

Support Information

Rh^{III}-Catalyzed Synthesis of Cyclopenta[*b*]carbazoles via Cascade C–H/C–C Bonds Cleavage and Cyclization Reactions: Using Amide as a Traceless Directing Group

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1. Experimental Section:

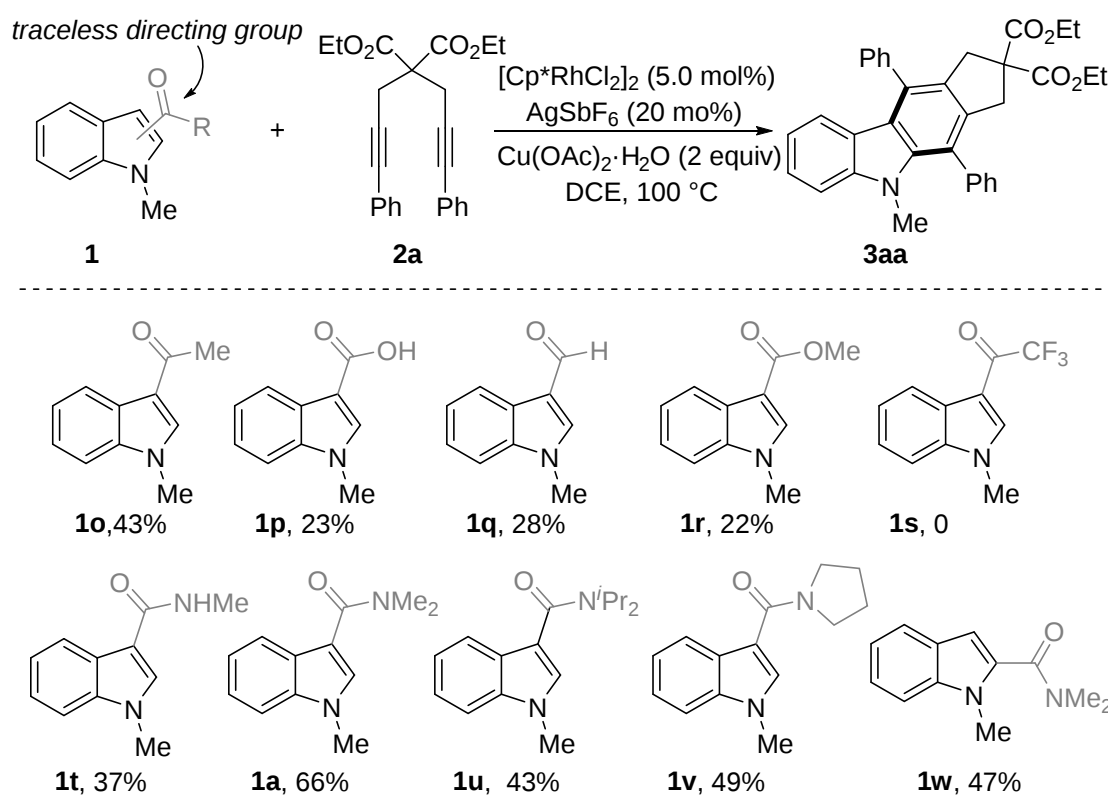
General Considerations: All the reactions were carried out under argon atmosphere using standard sealed Schlenk technique. ^1H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F (376 MHz) were recorded on Bruker AV400 NMR spectrometer with CDCl_3 and $\text{DMSO-}d_6$ as solvent. Chemical shifts of ^1H , ^{13}C and ^{19}F NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl_3 : $\delta \text{H} = 7.26$ ppm, $\delta \text{C} = 77.16$ ppm; $\text{DMSO-}d_6$: $\delta \text{H} = 2.50$ ppm, $\delta \text{C} = 39.43$ ppm). All coupling constants (J values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200–300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm and 365nm). High-resolution mass spectrometry (HRMS) was done on a FTICR-mass spectrometer. Aryl amides or heteroaryl amides **1**¹ were prepared from corresponding acids, and the diynes **2a-n**², **2o**³, **2p**⁵ were prepared according literature procedures. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available without any further purification.

2. Optimization studies.

The effect of directing groups on the cyclization reactions.

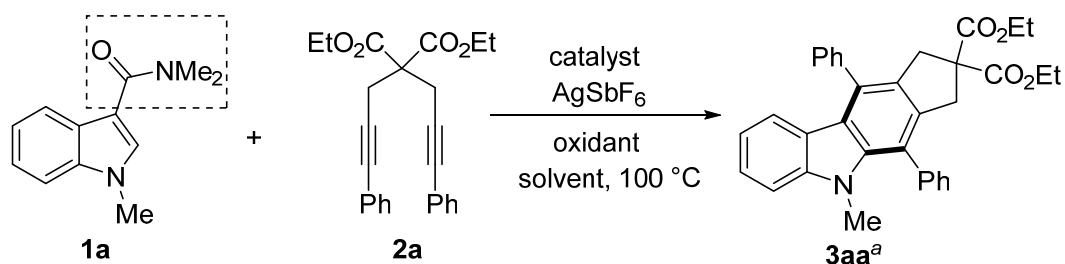
All the reactions were conducted according to the following procedure. A mixture of **1** (0.12 mmol, 1.2 equiv.), **2a** (0.1 mmol, 1.0 equiv), [Cp*RhCl₂]₂ (3.1 mg, 0.005 mmol, 5.0 mol %), AgSbF₆ (6.9 mg, 0.02 mmol, 20.0 mol%) and Cu(OAc)₂·H₂O (40 mg, 0.2 mmol, 2.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry 1,2-dichloroethane (DCE) (1.0 mL) was added and the mixture was stirred at 100 °C in a pre-heated oil bath for 12 h under Ar atmosphere. Afterwards, it was evaporated under reduced pressure and The residue was detected by ¹H NMR (0.1 mmol of 1,1,2,2-tetrachloroethane was added as an internal standard) and the ¹H NMR yields were reported.

Table S1 The effect of directing groups on cyclization reactions.^a



^a Reaction conditions: **1** (0.12 mmol, 1.2 equiv), **2a** (0.1 mmol, 1.0 equiv), [Cp*RhCl₂]₂ (5.0 mol %), AgSbF₆ (20.0 mol%), Cu(OAc)₂·H₂O (0.2 mmol, 2.0 equiv), DCE (1.0 mL), 100 °C, Ar atmosphere, 12 h. NMR yield of **3aa**, 1,1,2,2-tetrachloroethane as internal standard.

Table S2 Optimization of the reaction conditions.^a



Entry	Catalyst	Oxidant	Solvent	Yield (%) ^b
1	[Cp*RhCl ₂] ₂	Cu(OAc) ₂ ·H ₂ O	DCE	76(49) ^c
2	[Cp*RhCl ₂] ₂	Cu(OAc) ₂ ·H ₂ O	CH ₂ Cl ₂	28
3	[Cp*RhCl ₂] ₂	Cu(OAc) ₂ ·H ₂ O	CHCl ₃	62
4	[Cp*RhCl ₂] ₂	Cu(OAc) ₂ ·H ₂ O	dioxane	61
5	[Cp*RhCl ₂] ₂	Cu(OAc) ₂ ·H ₂ O	DMF	27
6	[Cp*RhCl ₂] ₂	Cu(OAc) ₂ ·H ₂ O	DCE	26 ^d , 65 ^e
7	[Cp*RhCl ₂] ₂	Cu(OAc) ₂	DCE	65
8	[Cp*RhCl ₂] ₂	CuOAc	DCE	70
9	[Cp*RhCl ₂] ₂	Ag ₂ CO ₃	DCE	56
10	[Cp*RhCl₂]₂	AgOAc	DCE	96(90)^f
11	[Cp*IrCl ₂] ₂	AgOAc	DCE	14
12	Cp*Co(CO)I ₂	AgOAc	DCE	trace
13	[Ru(<i>p</i> -cymene)Cl ₂] ₂	AgOAc	DCE	trace

^aReaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.12 mmol, 1.2 equiv), catalyst (5.0 mol %), AgSbF₆ (20.0 mol%), oxidant (0.2 mmol, 2.0 equiv), solvent (1.0 mL), 100 °C, Ar atmosphere, 12 h. ^bNMR yield, 1,1,2,2-tetrachloroethane as internal standard. ^cWithout AgSbF₆. ^d80 °C. ^e120 °C. ^fIsolated yield.

3. General Procedure for the Synthesis of 3

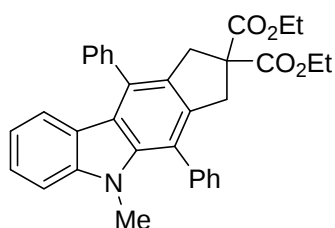
A mixture of **1** (20.2 mg, 0.1 mmol, 1.0 equiv), **2** (46.6 mg, 0.12 mmol, 1.2 equiv), [Cp*RhCl₂]₂ (3.1 mg, 0.005 mmol, 5.0 mol %), AgSbF₆ (6.9 mg, 0.02 mmol, 20.0 mol%) and AgOAc (33.4 mg, 0.2 mmol, 2.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.0 mL) was added and the mixture was stirred at 100 °C in a pre-heated oil bath

for 12 h under Ar atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was absorbed to small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/50 to 1/20).

4. 1.0 mmol Scale for the Synthesis of 3aa

A mixture of **1a** (202 mg, 1.0 mmol, 1.0 equiv), **2a** (466 mg, 1.2 mmol, 1.2 equiv), [Cp*RhCl₂]₂ (31 mg, 0.05 mmol, 5.0 mol %), AgSbF₆ (68.7 mg, 0.2 mmol, 20.0 mol%) and AgOAc (333.8 mg, 2 mmol, 2.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (5.0 mL) was added and the mixture was stirred at 100 °C in a pre-heated oil bath for 12 h under Ar atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was absorbed to small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/50 to 1/20) to give pure product **3aa** in 83% yield (429.1 mg).

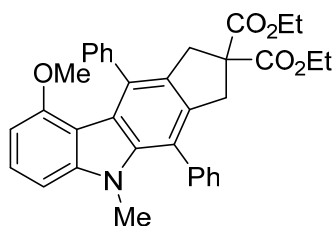
5. Characterization of Products 3



diethyl

5-methyl-4,10-diphenyl-3,5-dihydrocyclopenta[b]carbazole-2,2(1H)-dicarboxylate (3aa)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50 to 1/20), 46.7 mg, 90%, M.p.: 156-158 °C. **¹H NMR(CDCl₃, 400 MHz):** δ 7.58 – 7.43 (m, 10H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.21 (s, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 4H), 3.53 (s, 2H), 3.47 (s, 2H), 3.26 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 6H). **¹³C NMR (CDCl₃, 101 MHz):** δ 171.8, 142.3, 139.6, 138.5, 137.8, 132.2, 130.2, 129.6, 129.2, 128.9, 128.4, 127.5, 125.1, 122.4, 121.9, 121.4, 120.9, 118.6, 108.4, 61.6, 60.7, 40.3, 39.4, 32.4, 14.1. **HRMS (ESI):** Calcd for C₃₄H₃₂NO₄⁺ [M+H]⁺ 518.2326, Found: 518.2337.

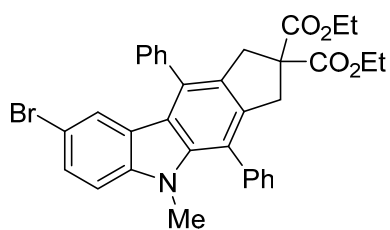


diethyl

9-methoxy-5-methyl-4,10-diphenyl-3,5-dihydrocyclopenta[b]carbazole-2,2(1H)-dicarboxylate (3ba)

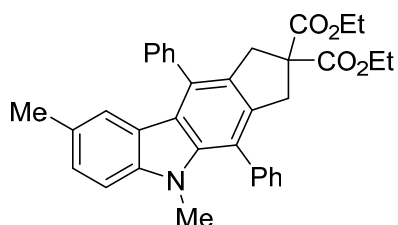
The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/20 to 1/8), 33 mg, 60%, M.p.: 124-126 °C. **¹H NMR(CDCl₃, 400**

¹H NMR (CDCl₃, 400 MHz): δ 7.55 – 7.43 (m, 7H), 7.42 – 7.36 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.42 (d, *J* = 7.9 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 4H), 3.45 (s, 4H), 3.27 (s, 3H), 3.18 (s, 3H), 1.24 – 1.17 (m, 6H). **¹³C NMR** (CDCl₃, 101 MHz): δ 171.8, 155.1, 144.2, 143.5, 138.8, 138.2, 136.6, 132.7, 130.5, 130.2, 129.1, 128.3, 127.3, 127.0, 126.1, 125.8, 121.4, 120.4, 111.4, 101.1, 100.0, 61.4, 60.4, 55.0, 40.5, 40.4, 32.9, 14.0. **HRMS (ESI)**: Calcd for C₃₅H₃₄NO₅⁺ [M+H]⁺ 548.2431, Found: 548.2442.



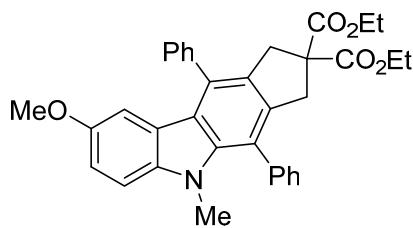
diethyl
8-bromo-5-methyl-4,10-diphenyl-3,5-dihydrocyclopenta[b]
carbazole-2,2(1H)-dicarboxylate (3ca)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50 to 1/20), 47 mg, 79%, M.p.: 205-207 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.62 – 7.45 (m, 10H), 7.38 (d, *J* = 8.7 Hz, 1H), 7.14 – 7.06 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 4H), 3.54 (s, 2H), 3.47 (s, 2H), 3.24 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃): δ 171.6, 140.9, 138.8, 138.7, 138.6, 138.0, 132.3, 130.1, 130.0, 128.9, 128.9, 128.4, 127.8, 127.6, 124.4, 124.0, 121.0, 120.4, 111.3, 109.8, 61.6, 60.5, 40.3, 39.3, 32.4, 14.0. **HRMS (ESI)**: Calcd for C₃₄H₃₁BrNO₄⁺ [M+H]⁺ 596.1431, Found: 596.1431.



diethyl
5,8-dimethyl-4,10-diphenyl-3,5-dihydrocyclopenta[b]car
bazole-2,2(1H)-dicarboxylate (3da)

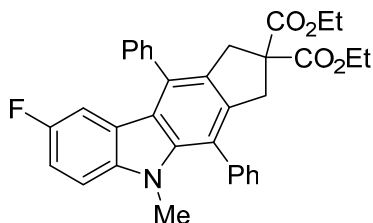
The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50 to 1/20), 35.1 mg, 66%, M.p.: 166-168 °C. **¹H NMR** (CDCl₃, 400 MHz): δ 7.59 – 7.45 (m, 10H), 7.13 (s, 2H), 6.79 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 4H), 3.54 (s, 2H), 3.48 (s, 2H), 3.25 (s, 3H), 2.25 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 6H). **¹³C NMR** (CDCl₃, 101 MHz): δ 171.7, 140.7, 139.6, 138.7, 138.5, 137.4, 132.1, 130.2, 129.2, 129.1, 128.7, 128.3, 127.6, 127.4, 127.4, 126.3, 122.4, 121.8, 121.2, 120.8, 108.0, 61.5, 60.6, 40.3, 39.3, 32.3, 21.4, 14.0. **HRMS (ESI)**: Calcd for C₃₅H₃₄NO₄⁺ [M+H]⁺ 532.2482, Found: 532.2484.



diethyl

8-methoxy-5-methyl-4,10-diphenyl-3,5-dihydrocyclopenta[b]carbazole-2,2(1H)-dicarboxylate (3ea)

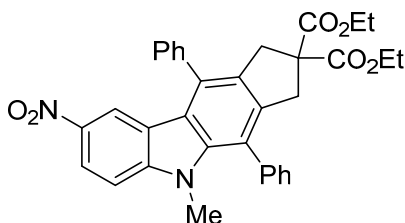
The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/20 to 1/8), 52 mg, 95%, M.p.: 157-159 °C. **¹H NMR(CDCl₃, 400 MHz):** δ 7.52 (m, 10H), 7.12 (s, 1H), 6.99 – 6.92 (m, 1H), 6.48 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 4H), 3.54 (d, *J* = 12.0 Hz, 5H), 3.48 (s, 2H), 3.24 (s, 3H), 1.23 – 1.17 (m, 6H). **¹³C NMR (CDCl₃, 101 MHz):** δ 171.7, 152.8, 139.4, 138.9, 138.4, 137.6, 137.3, 132.0, 130.2, 129.2, 129.0, 128.7, 128.3, 127.5, 127.4, 122.5, 121.1, 120.9, 114.1, 109.0, 104.5, 61.5, 60.6, 55.4, 40.2, 39.2, 32.4, 14.0. **HRMS (ESI):** Calcd for C₃₅H₃₄NO₅⁺ [M+H]⁺ 548.2431, Found: 548.2436.



diethyl

8-fluoro-5-methyl-4,10-diphenyl-3,5-dihydrocyclopenta[b]carbazole-2,2(1H)-dicarboxylate (3fa)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50 to 1/20), 43.9 mg, 82%, M.p.: 169-171 °C. **¹H NMR(CDCl₃, 400 MHz):** δ 7.53 (m, 10H), 7.14 (dd, *J* = 8.8, 4.3 Hz, 1H), 7.05 (t, *J* = 8.9 Hz, 1H), 6.67 (d, *J* = 9.9 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 4H), 3.53 (s, 2H), 3.47 (s, 2H), 3.25 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 6H). **¹³C NMR (CDCl₃, 101 MHz):** δ 171.6, 156.6 (d, *J* = 233.8 Hz), 139.3, 138.9, 138.7, 138.4, 138.1, 132.3, 130.1, 129.6, 128.9, 128.4, 127.8, 127.6, 122.5 (d, *J* = 10.0 Hz), 121.1, 120.8 (d, *J* = 4.2 Hz), 112.7 (d, *J* = 25.7 Hz), 108.8, 108.7, 107.5, 107.3, 61.6, 60.5, 40.3, 39.2, 32.4, 14.0. **¹⁹F NMR (CDCl₃, 376 MHz):** δ -125.3. **HRMS (ESI):** Calcd for C₃₄H₃₁FNO₄⁺ [M+H]⁺ 536.2232, Found: 536.3324.

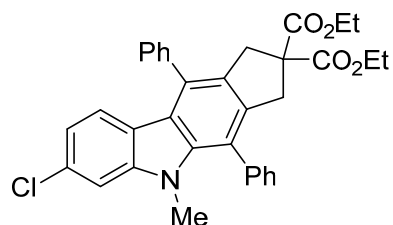


diethyl

5-methyl-8-nitro-4,10-diphenyl-3,5-dihydrocyclopenta[b]carbazole-2,2(1H)-dicarboxylate (3ga)

The title compound was isolated as a yellow solid (eluent: EtOAc/petroleum ether = 1/20 to 1/5), 31.7 mg, 56%, M.p.: 230-232 °C. **¹H NMR(CDCl₃, 400 MHz):** δ 8.21 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.92 (d, *J* = 2.2 Hz, 1H), 7.62 (td, *J* = 8.9, 4.5 Hz, 3H), 7.55 – 7.45 (m, 7H), 7.22 (d, *J* = 9.1 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 4H), 3.57

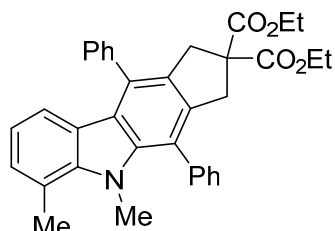
(s, 2H), 3.47 (s, 2H), 3.32 (s, 3H), 1.20 (t, $J = 7.1$ Hz, 6H). **^{13}C NMR (CDCl_3 , 101 MHz):** δ 171.5, 145.1, 140.3, 139.8, 139.4, 138.1, 137.4, 132.8, 131.5, 130.0, 129.3, 128.6, 128.6, 128.3, 128.0, 121.9, 121.3, 120.9, 118.6, 107.9, 61.7, 60.4, 40.3, 39.3, 32.8, 14.0. **HRMS (ESI):** Calcd for $\text{C}_{34}\text{H}_{31}\text{N}_2\text{O}_6^+ [\text{M}+\text{H}]^+$ 563.2177, Found: 563.2179.



diethyl

7-chloro-5-methyl-4,10-diphenyl-3,5-dihydrocyclopenta[b]carbazole-2,2(1H)-dicarboxylate (3ha)

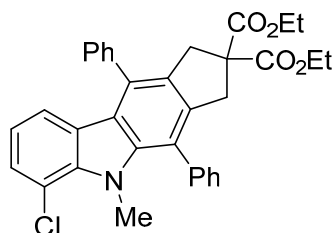
The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50 to 1/20), 39.7 mg, 72%, M.p.: 180-182 °C. **^1H NMR(CDCl_3 , 400 MHz):** δ 7.60 – 7.45 (m, 10H), 7.21 (d, $J = 1.5$ Hz, 1H), 6.90 (d, $J = 8.5$ Hz, 1H), 6.84 (dd, $J = 8.5$, 1.7 Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 4H), 3.53 (s, 2H), 3.47 (s, 2H), 3.23 (s, 3H), 1.20 (t, $J = 7.1$ Hz, 6H). **^{13}C NMR (CDCl_3 , 101 MHz):** δ 171.6, 142.9, 139.1, 138.7, 138.2, 138.1, 132.0, 130.9, 130.1, 130.1, 129.0, 128.9, 128.4, 127.7, 127.6, 122.6, 121.1, 120.9, 120.9, 119.0, 108.5, 61.6, 60.6, 40.3, 39.3, 32.4, 14.0. **HRMS (ESI):** Calcd for $\text{C}_{34}\text{H}_{31}\text{ClNO}_4^+ [\text{M}+\text{H}]^+$ 552.1936, Found: 552.1938.



diethyl

5,6-dimethyl-4,10-diphenyl-3,5-dihydrocyclopenta[b]carbazole-2,2(1H)-dicarboxylate (3ia)

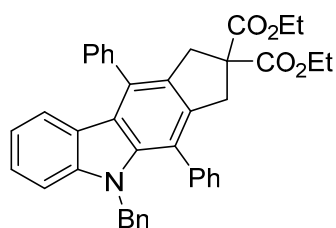
The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50 to 1/20), 43 mg, 81%, M.p.: 125-127 °C. **^1H NMR(CDCl_3 , 400 MHz):** δ 7.59 – 7.48 (m, 9H), 7.47 – 7.41 (m, 1H), 7.04 (d, $J = 7.1$ Hz, 1H), 6.84 (d, $J = 7.7$ Hz, 1H), 6.77 (t, $J = 7.5$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 4H), 3.53 (d, $J = 10.8$ Hz, 4H), 3.47 (s, 3H), 2.70 (s, 3H), 1.20 (t, $J = 7.1$ Hz, 6H). **^{13}C NMR (CDCl_3 , 101 MHz):** δ 171.7, 142.6, 140.7, 139.6, 138.8, 137.5, 131.9, 130.2, 129.9, 129.0, 128.8, 128.4, 127.4, 127.2, 123.8, 122.0, 121.3, 120.6, 119.8, 119.1, 61.5, 60.5, 40.4, 39.3, 36.4, 20.7, 14.0. **HRMS (ESI):** Calcd for $\text{C}_{35}\text{H}_{34}\text{NO}_4^+ [\text{M}+\text{H}]^+$ 532.2482, Found: 532.2488.



diethyl

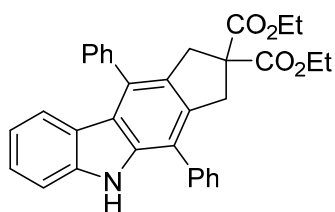
6-chloro-5-methyl-4,10-diphenyl-3,5-dihydrocyclopenta[b]carbazole-2,2(1H)-dicarboxylate (3ja)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50 to 1/20), 51.2 mg, 93%, M.p.: 126-128 °C. **¹H NMR(CDCl₃, 400 MHz):** δ 7.59 – 7.43 (m, 10H), 7.24 (dd, *J* = 7.7, 1.0 Hz, 1H), 6.86 (dd, *J* = 7.9, 1.0 Hz, 1H), 6.75 (t, *J* = 7.8 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 4H), 3.59 (s, 3H), 3.51 (d, *J* = 9.8 Hz, 4H), 1.19 (t, *J* = 7.1 Hz, 6H). **¹³C NMR (CDCl₃, 101 MHz):** δ 171.6, 140.7, 139.1, 138.7, 138.6, 138.3, 132.1, 130.9, 129.9, 128.9, 128.5, 127.7, 127.4, 127.1, 126.2, 121.6, 121.5, 120.4, 119.6, 116.2, 61.6, 60.5, 40.4, 39.3, 36.3, 14.0. **HRMS (ESI):** Calcd for C₃₄H₃₁ClNO₄⁺ [M+H]⁺ 552.1936, Found: 552.1942.



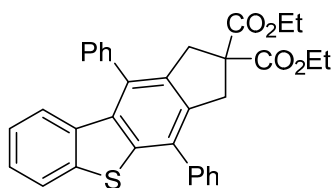
diethyl
5-benzyl-4,10-diphenyl-3,5-dihydrocyclopenta[b]carbazole-2,2(1H)-dicarboxylate (3ka)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50 to 1/20), 52.2 mg, 88%, M.p.: 71-73 °C. **¹H NMR(CDCl₃, 400 MHz):** δ 7.54 – 7.43 (m, 5H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.17 – 7.11 (m, 3H), 7.10 – 7.01 (m, 6H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.81 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 6.1 Hz, 3H), 4.96 (s, 2H), 4.05 (q, *J* = 7.1 Hz, 4H), 3.46 (s, 2H), 3.28 (s, 2H), 1.10 (t, *J* = 7.1 Hz, 6H). **¹³C NMR (CDCl₃, 101 MHz):** δ 171.7, 141.9, 139.5, 138.0, 137.7, 132.2, 129.8, 129.7, 129.1, 128.8, 128.1, 127.5, 127.3, 126.6, 125.5, 125.2, 122.5, 121.9, 121.6, 121.1, 118.9, 109.0, 61.5, 60.4, 47.6, 40.3, 39.4, 14.0. **HRMS (ESI):** Calcd for C₄₀H₃₆NO₄⁺ [M+H]⁺ 594.2639, Found: 594.2646.



diethyl
4,10-diphenyl-3,5-dihydrocyclopenta[b]carbazole-2,2(1H)-dicarboxylate (3la)

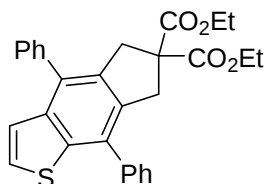
The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/30 to 1/10), 37.7 mg, 75%, M.p.: 179-181 °C. **¹H NMR(CDCl₃, 400 MHz):** δ 8.06 (s, 1H), 7.64 – 7.45 (m, 10H), 7.28 (dd, *J* = 10.0, 6.4 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.90 (t, *J* = 6.7 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 4H), 3.70 (s, 2H), 3.57 (s, 2H), 1.21 (t, *J* = 7.1 Hz, 6H). **¹³C NMR (CDCl₃, 101 MHz):** δ 171.7, 139.8, 139.3, 137.9, 136.9, 136.0, 132.1, 130.7, 129.2, 129.1, 128.7, 127.7, 127.5, 125.1, 123.3, 122.0, 121.0, 120.1, 119.0, 110.3, 61.6, 60.9, 39.9, 39.3, 14.0. **HRMS (ESI):** Calcd for C₃₃H₃₀NO₄⁺ [M+H]⁺ 504.2169, Found: 504.2167.



diethyl

4,10-diphenyl-1,3-dihydro-2H-benzo[b]indeno[5,6-d]thiophene-2,2-dicarboxylate (3ma)

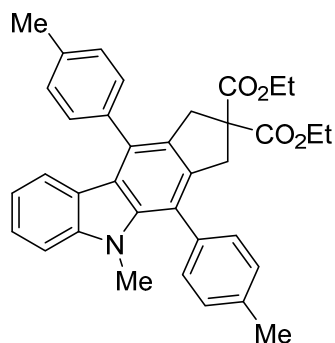
The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50 to 1/20), 47.8 mg, 92%, M.p.: 138-140 °C. **¹H NMR (CDCl₃, 400 MHz):** δ 7.73 (d, *J* = 7.9 Hz, 1H), 7.61 (dt, *J* = 21.0, 7.1 Hz, 7H), 7.52 – 7.44 (m, 3H), 7.31 – 7.26 (m, 1H), 7.08 – 7.01 (m, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 4H), 3.68 (s, 2H), 3.49 (s, 2H), 1.23 (t, *J* = 7.1 Hz, 6H). **¹³C NMR (CDCl₃, 101 MHz):** δ 171.4, 139.9, 139.6, 139.3, 138.8, 137.2, 136.6, 135.9, 134.0, 132.7, 131.9, 129.2, 128.8, 128.8, 128.8, 128.1, 127.8, 125.6, 124.5, 123.6, 122.4, 61.7, 60.5, 40.0, 39.7, 14.0. **HRMS (ESI):** Calcd for C₃₃H₂₉O₄S⁺ [M+H]⁺ 521.1781, Found: 521.1781.



diethyl

4,8-diphenyl-5,7-dihydro-6H-indeno[5,6-b]thiophene-6,6-dicarboxylate (3na)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50 to 1/20), 29 mg, 62%, M.p.: 107-109 °C. **¹H NMR (CDCl₃, 400 MHz):** δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 5.0 Hz, 1H), 7.29 – 7.20 (m, 4H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.34 (d, *J* = 5.4 Hz, 1H), 5.95 (s, 1H), 4.60 – 4.38 (m, 1H), 3.68 – 3.51 (m, 1H), 3.33 (dd, *J* = 10.1, 4.3 Hz, 1H), 2.51 (s, 3H), 2.17 (s, 3H). **¹³C NMR (CDCl₃, 101 MHz):** δ 152.9, 150.9, 143.4, 138.8, 138.7, 137.2, 134.0, 128.9, 128.8, 128.1, 128.0, 110.5, 59.2, 45.46, 13.9, 13.6. **HRMS (ESI):** Calcd for C₂₉H₂₇O₄S⁺ [M+H]⁺ 471.1625, Found: 471.1620.

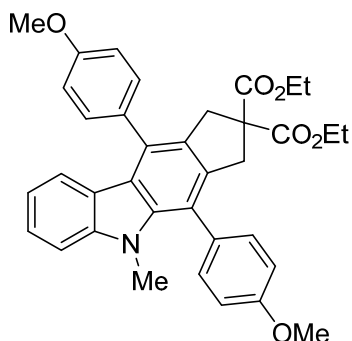


diethyl

5-methyl-4,10-di-p-tolyl-3,5-dihydrocyclopenta[b]carbazole-2,2(1H)-dicarboxylate (3ab)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50 to 1/20), 45.1 mg, 83%, M.p.: 144-146 °C. **¹H NMR (CDCl₃, 400 MHz):** δ 7.43 – 7.29 (m, 9H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 4H), 3.54 (s, 2H), 3.48 (s, 2H), 3.29 (s, 3H), 2.52 (s, 3H), 2.48 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 6H). **¹³C NMR (CDCl₃, 101 MHz):** δ 171.8, 142.3, 138.6, 137.9, 137.1, 137.1, 136.6, 135.5, 132.1,

131.6, 130.1, 129.7, 129.5, 129.0, 124.9, 122.5, 122.0, 121.4, 120.8, 118.5, 108.3, 61.5, 60.6, 40.4, 39.5, 32.4, 21.5, 21.4, 14.1. **HRMS (ESI):** Calcd for $C_{36}H_{36}NO_4^+$ $[M+H]^+$ 546.2639, Found: 546.2641.



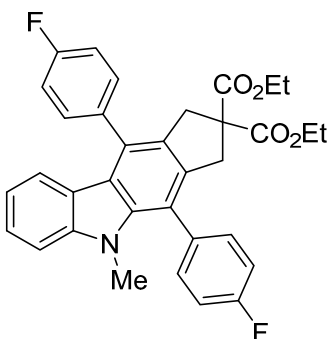
diethyl

4,10-bis(4-methoxyphenyl)-5-methyl-3,5-dihydrocyclopenta[b]carbazole-2,2(1H)-dicarboxylate (3ac)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/20 to 1/5), 41.5 mg, 72%, M.p.: 170-172 °C. **1H NMR (400 MHz, $CDCl_3$):** δ 7.46 (d, J = 8.5 Hz,

2H), 7.41 (d, J = 8.5 Hz, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.29 (s, 1H), 7.14 (t, J = 7.0 Hz, 3H), 7.07 (d, J = 8.5 Hz, 2H), 6.93 (t, J = 7.4 Hz, 1H), 4.18 (q, J = 7.1 Hz, 4H), 3.97 (d, J = 11.7 Hz, 6H), 3.57 (s, 2H), 3.51 (s, 2H), 3.33 (s, 3H), 1.23 (t, J = 7.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 171.8, 159.0, 159.0, 142.3, 138.8, 138.1, 131.8, 131.7, 131.2, 130.6, 130.3, 129.9, 125.0, 122.5, 121.9, 121.6, 120.4, 118.5, 114.2, 113.7, 108.3, 61.5, 60.6, 55.4, 40.4, 39.5, 32.3, 14.1.

HRMS (ESI): Calcd for $C_{36}H_{36}NO_6^+$ $[M+H]^+$ 578.2537, Found: 578.2543.

