Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Decarboxylative cyclization of *o*-chlorobenzoic acids with *C*,*C*-palladacycles formed by a aminopalladation/dealkylation to access dibenzo[*a*,*c*]carbazoles

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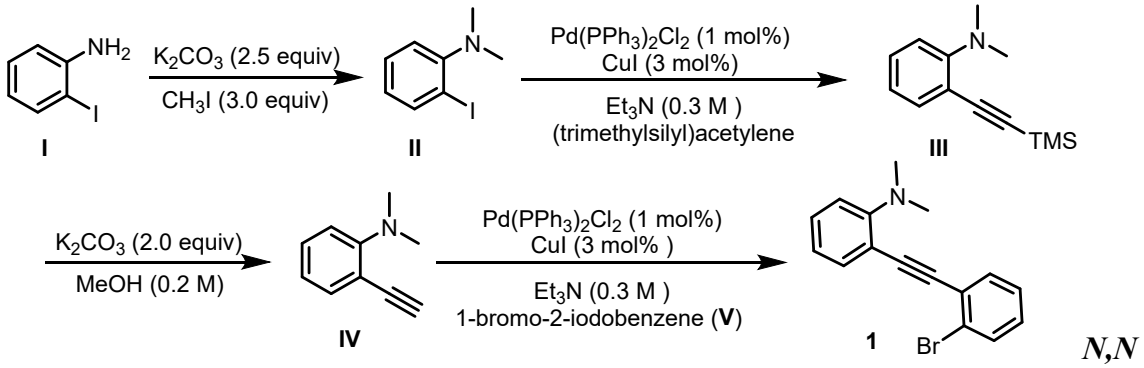
1 General Information

^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature using a Bruker Avance-500 instruments or Avance-400 instruments (^{1}H NMR at 500 MHz and ^{13}C NMR at 125 MHz), NMR spectra of all products were reported in ppm with reference to solvent signals [^{1}H NMR: $CDCl_3$ (7.26 ppm) or DMSO-d_6 (2.50 ppm), ^{13}C NMR: $CDCl_3$ (77.00 ppm) or DMSO-d_6 (39.60 ppm)]. Signal patterns are indicated as s, singlet; d, doublet; dd, doublets of doublet; t, triplet, and m, multiplet. HPLC/Q-TOF-MS analysis was performed with an Agilent 1290 LC system coupled with a 6530Q-TOF/MS accurate-mass spectrometer (Agilent Technologies, USA). The mass spectrometry was performed in the positive electrospray ionization (ESI+) mode. Reactions were monitored by thin-layer chromatography Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh). Analytical grade solvents and commercially available reagents were purchased from commercial sources and used directly without further purification unless otherwise stated.

2 General Procedure for the Synthesis of Starting Materials[1,2]



***N,N*-dimethyl-2-iodoaniline (II).**

A mixture of 2-iodoaniline **I** (2.2 g, 10.0 mmol, 1.0 equiv), K_2CO_3 (3.5 g, 25.0 mmol, 2.5 equiv) and iodomethane (1.9 mL, 30.0 mmol, 3.0 equiv) in 10.0 mL CH_3CN was stirred at reflux for 12 hours. After cooling down to room temperature, the mixture was treated with water (50.0 mL), then extracted with ethyl acetate

(2×30.0 mL). The organic phases were washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The crude sample was used for the next reaction without further purification.

***N,N*-dimethyl-2-((trimethylsilyl)ethynyl)aniline (III).**

To a solution of *N,N*-dimethyl-2-iodoaniline **II** (2.5 g, 10.0 mmol, 1.0 equiv) in 30.0 mL Et_3N, $PdCl_2(PPh_3)_2$ (70.1 mg, 0.1 mmol, 1 mol%), CuI (58.0 mg, 0.3 mmol, 3 mol%), and (trimethylsilyl)acetylene (1.8 ml, 13.0 mmol, 1.3 equiv), successively, under N_2. After being stirred for 3 ~ 4 hours at room temperature, saturated aqueous ammonium chloride solution (50.0 mL) and diethyl ether (50.0 mL) were added. The organic phase was washed with brine, dried over sodium sulfate, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate 100:1) to give *N,N*-dimethyl-2-((trimethylsilyl)ethynyl)aniline **III** (2.0 g, 90%).

2-ethynyl-*N,N*-dimethylaniline (IV).

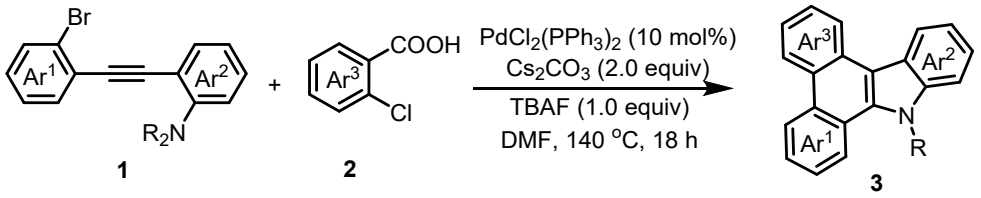
A mixture of *N,N*-dimethyl-2-((trimethylsilyl)ethynyl)aniline **III** (2.2 g, 10.0 mmol, 1.0 equiv) and K_2CO_3 (2.8 g, 20.0 mmol, 2.0 equiv) was dissolved in methanol (20.0 mL). After being stirred for 30 minutes at room temperature, the mixture was diluted with Et_2O and filtered. The filtrate was washed with H_2O and brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on silica gel (petroleum ether/ethyl acetate 100:1) to afford the title compound 2-ethynyl-*N,N*-dimethylaniline **IV** (1.2 g, 84%) as a yellow oil.

2-((2-bromophenyl)ethynyl)-*N,N*-dimethylaniline (1).

To a solution of 1-bromo-2-iodobenzene **V** (2.8 g, 10.0 mmol, 1.0 equiv) in Et_3N (30.0 mL) were successively added CuI (58.0 mg, 0.3 mmol, 3 mol%), $PdCl_2(PPh_3)_2$ (70.1 mg, 0.1 mmol, 1 mol%), and 2-ethynyl-*N,N*-dimethylaniline **IV** (1.6 g, 11.0 mmol, 1.1 equiv) at room temperature under N_2. The mixture was stirred at room temperature for 4 ~ 12 h and quenched by addition of saturated aqueous NH_4Cl at room temperature. The aqueous mixture was extracted with EtOAc, and the layers

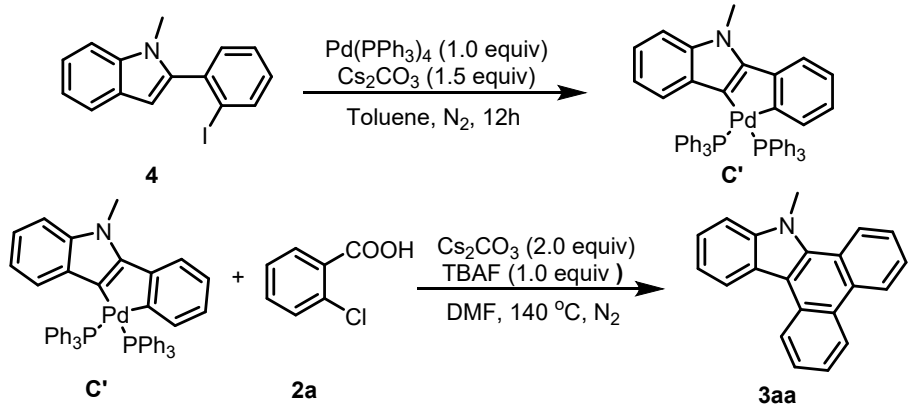
were separated. The organic layer was washed with brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography on silica gel with (petroleum ether/ethyl acetate 100:1) to afford 2-((2-bromophenyl)ethynyl)-*N,N*-dimethylaniline **1** (2.6 g, 86%) as a light yellow oil.

3 General Procedure for the Synthesis of dibenzo[*a,c*]carbazoles 3.



To a 25 mL Schlenk tube was added *o*-alkynylanilines **1** (60.0 mg, 0.2 mmol, 1.0 equiv), *o*-chlorobenzoic acids **2** (47.0 mg, 0.3 mmol, 1.5 equiv), $PdCl_2(PPh_3)_2$ (14.1 mg, 0.02 mmol, 10 mol%), Cs_2CO_3 (141.1 mg, 0.4 mmol, 2.0 equiv), TBAF (0.2 mmol, 1.0 equiv), and DMF (2.0 mL). Then the tube was evacuated briefly under high vacuum and charged with nitrogen, and was stirred at 140 °C (oil bath temperature) for 18 h. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate, dried over Na_2SO_4, filtrated. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatography (petroleum ether/ ethyl acetate) to give product **3**.

4 Mechanistic Studies[3]

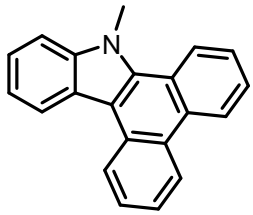


To a 25 mL Schlenk tube was added 2-(2-iodophenyl)-1-methyl-1*H*-indole **4** (66.6 mg, 0.2 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (231.1 mg, 0.2 mmol, 1.0 equiv), Cs_2CO_3 (97.8 mg, 0.3 mmol, 1.5 equiv), and toluene (2.0 mL). Then the tube was charged

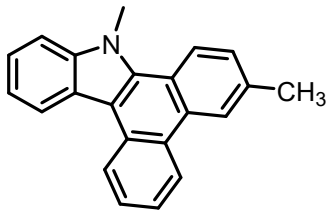
with nitrogen, and was stirred at 80 ~ 90 °C (oil bath temperature) for 12 h until complete consumption of starting material as monitored by TLC analysis. The reaction mixture was cooled to room temperature. Once cooled, the reaction was passed through a plug of celite using DCM and concentrated in vacuo. Once solidified, hexane was used to triturate the compound. The mixture was passed through glass wool and the collected solid was redissolved in DCM and concentrated in vacuo. The palladacycle **C'** then recrystallized Et_2O and hexanes to obtain a light yellow solid (120.3 mg, 72%).

To a 25 mL Schlenk tube was added palladacycles **C'** (83.5 mg, 0.1 mmol, 1.0 equiv), 2-chlorobenzoic acid **2a** (23.5 mg, 0.15 mmol, 1.5 equiv), Cs_2CO_3 (65.2 mg, 0.2 mmol, 2.0 equiv), TBAF (0.1 mmol, 1.0 equiv), and DMF (1.0 mL). Then the tube was charged with nitrogen, and was stirred at 140 °C (oil bath temperature for 2 h until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatography (petroleum ether/ ethyl acetate) to give product **3aa** (9.3 mg, 33%).

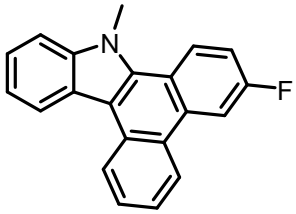
5 Characterization Data



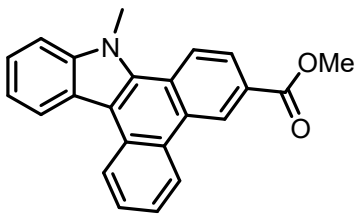
9-Methyl-9*H*-dibenzo[*a*,*c*]carbazole (3aa)[4]: white solid, isolated yield 71% (39.9 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.81 (d, *J* = 8.0 Hz, 1H), 8.78 (d, *J* = 9.0 Hz, 1H), 8.70 (d, *J* = 8.5 Hz, 1H), 8.58-8.55 (m, 2H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.62-7.57 (m, 2H), 7.55-7.50 (m, 2H), 7.47-7.44 (m, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 4.25 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.8, 134.7, 130.9, 130.0, 127.3, 126.9, 126.2, 125.6, 124.1, 123.9, 123.7, 123.6, 123.6, 123.5, 122.9, 121.9, 120.3, 113.4, 109.6, 34.5.



9,12-dimethyl-9*H*-dibenzo[*a,c*]carbazole (3ba): white solid, isolated yield 82% (48.4 mg); mp 161.8-163.2 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.82 (d, *J* = 8.5 Hz, 1H), 8.72 (d, *J* = 8.0 Hz, 1H), 8.58-8.56 (m, 2H), 8.49 (d, *J* = 8.5 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.55-7.53 (m, 2H), 7.47-7.44 (m, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 4.28 (s, 3H), 2.62 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.7, 135.3, 134.9, 131.1, 130.1, 127.7, 127.2, 126.7, 124.1, 123.6, 123.4, 122.8, 121.7, 120.2, 112.7, 109.5, 34.5, 22.0. HRMS (ESI) m/z calcd for $C_{22}H_{18}N^+$ $(M+H)^+$ 296.1434, found 296.1443.

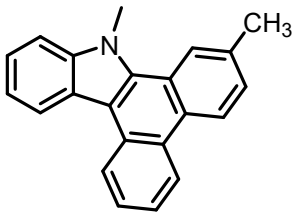


6-fluoro-9-methyl-9*H*-dibenzo[*a,c*]carbazole (3ca): white solid, isolated yield 64% (38.3 mg); mp 194.1-197.0 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.76 (d, *J* = 8.0 Hz, 1H), 8.53-8.47 (m, 3H), 8.33 (dd, *J* = 11.5 Hz, *J* = 2.5 Hz, 1H), 7.72 (t, *J* = 7.0 Hz, 1H), 7.54-7.45 (m, 3H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.31-7.28 (m, 1H), 4.18 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 160.7 (d, C-F, $^1J_{C\text{-}F}$ = 243.6 Hz), 140.5, 134.3, 132.9 (d, C-F, $^3J_{C\text{-}F}$ = 7.9 Hz), 130.3, 127.9, 126.1(d, C-F, $^4J_{C\text{-}F}$ = 3.8 Hz), 124.8 (d, C-F, $^3J_{C\text{-}F}$ = 8.5 Hz), 123.7, 123.6, 123.3, 121.7, 120.5, 120.4, 114.6 (d, C-F, $^2J_{C\text{-}F}$ = 23.0 Hz), 112.7, 109.5 (2C), 109.3, 34.4; **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -114.6; HRMS (ESI) m/z calcd for $C_{21}H_{15}FN^+$ $(M+H)^+$ 300.1189, found 300.1191.

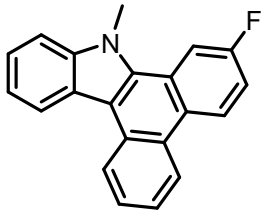


methyl 9-methyl-9*H*-dibenzo[*a,c*]carbazole-6-carboxylate (3da): white solid,

isolated yield 43% (29.2 mg); mp 182.4-183.7 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.40 (s, 1H), 8.75 (t, *J* = 7.5 Hz, 2H), 8.51 (t, *J* = 9.0 Hz, 2H), 8.13 (dd, *J* = 9.0 Hz, *J* = 1.5 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.52-7.48 (m, 2H), 7.39-7.36 (m, 1H), 4.20 (s, 3H), 4.04 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 167.3, 141.0, 133.6, 130.0, 129.9, 127.7, 126.8, 126.4, 126.2, 126.1, 126.0, 124.4, 124.0, 123.6, 123.0, 122.6, 122.1, 120.5, 115.1, 109.6, 52.3, 34.4. HRMS (ESI) m/z calcd for $C_{23}H_{17}NO_2^+$ (M^+) 339.1259, found 339.1253.

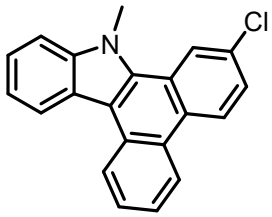


7,9-dimethyl-9*H*-dibenzo[*a,c*]carbazole (3ea): white solid, isolated yield 80% (47.2 mg); mp 143.1-144.8 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.77 (d, *J* = 8.0 Hz, 1H), 8.62 (d, *J* = 8.5 Hz, 1H), 8.58 (d, *J* = 8.5 Hz, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 8.21 (s, 1H), 7.68-7.65 (m, 1H), 7.52-7.48 (m, 1H), 7.45-7.40 (m, 2H), 7.36-7.33 (m, 2H), 4.13 (s, 3H), 2.50 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.7, 135.7, 134.5, 129.6, 128.7, 127.2, 127.0, 126.9, 124.0, 123.9, 123.6, 123.5, 123.2, 122.7, 121.8, 120.2, 113.4, 109.5, 34.4, 22.0. HRMS (ESI) m/z calcd for $C_{22}H_{18}N^+$ (M^+) 295.1361, found 295.1355.

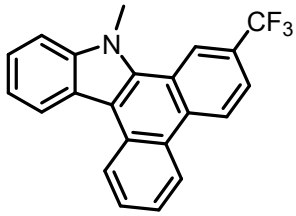


7-fluoro-9-methyl-9*H*-dibenzo[*a,c*]carbazole (3fa): white solid, isolated yield 56% (33.5 mg); mp 143.1-145.2 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.67 (d, *J* = 8.0 Hz, 1H), 8.56 (dd, *J* = 9.0 Hz, *J* = 6.0 Hz, 1H), 8.45 (dd, *J* = 14.5 Hz, *J* = 8.0 Hz, 2H), 7.98 (dd, *J* = 11.5 Hz, *J* = 2.5 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.49-7.46 (m, 1H), 7.44-7.38 (m, 2H), 7.34-7.31 (m, 1H), 7.22-7.19 (m, 1H), 4.01 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 160.9 (d, C-F, $^1J_{C\text{-}F}$ = 242.9 Hz), 140.6, 133.5 (d, C-F, $^4J_{C\text{-}F}$ = 3.1 Hz), 129.2, 127.1, 127.0, 126.4, 126.0 (d, C-F, $^3J_{C\text{-}F}$ = 9.0 Hz), 124.6 (d, C-F, $^3J_{C\text{-}F}$

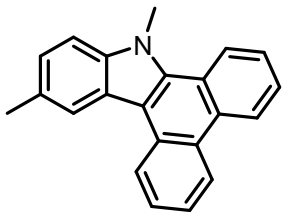
= 8.5 Hz), 124.0, 123.8, 123.6, 123.1, 123.0, 121.9, 120.3,114.0, 115.8 (d, C-F, $^2J_{C\text{-}F}$ = 22.9 Hz), 109.5, 107.9 (d, C-F, $^2J_{C\text{-}F}$ = 23.4 Hz), 33.9; **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -114.4; HRMS (ESI) m/z calcd for $C_{21}H_{14}FN^+$ (M^+) 299.1110, found 299.1104.



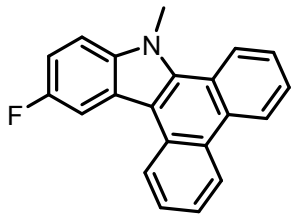
9,12-dimethyl-9*H*-dibenzo[*a,c*]carbazole (3ga)[4]: white solid, isolated yield 45% (28.4 mg); mp 167.8-169.1 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.70 (d, *J* = 8.5 Hz, 1H), 8.56-8.52 (m, 2H), 8.47 (d, *J* = 8.0 Hz, 1H), 8.37 (s, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.47-7.45 (m, 3H), 7.37-7.34 (m, 1H), 4.11 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.7, 133.2, 131.9, 129.7, 128.9, 127.5, 126.2, 125.6, 125.4, 124.6, 124.1, 123.9, 123.6, 123.3, 123.0, 122.1, 121.9, 120.4, 114.1, 109.6, 34.2.



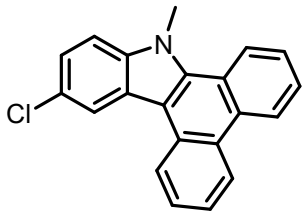
9-methyl-7-(trifluoromethyl)-9*H*-dibenzo[*a,c*]carbazole (3ha): white solid, isolated yield 50% (34.9 mg); mp 178.2-179.4 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.67-8.65 (m, 2H), 8.62 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 8.5 Hz, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.47-7.42 (m, 2H), 7.35-7.32 (m, 1H), 4.05 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.6, 133.5, 132.6, 130.3, 128.2, 127.4 (q, C-F, $^2J_{C\text{-}F}$ = 32.4 Hz), 125.7 (2C), 124.6, 124.2, 123.8, 123.7, 123.6, 122.9, 121.9, 121.1 (q, C-F, $^4J_{C\text{-}F}$ = 3.3 Hz), 120.5, 119.8 (q, C-F, $^4J_{C\text{-}F}$ = 4.4 Hz), 114.1, 109.5, 34.1; **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -61.9; HRMS (ESI) m/z calcd for $C_{22}H_{14}F_3N^+$ (M^+) 349.1078, found 349.1072.



9,12-dimethyl-9*H*-dibenzo[*a,c*]carbazole (3ia)[4]: white solid, isolated yield 73% (43.1 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.82-8.78 (m, 2H), 8.71 (d, *J* = 8.5 Hz, 1H), 8.59-8.57 (m, 1H), 8.33 (s, 1H), 7.72 (t, *J* = 7.0 Hz, 1H), 7.62-7.58 (m, 2H), 7.55-7.52 (m, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 4.24 (s, 3H), 2.62 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 139.3, 134.8, 130.9, 130.1, 129.5, 127.3, 126.8, 126.1, 125.5, 125.2, 124.1, 124.0, 123.6, 123.5, 123.4, 122.9, 121.7, 113.1, 109.2, 34.6, 21.9.

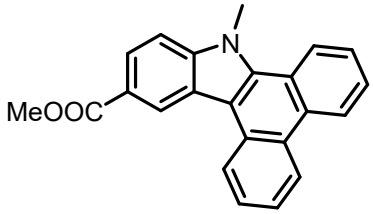


12-fluoro-9-methyl-9*H*-dibenzo[*a,c*]carbazole (3ja)[4]: white solid, isolated yield 76% (45.5 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.59 (d, *J* = 8.5 Hz, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 7.95 (dd, *J* = 10.0 Hz, *J* = 1.5 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.52-7.49 (m, 1H), 7.46-7.44 (m, 2H), 7.15-7.13 (m, 1), 7.07-7.03 (m, 1H), 3.88 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 157.9 (d, C-F, $^1J_{C\text{-}F}$ = 236.1 Hz), 136.9, 135.4, 130.9, 129.5, 127.3, 126.6, 126.0, 125.7, 123.9, 123.6 (d, C-F, $^3J_{C\text{-}F}$ = 8.4 Hz), 123.3, 123.1, 123.0, 122.7, 112.8, 112.7 (d, C-F, $^4J_{C\text{-}F}$ = 2.4 Hz), 111.4 (d, C-F, $^2J_{C\text{-}F}$ = 25.8 Hz), 109.8 (d, C-F, $^3J_{C\text{-}F}$ = 9.6 Hz), 106.9 (d, C-F, $^2J_{C\text{-}F}$ = 24.6 Hz), 34.3; **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -123.8.

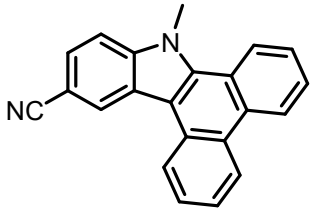


9,12-dimethyl-9*H*-dibenzo[*a,c*]carbazole (3ka)[4]: white solid, isolated yield 72% (45.4 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.62 (d, *J* = 8.5 Hz, 1H), 8.55 (d, *J* = 8.5

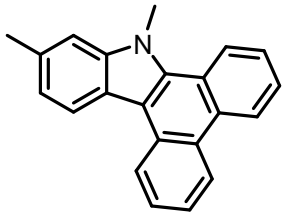
Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 8.25 (s, 1H), 7.64-7.61 (m, 1H), 7.56-7.53 (m, 1H), 7.51-7.46 (m, 2H), 7.27-7.23 (m, 1H), 7.17 (d, *J* = 8.5 Hz, 1H), 3.9 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 138.7, 135.0, 130.9, 129.3, 127.3, 126.7, 126.1, 125.8, 125.5, 123.9 (2C), 123.7, 123.5, 123.4, 123.3, 123.2, 122.7, 121.0, 112.3, 110.2, 34.3.



