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Supporting Information

Tribromide Enabled Step-up Generation of Spirolactams from Esters Employing Oxidative Dearomatization of Arenols

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TABLE OF CONTENTS

A. General Experimental

General Setup: Procedures employing commercially available nitrogen, Tarsons magnetic bead, Remi 5MLH stirrer and borosilicate glassware and/or moisture-sensitive materials were performed with anhydrous solvents using standard inert atmosphere techniques (atmosphere of anhydrous nitrogen or argon). Room temperature (rt) typically ranged between 25–30 °C, depending on the time of day.

NMR Spectroscopy: ^{1}H, ^{13}C{^{1}H}, ^{19}F spectra were recorded at 400 MHz, 100 MHz and 376 MHz respectively using a Bruker Advance spectrometer (400 MHz). Spectra were recorded at 298 K (25 °C) on the Bruker. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to residual solvent peaks. Chemical shifts are reported in parts per million (ppm) relative to residual chloroform (δ = 7.28 ppm, ^{1}H; 77.05 ppm, ^{13}C). All ^{13}C{^{1}H} resonances are assumed to be singlets, unless stated otherwise. Coupling constants, J, reported in Hertz (Hz), were calculated using Mestrenova to the nearest 0.1 Hz. The following abbreviations (and their combinations) are used to label the multiplicities: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), and m (multiplet).

Infrared Spectroscopy: Infrared (IR) spectra of neat compounds were recorded over the range 4000–650 cm^{-1} using a Shimadzu FTIR Spectrum 100 ATR-FTIR spectrometer. Peaks are reported in cm^{-1}.

Mass Spectrometry: Electrospray ionisation (ESI+) spectra were recorded on a Waters Xevo G2- XS QTof/Tof and 6200 series TOF/6500 series Q-TOF B.09.00 (B9044.1SP1) mass spectrometer with an orthogonal Z-spray-electrospray interface on a micro-mass spectrometer. Data are reported in the form of m/z (intensity relative to the base peak = 556.2771).

Chromatography: Analytical thin-layer chromatography was performed on Merck silica gel 60 F$_{254}$ aluminium-backed plates. Visualisation was accomplished with UV light (long range), iodine (I$_2$) on silica, ethanolic acidic vanillin solution and/or aqueous basic potassium permanganate (KMnO$_4$). Flash column chromatography (normal) was performed using high purity grade silica gel, pore size 60 Å, 100-200 mesh particle size (Sigma-Aldrich, Cat. No. 288594).

Crystal for X-ray Sample Preparation: Crystal suitable for X-ray were grown by dissolving the sample in a solvent which is soluble in CH_2Cl_2 and a second chamber placed outside containing a solvent which the compound is not soluble in distilled petroleum ether. The solvents slowly mixed causing crystallisation.

Crystallography: Single-crystal X-ray diffraction data were collected with a Rigaku X-ray diffractometer equipped with a micro-focus sealed X-ray tube and HyPix3000 CCD a CCD area detector and operated at 250 W power (50 kV, 0.8 mA) to generate Mo Kα radiation (λ = 0.71073 Å) and Mo Kα radiation (λ = 0.71073Å) at 298 K. The crystals were placed on top of a nylon Cryoloop (Hampton research) and then mounted in the diffractometer. Samples were initially scanned to obtain preliminary unit cell parameters and to assess the mosaicity (breadth of spots between frames) of the crystal. CrysAlisPro program software was used suite to carry out overlapping φ and ω scans at detector (2θ) settings (2θ, ~6 to ~60°with 0.3° scans in ω and 10 s per frame exposures). After the data collection, all the reflections were sampled from all regions of the Ewald sphere to re-determine the unit cell parameters for data integration. CrysAlisPro software was also used for the data integration with a narrow frame algorithm. SCALE3 ABSPACK3 scaling algorithm program was used for the subsequent data correction for adsorption. The structure was solved by a direct method and refined using the SHELXL 2016 software suite. Atoms were located from an iterative examination of difference F-maps following least-squares refinements of the earlier models. The final model was refined anisotropically (if the number of data permitted) until full convergence was achieved. The ellipsoids in ORTEP diagrams are displayed at the 50% probability level unless noted.

Polarimeter: Optical rotations were recorded on an AUTOPOL V digital polarimeter at 589 nm and are recorded as $[\alpha]_D^T$ (concentration in grams/mL solvent).

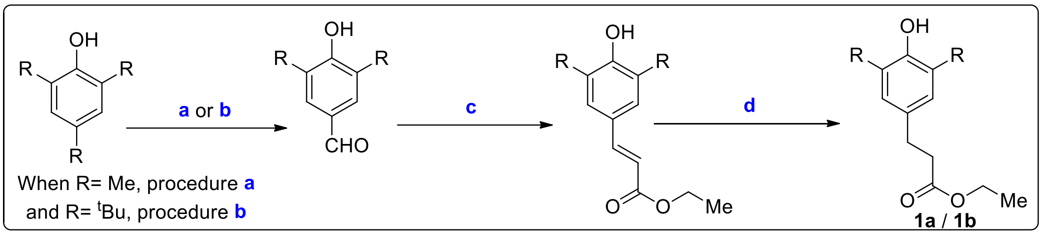
Solvents: Reaction solvents are dried following standard procedure. Tetrahydrofuran (THF), toluene (PhMe), methanol (MeOH), ethanol (EtOH), n-hexane, and tert-butanol (^{t}BuOH) are dried over sodium metal. Acetonitrile (MeCN), dichloromethane (DCM) and dichloroethane (DCE) were dried by phosphorus pentoxide (P_2O_5). Ethylacetate (EtOAc) and acetone were dried by potassium carbonate (K_2CO_3). Dimethyl formamide (DMF) and dimethyl sulfonyloxide (DMSO) were dried over calcium hydride (CaH_2) and stored all the solvent over 4 Å molecular sieves. Deuterated chloroform ($CDCl_3$) was used as received. Solvents for filtration, transfers, chromatography, including acetonitrile (MeCN), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), diethyl ether (Et_2O), ethyl acetate (EtOAc), hexane, methanol (MeOH), and 40–60° petroleum ether (petrol) were used after distillation.

Chemicals: Chemicals purchased from commercial suppliers were used as received. Mostly used Avra, HIMEDIA, Sigma, TCI chemicals.

Nomenclature: Atom numbers shown in chemical structures herein correspond to the IUPAC nomenclature, which was used to name each compound.

B. Preparation of Starting Materials

B.1.General Procedure for Synthesis of ethyl 3-(4-hydroxy-3,5-dialkylphenyl)propanoate(1a, 1b)



Reagents a) $K_2Cr_2O_7$, MeOH, H_2O, glacial AcOH. (b) $CHCl_3$, 10% aqueous NaOH solution, 60 ºC, 7 h, 65%. (c) $Ph_3P{=}CHCOOEt$, DCM, rt, 5 h. (d) H_2/ 10% Pd(C), high pressure, 2 h, 95%.

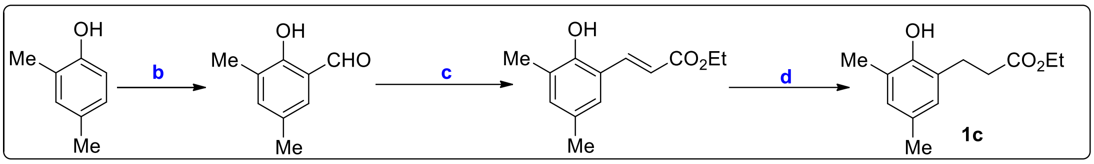
Synthetic procedure a: To a stirred methanolic solution (20 mL) of 2,4,6-trimethylphenol (1.36 g) aqueous solution (100 mL) of $K_2Cr_2O_7$ (3 g) was added. Then glacial AcOH (10 mL) was added dropwise. After the complete addition the reaction mixture was left for stirring for next 24 h at room temperature. White solid compound 4-hydroxy-3,5-dimethylbenzaldehyde was isolated by filtration and recrystallisation by aqueous MeOH.

Synthetic procedure b: To a stirred ethanolic solution (40 mL) of 2,6-di-tert-butylphenol (10 g) aqueous solution (30 mL) of NaOH (20 g) was added. Then $CHCl_3$ (18 mL) was added dropwise. After the complete addition of chloroform, it was left for stirring for next 6 h at 60 ºC.

Synthetic procedure c: The 2,6-dialkyl-4-hydroxy-benzaldehyde (1g, 6 mmol) was treated with Wittig salt ($Ph_3P{=}CHCOOEt$) (3.4 g, 9 mmol) in DCM at 0 ºC. The reaction mixture was allowed to stir for 4 h at room temperature. The reaction was quenched with water and the organic layer was extracted with DCM. The organic layer was washed with brine solution, dried over sodium sulphate, then concentrated over reduced pressure. The crude mixture was subjected to column chromatography over silica gel using 15% EtOAc to deliver (E)-ethyl 3-(4-hydroxy-3,5-alkylphenyl)acrylate (1.3 g, 90%) as yellow liquid $R_f = 0.5$ (20% EtOAc in petroleum ether).

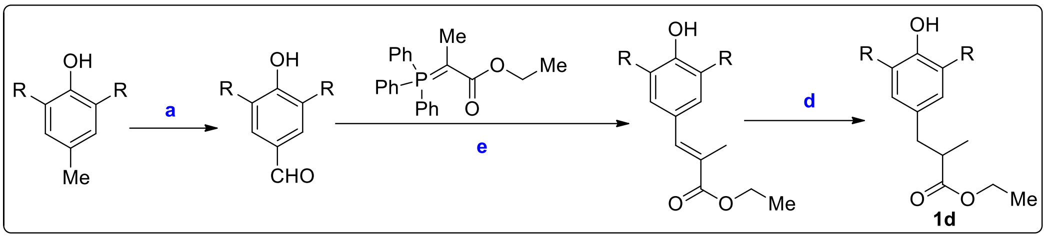
Synthetic procedure d: To a solution of (E)-ethyl 3-(4-hydroxy-3,5-alkylphenyl)acrylate (1.23 g, 0.005 mol) in MeOH, 10% Pd/C was added. After being stirred under hydrogen in high pressure reactor (6-8 bar) at room temperature for 4 h, then the reaction mixture was filtered by silica filtering-column to give ethyl 3-(4-hydroxy-3,5-alkylphenyl)propanoate (**1a** or **1b**) as a colourless liquid (1.12 g, 90%). Liquid $R_f = 0.5$ (20% EtOAc in petroleum ether).

B.2.General Procedure for Synthesis of ethyl 3-(2-hydroxy-3,5-dimethylphenyl)propanoate (1c)



Note: Compound ethyl 3-(2-hydroxy-3,5-dimethylphenyl) propanoate was synthesized according to the previously mentioned procedures b, c, and d.

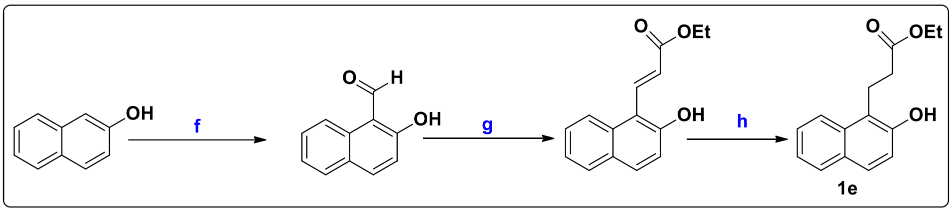
B.3.General Procedure for Synthesis of ethyl 3-(4-hydroxy-3,5-alkylphenyl)-2-methylpropanoate (1d)



Synthetic procedure e: The 2,6-dialkyl-4-hydroxy-benzaldehyde (1g, 6 mmol) was treated with Wittig salt ($Ph_3P{=}CHCH_3COOEt$) (3.4 g, 9 mmol) in DCM at 0 °C. The reaction mixture was allowed to stir for 4 h at room temperature. The reaction was quenched with water and the organic layer was extracted with DCM. The organic layer was washed with brine solution, dried over sodium sulphate, then concentrated over reduced pressure. The crude mixture was subjected to column chromatography over silica gel using 10% EtOAc to deliver (E)-ethyl 3-(4-hydroxy-3,5-alkylphenyl)-2-methylacrylate (1.3 g, 90%) as yellow liquid $R_f = 0.7$ (20% EtOAc in petroleum ether).

Note: Procedures a and d are mentioned in the previous section.

B.4.General Procedure for Synthesis of ethyl 3-(2-hydroxynaphthalen-1-yl)propanoate (1e)



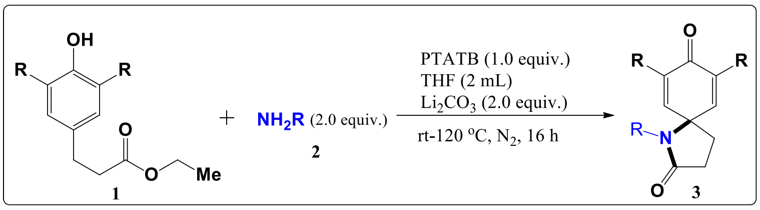
Reagents (f) $CHCl_3$, 10% aqueous NaOH solution, 60 °C, 7 h, 65%. (g) $Ph_3P{=}CHCOOEt$, DCM, rt, 5 h. (h) H_2/ 10% Pd(C), high pressure, 2 h, 95%.

Synthetic procedure f: To a stirred ethanolic solution (40 mL) of naphthalen-2-ol (10 g) aqueous solution (30 mL) of NaOH (20 g) was added. Then $CHCl_3$ (18 mL) was added dropwise. After the complete addition of chloroform, it was left for stirring for next 6 h at 60 °C.

Synthetic procedure g: The 2-hydroxy naphthaldehyde (1g, 6 mmol) was treated with Wittig salt ($Ph_3P{=}CHCOOEt$) (3.4 g, 9 mmol) in DCM at 0 °C. The reaction mixture was allowed to stir for 4 h at room temperature. The reaction was quenched with water and the organic layer was extracted with DCM. The organic layer was washed with brine solution, dried over sodium sulphate, then concentrated over reduced pressure. The crude mixture was subjected to column chromatography over silica gel using 15% EtOAc to deliver (E)-ethyl 3-(2-hydroxynaphthalen-1-yl)acrylate (1.3 g, 90%) as yellow liquid $R_f = 0.5$ (20% EtOAc in petroleum ether).

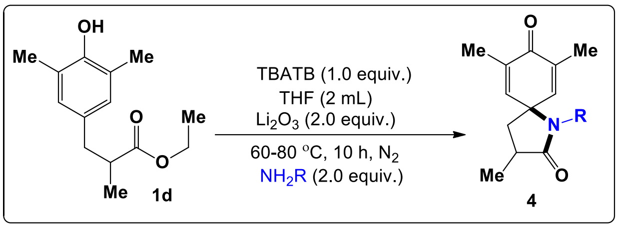
Synthetic procedure h: To a solution of (E)-ethyl 3-(2-hydroxynaphthalen-1-yl)acrylate (1.23 g, 0.005 mol) in MeOH, 10% Pd/C was added. After being stirred under hydrogen in high pressure reactor (6-8 bar) at room temperature for 4 h, then the reaction mixture was filtered by silica filtering-column to give ethyl 3-(2-hydroxynaphthalen-1-yl)propanoate as a colourless solid (1.12 g, 90%). Liquid $R_f = 0.5$ (20% EtOAc in petroleum ether).

C.1. General Procedure for Synthesis of Azaspirodienone for Phenols



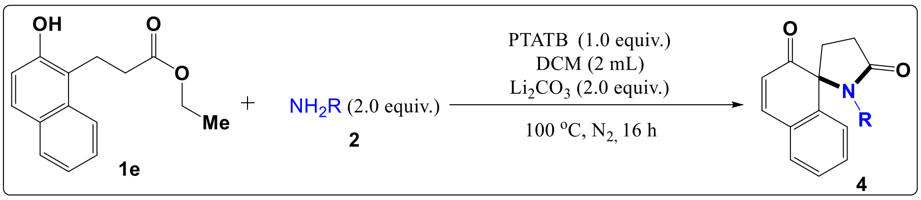
To an oven-dried reaction vial, ethyl 3-(4-hydroxy-3,5-alkylphenyl)propanoate (**1a, 1b, 1c**) (0.1 mmol) was dissolved in 2 mL of THF and the reaction vial was then sealed and flushed with nitrogen. Then 2.0 equiv. of Li_2CO_3 (0.2 mmol) and 2.0 equiv. primary amine (**2**, 0.2 mmol) were added to the reaction mixture and stirred for 10 min at room temperature. Then 1.0 equiv. of PTATB (0.1 mmol) was added and the reaction mixture was then stirred at room temperature to 120 °C (depending on the primary amines) until TLC revealed complete conversion of the starting material. The reaction mixture was then allowed to cool and diluted with H_2O and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, concentrated under vacuum, and purified by column chromatography using 100– 200 mesh size silica gels (petroleum ether/EtOAc) to afford the corresponding product.

C.2.General Procedure for Synthesis of Azaspirodienone for Substituted Phenols



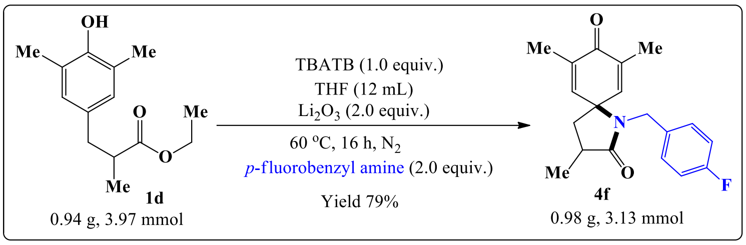
To an oven-dried reaction vial, ethyl 3-(4-hydroxy-3,5-dimethylphenyl)-2-methylpropanoate (**1d**) (0.1 mmol) was dissolved in 2 mL of THF and the reaction vial was then sealed and flushed with nitrogen. Then 2.0 equiv. of Li_2CO_3 (0.2 mmol) and 2.0 equiv. primary amine (**2**, 0.2 mmol) were added to the reaction mixture and stirred for 10 mins at room temperature. Then 1.0 equiv. of TBATB (0.1 mmol) was added and the reaction mixture was then stirred at room temperature to 60 °C -80 °C (depending on the primary amines) until TLC revealed complete conversion of the starting material. The reaction mixture was then allowed to cool and diluted with H_2O and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, concentrated under vacuum, and purified by column chromatography using 100– 200 mesh size silica gels (petroleum ether/EtOAc) to afford the corresponding product.

C.3.General Procedure for Synthesis of Azaspirodienone for Naphthols



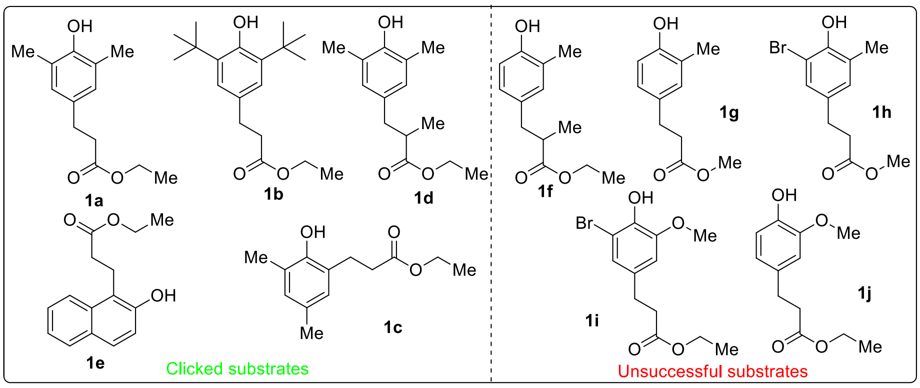
To an oven-dried reaction vial, ethyl 3-(2-hydroxynaphthalen-1-yl)propanoate (**1e**) (0.1 mmol) was dissolved in 2 mL of DCM and the reaction vial was then sealed and flushed with nitrogen. Then 2.0 equiv. of Li_2CO_3 (0.2 mmol) and 2.0 equiv. primary amine (**2**, 0.2 mmol) were added to the reaction mixture and stirred for 10 min at room temperature. Then 1.0 equiv. of PTATB (0.1 mmol) was added and the reaction mixture was then stirred at 60 °C- 100 °C (depending on the primary amines) until TLC revealed complete conversion of the starting material. The reaction mixture was then allowed to cool and diluted with H_2O and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, concentrated under vacuum, and purified by column chromatography using 100–200 mesh size silica gels (petroleum ether/EtOAc) to afford the corresponding product.

D. Typical Procedure for the Gram-scale Synthesis of 4f

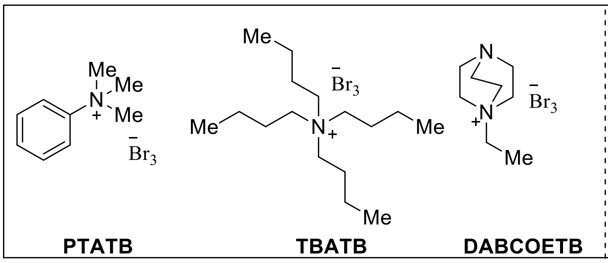


To an oven-dried reaction vial, ethyl 3-(4-hydroxy-3,5-dimethylphenyl)-2-methylpropanoate (**1d**) (3.97 mmol) was dissolved in 12 mL of THF and the reaction vial was then sealed and flushed with nitrogen. Then 2.0 equiv. of Li_2CO_3 (7.94 mmol) and 2.0 equiv. primary amine (7.94 mmol) were added to the reaction mixture and stirred for 10 min at room temperature. Then 1.0 equiv. of TBATB (3.97 mmol) was added and the reaction mixture was then stirred at room temperature to 60 °C until TLC revealed complete conversion of the starting material. The reaction mixture was then allowed to cool and diluted with H_2O and extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, concentrated under vacuum, and purified by column chromatography using 100– 200 mesh size silica gels (petroleum ether/EtOAc) to afford the corresponding product **4f** (0.98 g, 3.13 mmol).

E.1. Scope of Arenols:



E.2. Scope of QATBs:

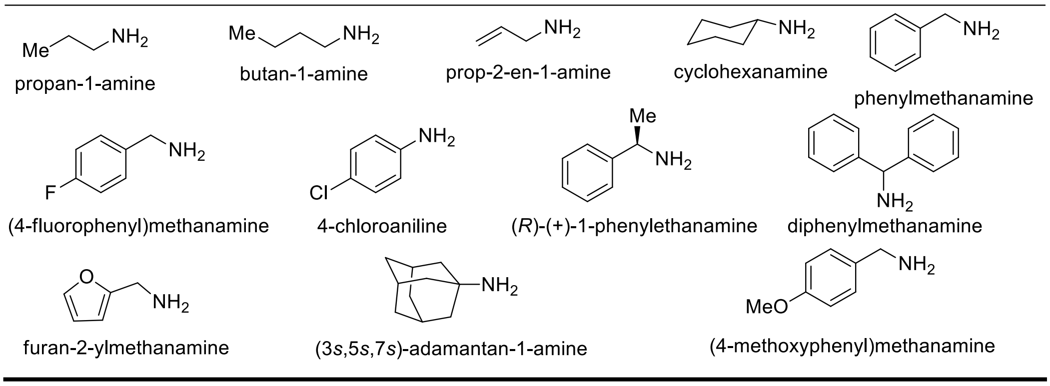


PTATB = Phenyl trimethyl ammonium tribromide

TBATB = Tetrabutyl ammonium tribromide

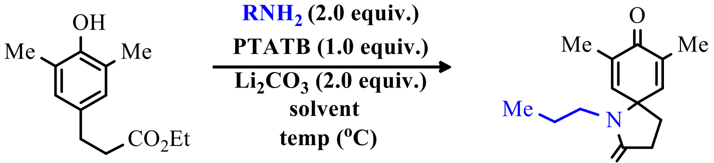
DABCOETB = 1,4-diazabicyclo[2.2.2]octane-1-ethyl ammonium tribromide

E.3. Scope of Amines:



F. Reaction Optimisation:

Table S1 Solvent optimisation[a]

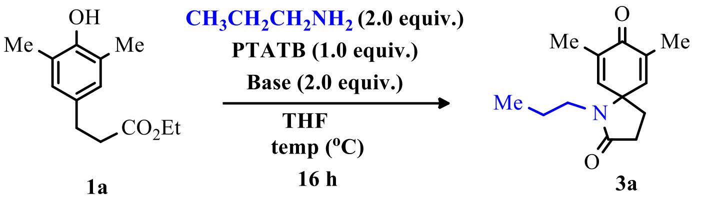


1a **3a**

entry	solvent	base	nucleophile (2)	time (h)	temp (^{o}C)	recoverd 1a (%)	yield of 3a
1.	**THF**	**Li_2CO_3**	**$CH_3CH_2CH_2NH_2$**	”	**100**	**0**	**86**
2.	THF	”	benzyl amine	10	120	0	84 (**3e**)
3.	DCE	”	$CH_3CH_2CH_2NH_2$	16	60	trace	60
4.	Benzene	”	”	”	”	100	0
5.	Toluene	”	”	”	”	100	0
6.	DCM	”	”	”	reflux	trace	72
7.	DMF	”	”	”	60	80	0
8.	Acetonitrile	”	”	”	”	0	66
9.	DMSO	”	”	”	”	85	0
10.	Et_2O	”	”	”	reflux	95	trace
11.	MeOH	”	”	”	”	90[c]	0
12.	EtOH	”	”	”	”	100	0

[a]Unless otherwise noted, the reactions were performed using **1a** (0.1 mmol), PTATB (0.1 mmol), Li_2CO_3 (0.2 mmol), and amine (0.2 mmol) in each solvent (2 mL) at a given temperature for a given period of time. [b]Isolated yield based on ethyl 3-(4-hydroxy-3,5-dimethyl phenyl)propanoate **1a**. [c]Isolated yield decreases due to transesterification of **1a.**

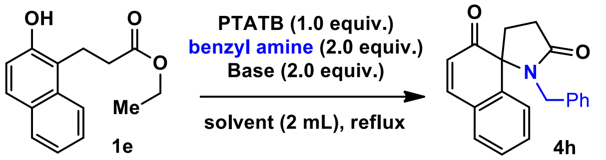
Table S2 Base and reaction temperature optimisation[a]



entry	solvent	base	nucleophile (2)	time (h)	temp (°C)	recoverd 1a (%)	yield of 3a (
1.	THF	K_2CO_3	$CH_3CH_2CH_2NH_2$	16	40	69	25
2.	THF	”	”	”	60	52	45
3.	THF	Cs_2CO_3	”	”	”	0	71
4.	THF	KO^{t}Bu	”	”	”	90	0
5.	THF	NaOMe	”	”	”	96	
6.	THF	KOH	”	”	”	0[c]	0
7.	THF	NaOH	”	”	”	0	0
8.	THF	Li_2CO_3	”	”	100	0	86
9.	THF	”	”	10	120	0	78

[a]Unless otherwise noted the reactions were performed using **1a** (0.1 mmol), PTATB (0.1 mmol), base (0.2 mmol), and propyl amine (0.2 mmol) in THF solvent (2 mL) at a given temperature for a given period. [b]Isolated yield based on ethyl 3-(4-hydroxy-3,5-dimethyl phenyl)propanoate **1a**. [c]**1a** decomposed due to hydrolysis.

Table S3 Reaction optimisation for naphthols[a]



entry	solvent	base	time[h]	temp [°C]	yield of 4h [in %][b]
1.	THF	K_2CO_3	16	40	trace
2.	THF	Li_2CO_3	16	40	26
3.	THF	Cs_2CO_3	16	40	65
4.	THF	Li_2CO_3	10	120	68
5.	DCM	K_2CO_3	16	rt	0
6.	DCM	K_2CO_3	16	40	trace
7.	DCM	Li_2CO_3	16	40	25
8.	DCM	”	16	100	82
9.	DCM	”	10	120	79
10.	Acetonitrile	”	10	reflux	45
11.	Et_2O	”	10	”	0
12.	Toluene	”	10	”	0
13.	DMF	”	10	”	0
14.	MeOH	”	10	”	0

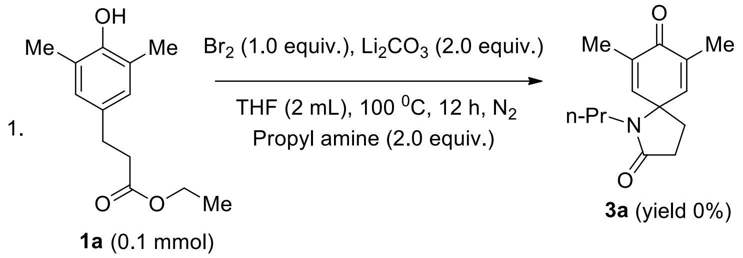
[a]Unless otherwise noted the reactions were performed using **1e** (0.1 mmol), PTATB (0.1 mmol), base (0.2 mmol), and propyl amine (0.2 mmol) in a given solvent (2 mL) at a given temperature for a given period. [b]Isolated yield based on ethyl 3-(4-hydroxy-3,5-dimethyl phenyl)propanoate **1e.**

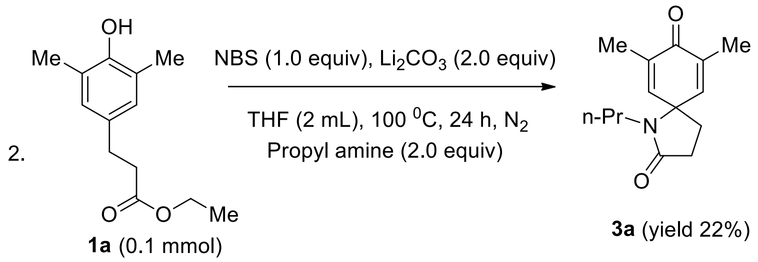
G. Mechanistic Investigation:

To validate a proposed mechanistic pathway for the dearomative spirolactamisation, we performed a series of mechanistic control experiments shown below.

G.1. Reaction with other bromine sources:

To determine the active species for the oxidation of arenols, two control experiments using bromine-based oxidants other than QATB were performed.



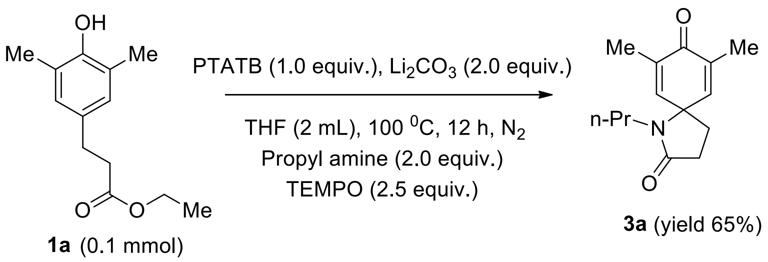


To an oven-dried reaction vial, ethyl 3-(4-hydroxy-3,5-dimethylphenyl)propanoate (**1a**, 0.1 mmol) was dissolved in 2 mL of THF and the reaction vial was then sealed and flushed with nitrogen. Then 2.0 equiv. of Li_2CO_3 (0.2 mmol) and 2.0 equiv. propyl amine (0.2 mmol) were added to the reaction mixture and stirred for 10 min at room temperature. Then 1.0 equiv. of Br_2 (0.1 mmol in THF) (reaction 1) or NBS (0.1 mmol) (reaction 2) was added, and the reaction mixture was then stirred at 100 °C for 12 h and the progress of the reactions were monitored by TLC.

In case of Br_2, however, no oxidation reaction proceeded at all (reaction 1), but oxidation of **1a** was happened in presence of NBS, afforded **3a** of 22% yield in 24 h which suggest the dipole-dipole interactions between arenol and tribromide enhance the oxidation step.

The previous observation insisted us to perform the radical trapping experiment to understand if the reaction proceeded via radical pathway.

G.2. TEMPO experiment:

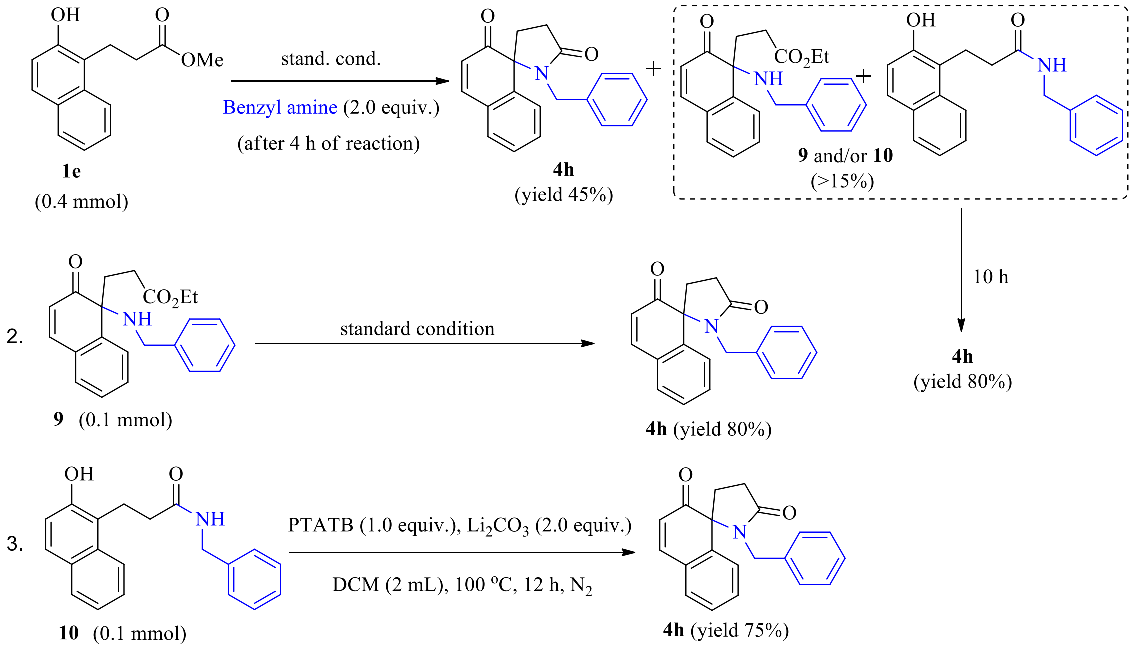


To an oven-dried reaction vial, ethyl 3-(4-hydroxy-3,5-dimethylphenyl)propanoate (**1a**, 0.1 mmol) was dissolved in 2 mL of THF and the reaction vial was then sealed and flushed with nitrogen. Then 2.0 equiv. of Li_2CO_3 (0.2 mmol) and 2.0 equiv. propyl amine (0.2 mmol) were added to the reaction mixture and stirred for 10 min at room temperature. Then 1.0 equiv. of PTATB followed by 2.5 equivalents of

2,2,6,6-tetramethyl-1-piperidinyloxy were added and the reaction mixture was then stirred at 100 °C for 12 h and the progress of the reaction were monitored by TLC. The product **3a** was isolated in a 65% yield, suggesting that this transformation might not proceed through a free radical pathway.

G.3. Detailed study of intermediates:

In case of naphthol, we found amide **10** or amminative dearomatized species **9** as intermediates during the lactamization reaction in presence of benzyl amine (reaction 1). To examine the potentiality of the intermediated products, we further performed some control experiments.



To an oven-dried reaction vial, ethyl 3-(2-hydroxynaphthalen-1-yl)propanoate (**1e**) (0.4 mmol) was dissolved in 4 mL of DCM and the reaction vial was then sealed and flushed with nitrogen. Then 2.0 equiv. of Li_2CO_3 (0.8 mmol) and 2.0 equiv. benzyl amine (0.8 mmol) were added to the reaction mixture and stirred for 10 min at room temperature. Then 1.0 equiv. of PTATB (0.4 mmol) was added and the reaction mixture was then stirred at 100 °C and after 4 h TLC revealed formation of the product **4h** along with two intermediates **9** and **10**. Then the reaction was again stirred at 100 °C for further 10 h for completion of the reaction which was confirmed by TLC.

To establish the reaction mechanism, we further synthesize those two intermediates separately according to the literature reports and under our optimized reaction condition, those two intermediates furnished the corresponding desired product smoothly.

Preparation of intermediate 9: To a well stirred solution of ethyl 3-(2-hydroxynaphthalen-1-yl) propanoate (**1e**) (0.2 mmol) and benzyl amine (0.5 mmol) in dry THF (4 mL), PTATB (0.2 mmol) was added and stirred for 16 h at room temperature. Then the mixture was quenched with H_2O followed by extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, concentrated under vacuum, and purified by column chromatography using 100– 200 mesh size silica gels (petroleum ether/EtOAc) to afford the corresponding product ethyl 3-(1-(benzylamino)-2-oxo-1,2-dihydronaphthalen-1-yl)propanoate **9** (yield 60%) and used in the next step.

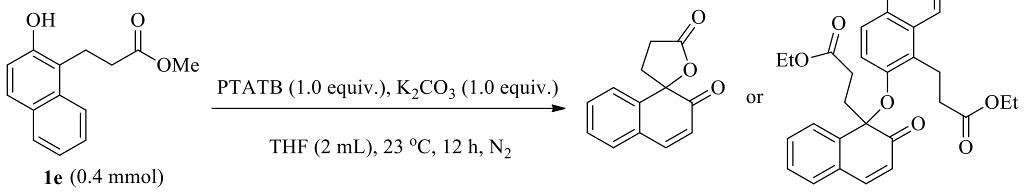
To an oven-dried reaction vial, **9** (0.1 mmol) was dissolved in 2 mL of DCM and the reaction vial was then sealed and flushed with nitrogen. Then 2.0 equiv. of Li_2CO_3 (0.2 mmol) was added to the reaction mixture and stirred for 10 min at room temperature. Then 1.0 equiv. of PTATB (0.1 mmol) was added and the reaction mixture was then stirred at room temperature to 100 °C until TLC revealed complete conversion of the starting material. The reaction mixture was then allowed to cool and diluted with H_2O

and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, concentrated under vacuum, and purified by column chromatography using 100– 200 mesh size silica gels (petroleum ether/EtOAc) to afford the desired product **4h** (yield 80%) (reaction 2).

*Preparation of intermediate **10**:* To a well stirred solution of ethyl 3-(2-hydroxynaphthalen-1-yl) propanoate (**1e**) (0.2 mmol) and benzyl amine (0.5 mmol) in dry DMF (3 mL), BOP (0.2 mmol), TEA (0.22 mmol) and DMAP (0.03 mmol) were added and stirred for 3 h at room temperature. Then the mixture was quenched with H_2O followed by extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, concentrated under vacuum, and purified by column chromatography using 100– 200 mesh size silica gels (petroleum ether/EtOAc) to afford the corresponding product N-benzyl-3-(2-hydroxynaphthalen-1-yl)propanamide **10** (yield 60%) and used in the next step.

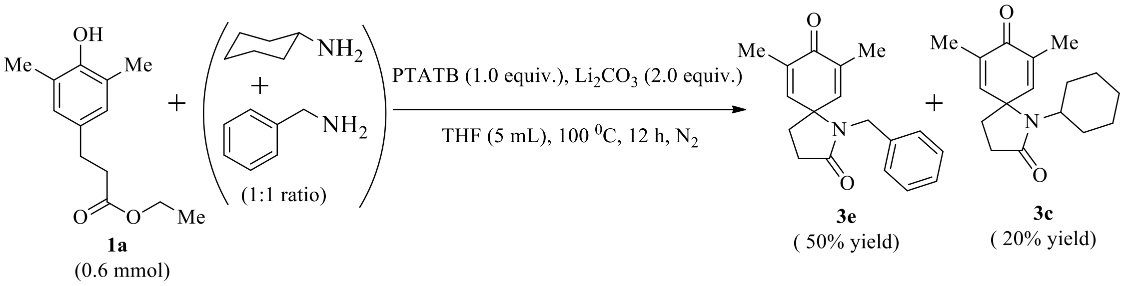
The next step was performed following the procedure mentioned in reaction 3.

G.4. Reaction in absence of amines:



Next, we also wanted to see our methodology in absence of any primary amines. We performed the synthetic procedure following our group's previous report and the compounds were matched with the reported literature (ref. 10b and 10d in manuscript).

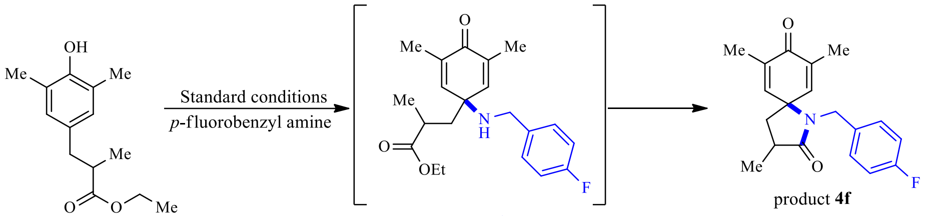
G.5. Competitive reaction between an aliphatic and aromatic amine:



To an oven-dried reaction vial, ethyl 3-(4-hydroxy-3,5-dimethylphenyl)propanoate (**1a**, 0.6 mmol) was dissolved in 5 mL of THF and the reaction vial was then sealed and flushed with nitrogen. Then 2.0 equiv. of Li_2CO_3 (0.2 mmol) and 2.0 equiv. of benzyl amine (1.2 mmol) and 2.0 equiv. of cyclohexyl amine (1.2 mmol) were added to the reaction mixture and stirred for 10 min at room temperature. Then 1.0 equiv. of PTATB (0.6 mmol) was added, and the reaction mixture was then stirred at 100 °C for 12 h and the progress of the reactions were monitored by TLC. The product **3c** and **3e** were isolated in 20% and 50% yield respectively.

G.6. Exploration of the possible pathways for generation of spirolactam using HRMS study at different time intervals:

With the continuation of our expedition on mechanistic outcomes, next, we studied the reaction at different time intervals via performing a series of HRMS studies. For this, to an oven-dried reaction vial, ethyl 3-(4-hydroxy-3,5-dimethylphenyl)-2-methylpropanoate (**1d**) (0.4 mmol) was dissolved in 4 mL of THF and the reaction vial was then sealed and flushed with nitrogen. Then 2.0 equiv. of Li_2CO_3 (0.8 mmol) and 2.0 equiv. of *p*-fluorobenzyl amine (0.8 mmol) were added to the reaction mixture and stirred for 10 min at room temperature. Then 1.0 equiv. of TBATB (0.4 mmol) was added and the reaction mixture was then stirred at 60 °C. In a first instance we took the first aliquot after 30 min from the reaction mixture and then immediately analysed by HRMS to detect the *in situ* generated intermediates.



1d (0.1 mmol)

intermediate7
detected by HRMS through out
the propagation of reaction

(calculated) m/z $[M+H]^+$: 360.1975
(**found**) m/z $[M+H]^+$: 360.1967

product **4f**

(calculated) m/z $[M+H]^+$: 314.1556
(**found**) m/z $[M+H]^+$: 314.1559

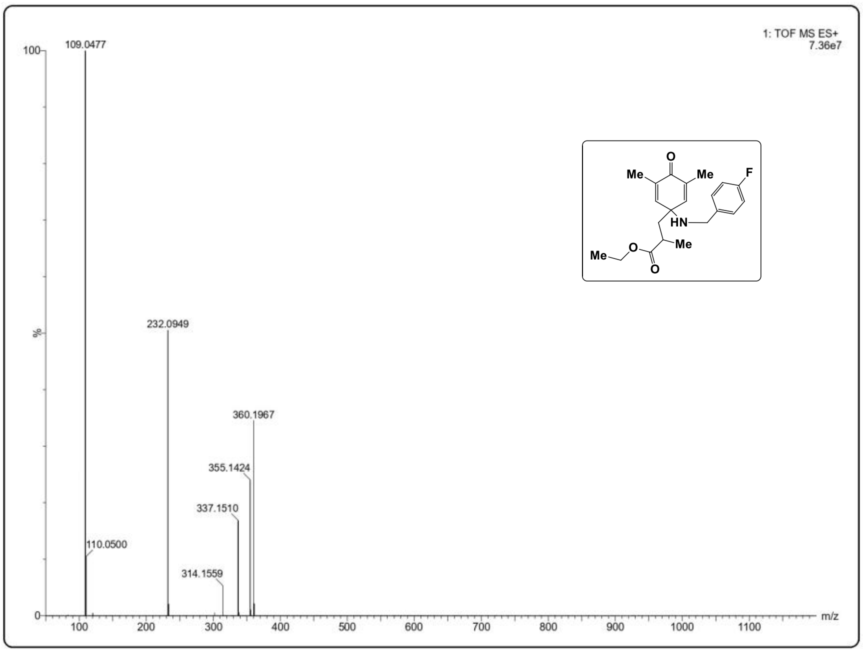
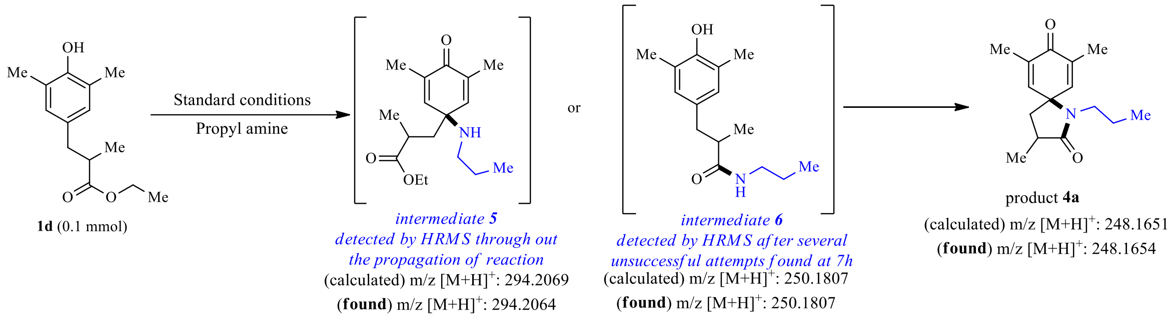


Figure S1 HRMS of the reaction mixture after 30 min showing the formation of dearomative intermediate

From HRMS study we found an intense peak at m/z = $[M+H]^+$ 360.1967 indicating the formation of dearomative intermediate (**IN5**), along with a very small peak of the corresponding product (**4f**) (m/z = $[M+H]^+$ 314.1559). This intermediate peak subsequently got diminished leading to the formation of product **4f** (In case of naphthol substrate **1e**, under the standard reaction condition, we isolated the corresponding dearomative intermediate **9** detected by Control Experiment G.3.).

Note: In case of naphthols, we were able to isolate the intermediates and characterized by NMR spectroscopy but for phenols, it was difficult to isolate the intermediates due to their lower stability under the reaction conditions.



1d (0.1 mmol)

intermediate 5
detected by HRMS through out the propagation of reaction
(calculated) m/z $[M+H]^+$: 294.2069
(**found**) m/z $[M+H]^+$: 294.2064

intermediate 6
detected by HRMS after several unsuccessful attempts found at 7h
(calculated) m/z $[M+H]^+$: 250.1807
(**found**) m/z $[M+H]^+$: 250.1807

product **4a**
(calculated) m/z $[M+H]^+$: 248.1651
(**found**) m/z $[M+H]^+$: 248.1654

Based on this result, we then explored the reaction between **1d** and any aliphatic alkylamine for example propyl amine and studied the HRMS study at different time intervals. For this, to an oven-dried reaction vial, ethyl 3-(4-hydroxy-3,5-dimethylphenyl)-2-methylpropanoate (**1d**) (0.4 mmol) was dissolved in 4 mL of THF and the reaction vial was then sealed and flushed with nitrogen. Then 2.0 equiv. of Li_2CO_3 (0.8 mmol) and 2.0 equiv. of propyl amine (0.8 mmol) were added to the reaction mixture and stirred for 10 min at room temperature. Then 1.0 equiv. of TBATB (0.4 mmol) was added and the reaction mixture was then stirred at 80 °C. The aliquots at different time intervals of 0.5, 2, 4, 7 h were taken from the reaction mixture and analysed by HRMS to detect the *in situ* generated intermediates.

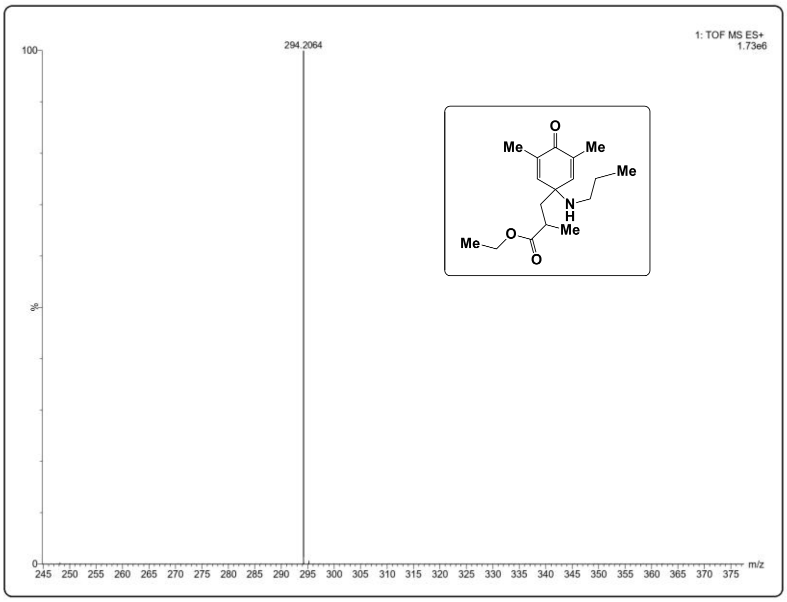


Figure S2 HRMS of the reaction mixture after 0.5 h showing the formation of dearomative intermediate

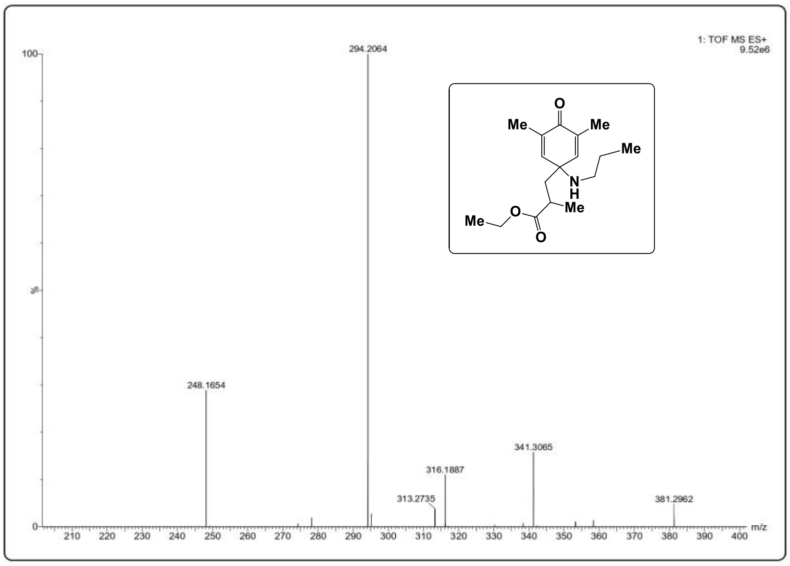


Figure S3 HRMS of the reaction mixture after 2 h showing the dearomative intermediate along with a small peak (30% with respect to the intermediate peak) of the corresponding product **4a** with m/z = $[M+H]^+$ 248.1654

From HRMS study we found an intense peak at m/z = $[M+H]^+$ 294.2064 indicating the formation of dearomative intermediate (**IN5´**). The HRMS data of aliquots after 4 h and 7 h is given below.

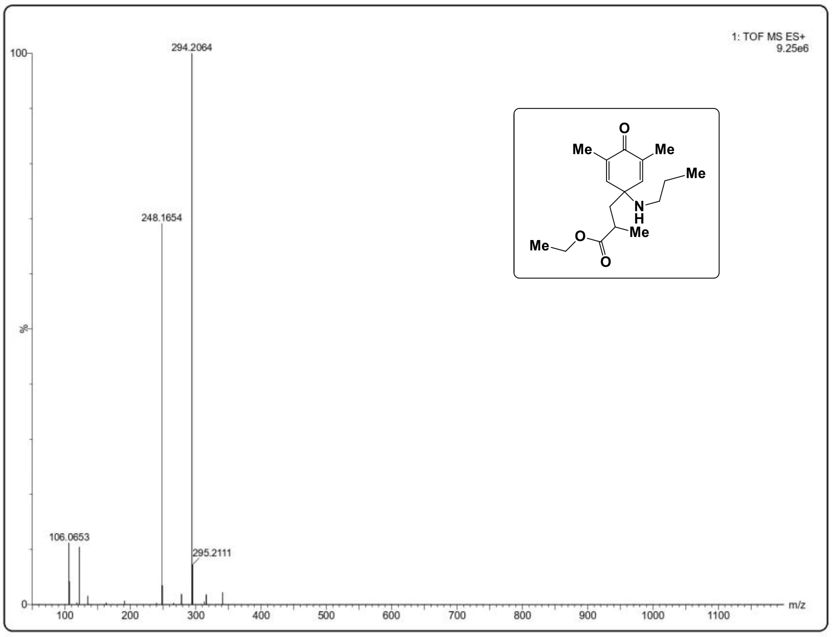


Figure S4 HRMS of the reaction mixture after 4 h showing the dearomative intermediate along with an intense peak (70% with respect to the intermediate peak) of the corresponding product **4a** with m/z = $[M+H]^+$ 248.1654

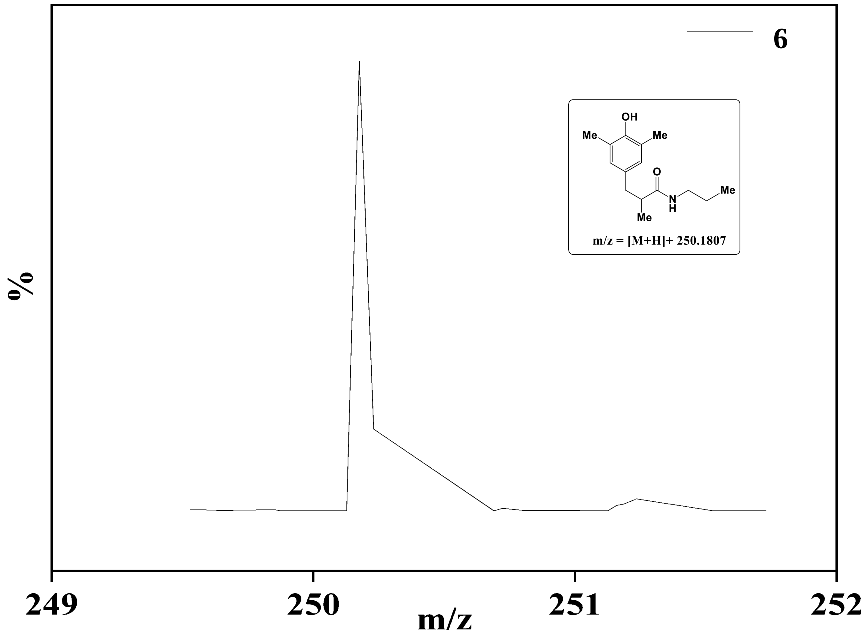


Figure S5 HRMS of the reaction mixture after 7 h showing the amide intermediate

In case of propyl amine, a small peak of amide intermediate, m/z = $[M+H]^+$ 250.1807 was observed along with a small dearomative intermediate peak when the aliquot was taken after 7 h from the reaction mixture. This intermediate peak also subsequently got diminished leading to the formation of product **4a**. (In case of naphthol substrate **1e**, under the standard reaction condition, we isolated the corresponding amide intermediate **10** detected by Control Experiment G.3.).