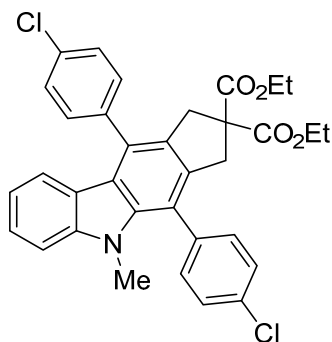


diethyl

4,10-bis(4-fluorophenyl)-5-methyl-3,5-dihydrocyclopenta[b]carbazole-2,2(1H)-dicarboxylate (3ad)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50 to 1/20), 48.9 mg, 88%, M.p.: 88-90 °C. **1H NMR($CDCl_3$, 400 MHz):** δ 7.55 – 7.44 (m, 4H),

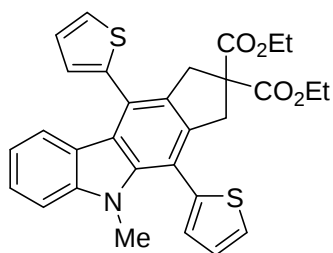
7.37 (t, J = 7.2 Hz, 1H), 7.32 – 7.22 (m, 5H), 7.06 (d, J = 7.9 Hz, 1H), 6.95 (t, J = 7.4 Hz, 1H), 4.19 (q, J = 7.1 Hz, 4H), 3.54 (s, 2H), 3.48 (s, 2H), 3.32 (s, 3H), 1.24 (t, J = 7.1 Hz, 6H). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 171.6, 162.4 (d, J = 246.2 Hz), 162.3 (d, J = 246.7 Hz), 142.3, 138.5, 137.9, 135.3 (d, J = 2.9 Hz), 134.2 (d, J = 3.6 Hz), 131.7 (d, J = 7.7 Hz), 131.2, 130.7 (d, J = 7.7 Hz), 129.8, 125.2, 122.1, 121.7, 121.5, 119.9, 118.7, 115.8 (d, J = 21.3 Hz), 115.4 (d, J = 21.5 Hz), 108.5, 61.6, 60.6, 40.3, 39.3, 32.4, 14.0. **^{19}F NMR ($CDCl_3$, 376 MHz):** δ -114.4, -114.7. **HRMS (ESI):** Calcd for $C_{34}H_{30}F_2NO_4^+$ $[M+H]^+$ 554.2137, Found: 554.2144.



diethyl

4,10-bis(4-chlorophenyl)-5-methyl-3,5-dihydrocyclopenta[b]carbazole-2,2(1H)-dicarboxylate (3ae)

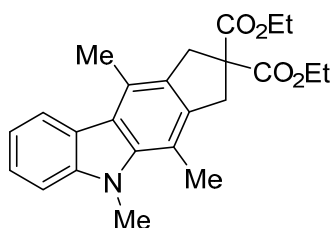
The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50 to 1/20), 43.9 mg, 75%, M.p.: 168-170 °C. **¹H NMR(CDCl₃, 400 MHz):** δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.43 (dd, *J* = 15.4, 8.3 Hz, 4H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 4.1 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 4.19 – 4.12 (m, 4H), 3.50 (s, 2H), 3.44 (s, 2H), 3.30 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 6H). **¹³C NMR (CDCl₃, 101 MHz):** δ 171.5, 142.3, 138.4, 137.8, 137.8, 136.8, 133.6, 133.6, 131.4, 131.1, 130.5, 129.7, 129.1, 128.6, 125.4, 122.0, 121.7, 121.3, 119.8, 118.8, 108.5, 61.6, 60.5, 40.2, 39.2, 32.5, 14.0. **HRMS (ESI):** Calcd for C₃₄H₃₀Cl₂NO₄⁺ [M+H]⁺ 586.1546, Found: 586.1546.



diethyl

5-methyl-4,10-di(thiophen-2-yl)-3,5-dihydrocyclopenta[b]carbazole-2,2(1H)-dicarboxylate (3af)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/30 to 1/10), 44.4 mg, 84%, M.p.: 116-118 °C. **¹H NMR (CDCl₃, 400 MHz):** δ 7.54 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.48 (dd, *J* = 4.8, 3.0 Hz, 1H), 7.38 (dd, *J* = 2.9, 1.1 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.27 – 7.22 (m, 2H), 7.22 – 7.14 (m, 2H), 6.95 (t, *J* = 7.5 Hz, 1H), 4.15 (q, *J* = 7.0 Hz, 4H), 3.54 (dd, *J* = 26.4, 11.2 Hz, 4H), 3.33 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 6H). **¹³C NMR (CDCl₃, 101 MHz):** δ 171.7, 142.2, 139.2, 138.9, 138.4, 137.9, 130.3, 129.9, 128.7, 127.2, 125.9, 125.5, 125.2, 123.9, 123.0, 122.2, 121.9, 121.7, 118.7, 115.7, 108.4, 61.6, 60.4, 40.4, 39.5, 31.6, 14.0. **HRMS (ESI):** Calcd for C₃₀H₂₈NO₄S₂⁺ [M+H]⁺ 530.1454, Found: 530.1457.

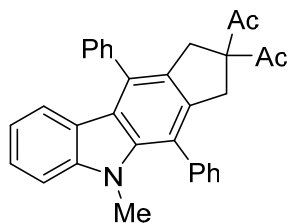


diethyl

4,5,10-trimethyl-3,5-dihydrocyclopenta[b]carbazole-2,2(1H)-dicarboxylate (3ag)

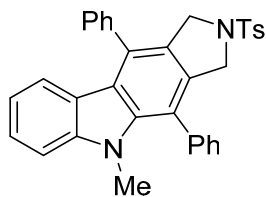
The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50 to 1/20), 20.3 mg, 52%, M.p.: 168-170 °C. **¹H NMR(CDCl₃, 400 MHz):** δ 8.16 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.20 (t,

$J = 7.4$ Hz, 1H), 4.28 – 4.20 (m, 4H), 4.07 (s, 3H), 3.73 (d, $J = 4.5$ Hz, 4H), 2.74 (d, $J = 7.8$ Hz, 6H), 1.29 (t, $J = 7.1$ Hz, 6H). **^{13}C NMR (CDCl₃, 101 MHz):** δ 172.0, 142.2, 139.9, 137.8, 130.0, 125.7, 124.4, 123.5, 122.2, 121.9, 118.6, 113.1, 108.2, 61.7, 59.8, 40.1, 39.1, 32.7, 17.1, 16.0, 14.1. **HRMS (ESI):** Calcd for C₂₄H₂₈NO₄⁺ [M+H]⁺ 394.2013, Found: 394.2013.



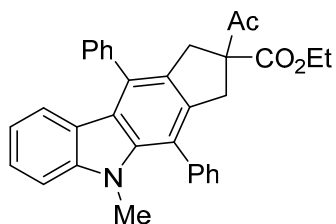
1,1'-(5-methyl-4,10-diphenyl-1,2,3,5-tetrahydrocyclopenta[b]carbazole-2,2-diyl)bis(ethan-1-one) (3ah)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/20 to 1/8), 43.6 mg, 95%, M.p.: 196-198 °C. **^1H NMR(CDCl₃, 400 MHz):** δ 7.52 (ddt, $J = 30.2, 15.0, 7.4$ Hz, 10H), 7.32 (t, $J = 7.6$ Hz, 1H), 7.26 – 7.22 (m, 1H), 6.98 (d, $J = 7.9$ Hz, 1H), 6.88 (t, $J = 7.4$ Hz, 1H), 3.43 (s, 2H), 3.37 (s, 2H), 3.26 (s, 3H), 2.08 (s, 6H). **^{13}C NMR (CDCl₃, 101 MHz):** δ 205.5, 142.3, 139.4, 138.4, 138.3, 137.3, 132.4, 130.0, 129.1, 129.0, 128.5, 127.7, 127.6, 125.2, 122.2, 121.8, 121.4, 121.1, 118.7, 108.4, 74.7, 37.6, 36.8, 32.3, 26.7. **HRMS (ESI):** Calcd for C₃₂H₂₈NO₂⁺ [M+H]⁺ 458.2115, Found: 458.2115



5-methyl-4,10-diphenyl-2-tosyl-1,2,3,5-tetrahydropyrrolo[3,4-b]carbazole (3ai)

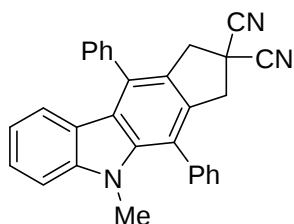
The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/20 to 1/8), 47 mg, 89%, M.p.: 241-243 °C. **^1H NMR(CDCl₃, 400 MHz):** δ 7.70 (d, $J = 8.2$ Hz, 3H), 7.55 (dd, $J = 21.1, 7.0$ Hz, 8H), 7.46 – 7.43 (m, 2H), 7.41 – 7.35 (m, 3H), 7.31 (d, $J = 8.3$ Hz, 2H), 7.27 (s, 1H), 7.02 (d, $J = 7.9$ Hz, 1H), 6.92 (t, $J = 7.4$ Hz, 1H), 4.58 (s, 2H), 4.53 (s, 2H), 3.28 (s, 3H), 2.42 (s, 3H). **^{13}C NMR (CDCl₃, 101 MHz):** δ 143.5, 142.4, 138.5, 138.3, 137.2, 133.7, 133.6, 131.0, 129.7, 129.7, 129.1, 128.6, 128.6, 128.1, 127.6, 125.7, 125.6, 122.0, 121.9, 119.5, 118.9, 108.5, 53.9, 53.3, 32.3, 21.5. **HRMS (ESI):** Calcd for C₃₄H₂₉N₂O₂S⁺ [M+H]⁺ 529.1944, Found: 529.1941.



ethyl 2-acetyl-5-methyl-4,10-diphenyl-1,2,3,5-tetrahydrocyclopenta[b]carbazole-2-carboxylate (3aj)

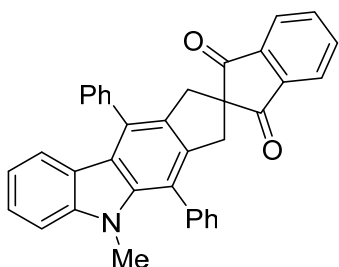
The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/30 to 1/10), 44.8 mg, 92%, M.p.: 181-183 °C. **^1H NMR(CDCl₃, 400 MHz):** δ 7.63 – 7.47 (m, 10H), 7.33 (t, $J = 7.6$ Hz, 2H), 7.25 (d, $J = 8.2$ Hz, 1H), 7.02 (d, J

= 7.2 Hz, 1H), 6.94 – 6.86 (m, 1H), 4.18 (q, J = 7.1 Hz, 3H), 3.54 (d, J = 16.3 Hz, 1H), 3.45 (d, J = 13.6 Hz, 3H), 3.28 (s, 3H), 2.16 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H). **^{13}C NMR (CDCl_3 , 101 MHz):** δ 203.2, 172.4, 142.2, 139.5, 138.4, 138.4, 137.5, 132.2, 130.1, 129.3, 129.0, 128.9, 128.4, 128.3, 127.5, 127.5, 125.0, 122.2, 121.8, 121.4, 120.9, 118.56, 108.3, 67.0, 61.6, 38.8, 38.0, 32.3, 26.2, 14.0. **HRMS (ESI):** Calcd for $\text{C}_{33}\text{H}_{30}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$ 488.2220, Found: 488.2227.



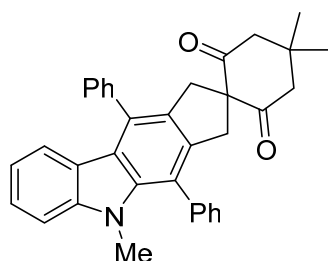
5-methyl-4,10-diphenyl-3,5-dihydrocyclopenta[*b*]carbazole-2,2(1*H*)-dicarbonitrile (3ak)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/30 to 1/10), 36.4 mg, 86%, M.p.: 240-242 °C. **^1H NMR(CDCl_3 , 400 MHz):** δ 7.63 – 7.43 (m, 10H), 7.38 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 8.3 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 3.68 (s, 2H), 3.61 (s, 2H), 3.31 (s, 3H). **^{13}C NMR (CDCl_3 , 101 MHz):** δ 142.6, 138.9, 138.3, 137.2, 133.5, 133.0, 129.9, 129.1, 128.8, 128.7, 128.2, 125.9, 125.6, 122.5, 122.1, 121.9, 121.5, 119.2, 116.5, 108.7, 44.5, 43.7, 33.8, 32.3. **HRMS (ESI):** Calcd for $\text{C}_{30}\text{H}_{22}\text{N}_3^+$ $[\text{M}+\text{H}]^+$ 424.1808, Found: 424.1809.



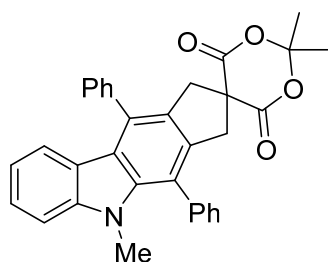
5-methyl-4,10-diphenyl-3,5-dihydro-1*H*-spiro[cyclopenta[*b*]carbazole-2,2'-indene]-1',3'-dione (3al)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/20 to 1/10), 38.7 mg, 77%, M.p.: 283-285 °C. **^1H NMR(CDCl_3 , 400 MHz):** δ 7.93 (dd, J = 5.6, 3.1 Hz, 2H), 7.79 (dd, J = 5.7, 3.1 Hz, 2H), 7.54 – 7.48 (m, 6H), 7.44 (t, J = 7.2 Hz, 3H), 7.38 (t, J = 7.1 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.24 (d, J = 6.0 Hz, 1H), 7.02 (d, J = 7.9 Hz, 1H), 6.88 (t, J = 7.5 Hz, 1H), 3.30 (d, J = 3.3 Hz, 5H), 3.24 (s, 2H). **^{13}C NMR (CDCl_3 , 101 MHz):** δ 203.0, 142.4, 141.4, 139.6, 138.8, 138.5, 138.2, 135.7, 132.0, 131.3, 130.2, 129.9, 129.1, 128.7, 128.3, 127.5, 125.1, 123.5, 122.4, 121.9, 121.8, 120.7, 118.6, 108.3, 58.9, 40.3, 40.1, 32.3. **HRMS (ESI):** Calcd for $\text{C}_{36}\text{H}_{26}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$ 504.1958, Found: 504.1961.



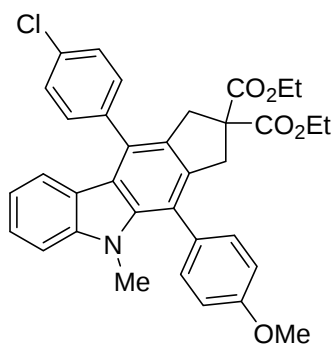
4,4,5'-trimethyl-4',10'-diphenyl-3',5'-dihydro-1*H*-spiro[cyclohexane-1,2'-cyclopenta[*b*]carbazole]-2,6-dione (3am)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/20 to 1/10), 35.6 mg, 72%, M.p.: 230-232 °C. **¹H NMR(CDCl₃, 400 MHz):** δ 7.58 – 7.53 (m, 2H), 7.49 (p, *J* = 4.2 Hz, 7H), 7.47 – 7.42 (m, 1H), 7.29 (t, *J* = 7.1 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 3.36 (d, *J* = 4.2 Hz, 4H), 3.24 (s, 3H), 2.66 (d, *J* = 14.1 Hz, 2H), 2.51 (d, *J* = 14.1 Hz, 2H), 0.98 (s, 3H), 0.88 (s, 3H). **¹³C NMR (CDCl₃, 101 MHz):** δ 206.9, 142.3, 139.6, 138.7, 138.5, 137.9, 132.0, 130.2, 129.1, 128.9, 128.3, 128.2, 127.5, 127.5, 125.0, 122.3, 121.7, 121.5, 120.7, 118.5, 108.3, 71.2, 51.3, 39.6, 36.9, 32.2, 30.5, 28.8, 27.6. **HRMS (ESI):** Calcd for C₃₅H₃₂NO₂⁺ [M+H]⁺ 498.2428, Found: 498.2433.



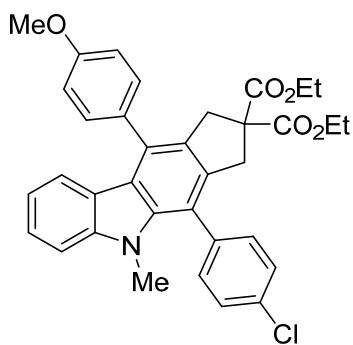
2,2',5-trimethyl-4,10-diphenyl-3,5-dihydro-1H-spiro[cyclopenta[b]carbazole-2,5'-[1,3]dioxane]-4',6'-dione (3an)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/20 to 1/5), 37.3 mg, 74%, M.p.: 178-180 °C. **¹H NMR(CDCl₃, 400 MHz):** δ 7.58 – 7.43 (m, 10H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.23 (s, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.88 (t, *J* = 7.2 Hz, 1H), 3.65 (s, 2H), 3.60 (s, 2H), 3.27 (s, 3H), 1.69 (d, *J* = 4.3 Hz, 6H). **¹³C NMR (CDCl₃, 101 MHz):** δ 170.9, 142.4, 139.2, 138.9, 138.1, 136.8, 131.9, 130.1, 129.0, 128.9, 128.4, 128.2, 127.7, 127.7, 125.3, 122.2, 122.0, 121.9, 120.5, 118.7, 108.4, 104.9, 52.46, 45.3, 45.0, 32.2, 29.0, 28.9. **HRMS (ESI):** Calcd for C₃₃H₂₈NO₄⁺ [M+H]⁺ 502.2013, Found: 502.2018.



1-((4-Chlorophenyl)sulfonyl)-5-phenylimidazolidin-2-one (3ao)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50), 32 mg, 55%, M.p.: 187-189 °C. **¹H NMR(CDCl₃, 400 MHz):** δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 5.9 Hz, 1H), 7.06 (dd, *J* = 10.7, 8.3 Hz, 3H), 6.96 – 6.89 (m, 1H), 4.15 (q, *J* = 7.1 Hz, 4H), 3.92 (s, 3H), 3.49 (d, *J* = 9.8 Hz, 4H), 3.31 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 6H). **¹³C NMR (CDCl₃, 101 MHz):** δ 171.7, 159.0, 142.3, 138.8, 138.2, 138.1, 133.5, 131.2, 130.7, 130.6, 130.4, 129.6, 129.1, 125.2, 122.1, 121.7, 121.1, 121.0, 118.7, 113.8, 108.5, 61.6, 60.6, 55.4, 40.3, 39.3, 32.4, 14.1. **HRMS (ESI):** Calcd for C₃₅H₃₃ClNO₅⁺ [M+H]⁺ 582.2024, Found: 582.2050.



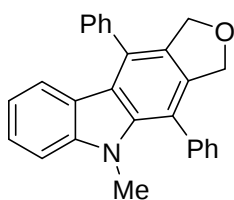
1-((4-Chlorophenyl)sulfonyl)-5-met

hylimidazolidin-2-one (3ao')

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50), 15.7 mg, 27%, M.p.: 168-170 °C.

¹H NMR(CDCl₃, 400 MHz): δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 4H), 7.33 (t, *J* = 7.1 Hz, 1H), 7.23 (s, 1H), 7.10 (dd, *J*

= 8.2, 3.5 Hz, 3H), 6.91 (t, *J* = 7.2 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 4H), 3.95 (s, 3H), 3.53 (s, 2H), 3.44 (s, 2H), 3.29 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 6H). **¹³C NMR (CDCl₃, 101 MHz):** δ 171.6, 159.0, 142.2, 138.4, 137.6, 137.0, 133.5, 132.2, 131.5, 131.5, 130.2, 130.0, 128.6, 125.1, 122.4, 121.9, 121.8, 119.2, 118.7, 114.2, 108.4, 61.6, 60.5, 55.3, 40.3, 39.4, 32.5, 14.0. **HRMS (ESI):** Calcd for C₃₅H₃₃ClNO₅⁺ [M+H]⁺ 582.2024, Found: 582.2048.



5-Methyl-4,10-diphenyl-3,5-dihydro-1H-fur

o[3,4-b]carbazole (3ap)

The title compound was isolated as a white solid (eluent: EtOAc/petroleum ether = 1/50 to 1/20), 15.8 mg, 42%, M.p.: 73-75 °C.

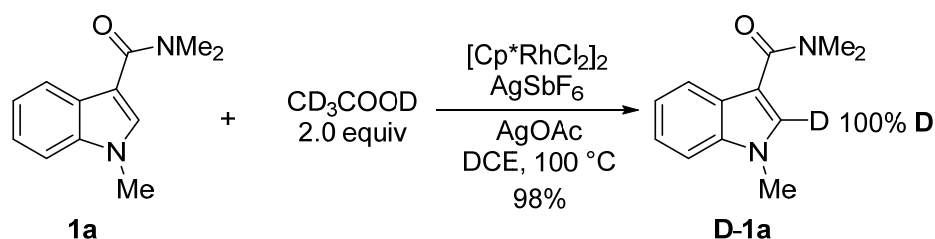
¹H NMR(CDCl₃, 400 MHz): δ 7.58 – 7.45 (m, 10H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 5.12 (s, 2H), 5.05 (s, 2H), 3.33 (s, 3H).

¹³C NMR (CDCl₃, 101 MHz): δ 142.6, 139.0, 138.8, 137.9, 137.2, 129.7, 129.7, 129.1, 128.9, 128.7, 128.4, 127.8, 127.6, 125.4, 122.2, 120.0, 121.8, 118.8, 118.2, 108.5, 73.9, 73.6, 32.5.

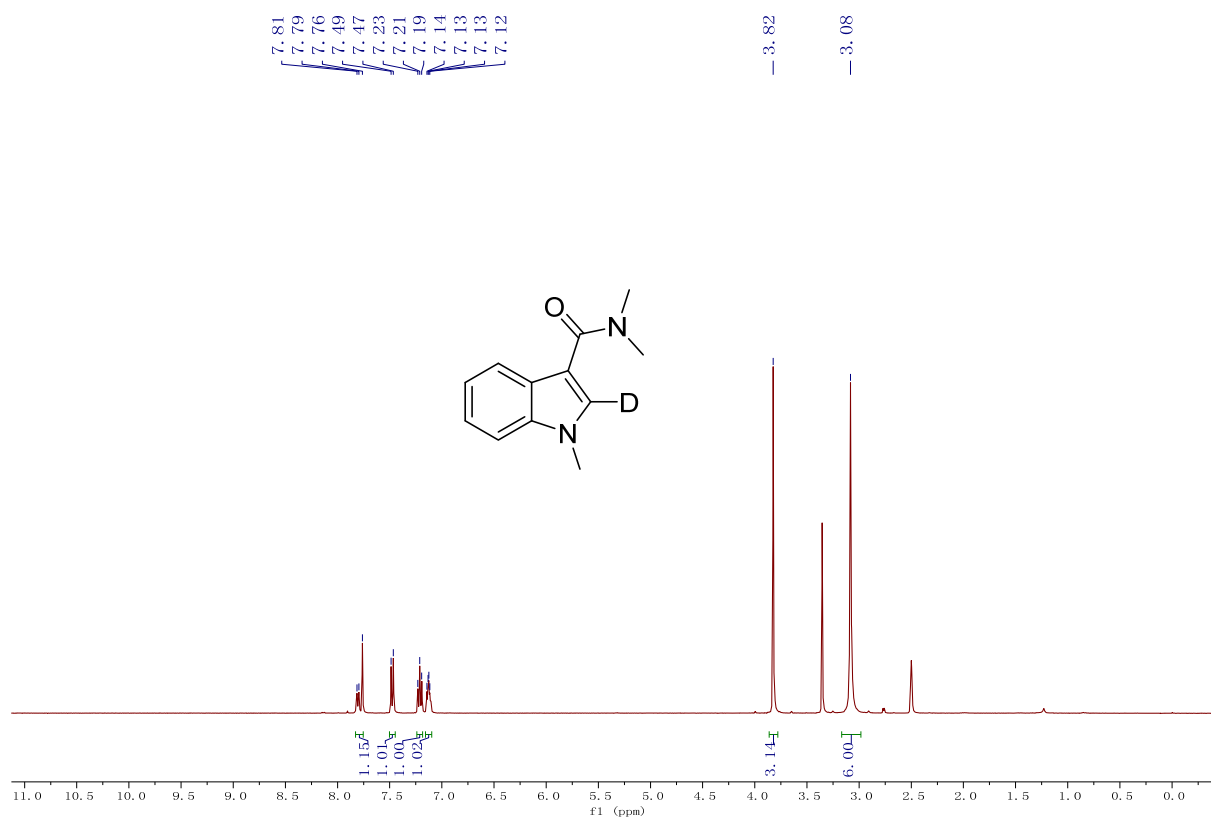
HRMS (ESI): Calcd for C₂₇H₂₂NO⁺ [M+H]⁺ 376.1696, Found: 376.1691.

6. Mechanism Research

H/D exchange experiments:



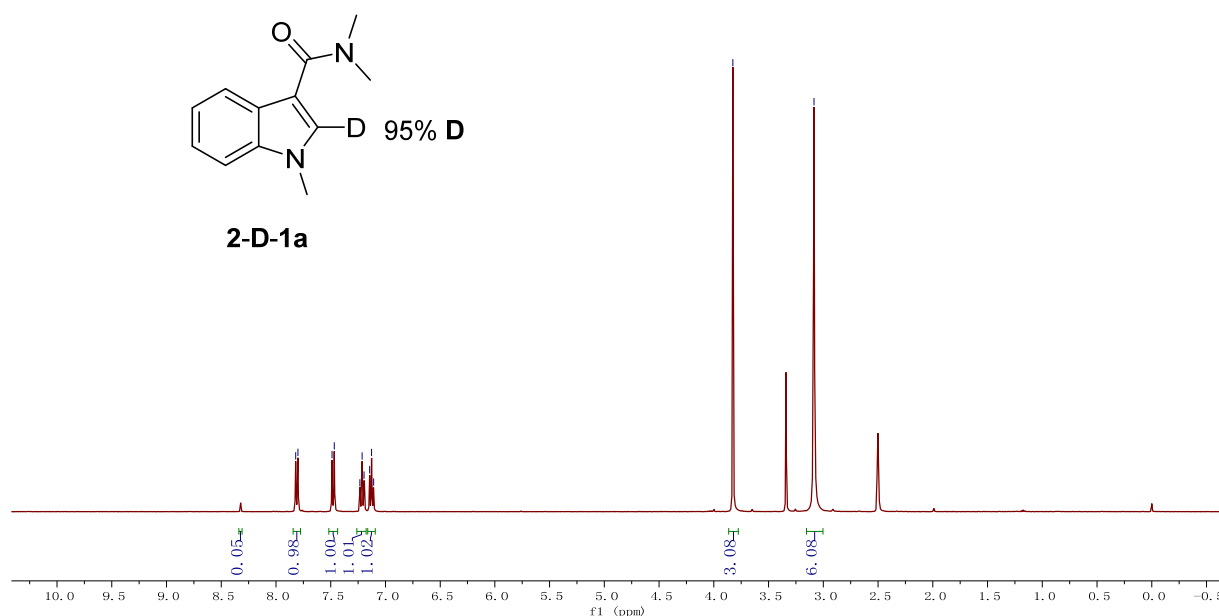
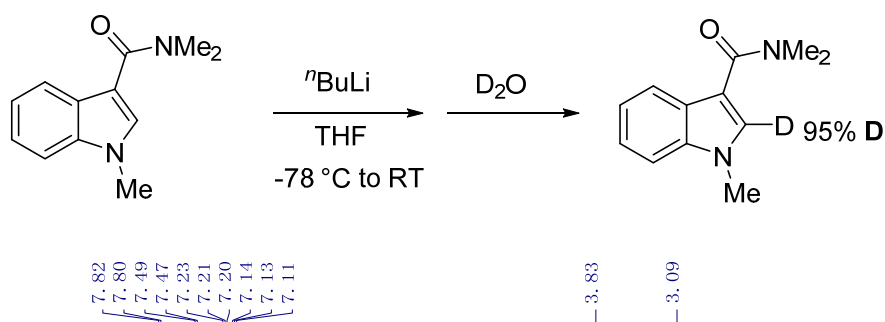
A mixture of **1** (20.2 mg, 0.1 mmol, 1.0 equiv), CD_3COOD (25.6 mg, 0.4 mmol, 2.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 0.005 mmol, 5.0 mol %), AgSbF_6 (6.9 mg, 0.02 mmol, 20.0 mol%) and AgOAc (33.4 mg, 0.2 mmol, 2.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.0 mL) was added and the mixture was stirred at 100°C in a pre-heated oil bath for 12 h under Ar atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was absorbed to small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/3 to 1/1). The ^1H NMR spectra of the **D-1a** was shown as below:



KIE experiments:

Procedure for the Preparation of 2-D-1a

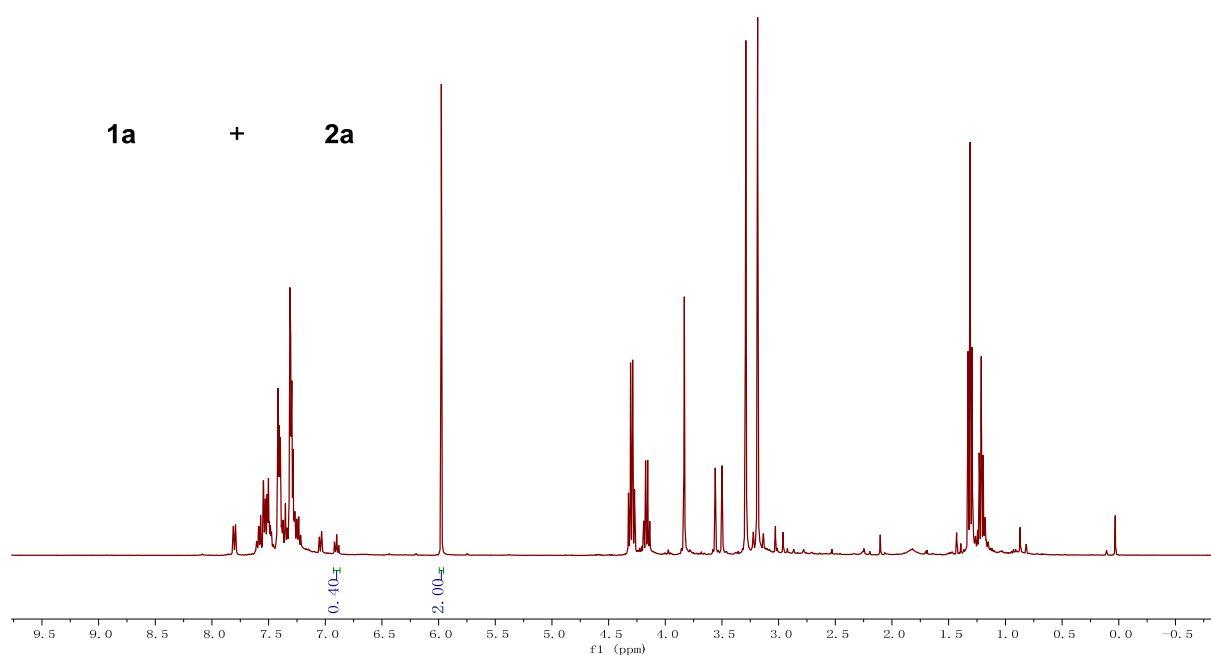
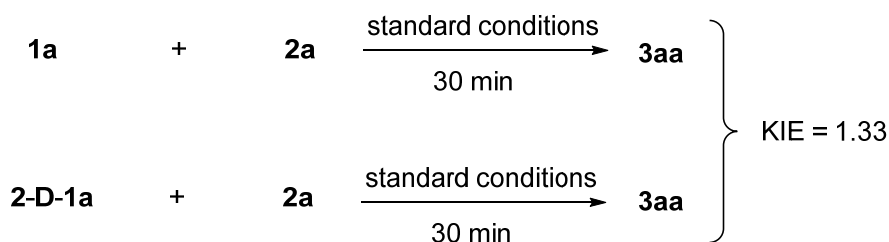
2-D-1a was prepared according the literature method with little improvement⁴. To a stirring solution of **1a** (606 mg, 3.0 mmol, 1.0 equiv) in dry THF (20 mL) under Ar atmosphere, n-butyllithium (2.5 M, 9.0 mmol, 3.0 equiv) was added dropwise at -78 °C. The reaction mixture was allowed to warm to room temperature stirred for 12 h. The solution was then re-cooled to -78 °C, and D₂O (2 mL) was added dropwise. The reaction was allowed again to warm to room temperature and stirred for 2 h during. The reaction was quenched with solid K₂CO₃ and stirred with 30 mL of anhydrous ether for 30 minutes. Then the reaction mixture was filtered and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography. Yield: 579 mg, 95%, as white solid.

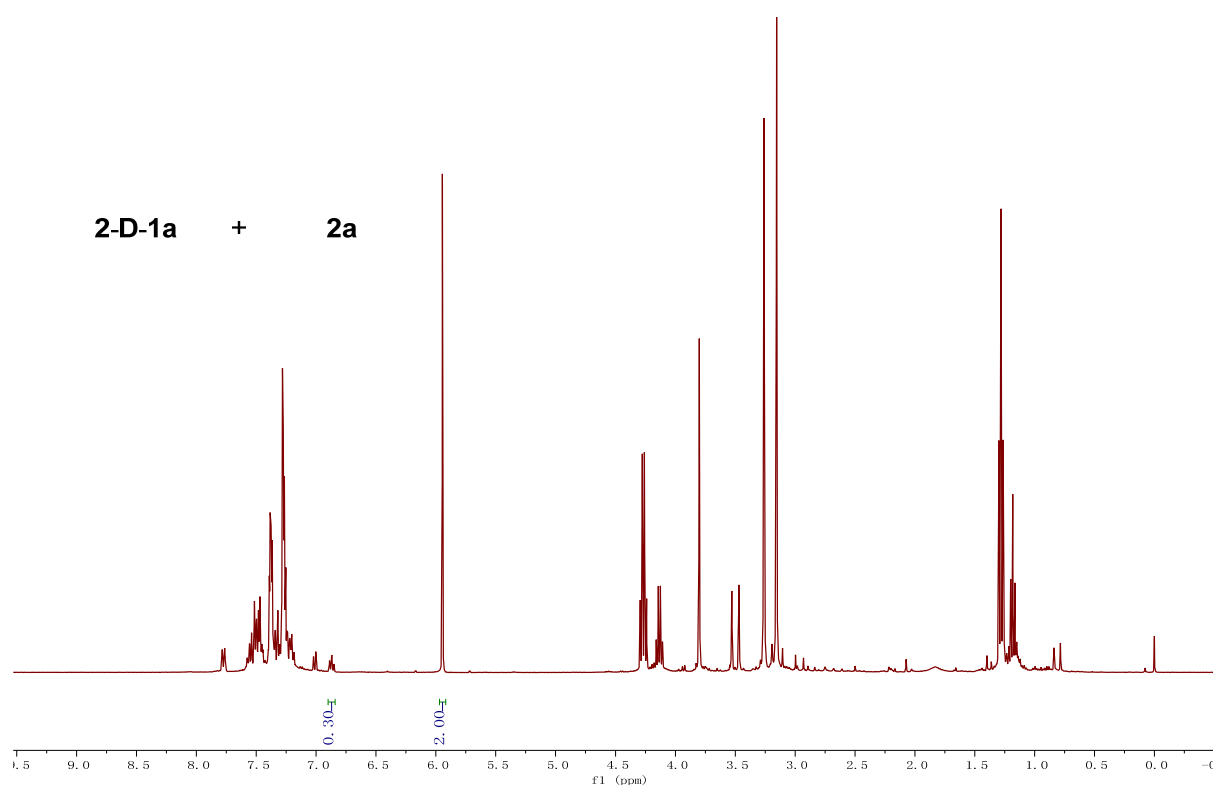


Parallel experiment:

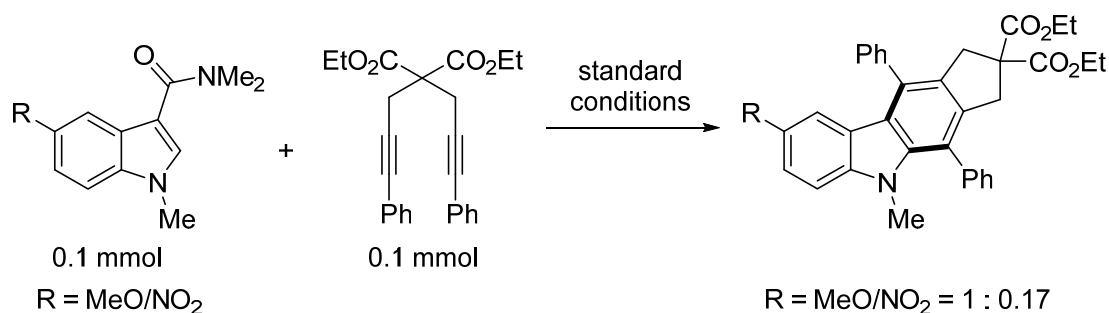
A mixture of amide **1a** (20.2 mg, 0.1 mmol) or **2-D-1a** (20.3 mg, 0.1 mmol), **2a** (46.6 mg,

0.12 mmol), [Cp*RhCl₂]₂ (3.1 mg, 0.005 mmol, 5.0 mol %), AgSbF₆ (6.9 mg, 0.02 mmol, 20.0 mol%) and AgOAc (33.4 mg, 0.2 mmol, 2.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.0 mL) was added and the mixture was stirred at 100 °C in a pre-heated oil bath for 12 h under Ar atmosphere. After 30 minutes, it was evaporated under reduced pressure and The residue was detected by ¹H NMR (0.1 mmol of 1,1,2,2-tetrachloroethane was added as an internal standard) and the ¹H NMR yields were reported respectively. The KIE value was calculated according to the isolated yields of **3aa**.