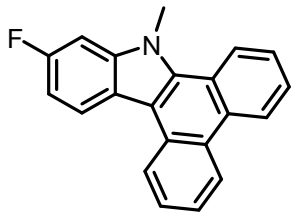
9-methyl-9*H*-dibenzo[*a,c*]carbazol-12-yl acetate (3la): white solid, isolated yield 41% (27.8 mg); mp 194.6-196.0 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.20 (s, 1H), 8.81 (d, *J* = 8.0 Hz, 1H), 8.77 (d, *J* = 8.0 Hz, 1H), 8.69 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 8.11 (dd, *J* = 8.5 Hz, *J* = 1.5 Hz, 1H), 7.75 (t, *J* = 8.0 Hz, 1H), 7.66-7.56 (m, 3H), 7.44 (d, *J* = 8.5 Hz, 1H), 4.23 (s, 3H), 4.03 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 168.1, 143.0, 135.4, 131.1, 129.3, 127.6, 127.1, 126.3, 126.0, 125.0, 124.4, 124.2, 124.1, 123.7, 123.5, 123.4, 122.9, 122.7, 121.9, 113.9, 109.0, 52.1, 34.7. HRMS (ESI) m/z calcd for $C_{23}H_{18}NO_2^+$ $(M+H)^+$ 340.1138, found 340.1145.



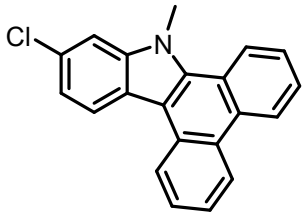
9-methyl-9*H*-dibenzo[*a,c*]carbazole-12-carbonitrile (3ma): white solid, isolated yield 57% (34.9 mg); mp 245.5-248.7 °C; **^{1}H NMR** (DMSO-d_6, 500 MHz) δ = 9.10 (s, 1H), 9.01-8.99 (m, 1H), 8.90 (t, *J* = 10.0 Hz, 2H), 8.86-8.84 (m, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.86-7.83 (m, 4H), 7.68 (t, *J* = 8.0 Hz, 1H), 4.42 (s, 3H); **^{13}C NMR** (DMSO-d_6, 125 MHz) δ = 142.1, 135.8, 131.1, 128.6, 128.4, 127.4, 127.3, 127.1, 126.9, 126.8, 125.0, 124.7, 124.2, 124.1, 124.0, 123.1, 122.5, 121.0, 112.6, 112.0, 102.7, 35.2. HRMS (ESI) m/z calcd for $C_{22}H_{15}N_2^+$ $(M+H)^+$ 307.1235, found 307.1238.



9,11-dimethyl-9*H*-dibenzo[*a,c*]carbazole (3na)[5]: white solid, isolated yield 81% (47.8 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.77 (d, *J* = 8.0 Hz, 2H), 8.70 (d, *J* = 8.0 Hz, 1H), 8.54-8.52 (m, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.60-7.55 (m, 2H), 7.54-7.51 (m, 1H), 7.25 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 4.18 (s, 3H), 2.57 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 141.3, 134.4, 133.7, 130.7, 129.9, 127.2, 126.9, 126.1, 125.3, 124.1, 124.0, 123.6, 123.5 (2C), 122.8, 122.0, 121.5, 121.3, 113.5, 109.7, 34.4, 22.2.

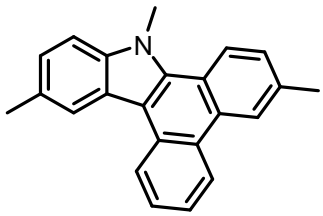


11-fluoro-9-methyl-9*H*-dibenzo[*a,c*]carbazole (3oa)[5]: white solid, isolated yield 60% (35.9 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.75 (d, *J* = 9.0 Hz, 1H), 8.68 (d, *J* = 8.5 Hz, 1H), 8.65 (d, *J* = 8.0 Hz, 1H), 8.47 (d, *J* = 9.0 Hz, 1H), 8.37 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.62-7.52 (m, 3H), 7.10 (dd, *J* = 10.0 Hz, *J* = 2.0 Hz, 1H), 7.08-7.04 (m, 1H), 4.12 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 160.7 (d, C-F, $^1J_{C\text{-}F}$ = 239.1 Hz), 141.3 (d, C-F, $^3J_{C\text{-}F}$ = 11.5 Hz), 135.0 (d, C-F, $^4J_{C\text{-}F}$ = 2.8 Hz), 130.5, 129.4, 127.3, 126.9, 126.2, 125.5, 124.0, 123.8, 123.6, 123.4 (d, C-F, $^2J_{C\text{-}F}$ = 22.9 Hz), 122.7, 122.6 (d, C-F, $^4J_{C\text{-}F}$ = 2.8 Hz), 119.9, 113.2, 108.5 (d, C-F, $^2J_{C\text{-}F}$ = 23.8 Hz), 96.2, 96.0, 34.3; **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -117.1.

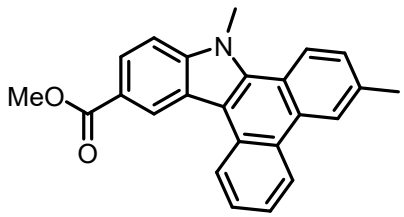


11-chloro-9-methyl-9*H*-dibenzo[*a,c*]carbazole (3pa): white solid, isolated yield 65% (40.9 mg); mp 162.2-163.5 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.65 (d, *J* = 8.0 Hz,

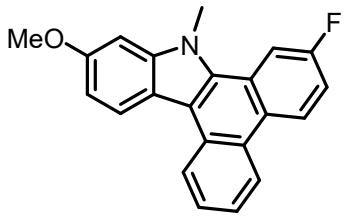
1H), 8.58 (d, *J* = 8.0 Hz, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.63-7.60 (m, 1H), 7.56-7.53 (m, 1H), 7.50-7.46 (m, 2H), 7.5 (s, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 3.9 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 141.0, 134.8, 130.8, 129.4, 129.3, 127.3, 126.9, 126.1, 125.7, 124.0, 123.8, 123.4 (2C), 123.3, 122.7, 122.4, 121.8, 120.6, 112.9, 109.5, 34.4. HRMS (ESI) m/z calcd for $C_{21}H_{14}ClN^+$ (M^+) 315.0815, found 315.0809.



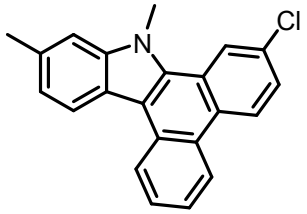
6,9,12-trimethyl-9*H*-dibenzo[*a,c*]carbazole (3qa): white solid, isolated yield 89% (55.0 mg); mp 191.4-192.6 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.79 (d, *J* = 8.0 Hz, 1H), 8.69 (d, *J* = 8.5 Hz, 1H), 8.55 (s, 1H), 8.41 (d, *J* = 8.5 Hz, 1H), 8.32 (s, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 1H), 4.17 (s, 3H), 2.62 (s, 3H), 2.59 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 139.1, 135.1, 135.0, 131.0, 130.3, 129.4, 127.6, 127.1, 126.6, 124.9, 124.0, 123.7, 123.6, 123.4, 123.3, 122.8, 121.8, 121.6, 112.3, 109.1, 34.4, 22.0, 21.9. HRMS (ESI) m/z calcd for $C_{23}H_{19}N^+$ (M^+) 309.1517, found 309.1511.



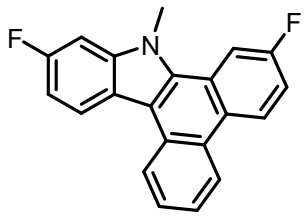
6,9-dimethyl-9*H*-dibenzo[*a,c*]carbazol-12-yl acetate (3ra): white solid, isolated yield 50% (35.3 mg); mp 164.2-166.2 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.25 (s, 1H), 8.84 (d, *J* = 8.0 Hz, 1H), 8.69-8.66 (m, 2H), 8.31 (s, 1H), 8.13 (dd, *J* = 9.0 Hz, *J* = 1.0 Hz, 1H), 7.76-7.73 (m, 1H), 7.60-7.57 (m, 1H), 7.49-7.46 (m, 2H), 4.26 (s, 3H), 4.04 (s, 3H), 2.60 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 168.1, 143.1, 136.0, 135.4, 129.0, 128.9, 127.6, 127.2 (2C), 124.9, 124.4, 124.0, 123.7, 123.6, 123.2, 123.0, 122.6, 121.9, 114.0, 109.0, 53.1, 34.8, 22.1. HRMS (ESI) m/z calcd for $C_{24}H_{19}NO_2^+$ (M^+) 353.1416, found 353.1410.



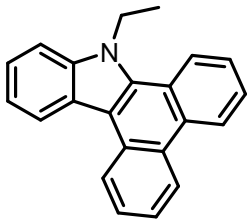
7-fluoro-11-methoxy-9-methyl-9*H*-dibenzo[*a,c*]carbazole (3sa): white solid, isolated yield 57% (37.5 mg); mp 226.7-229.5 °C; **^{1}H NMR** (DMSO-d_6, 500 MHz) δ = 9.02-8.99 (m, 1H), 8.82 (dd, *J* = 15.0 Hz, *J* = 8.5 Hz, 2H), 8.50 (d, *J* = 9.0 Hz, 1H), 8.44 (d, *J* = 11.5 Hz, 1H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.34 (s, 1H), 7.01 (d, *J* = 8.5 Hz, 1H), 4.34 (s, 3H), 3.97 (s, 3H); **^{13}C NMR** (DMSO-d_6 , 125 MHz) δ = 161.0 (d, C-F, $^{1}J_{C\text{-}F}$ = 241.0 Hz), 158.1, 142.3, 133.0 (d, C-F, $^{4}J_{C\text{-}F}$ = 2.6 Hz), 128.8, 127.8, 127.3 (d, C-F, $^{3}J_{C\text{-}F}$ = 9.1 Hz), 126.7, 126.5, 124.8 (d, C-F, $^{3}J_{C\text{-}F}$ = 8.8 Hz), 124.5, 124.2, 123.7, 122.9, 116.6, 114.1 (d, C-F, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 110.7, 108.3 (d, C-F, $^{2}J_{C\text{-}F}$ = 23.6 Hz), 94.2, 55.9, 34.5; **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -114.5; HRMS (ESI) m/z calcd for $C_{22}H_{17}FNO_2^+$ $(M+H)^+$ 330.1289, found 330.1298.



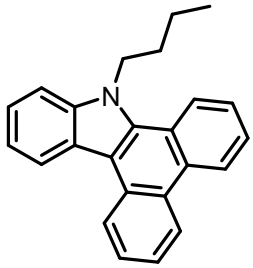
7-chloro-9,11-dimethyl-9*H*-dibenzo[*a,c*]carbazole (3ta): white solid, isolated yield 61% (40.1 mg); mp 209.1-211.6 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.72 (d, *J* = 6.5 Hz, 1H), 8.62 (d, *J* = 8.5 Hz, 1H), 8.58 (d, *J* = 7.0 Hz, 1H), 8.41 (s, 1H), 8.35 (d, *J* = 7.0 Hz, 1H), 7.70 (s, 1H), 7.52-7.48 (m, 2H), 7.24 (s, 1H), 7.17 (d, *J* = 7.0 Hz, 1H), 4.13 (s, 3H), 2.59 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 141.2, 134.2, 132.9, 131.9, 129.7, 128.8, 127.4, 126.2, 125.5, 125.4, 124.8, 123.8, 123.6, 123.3, 122.1, 122.0, 121.6, 120.9, 114.3, 109.7, 34.2, 22.2. HRMS (ESI) m/z calcd for $C_{22}H_{16}ClN^+$ $(M+H)^+$ 329.0971, found 329.0980.



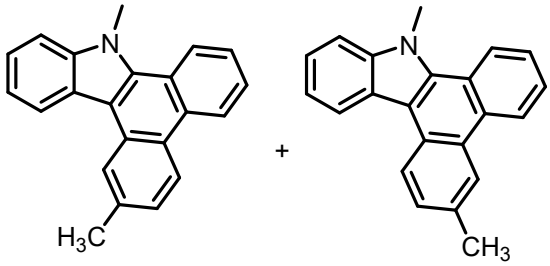
7,11-difluoro-9-methyl-9*H*-dibenzo[*a,c*]carbazole (3ua): white solid, isolated yield 55% (34.9 mg); mp 205.4-207.9 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.63 (dd, *J* = 9.0 Hz, *J* = 6.0 Hz, 2H), 8.58 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 8.31 (dd, *J* = 9.5 Hz, *J* = 5.5 Hz, 1H), 7.97 (dd, *J* = 11.5 Hz, *J* = 2.5 Hz, 1H), 7.67-7.64 (m, 1H), 7.54-7.51 (m, 1H), 7.29-7.26 (m, 1H), 7.07-7.03 (m, 1H), 3.99 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 160.9 (d, C-F, $^{1}J_{C\text{-}F}$ = 243.0 Hz), 160.9 (d, C-F, $^{1}J_{C\text{-}F}$ = 239.6 Hz), 141.2 (d, C-F, $^{3}J_{C\text{-}F}$ = 11.5 Hz), 133.9, 128.7, 127.0, 126.9 (d, C-F, $^{4}J_{C\text{-}F}$ = 1.6 Hz), 126.5, 126.1 (d, C-F, $^{3}J_{C\text{-}F}$ = 8.9 Hz), 124.4 (d, C-F, $^{3}J_{C\text{-}F}$ = 8.8 Hz), 124.1, 123.3, 123.2, 122.8 (d, C-F, $^{3}J_{C\text{-}F}$= 9.9 Hz), 119.5, 114.0, 113.8 (d, C-F, $^{2}J_{C\text{-}F}$ = 22.9 Hz), 108.7 (d, C-F, $^{2}J_{C\text{-}F}$ = 23.9 Hz), 107.6 (d, C-F, $^{2}J_{C\text{-}F}$ = 23.5 Hz), 96.1 (d, C-F, $^{2}J_{C\text{-}F}$ = 26.3 Hz), 34.1; **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -114.0, -116.9; HRMS (ESI) m/z calcd for $C_{22}H_{18}N^{+}$ (M^{+}) 307.1016, found 317.1010.



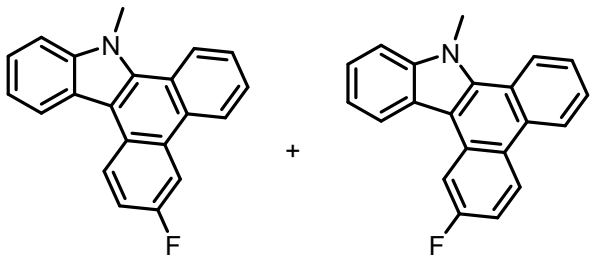
9-ethyl-9*H*-dibenzo[*a,c*]carbazole (3va)[6]: white solid, isolated yield 62% (36.6 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.85 (d, *J* = 8.0 Hz, 1H), 8.82-8.80 (m, 1H), 8.71 (d, *J* = 8.0 Hz, 1H), 8.60 (d, *J* = 8.0 Hz, 1H), 8.47-8.45 (m, 1H), 7.73-7.71 (m, 1H), 7.66-7.60 (m, 2H), 7.57-7.52 (m, 2H), 7.48-7.45 (m, 1H), 7.40-7.37 (m, 1H), 4.75 (q, *J* = 7.5 Hz, 2H), 1.65 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.2, 133.7, 131.0, 130.1, 127.4, 126.9, 126.5, 125.6, 124.3, 123.8, 123.7 (2C), 123.6, 123.5, 122.6, 122.0, 120.5, 113.7, 109.5, 41.0, 15.4.



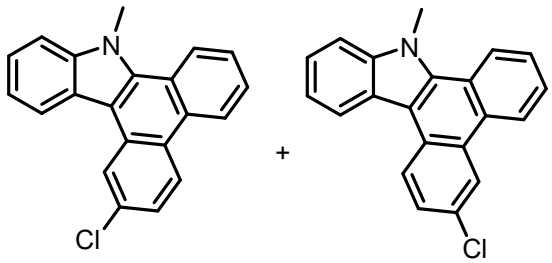
9-butyl-9*H*-dibenzo[a,c]carbazole (3wa): white solid, isolated yield 59% (38.1 mg); mp 115.3-116.7 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.80 (d, *J* = 8.0 Hz, 1H), 8.75 - 8.67 (m, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.54 (d, *J* = 7.5 Hz, 1H), 8.34 - 8.24 (m, 1H), 7.66 (t, *J* = 7.0 Hz, 1H), 7.59 - 7.42 (m, 4H), 7.39 (t, *J* = 7.0 Hz, 1H), 7.33 (t, *J* = 7.0 Hz, 1H), 4.48 (t, *J* = 7.5 Hz, 2H), 2.02 - 1.83 (m, 2H), 1.45 - 1.34 (m, 2H), 0.91 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.6, 133.7, 131.0, 130.1, 127.4, 127.0, 126.4, 125.6, 124.2, 123.7 (3C), 123.5 (2C), 122.6, 122.0, 120.4, 113.7, 109.8, 46.0, 32.2, 20.4, 14.0. HRMS (ESI) m/z calcd for $C_{24}H_{21}N^+$ $(M+H)^+$ 324.1752, found 324.1760.



2,9-dimethyl-9*H*-dibenzo[*a,c*]carbazole and **3,9-dimethyl-9*H*-dibenzo[*a,c*]carbazole (3ab)[4]:** white solid, isolated yield 86% (50.7 mg, 1:1); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.81-8.74 (m, 1H), 8.71 (d, *J* = 8.0 Hz, 0.5H), 8.61-8.58 (m, 2.5H), 8.56-8.51 (m, 1H), 7.62-7.56 (m, 2H), 7.55-7.52 (m, 1.5H), 7.48-7.45 (m, 1H), 7.39-7.35 (m, 1.5H), 4.29 (s, 1.5H), 4.29 (s, 1.5H), 2.66 (s, 1.5H), 2.62 (s, 1.5H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.8, 137.1, 134.9, 134.3, 133.0, 133.1, 130.7, 130.1, 128.9, 127.7, 127.0, 126.0, 125.7, 125.6, 125.4, 125.3, 124.8, 124.1, 124.0, 123.9, 123.6 (3C), 123.5 (3C), 123.4 (2C), 122.9 (2C), 121.9 (2C), 120.2 (2C), 113.5, 113.2, 109.5, 34.6, 22.1, 22.0.

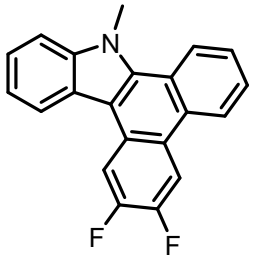


3-fluoro-9-methyl-9*H*-dibenzo[*a,c*]carbazole and **2-fluoro-9-methyl-9*H*-dibenzo[*a,c*]carbazole (3ac)[4]:** white solid, isolated yield 69% (41.3 mg, 2:1); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.65-8.58 (m, 1H), 6.56-8.53 (m, 1H), 8.50-8.47 (m, 1H), 8.40-8.36 (m, 1H), 8.27-8.20 (m, 1H), 7.60-7.53 (m, 2H), 7.49-7.43 (m, 2H), 7.41-7.32 (m, 1.5H), 7.22-7.18 (m, 0.5H), 4.17 (s, 1H), 4.16 (s, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 162.1 (d, C-F, $^1J_{C\text{-}F}$ = 243.6 Hz), 159.6 (d, C-F, $^1J_{C\text{-}F}$ = 240.1 Hz), 140.6 (d, C-F, $^3J_{C\text{-}F}$ = 8.1 Hz), 135.1, 133.9 (2C), 131.1 (d, C-F, $^3J_{C\text{-}F}$ = 9.4 Hz), 130.5, 130.0 (d, C-F, $^4J_{C\text{-}F}$ = 3.9 Hz), 128.4 (d, C-F, $^3J_{C\text{-}F}$ = 7.5 Hz), 126.6, 126.4, 125.8 (2C), 125.5 (3C), 125.2 (d, C-F, $^3J_{C\text{-}F}$ = 8.1 Hz), 124.2, 124.1, 123.8, 123.3 (2C), 123.2, 123.1, 123.0, 122.9, 122.8, 121.5, 121.3, 120.5, 120.3, 115.6 (d, C-F, $^2J_{C\text{-}F}$ = 23.0 Hz), 113.0, 112.7 (d, C-F, $^4J_{C\text{-}F}$ = 3.6 Hz), 111.9 (d, C-F, $^2J_{C\text{-}F}$ = 23.1 Hz), 109.6, 109.5, 108.6 (d, C-F, $^2J_{C\text{-}F}$ = 22.3 Hz), 108.3 (d, C-F, $^2J_{C\text{-}F}$ = 22.0 Hz), 34.4; **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -116.2, -120.1.

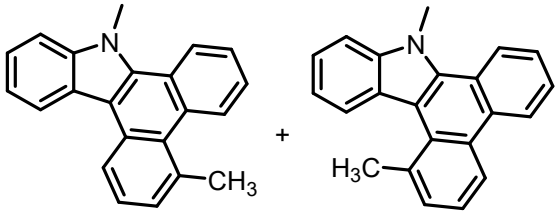


3-chloro-9-methyl-9*H*-dibenzo[*a,c*]carbazole and **2-chloro-9-methyl-9*H*-dibenzo[*a,c*]carbazole (3ad)[4]:** white solid, isolated yield 65% (40.9 mg, 1:1); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.51-8.47 (m, 1H), 8.45-8.43 (m, 1.5H), 8.39-8.35 (m, 1.5H), 8.28 (dd, *J* = 8.0 Hz, *J* = 2.5 Hz, 1H), 7.53-7.49 (m, 2.5H), 7.43-7.38 (m, 2H), 7.35-7.29 (m, 1.5H), 4.05 (s, 1.5H), 4.03 (s, 1.5H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.5, 140.4, 134.8, 134.3, 133.0, 130.7, 130.2, 129.6, 129.1, 127.9 (2C), 127.2, 126.5, 126.2, 125.7, 125.6, 124.9, 124.7 (2C), 123.9 (2C), 123.8 (2C), 123.6, 123.5, 122.9

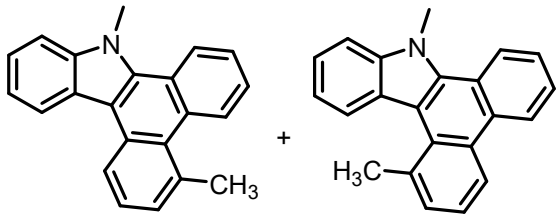
(3C), 122.8, 122.7, 122.6, 121.5, 121.4, 120.4, 120.3, 112.6, 112.1, 109.5, 109.4, 34.2 (2C).



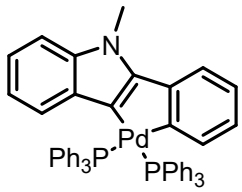
2,3-difluoro-9-methyl-9*H*-dibenzo[*a,c*]carbazole (3ae): white solid, isolated yield 45% (28.5 mg); mp 154.7-157.2 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.52-8.50 (m, 1H), 8.44-8.42 (m, 1H), 8.27-8.22 (m, 3H), 7.63-7.59 (m, 2H), 7.52-7.47 (m, 2H), 7.38-7.35 (m, 1H), 4.18 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.5, 134.4, 129.6 (d, C-F, $^{4}J_{C\text{-}F}$ = 3.5 Hz), 126.5 (d, C-F, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 126.4, 125.8, 124.0 (d, C-F, $^{4}J_{C\text{-}F}$ = 4.1 Hz), 123.6 (3C), 122.9, 122.6, 121.0, 120.5, 112.2, 111.1, 111.0, 110.5, 110.4, 109.6, 34.4; **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -137.5, -141.7; HRMS (ESI) m/z calcd for $C_{21}H_{13}F_2N^+$ (M^+) 317.1016, found 317.1010.



