Supporting Information

# Photocatalytic skeletal editing of bicyclic arenes to benzosemibullvalenes *via* energy transfer

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## 1. General information

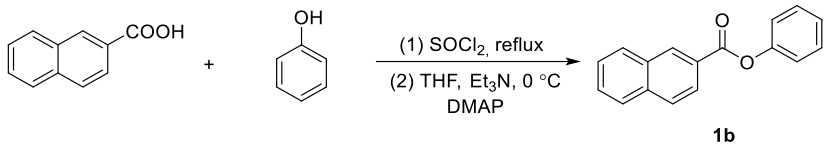
All reactions were carried out under Argon atmosphere in Schlenk tubes. Anhydrous solvents (including, MeCN,1,4-dioxane, DCM, THF, Water < 0.005%) were purchased from Energy and used as received. Solvent (including MeOH, HFIP, $Et_3N$ and EtOH, MeCN, THF, reagent grade) and commercially available compounds were purchased from Adamas-beta®, Aldrich, Energy Chemical, J&K, BiDe, ACMEC and TCI Chemical Company as reagent grade and used without further purification unless otherwise stated. $^{1}H$ NMR, $^{13}C$ NMR, $^{31}P$ NMR and $^{19}F$ NMR spectra were obtained with a Bruker AV II-400 spectrometer ($^{1}H$: 400 MHz, $^{13}C$: 101 MHz, $^{19}F$: 376 MHz, $^{31}P$: 162 MHz). The chemical shifts (δ) were expressed in ppm and J values were given in Hz using tetramethylsilane as the internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets ddt = doublet of doublets of triplets and br = broad. TLC was performed using commercially prepared silica gel plates (GF254), and visualized under UV light 254 nm. Flash column chromatography was performed on silica gel (200-300 mesh). All mixed solvent eluents are reported as v/v solutions. Emission intensities were recorded using SFQY-9000 Fluorescence Spectrometer. Cyclic voltammetry tests were carried out with a CHI700E electrochemical workstation. Mass analysis data were acquired on a SCIEX UPLC (EXion) – Q-TOF (X500R). Melting points were measured using a Hanon MP470 apparatus. X-Ray single-crystal diffraction data were collected on a Rigaku XtaLAB Synergy diffractometer.

## 2. The general synthetic route and characterization data of substrates

The naphthalene derivatives (**1a**, **1d-1l**), bicyclic substrates (**4a-4c**, **4g-4o**), and alkyne derivatives (**2f**, **2i**, **2r**) were purchased from Bide**,** Leyan, Energy Chemical, or Adamas-beta®, ACMEC, and were used directly without further purification. The synthesis of the naphthalene substrates (**1b**, **1c**), quinoline substrates (**4d-4f**), and alkyne substrates (**2e**, **2g**, **2h**, **2j-2q**, **2s**) was carried out according to the following procedures.

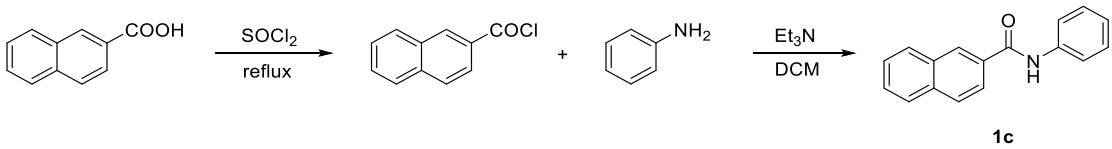
### 2.1 General Procedures for the synthesis of some substrates

### 2.1.1 Synthesis of 1b




Thionyl chloride (0.523 mL, 7.2 mmol, 1.2 eq.) was added to 2-naphthoic acid (1.033 g, 6 mmol, 1.0 eq.) and the mixture was stirred at reflux for 1 h. The solution was concentrated under vacuum. To a solution of the residue in THF (6 mL) was added triethylamine (1.0 mL, 7.2 mmol, 1.2 eq.). After cooling the mixture to 0 °C, phenol (564.0 mg, 6.0 mmol, 1.0 eq.) and a piece of 4,4-dimethylaminopyridine (DMAP) was added and then the reaction mixture was warmed to room temperature. After stirring the mixture for 1 h, the resulting mixture was passed through a short silica gel pad with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography. to afford **1b** as a white solid (96% yield).[1]

### 2.1.2 Synthesis of 1c

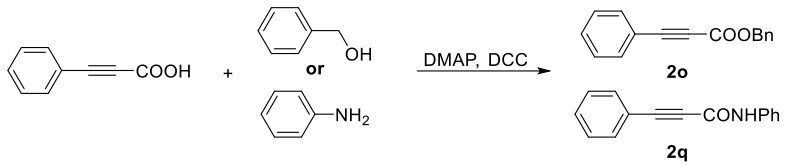



A 100 mL round-bottom flask was charged with 2-naphthic acid (1.033 g, 6.0 mmol, 1.0 eq.). Then thionyl chloride (0.522 mL, 7.2 mmol, 1.2 eq.) was added dropwise to the reaction mixture and stirred at 85 °C for 5 h. After cooling down to room temperature, the resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.[2]

Aniline (0.66 mL, 7.2 mmol, 1.2 eq.) in $CH_2Cl_2$ (12 mL) and $Et_3N$ (2.8 mL, 12.0 mmol, 2.0 eq.) were added dropwise to a solution of 2-naphthalenecarbonyl chloride in $CH_2Cl_2$ (10 mL) in a 50 mL two-necked flask at 0 ºC. The reaction mixture was warmed to rt, diluted with $CH_2Cl_2$ (80 mL), and washed with sat. $NH_4Cl$ aq. (40 mL). The aqueous layer was re-extracted with $CH_2Cl_2$ (40 mL

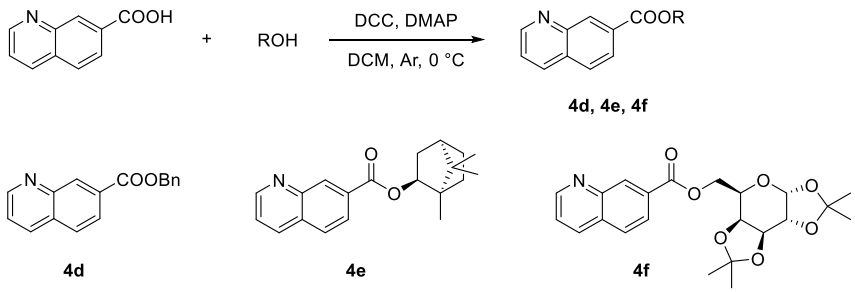
+ 50 mL), and the combined organic layer was washed with brine (40 mL), dried over $Na_2SO_4$, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EA) to afford **1c** as a white solid (83%).[3]

### 2.1.3 Synthesis of 2o, 2q



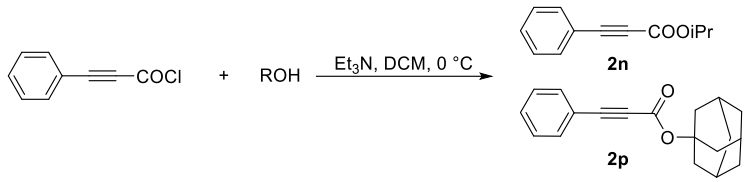

To a mixture of aniline or benzyl alcohol (10.0 mmol, 1.0 eq.) and phenylpropargylic acid (10.0 mmol, 1.0 eq.) in $CH_2Cl_2$ (0.1 M) was added a solution of DMAP (5 mol%) and DCC (12.0 mmol, 1.2 eq.) in $CH_2Cl_2$ (0.05 M) at 0°C. The reaction mixture was stirred for 12 h at room temperature. The solid was filtrated and washed with 0.1 N HCl (10 mL). The filtrate was concentrated in vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the product **2o** or **2q**.[4]

### 2.1.4 Synthesis of 4d, 4e, 4f



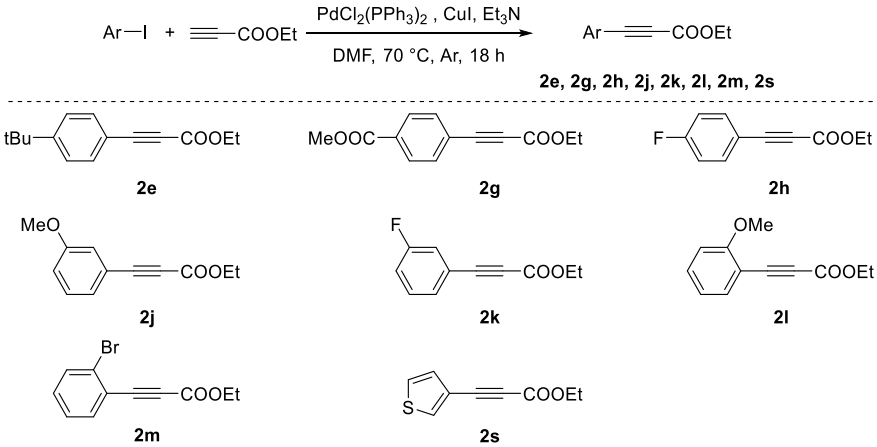

An oven dried round-bottom flask was charged with 7-quinolinecarboxylic acid (2.0 mmol, 1.0 eq.) and DMAP (10 mol %), and purged with argon for 10 minutes. The contents were dissolved in $CH_2Cl_2$ before the alcohol was added (0.9 eq.). The mixture was cooled to 0 °C and a $CH_2Cl_2$ solution of DCC (3.0 mmol, 1.5 eq.) was added drop-wise and the reaction was warmed to room temperature and stirred overnight (approximately 12 hours). The mixture was washed with three portions of aqueous $NaHCO_3$ and two portions of brine. The organic phase was separated and collected, then dried over magnesium sulfate. The excess solvent was removed under reduced pressure. Finally, the residue was purified by column chromatography on silica gel, using a petroleum ether and ethyl acetate mixture as the eluent to afford product **4d**, **4e** or **4f**.[5]

### 2.1.5 Synthesis of 2n, 2p




Alcohol (5.0 mmol, 1.5 eq.) was added to a solution of $Et_3N$ (6.6 mmol, 2.0 eq.) in DCM (0.2 M), and 3-phenyl-2-propynoyl chloride (5.0 mmol, 1.5 eq.) was slowly added dropwise to the reaction mixture while maintaining the temperature at 0 °C. After the addition was complete, the mixture was stirred overnight at room temperature. The reaction was quenched by the addition of aqueous $NaHCO_3$, and the mixture was extracted twice with ethyl acetate (EA). The organic layers were combined, dried over $Na_2SO_4$, and the solution was concentrated under reduced pressure. The crude product **2n** or **2p** was then purified by column chromatography on silica gel, using a petroleum ether/ethyl acetate mixture as the eluent.[3]

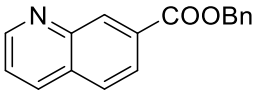
### 2.1.6 Synthesis of 2e, 2g, 2h, 2j, 2k, 2l, 2m and 2s




To a solution of aryl iodide (15.0 mmol, 1.5 eq.), ethyl propiolate (10.0 mmol, 1.0 eq.) and $K_2CO_3$ (4.15 g, 30.0 mmol, 3.0 eq.) in THF (80 mL) was added $PdCl_2(PPh_3)_2$ (140.4 mg, 0.2 mmol, 2 mol%). The mixture was stirred for 5 min. And CuI (19.2 mg, 0.1 mmol, 1 mol%) was added. The resulting mixture was then heated under a nitrogen atmosphere at 65 °C for 8 h. The mixture was cooled to room temperature, and the solid was removed by filtration. Then the filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as the eluent to provide the desired products.[6]

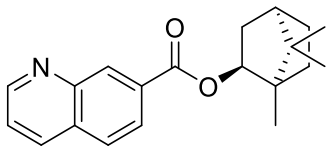
## 2.2 Characterization data of the substrates

Benzyl quinoline-7-carboxylate (**4d**)



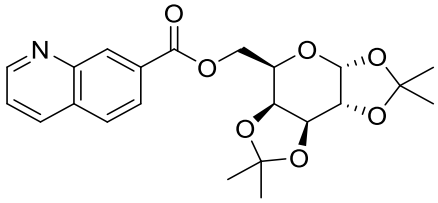
**Physical state:** White solid
**Melting Point:** 122.3-122.8 °C
**Yield：** 90%
**$R_f$** = 0.3 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 9.02 – 8.94 (m, 1H), 8.90 – 8.83 (m, 1H), 8.21 – 8.14 (m, 2H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.52 – 7.46 (m, 3H), 7.43 – 7.33 (m, 3H), 5.44 (s, 2H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.2, 151.5, 147.7, 135.9, 135.9, 132.3, 131.0, 130.8, 128.7, 128.4, 128.3, 128.2, 126.2, 122.9, 67.2.
**HRMS** (ESI)**:** calcd for $C_{17}H_{14}NO_2$ $[M+H]^+$ *m/z* 264.1019, found 264.1016.

(1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl quinoline-7-carboxylate (**4e**)



**Physical state:** White solid
**Melting Point:** 57.6 - 58.1 °C
**Yield：** 26%
**$R_f$** = 0.2 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 9.00 – 8.91 (m, 1H), 8.82 (s, 1H), 8.21 – 8.09 (m, 2H), 7.89 – 7.80 (m, 1H), 7.50 – 7.41 (m, 1H), 5.23 – 5.10 (m, 1H), 2.56 – 2.43 (m, 1H), 2.26 – 2.15 (m, 1H), 1.86 – 1.68 (m, 2H), 1.47 – 1.27 (m, 2H), 1.20 – 1.12 (m, 1H), 0.97 – 0.89 (m, 9H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.5, 151.4, 147.7, 136.0, 131.9, 131.8, 130.7, 128.1, 126.3, 122.8, 81.2, 49.3, 48.0, 45.1, 37.0, 28.2, 27.5, 19.8, 19.0, 13.7.
**HRMS** (ESI)**:** calcd for $C_{20}H_{24}NO_2$ $[M+H]^+$ *m/z* 310.1802, found 310.1806.

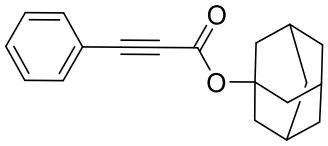
((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl quinoline-7-carboxylate (**4f**)



**Physical state**: White solid
**Melting Point:** 57.6 - 58.1 °C
**Yield：** 30%
**$R_f$** = 0.5 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 9.01 – 8.91 (m, 1H), 8.80 (d, *J* = 1.4 Hz, 1H), 8.18 – 8.07 (m, 2H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.51 – 7.40 (m, 1H), 5.55 (d, *J* = 5.0 Hz, 1H), 4.68 – 4.61 (m, 1H), 4.59 – 4.47 (m, 2H), 4.40 – 4.30 (m, 2H), 4.24 – 4.18 (m, 1H), 1.51 (s, 3H), 1.46 (s, 3H), 1.33 (s, 3H), 1.30 (s, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.1, 151.4, 147.6, 135.9, 132.2, 130.9, 130.8, 128.2, 126.2, 122.9, 109.7, 108.9, 96.4, 71.1, 70.8, 70.6, 66.0, 64.1, 26.1, 26.1, 25.0, 24.6.

**HRMS** (ESI)**:** calcd for $C_{22}H_{26}NO_7$ $[M+H]^+$ *m/z* 416.1704, found 416.1723.

Adamantan-1-yl 3-phenylpropiolate(**2p**)



**Physical state:** White oil
**Yield：** 23%
**Rf** = 0.5 in Petroleum ether/ethyl acetate (40:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.53 – 7.47 (m, 2H), 7.38 – 7.25 (m, 3H), 2.13 (s, 9H), 1.66 – 1.56 (m, 6H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 152.7, 132.9, 130.3, 128.5, 120.0, 83.8, 83.7, 82.1, 41.3, 36.1, 31.0.
**HRMS** (ESI)**:** calcd for $C_{19}H_{20}O_2$ $[M+H]^+$ *m/z* 281.1536, found 281.1543.

## 2.3 Involved substrates

## 2.3.1 Successful substrates

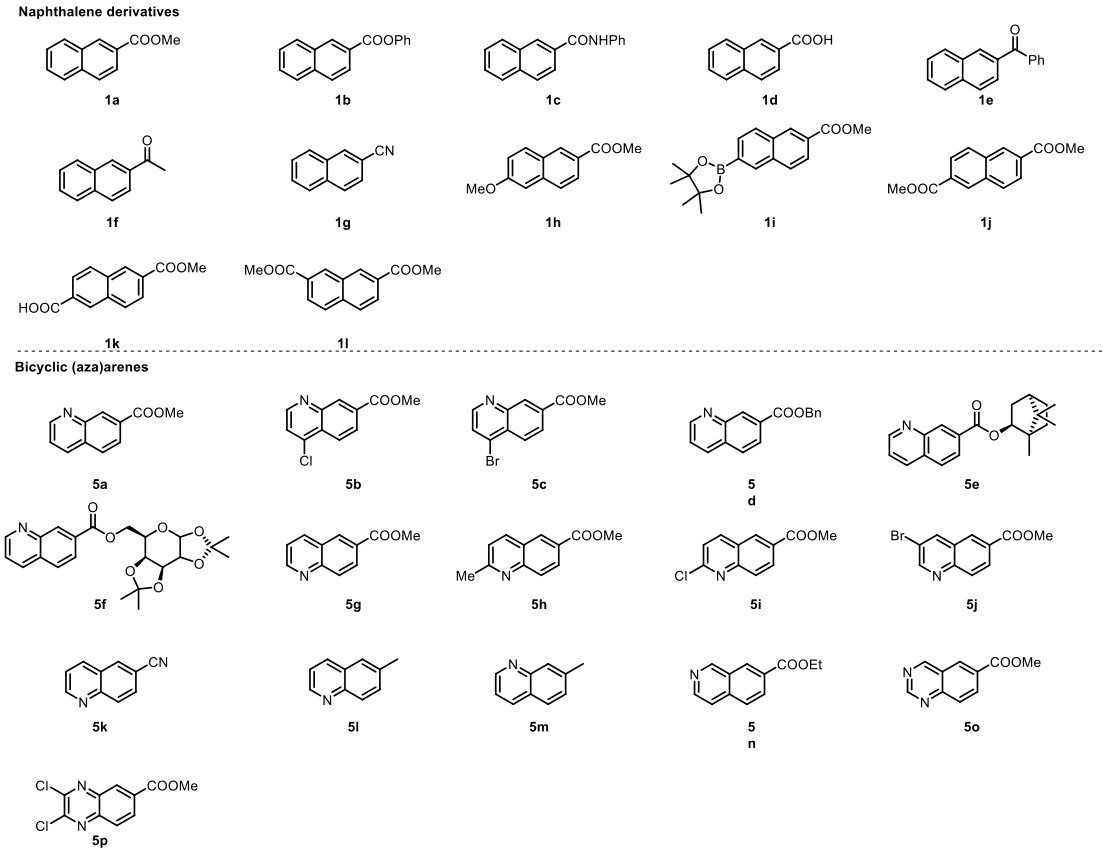



**Figure S1.** Structures of successful bicyclic (aza)arenes

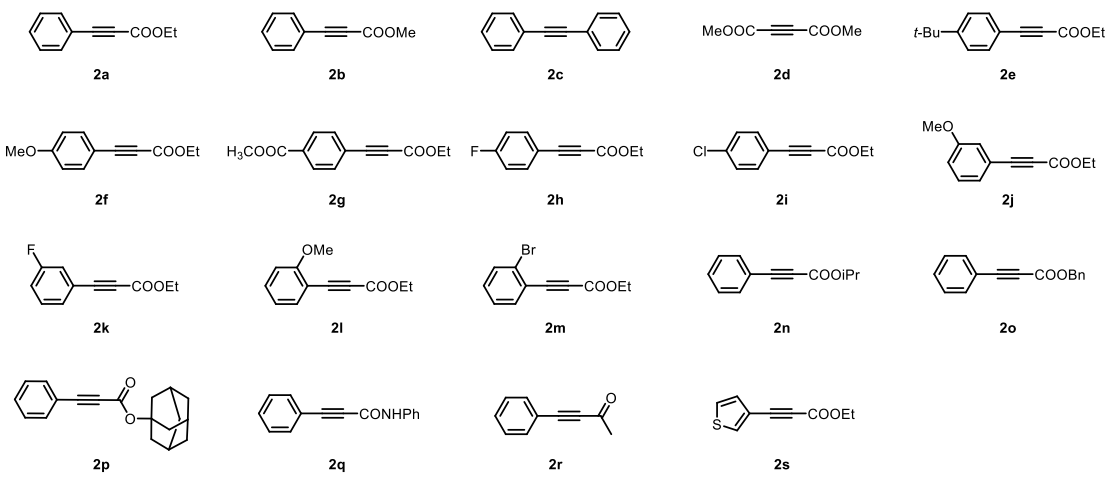



**Figure S2.** Structures of successful alkynes

### 2.3.2 Unsuccessful substrates and general procedures for the synthesis of commercial unavailable substrates

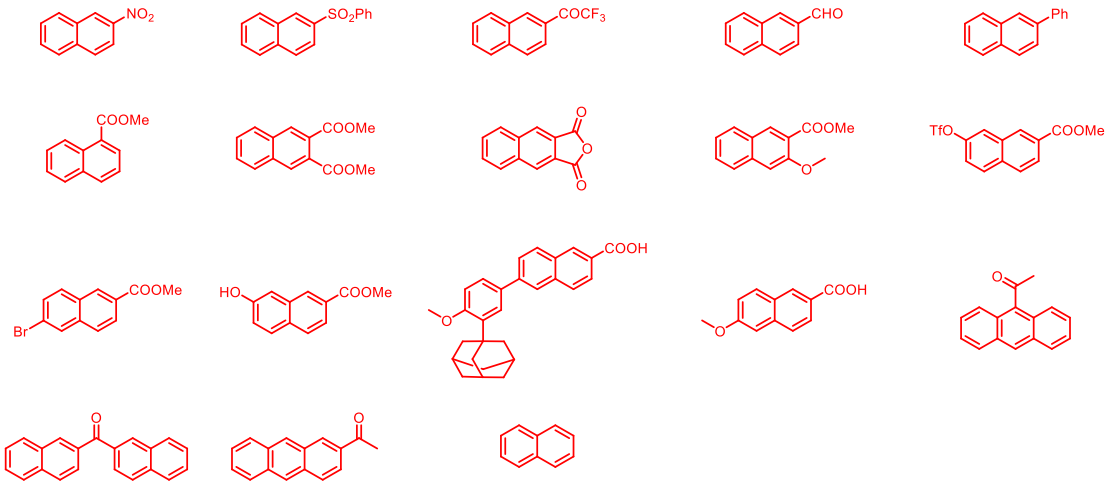
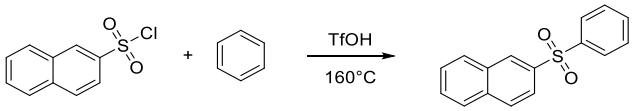
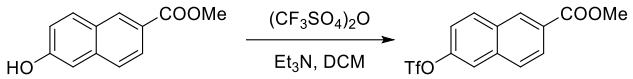



**Figure S3.** Unsuccessful substrates of naphthalene derivatives. Conditions: **1** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), [Ir(dF($CF_3$)ppy)$_2$(dtbbpy)][$PF_6$] (2 μmol, 2 mol%), MeCN:1,4-Dioxane (2 mL, 1:9, 0.1 M), 30 W 425 nm LEDs, 20-25 °C, 48 h.

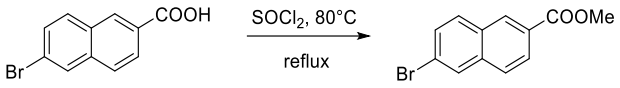



Inside an argon-filled glovebox, the corresponding aryl sulfonyl chloride 1 (454.0 mg, 2.0 mmol), and the benzene (624.0 mg, 8.0 mmol) were added to an oven-dried 10.0 mL pressure tube equipped with a Teflon coated magnetic stirring bar. The tube was transferred out of the glovebox and the trifluoromethanesulfonic acid (35.4 μL, 0.4 mmol, 20 mol%) was added. Once the addition completed, the tube was sealed and the reaction mixture stirred at 160 °C. After 24 h, the mixture

was cooled to 22 °C and ethanol (1.0 mL) followed by ethyl acetate (3.0 mL) were added. Remove the solvents under reduced pressure. Purify the crude mixture by flash chromatography (petroleum ether/ethyl acetate).[7]




The naphthalene derivative (505 mg, 2.5 mmol, 1.0 eq.) was dissolved in DCM (25.0 mL) and cooled to 0 °C. $Et_3N$ (0.52 mL, 3.75 mmol, 1.5 eq.) was added dropwise to the solution, which was followed by the addition of triflic anhydride (505.0 μL, 3.0 mmol, 1.2 eq.). After 5 mins, the ice bath was removed, and the reaction was monitored by TLC. Once the phenol was completely consumed, the reaction was stopped. The solvent was evaporated under vaccum and the residue was purified by flash chromatography to obtain the desired aryl triflate (petroleum ether/ethyl acetate 12/1, 700 mg, 86%).[8]




To a solution of 6-bromo-2-naphthoic acid (1.0 g, 4 mmol, 1 eq.) in MeOH (8.0 mL) was added $SOCl_2$ (0.57 ml, 8 mmol, 2 eq.). This mixture was heated to reflux for 3 h before evaporation. The residue was dissolved in DCM (30.0 mL), washed with aqueous $NaHCO_3$, water and brine, dried over anhydrous $Na_2SO_4$, and concentrated to give the desired product (1.023 g, 96.5%).[9]

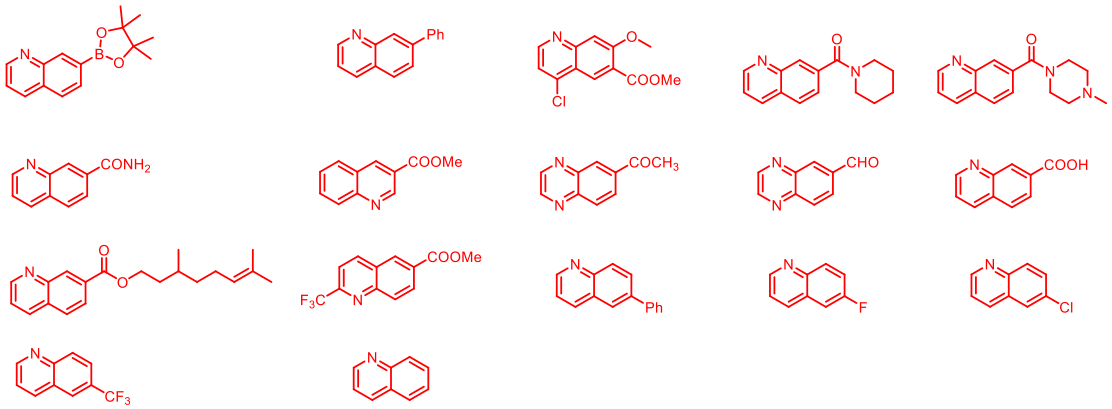
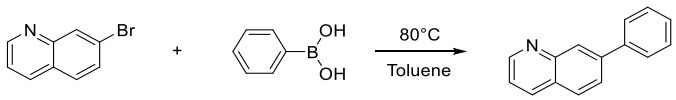
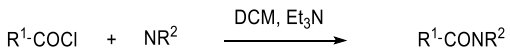



**Figure S4.** Unsuccessful substrates of bicyclic azaarenes. Conditions: **4** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 μmol, 2 mol%), HFIP (2 mL, 0.1 M), 30 W 450 nm LEDs, 20-25°C, 12 h.

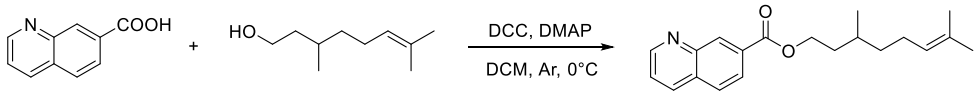



A Schlenk tube was charged with 7-bromoquinoline (1.040 g, 5.0 mmol, 1.0 eq.), phenylboronic acid (793.0 mg, 6.5 mmol, 1.3 eq.), and $Na_2CO_3$ (4.027 g, 38.0 mmol, 7.6 eq.). The tube was

evacuated and backfilled with argon three times before $Pd(PPh_3)_4$ (176 mg, 0.15 mmol, 3 mol%) was added. Subsequently, toluene (20.0 mL), $H_2O$ (20.0 mL), and ethanol (4.0 mL) were added, and the reaction mixture was heated to 80°C and stirred overnight. The mixture was allowed to cool to room temperature and quenched with $NH_4Cl$. The layer was extracted with EtOAc, and the combined organic layers were dried over $Na_2SO_4$, filtered and the solvent was removed under reduced pressure. Purification by silica gel column chromatography (petroleum ether/ethyl acetate) to obtain 7-phenylquinoline.[10]




Aniline derivatives (1.6 mmol, 0.8 eq.) in $CH_2Cl_2$ (8.0 mL) and $Et_3N$ (4.0 mmol, 2.0 eq.) were added dropwise to a solution of chloride (2 mmol, 1.0 eq.) in $CH_2Cl_2$ (10.0 mL) in a 50 mL two-necked flask at 0 ºC. The reaction mixture was warmed to rt, diluted with $CH_2Cl_2$ (80 mL), and washed with $NH_4Cl$. The aqueous layer was re-extracted with $CH_2Cl_2$, and the combined organic layer was washed with brine (40 mL), dried over $Na_2SO_4$, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford products.[3]




An oven dried round-bottom flask was charged with acid (1.0 eq.) and DMAP (10 mol %), and purged with argon for 10 minutes. The contents were dissolved in $CH_2Cl_2$ before the alcohol was added (0.9 eq.). The mixture was cooled to 0 °C and a $CH_2Cl_2$ solution of DCC (1.5 eq.) was added drop-wise and the reaction was warmed to room temperature and stirred overnight (approximately 12 hours). The mixture was washed with three portions of aqueous $NaHCO_3$ and two portions of brine. The organic phase was separated and collected, then dried over magnesium sulfate. The excess solvent was removed under reduced pressure. Finally, the product was purified by column chromatography on silica gel, using a petroleum ether/ethyl acetate mixture as the eluent.[5]

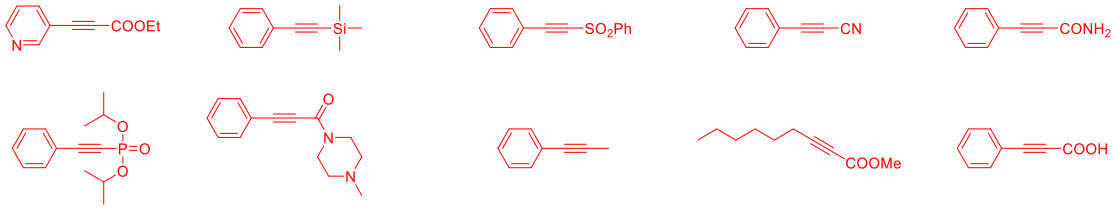
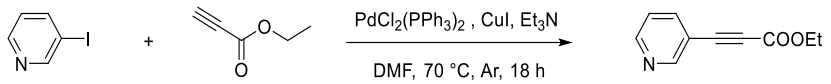
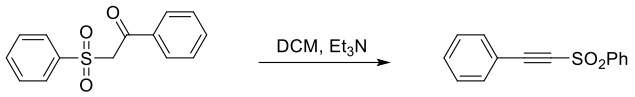


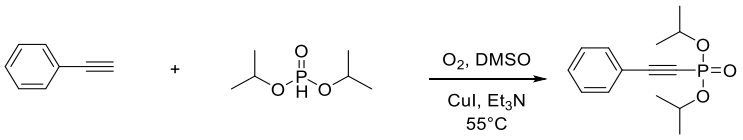

**Figure S5.** Unsuccessful substrates of alkynes. Conditions: **4a** (0.2 mmol, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 μmol, 2 mol%), HFIP (2 mL, 0.1 M), 30 W 450 nm LEDs, 20-25°C, 12 h.



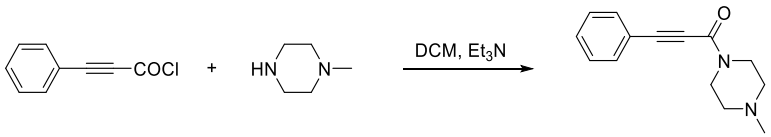

To a solution of aryl iodide (15.0 mmol, 1.5 eq.), alkyl propiolate (10.0 mmol, 1.0 eq.) and $K_2CO_3$ (4.15 g, 30.0 mmol, 3.0 eq.) in THF (80 mL) was added $PdCl_2(PPh_3)_2$ (140.4 mg, 0.2 mmol, 2 mol%). The mixture was stirred for 5 min. And CuI (19.2 mg, 0.1 mmol, 1 mol%) was added. The resulting mixture was then heated under a nitrogen atmosphere at 65 °C for 8 h. The mixture was cooled to room temperature, and the solid was removed by filtration. Then the filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as the eluent to provide the desired product.[6]




A stirred solution of substituted 1-phenyl-2-(phenylsulfonyl)ethan-1-one (1.3 g, 5.0 mmol, 1.0 eq.) and 2-Chloro-1-methylpyridinium iodide (1.53 g, 6.0 mmol, 1.2 eq.) in DCM (50 mL) was charged with $Et_3N$ (1.25 mL, 9.0 mmol, 1.8 eq.) dropwise. The mixture was stirred at room temperature for 3 h, then quenched with water (50 mL), washed with dichloromethane (3 × 50 mL). The organic layers were combined and then concentrated. The oily crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, 34 % yield). [11]



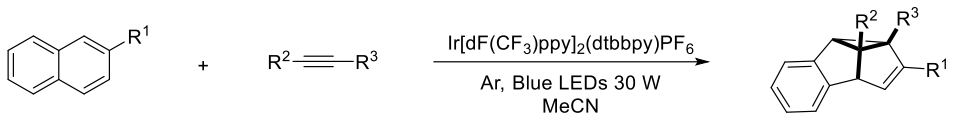

To a stirred solution of terminal alkyne (0.22 mL, 2.0 mmol, 1.0 eq.), H-phosphonate (0.4 mL, 2.4 mmol, 1.2 eq.), triethylamine (40.5 mg, 0.4 mmol, 0.2 eq), CuI (38.3 mg, 0.2 mmol, 0.1 eq.) in DMSO (4.0 mL) was heated under dry air at 55°C for 48 h. A yellow or orange suspension may generate and disappear later. After cooling to room temperature, the mixture was washed by water (15 mL) and then extracted with ethyl acetate (3×15 mL). The organic phase was washed by brine, dried over $Na_2SO_4$ and concentrated in vacuo. Purification of the residue by column chromatography (petroleum ether/ethyl acetate) gave the corresponding internal alkynylphosphonate.[12]



N-methylpiperazine (0.3 mL, 2.7 mmol, 0.9 eq.) was added to a solution of $Et_3N$ (0.83 mL, 6 mmol, 2.0 eq.) in DCM (0.2 M), and 2-propynoyl chloride (3.0 mmol, 1.0 eq.) was slowly added dropwise to the reaction mixture while maintaining the temperature at 0 °C. After the addition was complete, the mixture was stirred overnight at room temperature. Then, the reaction was quenched by the addition of aqueous $NaHCO_3$, and the mixture was extracted twice with ethyl acetate (EA). The organic layers were combined, dried over $MgSO_4$, and the solution was concentrated under reduced pressure. The product was then purified by column chromatography on silica gel, using a DCM/MeOH (50:1) mixture as the eluent (88 % yield).[3]

## 3. Reaction Optimization

**Table S1.** Initial feasibility screening[a]




**1** **2** **3**

| | | | | |
|---|---|---|---|---|
| | | | | |
| nBu | - | - | - | - |
| COOMe | - | - | - | - |
| MeOOC—≡—COOMe | 24 | - | - | - |
| | - | - | - | - |
| COOMe | 42 | 53 | - | - |
| COOEt | 43 | 64 | - | - |

[a] **1** (0.1 mmol), **2** (0.2 mmol), PC-4 (2 mol%), MeCN (1 mL), 425 nm Blue LEDs. Yields by were determined by $^1$H NMR using 1,3,5-Trimethoxybenzene as internal standard.

### 3.1 Reaction optimization with substrate methyl 2-naphthoate 1a

An oven-dried Schlenk tube (10 ml) containing a stirring bar was charged with the methyl 2-naphthoate **1a** (0.1 mmol), alkyne **2a** (0.2 mmol) and PC (2 mol %, 0.004 mmol). Then, the Schlenk tube was connected to a vacuum line where it was evacuated and back-filled with argon for 3 times. Afterwards, anhydrous solvent was added under argon flow. Finally, the reaction mixture in a sealed tube was placed at a distance of 2 - 3 cm from the blue LEDs (wavelength, power) and stirred at corresponding temperature for the indicated time (monitored by TLC, 48 h). After the reaction is

complete, the mixture was concentrated in vacuo. 1,3,5-Trimethoxybenzene (0.1 mmol) was added as internal standard, and the yield was determined by $^1$H NMR analysis. The results are compiled in Table S1-S13.

### 3.1.1 Conditions investigation on PC

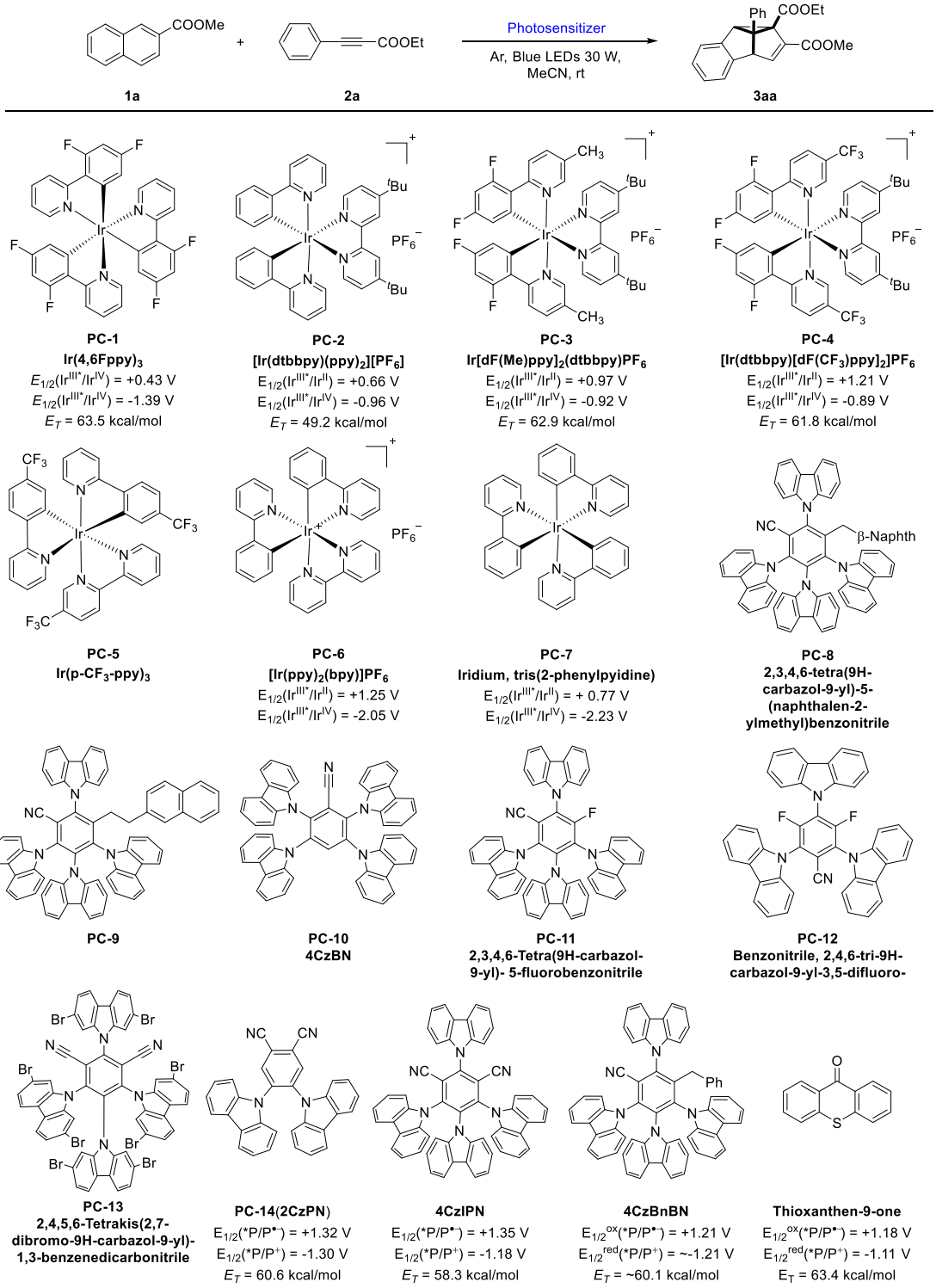



**Figure S6.** Information about photosensitizers. **PC-1**: 387859-70-3; **PC-2**: 676525-77-2; **PC-3**: 1335047-34-1; **PC-**

**4**: 870987-63-6; **PC-5**: 500295-52-3; **PC-6**: 106294-60-4; **PC-7**: 94928-86-6; **PC-8**[13]: 2766554-78-1; **PC-9**[13]; **PC-10**[14]: 1996609-93-8; **PC-11**[15]: 1819362-10-1; **PC-12**[15]: 1819362-09-8; **PC-13**[16]: 2750554-42-6; **PC-14** (**2CzPN**): 1416881-50-9; **4CzIPN**: 1416881-52-1; **4CzBnBN**: 2599844-24-1; **Thioxanthen-9-one**: 492-22-8.

**Table S2.** PC screening with 425 nm Blue LEDs[a]

| Entry | PC | Yields |
|---|---|---|
| **1** | PC-1 | 19 |
| **2** | PC-2 | 24 |
| **3** | PC-3 | 61 |
| **4** | PC-4 | 64 |
| **5** | PC-5 | 52 |
| **6** | PC-6 | N.D. |
| **7** | PC-7 | N.D. |
| **8** | PC-8 | 35 |
| **9** | PC-9 | 26 |
| **10** | PC-10 | 27 |
| **11** | PC-11 | 23 |
| **12** | PC-12 | 10 |
| **13** | PC-13 | 35 |
| **14** | PC-14 | 15 |

[a]1a (0.1 mmol), 2a (0.2 mmol) scale, PC (2 mol%), MeCN (1 mL) ,425 nm Blue LEDs. Yields were determined by crude $^1$H NMR using 1,3,5-Trimethoxybenzene as internal standard.

**Table S3.** PC screening with 465 nm Blue LEDs[a]

| Entry | PC | Yields |
|---|---|---|
| **1** | PC-8 | 16 |
| **2** | PC-9 | 15 |
| **3** | PC-10 | 19 |
| **4** | PC-11 | 22 |
| **5** | PC-12 | 6 |
| **6** | PC-13 | 19 |
| **7**[b] | Thioxanthen-9-one | N.D. |

[a] **1a** (0.1 mmol), **2a** (0.2 mmol) scale, PC (2 mol%), MeCN (1 mL), 465 nm Blue LEDs. Yields determined by $^1$H NMR using 1,3,5-Trimethoxybenzene as internal standard. [b] $\lambda_{max}$ = 365 nm, $\lambda_{max}$ = 390 nm, $\lambda_{max}$ = 405 nm, $\lambda_{max}$ = 425 nm.

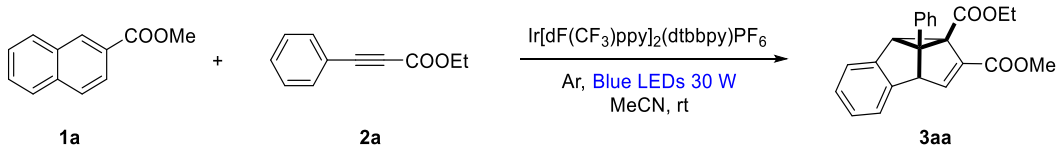
**Table S4.** PC screening using DMSO as the solvent[a]

| Entry | PC | Yields |
|---|---|---|
| **1** | 3CzClIPN | N.D. |
| **2** | 4CzPN | N.D. |
| **3** | 3,6-tBu-4CzIPN | N.D. |
| **4** | 4CzIPN | N.D. |
| **5** | 4CzPEBN | N.D. |
| **6** | 3CzEPAIPN | N.D. |
| **7** | 5CzIPN | N.D. |
| **8** | 3DPA2FBN | N.D. |
| **9** | 3DPAFIPN | N.D. |
| **10** | 4DPAIPN | N.D. |

[a] **1a** (0.1 mmol), **2a** (0.2 mmol) scale, PC (2 mol%), DMSO (1 mL), 465 nm Blue LEDs. Yield by crude $^1$H NMR using 1,3,5-Trimethoxybenzene as internal standard. **3CzClIPN**: 1469704-61-7; **4CzPN**: 1416881-51-0; **3,6-tBu-4CzIPN**: 1630263-99-8; **4CzIPN**: 1416881-52-1; **4CzPEBN**: 2365165-41-7; **3CzEPAIPN**: 2662263-39-8; **5CzIPN**: 1469700-24-0; **3DPA2FBN**: 1403850-00-9; **3DPAFIPN**: 2260543-73-3; **4DPAIPN**:

### 3.1.2 Condition investigations on wavelength

**Table S5.** Wavelength screening using PC-4 as the photocatalyst[a]




| Entry | Wavelength | Yields |
|---|---|---|
| **1** | 365 nm | N.D. |
| **2** | 390 nm | 63 |

| | | |
|---|---|---|
| **3** | 405 nm | 60 |
| **4** | 425 nm | 63 |
| **5**[b] | 425 nm | N.D. |
| **6**[c] | 425 nm | N.D. |
| **7** | 440 nm | 62 |
| **8** | 465 nm | 34 |

[a]**1a** (0.1 mmol), **2a** (0.2 mmol) scale, PC-4 (2 mol%), MeCN (1 mL). Yields by crude $^1$H NMR using 1,3,5-Trimethoxybenzene as internal standard. [b] In dark. [c] No photosensitizers.

### 3.1.3 Condition investigations on solvents

**Table S6.** Solvent screening[a]


| Entry | Solvent | Yields |
|---|---|---|
| **1** | MeCN | 64 |
| **2** | DMSO | 22 |
| **3** | DMA | 37 |
| **4** | DMF | 8 |
| **5** | DCE | 64 |
| **6** | DCM | 60 |
| **7** | HFIP | N.D. |
| **8** | TFA | N.D. |
| **9** | TFE | 29 |
| **10** | Acetone | 54 |
| **11** | MeOH | 52 |
| **12** | 1,4-Dioxane | 30 |
| **13** | $Et_2O$ | 24 |
| **14** | Toluene | 18 |
| **15** | THF | 30 |

[a] **1a** (0.1 mmol), **2a** (0.2 mmol), PC-4 (2 mol%), solvent (1 mL), 425 nm Blue LEDs. Yields by were determined $^1$H NMR using 1,3,5-Trimethoxybenzene as internal standard.

**Table S7.** Mixed solvent screening[a]

| Entry | Solvent (1:1) | Yields |
|---|---|---|
| **1** | MeCN : Acetone | 63 |
| **2** | MeCN : MeOH | 63 |
| **3** | MeCN : DCE | 64 |
| **4** | MeCN : DCM | 65 |
| **5** | DCE : MeOH | 66 |
| **6** | DCE : DCM | 65 |
| **7** | DCE : Acetone | 56 |
| **8** | Acetone : MeOH | 60 |

[a] **1a** (0.1 mmol), **2a** (0.2 mmol), PC-4 (2 mol%), solvent (1 mL), 425 nm Blue LEDs. Yields by crude $^{1}$H NMR using 1,3,5-Trimethoxybenzene as internal standard.

**Table S8.** Mixed solvent screening with 1,4-dioxane[a]

| Entry | Solvent (1:1) | Yields |
|---|---|---|
| **1** | 1,4-Dioxane: MeCN | 70 |
| **2** | 1,4-Dioxane: DCE | 65 |
| **3** | 1,4-Dioxane:DCM | 66 |
| **4** | 1,4-Dioxane: Acetone | 60 |
| **5** | 1,4-Dioxane:MeOH | 70 |

[a] **1a** (0.1 mmol), **2a** (0.2 mmol) scale, PC-4 (2 mol%), solvent (1 mL), 425 nm Blue LEDs. Yields were determined by $^{1}$H NMR using 1,3,5-Trimethoxybenzene as internal standard.

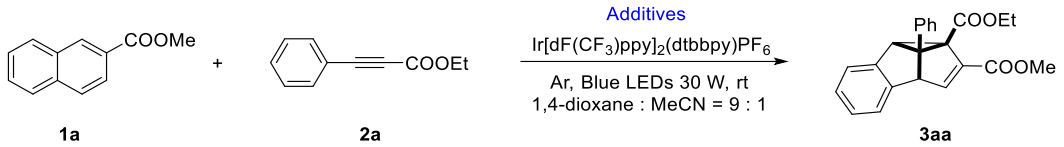
**Table S9.** The ratio screening of mixed solvent[a]

| Entry | Solvent | Proportions | Yields |
|---|---|---|---|
| **1** | 1,4-Dioxane : MeCN | 1 : 9 | 71 |
| **2** | 1,4-Dioxane : MeCN | 3 : 7 | 68 |
| **3** | 1,4-Dioxane : MeCN | 7 : 3 | 72 |
| **4** | 1,4-Dioxane : MeCN | 9 : 1 | 74 |
| **5** | 1,4-Dioxane : MeOH | 1 : 9 | 60 |
| **6** | 1,4-Dioxane : MeOH | 3 : 7 | 64 |
| **7** | 1,4-Dioxane : MeOH | 7 : 3 | 66 |
| **8** | 1,4-Dioxane : MeOH | 9 : 1 | 62 |

[a] **1a** (0.1 mmol), **2a** (0.2 mmol), PC-4 (2 mol%), solvent (1 mL), 425 nm Blue LEDs. Yields were determined by $^1$H NMR using 1,3,5-Trimethoxybenzene as internal standard.

### 3.1.4 Condition investigation on additives

**Table S10.** Additives screening[a]

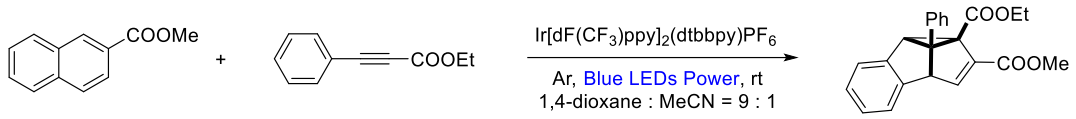



| Entry | Additives | Yields |
|---|---|---|
| **1** | LiOH | 60 |
| **2** | NaF | 68 |
| **3** | DIPEA | N.D. |
| **4** | $Cs_2CO_3$ | 72 |
| **5** | $K_2CO_3$ | 47 |
| **6** | $Et_3N$ | N.D. |
| **7** | DBU | N.D. |
| **8** | DMAP | Trace |
| **9** | NaOAc | 53 |
| **10** | $Cu(OAc)_2$ | 61 |
| **11** | CuO | 67 |
| **12** | $CuCl_2$ | N.D. |
| **13** | $CuSO_4$ | 74 |
| **14** | $FeCl_3$ | N.D. |
| **15** | $Fe(OTf)_3$ | N.D. |
| **16** | TFA | 67 |
| **17** | AcOH | 69 |
| **18** | Ethylene glycol | 72 |
| **19** | $Fe(OAc)_2$ | N.D. |
| **20** | $InCl_3$ | 54 |

[a] **1a** (0.1 mmol), **2a** (0.2 mmol), PC-4 (2 mol%), 1,4-Dioxane : MeCN = 9 : 1 (1 mL), 425 nm Blue LEDs. Yields were determined by crude $^1$H NMR using 1,3,5-Trimethoxybenzene as internal standard.

### 3.1.5 Condition investigation on LEDs Irradiating power

**Table S11.** Blue LEDs power screening[a]




**1a** **2a** **3aa**

| Entry | Irradiating power | Yield |
|---|---|---|
| **1** | 5w | 49 |
| **2** | 10w | 67 |
| **3** | 20w | 55 |
| **4** | 30w | 68 |

[a] **1a** (0.2 mmol), **2a** (0.4 mmol) scale, PC-4 (2 mol%), 1,4-Dioxane : MeCN = 9 : 1 (2 mL), 425 nm Blue LEDs. Yields by crude $^1$H NMR using 1,3,5-Trimethoxybenzene as internal standard.

### 3.1.6 Condition investigation on reaction temperature

**Table S12.** Temperature screening [a]

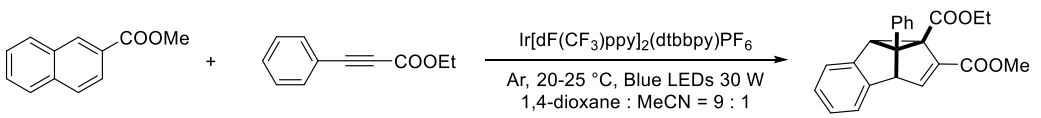

**1a** **2a** **3aa**

| Entry | Temperature | Yields |
|---|---|---|
| **1** | 0 °C | 49 |
| **2** | 20 °C | 74 |
| **3** | 30 °C | 67 |
| **4** | 40 °C | 55 |

[a] **1a** (0.2 mmol), **2a** (0.4 mmol), PC-4 (2 mol%), 1,4-Dioxane : MeCN = 9 : 1 (2 mL), 425 nm Blue LEDs. Yields were determined by $^1$H NMR using 1,3,5-Trimethoxybenzene as internal standard.

### 3.1.7 Water/Oxygen Sensitivity Test

**Table S13.** Water/oxygen sensitivity test[a]




**1a** **2a** **3aa**

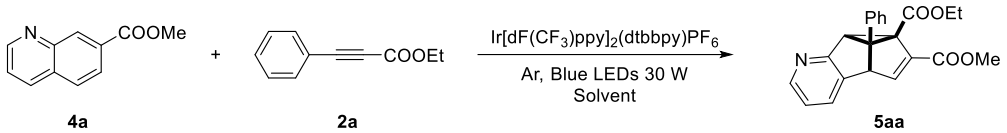
| Entry | Preconditions | Yields |
|---|---|---|
| **1** | $H_2O$ (10 μL) | 68 |
| **2** | Air | 12 |

[a] **1a** (0.1 mmol), **2a** (0.2 mmol), PC-4 (2 mol%), 1,4-Dioxane : MeCN = 9 : 1 (1 mL), 425 nm Blue LEDs. Yields were determined by $^1$H NMR using 1,3,5-Trimethoxybenzene as internal standard.

## 3.2 Reaction optimization with substrate methyl 7-quinolinecarboxylate 4a

An oven-dried Schlenk tube (10 ml) containing a stirring bar was charged with methyl 7-quinolinecarboxylate **4a** (0.1 mmol), alkyne **2a** (0.2 mmol) and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2 mol %, 0.004 mmol). Then, the Schlenk tube was connected to a vacuum line where it was evacuated and back-filled with argon for 3 times. Afterwards, solvent (2 ml, if HFIP is used as the solvent, it was bubbled with argon for 5 minutes) was added under argon flow. Finally, the reaction mixture in a sealed tube was placed at a distance of 2 - 3 cm from a 30 W blue LEDs (450 nm) and stirred at room temperature. After the reaction is complete (monitored by TLC), the mixture was concentrated in vacuo. 1,3,5-Trimethoxybenzene (0.1 mmol) was added as internal standard, and the yield was determined by $^1$H NMR analysis. The results are compiled in Table S14.

**Table S14.** Reaction optimization with substrate **4a**[a]



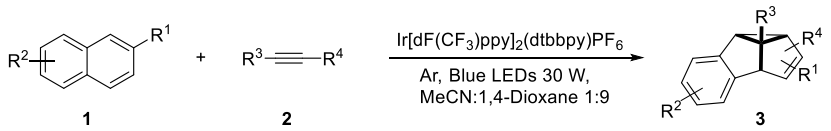

| Entry | Wavelength | Solvent | Additives | Yields |
|---|---|---|---|---|
| **1** | 450 nm | HFIP | - | 96 |
| **2** | 425 nm | DCE (TFA, 1.5 eq) | - | - |
| **3** | 425 nm | DCM | - | 63 |
| **4** | 465 nm | HFIP | - | 75 |
| **5** | 425 nm | HFIP | - | 77 |
| **6** | 425 nm | 1,4-Dioxane : MeCN = 9 : 1 | - | 65 |
| **7** | 425 nm | 1,4-Dioxane : MeCN = 9 : 1 | HFIP, 1.5 eq | 79 |
| **8** | 450 nm | 1,4-Dioxane : MeCN = 9 : 1 | - | 55 |
| **9** | 450 nm | 1,4-Dioxane : MeCN = 9 : 1 | HFIP, 1.5 eq | 54 |

[a] **4a** (0.1 mmol), **2a** (0.2 mmol) scale, PC-4 (2 mol%), solvent (1 mL). Yields were determined by crude $^1$H NMR using 1,3,5-Trimethoxybenzene as internal standard.

## 5. General procedures and characterization data of products

### 5.1 General procedures for the photoreactions

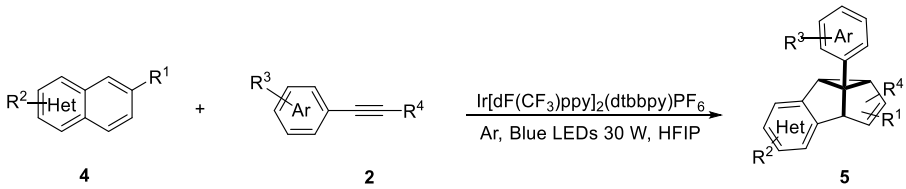
#### 5.1.1 General procedure for photoreactions using naphthalene derivatives as substrates




$R^1$=-COOR,-COR, -CN $R^3$=-Ph, -COOR
$R^2$=-COOR, -Bpin, -OMe, -H $R^4$=-Ph, -COOR

An oven-dried Schlenk tube (10 ml) containing a stirring bar was charged with the naphthalene **1** (0.2 mmol), alkyne **2** (0.4 mmol) and Ir[dF($CF_3$)ppy]$_2$(dtbbpy)$PF_6$ (2 mol %, 0.004 mmol, 4.5 mg). Then, the Schlenk tube was connected to a vacuum line where it was evacuated and back-filled with argon for 3 times. Afterwards, solvent (MeCN : 1,4-dioxane = 1:9, 2 ml) was added under argon flow. Finally, the reaction mixture in a sealed tube was placed at a distance of 2 - 3 cm from a 30 W blue LEDs (425 nm) and stirred at room temperature for the indicated time (monitored by TLC, 48 h). After finishing the reaction, the mixture was concentrated in vacuo and purified by silica gel flash chromatography to afford the corresponding product **3** (Petroleum ether/ethyl acetate).

#### 5.1.2 General procedure for photoreactions using bicyclic azaarenes as substrates

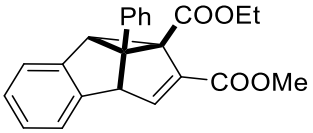



$R^1$ = -COOR, -CN, -Me $R^3$ = -EWG,- EDG, -X, -H
$R^2$ = -Me, -X $R^4$ = -COOR

An oven-dried Schlenk tube (10 ml) containing a stirring bar was charged with the quinoline **4** (0.2 mmol), alkyne **2** (0.4 mmol) and Ir[dF($CF_3$)ppy]$_2$(dtbbpy)$PF_6$ (2 mol %, 0.004 mmol). Then, the Schlenk tube was connected to a vacuum line where it was evacuated and back-filled with argon for 3 times. Afterwards, solvent (HFIP, 2 ml) which was bubbled with argon for 5 minutes was added under argon flow. Finally, the reaction mixture in a sealed tube was placed at a distance of 2 - 3 cm from a 30 W blue LEDs (450 nm) and stirred at room temperature for the indicated time (monitored by TLC, 8 to 16 h). After the reaction was complete, the mixture was concentrated in vacuo and purified by flash chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to afford the corresponding product **5**.

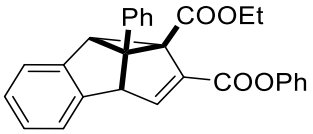
## 5.2 Characterization data for products

2a-ethyl 2-methyl 2a[1]-phenyl-2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2,2a(2a[1]*H*)-dicarboxylate (**3aa**)



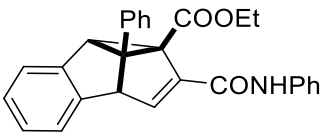

**Physical state:** Yellow oil
**Yield:** 61%
**R*f*** = 0.3 in Petroleum ether/ethyl acetate (20:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.2 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.24 – 7.21 (m, 3H), 7.20 – 7.12 (m, 2H), 6.65 (d, *J* = 2.6 Hz, 1H), 4.57 (s, 1H), 4.29 (d, *J* = 2.6 Hz, 1H), 4.02 – 3.91 (m, 2H), 3.64 (s, 3H), 0.94 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 167.1, 164.7, 146.7, 145.0, 137.5, 135.3, 128.4, 127.8, 127.6, 127.3, 126.8, 126.3, 126.2, 122.2, 70.0, 61.0, 60.8, 57.7, 51.6, 44.3, 13.9.
**HRMS (ESI):** calcd for $C_{23}H_{21}O_4$ $[M+H]^+$ *m/z* 361.1434, found 361.142.

2a-ethyl 2-phenyl 2a[1]-phenyl-2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2,2a(2a[1]*H*)-dicarboxylate (**3ba**)




**Physical state:** Yellow oil
**Yield:** 60%
**R*f*** = 0.2 in Petroleum ether/ethyl acetate (20:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.2 Hz, 1H), 7.34 – 7.27 (m, 6H), 7.25 – 7.14 (m, 4H), 7.06 – 7.00 (m, 2H), 6.86 (d, *J* = 2.7 Hz, 1H), 4.62 (s, 1H), 4.35 (d, *J* = 2.6 Hz, 1H), 4.04 – 3.93 (m, 2H), 0.94 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 167.0, 162.6, 150.6, 146.6, 146.4, 137.6, 135.2, 129.3, 128.4, 127.9, 127.7, 127.5, 127.0, 126.5, 125.7, 125.7, 122.4, 121.5, 70.2, 61.2, 61.0, 57.8, 44.5, 14.0.
**HRMS (ESI):** calcd for $C_{28}H_{23}O_4$ $[M+H]^+$ *m/z* 423.15909, found 423.16016.

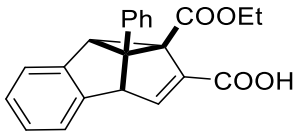
ethyl 2a[1]-phenyl-2-(phenylcarbamoyl)-2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2a(2a[1]*H*)-carboxylate (**3ca**)




**Physical state:** White solid
**Melting Point:** 332.6-333.1°C

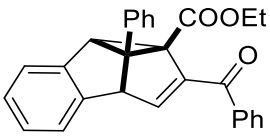
**Yield:** 60%
**R$_f$** = 0.2 in Petroleum ether/ethyl acetate (10:1).
**$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 10.04 (s, 1H), 7.66 – 7.53 (m, 3H), 7.38 – 7.16 (m, 10H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.55 (d, *J* = 2.6 Hz, 1H), 4.55 (s, 1H), 4.47 (d, *J* = 2.5 Hz, 1H), 3.84 (qt, *J* = 7.4, 3.8 Hz, 2H), 0.79 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 171.9, 168.0, 152.3, 144.6, 144.2, 142.3, 140.4, 135.2, 133.8, 133.6, 132.8, 132.4, 132.1, 131.8, 131.2, 128.4, 127.5, 124.7, 73.6, 65.5, 65.3, 63.8, 49.0, 18.9.
**HRMS (ESI):** calcd for $C_{28}H_{24}NO_3$ $[M+H]^+$ *m/z* 422.1751, found 422.1755.

2a-(ethoxycarbonyl)-2a$^1$-phenyl-2a,2a$^1$,2b,6b-tetrahydrobenzo[*a*]cyclopropa[*cd*]pentalene-2-carboxylic acid (**3da**)



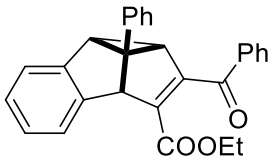

**Physical state:** Yellow oil
**Yield:** 55%
**R$_f$** = 0.2 in Petroleum ether/ethyl acetate (20:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.3 Hz, 1H), 7.32 – 7.09 (m, 9H), 6.74 (d, *J* = 2.6 Hz, 1H), 4.55 (s, 1H), 4.29 (d, *J* = 2.6 Hz, 1H), 4.01 – 3.88 (m, 2H), 0.90 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 169.3, 169.3, 167.0, 147.2, 146.2, 137.4, 135.2, 128.4, 127.8, 127.6, 127.5, 126.9, 126.4, 125.4, 122.3, 69.9, 61.2, 60.9, 57.4, 44.3, 13.8.
**HRMS (ESI):** calcd for $C_{22}H_{19}O_4$ $[M+H]^+$ *m/z* 347.1278, found 347.1287.

ethyl 2-benzoyl-2a$^1$-phenyl-2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2a(2a$^1$*H*)-carboxylate (**3ea-1**)



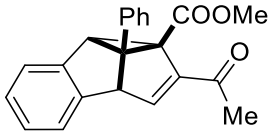

**Physical state:** Yellow solid
**Melting Point:** 184.2-184.7 °C
**Yield:** 34%
**R$_f$** = 0.1 in Petroleum ether/ethyl acetate (20:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.75 – 7.70 (m, 2H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.42 – 7.36 (m, 2H), 7.33 – 7.28 (m, 4H), 7.28 – 7.22 (m, 2H), 7.19 – 7.14 (m, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.40 (d, *J* = 2.6 Hz, 1H), 4.67 (s, 1H), 4.38 (d, *J* = 2.6 Hz, 1H), 3.81 (q, *J* = 7.1 Hz, 2H), 0.79 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 192.3, 167.1, 146.6, 144.1, 137.6, 137.4, 135.4, 134.6, 132.5, 128.8, 128.4, 128.3, 127.8, 127.7, 127.4, 127.1, 126.2, 122.2, 70.7, 61.4, 61.1, 59.3, 46.0, 13.7.
**HRMS (ESI):** calcd for $C_{28}H_{23}O_3$ $[M+H]^+$ *m/z* 407.1642, found 407.1627.

ethyl 2-benzoyl-2a[1]-phenyl-2a,2a[1],2b,6b-tetrahydrobenzo[*a*]cyclopropa[*cd*]pentalene-1-carboxylate (**3ea-2**)



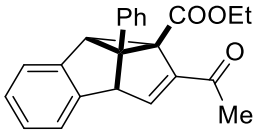

**Physical state:** White solid
**Melting Point:** 140.0-140.5 °C
**Yield:** 18%
**R*f*** = 0.3 in Petroleum ether/ethyl acetate (20:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.53 – 7.50 (m, 1H), 7.47 – 7.42 (m, 2H), 7.35 – 7.20 (m, 11H), 4.70 (d, *J* = 2.8 Hz, 1H), 3.99 – 3.86 (m, 2H), 3.78 – 3.71 (m, 1H), 3.38 – 3.32 (m, 1H), 0.90 – 0.83 (m, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 194.0, 162.2, 147.9, 143.4, 138.8, 137.2, 137.2, 136.3, 133.4, 128.7, 128.7, 128.4, 127.4, 127.2, 126.9, 125.8, 125.1, 122.8, 66.0, 60.7, 58.6, 47.5, 46.3, 13.5.
**HRMS (ESI):** calcd for $C_{28}H_{23}O_3$ $[M+H]^+$ *m/z* 407.1642, found 407.1632.

methyl 2-acetyl-2a[1]-phenyl-2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2a(2a[1]*H*)-carboxylate (**3fa**)




**Physical state:** White solid
**Melting Point:** 163.2-163.7 °C
**Yield:** 50%
**R*f*** = 0.4 in Petroleum ether/ethyl acetate (10:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.1 Hz, 1H), 7.31 – 7.10 (m, 8H), 6.57 (d, *J* = 2.0 Hz, 1H), 4.54 (s, 1H), 4.34 (d, *J* = 2.6 Hz, 1H), 3.45 (s, 3H), 2.17 (s, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 195.6, 167.8, 146.4, 144.4, 137.6, 135.6, 135.3, 128.5, 127.8, 127.4, 127.4, 126.9, 126.4, 122.2, 69.2, 61.0, 57.6, 52.1, 44.4, 26.9.
**HRMS (ESI):** calcd for $C_{22}H_{19}O_3$ $[M+H]^+$ *m/z* 331.1329, found 331.1334.

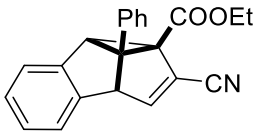
2-acetyl-2a[1]-phenyl-2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2a(2a[1]*H*)-carboxylate ()




**Physical state:** Yellow oil
**Yield:** 54%
**R*f*** = 0.2 in Petroleum ether/ethyl acetate (4:1).

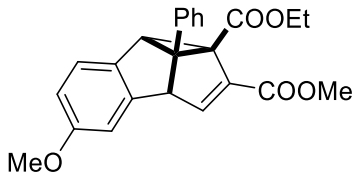
**$^1$H NMR** (400 MHz, Chloroform-d) δ 7.52 (d, J= 7.2 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.26 – 7.10 (m, 7H), 6.55 (d, J = 2.6 Hz, 1H), 4.55 (s, 1H), 4.34 (d, J = 2.6 Hz, 1H), 3.94 (q, J = 7.1 Hz, 2H), 2.19 (s, 3H), 0.90 (t, J = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 195.6, 167.2, 146.5, 144.0, 137.6, 135.8, 135.3, 128.4, 127.8, 127.5, 127.4, 126.8, 126.3, 122.1, 69.2, 61.0, 61.0, 57.7, 44.2, 27.0, 13.9.
**HRMS (ESI):** calcd for $C_{23}H_{21}NO_3$ $[M+H]^+$ m/z 345.14852, found 345.14081.

ethyl 2-cyano-2a$^1$-phenyl-2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2a(2a$^1$*H*)-carboxylate (**3ga**)



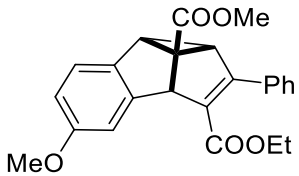

**Physical state:** Yellow oil
**Yield:** 42%
**R$_f$** = 0.3 in Petroleum ether/ethyl acetate (20:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.3 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.26 – 7.13 (m, 4H), 6.61 (d, *J* = 2.7 Hz, 1H), 4.56 (s, 1H), 4.30 (d, *J* = 2.7 Hz, 1H), 4.17 – 4.02 (m, 2H), 1.08 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.0, 150.4, 145.5, 136.6, 134.7, 128.5, 128.4, 128.2, 128.0, 127.8, 127.5, 126.6, 122.4, 115.5, 104.2, 70.8, 61.9, 61.7, 57.3, 46.9, 13.9.
**HRMS (ESI):** calcd for $C_{22}H_{18}NO_2$ $[M+H]^+$ *m/z* 328.1332, found 328.1346.

2a-ethyl 2-methyl 5-methoxy-2a$^1$-phenyl-2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2,2a(2a$^1$*H*)-dicarboxylate (**3ha-1**)



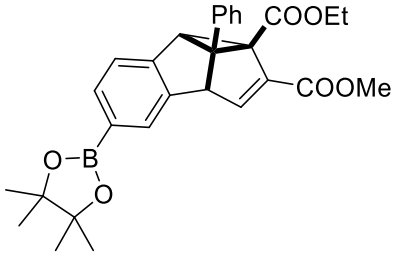

**Physical state:** Yellow oil
**Yield:** 13%
**R$_f$** = 0.5 in Petroleum ether/ethyl acetate (6:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.21 (m, 5H), 6.81 – 6.74 (m, 1H), 6.69 (d, *J* = 2.4 Hz, 1H), 6.63 (d, *J* = 2.6 Hz, 1H), 4.51 (s, 1H), 4.26 (d, *J* = 2.6 Hz, 1H), 4.03 – 3.89 (m, 2H), 3.76 (s, 3H), 3.64 (s, 3H), 0.93 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 167.3, 164.9, 159.2, 148.5, 145.0, 135.4, 129.8, 128.4, 127.8, 127.7, 126.8, 126.7, 112.6, 108.5, 69.8, 61.0, 57.4, 55.5, 51.7, 43.9, 14.0.
**HRMS (ESI):** calcd for $C_{24}H_{23}O_5$ $[M+H]^+$ *m/z* 391.1540, found 391.1527.

1-ethyl 2a$^1$-methyl 5-methoxy-2-phenyl-2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-1,2a$^1$(2a*H*)-dicarboxylate (**3ha-2**)



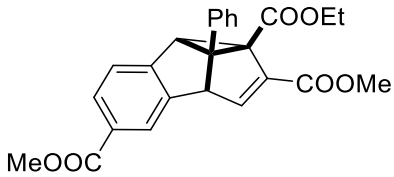

**Physical state:** White oil
**Yield:** 17%
**$R_f$** = 0.4 in Petroleum ether/ethyl acetate (6:1).
$^1$H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 1.6 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.18 (m, 3H), 7.16 – 7.12 (m, 2H), 4.52 (s, 1H), 4.13 – 3.96 (m, 2H), 3.82 (s, 3H), 3.69 (d, *J* = 8.0 Hz, 1H), 3.35 – 3.29 (m, 4H), 1.09 (t, *J* = 7.1 Hz, 3H).
$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 167.2, 163.2, 151.9, 146.0, 137.0, 135.8, 130.2, 129.1, 128.4, 128.3, 128.1, 127.6, 125.9, 122.6, 97.7, 60.3, 56.9, 56.3, 52.1, 50.9, 45.6, 14.1.
**HRMS (ESI):** calcd for $C_{24}H_{26}O_5$ $[M+H]^+$ *m/z* 391.15400, found 391.15394.

2a-ethyl 2-methyl 2a$^1$-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2,2a(2a$^1$*H*)-dicarboxylate (**3ja**)




**Physical state:** Yellow liquid
**Yield:** 68%
**$R_f$** = 0.5 in Petroleum ether/ethyl acetate (4:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.5 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.32 – 7.26 (m, 2H), 7.25 – 7.19 (m, 3H), 6.68 (d, *J* = 2.6 Hz, 1H), 4.57 (s, 1H), 4.27 (d, *J* = 2.6 Hz, 1H), 4.05 – 3.91 (m, 2H), 3.63 (s, 3H), 1.33 (d, *J* = 4.4 Hz, 12H), 0.94 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 167.2, 164.8, 146.0, 145.3, 140.8, 135.3, 134.1, 128.5, 128.4, 127.9, 127.7, 126.1, 125.9, 84.0, 70.2, 61.1, 60.8, 57.9, 51.7, 44.6, 25.0, 24.9, 14.0.
**HRMS (ESI):** calcd for $C_{29}H_{32}BO_6$ $[M+H]^+$ *m/z* 487.2287, found 487.2288.

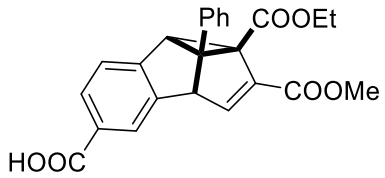
2a-ethyl 2,5-dimethyl 2a$^1$-phenyl-2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2,2a,5(2a$^1$*H*)-tricarboxylate (**3ja**)




**Physical state:** White oil

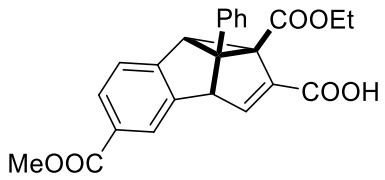
**Yield:** 66%
**$R_f$** = 0.3 in Petroleum ether/ethyl acetate (20:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.98 – 7.92 (m, 1H), 7.81 (d, *J* = 1.5 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.24 – 7.20 (m, 2H), 6.67 (d, *J* = 2.5 Hz, 1H), 4.59 (s, 1H), 4.33 (d, *J* = 2.6 Hz, 1H), 4.03 – 3.93 (m, 2H), 3.89 (s, 3H), 3.64 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.9, 166.8, 164.4, 146.8, 144.7, 142.6, 134.8, 129.2, 128.9, 128.5, 128.0, 127.5, 126.7, 126.1, 123.3, 70.6, 61.2, 60.6, 58.2, 52.2, 51.7, 44.3, 13.9.
**HRMS (ESI):** calcd for $C_{25}H_{23}O_6$ $[M+H]^+$ *m/z* 419.1489, found 419.1484.

2a-(ethoxycarbonyl)-2-(methoxycarbonyl)-2a$^1$-phenyl-2a,2a$^1$,2b,6b-tetrahydrobenzo[*a*]cyclopropa[*cd*]pentalene-5-carboxylic acid (**3ka-1**)




**Physical state:** Yellow oil
**Yield:** 32%
**$R_f$** = 0.5 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.06 – 7.99 (m, 1H), 7.88 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.25 (m, 3H), 7.26 – 7.18 (m, 2H), 6.70 (d, *J* = 2.6 Hz, 1H), 4.61 (s, 1H), 4.35 (d, *J* = 2.6 Hz, 1H), 4.08 – 3.90 (m, 2H), 3.65 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 171.9, 166.9, 164.6, 147.0, 144.8, 143.7, 134.8, 130.0, 128.6, 128.2, 128.2, 127.6, 126.8, 126.4, 123.9, 70.9, 61.4, 60.6, 58.4, 51.9, 44.4, 14.0.
**HRMS (ESI):** calcd for $C_{24}H_{21}O_6$ $[M+H]^+$ *m/z* 405.1333, found 405.1334.

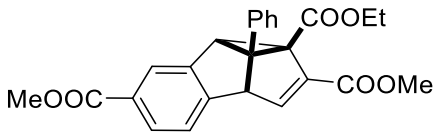
2a-(ethoxycarbonyl)-5-(methoxycarbonyl)-2a$^1$-phenyl-2a,2a$^1$,2b,6b-tetrahydrobenzo[*a*]cyclopropa[*cd*]pentalene-2-carboxylic acid **(3ka-2)**




**Physical state:** Yellow solid
**Melting Point:** 211.7-212.2 °C
**Yield:** 28%
**$R_f$** = 0.4 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.99 – 7.90 (m, 1H), 7.80 (d, *J* = 1.4 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.26 – 7.17 (m, 3H), 6.76 (d, *J* = 2.6 Hz, 1H), 4.57 (s, 1H), 4.33 (d, *J* = 2.6 Hz, 1H), 4.01 – 3.92 (m, 2H), 3.89 (s, 3H), 0.90 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 169.1, 167.0, 166.8, 146.9, 146.5, 142.7, 134.8, 129.4, 129.0, 128.6, 128.2, 127.6, 126.3, 123.5, 70.6, 61.4, 60.7, 58.0, 52.3, 44.3, 13.9.

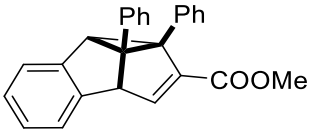
**HRMS (ESI):** calcd for $C_{24}H_{21}O_6$ $[M+H]^+$ *m/z* 405.1333, found 405.1347.

2a-ethyl 2,4-dimethyl 2a[1]-phenyl-2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2,2a,4(2a[1]*H*)-tricarboxylate (**3la**)



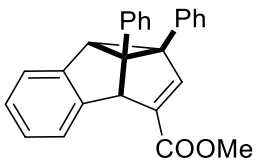

**Physical state:** Yellow oil
**Yield:** 83%
**R*f*** = 0.3 in Petroleum ether/ethyl acetate (20:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 1.5 Hz, 1H), 7.93 – 7.85 (m, 1H), 7.32 – 7.26 (m, 3H), 7.23 – 7.18 (m, 3H), 6.63 (d, *J* = 2.6 Hz, 1H), 4.61 (s, 1H), 4.33 (d, *J* = 2.6 Hz, 1H), 4.04 – 3.92 (m, 2H), 3.91 (s, 3H), 3.64 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.9, 166.7, 164.4, 151.4, 144.2, 137.7, 134.8, 129.6, 128.8, 128.5, 128.0, 127.5, 127.4, 127.3, 122.0, 70.2, 61.1, 60.8, 57.7, 52.2, 51.7, 44.0, 13.9.
**HRMS (ESI):** calcd for $C_{25}H_{23}O_6$ $[M+H]^+$ *m/z* 419.1489, found 419.1498.

methyl 2a,2a[1]-diphenyl-2a,2a[1],2b,6b-tetrahydrobenzo[*a*]cyclopropa[*cd*]pentalene-2-carboxylate (**3ac-1**)




**Physical state:** Yellow oil
**Yield:** 38%
**R*f*** = 0.5 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.4 Hz, 1H), 7.25 – 7.22 (m, 3H), 7.19 – 7.09 (m, 7H), 7.07 – 7.02 (m, 1H), 6.97 – 6.93 (m, 2H), 6.75 (d, *J* = 2.7 Hz, 1H), 4.48 (d, *J* = 2.7 Hz, 1H), 4.28 (s, 1H), 3.40 (s, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 164.8, 147.2, 144.3, 138.5, 137.5, 136.9, 130.1, 129.6, 128.2, 127.9, 127.1, 126.8, 126.6, 126.6, 126.4, 126.1, 122.3, 69.2, 61.1, 59.3, 51.4, 43.6.
**HRMS (ESI):** calcd for $C_{26}H_{21}O_2$ $[M+H]^+$ *m/z* 365.1536, found 365.1529.

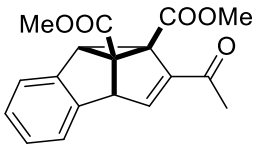
methyl 2a,2a[1]-diphenyl-2a,2a[1],2b,6b-tetrahydrobenzo[*a*]cyclopropa[*cd*]pentalene-1-carboxylate (**3ac-2**)




**Physical state:** Yellow oil

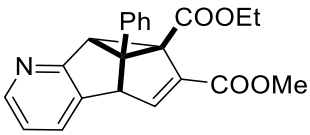
**Yield:** 4%
**$R_f$** = 0.3 in Petroleum ether/ethyl acetate (30:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.24 – 7.10 (m, 10H), 7.05 – 7.01 (m, 2H), 6.36 (s, 1H), 4.68 (s, 1H), 4.28 (s, 1H), 3.75 (s, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 164.1, 149.0, 139.4, 137.8, 137.6, 137.5, 136.8, 129.3, 128.4, 128.3, 127.1, 126.9, 126.9, 126.9, 126.5, 125.3, 122.9, 73.4, 60.8, 59.8, 51.7, 48.0.
**HRMS (ESI):** calcd for $C_{26}H_{21}O_2$ $[M+H]^+$ *m/z* 365.1536, found 365.1529.

dimethyl 2-acetyl-2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2a,2a$^1$-dicarboxylate (**3fd**)



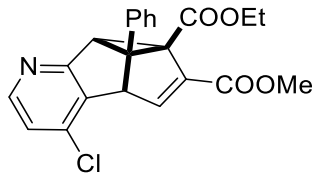

**Physical state:** Yellow oil
**Yield:** 30%
**$R_f$** = 0.4 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.52 – 7.45 (m, 1H), 7.25 – 7.16 (m, 3H), 6.65 (d, *J* = 2.7 Hz, 1H), 4.68 (d, *J* = 2.7 Hz, 1H), 4.58 (s, 1H), 3.83 (s, 3H), 3.63 (s, 3H), 2.12 (s, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 201.3, 168.0, 163.6, 145.9, 145.8, 135.8, 127.7, 127.6, 126.4, 125.2, 122.6, 74.4, 59.4, 54.9, 53.2, 52.0, 48.6, 27.3.
**HRMS (ESI):** calcd for $C_{18}H_{17}O_5$ $[M+H]^+$ *m/z* 313.1071, found 313.107.

2a-ethyl 2-methyl 2a$^1$-phenyl-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5aa**)




**Physical state:** Yellow oil
**Yield:** 85%
**$R_f$** = 0.3 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NM** (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 6.9 Hz, 1H), 7.31 – 7.10 (m, 9H), 6.65 (d, *J* = 2.6 Hz, 1H), 4.57 (s, 1H), 4.29 (d, *J* = 2.6 Hz, 1H), 4.03 – 3.91 (m, 2H), 3.64 (s, 3H), 0.94 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NM** (101 MHz, Chloroform-*d*) δ 167.1, 164.7, 146.7, 145.0, 137.5, 135.3, 128.4, 127.8, 127.6, 127.3, 126.8, 126.3, 126.2, 122.2, 70.0, 61.0, 60.8, 57.7, 51.6, 44.3, 13.9.
**HRMS (ESI):** calcd for $C_{22}H_{20}NO_4$ $[M+H]^+$ *m/z* 362.1387, found 362.1379.

2a-ethyl 2-methyl 6-chloro-2a$^1$-phenyl-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5ba**)




Physical state: Yellow oil

**Yield:** 78%

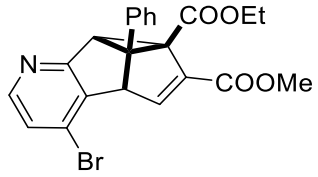
**R**$_f$ = 0.3 in Petroleum ether/ethyl acetate (3:1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 5.5 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.25 – 7.20 (m, 2H), 7.13 (d, *J* = 5.4 Hz, 1H), 6.81 (d, *J* = 2.6 Hz, 1H), 4.74 (s, 1H), 4.45 (d, *J* = 2.5 Hz, 1H), 4.00 – 3.93 (m, 2H), 3.67 (s, 3H), 0.94 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.0, 164.2, 158.8, 149.6, 141.8, 137.8, 134.1, 129.0, 128.6, 128.3, 127.5, 122.2, 77.2, 68.0, 61.3, 57.7, 57.5, 51.8, 45.6, 13.9.

**HRMS (ESI):** calcd for $C_{22}H_{19}ClNO_4$ $[M+H]^+$ *m/z* 396.0997, found 396.1009.

2a-ethyl 2-methyl 6-bromo-2a$^1$-phenyl-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5ca**)




Physical state: Yellow oil

**Yield:** 91%

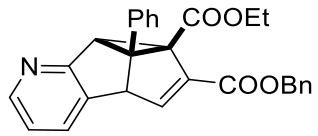
**R**$_f$ = 0.5 in Petroleum ether/ethyl acetate (3:1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 2.1 Hz, 1H), 7.96 (d, *J* = 2.1 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.23 – 7.18 (m, 2H), 6.71 (d, *J* = 2.6 Hz, 1H), 4.47 (s, 1H), 4.33 (d, *J* = 2.7 Hz, 1H), 4.04 – 3.94 (m, 2H), 3.68 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.4, 164.7, 164.1, 148.4, 144.3, 136.7, 134.2, 133.0, 128.6, 128.3, 128.2, 127.5, 119.4, 68.9, 61.4, 61.3, 58.0, 51.9, 40.2, 13.9.

**HRMS (ESI):** calcd for $C_{22}H_{19}BrNO_4$ $[M+H]^+$ *m/z* 440.0492, found 440.0478.

2-benzyl 2a-ethyl 2a$^1$-phenyl-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5da**)




Physical state: Yellow oil

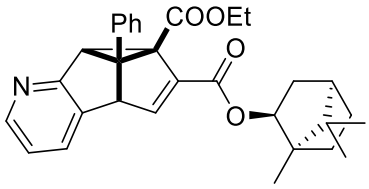
**Yield:** 84%

**R**$_f$ = 0.3 in Petroleum ether/ethyl acetate (3:1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.46 – 8.37 (m, 1H), 7.44 – 7.39 (m, 1H), 7.34 – 7.20 (m,

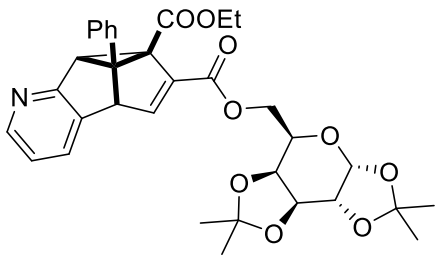
10H), 7.12 – 7.06 (m, 1H), 6.71 (d, $J$ = 2.6 Hz, 1H), 5.19 – 5.00 (m, 2H), 4.71 (s, 1H), 4.27 (d, $J$ = 2.6 Hz, 1H), 3.92 – 3.66 (m, 2H), 0.80 (t, $J$ = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.2, 163.7, 157.6, 148.5, 144.1, 139.6, 135.7, 134.6, 129.5, 128.5, 128.5, 128.2, 128.2, 128.1, 127.6, 127.5, 121.8, 68.7, 66.4, 61.1, 58.7, 57.7, 45.2, 13.8.
**HRMS (ESI):** calcd for $C_{28}H_{24}NO_4$ $[M+H]^+$ *m/z* 438.17, found 438.1716.

2a-ethyl 2-((1R,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl) 2a$^1$-phenyl-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5ea**)




Physical state: Yellow oil
**Yield:** 45%
**R$_f$** = 0.6 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.41 (d, $J$ = 5.1 Hz, 1H), 7.43 (d, $J$ = 7.6 Hz, 1H), 7.33 – 7.23 (m, 5H), 7.14 – 7.06 (m, 1H), 6.72 – 6.61 (m, 1H), 4.89 – 4.78 (m, 1H), 4.72 (d, $J$ = 2.4 Hz, 1H), 4.28 (d, $J$ = 2.6 Hz, 1H), 4.08 – 3.82 (m, 2H), 2.36 – 2.23 (m, 1H), 1.92 – 1.63 (m, 3H), 1.31 – 1.12 (m, 4H), 1.02 – 0.81 (m, 11H), 0.75 (d, $J$ = 17.2 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.3, 166.3, 164.3, 164.3, 157.6, 157.6, 148.4, 143.4, 143.3, 139.8, 134.7, 129.5, 129.4, 128.5, 128.3, 128.3, 128.0, 127.6, 121.7, 80.6, 80.5, 68.6, 68.5, 61.2, 61.1, 58.7, 58.6, 57.8, 57.8, 48.8, 47.8, 47.7, 45.0, 45.0, 44.8, 36.6, 36.3, 27.9, 27.1, 19.7, 18.8, 13.9, 13.8, 13.4, 13.4.
**HRMS (ESI):** calcd for $C_{31}H_{34}NO_4$ $[M+H]^+$ *m/z* 484.2482, found 484.2463.

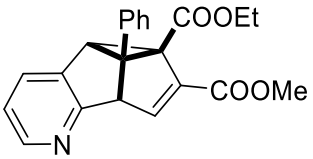
2a-ethyl 2-(((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl) 2a$^1$-phenyl-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5fa**)




**Physical state:** Yellow oil
**Yield:** 70%
**R$_f$** = 0.6 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.43 – 8.37 (m, 1H), 7.46 – 7.40 (m, 1H), 7.32 – 7.21 (m, 5H), 7.13 – 7.07 (m, 1H), 6.74 – 6.65 (m, 1H), 5.50 – 5.43 (m, 1H), 4.70 (s, 1H), 4.62 – 4.55 (m, 1H), 4.32 – 4.13 (m, 5H), 4.04 – 3.89 (m, 3H), 1.52 (s, 1H), 1.41 (d, $J$ = 4.7 Hz, 3H), 1.38 – 1.27

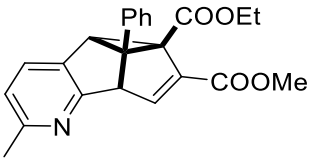
(m, 8H), 0.94 – 0.87 (m, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.1, 163.5, 163.5, 157.6, 148.5, 148.4, 144.3, 143.9, 139.6, 139.6, 134.6, 134.6, 129.6, 129.5, 128.5, 128.5, 128.1, 128.0, 127.5, 127.5, 127.5, 127.3, 121.7, 121.7, 109.5, 108.8, 108.7, 96.2, 70.9, 70.8, 70.6, 70.5, 70.5, 68.7, 68.7, 65.8, 65.7, 63.8, 63.3, 61.2, 58.7, 58.7, 57.6, 45.1, 45.1, 26.1, 25.9, 25.9, 25.0, 25.0, 24.4, 24.4, 13.8, 13.8.
**HRMS (ESI):** calcd for $C_{33}H_{36}NO_9$ $[M+H]^+$ *m/z* 590.2385, found 590.2365.

6c-ethyl 1-methyl 2a$^1$-phenyl-2a$^1$,6b-dihydrocyclopropa[3,4]pentaleno[1,2-*b*]pyridine-1,6c(2a*H*)-dicarboxylate (**5ga**)



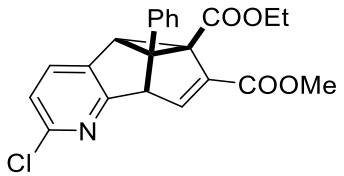

**Physical state:** Yellow oil
**Yield:** 72%
**$R_f$** = 0.3 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 5.0 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.25 – 7.21 (m, 2H), 7.17 – 7.12 (m, 1H), 6.74 (d, *J* = 2.7 Hz, 1H), 4.52 (s, 1H), 4.39 (d, *J* = 2.7 Hz, 1H), 4.04 – 3.93 (m, 2H), 3.66 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.7, 166.2, 164.3, 147.5, 144.7, 134.6, 134.0, 131.1, 128.5, 128.1, 127.8, 127.5, 122.1, 68.5, 61.9, 61.2, 57.9, 51.8, 40.8, 13.9.
**HRMS (ESI):** calcd for $C_{23}H_{22}NO_4$ $[M+H]^+$ *m/z* 362.1387, found 362.137.

6c-ethyl 1-methyl 4-methyl-2a$^1$-phenyl-2a$^1$,6b-dihydrocyclopropa[3,4]pentaleno[1,2-*b*]pyridine-1,6c(2a*H*)-dicarboxylate (**5ha**)



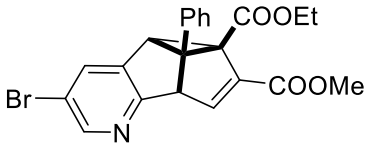

**Physical state:** Yellow oil
**Yield:** 51%
**$R_f$** = 0.4 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.24 (m, 3H), 7.25 – 7.18 (m, 2H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 2.7 Hz, 1H), 4.48 (s, 1H), 4.34 (d, *J* = 2.6 Hz, 1H), 4.04 – 3.91 (m, 2H), 3.66 (s, 3H), 2.51 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.9, 165.7, 164.4, 156.5, 144.8, 134.7, 134.2, 128.4, 128.0, 127.7, 127.5, 121.6, 68.3, 62.0, 61.2, 57.8, 51.7, 40.7, 24.0, 13.9.
**HRMS (ESI):** calcd for $C_{23}H_{22}NO_4$ $[M+H]^+$ *m/z* 376.1543, found 376.1557.

6c-ethyl 1-methyl 4-chloro-2a$^1$-phenyl-2a$^1$,6b-dihydrocyclopropa[3,4]pentaleno[1,2-*b*]pyridine-1,6c(2a*H*)-dicarboxylate (**5ia**)



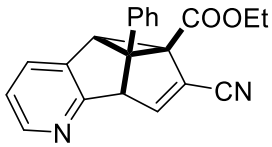

**Physical state:** Yellow oil
**Yield:** 96%
**$R_f$** = 0.7 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.22 – 7.16 (m, 3H), 6.74 (d, *J* = 2.5 Hz, 1H), 4.50 (s, 1H), 4.34 (d, *J* = 2.7 Hz, 1H), 4.03 – 3.93 (m, 2H), 3.68 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.5, 166.4, 164.1, 149.5, 144.1, 136.2, 134.2, 129.8, 128.5, 128.4, 128.2, 127.4, 122.4, 68.7, 61.6, 61.4, 58.0, 51.9, 40.3, 13.9.
**HRMS (ESI):** calcd for $C_{22}H_{19}ClNO_4$ $[M+H]^+$ *m/z* 396.0997, found 396.0984.

6c-ethyl 1-methyl 5-bromo-2a$^1$-phenyl-2a$^1$,6b-dihydrocyclopropa[3,4]pentaleno[1,2-*b*]pyridine-1,6c(2a*H*)-dicarboxylate (**5ja**)




**Physical state:** Yellow oil
**Yield:** 83%
**$R_f$** = 0.7 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 2.1 Hz, 1H), 7.95 (d, *J* = 2.1 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.25 – 7.18 (m, 2H), 6.72 (d, *J* = 2.7 Hz, 1H), 4.48 (s, 1H), 4.34 (d, *J* = 2.7 Hz, 1H), 4.04 – 3.93 (m, 2H), 3.68 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.4, 164.7, 164.1, 148.4, 144.3, 136.7, 134.2, 133.0, 128.6, 128.3, 128.2, 127.5, 119.4, 68.9, 61.4, 61.3, 58.0, 51.9, 40.2, 13.9.
**HRMS (ESI):** calcd for $C_{22}H_{19}BrNO_4$ $[M+H]^+$ *m/z* 440.0492, found 440.0504.

ethyl 1-cyano-2a$^1$-phenyl-2a$^1$,6b-dihydrocyclopropa[3,4]pentaleno[1,2-*b*]pyridine-6c(2a*H*)-carboxylate (**5ka**)



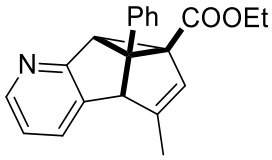

**Physical state:** Yellow oil
**Yield:** 77%
**$R_f$** = 0.5 in Petroleum ether/ethyl acetate (10:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.42 – 8.35 (m, 1H), 7.91 – 7.83 (m, 1H), 7.36 – 7.29 (m, 3H), 7.24 – 7.17 (m, 3H), 6.72 (d, *J* = 2.8 Hz, 1H), 4.52 (s, 1H), 4.39 (d, *J* = 2.8 Hz, 1H), 4.20 –

4.01 (m, 2H), 1.08 (t, $J$ = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 165.2, 150.8, 148.3, 134.5, 134.0, 130.3, 128.7, 128.6, 127.8, 122.8, 115.2, 105.9, 69.7, 63.0, 62.1, 57.7, 43.3, 13.9.

**HRMS (ESI):** calcd for $C_{21}H_{17}N_2O_2$ $[M+H]^+$ *m/z* 329.1285, found 329.1287.

ethyl 1-methyl-2a$^1$-phenyl-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2a(2a$^1$*H*)-carboxylate (**5la-1**)




**Physical state:** Yellow oil

**Yield:** 15%

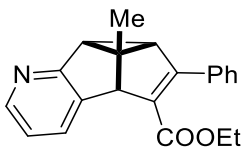
**R$_f$** = 0.6 in Petroleum ether/ethyl acetate (3:1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.29 – 8.24 (m, 1H), 7.81 – 7.73 (m, 1H), 7.33 – 7.27 (m, 2H), 7.26 – 7.19 (m, 3H), 7.12 – 7.05 (m, 1H), 5.57 (s, 1H), 4.38 (s, 1H), 4.16 (s, 1H), 4.04 – 3.90 (m, 2H), 1.77 (s, 3H), 0.95 (t, $J$ = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 168.9, 168.1, 146.7, 135.8, 133.4, 131.8, 131.1, 130.4, 128.3, 127.6, 127.6, 121.1, 69.3, 61.3, 60.9, 60.0, 41.6, 15.8, 14.0.

**HRMS (ESI):** calcd for $C_{21}H_{20}NO_2$ $[M+H]^+$ *m/z* 318.14886, found 318.14764.

ethyl 2a$^1$-methyl-2-phenyl-2a,2a$^1$,2b,6b-tetrahydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-1-carboxylate (**5la-2**)




**Physical state:** Yellow oil

**Yield:** 19%

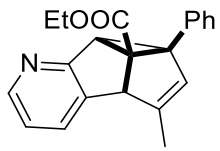
**R$_f$** = 0.4 in Petroleum ether/ethyl acetate (3:1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.30 (d, $J$ = 4.9 Hz, 1H), 7.55 (d, $J$ = 7.6 Hz, 1H), 7.37 – 7.22 (m, 5H), 7.07 – 6.97 (m, 1H), 4.21 – 4.00 (m, 3H), 3.27 (d, $J$ = 7.5 Hz, 1H), 2.88 (d, $J$ = 7.4 Hz, 1H), 1.46 (s, 3H), 1.17 (td, $J$ = 7.2, 0.9 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 163.6, 158.1, 147.8, 147.8, 141.7, 136.0, 130.3, 129.9, 128.8, 128.2, 127.5, 121.0, 60.1, 58.0, 56.1, 50.2, 45.9, 17.7, 14.1.

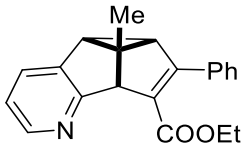
**HRMS (ESI):** calcd for $[M+H]^+$ *m/z* 318.14886, found 318.14993.

ethyl 1-methyl-2a-phenyl-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2a$^1$(2a*H*)-carboxylate (**5la-3**)



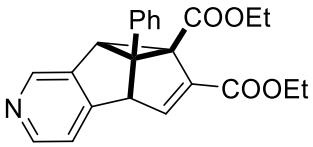

**Physical state:** White solid
**Melting Point:** 106.8-107.3°C
**Yield:** 18%
**R$_f$** = 0.5 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.40 – 8.36 (m, 1H), 7.50 – 7.45 (m, 2H), 7.44 – 7.40 (m, 1H), 7.37 – 7.31 (m, 2H), 7.30 – 7.27 (m, 1H), 7.11 – 7.07 (m, 1H), 4.96 (d, *J* = 1.6 Hz, 1H), 4.39 (s, 1H), 4.32 (s, 1H), 3.90 – 3.73 (m, 2H), 1.79 (d, *J* = 1.5 Hz, 3H), 0.77 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 169.4, 157.5, 147.3, 145.5, 142.4, 138.2, 129.4, 128.4, 128.3, 127.5, 122.0, 121.3, 66.2, 62.2, 60.5, 56.9, 48.0, 13.8, 13.8.
**HRMS (ESI):** calcd for $C_{21}H_{20}NO_2$ $[M+H]^+$ *m/z* 318.14886, found 318.15016.

ethyl 2a$^1$-methyl-1-phenyl-2a,2a$^1$,6b,6c-tetrahydrocyclopropa[3,4]pentaleno[1,2-*b*]pyridine-2-carboxylate (**5ma**)




**Physical state:** White solid
**Melting Point:** 138.5-139.0°C
**Yield:** 57%
**R$_f$** = 0.2 in Petroleum ether/ethyl acetate (6:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.21 – 8.14 (m, 1H), 7.63 – 7.54 (m, 1H), 7.20 – 7.18 (m, 5H), 7.00 – 6.94 (m, 1H), 4.17 (s, 1H), 4.14 – 3.98 (m, 2H), 2.95 (d, *J* = 7.0 Hz, 1H), 2.73 (d, *J* = 7.0 Hz, 1H), 1.41 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 167.7, 163.6, 146.4, 146.0, 136.2, 132.3, 131.8, 130.5, 128.4, 128.1, 127.6, 121.7, 61.0, 60.2, 56.5, 50.1, 41.0, 18.1, 14.1.
**HRMS (ESI):** calcd for $C_{21}H_{20}NO_2$ $[M+H]^+$ *m/z* 318.14886, found 318.14856.

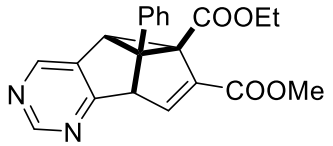
diethyl 2a$^1$-phenyl-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*c*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5na**)




**Physical state:** Yellow oil
**Yield:** 92%
**R$_f$** = 0.2 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.80 (s, 1H), 8.44 (d, *J* = 5.0 Hz, 1H), 7.31 – 7.27 (m, 3H),

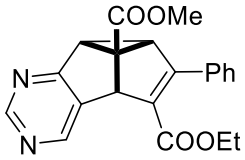
7.24 – 7.18 (m, 2H), 7.12 (d, $J$ = 5.0 Hz, 1H), 6.61 (d, $J$ = 2.7 Hz, 1H), 4.62 (s, 1H), 4.32 (d, $J$ = 2.6 Hz, 1H), 4.17 – 4.08 (m, 2H), 4.02 – 3.93 (m, 2H), 1.23 (t, $J$ = 7.1 Hz, 3H), 0.95 (t, $J$ = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.0, 150.4, 145.5, 136.6, 134.7, 128.5, 128.4, 128.2, 128.0, 127.8, 127.5, 126.6, 122.4, 115.5, 104.2, 70.8, 61.9, 61.7, 57.3, 46.9, 13.9.
**HRMS (ESI):** calcd for $C_{23}H_{22}NO_4$ $[M+H]^+$ *m/z* 376.1543, found 376.155.

6c-ethyl 1-methyl 2a$^1$-phenyl-2a$^1$,6b-dihydrocyclopropa[3,4]pentaleno[1,2-*d*]pyrimidine-1,6c(2a*H*)-dicarboxylate (**5oa-1**)



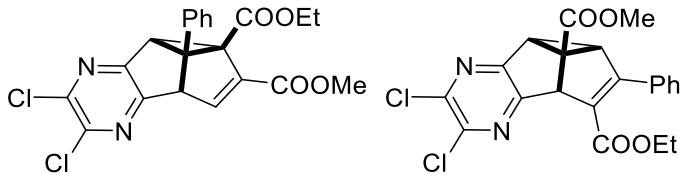

**Physical state:** Yellow solid
**Melting Point:** 120.1-120.5 °C
**Yield:** 37%
**R$_f$** = 0.1 in Petroleum ether/ethyl acetate (20:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.96 (s, 1H), 8.84 (s, 1H), 7.34 – 7.27 (m, 3H), 7.23 – 7.18 (m, 2H), 6.68 (d, $J$ = 2.6 Hz, 1H), 4.56 (s, 1H), 4.38 (d, $J$ = 2.7 Hz, 1H), 4.05 – 3.92 (m, 2H), 3.68 (s, 3H), 0.95 (t, $J$ = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 174.3, 166.2, 163.8, 156.8, 153.6, 143.3, 133.9, 129.7, 129.3, 128.7, 128.6, 127.6, 68.7, 62.0, 61.6, 58.2, 52.1, 39.0, 14.0.
**HRMS (ESI):** calcd for $C_{21}H_{19}N_2O_4$ $[M+H]^+$ *m/z* 363.1339, found 363.1337.

1-ethyl 2a$^1$-methyl 2-phenyl-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*d*]pyrimidine-1,2a$^1$(2a*H*)-dicarboxylate (**5oa-2**)



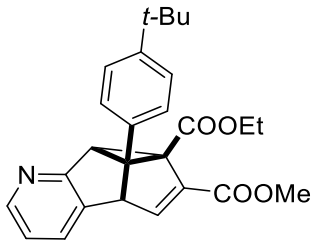

**Physical state:** Yellow oil
**Yield:** 56%
**R$_f$** = 0.2 in Petroleum ether/ethyl acetate (20:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.99 (s, 1H), 8.64 (s, 1H), 7.36 – 7.27 (m, 5H), 4.94 (s, 1H), 4.21 – 4.07 (m, 2H), 4.00 (d, $J$ = 8.2 Hz, 1H), 3.81 (d, $J$ = 8.2 Hz, 1H), 3.75 (s, 3H), 1.21 (t, $J$ = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 169.9, 164.0, 162.7, 157.8, 150.0, 145.4, 138.9, 134.1, 131.9, 129.2, 128.9, 127.9, 61.0, 58.9, 52.6, 51.8, 51.7, 47.1, 14.2.
**HRMS (ESI):** calcd for $C_{21}H_{19}N_2O_4$ $[M+H]^+$ *m/z* 363.1339, found 363.1331.

2a-ethyl 2-methyl 4,5-dichloro-2a$^1$-phenyl-2b,6b-dihydrocyclopropa[3,4]pentaleno[1,2-*b*]pyrazine-2,2a(2a$^1$*H*)-dicarboxylate **and** 1-ethyl 2a$^1$-methyl 4,5-dichloro-2-phenyl-2b,6b-dihydrocyclopropa[3,4]pentaleno[1,2-*b*]pyrazine-1,2a$^1$(2a*H*)-dicarboxylate (**5pa**)



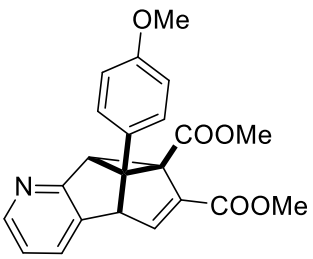

**Physical state:** Yellow oil
**Yield:** 68%
**$R_f$** = 0.3 in Petroleum ether/ethyl acetate (30:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.40 – 7.36 (m, 2H), 7.34 – 7.28 (m, 6H), 7.22 – 7.16 (m, 2H), 6.71 (d, *J* = 2.6 Hz, 1H), 4.98 (s, 1H), 4.60 (s, 1H), 4.34 (d, *J* = 2.7 Hz, 1H), 4.32 – 4.23 (m, 1H), 4.18 – 4.10 (m, 1H), 4.02 – 3.94 (m, 2H), 3.92 (d, *J* = 7.9 Hz, 1H), 3.81 (d, *J* = 7.6 Hz, 1H), 3.76 (s, 3H), 3.69 (s, 3H), 1.27 (t, *J* = 6.9 Hz, 3H), 0.94 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 169.3, 165.3, 163.5, 162.1, 158.2, 157.0, 149.8, 148.0, 146.0, 145.9, 145.6, 145.1, 145.0, 142.3, 133.6, 133.3, 130.2, 130.0, 129.4, 128.7, 128.7, 128.7, 127.9, 127.4, 68.6, 61.6, 61.0, 58.7, 58.5, 53.3, 52.6, 52.0, 51.4, 42.4, 40.8, 14.1, 13.9.
**HRMS (ESI):** calcd for $C_{21}H_{17}Cl_2N_2O_4$ $[M+H]^+$ *m/z* 431.056, found 431.0573.

2a-ethyl 2-methyl 2a$^1$-(4-(tert-butyl)phenyl)-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-$^b$]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5ae**)



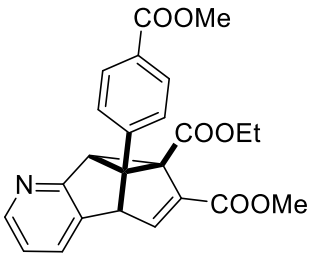

**Physical state:** Yellow oil
**Yield:** 66%
**$R_f$** = 0.3 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.46 – 8.36 (m, 1H), 7.44 – 7.40 (m, 1H), 7.34 – 7.29 (m, 2H), 7.19 – 7.13 (m, 2H), 7.12 – 7.06 (m, 1H), 6.67 (d, *J* = 1.9 Hz, 1H), 4.68 (s, 1H), 4.27 (d, *J* = 2.6 Hz, 1H), 4.08 – 3.89 (m, 2H), 3.65 (s, 3H), 1.27 (s, 9H), 0.89 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.3, 164.4, 157.6, 151.1, 148.4, 143.8, 139.8, 131.6, 129.5, 127.6, 127.2, 125.4, 121.7, 68.7, 61.1, 58.7, 57.6, 51.7, 45.3, 34.6, 31.3, 13.8.
**HRMS (ESI):** calcd for $C_{26}H_{28}NO_4$ $[M+H]^+$ *m/z* 418.2013, found 418.2013.

2a-ethyl 2-methyl 2a$^1$-(4-methoxyphenyl)-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$H)-dicarboxylate (**5af**)



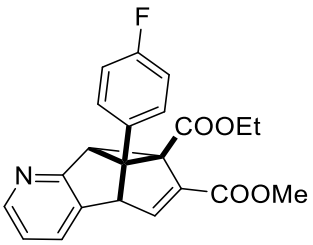

**Physical state:** Yellow oil
**Yield:** 50%
**$R_f$** = 0.1 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.42 – 8.37 (m, 1H), 7.45 – 7.39 (m, 1H), 7.15 – 7.06 (m, 3H), 6.85 – 6.78 (m, 2H), 6.65 (m, 1H), 4.63 (s, 1H), 4.21 (d, *J* = 2.6 Hz, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 3.51 (s, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 167.0, 164.3, 159.4, 157.5, 148.5, 143.8, 139.7, 129.5, 128.7, 127.4, 126.8, 121.8, 113.9, 68.6, 58.9, 57.5, 55.3, 52.3, 51.8, 45.5.
**HRMS (ESI):** calcd for $C_{22}H_{20}NO_5$ $[M+H]^+$ *m/z* 378.1336, found 378.1319.

2a-ethyl 2-methyl 2a$^1$-(4-(methoxycarbonyl)phenyl)-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5ag**)



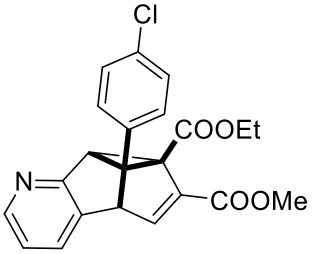

**Physical state:** Yellow oil
**Yield:** 70%
**$R_f$** = 0.2 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.45 – 8.39 (m, 1H), 8.02 – 7.91 (m, 2H), 7.48 – 7.40 (m, 1H), 7.33 – 7.26 (m, 2H), 7.15 – 7.07 (m, 1H), 6.68 (d, *J* = 2.6 Hz, 1H), 4.73 (s, 1H), 4.31 (d, *J* = 2.6 Hz, 1H), 4.00 – 3.89 (m, 2H), 3.89 (d, *J* = 1.0 Hz, 3H), 3.64 (s, 3H), 0.94 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.6, 166.0, 164.2, 157.1, 148.7, 143.7, 139.5, 139.4, 129.8, 129.6, 127.5, 127.5, 121.9, 68.2, 61.3, 58.3, 58.0, 52.2, 51.8, 45.4, 14.0.
**HRMS (ESI):** calcd for $C_{24}H_{22}NO_6$ $[M+H]^+$ *m/z* 420.1442, found 420.1451.

2a-ethyl 2-methyl 2a$^1$-(4-fluorophenyl)-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5ah**)



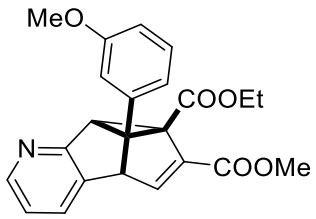

**Physical state:** Yellow oil
**Yield:** 88%
**R$_f$** = 0.3 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.45 – 8.35 (m, 1H), 7.45 – 7.39 (m, 1H), 7.23 – 7.15 (m, 2H), 7.13 – 7.07 (m, 1H), 7.02 – 6.92 (m, 2H), 6.65 (d, *J* = 2.6 Hz, 1H), 4.65 (s, 1H), 4.22 (d, *J* = 2.6 Hz, 1H), 4.02 – 3.91 (m, 2H), 3.63 (s, 3H), 0.96 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.2, 164.3, 162.5 (d, *J* = 248.5 Hz), 157.3, 148.6, 143.6, 139.5, 130.6 (d, *J* = 3.0 Hz), 129.6, 129.4(d, *J* = 8.1 Hz), 127.5, 121.9, 115.5 (d, *J* = 22.2 Hz), 68.0, 61.2, 58.8, 57.5, 51.8, 45.5, 14.0.
**$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -113.6.
**HRMS (ESI):** calcd for $C_{22}H_{19}FNO_4$ $[M+H]^+$ *m/z* 380.1293, found 380.1293.

2a-ethyl 2-methyl 2a$^1$-(4-chlorophenyl)-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5ai**)



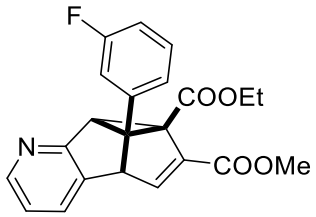

**Physical state:** Yellow oil
**Yield:** 72%
**R$_f$** = 0.2 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.49 – 8.40 (m, 1H), 7.48 – 7.42 (m, 1H), 7.31 – 7.25 (m, 2H), 7.20 – 7.09 (m, 3H), 6.66 (d, *J* = 2.4 Hz, 1H), 4.67 (s, 1H), 4.25 (d, *J* = 2.6 Hz, 1H), 4.08 – 3.92 (m, 2H), 3.65 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.1, 164.3, 157.2, 148.6, 143.6, 139.5, 134.1, 133.2, 129.6, 128.9, 128.7, 127.5, 121.9, 67.9, 61.3, 58.6, 57.6, 51.8, 45.4, 14.0.
**HRMS (ESI):** calcd for $C_{22}H_{19}ClNO_4$ $[M+H]^+$ *m/z* 396.0997, found 396.0999.

