Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

SUPPORTING INFORMATION

Peraryl-X-onium Ions of Nitrogen and Oxygen

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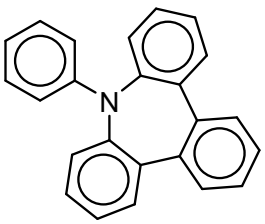
General Information

Unless otherwise stated, all reactions were carried out using reagents obtained from commercial sources and used without further purification. Column chromatography was performed on silica gel (200-300 mesh). High resolution mass data were collected by the Agilent 6230 TOF LC/MS and Thermo scientific Q Exactive HF. IR data were collected by Bruker Tensor 27. ^{1}H NMR, ^{19}F NMR, ^{13}C NMR spectra were recorded at 400 and 600 MHz on Bruker. ^{1}H NMR are referenced to the residual solvent peak at 7.26 ppm ($CDCl_3$), 2.50 ppm ($(CD_3)_2SO$) or 2.05 ppm ($(CD_3)_2CO$). ^{13}C NMR spectra, recorded at 101 and 151 MHz, are referenced to the solvent peak at 77.16 ppm ($CDCl_3$) or 29.84 ppm ($(CD_3)_2CO$). ^{19}F NMR spectra were recorded at 564 MHz in $CDCl_3$ and are referenced to the solvent peak at -162.2 ppm (C_6F_6). NMR data are represented as follows: chemical shift, multiplicity (br. = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hertz (Hz), integration.

Additional Data

Table 1. Product distribution between onium salts and neutral seven-membered rings (scaffold I, II, III).

Compound	Onium (%)	Neutral (%)	Onium/Neutral
1•Cb	62	27	2.3
1•I[13]	43	25-27	~1.7
2•Cb	75	23	3.3
3•Cb	63	20	3.1
3•I[13]	53-62	13-17	~4
4•Cb	56	15	3.7
4•I	55	18	3.1
5•Cb	52	19	2.7
5•I	60	20	3.0
6•I	62	22	2.8
7•Cb	55	20	2.75
7•I [13]	57-71	1.6-2.2	~35
8•Cb	68	22	3
9•Cb	29	15	1.9
10•Cb	62	14	4.4
10•I	60	18	3.3



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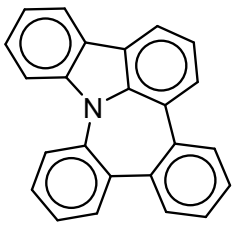

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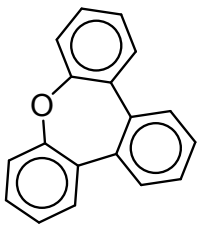


III

Figure 1. 1H NMR spectra (600 MHz, $CDCl_3$, parts) of **2**, **5**, **6**, **10** with BINPHAT salts. (a) **10**•AcO, (b) **10**•BINPHAT, (c) **2**•I, (d) **2**•BINPHAT, (e) **5**•I, (f) **5**•BINPHAT and **6**•AcO *vs* **6**•BINPHAT

#The full spectra of each salts are in the Spectra section and BINPHAT salts are at the spectra section.

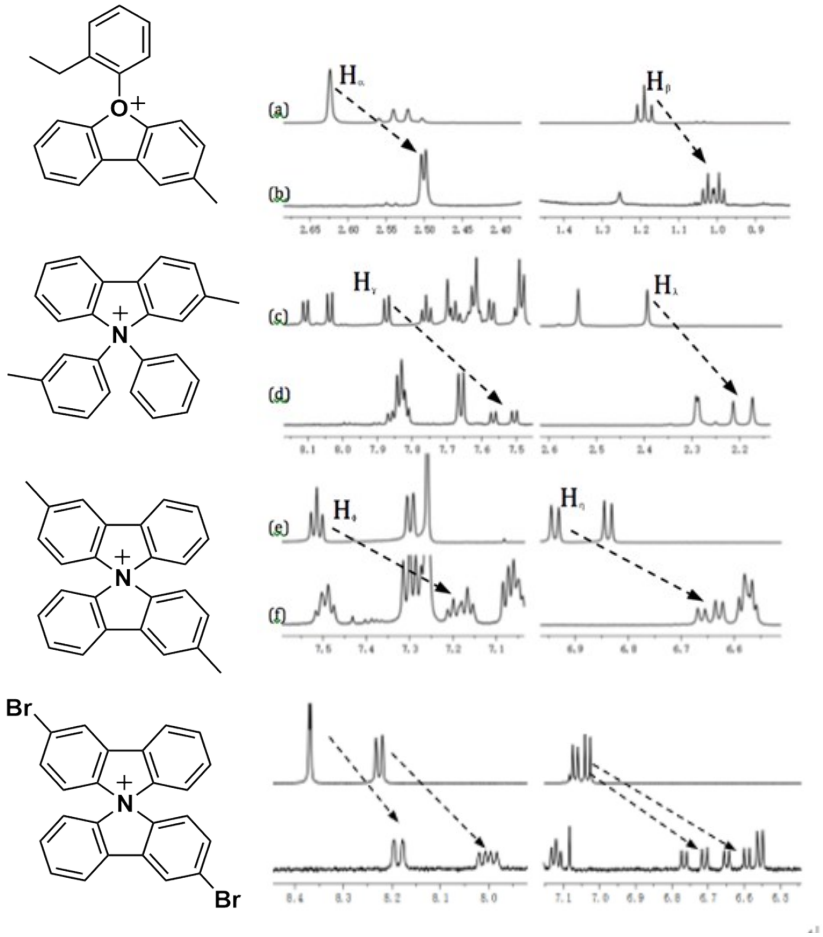
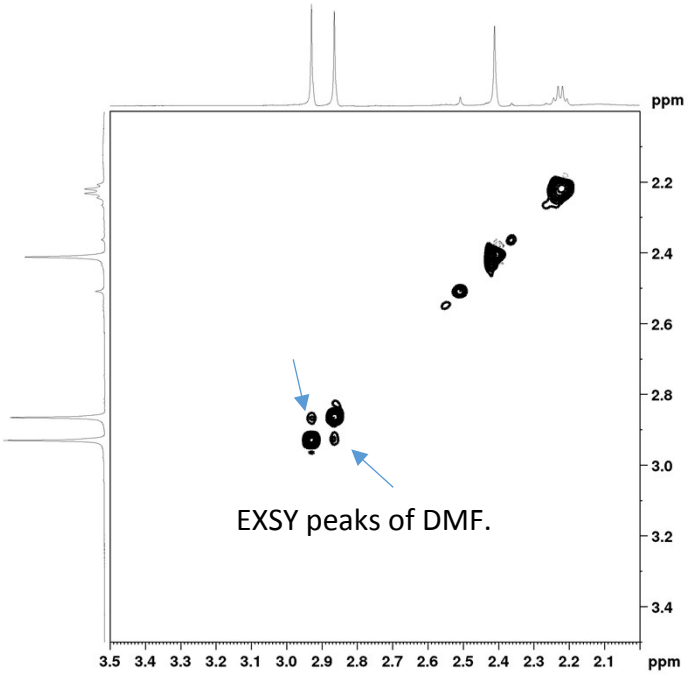


Figure 2. 2D NOESY spectra ($CDCl_3$, 600 MHz, 328 K, NS =16, t_m = 1 s, F1 = 512, F2 = 1024) of **10**•BINOL.



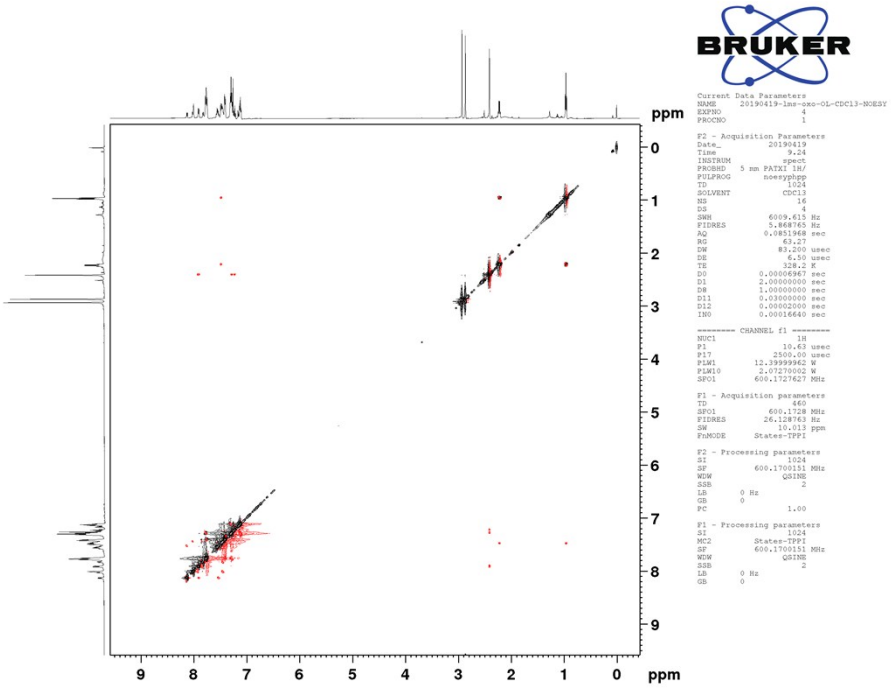


Figure 3. The proton assignment of **10**•AcO and **10**•BINOL.

#The supportive 2D NMR spectra were in the Spectra section.

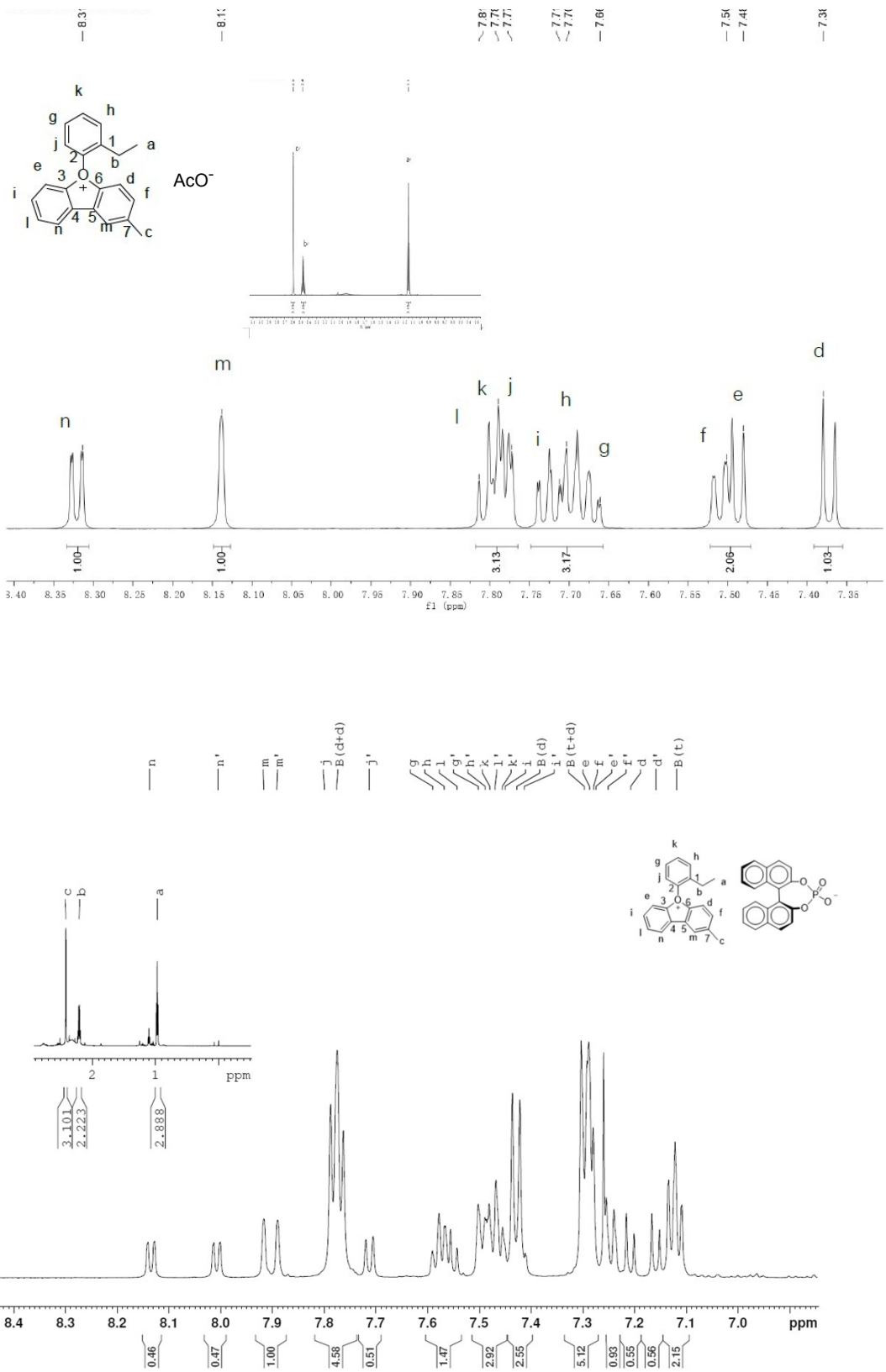


Figure 4. The carbon assignment of **10**•AcO and **10**•BINOL.

#The supportive 2D NMR spectra were in the Spectra section.

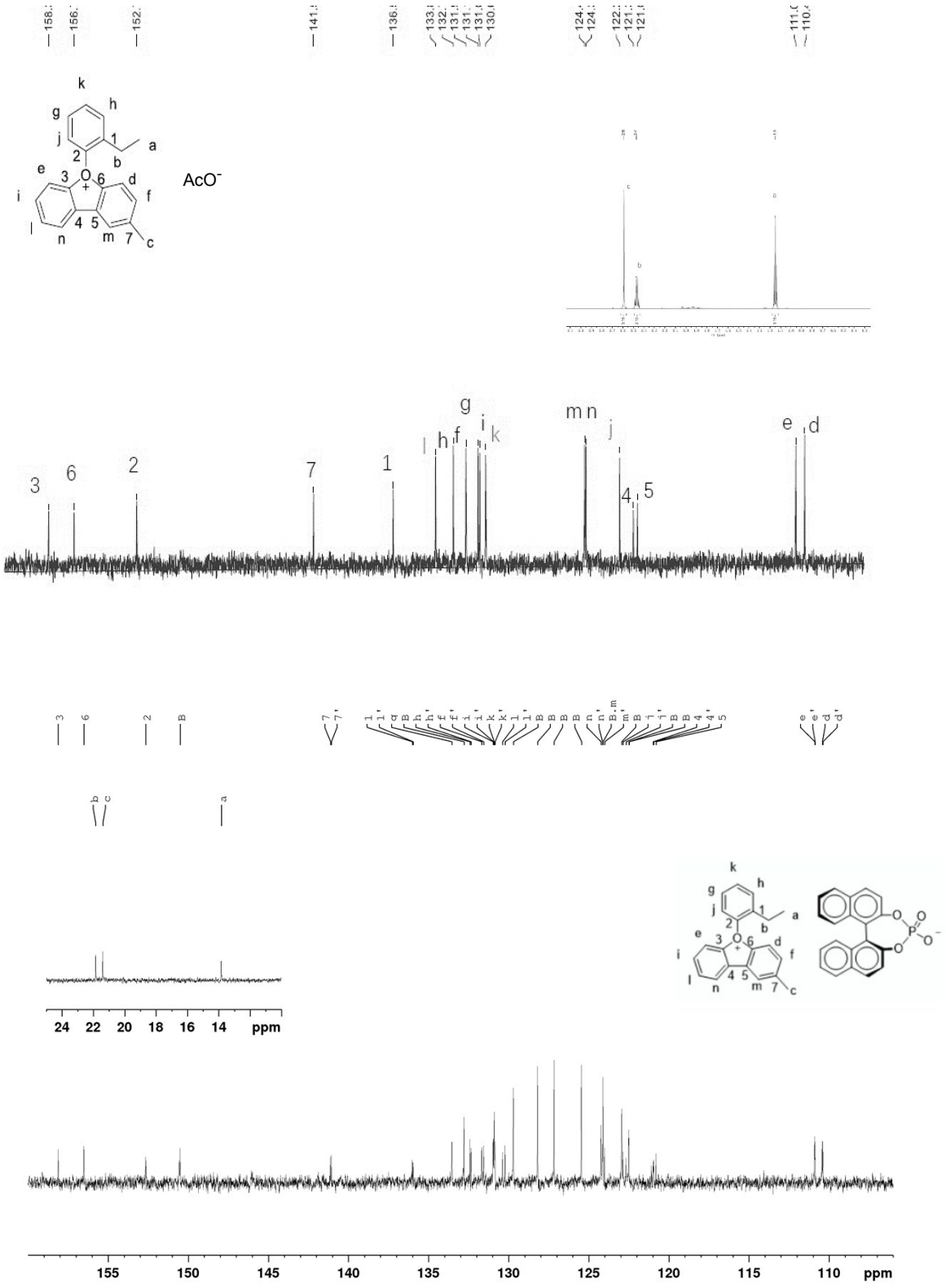
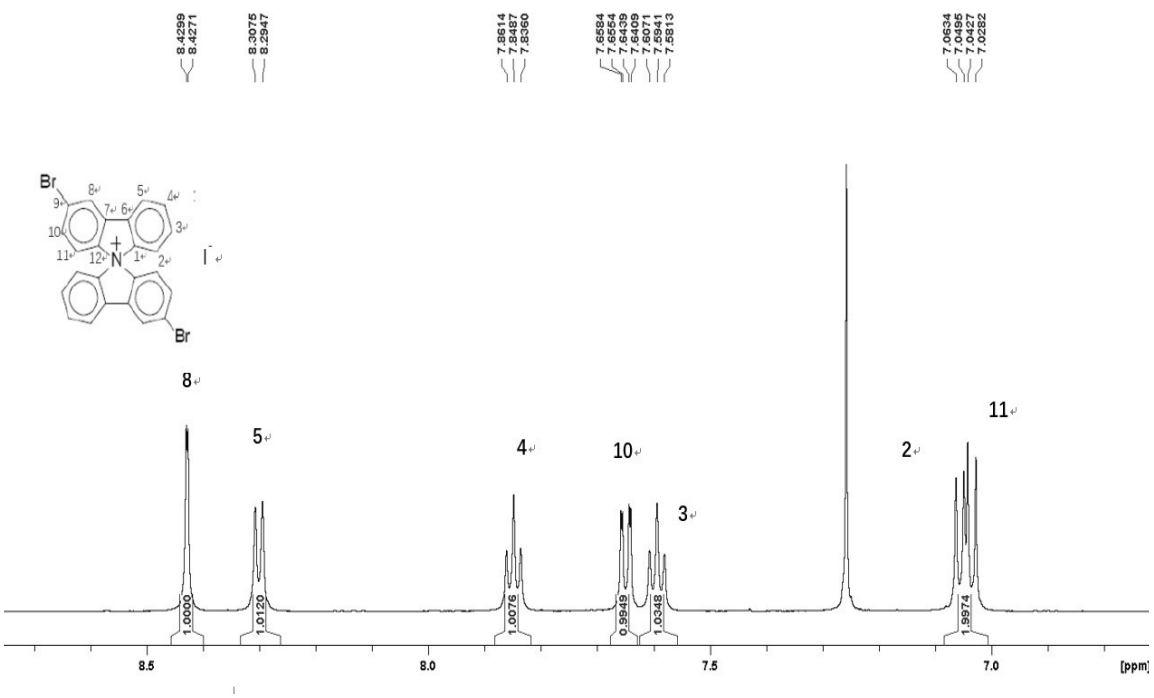


Figure 5. The proton assignment of **6**•I and **6**•BINOL.

#The supportive 2D NMR spectra were in the Spectra section.



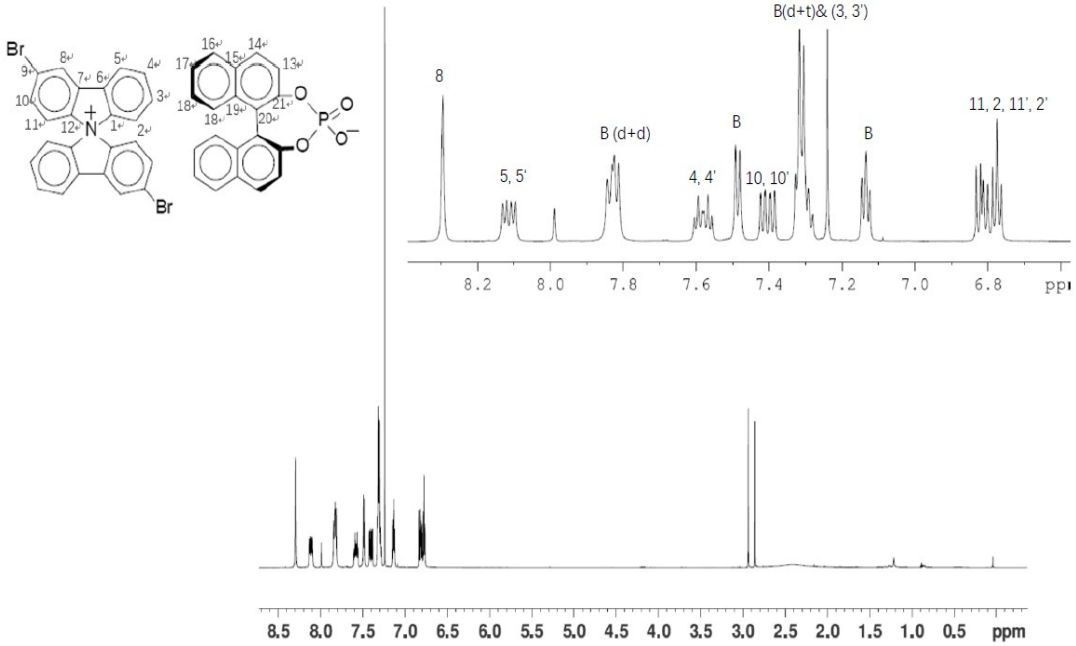
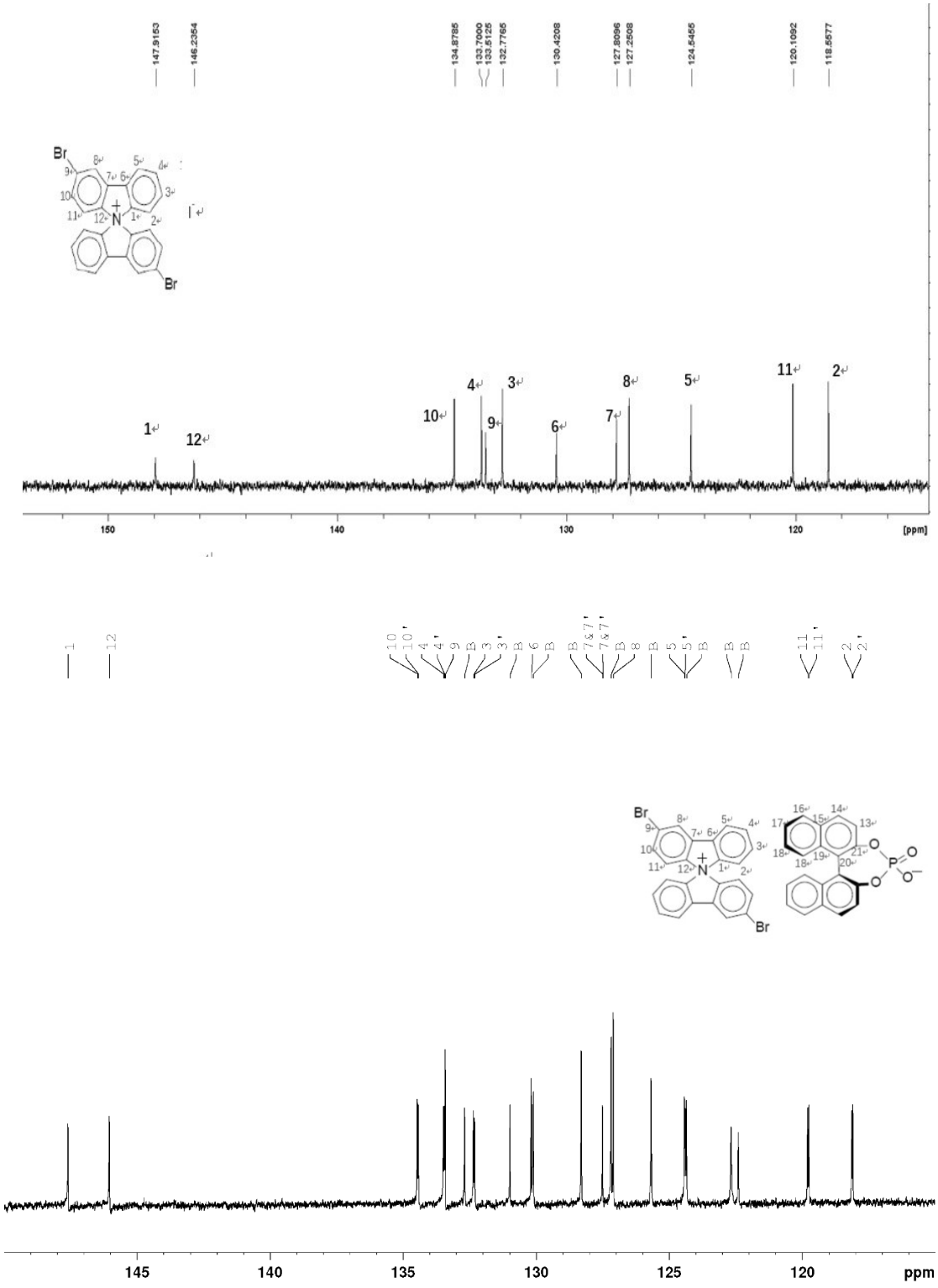


Figure 6. The carbon assignment of **6•I** and **6•**BINOL.

#The supportive 2D NMR spectra were in the Spectra section.



General procedure:

A. Buchwald amination[1]

A mixture of Palladium acetate ($Pd(OAc)_2$, 0.05 equiv.), Xantphos (0.05 equiv.), NaO^tBu (1.5 equiv.), 1-bromo-2- iodobenzene (1 equiv.), and phenylamines (1.2 equiv.) in toluene (Tol, 0.5 M) was stirred at 100 ^oC for 12 h under nitrogen atmosphere. The reaction was quenched with H_2O and extracted with DCM. The pure product was obtained by flash chromatography (cyclohexane).

B. Suzuki coupling[2]

A mixture of aryl bromide (1 equiv.), aryl boronic acid (1.5 equiv.), bis(triphenylphosphine)palladium (II) chloride ($Pd(PPh_3)_2Cl_2$, 0.1 equiv.) and potassium carbonate (K_2CO_3, 3 equiv.) in a solution of H_2O and dimethoxyethane (H_2O/DME, 1:8, 0.5 M) was stirred at 80 ^oC for 2 h under nitrogen atmosphere. The reaction was quenched with H_2O and extracted with DCM. The pure product was obtained by flash chromatography.

C. C-F activation[3]

A dried microwave tube was charged with fluoro starting material (1 equiv.) and triisopropylsilylium carborane $[^iPr_3Si][CHB_{11}H_5Cl_6]$ (1.2 equiv.) inside the glovebox. The compounds were dissolved in anhydrous chlorobenzene (PhCl, 0.1 M) to give a clear solution. The reaction mixture was subjected to Microwave (MW). After cooling to room temperature, the mixture was transferred with EtOAc. Removal of the solvent under reduced pressure gave the crude product, which was further purified by column chromatography (c-hex/DCM = 4/1 to DCM/^{i}PrOH = 10/1) to afford the product.

D. Arylation of Carbazoles[4]

A mixture of a fluorinated aryl halide (4 equiv.), a carbazole (1 equiv.) and cesium carbonate (Cs_2CO_3, 4 equiv.) in N,N-dimethylformide (DMF, 0.25 M) was heated to 150 ^oC and stirred under nitrogen atmosphere. After reaction completion, the mixture was quenched with brine and extracted with DCM. The pure product was obtained by flash chromatography.

E. Nucleophilic aromatic substitution (S_NAr) for carbazoles[5]

A mixture of nitroarene (1 equiv.) and carbazoles (1 equiv.) in dry THF (0.3 M) was added portion wise sodium hydride (NaH, 60% in mineral oil, 1.5 equiv.) at room temperature under nitrogen atmosphere. Then the solution was heated to 65 ^oC after no more bubbles formed. GC-MS was used as a detector. The reaction was quenched with H_2O and extracted with DCM. The pure product was obtained by flash chromatography (cyclohexane/THF = 100/1) to afford the product.

F. Nitro reduction[6]

To a refluxing mixture of nitroarene (1 equiv.) and EtOH (0.02 M) was added Pd/C (5%, 0.1 equiv.) under nitrogen atmosphere, the mixture was stirred for 5 min and Hydrazine hydrate ($N_2H_4 \cdot H_2O$, 80%, 10 equiv.) was added dropwise and the resulting solution was stirred for 5-30 min until no more nitroarene. Then the mixture was cooled to room temperature, filtered through celite and washed with MeOH. Removal of the MeOH by rote vapor, the residue was extracted with ether. The organic layer was combined and dried with Na_2SO_4 and concentrated under reduced pressure. The crude was subjected to the next step directly. (chromatography was used if necessary.)

G. Sandmeyer bromination[7]

To a 0 °C mixture of aniline (1 equiv.) and Acetonitrile (CH_3CN, 0.02 M) was added *p*-toluenesulfonic acid (TsOH, 3 equiv.) followed by Copper(I) bromide (CuBr, 2.5 equiv.) and Sodium nitrite ($NaNO_2$, 2 equiv.) in minimal H_2O was added dropwise. The mixture was warmed to room temperature gradually and kept stirring for 1 h in air. The reaction was quenched with $NaHCO_3$ (aq.) and extracted with DCM. The pure product was obtained by flash chromatography.

H. Nucleophilic aromatic substitution for phenols[8]

A mixture of nitroarene (1 equiv.) and phenols (1 equiv.) in dry DMF (0.3 M) was added K_2CO_3 (1.5 equiv.) at room temperature under nitrogen atmosphere. Then the solution was heated to 120 °C. GC-MS was used as a detector. The reaction was quenched with H_2O and extracted with EtOAc. The pure product was obtained by flash chromatography.

I. Amino reduction[9]

To a 0 °C mixture of aniline (1 equiv.), AcOH (0.2 M) and H_3PO_2 (10 equiv.) was added $NaNO_2$ (1.5 equiv.) portion wise. The mixture was warmed to room temperature and stirred overnight. After the completely consumption of diazonium intermediate, the mixture was poured into water and filtered, washing with water until neutral. The residue was collected by ether, dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane) to afford the product.

J. Aldehyde reduction[10]

A mixture of aldehydes (1 equiv.) and hydrazine monohydrate (4 equiv.) in ethylene glycol (0.24 M) was heated to 130 °C for 2 h under nitrogen atmosphere. After the mixture was cooled to room temperature, potassium hydroxide (82 mg, 1.47 mmol, 3 equiv.) was added to the mixture. The mixture was stirred at 160 °C for another 2 h. The reaction was quenched with H_2O and extracted with EtOAc. The pure product was obtained by flash chromatography to afford the product.

K. Suzuki coupling-II[11]

A mixture of aryl bromide (1 equiv.), aryl boronic acid (1.1 equiv.), $Pd(OAc)_2$ (0.05 equiv.), PPh_3 (0.15 equiv.) and K_2CO_3 (2 equiv.) was added Tol (0.11 M) followed by a 1:1 ethanol-water solution (0.56 M) was stirred at 100 ^oC under nitrogen atmosphere. The reaction was quenched with H_2O and extracted with DCM. The pure product was obtained by flash chromatography.

L. Nitro reduction[12]

To a stirred solution of nitrobenzene (1 equiv.) in DCM (0.08 M) was added activated zinc dust (60 equiv.) under nitrogen atmosphere. The solution was cooled down to 0 ^oC and acetic acid (AcOH, 1.5 M) was added drop wisely. After stirred for 10 min at 0 ^oC, the mixture was filtered through celite and washed with EtOAc. The filtrate was neutralized with saturated aqueous $NaHCO_3$ solution, dried over Na_2SO_4 and filtered. The filtrate was evaporated under reduced pressure and the resulting residue was purified by flash chromatography.

M. Hellwinkel's method[13]

To a stirring -5 ^oC mixture of aniline (1 equiv.), AcOH (0.27 M) and H_2O (1.31 M) was added $NaNO_2$ (1.5 equiv.) in a minimal amount of water dropwise in air. The mixture was stirred at 0 ^oC for 1 h and urea (0.51 equiv.) was added slowly to quench extra $NaNO_2$. The diazonium mixture was heated to 70 ^oC in a water bath. After complete consumption of the diazonium intermediate, the mixture was cooled to 40 ^oC and the AcOH was removed under vacuum. The crude was triturated three times with $CHCl_3$ and filtered each time. The combined organic filtrates were evaporated almost to dryness and then thoroughly triturated with ether. After decanting the by-product (liquid layer), the salt was collected as the remaining solid. The onium acetate salt was then dissolved in a minimum amount of warm water followed by an addition of KI (3.53 equiv.) in minimal water. The precipitate was washed with water and dried to give the finial onium iodide salt.

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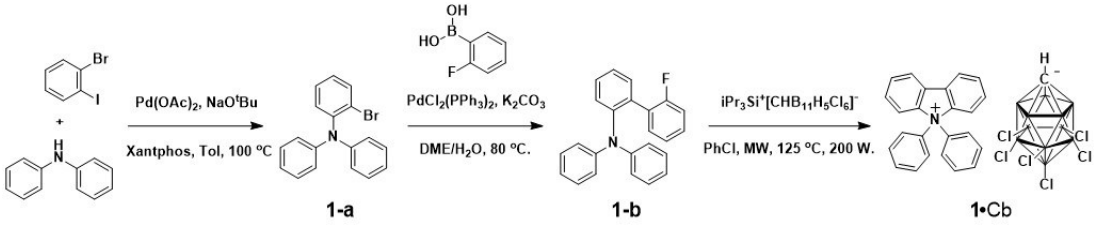
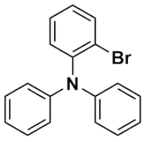
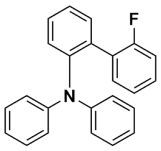
Organic Synthesis and Characterization



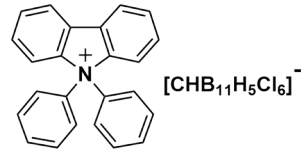
Scheme 1: Synthetic route for **1•**Cb



1-a: N-(2-bromophenyl)-N-phenylbenzenamine:
According to general procedure **A**, 1-bromo-2- iodobenzene (144 mg, 0.5 mmol) and diphenylamine (102 mg, 0.6 mmol) in toluene (0.5 mL) were stirred at 100 °C for 12 h. Purification afforded the pure product as a colorless oil (136 mg, 84 %).
R_f = 0.5 (c-hex).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (dd, *J* = 8 ,1 Hz, 1 H), 7.32 (td, *J* = 8, 1 Hz, 1 H),7.25-7.21 (m, 5 H), 7.11 (td, *J* = 8, 2 Hz, 1 H), 6.99-6.95 (m, 6 H).
Spectroscopic data matched those previously reported.[16]



1-b: 2-(N,N-diphenylamino)-1-(2-fluorophenyl)benzene:
According to general procedure **B**, 2-flurophenylboronic acid (64 mg, 0.45 mmol) and **1-a** (132 mg, 0.41 mmol) in the mixture of DME and H_2O (2.5 mL) were stirred at 80 °C and for 3 h. The pure product was obtained by flash chromatography (cyclohexane) as a colorless oil (135 mg, 97%).
R_f = 0.2 (c-hex).
^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.46-7.43 (m, 1 H), 7.30-7.29 (m, 2 H),7.24 (d, *J* = 8 Hz, 1 H), 7.14 (q, *J* = 8 Hz, 1 H), 7.08 (t, *J* = 8 Hz, 4 H), 7.02 (t, *J* = 8 Hz, 1 H), 6.94 (t, *J* = 8 Hz, 2 H), 6.83 (t, *J* = 8 Hz, 2 H), 6.72 (d, *J* = 8 Hz, 4 H).
^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.9 (d, $^1J_{C\text{-}F}$ = 246 Hz), 147.7, 146.4, 134.0, 132.5, 131.5, 131.5, 129.3, 128.8, 128.8, 128.8 (d, $^3J_{C\text{-}F}$ = 8 Hz), 128.7, 127.6 (d, $^2J_{C\text{-}F}$ = 15 Hz), 125.0, 123.5 (d, $^4J_{C\text{-}F}$ = 3 Hz), 122.6, 121.7, 115.2 (d, $^2J_{C\text{-}F}$ = 23 Hz),
^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -116.8.
IR (neat, cm^{-1}): 3056*w*, 1588*s*, 1493*s*, 1475*s*, 1327*m*, 747*s*, 693*m*, 502*w*.
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{24}H_{19}FN$) 340.1496; Found: 340.1474.



1•Cb**:**
According to general procedure **C**, a mixture of **1-b** (24 mg 0.07 mmol) and [^{i}Pr$_3$Si][$CHB_{11}H_5Cl_6$] (40 mg, 0.08 mmol) dissolved in chlorobenzene (1 mL) was subjected to MW (200 W, 125 °C) for 1 h. The crude was further purified by column chromatography (c-hex/DCM = 4/1 to DCM/^{i}PrOH = 10/1) to afford the product as a dark green solid

(29 mg, 62%). Crystals could be obtained from dissolving in acetone/ethanol and slow evaporation of the solvent.

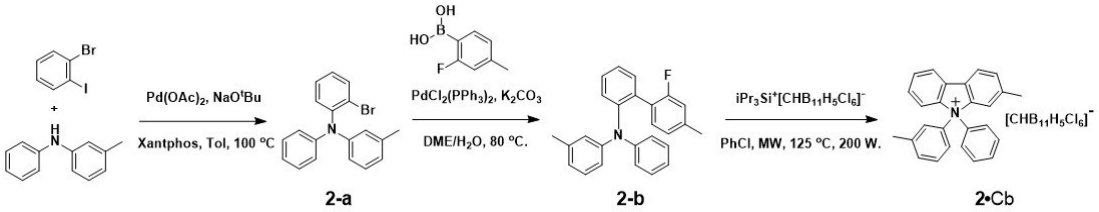
R_f = 0.5 (DCM).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8 Hz, 2 H), 7.79 (t, *J* = 8 Hz, 2 H), 7.70-7.66 (m, 4 H), 7.60-7.59 (m, 6 H), 7.36 (d, *J* = 7 Hz, 4 H).

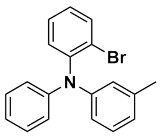
^{13}C NMR (151 MHz, $CDCl_3$): δ = 150.2, 146.4, 132.8, 132.1, 131.8, 131.6, 131.6, 130.3, 123.5, 122.3, 122.3, 121.7.

IR (cm^{-1}): 2917*m*, 2849*w*, 2599*w*, 1718*w*, 1461*w*, 1260*m*, 1093*m*, 1018*s*, 991*m*, 747*m*.

HR-MS (ESI): $[M-CH_6B_{11}Cl_6]^+$ Calculated: ($C_{24}H_{18}N$) 320.1434; Found: 320.1395. $[M-C_{24}H_{18}N]^-$ Calculated: ($CH_6B_{11}Cl_6$) 348.9630; Found: 348.9746.



Scheme 2: Synthetic route for **2•**Cb



2-a: N-(2-bromophenyl)phenyl-m-tolylamine:

According to general procedure **A**, 1-bromo-2- iodobenzene (144 mg, 0.5 mmol) and 3-methyldiphenylamine (113 mg, 0.6 mmol) in toluene (0.5 mL) were stirred at 100 °C for 12 h. Purification afforded the pure product as a colorless oil (96 mg, 57 %).

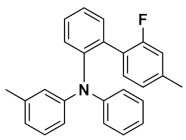
R_f = 0.2 (c-hex).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (dd, *J* = 8, 2 Hz, 1 H), 7.32 (td, *J* = 7, 1 Hz, 1 H), 7.24-7.20 (m, 3 H), 7.13-7.08 (m, 2 H), 6.98-6.94 (m, 3 H), 6.80-6.77 (m, 3 H), 2.25 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 147.2, 147.1, 145.7, 139.0, 134.6, 131.8, 129.1, 129.1, 129.0, 128.9, 127.3, 123.9, 123.2, 122.9, 122.0, 122.0, 122.0, 119.5, 21.7.

IR (neat, cm^{-1}): 3049*m*, 2790*m*, 2712*m*, 2450m, 1561*s*, 1551*s*, 1461*s*, 1427*m,* 1262*s*, 1200*m*.

HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{19}H_{17}BrN$) 338.0544; Found: 338.3915.



2-b:

According to general procedure **B**, 2-fluro-5-Methyl-phenylboronic acid (25 mg, 0.16 mmol) and **2-a** (47 mg, 0.14 mmol) in the mixture of DME and H_2O (1 mL) were stirred at 80 °C and for 3 h. The pure product was obtained by flash chromatography (hexane) as a colorless oil (42 mg, 82%).

R_f = 0.15.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.42 (td, *J* = 4, 2 Hz, 1 H), 7.29-7.26 (m, 2 H),7.22 (d, *J* = 8 Hz, 1 H), 7.08 (t, *J* = 8 Hz, 2 H), 6.97 (t, *J* = 8 Hz, 1 H), 6.88 (t, *J* =

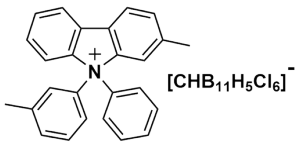
8 Hz, 1 H), 6.82 (t, J = 8 Hz, 1 H), 6.77 (t, J = 8 Hz, 2 H), 6.70 (d, J = 8 Hz, 2 H), 6.66 (d, J = 8 Hz, 1 H), 6.51 (d, J = 7.2 Hz, 1 H), 6.50 (s, 1 H), 2.1 9 (s, 3 H), 2.09 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.7 (d, $^1J_{C\text{-}F}$ = 244 Hz), 147.9, 147.6, 146.6, 139.1 (d, $^3J_{C\text{-}F}$ = 9 Hz), 138.4, 134.1, 132.6, 131.2 (d, $^4J_{C\text{-}F}$ = 4 Hz), 129.1, 128.7, 128.7, 128.5, 124.9, 124.5 (d, $^2J_{C\text{-}F}$ = 16 Hz), 124.2 (d, $^4J_{C\text{-}F}$ = 3 Hz), 123.5, 122.6, 122.5, 122.4, 122.4, 121.4, 120.1, 115.6 (d, $^2J_{C\text{-}F}$ = 22 Hz), 21.4, 21.1.

^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -117.5.

IR (neat, cm^{-1}): 3049*m*, 2998*m*, 2885*m*, 2801*w*, 2365*w*, 1590*s*, 1462*s*, 1304*s*, 1163*m*.

HR-MS (ESI): $[M]^+$ Calculated: ($C_{26}H_{22}FN$) 367.1736; Found: 367.1751.



2•Cb:

According to general procedure C, a mixture of **2-b** (14 mg, 0.04 mmol) and [^{i}Pr$_3$Si][$CHB_{11}H_5Cl_6$] (22 mg, 0.05 mmol) dissolved in chlorobenzene (0.50 mL) was subjected to MW (200 W, 125 °C) for 2 h. The crude was further purified by column chromatography (c-hex/DCM = 4/1 to DCM/^{i}PrOH = 10/1) to afford the product as a green solid (20 mg, 75%).

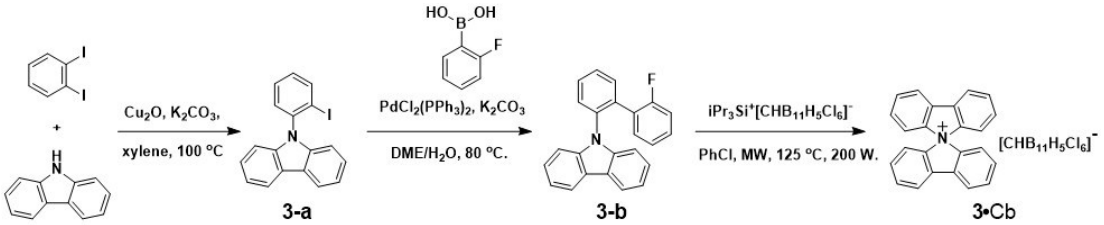
R_f = 0.5 (DCM).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.03 (d, J = 8 Hz, 1 H), 7.96 (d, J = 8 Hz, 1 H), 7.76 (t, J = 8 Hz, 1 H), 7.65-7.57 (m, 6 H), 7.48 (t, J = 8 Hz, 1 H), 7.41-7.40 (m, 2 H), 7.37 (d, J = 8 Hz, 2 H), 7.18 (d, J = 7 Hz, 1 H), 7.03 (s, 1 H), 2.51 (s, 3 H), 2.39 (s, 3 H).

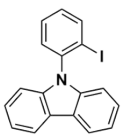
^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.5, 150.3, 146.5, 146.5, 143.1, 142.4, 133.8, 132.9, 132.7, 132.0, 131.5, 131.5, 131.3, 131.1, 130.5, 127.7, 123.0, 123.0, 122.4, 122.4, 122.2, 121.6, 121.6, 119.6, 22.4, 22.0.

IR (cm^{-1}): 3046*w*, 2924*w*, 2602*m*, 1581*w*, 1484*m*, 1467*m*, 1302*w*, 1019*s*, 991*m*, 866*s*.

HR-MS (ESI): $[M\text{-}CH_6B_{11}Cl_6]^+$ Calculated: ($C_{26}H_{22}N$) 348.1747; Found: 348.1762. $[M\text{-}C_{26}H_{22}N]^-$ Calculated: ($CH_6B_{11}Cl_6$) 348.9630; Found: 348.9661.



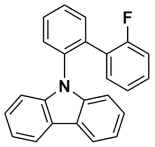
Scheme 3: Synthetic route for **3•Cb**



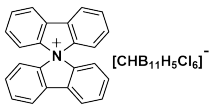
3-a: 9-(2-iodophenyl)-9H-carbazole:

Similar to general procedure **D**, 9-carbazole (835 mg, 5.0 mmol), 2-fluoro-iodobenzene (2.36 mL, 20.0 mmol) was heated at 150 °C in air for 1 day.

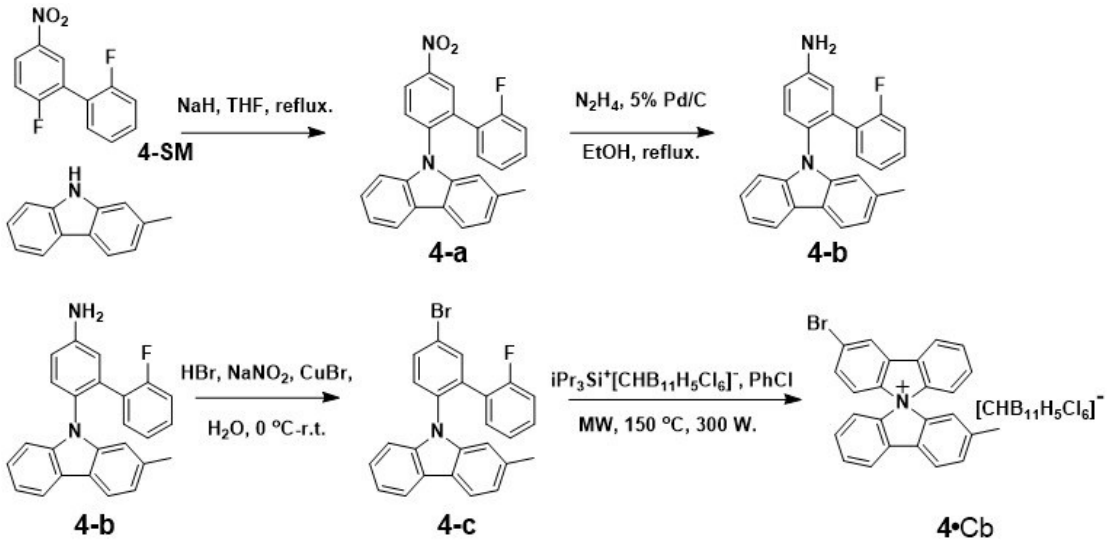
The pure product was obtained by flash chromatography (hexane) as a white solid (1.83 g, 99%).
R_f = 0.2.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 7 Hz, 2 H), 8.12 (d, *J* = 8 Hz, 1 H), 7.57 (t, *J* = 7 Hz, 1 H), 7.44 (d, *J* = 8 Hz, 1 H), 7.41 (t, *J* = 7 Hz, 2 H), 7.31 (t, *J* = 7 Hz, 2 H), 7.27 (t, *J* = 8 Hz, 1 H), 7.04 (d, *J* = 8 Hz, 2 H).
Spectroscopic data matched those previously reported[4].



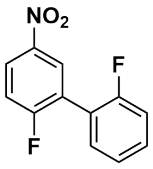
3-b: 9-(2'-fluoro-[1,1'-biphenyl]-2-yl)-9H-carbazole[14]
According to general procedure **B**, 2-flurophenylboronic acid (34 mg, 0.27 mmol) and **3-a** (70 mg, 0.18 mmol) in the mixture of DME and H_2O (0.5 mL) were stirred at 80 °C overnight. The pure product was obtained by flash chromatography (hexane) as a white solid (48 mg, 80%).
R_f = 0.2.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8 Hz, 2 H), 7.68-7.66 (m, 1 H),7.61-7.59 (m, 2 H), 7.55-7.53 (m, 1 H), 7.29 (t, *J* = 7 Hz, 2 H), 7.17 (t, *J* = 7 Hz, 2 H), 7.13 (d, *J* = 8 Hz, 2 H), 6.96 (q, *J* = 8 Hz, 1 H), 6.85-6.80 (m, 2 H), 6.64 (t, *J* = 7 Hz, 1 H).
^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.5 (d, $^1J_{C\text{-}F}$ = 244 Hz), 141.3, 136.0, 135.3, 132.6 (d, $^4J_{C\text{-}F}$ = 3 Hz), 130.4 (d, $^4J_{C\text{-}F}$ = 3 Hz), 129.7, 129.6, 129.5 (d, $^3J_{C\text{-}F}$ = 8 Hz), 128.4, 126.2 (d, $^2J_{C\text{-}F}$ = 15 Hz), 125.8, 123.7 (d, $^4J_{C\text{-}F}$ = 3 Hz), 123.2, 120.1, 119.7, 115.6 (d, $^2J_{C\text{-}F}$ = 22 Hz), 110.0.
^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -116.8.
IR (cm^{-1}): 3061*w*, 1597*w*, 1507*w*, 1491*w*, 1476*m*, 1451*s*, 1359*w*, 1336*w*, 1315*m*, 1231*m*, 1209*w*, 1177*w*, 824*w*, 748*s*, 724*m*, 630*w*, 423*w*.
MS (EI): m/z (%): 337.1 (100), 315.1 (8), 309.1 (8), 170 (17), 140 (15).



3•Cb Bis-2,2'-biphenylylene-ammonium hexachlorocarborane:[14]
According to general procedure **C**, a mixture of **3-b** (24 mg, 0.07 mmol) and [^{i}Pr$_3$Si][$CHB_{11}H_5Cl_6$] (39 mg, 0.08 mmol) dissolved in chlorobenzene (1 mL) was subjected to MW (200 W, 125 °C) for 2 h. The crude was further purified by column chromatography (c-hex/DCM = 4/1 to DCM/^{i}PrOH = 10/1) to afford the product as a brownish solid (29 mg, 63%). Crystals could be obtained from dissolving in acetone/hexane and slow evaporation of the solvent.
R_f = 0.5 (DCM).
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8 Hz, 4 H), 7.81 (t, *J* = 8 Hz, 4 H), 7.52 (t, *J* = 8 Hz, 4 H), 6.97 (d, *J* = 8 Hz, 4 H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 147.9, 133.4, 131.9, 131.6, 123.8, 118.4.
IR (cm^{-1}): 2918*w*, 1669*w*, 1618*w*, 1418*w*, 1166*m*, 1114*s*, 1018*m*, 747*w*.
HR-MS (ESI): [M-$CH_6B_{11}Cl_6$]$^+$ Calculated: ($C_{24}H_{16}N$) 318.1277; Found: 318.1281. [M-$C_{24}H_{16}N$]$^-$ Calculated: ($CH_6B_{11}Cl_6$) 348.9630; Found: 348.9677.



Scheme 4: Synthetic route for **4•**Cb



4-SM: 2,2'-difluoro-5-nitro-1,1'-biphenyl:
According to general procedure **B**, 2-flurophenylboronic acid (2.14 g, 15 mmol) and 3-bromo-4-fluro-nitrobenzene (2.27 g, 10 mmol) in the mixture of DME and H_2O (20 mL) were stirred at 80 °C for 1 h. The pure product was obtained by flash chromatography (cyclohexane) as an off-white solid (2.34 g, 99%).

