Electronic supporting information

Electrophilic fluorosulfoxonium cations as hidden Brønsted acid catalysts in (n+2) annulations of strained cycloalkanes

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General considerations

All reactions were performed in flame dried glassware using sealed tubes or Schlenk tubes. Liquids and solutions were transferred with syringes. Air- and moisture- sensitive materials were stored and handled under an atmosphere of argon with appropriate glassware. Dichloromethane (DCM) was distilled from calcium hydride prior to use. Technical-grade solvents for extraction and chromatography (cyclohexane, dichloromethane, *n*-pentane, ether and ethyl acetate) were used without purification. All reagents were purchased from standard suppliers (Sigma-Aldrich, Fluorochem, ABCR, Alfa Aesar, and Apollo scientific). Starting materials, if commercial, were purchased and used as such, provided that adequate checks (NMR) had confirmed the claimed purity.

Chromatography

Analytical thin-layer chromatography (TLC) analyses were performed on silica gel. Flash column chromatography purifications were performed on silica gel 60-F254.

Analytical data

^{1}H, ^{11}B, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ unless stated otherwise on Bruker Ascend 400 (^{1}H 400 MHz, ^{11}B 128 MHz, ^{13}C 100 MHz, ^{19}F NMR 377 MHz,) and Bruker Avance III HD 500 (^{1}H 500 MHz, ^{13}C 126 MHz, ^{11}B 160 MHz, ^{19}F NMR 470 MHz) instruments. ^{1}H, ^{13}C,^{11}B and ^{19}F NMR chemical shifts are reported in parts per million (ppm), either downfield from tetramethylsilane and referenced to the residual solvent resonance as the internal standard (e.g., chloroform residual signals δ [^{1}H] = 7.26 and accordingly δ [^{13}C] = 77.16 ppm). Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, coupling constant (Hz)) and integration. The spectra were processed with the program MestreNova (Mestrelab). High resolution mass spectrometry (HRMS) analyses were performed with a Bruker MicroTOF mass analyser under ESI in positive ionization mode detection (measurement accuracy ≤ 15 ppm) by the analytical facility at the University of Strasbourg.

Experimental procedures

Experimental procedure for the preparation of $[Ph_2S(F)O]^+[B(C_6F_5)_4]^-$ (Cat.1)

This procedure was carried out under exclusion of air at all times. In an argon-filled glovebox (GB), diphenyl sulfoxide (1 eq., 120 mg, 0.59 mmol) was dissolved in anhydrous and degassed DCM (0.2M) in a Schlenk tube. XeF_2 (1 eq., 101 mg, 0.60 mmol) and NEt_4Cl (5 mol%., 5 mg, 0.03 mmol) were added as solids and the tube was sealed with a rubber septum. The colourless solution was stirred at r.t. for 1 h out of the GB. The solution was then cooled to -78 °C and boron trifluoride etherate (1.06 eq., 0.08 mL, 0.63 mmol) was added dropwise. The mixture was stirred for 15 min at -78 °C before the argon line was switched to vacuum, still at -78 °C. The mixture was allowed to reach r.t., stirred for 18 h and was kept under vacuum through the whole process. A colourless solid residue was left. After placing again the reaction vessel in the GB, the residue was dissolved in DCM (4 mL) and potassium tetrakis(pentafluorophenyl)borate (1.02 eq., 433 mg, 0.60 mmol) was added as a solid. The vial was sealed and the pale yellow suspension was stirred at r.t. overnight, giving a red-ish solution and a white precipitate. The golden suspension was filtered through a cotton filled Pastor pipette before washing with clean DCM. The filtrate was taken out of the GB and concentrated in vacuo. A colorless residue was obtained, which was brought back to the GB. A minimum of DCM was added, followed by *n*-pentane dropwise until saturation. The vial was sealed and left at r.t. for 2 days. Colorless crystals were obtained, which were washed with *n*-pentane (491 mg, 0.55 mmol, 92%).

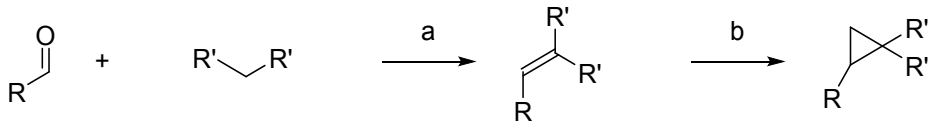
^{1}H NMR (400 MHz, CD_2Cl_2) δ = 8.25 (t, $^3J_{H4\text{-}H3}$ = 7.4 Hz, 2H, H4), 8.16 (d, $^3J_{H2\text{-}H3}$ = 8.1 Hz, 4H, H2), 7.99 (t, $^3J_{H3\text{-}H2/H4}$ = 7.9 Hz, 4H, H3).

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 142.2 (C1), 132.7 (C3), 129.7 (d, $^3J_{C2\text{-}F}$ = 1.7 Hz, C2), 126.0 (d, $^2J_{C1\text{-}F}$ = 10.7 Hz, C1). Signals corresponding to the $B(C_6F_5)_4$ anion are barely detected due to multiple C-F and C-B couplings and thus not reported.

^{19}F NMR (376 MHz, CD_2Cl_2) δ = 32.25 (s, 1F, F-S), -133.02–-133.29 (m, 8F, *o*-C_6F_5), -163.64 (t, $^3J_{F\text{-}F}$ = 20.3 Hz, 4F, *p*-C_6F_5), -167.54 (t, $^3J_{F\text{-}F}$ = 19.5 Hz, 8F, *m*-C_6F_5).

^{11}B NMR (128 MHz, CD_2Cl_2) δ = -16.73.

Experimental procedures for the preparation of D.A. cyclopropanes 1a–h[1]



a) piperidine, acetic acid, toluene, reflux, 12 - 48 h; b) $(CH)_3SOI$, NaH, DMSO, 0 °C to r.t.

General procedure A–Knoevenagel condensation

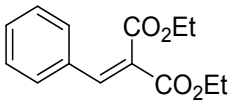
In a flame dried two-neck flask with a Dean-Stark apparatus were added the desired aldehyde (1 eq., 7.34 mmol), diethyl malonate (1.1 eq., 1.23 mL, 8.08 mmol), piperidine (6 mol%, 0.045 mL, 0.45 mmol), acetic acid (6mol%, 0.026 mL, 0.45 mmol) in toluene (8 mL). The reaction mixture was refluxed for 12-48 hours and conversion was monitored by TLC. The crude product was purified by silica gel chromatography but could be used directly for the next step.

General procedure B–Corey-Chaykovsky cyclopropanation

Under a hydrogen or argon atmosphere, trimethylsulfoxonium iodide (1.1 eq., 1.84 g, 8.36 mmol) was added in one portion to a stirred suspension of sodium hydride (1.1 eq., 0.33 g, 8.36 mmol) in anhydrous DMSO (19 mL), and the suspension was stirred until the frothing ceased. The resulting yellow mixture was cooled to 0 °C and a solution of the corresponding alkene (1 eq., 7.73 mmol) in anhydrous DMSO

(5 mL) was added portionwise. The reaction mixture was stirred for 15 min at the same temperature and then allowed to react at room temperature until the TLC showed the complete consumption of the starting material. The crude material was purified by flash chromatography.

Diethyl 2-benzylidenemalonate

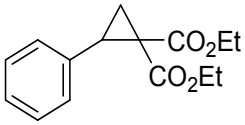


Following the general procedure A, the title compound was obtained as a colorless oil (4.79 g, 19.28 mmol, 58%). These data match previously reported values.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.47–7.43 (m, 2H), 7.40-7.35 (m, 3H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 164.3, 142.3, 133.1, 130.7, 129.6, 128.9, 126.5, 61.8, 61.8, 14.3, 14.0.

Diethyl 2-phenylcyclopropane-1,1-dicarboxylate (**1a**)

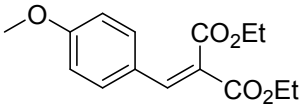


Following the general procedure B, the title compound was obtained as a colorless oil (0.51 g, 1.94 mmol, 96%). These data match previously reported values.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.18 (m, 3H), 4.34–4.16 (m, 2H), 3.84 (q, *J* = 7.2 Hz, 2H), 3.21 (t, *J* = 8.6 Hz, 1H), 2.17 (dd, *J* = 8.0, 5.2 Hz, 1H), 1.70 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 166.8, 134.8, 128.7, 128.2, 127.4, 61.8, 61.25, 37.6, 32.3, 18.8, 14.2, 13.8.

Diethyl 2-(4-methoxybenzylidene)malonate

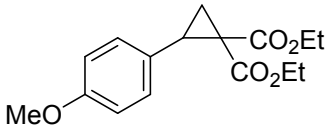


Following the general procedure A, the title compound was obtained as a yellow oil (1.52 g, 5.47 mmol, 74%). These data match previously reported values.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 164.7, 161.7, 141.9, 131.7, 125.6, 123.8, 114.4, 61.8, 61.6, 55.5, 14.3, 14.1.

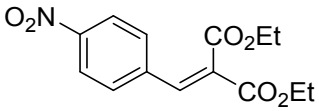
Diethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (**1b**)



Following the general procedure B, the title compound was obtained as a yellow oil (0.52 g, 1.77 mmol, 91%). These data match previously reported values.[3]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 4.32–4.14 (m, 2H), 3.86 (qd, *J* = 7.2, 2.4 Hz, 2H), 3.77 (s, 3H), 3.17 (t, *J* = 8.6 Hz, 1H), 2.12 (dd, *J* = 8.0, 5.1 Hz, 1H), 1.68 (dd, *J* = 9.2, 5.1 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.1 Hz, 3H).

Diethyl 2-(4-nitrobenzylidene)malonate (**3a**)

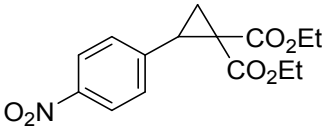


Following the general procedure A, the title compound was obtained as a yellow solid (0.53 g, 1.8 mmol, 54%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.76 (s, 1H), 7.61 (d, *J* = 8.7 Hz, 2H), 4.34 (q, *J* = 7.1, 2H), 4.33 (q, *J* = 7.1, 2H), 1.35 (t, *J* = 7.2, 3H), 1.28 (t, *J* = 7.1, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 163.5, 148.6, 139.4, 139.3, 130.2, 130.1, 124.1, 62.3, 62.3, 14.2, 14.1.

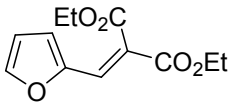
Diethyl 2-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate (**1c**)



Following the general procedure B, the title compound was obtained as a white solid (0.17 g, 0.55 mmol, 45%). These data match previously reported values.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 4.33–4.19 (m, 2H), 3.95–3.82 (m, 2H), 3.26 (t, *J* = 8.6 Hz, 1H), 2.20 (dd, *J* = 8.0, 5.4 Hz, 1H), 1.80 (dd, *J* = 9.1, 5.4 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.1 Hz, 3H).

Diethyl 2-(furan-2-ylmethylene)malonate

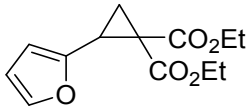


Following the general procedure A, the title compound was obtained as an orange liquid (1.54 g, 6.47 mmol, 77%). These data match previously reported values.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52–7.50 (m, 1H), 7.45 (s, 1H), 6.76 (d, *J* = 3.5 Hz, 1H), 6.49 (dd, *J* = 3.5, 1.8 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 164.3, 149.2, 146.2, 127.7, 122.2, 118.0, 112.7, 61.8, 61.7, 14.3, 14.2.

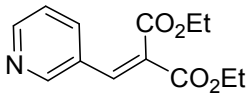
Diethyl 2-(furan-2-yl)cyclopropane-1,1-dicarboxylate (**1d**)



Following the general procedure B, the title compound was obtained as a yellow oil (1.0 g, 3.96 mmol, 93%). These data match previously reported values.[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.27 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.12 (m, 1H), 4.32–4.12 (m, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.14–3.03 (m, 1H), 2.05 (dd, *J* = 7.7, 5.0 Hz, 1H), 1.75 (dd, *J* = 9.5, 5.0 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H).

Diethyl 2-(pyridin-3-ylmethylene)malonate

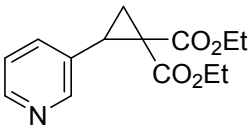


Following the general procedure A, the title compound was obtained as a yellow oil (1.54 g, 6.17 mmol, 73%). These data match previously reported values.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (d, *J* = 2.3 Hz, 1H), 8.61 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.77 (dd, *J* = 8.0, 1.6, 1H), 7.70 (s, 1H), 7.37–7.28 (m, 1H), 4.38–4.29 (m, 4H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 163.7, 151.2, 150.8, 138.7, 135.8, 129.1, 128.7, 123.9, 62.1, 62.1, 14.3, 14.1.

Diethyl 2-(pyridin-3-yl)cyclopropane-1,1-dicarboxylate (**1e**)

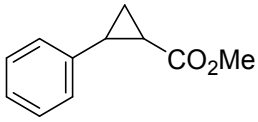


Following the general procedure B, the title compound was obtained as a colorless oil (0.67 g, 2.56 mmol, 71%). These data match the methyl analogue.[6]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (d, *J* = 2.0 Hz, 1H), 8.48 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.47 (dt, *J* = 7.9, 1.7 Hz, 1H), 7.19 (ddd, *J* = 7.8, 4.8, 0.9 Hz, 1H), 4.37–4.11 (m, 2H), 3.88 (app. qt, *J* = 7.2, 3.7 Hz, 2H), 3.19 (t, *J* = 8.6 Hz, 1H), 2.17 (dd, *J* = 7.9, 5.3 Hz, 1H), 1.75 (dd, *J* = 9.2, 5.3 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 169.6, 166.4, 150.8, 148.8, 135.7, 130.8, 123.0, 62.1, 61.6, 37.4, 29.4, 18.4, 14.2, 13.9.

Methyl 2-phenylcyclopropane-1-carboxylate (**1f**)

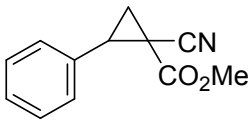


Following the general procedure B, the title compound was obtained as a yellow oil (0.13 g, 0.71 mmol, 6%). These data match previously reported values.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.25 (m, 2H), 7.25–7.16 (m, 1H), 7.12–7.07 (m, 2H), 3.72 (s, 3H), 2.53 (ddd, *J* = 9.2, 6.5, 4.2 Hz, 1H), 1.91 (ddd, *J* = 8.4, 5.3, 4.2 Hz, 1H), 1.61 (ddd, *J* = 9.2, 5.3, 4.6 Hz, 1H), 1.33 (ddd, *J* = 8.4, 6.5, 4.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 140.1, 128.6, 126.7, 126.4, 52.1, 26.4, 24.1, 17.2.

Methyl 1-cyano-2-phenylcyclopropane-1-carboxylate (**1g**)



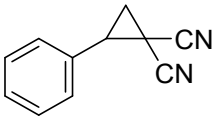
To a solution of dimethyl sulfide (1.75 eq., 2.2 g, 2.59 mL, 35 mmol) in acetonitrile (20 mL) maintained at 0 °C was added a solution of bromine (0.5 eq., 0.51 mL, 10 mmol) in CCl_4 (3 mL) to give a yellow precipitate. The styrene (1 eq., 2.3 mL, 20 mmol) was then added and stirring was continued for 60 min at the same temperature. The solution was then brought to room temperature and diethyl ether (30 mL), which led to the formation of a white precipitate. The latter was filtered and washed with diethyl ether to give the corresponding bromosulfonium bromide (1.53 g, 4.69 mmol, 23%).

To this compound (1 eq., 0.75 g, 2.3 mmol) in DCM (23 mL):H_2O (23 mL) (1:1 ratio) was added potassium carbonate (3 eq., 0.95 g, 6.9 mmol). Methyl cyanoacetate (2 eq., 0.41 mL, 4.6 mmol) was added and the reaction mixture was stirred for 8 h at room temperature. The organic layer was then separated and the aqueous layer was washed three times with DCM. The combined organic layers were dried over anhydrous sodium sulfate and concentrated. The residue was purified by column chromatography on silica gel to isolate the corresponding doubly activated cyclopropane **1g** as an inseparable mixture of diastereomers. Colorless liquid (0.346 g, 1.72 mmol, 75%, ratio *trans*/*cis* = 7:1).
These data match previously reported values.[8]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.34 (m, 3H), 7.31–7.27 (m, 2H), 3.87 (s, 3H), 3.18 (t, *J* = 8.8 Hz, 1H), 2.18 (dd, *J* = 9.3, 5.3 Hz, 1H), 2.12 (dd, *J* = 8.4, 5.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.00, 132.93, 128.93, 128.73, 128.44, 116.42, 53.85, 35.69, 22.99, 22.90.

2-Phenylcyclopropane-1,1-dicarbonitrile (**1h**)



Preparation of *t*-BuOCl
In a 500 mL Erlenmeyer flask with stirring bar was placed a 250 mL commercial household bleach solution (6°). The flask was placed in a pail of ice and the mixture was rapidly stirred until the temperature decreased below 10 °C. At this point the lights in the vicinity of the apparatus were turned off. A solution of *t*-BuOH (18.5 mL, 0.195 mol) and glacial acetic acid (12.25 mL, 0.215mol) were added in a single portion to the rapidly stirred bleach solution, and stirring was continued for about 3 min. The entire reaction mixture was poured into a 500 mL separatory funnel. The lower aqueous layer was discarded, and the oily yellow organic layer was washed first with a 25 mL portion of 10% aqueous sodium carbonate and then with 25 mL of water. The product was dried over 1 g calcium chloride and filtered. The product can be stored conveniently in a freezer or refrigerator over calcium chloride in amber glass bottles.

Procedure for the synthesis of **1h**
To a solution of styrene (1 eq., 1 mL, 8.7 mmol) in DCM (100 mL) were added malononitrile (1.2 eq., 0.69 g, 10 mmol), LiI (1.5 eq., 1.75 g, 13 mmol) and *t*-BuOCl (1.5 eq., 1.42 g, 13 mmol). The reaction was stirred at room temperature for 24 h. After reaction completion, the mixture was washed with 5% aqueous $Na_2S_2O_3$, and the aqueous layer was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. Purification by silica gel chromatography (Cyclohexane / Ethyl acetate 3:1) yielded analytically pure 1,1-dicyano-2-phenylcyclopropane **1h**.

The product was synthesized according to an already described protocol. These data match previously reported values.[9]

Yellow solid (1.30 g, 7.72 mmol, 89%)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.39 (m, 3H), 7.34–7.28 (m, 2H), 3.31 (t, *J* = 9.1 Hz, 1H), 2.29–2.23 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 130.7, 129.7, 129.3, 128.5, 115.5, 113.1, 35.3, 22.5, 7.4.

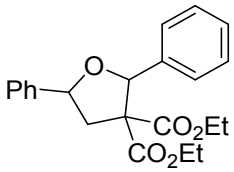
General procedure C for the (3+2) cyclisation of cyclopropanes, promoted by Electrophilic Sulfoxonium Cation Cat1

A flame-dried MW vial equipped with a magnetic stirrer was charged with the cyclopropane (1 eq., 0.38 mmol) and the reactant (2 eq., 0.76 mmol). In an argon-filled glovebox, the fluorosulfoxonium salt (5 mol%, 19 mmol) in anhydrous and degassed DCM (0.4 M) was added. The reaction mixture was stirred at 25 °C overnight. The vial was taken out the glovebox, volatiles were removed and the crude was purified by silica gel chromatography.

General procedure D for the (3+2) cyclisation of cyclopropanes, catalised by TfOH

A flame-dried MW vial equipped with a magnetic stirrer was charged with the cyclopropane (1 eq., 0.38 mmol) and the reactant (2 eq., 0.76 mmol). DCM (0.3 M) was added and then triflic acid (0.1 eq, 0.038 mmol). The reaction mixture was stirred at 25 °C for 0.25–12 h then quenched $NaHCO_3$. The aqueous and organic phases were separated, the aqueous phase was extracted three times with DCM. The organic phases were gathered, dried over Na_2SO_4 and concentrated under vacuum. The crude was purified by silica gel chromatography.

Diethyl 2,5-diphenyldihydrofuran-3,3(2*H*)-dicarboxylate (**2aa**)



Following the general procedure C, the title compound was obtained as a colorless liquid (108 mg, 0.29 mmol, 83%, d.r. = 13:1).

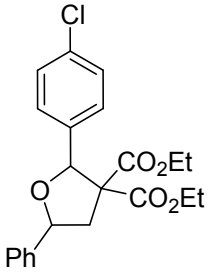
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.48 (m, 4H), 7.43–7.37 (m, 2H), 7.37–7.27 (m, 4H), 5.80 (s, 1H), 4.95 (dd, *J* = 10.6, 6.0 Hz, 1H), 4.36 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.27 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.71 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.41 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.01 (dd, *J* = 13.4, 10.7 Hz, 1H), 2.73 (dd, *J* = 13.4, 6.1 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.78 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.0, 169.0, 140.0, 137.8, 128.5, 128.1, 128.1, 127.8, 127.3, 126.6, 84.4, 79.8, 66.2, 61.9, 61.5, 43.0, 14.1, 13.4.

LRMS (APCI+) *m/z* 368 ($[M]^{+\bullet}$), 296 ($[M - CO_2Et + H]^{+\bullet}$), 264 ($[M - PhCHCH_2]^{+\bullet}$), 262 ($[M - PhCHO]^{+\bullet}$).

HRMS: 391.1516 calculated for $C_{22}H_{24}NaO_5$, found 391.1536.