Standard HRMS data of substrate and products

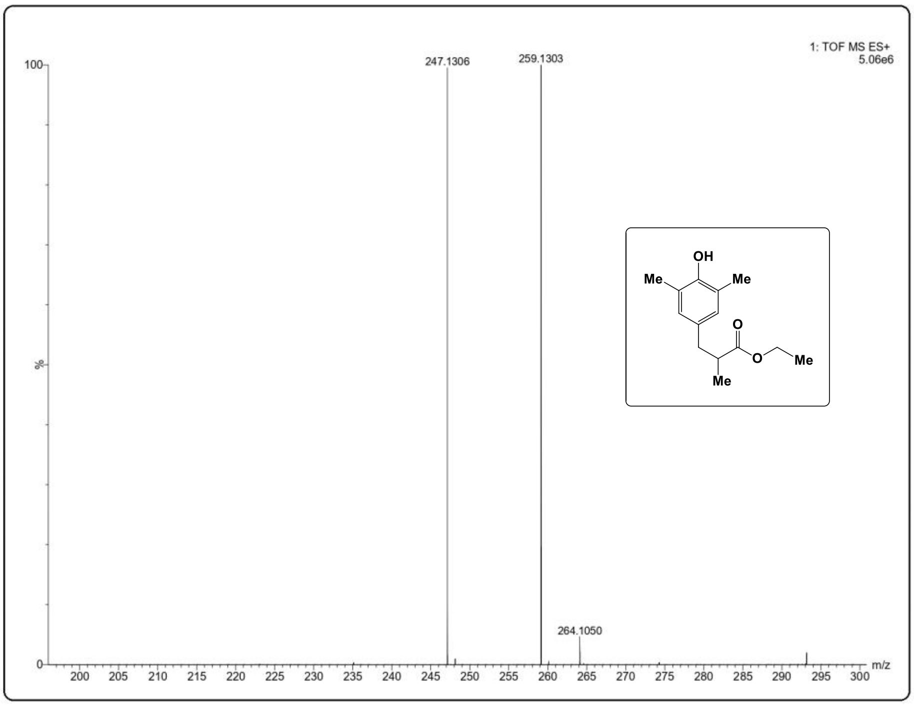


Figure S6 HRMS data of substrate **1d**

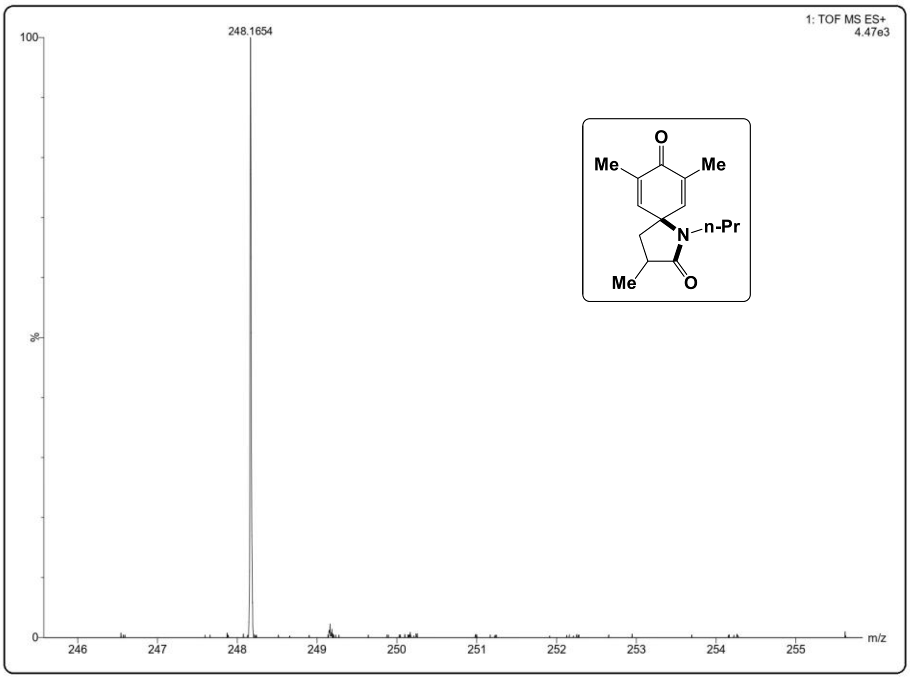


Figure S7 HRMS data of product **4a**

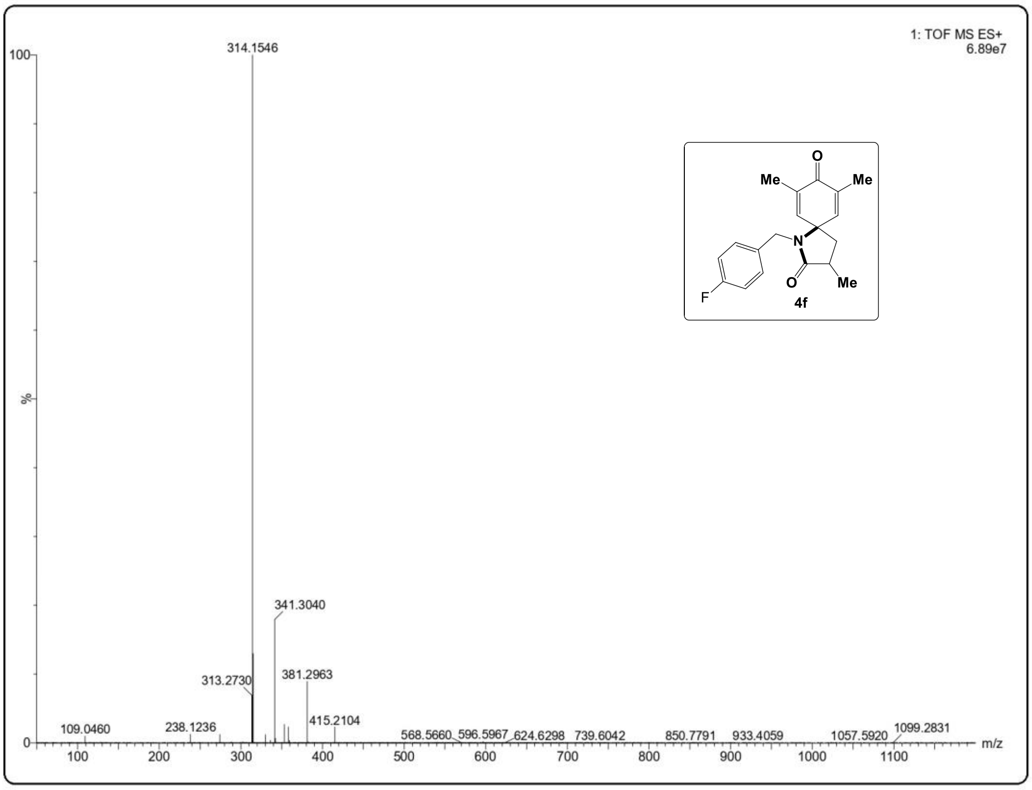
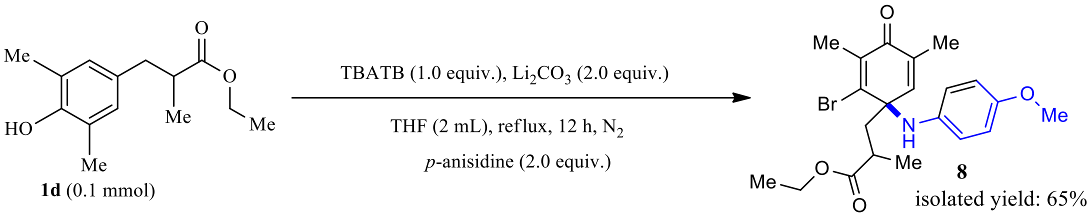


Figure S8 HRMS data of product **4f**

G.7. Trapping of dearomative intermediate of phenol



Based on the previous observation, we planned a reaction of **1d** with *p*-anisidine which produce the dearomative intermediated product (**8**).

To an oven-dried reaction vial, ethyl 3-(4-hydroxy-3,5-dimethylphenyl)-2-methylpropanoate (**1d**, 0.1 mmol) was dissolved in 2 mL of THF and the reaction vial was then sealed and flushed with nitrogen. Then 2.0 equiv. of Li_2CO_3 (0.2 mmol) and 2.0 equiv. *p*-anisidine (0.2 mmol) were added to the reaction mixture and stirred for 10 min at room temperature. Then 1.0 equiv. of TBATB (0.1 mmol) was added, and the reaction mixture was then stirred at 100 °C for 12 h and the progress of the reactions were monitored by TLC. The reaction mixture was then allowed to cool and diluted with H_2O and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, concentrated under vacuum, and purified by column chromatography using 100– 200 mesh size silica gels (petroleum ether/EtOAc) to afford the desired product **8** (yield 65%).

H. Plausible Reaction Mechanism:

Based on these above control experiments, a potential mechanistic pathway of these transformations is depicted in **Figure S9**.

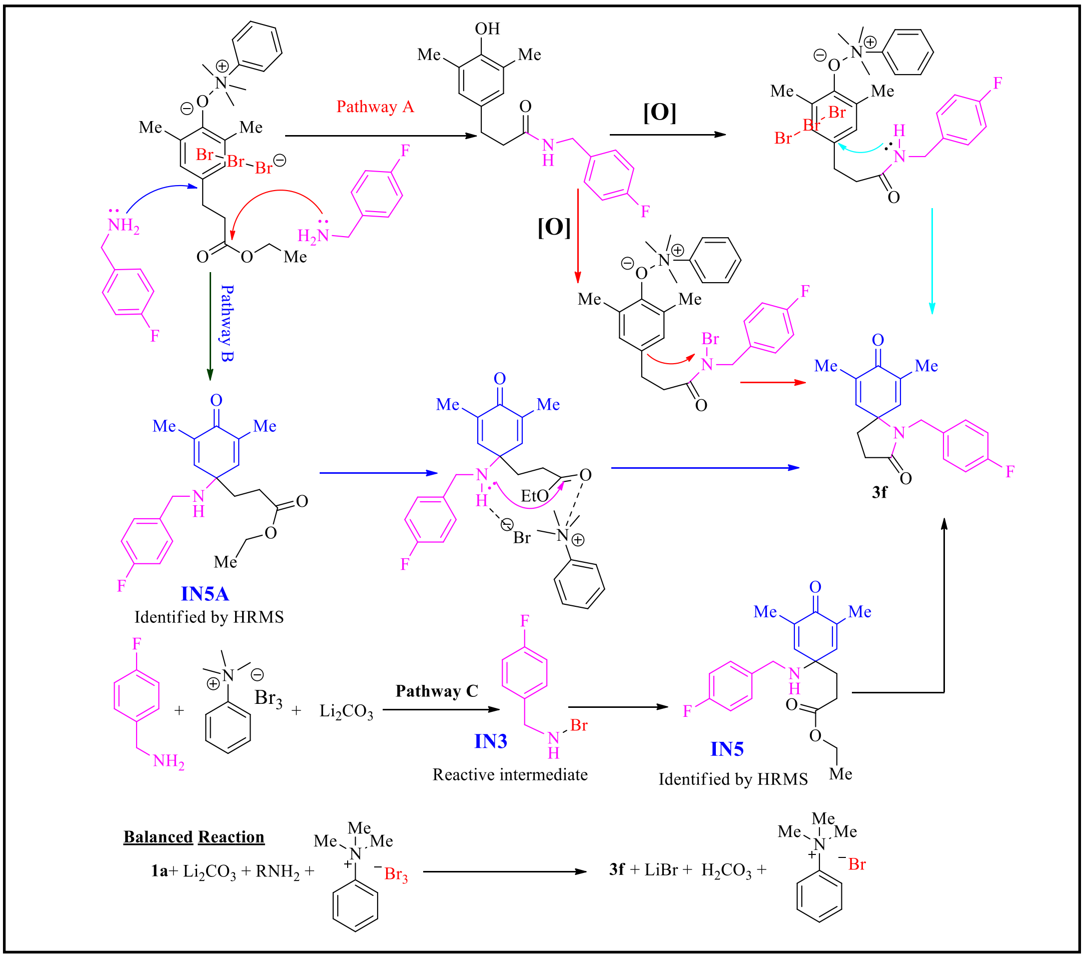


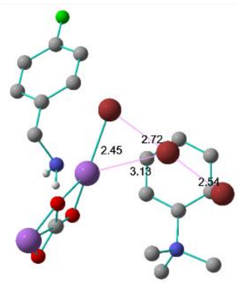
Figure S9 Proposed mechanism

I. DFT Calculation:

Computational Details:

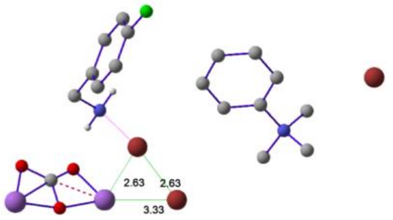
The Gaussian 16 suite of the quantum chemical program was employed in this study to perform all the calculations.[1] The hybrid density functional B3LYP-D3 (Grimmes's dispersion correction) and 6-31G** basis set used to optimize geometries of all reported reactants, intermediates, transition states, and at the DFT.[2-3] The frequency calculations performed to identify stationary points and the correct transition states were identified by the unique imaginary frequency calculations. The intrinsic reaction coordinate (IRC) calculations were employed to confirm the accuracy of these transition states.[4-5] The geometries obtained at the end of IRC on either side of the IRC trajectories to carry out the geometry optimization and to build the connection between the reactant and product arising from the transition state. A solvent continuum in tetrahydro furan (THF) was confirmed using the Cramer-Truhlar SMD continuum solvation model at 298K and 1 atm pressure.[6] The Gibbs free energies (298K) were obtained by employing thermal and entropic terms to the electronic energies in the condensed phase. The graphical user interface, CYLView was used for the visualization of optimized geometries of transition states and intermediates.[7]

Table S4



IN1
Electrical Energy: - -8825.381635
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

N	-3.73204	2.73714	0.32386
H	-4.22792	3.08638	1.14184
H	-3.16707	3.49856	-0.04408
C	-4.67647	2.25831	-0.68772
H	-5.46568	2.98349	-0.94673
H	-4.0977	2.08247	-1.60299
C	-5.32589	0.95357	-0.26382
C	-6.7144	0.78772	-0.28614
C	-4.52548	-0.12247	0.15766
C	-7.30515	-0.42251	0.09104
H	-7.34876	1.61223	-0.60119
C	-5.09418	-1.33634	0.53779
H	-3.44744	0.00224	0.17706
C	-6.479	-1.46199	0.49641
H	-8.38094	-0.56223	0.07918
H	-4.48791	-2.17698	0.85971
F	-7.03969	-2.64141	0.86752
C	2.22401	2.89978	1.70833
O	1.00972	2.5285	1.58656
O	2.81526	3.20111	2.80756
O	2.95555	2.96766	0.58666
Li	4.28376	3.55594	1.72994
Li	1.3853	2.37157	-0.28288
C	-0.45314	-2.67092	0.47471
C	-1.4606	-1.73693	0.71288
C	-1.18346	-0.60377	1.47953
C	0.09344	-0.40203	2.00064
C	1.09316	-1.35208	1.76233
C	0.82944	-2.48798	1.00116
H	-0.65145	-3.54994	-0.12979
H	-2.45253	-1.88345	0.29595
H	-1.95192	0.14058	1.65902
H	0.28925	0.49627	2.57224
H	1.59108	-3.22232	0.7801
N	2.46537	-1.10557	2.34074
C	3.07495	0.1323	1.70748
H	2.43293	0.9896	1.88832
H	4.05305	0.29937	2.16251
H	3.1743	-0.04388	0.63662
C	2.35389	-0.90475	3.83586
H	1.88747	-1.789	4.26752

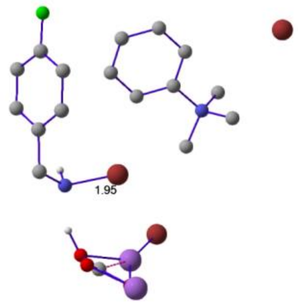


IN2
Electrical Energy: - -8825.361748
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Br	-2.34648	-0.37974	-0.67224
N	-4.02698	0.61879	-1.04659
H	-3.93222	0.99001	-1.99525
H	-4.75254	-0.35379	-0.95902
C	-4.33746	1.70152	-0.07053
H	-5.26492	2.14972	-0.44704
H	-4.56005	1.21087	0.87791
C	-3.23576	2.71876	0.05998
C	-2.9367	3.58401	-1.00279
C	-2.45529	2.76581	1.22205
C	-1.86353	4.46913	-0.9206
H	-3.5405	3.56066	-1.90658
C	-1.38431	3.65363	1.32746
H	-2.67834	2.09758	2.04869
C	-1.10868	4.48141	0.24723
H	-1.60886	5.13934	-1.73431
H	-0.76256	3.69748	2.21475
F	-0.04666	5.32004	0.3264
Br	-1.13012	-3.20402	-0.08865
C	-5.47235	-1.69733	0.55432
O	-4.97629	-2.7383	1.17132
O	-5.15412	-1.56494	-0.71245
O	-6.17677	-0.85395	1.18894
Li	-3.58028	-2.85634	-0.13602
Li	-5.86271	-1.99432	2.67799
C	3.23567	2.17941	0.10725
C	1.86058	2.41771	0.06082
C	0.98181	1.34001	-0.03872
C	1.4628	0.02771	-0.09031
C	2.84072	-0.18876	-0.04408
C	3.73673	0.87897	0.05503
H	3.93365	3.00785	0.18552
H	1.47931	3.43253	0.105
H	-0.08841	1.51031	-0.07487
H	0.75158	-0.78668	-0.16022
H	4.81532	0.71688	0.09509
N	3.41451	-1.5814	-0.09632
C	2.34872	-2.63727	-0.21371
H	1.77866	-2.48196	-1.12758
H	2.84829	-3.60455	-0.25063
H	1.69166	-2.59451	0.65183
C	4.33489	-1.70827	-1.29469

H	3.35732	-0.76302	4.23905
H	1.75049	-0.02157	4.03681
C	3.41616	-2.25527	2.10223
H	2.9993	-3.16749	2.53056
H	3.58246	-2.35547	1.03208
H	4.35079	-2.00992	2.60182
Br	1.17527	0.04649	-1.52896
Br	-1.02985	1.18474	-0.66257
Br	3.07097	-1.73739	-1.83119

H	5.20662	-1.06515	-1.15014
H	4.65806	-2.74859	-1.35448
H	3.76912	-1.43349	-2.18489
C	4.20473	-1.85174	1.16941
H	5.08179	-1.19999	1.19244
H	3.54593	-1.67895	2.02052
H	4.52754	-2.89348	1.14289
Br	7.28572	0.01768	0.19792



IN3

Electrical Energy: - - -8825.365644

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

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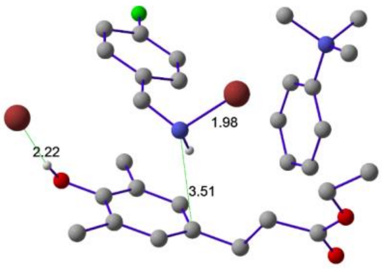
N	-4.02698	0.61879	-1.04659
H	-3.93222	0.99001	-1.99525
H	-4.75254	-0.35379	-0.95902
C	-4.33746	1.70152	-0.07053
H	-5.26492	2.14972	-0.44704
H	-4.56005	1.21087	0.87791
C	-3.23576	2.71876	0.05998
C	-2.9367	3.58401	-1.00279
C	-2.45529	2.76581	1.22205
C	-1.86353	4.46913	-0.9206
H	-3.5405	3.56066	-1.90658
C	-1.38431	3.65363	1.32746
H	-2.67834	2.09758	2.04869
C	-1.10868	4.48141	0.24723
H	-1.60886	5.13934	-1.73431
H	-0.76256	3.69748	2.21475
F	-0.04666	5.32004	0.3264
Br	-1.13012	-3.20402	-0.08865
C	-5.47235	-1.69733	0.55432
O	-4.97629	-2.7383	1.17132
O	-5.15412	-1.56494	-0.71245
O	-6.17677	-0.85395	1.18894
Li	-3.58028	-2.85634	-0.13602
Li	-5.86271	-1.99432	2.67799
C	3.23567	2.17941	0.10725
C	1.86058	2.41771	0.06082
C	0.98181	1.34001	-0.03872
C	1.4628	0.02771	-0.09031
C	2.84072	-0.18876	-0.04408
C	3.73673	0.87897	0.05503
H	3.93365	3.00785	0.18552
H	1.47931	3.43253	0.105
H	-0.08841	1.51031	-0.07487



IN4

Electrical Energy: - -6705.993996

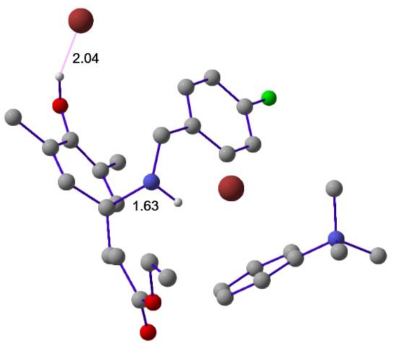
Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-0.73458	0.91109	2.38766
C	-1.46376	2.96948	1.38976
C	-2.74976	2.45366	1.20228
C	-3.01014	1.1235	1.60317
C	-2.00907	0.35504	2.2237
H	0.04428	0.30717	2.8473
H	-1.2631	3.99228	1.07635
O	-4.23989	0.55737	1.45806
C	-3.85321	3.29108	0.60909
H	-4.17082	2.89903	-0.36386
H	-4.74164	3.27085	1.25203
H	-3.53608	4.33132	0.48766
C	-2.32921	-1.04373	2.68318
H	-3.05241	-1.03254	3.50806
H	-2.78469	-1.6261	1.87688
H	-1.43059	-1.56435	3.02667
C	3.40264	-0.11543	1.70838
C	2.69789	-0.77108	2.71591
C	2.38572	-2.12484	2.57215
C	2.78121	-2.81949	1.42991
C	3.47969	-2.14932	0.42189
C	3.79253	-0.79808	0.55239
H	3.65792	0.93346	1.81088
H	2.39762	-0.23289	3.60917
H	1.83772	-2.64908	3.34842
H	2.53917	-3.8719	1.34327
H	4.33198	-0.2534	-0.20938
N	3.87716	-2.93216	-0.80491
C	4.79718	-4.06651	-0.40525
H	4.27318	-4.73794	0.27133
H	5.08891	-4.60316	-1.30832
H	5.66995	-3.63759	0.08655
C	2.63998	-3.48995	-1.47989
H	1.98067	-2.65829	-1.7246
H	2.95538	-4.0136	-2.3823

H	0.75158	-0.78668	-0.16022
H	4.81532	0.71688	0.09509
N	3.41451	-1.5814	-0.09632
C	2.34872	-2.63727	-0.21371
H	1.77866	-2.48196	-1.12758
H	2.84829	-3.60455	-0.25063
H	1.69166	-2.59451	0.65183
C	4.33489	-1.70827	-1.29469
H	5.20662	-1.06515	-1.15014
H	4.65806	-2.74859	-1.35448
H	3.76912	-1.43349	-2.18489
C	4.20473	-1.85174	1.16941
H	5.08179	-1.19999	1.19244
H	3.54593	-1.67895	2.02052
H	4.52754	-2.89348	1.14289
Br	7.28572	0.01768	0.19792

H	2.1359	-4.17891	-0.80728
C	4.60747	-2.09338	-1.82318
H	3.95898	-1.28274	-2.151
H	5.52344	-1.70339	-1.38271
H	4.845	-2.73787	-2.66868
Br	-5.06976	0.54452	-1.6377
C	-0.43607	2.21419	1.97088
C	0.96363	2.7716	2.1209
C	3.05479	3.44584	0.82978
H	0.9643	3.664	2.75907
C	1.57468	3.13763	0.7626
H	1.05211	3.9908	0.31685
H	1.60587	2.04368	2.62322
H	1.42516	2.31782	0.05428
O	3.72229	3.3551	1.84403
N	-0.50873	0.85586	-0.99026
C	-1.69188	0.04891	-1.26472
H	-2.52125	0.65715	-0.86644
H	-1.85078	0.03087	-2.34698
C	-1.81276	-1.35094	-0.68764
C	-0.82772	-1.95898	0.0972
C	-3.01608	-2.04015	-0.91424
C	-1.02519	-3.23589	0.63282
H	0.10244	-1.44861	0.3208
C	-3.22771	-3.31311	-0.3888
H	-3.80845	-1.54465	-1.47011
C	-2.21948	-3.89093	0.37453
H	-0.27636	-3.71014	1.25585
H	-4.1567	-3.84949	-0.55239
F	-2.41223	-5.13174	0.89172
H	-4.56471	0.66149	0.52148
O	3.68024	3.8159	-0.30896
C	2.96932	3.94182	-1.56762
H	2.47519	2.99552	-1.81215
H	2.20423	4.72135	-1.48268
C	3.99745	4.30227	-2.62076
H	4.7583	3.51989	-2.70414
H	3.50465	4.41233	-3.592
H	4.49355	5.24583	-2.37402
H	-0.25877	0.7526	-0.00162
Br	1.09819	0.17709	-1.91704



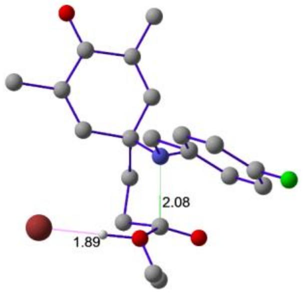
IN5

Electrical Energy: - -6706.012353

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	1.25911	-0.59571	2.15151
C	1.96365	-2.64467	1.03368



IN6

Electrical Energy: - - -3728.600279

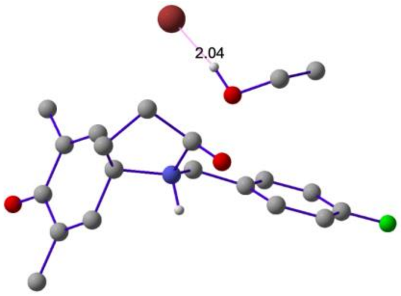
Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-2.52692	-1.7052	1.15516
C	-2.27912	0.41826	-0.17423
C	-3.26353	0.03013	-1.00133
C	-3.94008	-1.27884	-0.80322

C	3.25647	-2.17738	0.95268
C	3.54147	-0.85727	1.45089
C	2.54693	-0.09432	2.11327
H	0.47138	-0.00765	2.61611
H	1.73733	-3.64257	0.66959
O	4.7557	-0.3226	1.34813
C	4.37414	-3.02045	0.40274
H	4.75683	-2.59707	-0.53237
H	5.21656	-3.04988	1.10344
H	4.03413	-4.04322	0.21992
C	2.8972	1.26018	2.66556
H	3.63555	1.18281	3.47163
H	3.33965	1.88902	1.8873
H	2.00864	1.76382	3.05564
C	-3.09295	0.23002	2.10774
C	-2.45421	1.14459	2.94443
C	-2.38675	2.48968	2.57381
C	-2.96434	2.91891	1.37967
C	-3.59787	1.99213	0.54655
C	-3.65588	0.64523	0.89698
H	-3.15812	-0.81915	2.37682
H	-2.01384	0.81294	3.8799
H	-1.88826	3.21278	3.21138
H	-2.90363	3.96708	1.11175
H	-4.10568	-0.09746	0.25567
N	-4.18287	2.4877	-0.75122
C	-5.13089	3.6352	-0.48503
H	-4.58725	4.46875	-0.04742
H	-5.5651	3.94119	-1.43657
H	-5.90655	3.28728	0.19671
C	-3.06044	2.95121	-1.65949
H	-2.41753	2.09335	-1.86073
H	-3.50643	3.32567	-2.58155
H	-2.50344	3.74334	-1.16312
C	-4.95877	1.41957	-1.48505
H	-4.2784	0.61233	-1.75673
H	-5.76556	1.06484	-0.84478
H	-5.37029	1.87755	-2.38406
Br	5.53705	-0.18466	-1.61703
C	0.90221	-1.84212	1.54753
C	-0.43771	-2.45599	1.90551
C	-2.56169	-3.50932	1.03735
H	-0.31032	-3.0543	2.81581
C	-1.08015	-3.306	0.80452
H	-0.60768	-4.29296	0.72554
H	-1.12124	-1.64927	2.17562
H	-0.94072	-2.81089	-0.15914
O	-3.14593	-3.16764	2.05127
N	0.22174	-0.87691	-0.24808
C	1.25365	-0.07932	-0.8637
H	2.22585	-0.52146	-0.58122
H	1.19641	-0.29056	-1.94028
C	1.30614	1.41458	-0.6159
C	0.20117	2.14617	-0.16731
C	2.51804	2.08688	-0.8452
C	0.29896	3.52028	0.06771
H	-0.75417	1.65799	-0.0039
C	2.62783	3.45974	-0.62668
H	3.39115	1.52598	-1.17696
C	1.51204	4.15131	-0.16861
C	-3.49913	-2.13481	0.33488
H	-2.20801	-2.31894	1.9972
H	-1.7795	1.37009	-0.34486
O	-4.83741	-1.65199	-1.55816
C	-3.73057	0.86547	-2.1591
H	-4.78755	1.13052	-2.04369
H	-3.14201	1.78216	-2.24544
H	-3.65231	0.30241	-3.09537
C	-4.19858	-3.4529	0.49578
H	-5.27342	-3.30238	0.64464
H	-4.09338	-4.05634	-0.41226
H	-3.79999	-4.01548	1.34376
C	-1.8334	-0.38104	1.01997
C	-1.99244	0.48211	2.30919
C	0.40299	0.59234	2.07909
H	-2.9598	0.98715	2.30485
C	-0.81679	1.46262	2.3122
H	-0.69065	1.95749	3.2773
H	-1.9484	-0.16561	3.19125
H	-0.92164	2.22045	1.53314
O	1.37215	1.36757	0.84957
N	-0.32122	-0.62704	0.9607
C	0.21503	-0.81885	-0.41453
H	-0.47228	-1.49502	-0.93593
H	0.17014	0.14734	-0.9213
C	1.62294	-1.36775	-0.49554
C	2.41114	-1.71739	0.60574
C	2.16055	-1.51424	-1.7841
C	3.71038	-2.20355	0.4298
H	2.04977	-1.58192	1.61798
C	3.45359	-1.99387	-1.97719
H	1.56244	-1.23974	-2.64919
C	4.20792	-2.33162	-0.8583
H	4.33244	-2.46957	1.27781
H	3.87807	-2.10465	-2.96931
F	5.46776	-2.79784	-1.03445
H	-0.1347	-1.47406	1.50376
C	2.69293	1.82013	1.23388
H	2.61202	2.8277	1.65709
H	3.02622	1.13526	2.01579
C	3.60556	1.7843	0.02149
H	4.60404	2.13427	0.30517
H	3.68748	0.76686	-0.37001
H	3.21887	2.4358	-0.76779
O	1.10231	0.0819	2.91801
Br	-0.01833	3.28055	-1.00663
H	0.89112	2.06506	0.24952

H	-0.54488	4.09597	0.43094
H	3.56109	3.98814	-0.79254
F	1.61117	5.48588	0.06
H	5.13815	-0.42831	0.40734
O	-3.27731	-4.1155	0.06972
C	-2.69317	-4.43508	-1.221
H	-2.354	-3.50893	-1.69728
H	-1.83571	-5.10376	-1.08621
C	-3.77811	-5.1051	-2.03988
H	-4.63261	-4.43406	-2.17176
H	-3.38515	-5.36266	-3.02877
H	-4.12641	-6.02242	-1.5549
H	-0.4042	-0.29013	0.30867
Br	-1.84546	-0.62518	-1.92134



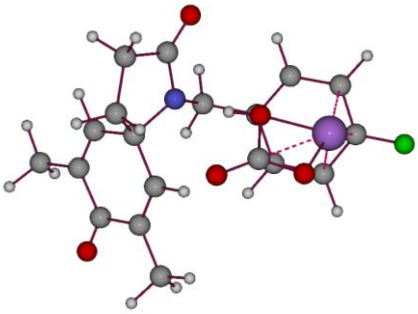
IN7

Electrical Energy: - - - -3728.590644

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-2.52692	-1.7052	1.15516
C	-2.27912	0.41826	-0.17423
C	-3.26353	0.03013	-1.00133
C	-3.94008	-1.27884	-0.80322
C	-3.49913	-2.13481	0.33488
H	-2.20801	-2.31894	1.9972
H	-1.7795	1.37009	-0.34486
O	-4.83741	-1.65199	-1.55816
C	-3.73057	0.86547	-2.1591
H	-4.78755	1.13052	-2.04369
H	-3.14201	1.78216	-2.24544
H	-3.65231	0.30241	-3.09537
C	-4.19858	-3.4529	0.49578
H	-5.27342	-3.30238	0.64464
H	-4.09338	-4.05634	-0.41226
H	-3.79999	-4.01548	1.34376
C	-1.8334	-0.38104	1.01997
C	-1.99244	0.48211	2.30919
C	0.40299	0.59234	2.07909
H	-2.9598	0.98715	2.30485
C	-0.81679	1.46262	2.3122
H	-0.69065	1.95749	3.2773
H	-1.9484	-0.16561	3.19125
H	-0.92164	2.22045	1.53314
O	1.37215	1.36757	0.84957
N	-0.32122	-0.62704	0.9607
C	0.21503	-0.81885	-0.41453
H	-0.47228	-1.49502	-0.93593
H	0.17014	0.14734	-0.9213
C	1.62294	-1.36775	-0.49554
C	2.41114	-1.71739	0.60574



IN8

Electronic Energy: -1273.617888

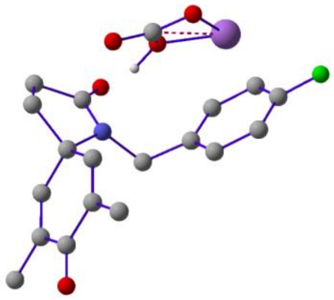
Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-2.25121	1.48058	0.
C	-3.10337	3.08249	-1.7531
C	-4.12225	2.25706	-2.04196
C	-4.26825	0.96861	-1.30541
C	-3.25685	0.63023	-0.26892
H	-1.48611	1.25623	0.73789
H	-3.00717	4.02334	-2.29241
O	-5.19868	0.2044	-1.5591
C	-5.15897	2.55411	-3.08543
H	-6.15821	2.57943	-2.6372
H	-4.9677	3.51123	-3.57736
H	-5.17958	1.76267	-3.84237
C	-3.43019	-0.68481	0.43479
H	-4.39389	-0.71921	0.95501
H	-3.43745	-1.51027	-0.28533
H	-2.63116	-0.85326	1.1609
C	-2.09757	2.81069	-0.67042
C	-2.02126	3.98851	0.35527
C	-0.45849	4.40893	-1.45491
H	-3.02078	4.29672	0.66241
C	-1.23356	5.09891	-0.36314
H	-0.52526	5.61068	0.29245
H	-1.45791	3.63078	1.21969
H	-1.87094	5.85429	-0.83306
N	-0.68435	2.9187	-1.26437
C	-0.33647	2.04258	-2.4371
H	-0.99592	1.17564	-2.37296
H	-0.57136	2.5978	-3.34583

C	2.16055	-1.51424	-1.7841
C	3.71038	-2.20355	0.4298
H	2.04977	-1.58192	1.61798
C	3.45359	-1.99387	-1.97719
H	1.56244	-1.23974	-2.64919
C	4.20792	-2.33162	-0.8583
H	4.33244	-2.46957	1.27781
H	3.87807	-2.10465	-2.96931
F	5.46776	-2.79784	-1.03445
H	-0.1347	-1.47406	1.50376
C	2.69293	1.82013	1.23388
H	2.61202	2.8277	1.65709
H	3.02622	1.13526	2.01579
C	3.60556	1.7843	0.02149
H	4.60404	2.13427	0.30517
H	3.68748	0.76686	-0.37001
H	3.21887	2.4358	-0.76779
O	1.10231	0.0819	2.91801
Br	-0.01833	3.28055	-1.00663
H	0.89112	2.06506	0.24952

C	1.1136	1.63142	-2.37791
C	1.49353	0.55844	-1.56082
C	2.09573	2.35248	-3.06644
C	2.83592	0.20983	-1.41842
H	0.73895	0.00722	-1.00839
C	3.44495	2.01639	-2.94057
H	1.80762	3.19624	-3.68398
C	3.78666	0.95061	-2.11269
H	3.14871	-0.61023	-0.78161
H	4.22122	2.55844	-3.47047
F	5.09499	0.62619	-1.97559
H	0.01688	2.7566	-0.47338
O	0.16281	4.83763	-2.38106
C	2.15386	2.49488	1.82343
O	3.30693	2.18848	2.32939
O	1.05836	1.93678	2.11908
O	2.16468	3.43749	0.8727
Li	3.97291	3.12694	0.89467



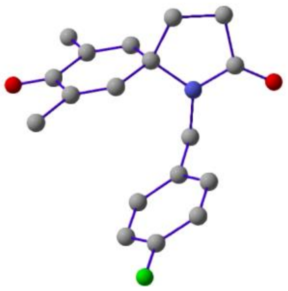
IN9

Electrical Energy: - -1273.617925

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-1.85476	-0.67184	1.07299
C	-2.70691	0.93007	-0.68011
C	-3.72579	0.10463	-0.96898
C	-3.87179	-1.18382	-0.23242
C	-2.8604	-1.52219	0.80406
H	-1.08966	-0.89619	1.81087
H	-2.61072	1.87092	-1.21942
O	-4.80222	-1.94802	-0.48612
C	-4.76251	0.40169	-2.01245
H	-5.76175	0.42701	-1.56421
H	-4.57124	1.3588	-2.50437
H	-4.78312	-0.38975	-2.76938
C	-3.03373	-2.83723	1.50778
H	-3.99743	-2.87164	2.028
H	-3.041	-3.66269	0.78766
H	-2.2347	-3.00569	2.23388
C	-1.70111	0.65827	0.40256
C	-1.62481	1.83609	1.42825
C	-0.06203	2.25651	-0.38193
H	-2.62433	2.1443	1.7354
C	-0.83711	2.94649	0.70984
H	-0.1288	3.45826	1.36544
H	-1.06146	1.47836	2.29267



Product

Electrical Energy: -1001.592062

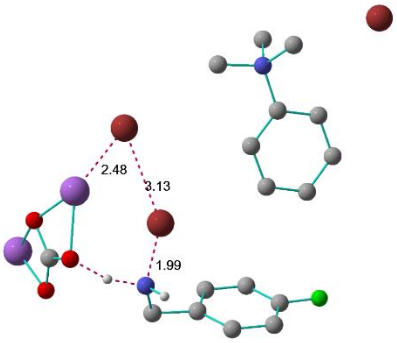
Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	0.56645	-0.46062	-1.07038
C	2.53623	0.25167	0.28784
C	2.87419	-1.02604	0.51325
C	2.05322	-2.11883	-0.06259
C	0.86916	-1.75147	-0.87275
H	-0.31753	-0.18732	-1.65203
H	3.13255	1.06013	0.71894
O	2.34254	-3.29438	0.13469
C	4.05344	-1.43472	1.33044
H	4.75009	-2.04001	0.73803
H	4.58851	-0.5614	1.71623
H	3.74649	-2.06114	2.17649
C	0.03529	-2.87183	-1.39597
H	0.61566	-3.5278	-2.05588
H	-0.32446	-3.50339	-0.57363
H	-0.83126	-2.49209	-1.94717
C	1.36296	0.68367	-0.53712
C	1.80929	1.63691	-1.67924
C	0.73014	2.91371	0.03619
H	2.78544	1.3456	-2.07763
C	1.77024	3.02429	-1.05669
H	1.51159	3.82261	-1.75767
H	1.07652	1.56971	-2.49249

H	-1.47448	3.70187	0.23993
N	-0.28789	0.76628	-0.19139
C	0.05999	-0.10984	-1.36412
H	-0.59947	-0.97678	-1.29997
H	-0.17491	0.44538	-2.27284
C	1.51006	-0.521	-1.30492
C	1.88999	-1.59398	-0.48783
C	2.49219	0.20006	-1.99345
C	3.23238	-1.9426	-0.34544
H	1.1354	-2.14521	0.0646
C	3.8414	-0.13603	-1.86758
H	2.20407	1.04382	-2.61099
C	4.18312	-1.20181	-1.03971
H	3.54517	-2.76266	0.29138
H	4.61768	0.40601	-2.39748
F	5.49145	-1.52623	-0.90261
H	0.41334	0.60417	0.59961
O	0.55927	2.68521	-1.30807
C	1.87151	0.42559	2.16684
O	3.02459	0.11919	2.67281
O	0.77601	-0.13251	2.4625
O	1.88233	1.3682	1.21611
Li	3.69056	1.05765	1.23808

H	2.72345	3.29935	-0.58526
O	0.18835	3.82579	0.63872
N	0.50559	1.58111	0.26002
C	-0.29511	1.10032	1.37131
H	0.29182	0.37156	1.94888
H	-0.47518	1.97149	2.01363
C	-1.59701	0.48602	0.9289
C	-2.50264	1.24465	0.1826
C	-1.89955	-0.84527	1.21036
C	-3.6854	0.68609	-0.28478
H	-2.26942	2.28582	-0.03863
C	-3.08051	-1.42355	0.75404
H	-1.19073	-1.44721	1.77894
C	-3.94918	-0.64349	0.00996
H	-4.40071	1.25962	-0.86843
H	-3.32597	-2.4629	0.95592
F	-5.08672	-1.19231	-0.4442



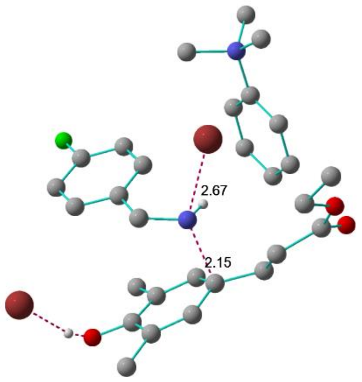
TS2-3

Electrical Energy: -8825.358745

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Br	2.45724	-0.49763	0.57349
N	3.65491	1.15209	1.07748
H	3.29922	1.54782	1.94941
H	4.92194	0.29509	1.25754
C	3.76593	2.16979	0.0141
H	4.50229	2.90849	0.35492
H	4.18196	1.67029	-0.86358
C	2.44672	2.8341	-0.29673
C	1.94164	3.82793	0.55438
C	1.67727	2.42632	-1.39462
C	0.69251	4.40309	0.32373
H	2.53138	4.15736	1.40615
C	0.42576	2.9908	-1.64281
H	2.05502	1.65527	-2.05958
C	-0.0438	3.96462	-0.771
H	0.28634	5.17153	0.97272
H	-0.18754	2.67859	-2.48112
F	-1.26996	4.49571	-0.98344
Br	1.60976	-2.88762	-0.00073
C	5.87436	-0.99612	-0.24432
O	5.55902	-2.08956	-0.8896



TS4-5

Electrical Energy: -6705.970134

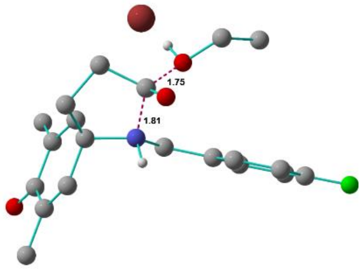
Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-1.27003	0.90038	2.15071
C	-1.88721	2.60977	0.5107
C	-3.20448	2.25677	0.63198
C	-3.56449	1.14243	1.46913
C	-2.59807	0.50997	2.27056
H	-0.51493	0.43821	2.78228
H	-1.62144	3.47078	-0.09704
O	-4.84623	0.72426	1.53793
C	-4.30045	3.00515	-0.07883
H	-4.7621	2.35577	-0.83186
H	-5.0919	3.29978	0.61942
H	-3.91186	3.90156	-0.57087
C	-3.01355	-0.60855	3.19159
H	-3.78575	-0.28344	3.89697
H	-3.44345	-1.43806	2.619
H	-2.16073	-0.98746	3.76313
C	2.50106	-0.20762	2.76193
C	1.7698	-1.16497	3.46355
C	1.67562	-2.46424	2.95978

O	5.56979	-0.98637	1.03993
O	6.39418	-0.01675	-0.85303
Li	4.21078	-2.42661	0.41914
Li	6.22892	-1.1258	-2.39004
C	-3.25193	1.83934	1.10533
C	-1.90629	2.13367	1.33156
C	-0.93279	1.18737	1.01614
C	-1.29232	-0.04996	0.47528
C	-2.64185	-0.32406	0.25061
C	-3.63137	0.61128	0.56346
H	-4.02117	2.56722	1.34578
H	-1.61618	3.09557	1.74193
H	0.11838	1.4044	1.17278
H	-0.50981	-0.76003	0.24499
H	-4.68907	0.40159	0.39518
N	-3.08179	-1.63975	-0.33943
C	-1.92167	-2.54492	-0.6527
H	-1.37747	-2.7715	0.2615
H	-2.32553	-3.46222	-1.07895
H	-1.26815	-2.06055	-1.37599
C	-3.98652	-2.35887	0.64267
H	-4.91213	-1.78974	0.76088
H	-4.2157	-3.34114	0.2262
H	-3.44774	-2.46085	1.58463
C	-3.8435	-1.39084	-1.62698
H	-4.77858	-0.8731	-1.39863
H	-3.20507	-0.80562	-2.2889
H	-4.06761	-2.36113	-2.07239
Br	-7.08394	-0.41069	-0.0792

C	2.32517	-2.80743	1.77499
C	3.06177	-1.83898	1.08621
C	3.1387	-0.53106	1.56013
H	2.58888	0.80811	3.12972
H	1.27474	-0.90195	4.39332
H	1.101	-3.21927	3.48694
H	2.24296	-3.8217	1.40292
H	3.66288	0.25521	1.03666
N	3.76634	-2.25405	-0.17978
C	4.72527	-3.38374	0.1228
H	4.17125	-4.23928	0.50267
H	5.23344	-3.65324	-0.80324
H	5.44151	-3.0349	0.86627
C	2.74536	-2.71543	-1.20137
H	2.04963	-1.89669	-1.37769
H	3.27707	-2.97543	-2.11729
H	2.2226	-3.58624	-0.81552
C	4.56648	-1.13195	-0.79493
H	3.89027	-0.3239	-1.07185
H	5.31696	-0.79449	-0.08145
H	5.05332	-1.5313	-1.68395
Br	-5.15535	-0.43686	-1.32802
C	-0.80232	1.84116	1.13459
C	0.42562	2.64581	1.58477
C	2.60986	3.27901	0.45188
H	0.10023	3.26519	2.4261
C	1.10878	3.51942	0.52097
H	0.97222	4.58789	0.73257
H	1.15824	1.94738	1.98968
H	0.67434	3.34934	-0.46368
O	3.2465	2.70407	1.31725
N	-0.19204	0.74306	0.03158
C	-1.2773	-0.02214	-0.6809
H	-2.21201	0.04498	-0.12186
H	-1.44974	0.48667	-1.62995
C	-0.95598	-1.48158	-0.88268
C	-0.91766	-2.34385	0.22257
C	-0.7342	-2.01161	-2.15971
C	-0.66271	-3.70595	0.06543
H	-1.09152	-1.94426	1.21771
C	-0.48167	-3.37295	-2.33955
H	-0.75819	-1.35307	-3.02203
C	-0.44973	-4.19347	-1.21868
H	-0.63555	-4.38353	0.91217
H	-0.31168	-3.79735	-3.32345
F	-0.18445	-5.51511	-1.38027
H	-5.1251	0.42945	0.60985
O	3.29095	3.79271	-0.59082
C	2.61379	4.3875	-1.72453
H	1.97356	3.63233	-2.19217
H	1.99226	5.22628	-1.39214
C	3.68973	4.85631	-2.68353
H	4.30705	4.01433	-3.01177
H	3.22557	5.3103	-3.56498
H	4.33799	5.60045	-2.21045
H	0.29696	0.08969	0.65211
Br	1.39529	0.78793	-1.42423



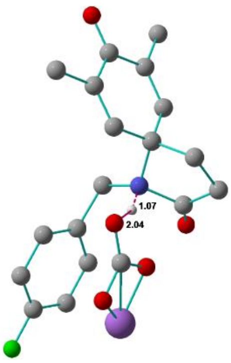
TS6-7

Electrical Energy: -3728.575035

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-2.49728	-1.68331	1.20711
C	-2.28627	0.40954	-0.18128
C	-3.25204	-0.02581	-1.00667
C	-3.89909	-1.3453	-0.77745
C	-3.45136	-2.15791	0.39059
H	-2.17464	-2.2622	2.07178
H	-1.80729	1.36882	-0.37048
O	-4.7778	-1.76185	-1.53052
C	-3.72737	0.76479	-2.19155
H	-4.79061	1.01006	-2.0912
H	-3.15778	1.69086	-2.3009
H	-3.62992	0.17553	-3.10965
C	-4.12424	-3.48456	0.58586
H	-5.2032	-3.35182	0.72087
H	-3.99803	-4.11245	-0.30263
H	-3.72163	-4.01243	1.45394
C	-1.83999	-0.34664	1.03904
C	-2.0061	0.55129	2.3016
C	0.35304	0.59186	2.01397
H	-2.96775	1.06584	2.27076
C	-0.81196	1.51337	2.27613
H	-0.64784	2.01206	3.23214
H	-1.97392	-0.07097	3.20154
H	-0.91832	2.26415	1.48934
O	1.40053	1.40381	0.76735
N	-0.30409	-0.57384	0.99217
C	0.23333	-0.78455	-0.38958
H	-0.46966	-1.46595	-0.87918
H	0.18251	0.17299	-0.90994
C	1.63255	-1.35372	-0.47615
C	2.45054	-1.64825	0.61959
C	2.12489	-1.58091	-1.77092
C	3.73603	-2.16467	0.43001
H	2.12078	-1.44119	1.63141
C	3.40516	-2.08893	-1.97613
H	1.50231	-1.34975	-2.63138
C	4.18988	-2.37423	-0.86365
H	4.38189	-2.39065	1.27184
H	3.79627	-2.26236	-2.97295
F	5.43659	-2.86962	-1.05216
H	-0.11137	-1.41701	1.54174
C	2.66501	1.91127	1.24663
H	2.5202	2.92852	1.62847
H	2.94806	1.26123	2.07726
C	3.67976	1.86874	0.11768
H	4.6439	2.24746	0.47425



TS8-9

Electrical Energy: -1273.567343

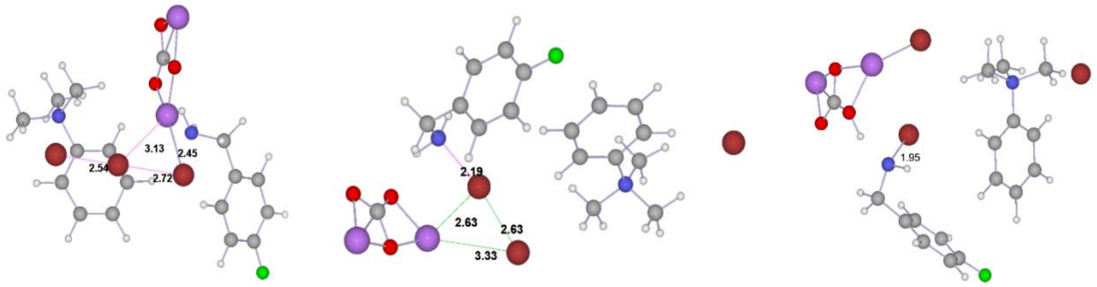
Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

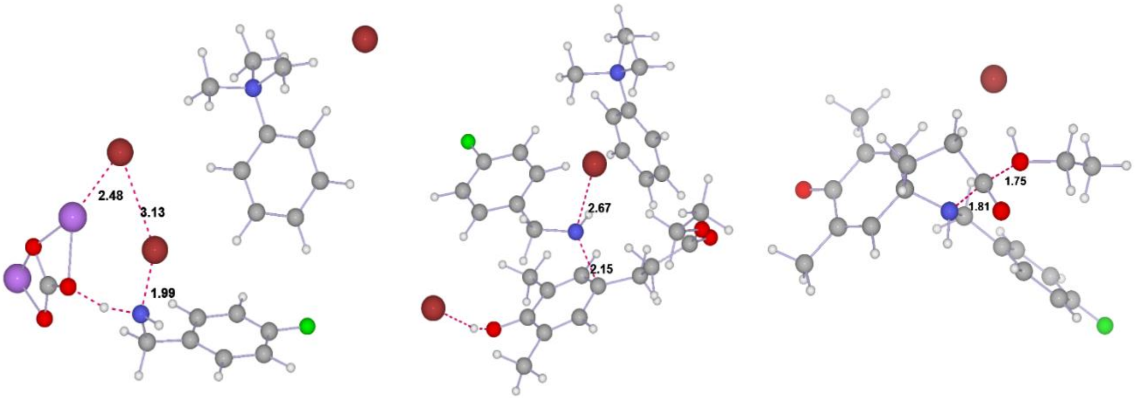
C	-1.73763	0.60014	-1.13508
C	-2.70624	-0.81835	0.70468
C	-3.6403	0.11071	0.9641
C	-3.67688	1.36854	0.16654
C	-2.65617	1.5533	-0.89715
H	-0.96914	0.71958	-1.8914
H	-2.68901	-1.73224	1.29658
O	-4.52503	2.23171	0.39349
C	-4.68102	-0.03661	2.03579
H	-5.6868	0.00785	1.6038
H	-4.56913	-0.9816	2.57363
H	-4.61534	0.78968	2.75186
C	-2.71472	2.84285	-1.66561
H	-3.67895	2.94535	-2.17596
H	-2.63052	3.70047	-0.98914
H	-1.9152	2.89701	-2.40878
C	-1.68609	-0.70249	-0.39844
C	-1.75404	-1.94642	-1.3386
C	-0.23937	-2.37287	0.5085
H	-2.78525	-2.16984	-1.61367
C	-1.07952	-3.07219	-0.53338
H	-0.42834	-3.70659	-1.14146
H	-1.17008	-1.71633	-2.23082
H	-1.78641	-3.72623	-0.01377
N	-0.28812	-0.91679	0.20197
C	0.07225	-0.00237	1.34662
H	-0.62138	0.83773	1.29752
H	-0.1046	-0.54562	2.2761
C	1.49522	0.48657	1.25874
C	1.7946	1.62128	0.4942
C	2.53551	-0.22491	1.86806
C	3.11436	2.03924	0.31849
H	0.99286	2.17021	0.0091
C	3.86482	0.17393	1.70381
H	2.30857	-1.11641	2.44335
C	4.12601	1.30197	0.92639
H	3.36472	2.90961	-0.27805
H	4.68487	-0.35937	2.17376
F	5.41166	1.69103	0.75642
H	0.58107	-0.93481	-0.57143
O	0.38099	-2.81536	1.43546
C	1.81203	-0.61692	-2.10067
O	2.95736	-0.30222	-2.59591

H 3.81512 0.84386 -0.23895 H 3.3505 2.49176 -0.71948 O 1.11196 0.0739 2.93718 Br -0.0779 3.2911 -1.06161 H 0.91201 2.09942 0.18078	O 0.67488 -0.27053 -2.49023 O 1.84542 -1.35593 -0.9716 Li 3.63468 -0.84134 -0.95481
EtOH EE: -154.997525 Symbolic Z-matrix: Charge = 0 Multiplicity = 1 C -0.08544 0.54187 0. C 1.21423 -0.21938 -0.00001 H -0.13568 1.20026 0.8836 H -0.13569 1.20027 -0.88359 H 2.0661 0.46615 -0.00004 H 1.29035 -0.85873 0.88481 H 1.29032 -0.85876 -0.88481 O -1.14726 -0.39821 0.00001 H -1.97005 0.10156 0.	HBr EE: -2572.023505 Symbolic Z-matrix: Charge = 0 Multiplicity = 1 Br 0. 0. 0.03938 H 0. 0. -1.37826
PTAB EE: -2977.410531 ---------- Symbolic Z-matrix: Charge = 0 Multiplicity = 1 C -2.05324 0.60057 2.2775 C -2.94038 1.67935 2.43545 C -3.60285 2.21101 1.31673 C -3.38632 1.66893 0.03806 C -2.50053 0.58429 -0.0912 C -1.8169 0.03844 1.01096 H -1.52915 0.18465 3.15398 H -3.11507 2.11024 3.4352 H -4.29759 3.05892 1.43081 H -3.91067 2.09868 -0.8272 H -1.10097 -0.82094 0.90438 N -2.20785 -0.0172 -1.48726 C -3.23698 0.42137 -2.54857 H -3.15056 1.5125 -2.70414 H -2.98396 -0.11632 -3.48201 H -4.24581 0.139 -2.19295 C -0.80991 0.45787 -1.95107 H -0.0418 0.12086 -1.21243 H -0.62975 0.01263 -2.94827 H -0.84322 1.56235 -2.01331 C -2.21911 -1.56739 -1.42847 H -1.35017 -1.92396 -0.79887 H -3.19511 -1.86724 -1.00286 H -2.12371 -1.92179 -2.47211 Br 0.29141 -2.49461 0.52405	PTATB EE: -8120.261269 ----------- Symbolic Z-matrix: Charge = 0 Multiplicity = 1 C 1.25889 1.01758 2.4018 C 2.35245 0.25679 2.79702 C 3.27053 -0.18137 1.84467 C 3.09527 0.14104 0.50436 C 1.99691 0.90986 0.12752 C 1.07056 1.35197 1.06151 H 0.52648 1.35039 3.13107 H 2.48726 -0.00275 3.84266 H 4.12468 -0.78302 2.13919 H 3.80874 -0.21381 -0.2335 H 0.1862 1.9131 0.77927 N 1.83654 1.22153 -1.3328 C 3.0426 1.96976 -1.82295 H 3.93227 1.35813 -1.6826 H 2.90171 2.18527 -2.88266 H 3.12832 2.89477 -1.2534 C 1.69327 -0.06229 -2.10403 H 0.82908 -0.60348 -1.71436 H 1.55766 0.18722 -3.15667 H 2.59505 -0.65834 -1.9732 C 0.63037 2.06401 -1.61398 H -0.26809 1.53257 -1.29639 H 0.72474 3.01037 -1.08277 H 0.60317 2.24377 -2.68805 Br -1.45546 -0.59903 -0.09126 Br -2.6976 1.89481 0.18775 Br -0.10314 -2.83579 -0.3443
p-fluorobenzyl amine EE: -426.061298 Symbolic Z-matrix: Charge = 0 Multiplicity = 1 N 3.14411 -0.63528 0.25879 C 2.37427 0.50378 -0.22062 H 2.61337 1.45761 0.28424	Ester EE: -731.717435

H 2.63378 0.65755 -1.27929 C 0.8883 0.27324 -0.11207 C 0.01992 1.36029 0.01535 C 0.34592 -1.01249 -0.16285 C -1.35749 1.18055 0.07821 H 0.42978 2.36864 0.06953 C -1.02893 -1.21483 -0.09529 H 1.01832 -1.8629 -0.25029 C -1.85638 -0.11058 0.02136 H -2.04184 2.01894 0.1793 H -1.46333 -2.21076 -0.13101 F -3.18564 -0.29689 0.08926 H 4.13333 -0.46531 0.1029 H 3.02493 -0.72464 1.26516	
Li_2CO_3 EE: -272.022716 Symbolic Z-matrix: Charge = 0 Multiplicity = 1 C 0. 0. -0.22877 O 0. -1.13221 -0.80887 O 0. 1.13221 -0.80887 O 0. 0. 1.10683 Li 0. 1.86129 0.90999 Li 0. -1.86129 0.90999	$LiHCO_3$ EE: -279.038369 Symbolic Z-matrix: Charge = 0 Multiplicity = 1 C 0. 0.10523 0. O 0.30146 1.42033 0. O -1.21566 -0.20585 0. O 0.94658 -0.73104 0. Li -0.50907 -1.99142 0. H 1.26813 1.47537 0.
ArCH$_2$NHBr EE: -2996.854192 Symbolic Z-matrix: Charge = 0 Multiplicity = 1 N 3.14411 -0.63528 0.25879 C 2.37427 0.50378 -0.22062 H 2.61337 1.45761 0.28424 H 2.63378 0.65755 -1.27929 C 0.8883 0.27324 -0.11207 C 0.01992 1.36029 0.01535 C 0.34592 -1.01249 -0.16285 C -1.35749 1.18055 0.07821 H 0.42978 2.36864 0.06953 C -1.02893 -1.21483 -0.09529 H 1.01832 -1.8629 -0.25029 C -1.85638 -0.11058 0.02136 H -2.04184 2.01894 0.1793 H -1.46333 -2.21076 -0.13101 F -3.18564 -0.29689 0.08926 H 3.02493 -0.72464 1.26516 Br 4.93605 -0.32738 -0.0236	



IN1 (0.0 kcal/mol) **IN2 (12.5 kcal/mol)** **IN3 (10.0kcal/mol)**



TS2-3 (14.4 kcal/mol) **TS4-5 (20.5 kcal/mol)** **TS6-7(10.9 kcal/mol)**

Figure S10 Optimized geometries of key intermediates and transition states. The bond lengths are in Å and relative Gibbs free energies are in parenthesis.