4,9-dimethyl-9*H*-dibenzo[*a,c*]carbazole and **1,9-dimethyl-9*H*-dibenzo[*a,c*]carbazole (3af)[4]:** white solid, isolated yield 64% (37.8 mg, 7:3); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.77 (d, *J* = 8.5 Hz, 0.7H), 8.71-8.67 (m, 1H), 8.54-8.47 (m, 2H), 8.11 (d, *J* = 8.0 Hz, 0.3H), 7.59-7.50 (m, 3H), 7.47-7.40 (m, 2H), 7.40-7.36 (m, 1H), 7.35-7.32 (m, 0.7H), 7.27-7.24 (m, 0.3H), 4.22 (s, 0.9H), 4.20 (s, 2.1H), 3.07 (s, 2.1H), 2.94 (s, 0.9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 141.3, 140.5, 136.0, 135.4, 134.9, 132.8, 131.9, 131.7, 131.4, 130.0, 129.2, 129.0, 128.5, 128.3, 127.7, 126.5, 126.0 (2C), 125.7, 124.8, 124.4, 124.3, 124.2, 123.7 (2C), 123.6 (2C), 123.2, 123.1, 122.8, 121.9, 121.5, 120.4, 119.1, 114.0, 113.5, 109.7, 109.3, 34.5, 27.3, 24.2.



4,9-dimethyl-9*H*-dibenzo[*a,c*]carbazole and **1,9-dimethyl-9*H*-dibenzo[*a,c*]carbazole (3af)[4]:** light yellow oil, isolated yield 57% (33.6 mg, 1:1); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.80-8.78 (m, 0.5H), 8.72-8.69 (m, 1H), 8.55-8.50 (m, 2H), 8.12 (d, *J* = 8.0 Hz, 0.5H), 7.60-7.57 (m, 1H), 7.56-7.55 (m, 1H), 7.52 (d, *J* = 7.0 Hz, 1H), 7.50-7.47 (m, 1.5H), 7.45-7.43 (m, 0.5H), 7.42-7.38 (m, 1H), 7.37-7.33 (m, 0.5H), 7.28-7.25 (m, 0.5H), 4.26 (s, 1.5H), 4.23 (s, 1.5H), 3.08 (s, 1.5H), 2.95 (s, 1.5H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 141.3, 140.5, 136.0, 135.4, 134.9, 132.8, 131.9, 131.7, 131.4, 130.1, 129.2, 129.0, 128.5, 128.3, 127.7, 126.5, 126.0 (2C), 125.7, 124.8, 124.4, 124.3, 124.2 (2C), 123.7 (2C), 123.6 (2C), 123.2, 123.1, 122.8, 121.9, 121.5, 120.4 (2C), 119.1, 114.0, 113.5, 109.7, 109.3, 34.6 (2C), 27.3, 24.2.



C': light yellow solid, isolated yield 72% (120.2 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.62-7.60 (m, 2H), 7.29-7.27 (m, 18H), 7.21-7.18 (m, 2H), 7.14-7.11 (m, 13H), 6.69 (d, *J* = 7.0 Hz, 1H), 6.63 (t, *J* = 7.5 Hz, 1H), 6.34 (t, *J* = 7.0 Hz, 1H), 2.67 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 158.6, 143.9, 140.3 (t, C-P, $J_{C\text{-}P}$ = 5.6 Hz), 137.8, 135.6 (t, C-P, $J_{C\text{-}P}$ = 3.9 Hz), 134.9 (t, C-P, $J_{C\text{-}P}$ = 6.1 Hz), 131.8 (t, C-P, $J_{C\text{-}P}$ = 22.4 Hz), 130.1, 129.8, 127.9 (t, C-P, $J_{C\text{-}P}$ = 5.1 Hz), 127.7, 126.3, 121.9, 121.4, 120.6, 119.7, 109.4, 102.6, 30.4; **^{31}P NMR** ($CDCl_3$, 202 MHz) δ = 20.9.

6 References

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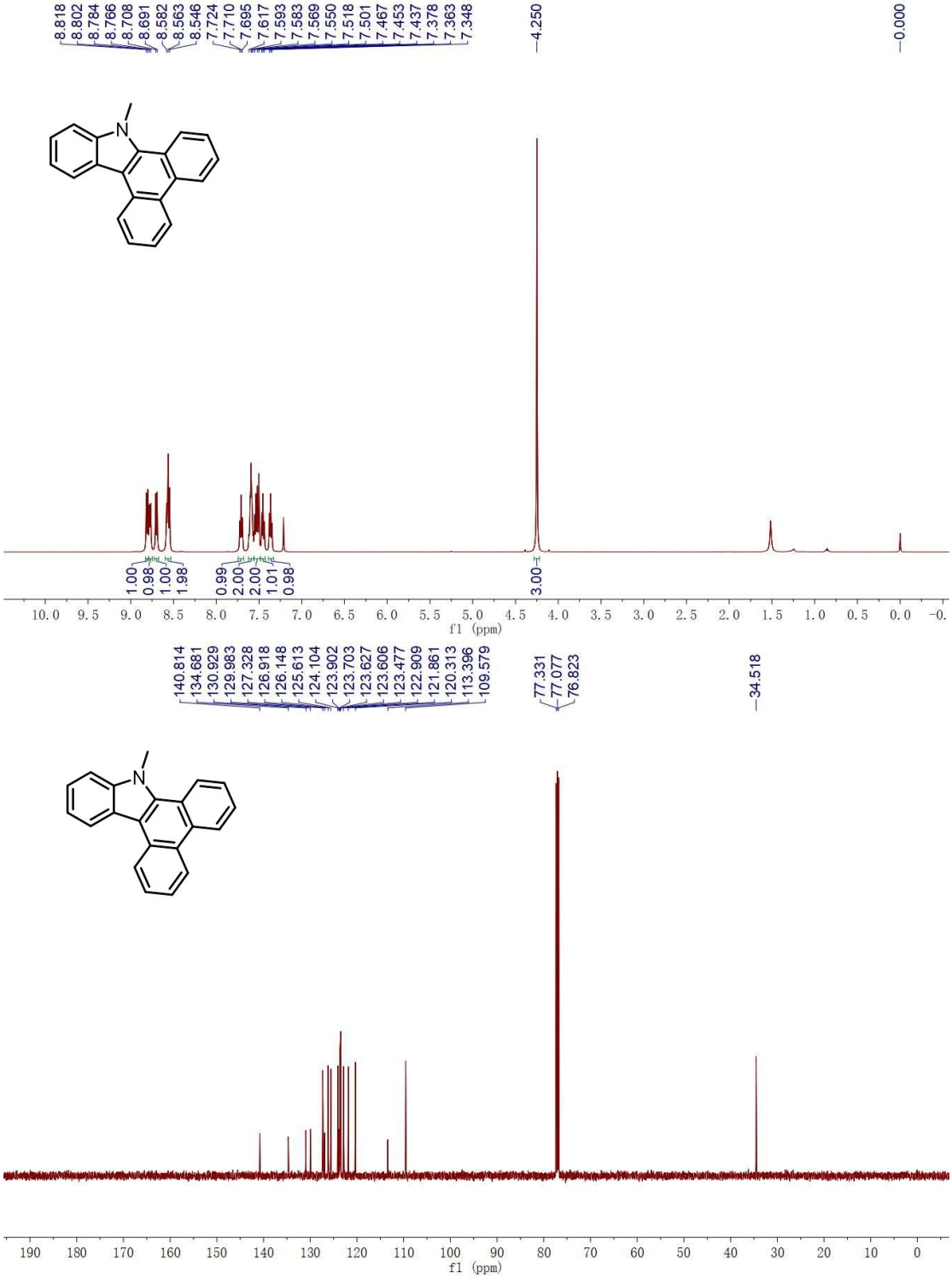
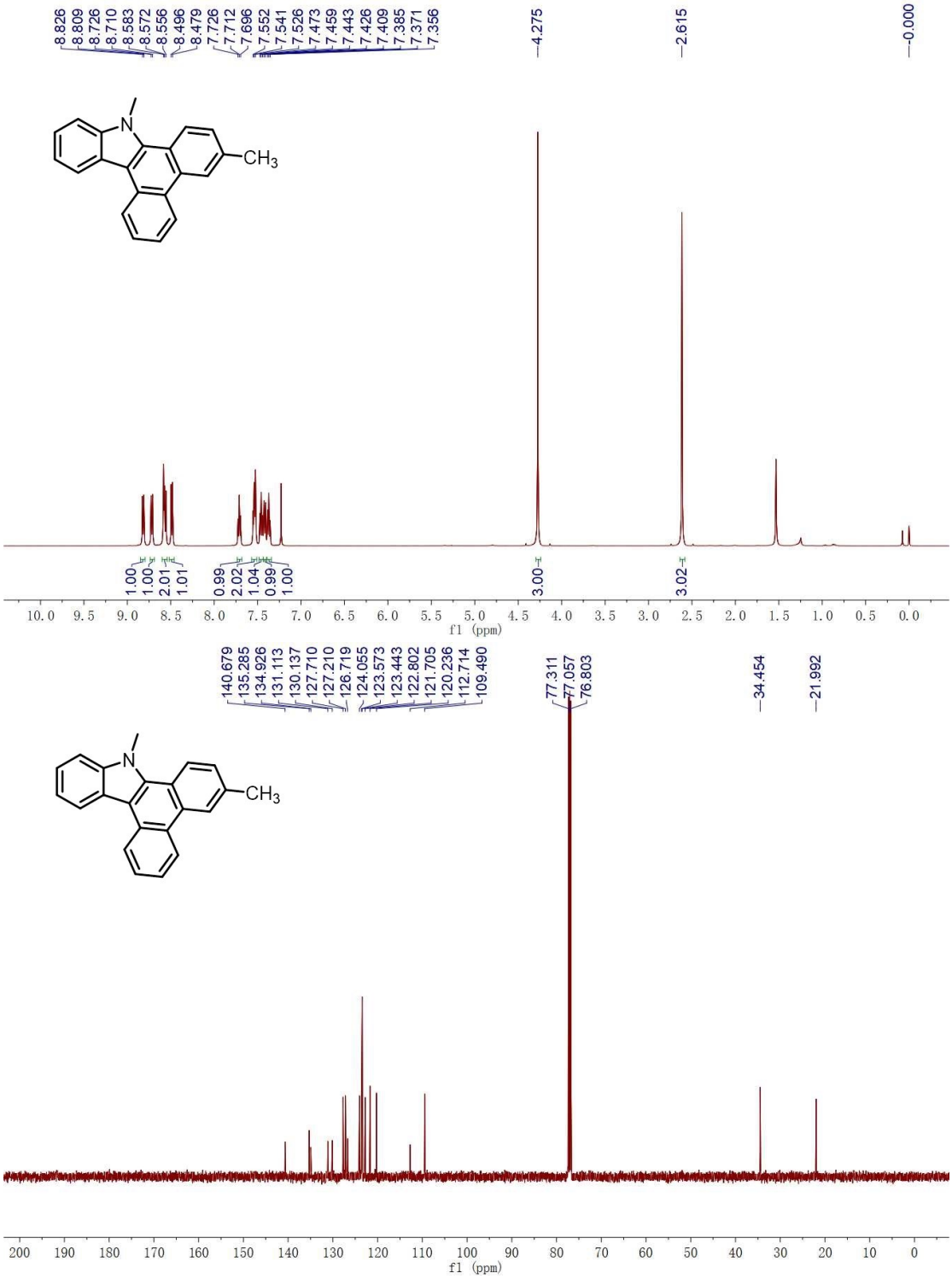
7 Scanned ^{1}H NMR and ^{13}C NMR Spectra of All Compounds

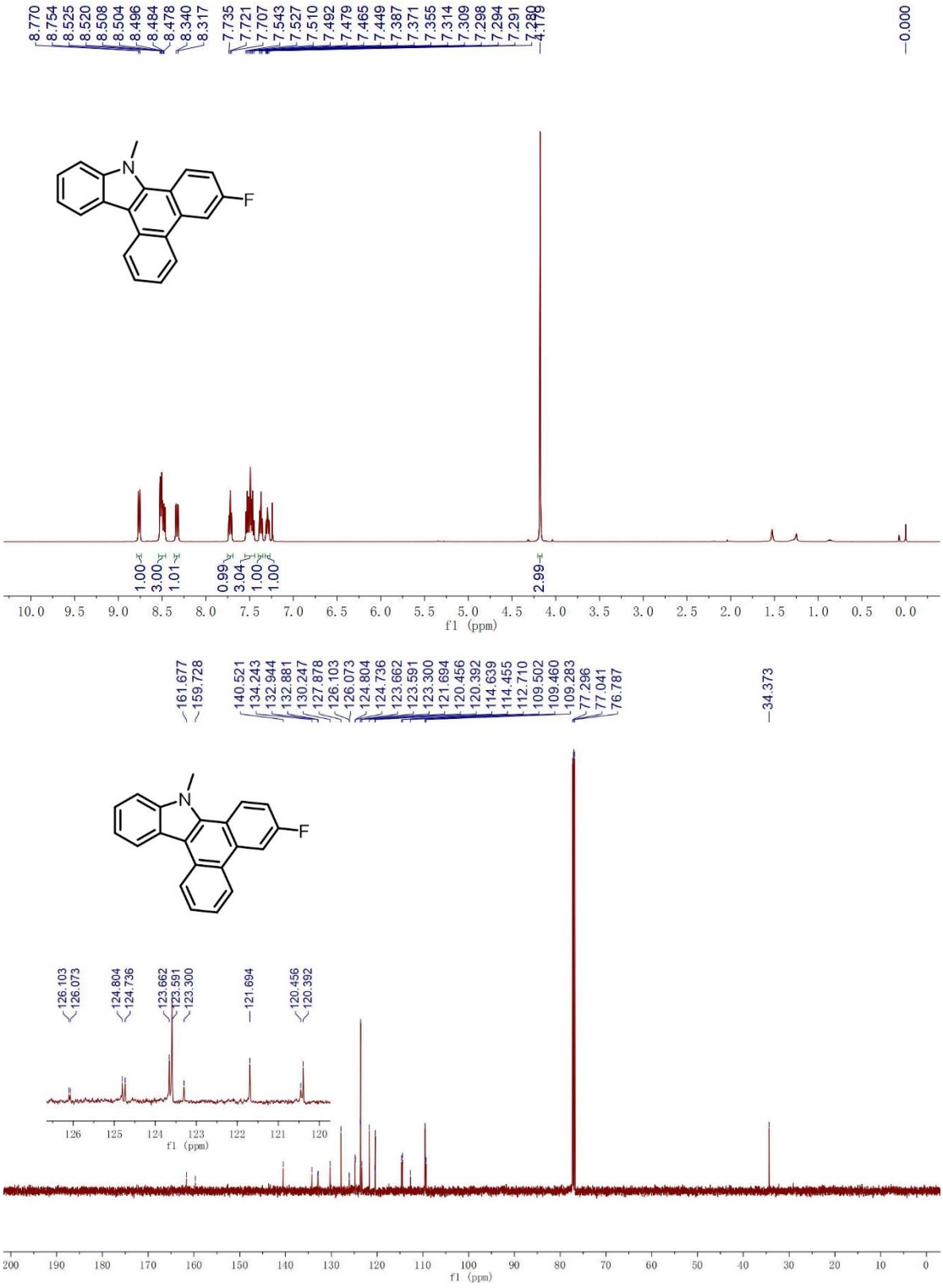
^{1}H NMR of **3aa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3aa** (125 MHz, $CDCl_3$)



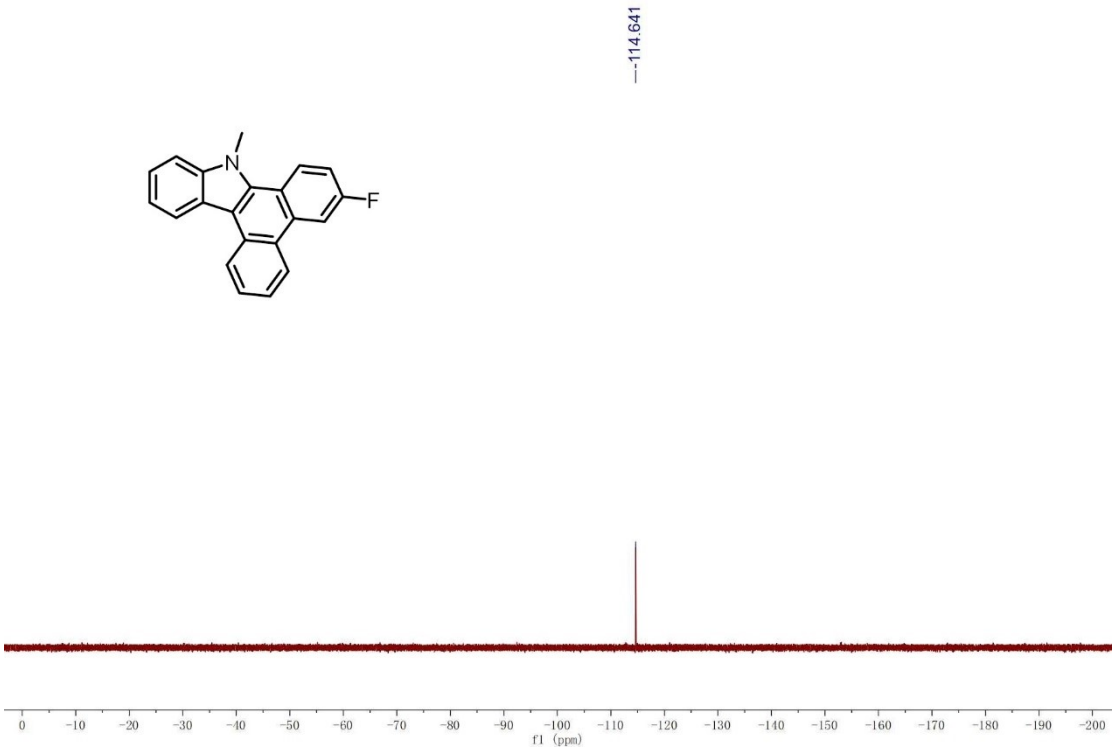
^{1}H NMR of **3ba** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ba** (125 MHz, $CDCl_3$)



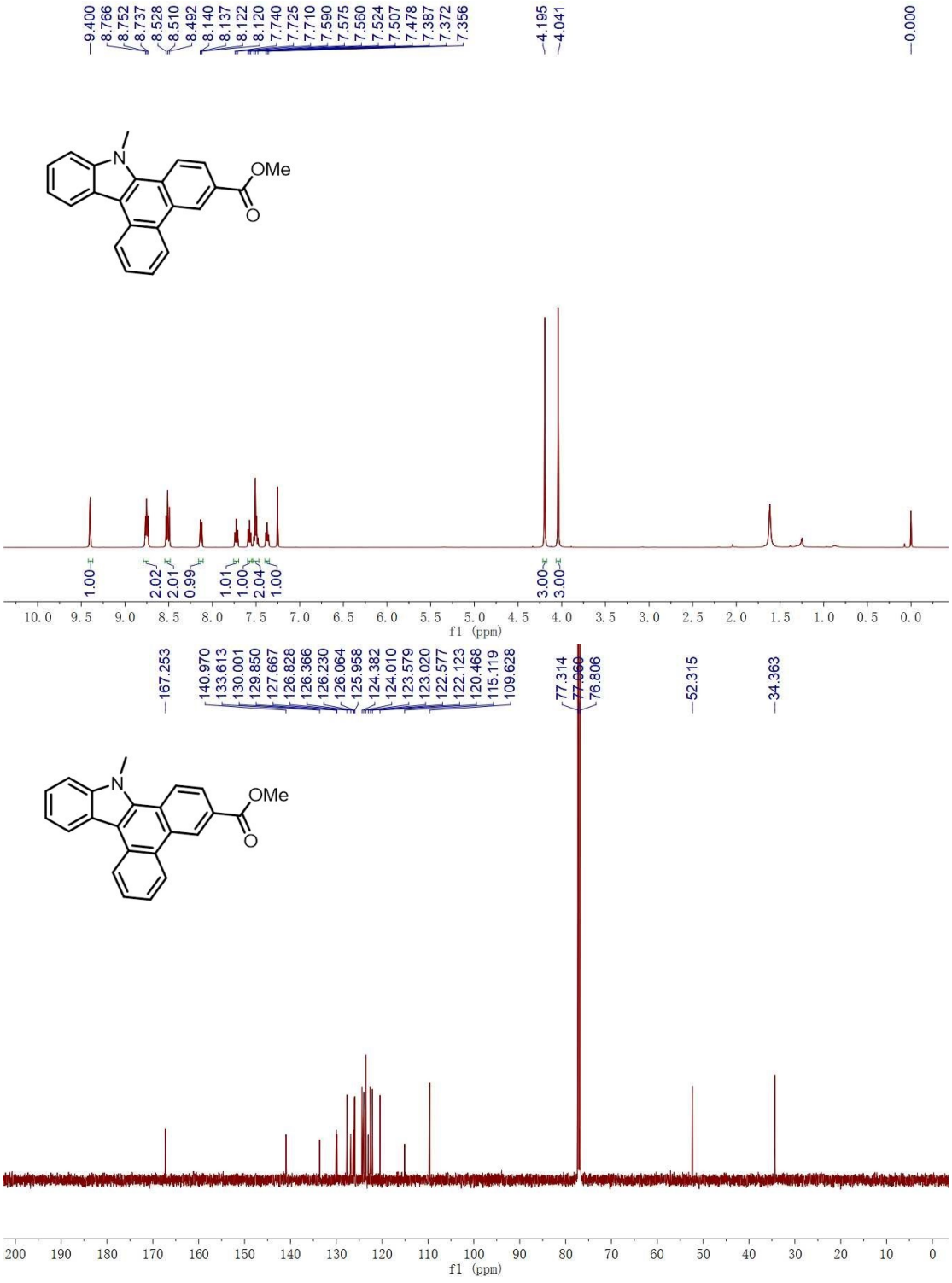
^{1}H NMR of **3ca** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ca** (125 MHz, $CDCl_3$)



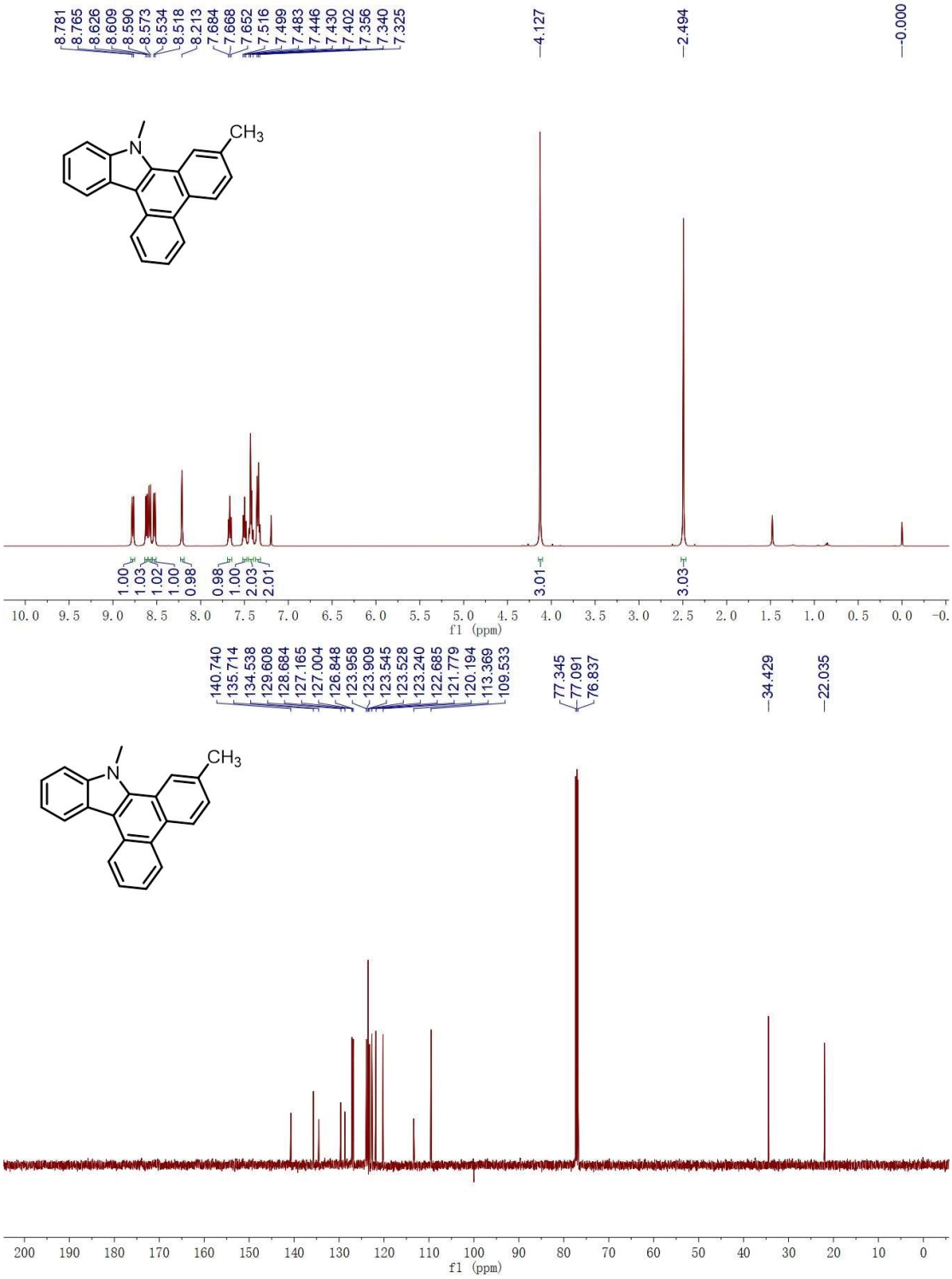
^{19}F NMR of **3ca** (470 MHz, $CDCl_3$)



