Highly Regio- and Diastereoselective (3 + 3)-Cycloannulation of Carbonyl Ylides and 2-(1-Alkynyl)-2-alken-1-ones Enabled by Silver Catalysis

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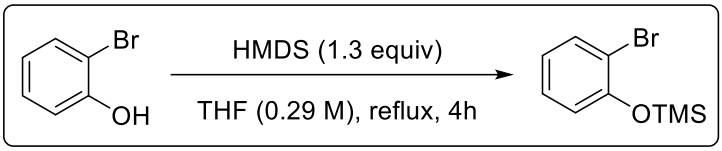
1.General Information:

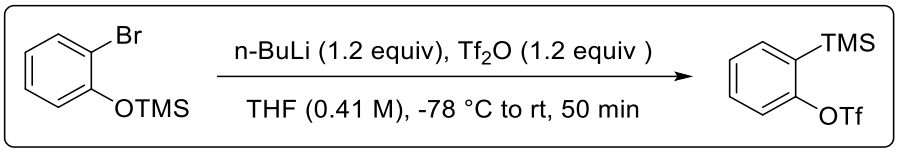
Chemicals and solvents were purchased from commercial suppliers and used as received. All dry solvents were dried using activated 4Å molecular sieves and stored under argon. 1H NMR spectra were recorded on 400 MHz, 500 MHz and 600 MHz spectrometer. 13C NMR spectra were recorded on 100 MHz, 125 MHz and 150 MHz. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.260), carbon (chloroform δ 77.23). Multiplicity was indicated as follows: s = singlet, d = doublet, dd = double doublet, ddd = doublet of doublet of doublets, t = triplet, q = quartet, dt = doublet of triplets, m = multiplet, bs = broad singlet. Coupling constants were reported in Hertz (Hz). Using ESI positive mode HRMS spectra were recorded. Enantiomeric ratios were determined by HPLC analysis performed on Chiral Columns using Daicel Chiral PAK IE Columns. For visualizing the products UV light was used. Silica gel (230-400 mesh size) was used for the flash column chromatography. Reactions were monitored by TLC on silica gel 60 with fluorescence indicator F254 (0.25 mm).

2.Preparation of Starting materials:

➢ *2.1 General procedure for the synthesis of α-diazoesters*: [1]

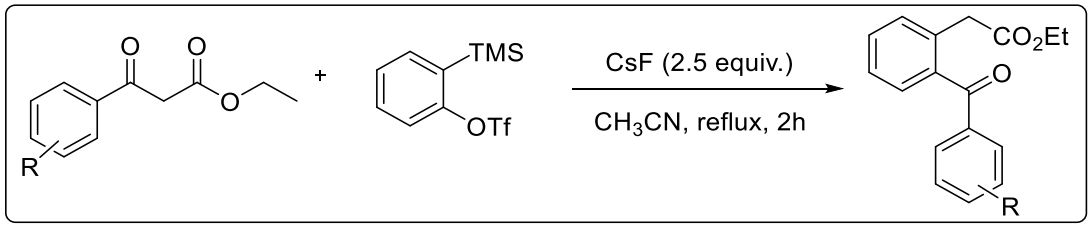


A mixture of 2-bromophenol (3.4ml, 28.9 mmol) and1,1,1,3,3,3-hexamethyl-disilazane (HMDS,7.8 ml, 37.6 mmol) in THF (×100ml) was stirred at 80 ºC under nitrogen atmosphere for 4 hours. Then, the volatile substances were removed under reduced pressure, affording the crude product as a yellow oil, which was used without further purification.

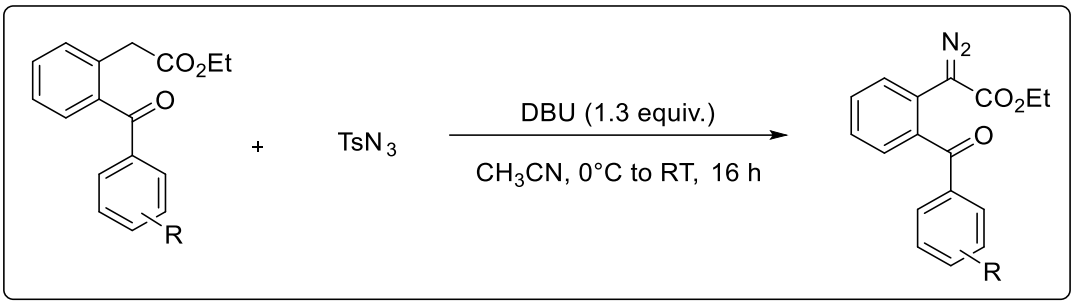


To a solution of the obtained crude material in THF (70ml) was added n-BuLi (13.9ml, 2.5M,34.7 mmol) at-78 ºC. after stirring under the same temperature for 30 min, to the mixture was added Tf_2O (5.8 ml,34.7 mmol) in a dropwise manner. The mixture was stirred for 20 min. after that, the mixture was quenched with NaHCO3 (aq.). the aqueous layer was extracted with ethyl acetate (3 ×40 ml). the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. After removal of the solvent in vacuo, the crude material was purified by flash column chromatography on silica gel to give 2- (trimethylsilyl)phenyl trifluoromethanesulfonate as light-yellow oil.

Yield: 4.76 g, 55% yield. (Rf= 0.60, eluent: hexane)

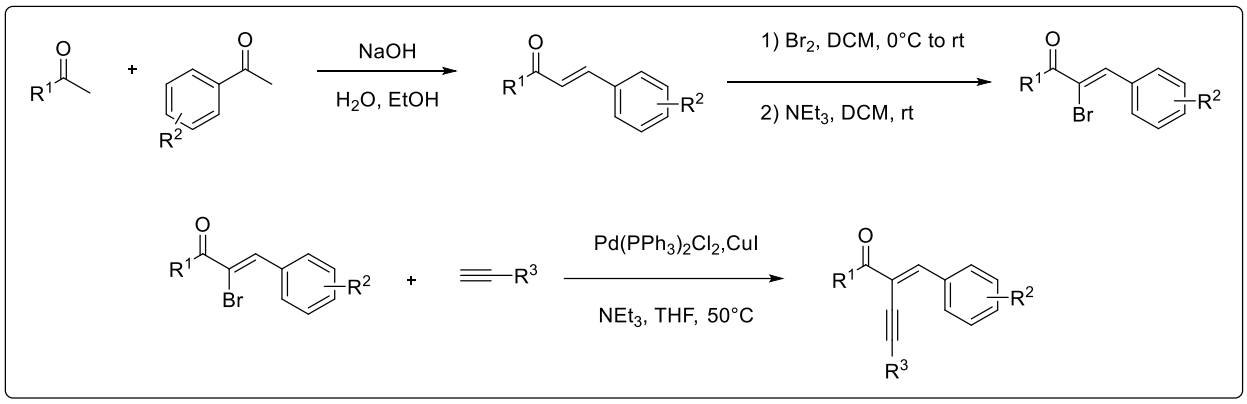


To a solution of benzoylacetates (1.0 equiv.) and 2-(trimethylsilyl) phenyl triflate (1.3 equiv.) in CH_3CN (4 mL/mmol) under Ar was added CsF (2.5 equiv.). The reaction mixture was refluxed for 2 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to RT and quenched by an aqueous solution of saturated NaCl (15 mL). The aqueous layer was extracted twice with EtOAc (15 mL each times). The combined organic layers were dried over Na_2SO_4 and conc. *in vacuo* to obtain crude product. The residue was purified over silica gel column chromatography using EtOAc/hexanes as eluent.

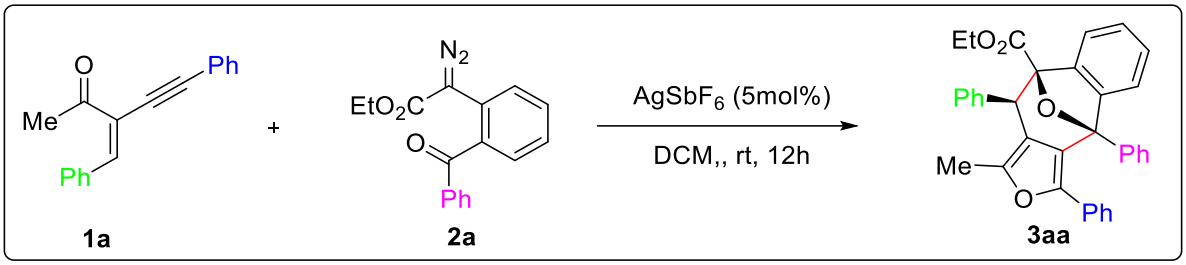


To a solution of acyl-alkyl derivative (1.0 equiv.) and TsN_3 (1.2 equiv.) in CH_3CN (3 mL/mmol) under Ar at 0 °C was slowly added DBU (1.3 equiv.). The reaction mixture was then stirred for 16h at RT. Upon completion of the reaction (monitored by TLC), the mixture was concentrated under reduced pressure to remove excess of CH_3CN. The residue was then purified by flash chromatography (using EtOAc/hexanes as eluent) to afford the desired diazoesters in high yields.

➢ 2.2 *General procedure for the synthesis of preparation of (E)-2-(1-alkynyl)-2-alken-1-one*: [2]



3.General Procedure for (3+3)-Cycloaddition:

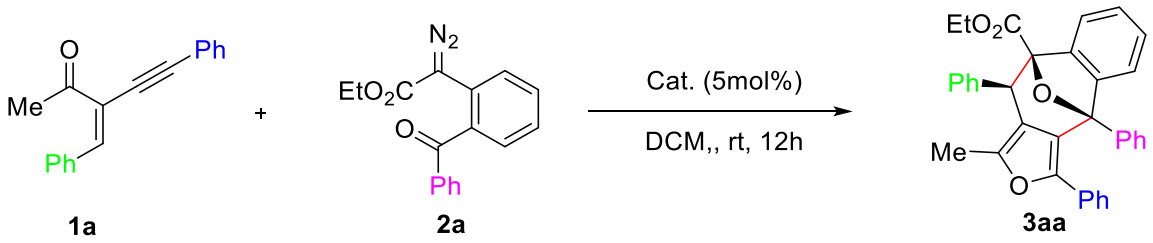


In a 10ml Rb enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat $AgSbF_6$ (1.7mg, 0.005mmol, 5 mol%), were suspended in dry DCM (2.0 mL). The reaction mixture was stirred at room temperature and a solution of α-diazo ester **2a** (30mg, 0.100 mmol, 1.0 eq.) dissolved in dry DCM (1.0 mL) was added dropwise and stirred at room temperature. After completed the reaction, check by TLC, the reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel eluting with ethyl-acetate: hexane (1 – 2 %) to afford the desired product.

4. Optimization Studies:

We began our study by conducting a model reaction in dichloromethane between (*E*)-3-benzylidene-5-phenylpent-4-yn-2-one (**1a**) and α-diazo ester **2a** using silver bis(trifluoromethanesulfonyl)imide catalyst (Table S1, entry 1). Gratifyingly, the required oxa-bridged polycyclic furan product **3aa** was produced in 80% yield with 1.5:1 d.r. after stirring for 12 hours at room temperature. Bismuth(III)trifluoromethanesulfonate was not suitable for the reaction and no product was formed (Table S1, entry 2). Silver triflate produced a decent yield of 80%, however silver acetate did not deliver any product (entries 3-4). Moderate yields and diastereoselectivities of **3aa** were attained with silver nitrate and silver nitrite (entries 5-6). Surprisingly, silver carobonate could not promote the reaction (entry 7). Then silver tetrafluoroborate was screened in the reaction. To our delight, a higher yield and perfect diastereoselectivity were found (entry 9). Silver hexafluoroantimonate catalyst ultimately turned out to be the most successful catalyst, yielding 3aa as a single diastereomer in 97% yield (entry 8). Other solvents were also tested but better results were not found (Table S2, entries 1-2).

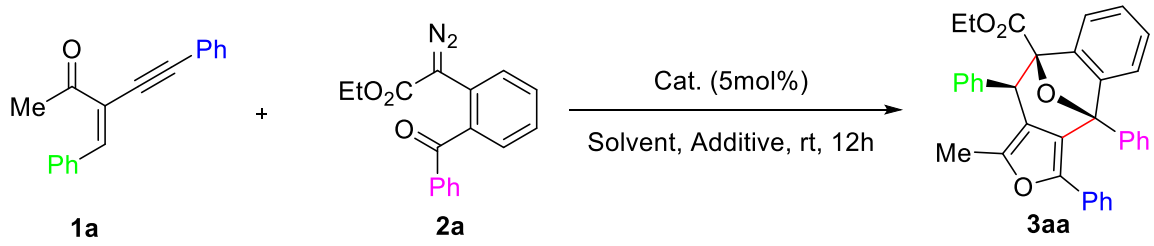
➢ **Table S1.** Catalyst Optimization:



Entry[a]	Catalyst	Yield (%) [b]	d.r[c]
1	$AgNTf_2$	80	1.5:1
2	$Bi(OTf)_3$	-	-
3	AgOTf	80	5:1
4	AgOAc	-	-
5	$AgNO_3$	60	3:1
6	$AgNO_2$	50	3:1
7	Ag_2CO_3	-	-
8	**$AgSbF_6$**	**97**	**20:1**
9	$AgBF_4$	85	20:1

[a] Reaction condition: 0.1 mmol of **1** and 0.1 mmol of **2** using 5 mol% of catalysts in 2 ml of DCM at room temperature. [b] Isolated yield after silica gel column chromatography. [c] Determined by NMR.

➢ **Table S2.** Optimization of Reaction Condition:

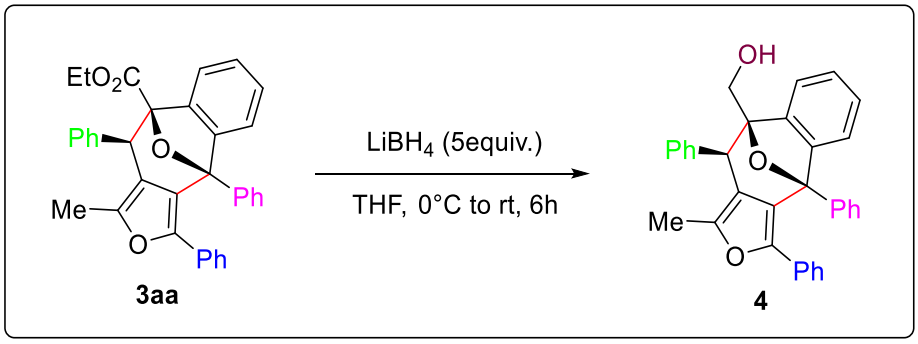


Entry[a]	Catalyst	Solvent	Additive	Yield (%) [b]	d.r[c]
1	$AgSbF_6$	MeOH	-	-	-
2	$AgSbF_6$	EtOAc	-	50	-

[a] Reaction condition: 0.1 mmol of **1** and 0.1 mmol of **2** using 5 mol% of catalysts in 1ml of DCM at room temperature. [b] Isolated yield after silica gel column chromatography. [c] Determined by NMR.

5. Synthetic Transformation:

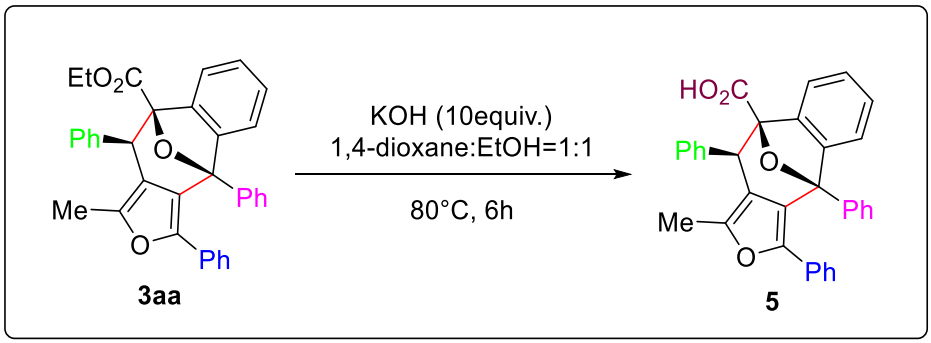
➢ *5.1 General procedure for the synthesis of compound **4*** [3]



3aa 26 mg (0.0500 mmol, 1.00 eq.) was dissolved in abs. THF (1.00 mL, 0.05M) in a sealed tube. The solution was cooled to 0°C and $LiBH_4$ (5.4 mg, 0.250 mmol, 5.00 eq.) was added. The solution

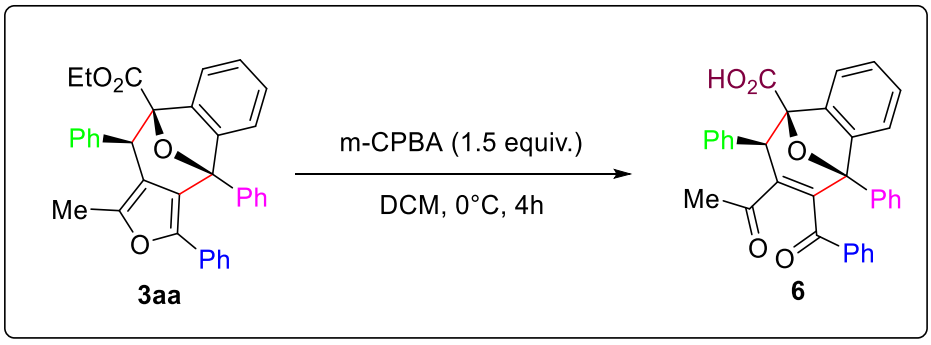
was warmed to room temperature and stirred for 6 h at the same temperature. Upon completion of the reaction, aq. NH_4Cl solution (5 mL) was added and the mixture was extracted with EtOAc (3 x 5 mL). The organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The product was obtained after column chromatography (hexane/EtOAc = 3:1, *v*/*v*) as a colourless solid (22mg, 93% Yield).

➢ *5.2 General procedure for the synthesis of compound* ***5*** [3]



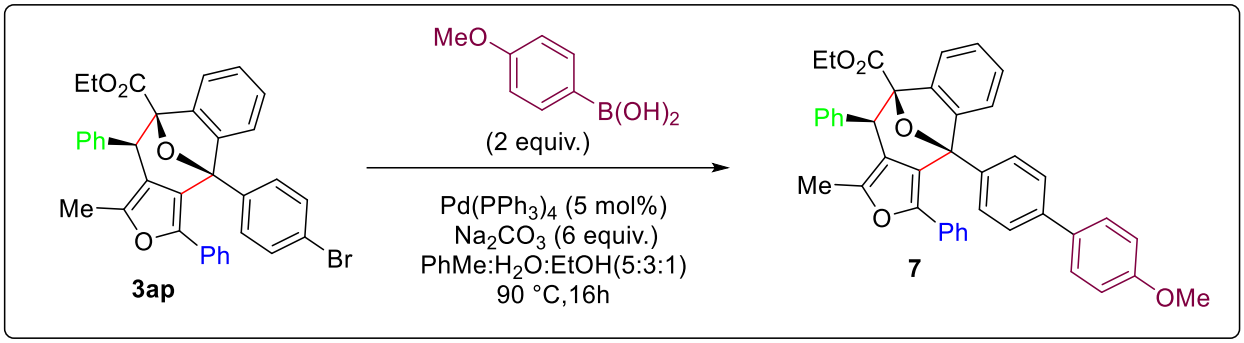
3aa 26 mg (0.0500 mmol, 1.00 eq.) was dissolved in a solvent mixture of 1,4-dioxane/EtOH (1:1, *v*/*v*, 1.00 mL, 0.05M) in a sealed tube. Subsequently, KOH (28.0 mg, 0.500 mmol, 10.0 eq) was added and the reaction was stirred for 4 h at 80 °C. Upon completion of the reaction, aq. NH_4Cl solution (5 mL) was added and the mixture was extracted with EtOAc (3 x 5 mL). The organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The product was obtained after column chromatography (CH_2Cl_2/MeOH = 20:1, *v*/*v*) as a yellow solid (18.4 mg, 75% Yield).

➢ *5.3 General procedure for the synthesis of compound* ***6*** [2]



Compound **6** was synthesized by an adapted literature procedure.[4] To a solution of **3aa** (26mg, 0.0500 mmol, 1.00 eq.) in DCM (1.5 mL) was added m-CPBA (18 mg, 0.1 mmol, 2.0 equiv.). The reaction mixture was stirred at room temperature under argon for 24 h. The completed reaction was concentrated. The residue was purified by column chromatography (Silica Gel, PE/EtOAc = 20/1) to afford 6 as a white solid (20.2 mg, 76% yield)

➢ *5.4 General procedure for the synthesis of compound **7*** [1]



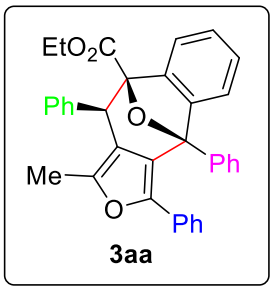
The bromo-substituted compound **3ap** (30 mg, 0.05 mmol, 1.0 equiv.), (4-methoxyphenyl)boronic acid (0.1 mmol, 2.0 equiv.), anhydrous Na_2CO_3 (0.3 mmol, 6.0 equiv.) and $Pd(PPh_3)_4$ (0.0025 mmol, 5 mol%) were suspended in a degassed solvent mixture of toluene/H_2O/EtOH (5:3:1 v/v/v) in a round bottom flask-fitted with a reflux condensor under Ar-atmosphere.The reaction mixture was refluxed at 90 °C until complete consumption of the starting material was indicated by TLC.The crude reaction mixture was directly purified by flash chromatography to deliver the desired compound **7** as a colourless solid (23.6mg, 76% yield).

6. References:

1. A. Suneja, H. J. Loui, C. Schneider, *Angew. Chem. Int. Ed*. 2020, **59**, 5536.
2. T. Yao, J.-E. She, T. Li, X. Qin, *Org. Lett*. 2024, **26**, 2018.
3. H. J. Loui, A. Suneja, C. Scheneider, *Org. Lett*. 2021, **23**, 2578.

7.Characterization of All Products:

Ethyl (4R,9R,10R)-1-methyl-3,4,10-triphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3aa)



3aa

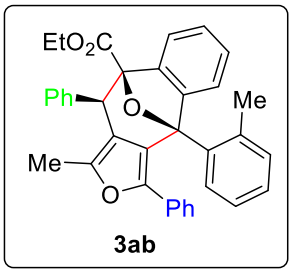
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (30 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 97% (49.6 mg), **d.r.** = 20:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 6.7, 2.2 Hz, 1H), 7.83 (dt, *J* = 6.9, 1.5 Hz, 2H), 7.68 – 7.59 (m, 3H), 7.48 (qt, *J* = 7.4, 3.7 Hz, 2H), 7.40 (td, *J* = 7.5, 6.8, 1.2 Hz, 3H), 7.36 – 7.31 (m, 3H), 7.25 (dt, *J* = 5.9, 3.7 Hz, 2H), 7.19 – 7.12 (m, 3H), 4.34 (s, 1H), 4.17 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.98 (dq, *J* = 10.8, 7.2 Hz, 1H), 1.95 (s, 3H), 1.07 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 148.5, 147.7, 143.6, 142.2, 140.7, 135.2, 130.9, 129.9, 129.6, 129.3, 128.9, 128.5, 128.3, 128.0, 127.7, 127.3, 127.0, 126.8, 123.2, 121.3, 118.9, 88.3, 61.4, 47.2, 14.0, 12.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{35}H_{29}O_4$: 513.2061, found 513.2055.

Ethyl (4R,9R,10R)-1-methyl-3,10-diphenyl-4-(o-tolyl)-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ab)



3ab

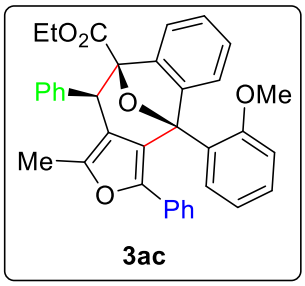
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2b** (31 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 80% (42 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 7.3 Hz, 1H), 7.50 (dd, *J* = 13.3, 7.3 Hz, 3H), 7.33 – 7.25 (m, 2H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.14 – 7.05 (m, 4H), 7.00 – 6.94 (m, 3H), 6.92 (d, *J* = 7.6 Hz, 1H), 4.08 (s, 1H), 4.03 – 3.95 (m, 1H), 3.86 – 3.76 (m, 1H), 2.26 (s, 3H), 1.76 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 148.7, 148.1, 142.9, 141.1, 140.7, 139.8, 133.8, 132.6, 130.7, 129.8, 129.4, 129.2, 128.8, 128.3, 127.8, 127.7, 127.2, 126.7, 126.1, 125.4, 123.0, 122.2, 122.0, 117.9, 88.4, 88.2, 61.3, 47.7, 22.3, 14.0, 12.2.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{36}H_{31}O_4$: 527.2217, found 527.2216.

Ethyl (4S,9R,10R)-4-(2-methoxyphenyl)-1-methyl-3,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ac)



3ac

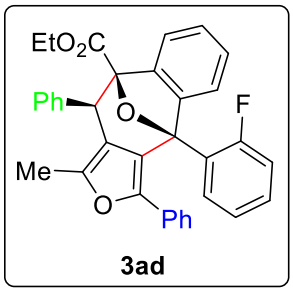
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2c** (32.5 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 85% (46 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.3 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.28 (q, *J* = 7.5 Hz, 3H), 7.25 – 7.20 (m, 1H), 7.17 – 7.10 (m, 2H), 7.04 (d, *J* = 4.1 Hz, 3H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 4.19 (s, 1H), 4.13 (ddt, *J* = 14.2, 10.7, 5.6 Hz, 1H), 3.93 (ddt, *J* = 10.8, 7.2, 3.4 Hz, 1H), 3.45 (s, 3H), 1.85 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 159.8, 147.7, 142.4, 141.3, 131.1, 130.8, 130.1, 128.7, 128.0, 127.5, 127.0, 126.3, 126.1, 123.6, 122.9, 122.1, 121.9, 120.1, 118.3, 112.2, 88.1, 86.4, 61.3, 55.4, 47.1, 14.0, 12.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{36}H_{31}O_5$: 543.2166, found 543.2167.

Ethyl (4R,9R,10R)-4-(2-fluorophenyl)-1-methyl-3,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ad)



3ad

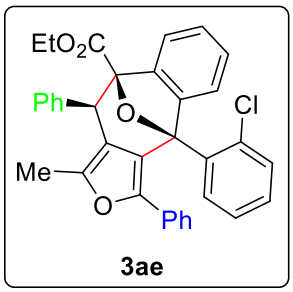
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2d** (31 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 78% (41.4 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 2H), 7.47 (dd, *J* = 19.1, 7.6 Hz, 3H), 7.30 (dt, *J* = 13.2, 7.4 Hz, 2H), 7.19 (q, *J* = 11.3, 9.4 Hz, 3H), 7.15 – 7.06 (m, 3H), 6.99 (dd, *J* = 15.3, 6.6 Hz, 4H), 6.79 – 6.70 (m, 1H), 4.11 (s, 1H), 4.00 (dq, *J* = 14.2, 7.2 Hz, 1H), 3.81 (dt, *J* = 10.8, 7.2 Hz, 1H), 1.73 (s, 3H), 0.90 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 163.6, 161.6, 148.2, 147.4, 143.0, 141.0, 140.7, 131.4, 131.4, 130.8, 130.6, 129.9, 128.9, 128.2, 128.0, 127.7, 127.2, 126.8, 126.5, 123.8, 123.7, 123.4, 123.3, 123.2, 121.4, 121.3, 118.0, 117.1, 116.9, 88.3, 85.3, 61.4, 47.2, 14.0, 12.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{35}H_{28}FO_4$: 531.1967, found 531.1935.

Ethyl (4R,9R,10R)-4-(2-chlorophenyl)-1-methyl-3,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ae)



3ae

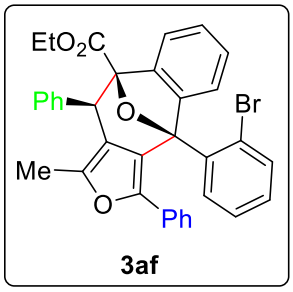
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2e** (33 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a colourless solid.
Yield = 80% (43 mg), **d.r.** = 20:1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 7.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.59 (dt, *J* = 23.9, 7.4 Hz, 2H), 7.52 – 7.45 (m, 3H), 7.45 – 7.40 (m, 2H), 7.40 – 7.33 (m, 3H), 7.26 (d, *J* = 6.5 Hz, 3H), 4.36 (s, 1H), 4.29 (dq, *J* = 14.1, 7.1 Hz, 1H), 4.10 (dd, *J* = 10.8, 7.2 Hz, 1H), 2.05 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 148.5, 147.5, 142.9, 141.2, 140.7, 136.1, 133.1, 132.1, 131.0, 130.9, 130.5, 130.1, 128.8, 128.2, 127.9, 127.7, 127.2, 126.7, 126.4, 126.2, 123.1, 121.9, 120.8, 118.0, 88.3, 87.4, 61.3, 47.6, 14.0, 12.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{35}H_{28}ClO_4$: 547.1671, found 547.1662.

Ethyl (4R,9R,10R)-4-(2-bromophenyl)-1-methyl-3,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3af)



3af

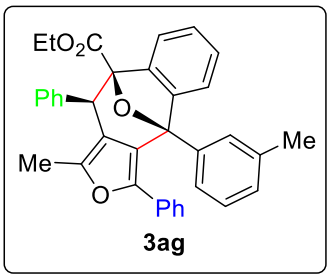
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2f** (37 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 92% (43 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.33 (dt, *J* = 20.3, 7.6 Hz, 3H), 7.23 (t, *J* = 7.5 Hz, 3H), 7.17 (q, *J* = 7.5 Hz, 1H), 7.12 – 7.05 (m, 3H), 7.03 – 6.97 (m, 3H), 4.08 (s, 1H), 4.02 (dq, *J* = 10.7, 7.0 Hz, 1H), 3.84 (dq, *J* = 10.8, 7.1 Hz, 1H), 1.79 (s, 3H), 0.92 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 148.7, 147.5, 143.0, 141.3, 140.8, 135.9, 134.5, 131.5, 131.0, 130.6, 130.2, 128.9, 128.2, 128.0, 127.7, 127.2, 127.0, 126.8, 126.3, 125.1, 123.1, 122.0, 120.6, 118.1, 88.4, 88.4, 61.4, 47.7, 14.0, 12.2.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{35}H_{28}BrO_4$: 591.1166, found 591.1129.

Ethyl (4R,9R,10R)-1-methyl-3,10-diphenyl-4-(m-tolyl)-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ag)



3ag

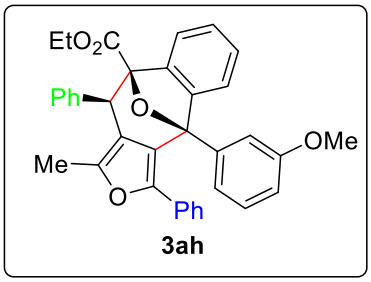
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2g** (31 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a colourless solid.
Yield = 78% (41 mg), **d.r.** = 20:1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.4 Hz, 1H), 7.76 – 7.64 (m, 5H), 7.57 (dt, *J* = 19.6, 7.3 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.42 (q, *J* = 7.3, 6.3 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.30 – 7.21 (m, 4H), 4.43 (s, 1H), 4.26 (dq, *J* = 14.2, 7.1 Hz, 1H), 4.06 (dq, *J* = 14.2, 7.1 Hz, 1H), 2.32 (s, 3H), 2.04 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 148.5, 147.9, 143.7, 142.2, 140.8, 138.1, 134.8, 131.1, 130.7, 129.9, 129.9, 128.9, 128.3, 128.3, 127.9, 127.6, 127.3, 127.2, 126.9, 126.5, 123.1, 121.4, 121.3, 118.9, 88.3, 88.3, 61.4, 47.2, 21.4, 14.0, 12.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{36}H_{31}O_4$: 527.2217, found 527.2211.

Ethyl (4R,9R,10R)-4-(3-methoxyphenyl)-1-methyl-3,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ah)



3ah

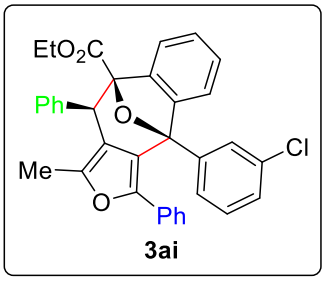
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2h** (32.5 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 75% (40 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.3 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 3H), 7.23 (t, *J* = 7.3 Hz, 2H), 7.16 (q, *J* = 7.8 Hz, 3H), 7.11 – 7.01 (m, 5H), 6.95 (d, *J* = 6.1 Hz, 3H), 6.70 (d, *J* = 8.7 Hz, 1H), 4.10 (s, 1H), 3.93 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.74 (dq, *J* = 14.0, 7.7, 7.2 Hz, 1H), 3.36 (s, 3H), 1.71 (s, 3H), 0.82 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.10, 159.76, 148.56, 147.77, 143.56, 142.06, 140.66, 136.43, 130.98, 129.85, 129.55, 128.90, 128.25, 127.98, 127.71, 127.28, 127.08, 126.96, 123.08, 122.00, 121.32, 121.13, 118.92, 115.89, 115.07, 88.34, 88.27, 61.40, 55.35, 47.17, 13.99, 12.05.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{36}H_{31}O_5$: 543.2166, found 543.2159.

Ethyl (4R,9R,10R)-4-(3-chlorophenyl)-1-methyl-3,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ai)



3ai

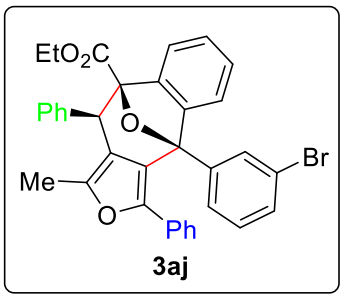
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2i** (33 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 95% (52 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.2 Hz, 1H), 7.72 (t, *J* = 2.0 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 3H), 7.44 (dt, *J* = 18.9, 6.9 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.22 – 7.13 (m, 6H), 4.28 (s, 1H), 4.12 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.93 (dq, *J* = 10.8, 7.1 Hz, 1H), 1.88 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 148.7, 147.1, 143.7, 142.0, 140.5, 137.1, 134.5, 130.7, 130.1, 129.8, 129.8, 129.4, 129.1, 128.3, 128.2, 127.8, 127.8, 127.4, 127.2, 127.2, 123.3, 121.1, 120.7, 118.7, 88.5, 87.6, 61.5, 47.1, 14.0, 12.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{35}H_{28}ClO_4$: 547.1671, found 547.1667.