Based on the results obtained from the time-dependent HRMS study and our previous findings, plausible mechanistic pathways of these transformations are depicted in **Figure S9**. We assume that due to the strong dipolar nature of tribromide, it polarizes the aromatic moiety of the phenoxide-ion which further strongly interacts with the tetra-substituted amine cation. As a result, local electron deficiency generates in the aromatic ring, and finally, selective nucleophilic addition of amide (Pathway A) or amine (Pathway B) results in the formation of the desired product. In Pathway C, the electron-rich aromatic ring promotes the attack at the electron-deficient nitrogen in R-NBr to provide the formation of the desired products. The HRMS study confirms the formation of **IN5**. Pathway B and Pathway C both show the formation of the key intermediate **IN5**. The selective formation of the intermediate **IN5** in the presence of tribromide remains unanswered. Moreover, the exact nature and source of the active species driving the oxidative dearomatization reaction are still unclear. Therefore, it is immensely necessary to probe into the correct mechanism using a density functional theoretical (DFT) study. In this context, the formation of **IN5** was considered the key evidence to design the mechanistic pathway, and compounds **1a** and **2** were considered as model substrates for the mechanistic study (**Figure S10**).

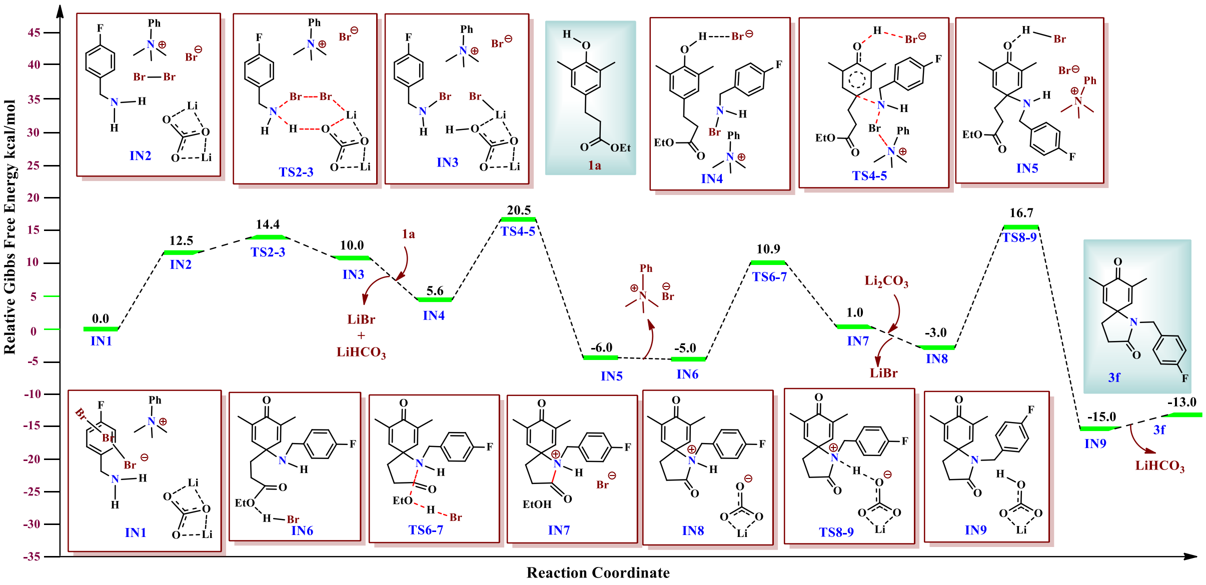


Figure S11 Solvent corrected relative Gibbs free energy profile. Calculations were carried out using SMD (THF)/ B3LYP-D3/6-31G** level of theory

After several unsuccessful attempts to make an electron-deficient aromatic ring using PTATB to validate Pathway A and B, all three compounds, PTATB, 4-flurobenzyl amine, and Li_2CO_3 were optimized together to find out the possible interactions between these three compounds, and the mystery of the mechanism was resolved (Figures **S11**). This study also eliminates the possible involvement of Pathway B in the reaction mechanism. Here, in the **IN1**, lithium facilitates the dissociation of tribromide by forming LiBr and further dissociation of dibromide takes place in the presence of quaternary ammonium cation. In short, the cations, $Li^{+,}$ and quaternary ammonium cation make third bromine highly electron deficient to facilitate the attack of the nucleophilic arylamine on it and to form the $ArCH_2NH_2Br$. Further, an anionic $LiCO_3^-$ abstracts proton from $ArCH_2NH_2Br$ cationic species to yield highly reactive intermediate $ArCH_2NHBr$, **IN3** along with $PhNMe_3Br$, LiBr, and $LiHCO_3$ through the transition state **TS2-3** with relative Gibbs free energy of 14.4 kcal/mol. In the intermediate **IN4**, $PhNMe_3Br$ facilitates the polarization of OH lone pair of phenolic ester **1a**; this promotes the *ipso*-attack of C-4 of compound **1a** on the nitrogen of $ArCH_2NH_2Br$ from the opposite side of ester substituent to get the intermediate **IN5** through the transition state **TS4-5** with an activation energy barrier of 20.5 kcal/mol. The attack of nucleophilic amine and elimination of Br^- take place simultaneously to provide the desired product. The **IN5** further undergoes cyclization in the presence of HBr and a second mole of Li_2CO_3 to get the spirolactamized product, **3f** through the transition states **TS6-7** and **TS8-9** with relative Gibbs free energy of 10.9 kcal/mol and 16.7 kcal/mol. Thus, DFT calculations establish the formation of the key reactive intermediate **IN3**, $ArCH_2NH_2Br$, and the aromatic nucleophilic substitution reaction at electrophilic N—Br through the S_N^2 pathway to provide product **3f** through Pathway C.

J. X-ray Crystallography Data

1-(4-fluorobenzyl)-8-hydroxy-3,7,9-trimethyl-1-azaspiro[4.5]deca-6,9-dien-2-one (**11b**)

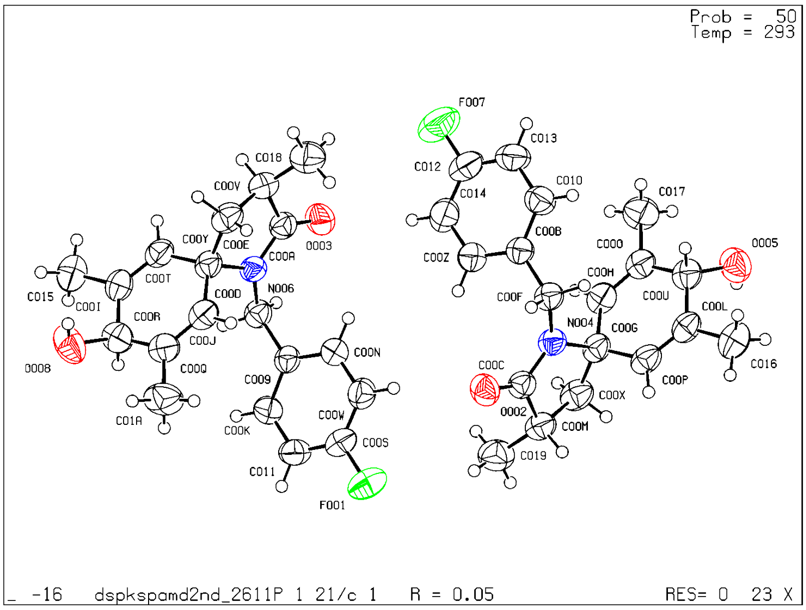


Figure S12 ORTEP diagram of **11b**. X-ray crystallographic coordinates have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with the accession code 2209185.

Colorless plates of **11b** were grown from a DCM solution of the compound at room temperature. A crystal of dimensions 0.18 x 0.16 x 0.08 mm was mounted on a Rigaku Oxford Diffraction, 2020 CCD-based X-ray diffractometer equipped with a low temperature device and Mo micro-focus rotating anode. Rigaku images were exported to CrysAlisPro 1.171.41.93a for processing and corrected for absorption. The integration of the data yielded a total of 19906 reflections. Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL[8] (version 2018/3) software package, using the space group P2(1)/c with Z = 4 for the formula $2(C_{19}H_{22}FNO_2)$. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. R_1 = 5.36 and wR_2 = 15.52% for all data. Additional details are presented in Table S5 and are given as Supporting Information in a CIF file.

Supplementary Table S5. Crystal data and structure refinement for **11b**

Identification code	dspkspamd2nd_261121
Empirical formula	$2(C_{19}H_{22}FNO_2)$
Formula weight	630.75
Temperature/K	293 (2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.6691(5)
b/Å	21.3606 (11)

c/Å	18.6802 (11)
α/°	90
β/°	99.169 (5)
γ/°	90
Volume/Å^3	3414.9 (3)
Z	4
ρ_{calc} g/cm^3	1.227
μ/mm^{-1}	0.086
F (000)	1344
Crystal size/mm^3	0.18 x 0.16 x 0.08
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	1.9100 to 26.2540
Index ranges	$-10 \leq h \leq 10$, $-17 \leq k \leq 27$, $-15 \leq l \leq 23$
Reflections collected	19906
Independent reflections	3861 [Rint = 0.0346, Rsigma = 0.0511]
Data/restraints/parameters	6971/0/426
Goodness-of-fit on F2	0.961
Final R indexes [I>=2σ (I)]	R1 = 0.0536, wR2 = 0.1552
Largest diff. peak/hole / e Å^{-3}	0.262/-0.161
Extinction coefficient	0.0024 (5)
Refinement method	Full-matrix F$_{sqd}$

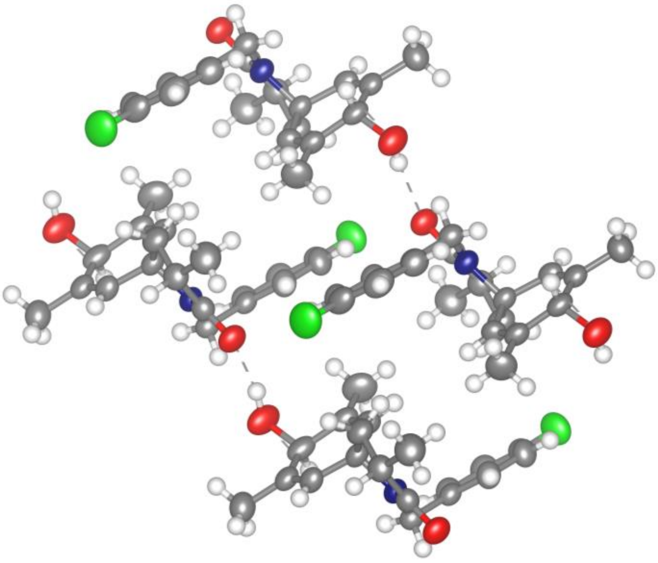


Figure S13 Cluster image of **11b** crystal (50% of ellipsoid), drawn by VESTA 3 [9]

Crystal surface properties

Hirshfeld surface plots for compounds **11b** in the crystal[a, 10]

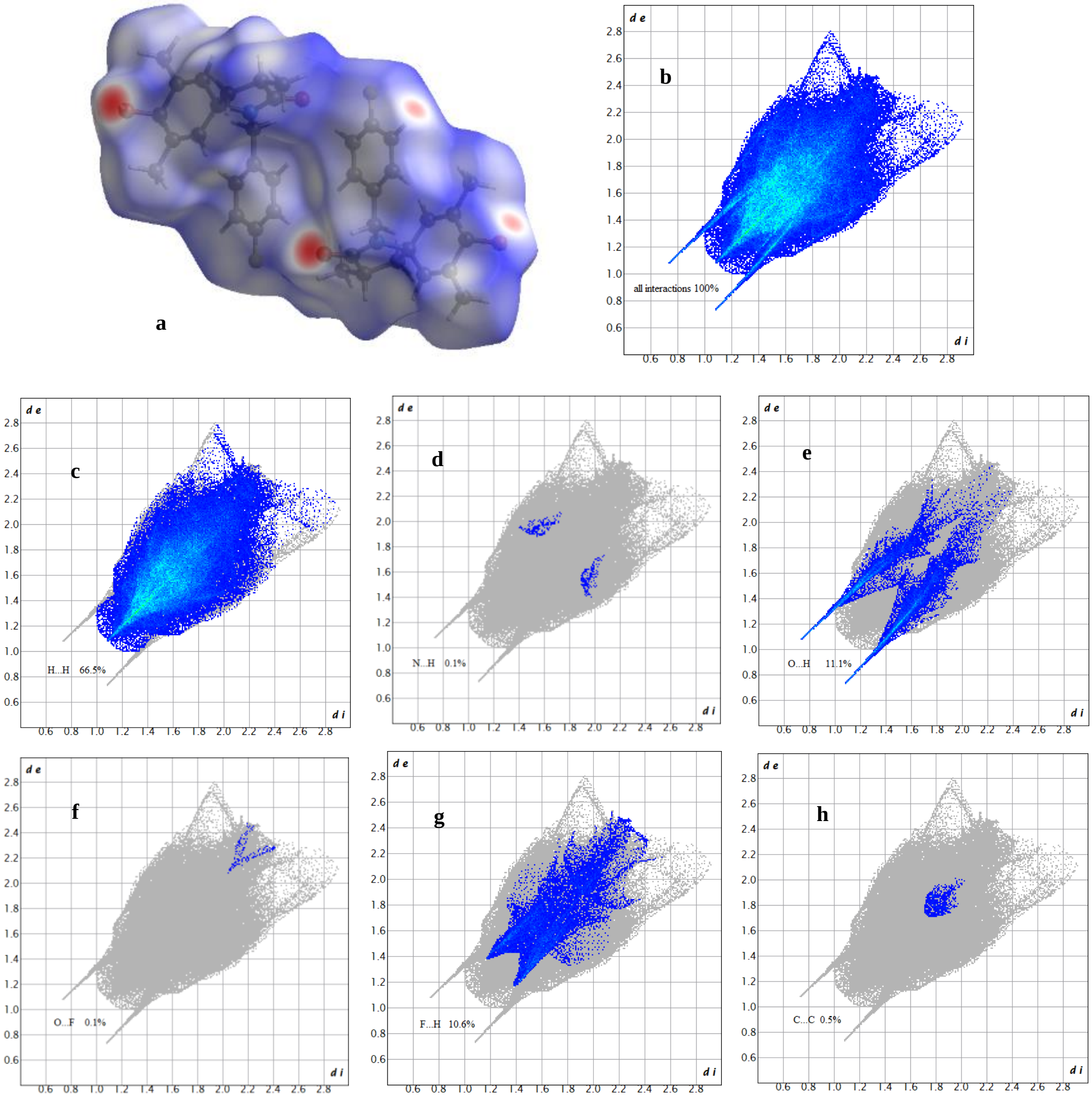


Figure S14 (a) Hirshfeld surface plots for compounds **11b** in the crystal. (b) 2D-fingerprint plot in crystal packing, showed *intra* and *inter* atomic all types of total interections in Hirshfeld surfaces. (c) 2D-fingerprint plot in crystal packing, showed *intra* and *inter* atomic H···H interections in Hirshfeld surfaces. (d) 2D-fingerprint plot in crystal packing, showed *intra* and *inter* atomic N···H/H···N interections in Hirshfeld surfaces. (e) 2D-fingerprint plot in crystal packing, showed *intra* and *inter* atomic H···O/O···H interections in Hirshfeld surfaces. (f) 2D-fingerprint plot in crystal packing, showed *intra* and *inter* atomic F···O/O···F interections in Hirshfeld surfaces. (g) 2D-fingerprint plot in crystal packing, showed *intra* and *inter* atomic H···F/F···H interections in Hirshfeld surfaces. (h) 2D-fingerprint plot in crystal packing, showed *intra* and *inter* atomic C···C interections in Hirshfeld surfaces. [a]All the data includes reciprocal contacts.

K. References:

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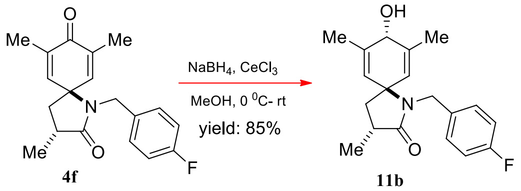
(11) Manuscript ref no. 10d.

(12) Manuscript ref no. 10c.

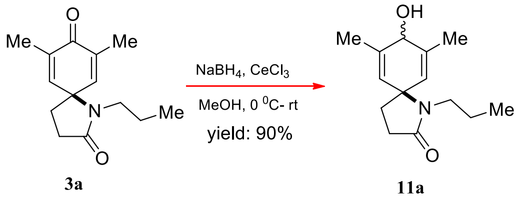
L. Synthetic Versatility of Azaspirodieneone

Synthesis of (3S,5r,8S)-1-(4-fluorobenzyl)-8-hydroxy-3,7,9-trimethyl-1-azaspiro[4.5]deca-6,9-dien-2-one (11b)



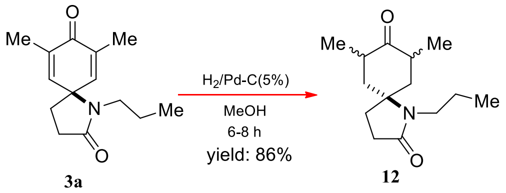
A solution of compound **4f** (80 mg, 0.255 mmol) in CH_3OH (8 mL) was cooled to 0 °C, $CeCl_3.7\ H_2O$ (114 mg, 0.306 mmol) was added and the mixture was stirred at 0 °C for 10 min, $NaBH_4$ (24.0 mg, 0.637 mmol) was added and the reaction was stirred overnight. It was quenched with saturated NH_4Cl (aq.) solution and the aqueous phase was extracted 3 times with ethyl acetate. The combined organic phases were dried over Na_2SO_4 and the solvent removed in vacuo. The crude compound was purified by silica gel chromatography (ethyl acetate/petroleum ether, v/v = 1:3 as eluent) to give the corresponding alcohol **11b** (65 mg, 0.208 mmol, 85 %) as colourless solid.

Synthesis of (8-hydroxy-7,9-dimethyl-1-propyl-1-azaspiro[4.5]deca-6,9-dien-2-one (11a + 11a´)



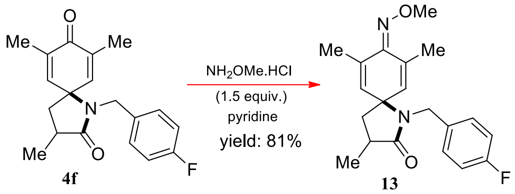
A solution of compound **3a** (30 mg, 0.121 mmol) in CH_3OH (3 mL) was cooled to 0 °C, $CeCl_3.7\ H_2O$ (54 mg, 0.145 mmol) was added and the mixture was stirred at 0 °C for 10 min, $NaBH_4$ (12.0 mg, 0.302 mmol) was added and the reaction was stirred overnight. It was quenched with saturated NH_4Cl (aq.) solution and the aqueous phase was extracted 3 times with ethyl acetate. The combined organic phases were dried over Na_2SO_4 and the solvent removed in vacuo. The crude compound was purified by silica gel chromatography (ethyl acetate/petroleum ether, v/v = 1:3 as eluent) to give the corresponding alcohol **11a + 11a´** (27 mg, 0.109 mmol, 90 %) as colourless liquid.

Synthesis of 3,7,9-trimethyl-1-propyl-1-azaspiro[4.5]decane-2,8-dione (12a + 12a´)



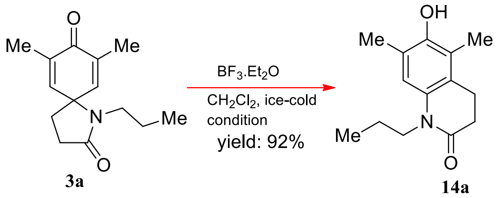
In an oven-dried round bottomed flask, a solution of compound **3a** (35 mg, 0.141 mmol) in CH_3OH (3 mL) was taken and purged with H_2. Then 5% Pd/C (15 mg, 0.141 mmol) was added and again purged with H_2. Then the reaction was stirred at room temperature for 10 h. Then the solution was diluted with CH_2Cl_2 and filtered to a round bottom flask. Silica was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:3as eluent) to give **12a + 12a´** (31 mg, 0.121 mmol, 86 %) as yellow liquid.

Synthesis of (3S,5S,Z)-1-(4-fluorobenzyl)-8-(methoxyimino)-3,7,9-trimethyl-1-azaspiro[4.5]deca-6,9-dien-2-one (13)



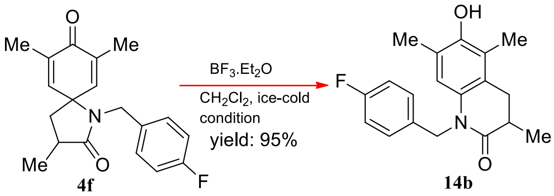
In an oven-dried round bottomed flask **4f** (42 mg, 0.134 mmol) was mixed with $NH_2OMe·HCl$ (14 mg, 0.201 mmol) in pyridine. The reaction mixture was heated to 80 °C in an oil bath for 5 h. The reaction mixture was then diluted with ethyl acetate and washed with 20% aqueous AcOH to remove pyridine (3 times). The combined organic layer was then neutralized with aqueous $NaHCO_3$, washed with brine solution, and dried over Na_2SO_4. The purification was performed by silica gel chromatography (eluent, EtOAc/hexane, 1:20) to give **13** (37 mg, 0.108 mmol, 81 %) as yellow liquid.

Synthesis of 6-hydroxy-5,7-dimethyl-1-propyl-3,4-dihydroquinolin-2(1H)-one (14a)



In an oven-dried round bottomed flask, a solution of compound **3a** (30 mg, 0.122 mmol) in DCM (3 mL) was taken and purged with N_2. Then $BF_3.Et_2O$ (0.045 mL, 0.366 mmol) was added. Then the reaction was stirred at room temperature for 6-8 h. The reaction was monitored by TLC. After that the reaction mixture was extracted with DCM and washed with brine solution, then dried over sodium sulphate and concentrated. The mass was subjected to column chromatography over silica gel afforded the desired product **14a** (27 mg, 0.111 mmol, 92 %) as yellow liquid.

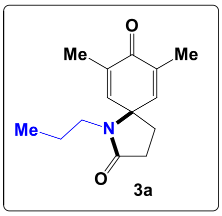
Synthesis of 1-(4-fluorobenzyl)-6-hydroxy-3,5,7-trimethyl-3,4-dihydroquinolin-2(1H)-one (14b)



In an oven-dried round bottomed flask, a solution of compound **4f** (30 mg, 0.096 mmol) in DCM (3 mL) was taken and purged with N_2. Then $BF_3.Et_2O$ (0.035 mL, 0.288 mmol) was added. Then the reaction was stirred at room temperature for 6-8 h. The reaction was monitored by TLC. After that the reaction mixture was extracted with DCM and washed with brine solution, then dried over sodium sulphate and concentrated. The mass was subjected to column chromatography over silica gel afforded the desired product **14b** (28 mg, 0.090 mmol, 95 %) as yellow liquid.

M. Product Characterizations

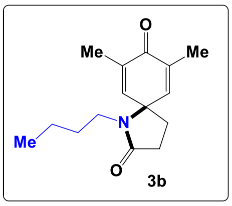
7,9-dimethyl-1-propyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3a)



3a

Total reaction time = 10 h. Temperature of reaction = 100 ˚C. Elution with 30% ethyl acetate in petroleum ether afforded colourless liquid, **1a** (30 mg, 0.135 mmol) → **3a** (27 mg, 0.116 mmol); 86% yield. **TLC**; R$_f$ = 0.3 (40% ethyl acetate in petroleum ether). **IR** (KBr) 3147, 2880, 1681, 1640, 1431, 1261, 1173, 1063, 759 cm^{-1}. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 6.39 (s, 2H), 2.87 – 2.83 (m, 2H), 2.47 – 2.43 (m, 2H), 2.02 – 1.97 (m, 2H), 1.83 (s, 6H), 1.38 – 1.33 (ddd, J = 10.2, 7.8, 5.4 Hz, 2H), 0.73 (t, J = 7.4 Hz, 3H).**^{13}C NMR** (100 MHz, CDCl$_3$) δ 186.05, 174.72, 144.74, 136.30, 62.42, 42.94, 30.40, 29.52, 23.03, 16.03, 11.46. **HRMS** (ESI) calc'd for $C_{14}H_{20}NO_2$ [M+H]$^+$: 234.1494, Found : 234.1493.

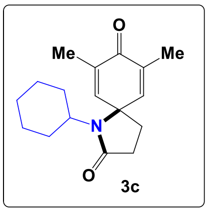
1-butyl-7,9-dimethyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3b)



3b

Total reaction time = 10 h. Temperature of reaction = 100 ˚C. Elution with 30% ethyl acetate in petroleum ether afforded yellow liquid, **1a** (30 mg, 0.135 mmol) → **3b** (26 mg, 0.105 mmol); 78% yield. **TLC**; R$_f$ = 0.3 (40% ethyl acetate in petroleum ether). **IR** (KBr) 3058, 2953, 1683, 1645, 1490, 1397, 1119, 1065, 883 cm^{-1}. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 6.40 (d, J = 12.2 Hz, 2H), 2.92 – 2.85 (m, 2H), 2.46 – 2.41 (dd, J = 14.2, 8.3 Hz, 2H), 2.01 – 1.96 (dd, J = 13.5, 8.7 Hz, 1H), 1.83 (d, J = 12.7 Hz, 6H), 1.45 – 1.23 (m, 4H), 1.17 – 1.11 (d, J = 8.6 Hz, 4H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 186.00, 174.66, 161.15, 144.71, 136.30, 62.43, 41.05, 31.85, 30.39, 29.49, 20.16, 15.96, 13.70. **HRMS** (ESI) calc'd for $C_{15}H_{22}NO_2$ [M+H]$^+$: 248.1651, Found : 248.1650.

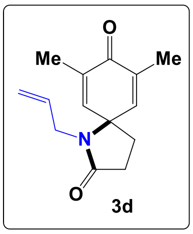
1-cyclohexyl-7,9-dimethyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3c)



3c

Total reaction time = 16 h. Temperature of reaction = 120 ˚C. Elution with 30% ethyl acetate in petroleum ether afforded yellow liquid, **1a** (30 mg, 0.135 mmol) → **3c** (28 mg, 0.102 mmol); 76% yield. **TLC**; R$_f$ = 0.4 (40% ethyl acetate in petroleum ether). **IR** (KBr) 2801, 1696, 1651, 1632, 1117, 974, 859 cm^{-1}. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 6.57 (s, 2H), 3.00 – 2.92 (m, 1H), 2.53 – 2.49 (m, 2H), 2.09 – 1.96 (m, 4H), 1.94 (s, 6H), 1.75 – 1.72 (m, 2H), 1.55 – 1.53 (m, 3H), 1.16 – 1.10 (m, 3H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 186.16, 174.36, 145.48, 135.66, 63.44, 54.52, 30.99, 30.64, 30.31, 26.16, 25.01, 16.06. **HRMS** (ESI) calc'd for $C_{17}H_{24}NO_2$ [M+H]$^+$: 274.1807, Found : 274.1800.

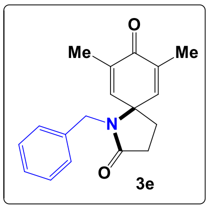
1-allyl-7,9-dimethyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3d)



3d

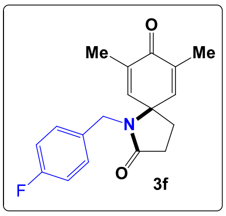
Total reaction time = 12 h. Temperature of reaction = 60 ˚C. Elution with 30% ethyl acetate in petroleum ether afforded sunset yellow liquid, **1a** (30 mg, 0.135 mmol) → **3d** (29 mg, 0.124 mmol); 92% yield. **TLC**; R$_f$ = 0.3 (25% ethyl acetate in petroleum ether). **IR** (KBr) 2924, 2853, 1686, 1641, 1433, 1306, 1155, 1038, 802 cm^{-1}. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 6.46 (s, 2H), 5.73 – 5.64 (ddt, J = 16.5, 10.3, 6.3 Hz, 1H), 5.08 – 4.97 (ddd, J = 19.0, 14.4, 2.0 Hz, 2H), 3.63 (d, J = 6.2 Hz, 2H), 2.58 – 2.54 (m, 2H), 2.12 – 2.08 (m, 2H), 1.89 (s, 6H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 185.97, 174.47, 144.41, 136.40, 133.88, 128.45, 117.66, 62.32, 43.45, 30.30, 29.35, 15.90. **HRMS** (ESI) calc'd for $C_{14}H_{18}NO_2$ [M+H]$^+$: 232.1338, Found : 232.1341.

1-benzyl-7,9-dimethyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3e)[11]


3e

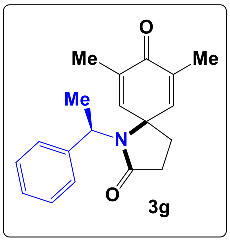
Total reaction time = 12 h. Temperature of reaction = 120 ˚C. Elution with 25% ethyl acetate in petroleum ether afforded pale yellow liquid, **1a** (31 mg, 0.139 mmol) → **3e** (32 mg, 0.111 mmol); 84% yield. **TLC**; R_f = 0.4 (40% ethyl acetate in petroleum ether). **IR** (KBr) 3015, 2954, 1678, 1650, 1639, 1473, 1057, 857 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.26 – 7.13 (m, 5H), 6.26 (s, 2H), 4.28 (s, 2H), 2.63 (t, J = 8 Hz, 2H), 2.08 (t, J = 8 Hz, 2H), 1.78(s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 185.8, 174.4, 144.2, 137.9, 136.0, 128.6, 128.2, 127.4, 62.0, 44.4, 30.1, 29.31, 15.7. **HRMS** (ESI) calc'd for $C_{18}H_{20}NO_2[M+H]^+$: 282.1494, Found: 282.1490.

1-(4-fluorobenzyl)-7,9-dimethyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3f)


3f

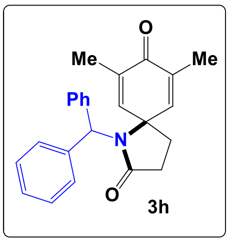
Total reaction time = 12 h. Temperature of reaction = 25 ˚C. Elution with 20% ethyl acetate in petroleum ether afforded colourless liquid, **1a** (30 mg, 0.135 mmol) → **3f** (37 mg, 0.124 mmol); 92% yield. **TLC**; R_f = 0.5 (30% ethyl acetate in petroleum ether). **IR** (KBr) 2970, 2904, 1687, 1662, 1641, 1325, 1022, 804, 716 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 – 7.11 (m, 2H), 6.97 – 6.93 (m, 2H), 6.27 (s, 2H), 4.25 (s, 2H), 2.63 (t, J = 8.1 Hz, 2H), 2.10 (t, J = 8.1 Hz, 2H), 1.81 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.89, 174.63, 163.34, 160.89, 144.30, 136.31, 133.99, 130.53, 130.45, 115.34, 115.13, 62.20, 43.81, 30.29, 29.37, 15.84. **HRMS** (ESI) calc'd for $C_{18}H_{18}FNNaO_2[M+Na]^+$: 322.1219, Found: 322.1218.

(R)-(+)-7,9-dimethyl-1-(1-phenylethyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3g)


3g

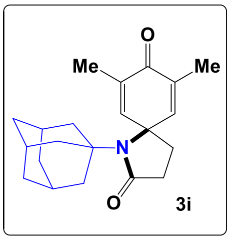
Total reaction time = 16 h. Temperature of reaction = 120 ˚C. Elution with 30% ethyl acetate in petroleum ether afforded pale red liquid, **1a** (30 mg, 0.135 mmol) → **3g** (30 mg, 0.101 mmol); 75% yield. **TLC**; R_f = 0.3 (40% ethyl acetate in petroleum ether). $[\alpha]_{589}^{26}$ = + 284.82 (*c* 0.02, $CHCl_3$). **IR** (KBr) 2812, 1673, 1633, 1473, 1255, 1138, 821 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.13 (m, 5H), 6.45 (m, 1H), 5.89 (m, 1H), 3.63 (q, J = 6.7 Hz, 1H), 2.17 – 2.12 (m, 2H), 1.98 – 1.93 (m, 4H), 1.91 – 1.89 (m, 1H), 1.46 (d, J = 1.9 Hz, 3H), 1.29 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.16, 173.19, 148.82, 148.22, 147.28, 136.94, 135.39, 128.24, 126.78, 126.53, 60.59, 58.29, 35.05, 28.93, 26.16, 16.07, 15.63. **HRMS** (ESI) calc'd for $C_{19}H_{22}NO_2$ $[M+H]^+$: 296.1651, Found : 296.1650.

1-benzhydryl-7,9-dimethyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3h)


3h

Total reaction time = 16 h. Temperature of reaction = 120 ˚C. Elution with 35% ethyl acetate in petroleum ether afforded pale yellow liquid, **1a** (44 mg, 0.198 mmol) → **3h** (57 mg, 0.158 mmol); 80% yield. **TLC**; R_f = 0.3 (40% ethyl acetate in petroleum ether). **IR** (KBr) 3430, 3022, 1676, 1655, 1493, 1028, 800 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.17 (m, 10H), 6.22 (s, 2H), 4.65 (s, 1H), 2.23 (t, J = 7.7 Hz, 2H), 2.02 (t, J = 7.7 Hz, 2H), 1.73 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.07, 173.12, 148.08, 145.08, 136.45, 128.42, 127.26, 126.97, 60.61, 58.55, 35.15, 29.05, 15.77. **HRMS** (ESI) calc'd for $C_{24}H_{24}NO_2$ $[M+H]^+$: 358.1807, Found : 358.1800.

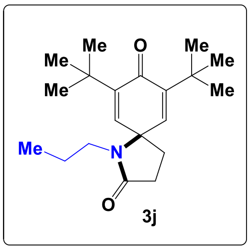
1-((3s,5s,7s)-adamantan-1-yl)-7,9-dimethyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3i)


3i

Total reaction time = 24 h. Temperature of reaction = 180 ˚C. Elution with 35% ethyl acetate in petroleum ether afforded yellow liquid, **1a** (52 mg, 0.234 mmol) → **3i** (55 mg, 0.168 mmol); 72% yield. **TLC**; Rf = 0.2 (40% ethyl acetate in petroleum ether). **IR** (KBr) 3447, 2924, 1717, 1597, 1368, 1153, 872 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.58 (s, 2H), 2.12 – 2.08 (m, 2H), 1.90 (m, 8H), 1.64 – 1.60 (m, 4H), 1.58 – 1.57 (m, 8H), 1.51 – 1.48 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$)

δ 187.30, 173.24, 151.74, 133.84, 76.71, 60.59, 57.03, 52.90, 45.48, 36.93, 36.35, 29.88, 28.63, 16.09, 14.19. **HRMS** (ESI) calc'd for $C_{21}H_{28}NO_2$ $[M+H]^+$: 326.2120, Found : 326.2122.

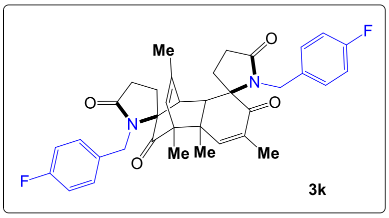
7,9-di-tert-butyl-1-propyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (3j)



3j

Total reaction time = 16 h. Temperature of reaction = 140 ˚C. Elution with 30% ethyl acetate in petroleum ether afforded colourless liquid, **1b** (27 mg, 0.088 mmol) → **3j** (23 mg, 0.072 mmol); 82% yield. **TLC**; R$_f$ = 0.4 (40% ethyl acetate in petroleum ether). **IR** (KBr) 2938, 1690, 1639, 1458, 1366, 1096, 881 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.41 (s, 2H), 2.96 – 2.92 (m, 2H), 2.59 (t, *J* = 8.1 Hz, 2H), 2.10 (t, *J* = 8.1 Hz, 2H), 1.50 – 1.44 (m, 2H), 1.25 (s, 18H), 0.86 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.32, 174.82, 148.27, 140.61, 62.09, 42.62, 34.92, 30.89, 29.55, 29.38, 23.06, 11.40. **HRMS** (ESI) calc'd for $C_{20}H_{32}NO_2$ $[M+H]^+$: 318.2433, Found : 318.2431.

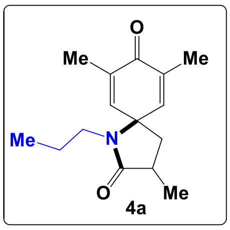
(1'R,4'R,4a'R,10'R)-1,1''-bis(4-fluorobenzyl)-2',4',4a',6'-tetramethyl-1',4',4a',8a'-tetrahydro-7'H-dispiro[pyrrolidine-2,8'-[1,4]ethanonaphthalene-10',2''-pyrrolidine]-5,5'',7',9'-tetraone (3k)



3k

Total reaction time = 18 h. Temperature of reaction = 100 ˚C. Elution with 25% ethyl acetate in petroleum ether afforded red liquid, **1c** (37 mg, 0.166 mmol) → **3k** (31 mg, 0.105 mmol); 63% yield. **TLC**; R$_f$ = 0.2 (20% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.14 – 7.10 (m, 2H), 7.02 – 6.96 (m, 4H), 6.85 (s, 1H), 6.72 (s, 1H), 6.57 (s, 1H), 6.54 (s, 1H), 4.39 (d, *J* = 5.9 Hz, 2H), 3.51 (s, 2H), 2.93 – 2.90 (m, 2H), 2.66 – 2.52 (m, 7H), 2.25 (s, 3H), 2.23 (s, 3H), 1.34 (s, 3H), 1.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.01, 186.15, 174.25, 173.02, 169.90, 163.47, 163.25, 160.90, 160.69, 150.73, 150.51, 149.76, 137.53, 135.50, 129.99, 129.69, 129.61, 129.50, 129.42, 128.94, 128.38, 127.02, 126.54, 115.67, 115.46, 115.30, 115.09, 60.38, 55.07, 48.05, 43.20, 37.37, 33.08, 29.72, 27.19, 25.25, 24.63, 20.44, 16.51, 16.00, 14.25.

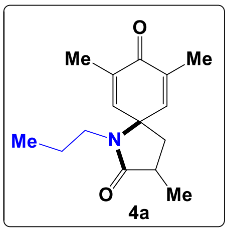
3,7,9-trimethyl-1-propyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (using PTATB; 4a with inseparable mixture, 1.24:1)



4a

Total reaction time = 10 h. Temperature of reaction = 90 ˚C. Elution with 25% ethyl acetate in petroleum ether afforded colourless liquid, **1d** (38 mg, 0.161 mmol) → **4a** (31 mg, 0.125 mmol); 78% yield. **TLC**; R$_f$ = 0.5 (40% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.67 (s, 1H), 6.50 (s, 1H), 6.40 (s, 1H), 5.97 (s, 1H), 3.02 (m, 1H), 2.91 – 2.79 (m, 1H), 2.71 – 2.49 (m, 4H), 2.31 – 2.17 (m, 6H), 2.16 – 2.01 (m, 3H), 1.90 (s, 4H), 1.87 (s, 5H), 1.78 – 1.72 (m, 3H), 1.45 – 1.33 (m, 6H), 1.25 – 1.06 (m, 18H), 0.84 – 0.78 (m, 8H).

3,7,9-trimethyl-1-propyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (using DABCOETB; 4a with inseparable mixture, 2:1)

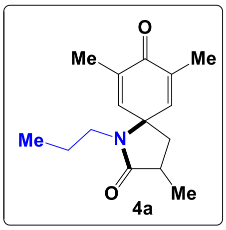


4a

Total reaction time = 10 h. Temperature of reaction = 90 ˚C. Elution with 25% ethyl acetate in petroleum ether afforded colourless liquid, **1d** (38 mg, 0.161 mmol) → **4a** (31 mg, 0.125 mmol); 78% yield. **TLC**; R$_f$ = 0.5 (40% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.67 (s, 1H), 6.50 (s, 2H), 6.40 (s, 2H), 5.97 (s, 1H), 3.02 (m, 2H), 2.91 – 2.79 (m, 2H), 2.71 – 2.49

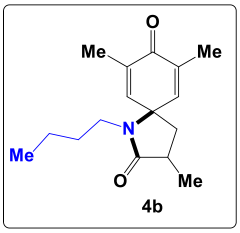
(m, 3H), 2.31 – 2.17 (m, 4H), 2.16 – 2.01 (m, 2H), 1.90 (s, 6H), 1.87 (s, 4H), 1.78 – 1.72 (m, 4H), 1.45 – 1.33 (m, 4H), 1.25 – 1.06 (m, 18H), 0.84 – 0.78 (m, 6H).

3,7,9-trimethyl-1-propyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (using TBATB; **4a** with inseparable mixture, 3.4:1**)**


4a

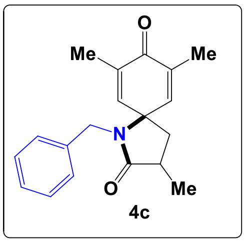
Total reaction time = 10 h. Temperature of reaction = 90 ˚C. Elution with 25% ethyl acetate in petroleum ether afforded colourless liquid, **1d** (38 mg, 0.161 mmol) → **4a** (29 mg, 0.119 mmol); 74% yield. **TLC**; R$_f$ = 0.5 (40% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 6.67 (s, 1H), 6.50 (s, 3H), 6.40 (s, 3H), 5.97 (s, 1H), 3.02 (m, 3H), 2.91 – 2.79 (m, 3H), 2.71 – 2.49 (m, 3H), 2.31 – 2.17 (m, 3H), 2.16 – 2.01 (m, 1H), 1.90 (s, 9H), 1.87 (s, 9H), 1.78 – 1.72 (m, 3H), 1.45 – 1.33 (m, 6H), 1.25 – 1.06 (m, 9H), 0.84 – 0.78 (m, 3H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 186.11, 177.05, 175.64, 145.99, 144.37, 141.43, 139.91, 136.83, 135.75, 132.97, 131.53, 64.27, 60.75, 60.50, 45.79, 41.20, 39.36, 39.10, 35.27, 32.63, 31.86, 29.69, 27.13, 20.32, 20.15, 16.79, 16.71, 16.06, 15.97, 15.08, 14.22, 13.88, 13.73. **HRMS** (ESI) calc'd for $C_{15}H_{22}NO_2$ $[M+H]^+$: 248.1651, Found : 248.1654.

1-butyl-3,7,9-trimethyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (using PTATB; **4b** with inseparable mixture, 1.8:1**)**


4b

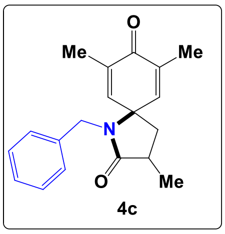
Total reaction time = 10 h. Temperature of reaction = 100 ˚C. Elution with 25% ethyl acetate in petroleum ether afforded colourless liquid, **1d** (30 mg, 0.127 mmol) → **4b** (25 mg, 0.094 mmol); 74% yield. **TLC**; Rf = 0.5 (40% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 6.71 (s, 1H), 6.53 (s, 2H), 6.44 (s, 2H), 6.03 (s, 1H), 3.14 – 3.04 (m, 2H), 2.99 – 2.87 (m, 2H), 2.72 – 2.53 (m, 5H), 2.33 – 2.21 (m, 6H), 1.95 (s, 6H), 1.92 (s, 6H), 1.79 (m, 3H), 1.46 – 1.36 (m, 6H), 1.31 – 1.25 (m, 16H), 1.20 – 1.13 (m, 8H), 0.89 – 0.85 (m, 5H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 207.89, 186.12, 177.04, 175.66, 147.22, 146.00, 144.38, 141.38, 141.29, 140.19, 136.84, 136.21, 135.77, 133.07, 131.43, 64.23, 60.74, 60.51, 45.82, 45.75, 41.21, 39.38, 39.20, 39.11, 39.06, 35.28, 32.79, 31.87, 27.28, 27.23, 20.34, 20.16, 16.77, 16.72, 16.07, 15.98, 15.09, 14.23, 13.93, 13.90, 13.73.

1-benzyl-3,7,9-trimethyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (using PTATB; **4c** with inseparable mixture, 3.84:1**)**


4c

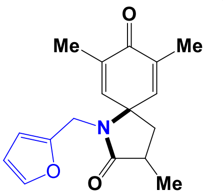
Total reaction time = 10 h. Temperature of reaction = 90 ˚C. Elution with 25% ethyl acetate in petroleum ether afforded pale yellow liquid, **1d** (30 mg, 0.127 mmol) → **4c** (30 mg, 0.103 mmol); 81% yield. **TLC**; R$_f$ = 0.3 (40% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.29 – 7.19 (m, 3H), 7.13 – 7.10 (m, 2H), 6.74 (s, 0.25H), 6.30 (m, 1H), 6.15 (m, 1H), 6.10 (s, 0.25H), 4.40 – 4.36 (d, *J* = 16 Hz, 1H), 4.18 – 4.15 (d, *J* = 12 Hz, 1H), 2.78 – 2.70 (m, 1H), 2.64 – 2.60 (m, 0.33H), 2.25 – 2.20 (m, 1H), 1.79 (s, 3H), 1.73 (m, 4H), 1.33 (d, *J* = 8 Hz, 3H).

1-benzyl-3,7,9-trimethyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (using TBATB; **4c** with inseparable mixture,16.7:1**)**


4c

Total reaction time = 10 h. Temperature of reaction = 90 ˚C. Elution with 25% ethyl acetate in petroleum ether afforded pale yellow liquid, **1d** (30 mg, 0.127 mmol) → **4c** (32 mg, 0.109 mmol); 86% yield. **TLC**; R$_f$ = 0.3 (40% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.29 – 7.19 (m, 3H), 7.13 – 7.10 (m, 2H), 6.30 (m, 1H), 6.15 (m, 1H), 4.40 – 4.36 (d, *J* = 16 Hz, 1H), 4.18 – 4.15 (d, *J* = 12 Hz, 1H), 2.78 – 2.70 (m, 1H), 2.25 – 2.20 (m, 1H), 1.79 (s, 3H), 1.73 (m, 4H), 1.33 (d, *J* = 8 Hz, 3H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 186.07, 176.99, 145.89, 143.81, 138.15, 136.64, 135.75, 128.74, 128.38, 127.53, 60.57, 44.79, 39.24, 35.25, 16.71, 15.88, 15.81.

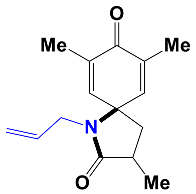
1-(furan-2-ylmethyl)-3,7,9-trimethyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (4d)



4d

Total reaction time = 12 h. Temperature of reaction = 80 ˚C. Elution with 30% ethyl acetate in petroleum ether afforded red liquid, **1d** (22 mg, 0.093 mmol) → **4d** (21 mg, 0.074 mmol); 80% yield. **TLC**; R$_f$ = 0.3 (40% ethyl acetate in petroleum ether). **IR** (KBr) 3031.31, 2931.10, 1672.16, 1647.32, 1438.07, 1403.46, 1118.72, 1037.01, 753.95 cm^{-1}. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.26 (d, *J* = 2.2 Hz, 1H), 6.36 (dd, *J* = 3.3, 1.3 Hz, 1H), 6.29 (dd, *J* = 3.1, 1.8 Hz, 1H), 6.24 (dd, *J* = 3.3, 2.0 Hz, 1H), 6.08 (d, *J* = 3.1 Hz, 1H), 4.31 (q, *J* = 15.4 Hz, 2H), 2.75 – 2.66 (m, 1H), 2.27 – 2.22 (m, 1H), 1.90 (s, 3H), 1.81 – 1.79 (m, 4H), 1.32 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 195.08, 186.02, 176.75, 150.28, 145.95, 145.12, 143.23, 142.02, 137.00, 136.72, 135.73, 110.56, 108.98, 60.13, 39.36, 37.12, 35.18, 16.06, 16.02. **HRMS** (ESI) calc'd for C$_{17}$H$_{20}$NO$_3$ [M+H]$^+$: 286.1443, Found : 286.1439.

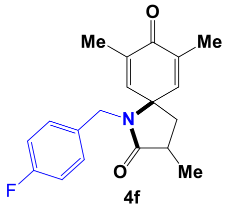
1-allyl-3,7,9-trimethyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (4e)



4e

Total reaction time = 8 h. Temperature of reaction = 60 ˚C. Elution with 20% ethyl acetate in petroleum ether afforded colourless liquid, **1d** (30 mg, 0.127 mmol) → **4e** (26 mg, 0.107 mmol); 84% yield. **TLC**; R$_f$ = 0.4 (40% ethyl acetate in petroleum ether). **IR** (KBr) 2931, 2831, 1681, 1637, 1491, 1396, 1173, 1065, 884 cm^{-1}. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 6.51 (s, 1H), 6.43 (s, 1H), 5.77 – 5.67 (m, 1H), 5.10 5.00 (m, 2H), 3.80 (dd, *J* = 15.3, 5.9 Hz, 1H), 3.56 (dd, *J* = 15.1, 6.3 Hz, 1H), 2.74 – 2.67 (m, 1H), 2.32 – 2.27 (m, 1H), 1.92 (d, *J* = 7.8 Hz, 6H), 1.85 – 1.79 (m, 1H), 1.32 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 186.23, 176.69, 145.84, 143.89, 136.82, 133.99, 117.64, 60.57, 43.66, 39.30, 35.18, 16.69, 15.92. **HRMS** (ESI) calc'd for C$_{15}$H$_{20}$NO$_2$ [M+H]$^+$: 246.1494, Found : 246.1490.