Diethyl 2-(4-chlorophenyl)-5-phenyldihydrofuran-3,3(2*H*)-dicarboxylate (**2ab**)



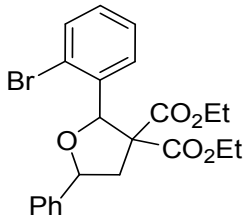
Following the general procedure C, the title compound was obtained as a colorless liquid (149.3 mg, 0.37 mmol, 97%, d.r. >20 :1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.48 (m, 2H), 7.46–7.41 (m, 2H), 7.39–7.34 (m, 2H), 7.32–7.28 (m, 1H), 7.27 - 7.22 (m, 2H), 5.71 (s, 1H), 4.91 (dd, *J* = 10.5, 6.3 Hz, 1H), 4.31 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.23 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.72 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.46 (dq, *J* = 10.7, 7.2 Hz, 1H), 2.96 (dd, *J* = 13.5, 10.5 Hz, 1H), 2.70 (dd, *J* = 13.5, 6.3 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.80 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 168.8, 139.9, 136.4, 134.0, 128.8, 128.7, 128.3, 128.1, 126.7, 83.8, 80.1, 66.2, 62.1, 61.8, 43.0, 14.2, 13.6.

HRMS: 425.1126 calculated for $C_{22}H_{23}ClNaO_5$, found 425.1120.

Diethyl 2-(2-bromophenyl)-5-phenyldihydrofuran-3,3(2*H*)-dicarboxylate (**2ac**)



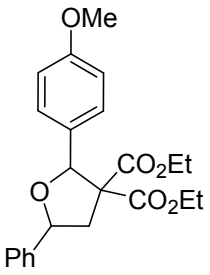
Following the general procedure C, the title compound was obtained as a yellow liquid (97.1 mg, 0.22 mmol, 71%, d.r. = 19:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56–7.48 (m, 4H), 7.43–7.37 (m, 2H), 7.37–7.32 (m, 1H), 7.29 (td, *J* = 7.6, 1.3 Hz, 1H), 7.13 (ddd, *J* = 7.9, 7.3, 1.7 Hz, 1H), 6.41 (s, 1H), 5.01 (dd, *J* = 11.8, 4.6 Hz, 1H), 4.40 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.29 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.76 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.40 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.05 (dd, *J* = 13.4, 11.8 Hz, 1H), 2.63 (dd, *J* = 13.3, 4.7 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 168.4, 139.2, 138.4, 132.4, 129.6, 129.6, 128.6, 128.2, 127.2, 126.3, 124.0, 82.8, 79.6, 66.0, 62.1, 61.6, 43.5, 14.1, 13.4.

HRMS: 485.0360 calculated for $C_{22}H_{23}BrKO_5$, found 485.0349.

Diethyl 2-(4-methoxyphenyl)-5-phenyldihydrofuran-3,3(2*H*)-dicarboxylate (**2ad**)



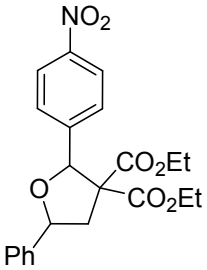
Following the general procedure C, the title compound was obtained as a colorless liquid. (22 mg, 0.055 mmol, 72%, d.r. = 3:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57–7.50 (m, 1H), 7.46–7.38 (m, 4H), 7.37–7.30 (m, 2H), 6.88–6.80 (m, 2H), 5.75 (s, 1H), 4.93 (dd, *J* = 10.7, 6.0 Hz, 1H), 4.35 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.29–4.21 (m, 1H), 3.79 (s, 3H), 3.77–3.70 (m, 1H), 3.48 (dq, *J* = 10.7, 7.2 Hz, 1H), 2.99 (dd, *J* = 13.4, 10.7 Hz, 1H), 2.72 (dd, *J* = 13.4, 6.1 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.84 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 169.1, 159.5, 140.1, 130.0, 128.5, 126.6, 113.2, 84.1, 79.7, 66.2, 61.8, 61.5, 55.3, 42.9, 29.7, 14.1, 13.5.

HRMS: 421.1621 calculated for $C_{23}H_{26}NaO_6$, found 421.1607.

Diethyl 2-(4-nitrophenyl)-5-phenyldihydrofuran-3,3(2*H*)-dicarboxylate (**2ae**)



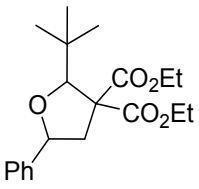
Following the general procedure C, the title compound was obtained as a yellow liquid (12 mg, 0.028 mmol, 43%, d.r. > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.42 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.39-7.31 (m, 1H), 5.82 (s, 1H) 4.99 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.85 (s, 3H), 3.15 (s, 3H), 3.00 (dd, *J* = 13.2, 10.8 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.82 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 168.6, 147.7, 145.1, 139.4, 128.7, 128.4, 128.2, 126.6, 123.0, 83.4, 80.3, 66.2, 62.2, 61.8, 43.0, 14.0, 13.5.

HRMS: 452.1106 calculated for $C_{22}H_{23}KNO_7$, found 452.1128.

Diethyl 2-(*tert*-butyl)-5-phenyldihydrofuran-3,3(2*H*)-dicarboxylate (**2af**)



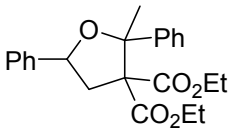
Following the general procedure C, the title compound was obtained as a colorless liquid (86 mg, 0.25 mmol, 65%, d.r. > 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.36 (m, 2H), 7.30–7.25 (m, 2H), 7.23–7.17 (m, 1H), 4.67 (dd, *J* = 9.8, 6.9 Hz, 1H), 4.34 (s, 1H), 4.27–4.12 (m, 3H), 4.05 (m, 1H), 2.77 (dd, *J* = 13.3, 9.8 Hz, 1H), 2.57 (dd, *J* = 13.3, 6.9 Hz, 1H), 1.24 -1.17 (m, 6H), 0.99 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 170.5, 141.3, 128.4, 127.7, 126.4, 90.6, 78.0 , 62.1, 61.7, 61.6, 45.2, 34.6, 26.9, 14.1, 13.8.

HRMS: 387.1568 calculated for $C_{20}H_{28}KO_5$, found 387.1568.

Diethyl 2-methyl-2,5-diphenyldihydrofuran-3,3(2*H*)-dicarboxylate (**2ag**)



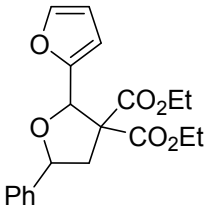
Following the general procedure C, the title compound was obtained as a colorless oil (0.213 g, 0.55 mmol, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.72 (m, 3H), 7.58 (dd, *J* = 7.4, 1.7 Hz, 2H), 7.29–7.15 (m, 5H), 5.24 (t, *J* = 8.0 Hz, 1H), 4.37–4.08 (m, 2H), 3.56 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.40 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.05 (dd, *J* = 13.8, 8.5 Hz, 1H), 2.73 (dd, *J* = 13.7, 7.5 Hz, 1H), 1.83 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.71 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 169.6, 142.9, 141.9, 128.5, 127.6, 127.6, 127.3, 126.6, 126.5, 126.3, 125.7, 87.9, 76.5, 68.9, 61.6, 61.4, 42.5, 26.7, 25.4, 14.1, 13.4.

HRMS: 405.1672 calculated for $C_{23}H_{26}NaO_5$, found 405.1670.

Diethyl 2-(furan-2-yl)-5-phenyldihydrofuran-3,3(2*H*)-dicarboxylate (**2ah**)



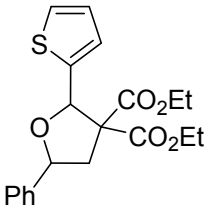
Following the general procedure C, the title compound was obtained as a yellow liquid (69.4 mg, 0.19 mmol, 51%, d.r. = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.90 (m, 1H), 7.59–7.27 (m, 5H), 6.38 (dd, *J* = 3.2, 0.9 Hz, 1H), 6.32 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.85 (s, 1H), 4.93 (dd, *J* = 11.3, 5.3 Hz, 1H), 4.44–4.21 (m, 2H), 3.97 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.84 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.05 (dd, *J* = 13.3, 11.3 Hz, 1H), 2.72 (dd, *J* = 13.3, 5.4 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 168.0, 151.7, 142.8, 140.1, 129.4, 128.6, 127.8, 126.6, 110.4, 109.4, 80.2, 77.9, 65.3, 62.4, 62.0, 42.0, 14.2, 13.9.

HRMS: 397.1048 calculated for $C_{20}H_{22}KO_6$, found 397.1075.

Diethyl 5-phenyl-2-(thiophen-2-yl)dihydrofuran-3,3(2*H*)-dicarboxylate (**2ai**)



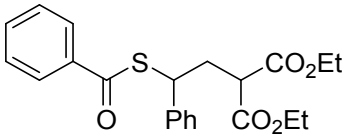
Following the general procedure C, the title compound was obtained as a yellow liquid (25.5 mg, 0.07 mmol, 18%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56–7.42 (m, 3H), 7.36 (ddd, *J* = 7.9, 6.7, 1.7 Hz, 2H), 7.30 (tt, *J* = 7.2, 1.5 Hz, 1H), 6.95 (dt, *J* = 3.7, 0.9 Hz, 1H), 6.77–6.73 (m, 1H), 5.94 (s, 1H), 4.90 (dd, *J* = 10.7, 5.9 Hz, 1H), 4.38–4.30 (m, 1H), 4.30–4.23 (m, 1H), 3.86 (dqdd, *J* = 10.9, 7.1, 3.7, 2.7 Hz, 1H), 3.72–3.63 (m, 1H), 2.93 (dd, *J* = 13.4, 10.7 Hz, 1H), 2.71 (dd, *J* = 13.5, 6.0 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 2H), 0.98–0.86 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 168.5, 146.9, 139.8, 129.5, 128.6, 128.2, 126.6, 125.4, 125.4, 81.1, 80.1, 66.3, 62.2, 62.1, 42.4, 14.2, 13.8.

HRMS: 397.1080 calculated for $C_{20}H_{22}NaO_5S$, found 397.1096.

Diethyl 2-(2-(benzoylthio)-2-phenylethyl)malonate (**2al**)



Following the general procedure C, the title compound was obtained as a colorless liquid (58.6 mg, 0.15 mmol, 73%).

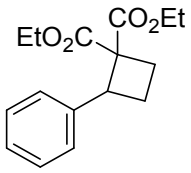
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.58–7.52 (m, 1H), 7.46–7.37 (m, 4H), 7.37–7.31 (m, 2H), 7.28 - 7.24 (m, 1H), 4.87 (t, *J* = 8.0 Hz, 1H), 4.24 (qd, *J* = 7.1, 1.7 Hz, 2H), 4.14 (qd, *J* = 7.2, 4.2 Hz, 2H), 3.40 (t, *J* = 7.3 Hz, 1H), 2.67 (d, *J* = 2.9 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 190.1, 168.9, 168.7, 140.5, 136.7, 133.5, 128.8, 128.6, 127.9, 127.8, 127.4, 61.7, 61.6, 50.2, 45.8, 35.3, 14.1, 14.0.

HRMS: 439.0976 calculated for $C_{22}H_{24}KO_5S$, found 439.097189.

General procedure E for the synthesis of D-A cyclobutanes.[10]

To a solution of diethyl malonate (1 eq., 2.05 mL, 13.5 mmol) in anhydrous THF (50 mL) under an inert atmosphere was added NaH (60% in mineral oil) (2.13 eq., 1.15 g, 28.68 mmol) at 0 °C. A solution of the substituted 1,3-dibromopropane (1 eq., 13.5 mmol) in anhydrous THF (12.5 mL) was added to the reaction mixture. The latter was heated under reflux overnight. The solvent was evaporated and the residue was taken up in ether and treated with ice. The organic layer was washed with water, dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography.

Diethyl 2-phenylcyclobutane-1,1-dicarboxylate (**3a**)

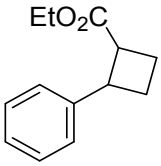


Following the general procedure E, the title compound was obtained as a colorless liquid (2.59 g, 9.37 mmol, 69%). These data match previously reported values.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.20 (m, 4H), 7.22–7.16 (m, 1H), 4.37 (t, *J* = 9.4 Hz, 1H), 4.33–4.13 (m, 2H), 3.78 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.66 (dq, *J* = 10.7, 7.1 Hz, 1H), 2.76–2.55 (m, 2H), 2.32–2.21 (m, 1H), 2.21–2.20 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.76 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 169.6, 139.4, 128.1, 127.9, 127.0, 61.4, 61.1, 59.7, 45.0, 25.8, 20.7, 14.2, 13.6.

Ethyl 2-phenylcyclobutane-1-carboxylate (**3b**)



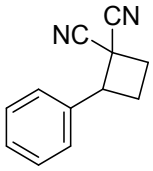
An adapted protocol from Varney's work has been used.[11] A micro-wave vial was charged with 1,1-diethyl 2-phenylcyclobutane-1,1-dicarboxylate **3a** (1 eq., 0.4 g, 1.45 mmol), LiCl (2.13 eq., 0.13 g, 3.076 mmol), DMSO (2.53 mL) and H_2O (0.03 mL) and heated under stirring at 170 °C for 30 min in the micro-wave reactor. The reaction mixture was diluted with diethyl ether then washed sequentially with a saturated solution of brine, water and a saturated solution of brine. The organic phase was dried, filtered and concentrated under vacuum. The crude was purified with silica gel chromatography to yield the desired product as a yellow liquid (168 mg, 0.8 mmol, 57%, d.r. = 1,2:1).

These data match previously reported values.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.13 (m, 5H), 4.16 (qd, *J* = 7.1, 1.0 Hz, 2H), 3.83–3.75 (m, 1H), 3.23–3.12 (m, 1H), 2.34–2.24 (m, 2H), 2.21–2.09 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 143.9, 128.5, 127.5, 126.5, 60.6, 45.6, 43.2, 25.4, 21.8, 14.4.

2-Phenylcyclobutane-1,1-dicarbonitrile (**3c**)

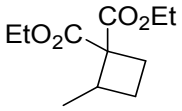


Following the general procedure E, the title compound was obtained as a colorless liquid (62 mg, 0.34 mmol, 4%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.29 (m, 2H), 7.29–7.24 (m, 1H), 7.23–7.18 (m, 2H), 4.13 (dd, *J* = 10.7, 8.4 Hz, 1H), 2.75–2.66 (m, 2H), 2.63–2.54 (m, 1H), 2.38–2.30 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.7, 129.4, 129.3, 127.4, 115.9, 114.7, 50.2, 34.1, 30.6, 23.6.

Diethyl 2-methylcyclobutane-1,1-dicarboxylate (**3d**)

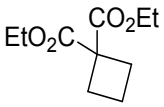


Following a procedure described in the US patent 2018/0050022 A1, the title product was obtained as a colorless liquid (0.39g, 1.8 mmol, 27%).[13]

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.29–4.16 (m, 4H), 3.17–3.07 (m, 1H), 2.71–2.61 (m, 1H), 2.17–2.00 (m, 2H), 1.74–1.67 (m, 1H), 1.26 (t, *J* = 9.4, 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.05 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.17, 170.43, 61.15, 57.03, 35.81, 25.81, 24.33, 17.25, 14.41, 14.22.

Diethyl cyclobutane-1,1-dicarboxylate (**3e**)



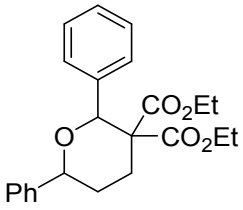
Following the general procedure E, the title compound was obtained as a colorless liquid (1.91 g, 9.54 mmol, 97%). These data match previously reported values.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20 (q, *J* = 7.1 Hz, 4H), 2.57–2.49 (m, 4H), 2.03–1.93 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 6H).

General procedure F for the (4+2) cyclisation of D-A cyclobutanes.

In an argon-filled glovebox, the cyclobutane (1 eq., 0.39 mmol) and the aldehyde (2 eq., 0.72 mmol) were placed into a flame-dried M.W. vial. DCM (1 mL) was added, followed by **Cat.1** (5 mol%, 24 mg, 0.026 mmol). The M.W. vial was sealed, taken out the glovebox and the mixture was stirred at 50 °C overnight. The crude material was directly purified by column chromatography on silica gel.

Diethyl 2,6-phenyldihydro-2*H*-pyran-3,3(4*H*)-dicarboxylate (**4aa**)



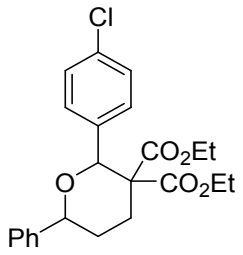
Following the general procedure F, the title compound was obtained as a colorless liquid (23 mg, 0.06 mmol, 62%, d.r. = 14:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.47 (m, 2H), 7.45–7.41 (m, 2H), 7.38–7.32 (m, 2H), 7.30–7.21 (m, 4H), 5.18 (s, 1H), 4.67 (dd, *J* = 11.6, 2.8 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.08 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.93 (dq, *J* = 10.7, 7.1 Hz, 1H), 2.73–2.62 (m, 1H), 2.30 (td, *J* = 13.4, 4.4 Hz, 1H), 2.14 (tdd, *J* = 13.4, 11.6, 4.0 Hz, 1H), 1.94 (ddt, *J* = 13.8, 4.4, 2.8 Hz, 1H), 1.17 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 168.9, 142.6, 139.8, 128.4, 127.7, 127.5, 127.3, 126.0, 82.2, 80.8, 61.5, 60.7, 58.5, 32.9, 30.3, 14.0, 13.8.

HRMS: 421.1411 calculated for $C_{23}H_{26}KO_5$, found 421.1401.

Diethyl 2-(4-chlorophenyl)-6-phenyldihydro-2*H*-pyran-3,3(4*H*)-dicarboxylate (**4ab**)

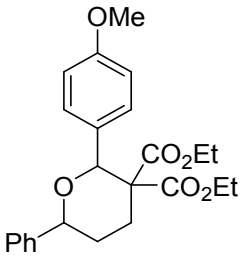


Following the general procedure F, the title compound was obtained as a colorless liquid (115 mg, 0.28 mmol, 76%, d.r.=19:1).

^{1}H NMR (400 MHz, $CDCl_3$)) δ 7.48–7.44 (m, 2H), 7.43–7.38 (m, 2H), 7.35 (ddd, *J* = 7.7, 6.7, 1.3 Hz, 2H), 7.32–7.22 (m, 3H), 5.16 (s, 1H), 4.66 (dd, *J* = 11.5, 2.8 Hz, 1H), 4.20–4.14 (m, 2H), 4.13–4.05 (m, 1H), 3.96 (dq, *J* = 10.8, 7.2 Hz, 1H), 2.69 (dt, *J* = 13.3, 3.7 Hz, 1H), 2.28 (td, *J* = 13.3, 4.2 Hz, 1H), 2.14 (tdd, *J* = 13.3, 11.4, 3.9 Hz, 1H), 1.94 (ddt, *J* = 13.8, 4.3, 2.7 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz $CDCl_3$) δ 171.0, 168.6, 142.3, 138.3, 133.2, 129.1, 128.4, 127.7, 127.4, 125.9, 81.6, 80.8, 61.6, 60.8, 58.4, 32.8, 30.1, 14.0, 13.8.

HRMS: 455.1022 calculated for $C_{23}H_{25}ClKO_5$, found 455.1017.

Diethyl 2-(4-methoxyphenyl)-6-phenyldihydro-2*H*-pyran-3,3(4*H*)-dicarboxylate (**4ac**)



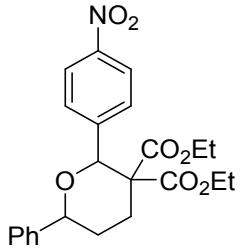
Following the general procedure F, the title compound was obtained as a colorless liquid (7 mg, 0.017 mmol, 5%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.39 (m, 4H), 7.36–7.30 (m, 2H), 7.29–7.23 (m, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 5.12 (s, 1H), 4.66 (dd, *J* = 11.6, 2.8 Hz, 1H), 4.19–4.04 (m, 3H), 3.97 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.78 (s, 3H), 2.72–2.62 (m, 1H), 2.28 (td, *J* = 13.3, 4.3 Hz, 1H), 2.20–2.05 (m, 1H), 1.97–1.87 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 169.0, 159.0, 142.6, 132.0, 128.9, 128.4, 127.6, 126.0, 112.7, 82.1, 80.8, 61.5, 60.7, 58.5, 55.4, 32.8, 30.3, 14.1, 13.9.

HRMS: 451.1517 calculated for $C_{24}H_{28}KO_6$ found 451.1517

Diethyl 2-(4-nitrophenyl)-6-phenyldihydro-2*H*-pyran-3,3(4*H*)-dicarboxylate (**4ad**)



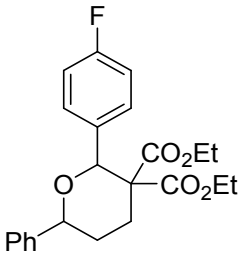
Following the general procedure F, the title compound was obtained as a yellow liquid (55 mg, 0.13 mmol, 36%, d.r. > 20:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.9 Hz, 2H), 7.72–7.65 (m, 2H), 7.45–7.35 (m, 4H), 7.34–7.27 (m, 1H), 5.27 (s, 1H), 4.69 (dd, *J* = 11.6, 2.7 Hz, 1H), 4.31–4.16 (m, 2H), 4.14–4.06 (m, 1H), 3.98–3.91 (m, 1H), 2.73 (ddd, *J* = 13.4, 4.1, 2.8 Hz, 1H), 2.31 (td, *J* = 13.4, 4.3 Hz, 1H), 2.14 (tdd, *J* = 13.4, 11.7, 4.1 Hz, 1H), 1.97 (ddt, *J* = 14.0, 4.4, 2.8 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 168.3, 147.3, 141.8, 129.4, 128.6, 128.6, 128.0, 125.9, 122.5, 81.3, 81.0, 61.9, 61.1, 58.6, 32.8, 30.0, 14.1, 13.9.

HRMS : 466.1262 calculated for $C_{23}H_{25}KNO_7$, found 466.1250

Diethyl 2-(4-fluorophenyl)-6-phenyldihydro-2*H*-pyran-3,3(4*H*)-dicarboxylate (**4ae**)



Following the general procedure F, the title compound was obtained as a yellow liquid (115 mg, 0.29 mmol, 73%, d.r. > 20:1).

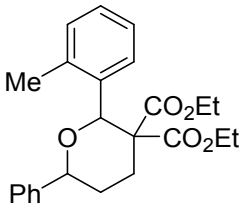
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.75 (m, 2H), 7.79-7.69 (m, 2H), 7.68-7.62 (m, 2H), 7.60–7.54 (m, 1H), 7.29-7.23 (m, 2H), 5.46 (s, 1H), 4.97 (dd, *J* = 11.4, 2.8 Hz, 1H), 4.50–4.35 (m, 3H), 4.29-4.20 (m, 1H), 2.99 (dt, *J* = 13.2, 3.5 Hz, 1H), 2.58 (td, *J* = 13.1, 4.1 Hz, 1H), 2.50–2.38 (m, 1H), 2.23 (dq, *J* = 13.8, 3.1 Hz, 1H), 1.48 (t, *J* = 7.1 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 168.7, 163.5, 161.1, 142.3, 135.6 (d, *J* = 3.3 Hz), 129.4 (d, *J* = 8.0 Hz), 128.4, 127.7, 125.9, 114.0 (d, *J* = 21.3 Hz), 81.6, 80.9, 61.5, 60.8, 58.4, 32.8, 30.2, 14.0, 13.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -115.44.

HRMS: 439.1297 calculated for $C_{23}H_{25}FKO_5$, found 439.1318.

Diethyl 6-phenyl-2-(*o*-tolyl)dihydro-2*H*-pyran-3,3(4*H*)-dicarboxylate (**4af**)



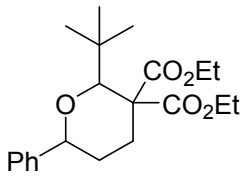
Following the general procedure F, the title compound was obtained as a colorless liquid (48.4 mg, 0.18 mmol, 48%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79-7.70 (m, 1H), 7.44–7.39 (m, 2H), 7.32 (m, 2H), 7.29–7.21 (m, 1H), 7.19–7.11 (m, 2H), 7.08 (m, 1H), 5.33 (s, 1H), 4.67 (dd, *J* = 11.0, 3.6 Hz, 1H), 4.19–4.04 (m, 3H), 3.97 (dq, *J* = 10.8, 7.1 Hz, 1H), 2.68 (dt, *J* = 13.6, 4.5 Hz, 1H), 2.39 (s, 3H), 2.36–2.32 (m, 1H), 2.13 (m, 1H), 1.94 (dtd, *J* = 13.9, 4.4, 3.5 Hz, 1H), 1.11 (t, *J* = 7.2, 3H), 1.10 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 169.3, 142.8, 137.2, 136.5, 130.1, 129.1, 128.4, 127.7, 127.6, 126.0, 125.2, 80.3, 79.6, 61.5, 60.9, 57.7, 32.1, 30.3, 20.3, 13.9, 13.8.

HRMS: 419.1829 calculated for $C_{24}H_{28}NaO_5$, found 419.1829

Diethyl 2-(tert-butyl)-6-phenyldihydro-2H-pyran-3,3(4H)-dicarboxylate (**4ag**)



Following the general procedure F, the title compound was obtained as a yellow liquid (46.9 mg, 0.13 mmol, 36%).

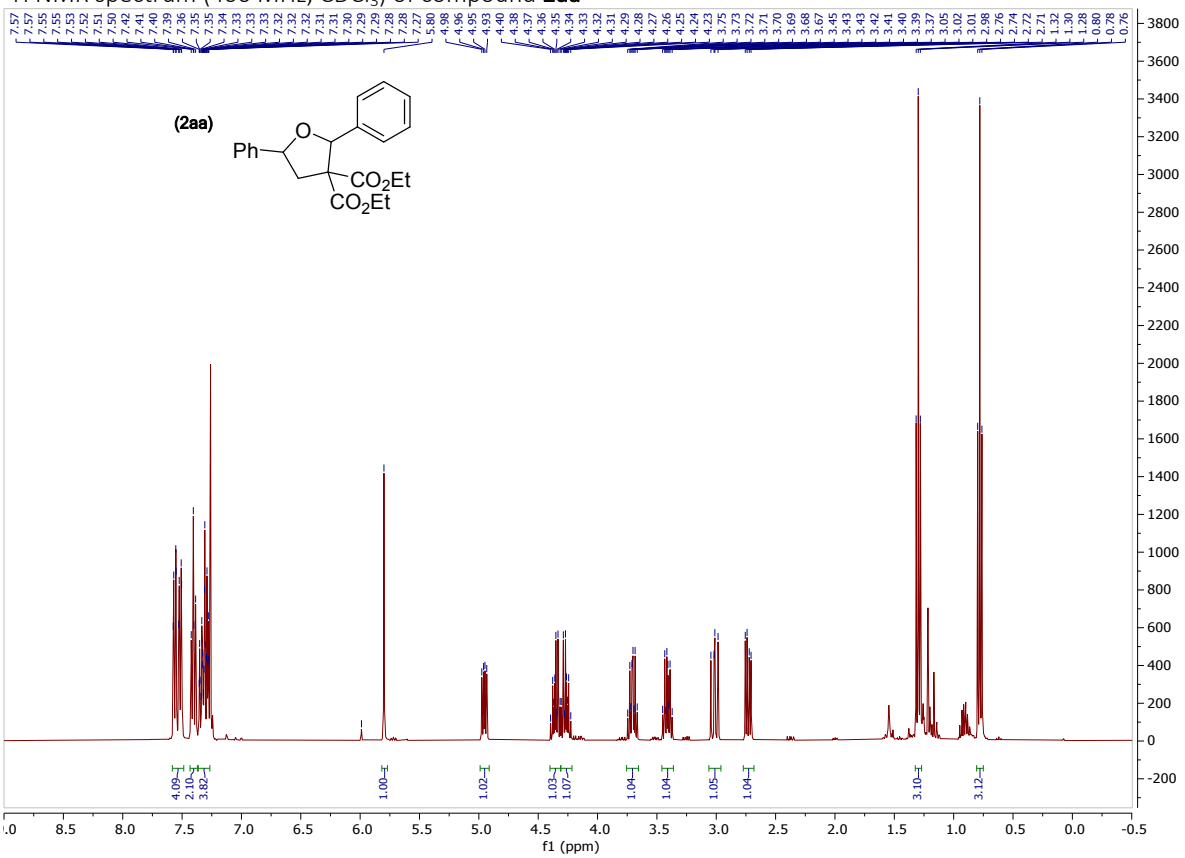
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.11 (m, 5), 4.40 (dd, *J* = 11.2, 2.7 Hz, 1H), 4.30–3.99 (m, 4H), 3.87 (s, 1H), 2.45 (ddd, *J* = 13.0, 3.5, 2.4 Hz, 1H), 2.07–1.89 (m, 2H), 1.78–1.72 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.2 Hz,3H), 0.98 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 169.9, 143.3, 128.3, 127.2, 125.6, 88.0, 80.5, 61.3, 60.9, 55.4, 36.9, 35.6, 30.4, 27.7, 14.1, 14.0.

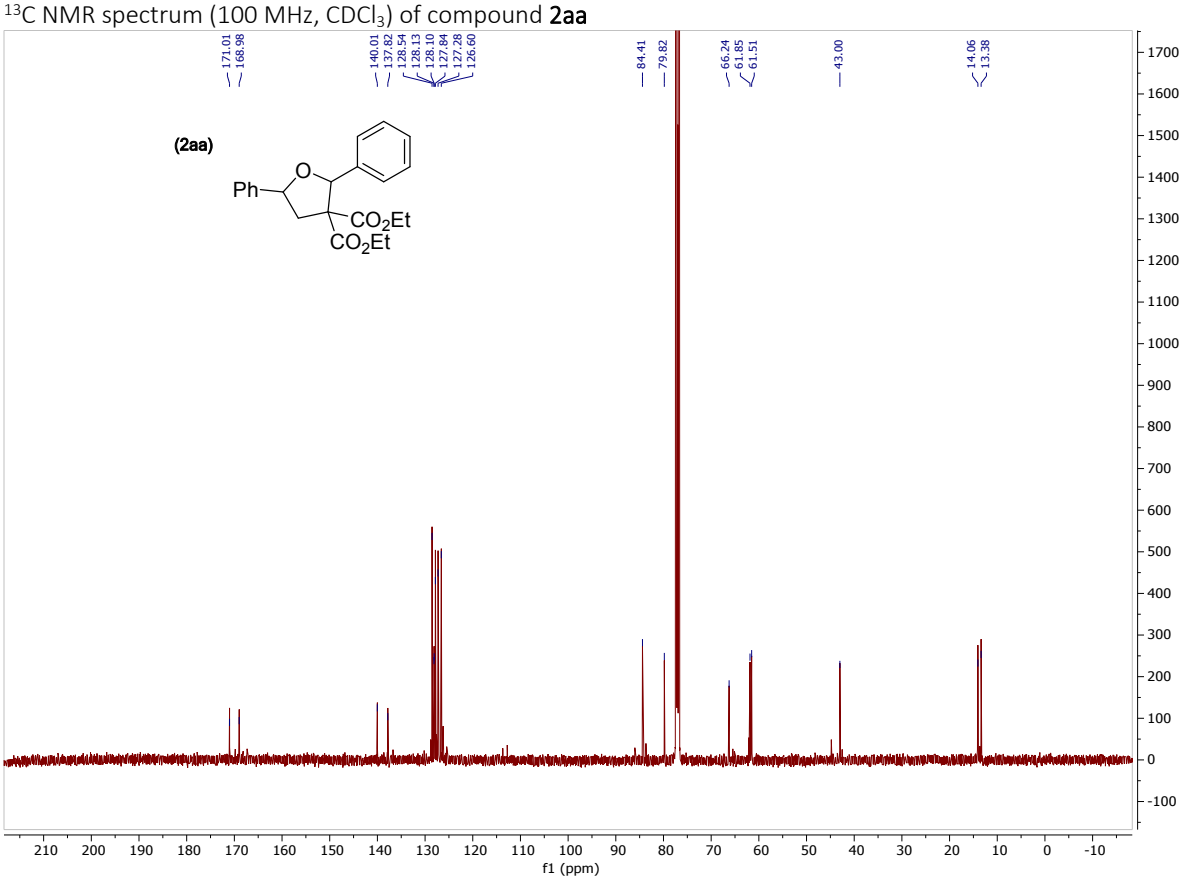
HRMS: 385.1985 calculated for $C_{21}H_{30}NaO_5$, found 385.1981.

NMR spectra

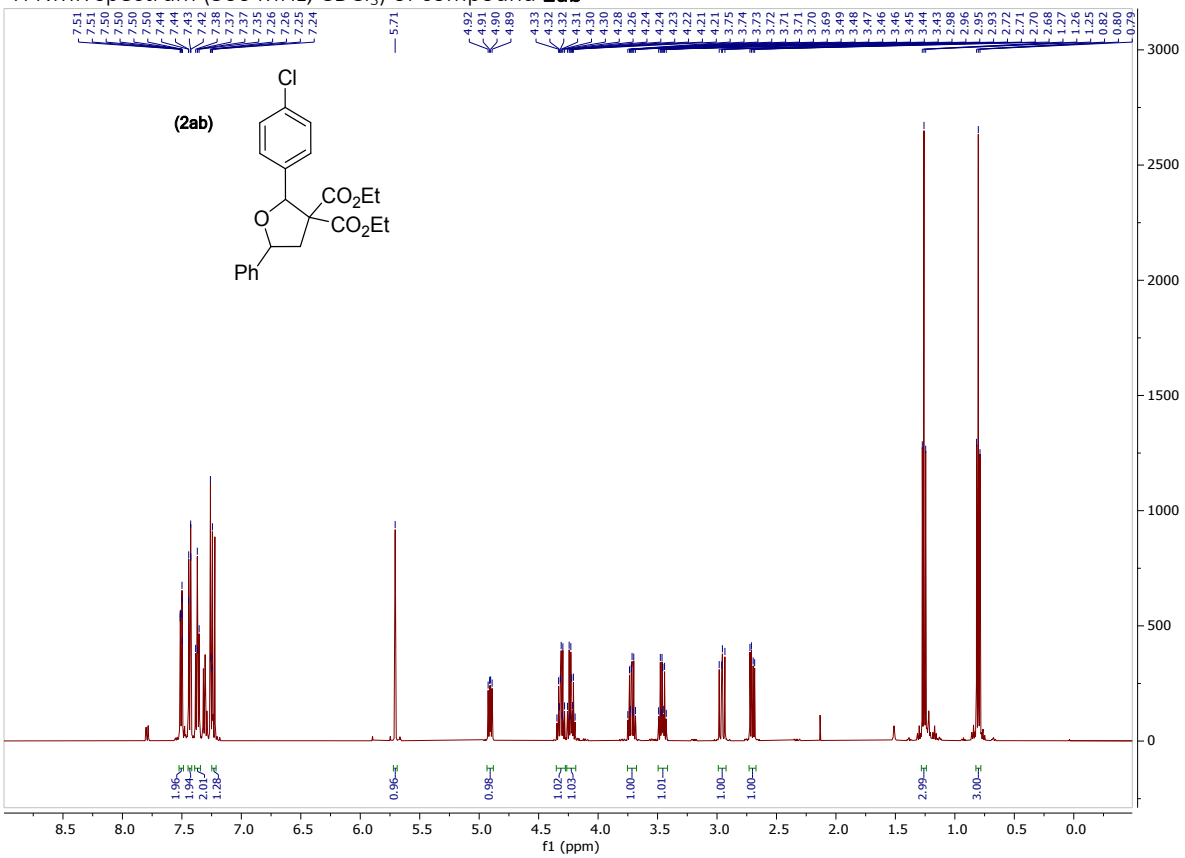
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2aa**



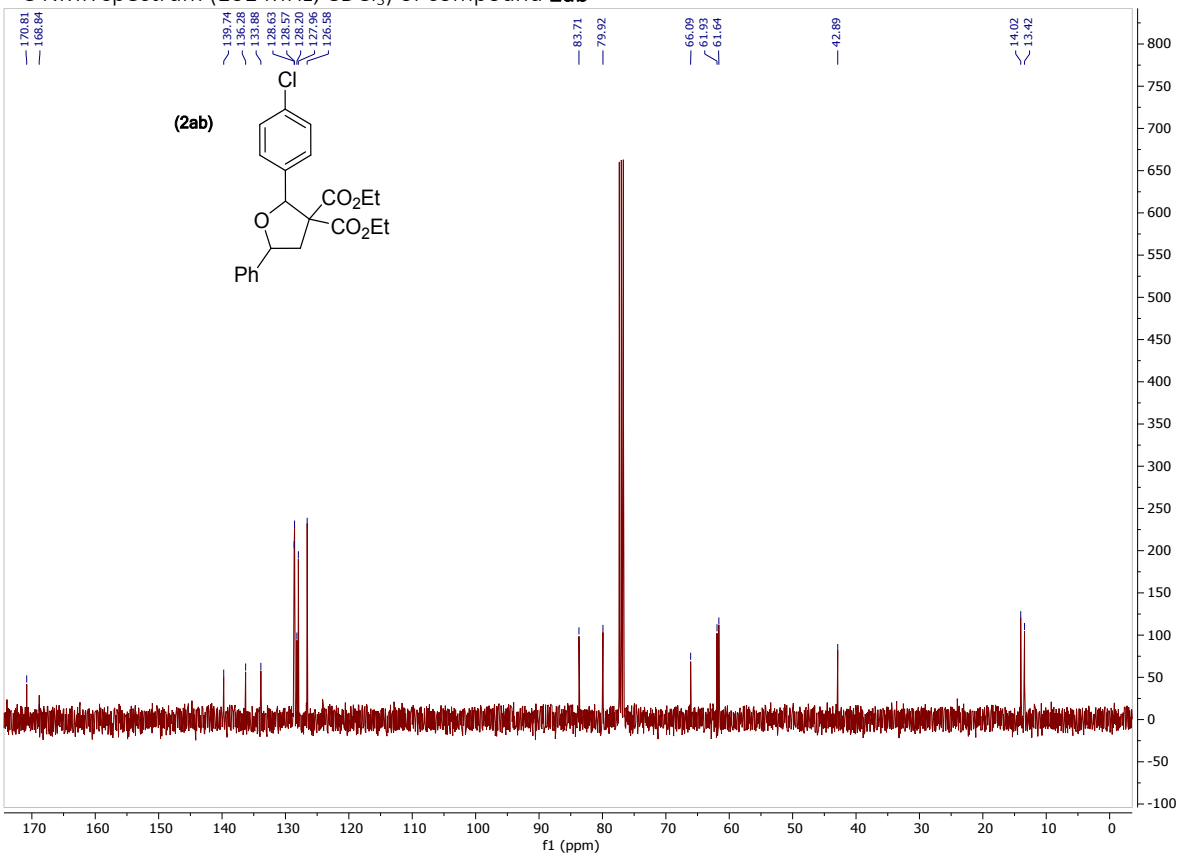
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **2aa**



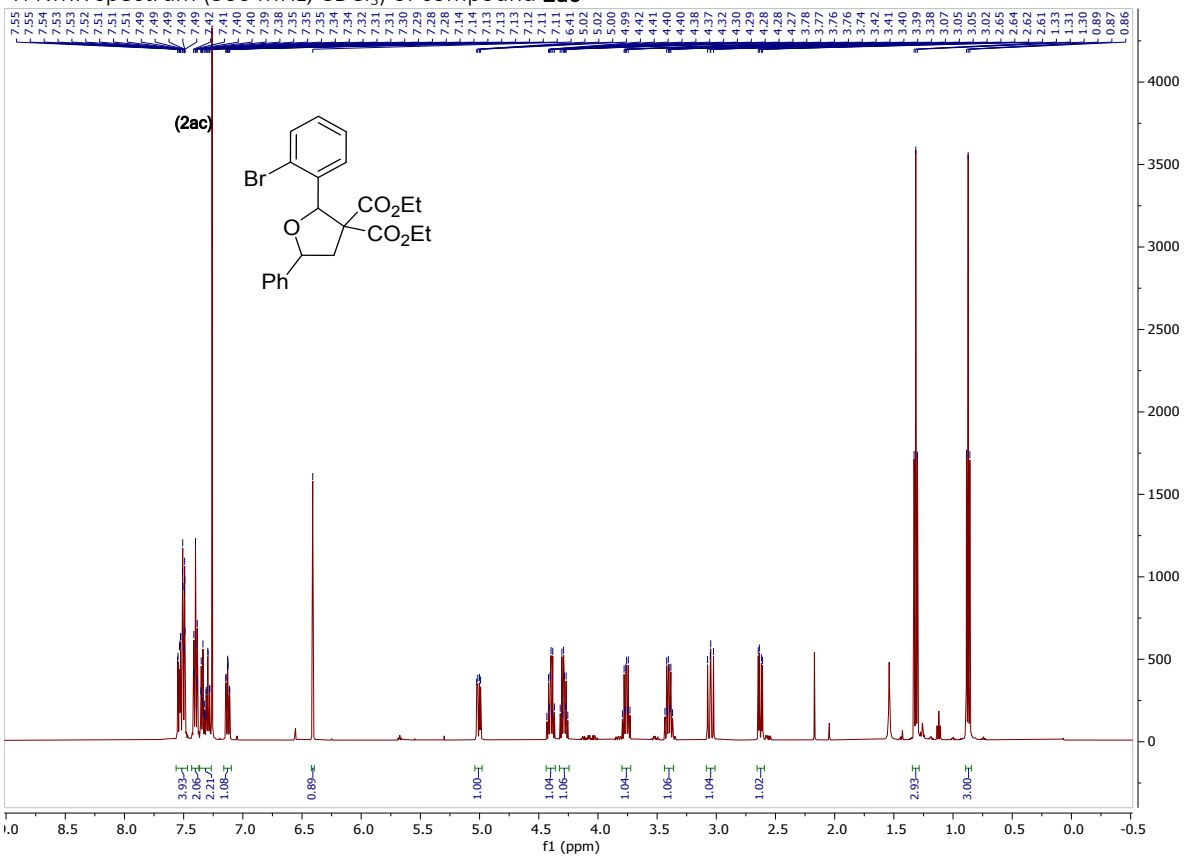
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **2ab**



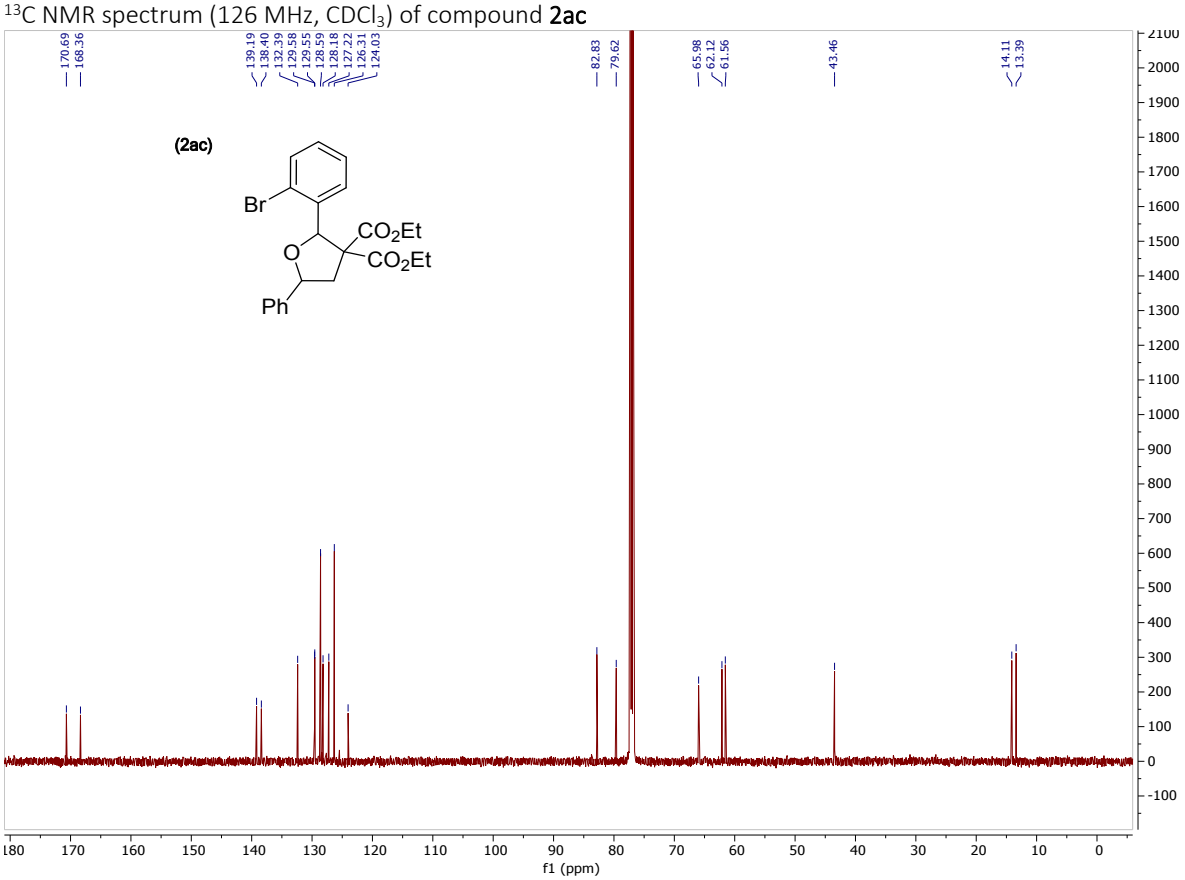
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **2ab**



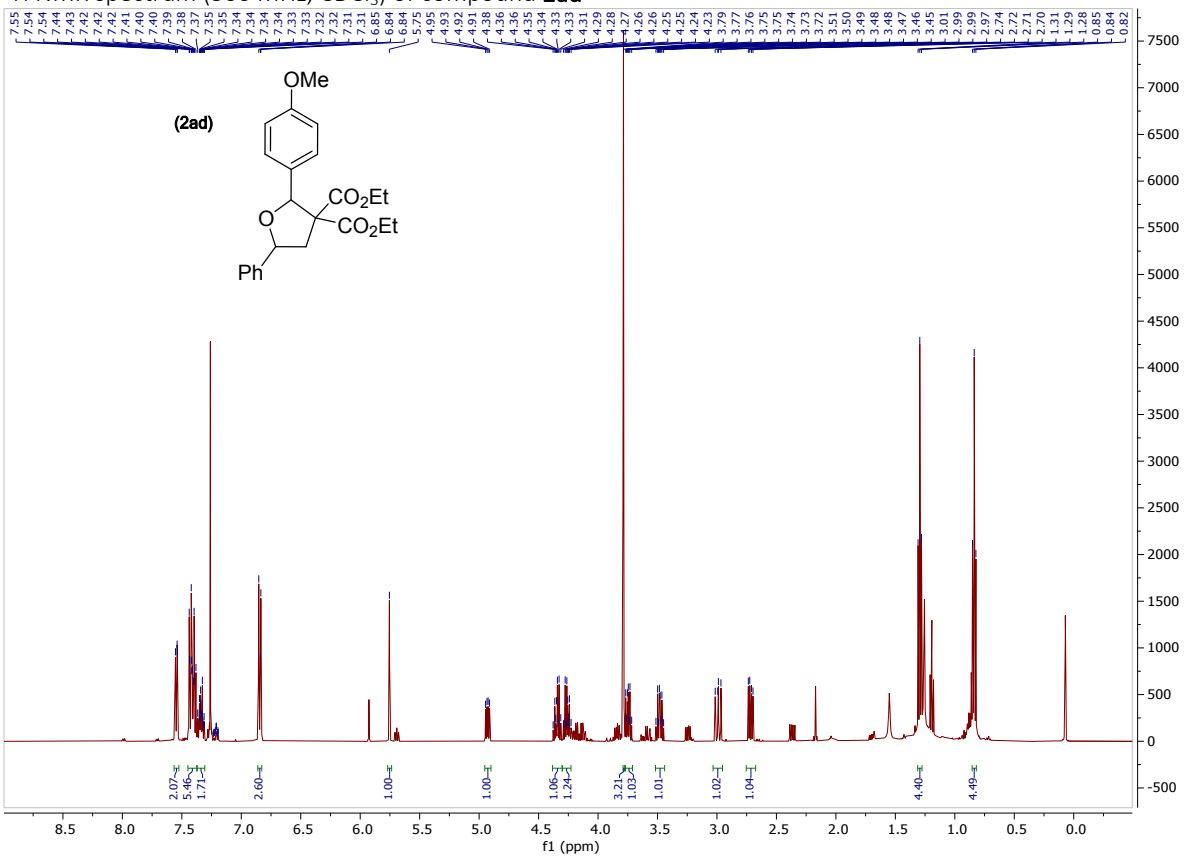
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **2ac**



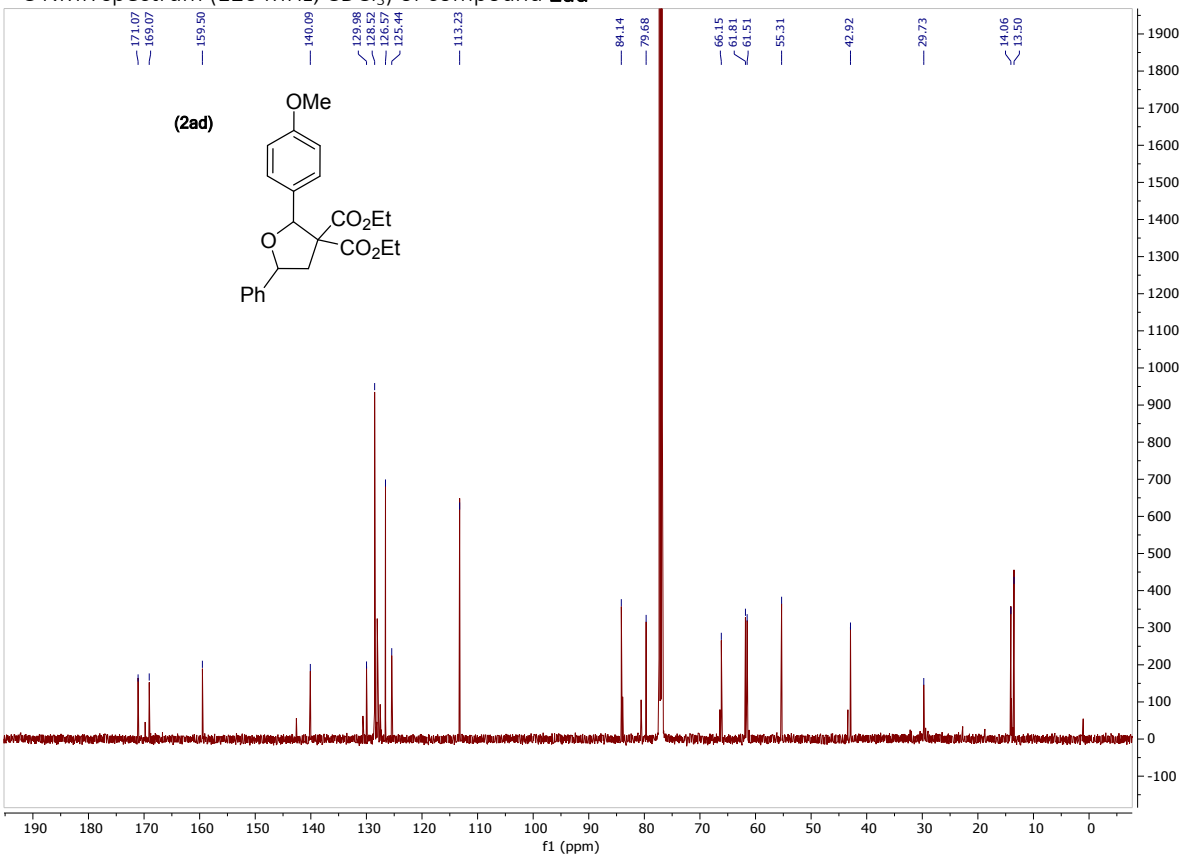
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **2ac**



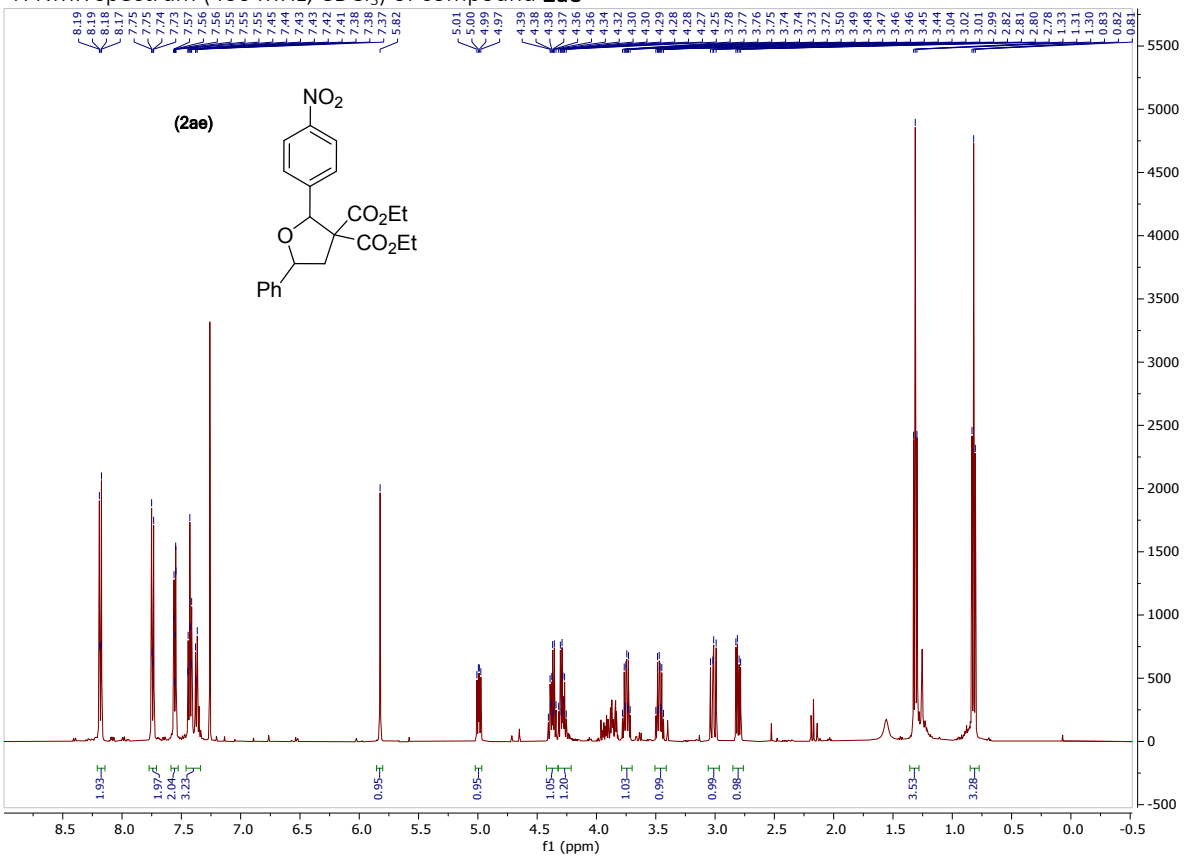
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **2ad**



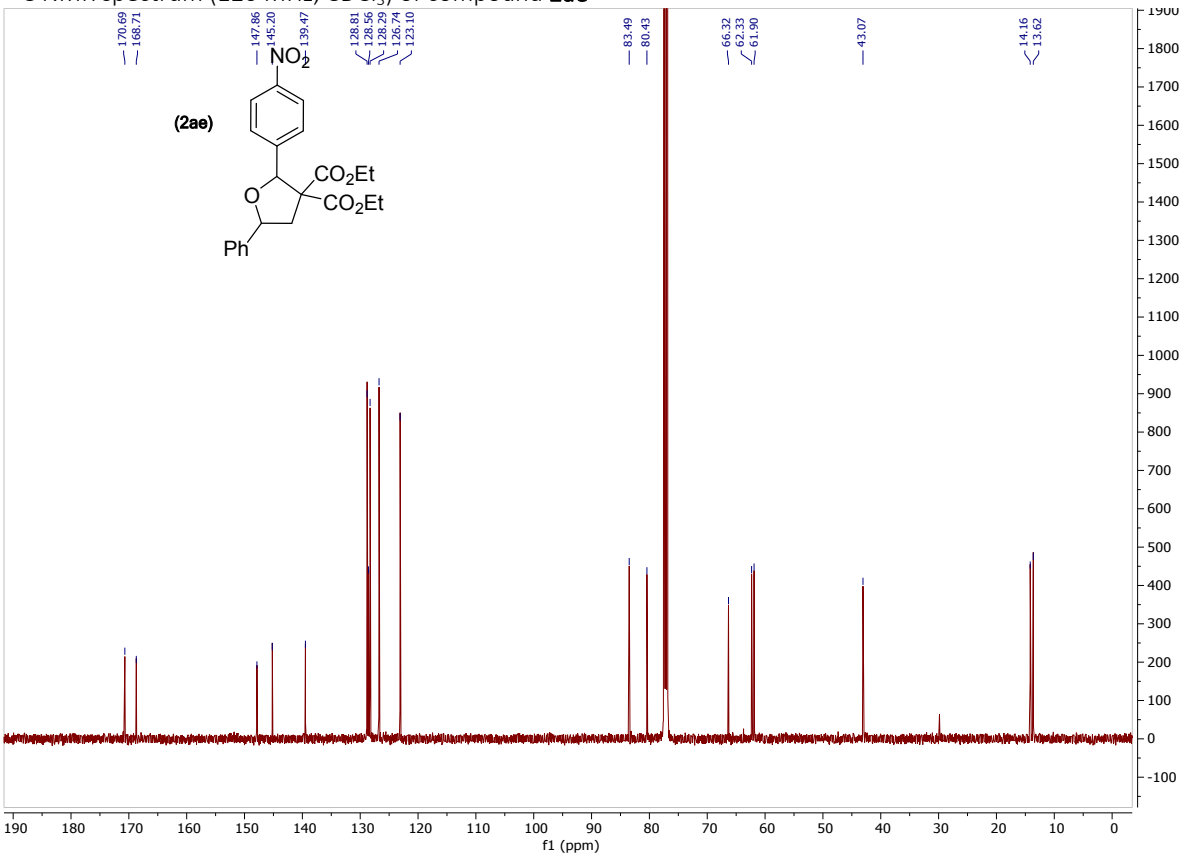
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **2ad**



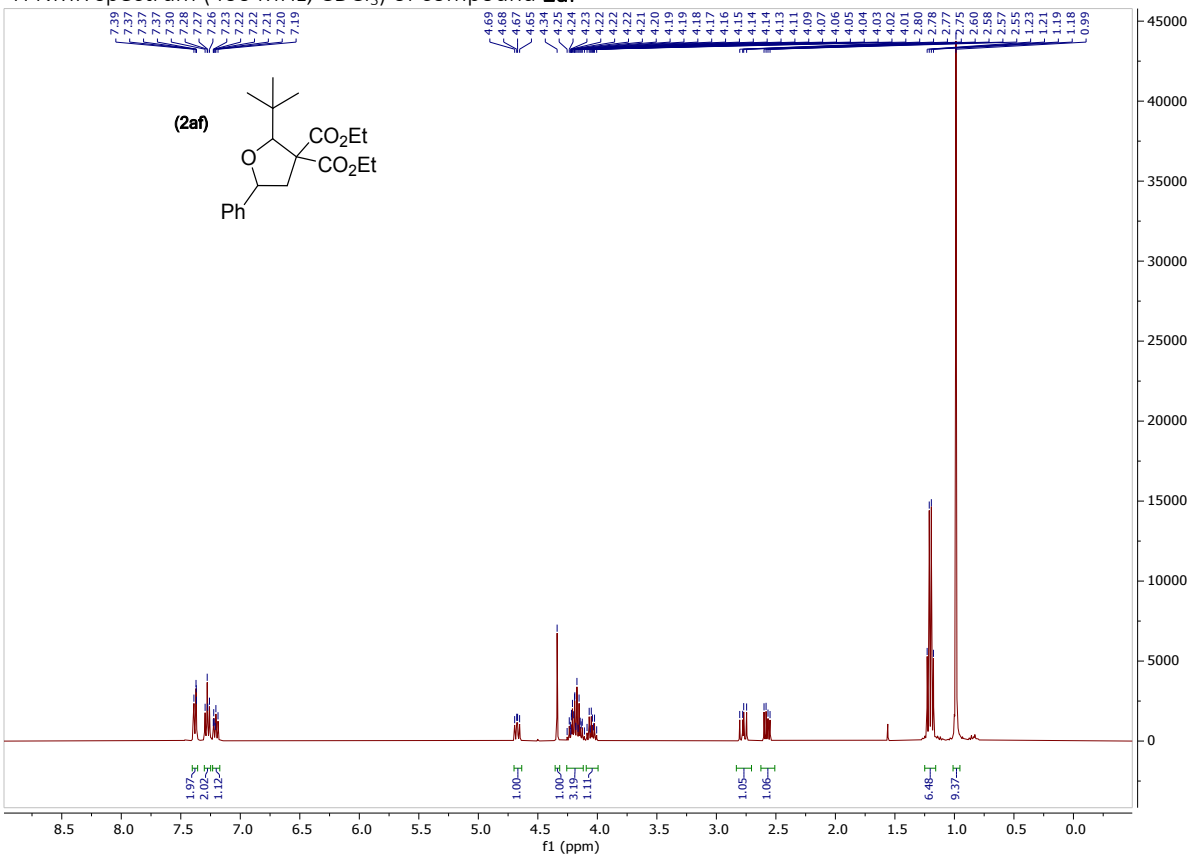
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2ae**



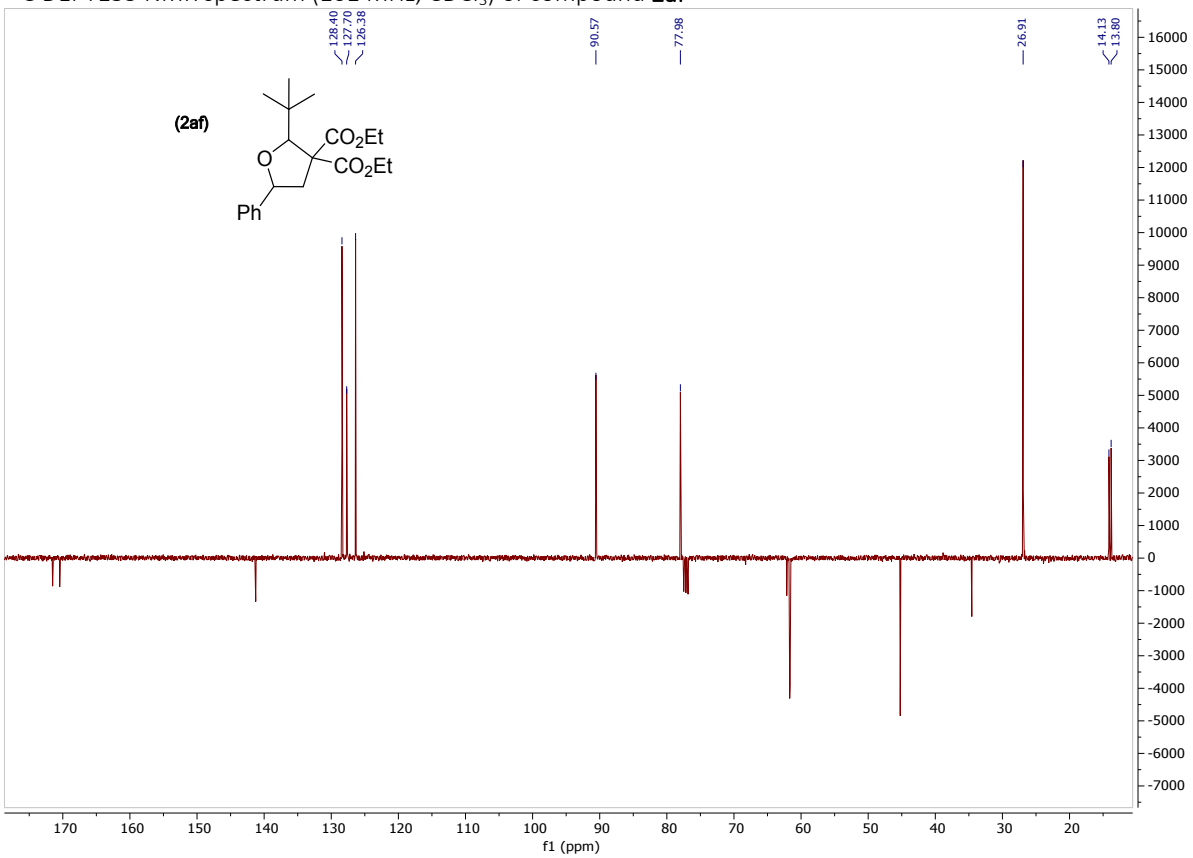
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **2ae**



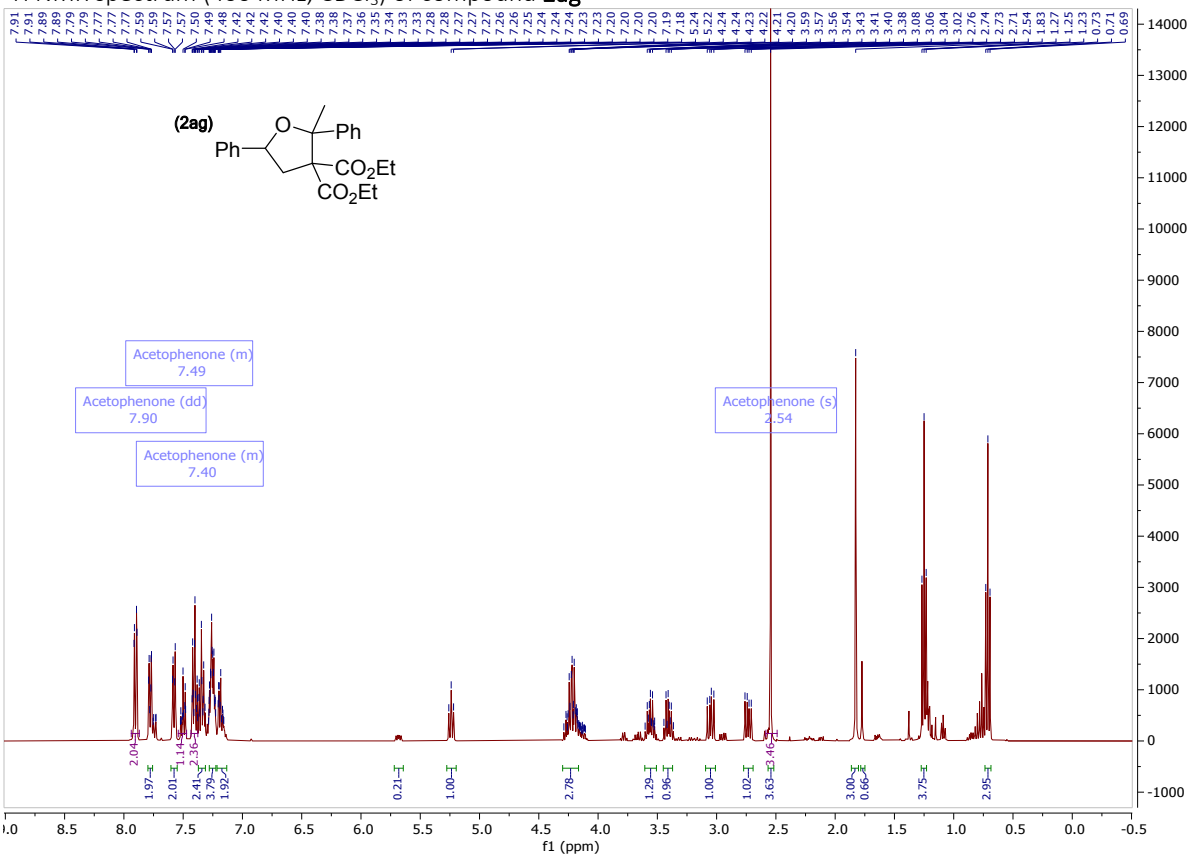
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2af**



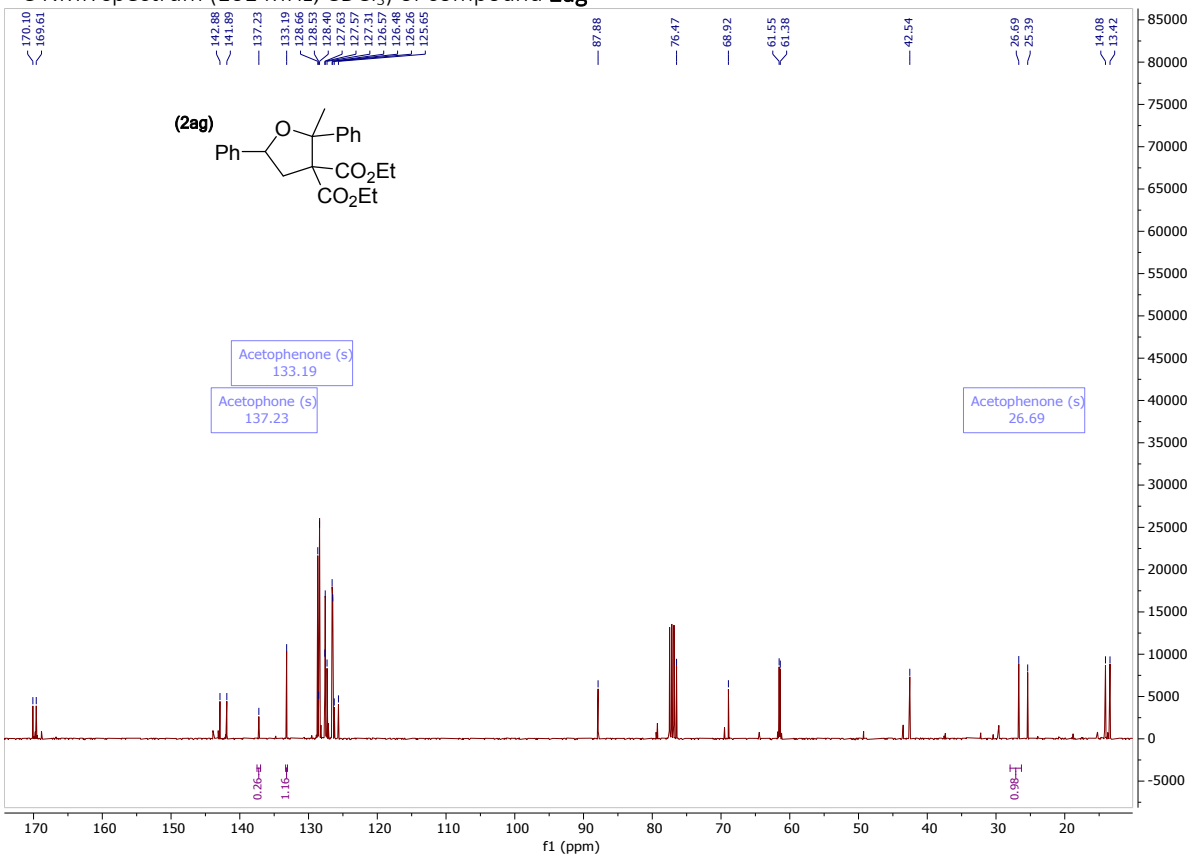
^{13}C DEPT135 NMR spectrum (101 MHz, $CDCl_3$) of compound **2af**



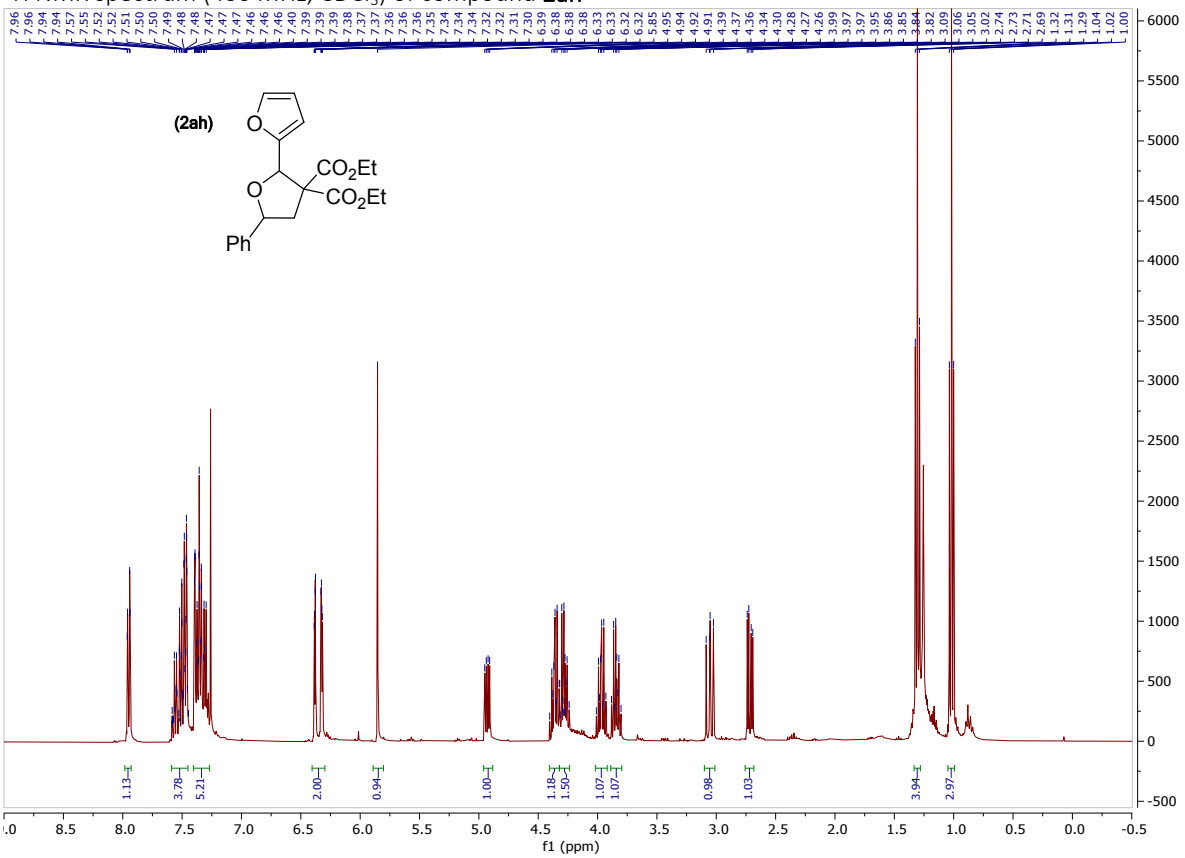
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2ag**



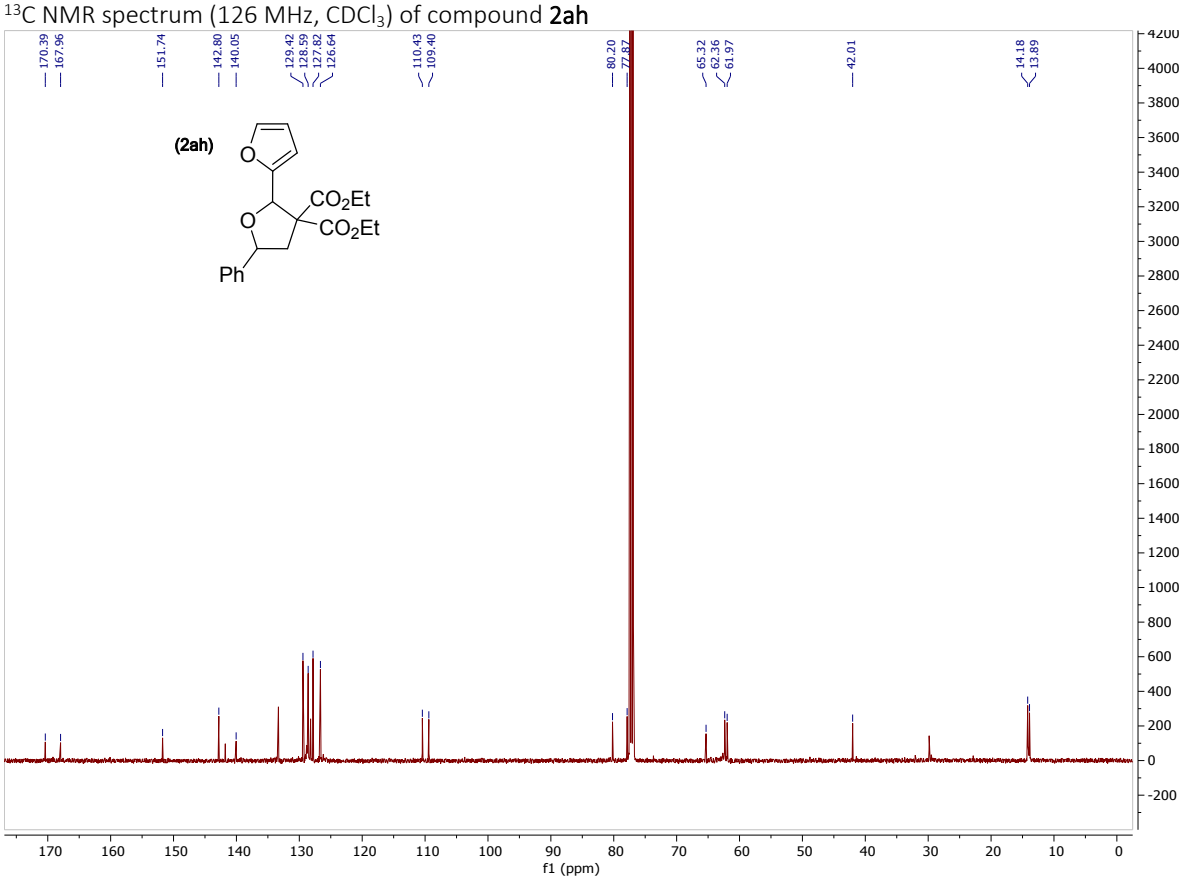
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **2ag**



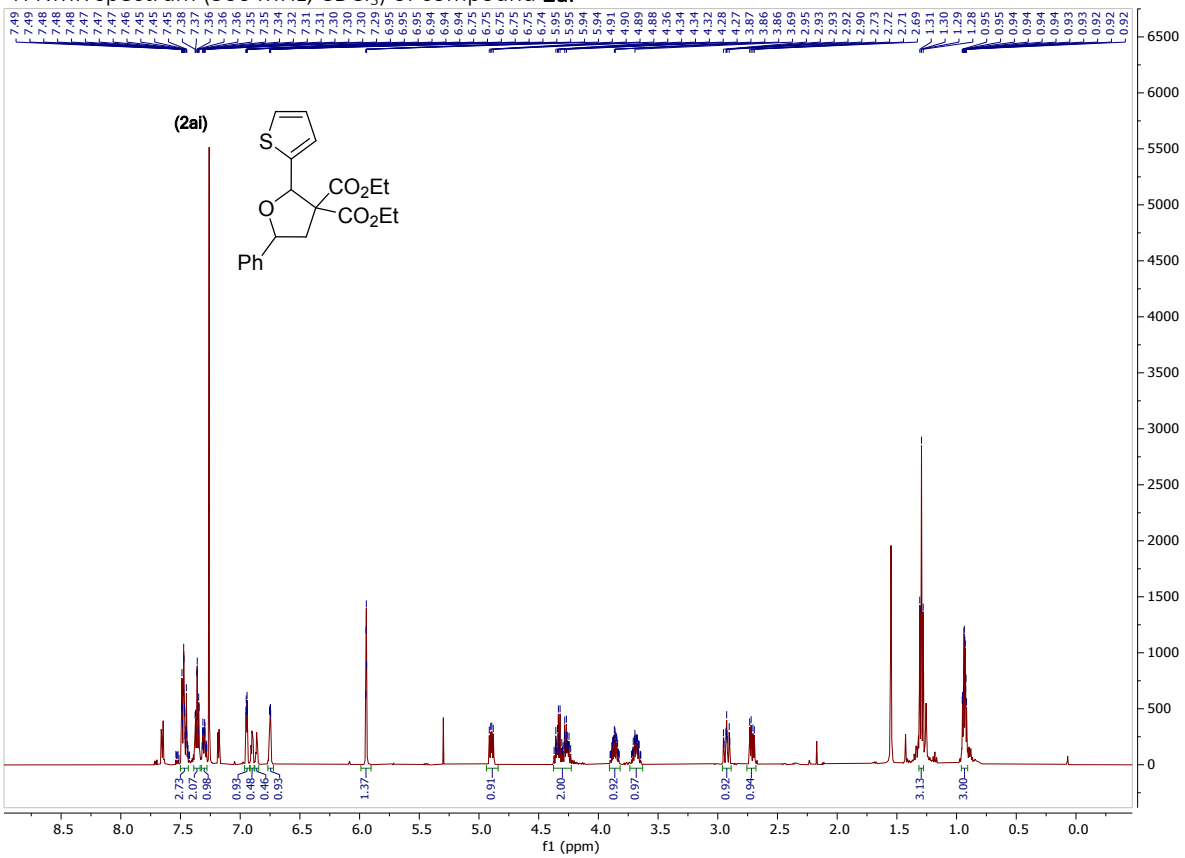
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2ah**



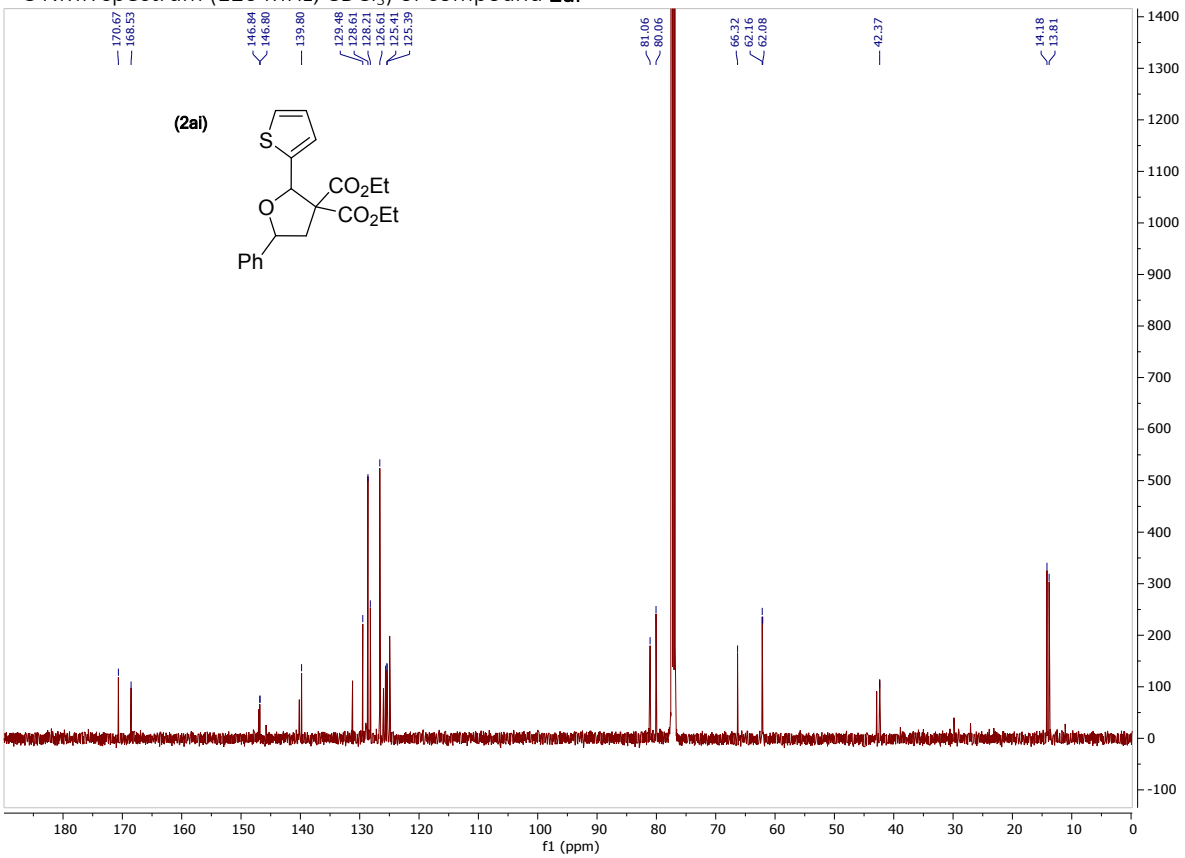
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **2ah**



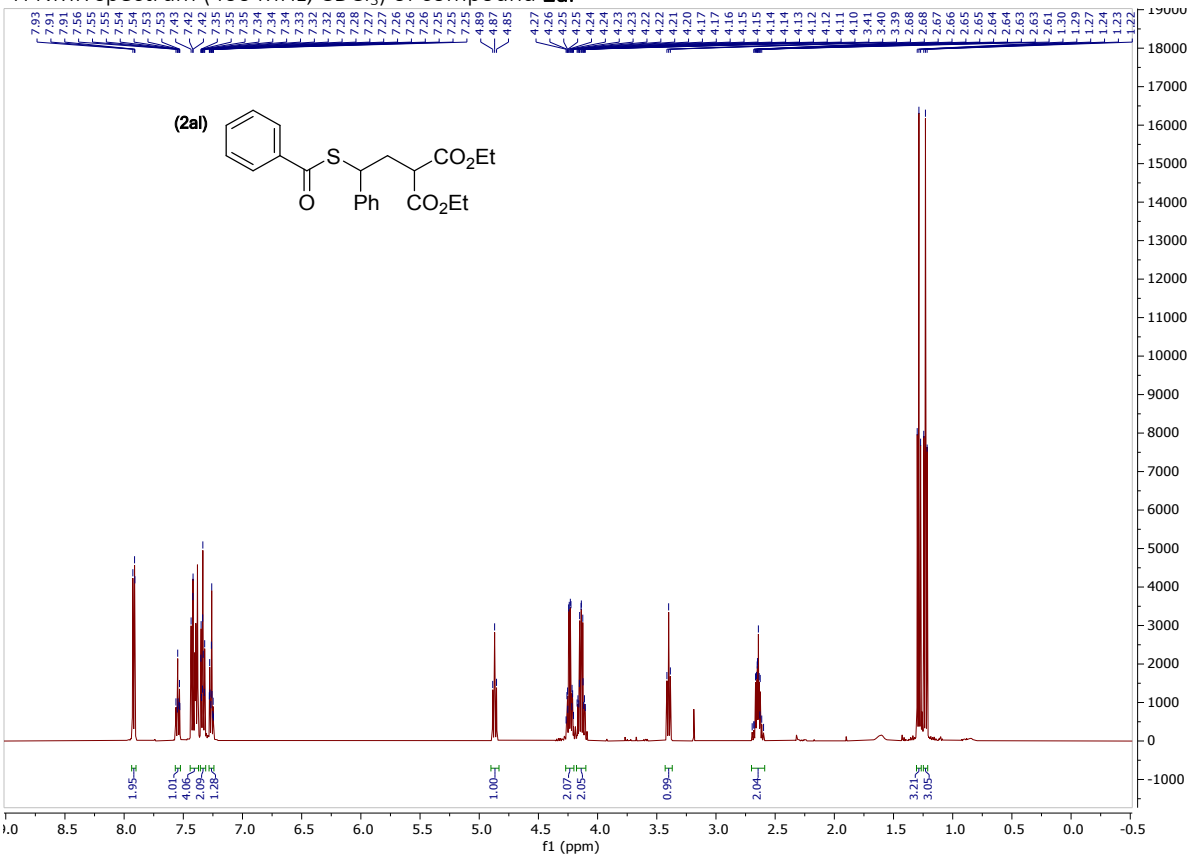
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **2ai**



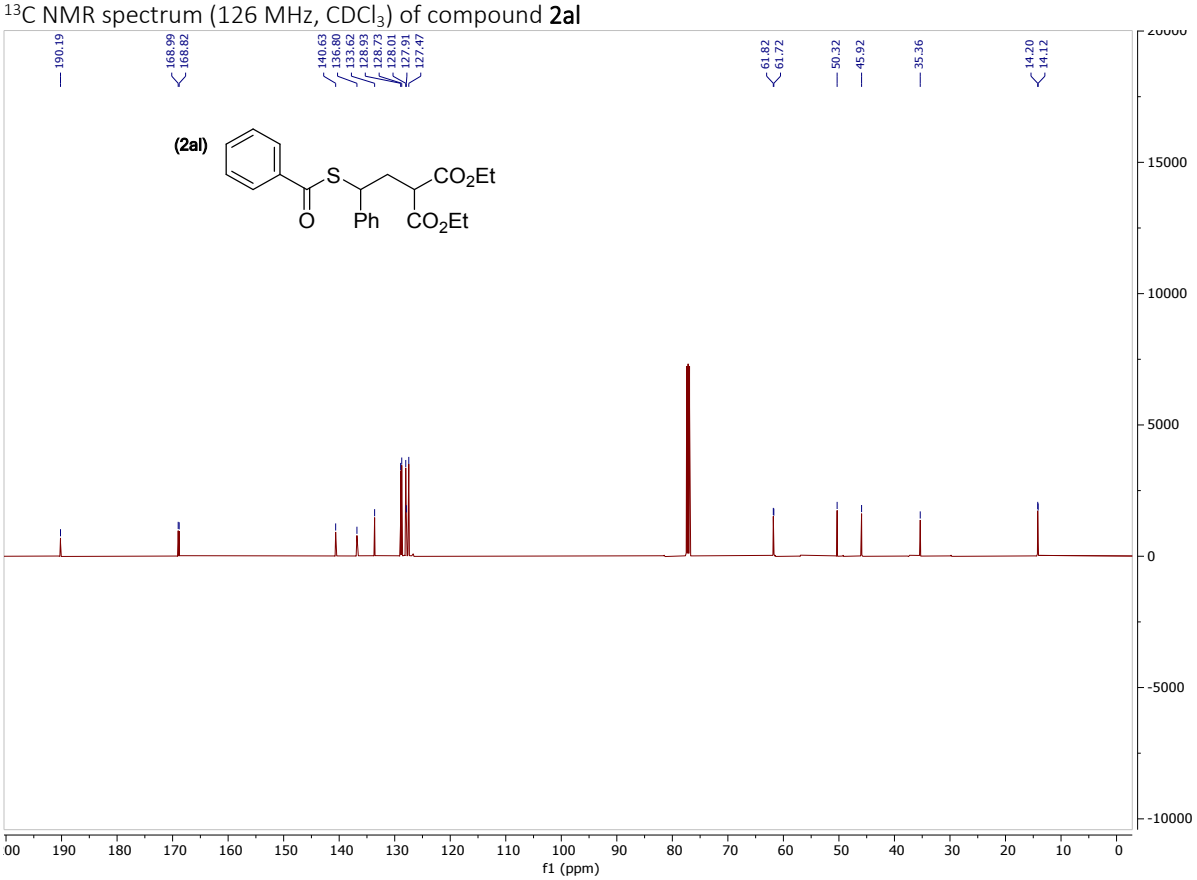
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **2ai**



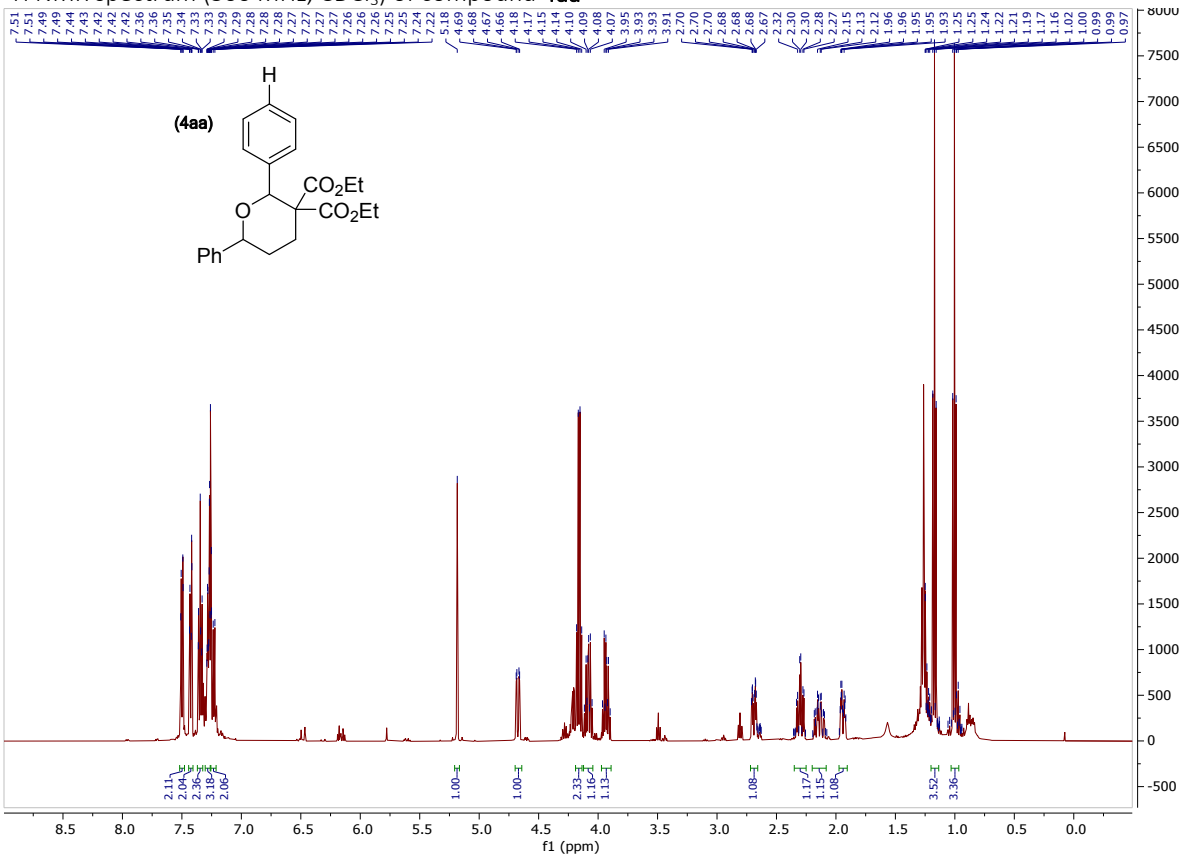
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2al**



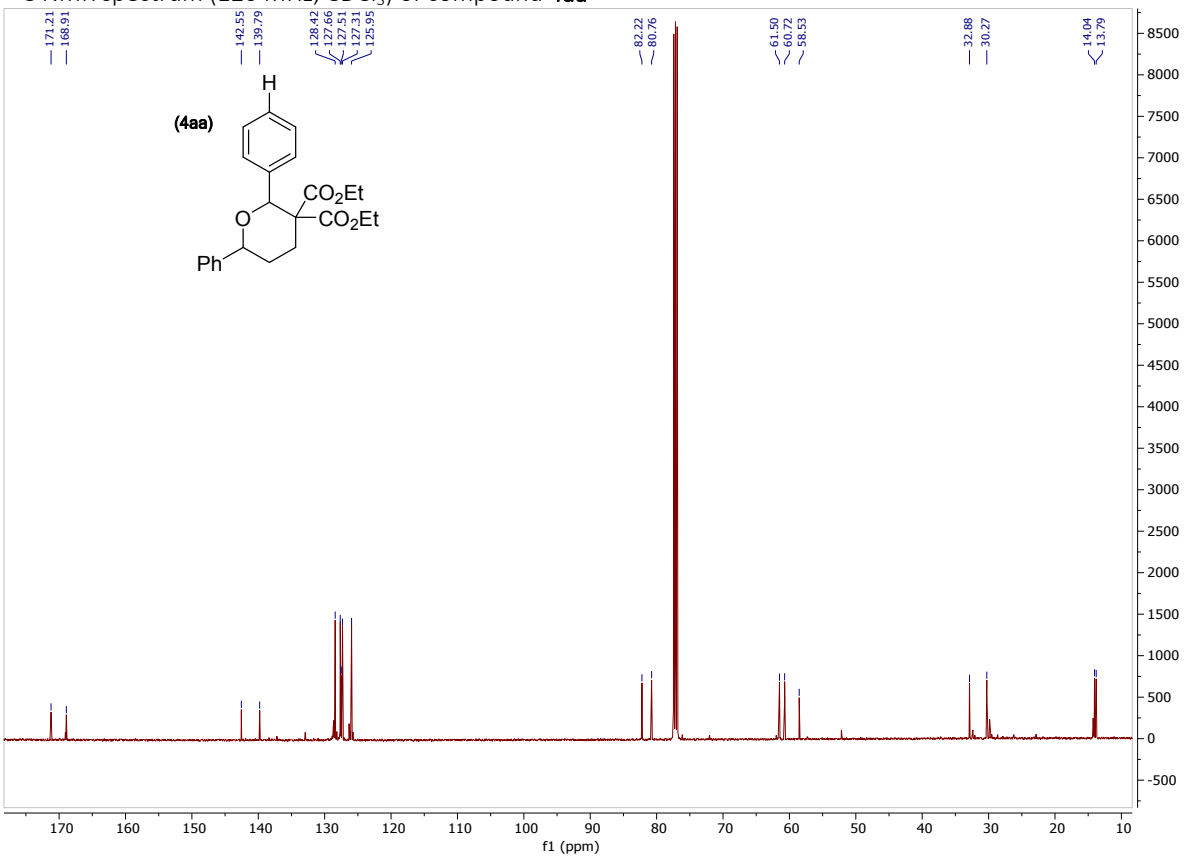
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **2al**



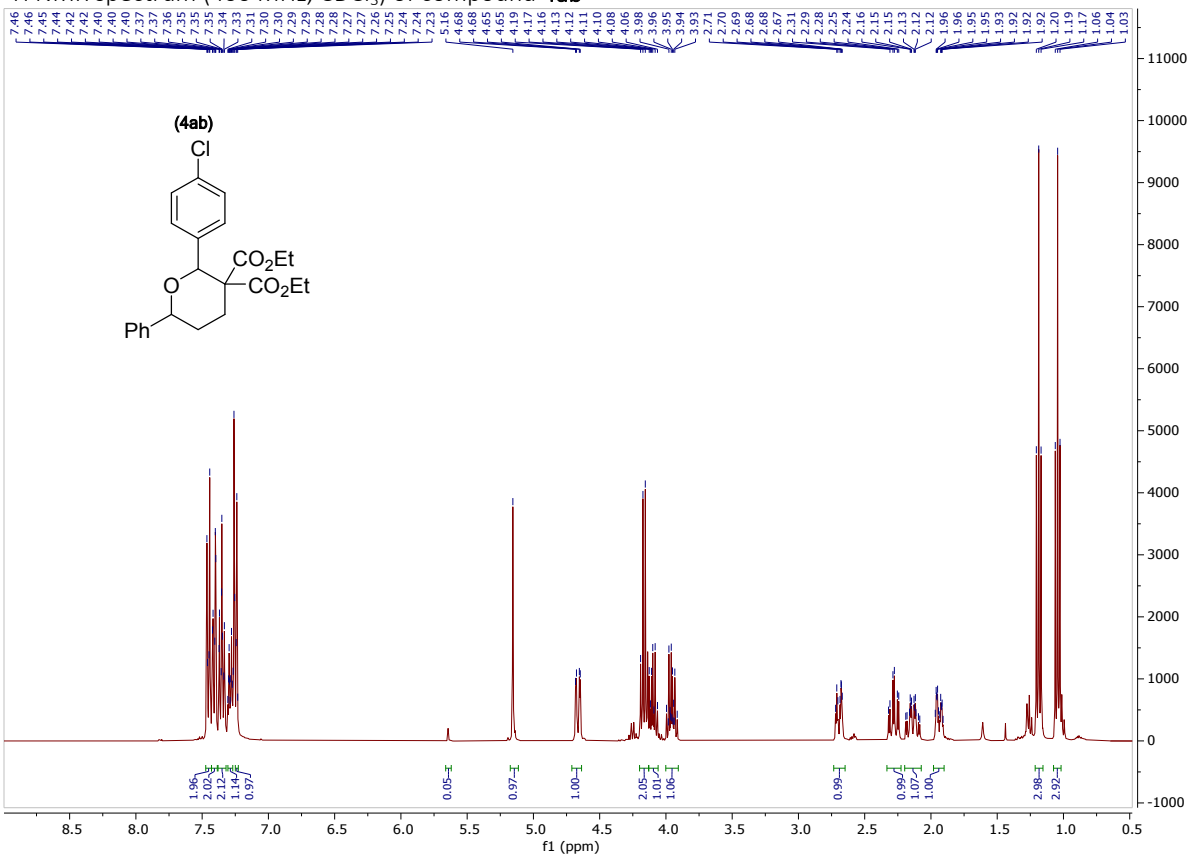
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **4aa**



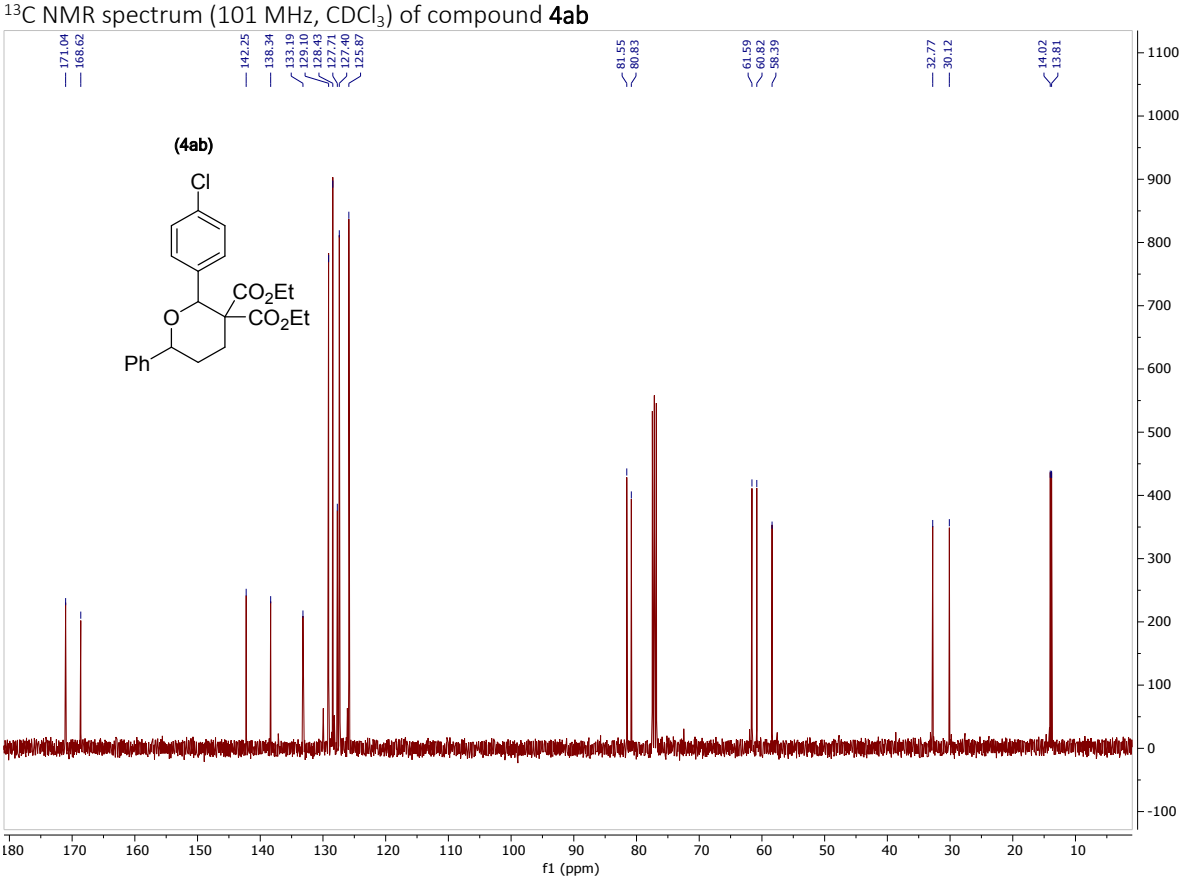
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **4aa**



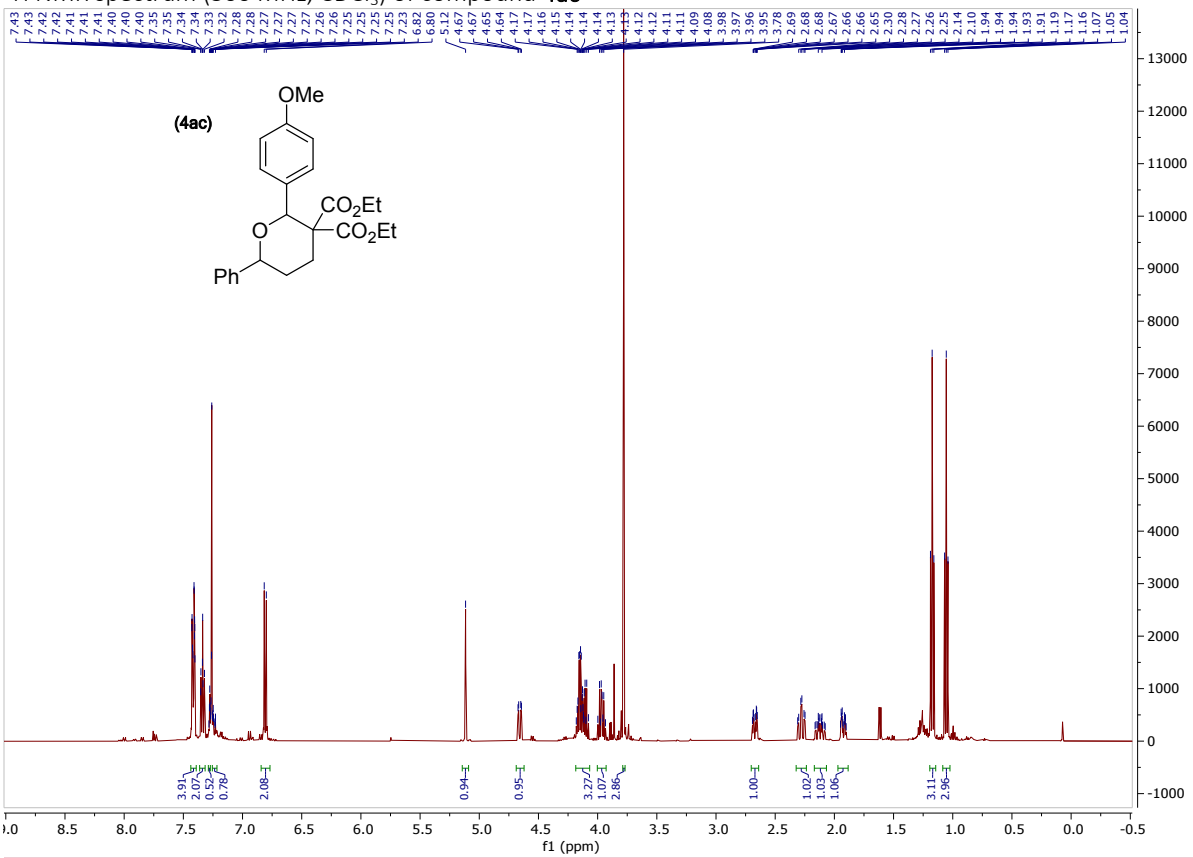
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ab**



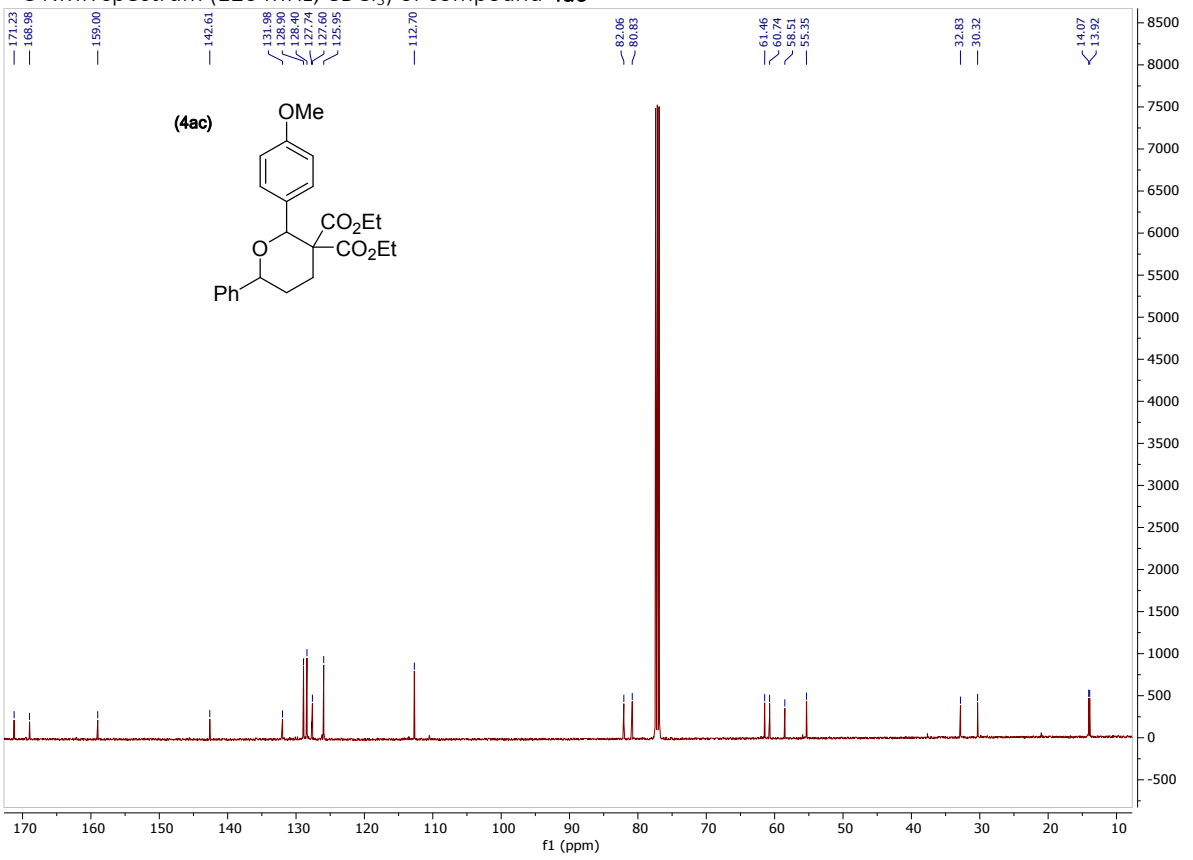
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **4ab**



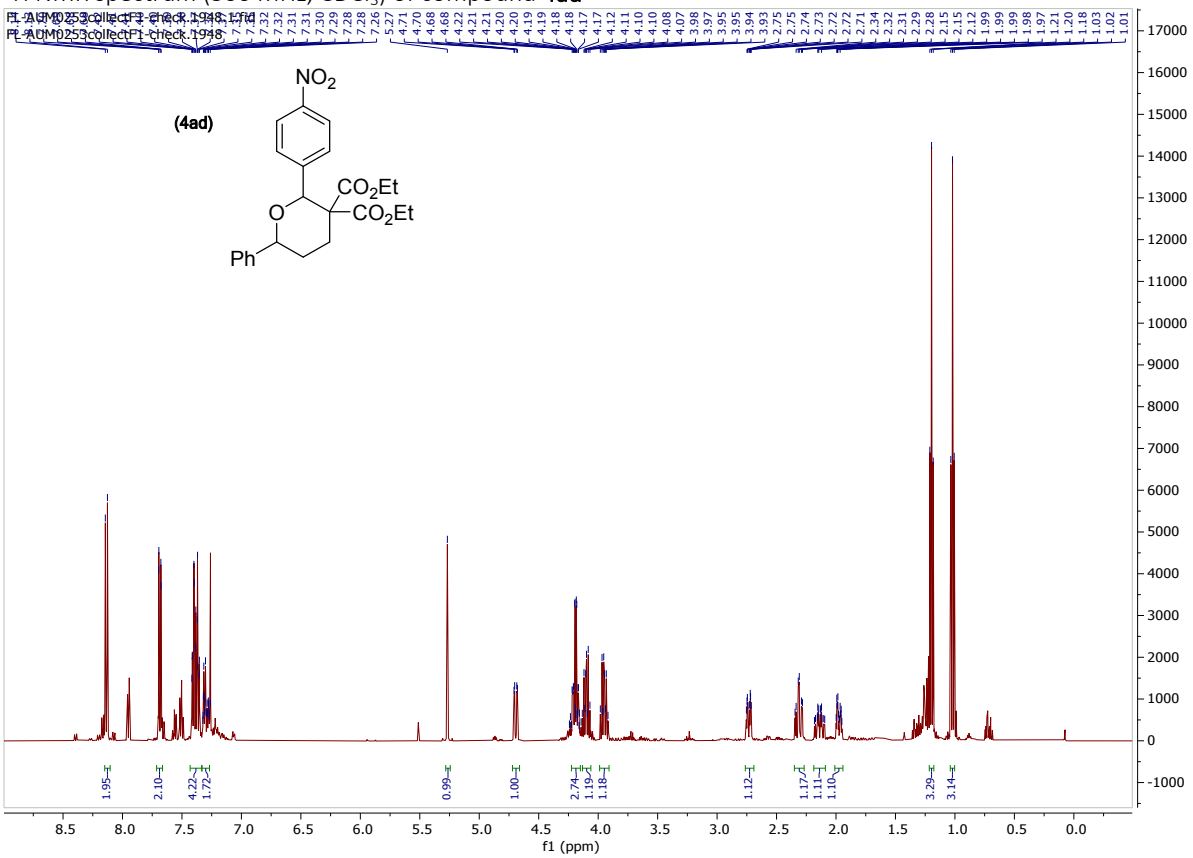
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **4ac**



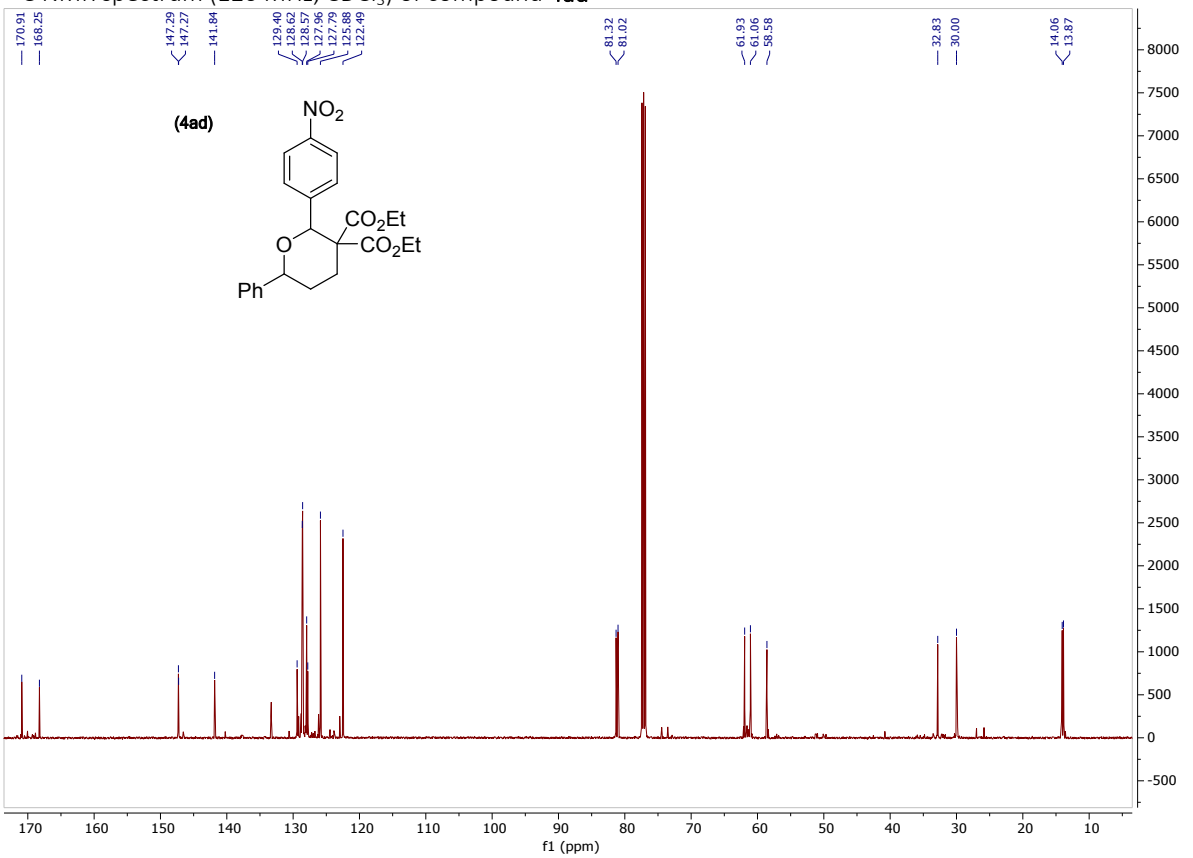
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **4ac**



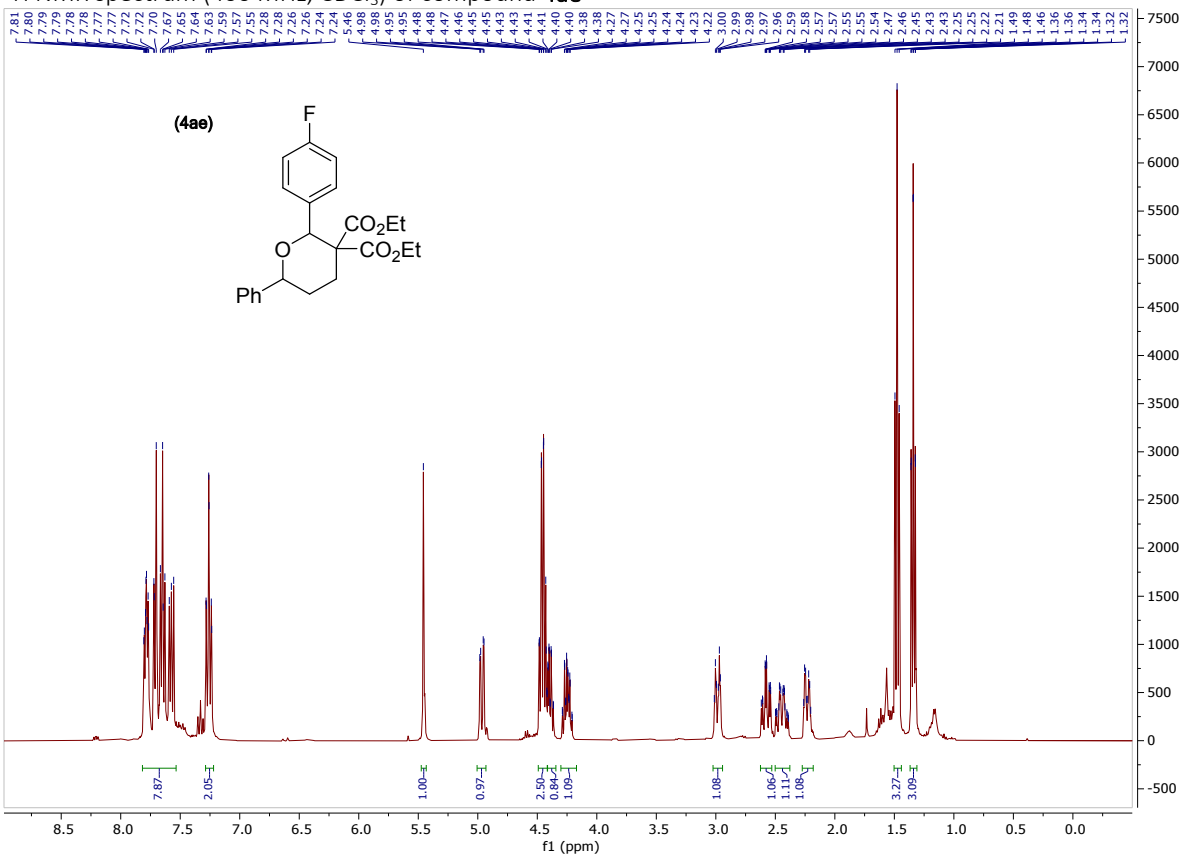
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **4ad**



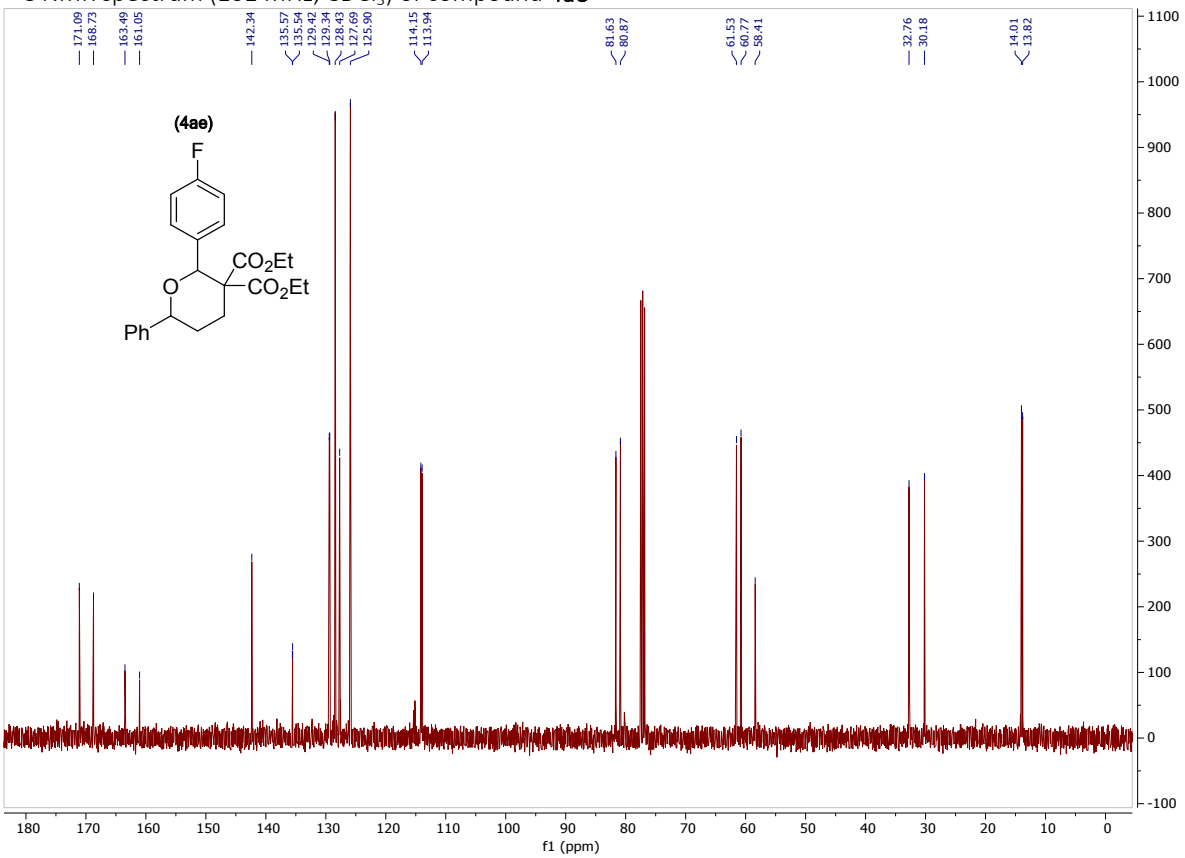
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **4ad**



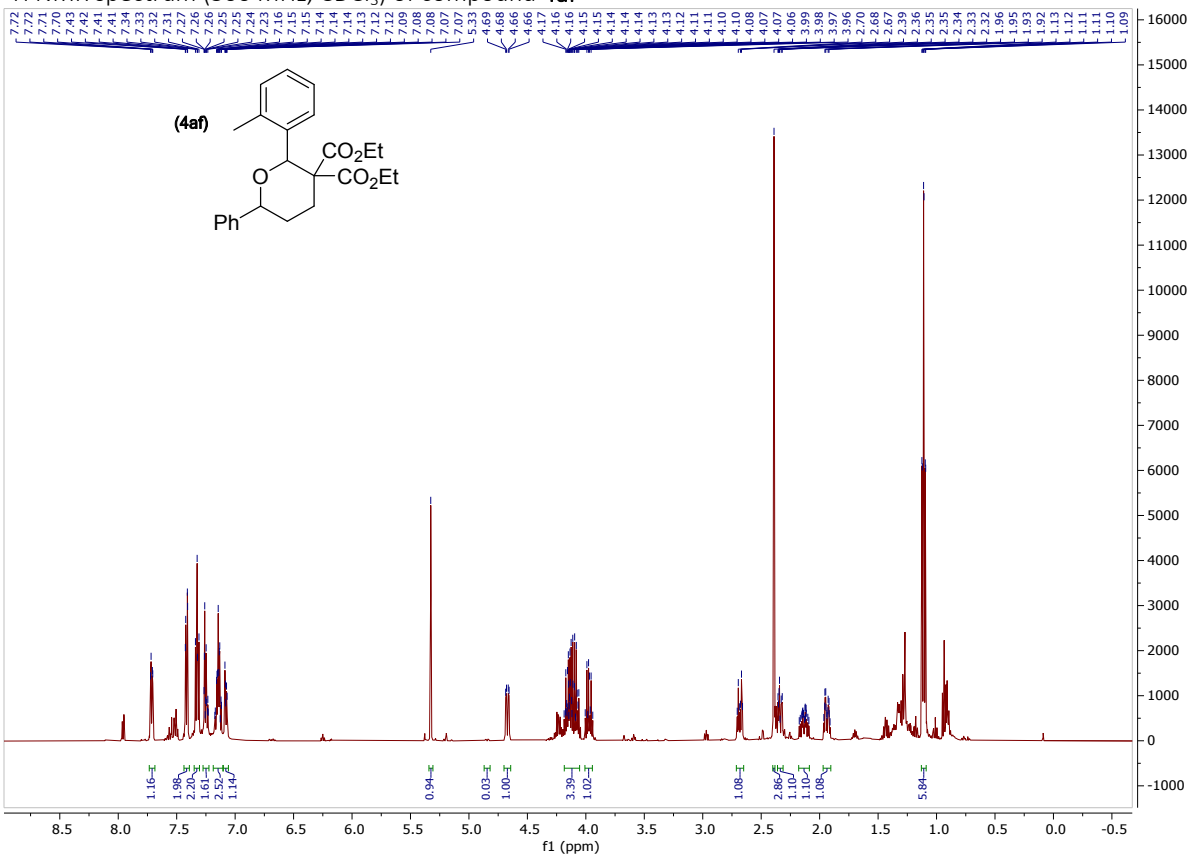
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ae**



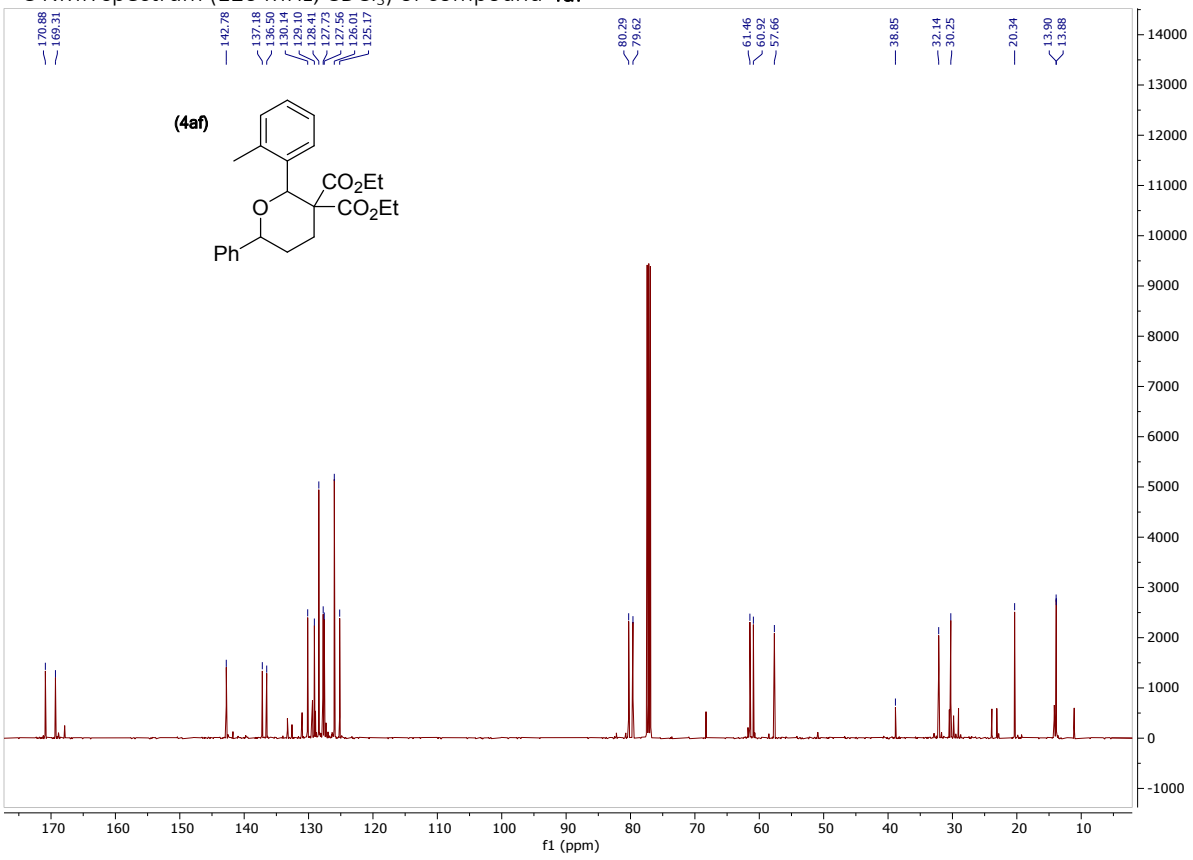
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **4ae**



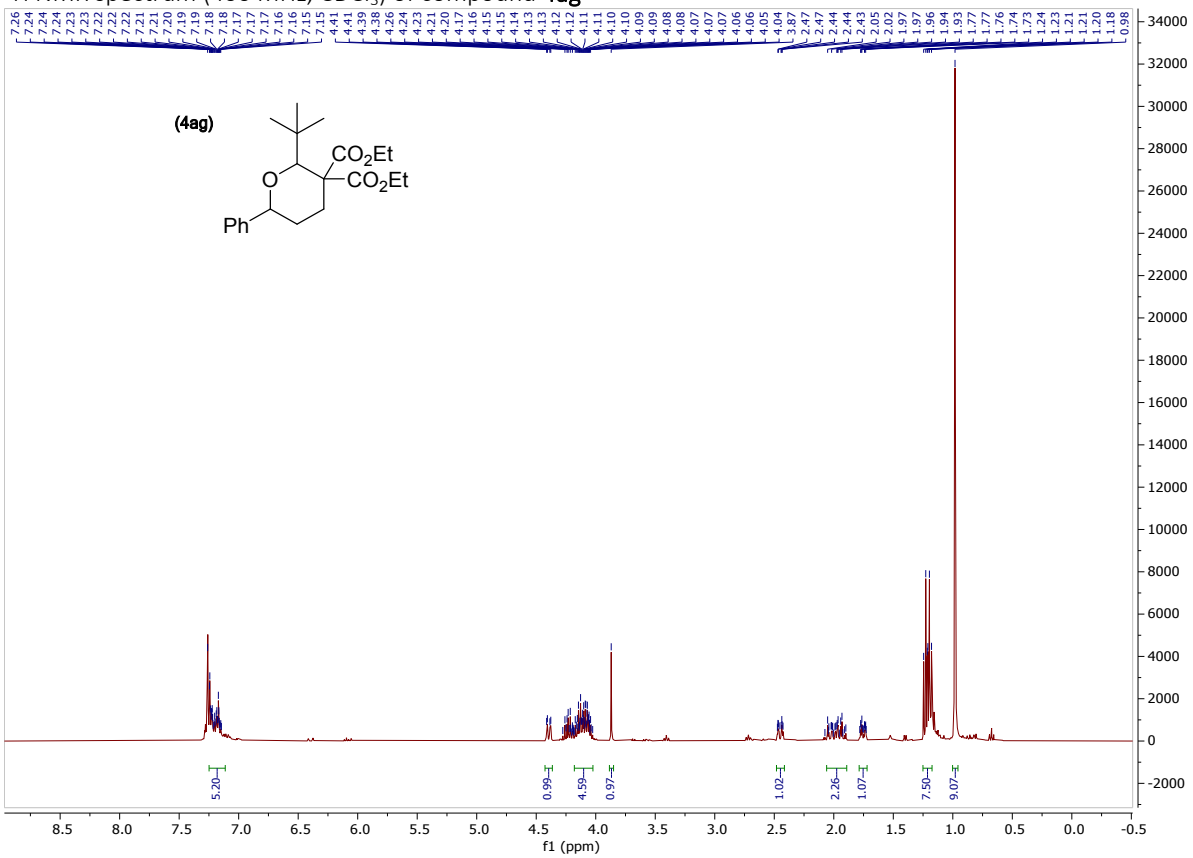
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **4af**



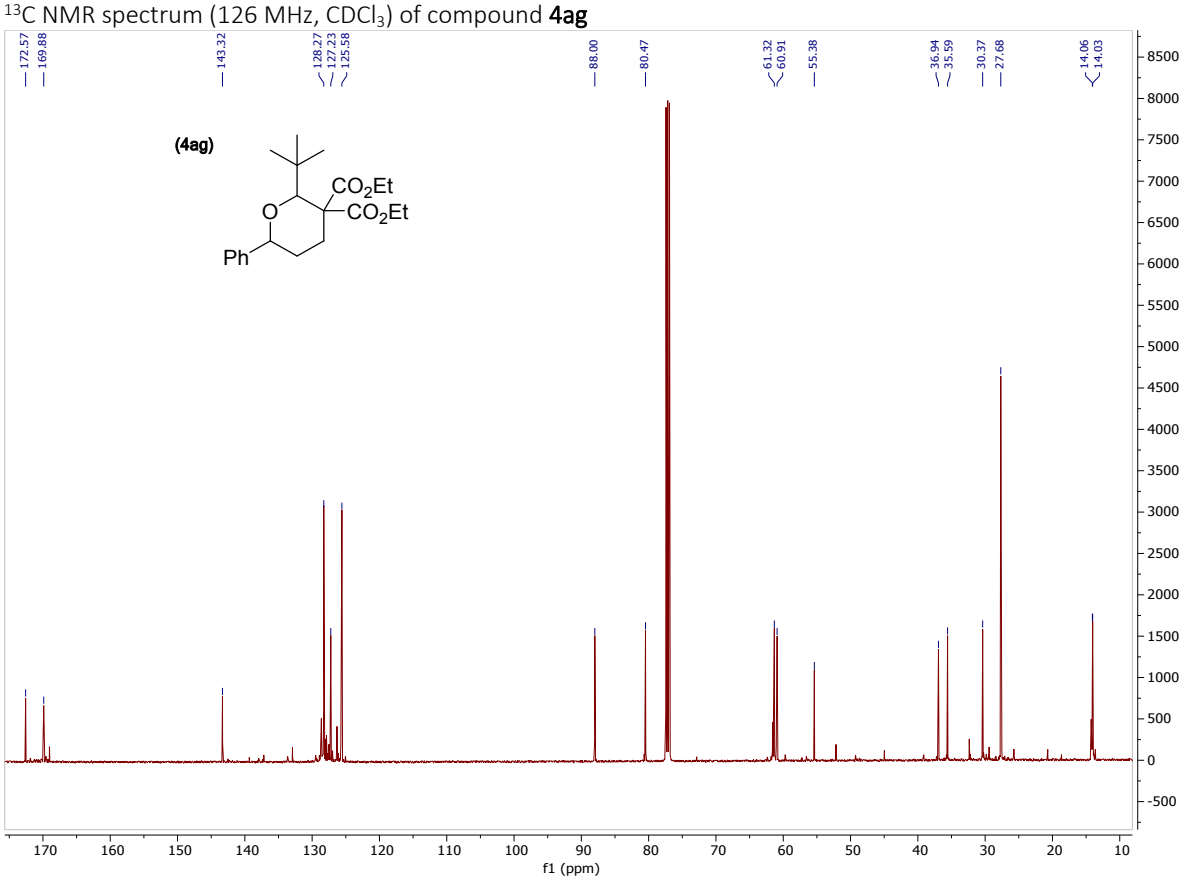
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **4af**

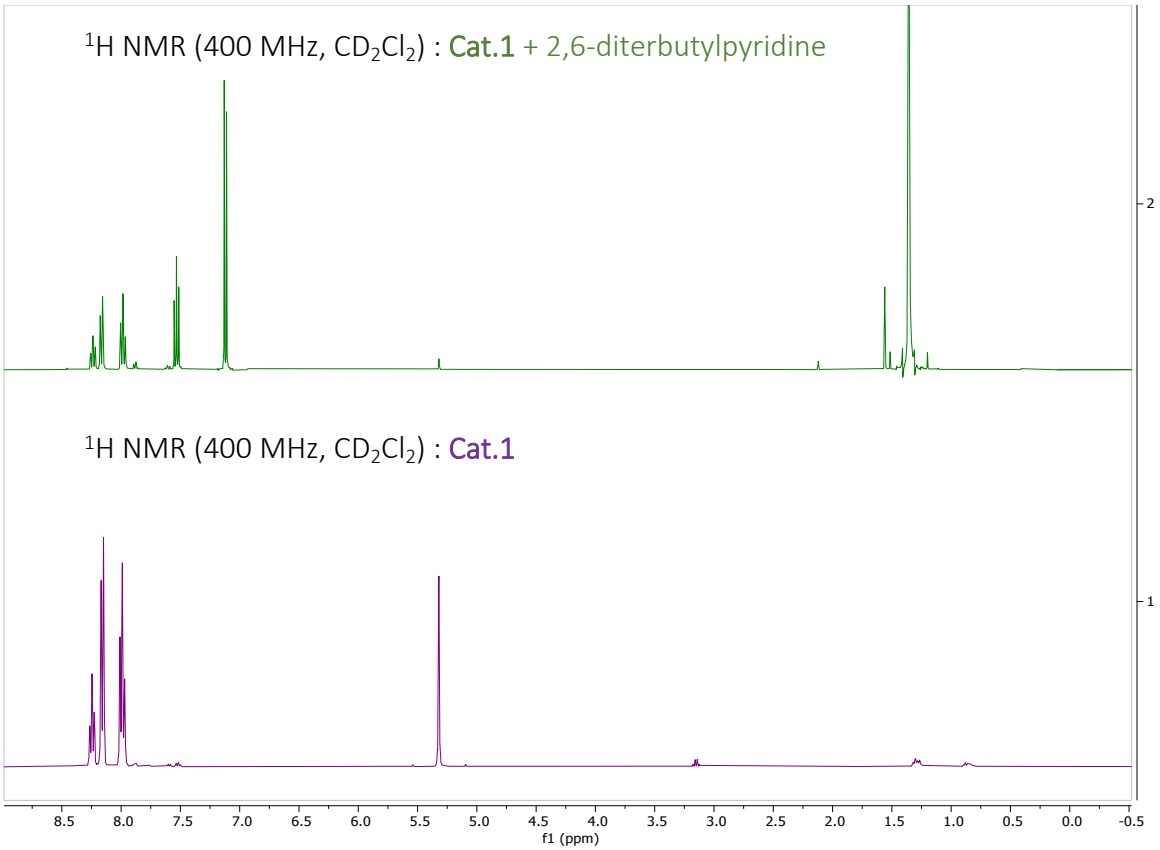


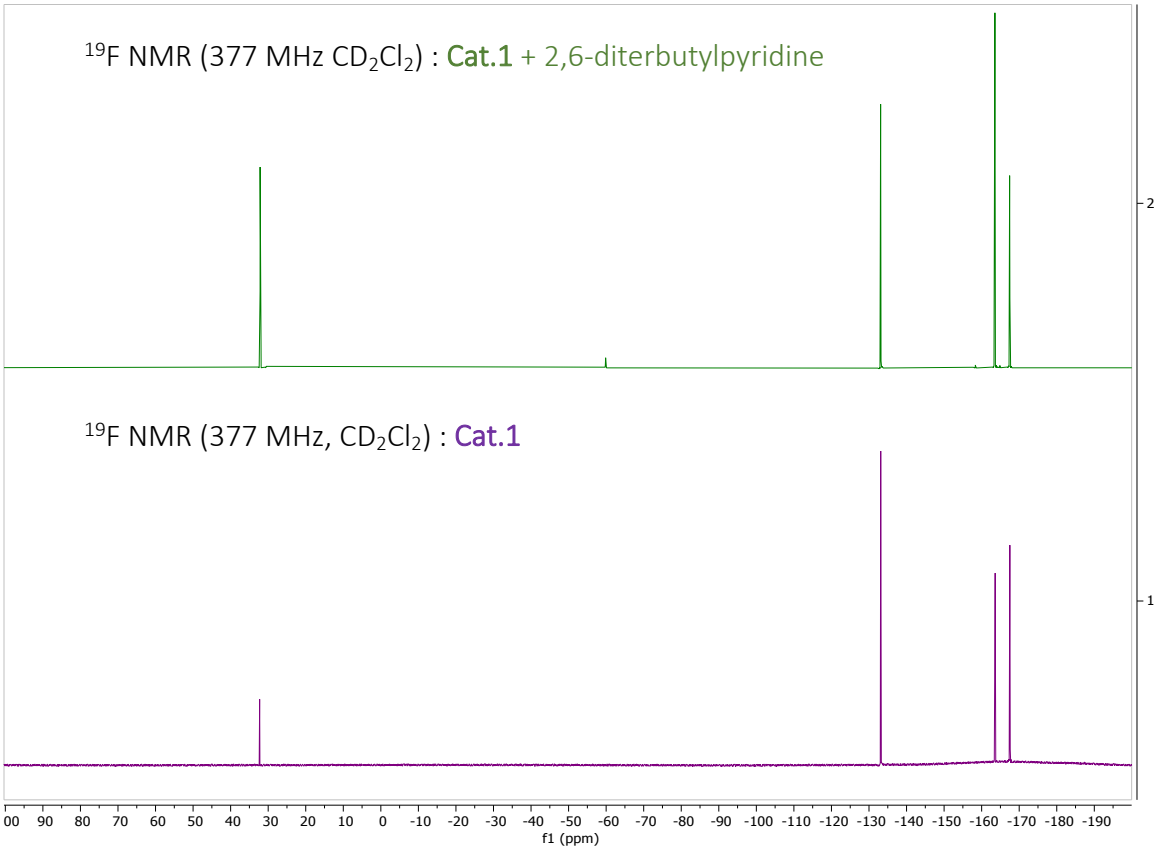
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ag**

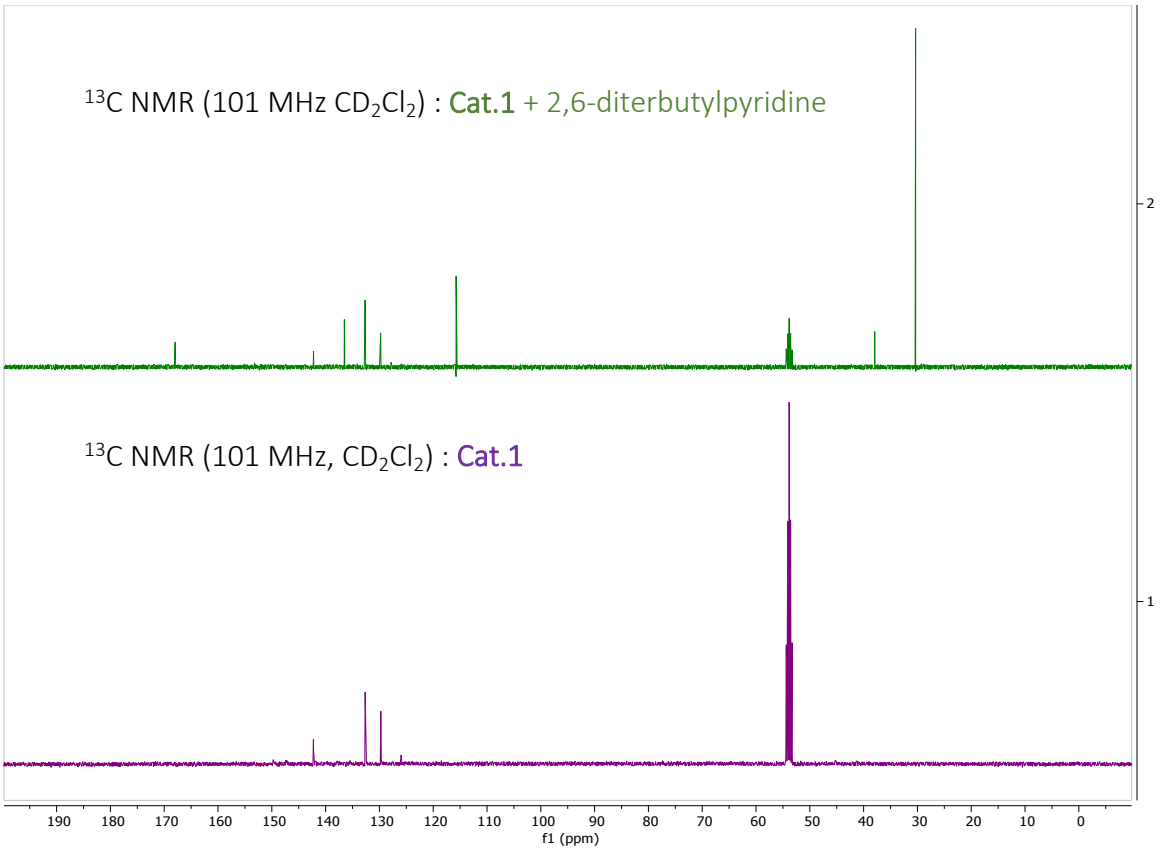


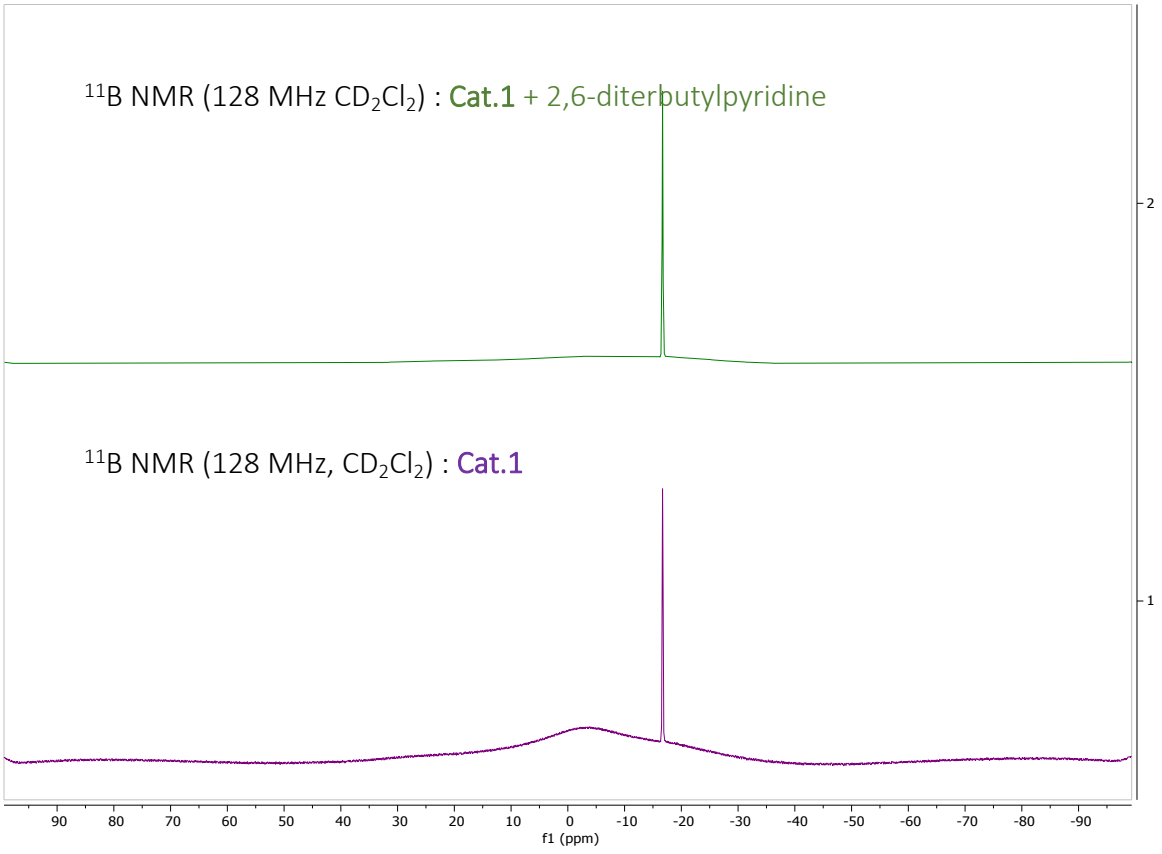
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **4ag**




^{1}H NMR (400 MHz, CD_2Cl_2) : Cat.1 + 2,6-diterbutylpyridine
^{1}H NMR (400 MHz, CD_2Cl_2) : Cat.1
2
1
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


^{19}F NMR (377 MHz CD_2Cl_2) : Cat.1 + 2,6-diterbutylpyridine
^{19}F NMR (377 MHz, CD_2Cl_2) : Cat.1
2
1
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


^{13}C NMR (101 MHz CD_2Cl_2) : Cat.1 + 2,6-diterbutylpyridine
^{13}C NMR (101 MHz, CD_2Cl_2) : Cat.1
2
1
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


^{11}B NMR (128 MHz CD_2Cl_2) : Cat.1 + 2,6-diterbutylpyridine
^{11}B NMR (128 MHz, CD_2Cl_2) : Cat.1
2
1
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

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