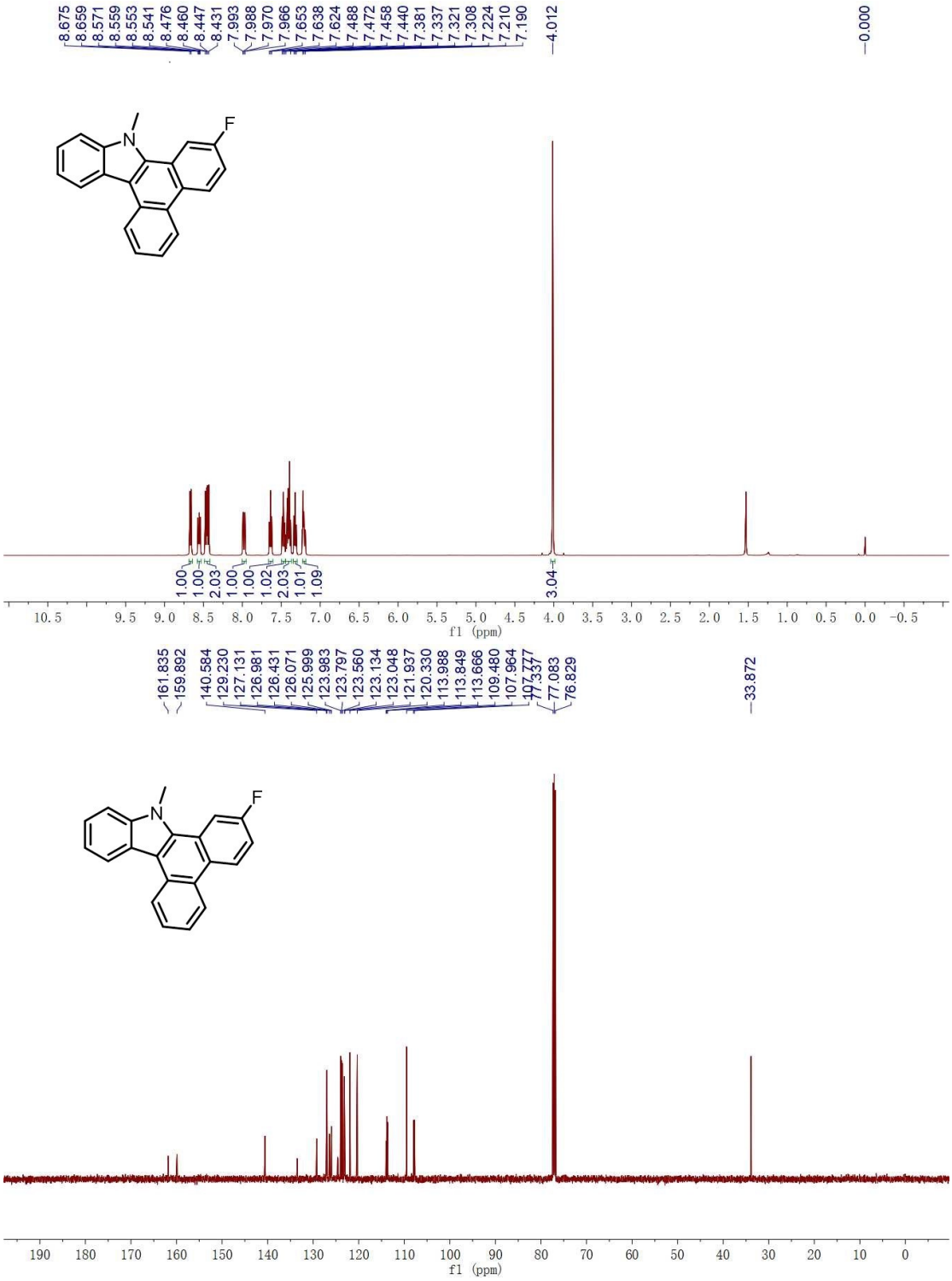
^{1}H NMR of **3da** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3da** (125 MHz, $CDCl_3$)



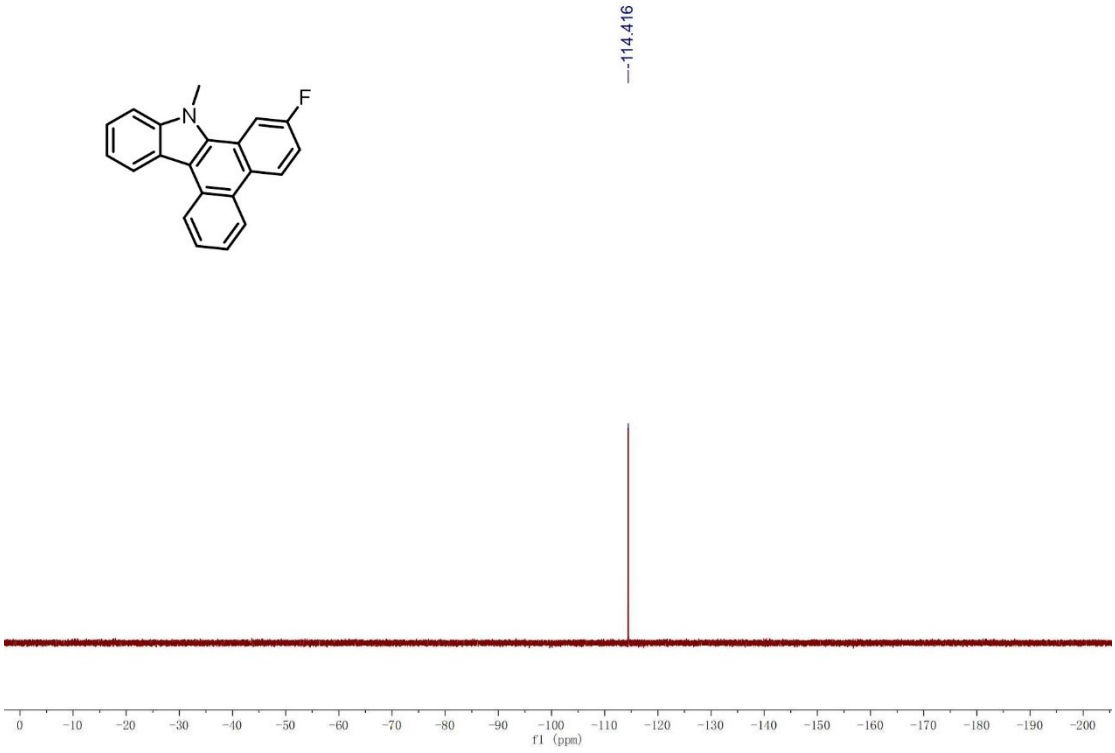
^{1}H NMR of **3ea** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ea** (125 MHz, $CDCl_3$)



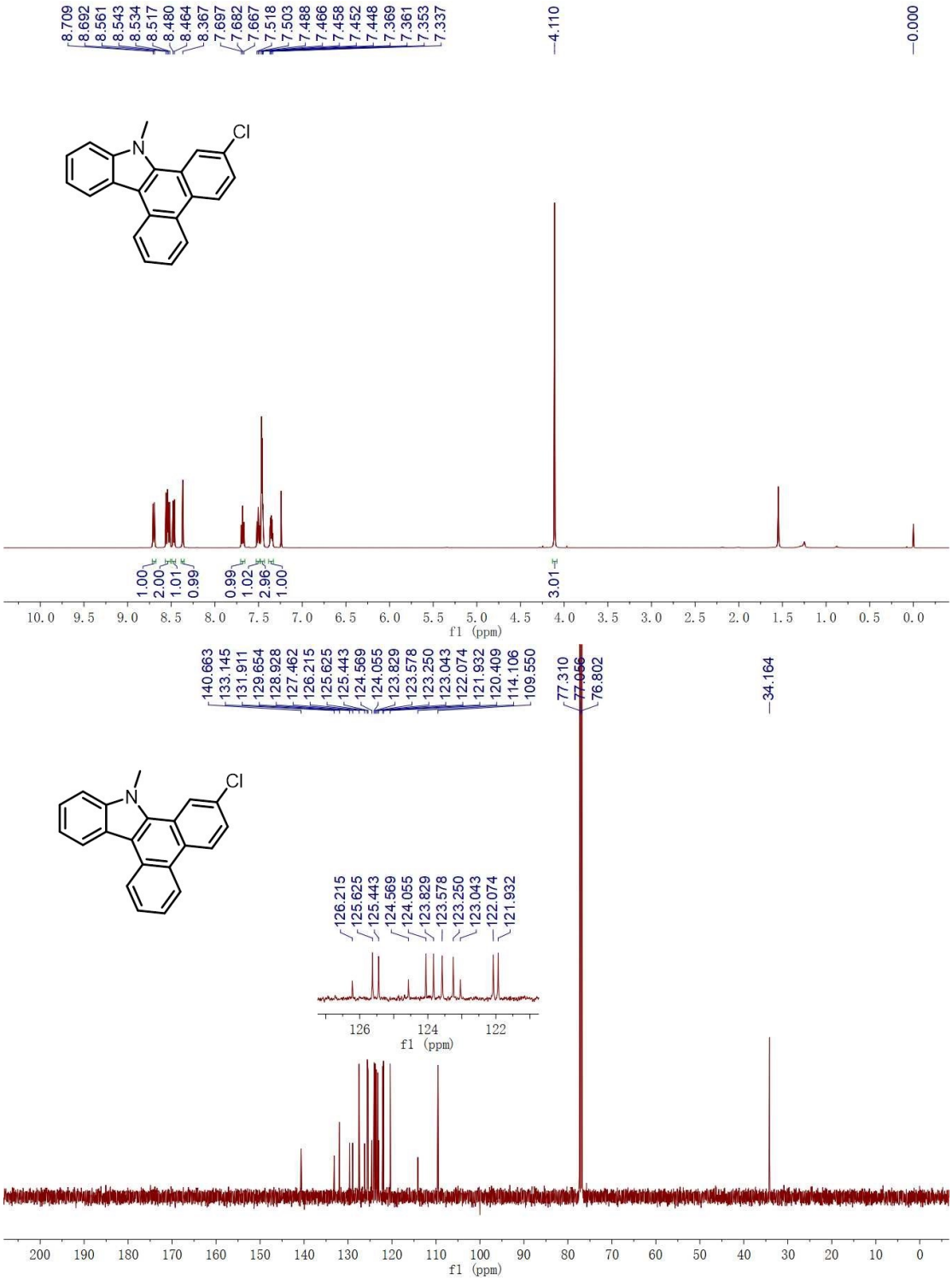
^{1}H NMR of **3fa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3fa** (125 MHz, $CDCl_3$)



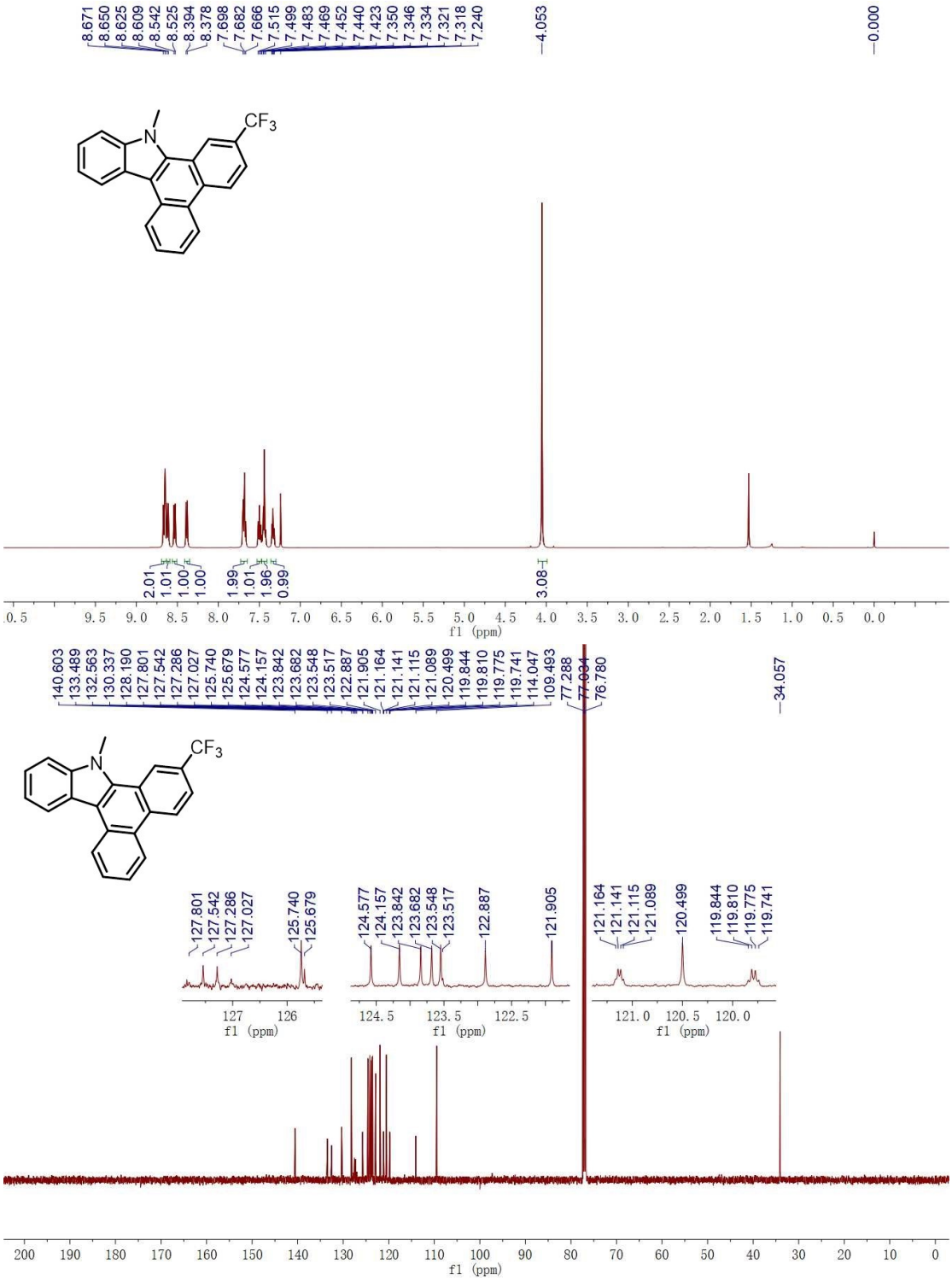
^{19}F NMR of **3fa** (470 MHz, $CDCl_3$)



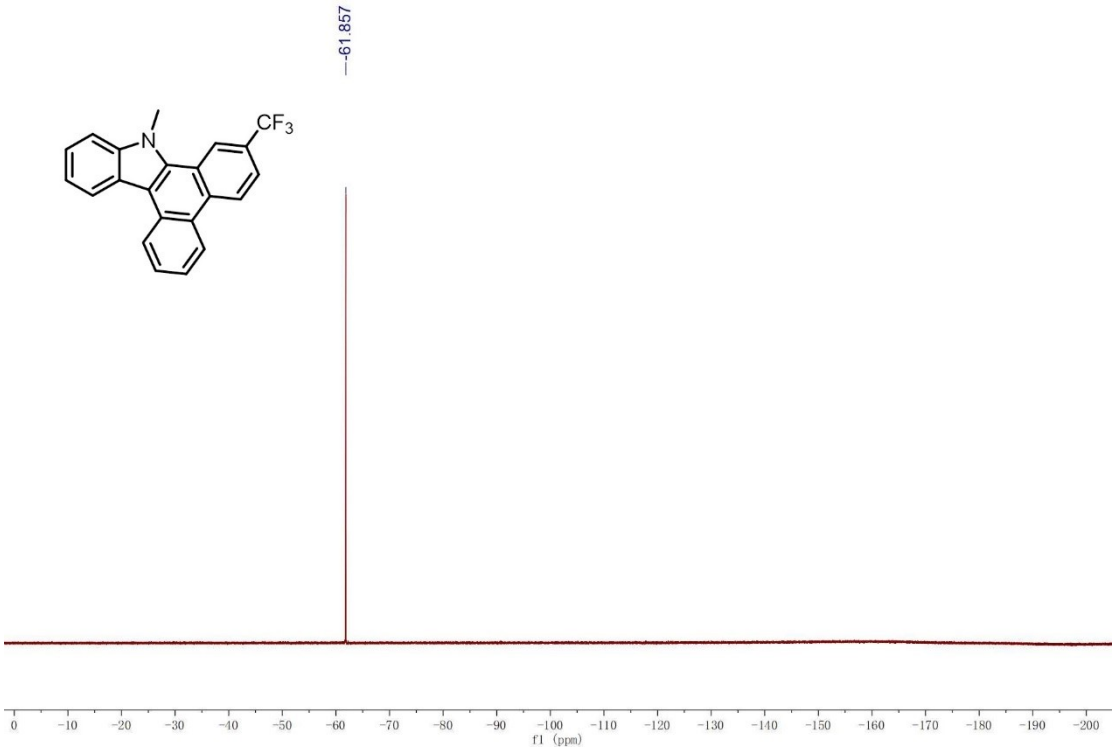
^{1}H NMR of **3ga** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ga** (125 MHz, $CDCl_3$)



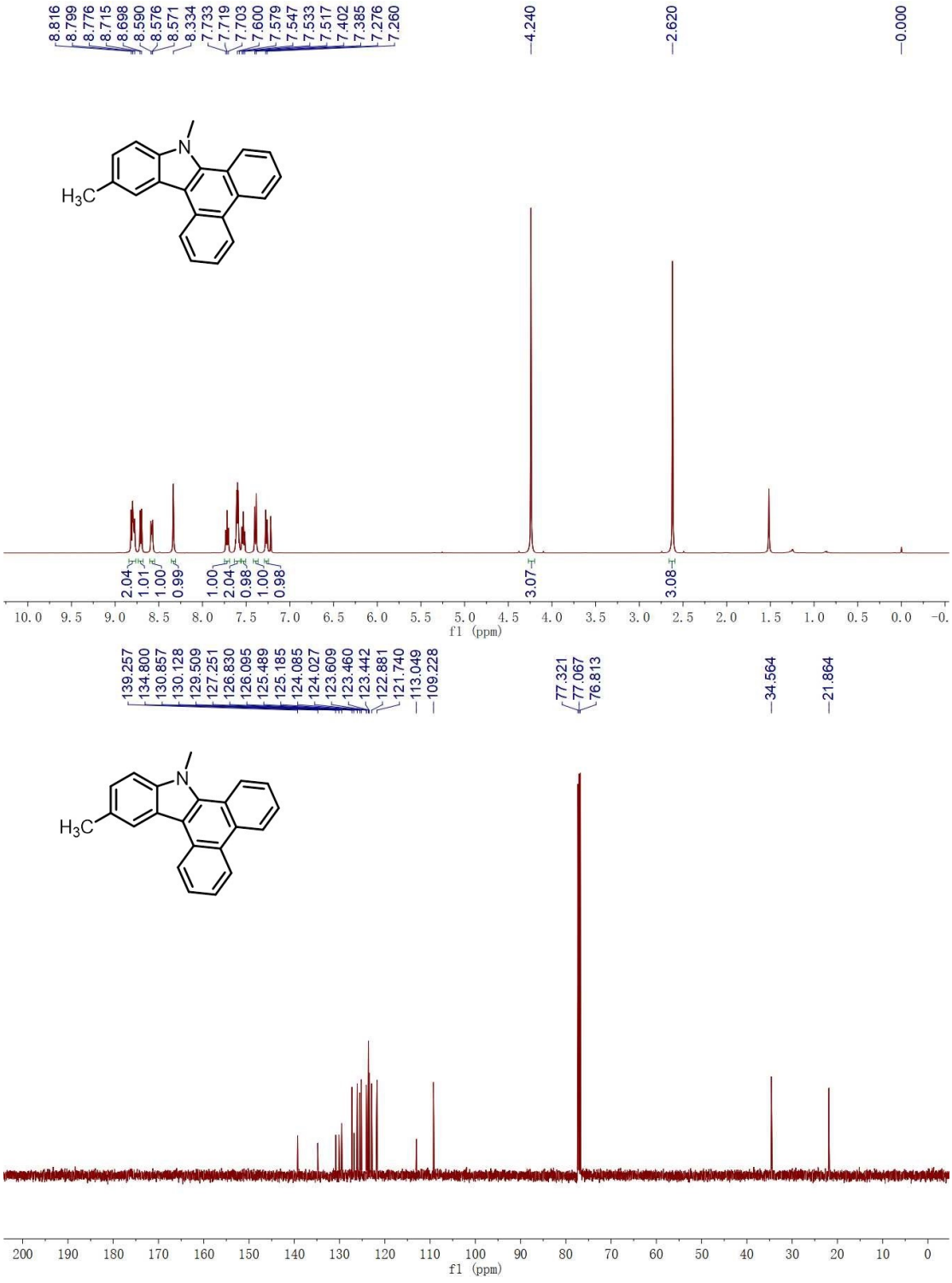
^{1}H NMR of **3ha** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ha** (125 MHz, $CDCl_3$)



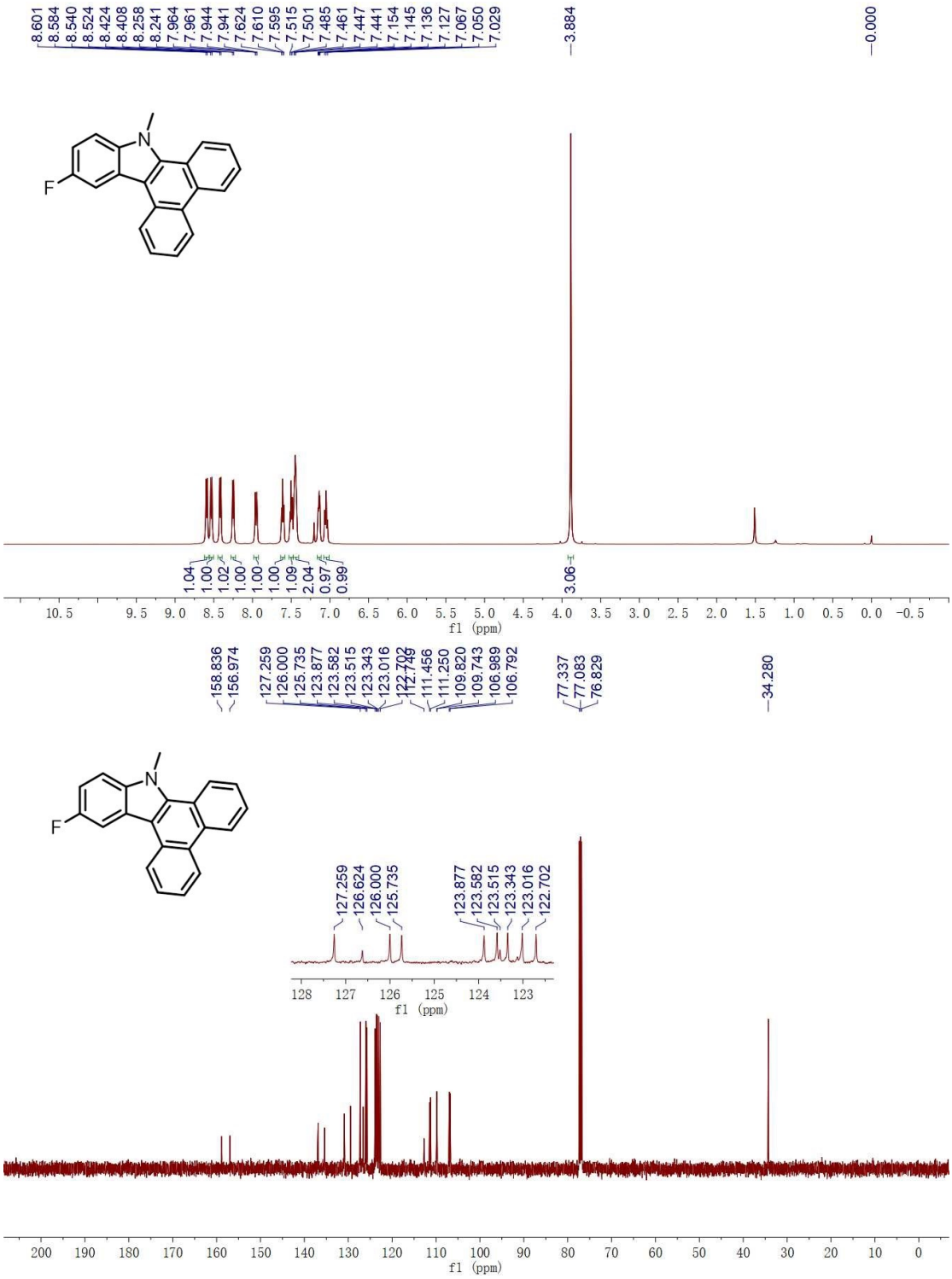
^{19}F NMR of **3ha** (470 MHz, $CDCl_3$)