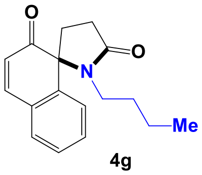
1-(4-fluorobenzyl)-3,7,9-trimethyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (4f)



4f

Total reaction time = 8 h. Temperature of reaction = 60 ˚C. Elution with 20% ethyl acetate in petroleum ether afforded colourless liquid, **1d** (60 mg, 0.254 mmol) → **4f** (65 mg, 0.208 mmol); 82% yield. **TLC**; R$_f$ = 0.5 (30% ethyl acetate in petroleum ether). **IR** (KBr) 2974, 2924, 1691, 1674, 1456, 1396, 1259, 1124, 907 cm^{-1}. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.13 – 7.10 (m, 2H), 6.94 (t, *J* = 8.7 Hz, 2H), 6.32 (dd, *J* = 2.9, 1.4 Hz, 1H), 6.16 (dd, *J* = 2.9, 1.4 Hz, 1H), 4.35 (d, *J* = 14.8 Hz, 1H), 4.14 (d, *J* = 14.8 Hz, 1H), 2.77 – 2.68 (m, 1H), 2.28 2.22 (m, 1H), 1.83 (d, *J* = 1.3 Hz, 3H), 1.80 – 1.74 (m, 4H), 1.33 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 185.91, 176.97, 163.31, 160.86, 145.75, 143.68, 136.75, 135.82, 134.12, 134.09, 130.52, 130.44, 115.30, 115.08, 60.54, 44.00, 39.23, 35.19, 16.64, 15.85, 15.76. **HRMS** (ESI) calc'd for C$_{19}$H$_{21}$NFO$_2$ [M+H]$^+$: 314.1550, Found : 314.1559.

1'-butyl-2H-spiro[naphthalene-1,2'-pyrrolidine]-2,5'-dione (4g)[12]

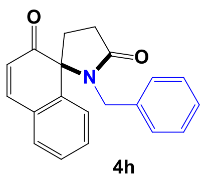


4g

Total reaction time = 14 h. Temperature of reaction = 120 ˚C. Elution with 35% ethyl acetate in petroleum ether afforded yellow liquid, **1e** (30 mg, 0.123 mmol) → **4g** (26 mg, 0.097 mmol); 79% yield. **TLC**; R$_f$ = 0.3 (40% ethyl acetate in petroleum ether). **IR** (KBr) 3313, 2855, 1748, 1646, 1451, 1096, 860, 745 cm^{-1}. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.55 (dddd, *J* = 12.5, 9.8, 6.0, 2.2 Hz, 3H), 7.45 – 7.31 (m, 2H), 6.22 (d, *J* = 10.0 Hz, 1H), 3.56 – 3.43 (m, 2H), 2.98 – 2.85 (m, 1H), 2.83 – 2.71 (m, 1H), 2.61 (ddd, *J* = 13.2, 9.1, 2.3 Hz, 1H), 2.15 – 2.05 (m, 1H), 1.79 – 1.62 (m, 2H), 1.57 – 1.39 (m, 1H), 1.10 – 0.92 (m, 3H).

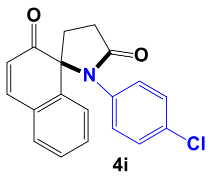
^{13}C NMR (100 MHz, $CDCl_3$) δ 199.13, 161.73, 145.30, 142.02, 130.81, 129.54, 128.78, 125.44, 123.20, 87.75, 50.75, 36.68, 33.07, 26.94, 20.67, 14.02. **HRMS** (ESI) calc'd for $C_{17}H_{19}NNaO_2$[M+Na]$^+$: 292.1313, Found: 292.1310.

1'-benzyl-2H-spiro[naphthalene-1,2'-pyrrolidine]-2,5'-dione (4h)[12]


4h

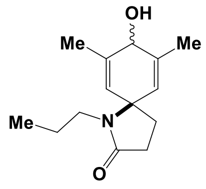
Total reaction time = 12 h. Temperature of reaction = 120 °C. Elution with 30% ethyl acetate in petroleum ether afforded yellow liquid, **1e** (30 mg, 0.123 mmol) → **4h** (31 mg, 0.100 mmol); 82% yield. **TLC**; R_f = 0.3 (40% ethyl acetate in petroleum ether). **IR** (KBr) 3001, 2952, 1745, 1685, 866, 754 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.34 (m, 5H), 7.34 – 7.26 (m, 1H), 7.26 – 7.06 (m, 2H), 6.94 (dd, *J* = 9.9, 2.8 Hz, 2H), 5.99 (d, *J* = 10.0 Hz, 1H), 4.64 (d, *J* = 14.3 Hz, 1H), 4.28 – 4.10 (m, 1H), 2.97 – 2.79 (m, 1H), 2.74 – 2.58 (m, 1H), 2.41 (ddd, *J* = 14.3, 8.3, 3.7 Hz, 1H), 2.11 – 1.93 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.87, 176.98, 144.94, 135.40, 130.55, 130.04, 129.96, 129.79, 128.44, 128.03, 127.77, 127.51, 123.84, 71.19, 45.69, 35.63, 28.59. **HRMS** (ESI) calc'd for $C_{20}H_{18}NO_2$ [M+H]$^+$: 304.1338, Found : 304.1330.

1'-(4-chlorophenyl)-2H-spiro[naphthalene-1,2'-pyrrolidine]-2,5'-dione (4i)[12]


4i

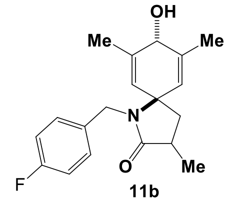
Total reaction time = 18 h. Temperature of reaction = 120 °C. Elution with 30% ethyl acetate in petroleum ether afforded yellow liquid, **1e** (38 mg, 0.155 mmol) → **4i** (30 mg, 0.093 mmol); 60% yield. **TLC**; R_f = 0.3 (40% ethyl acetate in petroleum ether). **IR** (KBr) 3126, 3032, 1740, 1693, 1296, 891, 767 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 10.0 Hz, 1H), 7.52 – 7.40 (m, 2H), 7.38 – 7.27 (m, 1H), 7.26 – 7.17 (m, 2H), 7.10 – 7.01 (m, 2H), 6.97 – 6.89 (m, 1H), 6.43 (d, *J* = 9.8 Hz, 1H), 2.97 (dt, *J* = 17.1, 9.5 Hz, 1H), 2.79 (ddd, *J* = 17.3, 9.2, 2.9 Hz, 1H), 2.73 – 2.59 (m, 1H), 2.23 – 2.12 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.05, 179.57, 175.56, 146.23, 141.75, 135.29, 131.28, 130.32, 129.63, 128.79, 128.62, 126.36, 124.38, 123.62, 120.55, 115.32, 73.61, 35.15, 29.13. **HRMS** (ESI) calc'd for $C_{19}H_{15}NClO_2$ [M+H]$^+$: 324.0791, Found : 324.0790.

8-hydroxy-7,9-dimethyl-1-propyl-1-azaspiro[4.5]deca-6,9-dien-2-one (11a + 11a′ = 2:1)


11a + 11a′

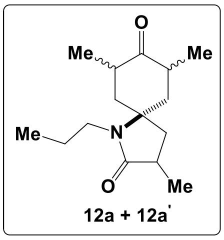
3a (30 mg, 0.121 mmol) → **11a+11a′** (27 mg, 0.109 mmol); 90% yield. **TLC**; R_f = 0.3 (40% ethyl acetate in petroleum ether). **IR** (KBr) 3393, 3164, 2829, 1654, 1614, 1431, 1219, 895 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.40 (s, 1H), 5.38 (s, 0.5H), 4.18 (s, 4H), 4.11 (s, 0.5H), 3.00 – 2.89 (m, 0.2H), 2.89 – 2.79 (m, 0.5H), 2.43 (t, *J* = 8.1 Hz, 1H), 1.98 – 1.84 (m, 6H), 1.44 (qd, *J* = 14.8, 7.5 Hz, 1H), 0.87 (t, *J* = 6.9 Hz, 0.5H), 0.82 (dt, *J* = 7.6, 5.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.84, 174.75, 137.87, 137.34, 127.50, 126.74, 68.27, 67.94, 63.00, 62.48, 42.16, 42.11, 33.48, 32.81, 31.91, 29.71, 29.68, 29.43, 29.35, 29.17, 24.94, 22.66, 19.93, 19.70, 14.12, 11.63, 11.55.

(3S,5r,8S)-1-(4-fluorobenzyl)-8-hydroxy-3,7,9-trimethyl-1-azaspiro[4.5]deca-6,9-dien-2-one (11b)


11b

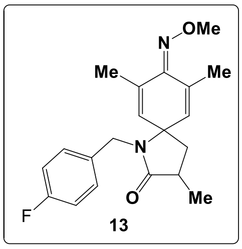
4f (80 mg, 0.255 mmol) → **11b** (65 mg, 0.208 mmol); 85% yield. **TLC**; R_f = 0.2 (30% ethyl acetate in petroleum ether). **IR** (KBr) 3373, 3065, 3044, 2926, 1649, 1605, 1412, 1040, 872 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 8.5, 5.5 Hz, 2H), 6.94 (t, *J* = 8.7 Hz, 2H), 5.28 (s, 1H), 5.13 (s, 1H), 4.27 (d, *J* = 14.7 Hz, 1H), 4.07 (dd, *J* = 16.7, 11.9 Hz, 2H), 2.76 – 2.56 (m, 1H), 2.16 (dd, *J* = 12.9, 8.6 Hz, 1H), 1.83 (s, 3H), 1.78 (s, 3H), 1.70 – 1.55 (m, 4H), 1.29 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.08, 163.08, 160.64, 138.29, 136.92, 134.94, 130.14, 130.06, 129.17, 126.84, 114.97, 114.76, 68.55, 60.95, 43.28, 41.87, 35.21, 19.62, 19.50, 16.74. **HRMS** (ESI) calc'd for $C_{19}H_{23}NFO_2$ [M+H]$^+$: 316.1707, Found : 316.1705.

3,7,9-trimethyl-1-propyl-1-azaspiro[4.5]decane-2,8-dione (12a + 12a′ = 2.3:1)


12a + 12a′

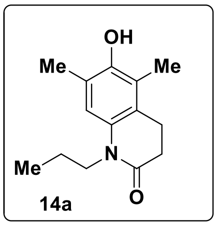
4a (35 mg, 0.141 mmol) → **12a+12a′** (31 mg, 0.121 mmol); 86% yield. **TLC**; $R_f = 0.4$ (30% ethyl acetate in petroleum ether). **IR** (KBr) 2970, 2878, 1711, 1663, 1410, 1299, 1155, 1005, 798 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.22 – 3.10 (m, 1H), 3.10 – 2.94 (m, 6H), 2.62 (dt, *J* = 12.4, 6.9 Hz, 6H), 2.48 (dd, *J* = 17.7, 10.0 Hz, 6H), 2.40 (t, *J* = 7.8 Hz, 2H), 2.26 (t, *J* = 7.7 Hz, 6H), 2.22 – 2.02 (m, 3H), 1.99 – 1.81 (m, 8H), 1.80 – 1.66 (m, 7H), 1.66 – 1.45 (m, 8H), 1.12 (dd, *J* = 17.9, 6.8 Hz, 7H), 1.04 (d, *J* = 6.2 Hz, 16H), 0.89 (dt, *J* = 14.5, 7.3 Hz, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.88, 211.88, 174.28, 174.24, 62.91, 62.24, 45.61, 44.26, 41.84, 41.43, 40.97, 40.85, 40.78, 40.71, 40.03, 38.58, 36.03, 33.62, 30.04, 29.65, 29.24, 29.17, 23.65, 23.17, 16.41, 15.51, 15.31, 14.37, 11.64, 11.51.

(3S,5S,Z)-1-(4-fluorobenzyl)-8-(methoxyimino)-3,7,9-trimethyl-1-azaspiro[4.5]deca-6,9-dien-2-one (13)


13

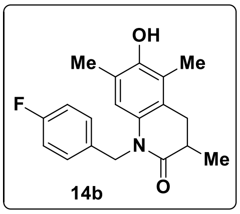
4f (42 mg, 0.134 mmol) → **13** (37 mg, 0.108 mmol); 81% yield. **TLC**; $R_f = 0.3$ (30% ethyl acetate in petroleum ether). **IR** (KBr) 3091, 2936, 1642, 1605, 1473, 1039, 870 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (ddd, *J* = 11.2, 5.3, 2.7 Hz, 2H), 7.00 – 6.86 (m, 2H), 5.66 – 5.19 (m, 2H), 4.34 (dd, *J* = 31.3, 14.7 Hz, 1H), 4.05 (dd, *J* = 39.6, 14.7 Hz, 1H), 3.94 (d, *J* = 6.3 Hz, 3H), 2.22 – 2.13 (m, 1H), 2.09 (dd, *J* = 13.2, 2.1 Hz, 4H), 1.86 (dd, *J* = 8.6, 1.8 Hz, 4H), 1.70 – 1.56 (m, 2H), 1.28 (d, *J* = 2.3 Hz, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.63, 160.66, 138.25, 138.02, 136.16, 134.94, 134.57, 132.50, 131.41, 130.55, 130.45, 130.33, 115.02, 114.81, 62.67, 61.46, 43.58, 41.67, 35.08, 24.03, 23.95, 18.47, 16.65. **HRMS** (ESI) calc'd for $C_{20}H_{23}N_2NaFO_2$ $[M+Na]^+$: 365.1641, Found : 365.1640.

6-hydroxy-5,7-dimethyl-1-propyl-3,4-dihydroquinolin-2(1H)-one (14a)


14a

3a (30 mg, 0.122 mmol) → **14a** (27 mg, 0.111 mmol); 92% yield. **TLC**; $R_f = 0.4$ (25% ethyl acetate in petroleum ether). **IR** (KBr) 3365 (brs), 2961, 1647, 1514, 1298, 1063, 853 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.67 (s, 1H), 4.94 (s, 1H), 3.94 – 3.81 (m, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.64 – 2.55 (m, 2H), 2.29 (s, 3H), 2.22 (s, 3H), 1.67 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.90, 167.49, 147.99, 145.21, 132.72, 124.51, 123.36, 121.57, 121.27, 114.99, 43.87, 31.75, 22.11, 20.57, 16.49, 11.94, 11.23. **HRMS** (ESI) calc'd for $C_{15}H_{22}NO_2$ $[M+H]^+$: 248.1651, Found : 248.1651.

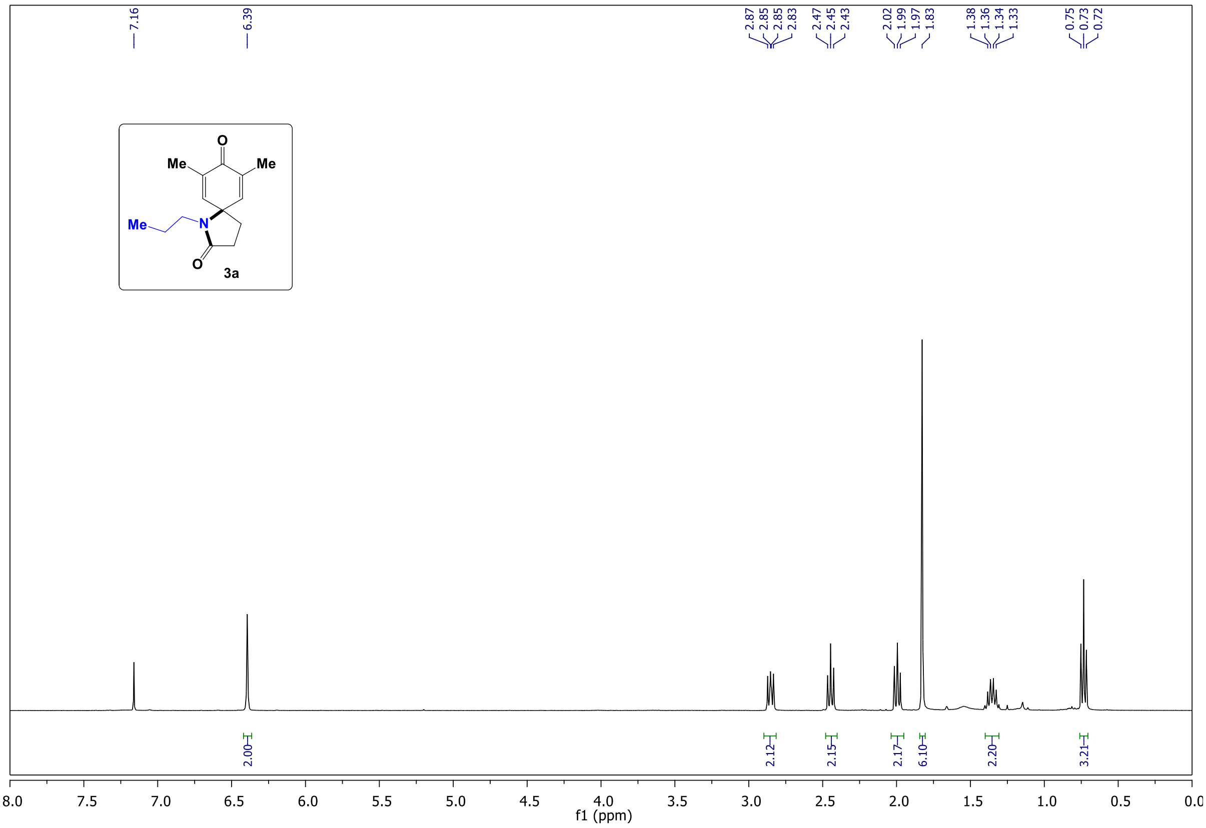
1-(4-fluorobenzyl)-6-hydroxy-3,5,7-trimethyl-3,4-dihydroquinolin-2(1H)-one (14b)


14b

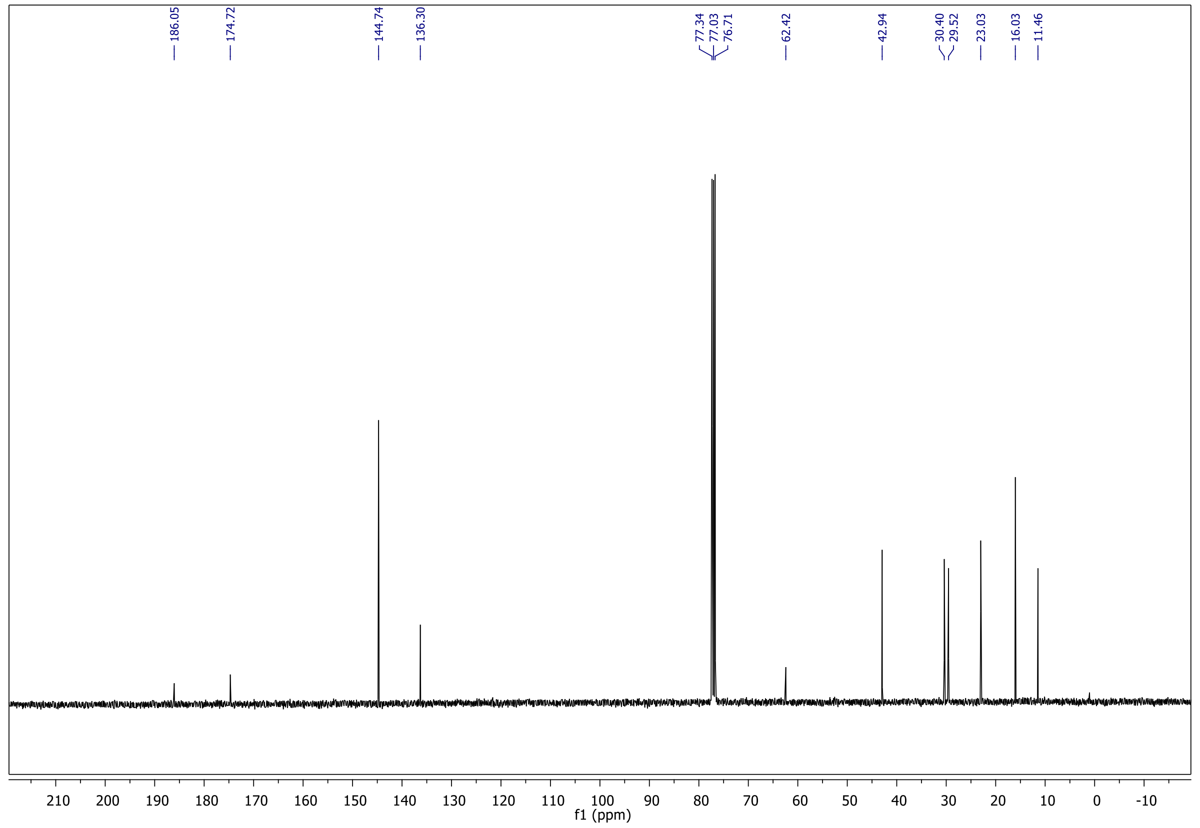
4f (30 mg, 0.096 mmol) → **14b** (28 mg, 0.090 mmol); 95% yield. **TLC**; $R_f = 0.4$ (25% ethyl acetate in petroleum ether). **IR** (KBr) 3385 (brs), 2930, 1641, 1611, 1391, 1186, 1078, 876 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.08 – 6.92 (m, 2H), 6.52 (s, 1H), 5.19 (d, *J* = 16.1 Hz, 1H), 5.00 (d, *J* = 16.1 Hz, 1H), 4.63 (s, 1H), 3.01 (dd, *J* = 15.0, 5.0 Hz, 1H), 2.80 – 2.53 (m, 2H), 2.19 (d, *J* = 27.9 Hz, 6H), 1.34 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.86, 148.10, 127.99, 127.91, 123.66, 121.09, 115.67, 115.45, 115.21, 77.36, 77.04, 76.72, 46.17, 35.30, 30.12, 16.35, 15.76, 11.92. **HRMS** (ESI) calc'd for $C_{19}H_{21}NFO_2$ $[M+H]^+$: 314.1556, Found : 314.1552.

N. ^{1}H, ^{13}C{^{1}H }, ^{19}F and nOe NMR Spectra

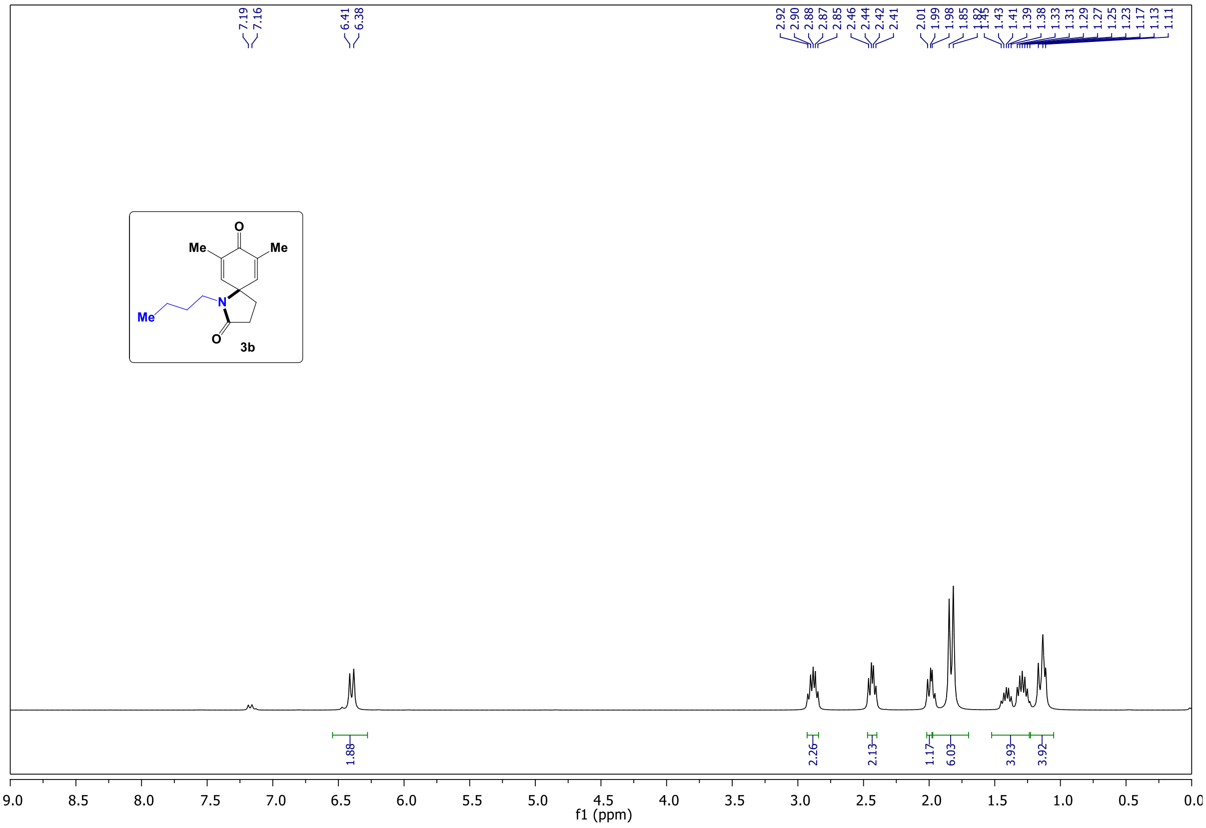
3a, ^{1}H NMR (CDCl$_3$, 400 MHz)



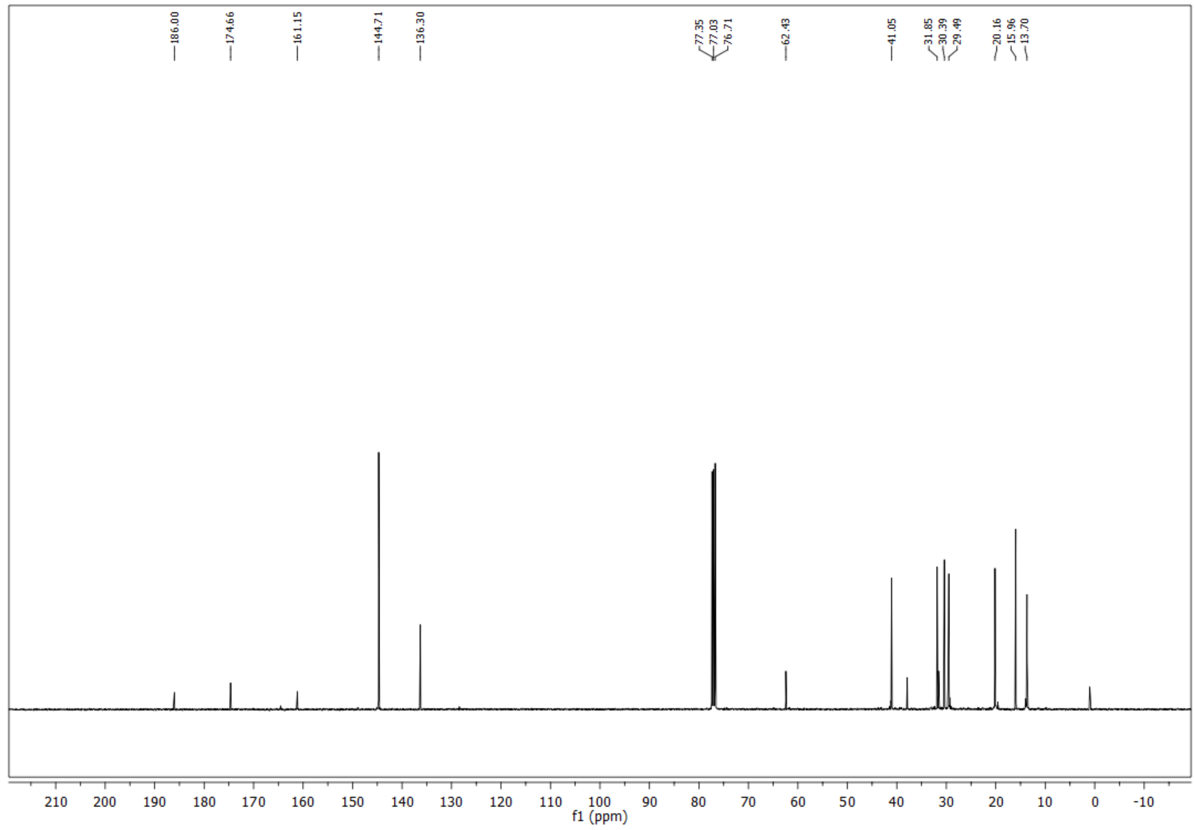
3a, ^{13}C NMR (CDCl$_3$, 100 MHz)



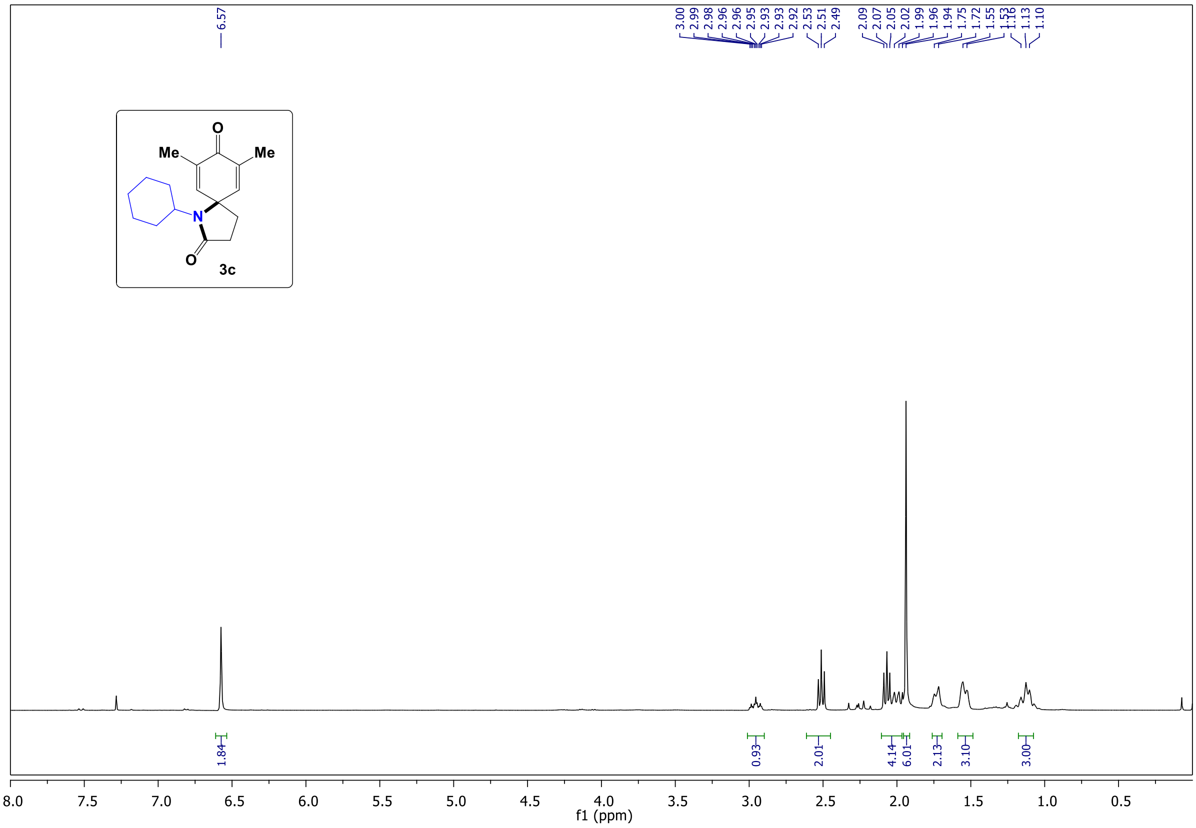
3b, ^{1}H NMR (CDCl$_3$, 400 MHz)



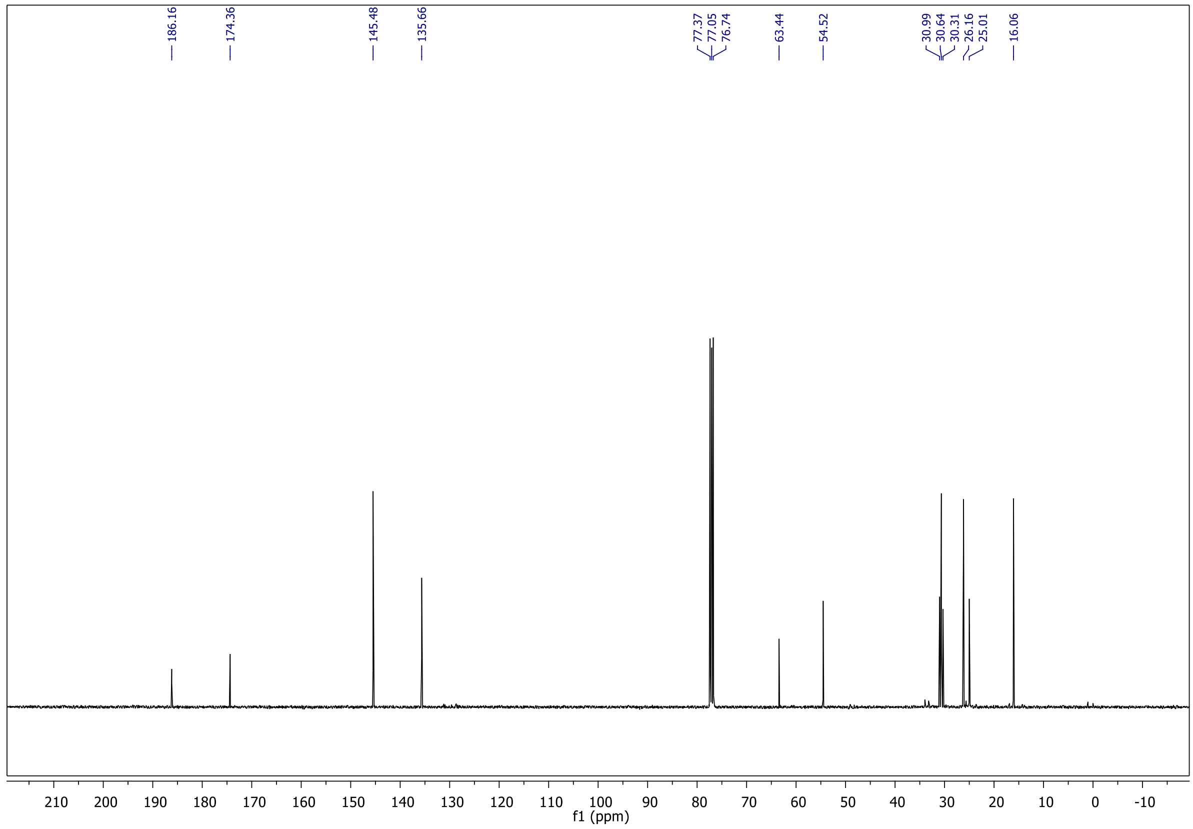
3b, ^{13}C NMR (CDCl$_3$, 100 MHz)



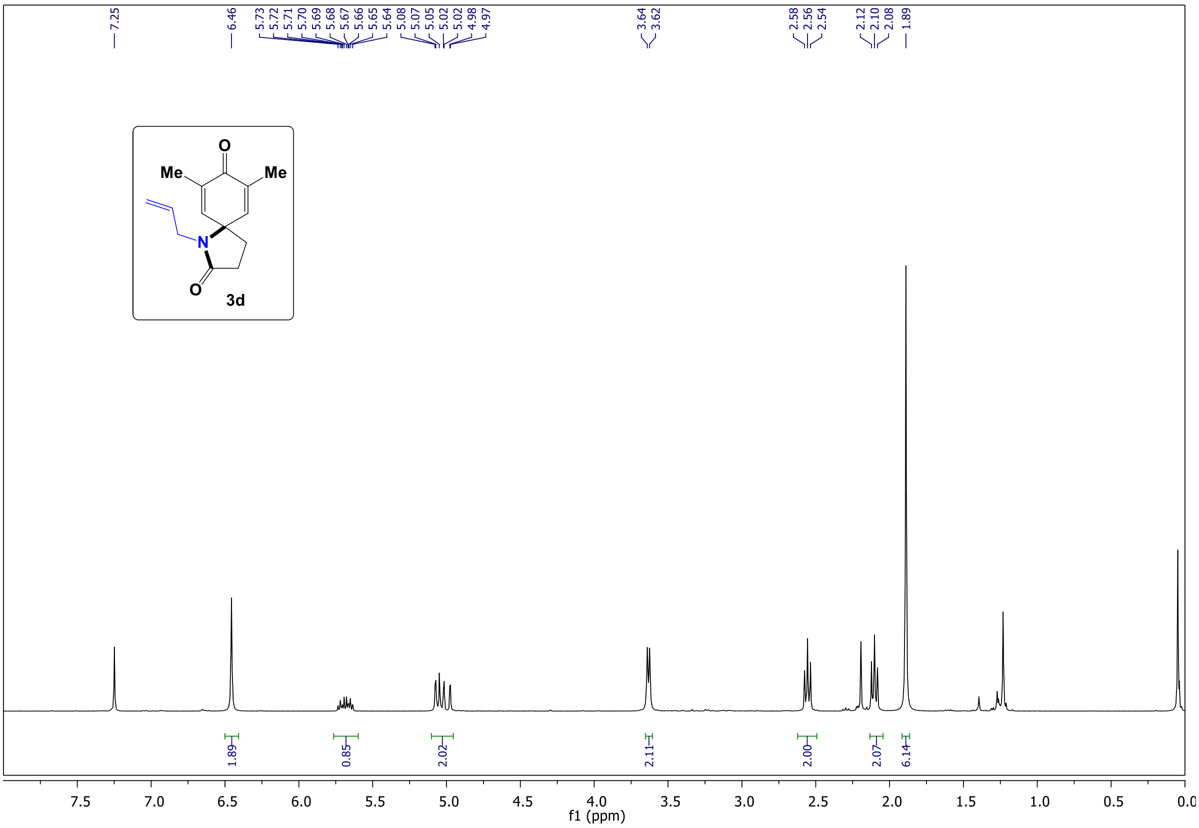
3c, ^{1}H NMR (CDCl$_3$, 400 MHz)



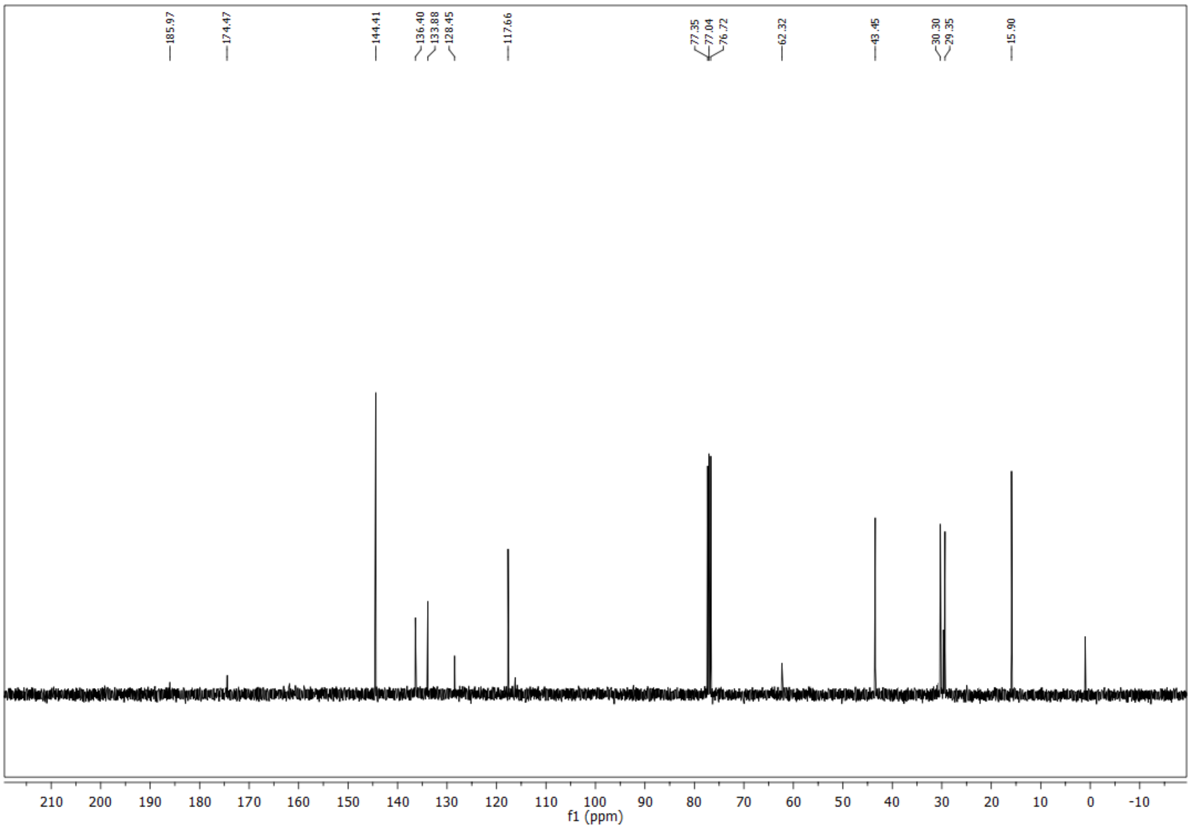
3c, ^{13}C NMR (CDCl$_3$, 100 MHz)



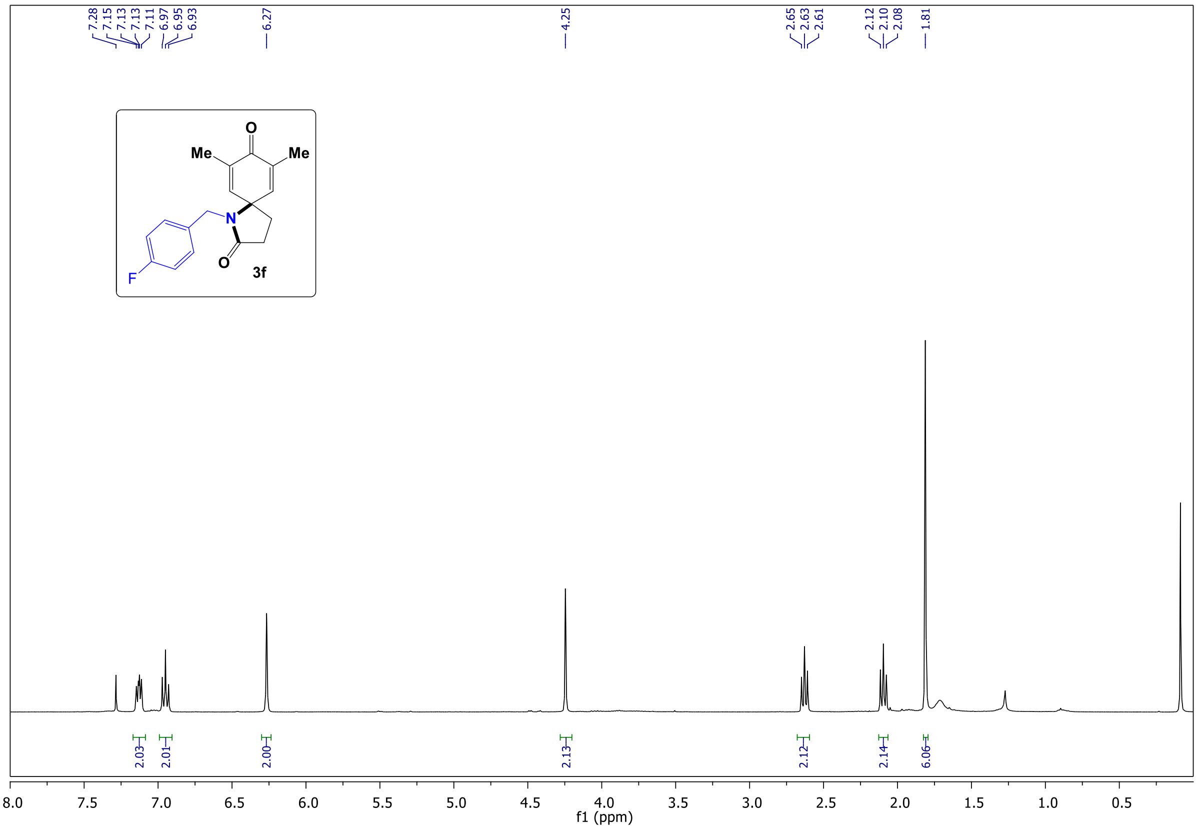
3d, ^{1}H NMR ($CDCl_3$, 400 MHz)



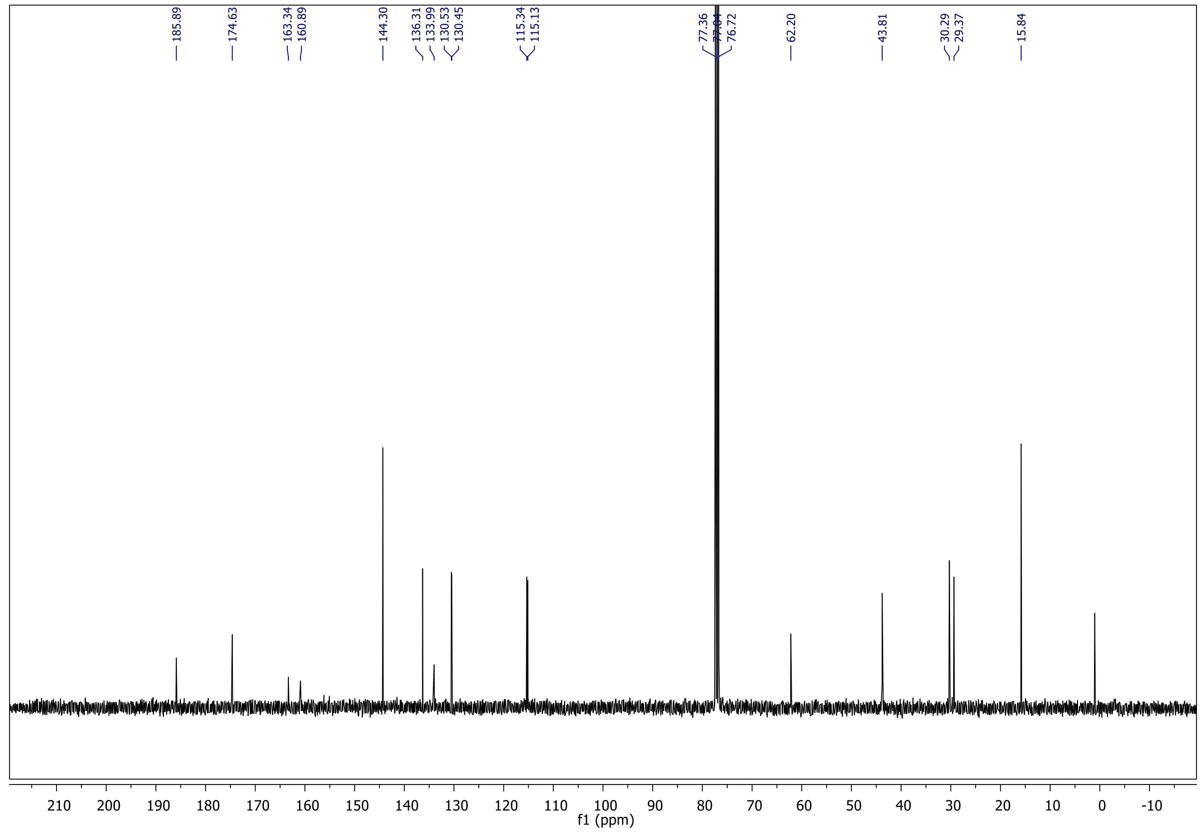
3d, ^{13}C NMR ($CDCl_3$, 100 MHz)



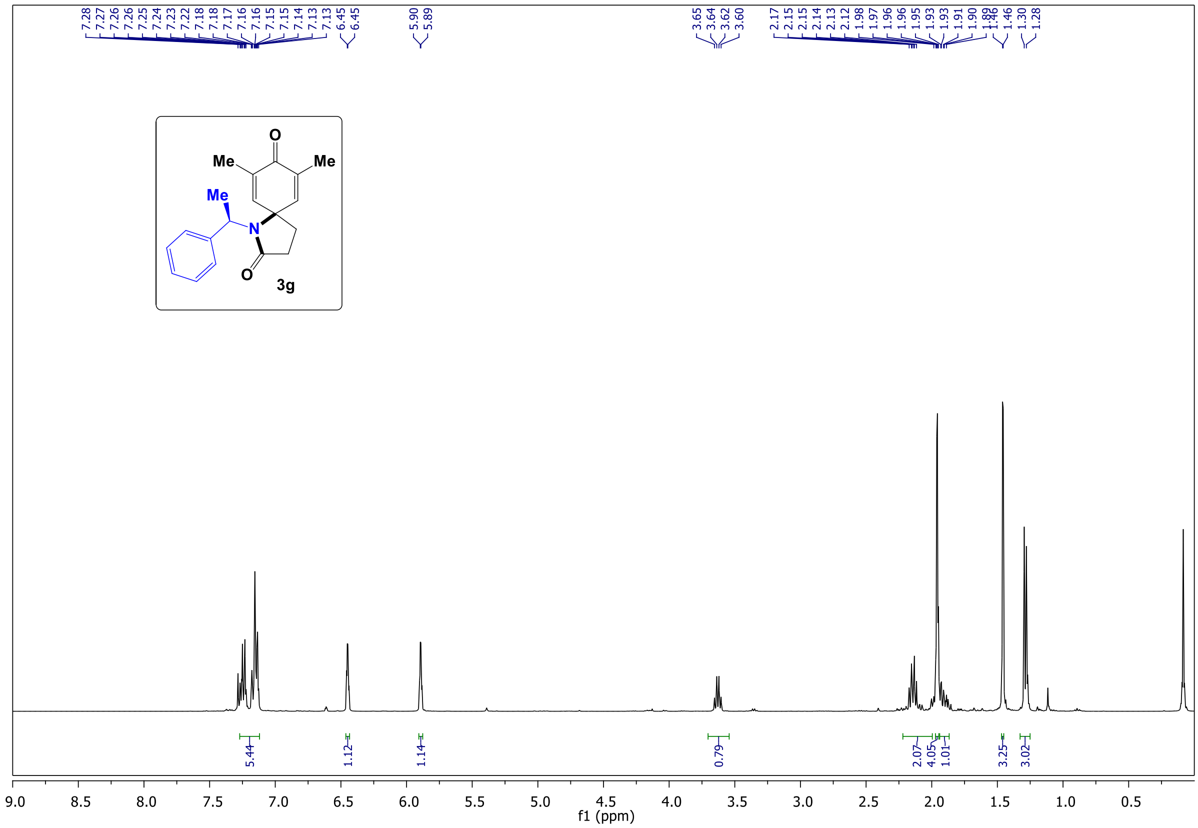
3f, ^{1}H NMR (CDCl$_3$, 400 MHz)



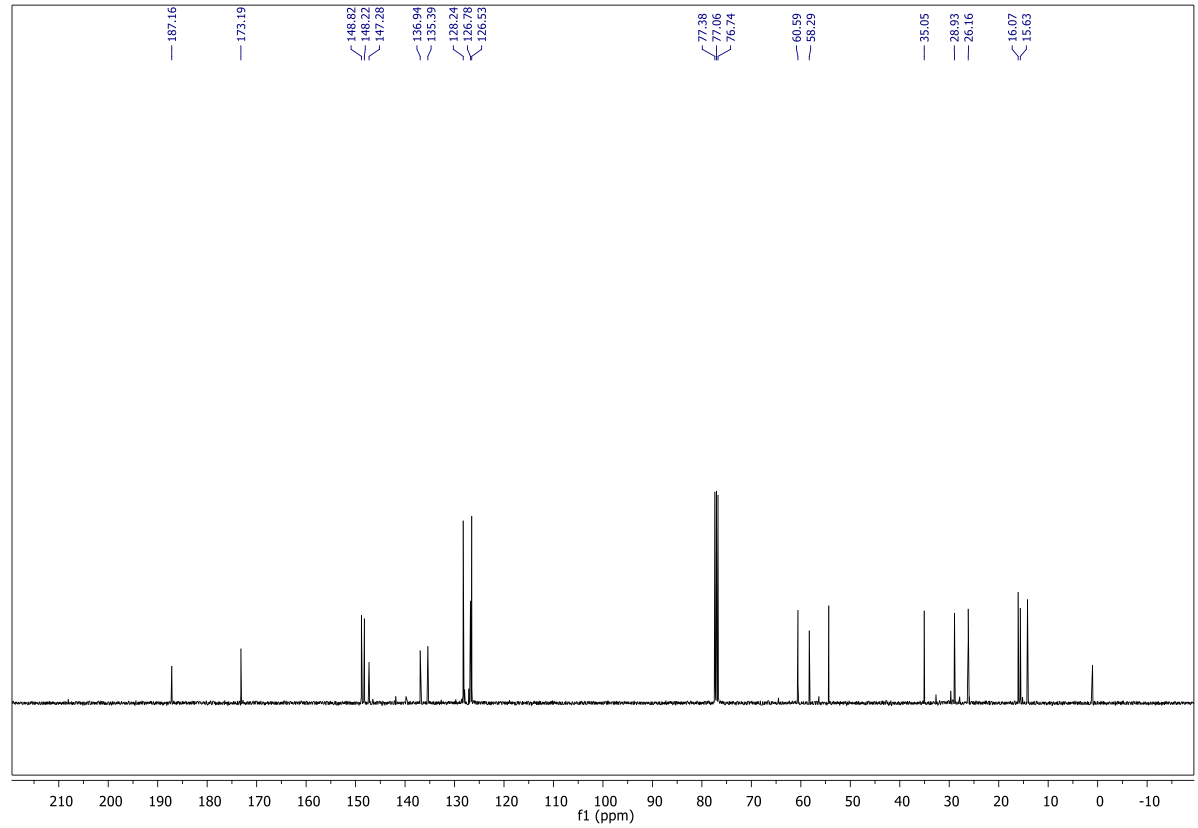
3f, ^{13}C NMR (CDCl$_3$, 100 MHz)



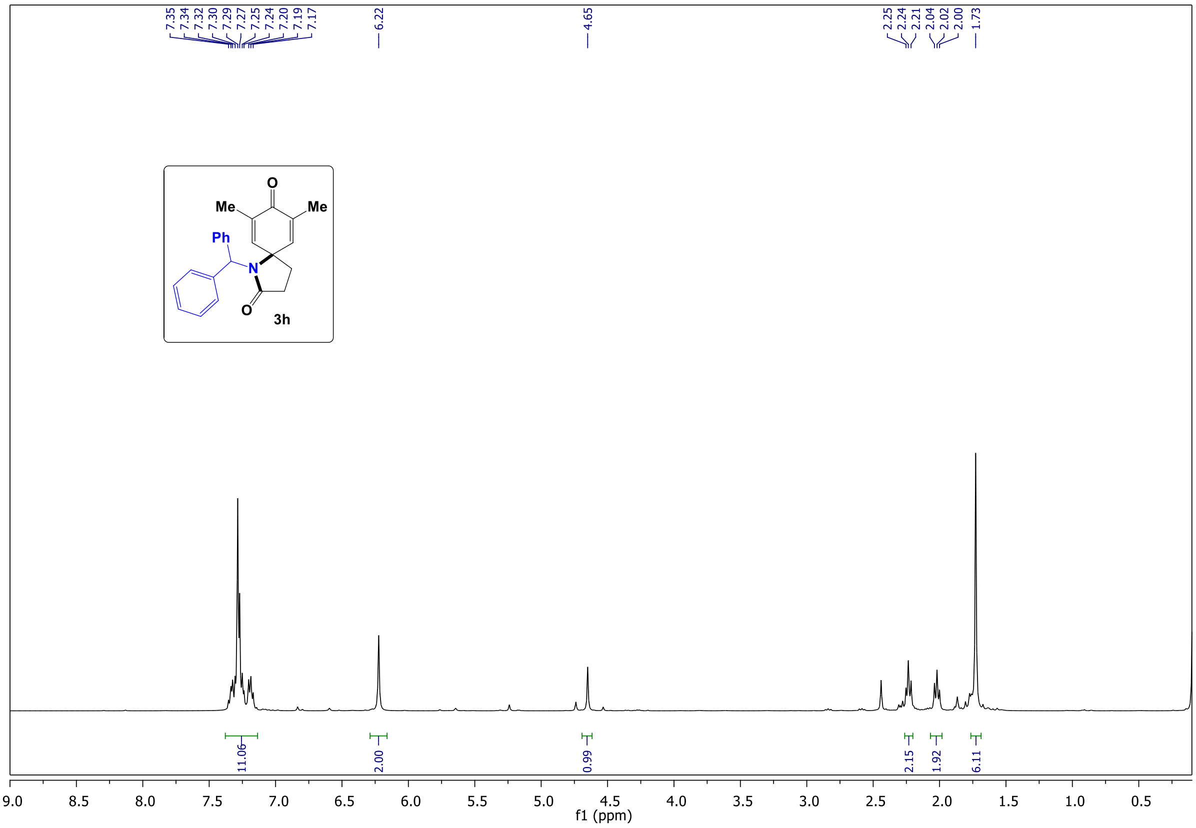
3g, ^{1}H NMR (CDCl$_3$, 400 MHz)