R_f = 0.1.

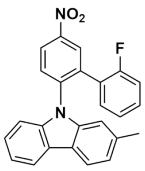
^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.40-8.38 (m, 1 H), 8.35-8.33 (m, 1 H), 7.67 (t, J = 9.0 Hz, 1 H), 7.60-7.56 (m, 2 H), 7.41-7.37 (m, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 163.5 (d, $^1J_{C-F}$ = 258 Hz), 159.8 (d, $^1J_{C-F}$ = 249 Hz), 144.4, 131.2 (t, $^4J_{C-F}$ = 3 Hz), 131.2 (d, $^3J_{C-F}$ = 7 Hz), 127.7 (dd, $^3J_{C-F}$ = 6 Hz, $^4J_{C-F}$ = 3 Hz), 125.6 (d, $^3J_{C-F}$ = 10 Hz), 125.2 (d, $^2J_{C-F}$ = 18 Hz), 124.6 (d, $^4J_{C-F}$ = 4 Hz), 121.3 (d, $^2J_{C-F}$ = 15 Hz), 117.0 (d, $^2J_{C-F}$ = 26 Hz), 116.2 (d, $^2J_{C-F}$ = 22 Hz).

^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -103.8, -114.9.

IR (cm^{-1}): 2378*w*, 2347*w*, 1750*w*, 1527*m*, 1507*m,* 1352*m*, 1094*w*, 767*w*, 640*w*.

HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{12}H_8F_2NO_2$) 236.0518; Found: 236.0518.

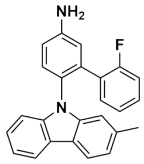


4-a: 9-(5-nitro-2'-fluoro[1,1'-biphenyl]-2-yl)-2-methyl-9H-carbazole:
According to general procedure **E**, **4-SM** (119 mg, 0.51 mmol) and 2-methyl carbazole[15](92 mg, 0.51 mmol) was heated at 65 °C and stirred for 2 h. The pure product was obtained by flash chromatography (cyclohexane/THF = 100/1) as a yellow solid (161 mg, 80%).

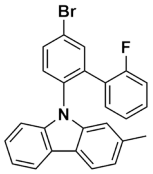
R_f = 0.2.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.52 (d, J = 9 Hz, 1 H), 8.49 (s,1 H), 8.05 (d, J = 8 Hz, 1 H), 7.98 (d, J = 8 Hz, 1 H), 7.95 (d, J = 9 Hz, 1 H), 7.26 (t, J = 7 Hz, 1 H),

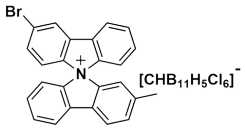
7.18-7.16 (m, 3 H), 7.09 (d, *J* = 8 Hz, 1 H), 7.03 (d, *J* = 8 Hz, 1 H), 6.98 (t, *J* = 9 Hz, 1 H), 6.95 (s, 1 H), 6.94 (t, *J* = 7 Hz, 1 H), 2.36 (s, 3 H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.3 (d, $^1J_{C\text{-}F}$ = 247 Hz), 147.0, 142.2, 140.7, 140.3, 136.5, 136.0, 130.6 (d, $^3J_{C\text{-}F}$ = 8 Hz), 130.5, 130.0 (d, $^4J_{C\text{-}F}$ = 3 Hz), 128.2, 128.2, 125.6, 124.5 (d, $^2J_{C\text{-}F}$ = 15 Hz), 124.5, 124.2 (d, $^4J_{C\text{-}F}$ = 3 Hz), 123.9, 122.1, 121.4, 120.6, 120.1 (d, $^4J_{C\text{-}F}$ = 2 Hz), 115.9 (d, $^2J_{C\text{-}F}$ = 22 Hz), 110.0, 109.6, 22.1.
^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -116.7.
IR (cm^{-1}): 2890*w*, 2349*s*, 1468*s*, 1442*s*, 1422*w*, 1357*s,* 1246*m*.
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{25}H_{18}FN_2O_2$) 397.1352; Found: 397.1892.



4-b: 9-(5-amino-2'-fluoro[1,1'-biphenyl]-2-yl)-2-methyl-carbazole: According to general procedure **F**, **4-a** (145 mg, 0.37 mmol) was heated at 80 °C and stirred for 15 min and after work up, the crude as a yellow solid (135 mg) was subjected to the next step directly.
^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.97 (d, *J* = 7 Hz, 1 H), 7.91 (d, *J* = 8 Hz, 1 H),7.22 (t, *J* = 8 Hz, 1 H), 7.10 (d, *J* = 8 Hz, 1 H), 7.07 (t, *J* = 8 Hz, 1 H), 7.04-7.00 (m, 2 H), 6.95-6.91 (m, 3 H), 6.88 (s, 1 H), 6.81 (dd, *J* = 8, 2 Hz, 1 H), 6.77-6.75 (m, 2 H), 5.59 (s, 2 H), 2.37 (s, 3 H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.5 (d, $^1J_{C\text{-}F}$ = 244 Hz), 146.3, 142.3, 141.8, 136.2, 135.8, 130.6, 130.3 (d, $^4J_{C\text{-}F}$ = 3 Hz), 129.2 (d, $^3J_{C\text{-}F}$ = 8 Hz), 126.5, 126.4 (d, $^2J_{C\text{-}F}$ = 15 Hz), 125.0, 123.5 (d, $^4J_{C\text{-}F}$ = 3 Hz), 123.0, 120.8, 120.7, 119.7, 119.7, 119.2,118.0 (d, $^4J_{C\text{-}F}$ = 2 Hz), 115.9, 115.4 (d, $^2J_{C\text{-}F}$ = 22 Hz), 110.2, 109.9, 22.2.
^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -116.7.
IR (cm^{-1}): 2349*s*, 1725*w*, 1665*w*, 1468*w,* 1462*w*, 990*w*.
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{25}H_{20}FN_2$) 367.1611; Found: 367.2112.



4-c: 9-(5-bromo-2'-fluoro[1,1'-biphenyl]-2-yl)-2-methyl-carbazole: **4-c** was synthesized according to general procedure **G**, purified by column chromatography (c-hexane) to afford the product as a white solid (84 mg, 53%).
R_f = 0.4.
^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.02 (d, *J* = 8 Hz, 1 H), 7.95 (d, *J* = 8 Hz, 1 H), 7.90-7.88 (m, 2 H), 7.54 (d, *J* = 9 Hz, 1 H), 7.24 (t, *J* = 7 Hz, 1 H), 7.13 (t, *J* = 7 Hz, 1 H), 7.10 (q, *J* = 8 Hz, 1 H), 7.06 (t, *J* = 8 Hz, 1 H), 7.04 (d, *J* = 8 Hz, 1 H), 7.00 (t, *J* = 8 Hz, 1 H), 6.95 (t, *J* = 8 Hz, 1 H), 6.91 (s, 1 H), 6.85 (t, *J* = 8 Hz, 1 H), 2.36 (s, 3 H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.4 (d, $^1J_{C\text{-}F}$ = 246 Hz), 141.4, 141.0, 137.0, 136.1, 135.4, 135.4, 135.2, 132.7, 131.2, 130.1(d, $^4J_{C\text{-}F}$ = 3 Hz), 130.0 (d, $^3J_{C\text{-}F}$ = 9 Hz), 125.3, 125.0 (d, $^2J_{C\text{-}F}$ = 15 Hz), 123.9 (d, $^4J_{C\text{-}F}$ = 4 Hz), 123.4, 121.8, 121.4, 121.0, 119.9, 119.8, 115.7 (d, $^2J_{C\text{-}F}$ = 22 Hz), 110.0, 109.7, 22.1.
^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -116.6.
IR (cm^{-1}): 2525*w*, 2310*w*, 1628*w*, 1547*m*, 1503*s,* 1470*m*, 1396*w*, 1324*m*, 761*s*.
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{25}H_{18}BrFN$) 430.0607; Found: 430.0599.



4•Cb**:**

According to general procedure **C**, a mixture of **4-c** (20 mg, 0.04 mmol) and [^{i}Pr$_3$Si][CHB$_{11}$H$_5$Cl$_6$] (26 mg, 0.05mmol) dissolved in chlorobenzene (0.5 mL) was subjected to MW (300 W, 150 ^{o}C) for 3 h. The crude was further purified by column chromatography (c-hex/DCM = 4/1 to DCM/^{i}PrOH = 10/1) to afford the product as a brownish solid (49 mg, 56%).

R_f = 0.4 (DCM).

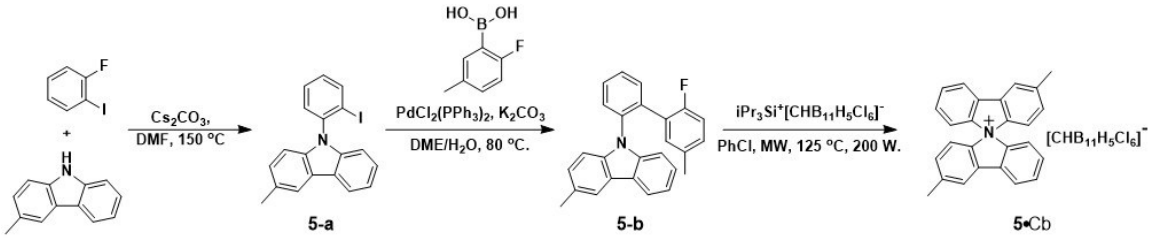
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.28 (s, 1 H), 8.14 (d, *J* = 8 Hz, 2 H), 8.07 (d, *J* = 8 Hz, 1 H), 7.83 (t, *J* = 8 Hz, 1 H), 7.79 (t, *J* = 8 Hz, 1 H), 7.63 (d, *J* = 9 Hz, 1 H), 7.60-7.57 (m, 2 H), 7.48 (t, *J* = 8 Hz, 1 H), 7.01 (d, *J* = 8 Hz, 1 H), 6.94 (d, *J* = 8 Hz, 1 H), 6.90 (d, *J* = 7 Hz, 1 H), 6.67 (s, 1 H), 2.36 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 148.3, 147.7, 147.4, 146.7, 143.4, 134.8, 134.5, 133.5, 133.4, 133.4, 132.7, 131.6, 131.4, 130.2, 128.8, 127.6, 126.7, 123.9, 123.6, 123.6, 120.0, 118.6, 118.2, 118.0, 22.0.

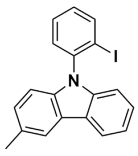
IR (cm^{-1}): 3007*m*, 2599*w*, 1724*w*, 1413*m*, 1260*m*, 1108*s*, 1018*m*, 865*w*, 801*m*.

HR-MS (ESI): [M-$CH_6B_{11}Cl_6$]$^{+}$ Calculated: ($C_{25}H_{17}BrN$) 410.0539; Found: 410.0548.

[M-$C_{25}H_{17}BrN$]$^{-}$ Calculated: ($CH_6B_{11}Cl_6$) 348.9630; Found: 348.9524.



Scheme 5: Synthetic route for **5•**Cb



5-a: 9-(2-iodophenyl)-3-methyl-9H-carbazole:

Similar to general procedure **D**, 3-methyl-carbazole[15](543 mg, 3.0 mmol,), 2-fluoro-iodobenzene (1.63 mL, 12.0 mmol) was heated at 150 ^{o}C in air for 1 day. The pure product was obtained by flash chromatography (hexane/DCM = 20/1) as a white solid (827 mg, 72%).

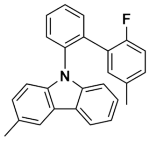
R_f = 0.2.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.11 (t, *J* = 9 Hz, 2 H), 7.95 (s, 1 H), 7.56 (t, *J* = 8 Hz, 1 H), 7.42 (d, *J* = 8 Hz, 1 H), 7.34 (t, *J* = 7 Hz, 1 H), 7.28-7.7.22 (m, 3 H), 7.00 (d, *J* = 8 Hz, 1 H), 6.93 (d, *J* = 8 Hz, 1 H), 2.55 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 141.0, 140.7, 140.6, 139.1, 130.8, 130.4, 129.9, 129.4, 127.4, 125.9, 123.5, 123.2, 120.5, 120.4, 119.9, 110.2, 110.0, 99.4, 21.6.

IR (cm^{-1}): 3744*w*, 2378*w*, 1641*m*, 1489*m*, 1233*w*, 744*w,* 668*w*.

HR-MS (ESI): [M+H]$^{+}$ Calculated: ($C_{19}H_{15}IN$) 384.0249; Found: 384.0240.



5-b: 9-(2'-fluoro-5'-methyl-[1,1'-biphenyl]-2-yl)-3-methylcarbazole: According to general procedure **B**, 2-fluro-5-methyl-phenylboronic acid (21 mg, 0.15 mmol) and **5-a** (47 mg, 0.12 mmol) in the mixture of DME and H_2O (0.5 mL) were stirred at 80 °C overnight. The pure product was obtained by flash chromatography (hexane) as a white solid (31 mg, 69%).

R_f = 0.2.

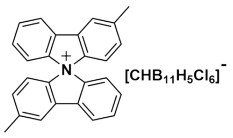
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.04 (d, *J* = 8 Hz, 1 H), 7.89 (s, 1 H), 7.69-7.65 (m, 3 H), 7.54-7.51 (m, 1 H), 7.26 (t, *J* = 8 Hz, 1 H), 7.13 (t, *J* = 8 Hz, 2 H), 7.01 (d, *J* = 8 Hz, 1 H), 6.94 (d, *J* = 8 Hz, 1 H), 6.87-6.84 (m, 2 H), 6.77 (t, *J* = 10 Hz, 1 H), 2.42 (s, 3 H), 1.92 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.7 (d, $^1J_{C\text{-}F}$ = 244 Hz), 136.3, 139.8, 136.3, 135.5, 132.9 (d, $^4J_{C\text{-}F}$ = 3 Hz), 132.4, 130.8 (d, $^4J_{C\text{-}F}$ = 3 Hz), 129.8 (d, $^3J_{C\text{-}F}$ = 8 Hz), 129.7, 129.4, 128.9, 128.3, 127.0, 125.7 (d, $^2J_{C\text{-}F}$ = 15 Hz), 125.5, 123.2, 123.0, 120.0, 119.9, 119.3, 115.1 (d, $^2J_{C\text{-}F}$ = 22 Hz), 110.0, 109.7, 21.5, 20.4.

^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -112.1.

IR (cm^{-1}): 3540*w*, 2904*w*, 2349*s*, 1530*m*, 1501*s*, 1442*w,* 1249*m*, 995*m*.

HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{26}H_{21}FN$) 366.1658; Found: 366.1651.



5•Cb**:**

According to general procedure **C**, a mixture of **5-b** (45 mg, 0.12 mmol) and [^{i}Pr$_3$Si][$CHB_{11}H_5Cl_6$] (62 mg, 0.12mmol) dissolved in chlorobenzene (1 mL) was subjected to MW (200 W, 125 °C) for 3 h. The crude was further purified by column chromatography (c-hex/DCM = 4/1 to DCM/^{i}PrOH = 10/1) to afford the product as a brownish solid (43 mg, 52%).

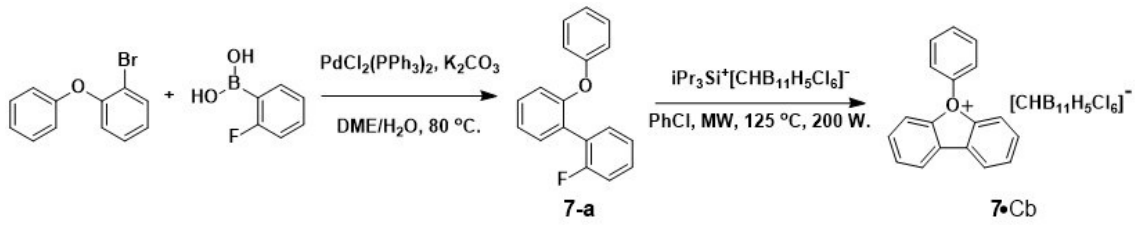
R_f = 0.5 (DCM).

^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ = 8.41 (d, *J* = 8 Hz, 2 H), 8.26 (s, 2 H), 7.90 (t, *J* = 7 Hz, 2 H), 7.60 (t, *J* = 8 Hz, 2 H), 7.42 (d, *J* = 8 Hz, 2 H), 7.31 (d, *J* = 8 Hz, 2 H), 7.21 (d, *J* = 8 Hz, 2 H), 2.57 (s, 6 H).

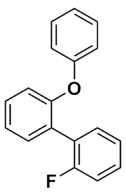
^{13}C NMR (151 MHz, $CDCl_3$): δ = 148.4, 145.6, 144.3, 144.3, 133.1, 132.5, 131.6, 131.4, 123.9, 123.5, 118.3, 117.9, 21.9.

IR (cm^{-1}): 3063*w*, 2928*m*, 2601*m*, 1486*m*, 1445*m*, 1131*w*, 1018*s*, 990*m*, 865*s*.

HR-MS (ESI): $[M\text{-}CH_6B_{11}Cl_6]^+$ Calculated: ($C_{26}H_{20}N$) 346.1590; Found: 346.1600. $[M\text{-}C_{26}H_{20}N]^-$ Calculated: ($CH_6B_{11}Cl_6$) 348.9630; Found: 348.9645.



Scheme 6: Synthetic route for **7•**Cb



7-a 2'-fluoro-2-phenoxybiphenyl:

According to general procedure **B**, 2-flurophenylboronic acid (104 mg, 0.75 mmol) and 1-bromo-2-phenoxy benzene (127 mg, 0.50 mmol) in the mixture of DME and H_2O (0.5 mL) were stirred at 80 °C for 2 h. The pure product was obtained by flash chromatography (cyclohexane) as a colorless oil (115 mg, 87%).

R_f = 0.25.

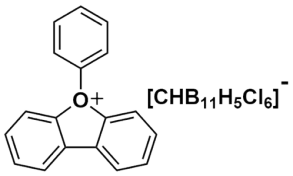
^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.44-7.36 (m, 4 H), 7.31 (t, *J* = 8 Hz, 2 H), 7.26 (t, *J* = 7 Hz, 1 H), 7.24-7.21 (m, 2 H), 7.06 (t, *J* = 7 Hz, 1 H), 6.97 (d, *J* = 8 Hz, 1 H), 6.90 (d, *J* = 8 Hz, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 160.2 (d, $^1J_{C\text{-}F}$ = 246 Hz), 157.5, 154.8, 132.0, 131.9 (d, $^4J_{C\text{-}F}$ = 3 Hz), 129.7, 129.5, 129.3 (d, $^3J_{C\text{-}F}$ = 8 Hz), 127.8, 125.7 (d, $^2J_{C\text{-}F}$ = 16 Hz), 123.9 (d, $^4J_{C\text{-}F}$ = 3 Hz), 123.4, 123.1, 119.1, 118.9, 115.6 (d, $^2J_{C\text{-}F}$ = 22 Hz).

^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -114.8.

IR (neat, cm^{-1}): 3744*w*, 3567*w*, 3065*w*, 2378*w*, 1588*m*, 1506*s*, 1477*s,* 1254*s*,1230*s*, 874*m*, 753*s*, 668*m*.

HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{18}H_{14}FO$) 265.1029; Found: 265.1006.



7•Cb**:**

According to general procedure **C**, a mixture of **7-a** (12 mg 0.04 mmol) and [^{i}Pr$_3$Si][$CHB_{11}H_5Cl_6$] (24 mg, 0.05 mmol) dissolved in chlorobenzene (0.5 mL) was subjected to MW (200 W, 125 °C) for 2 h. The crude was further purified by column chromatography (c-hex/DCM = 4/1 to DCM/^{i}PrOH = 10/1) to afford the product as a purple solid (16 mg, 55%). Crystals could be obtained from dissolving in DCM/MeOH and slow evaporation of the solvent.

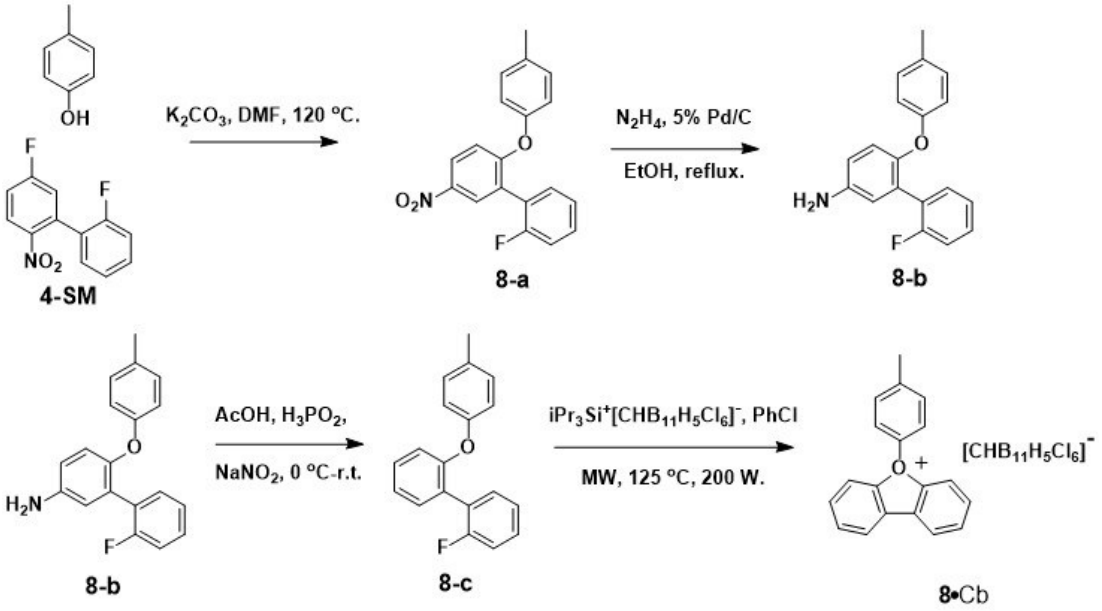
R_f = 0.5 (DCM).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 9 Hz, 2 H), 7.86-7.85 (m, 3 H), 7.82 (t, *J* = 8 Hz, 2 H), 7.76-7.70 (m, 4 H), 7.48 (d, *J* = 8 Hz, 2 H).

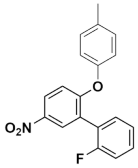
^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ = 159.8, 155.5, 134.4, 133.8, 131.9, 131.2, 124.8, 122.8, 122.5, 112.4.

IR (cm^{-1}): 3058*m*, 2602*m*, 1456*w*, 1129*w*, 1019*s*, 992*s*, 823*m,* 748*s*.

HR-MS (ESI): $[M\text{-}CH_6B_{11}Cl_6]^+$ Calculated: ($C_{18}H_{13}O$) 245.0961; Found: 245.0961. $[M\text{-}C_{18}H_{13}O)]^-$ Calculated: ($CH_6B_{11}Cl_6$) 348.9630; Found: 348.9692.



Scheme 7: Synthetic route for **8•**Cb



8-a:

According to general procedure **H**, **4-SM** (235 mg, 1 mmol) and 4-methyl phenol (109 mg, 1 mmol) was heated at 120 °C and stirred for 2 h. The pure product was obtained by flash chromatography (cyclohexane/DCM= 10/1) as a colorless oil (246 mg, 76%).

R_f = 0.1.

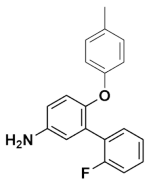
^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.27-8.24 (m, 2 H), 7.60 (t, J = 7 Hz, 1 H), 7.51 (q, J = 7 Hz, 1 H), 7.34 (t, J = 8 Hz, 2 H), 7.27 (d, J = 8 Hz, 2 H), 7.03 (d, J = 8 Hz, 2 H), 6.93 (d, J = 8 Hz, 1 H), 2.31 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.4, 160.2 (d, $^1J_{C\text{-}F}$ = 249 Hz), 152.8, 142.4, 135.2, 131.6 (d, $^4J_{C\text{-}F}$ = 3 Hz), 130.8, 130.4 (d, $^3J_{C\text{-}F}$ = 8 Hz), 127.6, 127.1, 125.2, 124.4, 124.4, 123.8 (d, $^3J_{C\text{-}F}$ = 7 Hz), 120.5, 116.0, 115.9, 115.9 (d, $^2J_{C\text{-}F}$ = 23 Hz), 21.0.

^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -116.7.

IR (neat, cm^{-1}): 3744*w*, 2377*w*, 1691*w*, 1549*m*, 1347*m*, 1257*m,* 1095*w*, 899*w*, 668*w*.

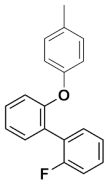
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{19}H_{15}FNO_3$) 324.1036; Found: 324.1039.



8-b:

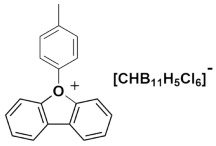
According to general procedure **F**, **8-a** (241 mg, 0.75 mmol) was heated at 80 °C and stirred for 10 min and after work up, the crude as a colorless oil (208 mg) was subjected to the next step directly.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.32-7.28 (m, 2 H), 7.18-7.13 (m, 2 H), 6.99 (d, J = 8 Hz, 2 H), 6.74 (d, J = 9 Hz, 1 H), 6.63-6.61 (m, 3 H), 6.57 (d, J = 2 Hz, 1 H), 5.09 (s, 2 H). 2.18 (s, 3 H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 160.0 (d, $^{1}J_{C\text{-}F}$ = 246 Hz), 156.6, 146.8, 142.5, 131.7 (d, $^{4}J_{C\text{-}F}$ =4 Hz), 131.4, 129.9, 129.9, 129.2 (d, $^{3}J_{C\text{-}F}$ =8 Hz), 129.0, 125.7 (d, $^{2}J_{C\text{-}F}$ = 15 Hz), 123.7 (d, $^{4}J_{C\text{-}F}$ = 4 Hz), 121.4, 118.1, 117.4, 117.4, 116.2, 115.6 (d, $^{2}J_{C\text{-}F}$ = 22 Hz), 20.7.
^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -115.0.
IR (neat, cm^{-1}): 3744*w*, 2378*w*, 1750*w*, 1507*m*, 1225*w*, 668*w*.
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{19}H_{17}FNO$) 294.1294; Found: 294.1216.



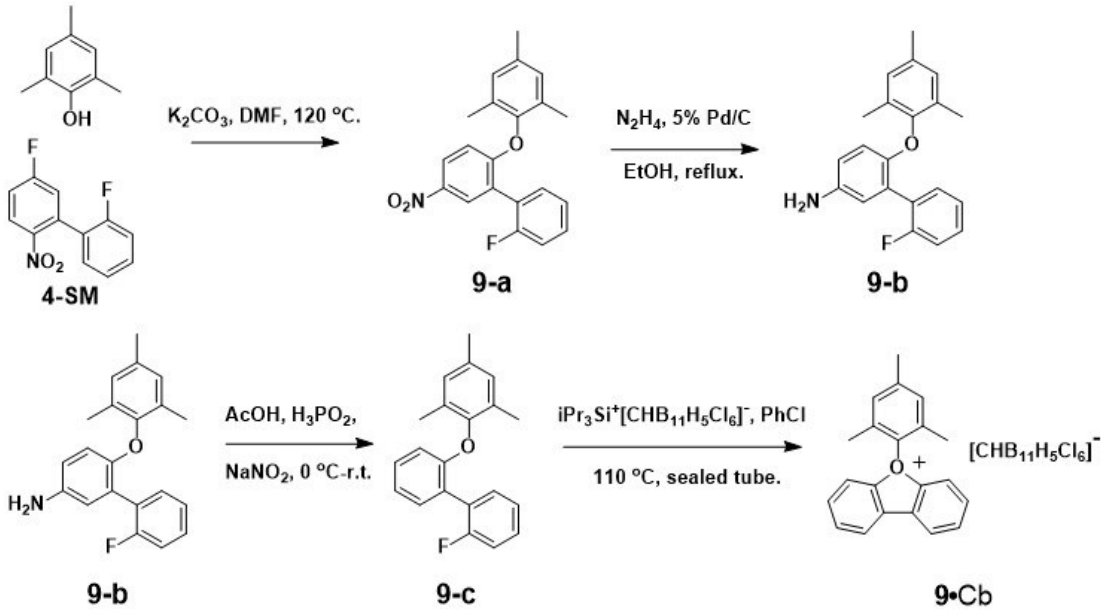
8-c:
8-c was synthesized according to general procedure **I**, purified by column chromatography (hexane) to afford the product as an off-white oil (62 mg, 30%).

R_f = 0.1.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41-7.38 (m, 2 H), 7.32-7.28 (m, 2 H), 7.16 (t, J = 8 Hz, 2 H), 7.10-7.07 (m, 3 H), 6.93 (d, J = 8 Hz, 1 H), 6.87 (d, J = 8 Hz, 2 H), 2.30 (s, 3 H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 160.2 (d, $^{1}J_{C\text{-}F}$ = 246 Hz), 155.3, 155.1, 132.7, 131.9 (d, $^{4}J_{C\text{-}F}$ = 3 Hz), 131.9, 130.2, 130.2, 129.4, 129.3 (d, $^{3}J_{C\text{-}F}$ = 8 Hz), 127.4, 125.8 (d, $^{2}J_{C\text{-}F}$ = 15 Hz), 123.9 (d, $^{4}J_{C\text{-}F}$ = 4 Hz), 123.0, 119.1, 119.1, 118.5, 115.6 (d, $^{2}J_{C\text{-}F}$ = 21 Hz), 20.8.
^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -114.7.
IR (neat, cm^{-1}): 2349*m*, 1552*w*, 1492*s*, 1462*s*, 1247*s*, 1178*w,* 1080*w*, 905*w*.
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{19}H_{16}FO$) 279.1185; Found: 279.1813.

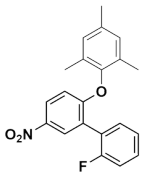


8•Cb**:**
According to general procedure C, a mixture of **8-c** (10 mg, 0.04 mmol) and [^{i}Pr$_3$Si][$CHB_{11}H_5Cl_6$] (22 mg, 0.05 mmol) dissolved in chlorobenzene (0.5 mL) was subjected to MW (200 W, 125 ^{o}C) for 1 h. The crude was further purified by column chromatography (c-hex/DCM = 4/1 to DCM/^{i}PrOH = 10/1) to afford the product as a brown solid (15 mg,68%). Crystals could be obtained from dissolving in Acetone and slow evaporation of the solvent.
R_f = 0.5 (DCM).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, J = 8 Hz, 2 H), 7.83 (t, J = 8 Hz, 2 H), 7.75 (t, J = 8 Hz, 2 H), 7.64 (s, 4 H), 7.52 (d, J = 12 Hz, 2 H), 2.57 (s, 3 H).
^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ = 159.8, 153.5, 145.3, 134.0, 131.9, 131.2, 124.8, 122.5, 122.4, 112.4, 21.3.
IR (cm^{-1}): 3074*m*, 2607*m*, 1490*w*, 1455*w*, 1430*w*, 1132*w*, 989*m*, 863*m*, 745*s*.

HR-MS (ESI): $[M\text{-}CH_6B_{11}Cl_6]^+$ Calculated: ($C_{19}H_{15}O$) 259.1117; Found: 259.1129. $[M\text{-}C_{19}H_{15}O]^-$ Calculated: ($CH_6B_{11}Cl_6$) 348.9630; Found: 348.9670.



Scheme 8: Synthetic route for **9•**Cb



9-a:

According to general procedure **H**, **4-SM** (235 mg, 1 mmol) and 2,4,6-trimethyl phenol (139 mg, 1 mmol) was heated at 120 °C and stirred for 2 h. The crude as a yellow solid (371 mg) was subjected to the next step directly.

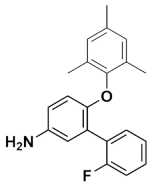
^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.22-8.21 (m, 2 H), 7.58 (t, J = 7 Hz, 1 H), 7.53 (q, J = 7 Hz, 1 H), 7.39-7.36 (m, 2 H), 7.00 (s, 2 H), 6.55 (d, J = 10 Hz, 1 H), 2.26 (s, 3 H), 1.95 (s, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 160.2 (d, $^1J_{C\text{-}F}$ = 248 Hz), 160.4, 148.1, 141.8, 135.6, 131.5 (d, $^4J_{C\text{-}F}$ = 3 Hz), 130.5, 130.4 (d, $^3J_{C\text{-}F}$ = 9 Hz), 130.0, 130.0, 127.7, 125.6, 124.3 (d, $^4J_{C\text{-}F}$ = 4 Hz), 124.0 (d, $^2J_{C\text{-}F}$ = 16 Hz), 115.9 (d, $^2J_{C\text{-}F}$ = 22 Hz), 112.4, 20.9, 16.1.

^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -113.5.

IR (cm^{-1}): 1610*s*, 1578*s*, 1517*m*, 1445*s,* 1350*s*, 1098*m*, 897*m*, 826*m*, 764*s*.741*m*.

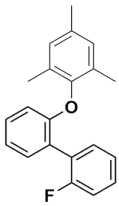
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{21}H_{19}FNO_3$) 352.1349; Found: 352.1341.



9-b:

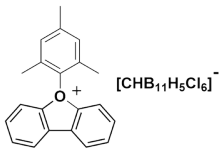
According to general procedure **F**, **9-a** (330 mg, 0.94 mmol) was heated at 80 °C and stirred for 30 min and after work up, the crude as a white solid (284 mg) was subjected to the next step directly.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.44-7.38 (m, 2 H), 7.28-7.25 (m, 2 H), 6.88 (s, 2 H), 6.54 (d, J = 2 Hz, 1 H), 6.42 (dd, J = 9, 3 Hz, 1 H), 6.01 (d, J = 8 Hz, 1 H), 4.77 (s, 2 H), 2.21 (s, 3 H), 1.93 (s, 6 H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.3 (d, $^{1}J_{C\text{-}F}$ = 246 Hz), 149.4, 148.4, 139.9, 134.1, 132.0 (d, $^{4}J_{C\text{-}F}$ =4 Hz), 131.3, 129.5, 129.1 (d, $^{3}J_{C\text{-}F}$ =8 Hz), 126.4 (d, $^{2}J_{C\text{-}F}$ = 17 Hz), 125.1, 123.8 (d, $^{4}J_{C\text{-}F}$ = 4 Hz), 118.9 (d, $^{4}J_{C\text{-}F}$ =2 Hz), 116.0, 115.6 (d, $^{2}J_{C\text{-}F}$ = 22 Hz), 113.2, 20.9, 16.3.
^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -114.1.
IR (cm^{-1}): 3751*w*, 2379*w*, 1750*w*, 1507*w*, 1489*m*, 1436*w*, 1221*w*.
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{21}H_{21}FNO$) 322.1607; Found: 322.1756.



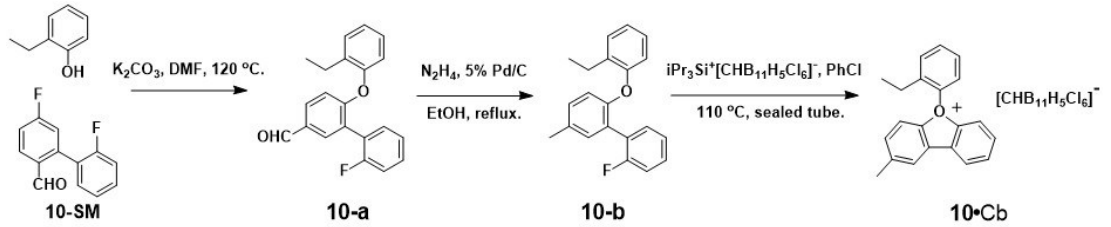
9-c:
9-c was synthesized according to general procedure I, purified by column chromatography (hexane) to afford the product as a white solid (175 mg, 61%).

R_f = 0.5.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.46 (t, J = 7 Hz, 1 H), 7.36-7.33 (m, 2 H), 7.21 (t, J = 7 Hz, 1 H), 7.19-7.14 (m, 2 H), 7.03 (t, J = 7 Hz, 1 H), 6.87 (s, 2 H), 6.42 (d, J = 8 Hz, 1 H), 2.28 (s, 3 H), 2.04 (s, 6 H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 160.4 (d, $^{1}J_{C\text{-}F}$ = 246 Hz), 155.2, 148.8, 134.4, 132.0 (d, $^{4}J_{C\text{-}F}$ = 3 Hz), 131.7, 131.1, 129.6, 129.4, 129.2 (d, $^{3}J_{C\text{-}F}$ = 9 Hz), 126.4 (d, $^{2}J_{C\text{-}F}$ = 15 Hz), 124.6, 123.8 (d, $^{4}J_{C\text{-}F}$ = 4 Hz), 121.0, 115.6 (d, $^{2}J_{C\text{-}F}$ = 22 Hz), 112.4, 20.9, 16.3.
^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -114.0.
IR (cm^{-1}): 3851*m*, 3743*m*, 3646*w*, 2378*w*, 1692*w*, 1550*w*, 1066*w*, 668*m*.
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{21}H_{20}FO$) 307.1498; Found: 307.1498.

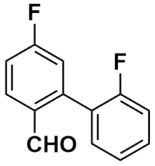


9•Cb**:**
A dried sealed tube was charged with **9-c** (10 mg, 0.03 mmol), [^{i}Pr$_3$Si][$CHB_{11}H_5Cl_6$] (20 mg, 0.04 mmol) inside the glovebox. The compounds were dissolved in anhydrous chlorobenzene (0.5 mL) to give a clear solution. The reaction mixture was heated to 110 ^{o}C for 1 h. After cooling to room temperature, the mixture was transferred with EtOAc. Removal of the solvent under reduced pressure gave the crude product, which was further purified by column chromatography (c-hex/DCM = 4/1 to DCM/^{i}PrOH = 10/1) to afford the product as a white solid (5 mg, 29 %).
9•Cb is unstable under microwave condition.
R_f = 0.5 (DCM).
^{1}H NMR (600 MHz, $(CD_3)_2CO$) δ = 8.63 (d, J = 8 Hz, 2 H), 8.00 (t, J = 7 Hz, 2 H), 7.95-7.90 (m, 4 H), 7.46 (s, 2 H), 2.50 (s, 3 H), 2.14 (s, 6 H).

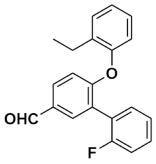
^{13}C NMR (151 MHz, $(CD_3)_2CO$) δ=157.3, 150.6, 144.8, 133.3, 132.4, 132.3, 131.3, 125.3, 121.9, 111.3, 21.1, 15.4.
IR (cm^{-1}): 2921*w*, 2850*w*, 1648*m*, 1384*m*, 1124*s*, 1090*s*, 1020*m*, 799*w*.
HR-MS (ESI): $[M\text{-}CH_6B_{11}Cl_6]^+$ Calculated: ($C_{21}H_{19}O$) 287.1430; Found: 287.1435. $[M\text{-}C_{21}H_{19}O]^-$ Calculated: ($CH_6B_{11}Cl_6$) 348.9630; Found: 348.9681.



Scheme 9: Synthetic route for **10•**Cb

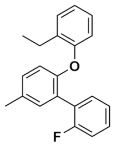


10-SM: 2,2'-difluoro-1,1'-biphenyl-5-carbaldehyde:
According to general procedure **B**, 2-flurophenylboronic acid (1 g, 7.1 mmol) and 3-bromo-4-fluorobenzaldehyde (986 mg, 4.8 mmol) in the mixture of DME and H_2O (9 mL) were stirred at 80 °C for 1 h. The pure product was obtained by flash chromatography (cyclohexane/EtOAc = 50/1) as a off-white solid (782 mg, 75%).
R_f = 0.1.
^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.95 (s, 1 H), 8.07-8.04 (m, 2 H), 7.60 (t, *J*= 9 Hz, 1 H), 7.57-7.54 (m, 2 H), 7.40-7.36 (m, 2 H).
^{13}C NMR (151 MHz, $CDCl_3$) δ = 190.4, 163.6 (d, $^1J_{C\text{-}F}$ = 258 Hz), 159.9 (d, $^1J_{C\text{-}F}$ = 249 Hz), 133.9 (dd, $^4J_{C\text{-}F}$ = 4 Hz, $^5J_{C\text{-}F}$ = 2 Hz), 133.1 (d, $^4J_{C\text{-}F}$ = 3 Hz), 131.5 (d, $^3J_{C\text{-}F}$ = 8 Hz), 131.5, 130.7 (d, $^3J_{C\text{-}F}$ = 9 Hz), 124.9 (d, $^2J_{C\text{-}F}$ = 18 Hz), 124.4 (d, $^4J_{C\text{-}F}$ = 4 Hz), 122.3 (d, $^2J_{C\text{-}F}$ = 16 Hz), 117.0 (d, $^2J_{C\text{-}F}$ = 24 Hz), 116.0 (d, $^2J_{C\text{-}F}$ = 22 Hz).
^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -104.5, -115.1.
IR (cm^{-1}): 3743*w*, 3566*w*, 2378*w*, 1703*s*, 1586*w*, 1550*w*, 1524*m*, 1100*w*, 824*m*, 758*m,* 668*w*.
HR-MS (ESI): $[M\text{-}H]^+$ Calculated: ($C_{13}H_7F_2O$) 217.0459; Found: 217.0503.



10-a:
According to general procedure **H**, **10-SM** (109 mg, 0.5 mmol) and 2-ethyl phenol (61 mg, 0.5 mmol) was heated at 120 °C and stirred overnight. The crude as a yellowish oil (152 mg) was subjected to the next step directly.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.95 (s, 1 H), 7.92 (s, 1 H), 7.78 (d, *J* = 8 Hz, 1 H), 7.46 (t, *J* = 8 Hz, 1 H), 7.38 (q, *J* = 8 Hz, 1 H), 7.28 (d, *J* = 7 Hz, 1 H), 7.24-7.19 (m, 2 H), 7.16 (t, *J* = 8 Hz, 2 H), 6.97 (d, *J* = 8 Hz, 1 H), 6.81 (d, *J* = 8 Hz, 1 H), 2.54 (q, *J* = 7 Hz, 2 H), 1.09 (t, *J* = 7 Hz, 3 H).

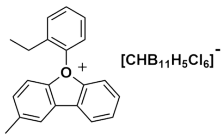
^{13}C NMR (151 MHz, $CDCl_3$): δ = 190.8, 161.0, 160.3 (d, $^1J_{C\text{-}F}$ = 248 Hz), 152.8, 136.5, 133.9, 131.7 (d, $^4J_{C\text{-}F}$ = 3 Hz), 131.4, 130.9, 130.2, 130.0 (d, $^3J_{C\text{-}F}$ = 8 Hz), 127.5, 126.8, 125.5, 124.7 (d, $^2J_{C\text{-}F}$ = 16 Hz), 124.2 (d, $^4J_{C\text{-}F}$ = 4 Hz), 120.8, 115.7 (d, $^2J_{C\text{-}F}$ = 22 Hz), 115.5, 23.2, 14.5.
^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -114.1.
IR (neat, cm^{-1}): 2969*w*, 2873*w*, 1695*s*, 1598*s*, 1576*s*, 1374s, 1174*w,* 816*m*, 751*s*.
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{21}H_{18}FO_2$) 321.1291; Found: 321.1279.



10-b:

10-b was synthesized according to general procedure **J**, purified by column chromatography (hexane) to afford the product as an off-white oil (92 mg, 65%).

R_f = 0.2.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39 (t, *J* = 8 Hz, 1 H), 7.28 (q, *J* = 7 Hz, 1 H), 7.21 (s, 1 H), 7.17 (d, *J* = 8 Hz, 1 H), 7.14 (t, *J* = 8 Hz, 1 H), 7.09-7.07 (m, 3 H), 6.99 (t, *J* = 7 Hz, 1 H), 6.81 (d, *J* = 8 Hz, 1 H), 6.77 (d, *J* = 8 Hz, 1 H), 2.59 (q, *J* = 7 Hz, 2 H), 2.38 (s, 3 H), 1.10 (t, *J* = 7 Hz, 3 H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 160.2 (d, $^1J_{C\text{-}F}$ = 246 Hz), 155.0, 152.8, 135.2, 132.3, 132.3, 131.9 (d, $^4J_{C\text{-}F}$ = 4 Hz), 130.0, 129.6, 129.2 (d, $^3J_{C\text{-}F}$ = 9 Hz), 127.0, 126.9, 126.0 (d, $^2J_{C\text{-}F}$ = 16 Hz), 123.8 (d, $^4J_{C\text{-}F}$ = 4 Hz), 123.3, 118.3, 117.9, 115.5 (d, $^2J_{C\text{-}F}$ = 22 Hz), 23.4, 20.8.14.5.
^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -114.7.
IR (neat, cm^{-1}): 3747*w*, 3033*w*, 2873*w*, 1502*m*, 1485*s*, 1461*s*, 1229*s*, 1185*w*, 753*m*.
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{21}H_{20}FO$) 307.1498; Found: 307.1489.

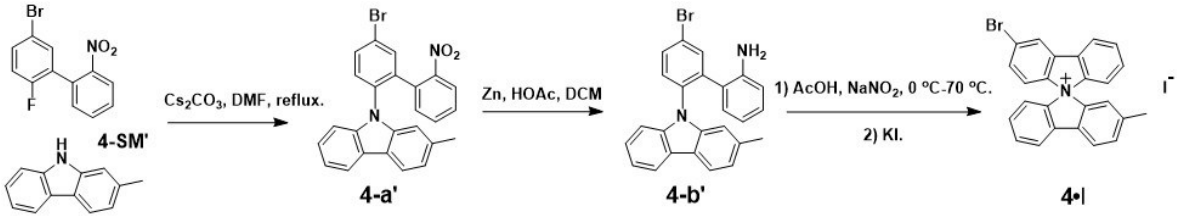


10•Cb:

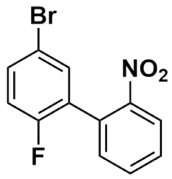
A dried sealed tube charged with **10-b** (30 mg, 0.1 mmol), [^{i}Pr$_3$Si][$CHB_{11}H_5Cl_6$] (60 mg, 0.12 mmol) and 1 mL anhydrous chlorobenzene inside the glovebox was heated to 110 °C for 1 h. After cooling to room temperature, the mixture was transferred with EtOAc. Removal of the solvent under reduced pressure gave the crude product, which was further purified by column chromatography (c-hex/DCM = 4/1 to DCM/^{i}PrOH = 10/1) to afford the product as a white solid (39 mg, 62 %).

R_f = 0.8 (DCM).
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.27 (d, *J* = 8 Hz, 1 H), 8.07 (s, 1 H), 7.85-7.80 (m, 2 H), 7.75 (t, *J* = 7 Hz, 2 H), 7.67 (t, *J* = 8 Hz, 1 H), 7.54 (d, *J* = 9 Hz, 1 H), 7.49 (d, *J* = 8 Hz, 1 H), 7.40 (d, *J* = 9 Hz, 1 H), 7.28 (d, *J* = 9 Hz, 1 H), 2.62 (s, 3 H), 2.58 (q, *J* = 7 Hz, 2 H), 1.23 (t, *J* = 7 Hz, 3 H).
^{13}C NMR (151 MHz, $(CD_3)_2CO$) δ = 159.7, 158.0, 154.1, 142.0, 138.4, 134.5, 133.7, 132.6, 131.9, 131.5, 131.2, 124.9, 124.9, 122.5, 122.3, 122.3, 112.2, 111.7, 22.8, 21.3, 14.5.
IR (cm^{-1}): 3005*w*, 2916*w*, 2530*w*, 1633*w*, 1435*w*, 1123*s*, 1053*m*, 991*m*.

HR-MS (ESI): $[M\text{-}CH_6B_{11}Cl_6]^+$ Calculated: ($C_{21}H_{19}O$) 287.1430; Found: 287.1429. $[M\text{-}C_{21}H_{19}O]^-$ Calculated: ($CH_6B_{11}Cl_6$) 348.9630; Found: 348.9669.



Scheme 10: Synthetic route for **4•I**



4-SM':

According to general procedure **K**, 5-bromo-2-fluorophenylboronic acid (1.23 g, 5.5 mmol) and 1-iodo-2-nitrobenzene (1.28 g, 5 mmol) in the mixture of Tol and ethanol solution (54 mL) were stirred at 100 °C for 24 h. The pure product was obtained by flash chromatography (hexane/DCM = 5/1) as an off-white solid (888 mg, 60%).

R_f = 0.2.

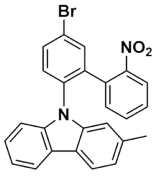
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 8 Hz, 1 H), 7.70 (t, *J* = 8 Hz, 1 H), 7.59 (t, *J* = 9 Hz, 1 H), 7.52-7.47 (m, 2 H), 7.42 (d, *J* = 8 Hz, 1 H), 7.02 (t, *J* = 9 Hz, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.6 (d, $^1J_{C\text{-}F}$ = 248 Hz), 148.8, 133.4, 131.1 (t, $^3J_{C\text{-}F}$ = 8 Hz), 132.8 (d, $^4J_{C\text{-}F}$ = 3 Hz), 132.5, 129.7, 129.4, 128.0 (d, $^2J_{C\text{-}F}$ = 18 Hz), 124.9, 117.3 (d, $^2J_{C\text{-}F}$ = 24 Hz), 117.0.

^{19}F NMR (564 MHz, C_6F_6 = -162.2 ppm): δ = -118.4.

IR (cm^{-1}): 2378*w*, 2311*w*, 1528*s*, 1497*w*, 1354*m,* 857*m,* 741*w*.

HR-MS (ESI): $[M\text{-}H]^-$ Calculated: ($C_{12}H_6BrFNO_2$) 293.9571; Found: 293.9568.



4-a':

According to general procedure **D**, 2-methyl-carbazole[14] (317 mg, 1.75 mmol) and **4-SM'** (1.04 g, 3.5 mmol) was heated at 150 °C for 1 day. The pure product was obtained by flash chromatography (hexane/EtOAc = 100/1) as a yellow solid (320 mg, 40%).

4-a' was existed as a pair of conformers caused by steric hindrance.

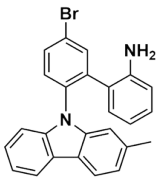
R_f = 0.1.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.99 (d, *J* = 8 Hz, 1 H), 7.95 (d, *J* = 2 Hz, 1 H), 7.92-7.88 (m, 2 H), 7.67-7.65 (m, 1 H), 7.54-7.47 (m, 3 H), 7.35-7.28 (m, 1 H), 7.26-7.24 (m, 1 H), 7.17-7.08 (m, 2 H), 7.00-6.95 (m, 1 H), 6.89 (s, 0.5 H), 6.76 (s, 0.5 H), 2.35-2.31 (m, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$) of conformers showed in spectrum.

IR (cm^{-1}): 2885*m*, 2808*m*, 2349*m*, 1725*w*, 1553*s*, 1444*m,* 921*w*.

HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{25}H_{18}BrN_2O_2$) 457.0552; Found: 457.0545.



4-b':

According to general procedure **L**, **4-a'** (122 mg, 0.27 mmol) was stirred at 0 °C for 20 minutes. The pure product was obtained by flash chromatography (hexane/DCM =1/1) as an off-white solid (86 mg, 75%).

4-b' was existed as a pair of conformers caused by steric hindrance.

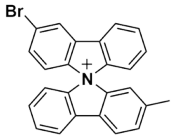
R_f = 0.2.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.03-7.90 (m, 2 H), 7.80-7.77 (m, 2 H),7.45 (d, *J* = 8 Hz, 1 H), 7.34-6.91 (m, 5 H), 6.68 (t, *J* = 8 Hz, 1 H), 6.50 (d, *J* = 8 Hz, 1 H), 6.38 (d, *J* = 8 Hz, 1 H), 6.00 (t, *J* = 8 Hz, 1 H), 5.07 (s, 2 H), 2.44 (s, 1.5 H), 2.32 (s, 1.5 H).

^{13}C NMR (151 MHz, $CDCl_3$) of conformers showed in spectrum.

IR (cm^{-1}): 3463*w*, 3375*m*, 1619*s*, 1501*m*, 1472*s*, 1454*s*, 1390*m,* 1187*w*, 807*m*, 746*s*, 726*m*, 507*m*.

HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{25}H_{20}BrN_2$) 427.0810; Found: 427.0926.



