Supporting Information

For

MeOTf/KI-catalyzed efficient synthesis of 2-arylnaphthalenes via cyclodimerization of styrene oxides

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Contents

1. General Procedure for the Synthesis of Starting Materials and Products

1.1. General Procedure for the Synthesis of Starting Materials 1

Aryl ethylene oxides **1b-1n** were prepared from trimethylsulfonium iodide with the corresponding cinnamaldehydes and aromatic aldehydes using the Johnson-Corey-Chaykovsky reaction. Sodium hydride (0.54 g, 22.5 mmol, 60% mineral oil dispersion) was washed with petroleum ether (3×5 mL). The residual petroleum ether was removed under vacuum. Under an atmosphere of nitrogen, dry THF (15 mL) and dry DMSO (15 mL) were added and the reaction mixture was cooled in an ice bath. A solution of trimethylsulfonium iodide (3.67 g, 18 mmol) in DMSO (4 mL) was added. After addition, aldehyde (15 mmol) was added in one portion. The reaction mixture was stirred at 0 °C for 30 min and at room temperature for an additional 12 h. The reaction mixture was slowly quenched with a mixture of water and ice (20 mL) and extracted with methylene chloride (3 x 10 mL). The combined organic extracts were washed with brine (2 x 30 mL), dried over sodium sulfate and filtered. The reaction mixture was directly subjected to flash column chromatography with ethyl acetate/ petroleum ether (1:25, v/v) to give the aryl ethylene oxides **1**.

1.2 . Procedure for the Synthesis of Compound 3

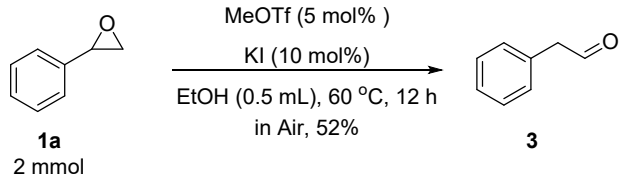


Figure S1. Procedure for the synthesis of **3**

A sealed tube was charged with KI (0.2 mmol) and 2-phenyloxirane 1a (2.0 mmol) stirred in ethanol (0.5 mL) for a while to completely dissolve, after dropwise added MeOTf (0.1 mmol) at 60 °C for 12 h under atmosphere. After completion, the crude product was concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel (petroleum ether) to obtain the corresponding product 3.

1.3. Procedure for the Synthesis of Compound 4

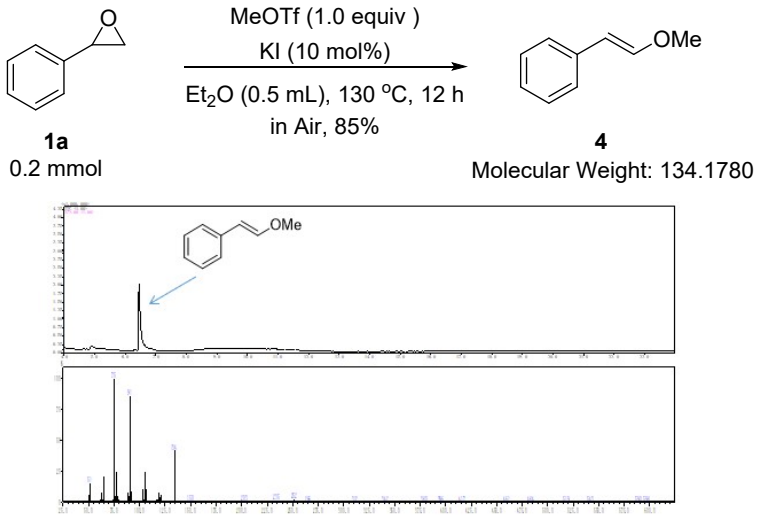


Figure S2. General procedure for the synthesis of **4**

A sealed tube was charged with KI (0.02 mmol) and 2-phenyloxirane 1a (0.2 mmol) stirred in ethyl ether (0.5 mL) for a while to completely dissolve, after dropwise added MeOTf (0.01 mmol) at 130 °C for 12 h under atmosphere. After completion, the crude product was concentrated under reduced pressure. The crude product was subjected to column chromatography on silica gel (petroleum ether) to obtain the corresponding product **4**.

1.4. General Procedure for the Cross-coupling Reaction

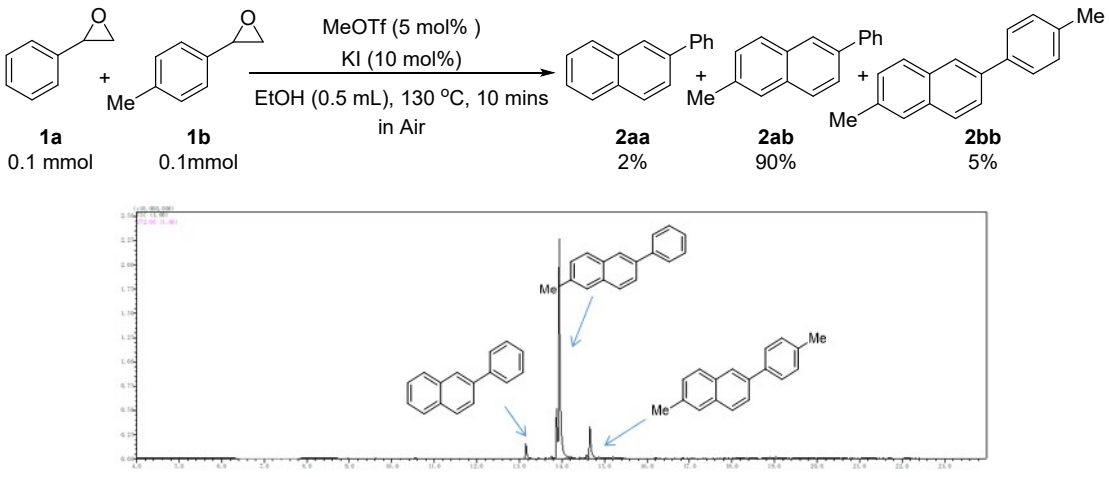


Figure S3. Cross-coupling experiment

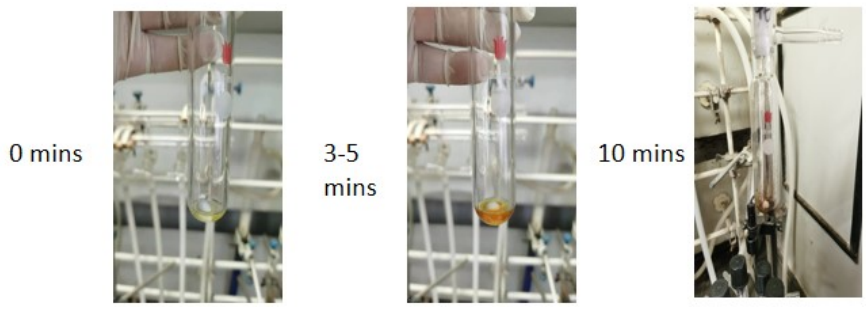
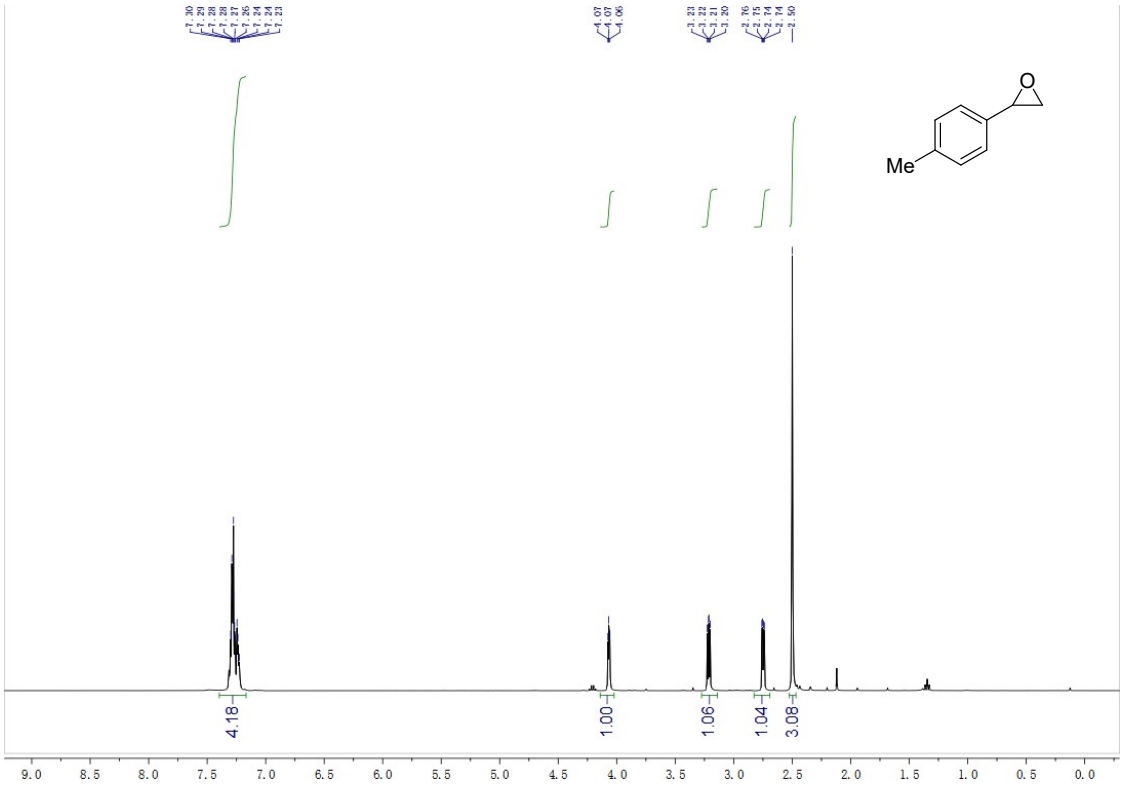


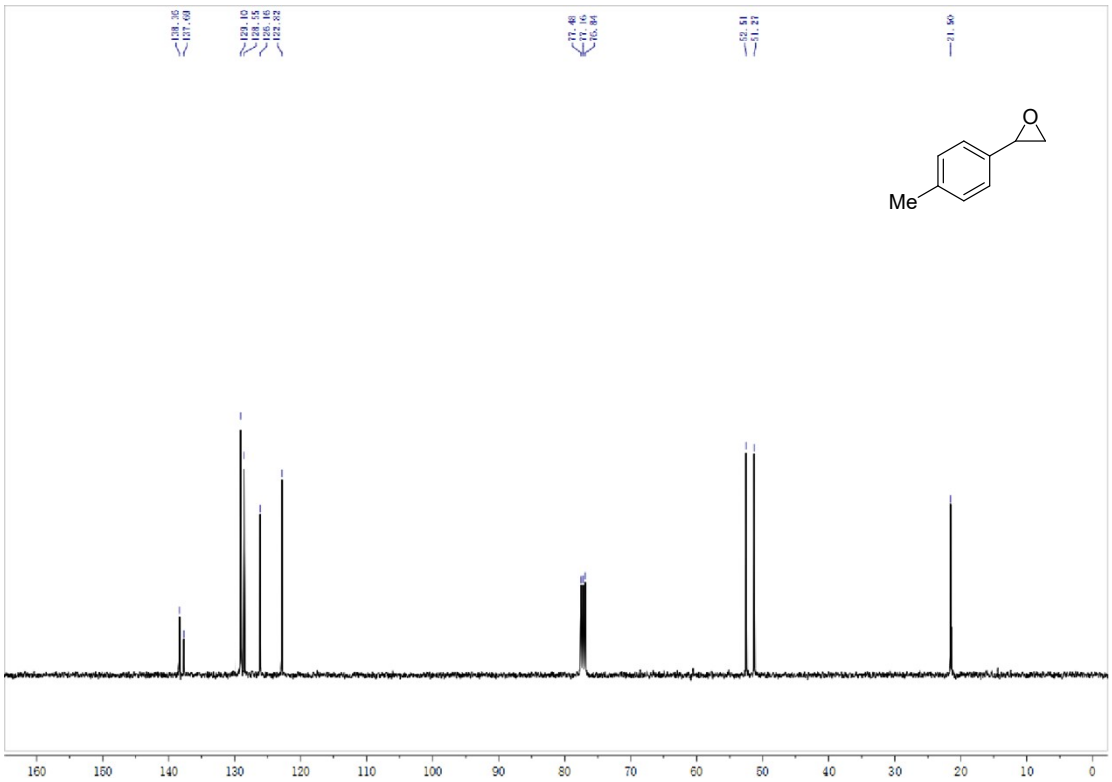
Figure S4. Reactor for Cross-coupling experiment

A sealed tube charged with KI (0.01 mmol) and 2-phenyloxirane **1a** (0.1 mmol) and 2-(*p*-tolyl)oxirane **1b** was stirred in enthanol (0.5 mL) for a while to completely dissolve, after dropwise added MeOTf (0.005 mmol) at 130 °C under atmosphere for indicated time. After completion, the main product 2ab (Cross-coupling product) was detected in 90% NMR yield. In addition, we could also judge the reaction time by the color change (colorless-brown-black, see Figure S4).

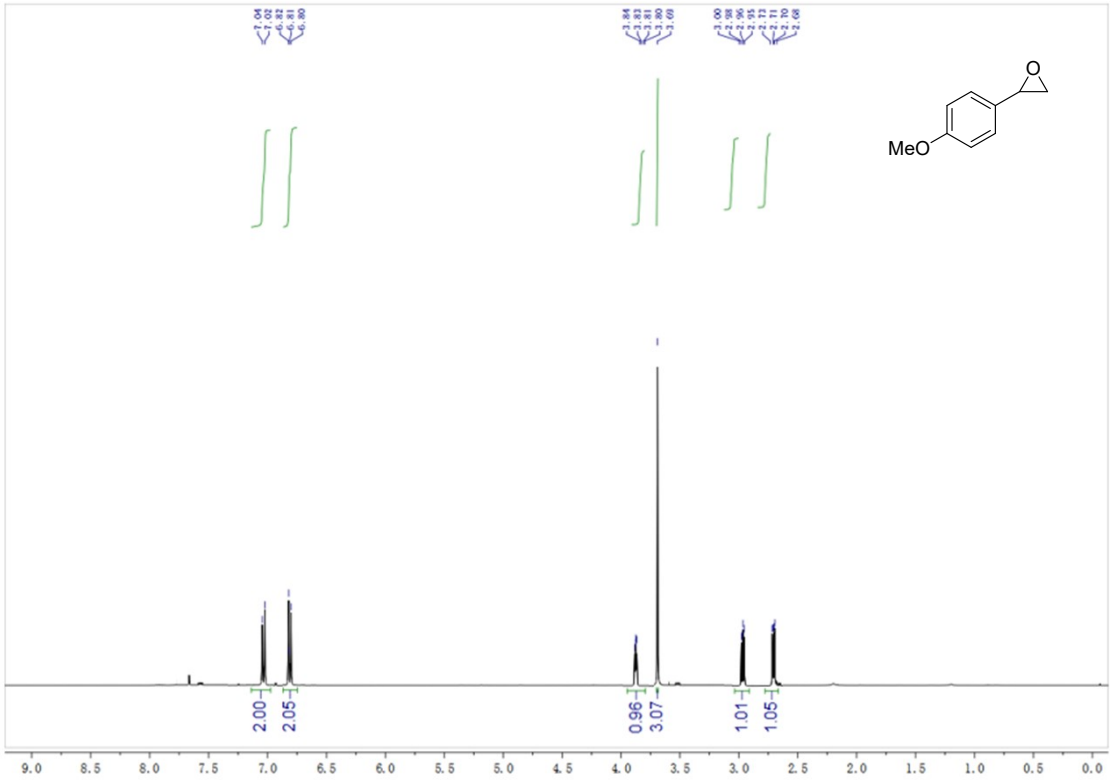
2. Copies of ^{1}H, $^{13}C\{^{1}H\}$, and ^{19}F NMR Spectra for Starting Materials



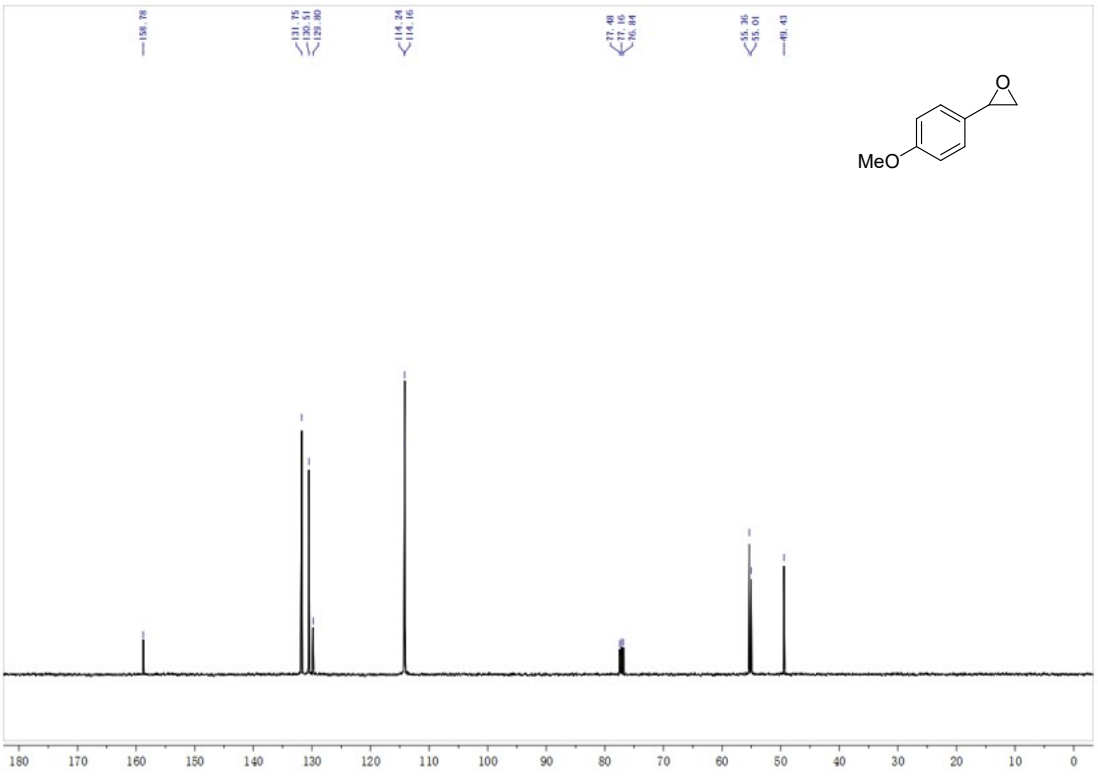
^{1}H NMR spectrum for compound **1b**



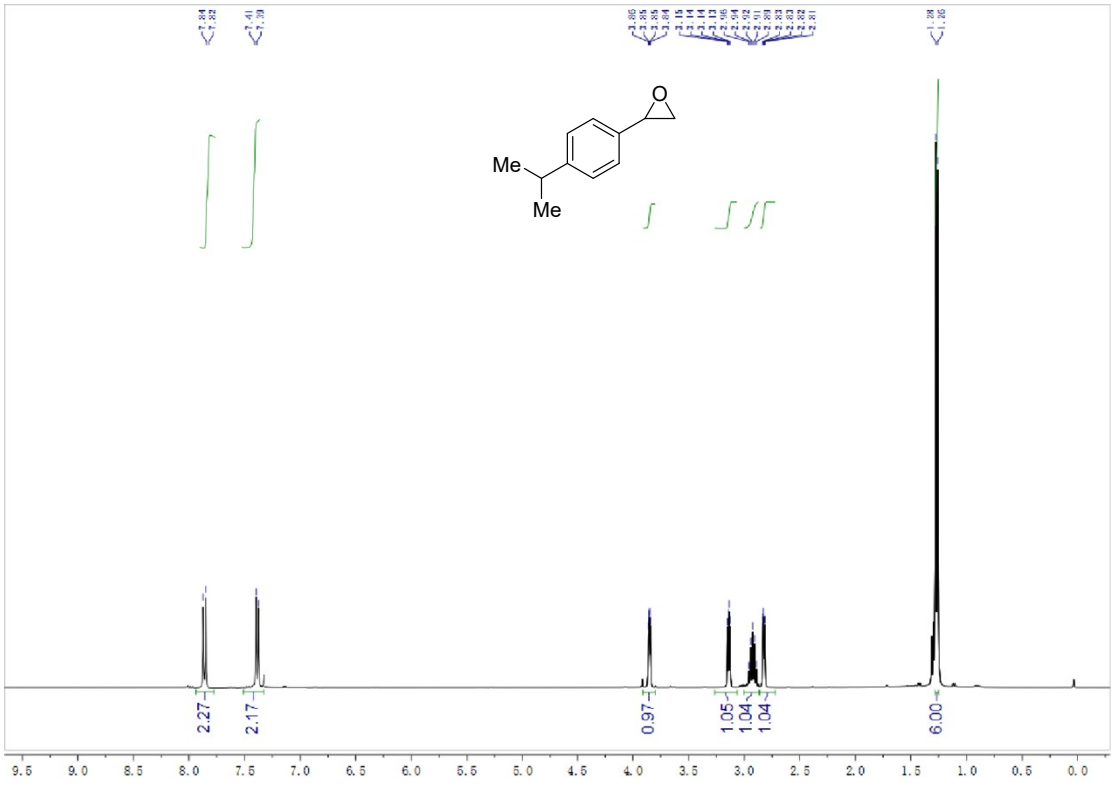
$^{13}C\{^{1}H\}$ NMR spectrum for compound **1b**