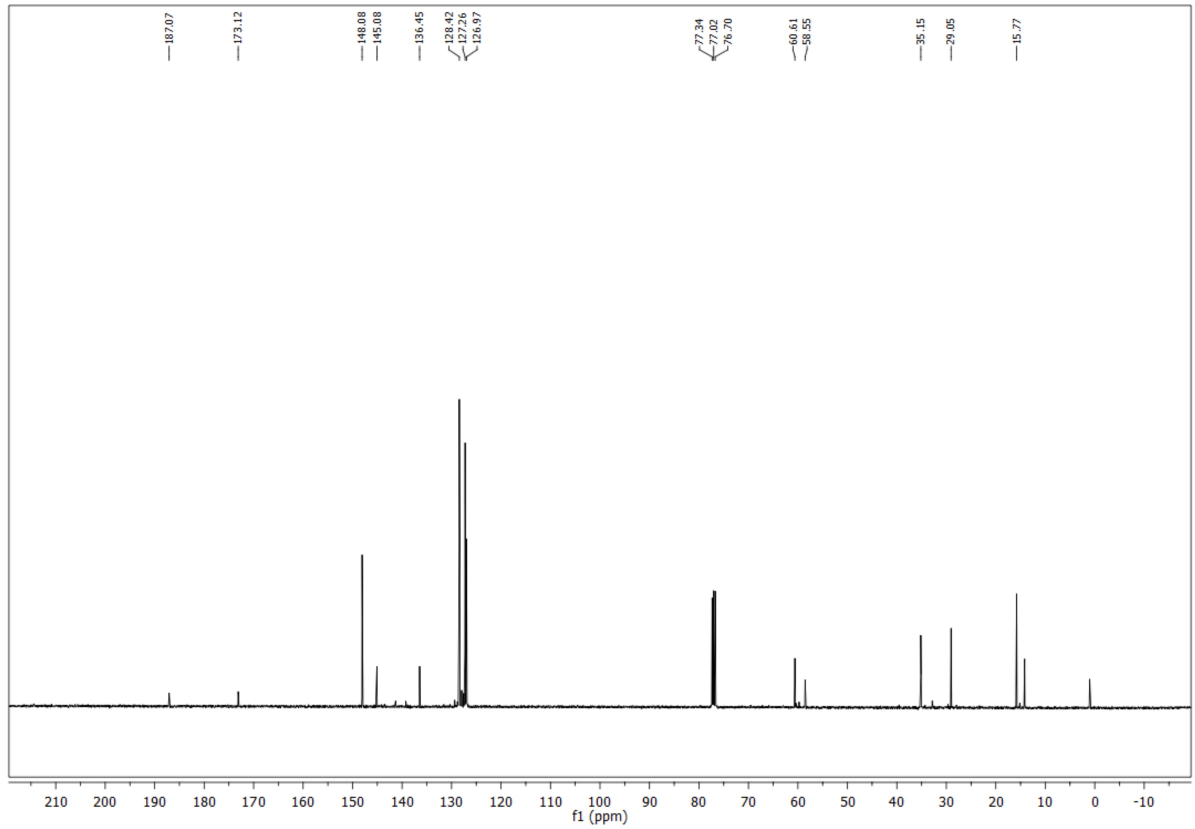
3g, ^{13}C NMR (CDCl$_3$, 100 MHz)



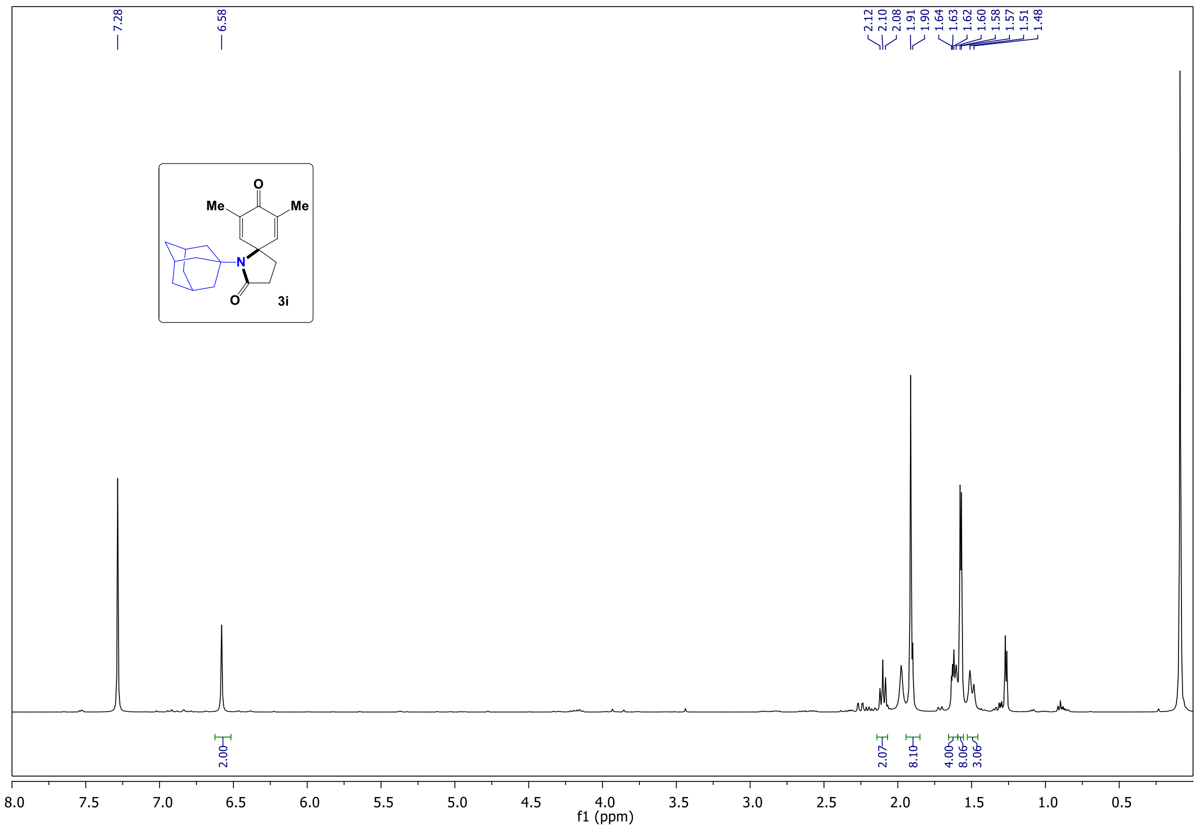
3h, ^{1}H NMR (CDCl$_3$, 400 MHz)



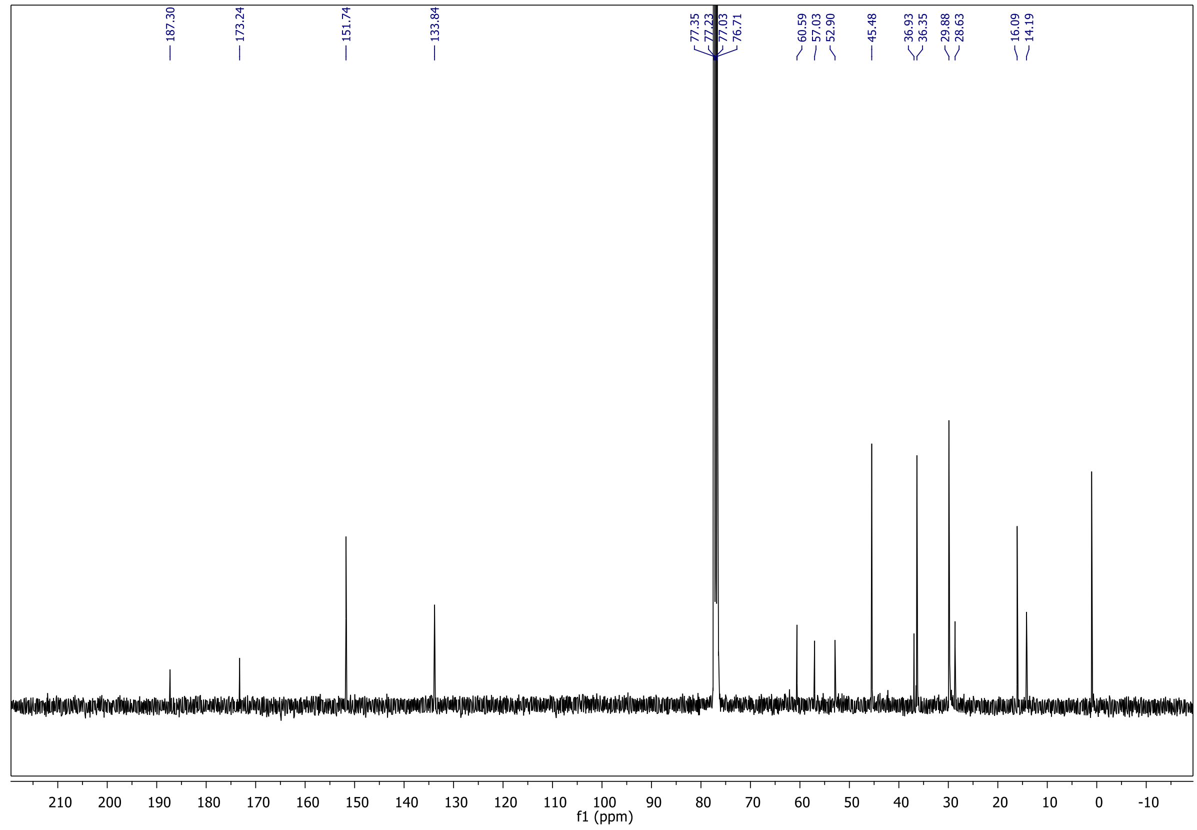
3h, ^{13}C NMR (CDCl$_3$, 100 MHz)



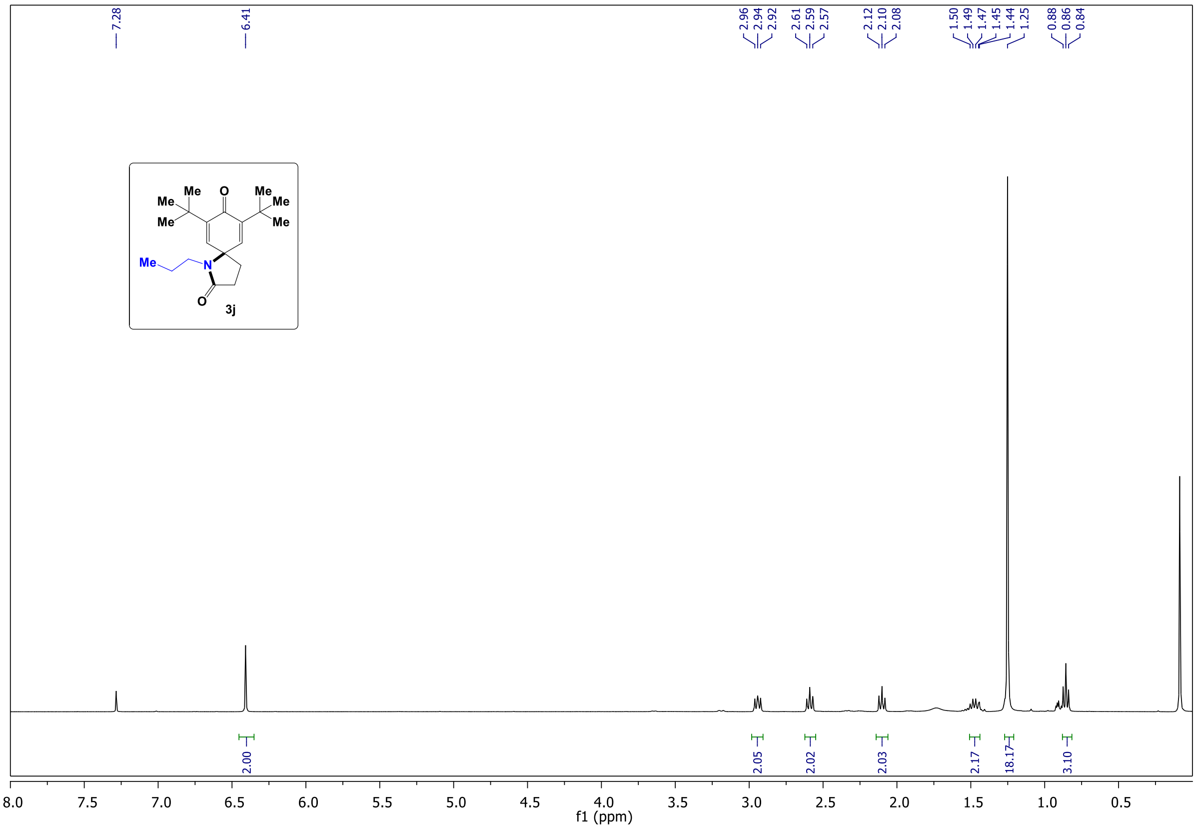
3i, ^{1}H NMR (CDCl$_3$, 400 MHz)



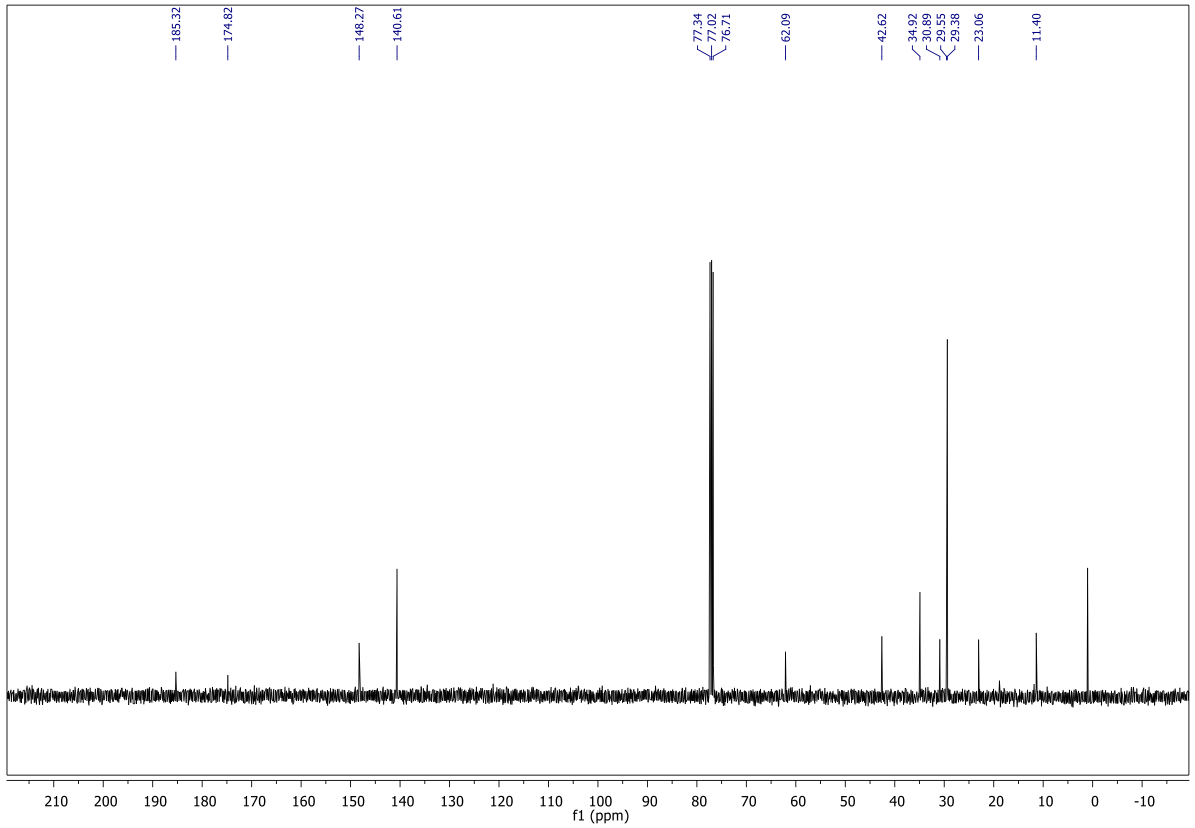
3i, ^{13}C NMR (CDCl$_3$, 100 MHz)



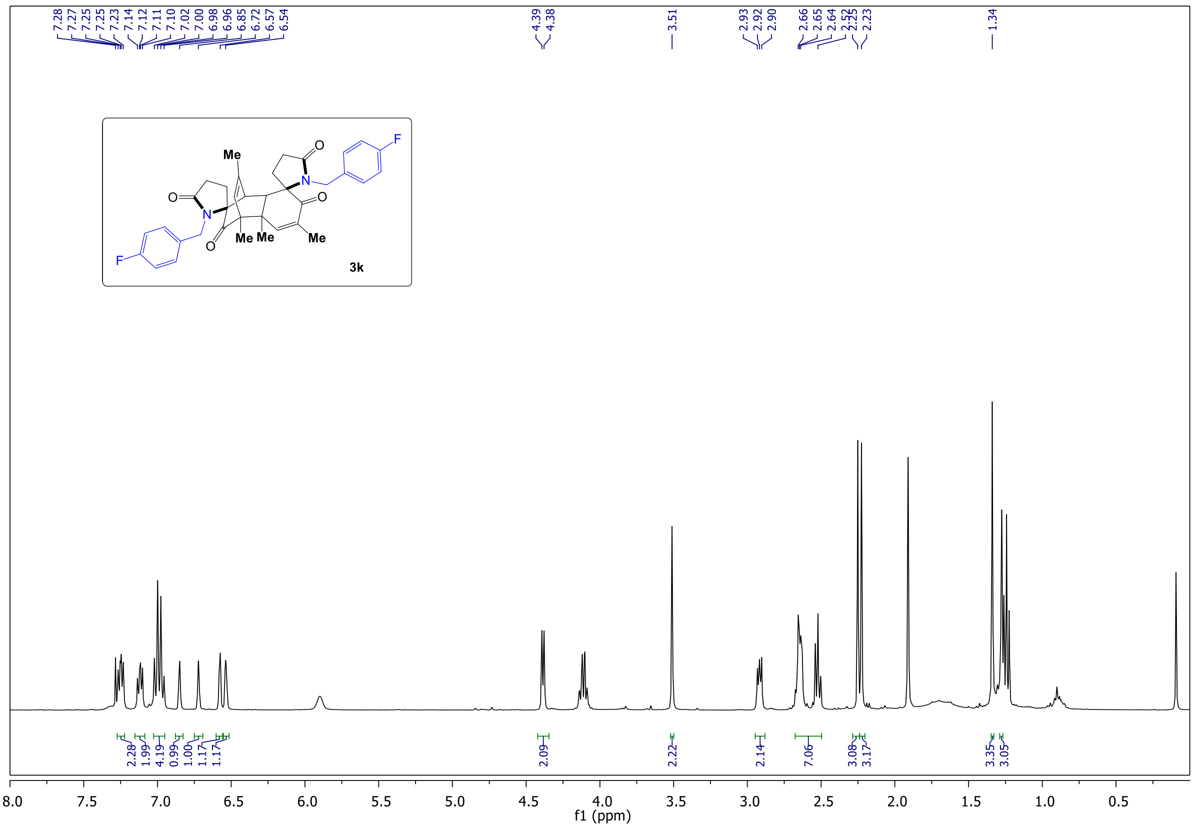
3j, ^{1}H NMR (CDCl$_3$, 400 MHz)



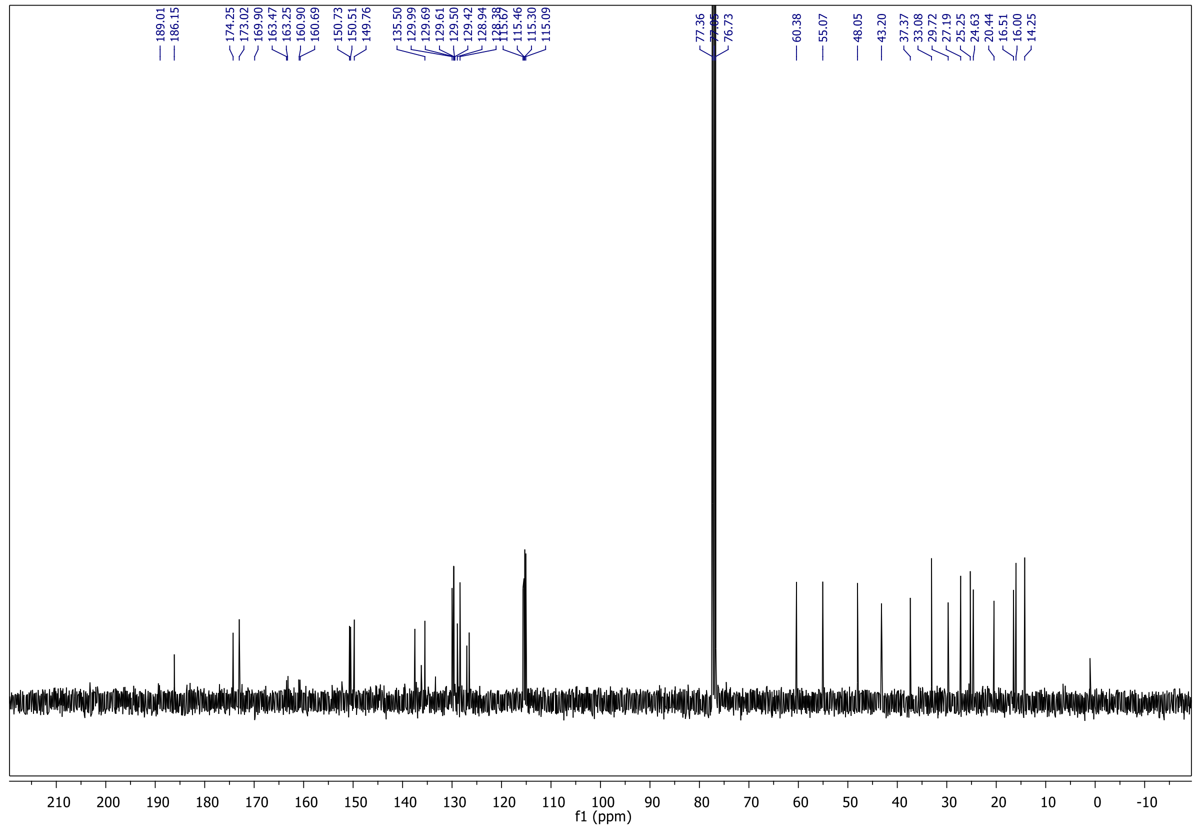
3j, ^{13}C NMR (CDCl$_3$, 100 MHz)



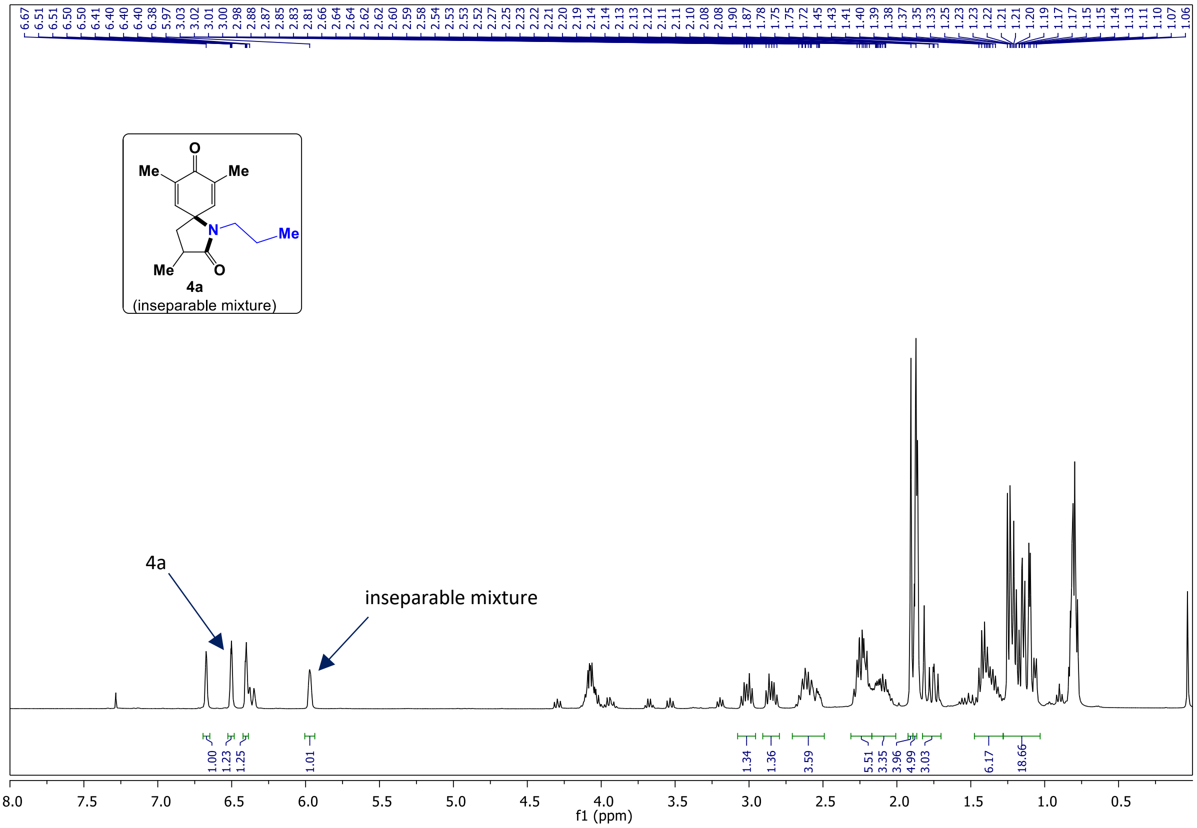
3k, ^{1}H NMR (CDCl$_3$, 400 MHz)



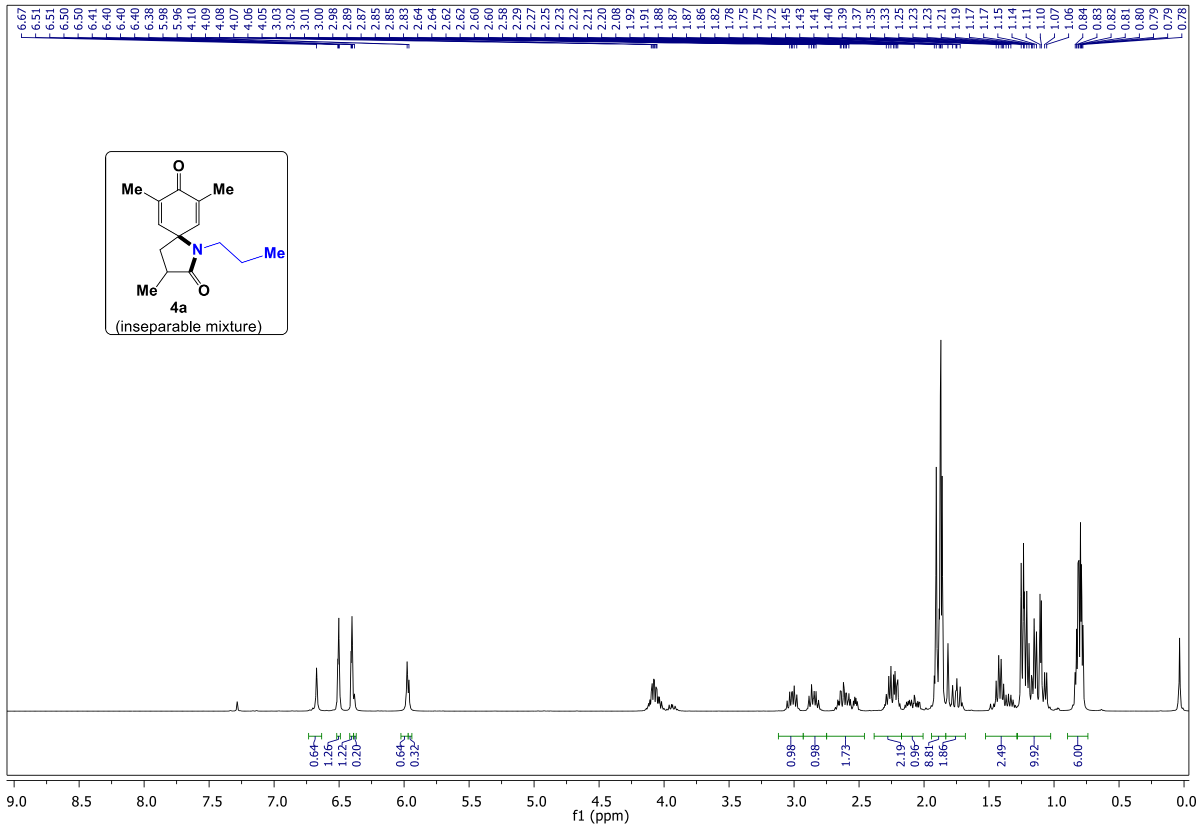
3k, ^{13}C NMR (CDCl$_3$, 100 MHz)



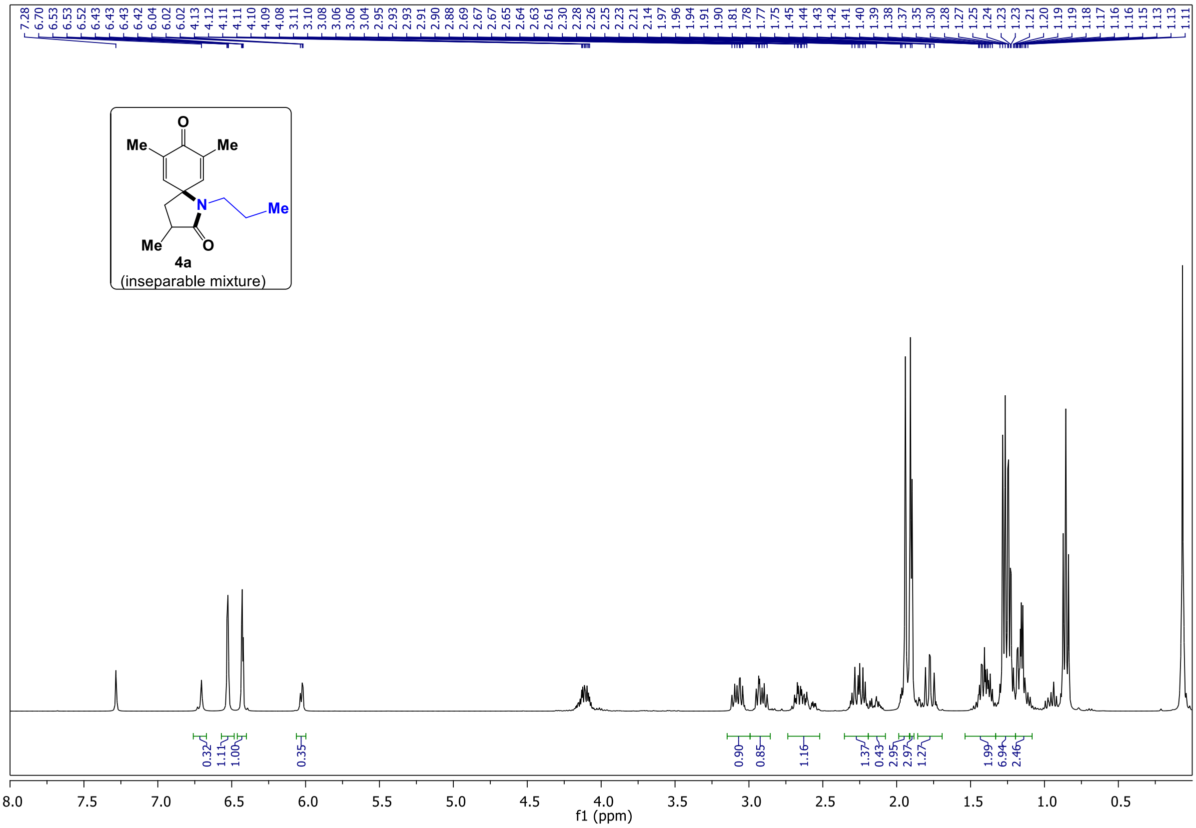
4a, ^{1}H NMR (CDCl$_3$, 400 MHz); PTATB



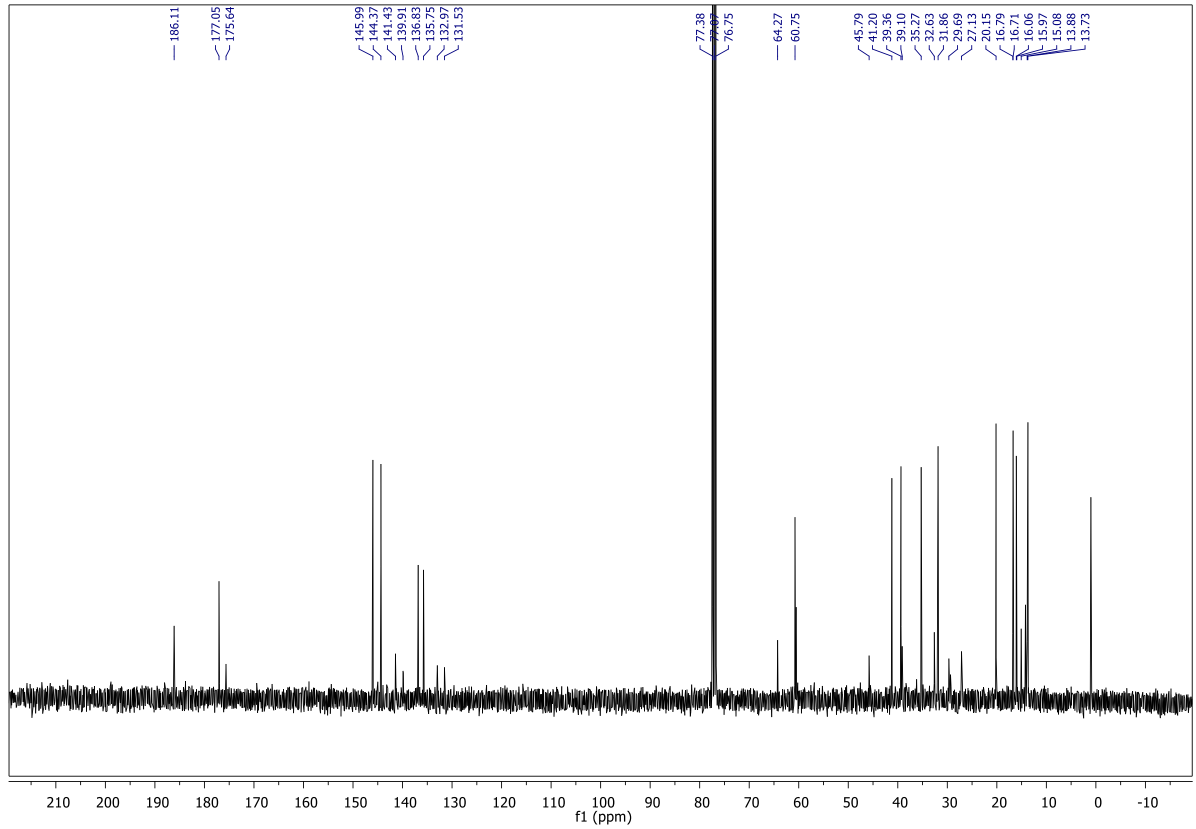
4a, ^{1}H NMR (CDCl$_3$, 400 MHz); DABCOTB



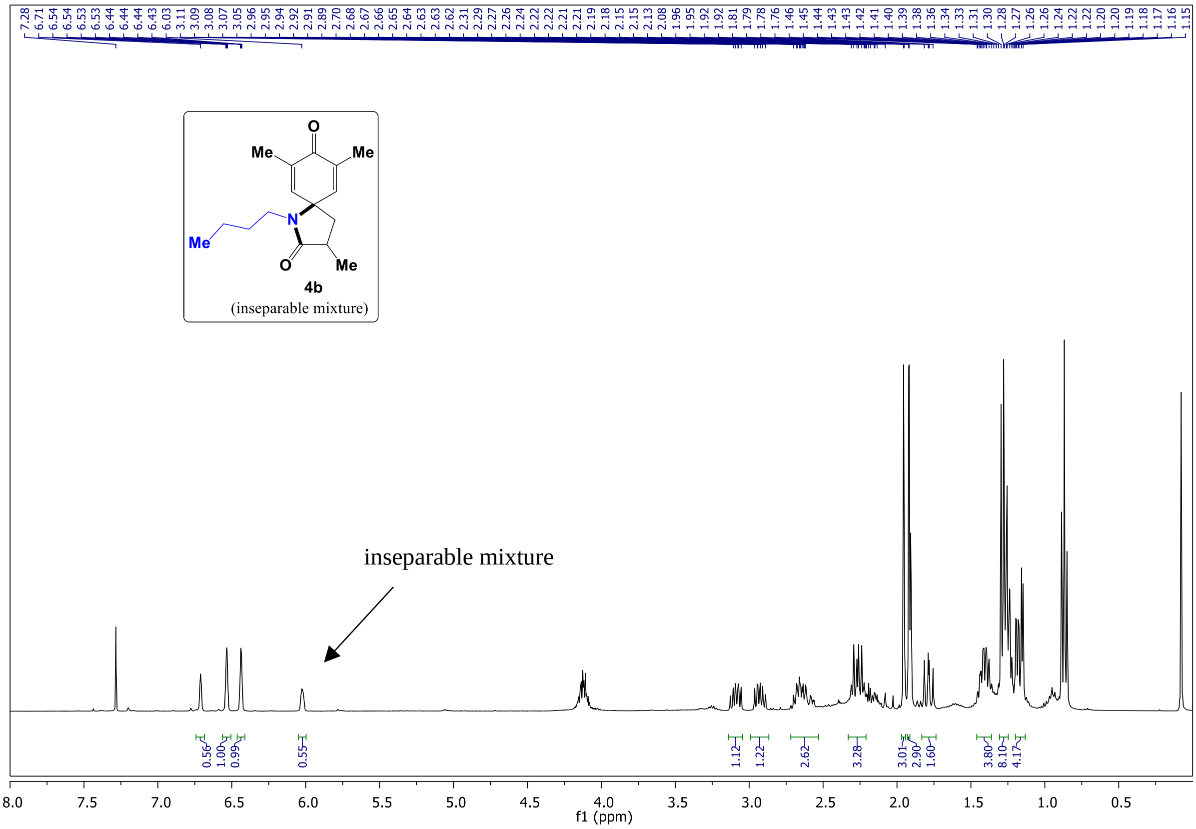
4a, ^{1}H NMR (CDCl$_3$, 400 MHz); TBATB



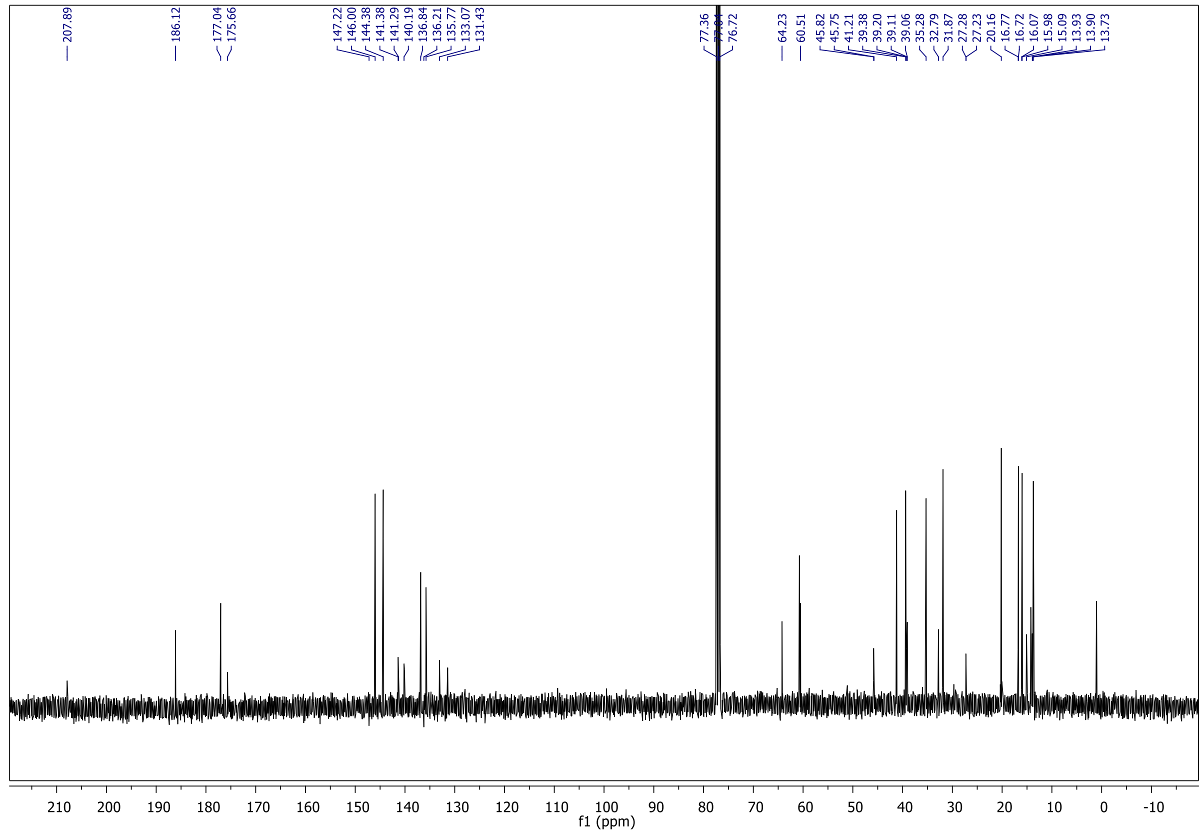
4a, ^{13}C NMR (CDCl$_3$, 100 MHz)



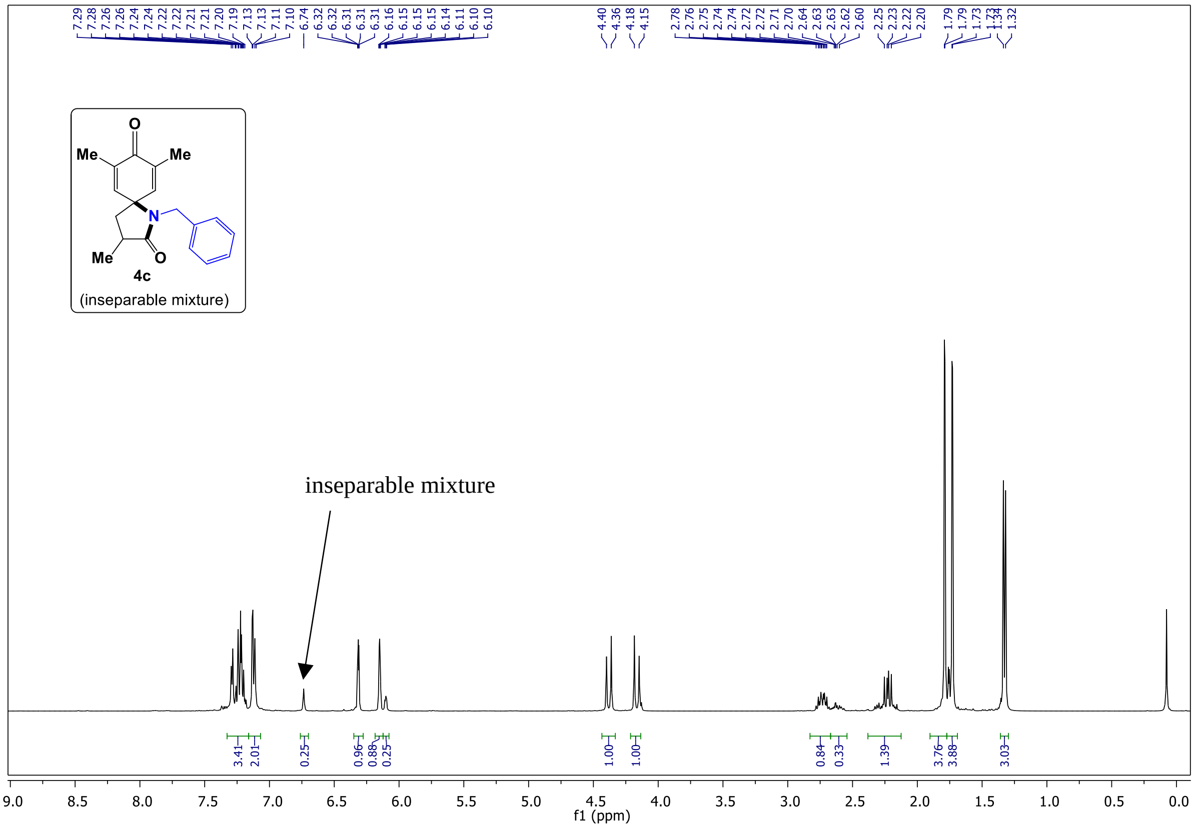
4b, ^{1}H NMR (CDCl$_3$, 400 MHz); PTATB



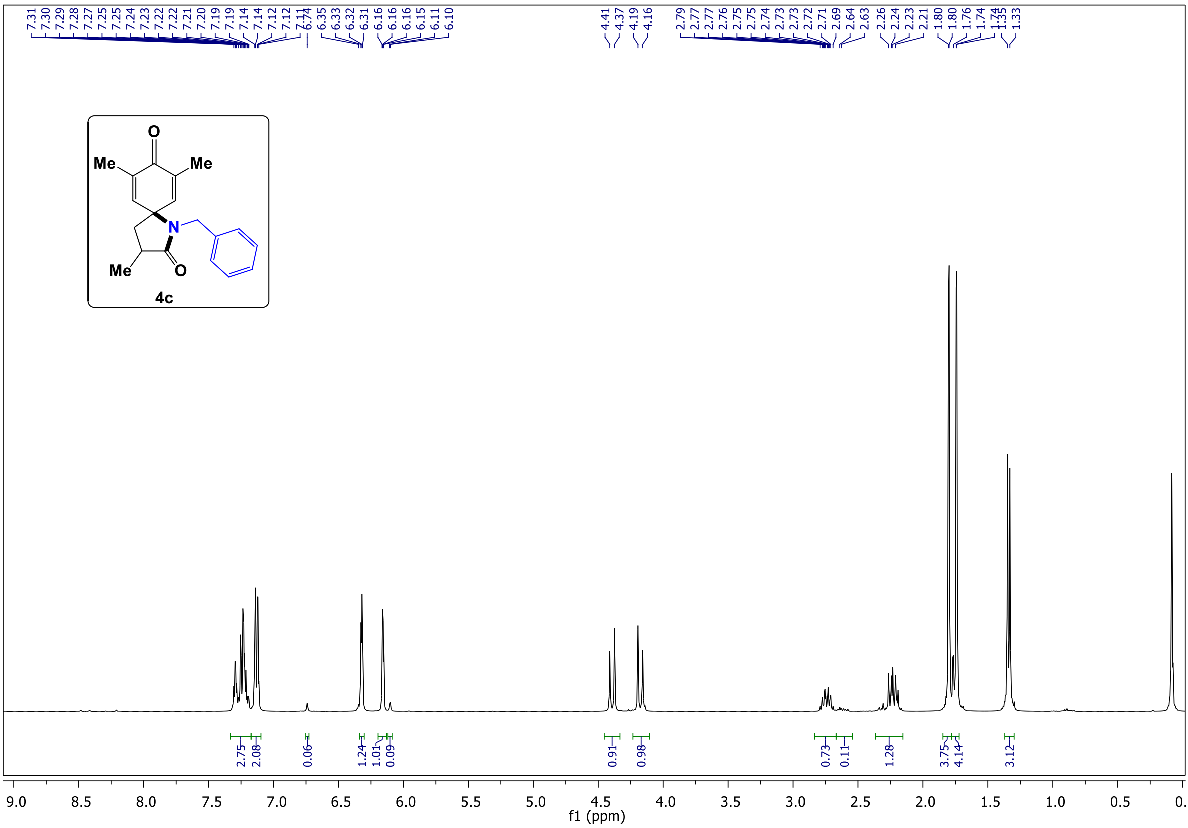
4b, ^{13}C NMR (CDCl$_3$, 100 MHz)



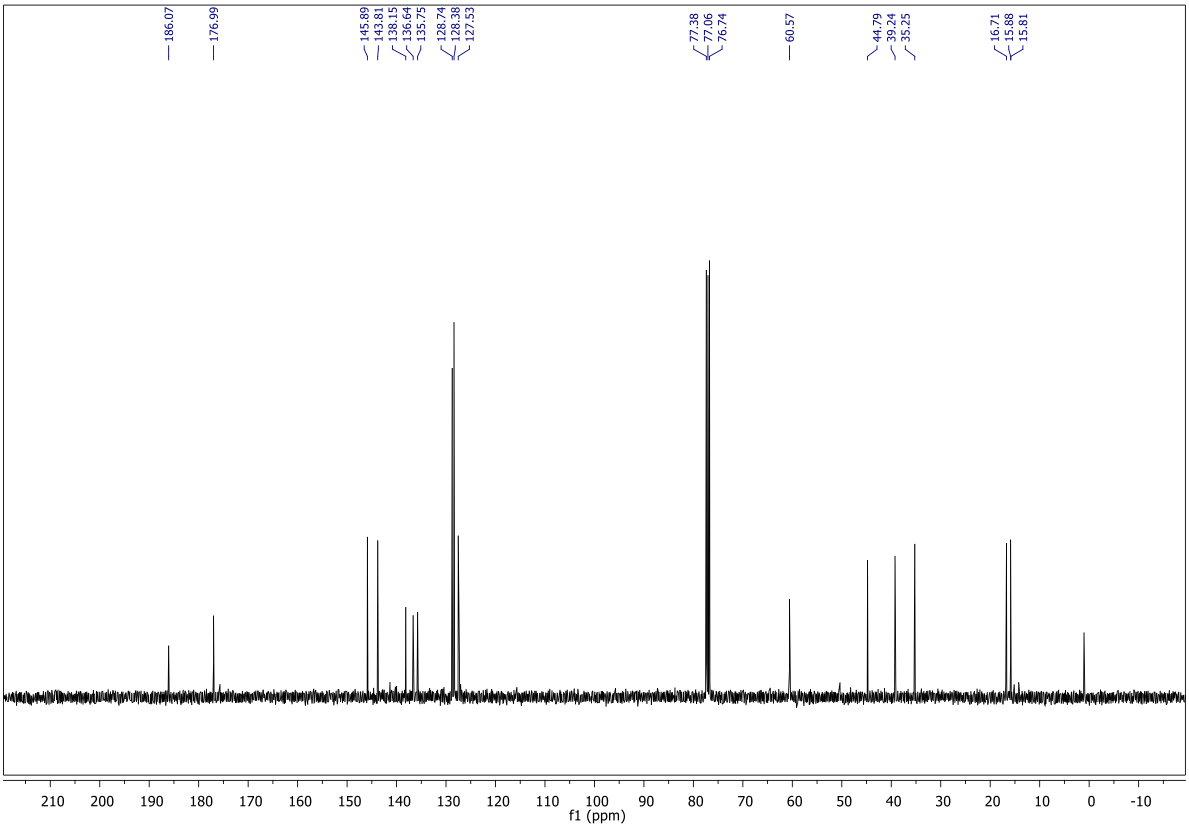
4c, ^{1}H NMR (CDCl$_3$, 400 MHz); PTATB



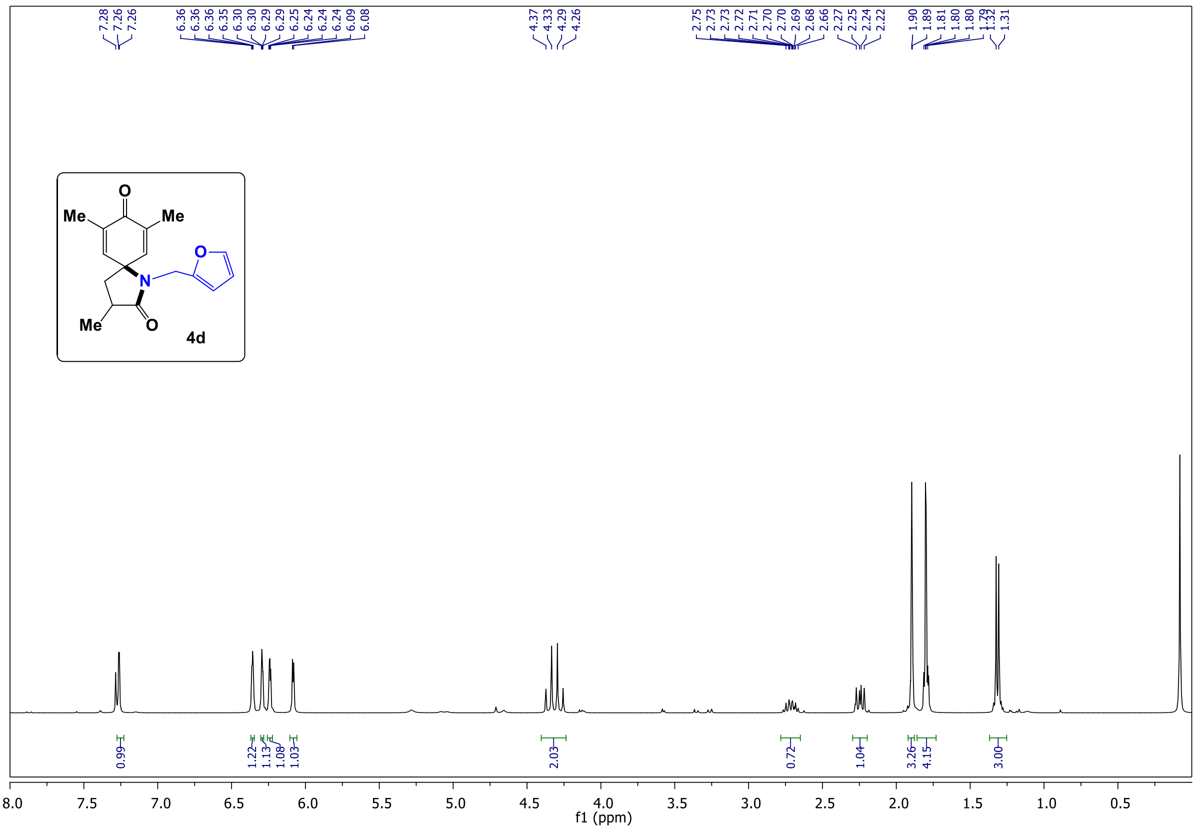
4c, ^{1}H NMR (CDCl$_3$, 400 MHz); TBATB