4•I:

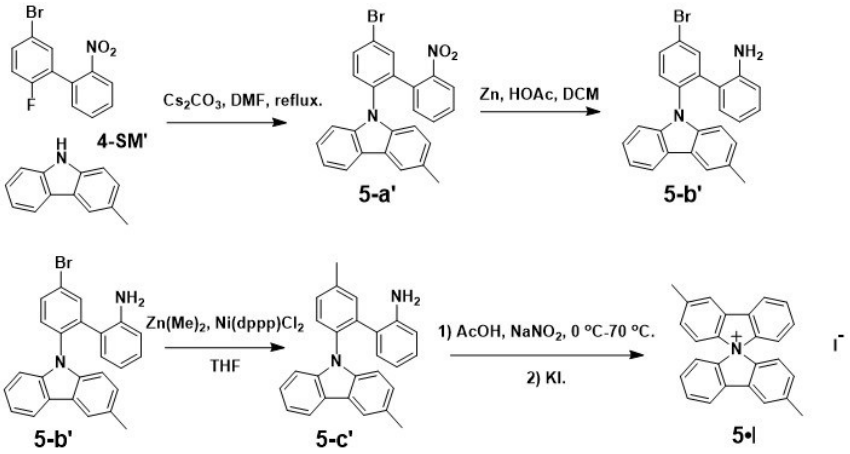
According to general procedure **M**, **4-b'** (300 mg, 0.7 mmol) was applied and **4•I** was obtained as a yellow solid (181 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.44 (d, *J* = 2 Hz, 1 H), 8.32-8.29 (m, 2 H), 8.21 (d, *J* = 8 Hz, 1 H), 7.87 (t, *J* = 8 Hz, 1 H), 7.81 (t, *J* = 8 Hz, 1 H), 7.66-7.59 (m, 3 H), 7.49 (t, *J* = 8 Hz, 1 H),7.03 (d, *J* = 8 Hz, 1 H), 6.97 (t, *J* = 8 Hz, 2 H), 6.79 (s, 1 H), 2.36 (s, 3 H).

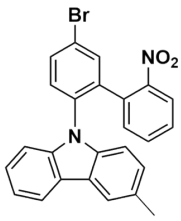
^{13}C NMR (151 MHz, $CDCl_3$): δ = 148.3, 147.8, 147.4, 146.7, 143.3, 134.8, 134.4, 133.6, 133.5, 133.4, 132.7, 131.7, 131.3, 130.3, 128.8, 127.5, 127.2, 124.5, 124.1, 124.0, 120.0, 118.5, 118.2, 118.2, 22.0.

IR (cm^{-1}): 3001*m*, 1622*w*, 1582*w*, 1466*s*, 1438*m*, 1408*m*, 1300*w*, 761*s*.

HR-MS (ESI): $[M-I]^+$ Calculated: ($C_{25}H_{17}BrN$) 410.0539; Found: 410.0540. [M-$C_{25}H_{17}BrN$]$^-$ Calculated: (I) 126.9050; Found: 126.9070.



Scheme 11: Synthetic route for **5•I**



5-a':

According to general procedure **D**, 3-methyl-carbazole[16](362 mg, 2.0 mmol) and **4-SM'** (596 mg, 2.0 mmol) was heated at 150 °C for 1 day. The pure product was obtained by flash chromatography (hexane/EtOAc = 100/1) as a yellow solid (275 mg, 30%). **5-a'** was existed as a pair of conformers caused by steric hindrance.

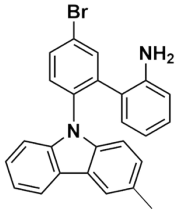
R_f = 0.1.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.01 (t, *J* = 8 Hz, 1 H), 7.95 (d, *J* = 2 Hz, 1 H), 7.88-7.85 (m, 2 H), 7.63 (d, *J* = 8 Hz, 1 H), 7.57-7.52 (m, 2 H), 7.44 (d, *J* = 8 Hz, 1 H), 7.34 (t, *J* = 8 Hz, 1 H), 7.29 (d, *J* = 8 Hz, 0.5 H), 7.17-7.14 (m, 1.5 H), 7.11-7.08 (m, 1 H), 7.01 (d, *J* = 8 Hz, 1 H),6.91 (d, *J* = 8 Hz, 0.5 H), 6.84 (d, *J* = 8 Hz, 0.5 H), 2.43(s, 1.5 H), 2.38(s, 1.5 H).

^{13}C NMR (101 MHz, $CDCl_3$) of conformers showed in spectrum.

IR (cm^{-1}): 3656*w*, 2335*s*, 1829*m*, 1684*m*, 1507*m*, 1457*m*, 1419*w,* 1362*w*, 1339*w*.

HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{25}H_{18}BrN_2O_2$) 457.0552; Found: 457.0544.



5-b':

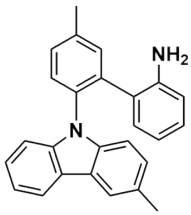
According to general procedure **L**, **5-a'** (260 mg, 0.61 mmol) was stirred at 0 °C for 20 minutes. The pure product was obtained by flash chromatography (hexane/DCM =1/1) as a white solid (171 mg, 70%). **5-b'** was existed as a pair of conformers caused by steric hindrance.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.06 (s, 0.5 H), 7.99 (s, 0.5 H), 7.91 (s, 0.5 H), 7.83 (s, 0.5 H), 7.79 (d, *J* = 2 Hz, 1 H), 7.76 (dd, *J* = 8, 2 Hz, 1 H), 7.43 (d, *J* = 8 Hz, 1 H), 7.36 (bs, 0.5 H), 7.24-7.17 (m, 3.5 H), 7.07 (s, 0.5 H), 7.00 (s, 0.5 H),6.68 (t, *J* = 8 Hz, 1 H), 6.49 (dd, *J* = 8, 2 Hz, 1 H), 6.39 (d, *J* = 7 Hz, 1 H), 6.00 (t, *J* = 8 Hz, 1 H), 5.06 (s, 2 H), 2.46-2.38 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) of conformers showed in spectrum.

IR (cm^{-1}): 3623*w*, 2834*w*, 2349*s*, 1597*m*, 1530*m*, 1256*w*, 924*m*.

HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{25}H_{20}BrN_2$) 427.0810; Found: 427.1365.

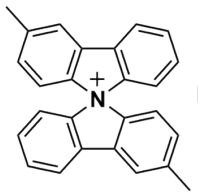


5-c':

A mixture of **5-b'** (100 mg, 0.23 mmol), dimethylzinc $Zn(Me)_2$ (1 M in Toluene, 0.46 mL, 0.46 mmol) and $Pd(dppf)Cl_2$ (19 mg, 0.023 mmol) in dry THF (4 mL, 0.06 M) was charged in 10 mL 2-necked flask at room temperature under nitrogen atmosphere. Then the solution was heated to 60 °C and stirred overnight. The reaction was quenched with H_2O and extracted with EtOAc. The pure product was obtained by flash chromatography (hexane/DCM = 1/1) as a brownish solid (68 mg, 80%).

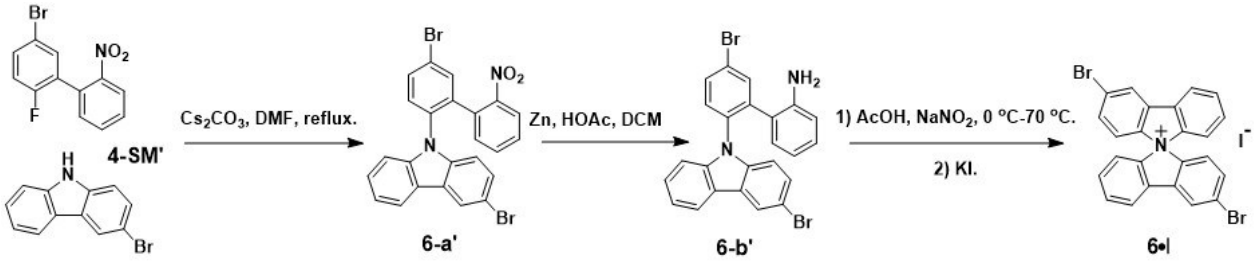
5_{DD}-c was existed as a pair of conformers caused by steric hindrance.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 7 Hz, 0.5 H), 7.95 (d, *J* = 7 Hz, 0.5 H), 7.82 (s, 0.5 H), 7.79 (s, 0.5 H), 7.47 (s, 1 H), 7.39 (d, *J* = 8 Hz, 1 H), 7.35 (d, *J* = 8 Hz, 1 H), 7.30-7.20 (m, 1 H), 7.16-7.01 (m, 4 H), 6.79 (t, *J* = 8 Hz, 1 H), 6.73 (d, *J* = 8 Hz, 0.5 H), 6.67 (d, *J* = 8 Hz, 0.5 H), 6.45 (bs, 1 H), 6.34-6.29 (m, 1 H), 2.51-2.45 (m, 6 H).
^{13}C NMR (101 MHz, $CDCl_3$) of conformers showed in spectrum.
IR (cm^{-1}): 3853*w*, 2970*w*, 2343*m*, 1653*w*, 1569*m*, 1499*s*, 1277*m,* 1202*m*, 1154*w*, 924*s*.
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{26}H_{23}N_2$) 363.1861; Found: 363.2175.

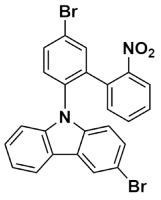


5•I:
According to general procedure **M**, **5-c'** (117 mg, 0.32 mmol) was applied and **5•I** was obtained as a yellow solid (91 mg, 60%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 8 Hz, 2 H), 8.12 (s, 2 H), 7.81 (t, *J* = 8 Hz, 2 H), 7.52 (t, *J* = 8 Hz, 2 H), 7.30 (d, *J* = 8 Hz, 2 H), 6.93 (d, *J* = 8 Hz, 2 H), 6.83 (d, *J* = 8 Hz, 2 H), 2.58 (s, 6 H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 148.4, 145.6, 144.3, 144.3, 133.2, 132.5, 131.6, 131.5, 124.2, 123.9, 118.3, 117.8, 21.9.
IR (cm^{-1}): 3024*w*, 2918*m*, 1614*m*, 1488*s*, 1455*s*, 1315*w*, 1231*m*, 1028*w*, 907*m*, 800*m*, 744*s*.
HR-MS (ESI): $[M-I]^+$ Calculated: ($C_{26}H_{20}N$) 346.1590; Found: 346.1490. [M-$C_{26}H_{20}N]^-$ Calculated: (I) 126.9050; Found: 126.9030.

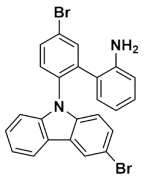


Scheme 12: Synthetic route for **6•I**

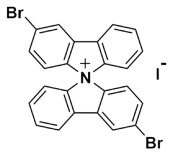


6-a':
According to general procedure **D**, 3-bromo carbazole (534 mg, 1.8 mmol) and **4-SM'** (534 mg, 1.8 mmol) in DMF (7 mL) were stirred at 150 °C for 24 h. The pure product was obtained by flash chromatography (hexane/acetone = 50/1) as a yellow solid (817 mg, 87%).
6-a' was existed as a pair of conformers caused by steric hindrance.
R_f = 0.2.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.09 (s, 1 H), 7.93 (t, *J* = 8 Hz, 1 H),7.75-7.71 (m, 2 H), 7.65-7.61 (m, 1 H), 7.39-7.30 (m, 4 H), 7.23-7.15 (m, 4 H), 6.94 (d, *J* = 8 Hz, 0.5 H), 6.79 (d, *J* = 8 Hz, 0.5 H).
^{13}C NMR (151 MHz, $CDCl_3$) of conformers showed in spectrum.
IR (cm^{-1}): 1524*s*, 1496*m*, 1468*m*, 1357*m*, 1019*m*, 876*w*, 802*w,* 768*m*, 704*w*.
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{24}H_{15}Br_2N_2O_2$) 520.9500; Found: 520.9502.

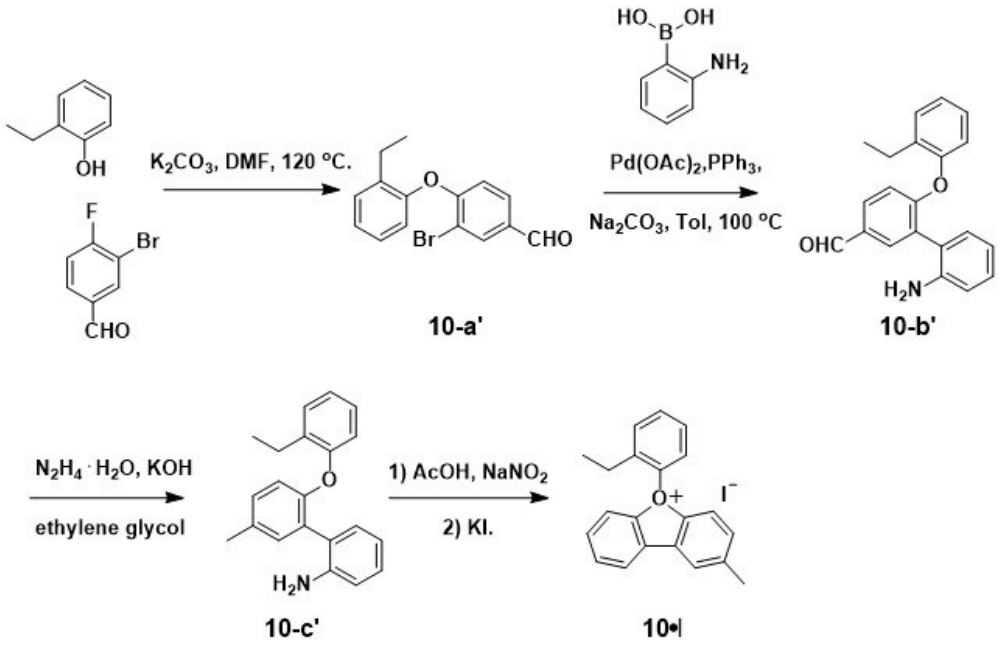


6-b':
According to general procedure **L**, **6-a'** (397 mg, 0.76 mmol) was stirred at 0 °C for 20 minutes. The pure product was obtained by flash chromatography (hexane/DCM =1/1) as a white solid (300 mg, 80%).
6-b' was existed as a pair of conformers caused by steric hindrance.
R_f = 0.2.
^{1}H NMR (400 MHz, DMSO-d_6): 8.37-8.31 (m, 1 H), 8.19-8.10 (m, 1 H), 7.80-7.78 (m, 2 H),7.50-7.13 (m, 6 H), 6.69 (t, *J* = 7 Hz, 1 H), 6.48 (d, *J* = 8 Hz, 1 H), 6.37 (s, 1 H), 6.01 (s, 1 H), 5.03 (s, 2 H).
^{13}C NMR (151 MHz, $CDCl_3$) of conformers showed in spectrum.
IR (cm^{-1}): 2349*s*, 1665*w*, 1591*w*, 1289*w*, 1255*w,* 923*w*.
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{24}H_{17}Br_2N_2$) 490.9758; Found: 490.9749.

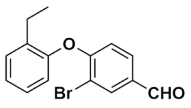


6•I:
According to general procedure **M**, **6-b'** (300 mg, 0.61 mmol) was applied and **6•**I was obtained as a white solid (201 mg, 62%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.43 (s, 2 H), 8.30 (d, *J* = 8 Hz, 2 H), 7.85 (t, *J* = 8 Hz, 2 H), 7.65 (d, *J* = 9 Hz, 2 H), 7.60 (t, *J* = 8 Hz, 2 H), 7.06 (d, *J* = 7 Hz, 2 H), 7.03 (d, *J* = 8 Hz, 2 H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 147.9, 146.2, 134.9, 133.7, 133.5, 132.8, 130.4, 127.8, 127.2, 124.5, 120.1, 118.6.
IR (cm^{-1}): 3005*w*, 2775*w*, 2530*w*, 1633*w*, 1444*w*, 1135*s*, 1054*m*, 857*w*.
HR-MS (ESI): $[M-I]^+$ Calculated: ($C_{24}H_{14}Br_2N$) 473.9488; Found: 473.9476. [M-$C_{24}H_{14}Br_2N]^-$ Calculated: (I) 126.9050; Found: 126.9086.



Scheme 13: Synthetic route for **10•**I



10-a':

According to general procedure **H**, 2-ethylphenol (356 mg, 3 mmol) and 3-bromo-4-fluorobenzaldehyde (621 mg, 3 mmol) in DMF (10 mL) were stirred at 120 °C under nitrogen atomosphere for 6 h. The pure product was obtained by flash chromatography (hexane/EtOAc= 10/1) as a colorless oil (818 mg, 89%).

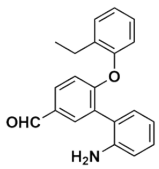
R_f = 0.2.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.86 (s, 1 H), 8.17 (d, *J* = 2 Hz, 1 H), 7.68 (dd, *J* = 8, 2 Hz, 1 H), 7.34 (dd, *J* = 8, 2 Hz, 1 H), 7.28-7.20 (m, 1 H), 6.97 (dd, *J* = 8, 2 Hz, 1 H), 6.73 (d, *J* = 8 Hz, 1 H), 2.57 (q, *J* = 8 Hz, 2 H), 1.19 (t, *J* = 8 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ =189.7, 160.1, 152.4, 136.3, 135.4, 132.0, 130.6, 130.5, 127.7, 126.1, 120.9, 116.1, 113.3, 23.3, 14.5.

IR (neat, cm^{-1}): 2969*m*, 2934*w*, 2874*w*, 1695*s*, 1595*s*, 1480*s*, 1452*m,* 1371*s*, 1250*m*, 1040*m*, 899*m*, 750*m*.

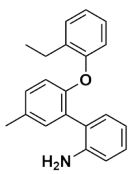
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{15}H_{14}BrO_2$) 305.0177; Found: 305.0190.



10-b':

According to general procedure **K**, **10-a'** (305 mg, 1 mmol) and 2-aminobenzeneboronic acid (169 mg, 1.2 mmol) in Tol (10 mL) were stirred at 100 °C under nitrogen atomosphere for 6 h. The crude was subjected to next step directly.

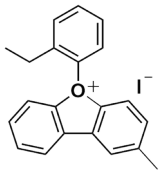
The **10-b'** were instable in air.



10-c':

According to general procedure **J**, **10-b'** (379 mg, 1.2 mmol) was applied and **10-c'** was obtained by flash chromatography (hexane/DCM= 5/1) as a yellowish oil (296 mg, 82%).

R_f = 0.2.
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.18 (d, *J* = 2 Hz, 1 H), 7.15 (dd, *J* = 8, 2 Hz, 1 H), 7.12-7.06 (m, 3 H), 7.05 (td, *J* = 8, 2 Hz, 1 H), 6.97 (td, *J* = 8, 2 Hz, 1 H), 6.80-6.74 (m, 4 H), 2.56 (q, *J* = 8 Hz, 2 H), 2.34 (s, 3 H), 1.08 (t, *J* = 8 Hz, 3 H).
^{13}C NMR (151 MHz, $CDCl_3$) δ = 155.1, 152.5, 144.0, 134.9, 133.2, 132.8, 131.1, 130.3, 129.6, 129.6, 128.6, 126.9, 124.8, 123.2, 118.7, 118.5, 118.0, 116.0, 23.4, 20.8, 14.4.
IR (neat, cm^{-1}): 2950*w*, 2812*w*, 2349*m*, 1653*m*, 1540*w,* 1498*s*, 1471*m*, 1219*s*, 905*w*.
HR-MS (ESI): $[M+H]^+$ Calculated: ($C_{21}H_{22}NO$) 304.1701; Found: 304.1701.

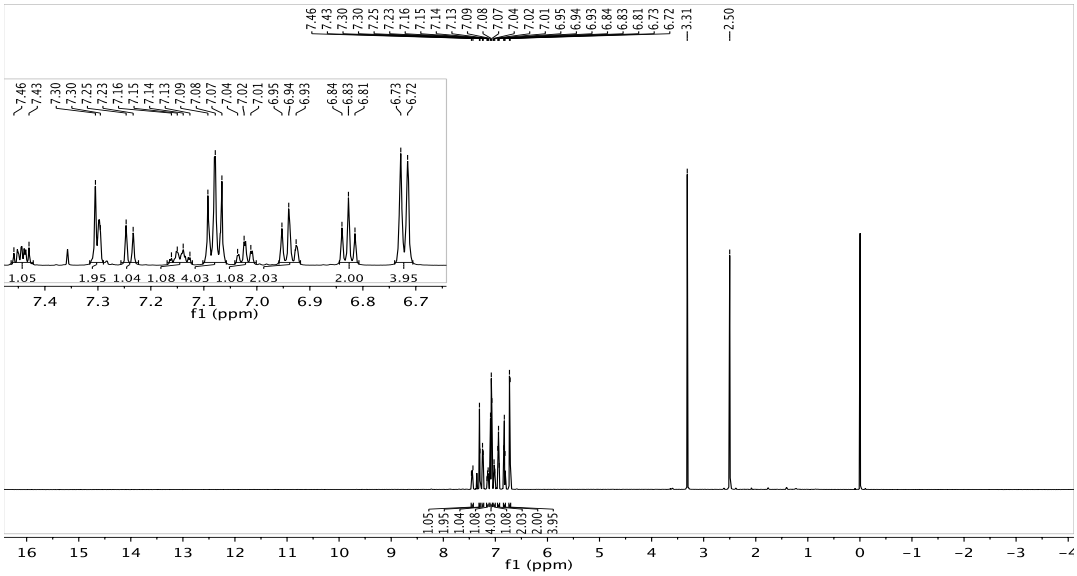


10•I:
Similar to general procedure **M**, **10-c'** (140 mg, 0.46 mmol) was applied. After adding KI, the solution was dried by rotary evaporator and the residue was purified by flash chromatography (hexane/DCM = 5/1 to DCM/MeOH= 10/1). **10•I** was obtained as a white solid (191 mg, 60%).
R_f = 0.1 (DCM).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (d, *J* = 7 Hz, 1 H), 8.21 (s, 1 H), 7.94 (d, *J* = 8 Hz, 1 H), 7.86-7.71 (m, 5 H), 7.55 (t, *J* = 7 Hz, 2 H), 7.43 (d, *J* = 8 Hz, 1 H), 2.62 (s, 3 H), 2.53 (q, *J* = 8 Hz, 2 H), 1.19 (t, *J* = 8 Hz, 3 H).
^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.1, 156.5, 152.5, 141.5, 136.5, 133.9, 132.9, 132.0, 131.2, 131.0, 130.7, 124.7, 124.7, 121.7, 121.1, 120.8, 110.9, 110.4, 22.1, 21.4, 14.1.
IR (cm^{-1}): 3005*w*, 2775*w*, 2530*w*, 1590*w*, 1463*w*, 1260*m*, 1111*s*, 1071*m*, 963*m*.
HR-MS (ESI): $[M-I]^+$ Calculated: ($C_{21}H_{19}O$) 287.1430; Found: 287.1341. $[M-C_{21}H_{19}O]^-$ Calculated: (I) 126.9050; Found: 126.9030.

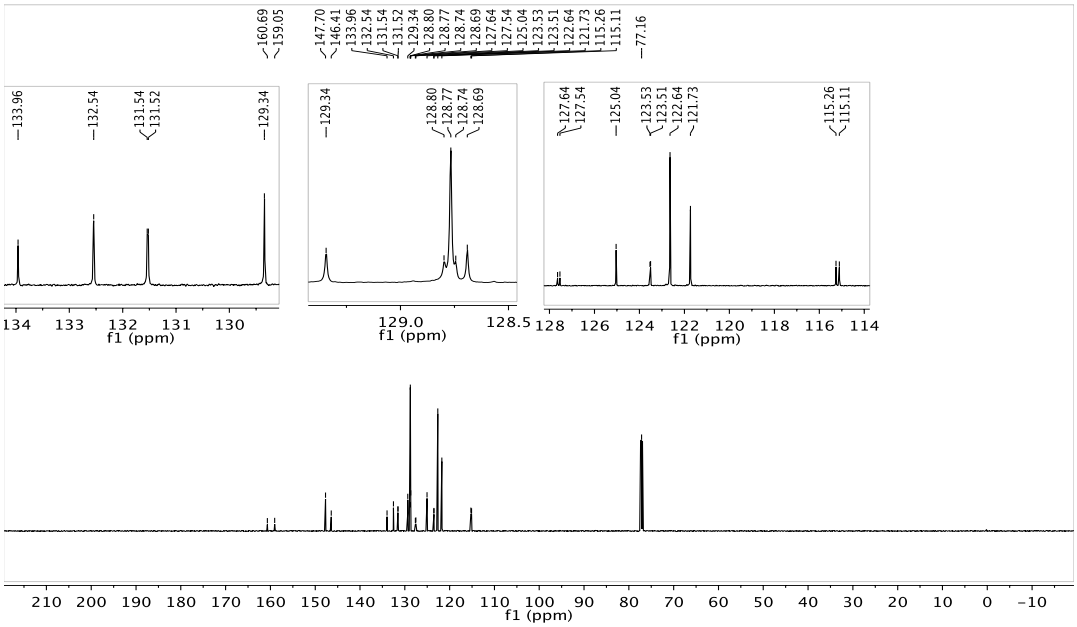
NMR spectra

Spectra for 1-5,7-10 by CFA.

1-b

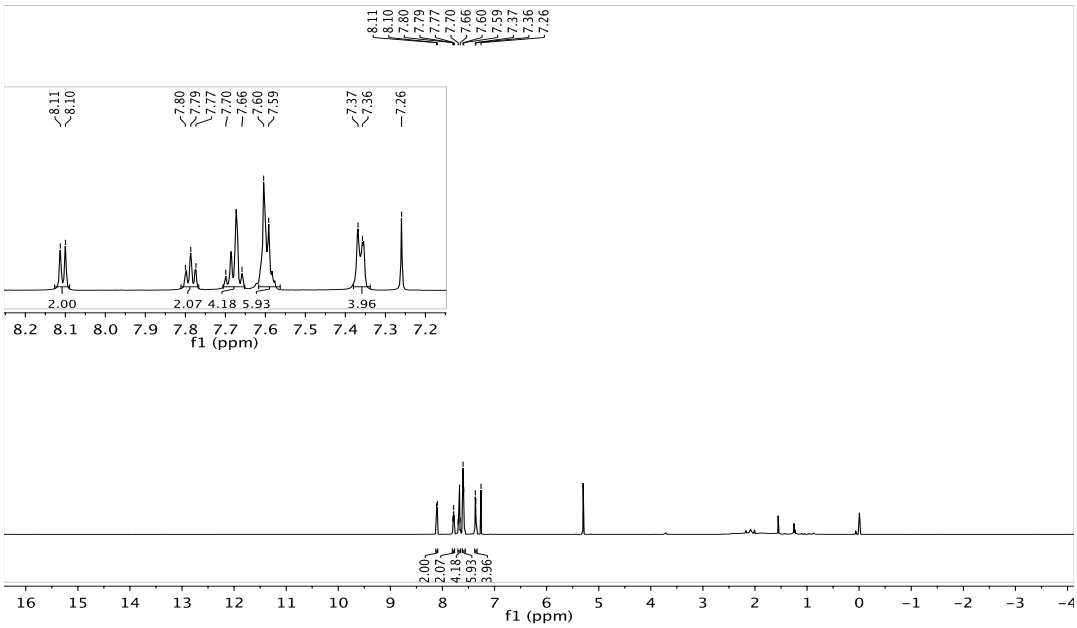


^{1}H-NMR (600 MHz, DMSO-d_6) spectrum of **1-b**.

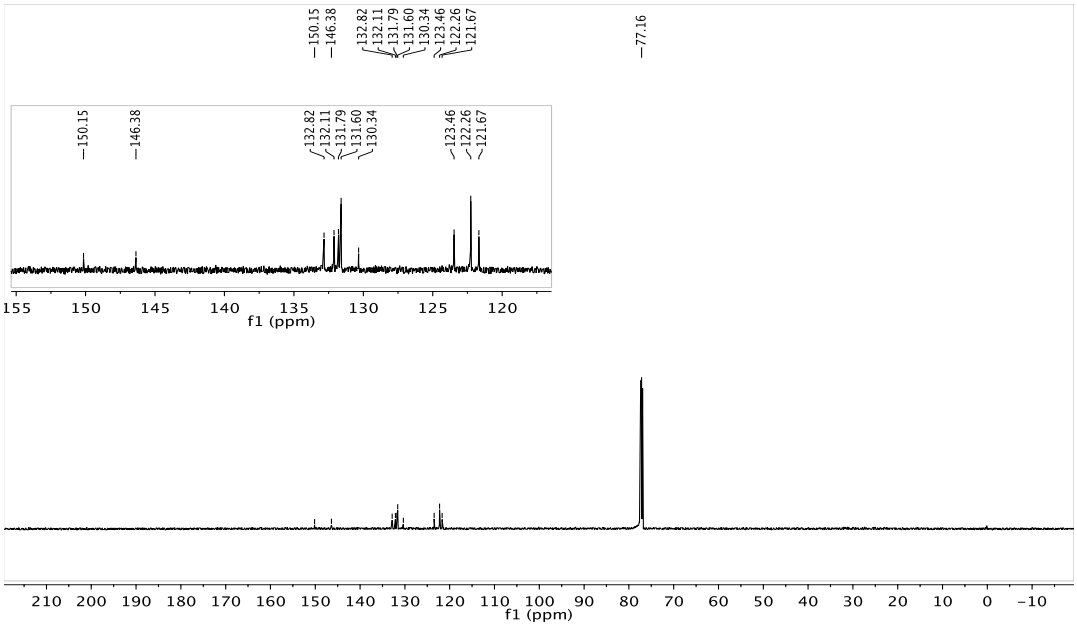


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **1-b**.

1•Cb

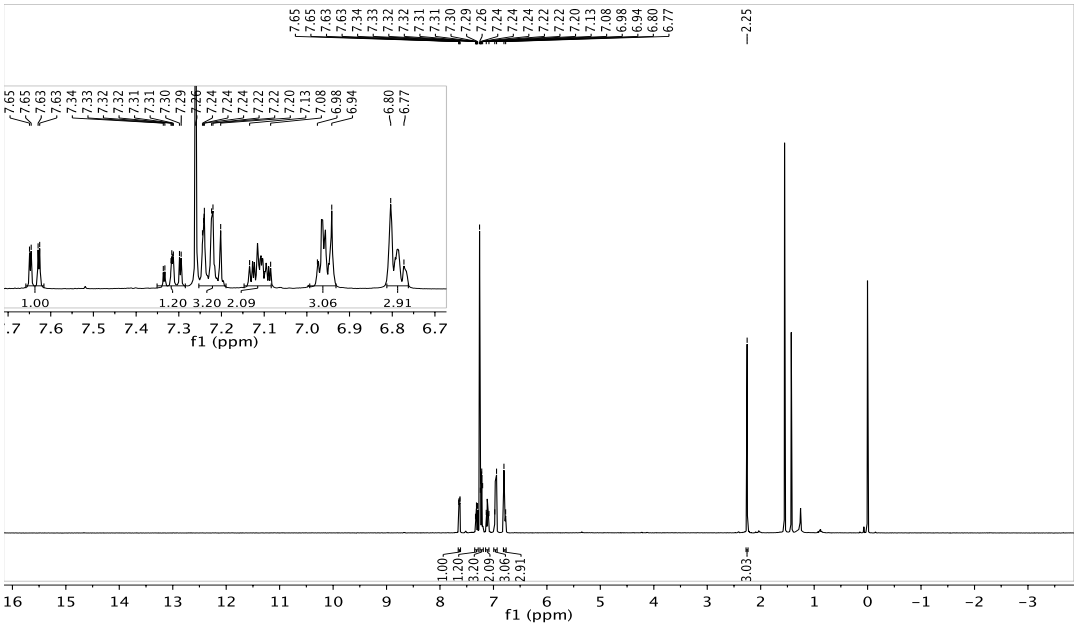


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **1**•Cb.

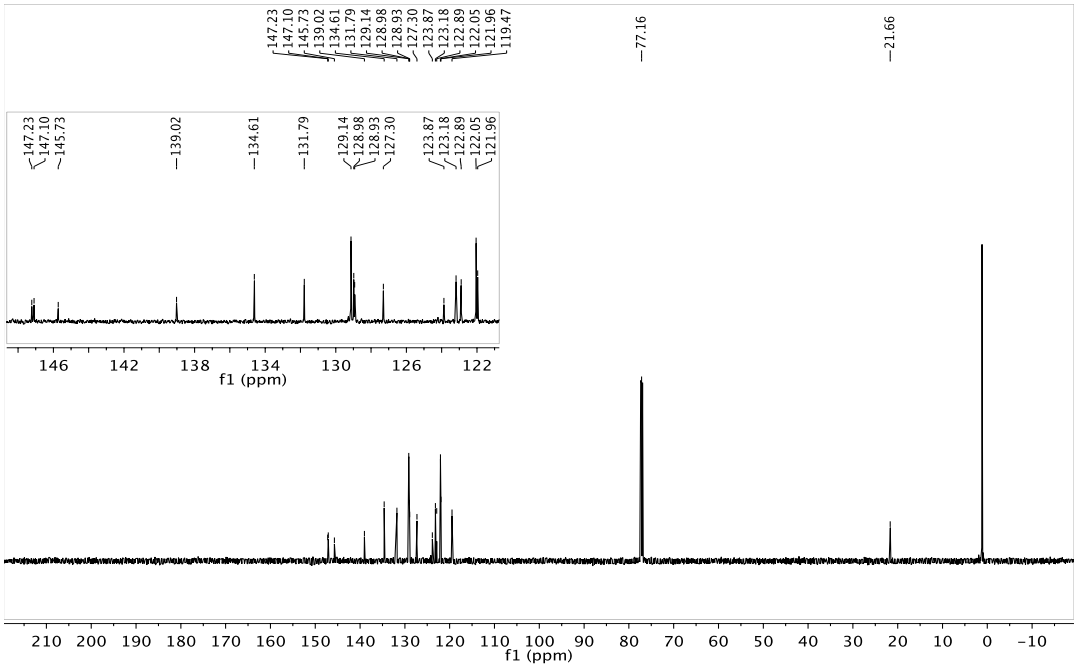


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **1**•Cb.

2-a

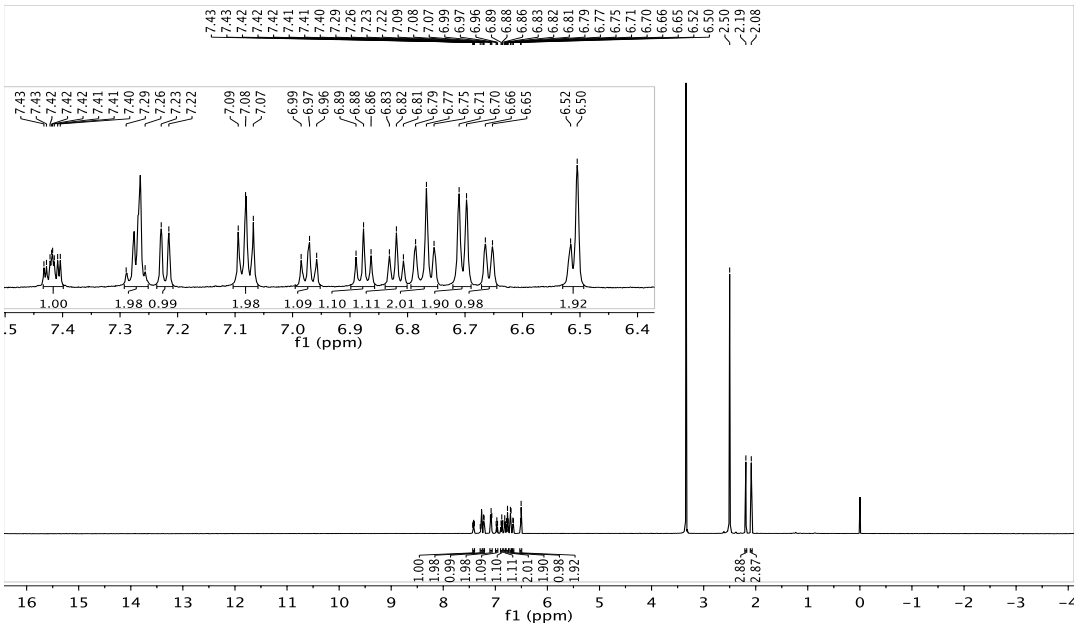


^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **2-a**.

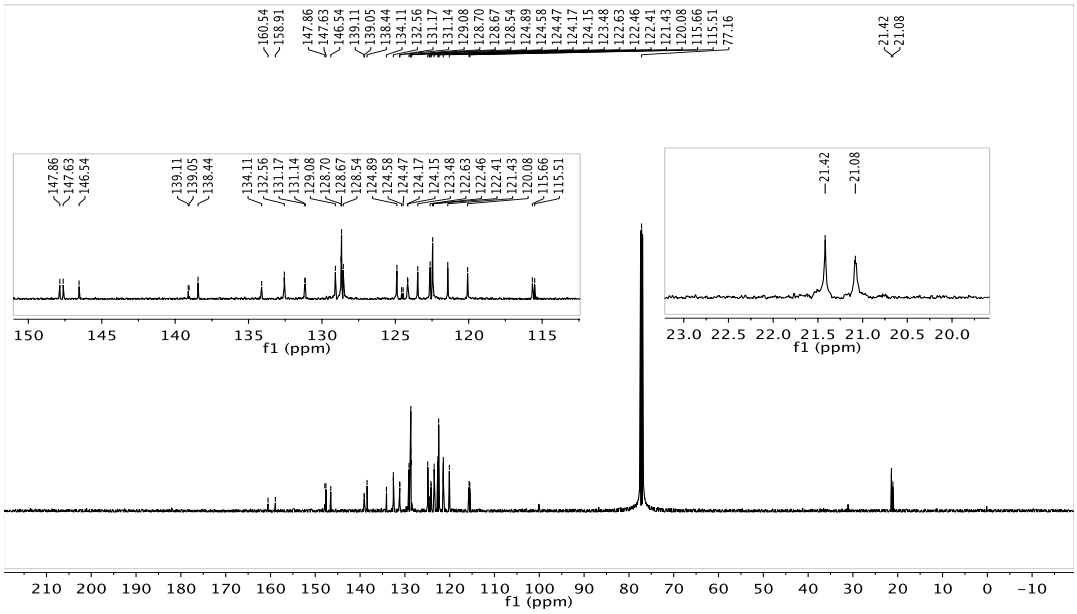


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **2-a**.

2-b

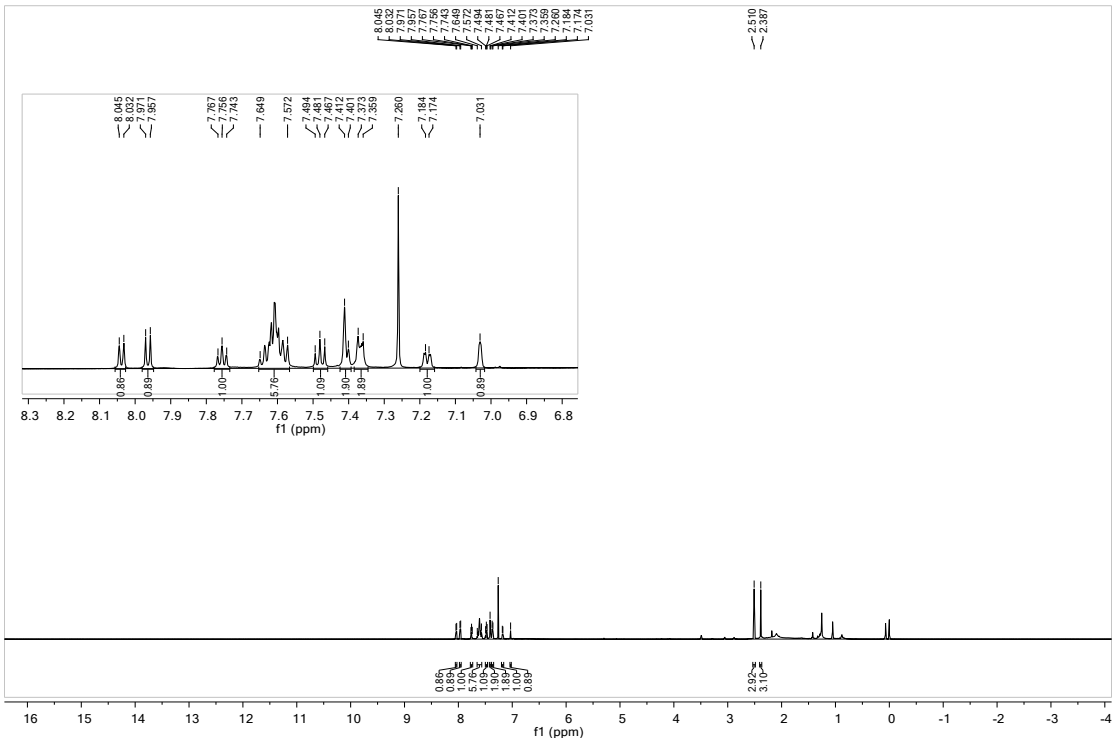


^{1}H-NMR (600 MHz, DMSO-d_6) spectrum of **2-b**.

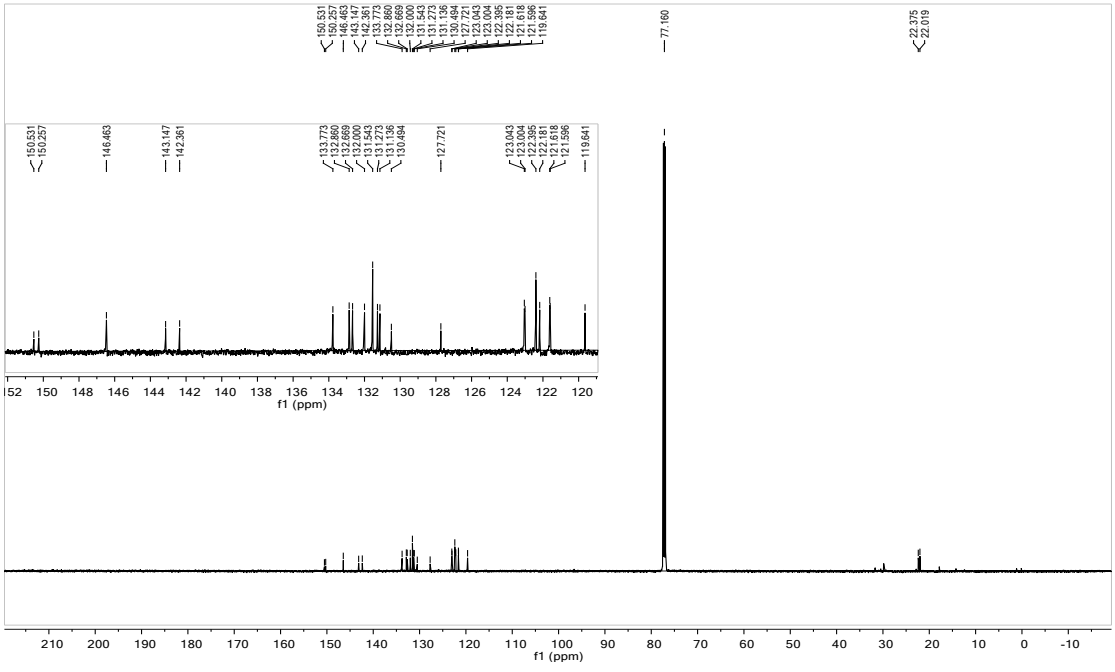


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **2-b**.

2•Cb

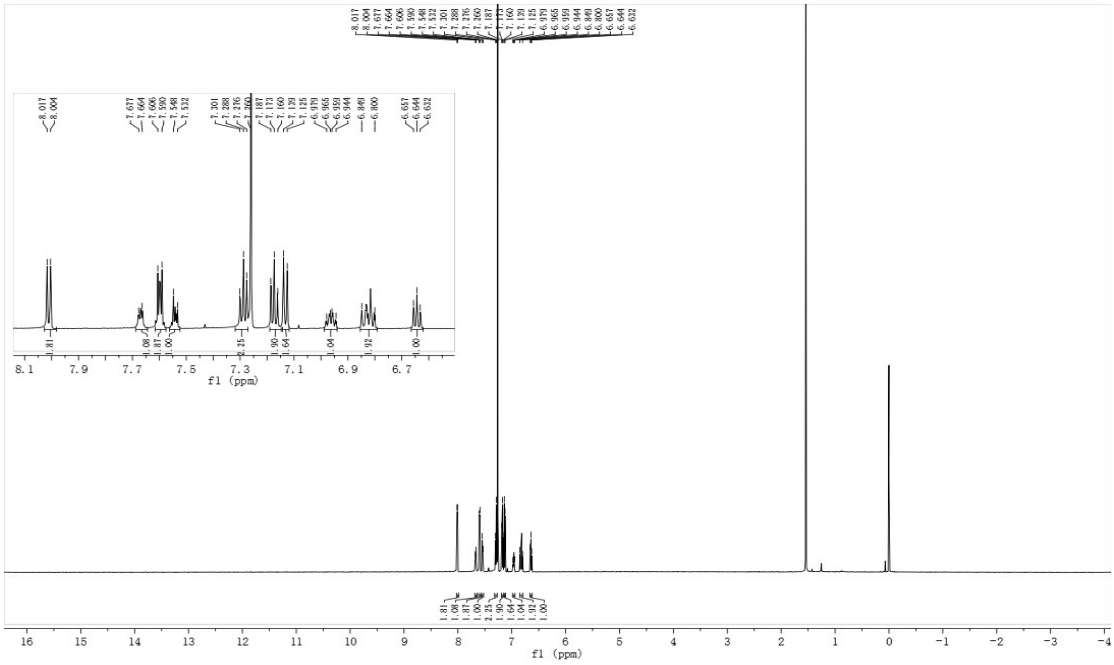


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **2**•Cb.

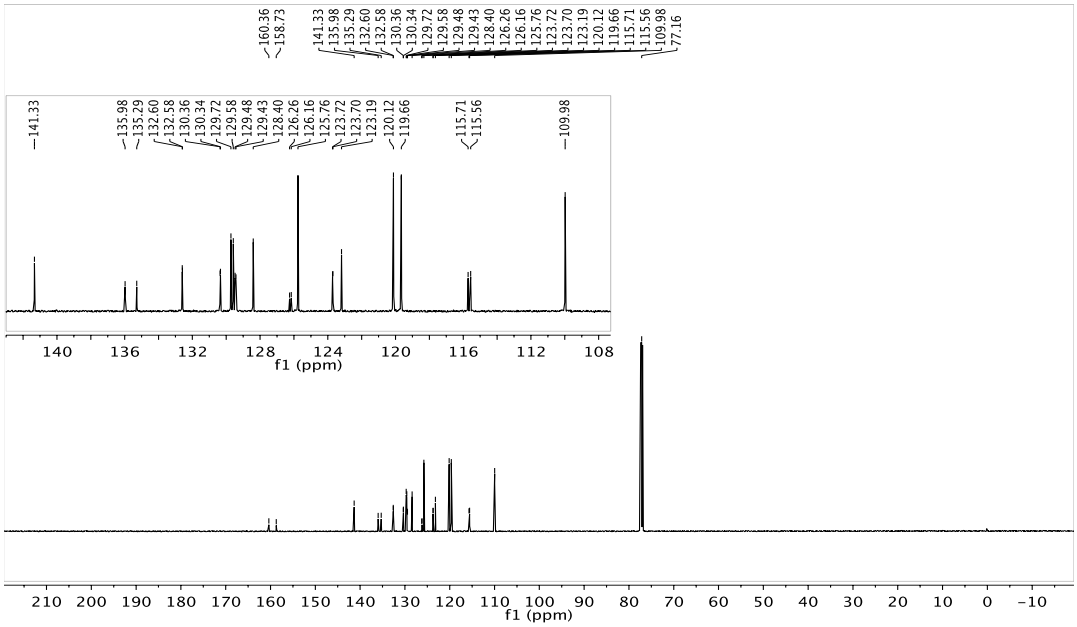


^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **2•**Cb.

3-b

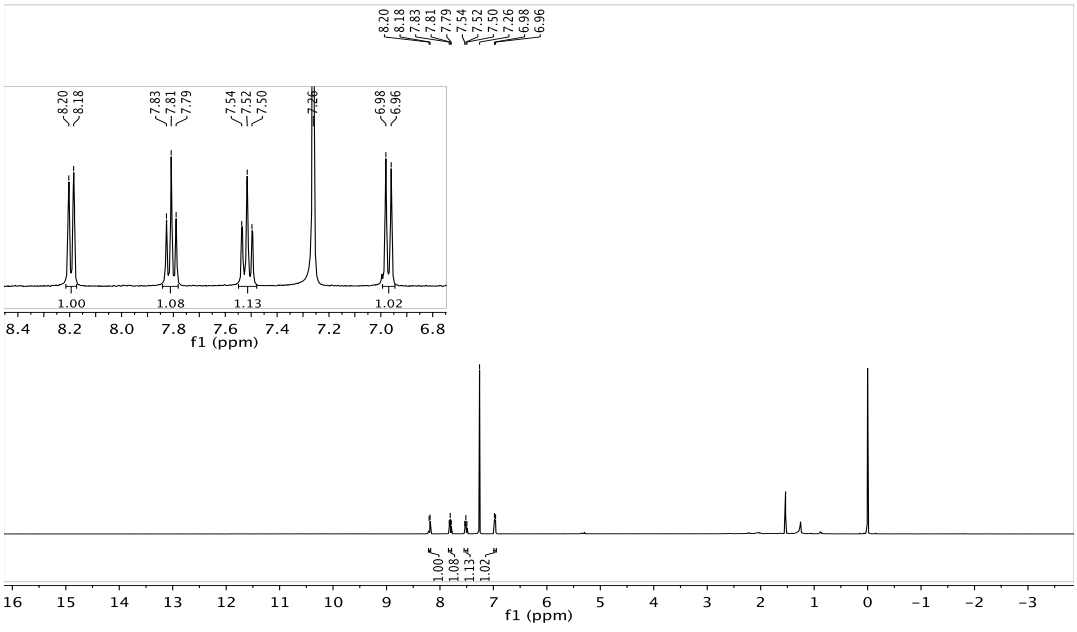


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **3-b**.

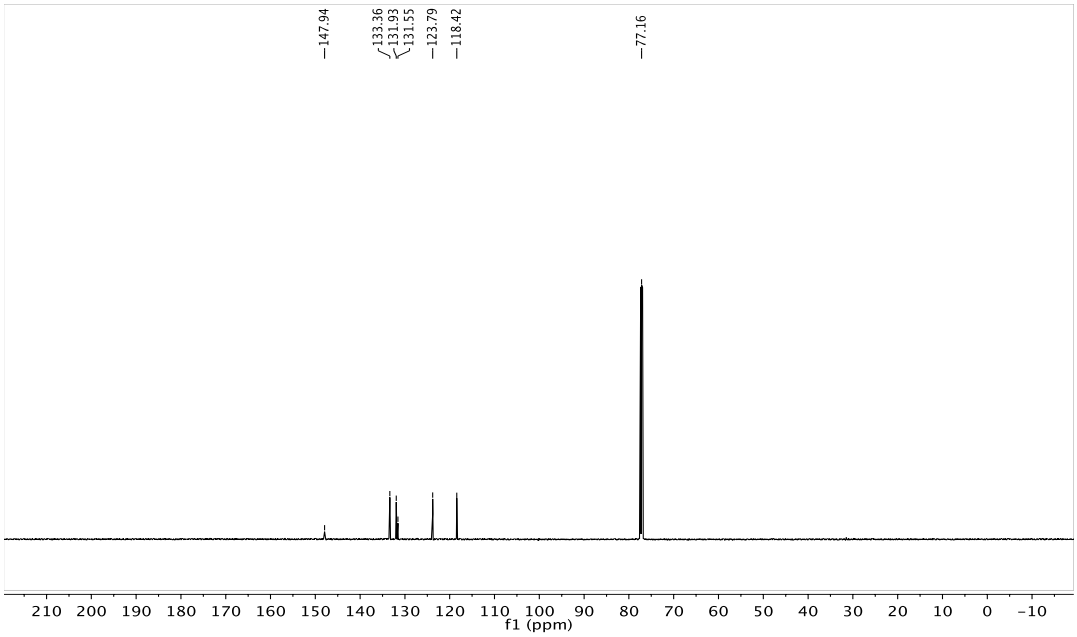


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **3-b**.