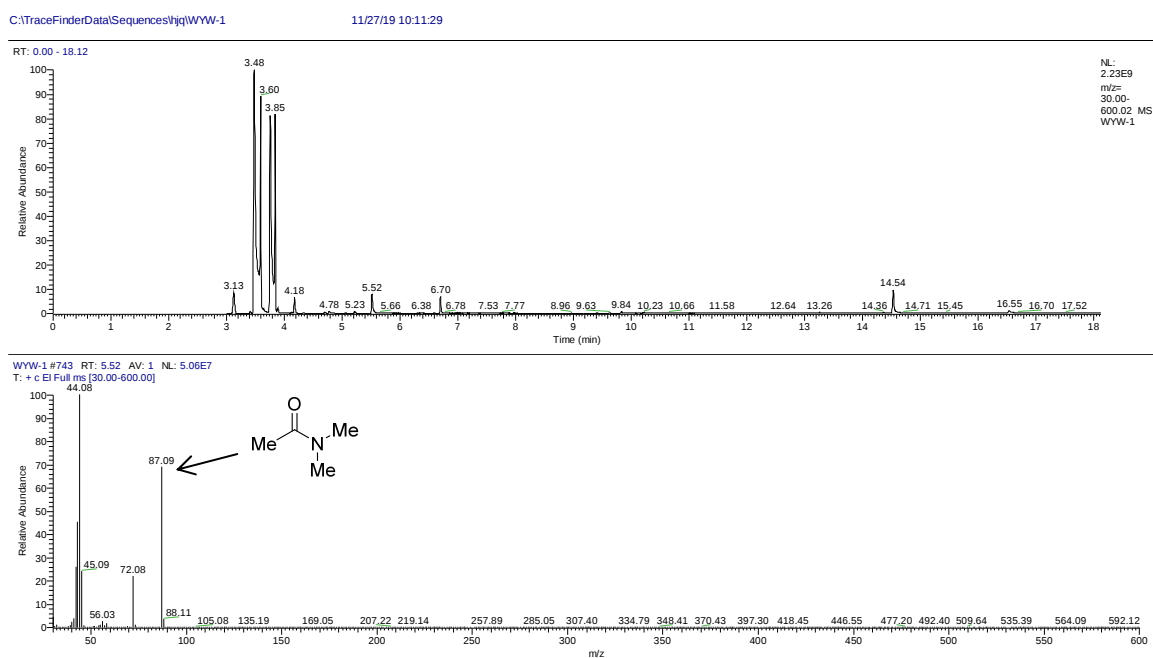
Competition experiments



A mixture of **1e** (23.2 mg, 0.1 mmol, 1.0 equiv), **1g** (24.7 mg, 0.1 mmol, 1.0 equiv), **2** (38.8 mg, 0.1 mmol, 1.0 equiv), [Cp*RhCl₂]₂ (3.1 mg, 0.005 mmol, 5.0 mol %), AgSbF₆ (6.9 mg, 0.02 mmol, 20.0 mol%) and AgOAc (33.4 mg, 0.2 mmol, 2.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.0 mL) was added and the mixture was stirred at 100 °C in a pre-heated oil bath for 12 h under Ar atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was absorbed to small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/50 to 1/20) to give the desired products **3ea** (yield: 45.9 %, 25.1 mg) and **3ga** (yield: 7.8 %, 4.4 mg).

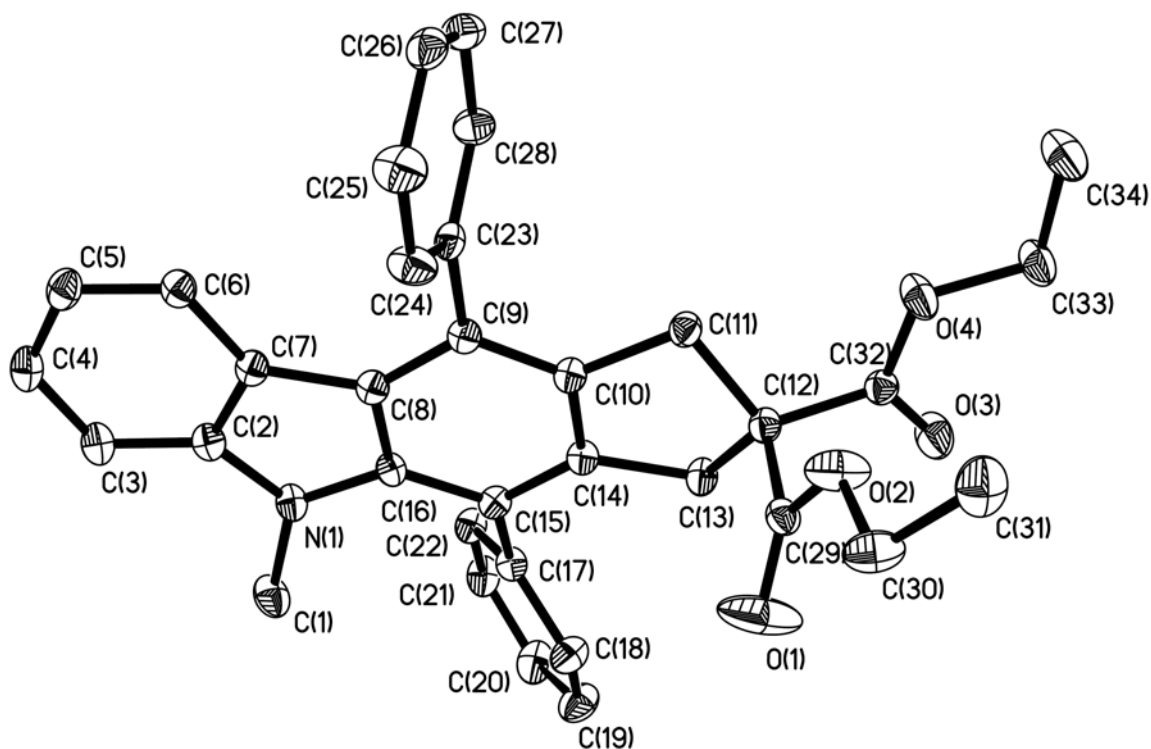
GC-MS analysis

A mixture of **1a** (20.2 mg, 0.1 mmol, 1.0 equiv), **2a** (46.6 mg, 0.12 mmol, 1.2 equiv), [Cp*RhCl₂]₂ (3.1 mg, 0.005 mmol, 5.0 mol %), AgSbF₆ (6.9 mg, 0.02 mmol, 20.0 mol%) and AgOAc (33.4 mg, 0.2 mmol, 2.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.0 mL) was added and the mixture was stirred at 100 °C for 12 h in a pre-heated oil bath under Ar atmosphere. Afterwards, the reaction mixture was cooled to room temperature and detected by GC-MS, and the *N,N*-dimethylacetamide was detected at 5.52 minute .



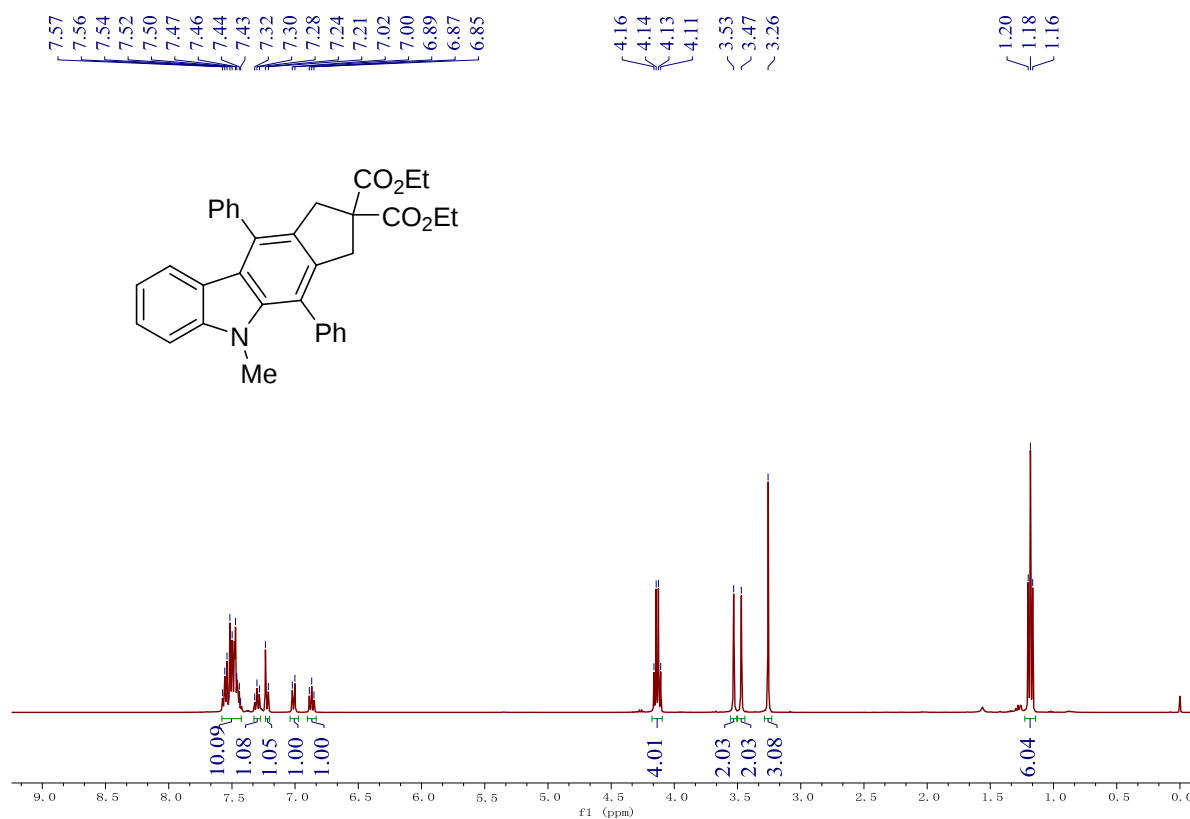
7. X-ray crystallography:

CCDC-1916286 (**3aa**), contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity.

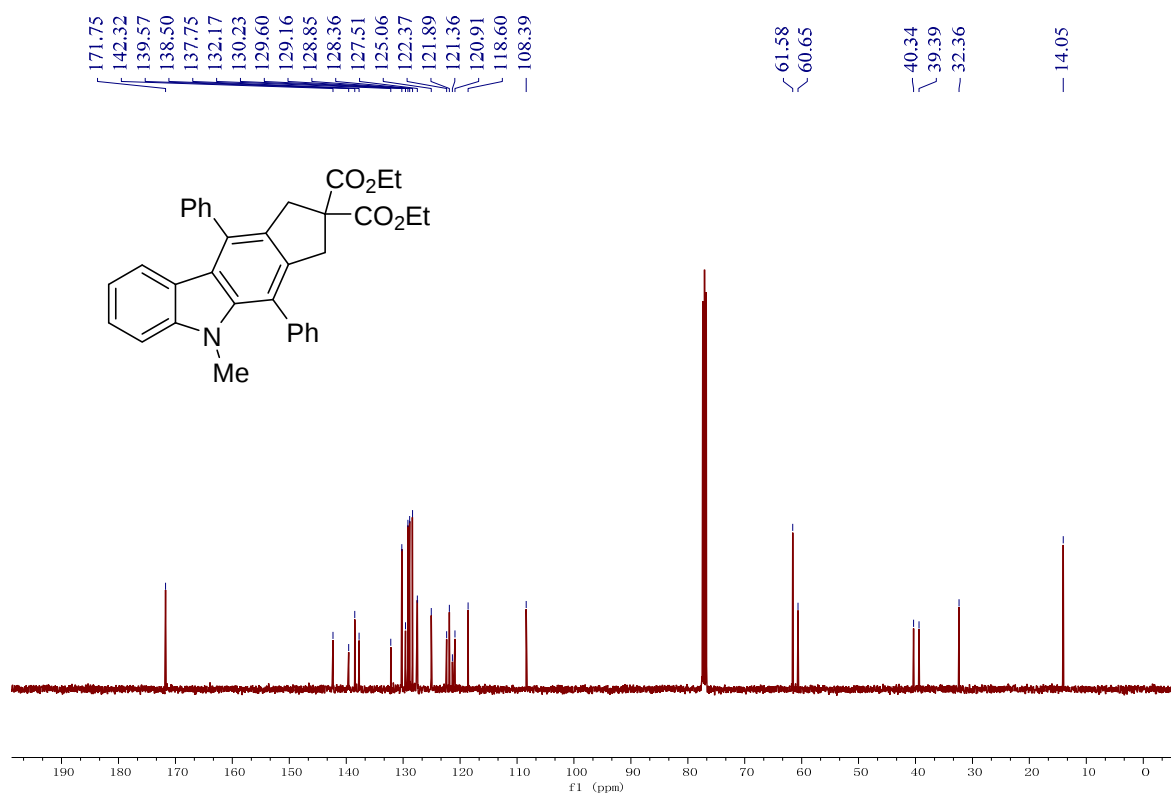


8. Copies of ^1H , ^{13}C and ^{19}F NMR Spectra for Compounds

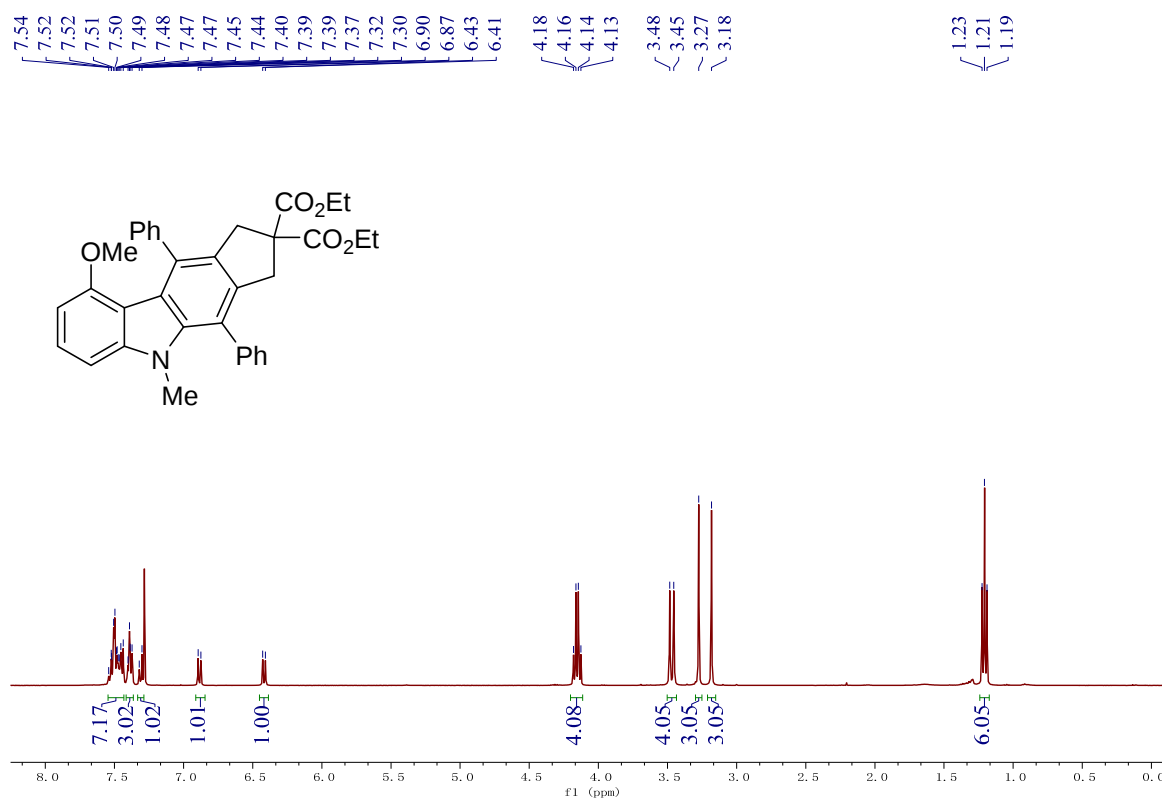
^1H NMR spectrum of **3aa**



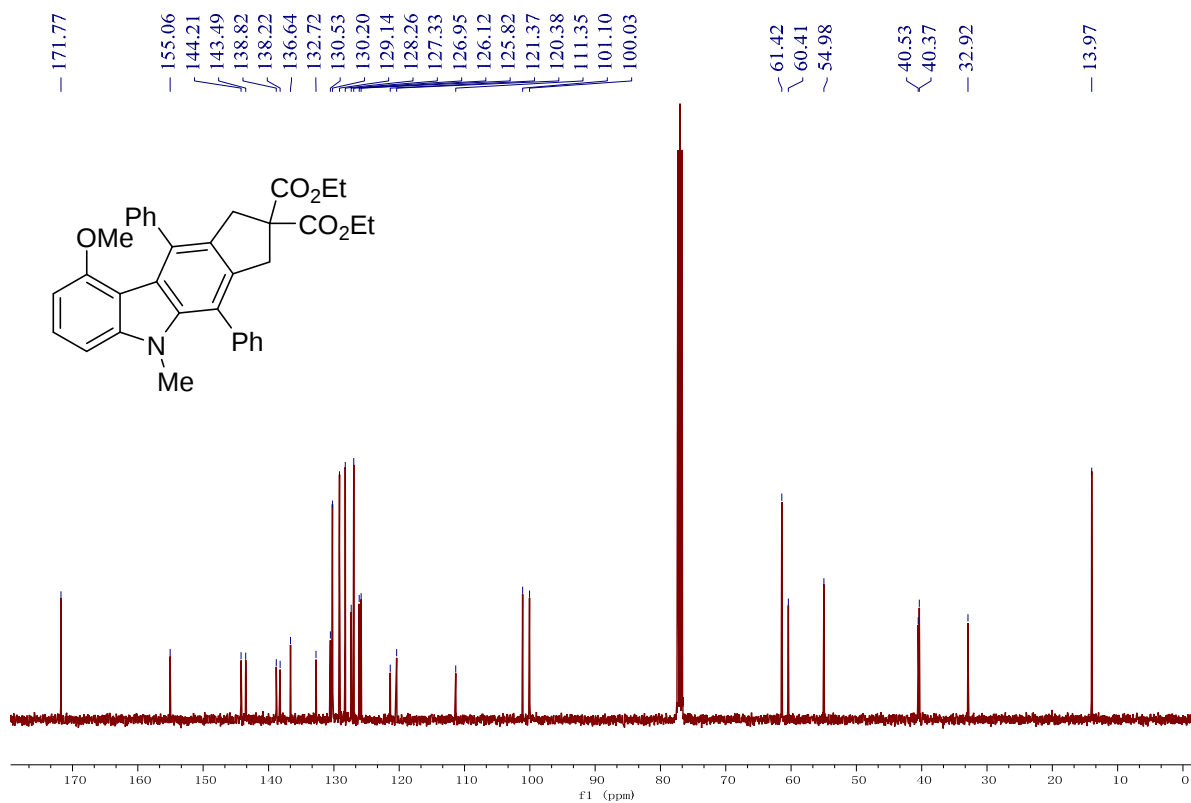
^{13}C NMR spectrum of **3aa**



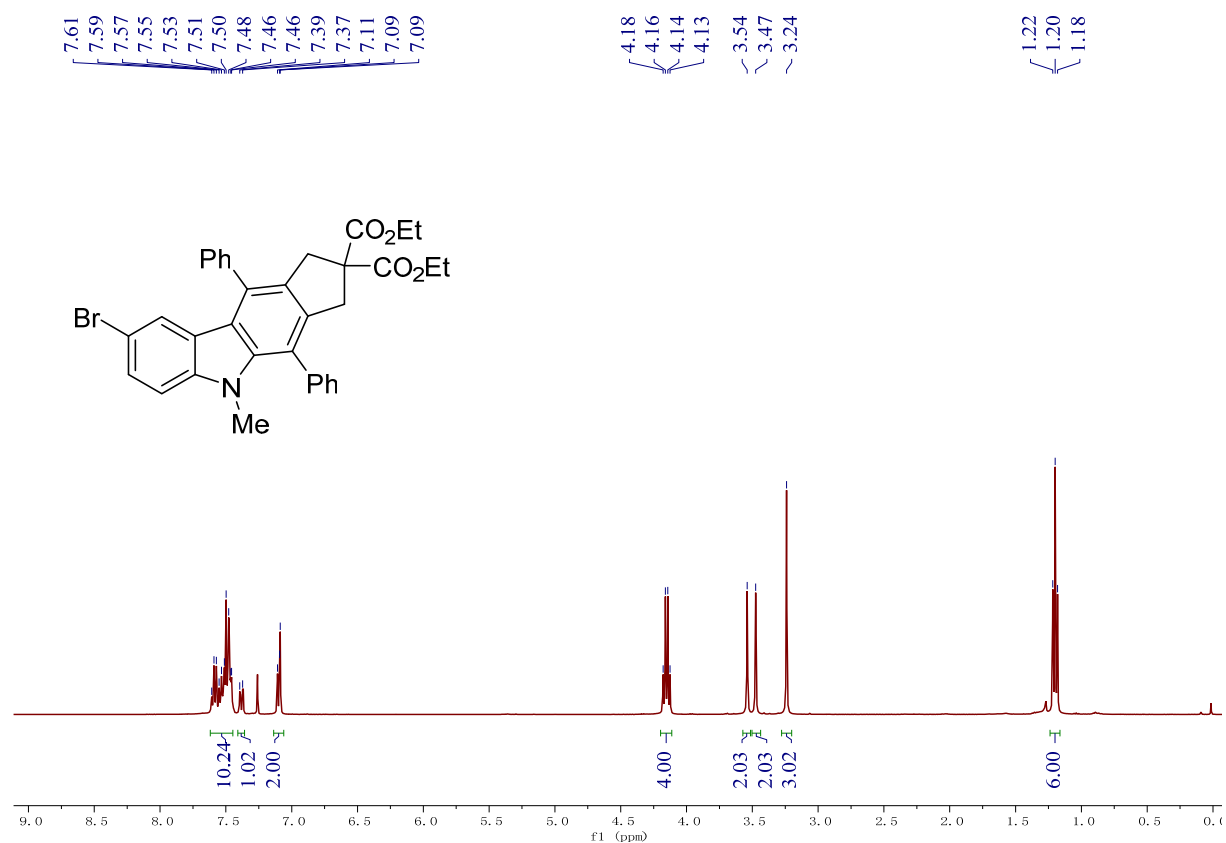
¹H NMR spectrum of **3ba**



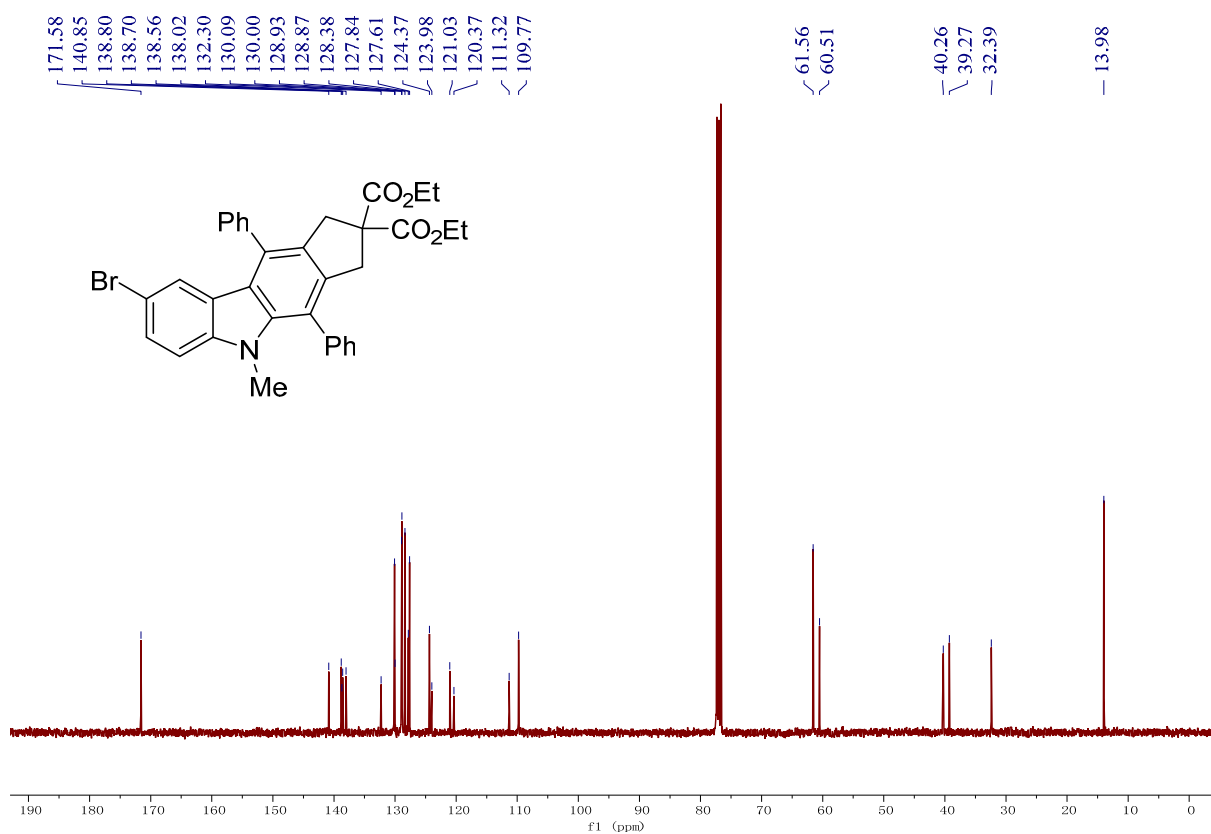
¹³C NMR spectrum of **3ba**



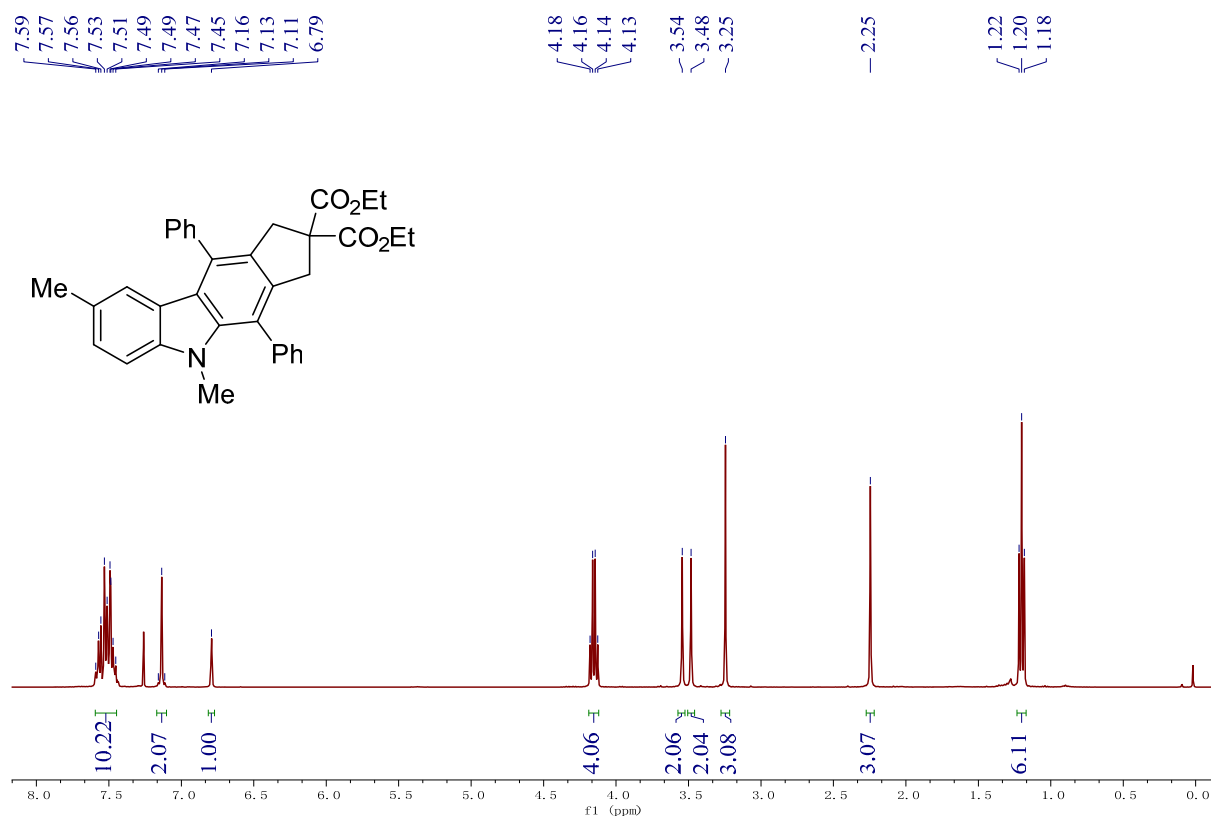
¹H NMR spectrum of **3ca**



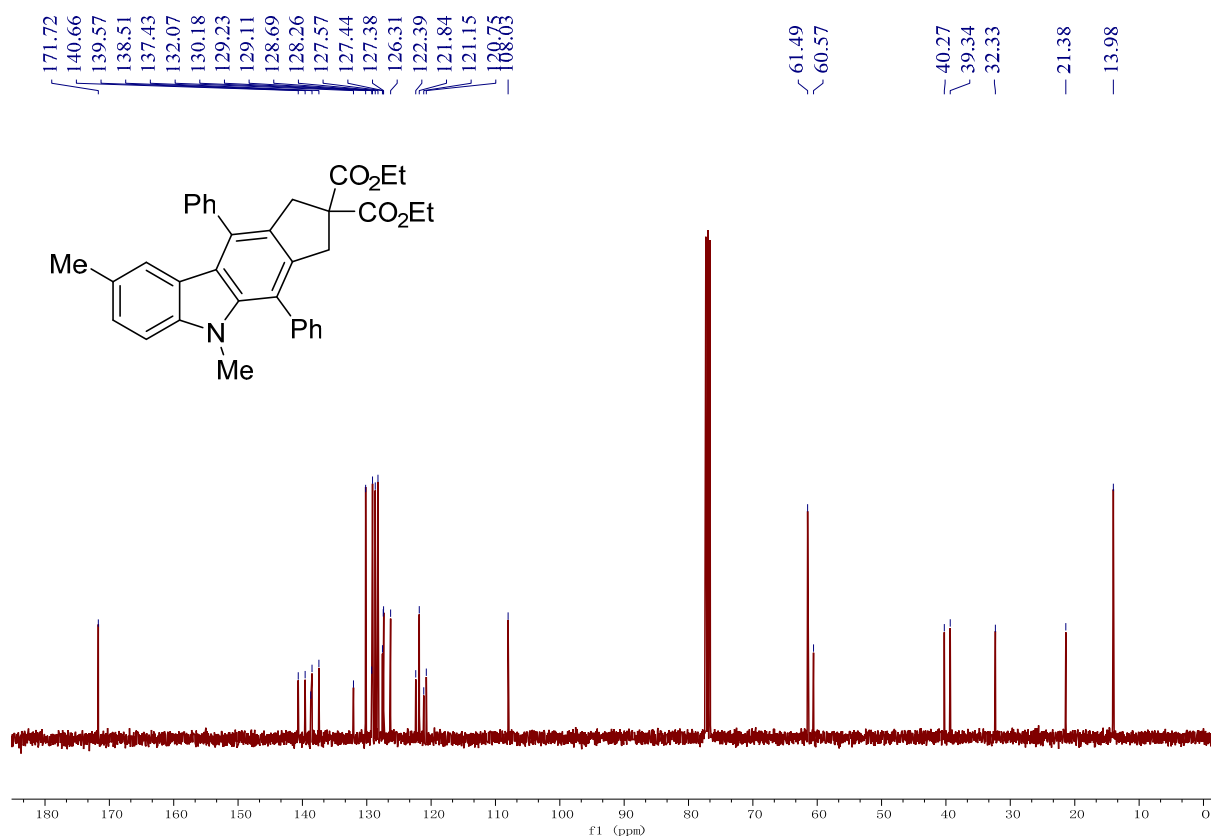
¹³C NMR spectrum of **3ca**



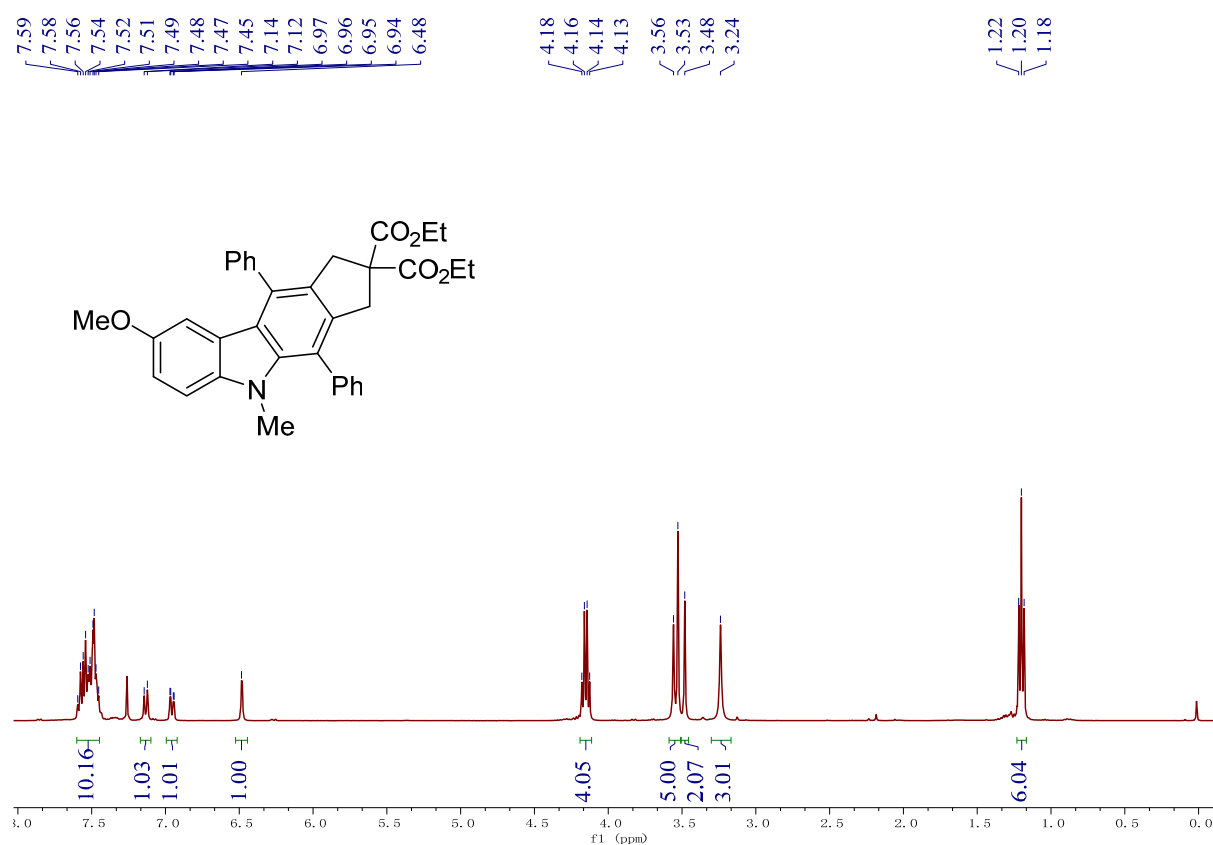
¹H NMR spectrum of **3da**



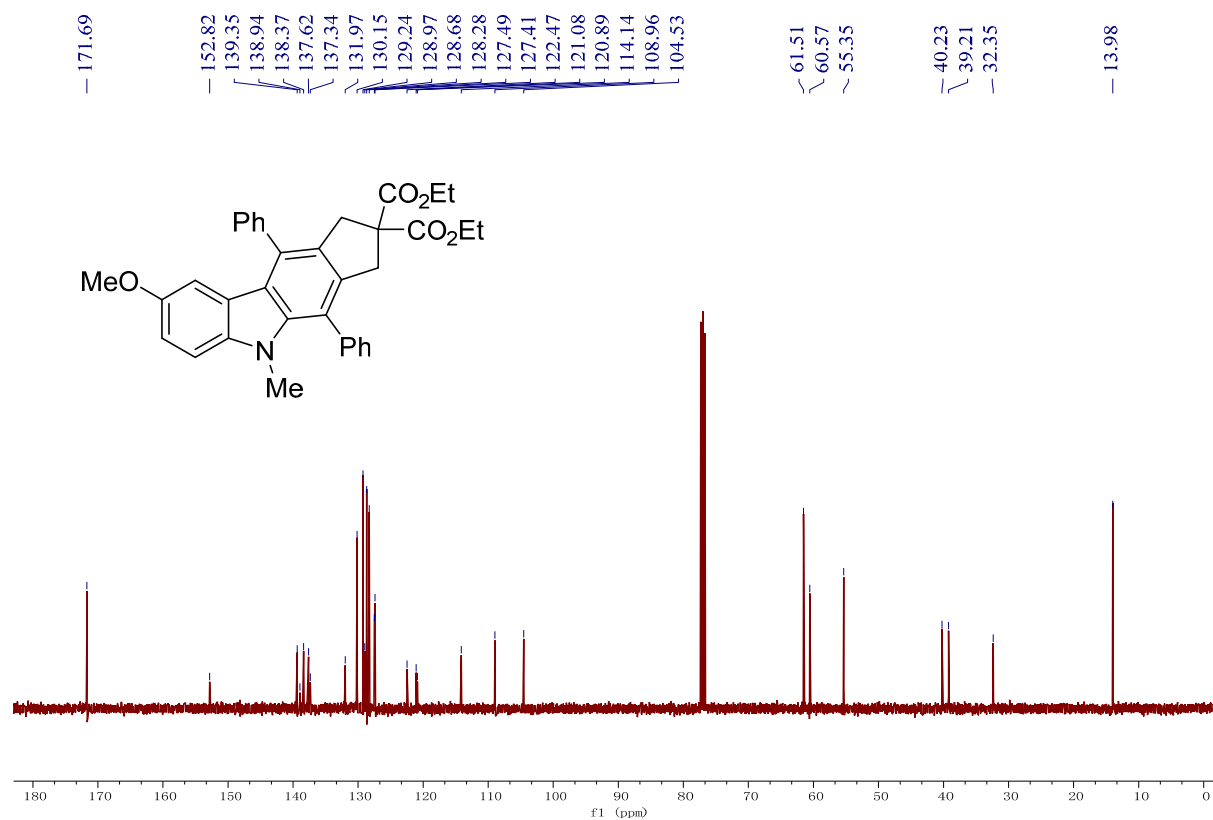
¹³C NMR spectrum of **3da**



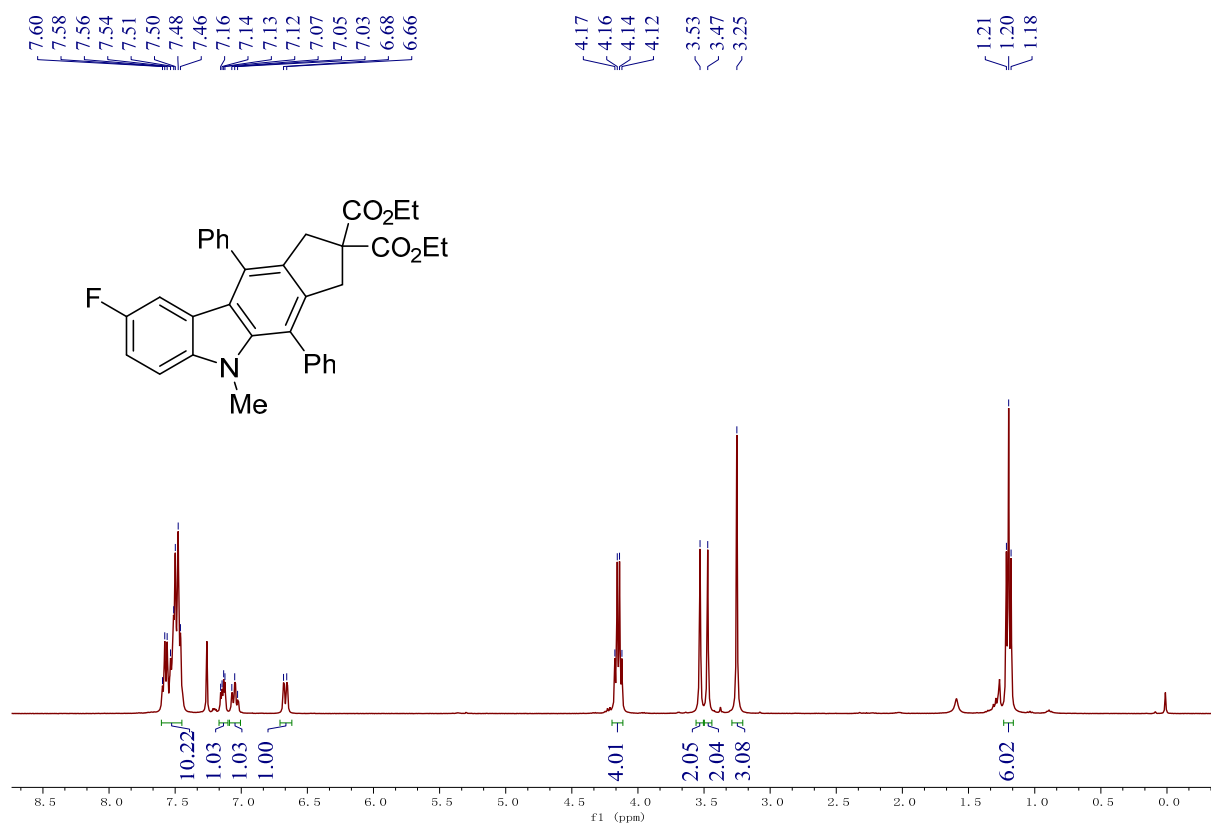
¹H NMR spectrum of **3ea**



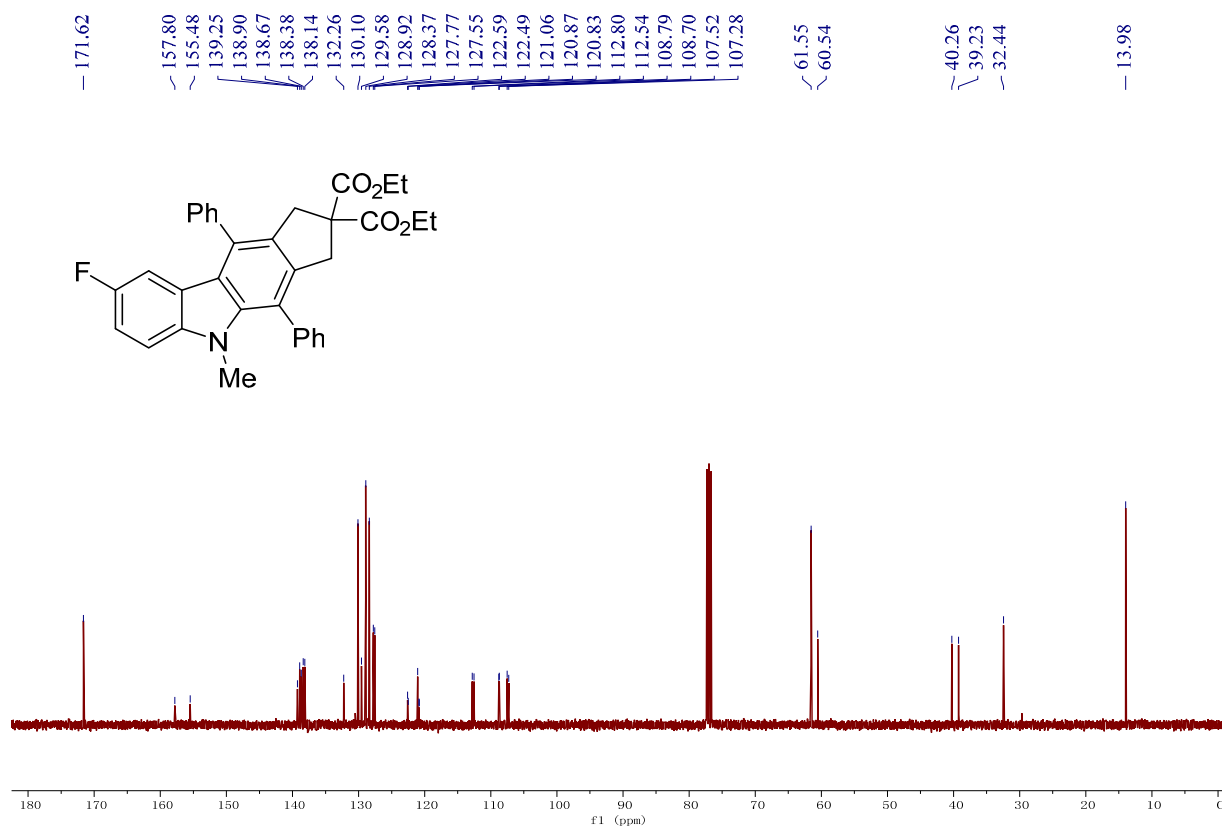
¹³C NMR spectrum of **3ea**



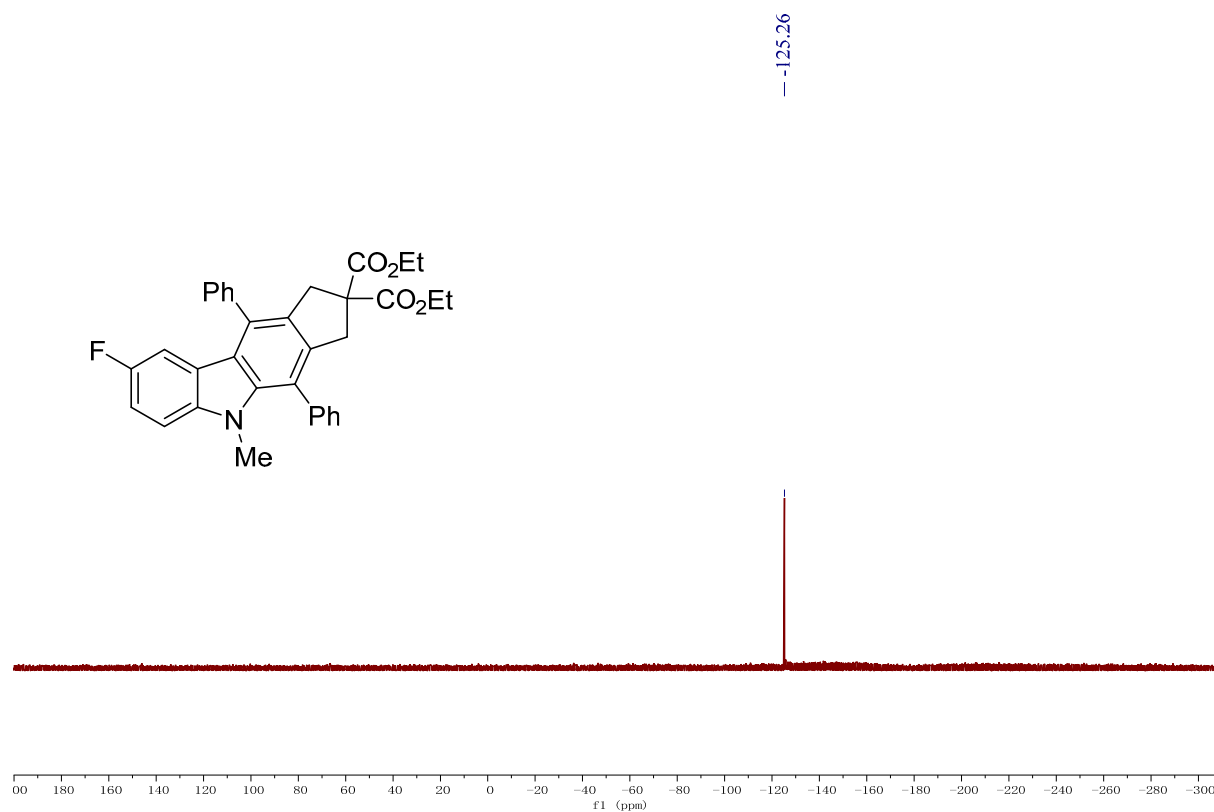
¹H NMR spectrum of **3fa**



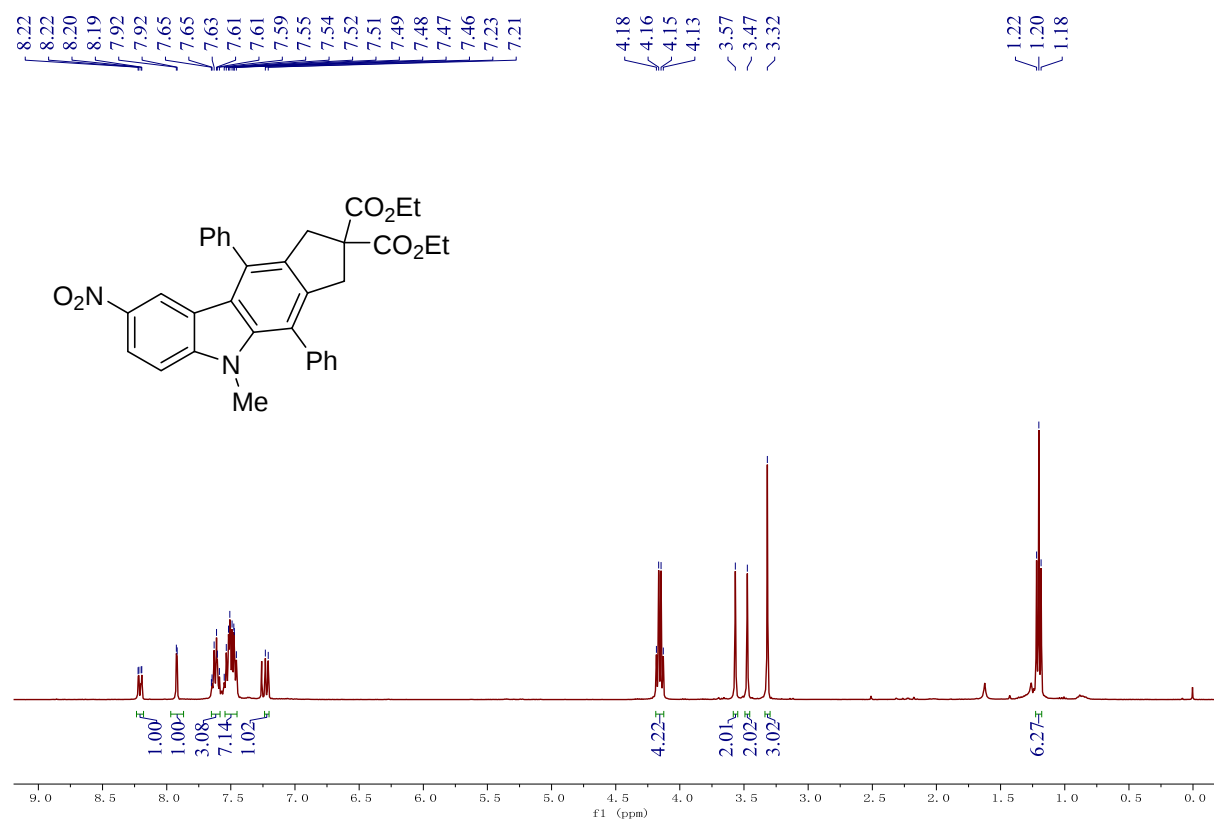