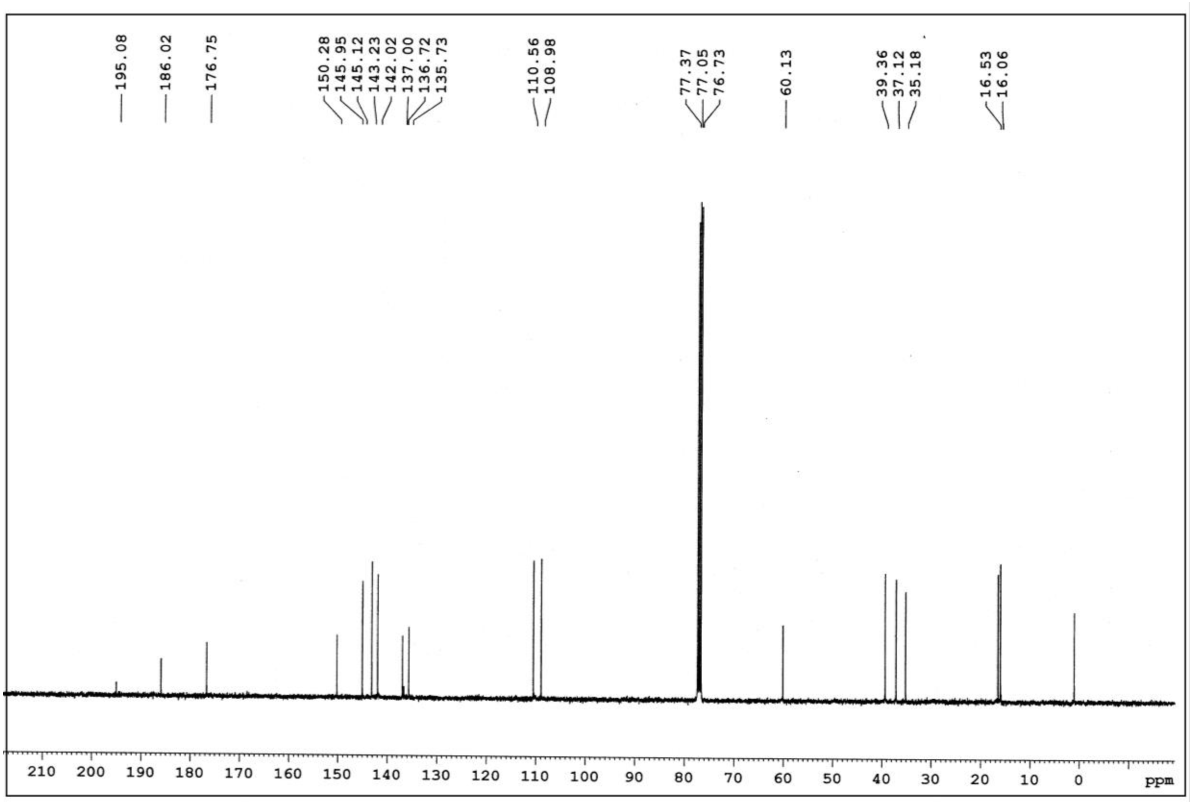
4c, ^{13}C NMR (CDCl$_3$, 100 MHz)



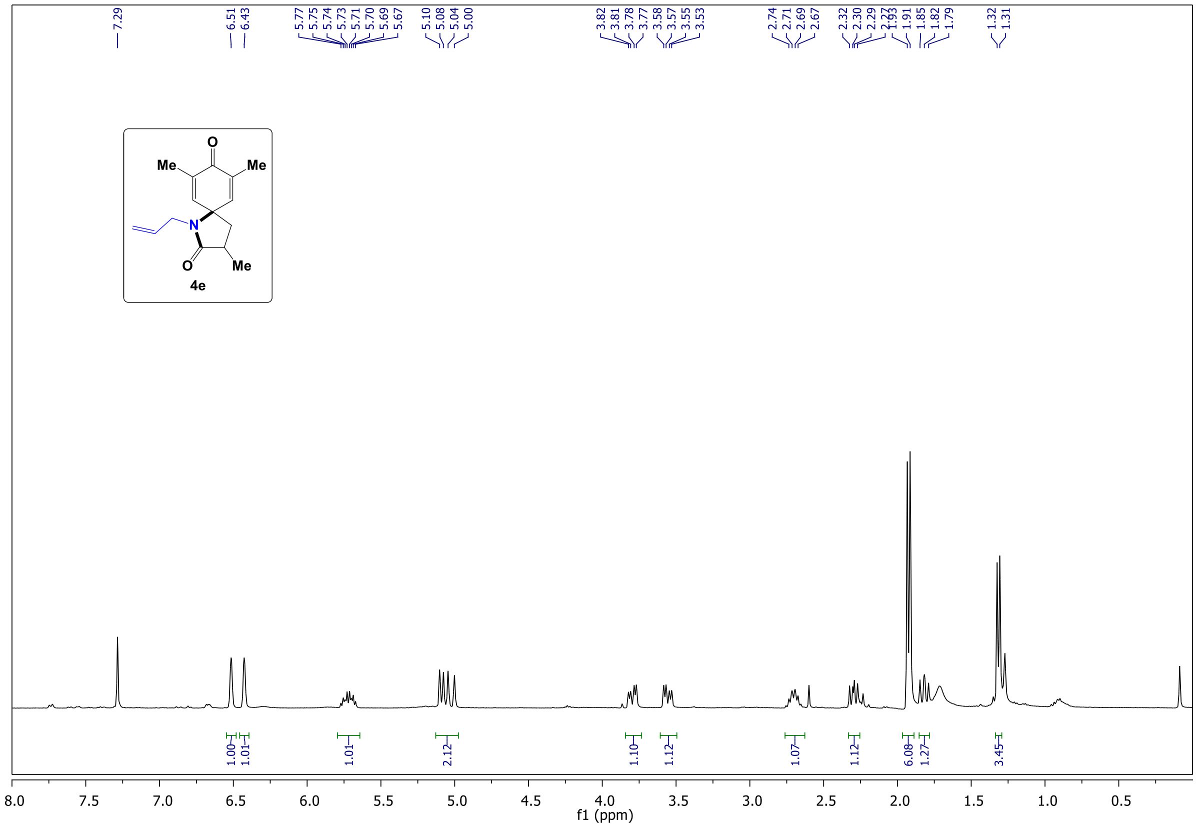
4d, ^{1}H NMR ($CDCl_3$, 400 MHz)



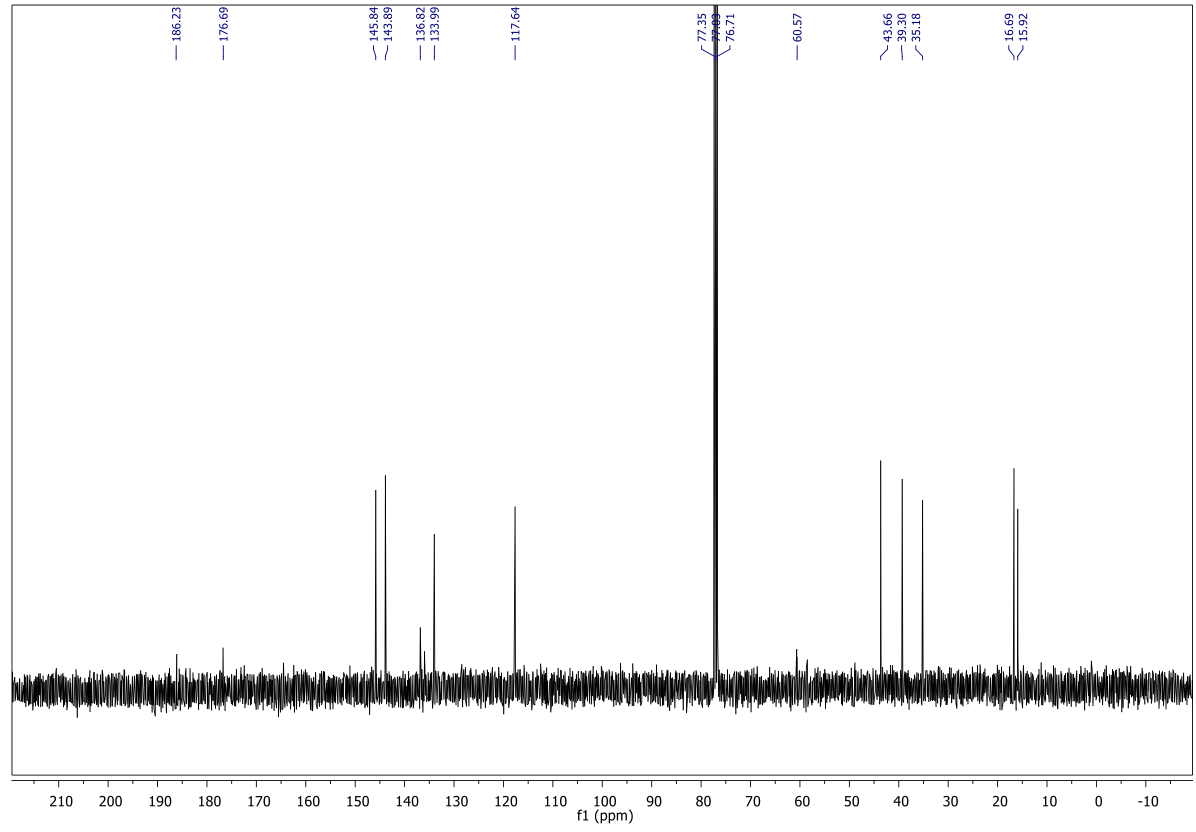
4d, ^{13}C NMR ($CDCl_3$, 100 MHz)



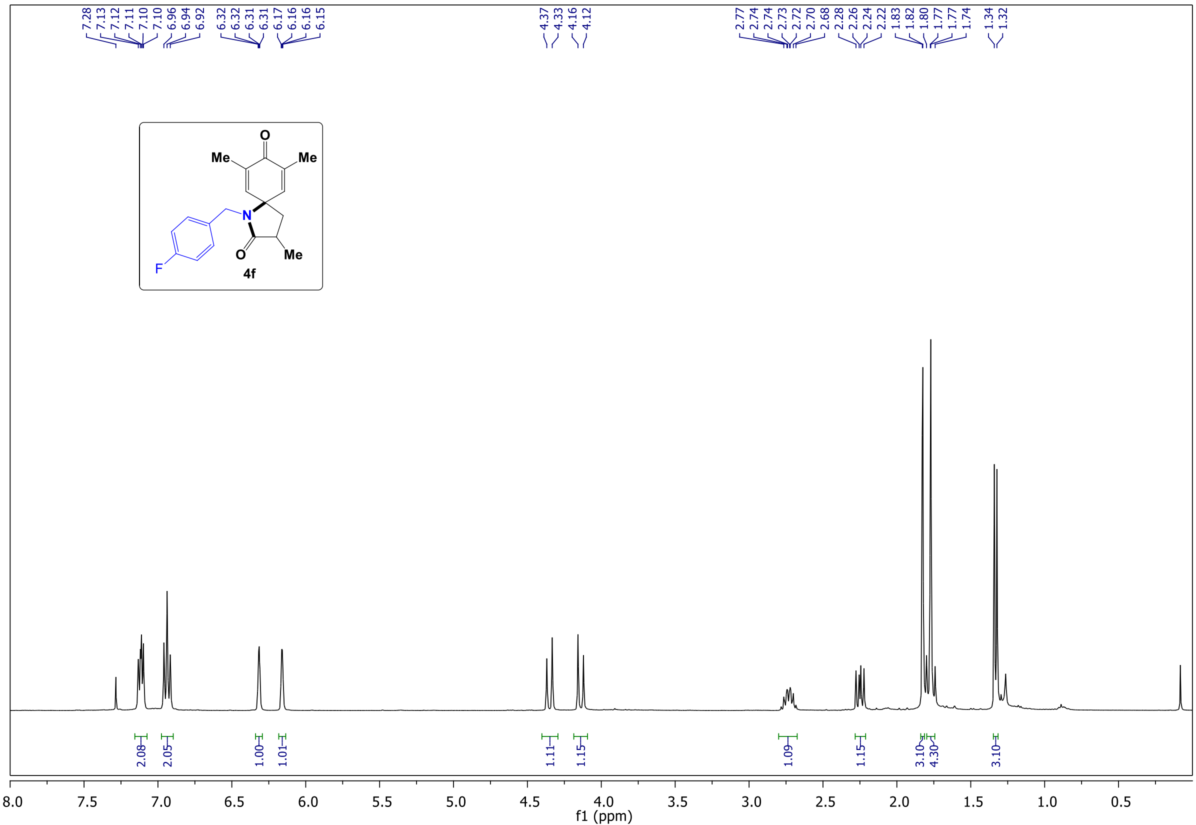
4e, ^{1}H NMR (CDCl$_3$, 400 MHz)



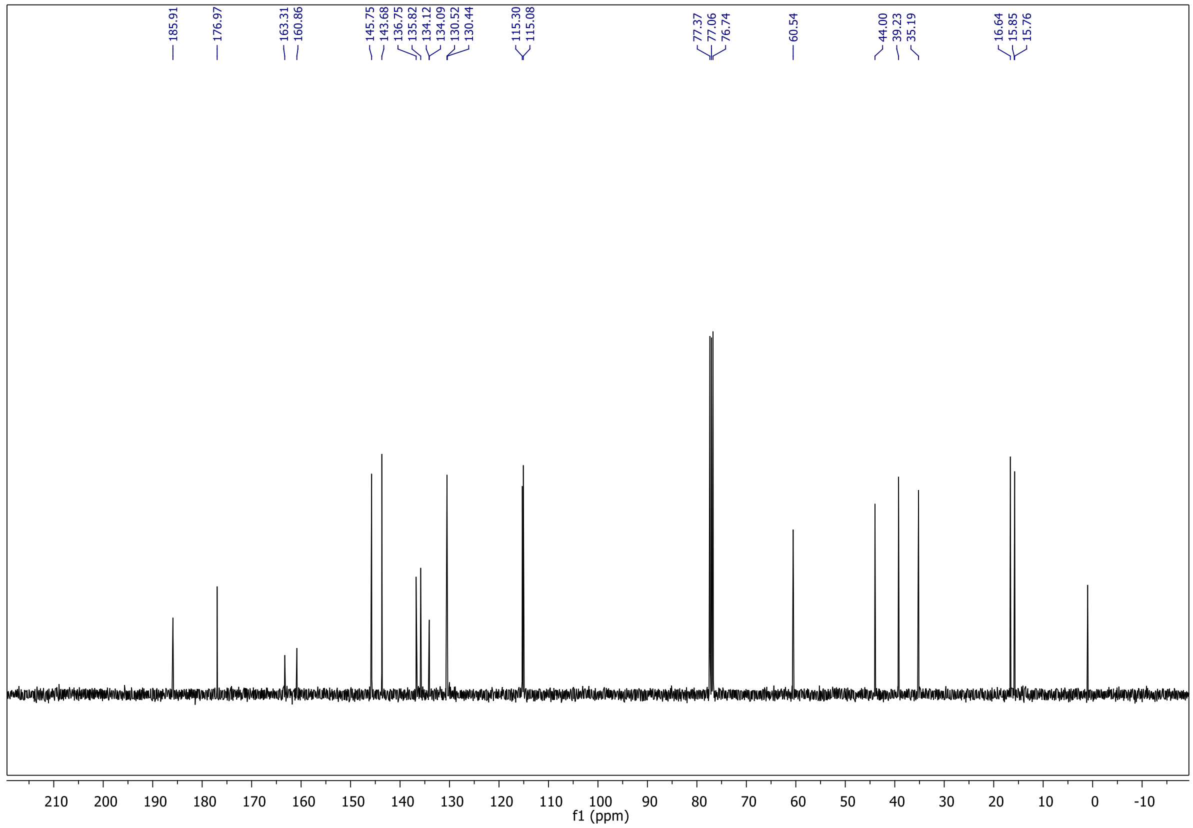
4e, ^{13}C NMR (CDCl$_3$, 100 MHz)



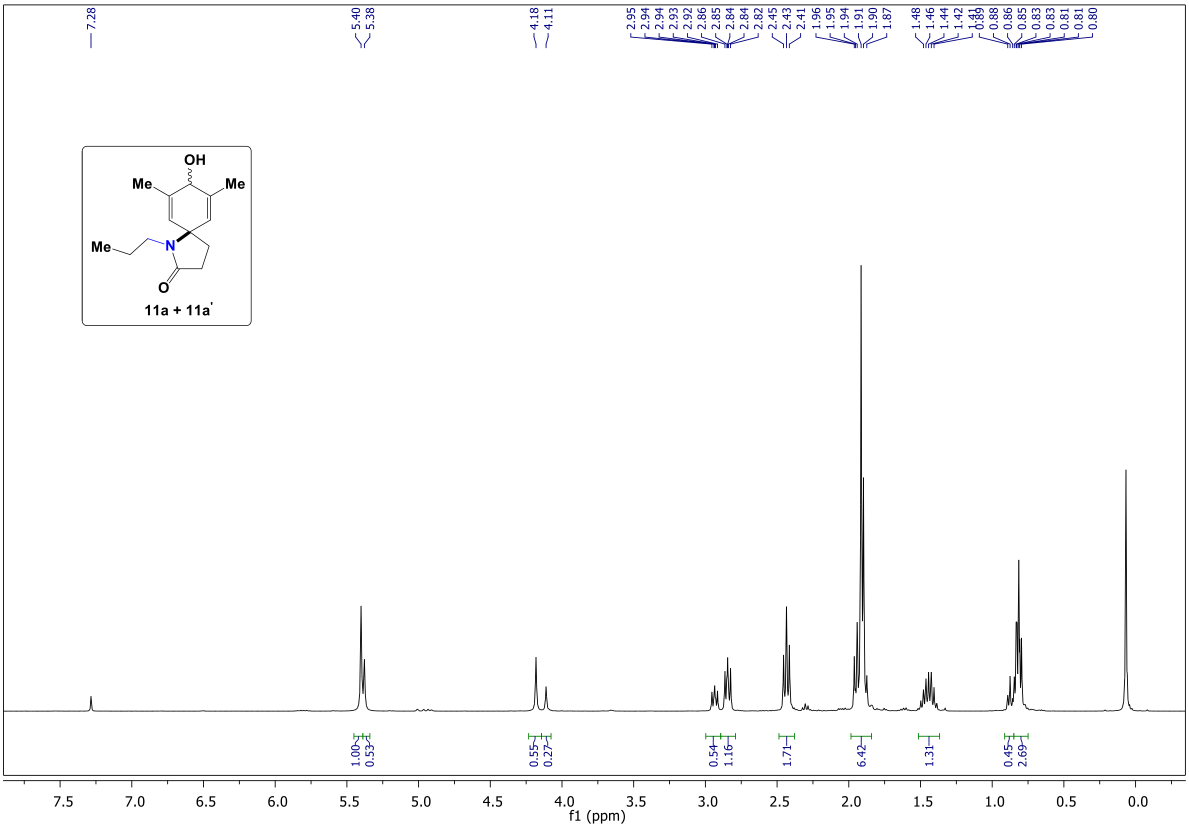
4f, ^{1}H NMR (CDCl$_3$, 400 MHz)



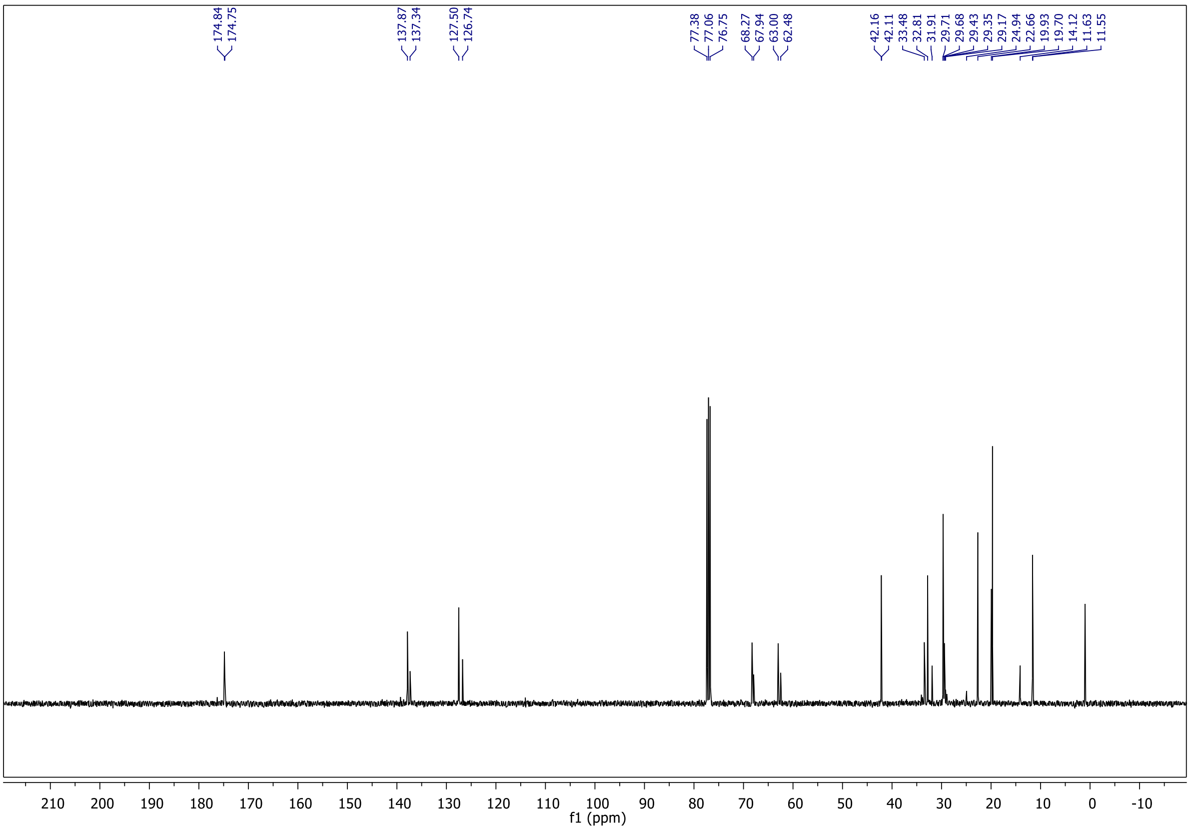
4f, ^{13}C NMR (CDCl$_3$, 100 MHz)



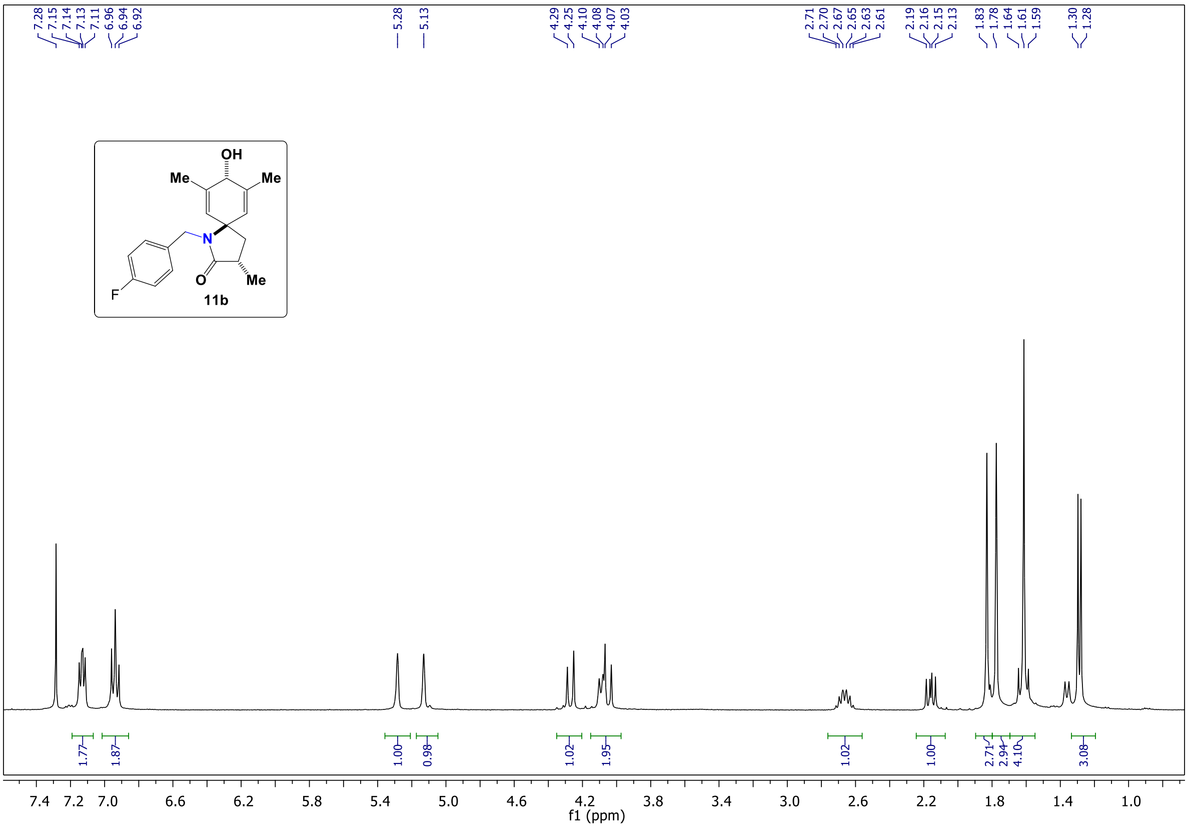
11a, ^{1}H NMR (CDCl$_3$, 400 MHz)



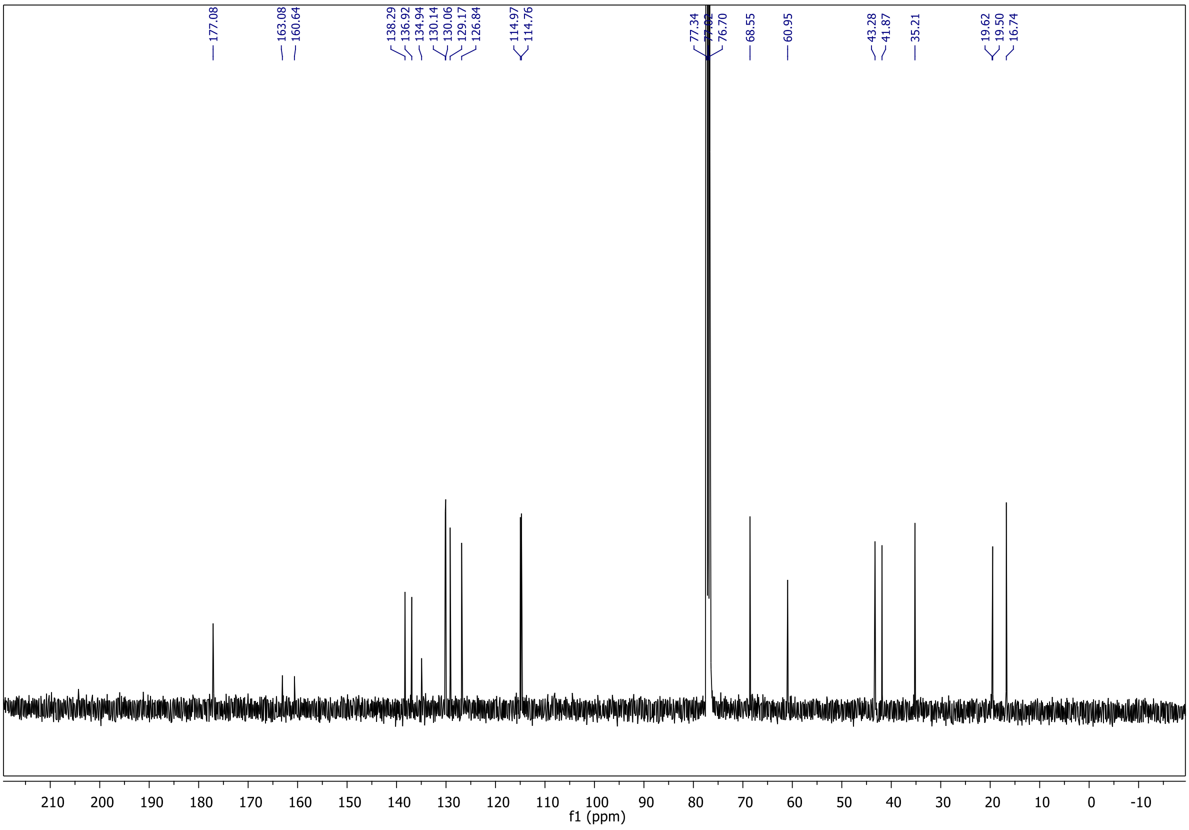
11a, ^{13}C NMR (CDCl$_3$, 100 MHz)



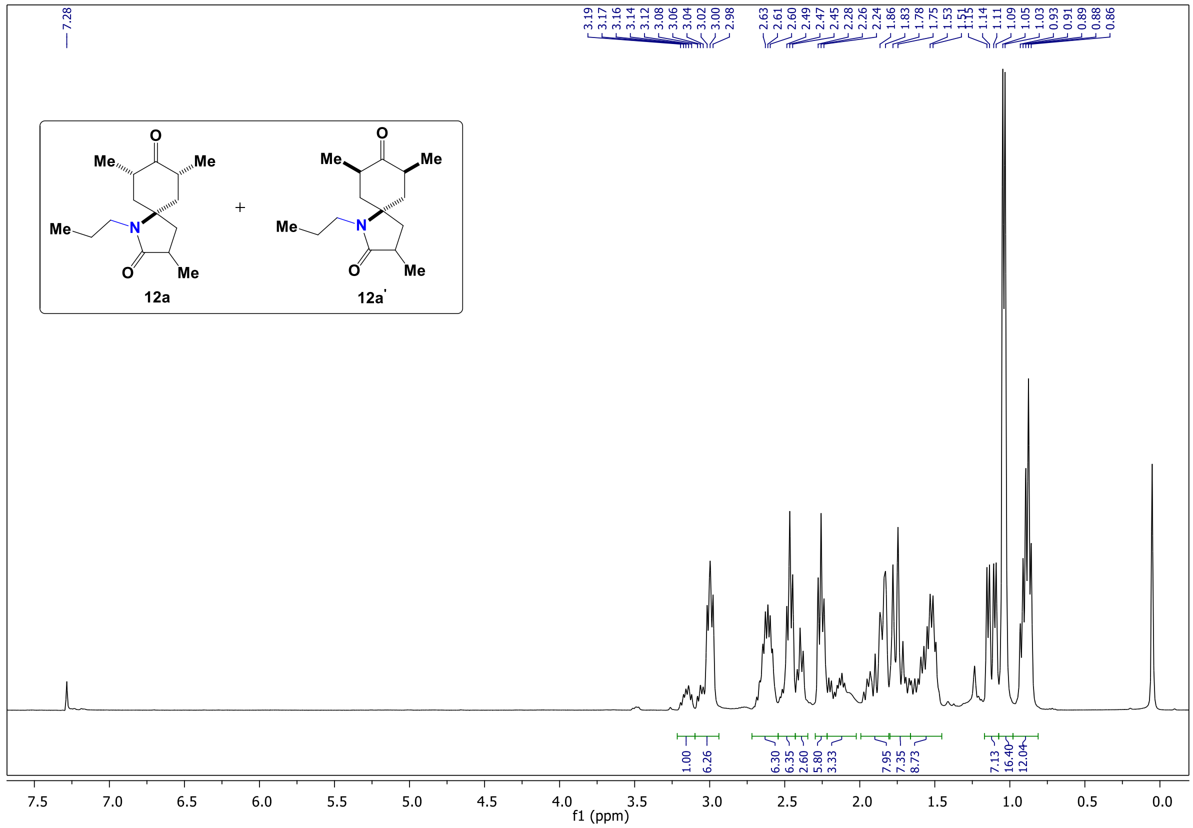
11b, ^{1}H NMR (CDCl$_3$, 400 MHz)



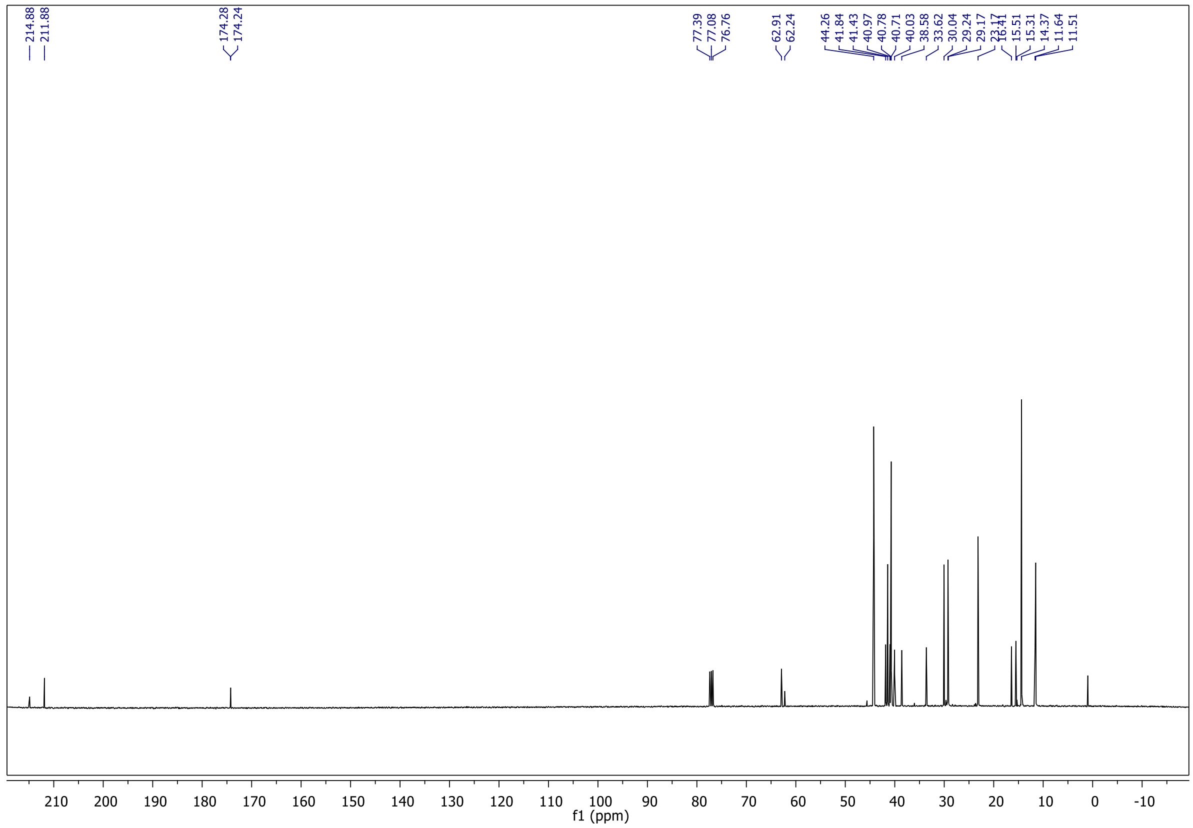
11b, ^{13}C NMR (CDCl$_3$, 100 MHz)



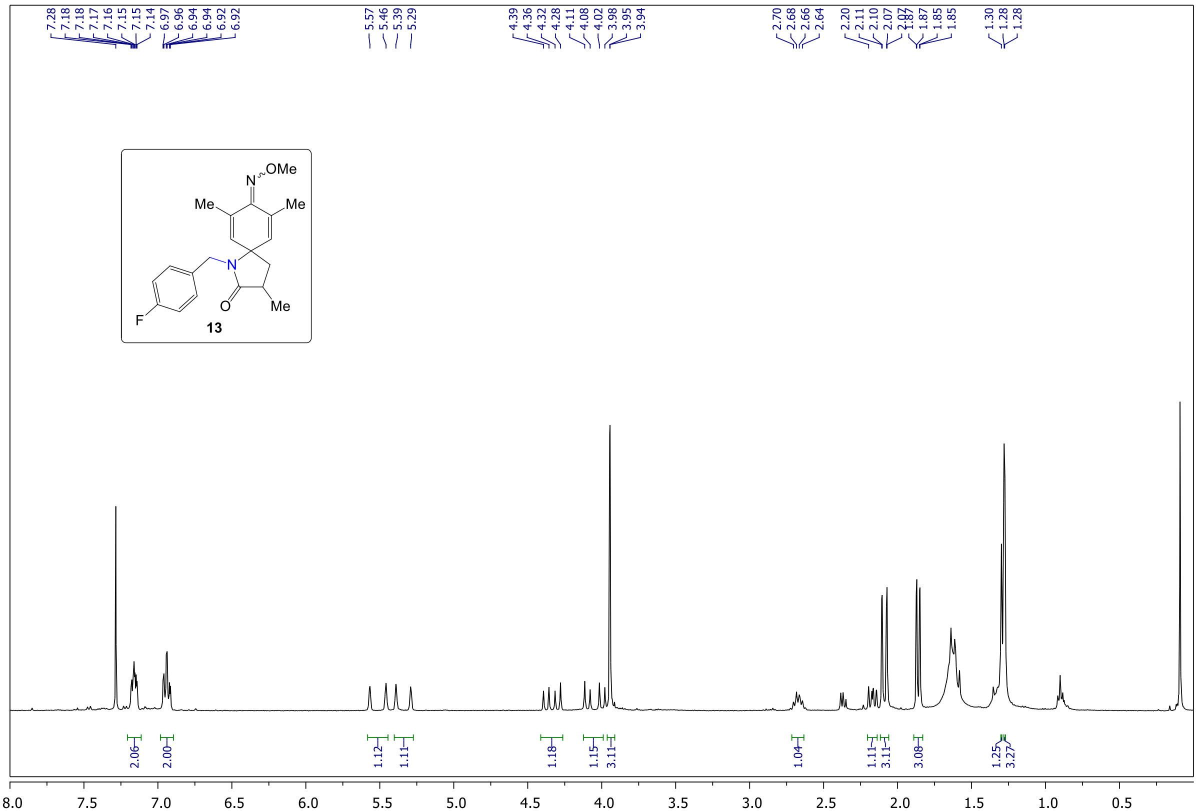
12, ^{1}H NMR (CDCl$_3$, 400 MHz)



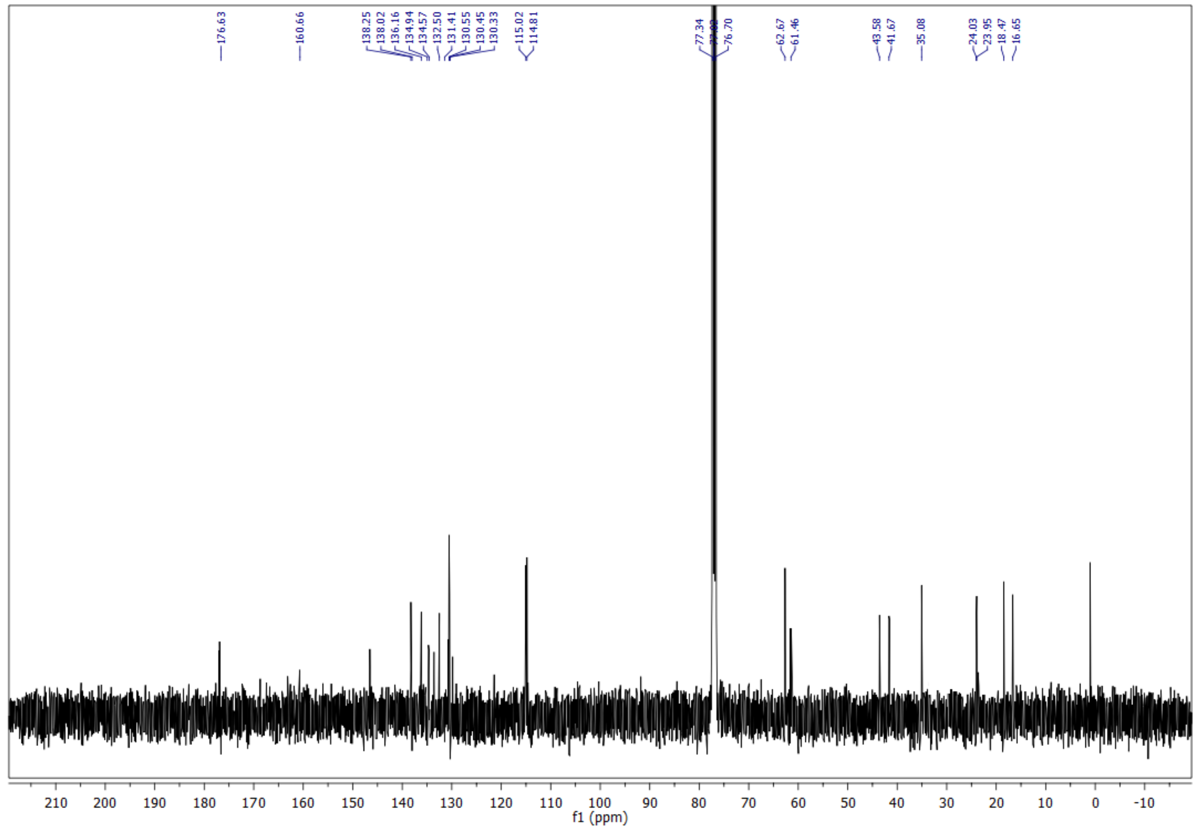
12, ^{13}C NMR (CDCl$_3$, 100 MHz)



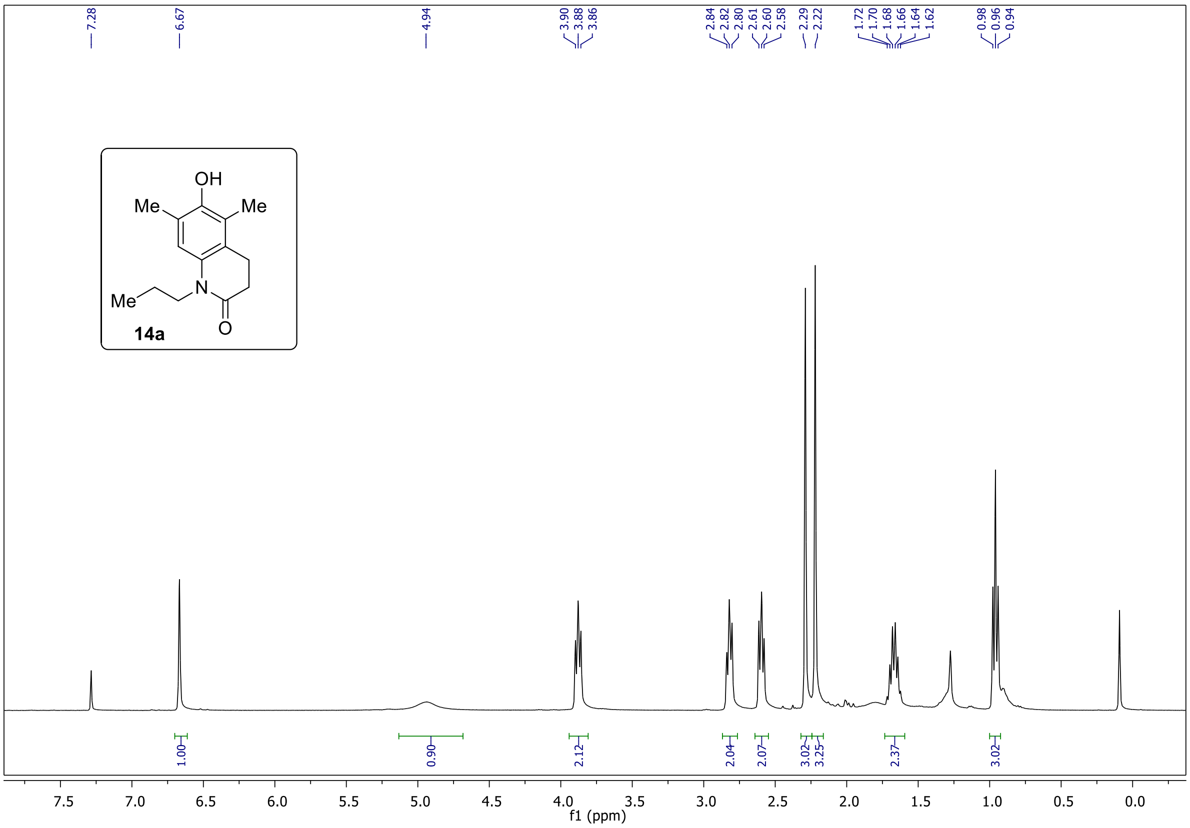
13, ^{1}H NMR (CDCl$_3$, 400 MHz)



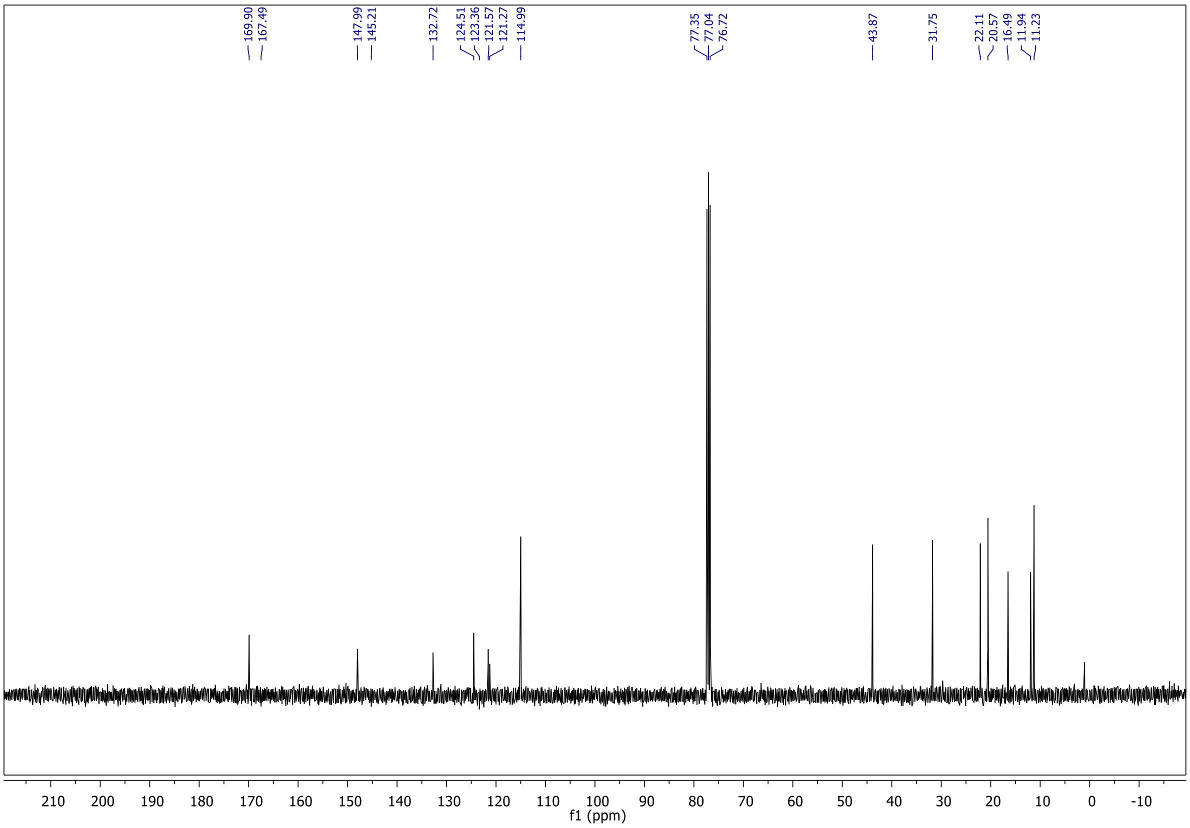
13, ^{13}C NMR (CDCl$_3$, 100 MHz)



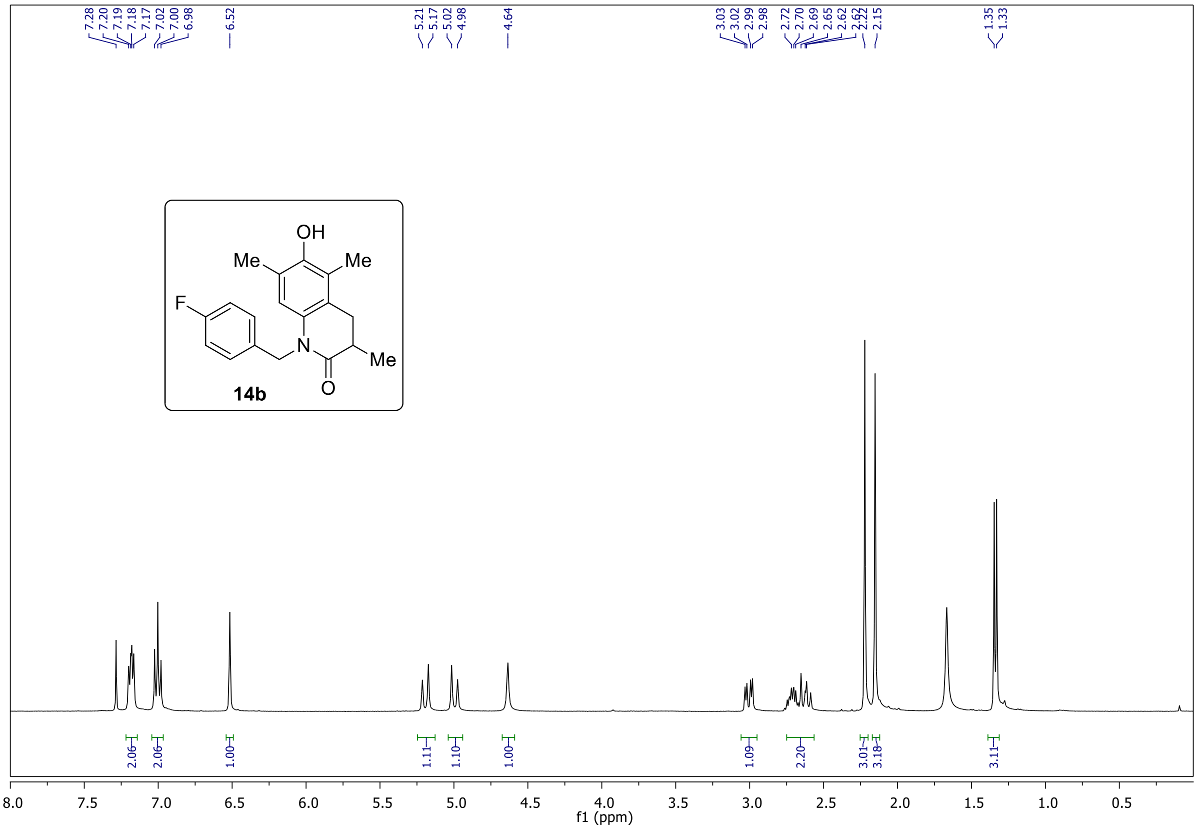
14a, ^{1}H NMR (CDCl$_3$, 400 MHz)



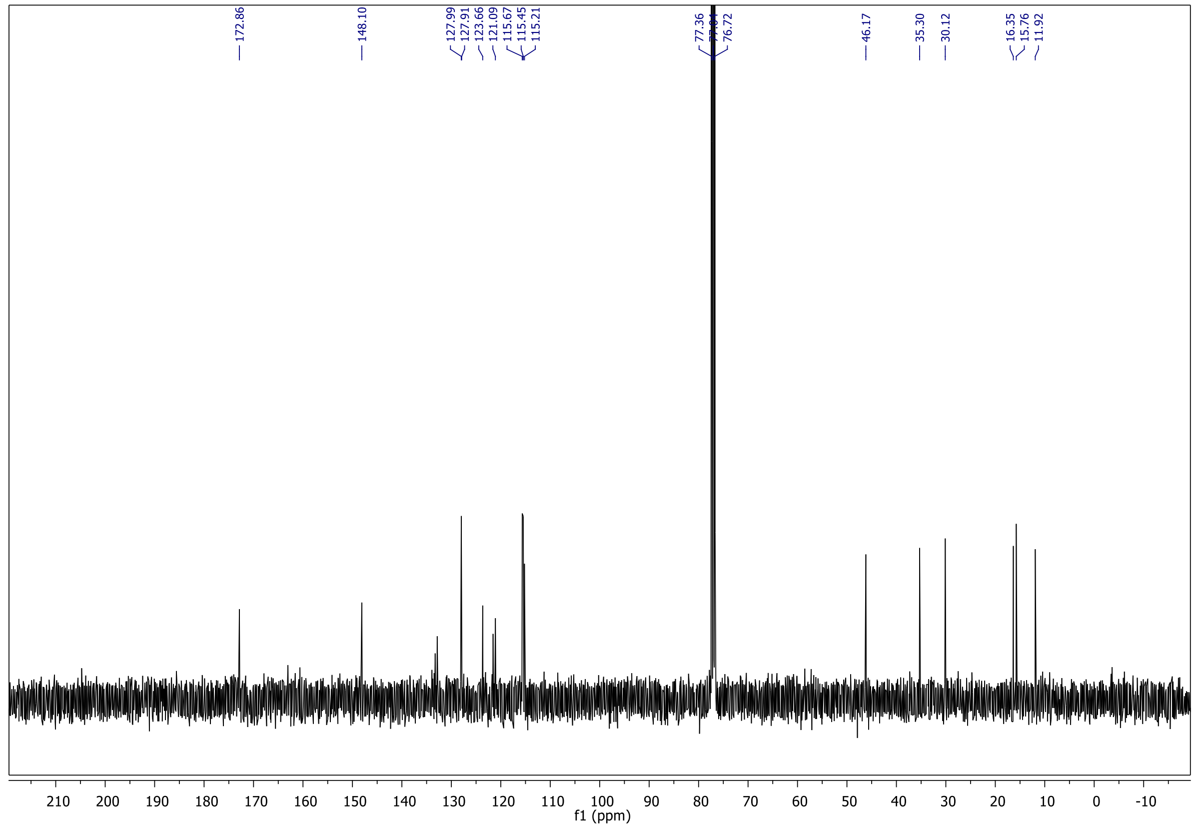
14a, ^{13}C NMR (CDCl$_3$, 100 MHz)