3•Cb

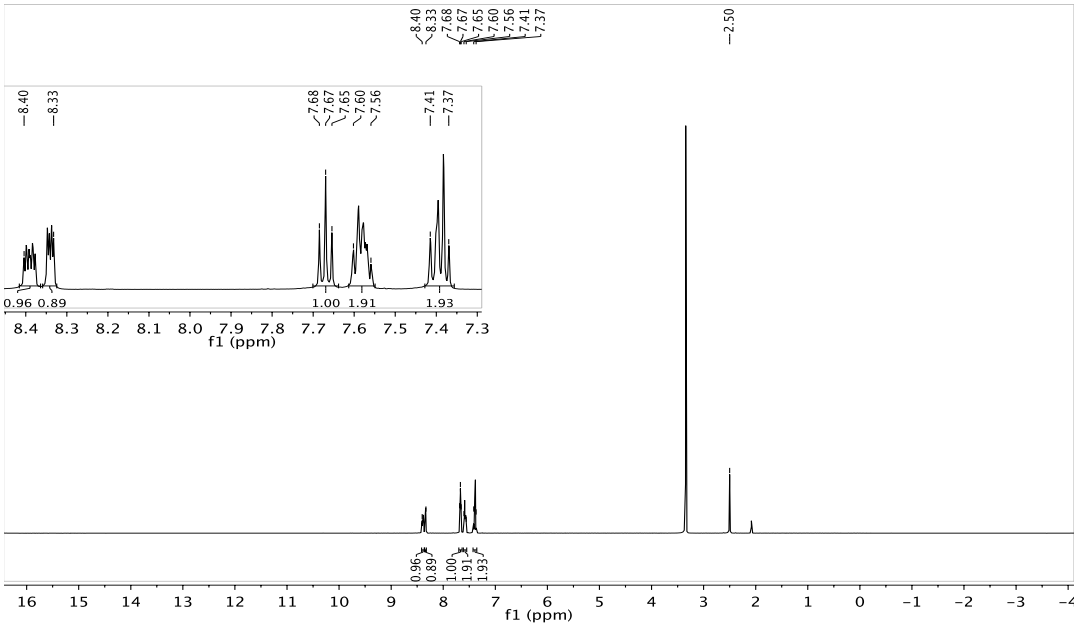


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **3**•Cb.

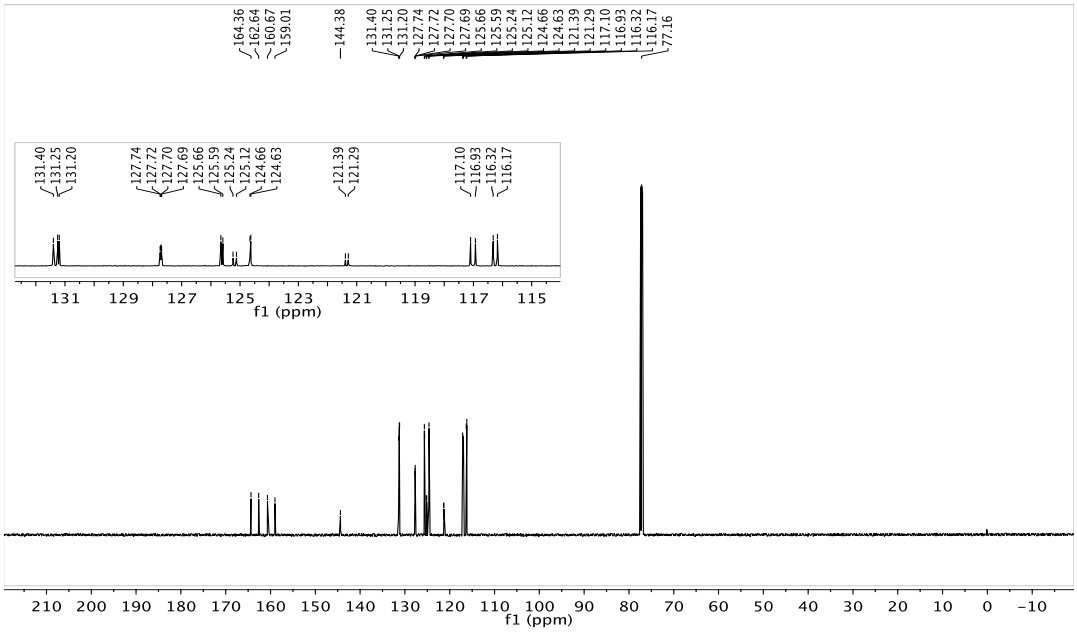


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **3**•Cb.

4-SM

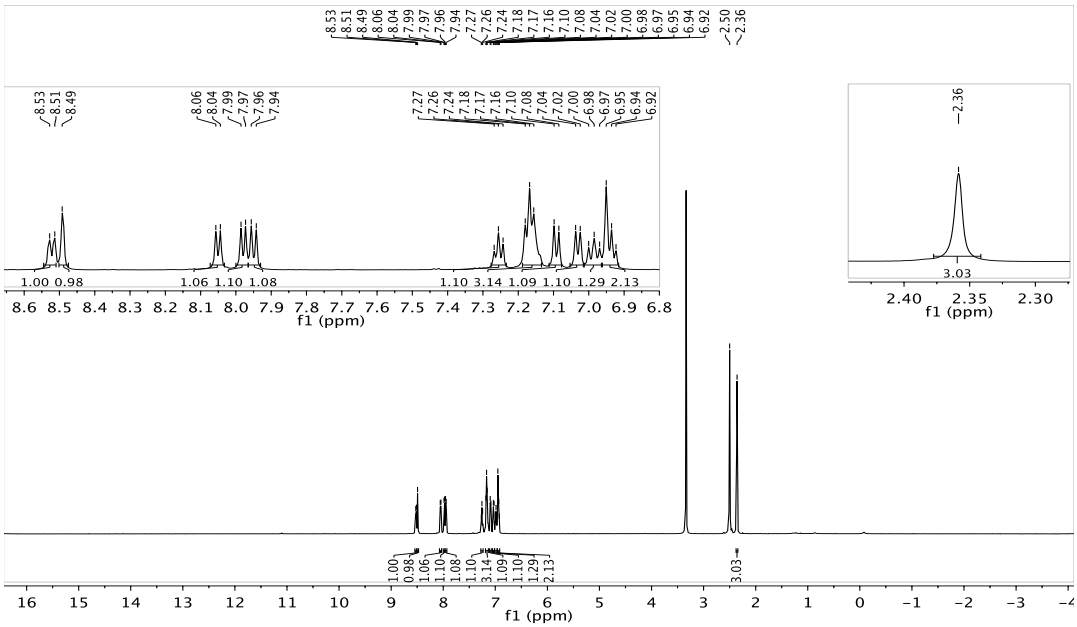


^{1}H-NMR (600 MHz, DMSO-d_6) spectrum of **4-SM**.

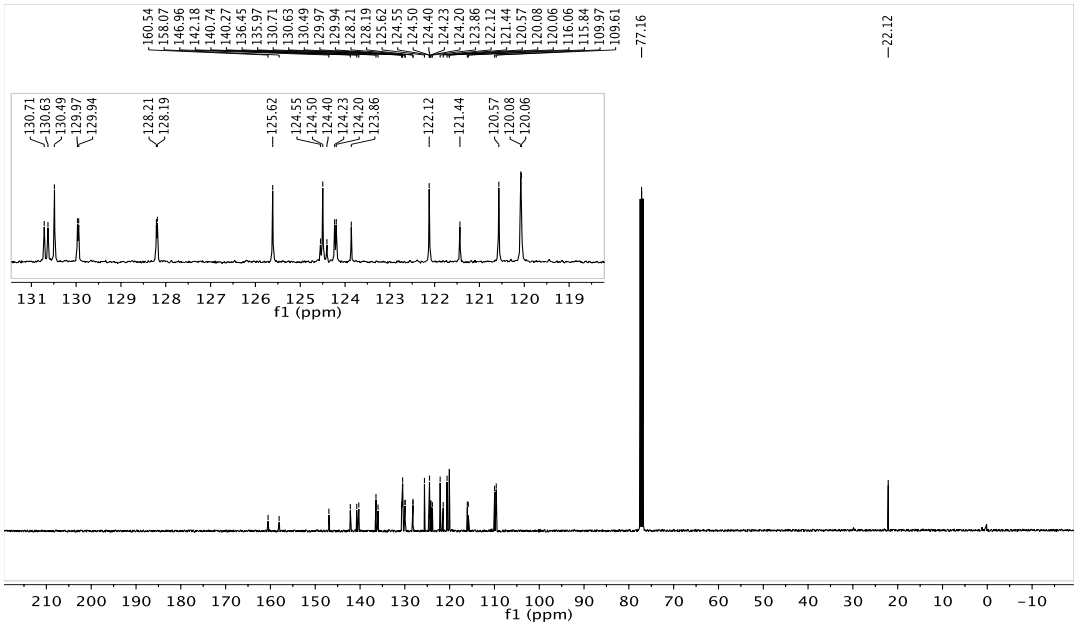


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **4-SM**.

4-a

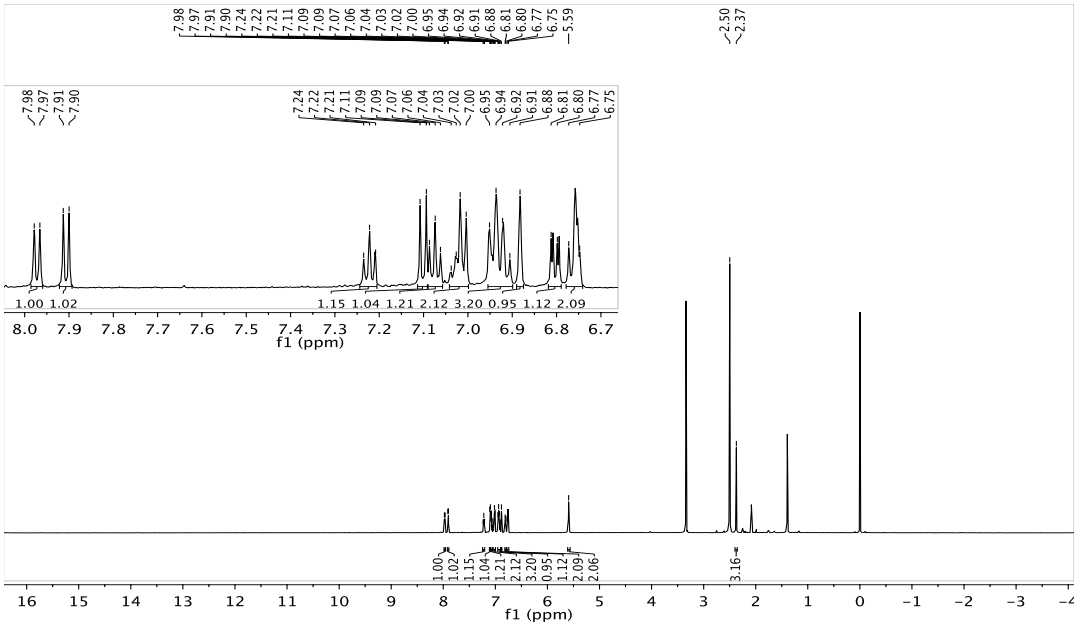


^{1}H-NMR (600 MHz, DMSO-d_6) spectrum of **4-a**.

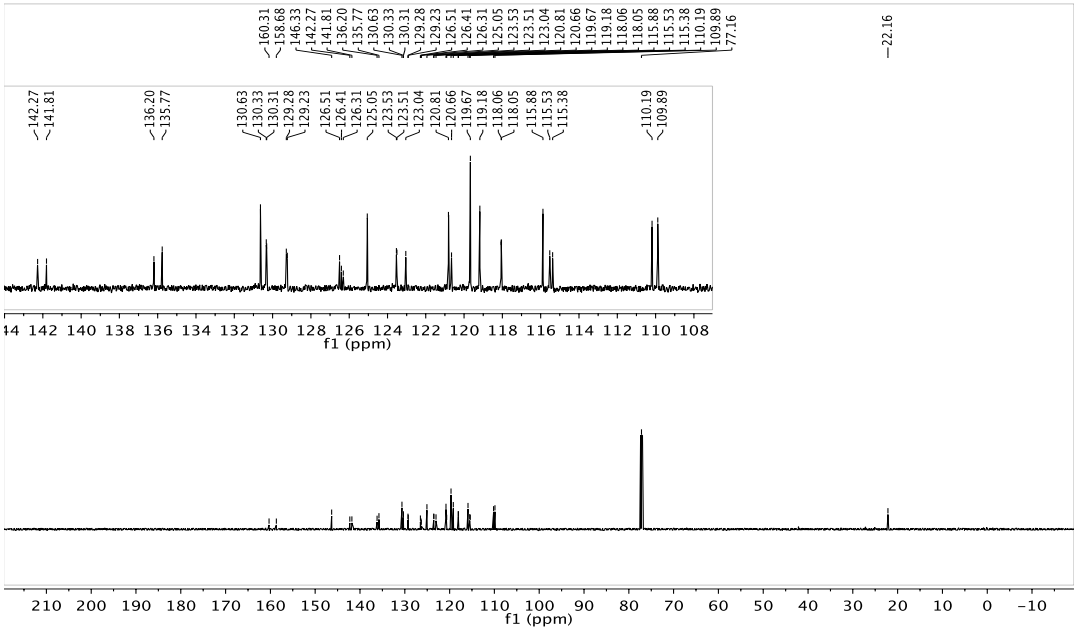


^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **4-a**.

4-b

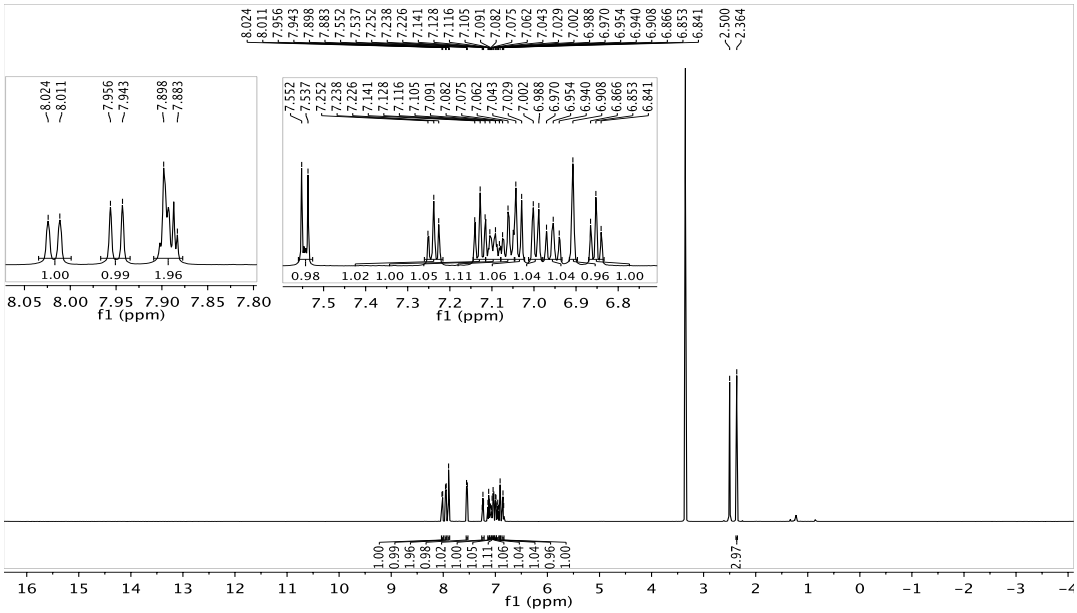


^{1}H-NMR (600 MHz, DMSO-d_6) spectrum of **4-b**.

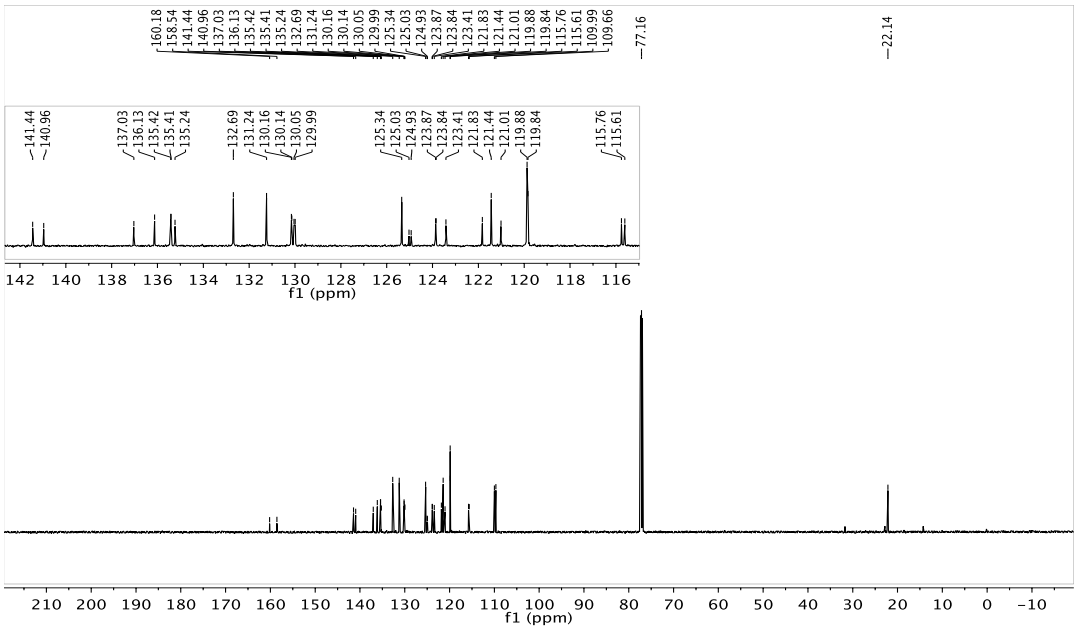


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **4-b**.

4-c

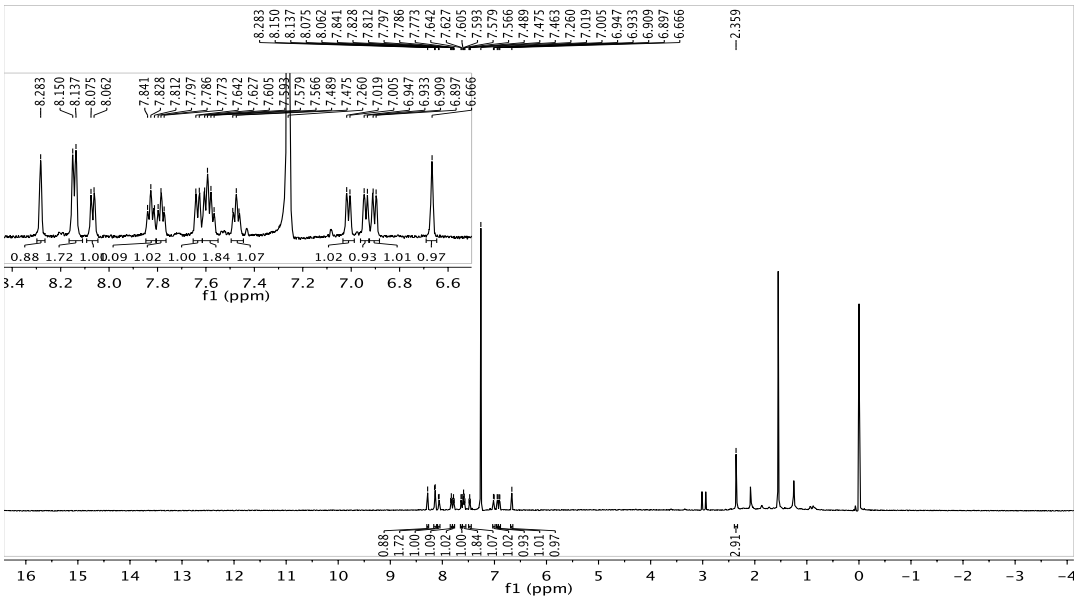


^{1}H-NMR (600 MHz, DMSO-d_6) spectrum of **4-c**.

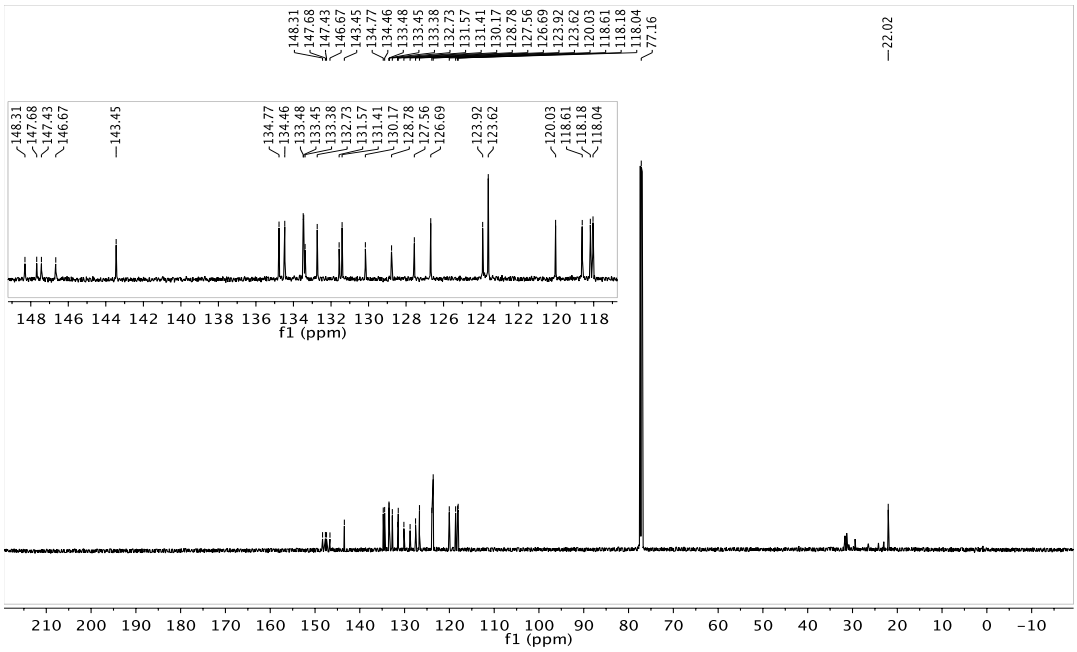


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **4-c**.

4•Cb

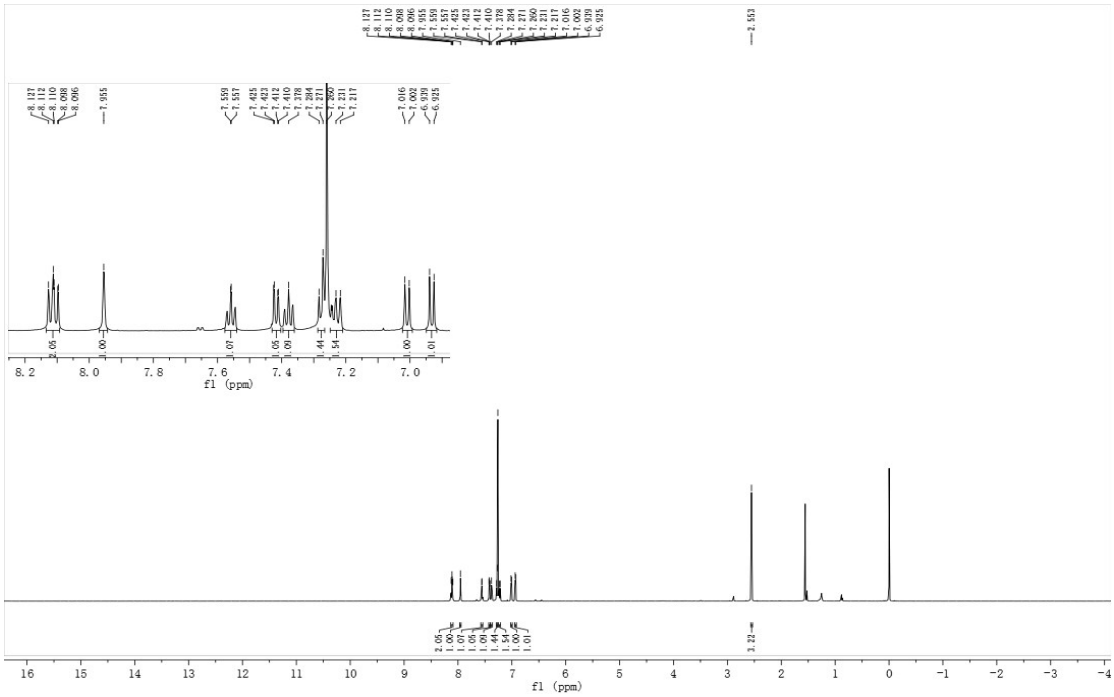


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **4**•Cb.

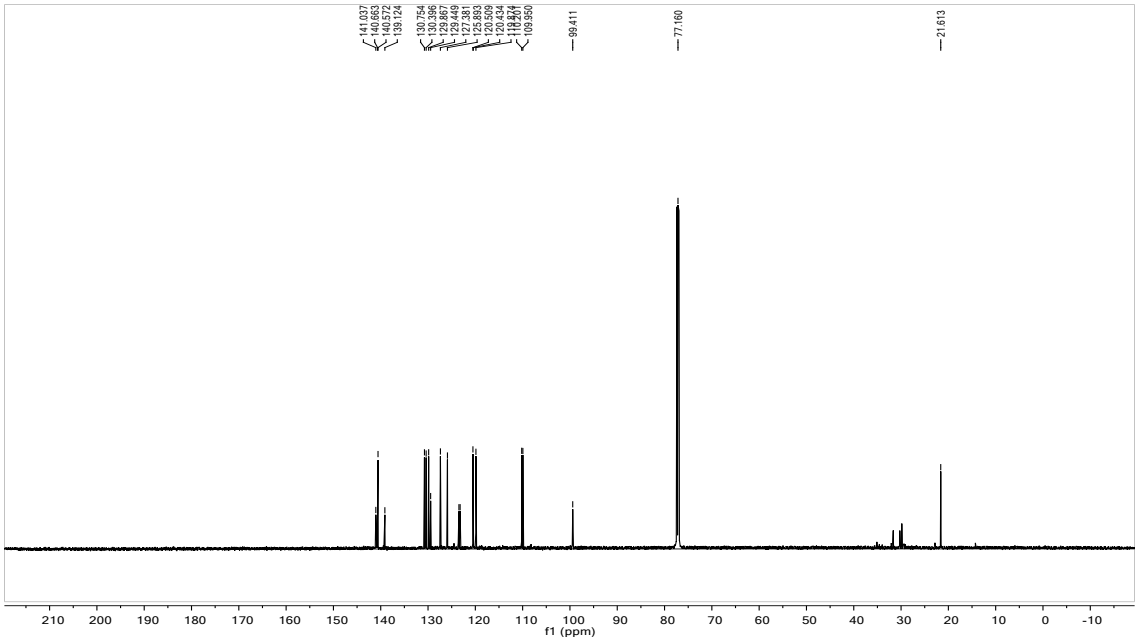


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **4**•Cb.

5-a

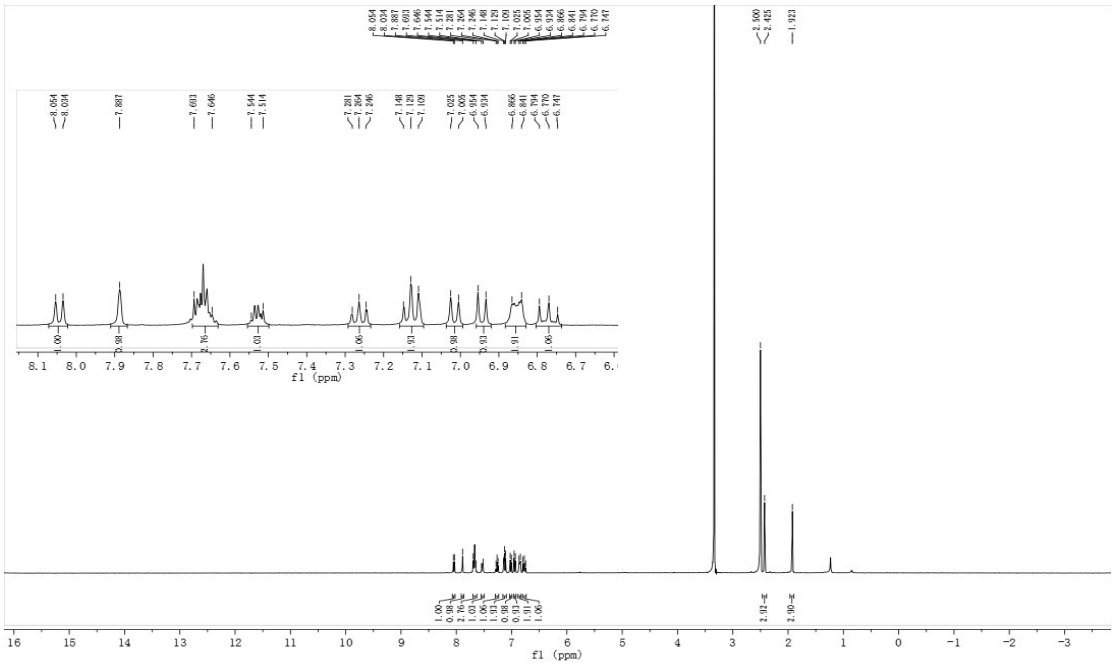


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **5-a**.

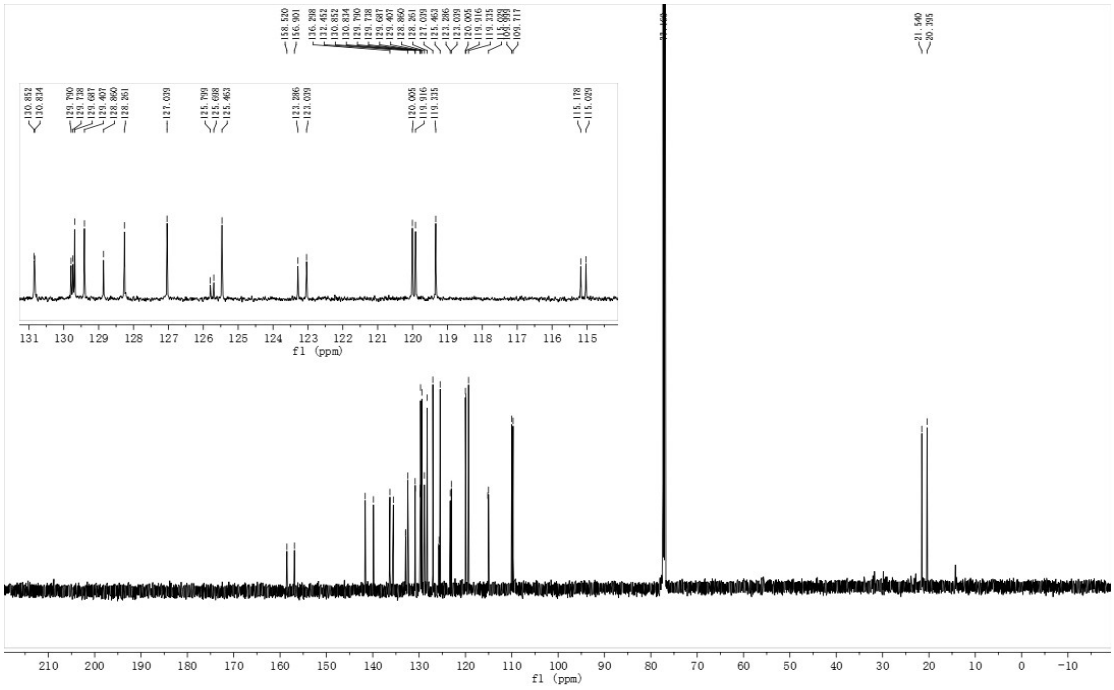


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **5-a**.

5-b

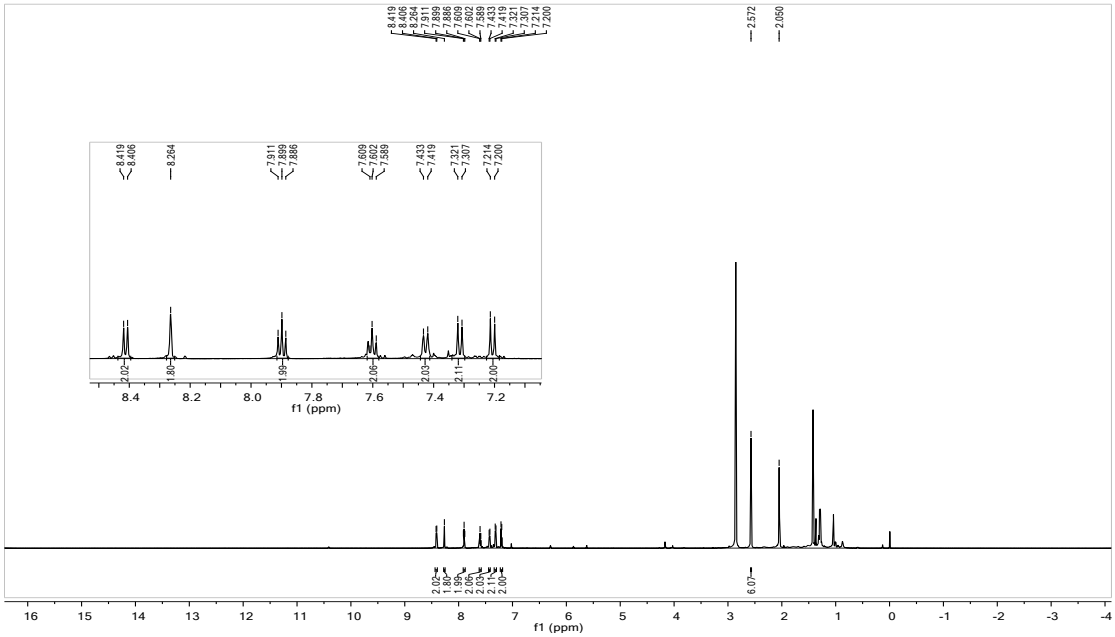


^{1}H-NMR (400 MHz, DMSO-d_6) spectrum of **5-b**.

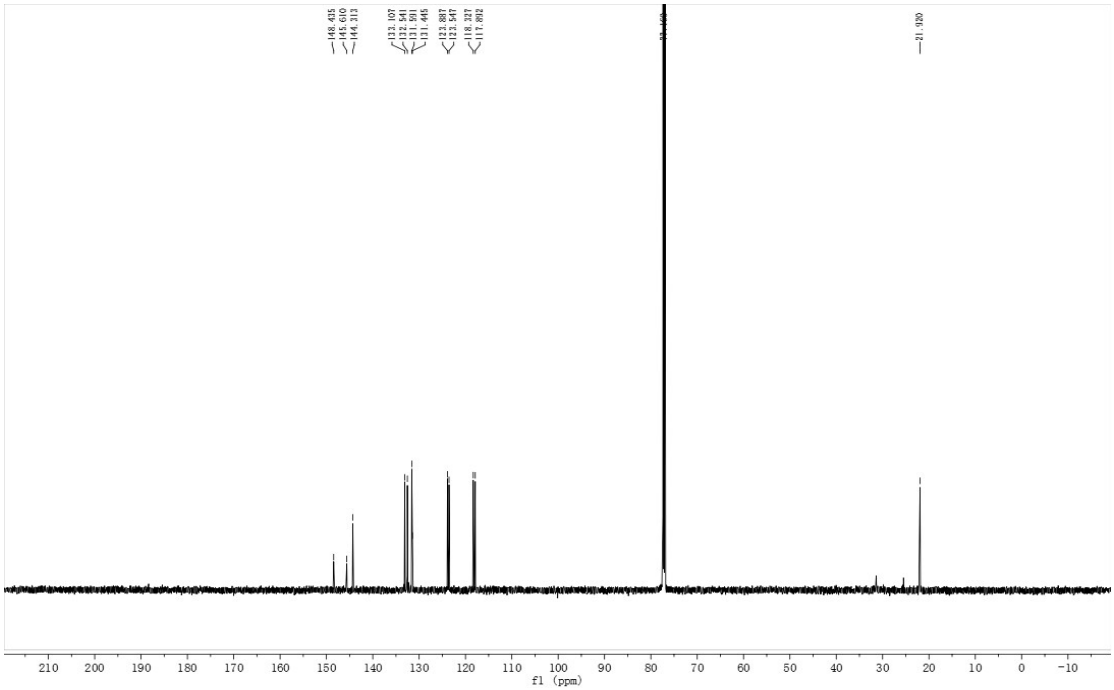


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **5-b**.

5•Cb

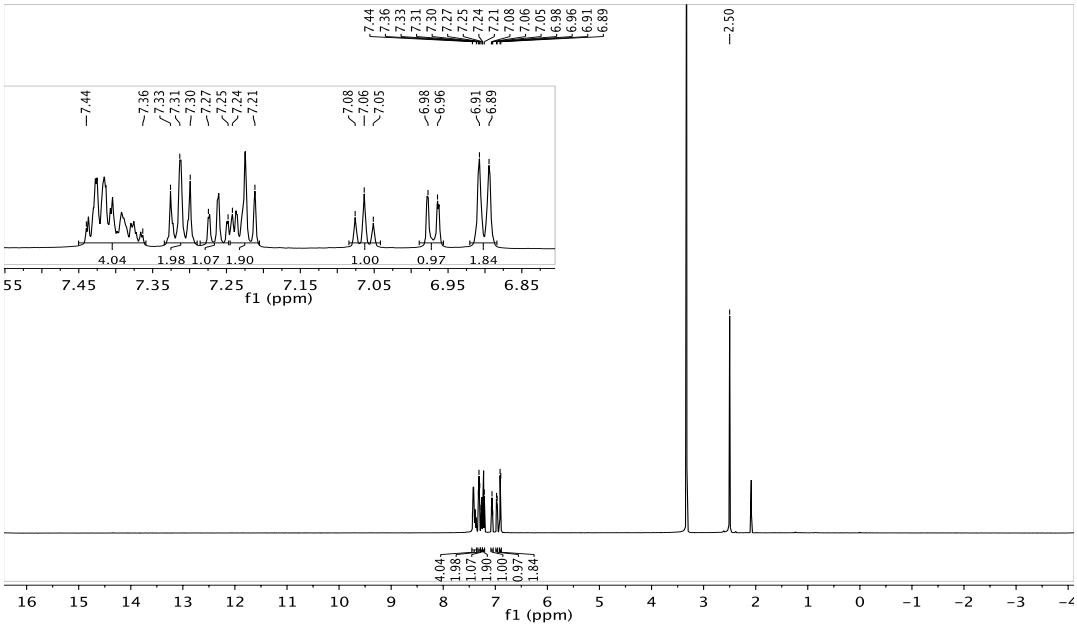


^{1}H-NMR (600 MHz, $(CD_3)_2CO$) spectrum of **5**•Cb.

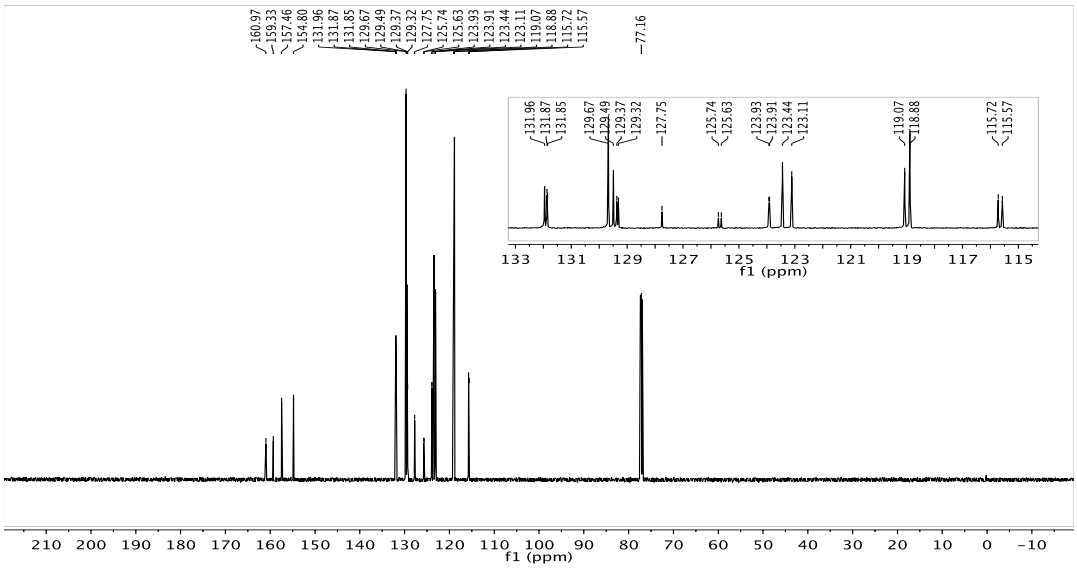


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **5**•Cb

7-a

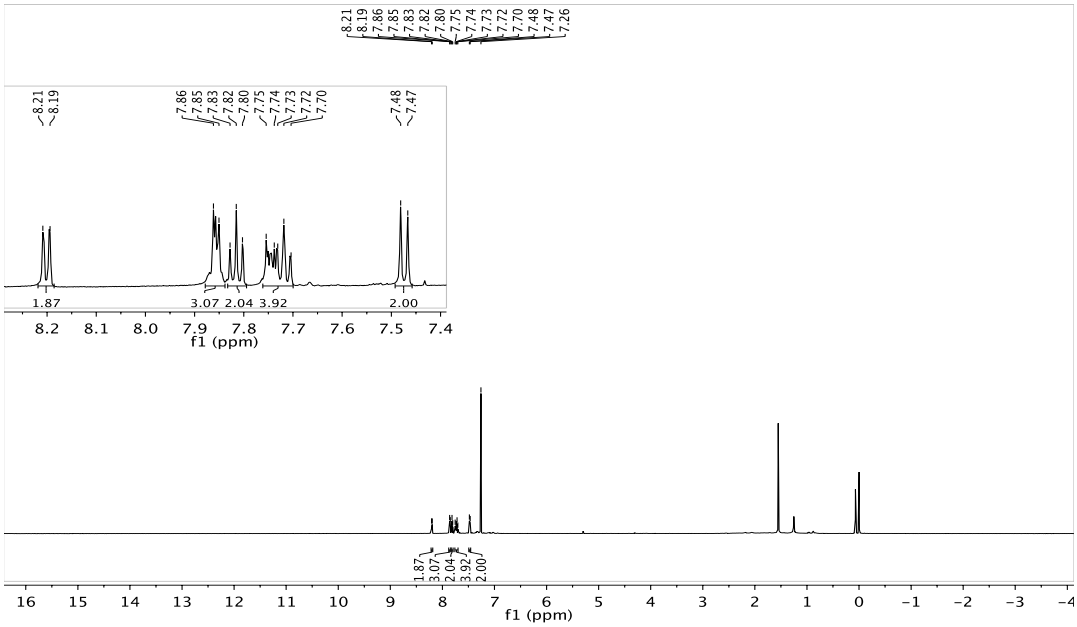


^{1}H-NMR (600 MHz, DMSO-d_6) spectrum of **7-a**.

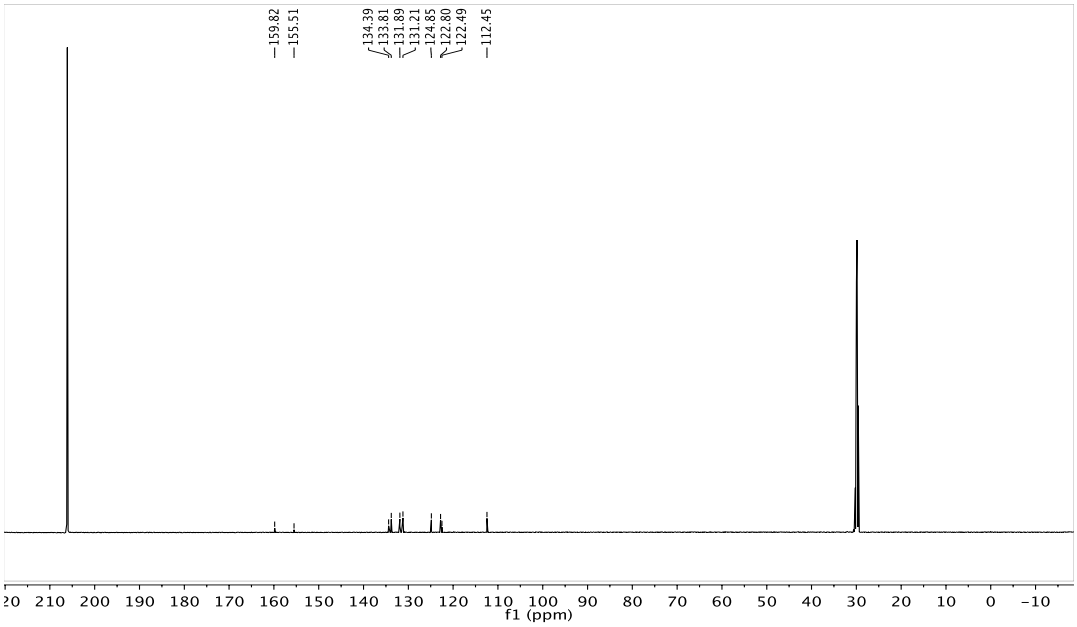


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **7-a**.

7•Cb

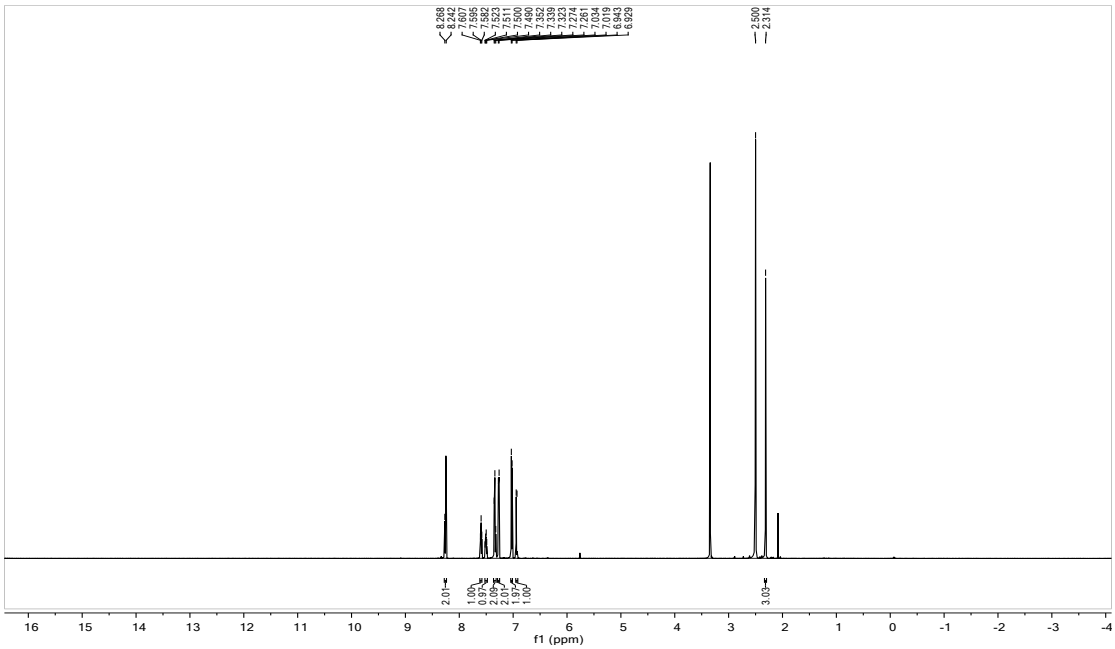


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **7**•Cb.

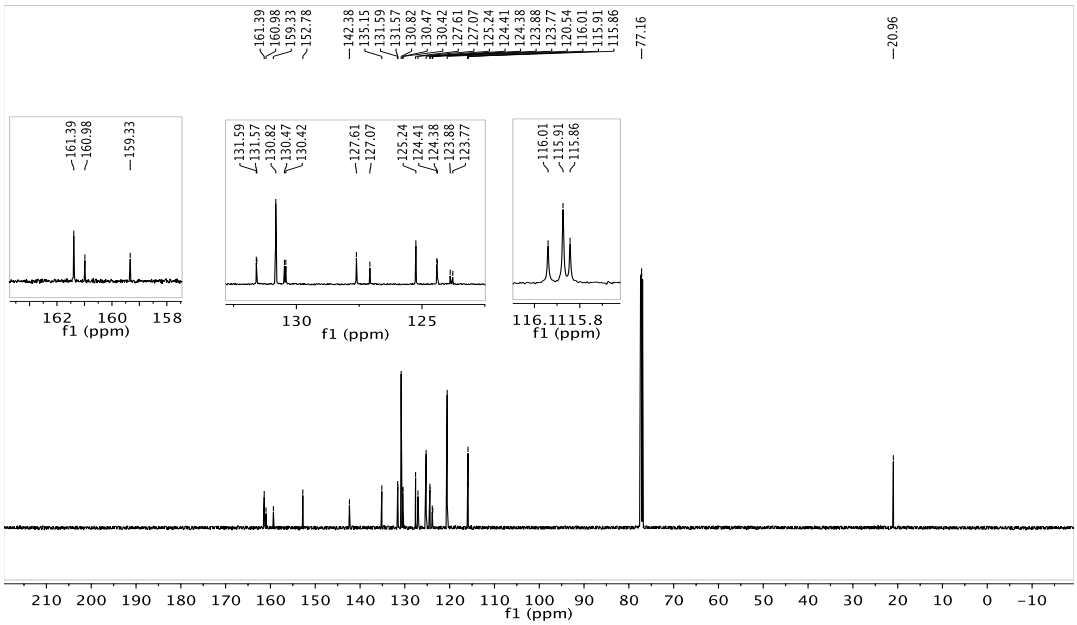


^{13}C-NMR (151 MHz, $(CD_3)_2CO$) spectrum of **7**•Cb.

8-a

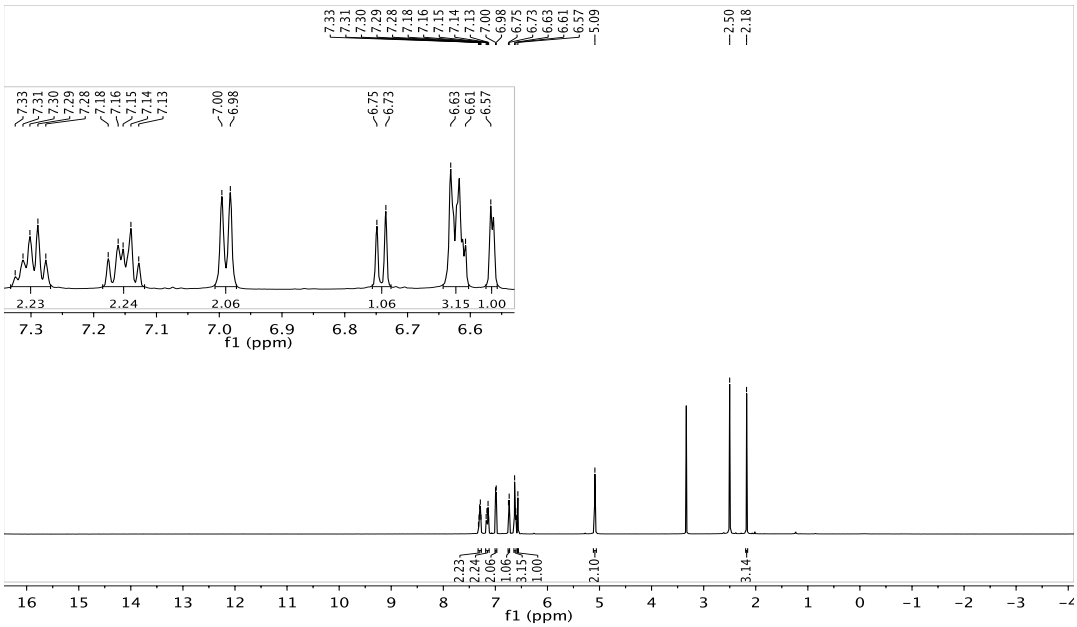


^{1}H-NMR (600 MHz, DMSO-d_6) spectrum of **8-a**.

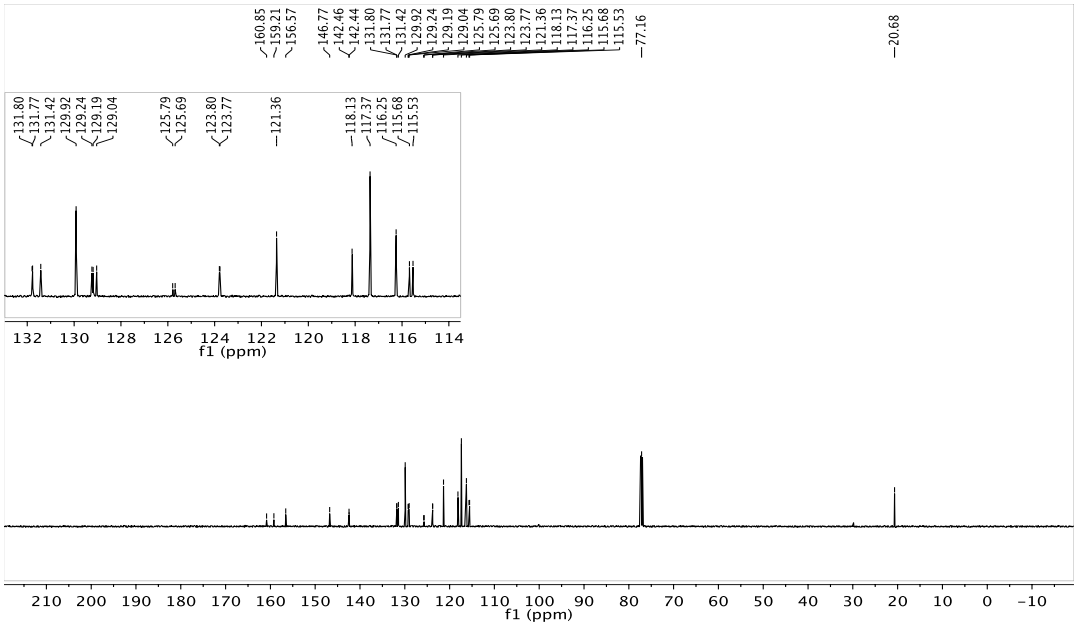


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **8-a**.