¹³C NMR spectrum of **3fa**



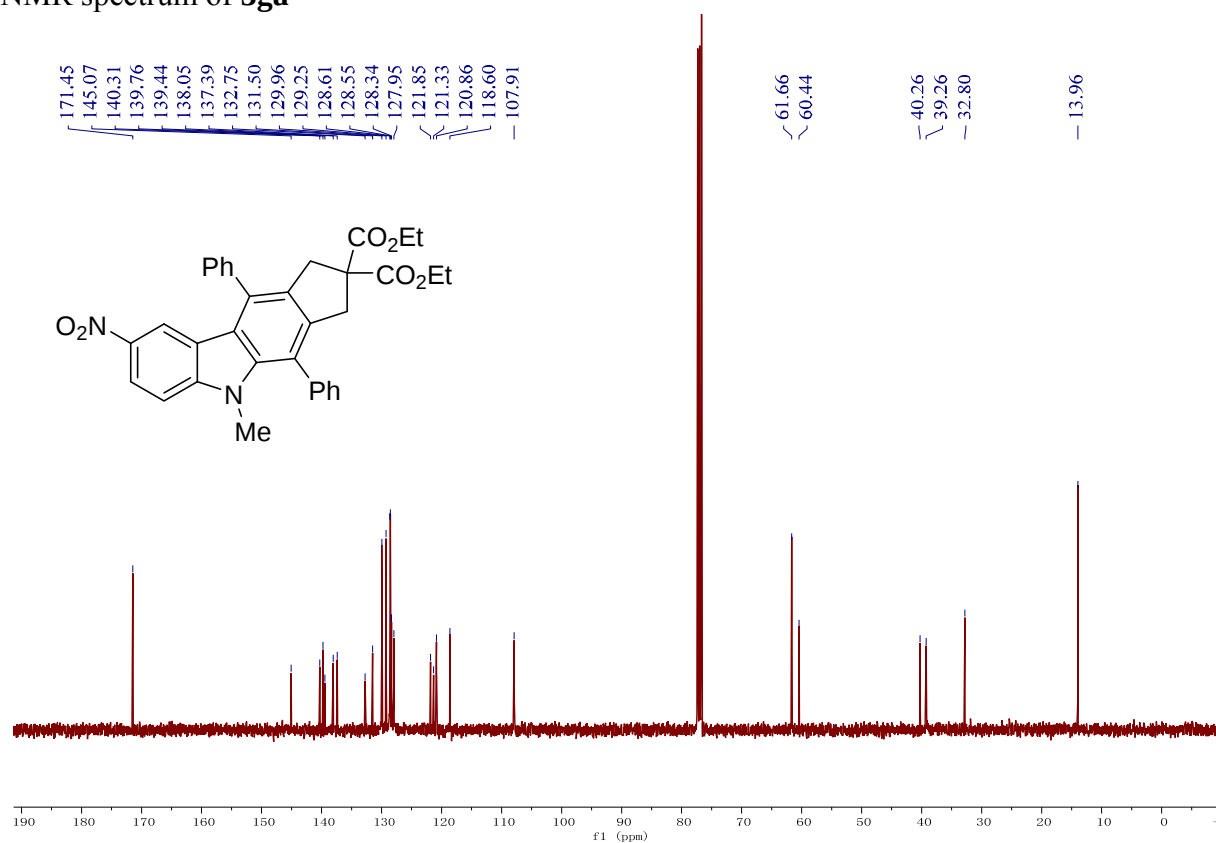
^{19}F NMR spectrum of **3fa**



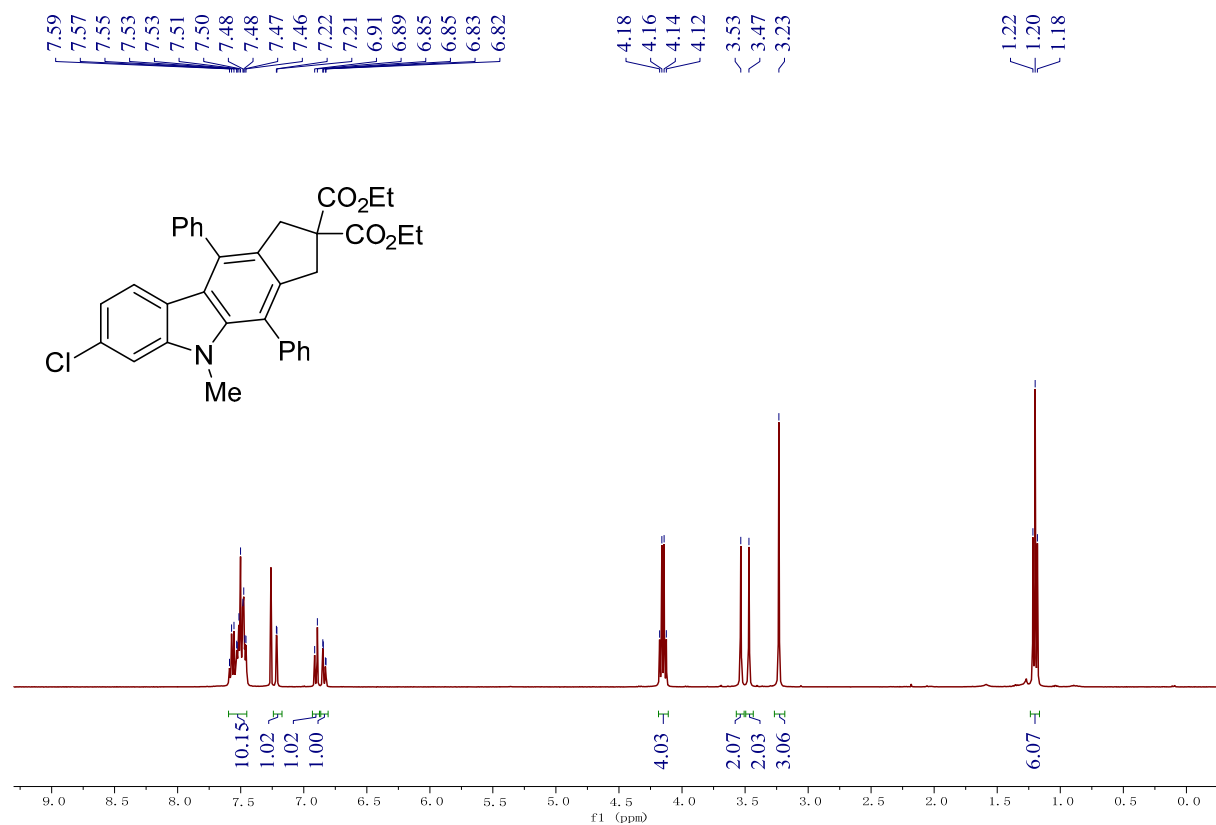
^1H NMR spectrum of **3ga**



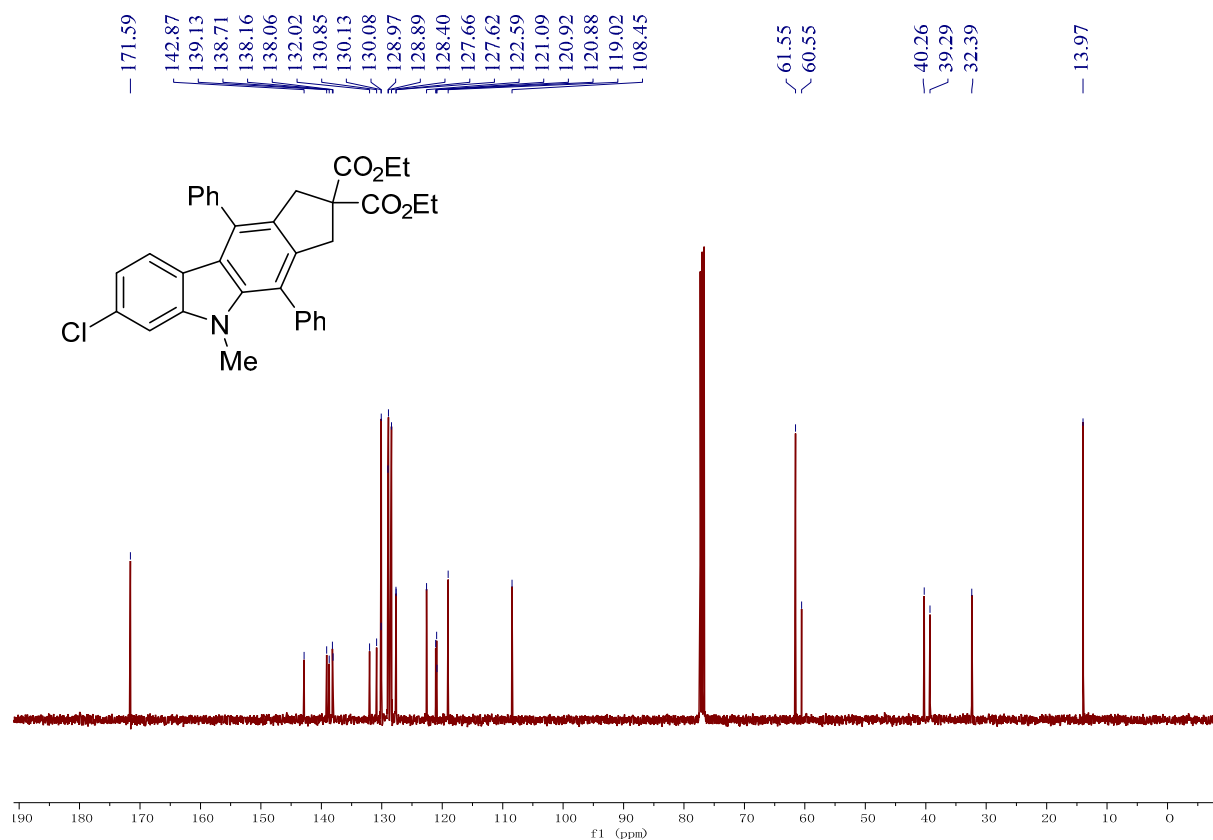
^{13}C NMR spectrum of **3ga**



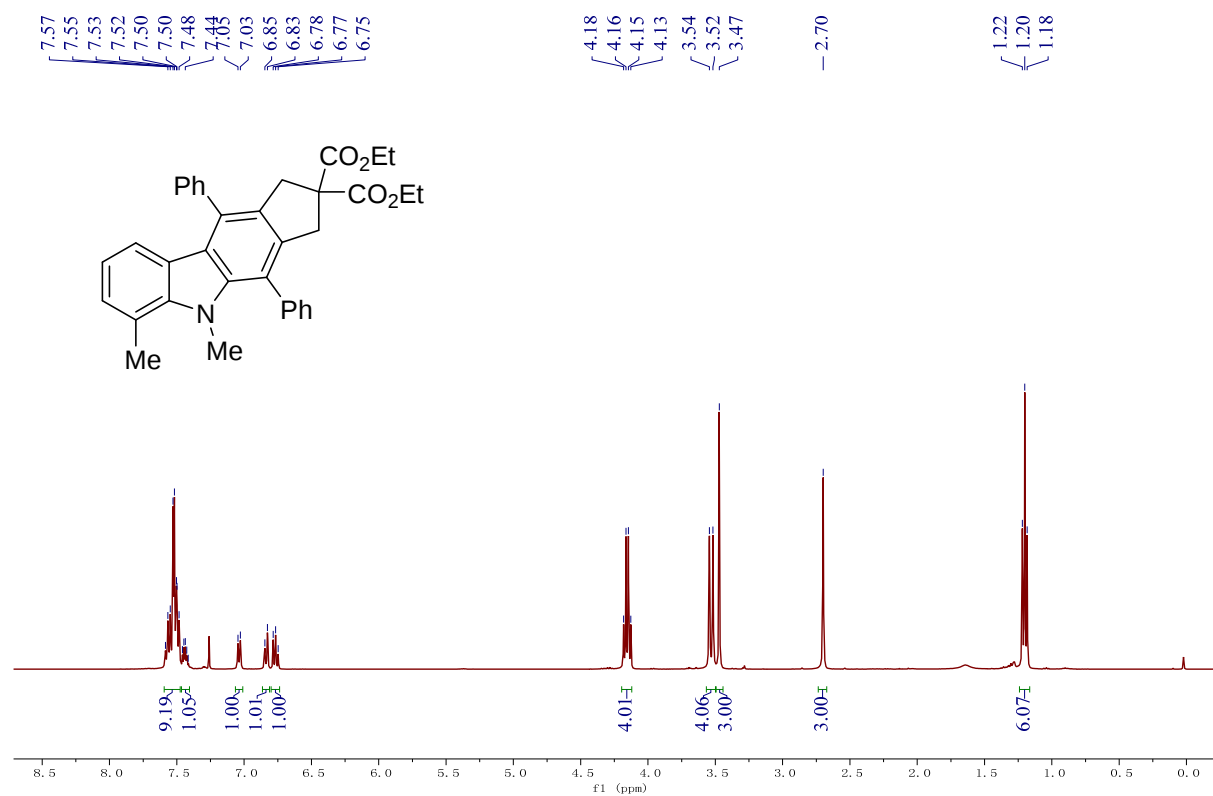
^1H NMR spectrum of **3ha**



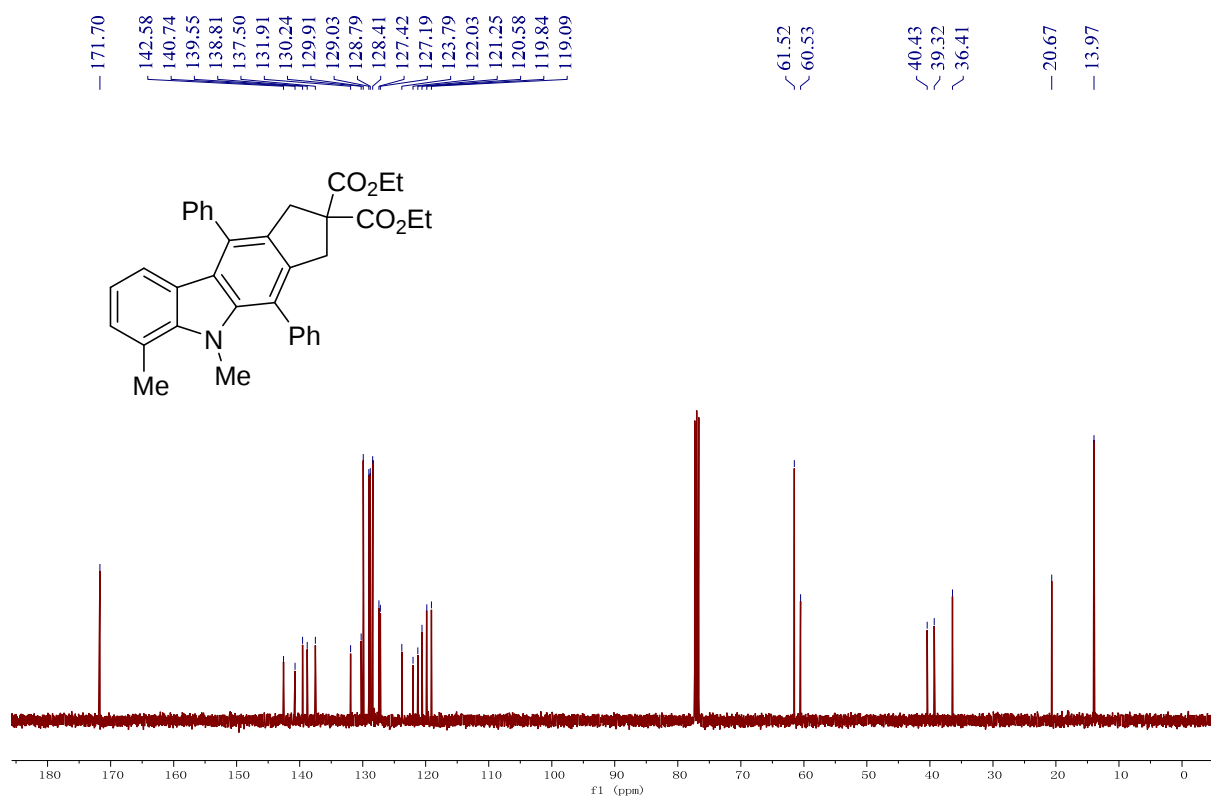
^{13}C NMR spectrum of **3ha**



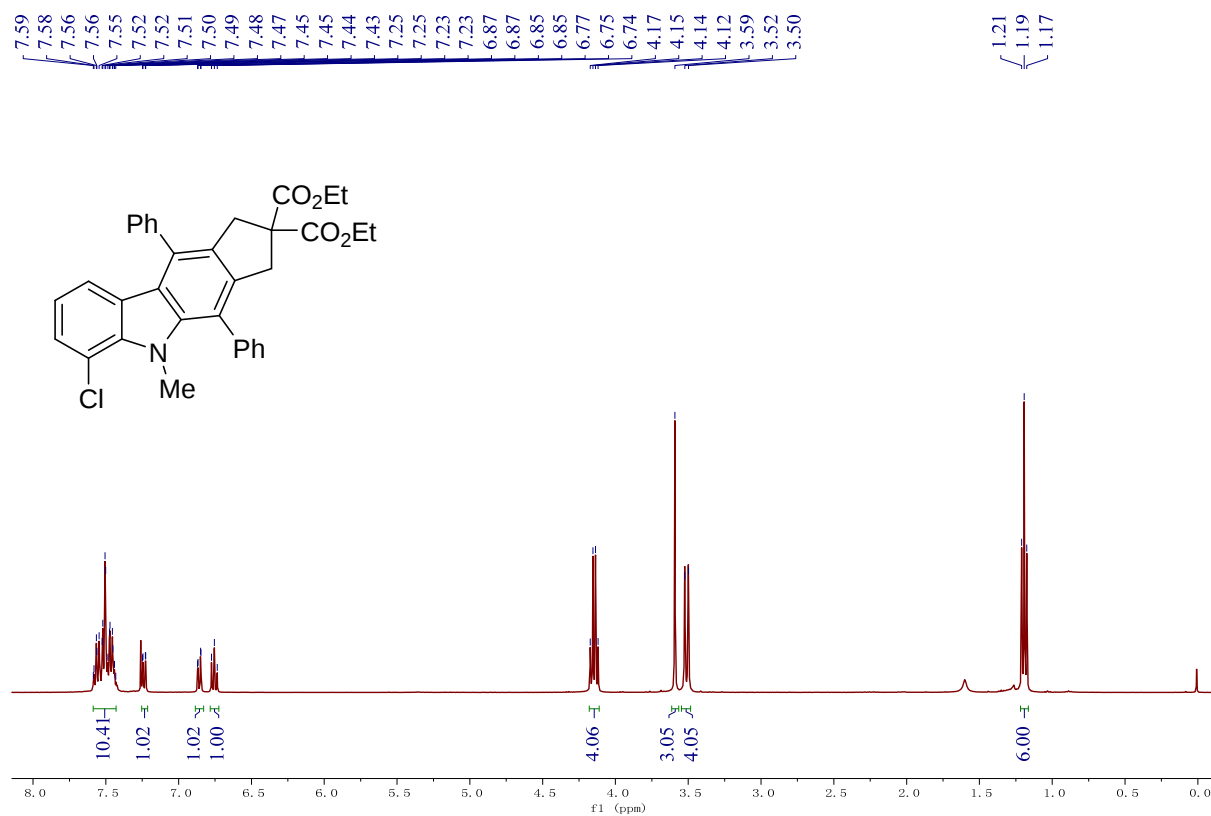
^1H NMR spectrum of **3ia**



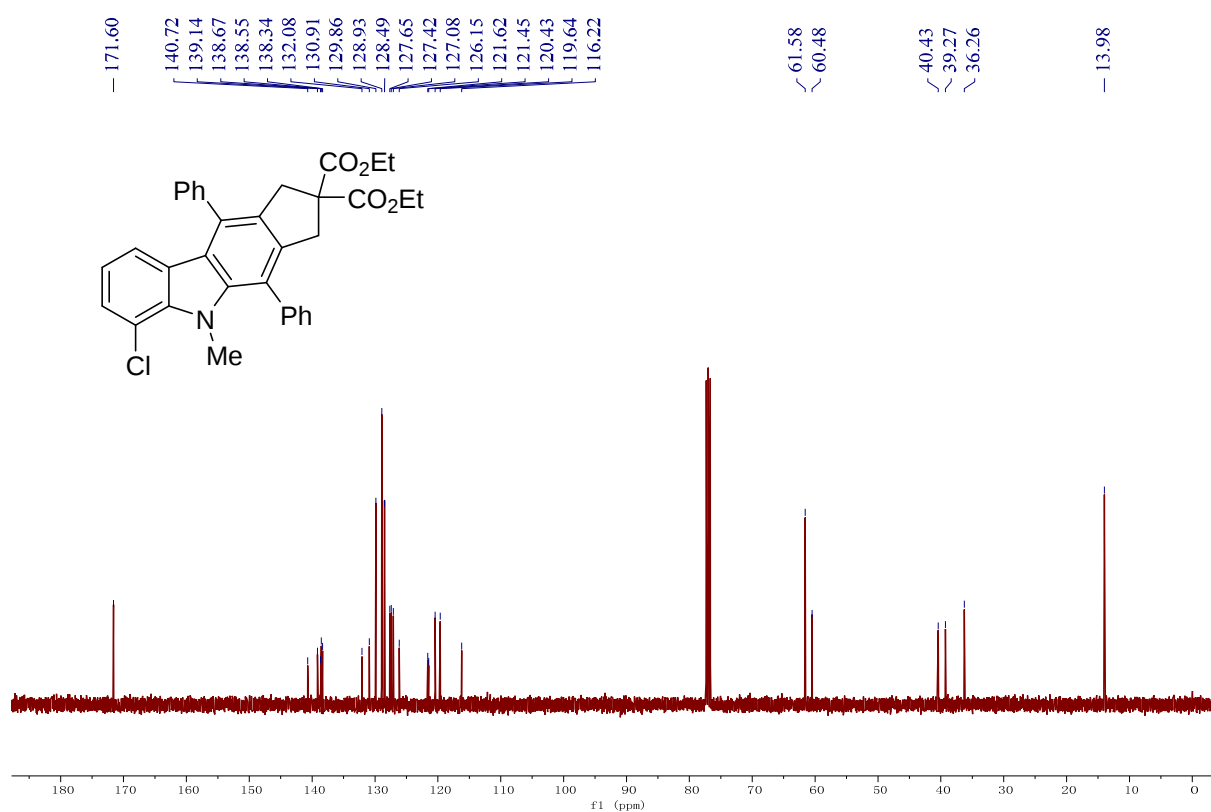
^{13}C NMR spectrum of **3ia**



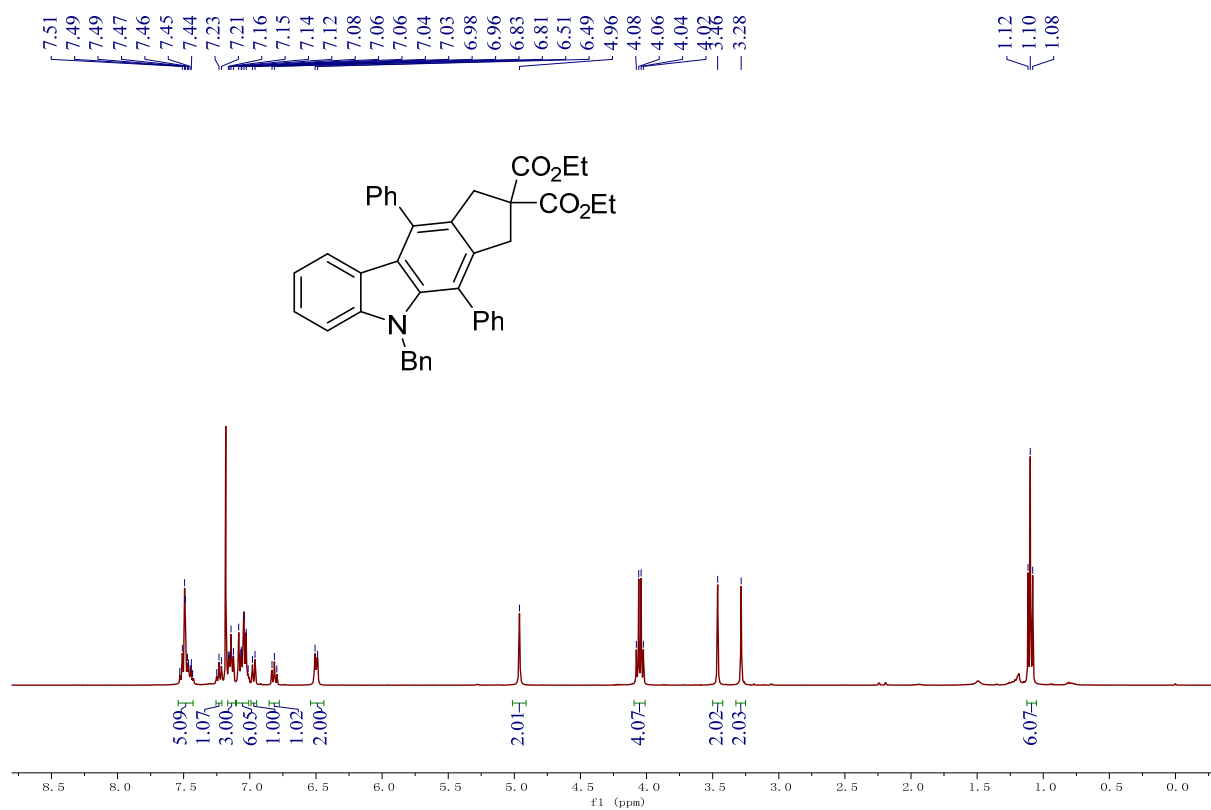
^1H NMR spectrum of **3ja**



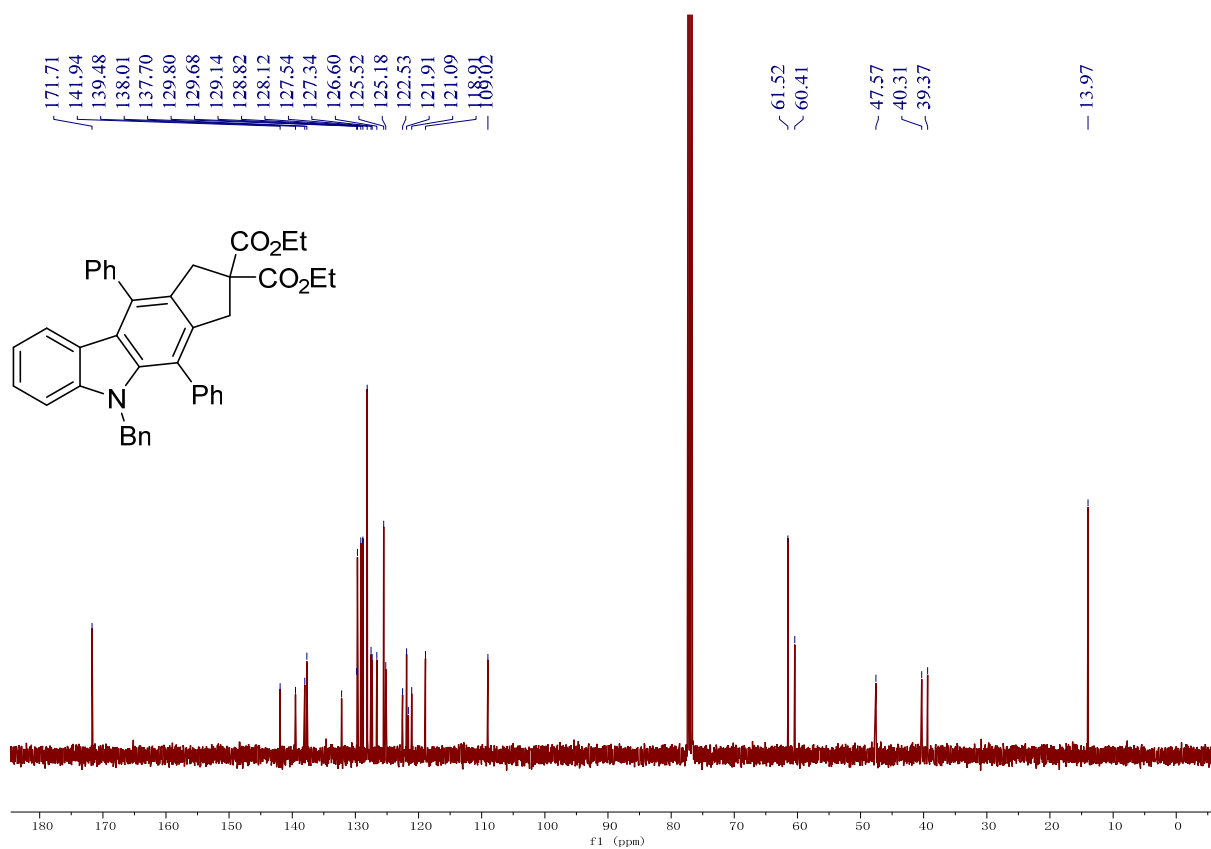
¹³C NMR spectrum of **3ja**



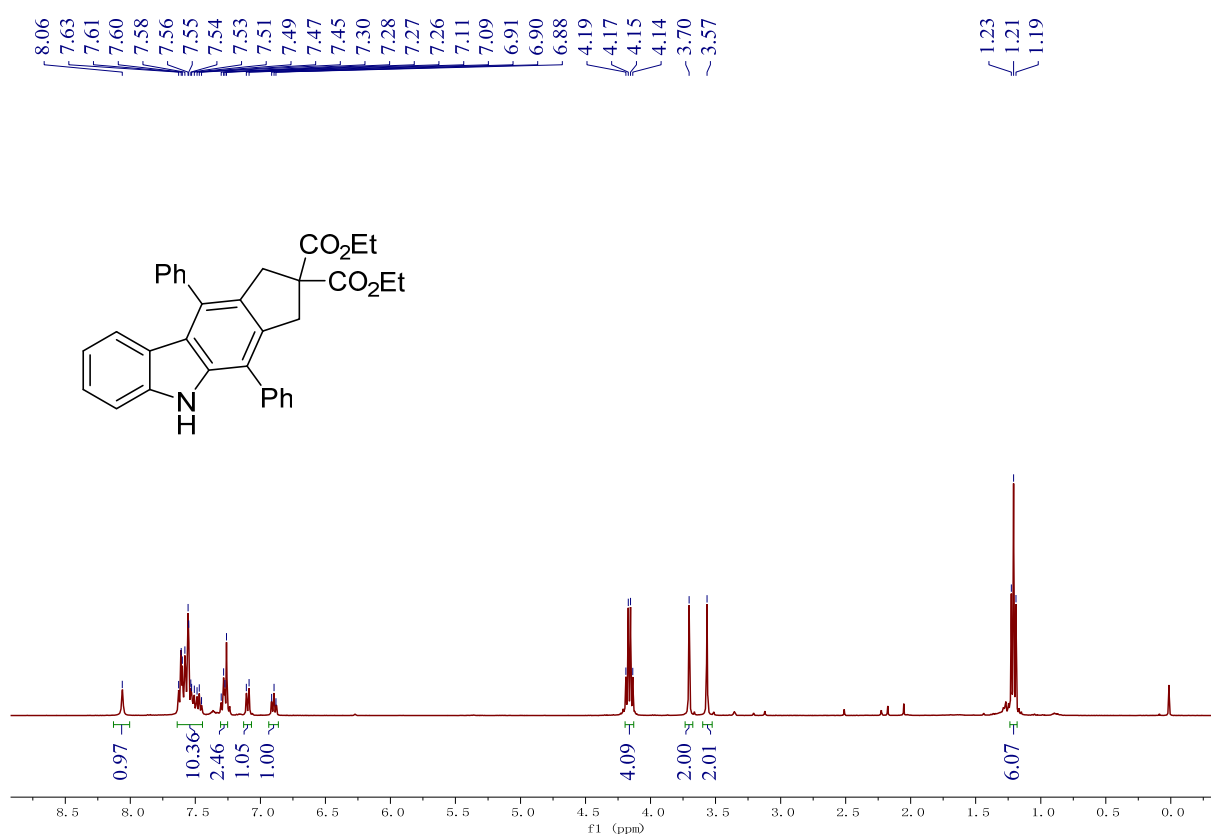
¹H NMR spectrum of **3ka**



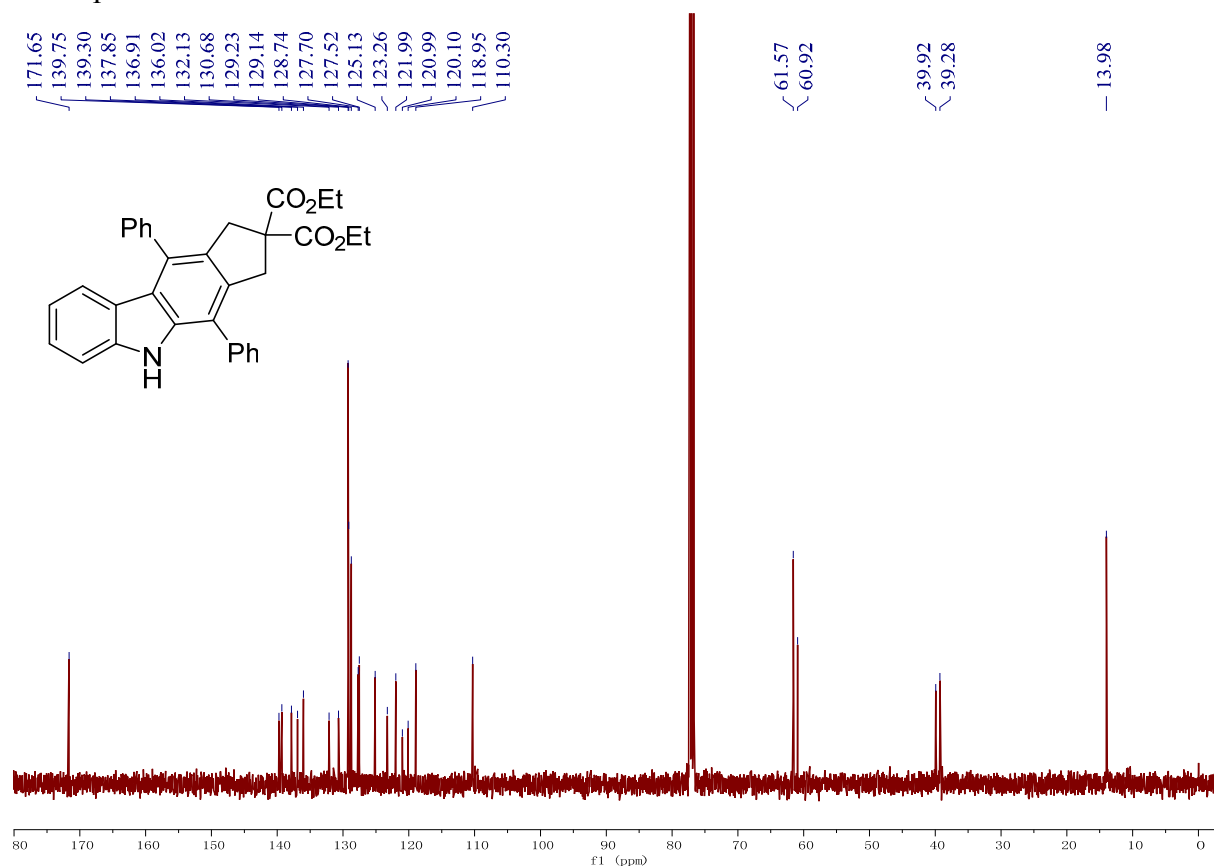
^{13}C NMR spectrum of **3ka**



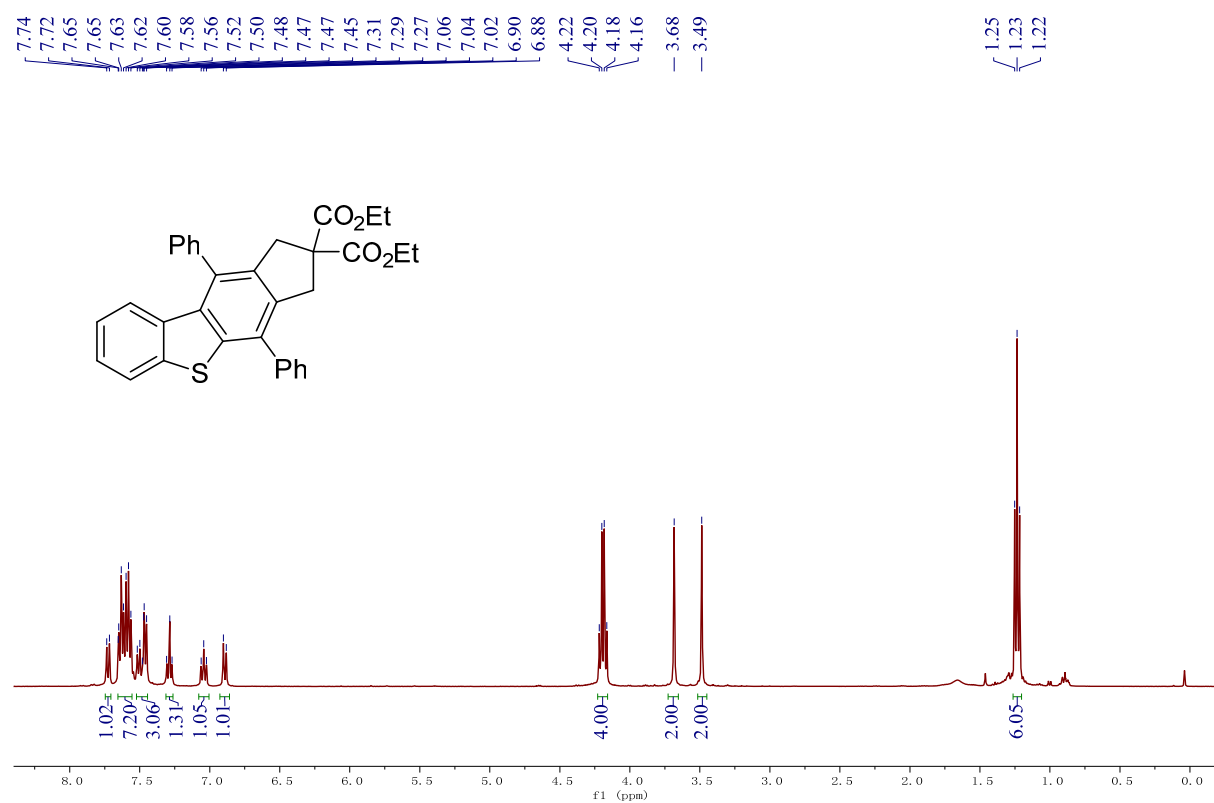
^1H NMR spectrum of **3la**



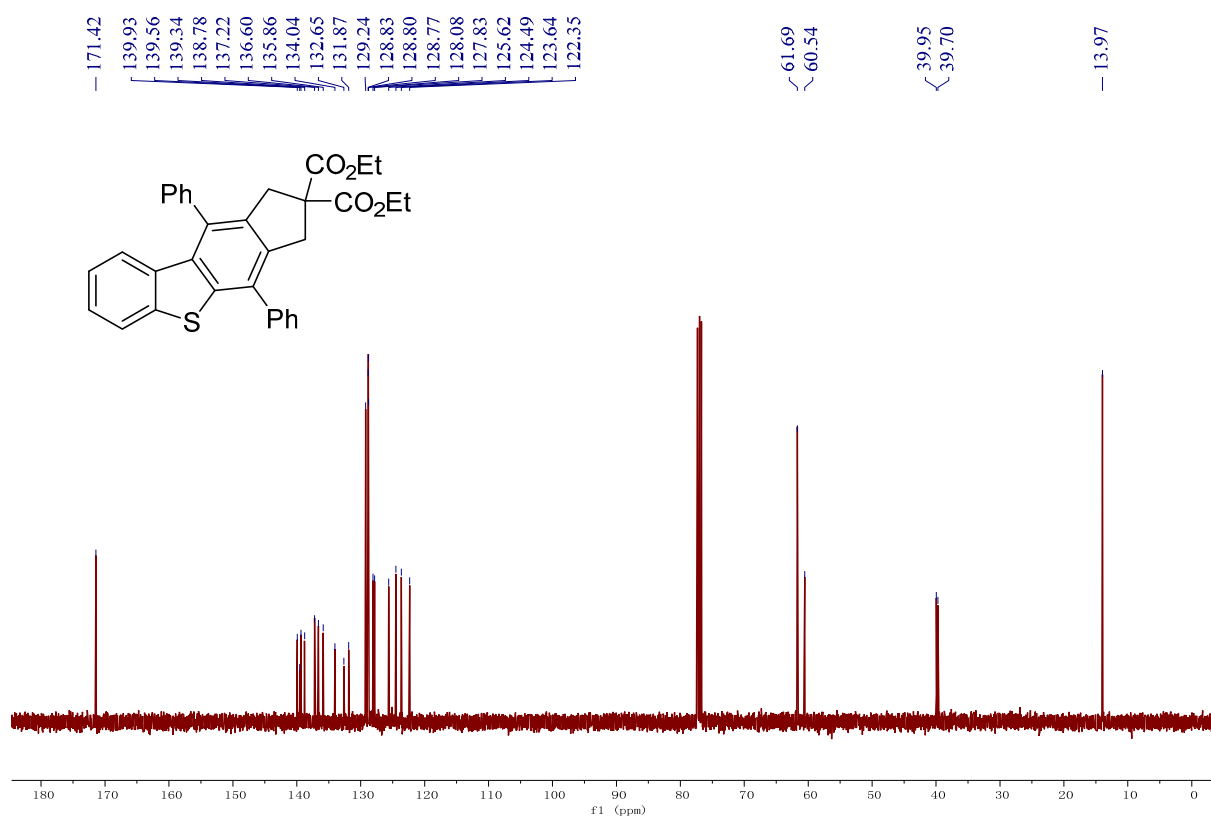
^{13}C NMR spectrum of **3la**



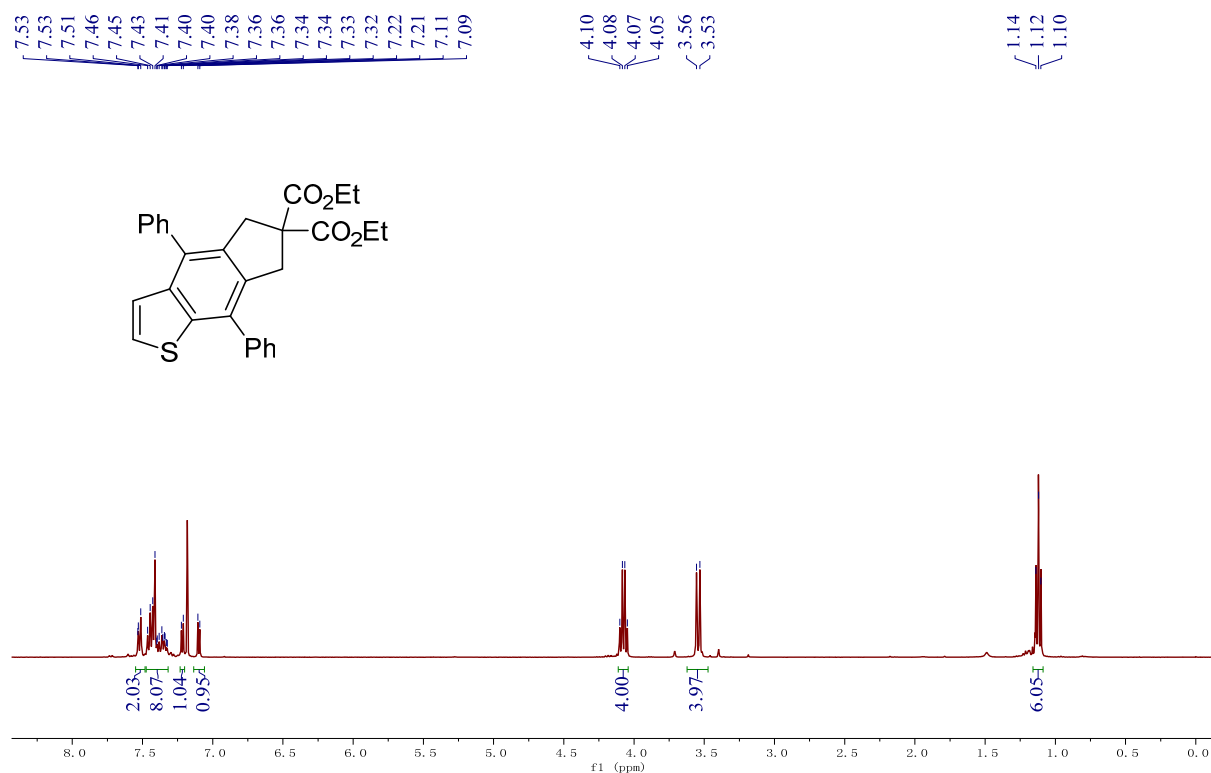
^1H NMR spectrum of **3ma**



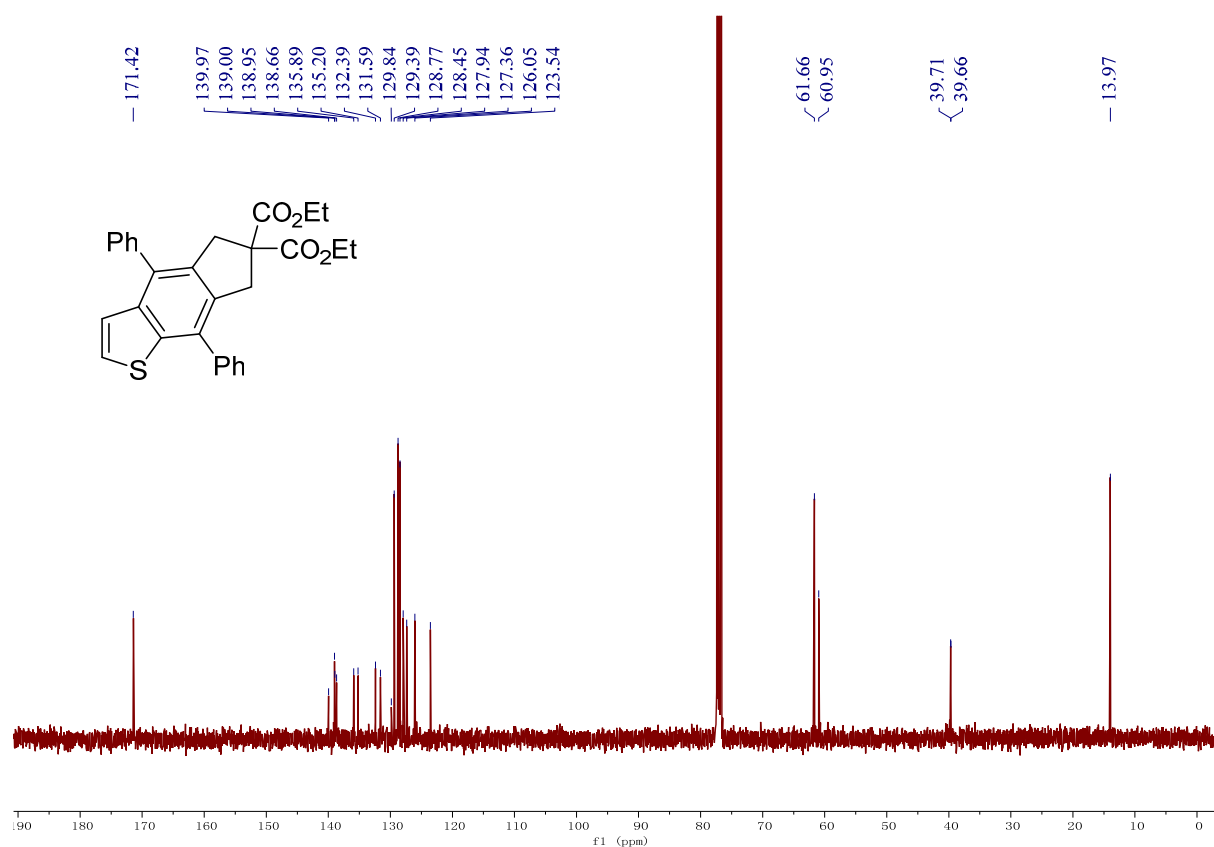
^{13}C NMR spectrum of **3ma**



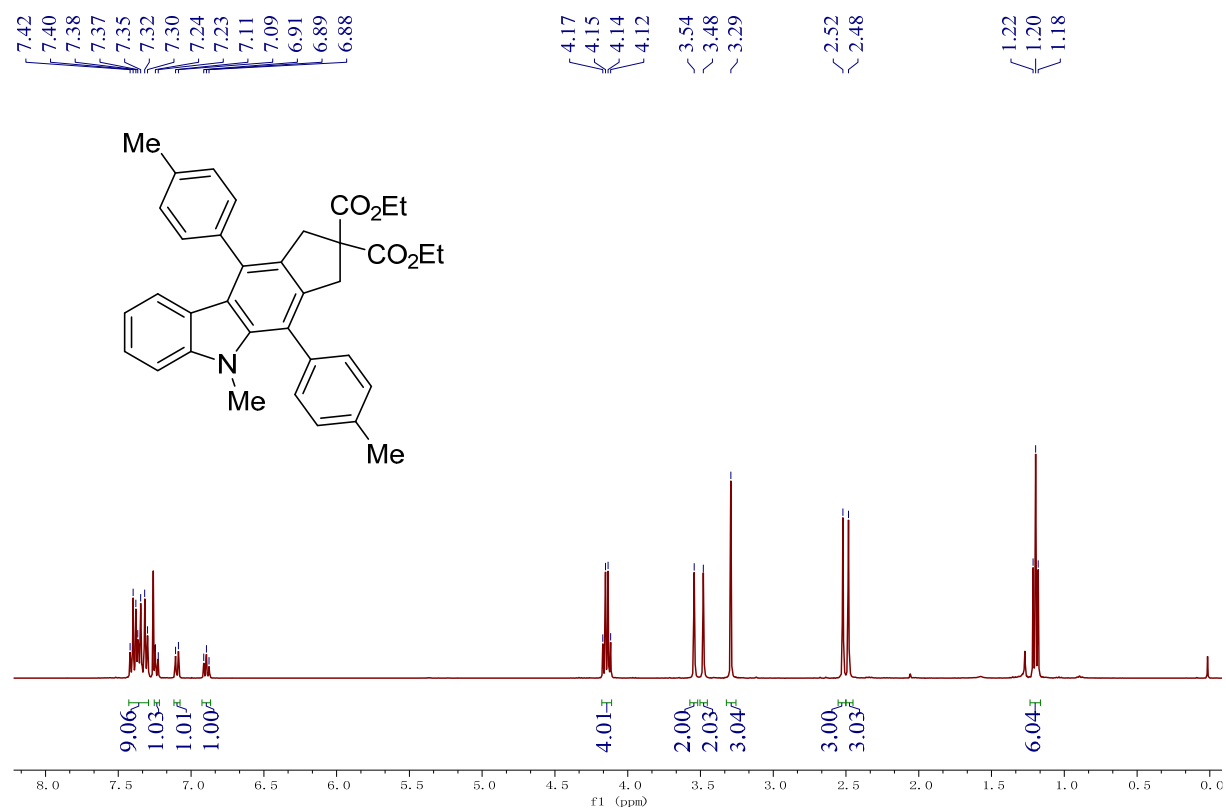
^1H NMR spectrum of **3na**



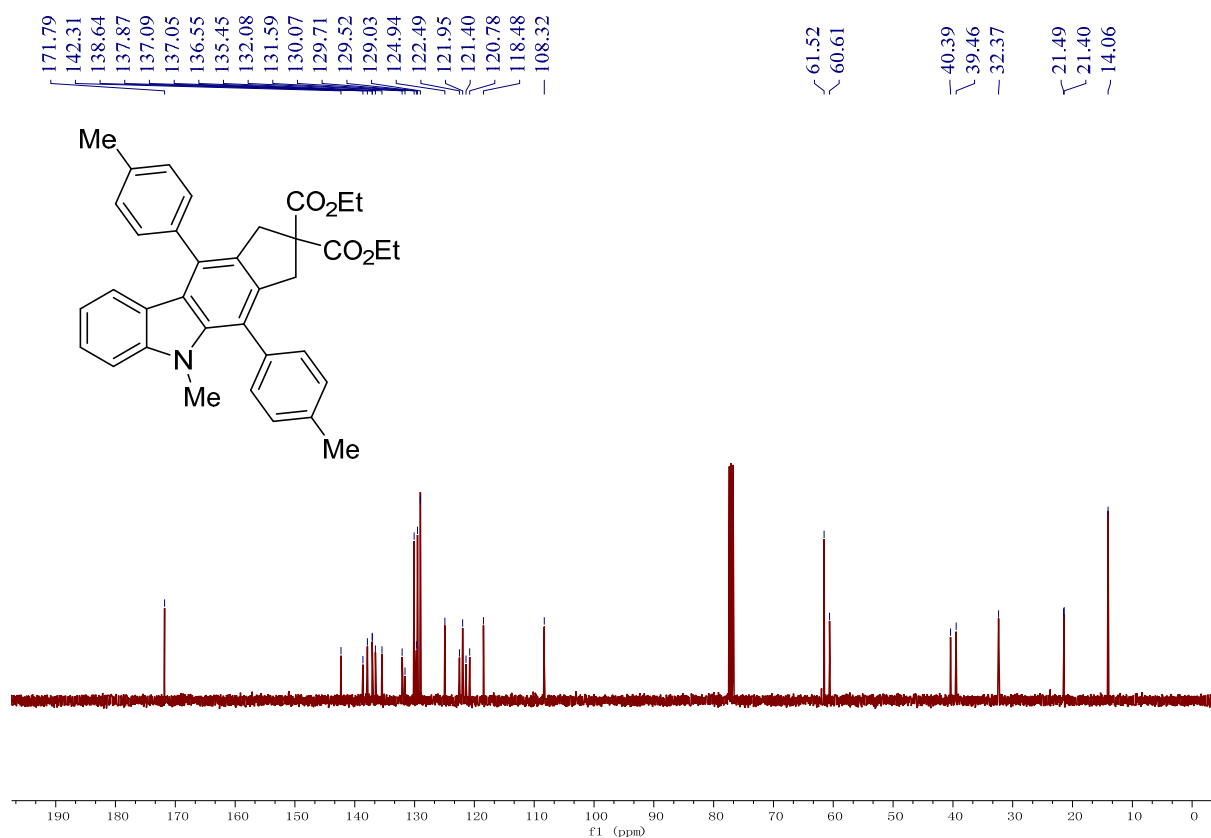
^{13}C NMR spectrum of **3na**



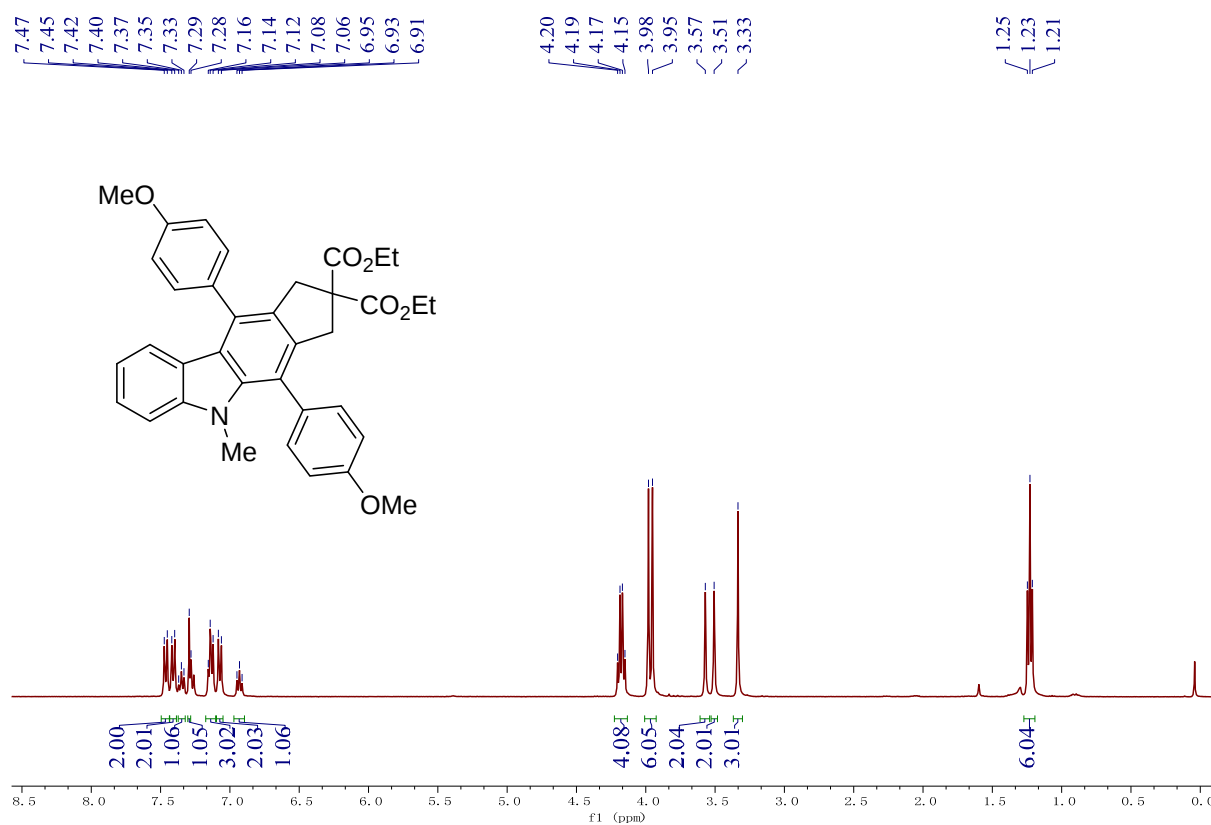
^1H NMR spectrum of **3ab**



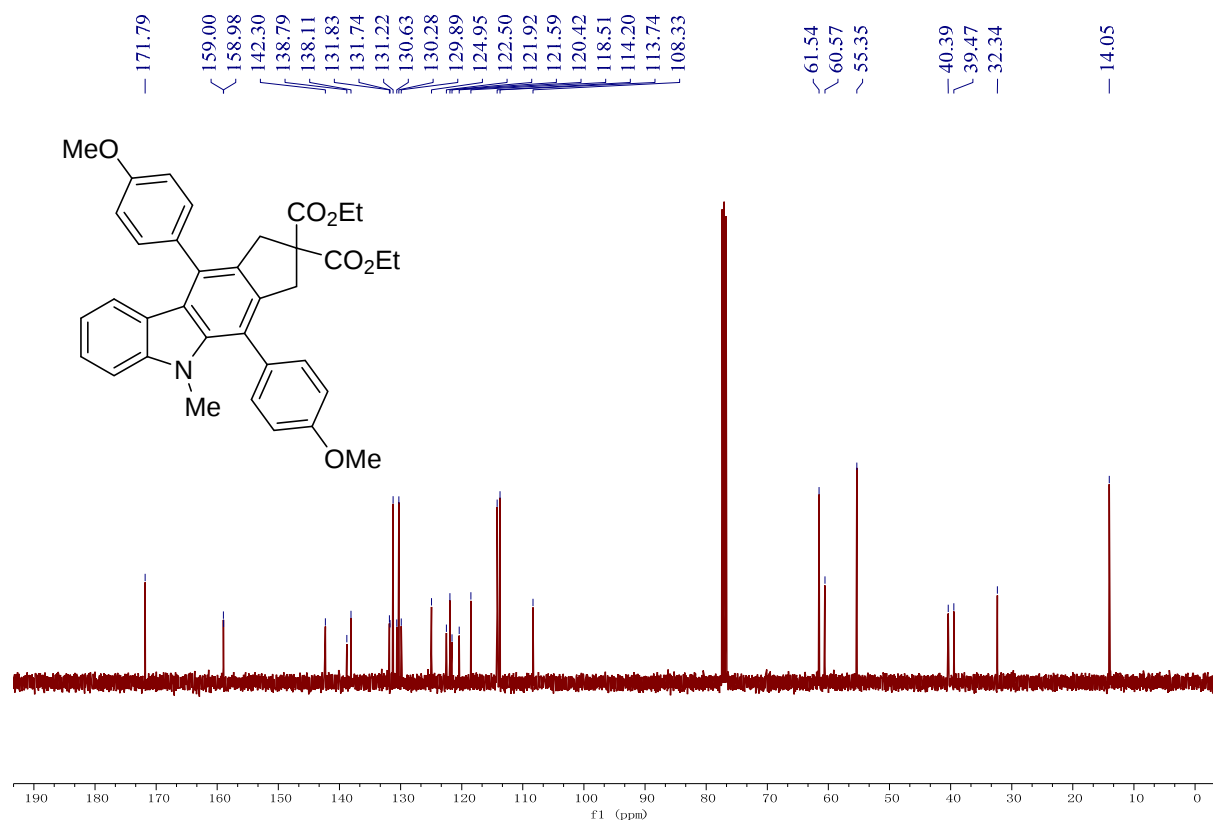
^{13}C NMR spectrum of **3ab**



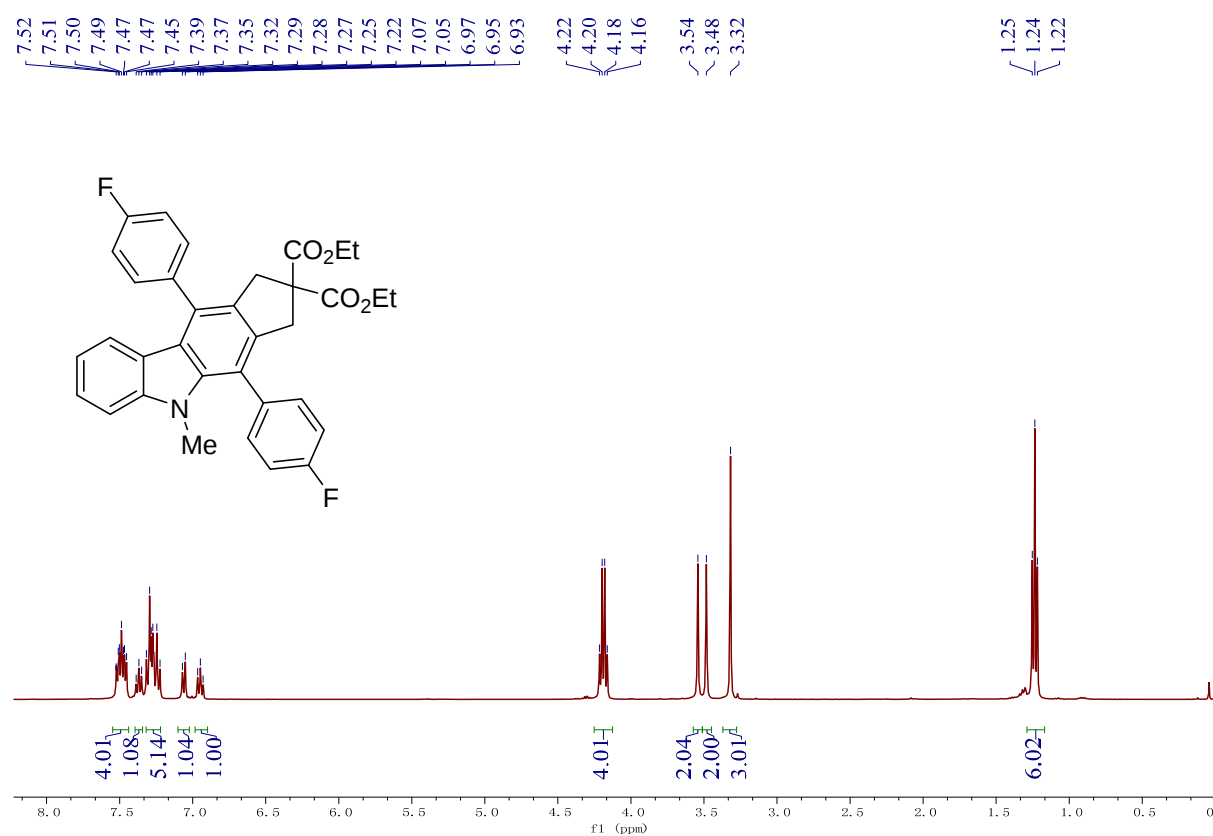
^1H NMR spectrum of **3ac**



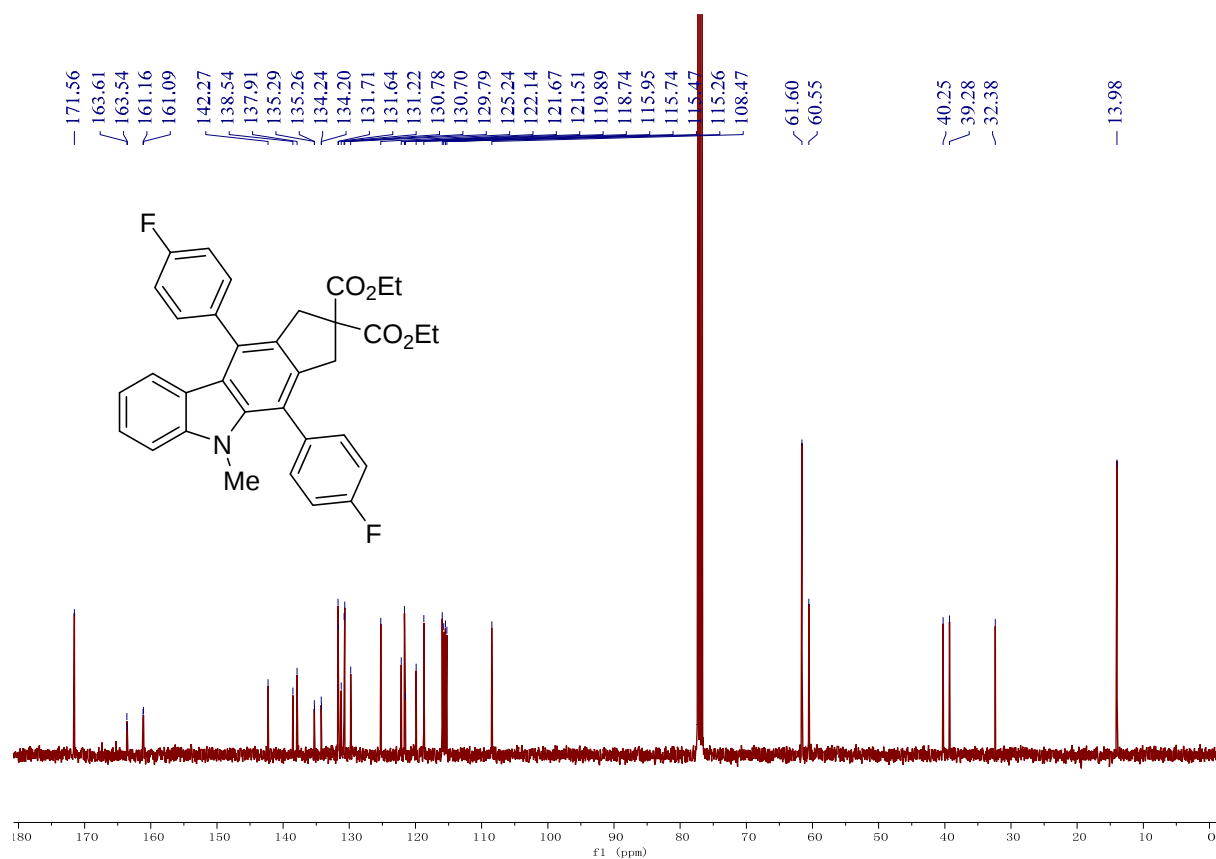
^{13}C NMR spectrum of **3ac**



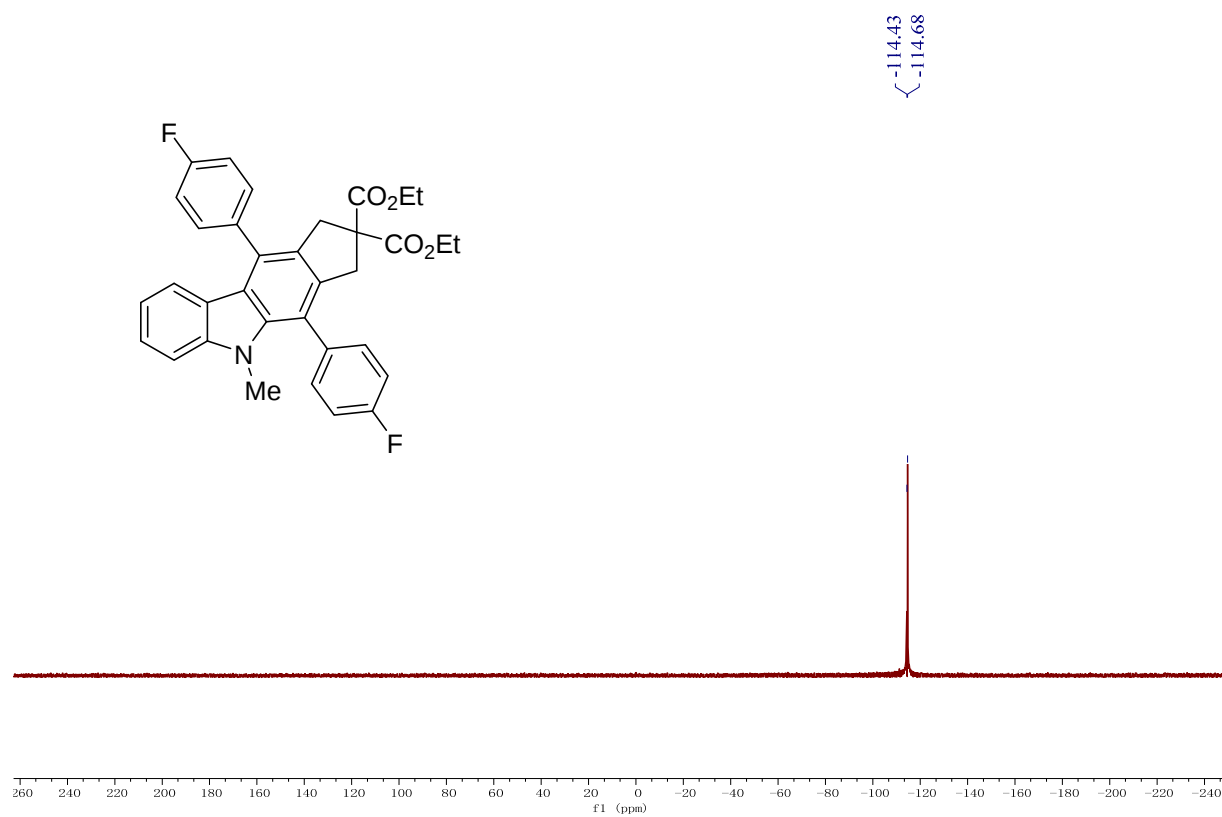
^1H NMR spectrum of **3ad**



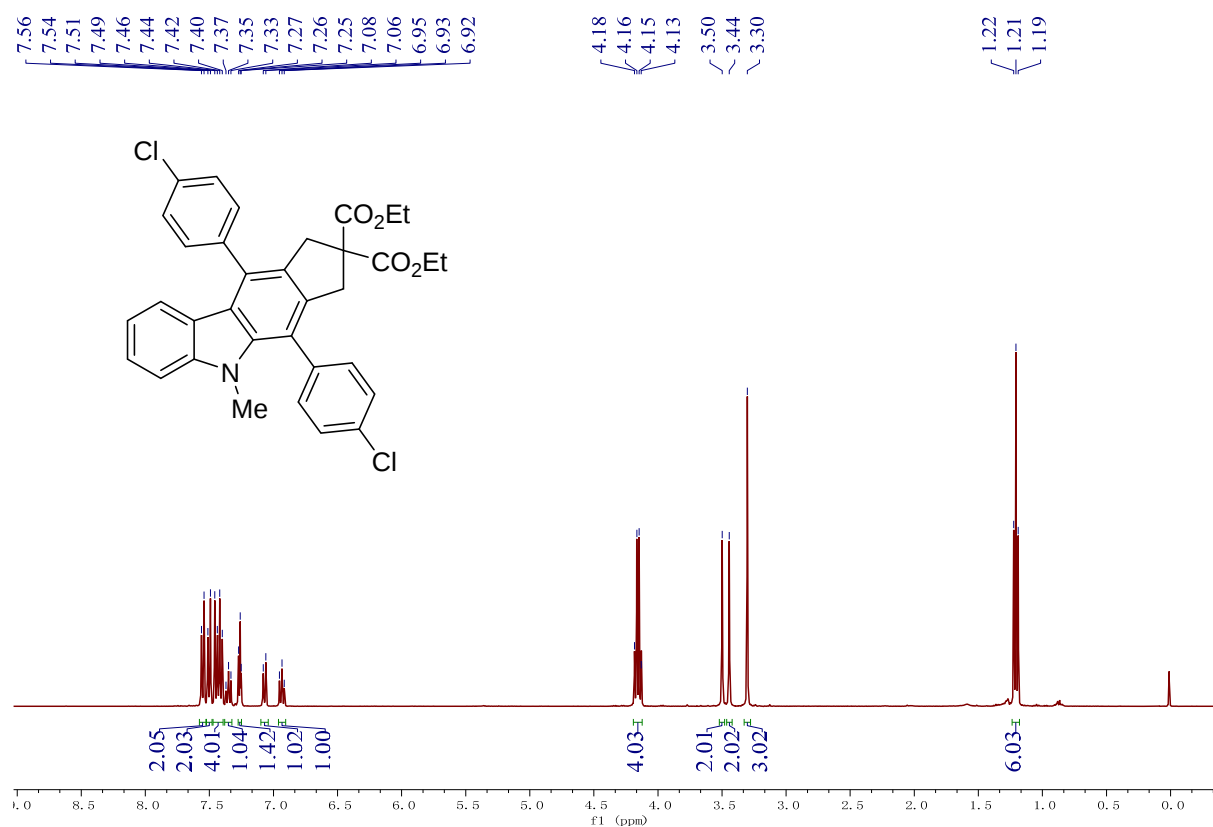
^{13}C NMR spectrum of **3ad**



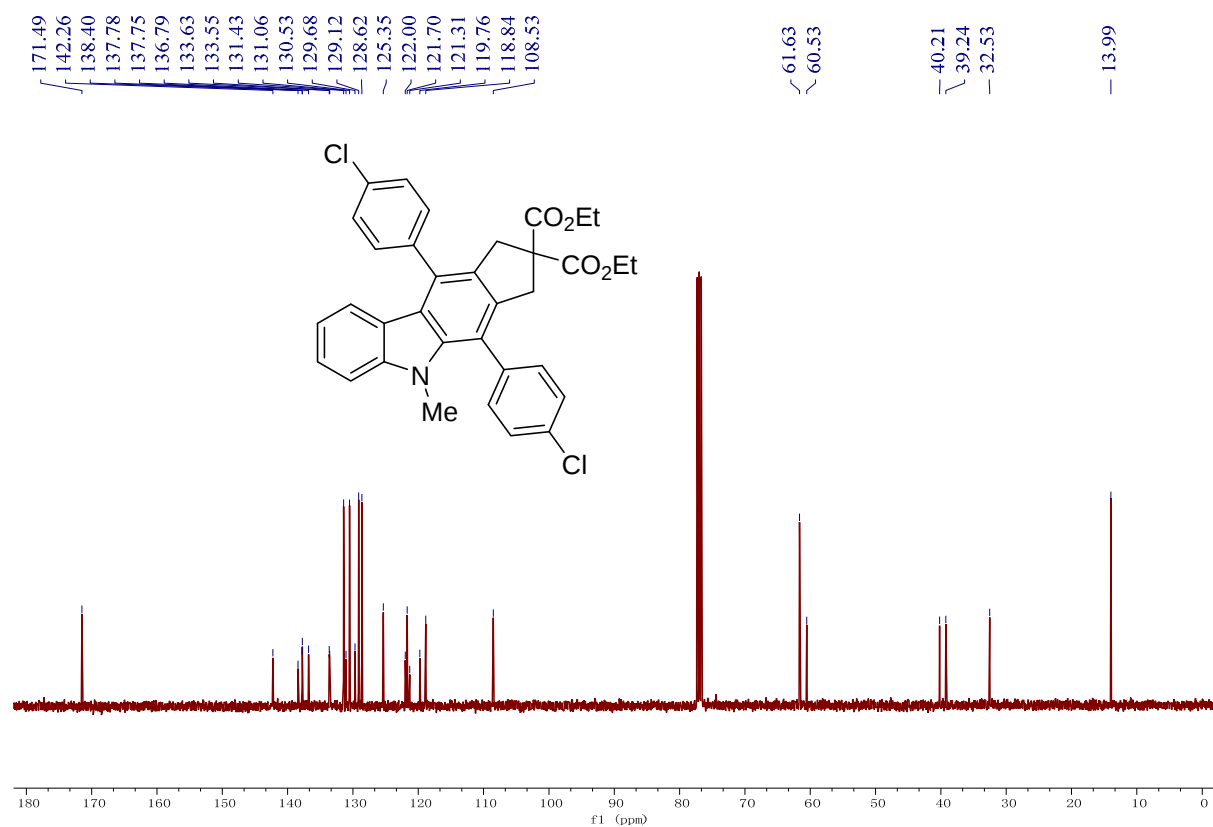
^{19}F NMR spectrum of **3ad**



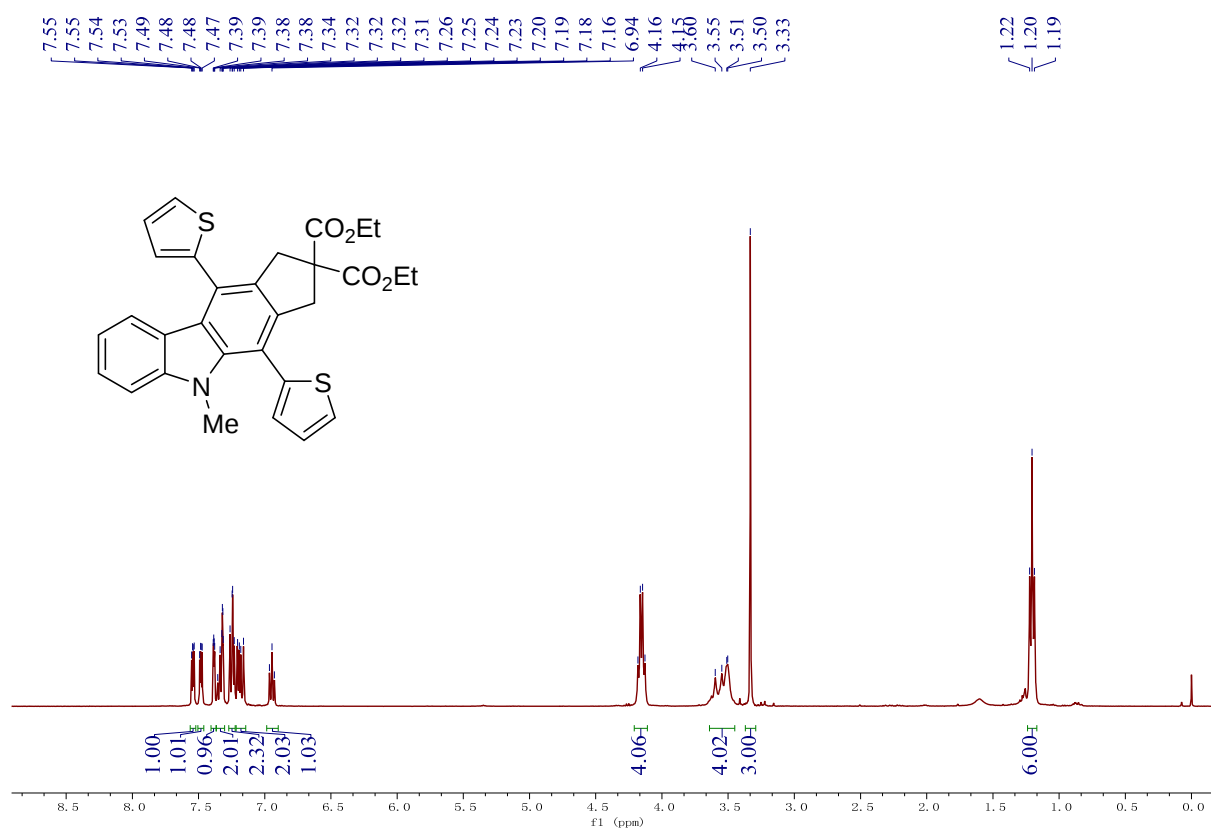
^1H NMR spectrum of **3ae**



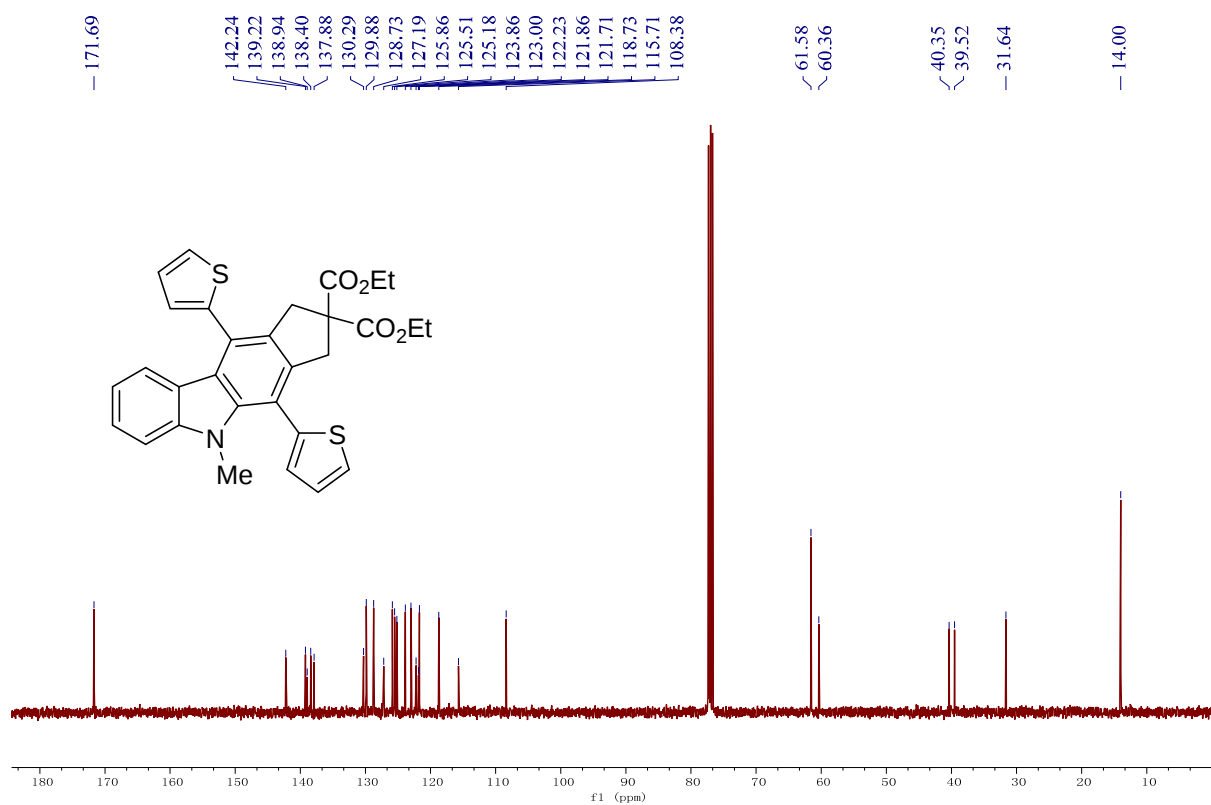