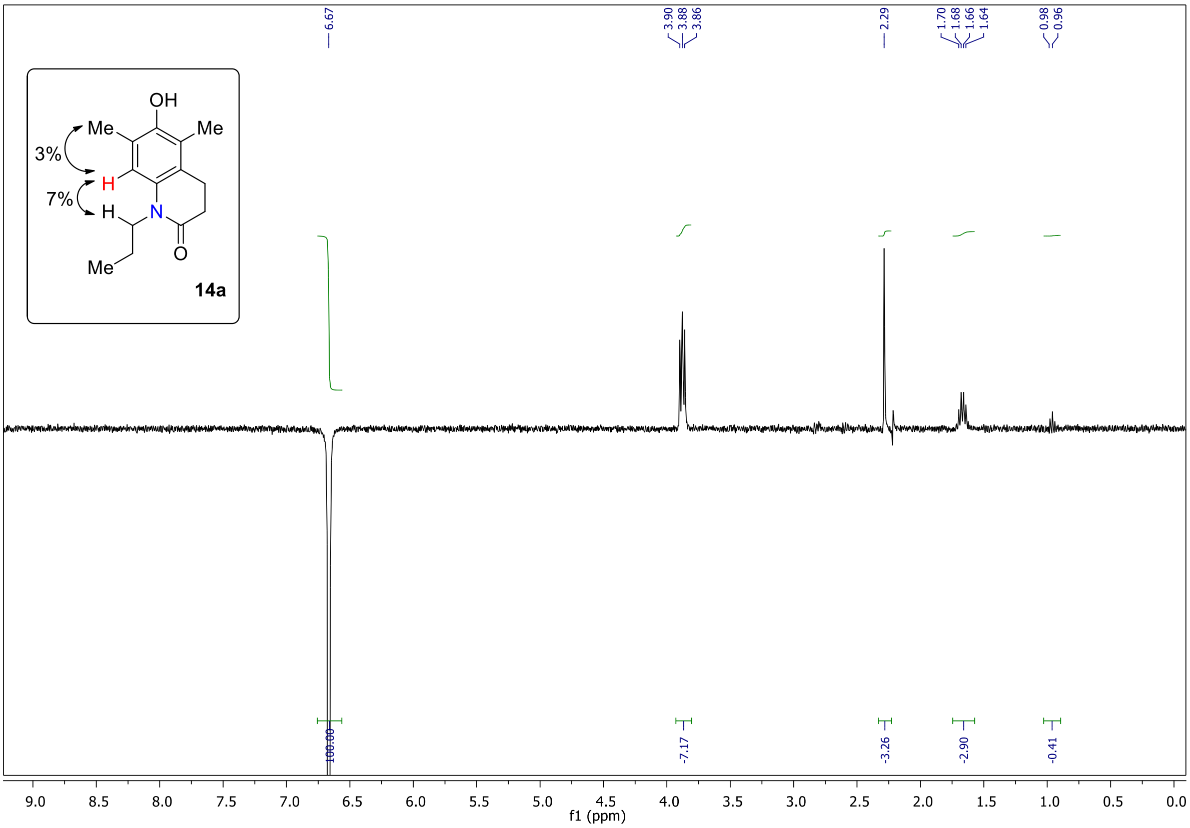
14b, ^{1}H NMR (CDCl$_3$, 400 MHz)

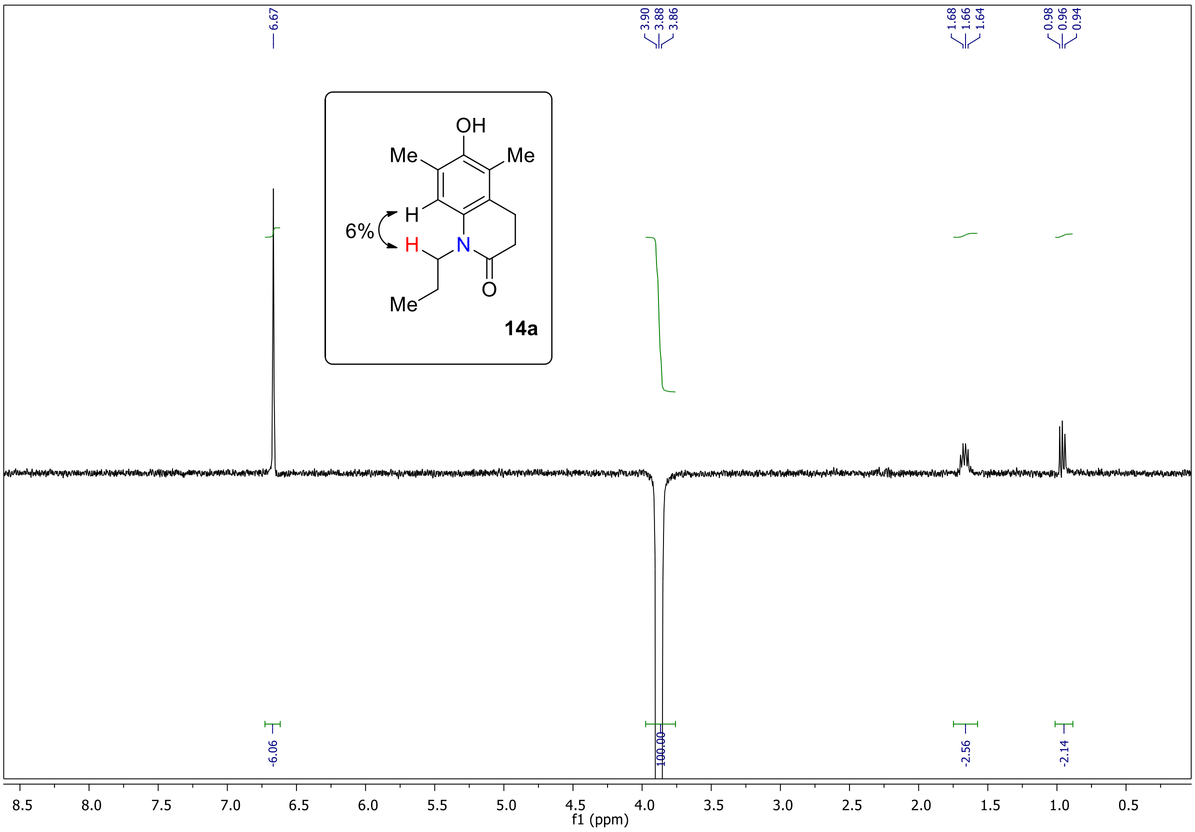


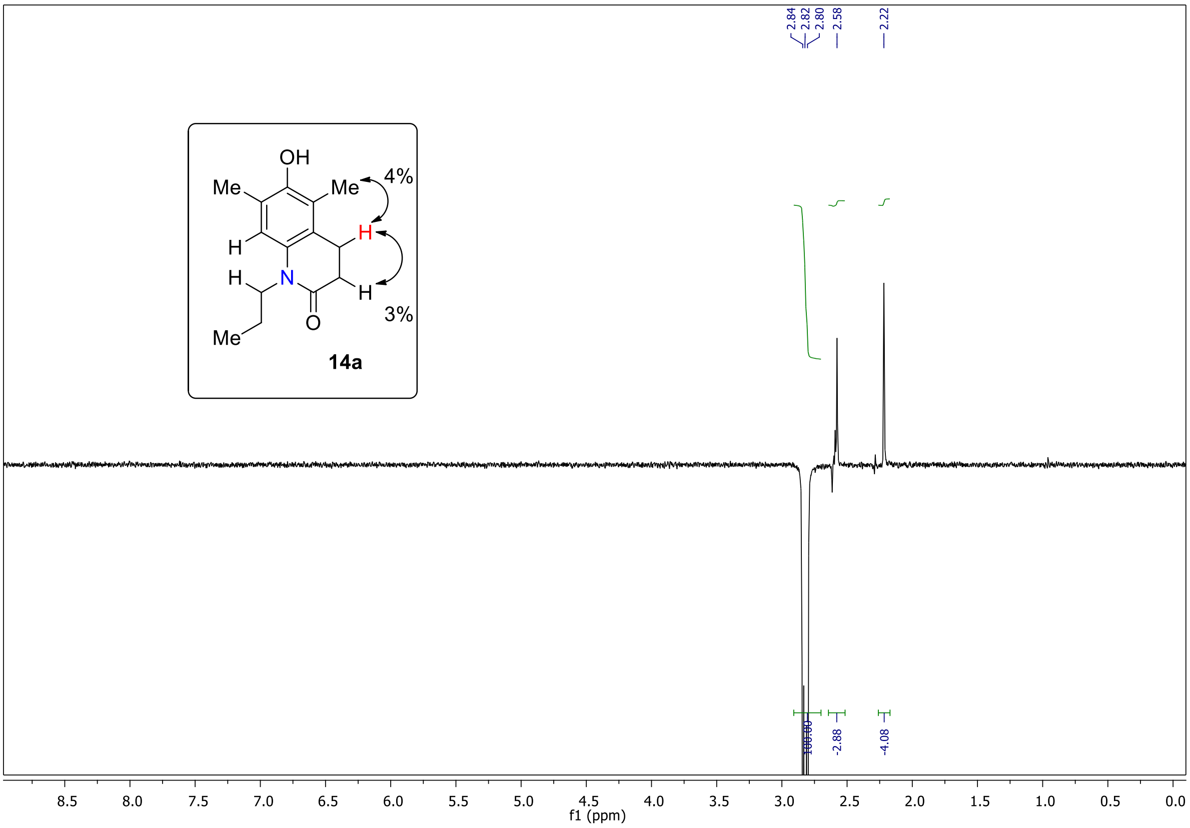
14b, ^{13}C NMR (CDCl$_3$, 100 MHz)

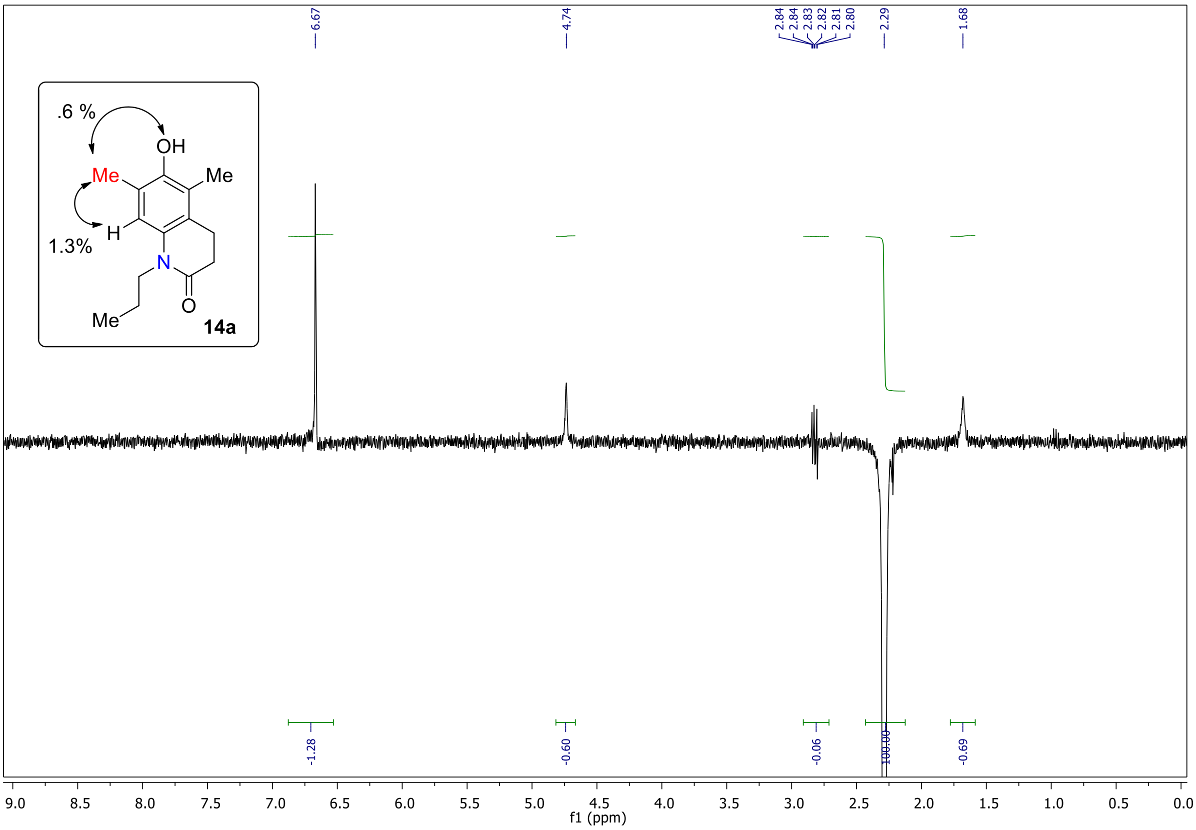


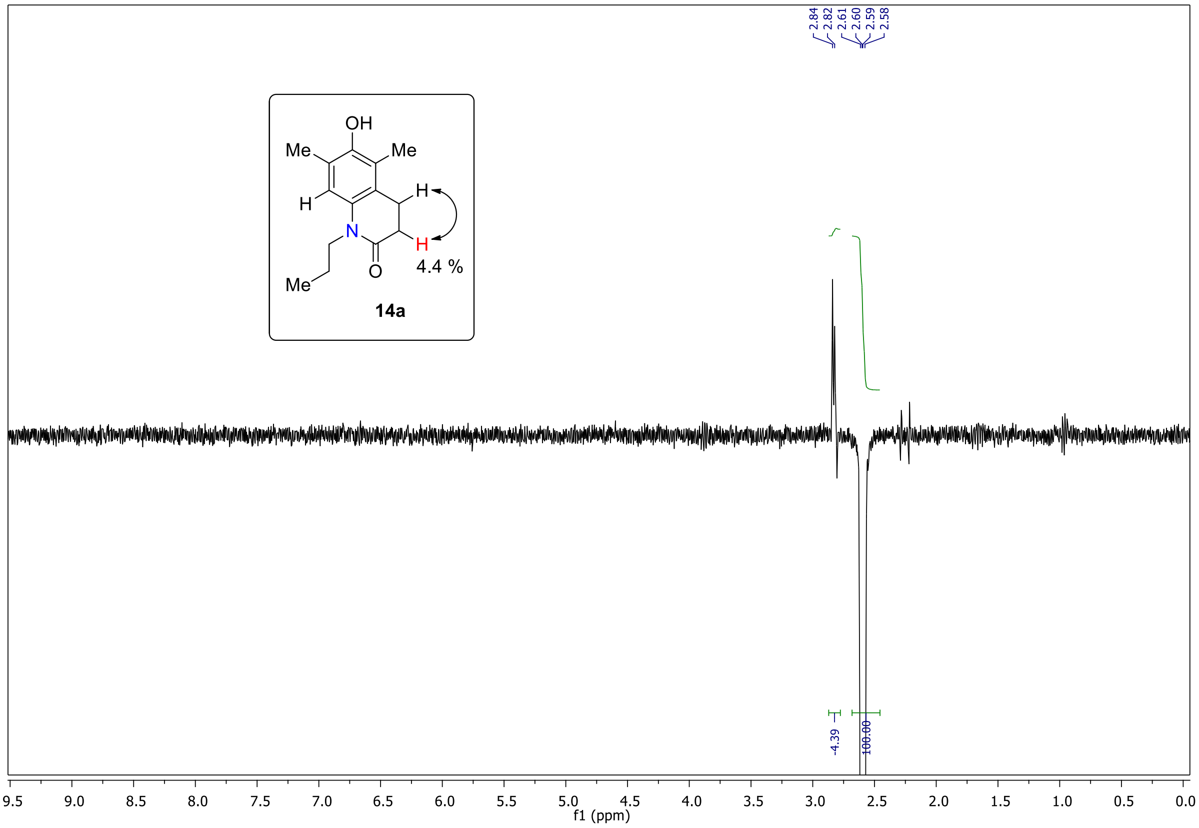
nOe of **14a** (CDCl$_3$, 400 MHz)

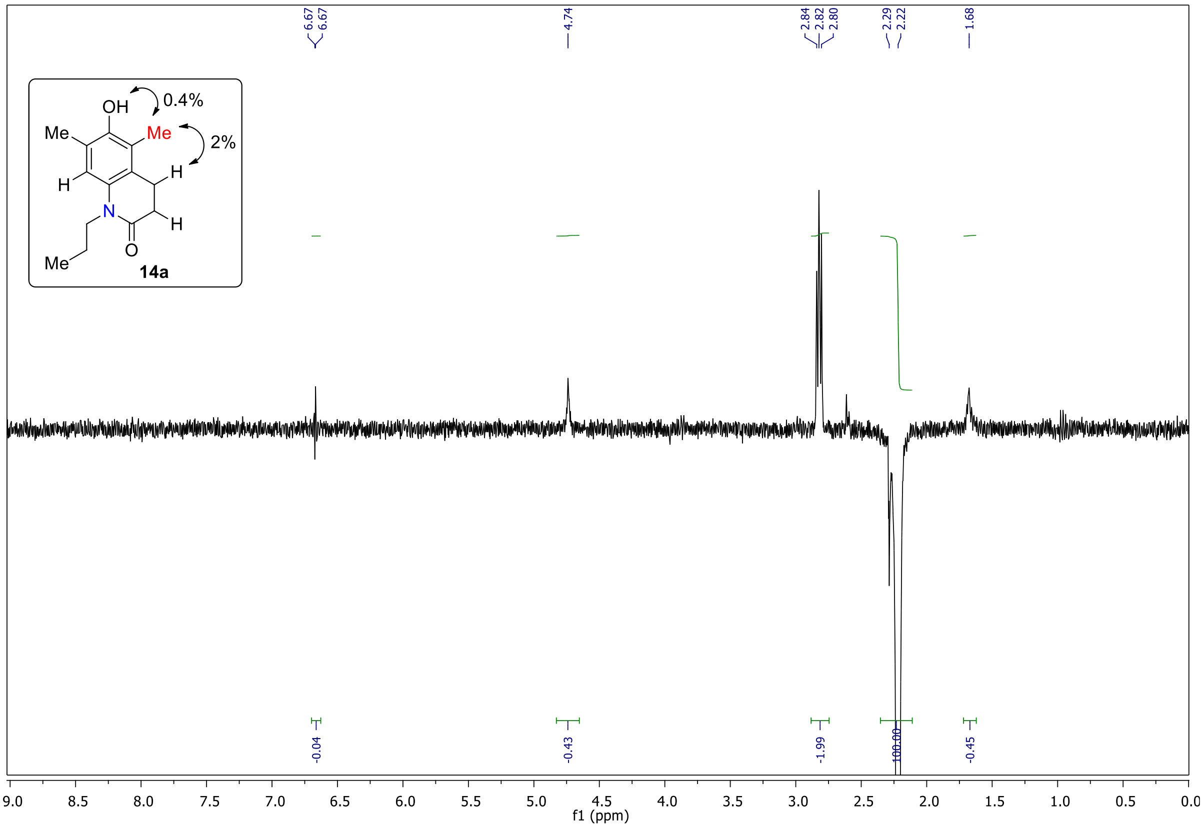


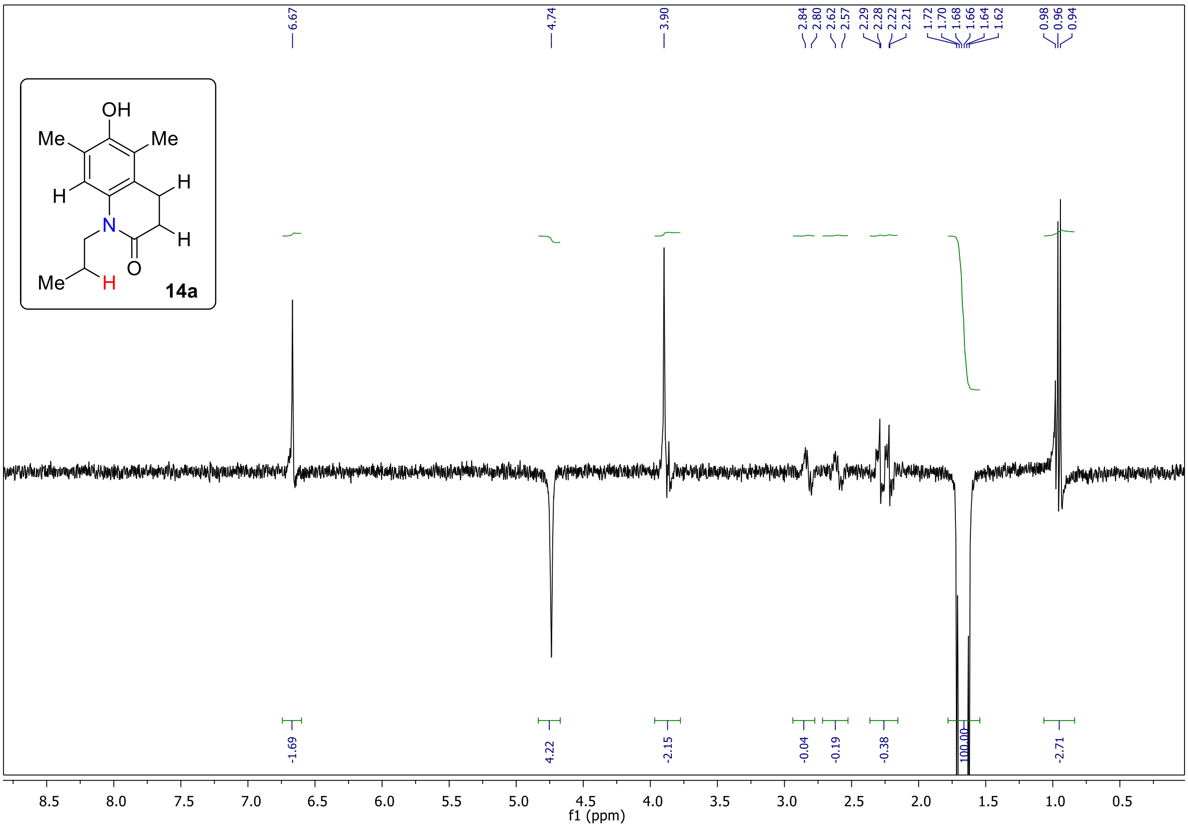



2.84
2.82
2.80
2.58
2.22
OH
Me
Me
4%
H
H
H
N
H
3%
O
Me
14a
100.00
-2.88
-4.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

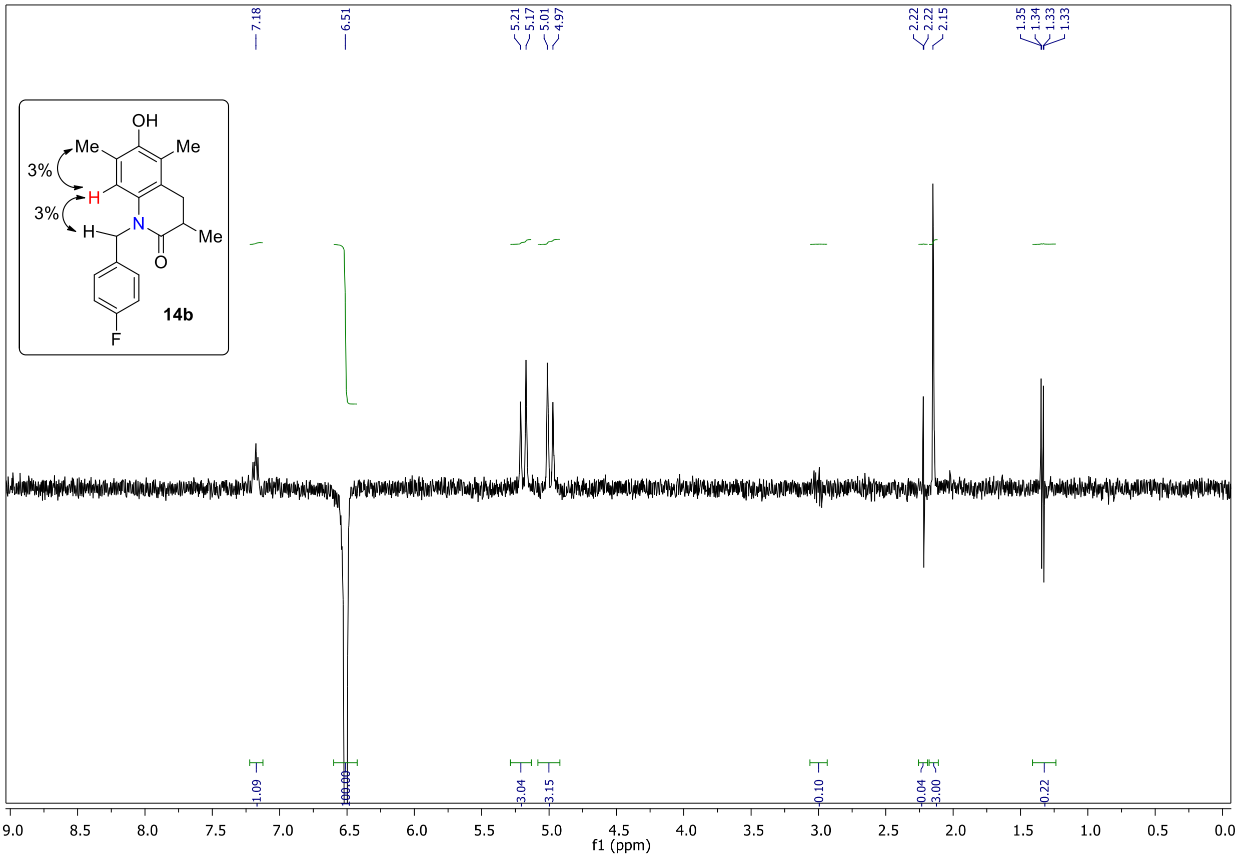

6.67
4.74
2.84
2.84
2.83
2.82
2.81
2.80
2.29
1.68
.6 %
OH
Me
Me
H
1.3%
N
O
Me
14a
-1.28
-0.60
-0.06
100.00
-0.69
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

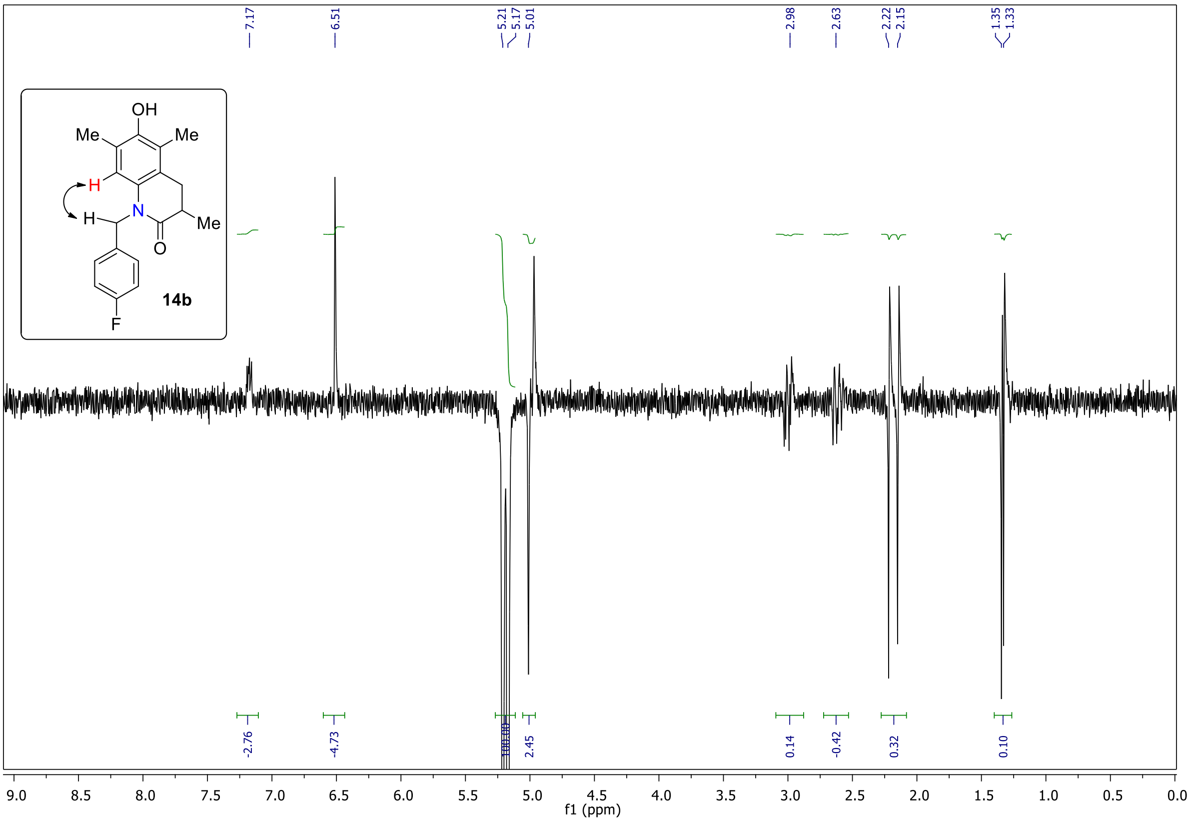

2.84
2.82
2.61
2.60
2.59
2.58
OH
Me
Me
H
H
N
H
4.4 %
O
Me
14a
-4.39
100.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

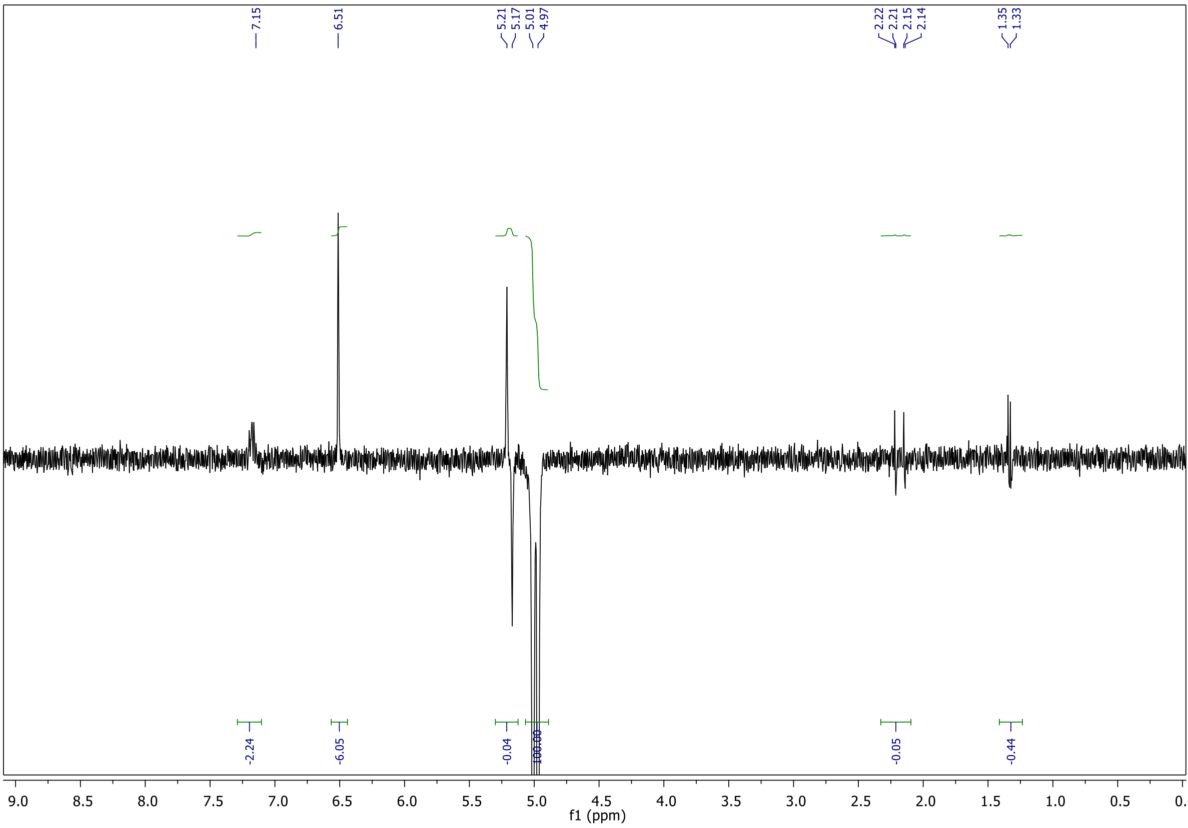

6.67
6.67
4.74
2.84
2.82
2.80
2.29
2.22
1.68
OH
0.4%
Me
Me
2%
H
H
N
H
O
Me
14a
-0.04
-0.43
-1.99
100.00
-0.45
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

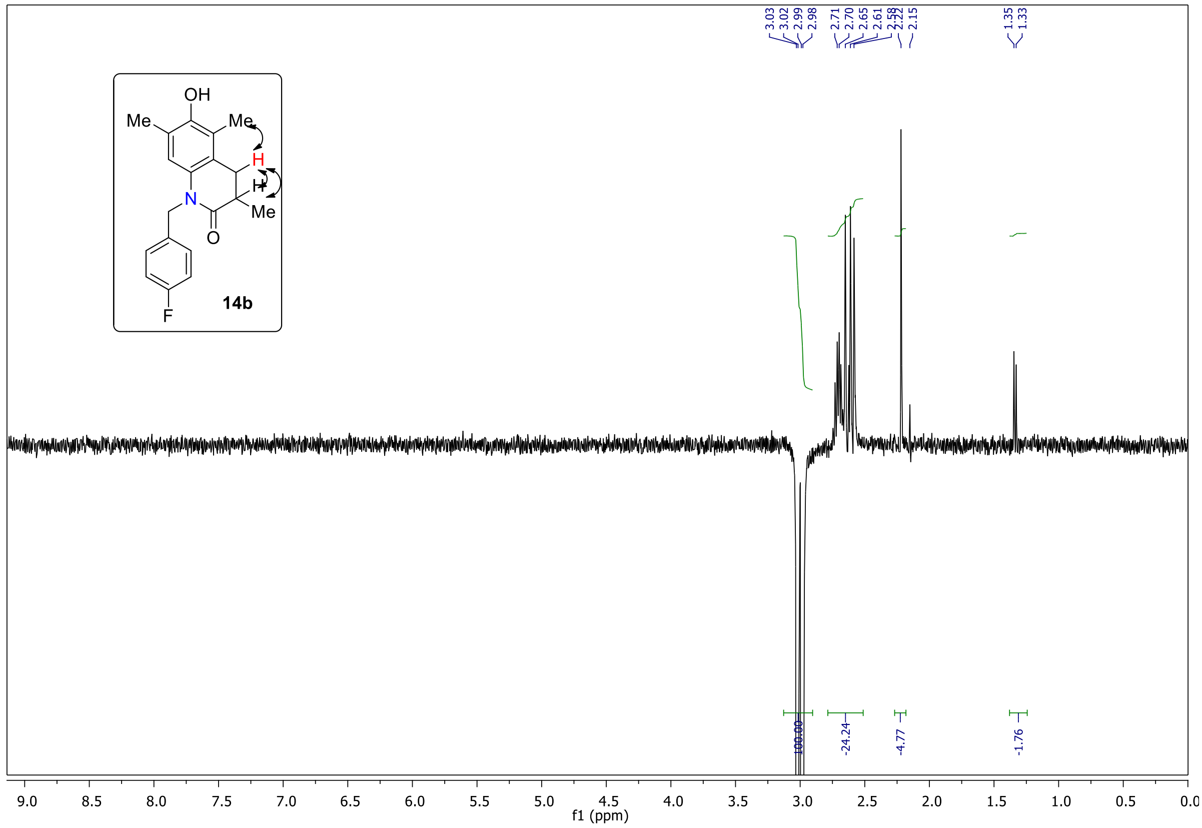


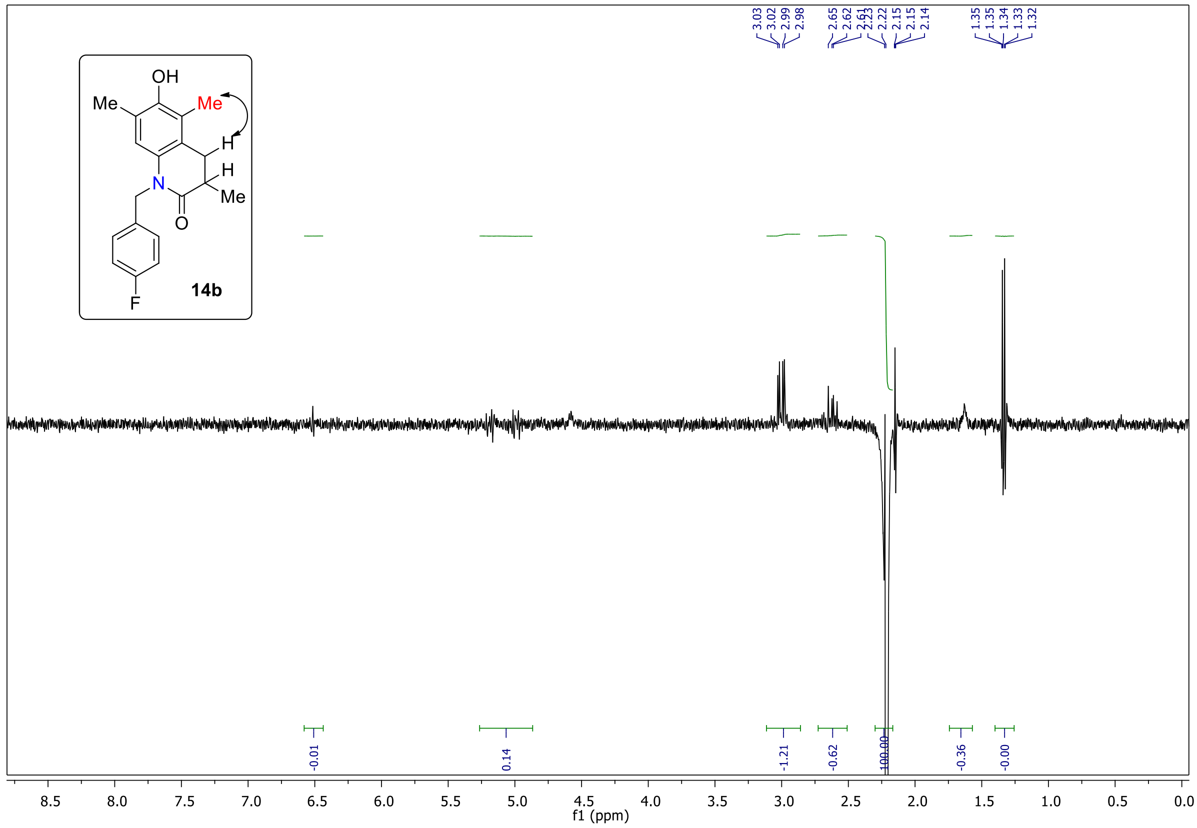
nOe of **14b** ($CDCl_3$, 400 MHz)

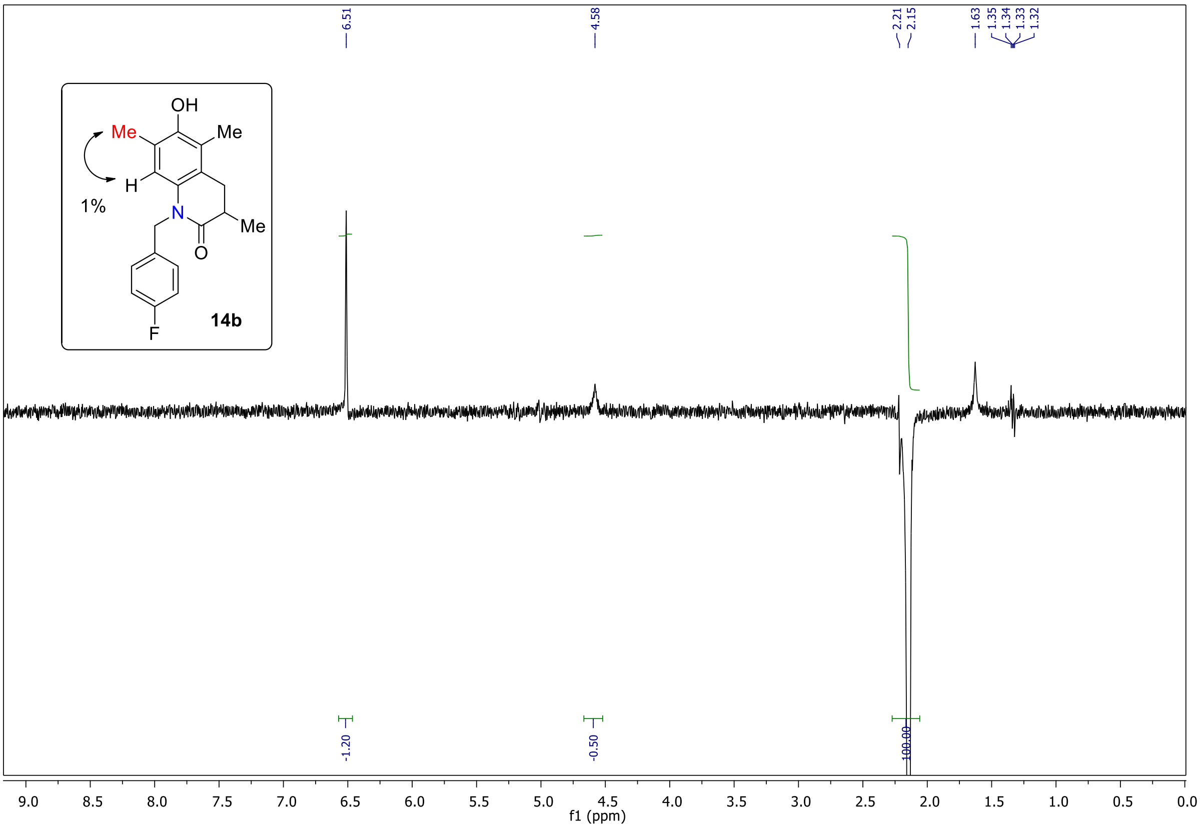



7.17
6.51
5.21
5.17
5.01
2.98
2.63
2.22
2.15
1.35
1.33
OH
Me
Me
H
H
N
Me
O
F
14b
-2.76
-4.73
100.00
2.45
0.14
-0.42
0.32
0.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

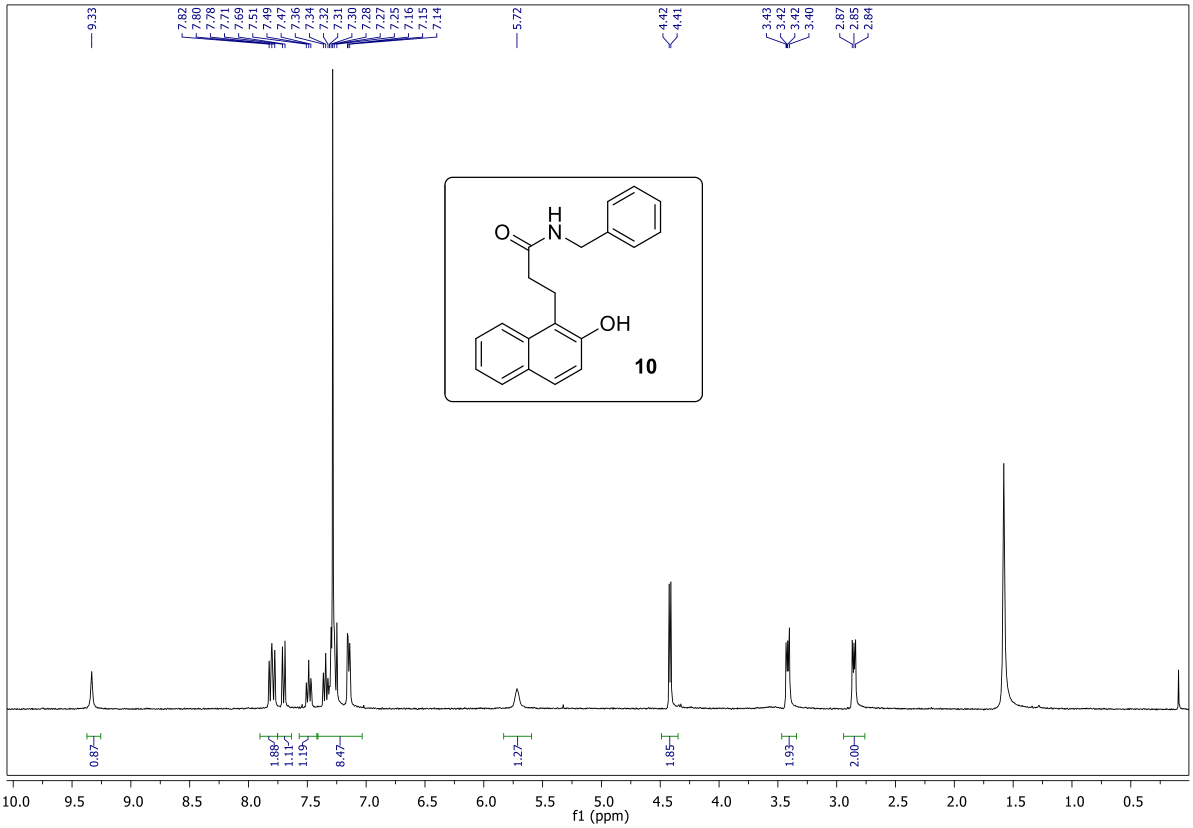

7.15
6.51
5.21
5.17
5.01
4.97
2.22
2.21
2.15
2.14
1.35
1.33
-2.24
-6.05
-0.04
100.00
-0.05
-0.44
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


3.03
3.02
2.99
2.98
2.71
2.70
2.65
2.61
2.58
2.22
2.15
1.35
1.33
OH
Me
Me
H
H
N
Me
O
F
14b
100.00
-24.24
-4.77
-1.76
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)

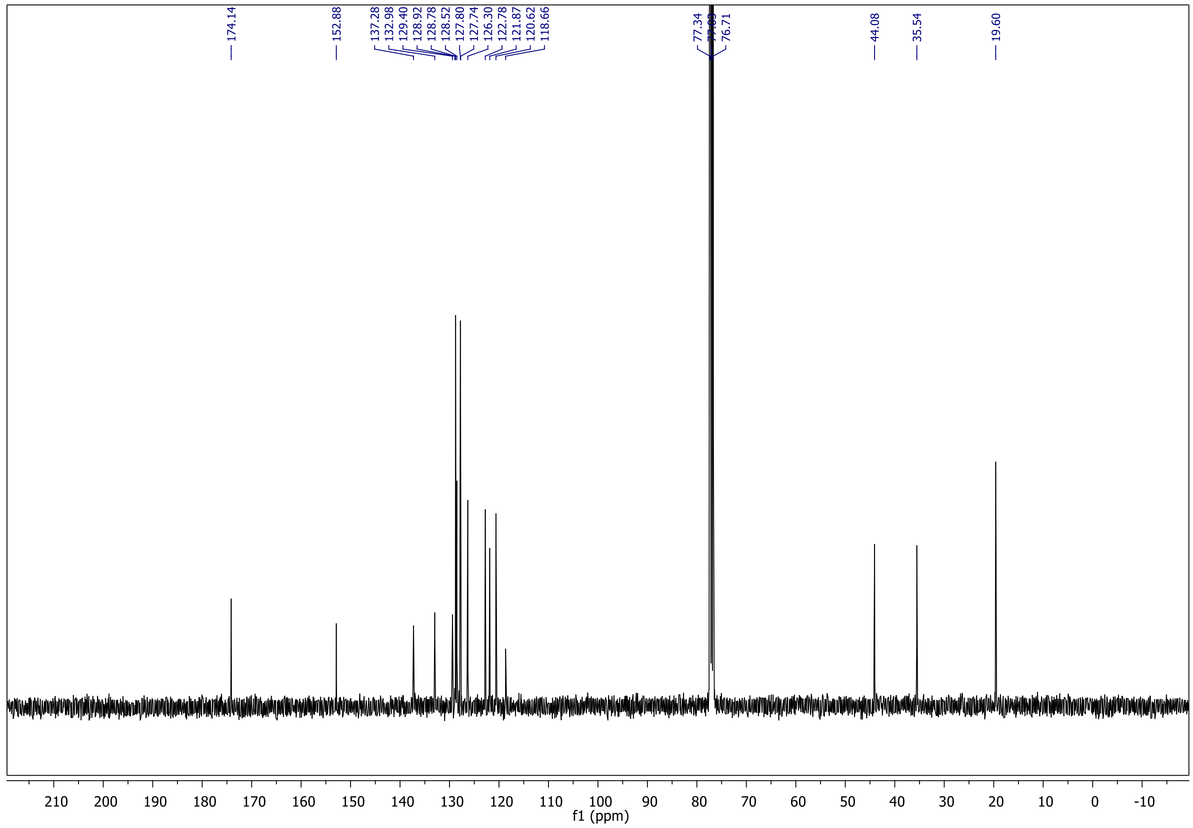

3.03
3.02
2.99
2.98
2.65
2.62
2.61
2.23
2.22
2.15
2.15
2.14
1.35
1.35
1.34
1.33
1.32
OH
Me
Me
H
H
N
Me
O
F
14b
-0.01
0.14
-1.21
-0.62
100.00
-0.36
-0.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


6.51
4.58
2.21
2.15
1.63
1.35
1.34
1.33
1.32
OH
Me
Me
H
1%
N
Me
O
F
14b
-1.20
-0.50
100.00
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)

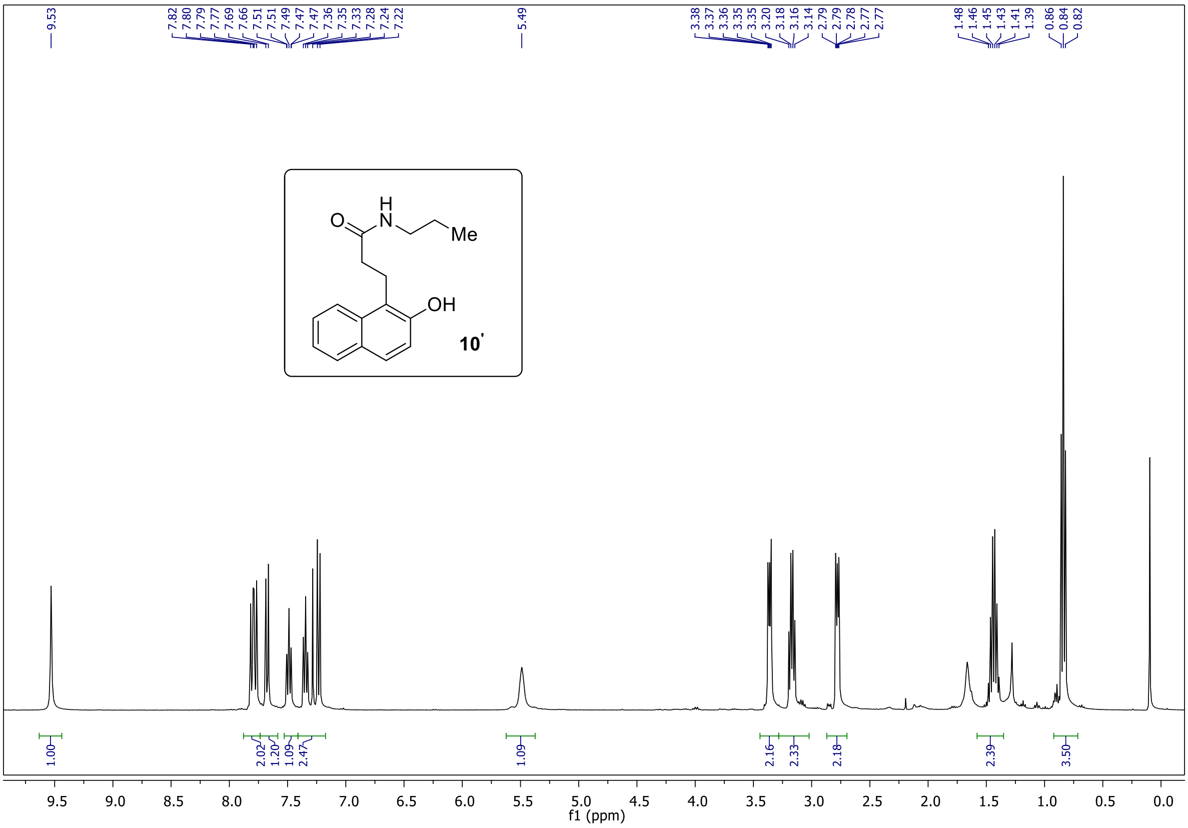
10, ^{1}H NMR (CDCl$_3$, 400 MHz)



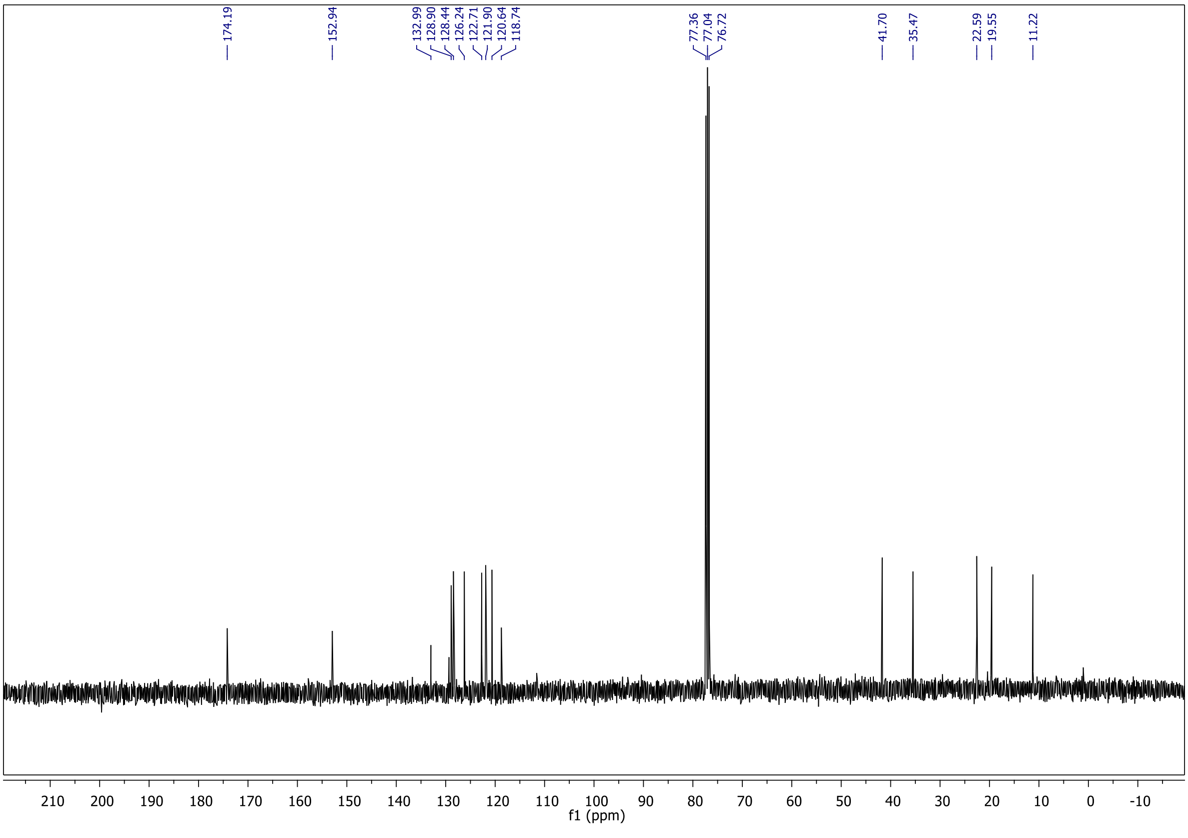
10, ^{13}C NMR (CDCl$_3$, 100 MHz)