8-b

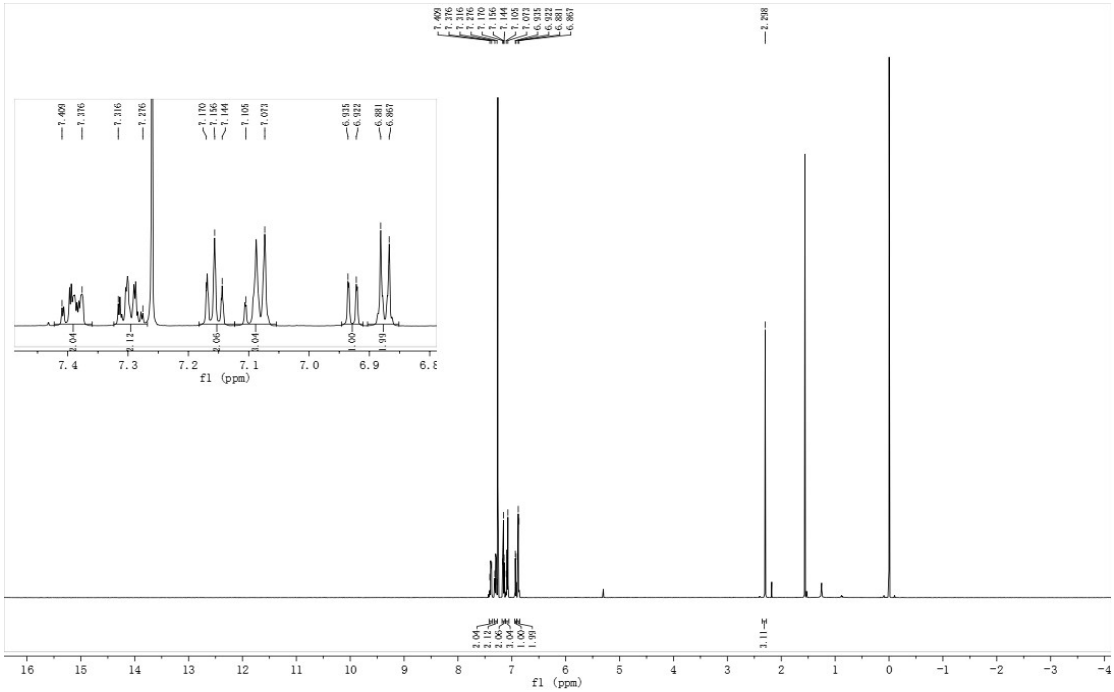


^{1}H-NMR (600 MHz, DMSO-d_6) spectrum of **8-b**.

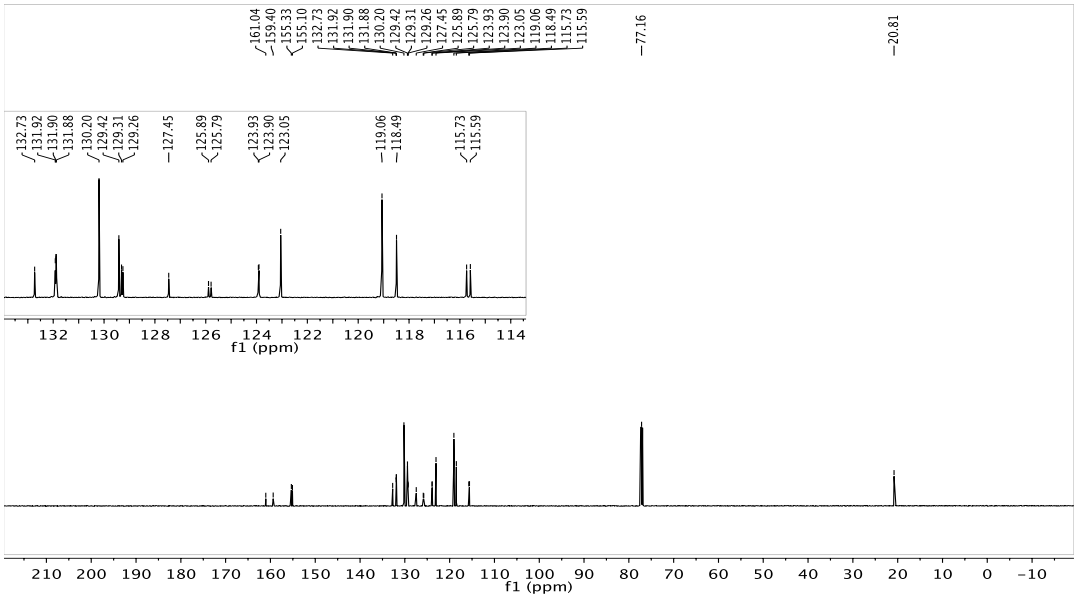


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **8-b**.

8-c

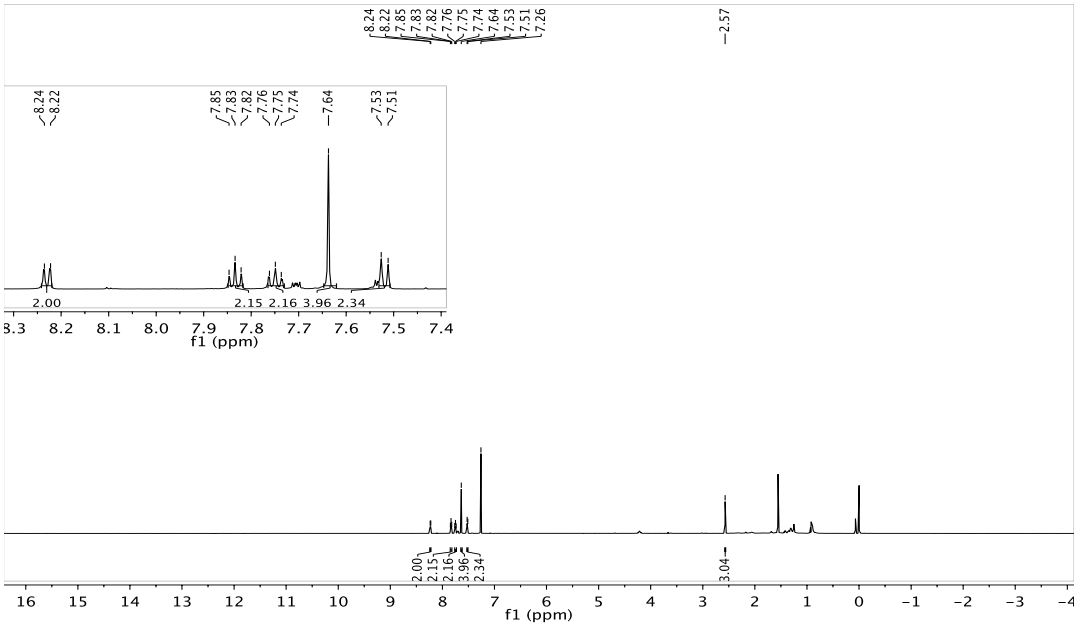


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **8-c**.

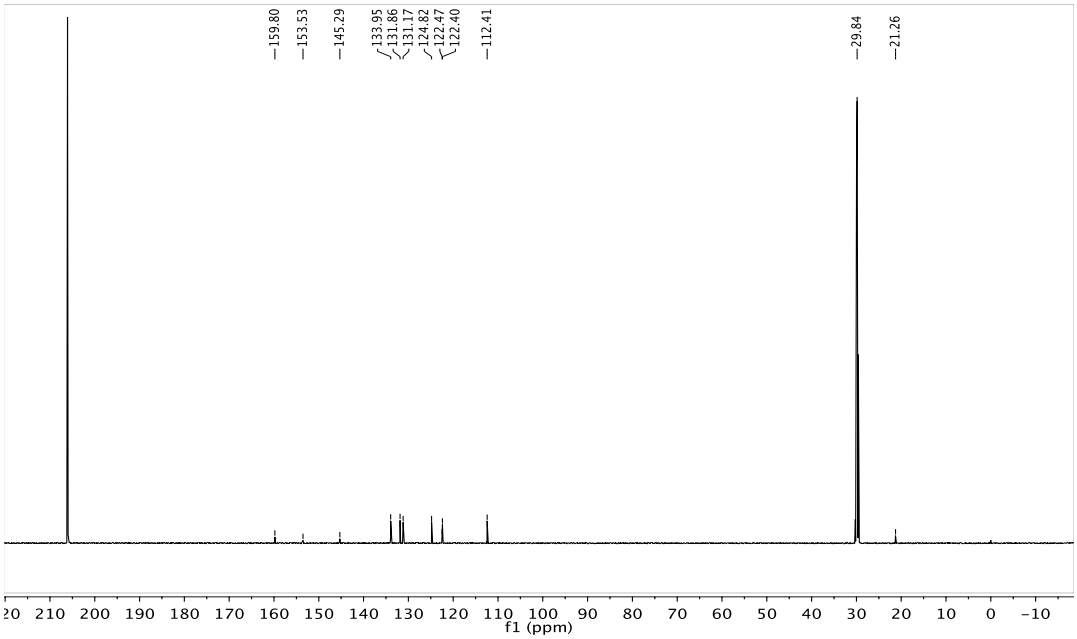


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **8-c**.

8•Cb

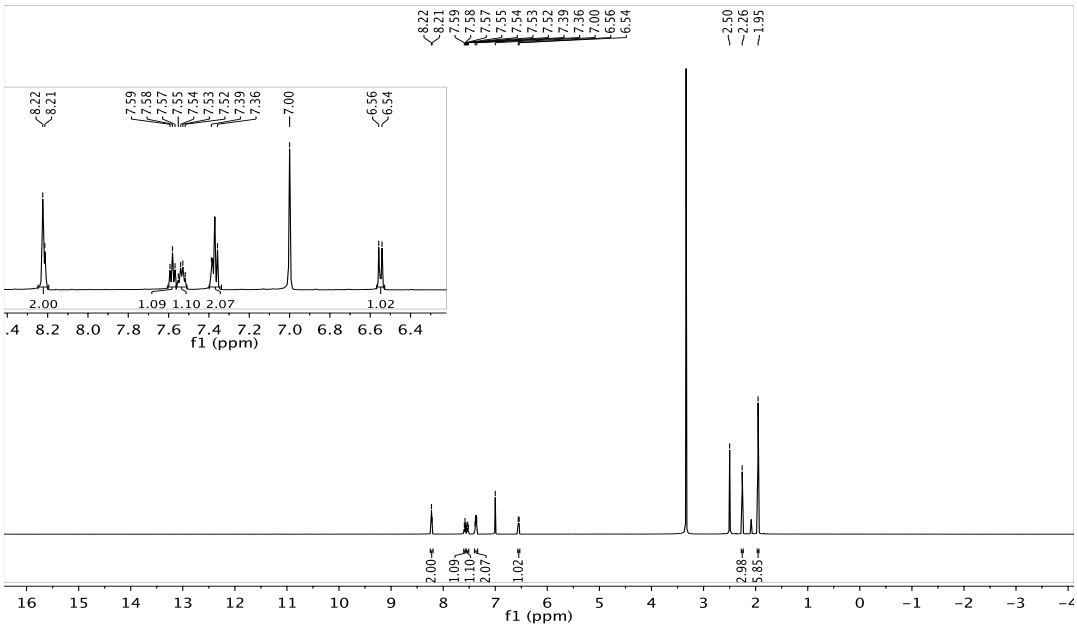


^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **8**•Cb.

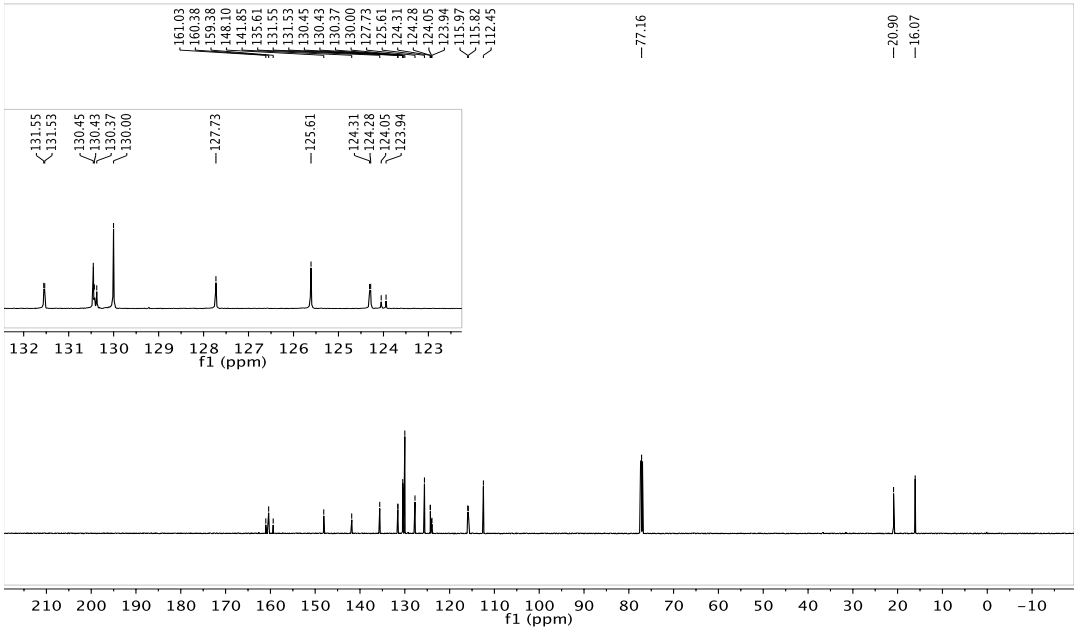


^{13}C-NMR (151 MHz, $(CD_3)_2CO$) spectrum of **8•**Cb.

9-a

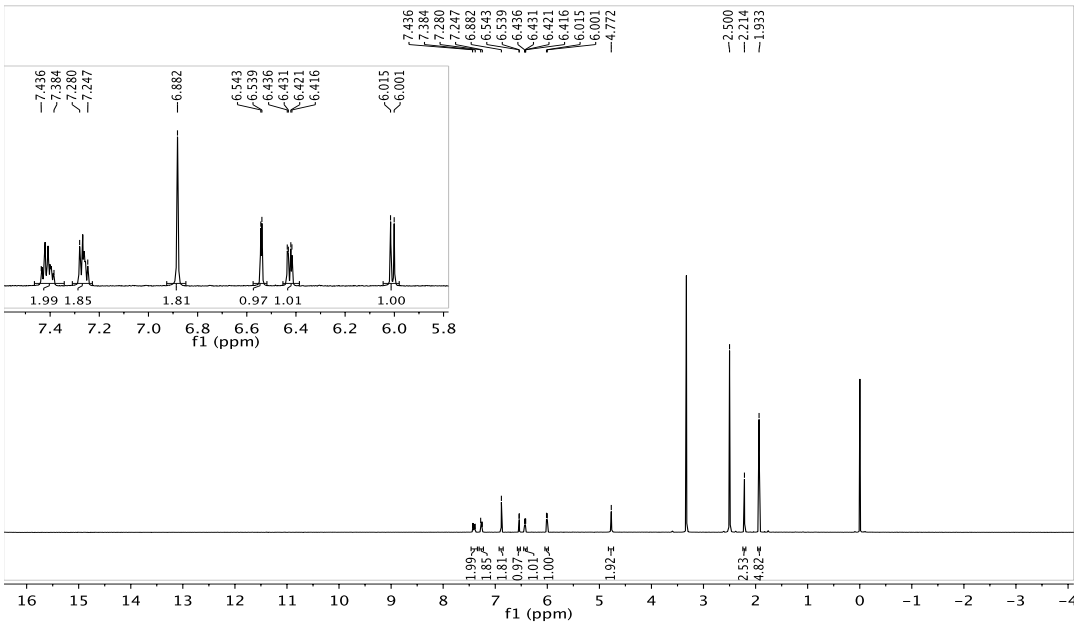


^{1}H-NMR (600 MHz, DMSO-d_6) spectrum of **9-a**.

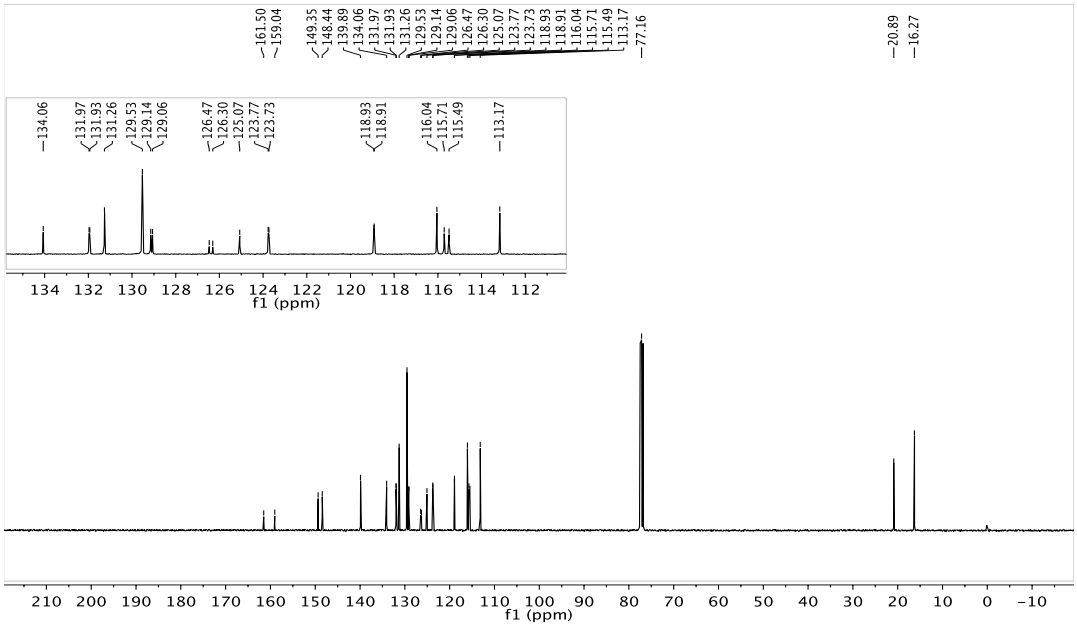


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **9-a**.

9-b

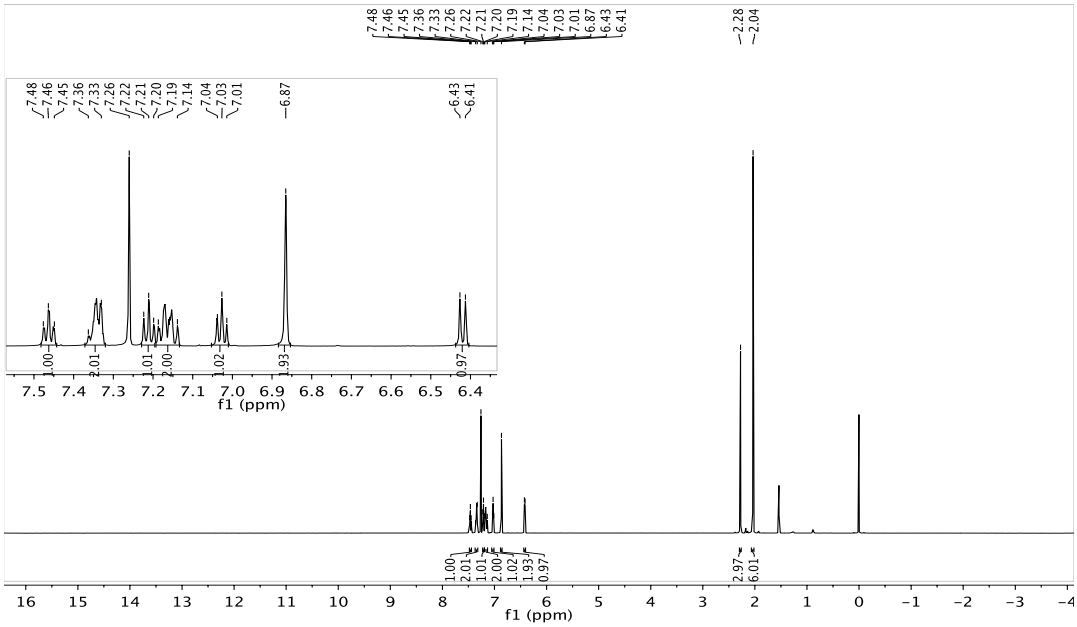


^{1}H-NMR (600 MHz, DMSO-d_6) spectrum of **9-b**.

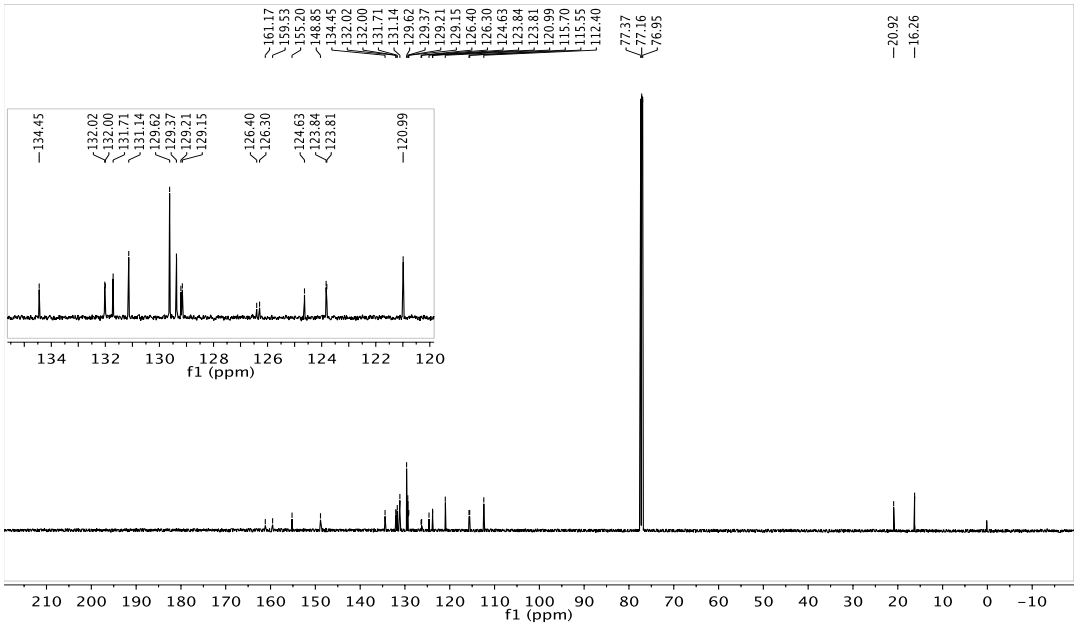


^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **9-b**.

9-c

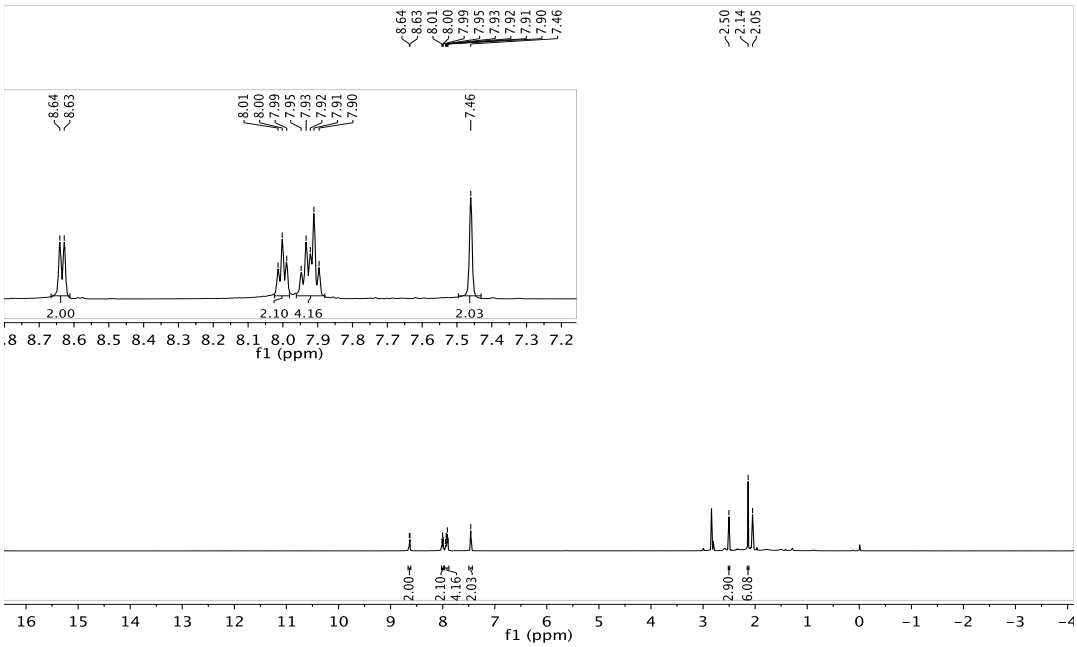


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **9-c**.

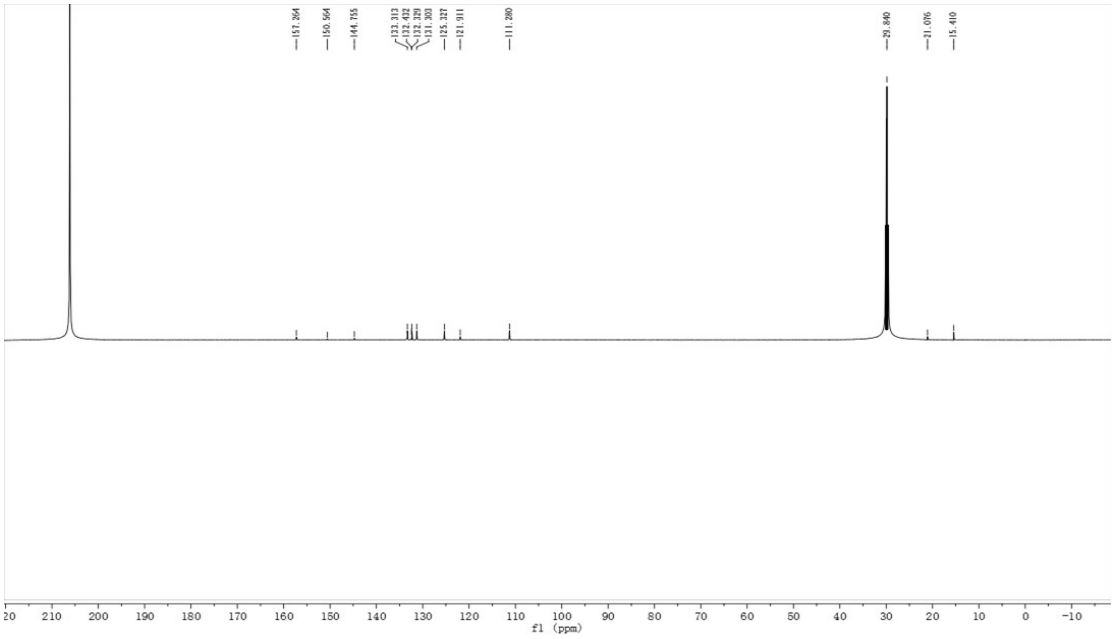


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **9-c**.

9•Cb

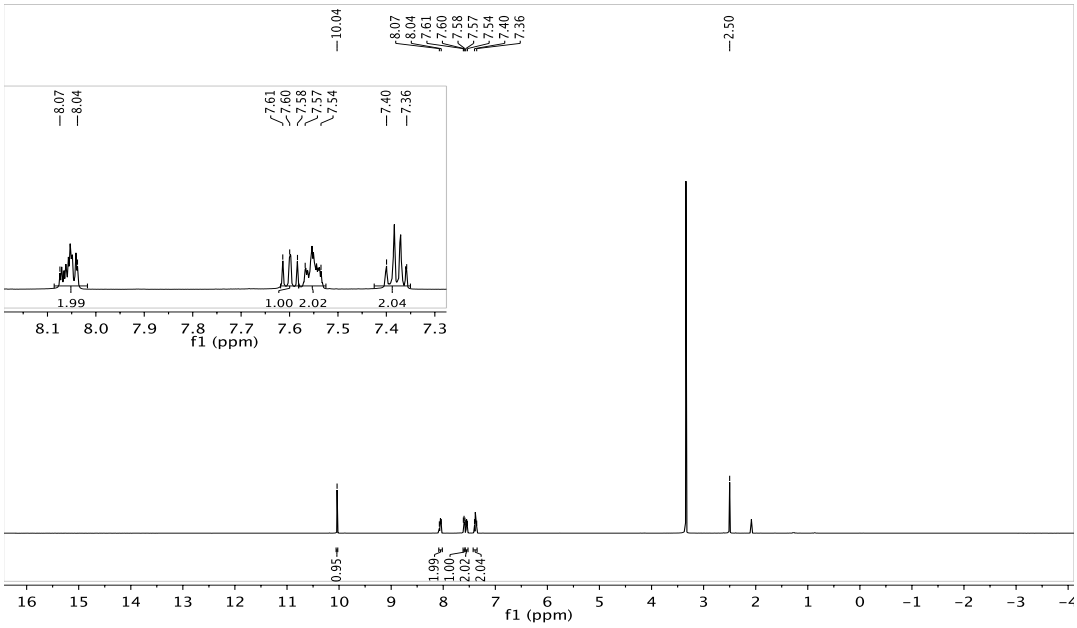


^{1}H-NMR (600 MHz, $(CD_3)_2CO$)) spectrum of **9**•Cb.

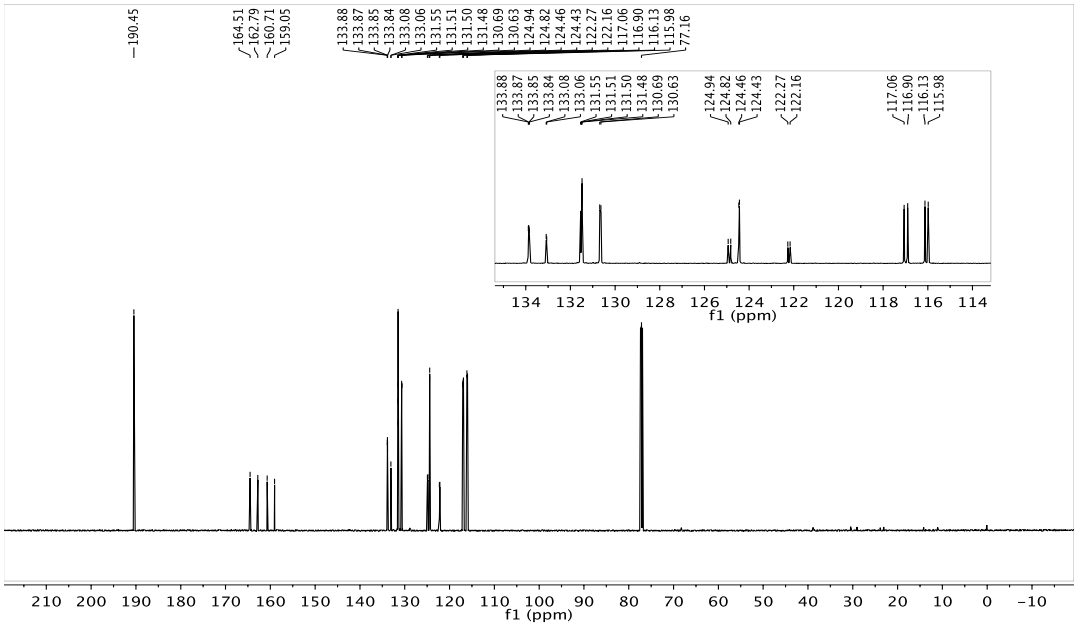


^{13}C-NMR (151 MHz, $(CD_3)_2CO$) spectrum of **9**•Cb.

10-SM

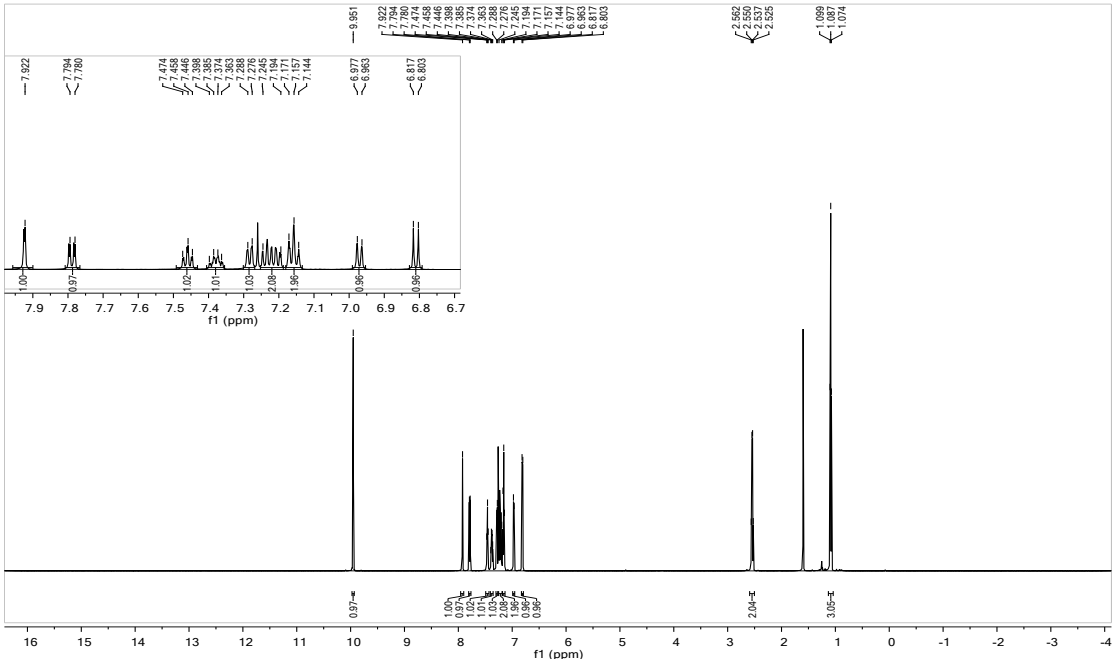


^{1}H-NMR (600 MHz, DMSO-d_6) spectrum of **10-SM**.

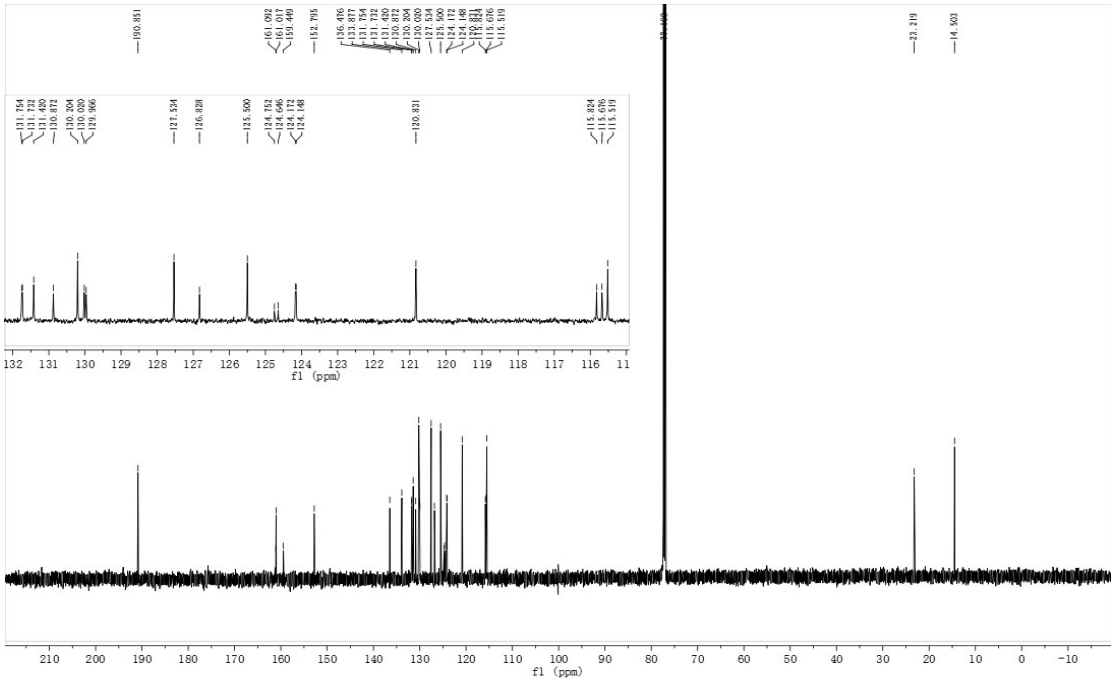


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **10-SM**.

10-a

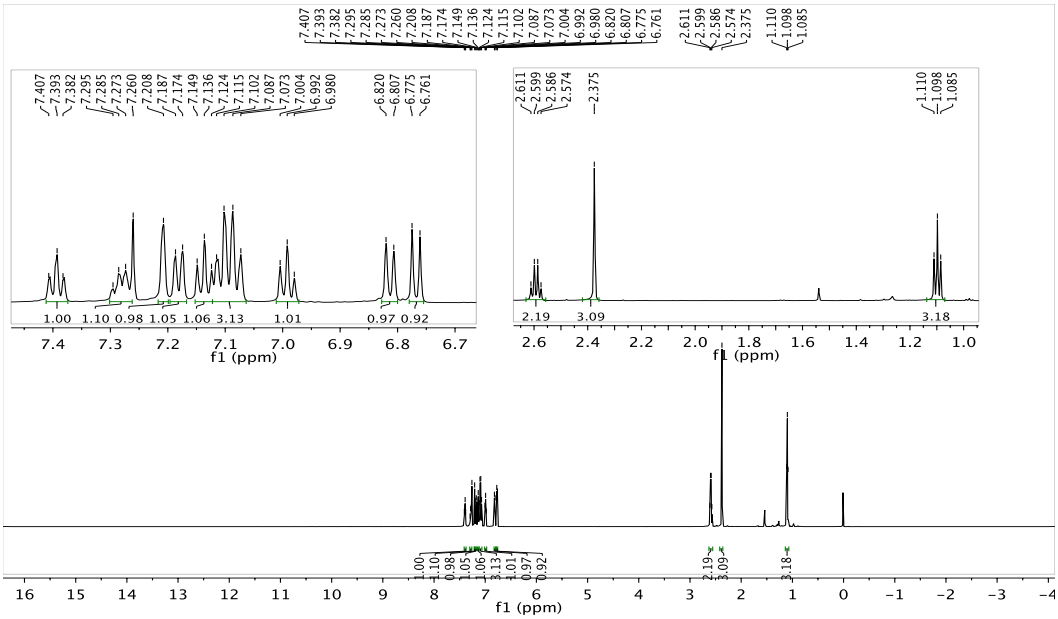


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **10-a**.

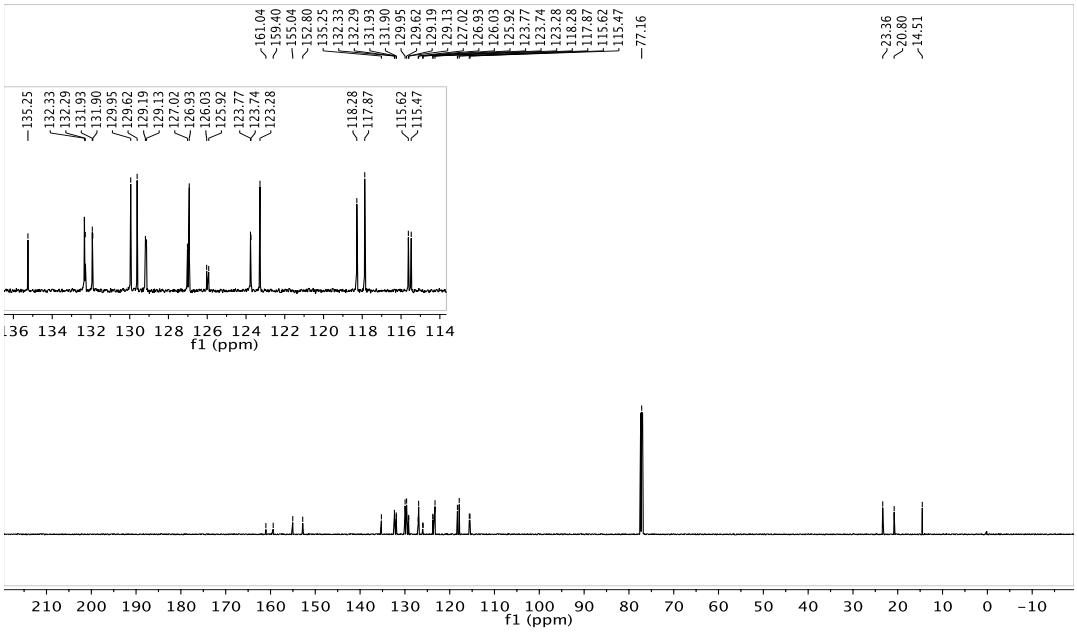


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **10-a**.

10-b

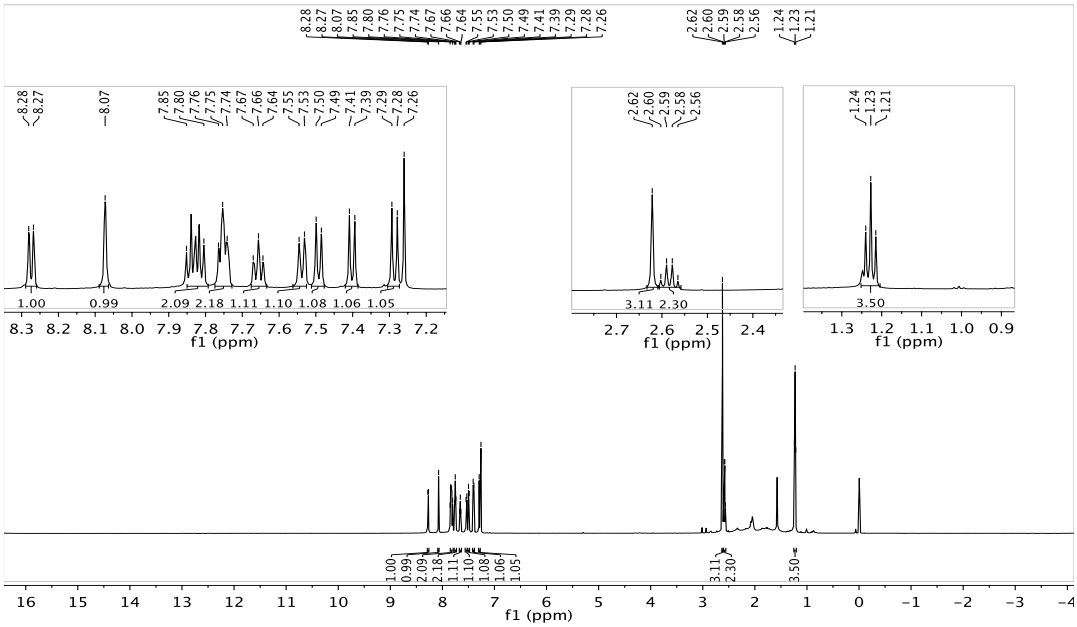


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **10-b**.

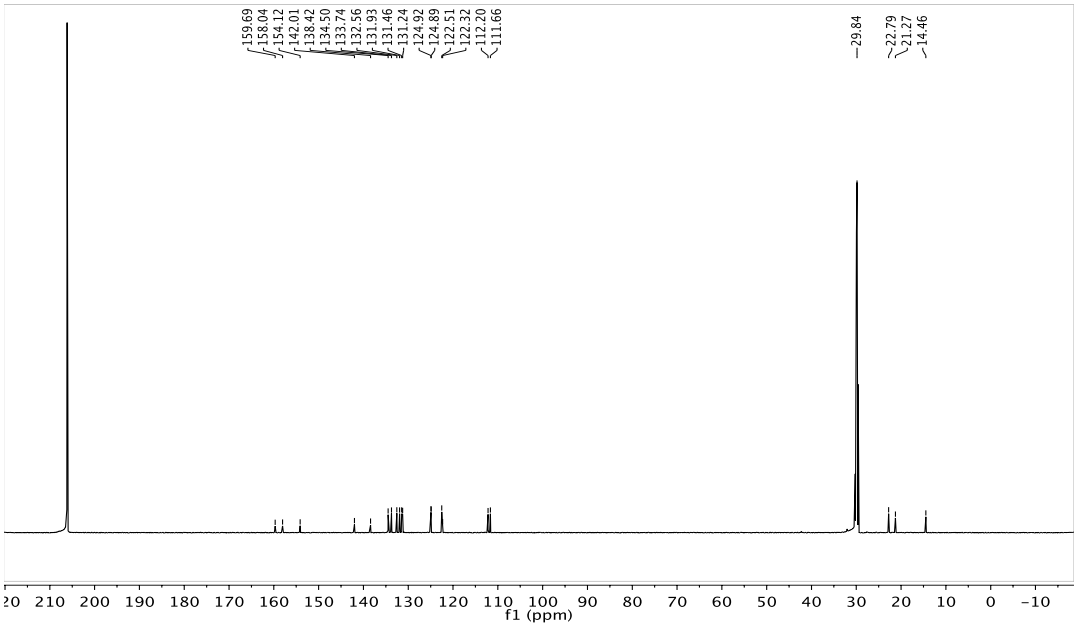


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **10-b**.

10•Cb



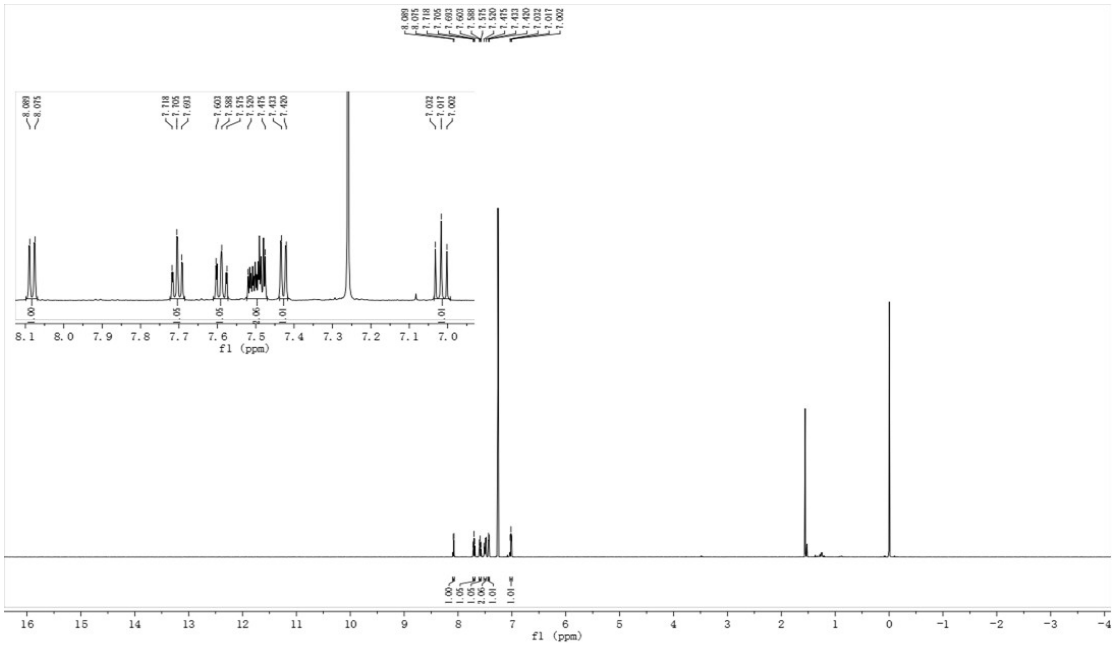
^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **10**•Cb.



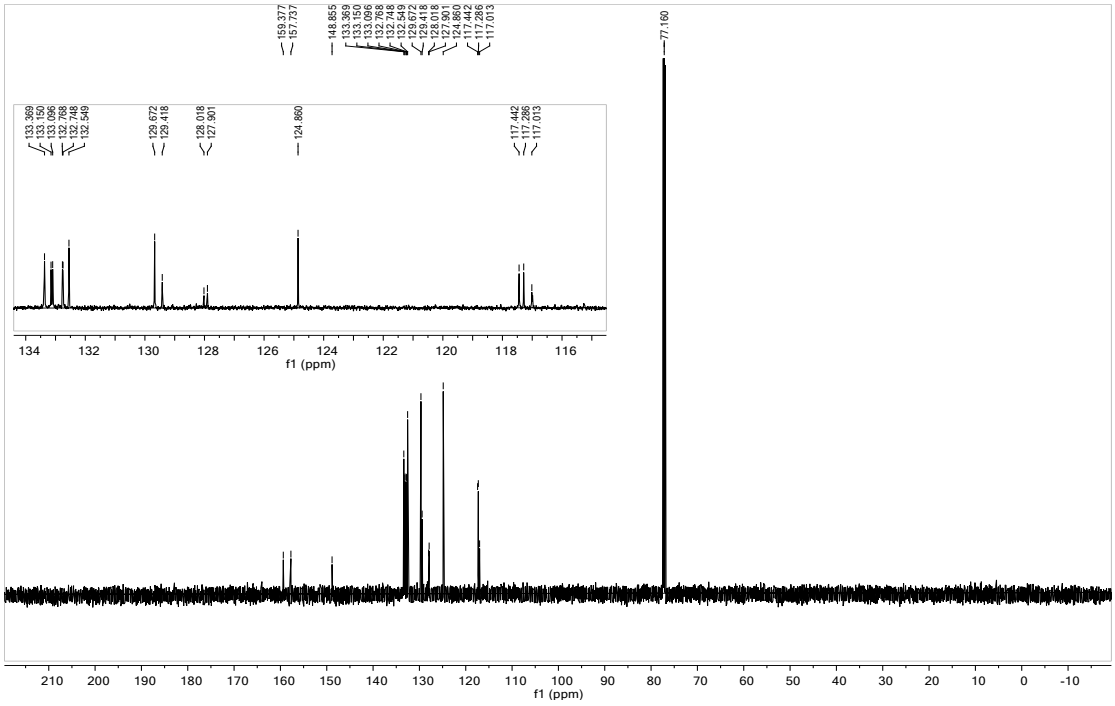
^{13}C-NMR (151 MHz, $(CD_3)_2CO$) spectrum of **10**•Cb.

Spectra for **4•I**, **5•I**, **6•I** and **10•I** by DSD.

4-SM'

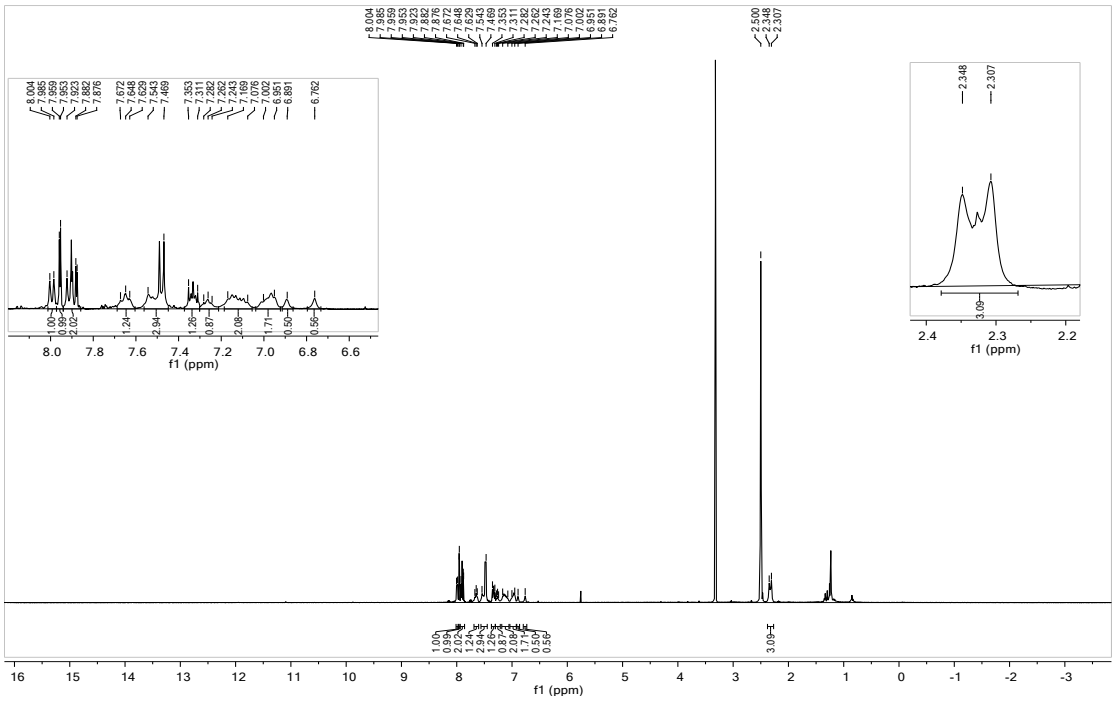


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **4-SM'**.

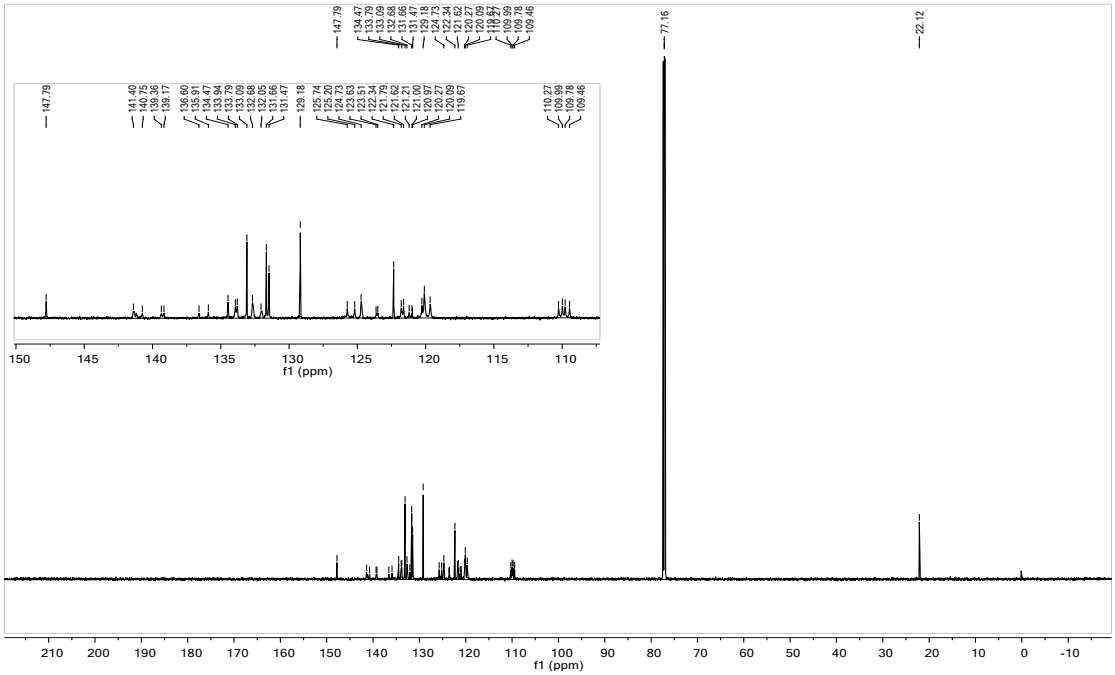


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **4-SM'**.

4-a'

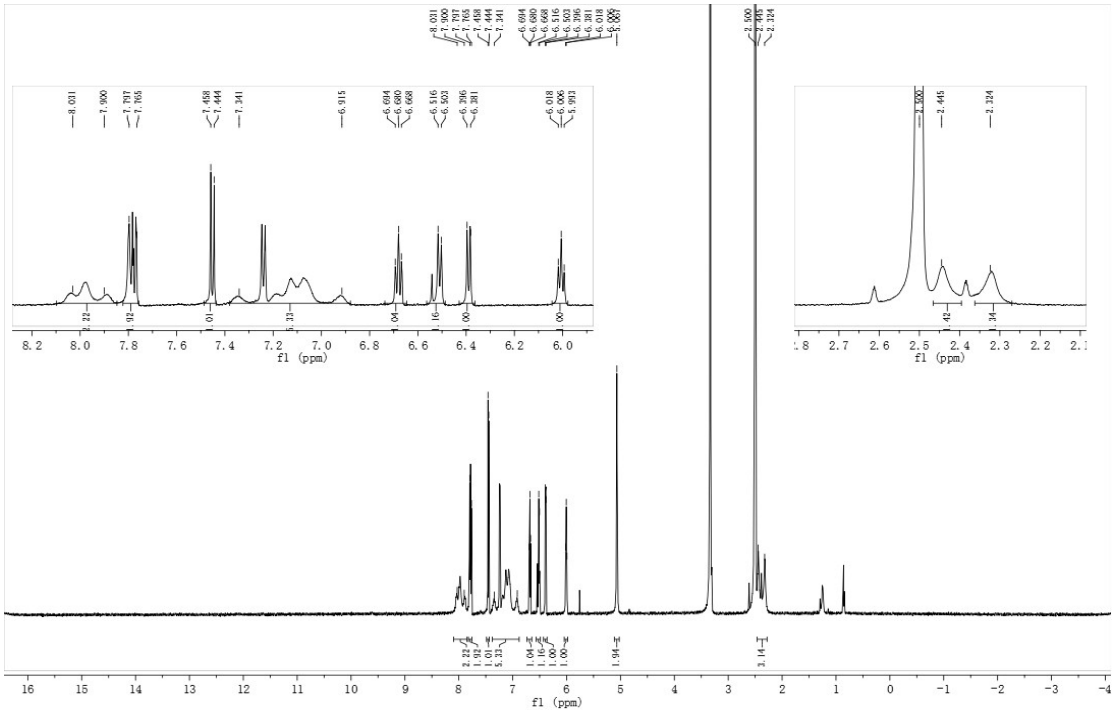


^{1}H-NMR (400 MHz, DMSO-d_6) spectrum of **4-a'**.

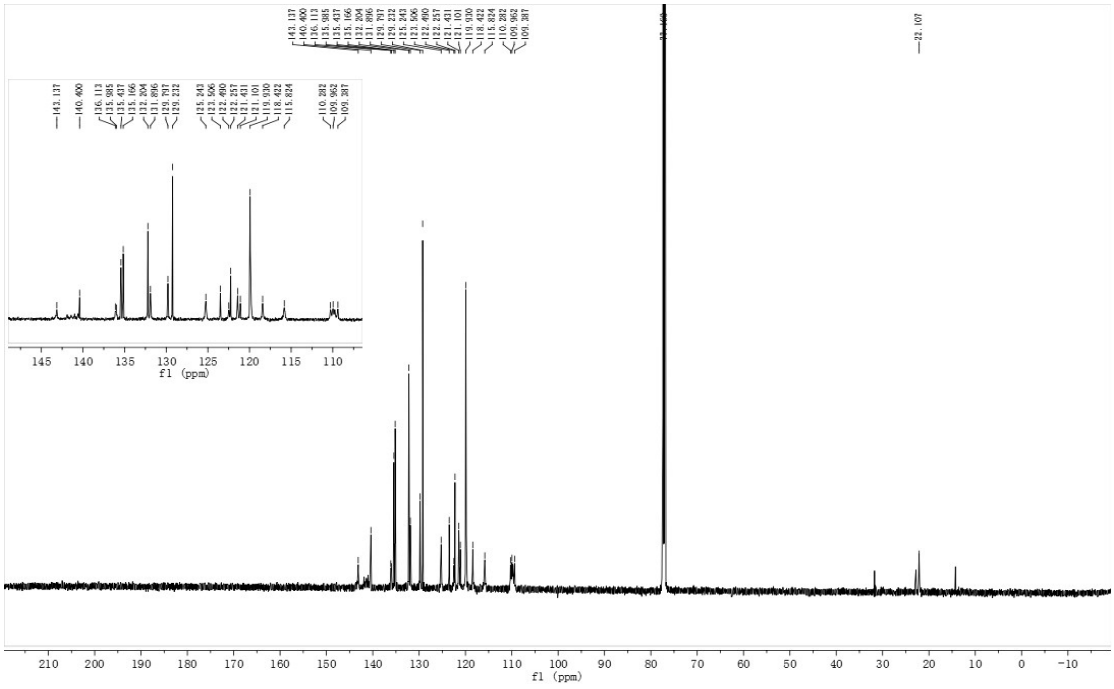


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **4-a'**.

4-b’

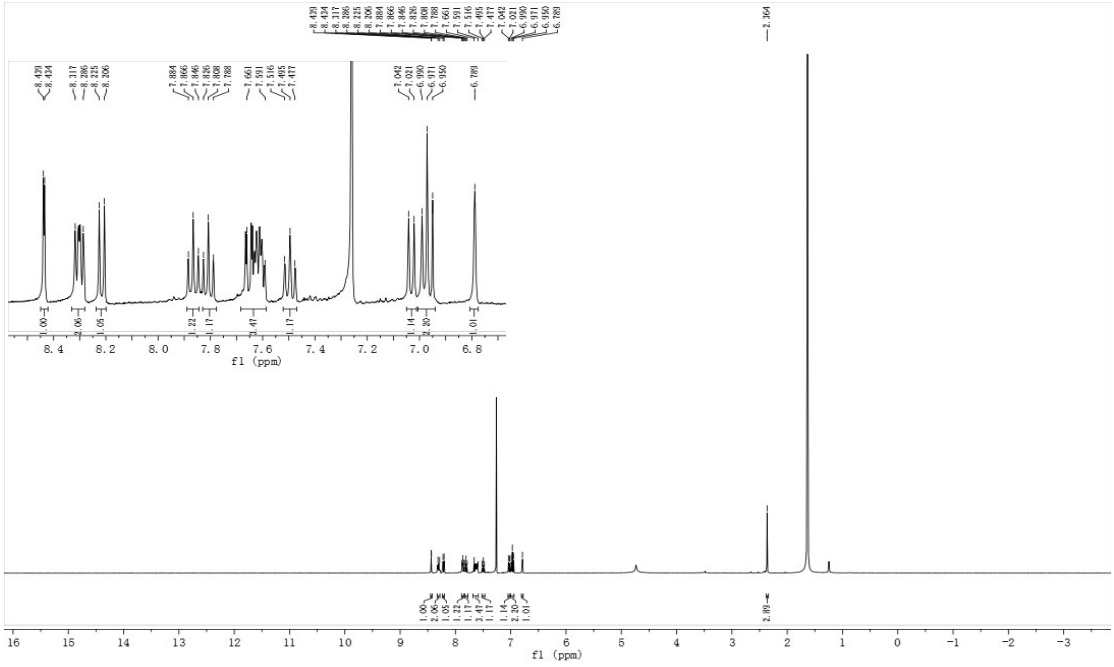


^{1}H-NMR (600 MHz, DMSO-d_6) spectrum of **4-b’**.

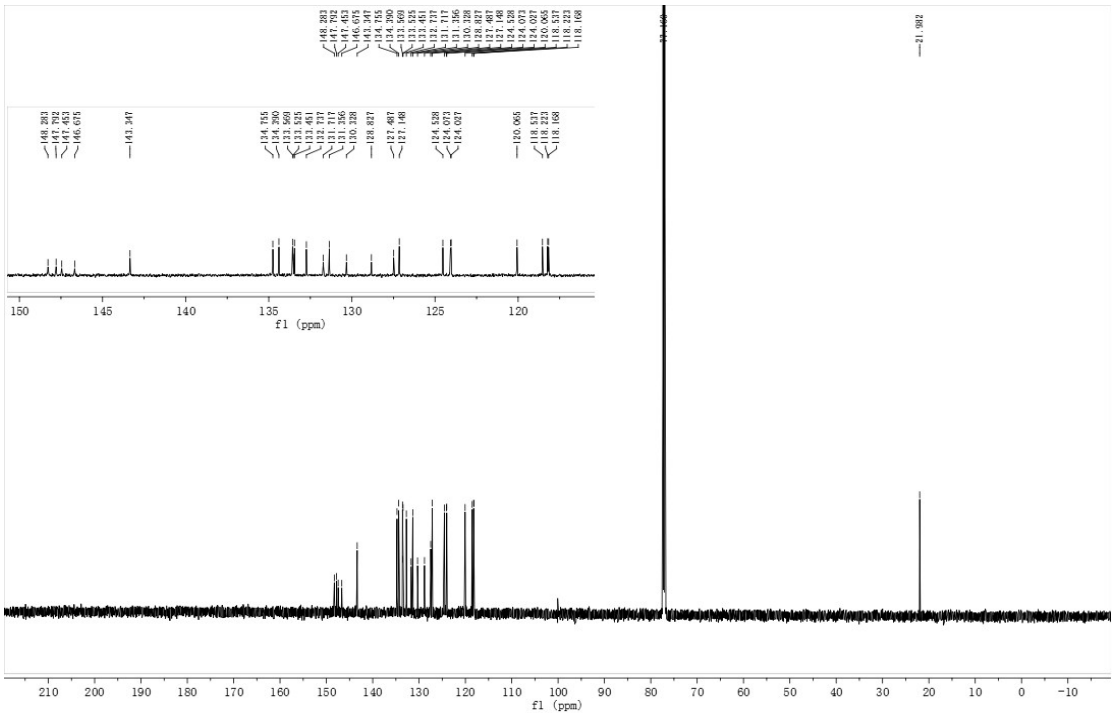


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **4-b'**.

4•I

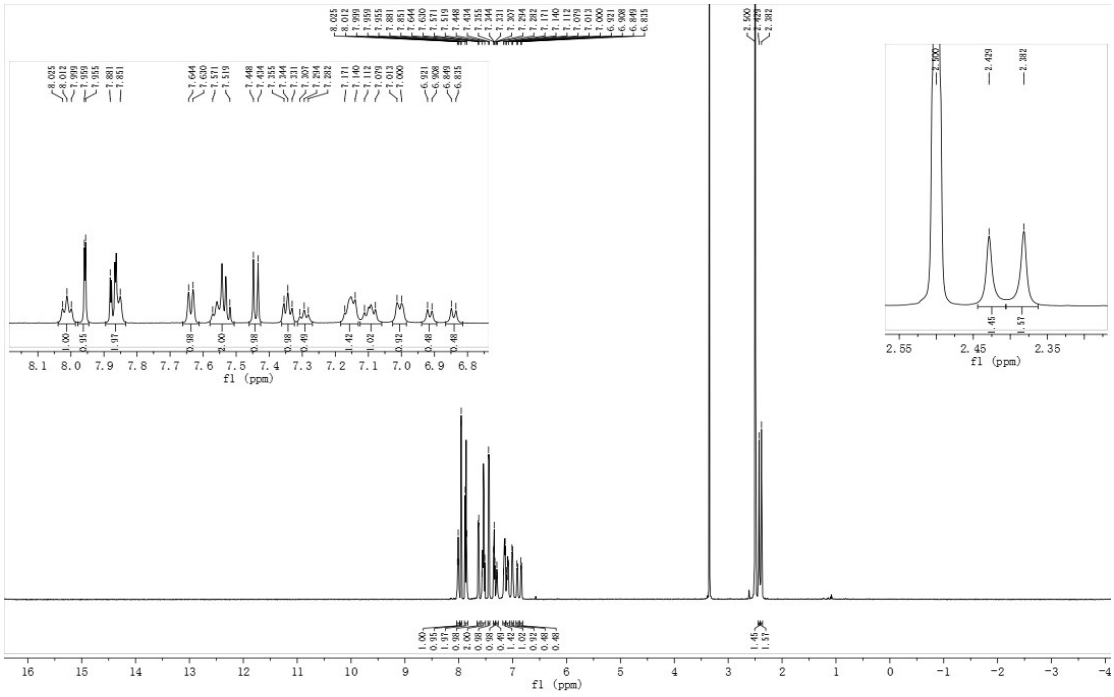


^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **4•I**.

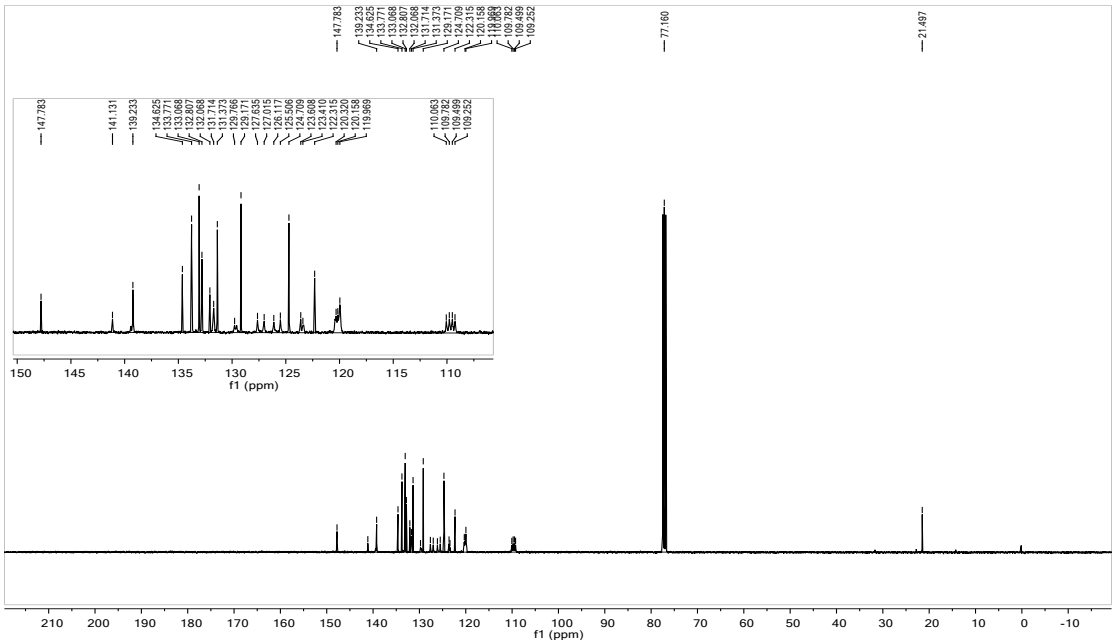


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **4•I**.

5-a’

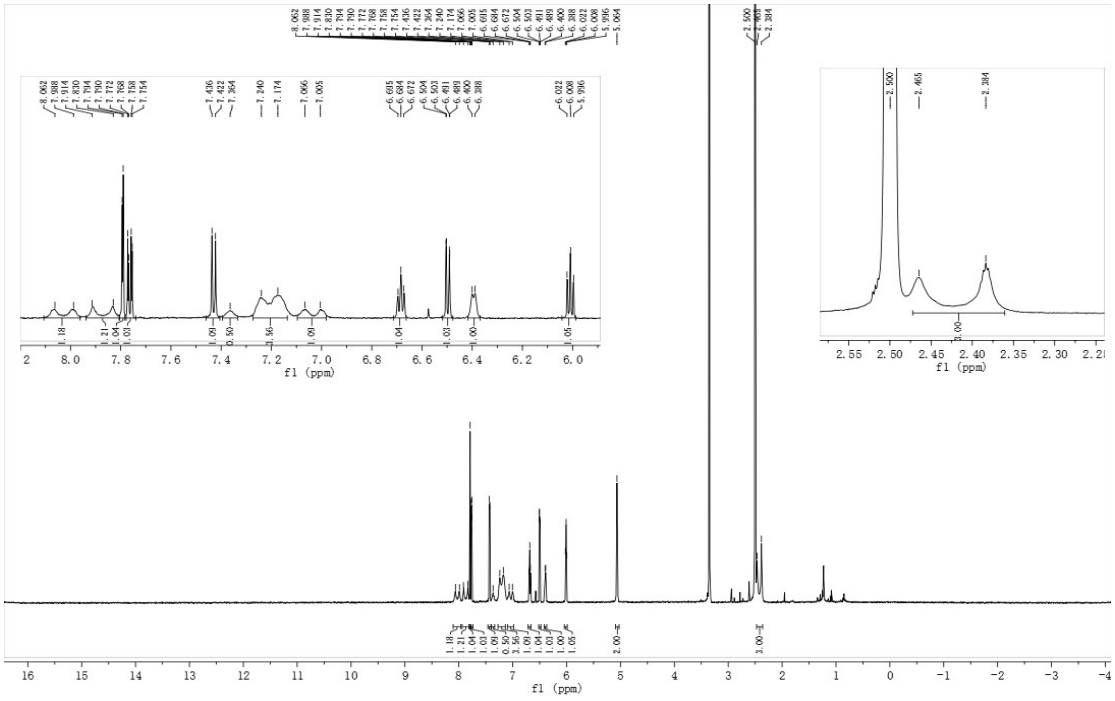


^{1}H-NMR (600 MHz, DMSO-d_6) spectrum of **5-a’**.

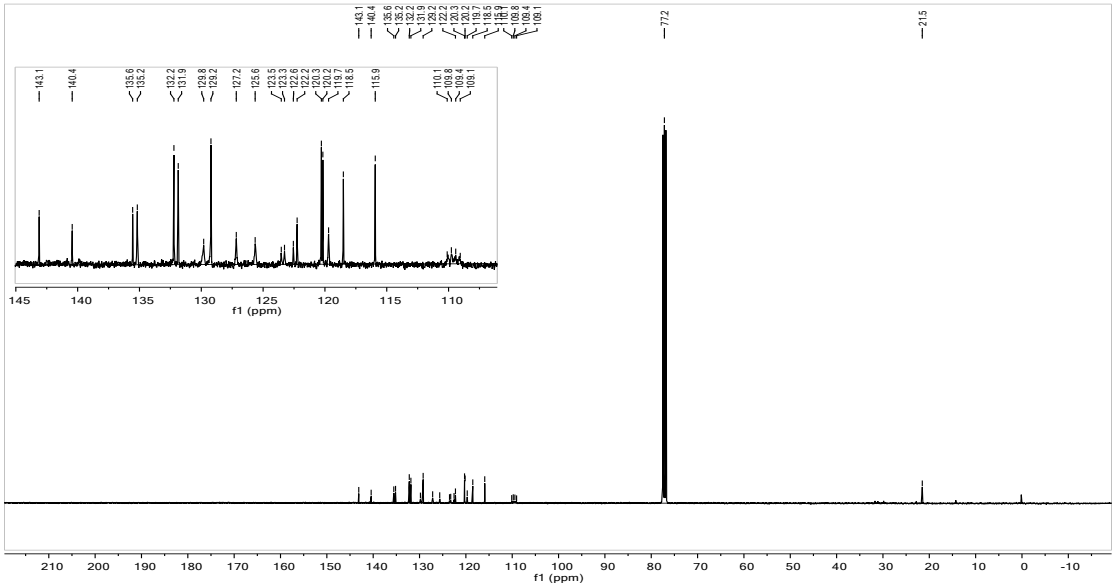


^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **5-a'**

5-b'

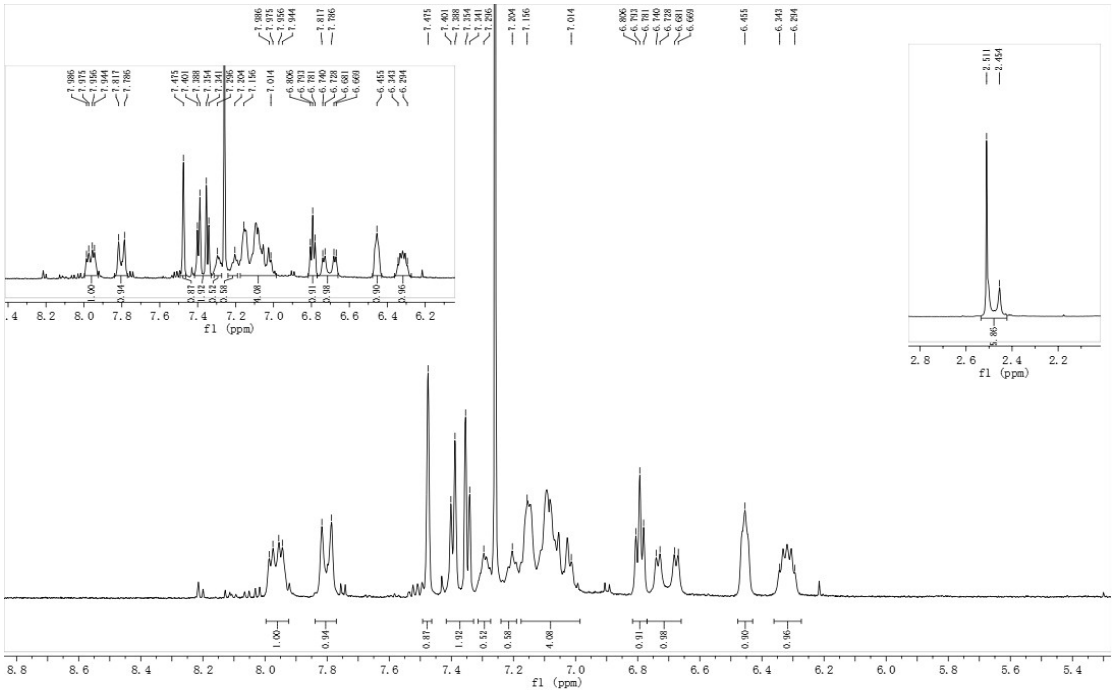


^{1}H-NMR (600 MHz, DMSO-d_6) spectrum of **5-b'**.

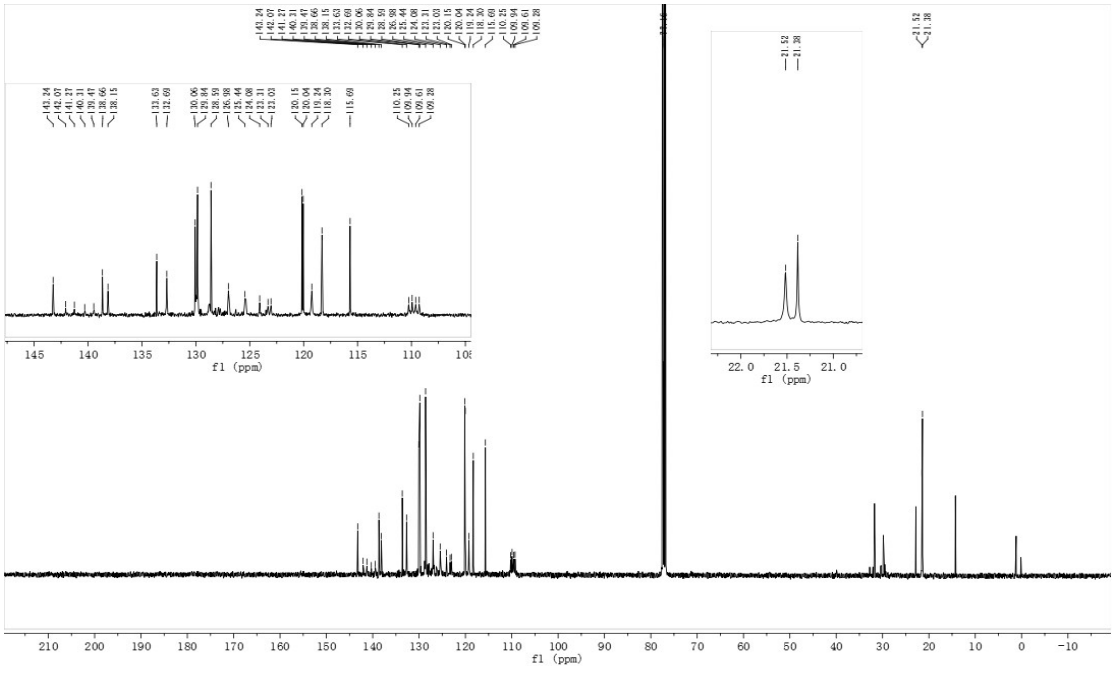


^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **5-b'**.

5-c'

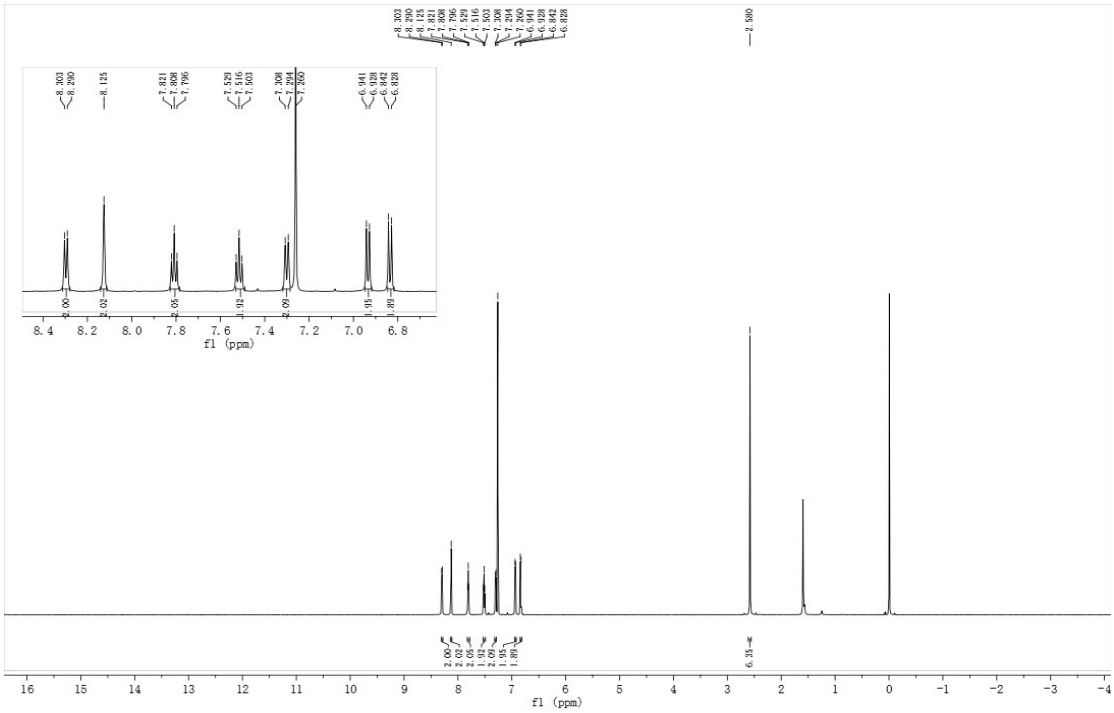


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **5-c'**.

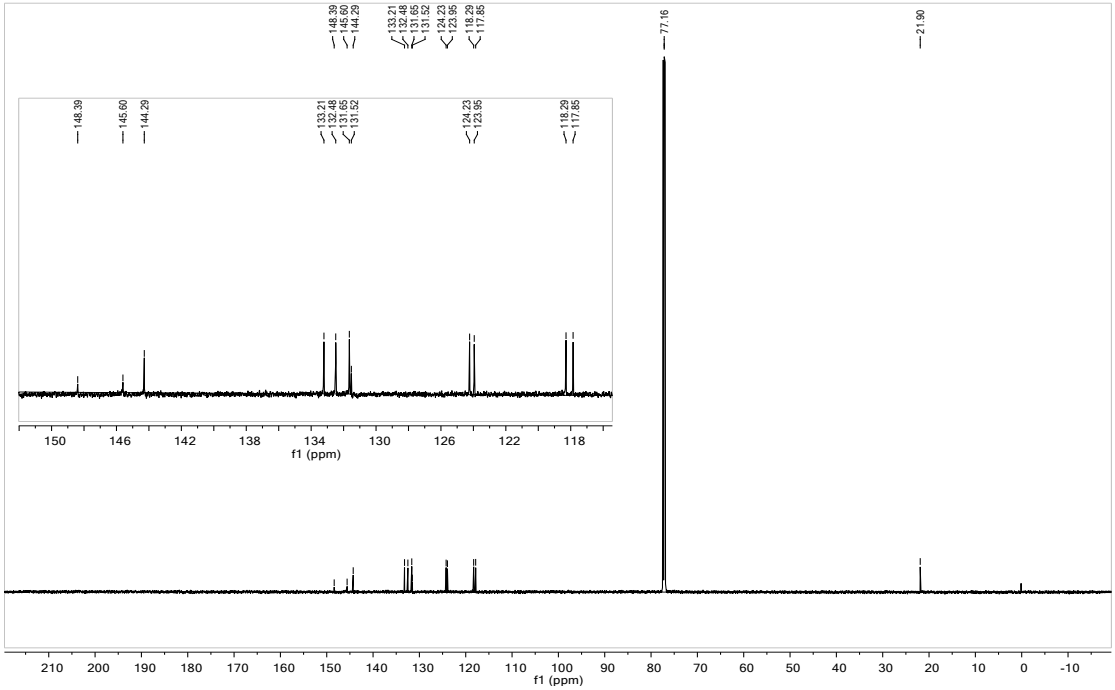


^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **5-c'**.

5•I

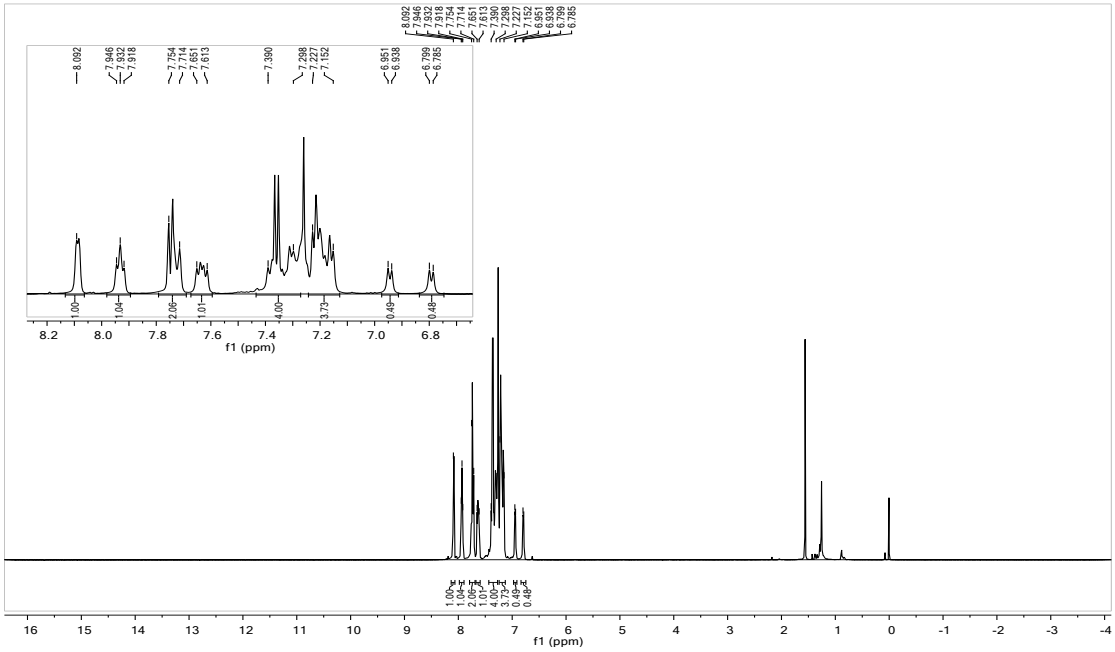


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **5•I**.

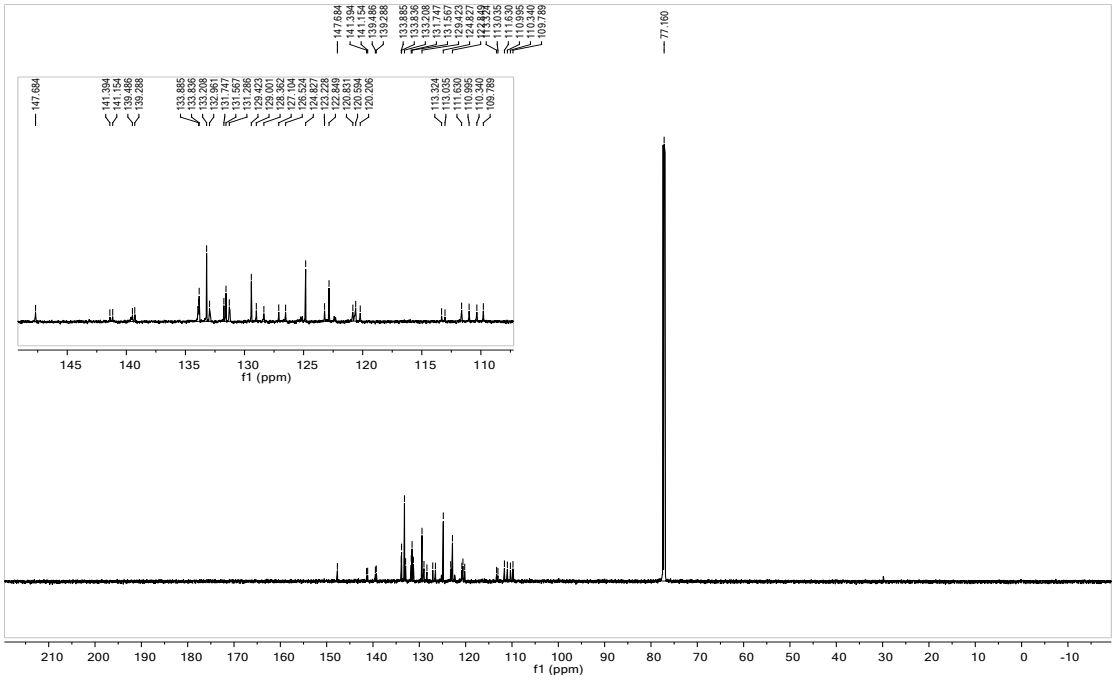


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **5•I**.

6-a'

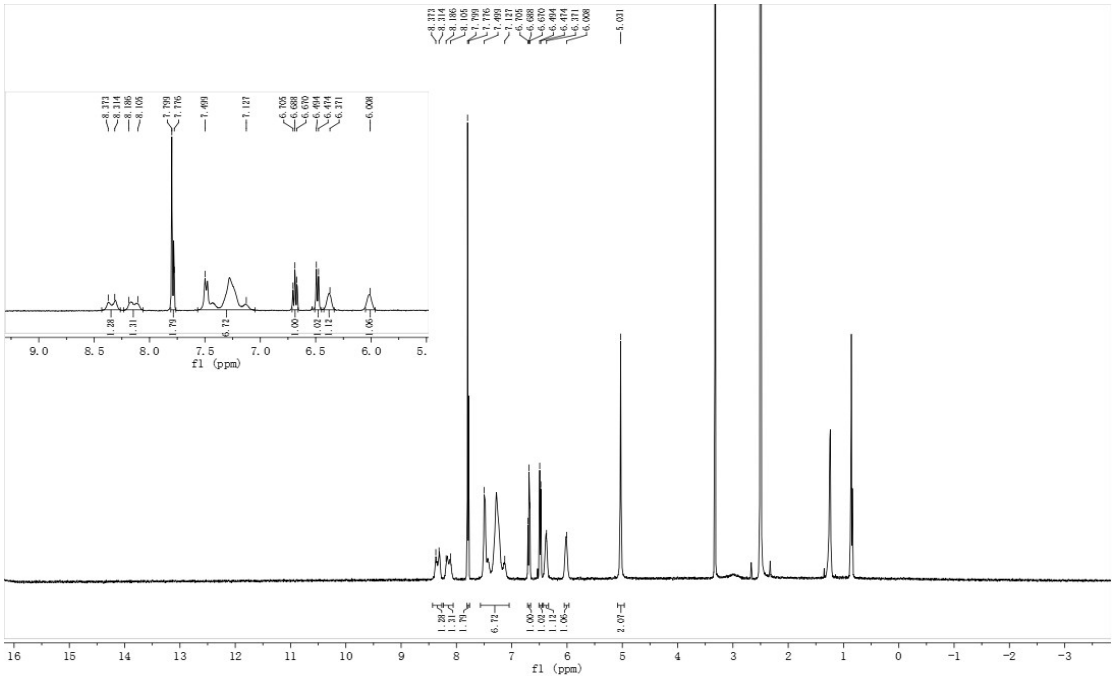


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **6-a'**.

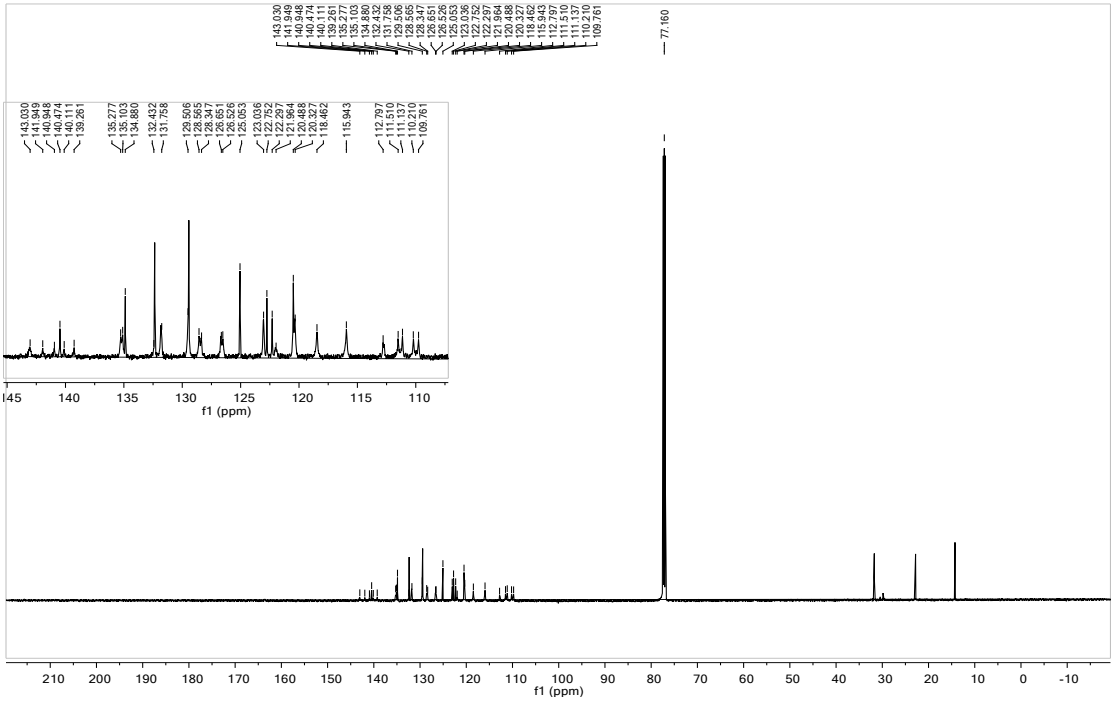


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **6-a'**.

6-b'

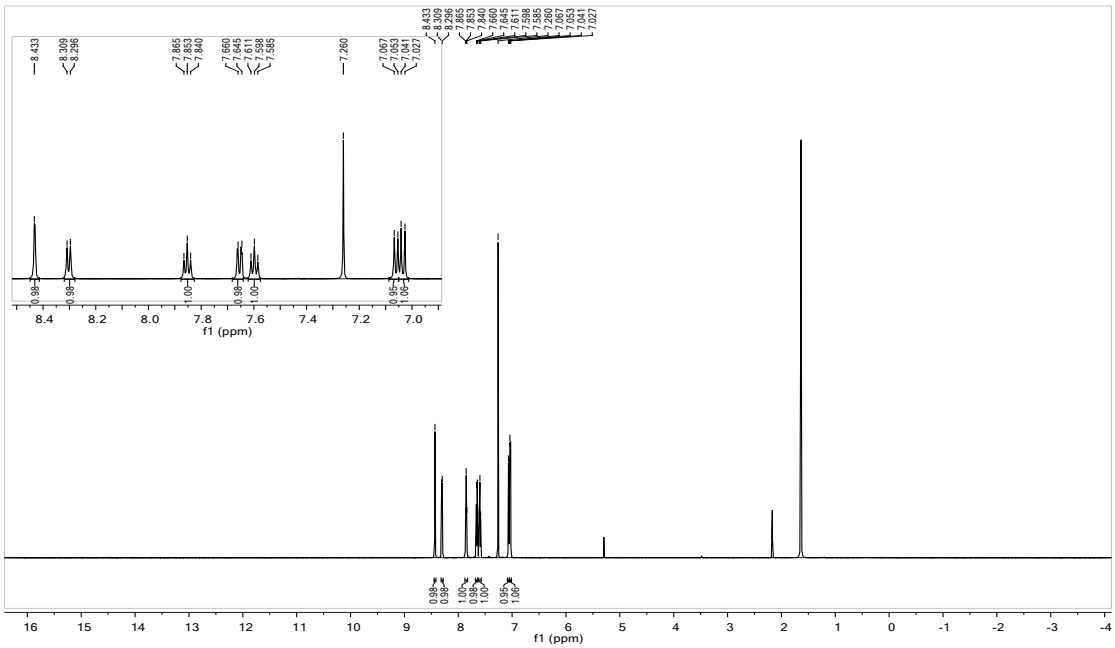


^{1}H-NMR (400 MHz, DMSO-d_6) spectrum of **6-b'**.

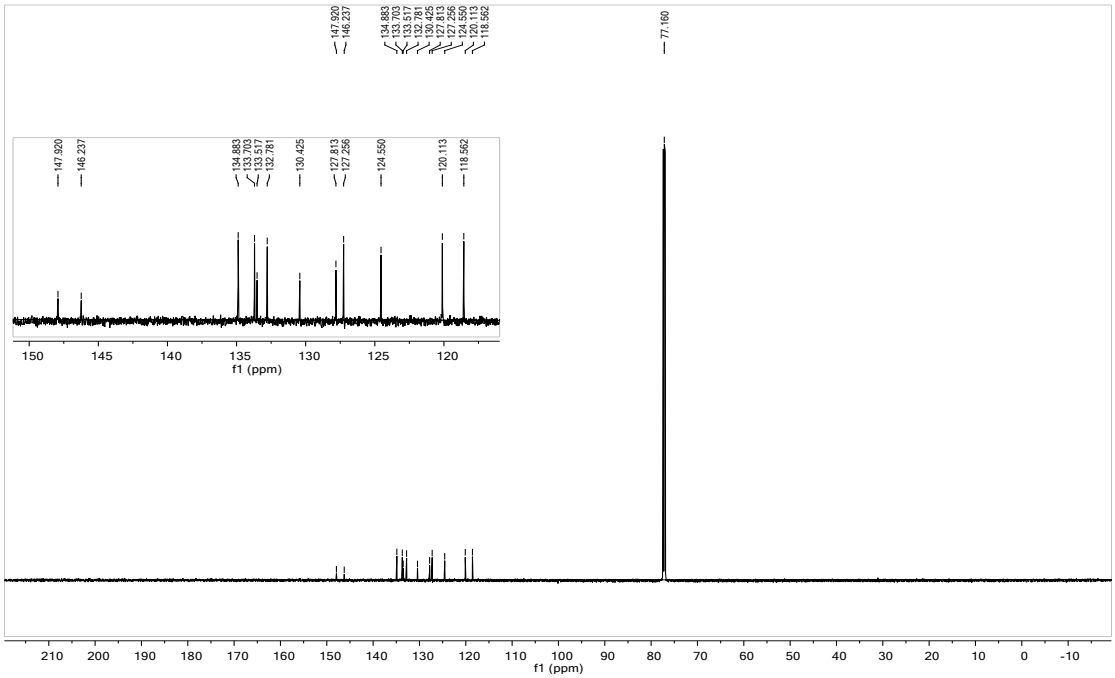


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **6-b'**.

6•I

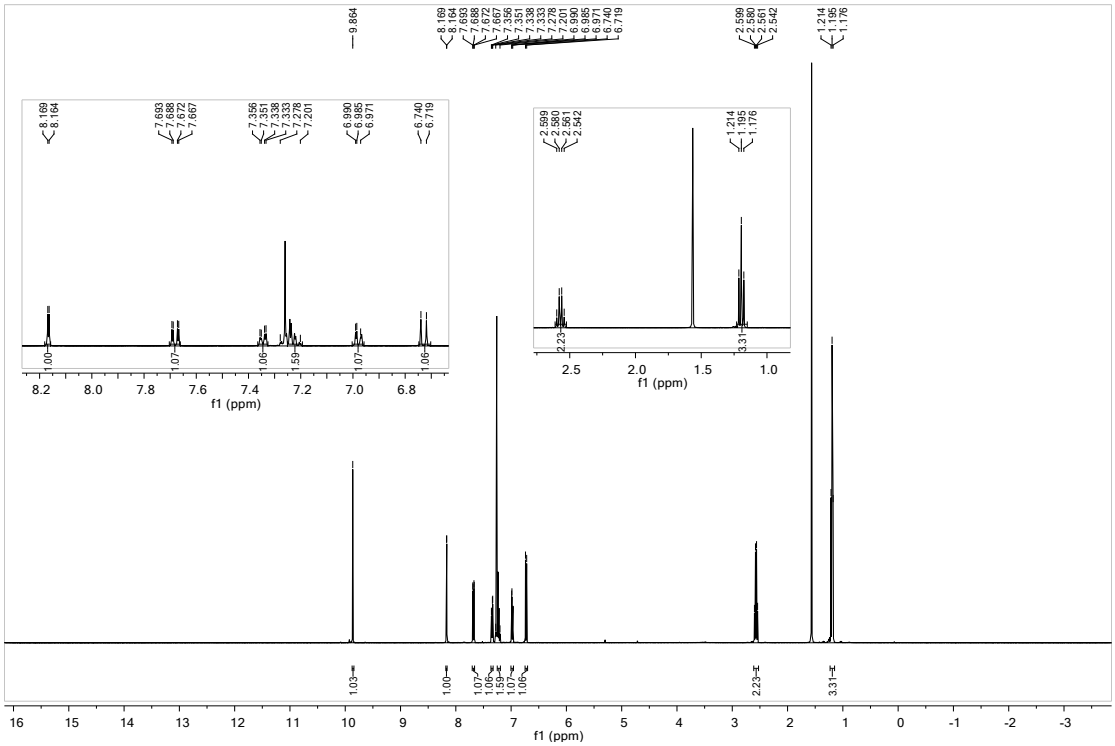


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **6•I**.

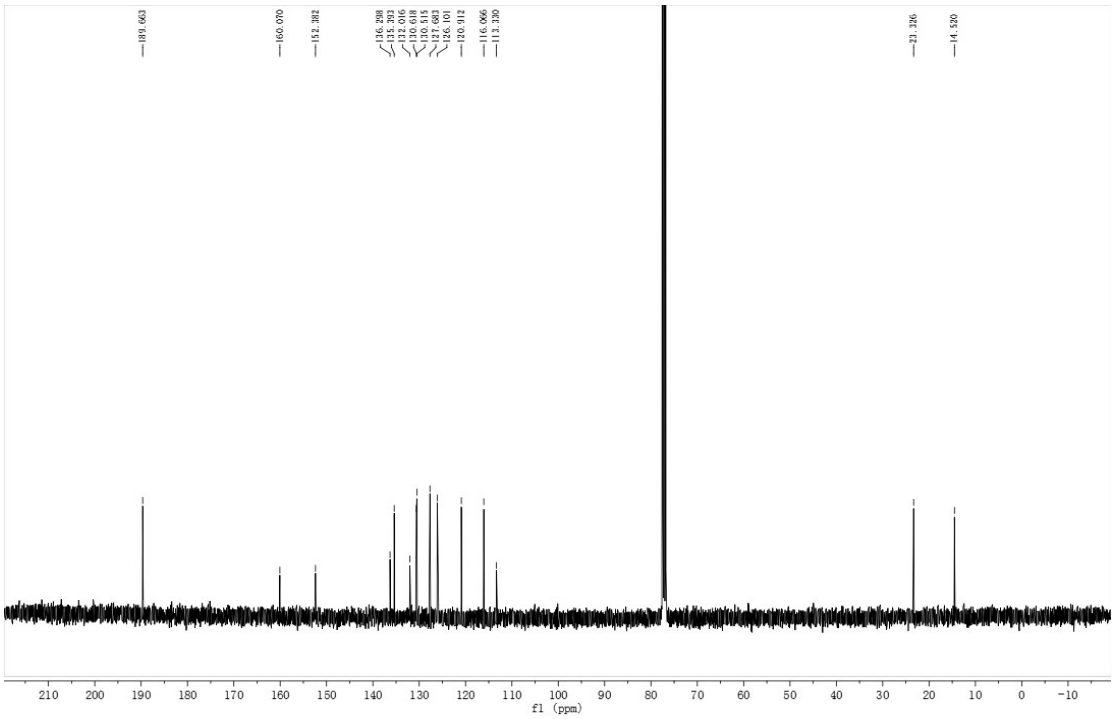


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **6•I.**

10-a’

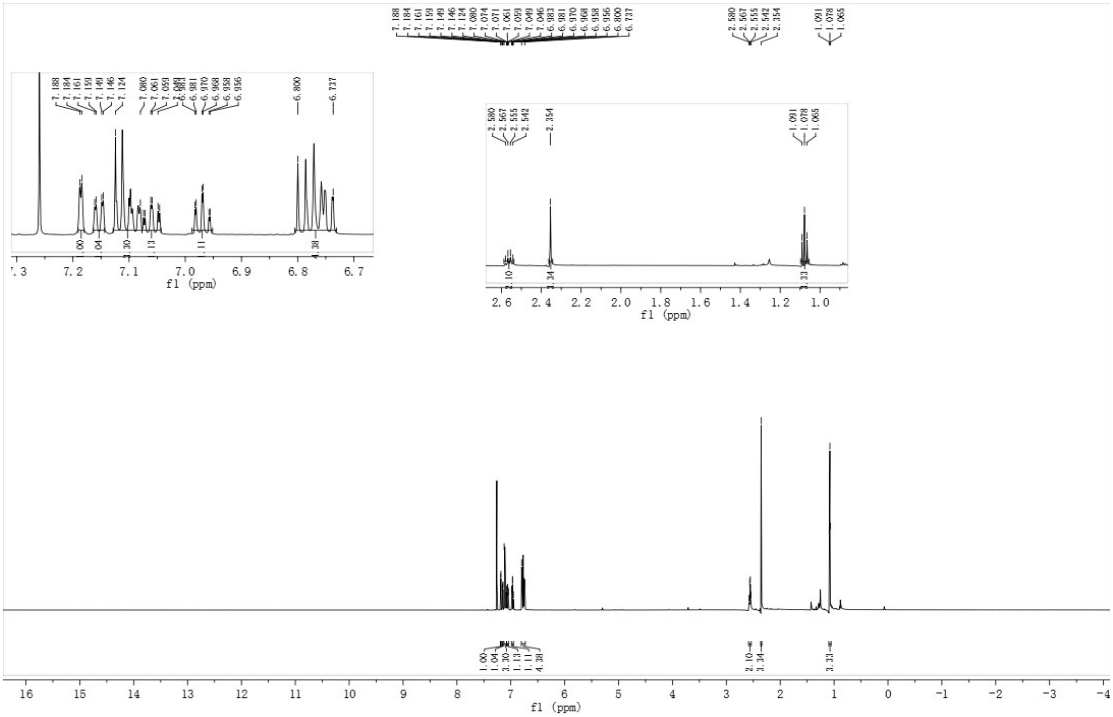


^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **10-a’**.