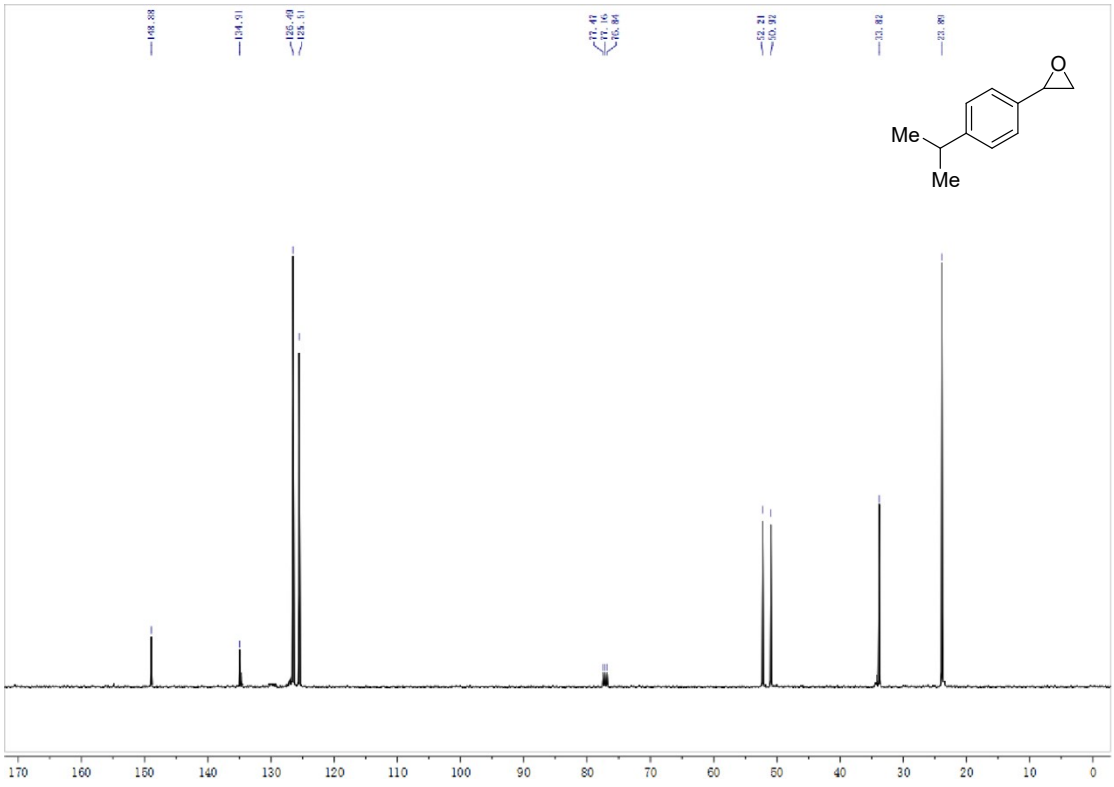
^{1}H NMR spectrum for compound **1c**



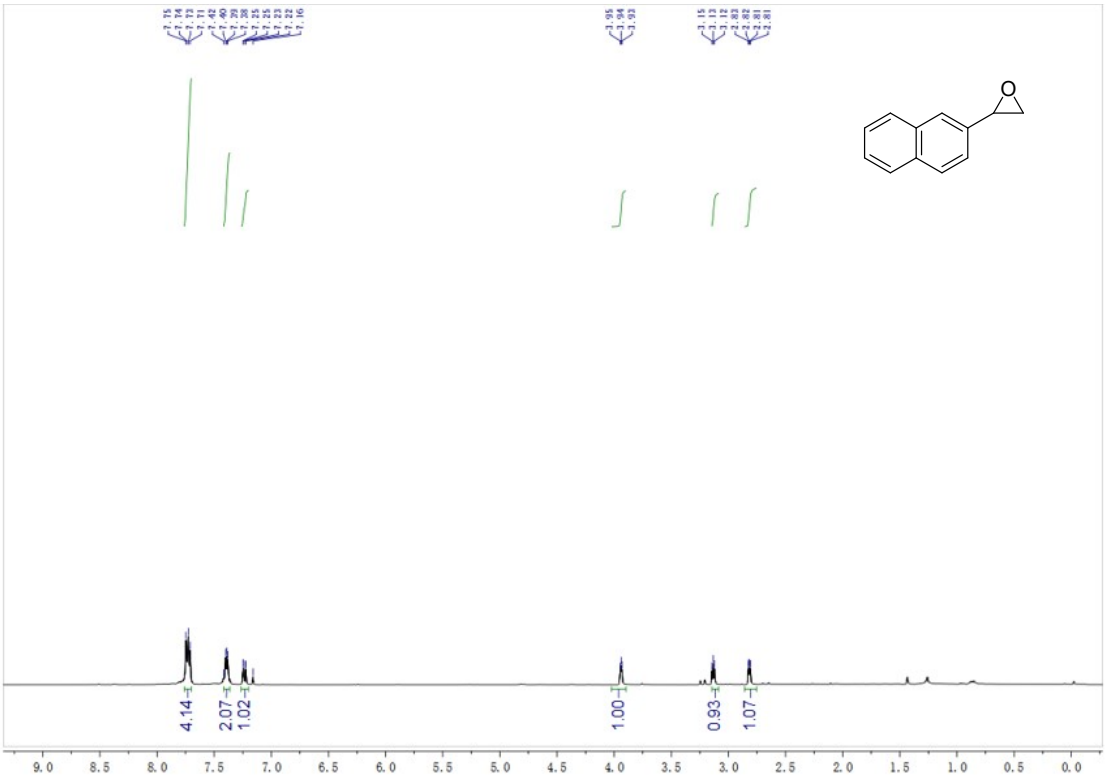
^{13}C{^{1}H} NMR spectrum for compound **1c**



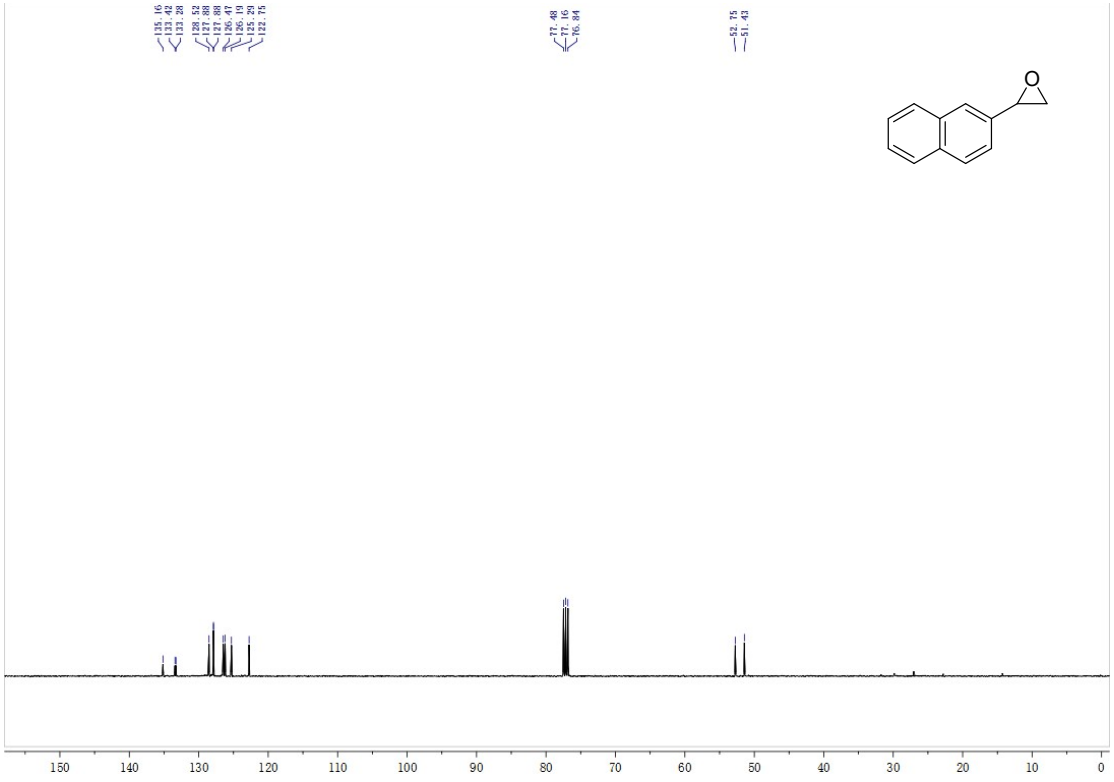
^{1}H NMR spectrum for compound **1d**



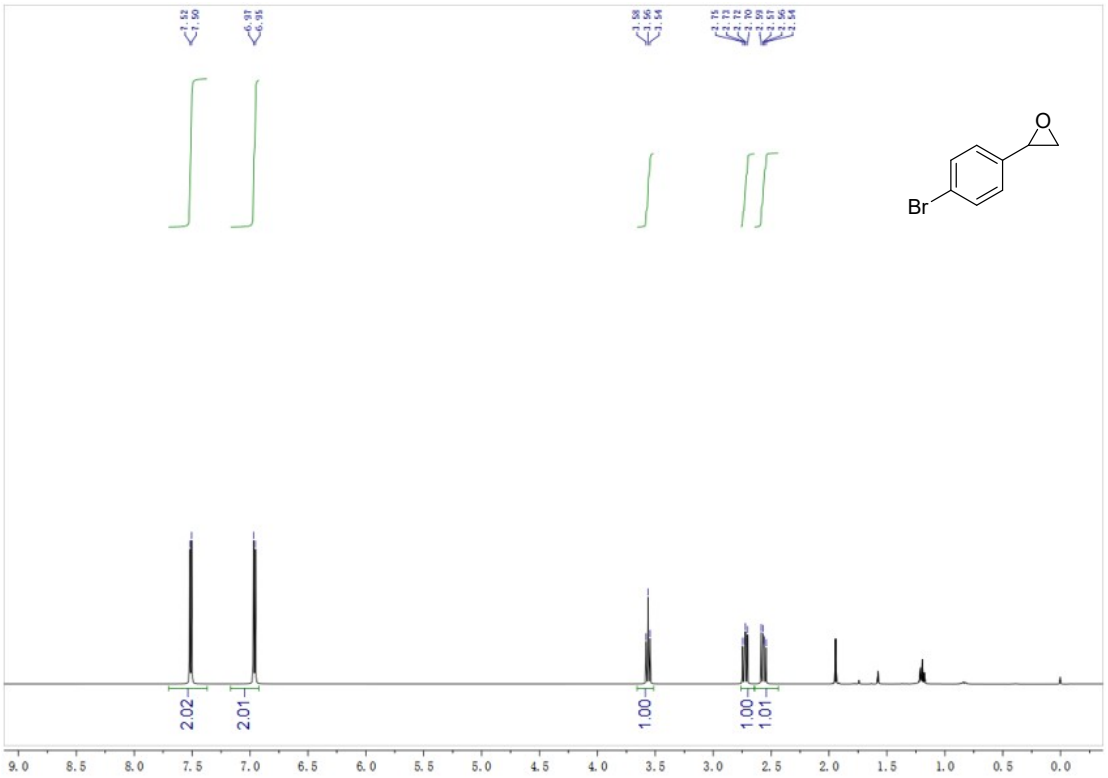
^{13}C{^{1}H} NMR spectrum for compound **1d**



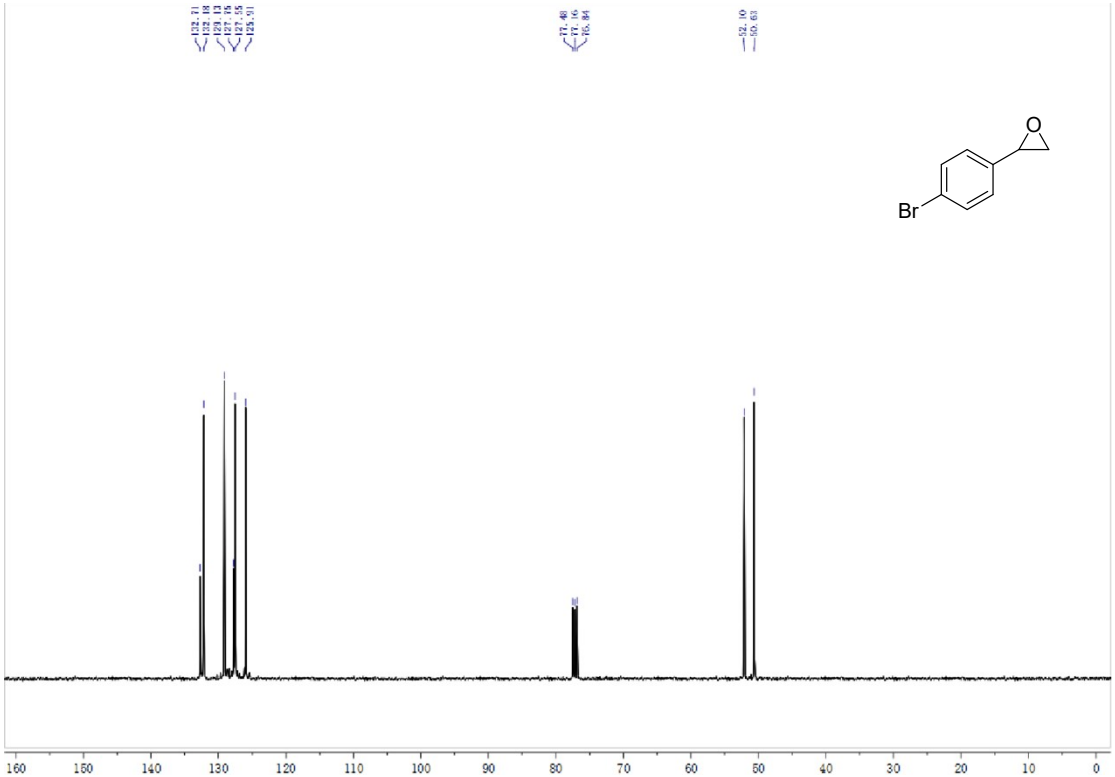
^{1}H NMR for compound **1e**



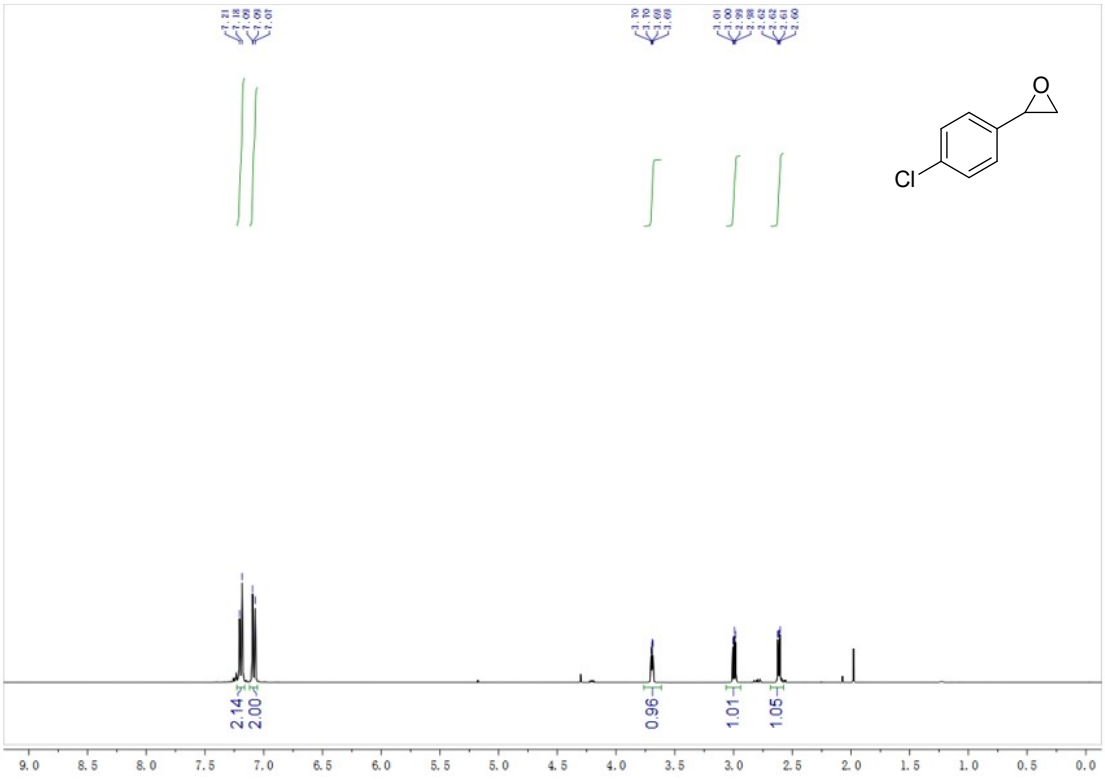
^{13}C{^{1}H} NMR spectrum for compound **1e**



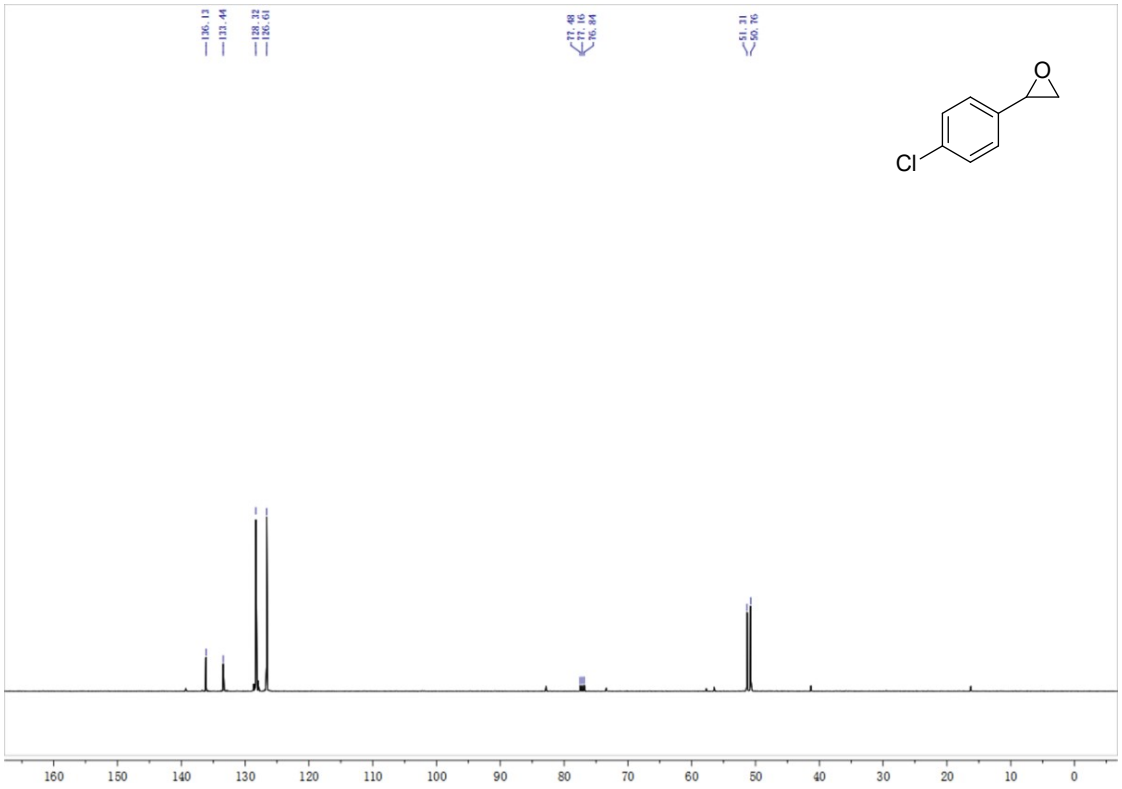
^{1}H NMR spectrum for compound **1f**



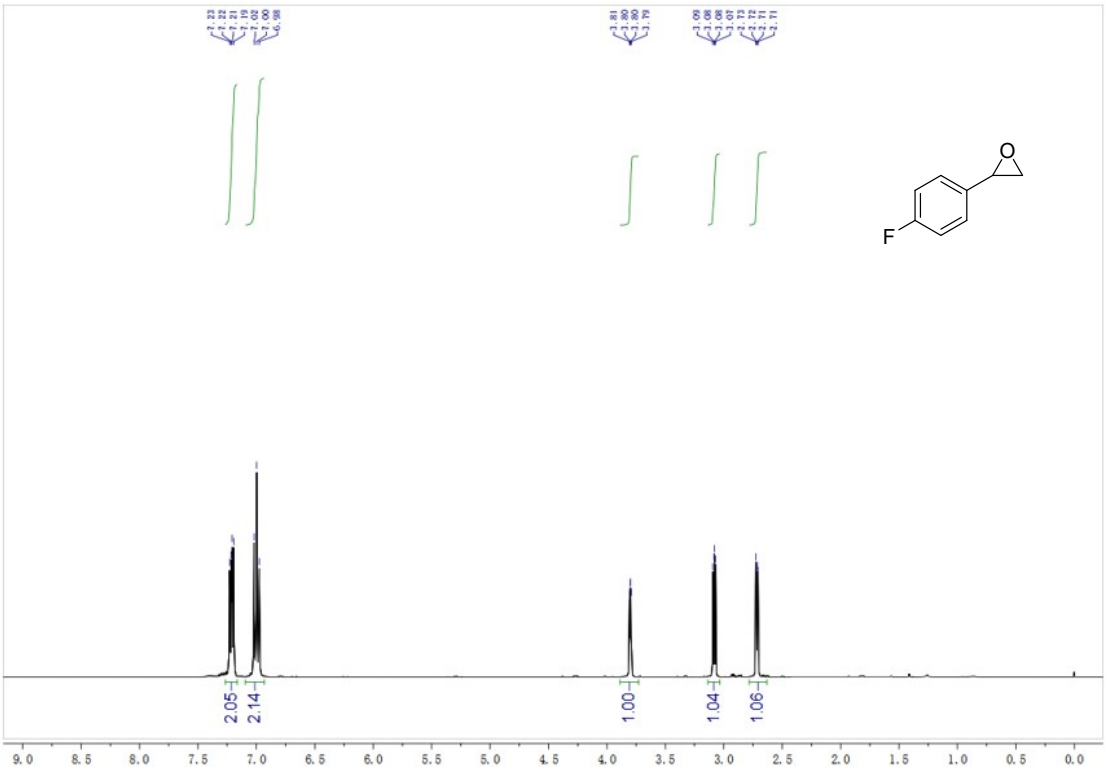
^{13}C{^{1}H} NMR spectrum for compound **1f**



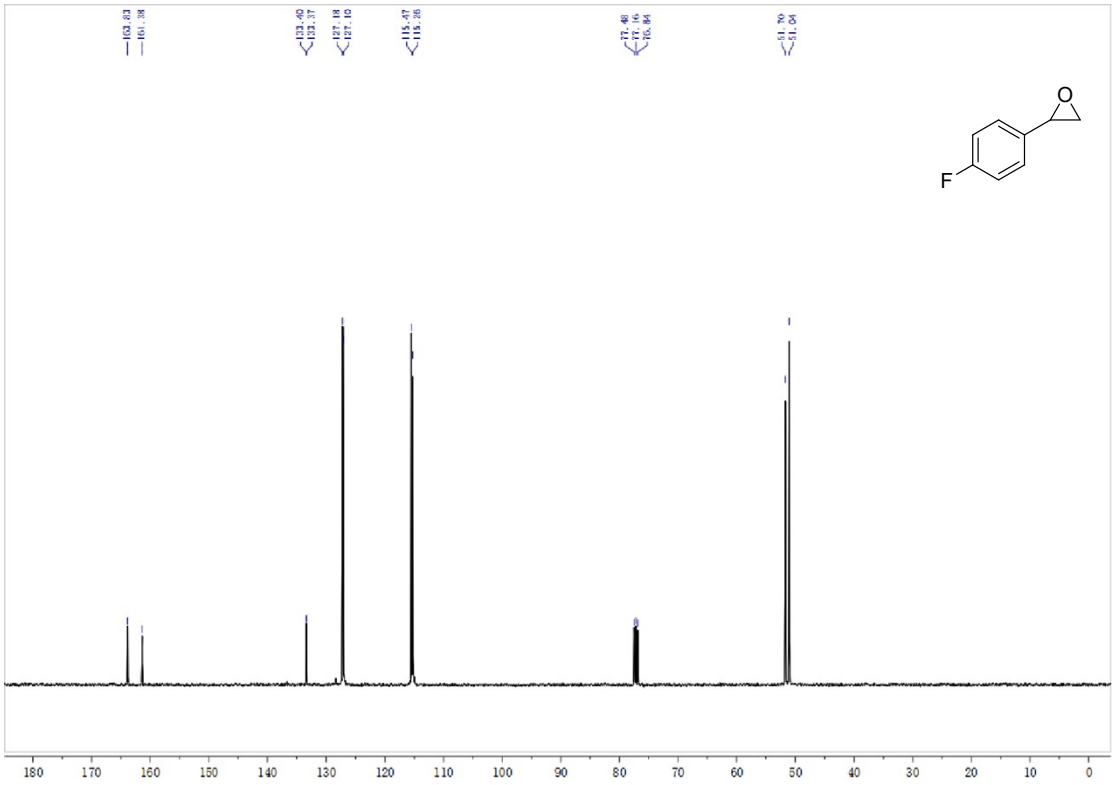
^{1}H NMR spectrum for compound **1g**



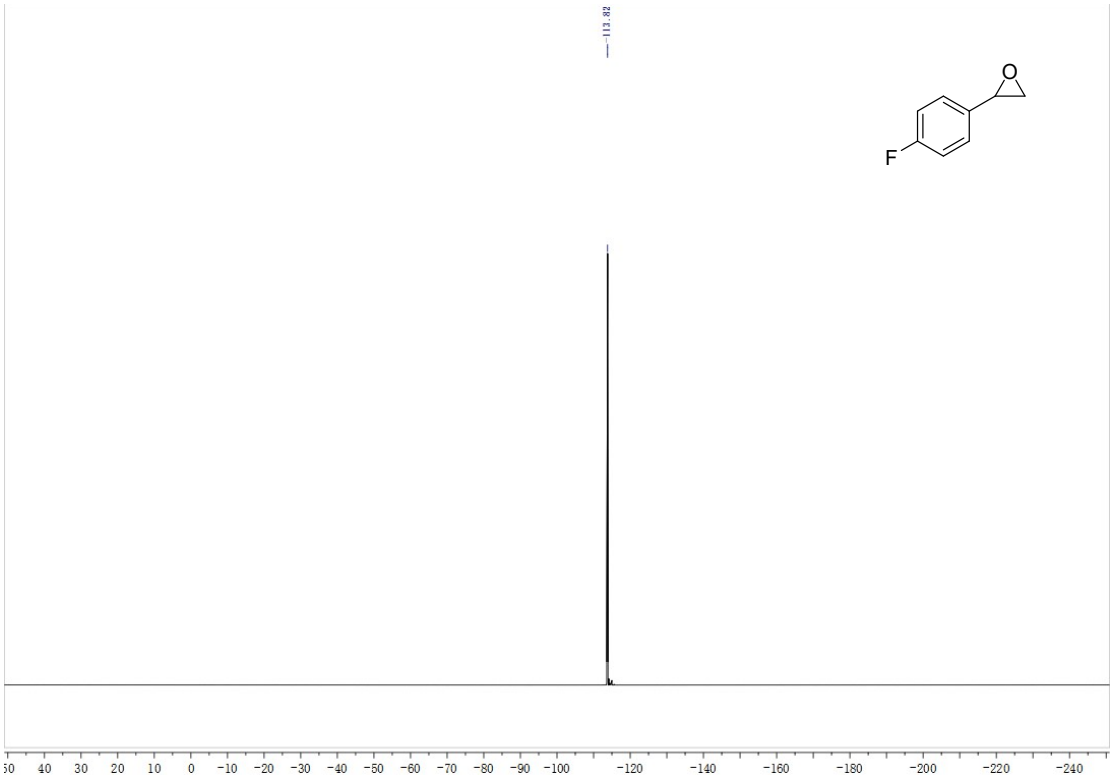
^{13}C{^{1}H} NMR spectrum for compound **1g**