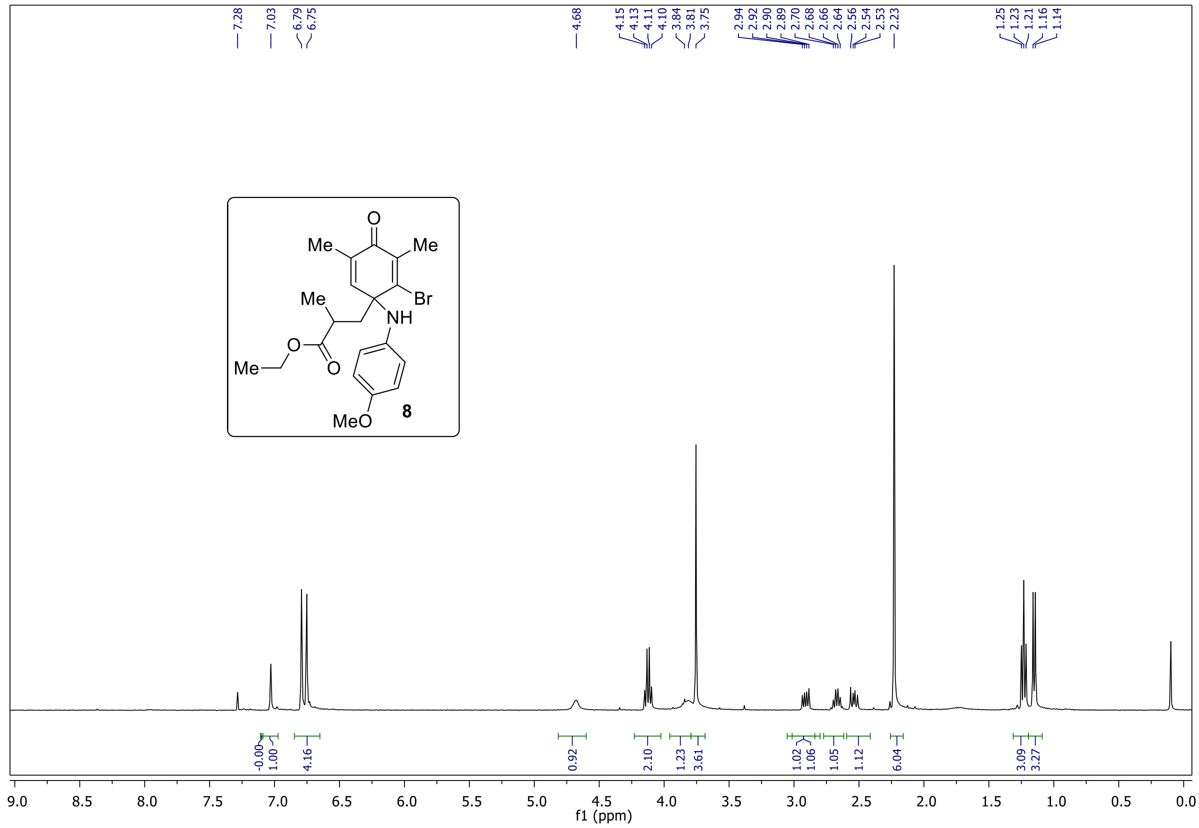
10´, ^{1}H NMR ($CDCl_3$, 400 MHz)



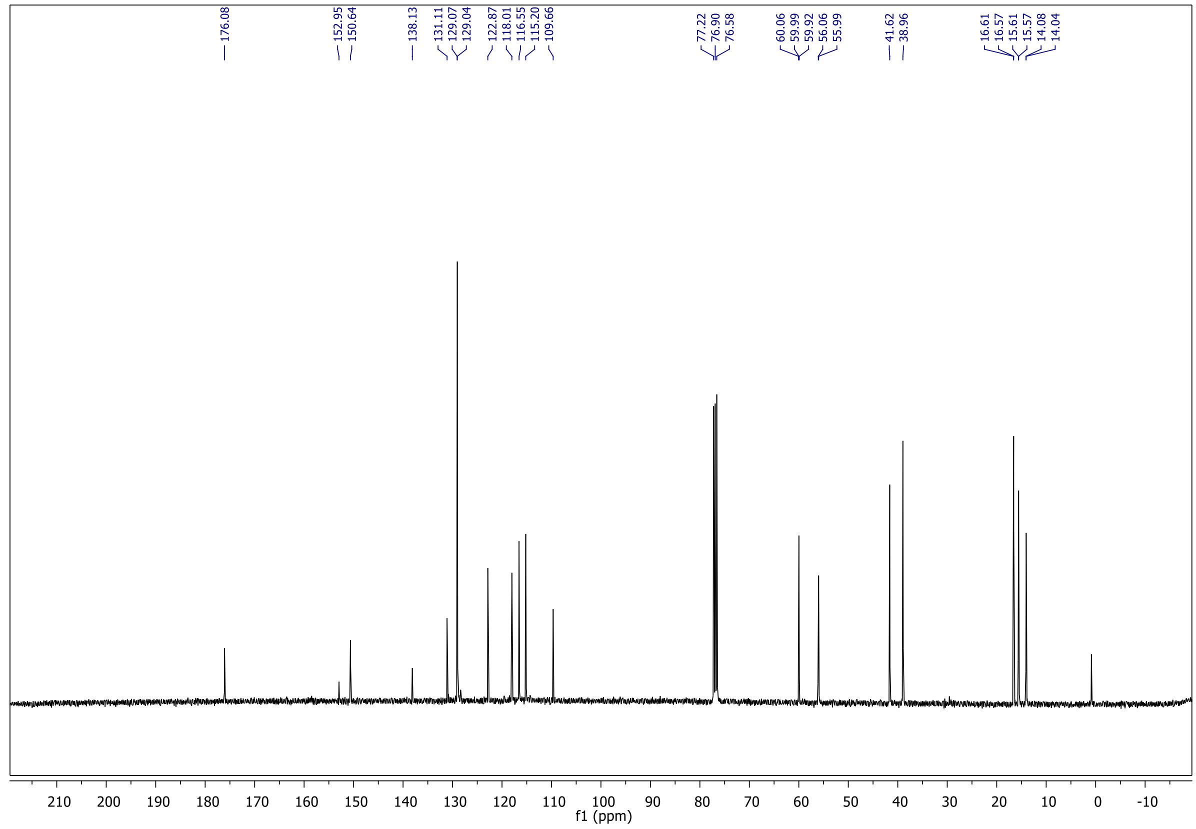
10´, ^{13}C NMR ($CDCl_3$, 100 MHz)



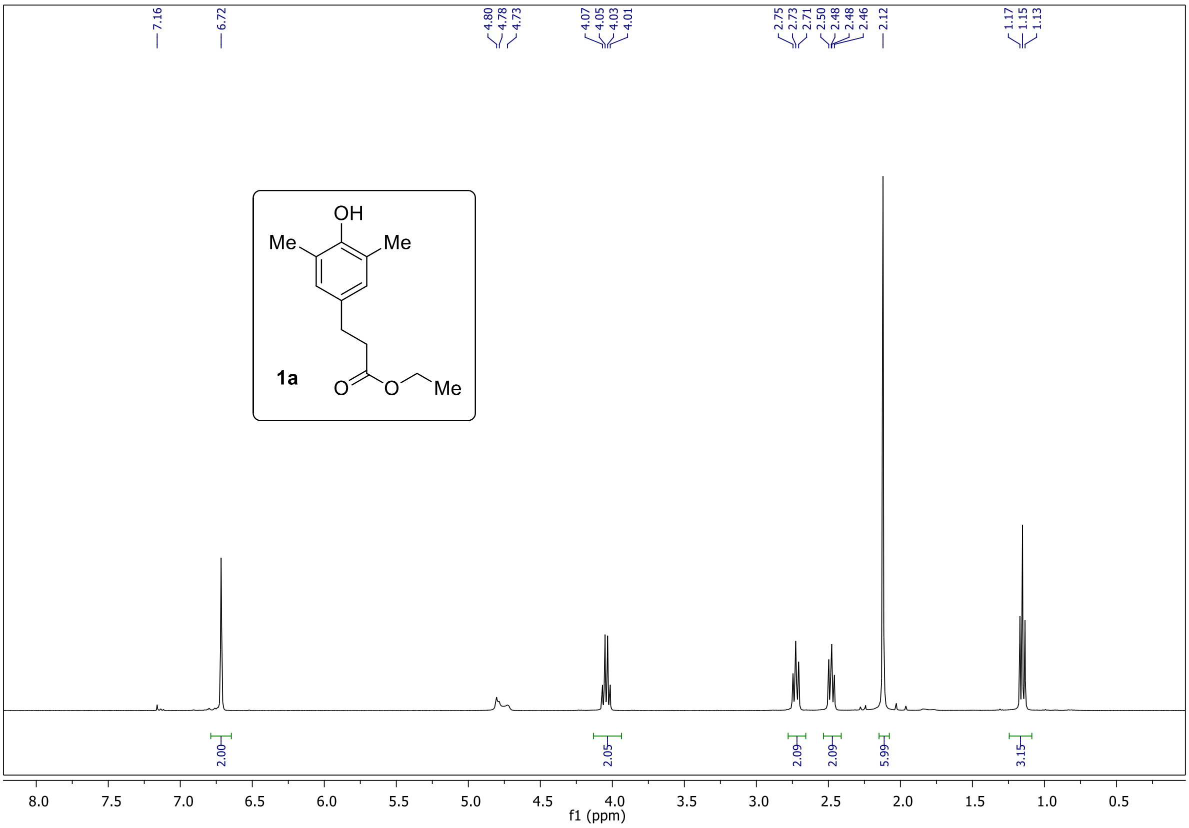
8, ^{1}H NMR (CDCl$_3$, 400 MHz)



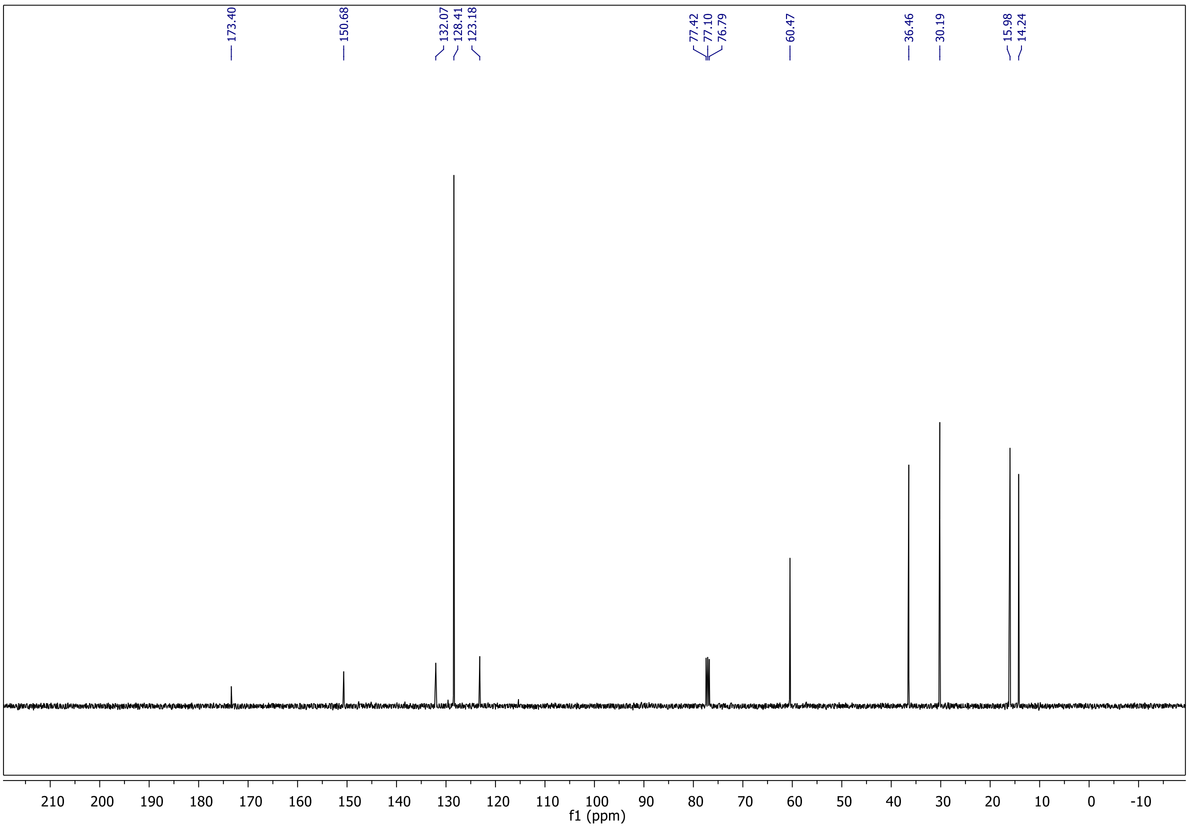
8, ^{13}C NMR (CDCl$_3$, 100 MHz)



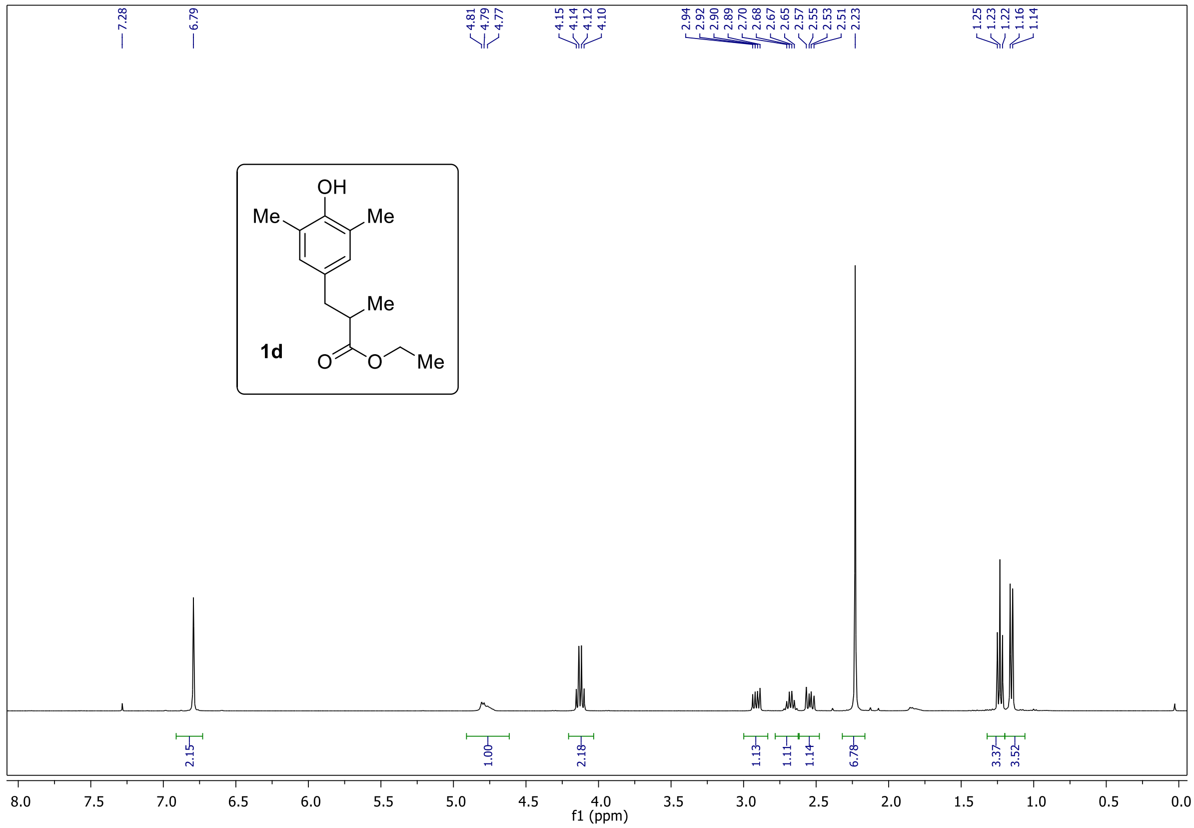
1a, ^{1}H NMR (CDCl$_3$, 400 MHz)



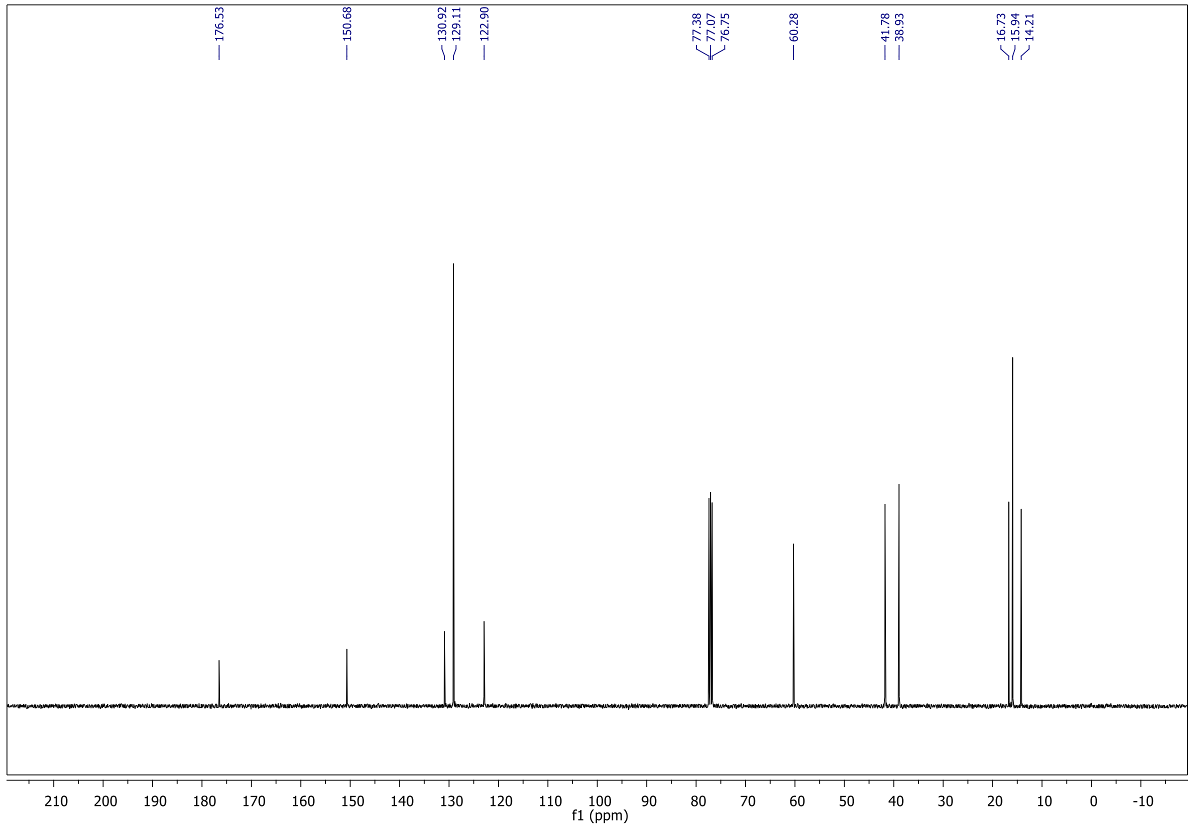
1a, ^{13}C NMR (CDCl$_3$, 100 MHz)



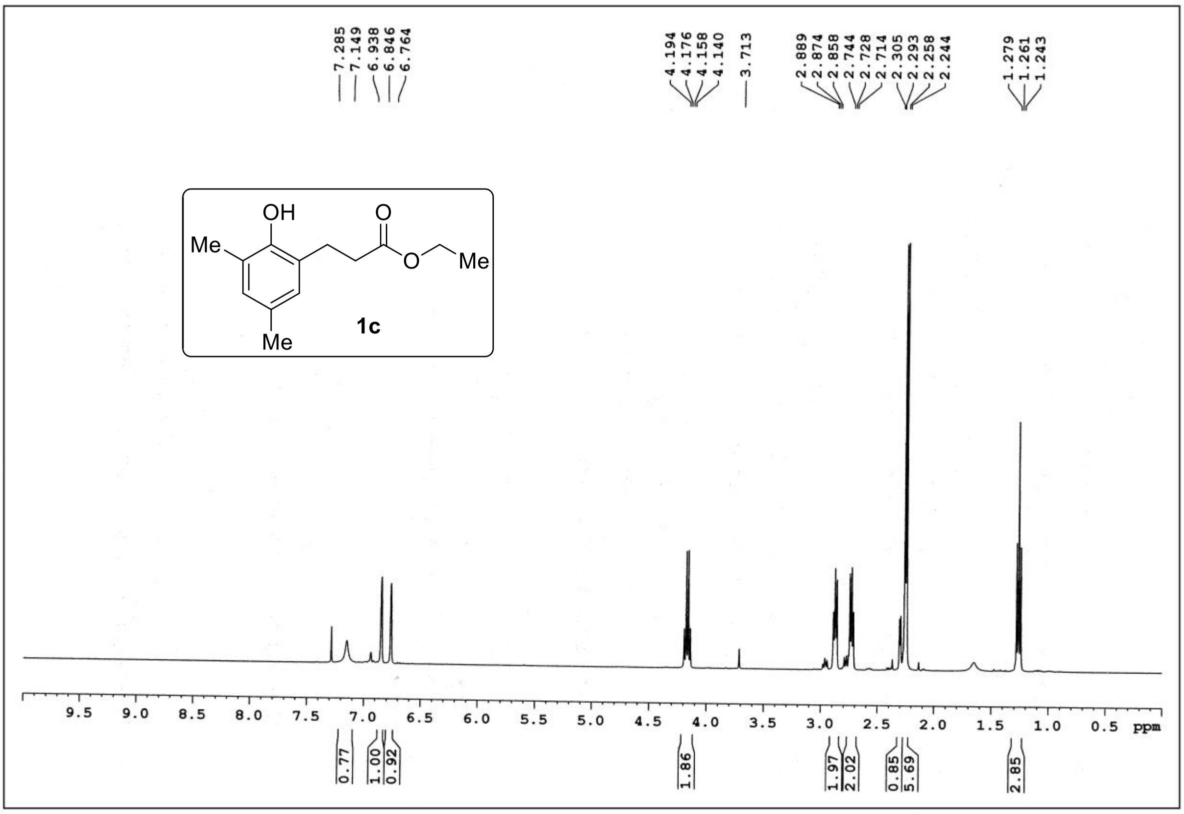
1d, ^{1}H NMR (CDCl$_3$, 400 MHz)



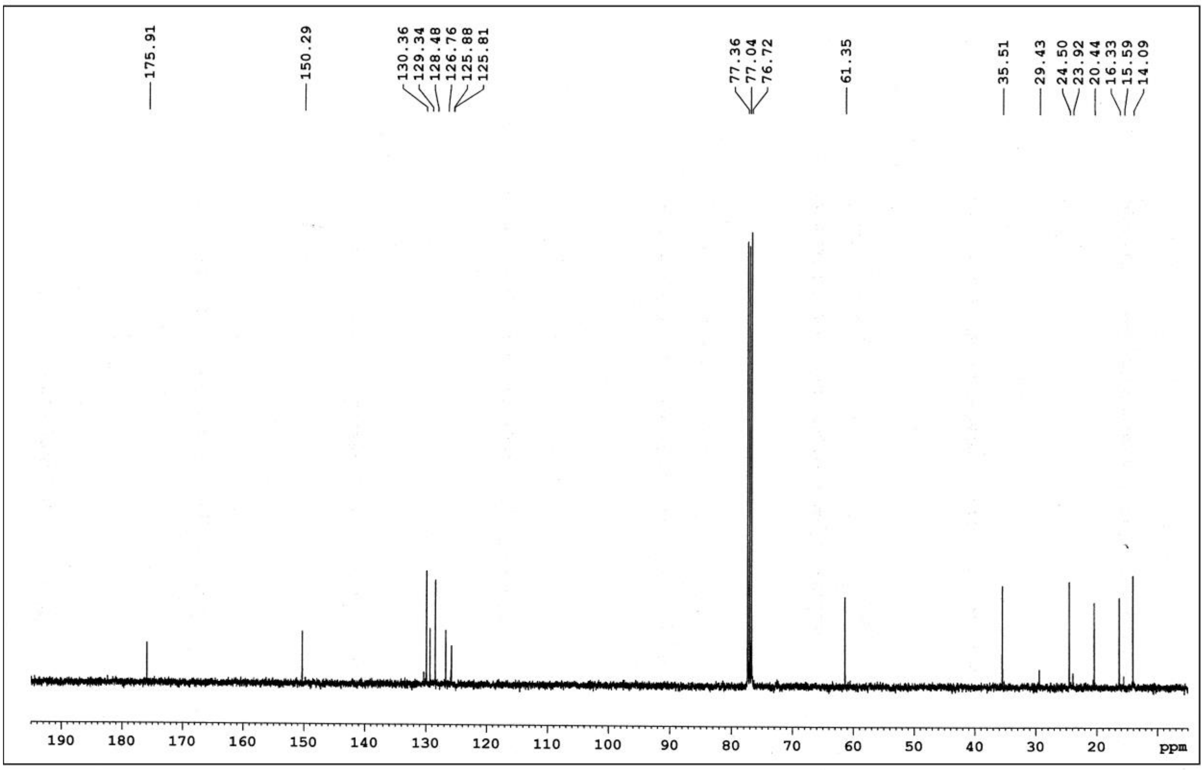
1d, ^{13}C NMR (CDCl$_3$, 100 MHz)



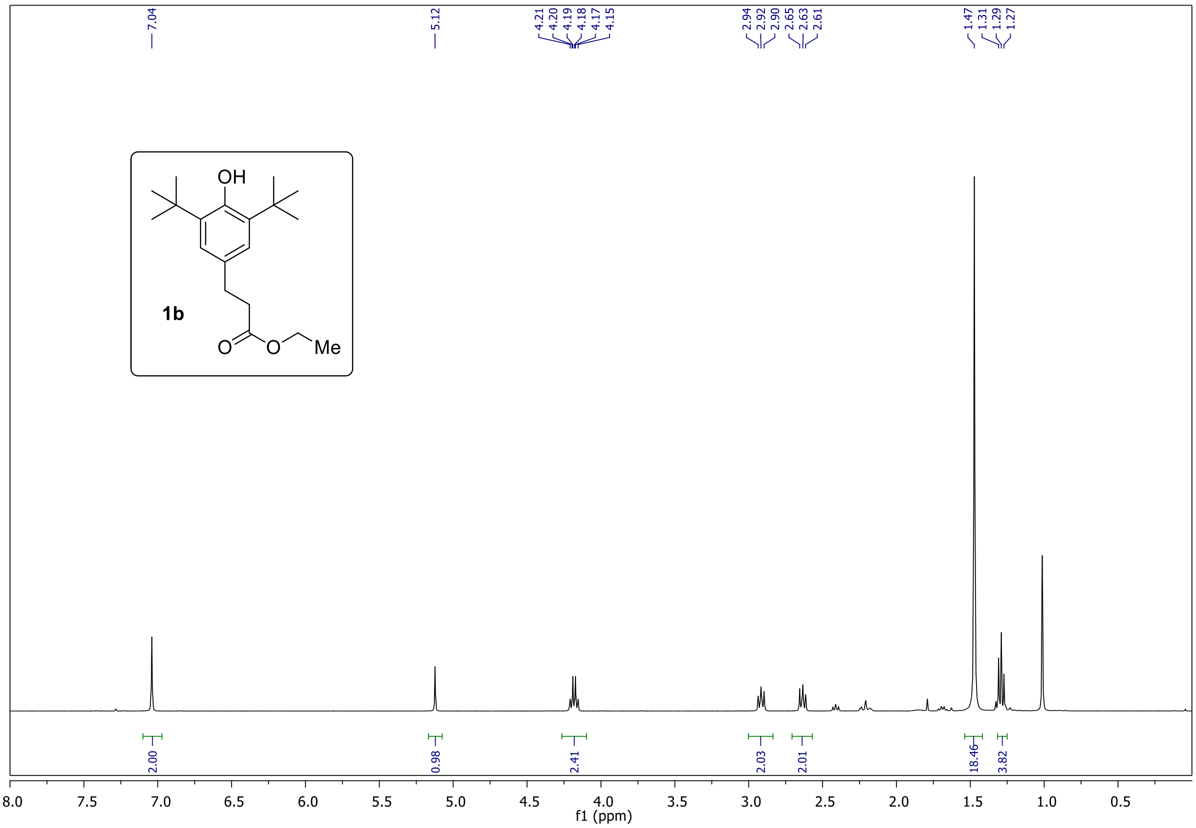
1c, ^{1}H NMR ($CDCl_3$, 400 MHz)



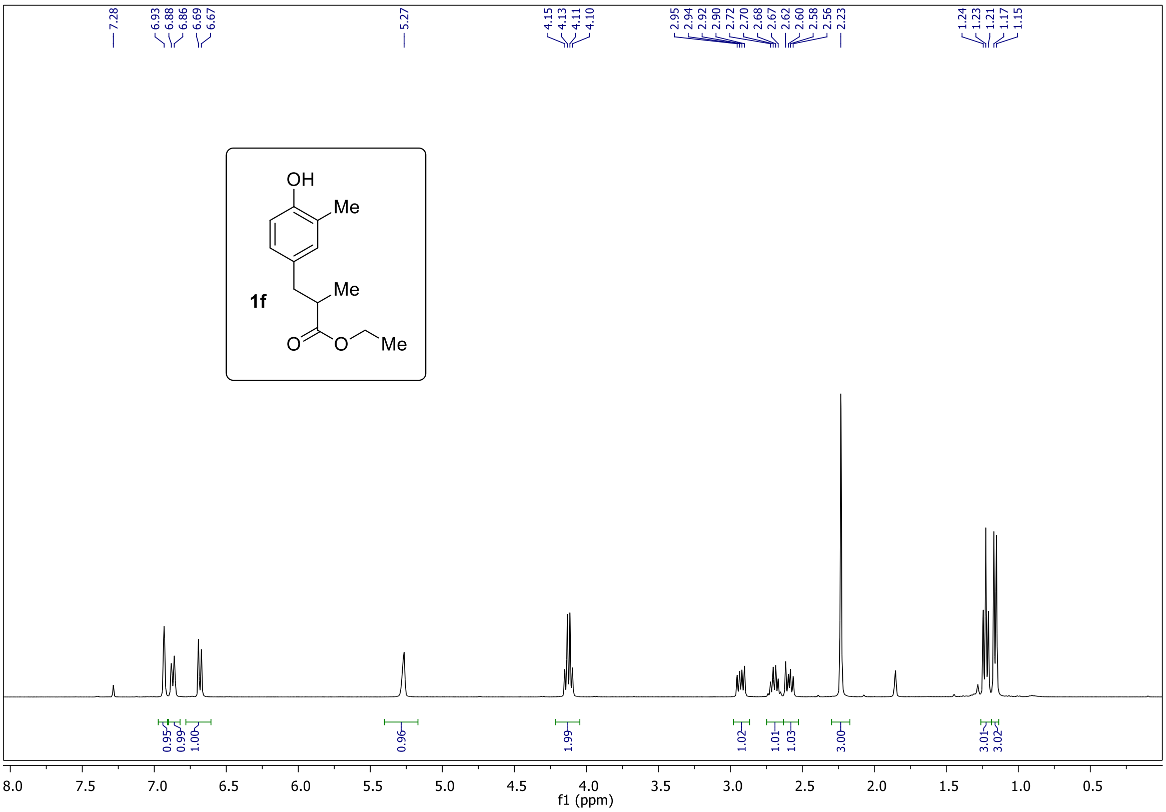
1c, ^{13}C NMR ($CDCl_3$, 100 MHz)



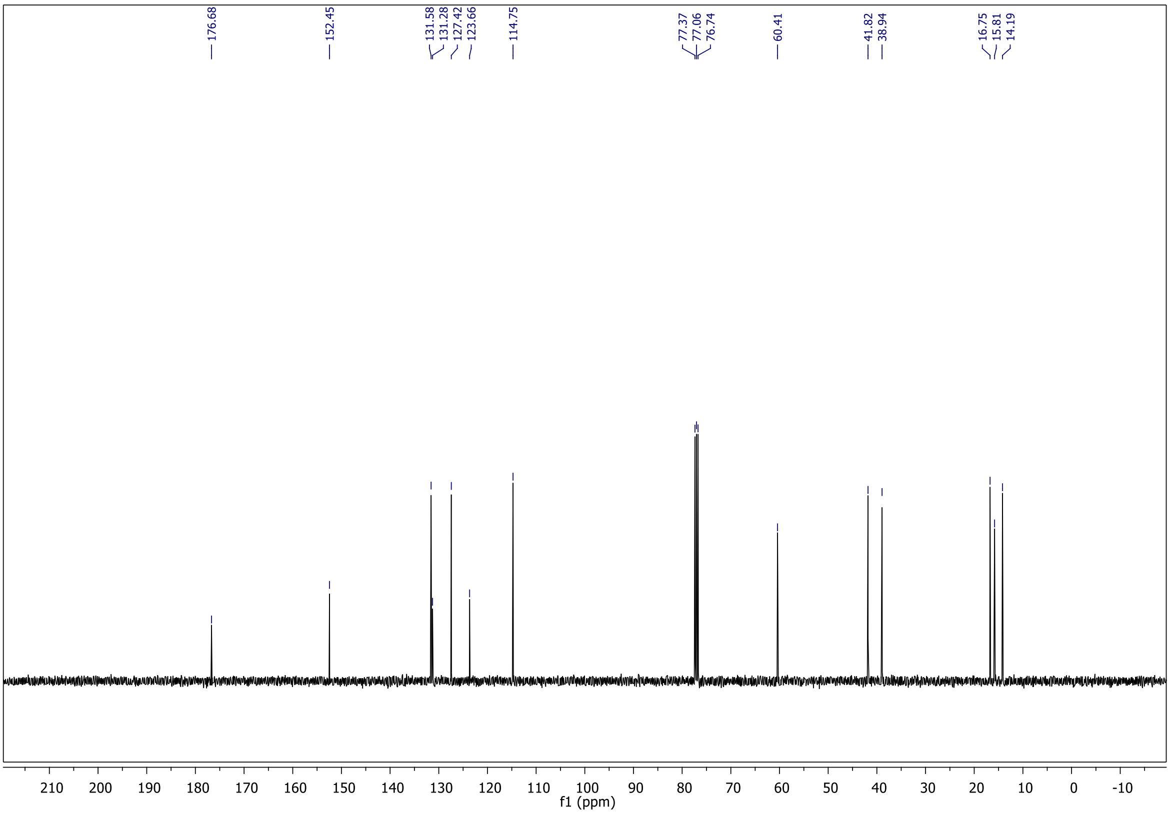
1b, ^{1}H NMR ($CDCl_3$, 400 MHz)



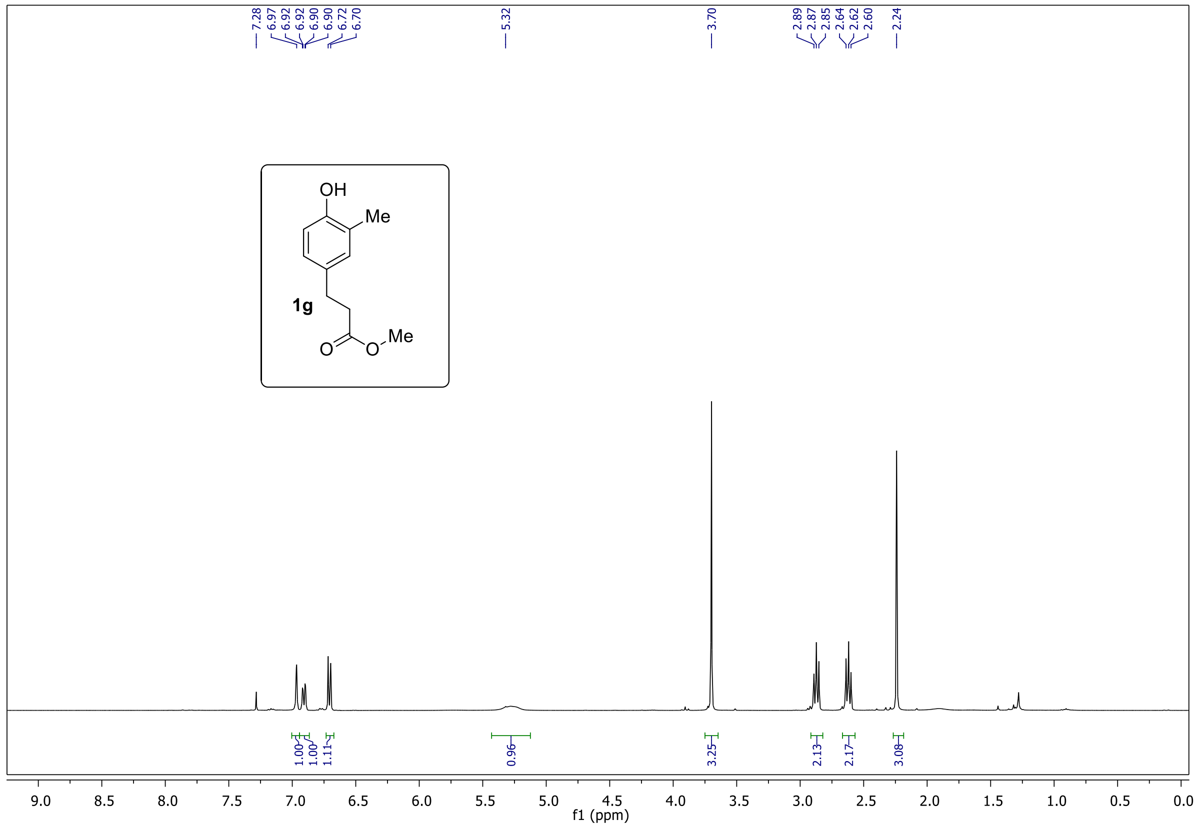
1f, ^{1}H NMR (CDCl$_3$, 400 MHz)



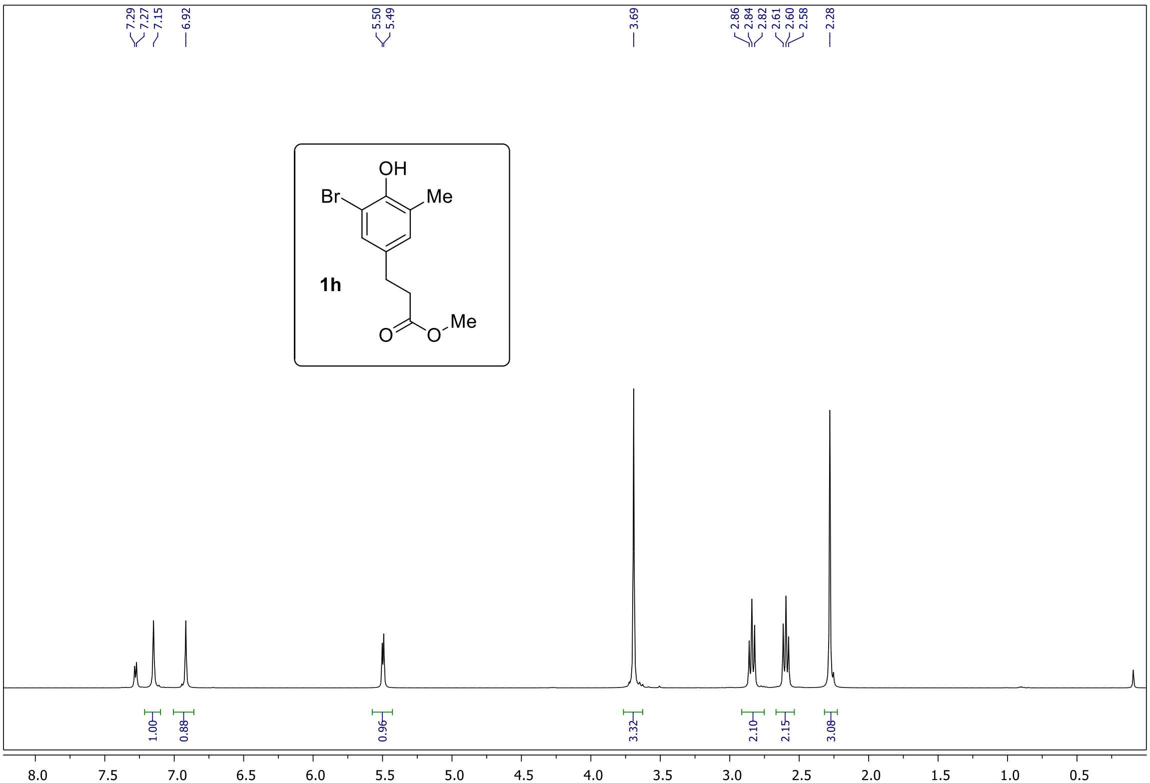
1f, ^{13}C NMR (CDCl$_3$, 100 MHz)



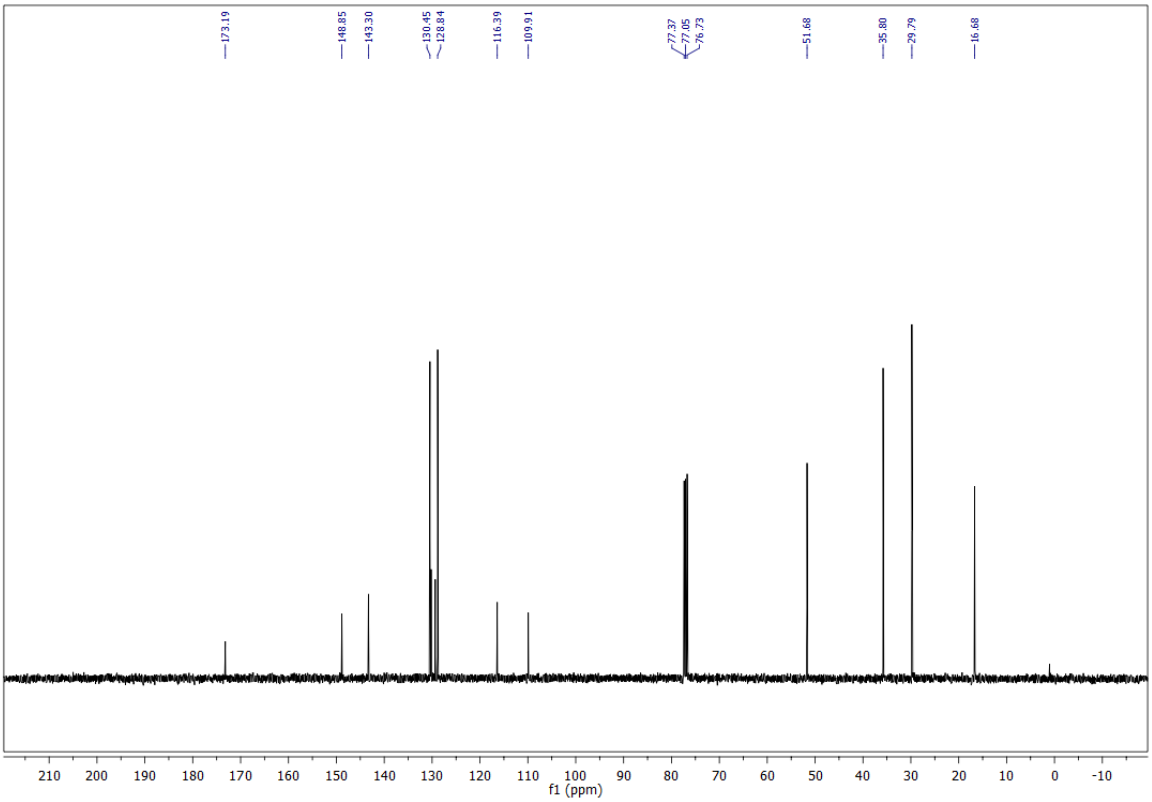
1g, ^{1}H NMR (CDCl$_3$, 400 MHz)



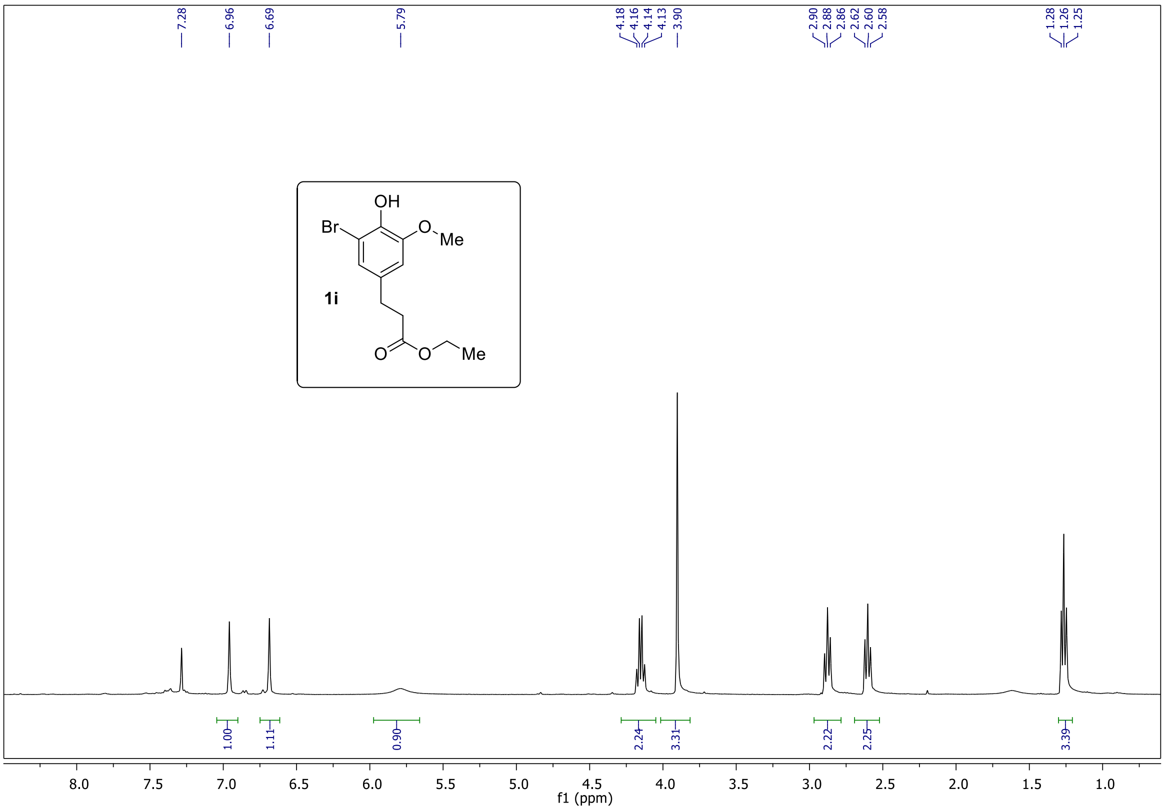
1h, ^{1}H NMR (CDCl$_3$, 400 MHz)



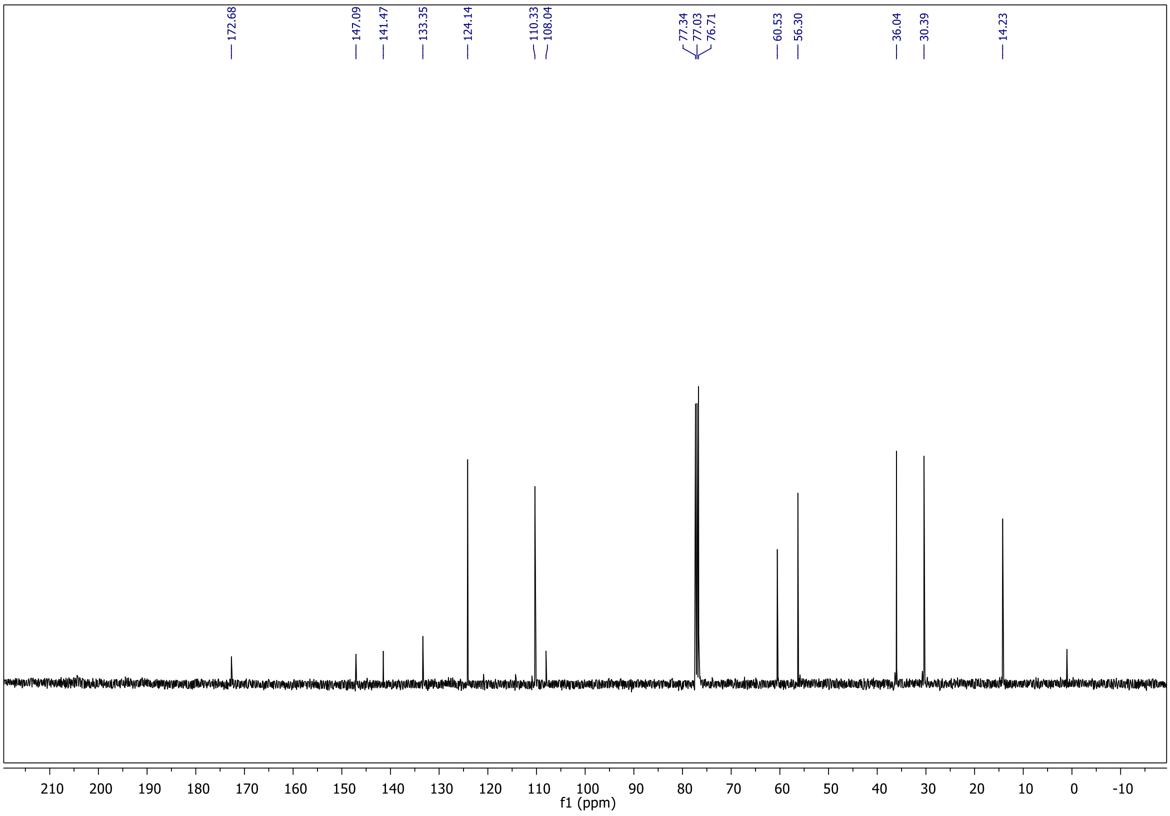
1h, ^{13}C NMR (CDCl$_3$, 100 MHz)



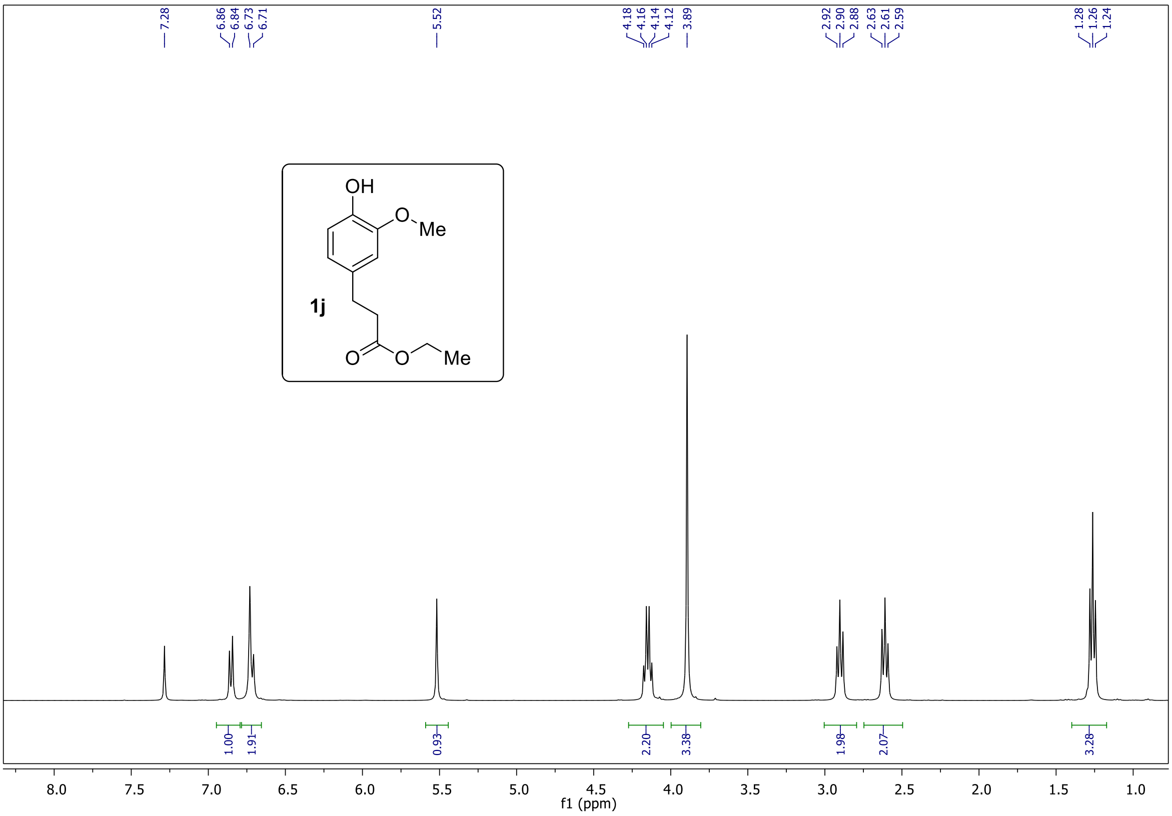
1i, ^{1}H NMR (CDCl$_3$, 400 MHz)



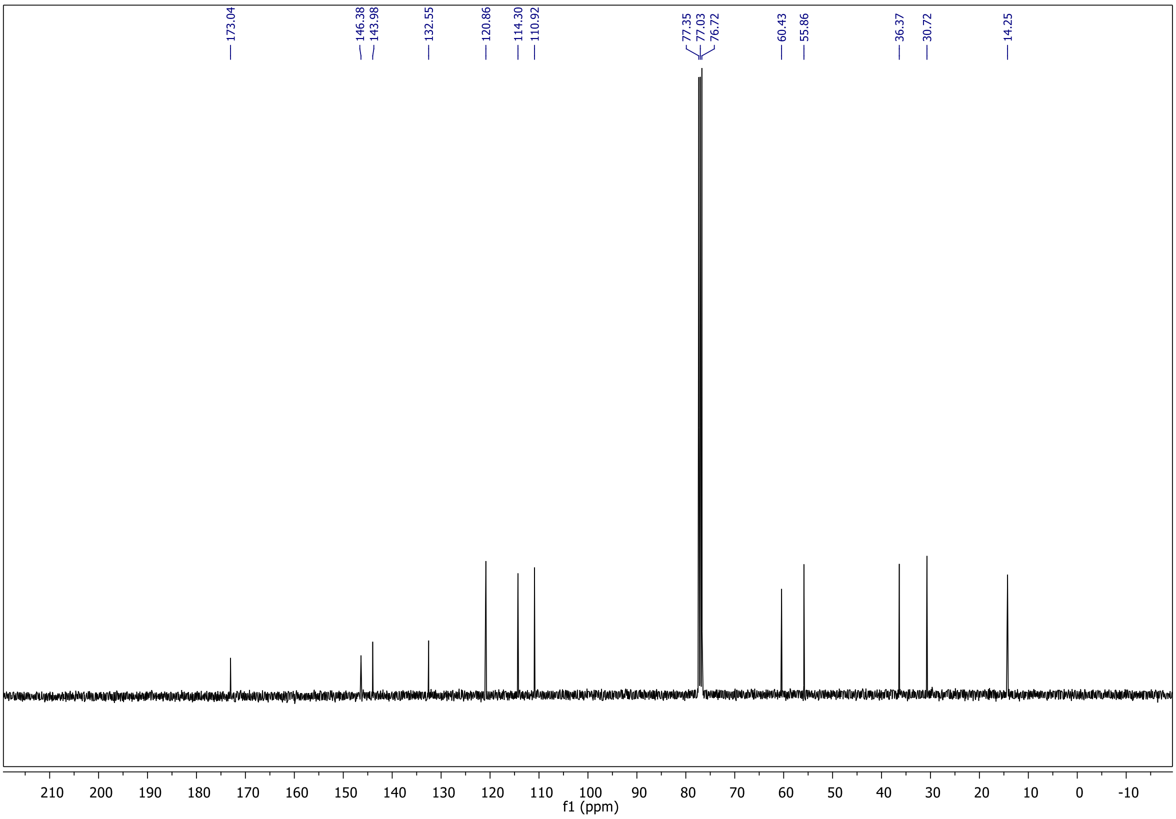
1i, ^{13}C NMR (CDCl$_3$, 100 MHz)



1j, ^{1}H NMR (CDCl$_3$, 400 MHz)



1j, ^{13}C NMR (CDCl$_3$, 100 MHz)



3k, ^{19}F NMR (CDCl$_3$, 376 MHz)