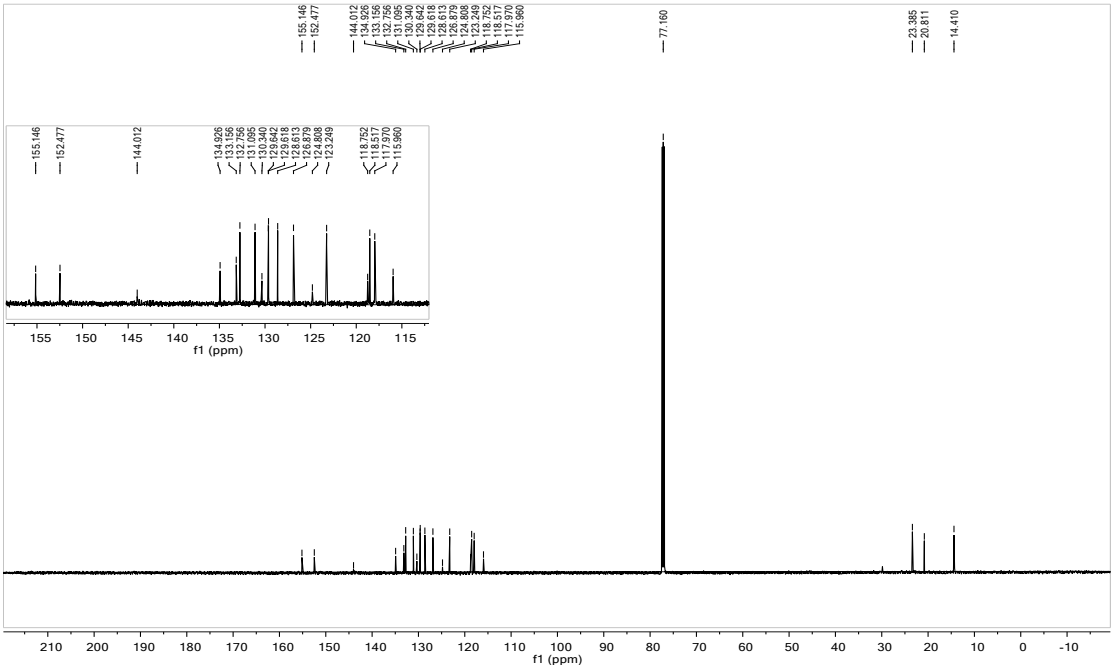


^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **10-a’**.

10-c'

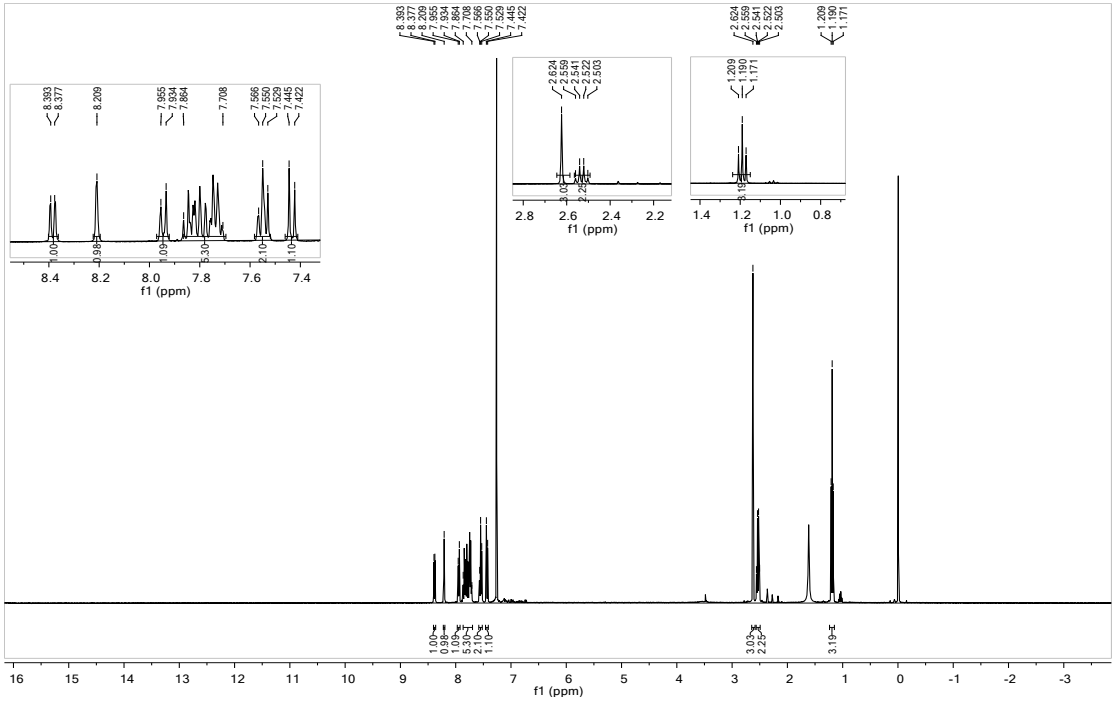


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **10-c'**.

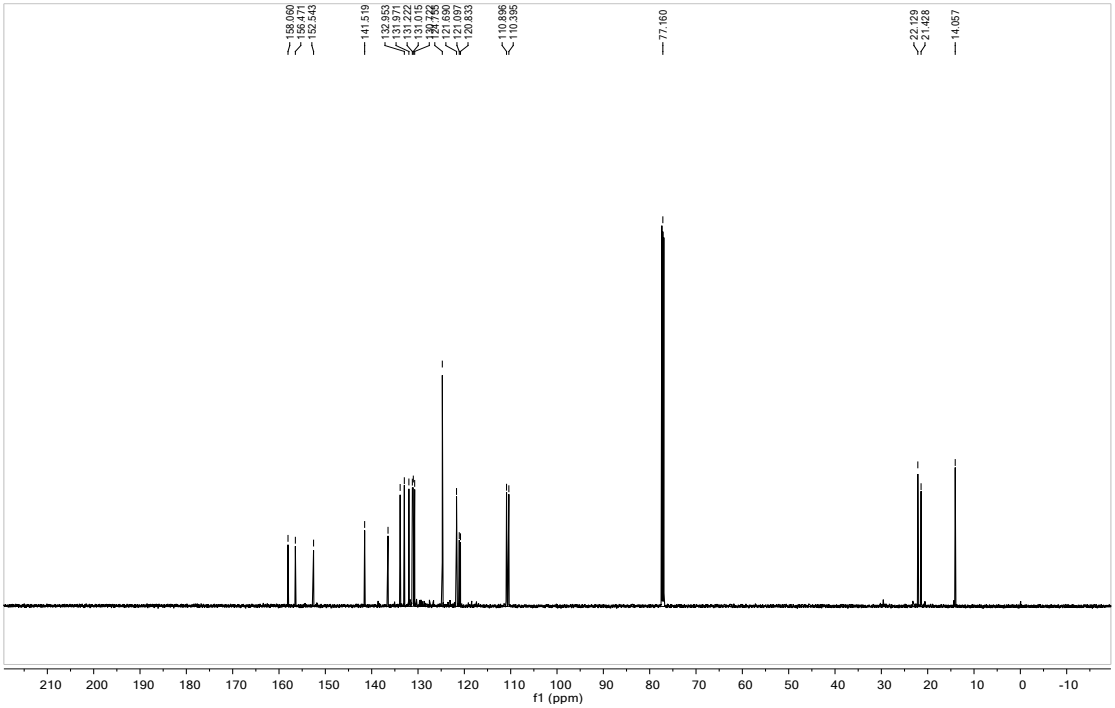


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **10-c'**.

10•I

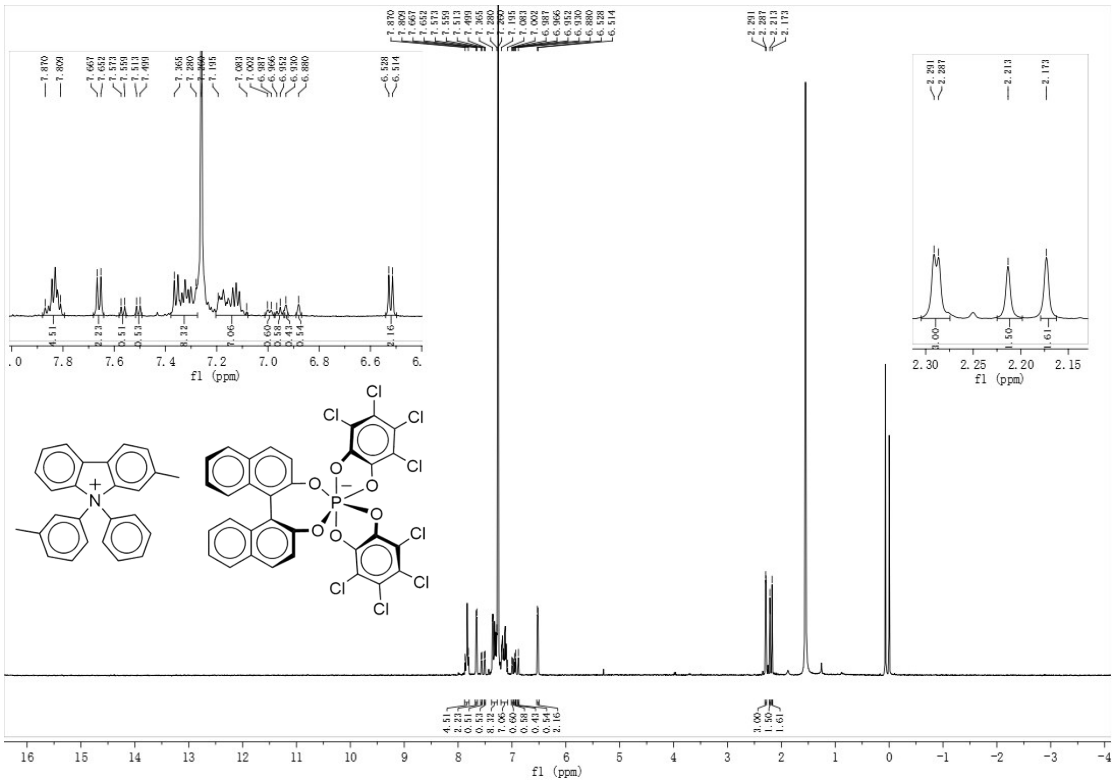


^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **10•I**.

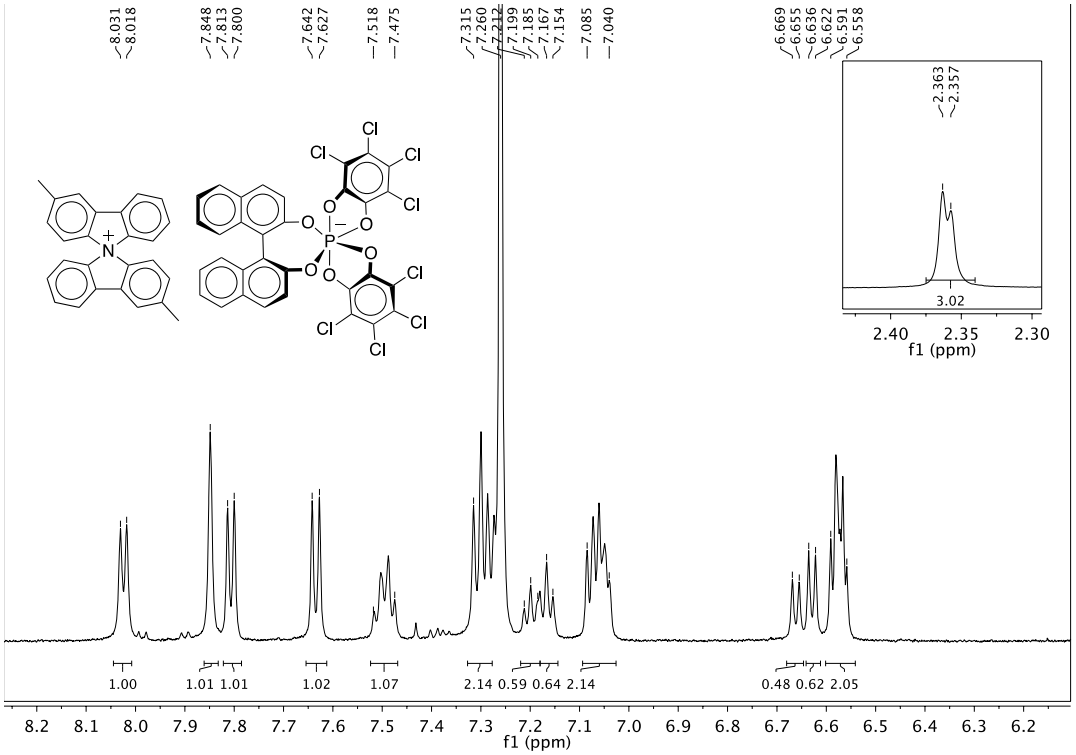


^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of **10•I**.

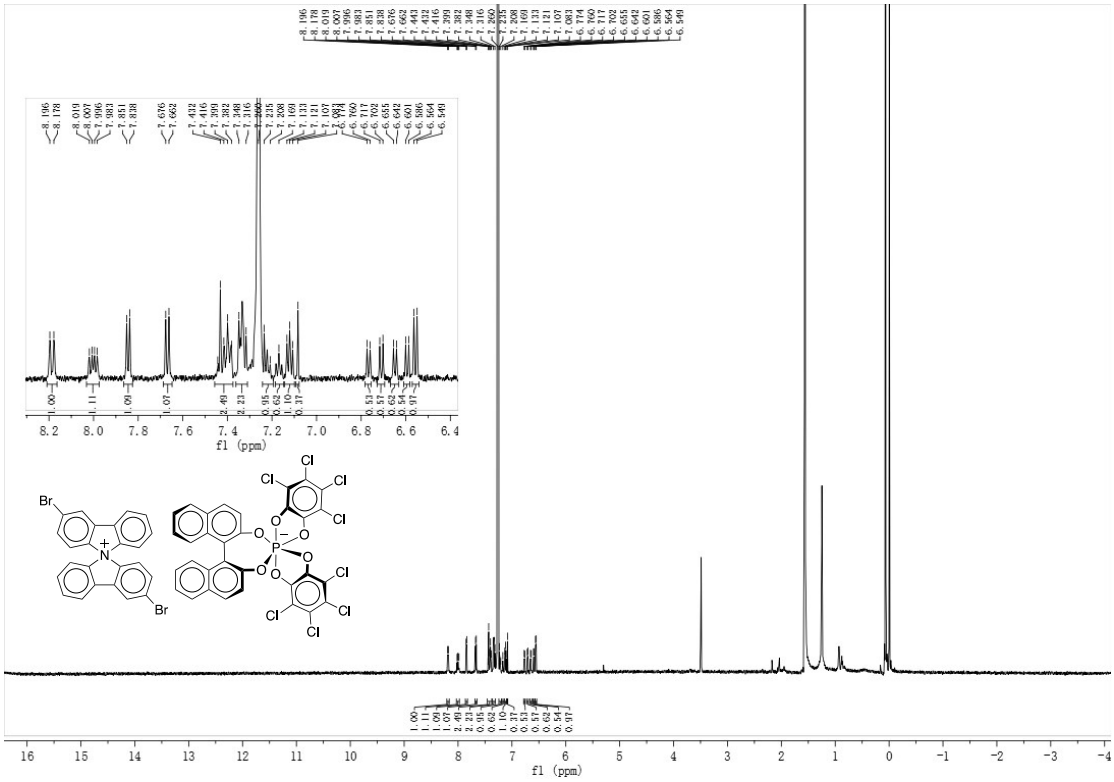
Spectra for BINPHAT salts.



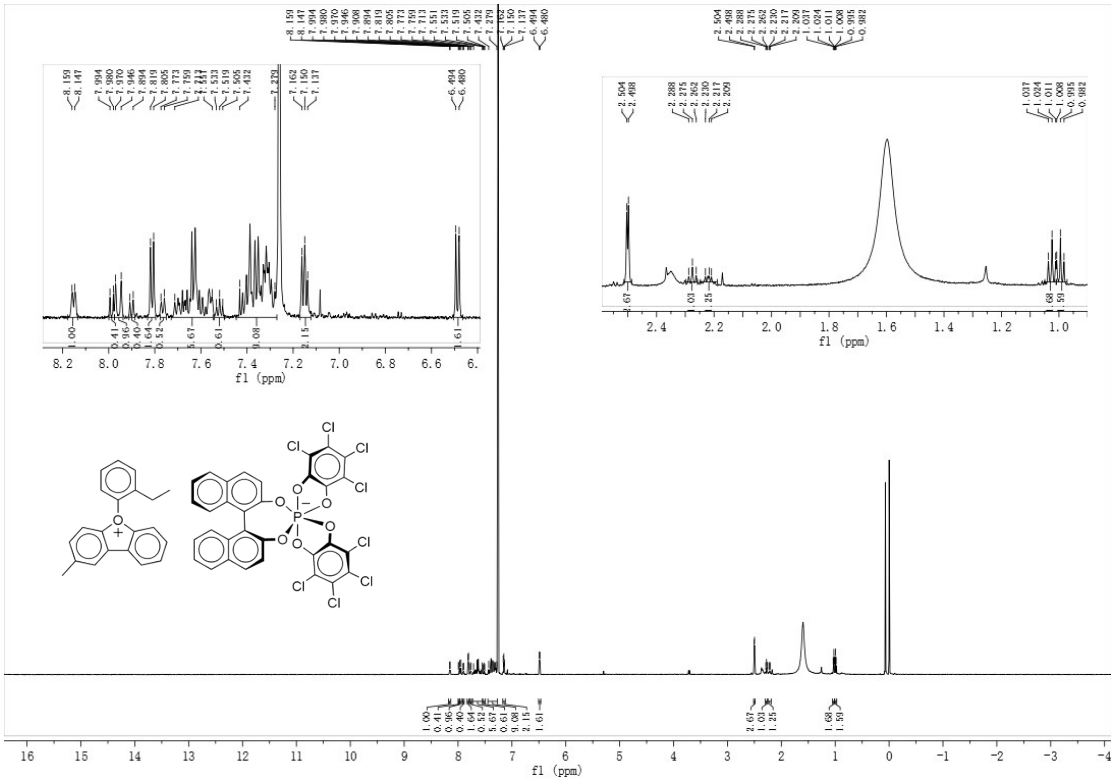
^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **2**•BINPHAT.



^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **5**•BINPHAT.

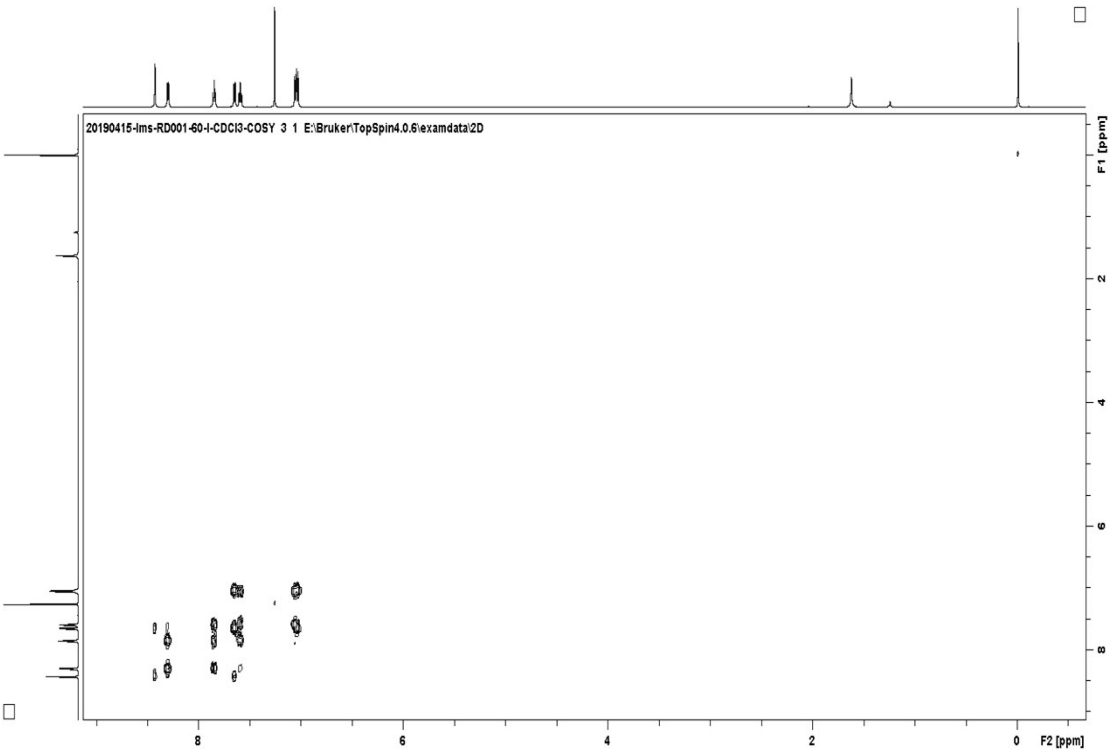


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **6**•BINPHAT.

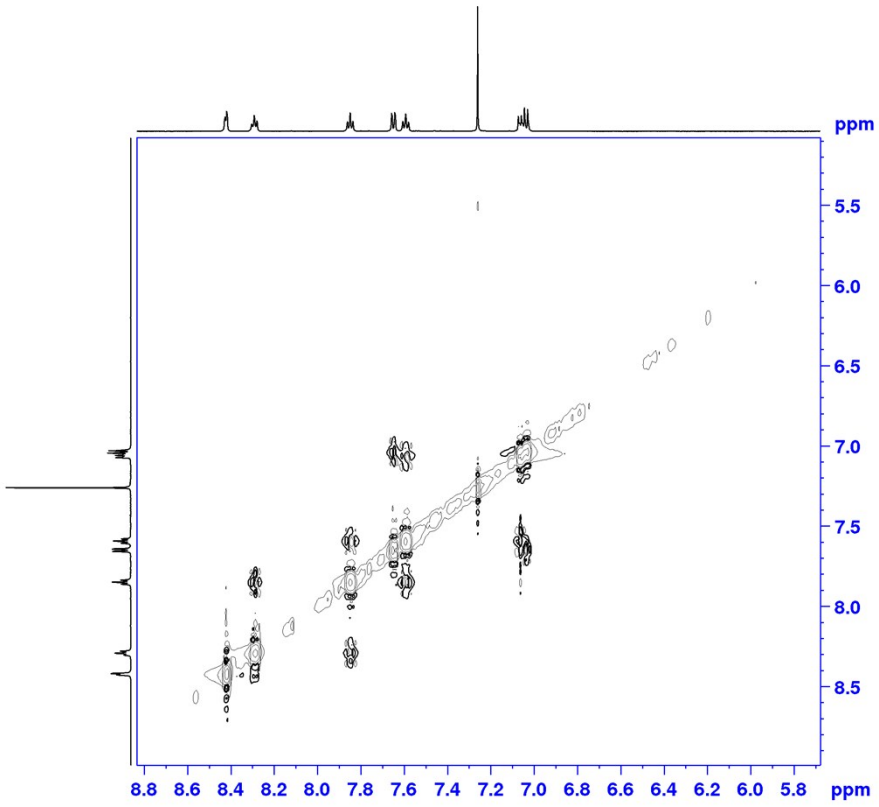


^{1}H-NMR (600 MHz, $CDCl_3$) spectrum of **10**•BINPHAT.

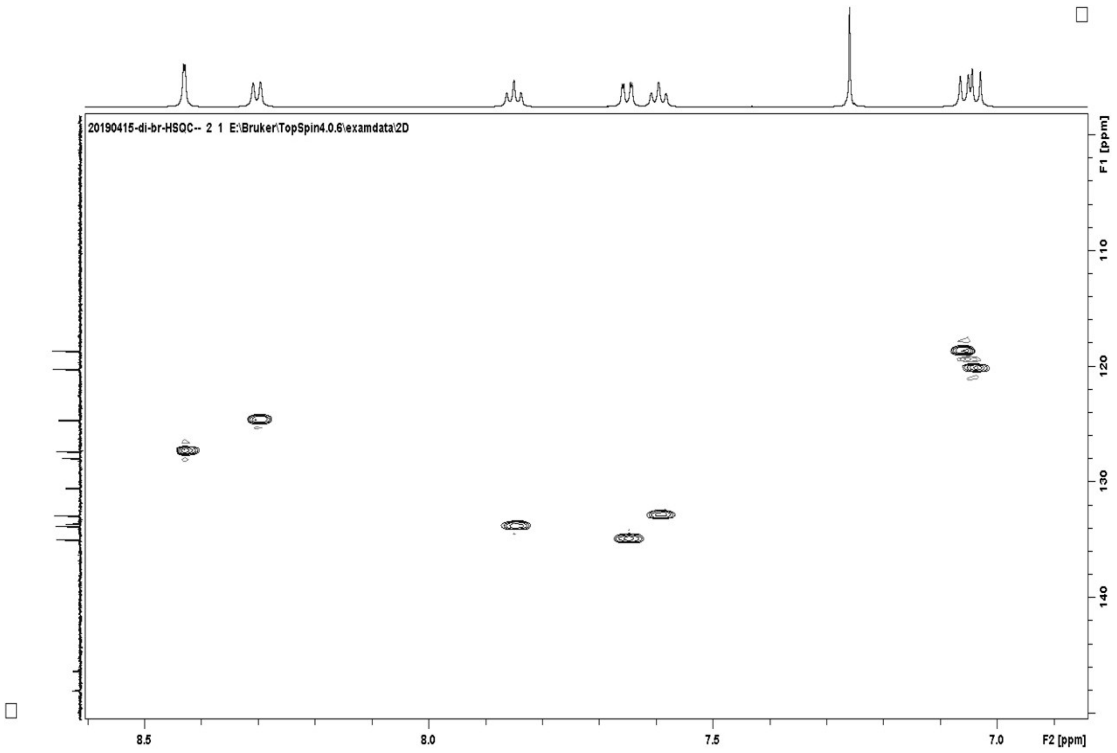
2D spectra (COSY, NOESY, HSQC and HMBC) of **6**•I, **6**•BINOL, **10**•AcO and **10**•BINOL.



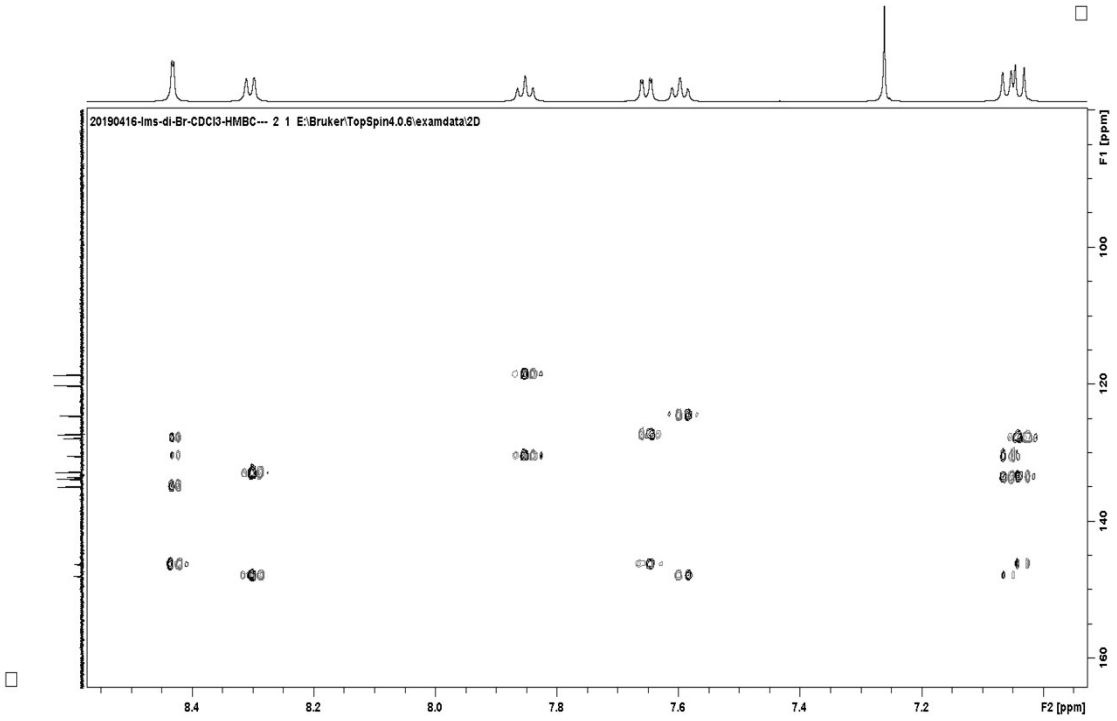
COSY (600 MHz, $CDCl_3$) spectrum of **6**•I.



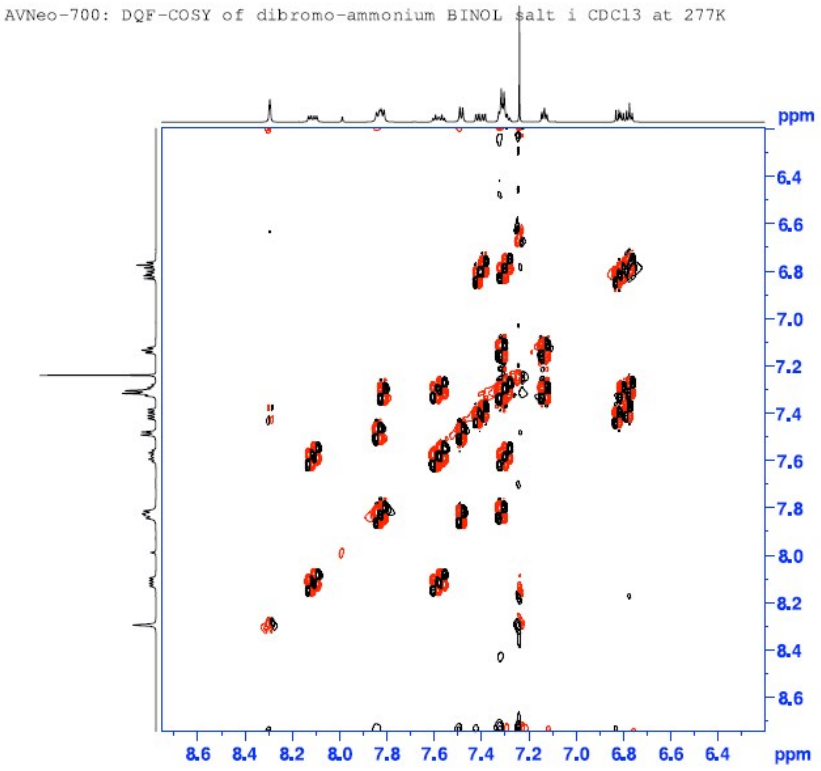
NOESY (600 MHz, $CDCl_3$) spectrum of **6**•I.



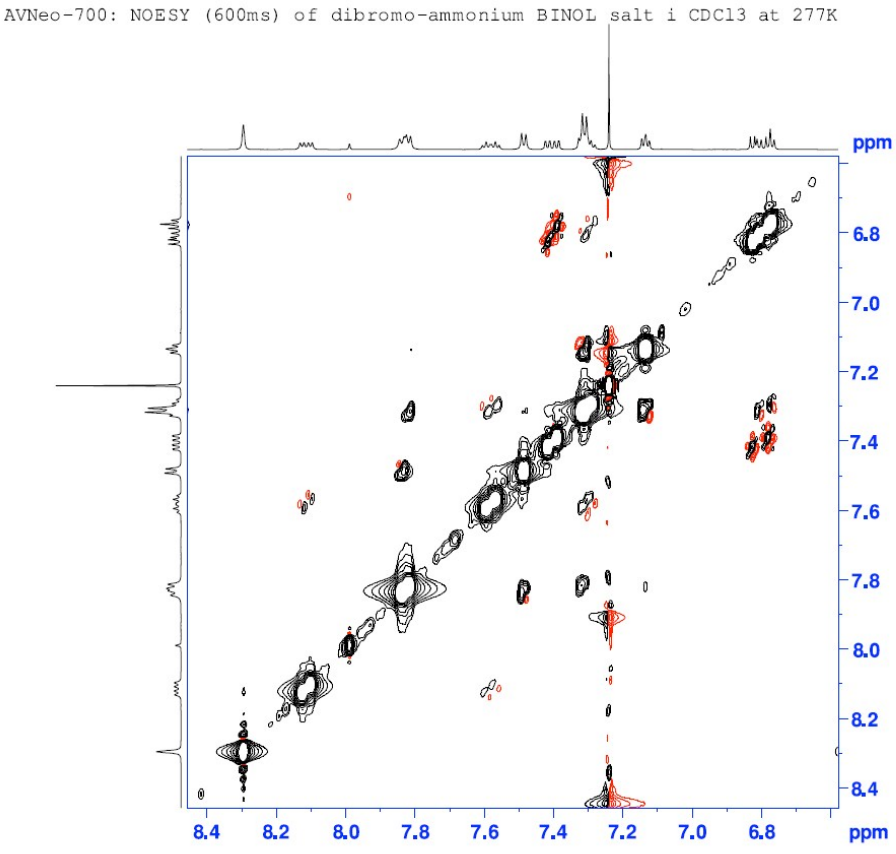
HSQC (600 MHz, $CDCl_3$) spectrum of **6•I**.



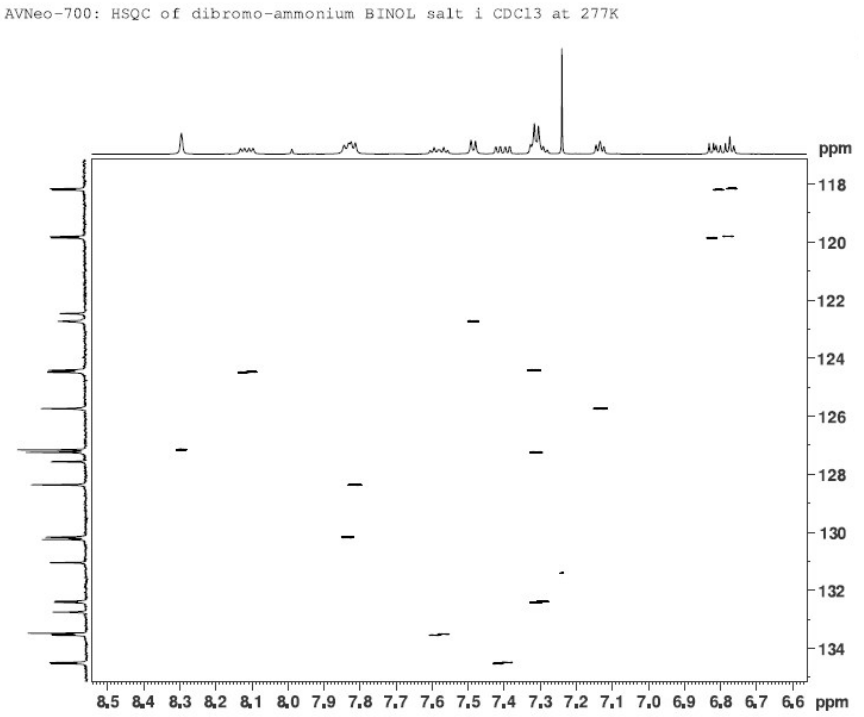
HMBC (600 MHz, $CDCl_3$) spectrum of **6•I**.



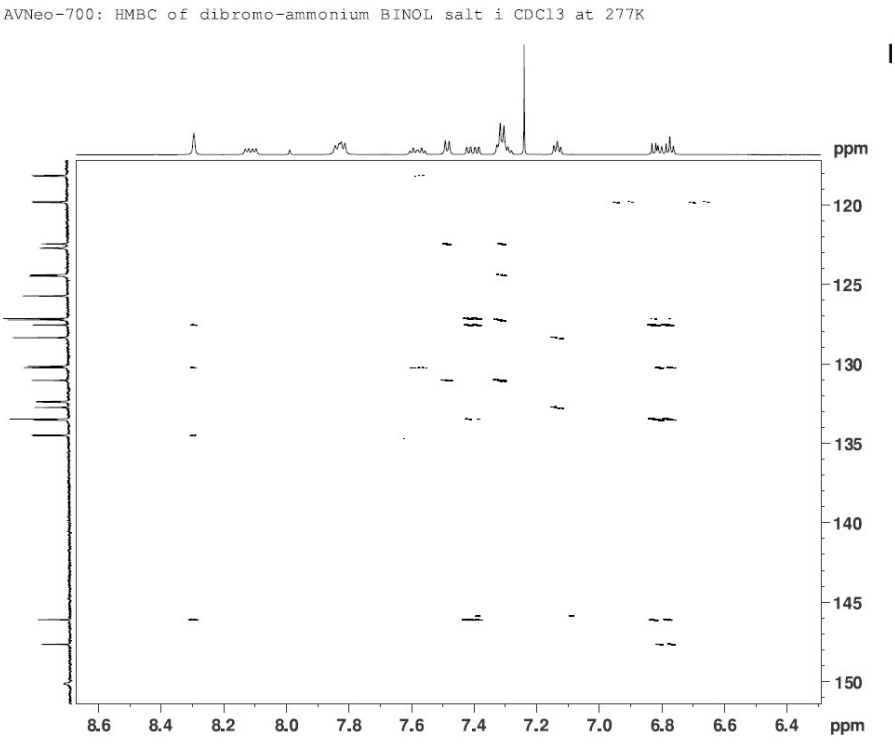
DQF-COSY (700 MHz, $CDCl_3$) spectrum of **6**•BINOL.



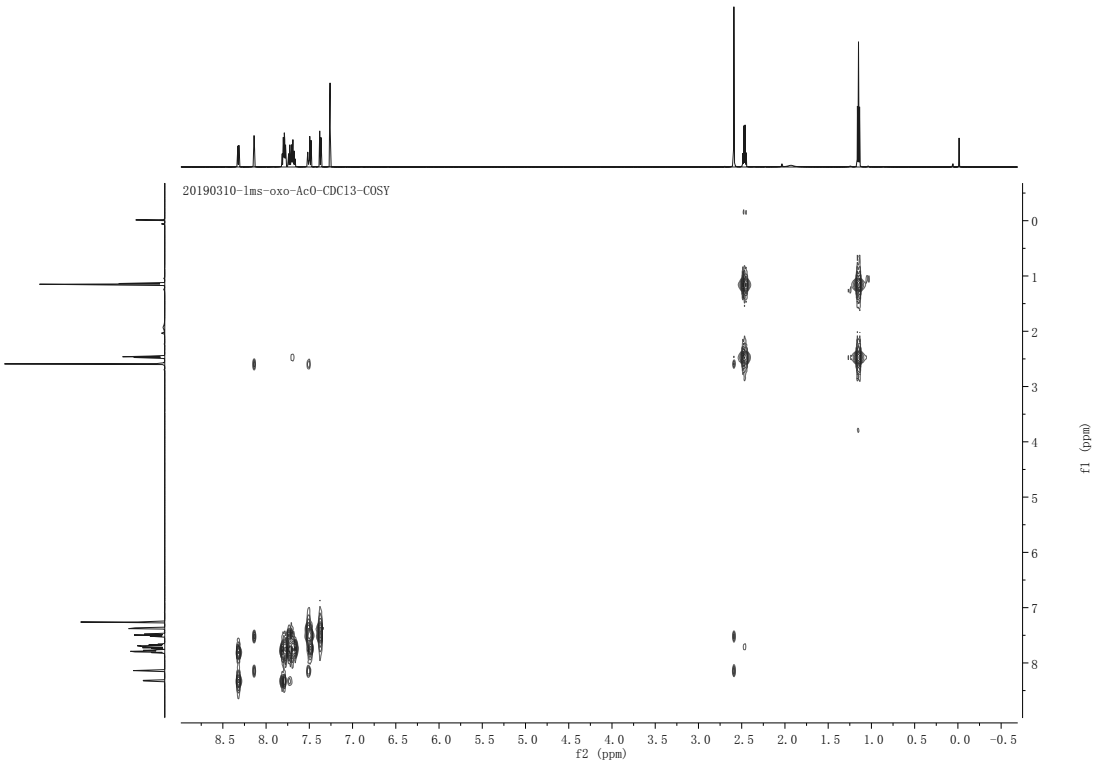
DQF-NOESY (700 MHz, $CDCl_3$) spectrum of **6**•BINOL.



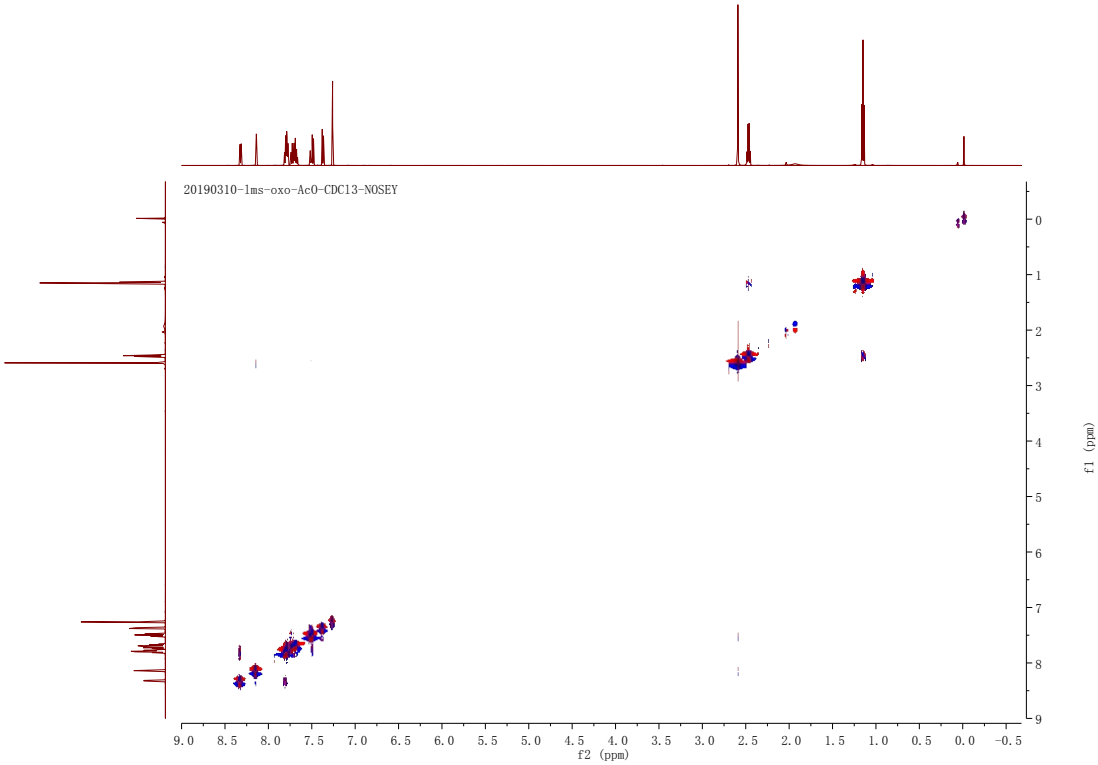
HSQC (700 MHz, $CDCl_3$) spectrum of **6**•BINOL.



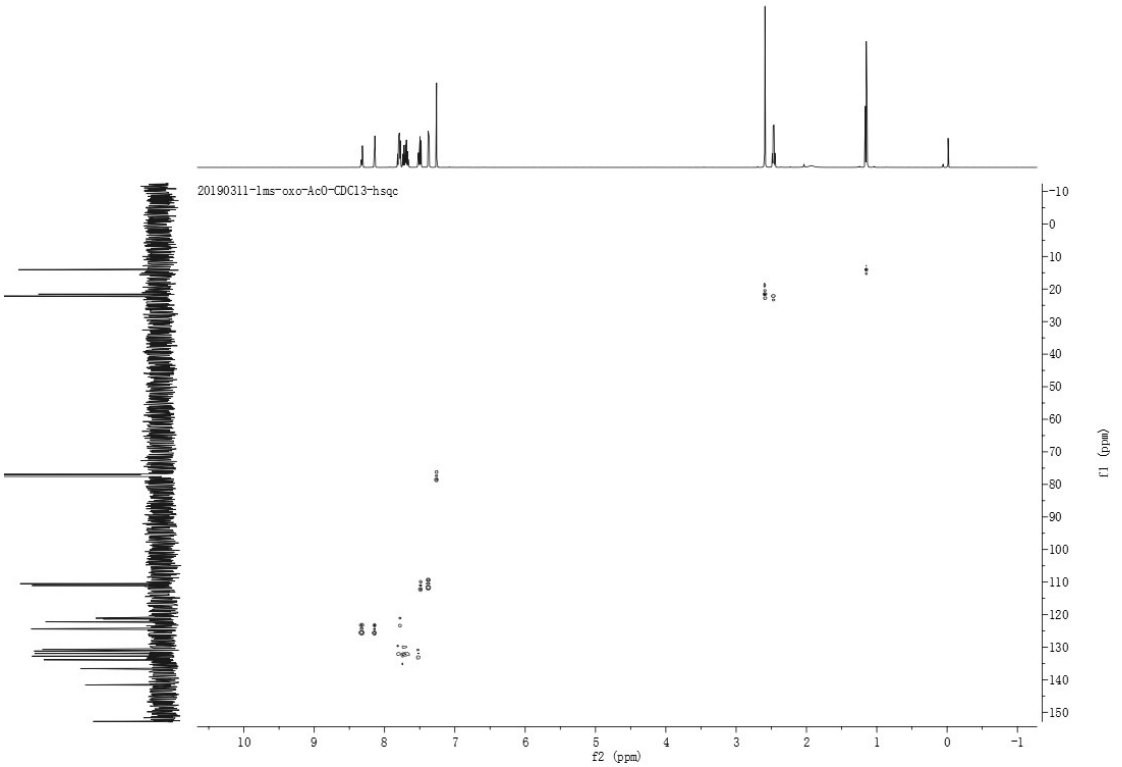
HSQC (700 MHz, $CDCl_3$) spectrum of **6**•BINOL.



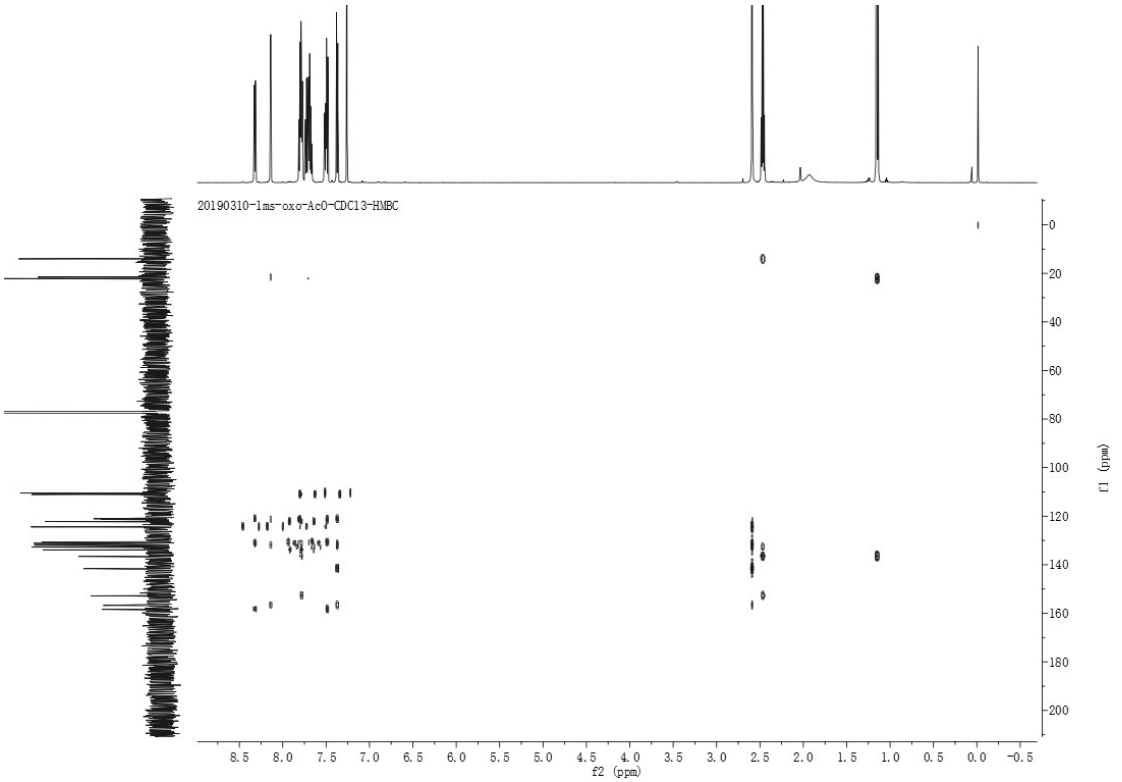
COSY (600 MHz, $CDCl_3$) spectrum of **10**•AcO.



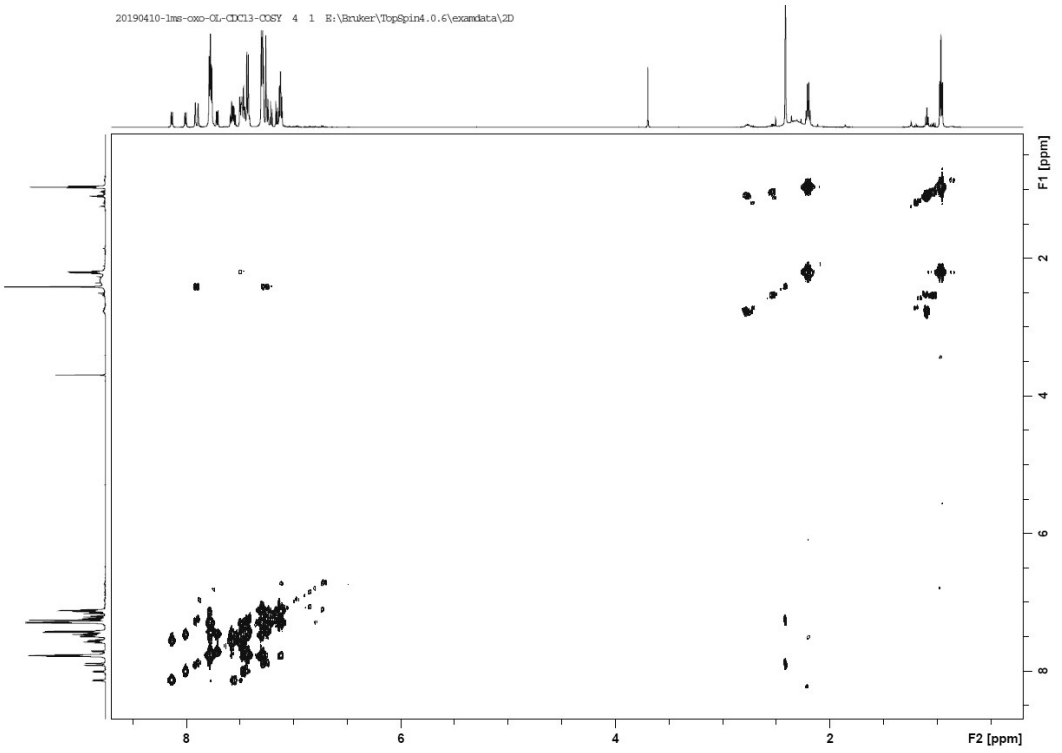
NOESY (600 MHz, $CDCl_3$) spectrum of **10**•AcO.



