Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Iron-catalyzed cascade C-C/C-O bond formation of 2,4-dienals with donor-acceptor cyclopropanes: access to functionalized hexahydrocyclopentapyrans

Table of Contents

General Information. $FeCl_3$ (98%), $Yb(OTf)_3$ (99.99%), $Cu(OTf)_2$ (98%), $Sc(OTf)_3$ (99%), $Zn(OTf)_2$ (98%), $CoCl_2$ (97%), TfOH (≥99%), $TsOH \cdot H_2O$ (≥98%), *trans,trans*-2,4-hexadienal (95%) and *trans,trans*-2,4-nonadienal (>85.0%) purchased from SRL Chemicals, Aldrich and TCI chemicals used as received. D-A cyclopropanes and 2,4-dienals were prepared according to literature.[1-4] Merck silica gel G/GF 254 plates were used for the analytical TLC and Rankem silica gel (100-200 mesh) was used for the column chromatography. NMR (^1H and ^{13}C) spectra were recorded in Bruker Avance III 400, 500 and 600 spectrometers using $CDCl_3$ as solvent and TMS as an internal standard. Chemical shifts (δ) and spin-spin coupling constants (*J*) are reported in ppm and in Hz, respectively, and other data are reported as follows: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, bt = broad triplet and m = multiplet. Melting points were determined using a Büchi B-540 apparatus and are uncorrected. IR spectra were collected on a Perkin Elmer Fourier Transform Infrared (FT-IR) spectrometer. Quadrupole time-of-flight electrospray ionization (ESI) mass spectrometer (model HAB 273) was used for mass spectra. Optical rotation was determined using a Rudolph Autopol I Automatic Polarimeter. HPLC analysis was carried out using Waters-2489 with YMC Chiral ART Cellulose-SC column using *iso*-propanol and hexane as eluent. Single-crystal X-ray data was collected using Brucker SMART APEX-II CCD area detector using Mo-Kα irradiation and the structure was solved by using *SHELXL-18* (Gottingen, Germany).

Crystal Data and Structure Refinement

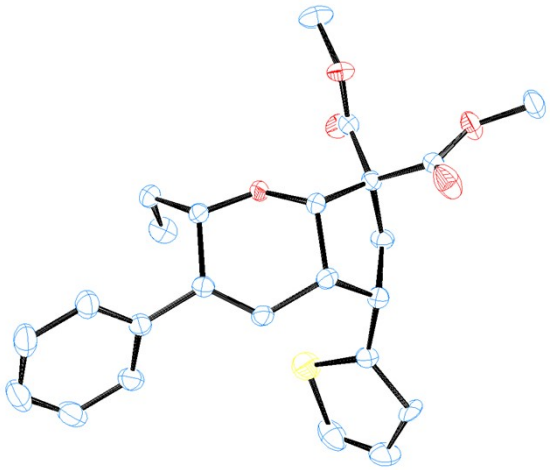
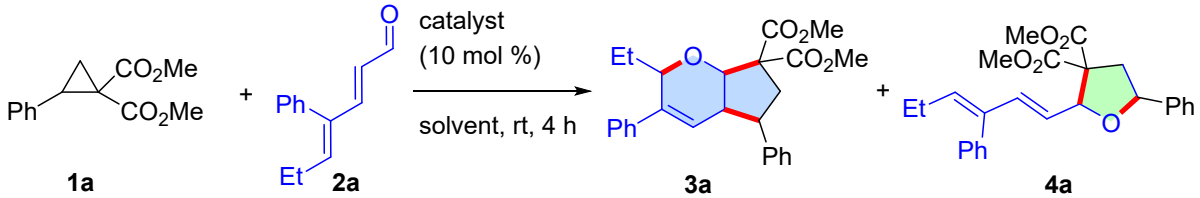


Figure S1. ORTEP diagram of **3k** (CCDC 2298985) with 50% ellipsoid. H-atoms are omitted for clarity.

Solvent and Method for Crystal Growth. Dimethyl 2-ethyl-3-phenyl-5-(thiophen-2-yl)-4a,5,6,7a-tetrahydrocyclopenta[b]pyran-7,7(2H)-dicarboxylate **3k** (5 mg) was dissolved in hot isopropanol (2 mL) and left at room temperature for slow evaporation. After 2 days, needle shaped colorless crystal growth was observed.

Identification code	**3k**
CCDC No.	**2298985**
Empirical formula	$C_{24}H_{26}O_5S$
Formula weight	426.15
Crystal habit, colour	Needle/colourless
Temperature,T/K	297 K
Wavelength, λ/Å	0.71073
Crystal System	monoclinic
Space group	'P 21/n'
Unit cell dimensions	a = 10.416(4)Å b = 19.090(8)Å c = 11.659(5)Å α = 90, β = 113.372(13), γ = 90
Volume, V/Å	2128.1(15)
Z	4
Calculated density, g·cm^{-3}	1.331
Absorption coefficient, μ/mm^{-1}	0.185
F(000)	904.0
θ range for data collection	2.22 to 27.10 °C
Limiting indices	–13≤ h ≤ 13, –24≤ k ≤ 24, –14≤ l ≤ 14
Reflection collected/unique	4194/4663
Completeness to *θ*	99% (*θ* = 27.10)
Absorption correction	none
Refinement method	'SHELXL-2018/3 (Sheldrick, 2015)'
Data / restraints / parameters	4663/0/274
Goodness-of-fit on F^2	1.043
Final *R* indices[I>2sigma(I)]	R1 = 0.0633, wR2 = 0.1866
R indices (all data)	R1 = 0.0689, wR2 = 0.1949

Table S1. Optimization of the Reaction Conditions.[a]



entry	Lewis acid (10 mol %)	solvent	yield **3a**[b]	yield **4a**[b]
1	$Cu(OTf)_2$	$(CH_2Cl)_2$	n.d.	58
2	$Yb(OTf)_3$	$(CH_2Cl)_2$	n.d.	65
3	$Sc(OTf)_3$	$(CH_2Cl)_2$	n.d.	62

4	$Zn(OTf)_2$	$(CH_2Cl)_2$	n.d.	trace
5	$CoCl_2$	$(CH_2Cl)_2$	n.d.	trace
6	$FeCl_3$	$(CH_2Cl)_2$	31	27
7	$FeCl_3$	CH_3CN	28	25
8	$FeCl_3$	THF	trace	12
9	$FeCl_3$	HFIP	n.d.	21
10	$FeCl_3$	toluene	35	27
11[c]	$FeCl_3$	toluene	47	38
12[d]	$FeCl_3$	toluene	51	40
13[e]	$FeCl_3$	toluene	45	52
14[f]	**$FeCl_3$**	**toluene**	**78**	**trace**
15[g]	$FeCl_3$	toluene	72	trace
16		toluene	n.d.	n.d.

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), Lewis acid (10 mol %), solvent (1.5 mL), 4 h, room temperature. [b]Isolated yield. [c]$FeCl_3$ (20 mol %). [d]$FeCl_3$ (30 mol %). [e]$FeCl_3$ (0.5 equiv). [f]$FeCl_3$ (20 mol %), 60 °C, 2 h. [g]$FeCl_3$ (20 mol %), 80 °C, 2 h. n.d. = not detected. HFIP = 1,1,1,3,3,3-Hexaflouro-2-propanol.

General Procedure for the Preparation of D-A Cyclopropanes.[2] To a stirred solution of aldehyde (5 mmol) in benzene (10 mL), dimethyl malonate (5 mmol, 660 mg), piperidine (0.5 mmol, 50 μL) and acetic acid (0.5 mmol, 28 μL) were added and the solution was heated to reflux in an oil bath. After completion, evaporation of the solvent gave a residue that was purified by silica gel column chromatography using ethyl acetate and hexane as an eluent. Sodium hydride (4 mmol, 60% dispersion in mineral oil, 96 mg) was suspended in DMF (10 mL) under nitrogen. Trimethylsulfoxonium iodide (3.85 mmol, 847 mg) was added, and the solution was stirred for 1 h at room temperature. A solution of the appropriate benzylidene malonate (3.5 mmol) in DMF (1 mL) was added, and the reaction mixture was stirred overnight at room temperature. After completion (monitored by TLC), the solution was poured into a mixture of ice and 2N HCl (5 mL) and extracted with ethyl acetate (2 x 25 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on a silica gel column chromatograph using ethyl acetate and hexane as an eluent to give cyclopropanes.

Procedure for the Synthesis of 1n-q.[3] **Step 1**: To a stirred solution of DCC (3.0 mmol, 618 mg) in CH_2Cl_2 (10 mL) was added 4-formylbenzoic acid (2.0 mmol, 300 mg) at room temperature. Then, a solution of the alcohol (2.0 mmol) and DMAP (0.3 mmol, 36 mg) in CH_2Cl_2 (5 mL) was added dropwise. The resultant mixture was allowed to stir for 12 h at room temperature and passed through a short pad of celite. The filtrate was washed with 1N HCl (20

mL), aqueous $NaHCO_3$ (20 mL) and brine (20 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was directly used for the next step without purification.

Step 2: To a stirred solution of the esters (1.5 mmol) in benzene (10 mL), dimethyl malonate (1.5 mmol, 200 mg), piperidine (0.15 mmol, 15 μL) and acetic acid (0.3 mmol, 17 μL) were added and the solution was heated to reflux in an oil bath. After completion, evaporation of the solvent gave a residue that was purified by silica gel column chromatography using ethyl acetate and hexane. Sodium hydride (1.7 mmol, 60% dispersion in mineral oil, 41 mg) was suspended in DMF (5 mL) under nitrogen. Trimethylsulfoxonium iodide (1.65 mmol, 363 mg) was added, and the solution was stirred for 1 h at room temperature. A solution of the benzylidene malonate (1.5 mmol) in DMF (2 mL) was added and the reaction mixture was stirred overnight at room temperature. After completion, the solution was poured onto a mixture of ice and 2N HCl (5 mL) and extracted with diethyl ether (2 x 25 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on a silica gel column chromatograph using ethyl acetate and hexane as an eluent to give cyclopropanes **1n-q**.

Preparation of Chiral Cyclopropane 1a′.[4] To a stirred solution of (*R*)-1-phenylethane-1,2-diol or (*S*)-1-phenylethane-1,2-diol (2.2 mmol, 304 mg) in CH_2Cl_2 (5 mL) at 0 °C was added NEt_3 (6.5 mmol, 1 mL). After 10 min, a solution of MsCl (5.4 mmol, 618 mg) in CH_2Cl_2 (1 mL) was added for 1 h dropwise. The resultant mixture was warmed to room temperature and the stirring was continued for an additional 4 h. The reaction mixture was then poured into 1N HCl (5 mL) and extracted using CH_2Cl_2 (2 x 30 mL). The combined organic layer was washed successively with 1N HCl (5 mL), saturated $NaHCO_3$ (5 mL) and water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue, which was used in the next step. To a suspension of sodium hydride (0.9 mmol, 60% dispersion in mineral oil, 22 mg) in THF (5 mL) was added a solution of dimethyl malonate (0.6 mmol, 79 mg) in THF (0.5 mL) for 20 min at 0 °C. The resultant mixture was treated with a solution of the above-prepared bismesylate (0.3 mmol, 88 mg) in THF (0.5 mL) dropwise (0 °C). The reaction mixture was then stirred under reflux for 24 h in an oil bath, poured into water (2 mL) and extracted with ethyl acetate (15 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on a silica gel column chromatograph using ethyl acetate and hexane as an eluent to afford (*R)*-**1a′** or (*S*)-**1a′**.

Procedure for 2,4-Dienal Preparation.[1] To a freshly prepared solution of Ph_3PCHCO_2Et (3 mmol, 1 g) in THF (20 mL) at 0 °C, sodium hydride (4.5 mmol, 60% dispersion in mineral oil,

110 mg) was added slowly followed by the enal (2.5 mmol). After completion (monitored by TLC), the reaction mixture was quenched with H_2O (15 mL). THF was evaporated under reduced pressure and the aqueous layer was extracted with CH_2Cl_2 (50 mL). The combined organic layer was washed with brine (10 mL), dried (Na_2SO_4), concentrated and used for next step without further purification.

The residue was diluted with 20 mL toluene at -78 °C under an argon atmosphere, and DIBAL-H (5.0 mL) was added dropwise. After completion (monitored by TLC), the reaction mixture was quenched with aqueous NH_4Cl. The solid was removed by filtration through celite using CH_2Cl_2 (50 mL). The combined organic layer was concentrated and used for next step without further purification.

The crude product was diluted in DMSO (5 mL), and IBX (4.5 mol, 1.2 g) was added. After completion (monitored by TLC), the solid was removed by filtration through celite using CH_2Cl_2 (30 mL). The combined organic layer was concentrated and the residue was purified by column chromatography using ethyl acetate and hexane to give **2a-h**.

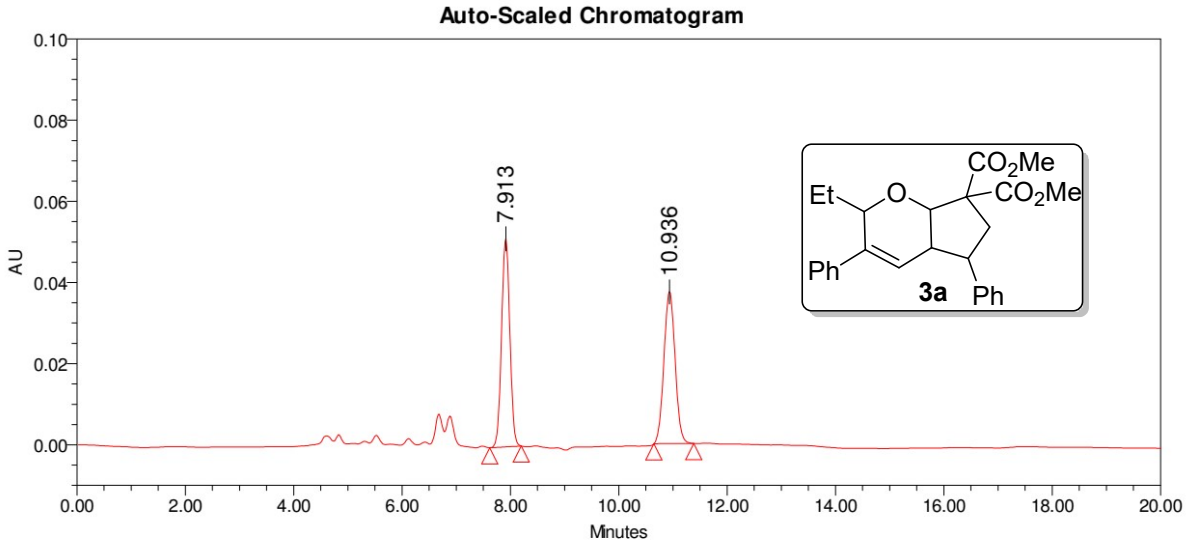
General Procedure for the Preparation of Hexahydrocyclopentapyrans 3. D-A cyclopropane **1a-q** (0.1 mmol), 2,4-dienal **2a-h** (0.11 mmol) and $FeCl_3$ (20 mol %, 3 mg) were stirred in toluene (1.5 mL) at 60 °C for 2 h in an oil bath. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with ethyl acetate (10 mL) and washed with water (2 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on a silica gel column chromatography using ethyl acetate and hexane as the eluent to give the cycloadduct **3a-y**.

Enantiospecific Synthesis of 3'. (*R*)-**1a'** or (*S*)-**1a'** (0.1 mmol, 23 mg), 2,4-dienal **2** (0.11 mmol) and $FeCl_3$ (0.02 mmol, 3.0 mg) were stirred at 60 ^oC for 2 h in an oil bath. The purification was carried out as above-described procedure. The *ee* was determined using chiral HPLC analysis. Compound **3a′**and **3z′** have prepared using (*R*)-**1a′**and compound **3v′** has been obstained using (*S*)-**1a′**

Gram-Scale Synthesis of 3a. Cyclopropane **1a** (3 mmol, 700 mg), 2,4-dienal **2a** (3.3 mmol, 613 mg) and $FeCl_3$ (20 mol %, 97 mg) were stirred in toluene (10 mL) at 60 °C for 2 h. The purification was carried out as described in general procedure to give **3a** in 62% yield (781 mg).

Synthesis of 6.[5] Compound **3a** (0.07 mmol, 30 mg), DMSO (2 mL), water (0.5 mL) and LiCl (0.21 mmol, 8.0 mg) were placed in a 10 mL round bottomed flask equipped with a magnetic stirrer and fitted with a condenser. The mixture was stirred at 130 ^{o}C in an oil bath for 8 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, poured into ice cold water and washed with brine (5 mL) and extracted using ethyl acetate (2 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent to give **6** in 68% yields (17 mg)**.**

HPLC Chromatogram



Peak Results

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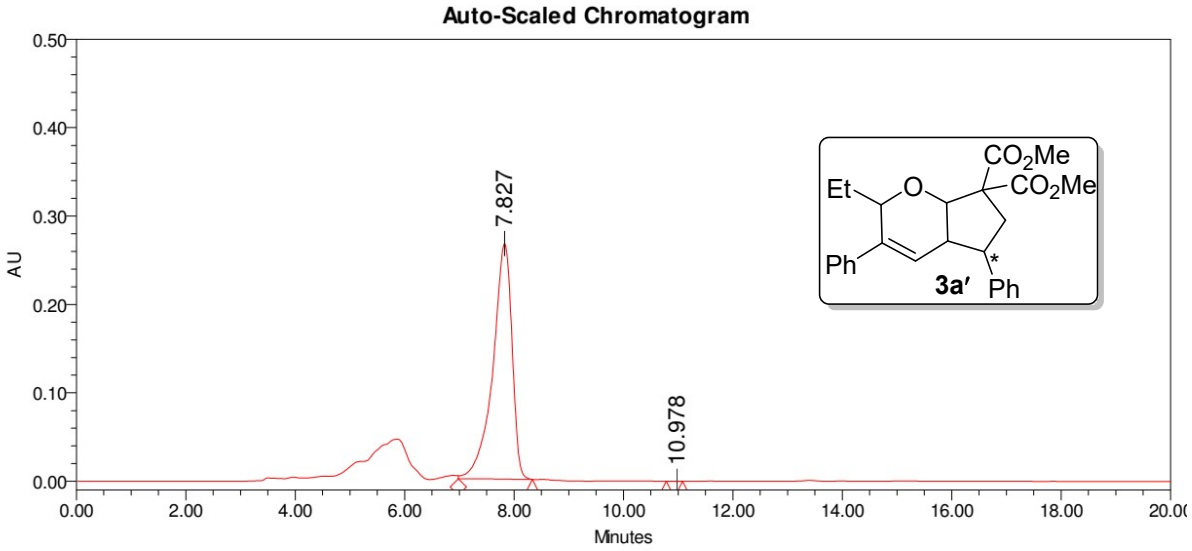

Peak Results

	Peak Codes	Start Time (min)	End Time (min)	RT	Height (μV)	% Area
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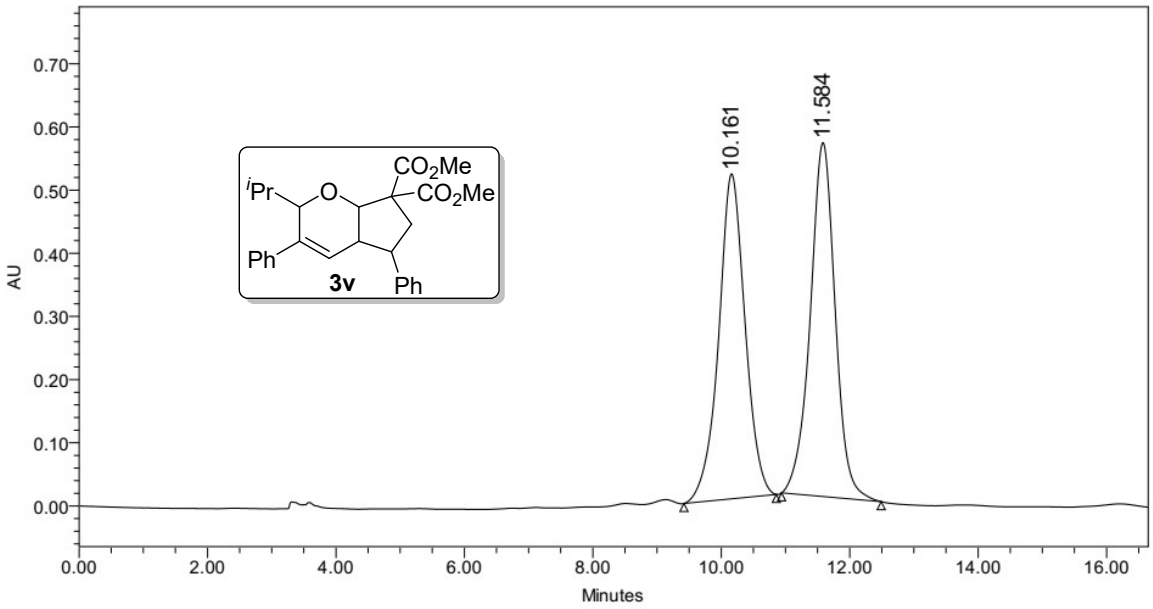
2	I37	10.783	11.083	10.978	8	0.00



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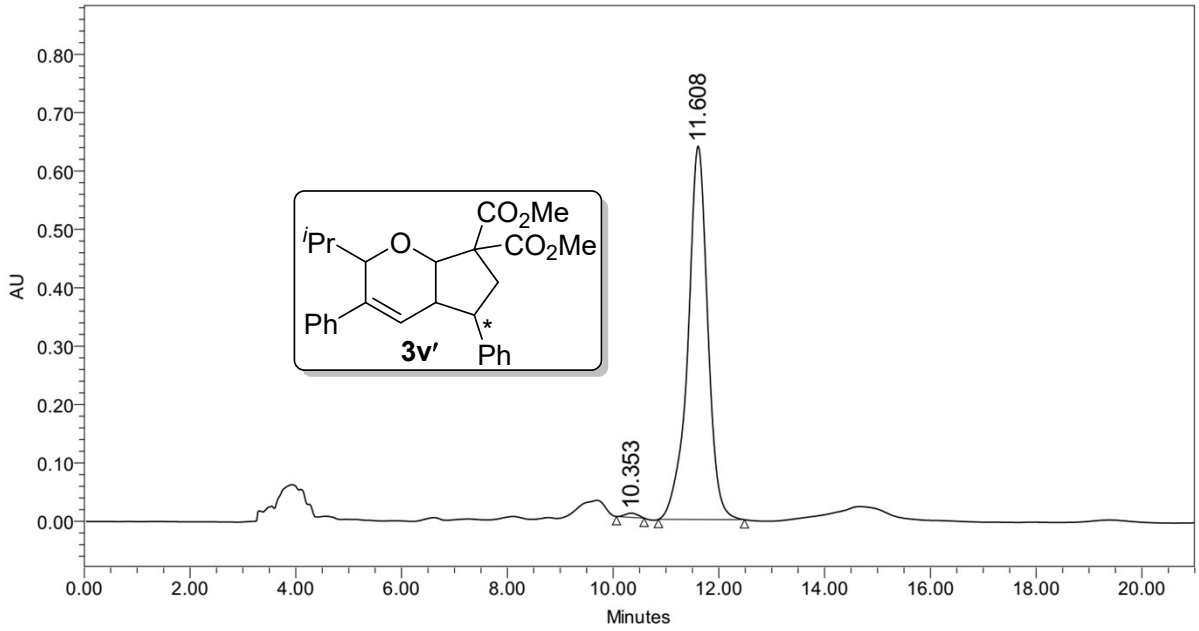
2	11.584	15134858	50.74	560121



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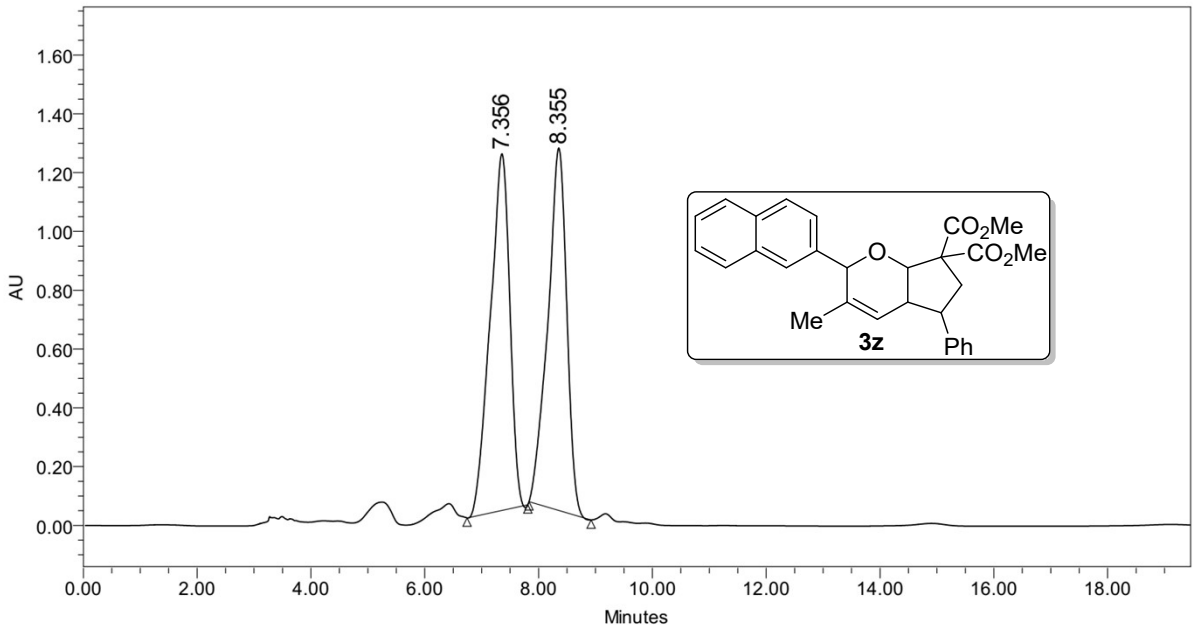

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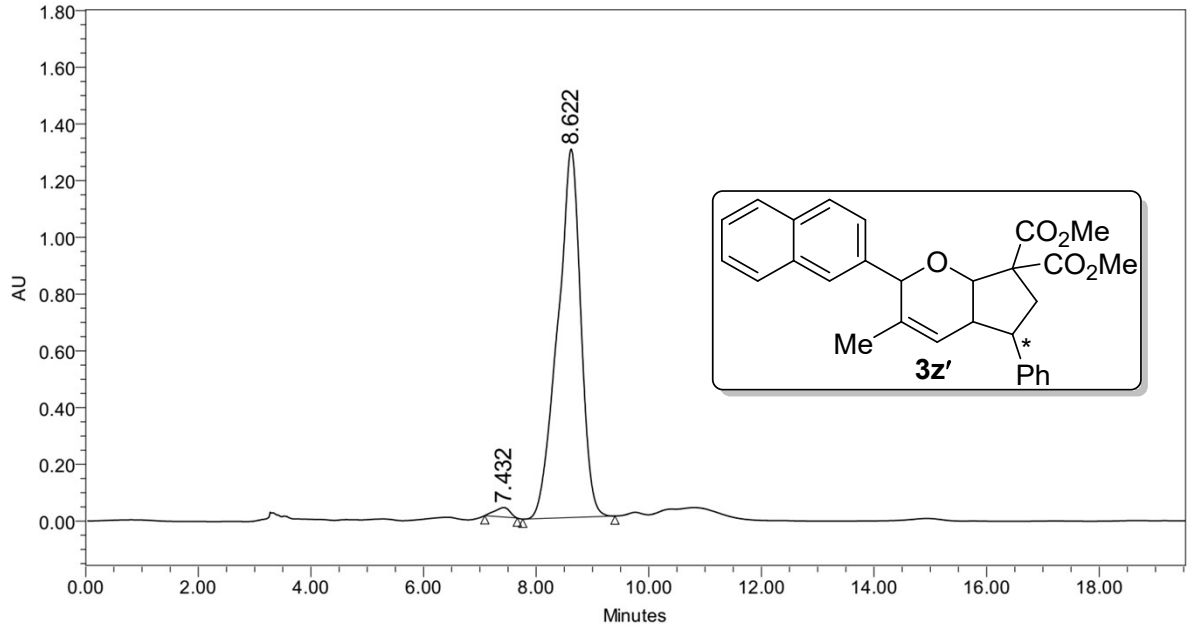

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1	7.432	620182	1.64	33514
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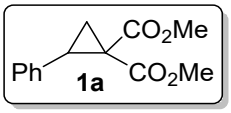
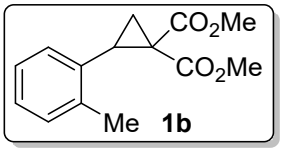
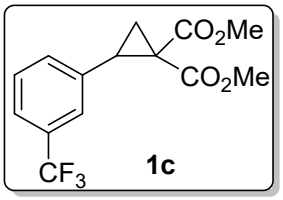
Characterization Data of the D-A Cyclopropanes



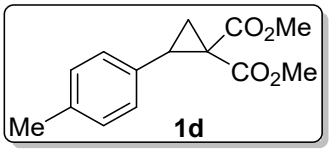
Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate 1a.[1a] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 3H), 7.19-7.17 (m, 2H), 3.78 (s, 3H), 3.35 (s, 3H), 3.22 (t, *J* = 8.4 Hz, 1H), 2.20 (dd, *J* = 5.2 Hz, 8.0 Hz, 1H), 1.74 (dd, *J* = 4.8 Hz, 9.2 Hz, 1H).



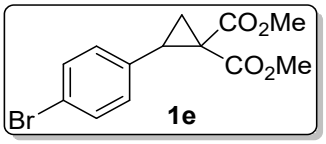
Dimethyl 2-(*o*-tolyl)-cyclopropane-1,1-dicarboxylate 1b.[1a] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.12 (m, 2H), 7.11-7.08 (m, 1H), 7.03-7.02 (m, 1H), 3.81 (s, 3H), 3.28 (s, 3H), 3.18 (t, *J* = 8.8 Hz, 1H), 2.35 (s, 3H), 2.31 (dd, *J* = 5.2 Hz, 8.0 Hz, 1H), 1.72 (dd, *J* = 5.2 Hz, 9.2 Hz, 1H).



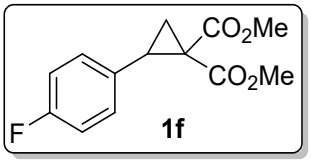
Dimethyl 2-(3-(tri-fluoromethyl)-phenyl)-cyclopropane-1,1-di-carboxylate 1c.[1a] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.49 (m, 1H), 7.46 (s, 1H), 7.40-7.39 (m, 2H), 3.80 (s, 3H), 3.38 (s, 3H), 3.26 (t, *J* = 8.4 Hz, 1H), 2.21 (dd, *J* = 5.2 Hz, 7.6 Hz, 1H), 1.79 (dd, *J* = 5.2 Hz, 9.2 Hz, 1H).



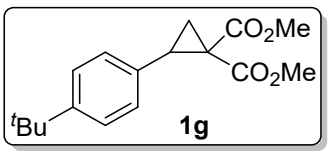
Dimethyl 2-(*p*-tolyl)cyclopropane-1,1-dicarboxylate 1d.[1a] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (s, 4H), 3.77 (s, 3H), 3.38 (s, 3H), 3.19 (t, *J* = 8.4 Hz, 1H), 2.29 (s, 3H), 2.17 (dd, *J* = 5.2 Hz, 8.0 Hz, 1H), 1.72 (dd, *J* = 4.8 Hz, 9.2 Hz, 1H).



Dimethyl 2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate 1e.[1b] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 3.41 (s, 3H), 3.16 (t, *J* = 8.4 Hz, 1H), 2.15 (dd, *J* = 5.2 Hz, 8.0 Hz, 1H), 1.74 (dd, *J* = 5.2 Hz, 9.2 Hz, 1H).

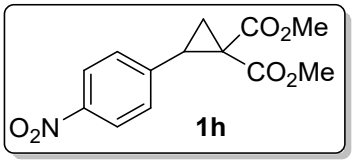


Dimethyl 2-(4-fluorophenyl) cyclopropane-1,1-dicarboxylate 1f.[1a] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.15 (m, 2H), 6.96 (t, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 3.39 (s, 3H), 3.19 (t, *J* = 8.8 Hz, 1H), 2.15 (dd, *J* = 5.2 Hz, 7.6 Hz, 1H), 1.74 (dd, *J* = 5.2 Hz, 9.2 Hz, 1H).

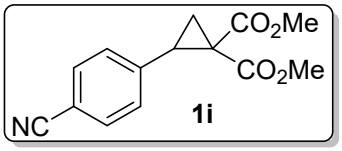


Dimethyl 2-(4-(*tert*-butyl)phenyl)cyclopropane-1,1-dicarboxylate 1g.[1b] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* =

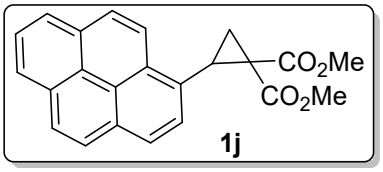
8.4 Hz, 2H), 3.78 (s, 3H), 3.34 (s, 3H), 3.19 (t, *J* = 8.8 Hz, 1H), 2.18 (dd, *J* = 5.2 Hz, 8.0 Hz, 1H), 1.73 (dd, *J* = 4.8 Hz, 9.2 Hz, 1H), 1.28 (s, 9H).



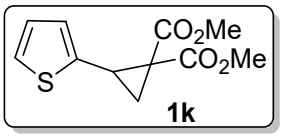
Dimethyl 2-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate 1h.[1b] Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H), 3.42 (s, 3H), 3.28 (t, *J* = 8.8 Hz, 1H), 2.23 (dd, *J* = 5.6 Hz, 8.0 Hz, 1H), 1.84 (dd, *J* = 5.2 Hz, 9.2 Hz, 1H).



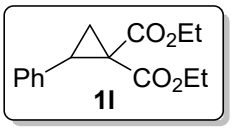
Dimethyl 2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate 1i.[1c] Colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H), 3.42 (s, 3H), 3.25 (t, *J* = 8.4 Hz, 1H), 2.21 (dd, *J* = 5.4 Hz, 8.4 Hz, 1H), 1.82 (dd, *J* = 5.4 Hz, 9.6 Hz, 1H).



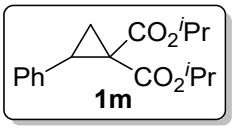
Dimethyl 2-(pyren-1-yl)cyclopropane-1,1-dicarboxylate 1j.[1b] Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 9.2 Hz, 1H), 8.21-8.14 (m, 3H) 8.11 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 3.6 Hz, 2H), 8.01-7.99 (m ,1H), 7.84 (d, *J* = 7.6 Hz, 1H), 3.98 (t, *J* = 8.8 Hz, 1H), 3.93 (s, 3H), 2.95 (s, 3H), 2.63 (dd, *J* = 4.8 Hz, 8.0 Hz, 1H), 1.99 (dd, *J* = 5.4 Hz, 9.2 Hz, 1H).



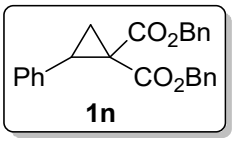
Dimethyl 2-(thiophen-2-yl)cyclopropane-1,1-dicarboxylate 1k.[1a] Dark brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 1.2 Hz, 5.2 Hz, 1H), 6.90-6.88 (m, 1H), 6.839-6.830 (m, 1H), 3.78 (s, 3H), 3.48 (s, 3H), 3.28 (t, *J* = 4.8 Hz, 1H), 2.14 (dd, *J* = 5.2 Hz, 7.6 Hz, 1H), 1.83 (dd, *J* = 5.2 Hz, 9.6 Hz, 1H).



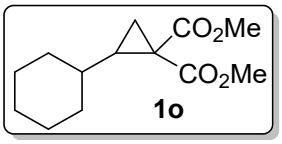
Diethyl 2-phenylcyclopropane-1,1-dicarboxylate 1l.[1a] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.19 (m, 5H), 4.29-4.19 (m, 2H), 3.84 (q, *J* = 7.2 Hz, 2H), 3.21 (t, *J* = 8.4 Hz, 1H), 2.17 (dd, *J* = 5.2 Hz, 8.0 Hz, 1H), 1.70 (dd, *J* = 5.2 Hz, 9.6 Hz, 1H), 1.29 (t, *J* = 6.8 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H).



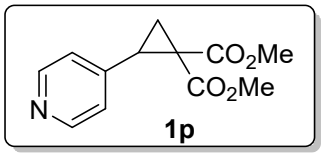
Di-*iso*-propyl 2-phenylcyclopropane-1,1-dicarboxylate 1m.[1a] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.23 (m, 2H), 7.20-7.19 (m, 3H), 5.13-5.04 (m, 1H), 4.76-4.67 (m, 1H), 3.17 (t, *J* = 8.8 Hz, 1H), 2.12 (dd, *J* = 5.2 Hz, 8.0 Hz, 1H), 1.64 (dd, *J* = 5.2 Hz, 9.2 Hz, 1H), 1.28-1.25 (m, 7H), 1.05 (d, *J* = 6.4 Hz, 3H), 0.69 (d, *J* = 6.4 Hz, 3H).



Dibenzyl 2-phenylcyclopropane-1,1-dicarboxylate 1n.[1a] Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.31 (m, 4H), 7.25-7.22 (m, 5H), 7.20-7.17(m, 3H), 6.93-6.91(m, 2H), 5.27 (d, *J* = 12.4 Hz, 1H), 5.16 (d, *J* = 12.4 Hz, 1H), 4.74 (s, 2H), 3.27 (t, *J* = 8.8 Hz, 1H), 2.23 (dd, *J* = 5.2 Hz, 8.0 Hz, 1H), 1.77 (dd, *J* = 5.2 Hz, 9.2 Hz, 1H), 1.28-1.25 (m, 7H), 1.05 (d, *J* = 6.4 Hz, 3H), 0.69 (d, *J* = 6.4 Hz, 3H).

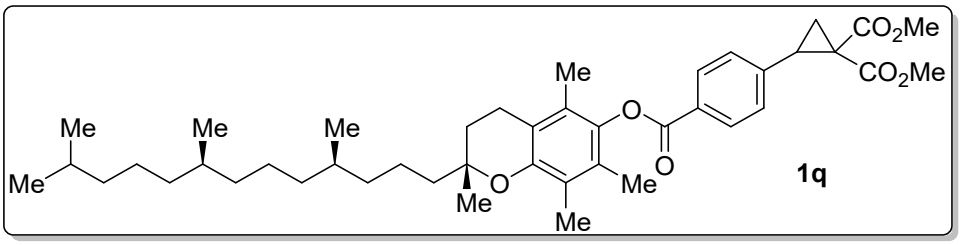


Dimethyl 2-cyclohexylcyclopropane-1,1-dicarboxylate 1o.[1d] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 3.71 (s, 3H), 1.78-1.71 (m. 4H), 1.67-1.62 (m, 2H), 1.42-1.39 (m, 1H), 1.36-1.32 (m, 1H), 1.19-1.08 (m, 5H), 0.82-0.77 (m, 1H).

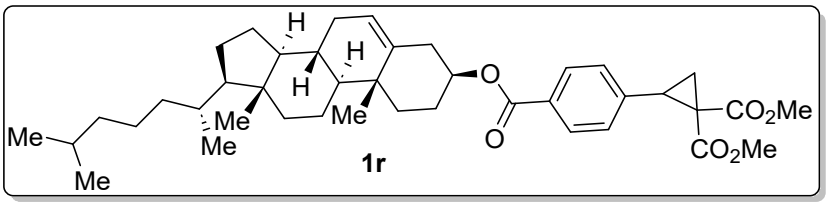


Dimethyl 2-(pyridin-4-yl) cyclopropane-1,1-dicarboxylate 1p. Black liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 6.4 Hz, 2H), 7.11 (d, *J* = 6.0 Hz, 2H), 3.80 (s, 3H), 3.42 (s, 3H), 3.15 (t, *J* = 8.4 Hz, 1H), 2.19 (dd, *J* = 5.6 Hz, 8.0 Hz, 1H), 1.79 (dd, *J* = 5.6 Hz, 9.2 Hz, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 166.5, 149.6, 144.3, 123.4,

53.1, 52.6, 37.8, 31.0, 18.9; FT-IR (neat) 2955, 1727, 1601, 1437, 1334, 1280, 1212, 1132, 1020 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{12}H_{14}NO_4^+$: 236.0918, found: 236.0918.

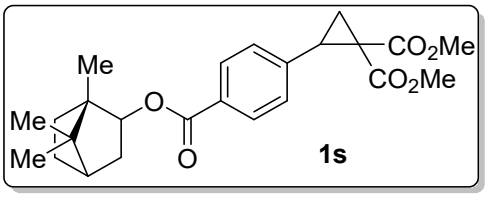


Dimethyl 2-(4-((((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy) carbonyl)phenyl)cyclopropane-1,1-dicarboxylate 1q. Yellow liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* =8.4 Hz, 2H), 3.84 (s, 3H), 3.47 (s, 3H), 3.31 (t, *J* = 8.4 Hz, 1H), 2.63 (t, *J* = 6.6 Hz, 1H), 2.28 (dd, *J* = 5.4 Hz, 8.4 Hz, 1H), 2.14 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.85-1.83 (m, 2H), 1.81-1.77 (m, 1H), 1.61-1.60 (m, 1H), 1.57-1.52 (m, 2H), 1.41 (s, 3H), 1.29-1.27 (m, 12H), 1.18-1.142 (m, 3H), 1.11-1.08 (m, 3H), 0.89-0.86 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 166.9, 165.0, 149.6, 140.7, 140.6, 130.1, 128.85, 128.80, 126.9, 125.2, 123.2, 117.6, 75.2, 53.1, 52.6, 39.5, 37.69, 37.67, 37.59, 37.58, 37.55, 37.52, 37.4, 32.9, 32.2, 28.1, 24.9, 24.5, 22.8, 22.7, 21.1, 20.7, 19.89, 19.82, 19.77, 19.74, 19.4, 13.1, 12.3, 11.9; FT-IR (neat) 2925, 1731, 1612, 1436, 1377, 1270, 1235, 1130, 1090 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{43}H_{63}O_7^+$:691.4568, found: 691.4571.

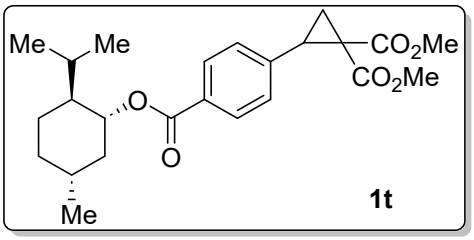


Dimethyl 2-(4-((((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)-oxy)carbonyl)-phenyl) cyclopropane-1,1-dicarboxylate 1r. Colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 5.43 (d, *J* = 4.2 Hz, 1H), 4.88-4.83 (m, 1H), 3.81 (s, 3H), 3.40 (s, 3H), 3.26 (t, *J* = 8.4 Hz, 1H), 2.47 (d, *J* = 7.8 Hz, 1H), 2.24 (dd, *J* = 5.4 Hz, 8.4 Hz, 1H), 2.05-1.99 (m, 3H), 1.94-1.91 (m, 1H), 1.87-1.83 (m, 1H), 1.80 (dd, *J* = 5.4 Hz, 9.6 Hz, 1H), 1.75 (d, *J* = 12.0 Hz, 1H), 1.62-1.58 (m, 3H), 1.56-1.52 (m, 3H), 1.50-1.45 (m, 2H), 1.36-1.35 (m, 2H), 1.27 (s, 2H), 1.22-1.19 (m, 2H), 1.18-1.14 (m, 2H), 1.13 (d, *J* = 9.6 Hz, 2H), 1.08 (s, 3H), 1.03-1.00 (m, 2H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.89 (dd, *J* = 2.4 Hz, 6.6 Hz, 6H), 0.70 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 166.9, 165.8,

139.9, 139.7, 130.0, 129.5, 128.4, 122.9, 74.8, 56.8, 56.2, 53.0, 52.5, 50.1, 42.4, 39.8, 39.6, 38.3, 37.6, 37.1, 36.7, 36.3, 35.9, 32.2, 32.0, 28.3, 28.1, 28.0, 24.4, 23.9, 22.9, 22.7, 21.1, 19.5, 19.3, 18.8, 12.0; FT-IR (neat) 2933, 1715, 1466, 1437, 1367, 1272, 1218, 1113, 1020 cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$calcd for $C_{41}H_{58}NaO_6^+$: 669.4126, found: 669.4125.

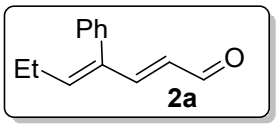


Dimethyl 2-(4-((((1*S*)-1,7,7-trimethyl bicyclo-[2.2.1]-heptan-2-yl)oxy)carbonyl)phenyl)cyclopropane-1,1-dicarboxylate 1s. Colorless liquid; ^1H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 5.11-5.09 (m, 1H), 3.81 (s, 3H), 3.41 (s, 3H), 3.26 (t, *J* = 8.4 Hz, 1H), 2.50-2.44 (m, 1H), 2.23 (dd, *J* = 5.4 Hz, 8.4 Hz, 1H), 2.14-2.10 (m, 1H), 1.83-1.81 (m, 1H), 1.80-1.79 (m, 1H), 1.74 (t, *J* = 4.2 Hz, 1H), 1.44-1.39 (m, 1H), 1.33-1.29 (m, 1H), 1.13-1.10 (m, 1H), 0.09 (s, 9H), 0.92 (d, *J* = 5.4 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 166.9, 166.6, 139.9, 130.0, 129.5, 128.5, 80.7, 53.0, 52.5, 49.19, 49.1, 47.9, 45.0, 37.6, 36.9, 32.2, 28.1, 27.4, 19.8, 19.3, 19.0, 13.7; FT-IR (neat) 2953, 1713, 1612, 1436, 1270, 1114, 1059 cm-1; HRMS (ESI) m/z $[M+Na]^+$calcd for $C_{24}H_{30}NaO_6^+$: 437.1935, found: 437.1936.

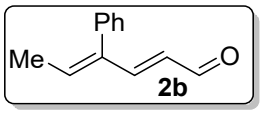


Dimethyl 2-(4-((((1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-cyclohexyl)oxy)carbonyl)phenyl) cyclopropane-1,1-dicarboxylate 1t. Colorless liquid; ^1H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 5.10 (d, *J* = 9.0 Hz, 1H), 3.81 (s, 3H), 3.42 (s, 3H), 3.27 (t, *J* = 8.4 Hz, 1H), 2.49-2.45 (m, 1H), 2.24-2.26 (m, 1H), 2.14-2.10 (m, 1H), 1.80 (dd, *J* = 4.8 Hz, 9.0 Hz, 2H), 1.74 (t, *J* = 4.8 Hz, 1H), 1.41 (bt, *J* = 12.0 Hz, 1H), 1.34-1.30 (m, 1H), 1.28-1.26 (m, 1H), 1.13-1.10 (m, 1H), 0.097 (s, 3H), 0.92 (d, *J* = 6.0 Hz, 6H), 0.88-0.86 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 166.9, 166.6, 139.9, 130.1, 129.5, 128.5, 80.7, 53.0, 52.5, 49.2, 49.1, 48.0, 45.1, 37.6, 37.0, 32.2, 28.2, 27.5, 19.8, 19.3, 19.0, 13.7; FT-IR (neat) 2953, 1713, 1612, 1436, 1369, 1330, 1268, 1217, 1178, 1111, 1038 cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{24}H_{32}NaO_6^+$: 439.2091, found: 439.2090.

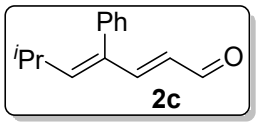
Characterization Data of the 2,4-Dienals



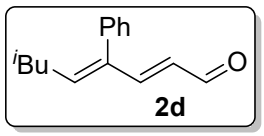
(2*E*,4*Z*)-4-Phenylhepta-2,4-dienal 2a.[4] Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (d, *J* = 8.0 Hz, 1H), 7.40-7.37 (m, 2H), 7.35-7.33 (m, 1H), 7.31 (d, *J* = 15.2 Hz, 1H), 7.10-7.08 (m, 2H), 6.25 (t, *J* = 7.6 Hz, 1H), 5.72 (dd, *J* = 8.0 Hz, 15.6 Hz, 1H), 2.11-2.03 (m, 2H), 1.00 (d, *J* = 7.6 Hz, 3H).



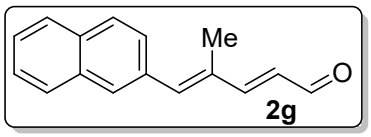
(2*E*,4*Z*)-4-Phenylhexa-2,4-dienal 2b.[4] Yellow liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.60 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.36-7.33 (m, 1H), 7.331 (d, *J* = 15.6 Hz, 1H), 7.11 (d, *J* = 1.2 Hz, 1H), 6.39 (q, *J* = 7.2 Hz, 1H), 5.74 (dd, *J* = 7.8 Hz, 15.6 Hz, 1H), 1.76 (d, *J* = 7.2 Hz, 3H).



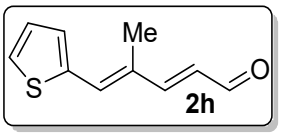
(2*E*,4*Z*)-6-Methyl-4-phenylhepta-2,4-dienal 2c. Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, *J* = 8.0 Hz, 1H), 7.40-7.36 (m, 2H), 7.34-7.32 (m, 1H), 7.29 (d, *J* = 15.6 Hz, 1H), 7.10-7.08 (m, 2H), 6.06 (d, *J* = 10.0 Hz, 1H), 5.68 (dd, *J* = 8.0 Hz, 15.2 Hz, 1H), 2.40-2.31 (m, 1H), 0.98 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.9, 156.9, 151.8, 138.3, 136.3, 129.9, 129.1, 128.6, 127.7, 29.0, 22.5; FT-IR (neat) 2962, 1676, 1618, 1599, 1443, 1362, 1120, 1074 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{17}O^+$: 201.1274, found: 201.1275.



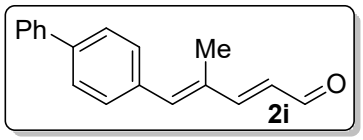
(2*E*,4*Z*)-7-Methyl-4-phenylocta-2,4-dienal 2d. Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (d, *J* = 7.6 Hz, 1H), 7.40-7.36 (m, 2H), 7.34-7.32 (m, 1H), 7.29-7.26 (m, 1H), 7.08-7.06 (m, 2H), 6.28 (t, *J* = 7.6 Hz, 1H), 5.69 (dd, *J* = 7.6 Hz, 15.2 Hz, 1H), 1.96 (t, *J* = 7.2 Hz, 2H), 1.75-1.69 (m, 1H), 0.87 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) 193.9, 156.7, 144.4, 141.2, 136.2, 129.6, 129.3, 128.6, 127.7, 38.9, 28.7, 22.5; FT-IR (neat) 2955, 1676, 1599, 1615, 1442, 1276, 1122, 1073 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{19}O^+$: 215.1430, found: 215.1431.



(2*E*,4*E*)-4-Methyl-5-(naphthalen-2-yl)penta-2,4-dienal 2g. Orange sticky liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (d, *J* = 8.0 Hz, 1H), 7.86-7.82 (m, 4H), 7.52-7.48 (m, 3H), 7.36 (d, *J* = 15.6 Hz, 1H), 7.09 (s, 1H), 6.32 (dd, *J* = 7.6 Hz, 15.6 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.0, 158.0, 140.9, 134.8, 133.8, 133.2, 132.9, 129.3, 128.4, 128.1, 127.8, 127.1, 126.9, 126.6, 14.2; FT-IR (neat) 2961, 2253, 1669, 1600, 1440, 1367, 1273, 1129, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{15}O^+$: 223.1117, found: 223.1115.

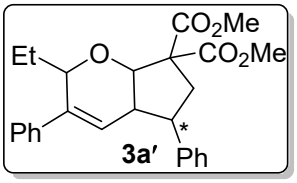


(2*E*,4*E*)-4-Methyl-5-(thiophen-2-yl)penta-2,4-dienal 2h. Black sticky liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 5.2 Hz, 1H), 7.27-7.23 (m, 2H), 7.12-7.10 (m, 1H), 7.08 (s, 1H), 6.28 (dd, *J* = 7.6 Hz, 15.2 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.8, 157.6, 139.8, 133.4, 131.8, 131.4, 129.1, 127.9, 127.6, 14.2; FT-IR (neat) 2923, 1666, 1586, 1419, 1257, 1127, 1051 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{10}H_{11}OS^+$: 179.0525, found: 179.0526.



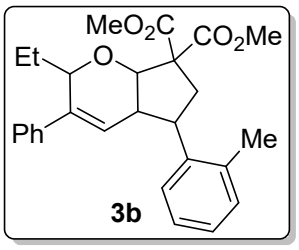
(2*E*,4*E*)-5-([1,1'-Biphenyl]-4-yl)-4-methylpenta-2,4-dienal 2i. Yellow liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.70 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.65-7.64 (m, 2H), 7.51-7.47 (m, 4H), 7.39 (t, *J* = 7.2Hz, 1H), 7.36 (d, *J* = 15.6 Hz, 1H), 7.00 (s, 1H), 6.33 (dd, *J* = 7.2 Hz, 15.0 Hz, 1H), 2.182-2.181 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.0, 158.0, 141.1, 140.5, 140.4, 135.3, 134.6, 130.3, 129.0, 128.3, 127.8, 127.2, 127.1, 14.2; FT-IR (neat) 2956, 1674, 1597, 1485, 1391, 1129, 1077 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{17}O^+$: 249.1274, found: 249.1276.

Characterization Data of the Products

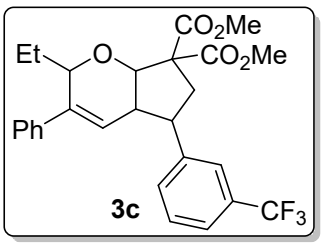


Dimethyl 2-ethyl-3,5-diphenyl-4a,5,6,7a-*tetra*-hydro-cyclopenta-[b]pyran-7,7(2H)-dicarboxylate 3a′. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane;

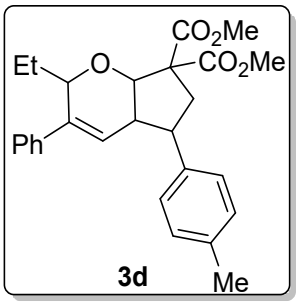
R_f = 0.45; yellow sticky liquid; yield 78% (34 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39-7.36 (m, 2H), 7.35-7.34 (m, 4H), 7.32-7.30 (m, 1H), 7.29-7.27 (m, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.67 (d, *J* = 15.6 Hz, 1H), 5.79 (t, *J* = 7.2 Hz, 1H), 5.37-5.35 (m, 2H), 5.12 (dd, *J* = 6.6 Hz, 15.6 Hz, 1H), 3.68 (s, 3H), 3.61 (s, 3H), 3.14 (dd, *J* = 7.2 Hz , 13.2 Hz, 1H), 2.26 (dd, *J* = 8.4 Hz, 13.2 Hz, 1H), 1.97-1.92 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 169.2, 142.3, 139.7, 138.1, 137.2, 136.8, 129.5, 128.5, 128.2, 127.6, 126.9, 125.5, 125.2, 83.3, 79.9, 65.1, 52.8, 52.6, 42.7, 22.6, 14.2; FT-IR (neat) 2955, 1732, 1608, 1515, 1435, 1259, 1167, 1074 cm^{-1}; $[\alpha]_D^{25}$ = +20 (*c* = 0.02, $CHCl_3$); HPLC analysis: 99% ee [YMC Chiral ART Cellulose-SC column, hexane/^{i}PrOH = 97:3, flow rate: 1 mL/min, λ = 254 nm, t_R = 7.82 min (major), 10.97 min (minor)]; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{29}O_5^+$: 421.2010, found: 421.2002.



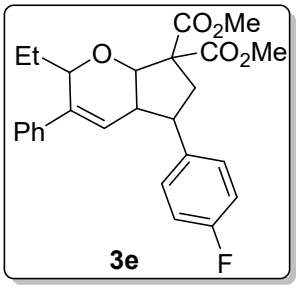
Dimethyl 2-ethyl-3-phenyl-5-(o-tolyl)-4a,5,6,7a-tetra-hydro-cyclopenta[b]pyran-7,7(2H)-dicarboxylate 3b. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.50; yellow sticky liquid; yield 72% (33 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.31-7.29 (m, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.13-7.11 (m, 3H), 6.69 (d, *J* = 15.6 Hz, 1H), 5.78 (t, *J* = 7.2 Hz, 1H), 5.52 (t, *J* = 7.8 Hz, 1H), 5.40 (d, *J* = 6.6 Hz, 1H), 5.13 (dd, *J* = 7.2 Hz, 15.6 Hz, 1H), 3.68 (s, 3H), 3.61 (s, 3H), 3.18 (dd, *J* = 7.2 Hz, 13.2 Hz, 1H), 2.31 (s, 3H), 2.08 (dd, *J* = 8.4 Hz, 13.2 Hz, 1H), 1.97-1.92 (m, 2H), 0.94 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ170.0, 169.3, 140.6, 139.8, 138.1, 137.1, 136.8, 134.2, ,130.4, 129.5, 128.2, 127.2, 126.9, 126.2, 125.3, 124.2, 83.2, 77.5, 65.0, 52.8, 52.6, 41.5, 22.6, 19.3, 14.2; FT-IR (neat) 2955, 1733, 1601, 1492, 1435, 1373, 1246, 1169, 1072 cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{27}H_{30}NaO_5^+$: 457.1985, found: 457.1980.



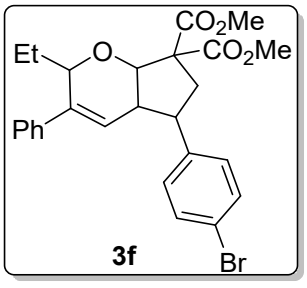
Dimethyl 2-ethyl-3-phenyl-5-(3-(trifluoromethyl)phenyl)-4a,5,6,7a-tetrahydrocyclopenta[b]pyran-7,7(2H)-dicarboxylate 3c. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.42; yellow sticky liquid; yield 76% (25 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.53 (t, *J* = 6.6 Hz, 2H), 7.48-7.45 (m, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 2H), 6.67 (d, *J* = 15.0 Hz, 1H), 5.80 (t, *J* = 7.8 Hz, 1H), 5.41 (t, *J* = 7.2 Hz, 1H), 5.38 (d, *J* = 7.2 Hz, 1H), 5.10 (dd, *J* = 6.6 Hz, 15.0 Hz, 1H), 3.68 (s, 3H), 3.62 (s, 3H), 3.17 (dd, *J* = 7.2 Hz, 13.2 Hz, 1H), 2.23 (dd, *J* = 7.8 Hz, 13.2 Hz, 1H), 1.97-1.92 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.9, 169.0, 143.4, 139.7, 138.0, 137.4,, 137.1, 131.2, 129.5, 129.0, 128.9, 128.2, 127.0, 126.9, 124.9, 124.4, 122.3, 83.5, 79.2, 65.0, 52.9, 52.7, 42.5, 22.6, 14.2; FT-IR (neat) 2956, 1732, 1601, 1493, 1328, 1258, 1164, 1072 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{22}H_{21}N_2O^+$: 329.1648, found: 329.1649.



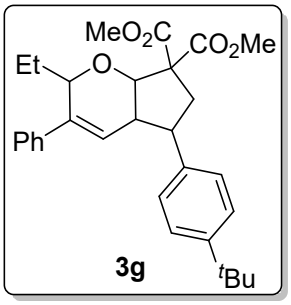
Dimethyl 2-ethyl-3-phenyl-5-(p-tolyl)-4a,5,6,7a-tetra-hydro-cyclopenta[b]pyran-7,7(2H)-dicarboxylate 3d. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.52; yellow sticky liquid; yield 78% (34 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.2 Hz, 2H), 7.28-7.20 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.13-7.11 (m, 2H), 7.09 (d, *J* = 6.8 Hz, 2H), 6.63 (d, *J* = 15.2 Hz, 1H), 5.74 (t, *J* = 7.6 Hz, 1H), 5.32-5.37 (m, 2H), 5.08 (dd, *J* = 6.8 Hz, 15.2 Hz, 1H), 3.66 (s, 3H), 3.57 (s, 3H), 3.08 (dd, *J* = 6.8 Hz 13.2 Hz, 1H) 2.31 (s, 3H), 2.21 (dd, *J* = 8.4 Hz, 13.2 Hz, 1H) 1.95-1.87 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.2, 169.3, 139.8, 139.2, 138.1, 137.2, 137.1, 136.7, 129.5, 129.2, 128.2, 126.9, 125.5, 125.3, 83.2, 79.8, 65.1, 52.8, 52.5, 42.7, 22.6, 21.2, 14.2; FT-IR (neat) 2960, 1732, 1683, 1518, 1488, 1249, 1203, 1071cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{27}H_{31}O_5^+$: 435.2166, found: 435.2164.



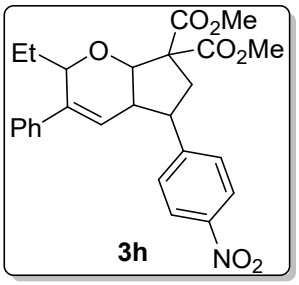
Dimethyl 2-ethyl-5-(4-fluorophenyl)-3-phenyl-4a,5,6,7a-tetra-hydrocyclopenta[b]pyran-7,7(2H)-dicarboxylate 3e. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.40; yellow sticky liquid; yield 75% (34 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.33 (m, 2H), 7.30-7.27 (m, 3H), 7.094-7.070 (m, 2H), 7.03-6.98 (m, 2H), 6.63 (d, *J* = 15.6 Hz, 1H), 5.76 (t, *J* = 7.6 Hz, 1H), 5.33-5.28 (m, 2H), 5.06 (dd, *J* = 6.8 Hz, 15.6 Hz, 1H), 3.66 (s, 3H), 3.58 (s, 3H), 3.08 (dd, *J* = 7.2 Hz, 13.2 Hz, 1H), 2.18 (dd, *J* = 8.0 Hz, 13.2 Hz, 1H) 1.95-1.87 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 169.2, 163.5, 161.0, 139.7, 138.0, 137.96, 137.93, 137.3, 137.0, 129.5, 128.2, 127.3, 127.2, 127.0, 125.0, 115.5, 115.3, 83.4, 79.4, 65.1, 52.9, 52.6, 42.7, 22.6, 14.2; FT-IR (neat) 2958, 1736, 1603, 1511, 1436, 1226, 1158, 1078 cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{26}H_{27}FNaO_5^+$: 461.1735, found: 461.1735.



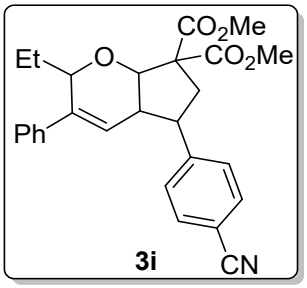
Dimethyl 5-(4-bromophenyl)-2-ethyl-3-phenyl-4a,5,6,7a-tetra-hydrocyclopenta[b]pyran-7,7(2H)-dicarboxylate 3f. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.40; yellow sticky liquid; yield 74% (36 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.65 (d, *J* = 15.6 Hz, 1H), 5.78 (t, *J* = 7.2 Hz, 1H), 5.33 (d, *J* = 7.2 Hz, 1H), 5.30 (t, *J* = 7.2 Hz, 1H), 5.08 (dd, *J* = 6.6 Hz, 15.0 Hz, 1H), 3.68 (s, 3H), 3.60 (s, 3H), 3.11 (dd, *J* = 7.2 Hz, 13.2 Hz, 1H), 2.18 (dd, *J* = 7.2 Hz, 13.2 Hz, 1H), 1.96-1.91 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.9, 169.1, 141.4, 139.7, 138.0, 137.4, 137.0, 131.6, 129.5, 128.2, 127.2, 127.0, 125.0, 121.3, 83.4, 79.2, 65.0, 52.9, 52.6, 42.5, 22.6, 14.2; FT-IR (neat) 2925, 1732, 1489, 1434, 1265, 1220, 1174, 1070 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{28}BrO_5^+$: 499.1115, found: 499.1113.



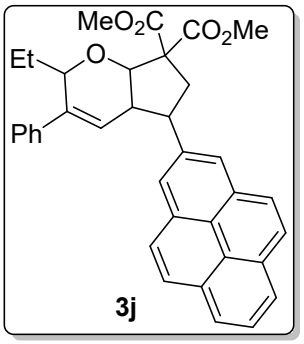
Dimethyl 5-(4-(tert-butyl)phenyl)-2-ethyl-3-phenyl-4a,5,6,7a-tetrahydrocyclopenta[b]pyran-7,7(2H)-dicarboxylate 3g. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.52; yellow sticky liquid; yield 76% (36 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.35 (m, 4H), 7.30-7.26 (m, 4H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.65 (d, *J* = 15.6 Hz, 1H), 5.76 (t, *J* = 7.2 Hz, 1H), 5.34-5.31 (m, 2H), 5.10 (dd, *J* = 6.6 Hz, 15.6 Hz, 1H), 3.68 (s, 3H), 3.60 (s, 3H), 3.10 (dd, *J* = 6.6 Hz, 13.2 Hz, 1H), 2.26 (dd, *J* = 8.4 Hz, 13.2 Hz, 1H), 1.96-1.91 (m, 2H), 1.32 (s, 9H), 0.93 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.2, 169.4, 150.6, 139.8, 139.1, 138.1, 137.1, 136.7, 129.5, 128.2, 126.9, 125.47, 125.43, 125.3, 83.2, 79.8, 65.1, 52.8, 52.6, 42.6, 34.6, 31.4, 22.6, 14.3; FT-IR (neat) 2957, 1734, 1681, 1513, 1490, 1434, 1254, 1198, 1068 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{30}H_{37}O_5^+$: 477.2636, found: 477.2654.



Dimethyl 2-ethyl-5-(4-nitrophenyl)-3-phenyl-4a,5,6,7a-tetrahydrocyclopenta[b]pyran-7,7(2H)-dicarboxylate 3h. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.35; red sticky liquid; yield 68% (31 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.38-7.34 (m, 3H), 7.10-7.07 (m, 2H), 6.65 (d, *J* = 15.6 Hz, 1H), 5.78 (t, *J* = 7.6 Hz, 1H), 5.41 (t, *J* = 7.6 Hz, 1H), 5.34 (d, *J* = 6.8 Hz, 1H), 5.06 (dd, *J* = 6.8 Hz, 15.6 Hz, 1H), 3.65 (s, 3H), 3.59 (s, 3H), 3.17 (dd, *J* = 7.2 Hz, 13.2 Hz, 1H), 2.16 (dd, *J* = 8.0 Hz, 13.2 Hz, 1H), 1.96-1.89 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 168.9, 149.9, 147.4, 139.6, 137.9, 137.7, 137.4, 129.5, 128.3, 127.0, 126.2, 124.6, 123.9, 83.8, 78.9, 64.9, 53.0, 52.8, 42.4, 22.7, 14.2; FT-IR (neat) 2956, 1734, 1684, 1601, 1520, 1435, 1380, 1258, 1178, 1075 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{28}NO_7^+$: 466.1860, found: 466.1872.

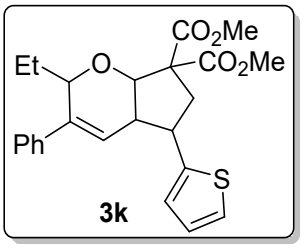


Dimethyl 5-(4-cyanophenyl)-2-ethyl-3-phenyl-4a,5,6,7a-tetrahydrocyclopenta[b]pyran-7,7(2H)-dicarboxylate 3i. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.45; red sticky liquid; yield 64% (28 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.30-7.29 (m, 1H), 7.09-7.07 (m, 2H), 6.64 (d, *J* = 15.6 Hz, 1H), 5.76 (t, *J* = 7.6 Hz, 1H), 5.36 (t, *J* = 7.6 Hz, 1H), 5.32 (d, *J* = 6.8 Hz, 1H), 5.06 (dd, *J* = 6.8 Hz, 15.6 Hz, 1H), 3.64 (s, 3H), 3.59 (s, 3H), 3.15 (dd, *J* = 7.2 Hz, 13.2 Hz, 1H), 2.15 (dd, *J* = 8.0 Hz, 13.2 Hz, 1H), 1.96-1.88 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 168.9, 147.9, 139.6, 137.9, 137.6, 137.3, 132.4, 129.5, 128.2, 127.0, 126.1, 124.6, 118.9, 111.4, 83.7, 79.0, 64.9, 53.0, 52.7, 42.4, 22.6, 14.2; FT-IR (neat) 2954, 2282, 1732, 1607, 1504, 1436, 1334, 1277, 1224, 1154 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{27}H_{28}NO_5^+$: 446.1962, found: 446.1957.

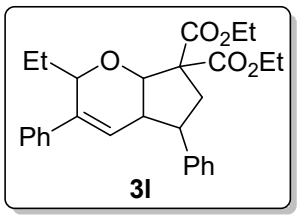


Dimethyl 2-ethyl-3-phenyl-5-(pyren-2-yl)-4a,5,6,7a-tetrahydrocyclopenta[b]pyran-7,7(2H)-dicarboxylate 3j. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.35; colorless solid; mp 160-161 °C; yield 73% (41 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 9.0 Hz, 1H), 8.24-8.19 (m, 4H), 8.07-8.03 (m, 4H), 7.20-7.17 (m, 3H), 7.069-7.05 (m, 2H), 5.794 (dd, *J* = 1.2 Hz, 6.0 Hz, 1H), 4.97 (d, *J* = 3.0 Hz, 1H), 4.843-4.83 (m, 1H), 4.65-4.60 (m, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 3.58 (dd, *J* = 7.8 Hz, 13.8 Hz, 1H), 3.16-3.12 (m, 1H), 2.24-2.20 (m, 1H), 1.77-1.73 (m, 1H), 1.56-1.51 (m, 1H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.1, 169.4, 141.6, 140.3, 135.4, 131.6, 131.1, 130.1, 129.8, 128.3, 127.6, 127.5, 127.2, 127.0, 126.3, 126.1, 125.4, 125.2, 125.1, 125.08, 125.00, 124.2, 123.5, 122.9, 80.3, 63.9, 52.9, 52.7, 47.4, 46.0, 42.1, 26.8, 9.1; FT-IR (neat) 2951, 1731,

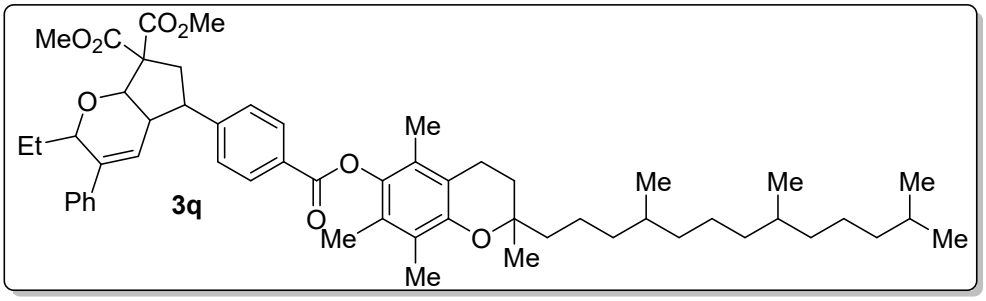
1602, 1492, 1244, 1171, 1068 cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{36}H_{32}NaO_5^+$: 567.2142, found: 567.2132.



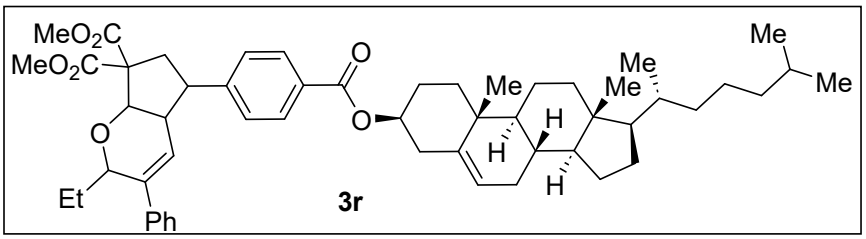
Dimethyl 2-ethyl-3-phenyl-5-(thiophen-2-yl)-4a,5,6,7a-tetrahydrocyclopenta[b]pyran-7,7(2H)-dicarboxylate 3k. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.50; colorless solid; mp 138-139 °C ; yield 77% (32 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.15 (m, 4H), 6.98-6.96 (m, 1H), 6.88-6.87 (m, 1H), 6.84-6.82 (m, 2H), 5.27 (dd, *J* = 2.0 Hz, 9.0 Hz, 1H), 4.58 (d, *J* = 4.0 Hz, 1H), 4.42-4.40 (m, 1H), 3.87-3.82 (m, 1H), 3.796-3.793 (m, 6H), 3.25-3.19 (m, 1H), 3.10-3.04 (m, 1H), 2.66 (dd, *J* = 7.6 Hz, 13.6 Hz, 1H), 1.56-1.51 (m, 2H), 0.82 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 168.8, 145.6, 141.5, 140.9, 128.1, 126.7, 126.5, 126.5, 125.5, 124.0, 123.7, 80.0, 75.1, 65.0, 52.9, 52.6, 41.6, 40.9, 39.9, 26.7, 9.8; FT-IR (neat) 2953, 1732, 1599, 1493, 1434, 1266, 1238, 1195, 1116, 1062 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{24}H_{27}O_5S^+$: 427.1586, found: 427.1584.



Diethyl 2-ethyl-3,5-diphenyl-4a,5,6,7a-tetrahydrocyclopenta[b]-pyran-7,7(2H)-dicarboxylate 3l. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.47; colorless liquid; yield 72% (30 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.31 (m, 5H), 7.29-7.21(m, 3H), 7.10-7.07 (m, 2H), 6.64 (d, *J* = 15.2 Hz, 2H), 5.74 (t, *J* = 7.6 Hz, 1H), 5.34-5.31 (m, 2H), 5.15 (dd, *J* = 6.8 Hz, 15.6 Hz, 1H), 4.17-4.04 (m, 3H), 3.99-3.91 (m, 1H), 3.10 (dd, *J* = 7.2 Hz, 13.2 Hz, 1H), 2.22 (dd, *J* = 8.0 Hz, 10.2 Hz, 1H), 1.95-1.88 (m, 2H), 1.15 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 168.9, 142.4, 139.7, 138.0, 137.2, 136.8, 129.5, 128.5, 128.2, 127.5, 126.9, 125.6, 125.2, 83.3, 79.8, 65.1, 61.76, 61.72, 42.7, 22.6, 14.3, 14.06, 14.03; FT-IR (neat) 2967, 1731, 1600, 1494, 1448, 1368, 1251, 1065 cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{28}H_{32}NaO_5$: 471.2142, found: 471.2156.

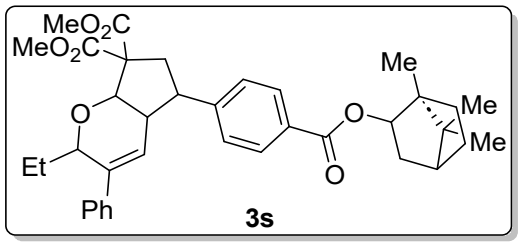


Dimethyl 2-ethyl-3-phenyl-5-(4-(((2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl)-oxy)carbonyl)phenyl)-4a,5,6,7a-tetrahydro cyclopenta[b]pyran-7,7(2H)-dicarboxylate 3q. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.60; yellow sticky liquid; yield 77% (67 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 15.0 Hz, 1H), 5.78 (t, *J* = 7.2 Hz, 1H), 5.42 (t, *J* = 7.2 Hz, 1H), 5.35 (d, *J* = 7.2 Hz, 1H), 5.09 (dd, *J* = 6.6 Hz, 15.0 Hz, 1H), 3.67 (s, 3H), 3.60 (s, 3H), 3.18 (dd, *J* = 7.2 Hz, 13.2 Hz, 1H), 2.61 (t, *J* = 6.0 Hz, 1H), 2.22 (dd, *J* = 7.8 Hz, 13.2 Hz, 1H), 2.11 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 1.95-1.90 (m, 2H), 1.84-1.81 (m, 1H), 1.78-1.75 (m, 1H), 1.54-1.50 (m, 2H), 1.39-1.37 (m, 4H), 1.28-1.24 (m, 10H), 1.15-1.11 (m, 3H), 1.10-1.06 (m, 3H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.87-0.84 (m, 14H) ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.9, 169.1, 165.0, 149.6, 148.2, 140.7, 139.7, 138.0, 137.5, 137.1, 130.5, 129.5, 128.8, 128.2, 127.0, 125.5, 125.2, 124.9, 123.2, 83.6, 79.4, 75.2, 65.0, 52.9, 52.7, 42.5, 39.5, 37.6, 37.5, 37.4, 32.93, 32.92, 28.1, 24.9, 24.5, 22.8, 22.7, 22.6, 21.1, 20.7, 19.89, 19.83, 14.2, 13.1, 12.3, 11.9; FT-IR (neat) 2926, 1733, 1612, 1576, 1457, 1435, 1333, 1270, 1174, 1089 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{56}H_{77}O_8^+$: 877.5613, found: 877.5625.



Dimethyl 5-(4-((((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)carbonyl)phenyl)-2-ethyl-3-phenyl-4a,5,6,7a-tetrahydrocyclopenta[b]pyran-7,7(2H)-dicarboxylate 3r. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.58; yellow sticky liquid; yield 76% (65 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 2H) 7.37-7.33 (m, 4H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.0 Hz, 1H), 6.64 (d, *J* = 15.5 Hz,

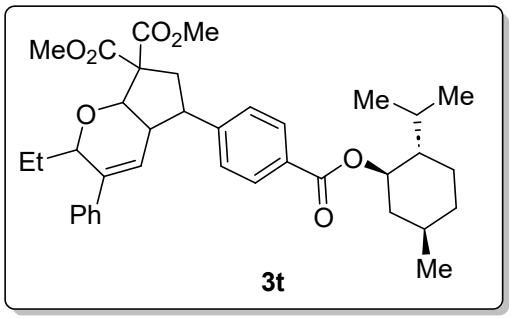
1H), 5.77 (t, *J* = 7.5 Hz, 1H), 5.417-5.410 (m, 1H), 5.37 (t, *J* = 7.5 Hz, 1H), 5.34 (d, *J* = 6.5 Hz, 1H), 5.07 (dd, *J* = 7.0 Hz, 15.5 Hz, 1H), 4.87-4.81 (m,1H), 3.76 (d, *J* = 8.5 Hz, 1H), 3.64 (s, 3H), 3.58 (s, 3H), 3.13 (dd, *J* = 7.0 Hz, 13.0 Hz, 1H), 2.46 (d, *J* = 8.0 Hz, 1H), 2.18 (dd, *J* = 8.0 Hz, 13.5 Hz, 1H), 2.03-1.97 (m, 4H), 1.92 (t, *J* = 7.5 Hz, 2H), 1.85-1.81 (m, 1H) 1.74-1.71 (m, 1H), 1.53-1.45 (m, 5H), 1.35-1.33 (m, 3H), 1.27-1.23 (m, 3H), 1.13-1.09 (m, 3H), 1.06 (s, 4H), 1.03-0.97 (m, 4H), 0.93-0.90 (m, 6H), 0.87 (dd, *J* = 2.0 Hz, 6.5 Hz, 6H), 0.68 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 169.1, 165.9, 147.4, 139.8, 139.7, 138.0, 137.4, 137.1, 130.1, 129.9, 129.5, 128.2, 127.0, 125.2, 125.0, 122.9, 83.6, 79.4, 74.7, 65.0, 56.8, 56.2, 52.9, 52.7, 50.2, 42.4, 39.8, 39.6, 38.3, 37.1, 36.8, 36.3, 35.9, 32.08, 32.03, 28.3, 28.1, 28.0, 24.4, 23.9, 22.9, 22.7, 22.6, 21.2, 19.5, 18.8, 14.2, 12.0; FT-IR (neat) 2949, 1735, 1717, 1613, 1436, 1374, 1272, 1177, 1111, 1017 cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{54}H_{72}NaO_7^+$: 855.5170, found: 855.5162.



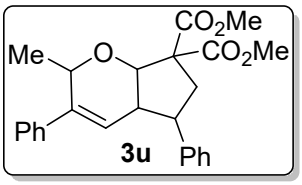
3s

Dimethyl 2-ethyl-3-phenyl-5-(4-((((1S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)carbonyl)phenyl)-4a,5,6,7a-tetrahydrocyclopenta-[b]pyran-7,7(2H)-dicarboxylate 3s. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.40; yellow sticky liquid; yield 80% (48 mg); 1:0.45 mixture of diastereomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.98 (m, 2.8H, major + minor), 7.40-7.33 (m, 5.7H, major + minor), 7.31-7.29 (m, 1.8H, major + minor), 7.24 (s, 0.7H, minor), 7.10-7.08 (m, 1.9H, major + minor), 6.65 (d, *J* = 15.6 Hz, 1H, major), 5.91 (t, *J* = 7.6 Hz, 0.4H, minor), 5.77 (t, *J* = 7.6 Hz, 1H, major), 5.72 (s, 0.4H, minor), 5.37 (t, *J* = 7.6 Hz, 1.4H, major + minor), 5.33 (d, *J* = 6.8 Hz, 1H, major), 5.08 (dd, *J* = 6.8 Hz, 15.6 Hz, 1H, major), 4.94-4.88 (m, 1.6H, major + minor), 3.64 (s, 3H, major), 3.59 (s, 3H, major), 3.53 (s, 1.2H, minor), 3.345-3.340 (s, 1.2H, minor), 3.14 (dd, *J* = 7.2 Hz, 13.2 Hz, 1.4H, major + minor), 2.34 (dd, *J* = 6.0 Hz, 12.8 Hz, 1H, major), 2.21-2.17 (m, 1.3H, major + minor), 2.158-2.155 (m, 1.7H, major + minor), 2.13-2.10 (m, 1.7H, major + minor), 2.01-1.94 (m, 1.7H, major + minor), 1.92-1.88(m, 2.6H, major + minor), 1.74 (d, *J* = 11.6 Hz, 3.3H, major + minor), 1.10 (d, *J* = 12.4 Hz, 2.6H, major + minor), 0.94 (s, 3H, major + minor), 0.93 (d, *J* = 4.8 Hz, 6H, major + minor), 0.90 (s, 3.3H, major + minor), 0.79 (d, *J* = 7.2 Hz, 4.2H, major + minor); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.98, 169.96, 169.12, 168.6, 166.07, 166.03, 147.9, 147.4, 139.7, 138.0, 137.4, 137.1, 136.6, 133.3, 129.93,

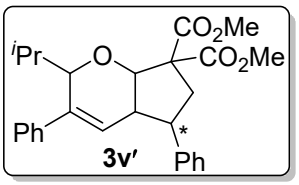
129.90, 129.8, 129.5, 128.2, 127.8, 127.1, 127.0, 125.3, 125.29, 125.26, 124.99, 86.57, 83.62, 83.61, 79.44, 79.15, 74.9, 65.03, 65.01, 52.99, 52.95, 52.69, 52.47, 47.42, 42.58, 42.55, 42.30, 41.15, 41.12, 34.48, 34.43, 32.0, 31.6, 29.84, 29.81, 26.7, 26.6, 23.86, 23.84, 22.8, 22.6, 22.18, 22.12, 20.89, 20.88, 16.74, 16.72, 16.6, 14.4, 14.27, 14.26; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{37}H_{45}O_7^+$: 601.3160, found: 601.3153.



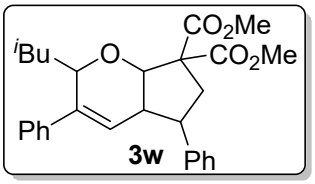
Dimethyl 2-ethyl-5-(4-((((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)phenyl)-3-phenyl-4a,5,6,7a-tetrahydrocyclopenta[b]-pyran-7,7(2H)-dicarboxylate 3t. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.38; yellow sticky liquid; yield 81% (51 mg); 1:0.25 mixture of diastereomers; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H, major), 7.97 (d, *J* = 8.4 Hz, 0.5H, minor), 7.40-7.33 (m, 4.33H, major + minor), 7.30-7.23 (m, 2.76H, major + minor), 7.10-7.08 (m, 2H, major), 6.97 (d, *J* = 15.2 Hz, 0.18H, minor), 6.65 (d, *J* = 15.2 Hz, 1H, major), 5.77 (t, *J* = 7.6 Hz, 1H, major), 5.57-5.44 (m, 0.34H, minor), 5.38 (t, *J* = 7.6 Hz, 1H, major), 5.34 (d, *J* = 6.8 Hz, 1H, major), 5.11-5.08 (m, 2H, major), 5.05 (d, *J* = 6.8 Hz, 0.41H, minor), 3.80 (s, 1H, minor), 3.65 (s, 3H, major), 3.59 (s, 3H, major), 3.40 (s, 1H, minor), 3.25(t, *J* = 8.8 Hz, 0.39H, minor), 3.15 (dd, J = 7.6 Hz, 13.2 Hz, 1H, major), 2.50-2.42 (m, 1.40H, major + minor), 2.24-2.16 (m, 1.35H, major + minor), 2.15-2.08 (m, 1.44H, major + minor), 1.96-1.88 (m, 2H, major), 1.83-1.77 (m, 2H, major + minor), 1.74-1.72 (m, 1.48H, major + minor), 1.43-1.36 (m, 2H, major + minor), 1.33-1.25 (m, 2.71H, major + minor), 1.13-1.08 (m, 2H, major + minor), 0.96 (s, 4H, major + minor), 0.94-0.90 (m, 12H, major + minor); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 169.8, 169.1, 169.0, 166.7, 166.6, 147.5, 139.7, 138.0, 137.5, 137.1, 130.2, 130.1, 129.8, 129.7, 129.5, 128.9, 128.5, 128.2, 127.6, 127.1, 127.0, 125.3, 124.9, 83.6, 80.9, 80.6, 79.4, 65.0, 64.4, 60.1, 53.04, 53.01, 52.9, 52.7, 49.3, 49.2, 48.05, 48.02, 45.1, 42.5, 38.7, 37.0, 35.8, 32.2, 29.86, 29.84, 28.2, 27.5, 26.8, 22.6, 21.6, 20.2, 19.8, 19.5, 19.0, 14.2, 13.7; FT-IR (neat) 2954, 1735, 1712, 1612, 1494, 1435, 1271, 1212, 1176, 1109, 1076 cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{37}H_{46}NaO_7^+$: 625.3136, found: 625.3154.



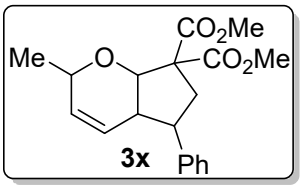
Dimethyl 2-methyl-3,5-diphenyl-4a,5,6,7a-tetrahydrocyclopenta[b]-pyran-7,7(2H)-dicarboxylate 3u. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.55; yellow sticky liquid; yield 61% (25 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 3H), 7.31-7.27 (m, 3H) 7.08 (d, *J* = 6.8 Hz, 2H), 6.66 (d, *J* = 14.8 Hz, 1H), 5.86 (q, *J* = 6.4 Hz, 1H), 5.12 (t, *J* = 7.2 Hz, 1H), 5.07 (t, *J* = 7.2 Hz, 1H), 4.81 (dd, *J* = 6.4 Hz, 10.4 Hz, 1H), 3.79 (s, 3H), 3.56 (s, 3H), 2.75-2.69 (m, 1H), 2.66-2.61 (m, 1H), 1.57-1.55 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 169.3, 142.3, 141.2, 137.9, 137.1, 129.6, 129.4, 128.5, 128.2, 127.6, 127.0, 125.5, 124.9, 83.4, 79.9, 65.1, 52.8, 52.6, 42.7, 15.1; FT-IR (neat) 2952, 1732, 1684, 1514, 1434, 1252, 1068 cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{25}H_{26}NaO_5^+$: 429.1672, found: 429.1671.



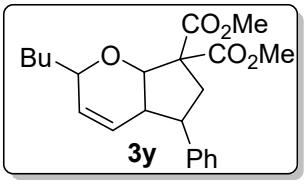
Dimethyl 2-isopropyl-3,5-diphenyl-4a,5,6,7a-tetrahydrocyclopenta[b]pyran-7,7(2H)-dicarboxylate 3v′. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.50; yellow sticky liquid; yield 74% (32 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.32 (m, 4H), 7.296-7.292 (m, 1H), 7.27-7.22 (m, 2H), 7.09 (d, *J* = 6.8 Hz, 2H), 6.62 (d, *J* = 15.6 Hz, 1H), 5.57 (d, *J* = 10.0 Hz, 1H), 5.34-5.31 (m, 1H), 5.04 (dd, *J* = 6.8 Hz, 15.2 Hz, 1H), 3.65 (s, 3H), 3.57 (s, 3H), 3.10 (dd, *J* = 13.2 Hz, 6.8 Hz, 1H), 2.25-2.16 (m, 2H), 0.90 (t, *J* = 5.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 169.3, 142.4, 142.3, 138.3, 138.0, 137.4, 129.4, 128.5, 128.2, 127.6, 126.9, 125.5, 125.4, 83.3, 79.9, 65.1, 52.8, 52.5, 42.7, 28.3, 23.0; FT-IR (neat) 2956, 1733, 1601, 1494, 1435, 1361, 1255, 1167, 1068 cm^{-1}; $[\alpha]_D^{25}$ = -45 (*c* = 0.02, $CHCl_3$); HPLC analysis: 98% ee [YMC Chiral ART Cellulose-SC column, hexane/^{i}PrOH = 97:3, flow rate: 1 mL/min, λ = 254 nm, t_R = 10.35 min (minor), 11.60 min (major)]; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{27}H_{31}O_5^+$: 435.2166, found: 435.2185.



Dimethyl 2-isobutyl-3,5-diphenyl-4a,5,6,7a-tetrahydrocyclopenta[b]pyran-7,7(2H)-dicarboxylate 3w. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.42; yellow sticky liquid; yield 76% (47 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.34 (m, 2H), 7.32-7.31 (m, 4H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 2H), 6.66 (d, *J* = 15.5 Hz, 1H), 5.78 (t, *J* = 7.5 Hz, 1H), 5.34-5.31 (m, 2H), 5.06 (dd, *J* = 7.0 Hz, 15.5 Hz, 1H), 3.65 (s, 3H), 3.58 (s, 3H), 3.10 (dd, *J* = 7.0 Hz, 13.0 Hz, 1H), 2.22 (dd, *J* = 8.0 Hz, 13.5 Hz, 1H), 1.81 (t, *J* = 7.0 Hz, 2H), 1.63-1.58 (m, 2H), 0.82 (dd, *J* = 1.0 Hz, 7.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 169.3, 142.3, 140.8, 137.3, 134.3, 129.6, 128.5, 128.1, 127.6, 126.9, 125.5, 125.1, 83.3, 79.9, 77.3, 65.1, 64.4, 52.8, 52.6, 42.7, 38.2, 28.8, 22.5, 14.2; FT-IR (neat) 2953, 1733, 1642, 1494, 1365, 1251, 1176, 1067 cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{28}H_{32}NaO_5^+$: 471.2142, found: 471.2155.

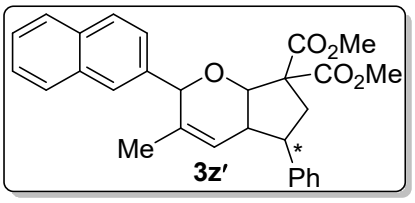


Dimethyl 2-methyl-5-phenyl-4a,5,6,7a-tetrahydrocyclopenta[b]pyran-7,7(2H)-dicarboxylate 3x. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.40; yellow sticky liquid; yield 83% (30 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.32 (m, 4H), 7.27-7.25 (m, 1H), 6.39 (dd, *J* = 10.8 Hz, 15.2 Hz, 1H), 6.08-6.01 (m, 1H), 5.78-5.70 (m, 1H), 5.58 (dd, *J* = 6.8 Hz, 15.2 Hz, 1H), 5.43-5.38 (m, 1H), 5.30 (d, *J* = 6.8 Hz, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 3.16 (dd, *J* = 13.2 Hz, 6.8 Hz, 1H) 2.31-2.26 (m, 1H), 1.77-1.74 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ170.2, 169.3, 142.3, 133.4, 131.1, 130.7, 128.6, 127.6, 125.5, 125.2, 83.0, ,79.8, 65.2, 52.9, 52.7, 42.6, 18.3; FT-IR (neat) 2953, 1732, 1660, 1495, 1254, 1210, 1174, 1066 cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{19}H_{22}NaO_5^+$: 353.1359, found: 353.1358.

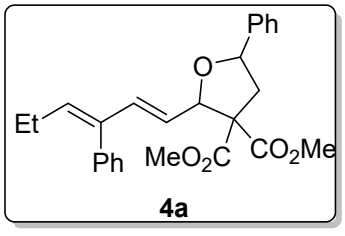


Dimethyl 2-butyl-5-phenyl-4a,5,6,7a-tetrahydrocyclopenta[b]pyran-7,7(2H)-dicarboxylate 3y. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.50; yellow sticky liquid; yield 86% (34 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.32 (m,

3H), 7.25 (s, 2H), 6.39 (dd, *J* = 10.4 Hz, 15.2 Hz, 1H), 6.03 (dd, *J* = 10.4 Hz, 15.2 Hz, 1H), 5.76-5.69 (m, 1H), 5.59 (dd, *J* = 6.8 Hz, 13.2 Hz, 1H), 5.40 (t, *J* = 7.2 Hz, 1H), 5.29-5.28 (m, 1H), 3.70 (s, 3H), 3.68 (s, 3H), 3.17 (dd, *J* = 7.2 Hz, 13.2 Hz, 1H), 2.31-2.26 (m, 1H), 2.09-2.04 (m, 2H), 1.36-1.28 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.2, 169.3, 142.4, 136.7, 133.6, 129.3, 128.6, 127.6, 125.5, 125.3, 83.0, 79.8, 65.3, 52.9, 52.7, 42.6, 32.4, 31.4, 22.3, 14.0; FT-IR (neat) 2954, 1733, 1658, 1495, 1434, 1253, 1176, 1065 cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{22}H_{28}NaO_5^+$: 395.1829, found: 395.1840.

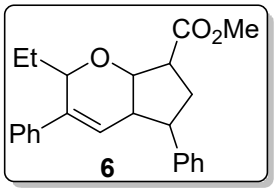


Dimethyl 3-methyl-2-(naphthalen-2-yl)-5-phenyl-4a,5,6,7a-tetrahydrocyclopenta[b]pyran-7,7(2H)-dicarboxylate 3z′. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.42; colorless liquid; yield 78% (37 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.78 (m, 3H), 7.73 (s, 1H), 7.48-7.43 (m, 2H), 7.42 (dd, *J* = 1.6 Hz, 8.4 Hz, 1H), 7.38-7.33 (m, 4H), 7.29-7.25 (m 1H), 6.71-6.67 (m, 2H), 5.58 (dd, *J* = 6.8 Hz, 15.6 Hz, 1H), 5.48 (t, *J* = 7.2 Hz, 1H), 5.45 (d, *J* = 6.4 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.22 (dd, *J* = 6.8 Hz, 13.2 Hz , 1H), 2.34 (dd, *J* = 8.4 Hz, 13.2 Hz , 1H), 2.07 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1 169.4, 142.3, 137.9, 135.27, 135.22, 133.3, 132.6, 132.3, 128.6, 128.1, 128.0, 127.7, 127.6, 126.2, 126.0, 125.5, 124.2, 83.3, 80.0, 65.4, 52.9, 52.7, 42.7, 14.1; FT-IR (neat) 2954, 1733, 1658, 1495, 1434, 1253, 1176, 1065 cm^{-1}; $[\alpha]_D^{25}$ = +25 (*c* = 0.02, $CHCl_3$); HPLC analysis: 97% ee [YMC Chiral ART Cellulose-SC column, hexane/^{i}PrOH = 97:3, flow rate: 1 mL/min, λ = 254 nm, t_R = 7.43 min (minor), 8.62 min (major)];.HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{29}H_{28}NaO_5^+$: 479.1829, found: 479.1830.



Dimethyl 5-phenyl-2-((1*E*,3*Z*)-3-phenyl hexa-1,3-dien-1-yl) dihydrofuran-3,3(2H)-dicarboxylate 4a. Analytical TLC on silica gel, 5:95 ethyl acetate/hexane; R_f = 0.45; yellow sticky liquid; yield 65% (27 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H), 7.36-7.31 (m, 4H), 7.30-7.27 (m, 2H), 7.08-7.06 (m, 2H), 6.66 (d, *J* = 14.8 Hz, 1H), 5.75 (t, *J* = 7.6 Hz, 1H), 5.14-5.05 (m, 2H), 4.81 (dd, *J* = 6.4 Hz, 10.2 Hz, 1H), 3.79 (s, 3H), 3.56 (s, 3H), 2.76-2.70 (m, 1H), 2.65-2.61 (m, 1H), 1.94-1.87 (m, 2H), 0.91

(t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.4, 140.0, 139.7, 138.0, 137.9, 137.0, 129.5, 128.5, 128.2, 128.1, 127.0, 126.6, 125.0, 83.4, 80.0, 65.0, 53.1, 52.6, 42.2, 22.6, 14.2; FT-IR (neat) 2970, 1736, 1599, 1494, 1435, 1365, 1264, 1228, 1217, 1091 cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{26}H_{28}O_5Na^+$: 443.1829, found: 443.1827.



6

Methyl 2-ethyl-3,5-diphenyl-2,4a,5,6,7,7a-hexahydrocyclopenta[b]-pyran-7-carboxylate 6. Analytical TLC on silica gel, 2:98 ethyl acetate/hexane; R_f = 0.45; colorless liquid; yield 67% (25 mg); 1:0.25 mixture of diastereomers; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.34 (m, 6H, major + minor), 7.32-7.30 (m, 2.5H, major + minor), 7.29-7.26 (m, 1.5H, major + minor), 7.14-7.12 (m, 2H, major), 7.09-7.07 (m, 0.5H, minor), 6.56-6.50 (m, 1.5H, major + minor), 5.73 (t, J = 7.6 Hz, 1.25H, major + minor), 5.34 (t, J = 7.2 Hz, 0.27H, minor), 5.23 (dd, J = 6.8 Hz, 15.2 Hz, 1H, major), 5.08 (t, J = 7.6 Hz, 0.28H, minor), 5.02 (dd, J = 6.0 Hz, 10.0 Hz, 1H, major), 4.93-4.90 (m, 0.28H, minor), 4.85 (t, J = 7.2 Hz, 0.28H, minor), 3.68 (s, 3H, major), 3.55 (s, 0.7H, minor), 3.28-3.23 (m, 0.26H, minor), 2.96-2.90 (m, 1H, major), 2.62-2.55 (m, 1.2H, major + minor), 2.25-2.17 (m, 1.26H, major + minor), 1.96-1.89 (m, 1.5H, major + minor), 0.92 (t, J = 7.2 Hz, 3.74H, major + minor); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.9, 142.0, 139.7, 138.1, 136.6, 136.4, 129.6, 128.7, 128.5, 128.2, 127.7, 126.9, 125.9, 125.5, 82.6, 80.6, 52.1, 51.4, 39.7, 31.7, 29.8, 22.6, 14.3; FT-IR (neat) 2926, 1736, 1601, 1494, 1436, 1369, 1261, 1168, 1048 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{24}H_{27}O_3^+$: 363.1955, found: 363.1952.

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1. (a) M. Mishra, P. B. De, S. Pradhan and T Punniyamurthy, *J. Org. Chem*., 2019, **84**, 10901. (b) P. Karjee, M. Mishra, B. Debnath and T. Punniyamurthy, *Chem. Commun.,* 2022, **58**, 8670. (c) E. Richmond, V. D. Vuković and J. Moran, *Org. Lett.,* 2018, **20**, 574. (d) L. Liu, X. Wang, W. Xiao, W. Chang and J. Li, *Chem.-Eur. J*., 2023, **29**, e202202544.
2. (a) M.-S. Liu and W. Shu, *ACS Catal.,* 2020, **10**, 12960. (b) C.-G. Wang, Y. Zhang, S. Wang, B. Chen, Y. Li, H.-L. Ni, Y. Gao, P. Hu, B.-Q. Wang and P. Cao, *Org. Lett.,* 2021, **23**, 535.
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4. A.-S. Marques, V. Coeffard, I. Chataigner, G. Vincent and X. Moreau, *Org. Lett.,* 2016, **18**, 5296.
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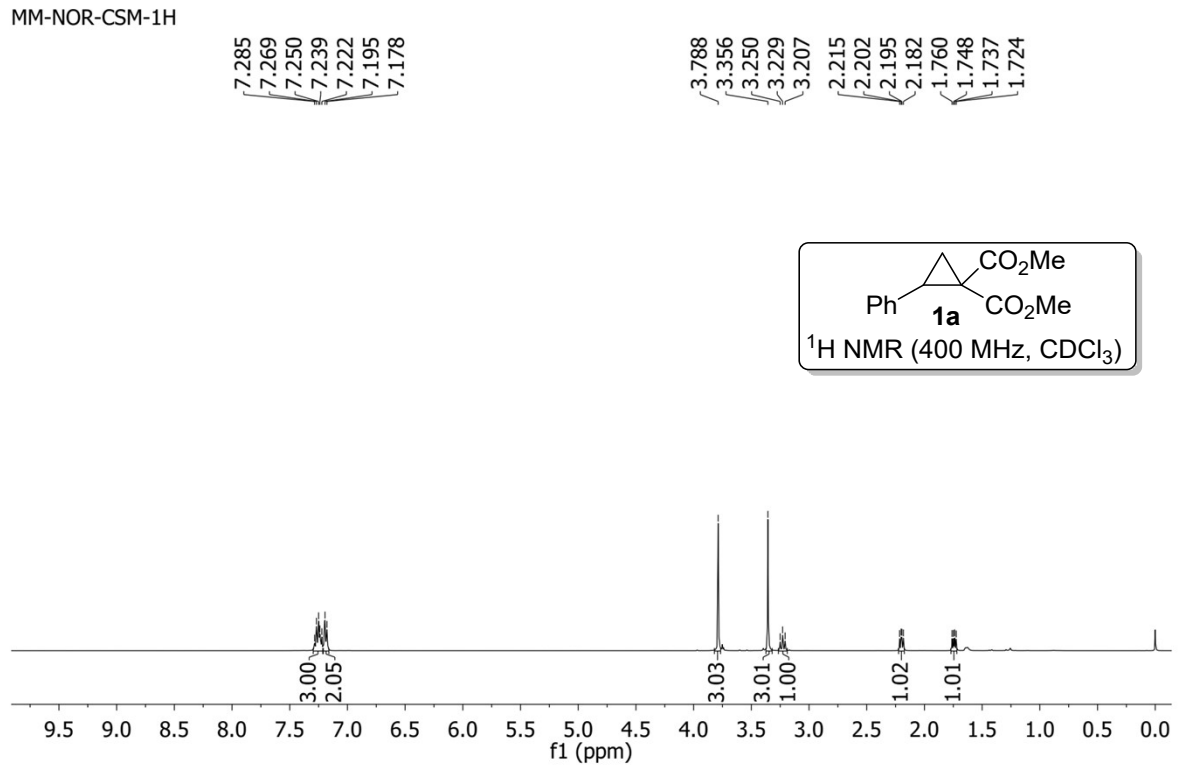
^{1}H and ^{13}C NMR Spectra



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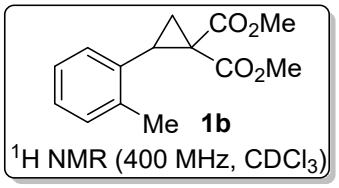

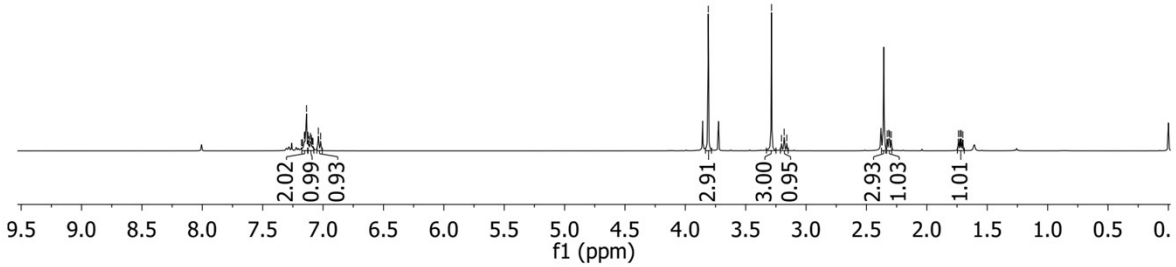

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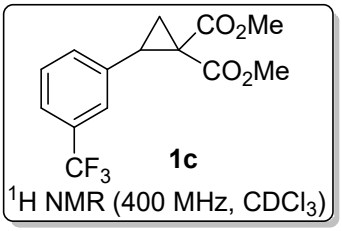

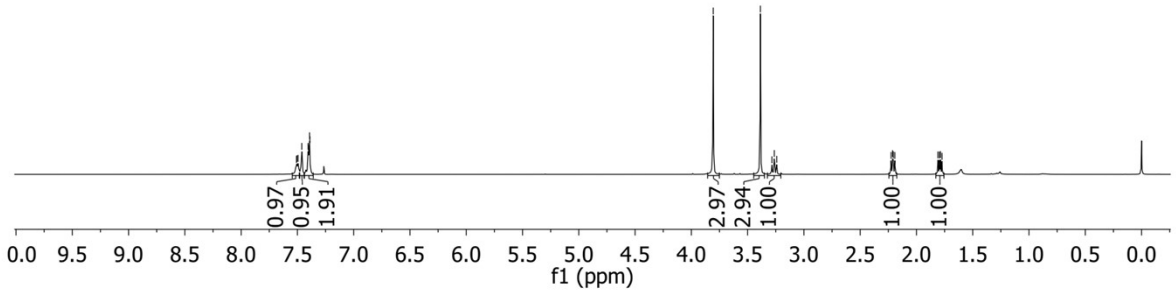

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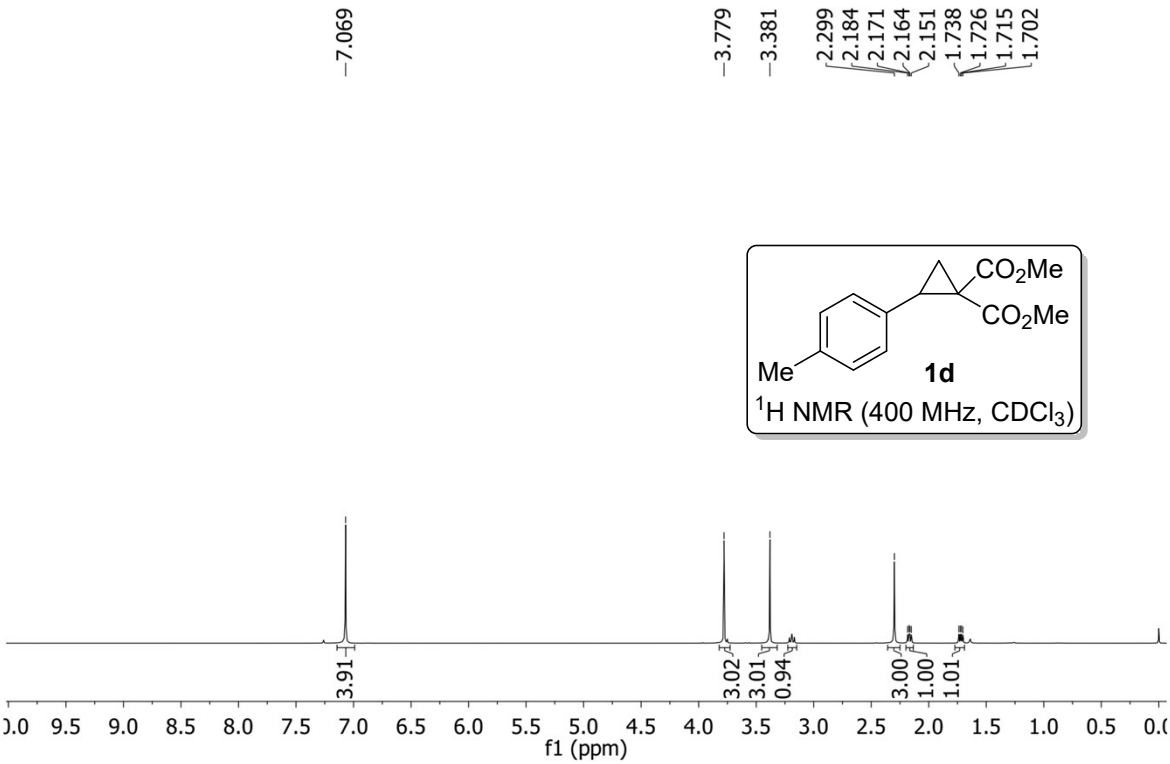

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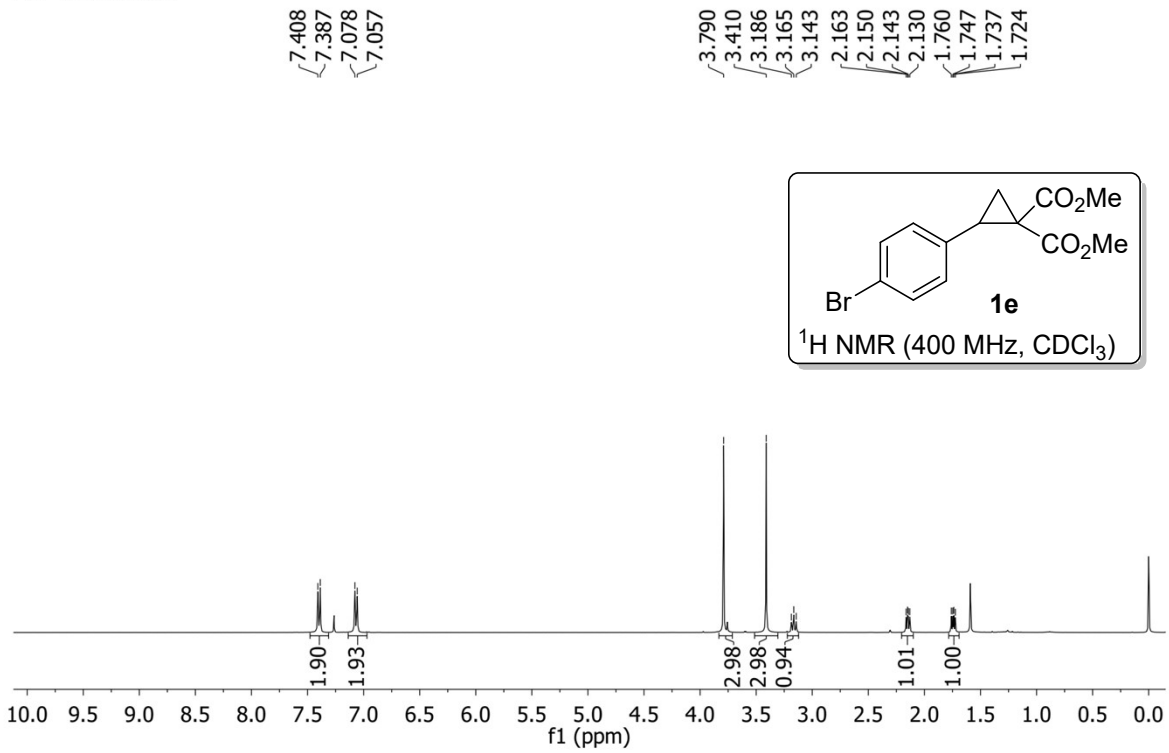

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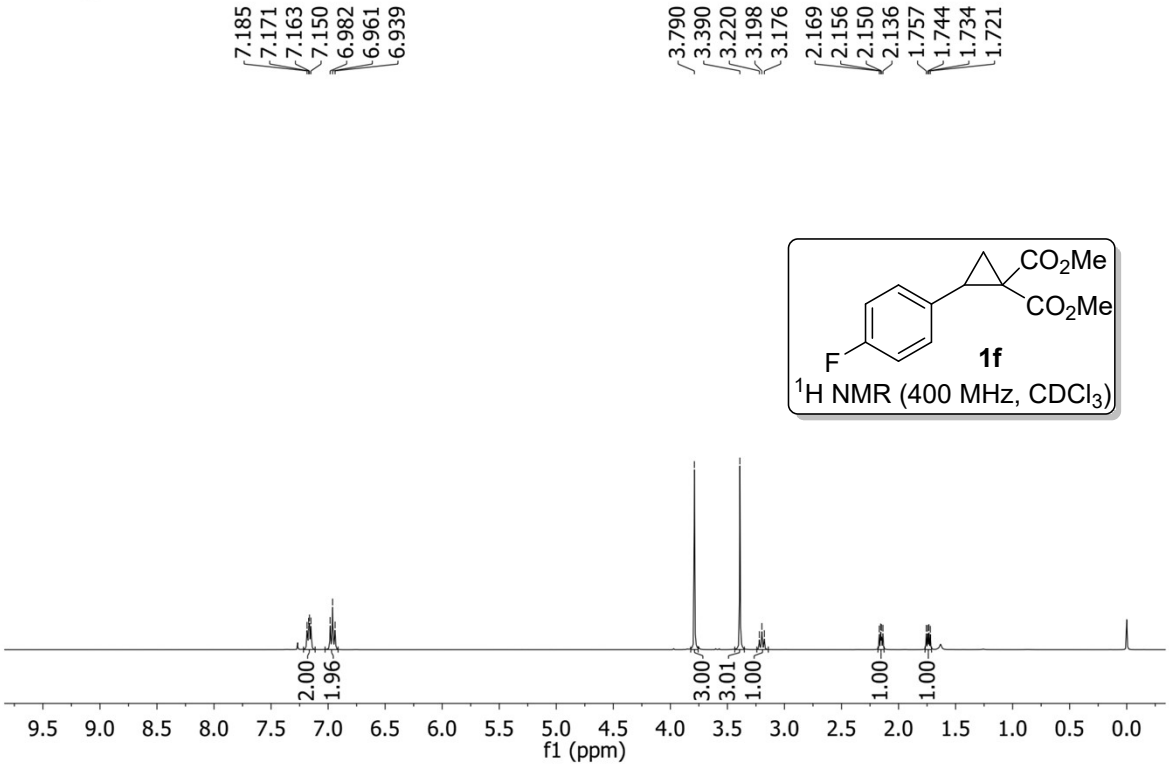

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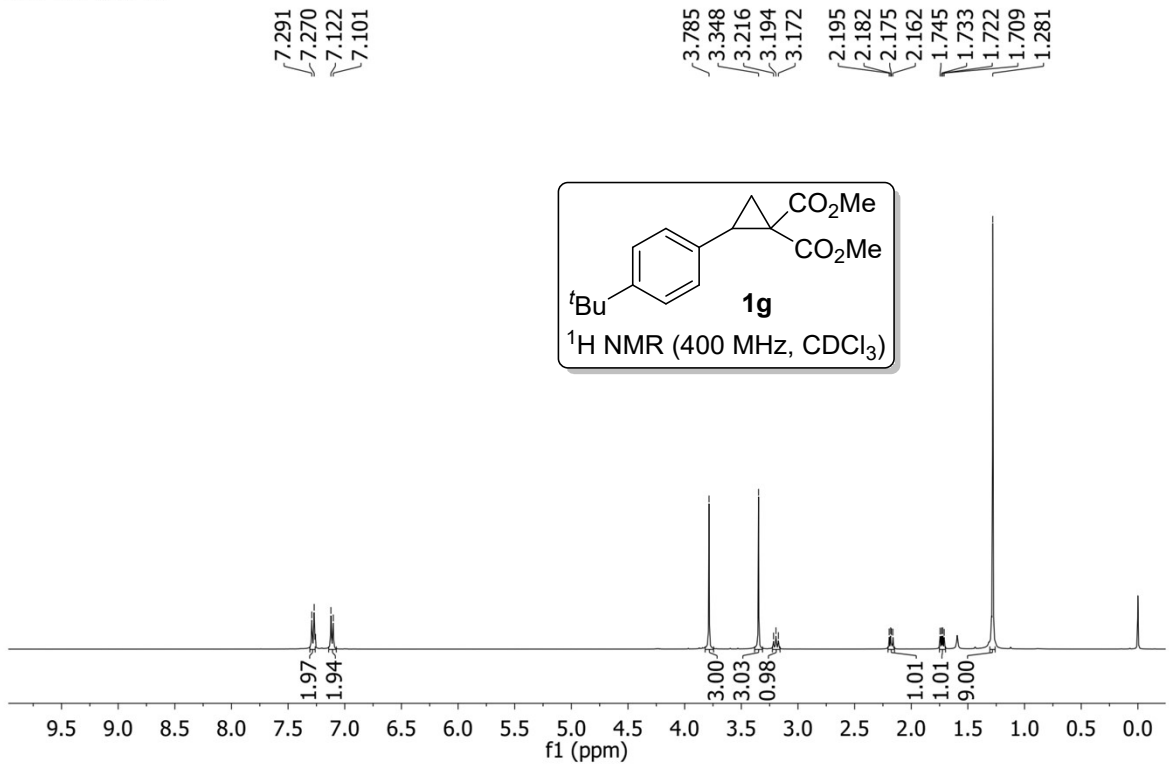

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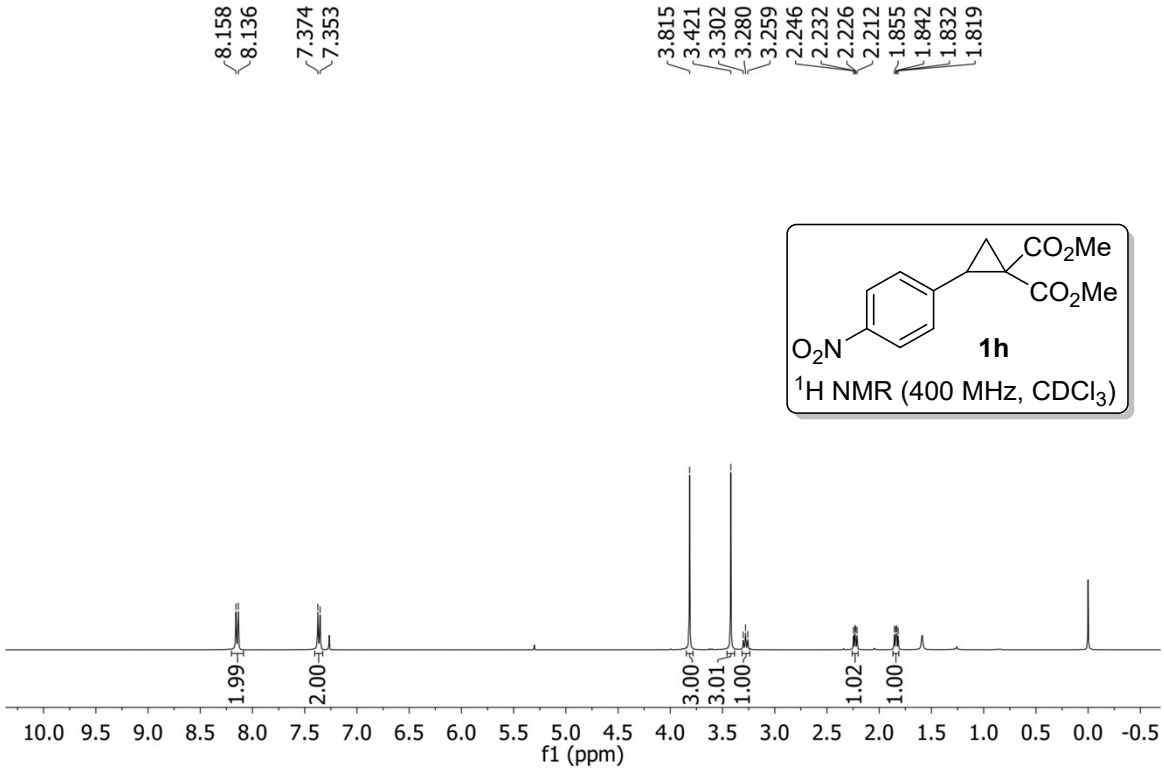

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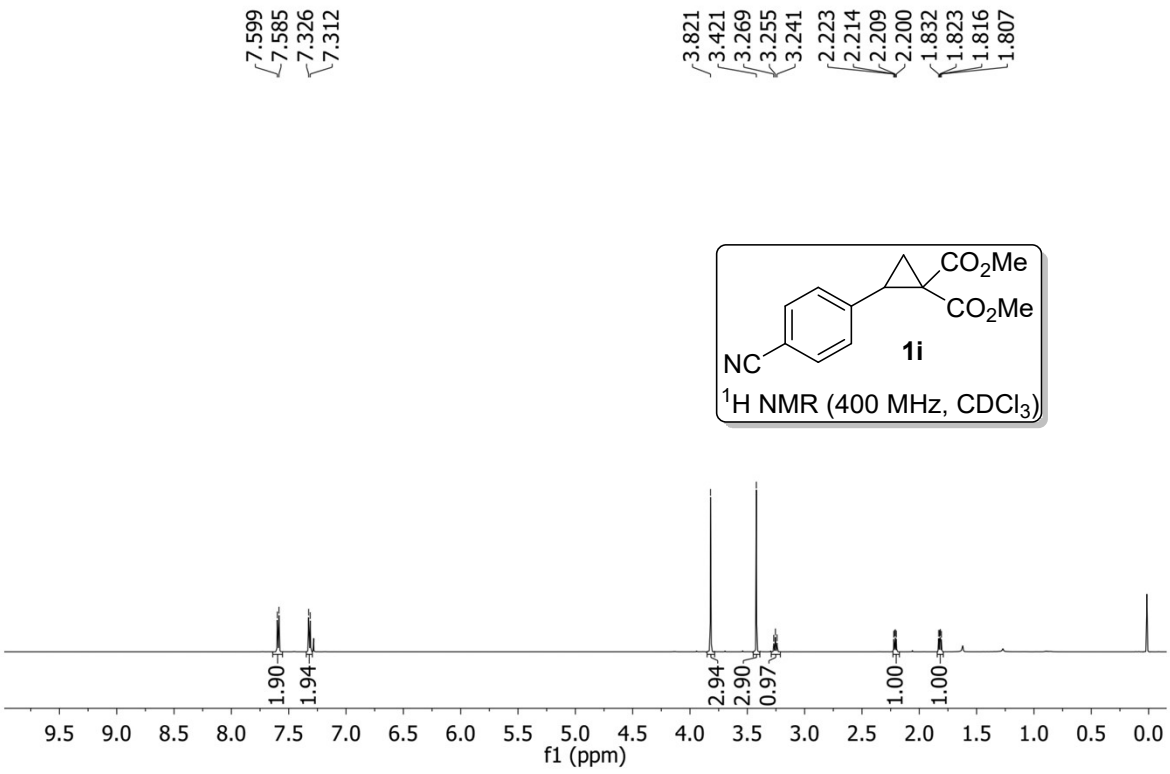

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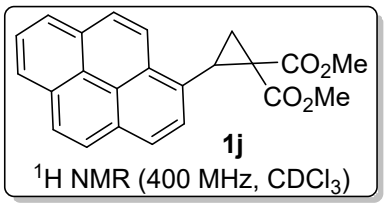

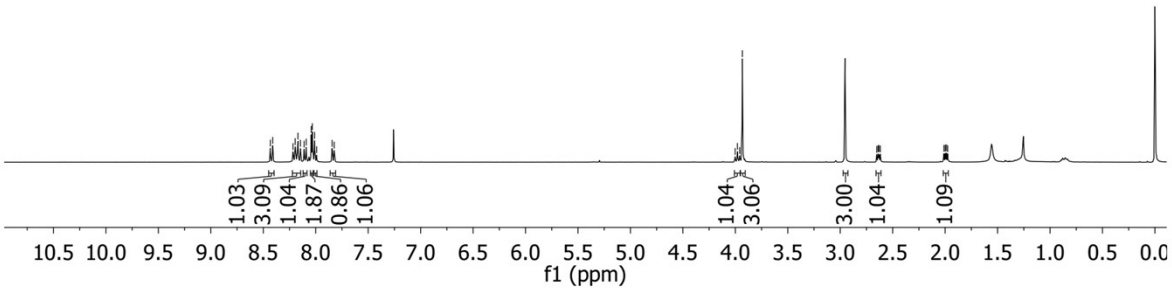

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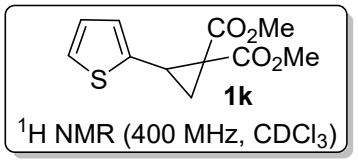

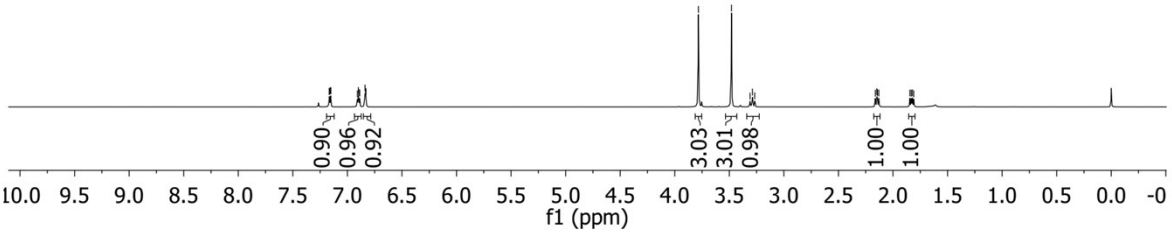

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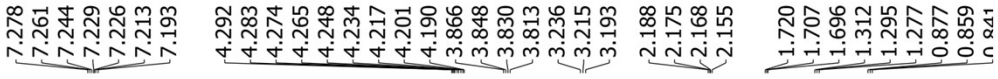
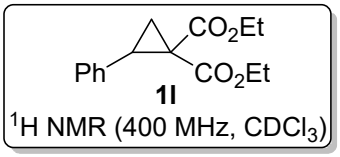
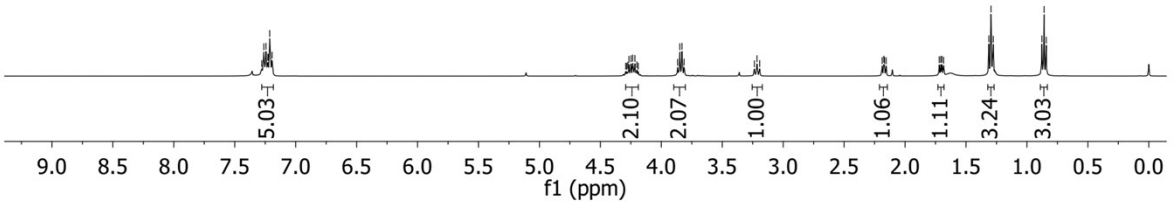




1l

^{1}H NMR (400 MHz, $CDCl_3$)



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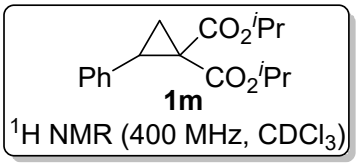
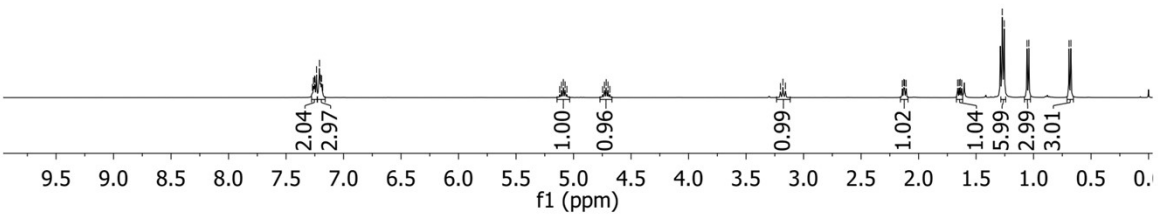


1m

^{1}H NMR (400 MHz, $CDCl_3$)



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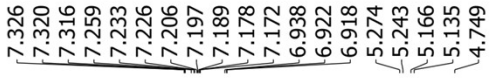

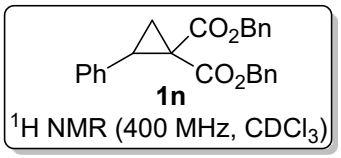

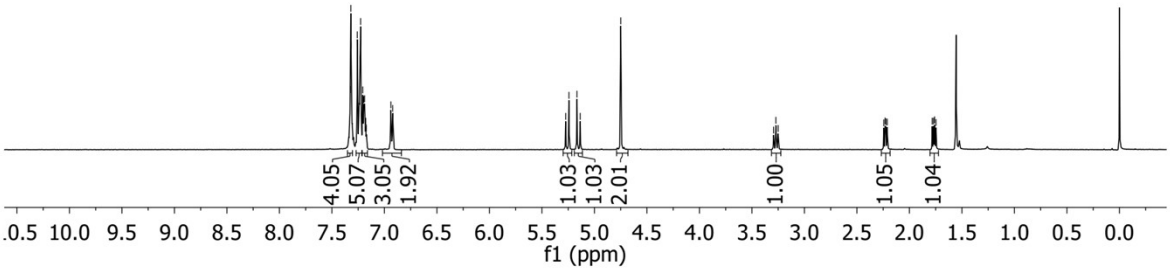

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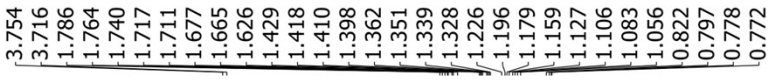

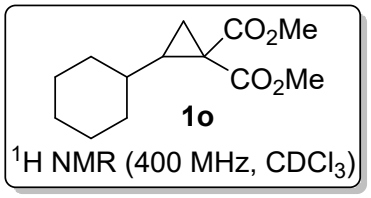

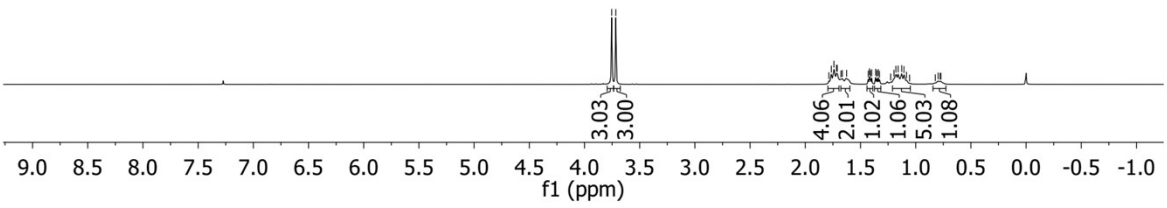

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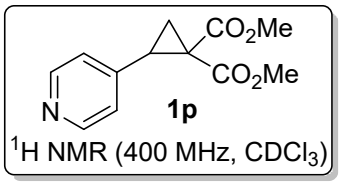
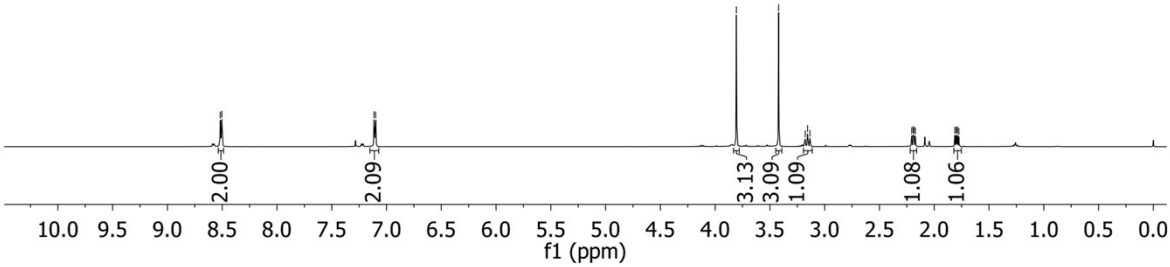
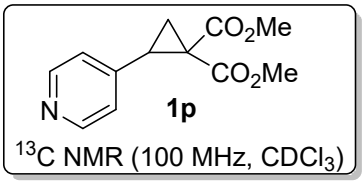
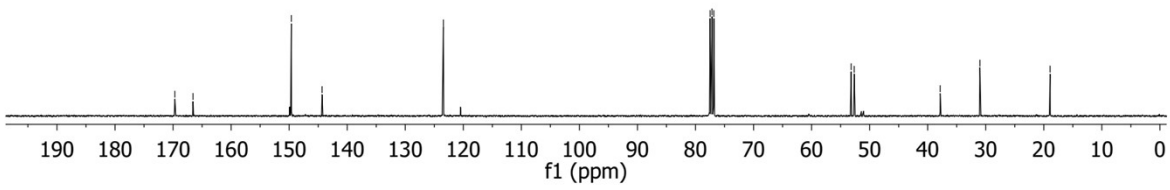


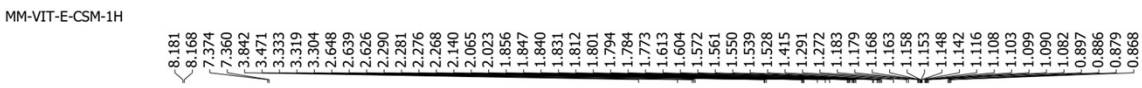


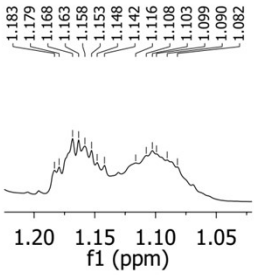
MM-PYR-CSM-13C

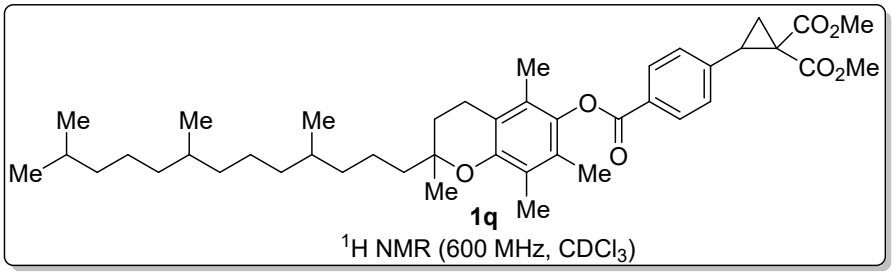




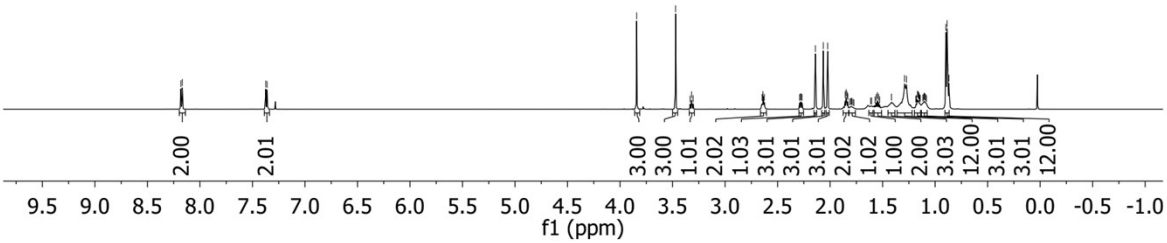
MM-VIT-E-CSM-1H



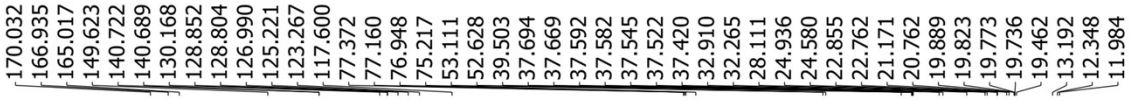


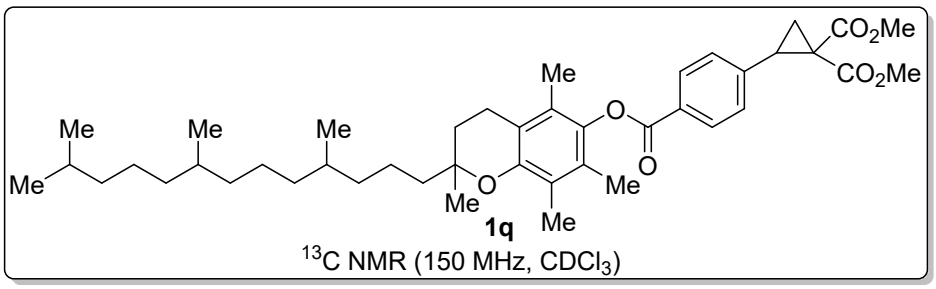


^{1}H NMR (600 MHz, $CDCl_3$)

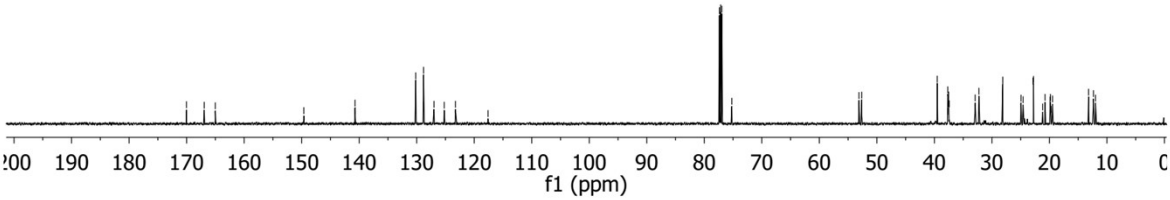


MM-VIT-E-CSM-13C

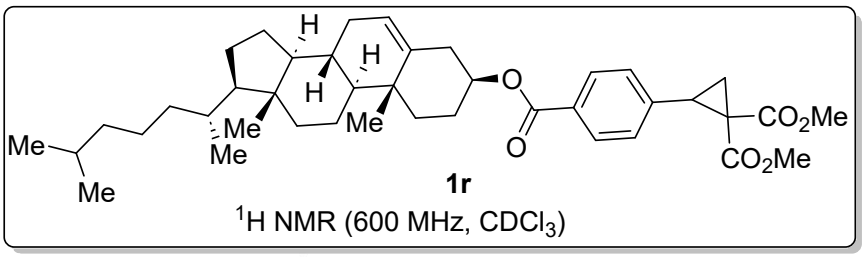




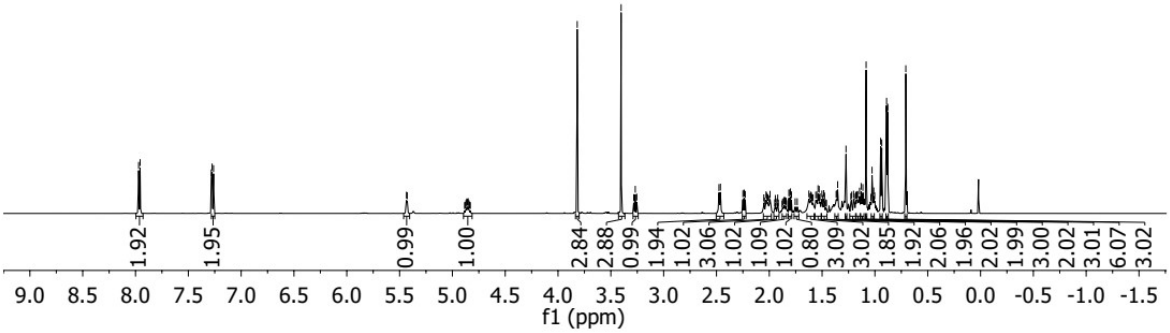
^{13}C NMR (150 MHz, $CDCl_3$)



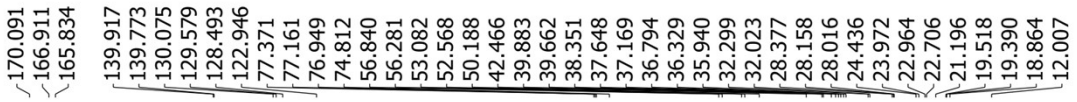
MM-CHOL-CSM-1H

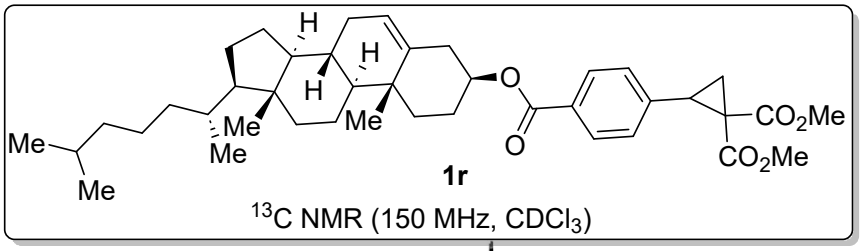


^{1}H NMR (600 MHz, $CDCl_3$)

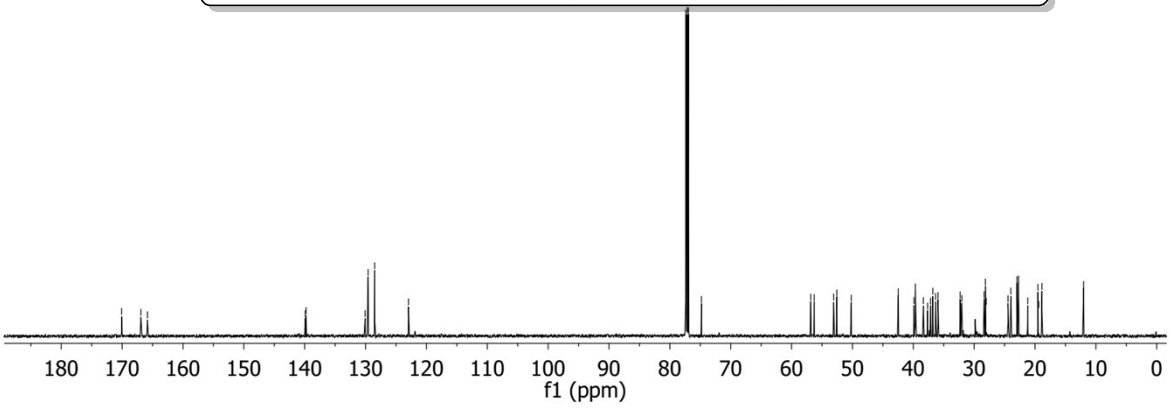


MM-CHOL-CSM-13C



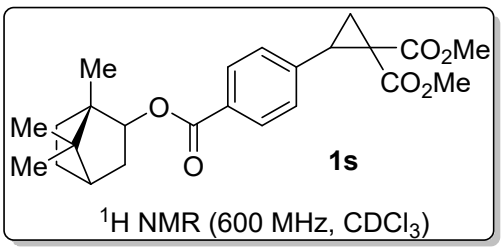


^{13}C NMR (150 MHz, $CDCl_3$)

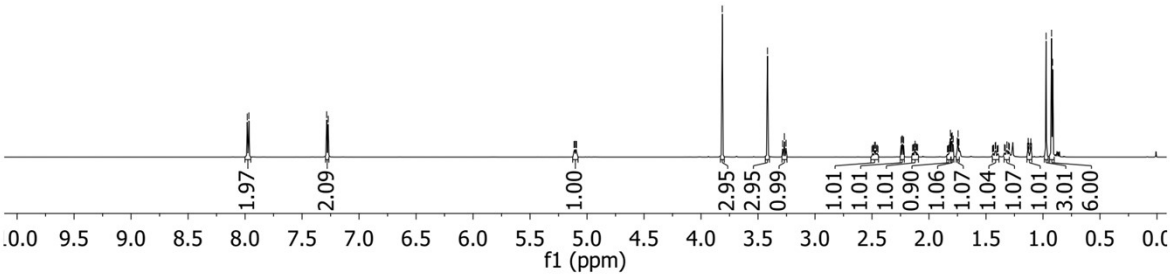


MM-450-CSM-1H

7.980 7.967 7.284 7.270 5.113 5.111 5.108 5.097 5.094 5.092 3.814 3.417 3.283 3.269 3.254 2.477 2.471 2.245 2.236 2.231 2.223 2.122 2.116 1.818 1.812 1.803 1.797 1.788 1.752 1.745 1.738 1.419 1.415 1.317 1.302 1.295 1.135 1.130 1.124 1.112 1.107 1.101 0.973 0.925 0.916

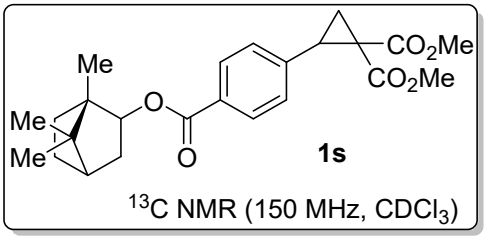


^{1}H NMR (600 MHz, $CDCl_3$)

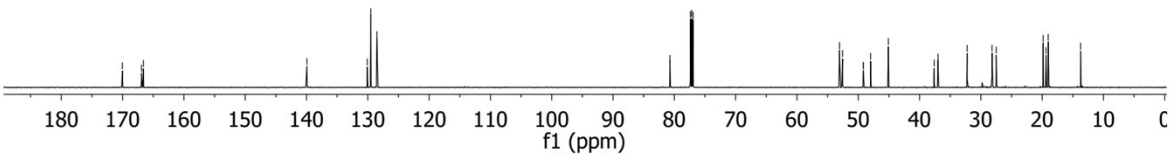


MM-450-CSM-13C

170.038 166.907 166.606 139.936 130.089 129.508 128.525 80.721 77.372 77.160 76.948 53.051 52.568 49.193 49.177 47.989 45.086 37.608 36.987 32.239 28.185 27.489 19.831 19.378 19.019 13.728

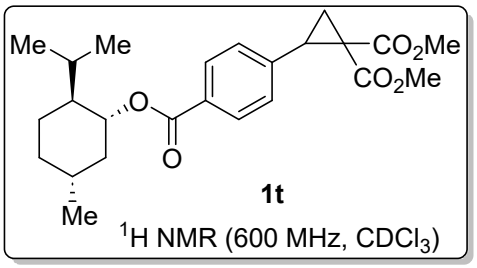


^{13}C NMR (150 MHz, $CDCl_3$)



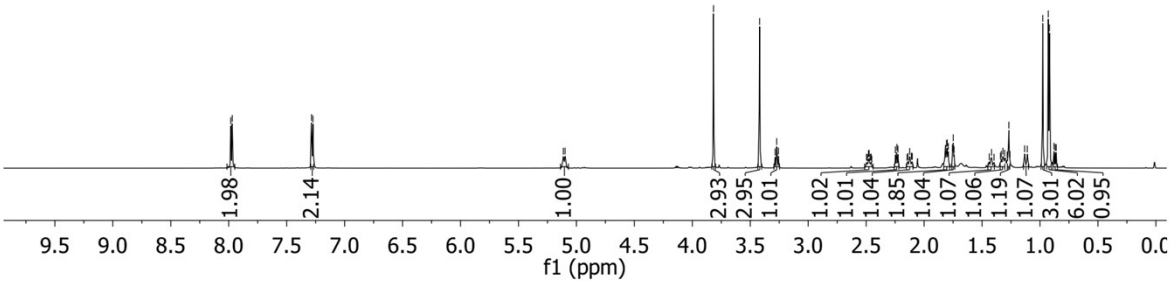
MM-444-CSM-1H

7.983 7.969 7.286 7.273 5.113 5.098 3.817 3.420 3.286 3.272 3.257 2.497 2.480 2.474 2.457 2.248 2.235 2.226 2.140 2.125 2.110 2.102 1.807 1.800 1.792 1.756 1.748 1.741 1.438 1.418 1.341 1.334 1.320 1.305 1.283 1.269 1.260 1.132 1.109 0.976 0.928 0.918 0.880 0.869 0.860



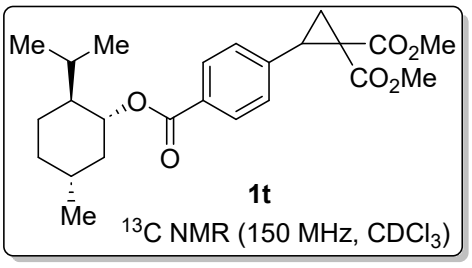
1t

^{1}H NMR (600 MHz, $CDCl_3$)



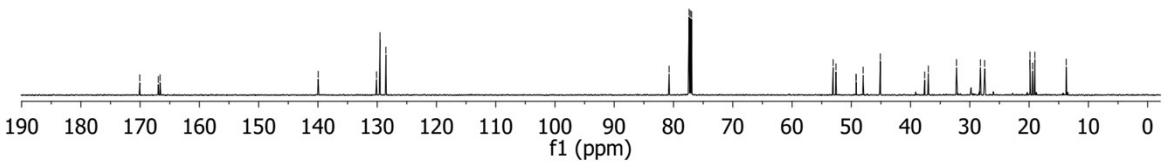
MM-444-CSM-13C

170.059 166.928 166.627 139.948 130.106 129.524 128.535 80.738 77.371 77.160 76.949 53.068 52.585 49.209 49.194 48.005 45.103 37.623 37.004 32.256 28.200 27.505 19.844 19.395 19.035 13.741

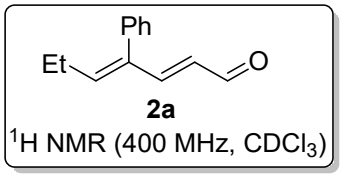


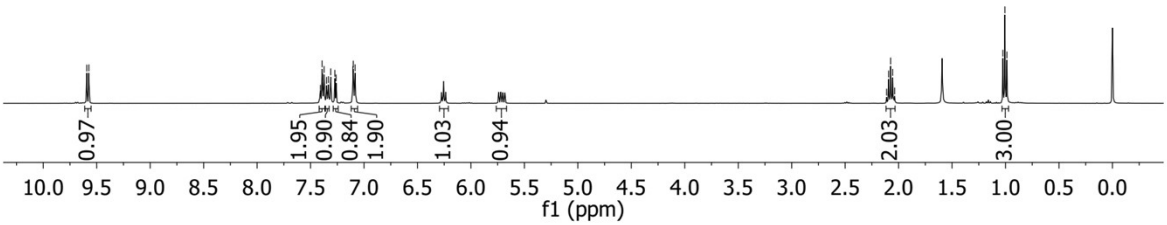
1t

^{13}C NMR (150 MHz, $CDCl_3$)

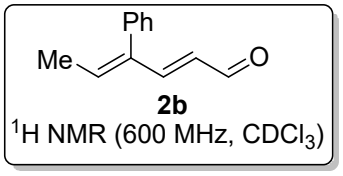


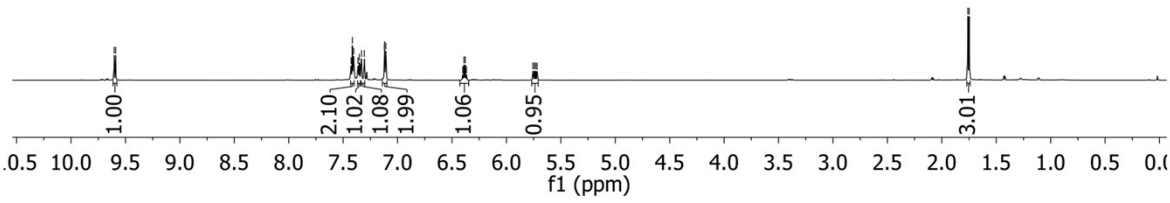
MM-ET-DIENAL-1H



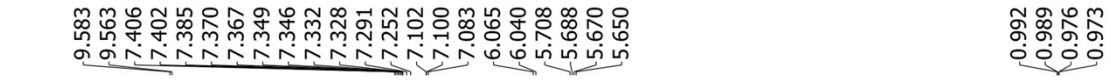


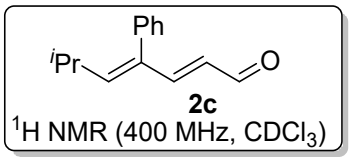
MM-ME-DSM-1H

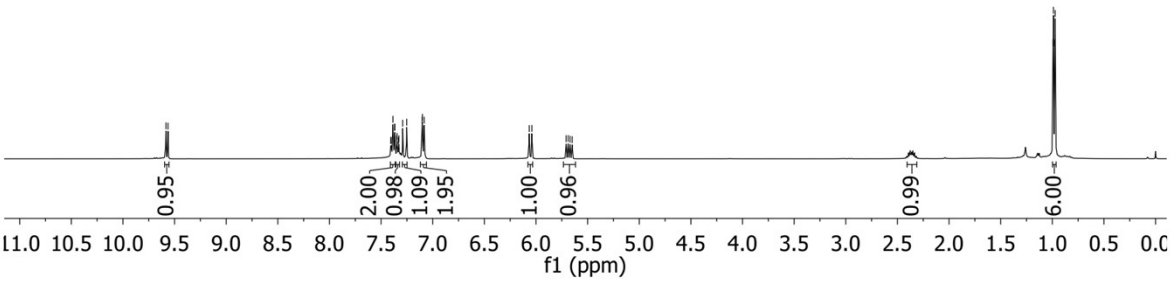




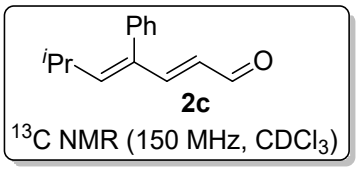
MM-390-DSM-1H

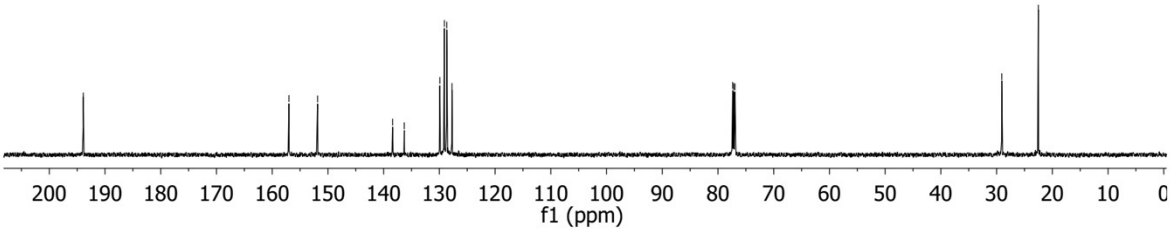






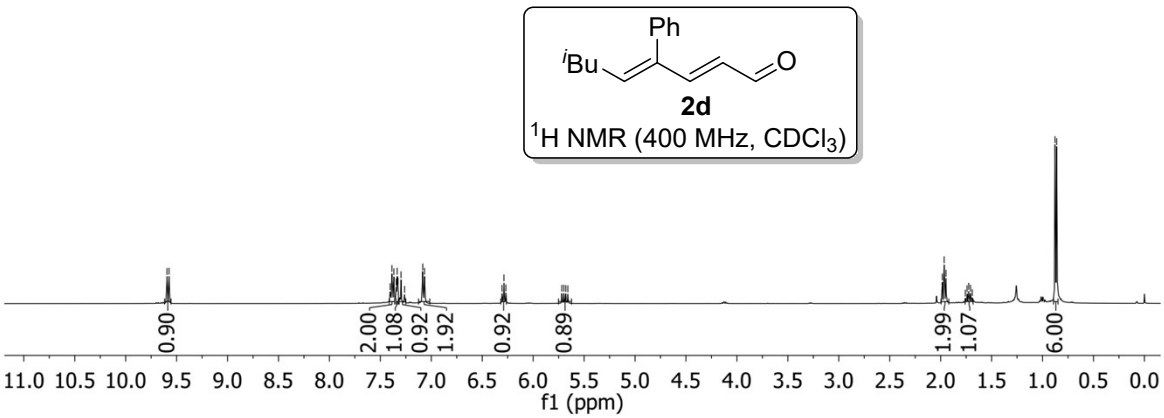
MM-390-DSM-13C





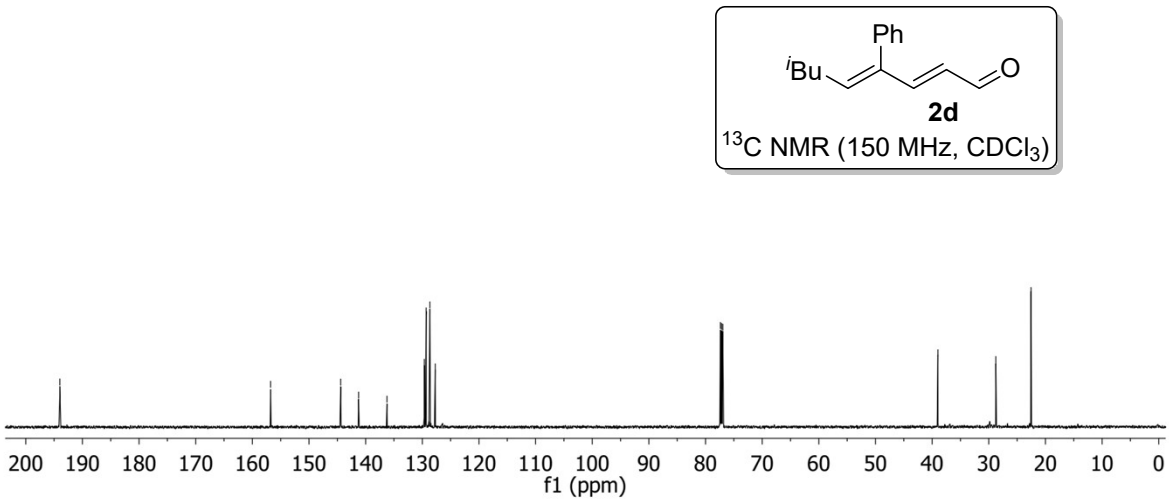
MM-391-DSM-1H

9.594 9.575 7.404 7.387 7.368 7.345 7.336 7.327 7.297 7.262 7.088 7.084 7.067 6.306 6.287 6.268 5.718 5.699 5.680 5.660 1.984 1.966 1.948 1.758 1.741 1.724 1.707 1.691 0.878 0.861

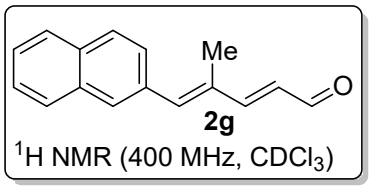


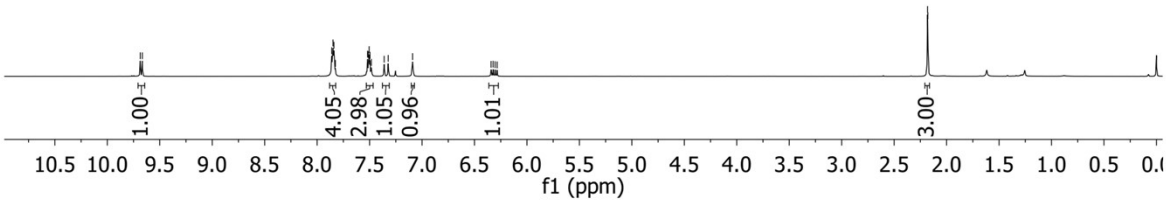
MM-391-DSM-13C

193.990 156.776 144.408 141.245 136.236 129.643 129.322 128.658 127.719 77.372 77.160 76.948 38.981 28.751 22.540

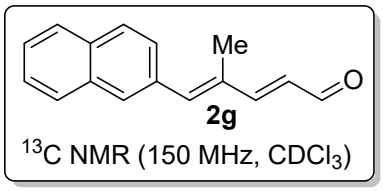


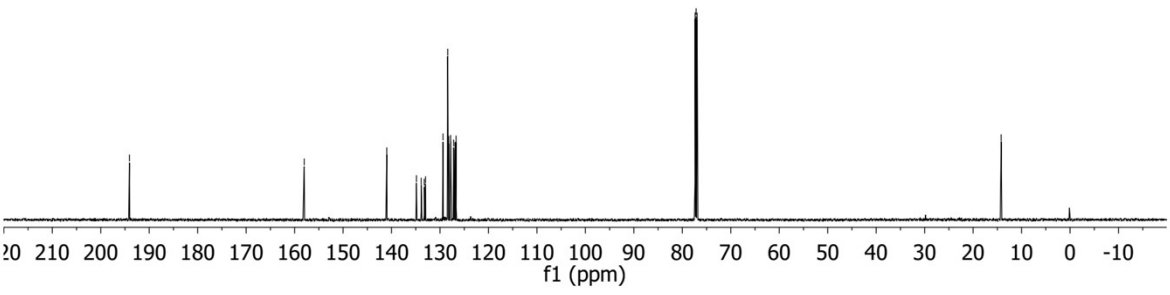
MM-2NAP-DSM-1H



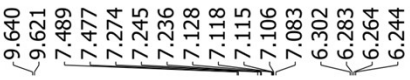


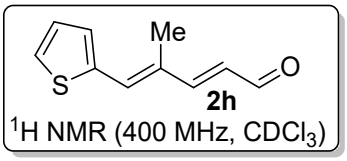
MM-2NAP-DSM-13C

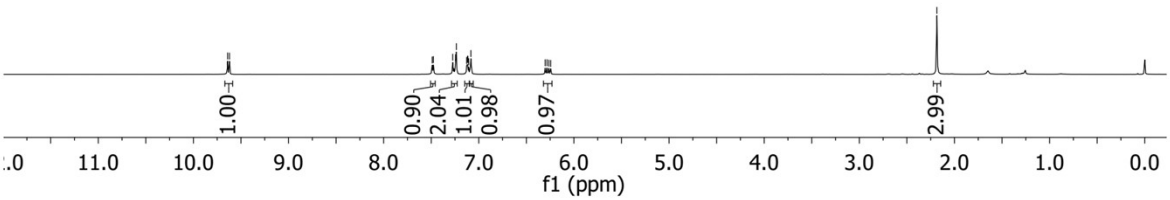




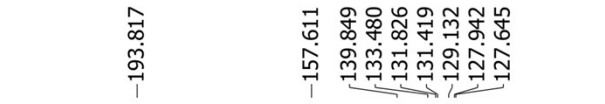
MM-2THIO-DSM-1H

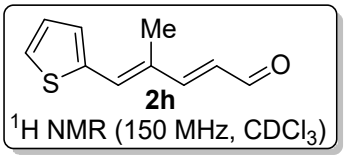


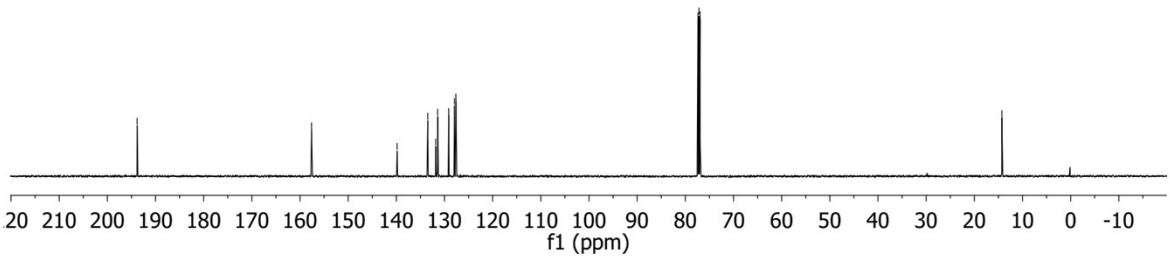




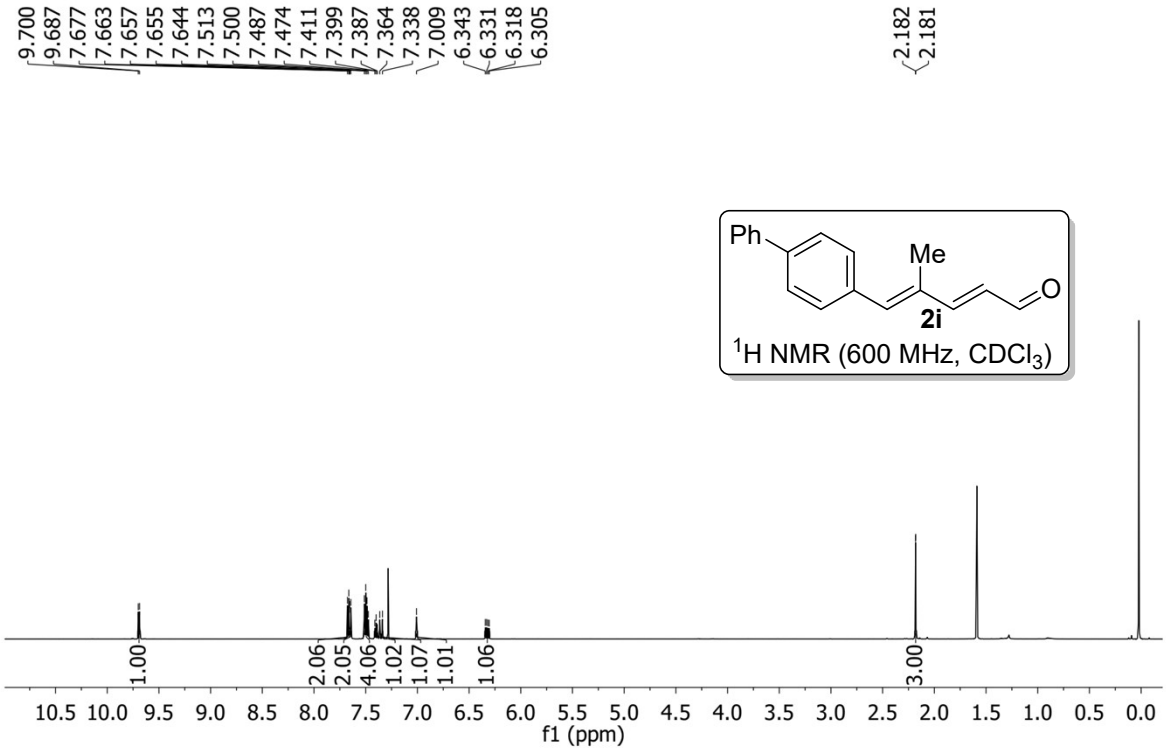
MM-2THIO-DSM-13C



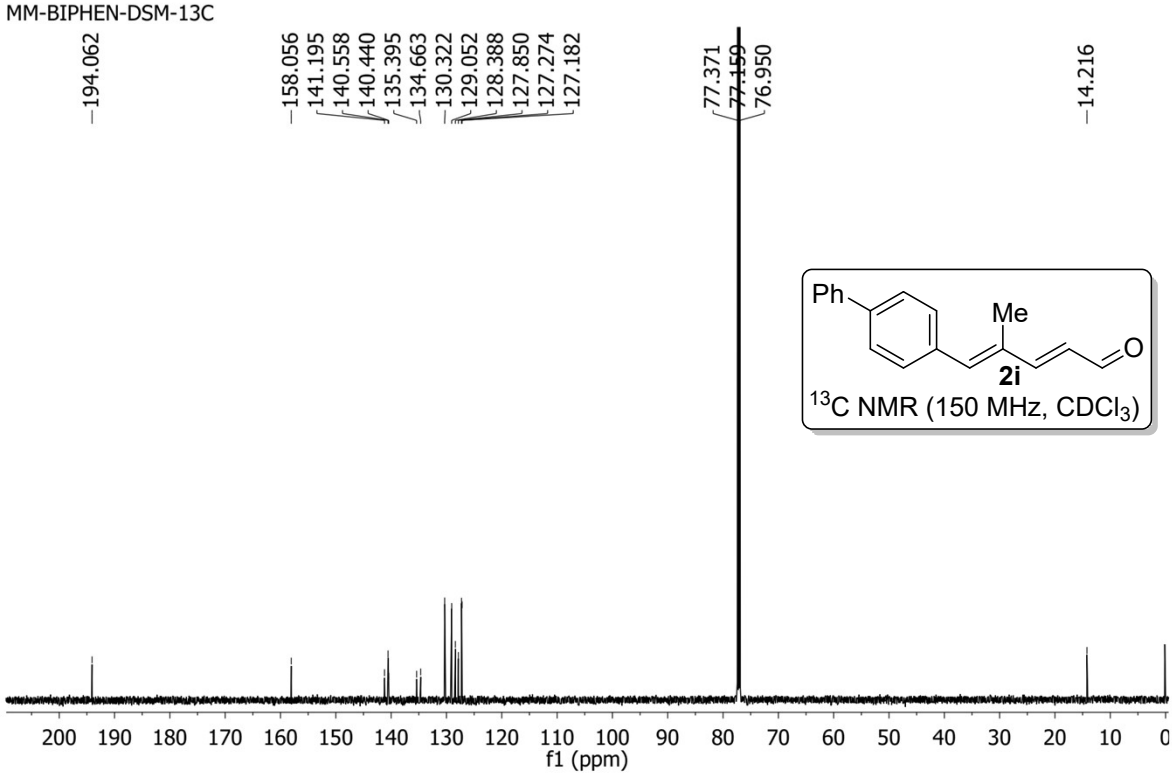




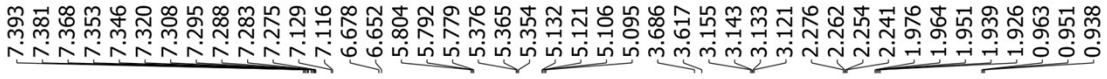
MM-BIPHEN-DSM-1H

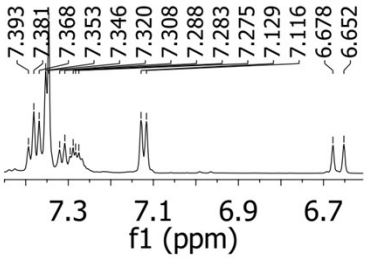


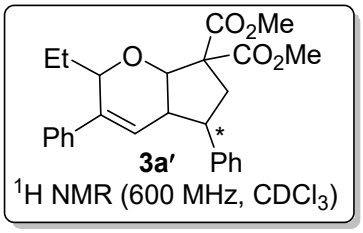
MM-BIPHEN-DSM-13C

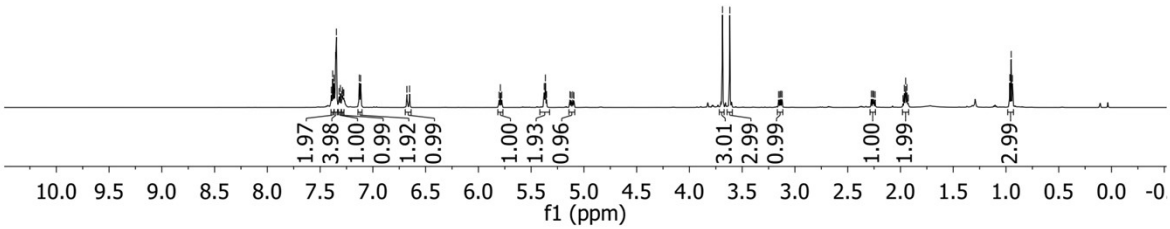


MM-343-A-1H

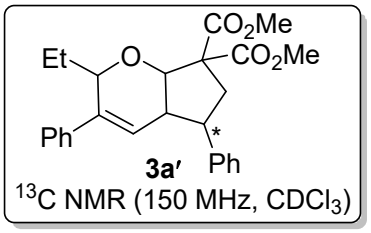


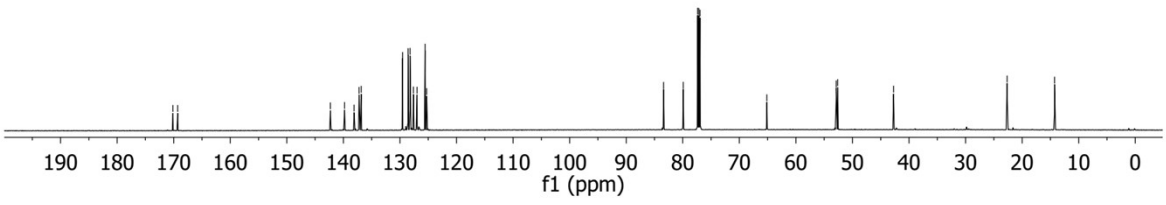




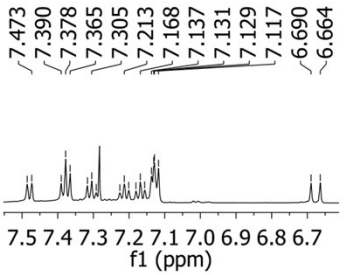


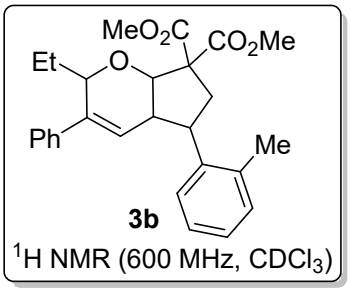
MM-343-A-13C

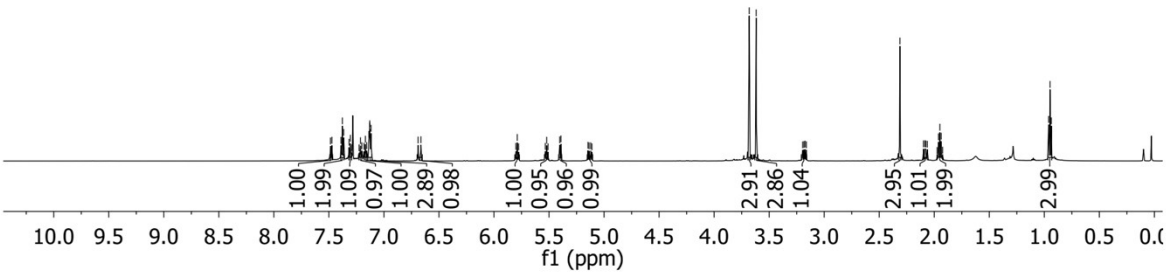




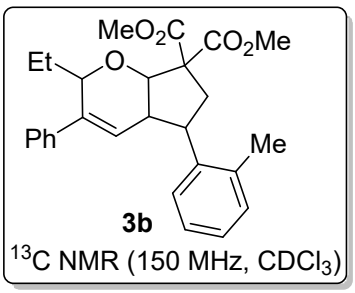
MM-448-A-1H

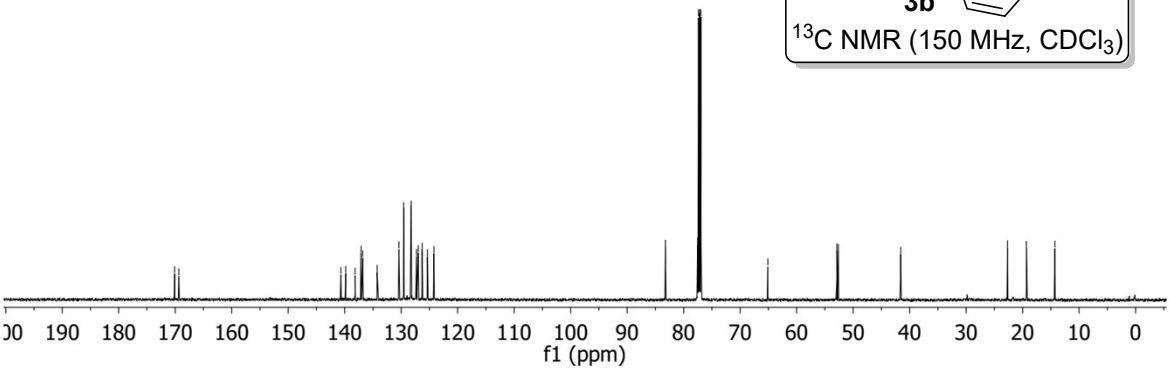




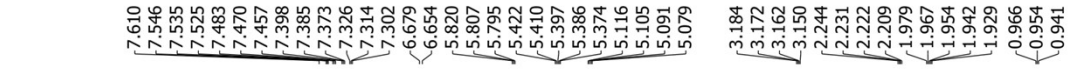


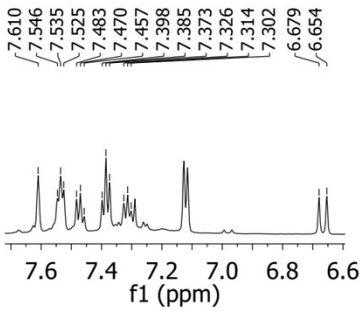
MM-448-A-13C

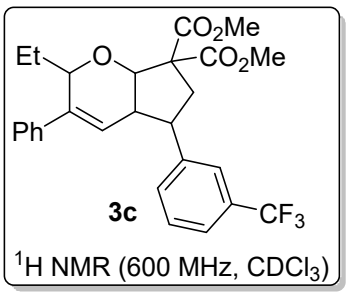


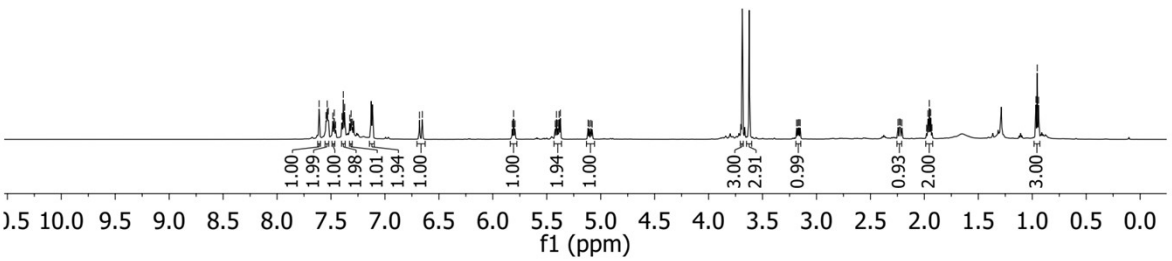


MM-374-1H

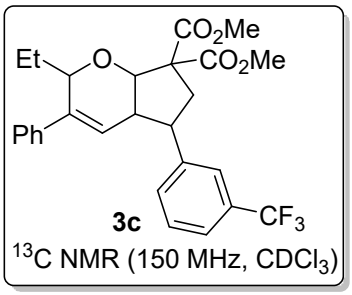




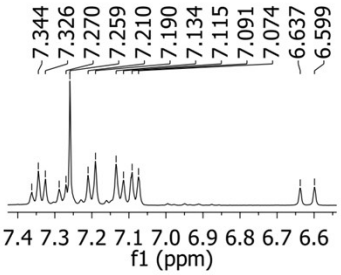


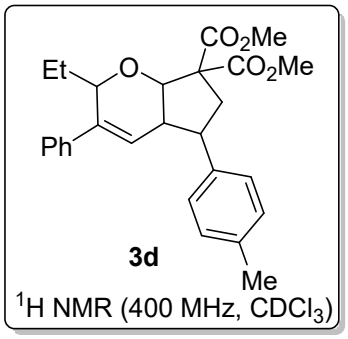


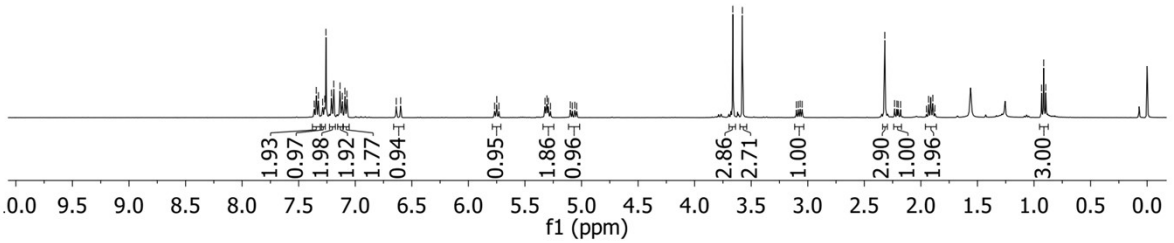
MM-374-13C



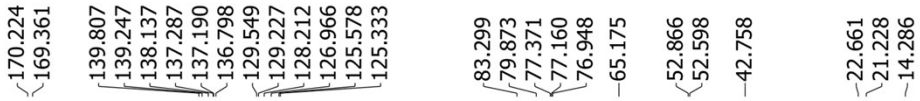
MM-344-A-1H

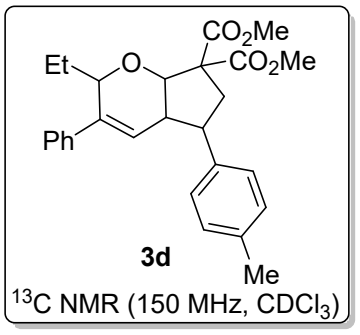


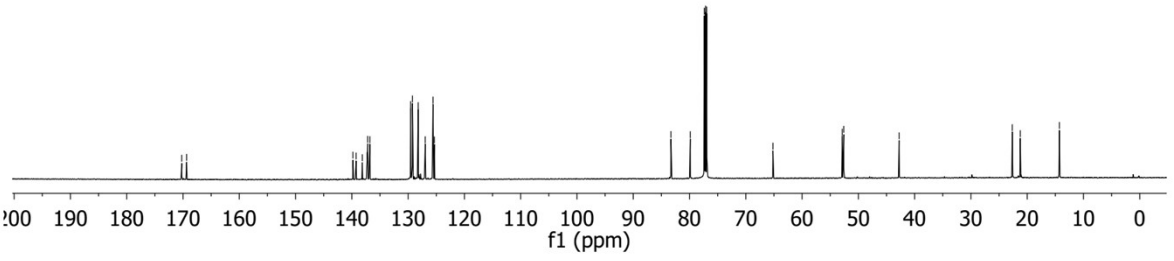




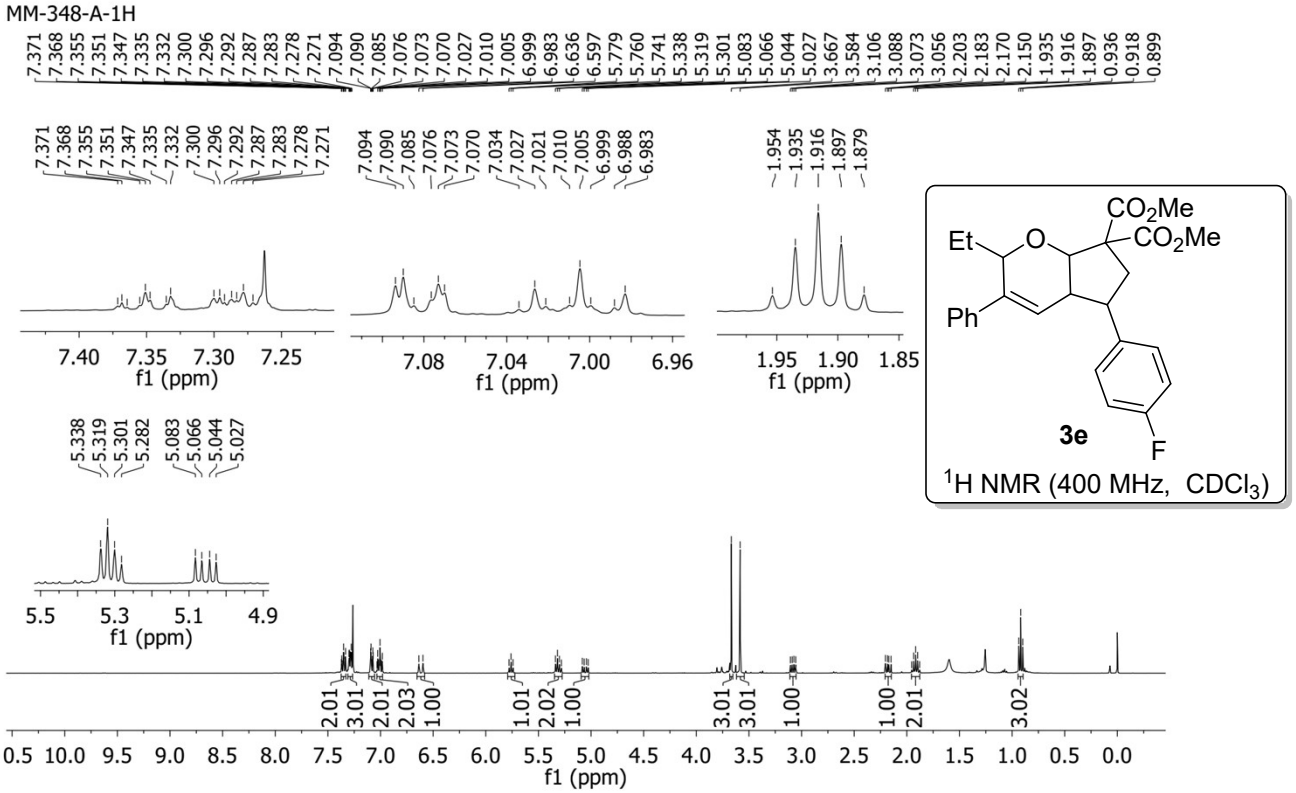
MM-344-A-13C



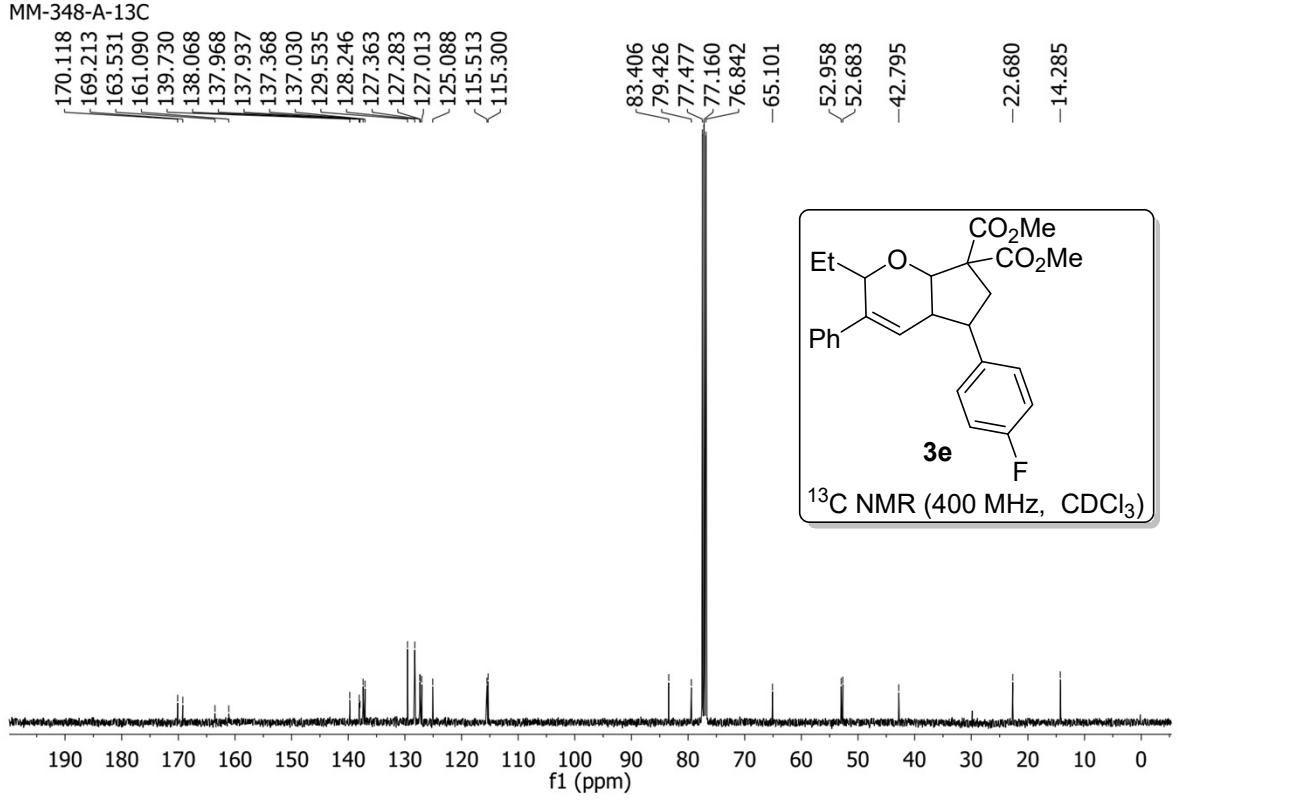




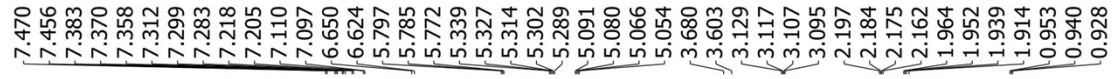
MM-348-A-1H

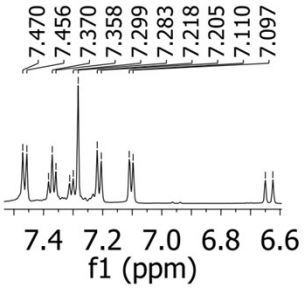


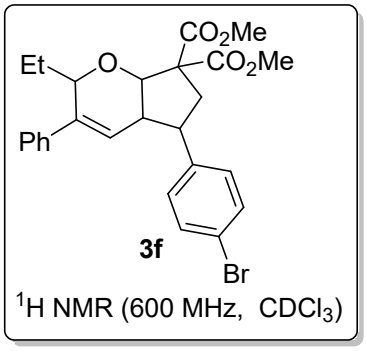
MM-348-A-13C



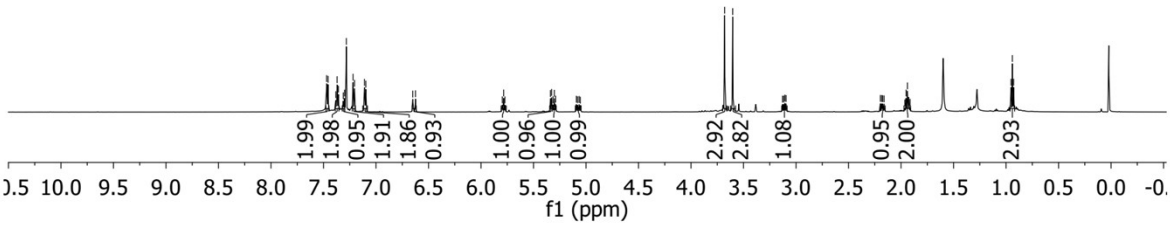
MM-365-1H



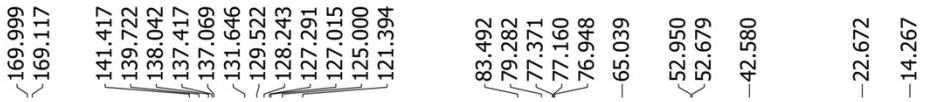


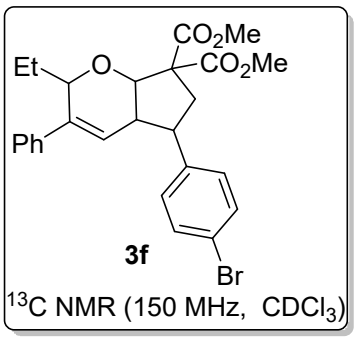


^{1}H NMR (600 MHz, $CDCl_3$)

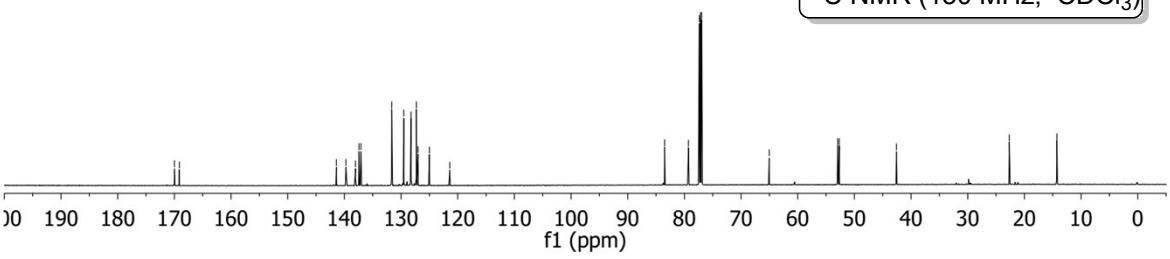


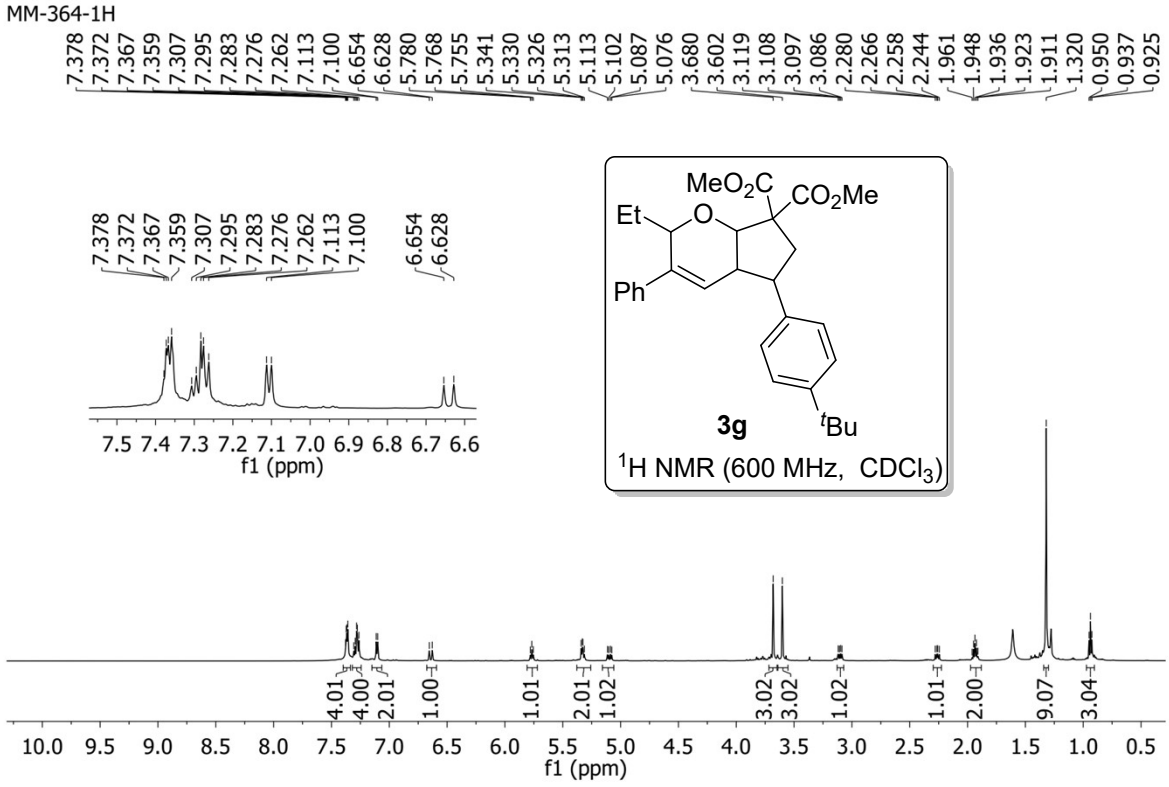
MM-365-A-13C

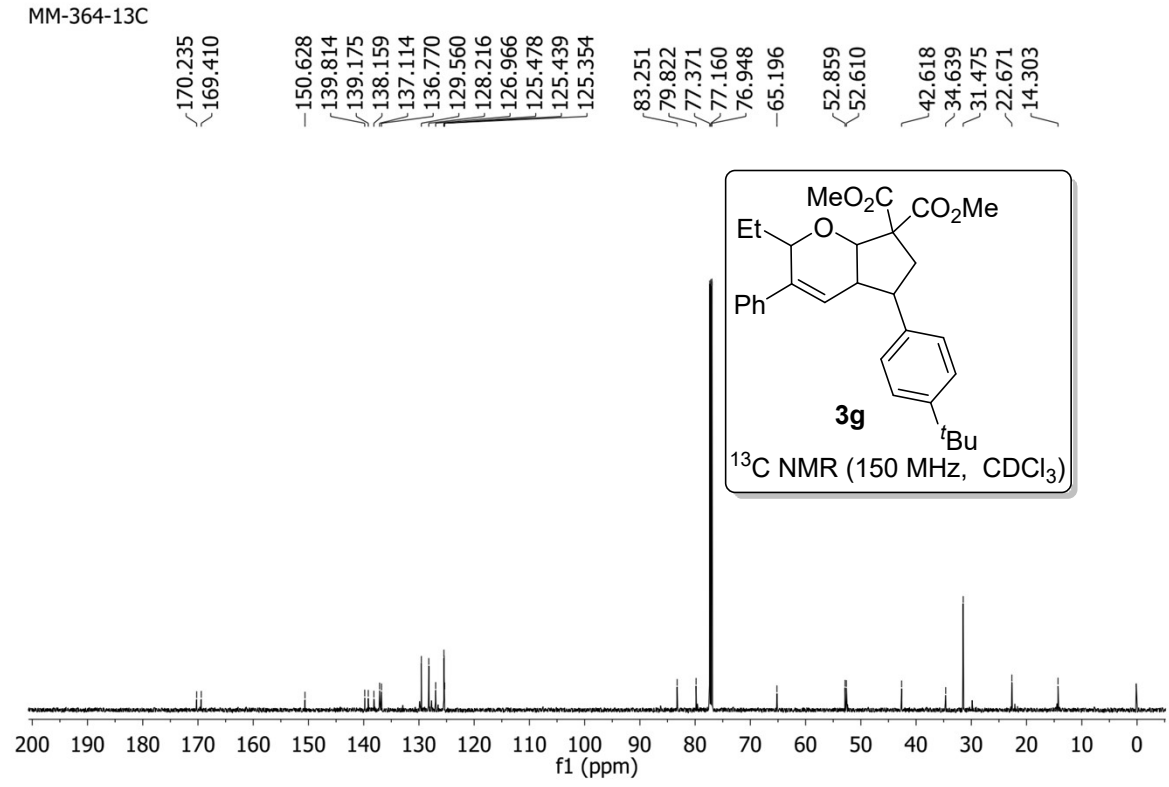




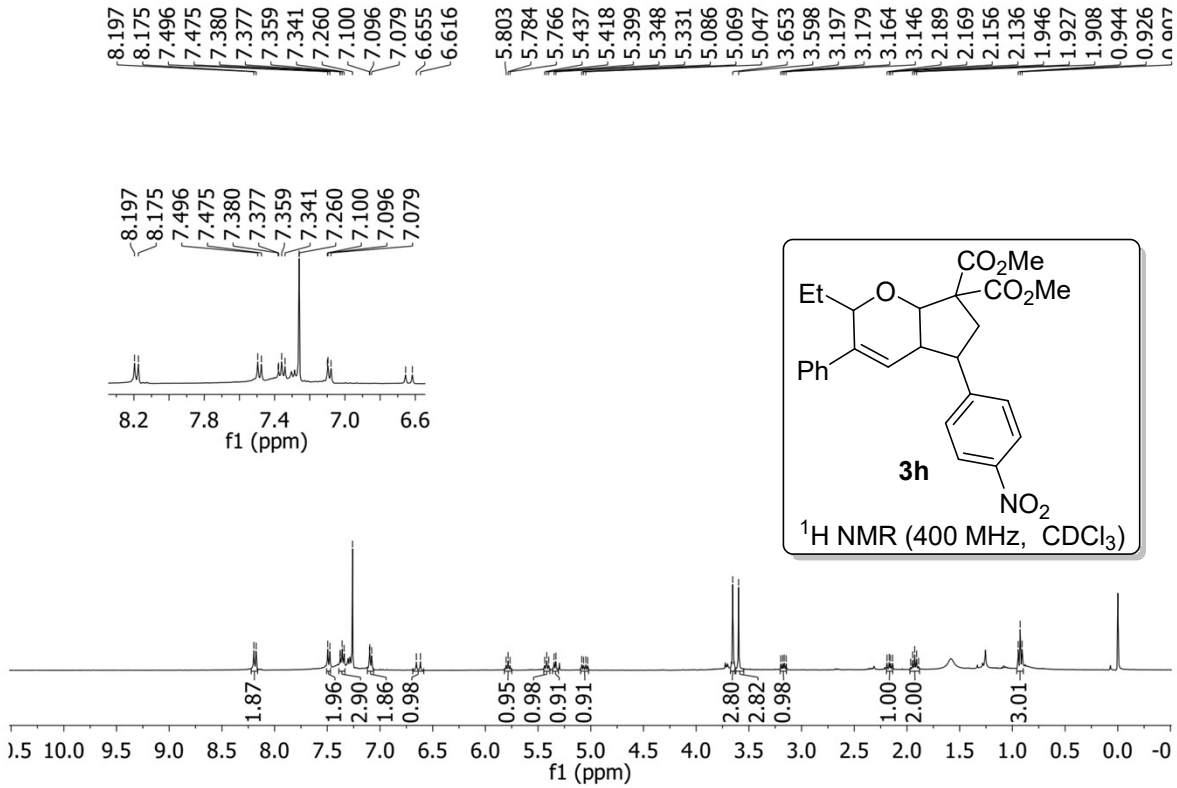
^{13}C NMR (150 MHz, $CDCl_3$)



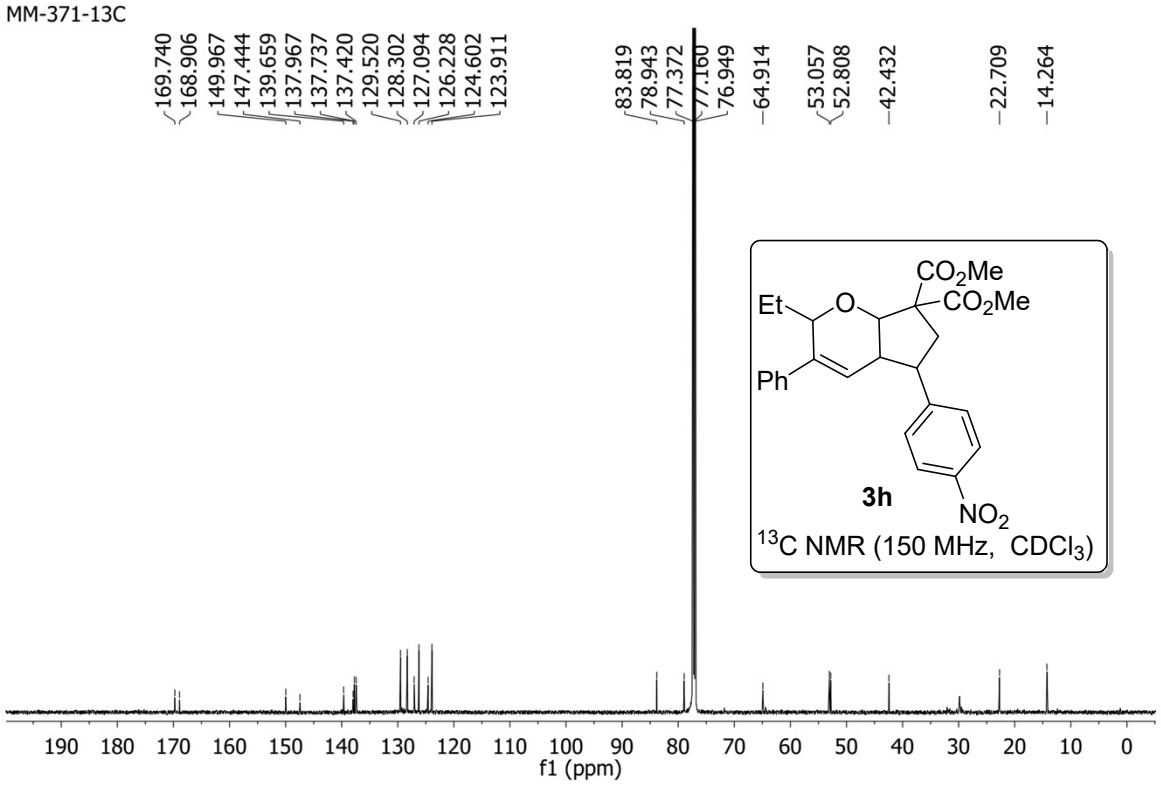

MM-364-1H
7.378 7.372 7.367 7.359 7.307 7.295 7.283 7.276 7.262 7.113 7.100 6.654 6.628 5.780 5.768 5.755 5.341 5.330 5.326 5.313 5.113 5.102 5.087 5.076 3.680 3.602 3.119 3.108 3.097 3.086 2.280 2.266 2.258 2.244 1.961 1.948 1.936 1.923 1.911 1.320 0.950 0.937 0.925
7.378 7.372 7.367 7.359 7.307 7.295 7.283 7.276 7.262 7.113 7.100 6.654 6.628
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
MeO2C
CO2Me
Et
O
Ph
3g
tBu
1H NMR (600 MHz, CDCl3)
4.01 4.00 2.01 1.00 1.01 2.01 1.02 3.02 3.02 1.02 1.01 2.00 9.07 3.04
10.0 9.5 9.0 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
f1 (ppm)


MM-364-13C
170.235 169.410 150.628 139.814 139.175 138.159 137.114 136.770 129.560 128.216 126.966 125.478 125.439 125.354 83.251 79.822 77.371 77.160 76.948 65.196 52.859 52.610 42.618 34.639 31.475 22.671 14.303
MeO2C
CO2Me
Et
O
Ph
3g
tBu
13C NMR (150 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

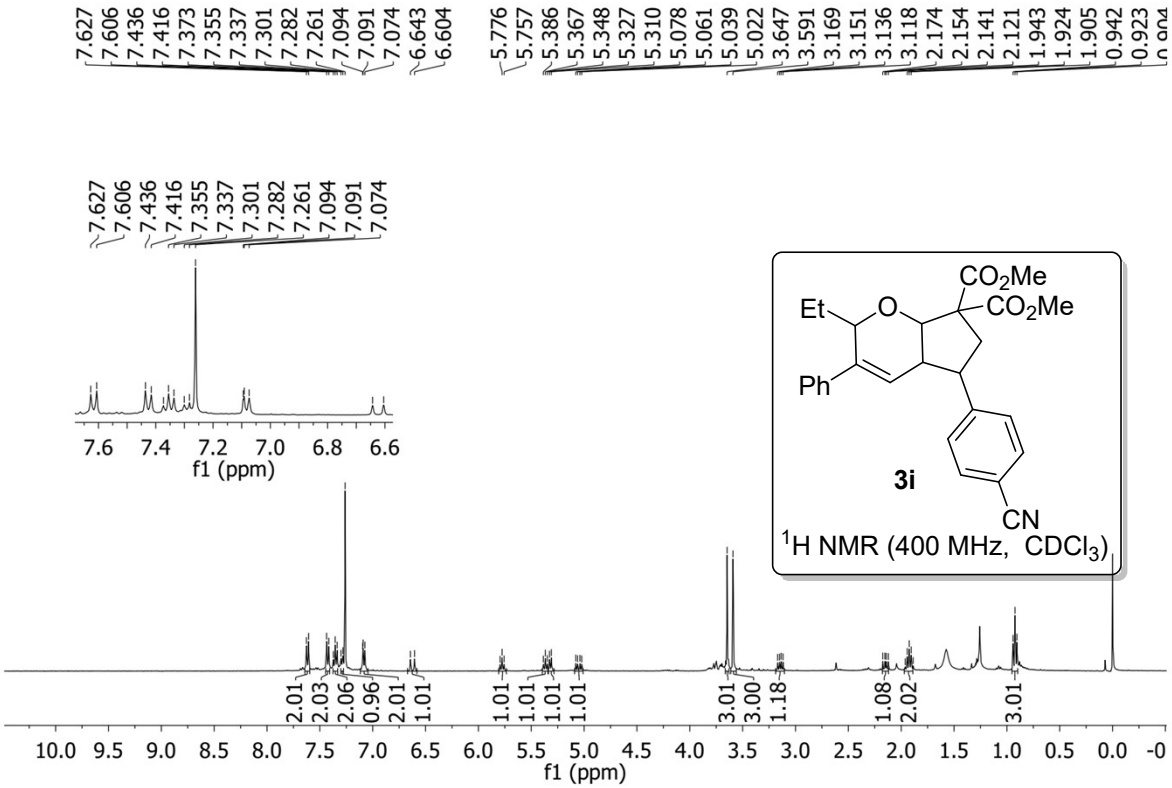
MM-371-1H



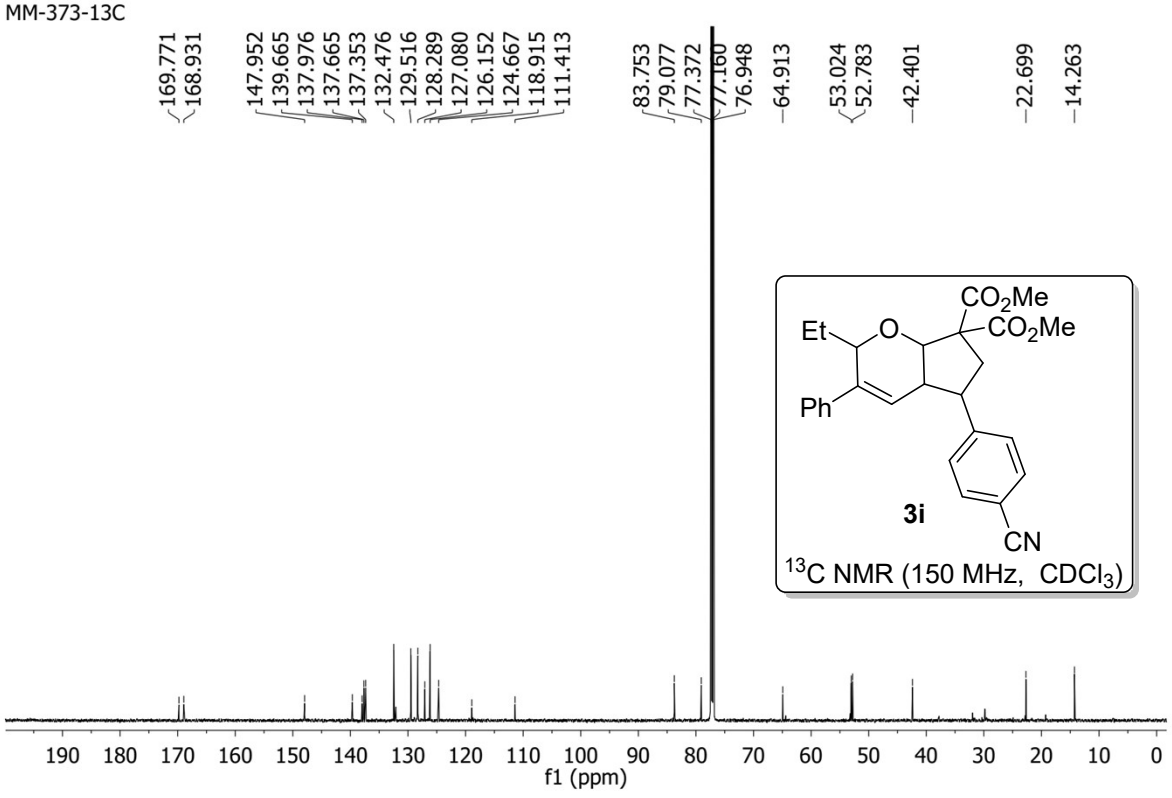
MM-371-13C

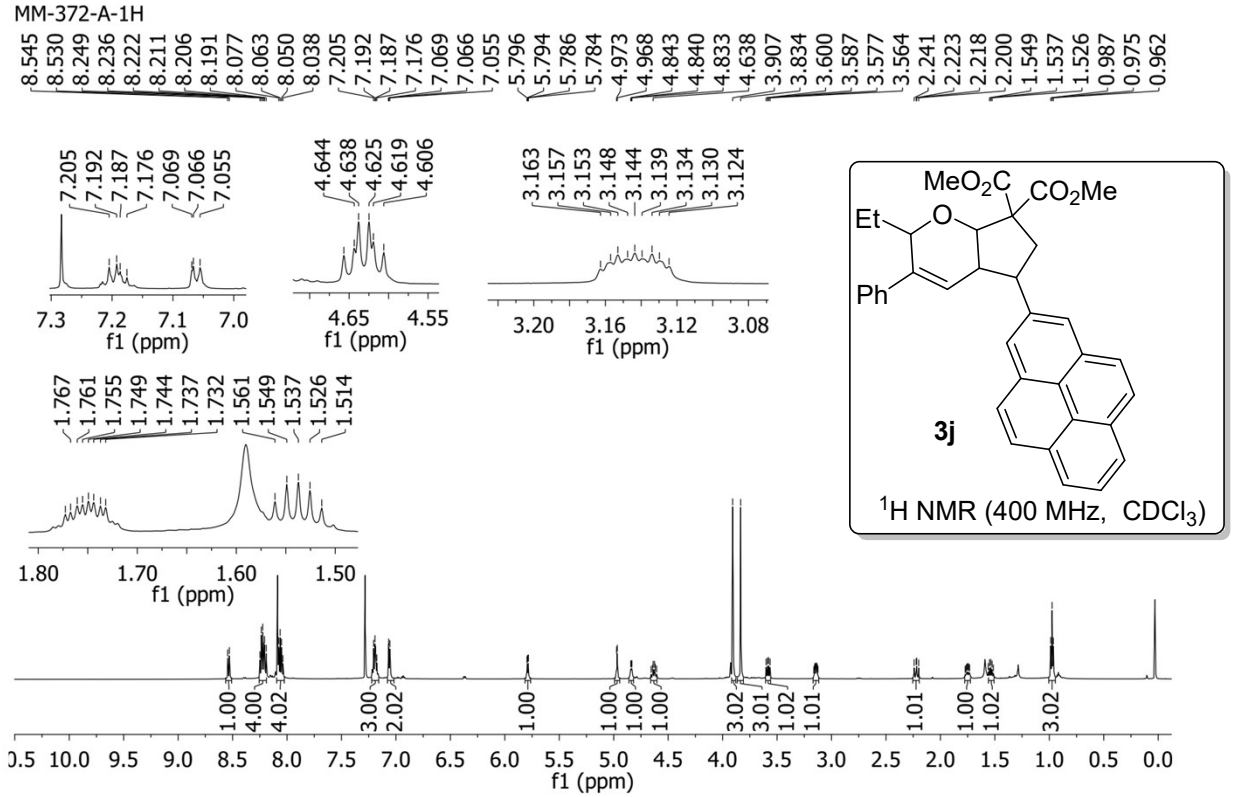


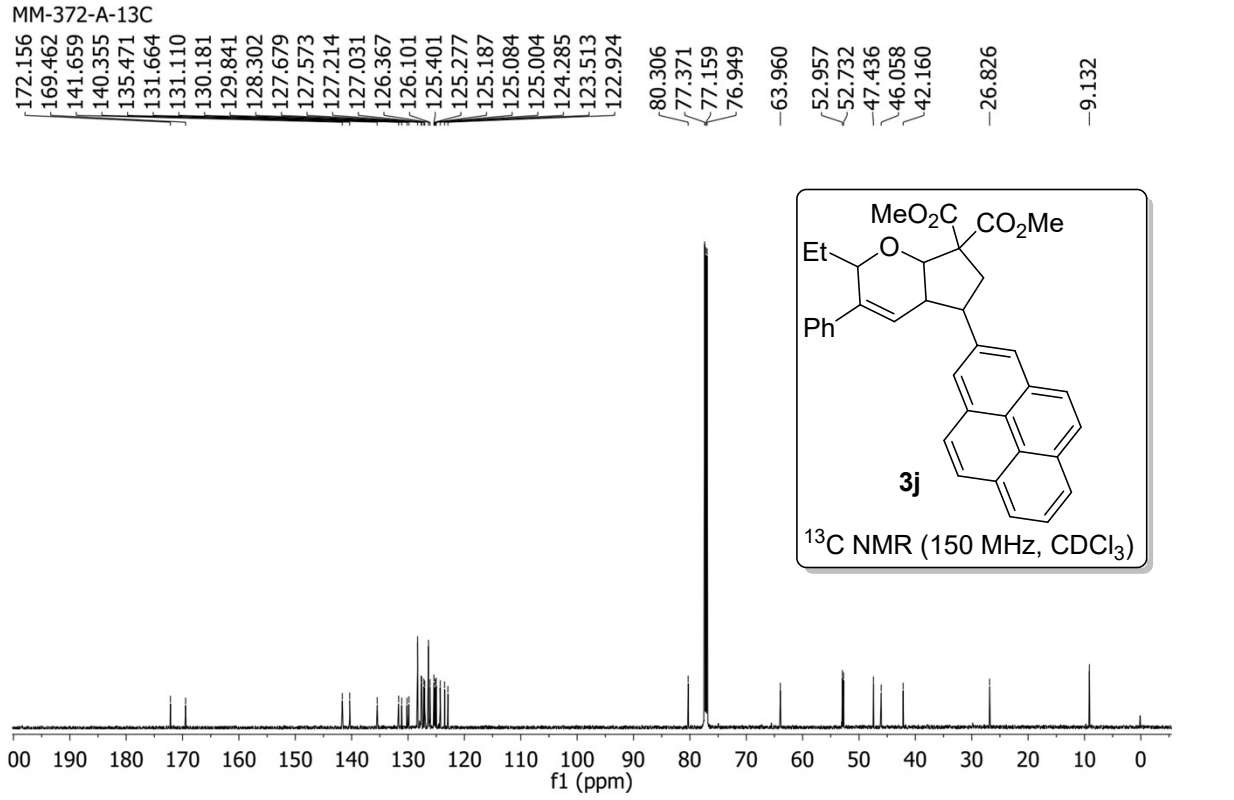
MM-373-1H

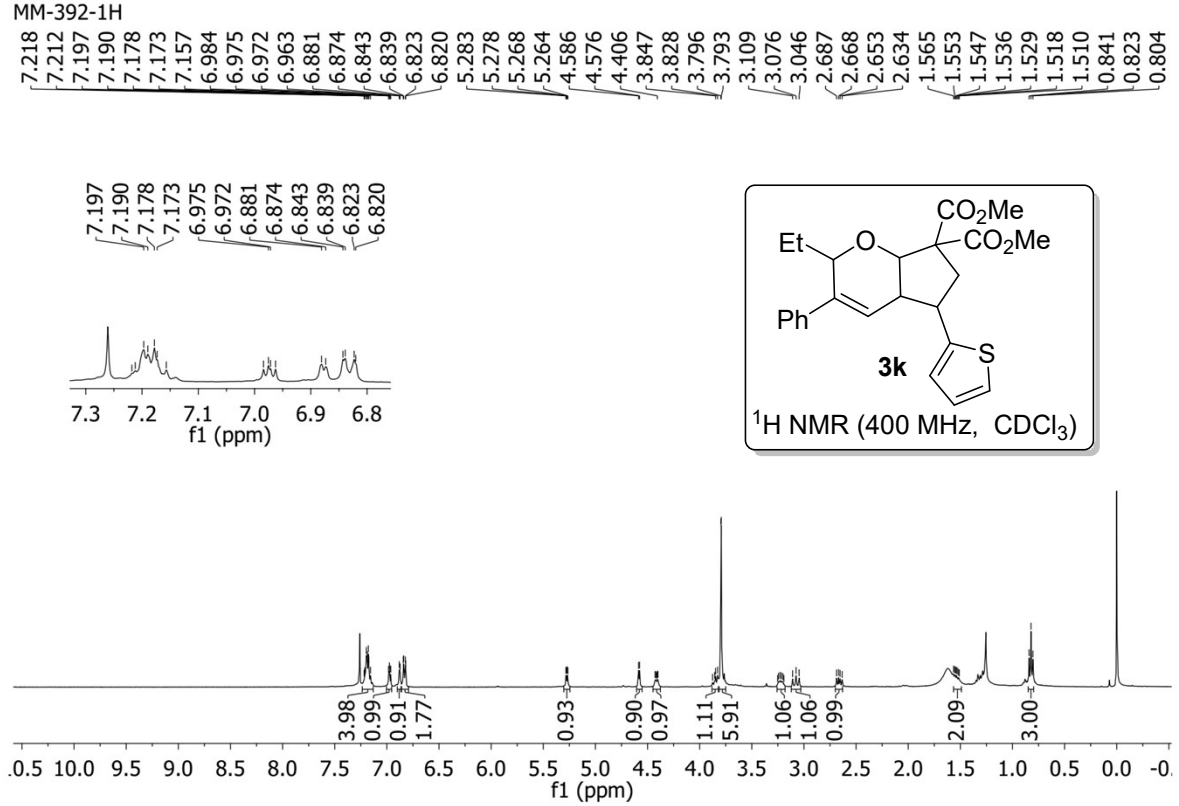


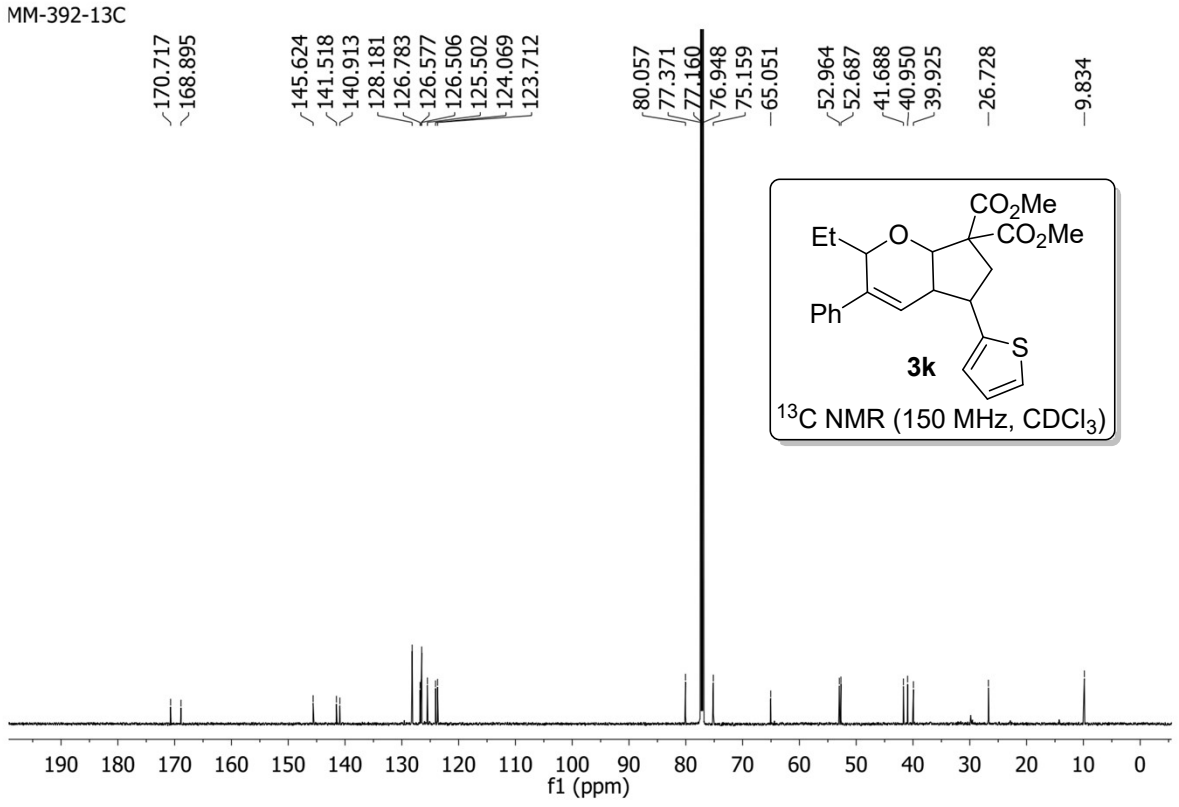
MM-373-13C



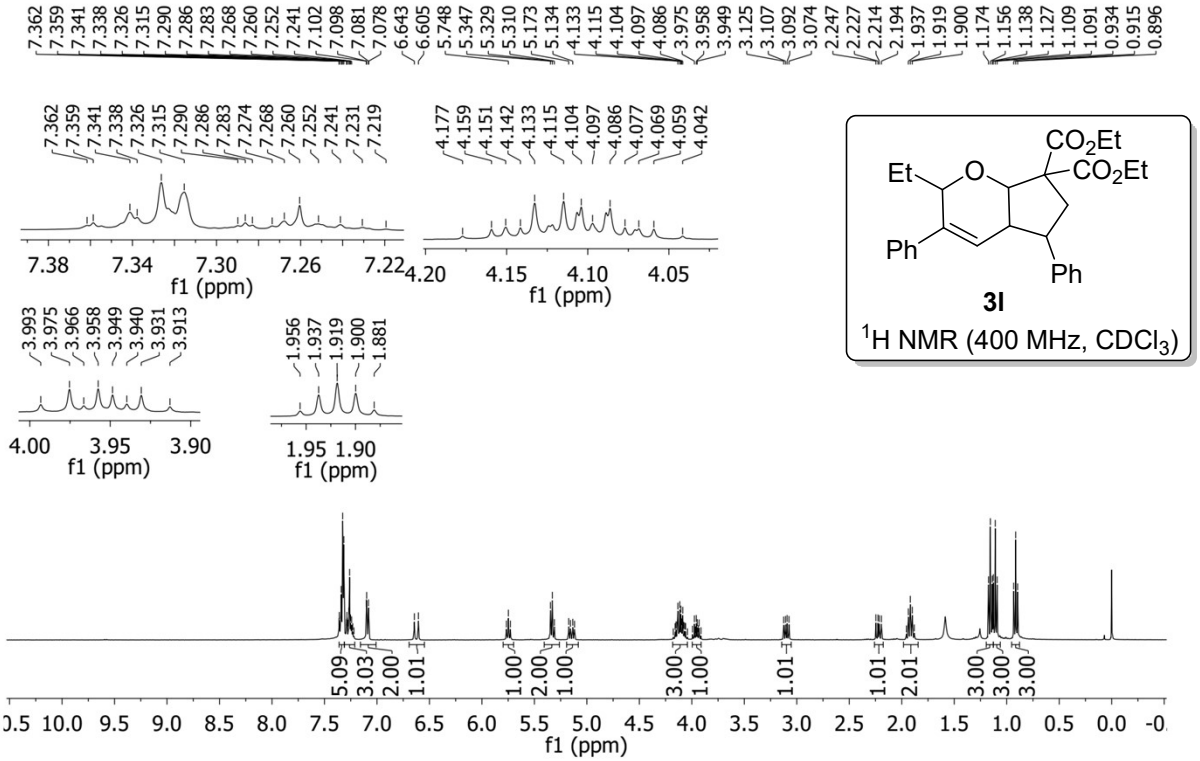

MM-372-A-1H
3j
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


MM-372-A-13C
3j
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)


MM-392-1H
7.218
7.212
7.197
7.190
7.178
7.173
7.157
6.984
6.975
6.972
6.963
6.881
6.874
6.843
6.839
6.823
6.820
5.283
5.278
5.268
5.264
4.586
4.576
4.406
3.847
3.828
3.796
3.793
3.109
3.076
3.046
2.687
2.668
2.653
2.634
1.565
1.553
1.547
1.536
1.529
1.518
1.510
0.841
0.823
0.804
7.197
7.190
7.178
7.173
6.975
6.972
6.881
6.874
6.843
6.839
6.823
6.820
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
CO2Me
Et
O
CO2Me
Ph
S
3k
1H NMR (400 MHz, CDCl3)
3.98
0.99
0.91
1.77
0.93
0.90
0.97
1.11
5.91
1.06
1.06
0.99
2.09
3.00
f1 (ppm)


MM-392-13C
170.717
168.895
145.624
141.518
140.913
128.181
126.783
126.577
126.506
125.502
124.069
123.712
80.057
77.371
77.160
76.948
75.159
65.051
52.964
52.687
41.688
40.950
39.925
26.728
9.834
CO2Me
Et
O
CO2Me
Ph
S
3k
13C NMR (150 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

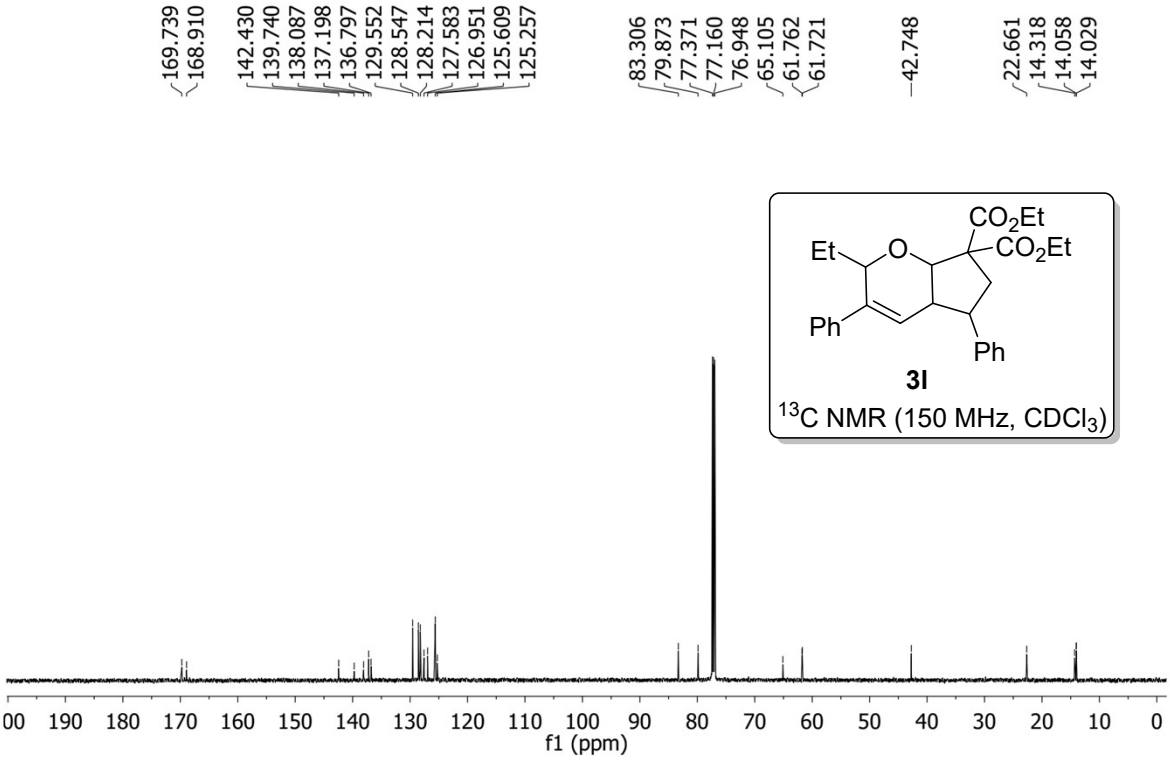
MM-417-1H



3l

^{1}H NMR (400 MHz, $CDCl_3$)

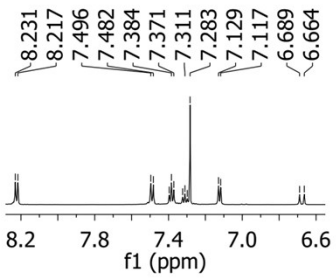
MM-417-13C

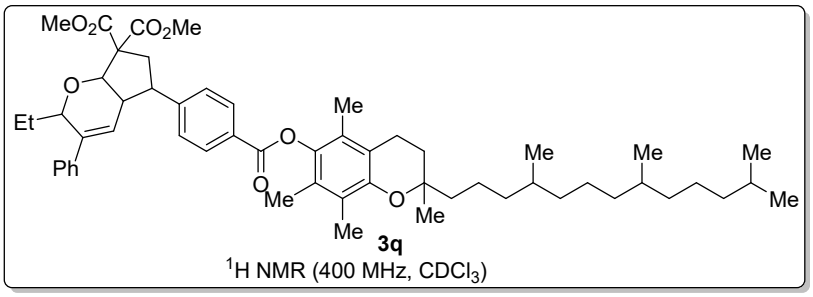


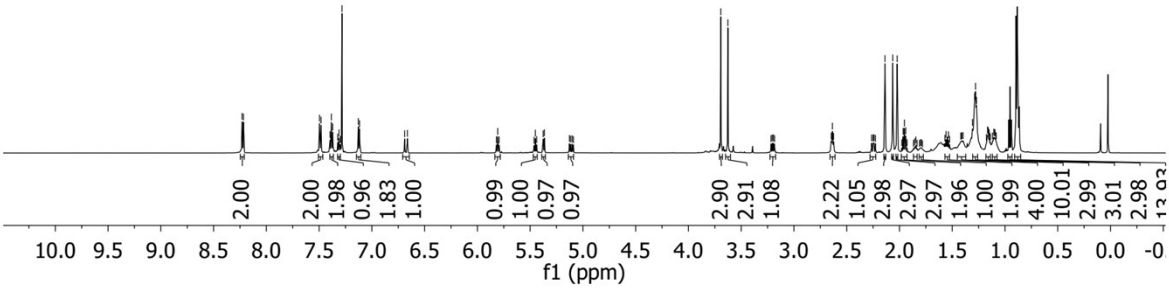
3l

^{13}C NMR (150 MHz, $CDCl_3$)

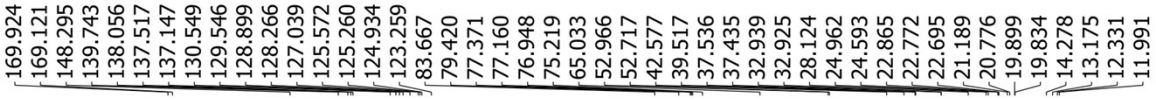
MM-443-A-1H

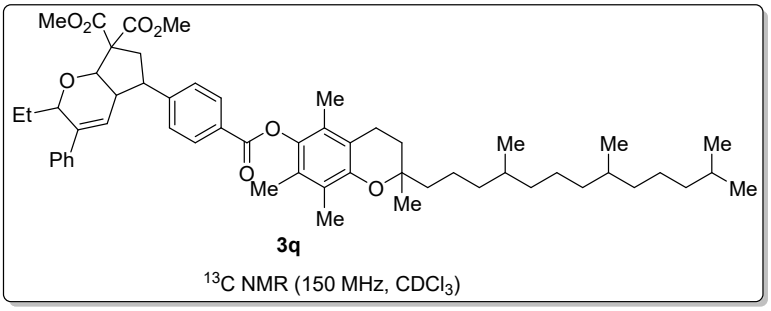


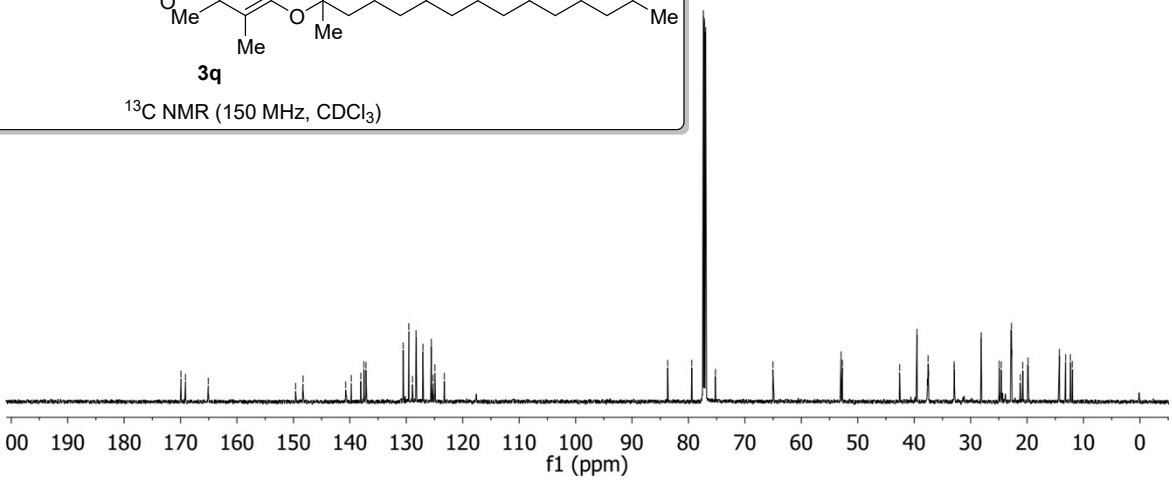


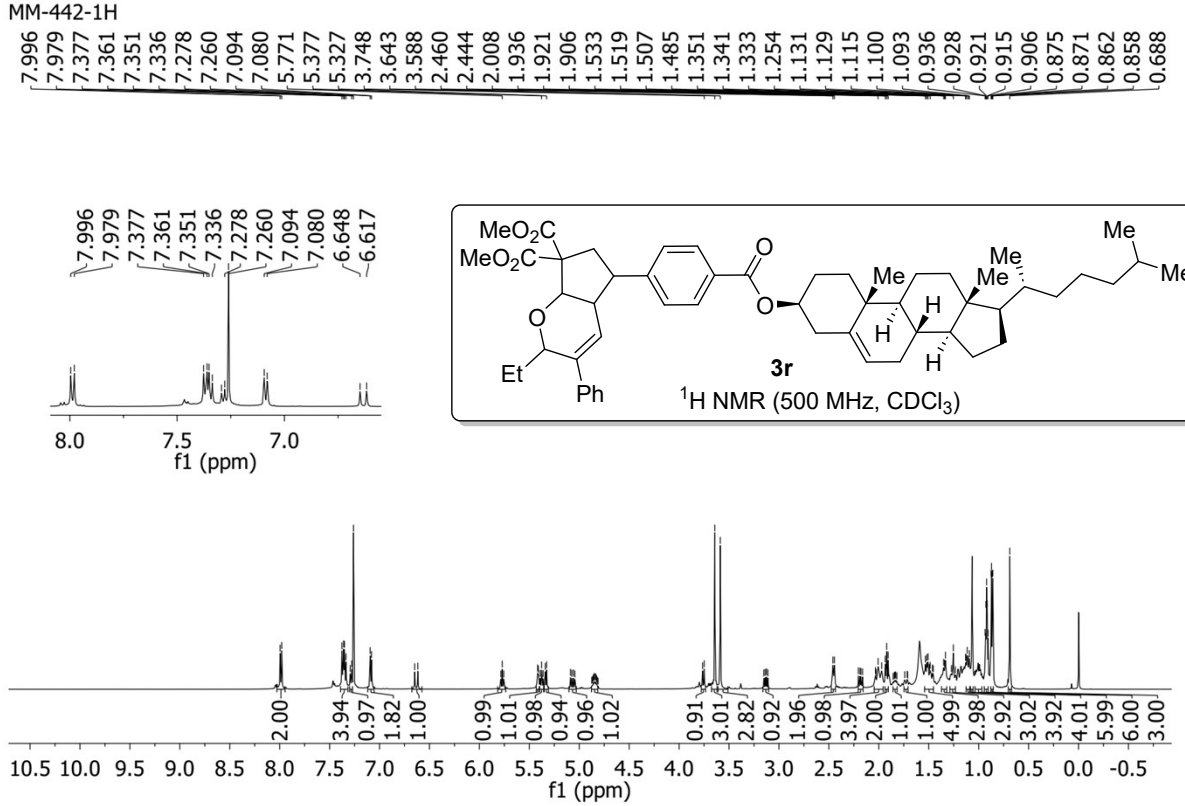


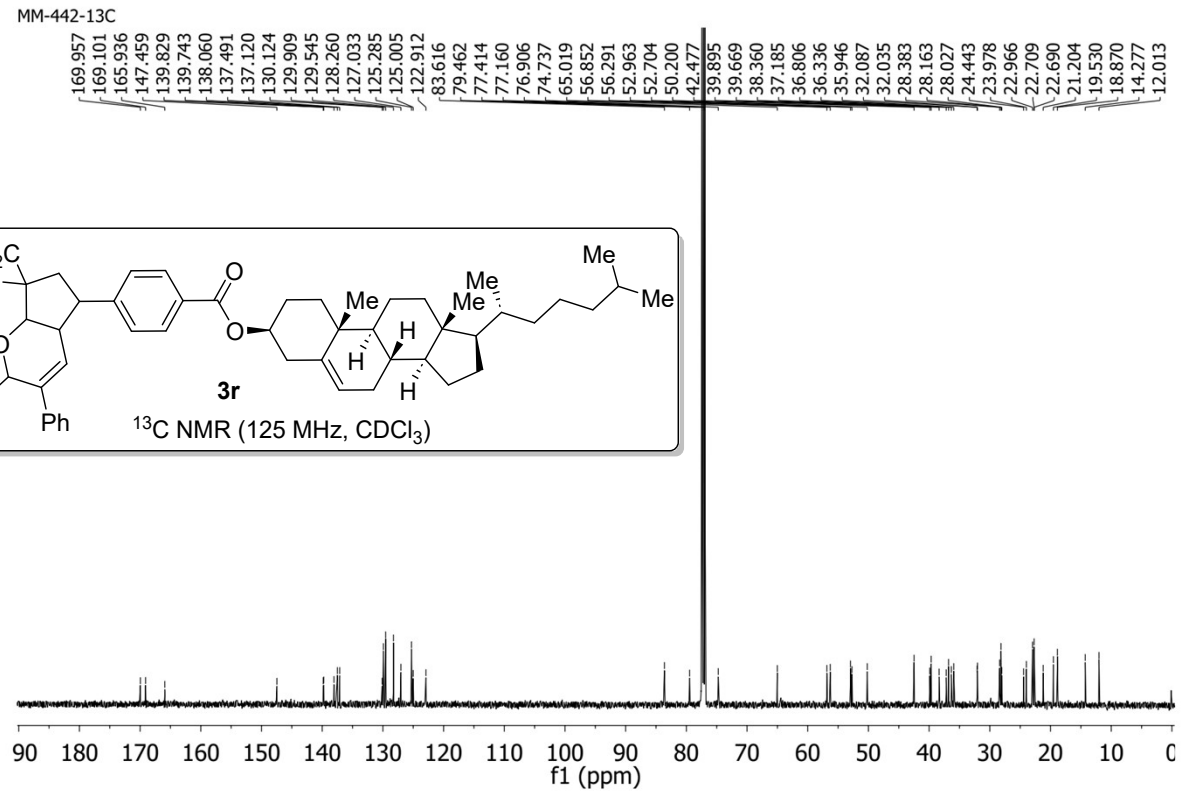
MM-443-A-13C

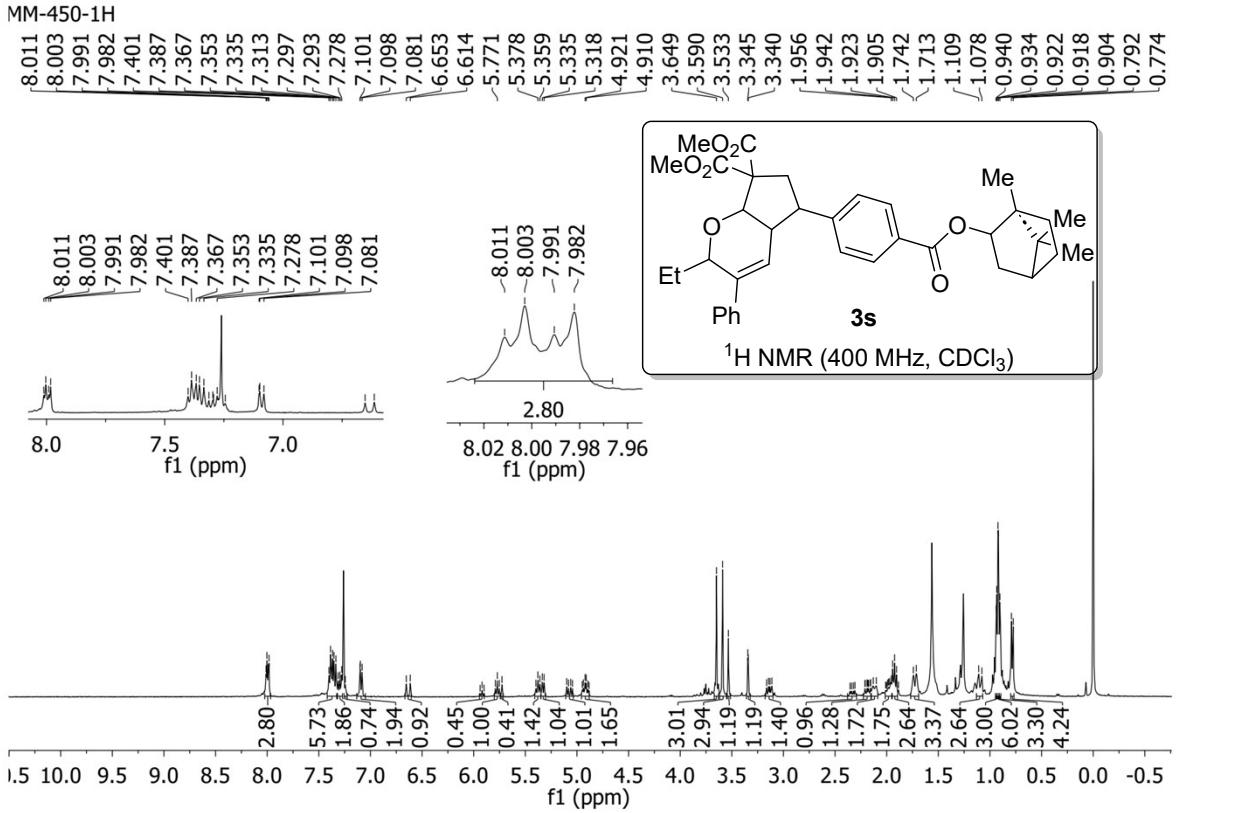


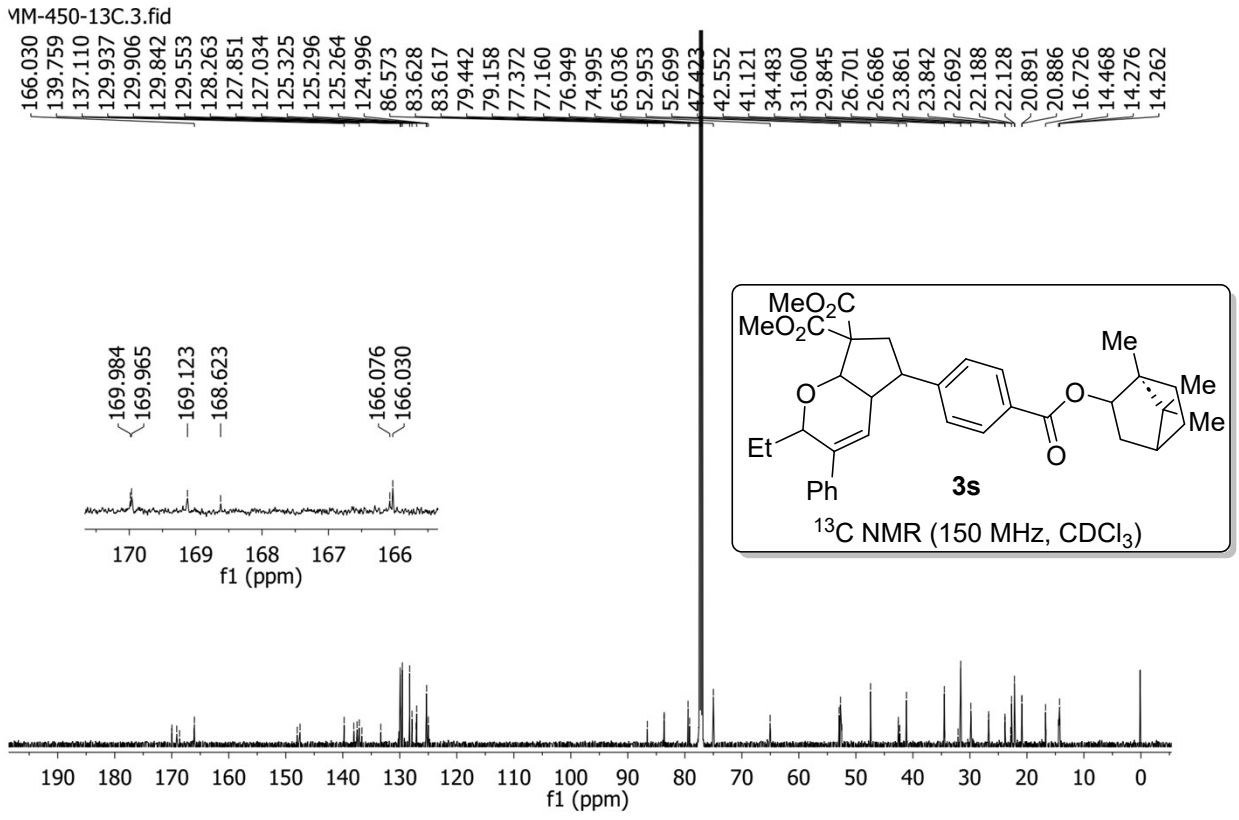




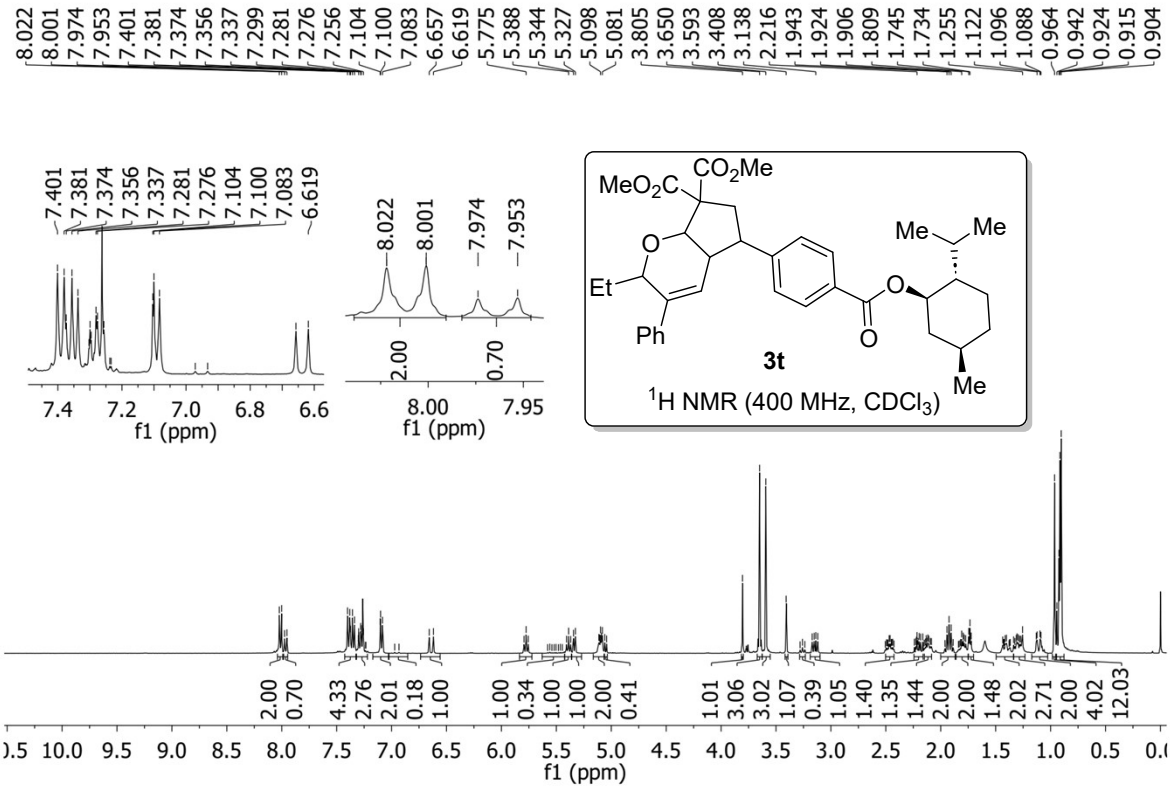

MM-442-1H
7.996 7.979 7.377 7.361 7.351 7.336 7.278 7.260 7.094 7.080 5.771 5.377 5.327 3.748 3.643 3.588 2.460 2.444 2.008 1.936 1.921 1.906 1.533 1.519 1.507 1.485 1.351 1.341 1.333 1.254 1.131 1.129 1.115 1.100 1.093 0.936 0.928 0.921 0.915 0.906 0.875 0.871 0.862 0.858 0.688
7.996 7.979 7.377 7.361 7.351 7.336 7.278 7.260 7.094 7.080 6.648 6.617
8.0 7.5 7.0
f1 (ppm)
MeO2C
MeO2C
O
O
Me
Me
Me
Me
H
H
H
O
Et
Ph
3r
1H NMR (500 MHz, CDCl3)
2.00 3.94 0.97 1.82 1.00 0.99 1.01 0.98 0.94 0.96 1.02 0.91 3.01 2.82 0.92 1.96 0.98 3.97 2.00 1.01 1.00 4.99 2.98 2.92 3.02 3.92 4.01 5.99 6.00 3.00
10.5 10.0 9.5 9.0 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)


MM-442-13C
169.957 169.101 165.936 147.459 139.829 139.743 138.060 137.491 137.120 130.124 129.909 129.545 128.260 127.033 125.285 125.005 122.912 83.616 79.462 77.414 77.160 76.906 74.737 65.019 56.852 56.291 52.963 52.704 50.200 42.477 39.895 39.669 38.360 37.185 36.806 36.336 35.946 32.087 32.035 28.383 28.163 28.027 24.443 23.978 22.966 22.709 22.690 21.204 19.530 18.870 14.277 12.013
MeO2C
MeO2C
O
O
Me
Me
Me
Me
H
H
H
O
Et
Ph
3r
13C NMR (125 MHz, CDCl3)
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

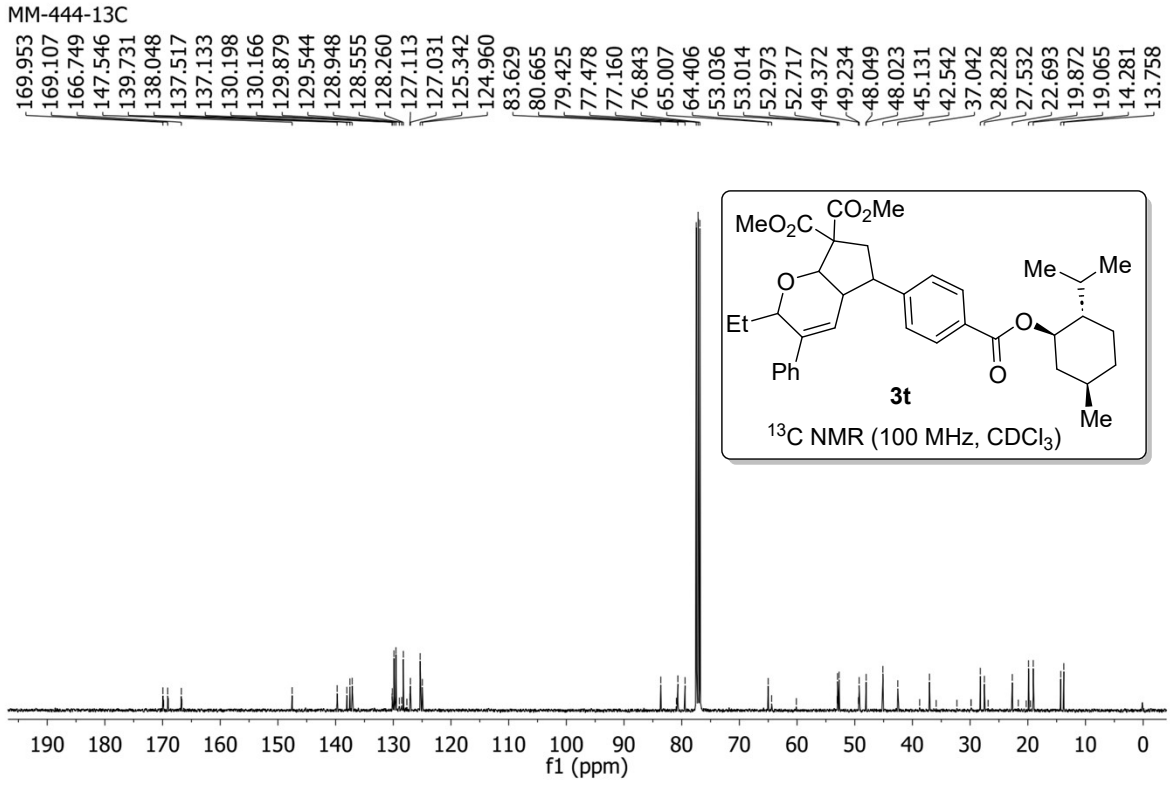

MM-450-1H
MeO2C
MeO2C
O
Et
Ph
O
O
Me
Me
Me
3s
1H NMR (400 MHz, CDCl3)
f1 (ppm)


MM-450-13C.3.fid
MeO2C
MeO2C
O
Et
Ph
O
O
Me
Me
Me
3s
13C NMR (150 MHz, CDCl3)
f1 (ppm)

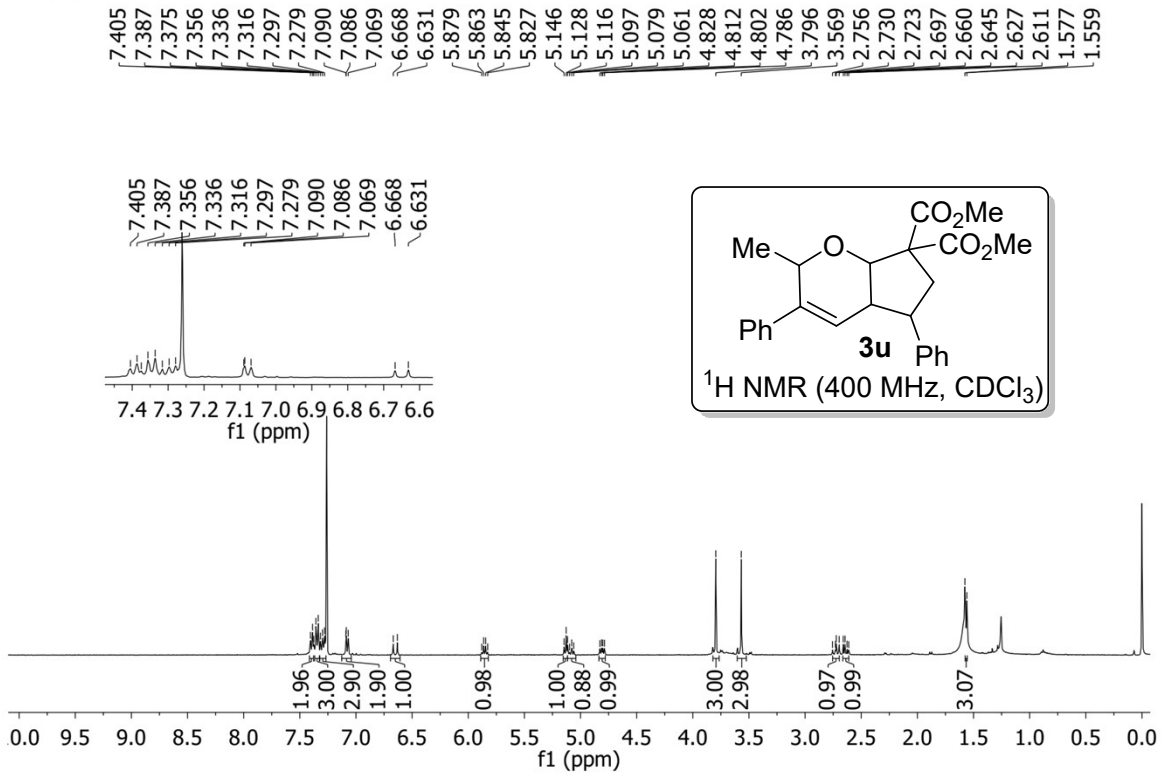
MM-444A-1H.1.fid



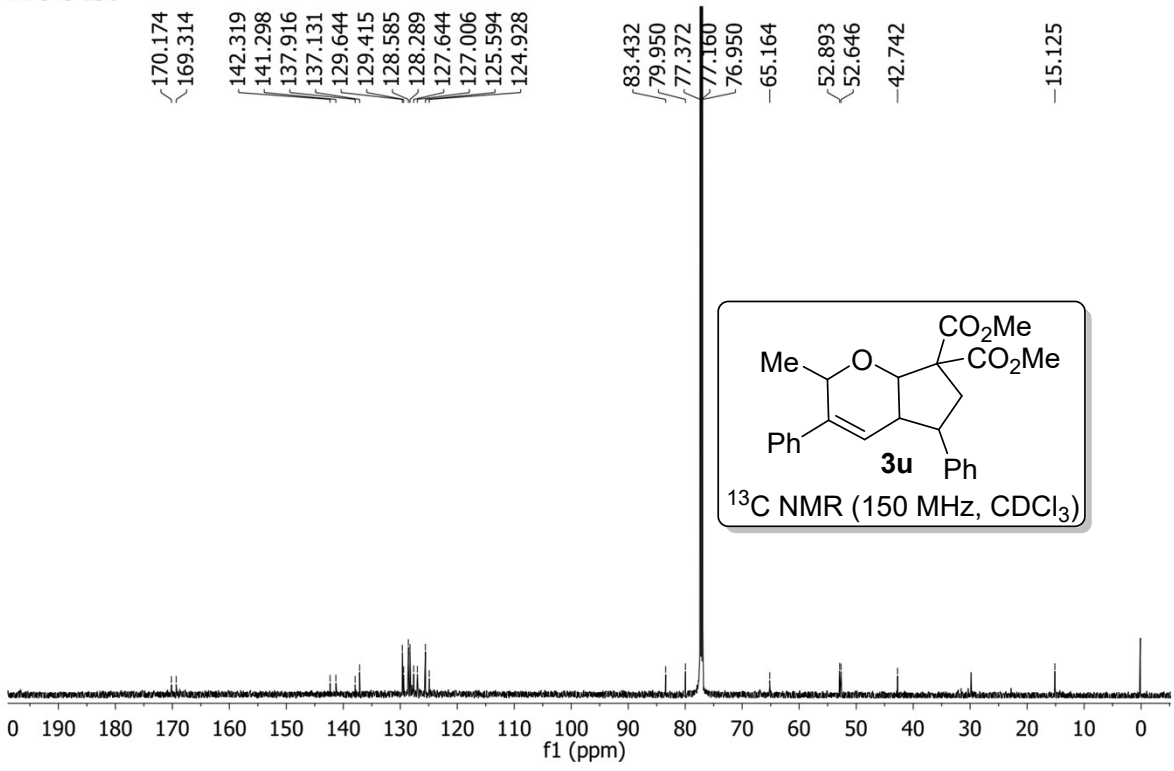
MM-444-13C



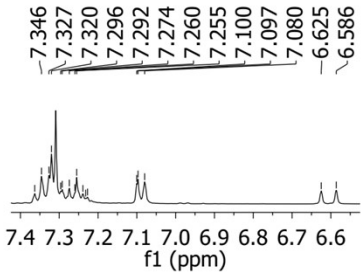
MM-345-A-1H

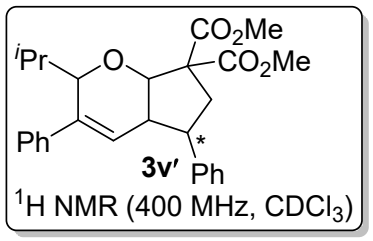


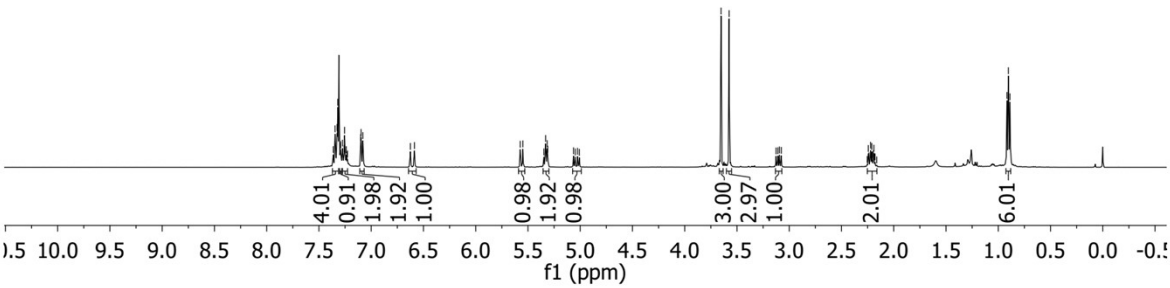
MM-345-13C



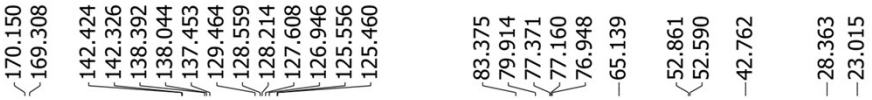
MM-401-A-1H

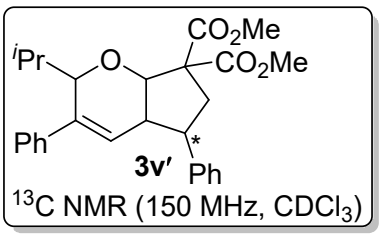


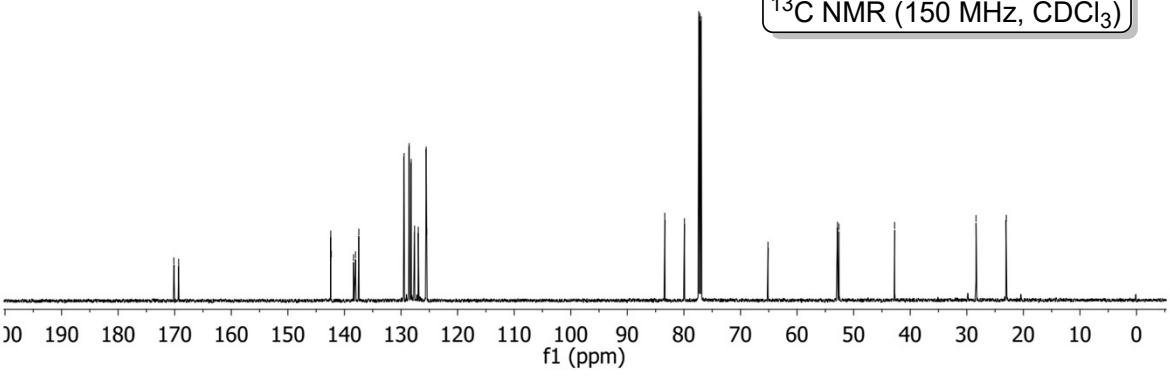




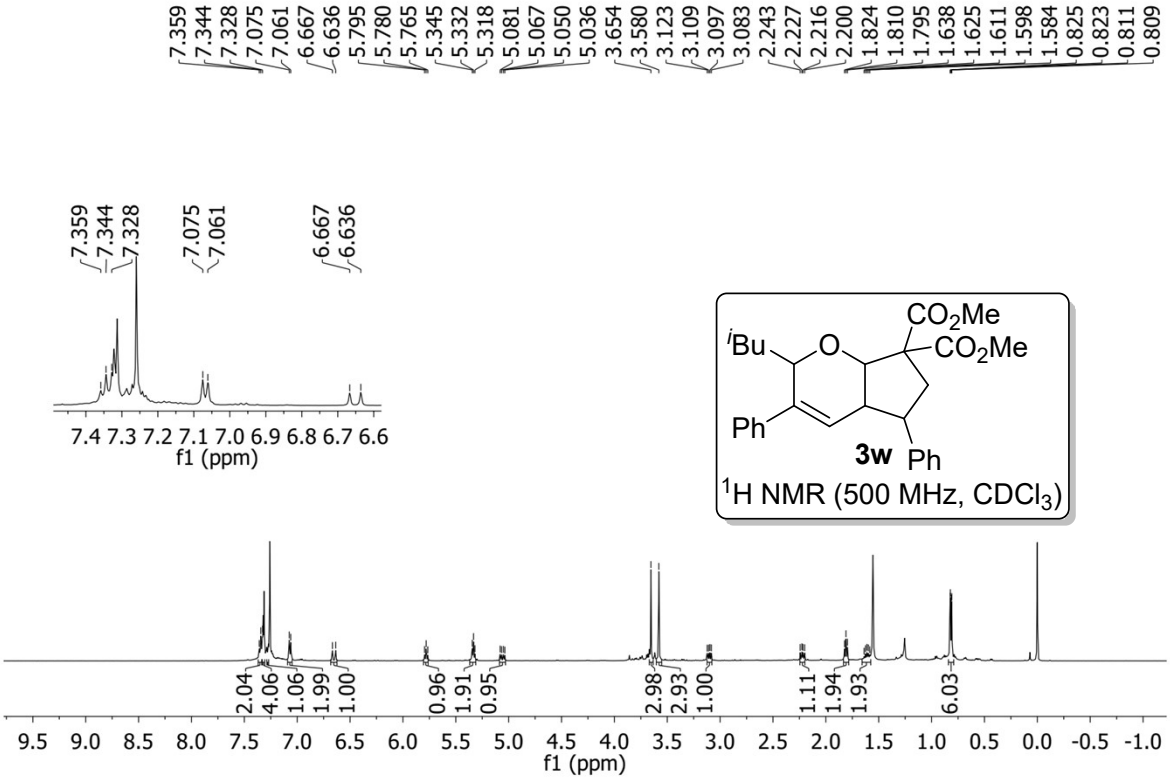
MM-401-A-13C



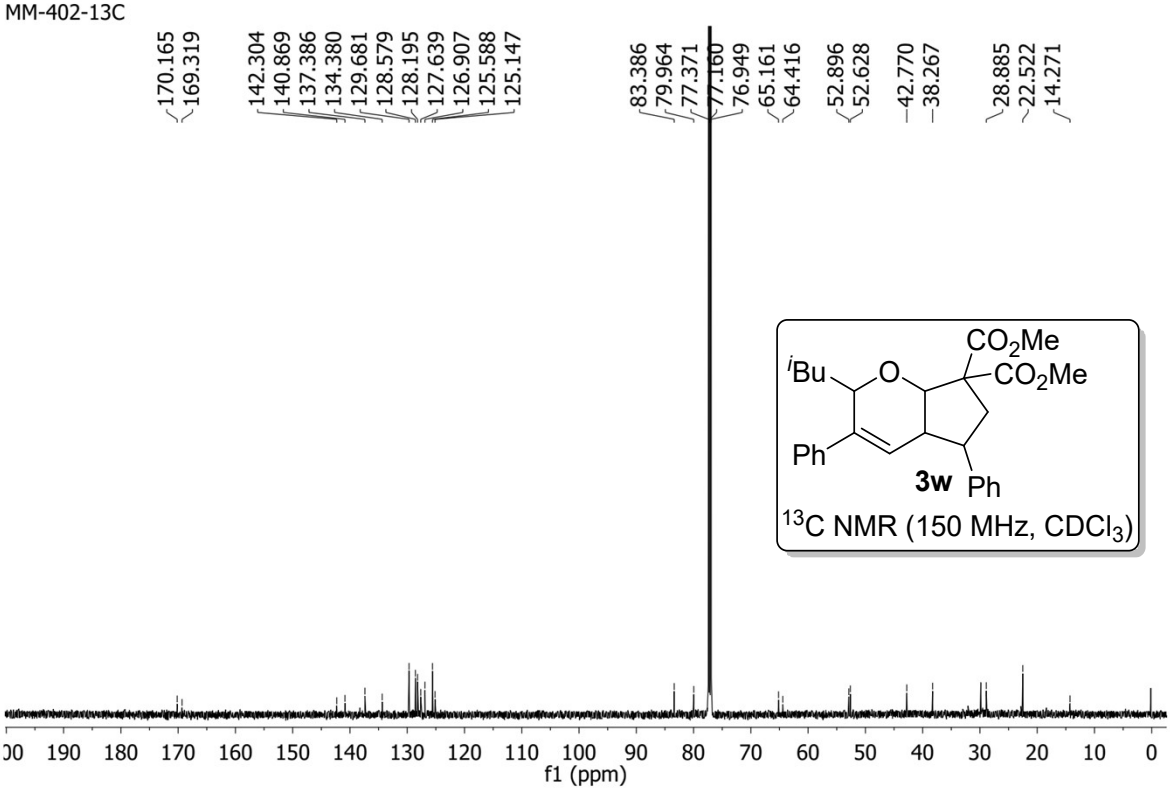


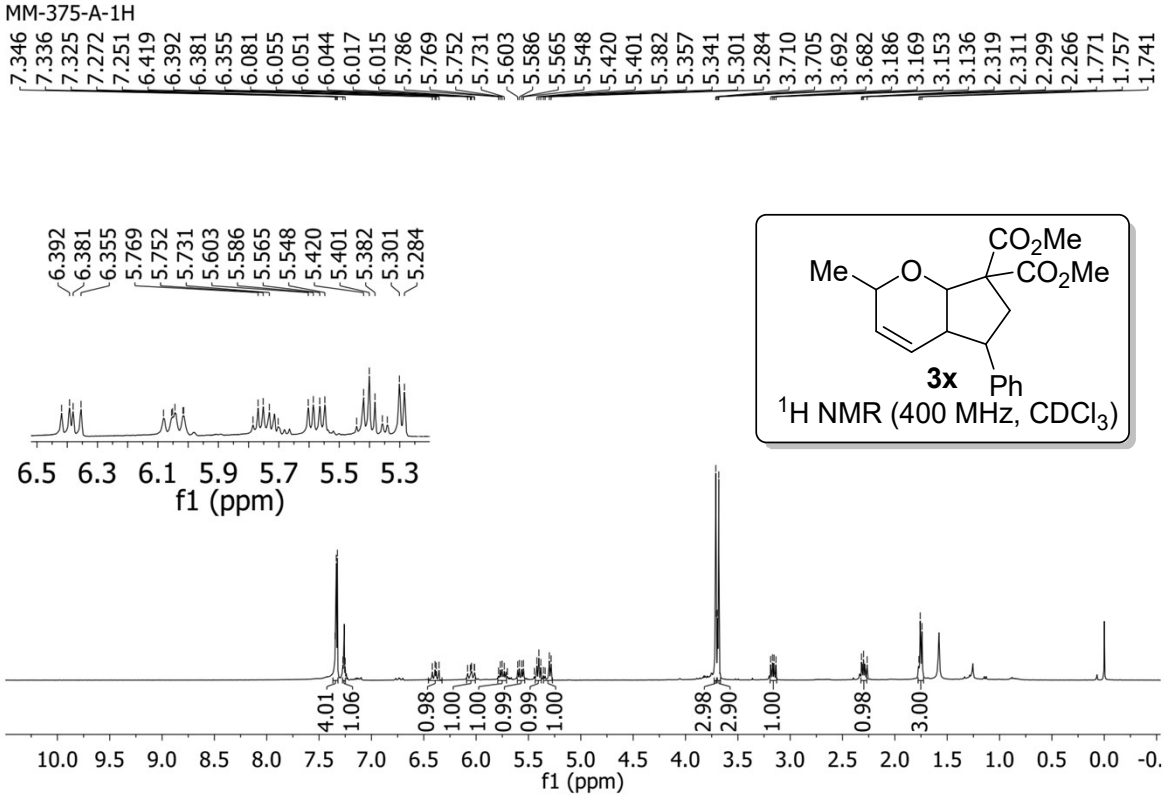


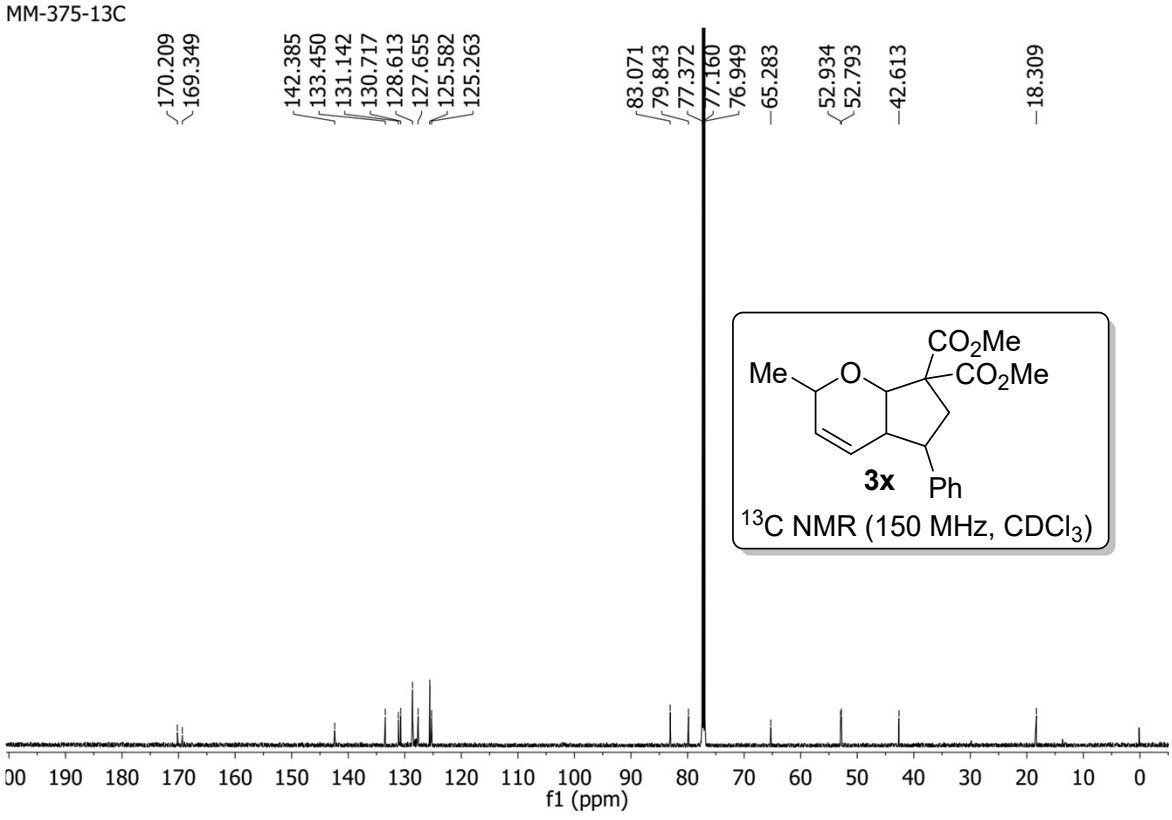
MM-402-1H



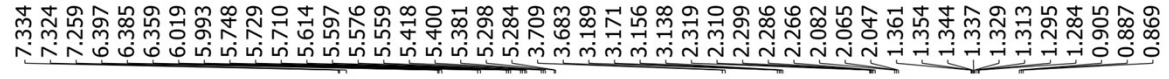
MM-402-13C

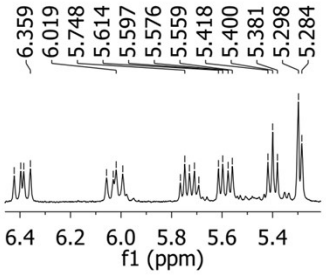


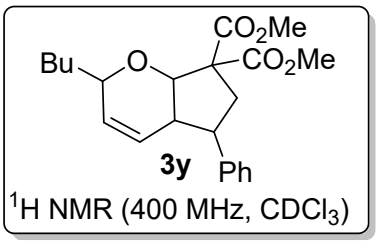

MM-375-A-1H
7.346 7.336 7.325 7.272 7.251 6.419 6.392 6.381 6.355 6.081 6.055 6.051 6.044 6.017 6.015 5.786 5.769 5.752 5.731 5.603 5.586 5.565 5.548 5.420 5.401 5.382 5.357 5.341 5.301 5.284 3.710 3.705 3.692 3.682 3.186 3.169 3.153 3.136 2.319 2.311 2.299 2.266 1.771 1.757 1.741
6.392 6.381 6.355 5.769 5.752 5.731 5.603 5.586 5.565 5.548 5.420 5.401 5.382 5.301 5.284
6.5 6.3 6.1 5.9 5.7 5.5 5.3
f1 (ppm)
Me O CO2Me CO2Me
3x Ph
1H NMR (400 MHz, CDCl3)
4.01 1.06 0.98 1.00 1.00 0.99 0.99 1.00 2.98 2.90 1.00 0.98 3.00
10.0 9.5 9.0 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
f1 (ppm)


MM-375-13C
170.209 169.349 142.385 133.450 131.142 130.717 128.613 127.655 125.582 125.263 83.071 79.843 77.372 77.160 76.949 65.283 52.934 52.793 42.613 18.309
Me O CO2Me CO2Me
3x Ph
13C NMR (150 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

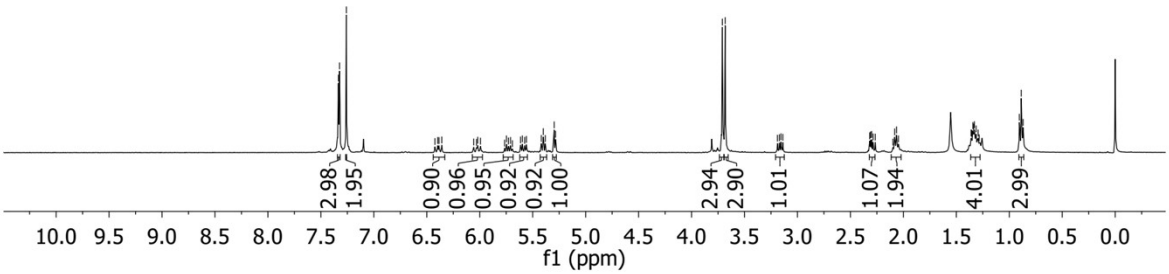
MM-385-1H



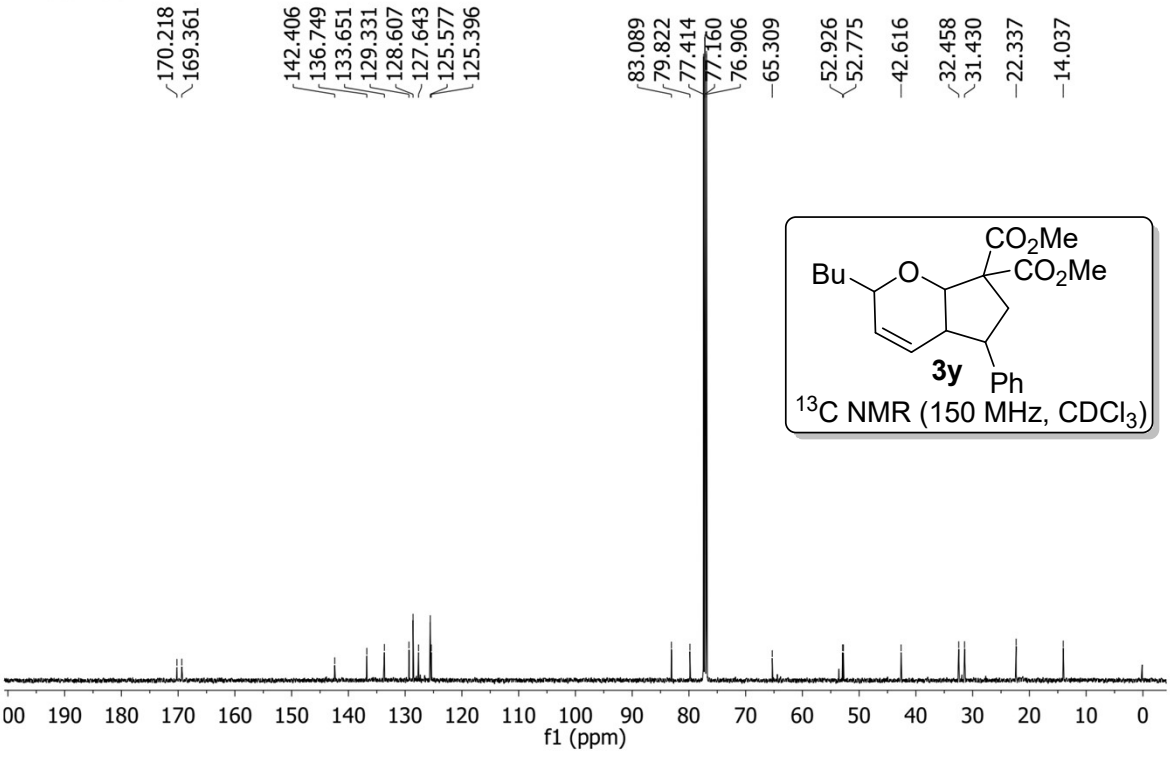




^{1}H NMR (400 MHz, $CDCl_3$)

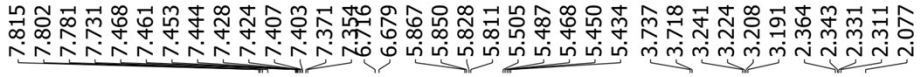


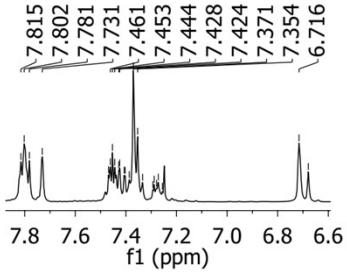
MM-385-13C

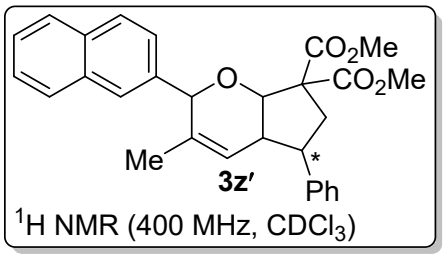


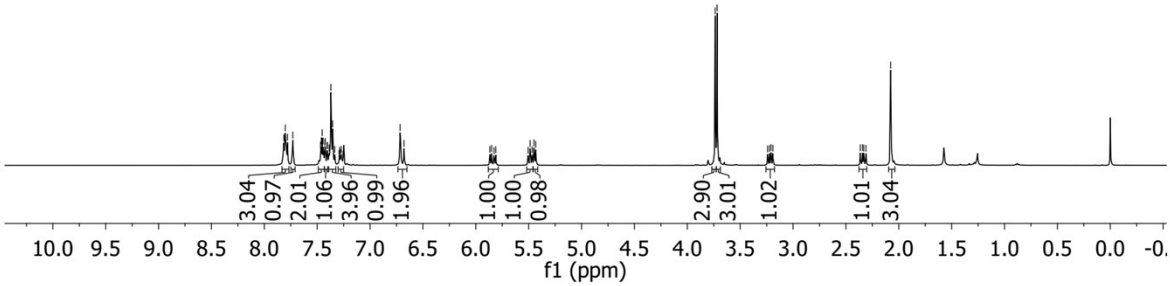
^{13}C NMR (150 MHz, $CDCl_3$)

MM-460-1H

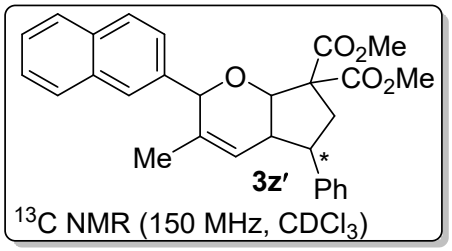


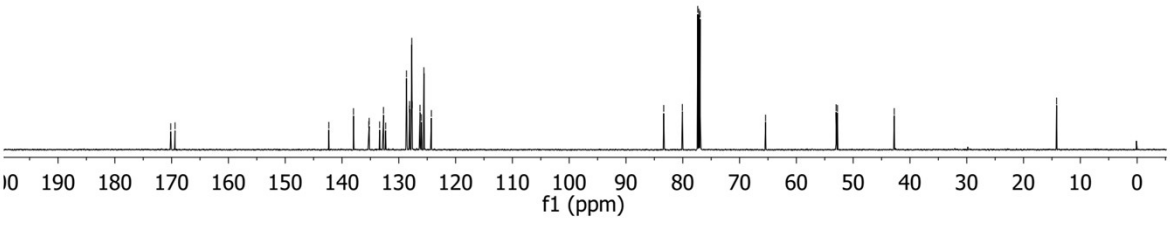




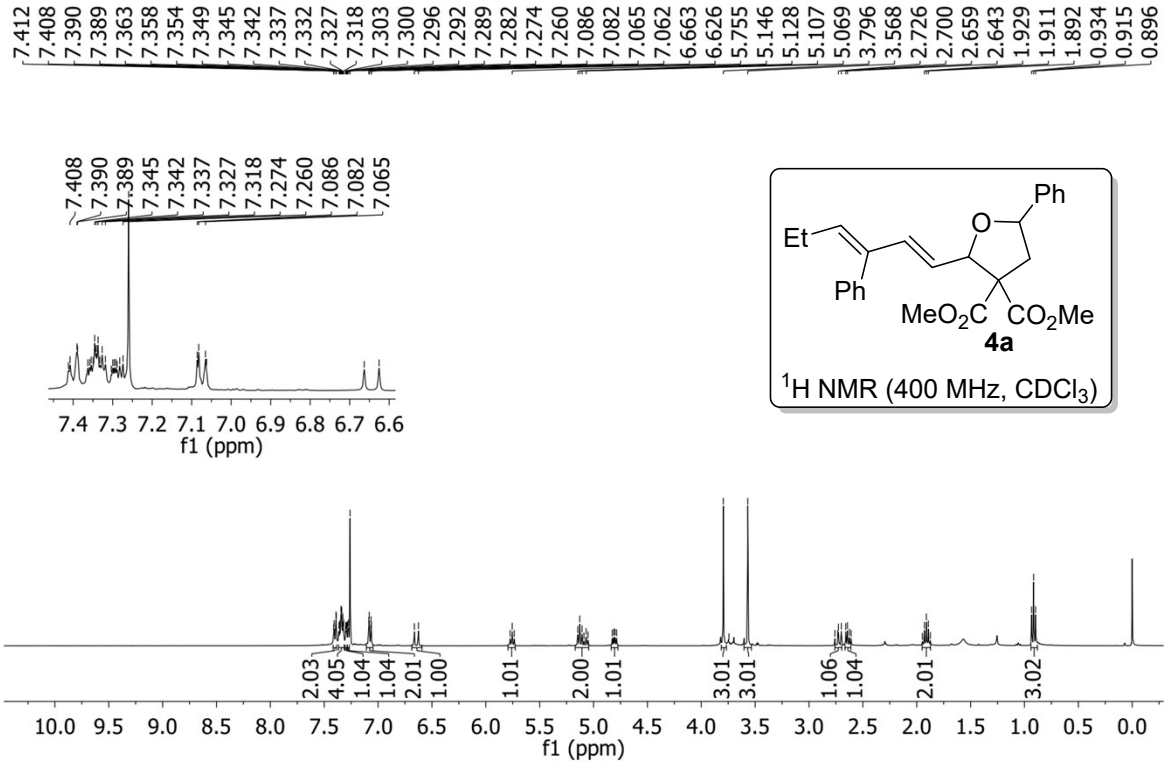


MM-460-13C

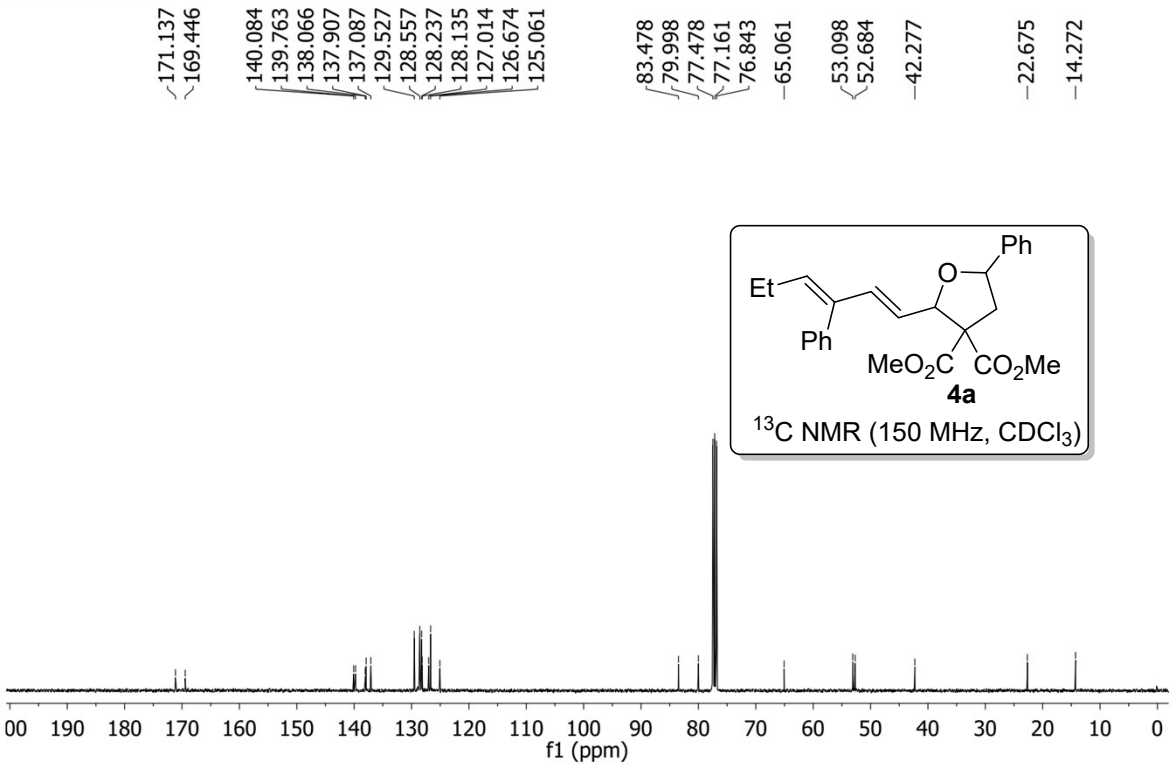




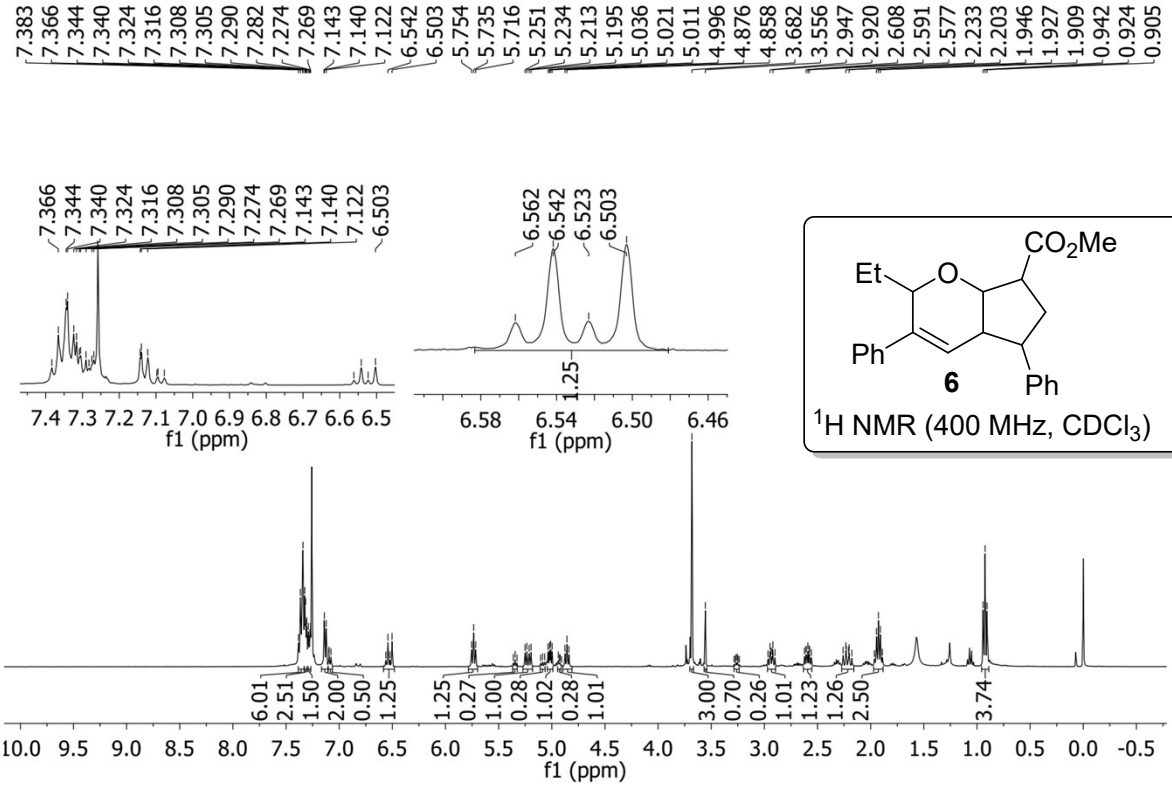
MM-343-B-1H



MM-343-B-13C



MM-KRA-1H



MM-KRA-13C