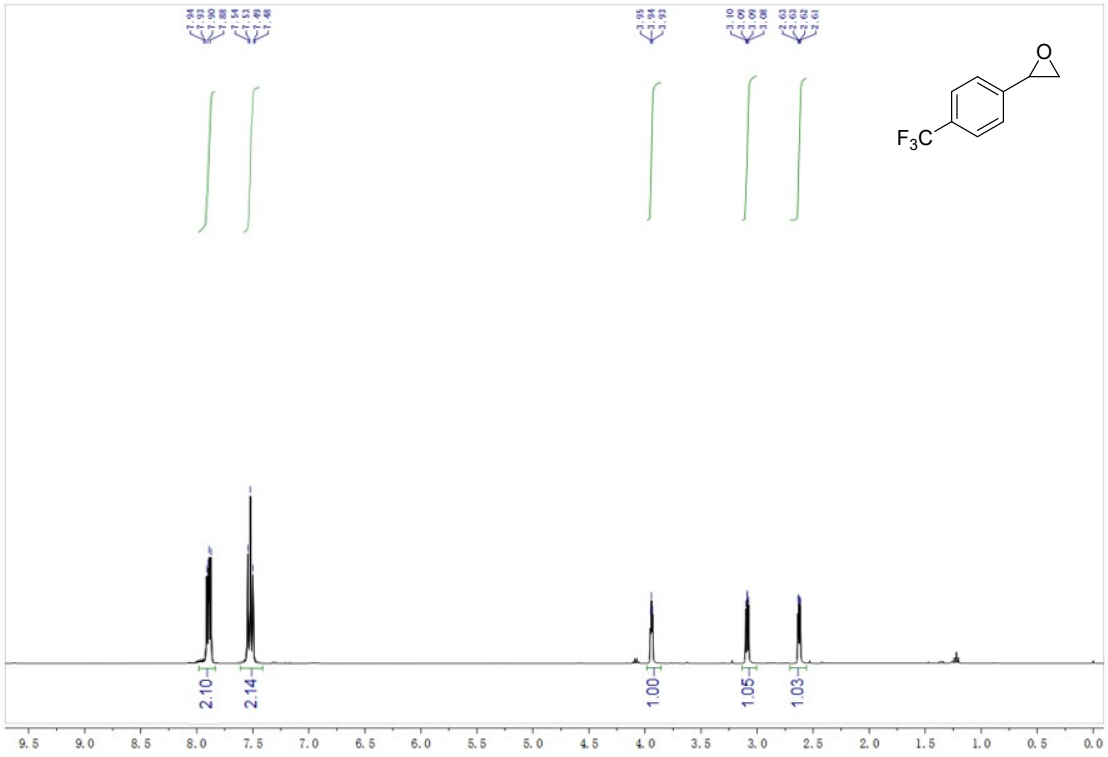
^{1}H NMR spectrum for compound 1**h**



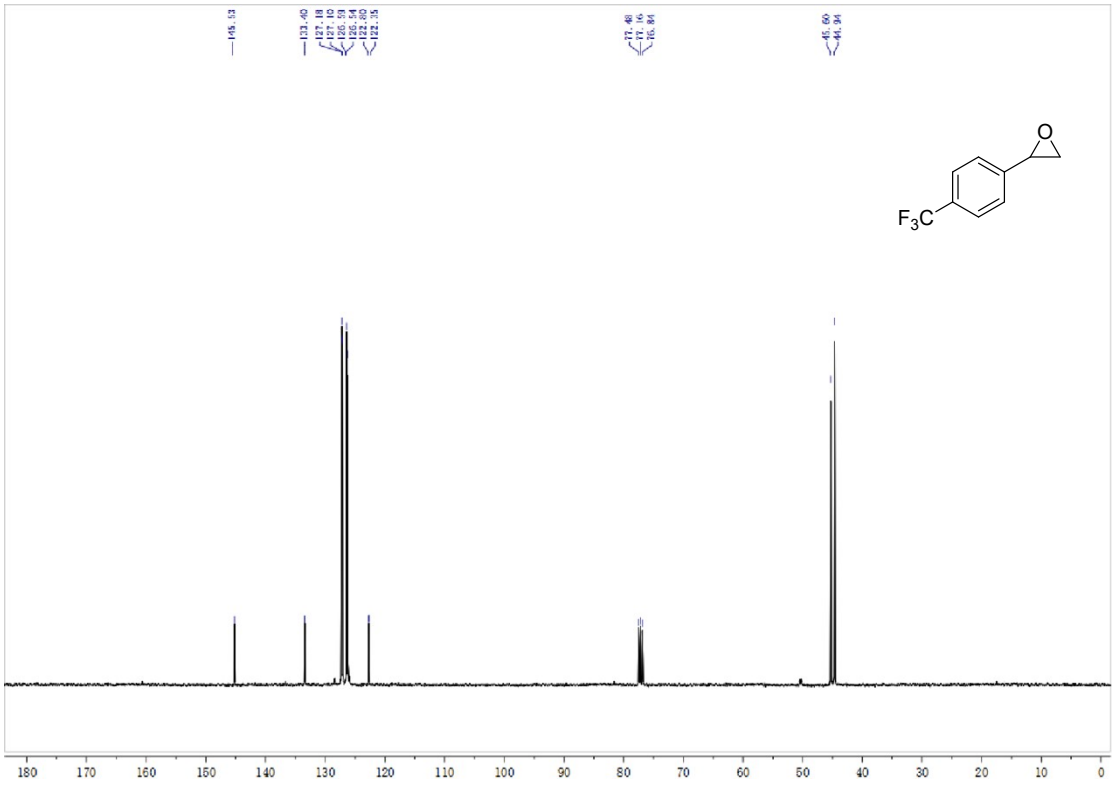
^{13}C{^{1}H} NMR spectrum for compound **1h**



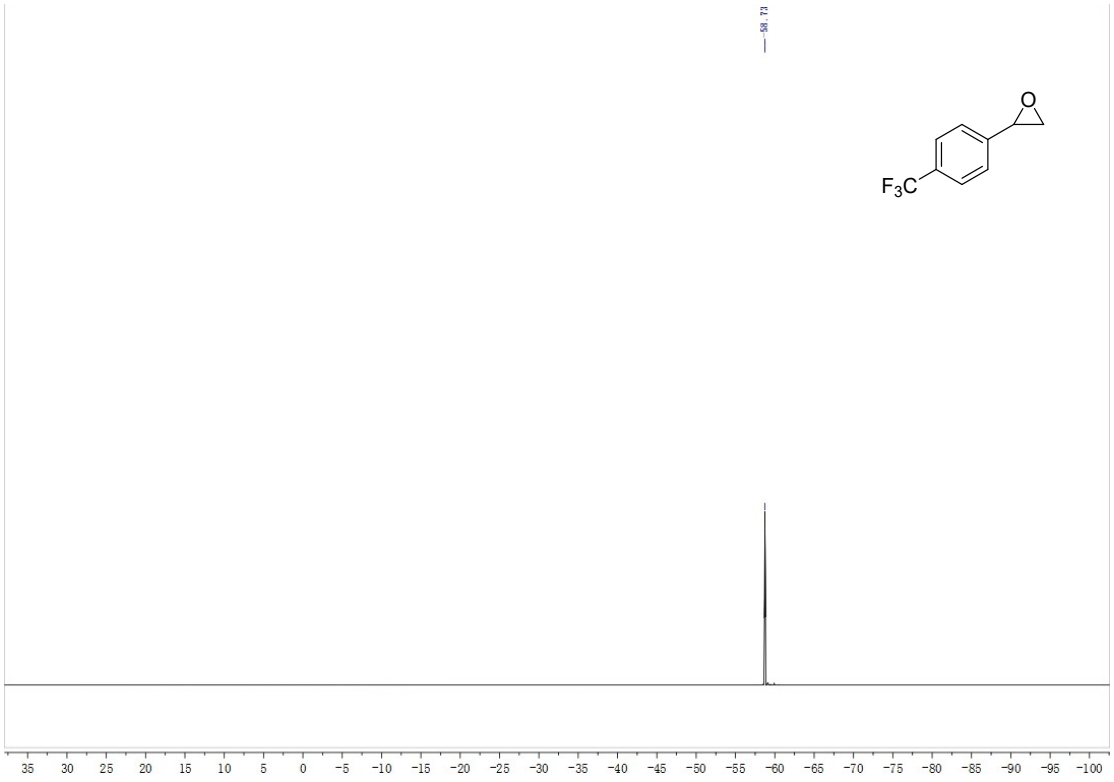
^{19}F NMR spectrum for compound **1h**



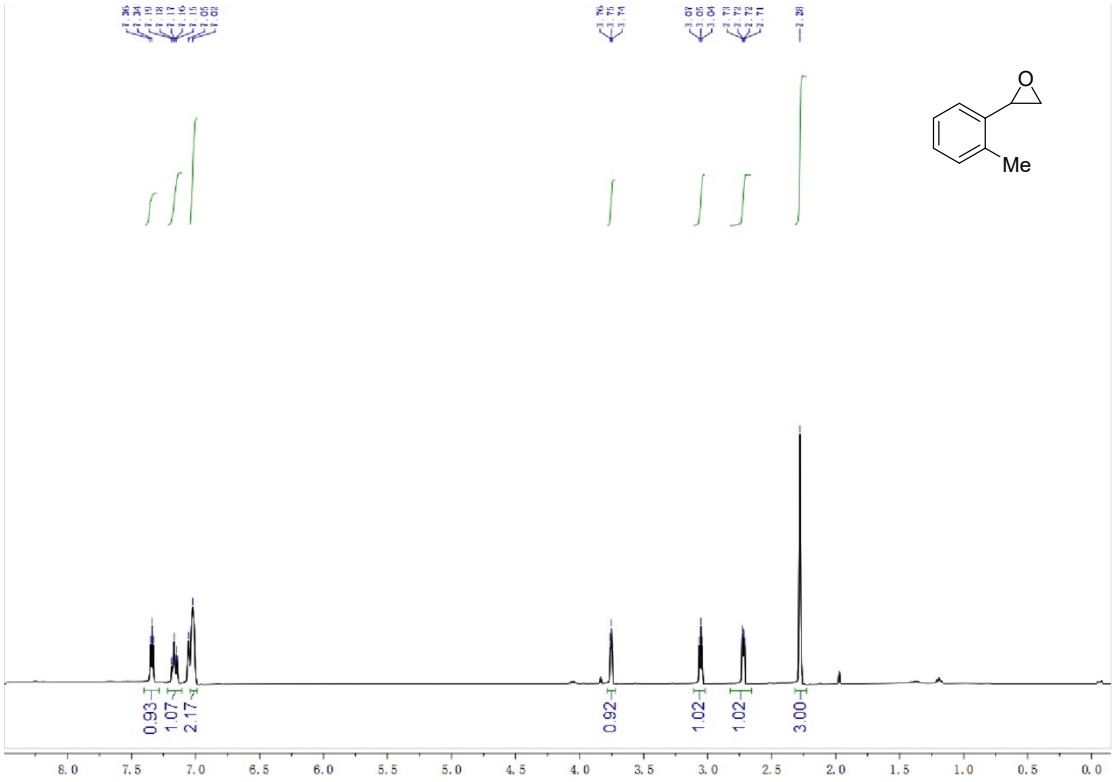
^{1}H NMR spectrum for compound **1i**



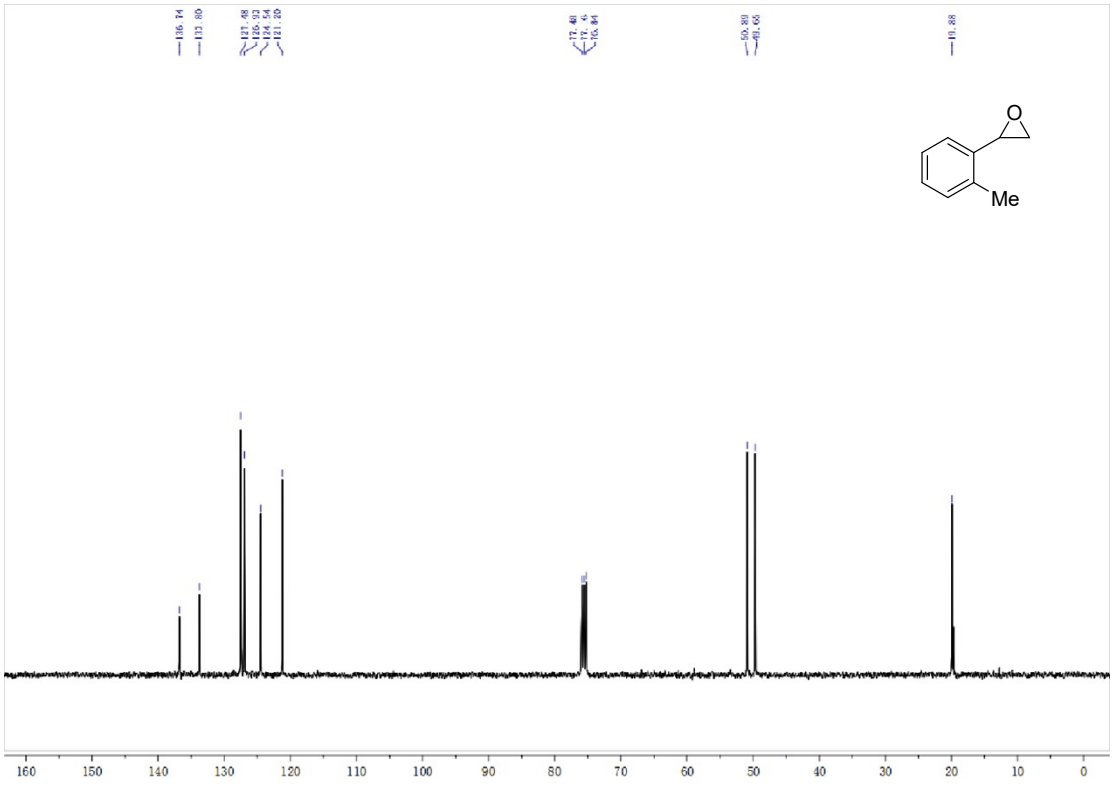
^{13}C{^{1}H} NMR spectrum for compound **1i**



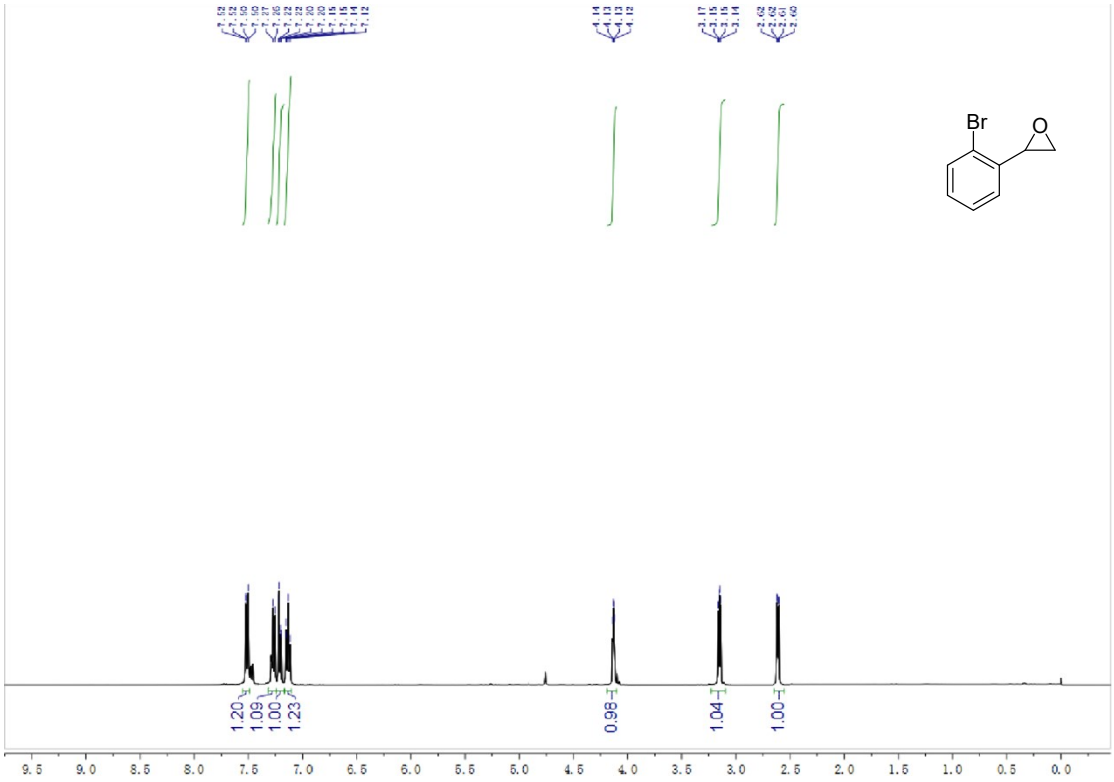
^{19}F NMR spectrum for compound **1i**



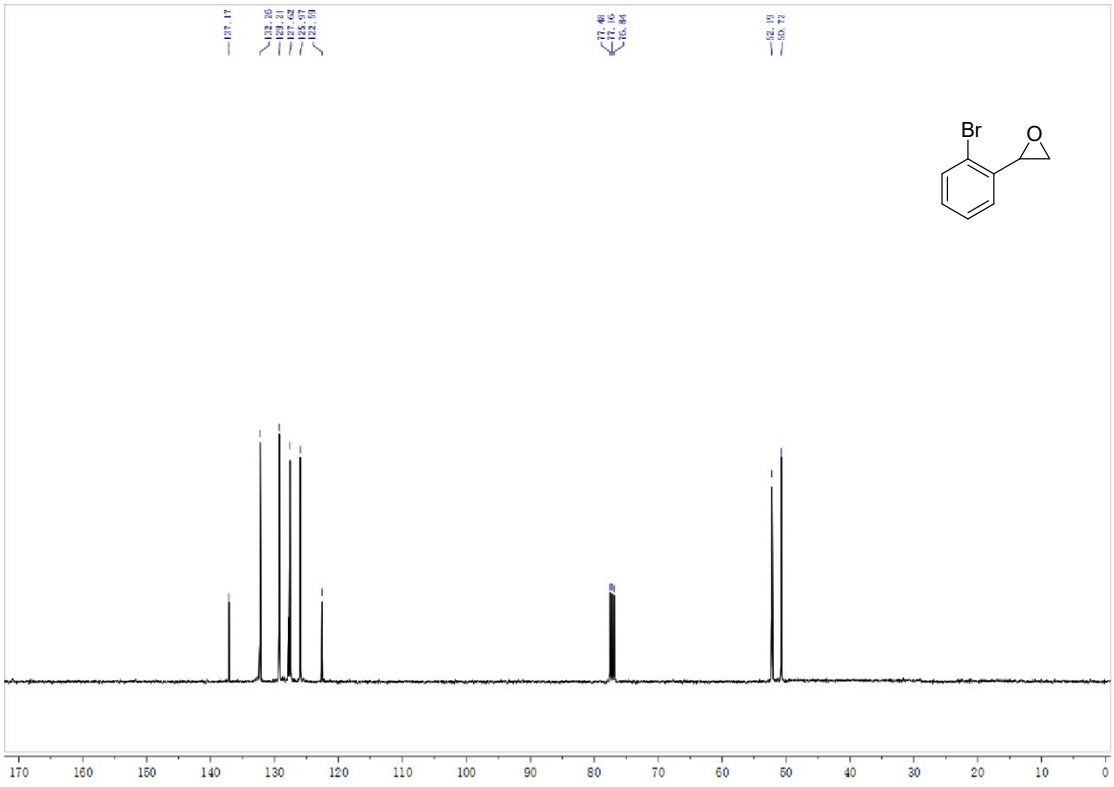
^{1}H NMR spectrum for compound **1j**



^{13}C{^{1}H} NMR spectrum for compound **1j**

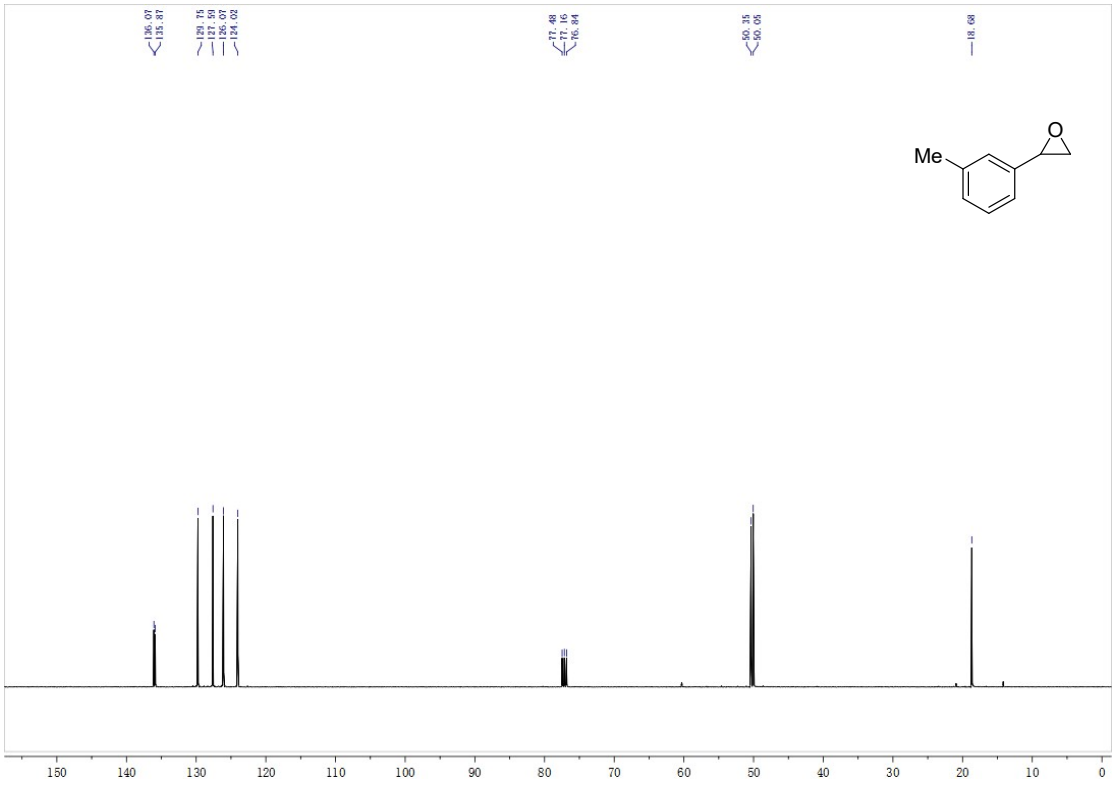


^{1}H NMR spectrum for compound **1k**

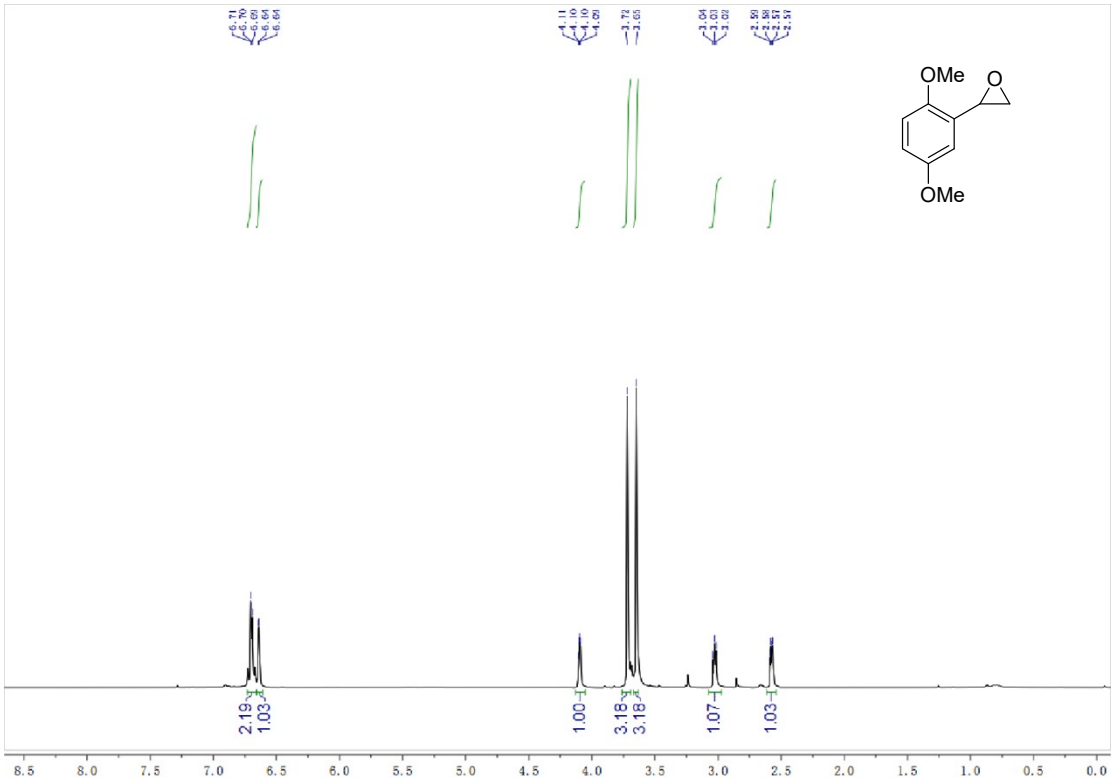


^{13}C{^{1}H} NMR spectrum for compound **1k**

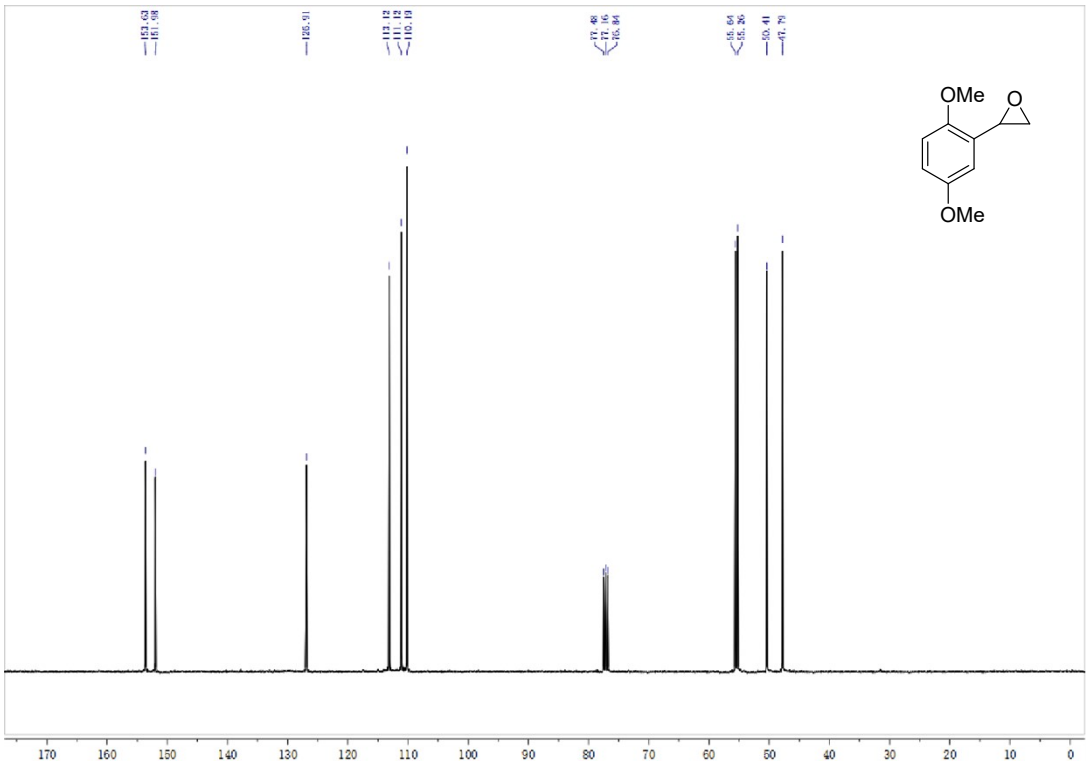
^{1}H NMR spectrum for compound **1l**



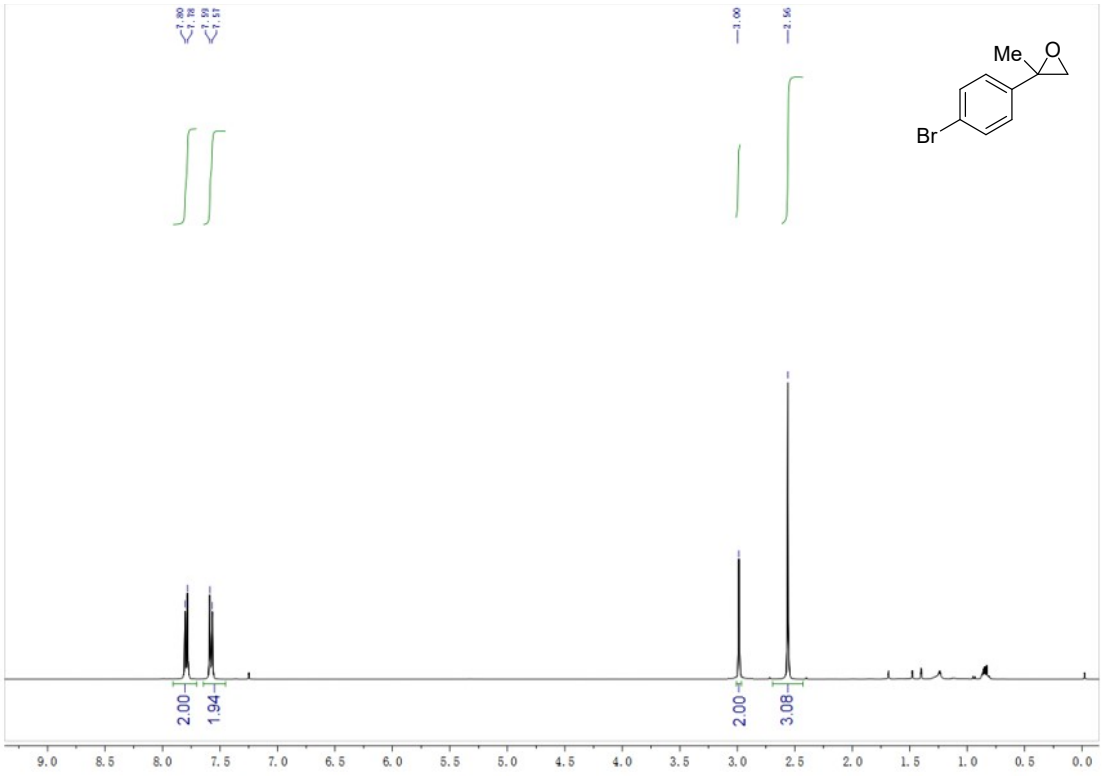
^{13}C{^{1}H} NMR spectrum for compound **1l**



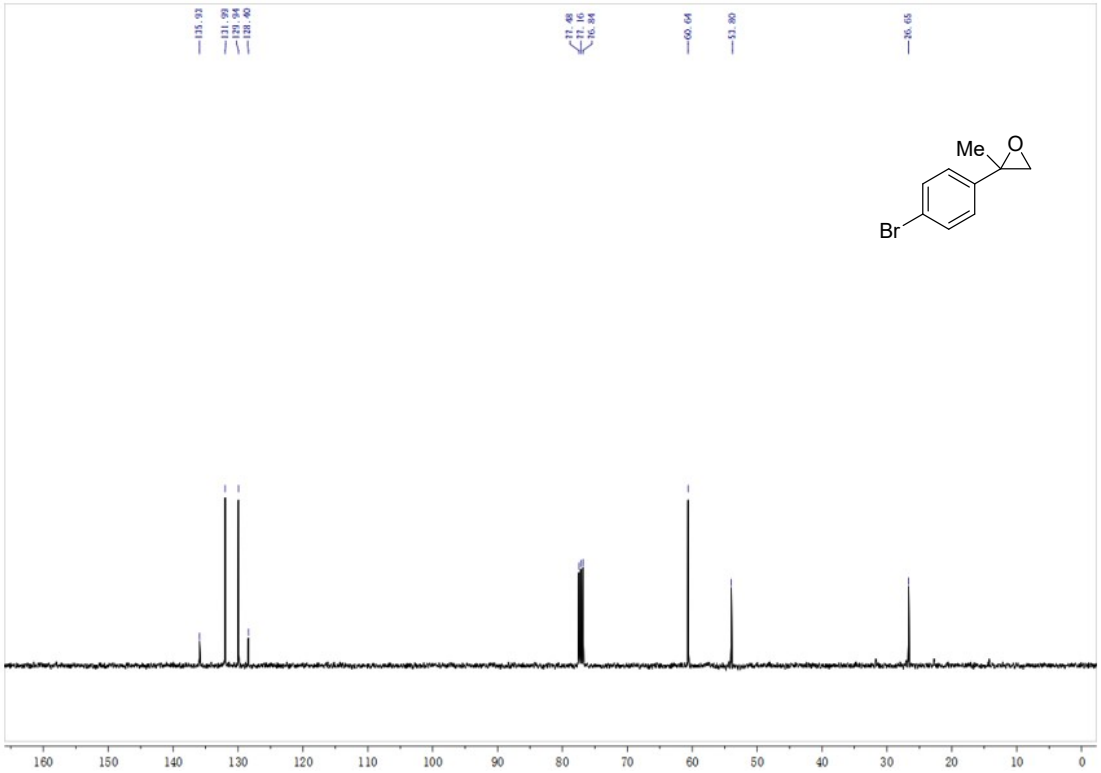
^{1}H NMR spectrum for compound **1m**



^{13}C{^{1}H} NMR spectrum for compound **1m**

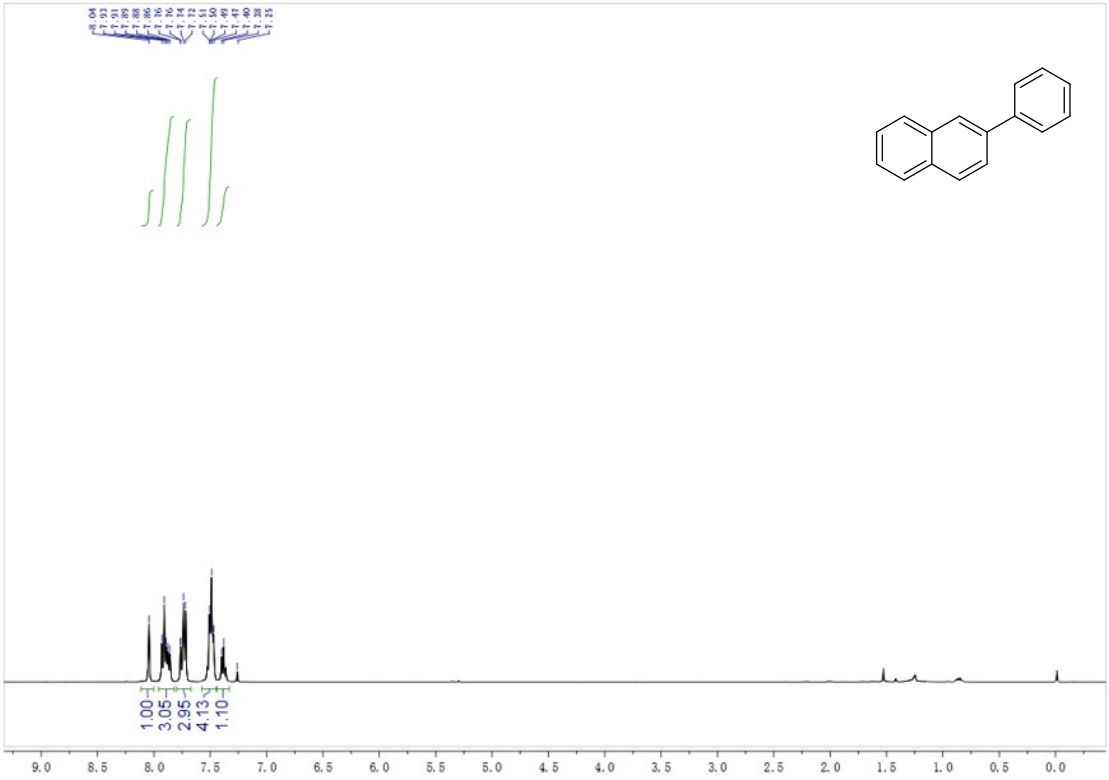


^{1}H NMR spectrum for compound **1p**

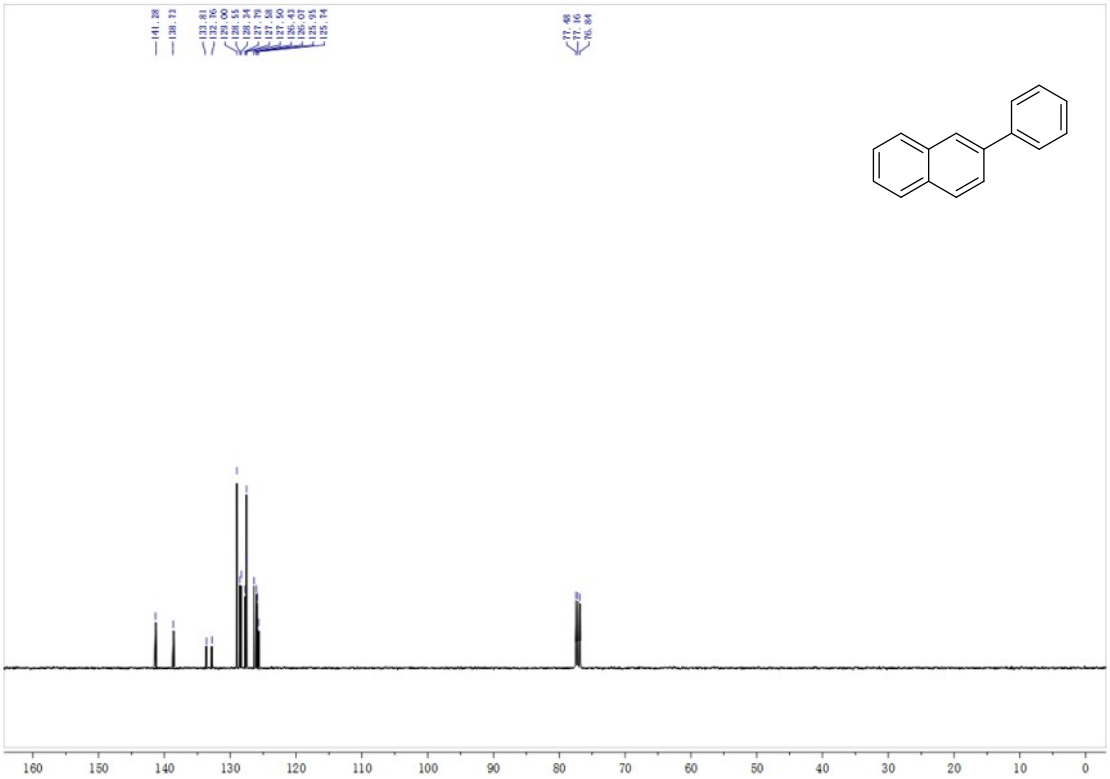


^{13}C{^{1}H} NMR spectrum for compound **1p**

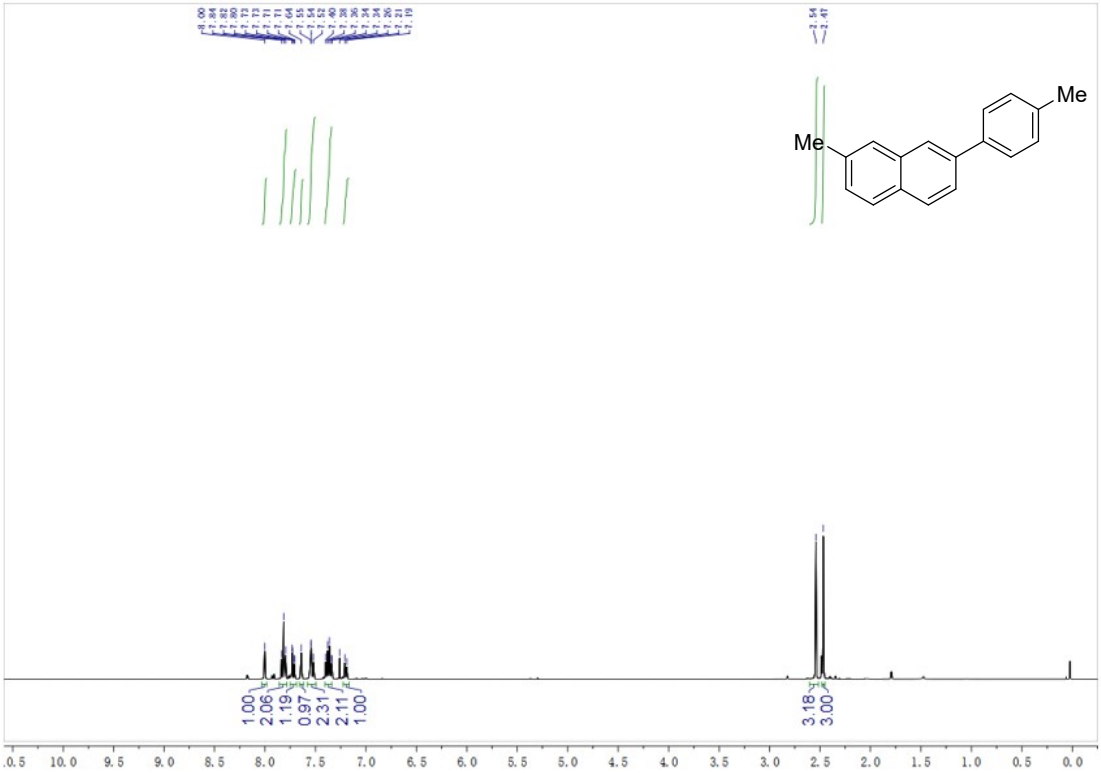
3. Copies of ^{1}H, $^{13}C\{^{1}H\}$, and ^{19}F NMR Spectra for Products



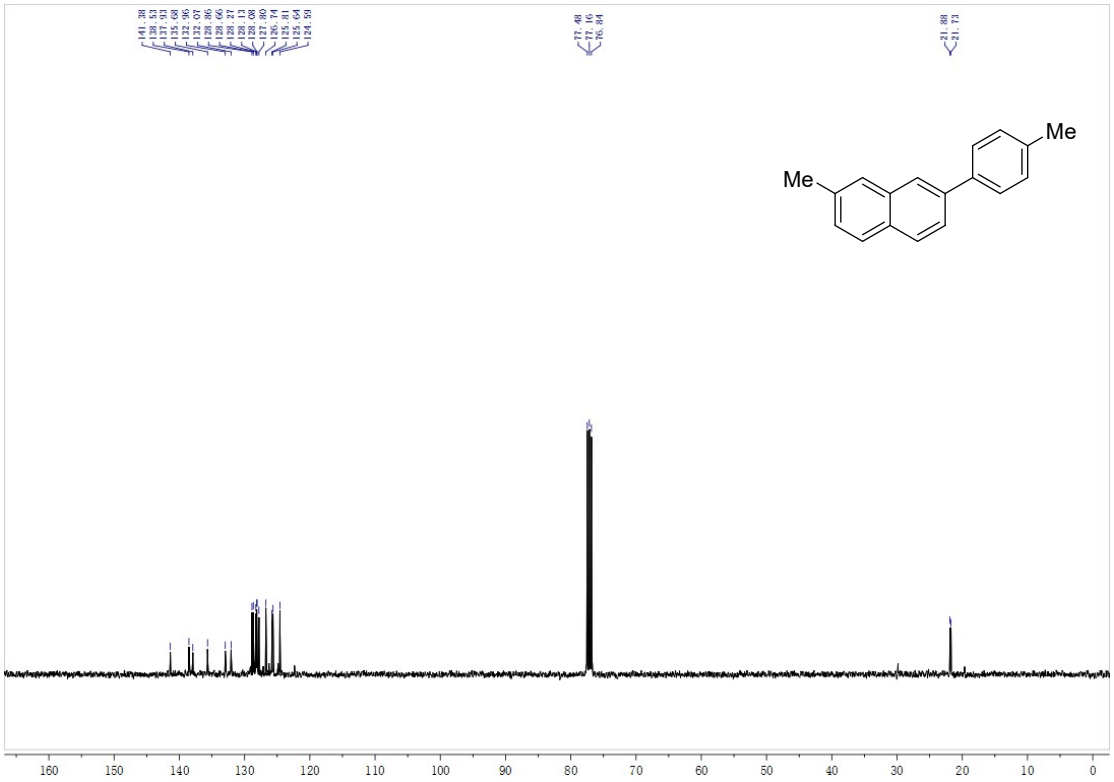
^{1}H NMR spectrum for compound **2aa**



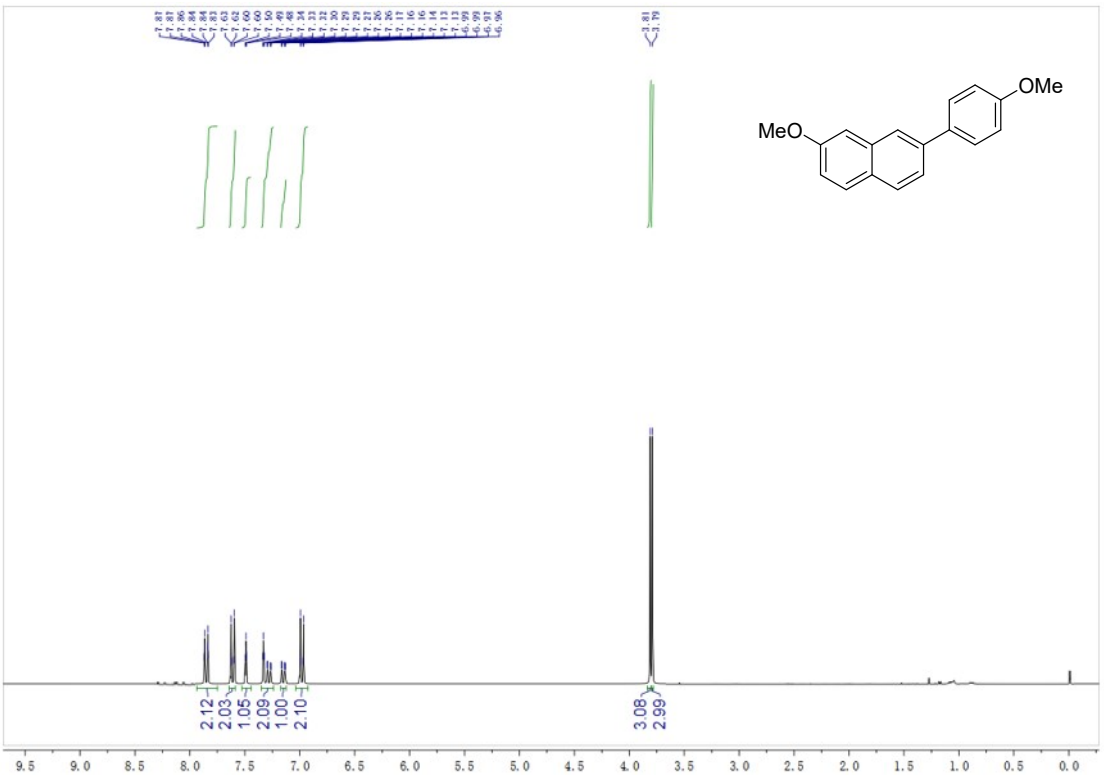
$^{13}C\{^{1}H\}$ NMR spectrum for compound **2aa**



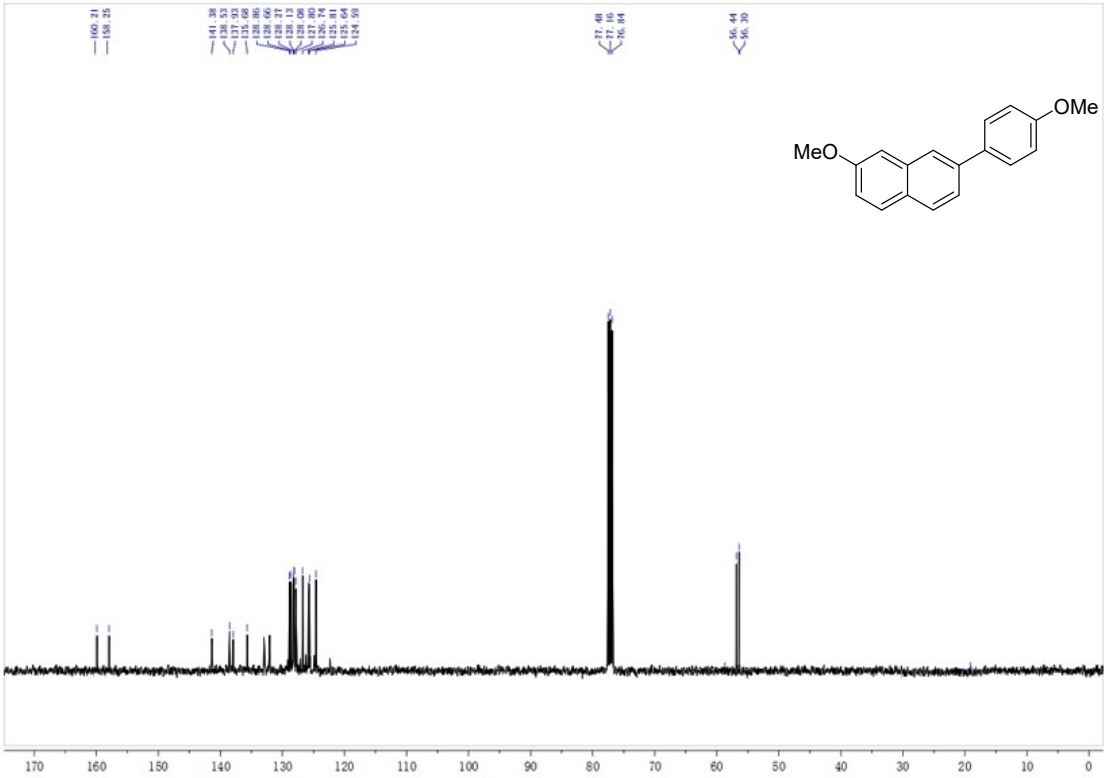
^{1}H NMR spectrum for compound **2bb**



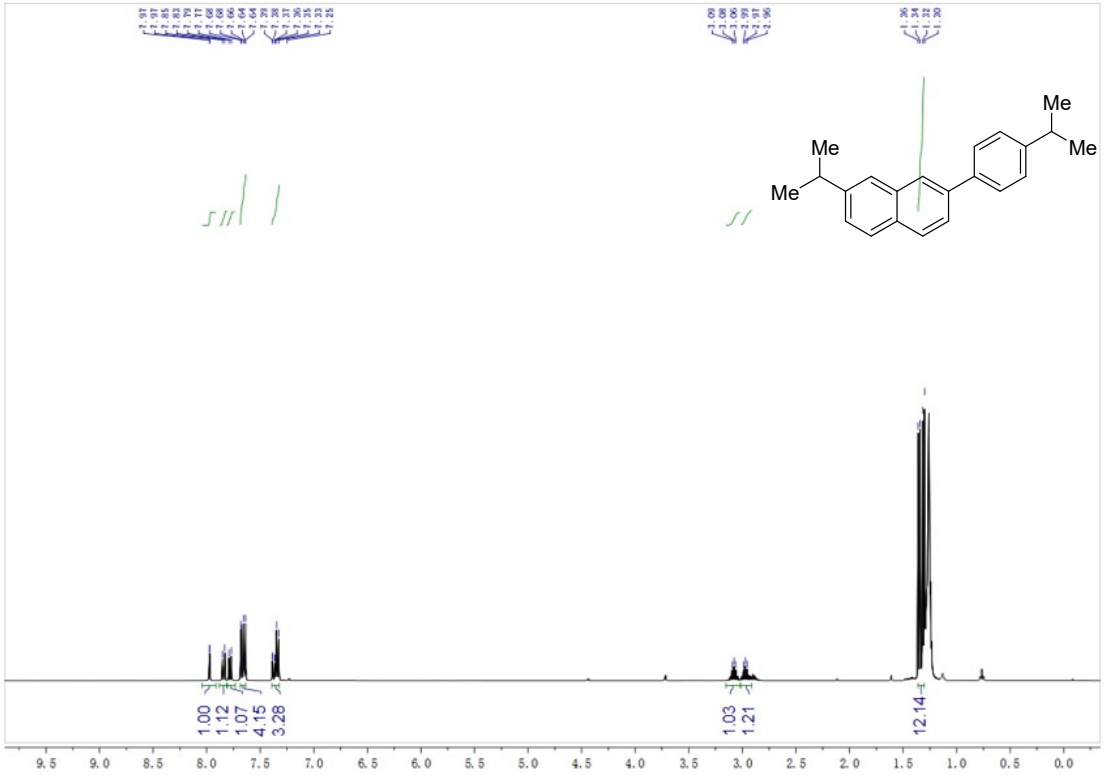
^{13}C{^{1}H} NMR spectrum for compound **2bb**



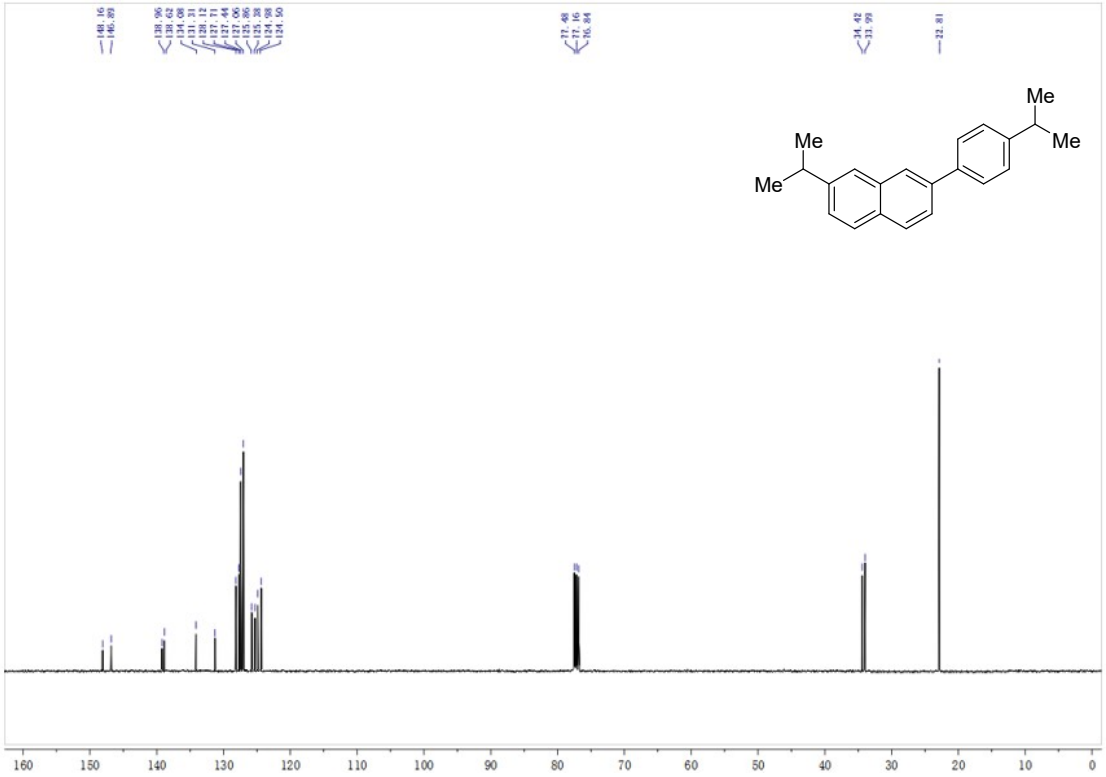
^{1}H NMR spectrum for compound **2cc**



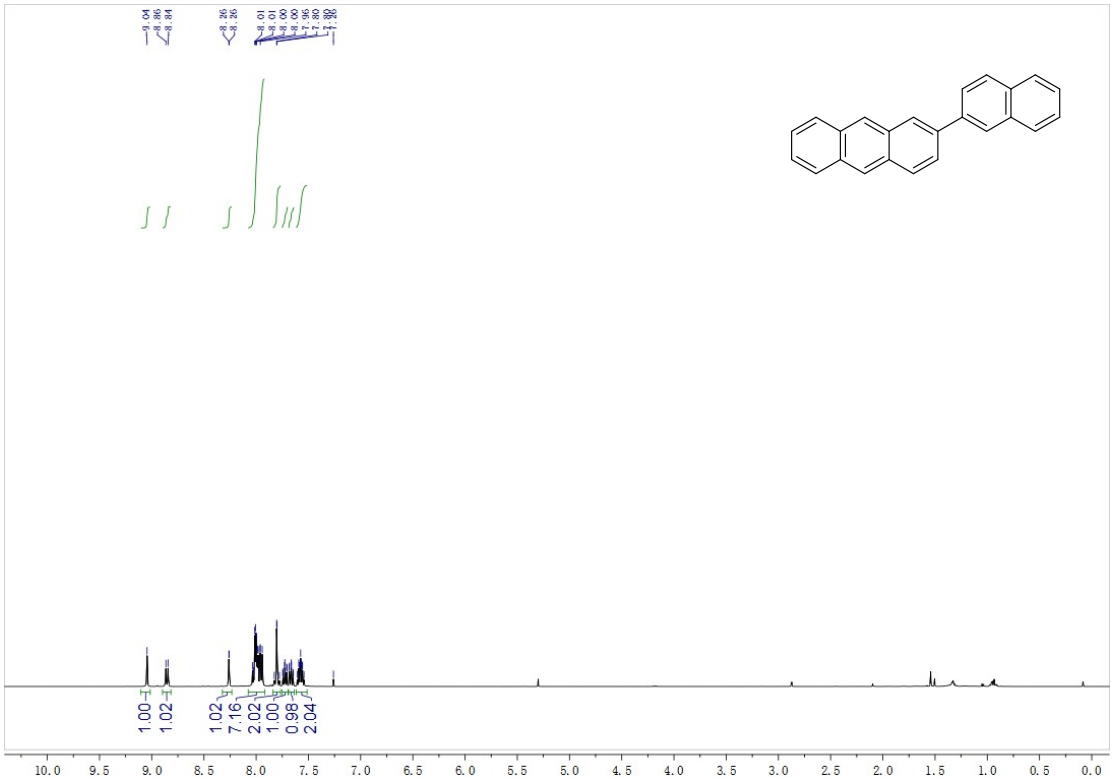
^{13}C{^{1}H} NMR spectrum for compound **2cc**



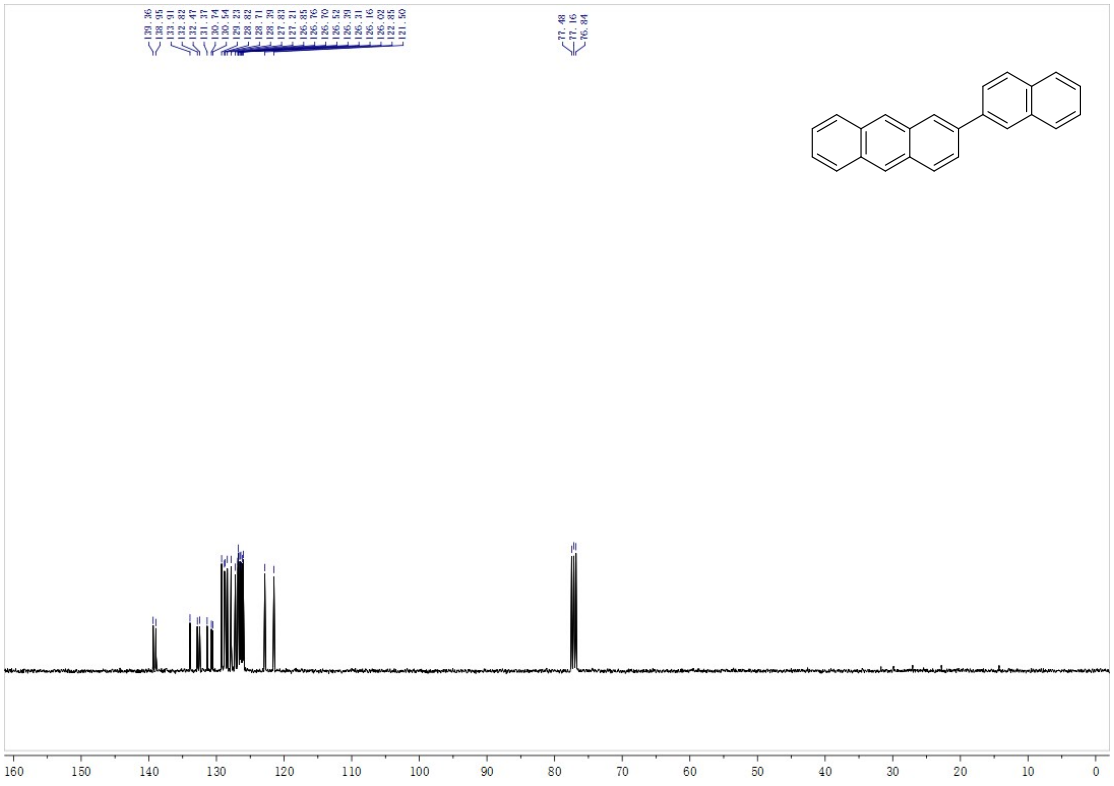
^{1}H NMR spectrum for compound **2dd**



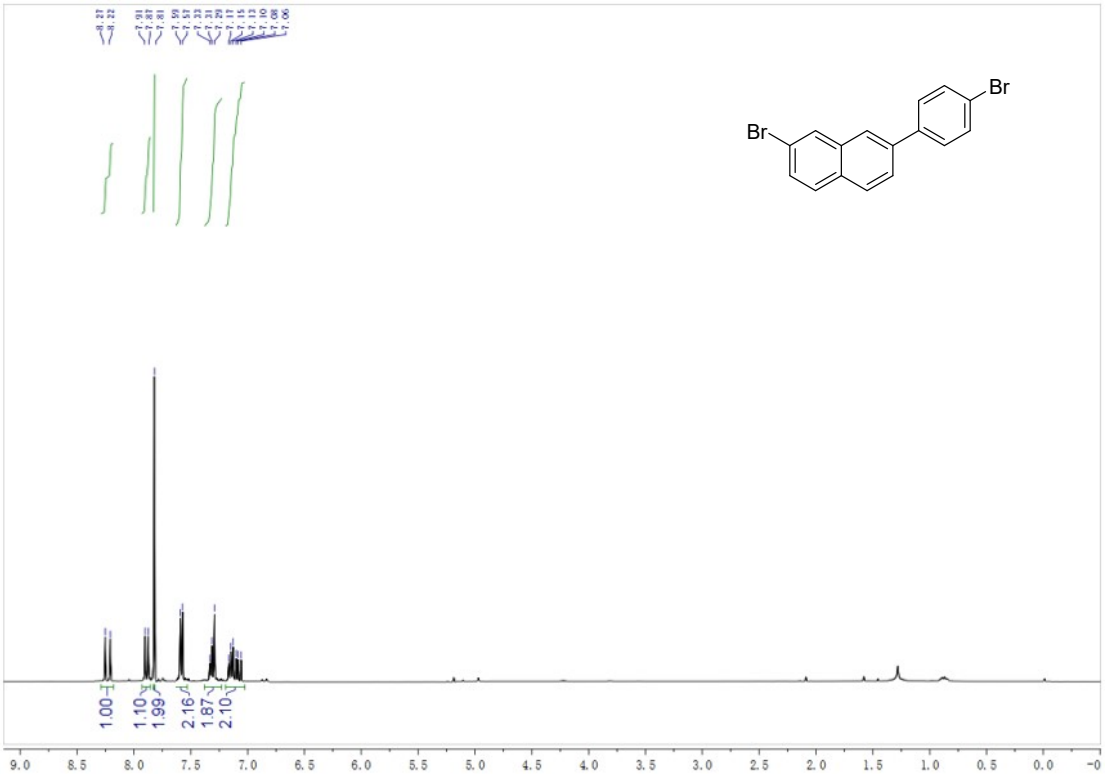
^{13}C{^{1}H} NMR spectrum for compound **2dd**



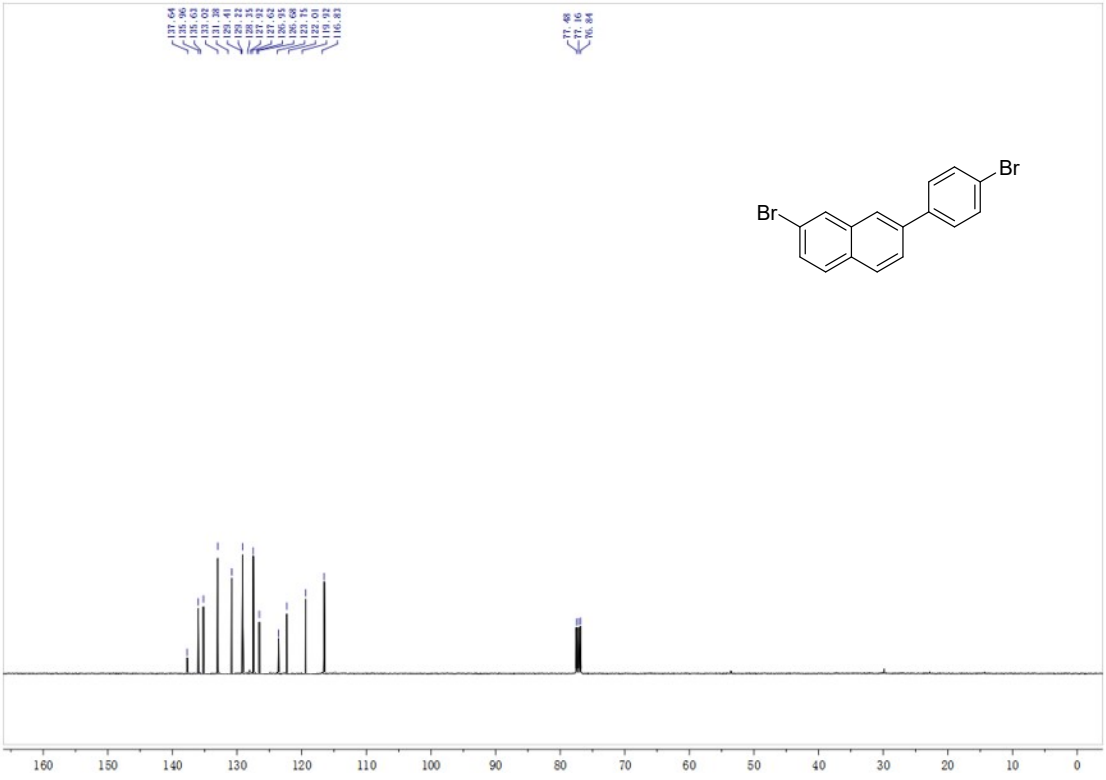
^{1}H NMR spectrum for compound **2ee**



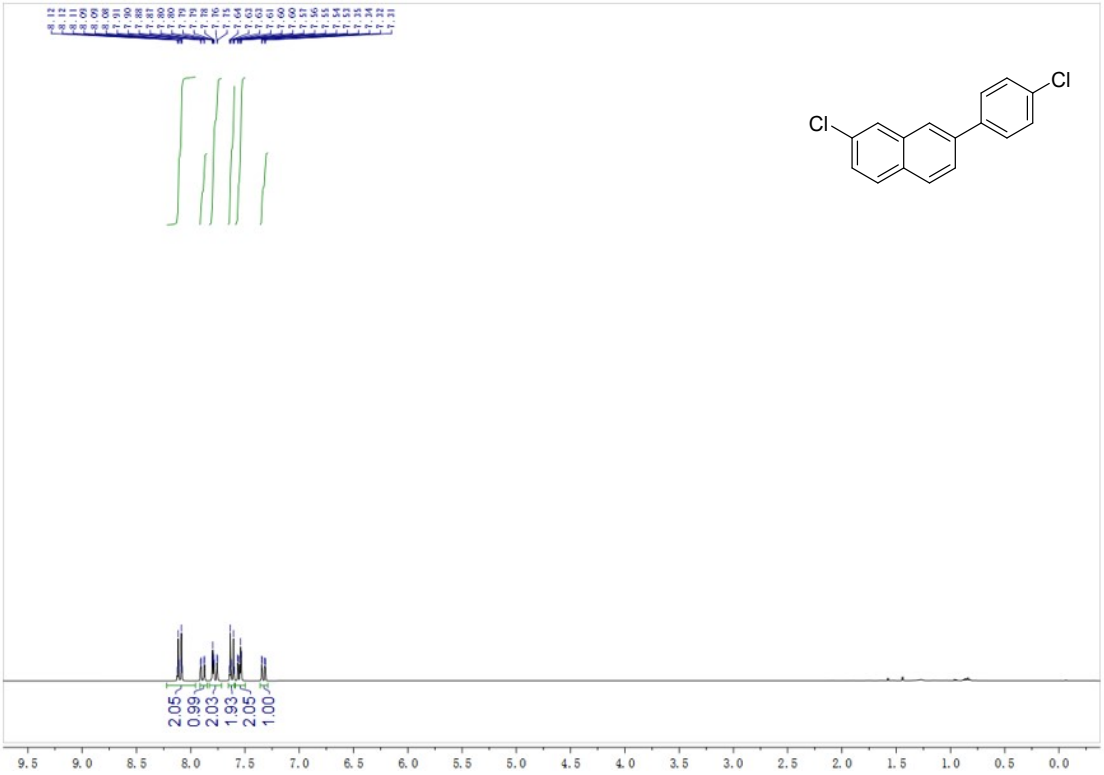
^{13}C{^{1}H} NMR spectrum for compound **2ee**



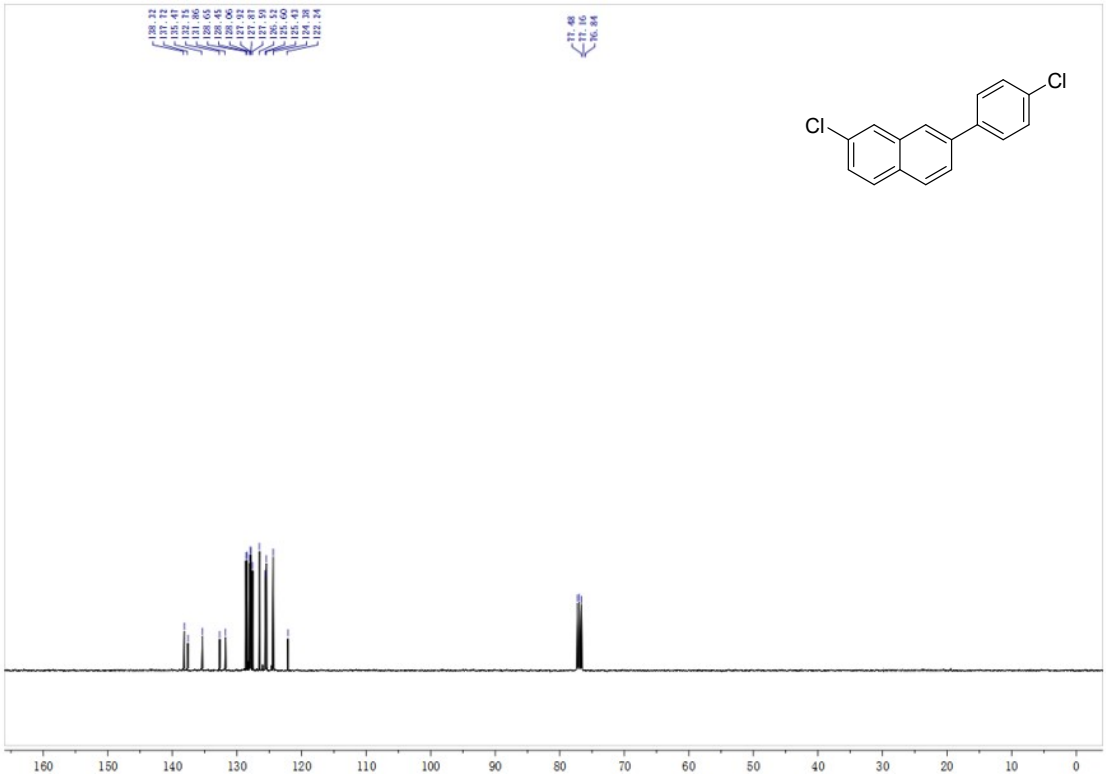
^{1}H NMR spectrum for compound **2ff**



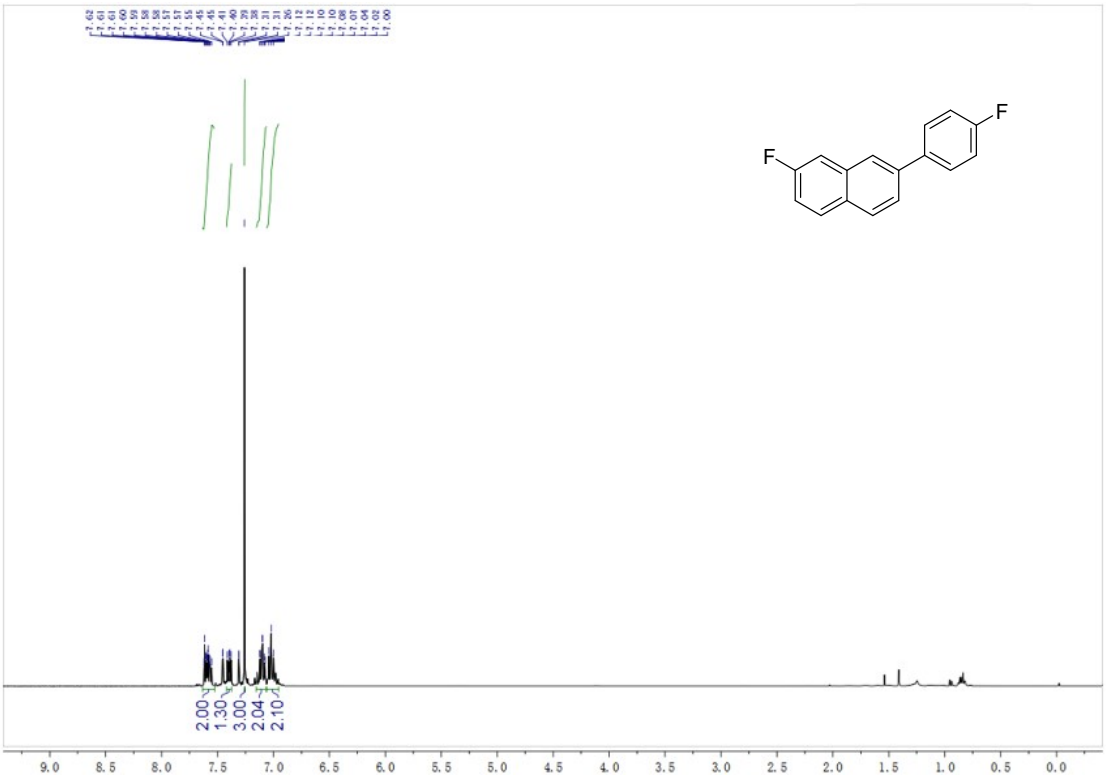
^{13}C{^{1}H} NMR spectrum for compound **2ff**



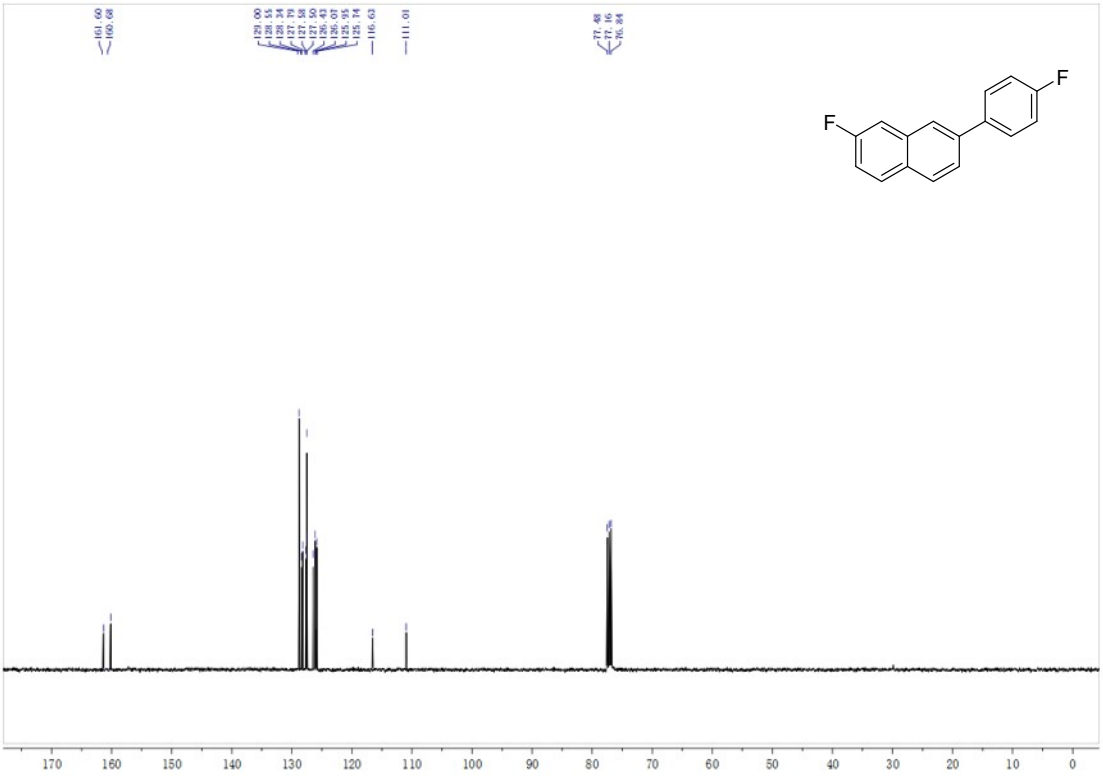
^{1}H NMR spectrum for compound **2gg**



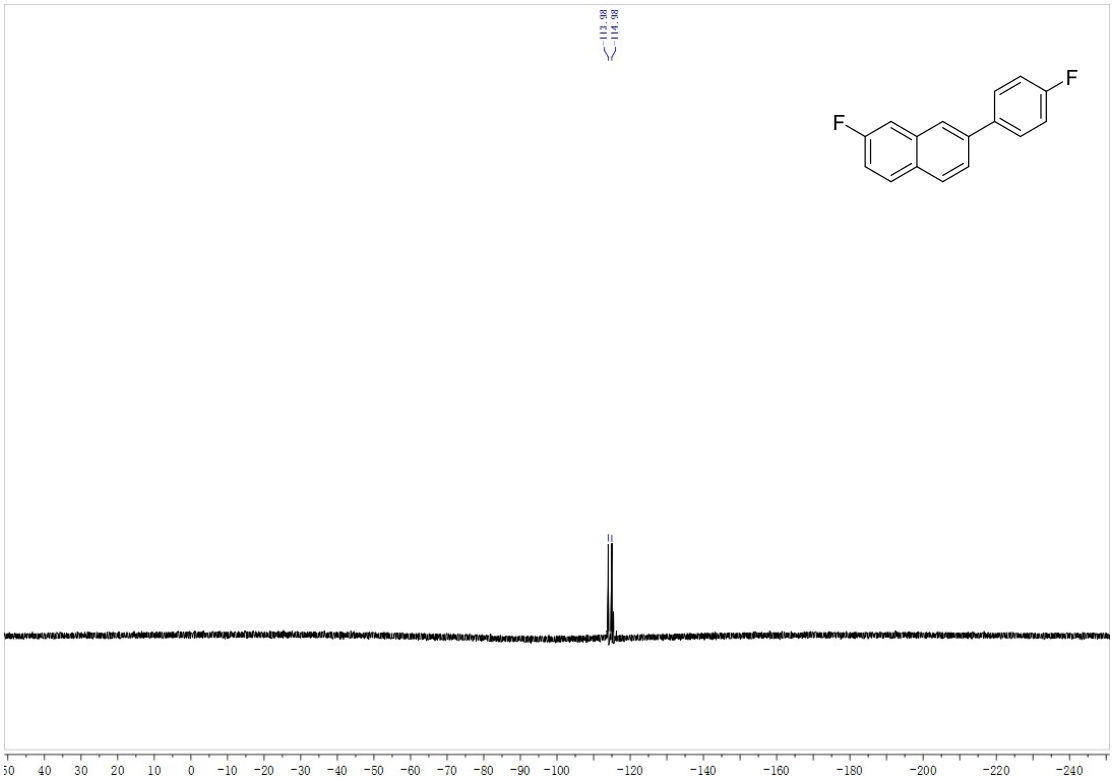
^{13}C{^{1}H} NMR spectrum for compound **2gg**



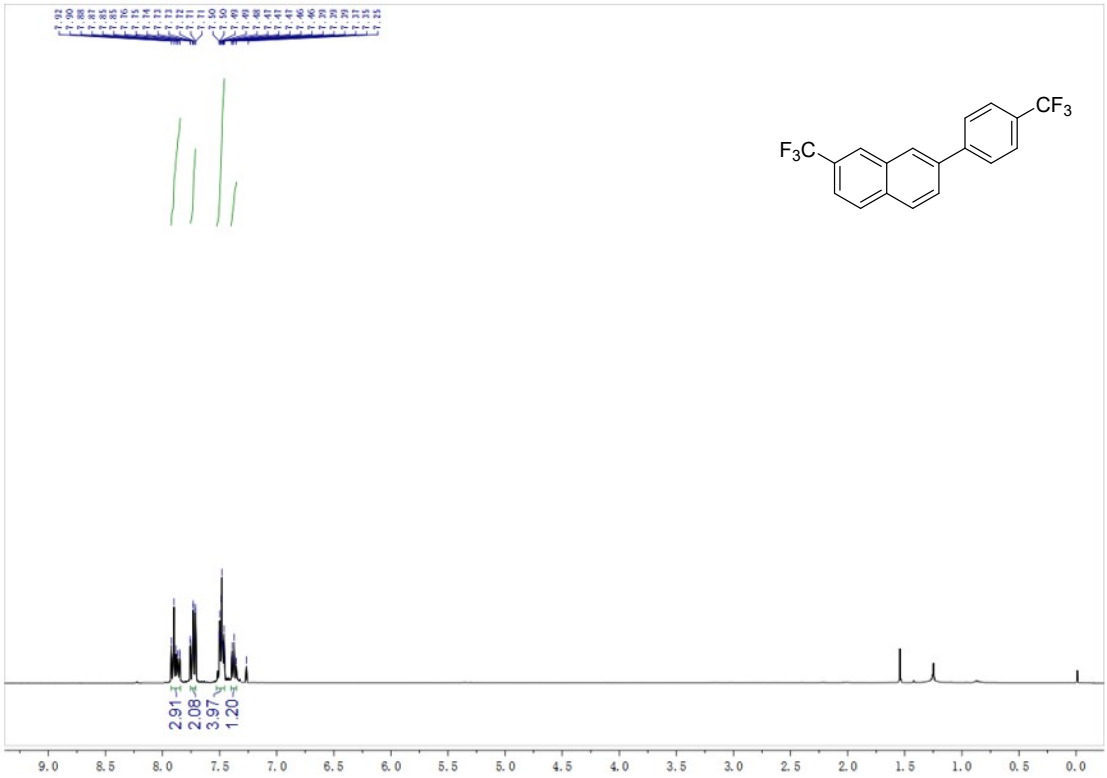
^{1}H NMR spectrum for compound **2hh**



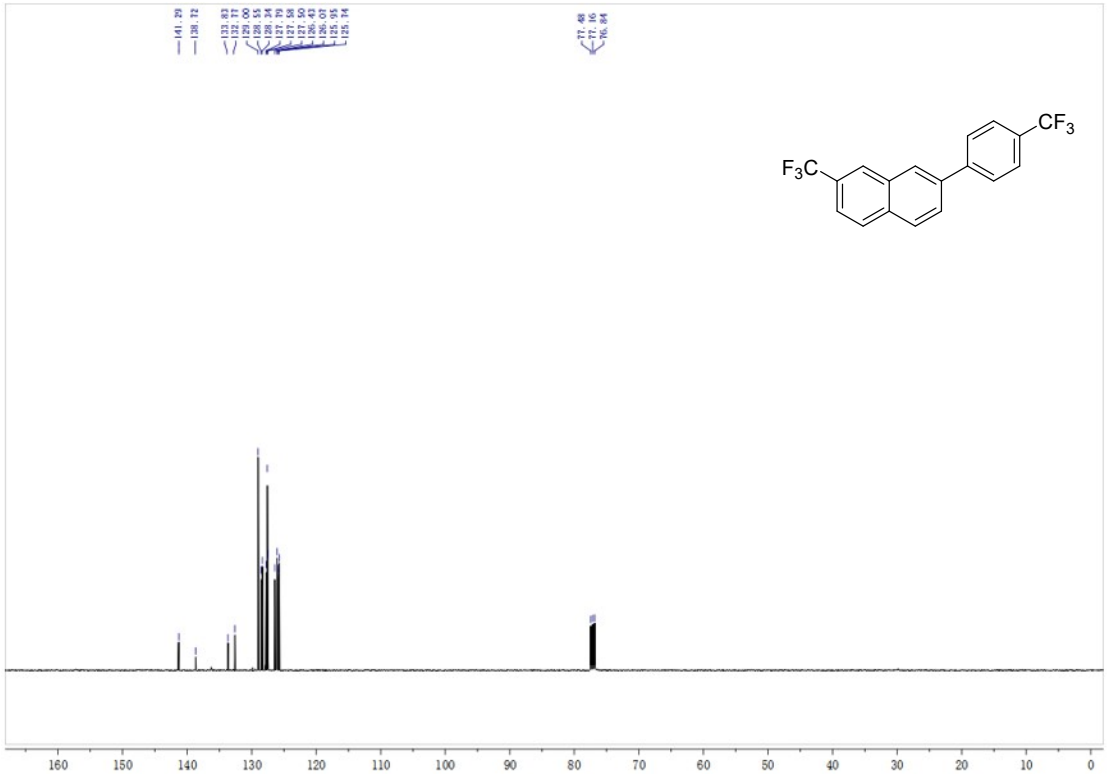
^{13}C{^{1}H} NMR spectrum for compound **2hh**



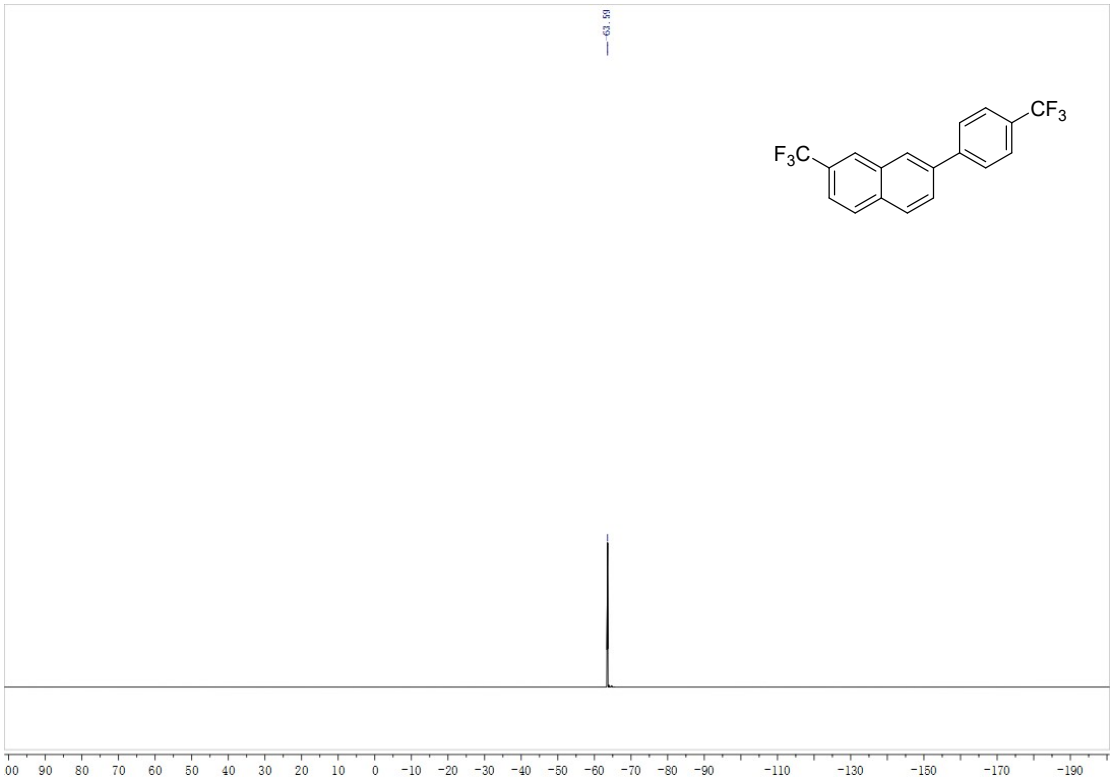
^{19}F NMR spectrum for compound **2hh**



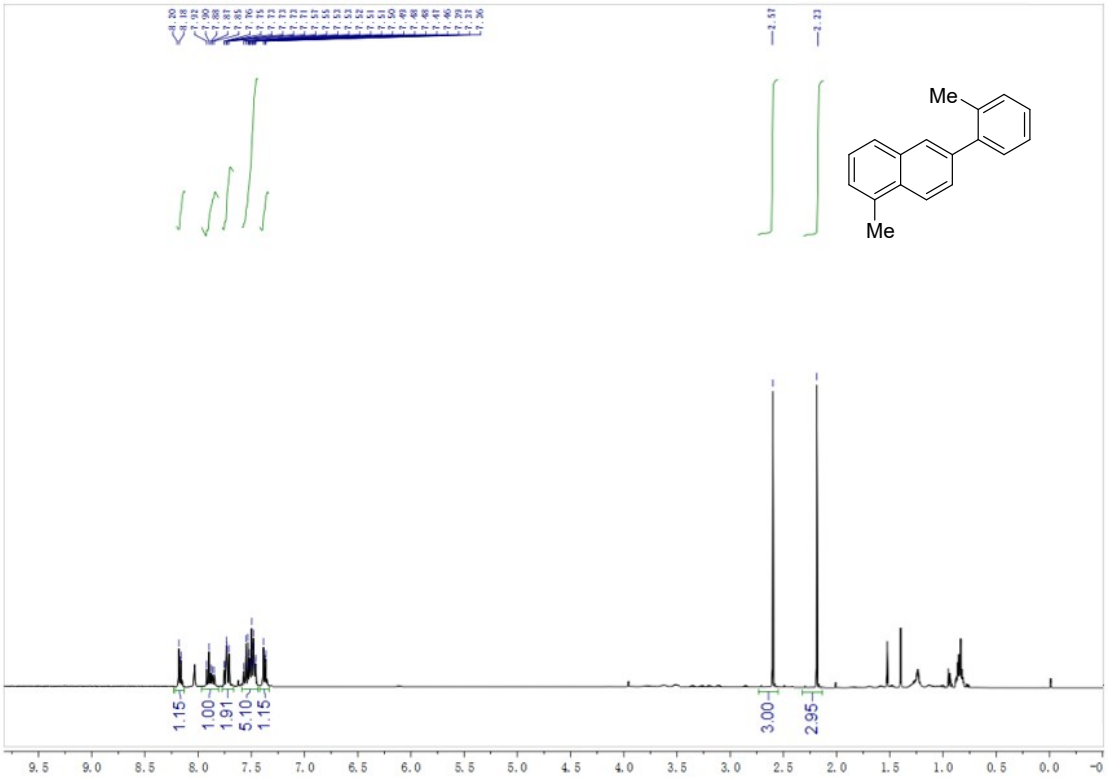
^{1}H NMR spectrum for compound **2ii**



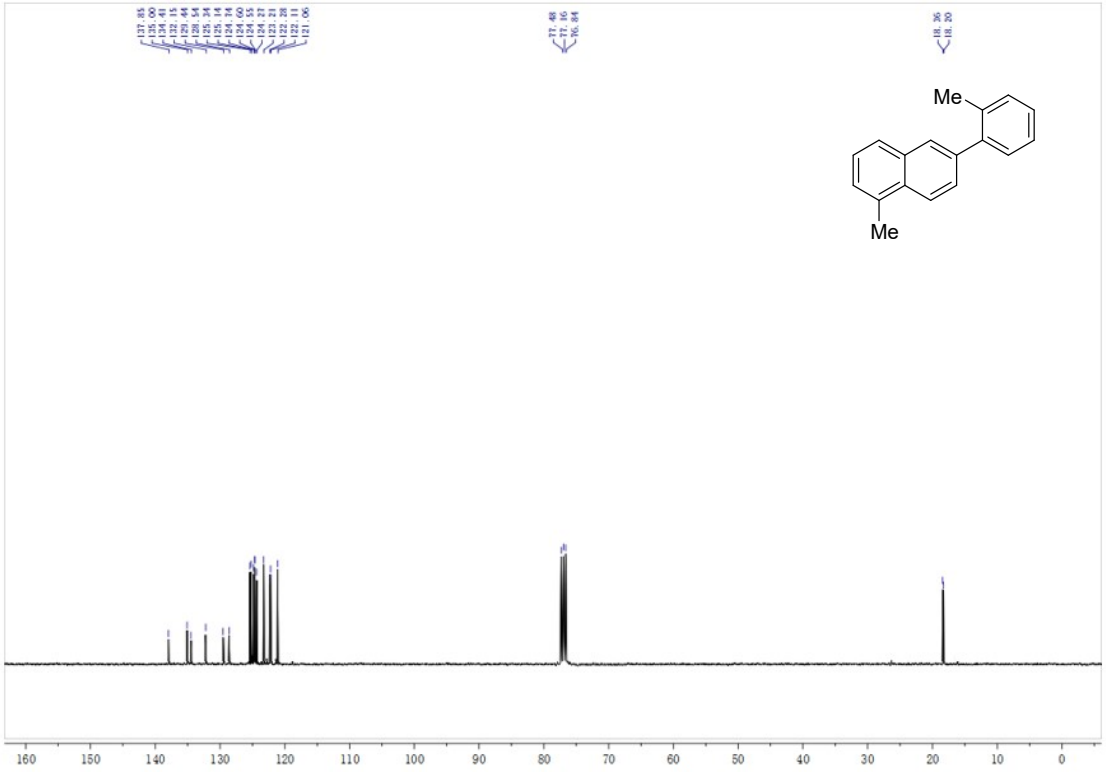
^{13}C{^{1}H} NMR spectrum for compound **2ii**



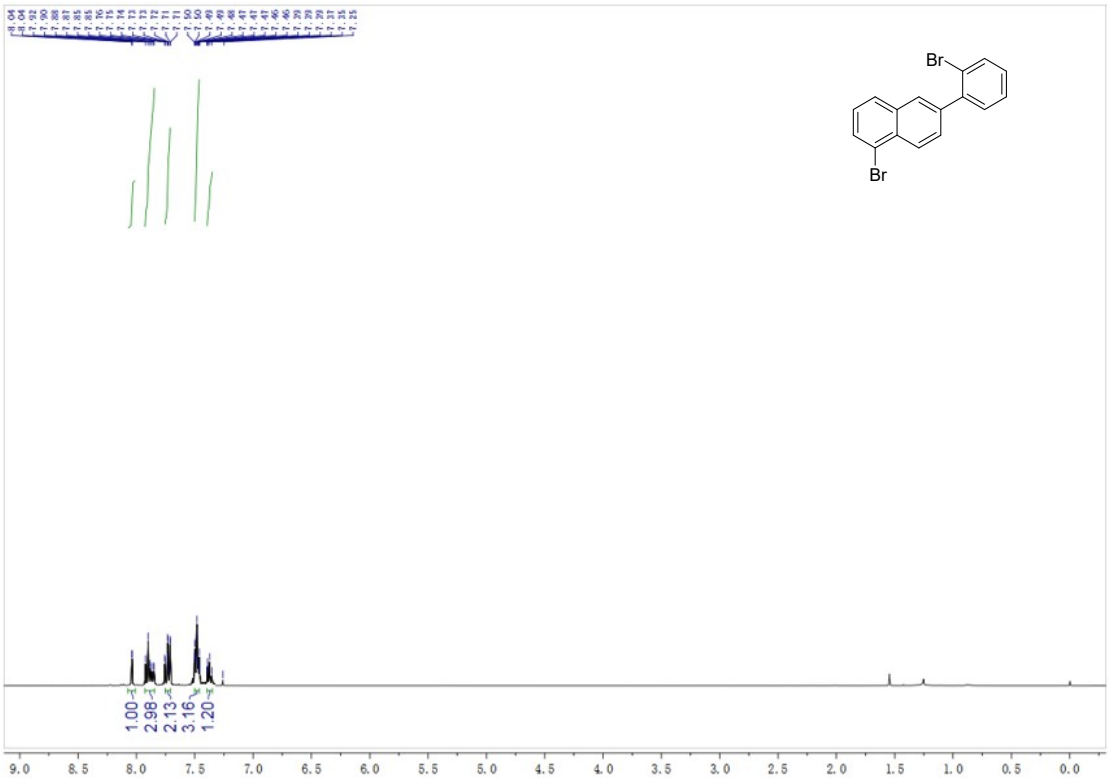
^{19}F NMR spectrum for compound **2ii**



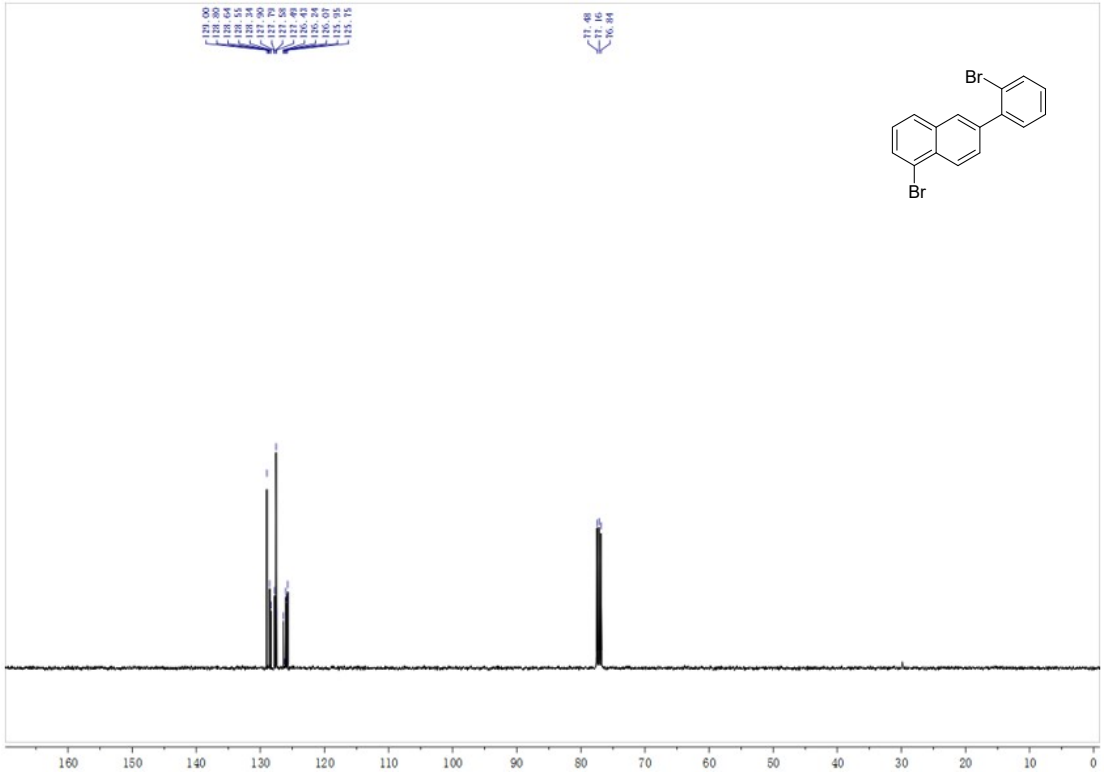
^{1}H NMR spectrum for compound **2jj**



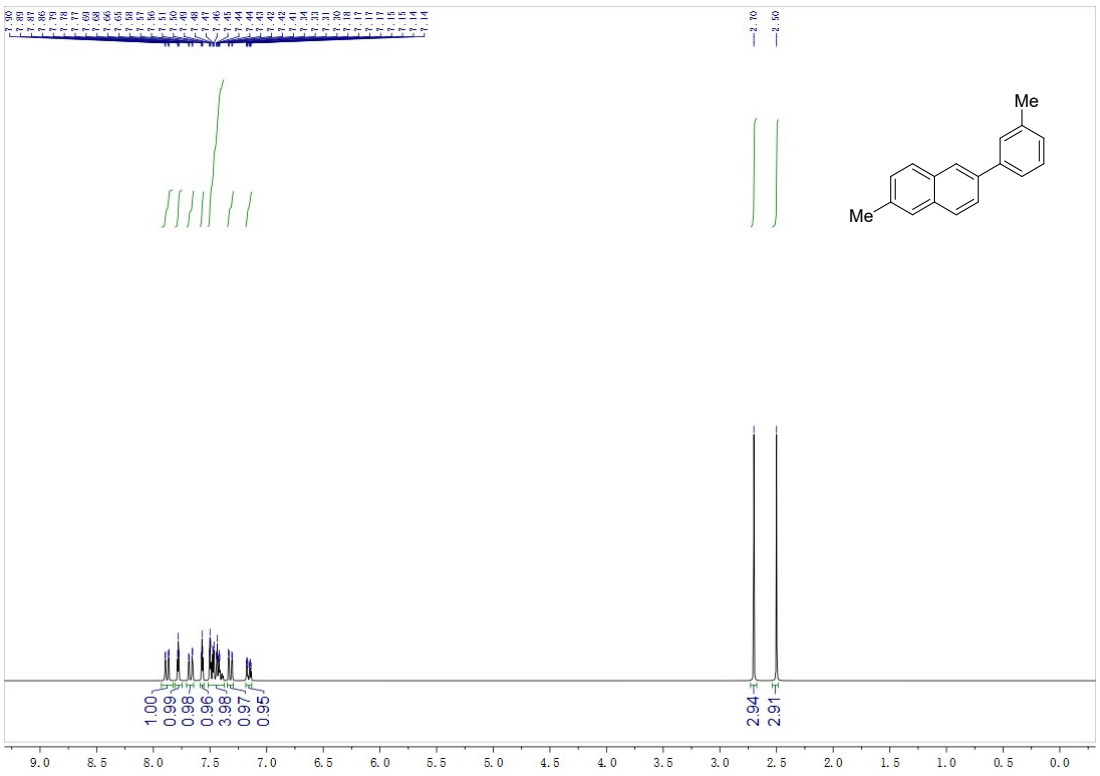
^{13}C{^{1}H} NMR spectrum for compound **2jj**



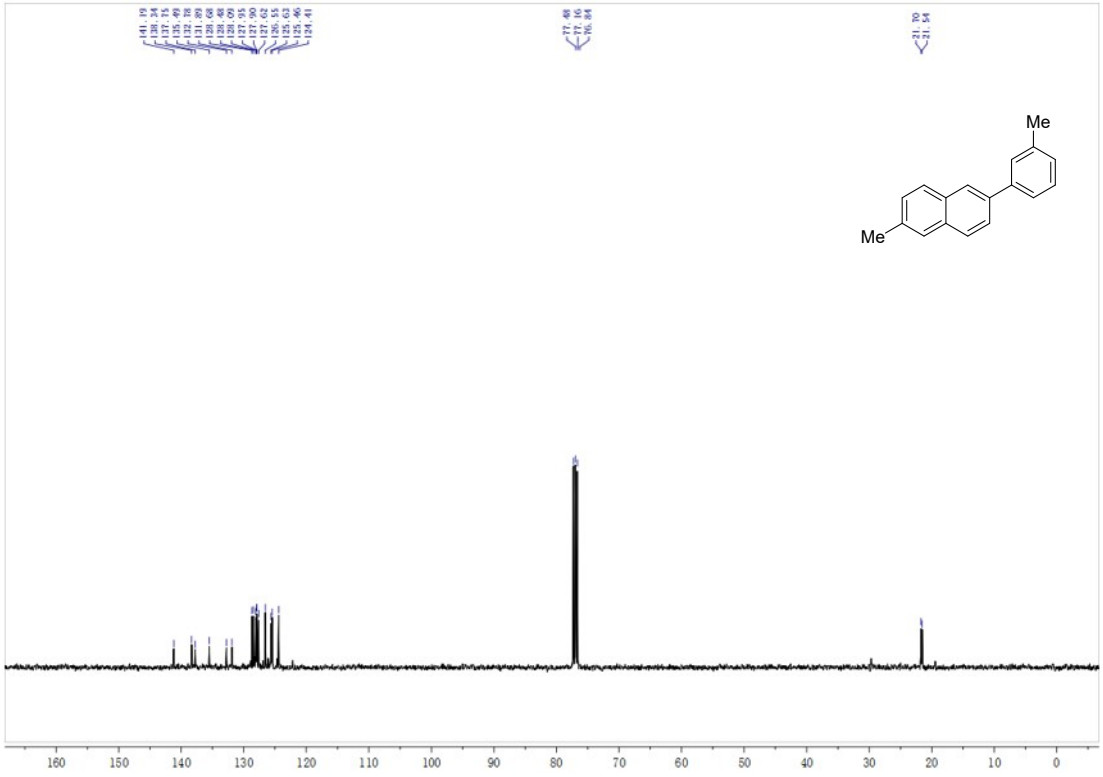
^{1}H NMR spectrum for compound **2kk**



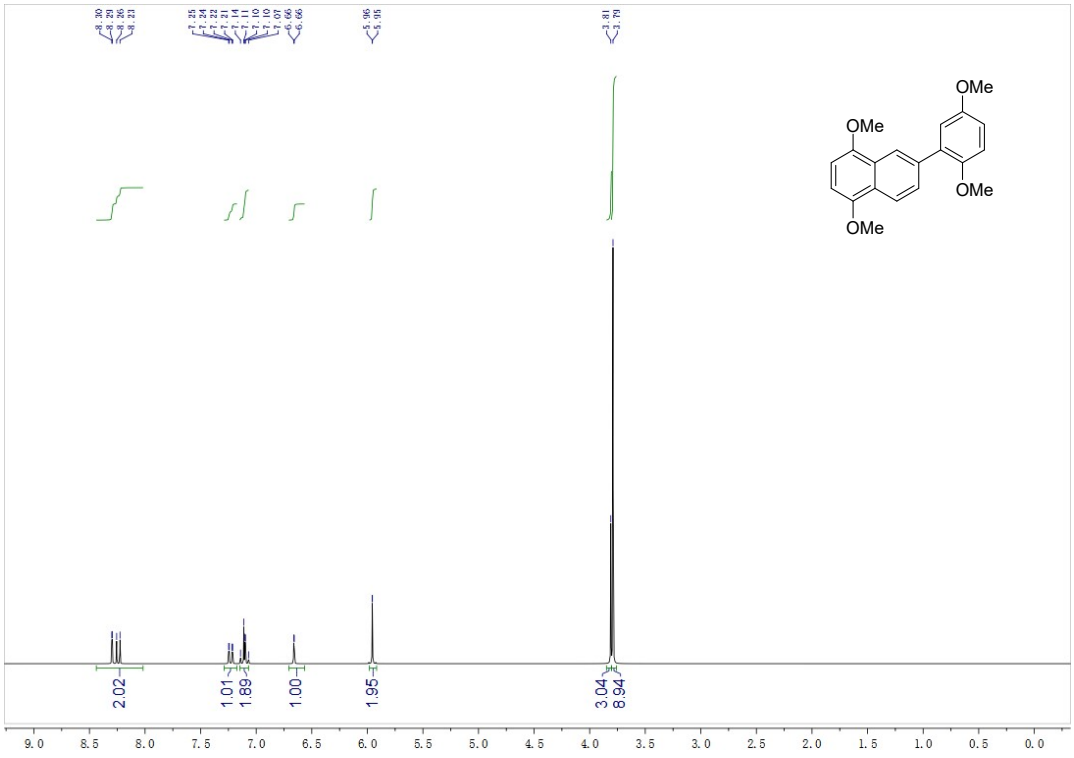
^{13}C{^{1}H} NMR spectrum for compound **2kk**



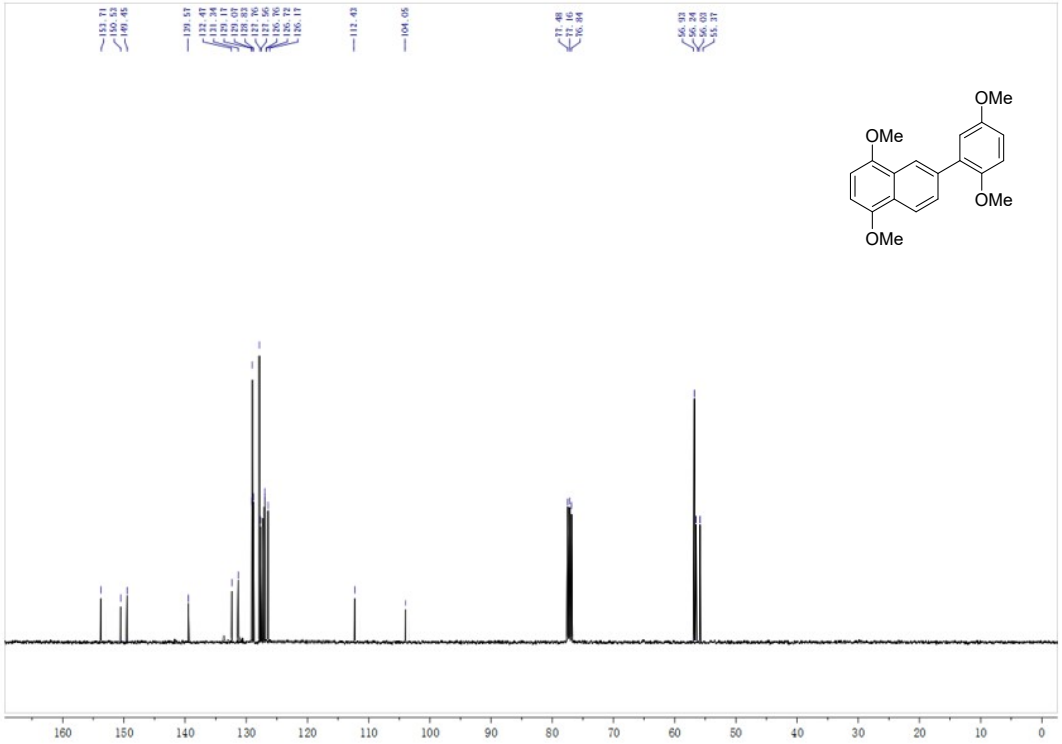
^{1}H NMR spectrum for compound **2ll**



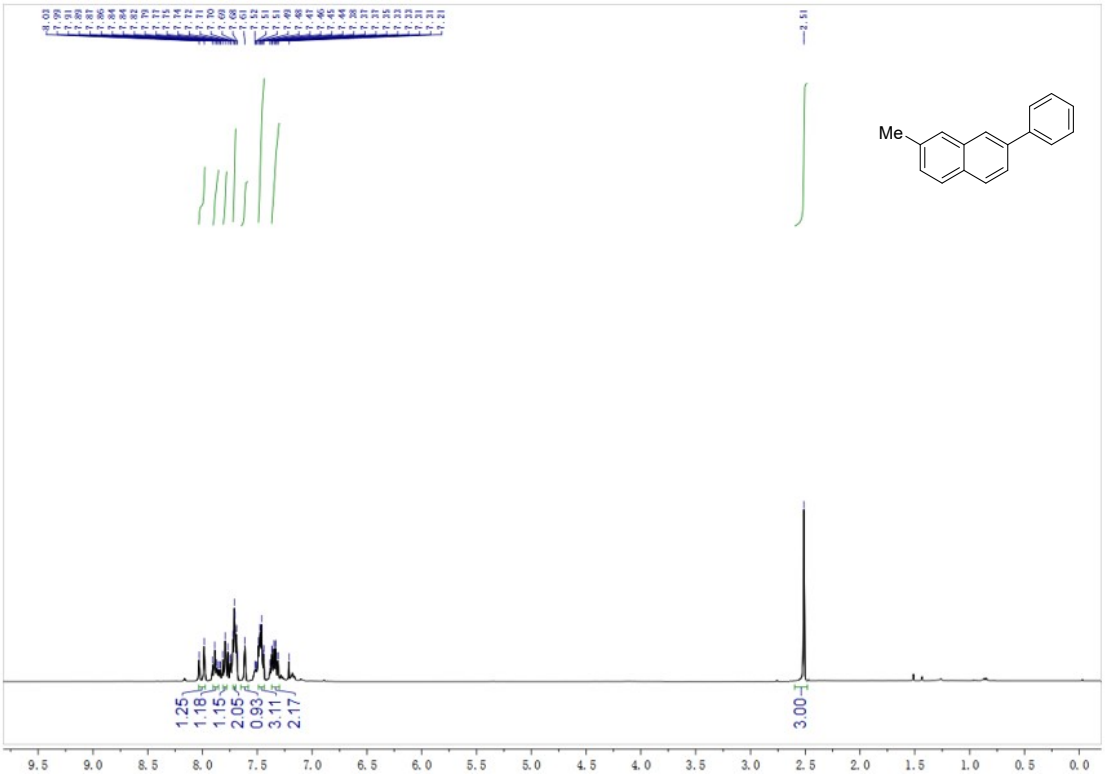
^{13}C{^{1}H} NMR spectrum for compound **2ll**



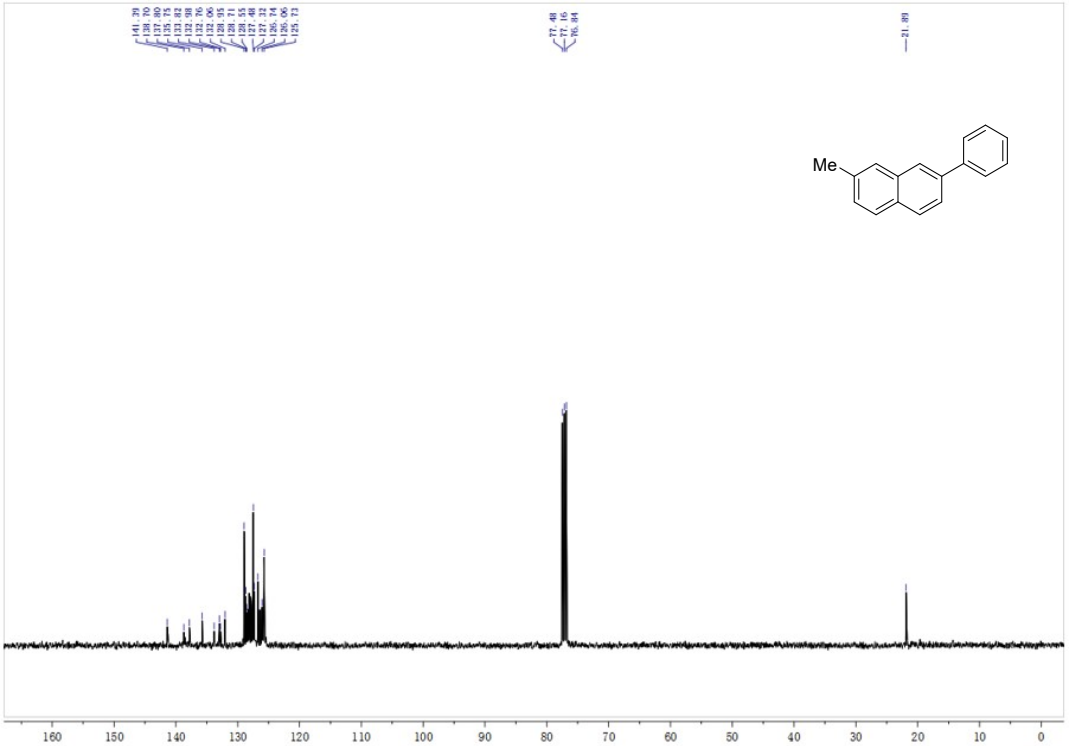
^{1}H NMR spectrum for compound **2mm**



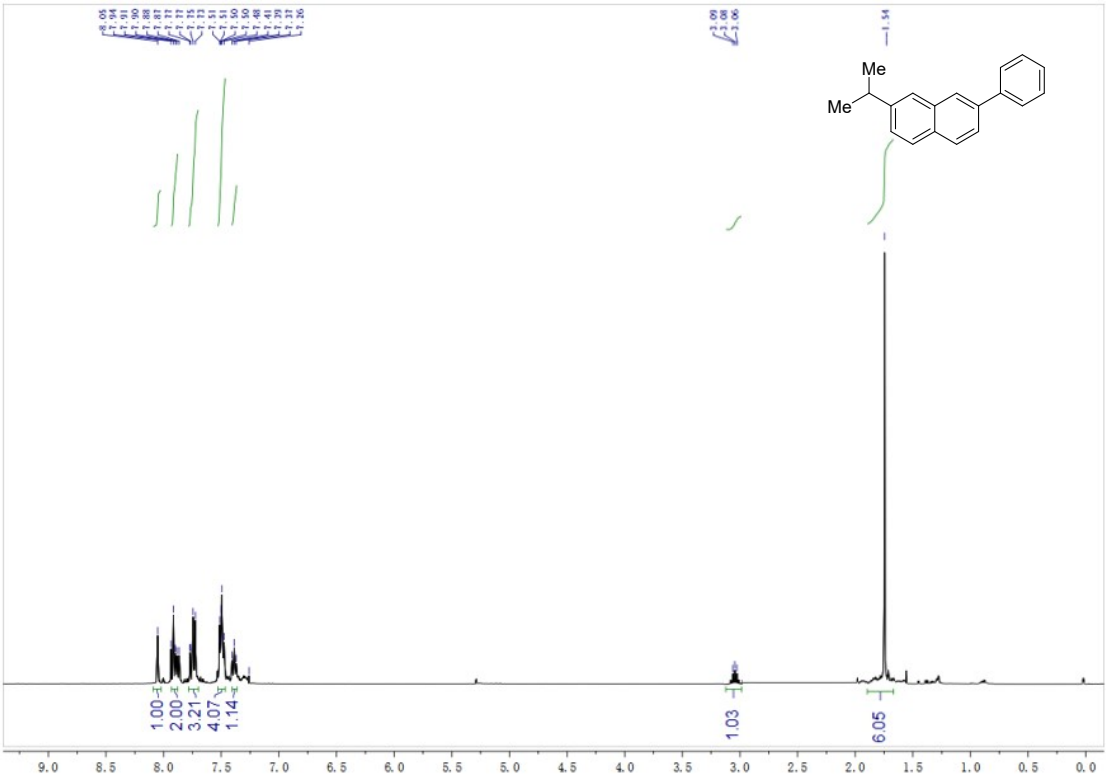
^{13}C{^{1}H} NMR spectrum for compound **2mm**



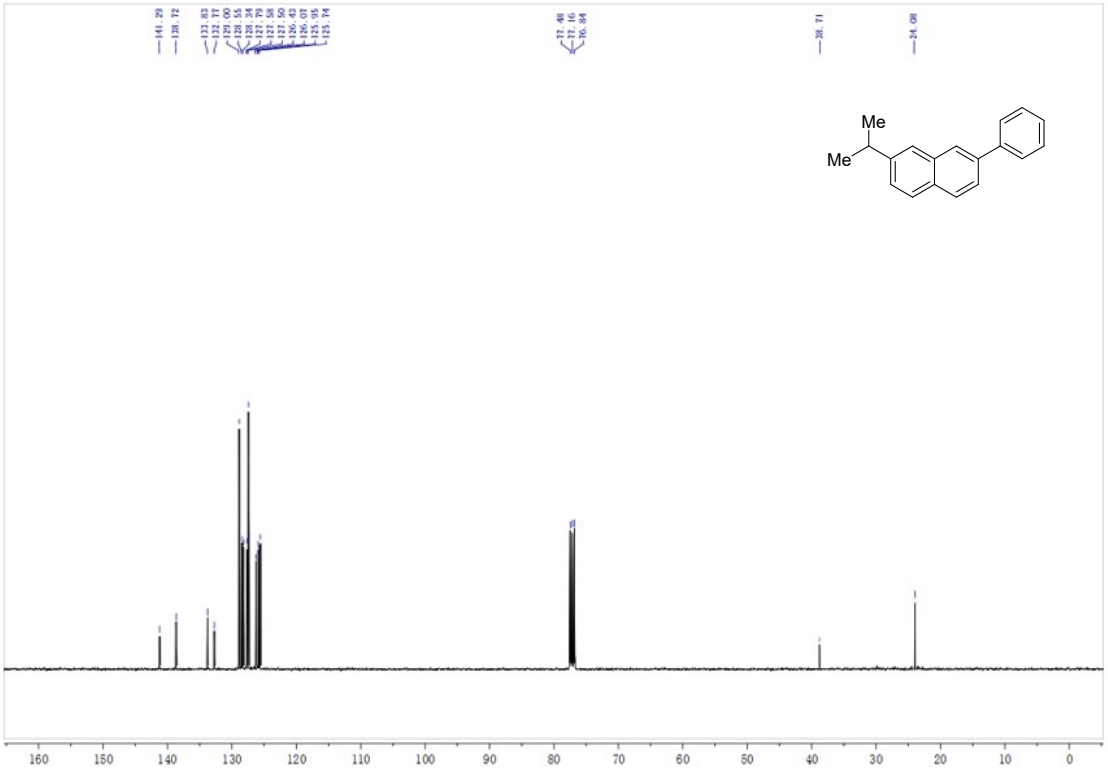
^{1}H NMR spectrum for compound **2ab**



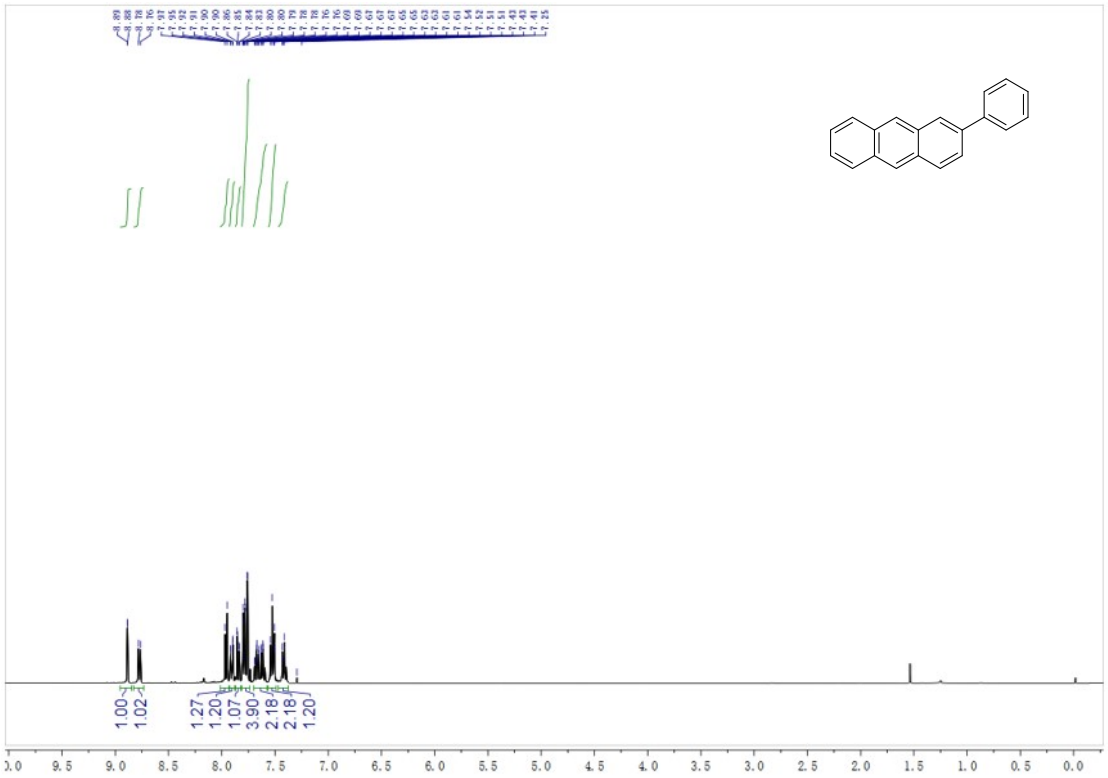
^{13}C{^{1}H} NMR spectrum for compound **2ab**



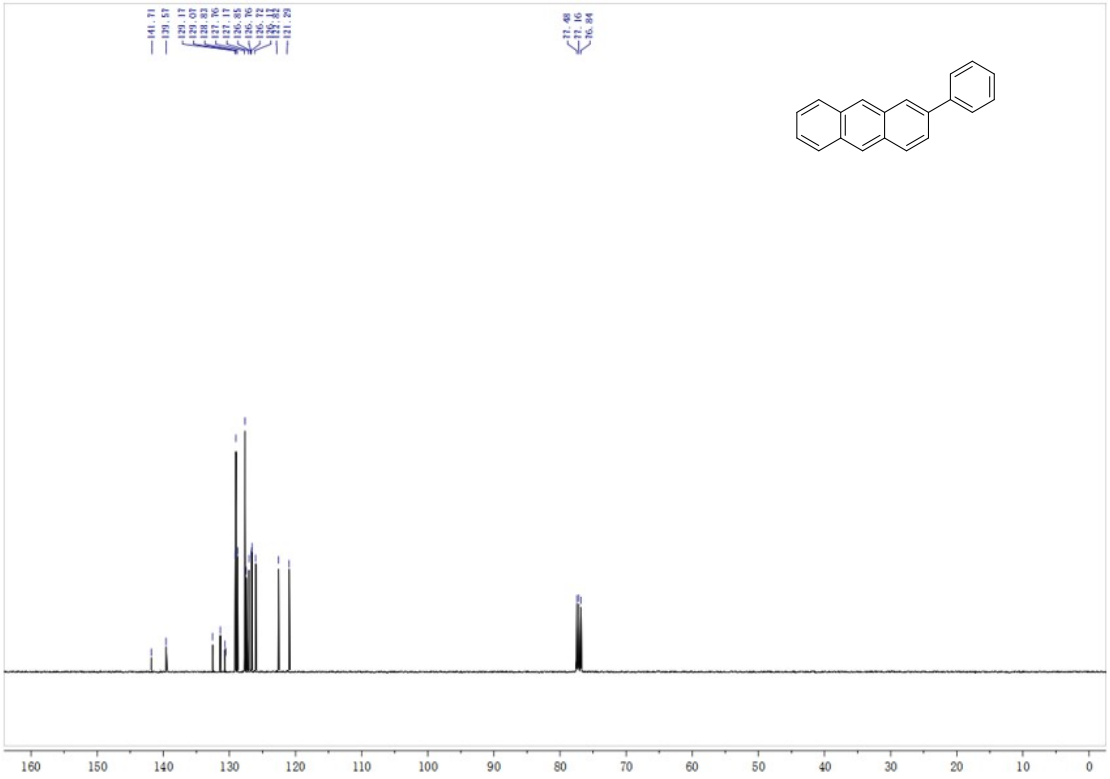
^{1}H NMR spectrum for compound **2ad**



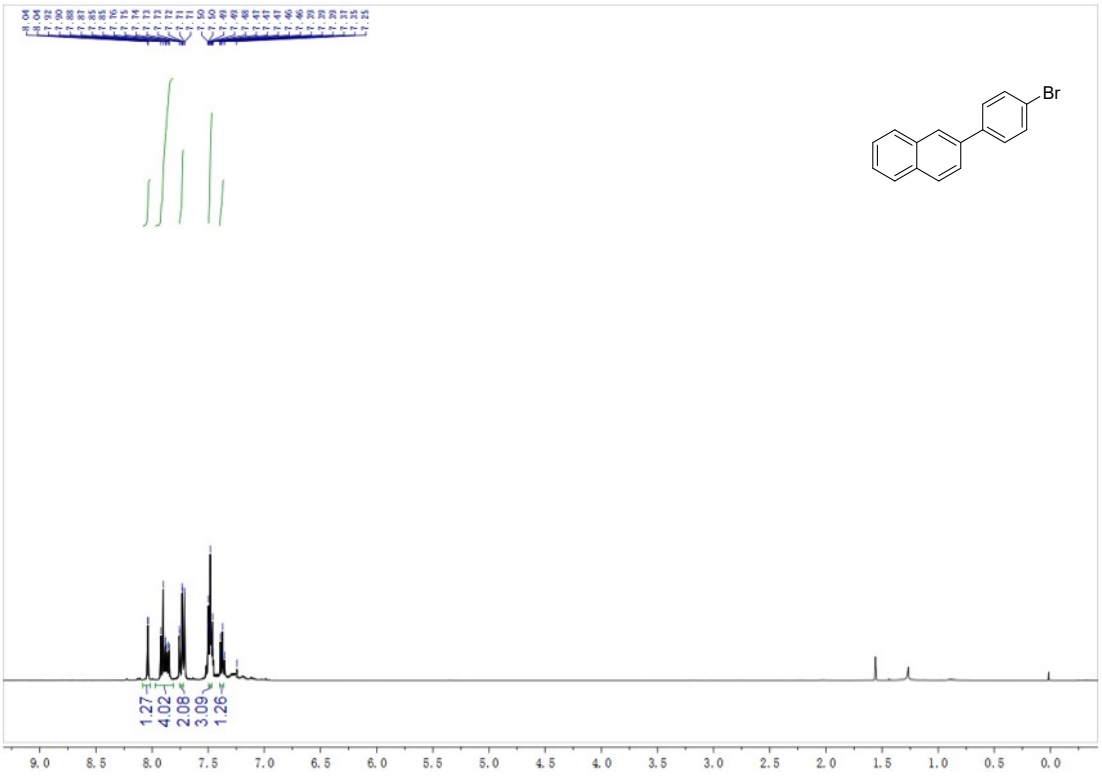
^{13}C{^{1}H} NMR spectrum for compound **2ad**



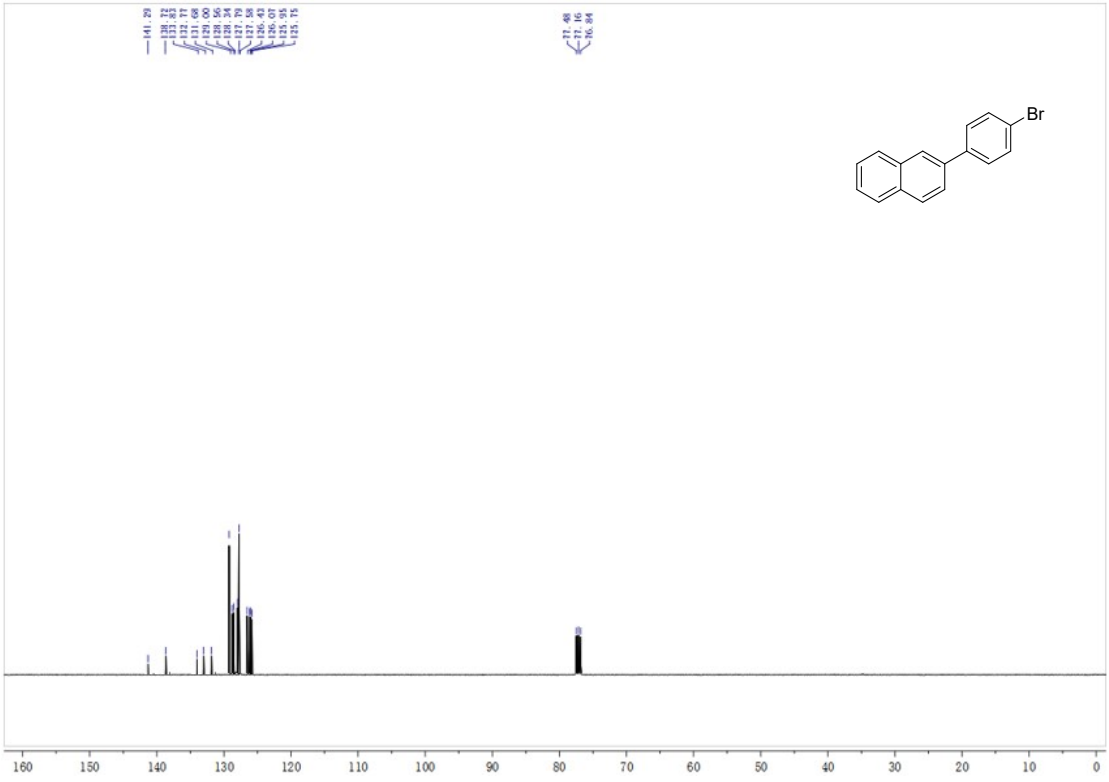
^{1}H NMR spectrum for compound **2ae**



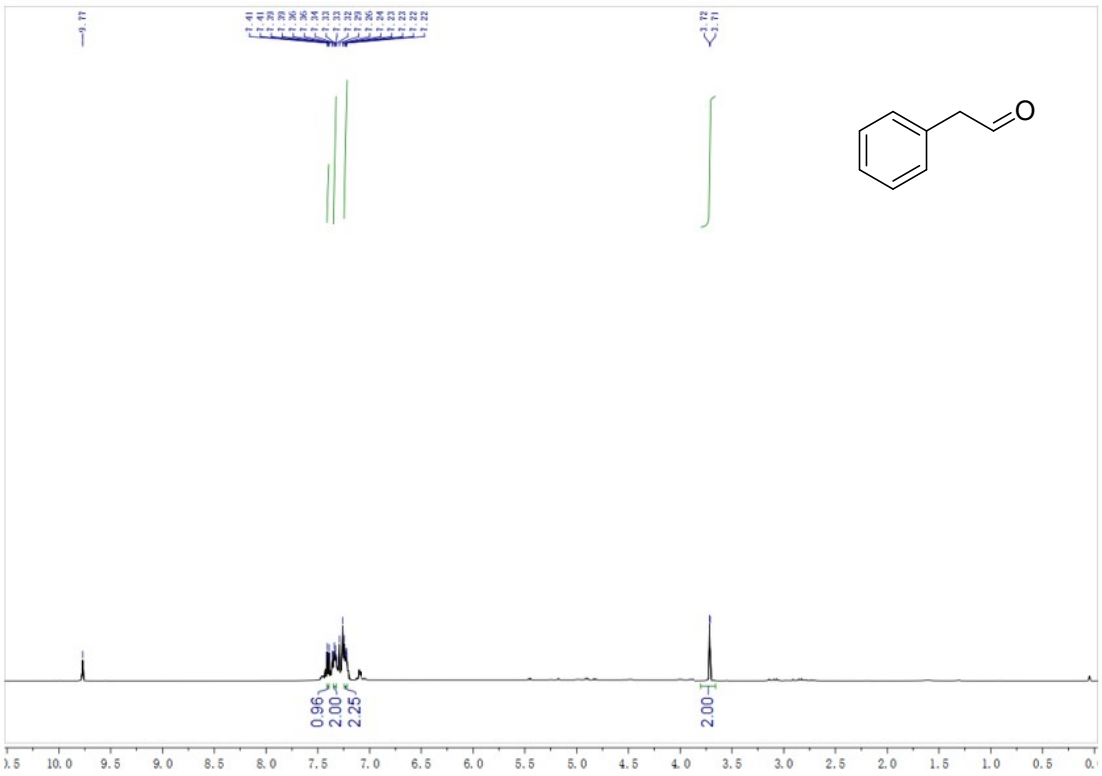
^{13}C{^{1}H} NMR spectrum for compound **2ae**



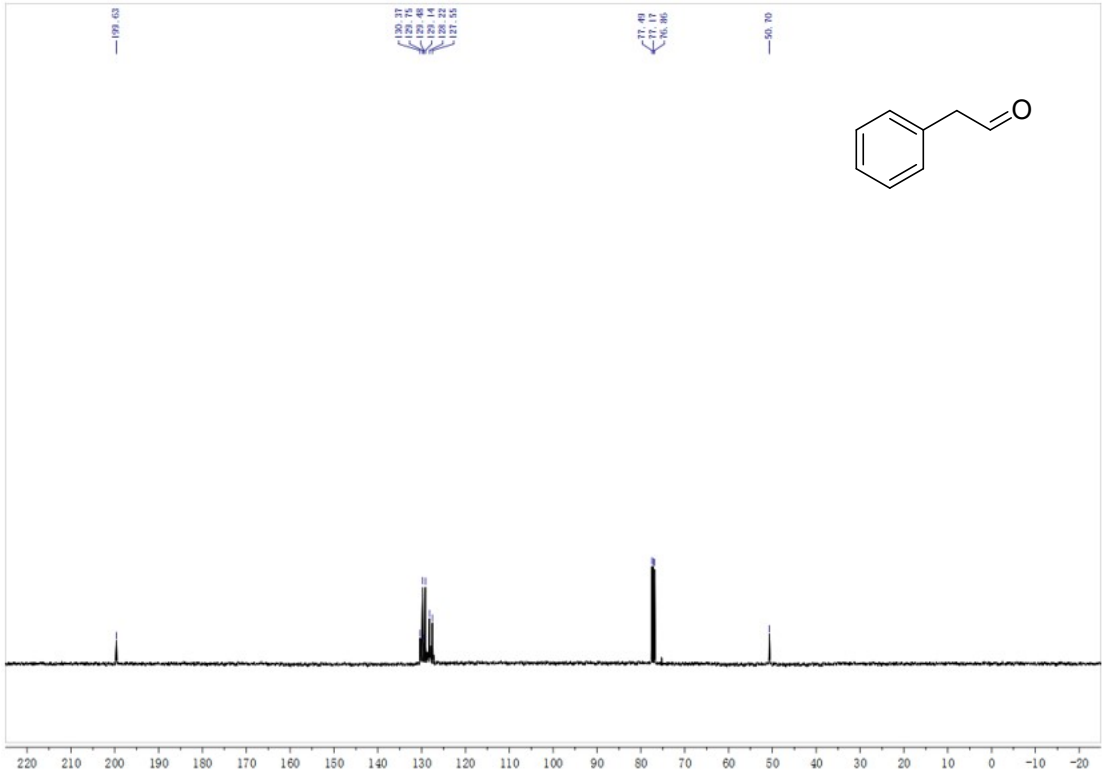
^{1}H NMR spectrum for compound **2af**



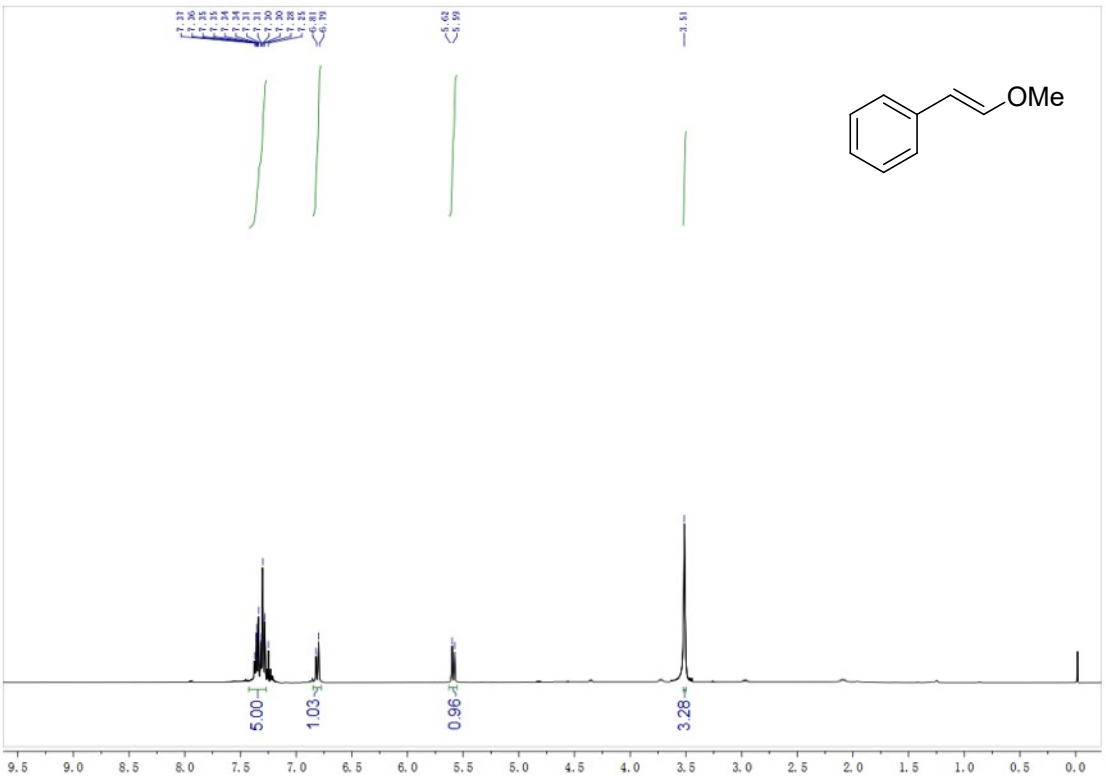
^{13}C{^{1}H} NMR spectrum for compound **2af**



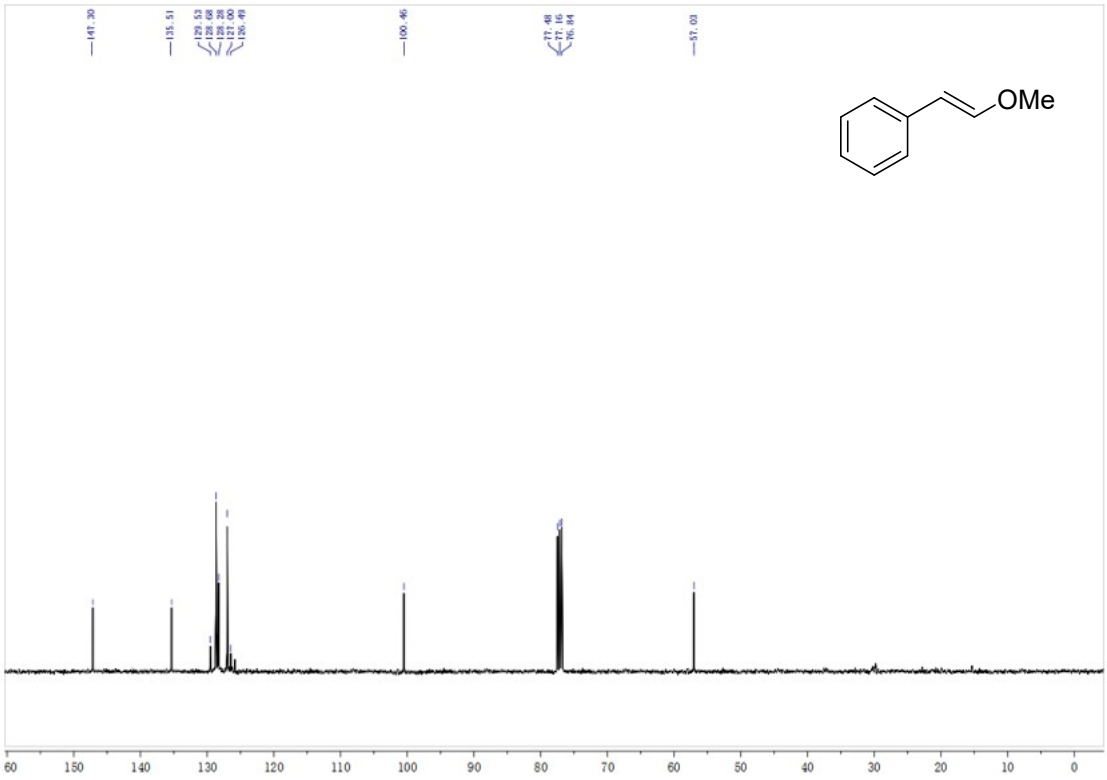
^{1}H NMR spectrum for compound **3**



^{13}C{^{1}H} NMR spectrum for compound **3**



^{1}H NMR spectrum for compound **4**



^{13}C{^{1}H} NMR spectrum for compound **4**