2a-ethyl 2-methyl 2a$^1$-(3-methoxyphenyl)-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5aj**)



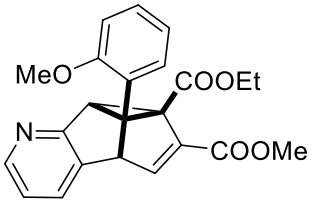

**Physical state:** Yellow oil
**Yield:** 73%
**R$_f$** = 0.2 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.45 – 8.39 (m, 1H), 7.46 – 7.40 (m, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.14 – 7.08 (m, 1H), 6.85 – 6.78 (m, 2H), 6.76 – 6.73 (m, 1H), 6.67 (d, *J* = 2.6 Hz, 1H), 4.68 (s, 1H), 4.27 (d, *J* = 2.6 Hz, 1H), 4.04 – 3.95 (m, 2H), 3.77 (s, 3H), 3.65 (s, 3H), 0.98 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.3, 164.5, 159.7, 157.6, 148.6, 143.9, 139.7, 136.2, 129.7, 129.6, 127.7, 121.9, 119.9, 113.9, 113.0, 68.8, 61.2, 58.9, 57.7, 55.4, 51.8, 45.5, 14.0.
**HRMS (ESI):** calcd for $C_{23}H_{22}NO_5$ $[M+H]^+$ *m/z* 392.1493, found 392.1508.

2a-ethyl 2-methyl 2a$^1$-(3-fluorophenyl)-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5ak**)



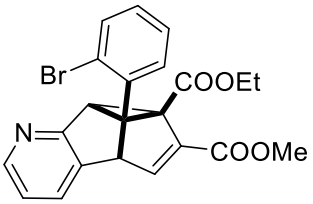

**Physical state:** Yellow oil
**Yield:** 82%
**R$_f$** = 0.3 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.43 – 8.37 (m, 1H), 7.46 – 7.39 (m, 1H), 7.29 – 7.20 (m, 1H), 7.12 – 7.07 (m, 1H), 7.02 – 6.89 (m, 3H), 6.65 (d, *J* = 1.9 Hz, 1H), 4.66 (s, 1H), 4.26 (d, *J* = 2.6 Hz, 1H), 4.06 – 3.91 (m, 2H), 3.63 (s, 3H), 0.96 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) *δ* 166.0, 164.2, 162.7 (d, *J* = 247.5 Hz), 157.2, 148.6, 143.7, 139.4, 137.0 (d, *J* = 8.1 Hz ), 130.1 (d, *J* = 9.1 Hz), 129.6, 127.5, 123.2 (d, *J* = 3.0 Hz), 121.9, 115.1 (d, *J* = 21.0 Hz), 114.6 (d, *J* = 22.2 Hz), 68.0 (d, *J* = 2.0 Hz), 61.3, 58.5, 57.7, 51.8, 45.4, 13.9.
**$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -112.6.
**HRMS (ESI):** calcd for $C_{22}H_{19}FNO_4$ $[M+H]^+$ *m/z* 380.1293, found 380.1286.

2a-ethyl 2-methyl 2a$^1$-(2-methoxyphenyl)-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5al**)



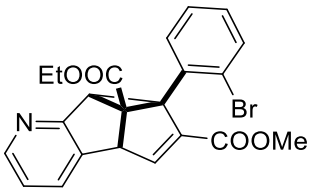

**Physical state:** Purple oil
**Yield:** 78%
**$R_f$** = 0.3 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.49 – 8.37 (m, 1H), 7.43 – 7.35 (m, 1H), 7.28 – 7.21 (m, 1H), 7.16 – 7.10 (m, 1H), 7.10 – 7.04 (m, 1H), 6.90 – 6.79 (m, 2H), 6.66 (d, *J* = 2.7 Hz, 1H), 4.57 (s, 1H), 4.09 (d, *J* = 2.7 Hz, 1H), 4.02 – 3.89 (m, 2H), 3.75 (s, 3H), 3.64 (s, 3H), 0.93 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.7, 165.0, 159.0, 158.1, 148.3, 144.5, 140.3, 129.7, 129.5, 129.5, 126.8, 123.5, 121.6, 120.2, 110.6, 66.6, 60.8, 58.3, 56.5, 55.6, 51.6, 45.5, 14.0.
**HRMS (ESI):** calcd for $C_{23}H_{22}NO_5$ $[M+H]^+$ *m/z* 392.1493, found 392.15.

2a-ethyl 2-methyl 2a$^1$-(2-bromophenyl)-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5am-1**)




**Physical state:** White solid
**Melting Point:** 174.1-174.6°C
**Yield:** 22%
**$R_f$** = 0.3 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.43 (d, *J* = 4.3 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.20 – 7.08 (m, 2H), 6.67 (d, *J* = 2.6 Hz, 1H), 4.63 (s, 1H), 4.16 (d, *J* = 2.6 Hz, 1H), 4.12 – 3.96 (m, 2H), 3.66 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.3, 164.7, 157.6, 148.5, 144.2, 139.9, 135.4, 133.2, 131.1, 130.0, 129.6, 127.2, 126.8, 125.1, 121.8, 69.2, 61.2, 58.0, 57.1, 51.7, 46.3, 13.9.
**HRMS (ESI):** calcd for $C_{22}H_{19}BrNO_4$ $[M+H]^+$ *m/z* 440.0492, found 440.0492.

2a$^1$-ethyl 1-methyl 2a-(2-bromophenyl)-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-1,2a$^1$(2a*H*)-dicarboxylate (**5am-2**)




**Physical state:** Yellow oil

**Yield:** 30%

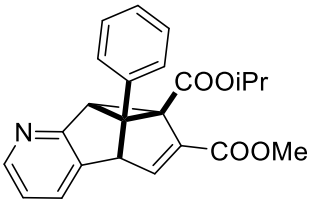
**$R_f$** = 0.4 in Petroleum ether/ethyl acetate (3:1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.39 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.25 – 7.16 (m, 2H), 7.11 – 7.01 (m, 2H), 5.90 (d, *J* = 2.4 Hz, 1H), 4.79 (s, 1H), 4.62 (d, *J* = 2.6 Hz, 1H), 4.16 – 3.98 (m, 2H), 3.72 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 169.1, 166.5, 156.1, 148.1, 140.9, 136.6, 135.4, 134.2, 133.0, 130.4, 129.2, 128.9, 127.2, 121.9, 121.2, 65.5, 61.6, 60.5, 53.1, 52.6, 49.6, 13.9.

**HRMS (ESI):** calcd for $C_{22}H_{19}BrNO_4$ $[M+H]^+$ *m/z* 440.0492, found 440.048.

2a-isopropyl 2-methyl 2a$^1$-phenyl-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5an**)




**Physical state:** Yellow oil

**Yield:** 67%

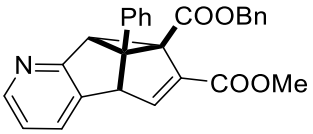
**$R_f$** = 0.3 in Petroleum ether/ethyl acetate (3:1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.46 – 8.39 (m, 1H), 7.48 – 7.40 (m, 1H), 7.33 – 7.28 (m, 3H), 7.26 – 7.22 (m, 2H), 7.13 – 7.09 (m, 1H), 6.68 (d, *J* = 2.6 Hz, 1H), 4.87 – 4.78 (m, 1H), 4.70 (s, 1H), 4.28 (d, *J* = 2.6 Hz, 1H), 3.66 (s, 3H), 0.93 (dd, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 164.4, 157.6, 148.4, 143.7, 139.7, 134.6, 129.5, 128.4, 128.1, 127.8, 127.6, 121.8, 68.8, 68.7, 58.7, 57.7, 51.7, 45.1, 21.5, 21.2.

**HRMS (ESI):** calcd for $C_{23}H_{22}NO_4$ $[M+H]^+$ *m/z* 376.1543, found 376.1558.

2a-benzyl 2-methyl 2a$^1$-phenyl-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5ao**)




**Physical state:** Yellow oil

**Yield:** 75%

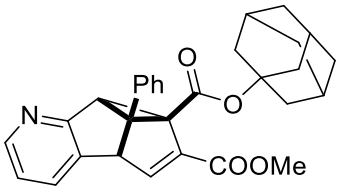
**$R_f$** = 0.2 in Petroleum ether/ethyl acetate (3:1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.44 – 8.38 (m, 1H), 7.45 – 7.39 (m, 1H), 7.27 – 7.24 (m, 6H), 7.21 – 7.16 (m, 2H), 7.12 – 7.07 (m, 1H), 7.06 – 7.01 (m, 2H), 6.68 – 6.64 (m, 1H), 4.93 (s, 2H), 4.72 (s, 1H), 4.27 (d, *J* = 2.6 Hz, 1H), 3.51 (s, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.4, 164.4, 157.5, 148.6, 144.0, 139.8, 135.6, 134.6, 129.6, 128.7, 128.5, 128.4, 128.3, 128.3, 128.2, 127.6, 127.6, 121.9, 69.1, 67.1, 58.9, 57.6, 51.8, 45.6.

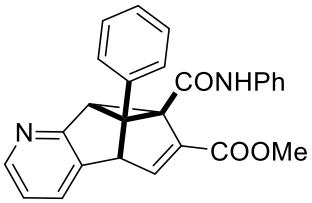
**HRMS (ESI):** calcd for $C_{27}H_{22}NO_4$ $[M+H]^+$ *m/z* 424.1543, found 424.1553.

2a-((3s,5s,7s)-adamantan-1-yl) 2-methyl 2a[1]-phenyl-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a[1]*H*)-dicarboxylate (**5ap**)



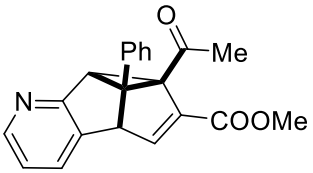

**Physical state:** White solid
**Melting Point:** 228.2-230.0 °C
**Yield:** 47%
**R*f*** = 0.3 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.45 – 8.36 (m, 1H), 7.45 – 7.38 (m, 1H), 7.34 – 7.27 (m, 3H), 7.26 – 7.22 (m, 2H), 7.11 – 7.05 (m, 1H), 6.62 (d, *J* = 2.5 Hz, 1H), 4.62 (s, 1H), 4.24 (d, *J* = 2.6 Hz, 1H), 3.67 (s, 3H), 2.05 – 2.00 (m, 3H), 1.83 – 1.71 (m, 6H), 1.57 – 1.50 (m, 6H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 164.8, 164.7, 157.9, 148.4, 143.3, 139.8, 134.9, 129.5, 128.5, 128.2, 128.1, 127.9, 121.7, 81.6, 68.8, 58.8, 58.5, 51.7, 45.3, 40.9, 36.1, 30.8.
**HRMS (ESI):** calcd for $C_{30}H_{30}NO_4$ $[M+H]^+$ *m/z* 468.2169, found 468.2169.

methyl 2a[1]-phenyl-2a-(phenylcarbamoyl)-2a,2a[1],2b,6b-tetrahydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2-carboxylate (**5aq**)



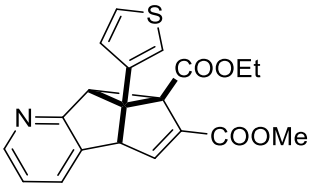

**Physical state:** White solid
**Melting Point:** ＞300°C
**Yield:** 30%
**R*f*** = 0.3 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.43 (d, *J* = 4.4 Hz, 1H), 7.88 (s, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.26 – 7.19 (m, 6H), 7.16 – 7.11 (m, 1H), 7.08 – 7.01 (m, 1H), 6.91 (d, *J* = 2.6 Hz, 1H), 4.73 (s, 1H), 4.38 (d, *J* = 2.6 Hz, 1H), 3.66 (s, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 164.4, 163.9, 157.6, 148.7, 146.7, 139.2, 137.6, 134.9, 129.8, 128.8, 128.7, 127.9, 126.9, 126.5, 124.5, 121.9, 120.6, 68.2, 60.3, 58.3, 52.2, 44.7.
**HRMS (ESI):** calcd for $C_{26}H_{21}N_2O_3$ $[M+H]^+$ *m/z* 409.1547, found 409.1553.

methyl 2a-acetyl-2a[1]-phenyl-2a,2a[1],2b,6b-tetrahydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2-carboxylate (**5ar**)




**Physical state:** Brown solid
**Melting Point:** 147.9-148.4℃
**Yield:** 72%
**$R_f$值:** 0.2 in Petroleum ether/ethyl acetate (6:1).
**$^1$H NMR** (400 MHz, Chloroform-d) δ 7.55 – 7.49 (m, 1H), 7.29 (m, J = 8.7, 1.5 Hz, 1H), 7.24 – 7.11 (m, 6H), 6.55 (d, J = 2.6 Hz, 1H), 4.55 (s, 1H), 4.34 (d, J = 2.6 Hz, 1H), 3.94 (q, J = 7.1 Hz, 2H), 2.19 (s, 3H), 0.90 (t, J = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 195.6, 167.2, 146.5, 144.0, 137.6, 135.8, 135.3, 128.4, 127.8, 127.5, 127.4, 126.8, 126.3, 122.1, 69.2, 61.0, 61.0, 57.7, 44.2, 27.0, 13.9.
**HRMS (ESI):** calcd for $C_{26}H_{21}N_2O_3$ $[M+H]^+$ *m/z* 332.12812, found 332.12648.

2a-ethyl 2-methyl 2a$^1$-(thiophen-3-yl)-2b,6b-dihydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2a$^1$*H*)-dicarboxylate (**5as**)

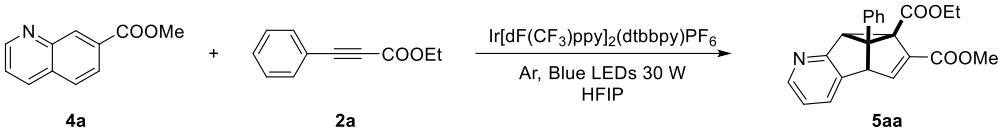



**Physical state:** Yellow liquid
**Yield:** 44%
**$R_f$** = 0.2 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.47 – 8.37 (m, 1H), 7.47 – 7.41 (m, 1H), 7.33 – 7.25 (m, 1H), 7.16 – 7.07 (m, 2H), 7.03 – 6.95 (m, 1H), 6.65 (d, *J* = 2.6 Hz, 1H), 4.62 (s, 1H), 4.26 (d, *J* = 2.6 Hz, 1H), 4.07 – 3.99 (m, 2H), 3.65 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.3, 164.3, 157.3, 148.6, 143.6, 139.6, 135.3, 129.6, 127.3, 126.7, 126.2, 122.6, 121.8, 64.8, 61.3, 58.1, 57.5, 51.8, 46.5, 14.0.
**HRMS (ESI):** calcd for $C_{20}H_{18}NO_4S$ $[M+H]^+$ *m/z* 368.0951, found 368.0956.

## 6. General Procedure for the synthetic application and characterization data of products

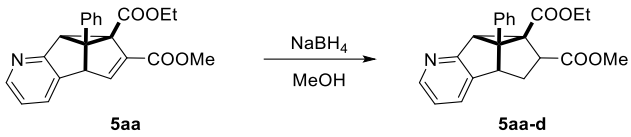
### 6.1 General procedures for the synthetic applications

#### 6.1.1 Gram scale reaction with substrate methyl 7-quinolinecarboxylate 4a



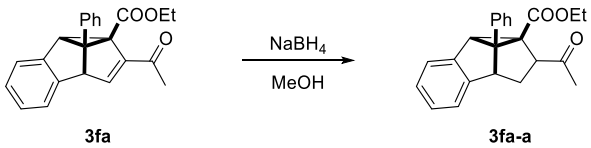

An oven-dried Schlenk tube (100 ml) containing a stirring bar was charged with the Methyl 7-quinolinecarboxylate **4a** (3.26 mmol, 0.61 g), **2a** ethyl phenylpropiolate (6.52 mmol, 1.07 mL) and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2 mol %, 73 mg). Then, the Schlenk tube was connected to a vacuum line where it was evacuated and back-filled with argon for 3 times. Afterwards, solvent (HFIP, 32 ml) which was bubbled with argon for 5 minutes was added under argon flow. Finally, the reaction mixture in a sealed tube was placed at a distance of 2 - 3 cm from a 30 W blue LEDs (450 nm) and stirred at room temperature for the indicated time (monitored by TLC, 12 h). After finishing the reaction, the mixture was concentrated in vacuo and purified by silica gel flash chromatography (Petroleum ether/ethyl acetate 3/1) to afford the corresponding product **5aa** (2.91 mmol, 1.05 g) as a yellow oil.

#### 6.1.2 Reduction reaction of 5aa with sodium borohydride




In a Schlenk tube equipped with a PTFE-coated stirring bar, compound **5aa** (72.3 mg, 0.20 mmol, 1.0 eq.), methanol (6 mL) was added, the solution was stirred at room temperature, $NaBH_4$ (18.2 mg, 0.48 mmol, 2.4 eq.) was added. The mixture was stirred 10 min and quenched with aqueous $NH_4Cl$, the aqueous layer was extracted three times with EA (5 ml each time). The combined organic extracts were dried over $Na_2SO_4$ and the solvent was removed in vacuo. The residue was purified by flash column chromatography on silica (Petroleum ether/ethyl acetate 6/1, $R_f$ = 0.4), affording compound **5aa-d** (72 mg, 0.2 mmol, 100%) as a white liquid.

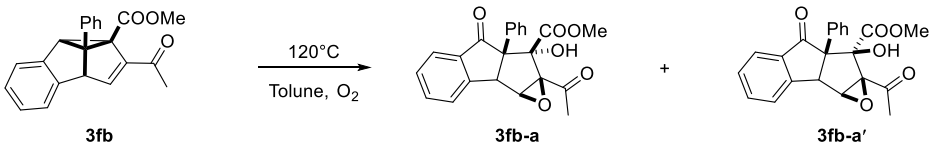
#### 6.1.3 Reduction reaction of 3fa with sodium borohydride




In a Schlenk tube equipped with a PTFE-coated stirring bar, **3fa** (33.7 mg, 0.10 mmol, 1.0 eq.), methanol (3 mL) was added, the solution was stirred at room temperature, $NaBH_4$ (9.1 mg, 0.24 mmol, 2.4 eq.) was added. The mixture was stirred 10 min and quenched with aqueous $NH_4Cl$, the

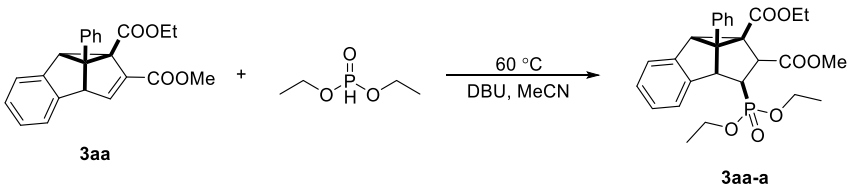
aqueous layer was extracted three times with EA (5 ml each time). The combined organic extracts were dried over $Na_2SO_4$ and the solvent was removed in vacuo. The residue was purified by flash column chromatography on silica (Petroleum ether/ethyl acetate 8/1, $R_f$ = 0.3), affording **3fa-a** (33 mg, 0.1 mmol, 100%) as a white liquid.

### 6.1.4 Thermal aerobic conversion of 3fb



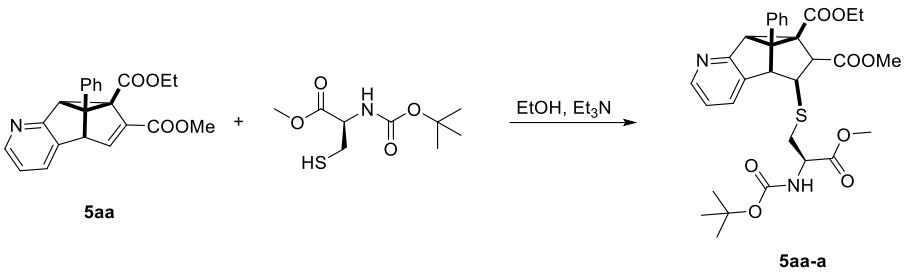

An oven-dried Schlenk tube (10 ml) containing a stirring bar was charged with the **3fb** (33.5 mg, 0.10 mmol, 1.0 eq.). Then, the Schlenk tube was connected to a vacuum line where it was evacuated and back-filled with oxygen for 3 times. Afterwards, solvent (toluene, 0.5 ml) was added under oxygen flow. Finally, the reaction mixture was warm to 120℃ stirred for the indicated time (monitored by TLC, 48 h). After finishing the reaction, the mixture was concentrated in vacuo and purified by silica gel flash chromatography (Petroleum ether/ethyl acetate 3/1), to afford the **3fb-a** (14.32 mg, 0.038 mmol, 38%, $R_f$ = 0.5) as a white solid, **3fb-a′** (17.75 mg, 0.047 mmol, 47%, $R_f$ = 0.4).

### 6.1.5 Michael addition reaction of 3aa with diethyl phosphite



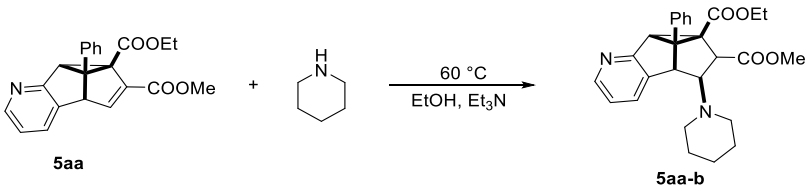

In a Schlenk tube equipped with a PTFE-coated stirring bar, **3aa** (72.1 mg, 0.20 mmol, 1.0 eq.), Diethyl phosphite (DEP) (66.5 mg, 0.40 mmol, 2.0 eq.) and DBU (30.5 mg, 0.20 mmol, 1.0 eq.) was dissolved in anhydrous $CH_3CN$ (1 ml), and the solution was warmed to 60 °C stirred for 8 hours. The reaction was carefully quenched with aqueous $NaHCO_3$, the aqueous layer was extracted three times with ethyl acetate (5 ml each time). The combined organic extracts were dried over $Na_2SO_4$ and the solvent was removed in vacuo. The residue was purified by flash column chromatography on silica (Petroleum ether/ethyl acetate 3/2, $R_f$ = 0.2), affording **3aa-a** (95.0 mg, 0.196 mmol, 98%) as a yellow oil.[17]

### 6.1.6 Michael addition reaction of 5aa with methyl cysteinate



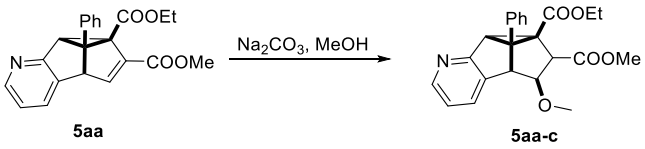

In a Schlenk tube equipped with a PTFE-coated stirring bar, Boc-DL-Cys-OMe (47.1 mg, 0.20 mmol, 1.0 eq.), **5aa** (72.3 mg, 0.20 mmol, 1.0 eq.), $Et_3N$ (30.4 mg, 0.3 mmol, 1.5 eq.) was dissolved in EtOH (2 mL), and the solution stirred at room temperature for 10 min. The mixture was concentrated through vacuum evaporation. The residue was purified by flash column chromatography on silica (Petroleum ether/ Acetone 5/1, $R_f$ = 0.3), affording **5aa-a** (105.0 mg, 0.176 mmol, 88%) as a yellow oil.[18]

### 6.1.7 Michael addition reaction of 5aa with piperidine



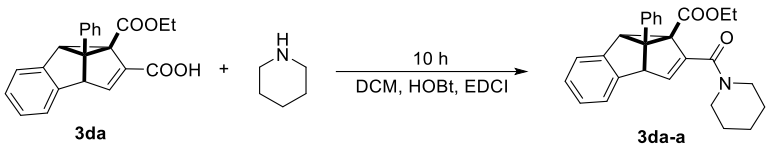

In a Schlenk tube equipped with a PTFE-coated stirring bar, piperidine (34.1 mg, 0.4 mmol, 2 eq.), **5aa** (72.3 mg, 0.20 mmol, 1.0 eq.), $Et_3N$ (30.4 mg, 0.3 mmol, 1.5 eq.) was dissolved in EtOH (2 mL), and the solution was warmed to 60 °C stirred for 12 hours. The mixture was concentrated through vacuum evaporation. The residue was purified by flash column chromatography on silica (Petroleum ether/ethyl acetate 3/1, $R_f$ = 0.3), affording **5aa-b** (85.0 mg, 0.196 mmol, 98%) as a yellow oil.[18]

### 6.1.8 Michael addition reaction of 5aa with methanol




In a Schlenk tube equipped with a PTFE-coated stirring bar, **5aa** (72.3 mg, 0.20 mmol, 1.0 eq.), methanol (1 mL) and $Na_2CO_3$ (0.16 ml, 0.05 M) was added, and the solution was stirred for 24 hours at room temperature. The mixture was concentrated through vacuum evaporation. The residue was purified by flash column chromatography on silica (Petroleum ether/ethyl acetate 3/1, $R_f$ = 0.3), affording **5aa-c** (65.3 mg, 0.166 mmol, 83%) as a white solid.[19]

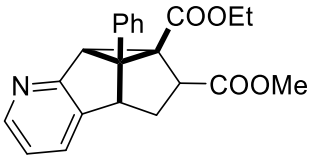
### 6.1.9 The amide formation reaction between compound 3da and piperidine




In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, compound **3da** (69.3 mg, 0.20 mmol, 1.0 eq.), piperidine (34.1 mg, 0.40 mmol, 2.0 eq.) was dissolved in anhydrous $CH_2Cl_2$ (2 ml), and the solution was cooled to 0 °C. HOBt (29.7 mg, 0.22 mmol, 1.1 eq.) and EDCI (42.2 mg, 0.22 mmol, 1.1 eq.) was added, and the reaction was warmed up to room temperature and stirred for 10 hours. The reaction was carefully quenched with aqueous $NaHCO_3$, the aqueous layer was extracted three times with $CH_2Cl_2$ (5 ml each time). The combined organic extracts were dried over $Na_2SO_4$ and the solvent was removed in vacuo. The residue was purified by flash column chromatography on silica (Petroleum ether/ethyl acetate 3/1, $R_f$ = 0.3), affording **3da-a** (80.7 mg, 0.18 mmol, 90%) as a yellow oil.[20]

## 6.2 Characterization data for products

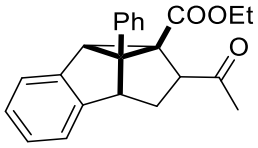
2a-ethyl 2-methyl 2a[1]-phenyl-1,2a[1],2b,6b-tetrahydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2*H*)-dicarboxylate (**5aa-d**)




**Physical state:** White oil
**Yield:** 100%
**$R_f$** = 0.3 in Petroleum ether/ethyl acetate (6:1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.32 – 8.25 (m, 1H), 7.30 – 7.18 (m, 66H), 7.03 – 6.97 (m, 1H), 4.20 (d, *J* = 9.9 Hz, 1H), 4.01 (s, 1H), 3.83 (q, *J* = 7.1 Hz, 2H), 3.74 (d, *J* = 5.4 Hz, 1H), 3.26 (s, 3H), 2.98 – 2.87 (m, 1H), 2.49 (d, *J* = 12.5 Hz, 1H), 0.77 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 173.1, 168.9, 160.7, 148.3, 140.5, 136.3, 131.4, 128.4, 128.1, 127.6, 122.1, 63.7, 61.1, 56.0, 51.9, 50.8, 45.2, 45.0, 44.7, 13.7.
**HRMS (ESI):** calcd for $C_{22}H_{22}NO_4$ $[M+H]^+$ *m/z* 364.15433, found 364.15377.

ethyl 2-acetyl-2a[1]-phenyl-1,2a[1],2b,6b-tetrahydrobenzo[*a*]cyclopropa[*cd*]pentalene-2a(2*H*)-carboxylate (**3fa-a**)



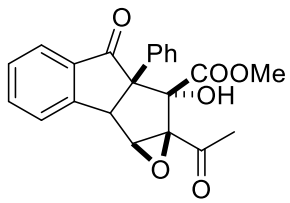

**Physical state:** White oil
**Yield:** 100%
**$R_f$** = 0.5 in Petroleum ether/ethyl acetate (6:1).
**$^1$H NMR** (400 MHz, Chloroform-d) δ 7.29 – 7.16 (m, 6H), 7.13 – 7.06 (m, 2H), 6.98 – 6.93

(m, 1H), 3.94 – 3.78 (m, 4H), 3.71 (d, $J$ = 5.5 Hz, 1H), 2.84 – 2.74 (m, 1H), 2.59 (d, $J$ = 12.3 Hz, 1H), 1.82 (s, 3H), 0.79 (t, $J$ = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-d) δ 206.3, 169.8, 148.1, 139.3, 136.9, 128.3, 128.2, 127.7, 127.4, 127.1, 125.0, 123.7, 64.9, 61.1, 57.8, 53.1, 50.7, 44.6, 44.6, 27.1, 13.8.

**HRMS (ESI):** calcd for $C_{23}H_{23}O_3$ $[M+H]^+$ *m/z* 347.16417, found 347.16351.

methyl (7*S*)-7a-acetyl-7-hydroxy-6-oxo-6a-phenyl-1a,1b,6,6a,7,7a-hexahydrobenzo[5,6]pentaleno[1,2-*b*]oxirene-7-carboxylate (**3fb-a**)




**Physical state:** White solid

**Yield:** 21%

**Melting point:** 167.6-168.1℃

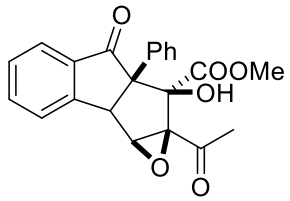
**R$_f$** = 0.5 in Petroleum ether/ethyl acetate (2:1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.96 – 7.88 (m, 2H), 7.83 (d, $J$ = 7.6 Hz, 1H), 7.71 – 7.59 (m, 2H), 7.47 (t, $J$ = 7.4 Hz, 1H), 7.32 (dd, $J$ = 8.5, 6.8 Hz, 2H), 7.26 – 7.20 (m, 1H), 4.87 (s, 1H), 4.47 (s, 1H), 4.45 (s, 1H), 3.31 (s, 3H), 2.12 (s, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 203.6, 199.9, 170.5, 147.6, 138.2, 136.7, 135.3, 129.2, 128.7, 128.0, 127.7, 125.0, 124.9, 84.9, 69.9, 67.6, 63.7, 52.7, 52.1, 25.6.

**HRMS (ESI):** calcd for $C_{23}H_{24}NO_5$ $[M+Na]^+$ *m/z* 401.09956, found 401.09932.

methyl (7*R*)-7a-acetyl-7-hydroxy-6-oxo-6a-phenyl-1a,1b,6,6a,7,7a-hexahydrobenzo[5,6]pentaleno[1,2-*b*]oxirene-7-carboxylate (**3fb-a′**)




**Physical state:** Yellow liquid

**Yield:** 17%

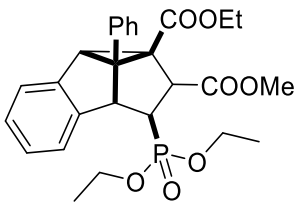
**R$_f$** = 0.4 in Petroleum ether/ethyl acetate (2:1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.82 – 7.76 (m, 3H), 7.75 – 7.69 (m, 1H), 7.65 – 7.61 (m, 1H), 7.48 (t, $J$ = 7.5 Hz, 1H), 7.38 – 7.26 (m, 3H), 4.86 (s, 1H), 4.36 (s, 1H), 3.57 (s, 1H), 3.46 (s, 3H), 2.05 (s, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 203.3, 200.9, 171.7, 148.3, 137.4, 135.8, 135.8, 129.6, 129.2, 128.1, 127.8, 125.5, 124.5, 81.9, 74.3, 69.4, 64.7, 54.1, 52.4, 24.7.

**HRMS (ESI):** calcd for $C_{23}H_{24}NO_5$ $[M+Na]^+$ *m/z* 401.09956, found 401.09785.

2a-ethyl 2-methyl 1-(diethoxyphosphoryl)-2a[1]-phenyl-1,2a[1],2b,6b-tetrahydrobenzo[*a*]cyclopropa[*cd*]pentalene-2,2a(2*H*)-dicarboxylate (**3aa-a**)




**Physical state:** Yellow liquid

**Yield:** 98%

**R*f*** = 0.2 in Petroleum ether/ethyl acetate (3:2).

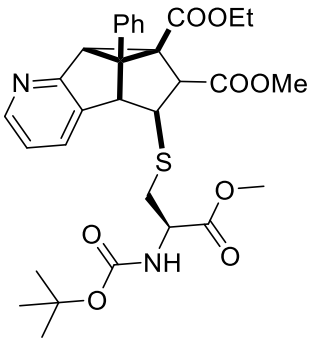
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.59 – 7.53 (m, 2H), 7.31 – 7.27 (m, 3H), 7.25 – 7.10 (m, 4H), 4.52 (d, *J* = 23.1 Hz, 1H), 4.29 (d, *J* = 10.3 Hz, 1H), 4.21 – 3.96 (m, 6H), 3.79 (s, 1H), 3.33 (s, 3H), 3.04 (d, *J* = 18.0 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 172.2 (d, *J* = 16.2 Hz), 168.7, 148.2(d, *J* = 17.0 Hz), 139.3, 135.8, 129.2, 127.9, 127.7, 127.3, 127.2, 124.9, 123.2, 63.6, 62.5 (d, *J* = 6.4 Hz), 61.8 (d, *J* = 7.4 Hz), 61.1, 57.8 (d, *J* = 1.7 Hz), 53.7 (d, *J* = 138.7 Hz),52.1, 52.1, 46.8 (d, *J* = 2.3 Hz), 45.4, 16.4 (d, *J* = 5.6 Hz), 16.2 (d, *J* = 6.2 Hz), 13.9.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 28.08.

**HRMS (ESI):** calcd for $C_{27}H_{32}O_7P$ $[M+H]^+$ *m/z* 499.18802, found 499.18624.

2a-ethyl 2-methyl 1-(((R)-2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)thio)-2a[1]-phenyl-1,2a[1],2b,6b-tetrahydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2*H*)-dicarboxylate (**5aa-a**)




**Physical state:** Yellow liquid

**Yield:** 88%

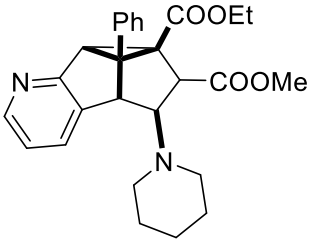
**R*f*** = 0.3 in Petroleum ether/ethyl acetate (3:1).

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 8.45 – 8.32 (m, 1H), 7.62 – 7.54 (m, 2H), 7.51 – 7.38 (m, 1H), 7.35 – 7.27 (m, 3H), 7.13 – 7.05 (m, 1H), 5.56 – 5.26 (m, 1H), 4.73 – 4.60 (m, 1H), 4.20 (d, *J* = 11.7 Hz, 1H), 4.00 – 3.89 (m, 3H), 3.86 – 3.72 (m, 5H), 3.35 (s, 3H), 3.17 – 3.05 (m, 2H), 1.45 (d, *J* = 9.2 Hz, 9H), 0.85 (q, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 171.3, 171.2, 171.2, 168.5, 168.5, 160.4, 160.3, 155.1, 148.9, 148.9, 138.8, 138.7, 135.6, 131.8, 131.7, 129.6, 128.3, 127.7, 127.7, 122.3, 122.2, 80.4, 80.2, 62.9, 62.9, 61.3, 61.2, 60.9, 60.6, 60.5, 53.4, 53.1, 52.9, 52.8, 52.7, 52.1, 52.1, 50.8, 50.7, 45.1, 45.0, 34.7, 34.5, 28.3, 13.7, 13.6.

**HRMS (ESI):** calcd for $C_{27}H_{27}N_2O_8S$ [M-*t*Bu]$^+$ *m/z* 541.16391, found 541.16396.

2a-ethyl 2-methyl 2a$^1$-phenyl-1-(piperidin-1-yl)-1,2a$^1$,2b,6b-tetrahydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2*H*)-dicarboxylate (**5aa-b**)




**Physical state:** Yellow liquid

**Yield:** 98%

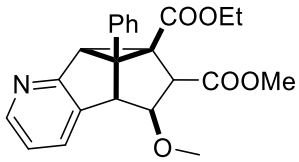
**R$_f$** = 0.3 in Petroleum ether/ethyl acetate (3:1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.38 – 8.29 (m, 1H), 7.52 – 7.42 (m, 2H), 7.38 – 7.24 (m, 3H), 7.28 – 7.20 (m, 1H), 7.09 – 7.00 (m, 1H), 4.39 (d, *J* = 1.8 Hz, 44H), 4.02 – 3.83 (m, 4H), 3.27 (d, *J* = 20.5 Hz, 4H), 2.58 (s, 4H), 1.72 – 1.56 (m, 4H), 1.54 – 1.43 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 172.3, 169.4, 161.5, 148.5, 138.8, 136.5, 131.9, 129.5, 128.1, 127.4, 121.8, 83.9, 61.9, 61.0, 57.0, 52.0, 51.6, 49.9, 49.5, 45.9, 26.0, 24.4, 13.7.

**HRMS (ESI):** calcd for $C_{27}H_{31}N_2O_4$ [M+H]$^+$ *m/z* 447.22783, found 447.22564.

2a-ethyl 2-methyl 1-methoxy-2a$^1$-phenyl-1,2a$^1$,2b,6b-tetrahydrocyclopropa[3,4]pentaleno[2,1-*b*]pyridine-2,2a(2*H*)-dicarboxylate (**5aa-c**)




**Physical state:** White solid

**Yield:** 83%

**Melting point:** 149.7-150.2℃

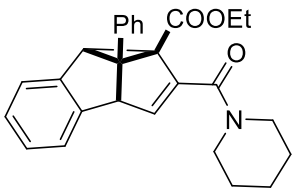
**R$_f$** = 0.3 in Petroleum ether/ethyl acetate (3:1).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.42 – 8.36 (m, 1H), 7.55 – 7.48 (m, 2H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.34 – 7.26 (m, 3H), 7.11 – 7.04 (m, 1H), 4.33 (d, *J* = 1.9 Hz, 1H), 4.25 (s, 1H), 4.10 (s, 1H), 3.97 – 3.84 (m, 3H), 3.53 (s, 3H), 3.32 (s, 3H), 0.83 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 171.1, 168.8, 161.3, 148.8, 136.2, 135.8, 132.2, 129.3, 128.2, 127.5, 121.9, 95.8, 63.1, 61.1, 59.7, 56.3, 51.6, 51.5, 50.1, 44.7, 13.6.

**HRMS (ESI):** calcd for $C_{23}H_{24}NO_5$ [M+H]$^+$ *m/z* 394.1649, found 394.16448.

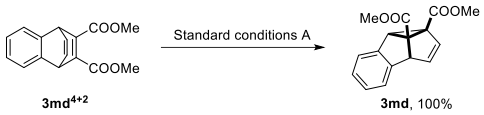
ethyl 2a$^1$-phenyl-2-(piperidine-1-carbonyl)-2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2a(2a$^1$*H*)-carboxylate (**3da-a**)




**Physical state:** Yellow liquid
**Yield:** 90%
**$R_f$** = 0.3 in Petroleum ether/ethyl acetate (3:1).
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.55 – 7.48 (m, 1H), 7.26 (m, 4H), 7.27 – 7.13 (m, 3H), 7.14 – 7.07 (m, 1H), 6.08 – 6.02 (m, 1H), 4.56 (s, 1H), 4.25 (d, *J* = 2.5 Hz, 1H), 4.08 – 3.89 (m, 2H), 3.45 (t, *J* = 5.5 Hz, 2H), 3.29 – 3.00 (m, 2H), 1.65 – 1.21 (m, 6H), 0.99 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 167.5, 165.7, 147.4, 137.9, 136.6, 135.6, 129.6, 128.3, 127.8, 127.7, 127.1, 127.0, 125.9, 121.8, 70.9, 61.0, 61.0, 58.9, 46.8, 46.8, 42.8, 26.2, 25.4, 24.6, 14.0.
**HRMS (ESI):** calcd for $C_{27}H_{28}NO_3$ $[M+H]^+$ *m/z* 414.2064, found 414.2055.

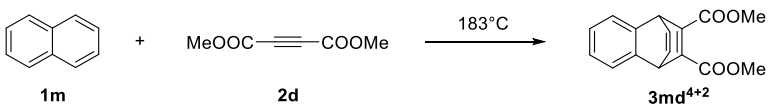
## 7. Preliminary mechanistic studies

### 7.1 Transformation of the [4+2] cycloaddition compound under standard conditions




The synthesis of 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (**3md$^{4+2}$**) was performed under thermochemical conditions, according to the literature,[21] with a yield of 15.4%. The compound's photochemical transformation was carried out following the photoreaction conditions used for naphthalene derivatives (65 mg), resulting in nearly quantitative conversion to the benzo semibullvalene derivative **3md**. (PE/EA 8/1, $R_f$ = 0.6, 65 mg, 100%). **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.44 – 7.37 (m, 1H), 7.22 – 7.10 (m, 3H), 5.81 (dd, *J* = 5.3, 2.5 Hz, 1H), 5.35 (d, *J* = 5.3 Hz, 1H), 4.56 – 4.41 (m, 2H), 3.82 (s, 3H), 3.70 (s, 3H). **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 169.0, 168.7, 148.6, 137.4, 135.0, 127.1, 126.8, 125.9, 121.6, 119.4, 67.0, 58.3, 56.6, 52.7, 52.3, 49.3.
**HRMS (ESI):** calcd for $C_{16}H_{15}O_4$ $[M+H]^+$ *m/z* 271.09469, found 271.09571.

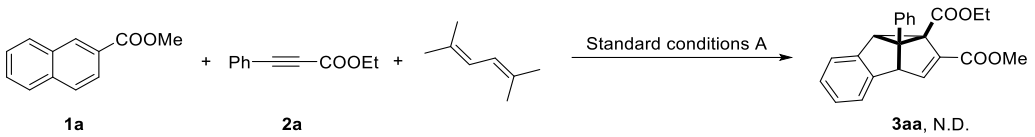
Synthesis of 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate:




Naphthalene **1m** (10 g, 78 mmol, 2 eq.), dimethyl butynedioate **2d** (4.8 mL, 39 mmol, 1 eq.) was added to a Schlenk tube (150 mL) containing a stirrer and heated to 183 °C with stirring for 48 hours. The residue was purified by flash column chromatography on silica (PE/EA), affording

benzobarrelene derivatives **3md**$^{4+2}$ 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (1.62 g, 5.99 mmol, 15.4 %) as a yellow oil.

## 7.2 Control experiment with triplet quencher




An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the **1a** (0.2 mmol), **2a** (0.4 mmol) and photosensitizer (2 mol%). The Schlenk tube was then connected to a vacuum line where it was evacuated and back-filled with argon for 3 times. Then, ultra-dry solvent (MeCN : 1,4-dioxane = 1:9, 2 mL) and 2,5-dimethylhexa-2,4-diene (0.2 mmol) were added to the reaction in sequence under argon flow. Finally, the reaction mixture in sealed tube was placed at a distance of 2 ~ 3 cm from a 30 W blue LED and stirred at room temperature for 48 h. Then, the mixture was concentrated in vacuo. The yield of the product was determined by $^{1}$H-NMR spectroscopy using 1,3,5-Trimethoxybenzene (0.2 mmol) as internal standard. The model condition was significantly inhibited in the presence of 1.0 equivalent of 2,5-dimethylhexa-2,4-diene.[22]

## 7.3 Stern-Volmer quenching studies

Stern-Volmer experiments were conducted on a SFQY-9000 Fluorescence Spectrophotometer. Before each set of experiments, each component was prepared in MeCN : 1,4-dioxane = 1 : 9 and HFIP. The solutions were irradiated at 440 nm and the luminescence was measured at 477 and 465 nm. Linear regression of $I_0/I$ against concentration was performed in Origin.[23]

**Table S15.** luminescence quenching experiment with substrate **1a** as the quenching species (Dioxane and MeCN)

| Species | Solvent | Concentration (M) |
|---|---|---|
| $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ | MeCN : 1,4-dioxane = 1:9 | 0.1 |
| **1a** | MeCN : 1,4-dioxane = 1:9 | Varied |

| **Substrate (M)** | 0 | 0.00005 | 0.0001 | 0.00015 | 0.0002 | 0.00025 |
|---|---|---|---|---|---|---|
| **$I_0/I$ in Solvent** | 1.000 | 1.225 | 1.457 | 1.732 | 2.073 | 2.447 |
| **Substrate (M)** | 0.0003 | 0.00035 | 0.0004 | 0.00045 | 0.0005 | |
| **$I_0/I$ in Solvent** | 2.700 | 3.089 | 3.486 | 3.946 | 4.370 | |

**Table S2.** Luminescence quenching experiment with substrate **2a** as the quenching species (Dioxane and MeCN)

| **Species** | **Solvent** | **Concentration (M)** |
|---|---|---|
| $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ | 1,4-dioxane : MeCN = 9 : 1 | 0.1 |
| **2a** | 1,4-dioxane : MeCN = 9 : 1 | Varied |

| **Substrate (M)** | 0 | 0.0001 | 0.0002 | 0.0003 | 0.0004 | 0.0005 | 0.0006 |
|---|---|---|---|---|---|---|---|
| **$I_0$/I in Solvent** | 1 | 1.021 | 1.021 | 1.025 | 1.035 | 1.034 | 1.041 |

**Table S3.** Luminescence quenching experiment with substrate **4a** as the quenching species (HFIP)

| **Species** | **Solvent** | **Concentration (M)** |
|---|---|---|
| $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ | HFIP | 0.1 |
| **4a** | HFIP | Varied |

| **Substrate (M)** | 0 | 0.00025 | 0.0005 | 0.00075 | 0.00010 | 0.000125 | 0.00015 |
|---|---|---|---|---|---|---|---|
| **$I_0$/I in Solvent** | 1 | 1.156 | 1.258 | 1.402 | 1.465 | 1.645 | 1.799 |

**Table S4.** Luminescence quenching experiment with substrate **2a** as the quenching species (HFIP)

| **Species** | **Solvent** | **Concentration (M)** |
|---|---|---|
| $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ | HFIP | 0.1 |
| **2a** | HFIP | Varied |

| **Substrate (M)** | 0 | 0.00025 | 0.0005 | 0.00075 | 0.00010 | 0.000125 | 0.00015 |
|---|---|---|---|---|---|---|---|
| **$I_0$/I in Solvent** | 1 | 1.020 | 1.029 | 1.042 | 1.067 | 1.070 | 1.082 |

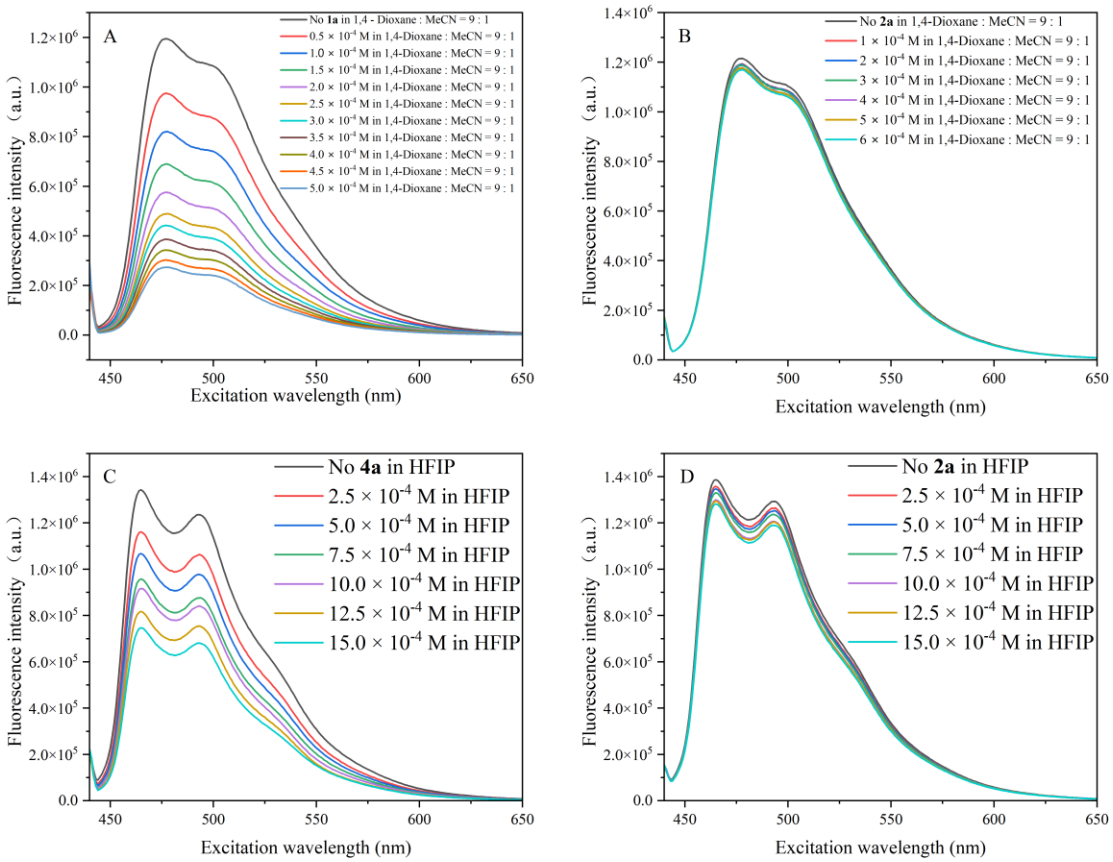



**Figure S7.** Stern-Volmer quenching curves. A: Quenching curves of PC by substrate **1a** under naphthalene ring conditions; B: Quenching curves of PC by substrate **2a** under naphthalene ring conditions; C: Quenching curves of PC by substrate **4a** under azabicyclic conditions; D: Quenching curves of PC by substrate **2a** under azabicyclic conditions

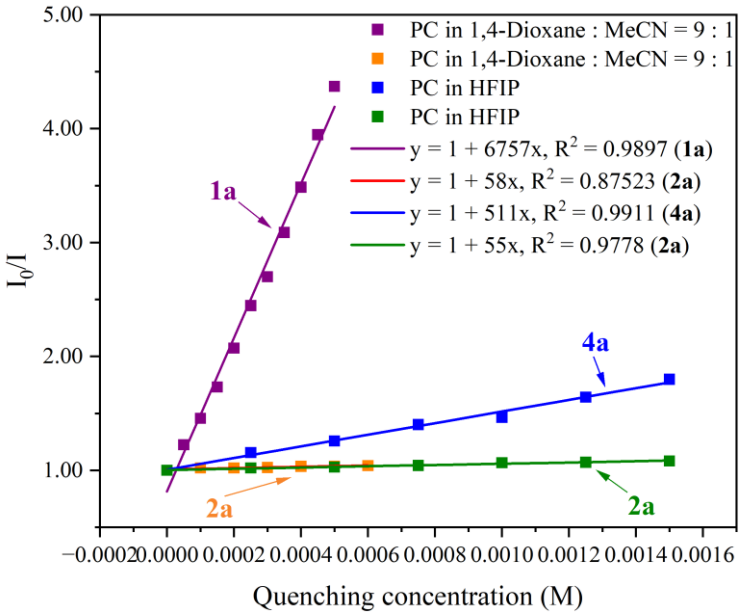



**Figure S8.** Stern-Volmer plots of the photosensitizer

## 7.4 Cyclic voltammetry test

Cyclic voltammetry test was performed in a three-electrode cell under argon at room temperature. All cyclic voltammograms were measured using $Ag/Ag^+$ (0.01 M $AgNO_3$ in $CH_3CN$) reference electrode, a platinum (Pt) wire counter electrode and a glassy carbon working electrode. The conditions of the experiments were as follows: testing compounds are in solution of 0.1 M tetrabutylammonium tetrafluoroborate ($nBu_4NBF_4$) in HFIP at a scan rate of 50 mV/s; Prior to each measurement, solutions were purged with argon (Ar) for 10 minutes to ensure the oxygen-free conditions. Measuring the $Fc/Fc^+$ redox couple afforded $E_{1/2}$ = +0.14 V vs $Ag/Ag^+$ under our experimental conditions. The obtained value was referenced to $Ag/Ag^+$ and converted to SCE by subtracting 0.28 V, providing a value of +0.42 V for the $Fc/Fc^+$ couple. The oxidation half-peak potential of **4a** in HFIP was measured as +0.942 V (vs $Ag/Ag^+$), and calculated to +1.222 V (vs SCE). The reduction half-peak potential of **4a** in HFIP was measured as -1.496 V (vs $Ag/Ag^+$), and calculated to -1.216 V (vs SCE).[24]

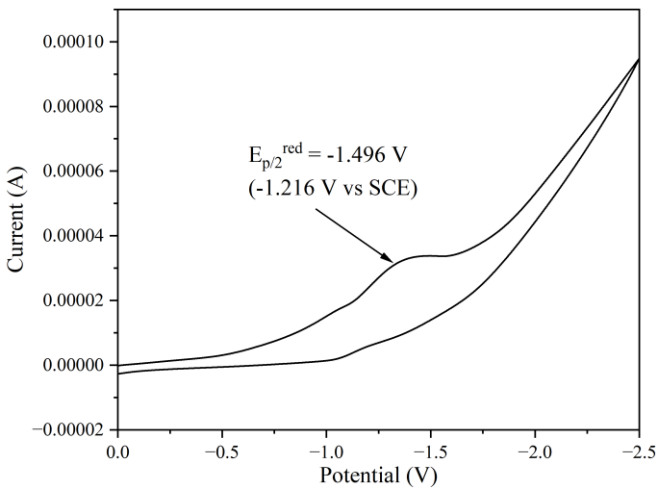



**Figure S9.** Cyclic voltammetry of **4a** (0.005 M) in HFIP (vs $Ag/Ag^+$) with $nBu4NPF_6$ (0.1 M) under argon at a glassy carbon electrode at a scan rate of 50 mV/s.

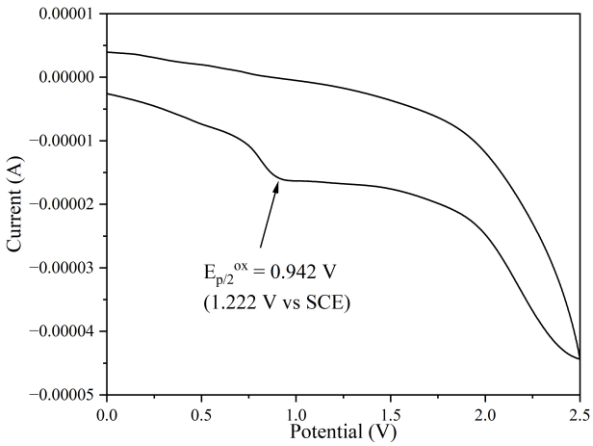


**Figure S10.** Cyclic voltammetry of **4a** (0.005 M) in HFIP (vs $Ag/Ag^+$) with $nBu4NPF_6$ (0.1 M) under argon at a glassy carbon electrode at a scan rate of 50 mV/s.

## 7.5 $^1$H NMR titration experiments

Substrate **4a** was dissolved in 0.5 ml $CDCl_3$, then HFIP (0, 0.1, 0.2, 0.5, 0.8, 1.0, 1.5, 2.0, 3.0, 4.0 equiv.) was added sequentially, and the $^1$H NMR of the obtained hydrogen bonded additives were recorded at 298 K on a Bruker AV II-400 spectrometer, respectively. As outlined in **Figure S11**, all compounds shows an obvious offset shift with the increasing of the concentration of HFIP.[25]

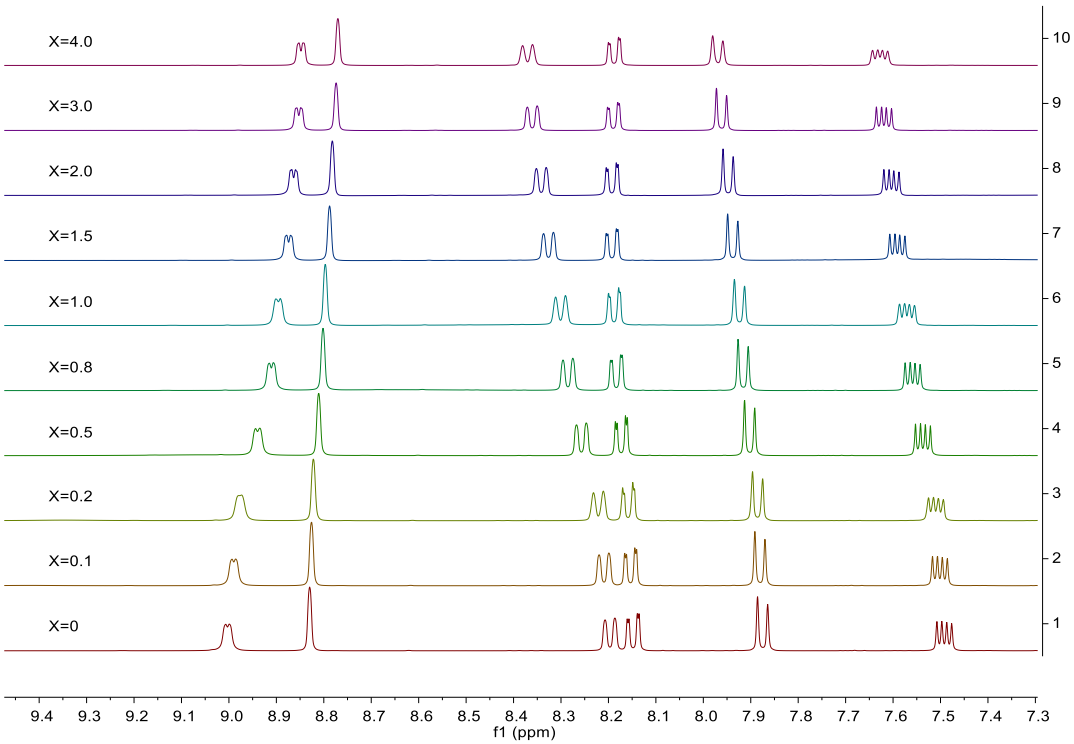



**Figure S1.** $^1$H NMR titration of **4a** with increasing amounts of HFIP

## 7.6 Possible benzosemibullvalene derivatives with different substitution mode

The cycloaddition reaction between bicyclic azaarenes and alkynes, followed by the Zimmerman di-π-methane rearrangement, can theoretically generate more than benzosemibullvalene derivatives with 20 different substitution patterns (Figure S12, **pathways a–p**, corresponding to products **1**–**14** and **1'**–**14'**). The structural diversity arises not only from the various addition modes between bicyclic azaarenes and asymmetric alkynes but also from the multiple regioselectivities inherent in the di-π-methane rearrangement. In addition, the resulting benzosemibullvalene derivatives may undergo further photoisomerization, further increasing the diversity of substitution patterns.

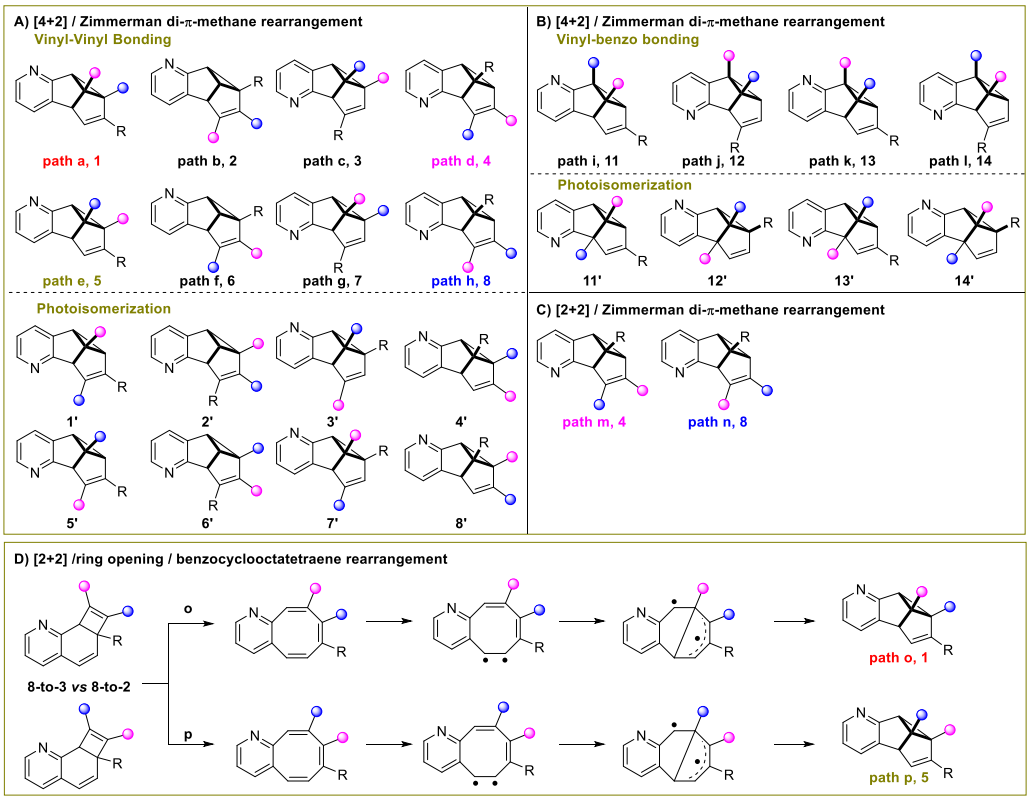


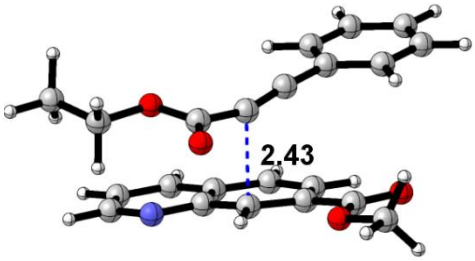

**Figure S12.** The structures of (aza)arenosemibullvalene derivatives with different substitution mode. Pathways **a** and **o**, **d** and **m**, **e** and **p**, as well as **h** and **n**, result in the same substitution pattern, producing the benzosemibullvalene derivatives **1**, **4**, **5**, and **8**, respectively.

## 7.7 Computational studies

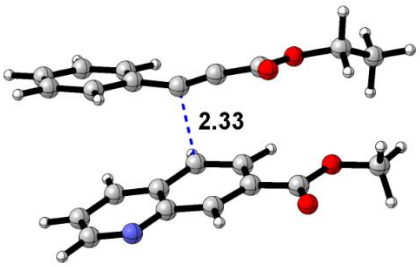
The proposed reaction mechanism is summarized as follows. The calculations and modeling were performed at the (U)ωB97X-D[26]/def2-TZVPP[27] level with the SMD solvation model (HFIP)[28]// (U)B3LYP[29]/6-31G(d)[30] empirical dispersion=GD3, using the Gaussian 16 program[31]. Implicit HFIP solvent was modeled using the parameters "solvent = generic, eps = 16.7, epsinf = 1.625" [32]. A modified version of the Harvey code[33] (sobMECP)[34], interfaced with Gaussian 16,[35] was employed to locate the minimum energy crossing point (MECP). Spin orbit coupling is calculated using Pysoc.[36] Additionally, Multiwfn and VMD are used to calculate spin density and isosurface maps[37] and CLYview20 and chemdraw20 are used for displaying structures.[38]

### 7.7.1 Calculated transition state structures, geometries and free energy barriers

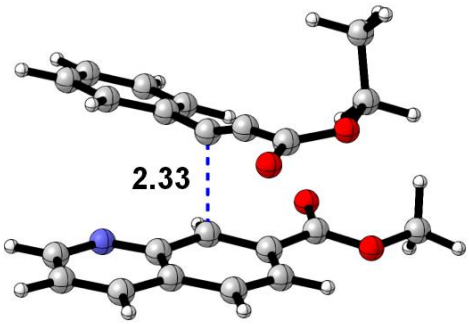
**Table S16.** Calculated structures of TSs and free energy barriers (Interatomic distances are in ångströms)



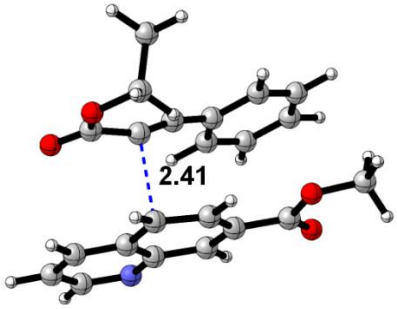

**TS**$^{P}_{8\text{-}2}$, ΔG = 13.1 kcal/mol



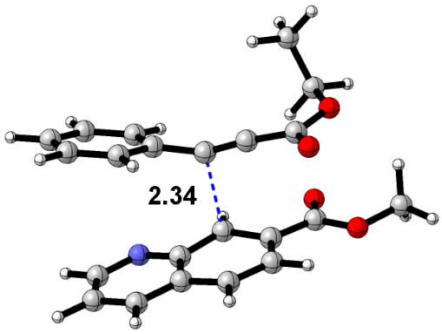

**TS**$^{P}_{5\text{-}3}$, ΔG = 21.0 kcal/mol



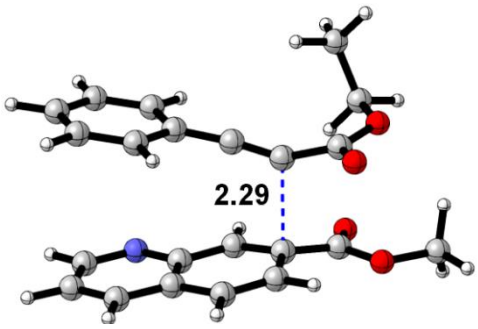

**TS**$^{P}_{8\text{-}3}$, ΔG = 19.6 kcal/mol



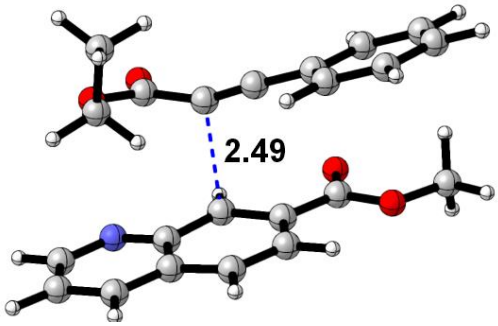

**TS**$^{P}_{5\text{-}2}$, ΔG = 21.0 kcal/mol



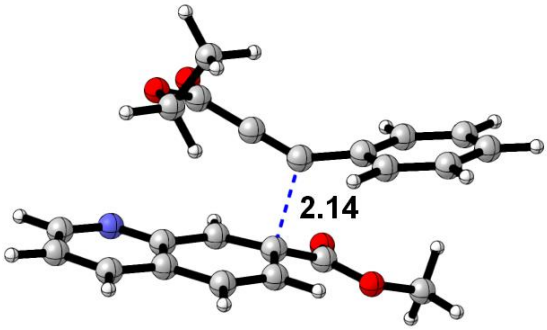

**TS**$^{O}_{8\text{-}3}$, ΔG = 19.4 kcal/mol



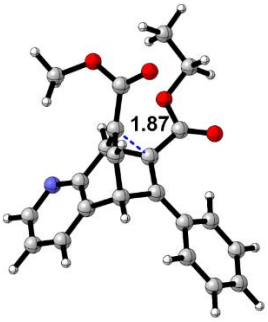

**TS**$^{O}_{7\text{-}2}$, ΔG = 21.9 kcal/mol



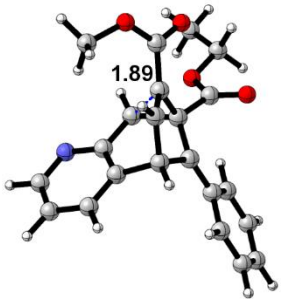

**TS**$^{O}_{8\text{-}2}$, ΔG = = 13.6 kcal/mol



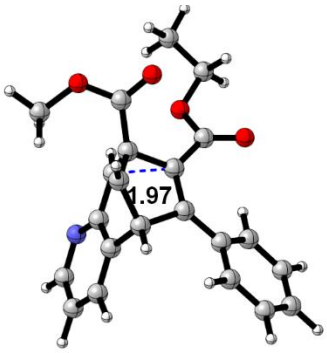

**TS**$^{O}_{7\text{-}3}$, ΔG = 22.0 kcal/mol



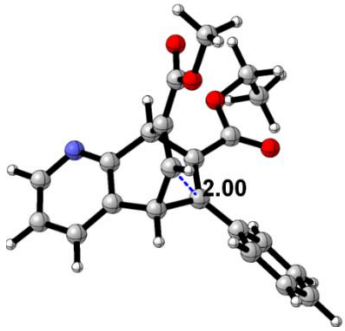

**TS3**, ΔG = 4.7 kcal/mol



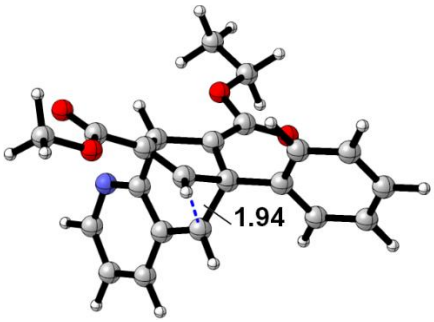

**TS4**, ΔG = 5.9 kcal/mol



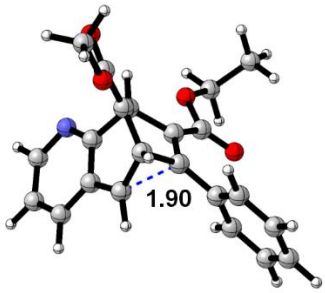

**TS10**, ΔG = 13.1 kcal/mol




**TS7**, ΔG = 9.2 kcal/mol




**TS8**, ΔG = 10.1 kcal/mol




**TS9**, ΔG = 11.3 kcal/mol

### 7.7.2 Calculated spin densities

**(1) Mulliken spin densities (T1) of selected substrates and pyridobarrelene derivative**

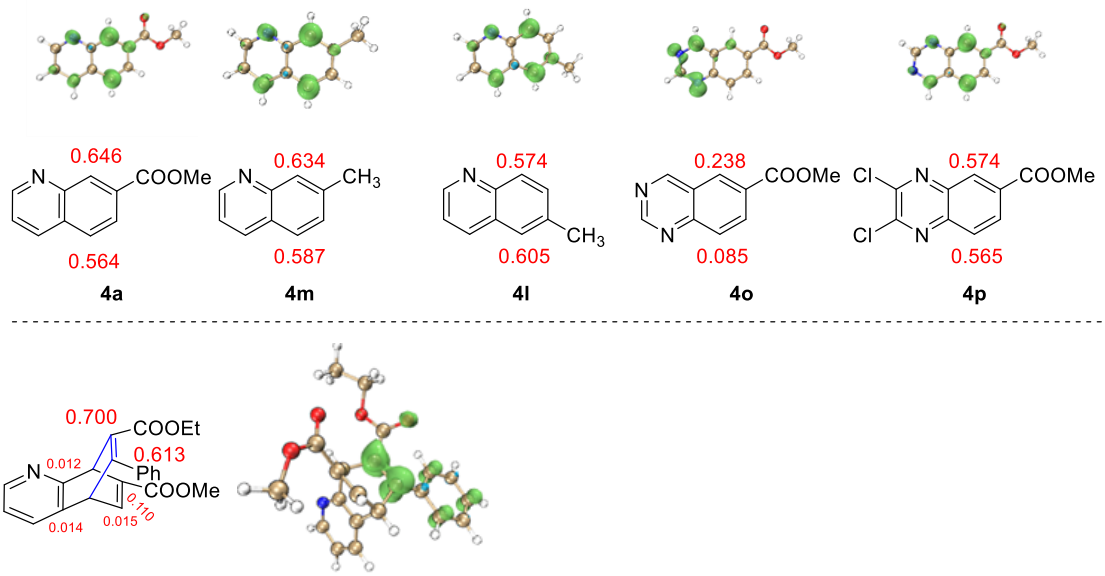



**Figure S13.** Mulliken spin densities (T1) of substrates **4a**, **4m**, **4l**, **4o** and **4p** (up); spin densities of pyridobarrelene derivative (T1, down)

**(2) Mulliken population analysis**

We have employed the Mulliken population analysis in Gaussian to calculate the atomic charges for the compounds **2a** and **2m**.

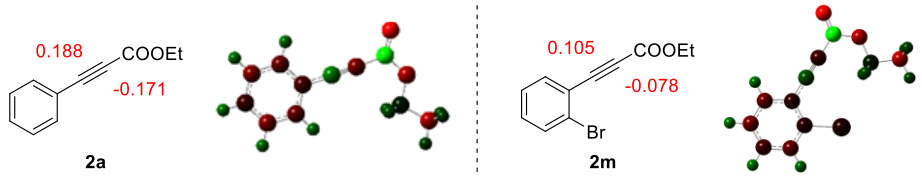



**Figure S14.** Calculated the atomic charges for the compounds **2a** and **2m**

### 7.7.3 Potential energy surfaces of the [4+2] cycloaddition/Zimmerman rearrangement (path a) and the [2+2] cycloaddition/ring opening/ring closure pathway *via* $TS^{O}_{8\text{-}3}$ (TS1)

We conducted a detailed analysis of the following reaction pathways: the **[4+2]** cycloaddition/Zimmerman rearrangement *via* transition state **TS1 ($TS^{P}_{8\text{-}2}$)** corresponding to **path a** (Figure S15); the [2+2] cycloaddition/ring opening/ring closure *via* **TS I ($TS^{O}_{8\text{-}3}$)** corresponding to **path o** (Figure S15); the [4+2] cycloaddition/Zimmerman rearrangement *via* **TS1 ($TS^{P}_{8\text{-}2}$)** for **path b** (Figure S16); the [2+2] cycloaddition/ring opening/ring closure *via* **TS V ($TS^{O}_{7\text{-}2}$)** as another variant of **path o** (Figure S17); the [4+2] cycloaddition/Zimmerman rearrangement via **TS IV ($TS^{P}_{5\text{-}3}$)** corresponding to **paths c** and **d** (Figure S18); and the [2+2] cycloaddition/Zimmerman rearrangement via **TS VII ($TS^{O}_{8\text{-}2}$)** corresponding to **path m** (Figure S19).

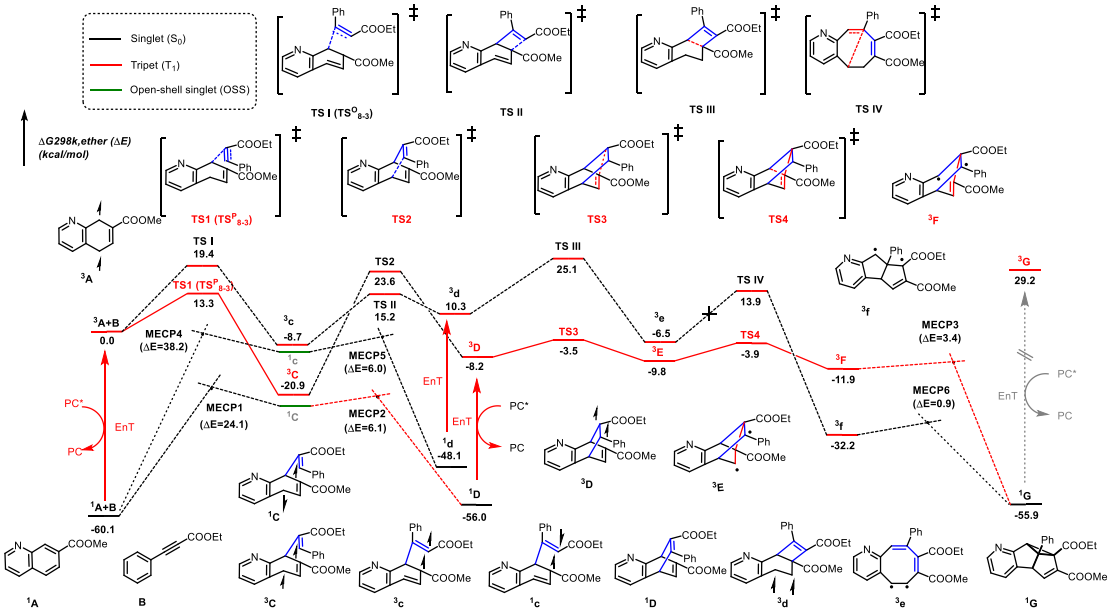



**Figure S2.** Calculated energy diagram. The value is measured in kcal $mol^{-1}$ at ωB97X-D/def2 TZVPP, SMD（HFIP）//(U)B3LYP/6-31G(d) empirical dispersion=GD3. Obtained at a theoretical level, used for [4+2] cycloaddition/Zimmerman rearrangement (path a) and [2+2] cycloaddition/opening/ring closure reaction *via* $TS^{O}_{8\text{-}3}$ (TS1) pathway between methyl 7-quinolinecarboxylate **4a** and ethyl phenylpropanoic acid **2a**

### 7.7.4 Potential energy surfaces of the possible reaction pathways

We examined the reaction pathway involving the transition state $\mathbf{TS}^{P}_{8\text{-}2}$ (**TS1**, ΔG = 13.3 kcal/mol) and the subsequent pathway **b**, leading to the formation of the pyridosemibullvalene derivatives $^{1}$**N** (Figure S16). The calculations showed that the transition state barriers along this pathway are relatively low. However, the energy crossing point (**MECP12**) leading to the final product exhibits a significantly higher barrier (ΔE = 7.7 kcal/mol). We also investigated the transformation of the intermediate $^{1}$**D** into the cage-like compound $^{1}$**O**. The results indicated that the energy crossing point (**MECP13**, ΔE = 14.2 kcal/mol) required for the formation of cage compound $^{1}$**O** has a high energy barrier, suggesting that the formation of this compound on the triplet potential energy surface is unlikely.

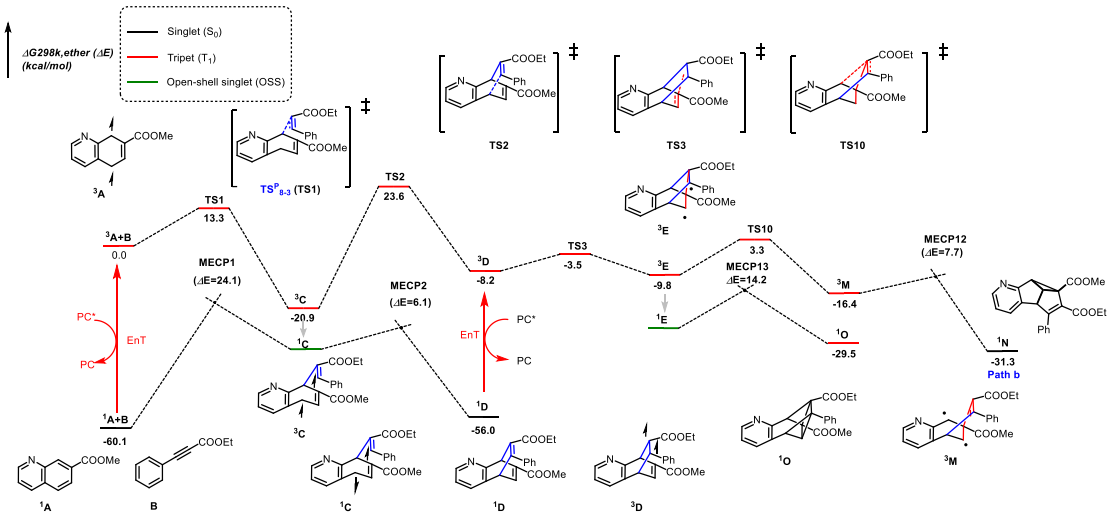



**Figure S16.** Energy profile of benzosemibullvalene derivatives $^{1}$**N** (transition state $\mathbf{TS}^{P}_{8\text{-}3}$ (**TS1**) and reaction pathway **b**) and cage compound $^{1}$**O**. The value is measured in kcal mol$^{-1}$ at ωB97X-D/def2 TZVPP, SMD（HFIP）//(U)B3LYP/6-31G(d) empirical dispersion=GD3

We investigated the reaction pathway involving the *ortho* [2+2] cycloaddition *via* $\mathbf{TS}^{O}_{7\text{-}2}$ (**TS V**) followed by the formation of a pyridocyclooctatetraene derivative intermediate (Figure S17). The calculations revealed that this pathway exhibits a significantly high transition state energy barrier.

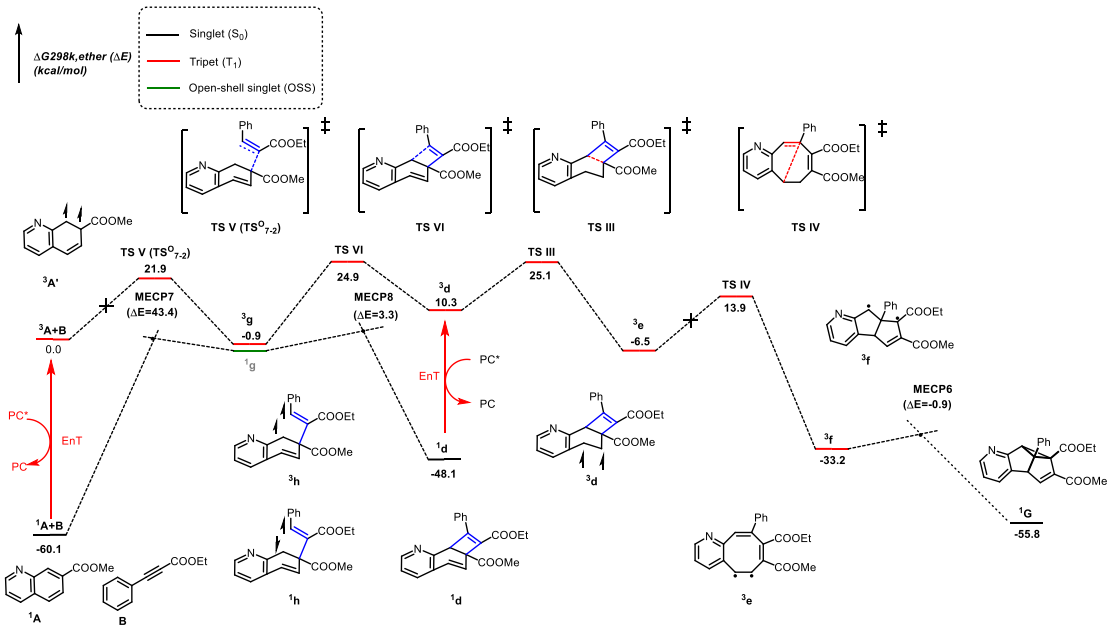



**Figure S17.** Energy profile for the calculated [2+2] cycloaddition/opening/ring closure reaction pathway *via* $\mathbf{TS^{O}_{7\text{-}2}}$ (**TS V**). The value is measured in kcal mol$^{-1}$ at ωB97X-D/def2 TZVPP, SMD（HFIP）//(U)B3LYP/6-31G(d) empirical dispersion=GD3

We examined the reaction pathway (Figure S18) involving the transition state $\mathbf{TS^{P}_{5\text{-}3}}$ (**TS5**, ΔG = 21.0 kcal/mol), which leads to the formation of the *para* [4+2] intermediate **$^1$D**, as well as pathways **c** and **d**, which yields the pyridosemibullvalene derivatives **$^1$K** and **$^1$Q**, respectively. The results showed that, in addition to the high energy barrier of **TS5**, the energy barriers **TS7** (0.9 kcal/mol, ΔG = 9.2 kcal/mol), **TS8** (-14.5 kcal/mol, ΔG = 10.1 kcal/mol) and **TS9** (-13.3 kcal/mol, ΔG = 11.3 kcal/mol) required to form the final product also has a relatively high barrier than pathway **a**.

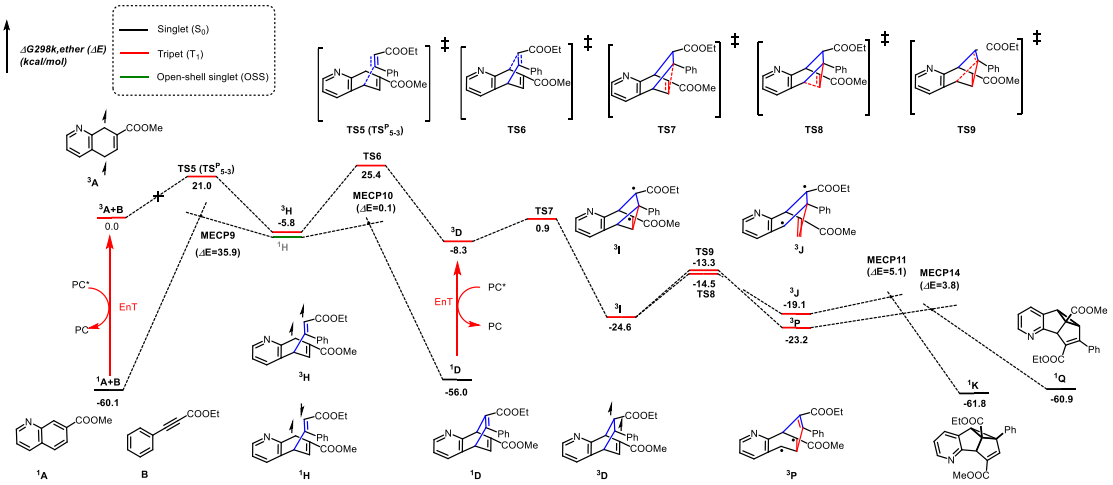



**Figure S18.** Energy profile of benzosemibullvalene derivatives **$^1$K** and **$^1$Q** formed *via* transition state $\mathbf{TS^{P}_{5\text{-}3}}$ **(TS5)** and reaction pathways **c** and **d**. The value is measured in kcal mol$^{-1}$ at ωB97X-D/def2 TZVPP, SMD（HFIP）//(U)B3LYP/6-31G(d) empirical dispersion = GD3

We examined a reaction pathway (Figure S19) in which the intermediate **$^1$i** is formed via transition state **TS VIII** (**TS$^{O}_{8\text{-}2}$**) through a [2+2] cycloaddition, followed by a Zimmerman rearrangement to give the pyridosemibullvalene derivative **$^1$R**. This pathway is characterized by relatively low activation barriers. These results suggest that, depending on the substituent type and position, the reaction may proceed through this route to yield arenosemibullvalene derivatives with alternative substitution patterns.

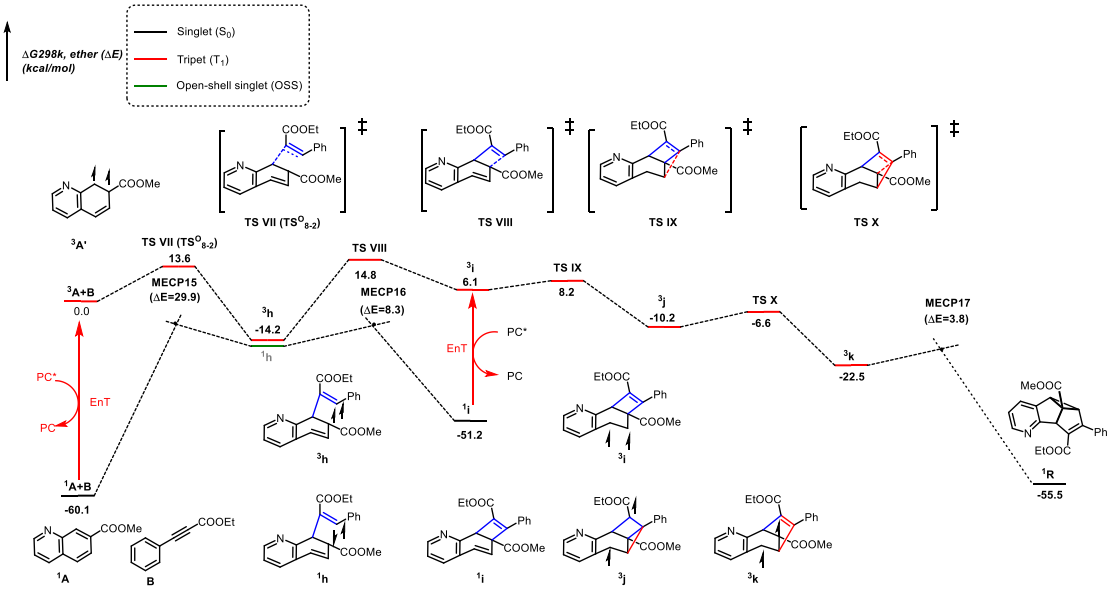



**Figure S19.** Calculated [2+2] cycloaddition and Zimmerman rearrangement energy diagram. The value is measured in kcal mol$^{-1}$ at ωB97X-D/def2 TZVPP, SMD（HFIP）//(U)B3LYP/6-31G(d) empirical dispersion=GD3

## 7.7.5 Summary of energies

| | Thermal Correction to Free Energy [(U)B3LYP/6-31G(d) empirical dispersion=GD3] | E [U)B3LYP/6-31G(d) empirical dispersion=GD3] | E [(U)ωB97X-D/def2-TZVPP, SMD(HFIP)] | G (Thermal Correction to Free Energy+ E [(U)ωB97X-D/def2-TZVPP, SMD(HFIP) |
|---|---|---|---|---|
| $^1$A | 0.141403 | -629.826842 | -629.849588 | -629.708185 |
| B | 0.140673 | -575.597082 | -575.626712 | -575.486039 |
| $^3$A | 0.134869 | -629.728183 | -629.747299 | -629.61243 |
| TS1 | 0.300249 | -1205.350955 | -1205.377567 | -1205.077318 |
| $^3$C | 0.301897 | -1205.394447 | -1205.433759 | -1205.131862 |
| TS2 | 0.302923 | -1205.325121 | -1205.363699 | -1205.060776 |
| $^1$D | 0.310427 | -1205.44474 | -1205.498216 | -1205.187789 |

| | | | | |
|---|---|---|---|---|
| $^3$D | 0.307263 | -1205.370199 | -1205.418862 | -1205.111599 |
| TS3 | 0.306967 | -1205.361358 | -1205.410979 | -1205.104012 |
| $^3$E | 0.30655 | -1205.367188 | -1205.420615 | -1205.114065 |
| TS4 | 0.30509 | -1205.357402 | -1205.409765 | -1205.104675 |
| $^3$F | 0.306103 | -1205.374731 | -1205.423584 | -1205.117481 |
| $^1$G | 0.311013 | -1205.439613 | -1205.498530 | -1205.187517 |
| MECP1 | | -1205.385512 | | |
| MECP2 | | -1205.368290 | | |
| MECP3 | | -1205.369164 | | |

| | Thermal Correction to Free Energy [(U)B3LYP/6-31G(d) empirical dispersion=GD3] | E [(U)B3LYP/6-31G(d) empirical dispersion=GD3] | E [(U)ωB97X-D/def2-TZVPP, SMD(HFIP)] | G (Thermal Correction to Free Energy+ E [(U)ωB97X-D/def2-TZVPP, SMD(HFIP) |
|---|---|---|---|---|
| $^1$A | 0.141403 | -629.826842 | -629.849588 | -629.708185 |
| B | 0.140673 | -575.597082 | -575.626712 | -575.486039 |
| $^3$A’ | 0.134869 | -629.728183 | -629.747299 | -629.61243 |
| TS Ⅰ | 0.301349 | -1205.341629 | -1205.368926 | -1205.067577 |
| $^3$c | 0.304479 | -1205.375506 | -1205.416799 | -1205.112320 |
| TS Ⅱ | 0.303626 | -1205.339049 | -1205.377943 | -1205.074317 |
| $^1$d | 0.310694 | -1205.440870 | -1205.485838 | -1205.175144 |
| $^3$d | 0.304117 | -1205.346408 | -1205.386203 | -1205.082086 |
| TSⅢ | 0.302809 | -1205.323908 | -1205.361295 | -1205.058486 |
| $^3$e | 0.305228 | -1205.375825 | -1205.414066 | -1205.108838 |
| TSⅣ | 0.303261 | -1205.337488 | -1205.379535 | -1205.076274 |
| $^3$f | 0.304883 | -1205.402012 | -1205.454722 | -1205.149839 |
| MECP4 | | -1205.363083 | | |
| MECP5 | | -1205.365914 | | |
| MECP6 | | -1205.400526 | | |

| | Thermal Correction to Free Energy [(U)B3LYP/6-31G(d) | E [(U)B3LYP/6-31G(d) empirical dispersion=GD3] | E [(U)ωB97X-D/def2-TZVPP, SMD(HFIP)] | G (Thermal Correction to Free Energy+ E |
|---|---|---|---|---|

| | empirical dispersion=GD3] | | | [(U)ωB97X-D/def2-TZVPP, SMD(HFIP) |
|---|---|---|---|---|
| $^{3}$H | 0.301831 | -1205.367273 | -1205.409590 | -1205.107759 |
| $^{3}$g | 0.302586 | -1205.362049 | -1205.402512 | -1205.099926 |
| $^{3}$h | 0.303366 | -1205.382621 | -1205.424438 | -1205.121072 |
| $^{3}$i | 0.303037 | -1205.345942 | -1205.391836 | -1205.088799 |
| $^{1}$i | 0.309799 | -1205.439326 | -1205.489828 | -1205.180029 |
| $^{3}$j | 0.305358 | -1205.367486 | -1205.420141 | -1205.114783 |
| $^{3}$k | 0.306597 | -1205.394777 | -1205.440894 | -1205.134297 |
| $^{3}$I | 0.306341 | -1205.389383 | -1205.444003 | -1205.137662 |
| $^{3}$J | 0.305663 | -1205.386546 | -1205.434584 | -1205.128921 |
| $^{1}$K | 0.310306 | -1205.452374 | -1205.507293 | -1205.196987 |
| $^{3}$M | 0.307447 | -1205.364765 | -1205.410967 | -1205.103520 |
| $^{1}$N | 0.312573 | -1205.439534 | -1205.494397 | -1205.181824 |
| $^{1}$O | 0.309716 | -1205.394456 | -1205.455235 | -1205.145519 |
| $^{3}$P | 0.306605 | -1205.397456 | -1205.441997 | -1205.135392 |
| $^{1}$Q | 0.312164 | -1205.458795 | -1205.507677 | -1205.195513 |
| TS5 | 0.300902 | -1205.341416 | -1205.365935 | -1205.065033 |
| TS6 | 0.304582 | -1205.329911 | -1205.362553 | -1205.057971 |
| TS7 | 0.307296 | -1205.356608 | -1205.404254 | -1205.096958 |
| TS8 | 0.304726 | -1205.375908 | -1205.426292 | -1205.121566 |
| TS9 | 0.306688 | -1205.379104 | -1205.426424 | -1205.119736 |
| TS10 | 0.305686 | -1205.351122 | -1205.398969 | -1205.093283 |
| TSV | 0.301965 | -1205.340705 | -1205.365514 | -1205.063549 |
| TSVI | 0.302805 | -1205.332611 | -1205.361522 | -1205.058717 |
| TSVII | 0.299261 | -1205.34199 | -1205.375981 | -1205.076720 |
| TSVIII | 0.301406 | -1205.334233 | -1205.376275 | -1205.074869 |
| TSIX | 0.3033 | -1205.352081 | -1205.388740 | -1205.085440 |
| TSX | 0.304895 | -1205.364361 | -1205.413951 | -1205.109056 |
| MECP7 | | -1205.35473 | | |
| MECP8 | | -1205.356711 | | |
| MECP9 | | -1205.366735 | | |
| MECP10 | | -1205.367055 | | |
| MECP11 | | -1205.368290 | | |

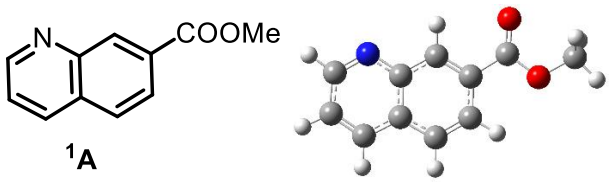
| | | | | |
|---|---|---|---|---|
| **MECP12** | | **-1205.352540** | | |
| **MECP13** | | **-1205.344527** | | |
| **MECP14** | | **-1205.391368** | | |
| **MECP15** | | **-1205.37629** | | |
| **MECP16** | | **-1205.36929** | | |
| **MECP17** | | **-1205.388717** | | |

| | **Thermal Correction to Free Energy [(U)B3LYP/6-31G(d) empirical dispersion=GD3]** | **E [U)B3LYP/6-31G(d) empirical dispersion=GD3]** | **E [(U)ωB97X-D/def2-TZVPP, SMD(HFIP)]** | **G (Thermal Correction to Free Energy+ E [(U)ωB97X-D/def2-TZVPP, SMD(HFIP)** |
|---|---|---|---|---|
| **TS1 ($TS^{p}_{8\text{-}3}$)** | **0.301339** | **-1205.341263** | **-1205.368635** | **-1205.067296** |
| **$TS^{p}_{5\text{-}2}$** | **0.300521** | **-1205.341496** | **-1205.367300** | **-1205.066779** |
| **TS VII ($TS^{o}_{8\text{-}2}$)** | **0.299261** | **-1205.34199** | **-1205.375981** | **-1205.076720** |
| **$TS^{o}_{7\text{-}3}$** | **0.300341** | **-1205.329761** | **-1205.363731** | **-1205.063390** |

## 7.7.6 Cartesian coordinates

**Cartesian coordinates and energies of all optimized structures**

At (U)ωB97X-D/def2-TZVPP, SMD(HFIP)// (U)B3LYP/ 6-31+G(d) empirical dispersion=GD3 level.




$^{1}$A

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SCF Done: E(ωB97XD) = -629.849588a.u.

Thermal Correction to Free Energy = 0.141403 (Hartree/Particle)

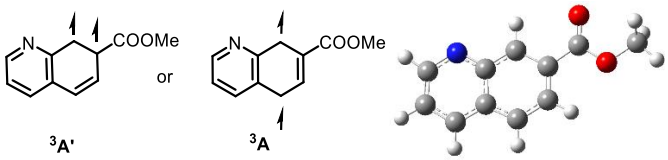
Sum of electronic and thermal Free Energies = -629.708185 a.u.

---

0 1

| | | | |
|---|---|---|---|
| C | -1.37838100 | -0.55898100 | 0.00001400 |
| C | -1.71594100 | 0.83313800 | -0.00003800 |
| C | -3.09307900 | 1.17246600 | -0.00020500 |
| C | -4.03053700 | 0.16753700 | -0.00030700 |
| C | -3.58729700 | -1.18191000 | -0.00024300 |
| N | -2.32232100 | -1.54786800 | -0.00008900 |

| | | | |
|---|---|---|---|
| C | -0.01282500 | -0.93377200 | 0.00017700 |
| C | 0.98069200 | 0.02689600 | 0.00029500 |
| C | 0.64348700 | 1.40902300 | 0.00023400 |
| C | -0.67453900 | 1.79835500 | 0.00007500 |
| C | 2.39752400 | -0.44069500 | 0.00049300 |
| O | 2.74161500 | -1.60597000 | 0.00010000 |
| O | 3.27741600 | 0.58870500 | 0.00006500 |
| C | 4.66189700 | 0.20454000 | -0.00032700 |
| H | -3.38693800 | 2.21953300 | -0.00024900 |
| H | -5.09425100 | 0.38589800 | -0.00043600 |
| H | -4.32220600 | -1.98634400 | -0.00032400 |
| H | 0.24353100 | -1.98736300 | 0.00021900 |
| H | 1.43773200 | 2.14630500 | 0.00032400 |
| H | -0.93621000 | 2.85378400 | 0.00003500 |
| H | 5.22495000 | 1.13852600 | -0.00067500 |
| H | 4.89598000 | -0.38821000 | 0.88874000 |
| H | 4.89539900 | -0.38852100 | -0.88933900 |




SCF Done: E(ωB97XD) = -629.747299 a.u.

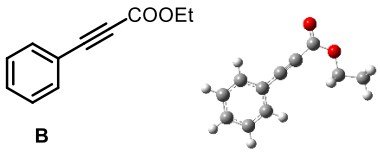
Thermal Correction to Free Energy = 0.134869 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -629.61243 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 1.40662700 | -0.56958100 | 0.00000100 |
| C | 1.74361400 | 0.83813400 | -0.00004400 |
| C | 3.08732200 | 1.18764200 | -0.00022900 |
| C | 4.07524000 | 0.15130900 | -0.00036400 |
| C | 3.65466400 | -1.15605400 | -0.00030600 |
| N | 2.34319700 | -1.54191200 | -0.00012800 |
| C | 0.04322100 | -0.94516200 | 0.00019600 |
| C | -1.02823100 | 0.06251700 | 0.00034900 |
| C | -0.68993200 | 1.39319800 | 0.00028700 |
| C | 0.67348100 | 1.79304000 | 0.00010500 |
| C | -2.41827600 | -0.41881200 | 0.00055400 |
| O | -2.73077900 | -1.59881300 | 0.00012800 |
| O | -3.32936300 | 0.58907300 | 0.00007200 |
| C | -4.69990500 | 0.16377800 | -0.00035500 |

| | | | |
|---|---|---|---|
| H | 3.38271300 | 2.23344400 | -0.00026800 |
| H | 5.13251700 | 0.39591300 | -0.00050700 |
| H | 4.37410500 | -1.97179600 | -0.00040300 |
| H | -0.21997800 | -1.99549500 | 0.00024300 |
| H | -1.46824500 | 2.14834500 | 0.00038600 |
| H | 0.91891200 | 2.85171000 | 0.00006900 |
| H | -5.29104400 | 1.08051000 | -0.00068700 |
| H | -4.91826900 | -0.43580800 | -0.88918500 |
| H | -4.91888700 | -0.43557000 | 0.88848200 |



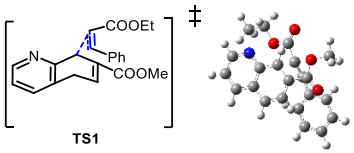

SCF Done: E(ωB97XD) = -575.626712 a.u.

Thermal Correction to Free Energy = 0.140673 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -575.486039 a.u.

0 1

| | | | |
|---|---|---|---|
| C | 3.96215400 | 0.81221800 | -0.00015500 |
| C | 4.34790500 | -0.53116700 | -0.00024300 |
| C | 3.37871500 | -1.53825300 | -0.00014600 |
| C | 2.02674100 | -1.20736300 | 0.00003500 |
| C | 1.62959500 | 0.14415800 | 0.00012000 |
| C | 2.61261400 | 1.15338300 | 0.00002600 |
| C | 0.24812100 | 0.48973400 | 0.00033100 |
| C | -0.92760400 | 0.79542700 | 0.00043400 |
| C | -2.30998700 | 1.22572700 | 0.00009400 |
| O | -2.63402300 | 2.39254500 | -0.00006500 |
| O | -3.25464500 | 0.25431000 | -0.00009700 |
| C | -4.15195800 | -1.94796500 | -0.00017900 |
| C | -2.86891100 | -1.13720700 | 0.00005400 |
| H | 4.71518100 | 1.59509200 | -0.00022600 |
| H | 5.40233900 | -0.79302900 | -0.00038500 |
| H | 3.67812400 | -2.58248400 | -0.00021100 |
| H | 1.26762700 | -1.98356700 | 0.00011400 |
| H | 2.30331900 | 2.19377800 | 0.00009900 |
| H | -3.91958300 | -3.01850400 | -0.00008100 |
| H | -4.75029000 | -1.71937800 | 0.88701900 |
| H | -4.74991700 | -1.71946100 | -0.88764800 |
| H | -2.26069500 | -1.34976000 | -0.88727200 |
| H | -2.26107300 | -1.34967500 | 0.88765900 |




SCF Done: E(ωB97XD) = -1205.377567 a.u.

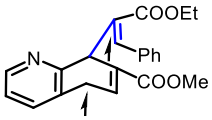
Thermal Correction to Free Energy = 0.300249 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.077318 a.u.

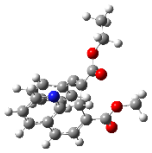
0 3

| | | | |
|---|---|---|---|
| C | -1.54790900 | 0.34221600 | -1.33832300 |
| C | -1.09782800 | 1.69131600 | -1.54093200 |
| C | -2.05939500 | 2.70066300 | -1.56780900 |
| C | -3.41529600 | 2.36347500 | -1.40944600 |
| C | -3.74731300 | 1.02541600 | -1.24338800 |
| N | -2.84771800 | 0.02242900 | -1.20234700 |
| C | -0.57414500 | -0.71017500 | -1.25404200 |
| C | 0.83624400 | -0.42569400 | -1.52397800 |
| C | 1.23777200 | 0.88437600 | -1.73857500 |
| C | 0.31252200 | 1.93108400 | -1.72828500 |
| C | 4.44492100 | 0.79159600 | 1.32661300 |
| C | 4.32618500 | 2.18484100 | 1.41577800 |
| C | 3.06059700 | 2.77743800 | 1.49550900 |
| C | 1.91747000 | 1.98887000 | 1.48776300 |
| C | 2.02732500 | 0.57583800 | 1.40108800 |
| C | 3.31394700 | -0.01197900 | 1.32128100 |
| C | 0.85815300 | -0.19863900 | 1.35156100 |
| C | -0.21702100 | -0.77273400 | 1.15366900 |
| C | 1.85765800 | -1.48078400 | -1.46592300 |
| O | 3.06482800 | -1.29272800 | -1.52991500 |
| O | 1.30776800 | -2.70835200 | -1.30120500 |
| C | 2.23981200 | -3.78694300 | -1.16115400 |
| C | -1.45640700 | -1.48483800 | 1.40397200 |
| O | -1.60473800 | -2.68417800 | 1.27588400 |
| O | -2.42858500 | -0.61548200 | 1.74093700 |
| C | -4.69141300 | -0.04049400 | 2.20354800 |
| C | -3.76512700 | -1.17153500 | 1.80067300 |
| H | -1.75740500 | 3.73417100 | -1.71970000 |
| H | -4.18771500 | 3.12580400 | -1.42739400 |
| H | -4.78823300 | 0.72594500 | -1.13632900 |
| H | -0.92191200 | -1.73432600 | -1.23008000 |
| H | 2.29435300 | 1.08263800 | -1.88463600 |
| H | 0.64964400 | 2.95276700 | -1.88123300 |
| H | 5.42702800 | 0.33423300 | 1.25059800 |
| H | 5.21764200 | 2.80573100 | 1.41961800 |
| H | 2.96902600 | 3.85814700 | 1.56132000 |

| | | | |
|---|---|---|---|
| H | 0.92971600 | 2.43489000 | 1.54219400 |
| H | 3.40058100 | -1.08780700 | 1.22455000 |
| H | 1.63240900 | -4.68490000 | -1.04481900 |
| H | 2.88103900 | -3.86238000 | -2.04444000 |
| H | 2.87164200 | -3.63701700 | -0.28005600 |
| H | -5.72525200 | -0.40070400 | 2.24551700 |
| H | -4.42058400 | 0.35317700 | 3.18863900 |
| H | -4.63414000 | 0.77653400 | 1.47772200 |
| H | -4.00502500 | -1.57184200 | 0.81114900 |
| H | -3.77749000 | -1.99602800 | 2.52059800 |




$^3$C



SCF Done: E(ωB97XD) = -1205.433759 a.u.

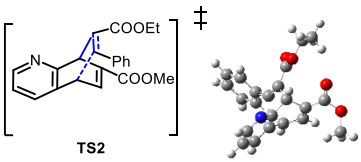
Thermal Correction to Free Energy = 0.301897 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.131862 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 0.98975400 | 1.56559400 | -1.03367600 |
| C | 2.35715000 | 1.19300500 | -1.11651600 |
| C | 3.31692600 | 2.18558700 | -0.83772700 |
| C | 2.89852600 | 3.46625800 | -0.50791700 |
| C | 1.52350300 | 3.72506500 | -0.46813400 |
| N | 0.58939700 | 2.80001600 | -0.71885800 |
| C | -0.11360100 | 0.54345500 | -1.24691400 |
| C | 0.38787700 | -0.80330100 | -1.71064700 |
| C | 1.73911400 | -1.10125400 | -1.76994000 |
| C | 2.71410400 | -0.15118800 | -1.47602500 |
| C | 1.99593400 | -2.98063200 | 2.00965000 |
| C | 2.95380800 | -2.27026100 | 2.74670800 |
| C | 2.80791700 | -0.88868900 | 2.93026500 |
| C | 1.71862800 | -0.21775000 | 2.39361400 |
| C | 0.73929000 | -0.92518700 | 1.64041200 |
| C | 0.89931200 | -2.32995100 | 1.46472500 |
| C | -0.35879200 | -0.25542900 | 1.09886700 |
| C | -0.90152000 | 0.36700100 | 0.07422800 |
| C | -0.57738900 | -1.87848500 | -1.99663800 |
| O | -0.29579100 | -3.05725200 | -2.15019900 |
| O | -1.84633700 | -1.40756300 | -2.05543100 |
| C | -2.86539400 | -2.39039300 | -2.27551300 |
| C | -2.28905400 | 0.91679600 | 0.09879800 |
| O | -2.84089100 | 1.42685600 | -0.85525300 |
| O | -2.87113700 | 0.77056900 | 1.30861500 |

| | | | |
|---|---|---|---|
| C | -4.68006200 | 1.01579900 | 2.83808300 |
| C | -4.22257900 | 1.26823600 | 1.41389100 |
| H | 4.37450400 | 1.93642800 | -0.88502500 |
| H | 3.61282500 | 4.25383200 | -0.28752500 |
| H | 1.15550700 | 4.71910700 | -0.22064000 |
| H | -0.83479600 | 0.95397800 | -1.96485700 |
| H | 2.02449900 | -2.11153100 | -2.04647600 |
| H | 3.76651300 | -0.41723800 | -1.52081200 |
| H | 2.11428700 | -4.04958800 | 1.85437300 |
| H | 3.80852300 | -2.78890100 | 3.17154300 |
| H | 3.55358300 | -0.33493400 | 3.49464400 |
| H | 1.60490700 | 0.85385100 | 2.52500500 |
| H | 0.17400300 | -2.87335800 | 0.86723700 |
| H | -3.80467700 | -1.83660000 | -2.27890900 |
| H | -2.71137000 | -2.89914400 | -3.23163900 |
| H | -2.85841400 | -3.13666500 | -1.47502400 |
| H | -5.70582800 | 1.37647700 | 2.97167900 |
| H | -4.65424100 | -0.05387500 | 3.06949100 |
| H | -4.03246800 | 1.53701100 | 3.55027100 |
| H | -4.22992700 | 2.33355400 | 1.15921600 |
| H | -4.85068200 | 0.75094500 | 0.68003700 |




SCF Done: E(ωB97XD) = -1205.363699 a.u.

Thermal Correction to Free Energy = 0.302923 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.060776 a.u.

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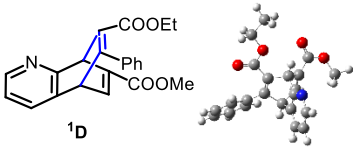
|---|---|---|---|
| C | -1.17155300 | 0.20826100 | -0.21978200 |
| C | -0.50076600 | -1.59875900 | -1.17012400 |
| C | 1.03351300 | -0.47043400 | 0.70546600 |
| C | 0.01001500 | 0.62165700 | 0.35509300 |
| C | 0.85294200 | -1.29110300 | -1.57721000 |
| H | 1.74891100 | -0.13222700 | 1.45178600 |
| H | -1.21980500 | -1.89514400 | -1.92774200 |
| C | -0.65637000 | -2.17228900 | 0.16407300 |
| C | 0.21235600 | -1.65516100 | 1.16314400 |
| C | -0.63131900 | -3.05008100 | 2.75001900 |
| H | -0.58953500 | -3.39596100 | 3.78085700 |
| C | -1.55526500 | -3.60707900 | 1.85729600 |
| H | -2.23940900 | -4.37901200 | 2.19621700 |
| C | -2.46524900 | 0.65251700 | -0.47400900 |

| | | | |
|---|---|---|---|
| C | -3.21977600 | 0.25674200 | -1.62012400 |
| C | -3.10971500 | 1.50539500 | 0.48182400 |
| C | -4.53026000 | 0.67319500 | -1.78457500 |
| H | -2.74360700 | -0.35418100 | -2.37899200 |
| C | -4.41935900 | 1.90938500 | 0.29968800 |
| H | -2.54400100 | 1.82929900 | 1.34921200 |
| C | -5.14549100 | 1.49605200 | -0.82934500 |
| H | -5.08216400 | 0.36659800 | -2.66929100 |
| H | -4.88608400 | 2.55890600 | 1.03546100 |
| H | -6.17244500 | 1.82090600 | -0.96798800 |
| C | 0.46192800 | 2.02872800 | 0.20528700 |
| O | -0.07758100 | 2.85598900 | -0.50900900 |
| O | 1.51963400 | 2.27836600 | 0.99756500 |
| C | 2.16892000 | 3.55751900 | 0.82718700 |
| H | 2.31809600 | 3.73164700 | -0.24287900 |
| H | 1.50546100 | 4.34383500 | 1.20571200 |
| C | 3.48286500 | 3.48421900 | 1.58076100 |
| H | 4.09104400 | 2.66898400 | 1.17999700 |
| H | 4.02887000 | 4.42824100 | 1.47400100 |
| H | 3.30981500 | 3.30261800 | 2.64680700 |
| C | 1.70564500 | -0.81055000 | -0.62930100 |
| C | 3.09407300 | -0.36818800 | -0.87002600 |
| O | 3.59795100 | 0.55890900 | -0.26944000 |
| O | 3.83040100 | -0.98678600 | -1.84065100 |
| C | 3.65267300 | -2.36807500 | -2.17522200 |
| H | 4.65543100 | -2.77997900 | -2.31687500 |
| H | 3.13760400 | -2.91828500 | -1.38284600 |
| H | 3.08973900 | -2.47281100 | -3.10894500 |
| H | 1.12676400 | -1.36876100 | -2.62447700 |
| N | 0.23209000 | -2.07301100 | 2.42470700 |
| C | -1.57705700 | -3.15744500 | 0.54042000 |
| H | -2.27906100 | -3.56246400 | -0.18392700 |




SCF Done: E(ωB97XD) = -1205.498216 a.u.

Thermal Correction to Free Energy = 0.310427 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.187789 a.u.

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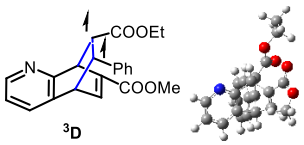
| | | | |
|---|---|---|---|
| C | -1.06580300 | -0.35457200 | -0.21513000 |
| C | -0.29262800 | -1.66519000 | -0.54023200 |
| C | 1.22513300 | 0.15438800 | 0.40496300 |

| | | | |
|---|---|---|---|
| C | -0.24629600 | 0.60510100 | 0.27333900 |
| C | 0.85810500 | -1.29053800 | -1.47535500 |
| H | 1.87269600 | 0.93249100 | 0.79468300 |
| H | -0.94678100 | -2.43594300 | -0.94757400 |
| C | 0.35207400 | -2.08467300 | 0.77516300 |
| C | 1.19545500 | -1.08728500 | 1.28934500 |
| C | 1.74330500 | -2.34711800 | 3.09363900 |
| H | 2.31206400 | -2.42763900 | 4.01770100 |
| C | 0.92808900 | -3.39640100 | 2.67627100 |
| H | 0.85527900 | -4.29994600 | 3.27403500 |
| C | -2.51780800 | -0.33945500 | -0.46473700 |
| C | -3.02098100 | -0.86728500 | -1.66726700 |
| C | -3.42745800 | 0.13467200 | 0.49429000 |
| C | -4.39164600 | -0.89671400 | -1.91600300 |
| H | -2.33141900 | -1.23197100 | -2.42468100 |
| C | -4.79798500 | 0.08583400 | 0.25253500 |
| H | -3.05094900 | 0.54366900 | 1.42332100 |
| C | -5.28554200 | -0.42467200 | -0.95288300 |
| H | -4.76065100 | -1.29058700 | -2.85912300 |
| H | -5.48793200 | 0.45223700 | 1.00764600 |
| H | -6.35552800 | -0.45541400 | -1.14005600 |
| C | -0.61703600 | 2.01468000 | 0.54583000 |
| O | -1.74112700 | 2.48128200 | 0.52461500 |
| O | 0.48294900 | 2.75679600 | 0.79568000 |
| C | 0.28100700 | 4.17637200 | 0.95662100 |
| H | -0.28349300 | 4.55106000 | 0.09646600 |
| H | -0.32654200 | 4.34946200 | 1.85210900 |
| C | 1.65974500 | 4.80112900 | 1.05658300 |
| H | 2.24723000 | 4.56352300 | 0.16428600 |
| H | 1.57455800 | 5.88956900 | 1.14668300 |
| H | 2.19567700 | 4.42025100 | 1.93198600 |
| C | 1.66080700 | -0.33855500 | -0.98187400 |
| C | 2.73936600 | 0.40218500 | -1.68981700 |
| O | 2.85540100 | 1.60078800 | -1.56292000 |
| O | 3.58550400 | -0.25700900 | -2.52308900 |
| C | 3.77348100 | -1.67622900 | -2.46165100 |
| H | 4.81374300 | -1.85154400 | -2.74478200 |
| H | 3.59180100 | -2.07052200 | -1.45814200 |
| H | 3.11815800 | -2.18677000 | -3.17550600 |
| H | 0.94497100 | -1.74577500 | -2.45510900 |
| C | 0.20793100 | -3.26724700 | 1.47857500 |
| N | 1.88935100 | -1.18951800 | 2.41551800 |
| H | -0.43804400 | -4.06493400 | 1.11991200 |

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SCF Done: E(ωB97XD) = -1205.418862 a.u.

Thermal Correction to Free Energy = 0.307263 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.111599 a.u.

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0 3

| | | | |
|---|---|---|---|
| C | 1.12147000 | 0.09247600 | 0.53504100 |
| C | 0.69968300 | -1.29444100 | 1.06093500 |
| C | -1.01851300 | -0.39660100 | -0.67068000 |
| C | 0.00478000 | 0.66369200 | -0.27596600 |
| C | -0.71472200 | -1.16271700 | 1.60266500 |
| H | -1.75667400 | -0.03381800 | -1.38047800 |
| H | 1.38390800 | -1.70999200 | 1.79916200 |
| C | 0.64066000 | -2.13138300 | -0.20863600 |
| C | -0.28079500 | -1.63232200 | -1.14718500 |
| C | 0.24033000 | -3.24531100 | -2.65871300 |
| H | 0.05879500 | -3.67500900 | -3.64175300 |
| C | 1.18813300 | -3.81468200 | -1.80646700 |
| H | 1.74957700 | -4.68816100 | -2.12421300 |
| C | 2.45361900 | 0.55496900 | 0.54792700 |
| C | 3.48495800 | -0.11393400 | 1.28561500 |
| C | 2.85225800 | 1.71137000 | -0.20120200 |
| C | 4.79201900 | 0.33640900 | 1.27110600 |
| H | 3.24398400 | -0.98892700 | 1.87930600 |
| C | 4.16801100 | 2.14213200 | -0.21297100 |
| H | 2.11021200 | 2.26108400 | -0.76238600 |
| C | 5.15299800 | 1.46723300 | 0.52048500 |
| H | 5.54599500 | -0.19314300 | 1.84791700 |
| H | 4.43365200 | 3.01988000 | -0.79608100 |
| H | 6.18151900 | 1.81595300 | 0.51360200 |
| C | -0.39922700 | 2.06343100 | -0.20596500 |
| O | 0.13016500 | 2.90167100 | 0.51528400 |
| O | -1.43034100 | 2.33011800 | -1.03900000 |
| C | -2.08418300 | 3.60338500 | -0.86124800 |
| H | -2.22349100 | 3.77966200 | 0.20962100 |
| H | -1.43235600 | 4.39475500 | -1.25018300 |
| C | -3.40758500 | 3.52259900 | -1.59779700 |
| H | -4.01383900 | 2.71611200 | -1.17585800 |
| H | -3.95177800 | 4.46836200 | -1.49773800 |
| H | -3.24927100 | 3.32482100 | -2.66329500 |
| C | -1.62042600 | -0.71375000 | 0.71285300 |
| C | -3.00720600 | -0.26819300 | 1.02564400 |

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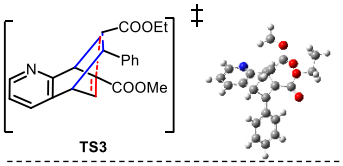
|---|---|---|---|
| O | -3.44059700 | 0.78695400 | 0.61978900 |
| O | -3.79549700 | -1.04639400 | 1.80937100 |
| C | -3.52255600 | -2.43768300 | 2.02881300 |
| H | -4.49616700 | -2.90928500 | 2.17753900 |
| H | -3.01649800 | -2.89482600 | 1.17403900 |
| H | -2.91340800 | -2.57913500 | 2.92736500 |
| H | -0.92819000 | -1.34638300 | 2.65011600 |
| N | -0.49250200 | -2.16011000 | -2.34945400 |
| C | 1.40189300 | -3.24168900 | -0.54823600 |
| H | 2.13811600 | -3.64990100 | 0.13984600 |



TS3

SCF Done: E(ωB97XD) = -1205.410979 a.u.

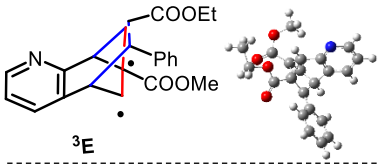
Thermal Correction to Free Energy = 0.306967 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.104012 a.u.

0 3

| | | | |
|---|---|---|---|
| C | -1.17797800 | -0.27753900 | 0.50159000 |
| C | -1.05848400 | 1.02103100 | 1.32571100 |
| C | 0.85812600 | 0.80528100 | -0.49132200 |
| C | 0.13380700 | -0.48905700 | -0.15182300 |
| C | 0.32081900 | 0.87761300 | 1.93104500 |
| H | 1.64188100 | 0.70289300 | -1.23269700 |
| H | -1.84224000 | 1.16115100 | 2.06923800 |
| C | -1.02914900 | 2.14864800 | 0.30568900 |
| C | -0.01571200 | 2.00909500 | -0.65795100 |
| C | -1.66654600 | 4.15412500 | -0.82501600 |
| H | -2.30223000 | 5.02678000 | -0.94100500 |
| C | -2.39931900 | -0.96076200 | 0.25975100 |
| C | -3.58634700 | -0.62711100 | 0.97895300 |
| C | -2.51706700 | -1.97846900 | -0.73392800 |
| C | -4.78994300 | -1.26652600 | 0.72676600 |
| H | -3.55513500 | 0.13580000 | 1.74922700 |
| C | -3.72910400 | -2.60404900 | -0.98128500 |
| H | -1.64482900 | -2.27190100 | -1.30059400 |
| C | -4.87691100 | -2.26047100 | -0.25633500 |
| H | -5.67153100 | -0.99037200 | 1.29957000 |
| H | -3.78207400 | -3.37226900 | -1.74819300 |
| H | -5.82211600 | -2.75846300 | -0.45238200 |
| C | 0.77261800 | -1.78969800 | -0.39563300 |
| O | 0.29944200 | -2.87244400 | -0.10203200 |
| O | 2.00145400 | -1.63302100 | -0.95581700 |

| | | | |
|---|---|---|---|
| C | 2.86392900 | -2.79445900 | -0.92744300 |
| H | 2.83252600 | -3.22194100 | 0.07879400 |
| H | 2.47552300 | -3.53987900 | -1.62957800 |
| C | 4.25408000 | -2.31271700 | -1.29677500 |
| H | 4.59756900 | -1.56394700 | -0.57640400 |
| H | 4.95522400 | -3.15429400 | -1.29016800 |
| H | 4.25910900 | -1.86625700 | -2.29698400 |
| C | 1.25654600 | 0.52786500 | 0.94210800 |
| C | 2.60608500 | -0.02984000 | 1.30639100 |
| O | 2.73683400 | -1.01239100 | 1.99781400 |
| O | 3.70704400 | 0.60499100 | 0.83723700 |
| C | 3.63483800 | 1.91685500 | 0.25662400 |
| H | 2.80985000 | 2.50300300 | 0.67149100 |
| H | 4.58302800 | 2.40097500 | 0.49828400 |
| H | 3.52492200 | 1.85256900 | -0.82962400 |
| H | 0.49427000 | 0.69901800 | 2.98452700 |
| C | -1.87809100 | 3.24410100 | 0.21563400 |
| H | -2.68140100 | 3.38755900 | 0.93419500 |
| C | -0.61906000 | 3.92802700 | -1.71922900 |
| H | -0.43114800 | 4.62548000 | -2.53297300 |
| N | 0.20825800 | 2.87076600 | -1.65049400 |




SCF Done: E(ωB97XD) = -1205.420615 a.u.

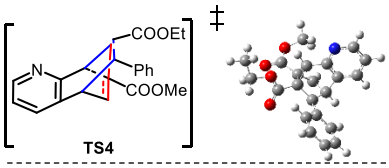
Thermal Correction to Free Energy = 0.30655 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.114065 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 1.05092500 | -0.33693200 | -0.70773400 |
| C | 1.02095700 | 1.05073700 | -1.36839500 |
| C | -0.81591400 | 0.76774000 | 0.58182700 |
| C | -0.31095800 | -0.51083500 | -0.12009000 |
| C | -0.39615400 | 1.14726900 | -1.87213300 |
| H | -1.56420500 | 0.62288900 | 1.35202000 |
| H | 1.77804300 | 1.22293300 | -2.13402500 |
| C | 1.13689700 | 2.04084300 | -0.21022800 |
| C | 0.16347100 | 1.86450800 | 0.79415200 |
| C | 0.98058000 | 3.60412400 | 2.01953700 |
| H | 0.89177100 | 4.21652600 | 2.91463600 |
| C | 1.99602300 | 3.85073200 | 1.09475000 |
| H | 2.70749400 | 4.65286500 | 1.26640600 |
| C | 2.25107800 | -1.04558800 | -0.41502800 |

| | | | |
|---|---|---|---|
| C | 3.47394400 | -0.68803300 | -1.05521400 |
| C | 2.31163000 | -2.10909000 | 0.53075700 |
| C | 4.66096200 | -1.34787000 | -0.77416400 |
| H | 3.48397400 | 0.11164300 | -1.78807700 |
| C | 3.50605900 | -2.75781200 | 0.80790500 |
| H | 1.41424800 | -2.42159900 | 1.04531100 |
| C | 4.69124100 | -2.38932300 | 0.16066700 |
| H | 5.57226400 | -1.05008500 | -1.28642200 |
| H | 3.51506500 | -3.56172700 | 1.53921100 |
| H | 5.62206100 | -2.90423700 | 0.38057800 |
| C | -0.92474100 | -1.83722000 | 0.19617400 |
| O | -0.53333100 | -2.89530400 | -0.24668300 |
| O | -2.00739400 | -1.69567300 | 0.98649600 |
| C | -2.89859700 | -2.83580700 | 1.06156300 |
| H | -2.95708100 | -3.29257900 | 0.07074500 |
| H | -2.46827500 | -3.56643700 | 1.75509300 |
| C | -4.24349800 | -2.31200500 | 1.52630200 |
| H | -4.63666300 | -1.59766400 | 0.79662200 |
| H | -4.95387700 | -3.14037700 | 1.62266200 |
| H | -4.15729700 | -1.81537300 | 2.49859800 |
| C | -1.24758400 | 0.50897200 | -0.86732700 |
| C | -2.69124700 | 0.20909000 | -1.18552100 |
| O | -3.09075800 | -0.87147700 | -1.54976600 |
| O | -3.56389300 | 1.23814700 | -1.08109100 |
| C | -3.14465000 | 2.53583100 | -0.62450200 |
| H | -4.00589600 | 3.18590600 | -0.78476100 |
| H | -2.88794000 | 2.51895700 | 0.43865300 |
| H | -2.28944200 | 2.90979000 | -1.19565300 |
| H | -0.69065600 | 1.32234800 | -2.89796300 |
| H | 2.84711900 | 3.21536500 | -0.79815600 |
| C | 2.07465600 | 3.05198800 | -0.05046400 |
| N | 0.06740300 | 2.62820100 | 1.88512500 |




SCF Done: E(ωB97XD) = -1205.409765 a.u.

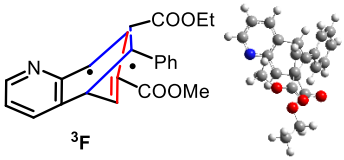
Thermal Correction to Free Energy = 0.30509 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.104675 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 1.00478300 | -0.09851400 | -0.80251500 |
| C | 0.85712800 | 1.33925000 | -1.28164300 |
| C | -0.80089000 | 0.53817300 | 0.78026100 |

| | | | |
|---|---|---|---|
| C | -0.35754500 | -0.44591600 | -0.26516700 |
| C | -0.56803700 | 1.37153300 | -1.78982600 |
| H | -1.59670900 | 0.26592500 | 1.46296000 |
| H | 1.60425900 | 1.68884300 | -1.99773600 |
| C | 0.85890400 | 2.18703600 | -0.00489900 |
| C | -0.03389600 | 1.75266100 | 1.01135500 |
| C | 0.48233300 | 3.54710800 | 2.33516700 |
| H | 0.30476700 | 4.07912000 | 3.26809800 |
| C | 1.41814000 | 4.03218100 | 1.41672700 |
| H | 1.97967600 | 4.93598300 | 1.63281200 |
| C | 2.23570300 | -0.75491700 | -0.53748100 |
| C | 3.44919500 | -0.28183400 | -1.11448400 |
| C | 2.32648100 | -1.89170500 | 0.31567400 |
| C | 4.66008700 | -0.91043200 | -0.86523200 |
| H | 3.42772700 | 0.57948700 | -1.77434700 |
| C | 3.54389400 | -2.50825800 | 0.56271800 |
| H | 1.43725300 | -2.26909200 | 0.80589200 |
| C | 4.72065900 | -2.03010300 | -0.02657100 |
| H | 5.56675800 | -0.52811500 | -1.32692900 |
| H | 3.57998700 | -3.36893500 | 1.22523100 |
| H | 5.67047300 | -2.51988500 | 0.16767700 |
| C | -0.76382700 | -1.90287000 | -0.18696900 |
| O | -0.47780000 | -2.71347600 | -1.03689100 |
| O | -1.47196200 | -2.16433500 | 0.92387300 |
| C | -2.12864900 | -3.45571200 | 0.95135000 |
| H | -2.69265500 | -3.56519900 | 0.02081900 |
| H | -1.36361600 | -4.23858700 | 0.98391300 |
| C | -3.02574600 | -3.46888700 | 2.17305700 |
| H | -3.77267700 | -2.67182200 | 2.10416800 |
| H | -3.54777300 | -4.42934500 | 2.24283400 |
| H | -2.44329600 | -3.32309900 | 3.08876900 |
| C | -1.31845100 | 0.46265300 | -1.03537900 |
| C | -2.77366900 | 0.15822500 | -1.13799800 |
| O | -3.20812500 | -0.97240300 | -1.10082000 |
| O | -3.64203800 | 1.18672400 | -1.30236400 |
| C | -3.31686000 | 2.53537100 | -0.93393800 |
| H | -4.25940400 | 2.98857800 | -0.61953200 |
| H | -2.59902600 | 2.57300800 | -0.11053600 |
| H | -2.92315500 | 3.08965800 | -1.79167000 |
| H | -0.96094100 | 2.15016400 | -2.42899700 |
| H | 2.29277900 | 3.70087100 | -0.54036200 |
| N | -0.24374600 | 2.43890600 | 2.14919200 |
| C | 1.59713000 | 3.34129200 | 0.21449600 |




SCF Done: E(ωB97XD) = -1205.423584 a.u.

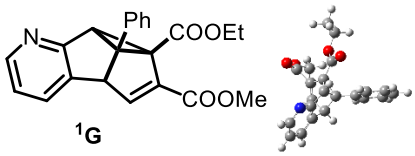
Thermal Correction to Free Energy = 0.306103 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.117481 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 0.96980200 | -0.39154500 | -0.76683100 |
| C | 1.04173700 | 0.99173500 | -1.39032900 |
| C | -0.28676000 | 0.54035400 | 1.10129800 |
| C | -0.40791000 | -0.37453900 | -0.10890500 |
| C | -0.38425300 | 1.19796000 | -1.87729300 |
| H | -0.86636900 | 0.36889800 | 2.00008900 |
| H | 1.80124700 | 1.13294500 | -2.16308900 |
| C | 1.26330100 | 1.95370100 | -0.21764900 |
| C | 0.54491400 | 1.68606900 | 0.99990200 |
| C | 1.42404100 | 3.57018700 | 1.99301900 |
| H | 1.46968100 | 4.20718100 | 2.87541000 |
| C | 2.18773600 | 3.89089700 | 0.85963700 |
| H | 2.82906900 | 4.76682700 | 0.86034800 |
| C | 2.09646600 | -1.19987100 | -0.45440300 |
| C | 3.34163300 | -0.97878100 | -1.11160500 |
| C | 2.06022900 | -2.23338400 | 0.52387200 |
| C | 4.46204800 | -1.74013400 | -0.81476000 |
| H | 3.41754300 | -0.20573300 | -1.86934000 |
| C | 3.18885400 | -2.98527900 | 0.81623900 |
| H | 1.14114600 | -2.43880400 | 1.05546700 |
| C | 4.39843900 | -2.75109200 | 0.15188200 |
| H | 5.39441900 | -1.54727900 | -1.33914100 |
| H | 3.12753600 | -3.76320400 | 1.57267000 |
| H | 5.27729000 | -3.34594400 | 0.38352800 |
| C | -1.10609700 | -1.70836100 | 0.14204600 |
| O | -0.82915800 | -2.74800300 | -0.40811400 |
| O | -2.12451800 | -1.53601200 | 1.00327400 |
| C | -3.09428600 | -2.61261200 | 1.08948300 |
| H | -3.18092100 | -3.07575500 | 0.10429100 |
| H | -2.71325100 | -3.35956400 | 1.79454200 |
| C | -4.40135800 | -1.99280900 | 1.54379800 |
| H | -4.74196700 | -1.26501000 | 0.80140500 |
| H | -5.16563200 | -2.77058000 | 1.64979600 |
| H | -4.28395000 | -1.48887000 | 2.50898700 |
| C | -1.22281600 | 0.44723900 | -1.15638000 |
| C | -2.71152000 | 0.37370700 | -1.25235100 |

| | | | |
|---|---|---|---|
| O | -3.28438000 | -0.66129800 | -1.51126500 |
| O | -3.43695900 | 1.49939300 | -1.05918400 |
| C | -2.84342300 | 2.68251600 | -0.49710700 |
| H | -3.68541200 | 3.29926200 | -0.17858100 |
| H | -2.21051800 | 2.44729900 | 0.36294700 |
| H | -2.25466200 | 3.22485600 | -1.24247500 |
| H | -0.65949600 | 1.93076900 | -2.62783900 |
| N | 0.62330900 | 2.51349700 | 2.08011000 |
| H | 2.65803900 | 3.28343800 | -1.16673200 |
| C | 2.09308400 | 3.06273400 | -0.26368800 |




**1G**

SCF Done: E(ωB97XD) = -1205.498530 a.u.

Thermal Correction to Free Energy = 0.311013 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.187517 a.u.

0 1

| | | | |
|---|---|---|---|
| C | -2.50116600 | 0.03340600 | 0.82110700 |
| C | -2.74201100 | -0.06894200 | -0.56333200 |
| C | -4.00346100 | 0.24621900 | -1.04689100 |
| C | -4.97372700 | 0.61845600 | -0.10877300 |
| C | -4.62743300 | 0.68775000 | 1.24337300 |
| N | -3.40422500 | 0.40690000 | 1.72424200 |
| C | -1.11765400 | -0.40072200 | 1.13291400 |
| C | -0.06031300 | 1.37723300 | -0.56301400 |
| C | -0.84035800 | 0.96473300 | -1.57696500 |
| C | -1.43992100 | -0.40266100 | -1.27769600 |
| C | 0.10823500 | 0.30437600 | 0.45504600 |
| C | -0.53265200 | -0.96689800 | -0.12723200 |
| C | 0.44016000 | 2.76253000 | -0.31207000 |
| O | 0.14863000 | 3.36233900 | 0.69520000 |
| O | 1.21826100 | 3.35720300 | -1.24984800 |
| C | 1.84348200 | 2.57009000 | -2.27466000 |
| C | 1.38642400 | 0.18167100 | 1.21535600 |
| O | 1.56983000 | -0.54389300 | 2.16984700 |
| O | 2.33852500 | 0.97182400 | 0.67294000 |
| C | 4.44599600 | 2.07321000 | 0.65754600 |
| C | 3.60872600 | 1.02471700 | 1.36471400 |
| C | 0.20284900 | -2.24973300 | -0.28644500 |
| C | 0.29687600 | -3.18206700 | 0.75335100 |
| C | 1.01610400 | -4.36487300 | 0.58002300 |
| C | 1.64778100 | -4.63355300 | -0.63520900 |

| | | | |
|---|---|---|---|
| C | 1.56133800 | -3.70827100 | -1.67827900 |
| C | 0.84665300 | -2.52462900 | -1.50305600 |
| H | -4.23774400 | 0.19432600 | -2.10740200 |
| H | -5.98723200 | 0.85249900 | -0.42030800 |
| H | -5.37071100 | 0.98193100 | 1.98170700 |
| H | -0.88616800 | -0.80265500 | 2.11281800 |
| H | -1.19371100 | 1.58869300 | -2.39219300 |
| H | -1.54572000 | -1.06814600 | -2.13832900 |
| H | 2.63957800 | 3.20035000 | -2.67615400 |
| H | 2.26938200 | 1.65268600 | -1.85997100 |
| H | 1.13966000 | 2.32074900 | -3.07482700 |
| H | 5.40986800 | 2.18865000 | 1.16450900 |
| H | 4.63560100 | 1.78426500 | -0.38170600 |
| H | 3.92921500 | 3.03804200 | 0.65947400 |
| H | 3.42277600 | 1.27937100 | 2.41267400 |
| H | 4.06544900 | 0.02993700 | 1.33633800 |
| H | -0.18936100 | -2.97847400 | 1.70128200 |
| H | 1.08029200 | -5.07805100 | 1.39726900 |
| H | 2.20451900 | -5.55701900 | -0.76942100 |
| H | 2.05314500 | -3.90702000 | -2.62689900 |
| H | 0.79320500 | -1.80046500 | -2.31250500 |

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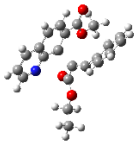

MECP1

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SCF Done: E(B3LYP) = -1205.385512 a.u.

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0 1 or 0 3

| | | | |
|---|---|---|---|
| C | -1.37993400 | 1.60695600 | -0.36192400 |
| C | -0.91690000 | 2.78120500 | 0.29448500 |
| C | -1.87804400 | 3.56775600 | 0.96773400 |
| C | -3.20544900 | 3.17968300 | 0.95788800 |
| C | -3.55125200 | 1.99933700 | 0.27922500 |
| N | -2.66823500 | 1.23148500 | -0.35852800 |
| C | -0.41159200 | 0.67141900 | -1.02438600 |
| C | 0.95481700 | 1.21064300 | -1.18110200 |
| C | 1.35488600 | 2.36903800 | -0.51737700 |
| C | 0.46609600 | 3.13187300 | 0.22614600 |
| C | 3.97147600 | -1.15868500 | 1.35487900 |
| C | 4.04672700 | -0.71728900 | 2.68136800 |
| C | 2.87297100 | -0.40064700 | 3.38230900 |
| C | 1.63390600 | -0.51744200 | 2.77275600 |
| C | 1.54078600 | -0.95257200 | 1.42068000 |
| C | 2.74114900 | -1.28516800 | 0.72686300 |

| | | | |
|---|---|---|---|
| C | 0.32624900 | -1.06094100 | 0.75480300 |
| C | -0.50542800 | -0.73439700 | -0.17364700 |
| C | 1.95627200 | 0.51910600 | -2.00694900 |
| O | 3.08771800 | 0.91940100 | -2.23147300 |
| O | 1.48113900 | -0.65380200 | -2.50746200 |
| C | 2.39408100 | -1.37269500 | -3.34553700 |
| C | -1.64457300 | -1.57842000 | -0.66038300 |
| O | -1.96437000 | -1.67088900 | -1.82640900 |
| O | -2.25401900 | -2.22361400 | 0.34998500 |
| C | -4.12137200 | -3.39150700 | 1.25808900 |
| C | -3.39157300 | -3.03586500 | -0.02332100 |
| H | -1.56137800 | 4.46992200 | 1.48593900 |
| H | -3.96824700 | 3.76424200 | 1.46321900 |
| H | -4.58505400 | 1.65880300 | 0.26083500 |
| H | -0.80986700 | 0.30250800 | -1.97709300 |
| H | 2.38954900 | 2.67859400 | -0.62456300 |
| H | 0.80290600 | 4.03828300 | 0.72207700 |
| H | 4.87934700 | -1.39808600 | 0.80826700 |
| H | 5.01265600 | -0.62227300 | 3.16875300 |
| H | 2.93557000 | -0.05944900 | 4.41221900 |
| H | 0.72345100 | -0.27075500 | 3.30959700 |
| H | 2.66894800 | -1.62646500 | -0.29966300 |
| H | 1.85933600 | -2.27092300 | -3.65613400 |
| H | 2.67859700 | -0.77120400 | -4.21381600 |
| H | 3.30214500 | -1.63552700 | -2.79279600 |
| H | -4.99414900 | -4.01330500 | 1.03129300 |
| H | -3.46679200 | -3.94503900 | 1.93890400 |
| H | -4.46275600 | -2.48545500 | 1.76869100 |
| H | -4.01983300 | -2.46679700 | -0.71523000 |
| H | -3.03032000 | -3.92457700 | -0.55352600 |

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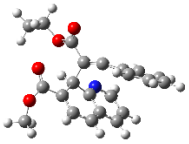

MECP2

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SCF Done: E(B3LYP) = 1205.368290 a.u.

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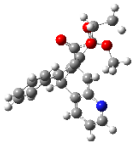
0 1 or 0 3

| | | | |
|---|---|---|---|
| C | 0.72276000 | -1.15379000 | -0.73069500 |
| C | 1.06603700 | 2.44118700 | -0.16989400 |
| C | -0.79621400 | 0.39275800 | 0.58619000 |
| C | -0.45595800 | -0.95264400 | -0.23481100 |
| C | -0.18054700 | 2.38209500 | -0.78407300 |
| H | -1.64460000 | 0.09732600 | 1.20462100 |

| | | | |
|---|---|---|---|
| H | 1.82294400 | 3.13017100 | -0.53493800 |
| C | 1.34254900 | 1.67221700 | 1.00830200 |
| C | 0.38142900 | 0.72858300 | 1.46103200 |
| C | 1.62436500 | 0.21941200 | 3.31849000 |
| H | 1.69417000 | -0.35663400 | 4.23914300 |
| C | 2.65865600 | 1.08574800 | 2.94237600 |
| H | 3.54721500 | 1.17850700 | 3.55963700 |
| C | 2.07306400 | -1.11071300 | -1.00565200 |
| C | 2.56436100 | -0.80406700 | -2.31024900 |
| C | 3.01505800 | -1.38881700 | 0.03239500 |
| C | 3.92811600 | -0.77259100 | -2.54868100 |
| H | 1.85223700 | -0.60698900 | -3.10495600 |
| C | 4.37480100 | -1.34333400 | -0.23048300 |
| H | 2.64324300 | -1.61165600 | 1.02697400 |
| C | 4.84184300 | -1.03873300 | -1.51649800 |
| H | 4.29247100 | -0.54493700 | -3.54679700 |
| H | 5.08205000 | -1.54682200 | 0.56946000 |
| H | 5.90933700 | -1.01058500 | -1.71500700 |
| C | -1.56208600 | -1.95959700 | -0.41260000 |
| O | -1.63187100 | -2.73037300 | -1.34433200 |
| O | -2.43852700 | -1.91588800 | 0.60513100 |
| C | -3.65082400 | -2.67885200 | 0.41337600 |
| H | -4.10738200 | -2.35508000 | -0.52705500 |
| H | -3.39328400 | -3.73914200 | 0.32184500 |
| C | -4.54095100 | -2.39969300 | 1.60848800 |
| H | -4.75708400 | -1.32877900 | 1.67656500 |
| H | -5.48848400 | -2.93999500 | 1.50527900 |
| H | -4.05777600 | -2.71812400 | 2.53821800 |
| C | -1.15902900 | 1.47636700 | -0.37502800 |
| C | -2.47411200 | 1.38417700 | -1.03219200 |
| O | -3.08405000 | 0.33573100 | -1.13343100 |
| O | -3.00556000 | 2.50671200 | -1.60866600 |
| C | -2.92939000 | 3.77895900 | -0.95353700 |
| H | -3.94535300 | 4.18399100 | -0.92774300 |
| H | -2.54664700 | 3.69173900 | 0.06778000 |
| H | -2.28663500 | 4.46095700 | -1.51985000 |
| H | -0.39373000 | 3.05307100 | -1.61089300 |
| N | 0.51667800 | 0.02912600 | 2.59051600 |
| C | 2.51490100 | 1.82081300 | 1.77473300 |
| H | 3.28763800 | 2.51272500 | 1.44856000 |



MECP3

SCF Done: E(B3LYP) = 1205.369164 a.u

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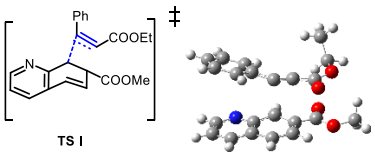
| | | | |
|---|---|---|---|
| C | 1.02067000 | -0.35485800 | -0.68857800 |
| C | 1.05269700 | 1.01530500 | -1.34983700 |
| C | -0.19122400 | 0.45509600 | 1.10689400 |
| C | -0.38542600 | -0.41226700 | -0.12094500 |
| C | -0.36930400 | 1.13986000 | -1.88832600 |
| H | -0.49909600 | 0.10407600 | 2.08521200 |
| H | 1.83043700 | 1.16146900 | -2.10332300 |
| C | 1.15259600 | 2.05091800 | -0.22543900 |
| C | 0.49006500 | 1.70358900 | 0.99853100 |
| C | 1.14318800 | 3.68868800 | 1.96322200 |
| H | 1.13819100 | 4.32212600 | 2.84970400 |
| C | 1.81100700 | 4.11150800 | 0.80811600 |
| H | 2.34062400 | 5.05876900 | 0.79374800 |
| C | 2.16832500 | -1.14031500 | -0.39744400 |
| C | 3.42579600 | -0.80536000 | -0.97839100 |
| C | 2.14263300 | -2.26273400 | 0.47968700 |
| C | 4.56589100 | -1.55164700 | -0.71638800 |
| H | 3.49928700 | 0.04252400 | -1.65021800 |
| C | 3.29151700 | -2.98972100 | 0.74592300 |
| H | 1.21616900 | -2.55211500 | 0.95549800 |
| C | 4.51227000 | -2.64861300 | 0.14904400 |
| H | 5.50554600 | -1.27344100 | -1.18634100 |
| H | 3.23827500 | -3.83596500 | 1.42558700 |
| H | 5.40653300 | -3.22907000 | 0.35701200 |
| C | -1.04534600 | -1.76419900 | 0.12410600 |
| O | -0.73969900 | -2.79604000 | -0.42696000 |
| O | -2.06698600 | -1.61739700 | 0.98354300 |
| C | -3.01360100 | -2.71587400 | 1.06079500 |
| H | -3.08374500 | -3.17682800 | 0.07317800 |
| H | -2.62022300 | -3.45662000 | 1.76561200 |
| C | -4.33634600 | -2.12591800 | 1.50827400 |
| H | -4.68292800 | -1.39823000 | 0.76875200 |
| H | -5.08632300 | -2.91944400 | 1.59874600 |
| H | -4.23773400 | -1.62858100 | 2.47884600 |
| C | -1.20093000 | 0.38042000 | -1.16917000 |
| C | -2.68883600 | 0.28152700 | -1.26715800 |
| O | -3.24399700 | -0.75811100 | -1.54729400 |
| O | -3.43230300 | 1.38909200 | -1.04528500 |

| | | | |
|---|---|---|---|
| C | -2.85385200 | 2.56378700 | -0.44814800 |
| H | -3.70560300 | 3.17020200 | -0.13680300 |
| H | -2.24006700 | 2.31265900 | 0.42131200 |
| H | -2.25099300 | 3.12258400 | -1.16973000 |
| H | -0.64882400 | 1.85905100 | -2.65070200 |
| N | 0.49610700 | 2.52840400 | 2.07759800 |
| H | 2.31938100 | 3.54999300 | -1.22594900 |
| C | 1.80024600 | 3.26875100 | -0.31233100 |




SCF Done: E(ωB97XD) = -1205.368926 a.u.

Thermal Correction to Free Energy = 0.301349 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.067577 a.u.

0 3

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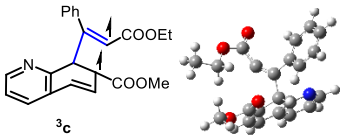
|---|---|---|---|
| C | -1.46098800 | -1.37461400 | -0.66697600 |
| C | -1.59375300 | -2.25529500 | 0.45341200 |
| C | -2.88419300 | -2.62674600 | 0.83572000 |
| C | -3.98075400 | -2.13238200 | 0.11596500 |
| C | -3.74025100 | -1.29163400 | -0.96802300 |
| N | -2.51466000 | -0.91387200 | -1.36661900 |
| C | -0.15371500 | -0.89625600 | -1.01684100 |
| C | 1.02983900 | -1.52665600 | -0.43190200 |
| C | 0.86943400 | -2.39412600 | 0.65361900 |
| C | -0.39720200 | -2.72853700 | 1.11068800 |
| C | 2.33885400 | -1.20009300 | -1.01422500 |
| O | 2.49629100 | -0.44004200 | -1.96184200 |
| O | 3.35856300 | -1.82238800 | -0.38050900 |
| H | -3.02854000 | -3.29487900 | 1.68140400 |
| H | -4.99653800 | -2.39842500 | 0.39118100 |
| H | -4.56834400 | -0.89124200 | -1.54921500 |
| H | -0.03898200 | -0.32168300 | -1.92732400 |
| H | 1.74931800 | -2.79510600 | 1.14196800 |
| H | -0.50586800 | -3.39119200 | 1.96526900 |
| C | -3.72774800 | 1.74497000 | 1.06485400 |
| C | -4.10357500 | 2.46873100 | -0.07064900 |
| C | -3.16590900 | 2.72967900 | -1.07422700 |
| C | -1.85956500 | 2.26822200 | -0.94996300 |
| C | -1.47037300 | 1.55062300 | 0.19625200 |
| C | -2.42196500 | 1.28534100 | 1.20170300 |
| C | -0.14815600 | 1.02272700 | 0.32587200 |
| C | 0.99488900 | 0.94248300 | 0.81334700 |

| | | | |
|---|---|---|---|
| C | 2.29843500 | 0.71959400 | 1.36480300 |
| O | 2.48141000 | 0.02966100 | 2.35322600 |
| O | 3.35747200 | 1.30113300 | 0.73839400 |
| C | 3.14402300 | 2.21775900 | -0.36345500 |
| H | -4.45557800 | 1.53584900 | 1.84391700 |
| H | -5.12473000 | 2.82496900 | -0.17518600 |
| H | -3.45759500 | 3.28547700 | -1.96084000 |
| H | -1.13298400 | 2.44734900 | -1.73632600 |
| H | -2.12247100 | 0.71319400 | 2.07380500 |
| H | 4.10161200 | 2.22086800 | -0.88947600 |
| H | 2.39306500 | 1.81065800 | -1.04441700 |
| C | 2.78198000 | 3.60764800 | 0.13847500 |
| H | 2.71793200 | 4.30518200 | -0.70461600 |
| H | 1.81312600 | 3.59931100 | 0.64859000 |
| H | 3.54013800 | 3.97381900 | 0.83803000 |
| C | 4.67728100 | -1.42555000 | -0.78673100 |
| H | 4.85858800 | -0.39205500 | -0.48034100 |
| H | 5.35700500 | -2.09990600 | -0.26474100 |
| H | 4.79406400 | -1.51732100 | -1.86982300 |




SCF Done: E(ωB97XD) = -1205.416799 a.u.

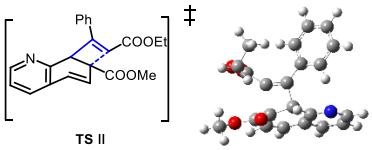
Thermal Correction to Free Energy = 0.304479 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.112320 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 1.75866000 | -1.51090200 | 0.28126600 |
| C | 1.58703600 | -2.74043900 | -0.40809700 |
| C | 2.73537000 | -3.33321600 | -0.96820100 |
| C | 3.96596800 | -2.71178600 | -0.81459100 |
| C | 4.02082800 | -1.51531700 | -0.08999600 |
| N | 2.94550700 | -0.92494600 | 0.44606300 |
| C | 0.55728400 | -0.76192100 | 0.82834600 |
| C | -0.71135200 | -1.57431800 | 0.84769500 |
| C | -0.81168200 | -2.77995200 | 0.17059600 |
| C | 0.28756600 | -3.34691800 | -0.47481700 |
| C | -1.83856400 | -0.95864500 | 1.55938600 |
| O | -1.75215300 | 0.06468600 | 2.22189400 |
| O | -3.01018500 | -1.62659300 | 1.39317800 |
| H | 2.64587600 | -4.27272600 | -1.50846300 |
| H | 4.87007300 | -3.14041000 | -1.23587800 |
| H | 4.97015700 | -1.00697600 | 0.06645800 |

| | | | |
|---|---|---|---|
| H | 0.79693300 | -0.42600800 | 1.84186200 |
| H | -1.76629700 | -3.29538300 | 0.15474800 |
| H | 0.17823100 | -4.28824400 | -1.00642100 |
| C | 2.29558300 | 3.76197900 | -0.18636900 |
| C | 2.24262800 | 4.18218300 | 1.14430200 |
| C | 1.56788100 | 3.40676800 | 2.09052700 |
| C | 0.96089800 | 2.20992300 | 1.71436100 |
| C | 1.02374900 | 1.77890900 | 0.38018600 |
| C | 1.68639400 | 2.56856200 | -0.57137600 |
| C | 0.35364100 | 0.51425100 | -0.03311000 |
| C | -0.39022300 | 0.44209400 | -1.11798700 |
| C | -0.96690500 | 1.13516600 | -2.24032700 |
| O | -0.28854400 | 1.63972200 | -3.12089200 |
| O | -2.31924400 | 1.18929300 | -2.31074000 |
| C | -3.09356900 | 0.62442900 | -1.22992000 |
| H | 2.81317400 | 4.36359100 | -0.92873200 |
| H | 2.71983300 | 5.11210300 | 1.44224500 |
| H | 1.50862300 | 3.73699000 | 3.12430500 |
| H | 0.40228800 | 1.62734300 | 2.44073500 |
| H | 1.71254500 | 2.24211900 | -1.60613200 |
| H | -2.86535100 | -0.44358200 | -1.13051400 |
| H | -2.82520200 | 1.11513400 | -0.28687600 |
| C | -4.55629400 | 0.84293700 | -1.57073400 |
| H | -5.18975200 | 0.42463900 | -0.78050300 |
| H | -4.77419400 | 1.91109600 | -1.66559500 |
| H | -4.80916400 | 0.35317900 | -2.51614400 |
| C | -4.13753300 | -1.05318000 | 2.07220200 |
| H | -4.97830200 | -1.71133400 | 1.85007900 |
| H | -3.95759500 | -1.00614600 | 3.14989500 |
| H | -4.33360900 | -0.04127000 | 1.70489400 |




SCF Done: E(ωB97XD) = -1205.377943 a.u.

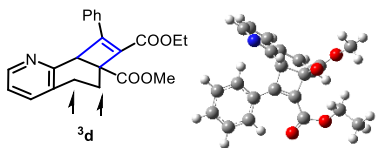
Thermal Correction to Free Energy = 0.303626 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.074317 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 1.78547700 | -1.47071100 | 0.44511300 |
| C | 1.89383800 | -2.34059300 | -0.71011200 |
| C | 3.21867100 | -2.71147700 | -1.10796000 |
| C | 4.29163100 | -2.29016100 | -0.36174900 |
| C | 4.05697800 | -1.49774900 | 0.78729600 |

| | | | |
|---|---|---|---|
| N | 2.83913300 | -1.09024800 | 1.16640000 |
| C | 0.46502300 | -0.85492900 | 0.79921900 |
| C | -0.76887400 | -1.53869600 | 0.17181100 |
| C | -0.57590400 | -2.52434500 | -0.80855300 |
| C | 0.74700000 | -2.80570200 | -1.34352500 |
| C | -2.00176300 | -1.59428000 | 1.02113400 |
| O | -2.05737300 | -1.25090900 | 2.18575900 |
| O | -3.07141200 | -2.01234200 | 0.31273700 |
| H | 3.35181300 | -3.33628500 | -1.98756700 |
| H | 5.30763100 | -2.56175600 | -0.63227700 |
| H | 4.88645800 | -1.17723900 | 1.41354900 |
| H | 0.36756900 | -0.76050900 | 1.88462500 |
| H | -1.43681400 | -3.03541900 | -1.22292200 |
| H | 0.83406500 | -3.45191800 | -2.21206700 |
| C | 1.60545800 | 3.85198500 | -0.87095400 |
| C | 2.47083200 | 4.10565900 | 0.19795500 |
| C | 2.60996200 | 3.16141500 | 1.21690800 |
| C | 1.88358600 | 1.97151000 | 1.17950700 |
| C | 1.00026200 | 1.71690500 | 0.11800300 |
| C | 0.87748500 | 2.66655100 | -0.91452000 |
| C | 0.20170100 | 0.48949200 | 0.07845000 |
| C | -0.92415700 | 0.20386500 | -0.56564600 |
| C | -1.90285500 | 0.66971800 | -1.53816000 |
| O | -1.74820300 | 0.49602900 | -2.73335500 |
| O | -3.06026700 | 1.21698400 | -1.08369300 |
| C | -3.19240300 | 1.63158500 | 0.29353300 |
| H | 1.50439800 | 4.57549900 | -1.67534200 |
| H | 3.03981800 | 5.03096500 | 0.23011400 |
| H | 3.28863500 | 3.34948900 | 2.04455900 |
| H | 2.01267900 | 1.22838400 | 1.95836700 |
| H | 0.22408300 | 2.45537500 | -1.75673900 |
| H | -4.26903600 | 1.59068200 | 0.48273000 |
| H | -2.69909700 | 0.92220100 | 0.96379400 |
| C | -2.65003100 | 3.03875800 | 0.49435100 |
| H | -2.83658200 | 3.37033300 | 1.52219900 |
| H | -1.57074300 | 3.06851600 | 0.31713700 |
| H | -3.13595400 | 3.73784400 | -0.19370100 |
| C | -4.31812700 | -2.02552800 | 1.02905300 |
| H | -5.05855700 | -2.38864700 | 0.31629300 |
| H | -4.25669200 | -2.68675400 | 1.89762400 |
| H | -4.57231100 | -1.01675000 | 1.36632900 |




SCF Done: E(ωB97XD) = -1205.386203 a.u.

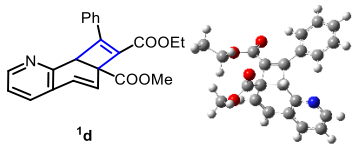
Thermal Correction to Free Energy = 0.304117 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.082086 a.u.

0 3

| | | | |
|---|---|---|---|
| C | -1.35549700 | 1.73517900 | 0.08127100 |
| C | -1.03258700 | 2.39443200 | -1.19018500 |
| C | -2.05648500 | 3.27178100 | -1.72313200 |
| C | -3.19096400 | 3.50294000 | -0.99875100 |
| C | -3.34881300 | 2.87218200 | 0.26757400 |
| N | -2.44988900 | 2.00434400 | 0.77316600 |
| C | -0.43606400 | 0.68813100 | 0.64069300 |
| C | 1.03275100 | 0.63082700 | 0.05268600 |
| C | 1.25213300 | 1.40715000 | -1.19223300 |
| C | 0.19180700 | 2.21814800 | -1.78350700 |
| C | 2.02718500 | 0.87069700 | 1.18850700 |
| O | 2.06319500 | 0.22169900 | 2.21195100 |
| O | 2.84686100 | 1.91274500 | 0.93963600 |
| H | -1.88886300 | 3.74923000 | -2.68519400 |
| H | -3.96827300 | 4.16627600 | -1.36715200 |
| H | -4.22611800 | 3.06554500 | 0.87886000 |
| H | -0.44442300 | 0.75654100 | 1.73283800 |
| H | 2.14764100 | 1.20126800 | -1.76876300 |
| H | 0.40372100 | 2.72192100 | -2.72361800 |
| C | -2.95130000 | -3.70403600 | -0.07135900 |
| C | -4.00756400 | -3.24986500 | 0.72413700 |
| C | -3.93395400 | -1.98890800 | 1.31987400 |
| C | -2.81321000 | -1.18654800 | 1.12541300 |
| C | -1.73843100 | -1.63694500 | 0.32820800 |
| C | -1.82467700 | -2.91270900 | -0.27060300 |
| C | -0.57962800 | -0.77481300 | 0.17445600 |
| C | 0.70515900 | -0.84651200 | -0.28111800 |
| C | 1.41416600 | -1.84293000 | -1.11294400 |
| O | 0.83198500 | -2.71724500 | -1.72551100 |
| O | 2.75663900 | -1.73234500 | -1.29799400 |
| C | 3.63898900 | -1.21254800 | -0.28371500 |
| H | -3.00666100 | -4.68171200 | -0.54255300 |
| H | -4.88411900 | -3.87459500 | 0.87568800 |
| H | -4.75178100 | -1.62773500 | 1.93756700 |
| H | -2.77192000 | -0.20267300 | 1.57990700 |
| H | -1.01326300 | -3.25518300 | -0.89939000 |

| | | | |
|---|---|---|---|
| H | 3.74009600 | -0.12809900 | -0.40866900 |
| H | 3.22835200 | -1.41465600 | 0.70938500 |
| C | 4.98285300 | -1.89569500 | -0.47055800 |
| H | 5.70197900 | -1.51633400 | 0.26429000 |
| H | 4.88318600 | -2.97731600 | -0.33974200 |
| H | 5.37443100 | -1.70413900 | -1.47444400 |
| C | 3.78660200 | 2.21428100 | 1.98860000 |
| H | 4.34928100 | 3.07866200 | 1.63552700 |
| H | 3.26036700 | 2.44561400 | 2.91838400 |
| H | 4.45132900 | 1.36270100 | 2.16038700 |
| H | -2.47386300 | 1.91389300 | 1.32545400 |




**1d**

SCF Done: E(ωB97XD) = -1205.485838 a.u.

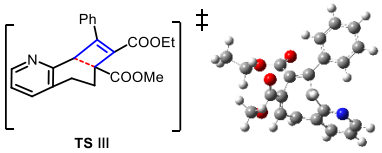
Thermal Correction to Free Energy = 0.310694 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.175144 a.u.

0 1

| | | | |
|---|---|---|---|
| C | 1.38376400 | -1.73920000 | 0.08610200 |
| C | 1.02937800 | -2.46333600 | -1.07338200 |
| C | 1.97738500 | -3.35499400 | -1.59081900 |
| C | 3.20282100 | -3.50751700 | -0.94858700 |
| C | 3.43418600 | -2.77055000 | 0.21237400 |
| N | 2.54565900 | -1.90854500 | 0.72383900 |
| C | 0.44272700 | -0.71134900 | 0.67282600 |
| C | -1.02429000 | -0.67954100 | 0.06708900 |
| C | -1.25839400 | -1.55324700 | -1.13288300 |
| C | -0.29810700 | -2.31876100 | -1.66848000 |
| C | -2.03865800 | -0.85593400 | 1.19384500 |
| O | -2.02480200 | -0.22335500 | 2.22803200 |
| O | -2.94553600 | -1.81984400 | 0.92677200 |
| H | 1.74539300 | -3.92619100 | -2.48681200 |
| H | 3.95736400 | -4.18916400 | -1.32908100 |
| H | 4.36869200 | -2.87390100 | 0.76027600 |
| H | 0.44961200 | -0.78576700 | 1.76426500 |
| H | -2.24052300 | -1.49771400 | -1.59293200 |
| H | -0.50143800 | -2.89201500 | -2.57057900 |
| C | 2.93077400 | 3.67782500 | -0.15616900 |
| C | 3.94379900 | 3.30442200 | 0.73144800 |
| C | 3.85776600 | 2.08529200 | 1.40706300 |
| C | 2.76573700 | 1.24654100 | 1.20193000 |
| C | 1.73247100 | 1.61740500 | 0.31555400 |

| | | | |
|---|---|---|---|
| C | 1.83385500 | 2.84779500 | -0.36738100 |
| C | 0.59002500 | 0.72719700 | 0.16842000 |
| C | -0.67986100 | 0.77089500 | -0.33346000 |
| C | -1.36138900 | 1.73188400 | -1.23004900 |
| O | -0.75135000 | 2.51113900 | -1.93644800 |
| O | -2.71376000 | 1.69113100 | -1.35776100 |
| C | -3.57800800 | 1.28659900 | -0.27813000 |
| H | 2.99737800 | 4.62084900 | -0.69215100 |
| H | 4.79823100 | 3.95737700 | 0.89040400 |
| H | 4.64406200 | 1.78448600 | 2.09419900 |
| H | 2.71868300 | 0.29075600 | 1.71122800 |
| H | 1.05889900 | 3.12702600 | -1.06927500 |
| H | -3.77933500 | 0.21248500 | -0.36117300 |
| H | -3.09464500 | 1.48018100 | 0.68381100 |
| C | -4.86532400 | 2.08226700 | -0.41184900 |
| H | -5.57079300 | 1.79000800 | 0.37434300 |
| H | -4.66331400 | 3.15383500 | -0.32249000 |
| H | -5.33045900 | 1.89890600 | -1.38538600 |
| C | -3.92097000 | -2.04657500 | 1.96101700 |
| H | -4.54883300 | -2.85986300 | 1.59669300 |
| H | -3.42809700 | -2.32356300 | 2.89643300 |
| H | -4.51502500 | -1.14318700 | 2.12770400 |




SCF Done: E(ωB97XD) = -1205.361295 a.u.

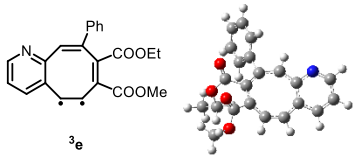
Thermal Correction to Free Energy = 0.302809 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.058486 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 1.48422100 | -1.74415700 | 0.14830000 |
| C | 1.12592200 | -2.24085300 | -1.15736700 |
| C | 2.14037600 | -2.92621800 | -1.86653200 |
| C | 3.36848900 | -3.17387000 | -1.26959700 |
| C | 3.56800300 | -2.73811900 | 0.04128000 |
| N | 2.65745300 | -2.02057600 | 0.72073700 |
| C | 0.64775300 | -0.75817300 | 0.90849800 |
| C | -1.29361400 | -0.79677300 | 0.07498400 |
| C | -1.29500100 | -1.90995700 | -0.75572800 |
| C | -0.18303500 | -2.08217700 | -1.70448100 |
| C | -2.12421500 | -0.77243700 | 1.32924500 |
| O | -2.21189400 | 0.17952900 | 2.07887200 |
| O | -2.75654900 | -1.94590600 | 1.55421100 |

| | | | |
|---|---|---|---|
| H | 1.92858200 | -3.28732100 | -2.86987400 |
| H | 4.15084900 | -3.71162200 | -1.79666800 |
| H | 4.49514500 | -2.95216000 | 0.56825000 |
| H | 0.69013100 | -0.85229800 | 1.99300500 |
| H | -1.82227900 | -2.80385000 | -0.42411000 |
| H | -0.34886200 | -2.25525200 | -2.76504700 |
| C | 2.26886500 | 3.95237700 | 0.26492300 |
| C | 3.47061700 | 3.62205400 | 0.89940200 |
| C | 3.69293600 | 2.30904000 | 1.31547900 |
| C | 2.72228100 | 1.33251000 | 1.10110400 |
| C | 1.51109800 | 1.65070300 | 0.45428400 |
| C | 1.29872300 | 2.98164300 | 0.04272000 |
| C | 0.50267400 | 0.60192000 | 0.28735900 |
| C | -0.68537000 | 0.51626900 | -0.36444400 |
| C | -1.19787300 | 1.35278800 | -1.48604800 |
| O | -0.45271500 | 1.96025000 | -2.22772800 |
| O | -2.52684600 | 1.36941900 | -1.76234500 |
| C | -3.53241100 | 1.10763300 | -0.76191300 |
| H | 2.08754900 | 4.97329800 | -0.05990500 |
| H | 4.22625800 | 4.38487700 | 1.06798200 |
| H | 4.62263100 | 2.04195900 | 1.81065300 |
| H | 2.90927800 | 0.31370700 | 1.42602400 |
| H | 0.38034000 | 3.25036400 | -0.46104400 |
| H | -3.72925700 | 0.02936400 | -0.72338500 |
| H | -3.17835100 | 1.43221900 | 0.22033900 |
| C | -4.77920200 | 1.86912300 | -1.17761100 |
| H | -5.58792000 | 1.68431400 | -0.46160500 |
| H | -4.57788600 | 2.94423900 | -1.21025700 |
| H | -5.11123200 | 1.55059100 | -2.17069000 |
| C | -3.53747700 | -1.99512400 | 2.76037700 |
| H | -3.97609900 | -2.99313200 | 2.78321700 |
| H | -2.90162500 | -1.83160400 | 3.63486000 |
| H | -4.31795400 | -1.22920900 | 2.74362100 |




SCF Done: E(ωB97XD) = -1205.414066 a.u.

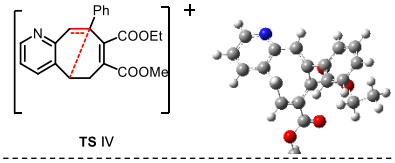
Thermal Correction to Free Energy = 0.305228 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.108838 a.u

0 3

| | | | |
|---|---|---|---|
| C | 2.95281000 | 0.22628100 | 0.11593500 |
| C | 3.10389700 | -1.09540800 | -0.44175500 |

| | | | |
|---|---|---|---|
| C | 4.42927200 | -1.48008900 | -0.79211300 |
| C | 5.51612100 | -0.67884700 | -0.52893300 |
| C | 5.26916100 | 0.55573600 | 0.10590000 |
| N | 4.06023600 | 0.99254400 | 0.38964600 |
| C | 1.77082200 | 0.99846300 | 0.33748400 |
| C | -0.24620100 | -1.63792100 | 0.30721000 |
| C | 0.80929000 | -2.35988800 | -0.25457600 |
| C | 2.12286100 | -2.11103400 | -0.65814300 |
| C | -1.34452100 | -2.50502600 | 0.86284700 |
| O | -1.89097100 | -2.29977900 | 1.92527600 |
| O | -1.65668200 | -3.55690400 | 0.06352500 |
| H | 4.57594500 | -2.45159300 | -1.25731100 |
| H | 6.52527500 | -0.98394100 | -0.78652700 |
| H | 6.09435700 | 1.21447600 | 0.37397300 |
| H | 2.07789000 | 2.01951900 | 0.54468500 |
| H | 0.54749500 | -3.40459900 | -0.40026700 |
| H | 2.55539700 | -2.98325400 | -1.14546900 |
| C | -0.82040800 | 4.41087900 | 1.10911300 |
| C | -1.51299300 | 4.74817200 | -0.05702500 |
| C | -1.59141200 | 3.82992800 | -1.10394900 |
| C | -0.98642400 | 2.57801800 | -0.98181300 |
| C | -0.29585100 | 2.23081900 | 0.18679500 |
| C | -0.21175800 | 3.16368900 | 1.22865600 |
| C | 0.36032200 | 0.87799600 | 0.29132400 |
| C | -0.50177300 | -0.21868300 | 0.38451900 |
| C | -1.96315100 | 0.13908100 | 0.63906500 |
| O | -2.33045500 | 0.73147100 | 1.62031300 |
| O | -2.88180900 | -0.27171500 | -0.27727200 |
| C | -2.51945700 | -0.69342400 | -1.60912100 |
| H | -0.76290200 | 5.11823200 | 1.93190700 |
| H | -1.98774000 | 5.72132200 | -0.14733800 |
| H | -2.11892300 | 4.08678500 | -2.01878400 |
| H | -1.03549200 | 1.87110500 | -1.80532600 |
| H | 0.30765900 | 2.89291900 | 2.14328000 |
| H | -1.49421000 | -0.38992100 | -1.84221200 |
| H | -2.55932000 | -1.78721300 | -1.64334400 |
| C | -3.50813800 | -0.05885200 | -2.57217100 |
| H | -3.29711800 | -0.37917900 | -3.59882500 |
| H | -4.53204600 | -0.34902300 | -2.31781000 |
| H | -3.43928400 | 1.03254500 | -2.51994400 |
| C | -2.67245700 | -4.42936400 | 0.59255300 |
| H | -2.81574900 | -5.20119000 | -0.16428800 |
| H | -2.34570800 | -4.86994300 | 1.53853900 |
| H | -3.59791500 | -3.87260000 | 0.76199800 |




TS IV

SCF Done: E(ωB97XD) = -1205.379535 a.u.

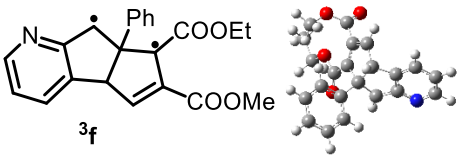
Thermal Correction to Free Energy = 0.303261 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.076274 a.u

0 3

| | | | |
|---|---|---|---|
| C | -2.31198500 | 1.72711500 | -0.42505500 |
| C | -2.67273000 | 0.98544800 | 0.73191400 |
| C | -4.02996400 | 0.76865200 | 0.96671200 |
| C | -4.96051800 | 1.29754600 | 0.07003400 |
| C | -4.49639100 | 2.04672000 | -1.01545300 |
| N | -3.20391000 | 2.27653800 | -1.26383200 |
| C | -0.88569300 | 1.97944700 | -0.54766900 |
| C | -0.51250600 | -1.37977700 | 0.46294200 |
| C | -1.28283700 | -0.94757000 | 1.53437600 |
| C | -1.55865700 | 0.49276400 | 1.58719800 |
| C | -0.32346000 | -2.82556500 | 0.14938400 |
| O | 0.38086400 | -3.24886800 | -0.74707300 |
| O | -1.02107900 | -3.62843000 | 0.97968600 |
| H | -4.35561600 | 0.20615100 | 1.83802100 |
| H | -6.02617500 | 1.14935900 | 0.21687100 |
| H | -5.20215500 | 2.48933100 | -1.71648800 |
| H | -0.57670400 | 3.00367300 | -0.74010300 |
| H | -1.77221800 | -1.66017000 | 2.19327200 |
| H | -1.27240200 | 1.08276500 | 2.45735400 |
| C | 3.33658800 | 2.96752900 | 0.01929200 |
| C | 3.88466200 | 2.53694900 | 1.22942900 |
| C | 3.18460300 | 1.61852300 | 2.01547100 |
| C | 1.94336200 | 1.14127900 | 1.59655100 |
| C | 1.37520300 | 1.58212200 | 0.39104500 |
| C | 2.09305800 | 2.49226000 | -0.39922400 |
| C | 0.02572800 | 1.06630200 | -0.02067000 |
| C | 0.07030000 | -0.40158500 | -0.35491600 |
| C | 0.73226800 | -0.66634300 | -1.68870100 |
| O | 0.08895900 | -0.46721300 | -2.69385700 |
| O | 2.03813500 | -0.96652500 | -1.76895900 |
| C | 2.79583300 | -1.45460300 | -0.64291400 |
| H | 3.88123600 | 3.66854200 | -0.60737600 |
| H | 4.85340900 | 2.90715000 | 1.55317900 |
| H | 3.60468400 | 1.27387100 | 2.95661700 |
| H | 1.39843200 | 0.42584500 | 2.20674400 |

| | | | |
|---|---|---|---|
| H | 1.68306900 | 2.81175600 | -1.35283400 |
| H | 2.28446200 | -1.21512700 | 0.29297700 |
| H | 2.84111100 | -2.54263100 | -0.74044400 |
| C | 4.16979100 | -0.81187100 | -0.68899800 |
| H | 4.79313800 | -1.20511300 | 0.12211000 |
| H | 4.66241500 | -1.02764900 | -1.64242800 |
| H | 4.08937100 | 0.27182200 | -0.57126800 |
| C | -0.87747700 | -5.03760800 | 0.72844500 |
| H | -1.50161900 | -5.53103800 | 1.47383900 |
| H | -1.21476900 | -5.28091900 | -0.28265600 |
| H | 0.16760300 | -5.34150800 | 0.83591200 |




$^3$f

SCF Done: E(ωB97XD) = -1205.454722 a.u.

Thermal Correction to Free Energy = 0.304883 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.149839 a.u

0 3

| | | | |
|---|---|---|---|
| C | 2.69395300 | 0.79842800 | -0.90520700 |
| C | 2.66083800 | 1.03847600 | 0.50171700 |
| C | 3.64350800 | 1.81951400 | 1.07630000 |
| C | 4.62838500 | 2.34816900 | 0.22596100 |
| C | 4.57213500 | 2.06308500 | -1.15017500 |
| N | 3.64320600 | 1.30750100 | -1.73344800 |
| C | 1.62121200 | -0.02295600 | -1.29444200 |
| C | -0.77806700 | 1.15519400 | 0.86084000 |
| C | 0.37992800 | 1.28110600 | 1.60265900 |
| C | 1.45816600 | 0.35070000 | 1.11311600 |
| C | -0.61553800 | 0.19565800 | -0.15555300 |
| C | 0.77942700 | -0.41722700 | -0.10206700 |
| C | -1.97128800 | 2.05264100 | 1.07810300 |
| O | -1.95955200 | 3.20829800 | 0.73219300 |
| O | -3.04122900 | 1.55354200 | 1.73539900 |
| C | -3.05796600 | 0.18180500 | 2.15087800 |
| C | -1.55212200 | -0.15788700 | -1.21471600 |
| O | -1.27686500 | -0.86450500 | -2.17090400 |
| O | -2.77055600 | 0.40451000 | -1.01573600 |
| C | -4.99190500 | 0.97928900 | -1.63352700 |
| C | -3.75591600 | 0.20726400 | -2.05393800 |
| C | 0.70861900 | -1.93203800 | 0.13589300 |
| C | 1.56985000 | -2.81769500 | -0.51895700 |
| C | 1.51852900 | -4.18736100 | -0.25253100 |

| | | | |
|---|---|---|---|
| C | 0.60844900 | -4.69127700 | 0.67688200 |
| C | -0.24989600 | -3.81349200 | 1.34248700 |
| C | -0.19823700 | -2.44669800 | 1.07348900 |
| H | 3.65757300 | 2.02657200 | 2.14375200 |
| H | 5.42598200 | 2.97256100 | 0.61611200 |
| H | 5.33327800 | 2.47440400 | -1.81204100 |
| H | 1.38414300 | -0.32484400 | -2.30548300 |
| H | 0.52155200 | 1.99102600 | 2.41031100 |
| H | 1.76697500 | -0.34381500 | 1.90588900 |
| H | -3.98175500 | 0.06233300 | 2.71913300 |
| H | -3.06765100 | -0.48527100 | 1.28534800 |
| H | -2.20317000 | -0.05147200 | 2.79537700 |
| H | -5.77494300 | 0.87607800 | -2.39231700 |
| H | -5.37809700 | 0.60387600 | -0.68041200 |
| H | -4.75718400 | 2.04096700 | -1.51088700 |
| H | -3.34246700 | 0.56663800 | -3.00215300 |
| H | -3.94615900 | -0.86626800 | -2.16044700 |
| H | 2.28410800 | -2.43600800 | -1.24196300 |
| H | 2.19278800 | -4.86023900 | -0.77567300 |
| H | 0.56761800 | -5.75760500 | 0.88162000 |
| H | -0.96233700 | -4.19313300 | 2.07043500 |
| H | -0.86947800 | -1.77125400 | 1.59663800 |

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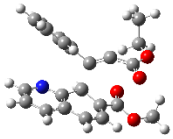

MECP4

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SCF Done: E(B3LYP) = -1205.363083 a.u.

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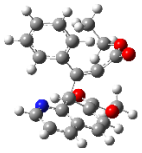
0 1 or 0 3

| | | | |
|---|---|---|---|
| C | -1.54332700 | -1.33617400 | -0.51449500 |
| C | -1.72185400 | -2.34450500 | 0.47439100 |
| C | -3.04485800 | -2.75194900 | 0.75304100 |
| C | -4.09029100 | -2.19102200 | 0.04128000 |
| C | -3.79215700 | -1.24709700 | -0.95515800 |
| N | -2.55637000 | -0.82681200 | -1.22799600 |
| C | -0.18542400 | -0.75865200 | -0.73911300 |
| C | 0.90946600 | -1.66925600 | -0.34996900 |
| C | 0.70318000 | -2.65803600 | 0.60962500 |
| C | -0.57386400 | -2.95396500 | 1.06964600 |
| C | 2.24322100 | -1.35640700 | -0.88045900 |
| O | 2.46701400 | -0.38435700 | -1.59193900 |
| O | 3.20357300 | -2.21169700 | -0.47806700 |
| H | -3.22542700 | -3.51130800 | 1.51025000 |
| H | -5.11991700 | -2.48006100 | 0.22871500 |

| | | | |
|---|---|---|---|
| H | -4.58808800 | -0.80871000 | -1.55380200 |
| H | -0.07674900 | -0.38740600 | -1.76161500 |
| H | 1.55958600 | -3.20352100 | 0.98836600 |
| H | -0.71784400 | -3.71508900 | 1.83230400 |
| C | -3.44711000 | 2.16707300 | 1.13050700 |
| C | -3.78341400 | 2.92022400 | 0.00367000 |
| C | -2.90746300 | 2.97048700 | -1.08322300 |
| C | -1.70635000 | 2.26345000 | -1.04899900 |
| C | -1.36706200 | 1.50563600 | 0.07746500 |
| C | -2.24208100 | 1.46587700 | 1.16997700 |
| C | -0.10768000 | 0.70948600 | 0.11707300 |
| C | 0.97730700 | 1.10186400 | 0.69937100 |
| C | 2.29411700 | 0.74677100 | 1.15652400 |
| O | 2.45943000 | -0.19226700 | 1.92340800 |
| O | 3.36325600 | 1.45810400 | 0.73758700 |
| C | 3.20370800 | 2.43659700 | -0.31529500 |
| H | -4.12168400 | 2.12608100 | 1.98170900 |
| H | -4.72195700 | 3.46783400 | -0.02681600 |
| H | -3.16064100 | 3.55828900 | -1.96167600 |
| H | -1.03025000 | 2.28903400 | -1.89861800 |
| H | -1.97564300 | 0.87495600 | 2.04119500 |
| H | 4.16922500 | 2.43475900 | -0.82785400 |
| H | 2.44589400 | 2.09091300 | -1.02291300 |
| C | 2.88075700 | 3.80686300 | 0.25926200 |
| H | 2.86035300 | 4.55454700 | -0.54190100 |
| H | 1.90238700 | 3.79839000 | 0.75054900 |
| H | 3.63785700 | 4.10198400 | 0.99291200 |
| C | 4.54749600 | -1.77924700 | -0.74945100 |
| H | 4.73932600 | -0.83312800 | -0.23513800 |
| H | 5.19094400 | -2.56707400 | -0.35780900 |
| H | 4.70313400 | -1.64916600 | -1.82383000 |



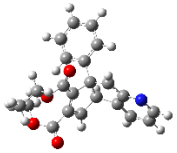
MECP5

SCF Done: E(B3LYP) = -1205.365914 a.u.

0 1 or 0 3

| | | | |
|---|---|---|---|
| C | -1.77539900 | -1.44071300 | -0.37815300 |
| C | -1.90702900 | -2.40525600 | 0.65612000 |
| C | -3.20970000 | -2.76794200 | 1.04279400 |
| C | -4.29698300 | -2.19249300 | 0.39723900 |
| C | -4.04999500 | -1.28544900 | -0.63700700 |
| N | -2.81882800 | -0.91726300 | -1.01998400 |

| | | | |
|---|---|---|---|
| C | -0.40288700 | -0.91342600 | -0.75541900 |
| C | 0.73857900 | -1.80441100 | -0.28758200 |
| C | 0.53163000 | -2.76528100 | 0.70757700 |
| C | -0.73224500 | -3.02361400 | 1.21078000 |
| C | 2.01903000 | -1.67878900 | -1.00494800 |
| O | 2.17459300 | -1.02331900 | -2.02389500 |
| O | 3.02034300 | -2.36833000 | -0.40761900 |
| H | -3.35315100 | -3.50270200 | 1.83162900 |
| H | -5.31567100 | -2.44612000 | 0.67355600 |
| H | -4.87326800 | -0.83289600 | -1.18573400 |
| H | -0.35337300 | -0.76743600 | -1.84065800 |
| H | 1.38438000 | -3.32446600 | 1.07625000 |
| H | -0.85907500 | -3.76290700 | 1.99686200 |
| C | -1.82445700 | 3.69205500 | 0.78930200 |
| C | -2.47002600 | 3.98986900 | -0.41337400 |
| C | -2.37168400 | 3.10489100 | -1.48905900 |
| C | -1.62854800 | 1.93112400 | -1.37023600 |
| C | -0.96636400 | 1.63020500 | -0.16915600 |
| C | -1.07992200 | 2.52121300 | 0.91377900 |
| C | -0.12346400 | 0.41663100 | -0.03446600 |
| C | 0.96403400 | 0.36507100 | 0.71852400 |
| C | 1.82796400 | 0.99006700 | 1.68781800 |
| O | 1.55756700 | 1.00180300 | 2.87954800 |
| O | 3.00887700 | 1.50492700 | 1.26299900 |
| C | 3.22928800 | 1.74710200 | -0.14604100 |
| H | -1.90954400 | 4.36648200 | 1.63706000 |
| H | -3.05221200 | 4.90251200 | -0.50916300 |
| H | -2.88037400 | 3.32489600 | -2.42393000 |
| H | -1.57362300 | 1.24227900 | -2.20429600 |
| H | -0.58958600 | 2.28308700 | 1.85364300 |
| H | 4.31823800 | 1.73959900 | -0.25009100 |
| H | 2.81960500 | 0.93242500 | -0.74907300 |
| C | 2.63937100 | 3.08632000 | -0.56321900 |
| H | 2.86990500 | 3.28618100 | -1.61588300 |
| H | 1.55063100 | 3.08367000 | -0.44822300 |
| H | 3.05237300 | 3.89557300 | 0.04745000 |
| C | 4.30770000 | -2.24221500 | -1.02907300 |
| H | 4.97296800 | -2.88575900 | -0.45284000 |
| H | 4.26798400 | -2.55999400 | -2.07453800 |
| H | 4.65118200 | -1.20400200 | -0.98760200 |



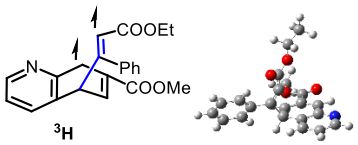
MECP6

SCF Done: E(B3LYP) = -1205.400526 a.u.

0 1 or 0 3

| | | | |
|---|---|---|---|
| C | 2.63296200 | -0.80711800 | 0.90741400 |
| C | 2.65346600 | -0.99436700 | -0.50701600 |
| C | 3.63896400 | -1.78503500 | -1.06887200 |
| C | 4.57241900 | -2.36496900 | -0.19854200 |
| C | 4.46066100 | -2.13337700 | 1.18666800 |
| N | 3.52598300 | -1.37955600 | 1.75806900 |
| C | 1.57969300 | 0.04511100 | 1.27655600 |
| C | -0.71356500 | -1.15617400 | -0.87758800 |
| C | 0.43331500 | -1.22232500 | -1.63846200 |
| C | 1.48713100 | -0.26754700 | -1.14092900 |
| C | -0.58411500 | -0.18751900 | 0.13908600 |
| C | 0.78242600 | 0.48128100 | 0.07240100 |
| C | -1.87989300 | -2.08652100 | -1.09890100 |
| O | -1.84684700 | -3.24322100 | -0.75850200 |
| O | -2.95549200 | -1.60523600 | -1.76274300 |
| C | -2.99739400 | -0.22982200 | -2.16589300 |
| C | -1.52965000 | 0.14191900 | 1.19872700 |
| O | -1.28518200 | 0.87775300 | 2.14198400 |
| O | -2.72641300 | -0.47204600 | 1.01332300 |
| C | -4.94130200 | -1.07757300 | 1.63746700 |
| C | -3.71450400 | -0.28800800 | 2.05193900 |
| C | 0.68178600 | 1.99092500 | -0.13665300 |
| C | 1.50169900 | 2.88059500 | 0.56178600 |
| C | 1.42415600 | 4.25402600 | 0.32381900 |
| C | 0.52856900 | 4.75583800 | -0.62103000 |
| C | -0.29321500 | 3.87303800 | -1.32551200 |
| C | -0.21593000 | 2.50217400 | -1.08410100 |
| H | 3.69146000 | -1.95551000 | -2.14150400 |
| H | 5.37299600 | -2.99285700 | -0.57693500 |
| H | 5.17903900 | -2.59397200 | 1.86351000 |
| H | 1.30409600 | 0.31369600 | 2.28724300 |
| H | 0.59795900 | -1.92415300 | -2.44858500 |
| H | 1.81788100 | 0.42821200 | -1.92151100 |
| H | -3.92136200 | -0.12322400 | -2.73572900 |
| H | -3.02240900 | 0.43067900 | -1.29535300 |
| H | -2.14530700 | 0.02704000 | -2.80512300 |
| H | -5.71587800 | -0.99799700 | 2.40802800 |
| H | -5.34710500 | -0.69740900 | 0.69466100 |

| | | | |
|---|---|---|---|
| H | -4.68851400 | -2.13312700 | 1.49856700 |
| H | -3.29508100 | -0.64096500 | 2.99980300 |
| H | -3.92050900 | 0.78211000 | 2.16030200 |
| H | 2.20144400 | 2.49790300 | 1.29897300 |
| H | 2.06519600 | 4.93221000 | 0.88020700 |
| H | 0.46614100 | 5.82518900 | -0.80370400 |
| H | -0.99619200 | 4.25286500 | -2.06236800 |
| H | -0.86032400 | 1.82088300 | -1.63363600 |




SCF Done: E(ωB97XD) = -1205.409590 a.u.

Thermal Correction to Free Energy = 0.301831 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.107759 a.u.

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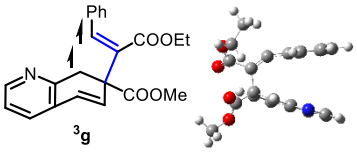
| | | | |
|---|---|---|---|
| C | -1.05882500 | -0.31018700 | 0.49716100 |
| C | 0.25928000 | -0.62564000 | 1.25867000 |
| C | 2.91205600 | 0.36808200 | 0.51627500 |
| C | -1.10830100 | 0.82613200 | -0.17466500 |
| C | 1.19141700 | -1.34108100 | 0.31636500 |
| H | 3.88367200 | 0.74704200 | 0.22505500 |
| H | -0.01260300 | -1.30731800 | 2.07973900 |
| C | 0.86411100 | 0.62731500 | 1.87195900 |
| C | 2.14510700 | 1.09469400 | 1.48185400 |
| C | 2.00580700 | 2.89357500 | 2.91096700 |
| H | 2.47769700 | 3.79339400 | 3.30373500 |
| C | 0.73965800 | 2.50508600 | 3.37301300 |
| H | 0.22221000 | 3.09345600 | 4.12438500 |
| C | -2.16476300 | -1.30934300 | 0.51777600 |
| C | -1.92457500 | -2.66286100 | 0.81437700 |
| C | -3.48907900 | -0.90625500 | 0.25876400 |
| C | -2.96971300 | -3.58663200 | 0.83221800 |
| H | -0.91942300 | -3.01322800 | 1.02284600 |
| C | -4.52868500 | -1.83182200 | 0.28198800 |
| H | -3.70167700 | 0.13931100 | 0.06191800 |
| C | -4.27566000 | -3.17663000 | 0.56494900 |
| H | -2.75846700 | -4.62861100 | 1.05693700 |
| H | -5.54406400 | -1.49785800 | 0.08614400 |
| H | -5.08986900 | -3.89586200 | 0.58344100 |
| C | -1.82117100 | 1.79190800 | -0.96283200 |
| O | -2.93649200 | 2.21711700 | -0.68593300 |
| O | -1.09877900 | 2.20548700 | -2.02335800 |

| | | | |
|---|---|---|---|
| C | -1.72449100 | 3.21050200 | -2.85691800 |
| H | -2.66428400 | 2.80827000 | -3.25071700 |
| H | -1.97091100 | 4.07959600 | -2.23732600 |
| C | -0.73859200 | 3.55024700 | -3.95800900 |
| H | -0.50302900 | 2.66324800 | -4.55447000 |
| H | -1.16664000 | 4.31112700 | -4.61956600 |
| H | 0.19328800 | 3.93955700 | -3.53631000 |
| C | 2.42199000 | -0.83243300 | -0.03524500 |
| C | 3.30221300 | -1.53434100 | -1.02194700 |
| O | 4.39284500 | -1.13253200 | -1.37330500 |
| O | 2.75149500 | -2.67845200 | -1.48893600 |
| C | 3.55126700 | -3.39231900 | -2.44513200 |
| H | 3.74222500 | -2.77161500 | -3.32514300 |
| H | 4.50911000 | -3.68276600 | -2.00418300 |
| H | 2.96779000 | -4.27337900 | -2.71451600 |
| H | 0.83985600 | -2.25922500 | -0.13794800 |
| C | 0.16832000 | 1.35454800 | 2.83622400 |
| N | 2.69966200 | 2.22290600 | 1.99853700 |
| H | -0.81930800 | 1.02628700 | 3.15161400 |




SCF Done: E(ωB97XD) = -1205.402512 a.u.

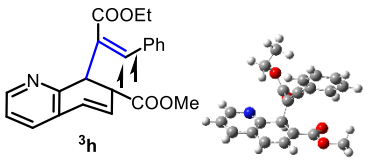
Thermal Correction to Free Energy = 0.302586 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.099926 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 1.47739000 | -1.38454100 | 0.63964000 |
| C | 1.77357300 | -1.92244300 | -0.66015300 |
| C | 3.09273600 | -2.29078600 | -0.92890800 |
| C | 4.06279600 | -2.12485700 | 0.05631200 |
| C | 3.67096300 | -1.60009300 | 1.30465500 |
| N | 2.43340400 | -1.24342000 | 1.60972300 |
| C | 0.17933800 | -0.95530400 | 0.93352400 |
| C | -0.92277600 | -0.92083200 | -0.09074500 |
| C | -0.55326300 | -1.62601300 | -1.37414800 |
| C | 0.69807900 | -2.05067900 | -1.62545300 |
| C | -2.17378000 | -1.50631000 | 0.59635500 |
| O | -2.84874700 | -0.87771700 | 1.38597500 |
| O | -2.38628500 | -2.78585200 | 0.26889900 |
| C | -3.53027500 | -3.39842800 | 0.89646600 |
| H | 3.35146800 | -2.69911400 | -1.90338500 |
| H | 5.09899700 | -2.39573300 | -0.12100700 |

| | | | |
|---|---|---|---|
| H | 4.41354100 | -1.46913900 | 2.09126700 |
| H | -0.02633600 | -0.53681200 | 1.91260000 |
| H | -1.34506500 | -1.70940700 | -2.10893000 |
| H | 0.93189200 | -2.50678800 | -2.58551500 |
| H | -3.41379400 | -3.39616900 | 1.98358100 |
| H | -4.44048300 | -2.85479500 | 0.63061900 |
| H | -3.56021200 | -4.41780300 | 0.51179600 |
| C | 3.29296500 | 1.90017600 | -1.14998100 |
| C | 3.74967300 | 2.49053100 | 0.03588800 |
| C | 2.84586500 | 2.76864800 | 1.07024300 |
| C | 1.50106100 | 2.46123800 | 0.93126100 |
| C | 1.02562600 | 1.84405400 | -0.25873900 |
| C | 1.95166600 | 1.58571000 | -1.30867800 |
| C | -0.31816200 | 1.48987200 | -0.40391500 |
| C | -1.25527600 | 0.57221300 | -0.42688700 |
| C | -2.64266700 | 0.81196100 | -0.96497500 |
| O | -3.12367400 | 0.04160300 | -1.77074100 |
| O | -3.33520000 | 1.89627500 | -0.57674700 |
| C | -2.43448800 | 3.91767600 | 0.45573200 |
| C | -3.07751100 | 2.56062100 | 0.68471300 |
| H | 3.99384800 | 1.67691300 | -1.94967300 |
| H | 4.80231500 | 2.73070000 | 0.15405600 |
| H | 3.19994800 | 3.22110600 | 1.99233400 |
| H | 0.80029300 | 2.66190100 | 1.73570000 |
| H | 1.59413800 | 1.10878700 | -2.21543700 |
| H | -2.34502200 | 4.45486000 | 1.40726900 |
| H | -1.43580800 | 3.80712700 | 0.02192500 |
| H | -3.04422500 | 4.51913700 | -0.22613600 |
| H | -4.06541600 | 2.66633400 | 1.14307700 |
| H | -2.47386300 | 1.91389300 | 1.32545400 |




SCF Done: E(ωB97XD) = -1205.424438 a.u.

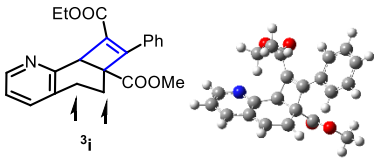
Thermal Correction to Free Energy = 0.303366 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.121072 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 2.22383700 | -0.91079300 | -0.02184000 |
| C | 2.37490200 | -1.70969100 | -1.18510800 |
| C | 3.59892000 | -1.62455200 | -1.87725800 |
| C | 4.59198100 | -0.77584000 | -1.41010900 |
| C | 4.33236200 | -0.02241900 | -0.26015700 |

| | | | |
|---|---|---|---|
| N | 3.17830200 | -0.08472200 | 0.41429900 |
| C | 0.92825000 | -0.91017600 | 0.77539000 |
| C | -0.10729300 | -1.87395600 | 0.25265800 |
| C | 0.10378700 | -2.62053600 | -0.89698000 |
| C | 1.29711900 | -2.55444400 | -1.61359700 |
| C | -1.34862900 | -1.99939000 | 1.03752000 |
| O | -1.53374200 | -1.46866200 | 2.11964300 |
| O | -2.28510000 | -2.76784300 | 0.42292900 |
| H | 3.75090800 | -2.22428100 | -2.77162100 |
| H | 5.54601700 | -0.68868200 | -1.92088300 |
| H | 5.07894300 | 0.66259100 | 0.13637300 |
| H | 1.15662500 | -1.15235200 | 1.82390700 |
| H | -0.68352700 | -3.28479100 | -1.23599600 |
| H | 1.42863800 | -3.15613900 | -2.50878300 |
| C | -4.30789500 | 0.99380900 | -0.38663900 |
| C | -4.36665600 | 1.40795900 | -1.72690100 |
| C | -3.17865200 | 1.66660100 | -2.42708800 |
| C | -1.94700700 | 1.51796100 | -1.81040700 |
| C | -1.86781200 | 1.09216300 | -0.44756700 |
| C | -3.09082600 | 0.83706200 | 0.25458300 |
| C | -0.65998500 | 0.94992200 | 0.19843900 |
| C | 0.40494300 | 0.54677200 | 0.83171700 |
| C | 1.13064000 | 1.42920300 | 1.83356600 |
| O | 1.29640300 | 1.04939400 | 2.96718500 |
| O | 1.51531200 | 2.67196600 | 1.47224300 |
| C | 1.69233500 | 3.06224200 | 0.09597500 |
| H | -5.22753800 | 0.79463200 | 0.15776600 |
| H | -5.32703800 | 1.52985300 | -2.21911300 |
| H | -3.22208600 | 1.98715900 | -3.46473700 |
| H | -1.02706100 | 1.71681800 | -2.35177700 |
| H | -3.03346400 | 0.50574100 | 1.28598500 |
| H | 2.69237400 | 3.50630900 | 0.05378000 |
| H | 1.68548600 | 2.18276400 | -0.55245000 |
| C | 0.62981800 | 4.07114100 | -0.30935600 |
| H | 0.83075700 | 4.44561600 | -1.32016100 |
| H | -0.36443000 | 3.61519700 | -0.29839300 |
| H | 0.62883600 | 4.92031200 | 0.38135000 |
| C | -3.53013200 | -2.88677100 | 1.12475800 |
| H | -3.37061100 | -3.25334300 | 2.14248500 |
| H | -4.03259900 | -1.91585200 | 1.16978700 |
| H | -4.12535800 | -3.59494400 | 0.54678900 |




SCF Done: E(ωB97XD) = -1205.391836 a.u.

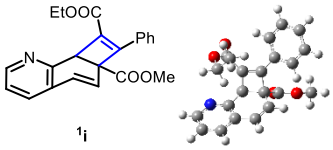
Thermal Correction to Free Energy = 0.303037 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.088799 a.u.

0 3

| | | | |
|---|---|---|---|
| C | -2.36087100 | -0.77162500 | -0.24075600 |
| C | -2.51608000 | -1.07165000 | 1.18584900 |
| C | -3.82618700 | -0.81562200 | 1.74399400 |
| C | -4.82213000 | -0.33668600 | 0.93853300 |
| C | -4.55008900 | -0.09790000 | -0.43714300 |
| N | -3.34298200 | -0.30148100 | -0.99487700 |
| C | -1.00919900 | -0.83607600 | -0.88923700 |
| C | 0.19292200 | -1.37511800 | -0.03401300 |
| C | -0.14860800 | -1.84080400 | 1.33014100 |
| C | -1.45614800 | -1.54111400 | 1.92411200 |
| C | 1.04571400 | -2.40490200 | -0.77419300 |
| O | 0.79202200 | -2.89394500 | -1.85139400 |
| O | 2.16417600 | -2.68108900 | -0.06869900 |
| H | -3.99563200 | -1.01363900 | 2.79949000 |
| H | -5.81559800 | -0.13884800 | 1.33078500 |
| H | -5.32845900 | 0.27325000 | -1.09879100 |
| H | -1.07645600 | -1.31336500 | -1.87051500 |
| H | 0.57717000 | -2.41546100 | 1.89238100 |
| H | -1.58834400 | -1.72945800 | 2.98705100 |
| C | 3.79126600 | 2.33802300 | -0.03765300 |
| C | 4.48652000 | 1.80234900 | 1.05039800 |
| C | 3.97970900 | 0.68255100 | 1.71392500 |
| C | 2.78192500 | 0.10369800 | 1.29991900 |
| C | 2.06815500 | 0.64321100 | 0.21634500 |
| C | 2.59460000 | 1.76337000 | -0.45755500 |
| C | 0.79918400 | 0.06832800 | -0.21137000 |
| C | -0.25333000 | 0.50247900 | -0.92545300 |
| C | -0.58176800 | 1.76843800 | -1.64284200 |
| O | -0.18693600 | 1.97268800 | -2.76912500 |
| O | -1.35709300 | 2.68523200 | -1.02545800 |
| C | -1.66613400 | 2.58648600 | 0.38254200 |
| H | 4.18716000 | 3.20032300 | -0.56708200 |
| H | 5.42177800 | 2.25102400 | 1.37405700 |
| H | 4.51971800 | 0.25813300 | 2.55615900 |
| H | 2.39201900 | -0.76888600 | 1.81170000 |
| H | 2.07076500 | 2.16123700 | -1.32168700 |

| | | | |
|---|---|---|---|
| H | -2.63782600 | 3.07667200 | 0.48255900 |
| H | -1.77997000 | 1.54245300 | 0.68157200 |
| C | -0.59773200 | 3.28012500 | 1.21349000 |
| H | -0.88234300 | 3.27476900 | 2.27201100 |
| H | 0.36460100 | 2.76848800 | 1.11363500 |
| H | -0.47409700 | 4.31828700 | 0.88955300 |
| C | 3.08261900 | -3.59144100 | -0.70104900 |
| H | 2.60865100 | -4.56384500 | -0.86061200 |
| H | 3.40966300 | -3.19153800 | -1.66444500 |
| H | 3.92469700 | -3.67904800 | -0.01418400 |

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SCF Done: E(ωB97XD) = -1205.489828 a.u.

Thermal Correction to Free Energy = 0.309799 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.180029 a.u.

0 1

| | | | |
|---|---|---|---|
| C | -2.39181300 | 0.65471200 | 0.25278600 |
| C | -2.56220000 | 1.03878800 | -1.09491600 |
| C | -3.83829300 | 0.88895800 | -1.65123000 |
| C | -4.86942900 | 0.37227500 | -0.87044300 |
| C | -4.58934600 | 0.02864400 | 0.45267800 |
| N | -3.37810800 | 0.16657600 | 1.00964400 |
| C | -1.03215000 | 0.71737100 | 0.90134100 |
| C | 0.15645300 | 1.31752700 | 0.05684900 |
| C | -0.19837500 | 1.71205100 | -1.35359700 |
| C | -1.43234900 | 1.56684600 | -1.85910300 |
| C | 0.93094600 | 2.41170800 | 0.78778200 |
| O | 0.69989400 | 2.81055400 | 1.90650500 |
| O | 1.96100400 | 2.85618800 | 0.03347700 |
| H | -4.01372800 | 1.17329600 | -2.68641600 |
| H | -5.86858300 | 0.24017200 | -1.27429200 |
| H | -5.36683700 | -0.37623300 | 1.09747900 |
| H | -1.10922200 | 1.15957800 | 1.89846000 |
| H | 0.59307400 | 2.13533200 | -1.96301900 |
| H | -1.62731500 | 1.85818100 | -2.88954700 |
| C | 3.86172300 | -2.28662600 | 0.03747900 |
| C | 4.61537500 | -1.65013500 | -0.95295900 |
| C | 4.13217400 | -0.48154200 | -1.54483500 |
| C | 2.90001900 | 0.04400300 | -1.16036700 |
| C | 2.12553700 | -0.59695700 | -0.17755800 |
| C | 2.63151500 | -1.76541900 | 0.42784000 |

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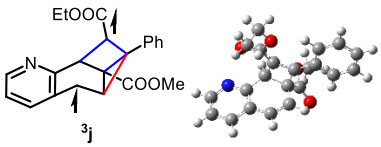
|---|---|---|---|
| C | 0.82236500 | -0.07613500 | 0.22207100 |
| C | -0.23555300 | -0.58489100 | 0.89007800 |
| C | -0.52501500 | -1.89573400 | 1.54590800 |
| O | -0.12675900 | -2.13973900 | 2.66297700 |
| O | -1.26855300 | -2.80795300 | 0.88464400 |
| C | -1.58208200 | -2.65128200 | -0.51732100 |
| H | 4.23851000 | -3.18640000 | 0.51603500 |
| H | 5.57664900 | -2.05765900 | -1.25390800 |
| H | 4.71685600 | 0.02410300 | -2.30876500 |
| H | 2.53854800 | 0.95839500 | -1.61509300 |
| H | 2.06857300 | -2.24341000 | 1.22342600 |
| H | -2.52146800 | -3.19495300 | -0.64574400 |
| H | -1.76253600 | -1.60124700 | -0.75725900 |
| C | -0.47519200 | -3.23232800 | -1.38363200 |
| H | -0.76243200 | -3.18699000 | -2.44047700 |
| H | 0.45466300 | -2.66959200 | -1.25603000 |
| H | -0.28799000 | -4.27717600 | -1.11663400 |
| C | 2.81591900 | 3.82528700 | 0.66823800 |
| H | 2.24750300 | 4.72107900 | 0.93233000 |
| H | 3.25892800 | 3.40370200 | 1.57438000 |
| H | 3.58750100 | 4.05865000 | -0.06580500 |




SCF Done: E(ωB97XD) = -1205.420141 a.u.

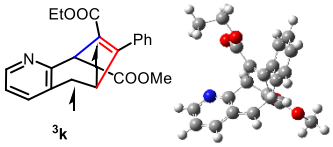
Thermal Correction to Free Energy = 0.305358 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.114783 a.u.

0 3

| | | | |
|---|---|---|---|
| C | -2.27997300 | -0.98809100 | -0.11532000 |
| C | -2.39952900 | -0.85782100 | 1.32083600 |
| C | -3.72697400 | -0.77173000 | 1.84498300 |
| C | -4.79304300 | -0.91040200 | 0.98338400 |
| C | -4.54522500 | -1.14634400 | -0.38557100 |
| N | -3.30994500 | -1.16718600 | -0.92375200 |
| C | -0.91500000 | -0.81475100 | -0.70617500 |
| C | 0.30558200 | -1.34811300 | 0.13795400 |
| C | 0.05432500 | -1.19128600 | 1.58438500 |
| C | -1.24623700 | -0.84734600 | 2.10605000 |
| C | 1.04176100 | -2.58761600 | -0.31674900 |
| O | 1.46291200 | -3.45474300 | 0.42122800 |
| O | 1.21424000 | -2.58416100 | -1.65131000 |
| H | -3.87451900 | -0.63664800 | 2.91345800 |

| | | | |
|---|---|---|---|
| H | -5.81573700 | -0.86839200 | 1.34660200 |
| H | -5.36953900 | -1.30899100 | -1.07553600 |
| H | -0.90458900 | -1.19468800 | -1.73117700 |
| H | 0.88865400 | -1.31372500 | 2.26409200 |
| H | -1.33252600 | -0.66218400 | 3.17367200 |
| C | 4.00097300 | 2.20436600 | 0.33979600 |
| C | 4.92623800 | 1.29086200 | 0.85078500 |
| C | 4.52918500 | -0.02930500 | 1.08423000 |
| C | 3.22680100 | -0.43152100 | 0.80920100 |
| C | 2.27870300 | 0.48464800 | 0.29824100 |
| C | 2.69254900 | 1.81414800 | 0.06859200 |
| C | 0.93320600 | 0.04584800 | -0.02076500 |
| C | -0.24137200 | 0.55277700 | -0.59910900 |
| C | -0.86377600 | 1.80175800 | -0.97039100 |
| O | -1.98536500 | 1.85834500 | -1.46025600 |
| O | -0.11382700 | 2.90741500 | -0.68932100 |
| C | -0.73653900 | 4.18171900 | -0.96441200 |
| H | 4.29975800 | 3.23263000 | 0.15254300 |
| H | 5.94515400 | 1.60218700 | 1.06402700 |
| H | 5.23926500 | -0.75116400 | 1.47898900 |
| H | 2.94443900 | -1.46333800 | 0.99231600 |
| H | 1.97781600 | 2.52638000 | -0.32285800 |
| H | 0.10095300 | 4.88052600 | -1.03910700 |
| H | -1.24988200 | 4.12758200 | -1.92856000 |
| C | -1.69818200 | 4.57626500 | 0.14760600 |
| H | -2.10370100 | 5.57677500 | -0.04259900 |
| H | -2.52840400 | 3.86672800 | 0.19340100 |
| H | -1.18401900 | 4.58724300 | 1.11444000 |
| C | 1.96696200 | -3.69092200 | -2.17975000 |
| H | 2.97368300 | -3.70257500 | -1.75266700 |
| H | 1.47024100 | -4.63680200 | -1.94736400 |
| H | 2.00627200 | -3.52894900 | -3.25694800 |




SCF Done: E(ωB97XD) = -1205.440894 a.u.

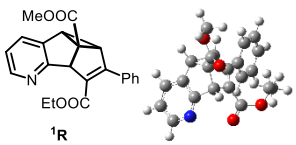
Thermal Correction to Free Energy = 0.306597 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.134297 a.u.

0 3

| | | | |
|---|---|---|---|
| C | -1.60722500 | -1.46740300 | -0.30577300 |
| C | -1.54366000 | -0.88560000 | -1.62478600 |
| C | -1.85390500 | -1.74368500 | -2.70846300 |

| | | | |
|---|---|---|---|
| C | -2.21278700 | -3.05759900 | -2.45372300 |
| C | -2.25569300 | -3.50265900 | -1.12538900 |
| N | -1.95671000 | -2.72283500 | -0.07102900 |
| C | -1.21055700 | -0.56946200 | 0.87181900 |
| C | -1.72761900 | 0.80021600 | 0.56017300 |
| C | -0.83777000 | 1.28700500 | -0.54731100 |
| C | -1.18644300 | 0.47342600 | -1.77982700 |
| C | -2.86993700 | 1.43554800 | 1.15759400 |
| O | -3.56287200 | 0.93672100 | 2.03533100 |
| O | -3.09631600 | 2.67705400 | 0.63569100 |
| H | -1.81502300 | -1.35965900 | -3.72509700 |
| H | -2.46275500 | -3.73656700 | -3.26362500 |
| H | -2.54193800 | -4.52626200 | -0.89369100 |
| H | -1.53522600 | -1.00729500 | 1.81449500 |
| H | -0.86679300 | 2.36099000 | -0.73482600 |
| H | -1.12418900 | 0.92002800 | -2.76799700 |
| C | 3.95789000 | 2.37087900 | 0.16338100 |
| C | 4.09966700 | 2.86873600 | -1.13487800 |
| C | 3.07656600 | 2.67287700 | -2.06411300 |
| C | 1.92103100 | 1.98552800 | -1.69760200 |
| C | 1.77590400 | 1.45829800 | -0.40175300 |
| C | 2.80984400 | 1.67373300 | 0.52740000 |
| C | 0.53635500 | 0.77544400 | -0.01633400 |
| C | 0.30137900 | -0.30736200 | 0.76985500 |
| C | 1.21501800 | -1.28874900 | 1.38823000 |
| O | 0.84071600 | -2.12143500 | 2.19344700 |
| O | 2.49106500 | -1.18448700 | 0.95231900 |
| C | 3.43696700 | -2.13365700 | 1.49712000 |
| H | 4.74285900 | 2.53228400 | 0.89730200 |
| H | 4.99740000 | 3.41206900 | -1.41685700 |
| H | 3.17518800 | 3.05924100 | -3.07493400 |
| H | 1.13205700 | 1.83547000 | -2.42842900 |
| H | 2.69933400 | 1.29653700 | 1.53724900 |
| H | 4.40830600 | -1.65490000 | 1.34871300 |
| H | 3.24856500 | -2.25163900 | 2.56800000 |
| C | 3.34954400 | -3.46878900 | 0.77259800 |
| H | 4.12210900 | -4.15021400 | 1.14697500 |
| H | 2.37074500 | -3.92508900 | 0.94178000 |
| H | 3.49825600 | -3.33173300 | -0.30347400 |
| C | -4.21666800 | 3.36887100 | 1.20283300 |
| H | -5.14157400 | 2.80637600 | 1.04198400 |
| H | -4.07933000 | 3.51293500 | 2.27902500 |
| H | -4.25916900 | 4.33086500 | 0.69000000 |




SCF Done: E(ωB97XD) = -1205.499328 a.u.

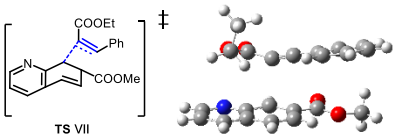
Thermal Correction to Free Energy = 0.312348 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.186980 a.u.

0 1

| | | | |
|---|---|---|---|
| C | 1.61211200 | 1.63369000 | 0.31756200 |
| C | 1.73134000 | 1.56641400 | -1.08677300 |
| C | 1.96221700 | 2.74299700 | -1.78637200 |
| C | 2.08665900 | 3.92070500 | -1.03959100 |
| C | 1.97430900 | 3.86508500 | 0.35150300 |
| N | 1.72712900 | 2.73721000 | 1.04076900 |
| C | 1.22676000 | 0.25812900 | 0.86150800 |
| C | 1.63905900 | -0.69549200 | -0.28280600 |
| C | 0.43814700 | -0.73517000 | -1.20507300 |
| C | 1.65137400 | 0.15901700 | -1.54571000 |
| C | 2.48890000 | -1.87462100 | -0.02107600 |
| O | 2.81662900 | -2.25331900 | 1.08563800 |
| O | 2.83179600 | -2.50914900 | -1.16705000 |
| H | 2.05657500 | 2.75119100 | -2.86925500 |
| H | 2.27978500 | 4.87040500 | -1.52927000 |
| H | 2.08855700 | 4.76880100 | 0.94649100 |
| H | 1.65264900 | 0.01961000 | 1.83658800 |
| H | 0.31225700 | -1.58050200 | -1.87378600 |
| H | 2.23375800 | -0.16631600 | -2.40232500 |
| C | -4.34031400 | 0.71002500 | -1.03658900 |
| C | -4.76869500 | -0.34071100 | -1.85051100 |
| C | -3.86862200 | -1.34668100 | -2.20888800 |
| C | -2.55234400 | -1.30380800 | -1.75348800 |
| C | -2.11082200 | -0.25746200 | -0.92346000 |
| C | -3.02469000 | 0.75616600 | -0.57995100 |
| C | -0.72763900 | -0.23183300 | -0.41390300 |
| C | -0.30519100 | 0.22414300 | 0.78909100 |
| C | -1.13002300 | 0.82834000 | 1.87913000 |
| O | -1.12788800 | 2.01562200 | 2.11258700 |
| O | -1.88732400 | 0.00506200 | 2.64240000 |
| C | -1.90010800 | -1.43084600 | 2.46356700 |
| H | -5.02948000 | 1.50387500 | -0.76213400 |
| H | -5.79435800 | -0.37300500 | -2.20767500 |
| H | -4.19219500 | -2.16777400 | -2.84301400 |
| H | -1.86792800 | -2.10102400 | -2.02944900 |
| H | -2.69355700 | 1.59182000 | 0.02778300 |

| | | | |
|---|---|---|---|
| H | -2.79908300 | -1.74076400 | 3.00259200 |
| H | -2.03729700 | -1.67958300 | 1.40801500 |
| C | -0.66488600 | -2.10199300 | 3.04934600 |
| H | -0.80624400 | -3.18913000 | 3.05740600 |
| H | 0.23786500 | -1.88909000 | 2.46891300 |
| H | -0.50485200 | -1.76815100 | 4.07949700 |
| C | 3.62422200 | -3.69711300 | -0.99360200 |
| H | 4.56871200 | -3.45817600 | -0.49719000 |
| H | 3.08492600 | -4.43375100 | -0.39137200 |
| H | 3.80370800 | -4.07850700 | -1.99927400 |




SCF Done: E(ωB97XD) = -1205.375981 a.u.

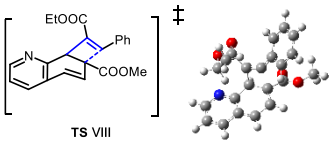
Thermal Correction to Free Energy = 0.299261 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.076720 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 2.10154400 | -1.28493400 | 0.17170000 |
| C | 2.14119300 | -1.41035600 | -1.26099700 |
| C | 3.37834100 | -1.30784400 | -1.89039800 |
| C | 4.53175000 | -1.08159100 | -1.11017400 |
| C | 4.38777600 | -0.99016400 | 0.26679600 |
| N | 3.20803800 | -1.09365100 | 0.91274700 |
| C | 0.83494500 | -1.31479400 | 0.83764000 |
| C | -0.38747400 | -1.63790100 | 0.08554100 |
| C | -0.31481000 | -1.76927500 | -1.29508900 |
| C | 0.90360700 | -1.63798500 | -1.96692800 |
| C | -1.63800800 | -1.80669200 | 0.83510000 |
| O | -1.73844400 | -1.68123900 | 2.04568700 |
| O | -2.69048700 | -2.12147100 | 0.03333300 |
| H | 3.44816500 | -1.40074900 | -2.97162300 |
| H | 5.50984800 | -0.99032400 | -1.57157100 |
| H | 5.25402900 | -0.82235800 | 0.90323600 |
| H | 0.80556100 | -1.30959600 | 1.91991100 |
| H | -1.21978500 | -1.97604200 | -1.85498900 |
| H | 0.93576100 | -1.73529200 | -3.04926500 |
| C | -4.46848600 | 1.21839900 | 0.19000400 |
| C | -4.64143400 | 1.35005200 | -1.19257800 |
| C | -3.52485000 | 1.44948000 | -2.03113200 |
| C | -2.24276400 | 1.42152800 | -1.49718500 |
| C | -2.05828600 | 1.28369500 | -0.10127400 |
| C | -3.19238600 | 1.18208500 | 0.73910900 |

| | | | |
|---|---|---|---|
| C | -0.76423200 | 1.24071600 | 0.45210400 |
| C | 0.36029200 | 1.12794500 | 0.94179700 |
| C | 1.56517300 | 1.51551200 | 1.66845800 |
| O | 1.64424400 | 1.43984900 | 2.87223300 |
| O | 2.61302000 | 1.95851200 | 0.93589100 |
| C | 2.50780600 | 2.12039600 | -0.49363600 |
| H | -5.33517700 | 1.14149100 | 0.84080600 |
| H | -5.64186000 | 1.37723100 | -1.61508800 |
| H | -3.65924400 | 1.55096700 | -3.10448600 |
| H | -1.37056700 | 1.49435300 | -2.13946600 |
| H | -3.04467700 | 1.05612200 | 1.80643500 |
| H | 3.53003700 | 1.98437100 | -0.85510600 |
| H | 1.89069300 | 1.32391800 | -0.91840400 |
| C | 1.96092900 | 3.49478900 | -0.84807600 |
| H | 1.97235200 | 3.63801400 | -1.93493300 |
| H | 0.92908000 | 3.59913200 | -0.49722100 |
| H | 2.56701000 | 4.28005400 | -0.38579400 |
| C | -3.92898900 | -2.34722500 | 0.71842600 |
| H | -3.83692500 | -3.18788600 | 1.41291600 |
| H | -4.22966900 | -1.45687700 | 1.27514200 |
| H | -4.65738400 | -2.57118400 | -0.06211900 |



TS VIII

SCF Done: E(ωB97XD) = -1205.376275 a.u.

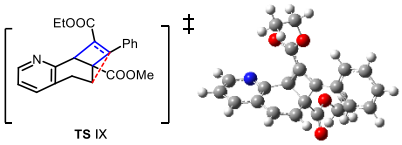
Thermal Correction to Free Energy = 0.301406 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.074869 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 2.39359700 | -0.79319800 | 0.27139800 |
| C | 2.60232300 | -1.19165100 | -1.10766600 |
| C | 3.90206100 | -0.92752600 | -1.65224000 |
| C | 4.85961000 | -0.33322300 | -0.86817600 |
| C | 4.53621400 | 0.01233000 | 0.46736200 |
| N | 3.33279000 | -0.20509000 | 1.01111800 |
| C | 1.03163100 | -0.87814500 | 0.89360000 |
| C | -0.05162800 | -1.57677900 | 0.04205300 |
| C | 0.29052900 | -2.09768200 | -1.21809200 |
| C | 1.57850000 | -1.79761400 | -1.82741100 |
| C | -1.14346900 | -2.25871300 | 0.81658400 |
| O | -1.13894800 | -2.43561400 | 2.01602800 |
| O | -2.16580400 | -2.61341900 | 0.00699000 |
| H | 4.10874100 | -1.20333800 | -2.68360100 |

| | | | |
|---|---|---|---|
| H | 5.85192000 | -0.12140700 | -1.25552000 |
| H | 5.27462400 | 0.48756900 | 1.10896500 |
| H | 1.08178400 | -1.27222100 | 1.91328900 |
| H | -0.43811600 | -2.68006300 | -1.76960600 |
| H | 1.75428200 | -2.09856000 | -2.85677900 |
| C | -4.09183100 | 1.84441800 | 0.23149000 |
| C | -4.56898300 | 1.59843600 | -1.06030100 |
| C | -3.78217500 | 0.88885100 | -1.97399700 |
| C | -2.52254800 | 0.42895200 | -1.60384000 |
| C | -2.02745000 | 0.68446600 | -0.30926700 |
| C | -2.83441200 | 1.38659000 | 0.61347200 |
| C | -0.74215200 | 0.19659800 | 0.09710500 |
| C | 0.31048300 | 0.47910400 | 0.84819800 |
| C | 0.67927500 | 1.71560900 | 1.60954500 |
| O | 0.39528000 | 1.82612900 | 2.77977900 |
| O | 1.33577200 | 2.70759400 | 0.97328100 |
| C | 1.64309700 | 2.63438500 | -0.43633500 |
| H | -4.70343300 | 2.39269200 | 0.94283600 |
| H | -5.55298000 | 1.95443300 | -1.35286400 |
| H | -4.15609100 | 0.69252500 | -2.97524200 |
| H | -1.90895400 | -0.13419200 | -2.30063300 |
| H | -2.45243500 | 1.56580800 | 1.61448700 |
| H | 2.59979300 | 3.15432500 | -0.53418700 |
| H | 1.78649400 | 1.59615100 | -0.74558400 |
| C | 0.55488000 | 3.30985600 | -1.25593300 |
| H | 0.84090600 | 3.33356100 | -2.31389900 |
| H | -0.39183500 | 2.76845800 | -1.16766000 |
| H | 0.40051600 | 4.33762600 | -0.91268900 |
| C | -3.29873700 | -3.19366300 | 0.67534900 |
| H | -3.71456300 | -2.48516000 | 1.39710700 |
| H | -4.02205400 | -3.40909700 | -0.11160400 |
| H | -3.01141800 | -4.10942500 | 1.19934100 |




SCF Done: E(ωB97XD) = -1205.388740 a.u.

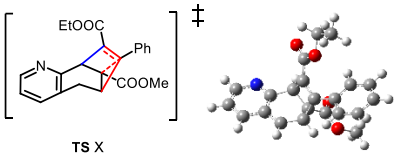
Thermal Correction to Free Energy = 0.3033 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.085440 a.u.

0 3

| | | | |
|---|---|---|---|
| C | -2.27997300 | -0.98809100 | -0.11532000 |
| C | -2.39952900 | -0.85782100 | 1.32083600 |
| C | -3.72697400 | -0.77173000 | 1.84498300 |

| | | | |
|---|---|---|---|
| C | -4.79304300 | -0.91040200 | 0.98338400 |
| C | -4.54522500 | -1.14634400 | -0.38557100 |
| N | -3.30994500 | -1.16718600 | -0.92375200 |
| C | -0.91500000 | -0.81475100 | -0.70617500 |
| C | 0.30558200 | -1.34811300 | 0.13795400 |
| C | 0.05432500 | -1.19128600 | 1.58438500 |
| C | -1.24623700 | -0.84734600 | 2.10605000 |
| C | 1.04176100 | -2.58761600 | -0.31674900 |
| O | 1.46291200 | -3.45474300 | 0.42122800 |
| O | 1.21424000 | -2.58416100 | -1.65131000 |
| H | -3.87451900 | -0.63664800 | 2.91345800 |
| H | -5.81573700 | -0.86839200 | 1.34660200 |
| H | -5.36953900 | -1.30899100 | -1.07553600 |
| H | -0.90458900 | -1.19468800 | -1.73117700 |
| H | 0.88865400 | -1.31372500 | 2.26409200 |
| H | -1.33252600 | -0.66218400 | 3.17367200 |
| C | 4.00097300 | 2.20436600 | 0.33979600 |
| C | 4.92623800 | 1.29086200 | 0.85078500 |
| C | 4.52918500 | -0.02930500 | 1.08423000 |
| C | 3.22680100 | -0.43152100 | 0.80920100 |
| C | 2.27870300 | 0.48464800 | 0.29824100 |
| C | 2.69254900 | 1.81414800 | 0.06859200 |
| C | 0.93320600 | 0.04584800 | -0.02076500 |
| C | -0.24137200 | 0.55277700 | -0.59910900 |
| C | -0.86377600 | 1.80175800 | -0.97039100 |
| O | -1.98536500 | 1.85834500 | -1.46025600 |
| O | -0.11382700 | 2.90741500 | -0.68932100 |
| C | -0.73653900 | 4.18171900 | -0.96441200 |
| H | 4.29975800 | 3.23263000 | 0.15254300 |
| H | 5.94515400 | 1.60218700 | 1.06402700 |
| H | 5.23926500 | -0.75116400 | 1.47898900 |
| H | 2.94443900 | -1.46333800 | 0.99231600 |
| H | 1.97781600 | 2.52638000 | -0.32285800 |
| H | 0.10095300 | 4.88052600 | -1.03910700 |
| H | -1.24988200 | 4.12758200 | -1.92856000 |
| C | -1.69818200 | 4.57626500 | 0.14760600 |
| H | -2.10370100 | 5.57677500 | -0.04259900 |
| H | -2.52840400 | 3.86672800 | 0.19340100 |
| H | -1.18401900 | 4.58724300 | 1.11444000 |
| C | 1.96696200 | -3.69092200 | -2.17975000 |
| H | 2.97368300 | -3.70257500 | -1.75266700 |
| H | 1.47024100 | -4.63680200 | -1.94736400 |
| H | 2.00627200 | -3.52894900 | -3.25694800 |




SCF Done: E(ωB97XD) = -1205.413951 a.u.

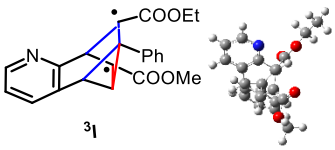
Thermal Correction to Free Energy = 0.304895 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.109056 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 2.81106200 | -0.11161700 | -0.17642100 |
| C | 2.89628300 | 0.19653800 | 1.22391500 |
| C | 4.11929900 | -0.11461600 | 1.86991300 |
| C | 5.15283400 | -0.66839000 | 1.13091100 |
| C | 4.96031900 | -0.89622300 | -0.23804500 |
| N | 3.80899600 | -0.62589000 | -0.88125300 |
| C | 1.48375900 | 0.12092000 | -0.85695900 |
| C | 0.76918900 | 1.37848700 | -0.35152500 |
| C | 0.58735000 | 1.22675500 | 1.12021500 |
| C | 1.79647300 | 0.79119600 | 1.87675400 |
| C | 0.17074900 | 2.38067900 | -1.21948900 |
| O | 0.29075100 | 2.40123400 | -2.43287600 |
| O | -0.58191000 | 3.27042400 | -0.51742800 |
| H | 4.23464000 | 0.09123900 | 2.93148000 |
| H | 6.10221000 | -0.91741000 | 1.59603100 |
| H | 5.75809800 | -1.31553000 | -0.84708600 |
| H | 1.58047100 | 0.05927400 | -1.94157500 |
| H | 0.04292200 | 2.04853500 | 1.58029800 |
| H | 1.84342500 | 0.99647200 | 2.94263300 |
| C | -4.08457200 | 0.16764300 | -0.16121400 |
| C | -4.59507900 | 0.50760200 | 1.09594400 |
| C | -3.72331800 | 0.75254300 | 2.15836600 |
| C | -2.34556100 | 0.65936900 | 1.96502700 |
| C | -1.82359600 | 0.30511300 | 0.71217600 |
| C | -2.71026500 | 0.06479800 | -0.35123200 |
| C | -0.36926400 | 0.20191600 | 0.50393400 |
| C | 0.33148400 | -0.72574200 | -0.33251400 |
| C | -0.06073900 | -2.00844400 | -0.87605900 |
| O | 0.54055500 | -2.58459000 | -1.77125500 |
| O | -1.16902000 | -2.51187800 | -0.26545000 |
| C | -1.66764400 | -3.75663400 | -0.79148600 |
| H | -4.75971400 | -0.01182700 | -0.99342700 |
| H | -5.66874100 | 0.58591700 | 1.24397300 |
| H | -4.11528300 | 1.01666300 | 3.13661500 |
| H | -1.66787900 | 0.84262400 | 2.79428100 |
| H | -2.30873900 | -0.19139800 | -1.32647100 |

| | | | |
|---|---|---|---|
| H | -1.82631800 | -3.65237200 | -1.87083700 |
| H | -0.91188400 | -4.53704500 | -0.64705900 |
| C | -2.95710100 | -4.06059700 | -0.05075000 |
| H | -3.39335300 | -4.99563700 | -0.41883400 |
| H | -2.77110100 | -4.16197300 | 1.02331700 |
| H | -3.68166700 | -3.25269600 | -0.19590500 |
| C | -1.29629500 | 4.22111400 | -1.32071100 |
| H | -1.84573000 | 4.84597700 | -0.61554900 |
| H | -0.60319800 | 4.82512300 | -1.91327800 |
| H | -1.98633500 | 3.70932100 | -1.99825000 |




$^3$I

SCF Done: E(ωB97XD) = -1205.444003 a.u.