^{13}C NMR spectrum of **3ae**



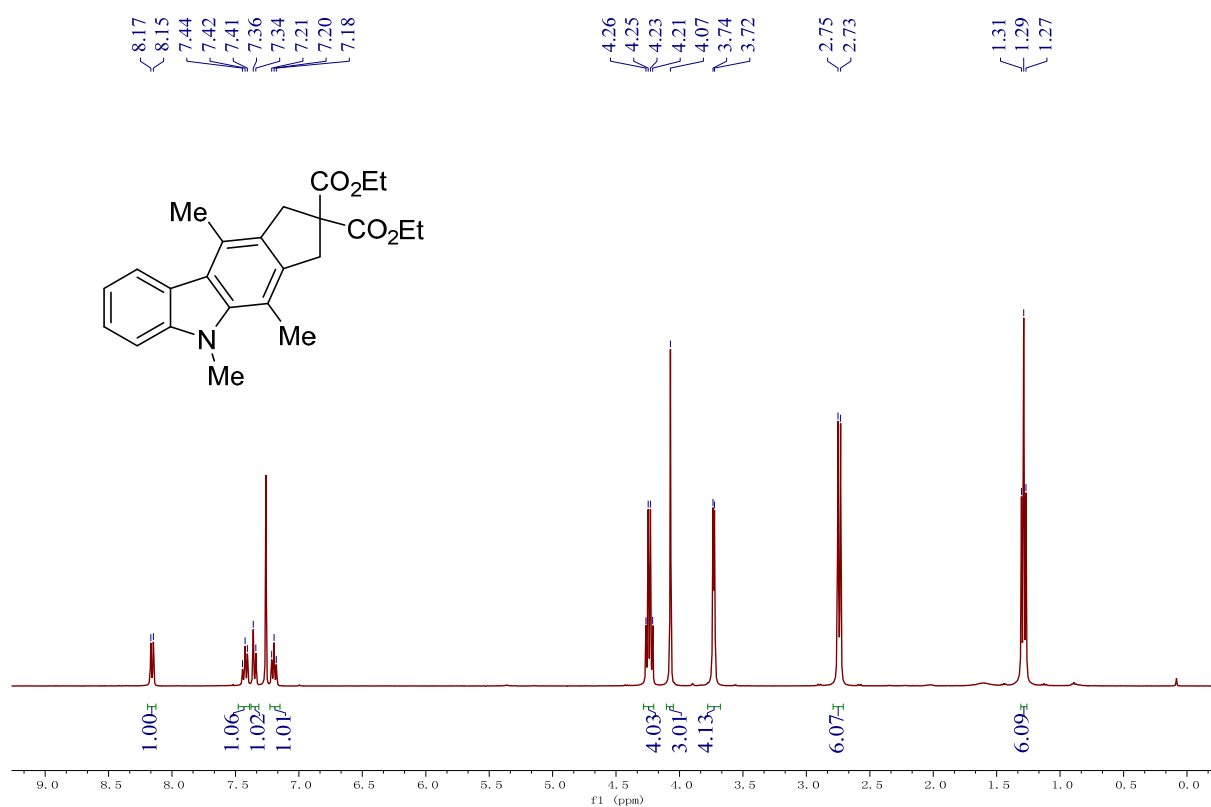
¹H NMR spectrum of **3af**



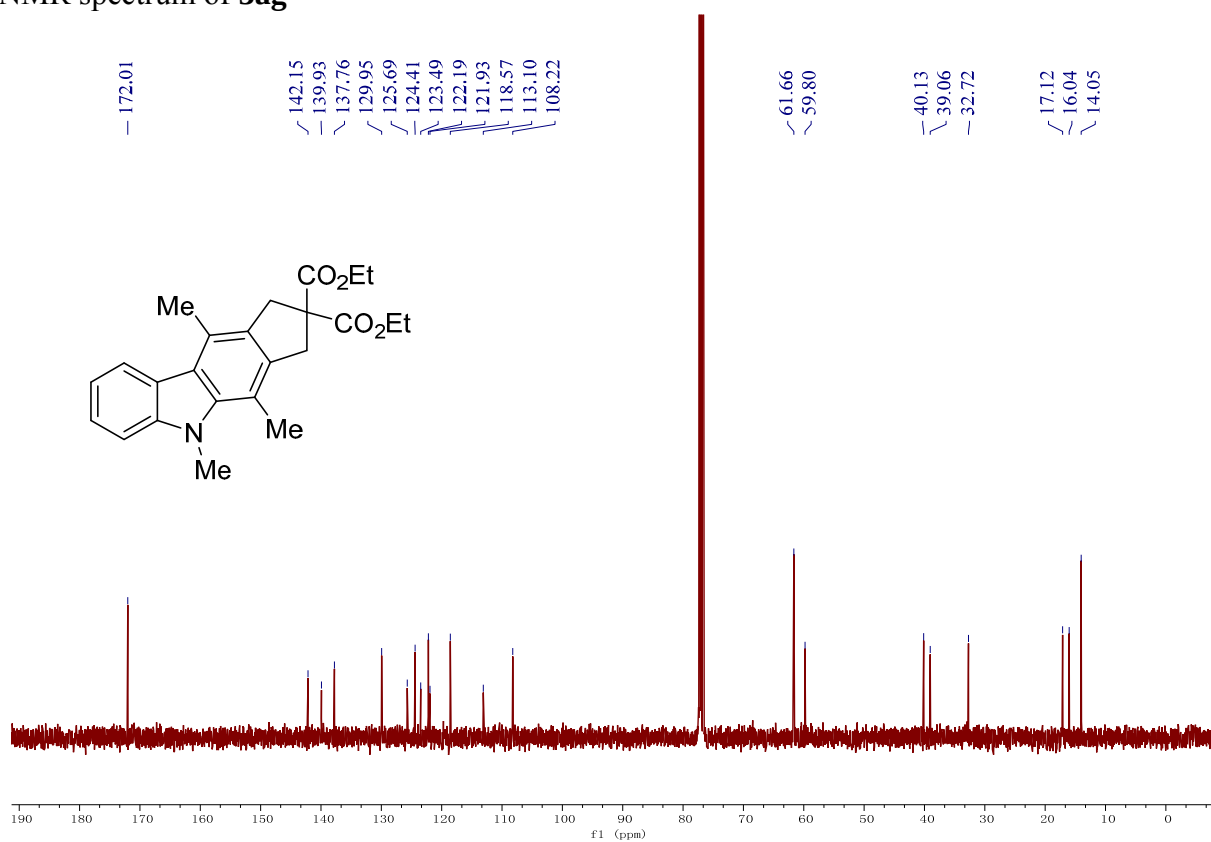
¹³C NMR spectrum of **3af**



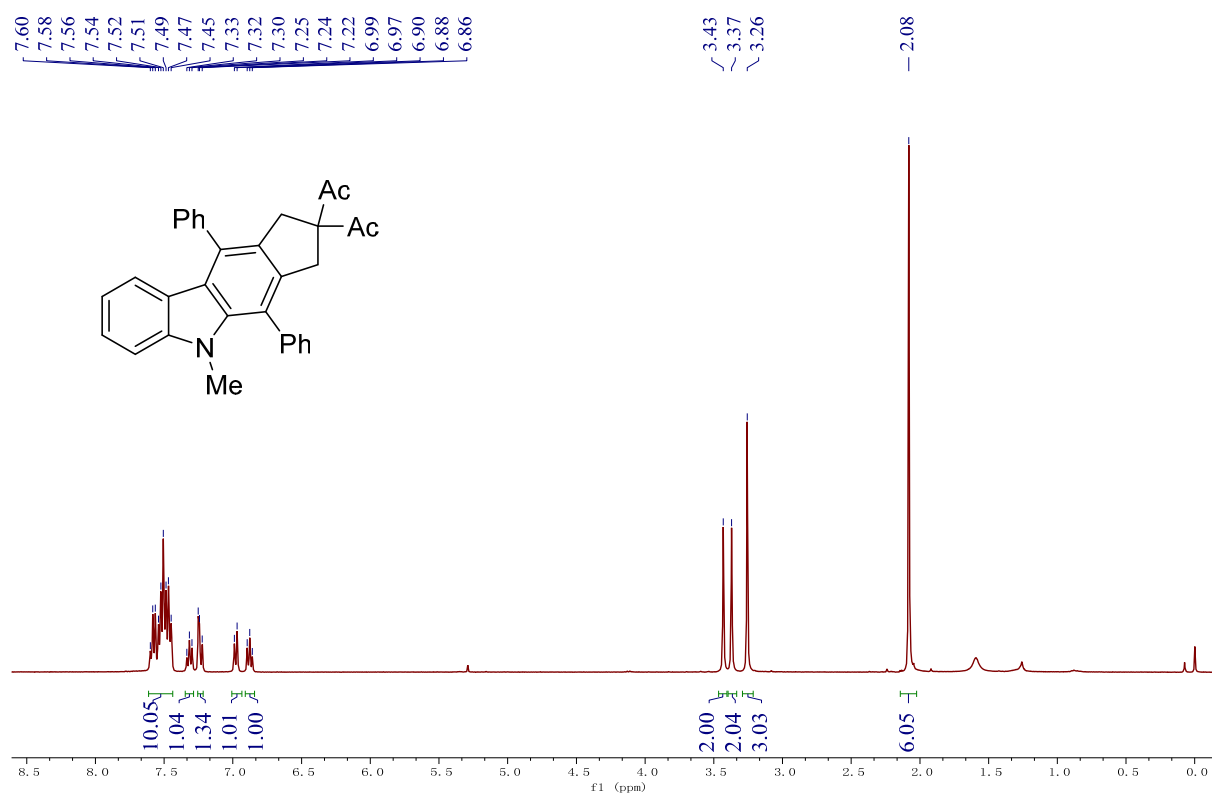
¹H NMR spectrum of **3ag**



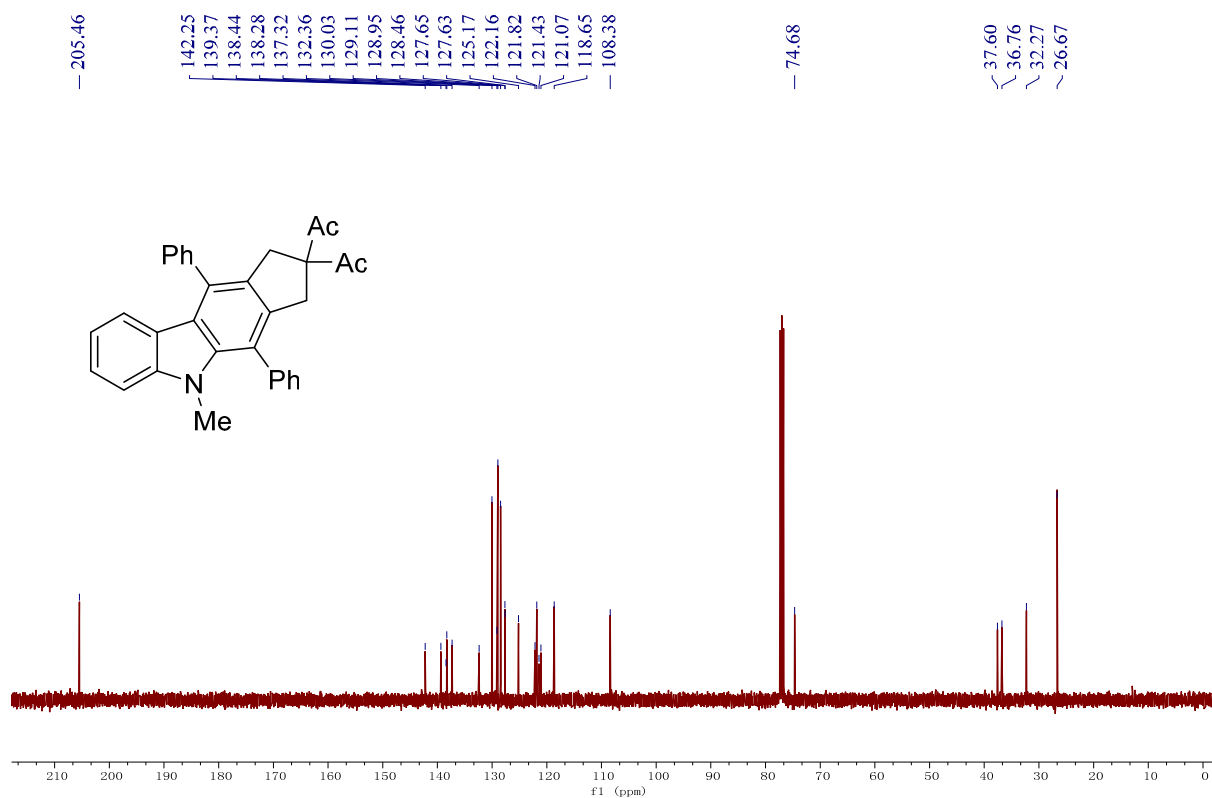
¹³C NMR spectrum of **3ag**



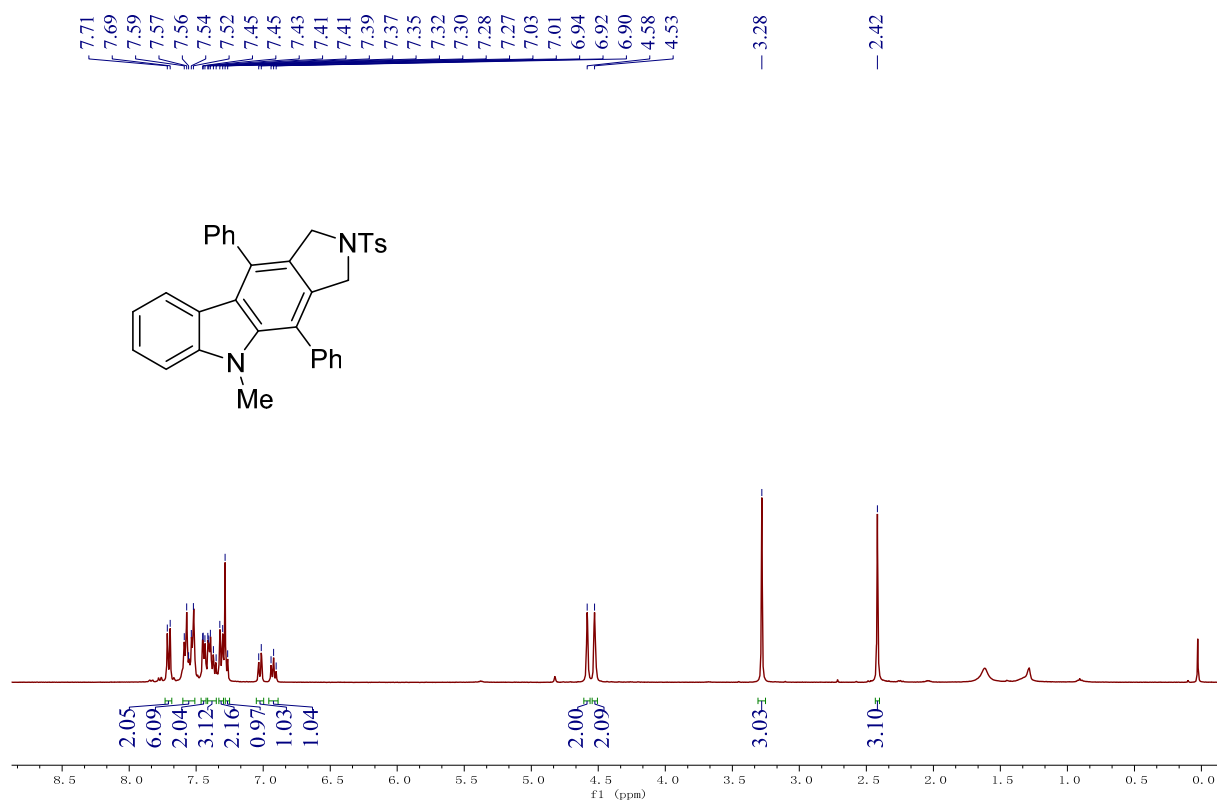
^1H NMR spectrum of **3ah**



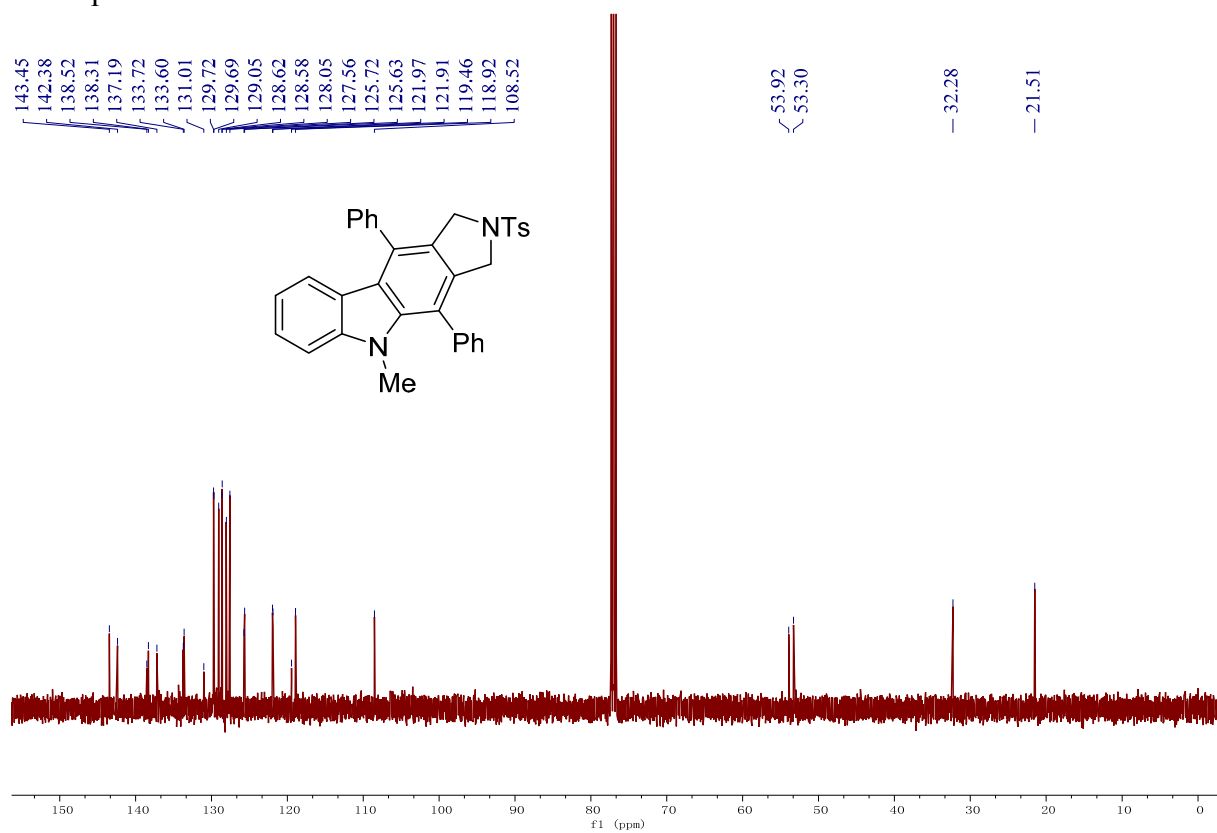
^{13}C NMR spectrum of **3ah**



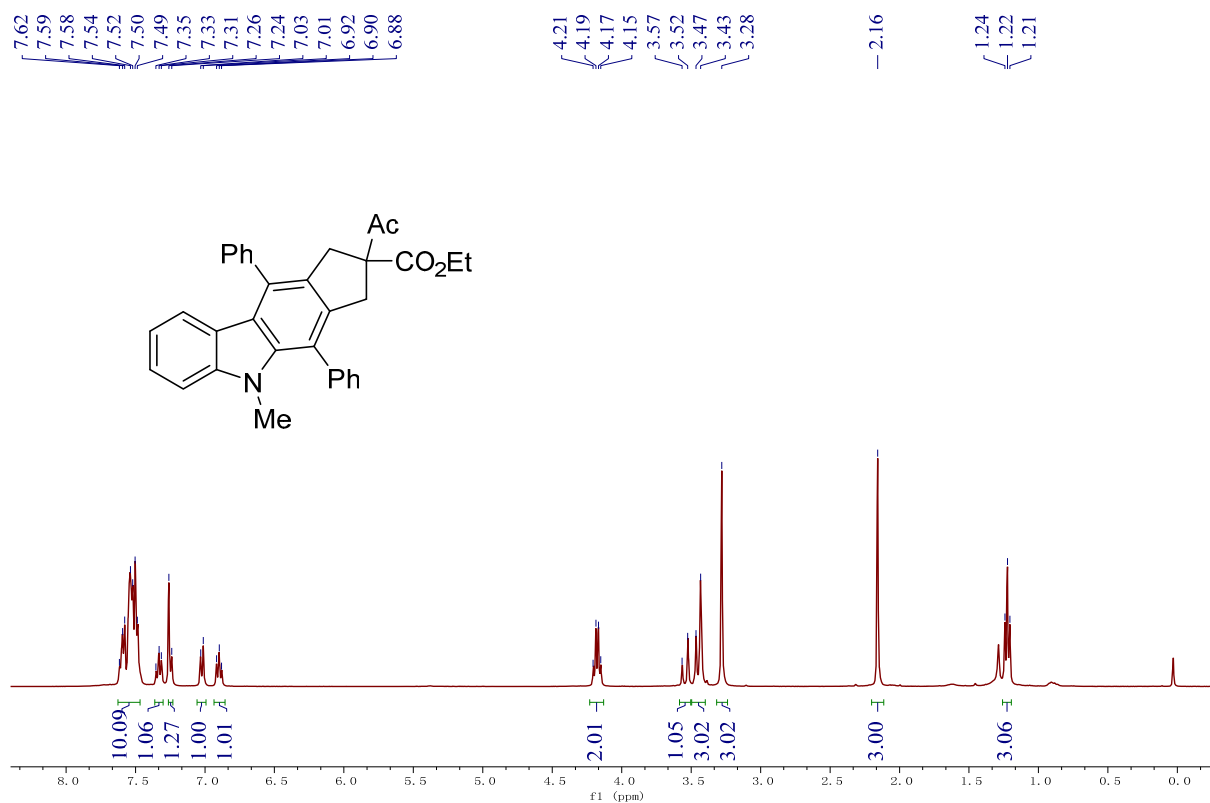
^1H NMR spectrum of **3ai**



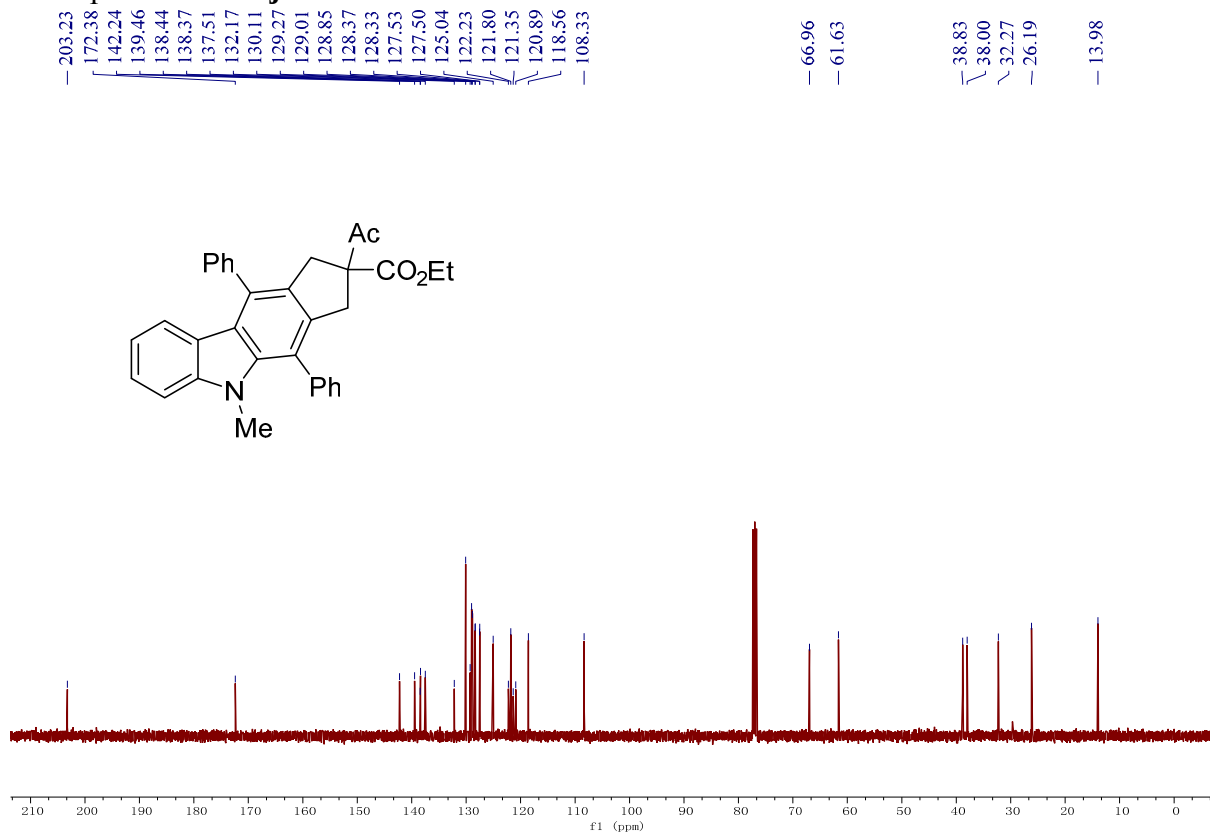
^{13}C NMR spectrum of **3ai**



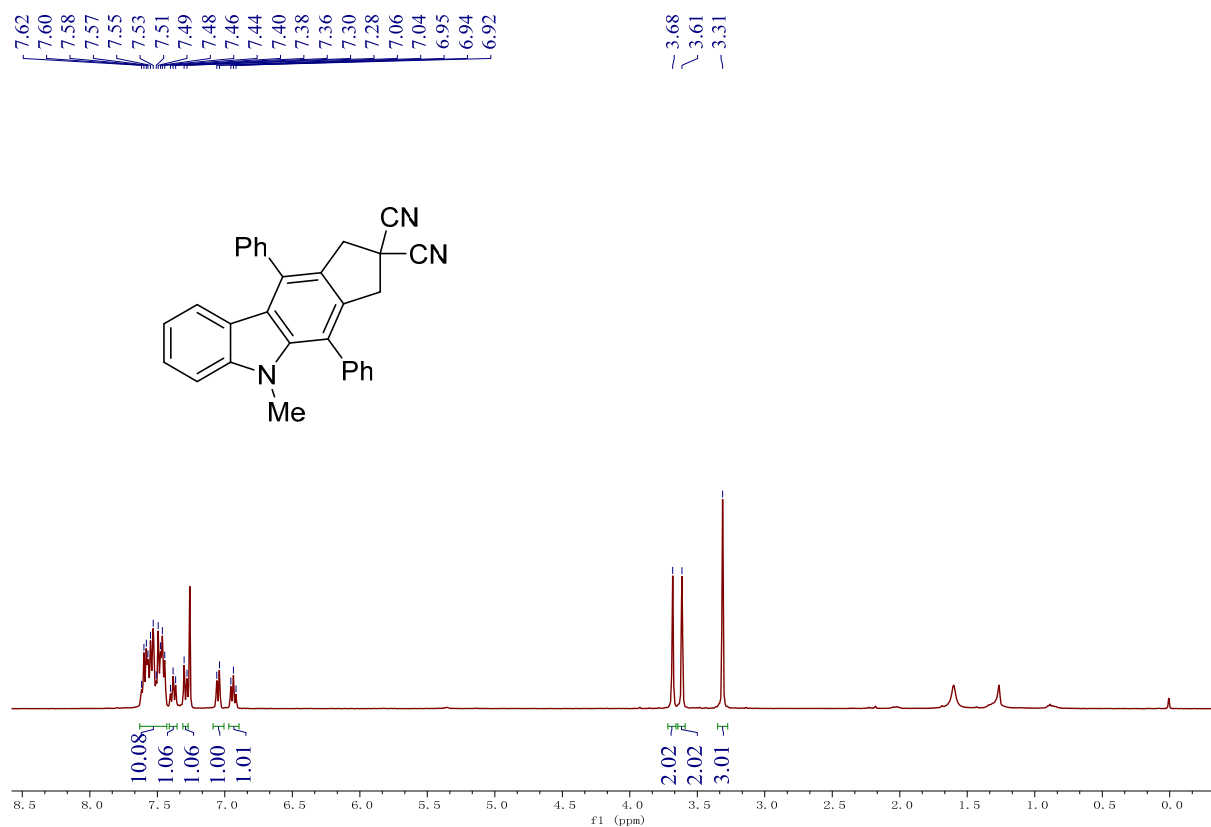
¹H NMR spectrum of **3aj**



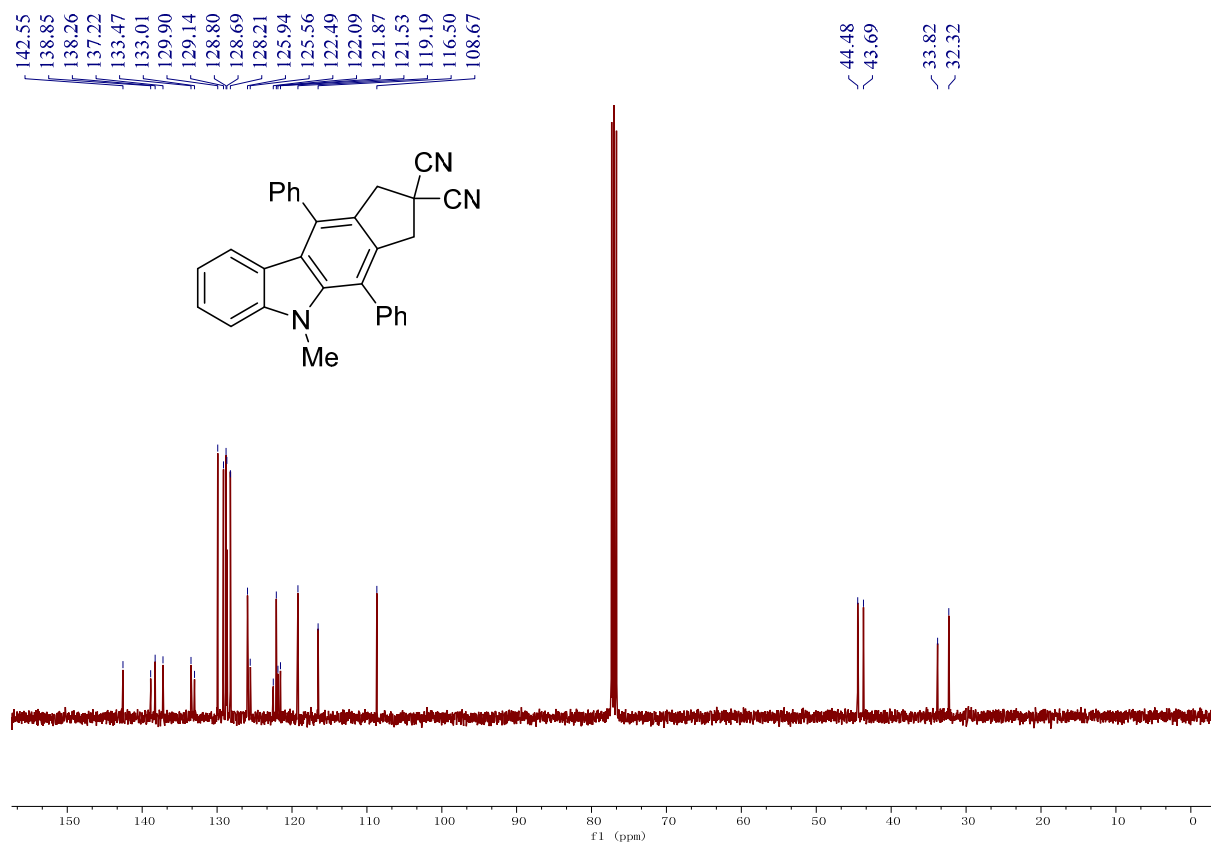
¹³C NMR spectrum of **3aj**



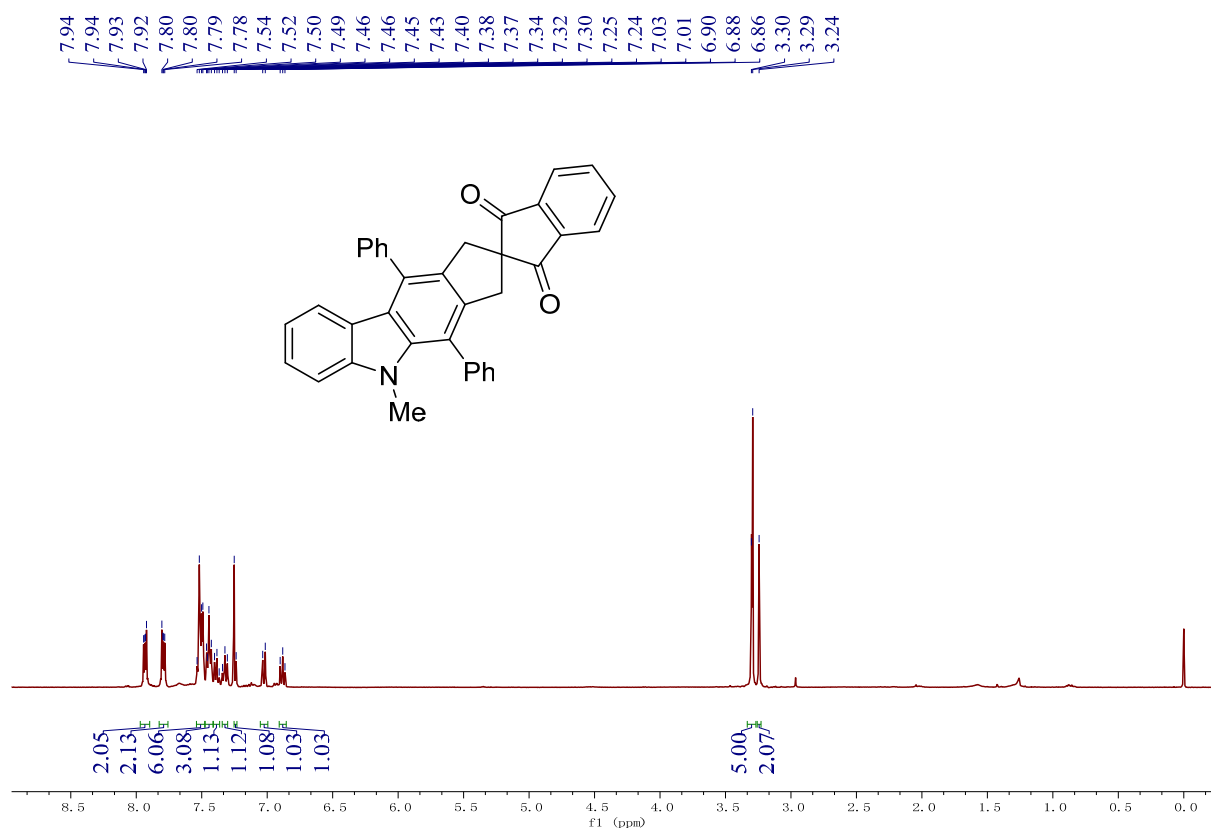
¹H NMR spectrum of **3ak**



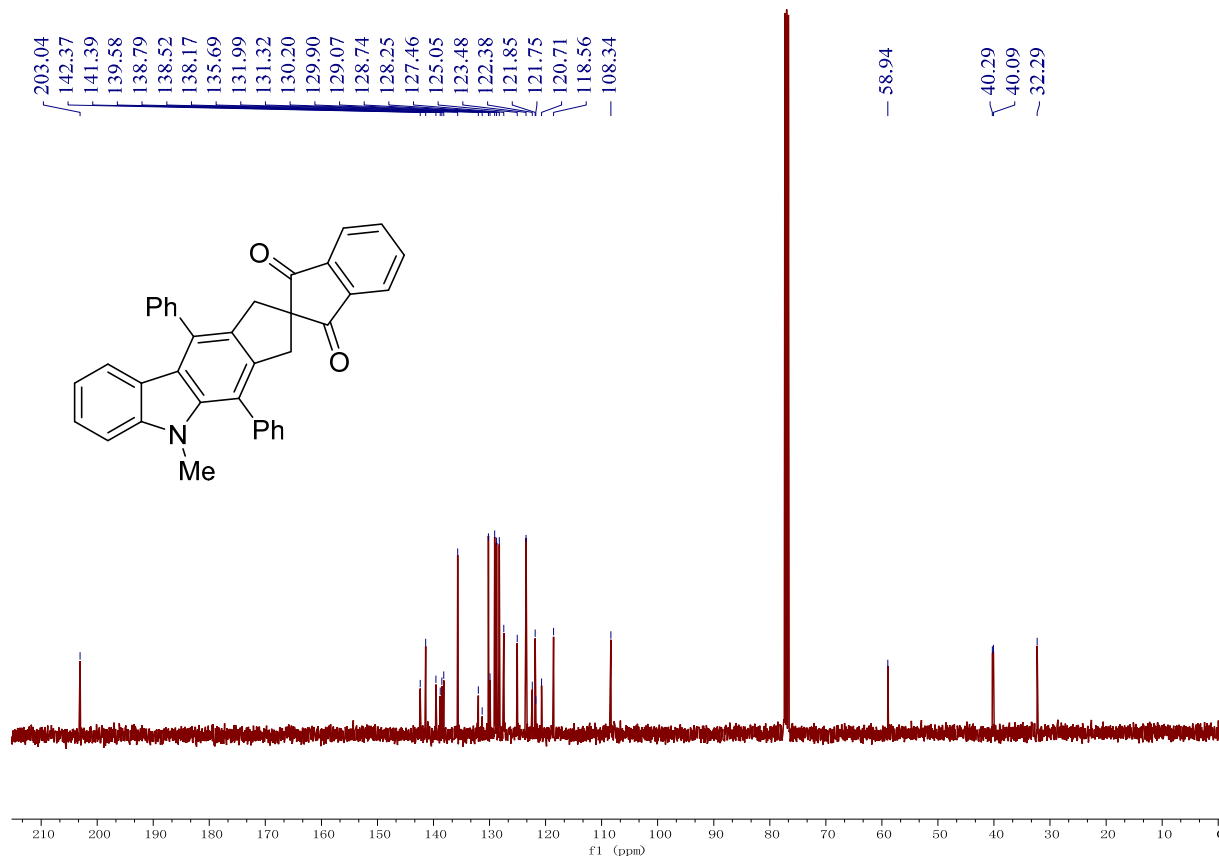
¹³C NMR spectrum of **3ak**



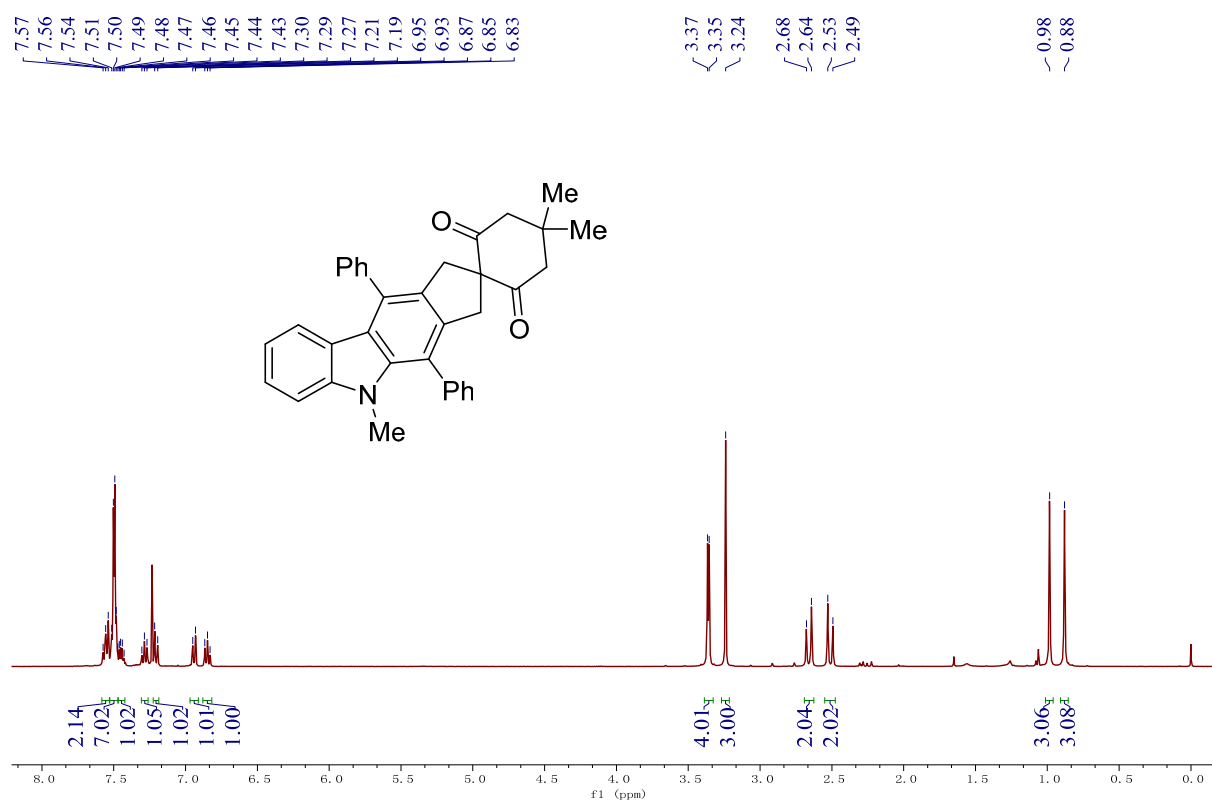
¹H NMR spectrum of **3al**



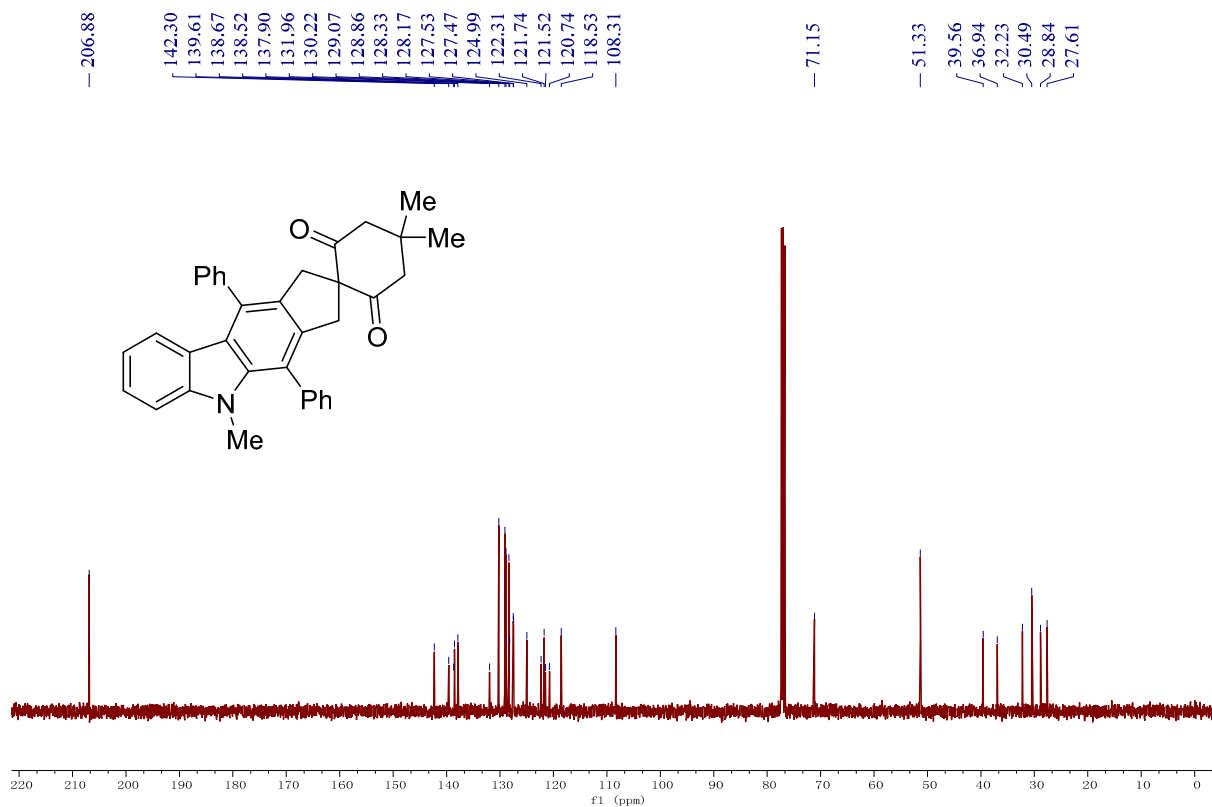
¹³C NMR spectrum of **3al**



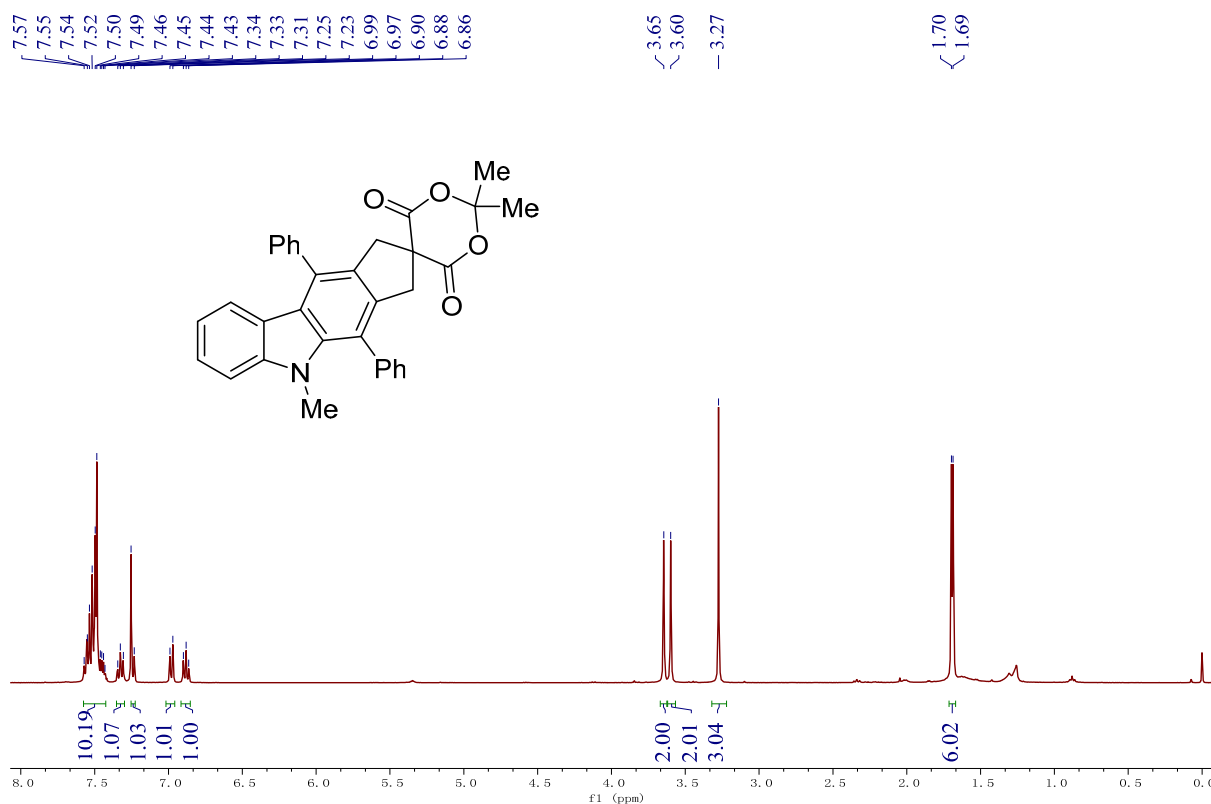
¹H NMR spectrum of **3am**



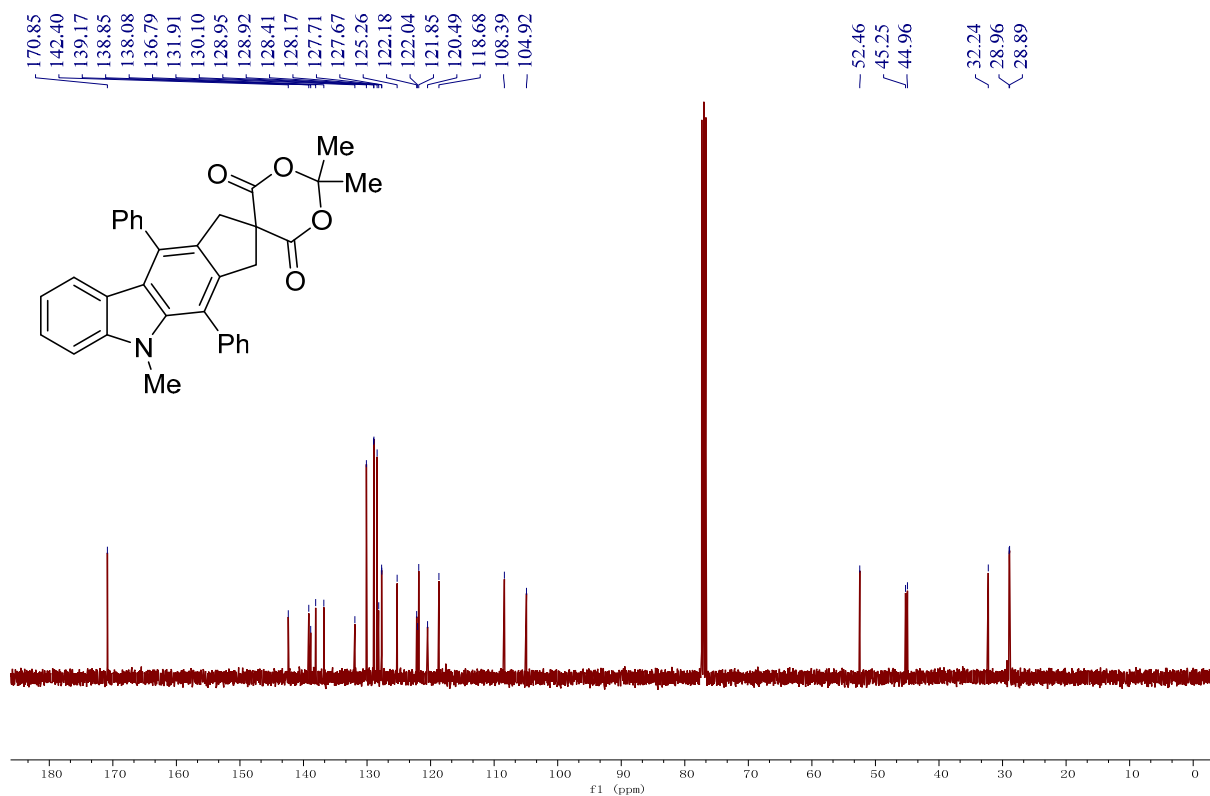
¹³C NMR spectrum of **3am**



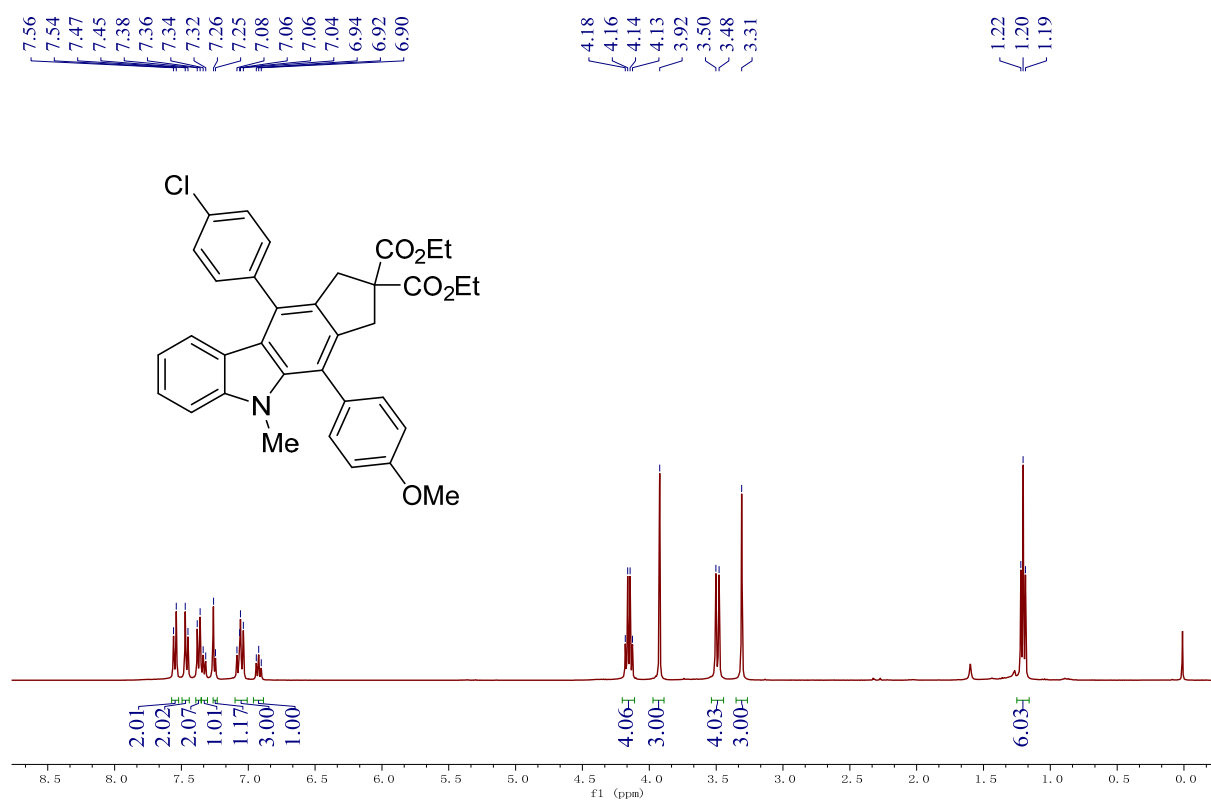
¹H NMR spectrum of **3an**



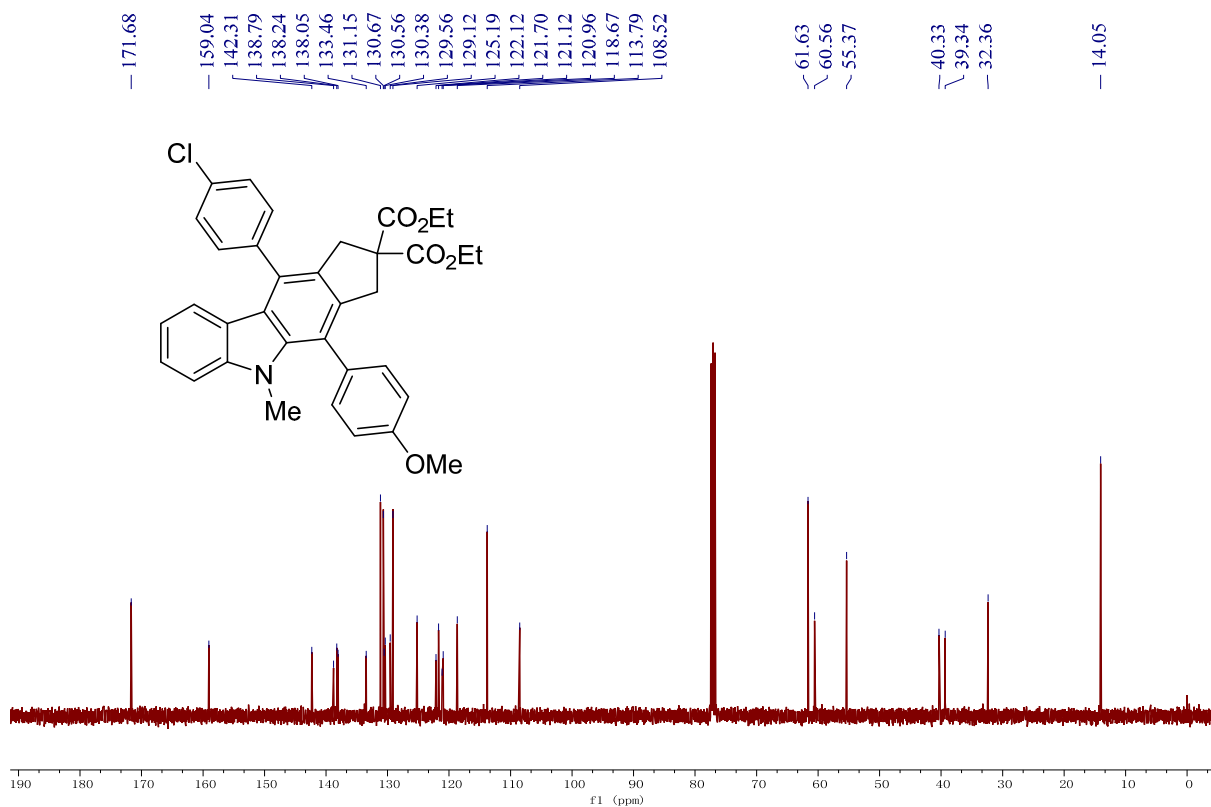
¹³C NMR spectrum of **3an**



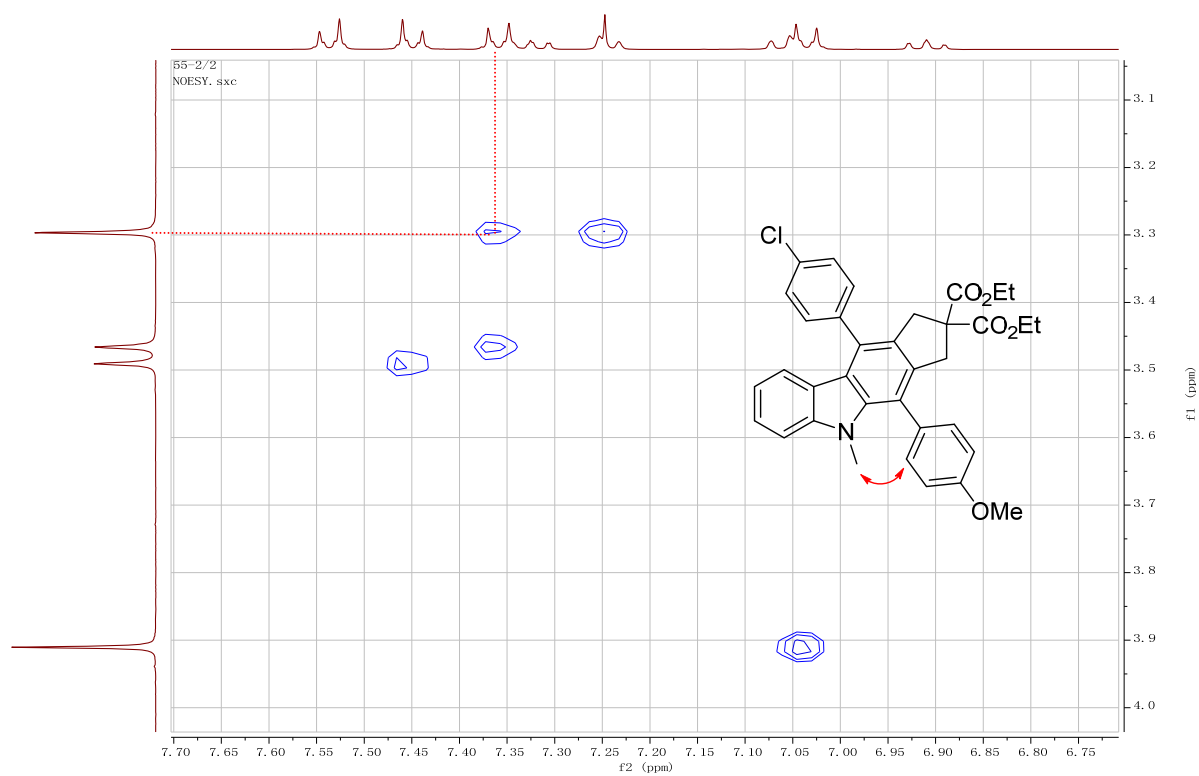
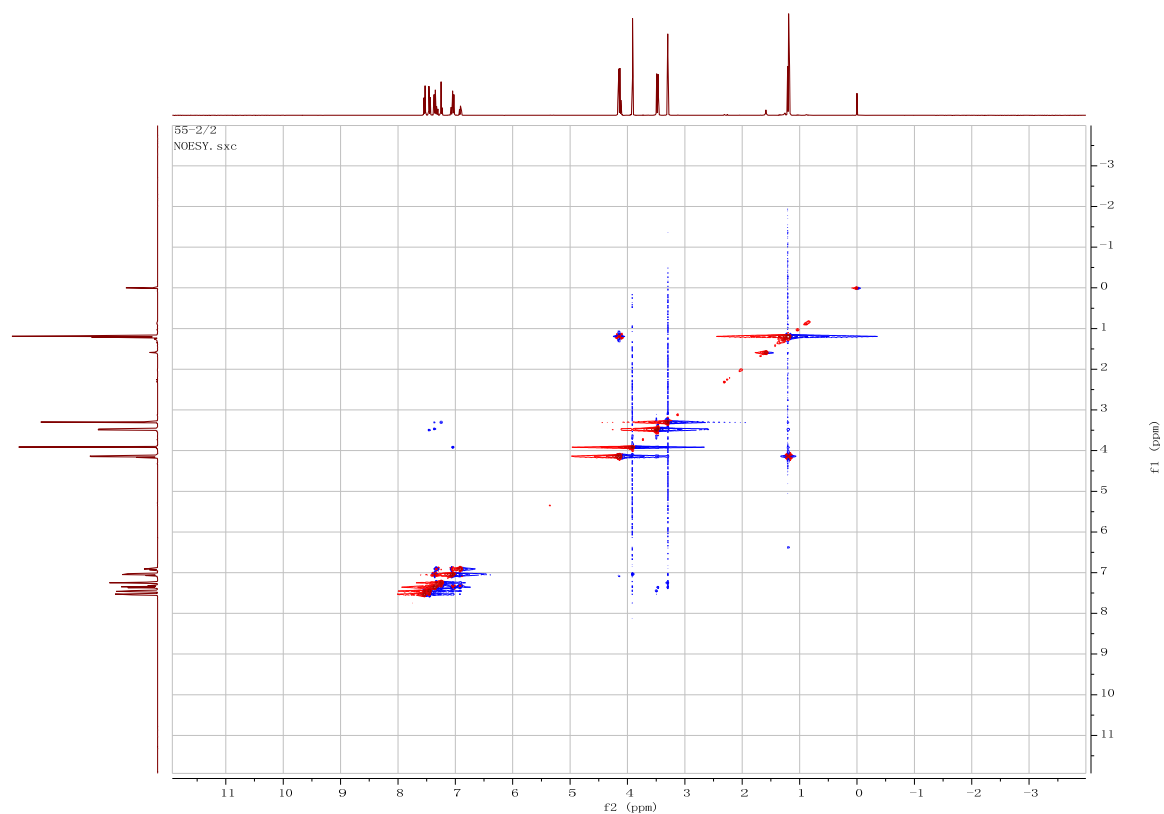
¹H NMR spectrum of **3ao**



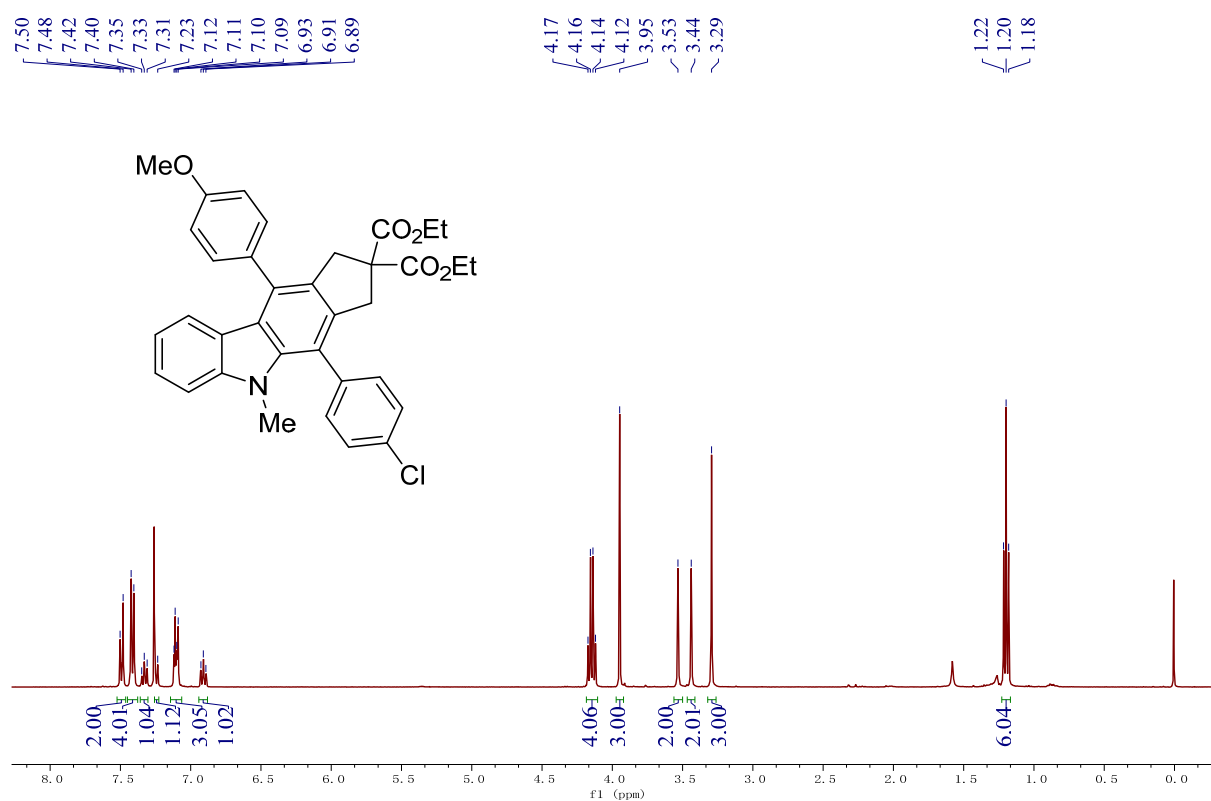
¹³C NMR spectrum of **3ao**



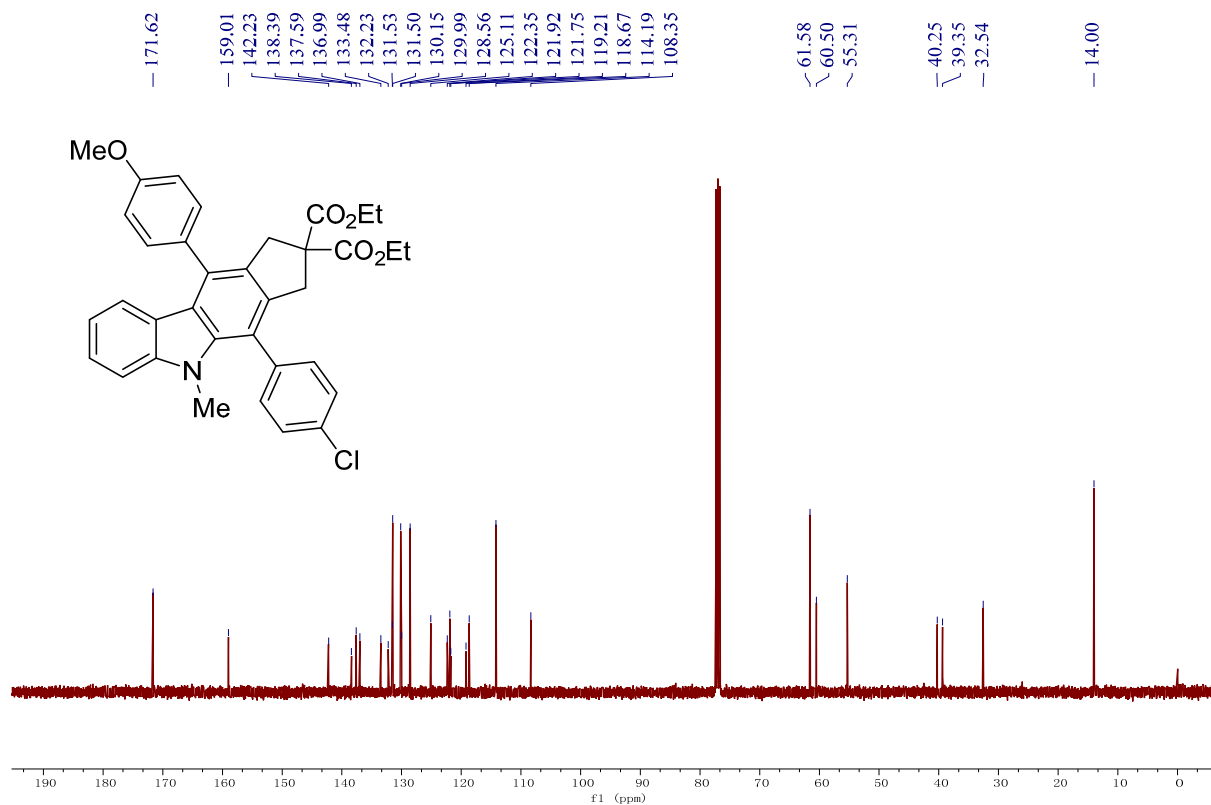
^1H - ^1H noesy spectrum of **3ao**



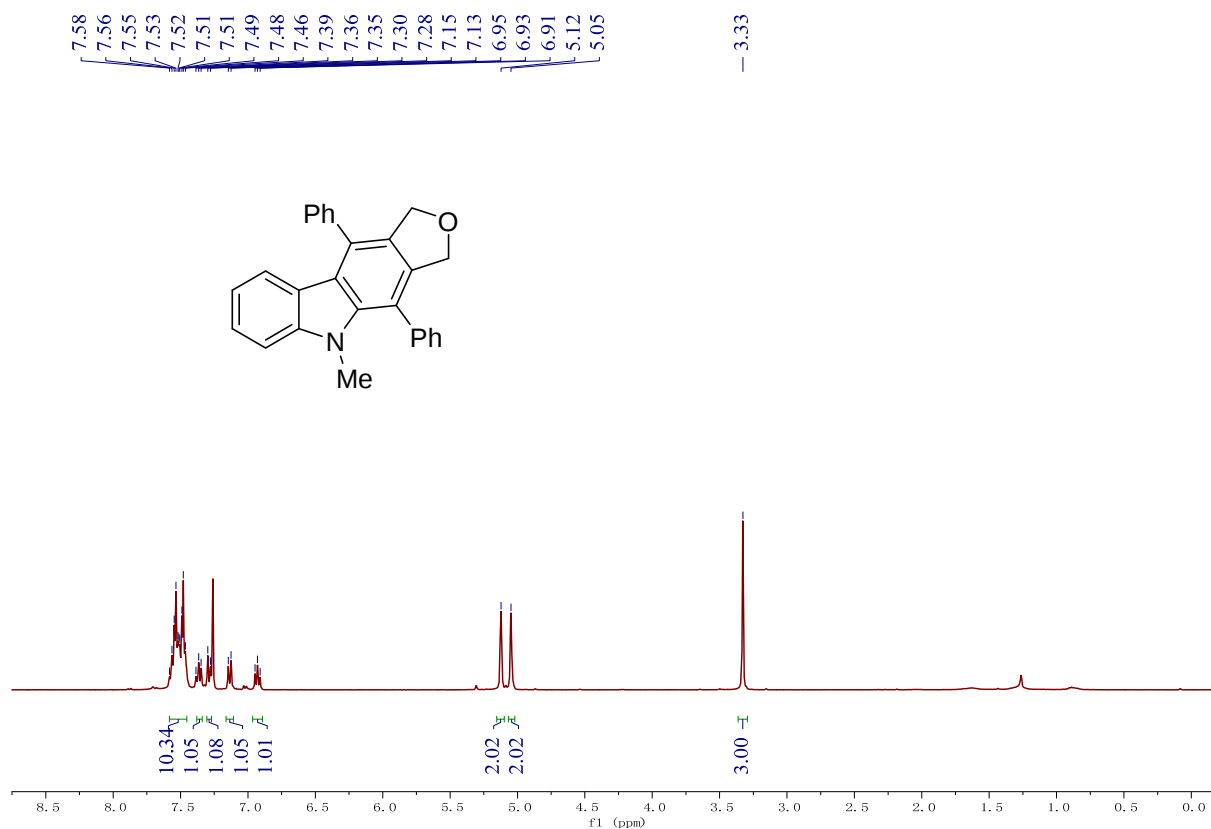
¹H NMR spectrum of **3ao'**



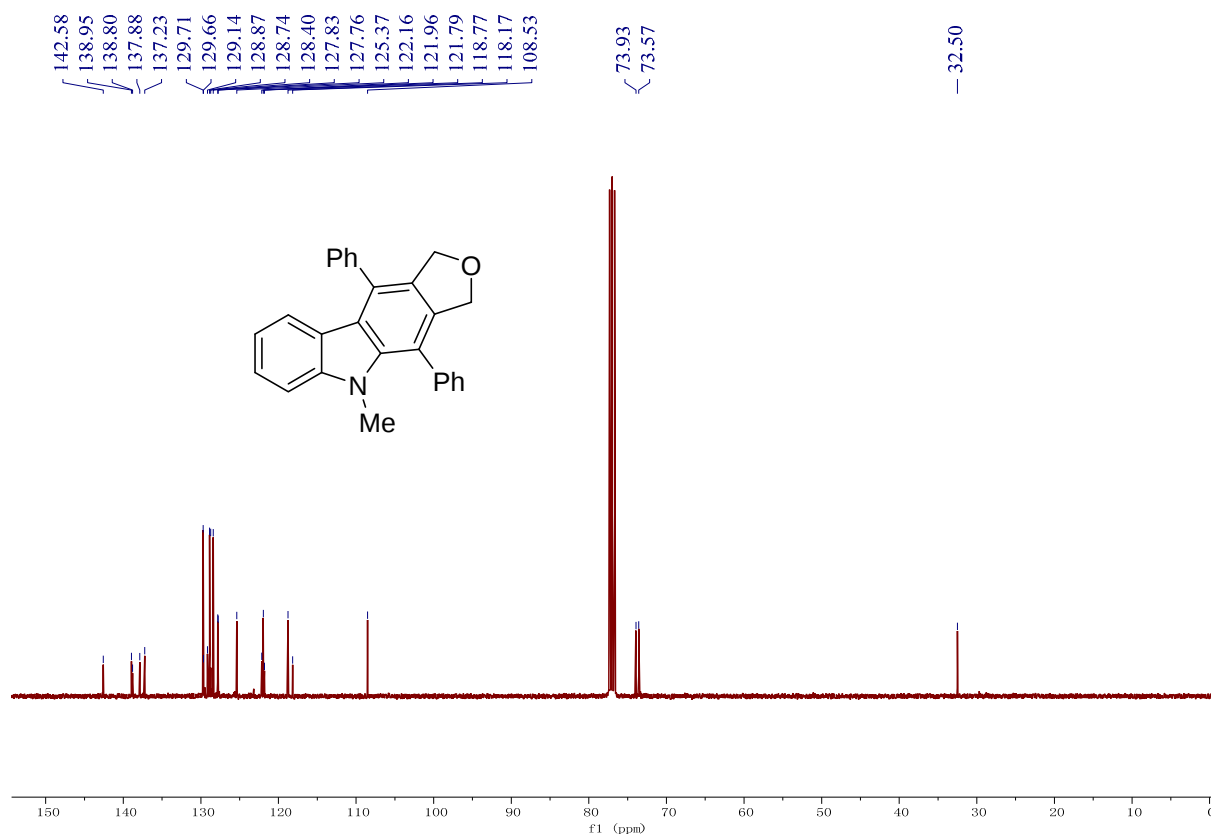
¹³C NMR spectrum of **3ao'**



¹H NMR spectrum of **3ap**



¹³C NMR spectrum of **3ap**



9. References:

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