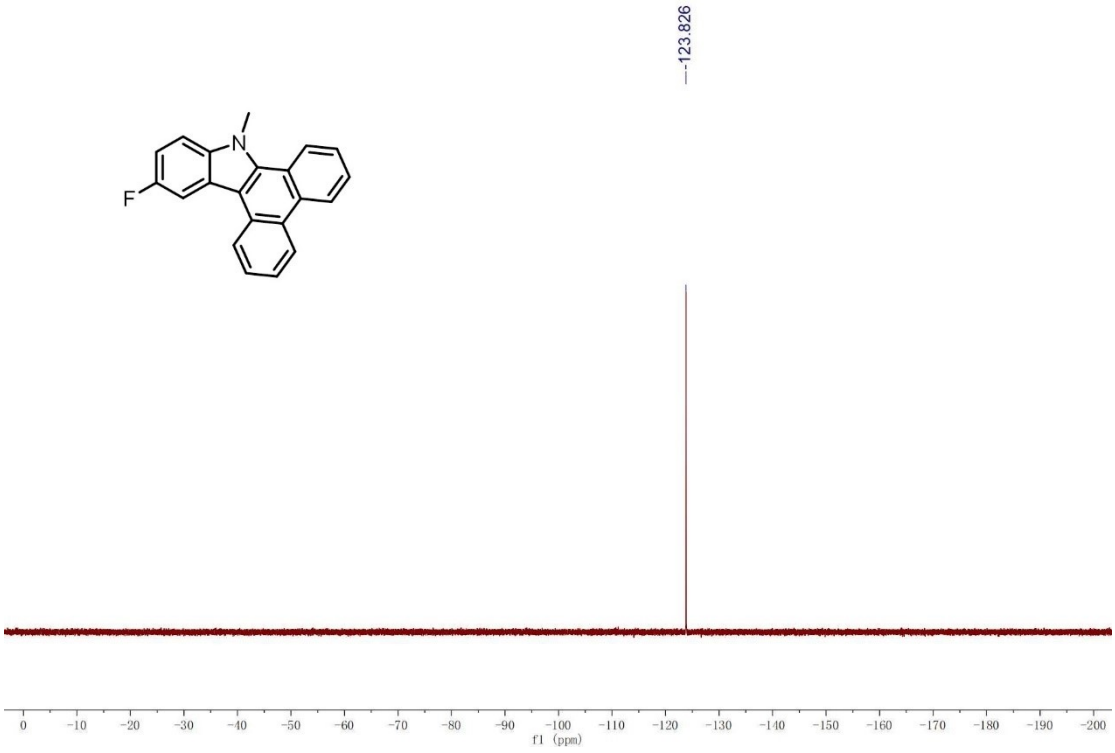
^{1}H NMR of **3ia** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ia** (125 MHz, $CDCl_3$)



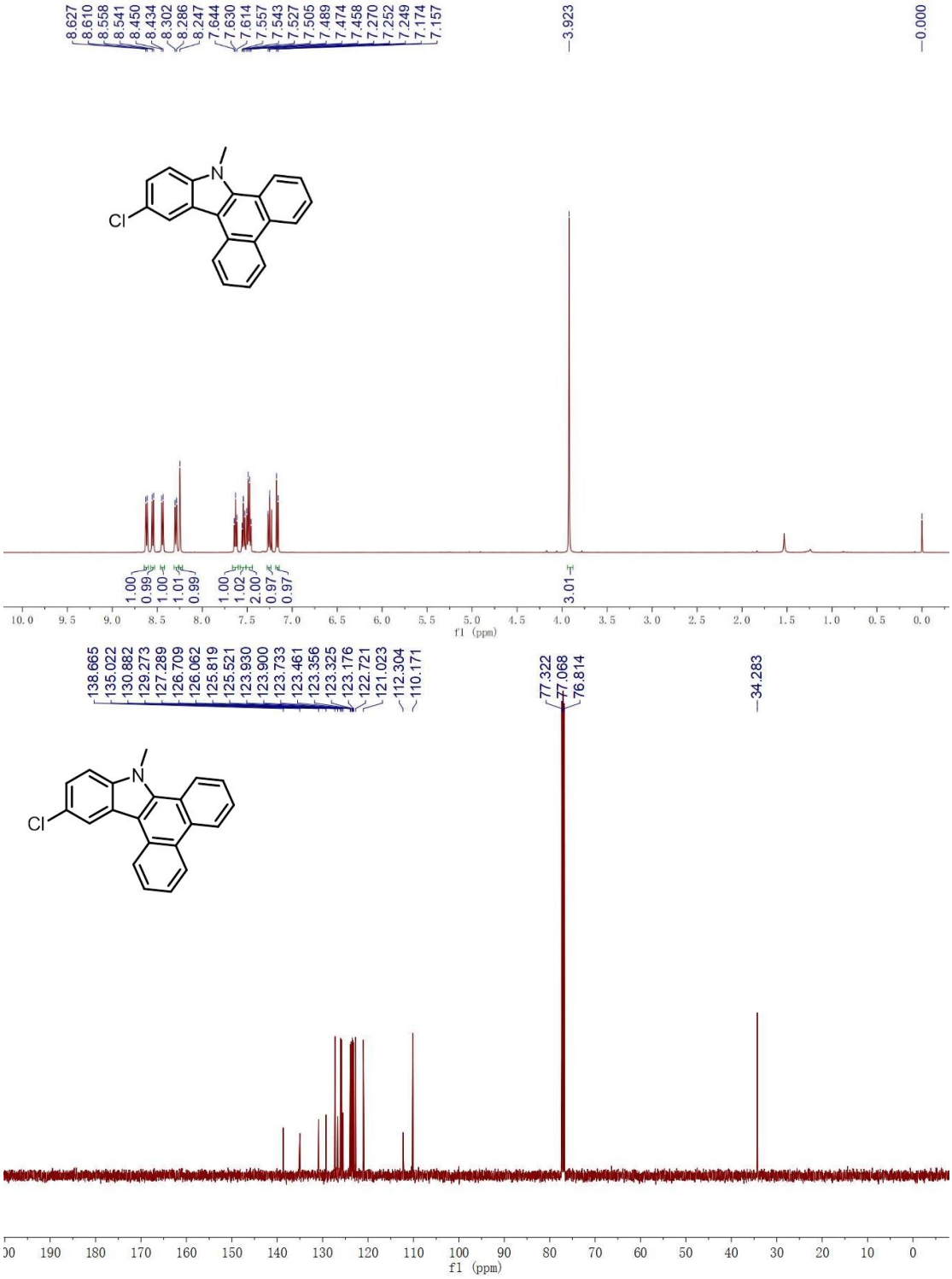
^{1}H NMR of **3ja** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ja** (125 MHz, $CDCl_3$)



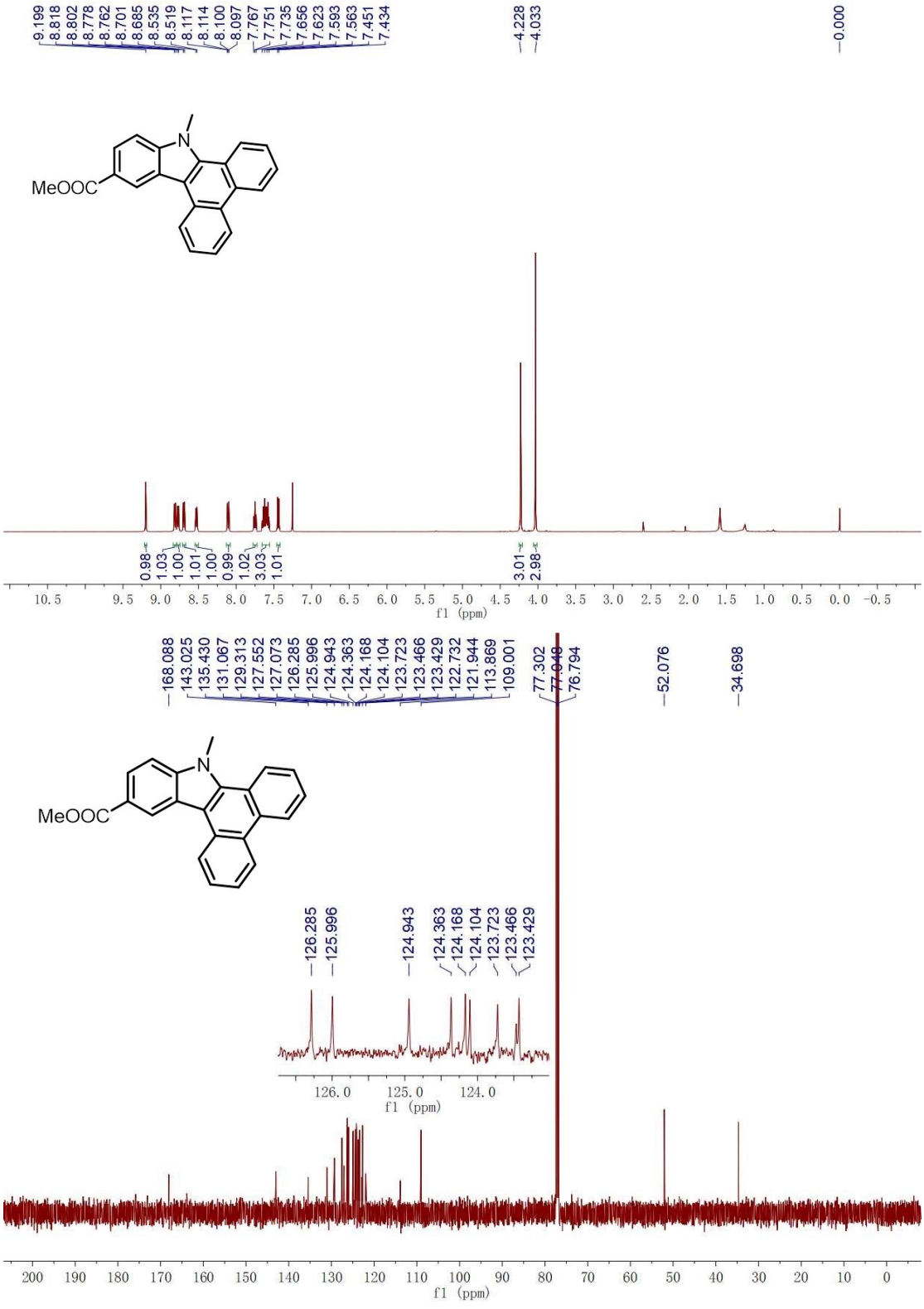
^{19}F NMR of **3ja** (470 MHz, $CDCl_3$)



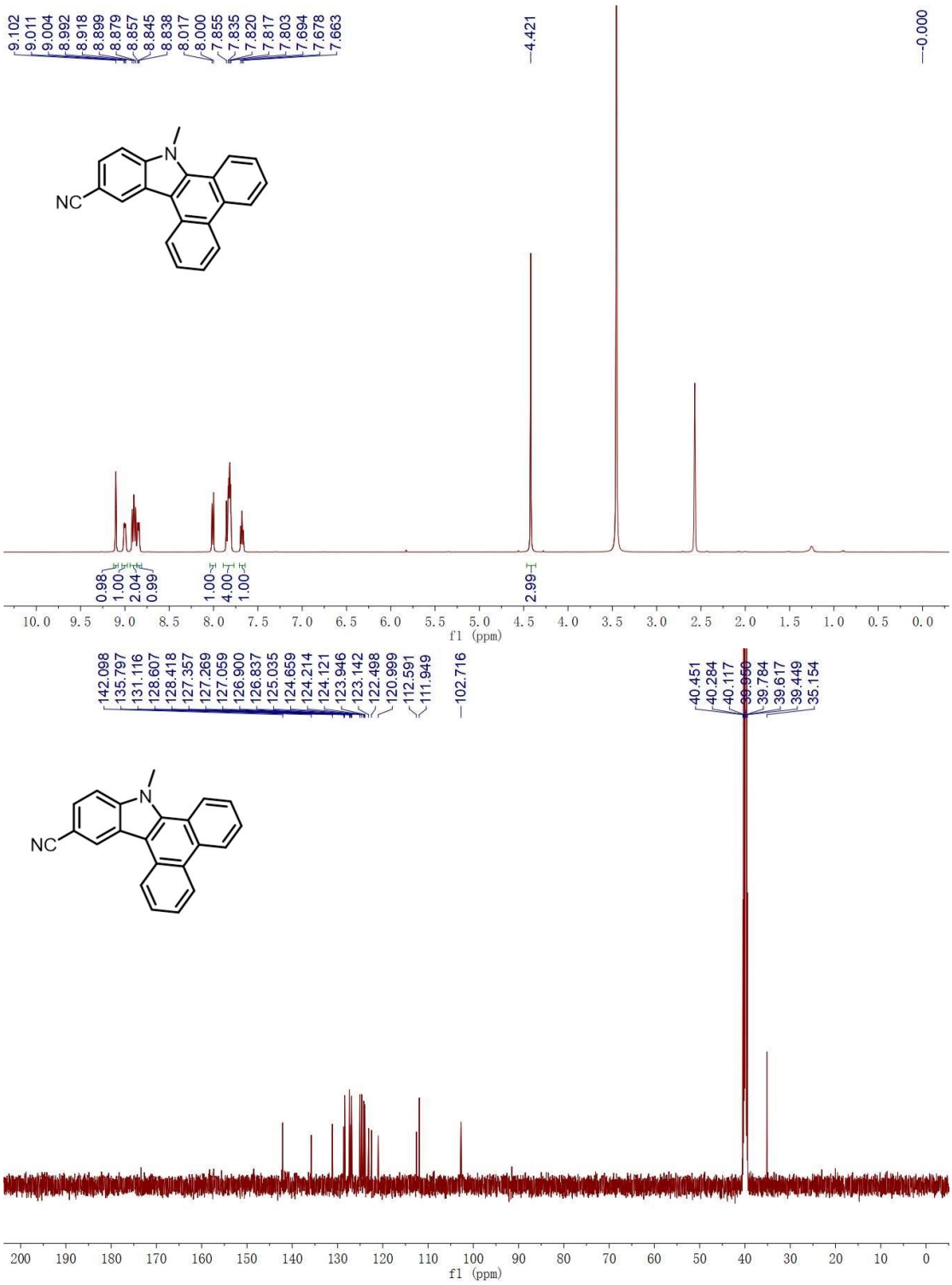
^{1}H NMR of **3ka** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ka** (125 MHz, $CDCl_3$)



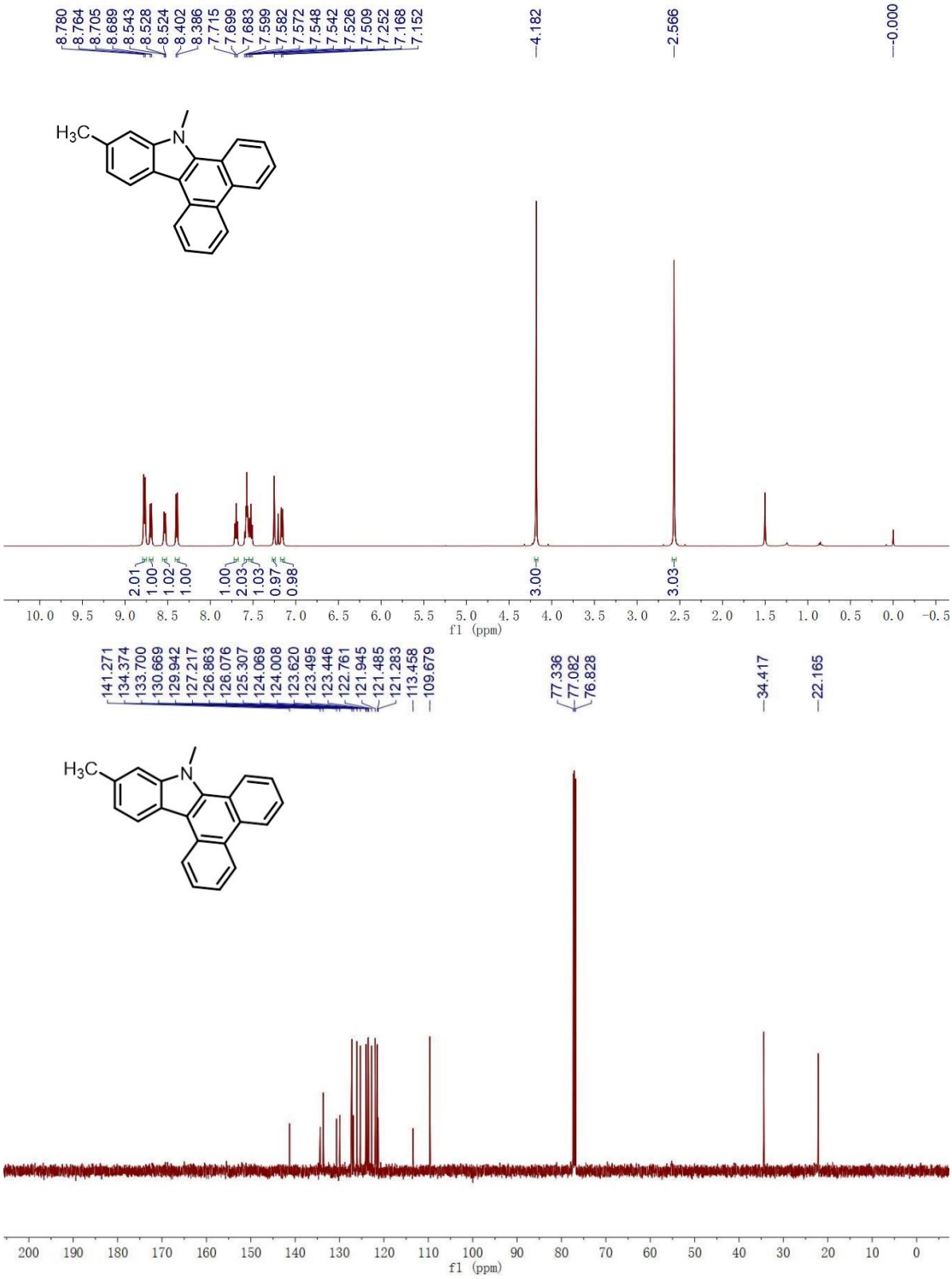
^{1}H NMR of **3la** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3la** (125 MHz, $CDCl_3$)



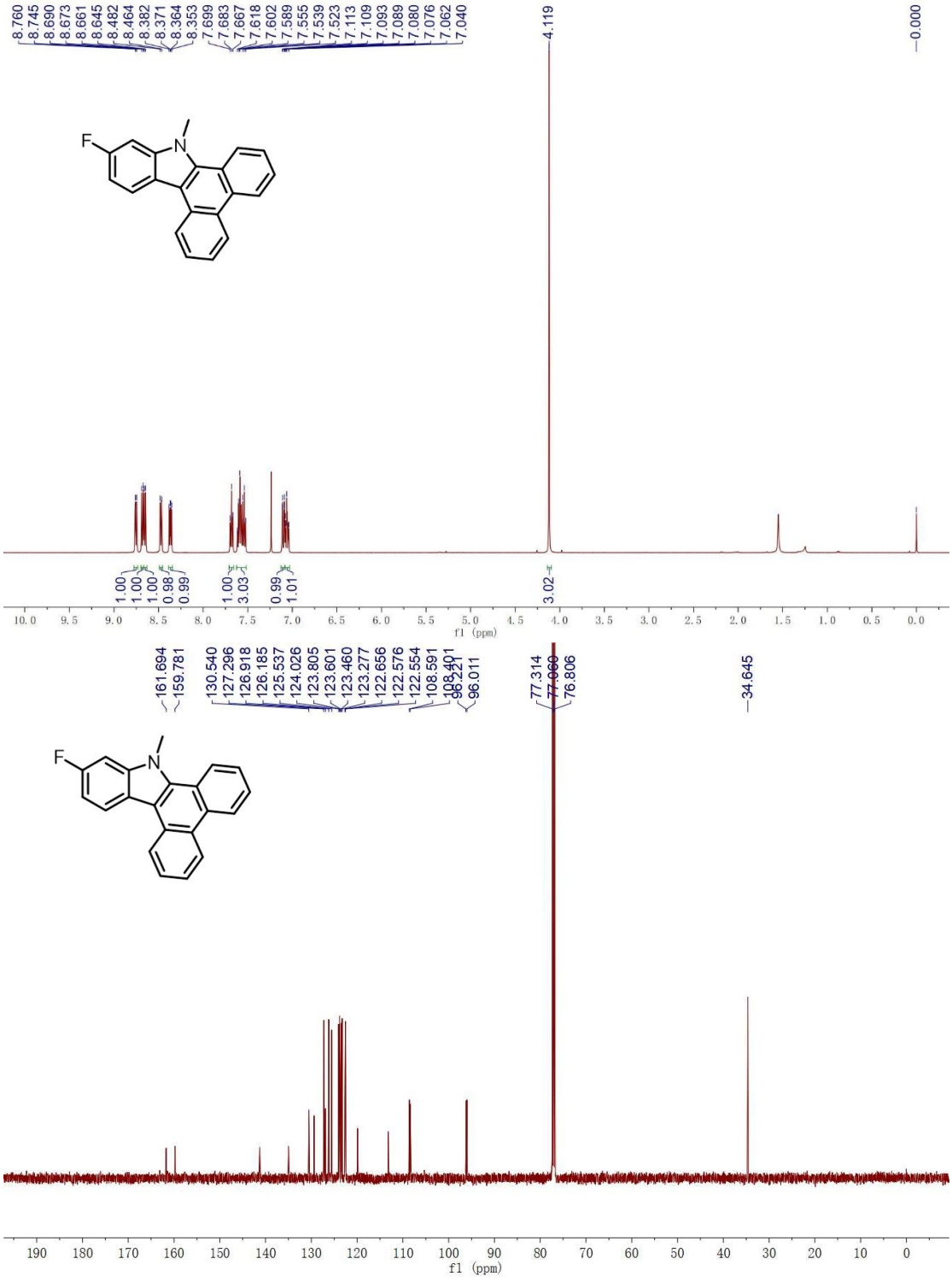
^{1}H NMR of **3ma** (500 MHz, DMSO-d_6) and ^{13}C NMR of **3ma** (125 MHz, DMSO-d_6)



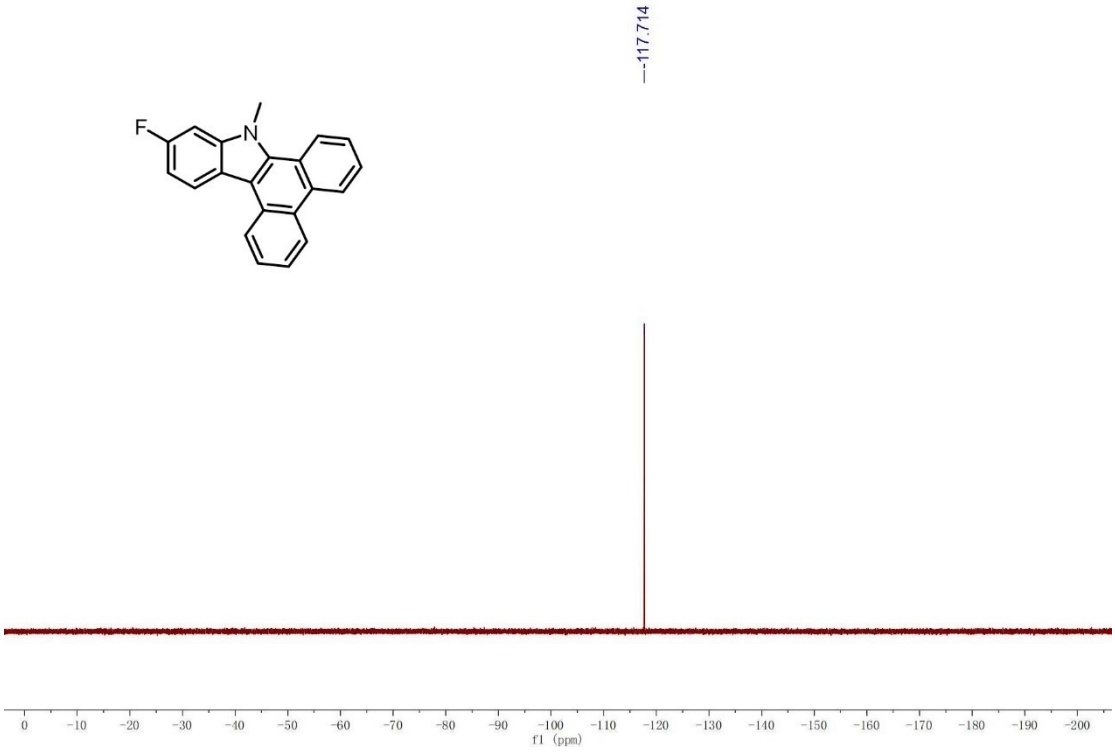
^{1}H NMR of **3na** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3na** (125 MHz, $CDCl_3$)



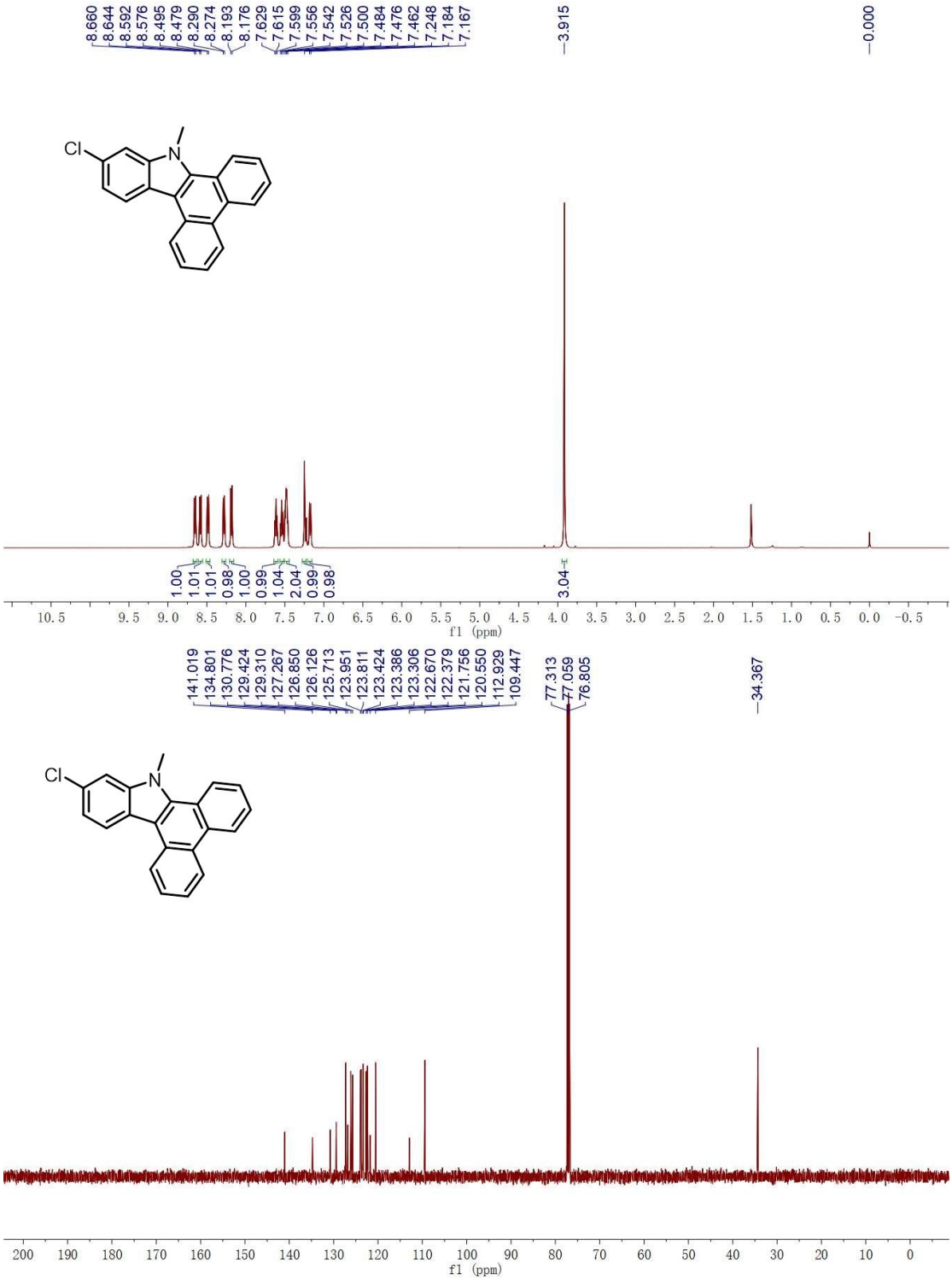
^{1}H NMR of **3oa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3oa** (125 MHz, $CDCl_3$)



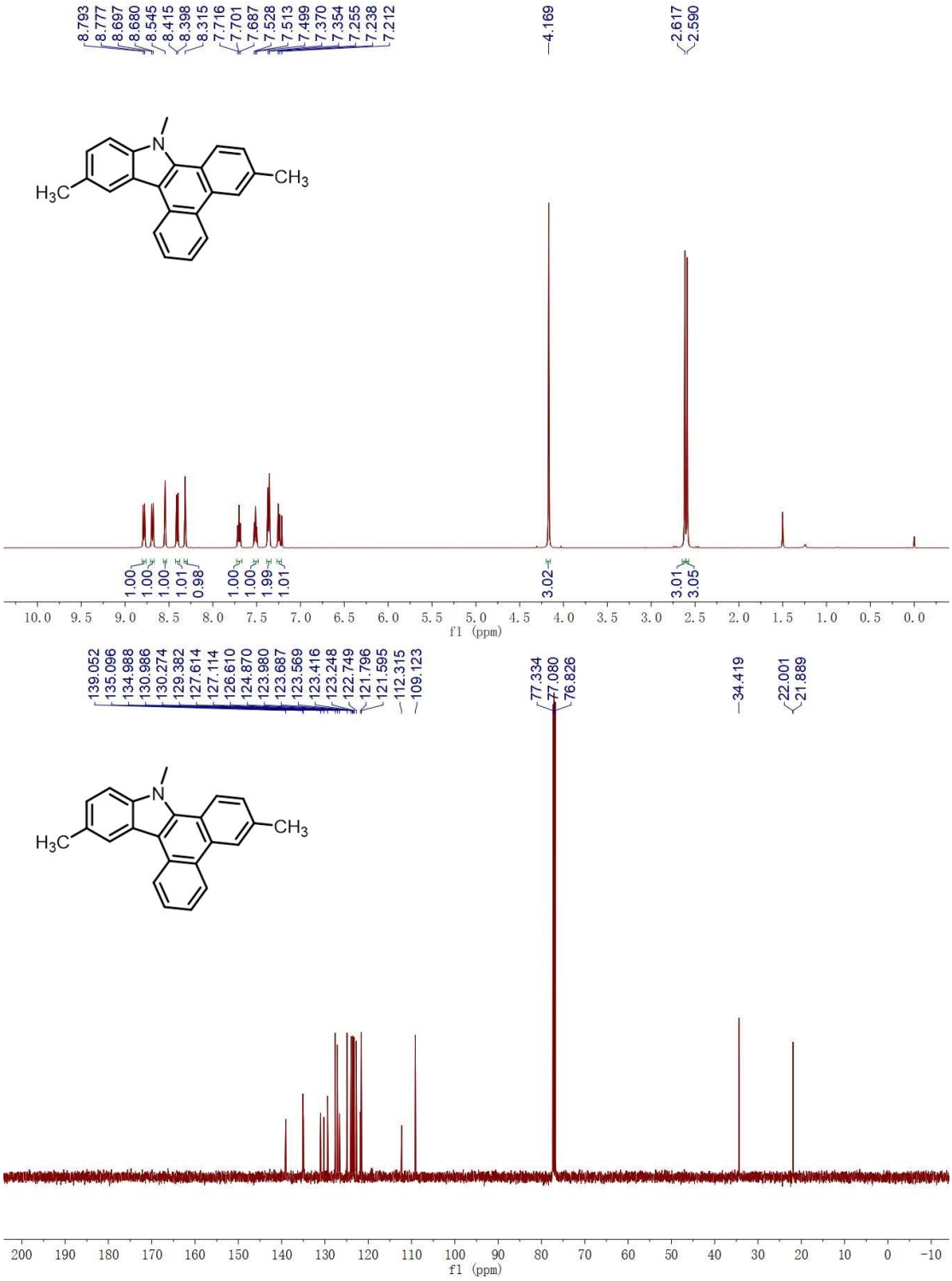
^{19}F NMR of **3oa** (470 MHz, $CDCl_3$)



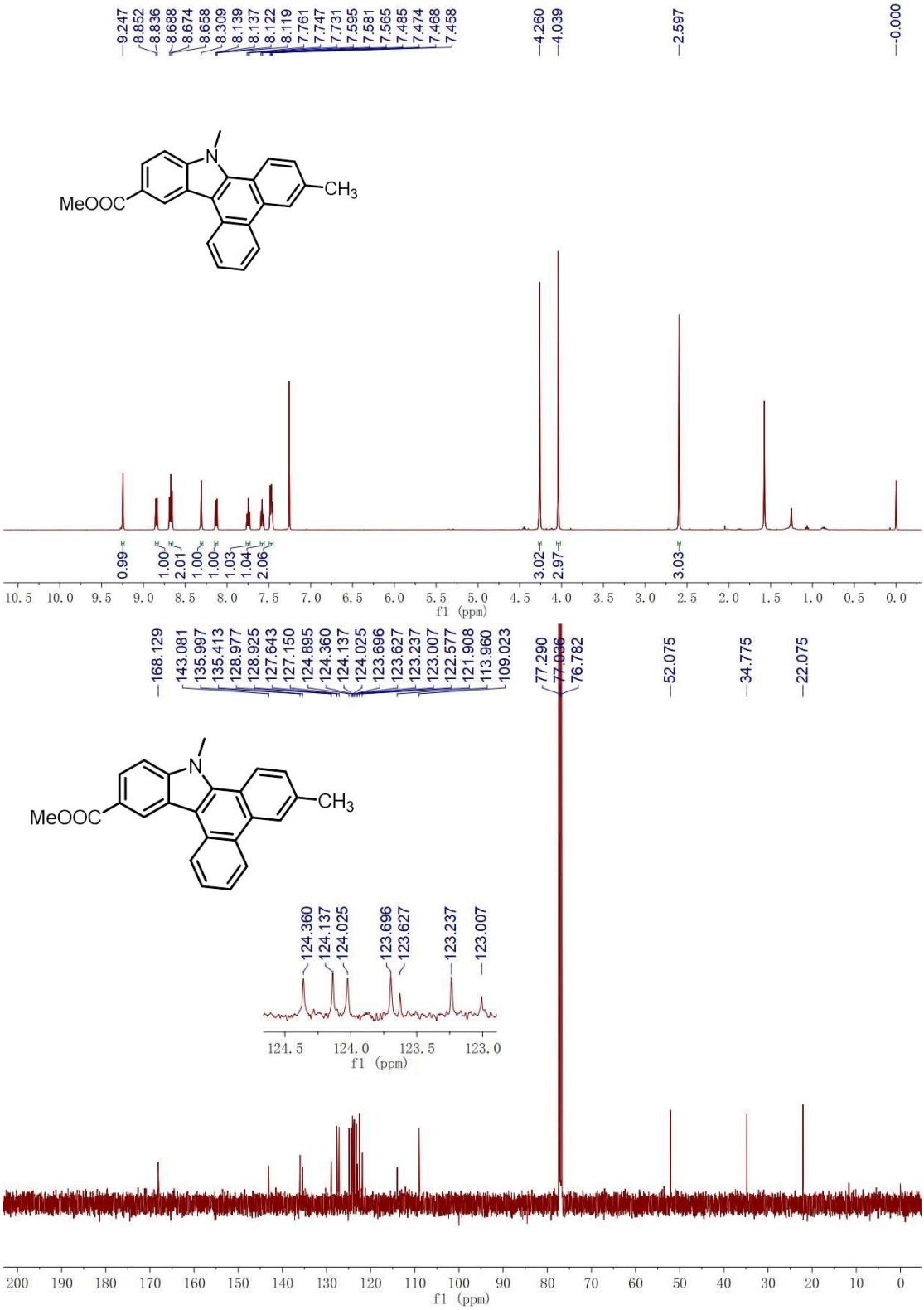
^{1}H NMR of **3pa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3pa** (125 MHz, $CDCl_3$)



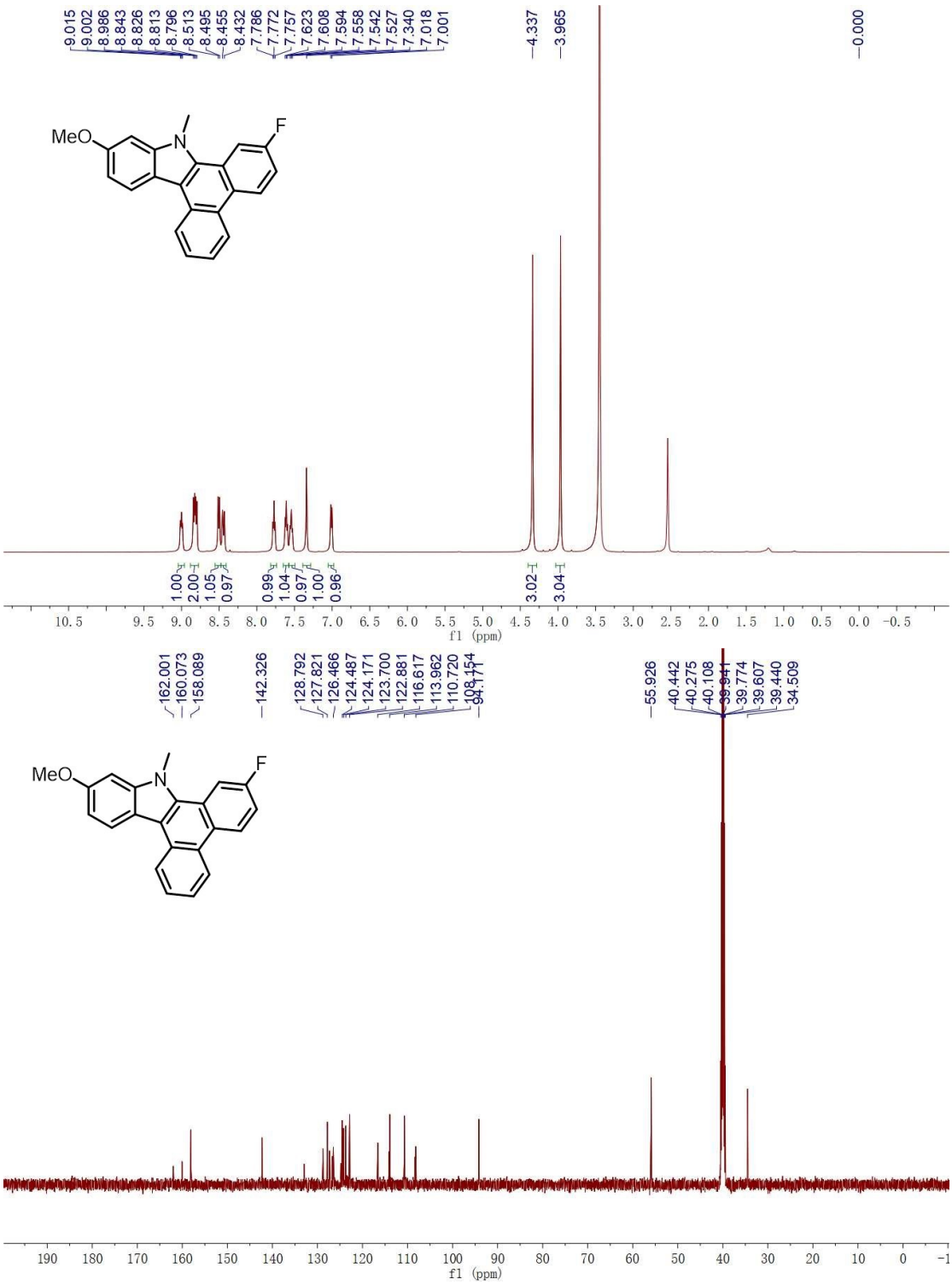
^{1}H NMR of **3qa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3qa** (125 MHz, $CDCl_3$)



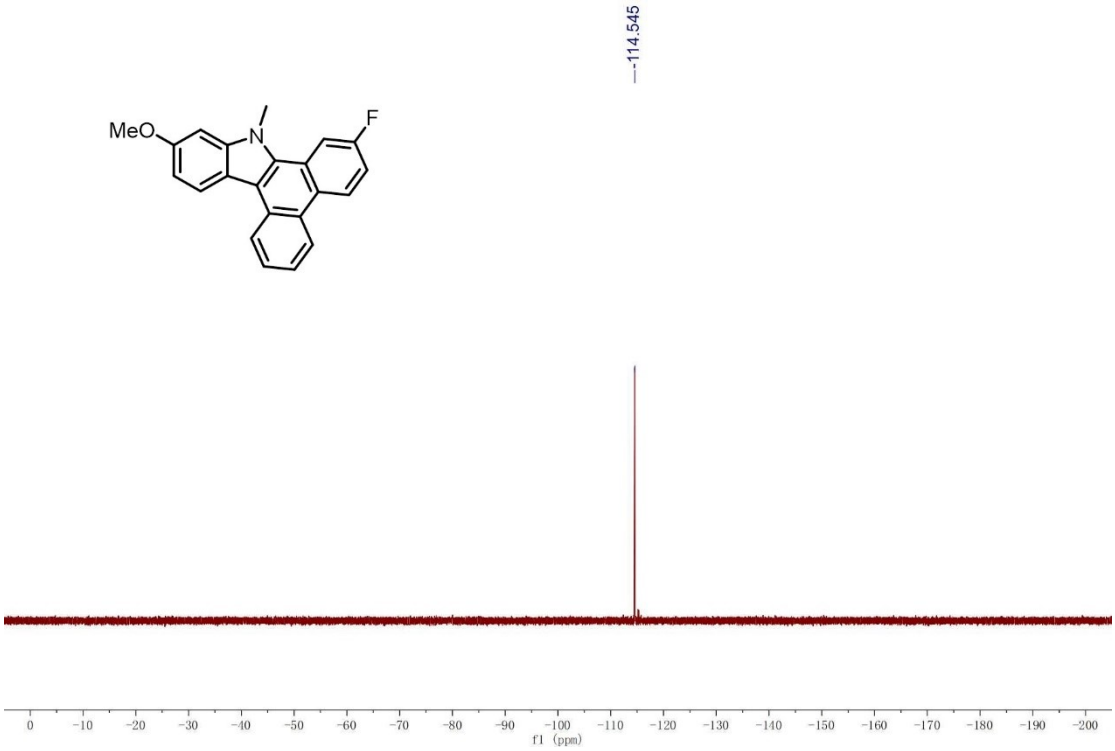
^{1}H NMR of **3ra** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ra** (125 MHz, $CDCl_3$)



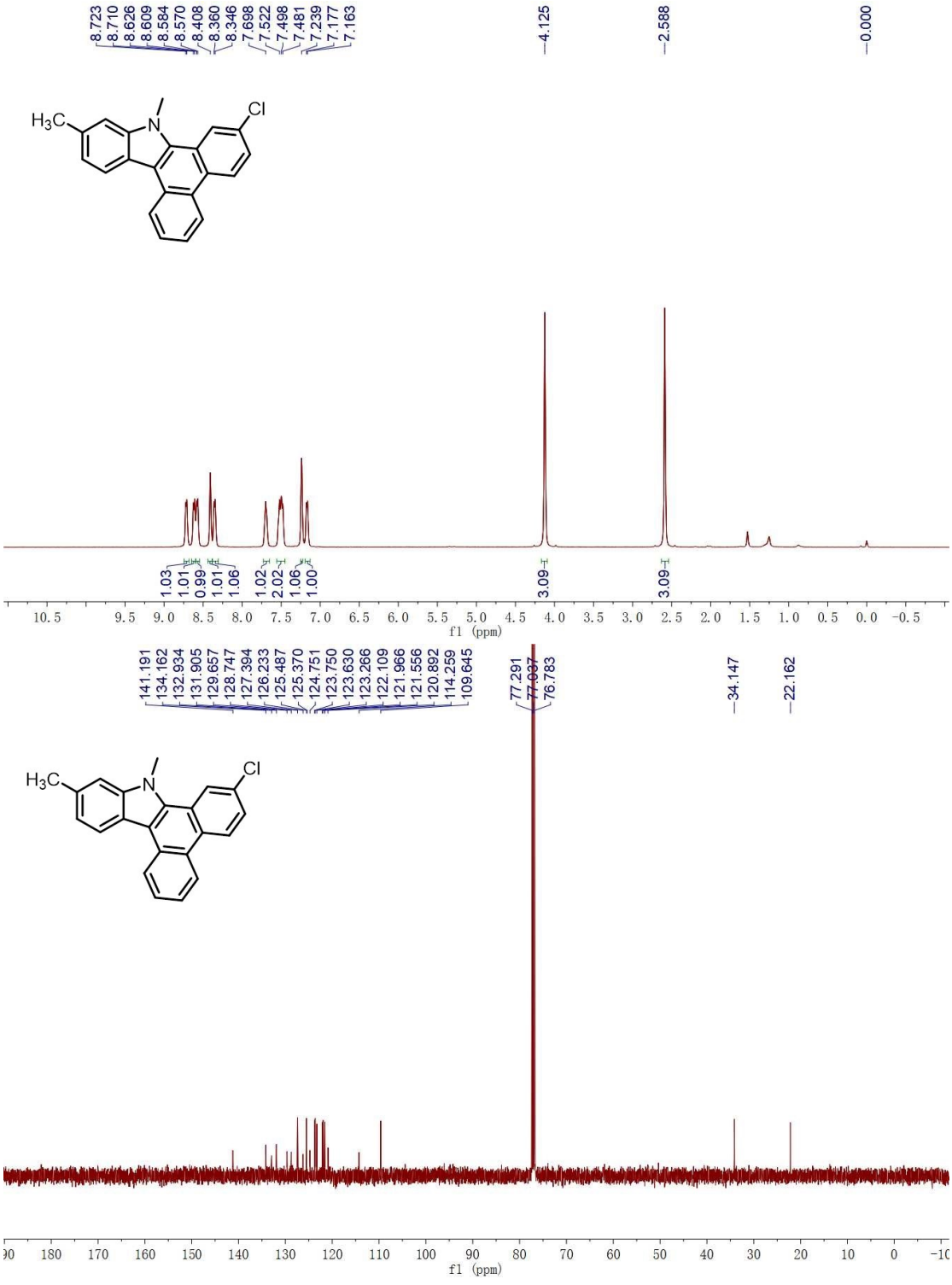
^{1}H NMR of **3sa** (500 MHz, DMSO-d_6) and ^{13}C NMR of **3sa** (125 MHz, DMSO-d_6)



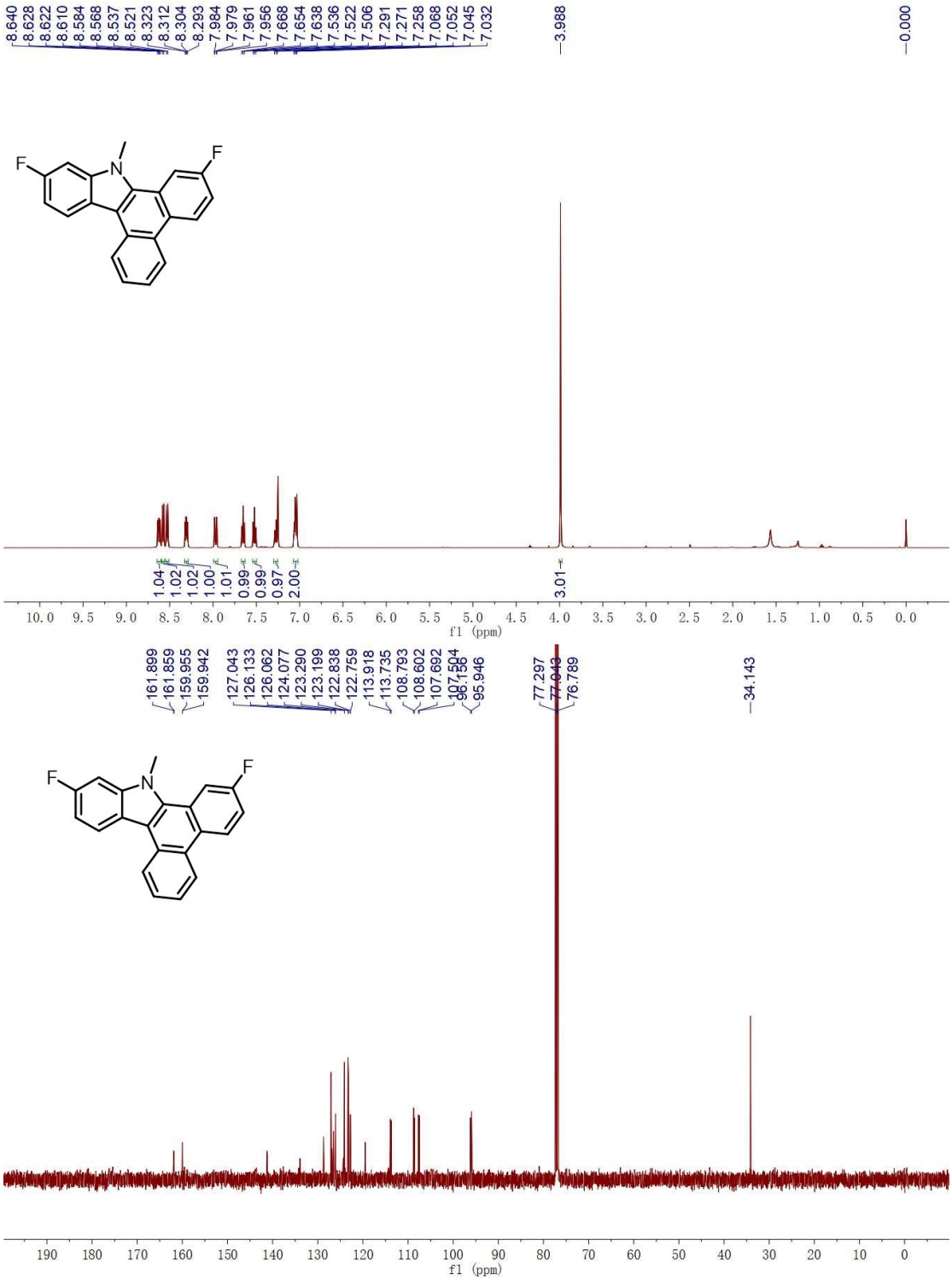
^{19}F NMR of **3sa** (470 MHz, $CDCl_3$)



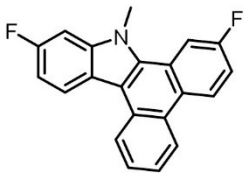
^{1}H NMR of **3ta** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ta** (125 MHz, $CDCl_3$)



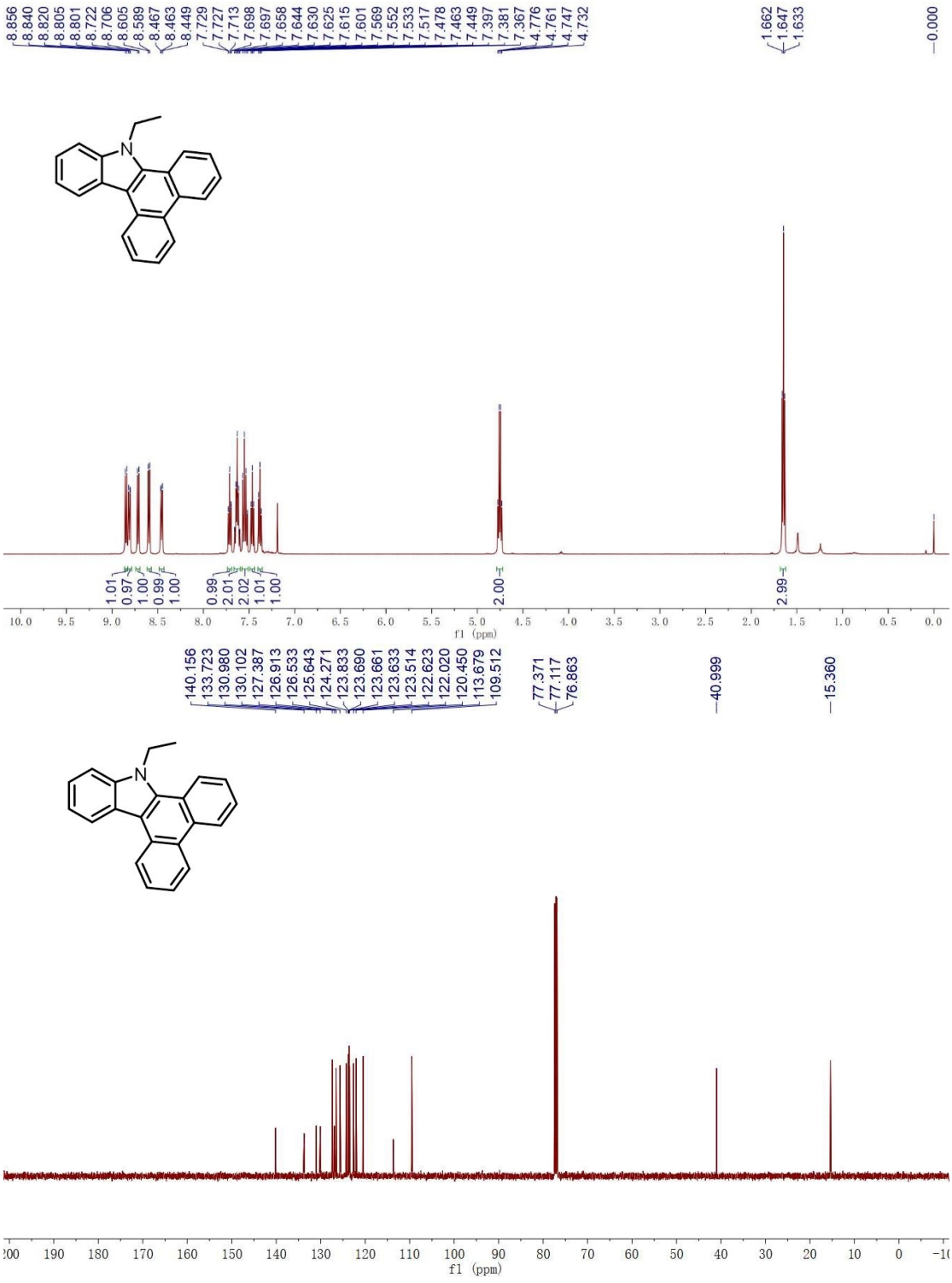
^{1}H NMR of **3ua** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ua** (125 MHz, $CDCl_3$)



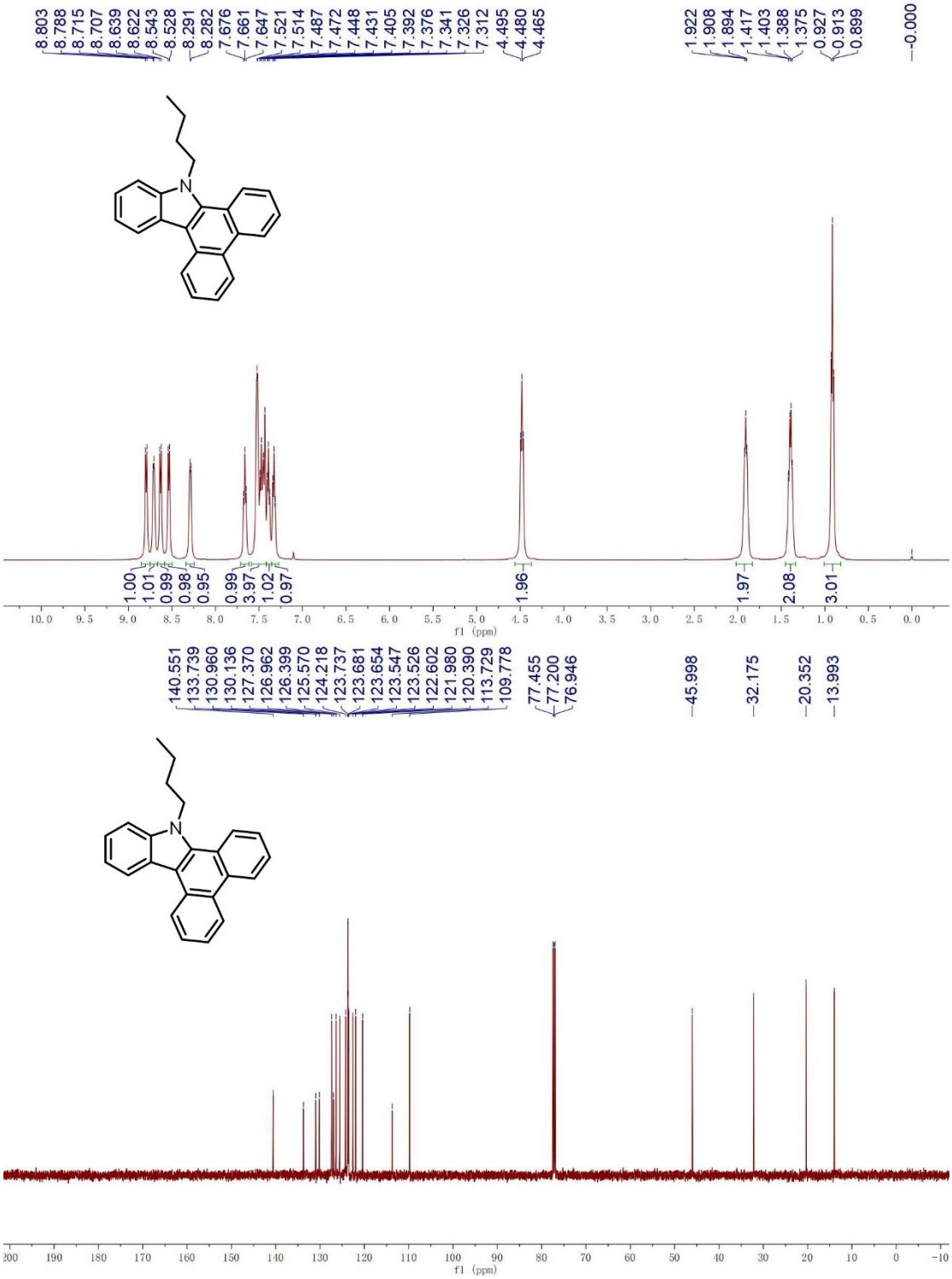
^{19}F NMR of **3ua** (470 MHz, $CDCl_3$)



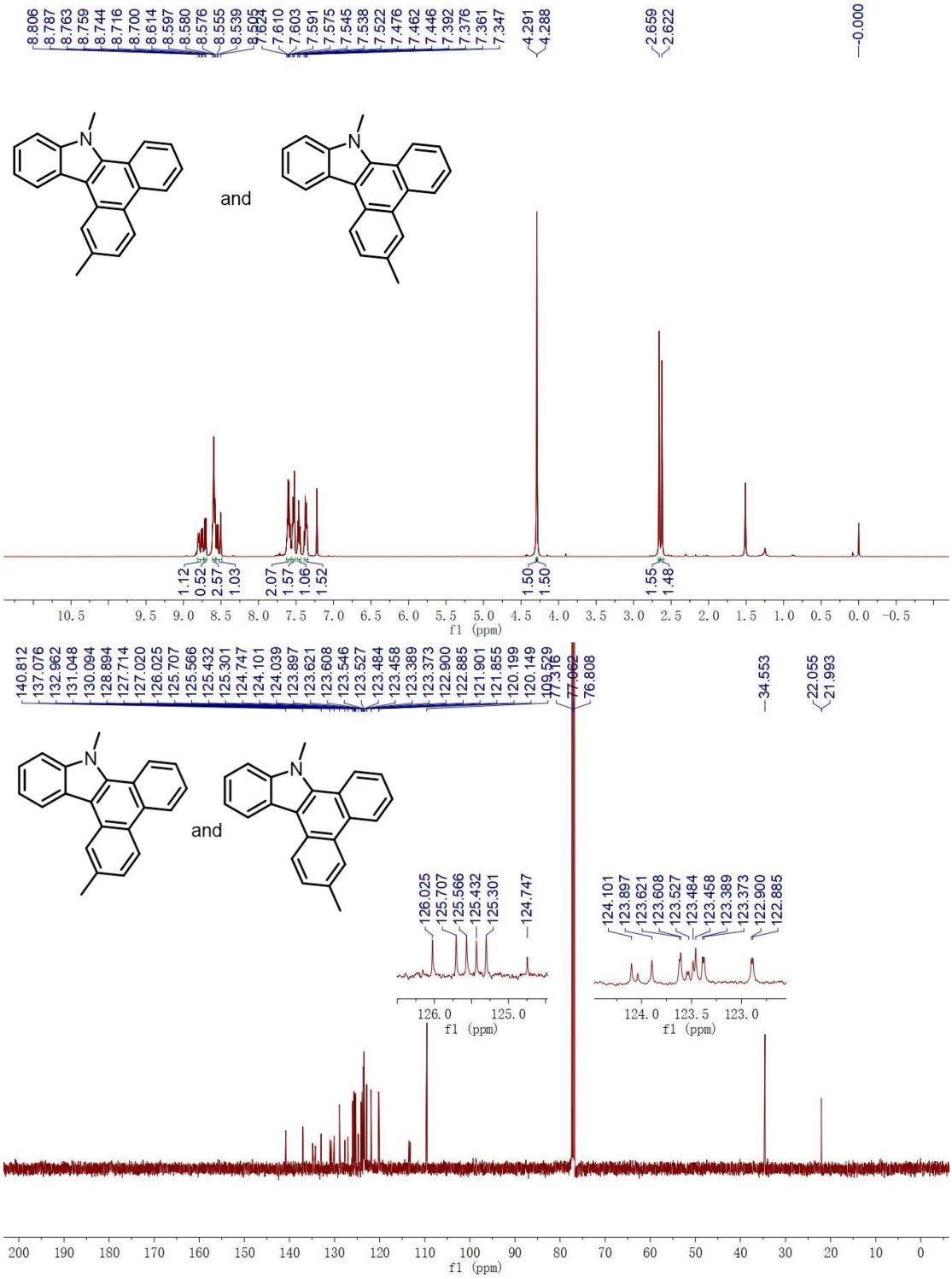
^{1}H NMR of **3va** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3va** (125 MHz, $CDCl_3$)



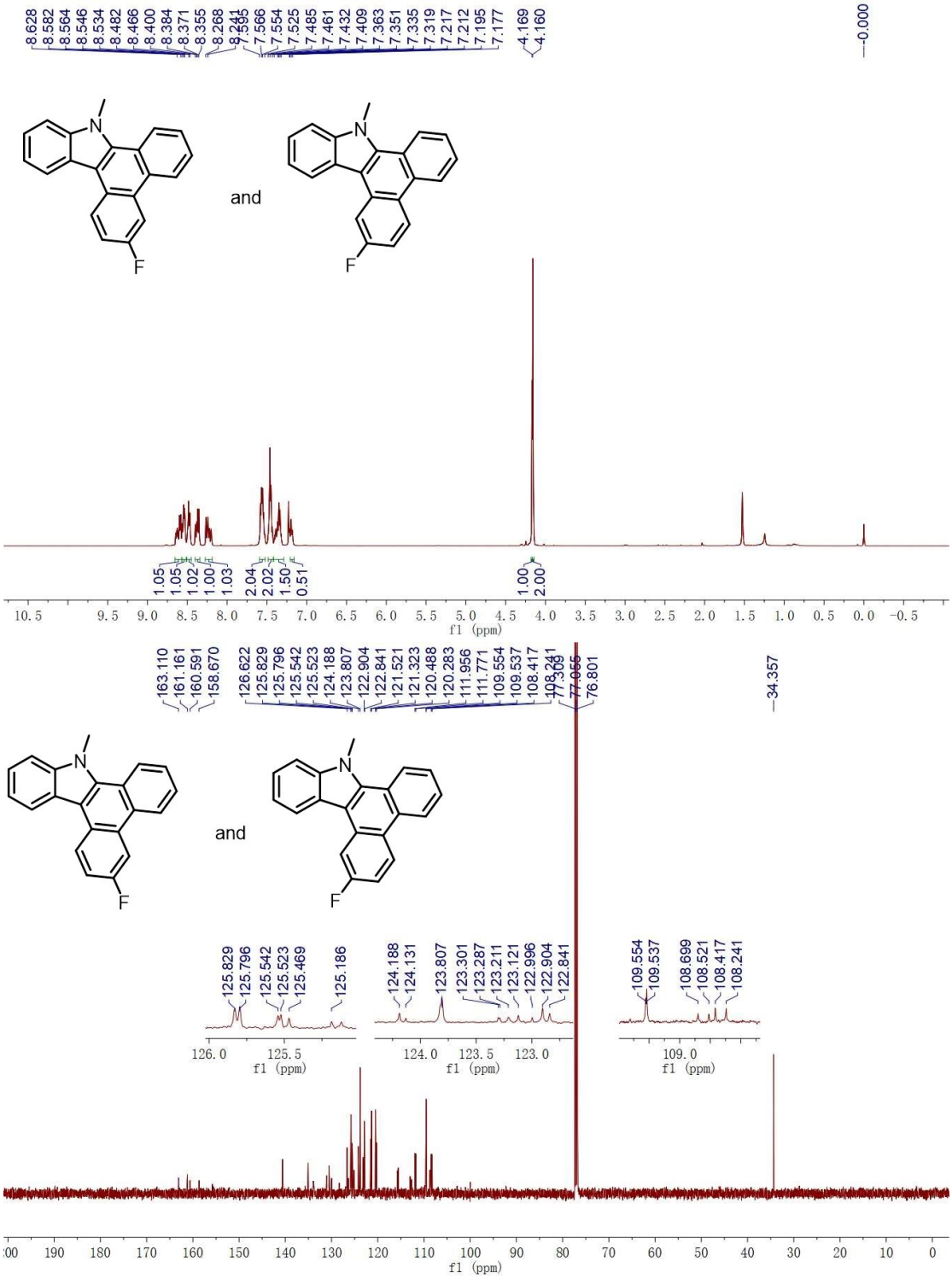
^{1}H NMR of **3wa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3wa** (125 MHz, $CDCl_3$)



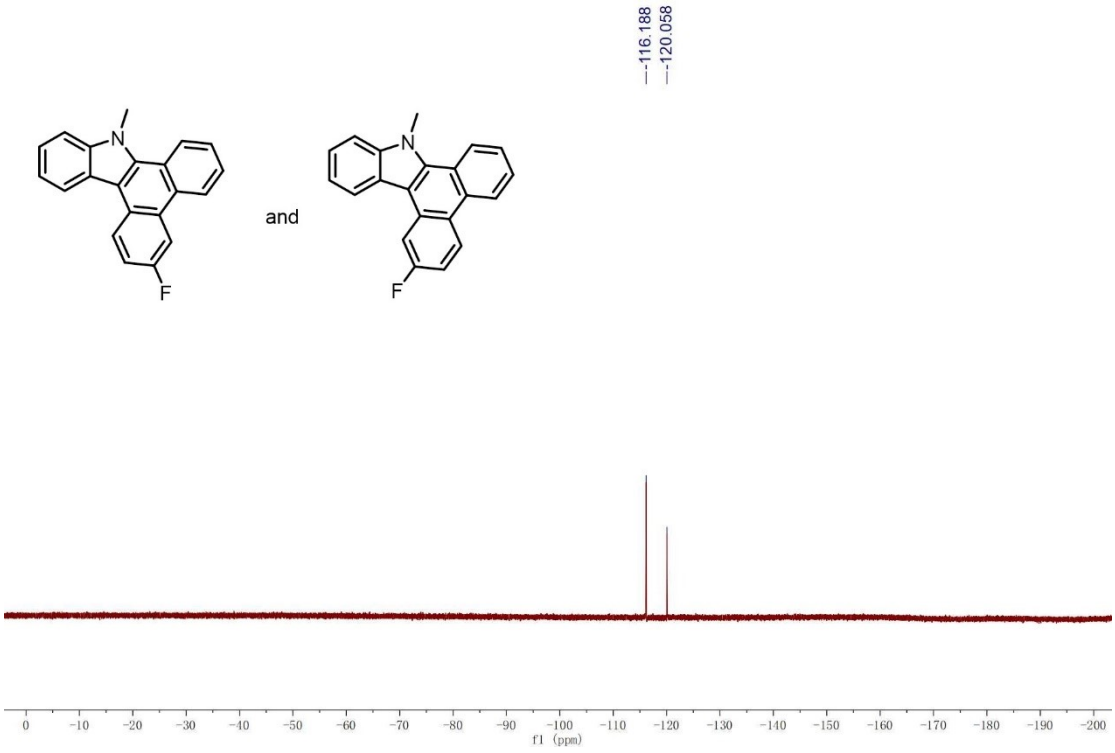
^{1}H NMR of **3ab** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ab** (125 MHz, $CDCl_3$)



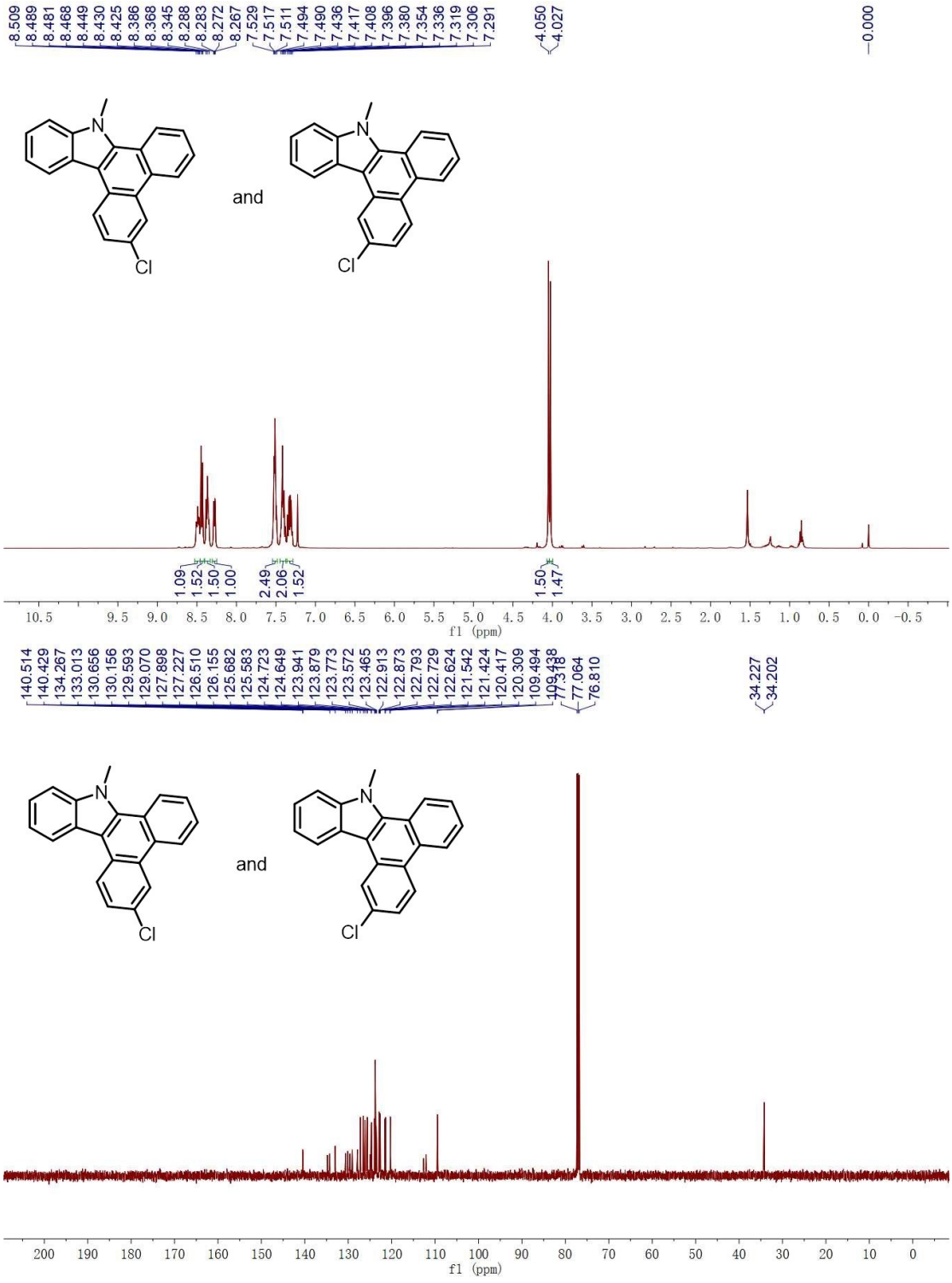
^{1}H NMR of **3ac** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ac** (125 MHz, $CDCl_3$)



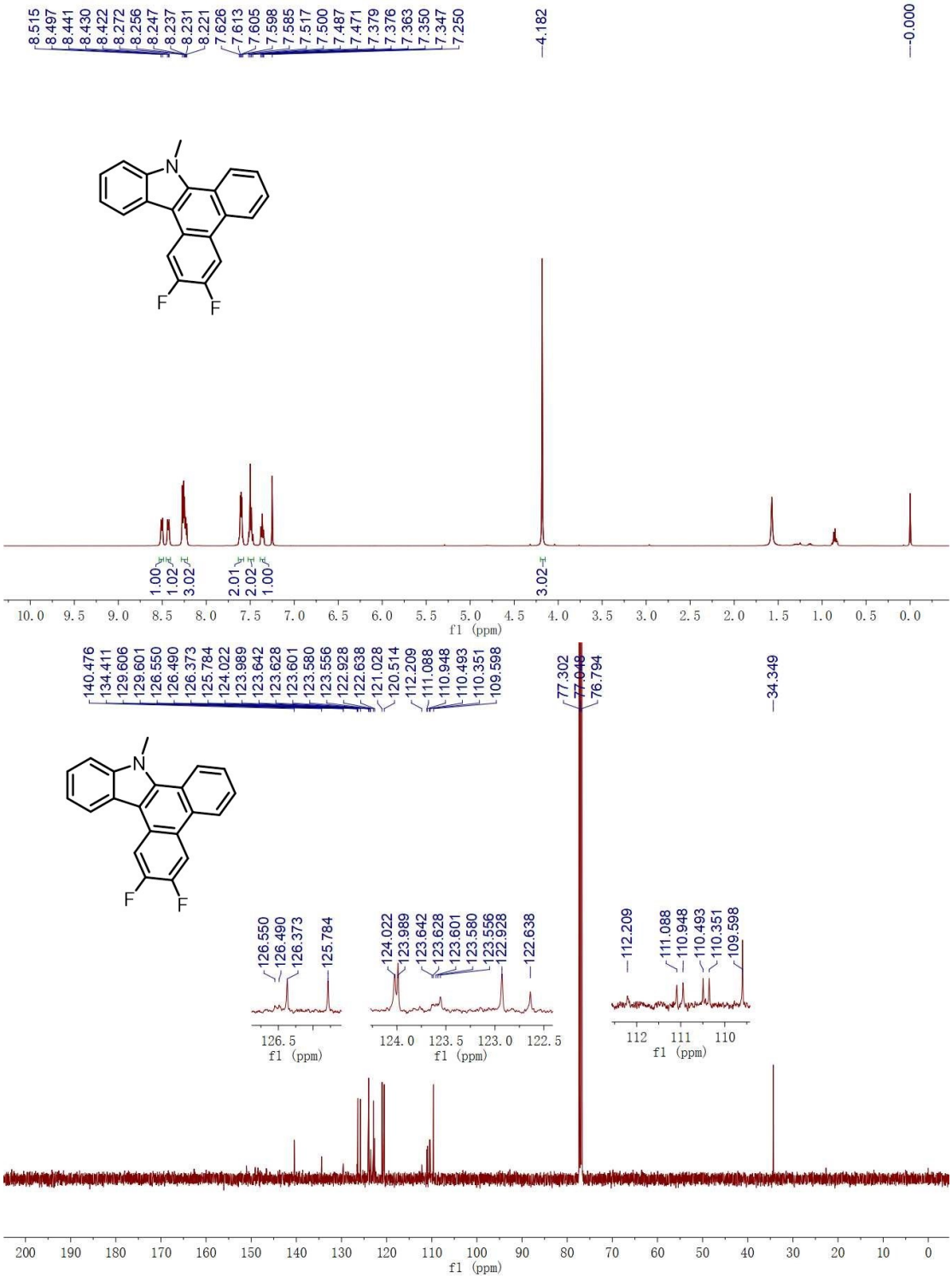
^{19}F NMR of **3ac** (470 MHz, $CDCl_3$)



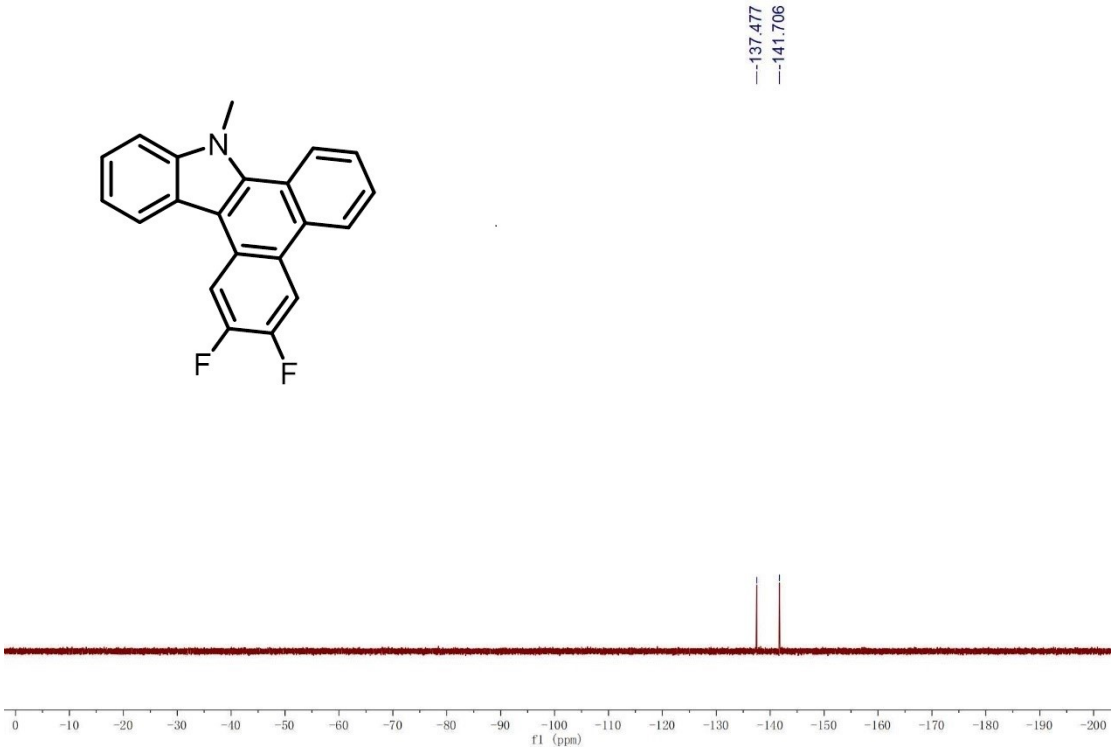
^{1}H NMR of **3ad** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ad** (125 MHz, $CDCl_3$)



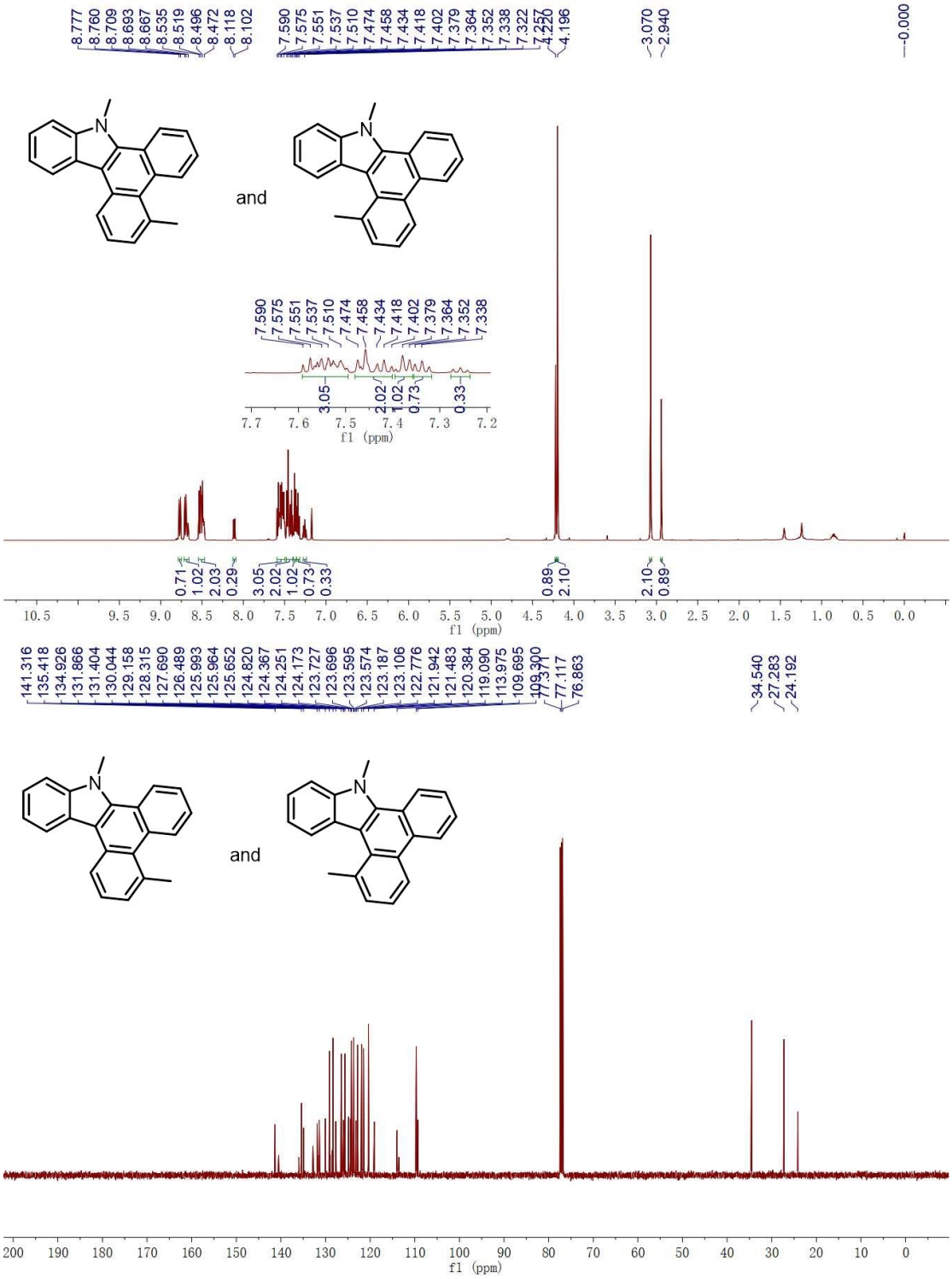
^{1}H NMR of **3ae** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ae** (125 MHz, $CDCl_3$)



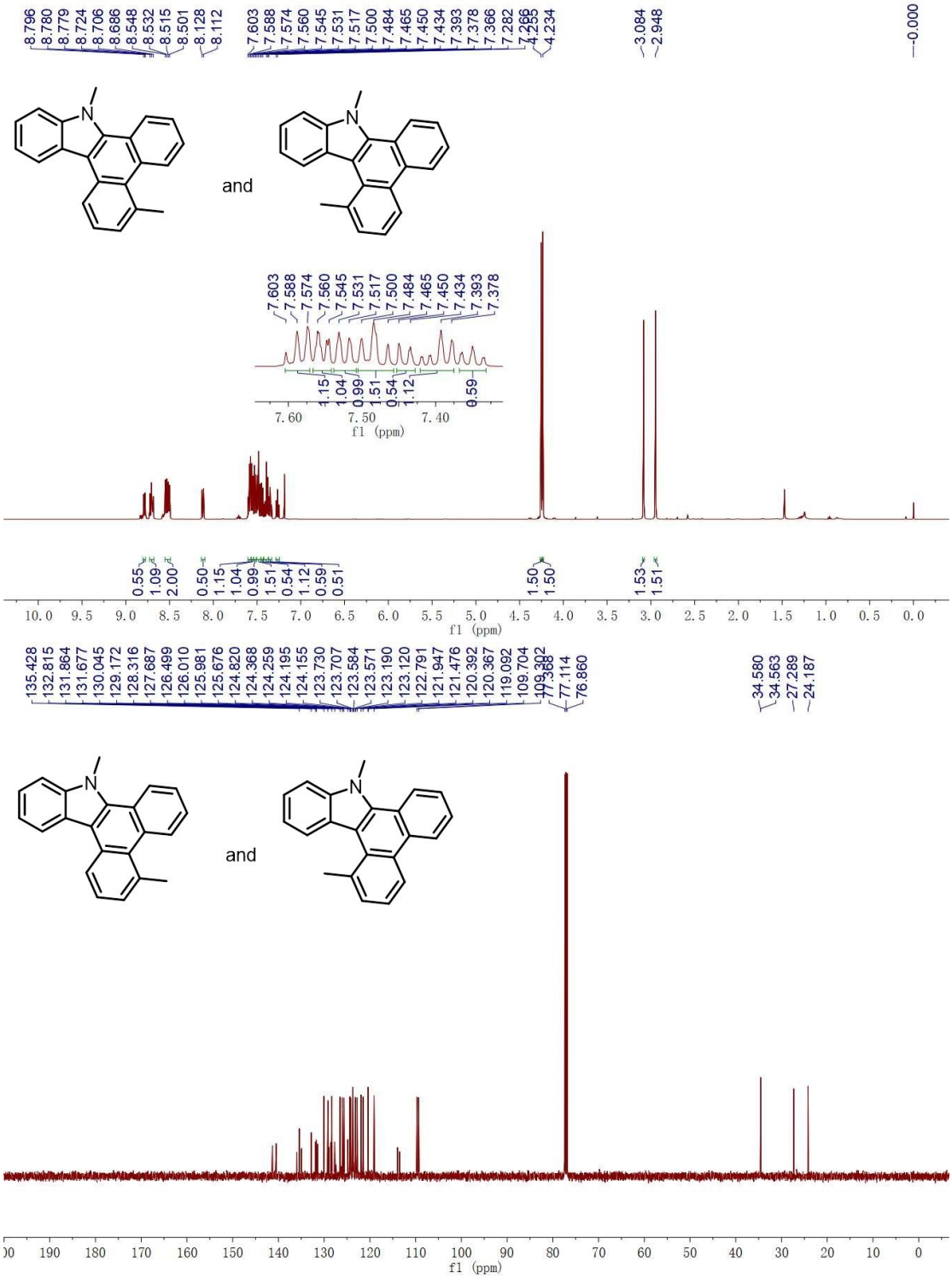
^{19}F NMR of **3ae** (470 MHz, $CDCl_3$)



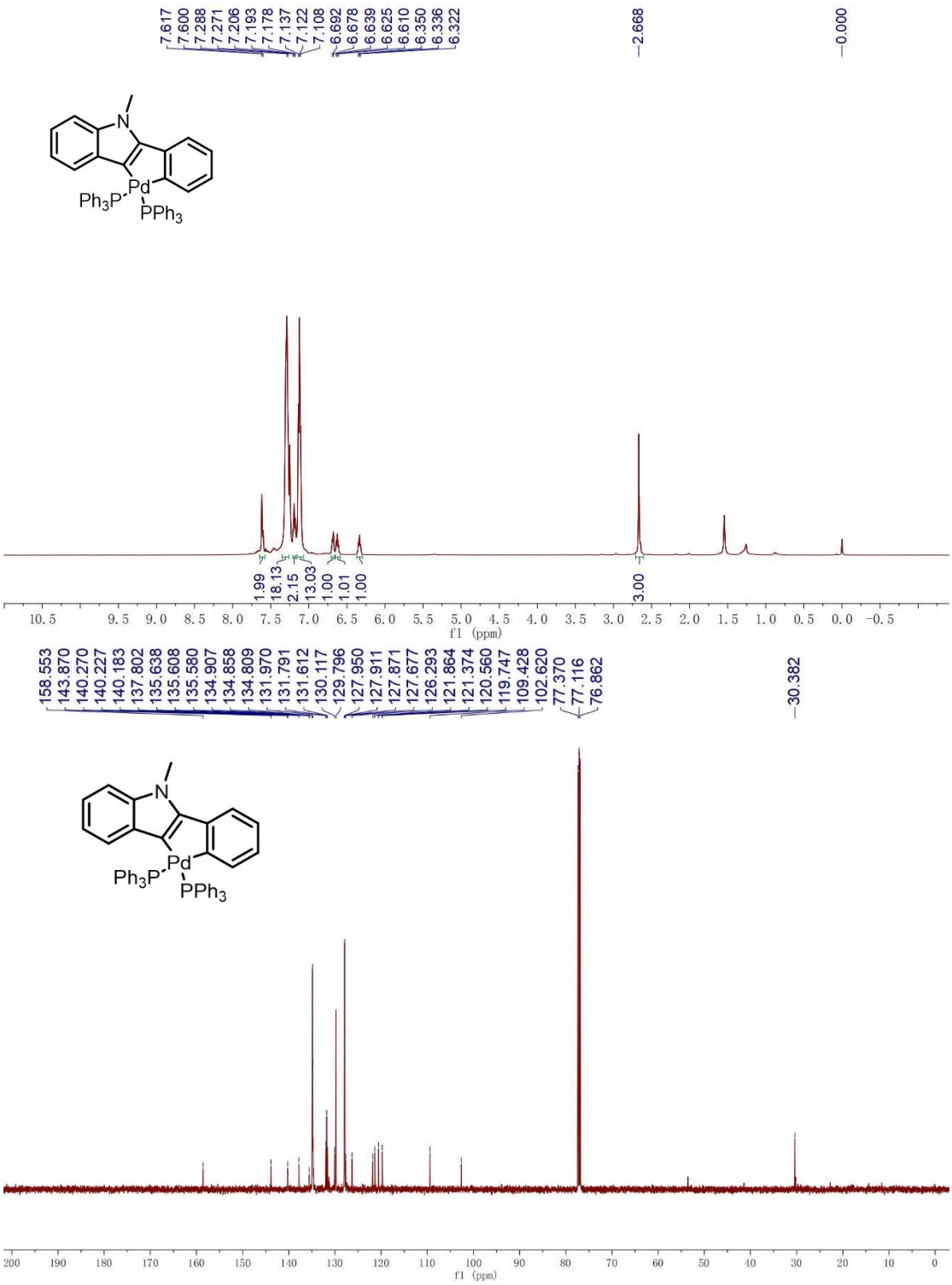
^{1}H NMR of **3af** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3af** (125 MHz, $CDCl_3$)

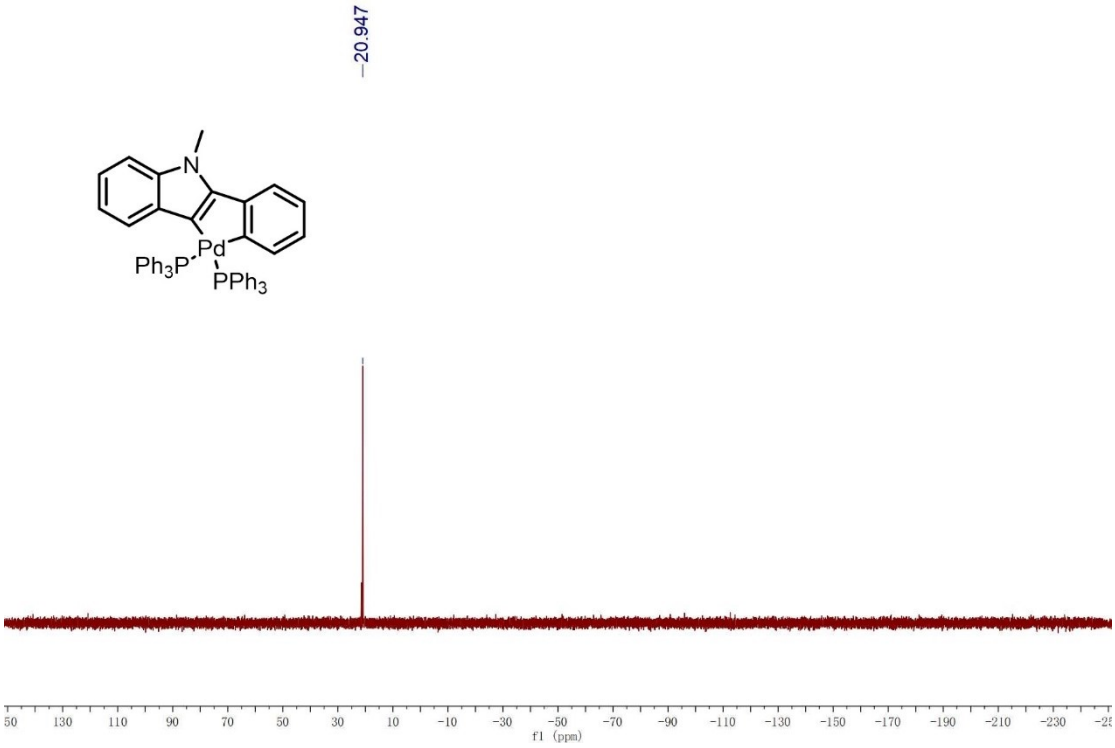


^{1}H NMR of **3af** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3af** (125 MHz, $CDCl_3$)



^{1}H NMR of **C'** (500 MHz, $CDCl_3$) and ^{13}C NMR of **C'** (125 MHz, $CDCl_3$) and ^{31}**P** NMR of **C'** (202 MHz, $CDCl_3$)




20.947
N
Pd
Ph3P
PPh3
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)