Thermal Correction to Free Energy = 0.306341 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.137662 a.u.

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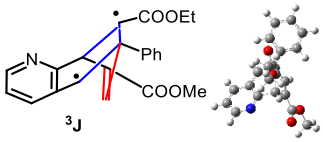
|---|---|---|---|
| C | -0.87220800 | -0.51366200 | 0.41441400 |
| C | -0.01929500 | -0.95692000 | 1.61651100 |
| C | 1.27356000 | 0.25216000 | -0.41352200 |
| C | -0.20943900 | 0.57166800 | -0.34465100 |
| C | 0.11605100 | -1.72161300 | 0.29179000 |
| H | 1.83899600 | 0.76668300 | -1.18712200 |
| H | -0.55976400 | -1.48152500 | 2.39925300 |
| C | 1.11458800 | -0.09018500 | 2.02571400 |
| C | 1.81725900 | 0.55771300 | 0.98816500 |
| C | 3.23906300 | 1.57763100 | 2.44065400 |
| H | 4.08659400 | 2.24656300 | 2.57535200 |
| C | 2.62097400 | 0.98822600 | 3.54301200 |
| H | 2.98171900 | 1.19348700 | 4.54628800 |
| C | -2.34877100 | -0.72511700 | 0.40950900 |
| C | -3.11730900 | -0.55103900 | 1.56453700 |
| C | -2.98318300 | -1.10710300 | -0.78038500 |
| C | -4.49716000 | -0.75778100 | 1.53409300 |
| H | -2.63531700 | -0.23442000 | 2.48546800 |
| C | -4.35999900 | -1.31299600 | -0.81292700 |
| H | -2.38732000 | -1.23981000 | -1.67986900 |
| C | -5.12147100 | -1.14040900 | 0.34641300 |
| H | -5.08405400 | -0.61401300 | 2.43733600 |
| H | -4.84027200 | -1.60901000 | -1.74169900 |
| H | -6.19580300 | -1.30166900 | 0.32205300 |
| C | -0.83365900 | 1.80447200 | -0.77438600 |

| | | | |
|---|---|---|---|
| O | -1.99880700 | 2.11452200 | -0.56443800 |
| O | 0.04450300 | 2.59251700 | -1.45036300 |
| C | -0.47350000 | 3.86037100 | -1.90142100 |
| H | -1.32425200 | 3.68088000 | -2.56865500 |
| H | -0.84873400 | 4.41945300 | -1.03694600 |
| C | 0.66307600 | 4.58182300 | -2.60073800 |
| H | 1.02219200 | 4.00095400 | -3.45631600 |
| H | 0.32205000 | 5.55843700 | -2.96135500 |
| H | 1.50170200 | 4.73622300 | -1.91444200 |
| C | 1.22049800 | -1.25147500 | -0.54098700 |
| C | 2.07182500 | -2.01874900 | -1.41309700 |
| O | 2.93518400 | -1.54243500 | -2.13883100 |
| O | 1.80252300 | -3.35547400 | -1.34461800 |
| C | 2.61585800 | -4.17492000 | -2.19499300 |
| H | 2.28159600 | -5.19917300 | -2.02376000 |
| H | 2.48154000 | -3.89728700 | -3.24505900 |
| H | 3.67438300 | -4.06805000 | -1.93872600 |
| H | -0.25457100 | -2.73734000 | 0.23338000 |
| N | 2.84948200 | 1.37233900 | 1.17044000 |
| C | 1.53327900 | 0.13482100 | 3.33229800 |
| H | 1.02547900 | -0.34129700 | 4.16773700 |




SCF Done: E(ωB97XD) = -1205.434584 a.u.

Thermal Correction to Free Energy = 0.305663 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.128921 a.u.

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| | | | |
|---|---|---|---|
| C | 0.82039500 | -0.67474600 | -0.43056400 |
| C | 0.26606900 | -0.31745100 | -1.80872200 |
| C | -1.11439800 | 0.28467900 | 0.61584200 |
| C | 0.37329700 | 0.46390200 | 0.47662800 |
| C | -0.13919300 | -1.77784400 | 0.05169000 |
| H | -1.59787500 | 0.80660300 | 1.44010200 |
| H | 0.76394500 | -0.69542600 | -2.69697800 |
| C | -0.95604500 | 0.39200300 | -1.91278700 |
| C | -1.68492700 | 0.76826500 | -0.72657000 |
| C | -3.30795200 | 1.83366700 | -1.93425100 |
| H | -4.22500400 | 2.41813600 | -1.90758100 |
| C | -2.71555800 | 1.49106400 | -3.15677400 |
| H | -3.17504900 | 1.80168100 | -4.09040300 |
| C | 2.29151200 | -1.04881000 | -0.40563900 |

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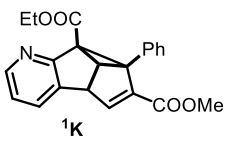
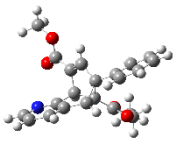
|---|---|---|---|
| C | 3.20503100 | -0.48577700 | -1.30367500 |
| C | 2.75910900 | -1.95808400 | 0.55042800 |
| C | 4.55212900 | -0.84084100 | -1.26130500 |
| H | 2.86546500 | 0.25707900 | -2.01823800 |
| C | 4.10784000 | -2.31309900 | 0.59742000 |
| H | 2.06448800 | -2.38740100 | 1.26811600 |
| C | 5.00809700 | -1.75959000 | -0.31357100 |
| H | 5.24858000 | -0.39118200 | -1.96391300 |
| H | 4.45260400 | -3.02212200 | 1.34545200 |
| H | 6.05862000 | -2.03587400 | -0.28114600 |
| C | 1.10580400 | 1.68652300 | 0.73251600 |
| O | 2.23142500 | 1.93970900 | 0.32574700 |
| O | 0.37157800 | 2.54424400 | 1.49075300 |
| C | 0.99351700 | 3.81317800 | 1.77919800 |
| H | 1.93143000 | 3.63602200 | 2.31763500 |
| H | 1.24709500 | 4.30794300 | 0.83493400 |
| C | 0.00296500 | 4.61810500 | 2.59908700 |
| H | -0.23633600 | 4.10126800 | 3.53393800 |
| H | 0.42635700 | 5.59879600 | 2.84211300 |
| H | -0.92712500 | 4.76768100 | 2.04163000 |
| C | -1.21590600 | -1.23875500 | 0.64753900 |
| C | -2.41371100 | -1.92554900 | 1.15479700 |
| O | -3.37102100 | -1.35835200 | 1.64418300 |
| O | -2.32224400 | -3.27312200 | 1.02873700 |
| C | -3.45643300 | -4.00390300 | 1.52060200 |
| H | -3.22471900 | -5.05559300 | 1.34789100 |
| H | -3.60554600 | -3.81225700 | 2.58730000 |
| H | -4.36386800 | -3.71555200 | 0.98193700 |
| H | 0.01613400 | -2.82586100 | -0.17383900 |
| N | -2.80529200 | 1.47281300 | -0.73998100 |
| C | -1.53514800 | 0.76393600 | -3.14963500 |
| H | -1.03902000 | 0.49128600 | -4.07796000 |





SCF Done: E(ωB97XD) = -1205.507293 a.u.

Thermal Correction to Free Energy = 0.310306 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.196987 a.u.

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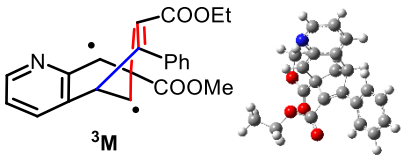
| | | | |
|---|---|---|---|
| C | 0.64929300 | 0.87770800 | 0.12607200 |
| C | 0.18394500 | 0.55199400 | 1.57596400 |
| C | -1.08807100 | -0.85755300 | 0.03323400 |

| | | | |
|---|---|---|---|
| C | 0.33726000 | -0.56549400 | 0.56592000 |
| C | -0.36214600 | 1.17949600 | -0.92390200 |
| H | -1.29205900 | -1.88129700 | -0.27547900 |
| H | 0.96091700 | 0.67002600 | 2.32549500 |
| C | -1.24357900 | 0.56615900 | 1.96701700 |
| C | -1.97884000 | -0.33477100 | 1.16541400 |
| C | -3.89719200 | 0.05954500 | 2.30096200 |
| H | -4.95391300 | -0.16834600 | 2.42657600 |
| C | -3.27123000 | 0.97522900 | 3.14885500 |
| H | -3.84123300 | 1.46468800 | 3.93283800 |
| C | 2.04391400 | 1.38130100 | -0.08051200 |
| C | 2.59452300 | 2.37234000 | 0.73755100 |
| C | 2.79898400 | 0.88695400 | -1.15287400 |
| C | 3.88026300 | 2.85809700 | 0.49430800 |
| H | 2.01163200 | 2.76476900 | 1.56650200 |
| C | 4.08342900 | 1.36871400 | -1.39676800 |
| H | 2.37248300 | 0.11418900 | -1.78799900 |
| C | 4.62771600 | 2.35688900 | -0.57232400 |
| H | 4.29734600 | 3.62740200 | 1.13864600 |
| H | 4.66153100 | 0.97139200 | -2.22678200 |
| H | 5.63007400 | 2.73225000 | -0.75991900 |
| C | 1.41969700 | -1.56902300 | 0.70320800 |
| O | 2.43391600 | -1.39754000 | 1.34889000 |
| O | 1.15342500 | -2.68317700 | -0.01030900 |
| C | 2.16320700 | -3.71884300 | 0.04155600 |
| H | 3.10854000 | -3.30533000 | -0.32550500 |
| H | 2.31475700 | -4.01116400 | 1.08599900 |
| C | 1.66583100 | -4.86917500 | -0.81224800 |
| H | 1.51303600 | -4.54639100 | -1.84703000 |
| H | 2.39889400 | -5.68309200 | -0.80645600 |
| H | 0.71583500 | -5.25425400 | -0.42834000 |
| C | -1.26942400 | 0.19434800 | -1.05612700 |
| C | -2.40323900 | 0.13408500 | -1.99570700 |
| O | -3.14563500 | -0.82111300 | -2.10621400 |
| O | -2.50634600 | 1.25708400 | -2.74977600 |
| C | -3.56850700 | 1.23865400 | -3.71576100 |
| H | -3.51518300 | 2.19982200 | -4.22858100 |
| H | -3.43232700 | 0.41602700 | -4.42420900 |
| H | -4.53644200 | 1.11856900 | -3.22055400 |
| H | -0.33561500 | 2.08983300 | -1.51109900 |
| N | -3.27349700 | -0.58844400 | 1.29970400 |
| C | -1.90843700 | 1.24721800 | 2.97732300 |
| H | -1.39104500 | 1.95475500 | 3.62027000 |




SCF Done: E(ωB97XD) = -1205.410967 a.u.

Thermal Correction to Free Energy = 0.307447 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.103520 a.u.

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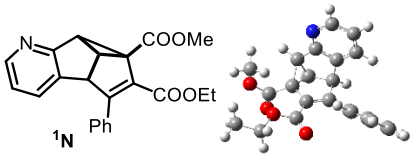
| | | | |
|---|---|---|---|
| C | 1.05276600 | -0.25246900 | -0.66966000 |
| C | 0.84253700 | 1.15387100 | -1.27894600 |
| C | -1.47134200 | 1.12645800 | 0.39003200 |
| C | -0.16956400 | -0.77846600 | -0.39904300 |
| C | -0.52754600 | 1.00103200 | -1.87350100 |
| H | -2.27436300 | 0.95437200 | 1.09696100 |
| H | 1.63513100 | 1.44201900 | -1.97615600 |
| C | 0.68082600 | 2.20166700 | -0.17107400 |
| C | -0.48409100 | 2.10707600 | 0.66436000 |
| C | 0.20606200 | 3.90384300 | 1.92847300 |
| H | 0.01386000 | 4.55785800 | 2.77804200 |
| C | 1.34025800 | 4.11329500 | 1.12797700 |
| H | 2.02083500 | 4.93116900 | 1.34306700 |
| C | 2.40388800 | -0.77203000 | -0.42445000 |
| C | 3.44720800 | 0.11312100 | -0.08653800 |
| C | 2.71075500 | -2.13725300 | -0.58208200 |
| C | 4.74384000 | -0.35230000 | 0.11410200 |
| H | 3.23570000 | 1.16725200 | 0.05180800 |
| C | 4.01232900 | -2.59566400 | -0.38949400 |
| H | 1.92282900 | -2.82778400 | -0.84994800 |
| C | 5.03300900 | -1.71018400 | -0.03855700 |
| H | 5.52928200 | 0.34646600 | 0.38972600 |
| H | 4.22846500 | -3.65268100 | -0.51864900 |
| H | 6.04616300 | -2.07348000 | 0.11163300 |
| C | -0.51657800 | -1.98532800 | 0.38599700 |
| O | 0.06686500 | -3.05099400 | 0.38021800 |
| O | -1.60903800 | -1.74139300 | 1.14547900 |
| C | -2.19274500 | -2.88594500 | 1.80601600 |
| H | -2.31742100 | -3.68510300 | 1.06891100 |
| H | -1.50083000 | -3.24161900 | 2.57700100 |
| C | -3.51821200 | -2.42851100 | 2.38414700 |
| H | -4.17846800 | -2.07543400 | 1.58548800 |
| H | -4.00984400 | -3.25970200 | 2.90115800 |
| H | -3.37026800 | -1.61370800 | 3.10070500 |
| C | -1.27815700 | 0.22063100 | -0.81756500 |
| C | -2.54378700 | -0.47785400 | -1.33196600 |

| | | | |
|---|---|---|---|
| O | -2.57840800 | -1.66323900 | -1.55764600 |
| O | -3.67449700 | 0.24803500 | -1.51966500 |
| C | -3.69270100 | 1.67475100 | -1.65434000 |
| H | -4.73654800 | 1.96681300 | -1.52676800 |
| H | -3.08023500 | 2.17767000 | -0.90051200 |
| H | -3.35890200 | 1.96350300 | -2.65711800 |
| H | -0.98540200 | 1.74783800 | -2.51242300 |
| H | 2.44771400 | 3.35841500 | -0.57288900 |
| C | 1.57274100 | 3.23870900 | 0.06243200 |
| N | -0.68800900 | 2.94373700 | 1.72070600 |




SCF Done: E(ωB97XD) = -1205.494397 a.u.

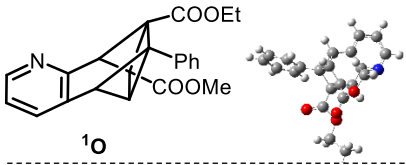
Thermal Correction to Free Energy = 0.312573 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.181824 a.u.

0 1

| | | | |
|---|---|---|---|
| C | 0.90351600 | -0.34503400 | -0.76444900 |
| C | 1.05773900 | 1.00120000 | -1.48580100 |
| C | -0.92263000 | 2.12350500 | -0.63785400 |
| C | -0.39266300 | -0.50067600 | -0.38004600 |
| C | -0.39151200 | 1.40762600 | -1.84913900 |
| H | -1.76251500 | 2.80641600 | -0.70616100 |
| H | 1.77358100 | 0.99451300 | -2.30997700 |
| C | 1.41882400 | 1.93769700 | -0.33670900 |
| C | 0.24133700 | 2.49545000 | 0.20041100 |
| C | 1.37158000 | 3.50754900 | 1.88257300 |
| H | 1.33513600 | 4.14468600 | 2.76418100 |
| C | 2.59497500 | 3.00040300 | 1.43659000 |
| H | 3.50831000 | 3.24494100 | 1.97041700 |
| C | 2.11040800 | -1.11712600 | -0.41990400 |
| C | 3.07529400 | -1.36331100 | -1.41162100 |
| C | 2.36945300 | -1.54438800 | 0.89241200 |
| C | 4.25407400 | -2.04234000 | -1.10641000 |
| H | 2.89090000 | -1.04092500 | -2.43279300 |
| C | 3.55368400 | -2.20808400 | 1.19960800 |
| H | 1.63667200 | -1.35077300 | 1.66653000 |
| C | 4.49838900 | -2.46305100 | 0.20189000 |
| H | 4.98151500 | -2.23884900 | -1.88923400 |
| H | 3.74014900 | -2.52806400 | 2.22103400 |
| H | 5.42041100 | -2.98471300 | 0.44386100 |
| C | -0.92957200 | -1.66467400 | 0.35847200 |

| | | | |
|---|---|---|---|
| O | -0.32986100 | -2.68614900 | 0.62919300 |
| O | -2.23352400 | -1.47117800 | 0.67544400 |
| C | -2.93083400 | -2.60277600 | 1.24399100 |
| H | -2.83864100 | -3.44729500 | 0.55352700 |
| H | -2.44173100 | -2.88539400 | 2.18206400 |
| C | -4.37420300 | -2.18057400 | 1.44306000 |
| H | -4.80376700 | -1.83301500 | 0.49856200 |
| H | -4.96377600 | -3.02744700 | 1.81003500 |
| H | -4.44535300 | -1.36940600 | 2.17488900 |
| C | -1.25625700 | 0.60987000 | -0.91302900 |
| C | -2.67538600 | 0.29731800 | -1.35305700 |
| O | -2.89581800 | -0.30109800 | -2.37918900 |
| O | -3.71722000 | 0.74276800 | -0.61320700 |
| C | -3.56054900 | 1.28383600 | 0.70666500 |
| H | -4.45220800 | 0.97875500 | 1.25820100 |
| H | -2.67503100 | 0.89624800 | 1.20916400 |
| H | -3.51764400 | 2.37646400 | 0.66464400 |
| H | -0.69636000 | 1.62729400 | -2.86699200 |
| H | 3.55241300 | 1.73112900 | -0.04625600 |
| C | 2.62475000 | 2.17159500 | 0.30845800 |
| N | 0.18954600 | 3.25808500 | 1.29138500 |




SCF Done: E(ωB97XD) = -1205.455235 a.u.

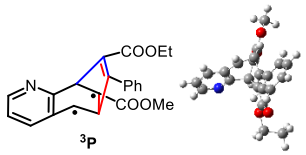
Thermal Correction to Free Energy = 0.309716 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.145519 a.u.

0 1

| | | | |
|---|---|---|---|
| C | -1.00002200 | 0.52480700 | 0.31789700 |
| C | -0.34237600 | 1.89634200 | 0.60027700 |
| C | 1.42656300 | 0.12517900 | -0.45068400 |
| C | 0.02579000 | -0.47347700 | -0.30323500 |
| C | -0.10478500 | 0.70977600 | 1.52048500 |
| H | 2.14257300 | -0.56566900 | -0.88181200 |
| H | -1.06711800 | 2.60526600 | 0.99461700 |
| C | 0.72129000 | 2.45826800 | -0.24473400 |
| C | 1.63791400 | 1.54444900 | -0.78394100 |
| C | 2.81957500 | 3.18892600 | -1.83238700 |
| H | 3.66669500 | 3.45223500 | -2.46291600 |
| C | 1.95615700 | 4.18231300 | -1.35949700 |
| H | 2.12428200 | 5.22237400 | -1.62218400 |
| C | -2.47719100 | 0.42556800 | 0.22789000 |

| | | | |
|---|---|---|---|
| C | -3.27234100 | 0.54457100 | 1.37334800 |
| C | -3.09987100 | 0.28043800 | -1.01952300 |
| C | -4.66485700 | 0.53009700 | 1.27596400 |
| H | -2.80024700 | 0.63736800 | 2.34818300 |
| C | -4.48859600 | 0.25889300 | -1.11637500 |
| H | -2.48971000 | 0.16832800 | -1.91040100 |
| C | -5.27707800 | 0.38746600 | 0.03071700 |
| H | -5.26868000 | 0.61949600 | 2.17519200 |
| H | -4.95781800 | 0.13738300 | -2.08896900 |
| H | -6.36078700 | 0.36875100 | -0.04668600 |
| C | -0.33226300 | -1.80288200 | -0.86528500 |
| O | -1.45403900 | -2.26395800 | -0.87176300 |
| O | 0.76193300 | -2.44584200 | -1.31524800 |
| C | 0.62914200 | -3.86839800 | -1.54522600 |
| H | -0.05855100 | -4.27966200 | -0.80188300 |
| H | 0.19113700 | -4.02038800 | -2.53811700 |
| C | 2.01968300 | -4.46209500 | -1.42443700 |
| H | 2.41403900 | -4.27415200 | -0.42134600 |
| H | 1.98249100 | -5.54387900 | -1.59410500 |
| H | 2.69989500 | -4.01937600 | -2.15978300 |
| C | 0.91013500 | -0.29129100 | 0.92469900 |
| C | 1.58726600 | -1.36071000 | 1.71978300 |
| O | 1.37926200 | -2.54364000 | 1.58426400 |
| O | 2.47668400 | -0.93927900 | 2.65444600 |
| C | 2.90798200 | 0.43117000 | 2.66974700 |
| H | 3.71312600 | 0.47118200 | 3.40481100 |
| H | 3.28786700 | 0.74245800 | 1.69165800 |
| H | 2.10282100 | 1.10644900 | 2.97745100 |
| H | -0.37057300 | 0.72300400 | 2.57219300 |
| H | 0.19365500 | 4.55119800 | -0.15496700 |
| C | 0.88596100 | 3.81006700 | -0.54746900 |
| N | 2.67653000 | 1.88607500 | -1.55751500 |




SCF Done: E(ωB97XD) = -1205.426424 a.u.

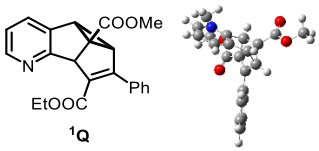
Thermal Correction to Free Energy = 0.306688 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.119736 a.u.

0 3

| | | | |
|---|---|---|---|
| C | -0.75320400 | -0.68986400 | 0.05547100 |
| C | 0.34913900 | -1.07741200 | 1.55716300 |
| C | 1.23515800 | 0.54849000 | -0.45508800 |

| | | | |
|---|---|---|---|
| C | -0.29680600 | 0.54782900 | -0.45868300 |
| C | 0.46003800 | -1.61648800 | 0.15900000 |
| H | 1.71008400 | 1.19941800 | -1.18566300 |
| H | -0.22192100 | -1.64898900 | 2.28082200 |
| C | 1.13904600 | 0.06070300 | 1.97981200 |
| C | 1.66355900 | 0.91429100 | 0.97170000 |
| C | 2.66771400 | 2.27636900 | 2.49669100 |
| H | 3.29156100 | 3.15078400 | 2.66926500 |
| C | 2.17156400 | 1.53515500 | 3.57074200 |
| H | 2.39960300 | 1.83148600 | 4.59010600 |
| C | -2.13326200 | -1.19002100 | 0.25382600 |
| C | -3.08262400 | -0.45677800 | 0.98294300 |
| C | -2.50022200 | -2.43972900 | -0.26859400 |
| C | -4.36484700 | -0.96210500 | 1.17921900 |
| H | -2.81025600 | 0.51358300 | 1.37935400 |
| C | -3.78738500 | -2.94252000 | -0.07590900 |
| H | -1.78049900 | -3.01497500 | -0.84454100 |
| C | -4.72275500 | -2.20596600 | 0.65133300 |
| H | -5.08876900 | -0.38210800 | 1.74509200 |
| H | -4.05698800 | -3.90814600 | -0.49518200 |
| H | -5.72492200 | -2.59683100 | 0.80572100 |
| C | -1.08849500 | 1.72072100 | -0.79776800 |
| O | -2.30171100 | 1.83038800 | -0.68573000 |
| O | -0.29200300 | 2.71096100 | -1.28528300 |
| C | -0.95568600 | 3.92963500 | -1.68274000 |
| H | -1.71941300 | 4.17901700 | -0.94025600 |
| H | -0.16599600 | 4.68465500 | -1.65789500 |
| C | -1.56472700 | 3.79780200 | -3.07162200 |
| H | -2.35599600 | 3.04354800 | -3.06534600 |
| H | -1.99745000 | 4.75510000 | -3.38452900 |
| H | -0.80057200 | 3.50742500 | -3.80010400 |
| C | 1.51523600 | -0.91916600 | -0.61213500 |
| C | 2.60431400 | -1.48406600 | -1.36458700 |
| O | 3.42255000 | -0.83123800 | -1.99858600 |
| O | 2.61794300 | -2.84751400 | -1.29841700 |
| C | 3.67759200 | -3.47266100 | -2.03603700 |
| H | 3.55047700 | -4.54508100 | -1.88195000 |
| H | 3.60678400 | -3.22574700 | -3.09980700 |
| H | 4.65322900 | -3.14373700 | -1.66541100 |
| H | 0.33570600 | -2.68722400 | 0.02906200 |
| N | 2.41169200 | 1.98152100 | 1.20953900 |
| C | 1.38791700 | 0.41102700 | 3.31130400 |
| H | 0.99167800 | -0.19507500 | 4.12237900 |




SCF Done: E(ωB97XD) = -1205.507677 a.u.

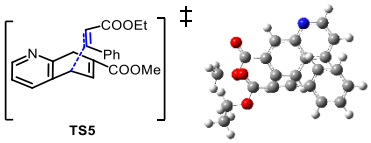
Thermal Correction to Free Energy = 0.312164 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.195513 a.u.

0 1

| | | | |
|---|---|---|---|
| C | -1.07382400 | -0.42654300 | -0.20486500 |
| C | 0.82608300 | -1.69183900 | 1.16989400 |
| C | 1.25249700 | 0.01586200 | -0.52453600 |
| C | -0.19565600 | 0.50808200 | -0.66993600 |
| C | -0.33592500 | -1.67819200 | 0.14263900 |
| H | 1.92756300 | 0.30421500 | -1.32796300 |
| H | 1.01417600 | -2.65891600 | 1.62566800 |
| C | 1.28749100 | -0.45177000 | 1.83291800 |
| C | 1.65231600 | 0.51421000 | 0.86865200 |
| C | 2.32486700 | 1.98332100 | 2.45943500 |
| H | 2.75515600 | 2.95655300 | 2.68730000 |
| C | 1.99205800 | 1.10560700 | 3.49199600 |
| H | 2.15668400 | 1.39662900 | 4.52499400 |
| C | -2.53171700 | -0.39076600 | -0.00887100 |
| C | -3.08356900 | -1.10747500 | 1.06996500 |
| C | -3.40351800 | 0.27806000 | -0.88503200 |
| C | -4.45991300 | -1.13126200 | 1.28439700 |
| H | -2.42315600 | -1.63066800 | 1.75621400 |
| C | -4.77964900 | 0.23953400 | -0.67722200 |
| H | -2.99789400 | 0.82870000 | -1.72313000 |
| C | -5.31407200 | -0.45892700 | 0.40847000 |
| H | -4.86451700 | -1.67748700 | 2.13230000 |
| H | -5.43855600 | 0.75949900 | -1.36723800 |
| H | -6.38874800 | -0.48119000 | 0.56847400 |
| C | -0.45962900 | 1.92607500 | -0.99894000 |
| O | -1.52191000 | 2.51603200 | -0.91886300 |
| O | 0.68613100 | 2.51460900 | -1.40406500 |
| C | 0.66290200 | 3.94693800 | -1.56462900 |
| H | 0.08490000 | 4.19585200 | -2.46224300 |
| H | 0.14830700 | 4.38872600 | -0.70544300 |
| C | 2.10999800 | 4.39348500 | -1.65754700 |
| H | 2.59754700 | 3.95317100 | -2.53349900 |
| H | 2.16578500 | 5.48459600 | -1.73978000 |
| H | 2.65127600 | 4.06947100 | -0.76359400 |
| C | 1.09238900 | -1.50303300 | -0.31779500 |
| C | 1.81912500 | -2.48104800 | -1.15689900 |

| | | | |
|---|---|---|---|
| O | 2.58951600 | -2.19107800 | -2.04760400 |
| O | 1.51648600 | -3.75503500 | -0.80550400 |
| C | 2.17769000 | -4.77296000 | -1.57634800 |
| H | 1.82526300 | -5.72221000 | -1.17145200 |
| H | 1.91570200 | -4.68372600 | -2.63434200 |
| H | 3.26312000 | -4.68826200 | -1.47287700 |
| H | -0.83321900 | -2.63429200 | 0.01475700 |
| N | 2.14868900 | 1.71272200 | 1.15250200 |
| C | 1.45003800 | -0.14615600 | 3.17692800 |
| H | 1.17811700 | -0.85315800 | 3.95658600 |




TS5

SCF Done: E(ωB97XD) = -1205.365935 a.u.

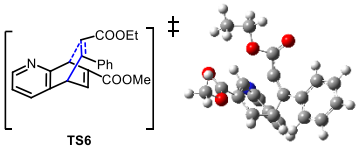
Thermal Correction to Free Energy = 0.300902 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.065033 a.u.

0 3

| | | | |
|---|---|---|---|
| C | -0.97147300 | 1.35754700 | -0.15855400 |
| C | -0.79781000 | -0.57606100 | -1.41182300 |
| C | 0.99987900 | -2.11546700 | 0.14155800 |
| C | 0.21080600 | 1.59188600 | 0.16284900 |
| C | 0.63157200 | -0.49858200 | -1.62976200 |
| H | 1.68311700 | -2.65887300 | 0.78252200 |
| H | -1.46206500 | -0.14629000 | -2.15486500 |
| C | -1.32613400 | -1.57516300 | -0.51746100 |
| C | -0.41327500 | -2.32416000 | 0.29989100 |
| C | -2.14966100 | -3.43661600 | 1.32701600 |
| H | -2.44281300 | -4.17346800 | 2.07247400 |
| C | -3.11338200 | -2.78007700 | 0.57055000 |
| H | -4.16759900 | -2.99717800 | 0.71167500 |
| C | -2.38614500 | 1.55848700 | -0.14729000 |
| C | -3.03157900 | 2.24157000 | -1.19993500 |
| C | -3.16485100 | 0.99608800 | 0.88603800 |
| C | -4.41586100 | 2.36908800 | -1.20576400 |
| H | -2.43336700 | 2.66885800 | -1.99943300 |
| C | -4.55211000 | 1.13300000 | 0.87043300 |
| H | -2.66954800 | 0.46415300 | 1.69117300 |
| C | -5.18207000 | 1.81490500 | -0.17208800 |
| H | -4.90311500 | 2.90373300 | -2.01655700 |
| H | -5.14134000 | 0.70147700 | 1.67493400 |
| H | -6.26358100 | 1.91696200 | -0.18242800 |
| C | 1.61161600 | 1.61783500 | 0.45099600 |

| | | | |
|---|---|---|---|
| O | 2.46977300 | 2.14212900 | -0.24860500 |
| O | 1.84910300 | 0.97626200 | 1.62277800 |
| C | 3.22525400 | 0.94498900 | 2.07887600 |
| H | 3.24024700 | 0.12477000 | 2.79955800 |
| H | 3.87530100 | 0.68251500 | 1.24282100 |
| C | 3.62305300 | 2.26887600 | 2.71435500 |
| H | 2.93859800 | 2.52838100 | 3.52875200 |
| H | 4.63719700 | 2.19496700 | 3.12381800 |
| H | 3.60692900 | 3.06801500 | 1.96838100 |
| C | 1.49696000 | -1.23201500 | -0.83970000 |
| C | 2.97064600 | -1.01922200 | -0.92178800 |
| O | 3.76247900 | -1.42591000 | -0.09164500 |
| O | 3.31936100 | -0.28697300 | -1.99639900 |
| C | 4.67354300 | 0.19444700 | -2.01352200 |
| H | 4.79045400 | 0.96191900 | -1.24351600 |
| H | 5.37850700 | -0.62216800 | -1.84063500 |
| H | 4.81604200 | 0.62888400 | -3.00341000 |
| H | 1.01908800 | 0.19397500 | -2.36558300 |
| C | -2.69339600 | -1.82719200 | -0.37123300 |
| N | -0.82397700 | -3.23181300 | 1.20253900 |
| H | -3.41343500 | -1.28699400 | -0.97833700 |




SCF Done: E(ωB97XD) = -1205.362553 a.u.

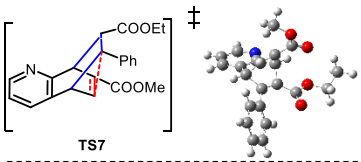
Thermal Correction to Free Energy = 0.304582 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.057971 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 1.22660400 | -0.02764900 | 0.01101800 |
| C | 1.17142600 | -1.18968000 | 1.03069300 |
| C | -1.27750400 | -1.45179300 | -0.12374400 |
| C | 0.19069500 | 0.00276200 | -0.88412300 |
| C | -0.01976000 | -0.66520600 | 1.79644100 |
| H | -2.15802600 | -1.41233800 | -0.75413600 |
| H | 2.08082300 | -1.23575200 | 1.62961100 |
| C | 0.87725900 | -2.50969400 | 0.37356700 |
| C | -0.36581400 | -2.59574900 | -0.27951600 |
| C | 0.08524000 | -4.68796000 | -1.06308900 |
| H | -0.25012400 | -5.53970600 | -1.65179800 |
| C | 1.33105500 | -4.71515000 | -0.43276500 |
| H | 1.97131200 | -5.58713500 | -0.52482800 |
| C | 2.28173000 | 0.99570300 | 0.13694400 |

| | | | |
|---|---|---|---|
| C | 2.90819300 | 1.25226900 | 1.37395800 |
| C | 2.70935500 | 1.72757900 | -0.98984800 |
| C | 3.91254900 | 2.21013800 | 1.48265900 |
| H | 2.58359700 | 0.73030000 | 2.26890900 |
| C | 3.72145800 | 2.67773400 | -0.87472100 |
| H | 2.25104500 | 1.53786600 | -1.95321900 |
| C | 4.32853700 | 2.92604200 | 0.35775300 |
| H | 4.36759300 | 2.40088800 | 2.45100100 |
| H | 4.03908600 | 3.22412400 | -1.75870200 |
| H | 5.11688300 | 3.66892200 | 0.44236200 |
| C | -0.41533100 | 0.97684700 | -1.75629500 |
| O | 0.12770400 | 1.42519300 | -2.76021700 |
| O | -1.67640500 | 1.28019800 | -1.37972500 |
| C | -2.43599000 | 2.13558600 | -2.26393700 |
| H | -1.83375000 | 3.01243700 | -2.52141000 |
| H | -2.63936100 | 1.58606800 | -3.19048500 |
| C | -3.71027400 | 2.50263000 | -1.52626200 |
| H | -3.47845600 | 3.09267300 | -0.63306900 |
| H | -4.36131800 | 3.09733600 | -2.17643100 |
| H | -4.24155600 | 1.60288700 | -1.20508100 |
| C | -1.26487100 | -0.71610200 | 1.06470100 |
| C | -2.43655700 | 0.12166400 | 1.38904800 |
| O | -3.51163900 | 0.07206500 | 0.81967200 |
| O | -2.18292400 | 0.95698600 | 2.42785200 |
| C | -3.28030700 | 1.80185800 | 2.80389600 |
| H | -3.56054900 | 2.45568400 | 1.97263400 |
| H | -4.15007000 | 1.20220700 | 3.08773200 |
| H | -2.92288900 | 2.38885500 | 3.65076100 |
| H | 0.10165900 | -0.02948400 | 2.66309000 |
| C | 1.73869700 | -3.59533000 | 0.29859400 |
| N | -0.76263200 | -3.65194500 | -0.99908400 |
| H | 2.71029300 | -3.56674500 | 0.78616800 |



TS7

SCF Done: E(ωB97XD) = -1205.404254 a.u.

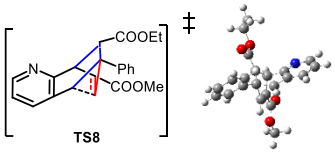
Thermal Correction to Free Energy = 0.307296 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.096958 a.u.

0 3

| | | | |
|---|---|---|---|
| C | -1.05430400 | 0.42736700 | -0.04455500 |
| C | -0.53147900 | 1.76924100 | 0.45700300 |

| | | | |
|---|---|---|---|
| C | 1.37585500 | 0.18668000 | -0.40290600 |
| C | -0.01286500 | -0.38782000 | -0.68095100 |
| C | 0.08144400 | 0.90025700 | 1.51668300 |
| H | 2.18013800 | -0.44731700 | -0.76003300 |
| H | -1.32756800 | 2.42136000 | 0.81065000 |
| C | 0.45108000 | 2.44157200 | -0.45035300 |
| C | 1.47851200 | 1.60447700 | -0.90424000 |
| C | 2.44185800 | 3.27814800 | -2.10200800 |
| H | 3.25071700 | 3.58839100 | -2.76075000 |
| C | 1.46104400 | 4.19434600 | -1.71456400 |
| H | 1.50129800 | 5.21914000 | -2.07103000 |
| C | -2.48770300 | 0.14105600 | 0.05209300 |
| C | -3.25493100 | 0.61585100 | 1.13621300 |
| C | -3.16173300 | -0.52817400 | -0.98968600 |
| C | -4.63204400 | 0.42246100 | 1.18298500 |
| H | -2.76573000 | 1.11285300 | 1.96964100 |
| C | -4.54135900 | -0.70461000 | -0.94665600 |
| H | -2.60100100 | -0.89981700 | -1.83714200 |
| C | -5.28522700 | -0.23632800 | 0.13861100 |
| H | -5.19516200 | 0.78231200 | 2.03987900 |
| H | -5.03690800 | -1.21681500 | -1.76673700 |
| H | -6.36065300 | -0.38624400 | 0.17271300 |
| C | -0.13613600 | -1.82869900 | -0.94097800 |
| O | -1.12094900 | -2.51186700 | -0.70196200 |
| O | 1.00503900 | -2.32188000 | -1.46962000 |
| C | 1.14312100 | -3.75910000 | -1.50284400 |
| H | 0.63609600 | -4.18261800 | -0.63160200 |
| H | 0.64230400 | -4.13677900 | -2.40232300 |
| C | 2.63112600 | -4.05568900 | -1.49513000 |
| H | 3.08086800 | -3.64278700 | -0.58756500 |
| H | 2.79881000 | -5.13834600 | -1.51834000 |
| H | 3.12288000 | -3.60957200 | -2.36600200 |
| C | 1.24089500 | 0.17870800 | 1.12180000 |
| C | 1.91393000 | -0.87309000 | 1.88724900 |
| O | 2.37483500 | -1.87093400 | 1.36088400 |
| O | 2.01026500 | -0.75366700 | 3.24525600 |
| C | 2.00343100 | 0.52378400 | 3.88913000 |
| H | 2.70863500 | 0.45043500 | 4.72099100 |
| H | 2.32022900 | 1.32400700 | 3.21231900 |
| H | 1.01010400 | 0.75936000 | 4.28751100 |
| H | -0.39712100 | 0.79523300 | 2.48173400 |
| N | 2.46532200 | 1.99350100 | -1.71167000 |
| C | 0.43658400 | 3.76788900 | -0.86522600 |
| H | -0.34529800 | 4.44953800 | -0.53870500 |




SCF Done: E(ωB97XD) = -1205.426292a.u.

Thermal Correction to Free Energy = 0.304726 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.121566 a.u.

0 3

| | | | |
|---|---|---|---|
| C | -0.83688800 | -0.69505800 | 0.30725600 |
| C | -0.05980300 | -0.77879200 | 1.59755400 |
| C | 1.11386300 | 0.38051500 | -0.61238600 |
| C | -0.38412500 | 0.51419000 | -0.46474400 |
| C | 0.20722000 | -1.73126300 | -0.06577400 |
| H | 1.58366800 | 0.97089700 | -1.39699200 |
| H | -0.43044100 | -1.44825500 | 2.36794800 |
| C | 1.04952800 | 0.11146900 | 1.86691300 |
| C | 1.66610200 | 0.77422800 | 0.76790700 |
| C | 3.13777000 | 1.87284700 | 2.11726600 |
| H | 3.95153900 | 2.59155200 | 2.18627000 |
| C | 2.64636100 | 1.24368800 | 3.26287400 |
| H | 3.07956200 | 1.46207100 | 4.23423100 |
| C | -2.28700500 | -1.09291700 | 0.32127100 |
| C | -3.13193100 | -0.69844500 | 1.36285100 |
| C | -2.80433200 | -1.85919700 | -0.72835000 |
| C | -4.47553500 | -1.06897900 | 1.35839700 |
| H | -2.73546900 | -0.08361500 | 2.16585300 |
| C | -4.14947500 | -2.22904300 | -0.73594000 |
| H | -2.14789100 | -2.16486700 | -1.53944600 |
| C | -4.98746700 | -1.83655200 | 0.30951000 |
| H | -5.12496100 | -0.75363500 | 2.17055300 |
| H | -4.54129400 | -2.82525400 | -1.55568600 |
| H | -6.03492000 | -2.12597500 | 0.30668400 |
| C | -1.15284700 | 1.72474400 | -0.66446800 |
| O | -2.29509500 | 1.90961700 | -0.26645400 |
| O | -0.43686600 | 2.65061000 | -1.35412900 |
| C | -1.09686300 | 3.91368400 | -1.57788200 |
| H | -2.01637200 | 3.73878200 | -2.14792600 |
| H | -1.38728400 | 4.33893400 | -0.61071100 |
| C | -0.11766800 | 4.80099700 | -2.32280100 |
| H | 0.15877600 | 4.35256200 | -3.28239500 |
| H | -0.56945400 | 5.78055700 | -2.51364900 |
| H | 0.79471900 | 4.94519600 | -1.73555600 |
| C | 1.26706300 | -1.12733800 | -0.73256500 |

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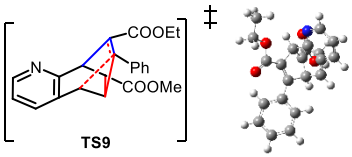
|---|---|---|---|
| C | 2.46066300 | -1.75128300 | -1.27638500 |
| O | 3.38143000 | -1.14574400 | -1.80082900 |
| O | 2.42768700 | -3.10888600 | -1.15864400 |
| C | 3.57281000 | -3.78581100 | -1.69472600 |
| H | 3.39361700 | -4.84815900 | -1.52277200 |
| H | 3.67763000 | -3.58212600 | -2.76477500 |
| H | 4.48686200 | -3.46321400 | -1.18691900 |
| H | 0.06423400 | -2.79180600 | 0.08904400 |
| N | 2.66434900 | 1.63746700 | 0.88089000 |
| C | 1.58888900 | 0.34391700 | 3.13770400 |
| H | 1.17180600 | -0.15428300 | 4.00956700 |




SCF Done: E(ωB97XD) = -1205.441997 a.u.

Thermal Correction to Free Energy = 0.306605 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.135392 a.u.

0 3

| | | | |
|---|---|---|---|
| C | -1.18228600 | -0.13076600 | -0.08686300 |
| C | -0.00458100 | -1.35221700 | 1.73112000 |
| C | 1.13681400 | -0.23495700 | -0.62177000 |
| C | -0.16151600 | 0.59936500 | -0.61739800 |
| C | -0.60120500 | -1.51291200 | 0.34424700 |
| H | 1.82302500 | -0.02157600 | -1.43931600 |
| H | -0.50776100 | -1.77254800 | 2.59698300 |
| C | 1.18478300 | -0.60403900 | 1.88525800 |
| C | 1.83432400 | -0.03884500 | 0.72783600 |
| C | 3.53129300 | 0.84011000 | 1.98645000 |
| H | 4.46257200 | 1.40250300 | 1.99126300 |
| C | 2.98391600 | 0.35950000 | 3.18383500 |
| H | 3.48550500 | 0.55219800 | 4.12757600 |
| C | -2.59509400 | 0.17366300 | 0.15839600 |
| C | -3.26119100 | -0.42404300 | 1.24714200 |
| C | -3.34127400 | 0.99296900 | -0.70992800 |
| C | -4.61309200 | -0.18586500 | 1.47966400 |
| H | -2.71179900 | -1.06400500 | 1.93020800 |
| C | -4.69623400 | 1.21720600 | -0.48232100 |
| H | -2.85083700 | 1.45419700 | -1.55580100 |
| C | -5.33762100 | 0.63558900 | 0.61367300 |
| H | -5.10150100 | -0.64578600 | 2.33448600 |
| H | -5.25389700 | 1.85076300 | -1.16651500 |
| H | -6.39453100 | 0.81725700 | 0.78918700 |

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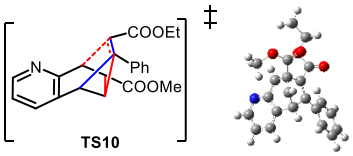
|---|---|---|---|
| C | -0.12571200 | 2.03702400 | -0.95123200 |
| O | -1.06391900 | 2.81365800 | -0.98433500 |
| O | 1.14870900 | 2.40849600 | -1.20746200 |
| C | 1.38029800 | 3.81130000 | -1.44585100 |
| H | 0.82704500 | 4.11808700 | -2.34060200 |
| H | 0.98217500 | 4.38306300 | -0.60044800 |
| C | 2.88006200 | 3.98077000 | -1.60064000 |
| H | 3.24548100 | 3.41946800 | -2.46639000 |
| H | 3.12893700 | 5.03857100 | -1.73900600 |
| H | 3.39519300 | 3.60481200 | -0.71142700 |
| C | 0.54981800 | -1.60990900 | -0.61172200 |
| C | 1.04604900 | -2.74849000 | -1.33443500 |
| O | 2.01711200 | -2.72756600 | -2.08085200 |
| O | 0.30261900 | -3.86897400 | -1.09961300 |
| C | 0.74064900 | -5.03709400 | -1.80620900 |
| H | 0.05122300 | -5.83172100 | -1.51740800 |
| H | 0.70542700 | -4.87215800 | -2.88757000 |
| H | 1.76618300 | -5.29744400 | -1.52655900 |
| H | -1.32098400 | -2.33046600 | 0.29244000 |
| N | 2.96645400 | 0.64780300 | 0.78088500 |
| C | 1.80429600 | -0.36565100 | 3.13697100 |
| H | 1.35221900 | -0.76099800 | 4.04345600 |




SCF Done: E(ωB97XD) = -1205.398969 a.u.

Thermal Correction to Free Energy = 0.305686 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.093283 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 0.96873400 | -0.36497700 | -0.77889900 |
| C | 0.96585500 | 1.05381200 | -1.39585600 |
| C | -0.97825400 | 1.04506300 | 0.56125200 |
| C | -0.34783000 | -0.60451800 | -0.32298400 |
| C | -0.45433900 | 1.18605100 | -1.87018500 |
| H | -1.64086700 | 0.80097500 | 1.38075600 |
| H | 1.71863500 | 1.22249100 | -2.16689800 |
| C | 1.14463900 | 2.00739800 | -0.21748400 |
| C | 0.13520100 | 1.94340500 | 0.77793300 |
| C | 1.23856300 | 3.44957900 | 2.10104200 |
| H | 1.25893200 | 4.00934300 | 3.03463800 |
| C | 2.27356600 | 3.59847600 | 1.17136400 |
| H | 3.10005000 | 4.27215300 | 1.37567900 |

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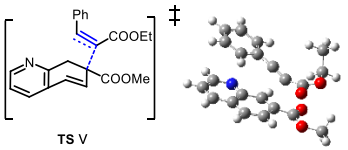
|---|---|---|---|
| C | 2.20877400 | -1.05368900 | -0.47733800 |
| C | 3.36542500 | -0.79628500 | -1.25245400 |
| C | 2.33608600 | -1.96779700 | 0.59524000 |
| C | 4.57538400 | -1.42426200 | -0.97941700 |
| H | 3.31021300 | -0.11354700 | -2.09405100 |
| C | 3.55043100 | -2.58541400 | 0.86910700 |
| H | 1.48126100 | -2.18605000 | 1.21958000 |
| C | 4.67803400 | -2.32281600 | 0.08547700 |
| H | 5.44156400 | -1.21253100 | -1.60073600 |
| H | 3.61817100 | -3.27661100 | 1.70486300 |
| H | 5.62382700 | -2.81148500 | 0.30232400 |
| C | -0.92655700 | -1.83628500 | 0.26533300 |
| O | -0.47569400 | -2.95284900 | 0.11067100 |
| O | -2.06022100 | -1.57242200 | 0.95111200 |
| C | -2.90929700 | -2.70488100 | 1.25291500 |
| H | -2.92125300 | -3.37063800 | 0.38593300 |
| H | -2.47629500 | -3.25138400 | 2.09788300 |
| C | -4.28564100 | -2.14792500 | 1.56288500 |
| H | -4.67528400 | -1.61022900 | 0.69310700 |
| H | -4.97346900 | -2.96416300 | 1.80919300 |
| H | -4.24698300 | -1.46005700 | 2.41430500 |
| C | -1.27286200 | 0.52349400 | -0.80883500 |
| C | -2.69628800 | 0.17820500 | -1.21740700 |
| O | -3.00704200 | -0.90277400 | -1.65689400 |
| O | -3.63164700 | 1.15082600 | -1.12817800 |
| C | -3.30870800 | 2.48818000 | -0.71204100 |
| H | -4.17515600 | 3.09066100 | -0.99012100 |
| H | -3.15665400 | 2.53930200 | 0.36992000 |
| H | -2.41849700 | 2.86895900 | -1.22194600 |
| H | -0.75313800 | 1.19528300 | -2.91163600 |
| H | 3.02495600 | 2.91319300 | -0.74379300 |
| C | 2.22665600 | 2.85038400 | -0.00801700 |
| N | 0.19019800 | 2.63870100 | 1.93107500 |




SCF Done: E(ωB97XD) = -1205.365514 a.u.

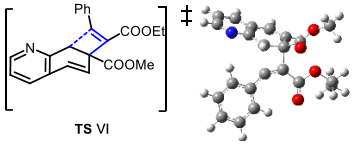
Thermal Correction to Free Energy = 0.301965 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.063549 a.u.

0 3

| | | | |
|---|---|---|---|
| C | -1.43930300 | -1.38047100 | -0.80402500 |
| C | -1.68025100 | -2.09454400 | 0.42018400 |

| | | | |
|---|---|---|---|
| C | -3.00369800 | -2.37051100 | 0.76143700 |
| C | -4.03233300 | -1.94053600 | -0.08349500 |
| C | -3.69408000 | -1.24108100 | -1.25155500 |
| N | -2.44798100 | -0.96523500 | -1.62425700 |
| C | -0.11952100 | -1.05768800 | -1.15984800 |
| C | 0.99622100 | -1.38430400 | -0.29114400 |
| C | 0.73221200 | -2.15677900 | 0.89402700 |
| C | -0.54563200 | -2.48187100 | 1.23533400 |
| C | 2.35610300 | -1.28228800 | -0.87402100 |
| O | 2.60635400 | -0.75036200 | -1.94496600 |
| O | 3.29792800 | -1.80684000 | -0.06172500 |
| C | 4.66017900 | -1.58510700 | -0.46407200 |
| H | -3.22562700 | -2.91171100 | 1.67828800 |
| H | -5.07304700 | -2.13671100 | 0.15478200 |
| H | -4.47921900 | -0.88702100 | -1.91795900 |
| H | 0.07219200 | -0.53941700 | -2.09082900 |
| H | 1.56813700 | -2.43460800 | 1.52372300 |
| H | -0.73908300 | -3.04571600 | 2.14473800 |
| H | 4.82760000 | -1.95516500 | -1.47888600 |
| H | 4.88705800 | -0.51717400 | -0.41680000 |
| H | 5.26676200 | -2.13432400 | 0.25619600 |
| C | -3.66898300 | 1.49369100 | 1.22085300 |
| C | -4.11311600 | 2.22849000 | 0.11318700 |
| C | -3.19839500 | 2.64197100 | -0.86606700 |
| C | -1.85484400 | 2.32373000 | -0.75103000 |
| C | -1.39013300 | 1.57682600 | 0.36628100 |
| C | -2.32873700 | 1.16886000 | 1.35650100 |
| C | -0.05973300 | 1.18638300 | 0.47981000 |
| C | 1.08900800 | 0.70661900 | 0.62806200 |
| C | 2.41144600 | 0.78508700 | 1.24246400 |
| O | 2.66240100 | 0.25567200 | 2.30416200 |
| O | 3.39362800 | 1.39783100 | 0.53574400 |
| C | 2.59247400 | 3.54814600 | -0.32310600 |
| C | 3.08352600 | 2.15017700 | -0.66460400 |
| H | -4.37894400 | 1.16839300 | 1.97600300 |
| H | -5.16574300 | 2.47667200 | 0.01214000 |
| H | -3.54474000 | 3.20471000 | -1.72822400 |
| H | -1.14572900 | 2.62051900 | -1.51711000 |
| H | -1.97691900 | 0.58983700 | 2.20343500 |
| H | 2.45724900 | 4.13158300 | -1.24117400 |
| H | 1.63201600 | 3.50671800 | 0.20079800 |
| H | 3.31568800 | 4.06507500 | 0.31555000 |
| H | 4.03249400 | 2.18066100 | -1.20490300 |
| H | 2.36877400 | 1.59513800 | -1.27672100 |




SCF Done: E(ωB97XD) = -1205.361522 a.u.

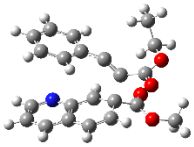
Thermal Correction to Free Energy = 0.302805 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.058717 a.u.

0 3

| | | | |
|---|---|---|---|
| C | -1.52719000 | 1.86125300 | 0.14364400 |
| C | -1.19222800 | 2.43539400 | -1.17919900 |
| C | -2.22124200 | 3.14495400 | -1.85713200 |
| C | -3.44980500 | 3.28482300 | -1.27254700 |
| C | -3.67249200 | 2.69475000 | 0.03343800 |
| N | -2.78109800 | 2.02223300 | 0.70591700 |
| C | -0.60817200 | 1.04764200 | 0.80753100 |
| C | 0.82949200 | 0.89377100 | 0.29352800 |
| C | 1.10264400 | 1.62496100 | -0.96843000 |
| C | 0.10872500 | 2.29555600 | -1.67279300 |
| C | 1.84408400 | 1.13008400 | 1.42525600 |
| O | 1.73374800 | 0.64791400 | 2.53055700 |
| O | 2.86679700 | 1.92007500 | 1.05077800 |
| H | -2.01084000 | 3.57390100 | -2.83471500 |
| H | -4.25745200 | 3.82152500 | -1.75985000 |
| H | -4.65170500 | 2.80728800 | 0.49938400 |
| H | -0.76296300 | 0.85787800 | 1.86595500 |
| H | 2.09943100 | 1.52672100 | -1.38101900 |
| H | 0.35321800 | 2.74376400 | -2.63377100 |
| C | -2.47405800 | -4.11083700 | -0.03277100 |
| C | -3.73929400 | -3.71190700 | 0.41061300 |
| C | -3.95867000 | -2.38823000 | 0.80162800 |
| C | -2.92255900 | -1.46047600 | 0.74610800 |
| C | -1.64213100 | -1.85591200 | 0.30383700 |
| C | -1.42474900 | -3.19858200 | -0.08364300 |
| C | -0.59090700 | -0.88604100 | 0.24636100 |
| C | 0.69823100 | -0.64165300 | 0.02488900 |
| C | 1.80045400 | -1.53108000 | -0.36484100 |
| O | 1.70751300 | -2.71976100 | -0.61673300 |
| O | 2.97185400 | -0.84418200 | -0.40187500 |
| C | 4.15105100 | -1.59164200 | -0.77946800 |
| H | -2.30336300 | -5.14102800 | -0.33413000 |
| H | -4.55199900 | -4.43249200 | 0.45198800 |
| H | -4.94101800 | -2.07766100 | 1.14704000 |
| H | -3.08716100 | -0.42790300 | 1.03958200 |

| | | | |
|---|---|---|---|
| H | -0.43604900 | -3.49612300 | -0.41489400 |
| H | 4.97976000 | -1.00519300 | -0.37500500 |
| H | 4.12351700 | -2.56830800 | -0.28852800 |
| C | 4.24593500 | -1.73493000 | -2.29107500 |
| H | 4.23035000 | -0.75163400 | -2.77284200 |
| H | 5.17999200 | -2.23986600 | -2.56250200 |
| H | 3.40815100 | -2.32833200 | -2.66656300 |
| C | 3.88327200 | 2.10916900 | 2.05074800 |
| H | 3.45969300 | 2.57036800 | 2.94698600 |
| H | 4.32962700 | 1.14844400 | 2.32311300 |
| H | 4.62486400 | 2.76424800 | 1.59244400 |

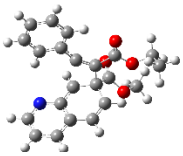
MECP7 

SCF Done: E(B3LYP) = -1205.35473 a.u.

0 1 or 0 3

| | | | |
|---|---|---|---|
| C | -1.56647300 | -1.38568000 | -0.73504500 |
| C | -1.79510400 | -2.06808700 | 0.51171900 |
| C | -3.10939600 | -2.43514700 | 0.82522700 |
| C | -4.13116700 | -2.13165100 | -0.06419100 |
| C | -3.80143800 | -1.48184700 | -1.27609600 |
| N | -2.57935600 | -1.12329500 | -1.62271300 |
| C | -0.27462100 | -0.97550500 | -1.07026000 |
| C | 0.84391800 | -1.05041600 | -0.11121800 |
| C | 0.58022000 | -1.92087800 | 1.07346600 |
| C | -0.66800700 | -2.34884100 | 1.36639100 |
| C | 2.16264500 | -1.30355000 | -0.85484800 |
| O | 2.43606600 | -0.80715300 | -1.92832100 |
| O | 3.00649200 | -2.06233600 | -0.14195500 |
| C | 4.34449000 | -2.16893200 | -0.66647300 |
| H | -3.31592100 | -2.95028400 | 1.76077600 |
| H | -5.16278800 | -2.39428000 | 0.14901600 |
| H | -4.58963300 | -1.24988000 | -1.99224800 |
| H | -0.10133500 | -0.50188200 | -2.02878900 |
| H | 1.41315900 | -2.11238900 | 1.73720600 |
| H | -0.84431000 | -2.92518100 | 2.27224500 |
| H | 4.33047300 | -2.62144600 | -1.66102700 |
| H | 4.79842200 | -1.17581200 | -0.72033900 |
| H | 4.88098100 | -2.79852000 | 0.04296500 |
| C | -3.45678700 | 1.84425700 | 1.13801800 |
| C | -3.80182300 | 2.56715500 | -0.01260600 |
| C | -2.81367400 | 2.91384100 | -0.94266300 |

| | | | |
|---|---|---|---|
| C | -1.49293200 | 2.54437800 | -0.73587700 |
| C | -1.13075600 | 1.79514300 | 0.41704500 |
| C | -2.14245200 | 1.46711700 | 1.36323600 |
| C | 0.18381600 | 1.37130900 | 0.61132100 |
| C | 1.12103100 | 0.48626600 | 0.54788400 |
| C | 2.48609600 | 0.62085300 | 1.17400100 |
| O | 2.77036400 | 0.05531800 | 2.20426300 |
| O | 3.42518100 | 1.33634600 | 0.51842300 |
| C | 2.68631700 | 3.50310600 | -0.33558700 |
| C | 3.12649500 | 2.09095200 | -0.68415800 |
| H | -4.22457400 | 1.56874300 | 1.85570500 |
| H | -4.83461600 | 2.85693700 | -0.18297000 |
| H | -3.08201200 | 3.46985700 | -1.83644200 |
| H | -0.72481400 | 2.80070000 | -1.45887300 |
| H | -1.87022000 | 0.89105500 | 2.24166300 |
| H | 2.53975100 | 4.08621600 | -1.25233600 |
| H | 1.74161800 | 3.48432900 | 0.21749200 |
| H | 3.44109900 | 4.00243800 | 0.28006000 |
| H | 4.06978200 | 2.09006900 | -1.23661200 |
| H | 2.38323000 | 1.56194800 | -1.28350700 |



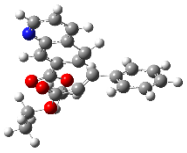
MECP8

SCF Done: E(B3LYP) = -1205.356711 a.u.

0 1 or 0 3

| | | | |
|---|---|---|---|
| C | -1.29458200 | -2.16318800 | -0.19399200 |
| C | -0.94981600 | -2.59841500 | 1.13158300 |
| C | -1.88468400 | -3.36335400 | 1.83114100 |
| C | -3.10354900 | -3.67185700 | 1.23324100 |
| C | -3.34528200 | -3.20704300 | -0.07439100 |
| N | -2.48879000 | -2.48445200 | -0.78119700 |
| C | -0.40393500 | -1.35544500 | -0.91580600 |
| C | 0.87950800 | -0.81446800 | -0.31606100 |
| C | 1.20668700 | -1.43720000 | 1.02004600 |
| C | 0.34203100 | -2.22953200 | 1.67843600 |
| C | 2.00186900 | -0.95195600 | -1.36494900 |
| O | 1.96470700 | -0.41348400 | -2.44822200 |
| O | 3.00274000 | -1.75193400 | -0.95499700 |
| H | -1.65477700 | -3.70807900 | 2.83675300 |
| H | -3.85690400 | -4.25272200 | 1.75556800 |
| H | -4.29076800 | -3.43873300 | -0.56385500 |
| H | -0.61754300 | -1.11410900 | -1.95030900 |

| | | | |
|---|---|---|---|
| H | 2.15920900 | -1.16103900 | 1.45580500 |
| H | 0.59863700 | -2.61048600 | 2.66490900 |
| C | -2.84019000 | 4.05782000 | 0.05391100 |
| C | -4.07920600 | 3.55438200 | -0.35475500 |
| C | -4.20097900 | 2.21535500 | -0.73821300 |
| C | -3.09018000 | 1.37797600 | -0.71168300 |
| C | -1.83352300 | 1.87884900 | -0.30175600 |
| C | -1.71853000 | 3.23489800 | 0.08295600 |
| C | -0.72513300 | 0.98613300 | -0.28918700 |
| C | 0.55866700 | 0.68719300 | -0.10849500 |
| C | 1.59418900 | 1.66726300 | 0.29599700 |
| O | 1.40175600 | 2.84407200 | 0.54475600 |
| O | 2.81836900 | 1.08212500 | 0.35620500 |
| C | 3.92424300 | 1.92147200 | 0.76334600 |
| H | -2.74619600 | 5.09997900 | 0.34769700 |
| H | -4.94840200 | 4.20652900 | -0.37519900 |
| H | -5.16278000 | 1.82476300 | -1.05904800 |
| H | -3.17218400 | 0.33312400 | -0.99894700 |
| H | -0.74932300 | 3.60887200 | 0.39137700 |
| H | 4.80637600 | 1.41438200 | 0.36437000 |
| H | 3.82140400 | 2.89955700 | 0.28602100 |
| C | 3.97993000 | 2.04635600 | 2.27845200 |
| H | 4.02387400 | 1.05674600 | 2.74571500 |
| H | 4.87072100 | 2.61032500 | 2.57762300 |
| H | 3.09488800 | 2.57247200 | 2.64580700 |
| C | 4.09160800 | -1.88192700 | -1.88623100 |
| H | 3.73525200 | -2.27727400 | -2.84060400 |
| H | 4.55866500 | -0.90751000 | -2.05871400 |
| H | 4.79594500 | -2.57174000 | -1.42006400 |



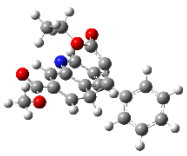
MECP9

SCF Done: E(B3LYP) = -1205.366735 a.u.

0 1 or 0 3

| | | | |
|---|---|---|---|
| C | 1.48790500 | -0.14338900 | 0.29316400 |
| C | 0.82228000 | 0.35045800 | -1.11399100 |
| C | -1.96390000 | 1.00955500 | -0.88289500 |
| C | 0.80784000 | -0.02065900 | 1.39970000 |
| C | -0.24894200 | -0.62140600 | -1.42117300 |
| H | -3.00622400 | 1.24079100 | -0.69830400 |
| H | 1.65156000 | 0.27253200 | -1.82436500 |
| C | 0.36710600 | 1.77605400 | -1.02239500 |

| | | | |
|---|---|---|---|
| C | -1.01035800 | 2.07278100 | -0.86042000 |
| C | -0.58617700 | 4.32088800 | -0.68730700 |
| H | -0.98272400 | 5.32520000 | -0.54540300 |
| C | 0.79709300 | 4.13107100 | -0.85288000 |
| H | 1.47112700 | 4.98171000 | -0.84114500 |
| C | 2.84835000 | -0.73045100 | 0.20468700 |
| C | 3.26305100 | -1.48579100 | -0.90357000 |
| C | 3.75578600 | -0.53520200 | 1.26109200 |
| C | 4.54835500 | -2.02553700 | -0.95643000 |
| H | 2.57523700 | -1.67922500 | -1.72242100 |
| C | 5.03980200 | -1.07004800 | 1.20329800 |
| H | 3.44118800 | 0.05245300 | 2.11810300 |
| C | 5.44408200 | -1.81517900 | 0.09245200 |
| H | 4.84548200 | -2.61786900 | -1.81746800 |
| H | 5.72837800 | -0.90147300 | 2.02703600 |
| H | 6.44846200 | -2.22637600 | 0.04524200 |
| C | -0.43343700 | 0.42452400 | 1.97069300 |
| O | -0.65554000 | 1.57730900 | 2.31045100 |
| O | -1.31767900 | -0.59594100 | 2.09947400 |
| C | -2.63617900 | -0.21550100 | 2.55915000 |
| H | -2.54408800 | 0.28874300 | 3.52695100 |
| H | -3.05729800 | 0.50164600 | 1.84607900 |
| C | -3.46947100 | -1.47968500 | 2.63798600 |
| H | -3.00841600 | -2.20799500 | 3.31247800 |
| H | -4.46873300 | -1.23868800 | 3.01657200 |
| H | -3.57903600 | -1.92477700 | 1.64566300 |
| C | -1.57609000 | -0.30586800 | -1.18844400 |
| C | -2.64290400 | -1.35051400 | -1.19852200 |
| O | -3.77353200 | -1.17402500 | -0.78697100 |
| O | -2.20943300 | -2.53014800 | -1.69053700 |
| C | -3.17182100 | -3.59746400 | -1.66326600 |
| H | -3.45536700 | -3.82842800 | -0.63254900 |
| H | -4.06818500 | -3.32196800 | -2.22481600 |
| H | -2.67426000 | -4.45149100 | -2.12310300 |
| H | 0.03242400 | -1.63584400 | -1.67794100 |
| C | 1.27303600 | 2.83629700 | -1.02103500 |
| N | -1.47568800 | 3.33754500 | -0.69387400 |
| H | 2.33732700 | 2.64106000 | -1.13219900 |



MECP10

SCF Done: E(B3LYP) = -1205.367055 a.u.

0 1 or 0 3

| | | | |
|---|---|---|---|
| C | 1.51287000 | -0.03283700 | 0.29345800 |
| C | 0.79705800 | 0.30627700 | -1.13343000 |
| C | -2.03617600 | 0.76477100 | -0.94695400 |
| C | 0.85781700 | 0.18916800 | 1.40016200 |
| C | -0.19792500 | -0.76711000 | -1.34884700 |
| H | -3.09527200 | 0.92918000 | -0.79008300 |
| H | 1.62361600 | 0.23943800 | -1.84914400 |
| C | 0.23021800 | 1.69552700 | -1.14187200 |
| C | -1.16640000 | 1.89530300 | -0.99546500 |
| C | -0.92030000 | 4.17596500 | -0.96381500 |
| H | -1.39418500 | 5.15292500 | -0.87982600 |
| C | 0.47321300 | 4.08406200 | -1.12815300 |
| H | 1.07876200 | 4.98401000 | -1.17123000 |
| C | 2.88395300 | -0.59776700 | 0.22810500 |
| C | 3.30949800 | -1.41868000 | -0.82829400 |
| C | 3.79595200 | -0.30650400 | 1.25896000 |
| C | 4.60879300 | -1.92740700 | -0.85609000 |
| H | 2.62239200 | -1.68908600 | -1.62534400 |
| C | 5.09239100 | -0.81166800 | 1.22663100 |
| H | 3.47247800 | 0.33206200 | 2.07538800 |
| C | 5.50654200 | -1.62397500 | 0.16744800 |
| H | 4.91690800 | -2.56566400 | -1.67976300 |
| H | 5.78468400 | -0.56448600 | 2.02687700 |
| H | 6.51955700 | -2.01556700 | 0.14115100 |
| C | -0.38140800 | 0.67067000 | 1.94540300 |
| O | -0.61606600 | 1.84741000 | 2.17954900 |
| O | -1.25046000 | -0.34381700 | 2.17702400 |
| C | -2.57044300 | 0.06075500 | 2.60955300 |
| H | -2.48250300 | 0.61112200 | 3.55311200 |
| H | -2.98570500 | 0.74649900 | 1.86205100 |
| C | -3.40395900 | -1.19938100 | 2.74228300 |
| H | -2.94900200 | -1.89430300 | 3.45577200 |
| H | -4.40623000 | -0.94106400 | 3.10127000 |
| H | -3.50482100 | -1.69530300 | 1.77268500 |
| C | -1.54748800 | -0.53622400 | -1.14899500 |
| C | -2.53961800 | -1.65052700 | -1.09746600 |
| O | -3.69273400 | -1.51786300 | -0.73369600 |
| O | -2.01669900 | -2.83535500 | -1.47723000 |
| C | -2.91760800 | -3.95228900 | -1.38627700 |
| H | -3.20977900 | -4.11911500 | -0.34527900 |
| H | -3.81587700 | -3.76902000 | -1.98180700 |
| H | -2.36413200 | -4.80868000 | -1.77239800 |
| H | 0.16145200 | -1.77530100 | -1.51659800 |

| | | | |
|---|---|---|---|
| C | 1.04921600 | 2.82198200 | -1.21297700 |
| N | -1.72965100 | 3.12778100 | -0.90400600 |
| H | 2.12571400 | 2.70421800 | -1.31416100 |

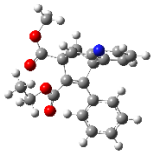
MECP11

SCF Done: E(B3LYP) = -1205.368290 a.u.

0 1 or 0 3

| | | | |
|---|---|---|---|
| C | -0.83086700 | -0.66531700 | 0.47493700 |
| C | -0.32255300 | -0.07432200 | 1.78237300 |
| C | 1.08663900 | 0.29893700 | -0.60918700 |
| C | -0.39777900 | 0.48294500 | -0.42274900 |
| C | 0.13822100 | -1.76238700 | 0.02667500 |
| H | 1.53376000 | 0.81086600 | -1.46029800 |
| H | -0.98818300 | -0.02929400 | 2.63908000 |
| C | 0.97336400 | 0.50515600 | 1.88670100 |
| C | 1.75669900 | 0.72870500 | 0.70285200 |
| C | 3.48981100 | 1.62508700 | 1.88502400 |
| H | 4.48840300 | 2.05446500 | 1.84802600 |
| C | 2.81014300 | 1.49815400 | 3.09998300 |
| H | 3.27010600 | 1.84526100 | 4.02012800 |
| C | -2.29870200 | -1.05991600 | 0.45027800 |
| C | -3.24954600 | -0.46158100 | 1.28491800 |
| C | -2.72866100 | -2.02042500 | -0.47366900 |
| C | -4.58960400 | -0.83953000 | 1.22148000 |
| H | -2.95850200 | 0.33563200 | 1.95939400 |
| C | -4.07069700 | -2.39544400 | -0.54426400 |
| H | -2.01005600 | -2.46970100 | -1.15403400 |
| C | -5.00550000 | -1.81310500 | 0.31207300 |
| H | -5.31245300 | -0.35796300 | 1.87416400 |
| H | -4.38383600 | -3.13900000 | -1.27242700 |
| H | -6.05028600 | -2.10673200 | 0.26442800 |
| C | -1.13520400 | 1.69812000 | -0.68271100 |
| O | -2.25609200 | 1.96806700 | -0.27172600 |
| O | -0.40254900 | 2.53799400 | -1.46736600 |
| C | -1.03446200 | 3.78589300 | -1.81225000 |
| H | -1.96819200 | 3.57821000 | -2.34672300 |
| H | -1.29727100 | 4.31966900 | -0.89228200 |
| C | -0.04387200 | 4.55847300 | -2.66306200 |
| H | 0.21087700 | 3.99332700 | -3.56550000 |
| H | -0.47068600 | 5.52151200 | -2.96316300 |
| H | 0.87885100 | 4.74461300 | -2.10431200 |

| | | | |
|---|---|---|---|
| C | 1.18209600 | -1.23032800 | -0.62528100 |
| C | 2.37107200 | -1.91355800 | -1.16350500 |
| O | 3.29880400 | -1.34127700 | -1.69998500 |
| O | 2.30724000 | -3.25818300 | -1.00537400 |
| C | 3.44671600 | -3.97578600 | -1.50758000 |
| H | 3.23601300 | -5.02973600 | -1.32418100 |
| H | 3.57979600 | -3.78929000 | -2.57712900 |
| H | 4.35527200 | -3.66791800 | -0.98156000 |
| H | 0.00631900 | -2.80618000 | 0.28466000 |
| N | 2.96881800 | 1.24847700 | 0.69962400 |
| C | 1.54157600 | 0.92916300 | 3.10646600 |
| H | 0.98577200 | 0.80648500 | 4.03296700 |



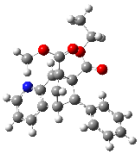
MECP12

SCF Done: E(B3LYP) = -1205.352540 a.u.

0 1 or 0 3

| | | | |
|---|---|---|---|
| C | 1.05217200 | -0.21888700 | -0.66307500 |
| C | 0.81181900 | 1.18877600 | -1.28464600 |
| C | -1.56125600 | 1.27786500 | 0.19121300 |
| C | -0.15388400 | -0.73995800 | -0.32358400 |
| C | -0.56677300 | 0.99972900 | -1.84302200 |
| H | -2.55338200 | 1.41651100 | 0.60864300 |
| H | 1.57332500 | 1.48455600 | -2.01346200 |
| C | 0.70596000 | 2.20910300 | -0.14163600 |
| C | -0.52868600 | 2.19106000 | 0.57936100 |
| C | 0.16575500 | 3.92488000 | 1.92007100 |
| H | -0.06971500 | 4.59845800 | 2.74285500 |
| C | 1.39304600 | 4.03054700 | 1.26112200 |
| H | 2.10725600 | 4.79699100 | 1.54468300 |
| C | 2.40716400 | -0.74843600 | -0.45779200 |
| C | 3.48341100 | 0.11505300 | -0.17785100 |
| C | 2.67632400 | -2.12408400 | -0.59570100 |
| C | 4.77407200 | -0.37876400 | -0.00686700 |
| H | 3.30567200 | 1.17602300 | -0.06077700 |
| C | 3.96952500 | -2.61364400 | -0.42804700 |
| H | 1.86390000 | -2.79894500 | -0.82546100 |
| C | 5.02313500 | -1.74713300 | -0.13099300 |
| H | 5.58572600 | 0.30684200 | 0.22173700 |
| H | 4.15242500 | -3.67948100 | -0.53355100 |
| H | 6.03080500 | -2.13343500 | -0.00341500 |
| C | -0.46820000 | -1.90002000 | 0.54037700 |

| | | | |
|---|---|---|---|
| O | 0.13674900 | -2.95176100 | 0.60719300 |
| O | -1.57007200 | -1.62893600 | 1.27620500 |
| C | -2.17108800 | -2.75606500 | 1.95118200 |
| H | -2.24895400 | -3.58275800 | 1.23825600 |
| H | -1.51641600 | -3.07435700 | 2.76901500 |
| C | -3.52999700 | -2.29439400 | 2.44145500 |
| H | -4.14541700 | -1.97484600 | 1.59484600 |
| H | -4.04256500 | -3.11411500 | 2.95646400 |
| H | -3.43084200 | -1.45490900 | 3.13731400 |
| C | -1.28384000 | 0.18130200 | -0.80431700 |
| C | -2.51368400 | -0.60026800 | -1.28994800 |
| O | -2.49868400 | -1.80010800 | -1.41429400 |
| O | -3.67848300 | 0.06058900 | -1.52662700 |
| C | -3.74672400 | 1.39492500 | -2.04570400 |
| H | -4.79900300 | 1.67727100 | -1.98359300 |
| H | -3.14723800 | 2.10817200 | -1.47367300 |
| H | -3.43363100 | 1.40255600 | -3.09589100 |
| H | -1.02819600 | 1.64239300 | -2.58033800 |
| H | 2.58829600 | 3.22315900 | -0.35679700 |
| C | 1.66057400 | 3.14629200 | 0.20556400 |
| N | -0.78586800 | 3.04491000 | 1.59862100 |



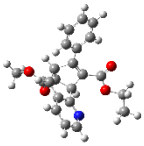
MECP13

SCF Done: E(B3LYP) = -1205.344527 a.u.

0 1 or 0 3

| | | | |
|---|---|---|---|
| C | -1.20895300 | 0.17944800 | 0.28595800 |
| C | -0.87111400 | 1.50452400 | 0.93683600 |
| C | 1.19071300 | 0.58388100 | -0.52897100 |
| C | 0.10318000 | -0.45777700 | -0.18592400 |
| C | 0.15322100 | 0.82267600 | 1.80279400 |
| H | 2.01747900 | 0.20339500 | -1.11701100 |
| H | -1.70520700 | 1.93314700 | 1.48983800 |
| C | -0.26510400 | 2.48800400 | -0.02796200 |
| C | 0.80472200 | 1.98899700 | -0.78476300 |
| C | 1.10427700 | 3.97915700 | -1.85339500 |
| H | 1.67114300 | 4.55153000 | -2.58456500 |
| C | 0.04534500 | 4.57089800 | -1.16183600 |
| H | -0.22105700 | 5.60585200 | -1.35354100 |
| C | -2.53917700 | -0.35828000 | 0.22693800 |
| C | -3.54635100 | 0.05699700 | 1.13862200 |
| C | -2.92945400 | -1.24540400 | -0.80985700 |

| | | | |
|---|---|---|---|
| C | -4.85460400 | -0.39054500 | 1.02183000 |
| H | -3.28641800 | 0.70283600 | 1.97188100 |
| C | -4.24708200 | -1.66963100 | -0.93059600 |
| H | -2.19998600 | -1.57617400 | -1.53487000 |
| C | -5.21880700 | -1.25529200 | -0.01631200 |
| H | -5.59657300 | -0.06630600 | 1.74654300 |
| H | -4.51524700 | -2.33552800 | -1.74643200 |
| H | -6.24418700 | -1.60281800 | -0.10728700 |
| C | 0.26807200 | -1.88284200 | -0.58852000 |
| O | -0.53551400 | -2.76518700 | -0.37024300 |
| O | 1.47686700 | -2.08599200 | -1.15474500 |
| C | 1.91275700 | -3.46517200 | -1.22898000 |
| H | 1.65207600 | -3.95906100 | -0.29004400 |
| H | 1.37100500 | -3.95806600 | -2.04346600 |
| C | 3.41109800 | -3.44376900 | -1.45918900 |
| H | 3.91440100 | -2.96730800 | -0.61243000 |
| H | 3.78697100 | -4.46806900 | -1.55585200 |
| H | 3.66230600 | -2.89650800 | -2.37354500 |
| C | 1.06510400 | 0.04012000 | 0.89314300 |
| C | 2.16615000 | -0.79269200 | 1.49488300 |
| O | 2.08987000 | -1.98440600 | 1.68249800 |
| O | 3.28543700 | -0.13062000 | 1.86751300 |
| C | 3.42019600 | 1.28219500 | 1.63136400 |
| H | 4.33893300 | 1.57093900 | 2.14419300 |
| H | 3.51086900 | 1.49782400 | 0.56276000 |
| H | 2.57291200 | 1.84058100 | 2.04245900 |
| H | -0.09990700 | 0.41378600 | 2.77465400 |
| H | -1.48049400 | 4.23184500 | 0.34103500 |
| C | -0.65410300 | 3.80731800 | -0.22389100 |
| N | 1.49388400 | 2.70726900 | -1.67822000 |



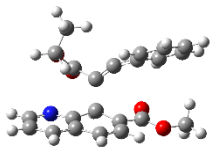
MECP14

SCF Done: E(B3LYP) = -1205.391368 a.u.

0 1 or 0 3

| | | | |
|---|---|---|---|
| C | 1.16272900 | 0.21233700 | -0.16712000 |
| C | -0.11065600 | 1.58479300 | 1.55178900 |
| C | -1.18657600 | 0.11467200 | -0.57661800 |
| C | 0.18392300 | -0.60802600 | -0.63600900 |
| C | 0.51314500 | 1.57333600 | 0.17196000 |
| H | -1.91485100 | -0.18723000 | -1.32666300 |
| H | 0.16868000 | 2.35645500 | 2.26430200 |

| | | | |
|---|---|---|---|
| C | -1.12994000 | 0.65231500 | 1.88079200 |
| C | -1.72005100 | -0.14315600 | 0.83768700 |
| C | -3.08797500 | -1.23583200 | 2.30594500 |
| H | -3.85284700 | -1.99721700 | 2.44091800 |
| C | -2.62605700 | -0.48922200 | 3.39461600 |
| H | -3.03665800 | -0.66081600 | 4.38519000 |
| C | 2.59576500 | 0.02050900 | 0.07637700 |
| C | 3.21225200 | 0.72429700 | 1.13105400 |
| C | 3.40188300 | -0.78505000 | -0.74890400 |
| C | 4.57944300 | 0.61045400 | 1.36611300 |
| H | 2.61044000 | 1.34979300 | 1.78393000 |
| C | 4.77196000 | -0.88303500 | -0.52000000 |
| H | 2.94842400 | -1.33298400 | -1.56306000 |
| C | 5.36730500 | -0.19020000 | 0.53625500 |
| H | 5.03051100 | 1.15316400 | 2.19228500 |
| H | 5.37779100 | -1.50439800 | -1.17345800 |
| H | 6.43730500 | -0.26869800 | 0.70866100 |
| C | 0.24548200 | -2.04990800 | -0.95172600 |
| O | 1.23671400 | -2.75768800 | -0.97720300 |
| O | -0.99815600 | -2.50864500 | -1.20898400 |
| C | -1.14049300 | -3.92521800 | -1.43322100 |
| H | -0.57523200 | -4.20395100 | -2.32979600 |
| H | -0.70138300 | -4.46180400 | -0.58528800 |
| C | -2.62807500 | -4.18980900 | -1.57467000 |
| H | -3.03818500 | -3.64533300 | -2.43145300 |
| H | -2.81000900 | -5.25969300 | -1.72225200 |
| H | -3.15646500 | -3.85638000 | -0.67636400 |
| C | -0.73021600 | 1.53553300 | -0.65997700 |
| C | -1.41482900 | 2.60344700 | -1.33174500 |
| O | -2.44408500 | 2.46767300 | -1.98324500 |
| O | -0.76935700 | 3.79940500 | -1.18854800 |
| C | -1.37716900 | 4.89527400 | -1.88402200 |
| H | -0.72788700 | 5.75368300 | -1.70408200 |
| H | -1.44642700 | 4.68299200 | -2.95554300 |
| H | -2.38448300 | 5.08966700 | -1.50229800 |
| H | 1.16766800 | 2.43071200 | 0.01487900 |
| N | -2.64797200 | -1.06147900 | 1.04433700 |
| C | -1.63578000 | 0.46204400 | 3.18543600 |
| H | -1.23793400 | 1.04911200 | 4.00950200 |



MECP15

SCF Done: E(B3LYP) = -1205.37629 a.u.

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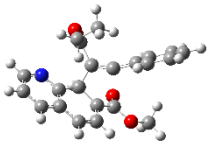
0 1 or 0 3

| | | | |
|---|---|---|---|
| C | 2.03963000 | -1.14693900 | 0.04242100 |
| C | 2.08186300 | -1.54532700 | -1.32447500 |
| C | 3.33705700 | -1.49470500 | -1.97117800 |
| C | 4.45399000 | -1.08731100 | -1.26288800 |
| C | 4.29961500 | -0.73691900 | 0.08852800 |
| N | 3.12672200 | -0.75789500 | 0.72155200 |
| C | 0.72973100 | -1.03082300 | 0.75389500 |
| C | -0.37638800 | -1.76045000 | 0.10445900 |
| C | -0.28989800 | -2.14305700 | -1.23295800 |
| C | 0.88792900 | -2.00493100 | -1.95906700 |
| C | -1.61320600 | -1.90928500 | 0.88127400 |
| O | -1.75395200 | -1.51284800 | 2.02799600 |
| O | -2.61008700 | -2.51793100 | 0.18512800 |
| H | 3.41083900 | -1.77901700 | -3.01820300 |
| H | 5.43199100 | -1.03649900 | -1.73219700 |
| H | 5.15534800 | -0.41531300 | 0.67857600 |
| H | 0.81679200 | -1.25938600 | 1.82149800 |
| H | -1.16259600 | -2.58218200 | -1.70416300 |
| H | 0.92618900 | -2.30766100 | -3.00193500 |
| C | -4.26865600 | 1.28639400 | -0.02666700 |
| C | -4.38827300 | 1.67489000 | -1.36858400 |
| C | -3.23748500 | 1.90252900 | -2.13604200 |
| C | -1.97763100 | 1.74745400 | -1.57792100 |
| C | -1.83846000 | 1.34722200 | -0.21788600 |
| C | -3.01929600 | 1.12344200 | 0.55210500 |
| C | -0.59104600 | 1.18289300 | 0.36686900 |
| C | 0.43995500 | 0.60696400 | 0.86810100 |
| C | 1.43356100 | 1.28726000 | 1.78978500 |
| O | 1.46252500 | 1.02638000 | 2.96523000 |
| O | 2.25518700 | 2.22432000 | 1.27228400 |
| C | 2.37796600 | 2.44387000 | -0.14771600 |
| H | -5.16172500 | 1.10860600 | 0.56710100 |
| H | -5.37132000 | 1.79957500 | -1.81325800 |
| H | -3.33187600 | 2.20245100 | -3.17645700 |
| H | -1.08299000 | 1.92156500 | -2.16758100 |
| H | -2.91259600 | 0.79508400 | 1.58008200 |
| H | 3.45179600 | 2.56251100 | -0.32022300 |
| H | 2.03915600 | 1.56425500 | -0.70110400 |
| C | 1.60732000 | 3.68691900 | -0.56106800 |
| H | 1.76677400 | 3.89566700 | -1.62546800 |
| H | 0.53550300 | 3.54532100 | -0.38915100 |
| H | 1.93885700 | 4.55545800 | 0.01688500 |

| | | | |
|---|---|---|---|
| C | -3.86095100 | -2.61360200 | 0.87610400 |
| H | -3.74499400 | -3.15826500 | 1.81733500 |
| H | -4.25664700 | -1.61540000 | 1.08963100 |
| H | -4.52889500 | -3.14979900 | 0.20012300 |



MECP16

SCF Done: E(B3LYP) = -1205.36929 a.u.

0 1 or 0 3

| | | | |
|---|---|---|---|
| C | -2.39387200 | 0.77152300 | 0.22604900 |
| C | -2.68636100 | 1.24889400 | -1.07651500 |
| C | -3.96619000 | 0.97100300 | -1.58787900 |
| C | -4.87383200 | 0.25528900 | -0.81443200 |
| C | -4.48051700 | -0.15822500 | 0.46031800 |
| N | -3.26518100 | 0.09240200 | 0.97085400 |
| C | -1.00153200 | 0.93047400 | 0.81680900 |
| C | -0.06776600 | 1.81910500 | 0.00252400 |
| C | -0.44938500 | 2.27390700 | -1.26802000 |
| C | -1.68885500 | 1.99130200 | -1.80807800 |
| C | 1.16286400 | 2.27447200 | 0.66655500 |
| O | 1.42670900 | 2.09306600 | 1.84496500 |
| O | 2.00746400 | 2.91429100 | -0.18777500 |
| H | -4.23449600 | 1.31857700 | -2.58294100 |
| H | -5.86745500 | 0.02396000 | -1.18533500 |
| H | -5.16038800 | -0.71435600 | 1.10184100 |
| H | -1.08211800 | 1.27410900 | 1.85567100 |
| H | 0.25588300 | 2.87495200 | -1.83157600 |
| H | -1.94603200 | 2.35926800 | -2.79789200 |
| C | 4.44256000 | -1.11382400 | 0.33328600 |
| C | 4.71441100 | -1.61568600 | -0.94759600 |
| C | 3.68463100 | -1.71978500 | -1.89374600 |
| C | 2.39191500 | -1.33655100 | -1.57016000 |
| C | 2.09402600 | -0.85096000 | -0.26535300 |
| C | 3.15664400 | -0.72896500 | 0.68055300 |
| C | 0.82008500 | -0.43559500 | 0.10017300 |
| C | -0.29096700 | -0.41056000 | 0.80048800 |
| C | -0.79362700 | -1.55753200 | 1.65946300 |
| O | -0.67675300 | -1.51782100 | 2.85874200 |
| O | -1.35926900 | -2.62628500 | 1.05996300 |
| C | -1.61377900 | -2.66861100 | -0.35932600 |
| H | 5.24147000 | -1.03468400 | 1.06617200 |
| H | 5.72273600 | -1.92409600 | -1.20748600 |

| | | | |
|---|---|---|---|
| H | 3.89833200 | -2.10434800 | -2.88718900 |
| H | 1.59094400 | -1.40803600 | -2.29980000 |
| H | 2.93030800 | -0.33123300 | 1.66453400 |
| H | -2.63255800 | -3.05523900 | -0.45523500 |
| H | -1.59142600 | -1.66234000 | -0.78452800 |
| C | -0.60614200 | -3.58090500 | -1.03925700 |
| H | -0.81944400 | -3.64965200 | -2.11265200 |
| H | 0.41104900 | -3.19855400 | -0.91076400 |
| H | -0.65060800 | -4.58627500 | -0.60992600 |
| C | 3.25950900 | 3.31226600 | 0.38772600 |
| H | 3.83023400 | 2.43273100 | 0.70044300 |
| H | 3.78914800 | 3.84651800 | -0.40283700 |
| H | 3.10256600 | 3.95966100 | 1.25487800 |

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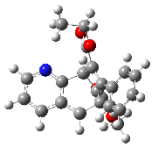

MECP17

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SCF Done: E(B3LYP) = -1205.388717 a.u.

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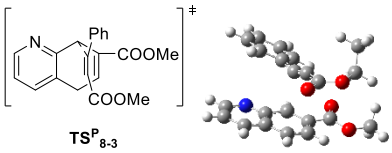
0 1 or 0 3

| | | | |
|---|---|---|---|
| C | -1.44050700 | 1.48429800 | 0.32456000 |
| C | -1.55189400 | 0.74229500 | 1.55325300 |
| C | -1.86617100 | 1.48531300 | 2.71166700 |
| C | -2.01762200 | 2.86289600 | 2.61234900 |
| C | -1.84675400 | 3.47529300 | 1.36704400 |
| N | -1.56406800 | 2.79589000 | 0.23779000 |
| C | -1.13783500 | 0.65215600 | -0.93102800 |
| C | -1.74148300 | -0.70368800 | -0.72767600 |
| C | -0.85284700 | -1.35378800 | 0.28936500 |
| C | -1.37370900 | -0.66779800 | 1.53612600 |
| C | -3.03781600 | -1.12621600 | -1.18199400 |
| O | -3.75857800 | -0.48067000 | -1.93255000 |
| O | -3.37595000 | -2.35656800 | -0.69002100 |
| H | -1.97896200 | 0.97756500 | 3.66683600 |
| H | -2.26407800 | 3.46133800 | 3.48457900 |
| H | -1.95234500 | 4.55248400 | 1.25948600 |
| H | -1.43669900 | 1.18472800 | -1.83296500 |
| H | -0.91958000 | -2.43919400 | 0.36683000 |
| H | -1.70713800 | -1.26907200 | 2.37802600 |
| C | 3.92479600 | -2.51312700 | -0.20752300 |
| C | 3.97400300 | -3.09089200 | 1.06429200 |
| C | 2.90475300 | -2.91383200 | 1.94434900 |
| C | 1.79363900 | -2.16891400 | 1.55329100 |
| C | 1.74101000 | -1.56612000 | 0.28360800 |

| | | | |
|---|---|---|---|
| C | 2.82185700 | -1.75753700 | -0.59485300 |
| C | 0.53802800 | -0.82954200 | -0.12043000 |
| C | 0.36205600 | 0.30977300 | -0.83476900 |
| C | 1.33007200 | 1.29628000 | -1.35861400 |
| O | 1.02095000 | 2.17724300 | -2.13875100 |
| O | 2.57702900 | 1.13030900 | -0.86344700 |
| C | 3.58026500 | 2.07293900 | -1.30701900 |
| H | 4.74700800 | -2.65776900 | -0.90310300 |
| H | 4.83591000 | -3.68059600 | 1.36378700 |
| H | 2.93289800 | -3.36007300 | 2.93461800 |
| H | 0.96507800 | -2.03297800 | 2.24302500 |
| H | 2.78285200 | -1.31862500 | -1.58494700 |
| H | 4.52649600 | 1.55113400 | -1.14308500 |
| H | 3.44923100 | 2.26000900 | -2.37646100 |
| C | 3.50250400 | 3.36476200 | -0.50700600 |
| H | 4.31015800 | 4.04218000 | -0.80729600 |
| H | 2.54514900 | 3.86086500 | -0.68622300 |
| H | 3.60125700 | 3.15961900 | 0.56382900 |
| C | -4.65367900 | -2.84033300 | -1.12239000 |
| H | -5.45217400 | -2.15882200 | -0.81287700 |
| H | -4.68334100 | -2.93647600 | -2.21223500 |
| H | -4.77685400 | -3.81536900 | -0.64780800 |




$TS^{P}_{8\text{-}3}$

SCF Done: E(ωB97XD) = -1205.368635 a.u.

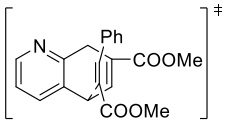
Thermal Correction to Free Energy = 0.301339 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.067296 a.u.

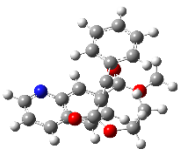
0 3

| | | | |
|---|---|---|---|
| C | -1.45623900 | -1.47661400 | -0.68269300 |
| C | -1.04984300 | -2.72381400 | -0.10736300 |
| C | -2.04562400 | -3.55288500 | 0.41395900 |
| C | -3.38364600 | -3.14205900 | 0.34576900 |
| C | -3.67300400 | -1.92337400 | -0.26025300 |
| N | -2.74173300 | -1.09712700 | -0.77139600 |
| C | -0.44377000 | -0.56370500 | -1.15703000 |
| C | 0.95524000 | -0.99279900 | -1.19684500 |
| C | 1.30658700 | -2.23795900 | -0.69535900 |
| C | 0.34572100 | -3.07845300 | -0.12491400 |
| C | 1.93275900 | -0.02228500 | -1.70025400 |
| O | 1.65510800 | 1.12592800 | -2.02485500 |
| O | 3.19871500 | -0.51028000 | -1.74651700 |

| | | | |
|---|---|---|---|
| H | -1.77680400 | -4.50613200 | 0.86191900 |
| H | -4.18060100 | -3.76168100 | 0.74485300 |
| H | -4.70252800 | -1.58065300 | -0.34620100 |
| H | -0.75180300 | 0.26599100 | -1.77946800 |
| H | 2.34897000 | -2.53522500 | -0.69393400 |
| H | 0.64934100 | -4.02258700 | 0.31606400 |
| C | -3.67705900 | 2.61055700 | 0.54718200 |
| C | -3.39937900 | 3.63415500 | -0.36182000 |
| C | -2.12569700 | 3.73865600 | -0.93228200 |
| C | -1.12872000 | 2.83034000 | -0.59305100 |
| C | -1.40141800 | 1.80684500 | 0.33658200 |
| C | -2.68839700 | 1.69325100 | 0.89410300 |
| C | -0.37818300 | 0.86754200 | 0.67764100 |
| C | 0.53155100 | 0.35978100 | 1.35706900 |
| C | 1.51342800 | -0.53603100 | 1.88387800 |
| O | 1.21469500 | -1.62427400 | 2.35525700 |
| O | 2.81848100 | -0.16152200 | 1.83827000 |
| C | 3.18032200 | 1.14251100 | 1.33570100 |
| H | -4.66827000 | 2.52343400 | 0.98353900 |
| H | -4.17506900 | 4.34550700 | -0.63206600 |
| H | -1.91310500 | 4.52821800 | -1.64777300 |
| H | -0.14510100 | 2.87485800 | -1.05096000 |
| H | -2.89480100 | 0.88982200 | 1.59289200 |
| H | 4.21436000 | 1.02066500 | 1.00204700 |
| H | 2.56711700 | 1.40011300 | 0.46667200 |
| C | 3.07138200 | 2.20233800 | 2.42263100 |
| H | 3.42671100 | 3.16796400 | 2.04504500 |
| H | 2.03094300 | 2.32143900 | 2.74169800 |
| H | 3.67341600 | 1.92255800 | 3.29282300 |
| C | 4.19035800 | 0.41220900 | -2.21637500 |
| H | 4.25249800 | 1.28261300 | -1.55629500 |
| H | 5.13055000 | -0.14047100 | -2.20869400 |
| H | 3.95209800 | 0.75540500 | -3.22728300 |




**TS$^{P}_{5\text{-}2}$**



SCF Done: E(ωB97XD) = -1205.367300 a.u.

Thermal Correction to Free Energy = 0.300521 (Hartree/Particle)

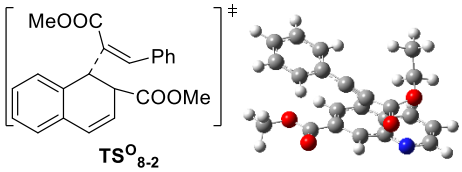
Sum of electronic and thermal Free Energies = -1205.066779 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 0.84937000 | -2.35460800 | -0.31034900 |

| | | | |
|---|---|---|---|
| C | 1.84221000 | -1.42886600 | -0.77295300 |
| C | 3.18406500 | -1.73087100 | -0.53375400 |
| C | 3.49951300 | -2.91079800 | 0.15415100 |
| C | 2.46139800 | -3.73841200 | 0.57603300 |
| N | 1.16118700 | -3.48641100 | 0.35522800 |
| C | -0.53184700 | -2.07726300 | -0.55651900 |
| C | -0.92606900 | -0.90737300 | -1.26983100 |
| C | 0.02173200 | -0.01883900 | -1.72853900 |
| C | 1.40638200 | -0.21119100 | -1.41855700 |
| C | -2.38303900 | -0.67360700 | -1.43917000 |
| O | -3.24682700 | -1.45735400 | -1.09664100 |
| O | -2.65667000 | 0.53314900 | -1.99282800 |
| H | 3.96213400 | -1.04514900 | -0.85126100 |
| H | 4.53136500 | -3.17208700 | 0.36588900 |
| H | 2.67765400 | -4.65571500 | 1.12071000 |
| H | -1.28114900 | -2.77907800 | -0.21421300 |
| H | -0.28359500 | 0.87067800 | -2.26663100 |
| H | 2.15005000 | 0.41496900 | -1.90162700 |
| C | -2.54117900 | -1.02207700 | 2.39567400 |
| C | -3.64222100 | -0.19523900 | 2.16023000 |
| C | -3.45739700 | 1.07482200 | 1.58076300 |
| C | -2.19356900 | 1.51056600 | 1.22994500 |
| C | -1.06115400 | 0.67405600 | 1.45332000 |
| C | -1.25929200 | -0.60432900 | 2.05828900 |
| C | 0.21598600 | 1.05732200 | 1.05623700 |
| C | 1.33531100 | 1.19651200 | 0.53024000 |
| C | 2.72579100 | 1.57928200 | 0.43025100 |
| O | 3.63181600 | 0.89348800 | 0.86425000 |
| O | 3.01643500 | 2.70373000 | -0.28174000 |
| C | 1.95768100 | 3.57904500 | -0.72128100 |
| H | -2.68351800 | -2.00396800 | 2.83746000 |
| H | -4.64143800 | -0.53224800 | 2.41834500 |
| H | -4.31622800 | 1.71686800 | 1.40400000 |
| H | -2.04674600 | 2.48017900 | 0.76480200 |
| H | -0.39963100 | -1.23905600 | 2.24178200 |
| H | 2.39830300 | 4.13523800 | -1.55290900 |
| H | 1.11847900 | 2.98811900 | -1.10652300 |
| C | 1.50668300 | 4.51518400 | 0.39069400 |
| H | 0.76952900 | 5.22976300 | 0.00652300 |
| H | 1.04662700 | 3.95083800 | 1.20770000 |
| H | 2.36019400 | 5.07321900 | 0.78789400 |
| C | -4.05429700 | 0.82860300 | -2.13012100 |
| H | -4.53745100 | 0.83037300 | -1.14909800 |
| H | -4.10111000 | 1.81868800 | -2.58558000 |

| | | | |
|---|---|---|---|
| H | -4.54616100 | 0.08764700 | -2.76668100 |




SCF Done: E(ωB97XD) = -1205.375981 a.u.

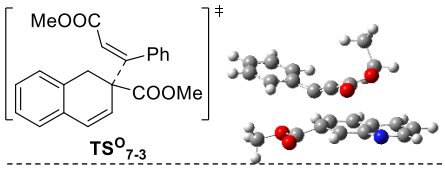
Thermal Correction to Free Energy = 0.299261 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.076720 a.u.

0 3

| | | | |
|---|---|---|---|
| C | 2.10154400 | -1.28493400 | 0.17170000 |
| C | 2.14119300 | -1.41035600 | -1.26099700 |
| C | 3.37834100 | -1.30784400 | -1.89039800 |
| C | 4.53175000 | -1.08159100 | -1.11017400 |
| C | 4.38777600 | -0.99016400 | 0.26679600 |
| N | 3.20803800 | -1.09365100 | 0.91274700 |
| C | 0.83494500 | -1.31479400 | 0.83764000 |
| C | -0.38747400 | -1.63790100 | 0.08554100 |
| C | -0.31481000 | -1.76927500 | -1.29508900 |
| C | 0.90360700 | -1.63798500 | -1.96692800 |
| C | -1.63800800 | -1.80669200 | 0.83510000 |
| O | -1.73844400 | -1.68123900 | 2.04568700 |
| O | -2.69048700 | -2.12147100 | 0.03333300 |
| H | 3.44816500 | -1.40074900 | -2.97162300 |
| H | 5.50984800 | -0.99032400 | -1.57157100 |
| H | 5.25402900 | -0.82235800 | 0.90323600 |
| H | 0.80556100 | -1.30959600 | 1.91991100 |
| H | -1.21978500 | -1.97604200 | -1.85498900 |
| H | 0.93576100 | -1.73529200 | -3.04926500 |
| C | -4.46848600 | 1.21839900 | 0.19000400 |
| C | -4.64143400 | 1.35005200 | -1.19257800 |
| C | -3.52485000 | 1.44948000 | -2.03113200 |
| C | -2.24276400 | 1.42152800 | -1.49718500 |
| C | -2.05828600 | 1.28369500 | -0.10127400 |
| C | -3.19238600 | 1.18208500 | 0.73910900 |
| C | -0.76423200 | 1.24071600 | 0.45210400 |
| C | 0.36029200 | 1.12794500 | 0.94179700 |
| C | 1.56517300 | 1.51551200 | 1.66845800 |
| O | 1.64424400 | 1.43984900 | 2.87223300 |
| O | 2.61302000 | 1.95851200 | 0.93589100 |
| C | 2.50780600 | 2.12039600 | -0.49363600 |
| H | -5.33517700 | 1.14149100 | 0.84080600 |
| H | -5.64186000 | 1.37723100 | -1.61508800 |

| | | | |
|---|---|---|---|
| H | -3.65924400 | 1.55096700 | -3.10448600 |
| H | -1.37056700 | 1.49435300 | -2.13946600 |
| H | -3.04467700 | 1.05612200 | 1.80643500 |
| H | 3.53003700 | 1.98437100 | -0.85510600 |
| H | 1.89069300 | 1.32391800 | -0.91840400 |
| C | 1.96092900 | 3.49478900 | -0.84807600 |
| H | 1.97235200 | 3.63801400 | -1.93493300 |
| H | 0.92908000 | 3.59913200 | -0.49722100 |
| H | 2.56701000 | 4.28005400 | -0.38579400 |
| C | -3.92898900 | -2.34722500 | 0.71842600 |
| H | -3.83692500 | -3.18788600 | 1.41291600 |
| H | -4.22966900 | -1.45687700 | 1.27514200 |
| H | -4.65738400 | -2.57118400 | -0.06211900 |




SCF Done: E(ωB97XD) = -1205.363731 a.u.

Thermal Correction to Free Energy = 0.300341 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1205.063390 a.u.

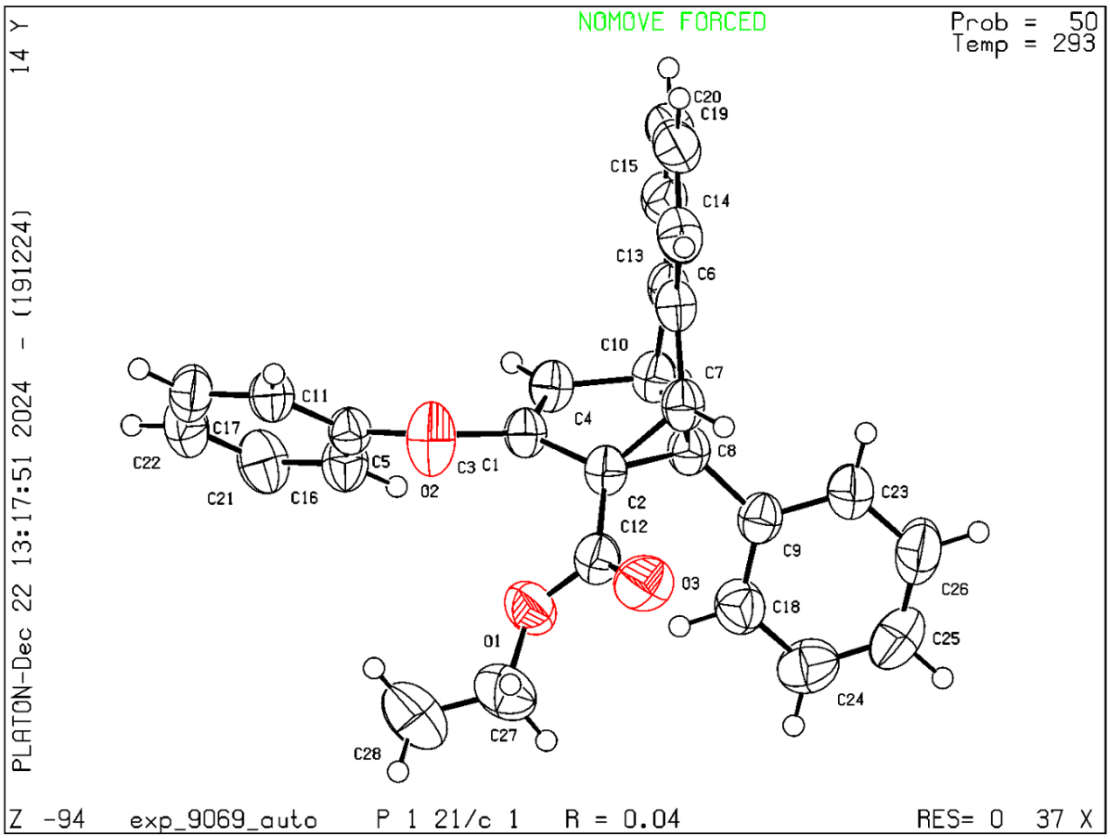
0 3

| | | | |
|---|---|---|---|
| C | 2.24547000 | -1.23310000 | 0.21572500 |
| C | 2.33942000 | -1.19293900 | -1.21593100 |
| C | 3.60746200 | -1.04008000 | -1.78367100 |
| C | 4.71818400 | -0.92803500 | -0.94999900 |
| C | 4.52152200 | -0.99211400 | 0.44100300 |
| N | 3.33825700 | -1.14877400 | 1.02177800 |
| C | 0.97531200 | -1.35152400 | 0.82610300 |
| C | -0.24148600 | -1.36433300 | 0.02890800 |
| C | -0.09695800 | -1.41260000 | -1.41093200 |
| C | 1.12671800 | -1.30867000 | -1.99610700 |
| C | -1.46517000 | -1.90791700 | 0.68650700 |
| O | -1.59019500 | -2.07220700 | 1.88455000 |
| O | -2.44871000 | -2.15508300 | -0.20901700 |
| H | 3.71538600 | -1.00607900 | -2.86555500 |
| H | 5.71681200 | -0.80112400 | -1.35596900 |
| H | 5.37443100 | -0.91350000 | 1.11331400 |
| H | 0.90452800 | -1.43582600 | 1.90326500 |
| H | -0.99328900 | -1.51249600 | -2.01103300 |
| H | 1.21491800 | -1.32422100 | -3.08024000 |
| C | -4.51461000 | 1.13098400 | 0.49553600 |
| C | -4.81273500 | 1.32292400 | -0.85726200 |

| | | | |
|---|---|---|---|
| C | -3.78446500 | 1.31998100 | -1.80542600 |
| C | -2.46519800 | 1.12365100 | -1.40873200 |
| C | -2.15792200 | 0.93217700 | -0.04777000 |
| C | -3.19846000 | 0.93200300 | 0.90347900 |
| C | -0.80806400 | 0.67009800 | 0.37506000 |
| C | 0.22520200 | 1.14079400 | 0.93056300 |
| C | 1.37770200 | 1.66310500 | 1.59857800 |
| O | 1.48655600 | 1.65347000 | 2.81187400 |
| O | 2.38174500 | 2.16353500 | 0.82836900 |
| C | 2.20153100 | 2.31693200 | -0.59360600 |
| H | -5.31081600 | 1.13792000 | 1.23497700 |
| H | -5.84128200 | 1.47715100 | -1.17124800 |
| H | -4.01374600 | 1.47254800 | -2.85652800 |
| H | -1.66197700 | 1.11394800 | -2.13906200 |
| H | -2.95652900 | 0.76682200 | 1.94846800 |
| H | 3.21957700 | 2.34579400 | -0.99000600 |
| H | 1.70311900 | 1.43596100 | -1.00925400 |
| C | 1.43726800 | 3.59154000 | -0.92316800 |
| H | 1.39359900 | 3.73637300 | -2.00893600 |
| H | 0.41103900 | 3.53810000 | -0.54413400 |
| H | 1.92832400 | 4.46011200 | -0.47352500 |
| C | -3.69572200 | -2.59216900 | 0.35544500 |
| H | -4.10314300 | -1.82070200 | 1.01317200 |
| H | -4.35745300 | -2.75541500 | -0.49564000 |
| H | -3.55646500 | -3.51591000 | 0.92345400 |

## 8. X-ray Analysis

**X-ray crystal data of 3ea-1** (CCDC 2413434), Chloroform / Hexane 1/1




Bond precision: C-C = 0.0021 A Wavelength=1.54184

Cell: a=12.5942(2) b=10.7849(2) c=15.9030(2)

alpha=90 beta=93.996(2) gamma=90

Temperature: 293 K

| | Calculated | Reported |
|---|---|---|
| Volume | 2154.81(6) | 2154.81(6) |
| Space group | P 21/c | P 1 21/c 1 |
| Hall group | -P 2ybc | -P 2ybc |
| Moiety formula | $C_{28}H_{22}O_3$ | $C_{28}H_{22}O_3$ |
| Sum formula | $C_{28}H_{22}O_3$ | $C_{28}H_{22}O_3$ |
| Mr | 406.46 | 406.45 |
| Dx,g $cm^{-3}$ | 1.253 | 1.253 |
| Z | 4 | 4 |
| Mu ($mm^{-1}$) | 0.639 | 0.639 |

| | | |
|---|---|---|
| F000 | 856.0 | 856.0 |
| F000’ | 858.52 | |
| h,k,$l_{max}$ | 15,13,20 | 15,13,19 |
| Nref | 4484 | 4399 |
| $T_{min}$,$T_{max}$ | 0.858,0.891 | 0.700,1.000 |
| $T_{min'}$ | 0.852 | |

Correction method= # Reported T Limits: $T_{min}$=0.700 $T_{max}$=1.000

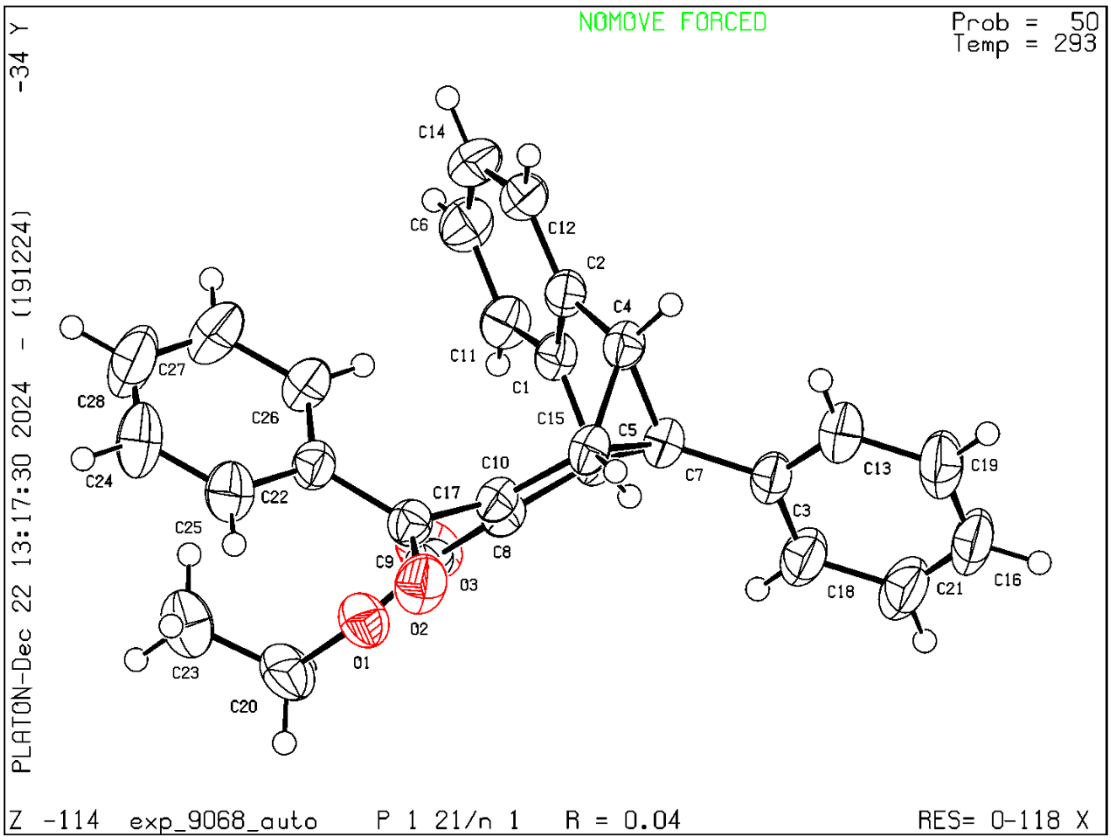
AbsCorr = MULTI-SCAN

Data completeness= 0.981 Theta(max)= 75.825

R(reflections)= 0.0439( 3763) wR2(reflections)= 0.1279( 4399)

S = 1.075 Npar= 281

**X-ray crystal data of 3ea-2** (CCDC 2413433) Ethyl acetate/Hexane 1/1




Bond precision: C-C = 0.0020 A Wavelength=1.54184

| | | | |
|---|---|---|---|
| Cell: | a=13.00613(13) | b=7.65855(6) | c=21.76921(19) |
| | alpha=90 | beta=103.5843(9) | gamma=90 |

Temperature: 293 K

| | Calculated | Reported |
|---|---|---|
| Volume | 2107.73(3) | 2107.73(3) |
| Space group | P 21/n | P 1 21/n 1 |
| Hall group | -P 2yn | -P 2yn |
| Moiety formula | $C_{28}H_{22}O_3$ | $C_{28}H_{22}O_3$ |
| Sum formula | $C_{28}H_{22}O_3$ | $C_{28}H_{22}O_3$ |
| Mr | 406.46 | 406.45 |
| Dx,g $cm^{-3}$ | 1.281 | 1.281 |
| Z | 4 | 4 |
| Mu ($mm^{-1}$) | 0.654 | 0.654 |
| F000 | 856.0 | 856.0 |
| F000’ | 858.52 | |
| $h,k,l_{max}$ | 16,9,27 | 16,9,27 |
| Nref | 4398 | 4290 |
| $T_{min},T_{max}$ | 0.877,0.901 | 0.706,1.000 |
| $T_{min'}$ | 0.877 | |

Correction method= # Reported T Limits: $T_{min}$=0.706 $T_{max}$=1.000

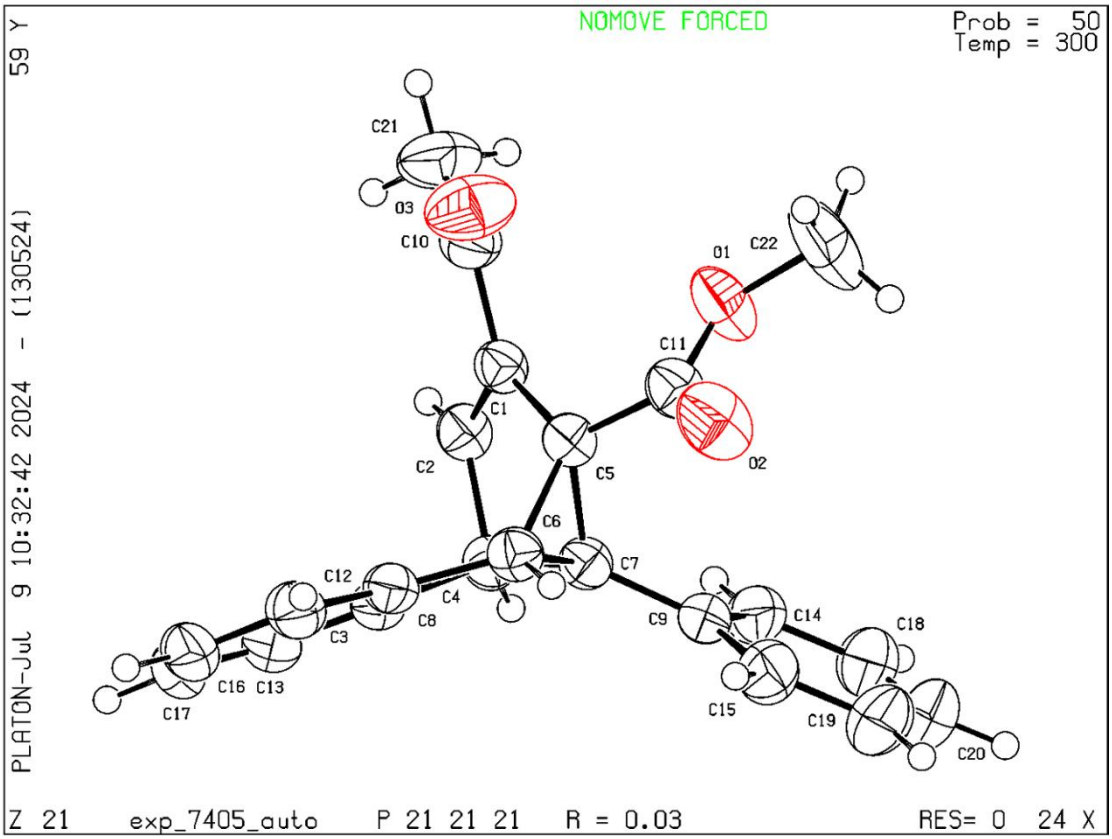
AbsCorr = MULTI-SCAN

Data completeness= 0.975 Theta(max)= 75.957

R(reflections)= 0.0440( 3940) wR2(reflections)= 0.1267( 4290)

S = 1.041 Npar= 281

**X-ray crystal data of 3fb** (CCDC 2392226) Chloroform / Hexane 1/1




Bond precision: C-C = 0.0026 A Wavelength=1.54184

Cell: a=7.6729(1) b=15.1105(1) c=15.2900(2)

alpha=90 beta=90 gamma=90

Temperature: 300 K

| | Calculated | Reported |
|---|---|---|
| Volume | 1772.74(3) | 1772.74(3) |
| Space group | P 21 21 21 | P 21 21 21 |
| Hall group | P 2ac 2ab | P 2ac 2ab |
| Moiety formula | $C_{22}H_{18}O_3$ | $C_{22}H_{18}O_3$ |
| Sum formula | $C_{22}H_{18}O_3$ | $C_{22}H_{18}O_3$ |
| Mr | 330.36 | 330.36 |
| Dx,g $cm^{-3}$ | 1.238 | 1.238 |
| Z | 4 | 4 |
| Mu ($mm^{-1}$) | 0.655 | |
| F000 | 696.0 | 696.0 |
| F000’ | 698.10 | 0.655 |

| | | |
|---|---|---|
| $h,k,l_{max}$ | 9,18,19 | 9,18,18 |
| Nref | 3689[ 2119] | 3632 |
| $T_{min},T_{max}$ | 0.877,0.906 | 0.377,1.000 |
| $T_{min'}$ | 0.877 | |

Correction method= # Reported T Limits: $T_{min}$=0.377 $T_{max}$=1.000

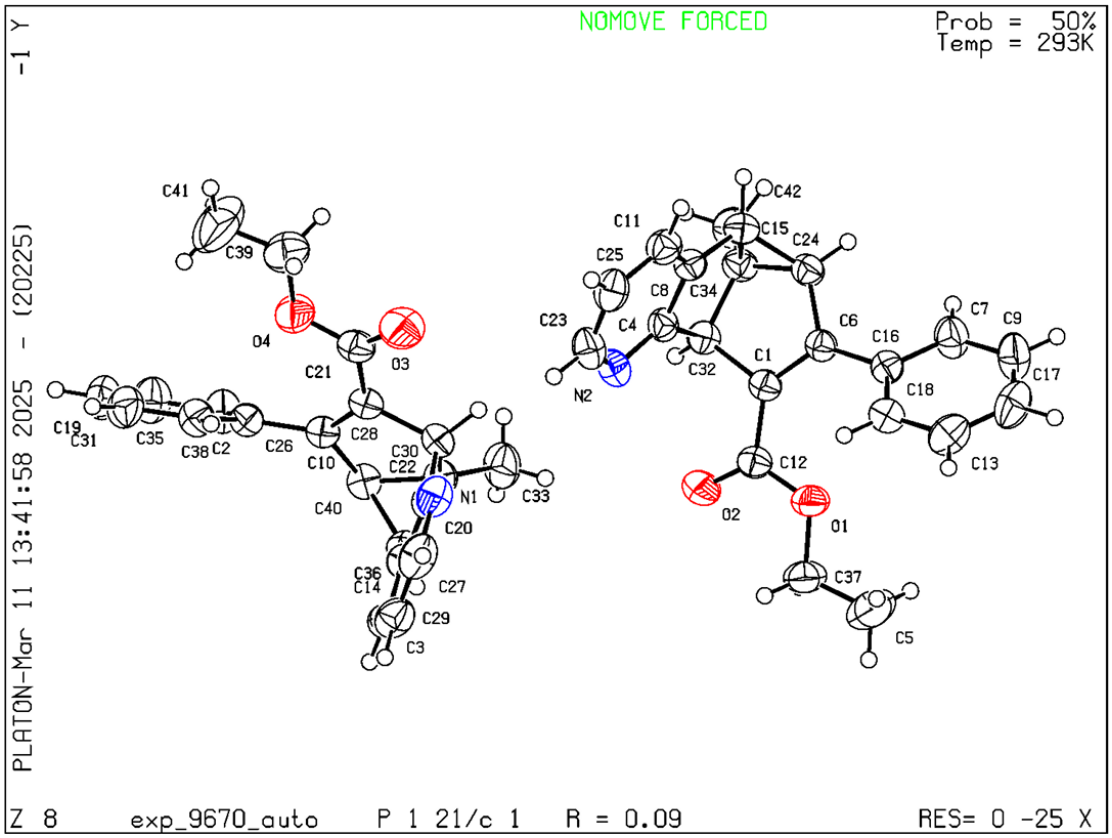
AbsCorr = MULTI-SCAN

Data completeness= 1.71/0.98 Theta(max)= 75.582

R(reflections)= 0.0310( 3493) wR2(reflections)= 0.0860( 3632)

S = 1.043 Npar= 229

**X-ray crystal data of 5** (CCDC 2432125) Acetone / Hexane 1/1




Bond precision: C-C = 0.0045 A Wavelength=1.54184

| | | | |
|---|---|---|---|
| Cell: | a=22.6047(3) | b=8.1436(1) | c=19.0805(3) |
| | alpha=90 | beta=110.010(2) | gamma=90 |
| Temperature: | 293 K | | |

| | Calculated | Reported |
|---|---|---|
| Volume | 3300.38(9) | 3300.37(9) |
| Space group | P 21/c | P 1 21/c 1 |
| Hall group | -P 2ybc | -P 2ybc |
| Moiety formula | $C_{21}H_{19}NO_2$ | $C_{21}H_{19}NO_2$ |
| Sum formula | $C_{21}H_{19}NO_2$ | $C_{21}H_{19}NO_2$ |
| Mr | 317.37 | 317.37 |
| Dx,g $cm^{-3}$ | 1.278 | 1.277 |
| Z | 8 | 8 |
| Mu ($mm^{-1}$) | 0.650 | 0.650 |
| F000 | 1344.0 | 1344.0 |
| F000’ | 1347.88 | |
| $h,k,l_{max}$ | 28,10,24 | 27,9,24 |
| Nref | 6870 | 6472 |
| $T_{min},T_{max}$ | 0.856,0.890 | 0.669,1.000 |
| $T_{min'}$ | 0.850 | |

Correction method= # Reported T Limits: $T_{min}$=0.669 $T_{max}$=1.000

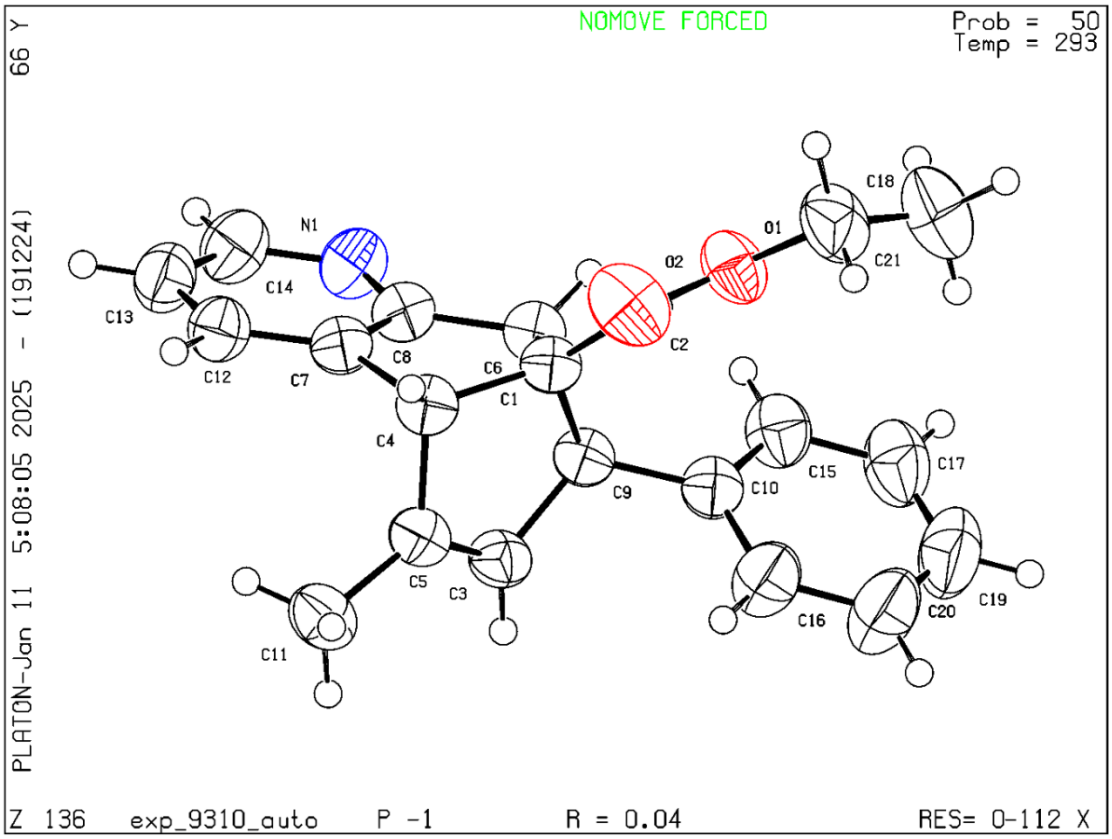
AbsCorr = MULTI-SCAN

Data completeness= 0.942 Theta(max)= 75.868

R(reflections)= 0.0899( 5667) wR2(reflections)= 0.2709( 6472)

S = 1.034 Npar= 437

**X-ray crystal data of 5ga-3** (CCDC 2416776) Ethyl acetate/Hexane 1/1




Bond precision: C-C = 0.0021 A Wavelength=1.54184

Cell: a=6.3303(2) b=7.7628(2) c=18.0636(4)

alpha=88.960(2) beta=87.618(2) gamma=71.409(3)

Temperature: 293 K

| | Calculated | Reported |
|---|---|---|
| Volume | 840.60(4) | 840.60(4) |
| Space group | P -1 | P -1 |
| Hall group | -P 1 | -P 1 |
| Moiety formula | $C_{21}H_{19}NO_2$ | $C_{21}H_{19}NO_2$ |
| Sum formula | $C_{21}H_{19}NO_2$ | $C_{21}H_{19}NO_2$ |
| Mr | 317.37 | 317.37 |
| Dx,g $cm^{-3}$ | 1.254 | 1.254 |
| Z | 2 | 2 |
| Mu ($mm^{-1}$) | 0.638 | 0.638 |
| F000 | 336.0 | 336.0 |
| F000’ | 336.97 | |

| | | |
|---|---|---|
| $h,k,l_{max}$ | 7,9,22 | 7,9,22 |
| Nref | 3496 | 3307 |
| $T_{min},T_{max}$ | 0.892,0.915 | 0.709,1.000 |
| $T_{min'}$ | 0.892 | |

Correction method= # Reported T Limits: $T_{min}$=0.709 $T_{max}$=1.000

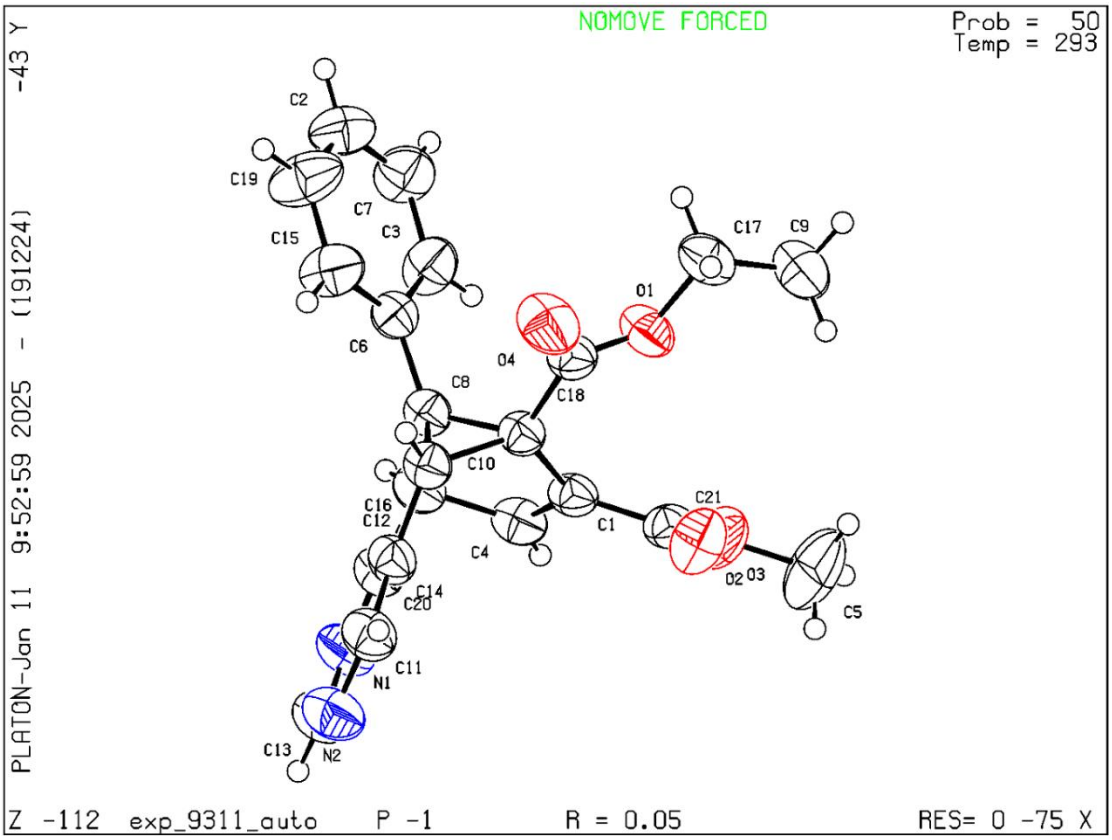
AbsCorr = MULTI-SCAN

Data completeness= 0.946 Theta(max)= 75.468

R(reflections)= 0.0440( 2828) wR2(reflections)= 0.1289( 3307)

S = 1.073 Npar= 219

**X-ray crystal data of 5na-1** (CCDC 2416775) Chloroform / Hexane1/1




Bond precision: C-C = 0.0021 A Wavelength=1.54184

Cell: a=8.1518(3) b=9.2515(2) c=12.5992(3)

alpha=86.134(2) beta=89.926(2) gamma=78.178(2)

Temperature: 293 K

| | Calculated | Reported |
|---|---|---|
| Volume | 927.84(5) | 927.84(5) |
| Space group | P -1 | P -1 |
| Hall group | -P 1 | -P 1 |
| Moiety formula | $C_{21}H_{18}N_2O_4$ | $C_{21}H_{18}N_2O_4$ |
| Sum formula | $C_{21}H_{18}N_2O_4$ | $C_{21}H_{18}N_2O_4$ |
| Mr | 362.37 | 362.37 |
| Dx,g $cm^{-3}$ | 1.297 | 1.297 |
| Z | 2 | 2 |
| Mu ($mm^{-1}$) | 0.746 | 0.746 |
| F000 | 380.0 | 380.0 |
| F000' | 381.22 | |
| h,k,$l_{max}$ | 10,11,15 | 9,11,15 |
| Nref | 3862 | 3623 |
| $T_{min}$, $T_{max}$ | 0.874,0.894 | 0.613,1.000 |
| $T_{min'}$ | 0.874 | |

Correction method= # Reported T Limits: $T_{min}$=0.613 $T_{max}$=1.000

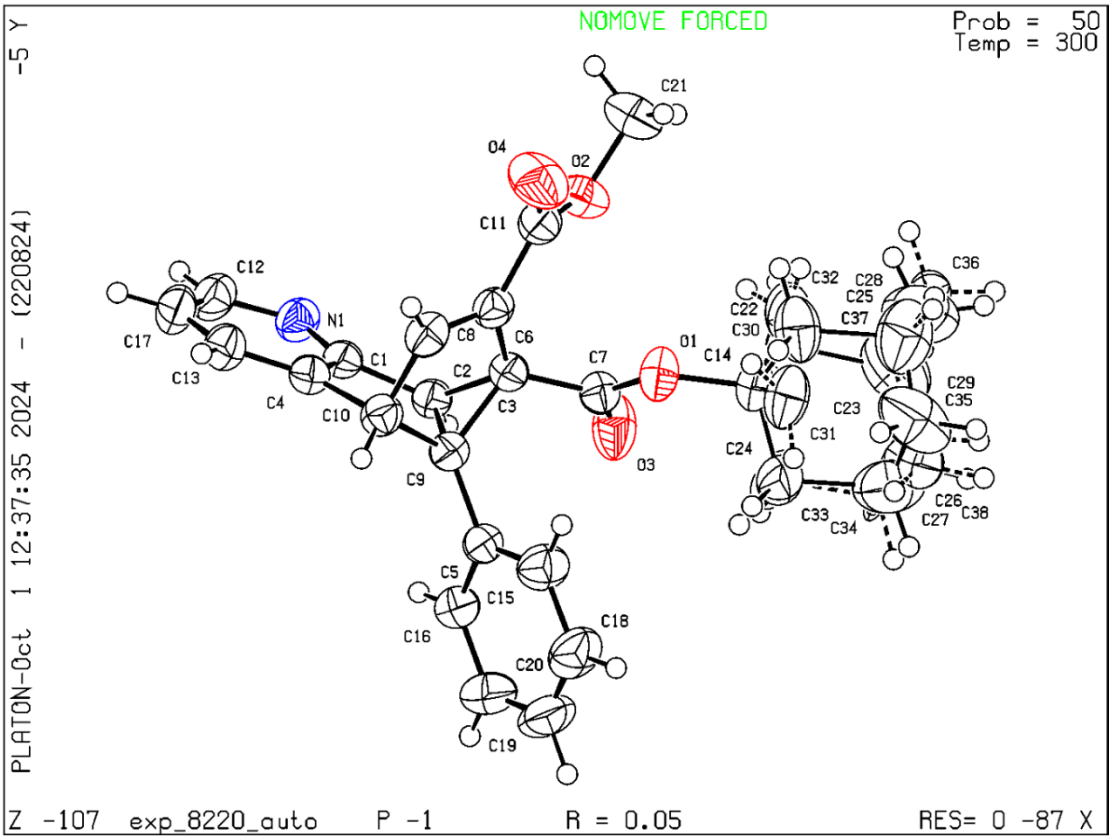
AbsCorr = MULTI-SCAN

Data completeness= 0.938 Theta(max)= 75.766

R(reflections)= 0.0498( 3210) wR2(reflections)= 0.1516( 3623)

S = 1.089 Npar= 246

**X-ray crystal data of 5ap** (CCDC 2392227) Chloroform / Hexane 1/1




Bond precision: C-C = 0.0024 A Wavelength=1.54184

Cell: a=9.8021(1) b=11.6463(1) c=11.6521(1)

alpha=86.529(1) beta=86.782(1) gamma=65.357(1)

Temperature: 300 K

| | Calculated | Reported |
|---|---|---|
| Volume | 1206.12(2) | 1206.12(2) |
| Space group | P -1 | P -1 |
| Hall group | -P 1 | -P 1 |
| Moiety formula | $C_{30}H_{29}NO_4$ | $C_{30}H_{29}NO_4$ |
| Sum formula | $C_{30}H_{29}NO_4$ | $C_{30}H_{29}NO_4$ |
| Mr | 467.54 | 467.54 |
| Dx,g $cm^{-3}$ | 1.287 | 1.287 |
| Z | 2 | 2 |
| Mu ($mm^{-1}$) | 0.681 | 0.681 |
| F000 | 496.0 | 496.0 |
| F000’ | 497.48 | |

| | | |
|---|---|---|
| $h,k,l_{max}$ | 12,14,14 | 12,14,14 |
| Nref | 5028 | 4813 |
| $T_{min}$, $T_{max}$ | 0.838,0.873 | 0.927,1.000 |
| $T_{min'}$ | 0.838 | |

Correction method= # Reported T Limits: $T_{min}$=0.927 $T_{max}$=1.000

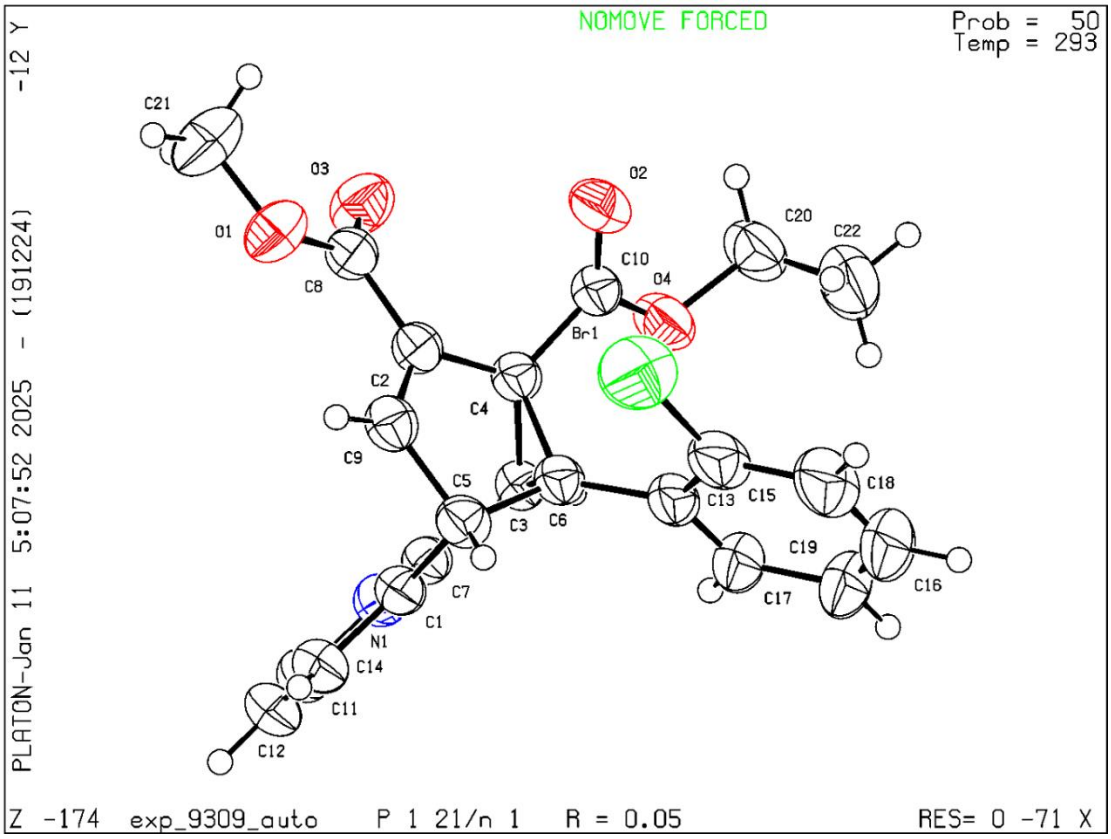
AbsCorr = MULTI-SCAN

Data completeness= 0.957 Theta(max)= 75.698

R(reflections)= 0.0533( 4451) wR2(reflections)= 0.1463( 4813)

S = 1.046 Npar= 391

**X-ray crystal data of 5am-1** (CCDC 2416777) Chloroform / Hexane 1/1




Bond precision: C-C = 0.0037 A Wavelength=1.54184

| | | | |
|---|---|---|---|
| Cell: | a=9.81144(17) | b=11.1752(3) | c=17.8620(3) |
| | alpha=90 | beta=94.4374(16) | gamma=90 |

Temperature: 293 K

| | Calculated | Reported |
|---|---|---|
| Volume | 1952.61(7) | 1952.61(7) |
| Space group | P 21/n | P 1 21/n 1 |
| Hall group | -P 2yn | -P 2yn |
| Moiety formula | $C_{22}H_{18}BrNO_4$ | $C_{22}H_{18}BrNO_4$ |
| Sum formula | $C_{22}H_{18}BrNO_4$ | $C_{22}H_{18}BrNO_4$ |
| Mr | 440.27 | 441.29 |
| Dx,g $cm^{-3}$ | 1.498 | 1.501 |
| Z | 4 | 4 |
| Mu ($mm^{-1}$) | 3.109 | 3.110 |
| F000 | 896.0 | 900.0 |
| F000' | 895.69 | |
| $h,k,l_{max}$ | 12,14,22 | 12,13,21 |
| Nref | 4065 | 3871 |
| $T_{min},T_{max}$ | 0.600,0.627 | 0.251,1.000 |
| $T_{min'}$ | 0.544 | |

Correction method= # Reported T Limits: $T_{min}$=0.251 $T_{max}$=1.000

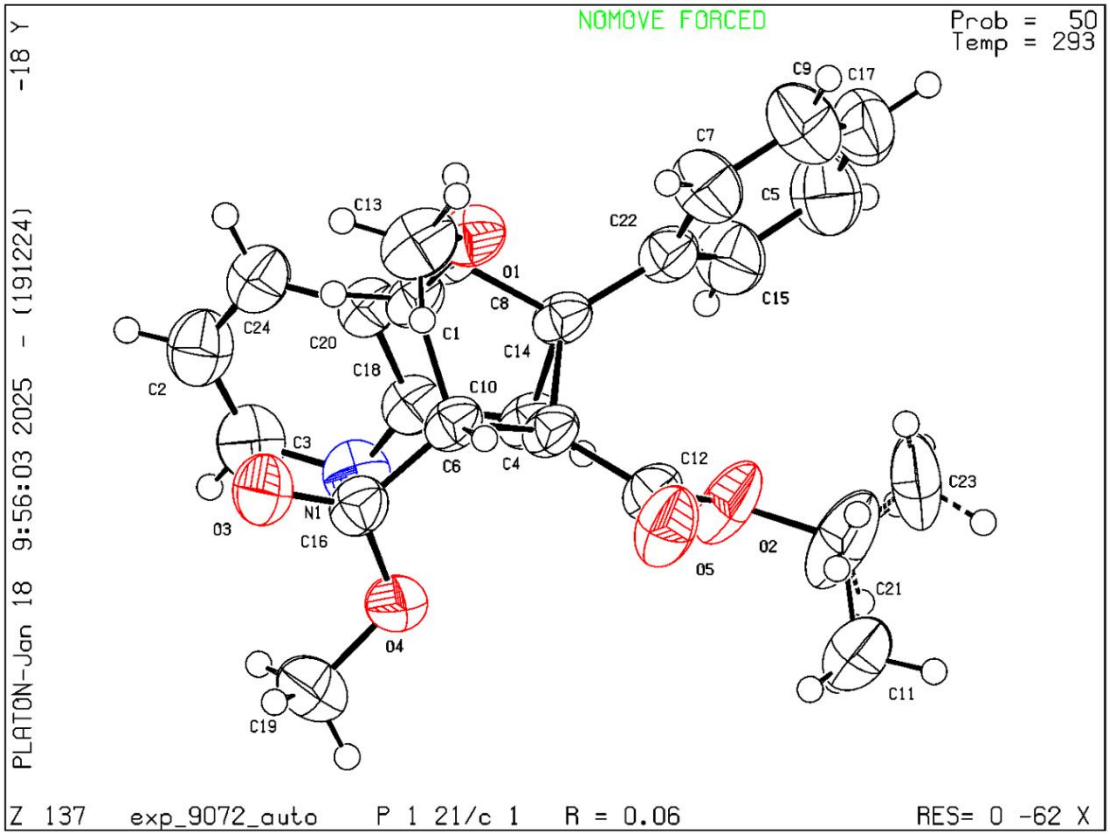
AbsCorr = MULTI-SCAN

Data completeness= 0.952 Theta(max)= 75.685

R(reflections)= 0.0474( 3322) wR2(reflections)= 0.1416( 3871)

S = 1.046 Npar= 255

**X-ray crystal data of 5aa-c** (CCDC 2413435) Chloroform / Hexane 1/1




| | | | |
|---|---|---|---|
| Bond precision: | C-C = 0.0030 A | | Wavelength=1.54184 |
| Cell: | a=11.65139(12) | b=15.13875(13) | c=12.38448(12) |
| | alpha=90 | beta=112.0248(12) | gamma=90 |
| Temperature: | 293 K | | |

| | Calculated | Reported |
|---|---|---|
| Volume | 2025.05(4) | 2025.05(4) |
| Space group | P 21/c | P 1 21/c 1 |
| Hall group | -P 2ybc | -P 2ybc |
| Moiety formula | $C_{23}H_{23}NO_5$ | $C_{23}H_{23}NO_5$ |
| Sum formula | $C_{23}H_{23}NO_5$ | $C_{23}H_{23}NO_5$ |
| Mr | 393.42 | 393.42 |
| Dx,g $cm^{-3}$ | 1.290 | 1.290 |
| Z | 4 | 4 |
| Mu ($mm^{-1}$) | 0.746 | 0.746 |
| F000 | 832.0 | 832.0 |
| F000’ | 834.66 | |
| h,k,$l_{max}$ | 14,19,15 | 14,18,15 |

| | | |
|---|---|---|
| Nref | 4224 | 4076 |
| $T_{min}$,$T_{max}$ | 0.851,0.887 | 0.289,1.000 |
| $T_{min'}$ | 0.830 | |

Correction method= # Reported T Limits: $T_{min}$=0.289 $T_{max}$=1.000

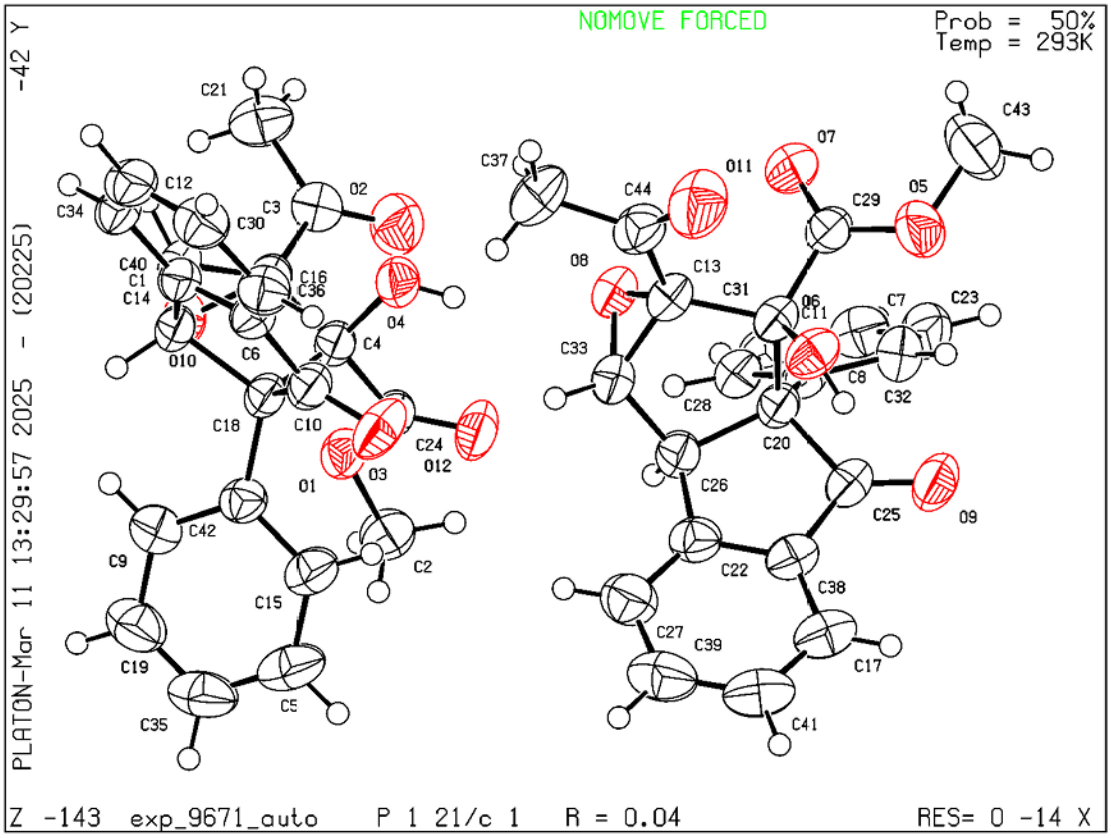
AbsCorr = MULTI-SCAN

Data completeness= 0.965 Theta(max)= 75.905

R(reflections)= 0.0583( 3766) wR2(reflections)= 0.1515( 4076)

S = 1.043 Npar= 276

**X-ray crystal data of** (CCDC 2432126) Chloroform / Hexane 1/1




Bond precision: C-C = 0.0021 A Wavelength=1.54184

| | | | |
|---|---|---|---|
| Cell: | a=12.53747(9) | b=13.30629(12) | c=21.80649(16) |
| | alpha=90 | beta=90.5945(6) | gamma=90 |
| Temperature: | 293 K | | |

| | Calculated | Reported |
|---|---|---|
| Volume | 3637.72(5) | 3637.72(5) |
| Space group | P 21/c | P 1 21/c 1 |
| Hall group | -P 2ybc | -P 2ybc |
| Moiety formula | $C_{22}H_{18}O_6$ | $C_{22}H_{18}O_6$ |
| Sum formula | $C_{22}H_{18}O_6$ | $C_{22}H_{18}O_6$ |
| Mr | 378.36 | 378.36 |
| Dx,g $cm^{-3}$ | 1.382 | 1.382 |
| Z | 8 | 8 |
| Mu ($mm^{-1}$) | 0.839 | 0.839 |
| F000 | 1584.0 | 1584.0 |
| F000’ | 1589.37 | |
| $h,k,l_{max}$ | 15,16,27 | 15,16,26 |
| Nref | 7575 | 7270 |
| $T_{min},T_{max}$ | 0.818,0.860 | 0.667,1.000 |
| $T_{min'}$ | 0.811 | |

Correction method= # Reported

T Limits: $T_{min}$=0.667 $T_{max}$=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.960

Theta(max)= 75.885

R(reflections)= 0.0420( 6459)

wR2(reflections)= 0.1211( 7270)

S = 1.040

Npar= 511

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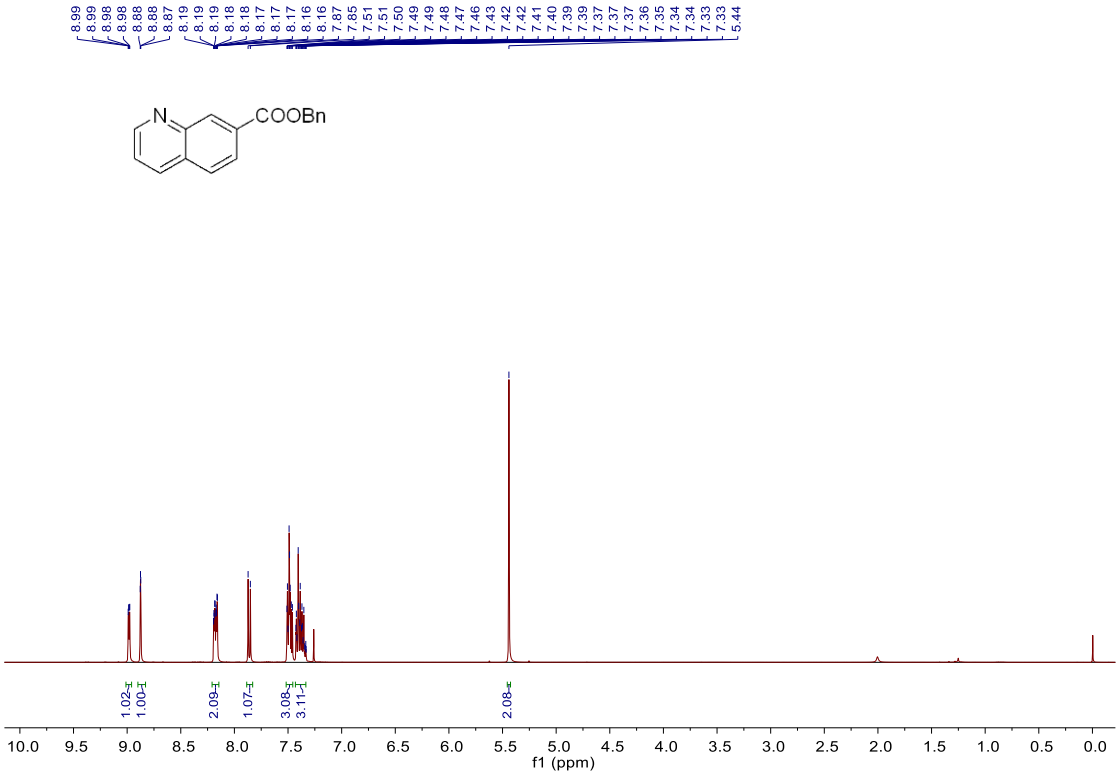
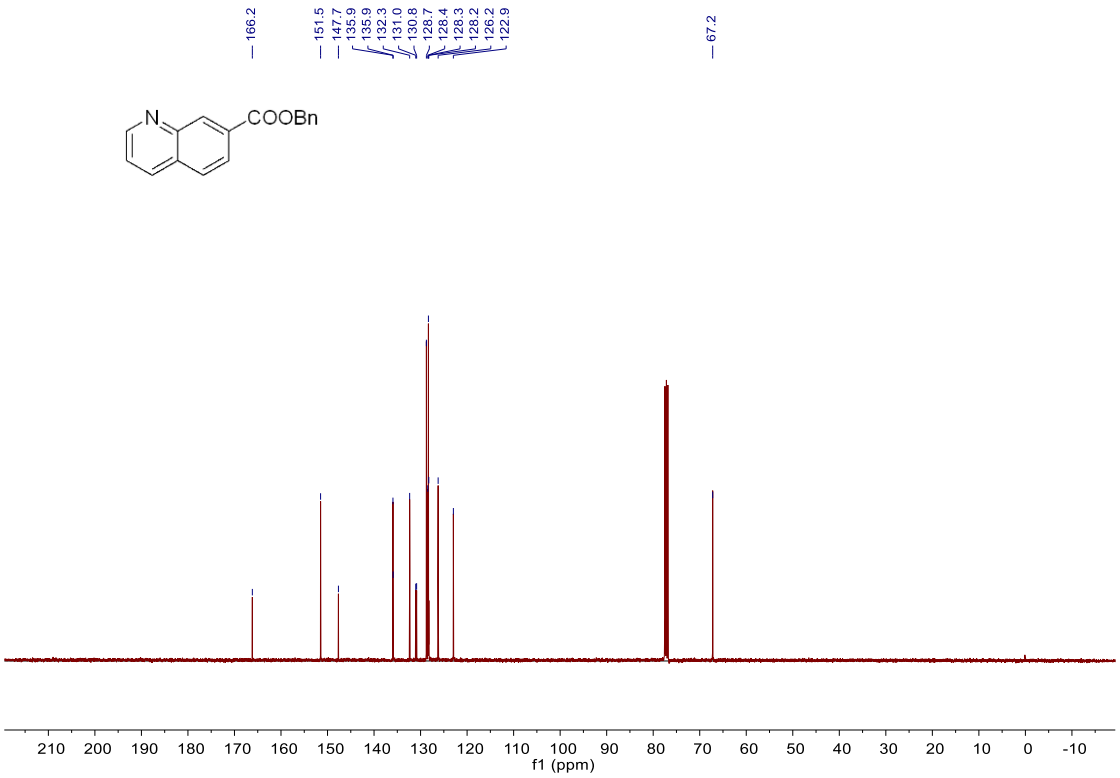
## 10. Copies of NMR spectra for substrates

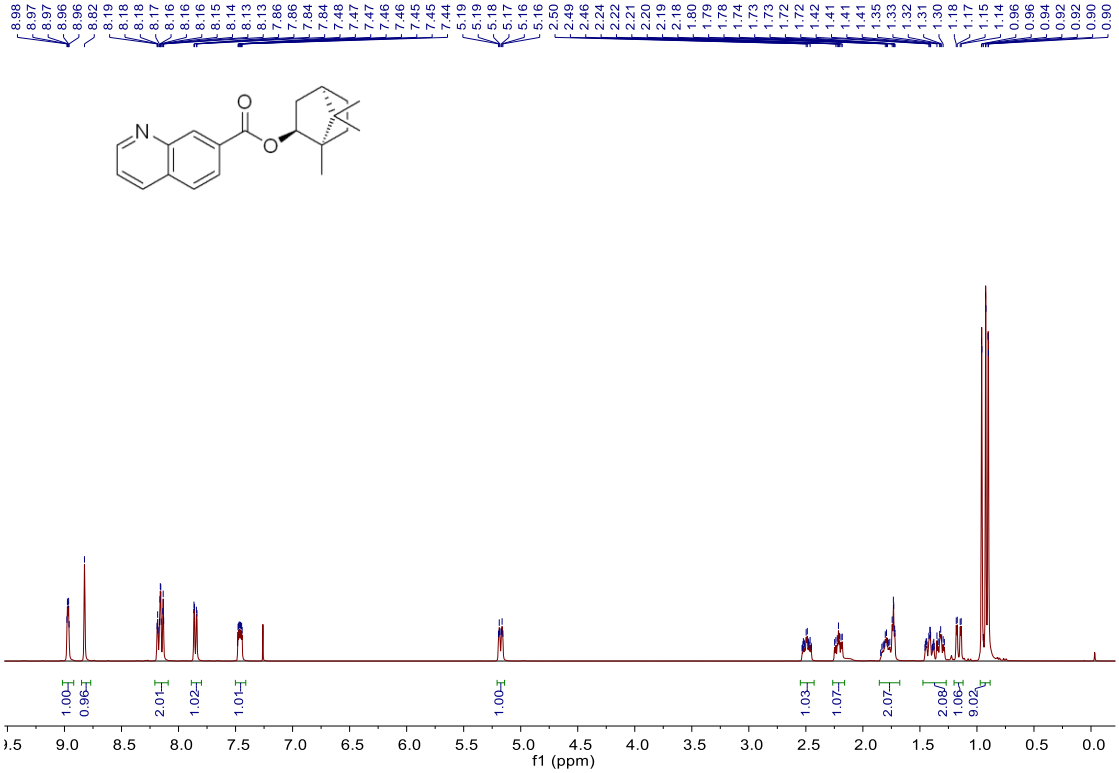
$^{1}$H NMR spectrum of **4d**



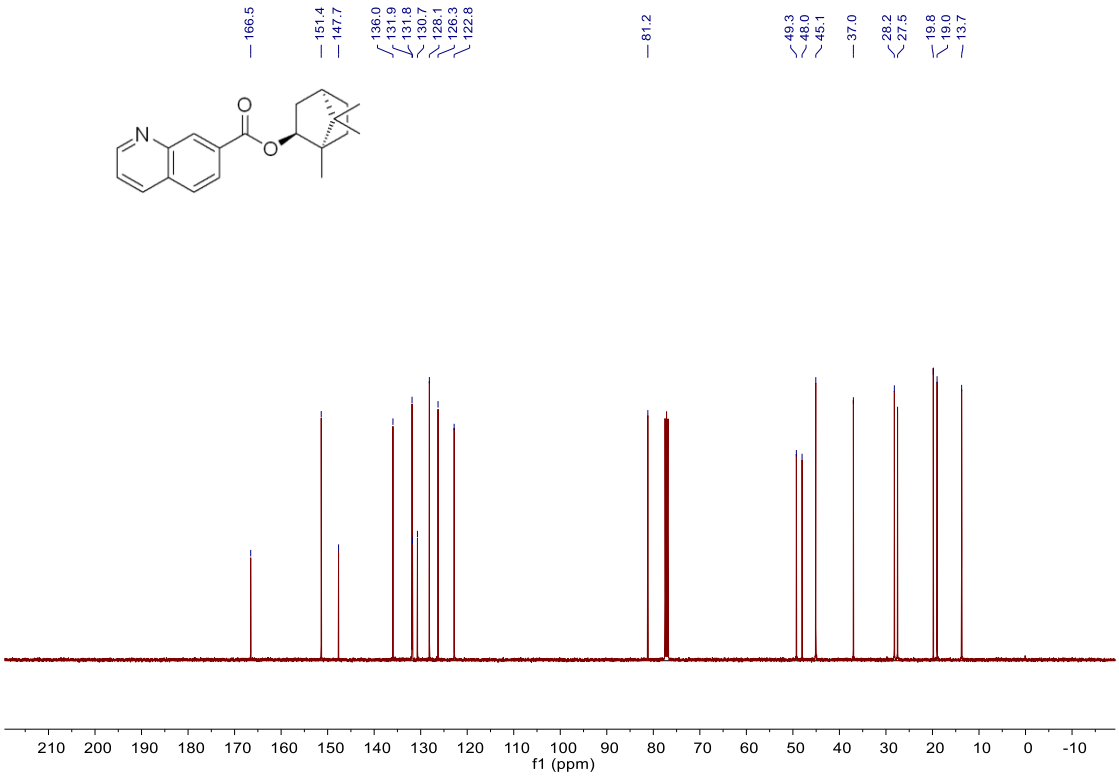

$^{13}$C NMR spectrum of **4d**



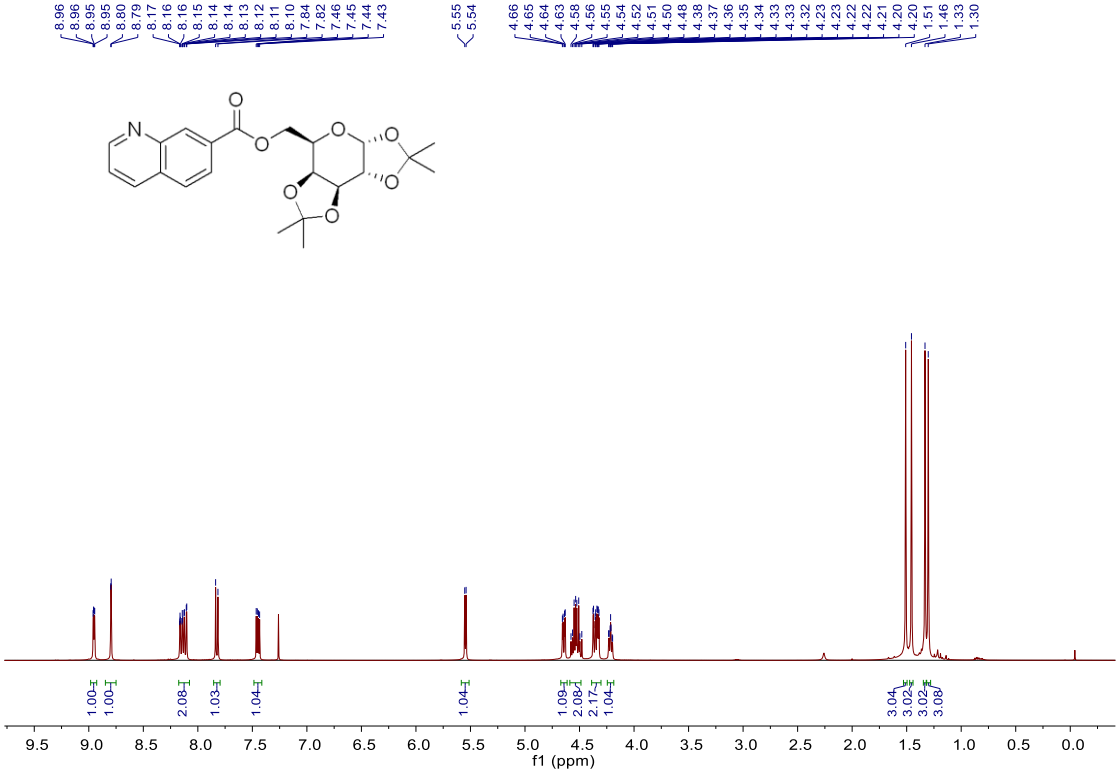
$^{1}$H NMR spectrum of **4e**



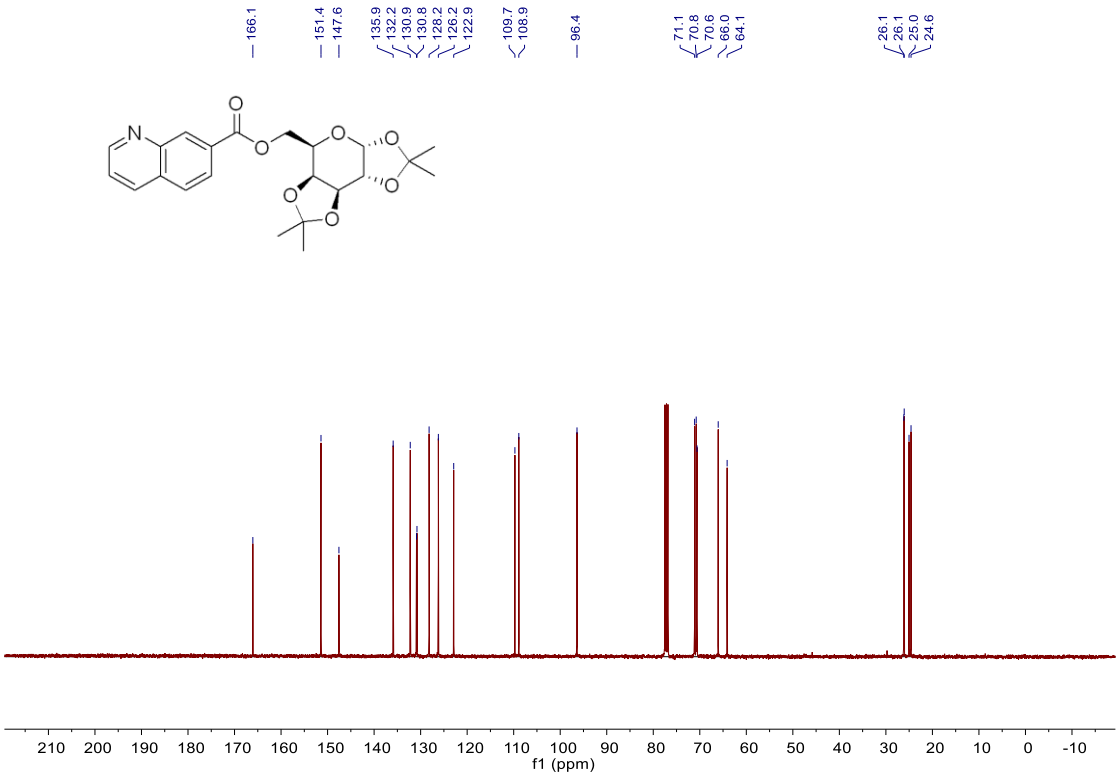

$^{13}$C NMR spectrum of **4e**



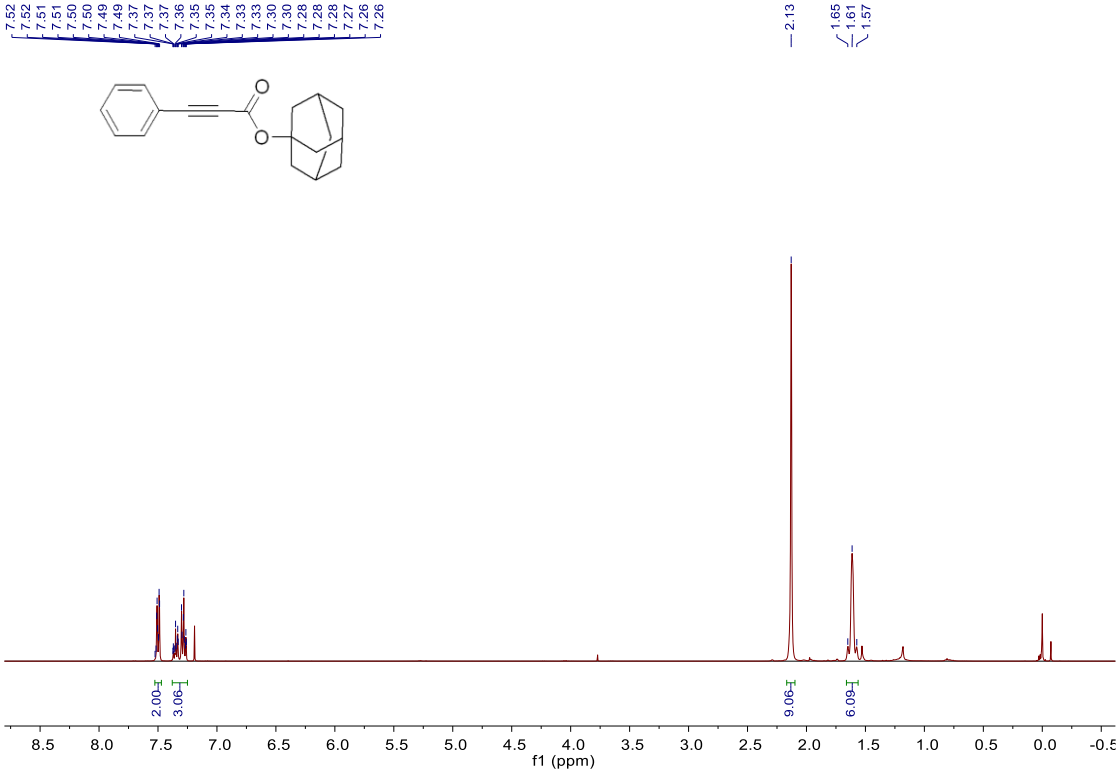
$^{1}$H NMR spectrum of **4f**



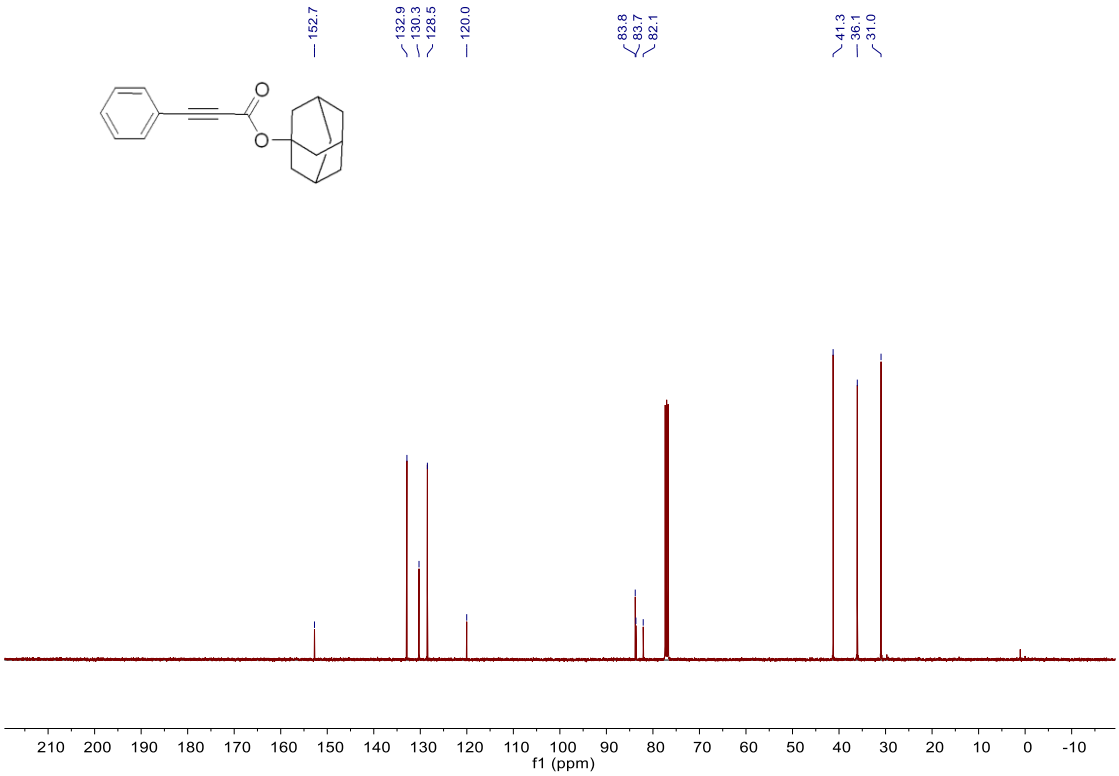

$^{13}$C NMR spectrum of **4f**



$^{1}$H NMR spectrum of **2P**

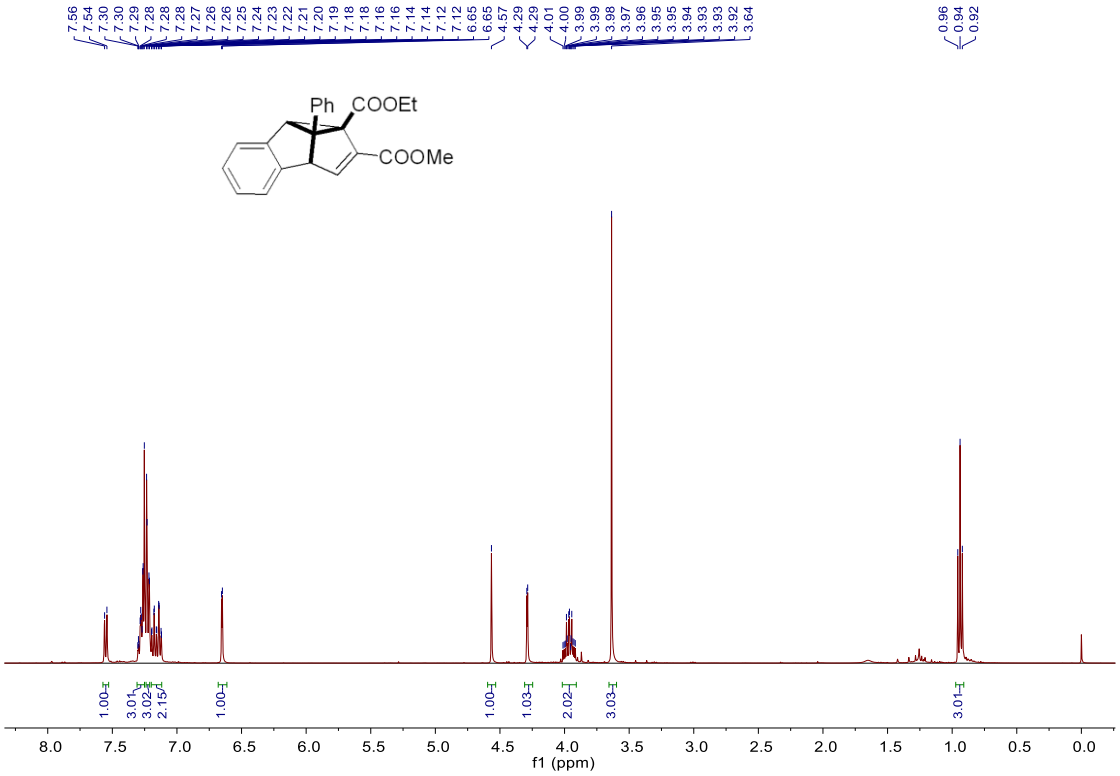



$^{13}$C NMR spectrum of **2P**

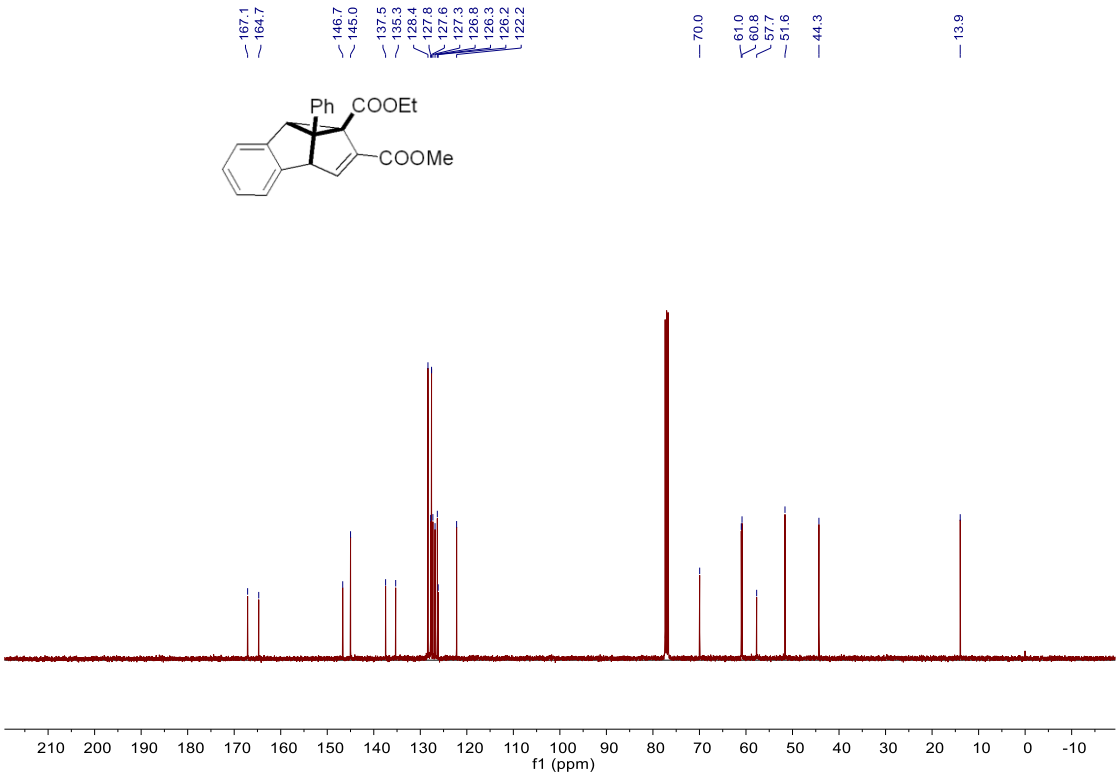


## 11. Copies of NMR spectra for the products

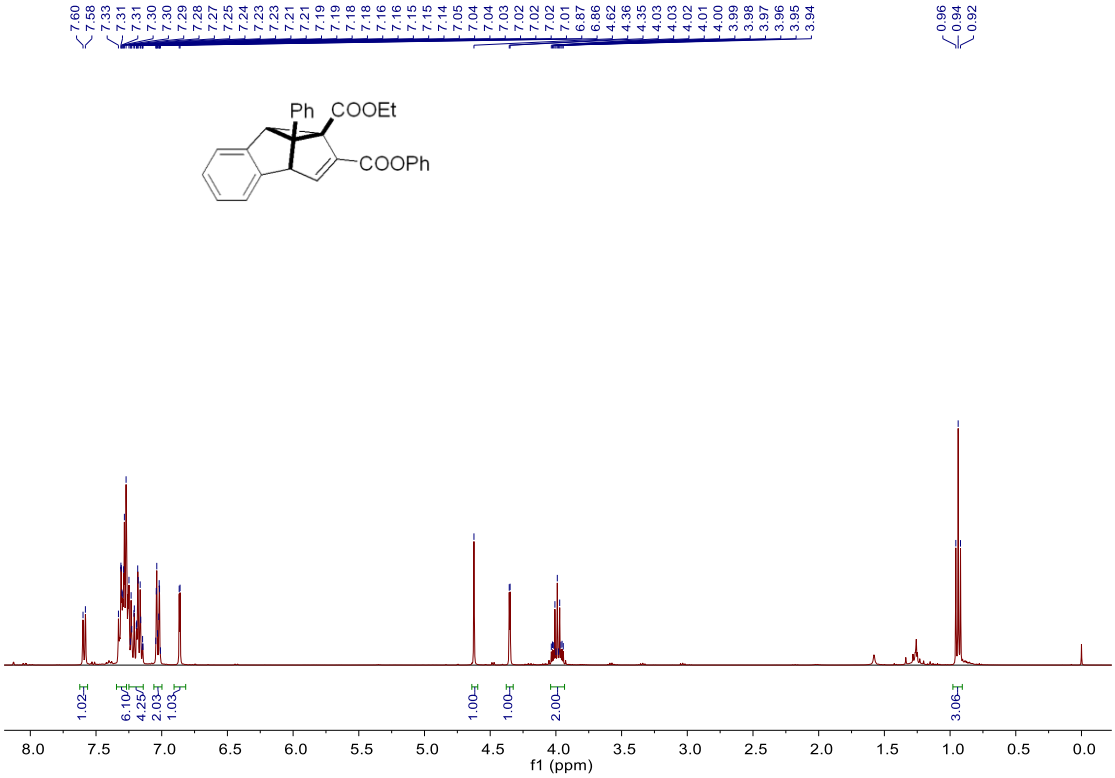
$^{1}$H NMR spectrum of **3aa**



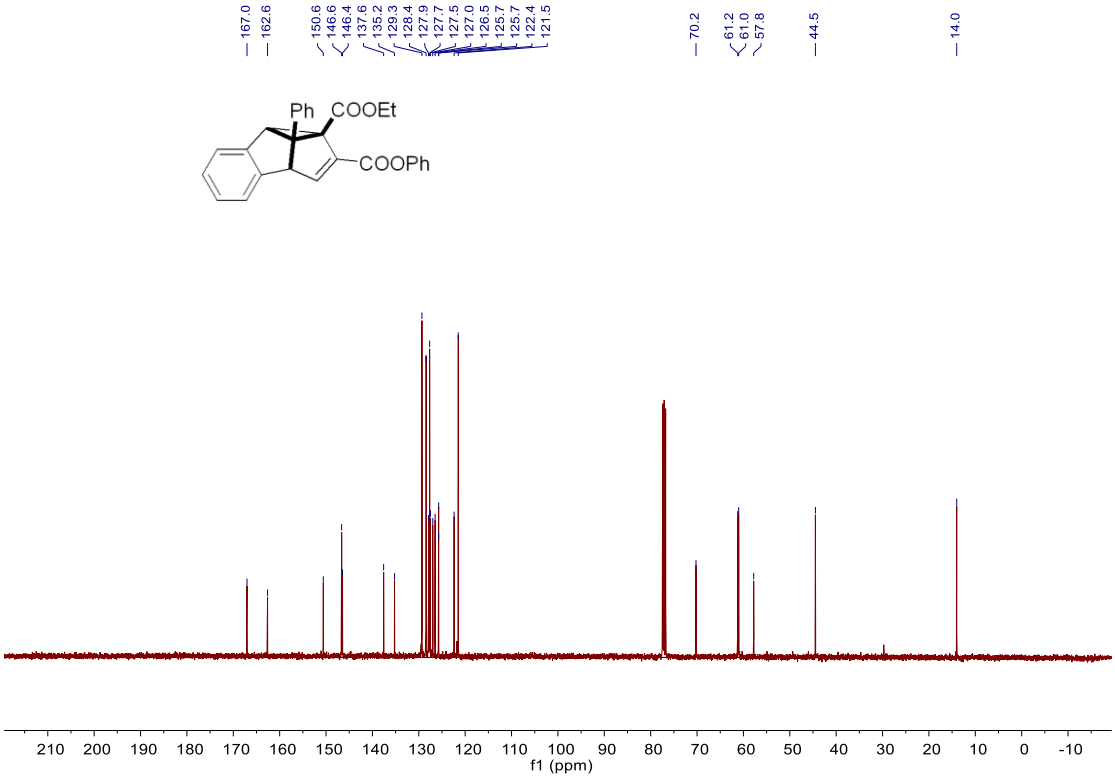

$^{13}$C NMR spectrum of **3aa**



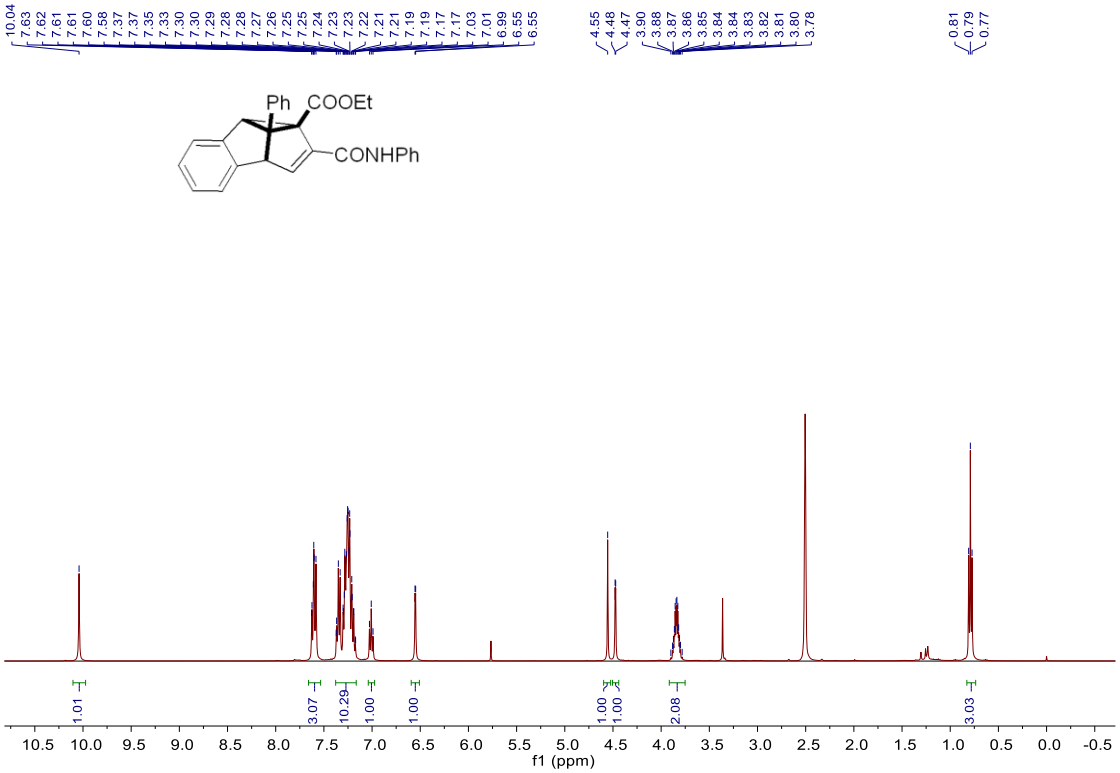
$^{1}$H NMR spectrum of **3ba**



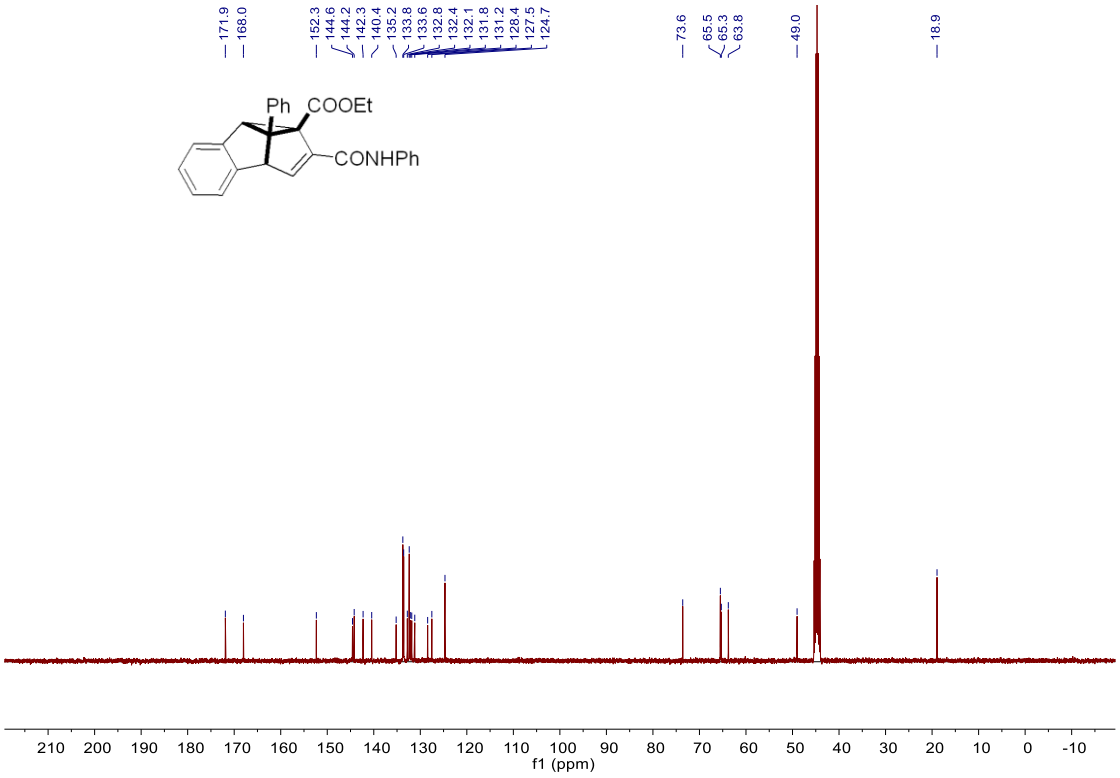

$^{13}$C NMR spectrum of **3ba**



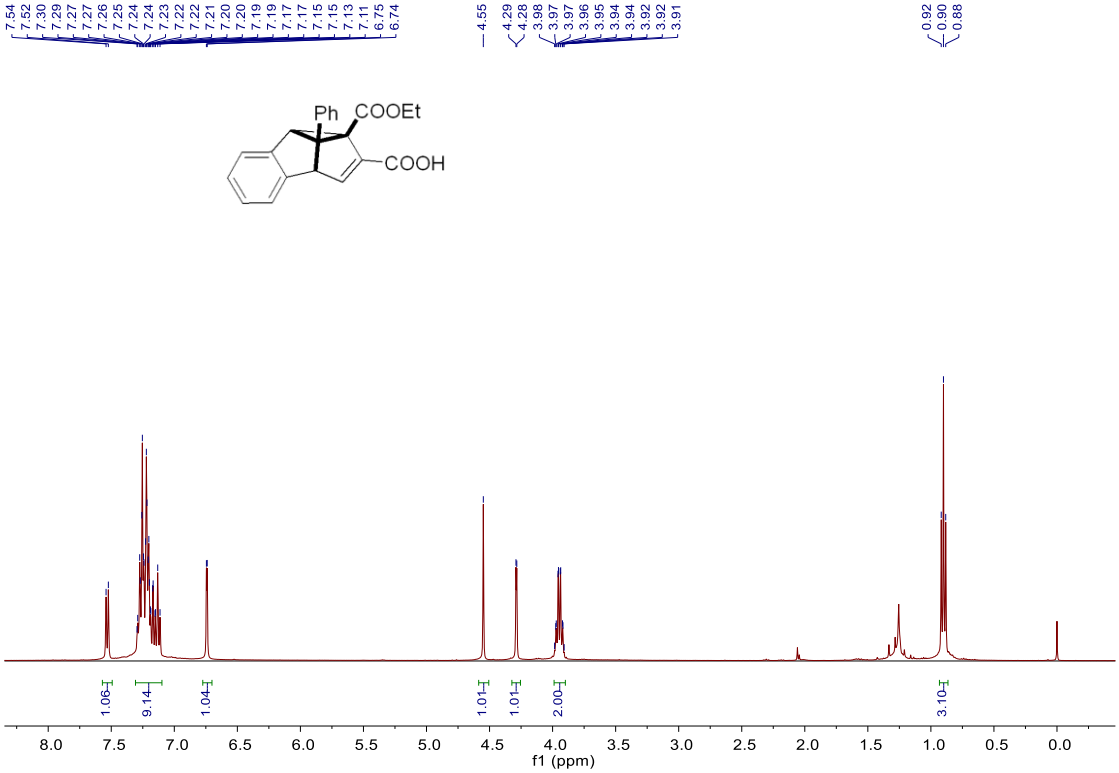
$^{1}$H NMR spectrum of **3ca**



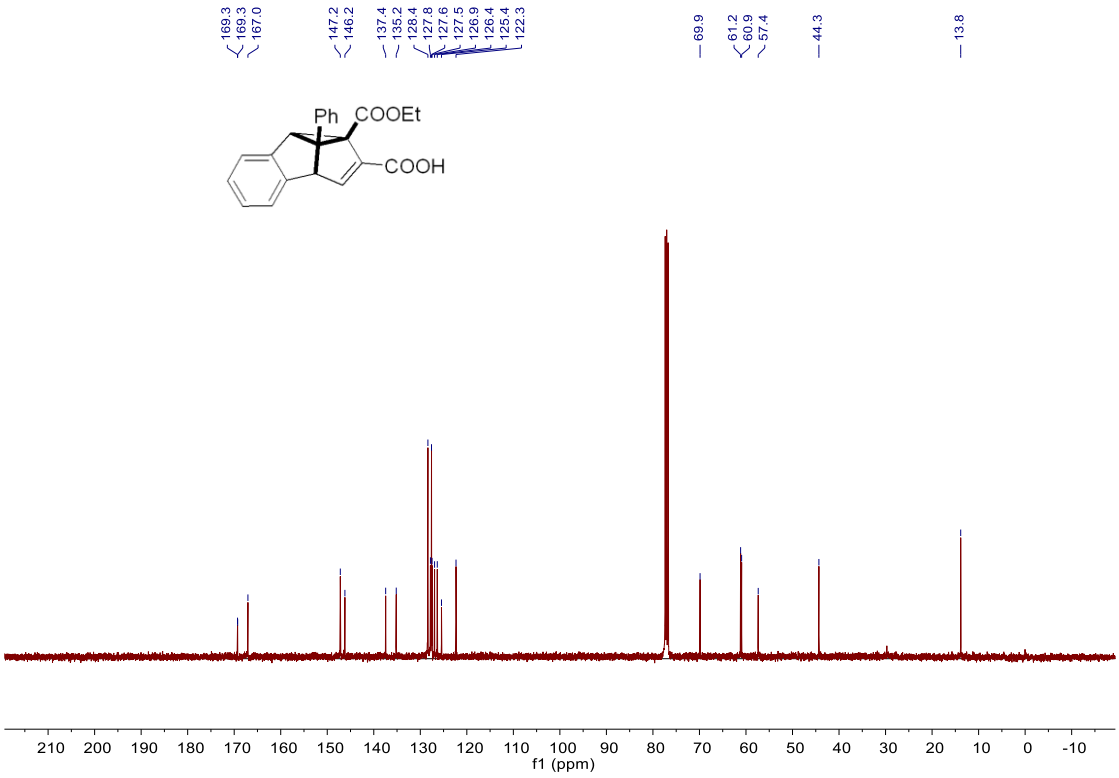

$^{13}$C NMR spectrum of **3ca**



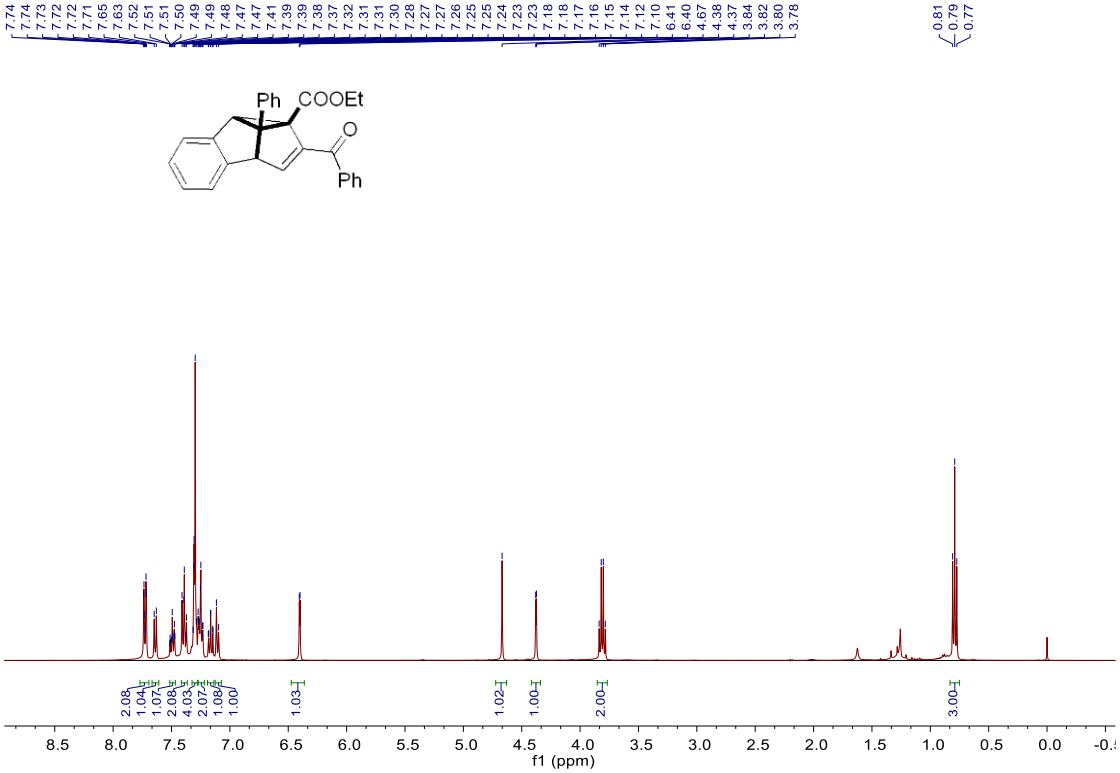
$^{1}$H NMR spectrum of **3da**



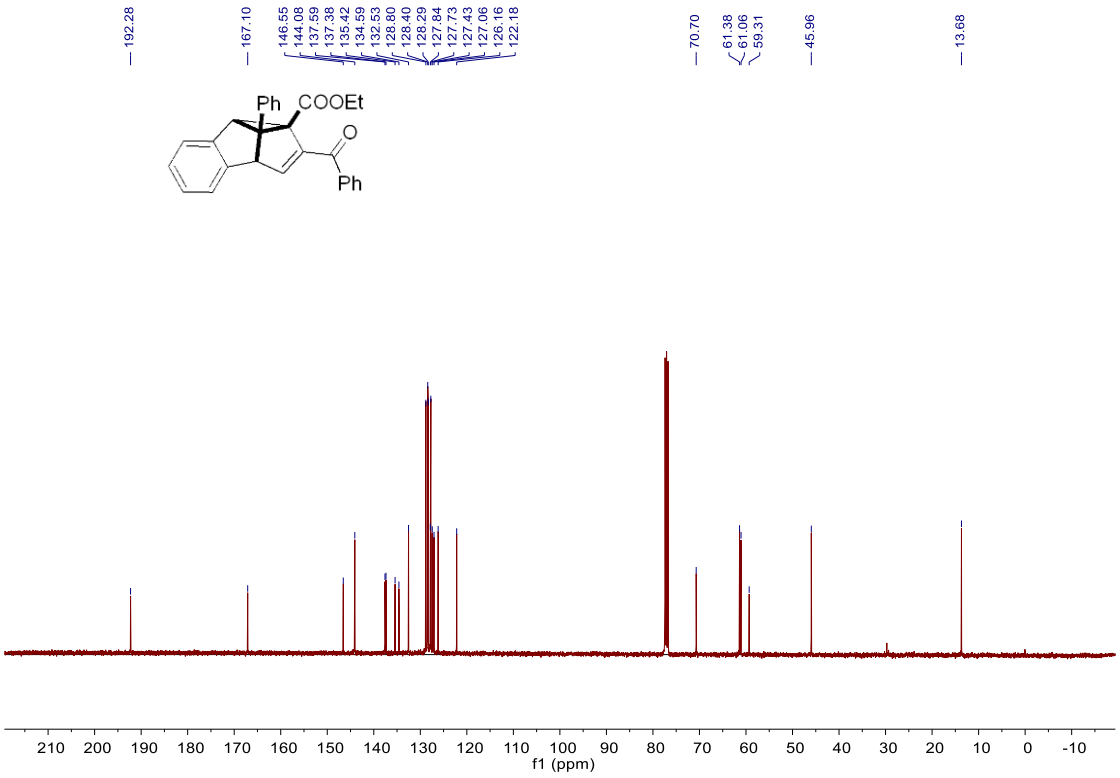

$^{13}$C NMR spectrum of **3da**



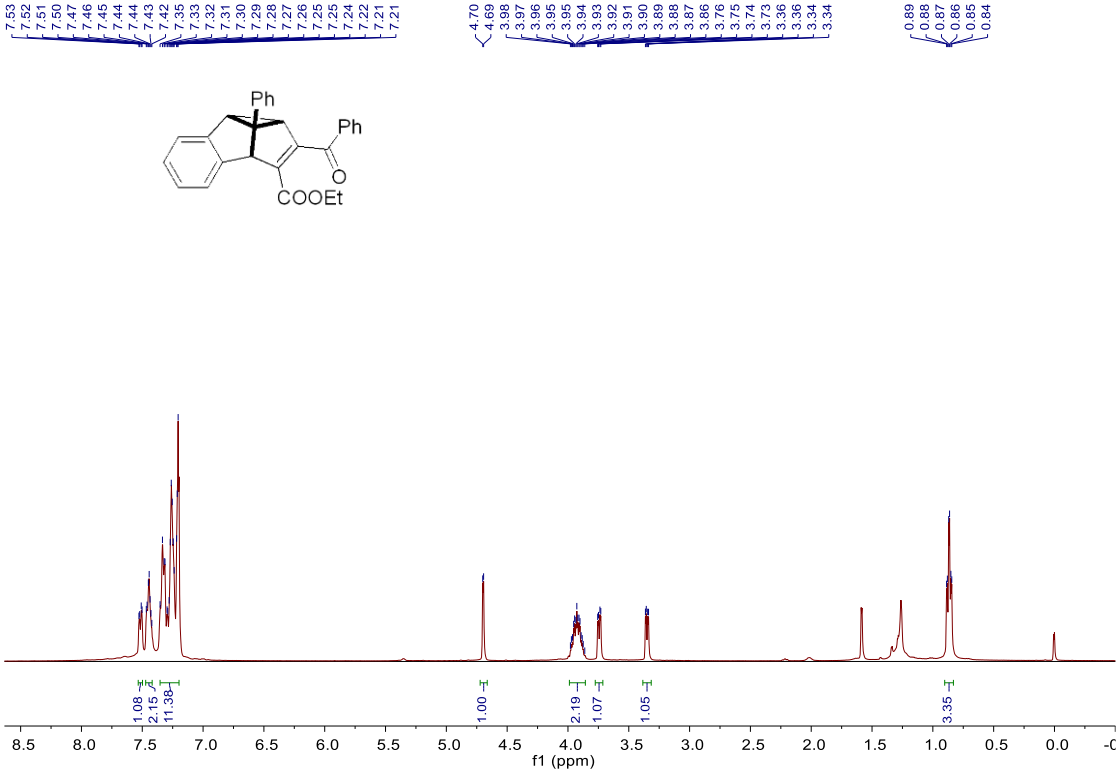
$^{1}$H NMR spectrum of **3ea-1**



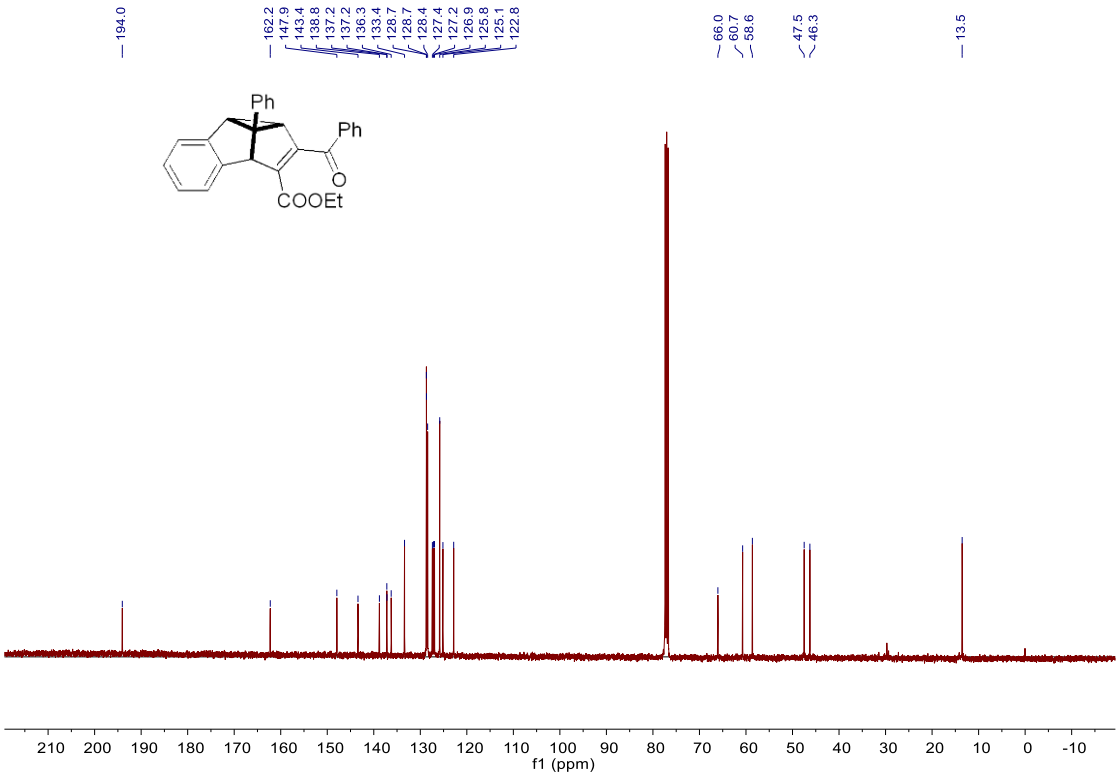

$^{13}$C NMR spectrum of **3ea-1**



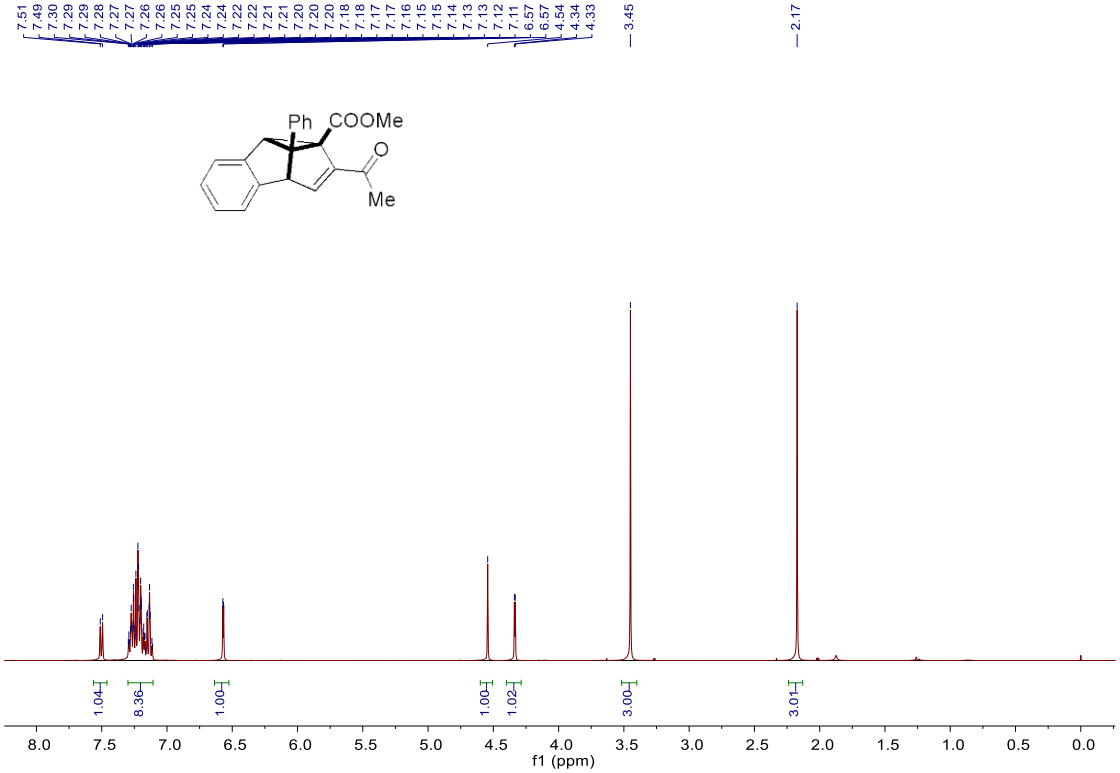
$^{1}$H NMR spectrum of **3ea-2**



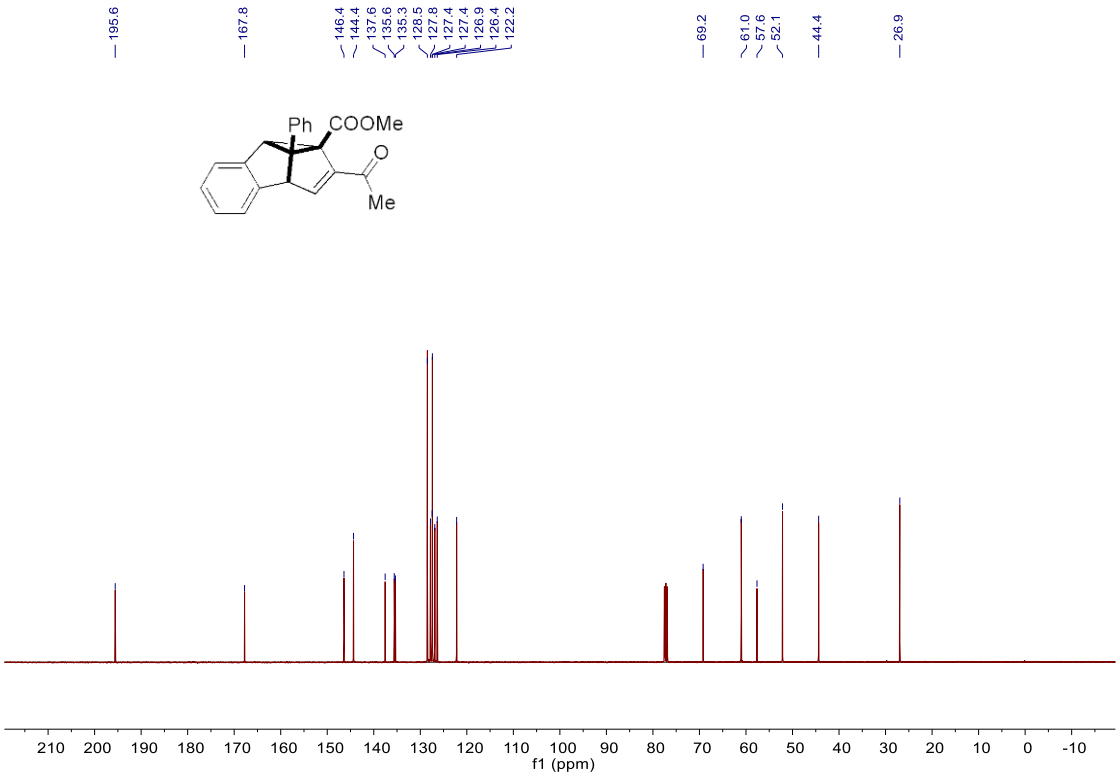

$^{13}$C NMR spectrum of **3ea-2**



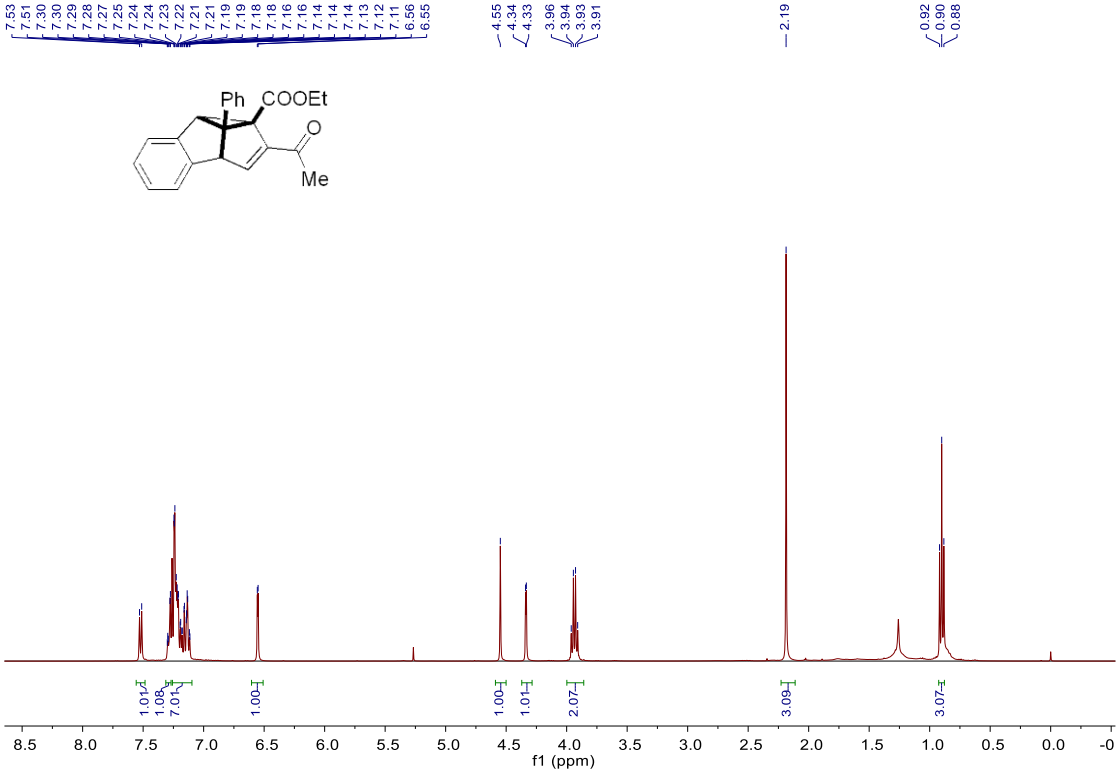
$^{1}$H NMR spectrum of **3fb**



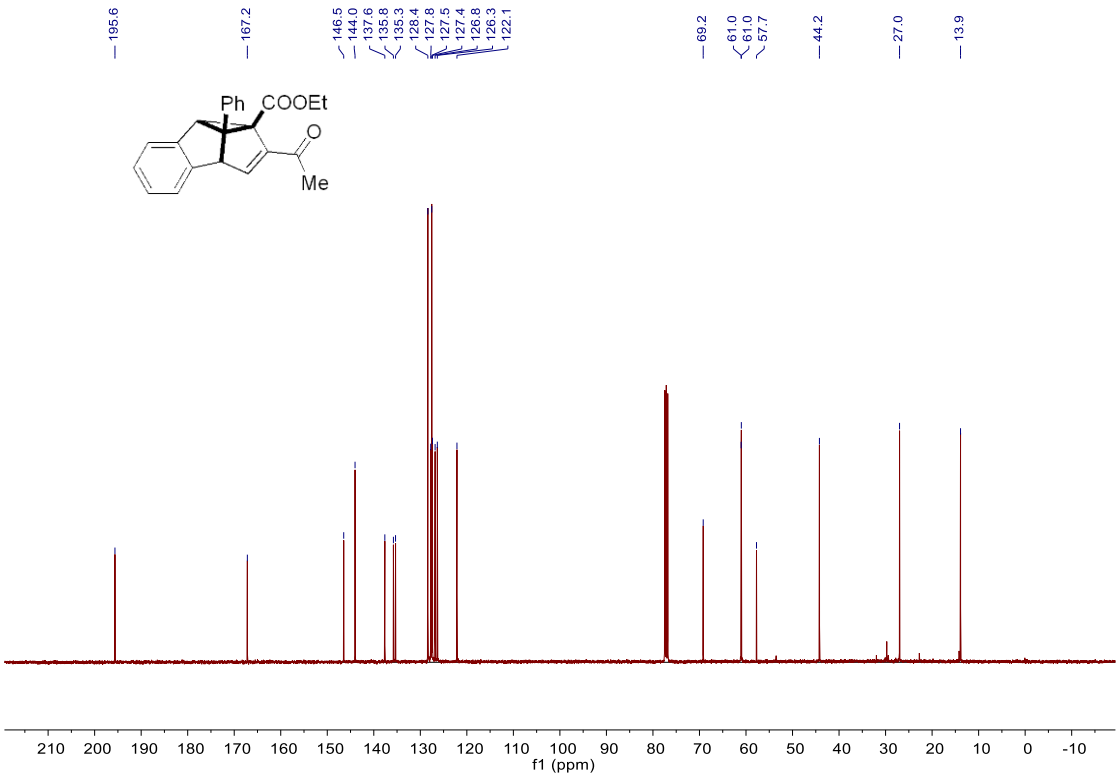

$^{13}$C NMR spectrum of **3fb**



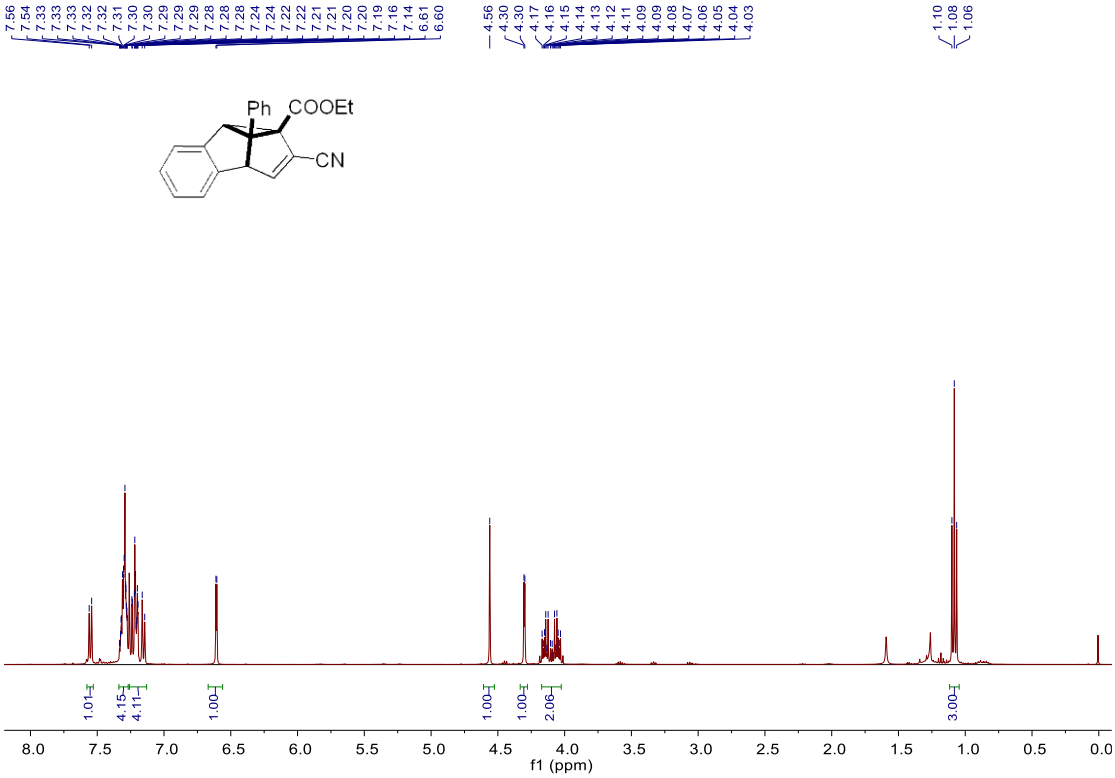
$^{1}$H NMR spectrum of **3fa**



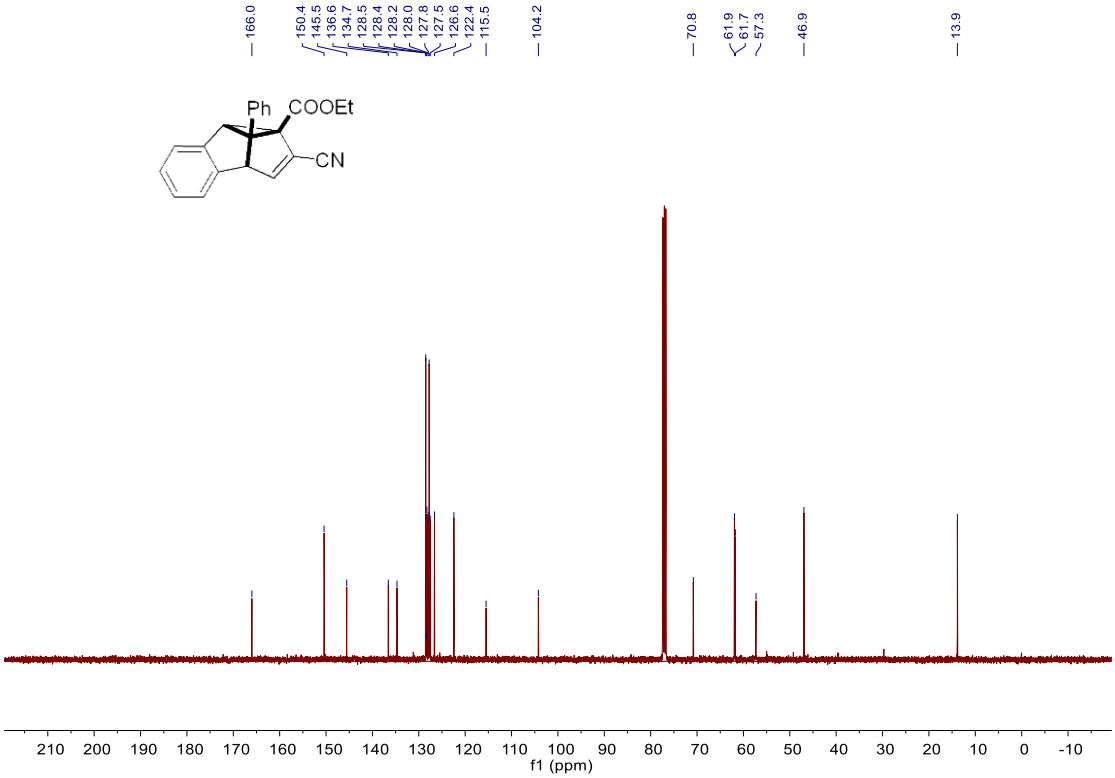

$^{13}$C NMR spectrum of **3fa**



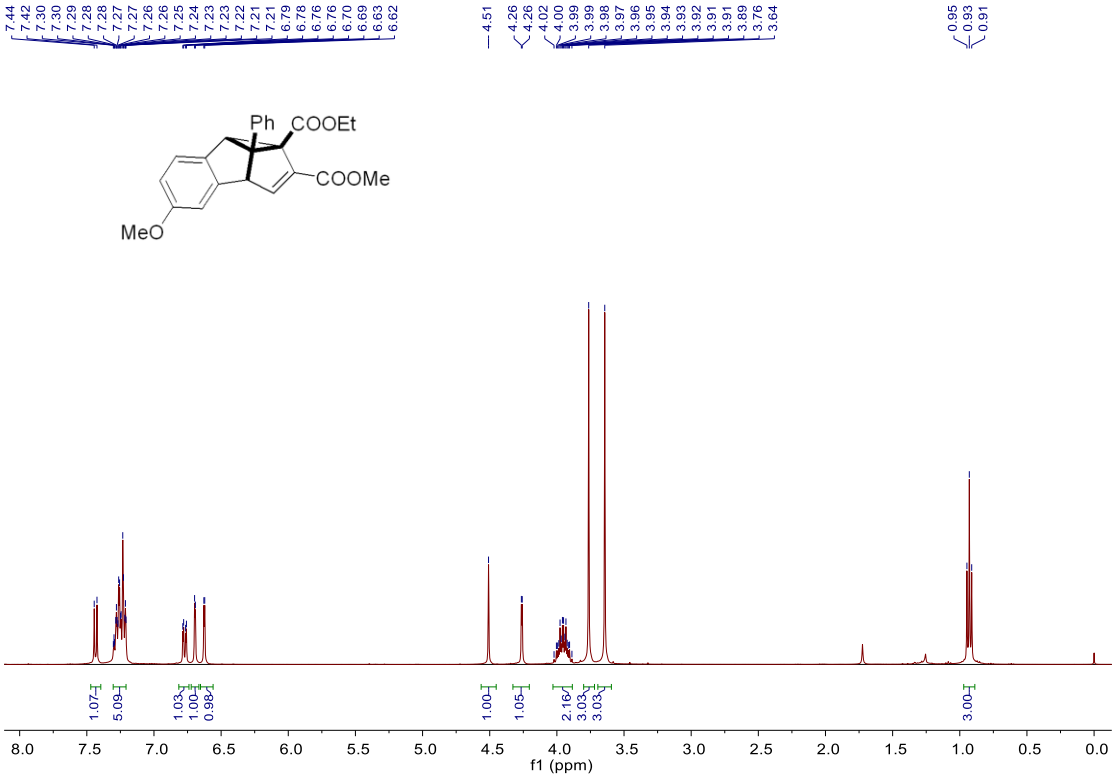
$^{1}$H NMR spectrum of **3ga**



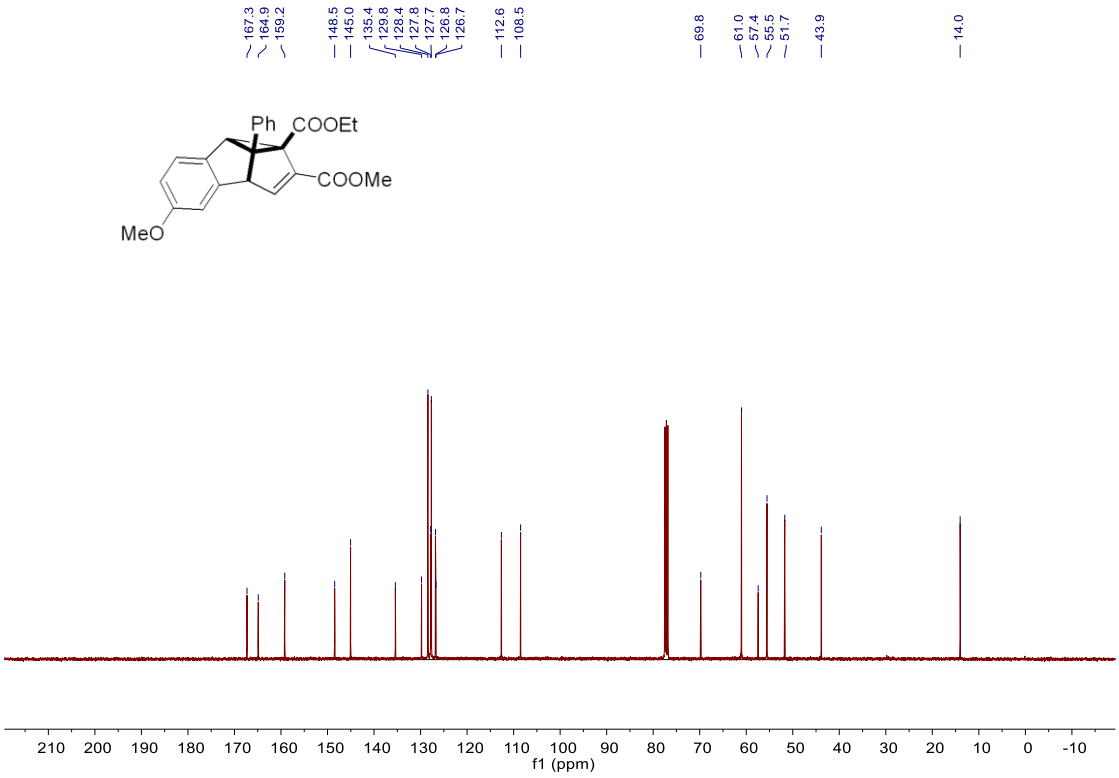

$^{13}$C NMR spectrum of **3ga**



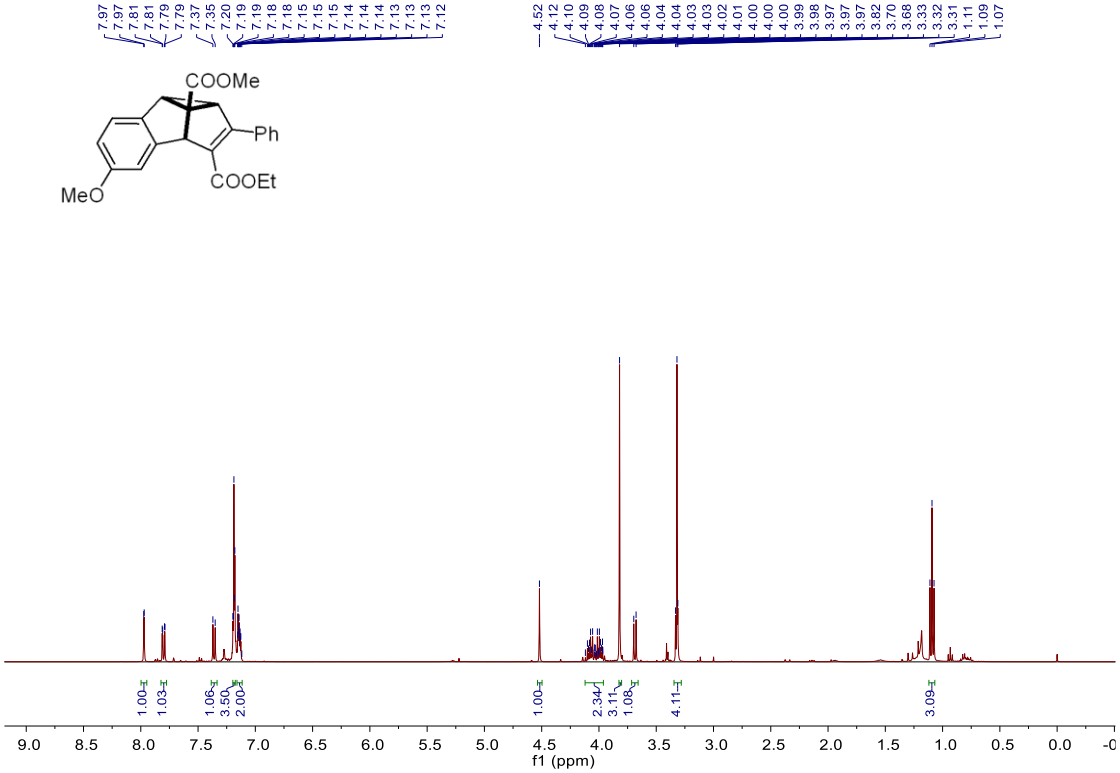
$^{1}$H NMR spectrum of **3ha-1**



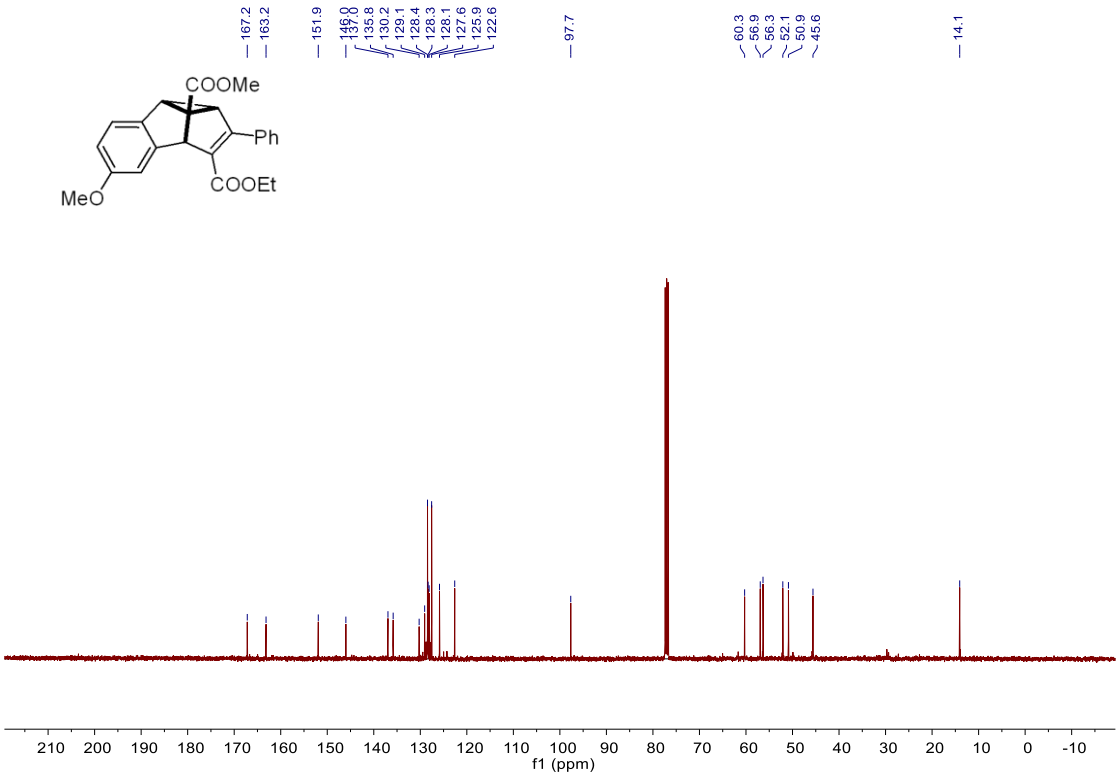

$^{13}$C NMR spectrum of **3ha-1**



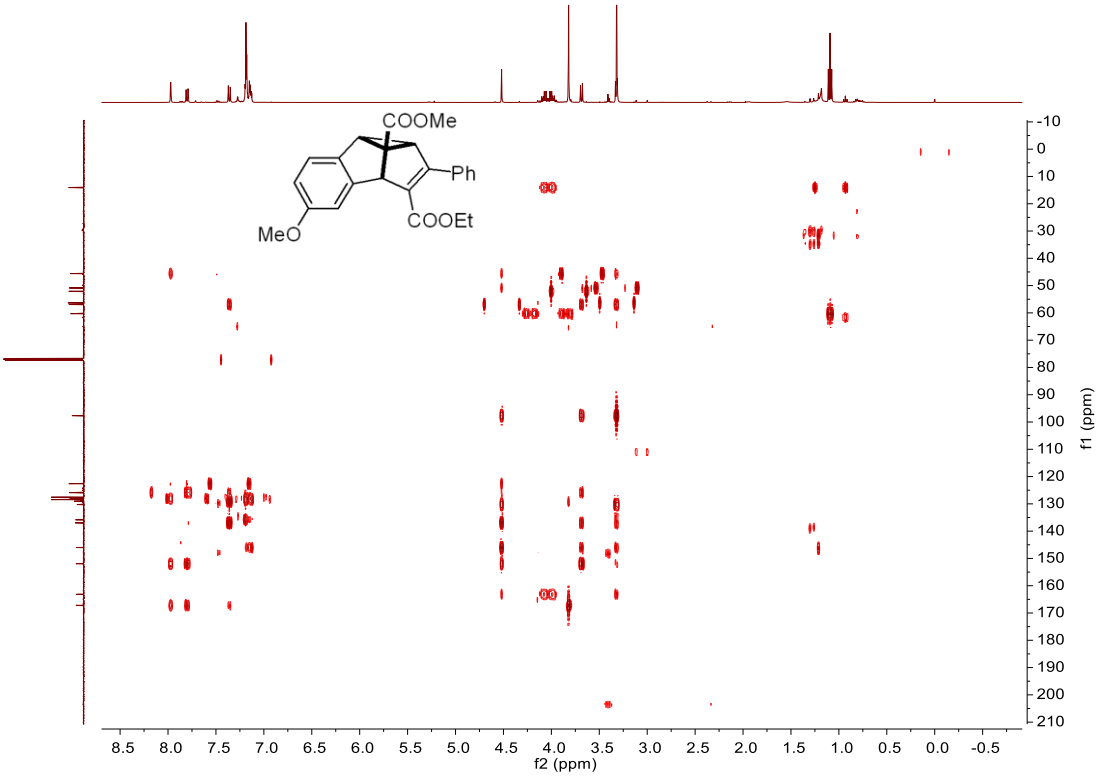
$^{1}$H NMR spectrum of **3ha-2**



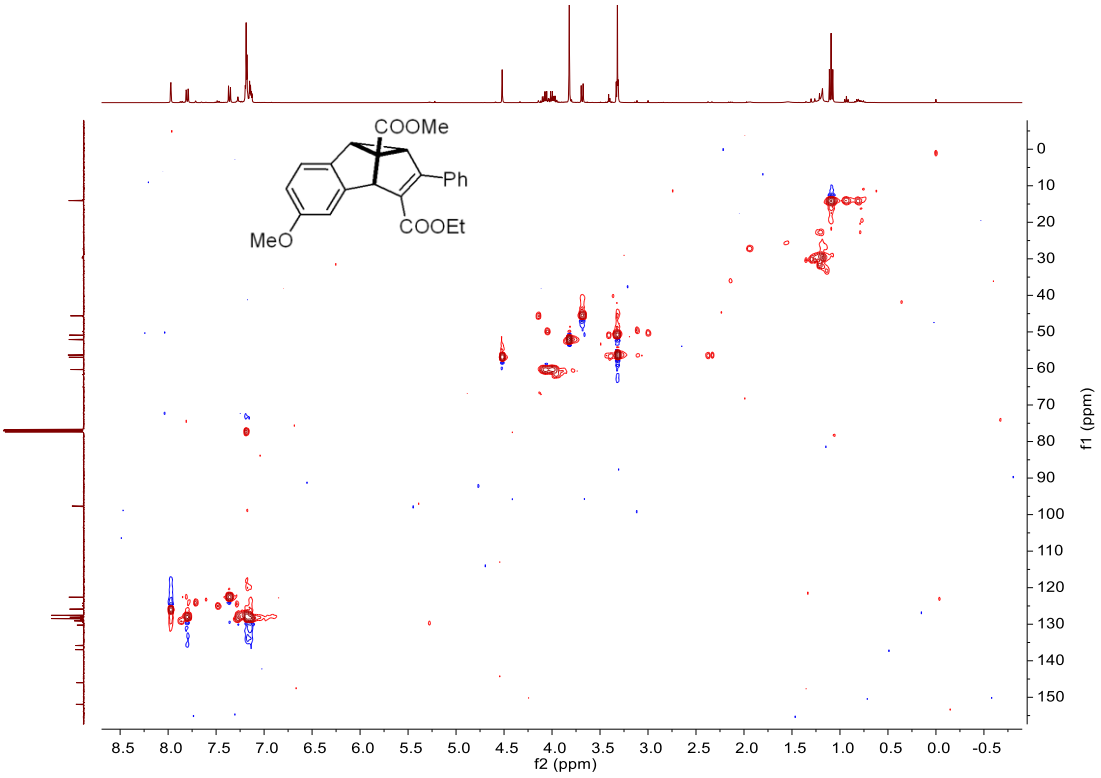

$^{13}$C NMR spectrum of **3ha-2**



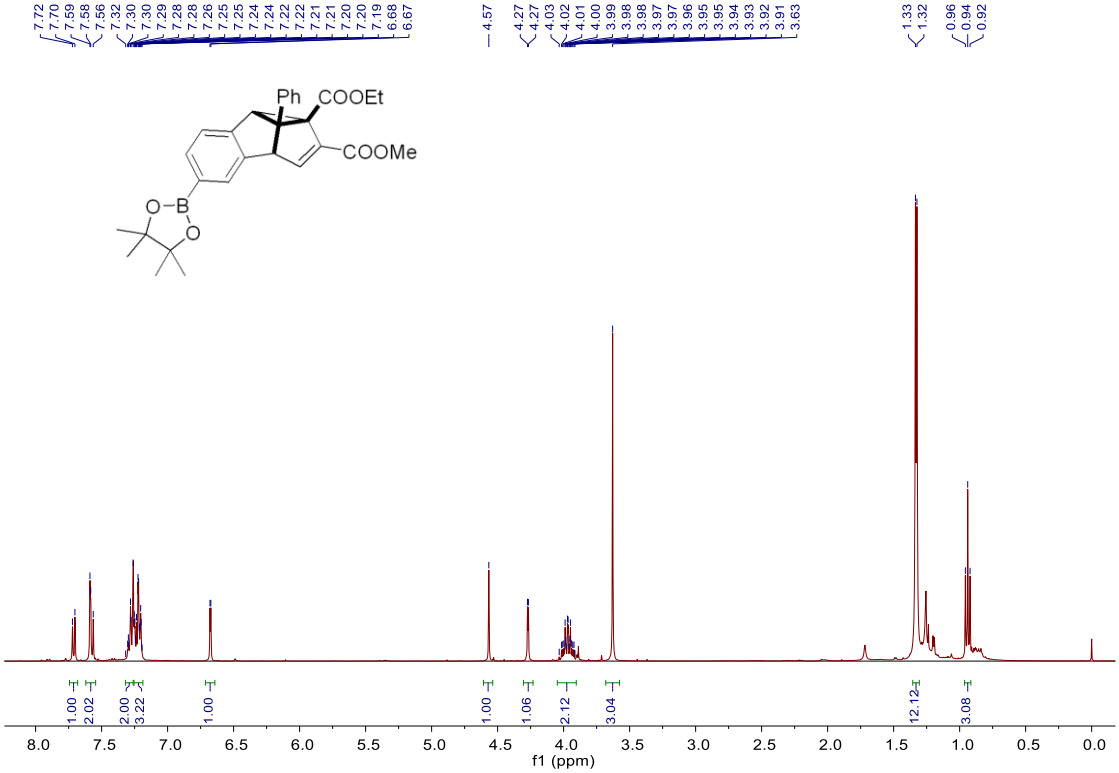
HMBC NMR spectrum of **3ha-2**



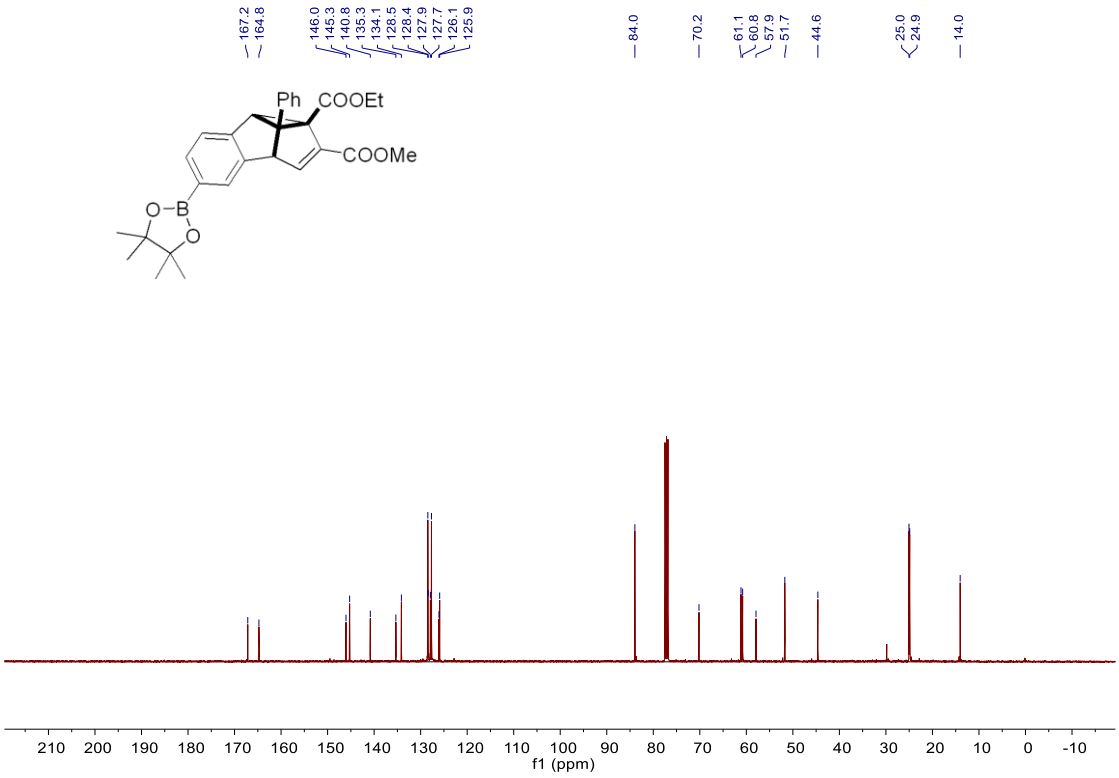

HSQC NMR spectrum of **3ha-2**



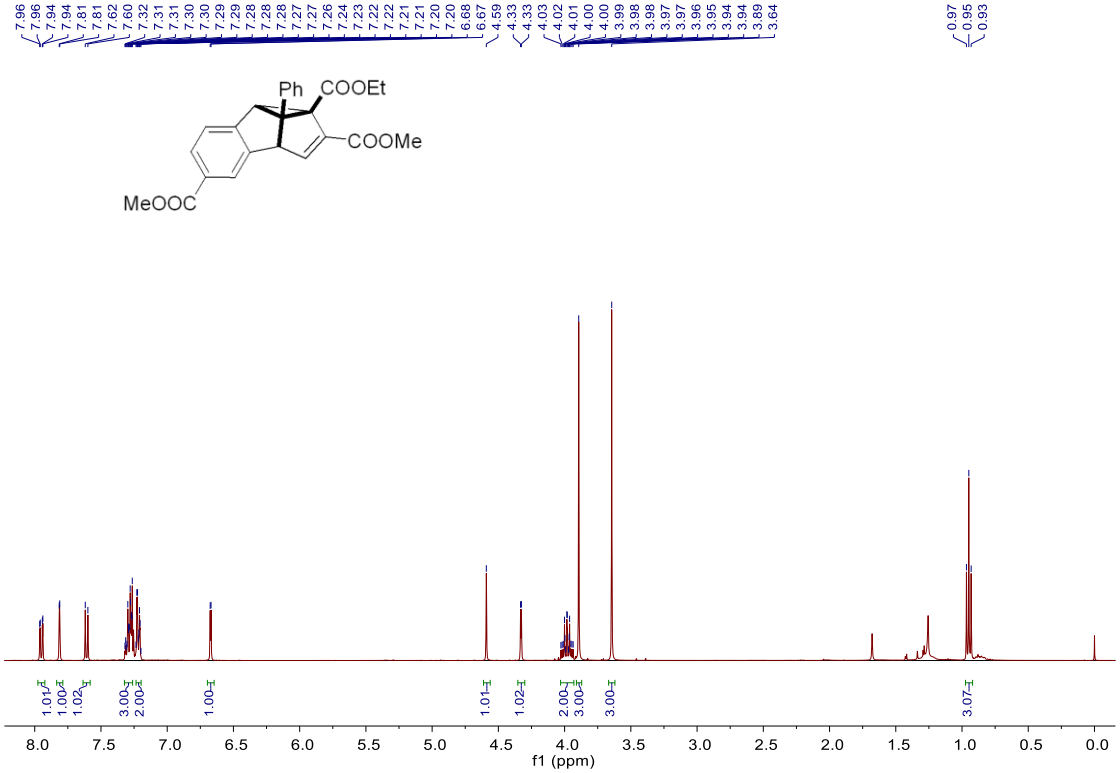
$^{1}$H NMR spectrum of **3ia**



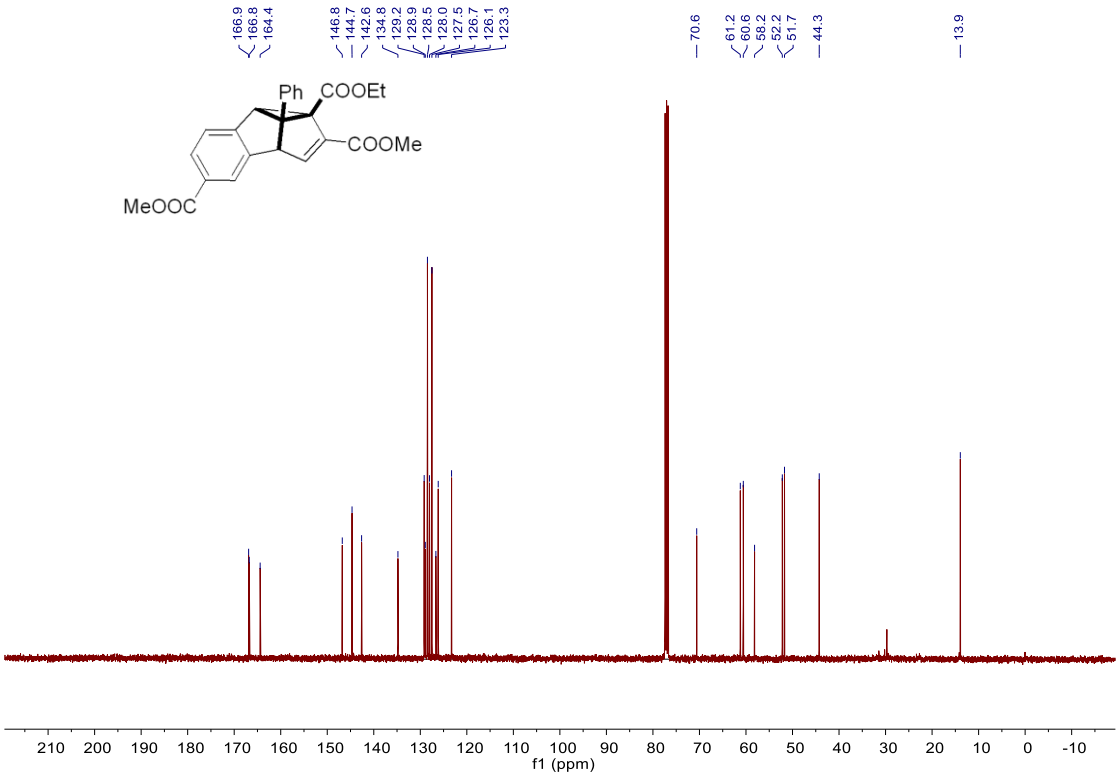

$^{13}$C NMR spectrum of **3ia**



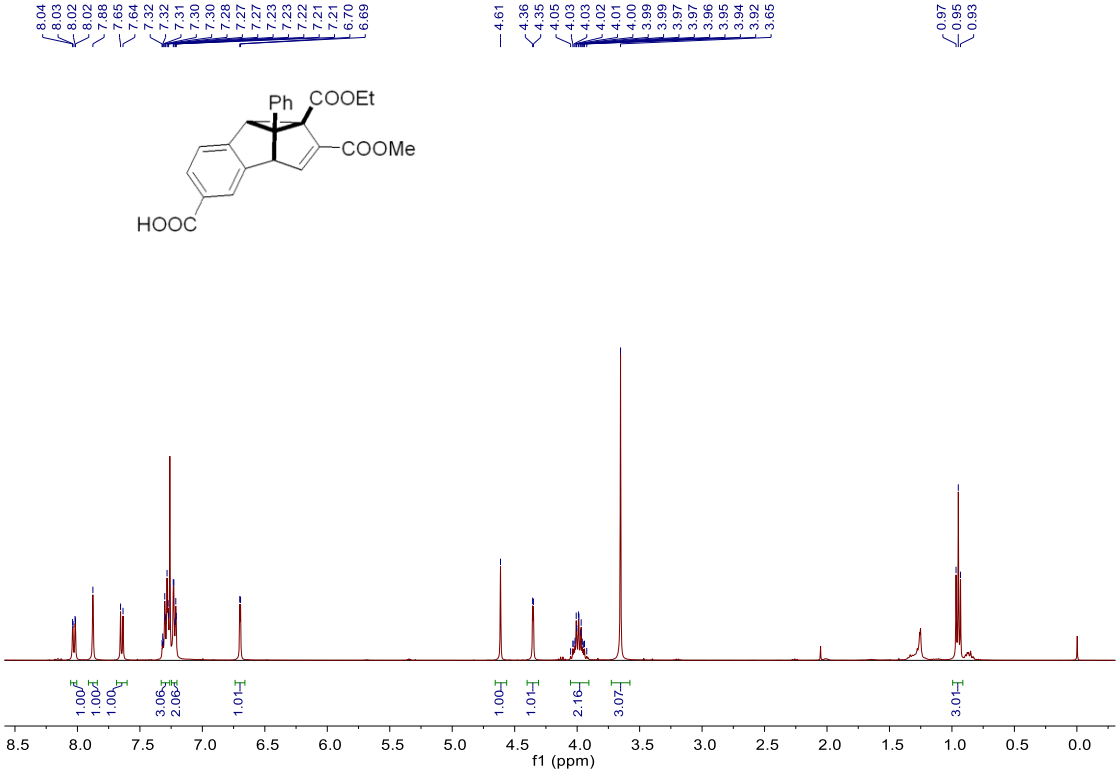
$^{1}$H NMR spectrum of **3ja**



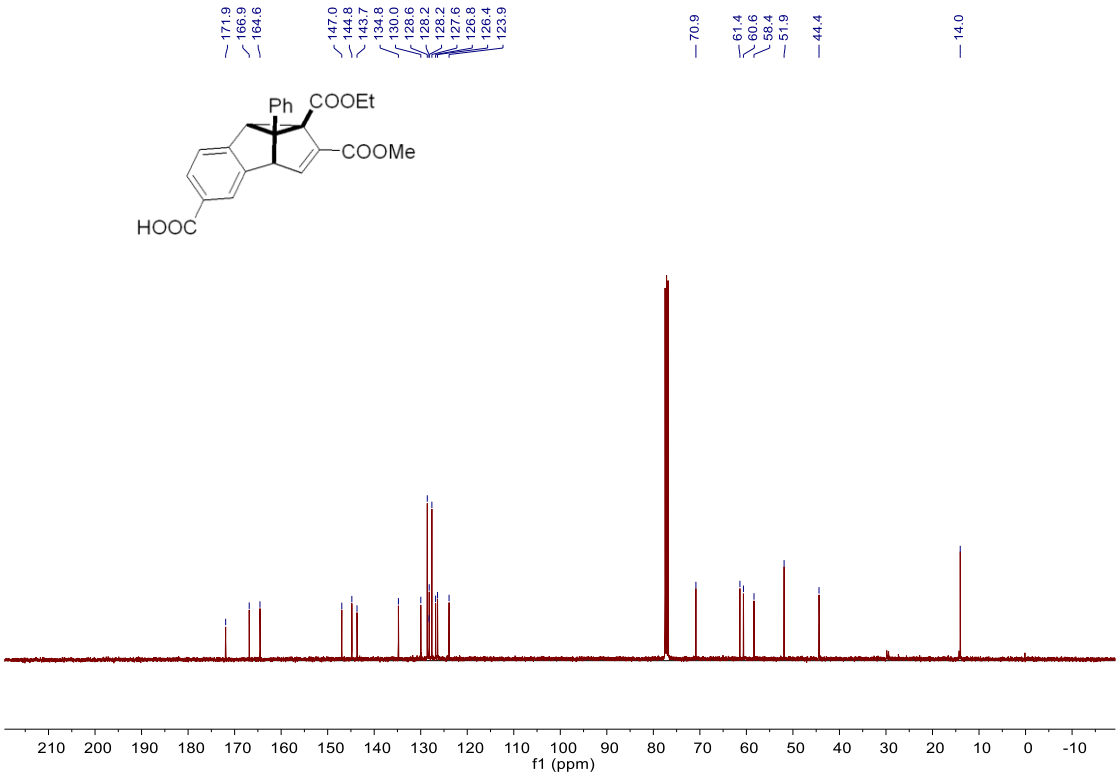

$^{13}$C NMR spectrum of **3ja**



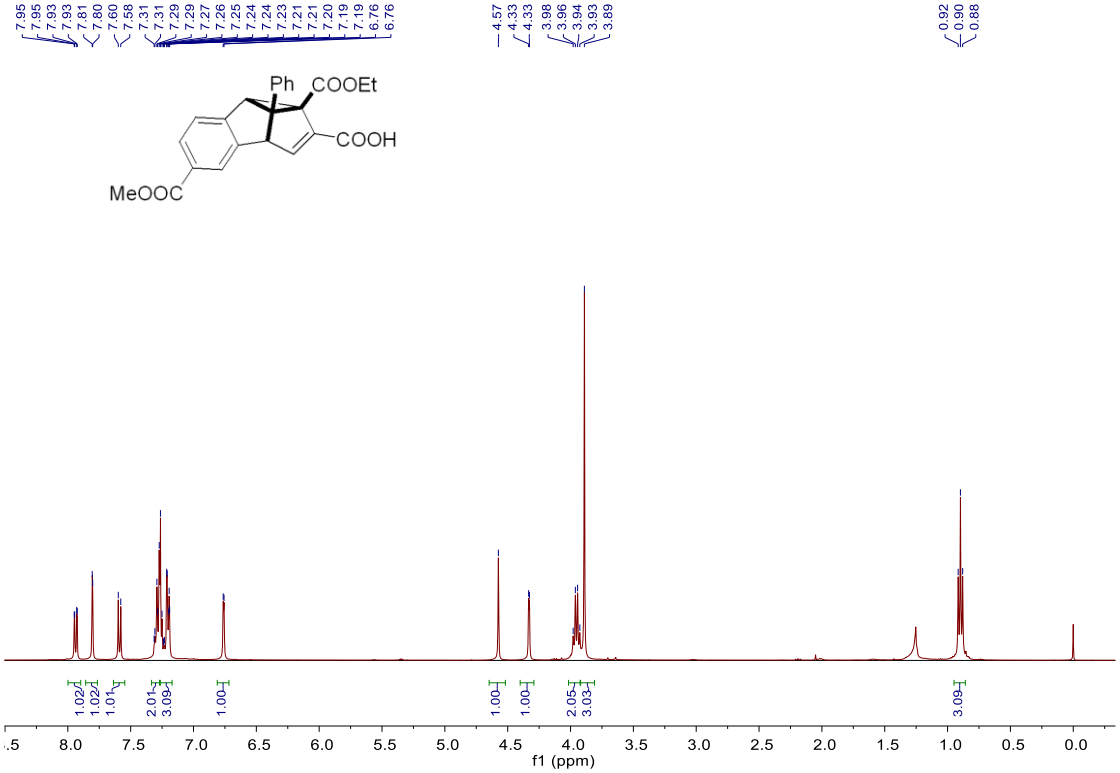
$^{1}$H NMR spectrum of **3ka-1**



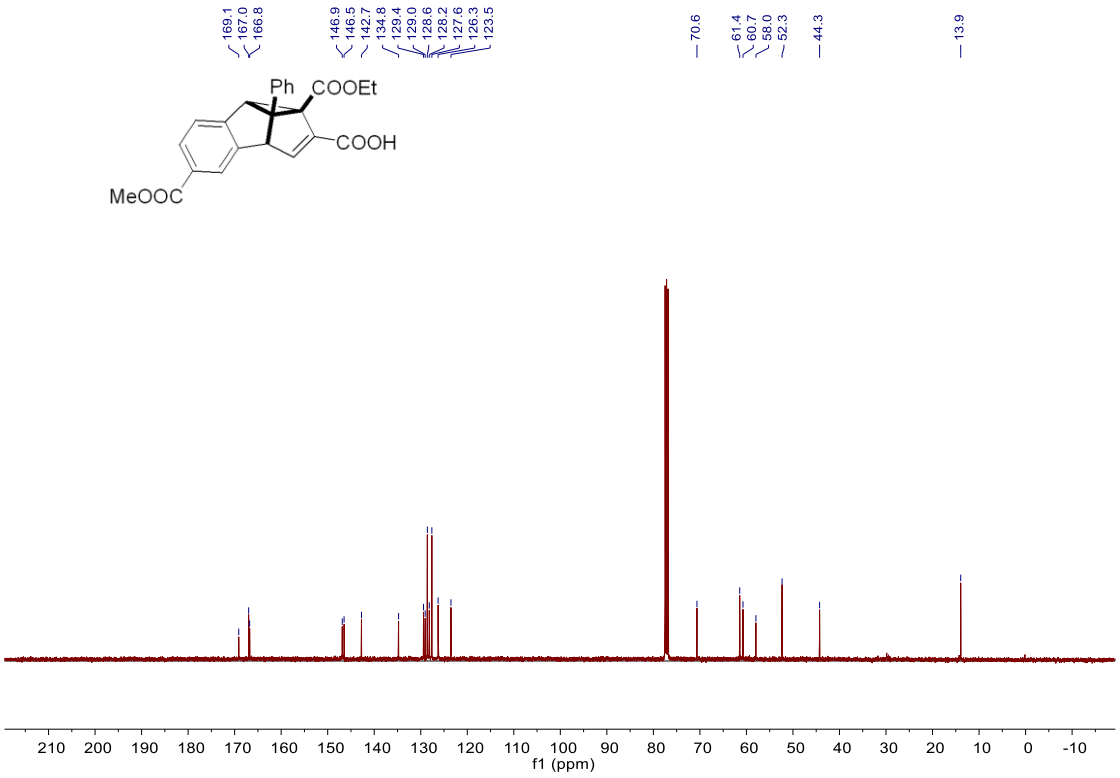

$^{13}$C NMR spectrum of **3ka-1**



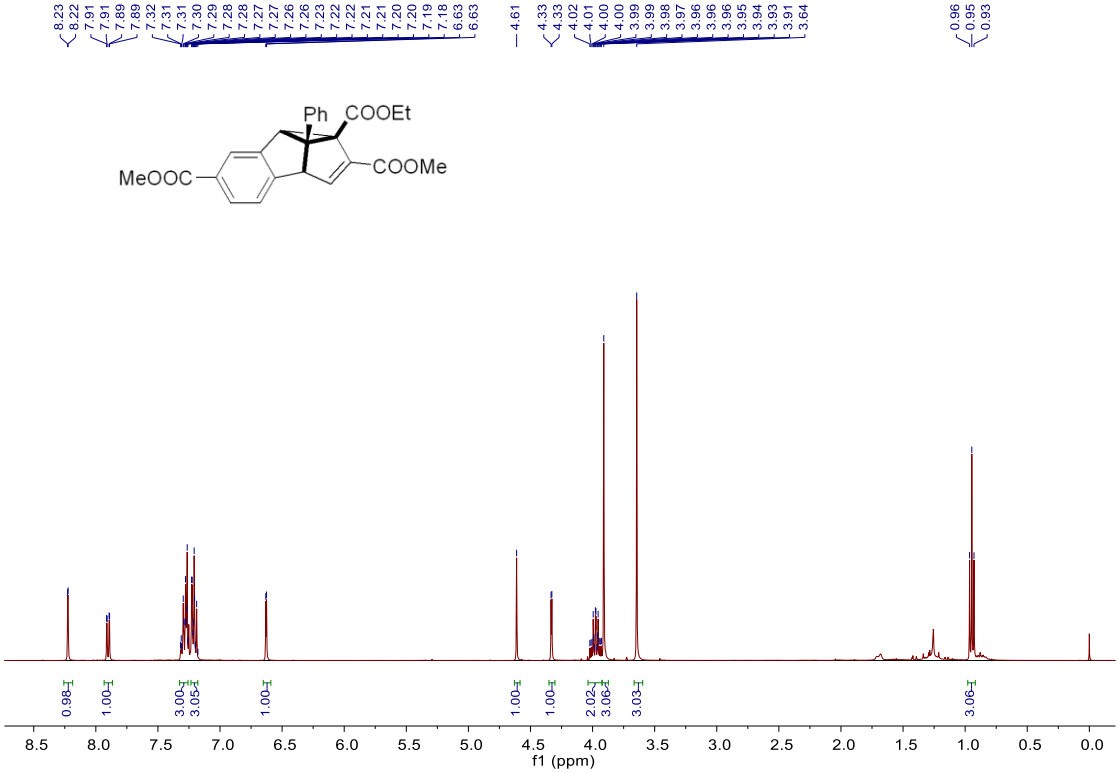
$^{1}$H NMR spectrum of **3ka-2**



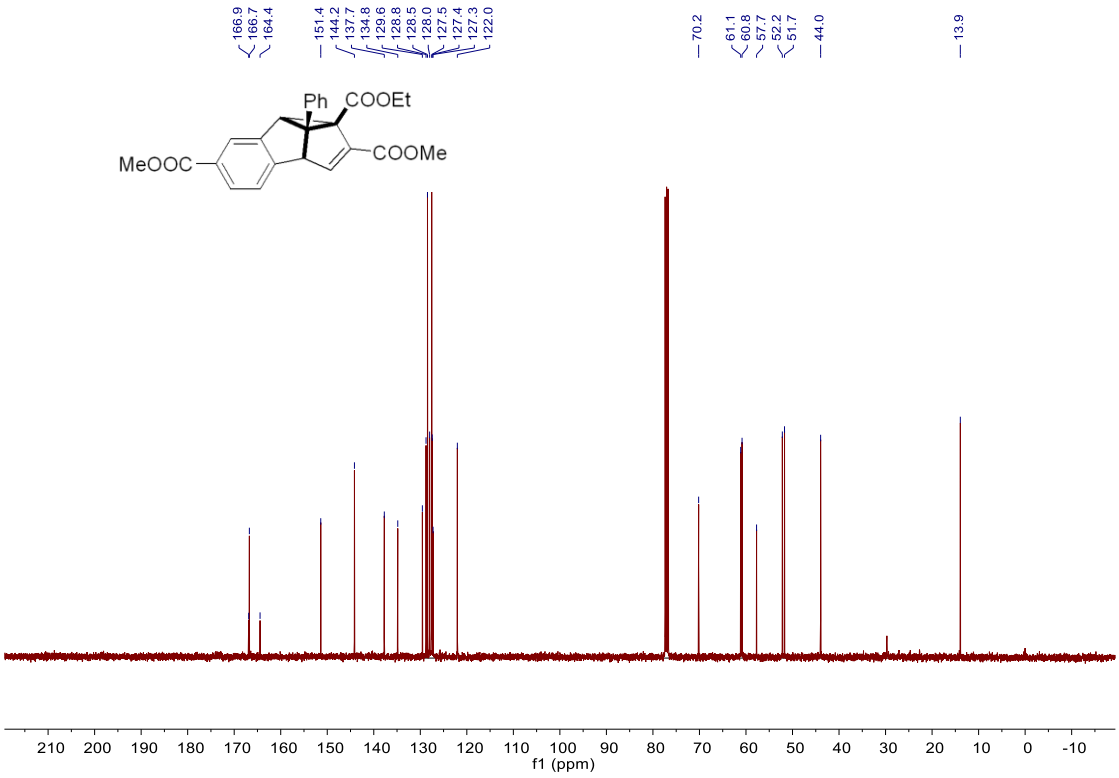

$^{13}$C NMR spectrum of **3ka-2**



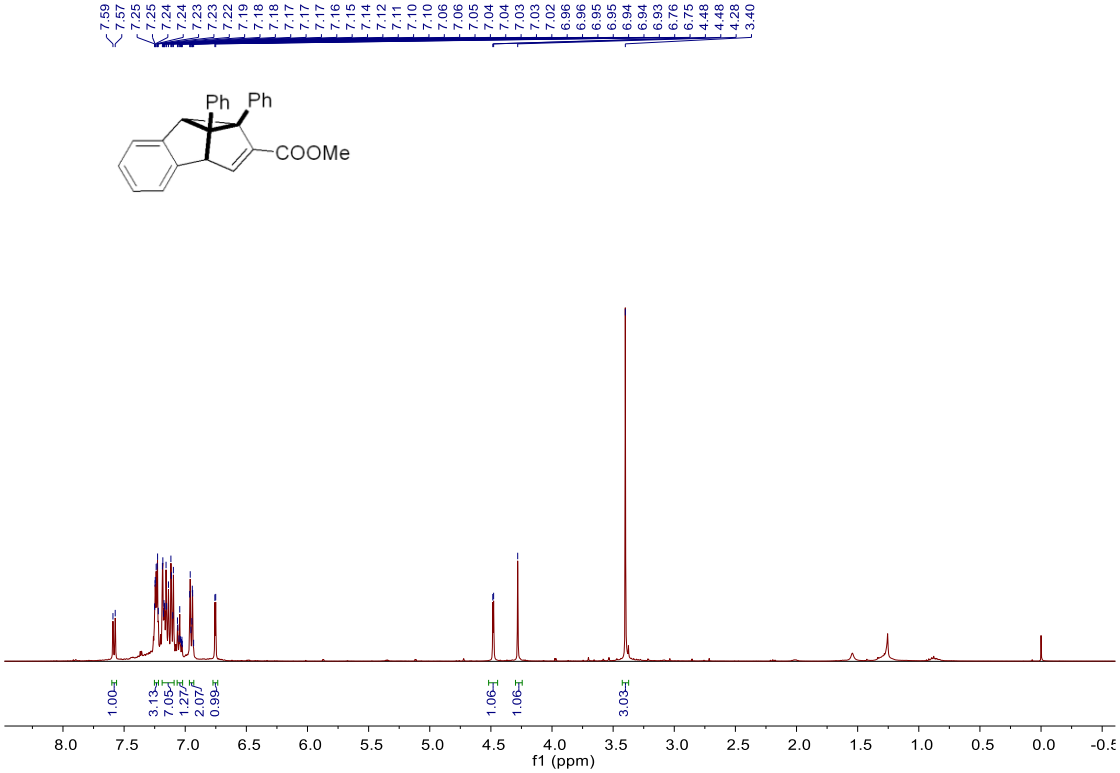
$^{1}$H NMR spectrum of **3la**



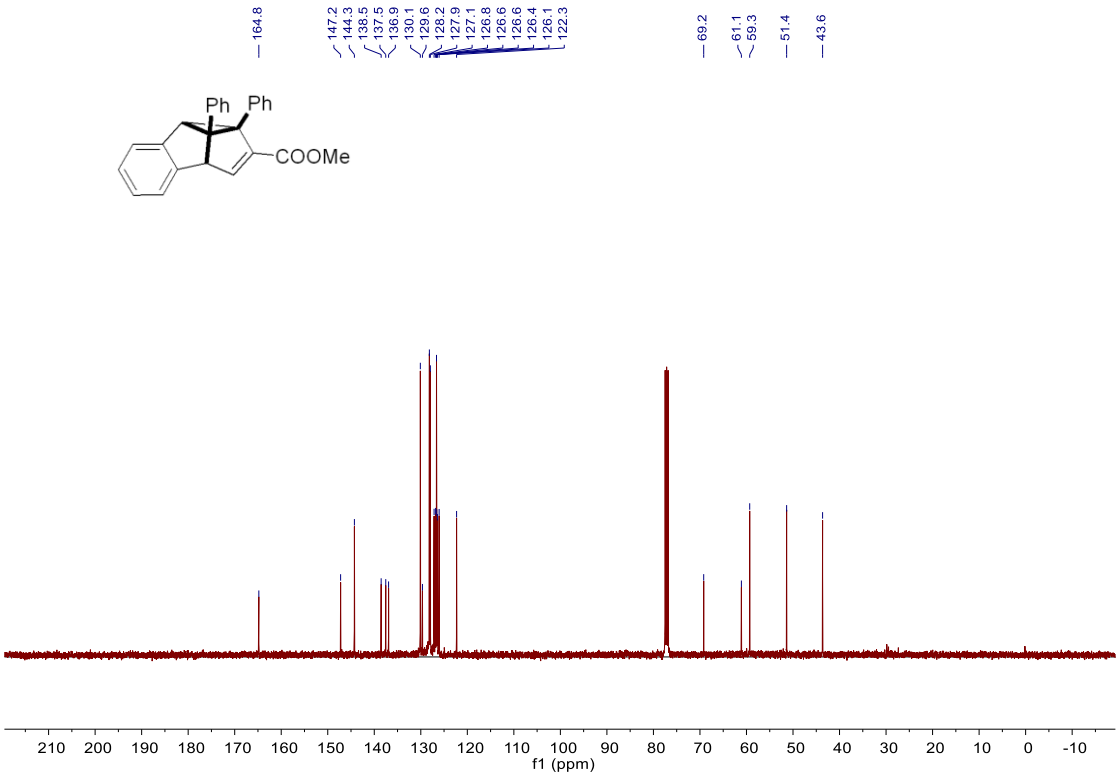

$^{13}$C NMR spectrum of **3la**



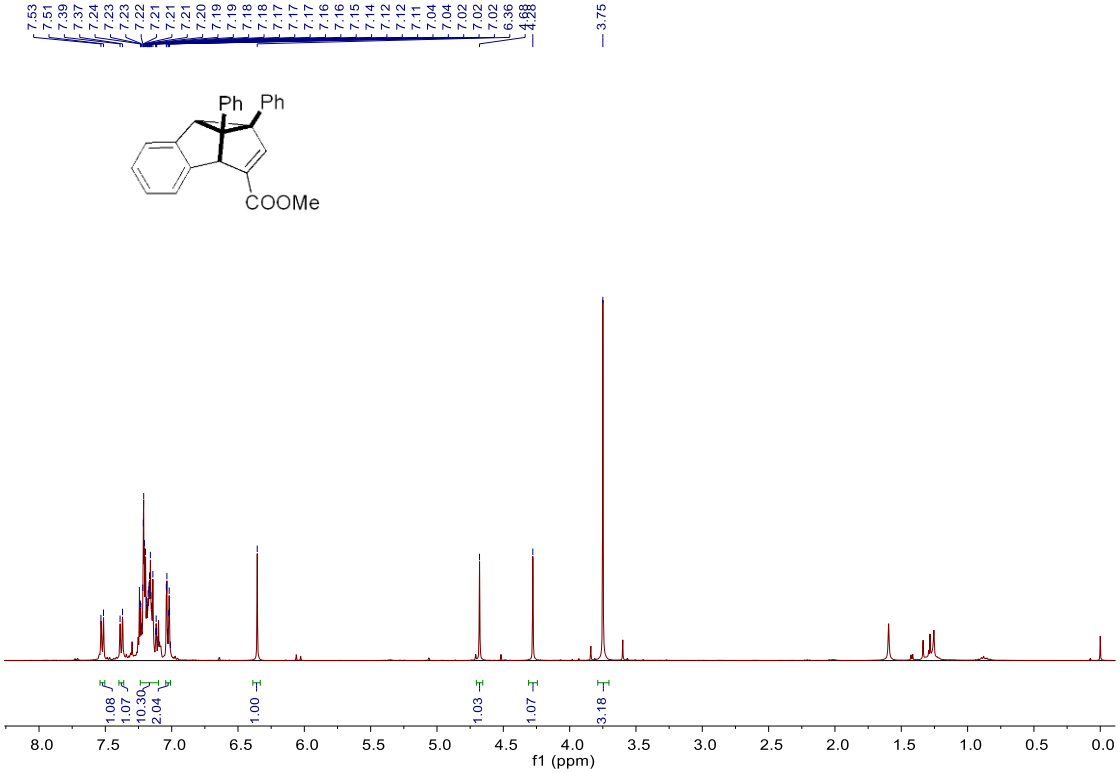
$^{1}$H NMR spectrum of **3ac-1**



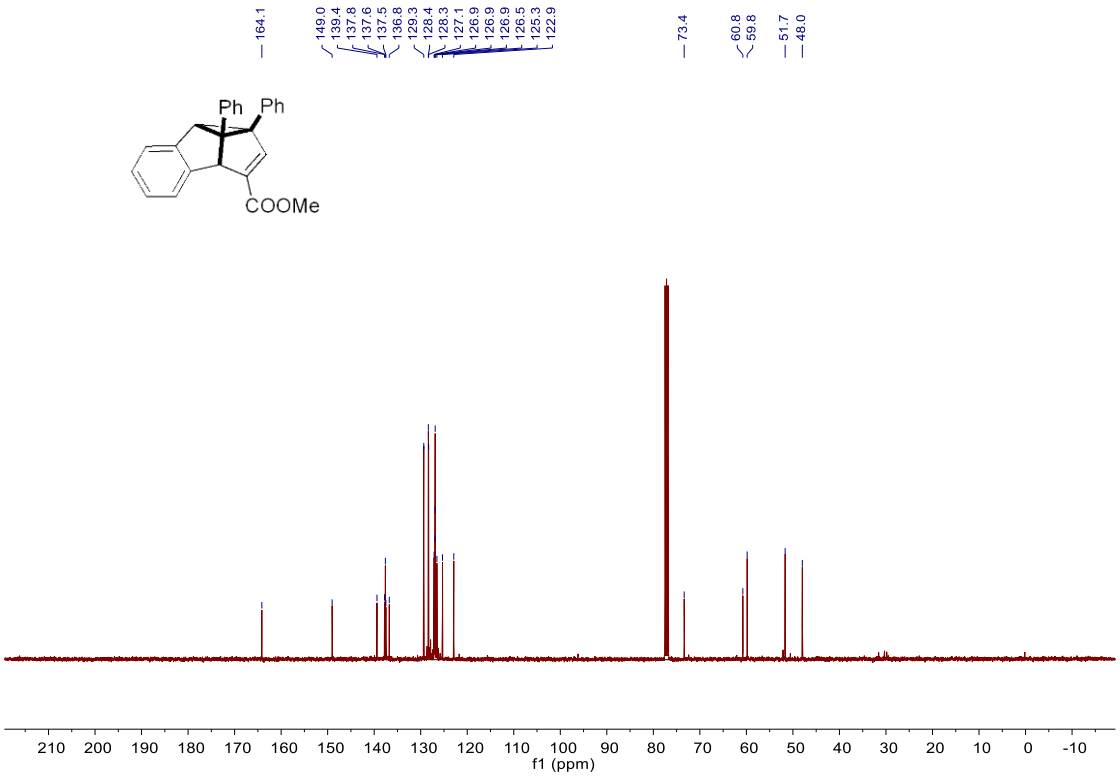

$^{13}$C NMR spectrum of **3ac-1**



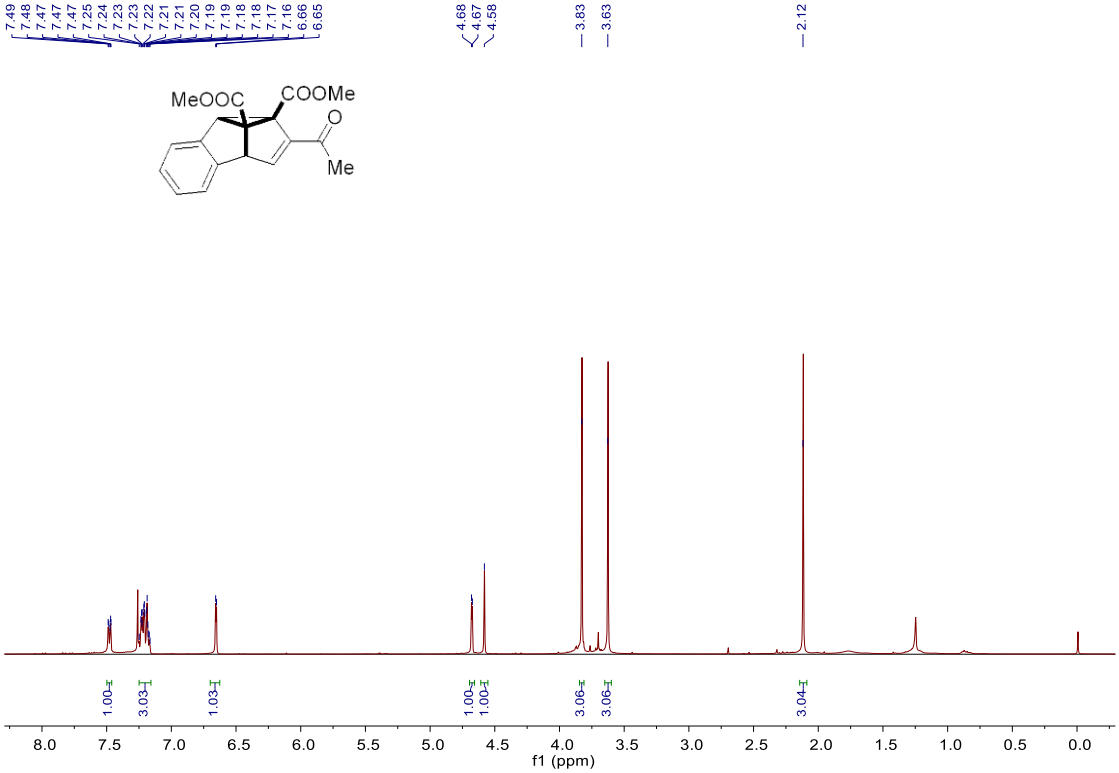
$^{1}$H NMR spectrum of **3ac-2**



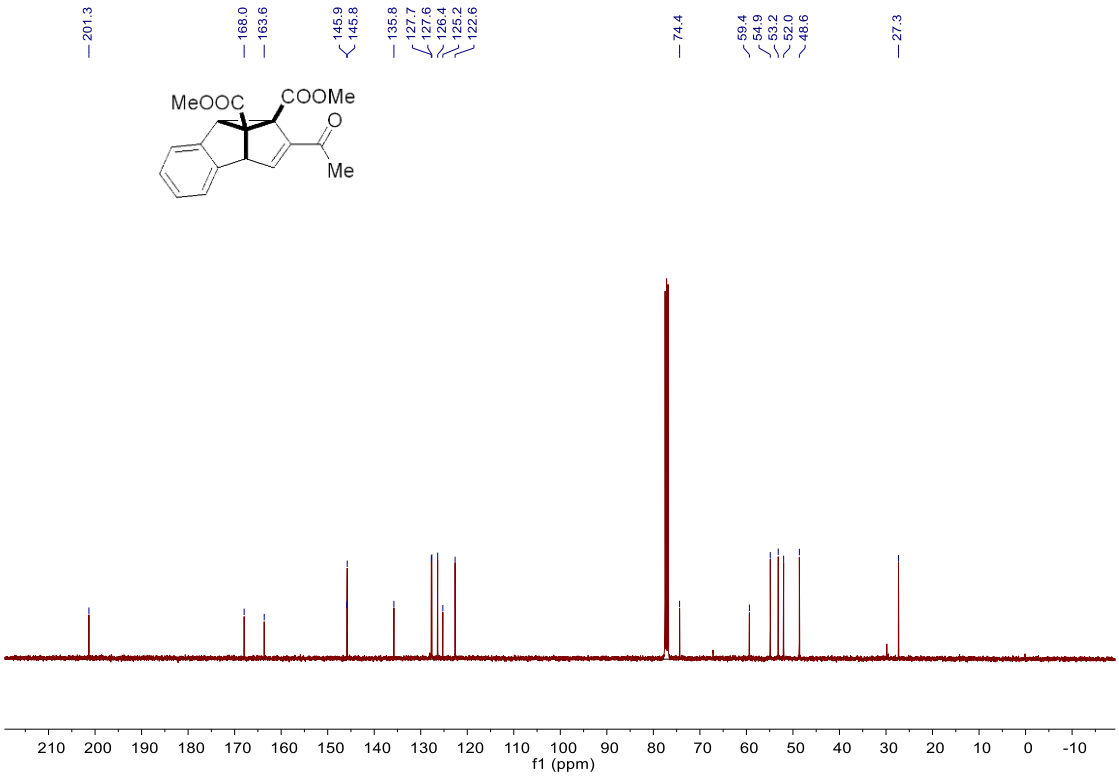

$^{13}$C NMR spectrum of **3ac-2**



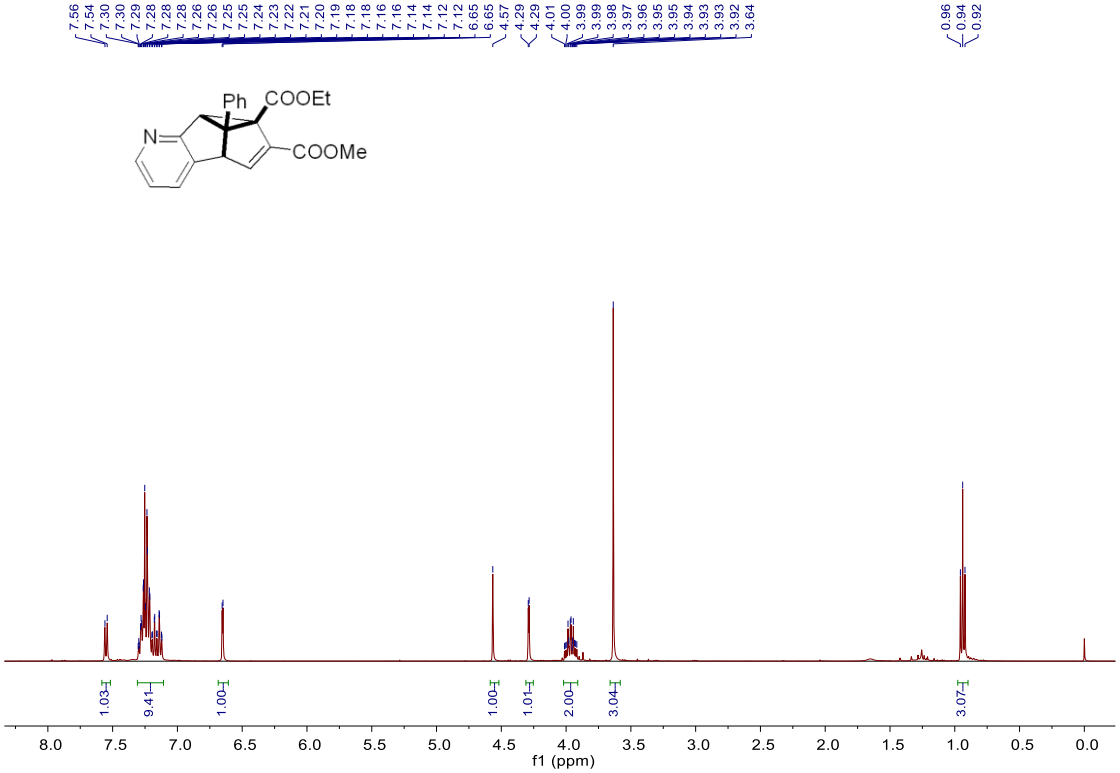
$^{1}$H NMR spectrum of **3fd**



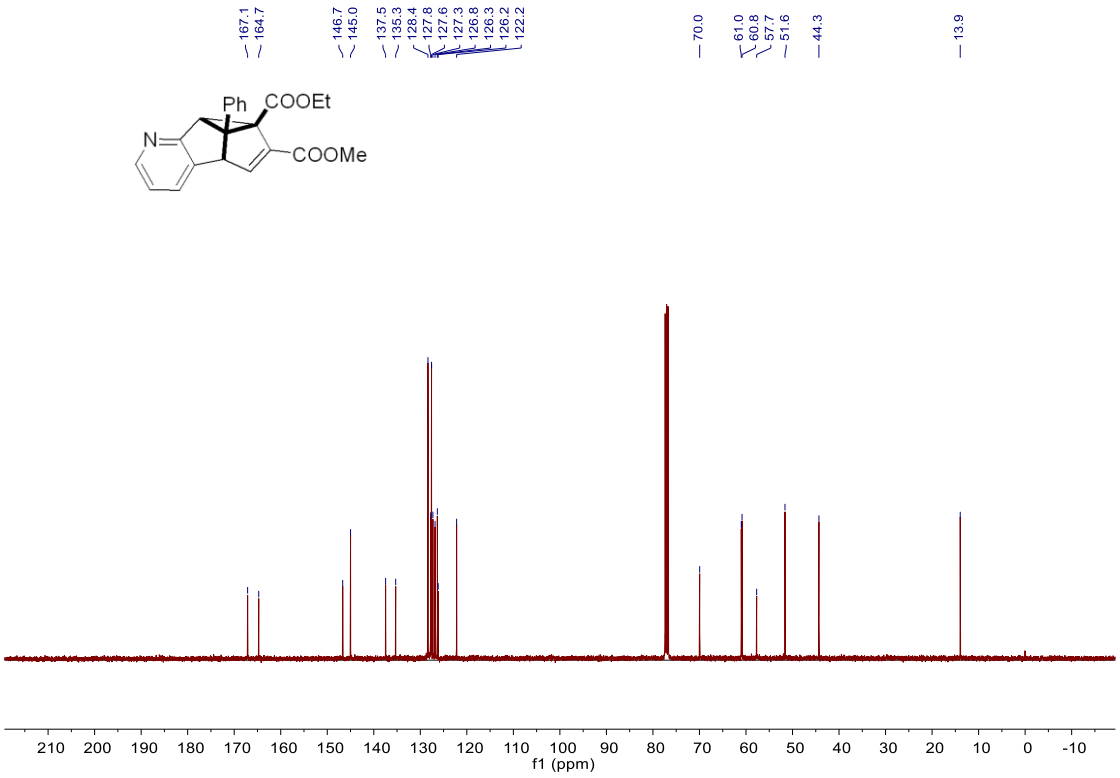

$^{13}$C NMR spectrum of **3fd**



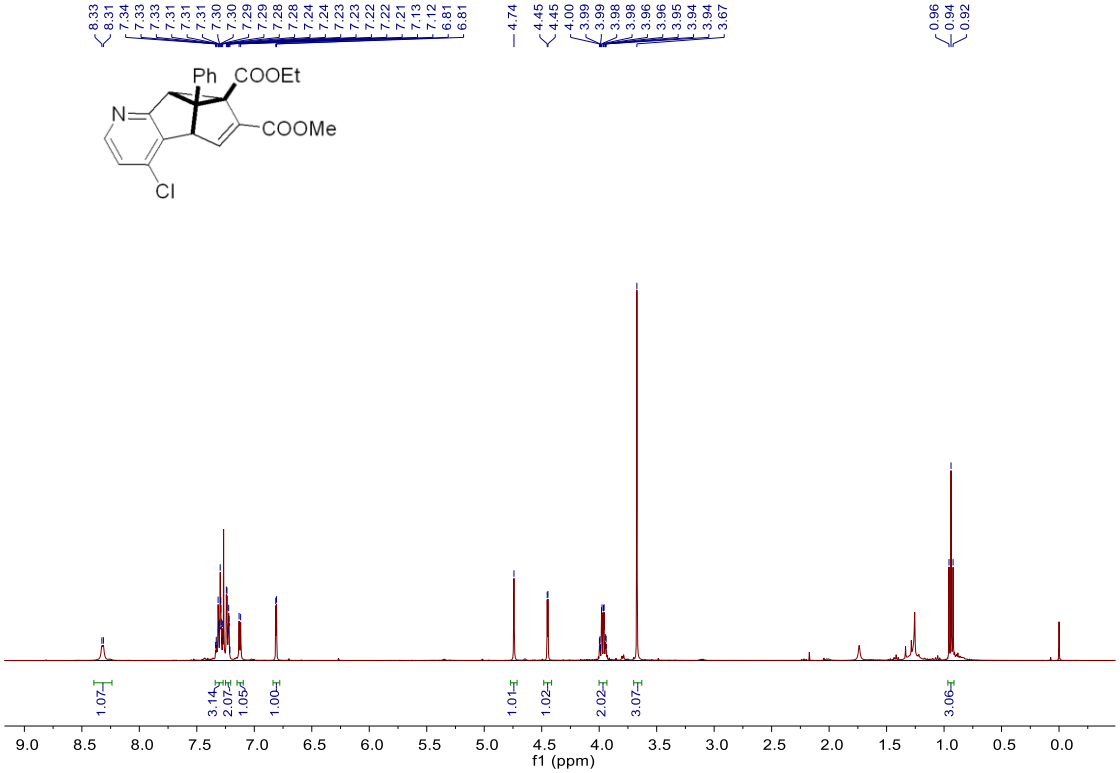
$^{1}$H NMR spectrum of **5aa**



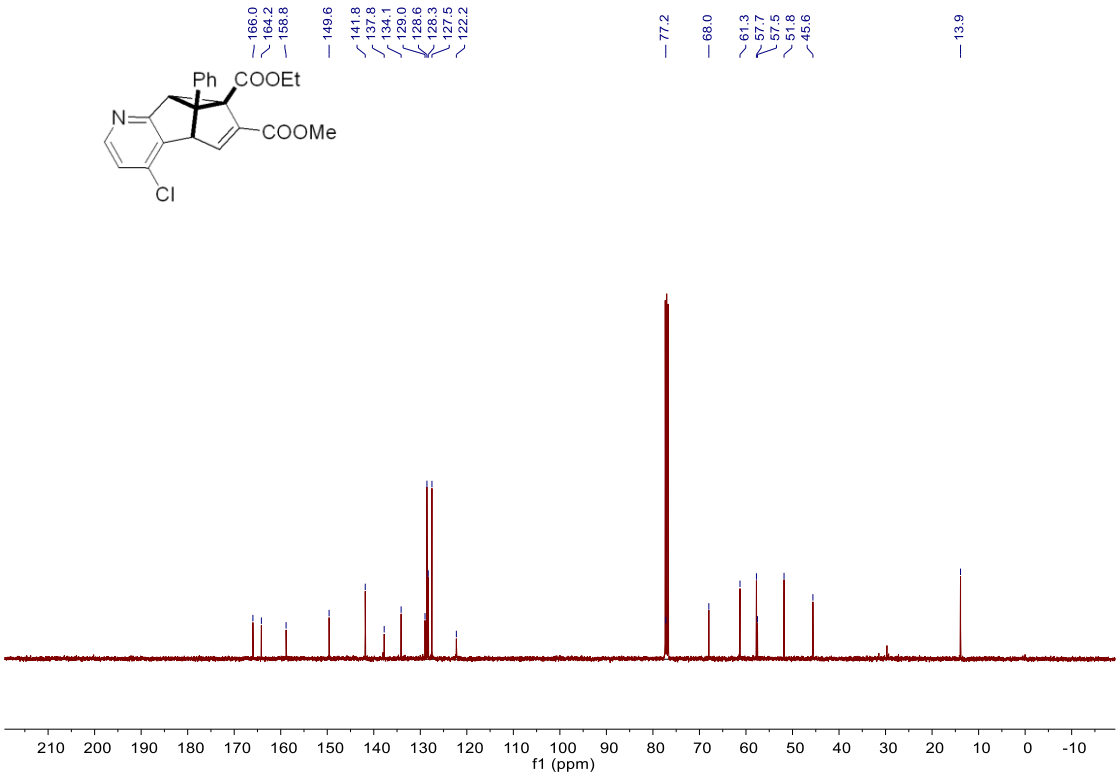

$^{13}$C NMR spectrum of **5aa**



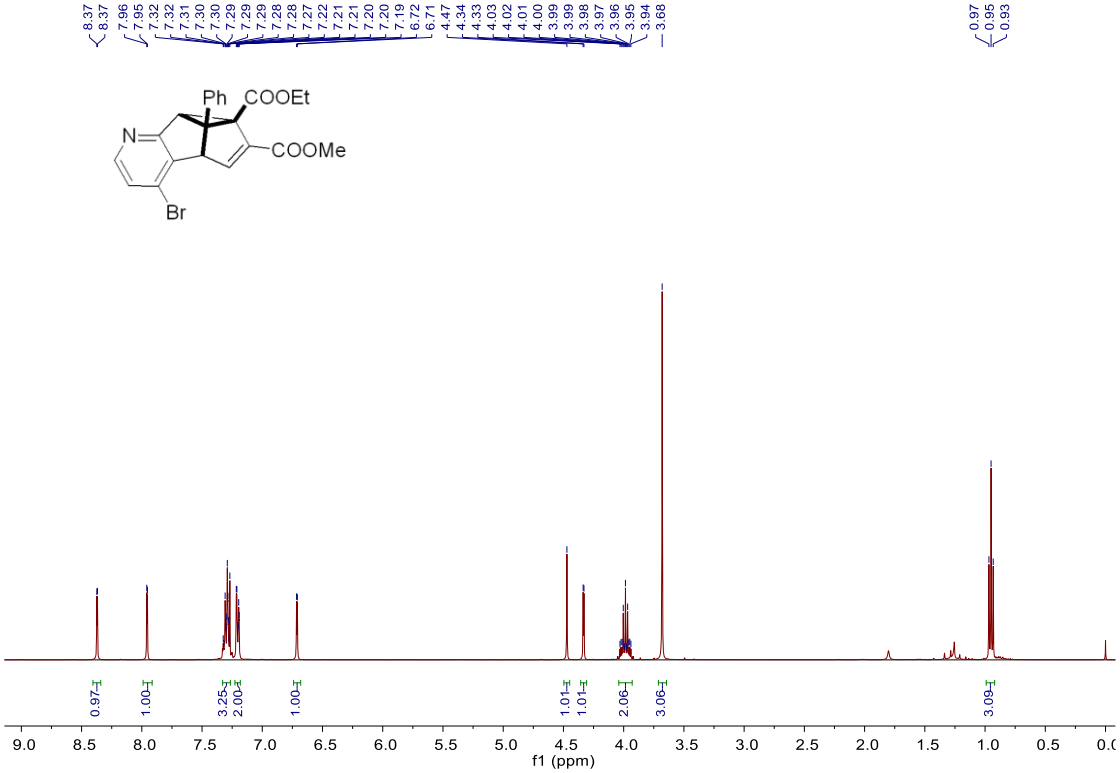
$^{1}$H NMR spectrum of **5ba**



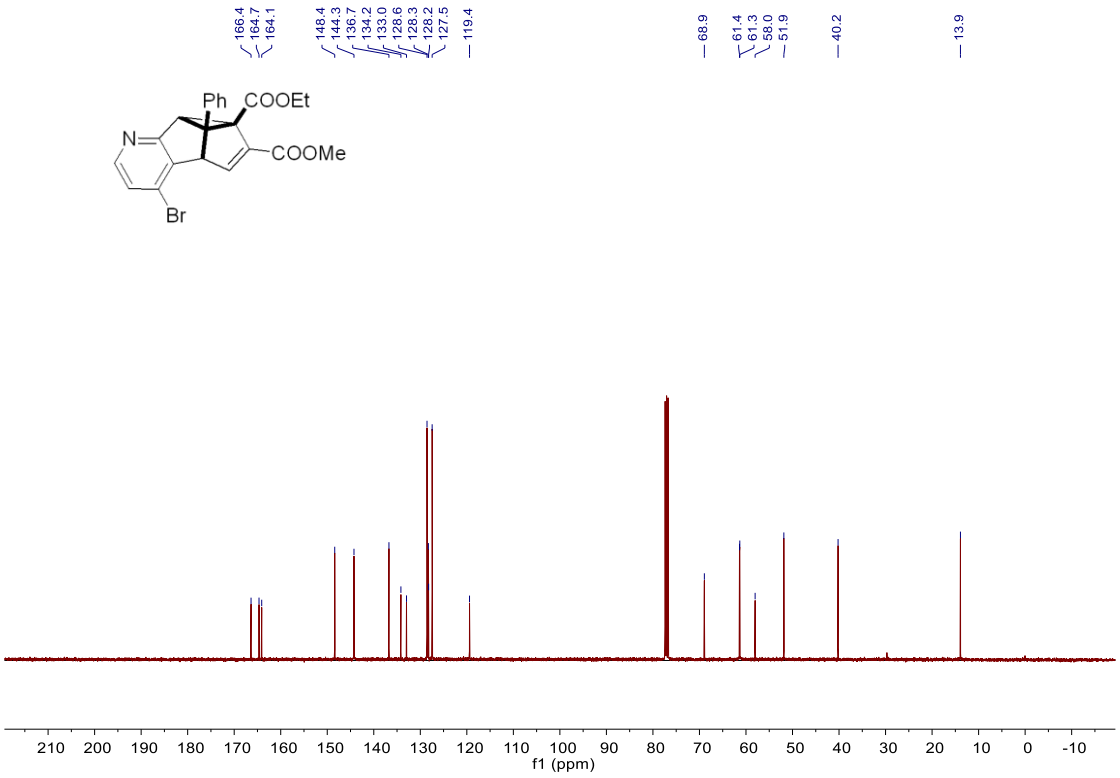

$^{13}$C NMR spectrum of **5ba**



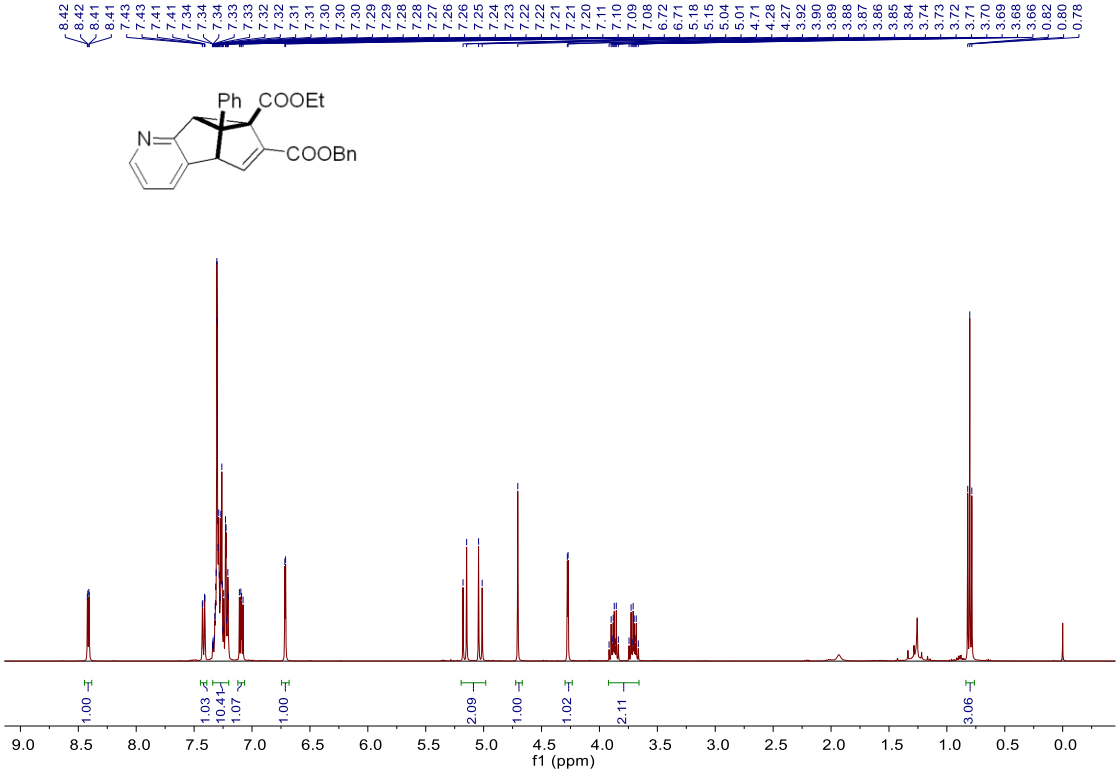
$^{1}$H NMR spectrum of **5ca**



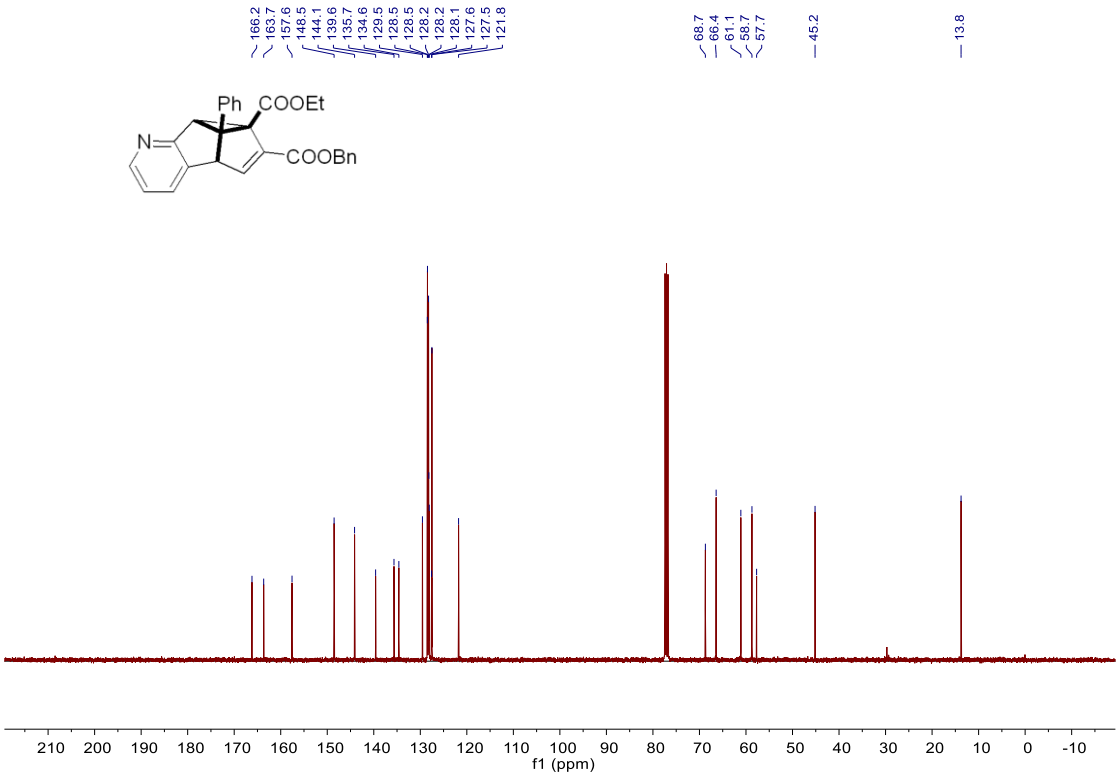

$^{13}$C NMR spectrum of **5ca**



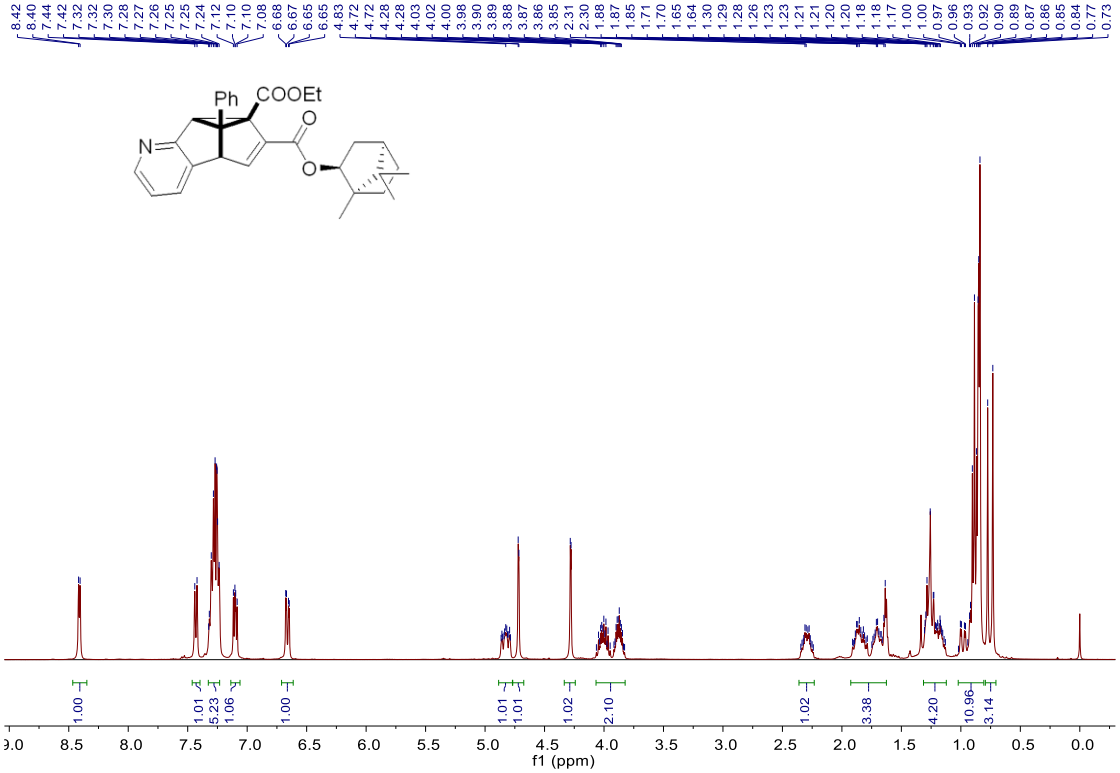
$^{1}$H NMR spectrum of **5da**



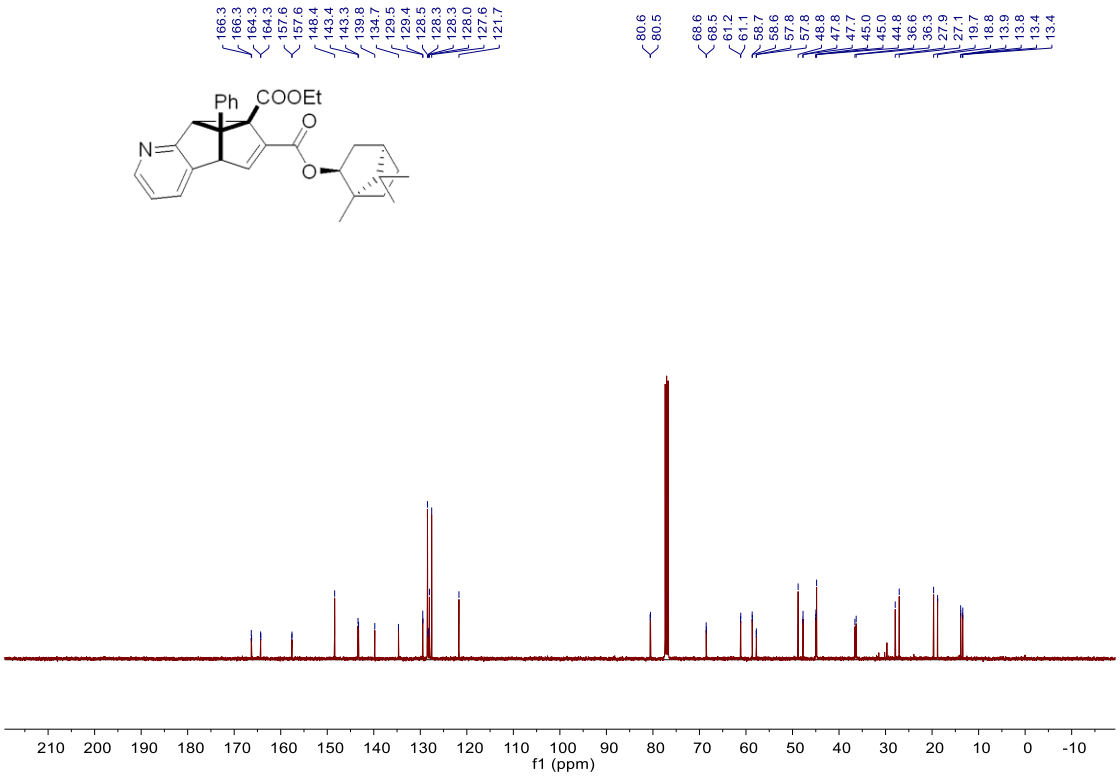

$^{13}$C NMR spectrum of **5da**



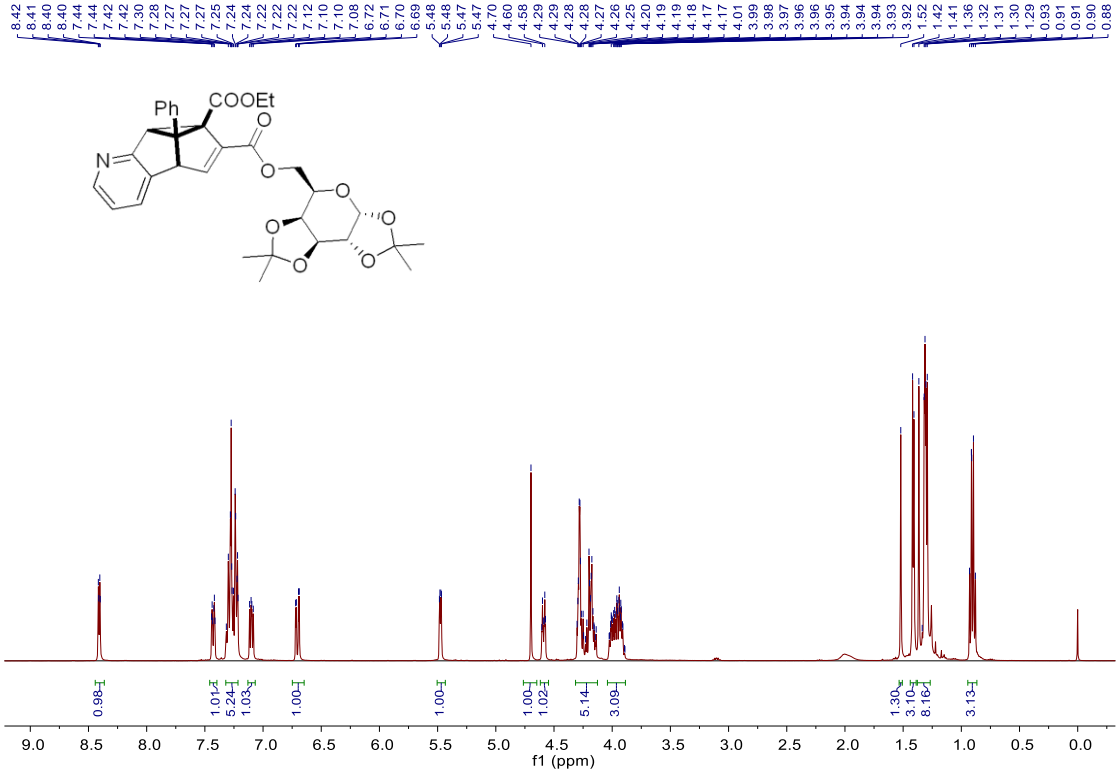
$^{1}$H NMR spectrum of **5ea**



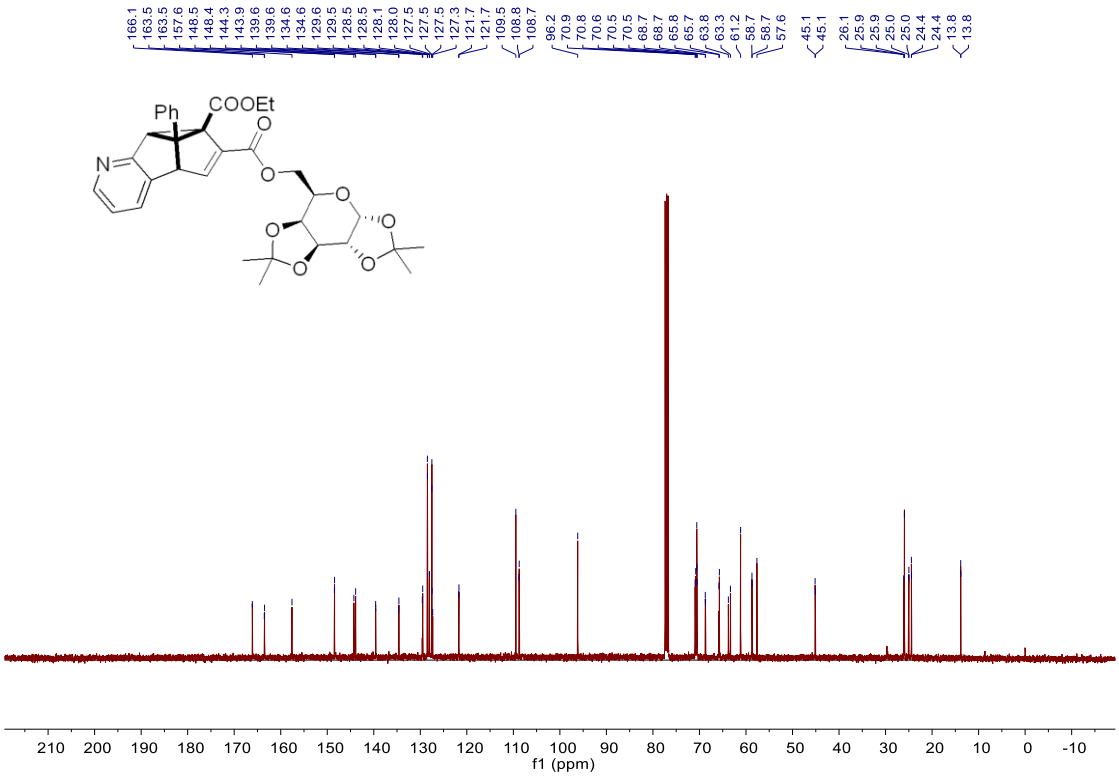

$^{13}$C NMR spectrum of **5ea**



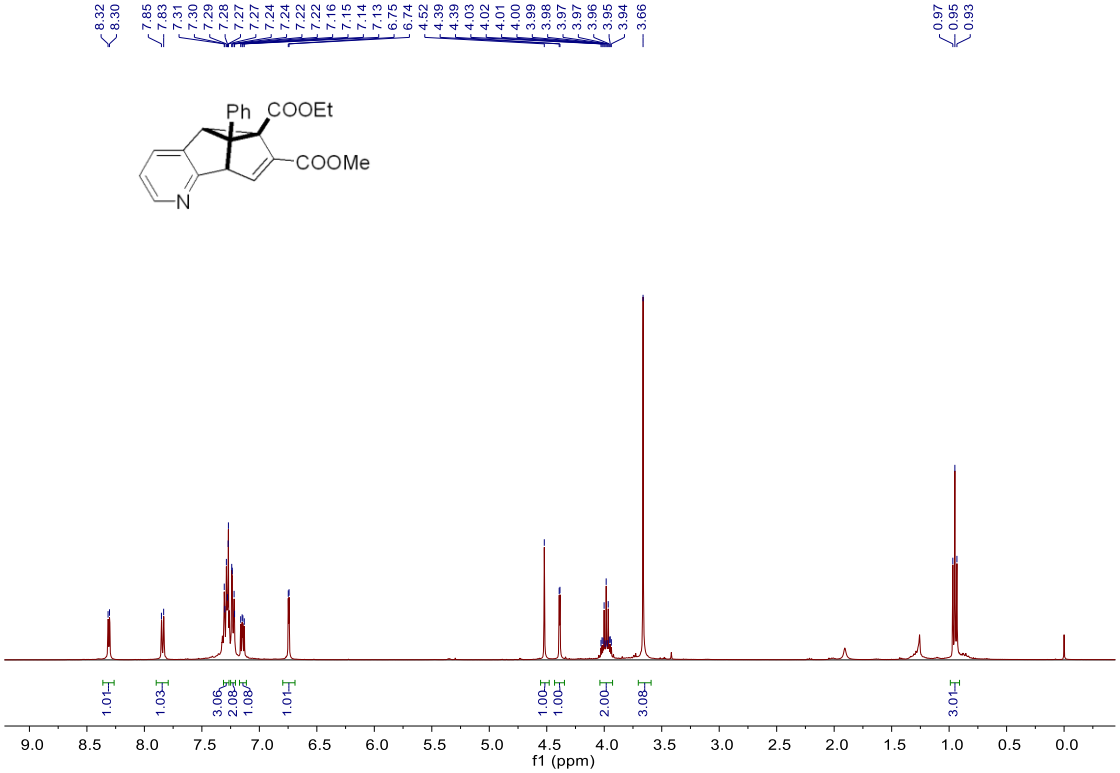
$^{1}$H NMR spectrum of **5fa**



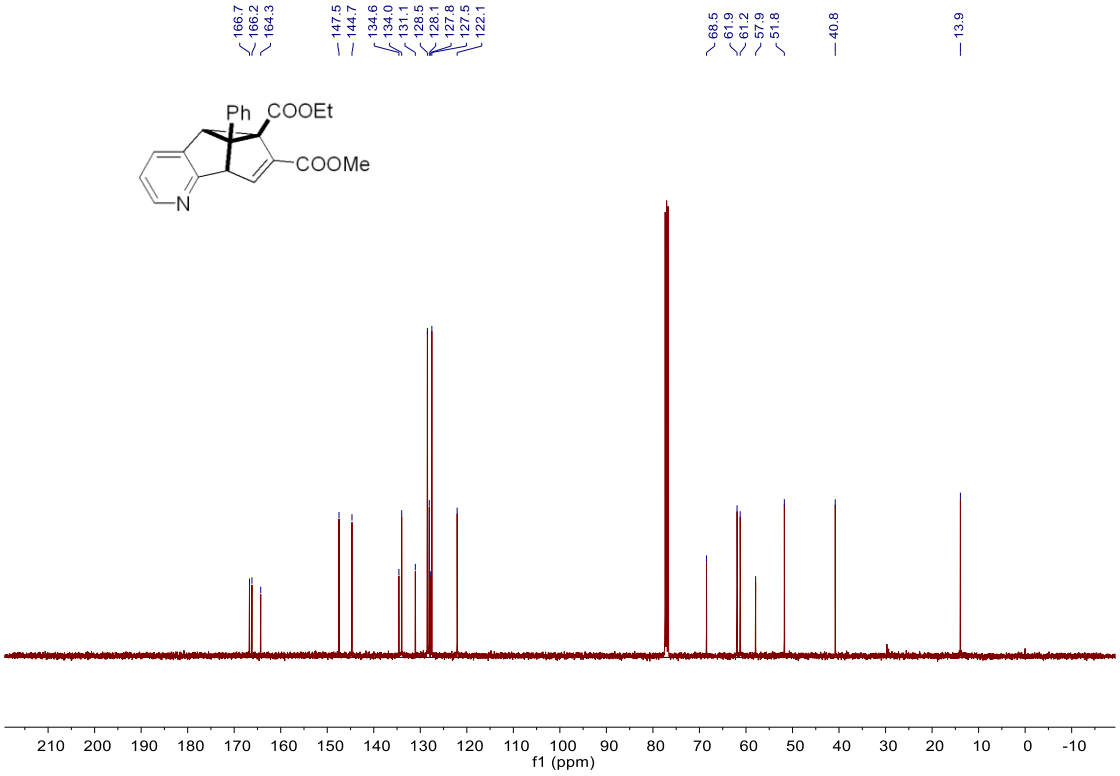

$^{13}$C NMR spectrum of **5fa**



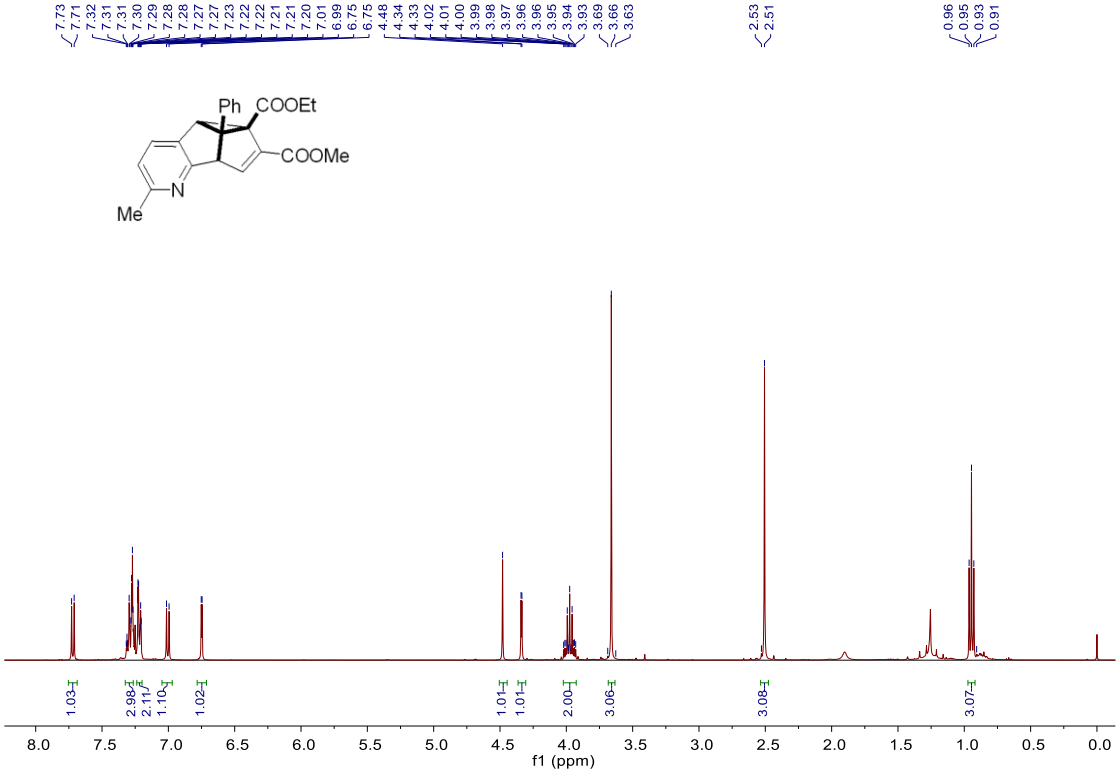
$^{1}$H NMR spectrum of **5ga**



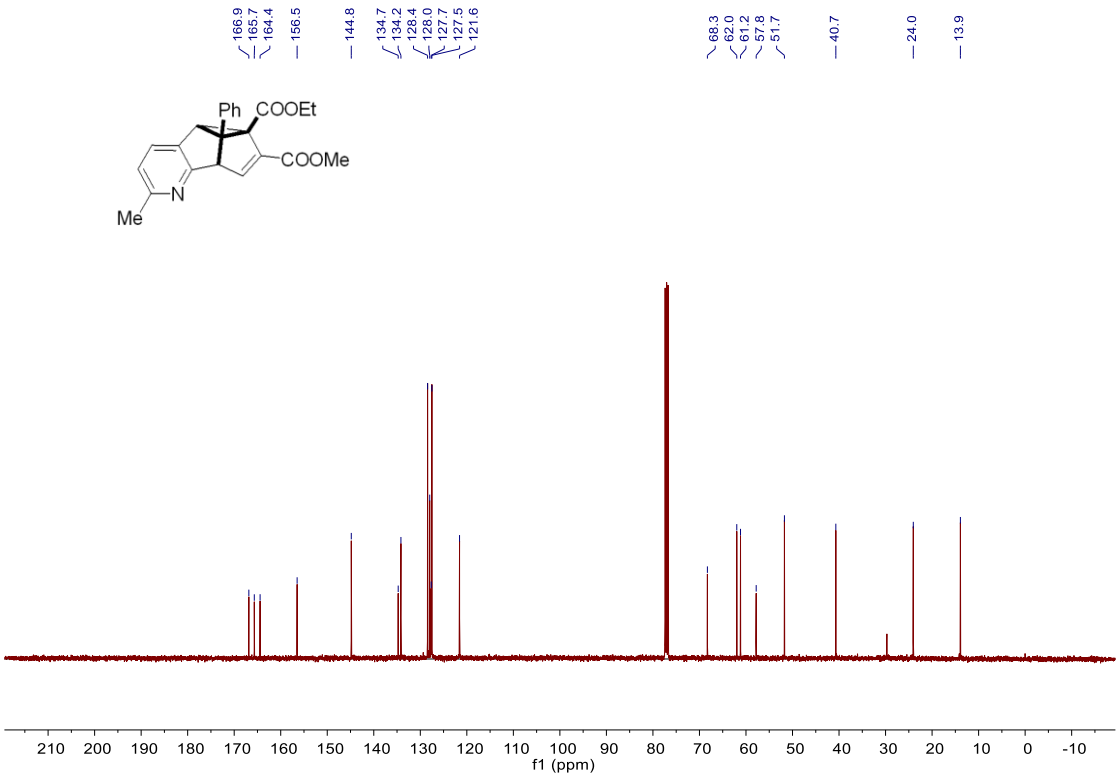

$^{13}$C NMR spectrum of **5ga**



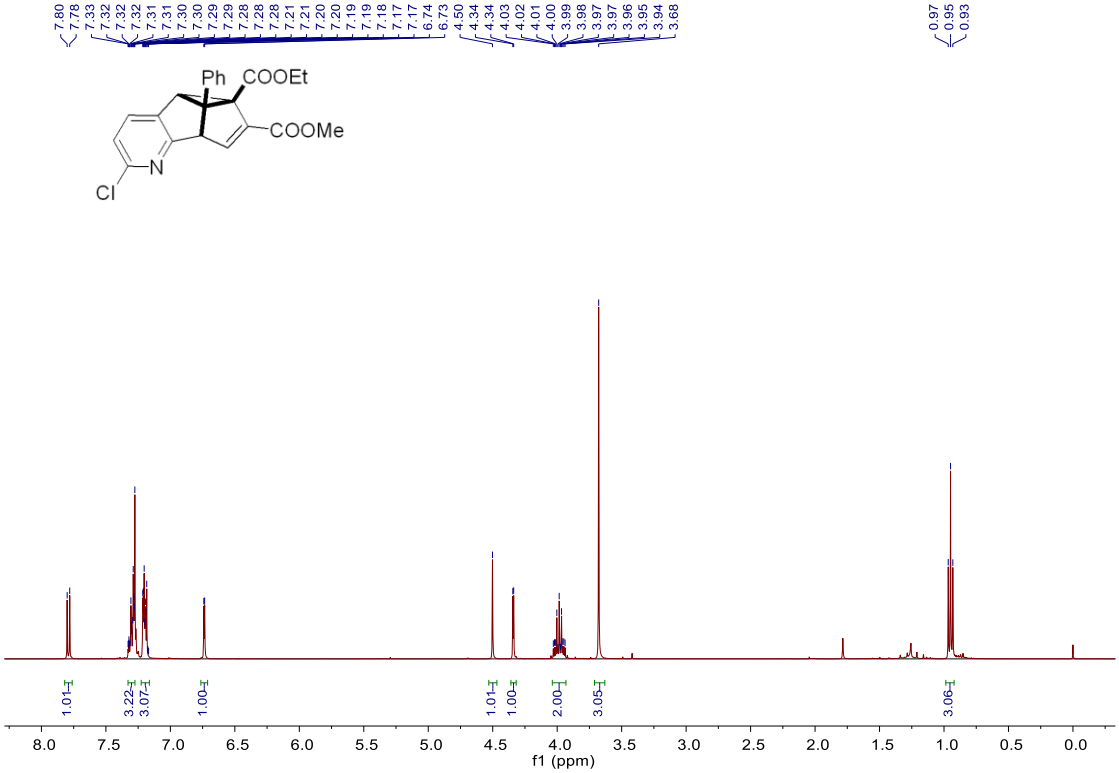
$^{1}$H NMR spectrum of **5ha**



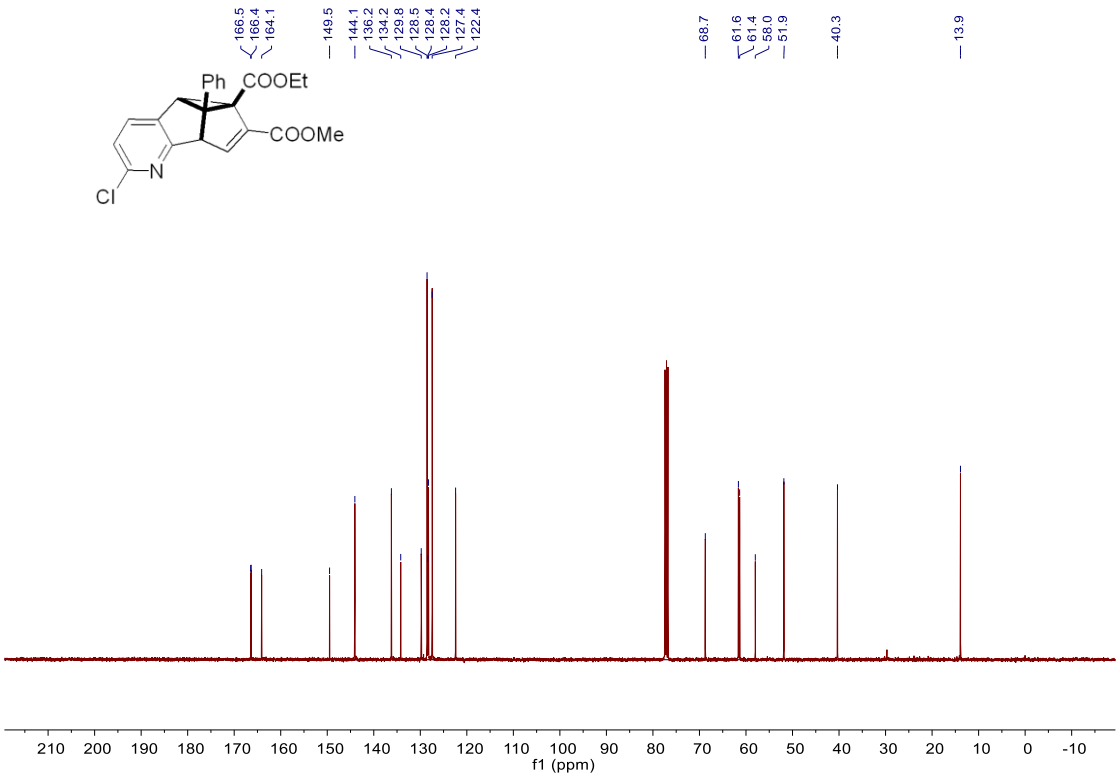

$^{13}$C NMR spectrum of **5ha**



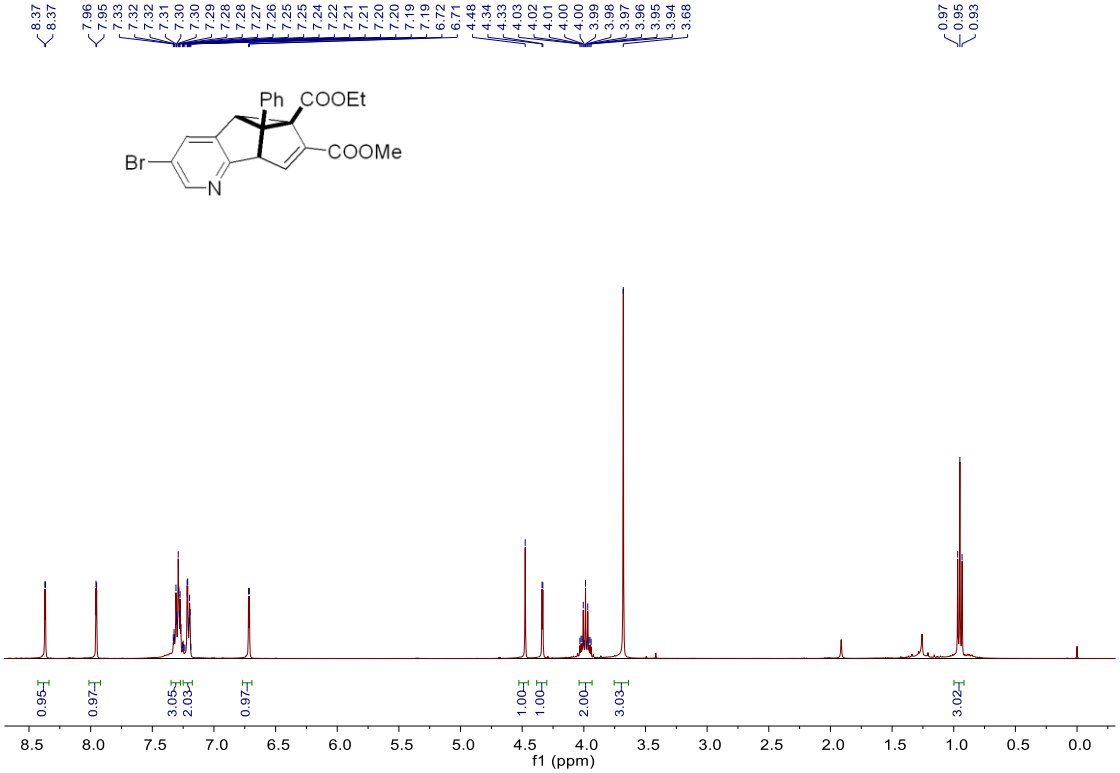
$^{1}$H NMR spectrum of **5ia**



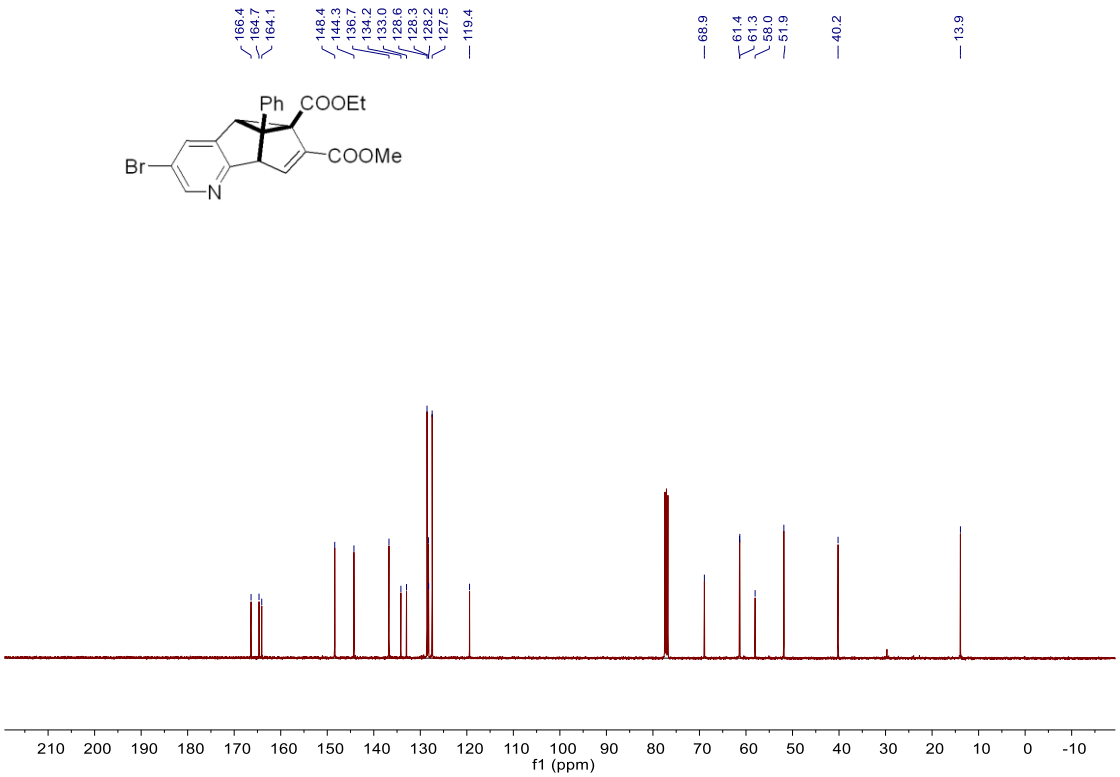

$^{13}$C NMR spectrum of **5ia**



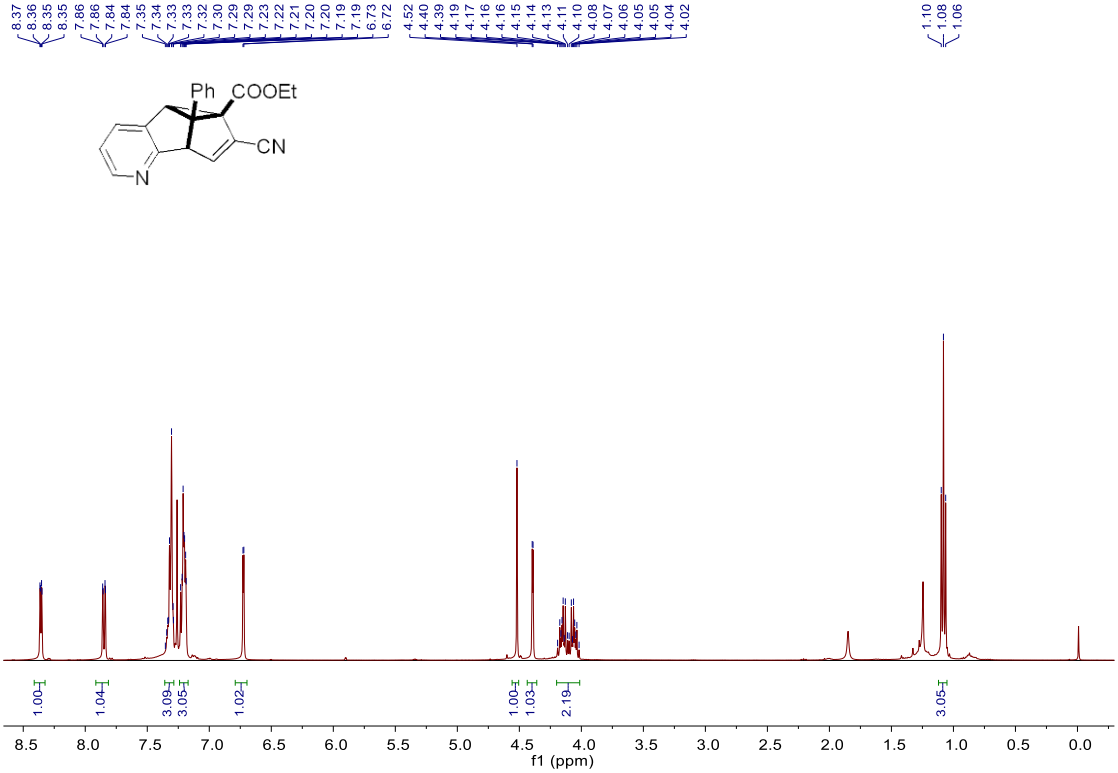
$^{1}$H NMR spectrum of **5ja**



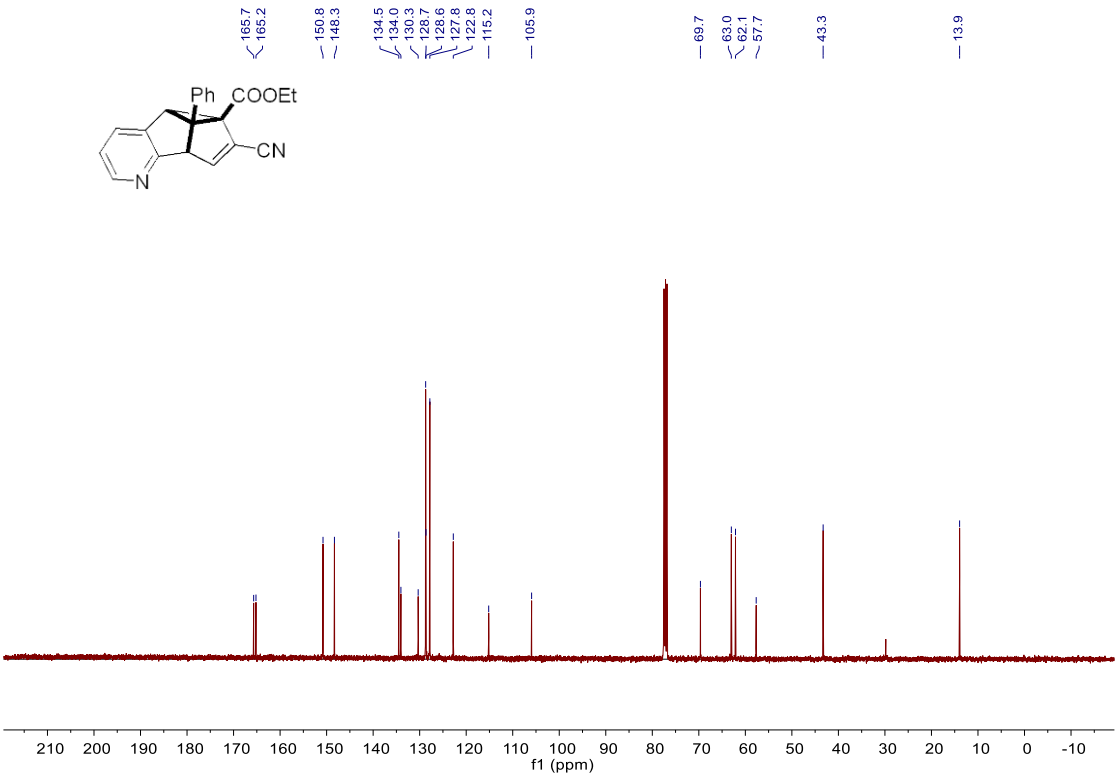

$^{13}$C NMR spectrum of **5ja**



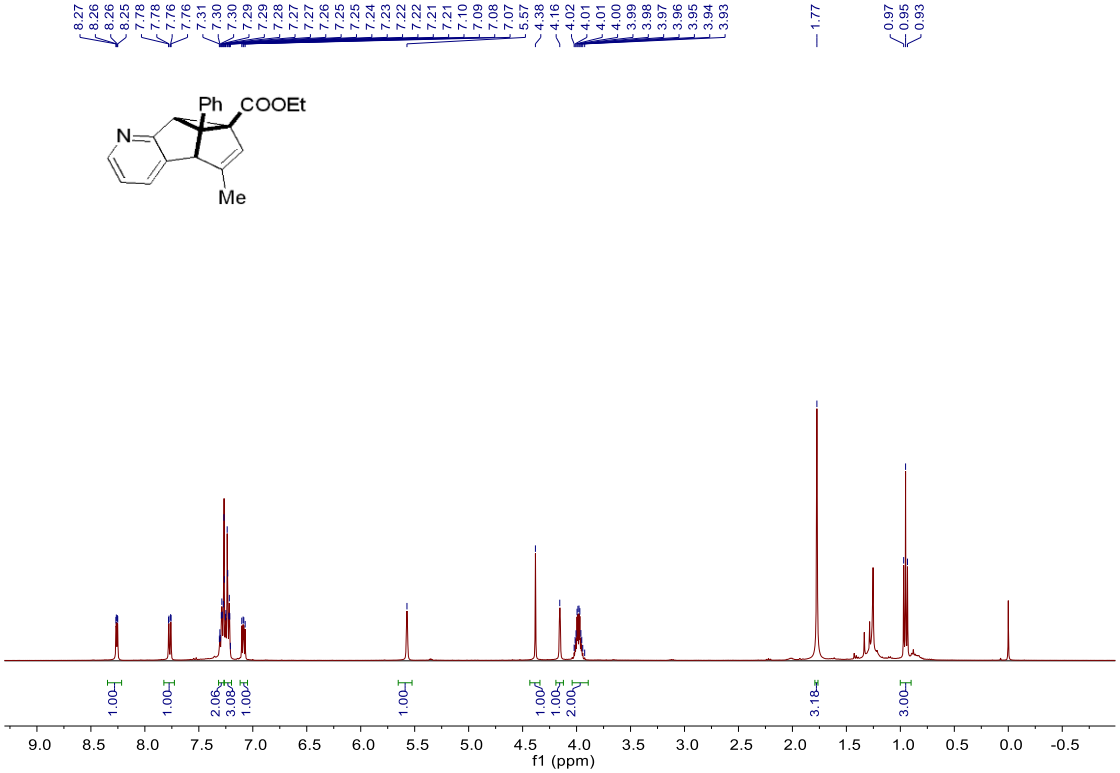
$^{1}$H NMR spectrum of **5ka**



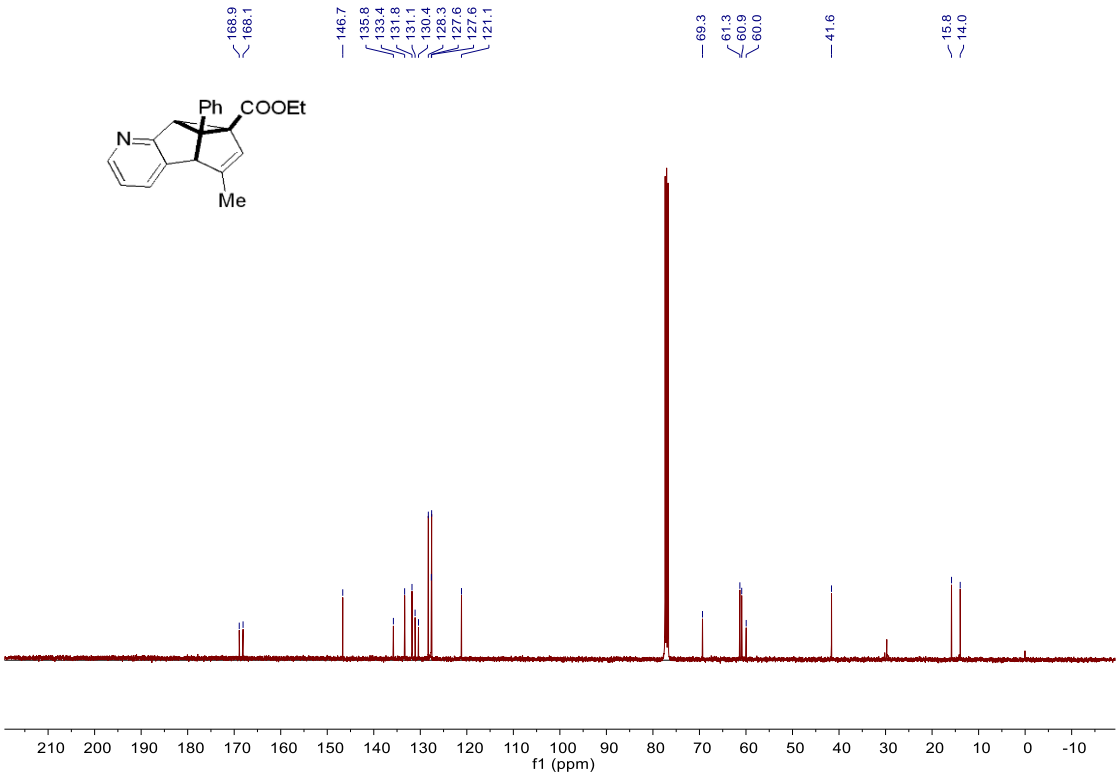

$^{13}$C NMR spectrum of **5ka**



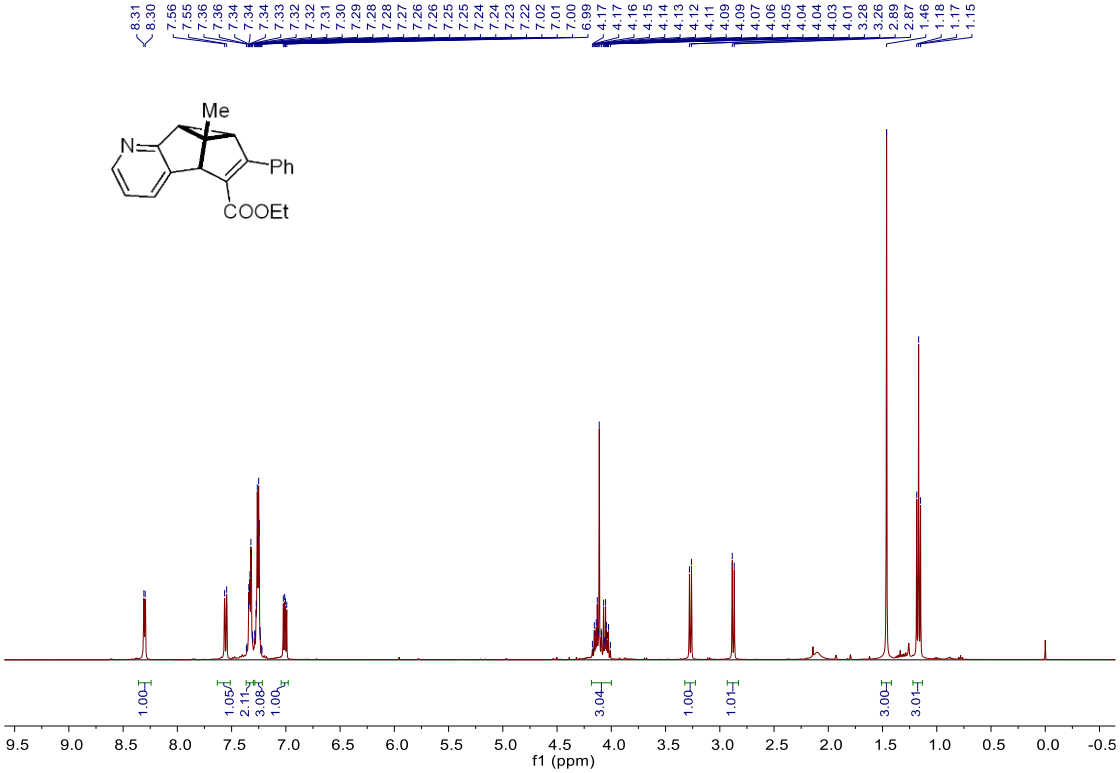
$^{1}$H NMR spectrum of **5la-1**



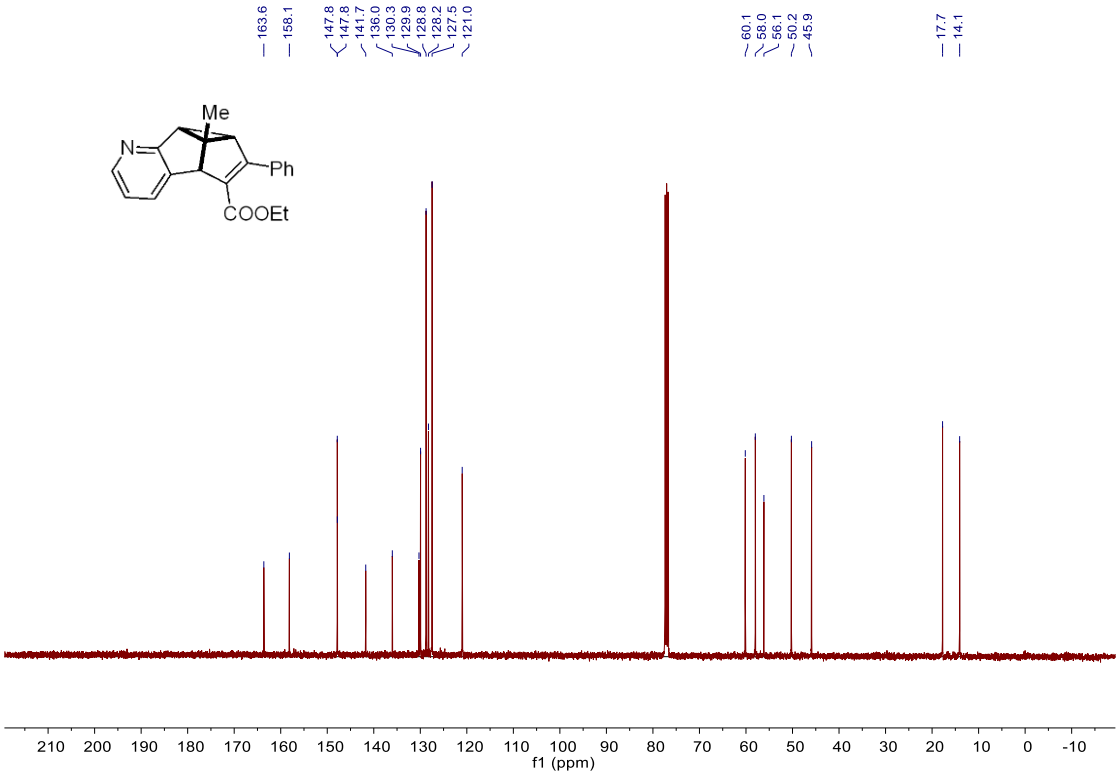

$^{13}$C NMR spectrum of **5la-1**



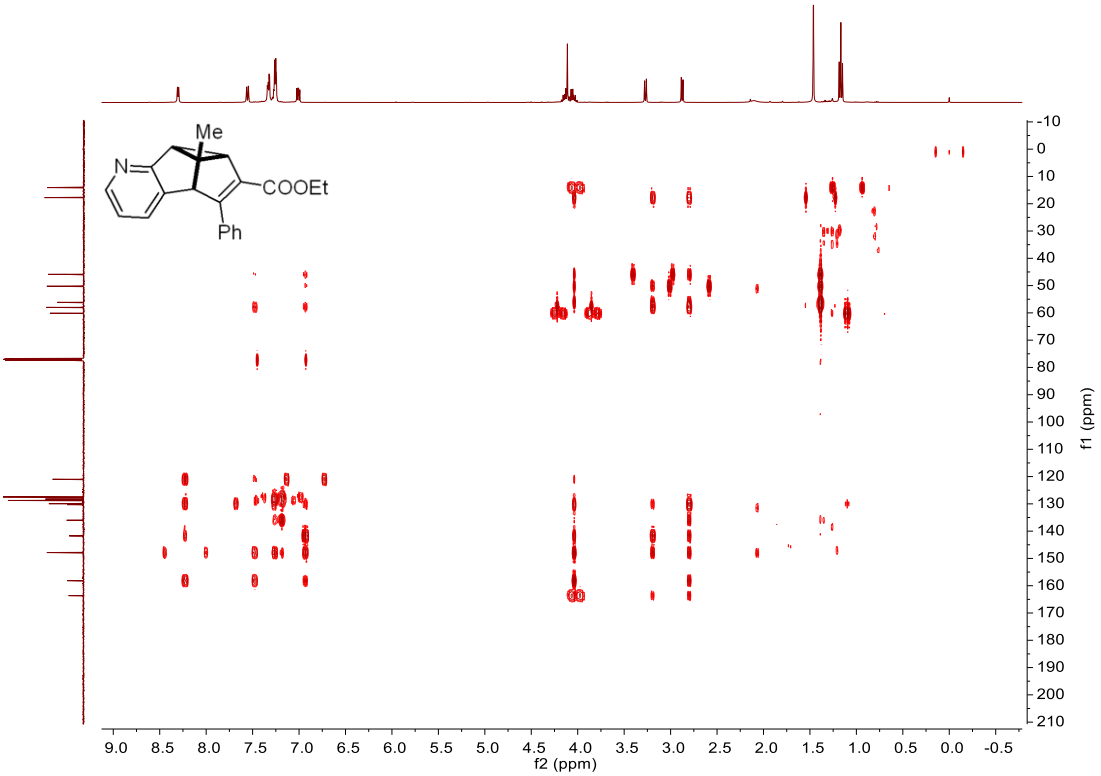
$^{1}$H NMR spectrum of **5la-2**



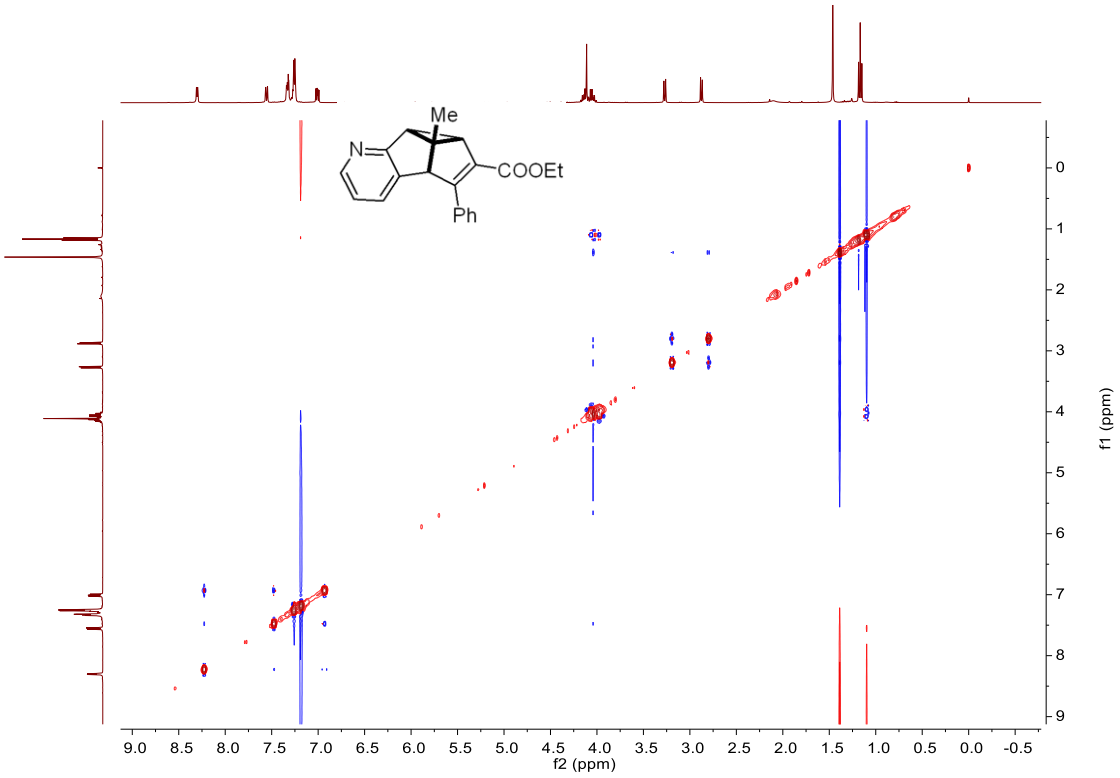

$^{13}$C NMR spectrum of **5la-2**



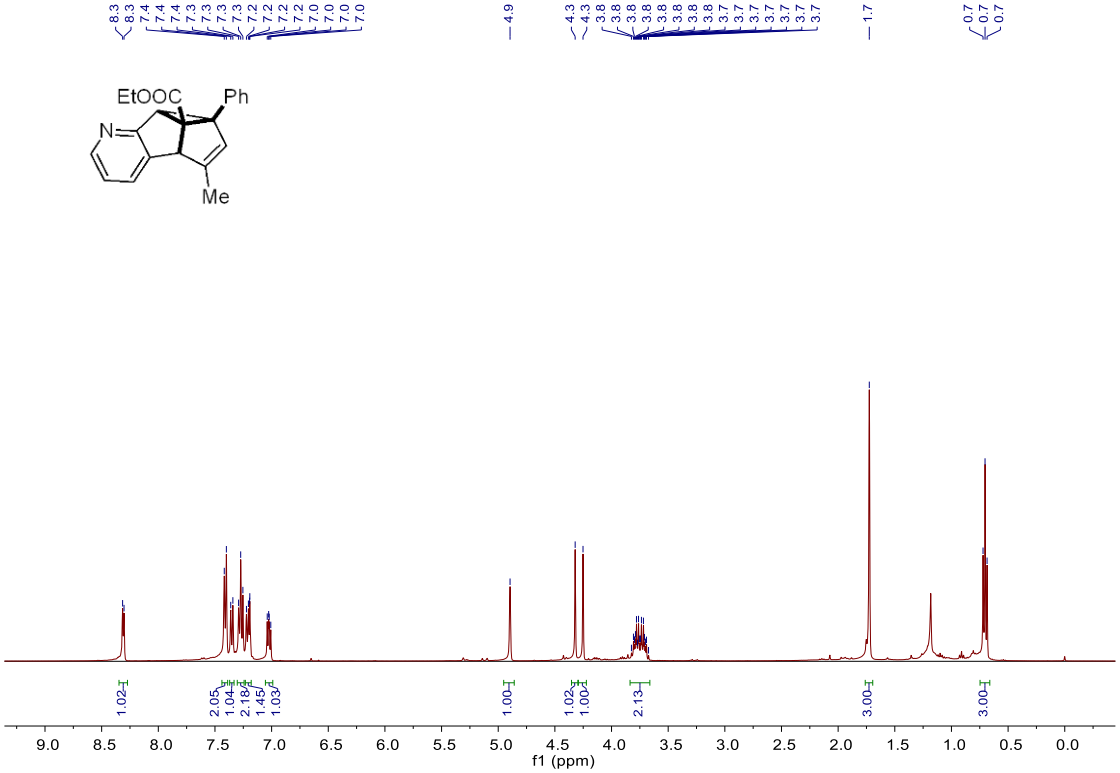
HMBC NMR spectrum of **5la-2**



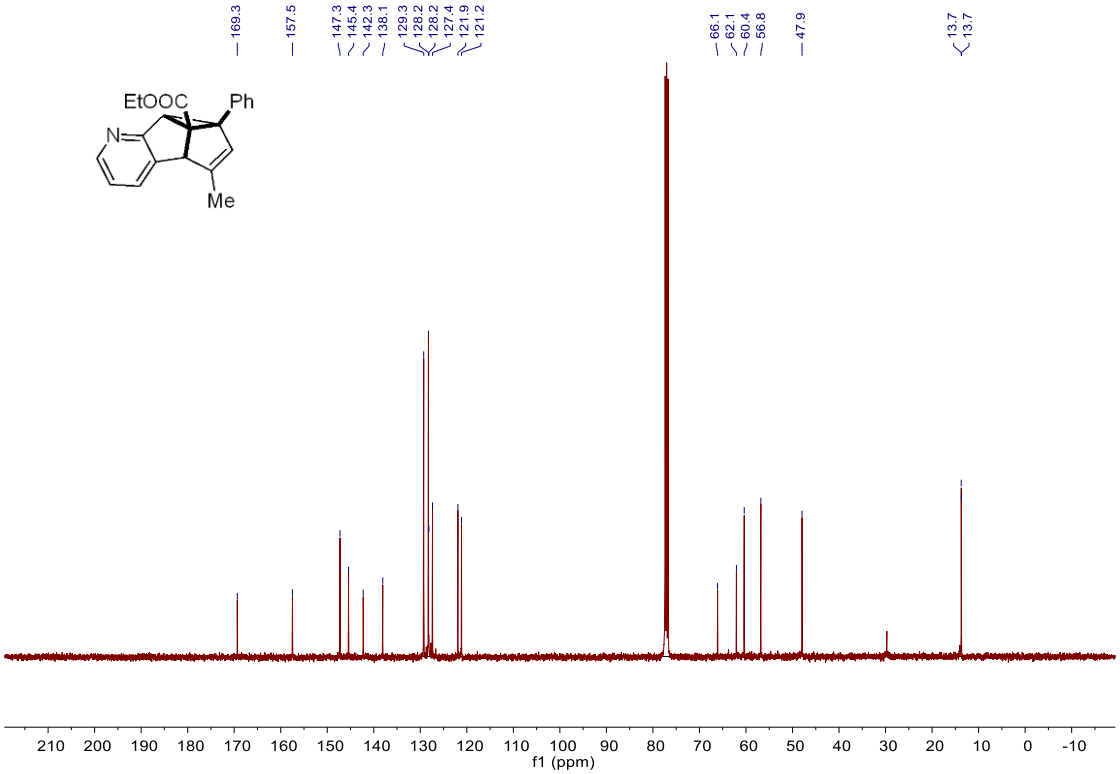

HSQC NMR spectrum of **5la-2**



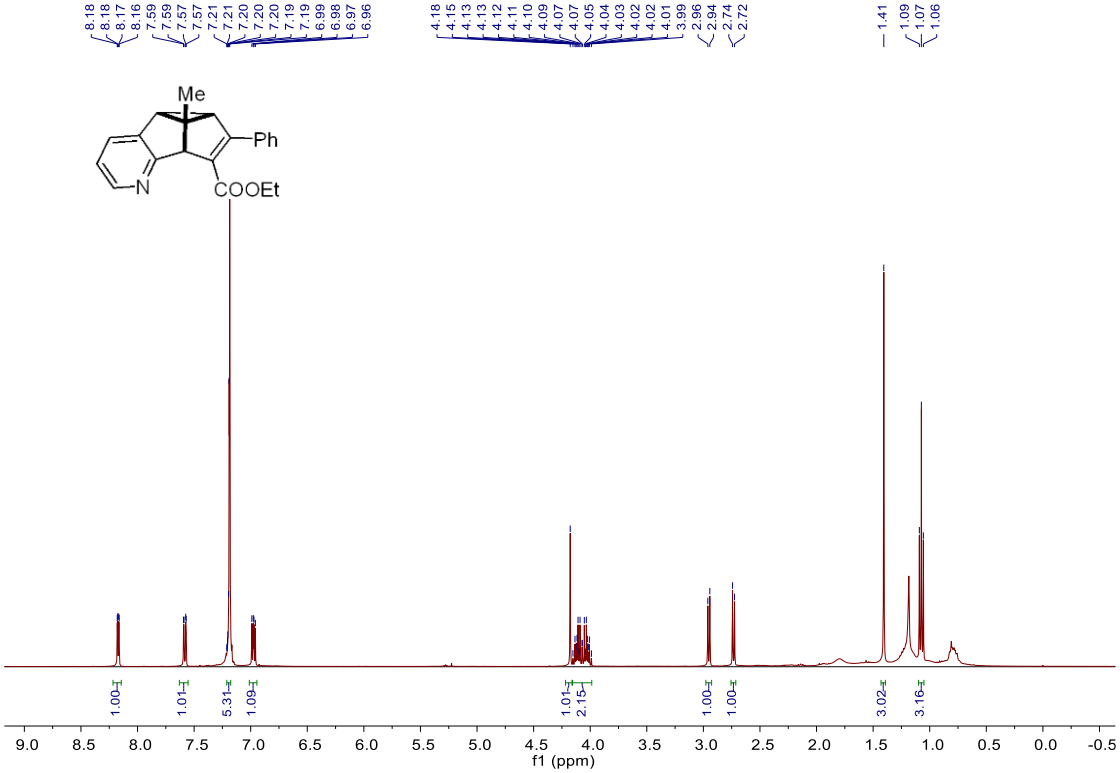
$^{1}$H NMR spectrum of **5la-3**



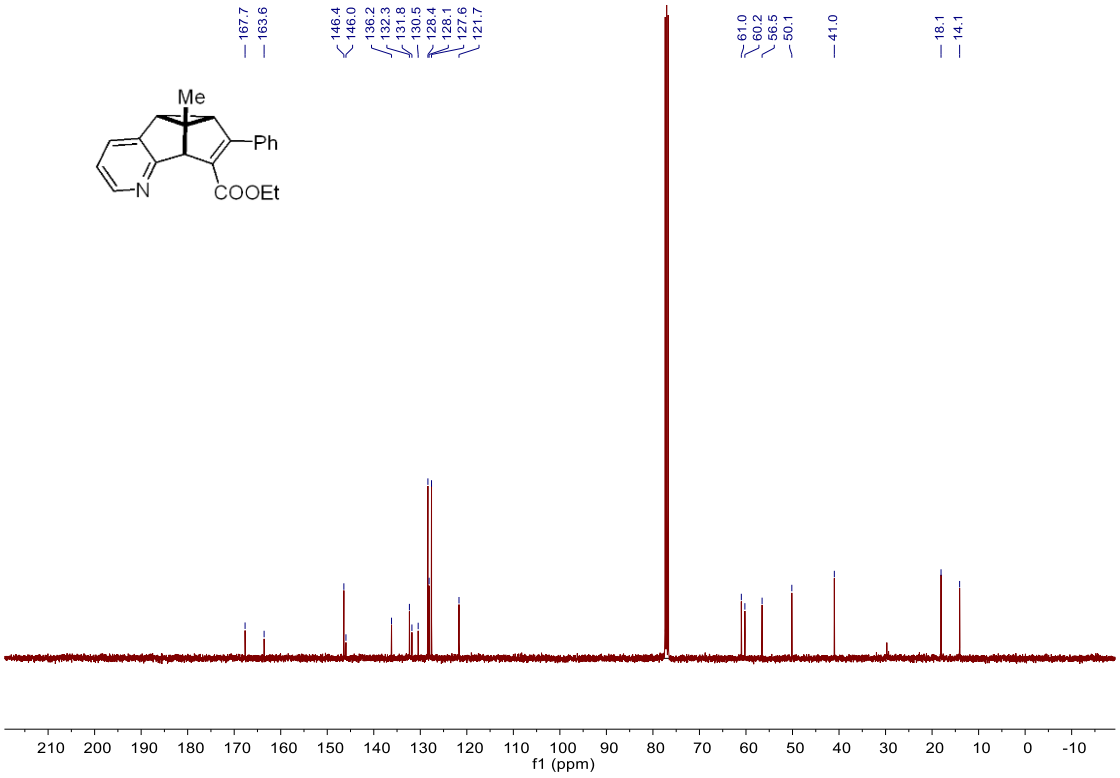

$^{13}$C NMR spectrum of **5la-3**



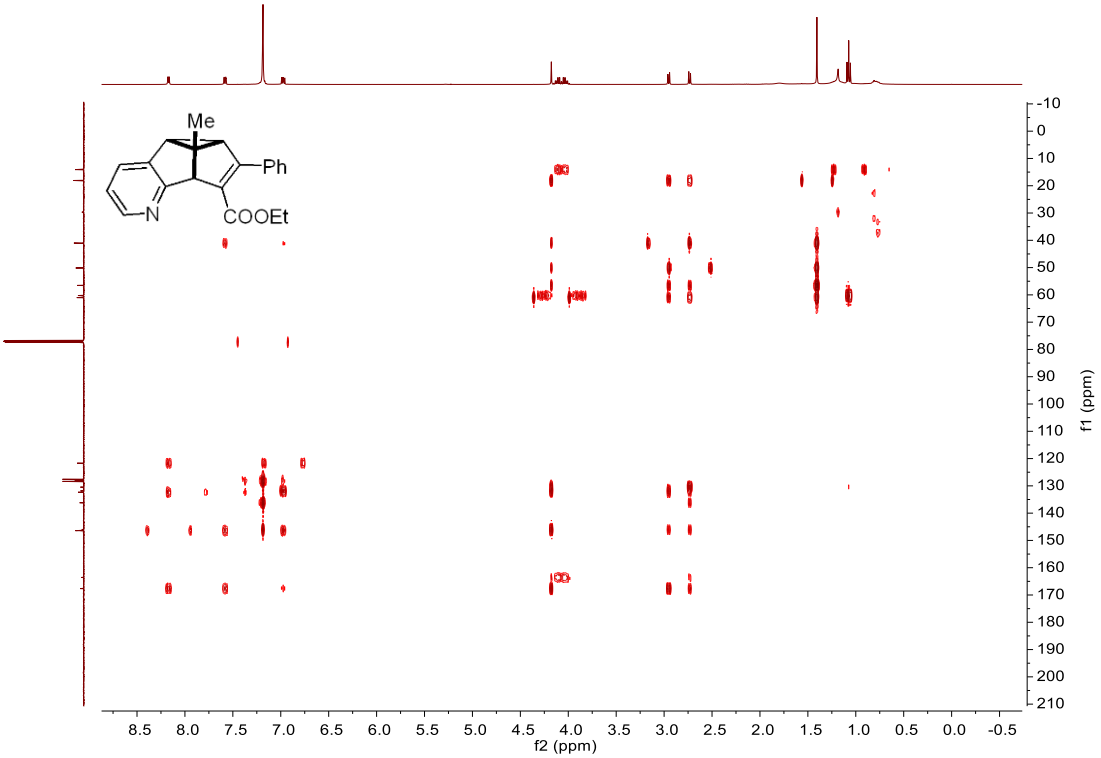
$^{1}$H NMR spectrum of **5ma**



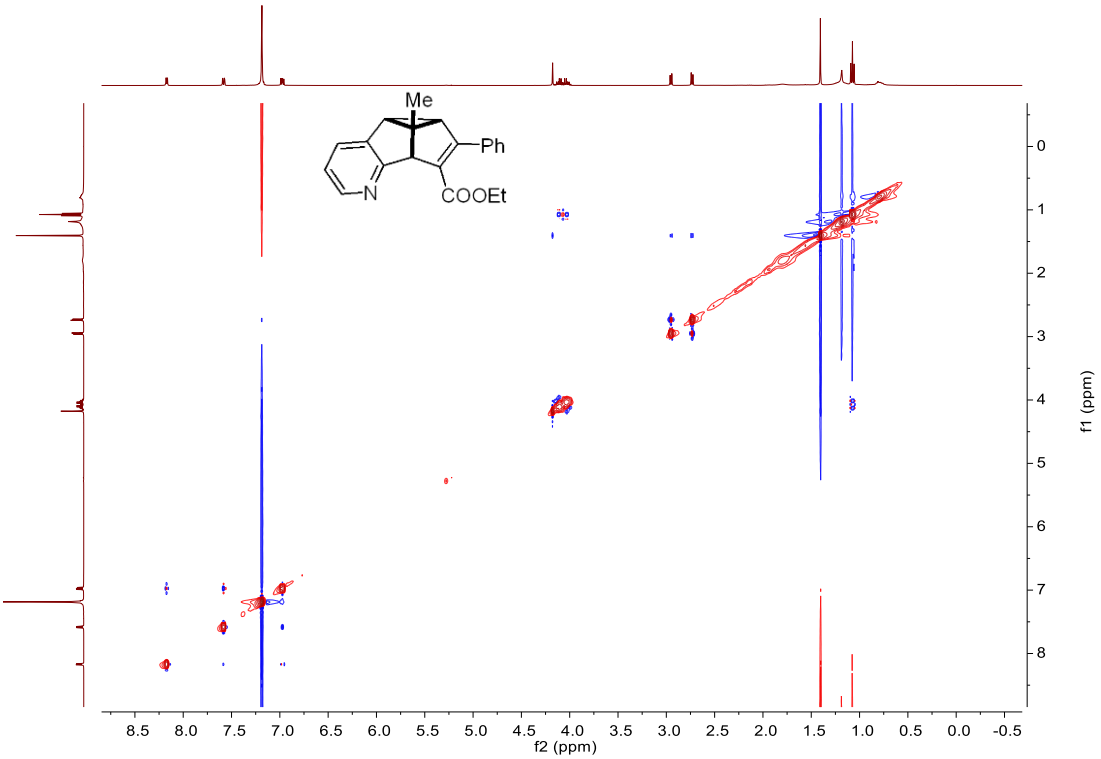

$^{13}$C NMR spectrum of **5ma**



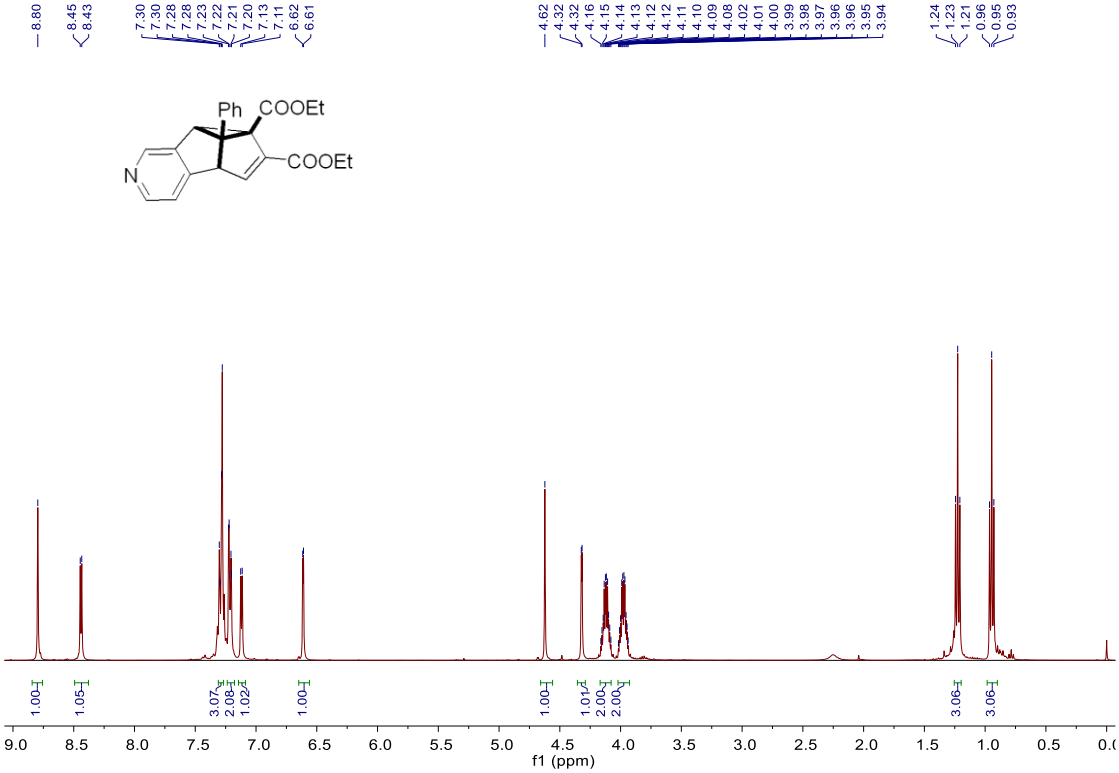
HMBC NMR spectrum of **5ma**



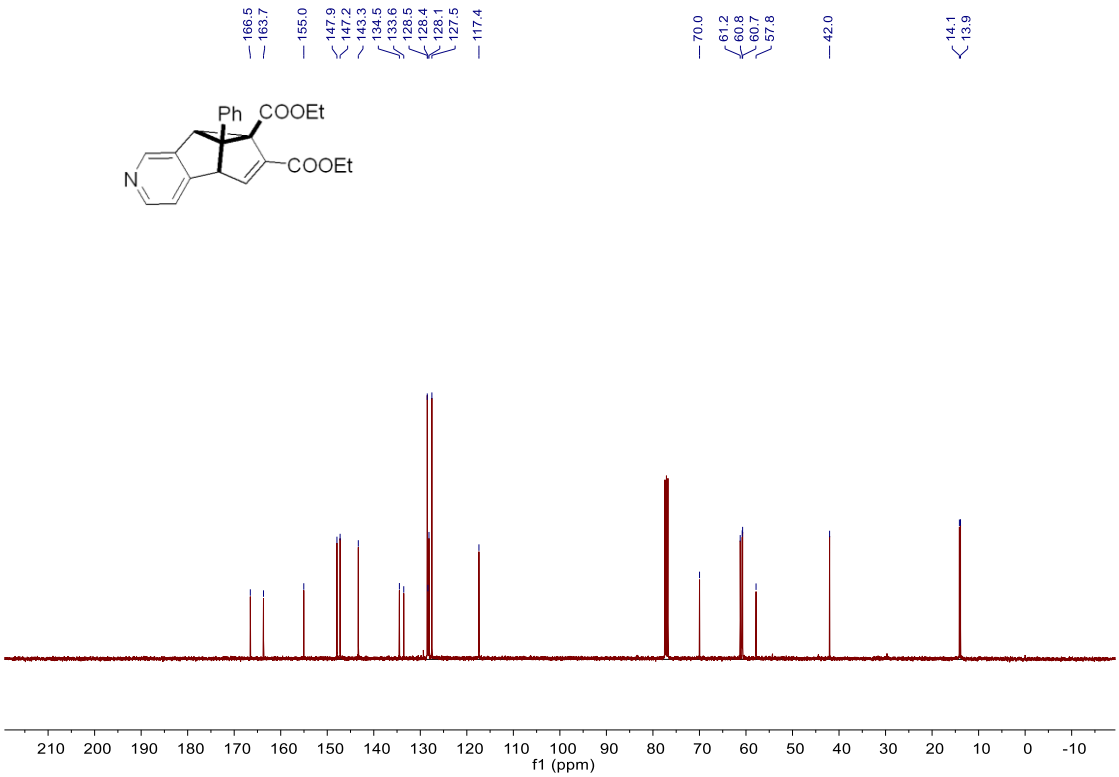

HSQC NMR spectrum of **5ma**



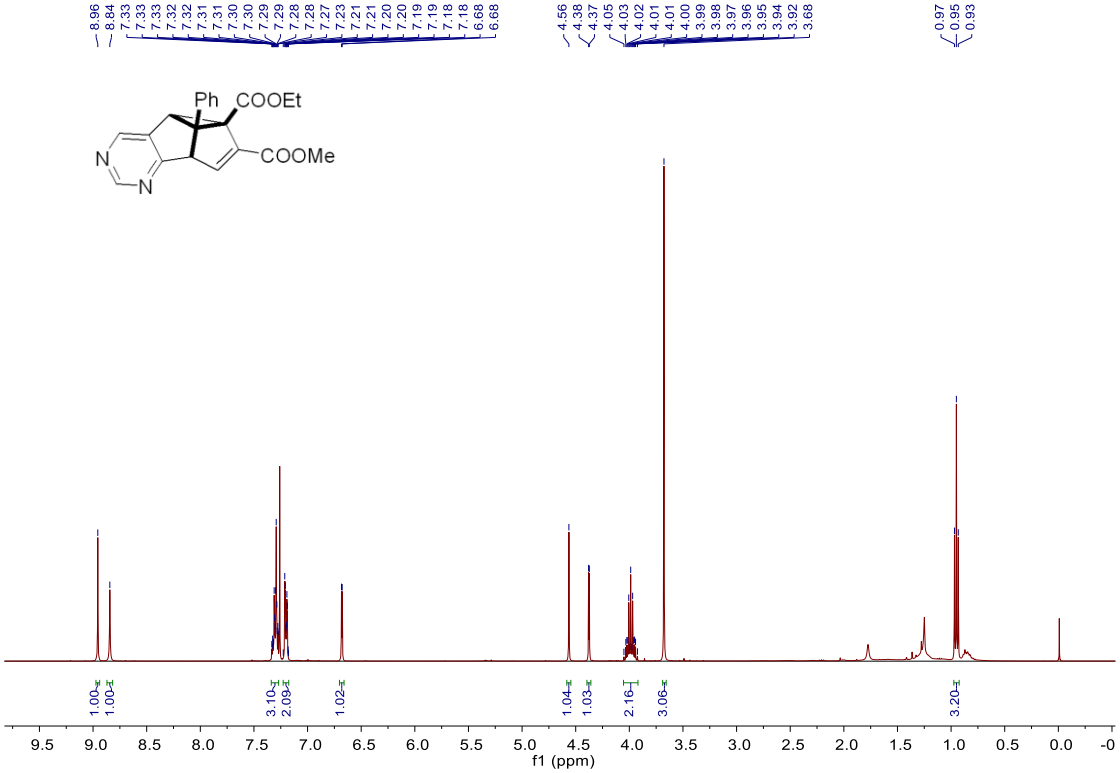
$^{1}$H NMR spectrum of **5na**



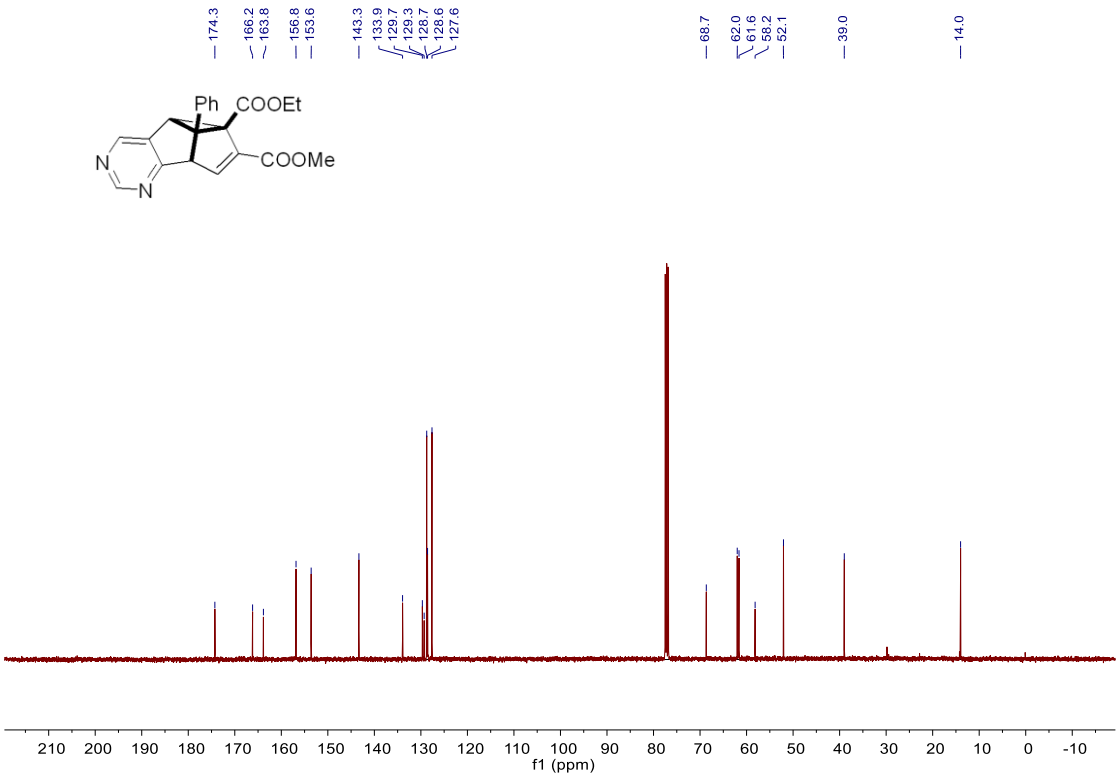

$^{13}$C NMR spectrum of **5na**



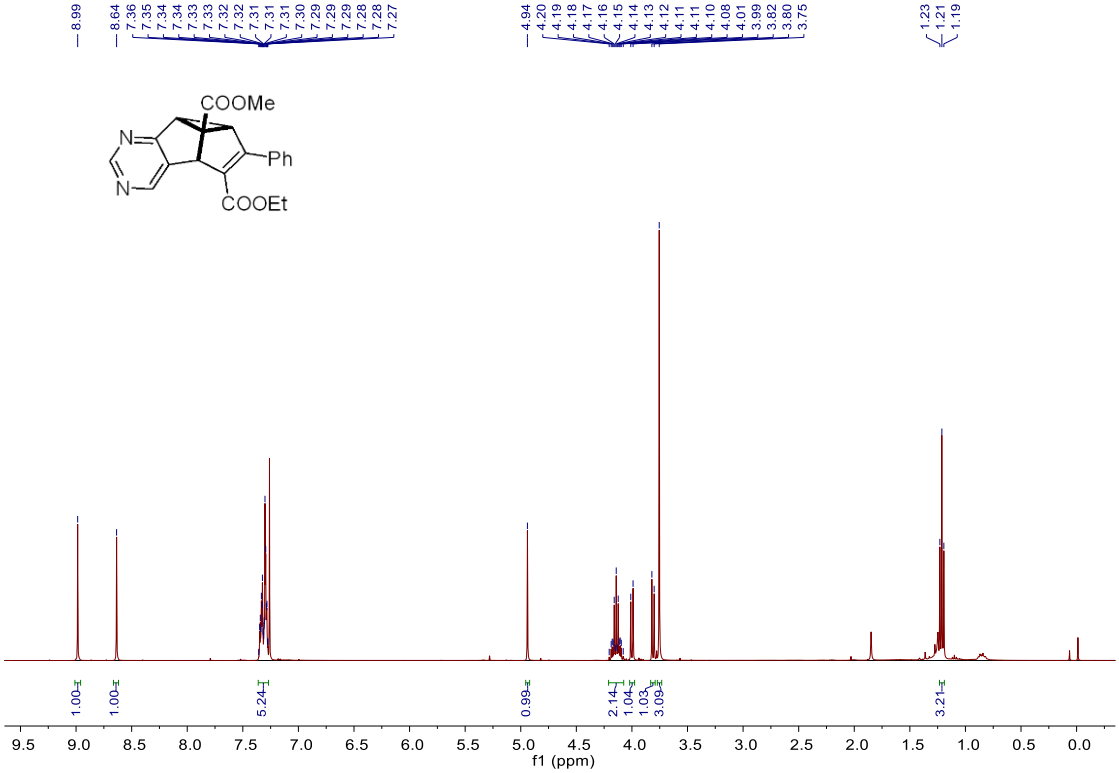
$^{1}$H NMR spectrum of **5oa-1**



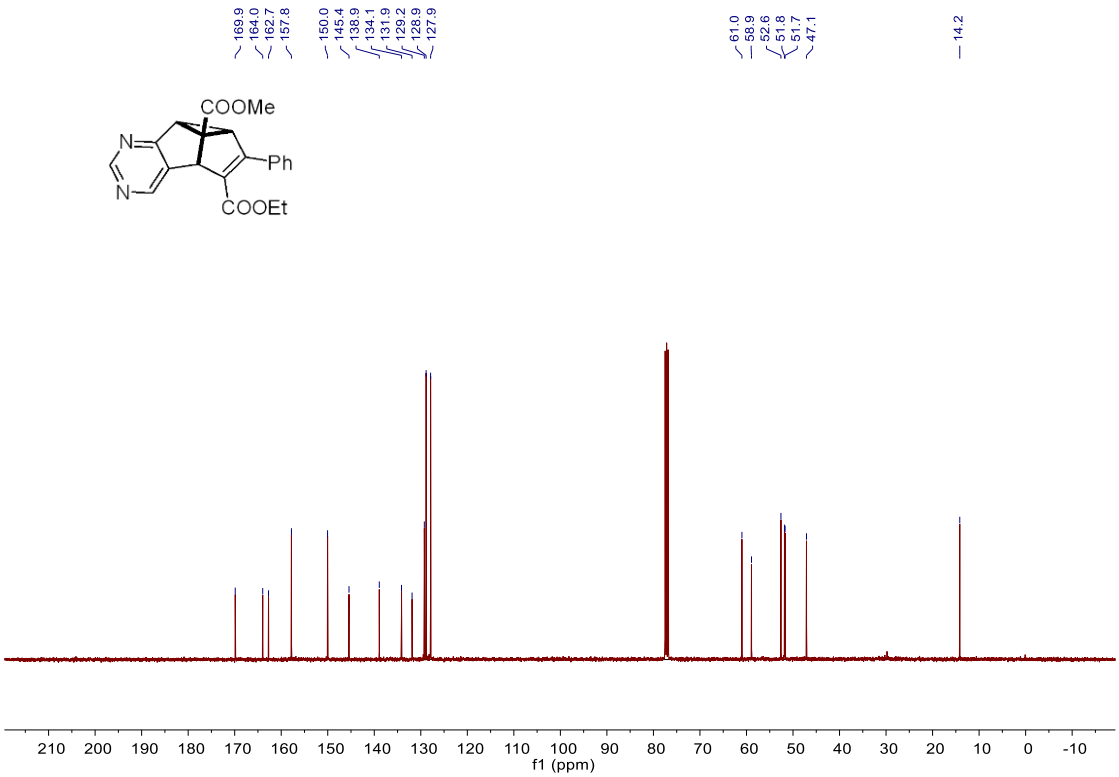

$^{13}$C NMR spectrum of **5oa-1**



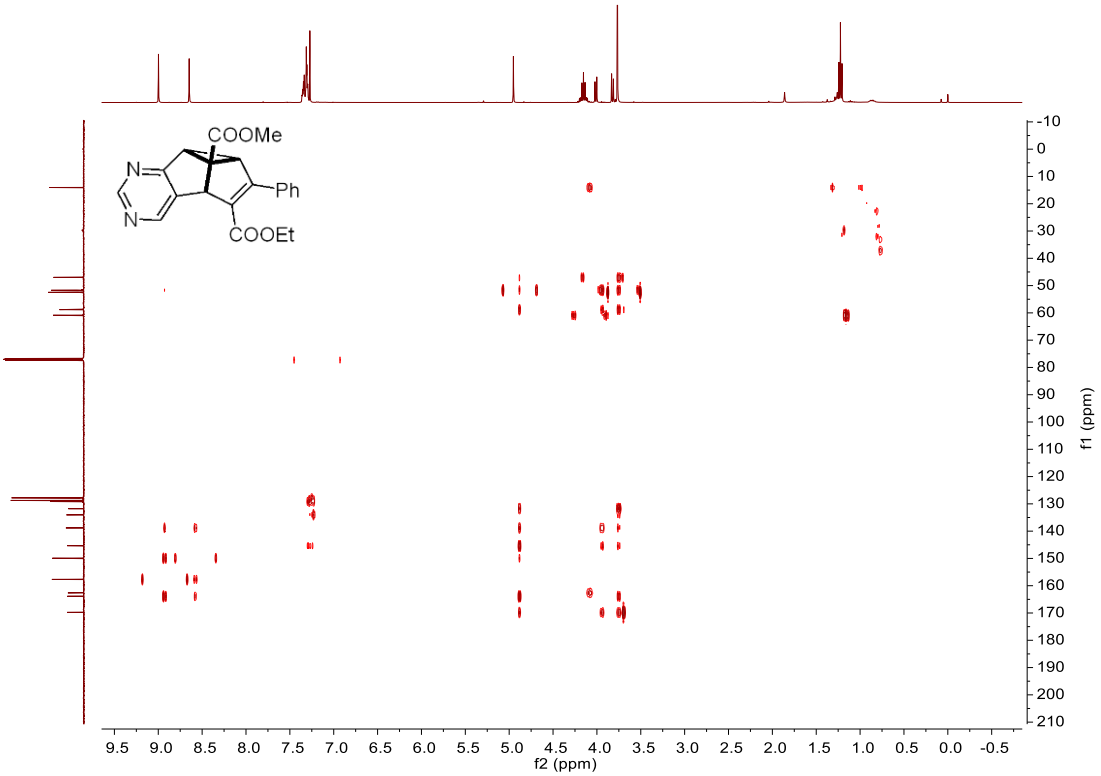
$^{1}$H NMR spectrum of **5oa-2**



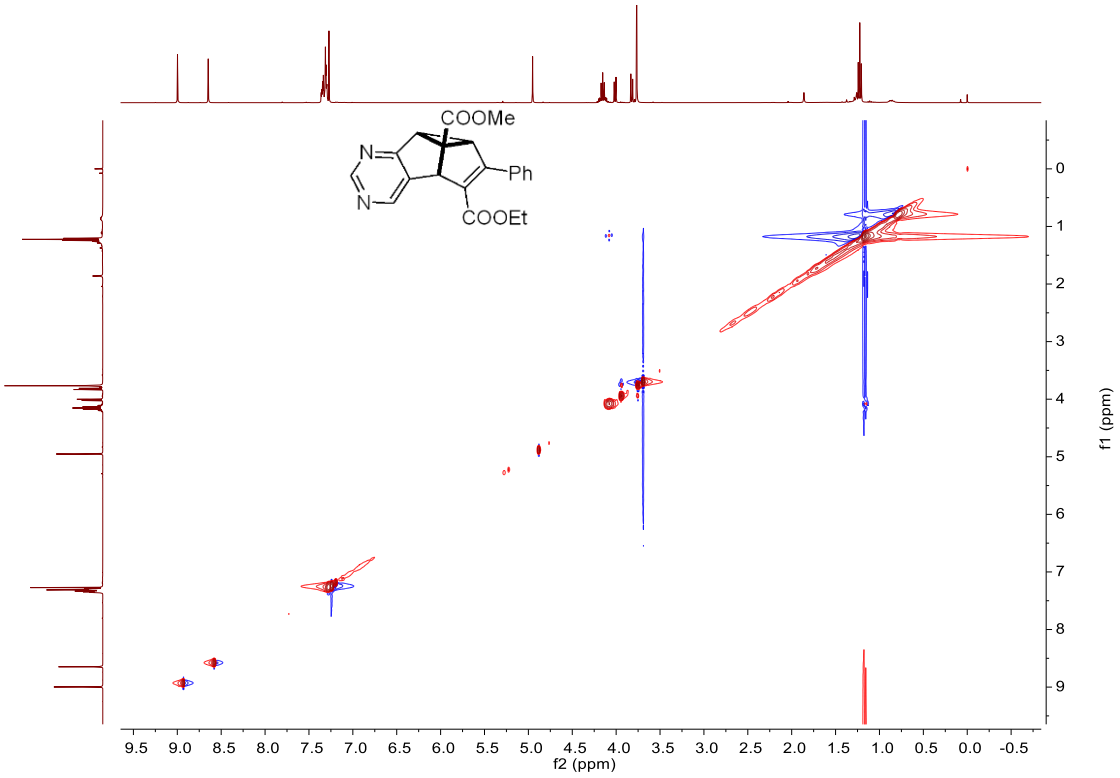

$^{13}$C NMR spectrum of **5oa-2**



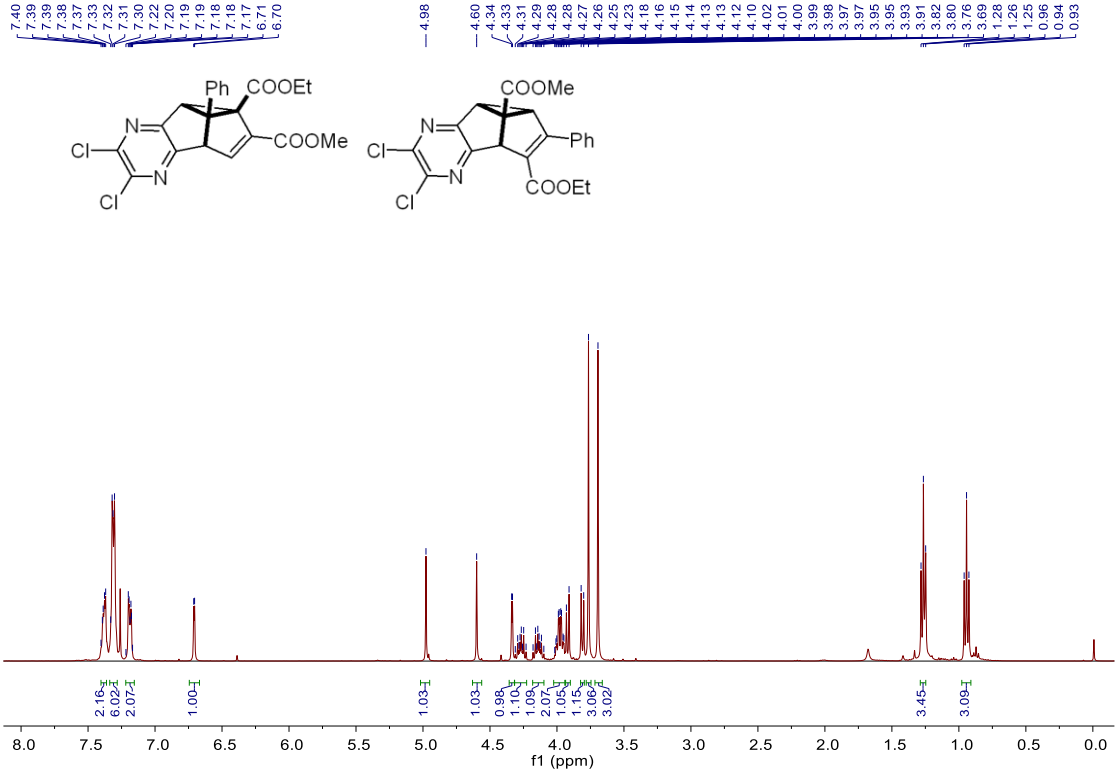
HMBC NMR spectrum of **5oa-2**



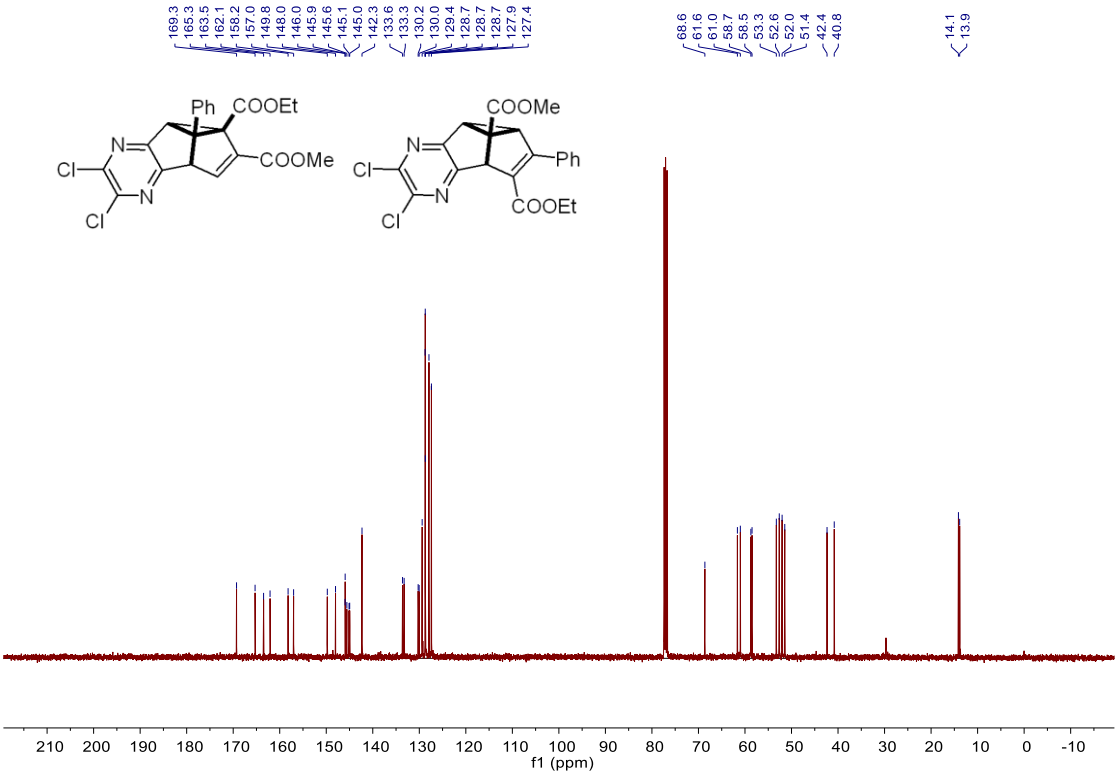

HSQC NMR spectrum of **5oa-2**



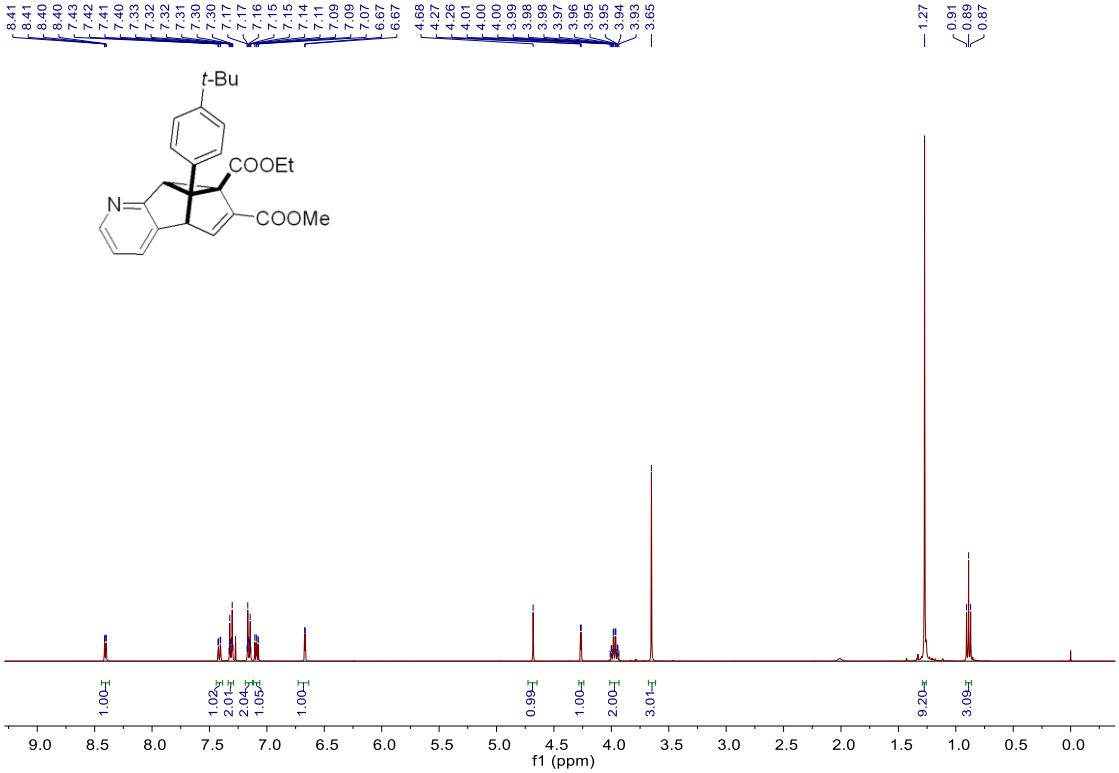
$^{1}$H NMR spectrum of **5pa**



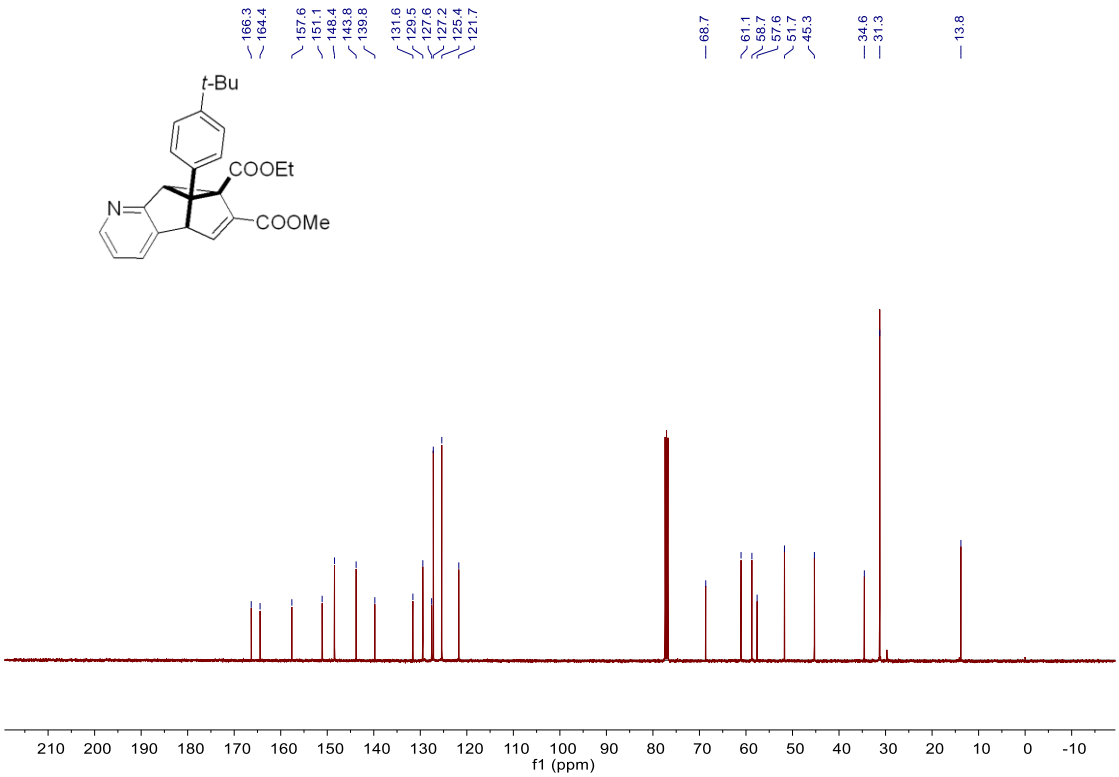

$^{13}$C NMR spectrum of **5pa**



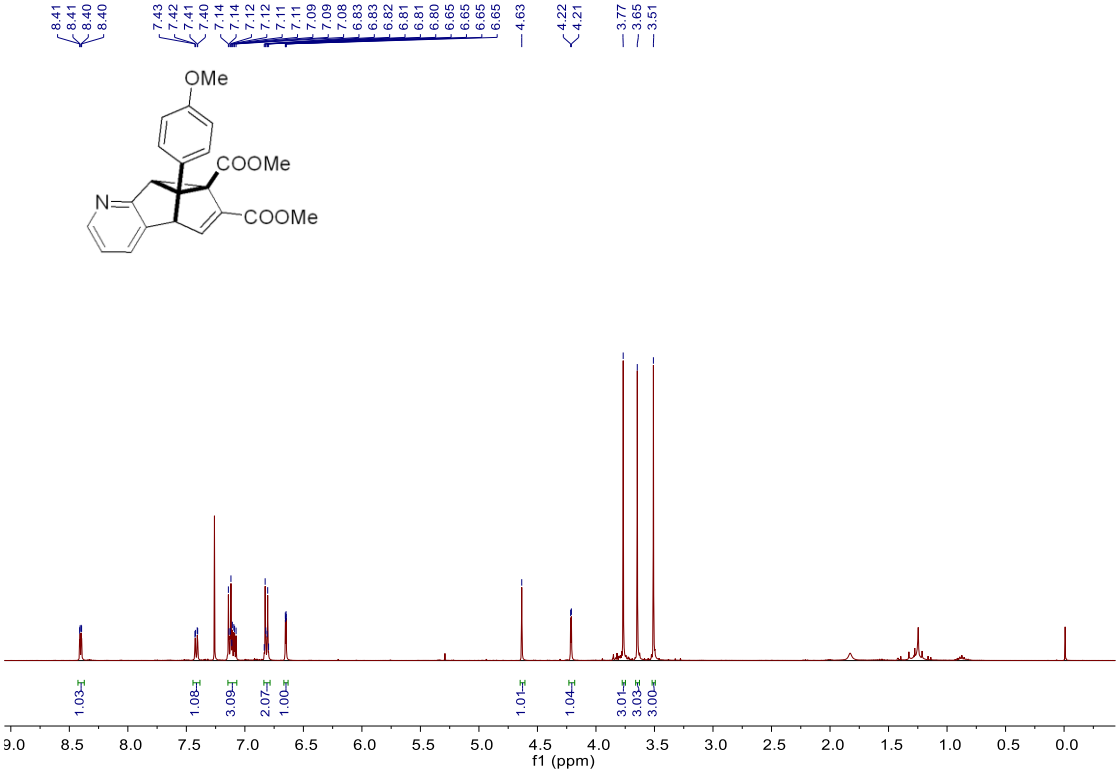
$^{1}$H NMR spectrum of **5ae**



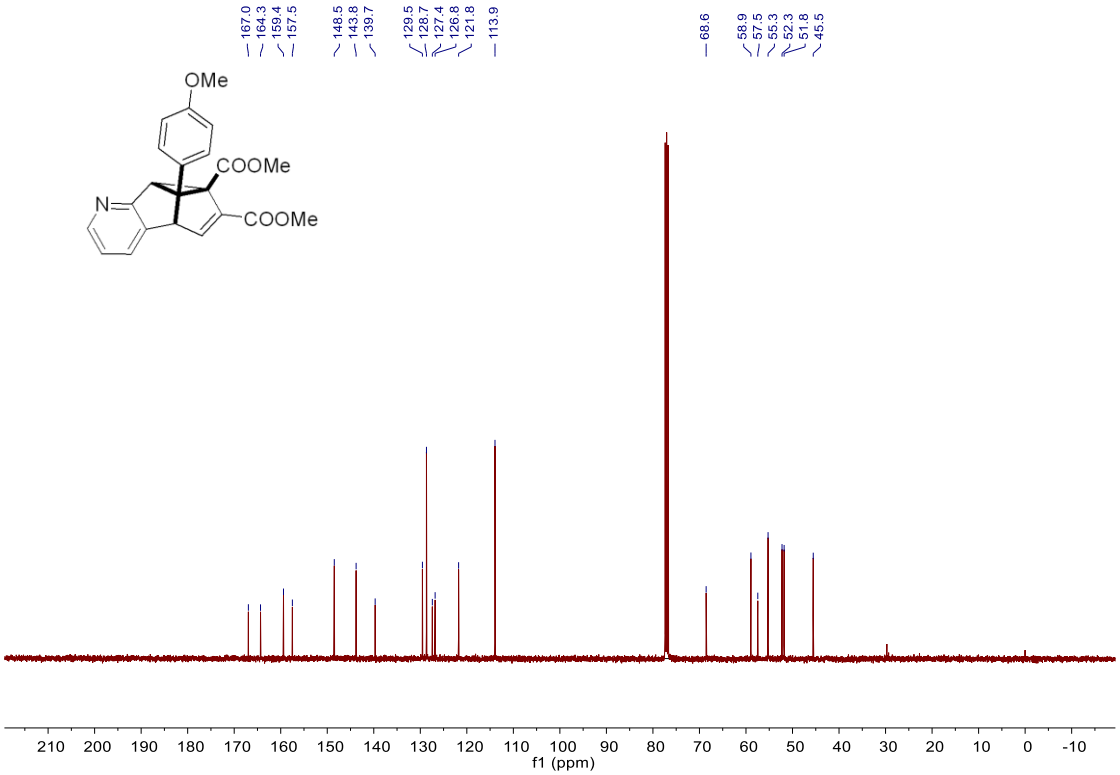

$^{13}$C NMR spectrum of **5ae**



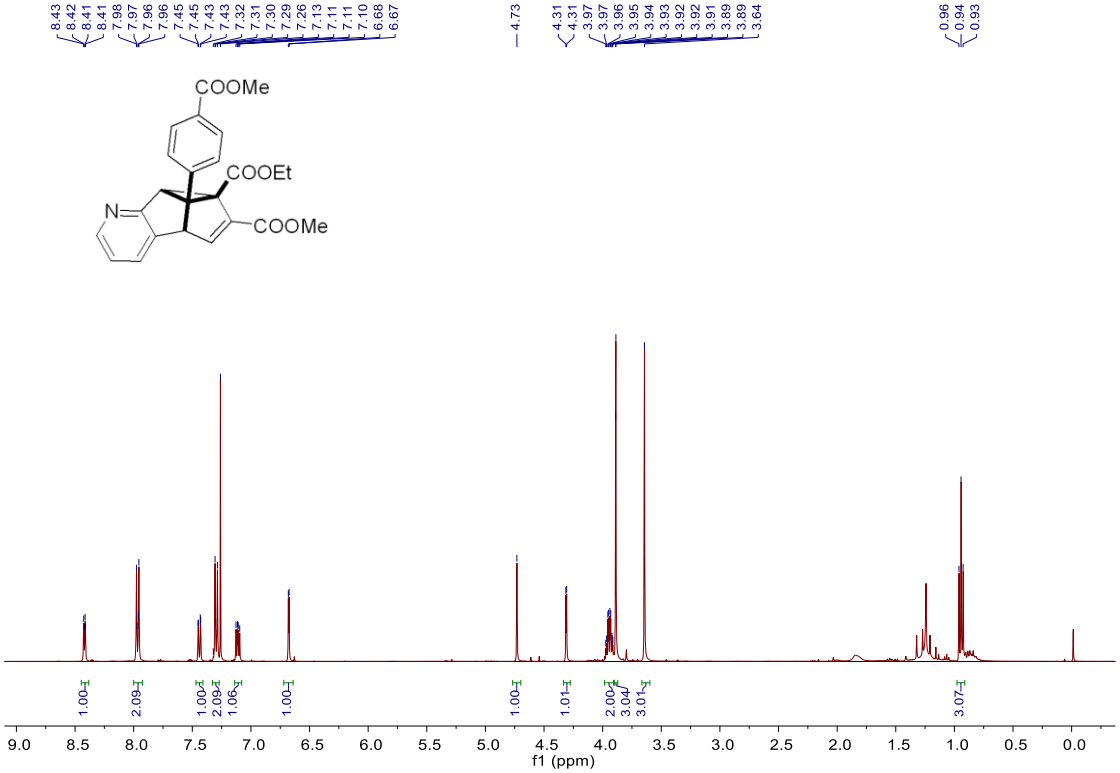
$^{1}$H NMR spectrum of **5af**



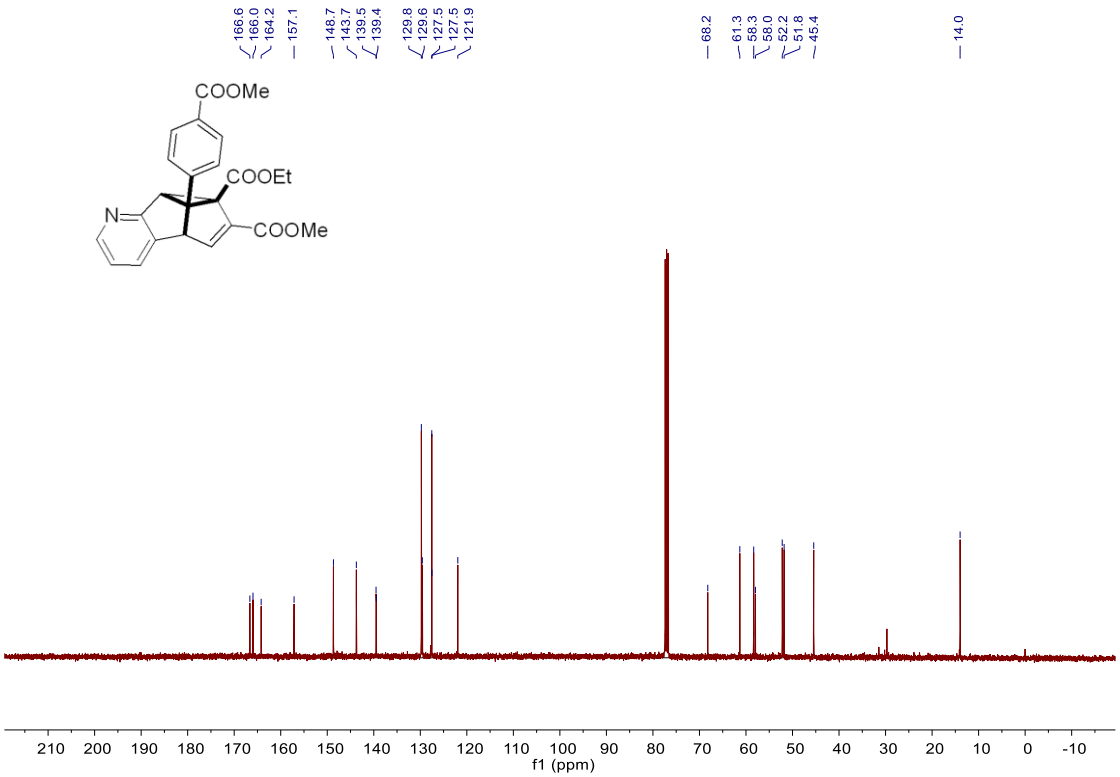

$^{13}$C NMR spectrum of **5af**



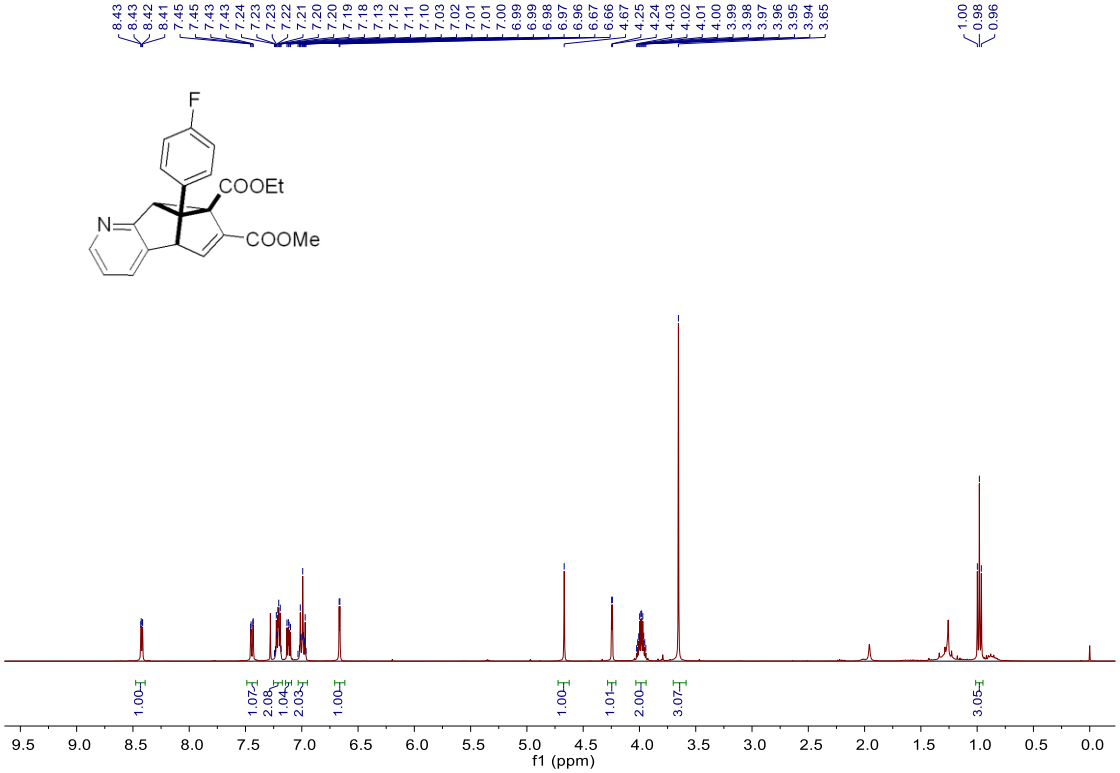
$^{1}$H NMR spectrum of **5ag**



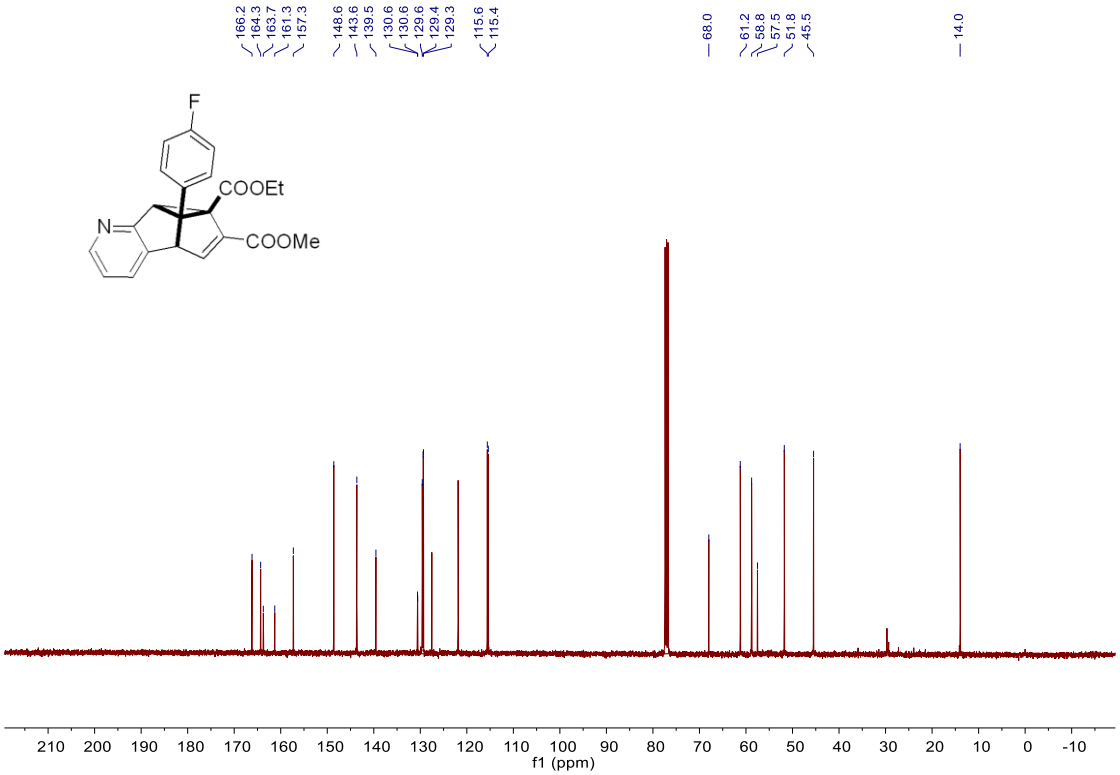

$^{13}$C NMR spectrum of **5ag**



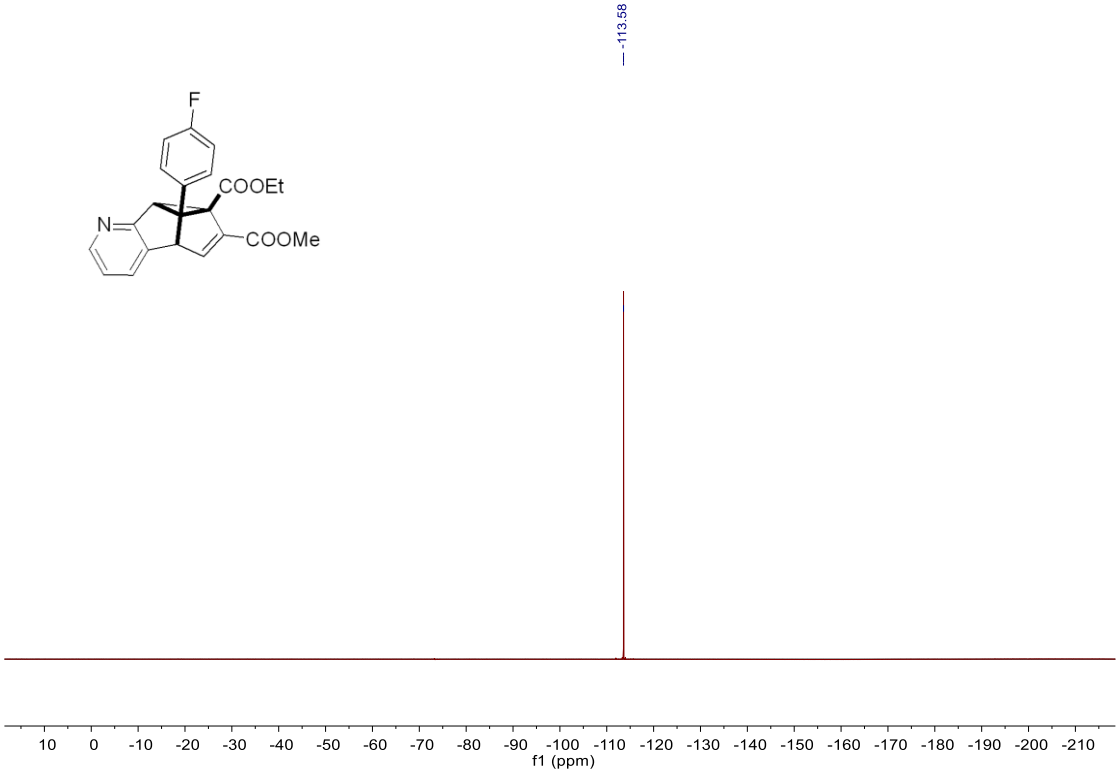
$^{1}$H NMR spectrum of **5ah**



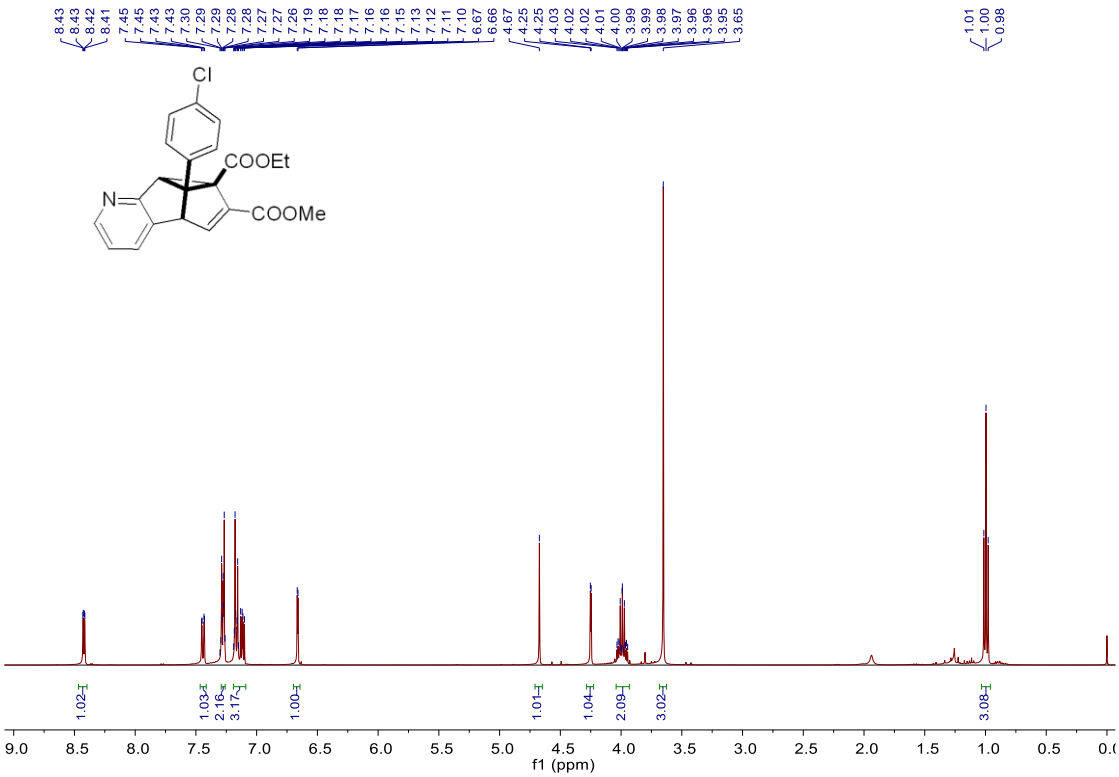

$^{13}$C NMR spectrum of **5ah**



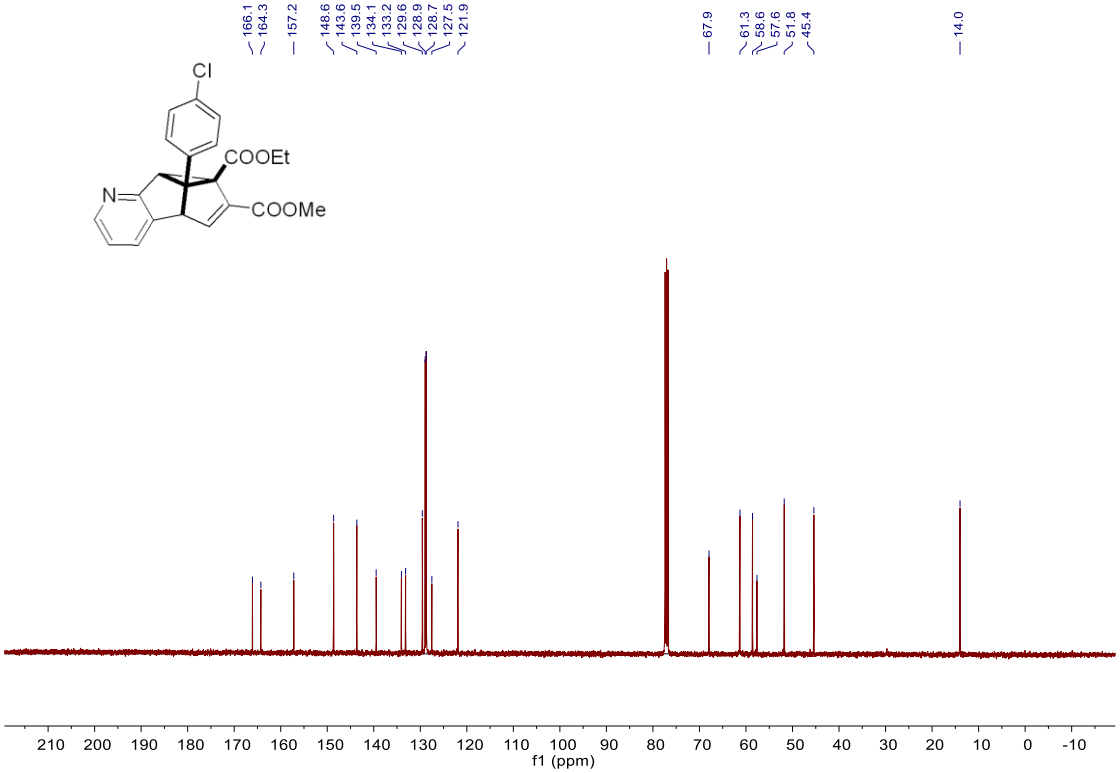
$^{19}$F NMR spectrum of **5ah**



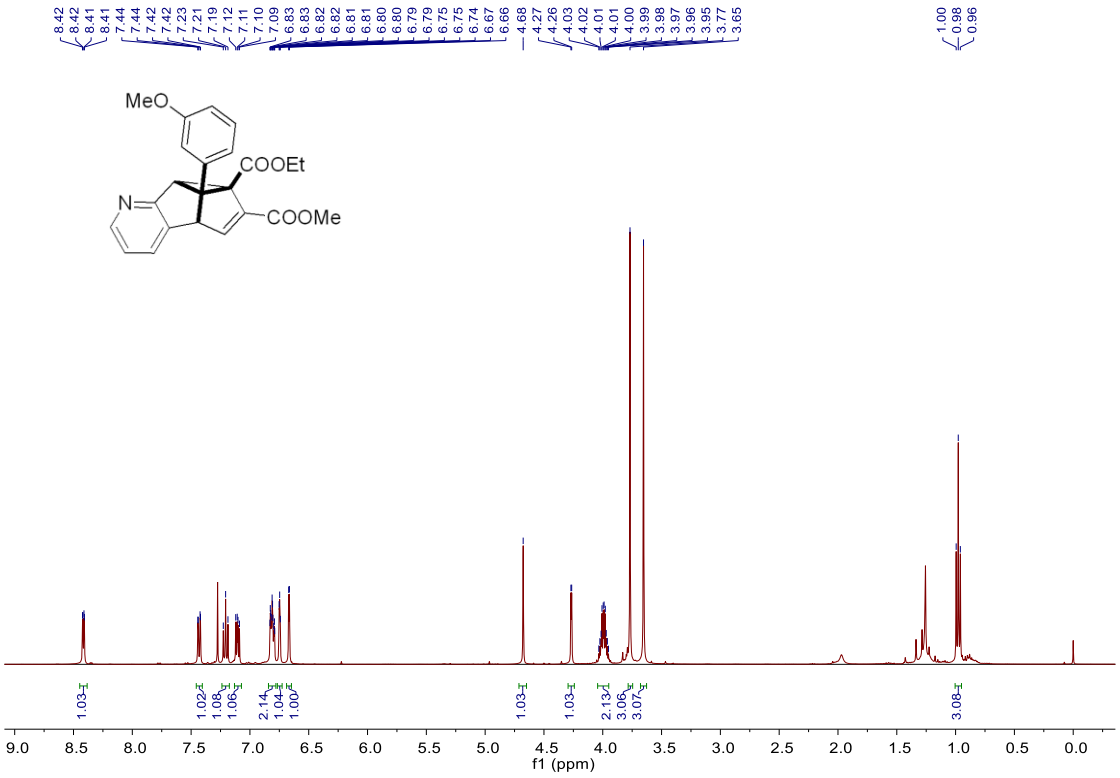

$^{1}$H NMR spectrum of **5ai**



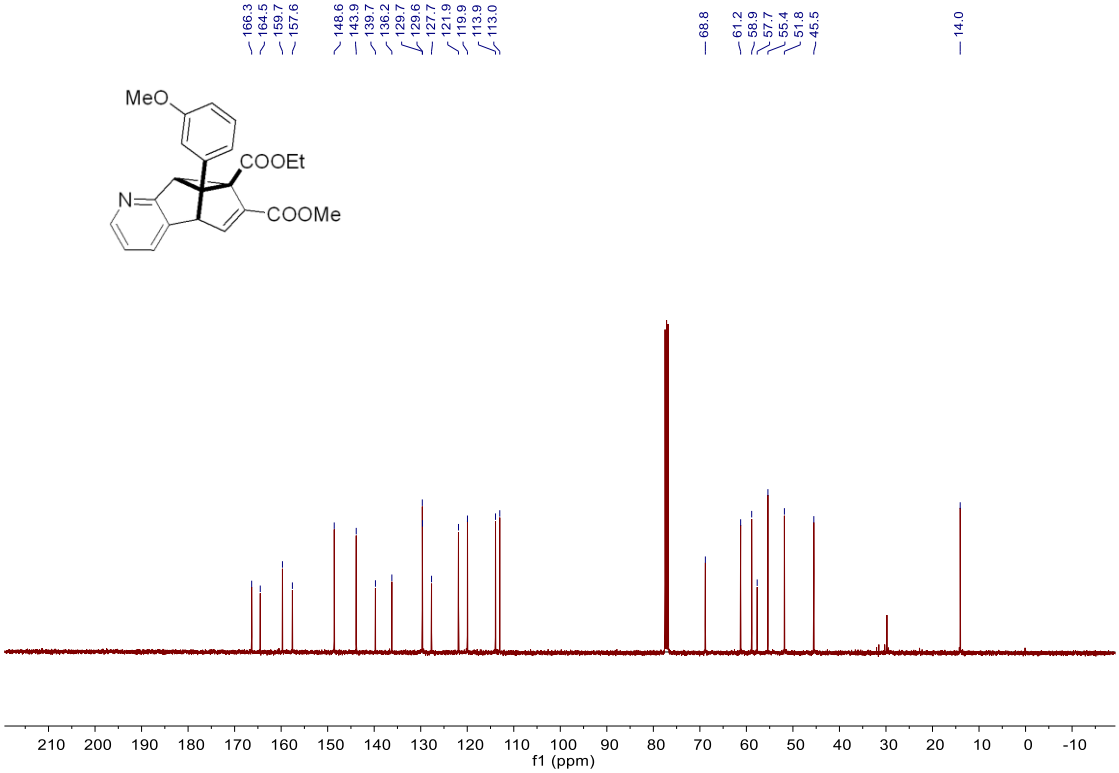
$^{13}$C NMR spectrum of **5ai**



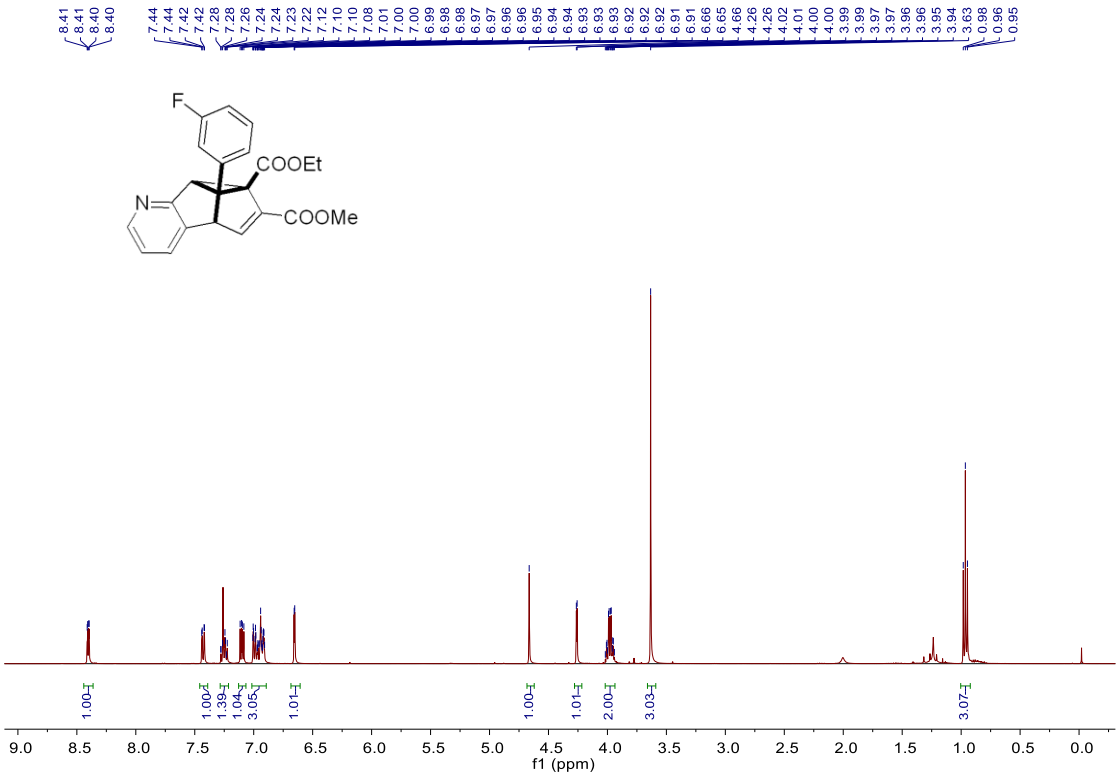

$^{1}$H NMR spectrum of **5aj**



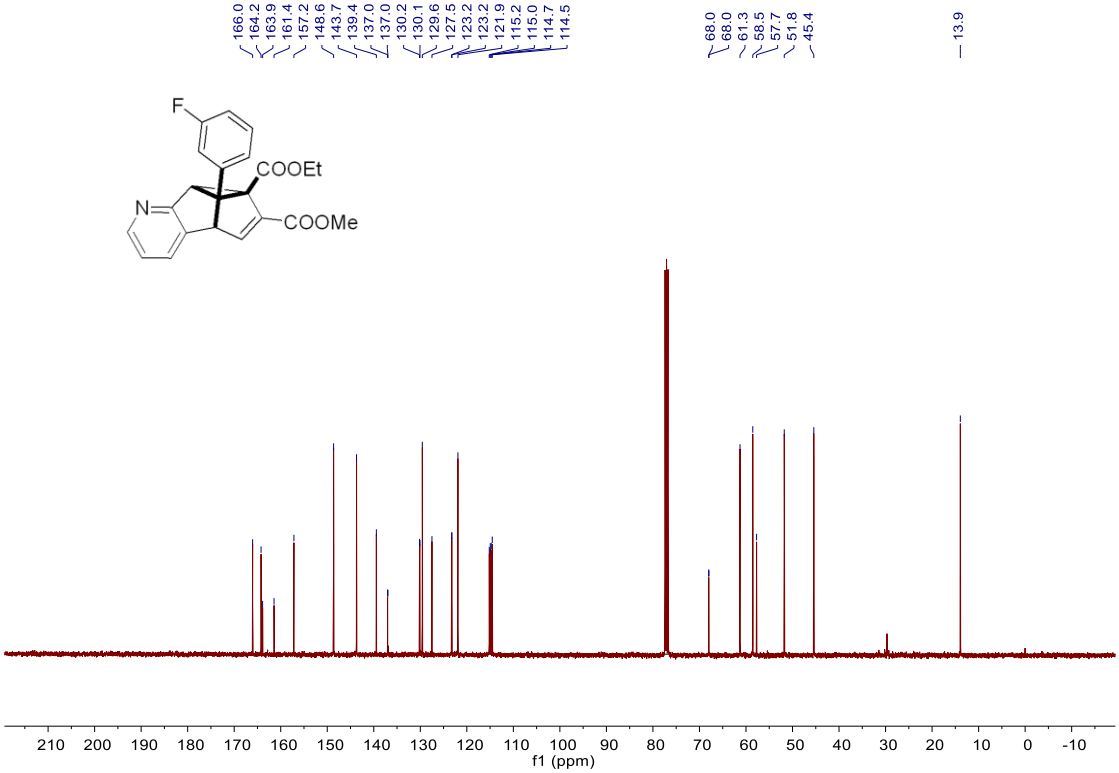
$^{13}$C NMR spectrum of **5aj**