Ethyl (4R,9R,10R)-4-(3-bromophenyl)-1-methyl-3,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3aj)



3aj

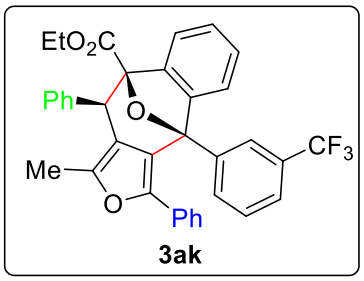
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2j** (37 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 85% (50 mg), **d.r.** = 20:1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.4 Hz, 1H), 7.86 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.57 – 7.52 (m, 3H), 7.47 – 7.40 (m, 3H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.22 – 7.19 (m, 2H), 7.18 – 7.12 (m, 4H), 4.28 (s, 1H), 4.14 – 4.08 (m, 1H), 3.95 – 3.88 (m, 1H), 1.88 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 148.7, 147.2, 143.7, 142.0, 140.5, 137.3, 133.0, 132.3, 130.7, 130.0, 129.8, 129.1, 128.3, 128.2, 127.9, 127.4, 127.3, 127.2, 123.3, 122.6, 121.1, 120.7, 118.6, 88.5, 87.6, 61.5, 47.1, 14.0, 12.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{35}H_{28}BrO_4$: 591.1166, found 591.1145.

Ethyl (4R,9R,10R)-1-methyl-3,10-diphenyl-4-(3-(trifluoromethyl)phenyl)-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ak)



3ak

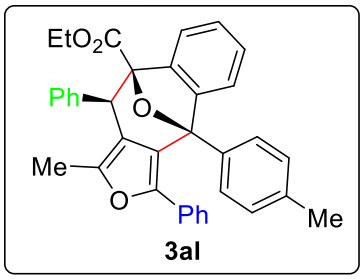
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2k** (36 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a light-yellow solid.
Yield = 80% (46.4 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.02 (dd, *J* = 8.0, 4.5 Hz, 2H), 7.66 (q, *J* = 7.3, 5.5 Hz, 4H), 7.61 – 7.49 (m, 3H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 (dd, *J* = 11.8, 4.7 Hz, 1H), 7.29 – 7.17 (m, 5H), 4.40 (s, 1H), 4.23 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.04 (dq, *J* = 10.8, 7.1 Hz, 1H), 2.00 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 148.9, 147.1, 143.8, 142.1, 140.5, 136.0, 133.1, 130.6, 129.8, 129.2, 129.0, 128.4, 128.3, 127.7, 127.5, 127.4, 127.3, 127.0, 127.0, 126.2, 126.1, 123.4, 121.1, 120.5, 118.6, 88.6, 87.7, 61.6, 47.2, 14.0, 12.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{36}H_{28}F_3O_4$: 581.1935, found 581.1936.

Ethyl (4R,9R,10R)-1-methyl-3,10-diphenyl-4-(p-tolyl)-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3al)



3al

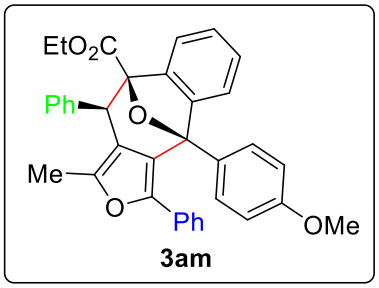
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2l** (31 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 95% (50 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.39 (t, *J* = 5.9 Hz, 3H), 7.23 (q, *J* = 7.4 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.07 (dd, *J* = 19.6, 7.8 Hz, 3H), 6.93 (dd, *J* = 14.6, 7.1 Hz, 5H), 4.10 (s, 1H), 3.93 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.73 (dq, *J* = 14.1, 7.1 Hz, 1H), 2.16 (s, 3H), 1.71 (s, 3H), 0.82 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 148.4, 147.9, 143.6, 142.2, 140.8, 139.1, 132.4, 130.9, 129.9, 129.5, 129.2, 128.8, 128.2, 127.9, 127.7, 127.2, 127.0, 126.8, 123.1, 121.4, 121.2, 119.0, 88.2, 88.2, 61.3, 47.1, 21.4, 14.0, 12.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{36}H_{31}O_4$: 527.2217, found 527.2210.

Ethyl (4R,9R,10R)-4-(4-methoxyphenyl)-1-methyl-3,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3am)



3am

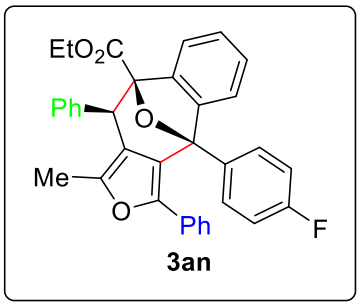
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2m** (32.5 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 90% (48.5 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.1 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.40 – 7.35 (m, 3H), 7.22 (q, *J* = 7.7, 7.2 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 2H), 7.07 (dd, *J* = 15.5, 7.9 Hz, 3H), 6.95 (d, *J* = 7.8 Hz, 3H), 6.62 (d, *J* = 8.8 Hz, 2H), 4.08 (s, 1H), 3.93 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.76 – 3.71 (m, 1H), 3.62 (s, 3H), 1.70 (s, 3H), 0.82 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 160.5, 148.4, 148.0, 143.6, 142.2, 140.8, 131.0, 131.0, 129.9, 128.9, 128.2, 127.9, 127.8, 127.6, 127.3, 127.1, 126.8, 123.1, 121.5, 121.2, 119.0, 113.9, 88.2, 88.0, 61.4, 55.5, 47.1, 14.0, 12.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{36}H_{31}O_5$: 543.2166, found 543.2155.

Ethyl (4R,9R,10R)-4-(4-fluorophenyl)-1-methyl-3,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3an)



3an

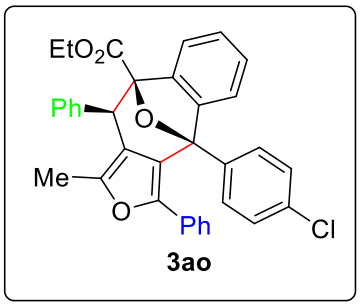
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2n** (31 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 94% (50 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.2 Hz, 1H), 7.70 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 3H), 7.40 (p, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.17 (dd, *J* = 6.8, 3.0 Hz, 2H), 7.14 – 7.07 (m, 3H), 6.92 (t, *J* = 8.7 Hz, 2H), 4.24 (s, 1H), 4.12 – 4.04 (m, 1H), 3.89 (dt, *J* = 10.8, 7.1 Hz, 1H), 1.85 (s, 3H), 0.99 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 164.5, 162.5, 148.7, 147.6, 143.6, 142.1, 140.6, 131.7, 131.6, 131.4, 131.3, 130.8, 129.8, 129.0, 128.3, 128.1, 127.8, 127.3, 127.1, 123.2, 121.2, 121.1, 118.8, 115.5, 115.3, 88.4, 87.7, 61.5, 47.1, 14.0, 12.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{35}H_{28}FO_4$: 531.1967, found 531.1967.

Ethyl (4R,9R,10R)-4-(4-chlorophenyl)-1-methyl-3,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ao)



3ao

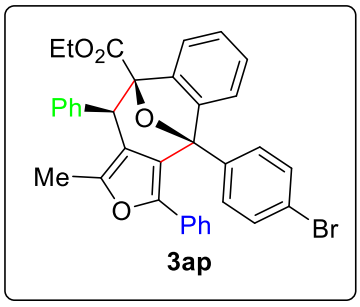
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2o** (33 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 93% (51 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.0 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.61 (dt, *J* = 6.8, 2.5 Hz, 3H), 7.50 (dt, *J* = 14.5, 7.4 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.36 – 7.30 (m, 3H), 7.28 (dd, *J* = 6.6, 3.4 Hz, 2H), 7.22 (dd, *J* = 5.0, 2.1 Hz, 3H), 4.34 (s, 1H), 4.18 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.99 (dq, *J* = 10.8, 7.2 Hz, 1H), 1.95 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.0, 148.7, 147.3, 143.6, 142.1, 140.5, 135.4, 133.9, 131.1, 130.7, 129.8, 129.0, 128.7, 128.3, 128.1, 127.8, 127.4, 127.2, 127.1, 123.3, 121.0, 120.9, 118.8, 88.4, 87.7, 61.5, 47.1, 14.0, 12.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{35}H_{28}ClO_4$: 547.1671, found 547.1670.

Ethyl (4R,9R,10R)-4-(4-bromophenyl)-1-methyl-3,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ap)



3ap

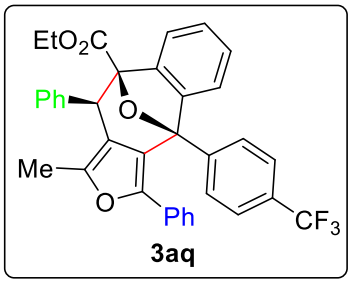
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2p** (37 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 90% (53 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.0 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.63 – 7.58 (m, 3H), 7.51 – 7.44 (m, 4H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.21 (dd, *J* = 5.1, 2.2 Hz, 3H), 4.34 (s, 1H), 4.16 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.97 (dq, *J* = 10.8, 7.1 Hz, 1H), 1.93 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 148.7, 147.2, 143.6, 142.0, 140.5, 134.4, 131.6, 131.4, 130.6, 129.8, 129.0, 128.2, 128.1, 127.8, 127.3, 127.18, 127.0, 123.7, 123.2, 121.0, 120.8, 118.7, 88.3, 87.7, 61.4, 47.1, 14.0, 12.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{35}H_{28}BrO_4$: 591.1166, found 591.1142.

Ethyl (4R,9R,10R)-1-methyl-3,10-diphenyl-4-(4-(trifluoromethyl)phenyl)-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3aq)



3aq

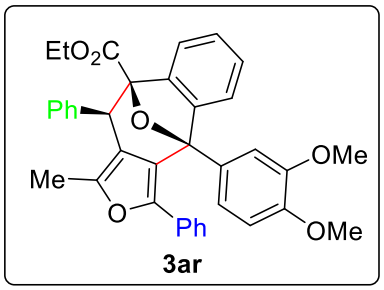
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2q** (36 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 90% (52.3 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 16.2, 7.6 Hz, 3H), 7.58 – 7.50 (m, 5H), 7.45 (p, *J* = 7.4 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.18 – 7.08 (m, 5H), 4.29 (s, 1H), 4.11 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.92 (dq, *J* = 10.7, 7.1 Hz, 1H), 1.89 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 148.9, 147.1, 143.7, 142.1, 140.5, 139.2, 130.6, 130.1, 129.8, 129.1, 128.3, 128.3, 127.9, 127.4, 127.3, 127.1, 125.5, 125.5, 123.4, 121.1, 120.7, 118.7, 88.6, 87.6, 61.5, 47.2, 14.0, 12.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{36}H_{28}F_3O_4$: 581.1935, found 581.1907.

Ethyl (4R,9R,10R)-4-(3,4-dimethoxyphenyl)-1-methyl-3,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ar)



3ar

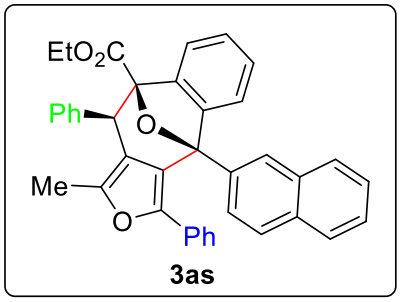
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2r** (35 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 70% (40 mg), **d.r.** = 20:1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 1H), 7.61 (dd, *J* = 14.5, 7.4 Hz, 3H), 7.48 (p, *J* = 7.3 Hz, 2H), 7.39 (q, *J* = 7.7 Hz, 3H), 7.32 (dd, *J* = 13.4, 7.1 Hz, 3H), 7.21 (q, *J* = 7.3, 6.8 Hz, 3H), 6.90 (d, *J* = 8.3 Hz, 1H), 4.33 (s, 1H), 4.18 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.95 (s, 4H), 3.55 (s, 3H), 1.96 (s, 3H), 1.06 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 150.1, 148.9, 148.7, 148.2, 143.6, 142.2, 140.8, 131.1, 129.9, 128.9, 128.3, 128.0, 127.8, 127.7, 127.3, 127.26, 127.16, 123.1, 122.5, 121.27, 121.2, 119.1, 113.8, 111.2, 88.4, 88.3, 61.4, 56.2, 55.9, 47.2, 14.0, 12.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{37}H_{33}O_6$: 573.2272, found 573.2266.

Ethyl (4R,9R,10R)-1-methyl-4-(naphthalen-2-yl)-3,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3as)



3as

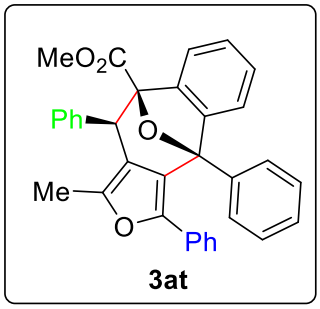
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2t** (34.5 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 94% (53 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.69 (dd, *J* = 12.9, 8.3 Hz, 2H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.44 (dt, *J* = 17.2, 6.1 Hz, 4H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.16 (m, 3H), 6.95 (d, *J* = 5.7 Hz, 3H), 4.30 (s, 1H), 4.08 (dq, *J* = 14.3, 7.2 Hz, 1H), 3.88 (dq, *J* = 14.2, 7.2 Hz, 1H), 1.90 (s, 3H), 0.97 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 148.6, 147.9, 143.7, 142.2, 140.7, 133.8, 133.3, 132.8, 130.9, 129.9, 129.5, 129.0, 128.6, 128.3, 128.3, 128.1, 127.7, 127.6, 127.3, 127.0, 127.0, 126.9, 126.6, 126.0, 123.2, 121.3, 121.2, 119.0, 88.5, 88.4, 61.4, 47.3, 14.0, 12.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{39}H_{31}O_4$: 563.2217, found 563.2210.

Methyl (4R,9R,10R)-1-methyl-3,4,10-triphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3at)



3at

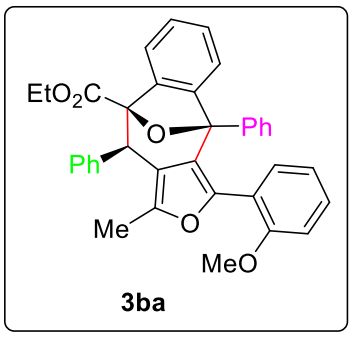
Prepared according to the general procedure using enynone **1a** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2u** (28 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 85% (43 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.3 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.42 (p, *J* = 7.2 Hz, 2H), 7.33 (q, *J* = 7.6 Hz, 3H), 7.28 (d, *J* = 7.6 Hz, 3H), 7.22 – 7.17 (m, 2H), 7.11 (q, *J* = 3.3, 2.3 Hz, 3H), 4.30 (s, 1H), 3.48 (s, 3H), 1.89 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 148.5, 147.6, 143.6, 141.9, 140.6, 135.1, 130.8, 129.7, 129.5, 129.4, 128.9, 128.6, 128.3, 128.0, 127.7, 127.3, 127.0, 126.9, 123.2, 121.3, 121.3, 118.7, 88.6, 88.4, 52.2, 47.2, 12.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{34}H_{27}O_4$: 499.1904, found 499.1895.

Ethyl (4R,9R,10R)-3-(2-methoxyphenyl)-1-methyl-4,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ba)



3ba

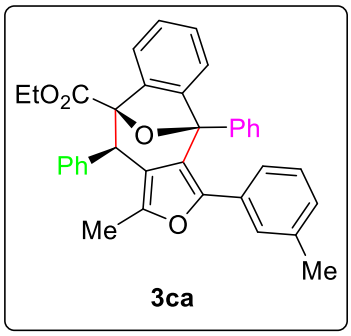
Prepared according to the general procedure using enynone **1b** (28mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (30 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a colourless solid. **Yield** = 90% (49 mg), **rotamer ratio** = 2:1.

^{1}H NMR (500 MHz, $CDCl_3$) (*major+minor*) δ 7.83 (d, *J* = 7.5 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 4H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.41 (q, *J* = 9.1, 7.4 Hz, 2H), 7.31 (dt, *J* = 23.4, 7.7 Hz, 6H), 7.25 – 7.19 (m, 2H), 7.18 – 7.10 (m, 4H), 7.08 (t, *J* = 8.1 Hz, 3H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.92 – 6.83 (m, 2H), 6.78 – 6.66 (m, 2H), 4.23 (s, 1H), 4.08 – 4.01 (m, 1H), 3.99 – 3.81 (m, 3H), 3.68 (s, 3H), 3.54 (s, 1H), 2.02 (s, 1H), 1.82 (s, 3H), 0.92 (dq, *J* = 28.5, 7.1 Hz, 7H).

^{13}C NMR (125 MHz, $CDCl_3$) (*major+minor*) δ 174.6, 169.3, 157.4, 155.4, 155.1, 148.5, 148.1, 148.0, 147.8, 146.7, 144.0, 142.3, 141.5, 141.0, 140.9, 140.3, 140.1, 135.4, 131.9, 130.0, 129.9, 129.86, 129.4, 129.3, 129.2, 128.9, 128.9, 128.7, 128.6, 128.5, 128.5, 128.3, 128.2, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 127.2, 127.1, 127.0, 126.8, 126.6, 125.8, 125.0, 124.2, 123.7, 123.0, 122.8, 122.3, 122.1, 121.9, 121.2, 120.6, 120.5, 120.2, 120.0, 119.4, 119.3, 117.8, 114.9, 112.2, 111.1, 111.0, 110.8, 110.3, 109.8, 93.5, 93.4, 88.4, 88.0, 62.5, 61.6, 61.3, 55.6, 55.5, 55.1, 51.3, 48.4, 47.3, 29.9, 13.8, 13.7, 12.5, 12.2.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{36}H_{31}O_5$: 543.2166, found 543.2162.

Ethyl (4R,9R,10R)-1-methyl-4,10-diphenyl-3-(m-tolyl)-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ca)



3ca

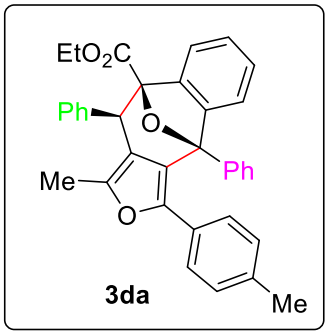
Prepared according to the general procedure using enynone **1c** (26mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (30 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a colourless solid. **Yield** = 88% (46.4 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.3 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 3H), 7.29 (t, *J* = 8.3 Hz, 2H), 7.18 (dq, *J* = 23.0, 7.6 Hz, 6H), 6.94 – 6.83 (m, 3H), 6.79 (d, *J* = 7.5 Hz, 1H), 4.16 (s, 1H), 3.99 (dq, *J* = 14.5, 7.1 Hz, 1H), 3.79 (dq, *J* = 14.5, 7.1 Hz, 1H), 2.03 (s, 3H), 1.76 (s, 3H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 148.3, 147.7, 143.7, 142.1, 140.7, 137.1, 135.4, 130.6, 129.8, 129.5, 129.2, 128.8, 128.5, 128.2, 127.9, 127.8, 127.6, 127.2, 123.9, 123.1, 121.3, 121.2, 118.8, 88.3, 88.3, 61.3, 47.1, 21.4, 14.0, 12.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{36}H_{31}O_4$: 527.2217, found 527.2211.

Ethyl (4R,9R,10R)-1-methyl-4,10-diphenyl-3-(p-tolyl)-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3da)



3da

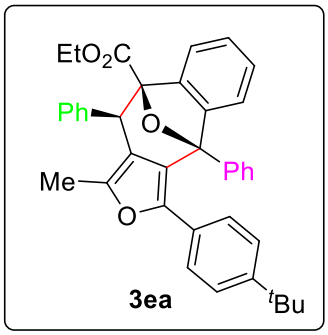
Prepared according to the general procedure using enynone **1d** (26mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (30 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a colourless solid. **Yield** = 80% (42 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 6.9 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.52 – 7.47 (m, 3H), 7.34 (p, *J* = 7.3 Hz, 2H), 7.29 – 7.18 (m, 6H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 8.1 Hz, 2H), 4.20 (s, 1H), 4.04 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.85 (dq, *J* = 10.7, 7.1 Hz, 1H), 2.20 (s, 3H), 1.81 (s, 3H), 0.94 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 148.1, 147.8, 143.8, 142.1, 140.8, 136.6, 135.4, 129.9, 129.6, 129.3, 128.9, 128.6, 128.4, 128.2, 128.1, 127.9, 127.2, 126.8, 123.1, 121.2, 120.6, 118.8, 88.4, 88.3, 61.4, 47.2, 21.3, 14.0, 12.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{36}H_{31}O_4$: 527.2217, found 527.2214.

Ethyl (4R,9R,10R)-3-(4-(tert-butyl)phenyl)-1-methyl-4,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ea)



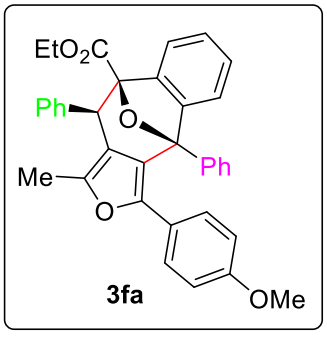
Prepared according to the general procedure using enynone **1e** (30mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (30 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a colourless solid.
Yield = 80% (45.6 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 6.9 Hz, 1H), 7.73 (d, *J* = 7.3 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 3H), 7.42 – 7.36 (m, 2H), 7.31 (q, *J* = 7.2 Hz, 3H), 7.24 (d, *J* = 6.9 Hz, 3H), 7.09 (s, 4H), 4.25 (s, 1H), 4.09 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.90 (dq, *J* = 10.8, 7.2 Hz, 1H), 1.86 (s, 3H), 1.26 (s, 9H), 0.99 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 149.8, 148.1, 147.9, 143.8, 142.1, 140.8, 135.2, 129.9, 129.6, 129.2, 128.8, 128.5, 128.2, 128.1, 127.9, 127.2, 126.7, 124.6, 123.1, 121.3, 120.7, 118.7, 88.3, 88.3, 61.4, 47.2, 34.6, 31.4, 14.0, 12.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{39}H_{37}O_4$: 569.2687, found 569.2685.

Ethyl (4R,9R,10R)-3-(4-methoxyphenyl)-1-methyl-4,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3fa)



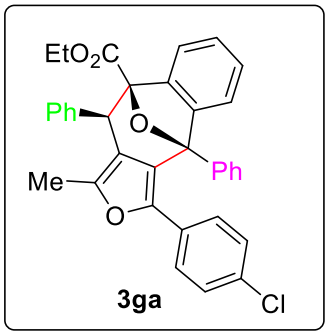
Prepared according to the general procedure using enynone **1f** (28mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (30 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a light-yellow solid.
Yield = 86% (46.8 mg), **d.r.** = 20:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 6.8 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 3H), 7.36 – 7.29 (m, 2H), 7.21 (td, *J* = 12.0, 11.2, 5.4 Hz, 6H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 4.18 (s, 1H), 4.02 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.83 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.68 (s, 3H), 1.79 (s, 3H), 0.93 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 158.6, 147.9, 147.8, 143.6, 142.2, 140.8, 135.2, 129.9, 129.7, 129.3, 128.8, 128.6, 128.4, 128.2, 127.9, 127.2, 123.9, 123.1, 121.2, 119.9, 118.7, 113.2, 88.3, 61.4, 55.4, 47.2, 14.0, 12.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{36}H_{31}O_5$: 543.2166, found 543.2159.

Ethyl (4R,9R,10R)-3-(4-chlorophenyl)-1-methyl-4,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ga)



3ga

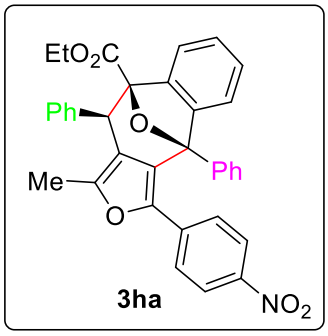
Prepared according to the general procedure using enynone **1g** (28mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (30 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 82% (44.8 mg), **d.r.** = 20:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 6.2, 2.6 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.39 – 7.31 (m, 3H), 7.23 (ddd, *J* = 6.3, 4.0, 1.6 Hz, 2H), 7.18 – 7.07 (m, 6H), 6.93 – 6.85 (m, 4H), 4.07 (s, 1H), 3.91 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.72 (dq, *J* = 10.8, 7.1 Hz, 1H), 1.68 (s, 3H), 0.81 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.03, 148.86, 147.46, 142.45, 142.11, 140.54, 135.16, 132.56, 129.85, 129.57, 129.49, 129.37, 128.94, 128.77, 128.30, 128.09, 127.96, 127.92, 127.35, 123.25, 122.06, 121.16, 119.15, 88.30, 88.15, 61.44, 47.10, 14.01, 12.05.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{35}H_{28}ClO_4$: 547.1671, found 547.1667.

Ethyl (4R,9R,10R)-1-methyl-3-(4-nitrophenyl)-4,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ha)



3ha

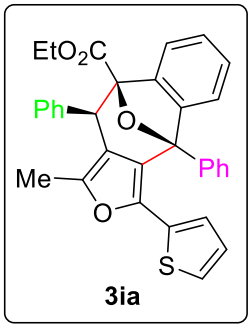
Prepared according to the general procedure using enynone **1h** (29mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (30 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a yellow solid.
Yield = 90% (50.2 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 16.3, 7.8 Hz, 3H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 3H), 7.47 (p, *J* = 7.5 Hz, 3H), 7.37 (t, *J* = 7.4 Hz, 4H), 7.32 (d, *J* = 8.6 Hz, 3H), 4.30 (s, 1H), 4.14 (dq, *J* = 14.6, 7.2 Hz, 1H), 3.99 – 3.91 (m, 1H), 1.95 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 151.0, 146.9, 145.7, 142.0, 141.3, 140.1, 136.6, 135.2, 129.9, 129.8, 129.2, 129.1, 129.1, 129.0, 128.9, 128.4, 128.4, 127.5, 126.5, 125.9, 123.4, 123.2, 123.2, 121.1, 120.1, 88.2, 88.0, 61.5, 47.0, 14.0, 12.2.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{35}H_{28}NO_6$: 558.1912, found 558.1901.

Ethyl (4R,9R,10R)-1-methyl-4,10-diphenyl-3-(thiophen-2-yl)-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ia)



3ia

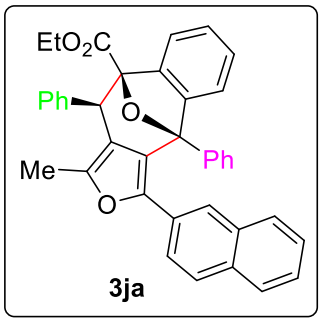
Prepared according to the general procedure using enynone **1i** (33mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (30 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a colourless solid.
Yield = 85% (44 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.2 Hz, 3H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 4.7 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 5H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 5.1 Hz, 1H), 6.74 (t, *J* = 4.5 Hz, 1H), 6.48 (d, *J* = 3.9 Hz, 1H), 4.21 (s, 1H), 4.08 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.89 (dq, *J* = 14.2, 7.1 Hz, 1H), 1.85 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 148.3, 147.6, 141.9, 140.4, 139.0, 135.0, 133.3, 129.9, 129.8, 129.6, 128.9, 128.8, 128.3, 128.0, 127.3, 126.9, 124.9, 124.8, 123.1, 121.2, 121.17, 118.8, 88.3, 87.9, 61.4, 47.0, 14.0, 12.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{33}H_{27}O_4S$: 519.1625, found 519.1623.

Ethyl (4R,9R,10R)-1-methyl-3-(naphthalen-2-yl)-4,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ja)



3ja

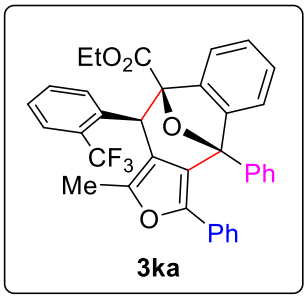
Prepared according to the general procedure using enynone **1j** (37mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (30 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a yellow solid.
Yield = 90% (50.6 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.71 – 7.63 (m, 2H), 7.62 – 7.49 (m, 5H), 7.44 – 7.36 (m, 5H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 6.3 Hz, 4H), 4.31 (s, 1H), 4.11 (dq, *J* = 13.9, 7.1 Hz, 1H), 3.91 (dd, *J* = 11.1, 6.9 Hz, 1H), 1.91 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 148.7, 147.6, 143.5, 142.1, 140.6, 135.4, 133.0, 132.1, 129.9, 129.4, 129.42, 128.9, 128.7, 128.3, 128.2, 128.1, 128.0, 127.6, 127.3, 127.1, 126.1, 125.9, 125.8, 124.7, 123.2, 122.0, 121.2, 119.2, 88.4, 88.3, 61.4, 47.2, 14.0, 12.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{39}H_{31}O_4$: 563.2217, found 563.2214.

Ethyl (4R,9R,10R)-1-methyl-3,4-diphenyl-10-(2-(trifluoromethyl)phenyl)-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ka)



3ka

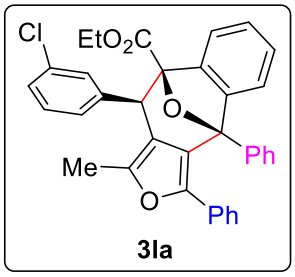
Prepared according to the general procedure using enynone **1k** (25mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (36 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a white solid.
Yield = 82% (47.5 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 7.0 Hz, 1H), 7.81 (dd, *J* = 17.9, 8.0 Hz, 3H), 7.69 (d, *J* = 6.8 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.54 (p, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.27 (dd, *J* = 6.5, 2.8 Hz, 2H), 7.21 – 7.15 (m, 3H), 4.83 (s, 1H), 4.23 – 4.15 (m, 1H), 3.96 – 3.88 (m, 1H), 1.93 (s, 3H), 1.05 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 148.9, 147.1, 143.7, 142.5, 139.7, 135.1, 132.4, 132.3, 130.8, 129.5, 129.3, 129.0, 128.5, 128.3, 127.7, 127.4, 127.1, 127.0, 125.7, 125.6, 125.6, 125.5, 123.7, 121.6, 121.2, 118.9, 88.05, 88.0, 61.5, 42.05, 42.03, 42.01, 13.77, 12.05, 12.03, 12.01.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{36}H_{28}F_3O_4$: 581.1935, found 581.1934.

Ethyl (4R,9R,10R)-10-(3-chlorophenyl)-1-methyl-3,4-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3la)



3la

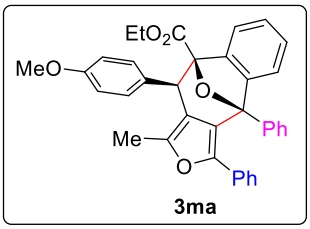
Prepared according to the general procedure using enynone **1l** (28mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (30 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a light-yellow solid.
Yield = 84% (46 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.4 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.40 (d, *J* = 6.3 Hz, 1H), 7.34 (dt, *J* = 14.6, 7.3 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.21 – 7.15 (m, 4H), 7.13 – 7.08 (m, 2H), 7.06 – 6.99 (m, 3H), 4.17 (s, 1H), 4.07 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.89 (dq, *J* = 14.2, 7.1 Hz, 1H), 1.82 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 148.6, 147.7, 143.9, 142.8, 141.9, 135.1, 133.9, 130.8, 129.9, 129.6, 129.6, 129.4, 129.0, 128.6, 128.2, 128.1, 127.7, 127.5, 127.0, 127.0, 123.1, 121.4, 121.2, 118.3, 88.4, 88.1, 61.5, 46.8, 14.0, 12.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{35}H_{28}ClO_4$: 547.1671, found 547.1672.

Ethyl (4R,9R,10R)-10-(4-methoxyphenyl)-1-methyl-3,4-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3ma)



3ma

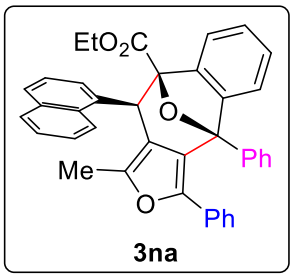
Prepared according to the general procedure using enynone **1m** (28mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (30 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a yellow solid.
Yield = 85% (46.2 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.2 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.14 (dt, *J* = 17.9, 7.4 Hz, 2H), 7.02 (dt, *J* = 17.4, 7.3 Hz, 4H), 6.94 – 6.89 (m, 2H), 6.86 – 6.79 (m, 3H), 6.60 (d, *J* = 8.6 Hz, 1H), 3.95 – 3.86 (m, 2H), 3.77 – 3.71 (m, 1H), 3.62 (s, 3H), 1.63 (s, 3H), 0.85 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, CD_3CN) δ 168.9, 155.1, 148.5, 147.7, 143.7, 141.8, 135.1, 134.4, 130.8, 129.9, 129.5, 129.4, 129.0, 128.6, 128.0, 127.7, 127.0, 126.9, 123.1, 121.4, 121.3, 118.6, 111.9, 111.0, 88.3, 88.3, 77.5, 77.2, 77.0, 61.6, 56.4, 45.9, 14.2, 12.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{36}H_{31}O_5$: 543.2166, found 543.2157.