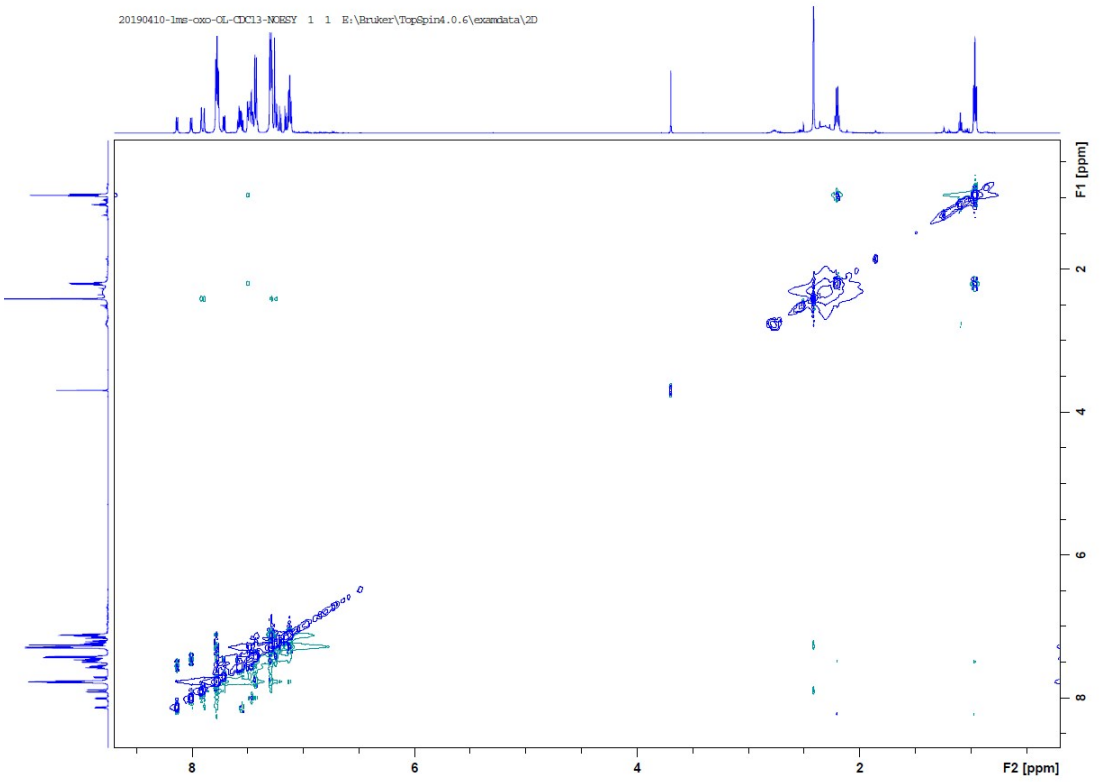
HSQC (600 MHz, $CDCl_3$) spectrum of **10**•AcO.



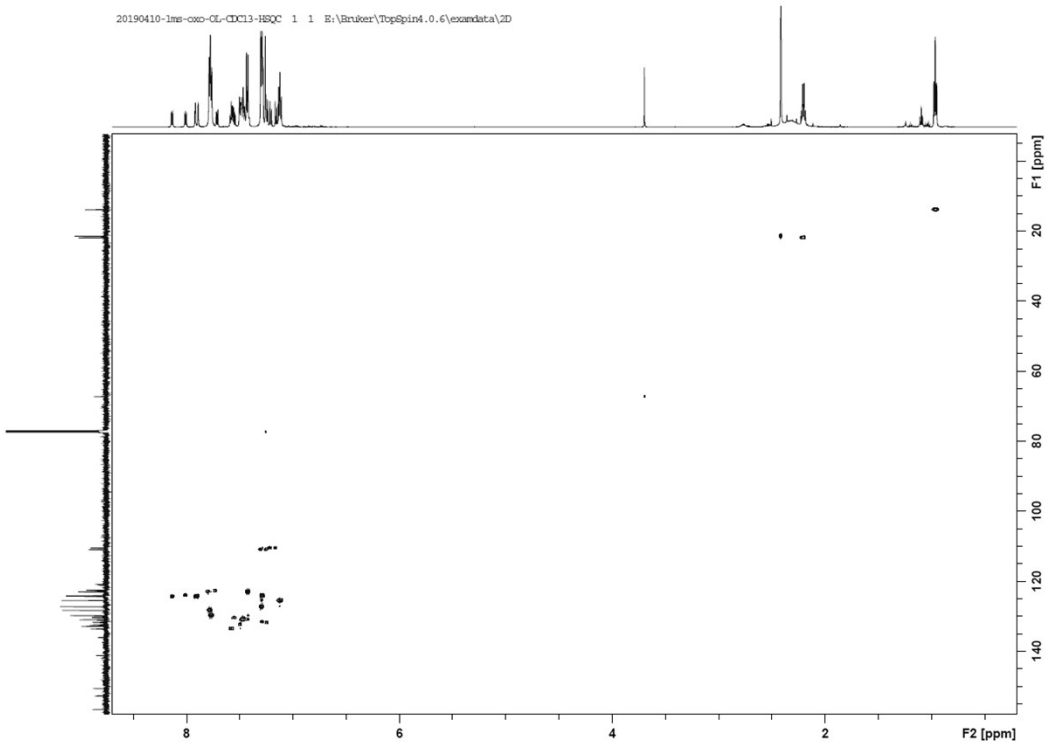
HMBC (600 MHz, $CDCl_3$) spectrum of **10**•AcO.



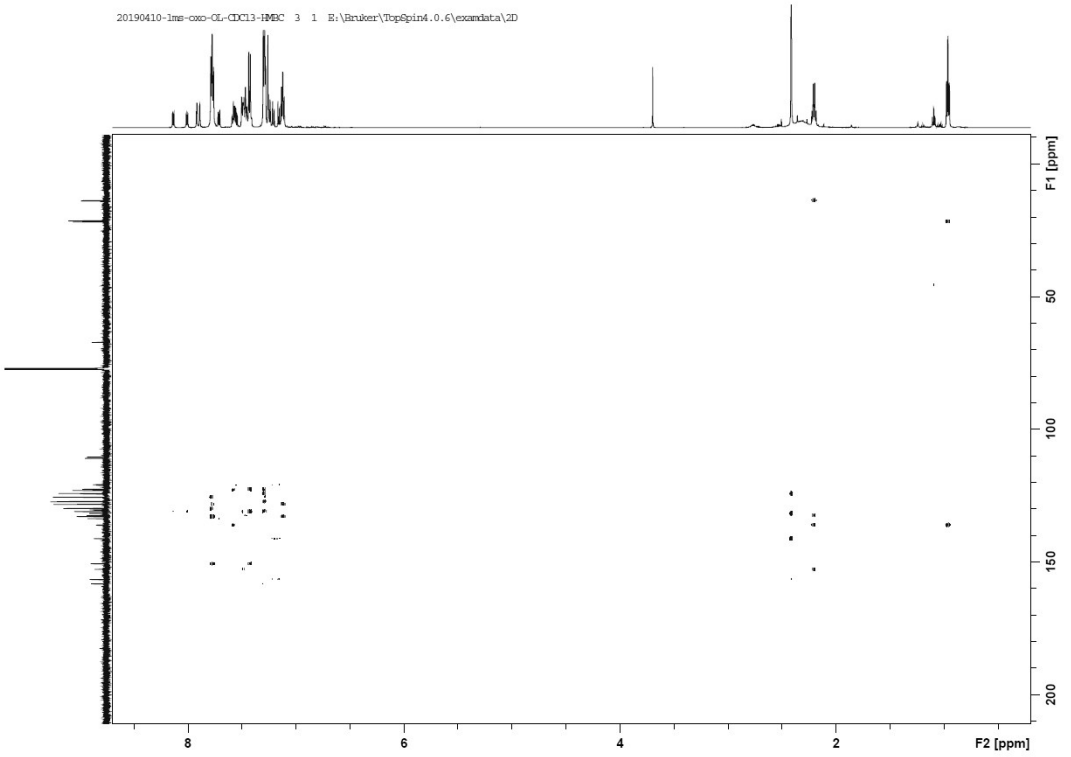
COSY (600 MHz, $CDCl_3$) spectrum of **10**•BINOL.



NOESY (600 MHz, $CDCl_3$) spectrum of **10**•BINOL.

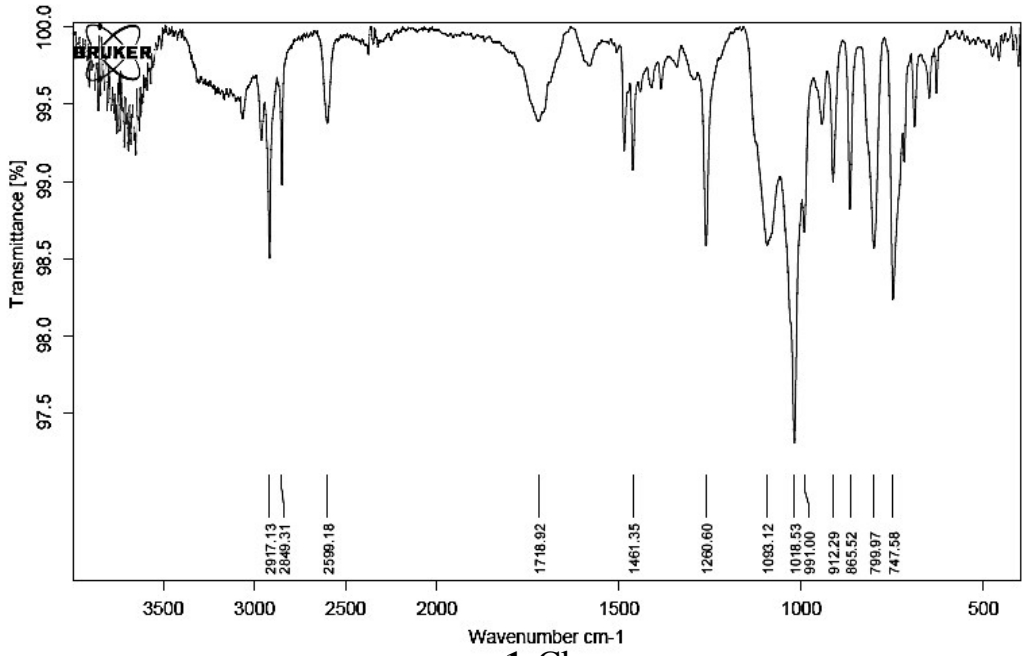


HSQC (600 MHz, $CDCl_3$) spectrum of **10**•BINOL.

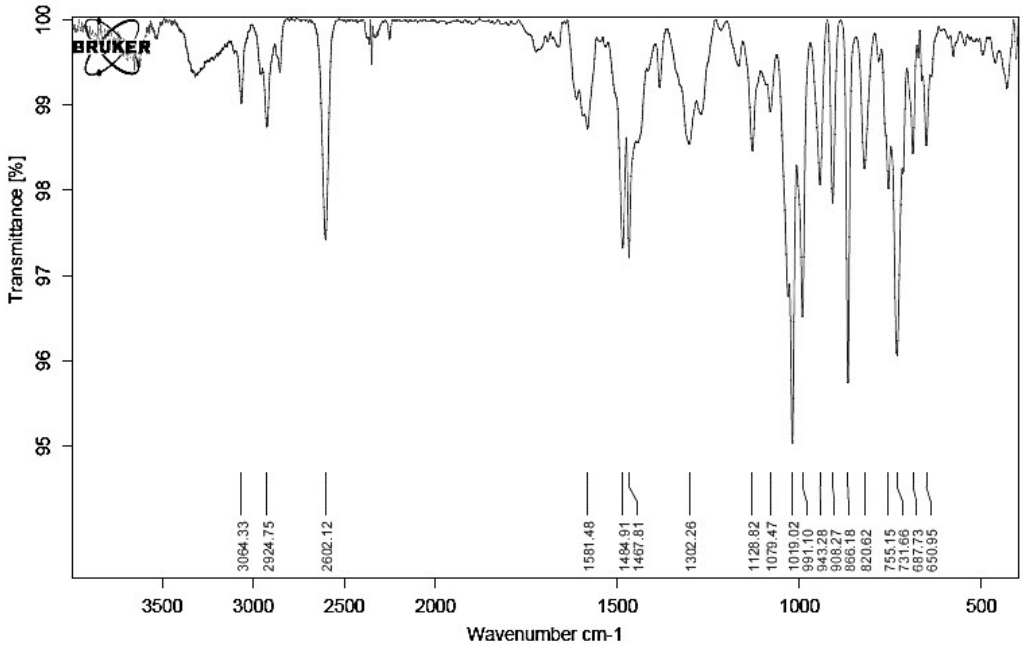


HMBC (600 MHz, $CDCl_3$) spectrum of **10**•BINOL.

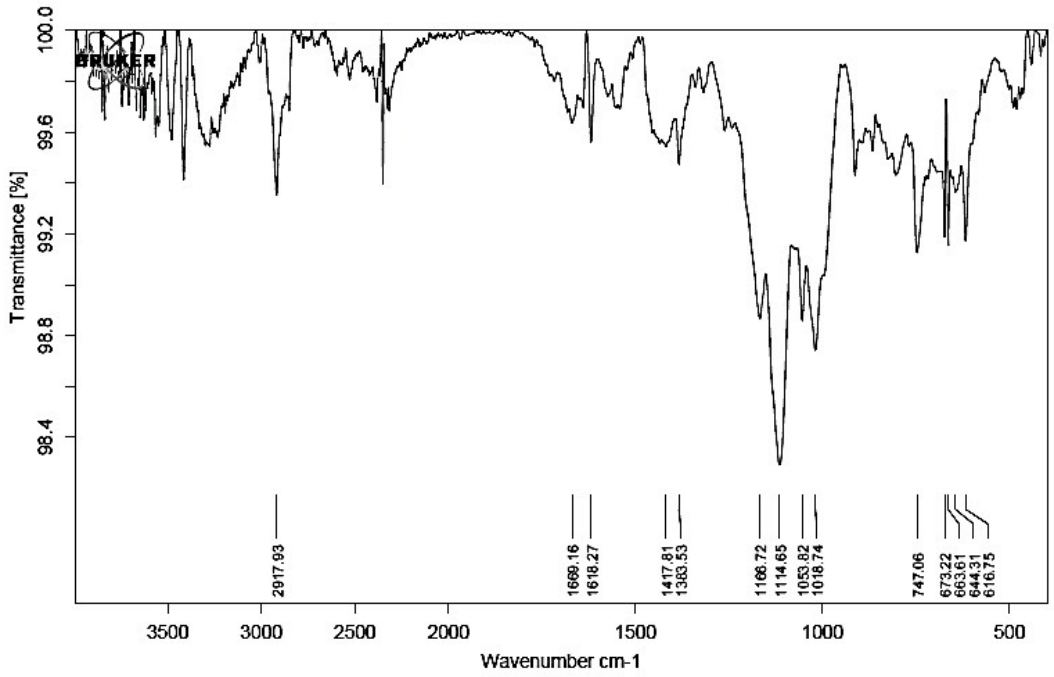
IR spectra



1•Cb



2•Cb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98.4
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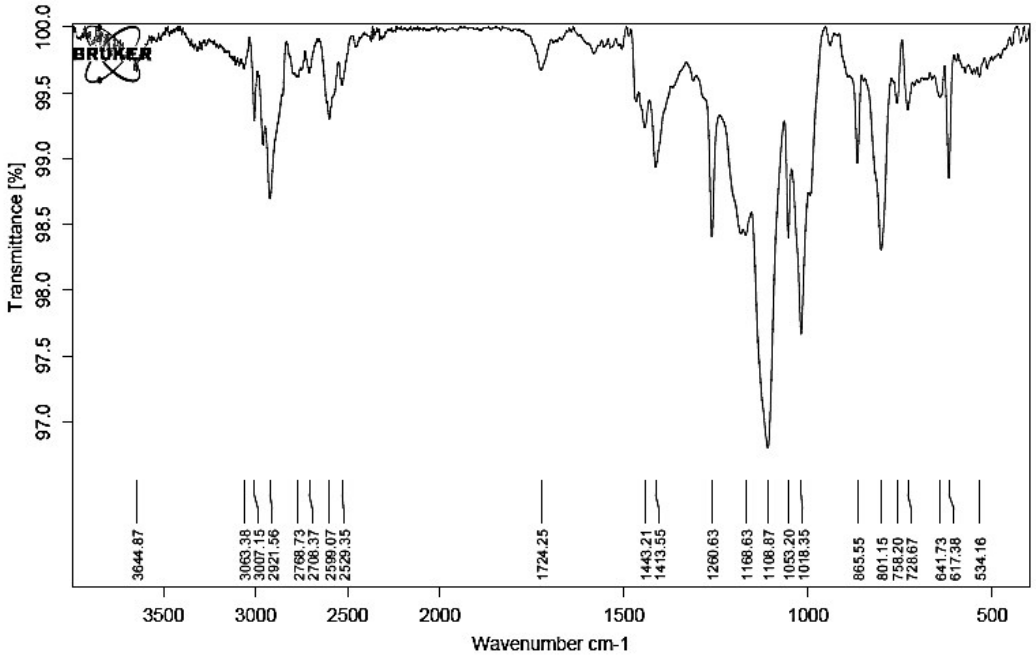
1383.53
1166.72
1114.65
1053.82
1018.74
747.06
673.22
663.61
644.31
616.75
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

3•Cb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2708.37
2599.07
2529.35
1724.25
1443.21
1413.55
1260.63
1168.63
1108.87
1053.20
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865.55
801.15
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3500
3000
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1500
1000
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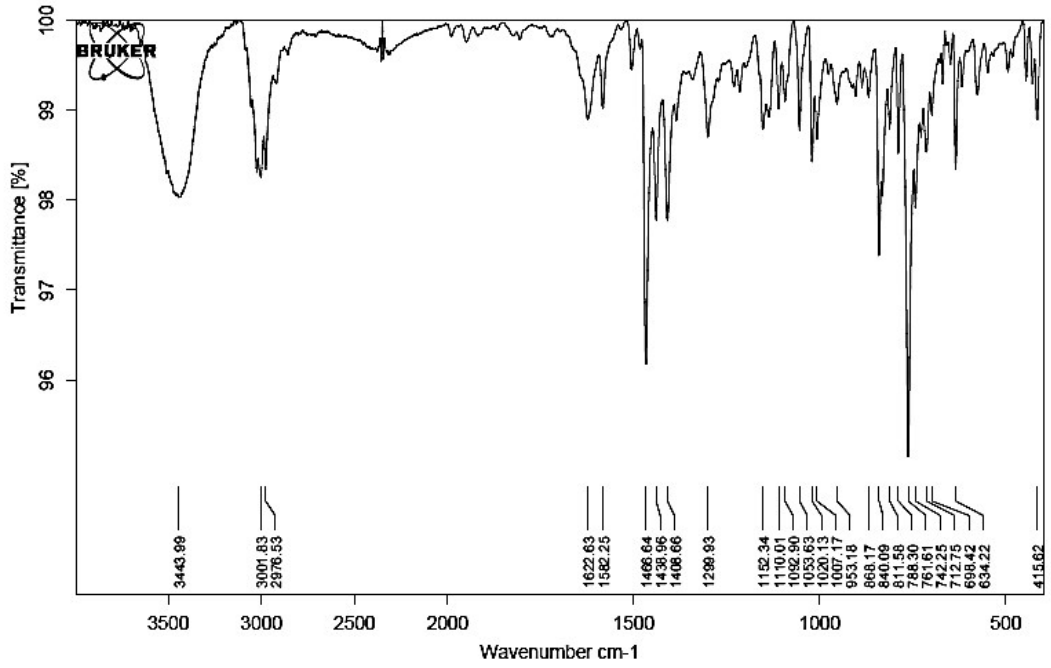
Wavenumber cm-1

4•Cb


BRUKER
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1110.01
1092.90
1053.63
1020.13
1007.17
953.18
868.17
840.09
811.58
788.30
761.61
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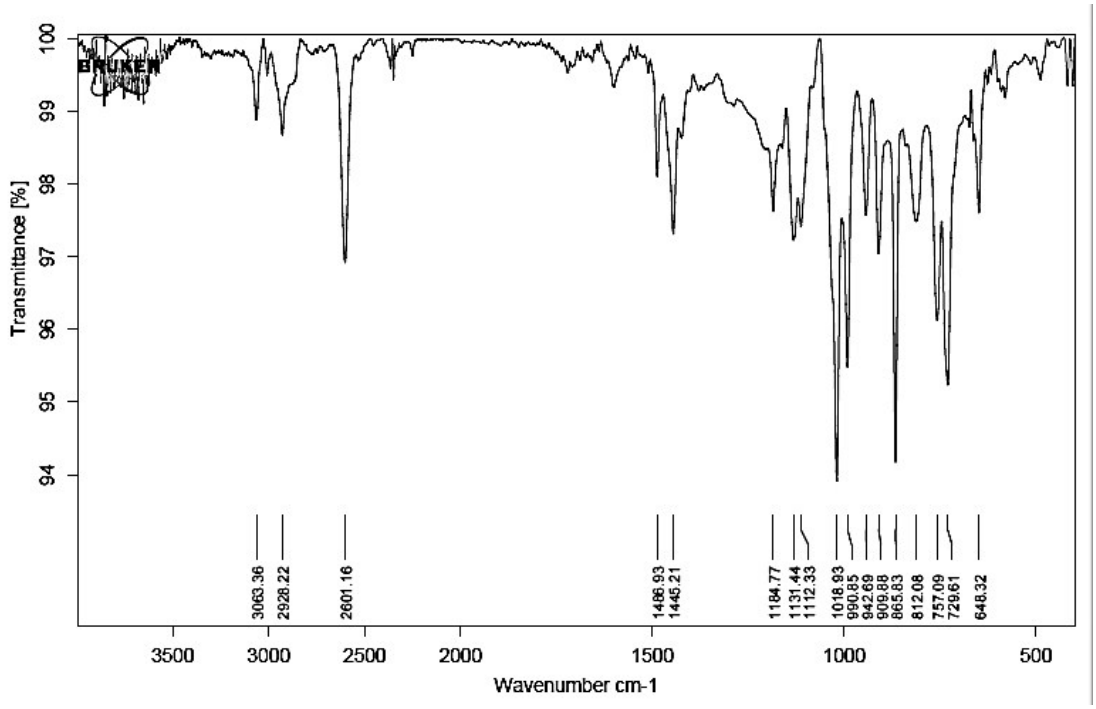
Wavenumber cm-1

4•I


BRUKER
Transmittance [%]
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990.85
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909.88
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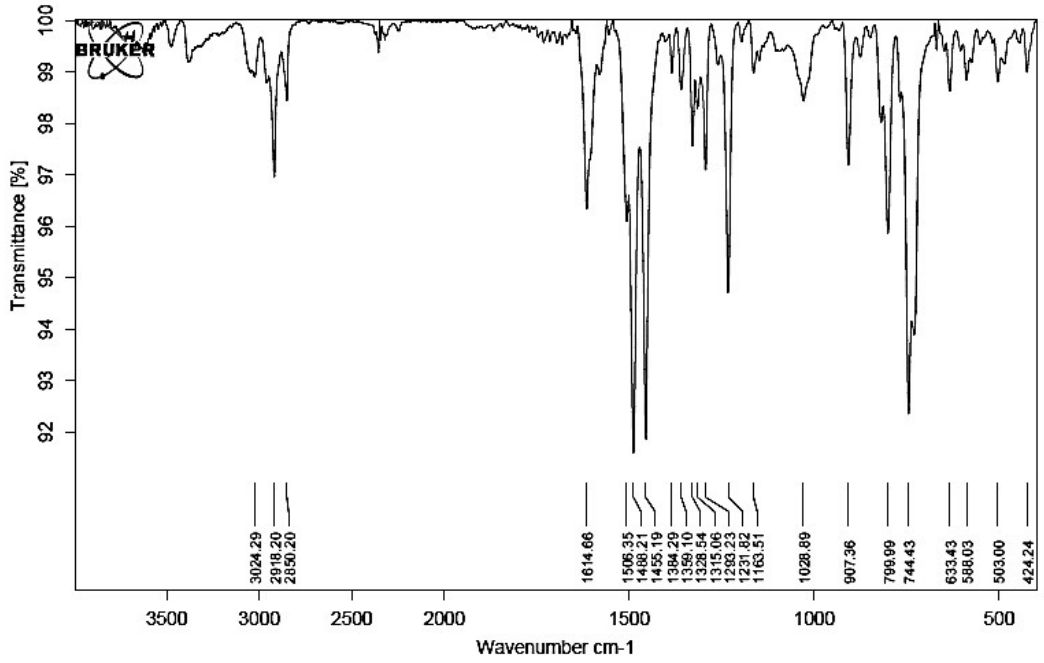
Wavenumber cm-1

5•Cb


BRUKER
Transmittance [%]
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1384.29
1359.10
1328.54
1315.06
1283.23
1231.82
1163.51
1028.89
907.36
799.99
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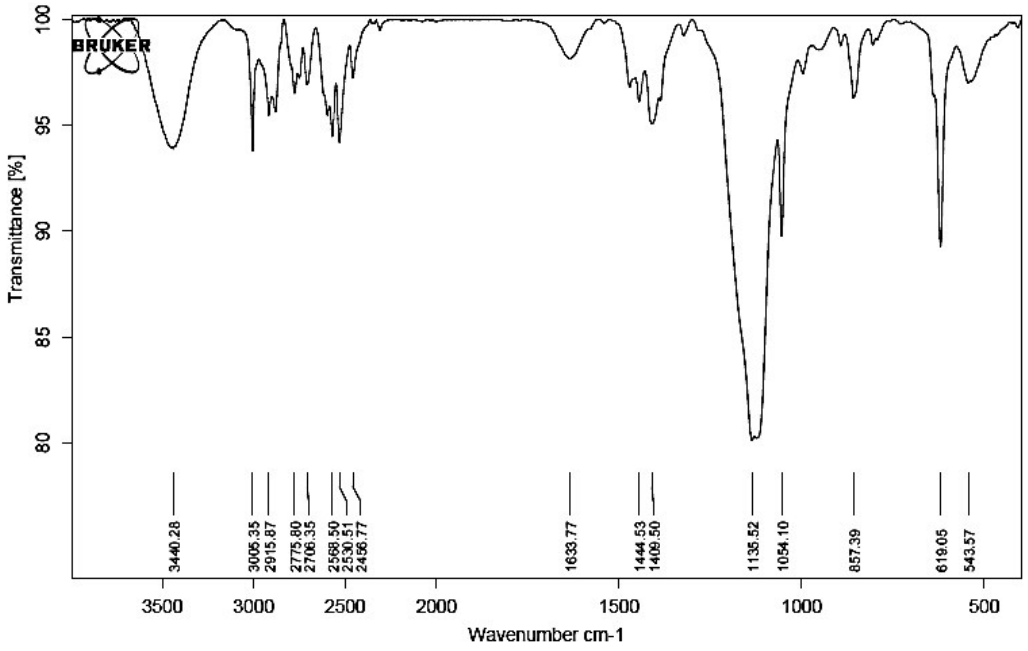
588.03
503.00
424.24
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

5•I


BRUKER
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90
85
80
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1444.53
1409.50
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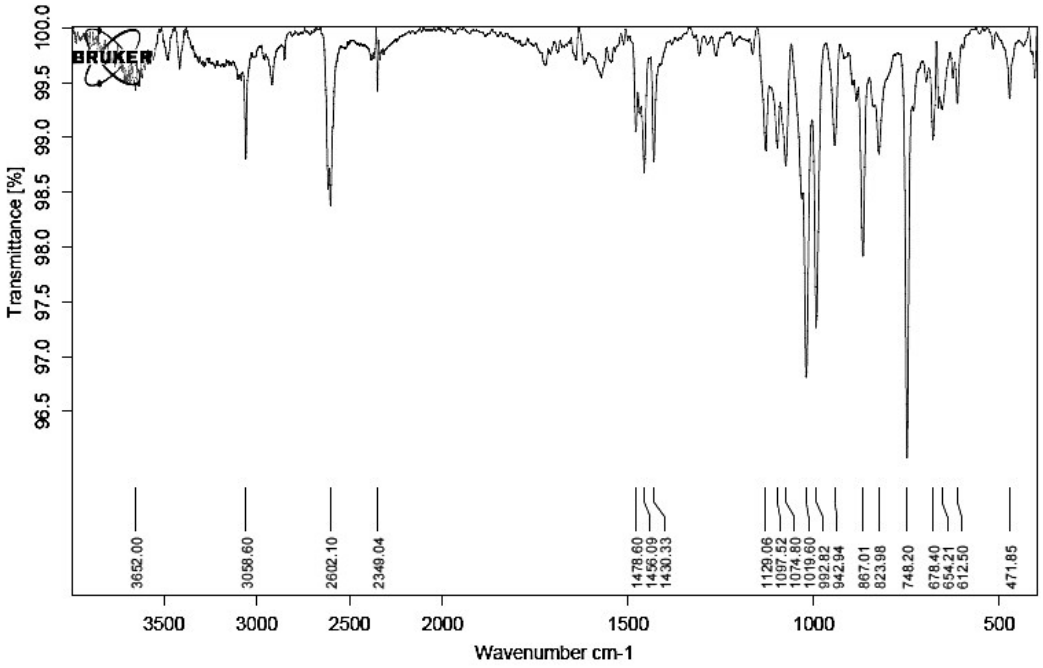
Wavenumber cm-1

6•I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1456.09
1430.33
1129.06
1097.52
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942.94
867.01
823.98
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2000
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1000
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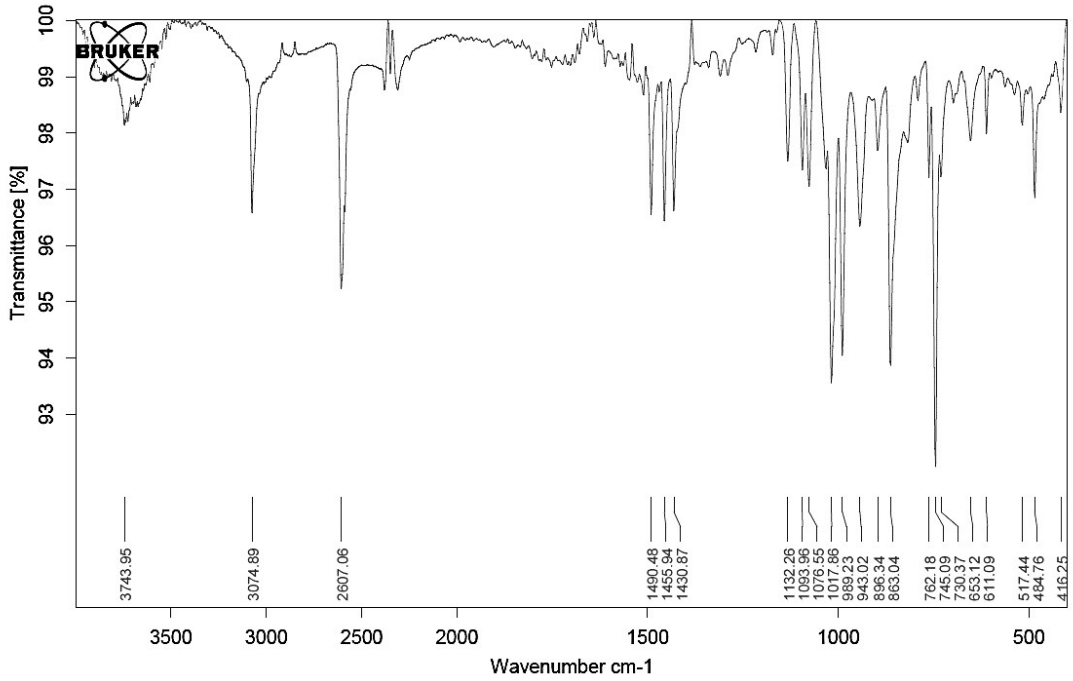
Wavenumber cm-1

7•Cb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Transmittance [%]
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98
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96
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94
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1093.96
1076.55
1017.86
989.23
943.02
896.34
863.04
762.18
745.09
730.37
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416.25
3500
3000
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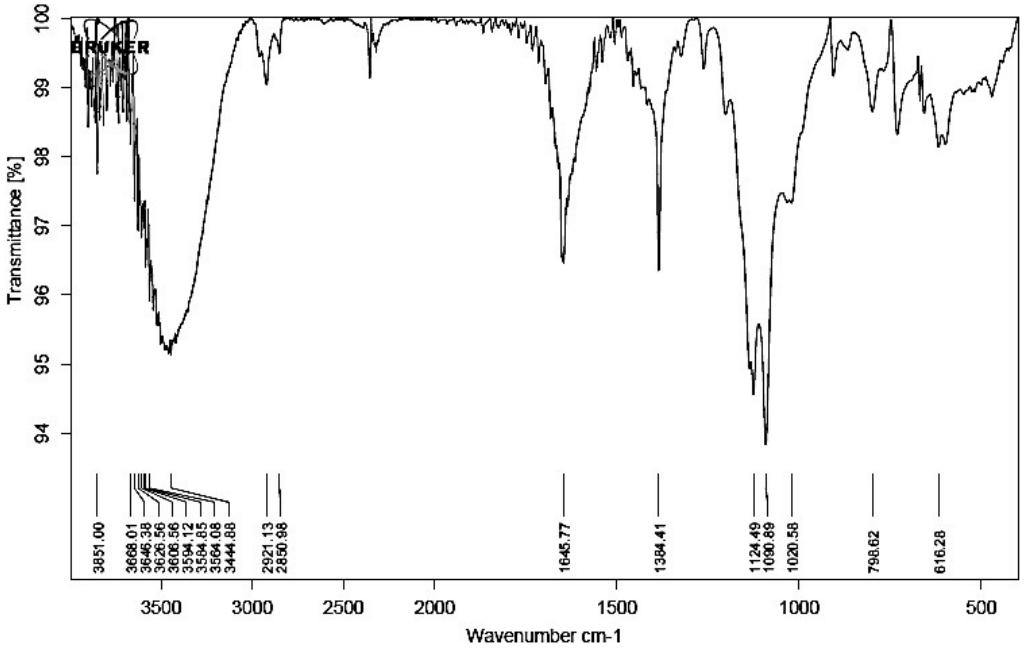
2000
1500
1000
500
Wavenumber cm-1

8•Cb


BRUKER
Transmittance [%]
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98
97
96
95
94
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3606.56
3594.12
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3564.08
3444.88
2921.13
2850.98
1645.77
1384.41
1124.49
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3000
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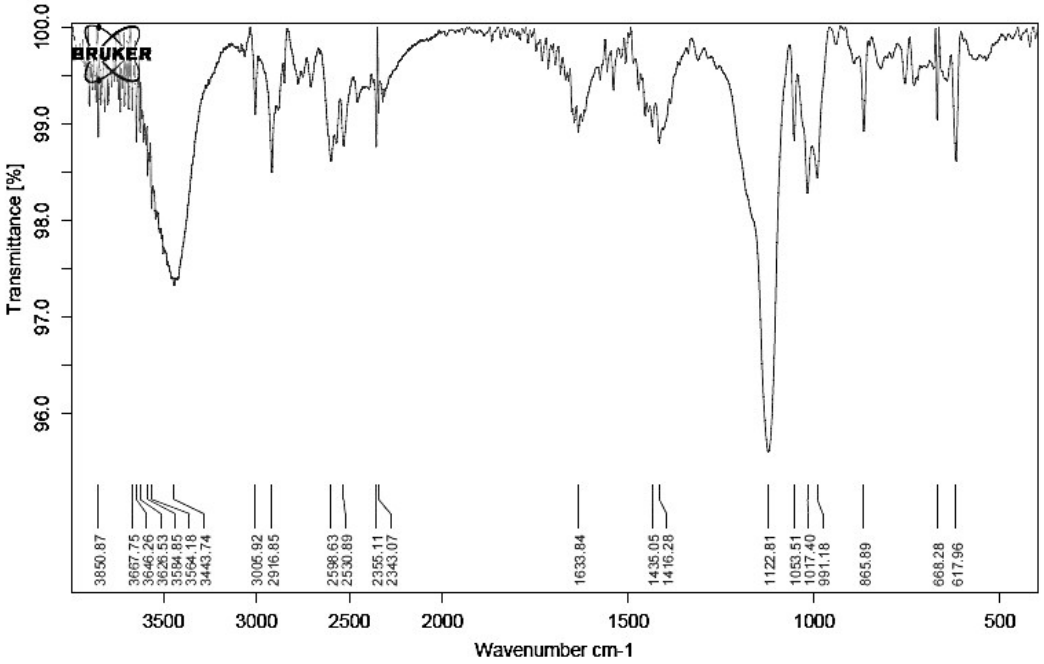
2000
1500
1000
500
Wavenumber cm-1

9•Cb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3005.92
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2343.07
1633.84
1435.05
1416.28
1122.81
1053.51
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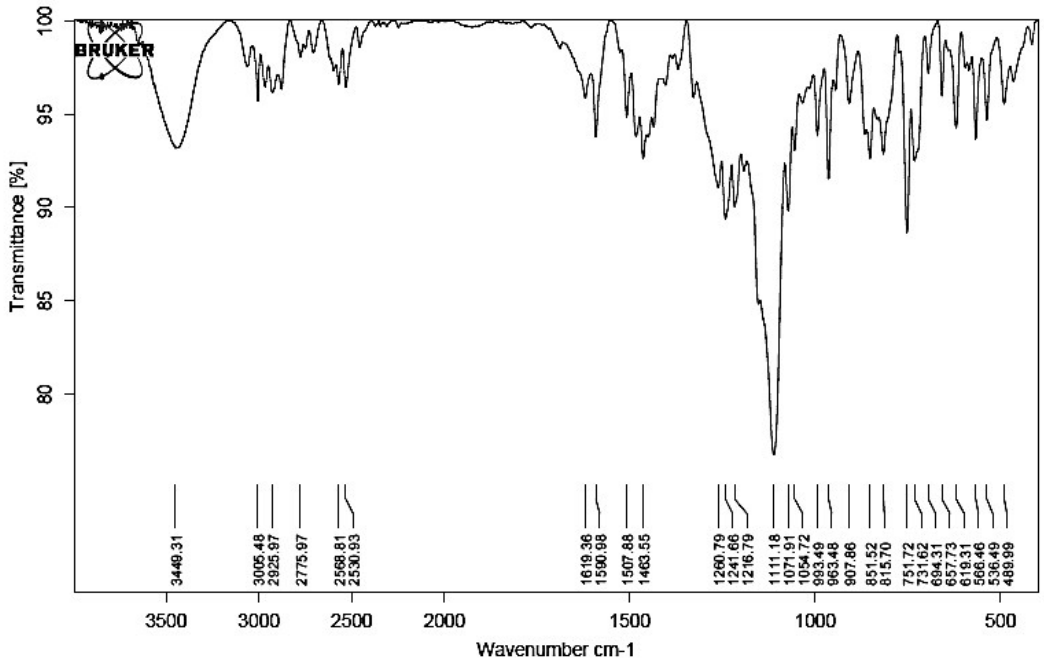
1500
1000
500
Wavenumber cm-1

10•Cb


BRUKER
Transmittance [%]
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85
80
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1619.36
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1507.88
1463.55
1260.79
1241.66
1216.79
1111.18
1071.91
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993.49
963.48
907.86
851.52
815.70
751.72
731.62
694.31
657.73
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500
Wavenumber cm-1

10•I

Crystal data

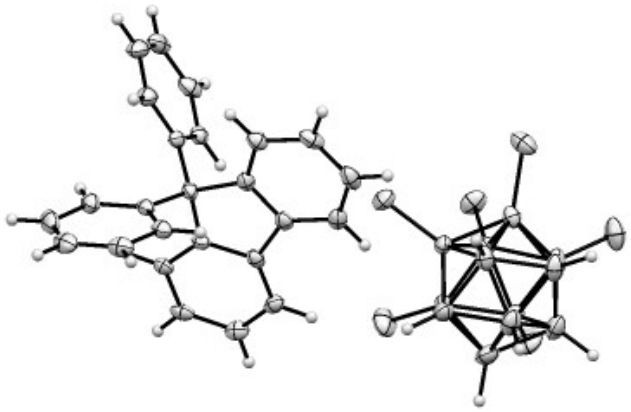

Table 2, Crystal data and structure refinement for **1**•Cb

Identification code	**1**•Cb	
Crystallised from	acetone / ethanol	
Empirical formula	$C_{25}H_{24}B_{11}Cl_6N$	
Formula weight [g·mol^{-1}]	670.06	
Crystal color	colourless	
Crystal dimensions [mm]	0.16 × 0.18 × 0.22	
Temperature [K]	133.15	
Crystal system, space group	Monoclinic, $P2_1/c$ (No. 14)	
Z	16	
Reflections for cell determination	16297	
2θ range for cell determination [°]	6.2-55	
Unit cell parameters	a [Å]	31.445(2)
	b [Å]	13.6072(8)
	c [Å]	32.634(2)
	α [°]	90
	β [°]	116.6660(10)
	γ [°]	90
	V [Å^3]	12478.3(15)
F(000)	5408	
Dx [g·cm^{-3}]	1.427	
μ(Mo Kα) [mm^{-1}]	0.572	
Scan type	ω	
$2\theta_{(max)}$ [°]	55.1	
Transmission factors (min; max)	0.891; 1.000	

Total reflections measured	124044	
Symmetry independent reflections	28478	
R_{int}	0.073	
Reflections with $I > 2\sigma(I)$	21156	
Reflections used in refinement	28478	
Parameters refined	1565	
Final	R(F) [$I > 2\sigma(I)$ reflections]	0.0711
	$wR(F^2)$ (all data)	0.1534
Weights: where $P = (F_o^2 + 2F_c^2)/3$	$w = [\sigma^2(F_o^2) + (0.0241P)^2 + 39.1817P]^{-1}$	
Goodness of fit	1.179	
$\Delta\rho$ (max; min) [e Å^{-3}]	1.452; -0.684	

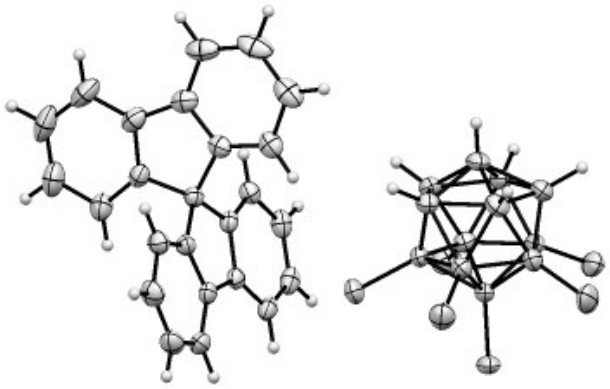

Table 3, Crystal data and structure refinement for **3**•Cb **β**[14]

Identification code	**3**•Cb **β**	
Crystallised from	acetone / hexane	
Empirical formula	$C_{25}H_{22}B_{11}Cl_6N$	
Formula weight [g·mol^{-1}]	668.08	
Crystal color	colourless	
Crystal dimensions [mm]	0.22 × 0.25 × 0.25	
Temperature [K]	160(2)	
Crystal system, space group	Orthorhombic, *Pbcn* (No. 60)	
Z	8	
Reflections for cell determination	75479	
2θ range for cell determination [°]	4-55	
Unit cell parameters	*a* [Å]	18.0150(2)
	b [Å]	14.8013(2)
	c [Å]	23.3476(2)
	α [°]	90

	β [°]	90	
	γ [°]	90	
	V [Å^3]	6225.53(12)	
F(000)	2688		
Dx [g·cm^{-3}]	1.426		
μ(Mo Kα) [mm^{-1}]	0.573		
Scan type	ϕ and ω		
$2\theta_{(max)}$ [°]	55		
Transmission factors (min; max)	0.813; 0.887		
Total reflections measured	78563		
Symmetry independent reflections	7125		
R_{int}	0.0461		
Reflections with $I > 2\sigma(I)$	5755		
Reflections used in refinement	7120		
Parameters refined	388		
Final	R(F) [$I > 2\sigma(I)$ reflections]	0.0396	
	$wR(F^2)$ (all data)	0.1059	
Weights: where $P = (F_o^2 + 2F_c^2)/3$	$w = [\sigma^2(F_o^2) + (0.0458P)^2 + 5.1407P]^{-1}$		
Goodness of fit	1.024		
Final Δ_{max}/σ	0.001		
$\Delta\rho$ (max; min) [e Å^{-3}]	0.73; -0.48		
$\sigma(d$(C–C)) [Å]	0.003-0.004		

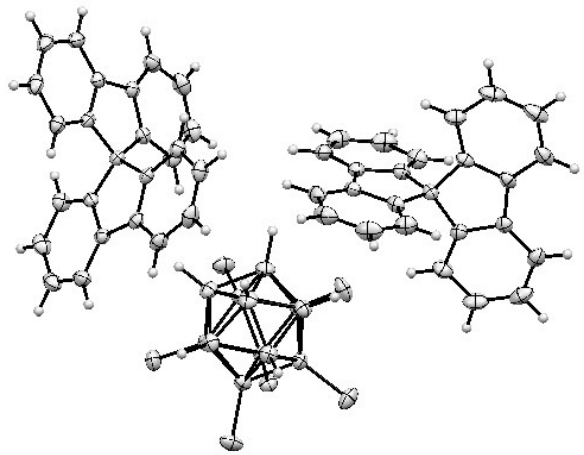

Table 4, Crystal data and structure refinement for **3**•Cb α[14]

Identification code	**3**•Cb α
Crystallised from	deuterochloroform / hexane

Empirical formula	$C_{25}H_{22}B_{11}Cl_6N$	
Formula weight [g·mol^{-1}]	668.04	
Crystal color	colourless	
Crystal dimensions [mm]	0.21 × 0.22 × 0.23	
Temperature [K]	160(2)	
Crystal system, space group	Orthorhombic, *Pbcn* (No. 60)	
Z	8	
Reflections for cell determination	21201	
2θ range for cell determination [°]	5-60.8	
Unit cell parameters	*a* [Å]	18. 70332(19)
	b [Å]	18.4574(3)
	c [Å]	18.40020(17)
	α [°]	90
	β [°]	90
	γ [°]	90
	V [Å^3]	6352.02(13)
F(000)	2688	
D*x* [g·cm^{-3}]	1.397	
μ(Mo Kα) [mm^{-1}]	0.562	
Scan type	ω	
$2\theta_{(max)}$ [°]	61	
Transmission factors (min; max)	0.866; 1.000	
Total reflections measured	39043	
Symmetry independent reflections	8322	
R_{int}	0.021	
Reflections with $I > 2\sigma(I)$	7016	
Reflections used in refinement	8322	
Parameters refined	389	
Final	R(F) [$I > 2\sigma(I)$ reflections]	0.0307
	wR(F^2) (all data)	0.0833
Weights: where $P = (F_o^2 + 2F_c^2)/3$	$w = [\sigma^2(F_o^2) + (0.0403P)^2 + 2.4228P]^{-1}$	
Goodness of fit	1.024	
Final Δ_{max}/σ	0.001	
$\Delta\rho$ (max; min) [e Å^{-3}]	0.34; -0.44	
σ(*d*(C–C)) [Å]	0.0018-0.003	

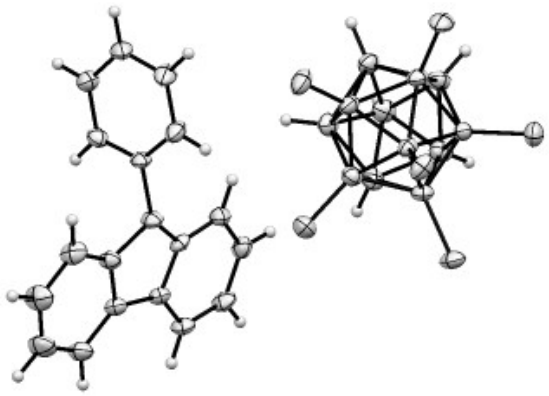

Table 5, Crystal data and structure refinement for **7**•Cb

Identification code	**7**•Cb	
Crystallised from	DCM/methanol	
Empirical formula	$C_{19}H_{19}B_{11}Cl_6O$	
Formula weight [g·mol^{-1}]	594.95	
Crystal color	colourless	
Crystal dimensions [mm]	0.12 × 0.18 × 0.20	
Temperature [K]	113.15	
Crystal system, space group	Monoclinic, $P2_1/c$ (No. 14)	
Z	8	
Reflections for cell determination	9306	
2θ range for cell determination [°]	6-55	
Unit cell parameters	a [Å]	17.251(2)
	b [Å]	12.1706(17)
	c [Å]	26.112(4)
	α [°]	90
	β [°]	91.879(3)
	γ [°]	90
	V [Å^3]	5479.3(14)
F(000)	2384	
Dx [g·cm^{-3}]	1.442	
μ(Mo Kα) [mm^{-1}]	0.643	
Scan type	ω	
$2\theta_{(max)}$ [°]	55	
Transmission factors (min; max)	0.882; 0.927	
Total reflections measured	54514	
Symmetry independent reflections	12534	
R_{int}	0.0525	

Reflections with $I > 2\sigma(I)$	9728	
Reflections used in refinement	12534	
Parameters refined	703	
Final	R(F) [$I > 2\sigma(I)$ reflections]	0.0467
	$wR(F^2)$ (all data)	0.1119
Weights: where $P = (F_o^2 + 2F_c^2)/3$	$w = [\sigma^2(F_o^2) + (0.0344P)^2 + 8.4146P]^{-1}$	
Goodness of fit	1.083	
$\Delta\rho$ (max; min) [e Å^{-3}]	0.650; -0.445	

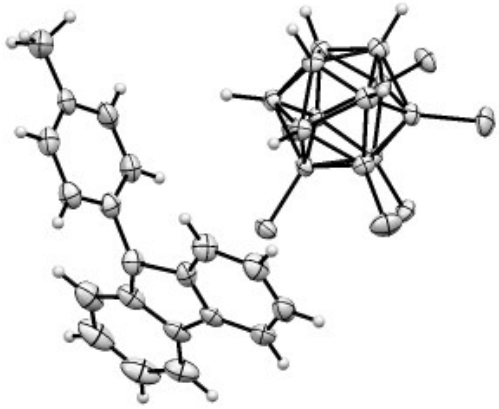

Table 6, Crystal data and structure refinement for **8**•Cb

Identification code	**8**•Cb	
Crystallised from	Acetone	
Empirical formula	$C_{20}H_{21}B_{11}Cl_6O$	
Formula weight [g·mol^{-1}]	608.98	
Crystal color	colourless	
Crystal dimensions [mm]	0.20 × 0.20 × 0.20	
Temperature [K]	113.15	
Crystal system, space group	Orthorhombic, *Pbca* (No. 61)	
Z	8	
Reflections for cell determination	29092	
2θ range for cell determination [°]	4-66	
Unit cell parameters	a [Å]	19.0146(6)
	b [Å]	13.8372(3)
	c [Å]	21.2518(5)
	α [°]	90
	β [°]	90
	γ [°]	90

	V [Å^3]	5691.5(3)
F(000)	2448	
Dx [g·cm^{-3}]	1.447	
μ(Mo Kα) [mm^{-1}]	0.632	
Scan type	ω	
$2\theta_{(max)}$ [°]	50.0	
Transmission factors (min; max)	0.822; 1.000	
Total reflections measured	49304	
Symmetry independent reflections	4854	
R_{int}	0.0511	
Reflections with $I > 2\sigma(I)$	4302	
Reflections used in refinement	4854	
Parameters refined	348	
Final	R(F) [$I > 2\sigma(I)$ reflections]	0.0392
	$wR(F^2)$ (all data)	0.1098
Weights: where $P = (F_o^2 + 2F_c^2)/3$	$w = [\sigma^2(F_o^2) + (0.0542P)^2 + 7.2759P]^{-1}$	
Goodness of fit	1.043	
$\Delta\rho$ (max; min) [e Å^{-3}]	1.444; -0.629	