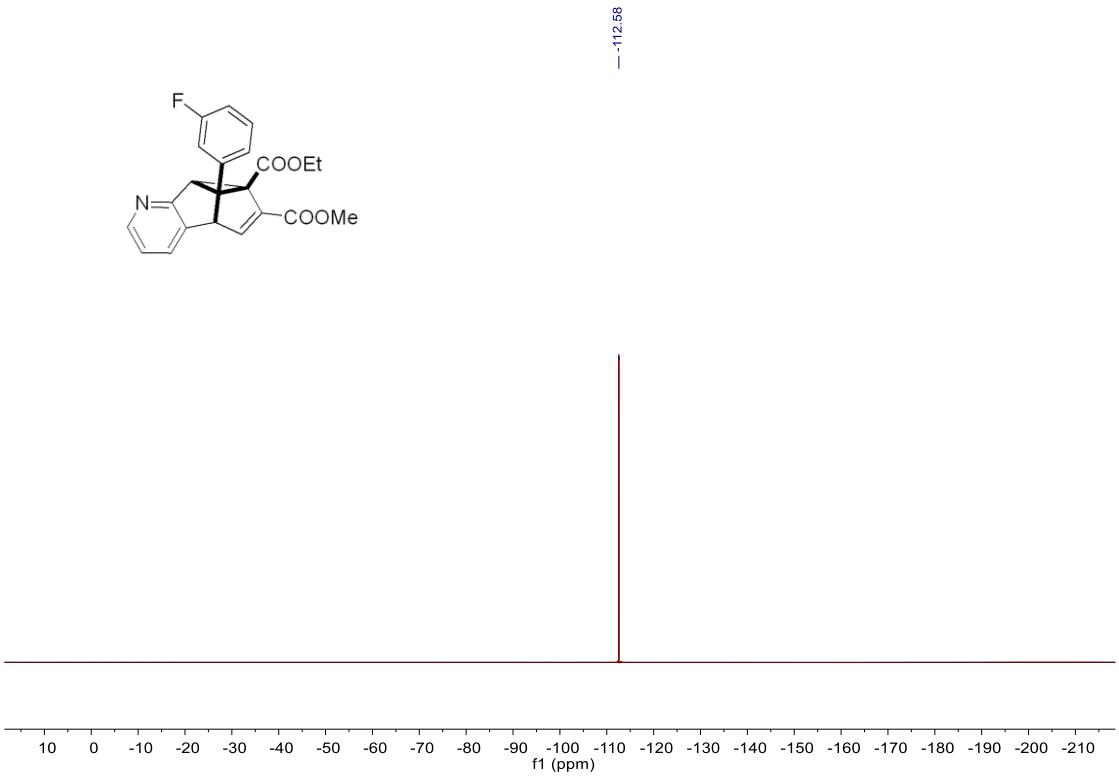

$^{1}$H NMR spectrum of **5ak**



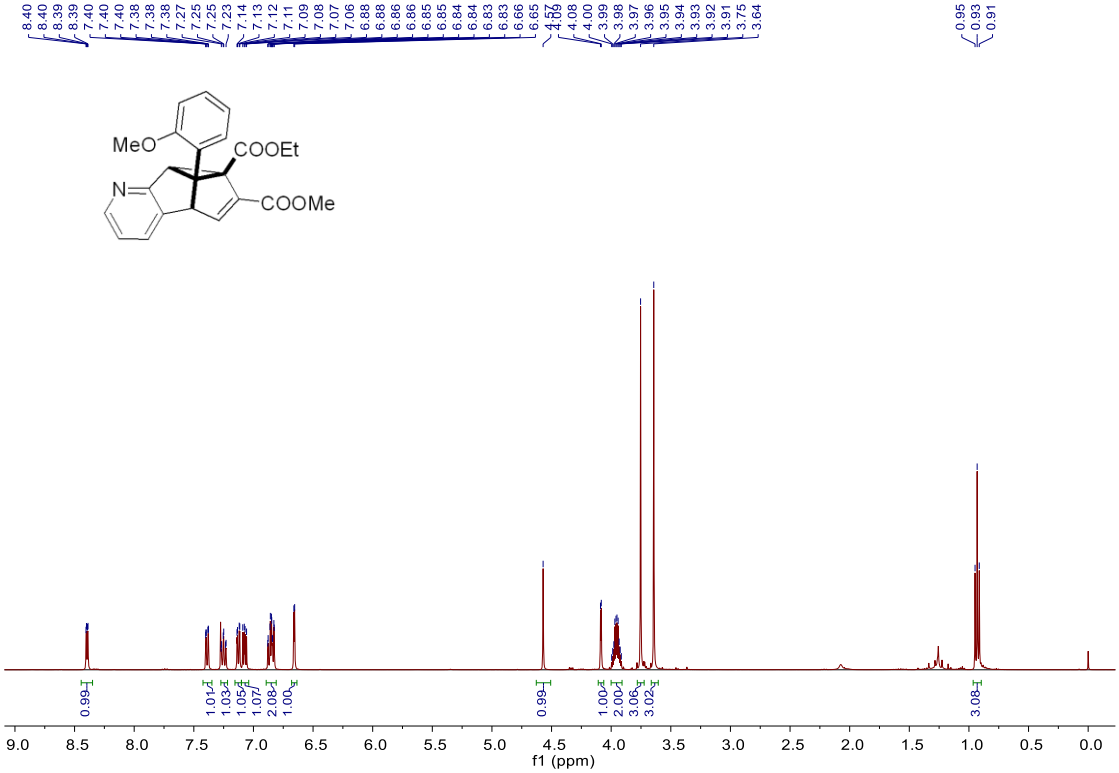
$^{13}$C NMR spectrum of **5ak**



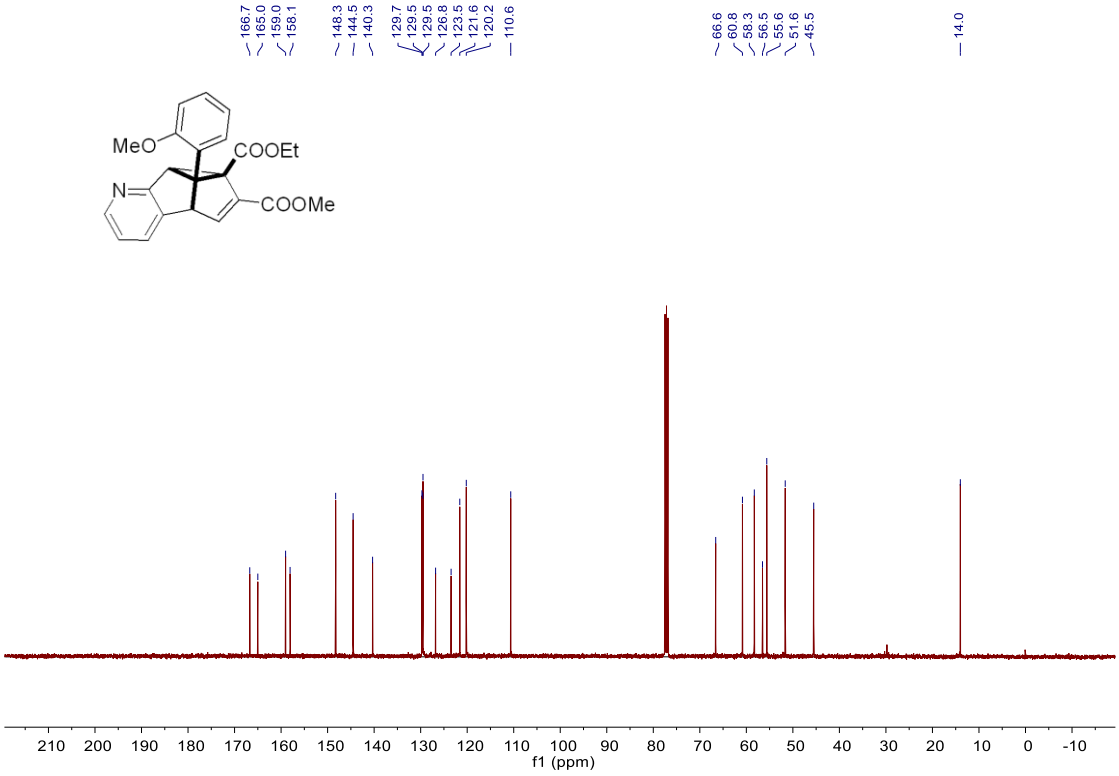

$^{19}$F NMR spectrum of **5ak**



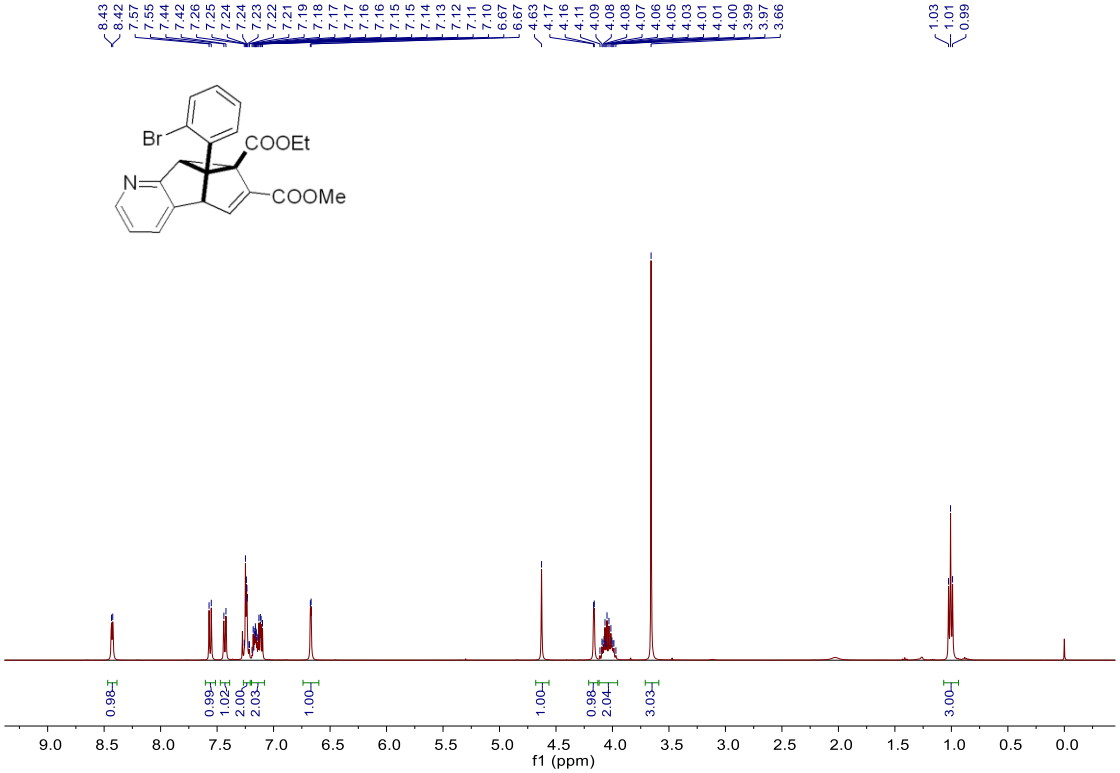
$^{1}$H NMR spectrum of **5al**



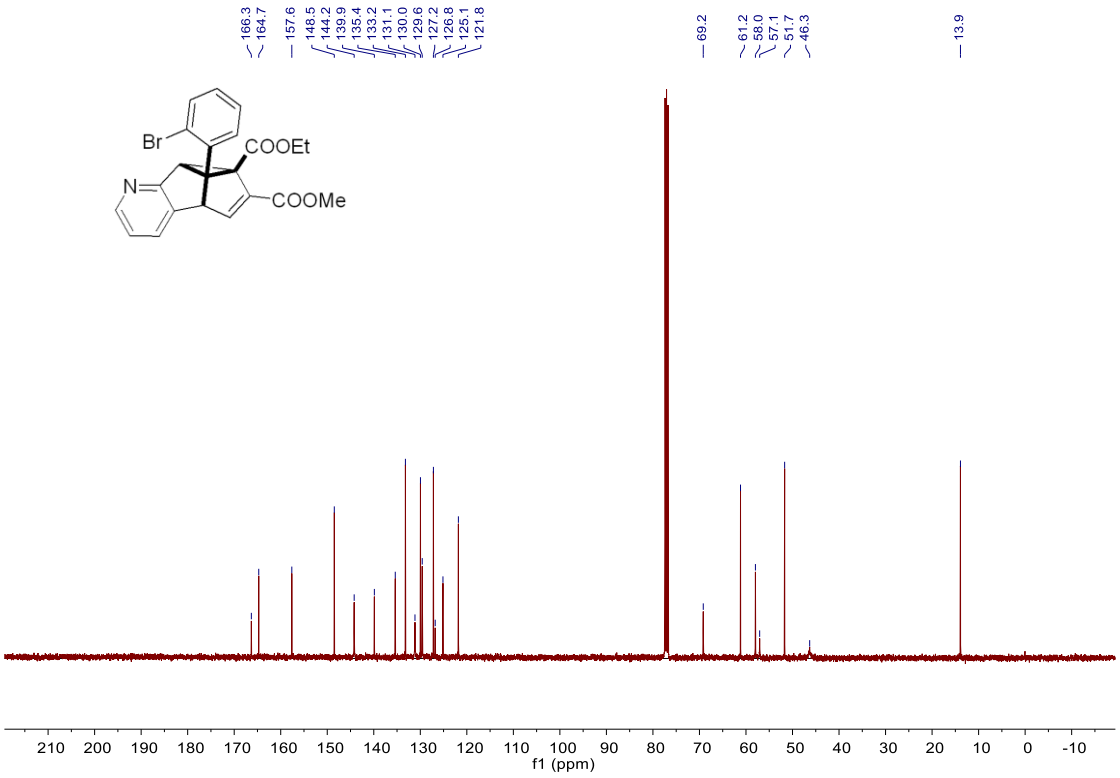

$^{13}$C NMR spectrum of **5al**



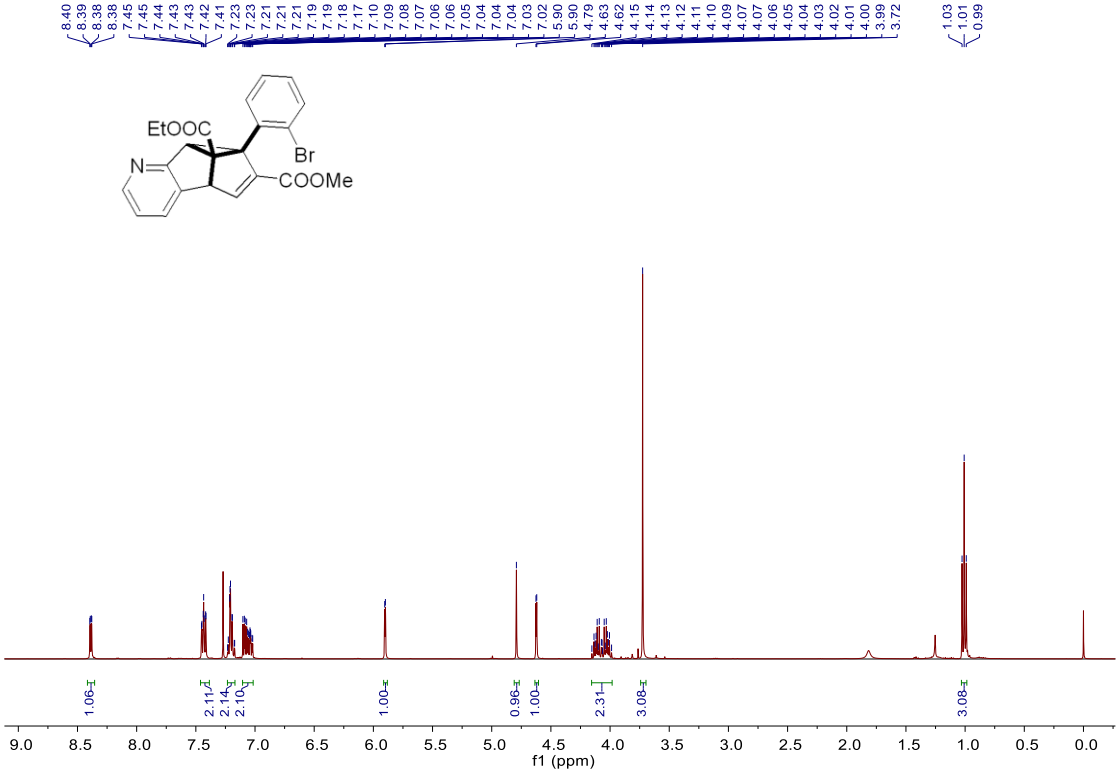
$^{1}$H NMR spectrum of **5am-1**



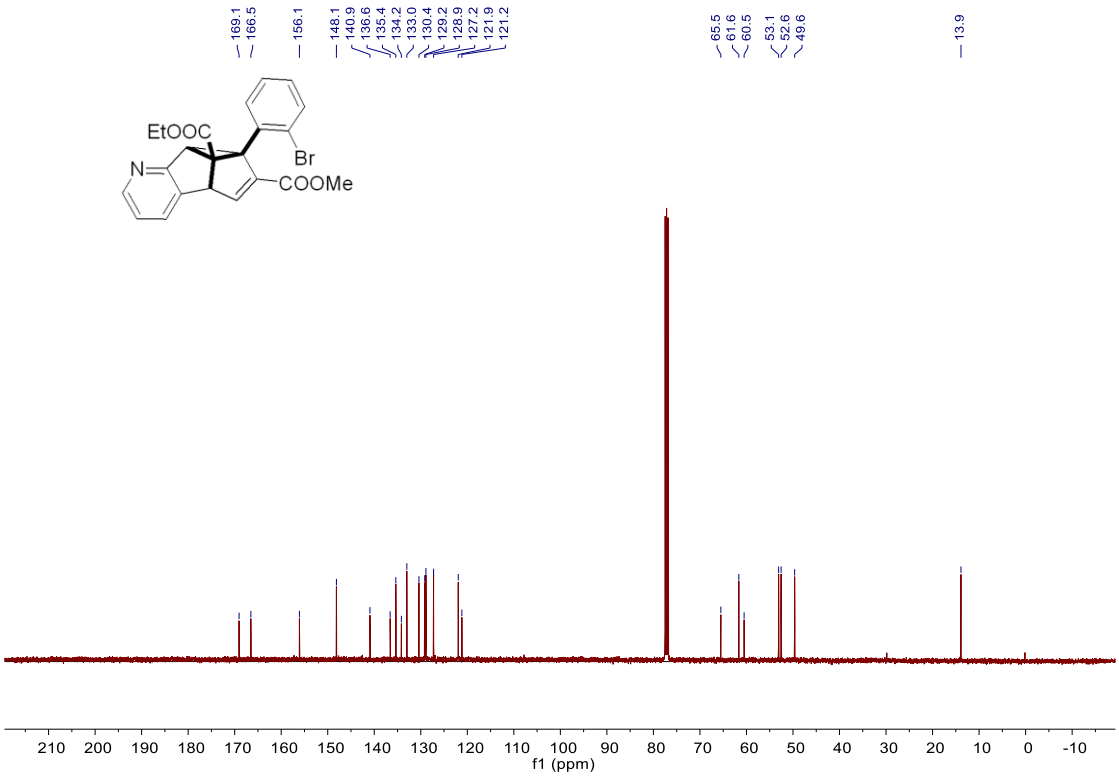

$^{13}$C NMR spectrum of **5am-1**



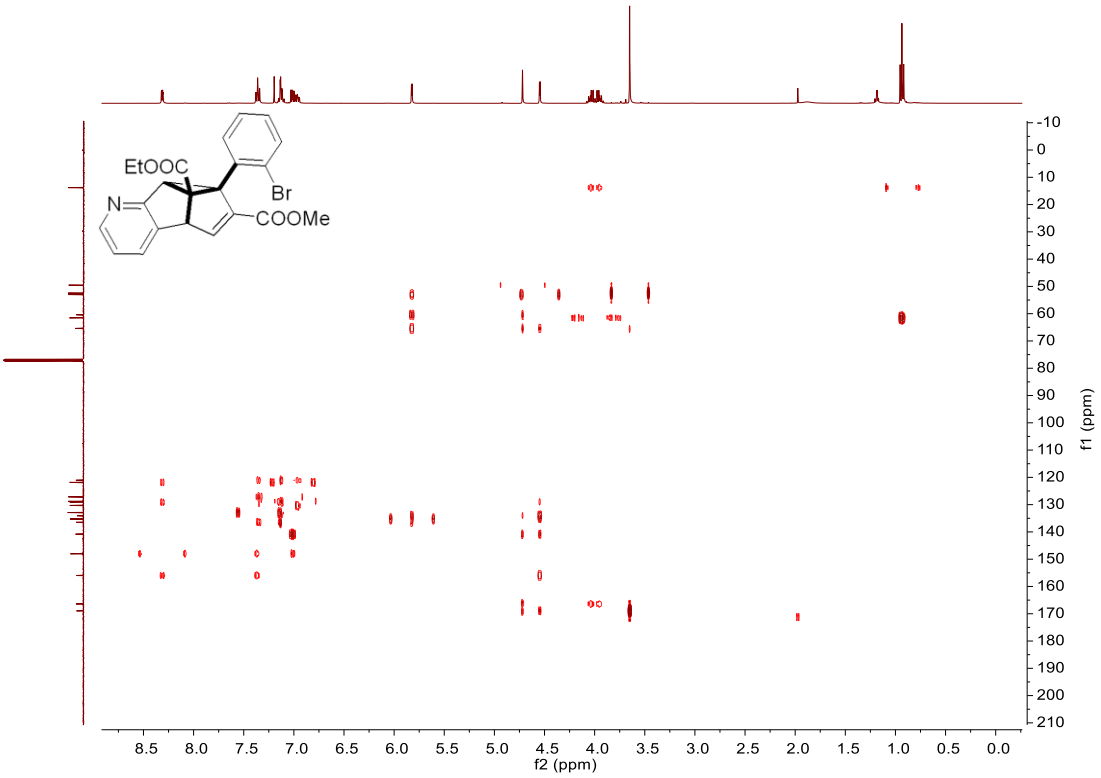
$^{1}$H NMR spectrum of **5am-2**



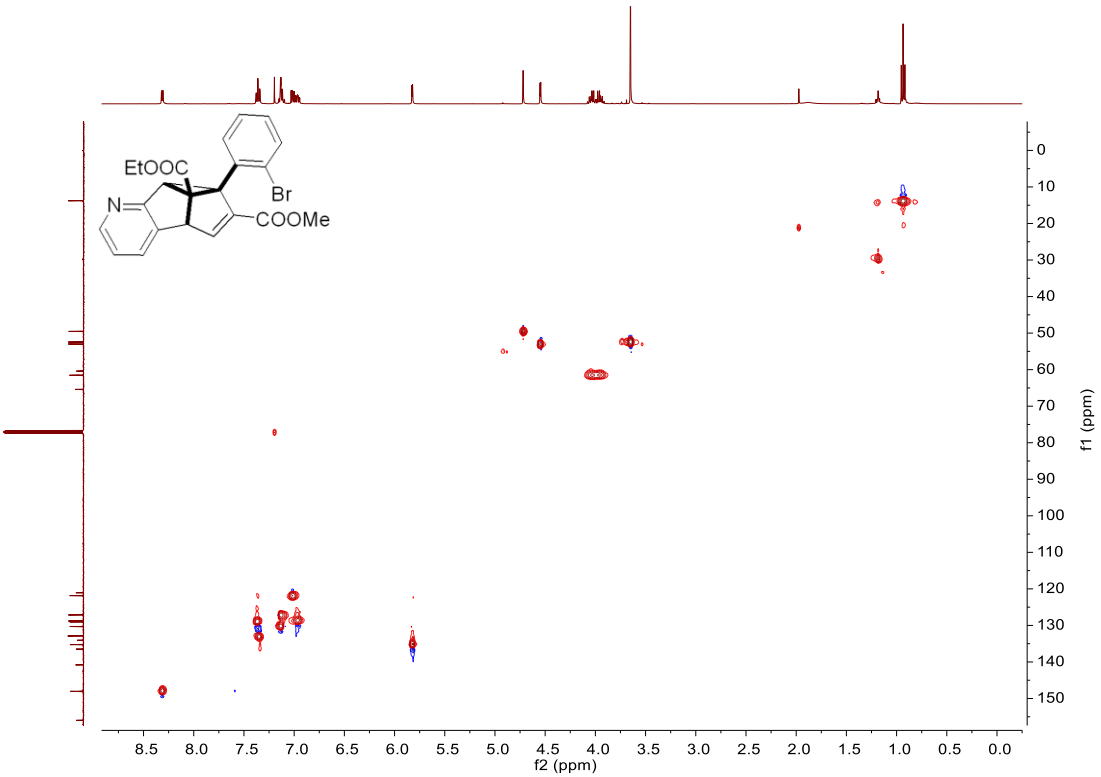

$^{13}$C NMR spectrum of **5am-2**



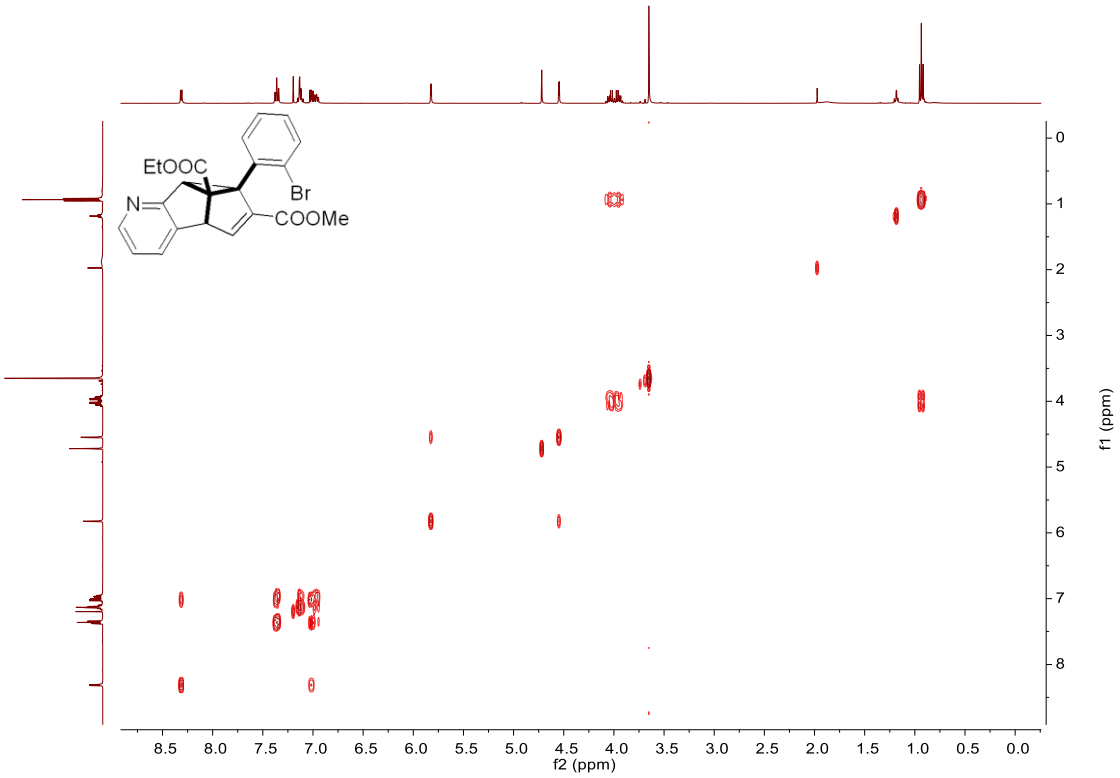
HMBC NMR spectrum of **5am-2**



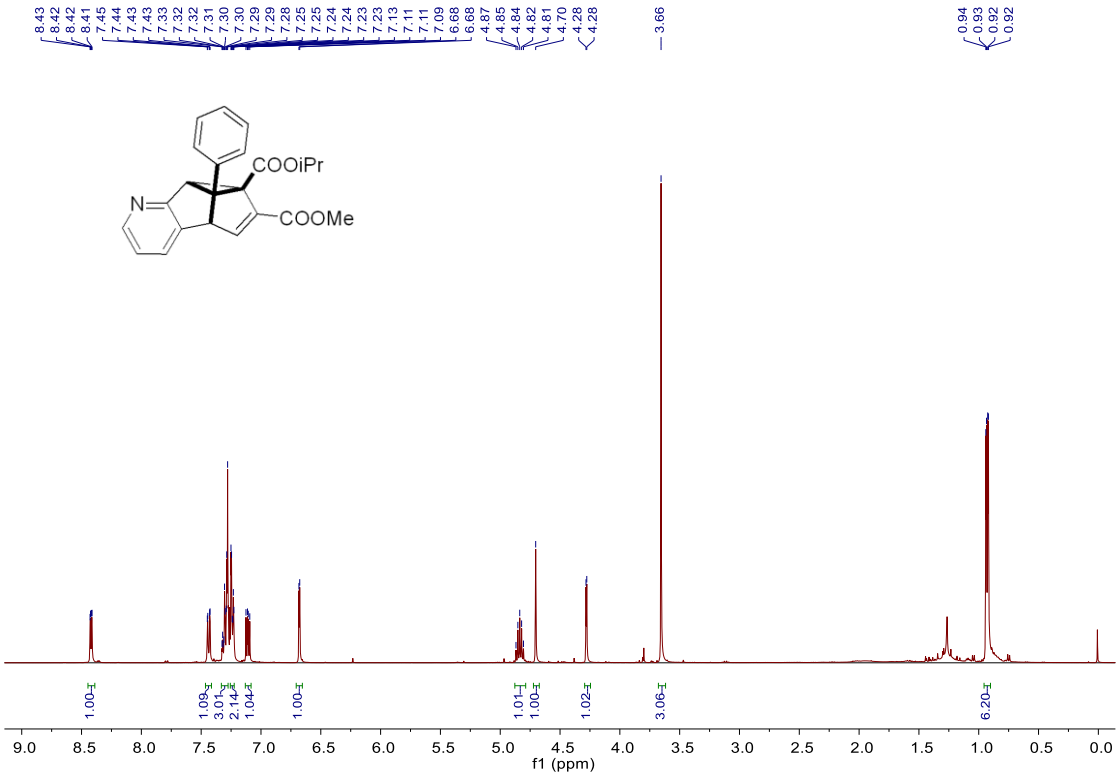

HSQC NMR spectrum of **5am-2**



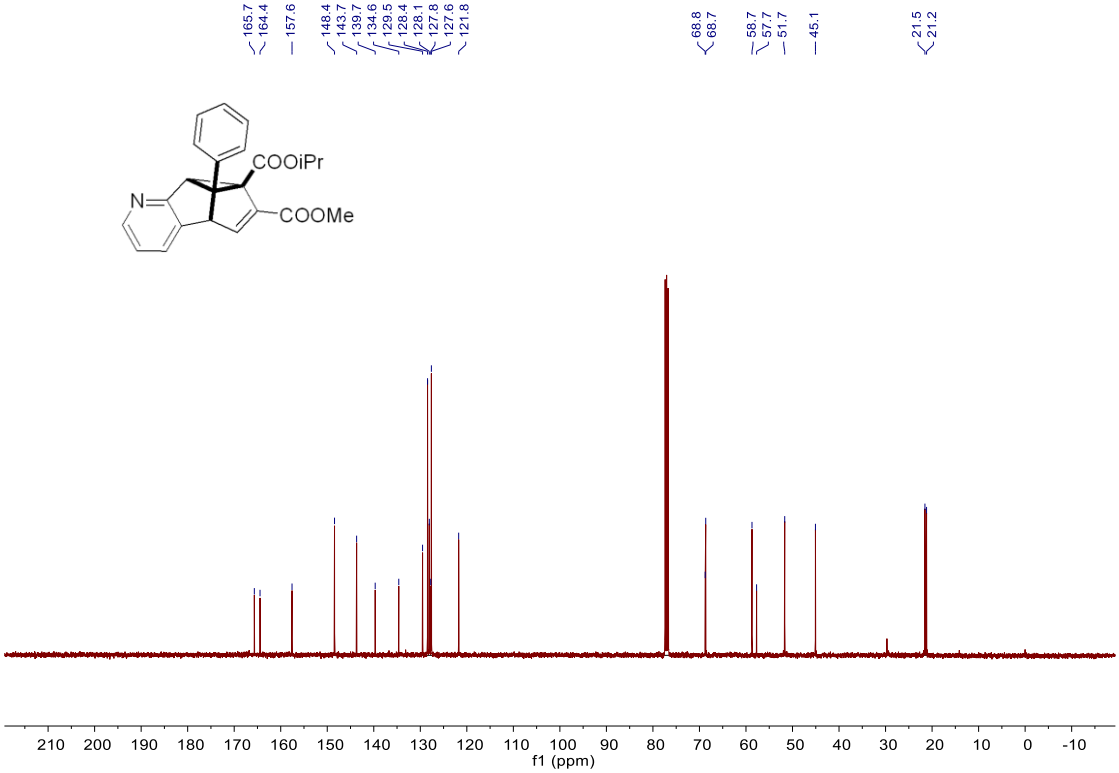
H-H COSY NMR spectrum of **5am-2**



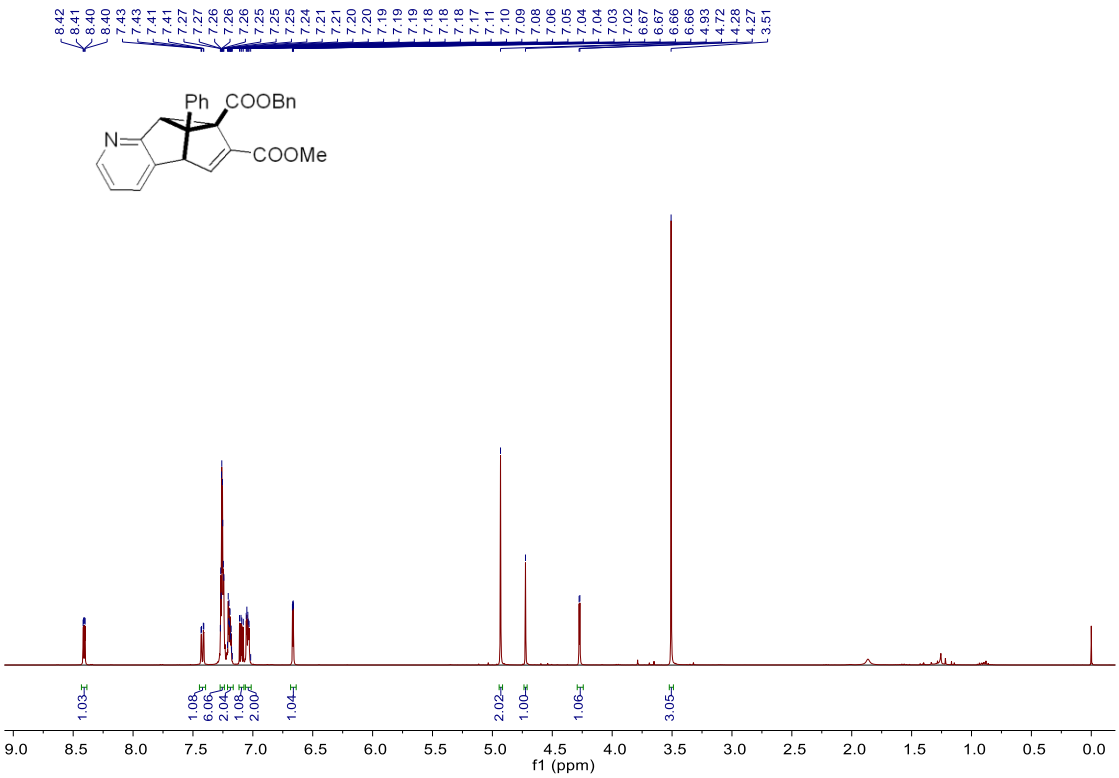

$^{1}$H NMR spectrum of **5an**



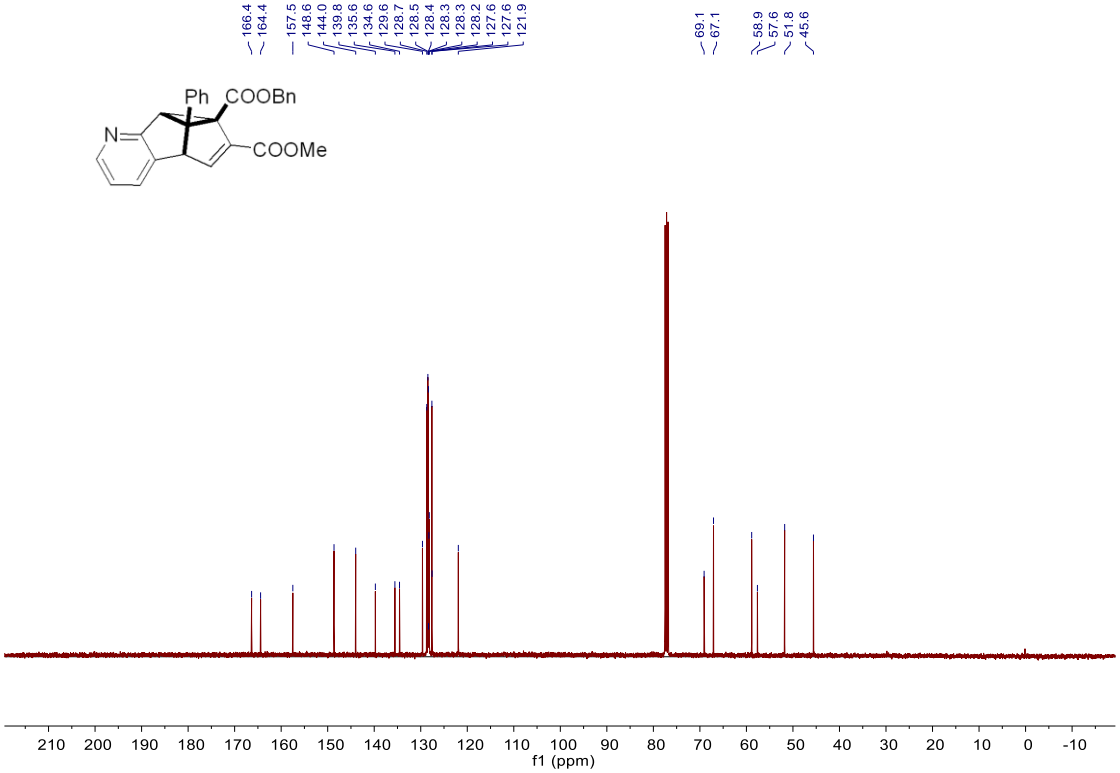
$^{13}$C NMR spectrum of **5an**



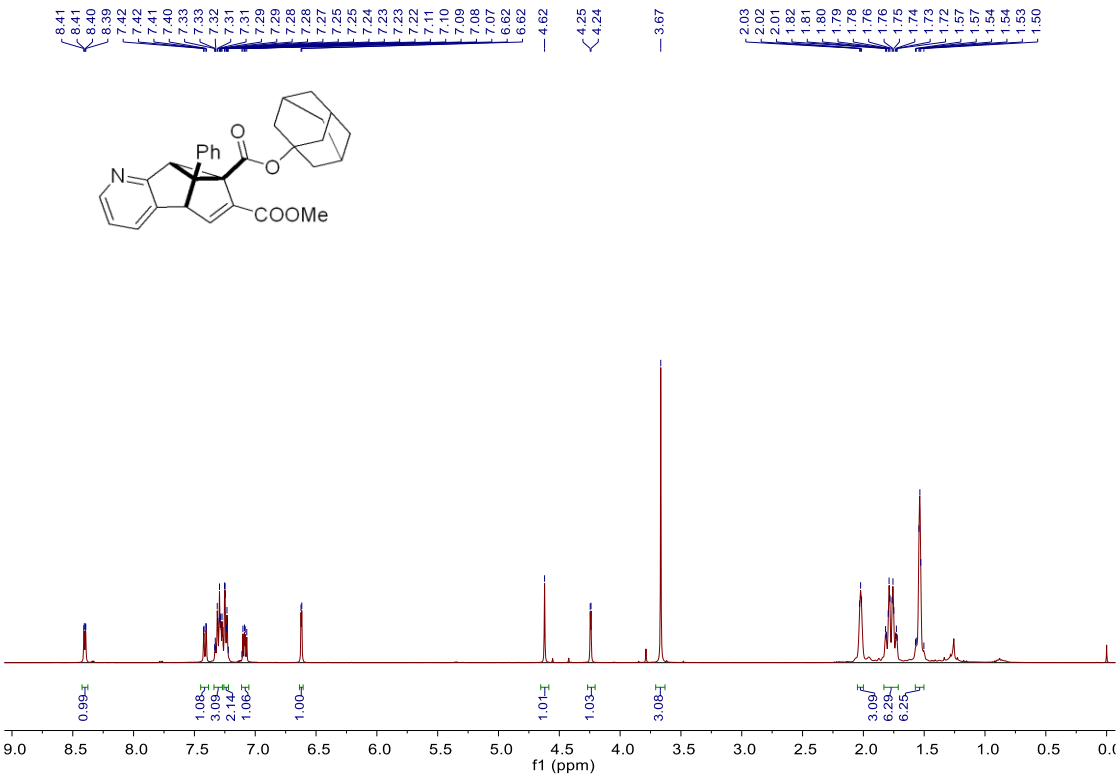

$^{1}$H NMR spectrum of **5ao**



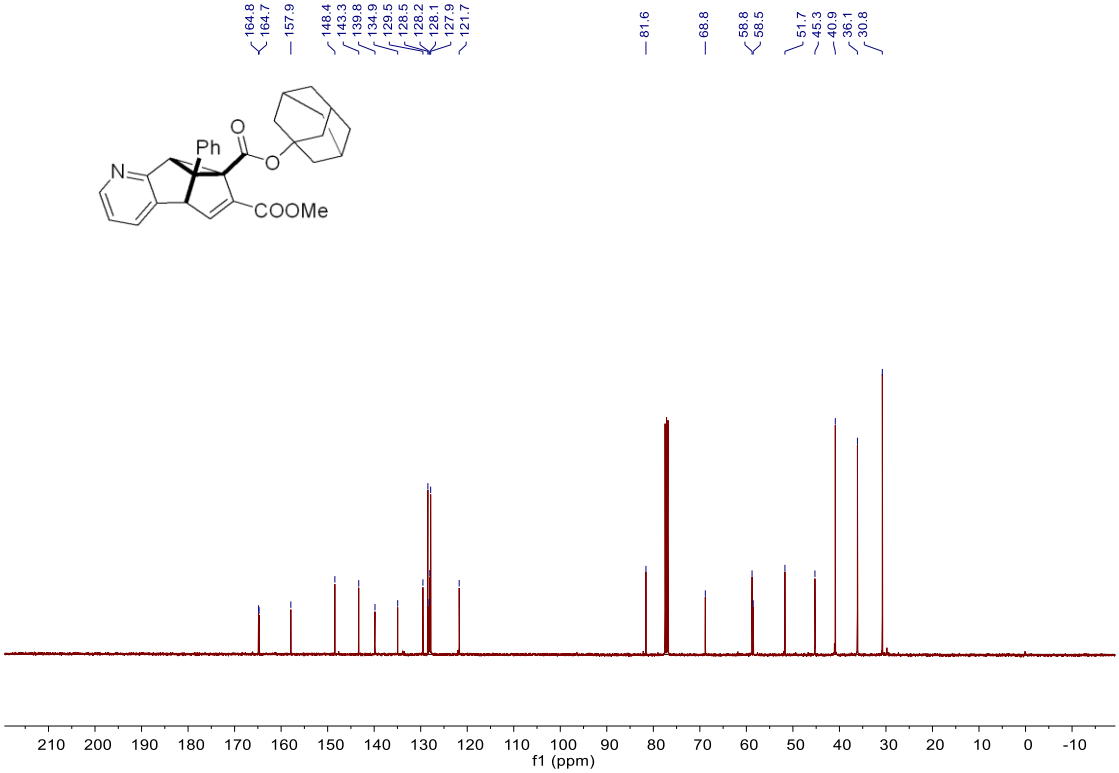
$^{13}$C NMR spectrum of **5ao**



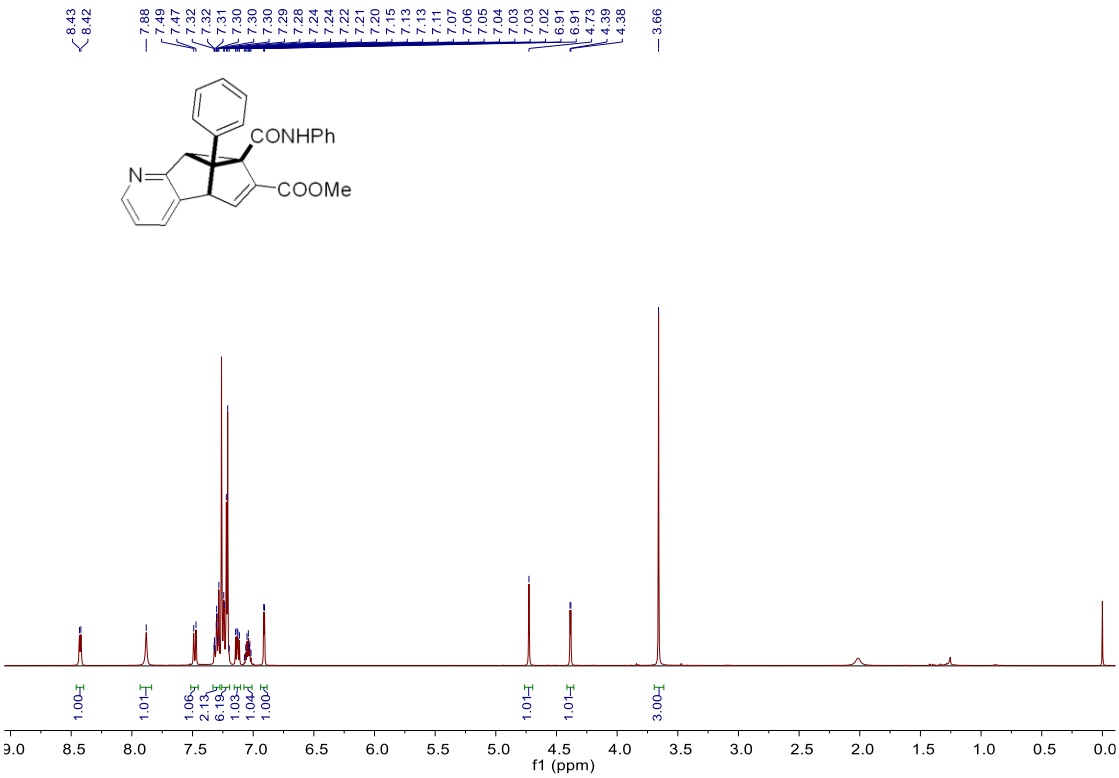

$^{1}$H NMR spectrum of **5ap**



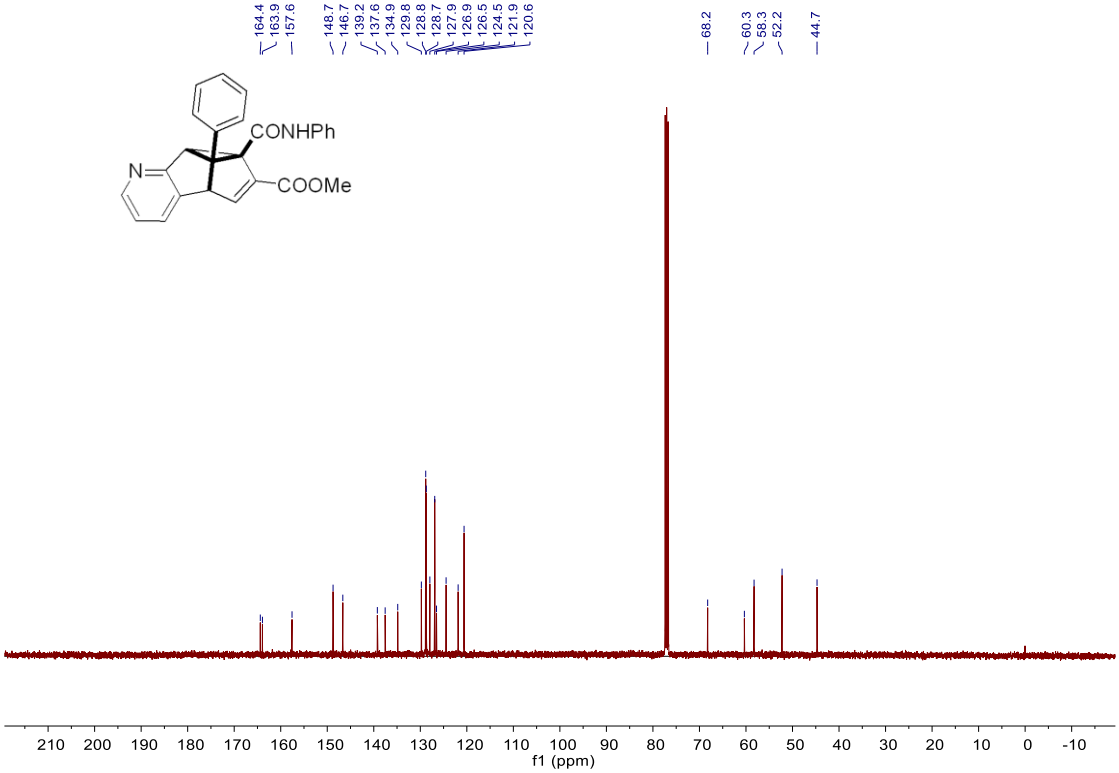
$^{13}$C NMR spectrum of **5ap**



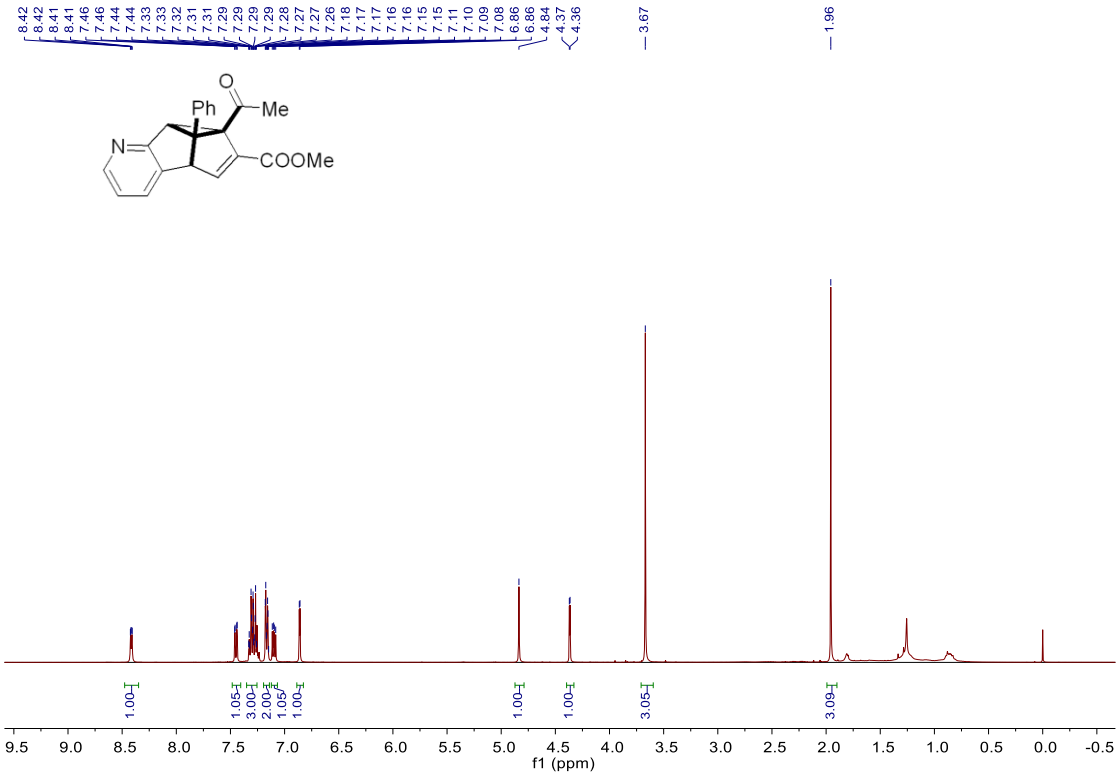

$^{1}$H NMR spectrum of **5aq**



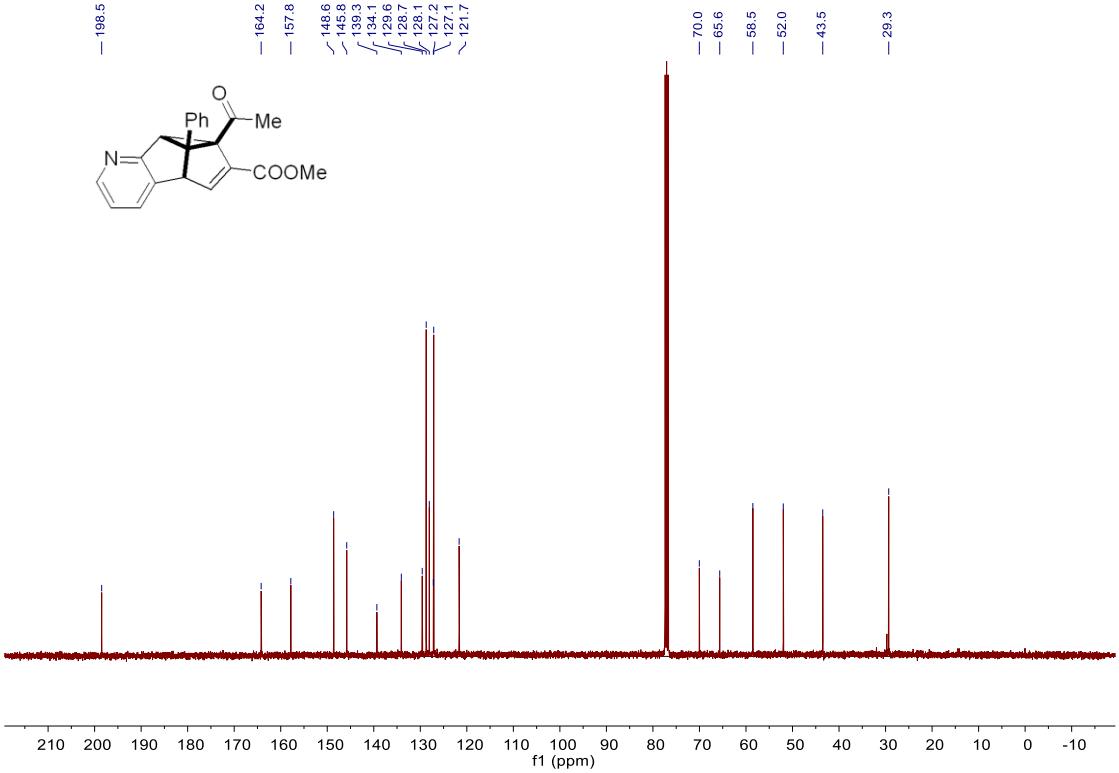
$^{13}$C NMR spectrum of **5aq**



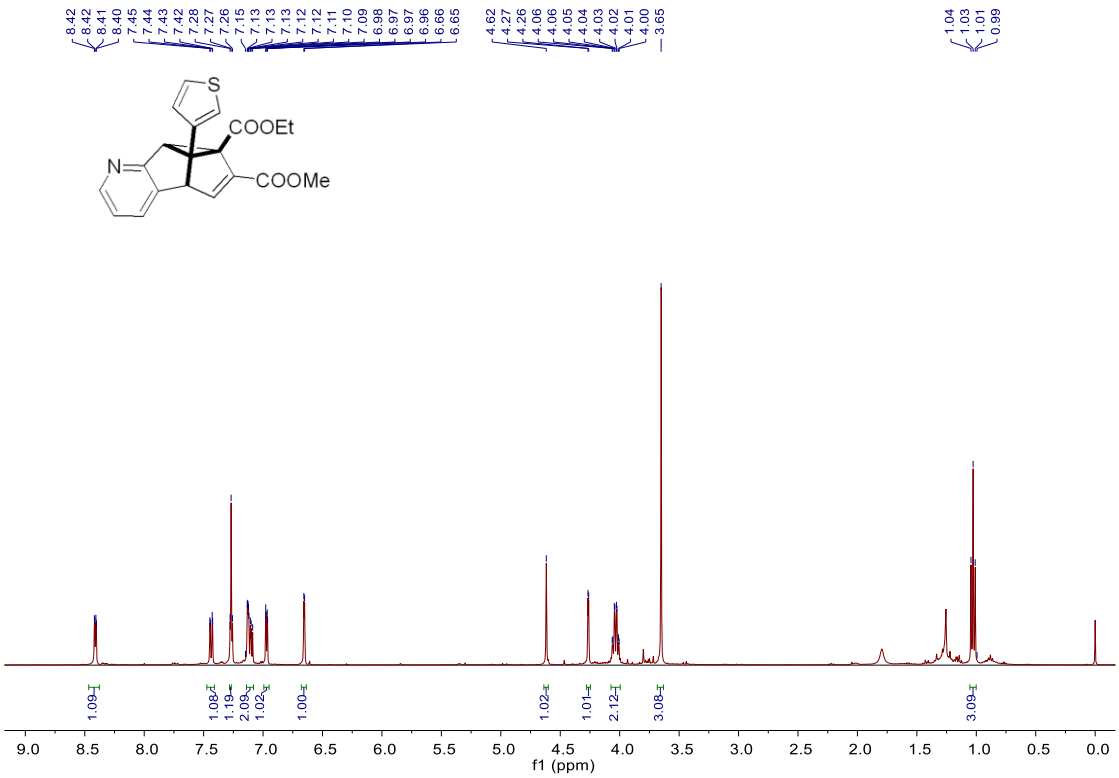

$^{1}$H NMR spectrum of **5ar**



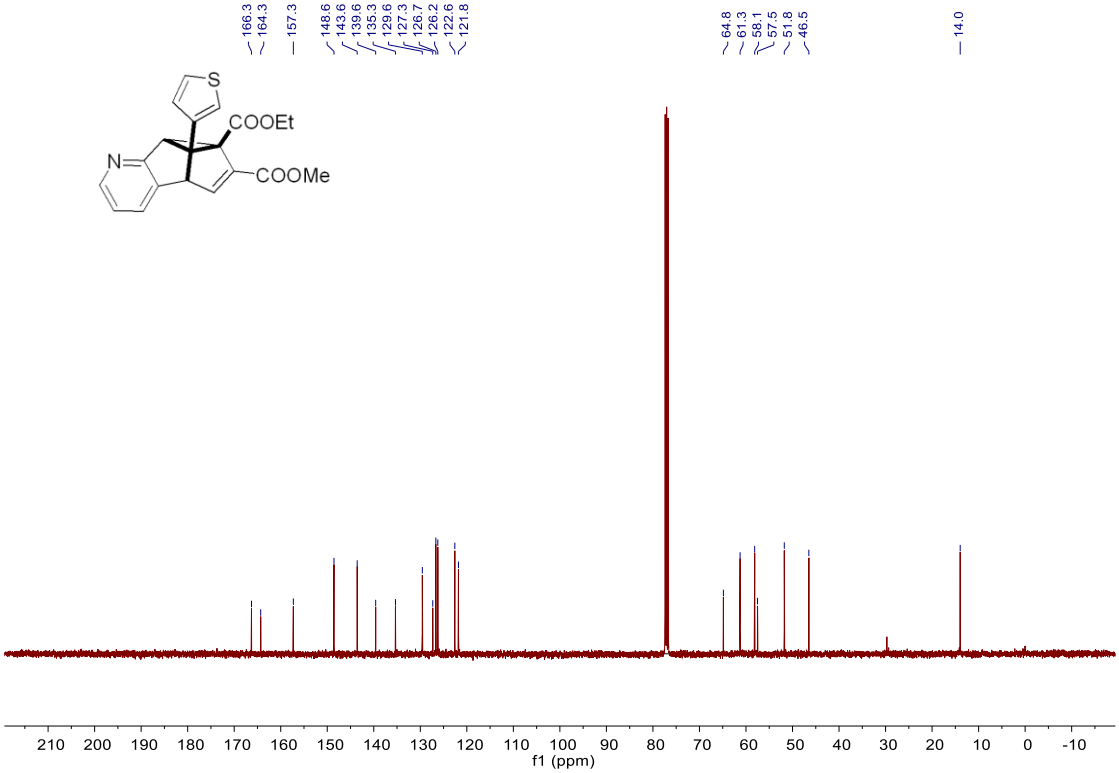
$^{13}$C NMR spectrum of **5ar**



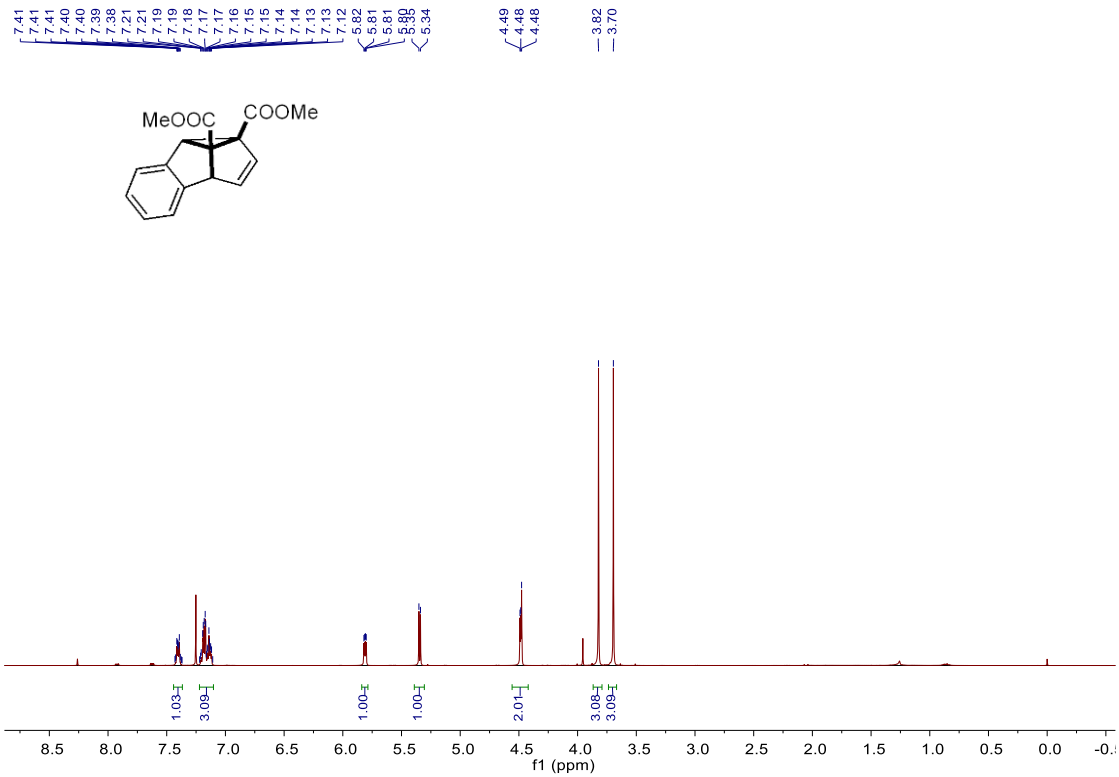

$^{1}$H NMR spectrum of **5as**



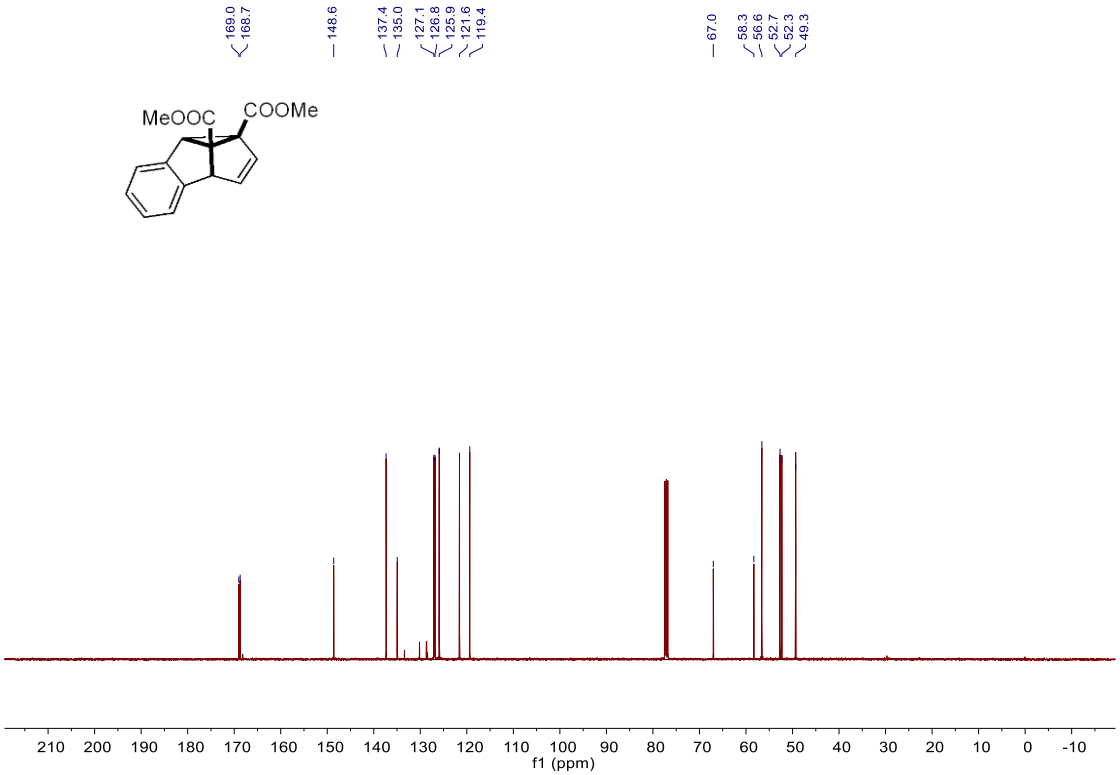
$^{13}$C NMR spectrum of **5as**




$^{1}$H NMR spectrum of **dimethyl 2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2a,2a$^{1}$-dicarboxylate**

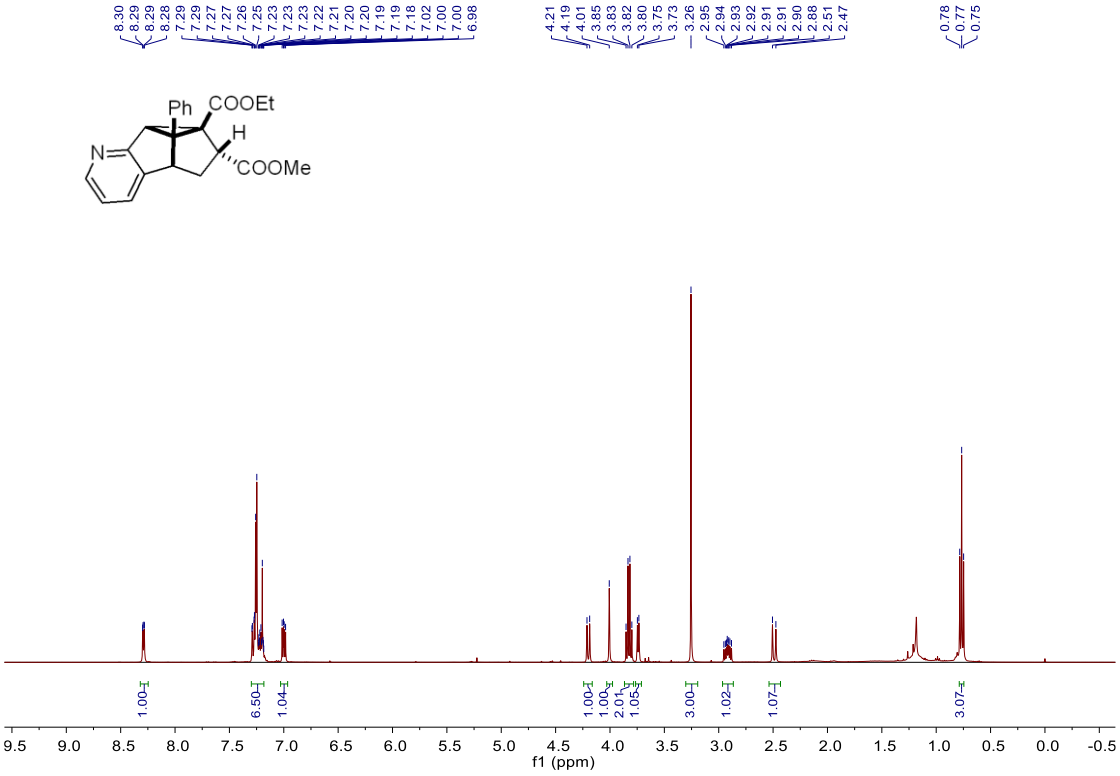


$^{13}$C NMR spectrum of **dimethyl 2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2a,2a$^{1}$-dicarboxylate**

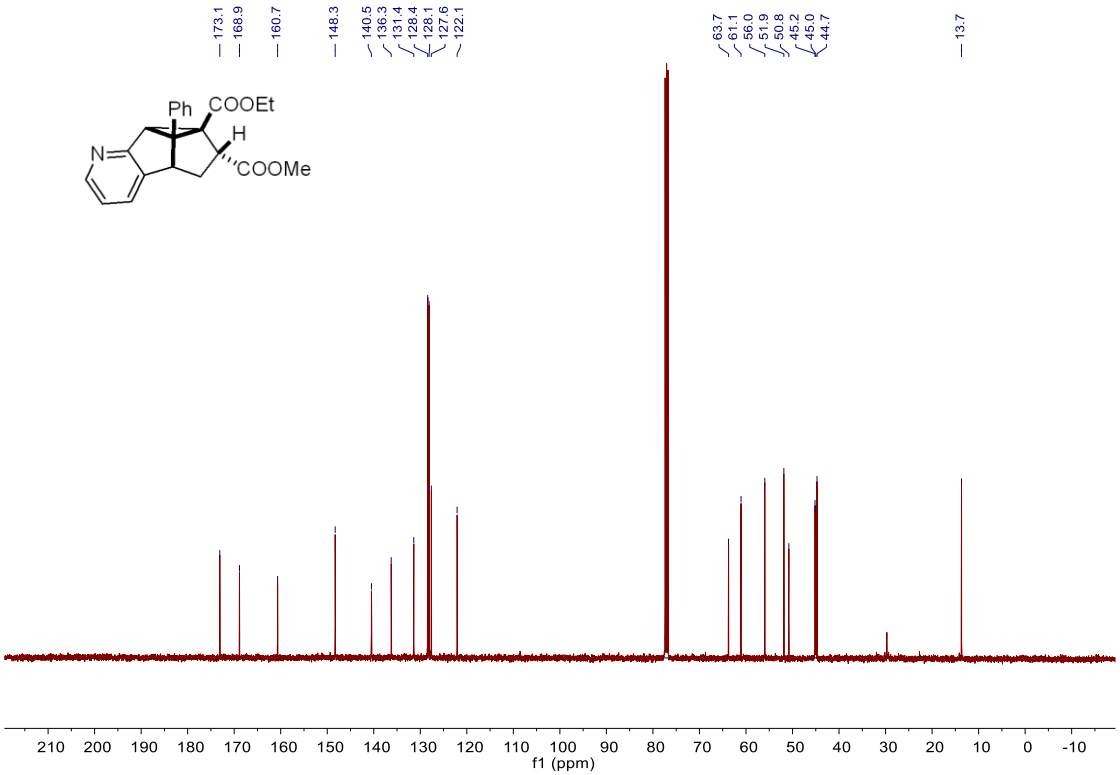


## 12. Copies of NMR spectra for the application and characterization products

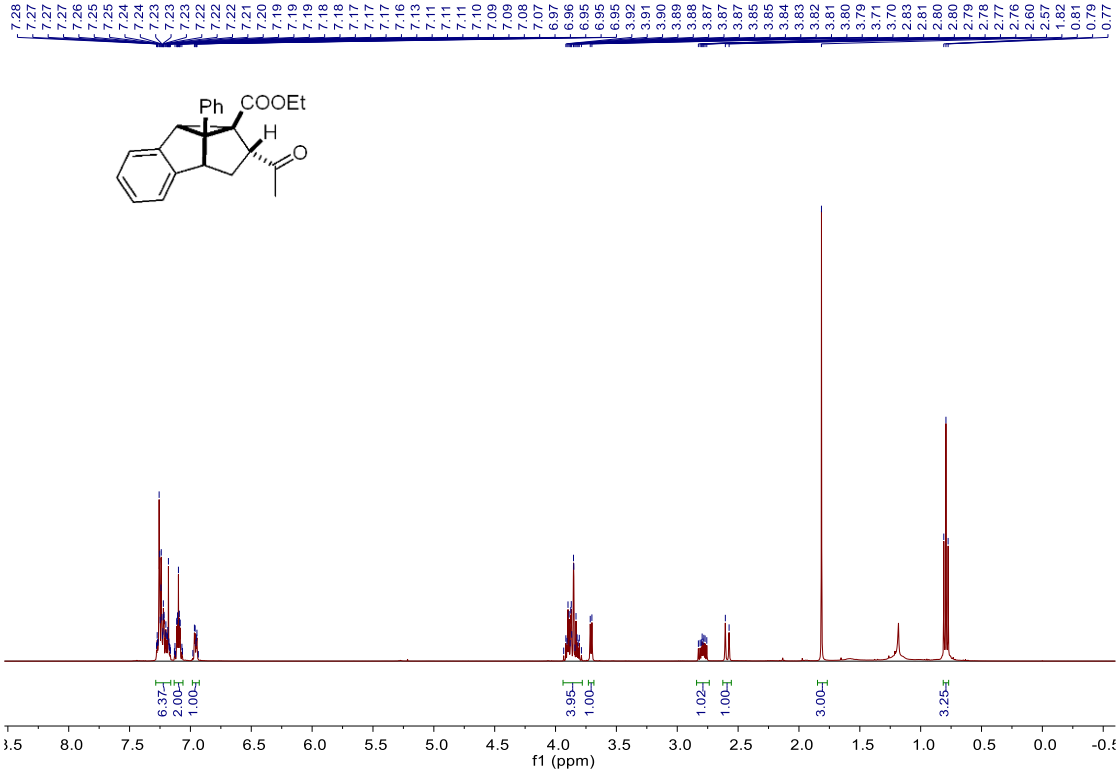
$^{1}$H NMR spectrum of **5aa-d**



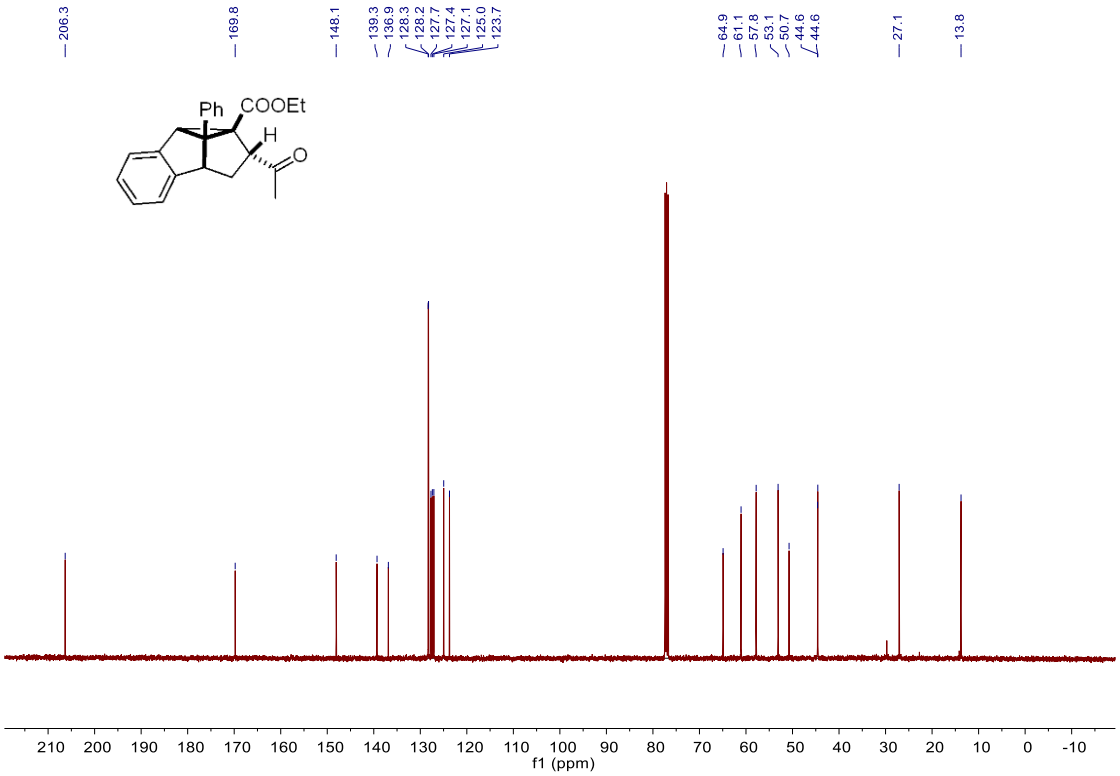

$^{13}$C NMR spectrum of **5aa-d**



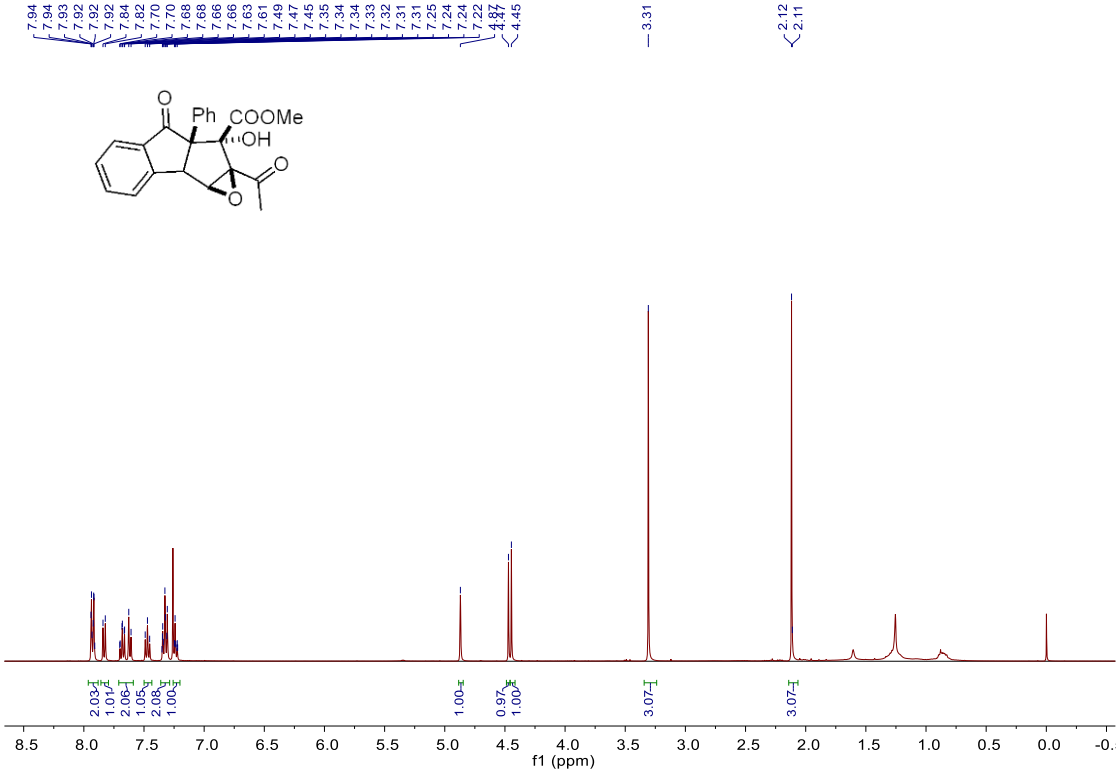
$^{1}$H NMR spectrum of **3fa-a**



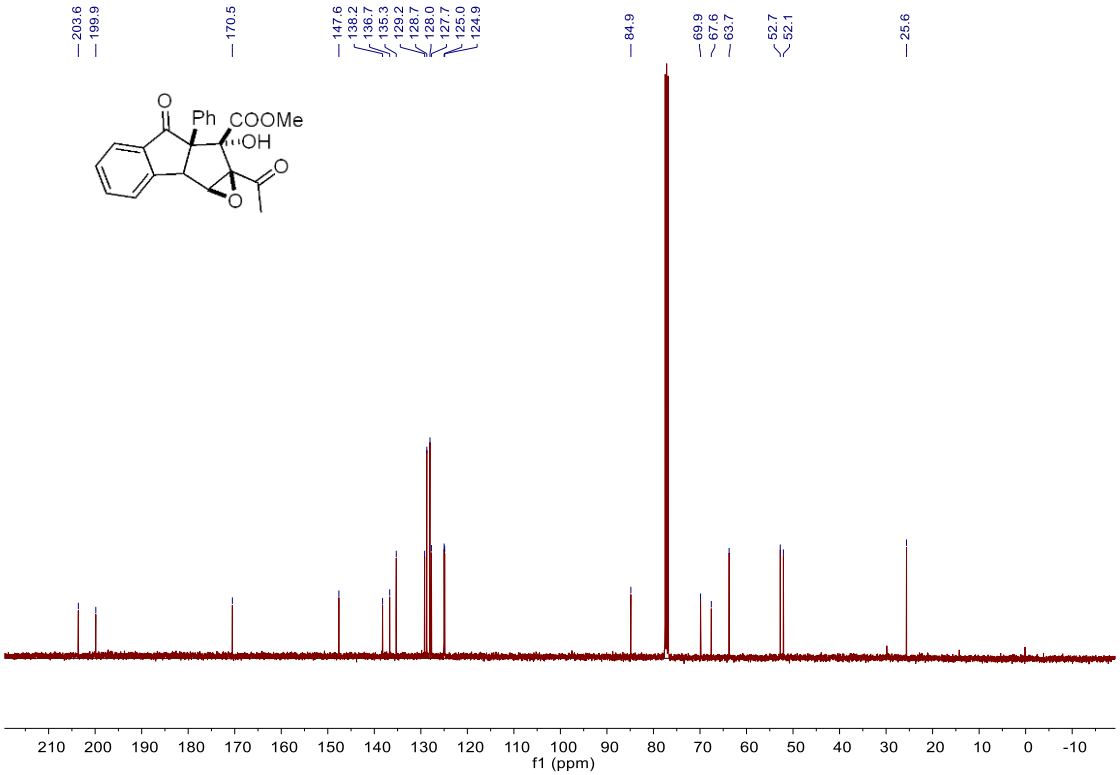

$^{13}$C NMR spectrum of **3fa-a**



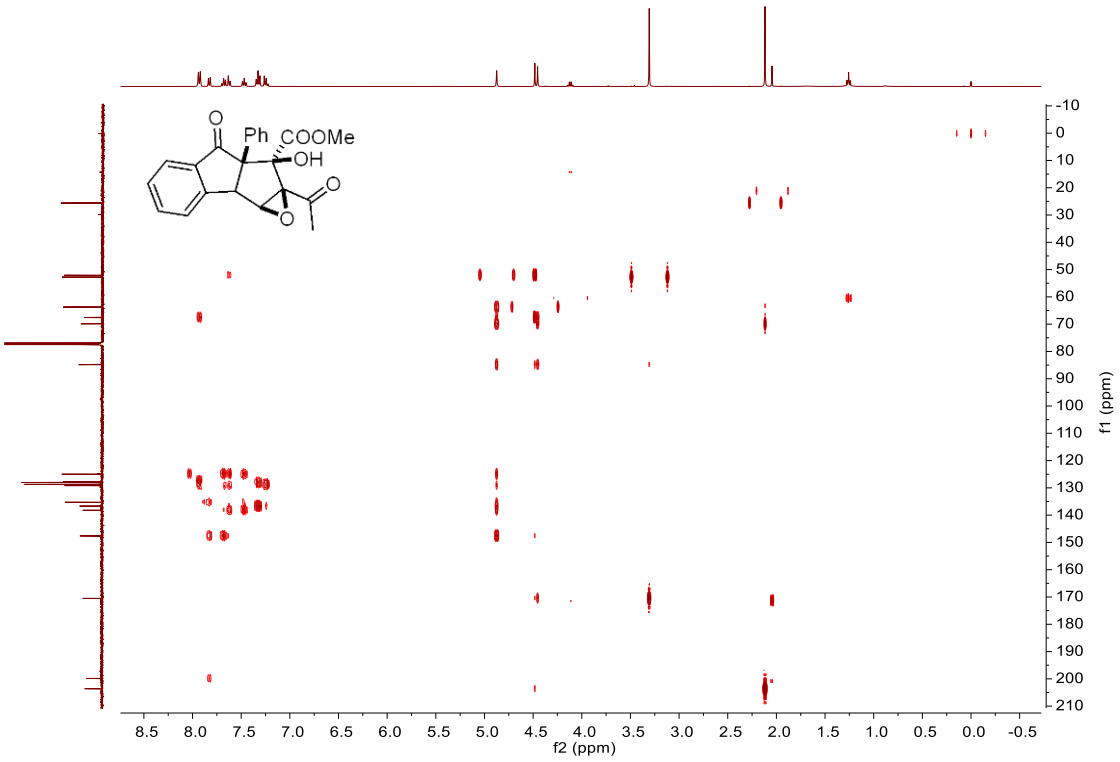
$^{1}$H NMR spectrum of **3fb-a**



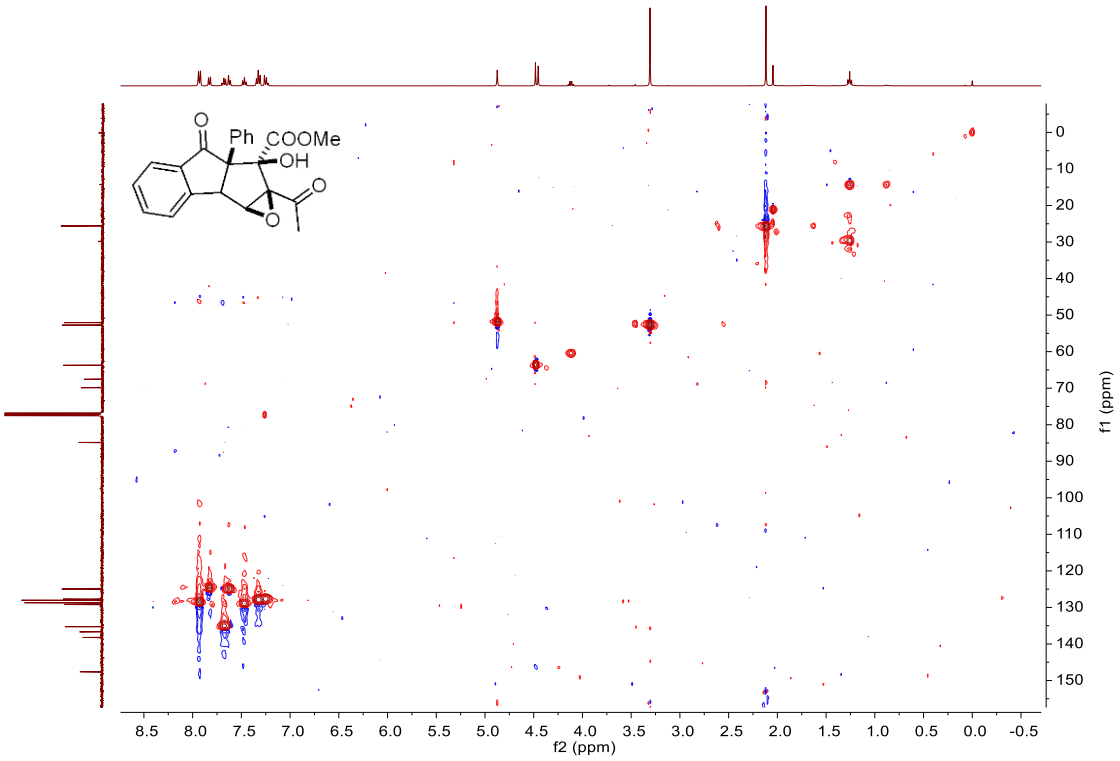

$^{13}$C NMR spectrum of **3fb-a**



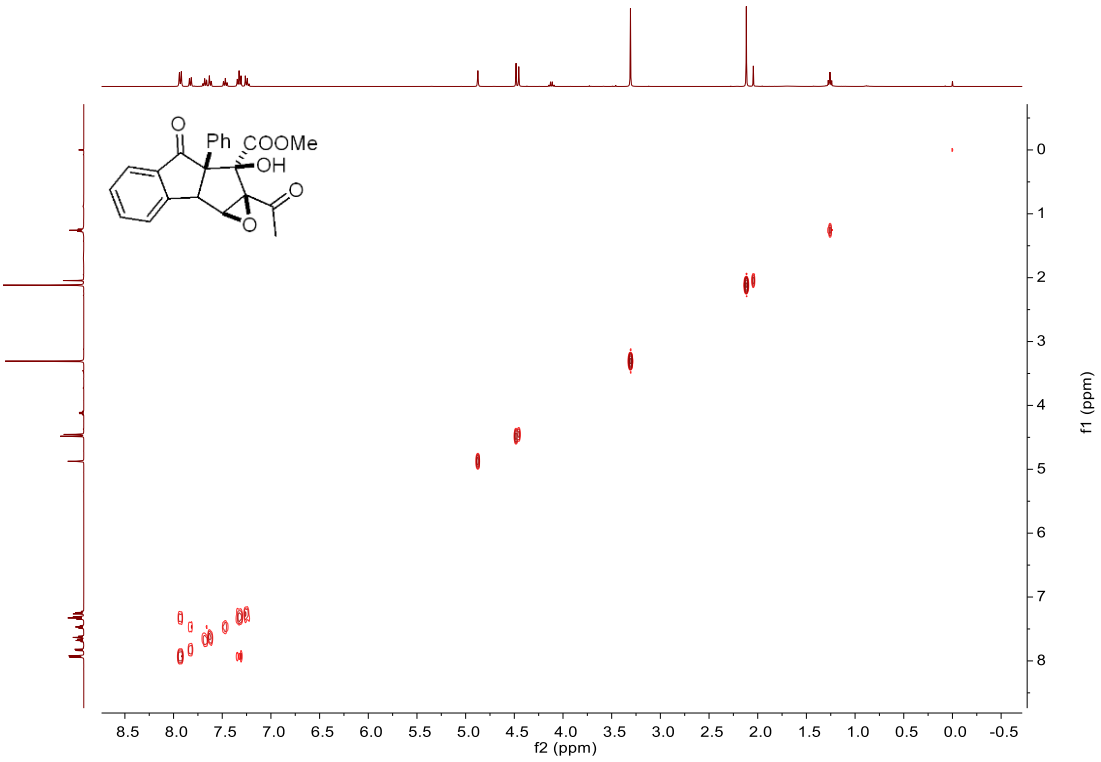
HMBC NMR spectrum of **3fb-a**



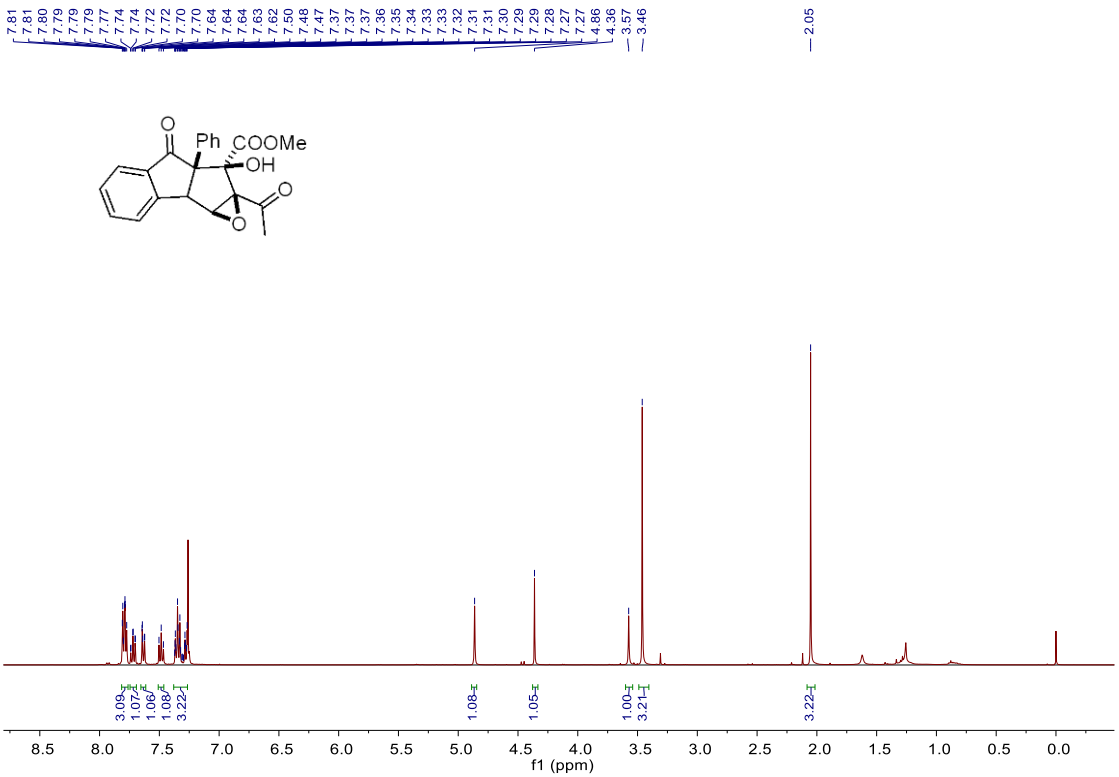

HSQC NMR spectrum of **3fb-a**



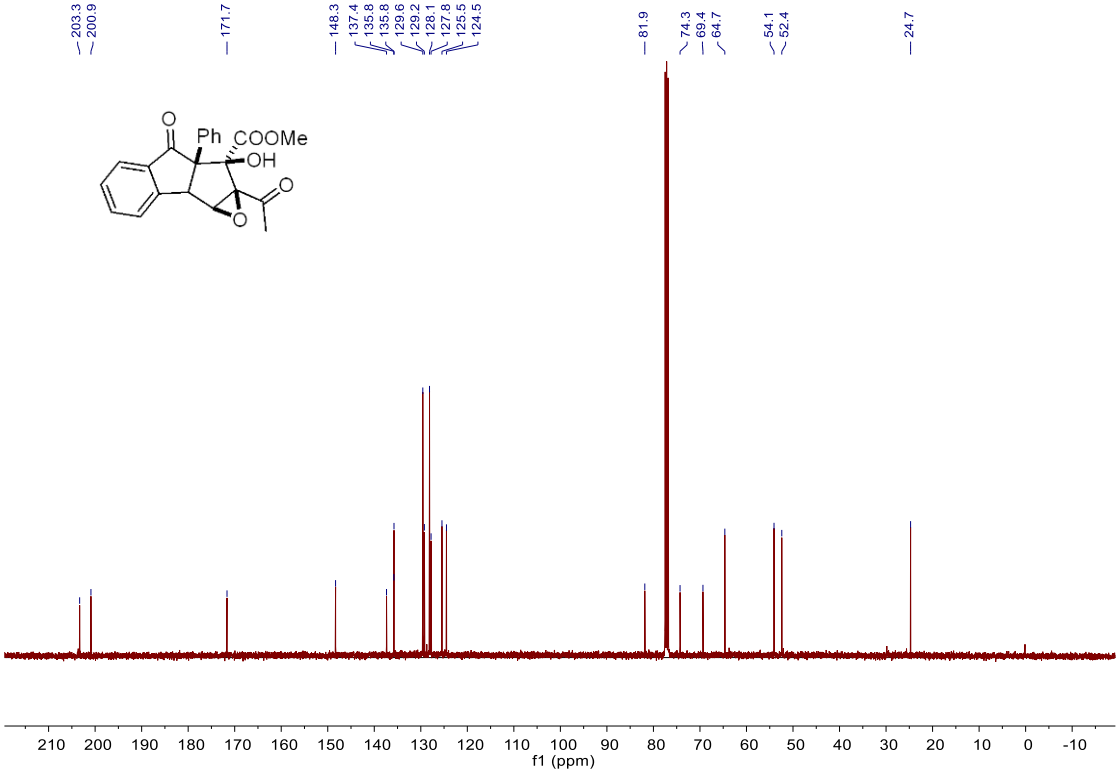
H-H COSY NMR spectrum of **3fb-a**



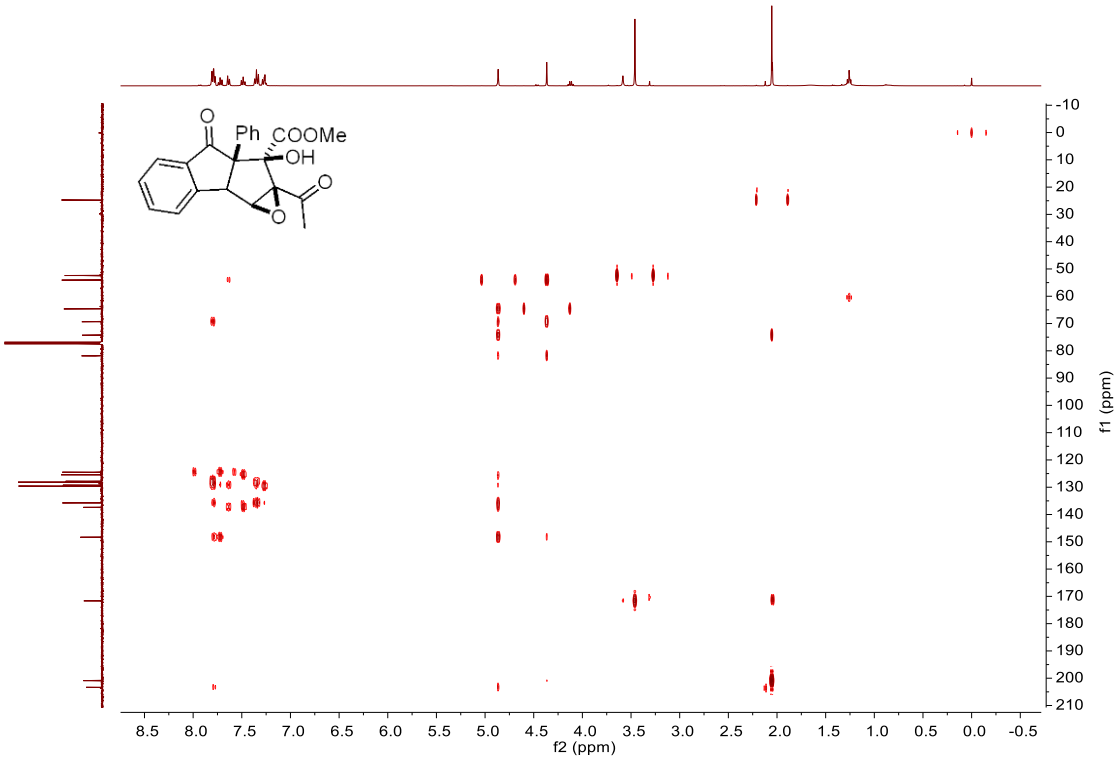

$^{1}$H NMR spectrum of **3fb-a´**



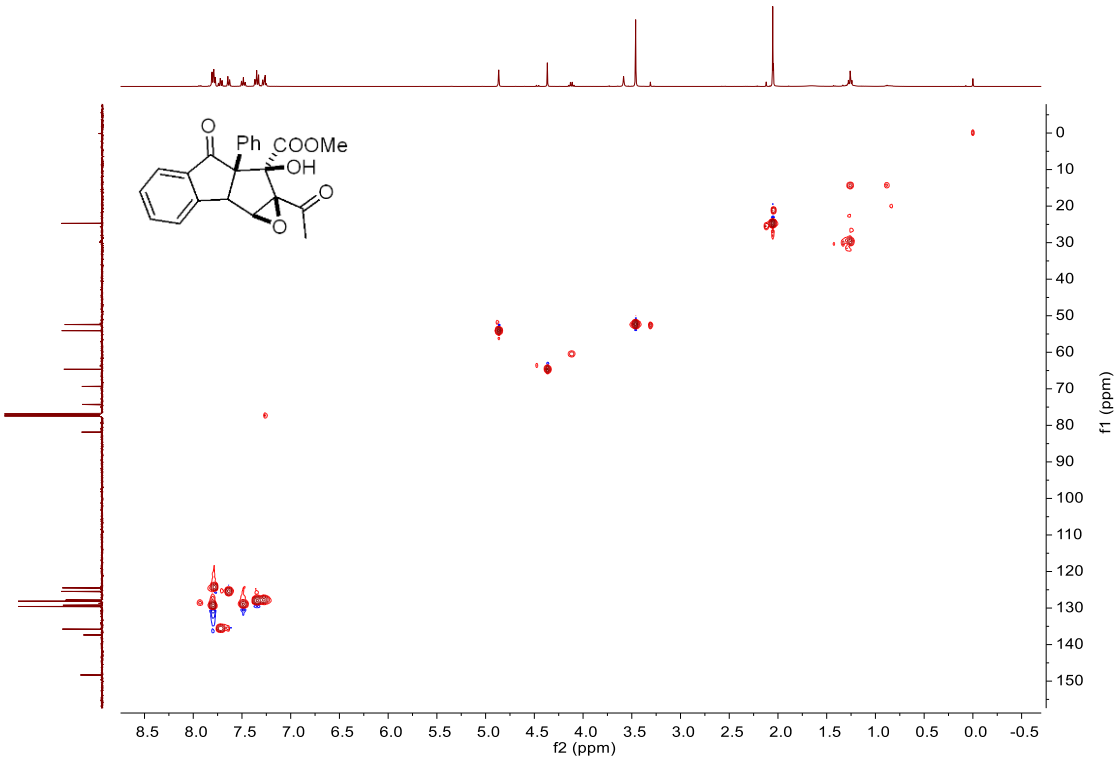
$^{13}$C NMR spectrum of **3fb-a′**



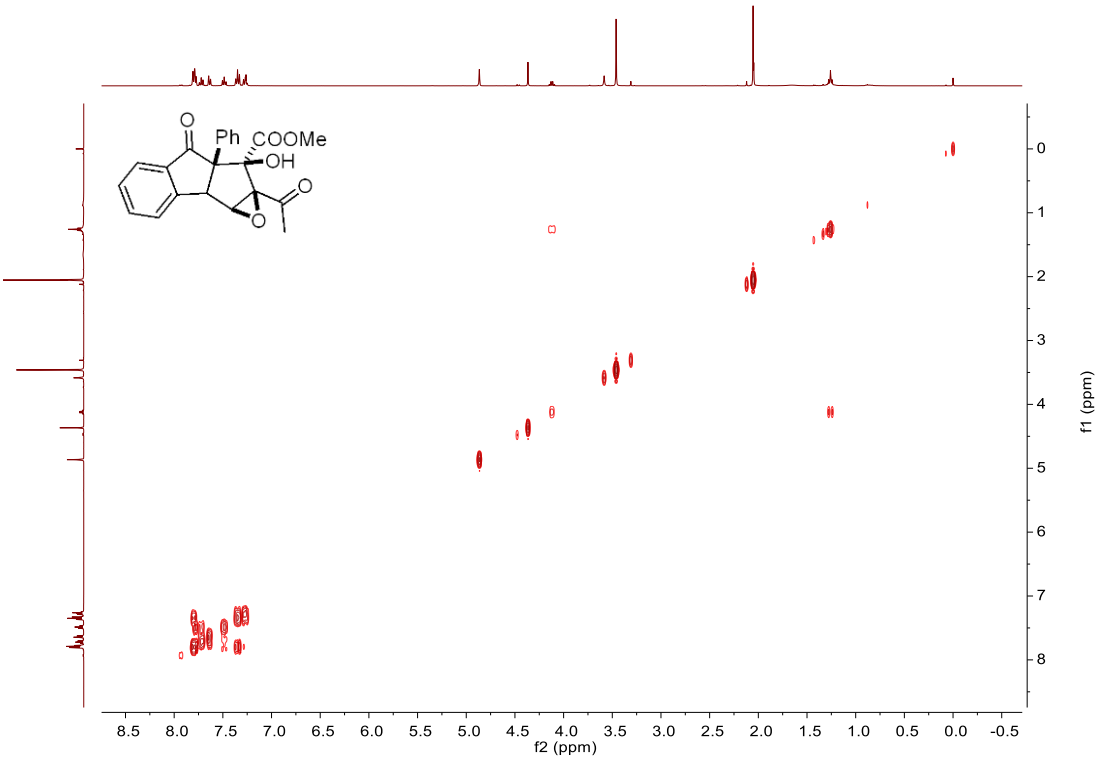

HMBC NMR spectrum of **3fb-a′**



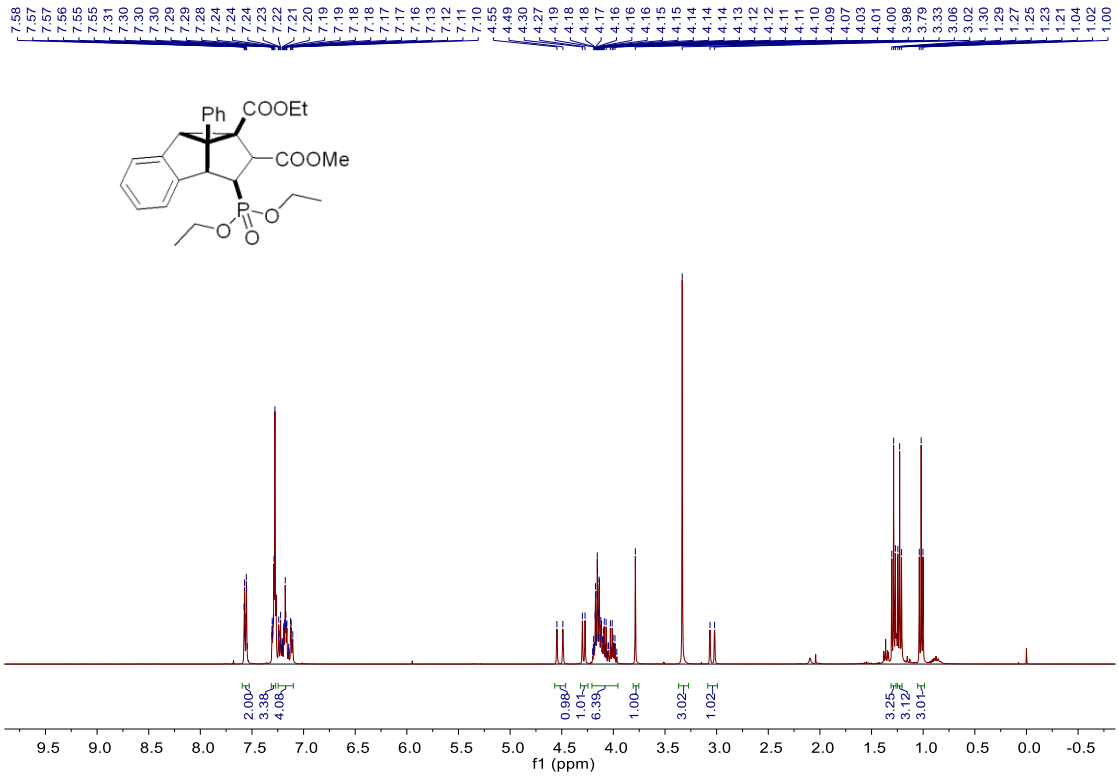
HSQC NMR spectrum of **3fb-a′**



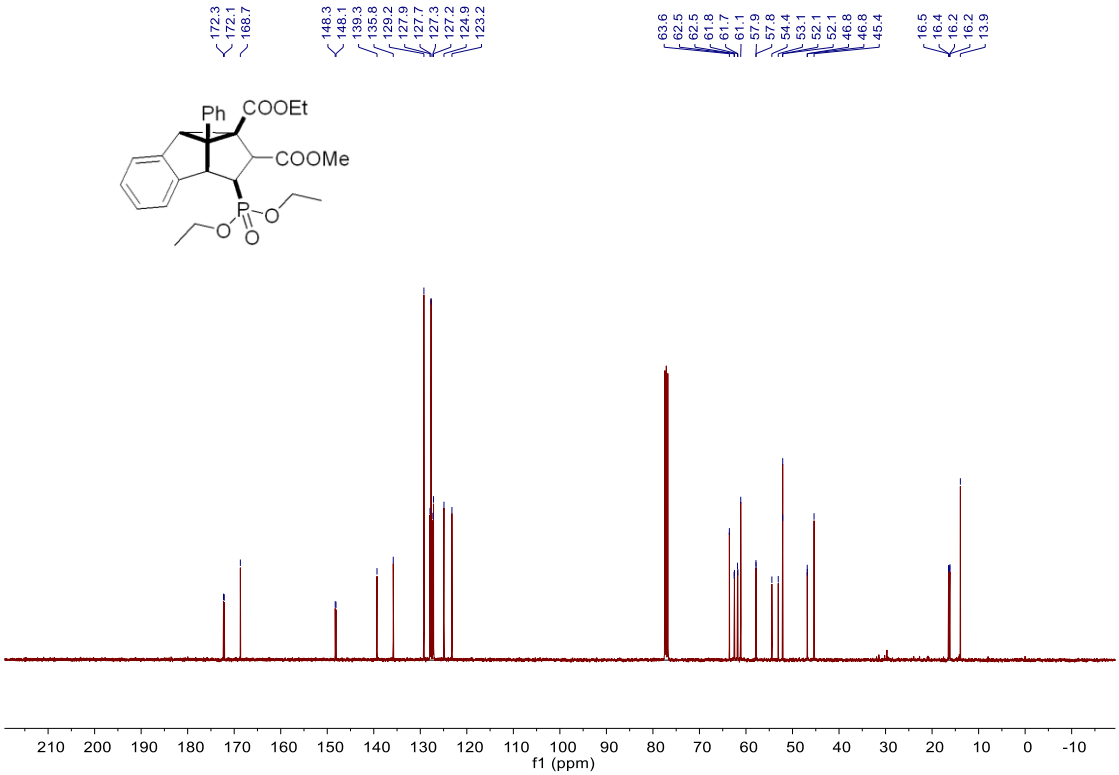

H-H COSY NMR spectrum of **3fb-a′**



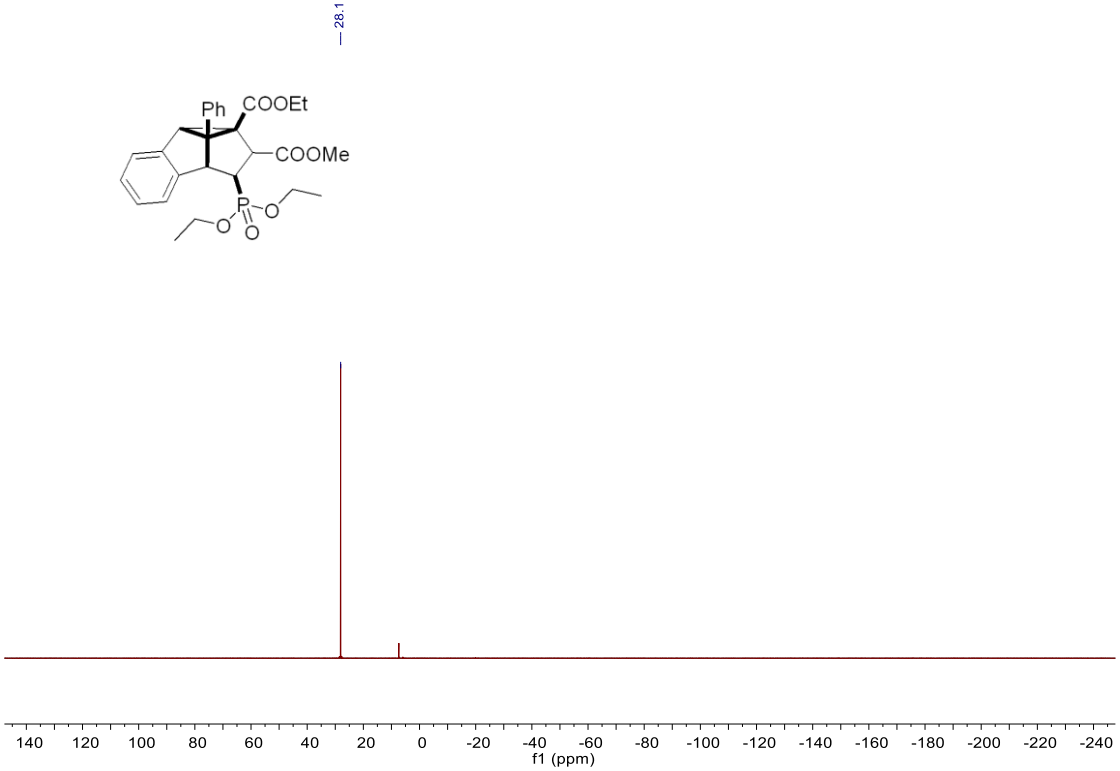
$^{1}$H NMR spectrum of **3aa-a**



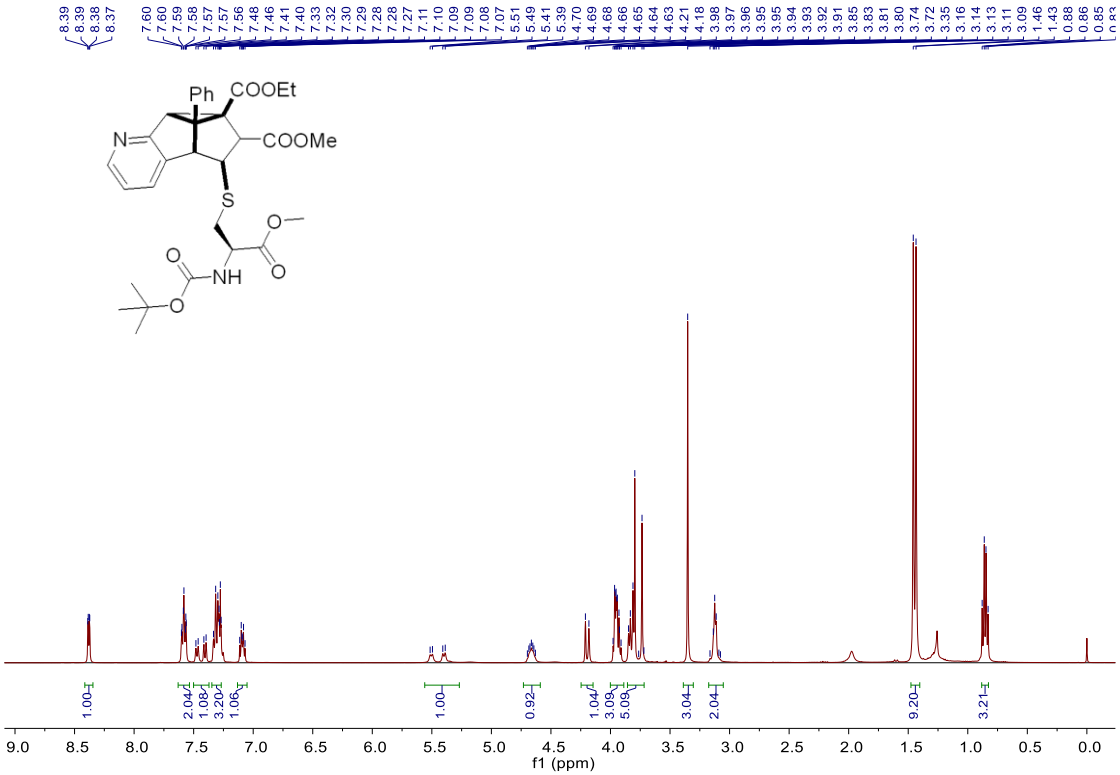

$^{13}$C NMR spectrum of **3aa-a**



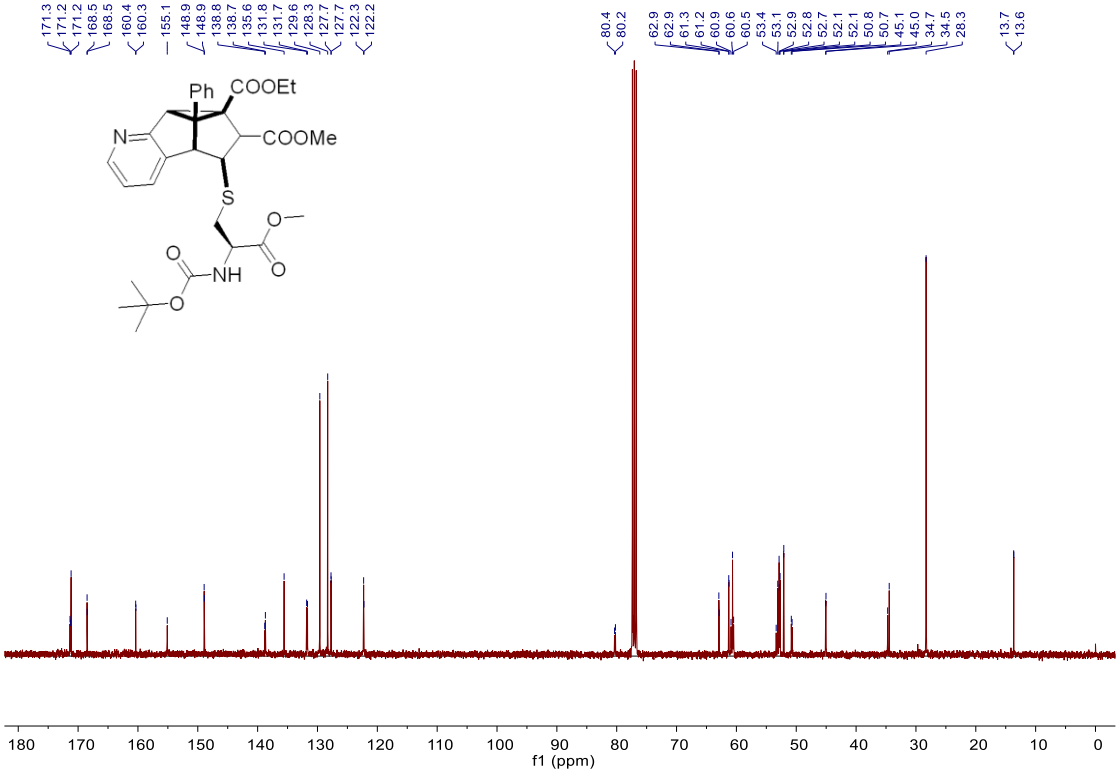
$^{31}$P NMR spectrum of **3aa-a**



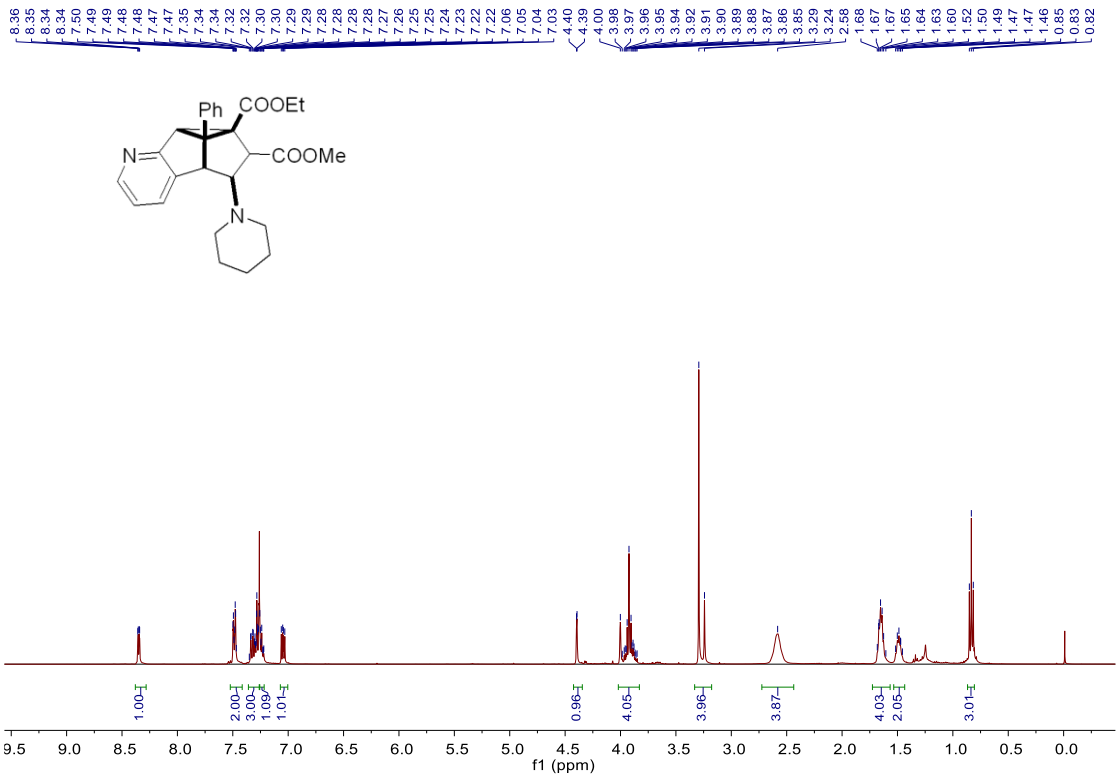

$^{1}$H NMR spectrum of **5aa-a**



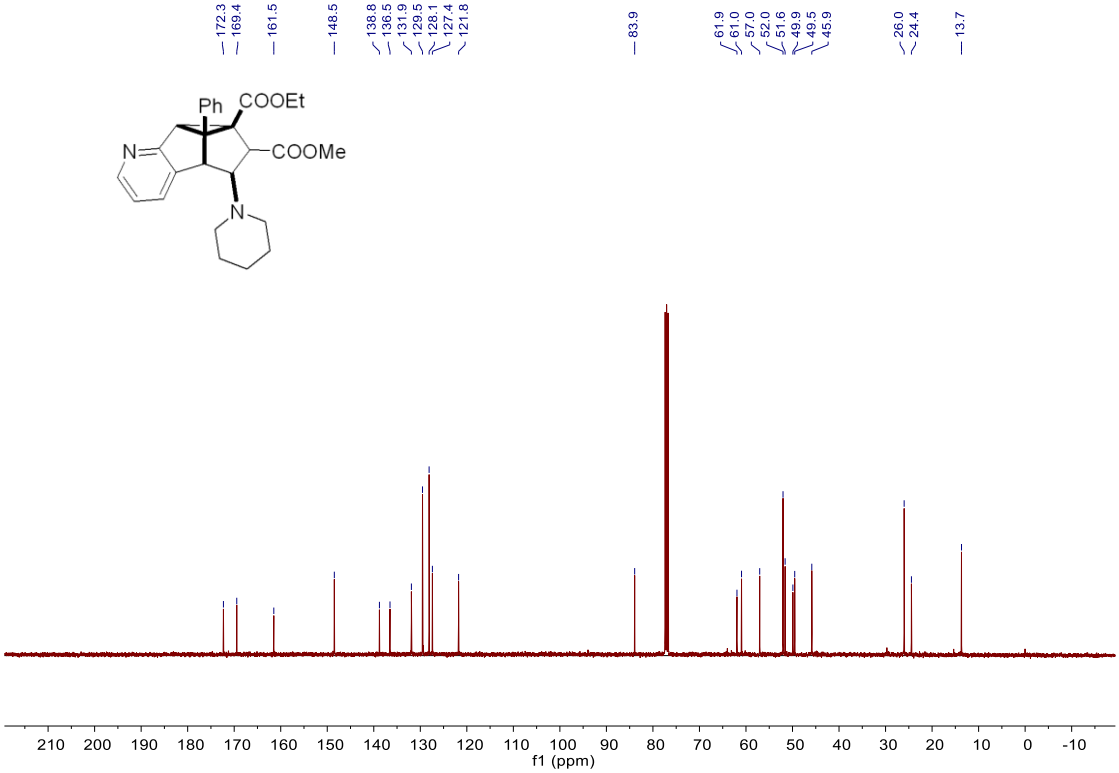
$^{13}$C NMR spectrum of **5aa-a**



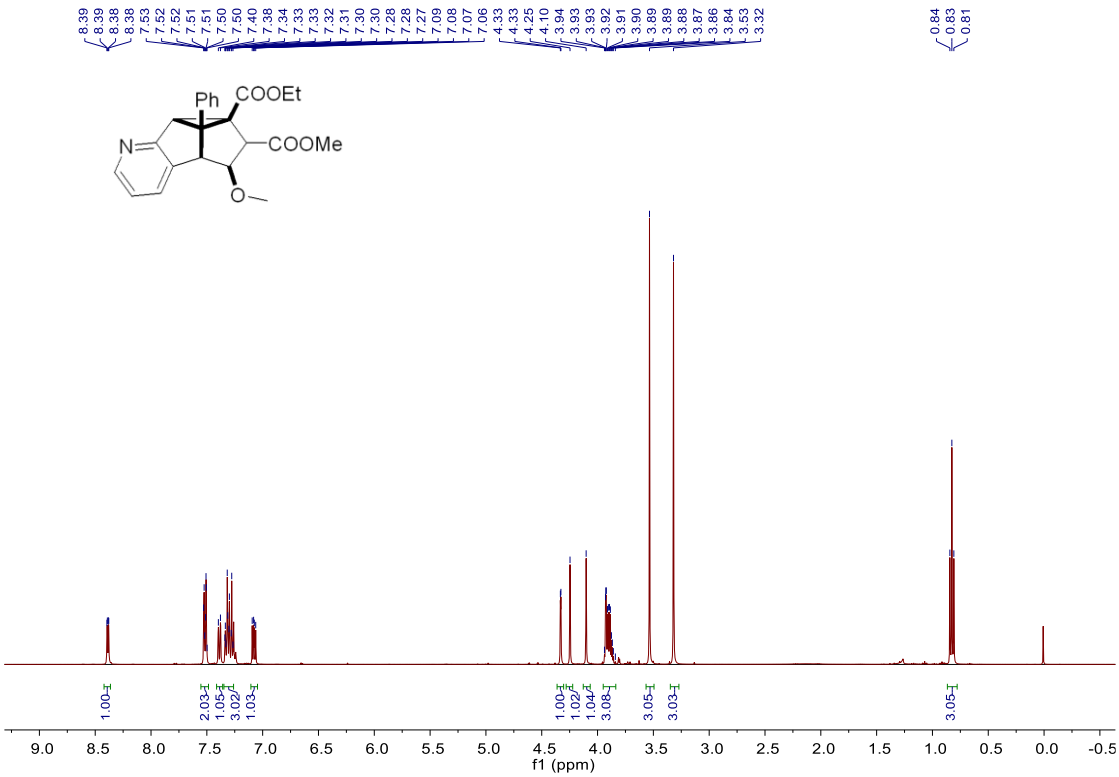

$^{1}$H NMR spectrum of **5aa-b**



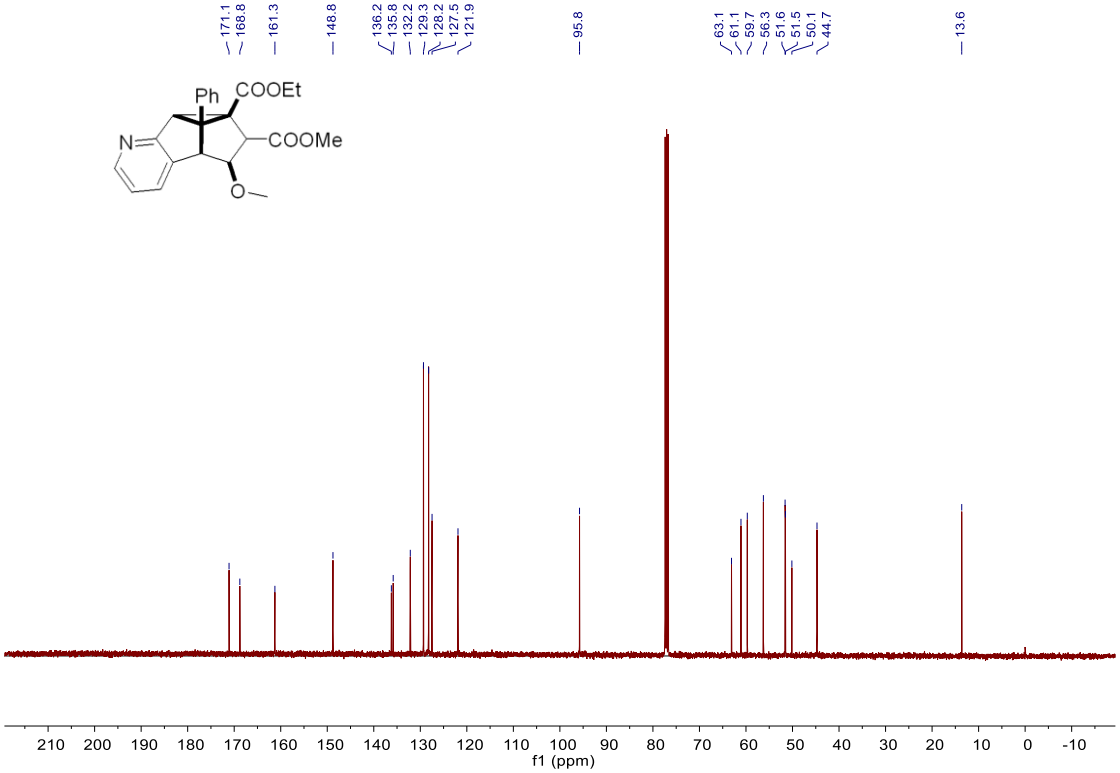
$^{13}$C NMR spectrum of **5aa-b**



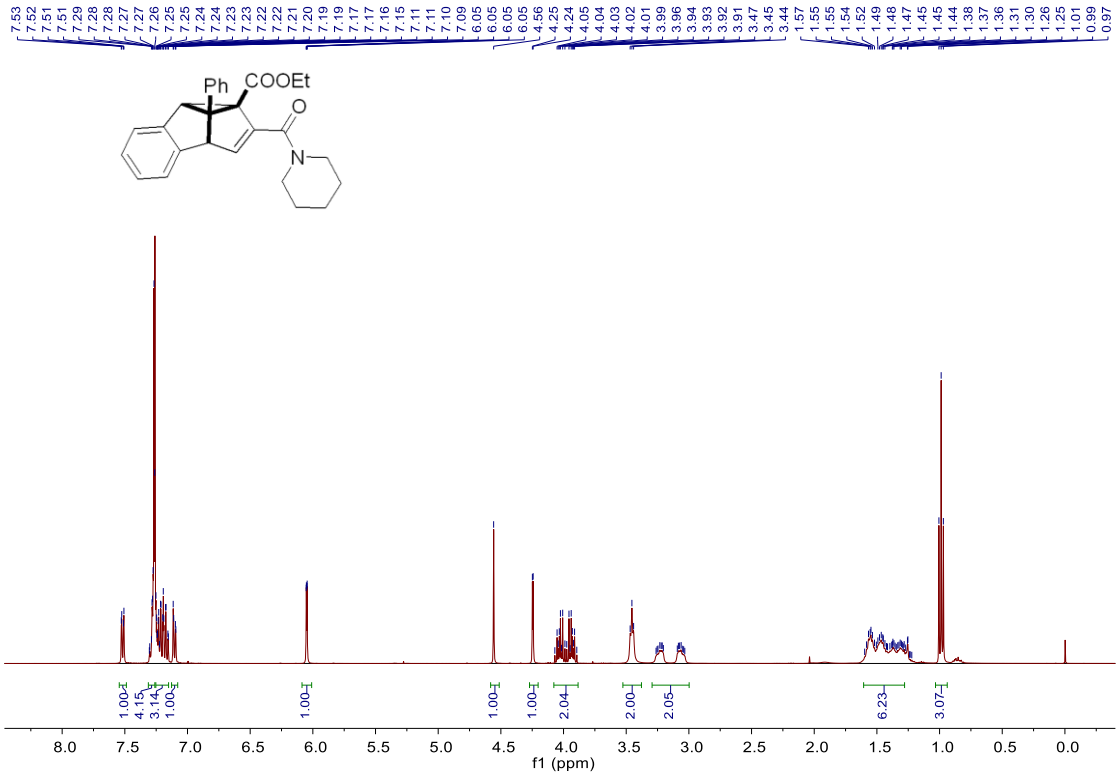

$^{1}$H NMR spectrum of **5aa-c**



$^{13}$C NMR spectrum of **5aa-c**




$^{1}$H NMR spectrum of **3da-a**



$^{13}$C NMR spectrum of **3da-a**