Ethyl (4R,9R,10R)-1-methyl-10-(naphthalen-1-yl)-3,4-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3na)



3na

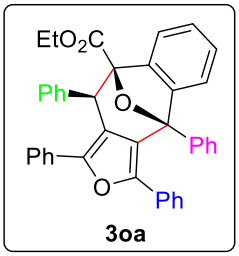
Prepared according to the general procedure using enynone **1n** (37mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (30 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a colourless solid.
Yield = 80% (45 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 7.4 Hz, 1H), 7.85 (d, *J* = 6.8 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 3H), 7.57 – 7.49 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.35 (dt, *J* = 13.7, 7.4 Hz, 3H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 9.2 Hz, 2H), 7.09 (d, *J* = 6.6 Hz, 2H), 6.99 (d, *J* = 6.2 Hz, 3H), 5.16 (s, 1H), 3.73 – 3.65 (m, 1H), 3.36 – 3.27 (m, 1H), 1.56 (s, 3H), 0.45 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 148.3, 147.7, 143.7, 142.6, 137.3, 135.2, 133.7, 132.0, 130.9, 129.7, 129.4, 129.1, 129.0, 128.6, 128.4, 128.1, 127.7, 127.7, 127.0, 126.9, 126.2, 126.1, 125.4, 123.6, 1231, 121.5, 121.4, 120.2, 88.3, 88.3, 61.2, 39.9, 13.4, 12.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{39}H_{31}O_4$: 563.2217, found 563.2207.

Ethyl (4R,9R,10R)-1,3,4,10-tetraphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3oa)



3oa

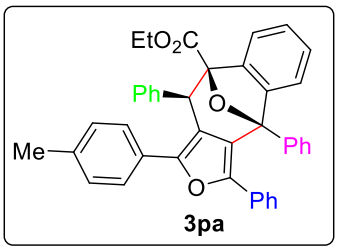
Prepared according to the general procedure using enynone **1o** (31mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (30 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a colourless solid.
Yield = 90% (51.8 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.76 – 7.70 (m, 3H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.51 (dt, *J* = 16.3, 7.6 Hz, 3H), 7.45 – 7.40 (m, 6H), 7.34 (t, *J* = 7.9 Hz, 3H), 4.80 (s, 1H), 4.24 (p, *J* = 7.3 Hz, 1H), 4.08 (q, *J* = 10.7, 9.0 Hz, 1H), 1.17 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 148.4, 148.1, 144.4, 141.5, 140.0, 135.1, 130.6, 130.4, 130.3, 129.6, 129.4, 129.0, 128.6, 128.3, 128.2, 128.0, 127.7, 127.45, 127.42, 127.36, 127.31, 125.3, 123.5, 123.0, 121.0, 120.1, 88.3, 88.2, 61.5, 48.1, 14.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{40}H_{31}O_4$: 575.2217, found 575.2216.

Ethyl (4R,9R,10R)-3,4,10-triphenyl-1-(p-tolyl)-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3pa)



3pa

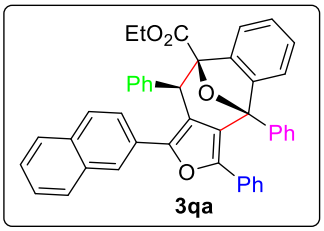
Prepared according to the general procedure using enynone **1p** (32mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (30 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a colourless solid.
Yield = 84% (49.4 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.4 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.67 (dd, *J* = 15.4, 7.5 Hz, 3H), 7.45 (dd, *J* = 13.0, 7.4 Hz, 4H), 7.37 (p, *J* = 8.0, 7.5 Hz, 7H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 5.9 Hz, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.74 (s, 1H), 4.19 (dq, *J* = 15.0, 7.2 Hz, 1H), 4.06 – 3.96 (m, 1H), 2.32 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 148.7, 148.1, 144.0, 141.5, 140.2, 137.1, 135.1, 130.6, 130.4, 129.5, 129.4, 129.0, 128.9, 128.6, 128.2, 128.0, 127.7, 127.6, 127.4, 127.3, 127.2, 125.2, 123.5, 122.9, 121.0, 119.2, 88.3, 88.2, 61.5, 48.1, 21.3, 14.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{41}H_{33}O_4$: 589.2374, found .

Ethyl (4R,9R,10R)-1-(naphthalen-2-yl)-3,4,10-triphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (3qa)



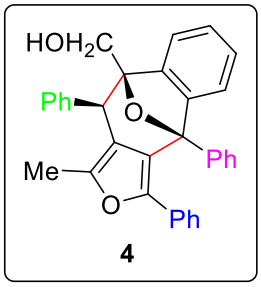
Prepared according to the general procedure using enynone **1q** (36mg, 0.1 mmol, 1.0 eq.), cat **$AgSbF_6$** (1.7mg, 0.005mmol, 5 mol%) and α-diazo ester **2a** (30 mg, 0.1 mmol, 1.0 eq.) in dry DCM. The product was obtained after column chromatography (hexane/EtOAc =20:1) as a colourless solid. **Yield** = 88% (55 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 6.8 Hz, 3H), 7.65 (q, *J* = 9.3, 8.7 Hz, 6H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.37 (dt, *J* = 13.5, 7.1 Hz, 5H), 7.29 (dt, *J* = 15.4, 8.5 Hz, 7H), 7.13 (d, *J* = 5.0 Hz, 3H), 4.73 (s, 1H), 4.10 (p, *J* = 7.2 Hz, 1H), 3.93 (p, *J* = 7.3 Hz, 1H), 1.03 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 148.6, 148.1, 144.7, 141.6, 140.3, 135.1, 133.2, 132.4, 130.6, 130.6, 129.6, 129.5, 129.0, 128.7, 128.3, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 126.4, 126.2, 124.4, 123.6, 123.3, 123.2, 121.1, 120.5, 88.4, 88.2, 61.6, 48.3, 14.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{44}H_{33}O_4$: 625.2374, found 625.2374.

((4R,9R,10R)-1-methyl-3,4,10-triphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-yl)methanol (4)



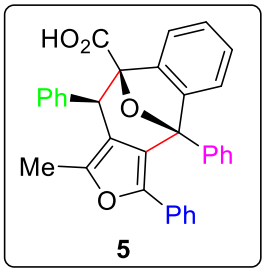
Colourless solid, **Yield** = 93% (22 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.52 (t, *J* = 7.0 Hz, 3H), 7.35 (t, *J* = 6.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 4H), 7.23 (t, *J* = 7.6 Hz, 3H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 5.7 Hz, 3H), 3.85 (s, 1H), 3.79 (d, *J* = 12.5 Hz, 1H), 3.41 (d, *J* = 12.4 Hz, 1H), 1.76 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 148.3, 144.5, 143.2, 141.0, 136.0, 130.9, 129.4, 129.4, 129.1, 128.7, 128.2, 128.0, 127.7, 127.2, 126.9, 126.8, 122.4, 122.4, 121.2, 119.7, 87.7, 87.6, 64.5, 45.9, 12.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{33}H_{27}O_3$: 471.1955, found 471.1955.

(4R,9R,10R)-1-methyl-3,4,10-triphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylic acid (5)



5

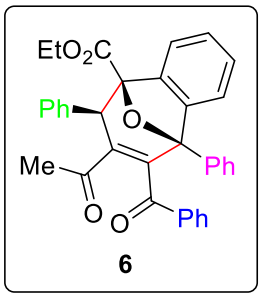
Yellow solid, **Yield** = 75% (19 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.64 (dt, *J* = 16.4, 7.2 Hz, 4H), 7.57 (t, *J* = 6.6 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.46 (q, *J* = 7.2 Hz, 4H), 7.36 – 7.32 (m, 2H), 7.26 (s, 3H), 4.48 (s, 1H), 4.00 (s, 1H), 2.03 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 199.5, 148.8, 146.9, 143.7, 140.9, 140.0, 137.6, 137.3, 134.8, 134.2, 133.8, 132.2, 132.0, 131.1, 131.0, 130.6, 129.8, 129.7, 129.3, 129.3, 128.7, 128.6, 128.4, 128.3, 127.8, 127.5, 127.05, 127.00, 126.96, 123.3, 121.2, 121.0, 118.6, 89.4, 88.2, 46.3, 12.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{33}H_{25}O_4$: 485.1748, found 485.1737.

Ethyl (5R,6R,9R)-7-acetyl-8-benzoyl-6,9-diphenyl-6,9-dihydro-5H-5,9-epoxybenzo[7]annulene-5-carboxylate (6)



6

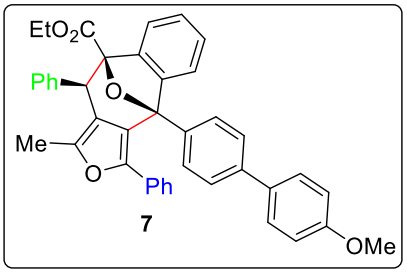
White solid, **Yield** = 76% (19 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.70 (q, *J* = 6.4, 5.4 Hz, 3H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.48 (p, *J* = 7.4 Hz, 4H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 4.28 – 4.20 (m, 1H), 4.18 (s, 1H), 4.09 – 4.01 (m, 1H), 1.86 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 198.6, 197.3, 168.1, 152.8, 148.7, 139.9, 137.1, 137.1, 135.5, 134.6, 133.9, 133.0, 130.6, 130.4, 130.0, 129.0, 128.8, 128.7, 128.63, 128.59, 128.4, 128.3, 127.4, 122.6, 122.0, 87.7, 87.3, 61.7, 48.3, 28.9, 14.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{35}H_{29}O_5$: 529.2010, found 529.2006.

Ethyl (4R,9R,10R)-4-(4'-methoxy-[1,1'-biphenyl]-4-yl)-1-methyl-3,10-diphenyl-4H-4,9-epoxybenzo[4,5]cyclohepta[1,2-c]furan-9(10H)-carboxylate (7)



7

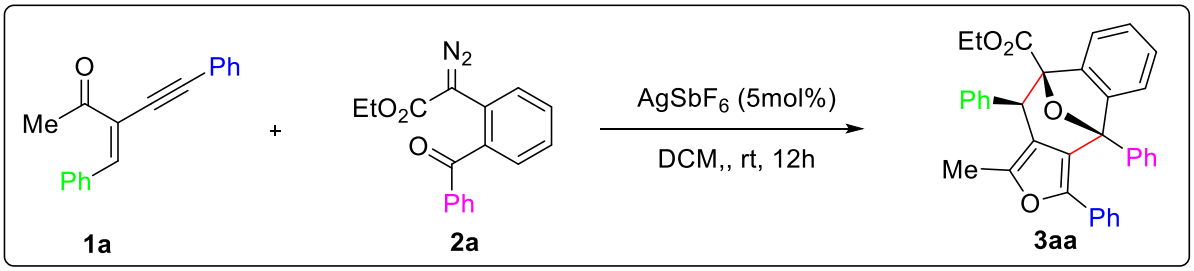
White solid, **Yield** = 76% (23.6 mg), **d.r.** = 20:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.39 (dd, *J* = 13.0, 7.4 Hz, 3H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.26 – 7.19 (m, 4H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 2H), 6.89 (q, *J* = 7.9, 7.2 Hz, 3H), 6.80 (d, *J* = 8.6 Hz, 2H), 4.08 (s, 1H), 3.91 (dd, *J* = 10.9, 7.1 Hz, 1H), 3.68 (s, 4H), 1.69 (s, 3H), 0.80 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.96, 158.23, 147.30, 146.58, 142.43, 140.97, 140.53, 139.51, 132.46, 132.41, 129.68, 128.79, 128.68, 127.69, 127.17, 127.04, 126.76, 126.49, 126.06, 125.86, 125.69, 125.65, 121.94, 120.10, 120.08, 117.73, 113.15, 87.10, 86.90, 60.17, 54.35, 45.97, 12.79, 10.85.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{42}H_{35}O_5$: 619.2479, found 619.2470.

8. Scale-up reaction for compound 3aa:



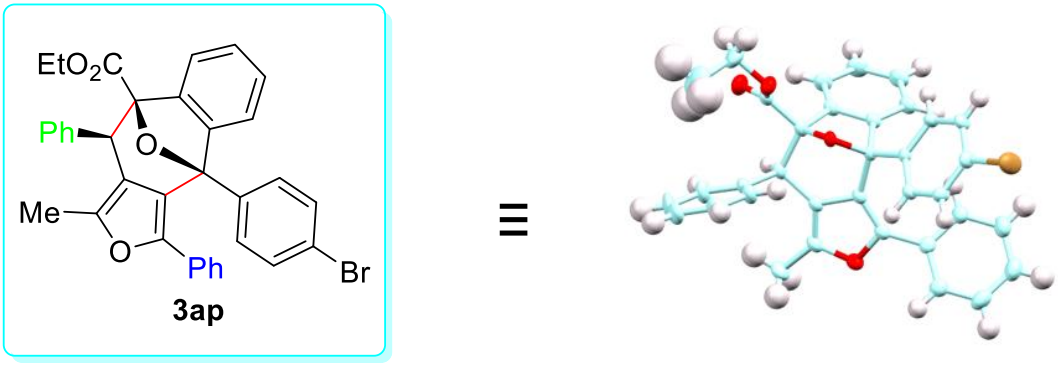
In a 10ml Rb Enynone **1a** (250mg, 1 mmol, 1.0 eq.), cat $AgSbF_6$ (17mg, 0.05mmol, 5 mol%), were suspended in dry DCM (20 mL). The reaction mixture was stirred at room temperature and a solution of α-diazo ester **2a** (300mg, 1 mmol, 1.0 eq.) dissolved in dry DCM (10 mL) was added dropwise and stirred at room temperature. After completed the reaction, check by TLC, the reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel eluting with ethyl-acetate: hexane (1 – 2 %) to afford the desired product with 94% (482 mg) yield. A little amount of yield is decreased with scale-up reaction.

9. Single crystal X-ray diffraction analysis:

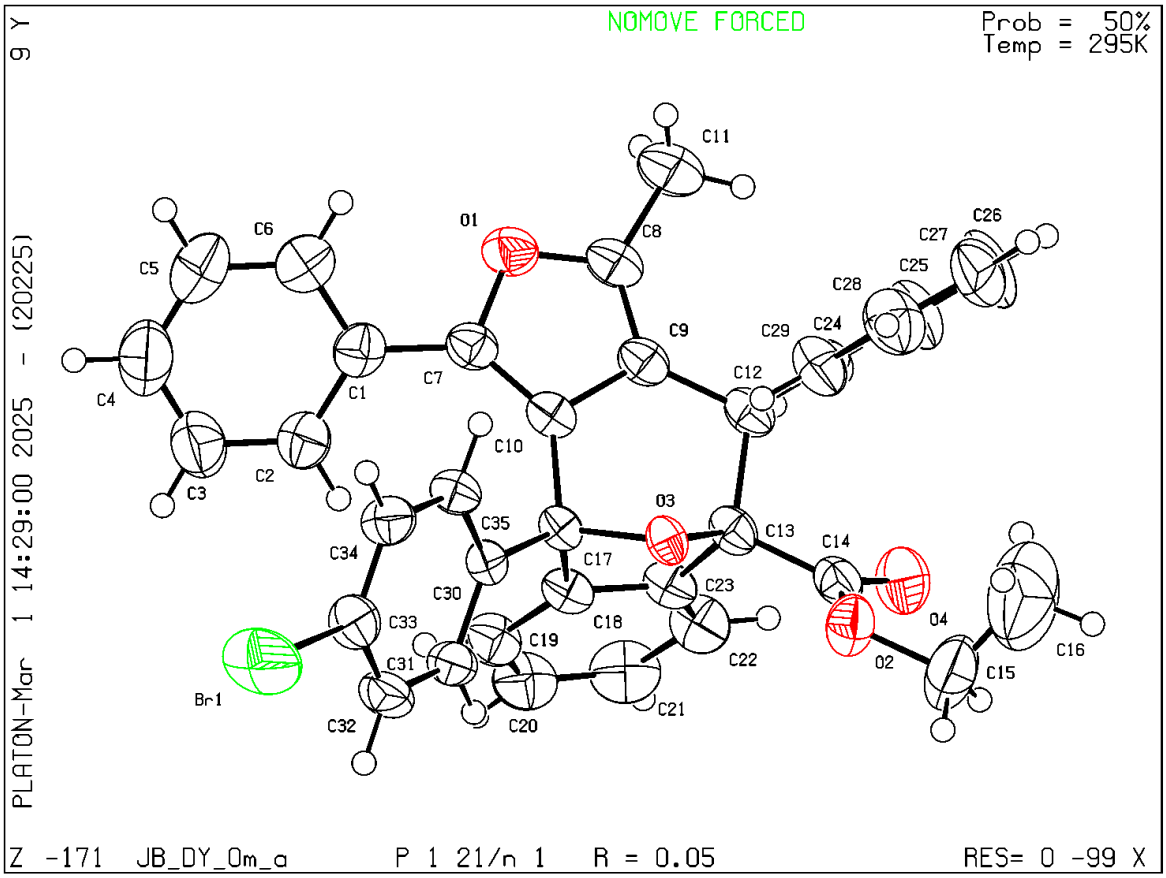
Method for crystal growth:

In a round bottom flask, compound **3ap** dissolved in minimum amount of hexane/DCM (3:1) and it kept in dark place at room temperature for slow evaporation to get colourless crystal of compound **3ap**. X-ray crystallographic data were collected using Bruker D8 QUEST diffractometer. Data refinement and cell reduction were carried out by APEX4. Structures were solved by direct methods using Olex2 v1.5 and refined by a full-matrix least-squares method using Olex2 v1.5. The ORTEP diagram was obtained with ORTEP3 software with 30% thermal ellipsoid. The crystallographic parameters and refinement data are:

CCDC No.	**2428178**
Empirical formula	$C_{35}H_{27}BrO_4$
Formula weight	591.505
Temperature/K	295.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	17.213(5)
b/Å	7.777(2)
c/Å	25.463(7)
α/°	90
β/°	105.237(8)
γ/°	90
Volume/Å^3	3288.9(16)
Z	4
ρ_{calc}g/cm^3	1.195
μ/mm^{-1}	1.283
F(000)	1215.9
Crystal size/mm^3	0.31 × 0.26 × 0.21
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.94 to 50.8
Index ranges	$-20 \le h \le 20$, $-9 \le k \le 9$, $-30 \le l \le 30$
Reflections collected	77508
Independent reflections	6001 [R_{int} = 0.0487, R_{sigma} = 0.0246]
Data/restraints/parameters	6001/0/363
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0641, wR_2 = 0.1951
Final R indexes [all data]	R_1 = 0.0793, wR_2 = 0.2106
Largest diff. peak/hole / e Å^{-3}	1.10/-0.69

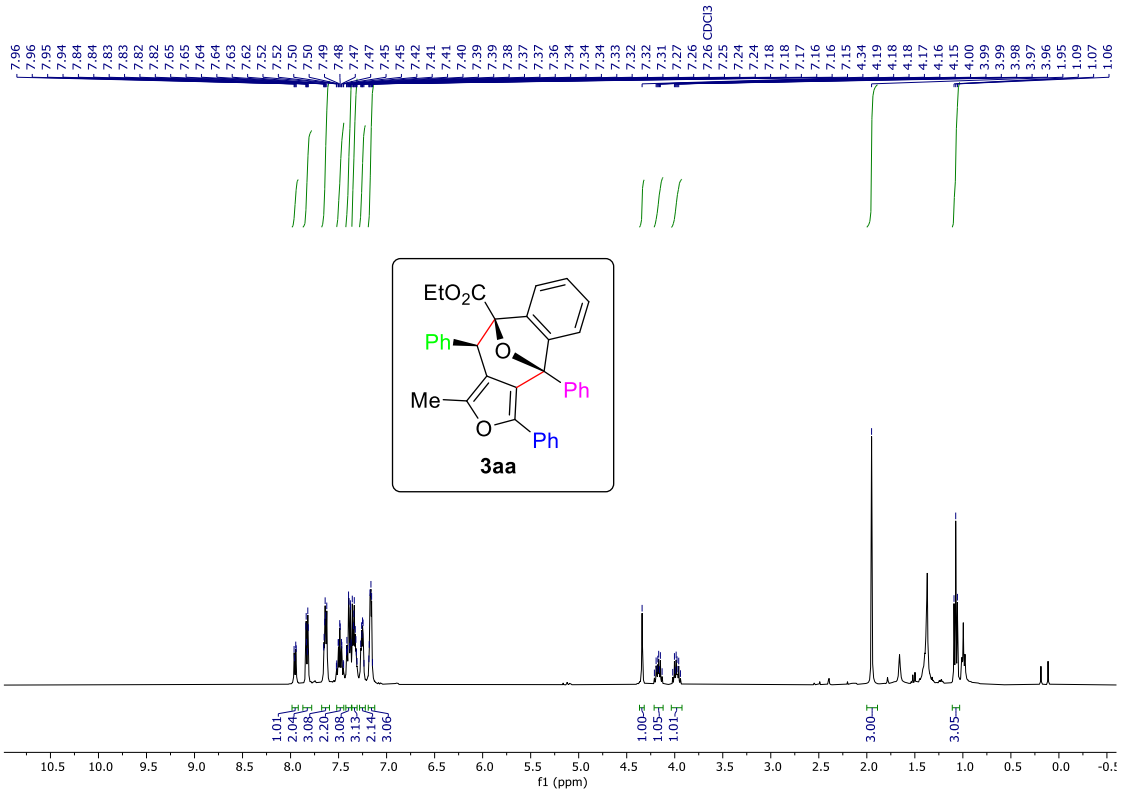


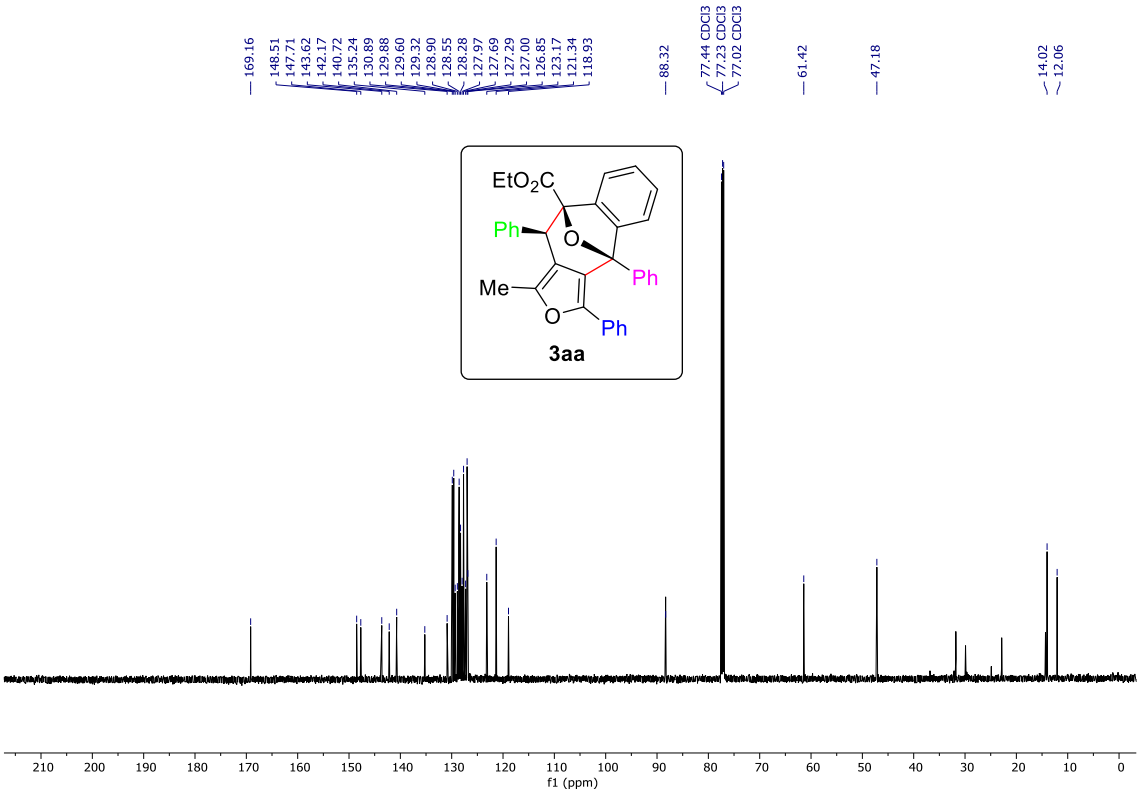
Ortep Diagram with 30 % ellipsoid probability of compound 3ap



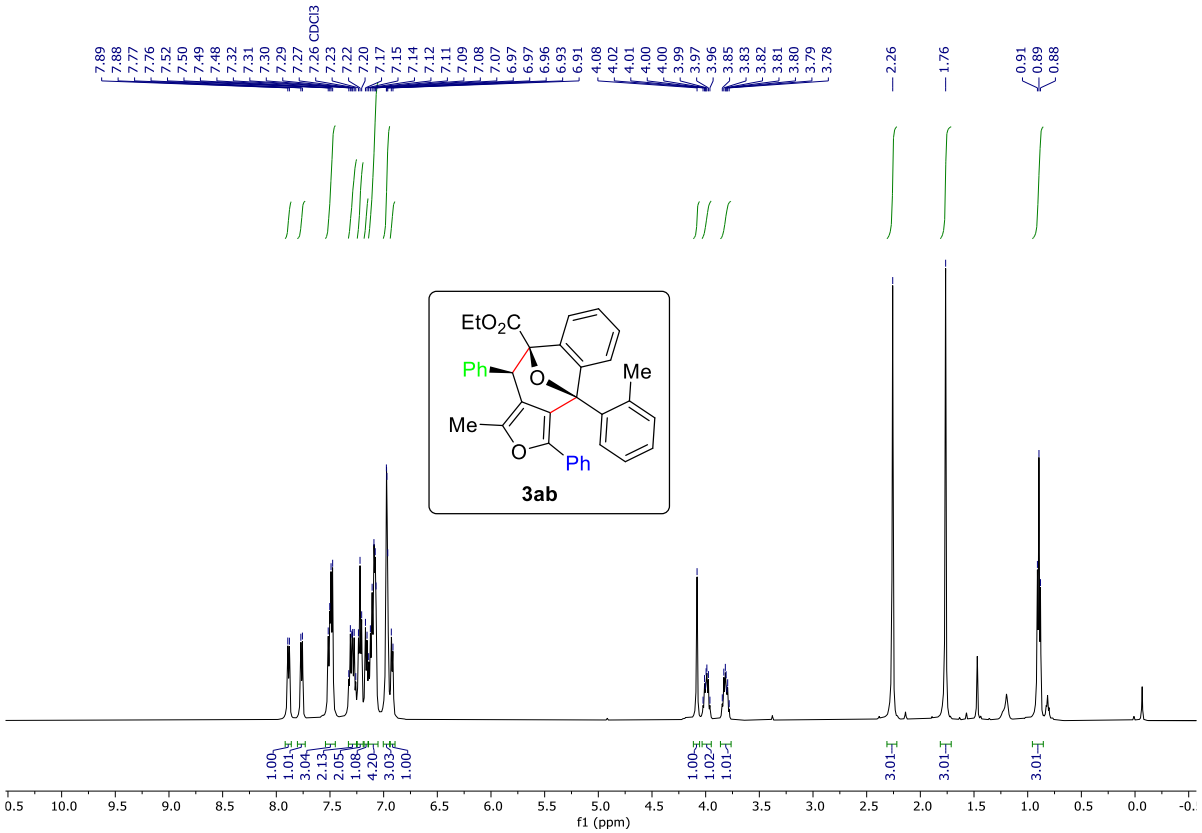
10. ^{1}H-NMR & ^{13}C NMR Spectra of product:

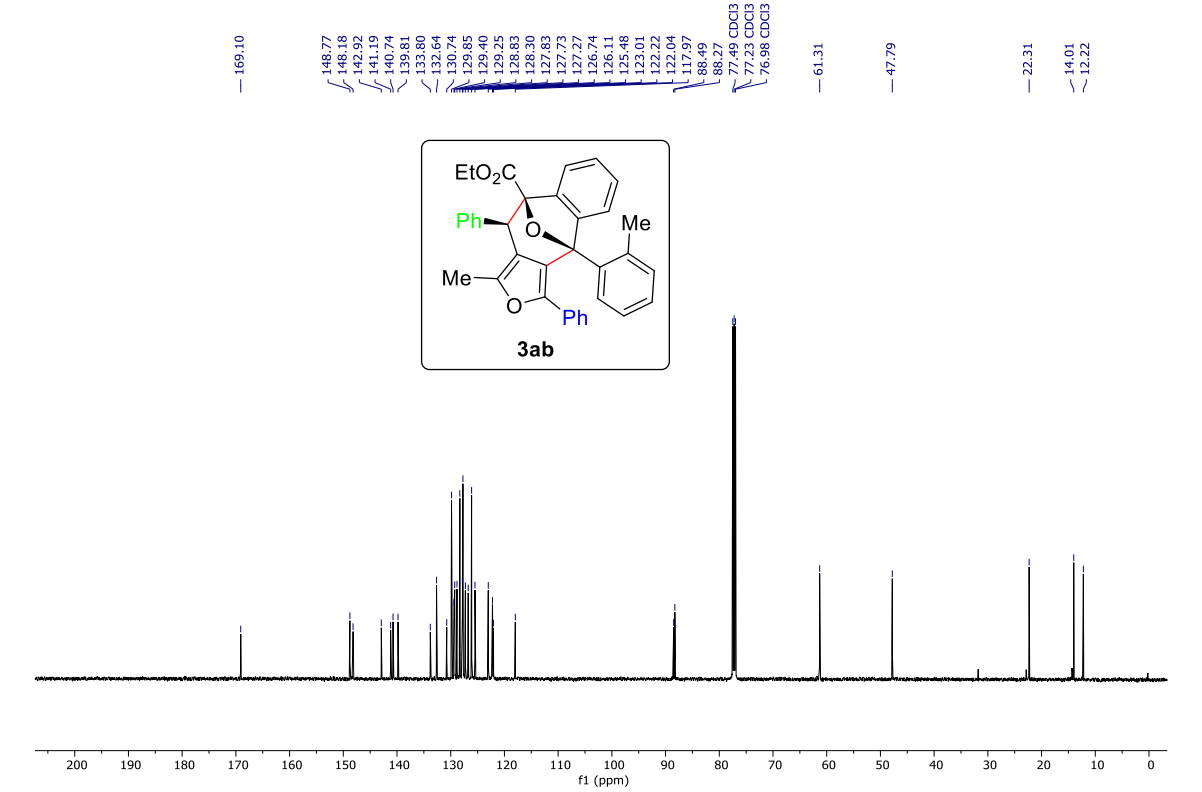
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3aa:



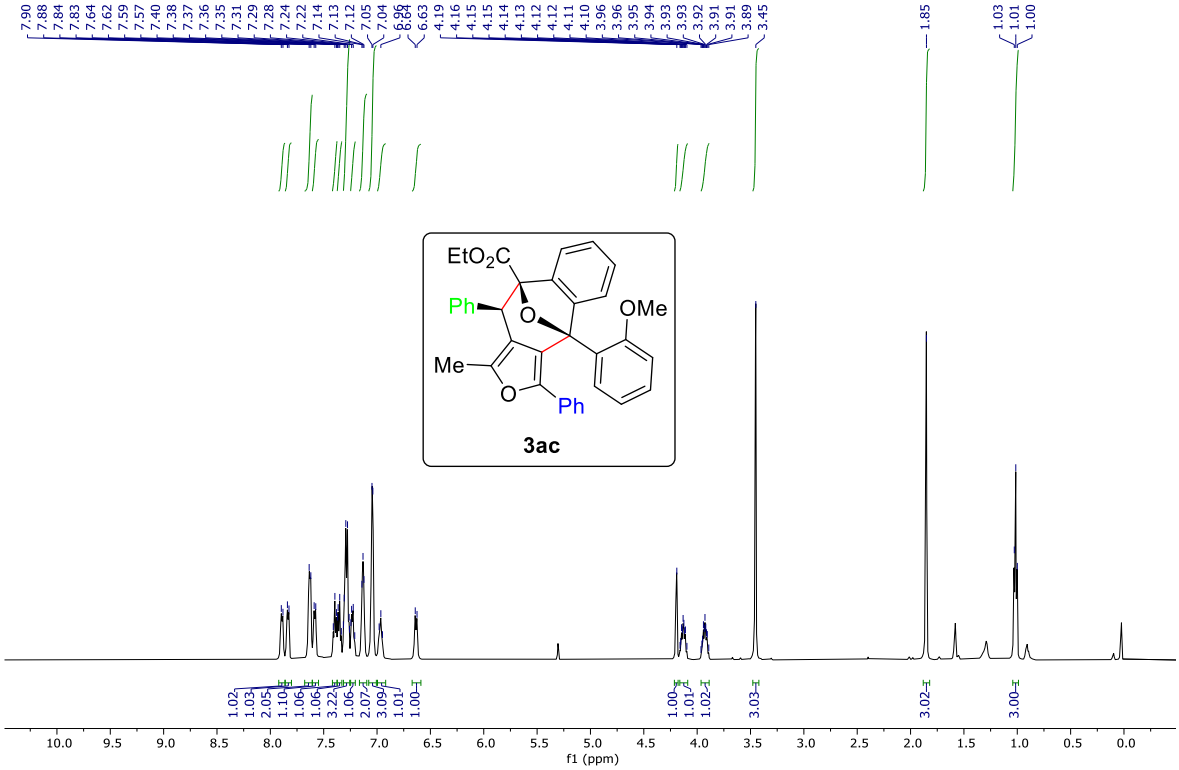


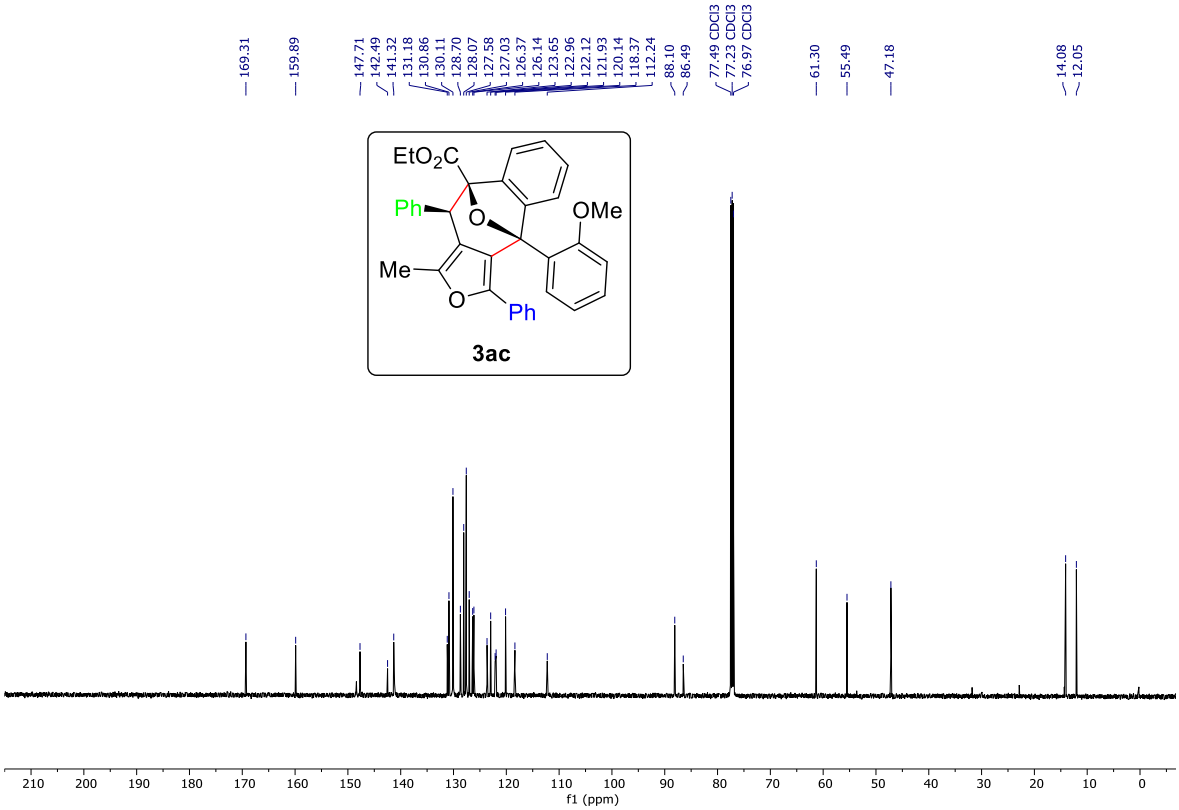
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3ab:



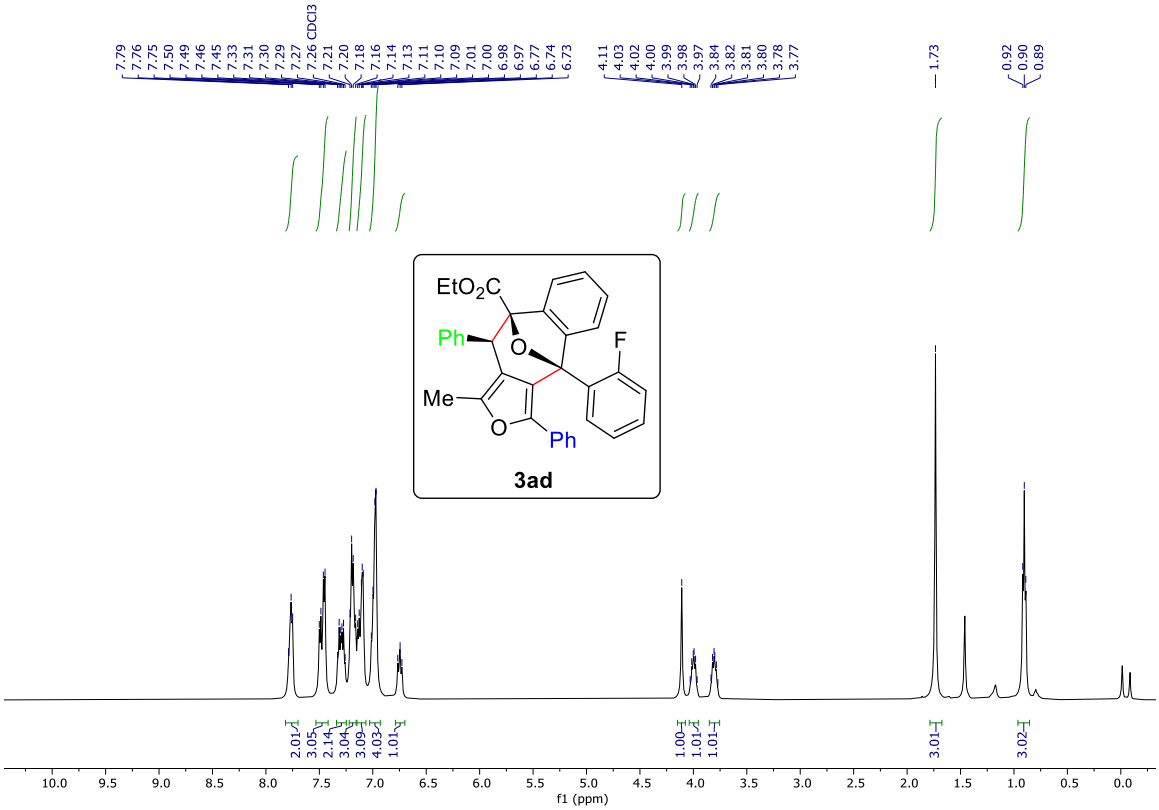


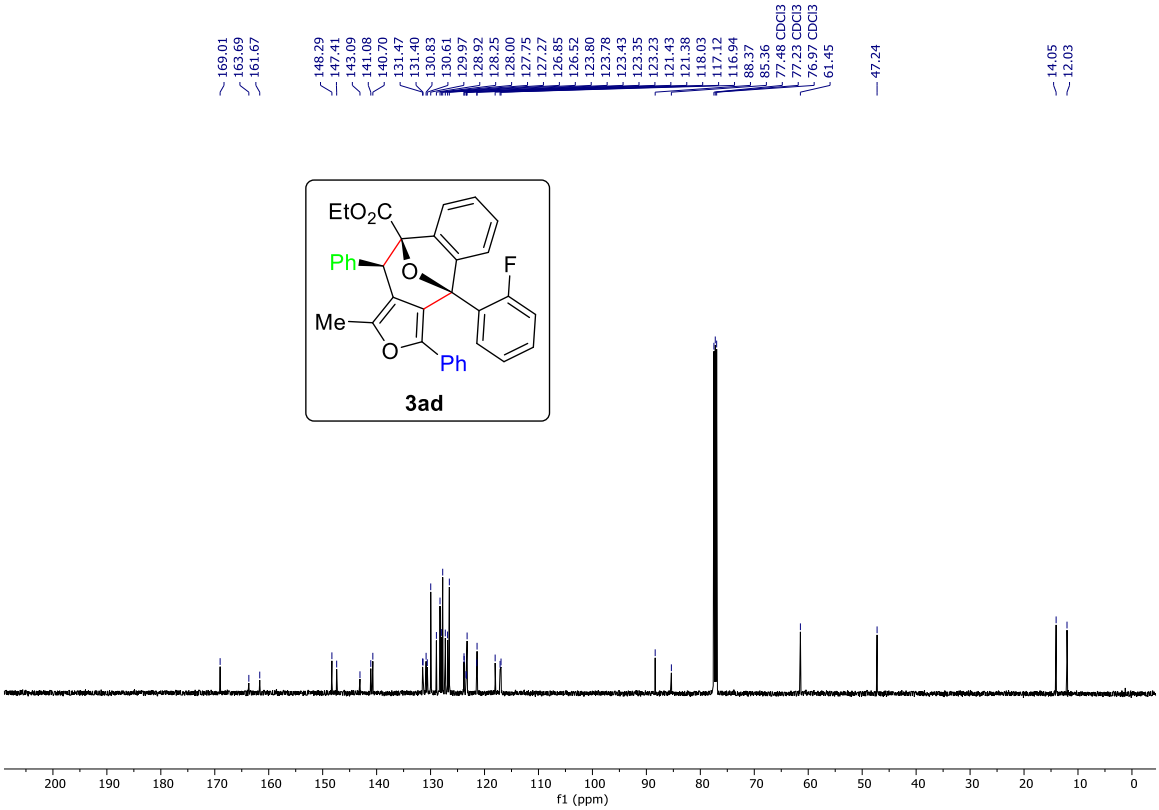
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3ac:



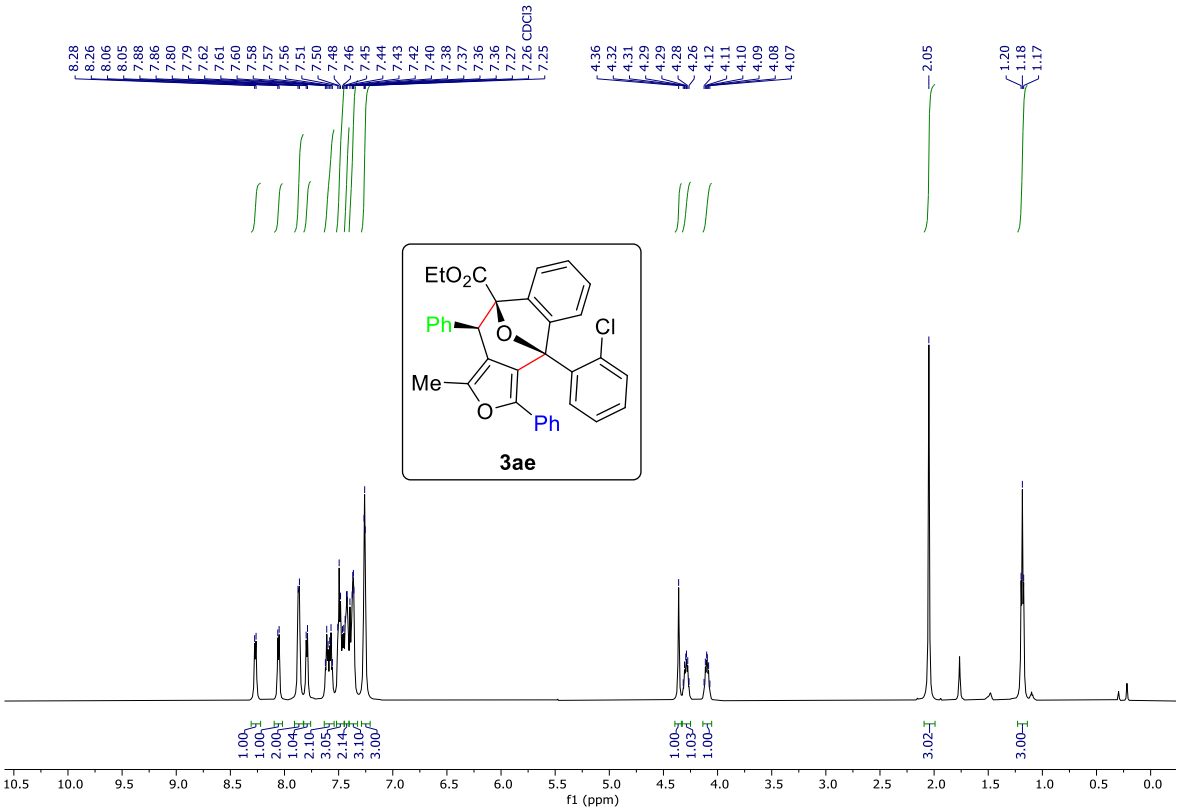


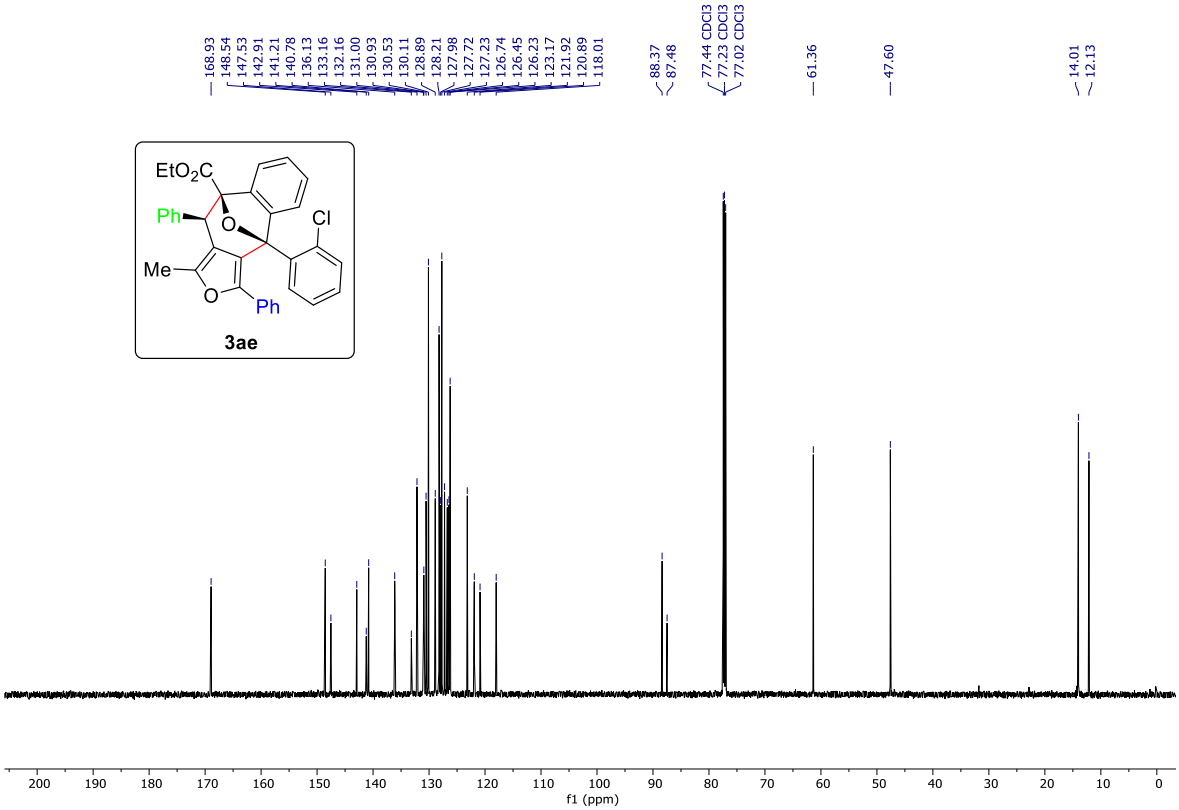
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3ad:



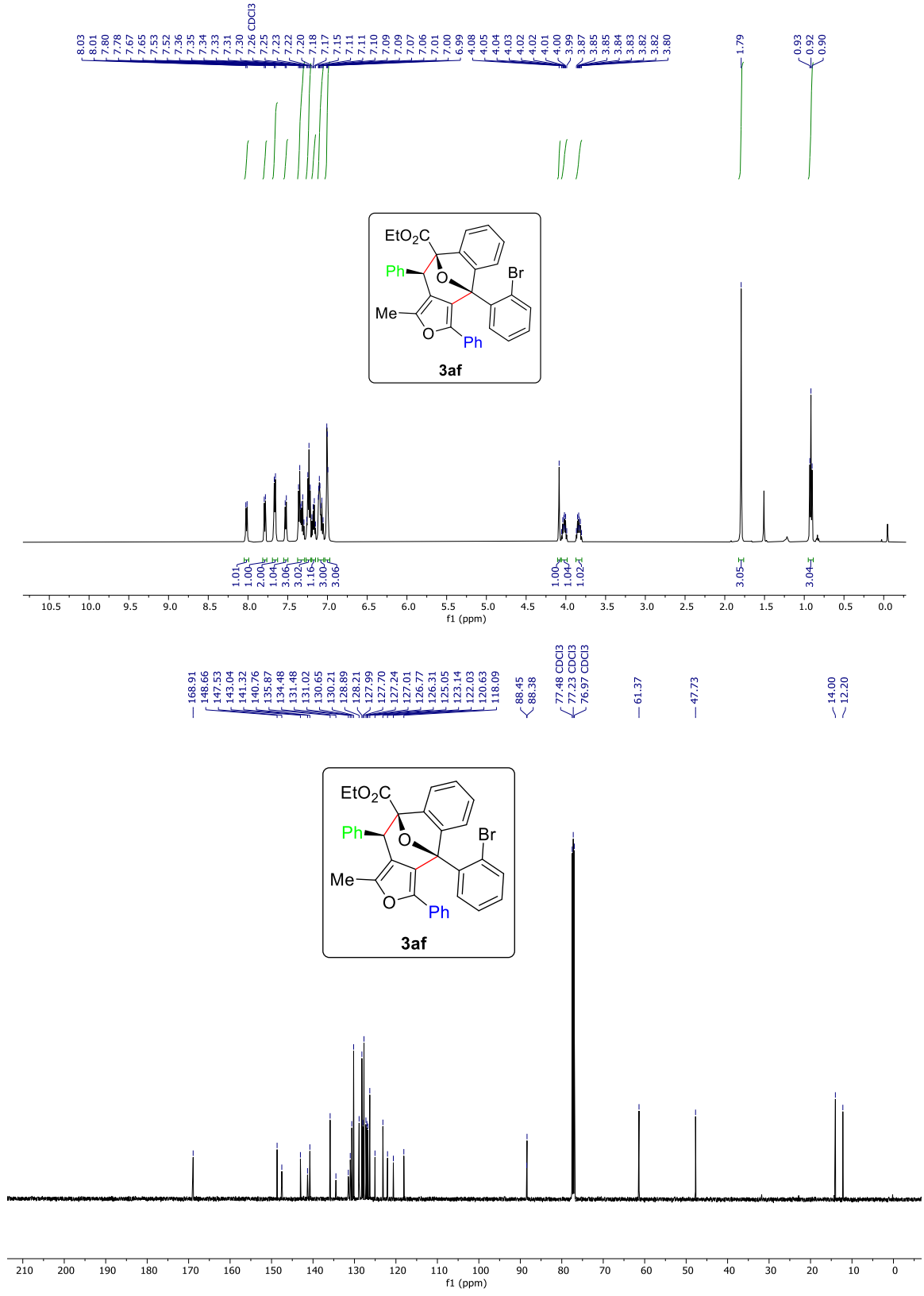


1H (600 MHz, $CDCl_3$) and 13C{H} (150 MHz, $CDCl_3$) NMR of 3ae:

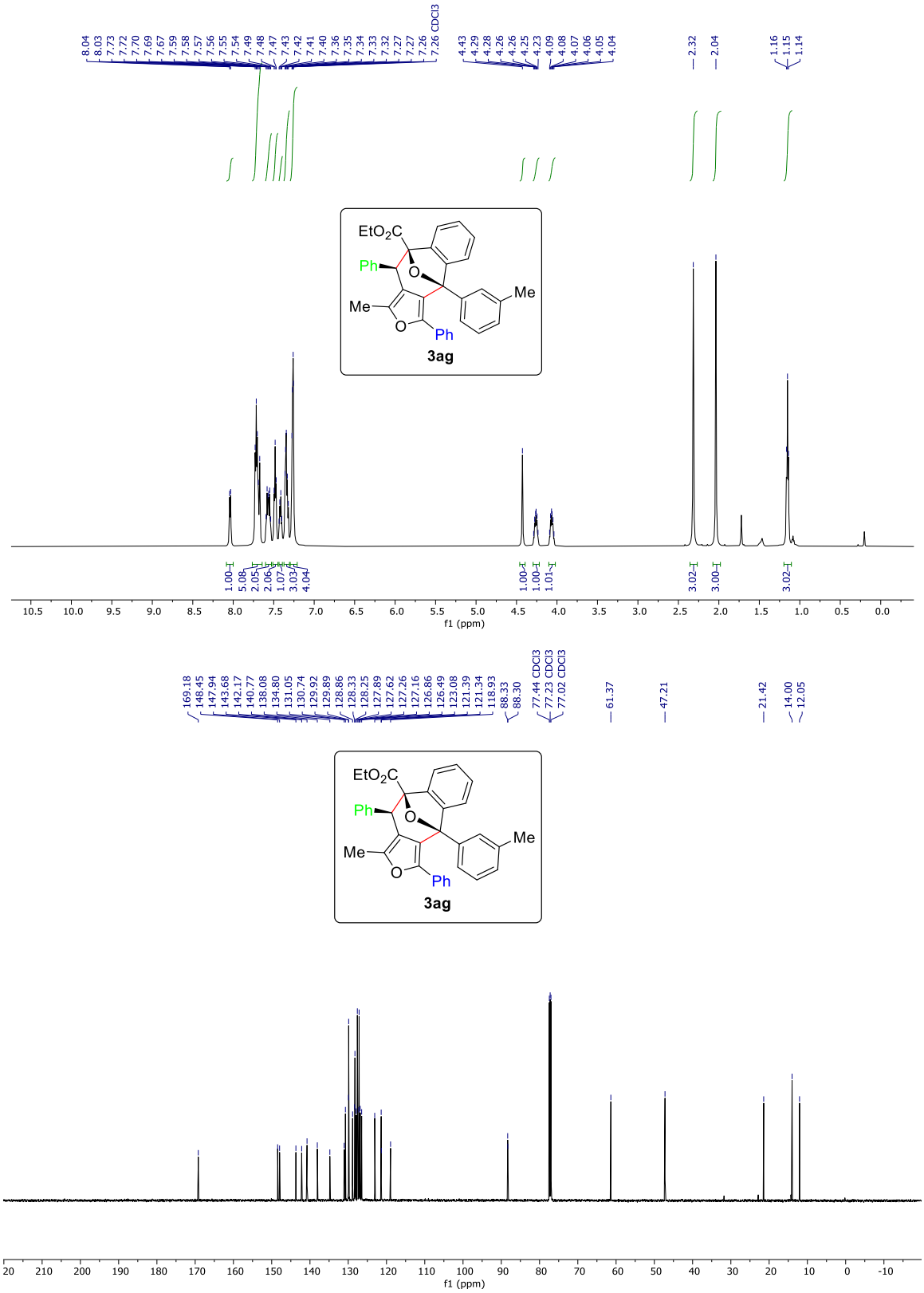




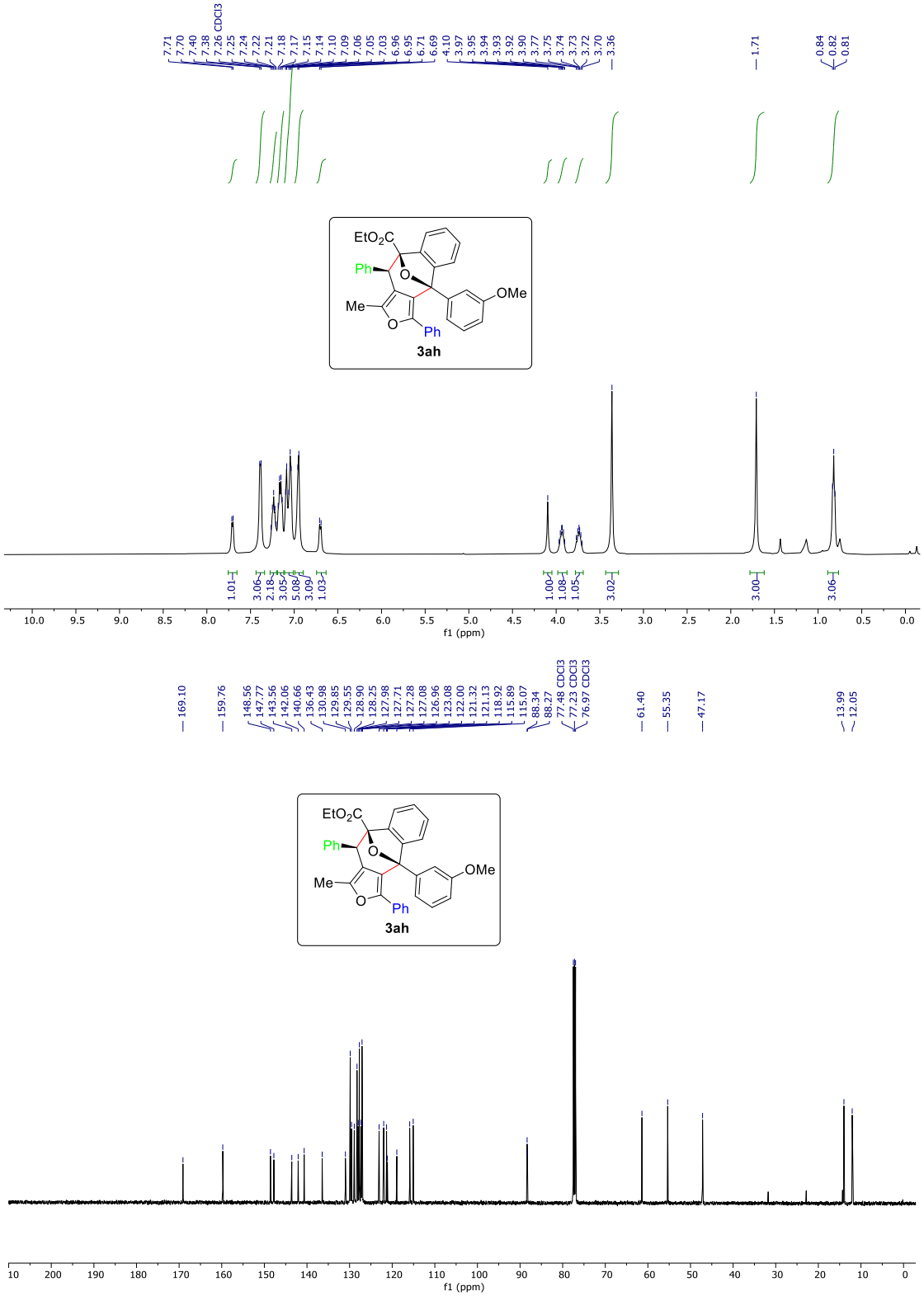
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3af:



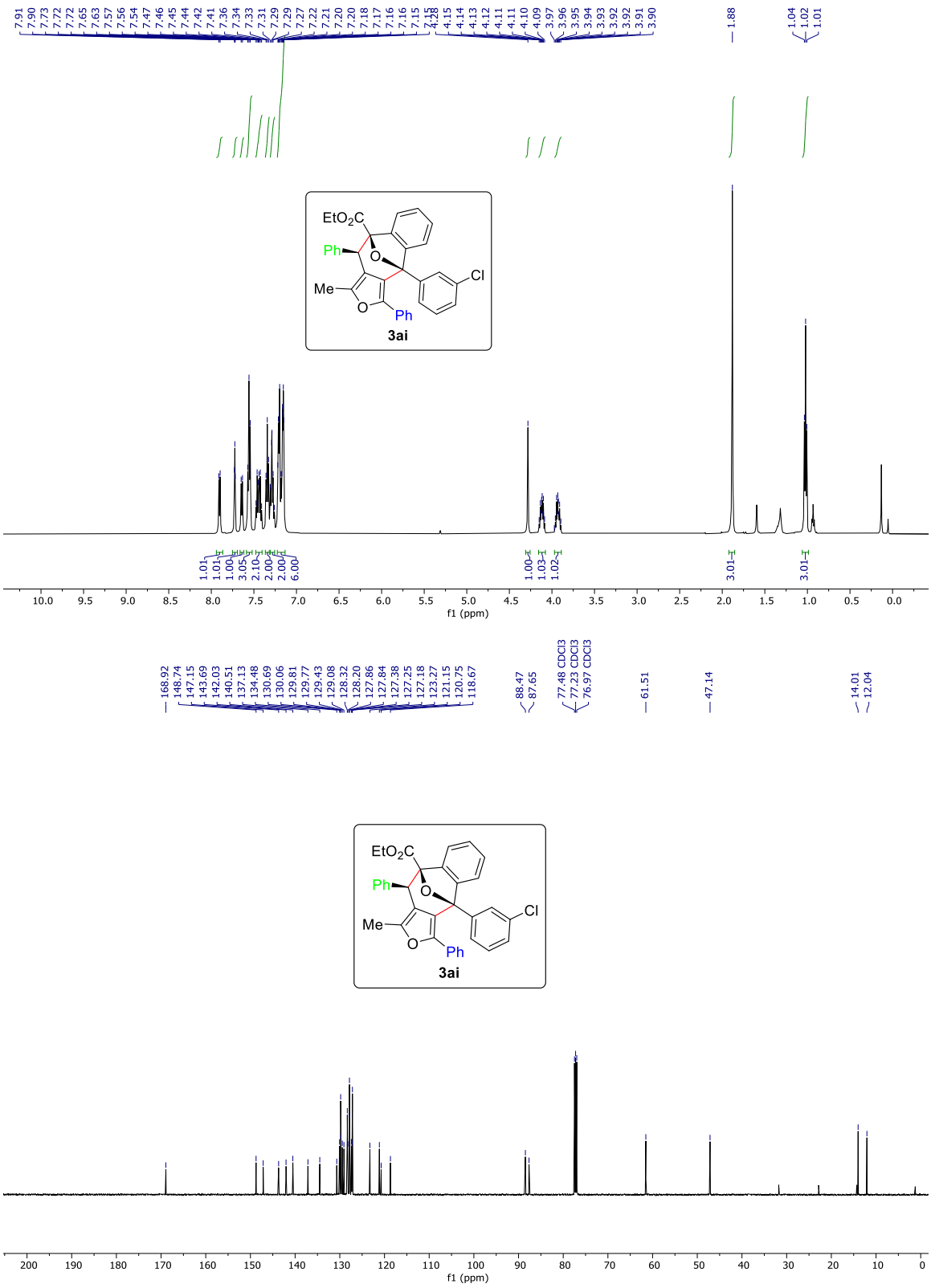
1H (600 MHz, $CDCl_3$) and 13C{H} (150 MHz, $CDCl_3$) NMR of 3ag:



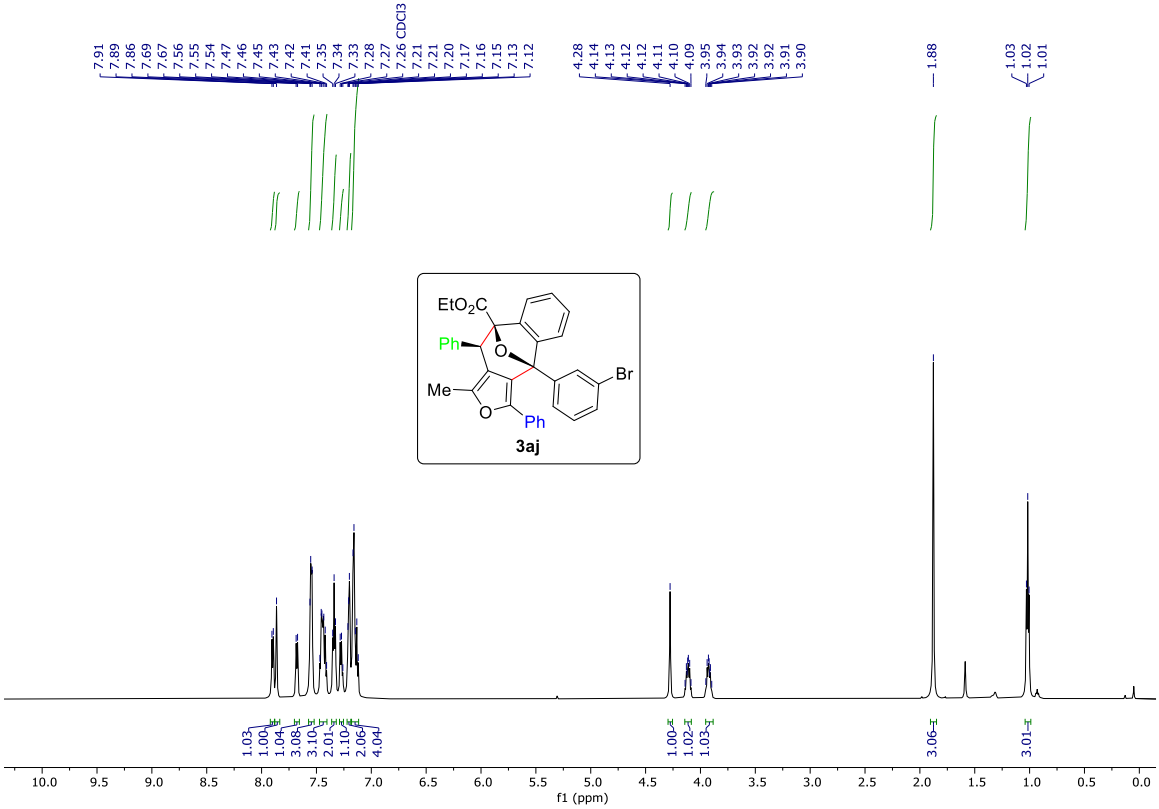
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3ah:

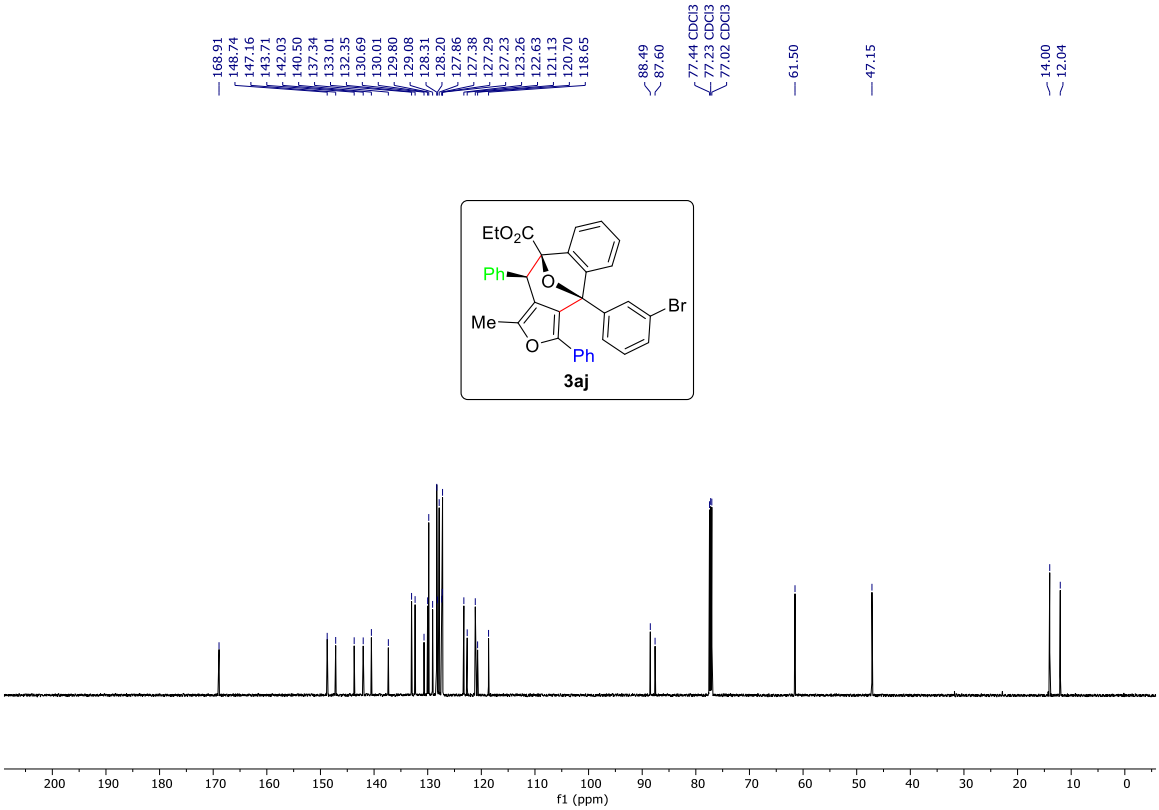


1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3ai:

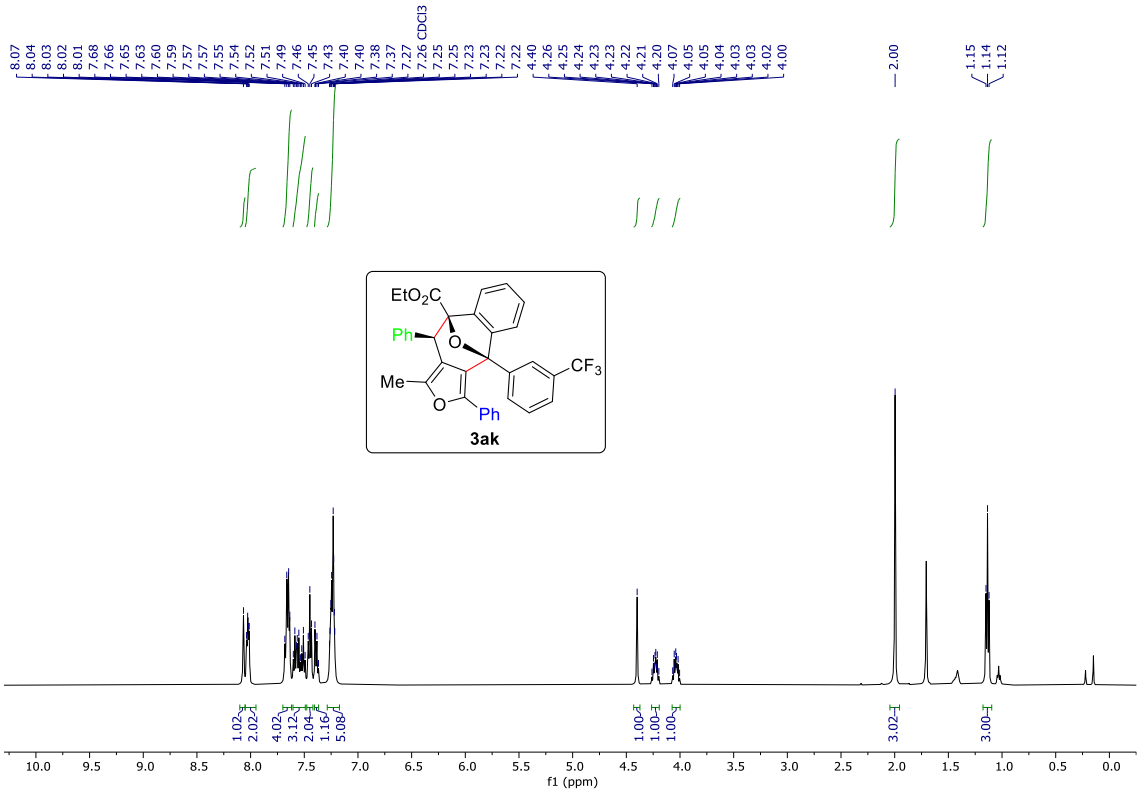


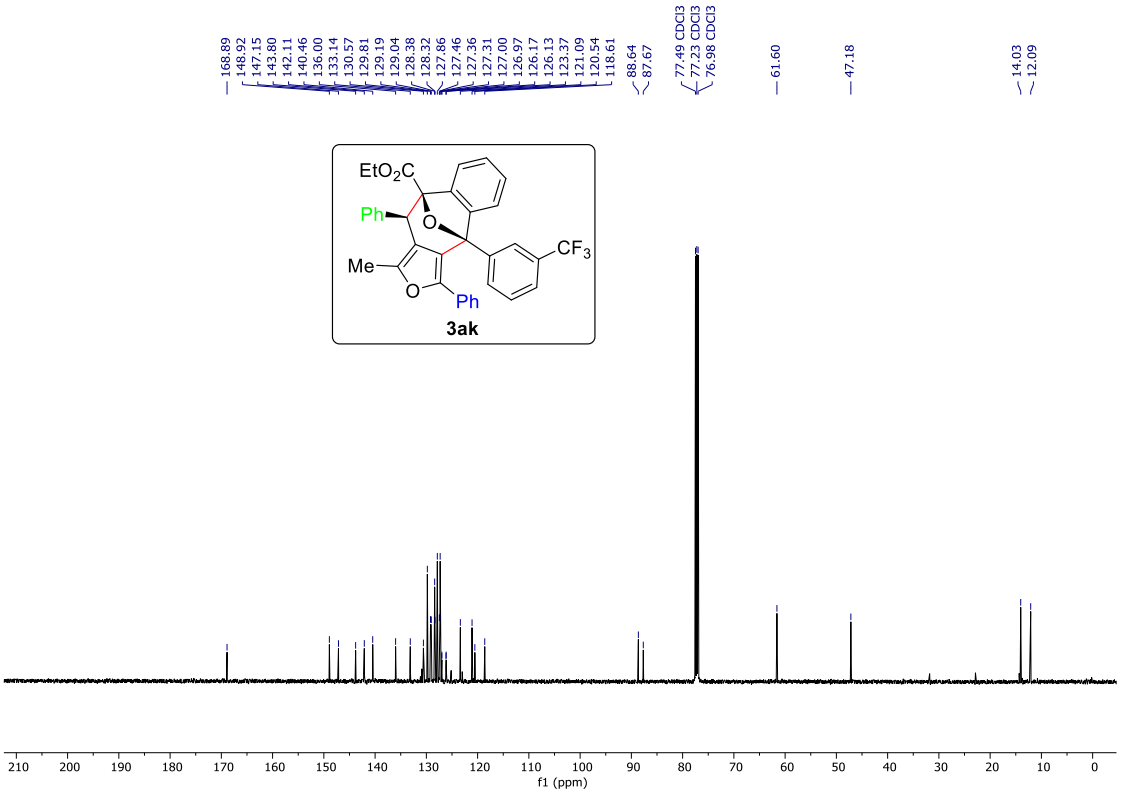
1H (600 MHz, $CDCl_3$) and 13C{H} (150 MHz, $CDCl_3$) NMR of 3aj:



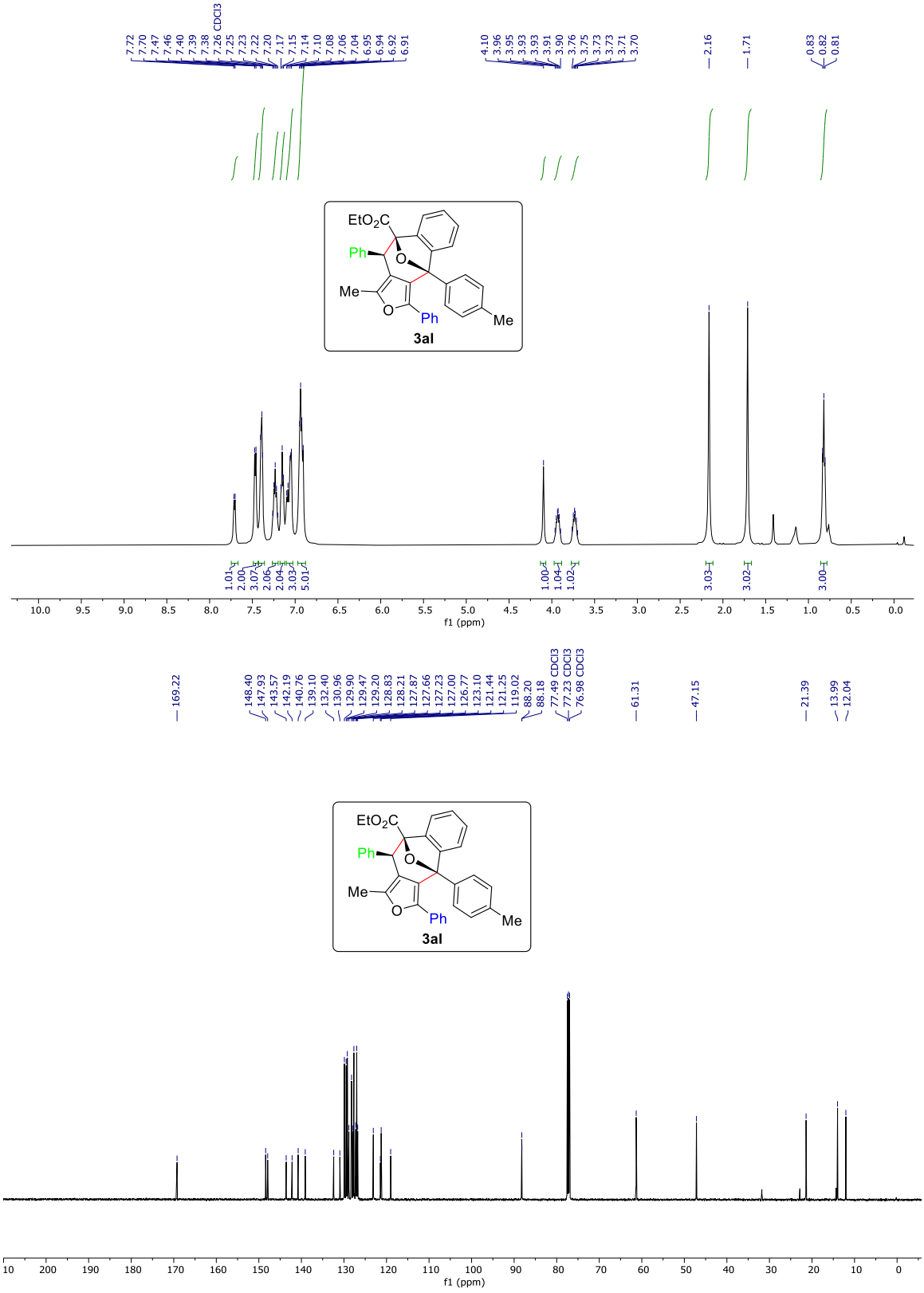


1H (600 MHz, $CDCl_3$) and 13C{H} (150 MHz, $CDCl_3$) NMR of 3ak:

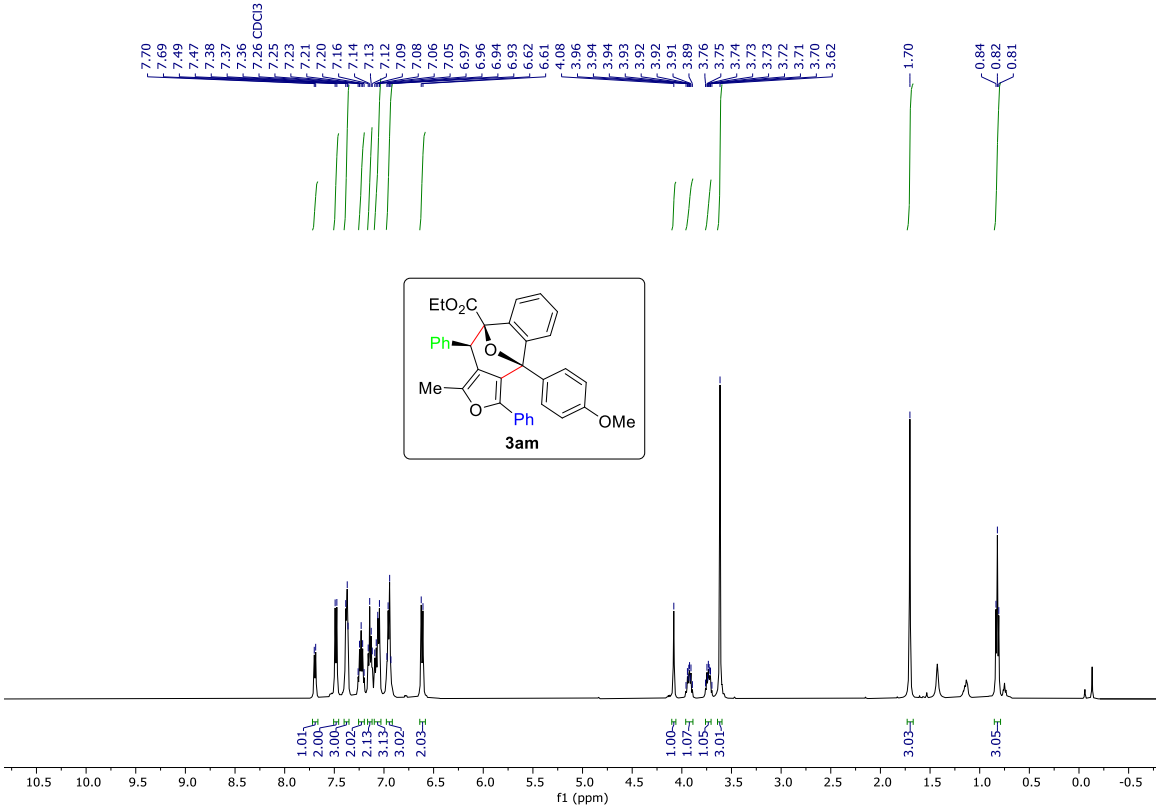


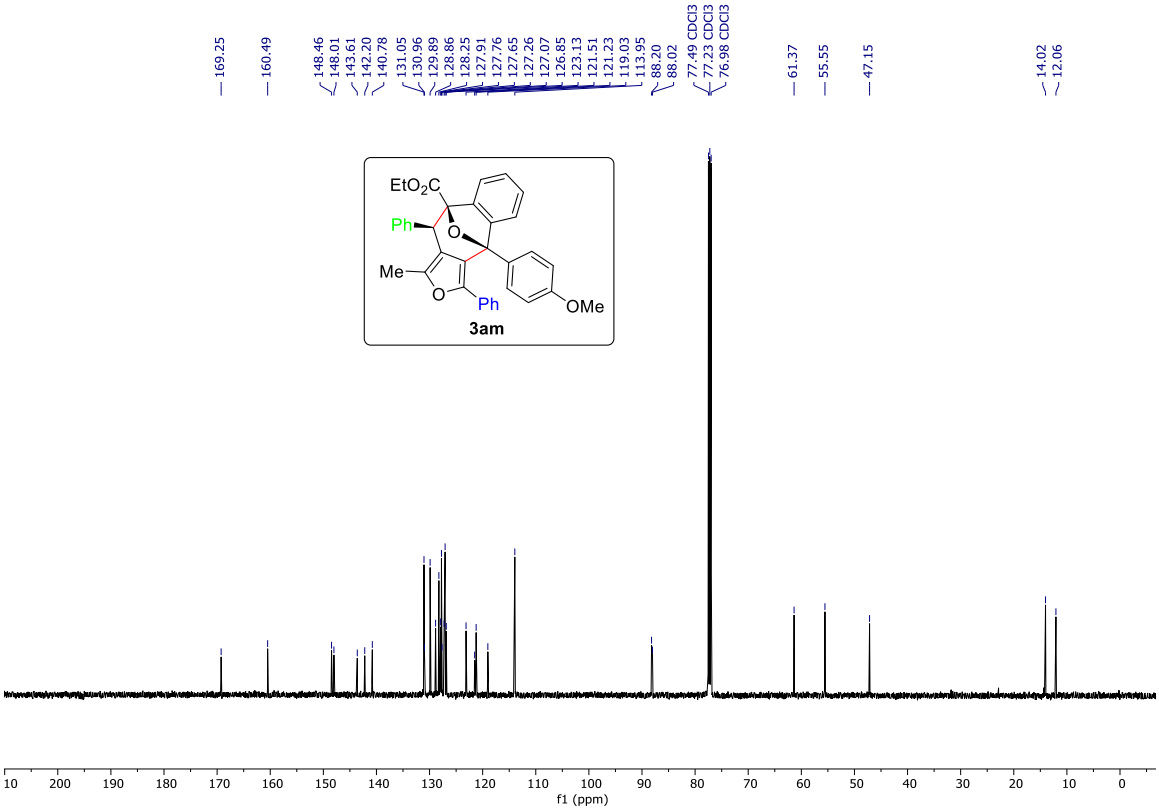


1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3al:

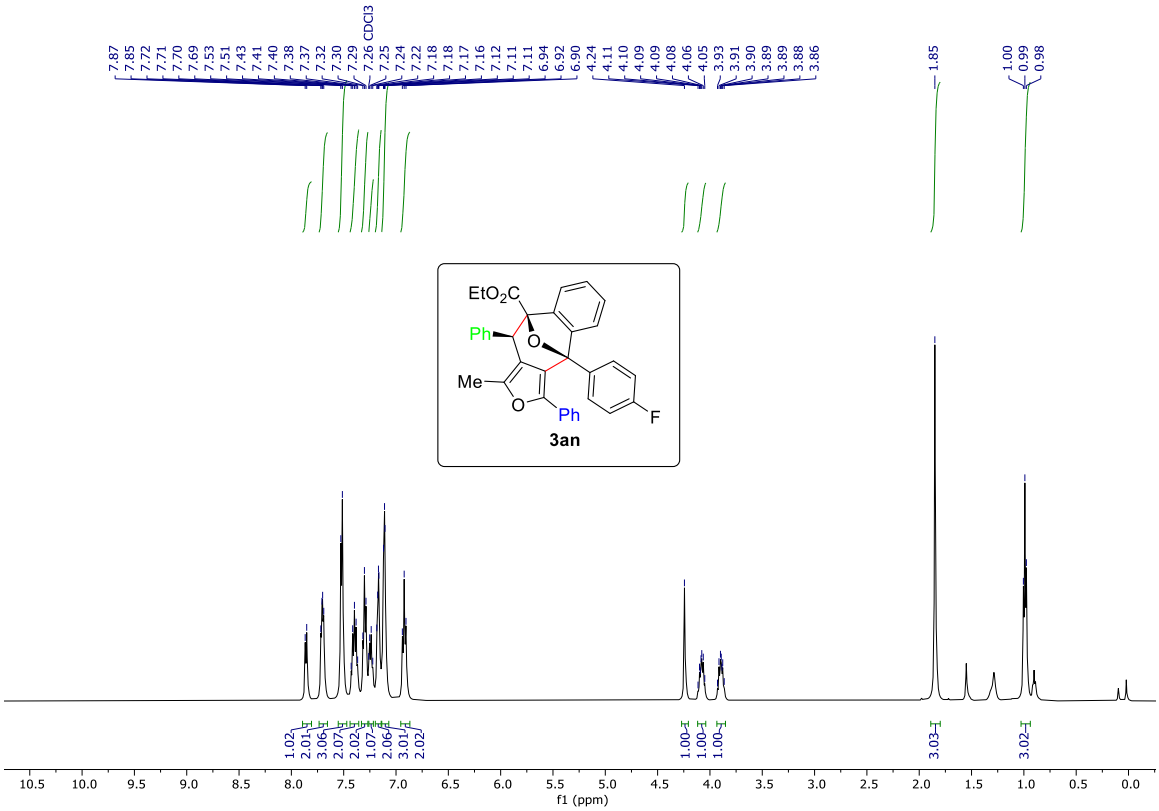


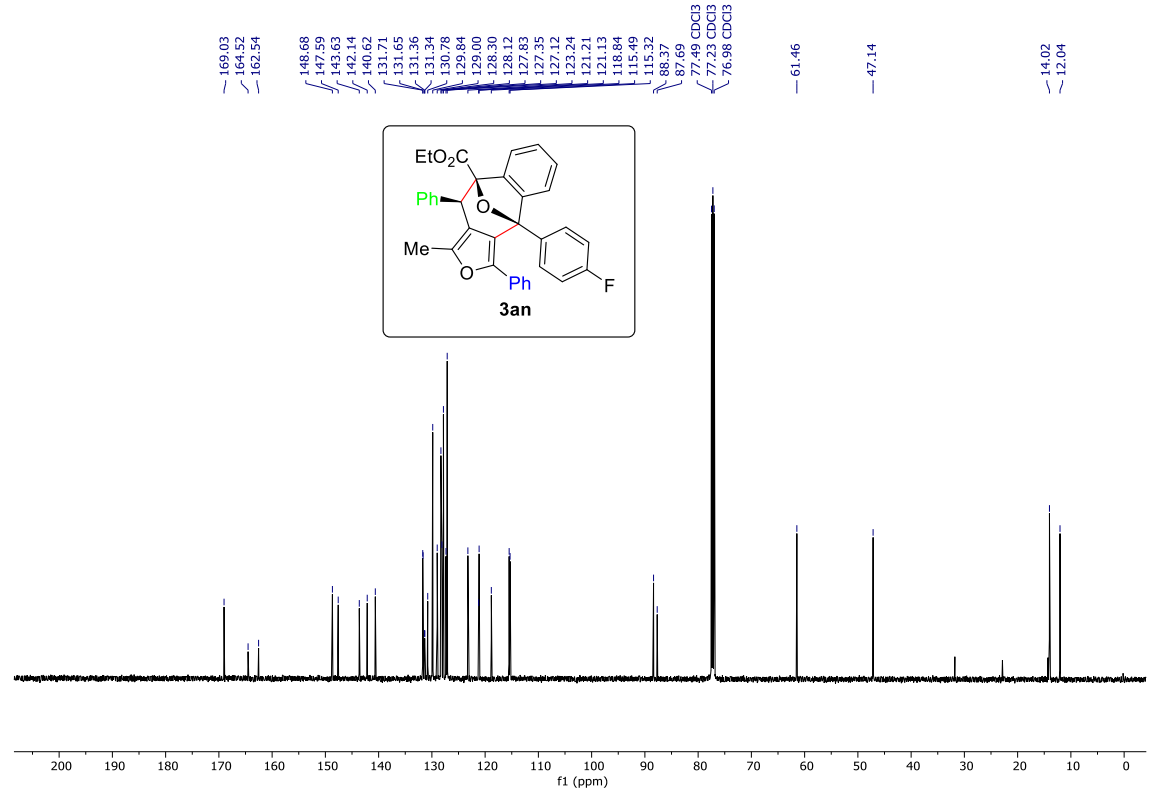
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3am:



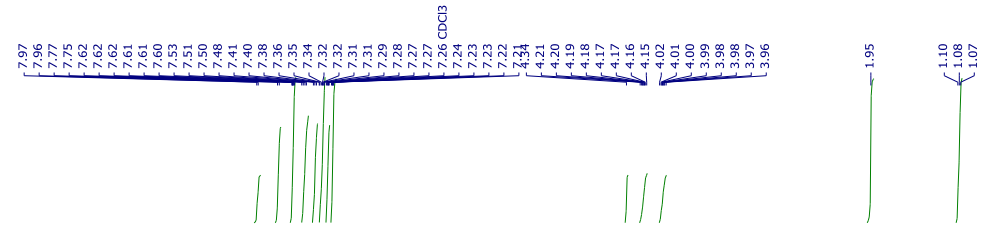


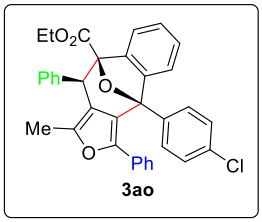
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3an:

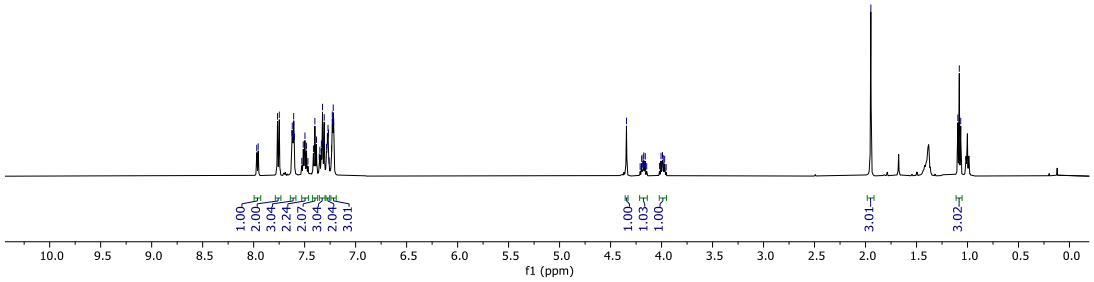


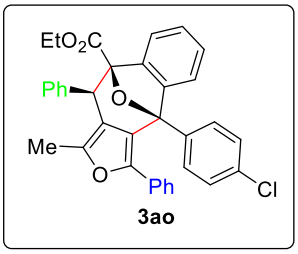


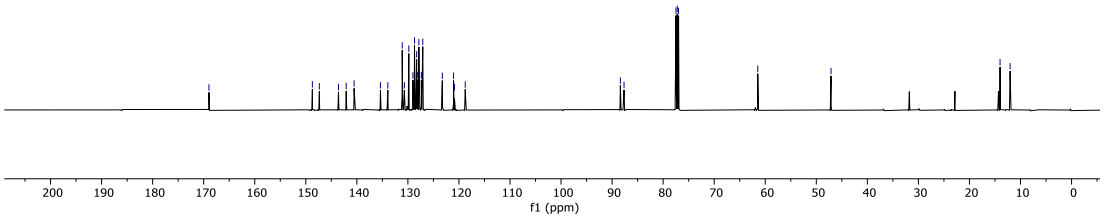
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3ao:



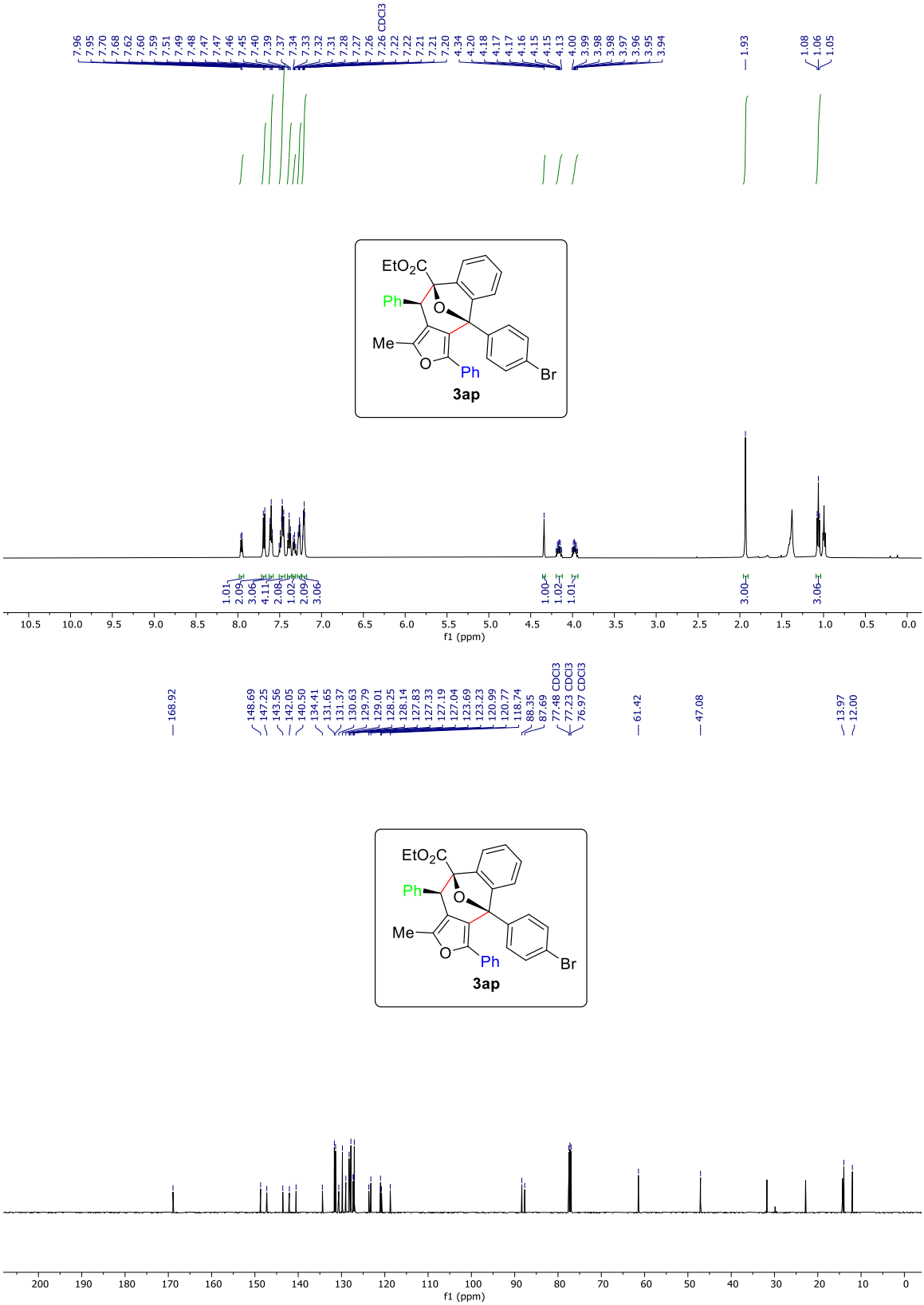




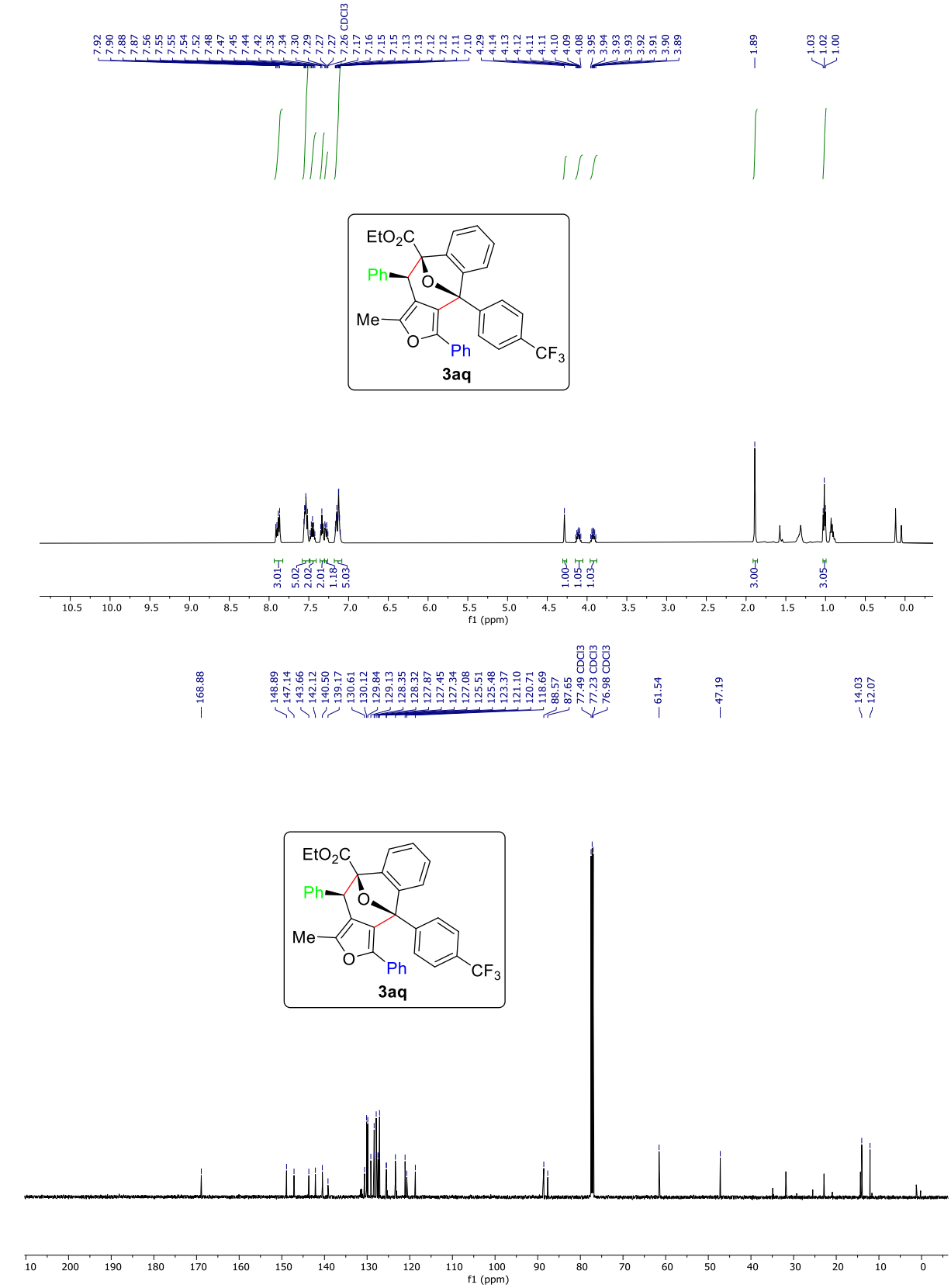




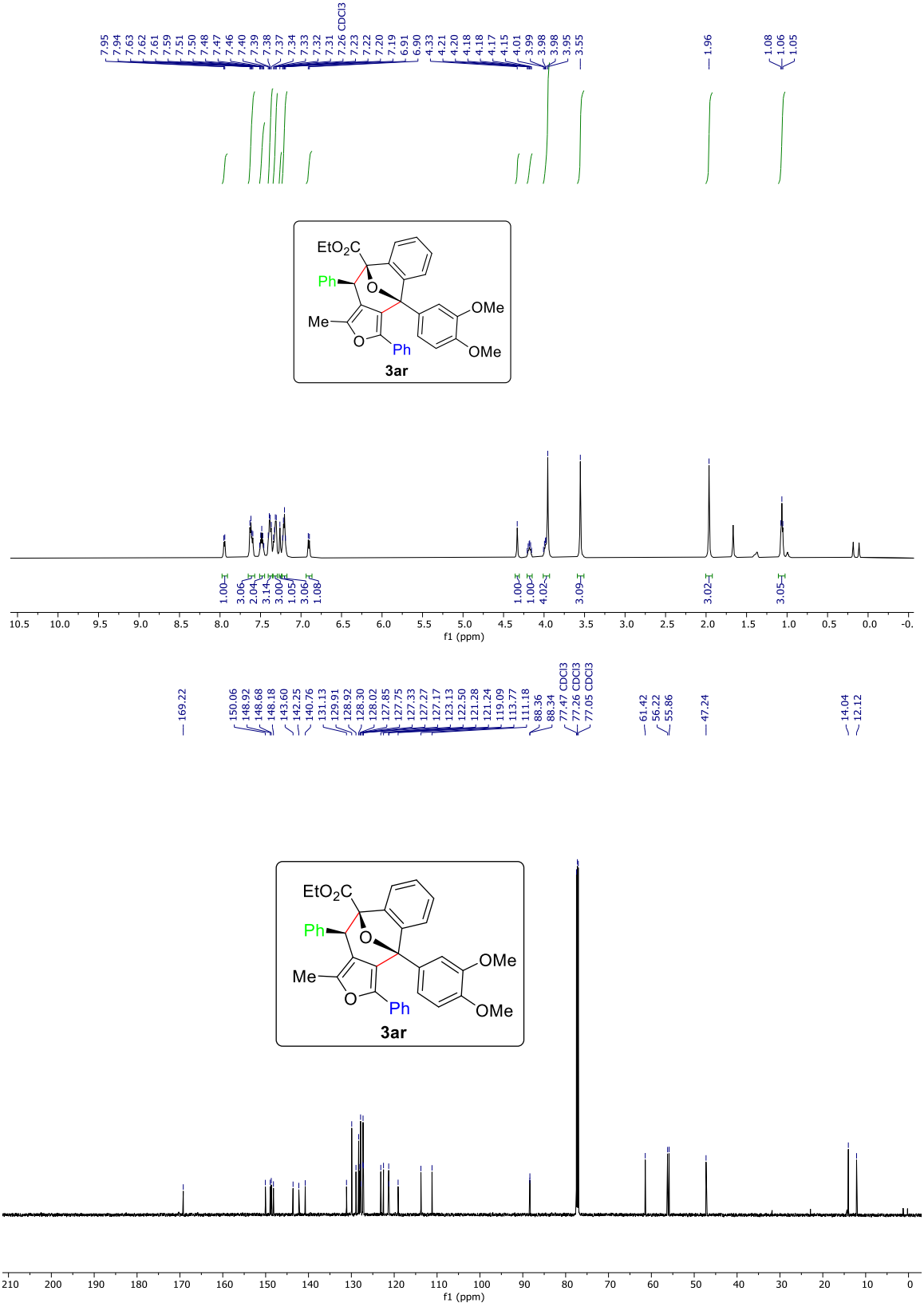
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3ap:



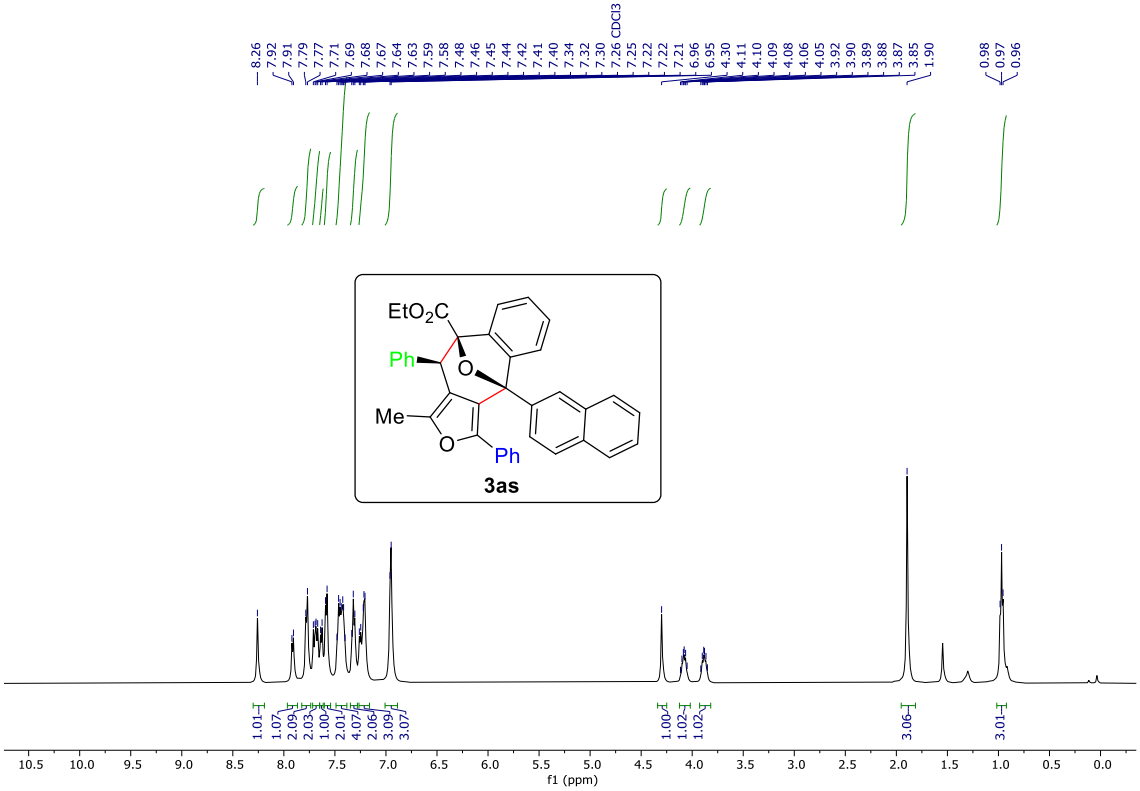
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3aq:

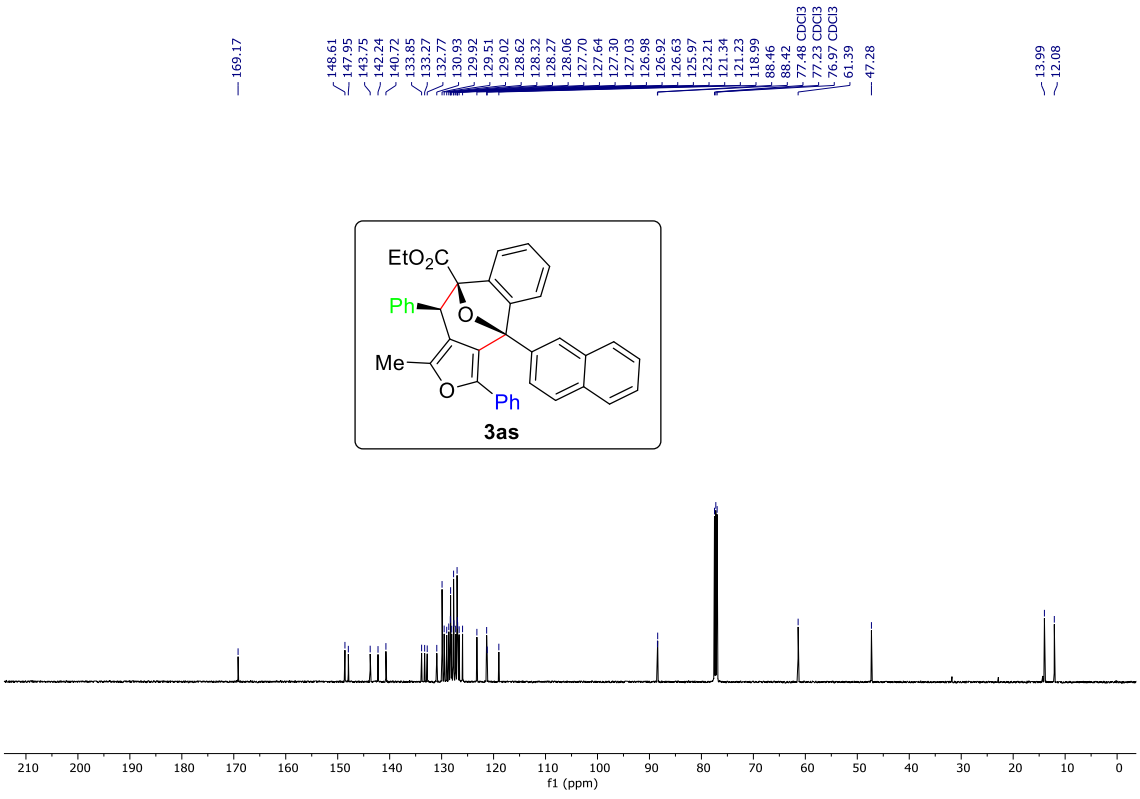


1H (600 MHz, $CDCl_3$) and 13C{H} (150 MHz, $CDCl_3$) NMR of 3ar:

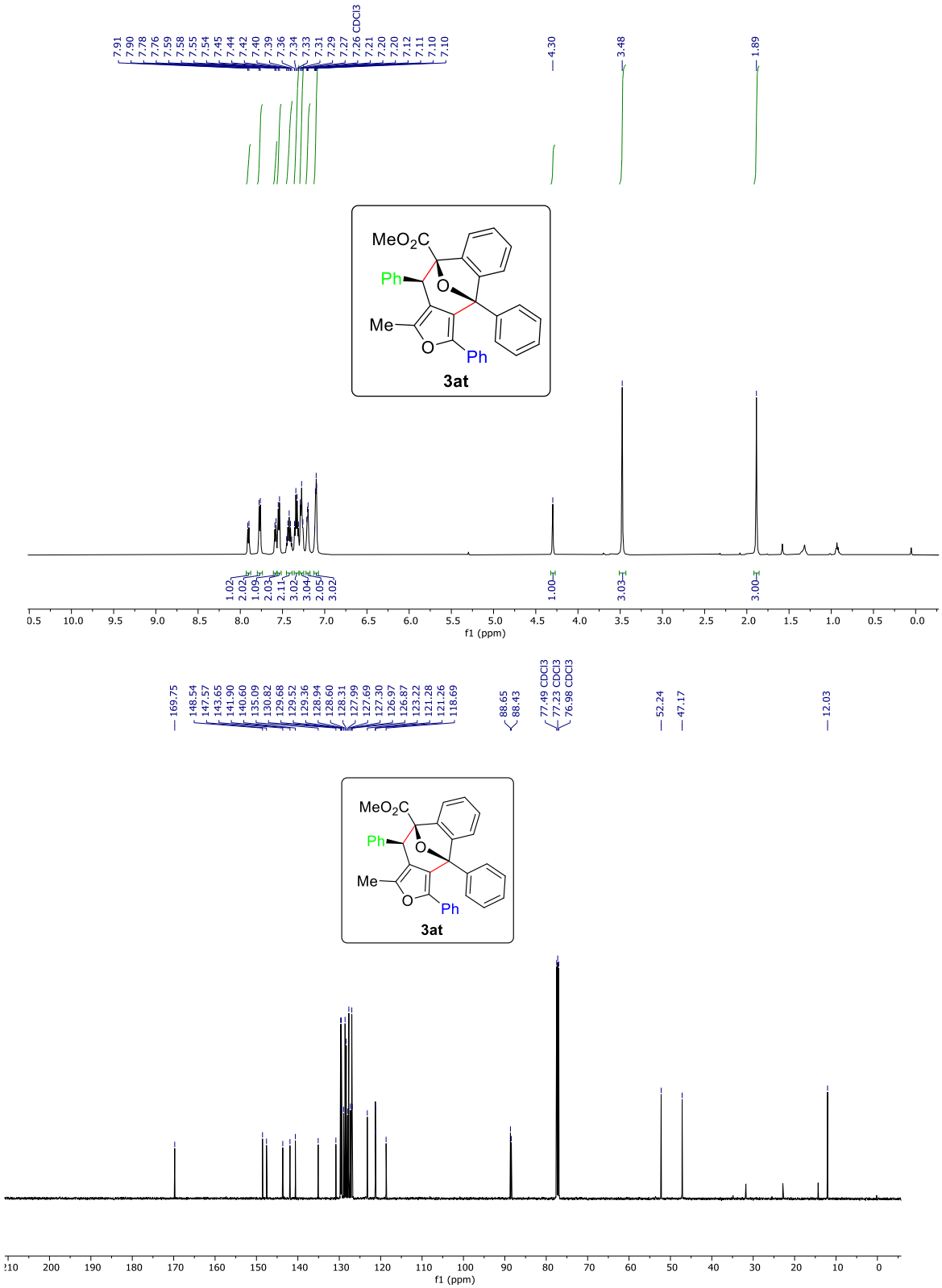


1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3as:

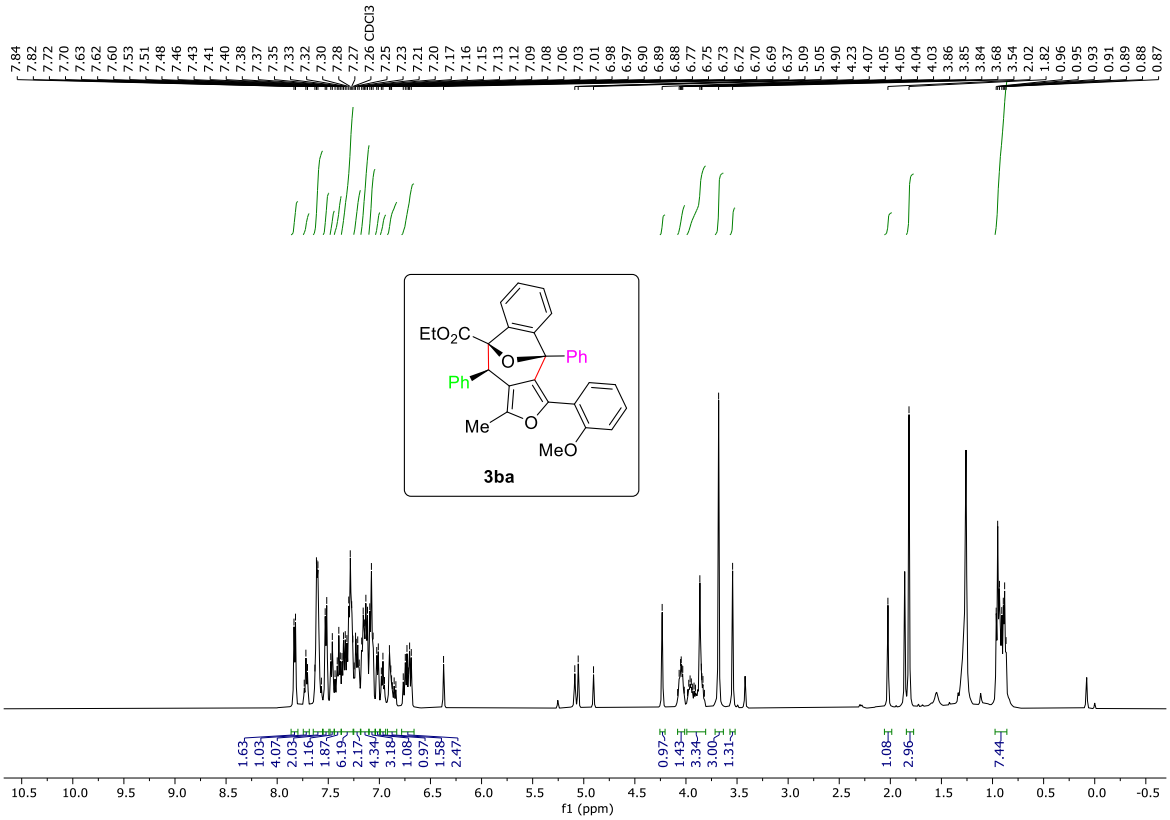


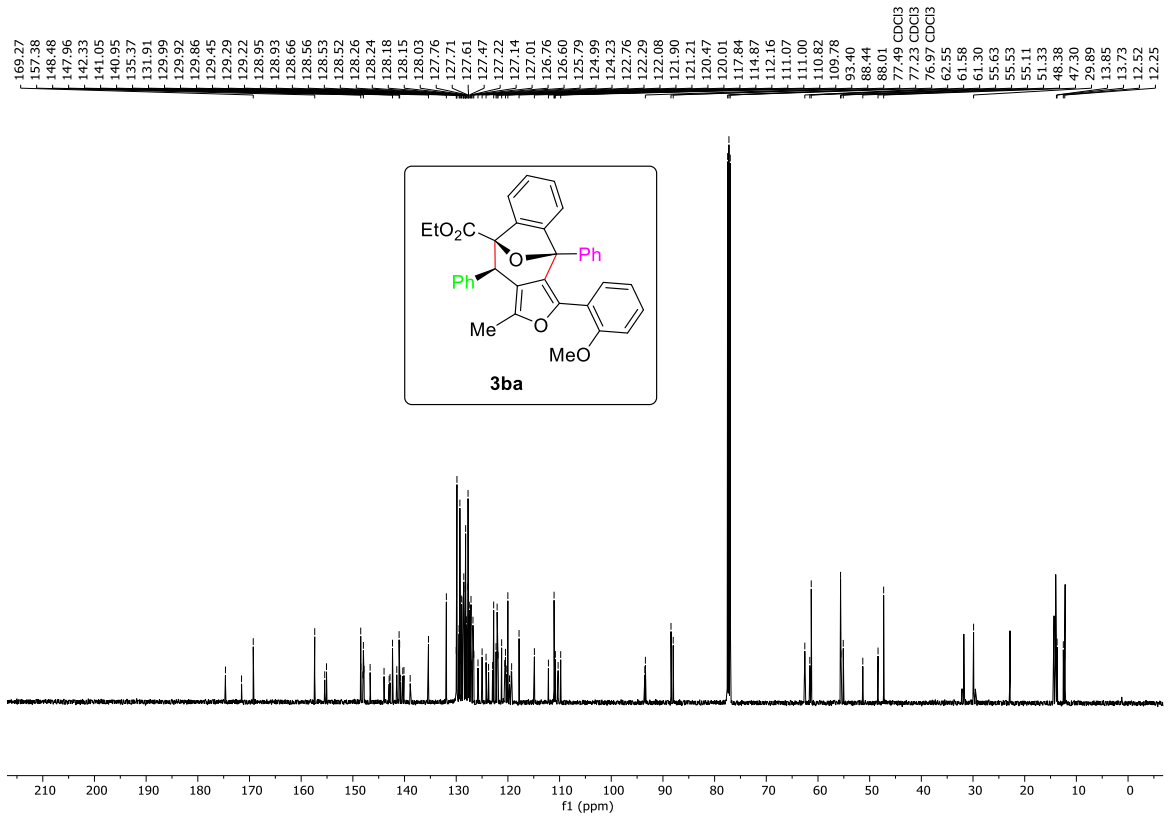


1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3at:

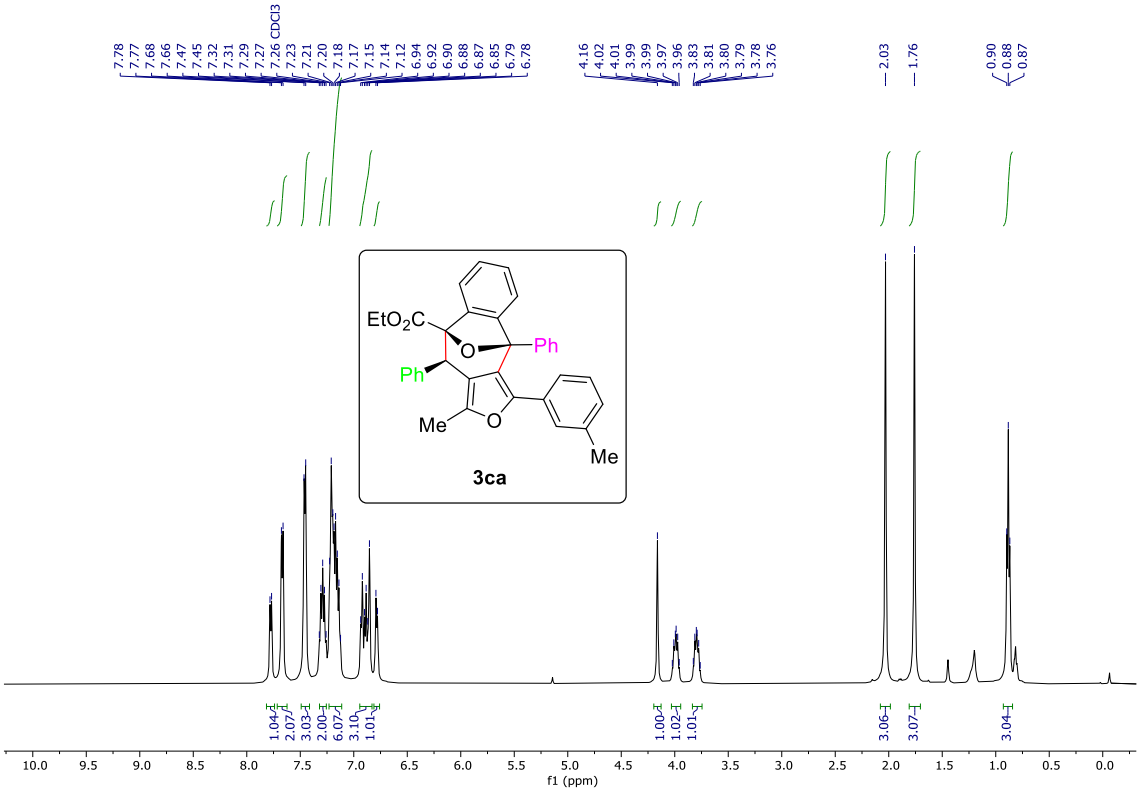


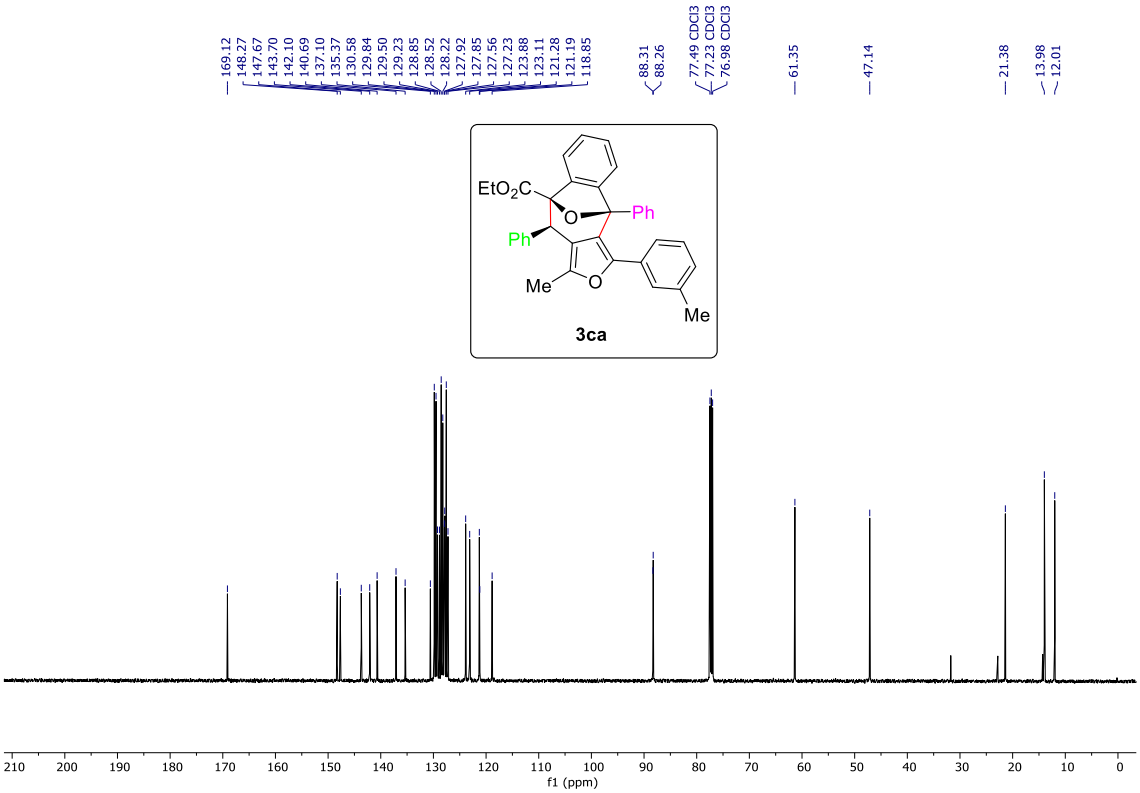
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3ba:



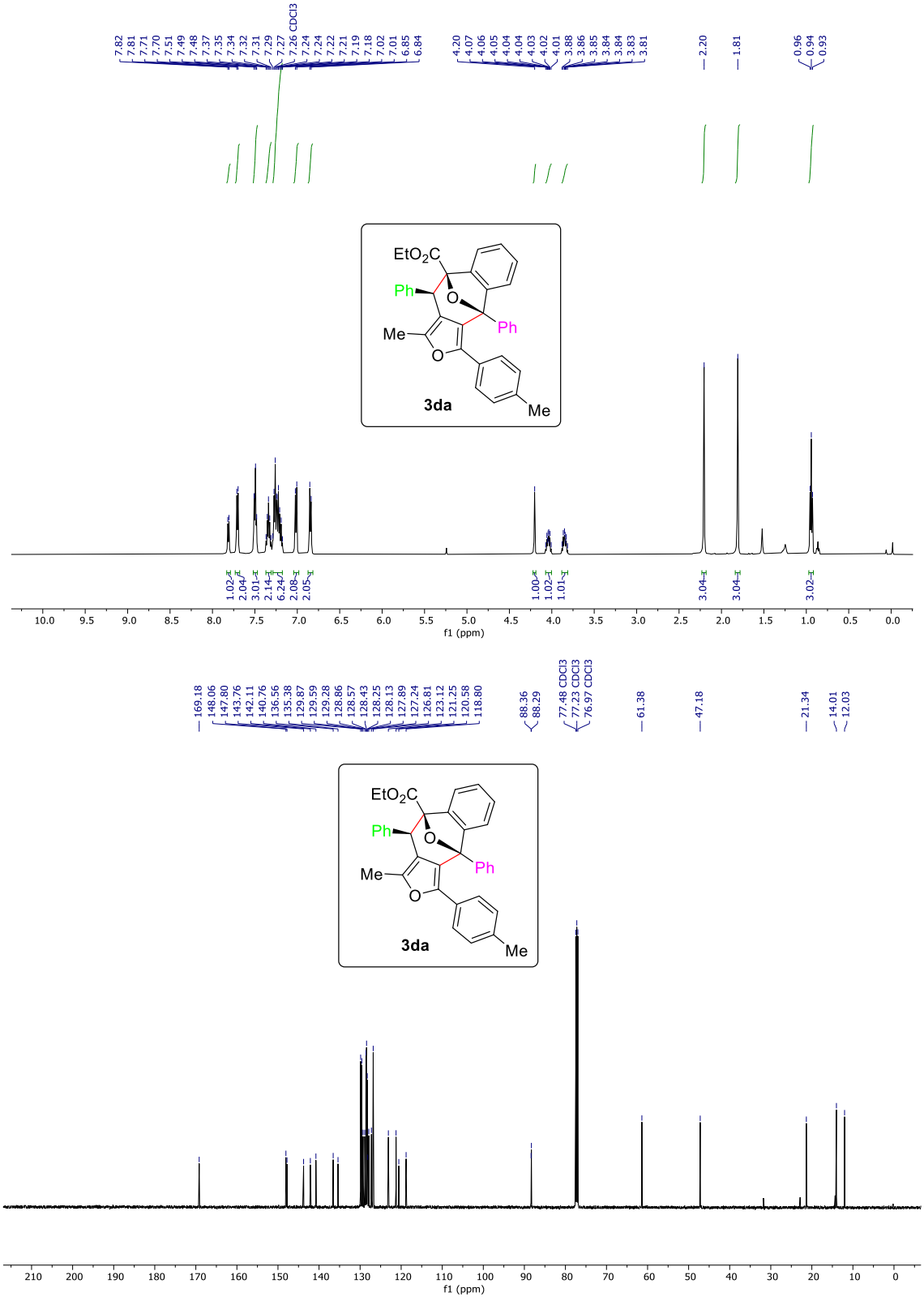


1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3ca:

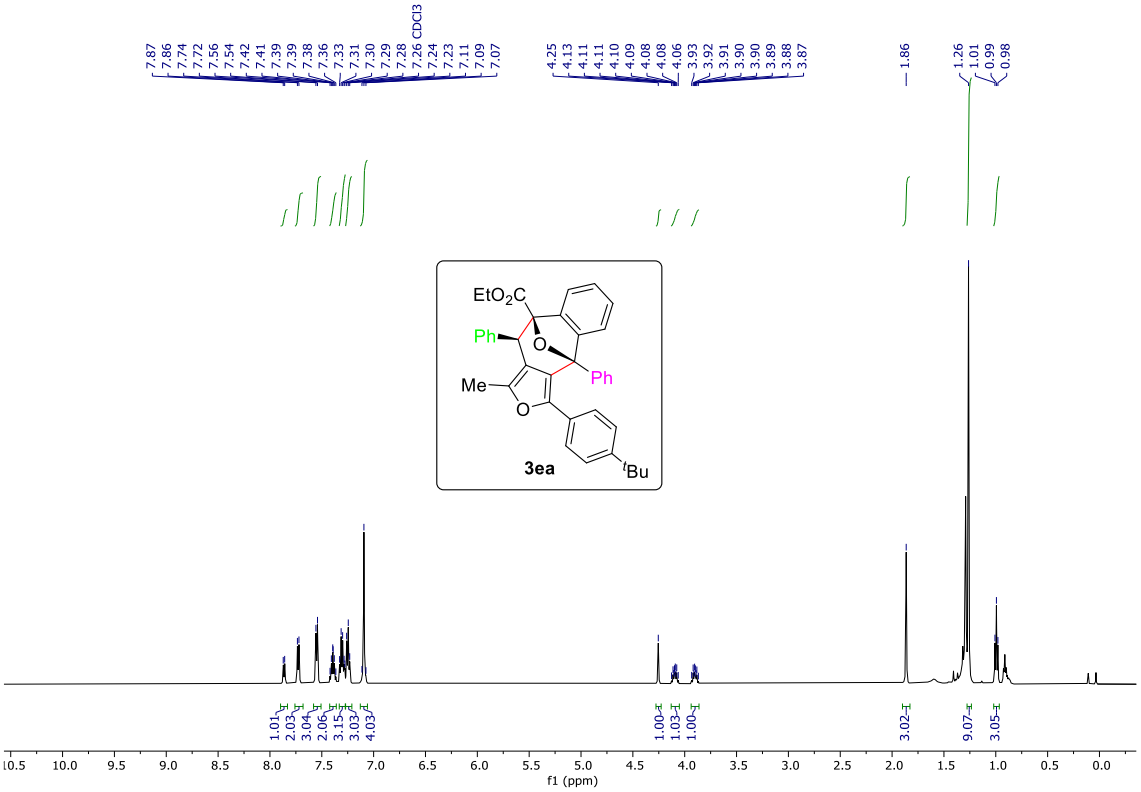


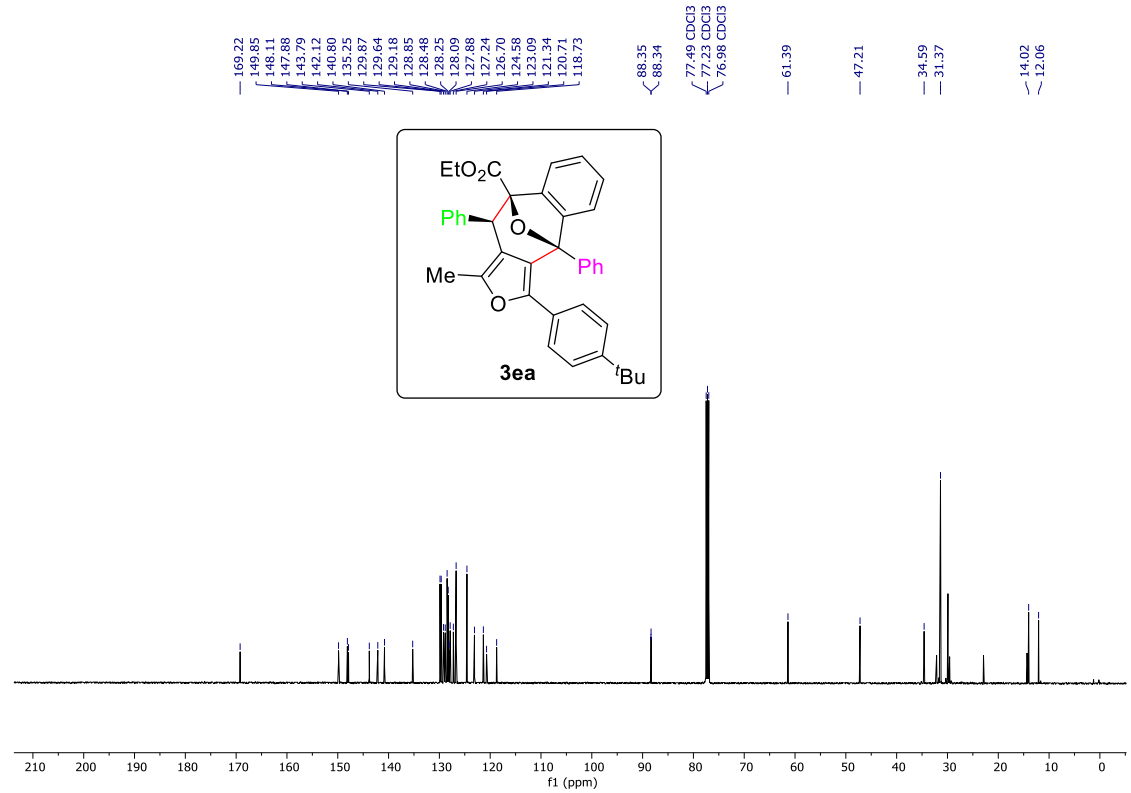


1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3da:

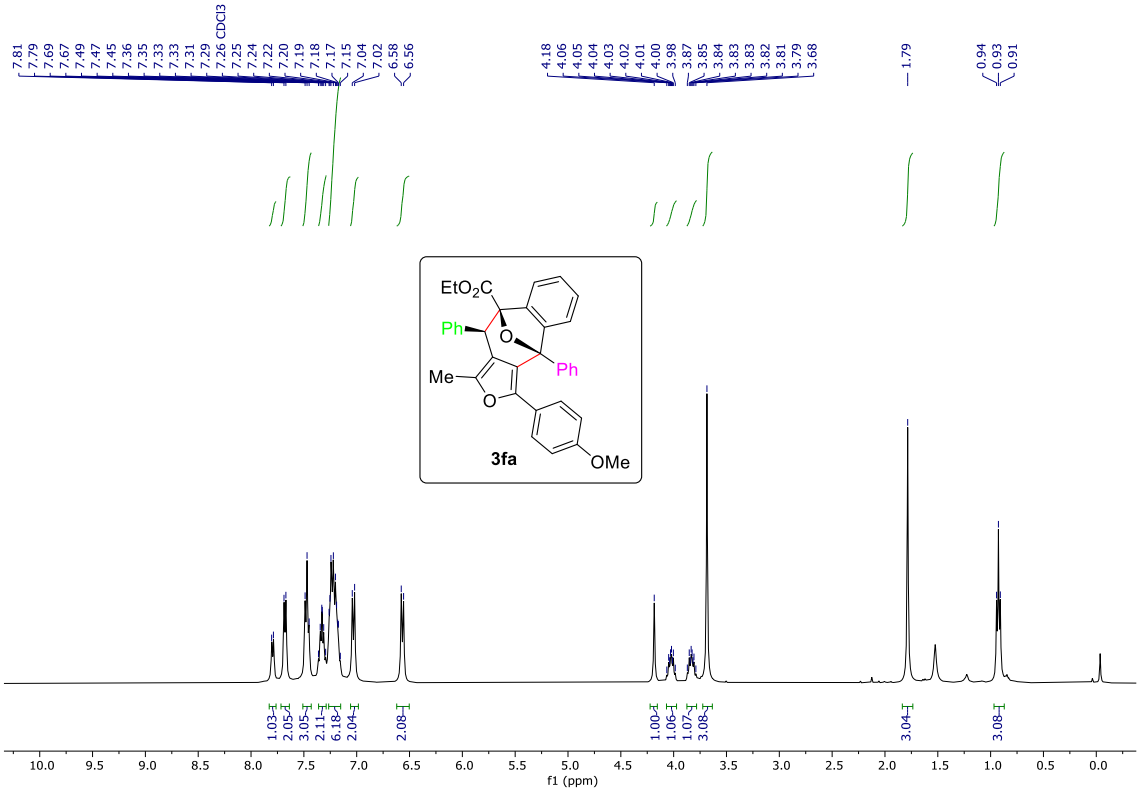


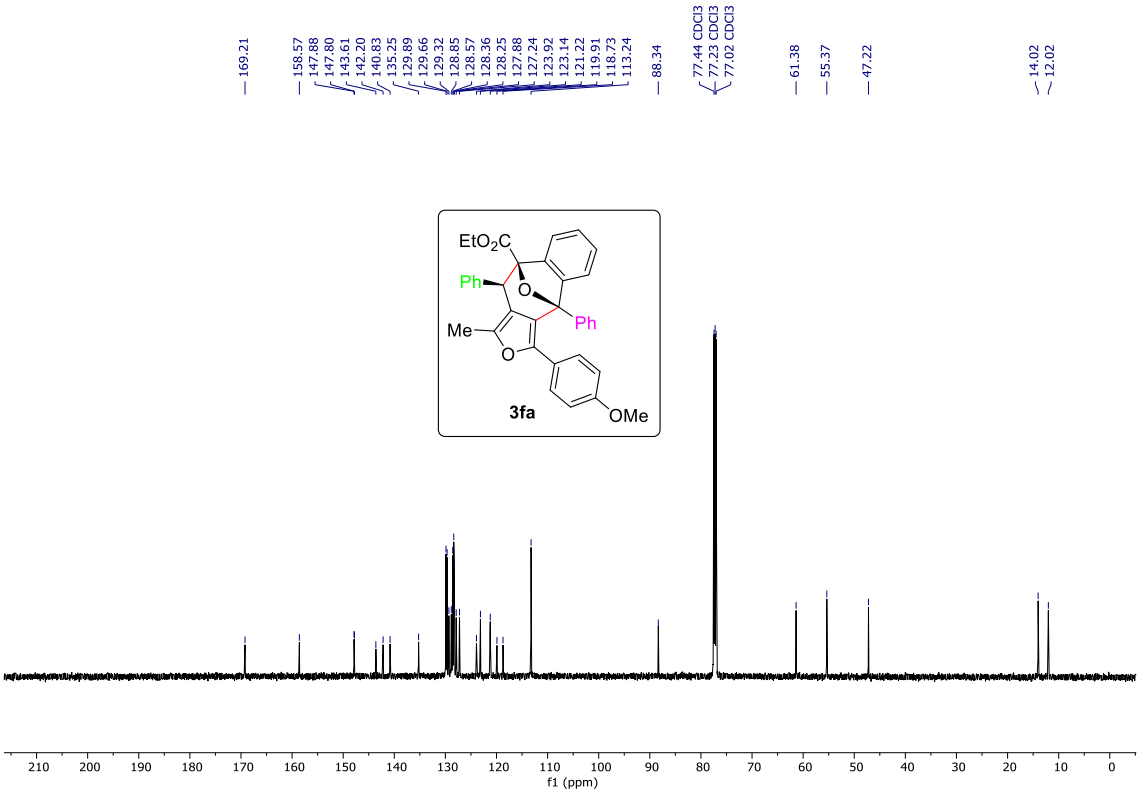
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3ea:



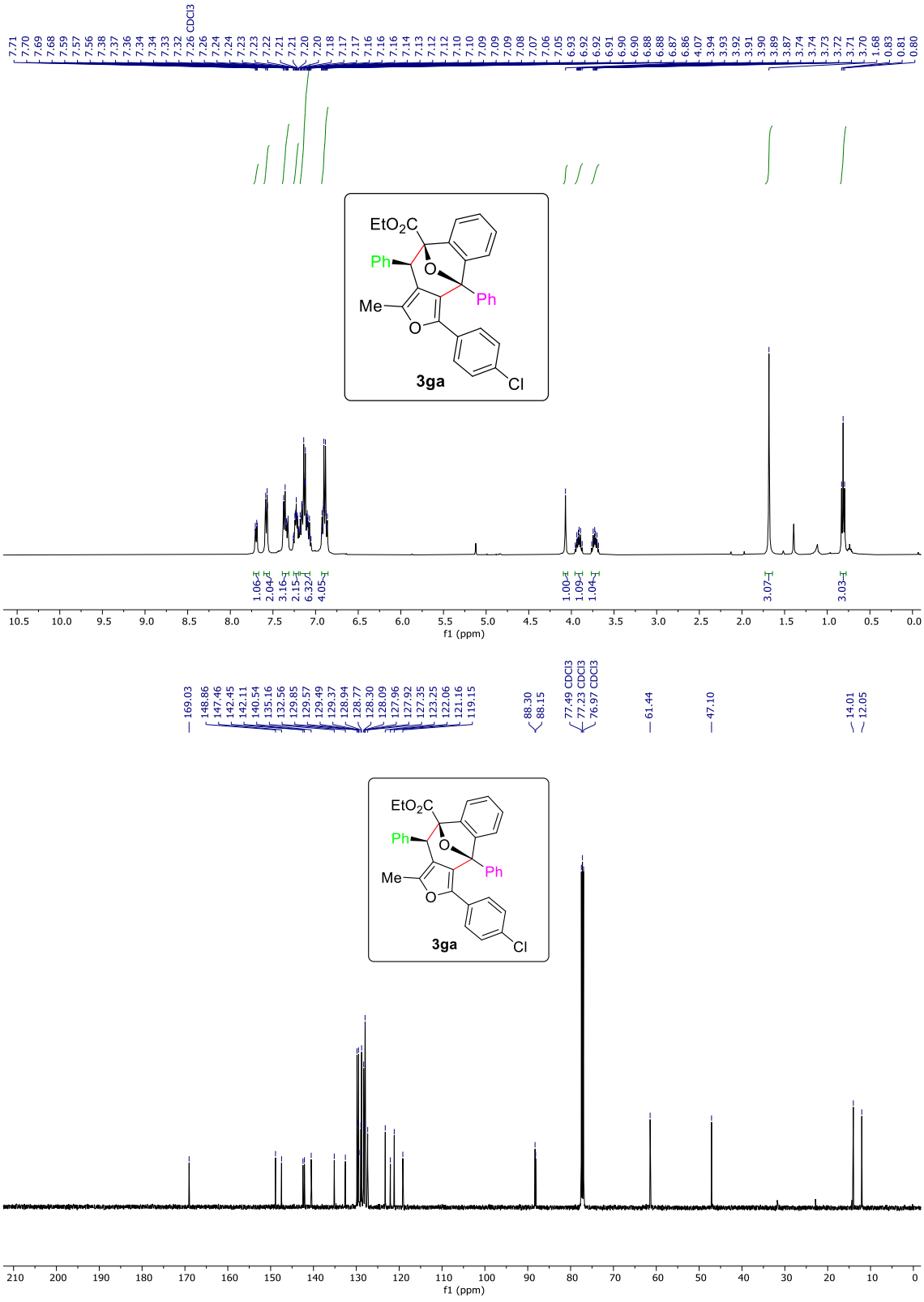


1H (400 MHz, $CDCl_3$) and 13C{H} (150 MHz, $CDCl_3$) NMR of 3fa:

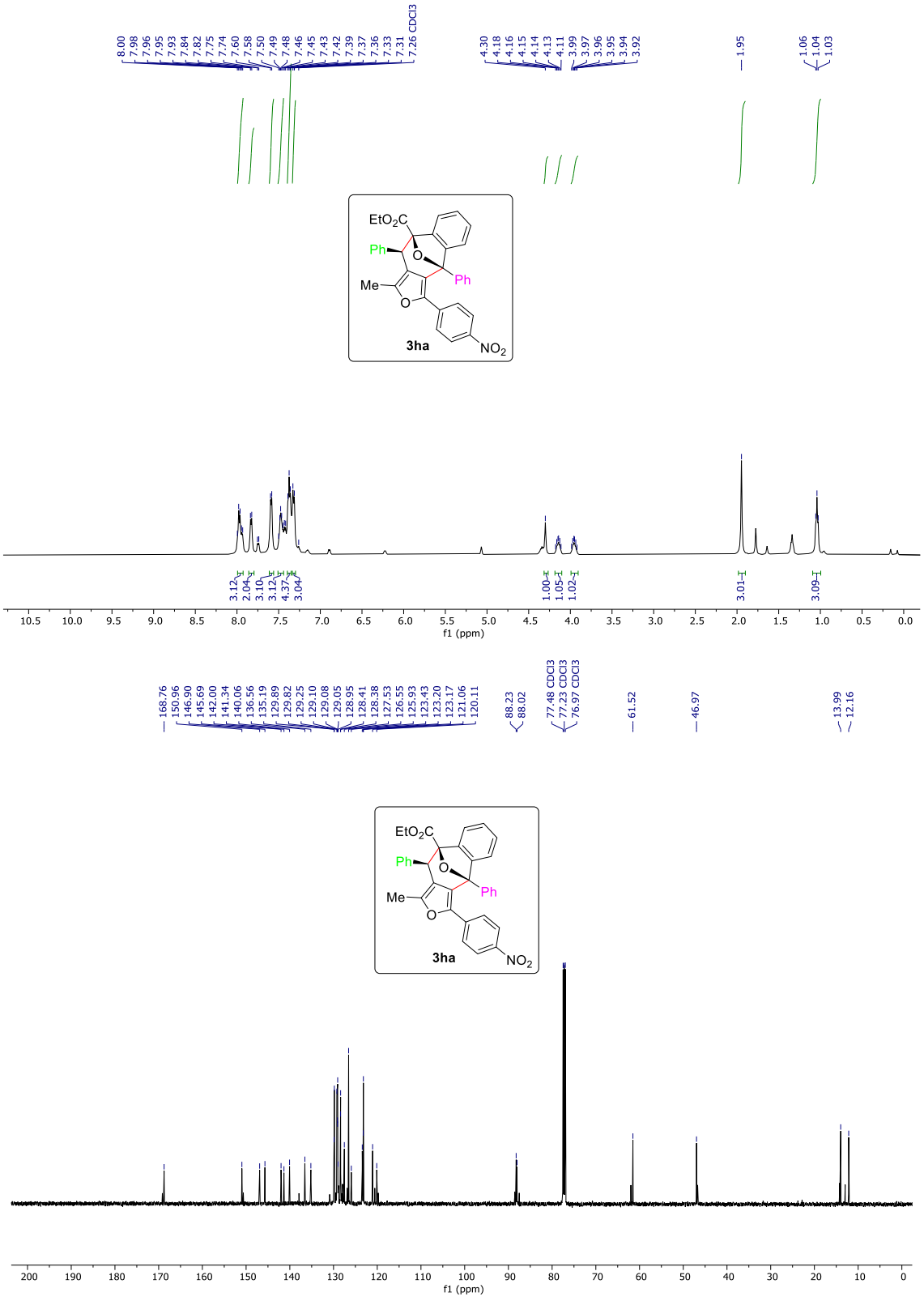




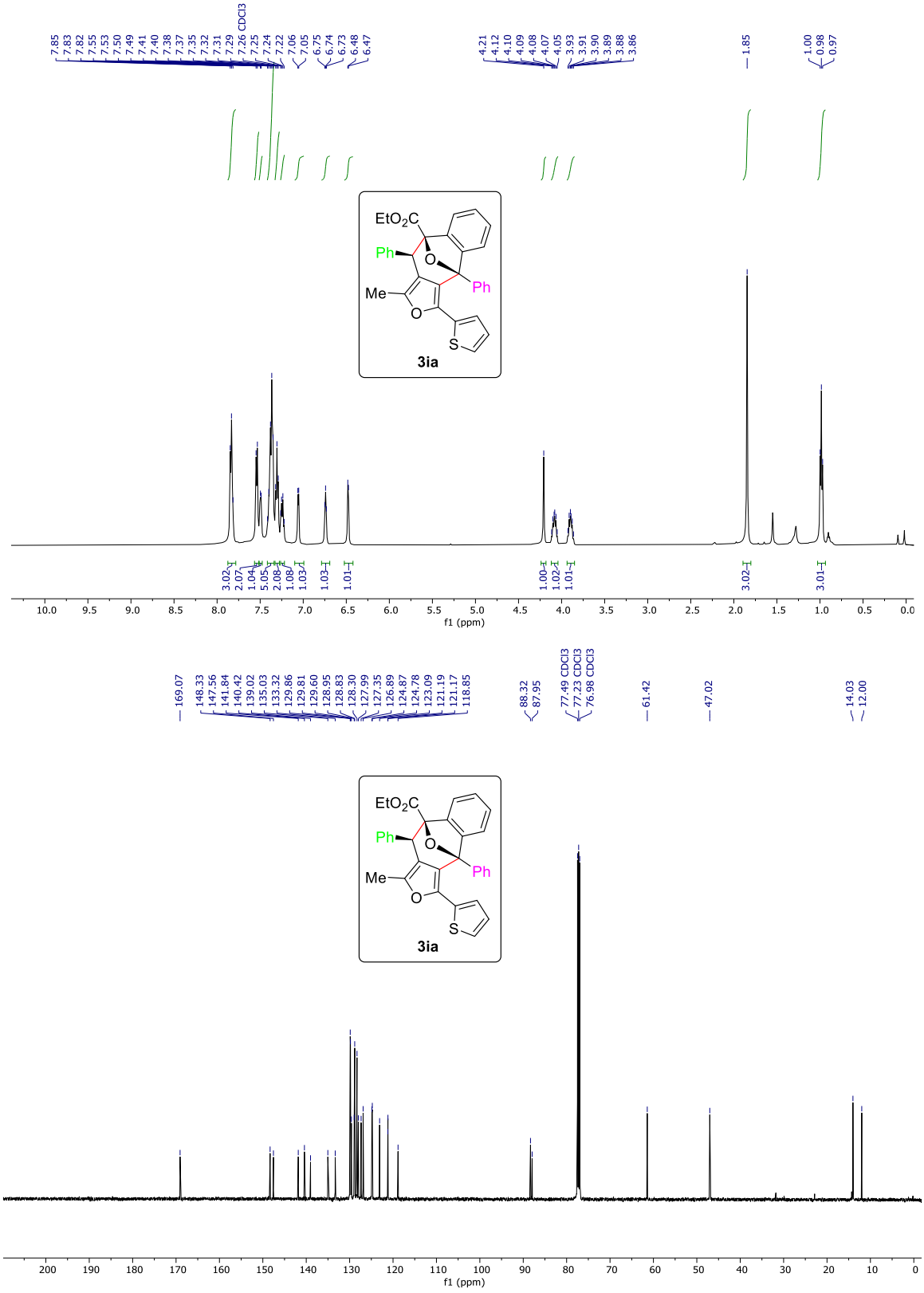
1H (400 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3ga:



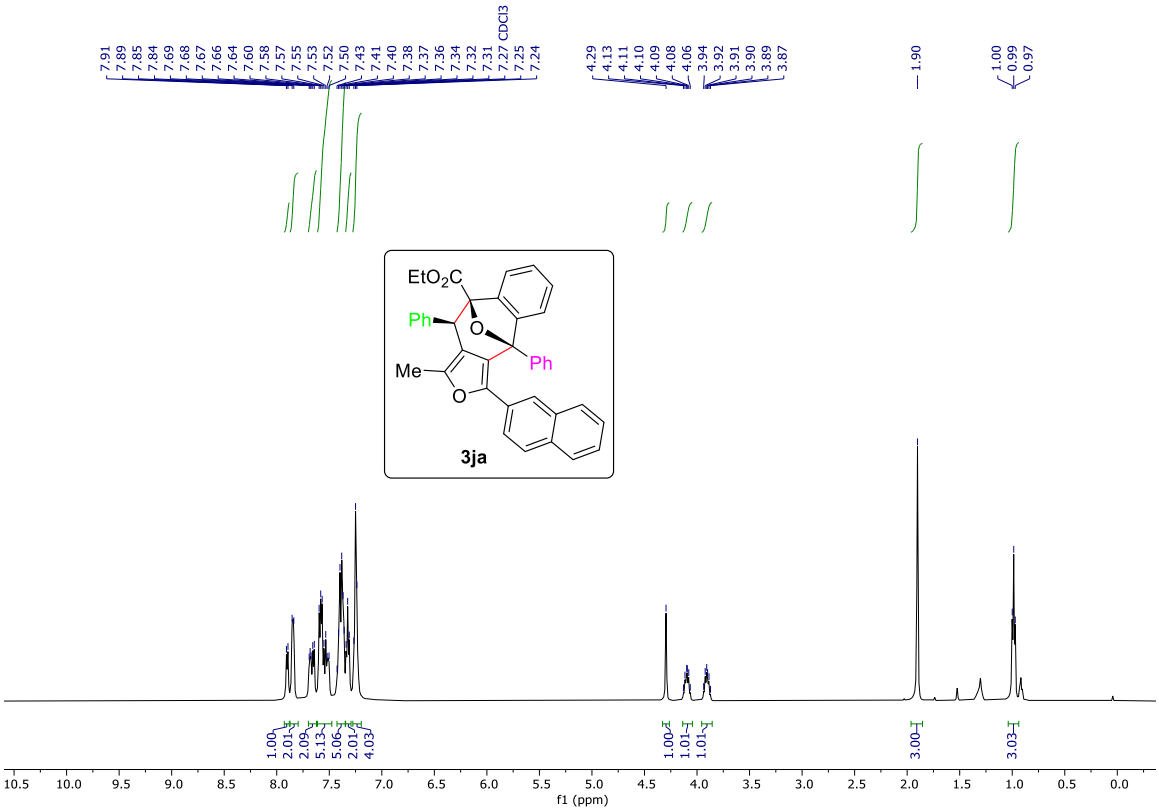
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3ha:

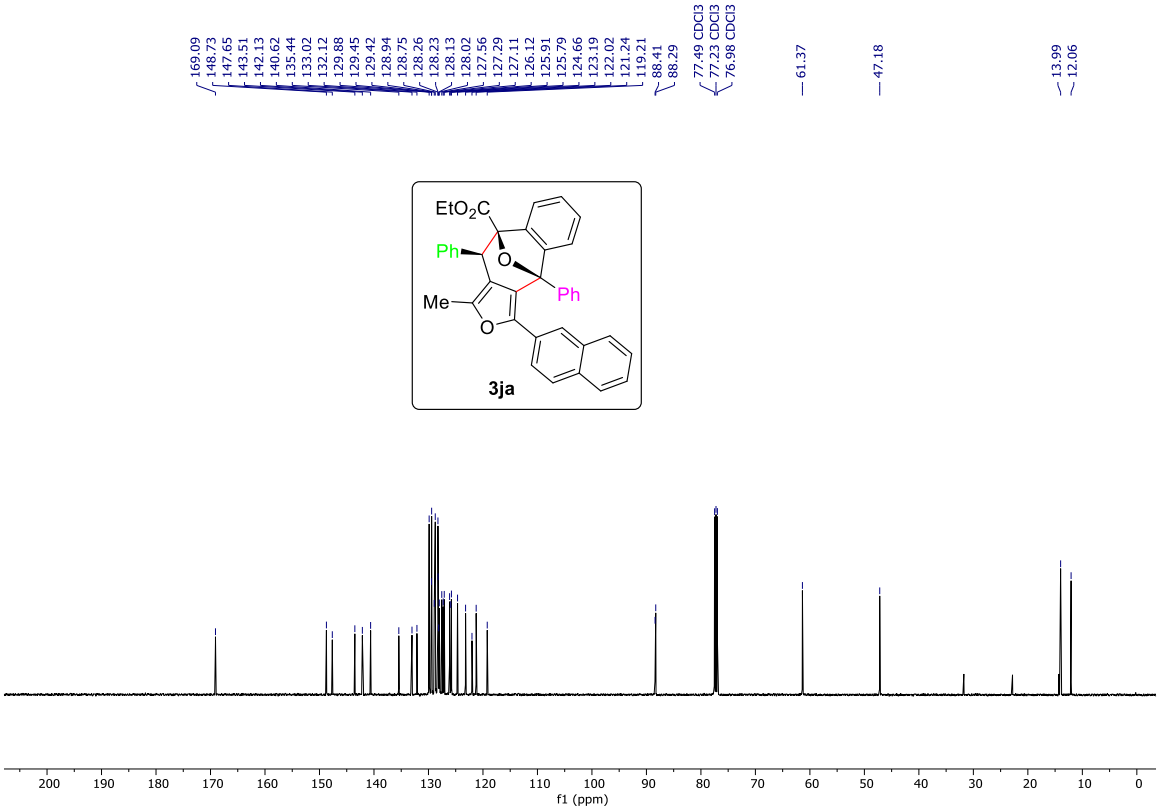


1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3ia:

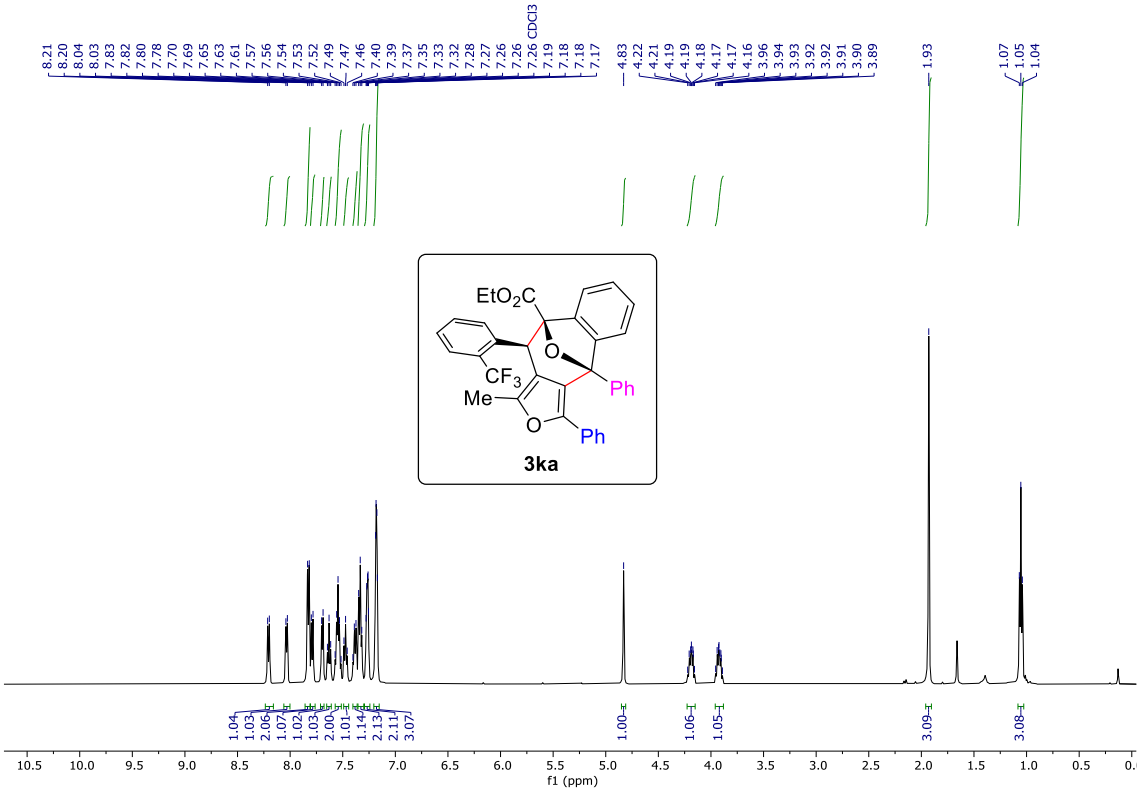


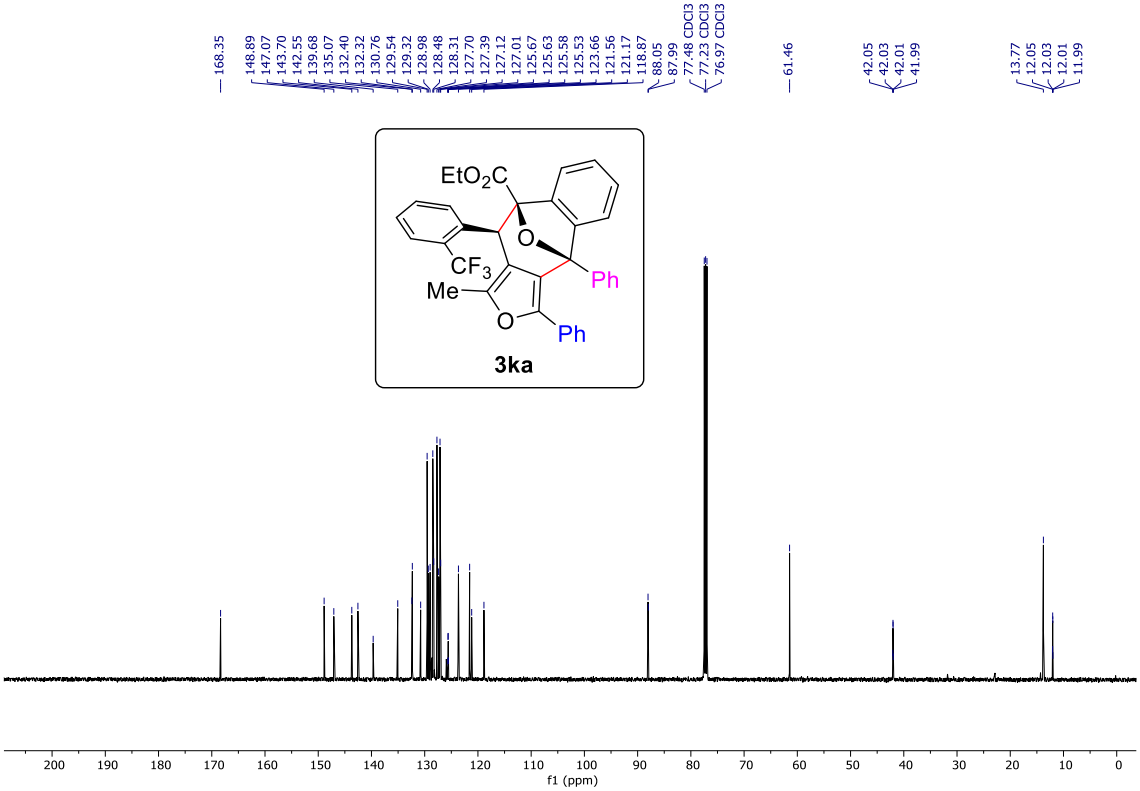
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3ja:



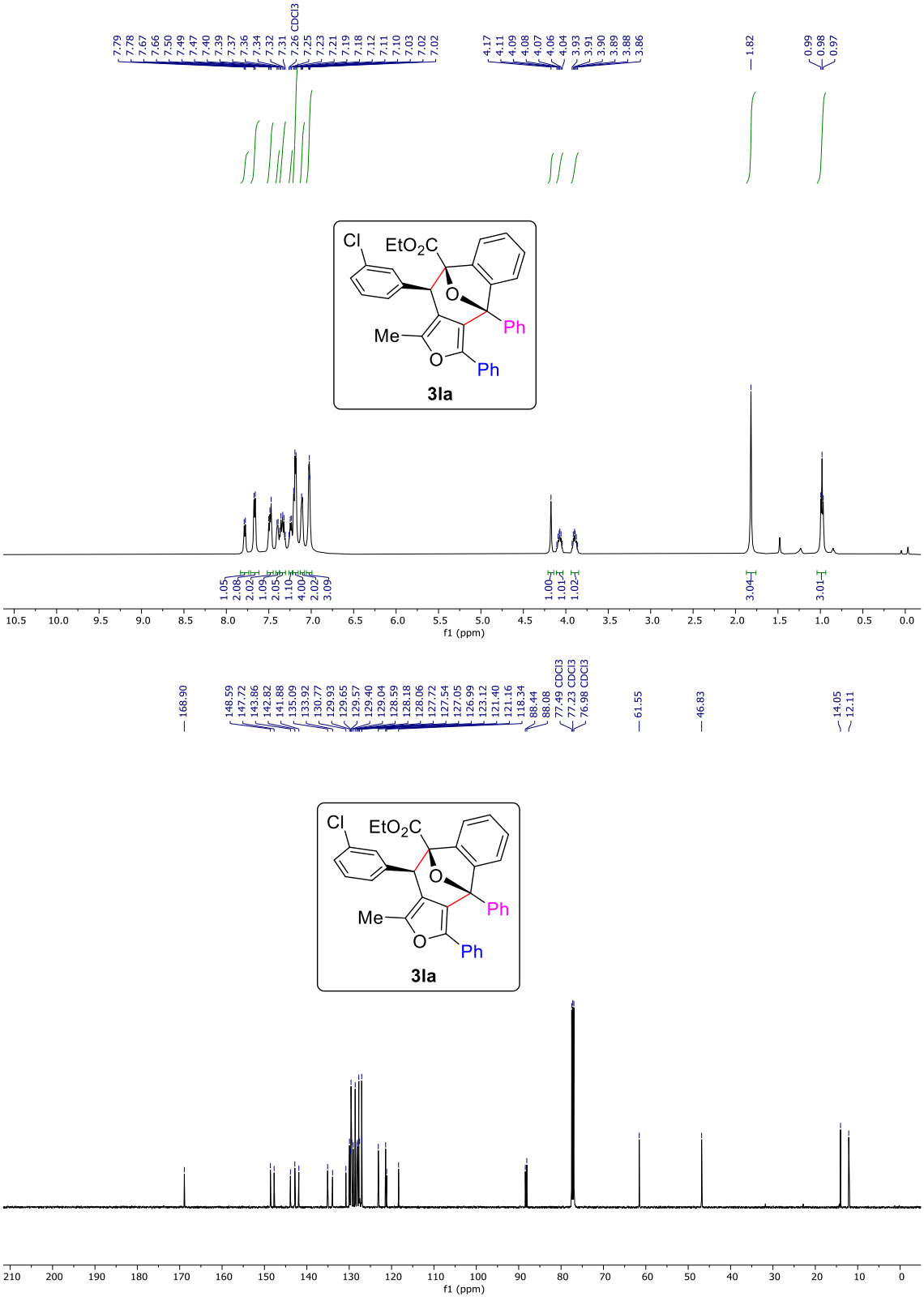


1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3ka:

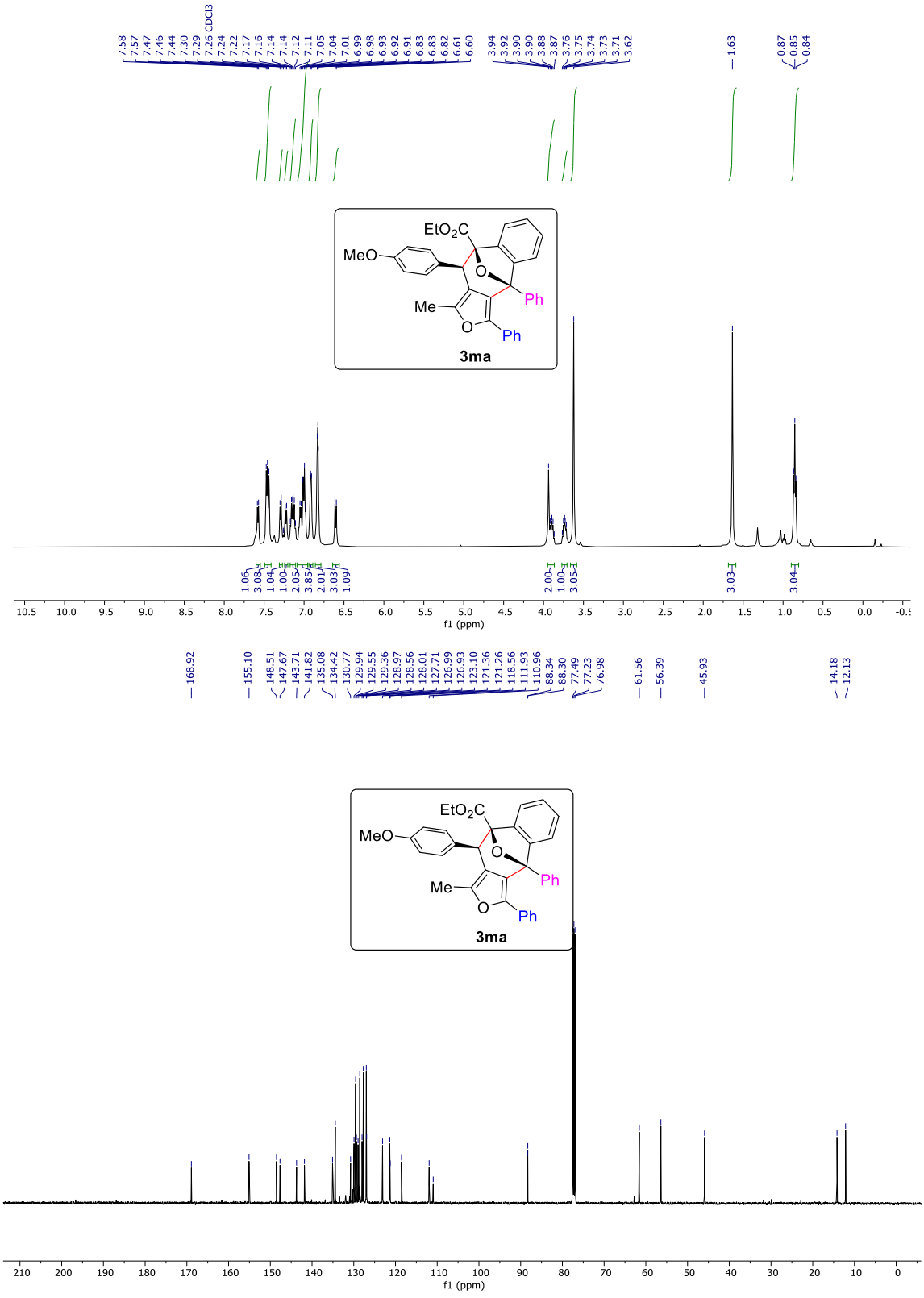




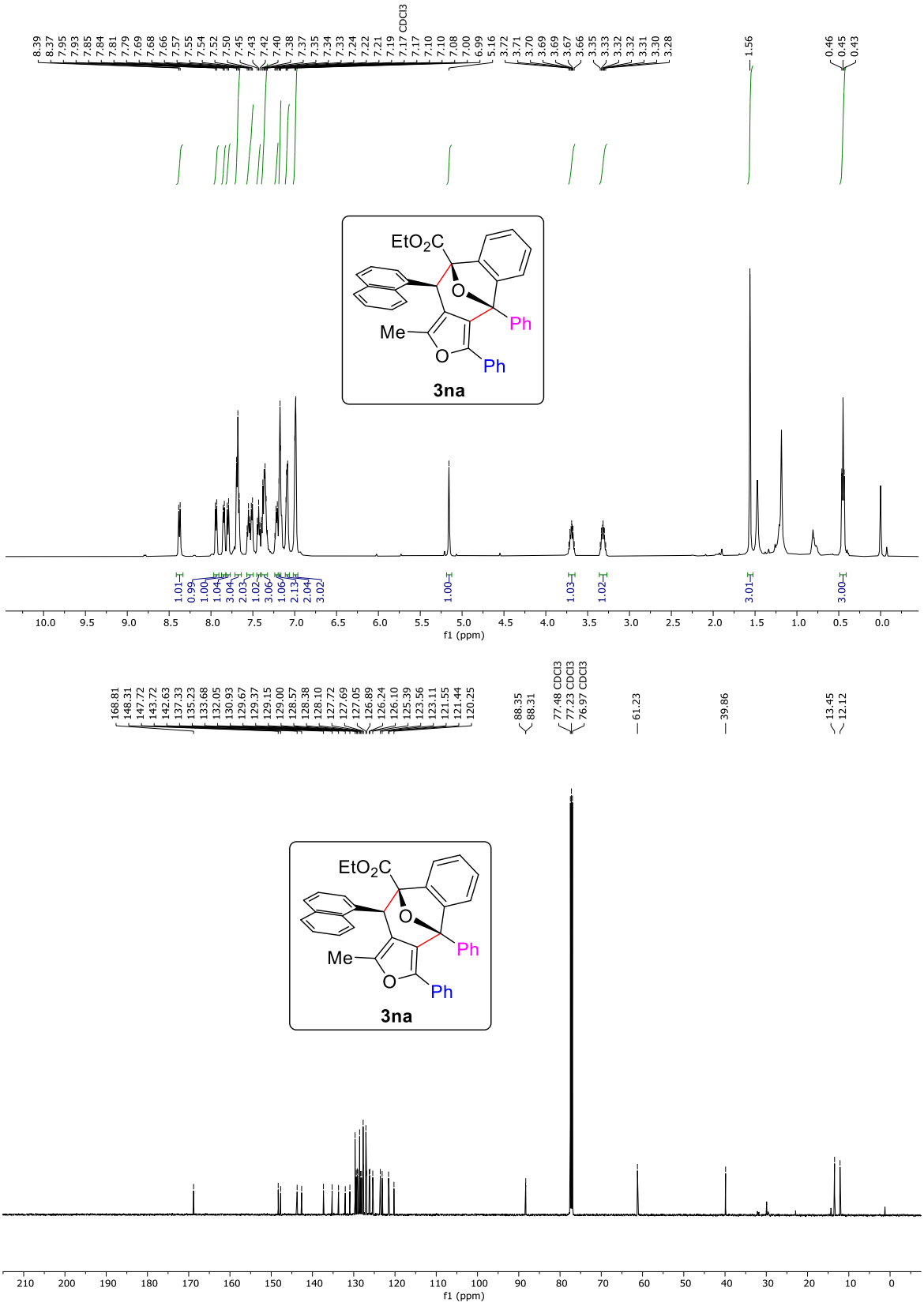
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3la:



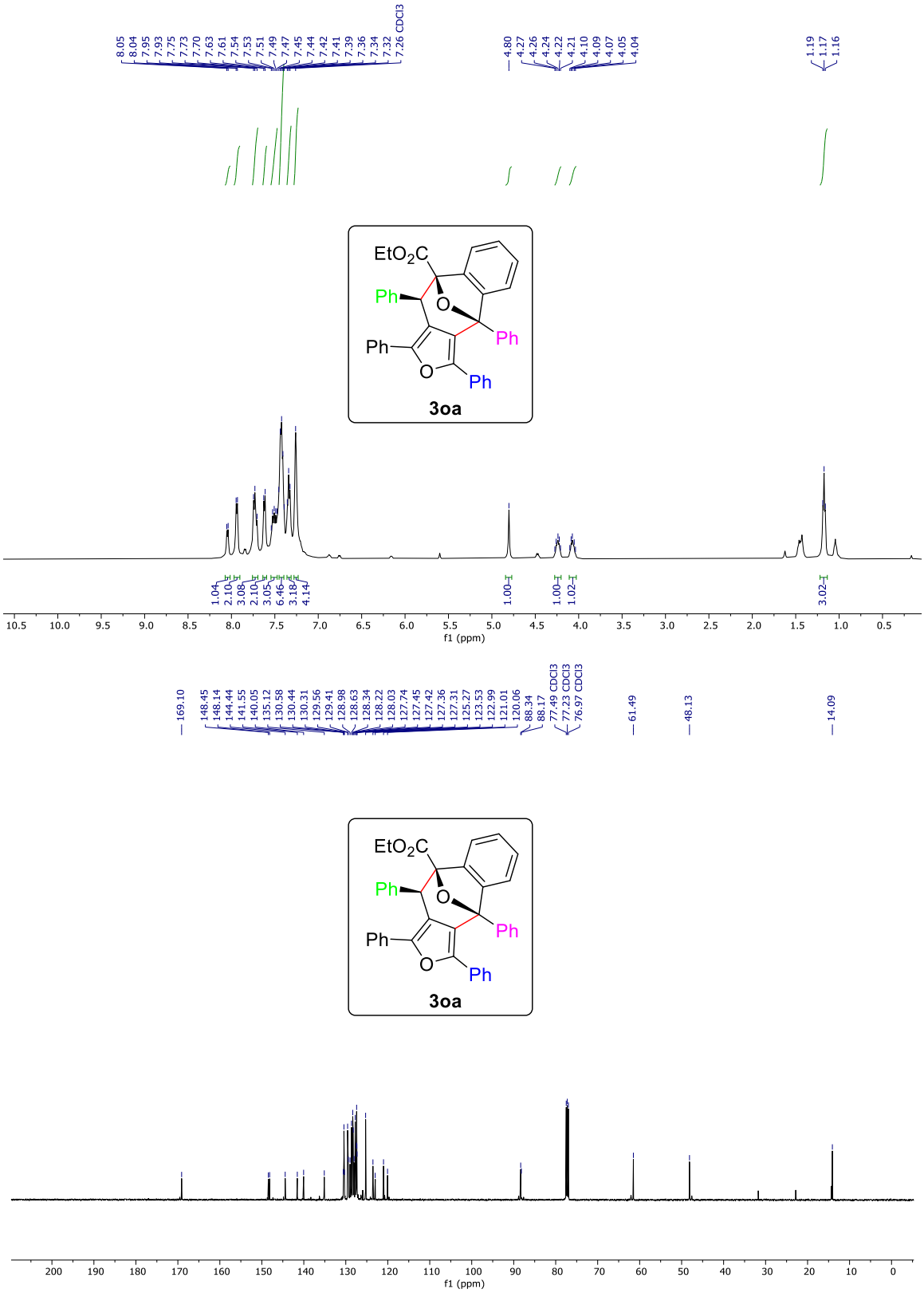
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3ma:



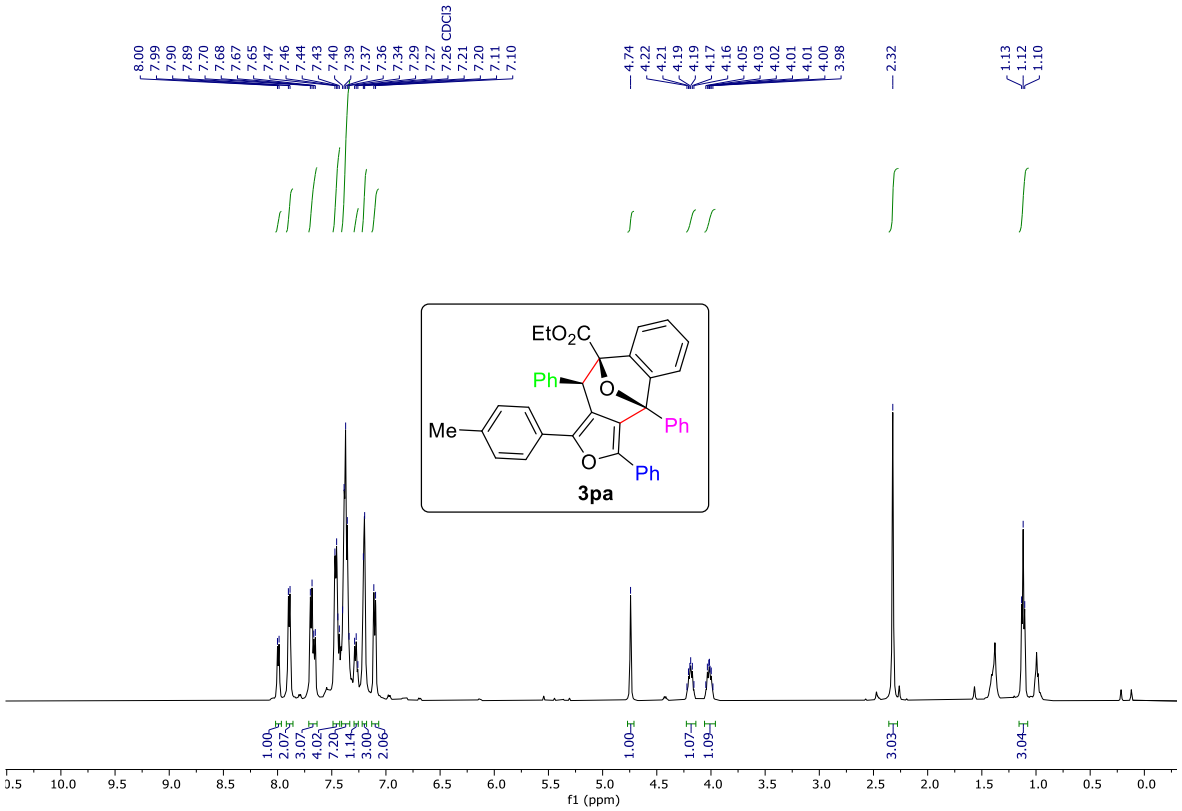
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3na:

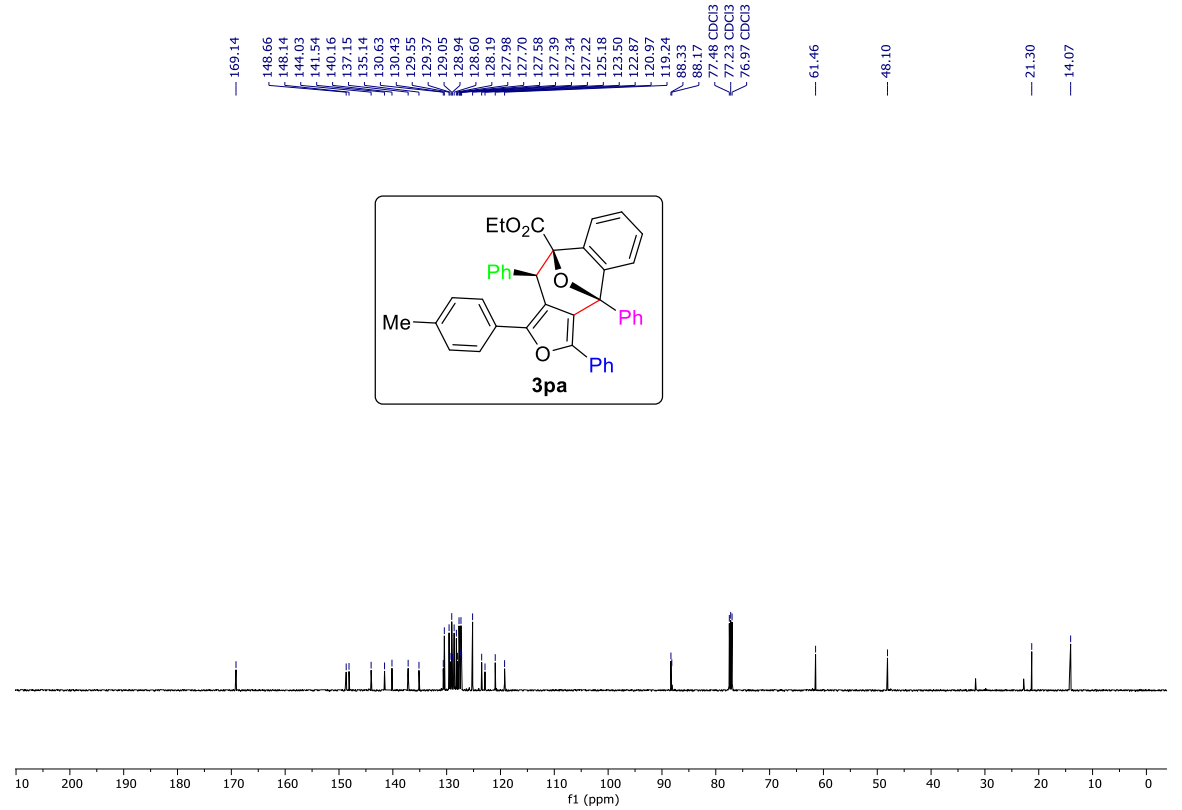


1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3oa:

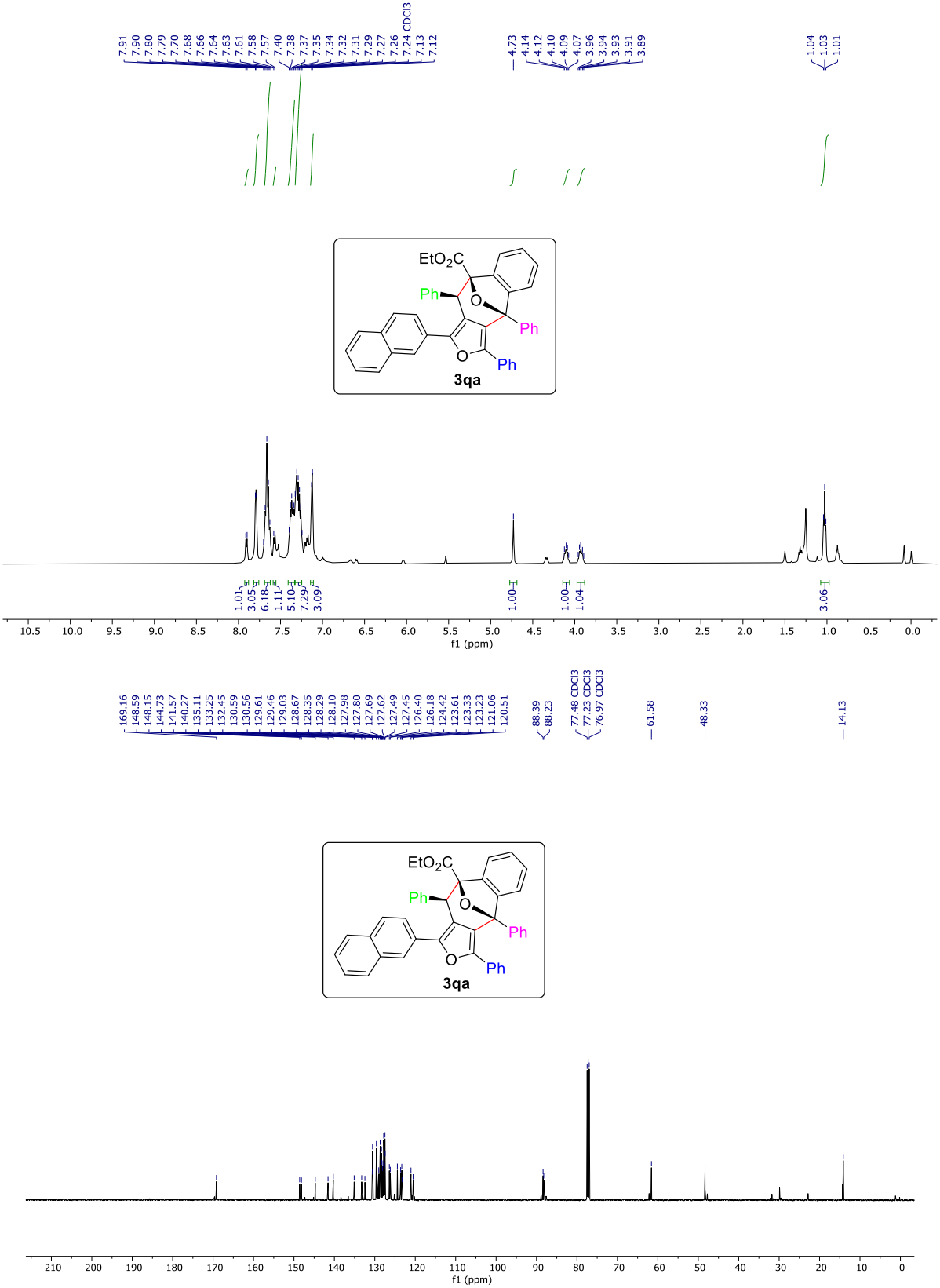


1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3pa:

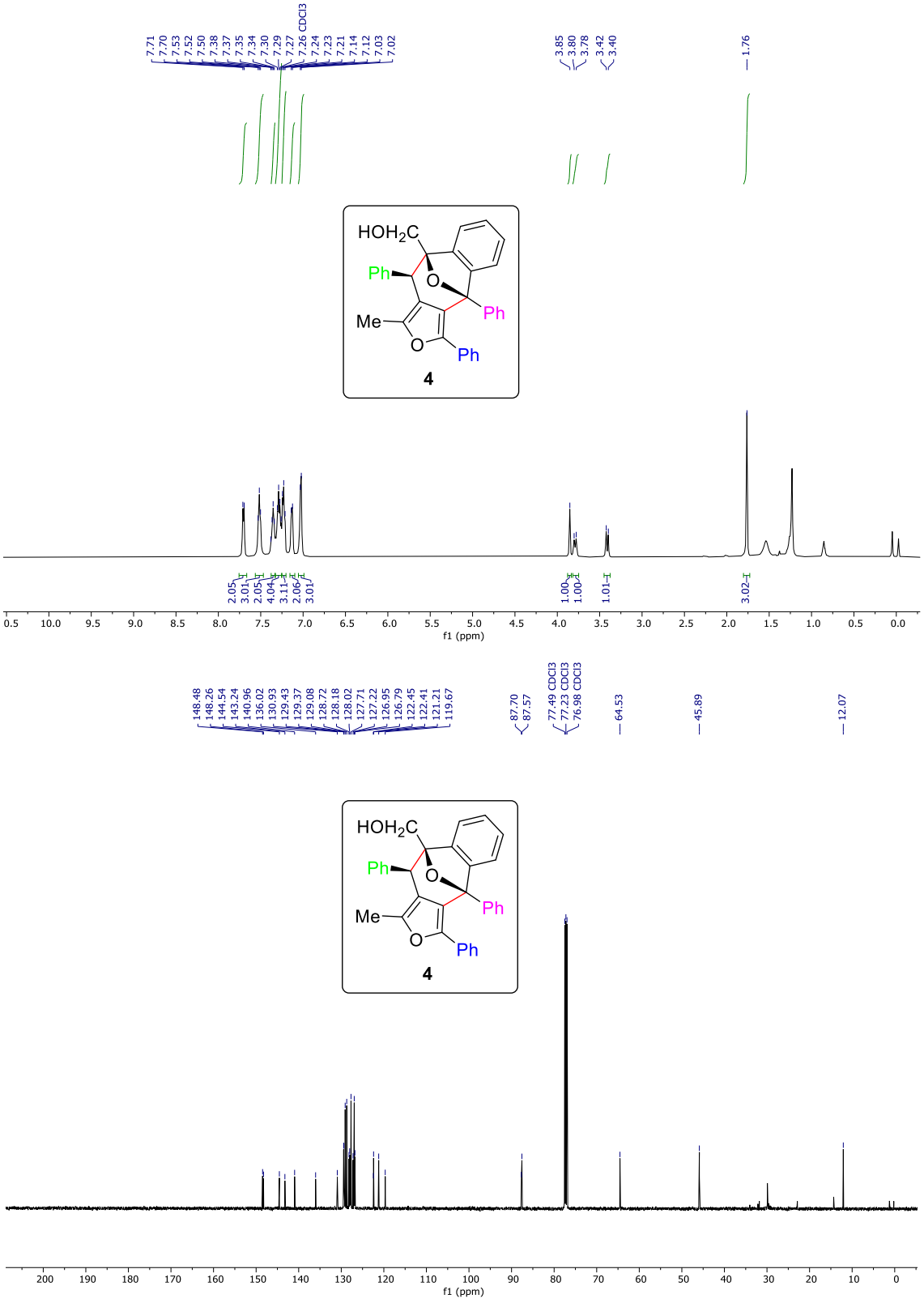




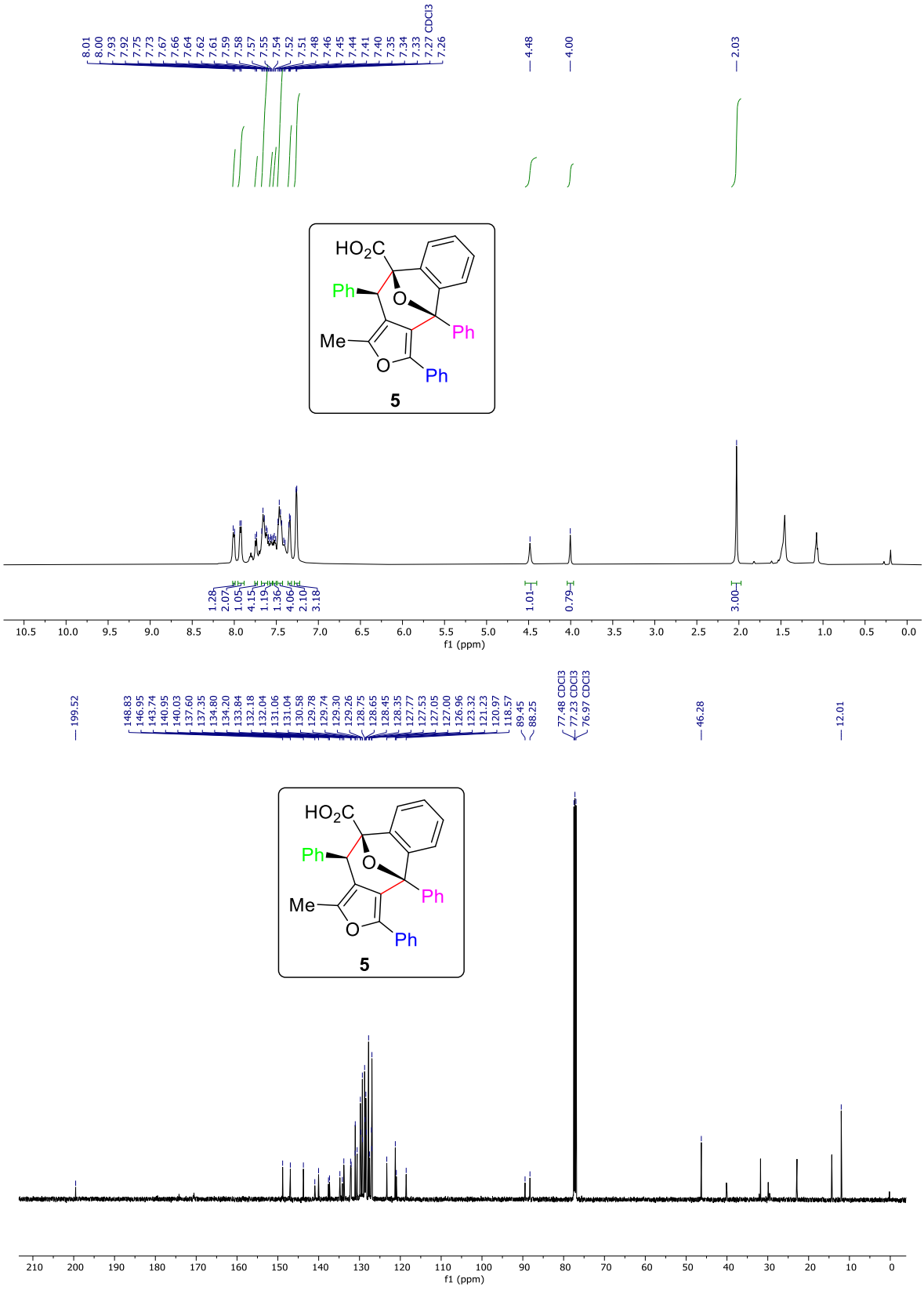
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of 3qa:



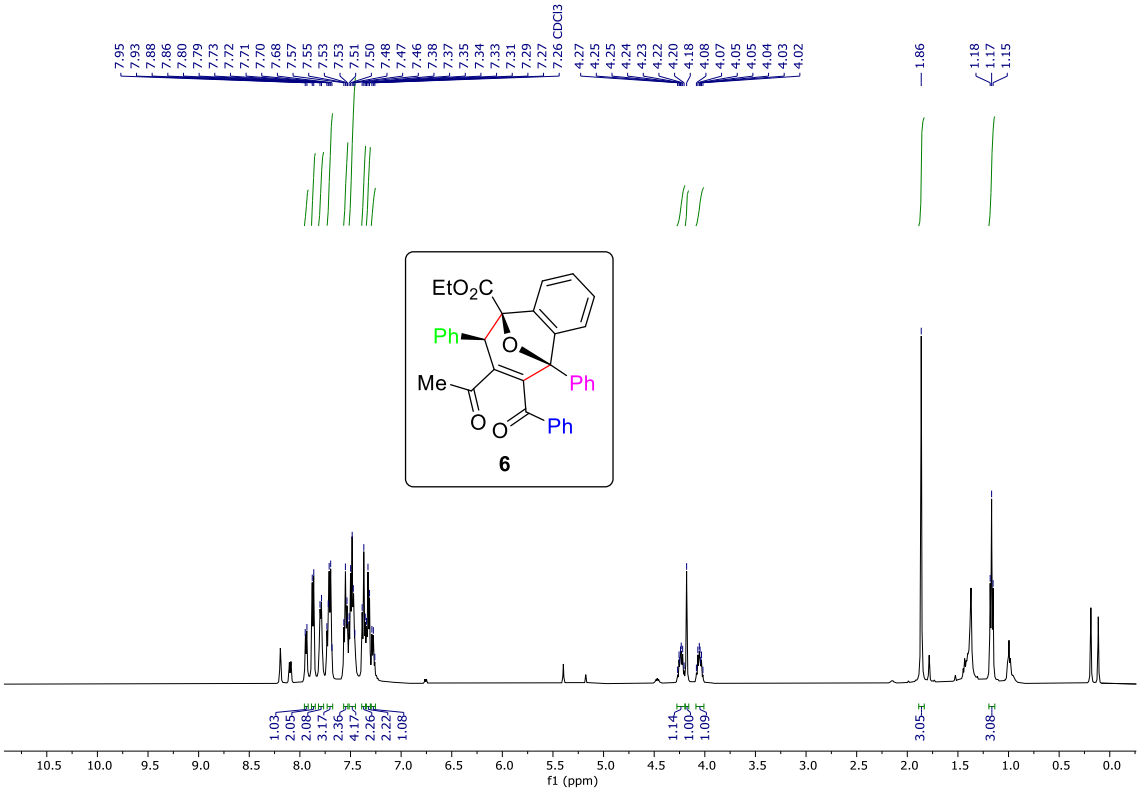
1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of Compound 4:

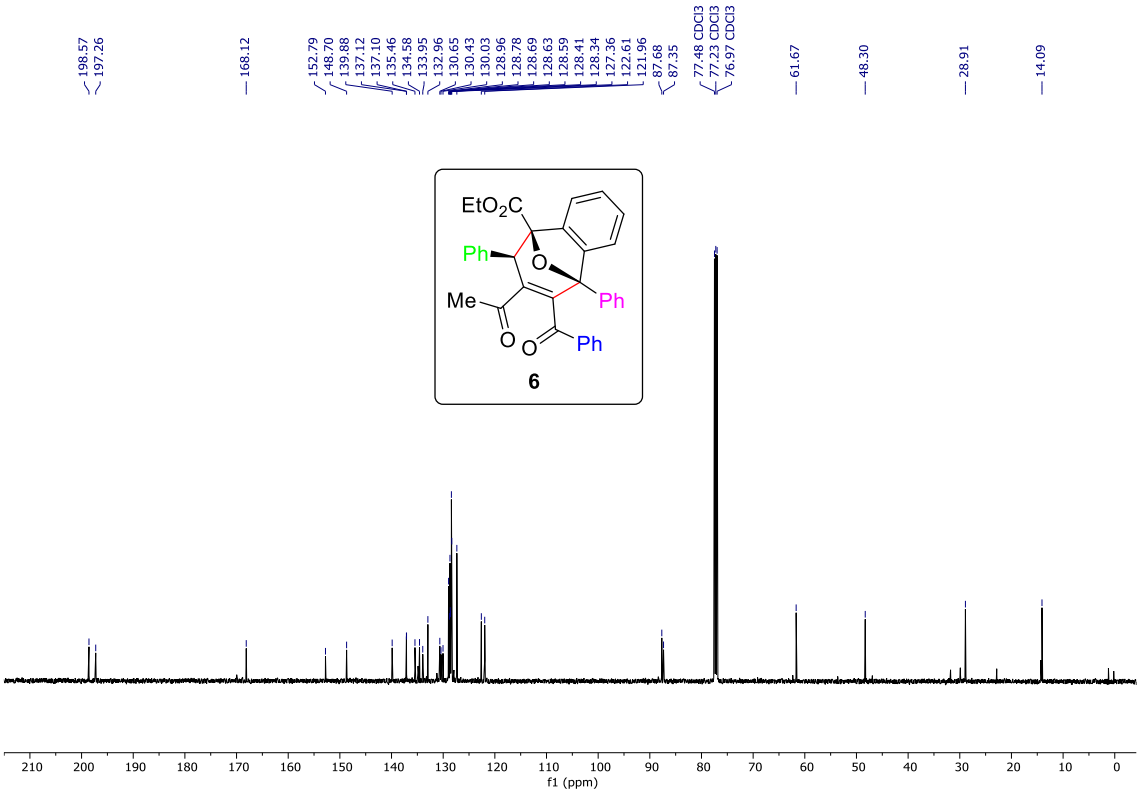


1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of Compound 5:



1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of Compound 6:





1H (500 MHz, $CDCl_3$) and 13C{H} (125 MHz, $CDCl_3$) NMR of Compound 7: