Supporting Information

Expedient (3+3)-annulation of carbonyl ylides with azaoxyallyl cations: formal access to oxa-benzo[*c*]azepin-3-ones

Table of Contents

General Information: Ethyl benzoyl acetate, acetophenones, *o*-benzylhydroxylamine hydrochloride, HFIP (≥99%), NaH (60 % dispersion in mineral oil), diethyl carbonate (99%), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (>95%), 2-bromoisobutyryl bromide (>98%), $Rh_2(OAc)_4$, $Pd(PPh_3)_4$ (99 %), $Pd(PPh_3)_2Cl_2$ (99 %) and TEMPO (98%) were purchased from Aldrich and TCI, and used as received. Na_2CO_3 (>99%), K_2CO_3 (98%), Cs_2CO_3 (99%), DIPEA (≥99%), DBU (≥99%), DABCO (99%) and Et_3N (>99%) were procured from Merck and used as received. CH_3CN and CH_2Cl_2 were dried prior as per the standard procedure prior to use. SRL silica gel G/GF 254 plates were used for analytical TLC and SRL silica gel (100-200 mesh) was used for column chromatography. Bruker Avance III 400, 500 and 600 MHz NMR spectrometers were used to record (^1H, ^{13}C and ^{19}F) spectra using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) and spin-spin coupling constant (*J*) are reported in parts per million and hertz (Hz), respectively, and to describe peak patterns following abbreviations used when appropriate: s = singlet, d = doublet, t = triplet, q= quartet and m = multiplet. Melting point of the products was measured on Büchi melting point apparatus, MPB-540. Open capillary tubes were used for the measurements and are uncorrected. Mestre nova software was used throughout the spectral analysis. Q-Tof ESI-MS instrument Agilent (model: 6546 LC/Q-TOF) was used for recording HRMS data. Infrared spectra were recorded on Perkin Elmer FT-IR instrument. Single crystal X-ray data of **3ra** was collected on a Bruker SMART APEX equipped with a CCD area detector using Mo/-Kα radiation and the structure was solved by direct method using SHELXL-19 (Göttingen, Germany).

Sample Preparation for Crystal Growth. The compound **3ra** (10 mg) was dissolved in a mixture of $CHCl_3$ (1.0 ml) and CH_3CN (1.0 ml) and kept at room temperature for slow evaporation (2 days). Block shaped colorless crystals were formed, which was subjected to *X*-ray diffraction.

Crystal Structure and Data of 3ra.

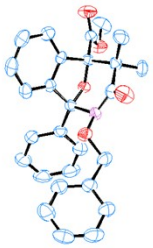
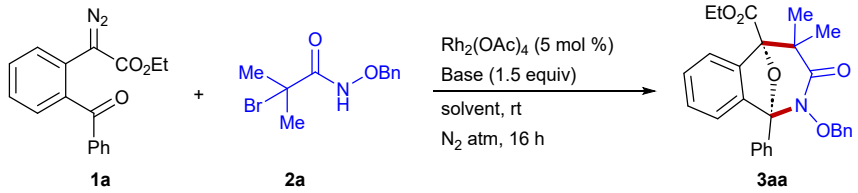


Figure S1. ORTEP diagram of methyl 2-(benzyloxy)-4,4-dimethyl-3-oxo-1-phenyl-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate **3ra** (CCDC 2372696) with 50% ellipsoid. H-omitted for clarity.

Identification code	**3ra**
Empirical formula	'C27 H25 N O5 '
Formula weight	443.48
Crystal habit, colour	Block/Colorless
Temperature, *T*/K	299 K
Wavelength, λ/Å	0.71073
Crystal system	'orthorhombic'
Space group	'P c a 21'
Unit cell dimensions	a = 18.656(4) Å b = 9.9609(18) Å c = 12.339(2) Å α = 90 β = 90 γ = 90
Volume, *V*/Å^3	2293.0(7)
Z	4
Calculated density, Mg·m^{-3}	1.285
Absorption coefficient, μ/mm^{-1}	0.089
F(000)	936
θ range for data collection	2.183 to 27.481
Limiting indices	-24 ≤ h ≤24, –12 ≤ k ≤ 12, –16 ≤ l ≤ 16
Reflection collected / unique	5248/3994
Completeness to θ	99.9%
Absorption correction	Multi-scan

Refinement method	'SHELXL-2019/1 (Sheldrick 2019)'
Data / restraints / parameters	5248/1/ 301
Goodness–of–fit on F^2	1.201
Final *R* indices [*I*>2sigma(*I*)]	R1 =0.0603, wR2 = 0.1014
R indices (all data)	R1 = 0.0922, wR2 = 0.1133

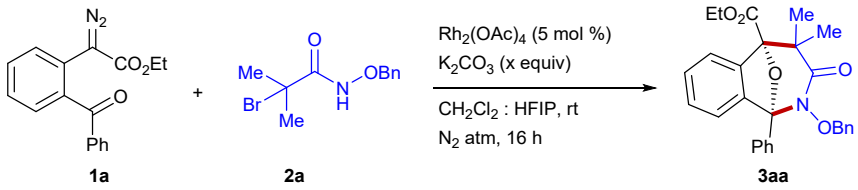
Table S1 Optimization of the reaction conditions[a]



Entry	Catalyst	Base	Solvent	Yield (%)[b]
1	$Rh_2(OAc)_4$	Cs_2CO_3	$CHCl_3$	43
2	$Rh_2(OAc)_4$	K_2CO_3	$CHCl_3$	65
3	$Rh_2(OAc)_4$	Na_2CO_3	$CHCl_3$	30
4	$Rh_2(OAc)_4$	$NaHCO_3$	$CHCl_3$	trace
5	$Rh_2(OAc)_4$	NEt_3	$CHCl_3$	trace
6	$Rh_2(OAc)_4$	DIPEA	$CHCl_3$	53
7	$Rh_2(OAc)_4$	DBU	$CHCl_3$	58
8	$Rh_2(OAc)_4$	DABCO	$CHCl_3$	46
9	$Rh_2(OAc)_4$	K_2CO_3	CH_2Cl_2	73
10	$Rh_2(OAc)_4$	K_2CO_3	$(CH_2Cl)_2$	61
11	$Rh_2(OAc)_4$	K_2CO_3	Toluene	n.d.
12	$Rh_2(OAc)_4$	K_2CO_3	THF	n.d.
13	$Rh_2(OAc)_4$	K_2CO_3	CH_3CN	n.d.
14	$Rh_2(OAc)_4$	K_2CO_3	TFE	trace
15	$Rh_2(OAc)_4$	K_2CO_3	MeOH	n.d.
16	$Rh_2(OAc)_4$	K_2CO_3	HFIP	68
17	**$Rh_2(OAc)_4$**	**K_2CO_3**	**CH_2Cl_2: HFIP**	**86**
18	$Rh_2(OAc)_4$	K_2CO_3	$CHCl_3$: HFIP	78
19	$Rh_2(OAc)_4$	K_2CO_3	$(CH_2Cl)_2$: HFIP	58

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.11 mmol), $Rh_2(OAc)_4$ (5 mol %), base (1.5 equiv), solvent (2 mL), N_2 atm 16 h. [b]Isolated yield. n.d. = not detected. HFIP = 1,1,1,3,3,3-Hexafluoroisopropanol. TFE =2,2,2- Trifluoroethanol.

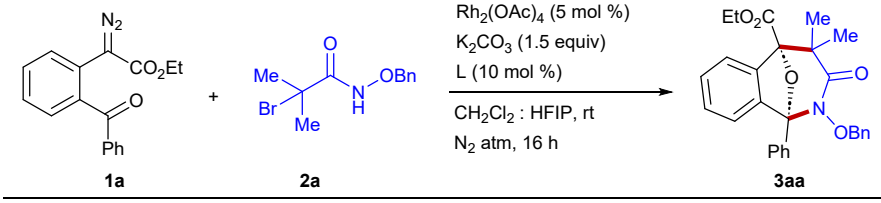
Table S2 Screening of the equivalent of K_2CO_3[a]

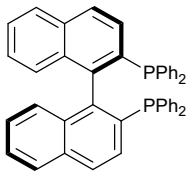


Entry	Catalyst	Equivalent	Yield (%)[b]
1	K_2CO_3	0.2	n.d.
2	K_2CO_3	0.5	trace
3	K_2CO_3	1	34
4	K_2CO_3	1.2	73
5	K_2CO_3	1.5	86
6	K_2CO_3	1.7	75
7	K_2CO_3	2.0	77

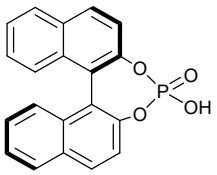
[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.11 mmol), $Rh_2(OAc)_4$ (5 mol %), K_2CO_3 (x equiv) CH_2Cl_2:HFIP (1:1, 2 mL), rt, N_2 atm 16 h. [b]Isolated yield.

Table S3 HPLC Analysis[a]





L1

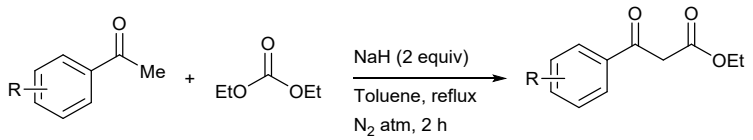


L2

Entry	Ligand	ee (%)[b]
1	L1	0
2	L2	0

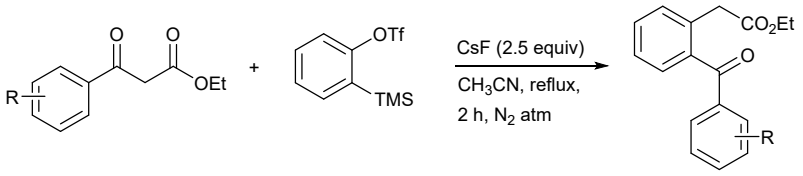
[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.11 mmol), $Rh_2(OAc)_4$ (5 mol %), K_2CO_3 (1.5 equiv), L (10 mol %), CH_2Cl_2:HFIP (1:1, 2 mL), rt, N_2 atm 16 h. [b]Chiral HPLC Analysis.

Procedure for the Preparation of *α*-Diazoesters 1[1]



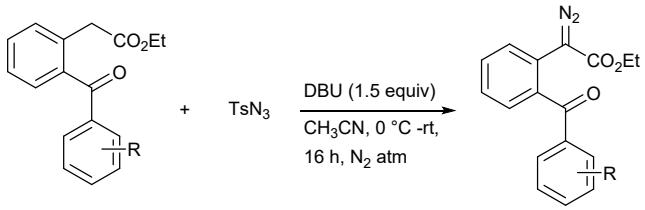
Scheme S1

Step-I: To a stirred suspension of NaH (6 mmol, 144 mg, 60% dispersion in mineral oil) in toluene (10 ml), acetophenone (3 mmol) was added at room temperature and stirred for 10 min. After that diethyl carbonate (12 mmol, 1416 mg) was added dropwise and refluxed for 2 h under N_2 atm. After completion (monitored by TLC), the reaction mixture cooled to room temperature and quenched with cold water, acidified with 2 M HCl solution and then extracted with ethyl acetate (3 x 30 mL). The combined organic layer was washed with brine (20 ml) and dried (Na_2SO_4). Evaporation of the solvent gave a residue that was purified on a silica gel column chromatography using ethyl acetate and hexane as an eluent to afford benzoyl acetates.



Scheme S2

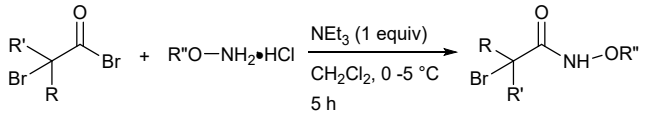
Step-II: To a stirred solution of benzoyl acetate (2 mmol) and 2-(trimethylsilyl)-phenyl triflate (2.6 mmol, 775 mg) in CH_3CN (8 ml), CsF (5 mmol, 760 mg) was added under N_2 atm in one portion and refluxed for 2 h. After completion (monitored by TLC), the reaction was cooled to room temperature and quenched with brine (20 ml) and extracted with ethyl acetate (3 x 20 mL). The combined organic solution was dried (Na_2SO_4) and the solvent was evaporated to give a residue that was purified on a silica gel column chromatography using ethyl acetate and hexane as eluent to afford benzoyl phenyl acetate.



Scheme S3

Step-III: To a stirred solution of benzoyl phenyl acetate (2 mmol) and TsN_3 (2.4 mmol, 473 mg) in CH_3CN (8 mL), was added DBU (3.0 mmol, 456 mg) dropwise at 0 ºC and after 5 min, the reaction mixture was allowed to stir at room temperature for 16 h under N_2 atm. After completion (monitored by TLC), the reaction mixture was concentrated and purified on a silica gel column chromatography using ethyl acetate and hexane as eluent to afford diazoesters **1a-s**.

Procedure for the Preparation of *α*-Halohydroxamate 2[2]



Scheme S4

To a stirred solution of *o*-hydroxylamine HCl (3 mmol) in CH_2Cl_2 (10 mL), NEt_3 (3 mmol, 0.4 mL) was added at 0 ºC. After 5 mins, corresponding bromide (3 mmol) was added dropwise and allowed to stir for 5 h. After completion (monitored by TLC), the reaction mixture was quenched with water and the organic layer washed with water (3 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on a silica gel column chromatography using ethyl acetate and hexane as eluent to afford halo hydroxamates **2a-k**.

General Procedure for the Synthesis of 3. To a stirred solution of *α*-diazo esters **1** (0.1 mmol) and *α*-halo-hydroxamate **2** (0.11 mmol) in CH_2Cl_2: HFIP (1:1, 2 mL), K_2CO_3 (0.15 mmol, 21 mg) and $Rh_2(OAc)_4$ (0.005 mmol, 2.3 mg) were added and the reaction mixture was allowed to stir at room temperature for 16 h under N_2 atm. After completion (monitored by TLC), the reaction mixture diluted with CH_2Cl_2 (5 mL) and passed through a short bed of celite. The solvent was evaporated and the residue was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford **3aa-sa** and **3ab-ai**.

Scale-up Synthesis of 3aa. *α*-Diazo esters **3a** (1.0 mmol, 294 mg), *α* halohydroxamate **2a** (1.1 mmol, 298 mg), K_2CO_3 (1.5 mmol, 207 mg) and $Rh_2(OAc)_4$ (0.05 mmol, 22 mg) were subjected to above-described procedure to afford **3aa** in 68% (312 mg) yield.

Synthesis of 5.[3] To a stirred solution of ethyl -2-(benzyloxy)-1-(4-bromophenyl)-4,4-dimethyl-3-oxo-1,2,3,4-tetrahydro-5H-1,5-epoxybenzo[*c*]azepine-5-carboxylate **3fa** (0.1 mmol, 53 mg) and phenylacetylene (0.3 mmol, 30 mg) in DMF (2 mL), CuBr (0.005 mmol, 1 mg), DIPEA (0.3 mmol, 38 mg) and $Pd(PPh_3)_2Cl_2$ (0.01 mmol, 7 mg) were added and the reaction mixture was allowed to stir at 100 ºC for 12 h under N_2 atm. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with ethyl acetate (5 mL) and washed

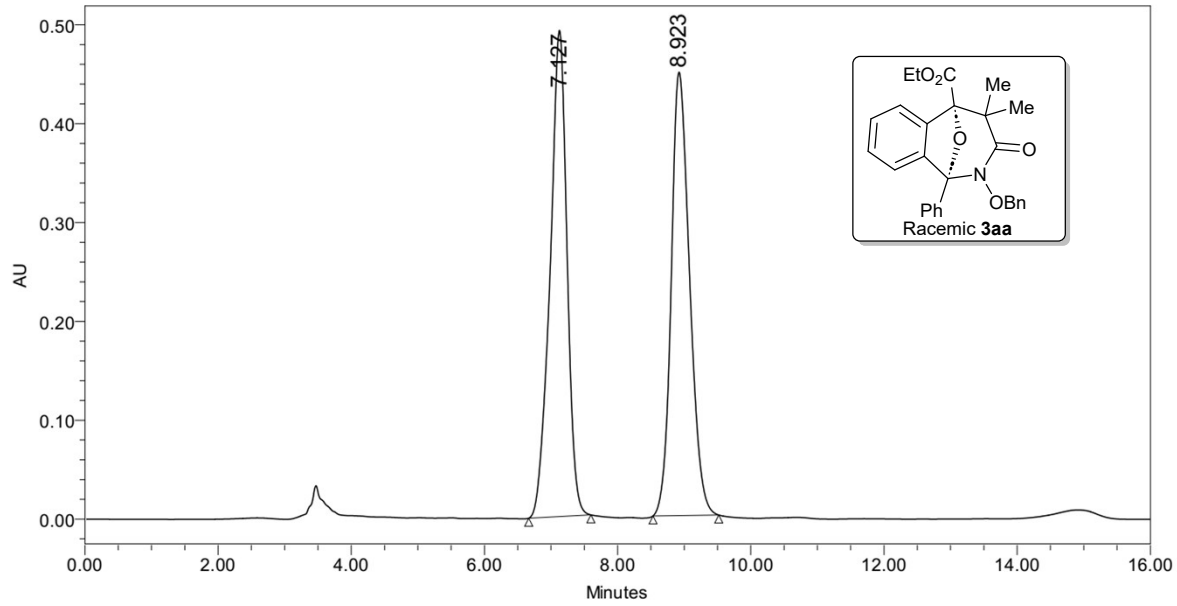
with water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on a silica gel column chromatography using ethyl acetate and hexane as eluent to afford **5** in 85% (48 mg) yield.

Synthesis of 6.[4] To a stirred solution of ethyl -2-(benzyloxy)-1-(4-bromophenyl)-4,4-dimethyl-3-oxo-1,2,3,4-tetrahydro-5H-1,5-epoxybenzo[*c*]azepine-5-carboxylate **3fa** (0.1 mmol, 53 mg) and phenyl boronic acid (0.11 mmol, 14 mg) in 1,4 dioxane (2 ml), K_2CO_3 (0.2 mmol, 27 mg), $Pd(PPh_3)_4$ (0.005 mmol, 5 mg) and H_2O (0.2 mL) were added and the reaction mixture was allowed to stir at 90 ºC for 8 h under N_2 atm. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with ethyl acetate (5 mL) and washed with water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on a silica gel column chromatography using ethyl acetate and hexane as eluent to afford **6** in 82% (43 mg) yield.

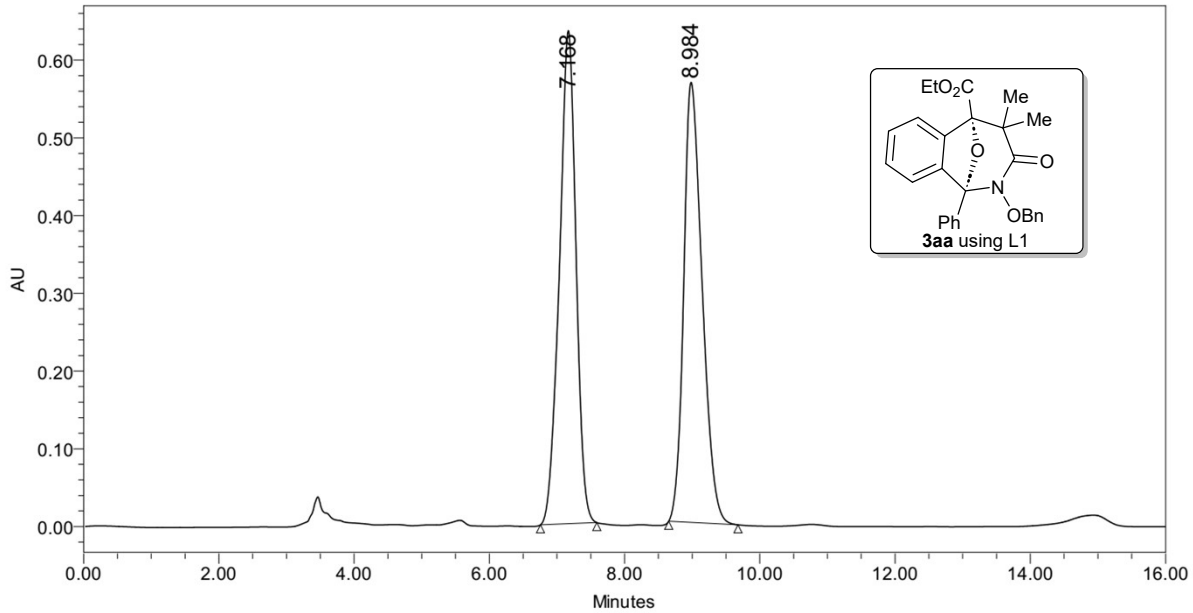
Synthesis of 7.[5] To a stirred solution of ethyl 2-(benzyloxy)-4,4-dimethyl-3-oxo-1-phenyl-1,2,3,4-tetrahydro-5H-1,5-epoxybenzo[*c*]azepine-5-carboxylate **3aa** (0.1 mmol, 45 mg) in THF (2 mL) at 0 ºC, $LiBH_4$ (0.5 mmol, 11 mg) was added. The resulting reaction mixture was allowed warm up to room temperature and continued the stirring for 5 h under N_2 atm. After completion (monitored by TLC), the reaction was quenched by saturated NH_4Cl (5 mL) and extracted with ethyl acetate (2 x 5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on a silica gel column chromatography using ethyl acetate and hexane as eluent to afford **7** in 79% (33 mg) yield.

Synthesis of 8.[6] To a stirred solution of ethyl 2-(benzyloxy)-4,4-dimethyl-3-oxo-1-phenyl-1,2,3,4-tetrahydro-5H-1,5-epoxybenzo[*c*]azepine-5-carboxylate **3aa** (0.1 mmol, 45 mg) in CH_3CN: H_2O (9:1, 2 mL), $Mo(CO)_6$ (0.12 mmol, 32 mg) was added. The resulting mixture was then stirred at 90 ºC for 6 h. After completion (monitored by TLC), the reaction mixture diluted with ethyl acetate (5 mL) and passed through a short bed of celite. The solvent was evaporated and the residue was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to afford **8** in 75% (26 mg) yield.

HPLC Chromatogram:



	RT	Area	% Area	Height
1	7.127	8661704	50.22	491654
2	8.923	8584170	49.78	448483



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1	7.168	10796391	50.15	634207
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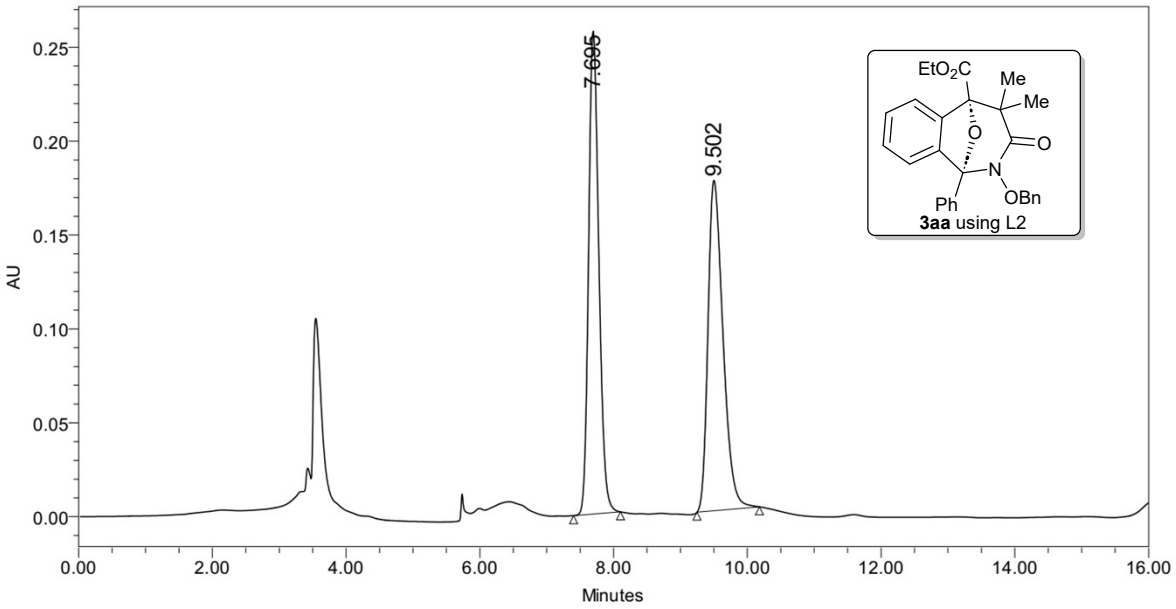

	RT	Area	% Area	Height
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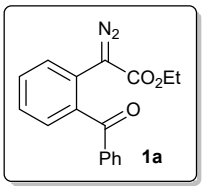
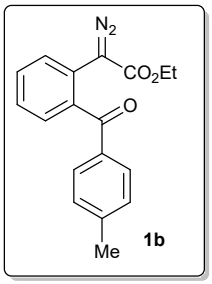
2	9.502	2744964	50.11	175989

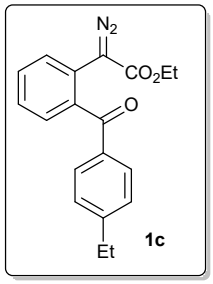
Characterization Data of the *α*-Diazo esters



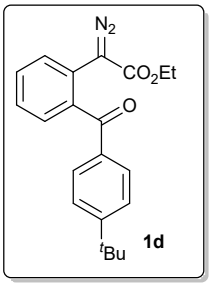
Ethyl 2-(2-benzoylphenyl)-2-diazoacetate 1a.[1a] Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 2H), 7.60-7.54 (m, 2H), 7.53-7.50 (m, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.42-7.38 (m, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 1.13 (t, *J* = 7.2 Hz, 3H).



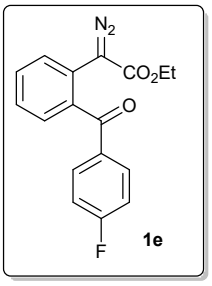
Ethyl 2-diazo-2-(2-(4-methyl-benzoyl)-phenyl)-acetate 1b.[1a] Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.55-7.48 (m, 3H), 7.40-7.36 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H).



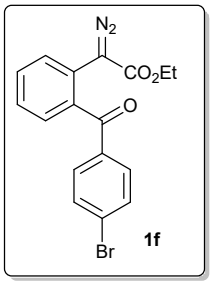
Ethyl 2-diazo-2-(2-(4-ethyl-benzoyl)-phenyl)acetate 1c. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.40; yellow viscous liquid; yield 85% (230 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.57-7.49 (m, 3H), 7.40-7.36 (m, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 165.4, 150.3, 138.0, 134.8, 131.0, 130.4, 130.2, 129.8, 128.0, 127.6, 125.1, 61.2, 29.1, 15.3, 14.4; FT-IR (neat) 2965, 2829, 2070, 1718, 1665, 1255, 1111, 1065, 1010 cm-1; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{19}H_{18}N_2NaO_3$: 345.1210, found: 345.1209.



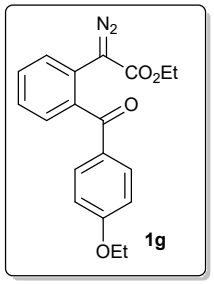
Ethyl 2-(2-(4-(*tert*-butyl)-benzoyl)-phenyl)-2-diazoacetate 1d. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; yellow viscous liquid; yield 90% (240 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.57-7.52 (m, 2H), 7.51-7.49 (m, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.40-7.36 (m, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 1.34 (s, 9H), 1.12 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.5, 165.5, 157.0, 137.9, 134.5, 131.0, 130.3, 130.1, 129.9, 127.6, 125.4, 125.1, 122.5, 61.2, 35.3, 31.2, 14.4; FT-IR (neat) 2945, 2829, 2010, 1714, 1686, 1565, 1255, 1164, 1103 cm-1; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{21}H_{22}N_2NaO_3$: 373.1523, found: 373.1520.



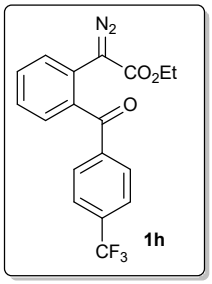
Ethyl 2-diazo-2-(2-(4-fluorobenzoyl)-phenyl)-acetate 1e.[1a] Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.82 (m, 2H), 7.58-7.54 (m, 1H), 7.50-7.47 (m, 2H), 7.41-7.37 (m, 1H), 7.12 (t, *J* = 8.4 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 3H).



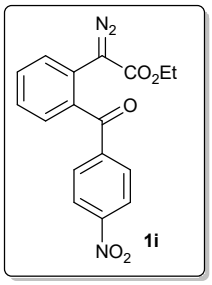
Ethyl 2-(2-(4-bromo-benzoyl)-phenyl)-2-diazoacetate 1f.[1a] Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.8 Hz, 2H), 7.60-7.55 (m, 3H), 7.49-7.46 (m, 2H), 7.41-7.37 (m, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 1.15 (t, *J* = 6.8 Hz, 3H).



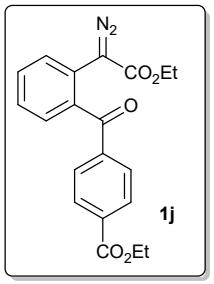
Ethyl 2-diazo-2-(2-(4-ethoxy-benzoyl)-phenyl)acetate 1g. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.40; yellow viscous liquid; yield 93% (260 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.56-7.51 (m, 2H), 7.49-7.47 (m, 1H), 7.40-7.36 (m, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.13-4.07 (m, 4H), 1.44 (t, *J* = 6.8 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.4, 165.5, 163.3, 138.2, 132.5, 130.8, 130.0, 129.9, 129.7, 127.7, 124.9, 114.2, 63.9, 61.3, 14.8, 14.5; FT-IR (KBr) 2940, 2889, 2066, 1788, 1765, 1455, 1211, 1165 cm-1; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{19}H_{18}N_2NaO_4$: 361.1159, found: 361.1159.



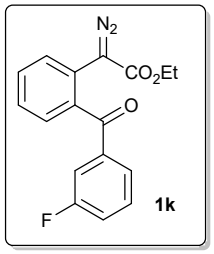
Ethyl 2-diazo-2-(2-(4-(trifluoromethyl)-benzoyl)-phenyl)-acetate 1h.[1a] Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.42-7.39 (m, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 3H).



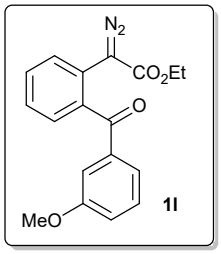
Ethyl 2-diazo-2-(2-(4-nitro-benzoyl)-phenyl)-acetate 1i.[1c] Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.63-7.59 (m, 1H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.43-7.39 (m, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 1.15 (t, *J* = 7.2 Hz, 3H).



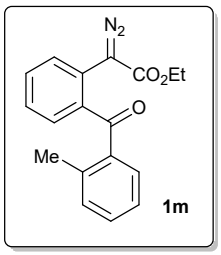
Ethyl 4-(2-(1-diazo-2-ethoxy-2-oxoethyl)-benzoyl)-benzoate 1j. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.20; yellow viscous liquid; yield 85% (240 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.60-7.56 (m, 1H), 7.51-7.47 (m, 2H), 7.42-7.38 (m, 1H), 4.42 (q, *J* = 7.2 Hz 2H), 4.08 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.0, 165.9, 165.3, 140.7, 137.1, 134.2, 131.6, 130.4, 129.9, 129.6, 129.4, 127.7, 125.4, 61.6, 61.4, 14.44, 14.40; FT-IR (neat) 2982, 2940, 2089, 1716, 1672, 1271, 1103, 1024 cm-1; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{20}H_{18}N_2NaO_5$: 389.1108, found: 389.1103.



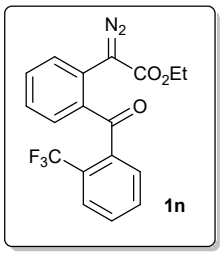
Ethyl 2-diazo-2-(2-(3-fluoro-benzoyl)-phenyl)-acetate 1k.[1d] Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.54 (m, 2H), 7.52-7.48 (m, 2H), 7.45-7.38 (m, 3H), 7.30-7.27 (m, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 1.15 (t, *J* = 7.2 Hz, 3H).



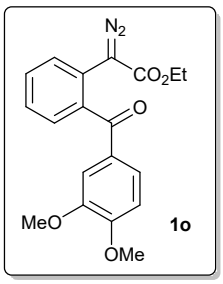
Ethyl 2-diazo-2-(2-(3-methoxy-benzoyl)-phenyl)-acetate 1l.[1b] Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.42 (m, 3H), 7.34-7.28 (m, 3H), 7.24-7.23 (m, 1H), 7.06-7.03 (m, 1H), 4.04 (q, *J* = 6.8 Hz, 2H), 3.76 (s, 3H), 1.06 (t, *J* = 6.8 Hz, 3H).



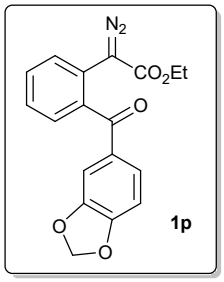
Ethyl 2-diazo-2-(2-(2-methyl-benzoyl)-phenyl)-acetate 1m. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.40; yellow viscous liquid; yield 78% (180 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.49 (m, 3H), 7.39-7.34 (m, 3H), 7.22-7.18 (m, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.48 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.4, 165.5, 139.2, 138.4, 137.5, 131.71, 131.70, 131.6, 131.4, 130.9, 130.3, 128.0, 125.6, 125.4, 61.2, 20.8, 14.5; FT-IR (neat) 2983, 2925, 2088, 1696, 1664, 1294, 1177, 762 cm-1; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{18}H_{16}N_2NaO_3$: 331.1053, found: 331.1041.



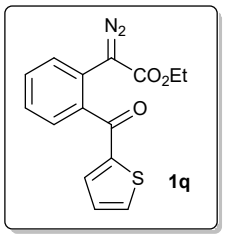
Ethyl 2-diazo-2-(2-(2-(trifluoromethyl)-benzoyl)-phenyl)-acetate 1n. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.30; yellow viscous liquid; yield 81% (210 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.77 (m, 1H), 7.62-7.57 (m, 4H), 7.56-7.52 (m, 1H), 7.39-7.37 (m, 1H), 7.33-7.29 (m, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.5, 165.7, 138.8, 135.3, 133.0, 132.8, 131.6, 131.0, 130.5, 129.6, 128.8 (J_{C-F} = 32.1 Hz), 127.6, 126.9 (J_{C-F} = 4.8 Hz), 126.6, 124.8 (J_{C-F} = 272.2 Hz), 61.3, 14.5; FT-IR (neat) 3063, 1978, 2088, 1679, 1309, 1294, 1162, 1032, 767 cm-1; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{18}H_{13}F_3N_2NaO_3$: 385.0770, found: 385.0767.



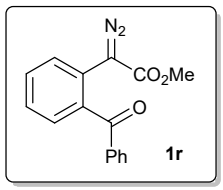
Ethyl 2-diazo-2-(2-(3,4-dimethoxy-benzoyl)-phenyl)-acetate 1o.[1a] Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.52 (m, 2H), 7.49-7.48 (m, 2H), 7.41-7.37 (m, 1H), 7.33-7.30 (m, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.94 (s, 3H), 3.92 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H).



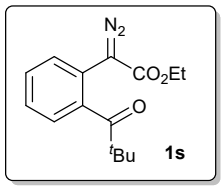
Ethyl 2-(2-(benzo[*d*][1,3] dioxole-5-carbonyl)-phenyl)-2-diazoacetate 1p.[1b] Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.51 (m, 2H), 7.47-7.45 (m, 1H), 7.40-7.36 (m, 2H), 7.33-7.31 (m, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.05 (s, 2H), 4.12 (q, J = 7.2 Hz, 2H), 1.17 (t, J = 7.2 Hz, 3H).



Ethyl 2-diazo-2-(2-(thiophene-2-carbonyl)-phenyl)-acetate 1q.[1a] Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.70 (m, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.55-7.54 (m, 2H), 7.50-7.49 (m, 1H), 7.41-7.37 (m, 1H), 7.12-7.10 (m, 1H), 4.14 (q, J = 6.8 Hz, 2H), 1.15 (t, J = 6.8 Hz, 3H).

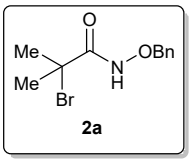


Methyl 2-(2-benzoyl-phenyl)-2-diazoacetate 1r.[1b] Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.2 Hz, 2H), 7.59-7.54 (m, 2H), 7.51-7.49 (m, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.41-7.37 (m, 1H), 3.59 (s, 3H).

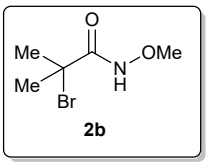


Ethyl 2-diazo-2-(2-pivaloylphenyl)acetate 1s.[1a] Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.42 (m, 1H), 7.36-7.29 (m, 3H), 4.27 (q, J = 7.2 Hz, 2H), 1.29-1.23 (m, 12H).

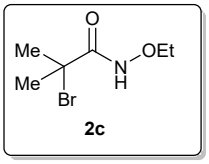
Characterization Data of the *α*-halo-hydroxamate:



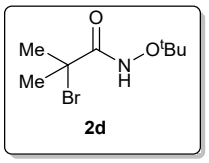
***N*-(benzyloxy)-2-bromo-2-methyl-propanamide 2a.**[2a] Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (bs, 1H), 7.43-7.38 (m, 5H), 4.94 (s, 2H), 1.93 (s, 6H).



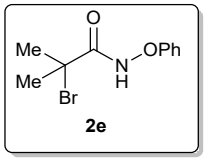
2-Bromo-*N*-methoxy-2-methyl-propanamide 2b.[2b] Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (bs, 1H), 3.79 (s, 3H), 1.96 (s, 6H).



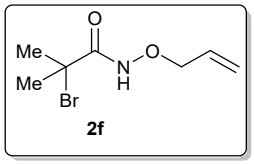
2-Bromo-*N*-ethoxy-2-methyl-propanamide 2c.[2b] Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (bs, 1H), 4.00 (q, J = 7.2 Hz, 2H), 1.96 (s, 6H), 1.29 (t, J = 6.8 Hz, 3H).



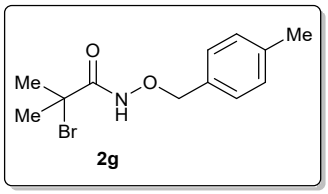
2-Bromo-*N*-(*tert*-butoxy)-2-methyl-propanamide 2d.[2c] Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (bs, 1H), 1.98 (s, 6H), 1.30 (s, 9H).



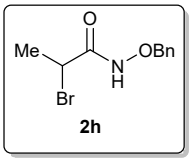
2-Bromo-2-methyl-*N*-phenoxy-propanamide 2e.[2d] Grey solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, J = 7.6 Hz, 2H), 7.09-7.05 (m, 3H), 2.05 (s, 6H).



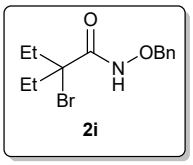
***N*-(Allyloxy)-2-bromo-2-methyl-propanamide 2f.**[2c] Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (bs, 1H), 6.04-5.94 (m, 1H), 5.40-5.35 (m, 2H), 4.41 (d, J = 6.4 Hz, 2H), 1.95 (s, 6H).



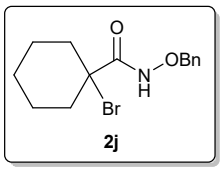
2-Bromo-2-methyl-*N*-((4-methyl-benzyl) oxy)-propenamide 2g.[2b] Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (bs, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 4.89 (s, 2H), 2.37 (s, 3H), 1.93 (s, 6H).



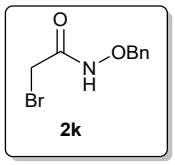
***N*-(Benzyloxy)-2-bromo-propanamide 2h.**[2a] Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (bs, 1H), 7.42-7.38 (m, 5H), 4.94 (s, 2H), 4.37-4.32 (m, 1H), 1.71 (d, J = 5.6 Hz, 3H).



***N*-(Benzyloxy)-2-bromo-2-ethylbutanamide 2i.** Analytical TLC on silica gel, 2:8 ethyl acetate/hexane R_f = 0.30; yellow oil; yield 75% (150 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (bs, 1H), 7.44-7.35 (m, 5H), 4.93 (s, 2H), 2.26-2.17 (m, 2H), 1.98-1.89 (m, 2H), 1.00 (t, J = 7.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 134.9, 129.5, 129.1, 128.8, 78.7, 76.3, 36.2, 10.4; FT-IR (neat) 3063, 1978, 2088, 1679, 1309, 1294, 1162, 1032, 767 cm-1; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{13}H_{19}BrNO_2$: 300.0594, found: 300.0590.

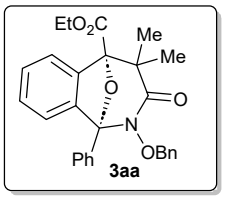


***N*-(Benzyloxy)-1-bromocyclohexane-1-carboxamide 2j.**[2b] Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (bs, 1H), 7.44-7.36 (m, 5H), 4.94 (s, 2H), 2.16-2.09 (m, 2H), 2.02-1.97 (m, 2H), 1.77-1.63 (m, 5H), 1.36-1.27 (m, 1H).

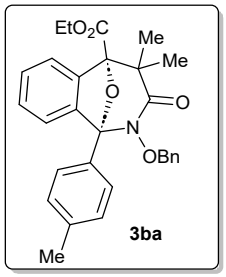


***N*-(Benzyloxy)-2-bromo-acetamide 2k.**[2a] Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (bs, 1H), 7.41 (s, 5H), 4.94 (s, 2H), 3.79 (s, 2H).

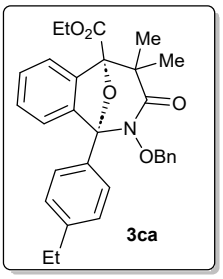
Characterization Data of Products



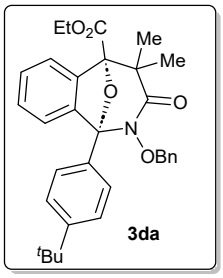
Ethyl 2-(benzyloxy)-4,4-dimethyl-3-oxo-1-phenyl-1,2,3,4-tetra-hydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3aa. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.40; colorless sticky solid; yield 86% (40 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.73-7.71 (m, 1H), 7.60-7.58 (m, 1H), 7.54-7.52 (m, 3H), 7.36-7.34 (m, 2H), 7.24-7.20 (m, 3H), 7.02-7.00 (m, 2H), 4.95 (d, *J* = 8.8 Hz, 1H), 4.56 (d, *J* = 9.2 Hz, 1H), 4.44-4.32 (m, 2H), 1.66 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6, 167.4, 142.7, 139.0, 135.0, 134.3, 129.9, 129.4, 128.9, 128.6, 128.5, 128.4, 128.3, 124.8, 123.4, 98.6, 89.7, 78.1, 62.1, 52.5, 24.5, 19.9, 14.4; FT-IR (neat) 2927, 2837, 1731, 1703, 1458, 1304, 1048, 752, 699, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{28}H_{28}NO_5$: 458.1962, found: 458.1968.



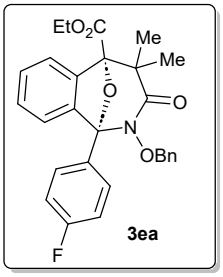
Ethyl 2-(benzyloxy)-4,4-dimethyl-3-oxo-1-(*p*-tolyl)-1,2,3,4-tetra-hydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3ba. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; colorless sticky liquid; yield 84% (40 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.72-7.70 (m, 1H), 7.58-7.56 (m, 1H), 7.34-7.30 (m, 4H), 7.25-7.18 (m, 3H), 7.05-7.03 (m, 2H), 4.94 (d, *J* = 9.2 Hz, 1H), 4.58 (d, J = 9.2 Hz, 1H), 4.44-4.27 (m, 2H), 2.43 (s, 3H), 1.65 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.5, 167.4, 142.9, 139.8, 139.1, 135.2, 131.4, 129.4, 129.2, 128.8, 128.4, 128.3, 128.2, 124.8, 123.3, 98.6, 89.6, 78.0, 62.0, 52.4, 24.5, 21.4, 19.9, 14.4; FT-IR (neat) 3030, 2985, 2936, 1737, 1704, 1460, 1214, 1048, 753, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{29}H_{30}NO_5$: 472.2118, found: 472.2112.



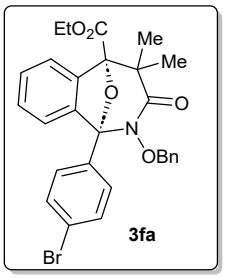
Ethyl 2-(benzyloxy)-1-(4-ethylphenyl)-4,4-dimethyl-3-oxo-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3ca. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; colorless sticky solid; yield 81% (39 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.73-7.71 (m, 1H), 7.59-7.57 (m, 1H), 7.36-7.33 (m, 4H), 7.24-7.18 (m, 3H), 7.02-6.99 (m, 2H), 4.96 (d, *J* = 9.2 Hz, 1H), 4.59 (d, *J* = 9.2 Hz, 1H), 4.45-4.29 (m, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.66 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.34 (s, 3H), 1.30 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.6, 167.4, 146.2, 142.8, 139.0, 135.2, 131.6, 129.4, 128.8, 128.5, 128.4, 128.3, 128.2, 128.0, 124.8, 123.4, 98.7, 89.6, 78.0, 62.0, 52.4, 28.9, 24.5, 19.9, 15.9, 14.4; FT-IR (neat) 2967, 2935, 2873, 1730, 1701, 1459, 1304, 1047, 752, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{30}H_{32}NO_5$: 486.2275, found: 486.2277.



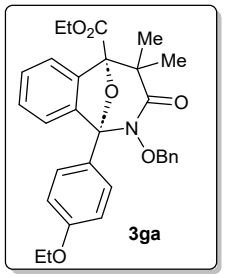
Ethyl 2-(benzyloxy)-1-(4-(*tert*-butyl)phenyl)-4,4-dimethyl-3-oxo-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3da. Analytical TLC on silica gel, 1:6.5 ethyl acetate/hexane R_f = 0.40; colorless solid; mp 163-165 ºC yield 73% (37 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.8 Hz, 2H), 7.72-7.70 (m, 1H), 7.59-7.57 (m, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.36-7.32 (m, 2H), 7.23-7.16 (m, 3H), 6.94-6.92 (m, 2H), 4.97 (d, *J* = 9.2 Hz, 1H), 4.59 (d, *J* = 9.2 Hz, 1H), 4.45-4.28 (m, 2H), 1.66 (s, 3H), 1.39-1.36 (m, 12H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6, 167.4, 153.0, 142.8, 139.1, 135.2, 131.4, 129.4, 128.8, 128.4, 128.3, 128.2, 125.5, 124.8, 123.4, 98.8, 89.6, 78.1, 62.0, 52.5, 34.9, 31.5, 24.5, 19.9, 14.4; FT-IR (neat) 2986, 2935, 2883, 1730, 1700, 1459, 1212, 1047, 748, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{32}H_{36}NO_5$: 514.2588, found: 514.2586.



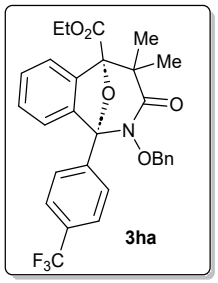
Ethyl 2-(benzyloxy)-1-(4-fluorophenyl)-4,4-dimethyl-3-oxo-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3ea. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; colorless sticky solid; yield 77% (36 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.96 (m, 2H), 7.73-7.71 (m, 1H), 7.55-7.53 (m, 1H), 7.38-7.34 (m, 2H), 7.25-7.17 (m, 5H), 7.07-7.04 (m, 2H), 4.96 (d, *J* = 9.2 Hz, 1H), 4.54 (d, *J* = 9.2 Hz, 1H), 4.46-4.30 (m, 2H), 1.64 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.6, 167.2, 164.4 ($J_{C\text{-}F}$ = 247.8 Hz), 142.5, 139.0, 135.0, 130.5 ($J_{C\text{-}F}$ = 8.4 Hz), 130.4 ($J_{C\text{-}F}$ = 3.3 Hz), 129.8, 129.3, 129.0, 128.6, 128.4, 124.9, 123.2, 115.6 ($J_{C\text{-}F}$ = 21.6 Hz), 98.1, 89.7, 78.1, 62.2, 52.5, 24.5, 19.9, 14.4; ^{19}F NMR (565 MHz, $CDCl_3$) δ -111.39; FT-IR (neat) 3065, 2985, 2931, 1732, 1706, 1513, 1305, 1230, 1049, 753, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{28}H_{27}FNO_5$: 476.1868, found: 476.1873.



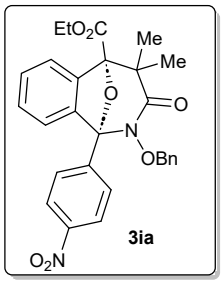
Ethyl 2-(benzyloxy)-1-(4-bromophenyl)-4,4-dimethyl-3-oxo-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3fa. Analytical TLC on silica gel, 1:6.5 ethyl acetate/hexane R_f = 0.40; yellow sticky solid; yield 82% (43 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.84 (m, 2H), 7.72-7.69 (m, 1H), 7.65-7.62 (m, 2H), 7.53-7.50 (m, 1H), 7.37-7.31 (m, 2H), 7.26-7.21 (m, 3H), 7.07-7.05 (m, 2H), 4.96 (d, *J* = 9.2 Hz, 1H), 4.55 (d, *J* = 9.2 Hz, 1H), 4.43-4.31 (m, 2H), 1.64 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.5, 167.2, 142.2, 138.9, 134.9, 133.4, 131.7, 130.1, 129.3, 129.0, 128.6, 128.5, 128.4, 124.9, 124.2, 123.1, 98.1, 89.7, 78.1, 62.1, 52.6, 24.4, 19.8, 14.4; FT-IR (neat) 2965, 2915, 1742, 1716, 1532, 1345, 1210, 1029, 780,cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{28}H_{27}BrNO_5$: 536.1067, found: 536.1061.



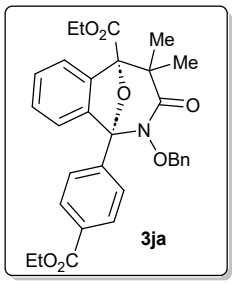
Ethyl 2-(benzyloxy)-1-(4-ethoxyphenyl)-4,4-dimethyl-3-oxo-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3ga. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; colorless sticky liquid; yield 80% (40 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.72-7.69 (m, 1H), 7.58-7.56 (m, 1H), 7.34-7.32 (m, 2H), 7.25-7.21 (m, 3H), 7.08-7.05 (m, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.94 (d, *J* = 8.8 Hz, 1H), 4.57 (d, *J* = 9.2 Hz, 1H), 4.45-4.29 (m, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 1.64 (s, 3H), 1.46 (t, *J* = 6.8 Hz, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.5, 167.5, 160.1, 142.9, 139.0, 135.2, 129.9, 129.4, 128.8, 128.4, 128.34, 128.32, 126.4, 124.8, 123.3, 114.4, 98.6, 89.5, 78.0, 63.7, 62.0, 52.4, 24.5, 19.9, 14.9, 14.4; FT-IR (neat) 2982, 2933, 1731, 1702, 1304, 1249, 1047, 754, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{30}H_{32}NO_6$: 502.2224, found: 502.2231.



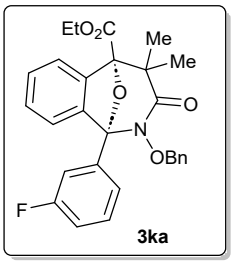
Ethyl 2-(benzyloxy)-4,4-dimethyl-3-oxo-1-(4-(trifluoro-methyl)-phenyl)-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3ha. Analytical TLC on silica gel, 1:6.5 ethyl acetate/hexane R_f = 0.50; yellow sticky liquid; yield 76% (39 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.77-7.72 (m, 3H), 7.55-7.53 (m, 1H), 7.40-7.34 (m, 2H), 7.24-7.20 (m, 3H), 7.03-7.00 (m, 2H), 4.99 (d, *J* = 9.6 Hz, 1H), 4.54 (d, *J* = 9.2 Hz, 1H), 4.46-4.30 (m, 2H), 1.66 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 167.1, 142.1, 139.0, 138.2, 134.8, 132.0 ($J_{C\text{-}F}$ = 32.5 Hz), 129.3, 129.1, 128.9, 128.8, 128.7, 128.4, 125.5 ($J_{C\text{-}F}$ = 3.6 Hz), 125.0, 124.9, 123.1, 97.8, 89.9, 78.2, 62.2, 52.7, 24.4, 19.9, 14.4; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.68.; FT-IR (neat) 2926, 2855, 1734, 1711, 1323, 1169, 1066, 753, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{29}H_{27}NF_3O_5$: 526.1836, found: 526.1841.



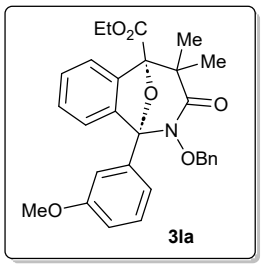
Ethyl 2-(benzyloxy)-4,4-dimethyl-1-(4-nitrophenyl)-3-oxo-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3ia. Analytical TLC on silica gel, 1:5 ethyl acetate/hexane R_f = 0.4; yellow sticky solid; yield 64% (32 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2H), 8.14 (d, *J* = 8.8 Hz, 2H), 7.75-7.73 (m, 1H), 7.54-7.52 (m, 1H), 7.40-7.37 (m, 2H), 7.25-7.21 (m, 3H), 7.07-7.05 (m, 2H), 5.00 (d, *J* = 9.6 Hz, 1H), 4.53 (d, *J* = 9.6 Hz, 1H), 4.44-4.33 (m, 2H), 1.65 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6, 166.9, 148.7, 141.8, 141.0, 138.9, 134.7, 129.5, 129.3, 129.2, 129.0, 128.7, 128.5, 125.1, 123.6, 122.9, 97.4, 90.0, 78.3, 62.3, 52.9, 24.4, 19.9, 14.4; FT-IR (neat) 3065, 2961, 2870, 1731, 1704, 1461, 1306, 1049, 755, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{28}H_{27}N_2O_7$: 503.1813, found: 5023.1810.



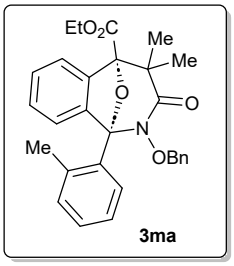
Ethyl 2-(benzyloxy)-1-(4-(ethoxycarbonyl)-phenyl)-4,4-dimethyl-3-oxo-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3ja. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.45; yellow sticky liquid; yield 77% (41 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 9.0 Hz, 2H), 8.06 (d, *J* = 9.0 Hz, 2H), 7.73-7.72 (m, 1H), 7.56-7.55 (m, 1H), 7.37-7.35 (m, 2H), 7.25-7.20 (m, 3H), 7.05-7.04 (m, 2H), 4.95 (d, *J* = 9.0 Hz, 1H), 4.53 (d, *J* = 9.0 Hz, 1H), 4.46-4.32 (m, 4H), 1.65 (s, 3H), 1.44 (t, *J* = 7.0 Hz, 3H), 1.38 (t, *J* = 7.0 Hz, 3H), 1.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6, 167.2, 166.3, 142.3, 139.0, 138.9, 134.9, 131.8, 129.7, 129.4, 129.0, 128.7, 128.6, 128.5, 128.4, 124.9, 123.2, 98.0, 89.8, 78.1, 62.1, 61.4, 52.7, 24.5, 19.9, 14.5, 14.4. FT-IR (neat) 3005, 2951, 2850, 1732, 1715, 1431, 1356, 1055, 754, 715 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{31}H_{32}NO_7$: 530.2173, found: 530.2165.



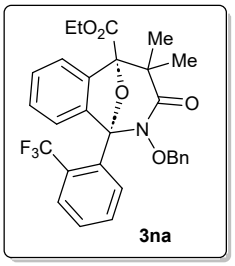
Ethyl 2-(benzyloxy)-1-(3-fluorophenyl)-4,4-dimethyl-3-oxo-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3ka. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.40; colorless sticky liquid; yield 82% (39 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.77 (m, 1H), 7.73-7.69 (m, 2H), 7.56-7.54 (m, 1H), 7.52-7.46 (m, 1H), 7.38-7.33 (m, 2H), 7.25-7.18 (m, 4H), 7.08-7.05 (m, 2H), 4.98 (d, *J* = 9.2 Hz, 1H), 4.56 (d, *J* = 9.2 Hz, 1H), 4.46-4.30 (m, 2H), 1.65 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6, 167.2, 163.8 ($J_{C\text{-}F}$ = 244.7 Hz), 142.2, 139.0, 136.9 ($J_{C\text{-}F}$ = 7.3 Hz), 134.9, 130.2 ($J_{C\text{-}F}$ = 7.8 Hz), 129.4, 129.0, 128.7, 128.6, 128.4, 124.9, 124.1 ($J_{C\text{-}F}$ = 3.0 Hz), 123.1, 116.9 ($J_{C\text{-}F}$ = 20.8 Hz), 115.9 ($J_{C\text{-}F}$ = 23.2 Hz), 97.8 ($J_{C\text{-}F}$ = 2.2 Hz), 89.8, 78.2, 62.1, 52.6, 24.4, 19.9, 14.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ -111.95; FT-IR (neat)2987, 2935, 1731, 1704, 1305, 1217, 1049, 750, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{28}H_{27}FNO_5$: 476.1868, found: 476.1866.



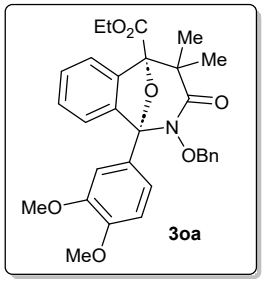
Ethyl 2-(benzyloxy)-1-(3-methoxyphenyl)-4,4-dimethyl-3-oxo-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3la. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.40; colorless sticky solid; yield 78% (38 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.70 (m, 1H), 7.60-7.58 (m, 2H), 7.55-7.54 (m, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.35-7.32 (m, 2H), 7.24-7.20 (m, 3H), 7.06-7.03 (m, 3H), 4.98 (d, *J* = 8.8 Hz, 1H), 4.61 (d, *J* = 9.2 Hz, 1H), 4.45-4.29 (m, 2H), 3.86 (s, 3H), 1.65 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6, 167.4, 159.7, 142.6, 139.0, 135.8, 135.1, 129.6, 129.4, 128.9, 128.5, 128.3, 124.8, 123.3, 120.8, 115.1, 114.6, 98.5, 89.6, 78.1, 62.0, 55.5, 52.5, 24.5, 19.9, 14.4; FT-IR (neat)3065, 2932, 1731, 1702, 1460, 1305, 1046, 751, cm^{-1}HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{29}H_{30}NO_6$: 488.2068, found: 488.2064.



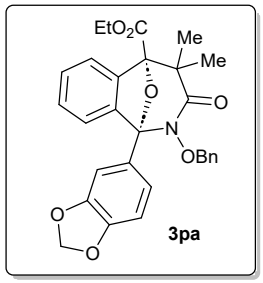
Ethyl 2-(benzyloxy)-4,4-dimethyl-3-oxo-1-(*o*-tolyl)-1,2,3,4-tetra-hydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3ma. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; colorless sticky liquid; yield 75% (35 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.75-7.73 (m, 1H), 7.69-7.67 (m, 1H), 7.44-7.40 (m, 1H), 7.37-7.35 (m, 3H), 7.31-7.27 (m, 1H), 7.22-7.16 (m, 3H), 6.91-6.89 (m, 2H), 4.92 (d, *J* = 9.2 Hz, 1H), 4.50 (d, *J* = 8.8 Hz, 1H), 4.44-4.30 (m, 2H), 2.85 (s, 3H), 1.66 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.0, 167.4, 143.1, 139.5, 138.3, 135.1, 133.1, 132.0, 130.0, 129.4, 129.3, 128.8, 128.4, 128.3, 128.2, 125.5, 124.8, 124.5, 99.8, 89.4, 77.4, 62.0, 52.6, 23.7, 21.9, 20.0, 14.4; FT-IR (neat) 2986, 2935, 1731, 1699, 1459, 1302, 1079, 1047, 752, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{29}H_{30}NO_5$: 472.2118, found: 472.2120.



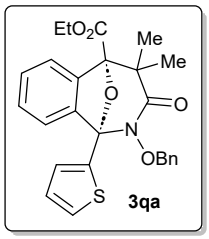
Ethyl 2-(benzyloxy)-4,4-dimethyl-3-oxo-1-(2-(trifluoromethyl)-phenyl)-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3na. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; colorless sticky liquid; yield 66% (34 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43-8.41 (m, 1H), 7.98-7.96 (m, 1H), 7.75-7.73 (m, 1H), 7.68-7.64 (m, 3H), 7.36-7.34 (m, 2H), 7.23-7.18 (m, 3H), 6.99-6.96 (m, 2H), 4.94 (d, *J* = 9.6 Hz, 1H), 4.45-4.26 (m, 3H), 1.64 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.4, 167.2, 143.6, 138.1, 135.1, 131.4, 131.2, 130.5 ($J_{C\text{-}F}$ = 32.5 Hz), 130.1, 129.4 ($J_{C\text{-}F}$ = 6.7 Hz), 129.2, 128.8, 128.7 ($J_{C\text{-}F}$ = 66.6 Hz), 128.5, 128.4, 128.3, 125.1 ($J_{C\text{-}F}$ = 272.9 Hz), 124.8, 123.9, 98.1, 89.8, 77.8, 62.0, 52.7, 23.6, 20.3, 14.2; ^{19}F NMR (470 MHz, $CDCl_3$) δ -54.16; FT-IR (neat) 2988, 2933, 1733, 1699, 1460, 1302, 1158, 1043, 752, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{29}H_{27}NF_3O_5$: 526.1836, found: 526.1840.



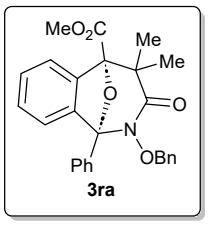
Ethyl 2-(benzyloxy)-1-(3,4-dimethoxyphenyl)-4,4-dimethyl-3-oxo -1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3oa. Analytical TLC on silica gel, 1:6.5 ethyl acetate/hexane R_f = 0.50; colorless sticky liquid; yield 63% (32 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.70 (m, 1H), 7.57-7.52 (m, 2H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.37-7.32 (m, 3H), 7.24-7.21 (m, 2H), 7.08-7.05 (m, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 4.99 (d, *J* = 9.2 Hz, 1H), 4.63 (d, *J* = 9.2 Hz, 1H), 4.45-4.29 (m, 2H), 3.95 (s, 3H), 3.91 (s, 3H), 1.65 (s, 3H), 1.38 (t, *J* = 6.8 Hz, 3H), 1.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.6, 167.4, 150.2, 148.9, 142.9, 139.0, 135.2, 129.2, 128.9, 128.5, 128.4, 128.3, 127.4, 124.9, 123.2, 121.4, 111.6, 110.8, 98.7, 89.6, 78.0, 62.1, 56.2, 56.1, 52.4, 24.5, 19.9, 14.4; FT-IR (neat) 2931, 2850, 1732, 1703, 1517, 1461, 1271, 1231, 1024, 755, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{30}H_{32}NO_7$: 518.2173, found: 518.2182.



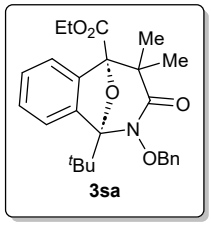
Ethyl 1-(benzo[*d*][1,3]dioxol-5-yl)-2-(benzyloxy)-4,4-dimethyl-3-oxo-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3pa. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.60; yellow sticky solid; yield 80% (40 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.69 (m, 1H), 7.56-7.54 (m, 1H), 7.48-7.45 (m, 2H), 7.34-7.32 (m, 2H), 7.25-7.23 (m, 3H), 7.11-7.09 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.03-6.02 (m, 2H), 4.97 (d, *J* = 9.2 Hz, 1H), 4.64 (d, *J* = 9.2 Hz, 1H), 4.43-4.30 (m, 2H), 1.63 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 167.3, 148.8, 147.9, 142.5, 139.0, 135.2, 129.5, 129.3, 128.9, 128.4, 128.3, 128.2, 124.8, 123.3, 122.5, 109.1, 108.1, 101.6, 98.6, 89.5, 78.0, 62.1, 52.4, 24.4, 19.8, 14.4; FT-IR (neat) 1986, 1958, 1731, 1701, 1442, 1232, 1041, 753, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{29}H_{28}NO_7$: 502.1860, found: 502.1852.



Ethyl 2-(benzyloxy)-4,4-dimethyl-3-oxo-1-(thiophen-2-yl)-1,2,3,4-tetra-hydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3qa. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.60; yellow sticky solid; yield 81% (38 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.68 (m, 1H), 7.63-7.60 (m, 2H), 7.51-7.50 (m, 1H), 7.34-7.32 (m, 2H), 7.26-7.24 (m, 3H), 7.16-7.11 (m, 3H), 4.99 (d, *J* = 9.2 Hz, 1H), 4.70 (d, *J* = 9.2 Hz, 1H), 4.45-4.29 (m, 2H), 1.64 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.2, 167.1, 142.9, 138.4, 137.2, 135.1, 129.4, 129.0, 128.7, 128.6, 128.5, 128.3, 127.6, 127.0, 124.7, 122.6, 96.4, 89.9, 78.4, 62.1, 52.6, 24.4, 19.8, 14.4; FT-IR (neat) 2986, 2940, 1730, 1704, 1294, 1044, 750, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{26}NO_5S$: 464.1526, found: 464.1523.

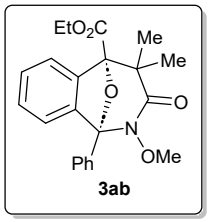


Methyl 2-(benzyloxy)-4,4-dimethyl-3-oxo-1-phenyl-1,2,3,4-tetra-hydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3ra. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.40; colorless solid; mp 148-149 ^{o}C yield 83% (37 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.74-7.72 (m, 1H), 7.60-7.58 (m, 1H), 7.54-7.52 (m, 3H), 7.36-7.34 (m, 2H), 7.23-7.19 (m, 3H), 7.02-7.00 (m, 2H), 4.98 (d, *J* = 9.2 Hz, 1H), 4.58 (d, *J* = 9.2 Hz, 1H), 3.87 (s, 3H), 1.66 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6, 168.0, 142.4, 139.0, 135.1, 134.3, 129.9, 129.3, 128.9, 128.6, 128.5, 128.4, 128.3, 124.8, 123.4, 98.8, 89.8, 78.0, 52.7, 52.5, 24.5, 19.7; FT-IR (neat) 3030, 2951, 1737, 1701, 1304, 1050, 751, cm^{-1} ; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{27}H_{26}NO_5$: 444.1805, found: 444.1809.



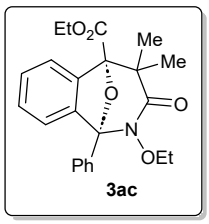
Ethyl-2-(benzyloxy)-1-(*tert*-butyl)-4,4-dimethyl-3-oxo-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3sa. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.70; colorless liquid; yield 74% (33 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ

7.63-7.60 (m, 2H), 7.45-7.43 (m, 2H), 7.35-7.30 (m, 3H), 7.29-7.26 (m, 2H), 5.05 (d, J = 9.0 Hz, 1H), 4.96 (d, J = 9.5 Hz, 1H), 4.36-4.32 (m, 2H), 1.52 (s, 3H), 1.39-1.35 (m, 12H), 1.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 167.9, 144.1, 139.3, 135.3, 129.4, 128.7, 128.54, 128.53, 128.0, 124.6, 122.3, 102.8, 88.2, 76.5, 61.7, 52.4, 37.8, 26.9, 24.2, 20.0, 14.4; FT-IR (neat) 3025, 2981, 1767, 1731, 1324, 1150, 791, cm^{-1} ; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{32}NO_5$: 438.2275, found: 438.2270.



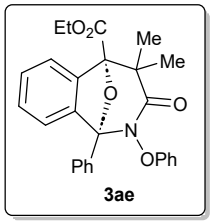
3ab

Ethyl 2-methoxy-4,4-dimethyl-3-oxo-1-phenyl-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3ab. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; yellow sticky liquid; yield 82% (31 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.90 (m, 2H), 7.74-7.72 (m, 1H), 7.61-7.59 (m, 1H), 7.50-7.48 (m, 3H), 7.40-7.37 (m, 2H), 4.44-4.28 (m, 2H), 3.63 (s, 3H), 1.62 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.9, 167.3, 142.6, 139.1, 134.3, 129.8, 128.8, 128.5, 128.4, 128.3, 124.9, 123.2, 98.9, 89.6, 63.7, 62.0, 52.4, 24.3, 19.8, 14.4; FT-IR (neat) 2986, 2937, 1730, 1701, 1459, 1302, 1211, 1046, 753, 701, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{22}H_{24}NO_5$: 382.1649, found: 382.1656.

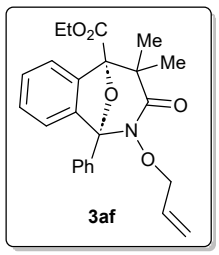


3ac

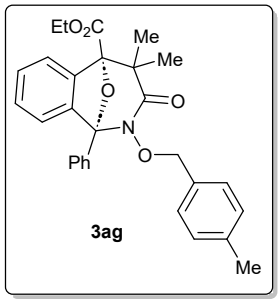
Ethyl 2-ethoxy-4,4-dimethyl-3-oxo-1-phenyl-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3ac. Analytical TLC on silica gel, 1:6.5 ethyl acetate/hexane R_f = 0.40; yellow sticky solid; yield 75% (29 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.93 (m, 2H), 7.73-7.71 (m, 1H), 7.65-7.63 (m, 1H), 7.51-7.47 (m, 3H), 7.41-7.34 (m, 2H), 4.44-4.28 (m, 2H), 4.02-3.94 (m, 1H), 3.66-3.58 (m, 1H), 1.61 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H), 1.32 (s, 3H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.3, 167.4, 143.0, 139.0, 134.4, 129.7, 128.8, 128.4, 128.2, 124.8, 123.1, 98.4, 89.6, 71.9, 62.0, 52.3, 24.4, 19.9, 14.4, 13.4; FT-IR (neat) 2983, 2935, 1730, 1700, 1460, 1213, 1045, 752, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{23}H_{26}NO_5$: 396.1805, found: 396.1804.



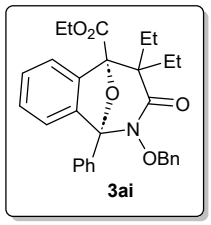
Ethyl 4,4-dimethyl-3-oxo-2-phenoxy-1-phenyl-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3ae. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.40; colorless sticky liquid; yield 81% (36 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.78 (m, 1H), 7.68-7.65 (m, 3H), 7.50-7.42 (m, 2H), 7.34-7.29 (m, 1H), 7.27-7.23 (m, 2H), 7.21-7.17 (m, 2H), 6.97-6.93 (m, 1H), 6.84-6.82 (m, 2H), 4.47-4.31 (m, 2H), 1.74 (s, 3H), 1.41-1.37 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 167.1, 159.3, 142.7, 139.2, 133.3, 129.8, 129.2, 129.1, 128.8, 128.4, 128.3, 124.8, 123.7, 122.5, 114.0, 100.5, 89.9, 62.2, 53.4, 24.3, 19.8, 14.4; FT-IR (neat) 2987, 2935, 1788, 1722, 1303, 1213, 1049, 752, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{27}H_{26}NO_5$: 444.1805, found: 444.1809.



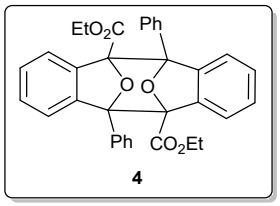
Ethyl 2-(allyloxy)-4,4-dimethyl-3-oxo-1-phenyl-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3af. Analytical TLC on silica gel, 1:6.5 ethyl acetate/hexane R_f = 0.30; colorless sticky liquid; yield 68% (28 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2H), 7.73-7.71 (m, 1H), 7.65-7.63 (m, 1H), 7.50-7.48 (m, 3H), 7.40-7.36 (m, 2H), 5.74-5.64 (m, 1H), 5.10-5.09 (m, 1H), 5.07-5.05 (m, 1H), 4.42-4.30 (m, 3H), 4.12-4.08 (m, 1H), 1.61 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 167.4, 142.8, 139.0, 134.3, 132.1, 131.4, 129.8, 128.9, 128.5, 128.3, 124.9, 123.2, 119.6, 98.6, 89.6, 77.4, 62.1, 52.5, 24.4, 19.9, 14.4; FT-IR (neat) 2988, 2927, 2855, 1732, 1705, 1463, 1304, 1049, 760, 703, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{24}H_{26}NO_5$: 408.1805, found: 408.1809.



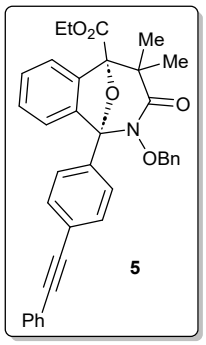
Ethyl 4,4-dimethyl-2-((4-methylbenzyl)oxy)-3-oxo-1-phenyl-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3ag. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.50; colorless sticky solid; yield 78% (36 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.99 (m, 2H), 7.72-7.70 (m, 1H), 7.59-7.57 (m, 1H), 7.53-7.51 (m, 3H), 7.34-7.32 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 4.91 (d, *J* = 9.2 Hz, 1H), 4.50 (d, *J* = 8.8 Hz, 1H), 4.42-4.31 (m, 2H), 2.28 (s, 3H), 1.65 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 167.4, 142.8, 139.1, 138.3, 134.4, 132.1, 129.8, 129.5, 129.0, 128.8, 128.5, 128.47, 128.40, 124.8, 123.4, 98.5, 89.7, 77.9, 62.0, 52.5, 24.5, 21.4, 19.9, 14.4; FT-IR (neat) 2985, 2928, 1731, 1704, 1462, 1304, 1049, 758, 702, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{29}H_{30}NO_5$: 472.2118, found: 472.2116.



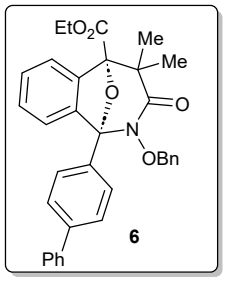
Ethyl-2-(benzyloxy)-4,4-diethyl-3-oxo-1-phenyl-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 3ai. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.70; colorless liquid; yield 70% (34 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99-7.97 (m, 2H), 7.79-7.77 (m, 1H), 7.59-7.57 (m, 1H), 7.52-7.50 (m, 3H), 7.34-7.33 (m, 2H), 7.23-7.19 (m, 3H), 7.00 (d, *J* = 6.5 Hz, 2H), 4.95 (d, *J* = 9.5 Hz, 1H), 4.55 (d, *J* = 9.0 Hz, 1H), 4.44-4.37 (m, 1H), 4.28-4.22 (m, 1H), 2.32-2.25 (m, 1H), 2.12-2.05 (m, 1H), 1.87 (q, *J* = 7.5 Hz, 2H), 1.37 (t, *J* = 7.5 Hz, 3H), 1.15 (t, *J* = 7.5 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.2, 167.9, 143.2, 139.8, 135.2, 134.6, 129.3, 128.6, 128.5, 128.45, 128.41, 128.34, 128.30, 128.2, 125.6, 123.3, 98.4, 89.9, 77.9, 62.1, 59.2, 27.1, 24.1, 14.3, 10.8, 9.5; FT-IR (neat) 2943, 2935, 1770, 1710, 1450, 1203, 1015, 782, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{30}H_{32}NO_5$: 486.2275, found: 486.2268.



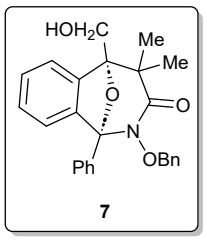
Diethyl 6,12-diphenyl-5,12:6,11-diepoxy-dibenzo-[*a,e*][8]-annulene-5,11(6*H*,12*H*)-dicarboxylate 4. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.30; colorless liquid; yield 58% (30 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.5 Hz, 6H), 7.70-7.67 (m, 2H), 7.65-7.60 (m, 6H), 7.50 (t, *J* = 7.5 Hz, 4H), 4.19 (q, *J* = 7.0 Hz, 4H), 1.22 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.6, , 186.9, 161.6, 140.1, 136.9, 136.8, 133.4, 131.91, 131.88, 130.9, 130.3, 130.2, 128.7, 62.7, 14.0; FT-IR (neat) 2984, 2928, 1708, 1649, 1284, 1201, 1020, 752, cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{34}H_{28}NaO_6$: 550.1778, found: 550.1785.



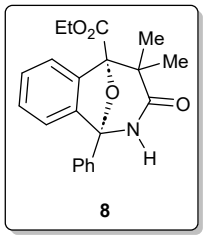
Ethyl 2-(benzyloxy)-4,4-dimethyl-3-oxo-1-(4-(phenylethynyl)-phenyl)-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 5. Analytical TLC on silica gel, 1:6.5 ethyl acetate/hexane R_f = 0.30; yellow sticky liquid; yield 85% (48 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.74-7.71 (m, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.59-7.56 (m, 3H), 7.38-7.35 (m, 5H), 7.26-7.24 (m, 3H), 7.09-7.07 (m, 2H), 4.96 (d, *J* = 9.2 Hz, 1H), 4.57 (d, *J* = 9.2 Hz, 1H), 4.46-4.31 (m, 2H), 1.66 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.5, 167.3, 142.5, 139.0, 135.0, 134.2, 131.9, 131.7, 129.4, 129.0, 128.7, 128.6, 128.5, 128.4, 124.94, 124.90, 123.2, 123.1, 98.2, 90.8, 89.8, 89.0, 78.2, 62.1, 52.6, 24.5, 19.9, 14.4; FT-IR (neat) 2985, 2927, 2855, 1732, 1705, 1304, 1048, 754, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{36}H_{32}NO_5$: 558.2275, found: 558.2279.



Ethyl 1-([1,1'-biphenyl]-4-yl)-2-(benzyloxy)-4,4-dimethyl-3-oxo-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 6. Analytical TLC on silica gel, 1:6.5 ethyl acetate/hexane R_f = 0.40; colorless sticky solid; yield 82% (43 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 3H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.64-7.62 (m, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.43-7.41 (m, 1H), 7.38-7.36 (m, 2H), 7.24-7.20 (m, 3H), 7.07-7.05 (m, 2H), 5.01 (d, *J* = 9.2 Hz, 1H), 4.65 (d, *J* = 9.2 Hz, 1H), 4.47-4.31 (m, 2H), 1.69 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6, 167.4, 142.7, 140.6, 139.1, 135.1, 133.3, 129.34, 129.0, 128.90, 128.88, 128.5, 128.3, 127.9, 127.4, 127.2, 124.8, 123.3, 98.5, 89.7, 78.1, 62.1, 52.5, 24.5, 19.9, 14.4; FT-IR (neat) 2986, 2940, 1730, 1700, 1304, 1048, 750, 697, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{34}H_{32}NO_5$: 534.2275, found: 534.2269.



2-(Benzyloxy)-5-(hydroxymethyl)-4,4-dimethyl-1-phenyl-1,2,4,5-tetra-hydro-3*H*-1,5-epoxybenzo[*c*]azepin-3-one 7. Analytical TLC on silica gel, 2:8 ethyl acetate/hexane R_f = 0.30; colorless sticky liquid; yield 79% (33 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99-7.97 (m, 2H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.55-7.53 (m, 3H), 7.38-7.31 (m, 3H), 7.23-7.18 (m, 3H), 6.99-6.98 (m, 2H), 4.96 (d, *J* = 9.0 Hz, 1H), 4.60 (d, *J* = 9.0 Hz, 1H), 4.21 (d, *J* = 12.0 Hz, 1H), 4.14 (d, *J* = 12.6 Hz, 1H), 1.66 (s, 4H), 1.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.4, 143.7, 140.8, 135.4, 135.0, 129.9, 129.2, 128.6, 128.4, 128.34, 128.30, 128.28, 123.9, 123.5, 99.5, 90.9, 77.8, 60.2, 50.7, 23.9, 19.6; FT-IR (neat) 2975, 2917, 1762, 1356, 1148, 734, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{26}H_{26}NO_4$: 416.1856, found: 416.1850.



Ethyl-4,4-dimethyl-3-oxo-1-phenyl-1,2,3,4-tetrahydro-5*H*-1,5-epoxybenzo[*c*]azepine-5-carboxylate 8. Analytical TLC on silica gel, 2:8 ethyl acetate/hexane R_f = 0.30; colorless sticky solid; yield 75% (26 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72-7.67 (m, 3H), 7.50-7.47 (m, 3H), 7.34-7.26 (m, 2H), 7.15-7.13 (m, 1H), 7.03 (d, *J* = 7.0 Hz, 1H), 4.46-4.33 (m, 2H), 1.53 (s, 3H), 1.40 (t, *J* = 7.0 Hz, 3H), 1.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.4, 168.0, 147.6, 138.3, 135.3, 129.9, 129.0, 128.9, 128.0, 126.6, 124.7, 120.2, 92.5, 90.0, 62.0, 48.9, 24.3, 20.6, 14.4; FT-IR (neat) 2925, 2907, 1782, 1754, 1340, 1188, 788, cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{21}H_{22}NO_4$: 352.1543, found: 352.1547.

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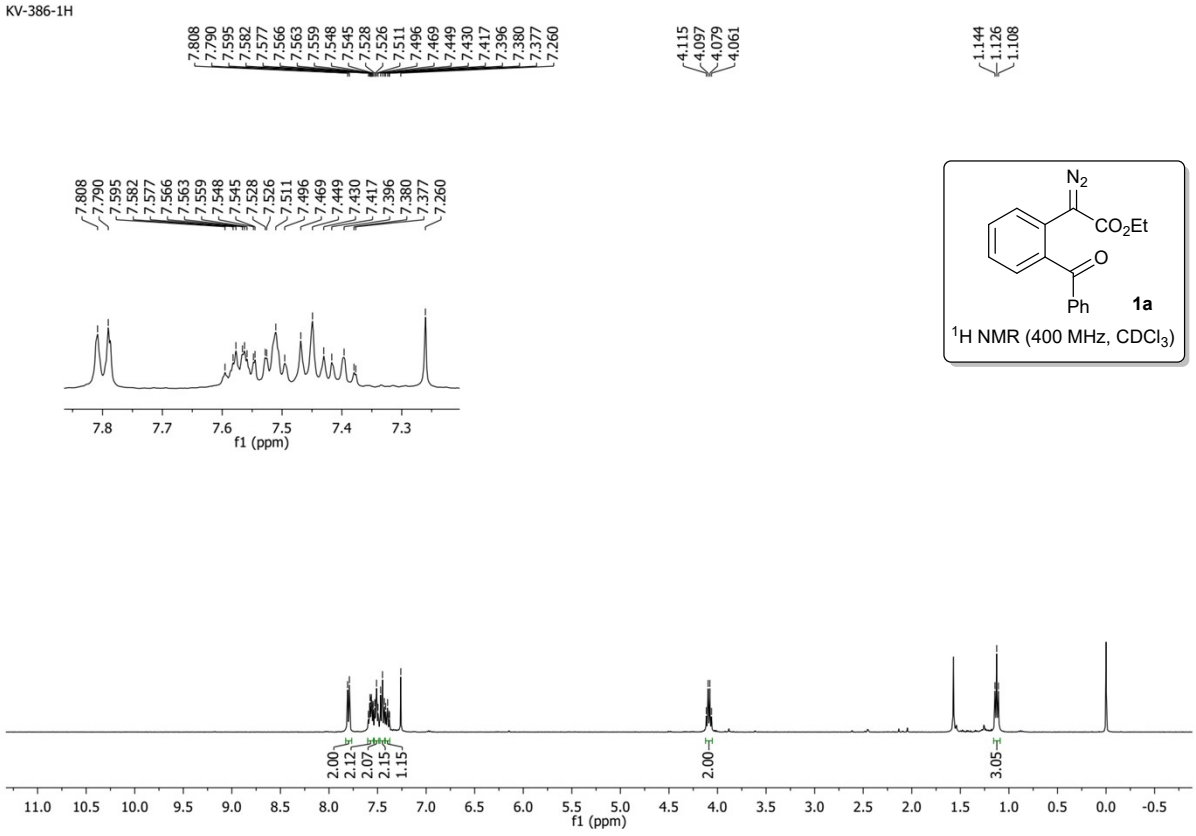
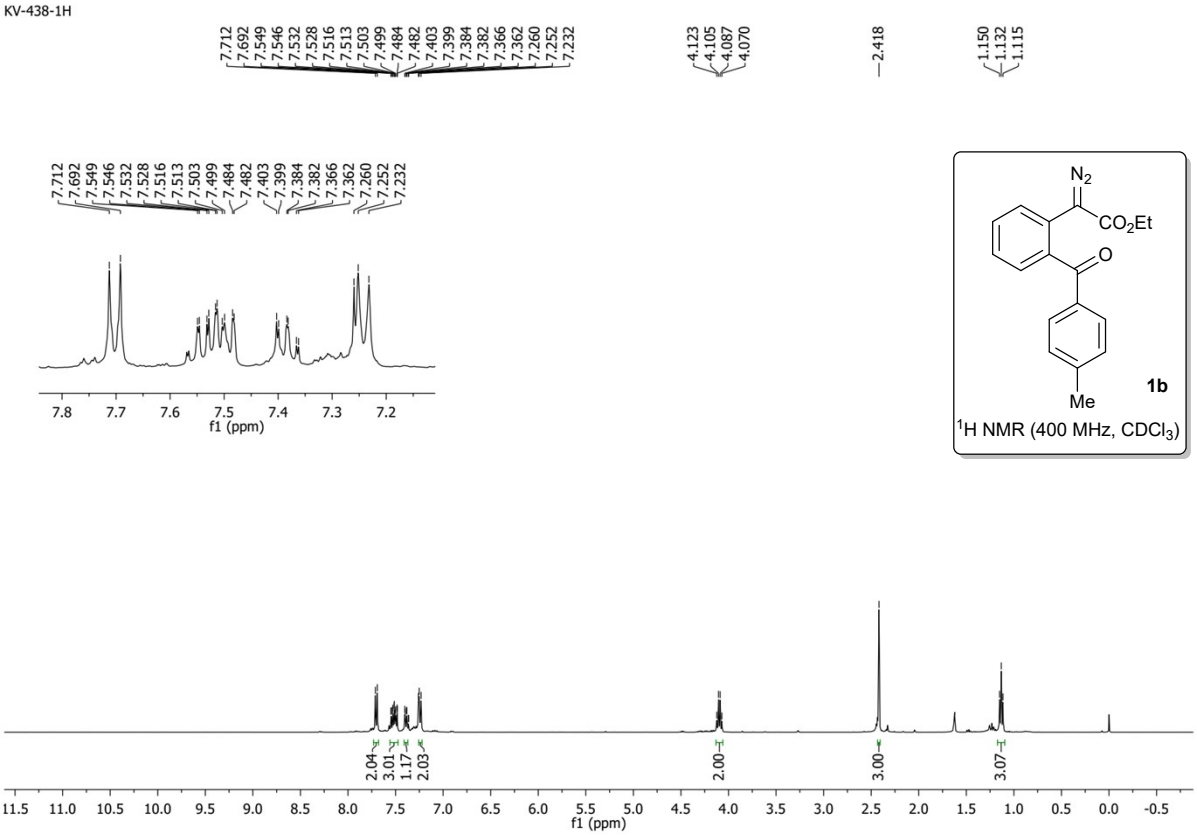
(5) H. J. Loui, A. Suneja and C. Schneider, *Org. Lett.*, 2021, **23**, 2578.

(6) M. C. DiPoto, R. P. Hughes and J. Wu, *J. Am. Chem. Soc.*, 2015, **137**, 14861.

^{1}H ,^{13}C and ^{19}F NMR spectra





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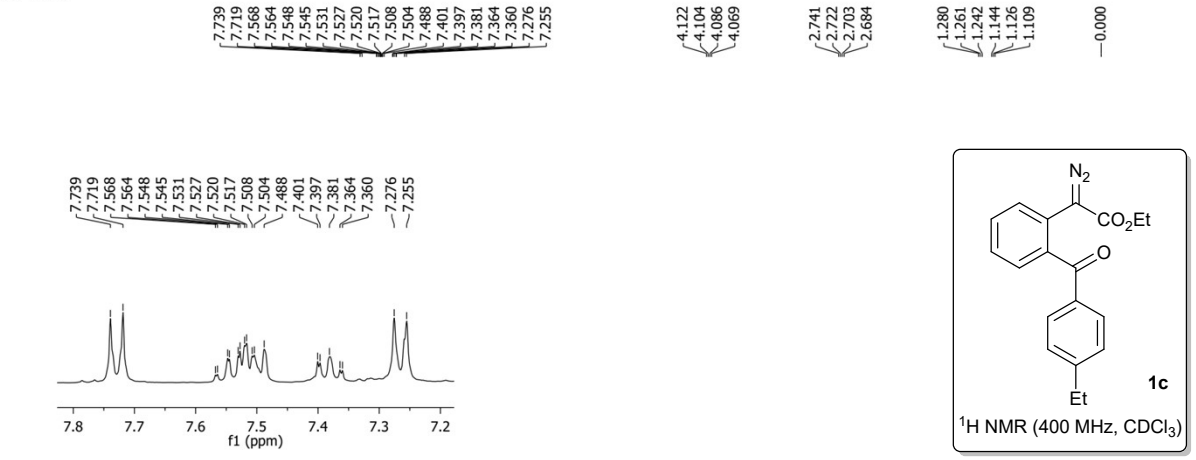
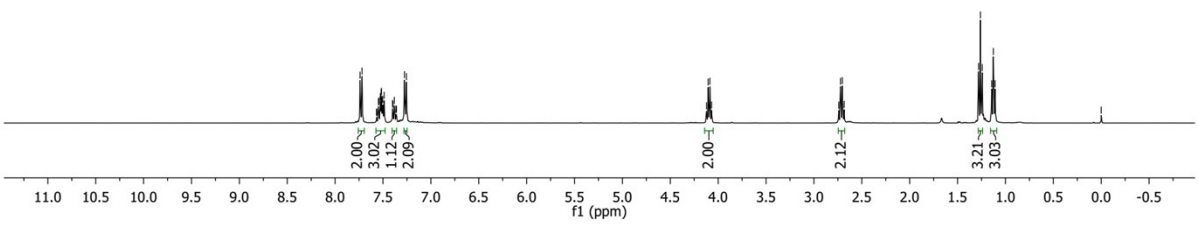
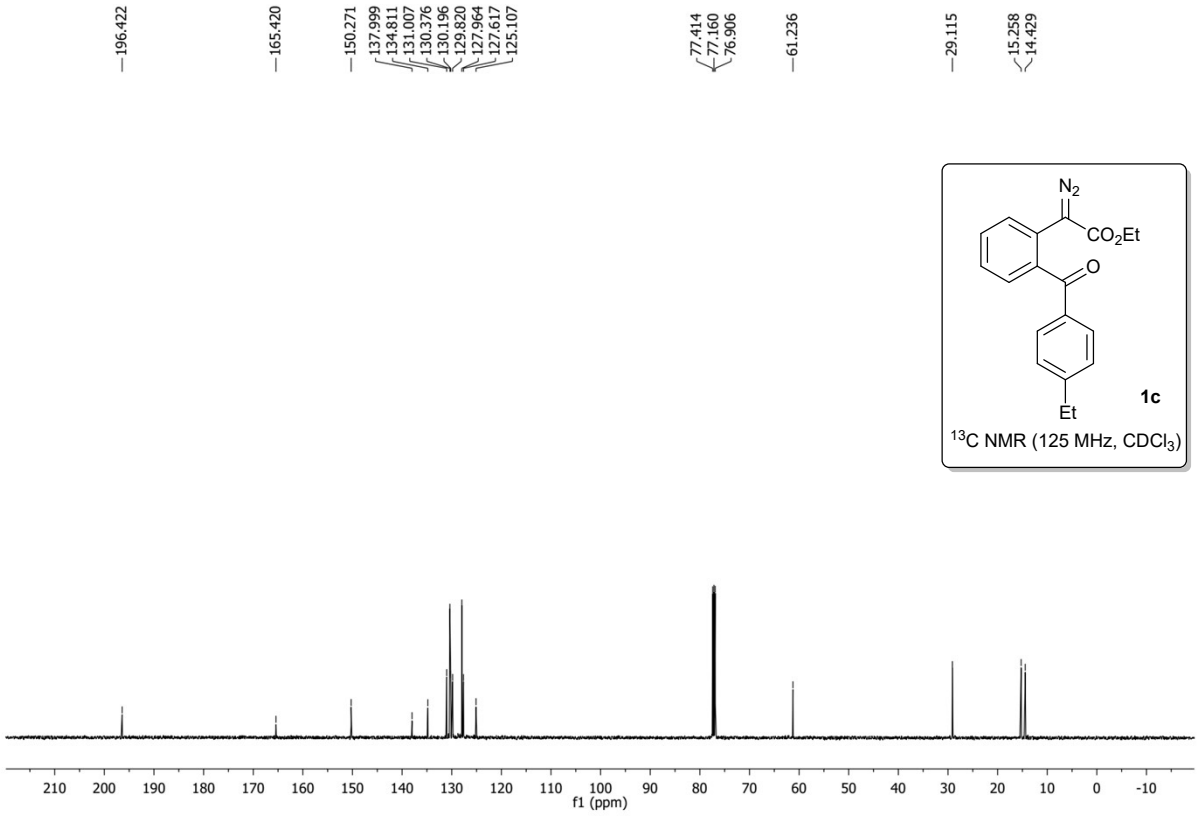




^{1}H NMR (400 MHz, $CDCl_3$)

KV-419-13C



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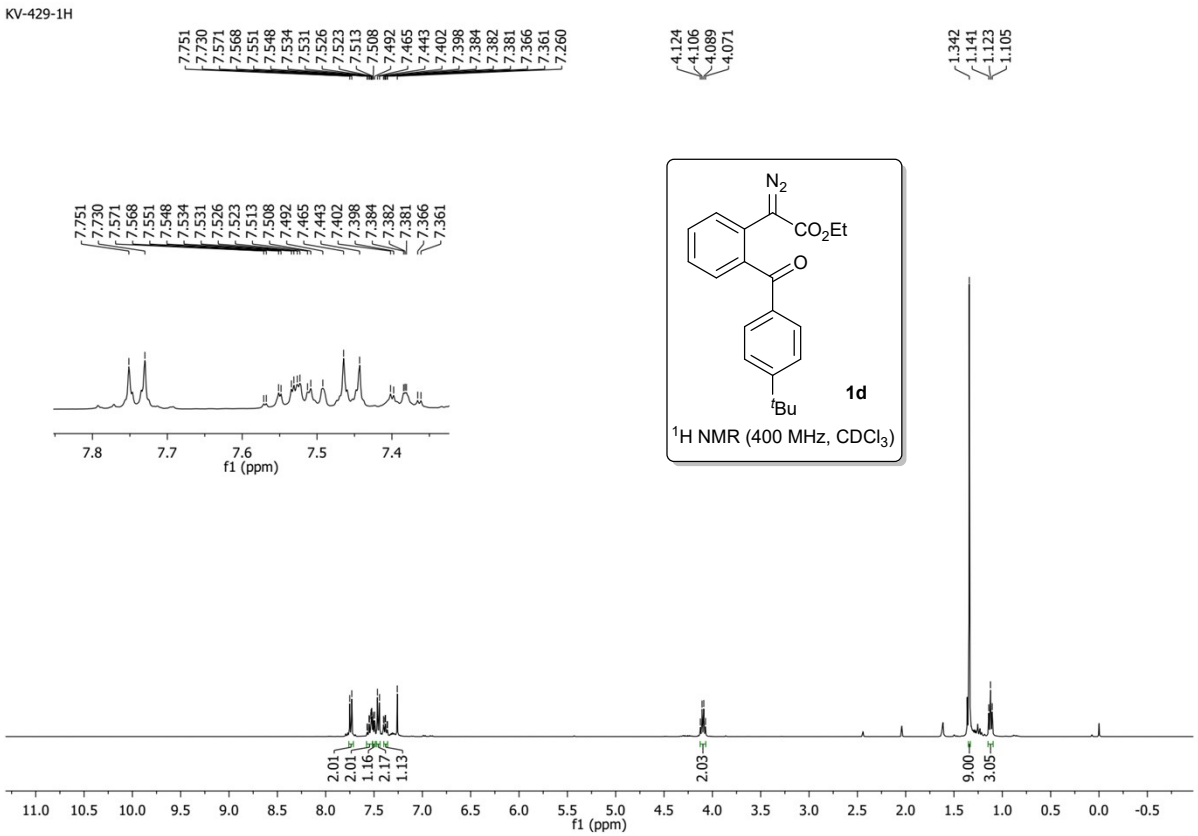

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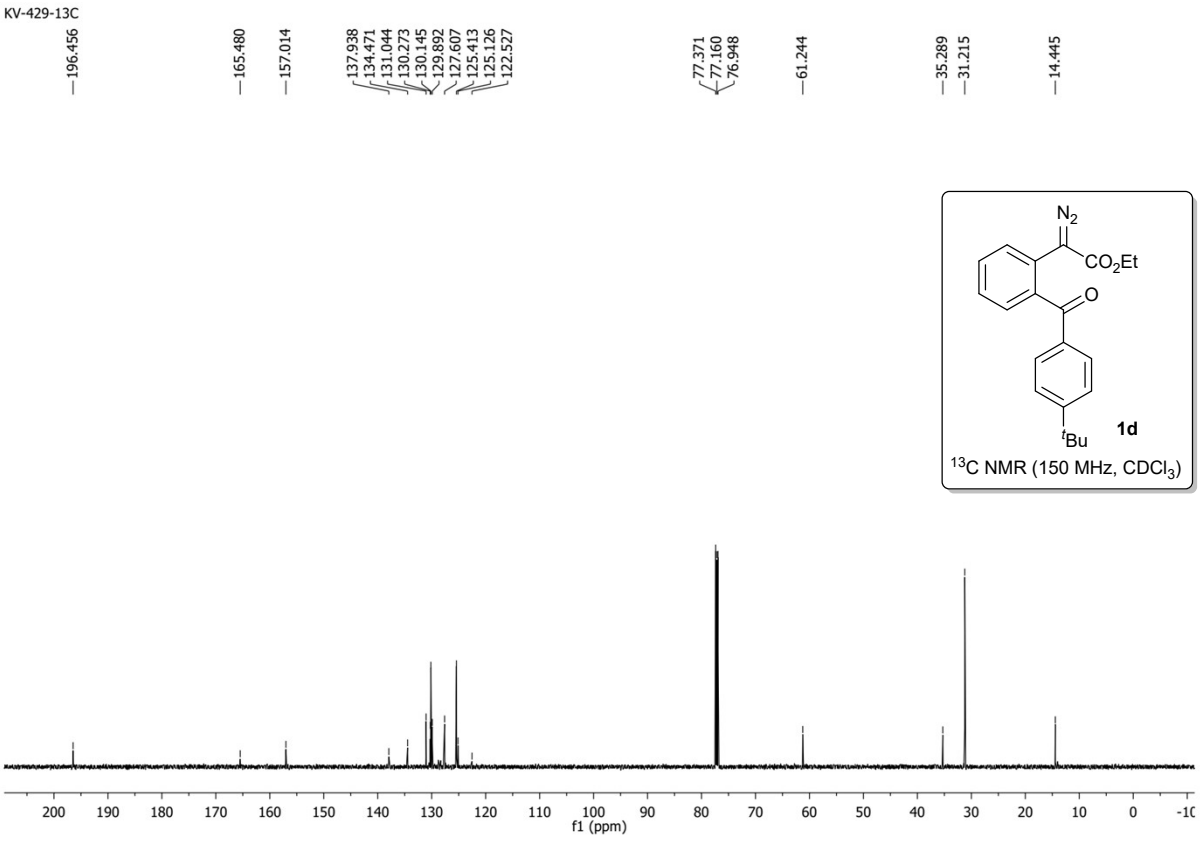

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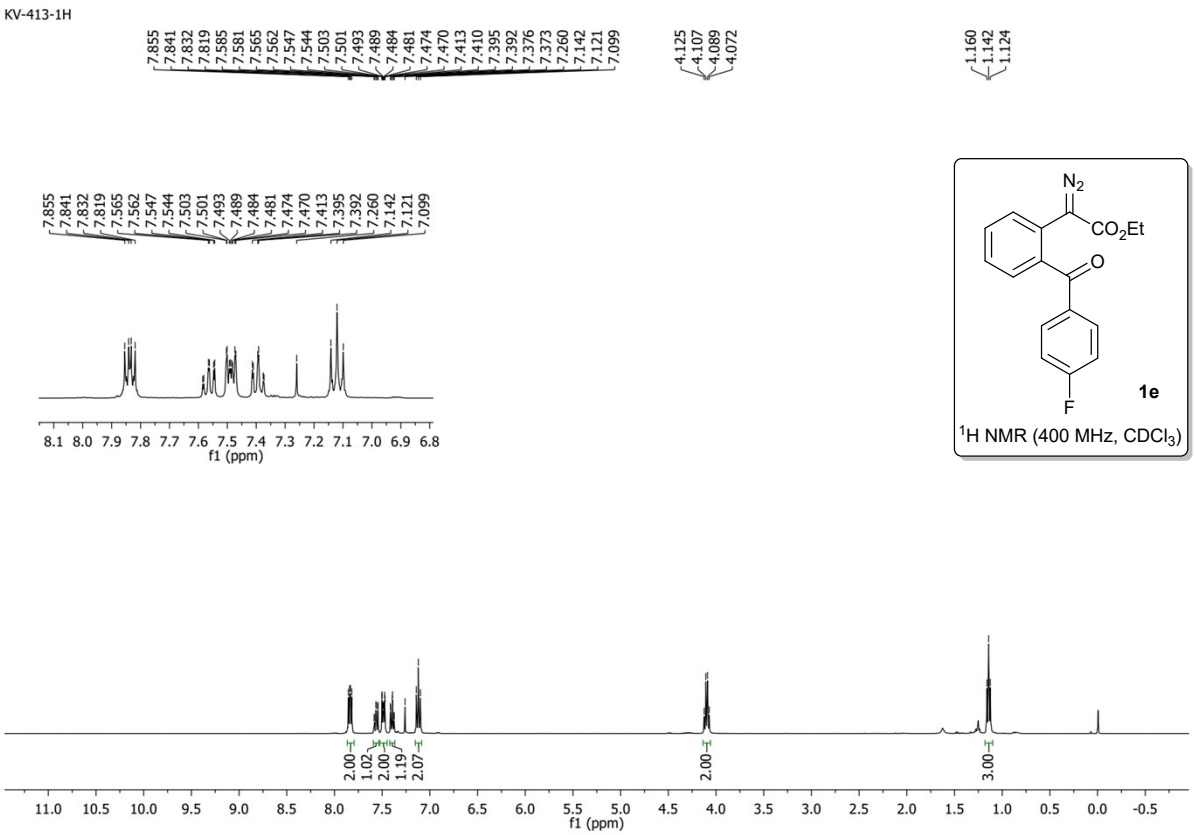

^{1}H NMR (400 MHz, $CDCl_3$)

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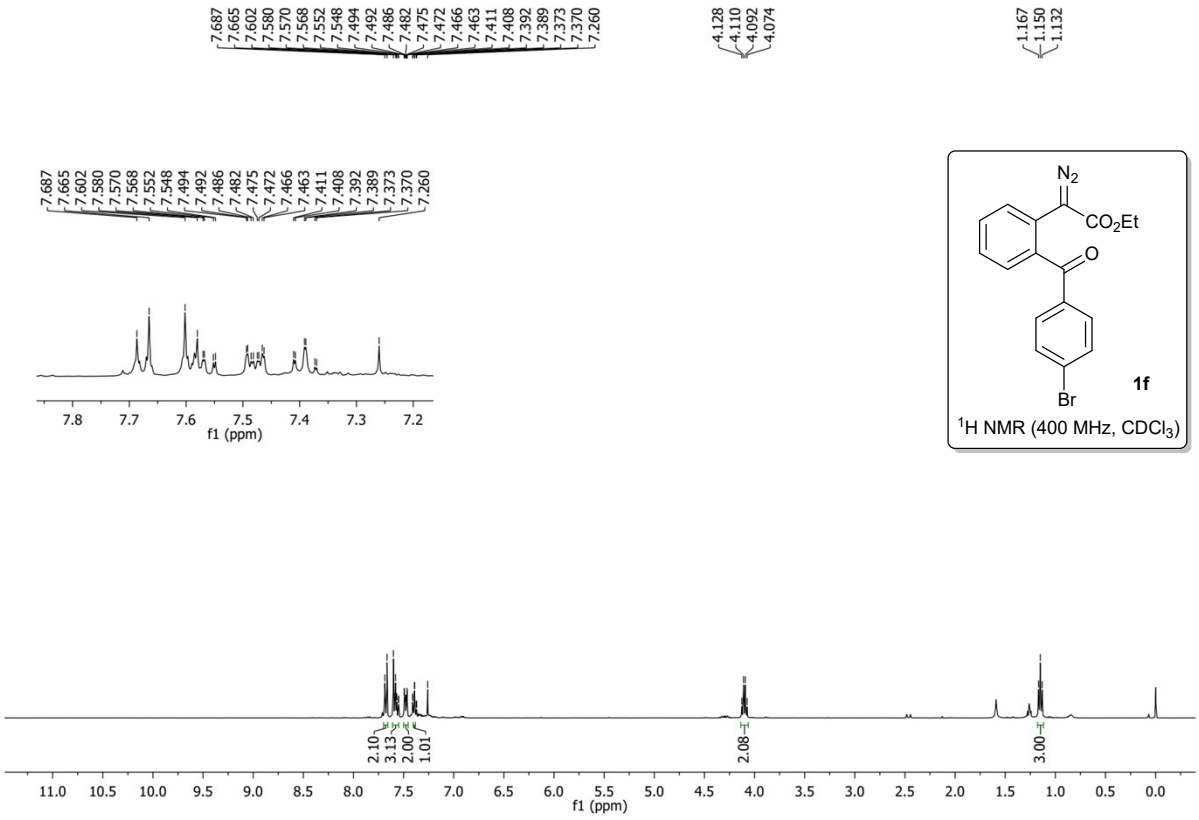

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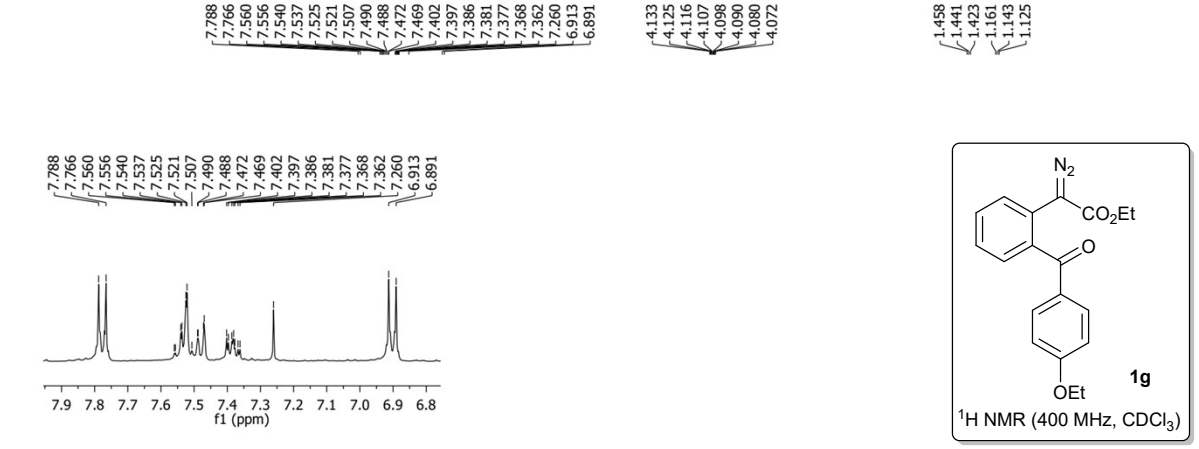

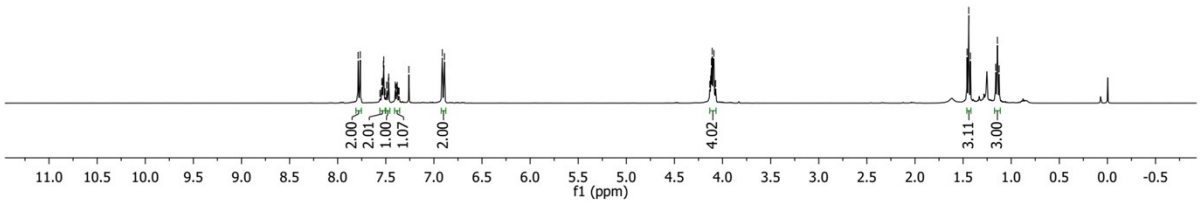

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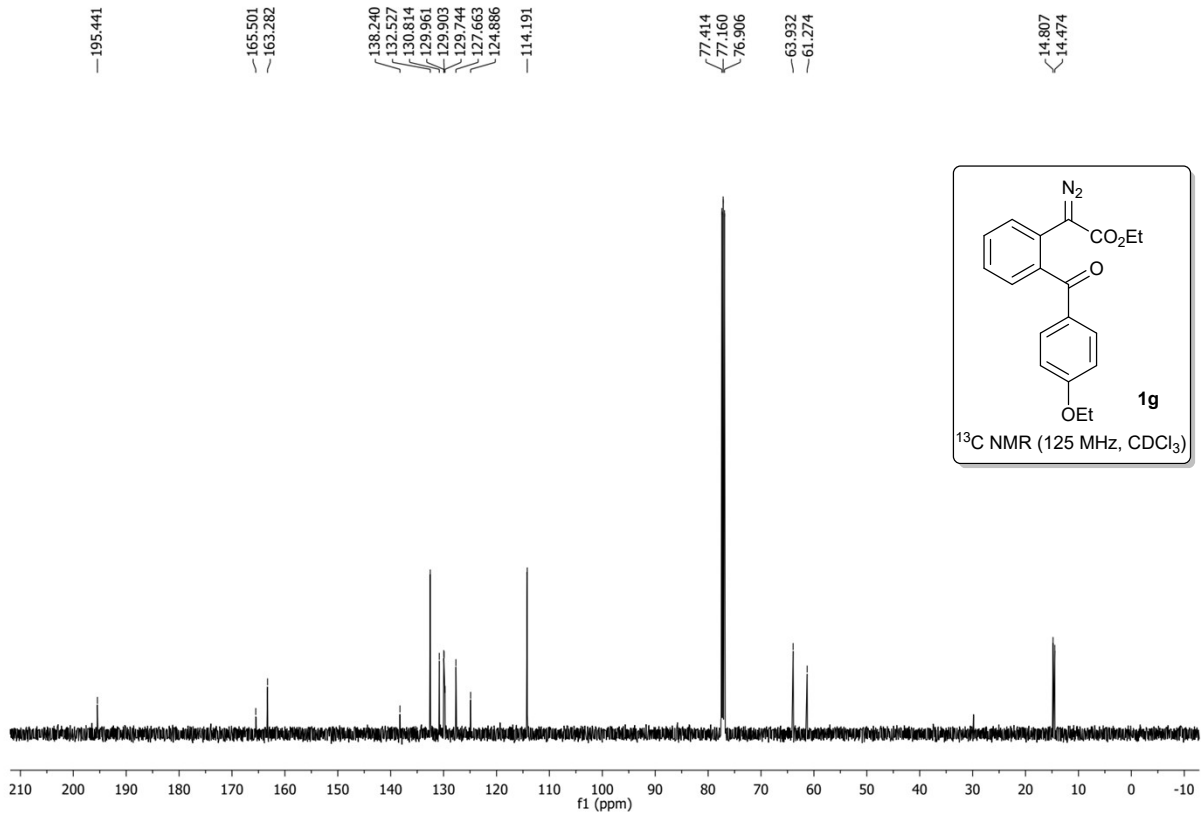

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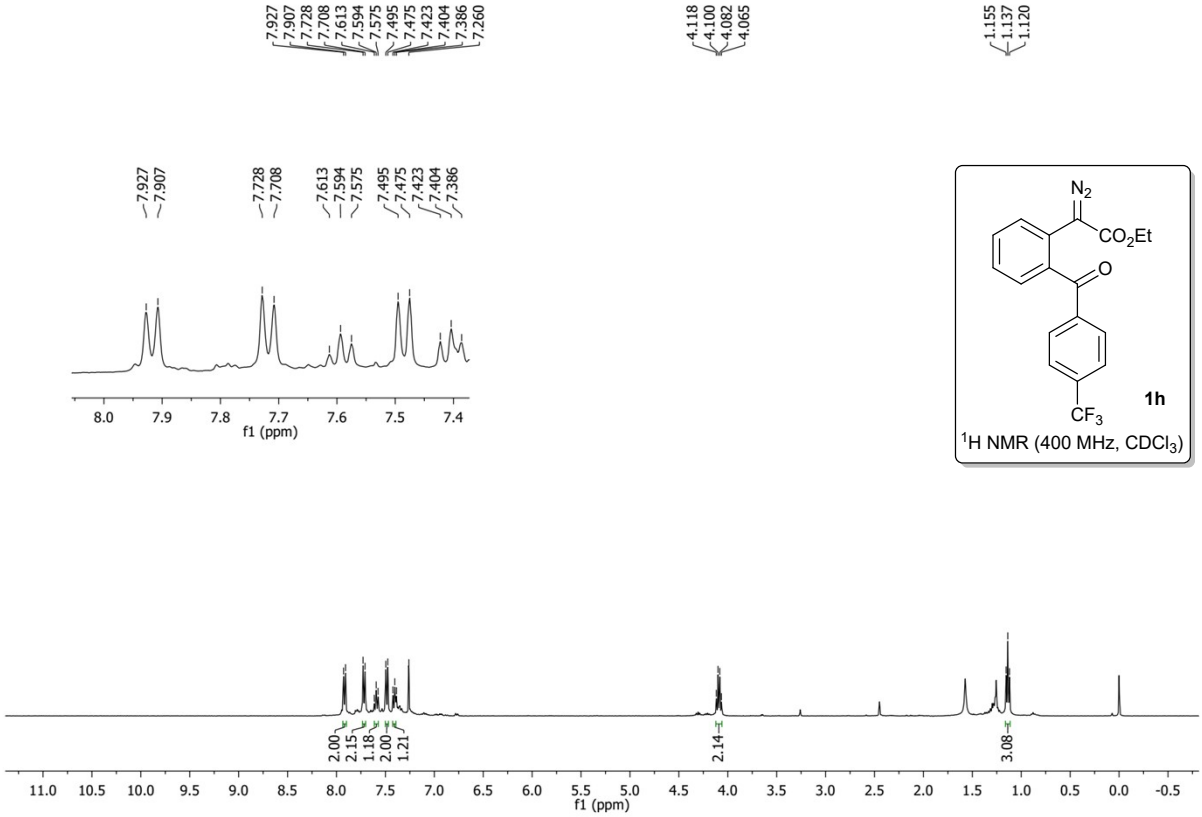

^{1}H NMR (400 MHz, $CDCl_3$)

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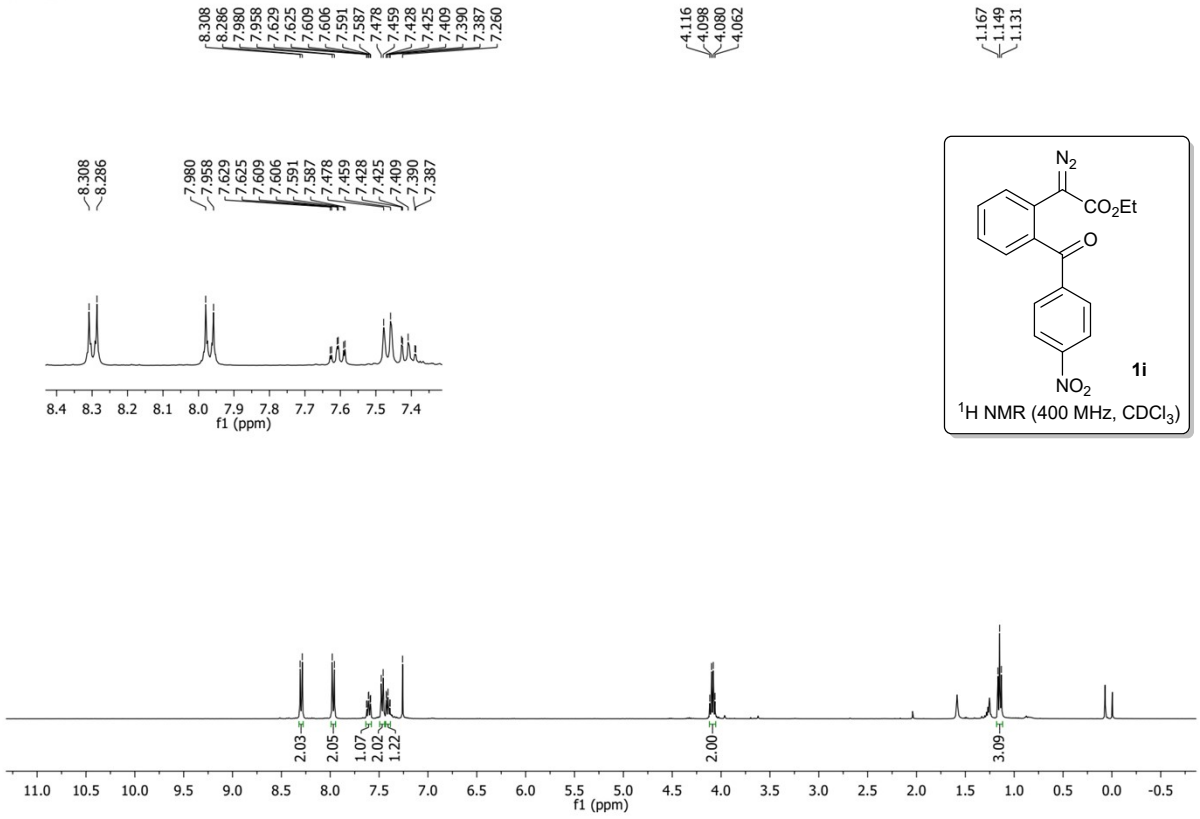
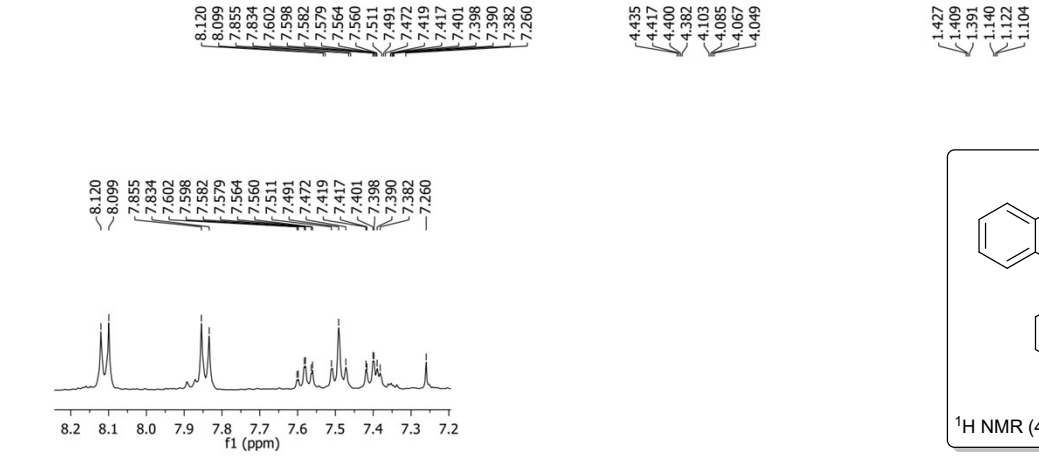
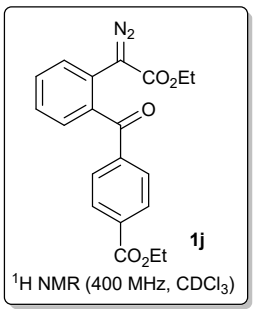


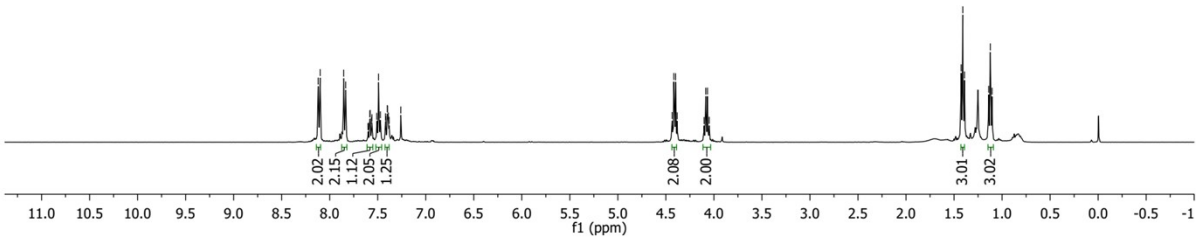
^{1}H NMR (400 MHz, $CDCl_3$)

KV-ESTER-1H





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



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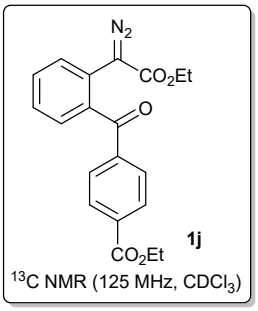
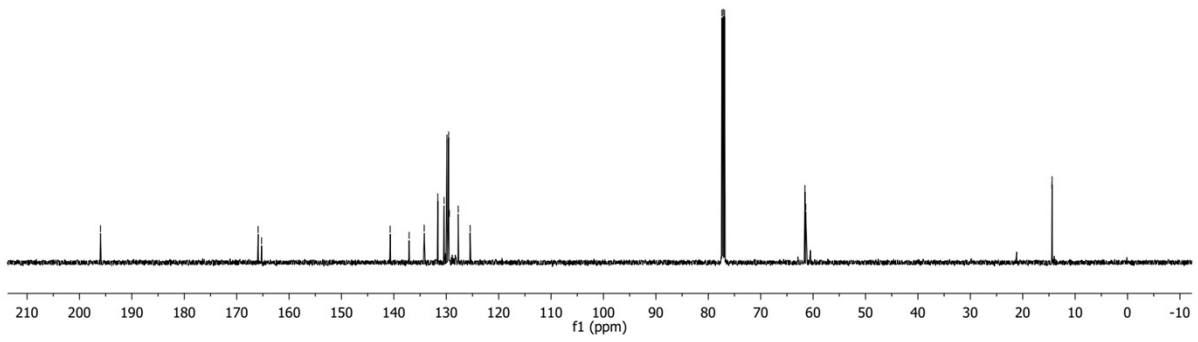
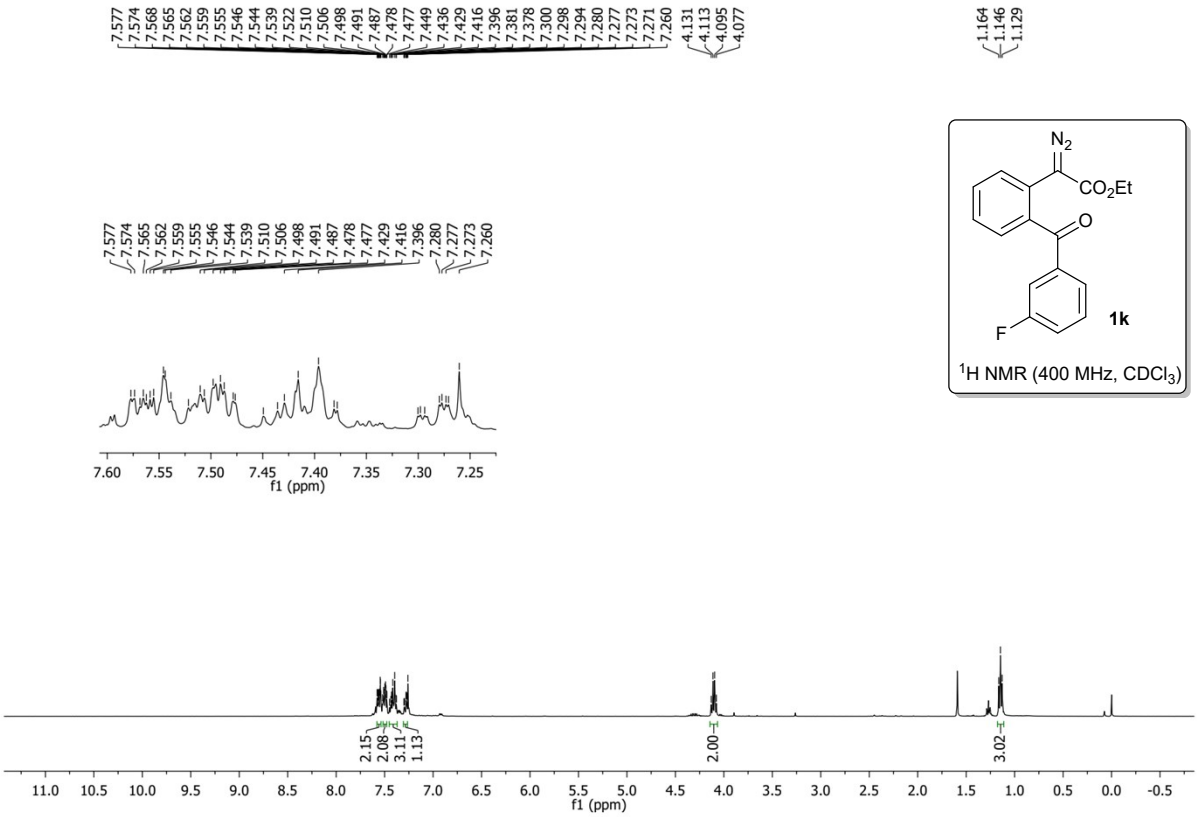


^{13}C NMR (125 MHz, $CDCl_3$)

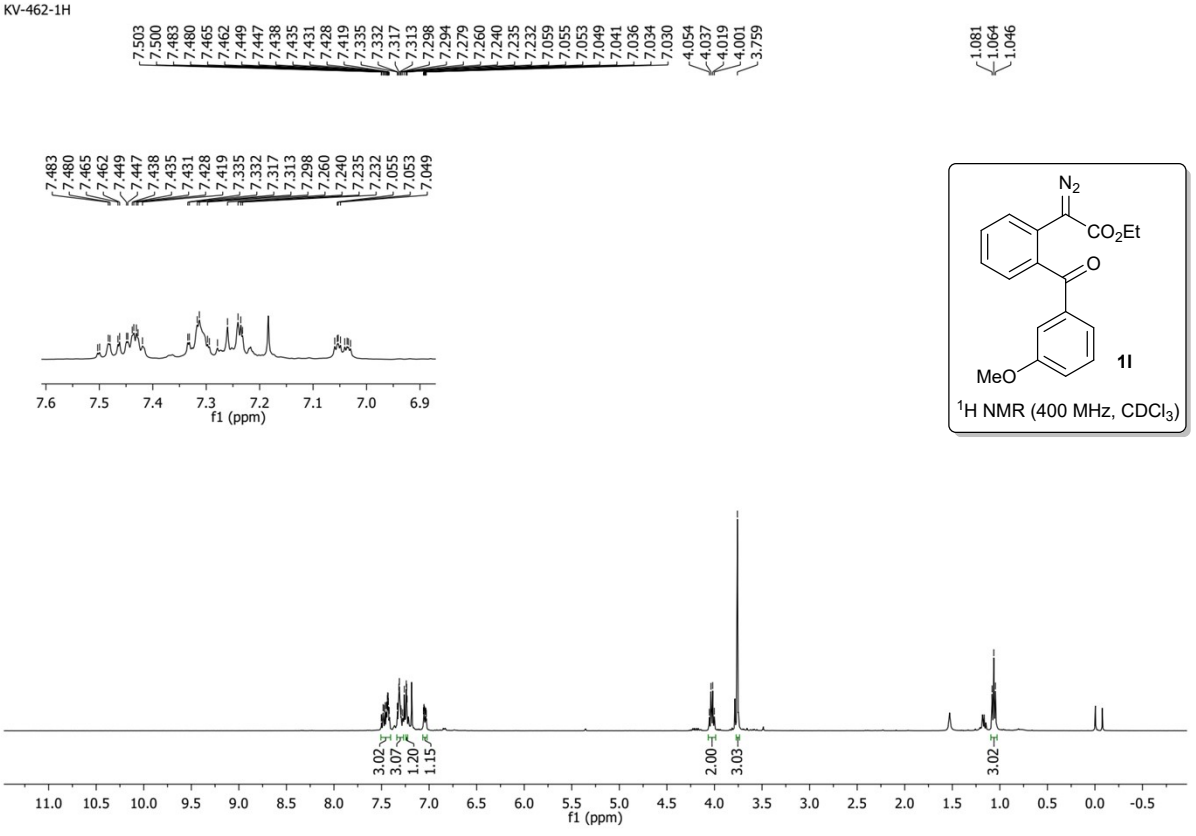


KV-445-1H



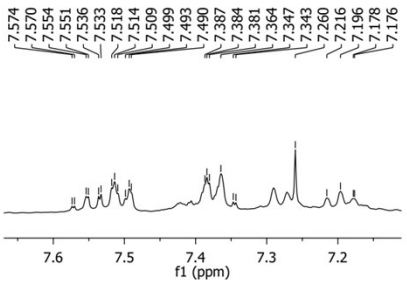
^{1}H NMR (400 MHz, $CDCl_3$)

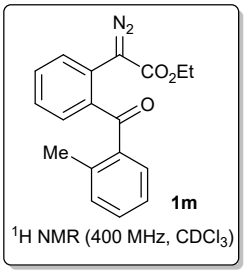
KV-462-1H



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

KV-437-1H





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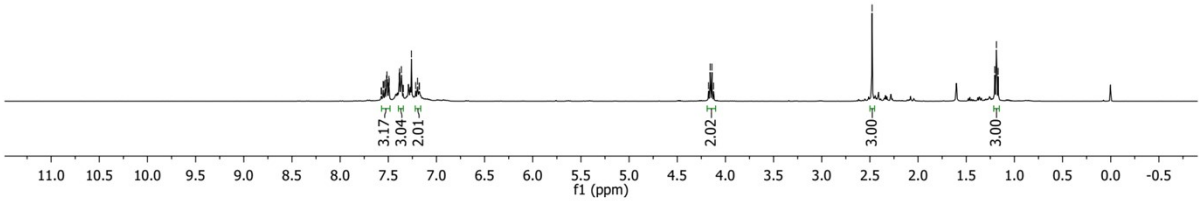
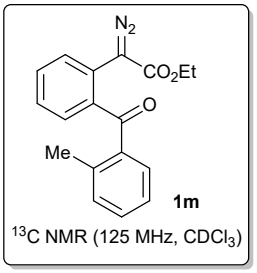
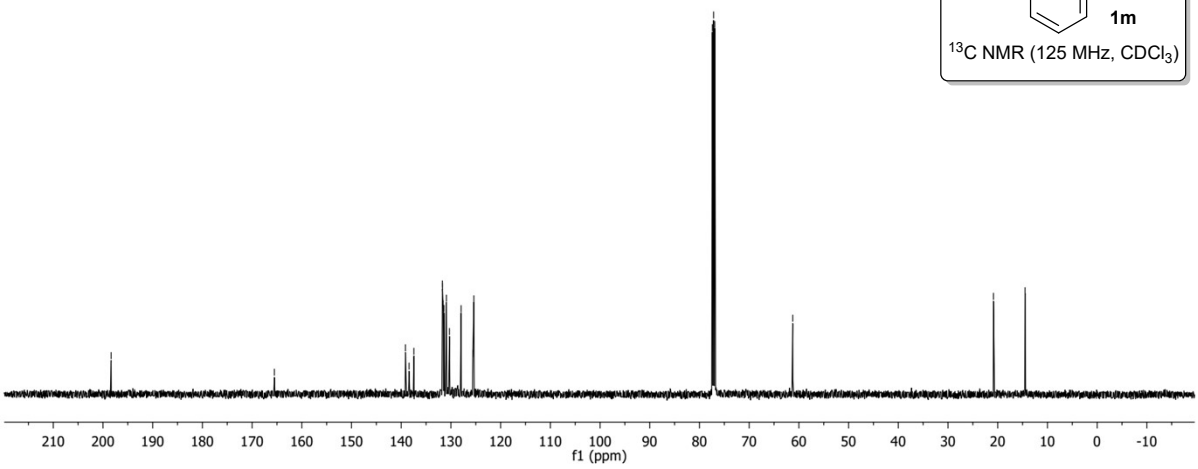


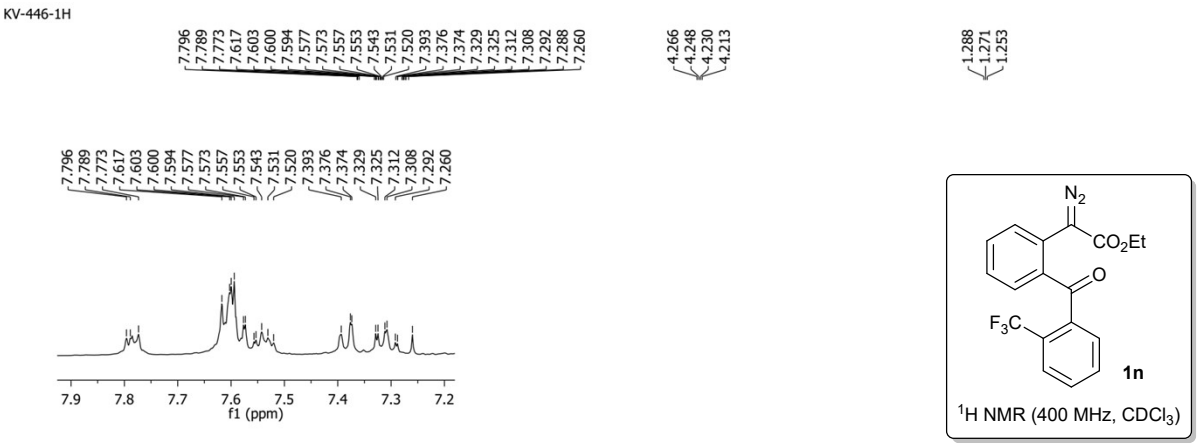
KV-437-13C



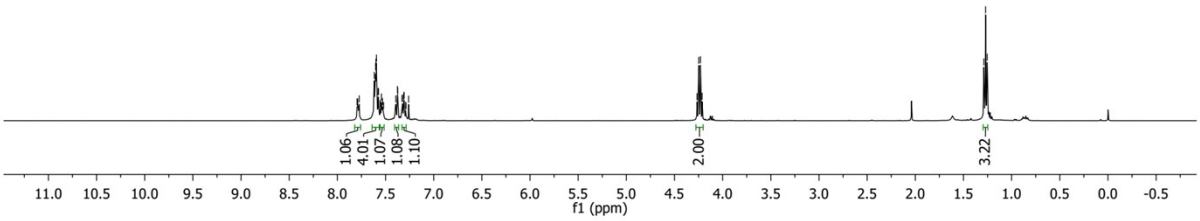
^{13}C NMR (125 MHz, $CDCl_3$)



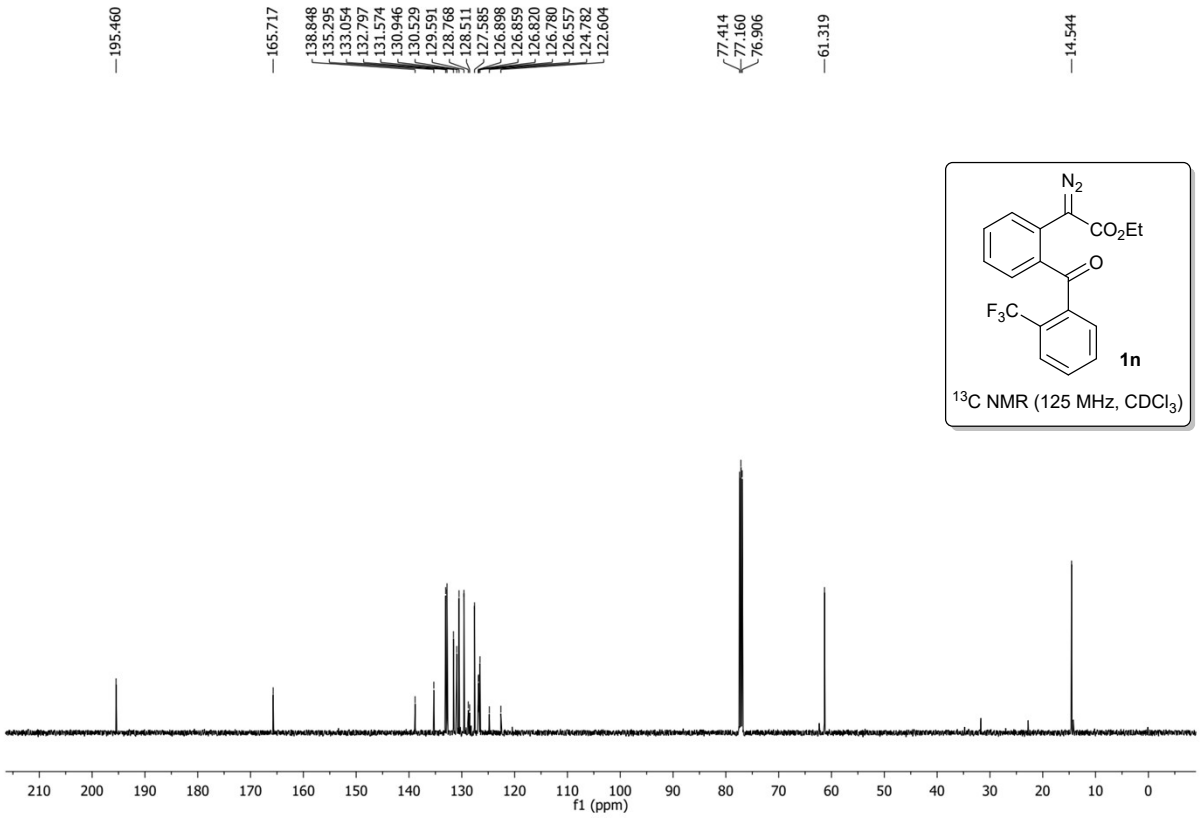
KV-446-1H



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

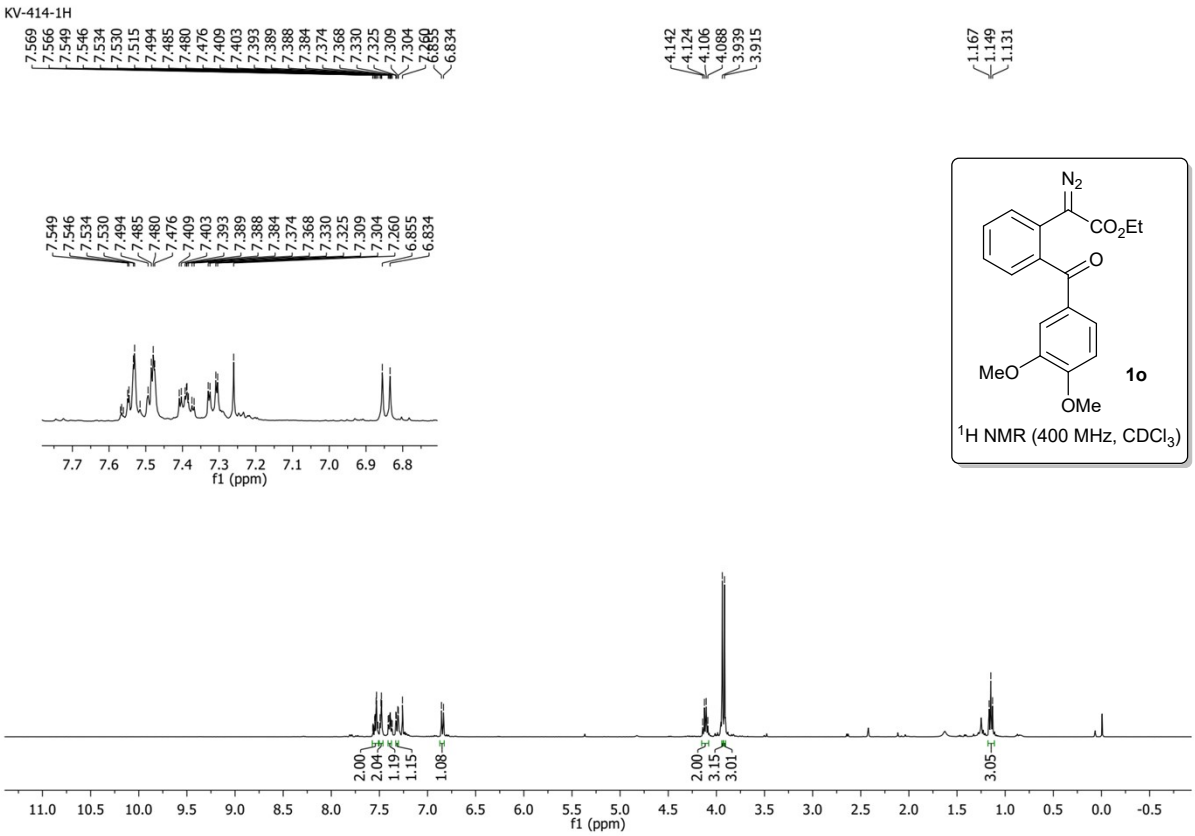


KV-446-13C



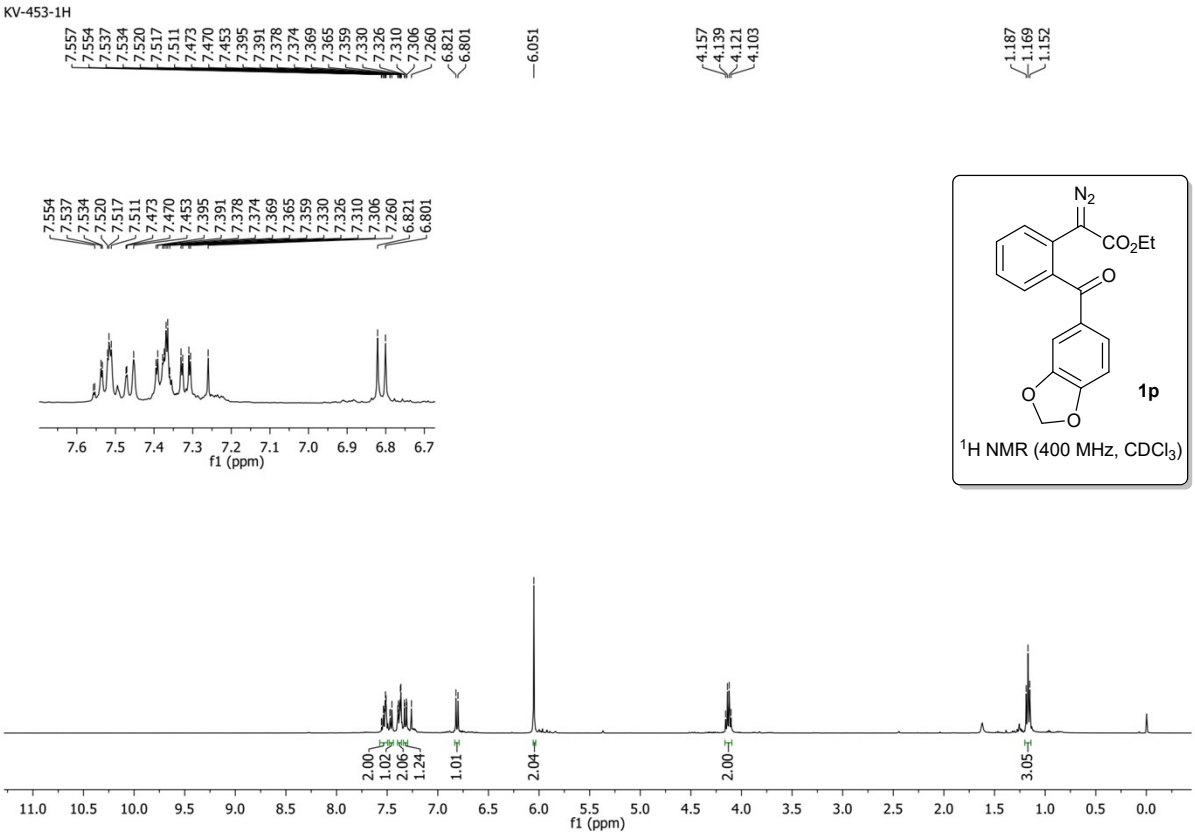
^{13}C NMR (125 MHz, $CDCl_3$)

KV-414-1H



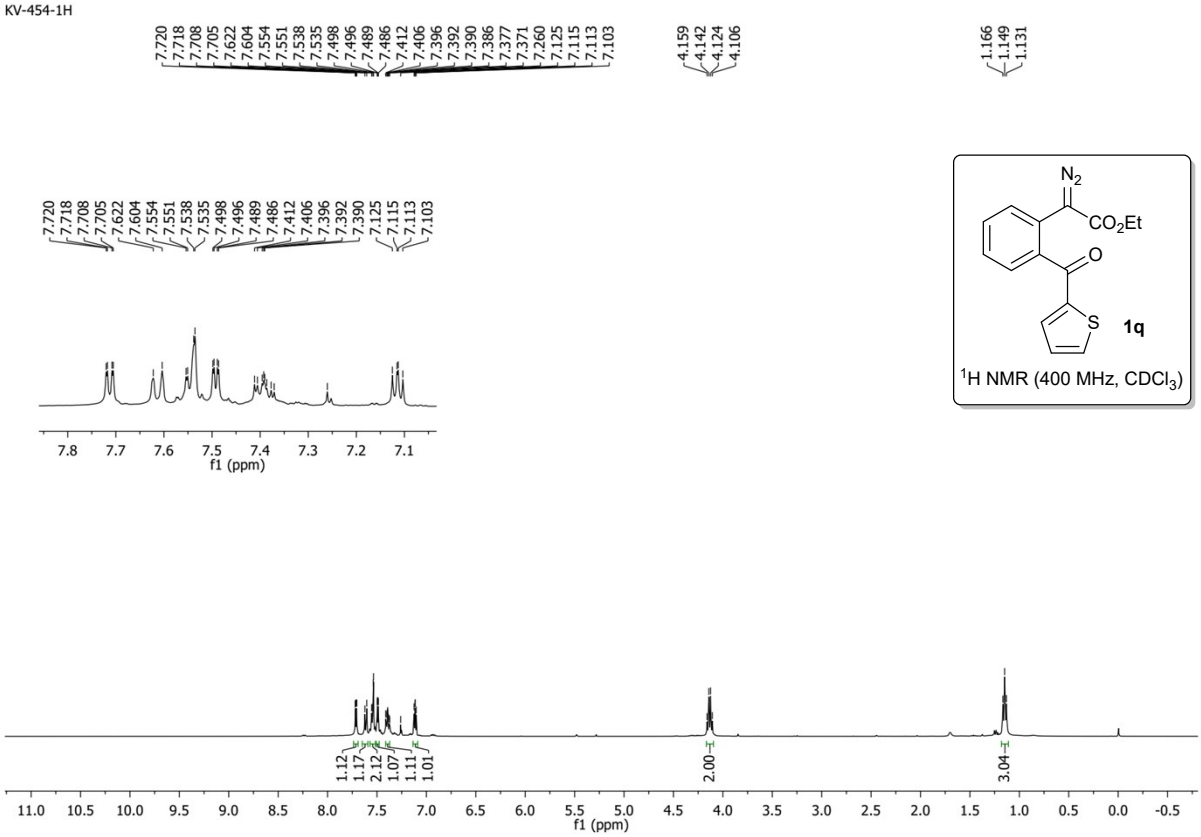
^{1}H NMR (400 MHz, $CDCl_3$)

KV-453-1H



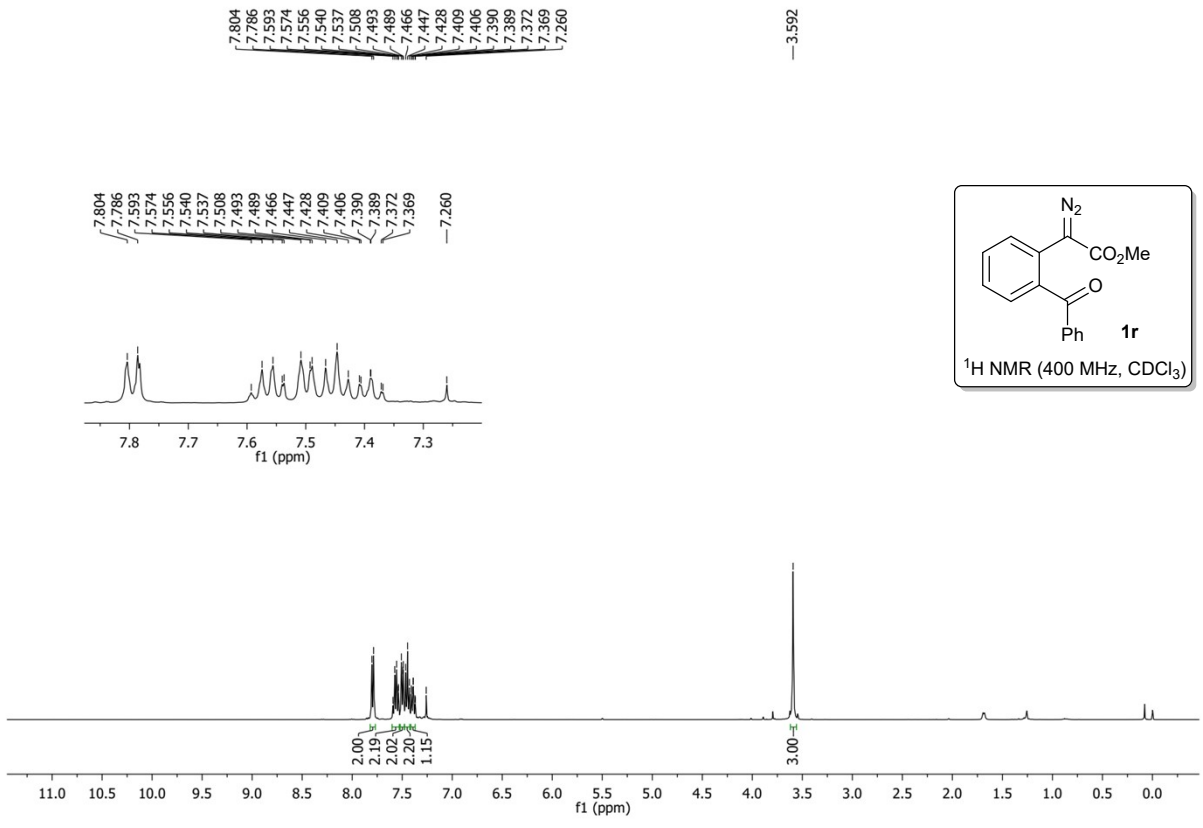
^{1}H NMR (400 MHz, $CDCl_3$)

KV-454-1H



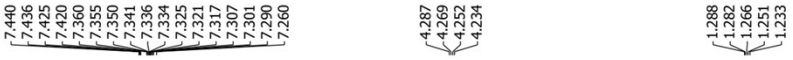
^{1}H NMR (400 MHz, $CDCl_3$)

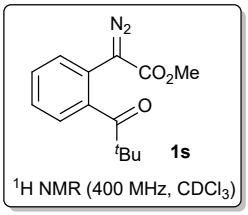
KV-467-1H



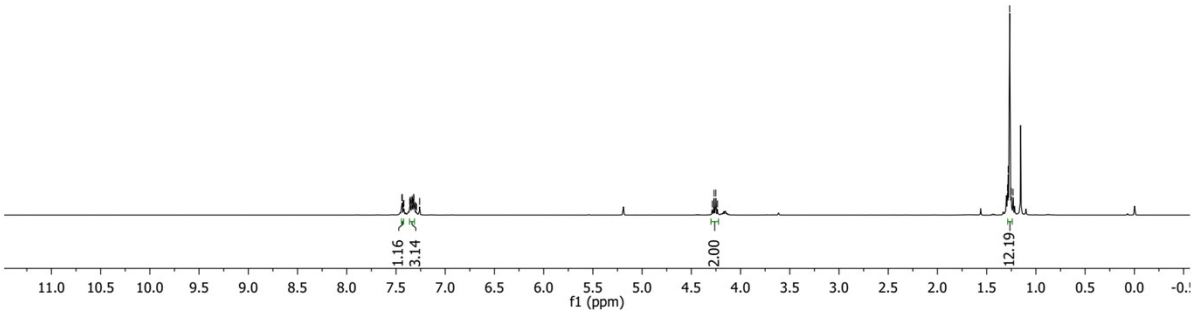
^{1}H NMR (400 MHz, $CDCl_3$)

KV-520-1H

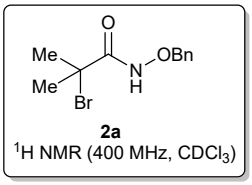




^{1}H NMR (400 MHz, $CDCl_3$)

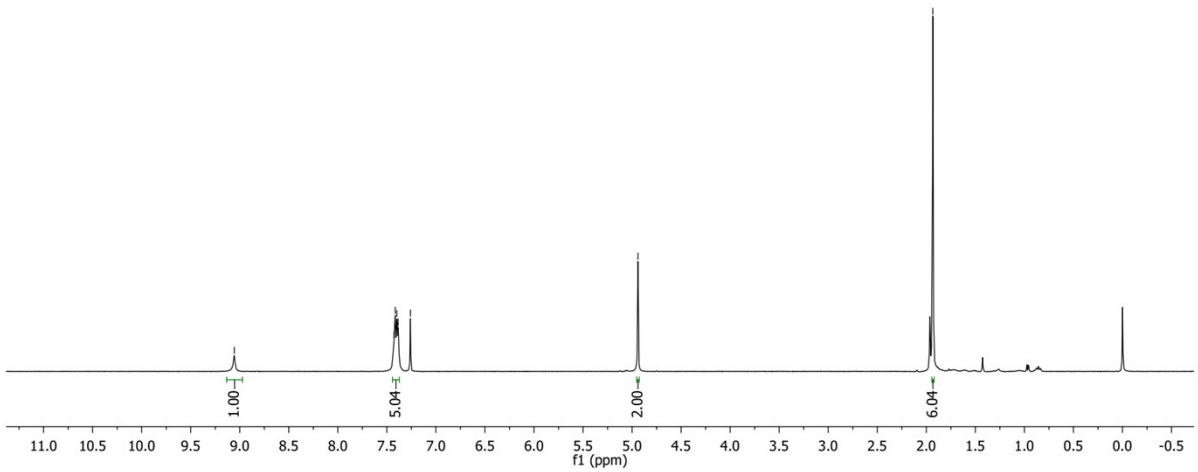


KV-364-1H

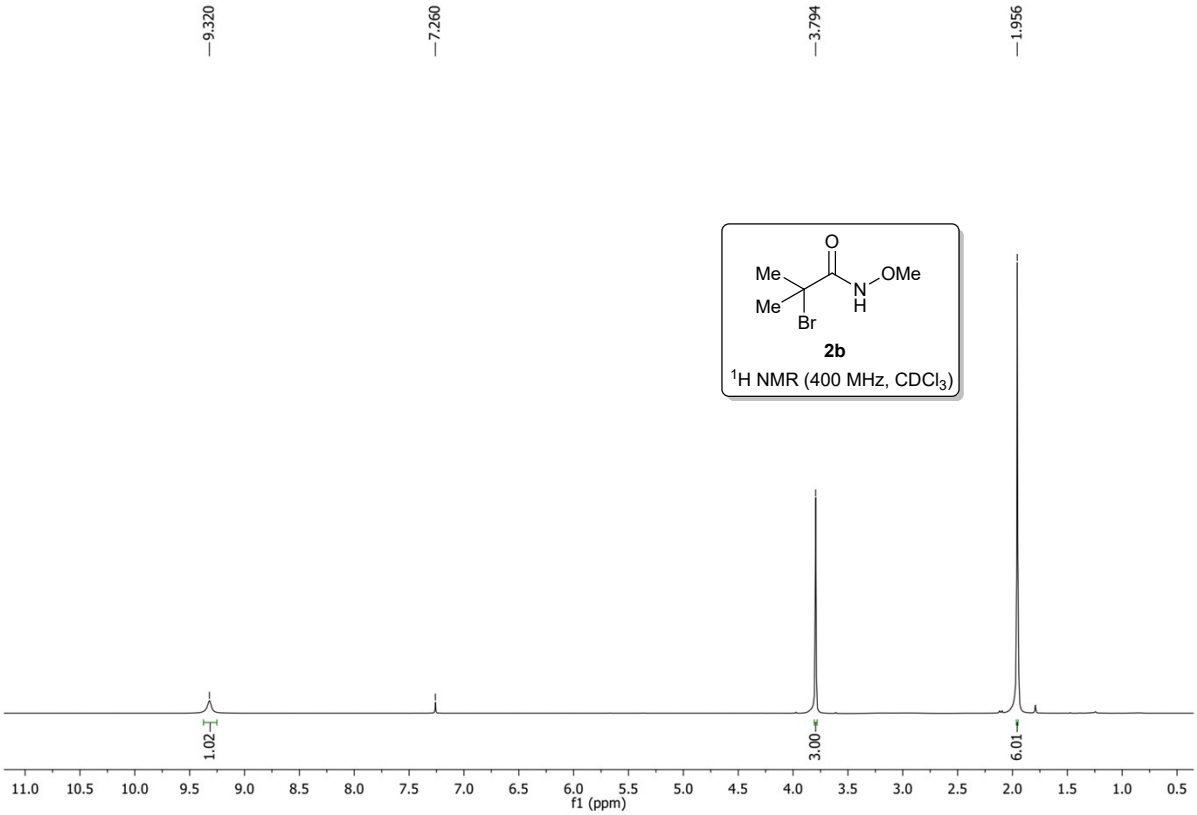


2a

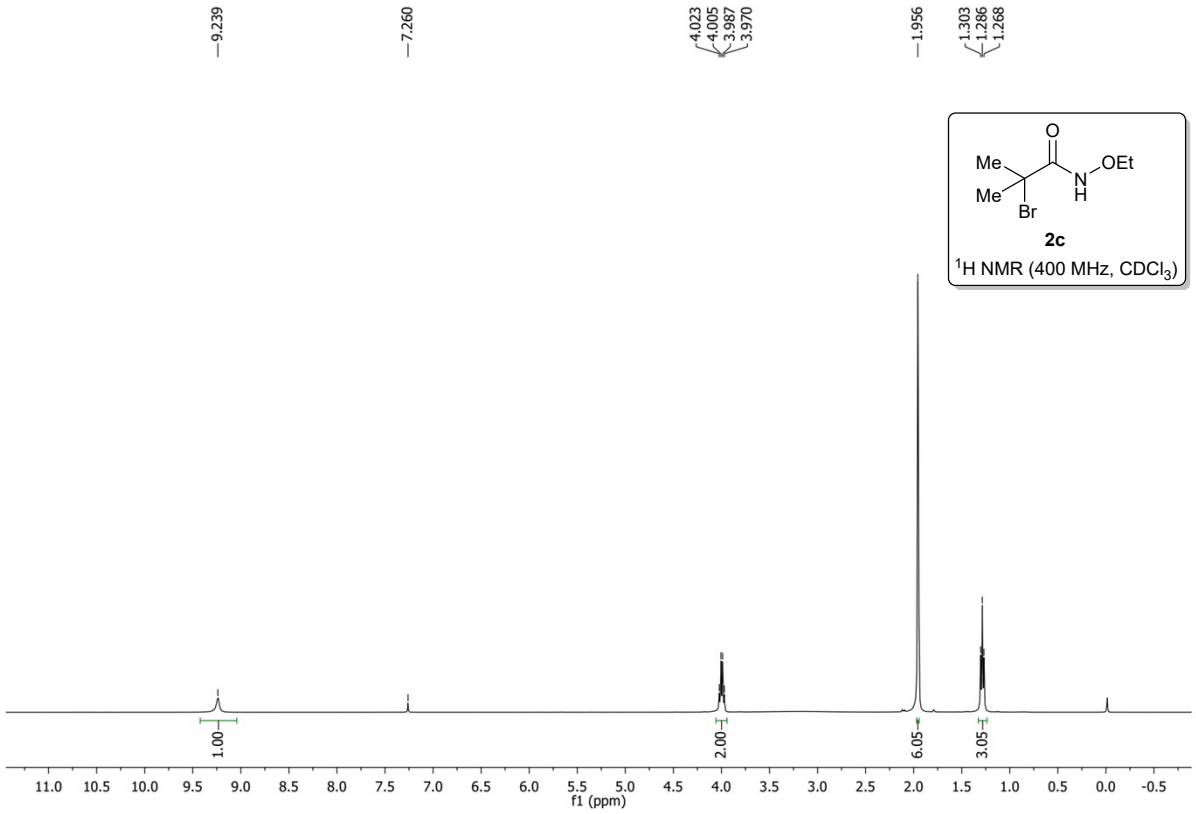
^{1}H NMR (400 MHz, $CDCl_3$)



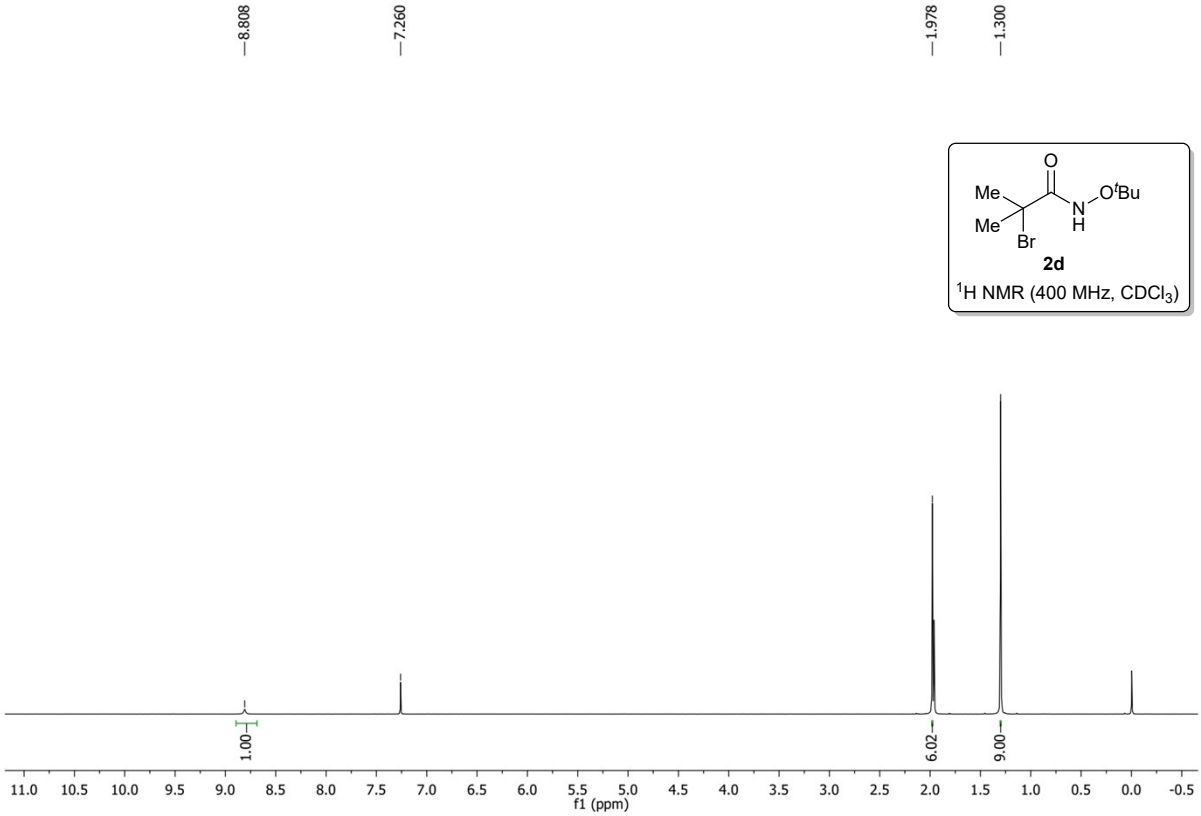
KV-398-1H



KV-399-1H



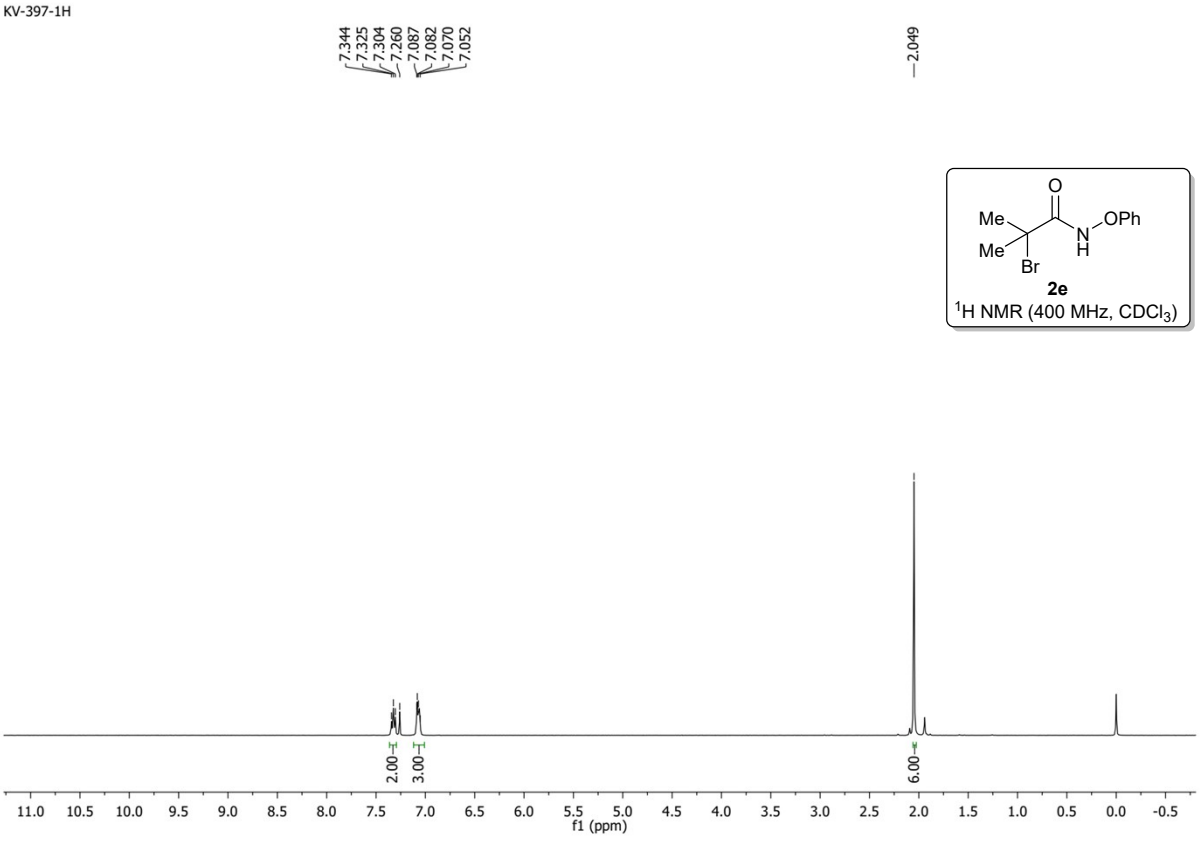
KV-477-1H



2d

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

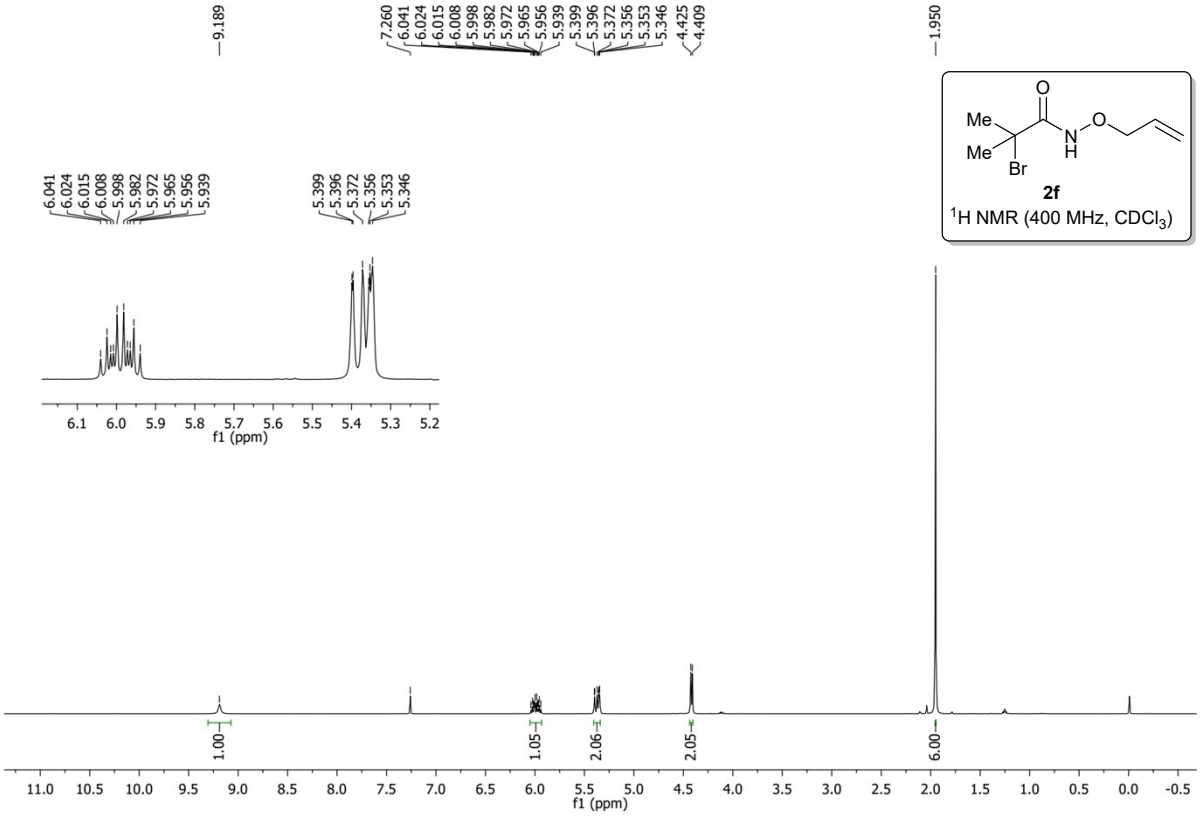
KV-397-1H



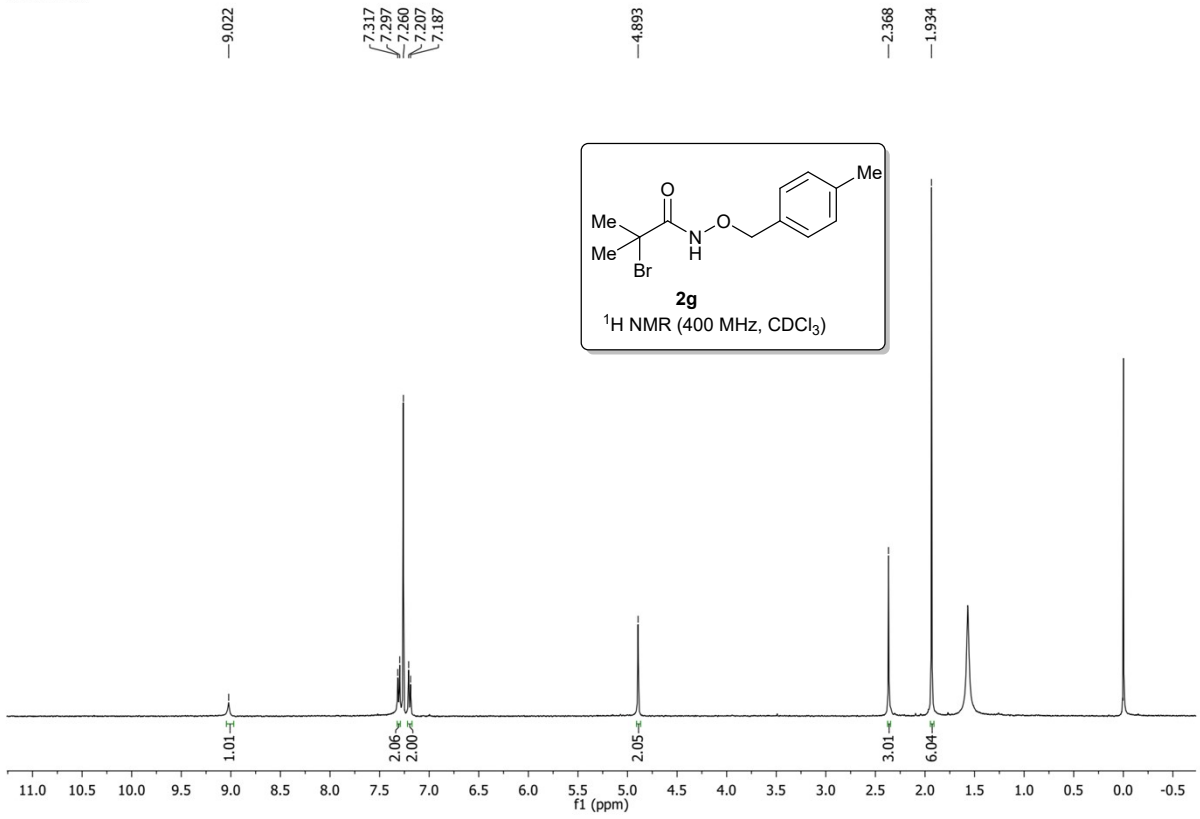
2e

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

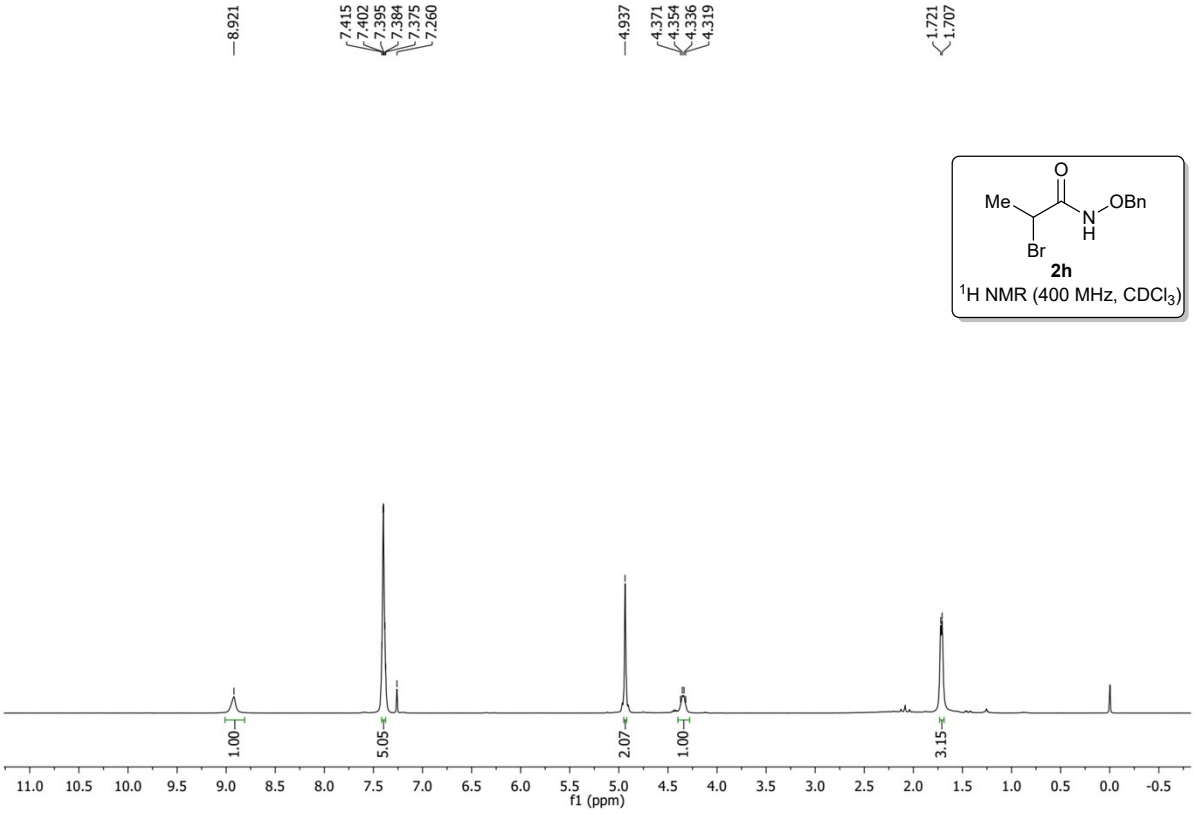
KV-463-1H



KV-4AME-1H



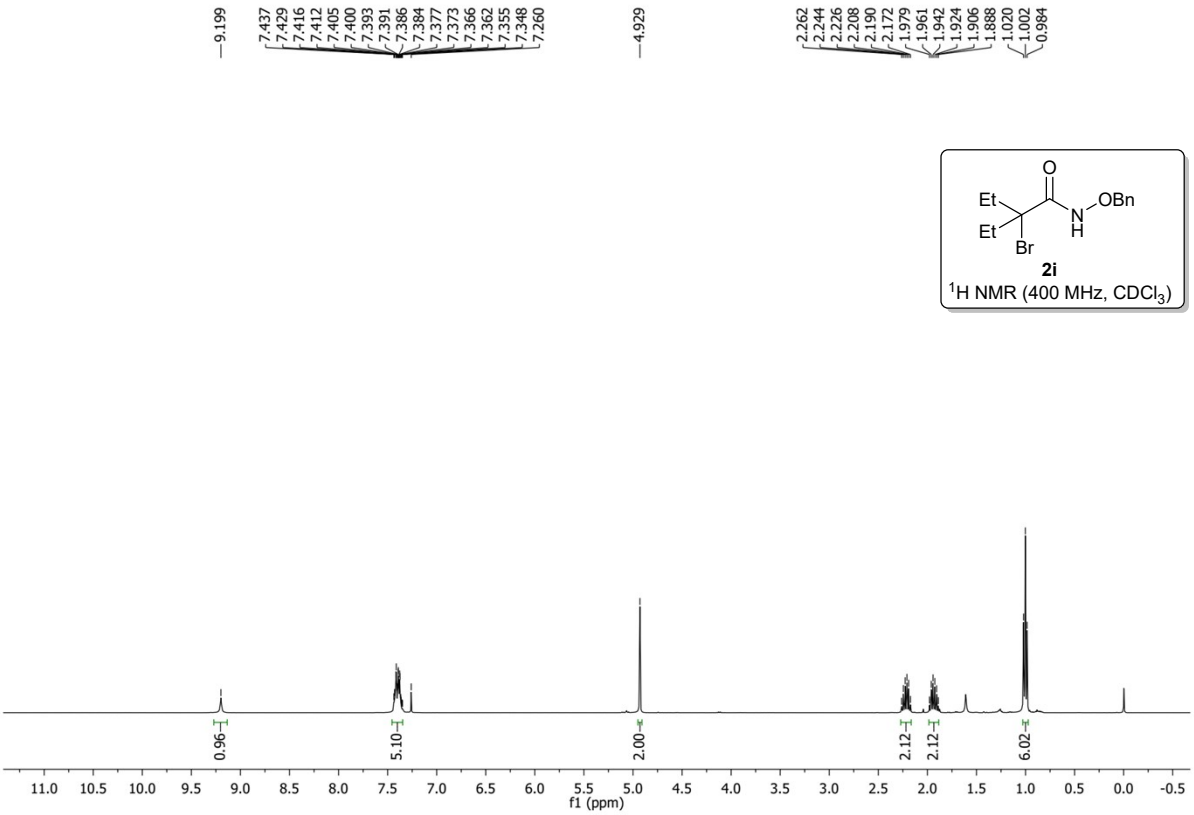
KV-391-1H



2h

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

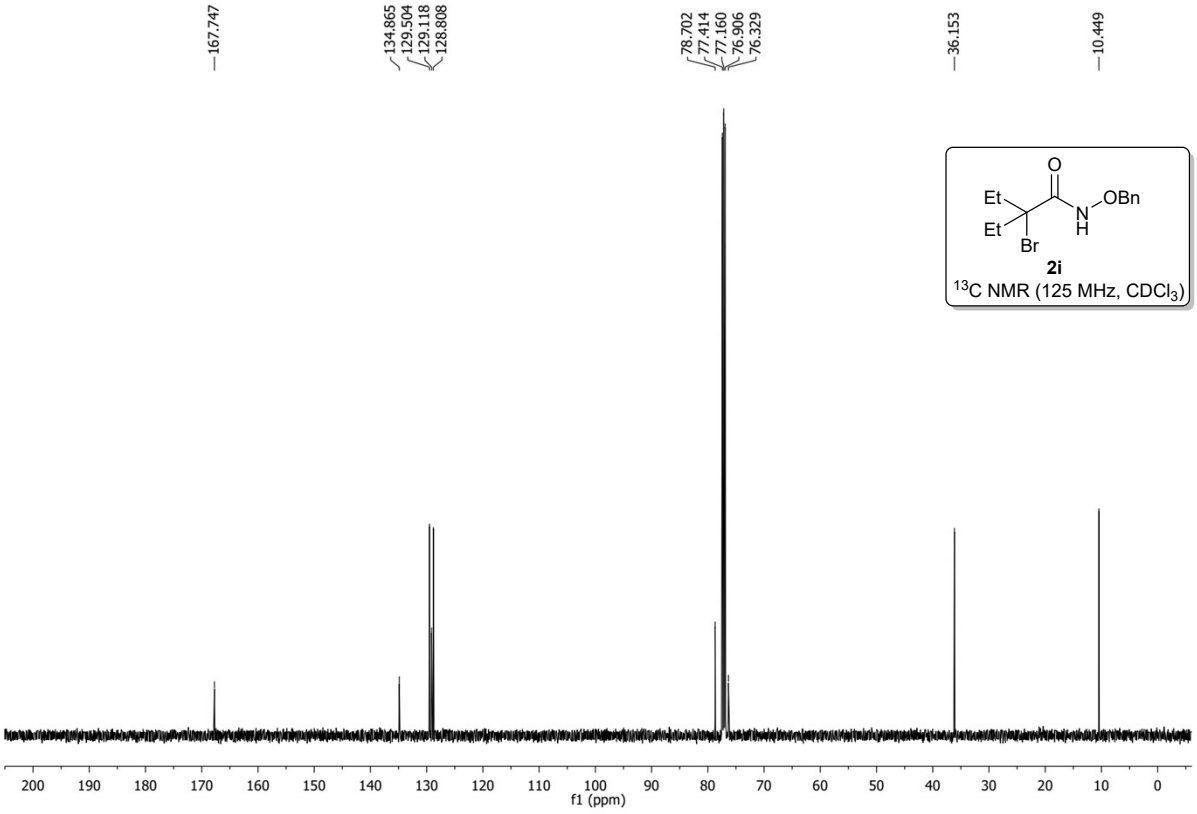
KV-DIETHYL-1H



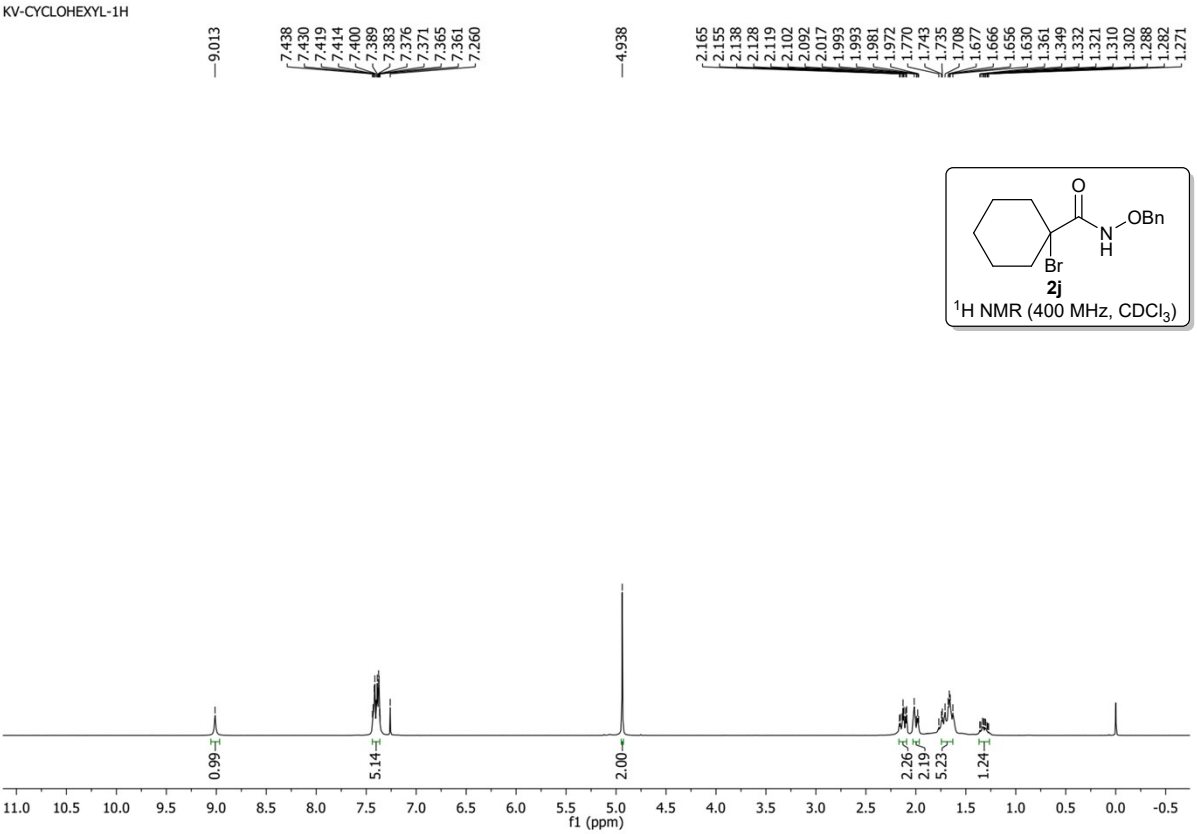
2i

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

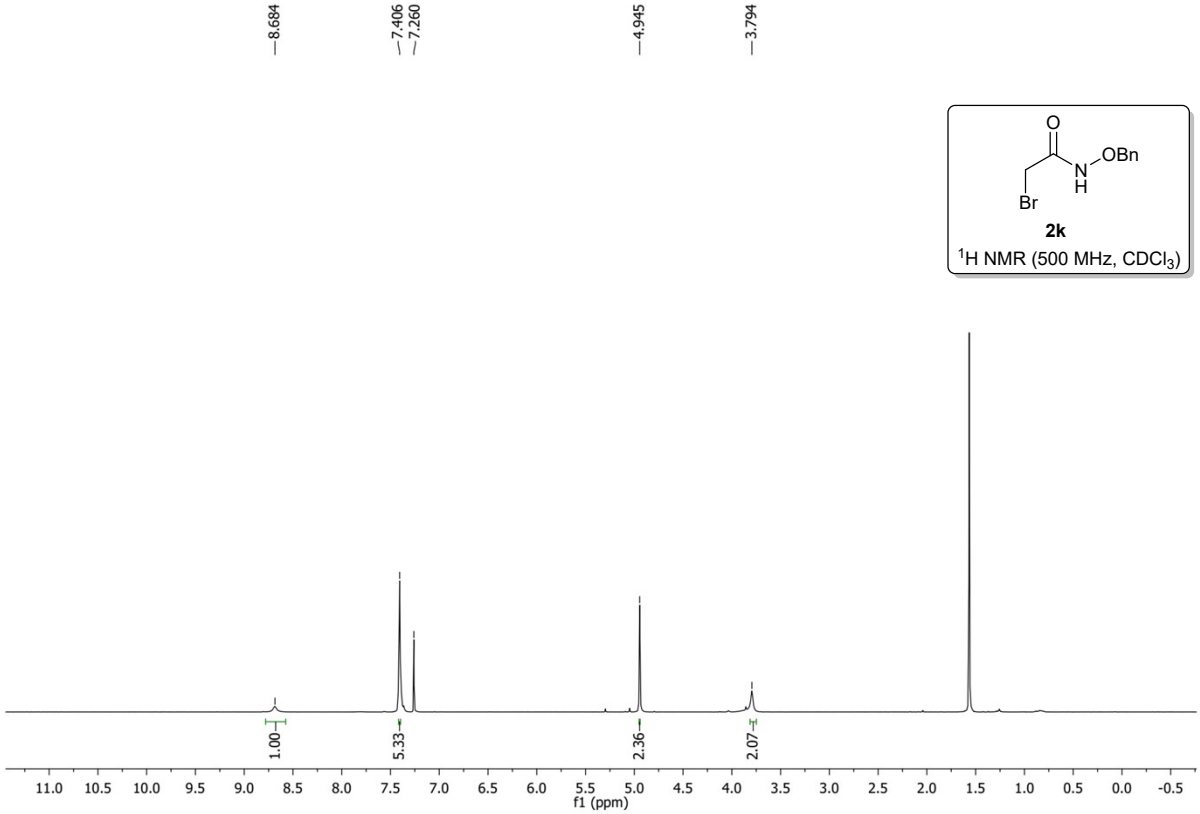
KV-DIETHYL-13C



KV-CYCLOHEXYL-1H



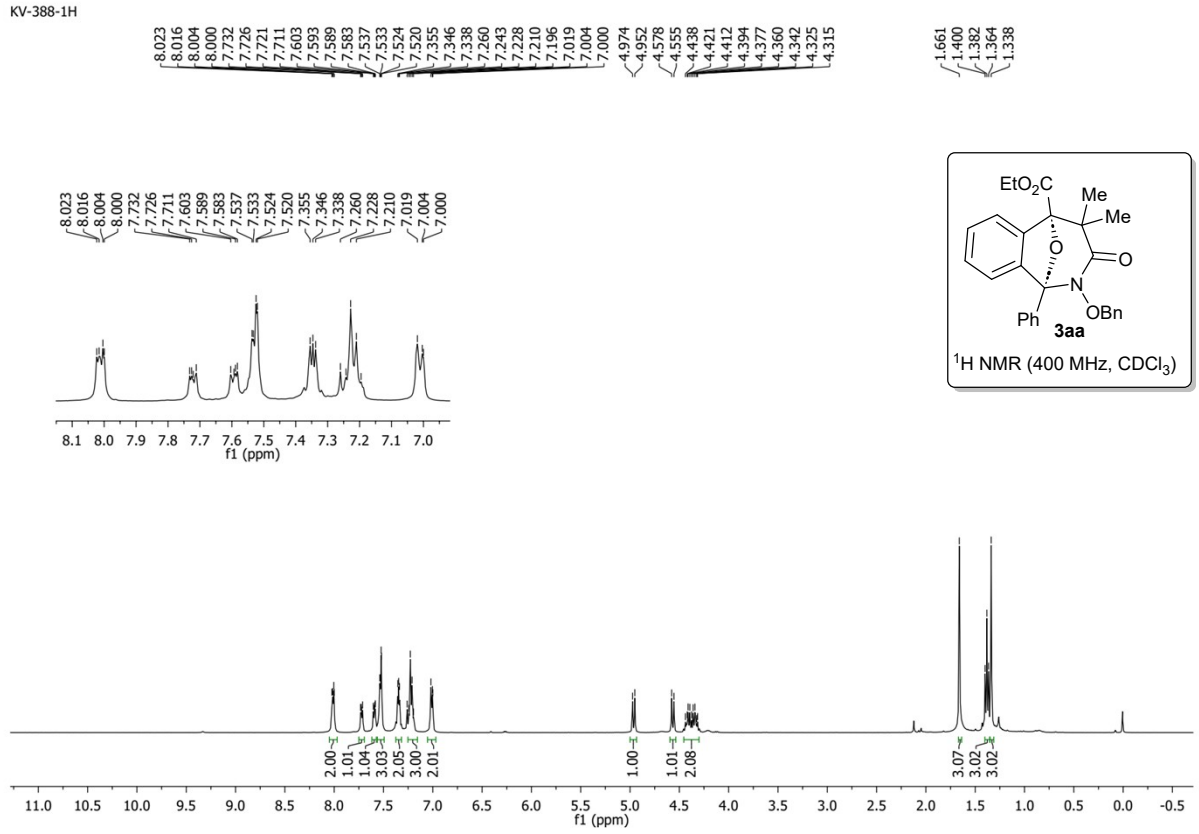
KV-83-1H



2k

^{1}H NMR (500 MHz, $CDCl_3$)

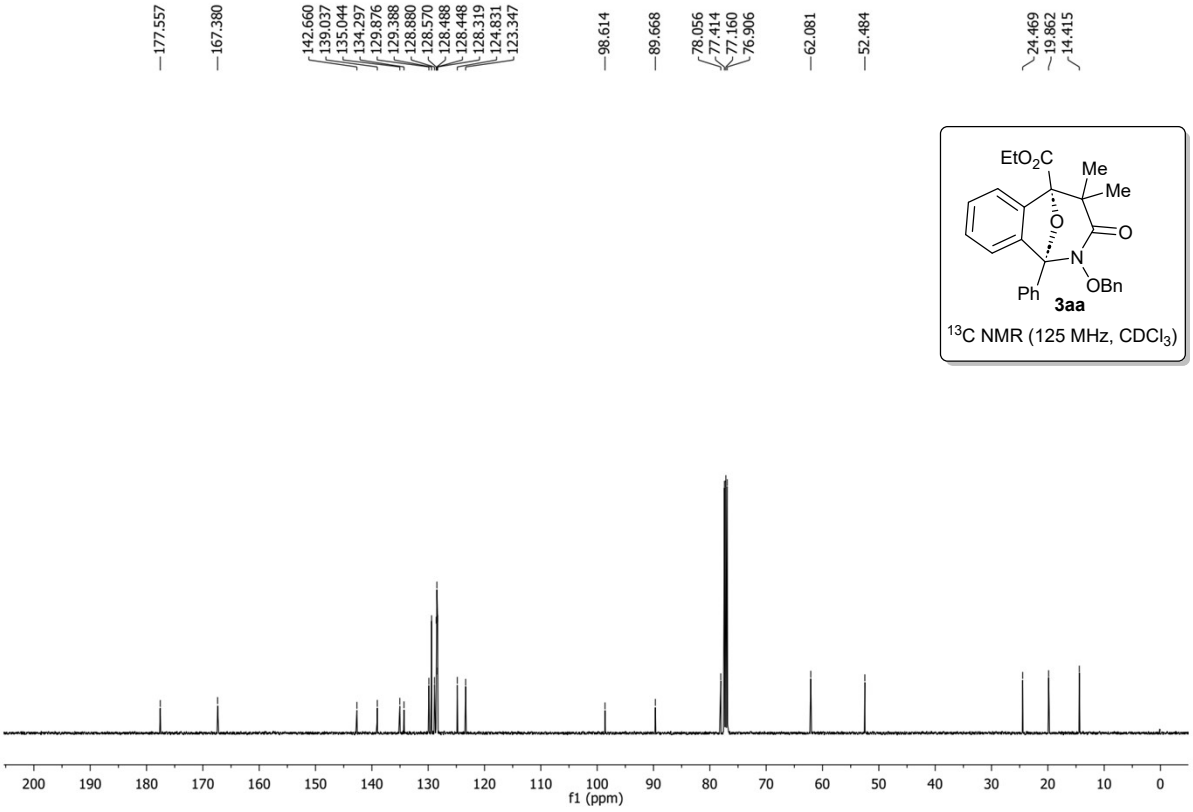
KV-388-1H



3aa

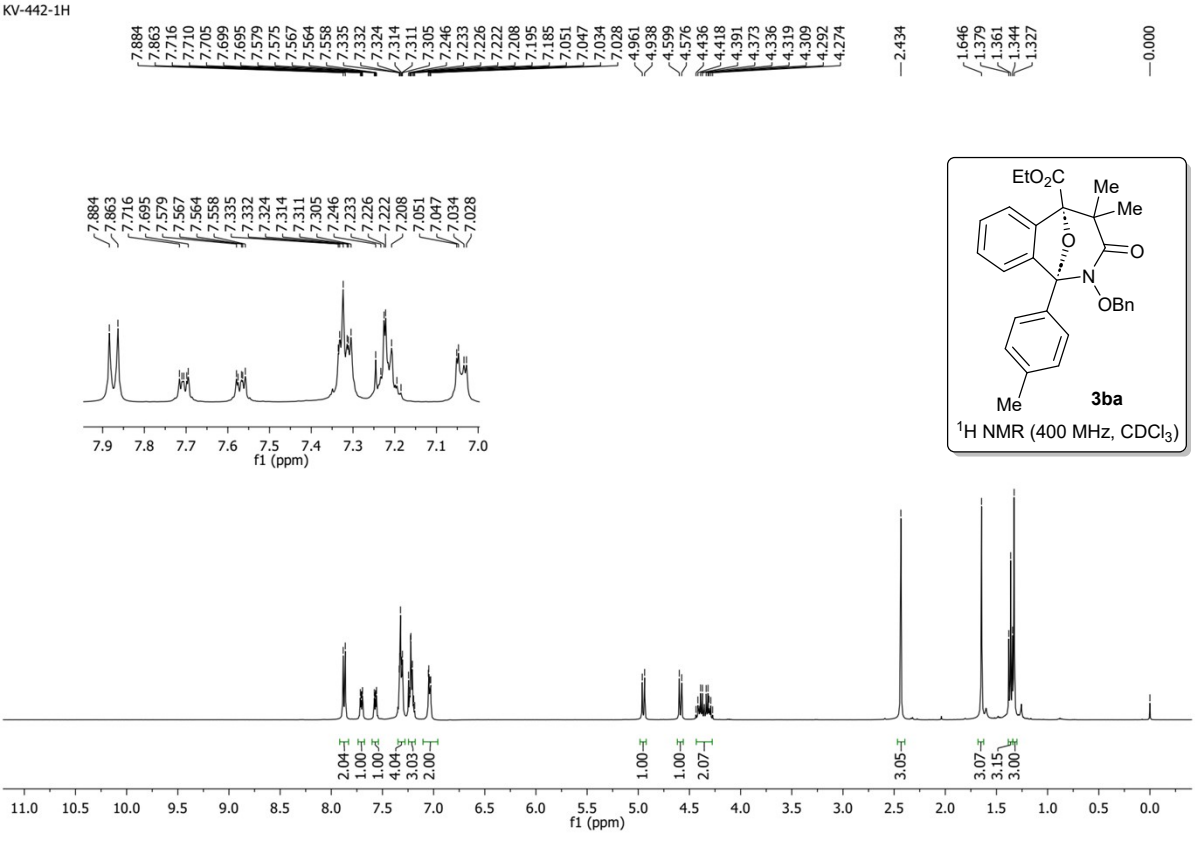
^{1}H NMR (400 MHz, $CDCl_3$)

KV-388-13C



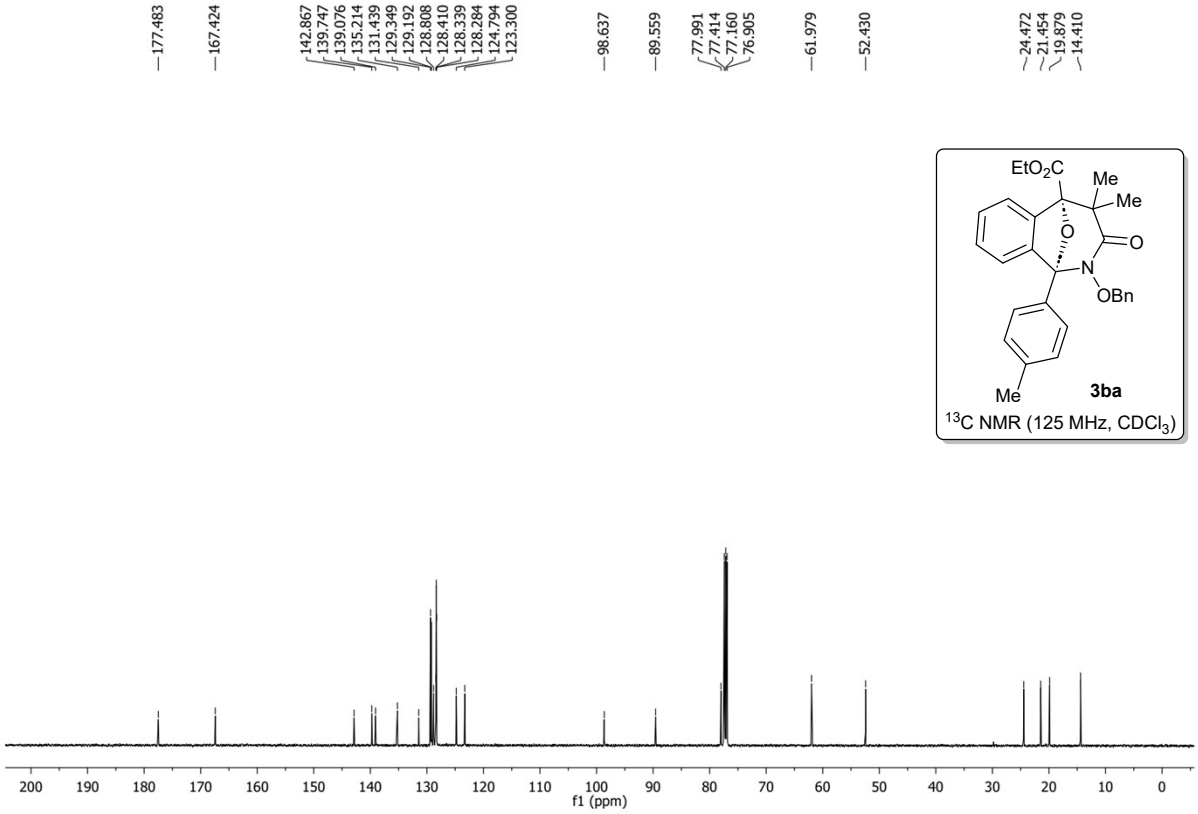
^{13}C NMR (125 MHz, $CDCl_3$)

KV-442-1H



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

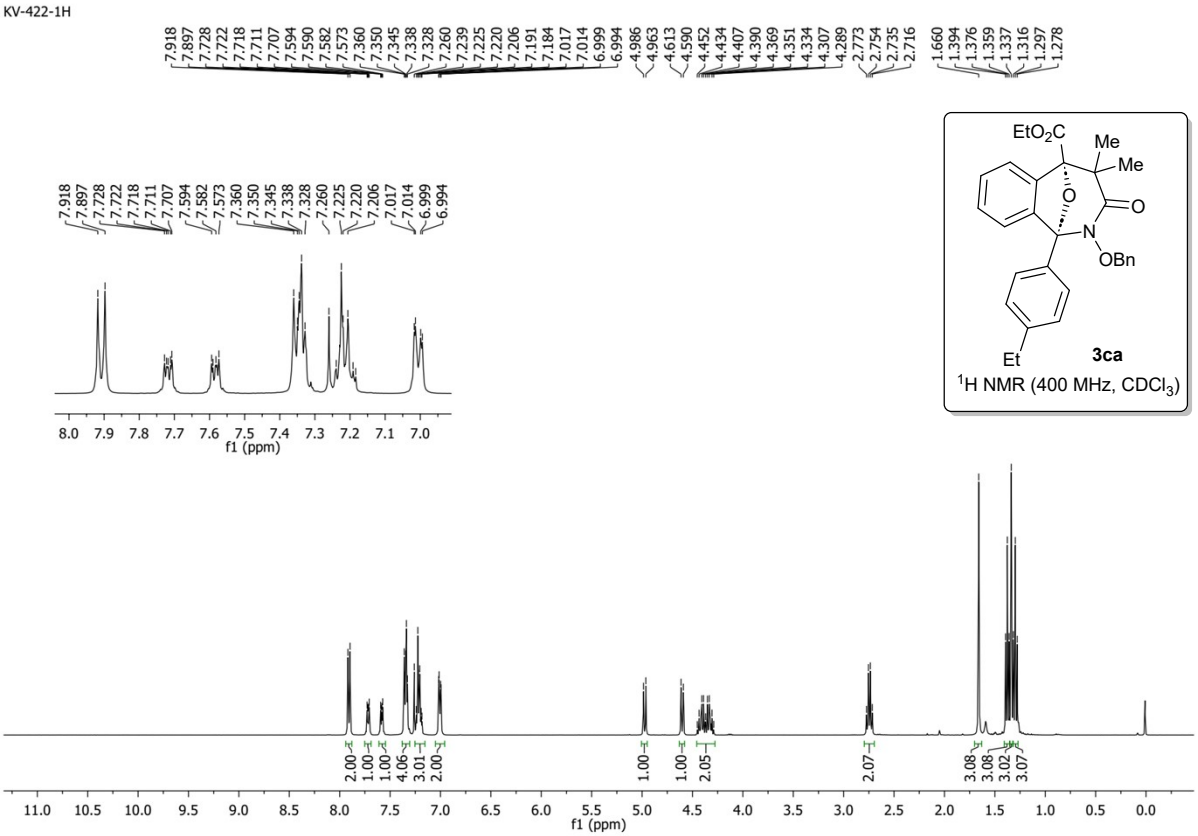
KV-442-13C



3ba

^{13}C NMR (125 MHz, $CDCl_3$)

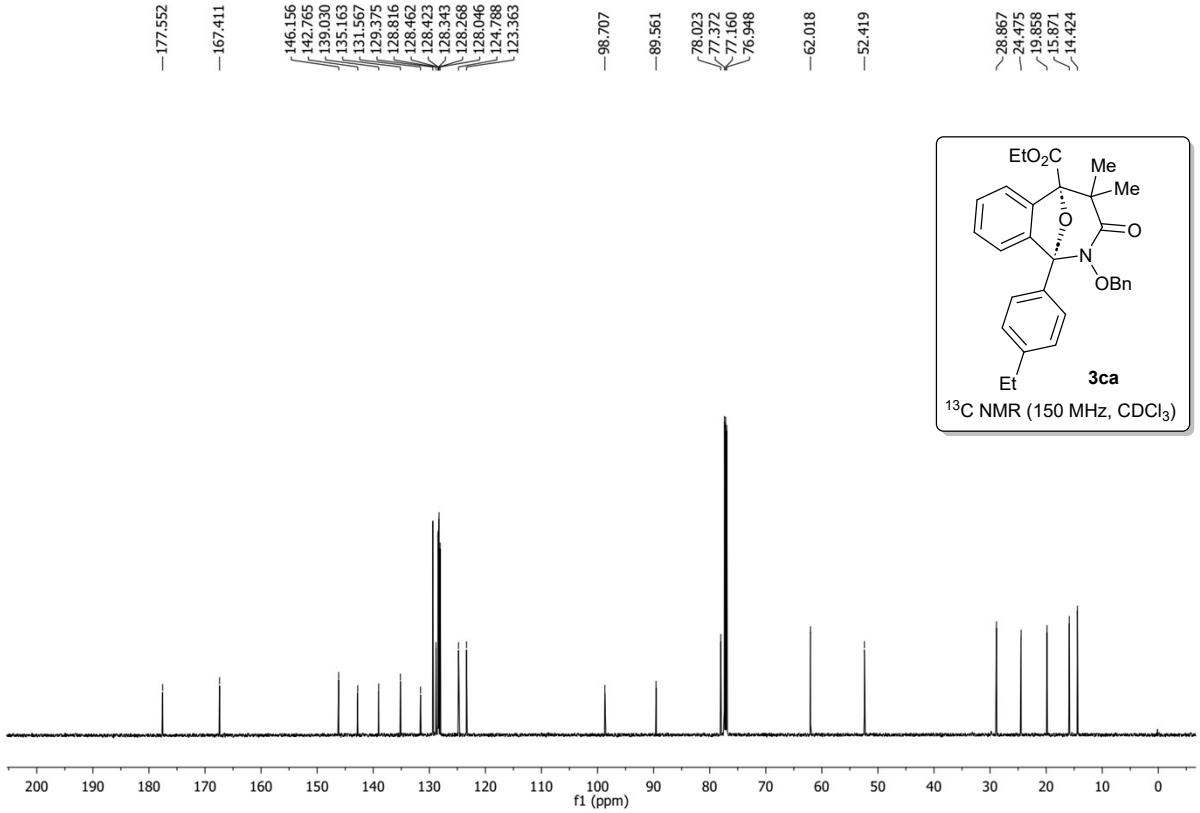
KV-422-1H



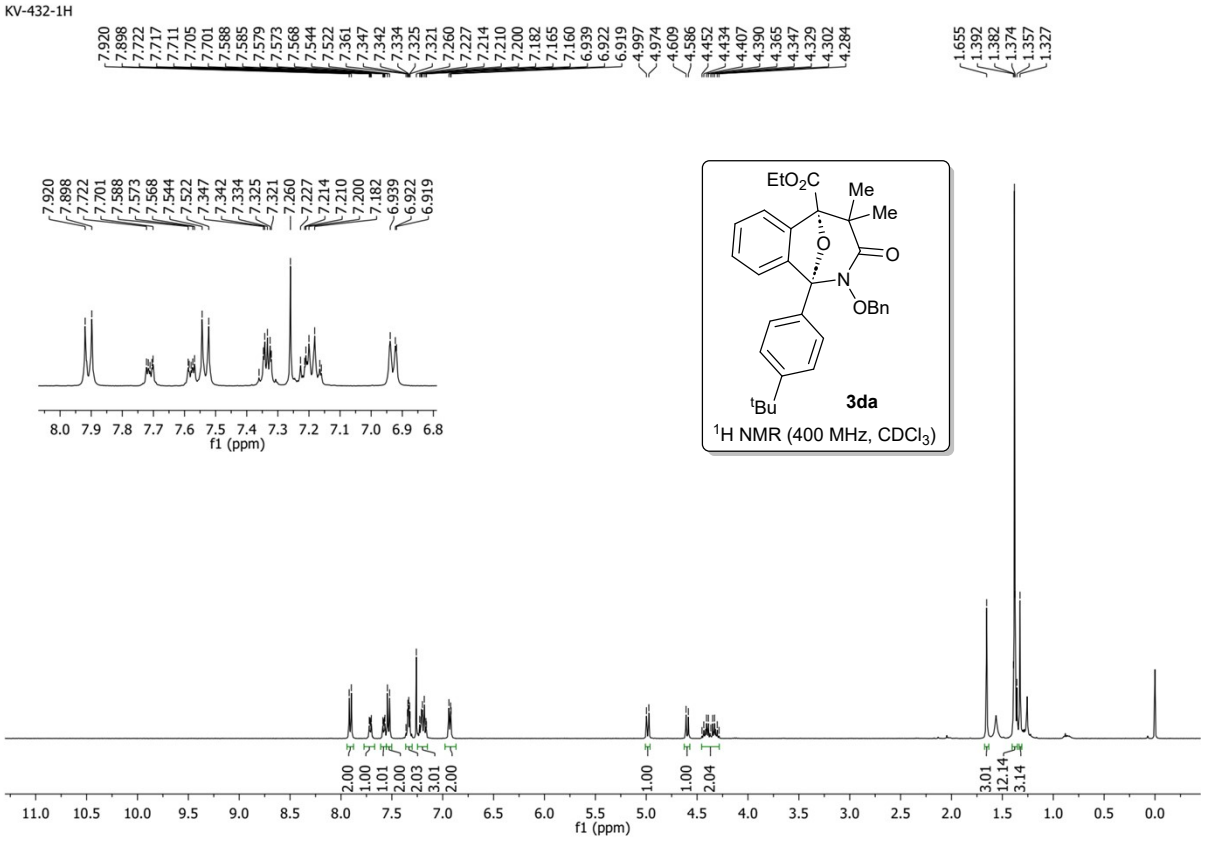
3ca

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

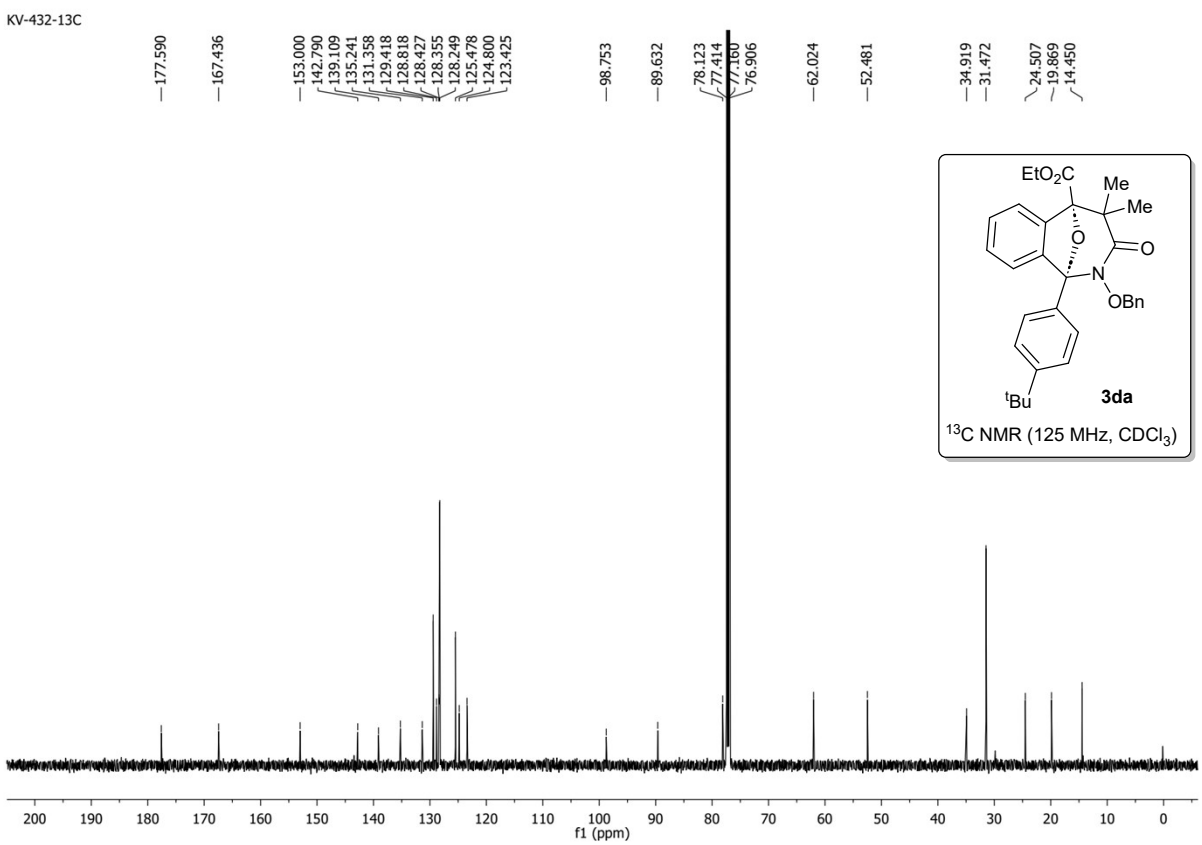
KV-422-13C



KV-432-1H



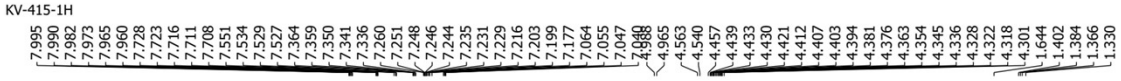
KV-432-13C

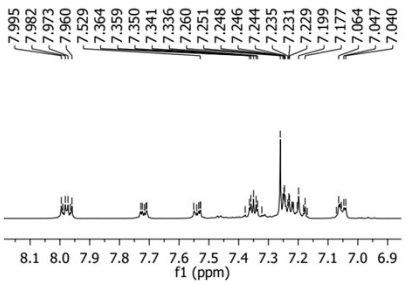


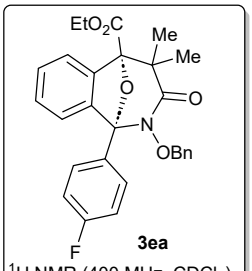
3da

^{13}C NMR (125 MHz, $CDCl_3$)

KV-415-1H

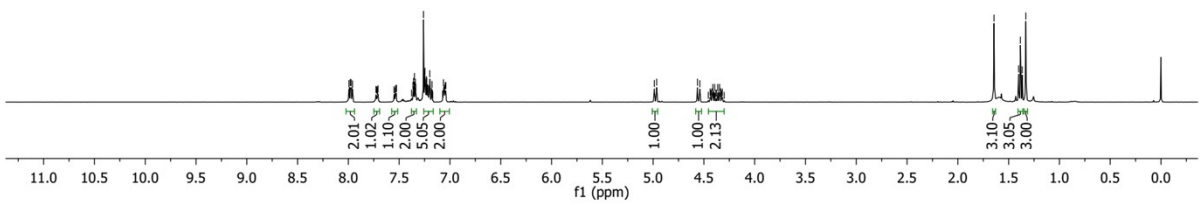




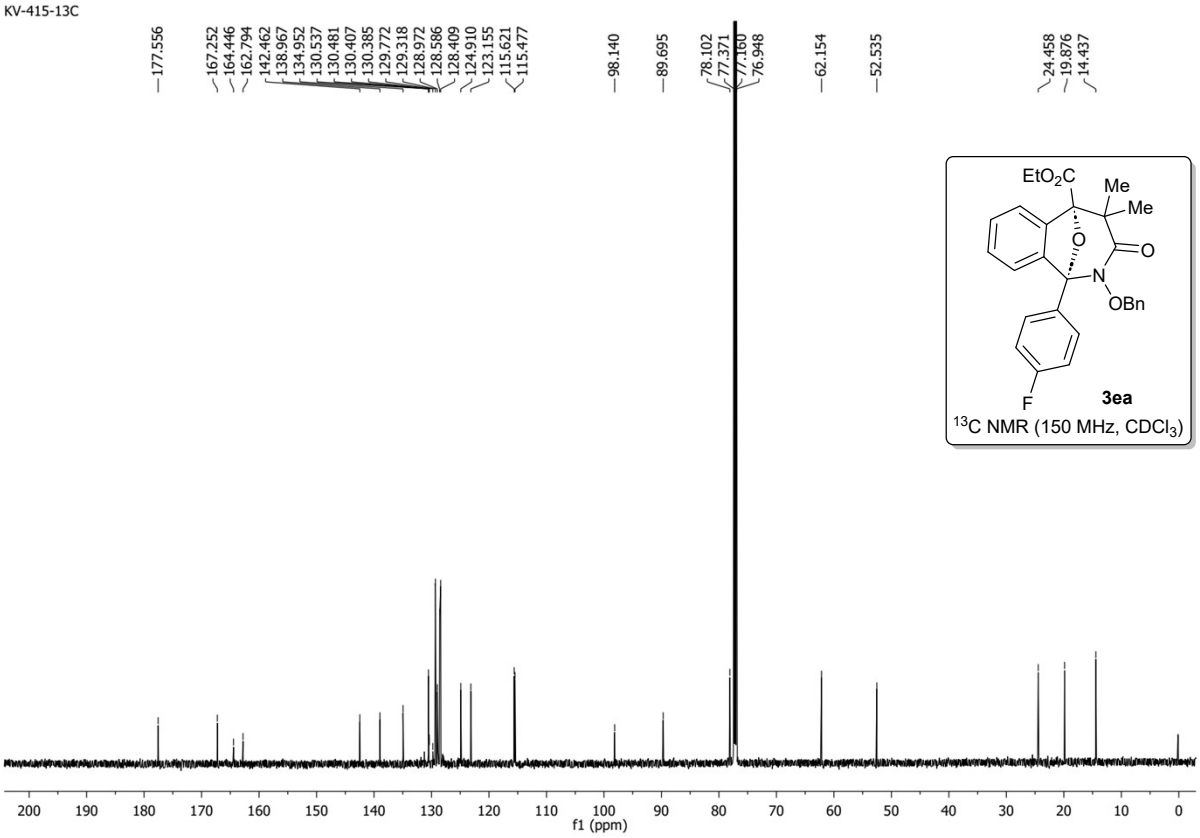


3ea

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



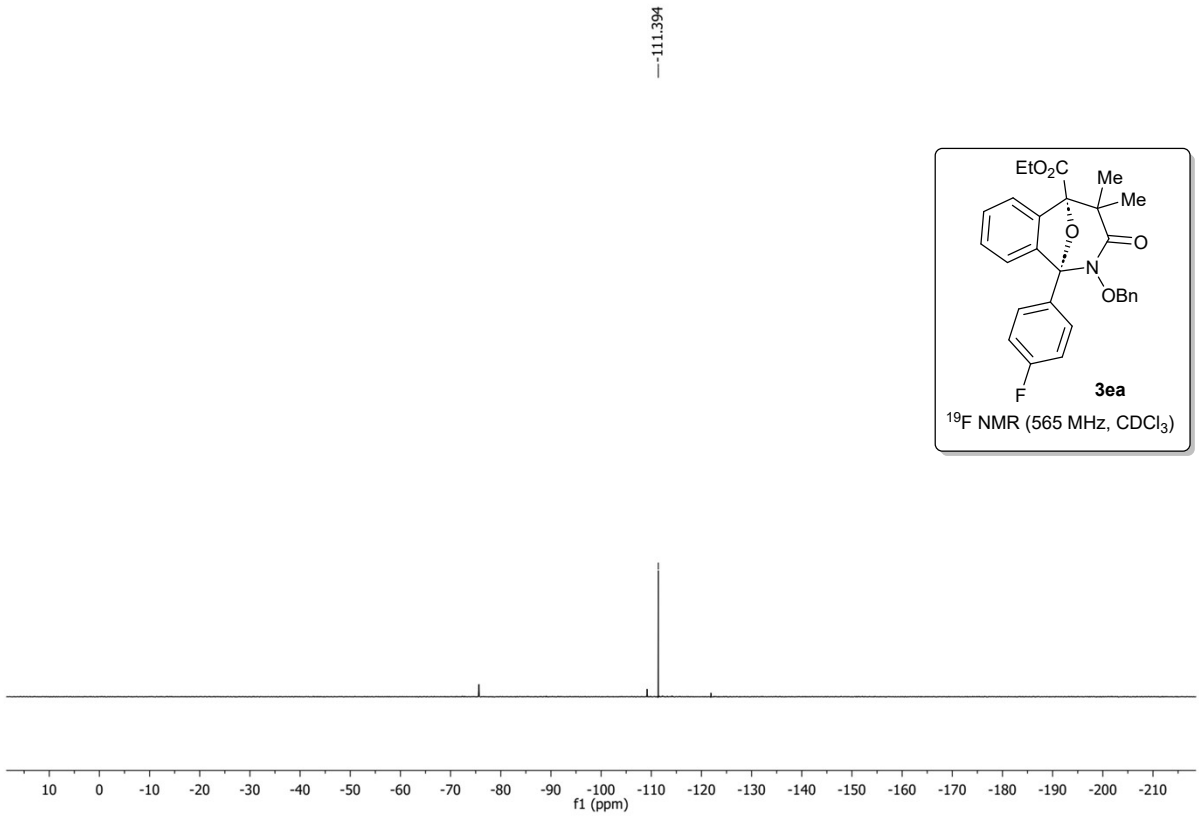
KV-415-13C



3ea

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

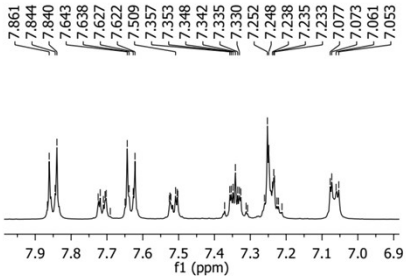
KV-415-19F

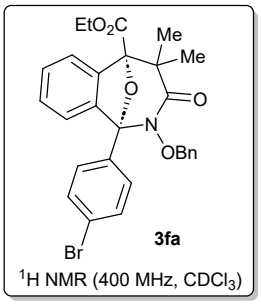


3ea

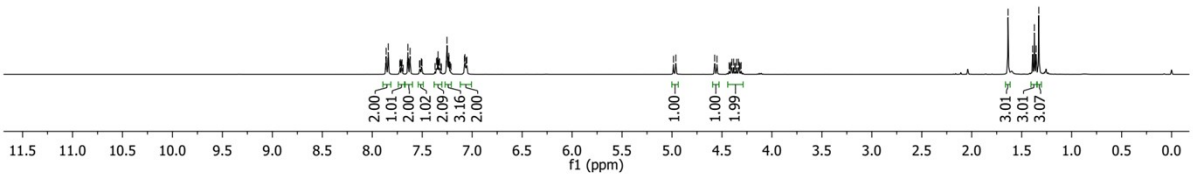
^{19}F NMR (565 MHz, $CDCl_3$)

KV-408-1H

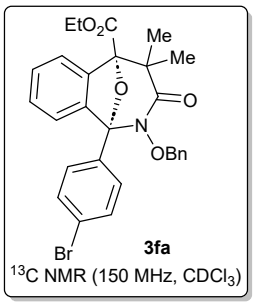




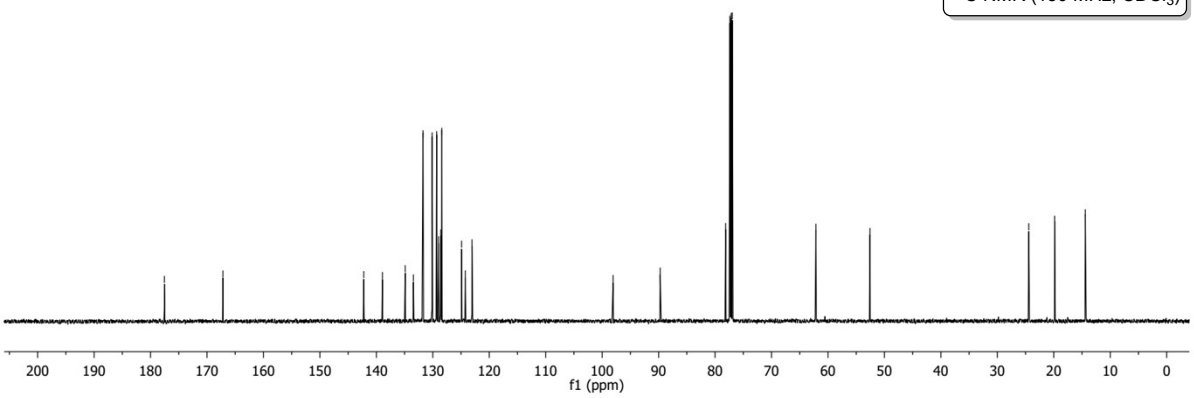
^{1}H NMR (400 MHz, $CDCl_3$)



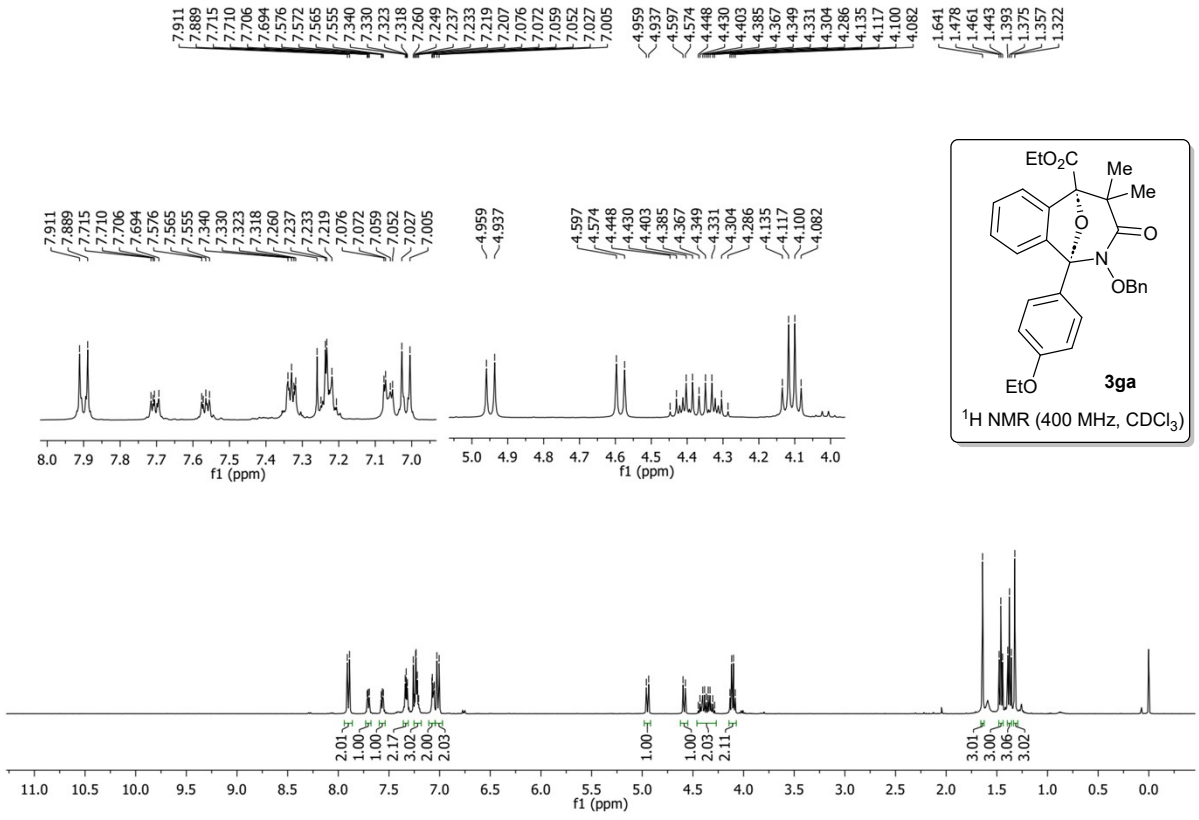
KV-408-13C



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

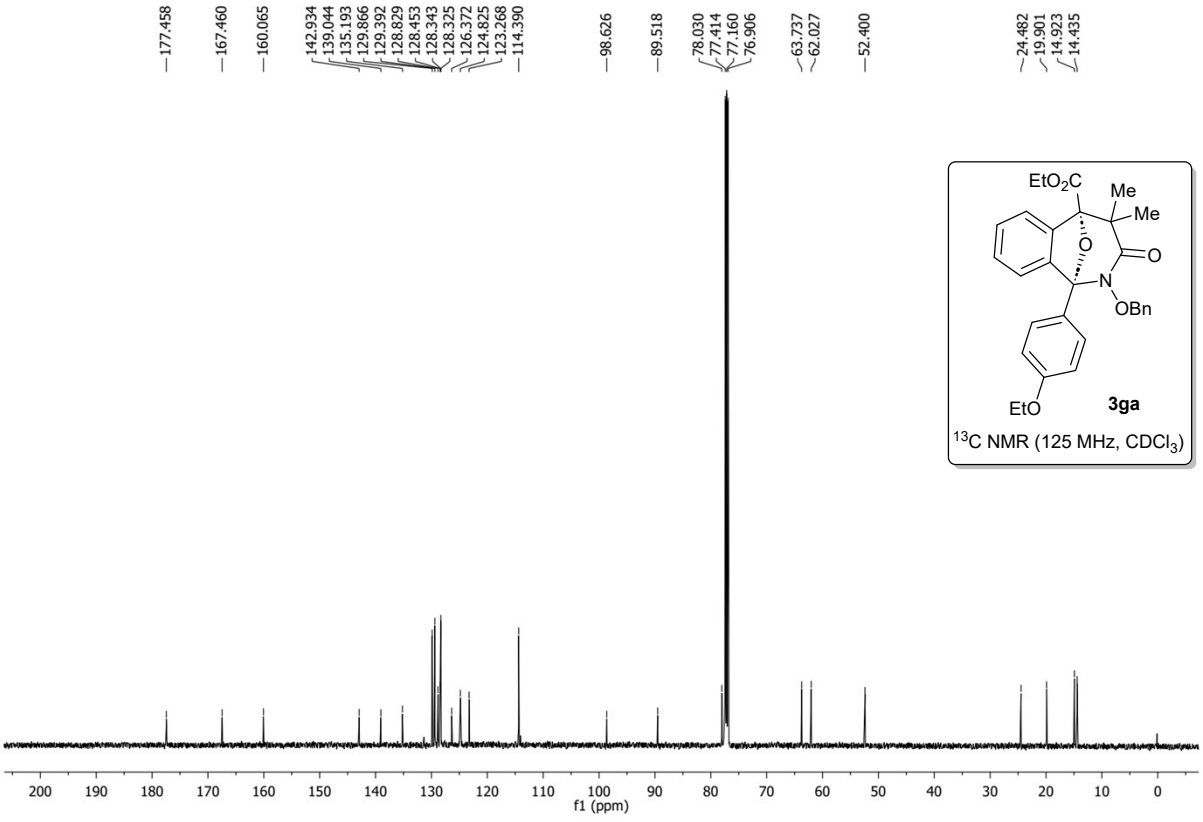


KV-407-1H



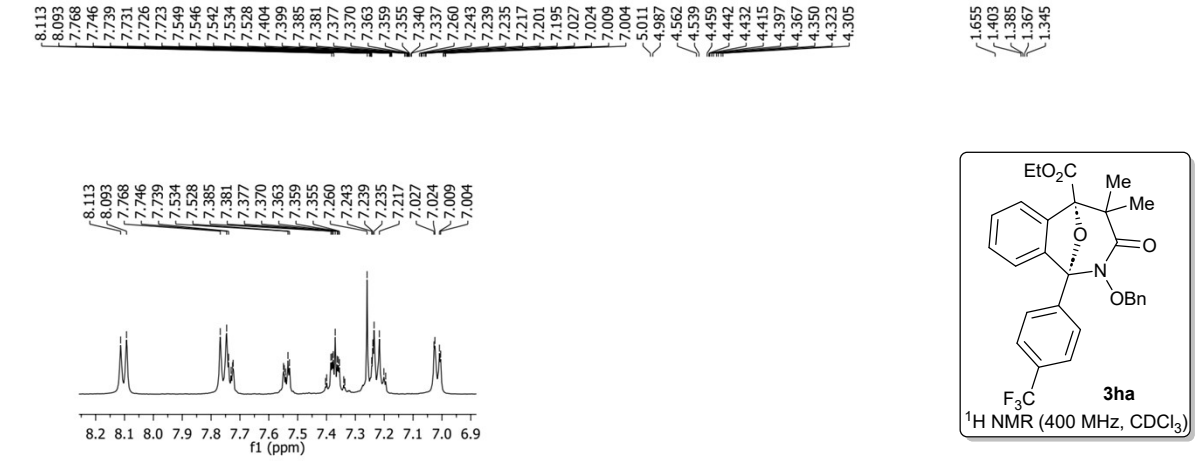
^{1}H NMR (400 MHz, $CDCl_3$)

KV-407-13C



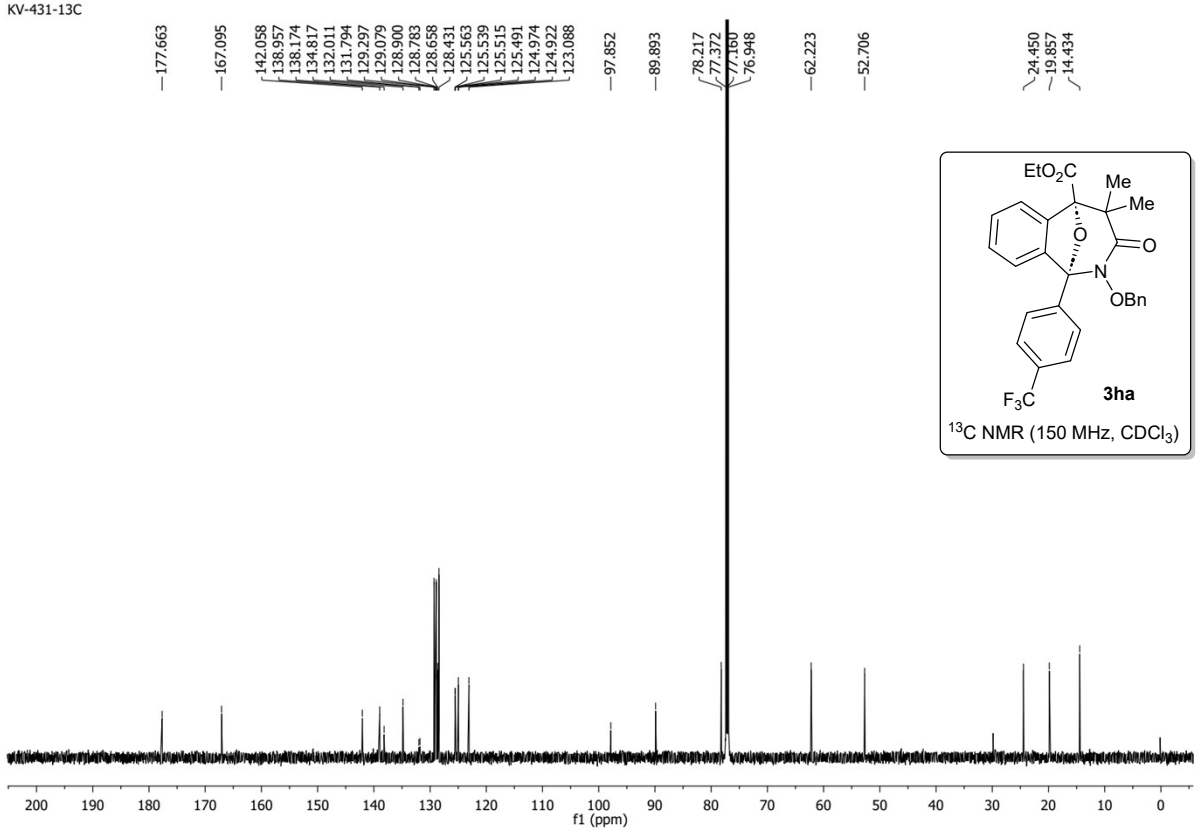
^{13}C NMR (125 MHz, $CDCl_3$)

KV-431-1H



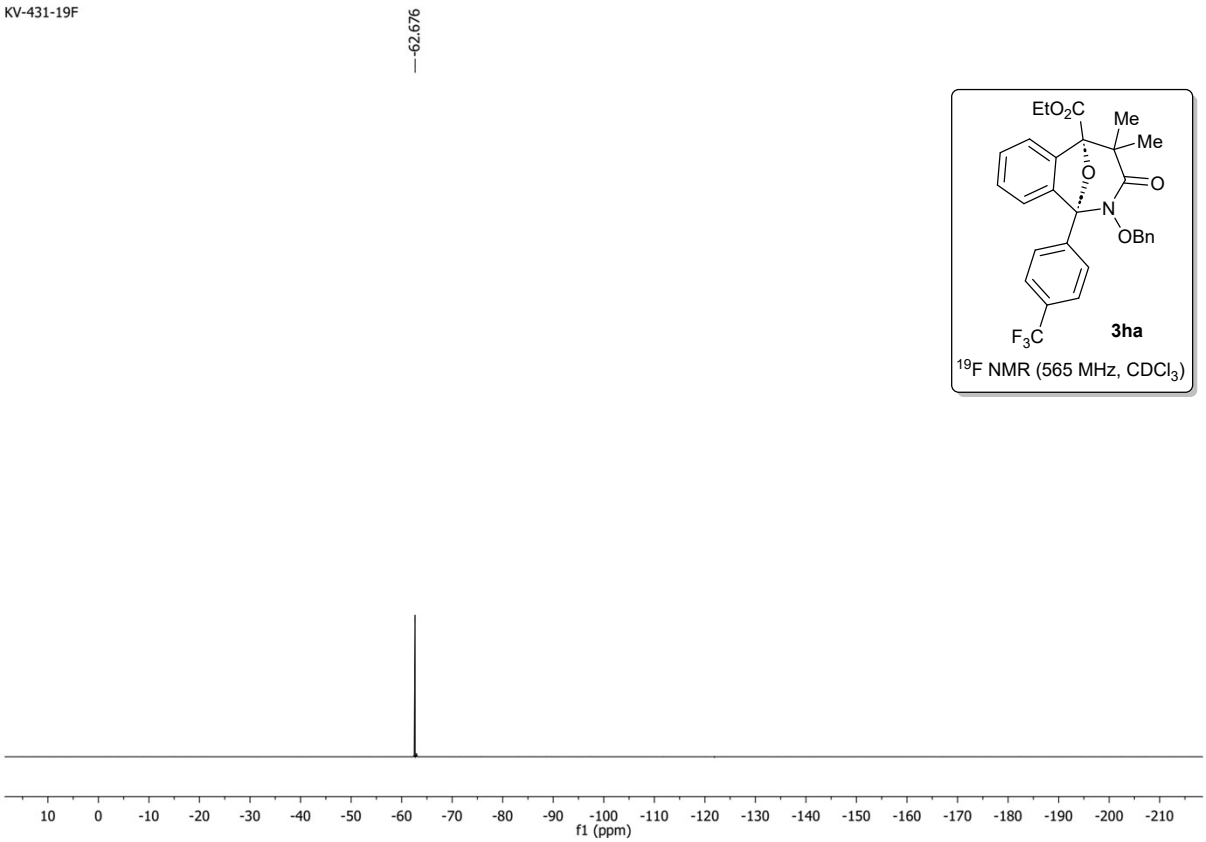
^{1}H NMR (400 MHz, $CDCl_3$)

KV-431-13C



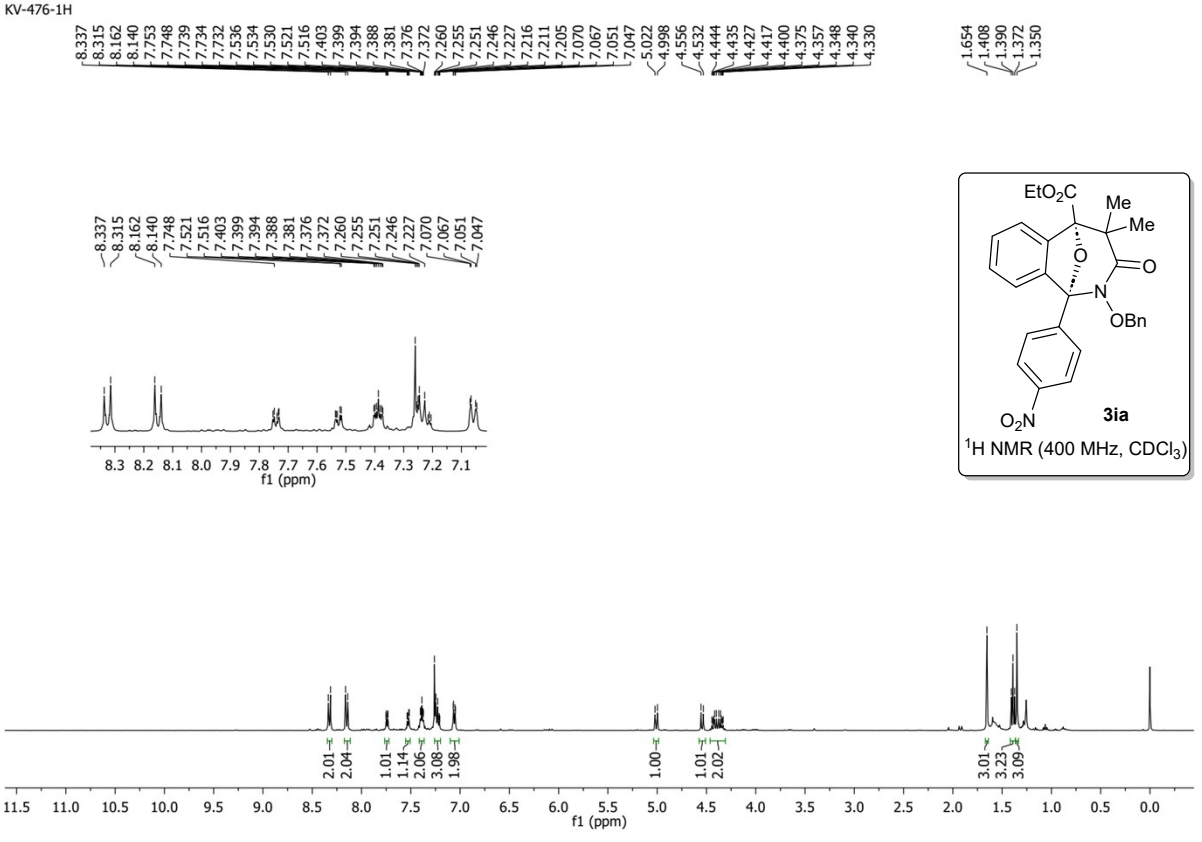
^{13}C NMR (150 MHz, $CDCl_3$)

KV-431-19F



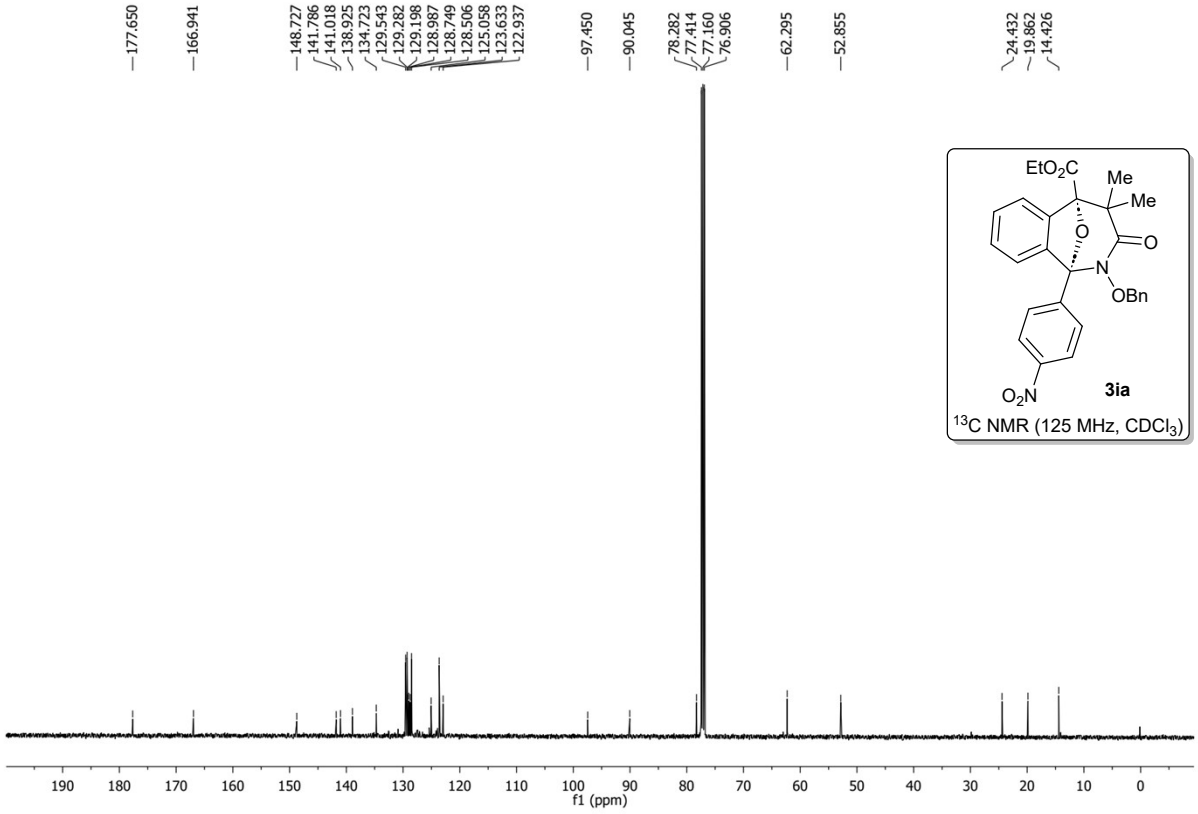
^{19}F NMR (565 MHz, $CDCl_3$)

KV-476-1H



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

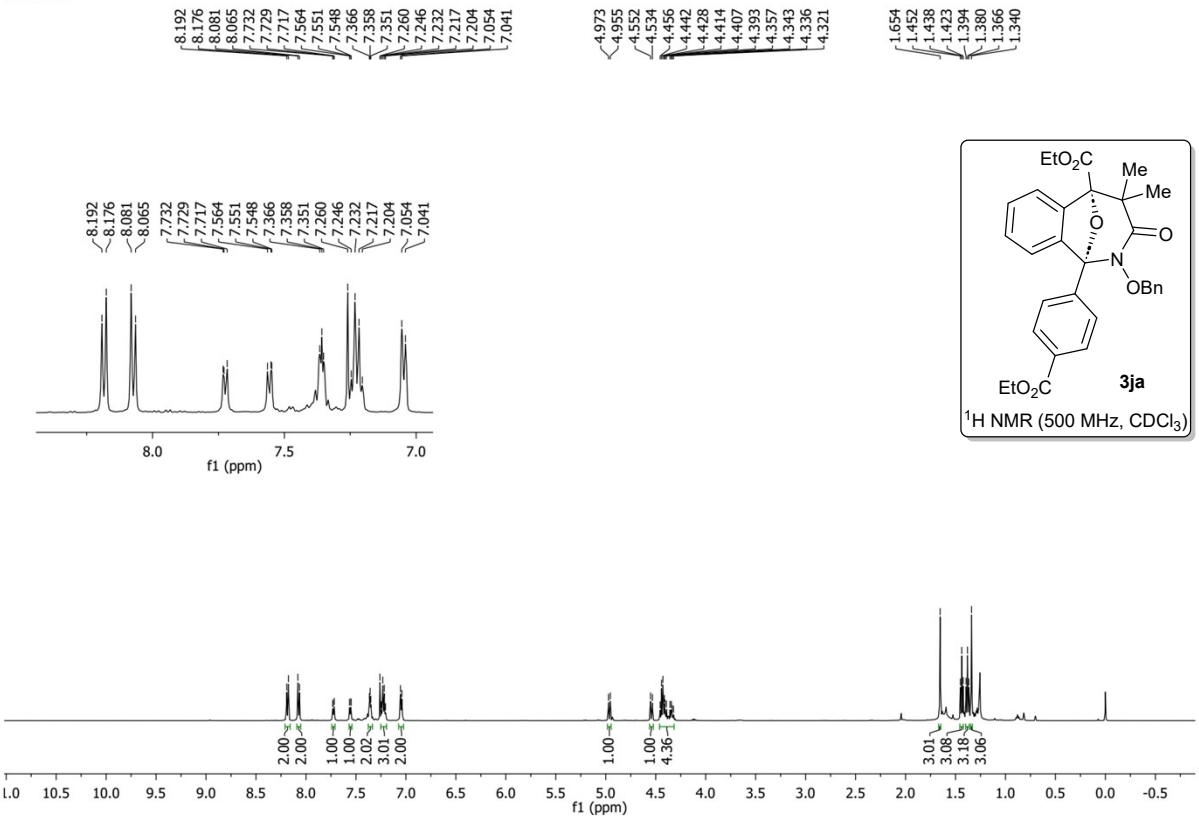
KV-476-13C



3ia

^{13}C NMR (125 MHz, $CDCl_3$)

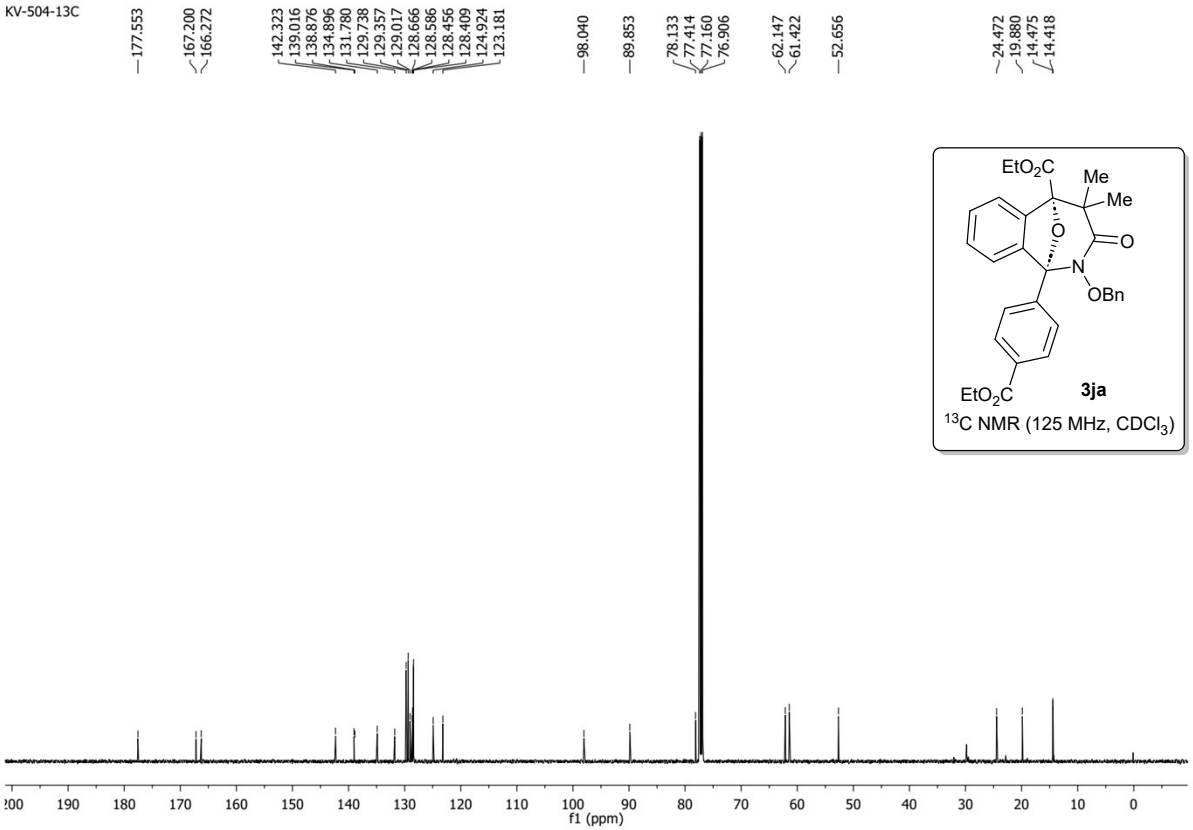
KV-504-1H



3ja

^{1}H NMR (500 MHz, $CDCl_3$)

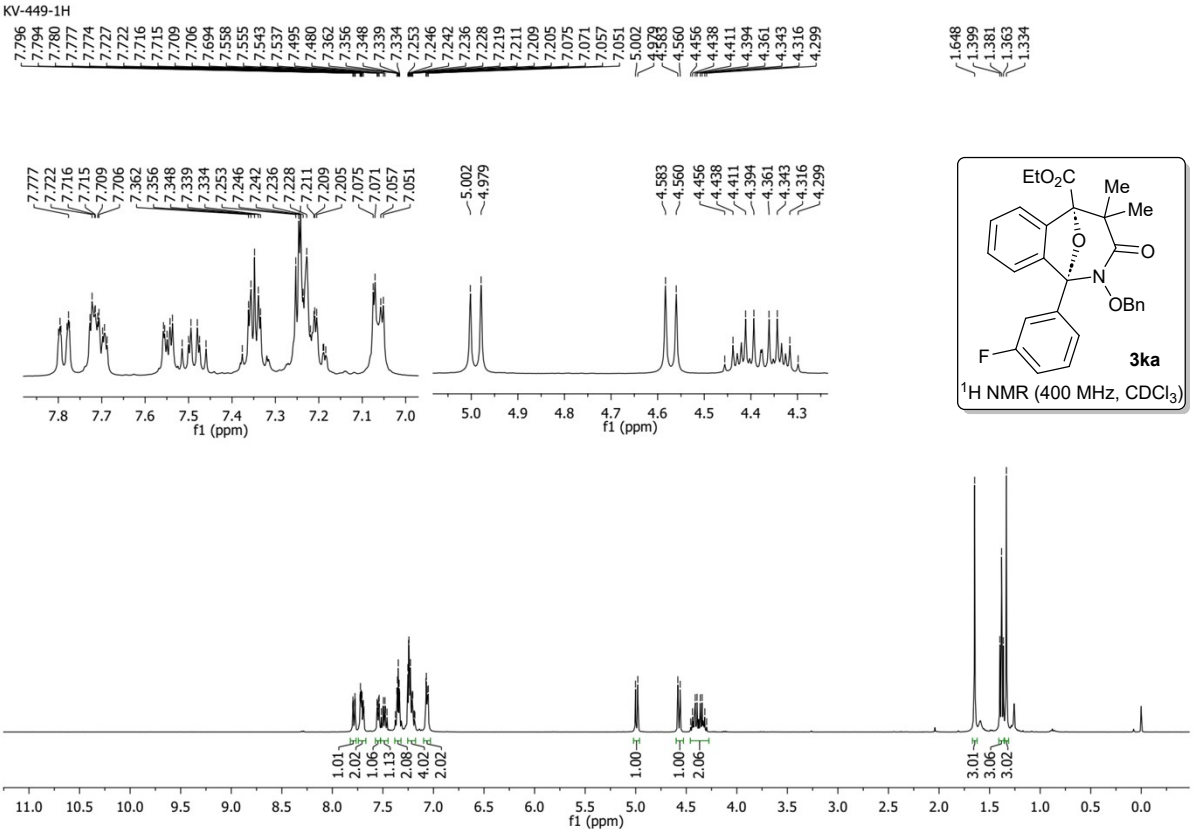
KV-504-13C



3ja

^{13}C NMR (125 MHz, $CDCl_3$)

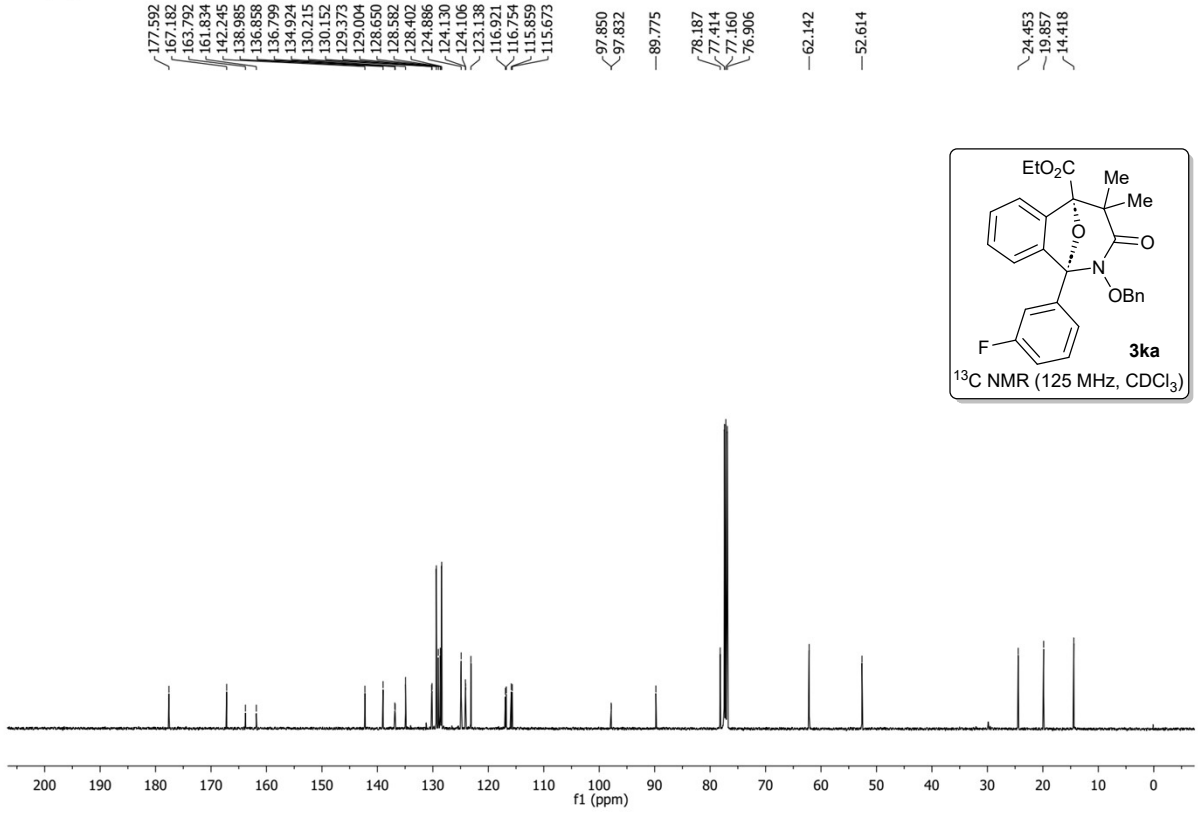
KV-449-1H



3ka

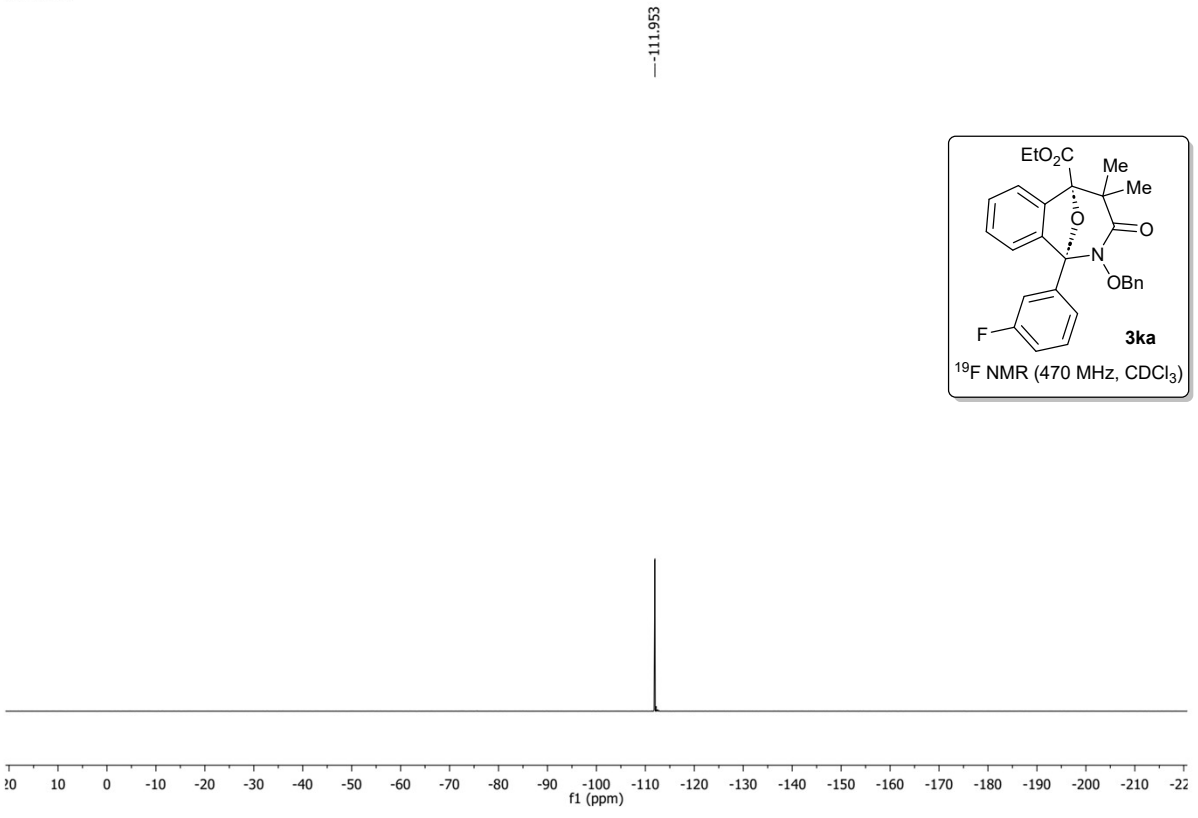
^{1}H NMR (400 MHz, $CDCl_3$)

KV-449-13C



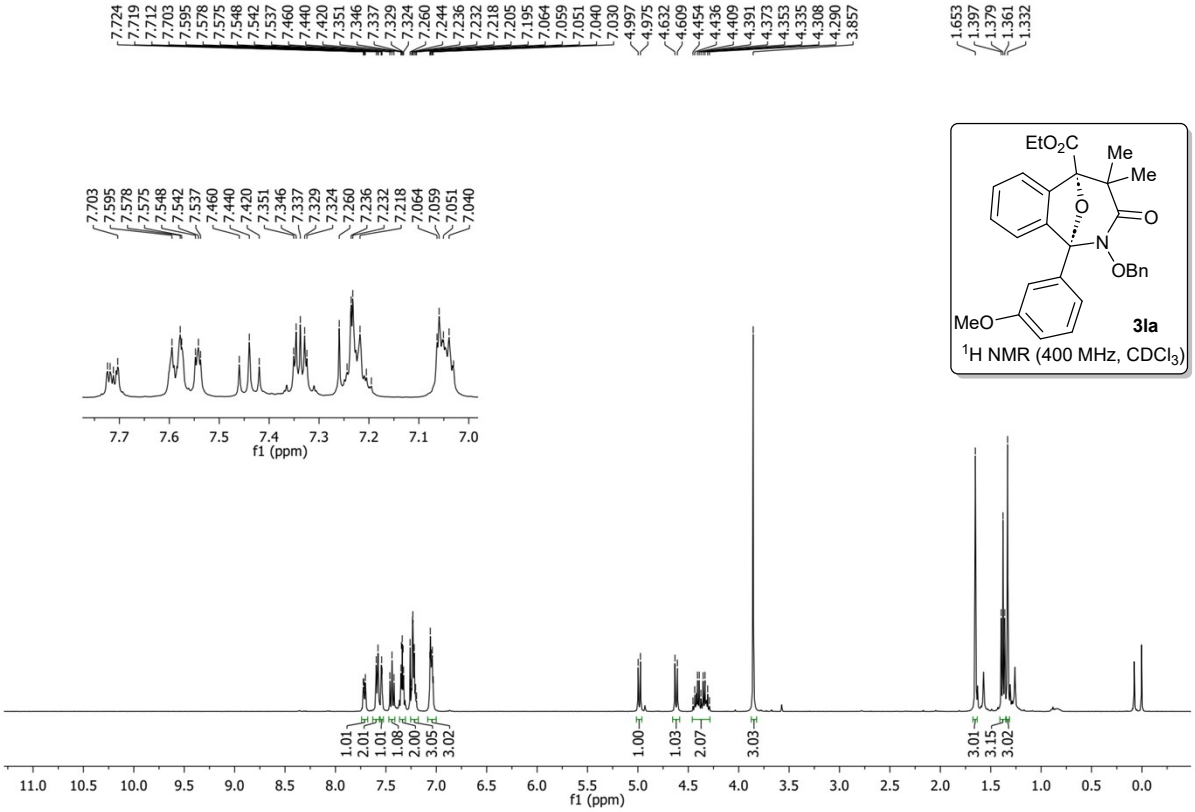
^{13}C NMR (125 MHz, $CDCl_3$)

KV-449-19F



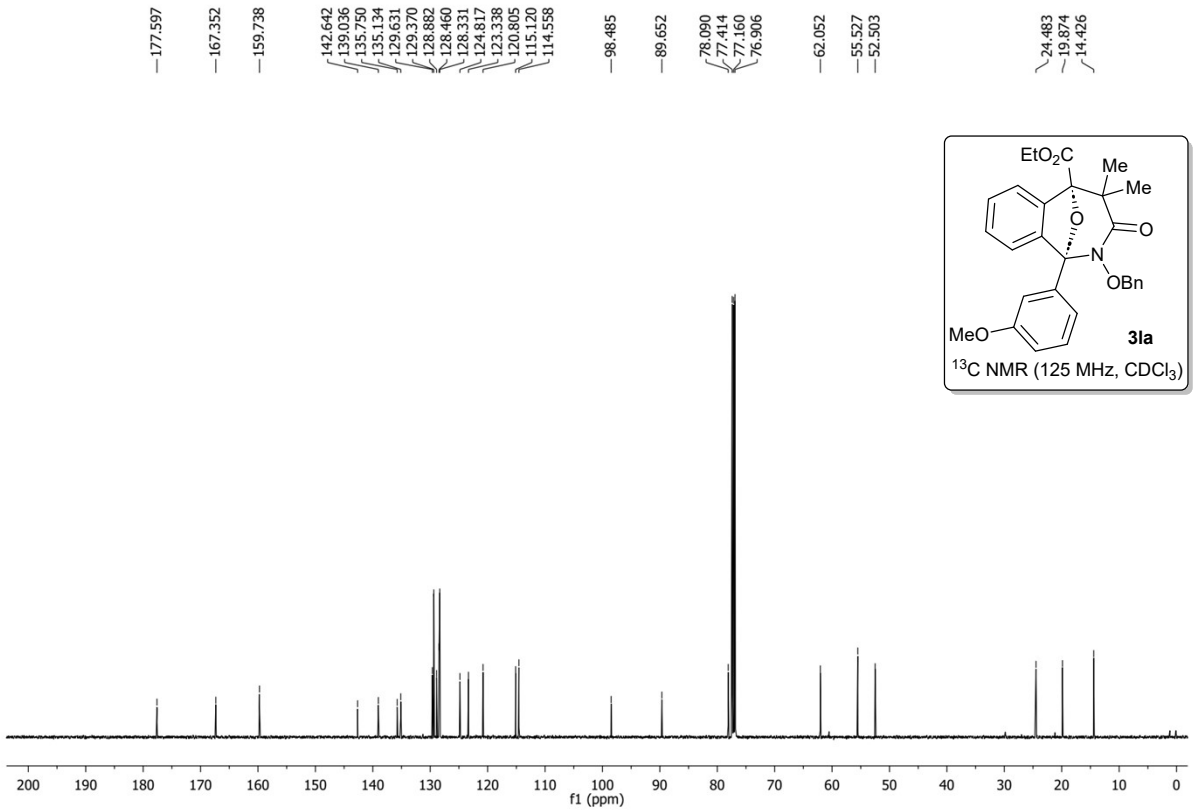
^{19}F NMR (470 MHz, $CDCl_3$)

KV-469-1H



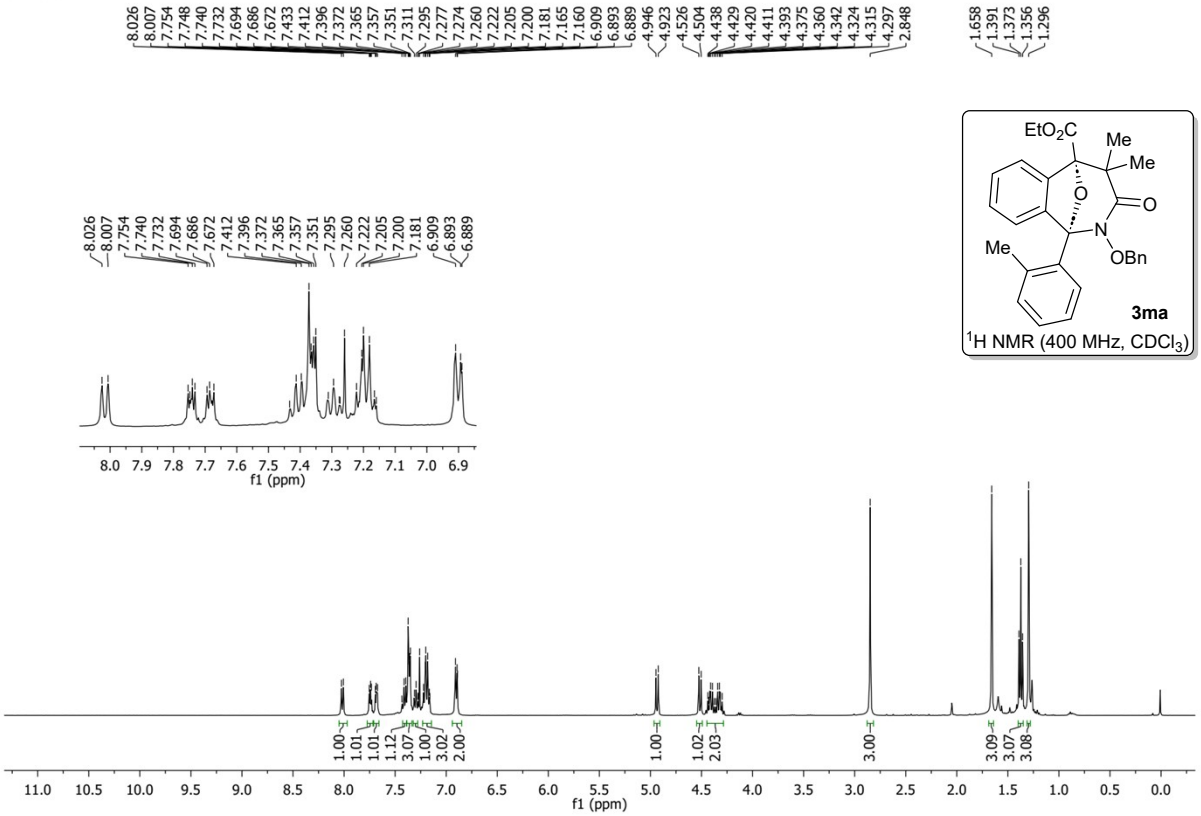
^{1}H NMR (400 MHz, $CDCl_3$)

KV-469-13C



^{13}C NMR (125 MHz, $CDCl_3$)

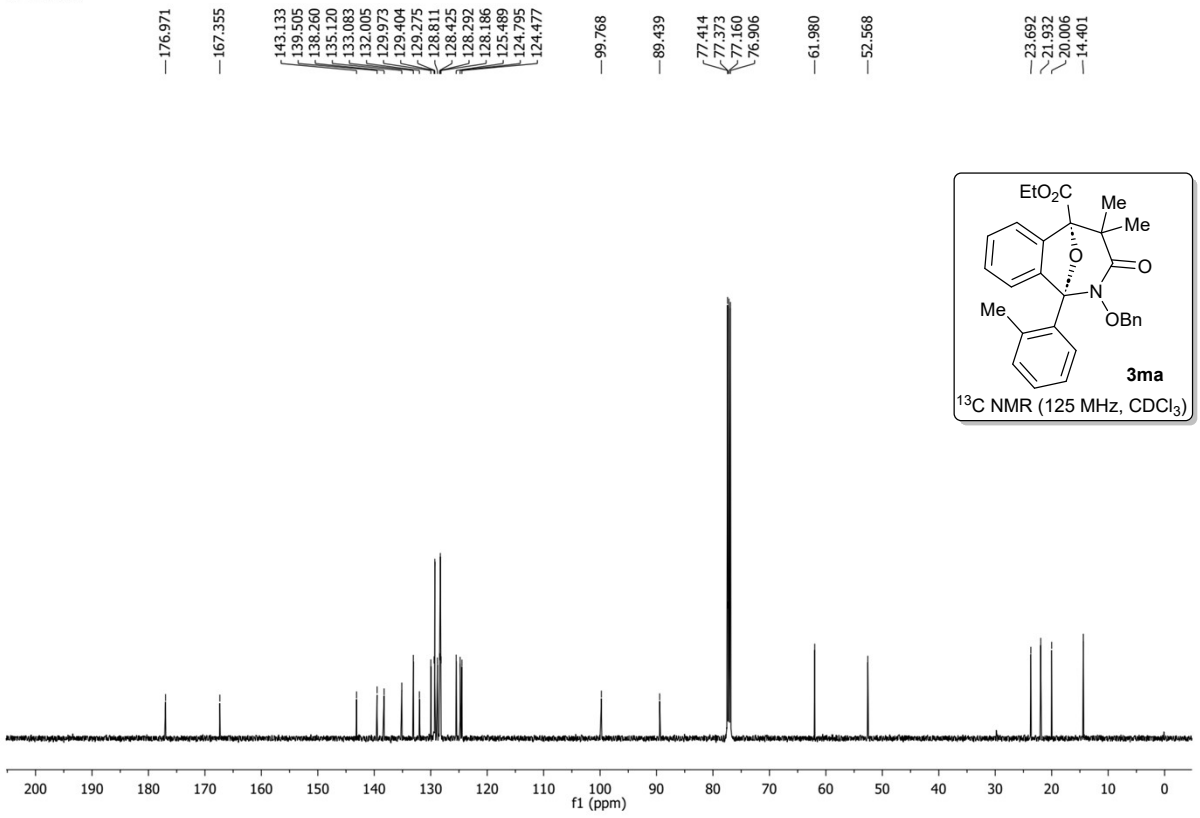
KV-441-1H



3ma

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

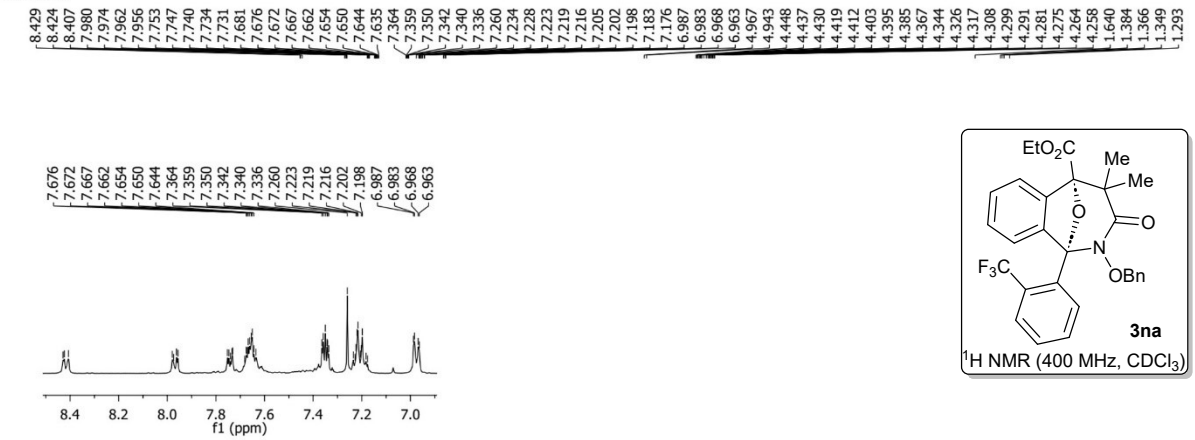
KV-441-13C



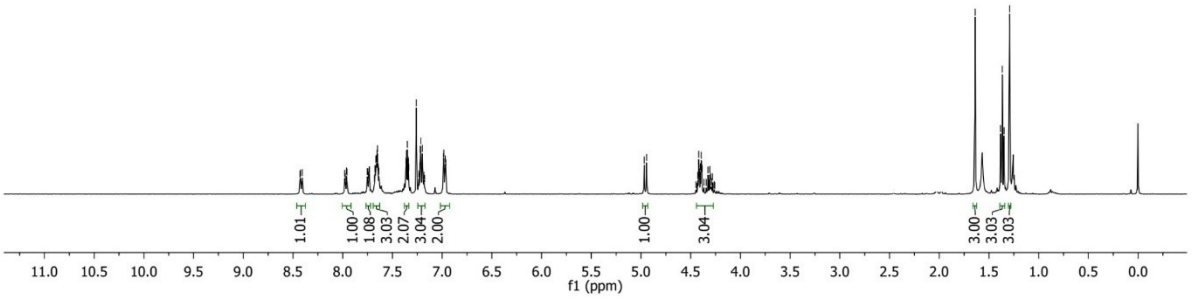
3ma

^{13}C NMR (125 MHz, $CDCl_3$)

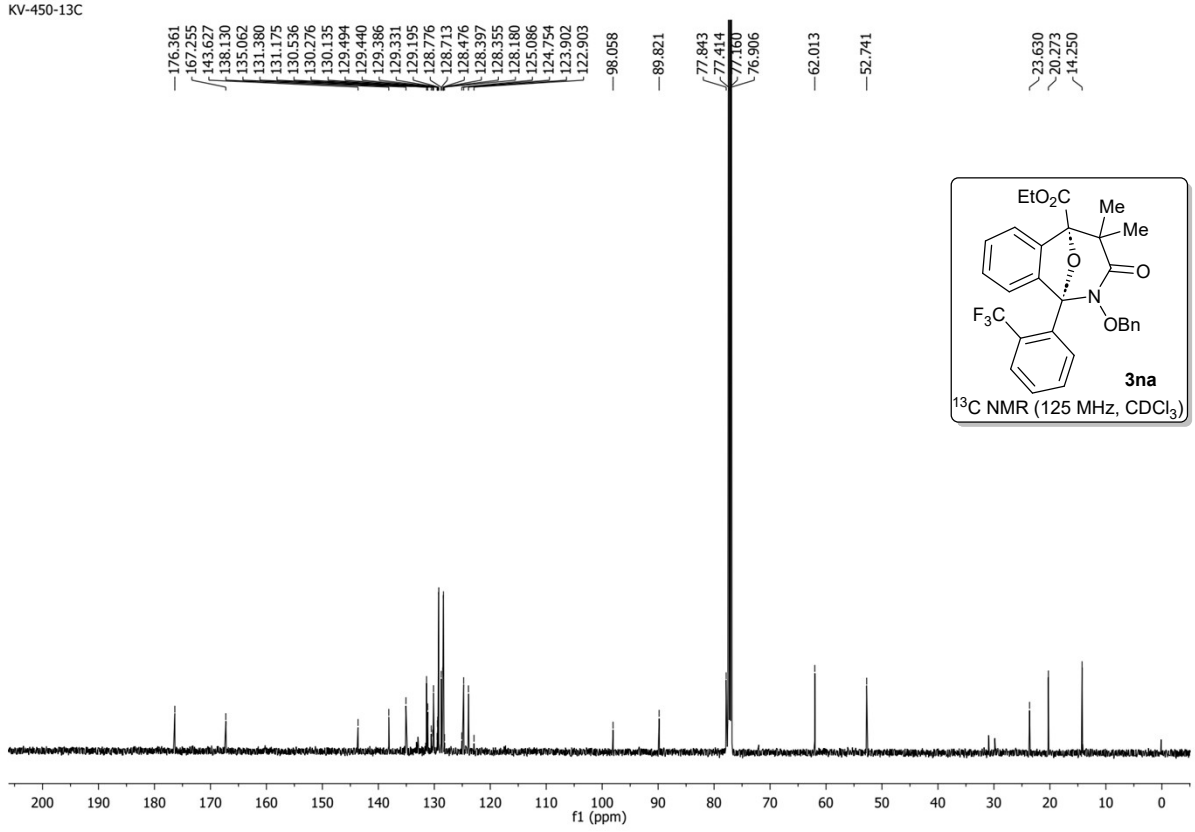
KV-450-1H



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

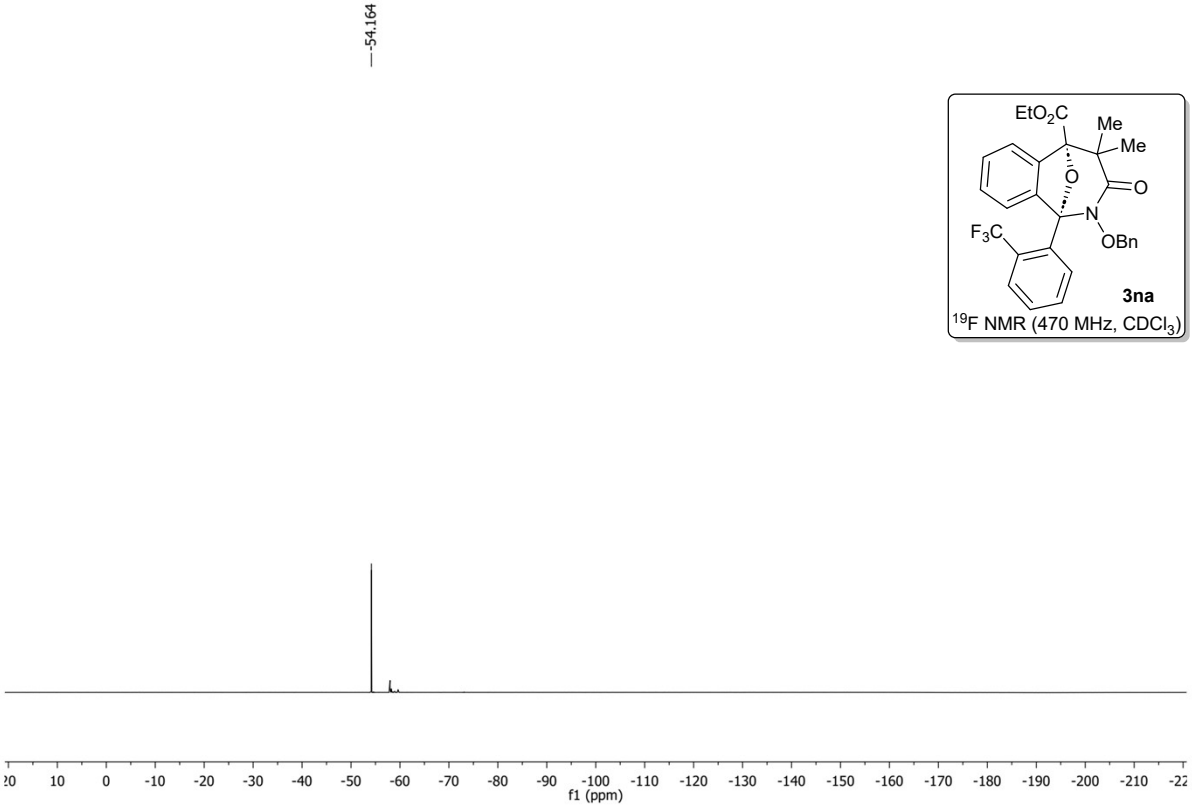


KV-450-13C



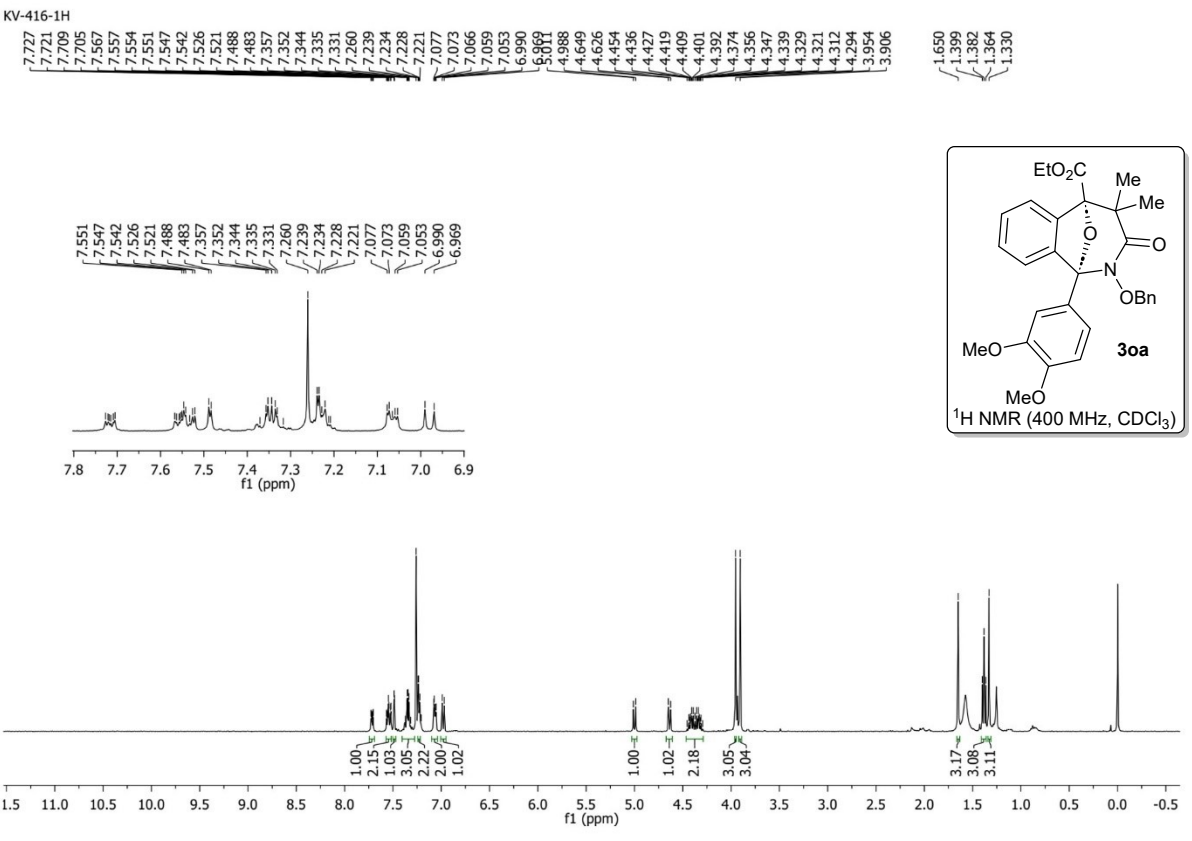
^{13}C NMR (125 MHz, $CDCl_3$)

KV-450-19F



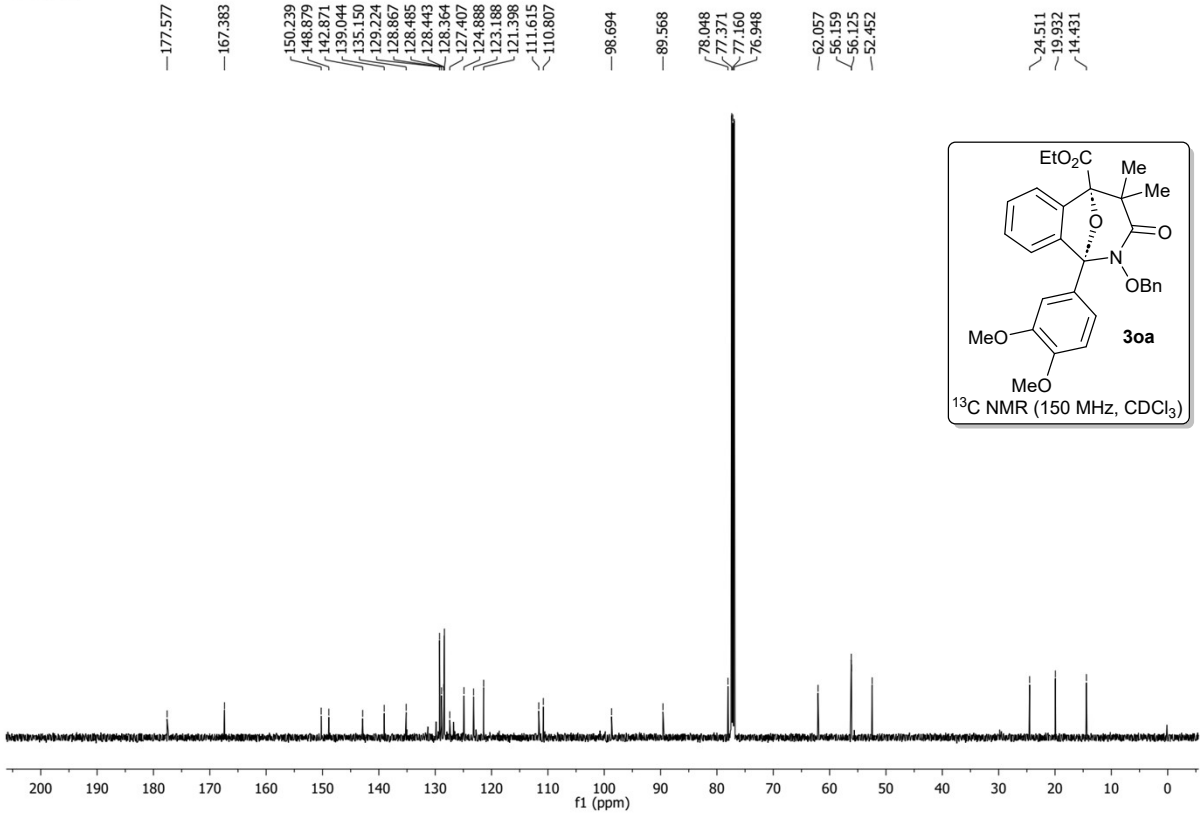
^{19}F NMR (470 MHz, $CDCl_3$)

KV-416-1H



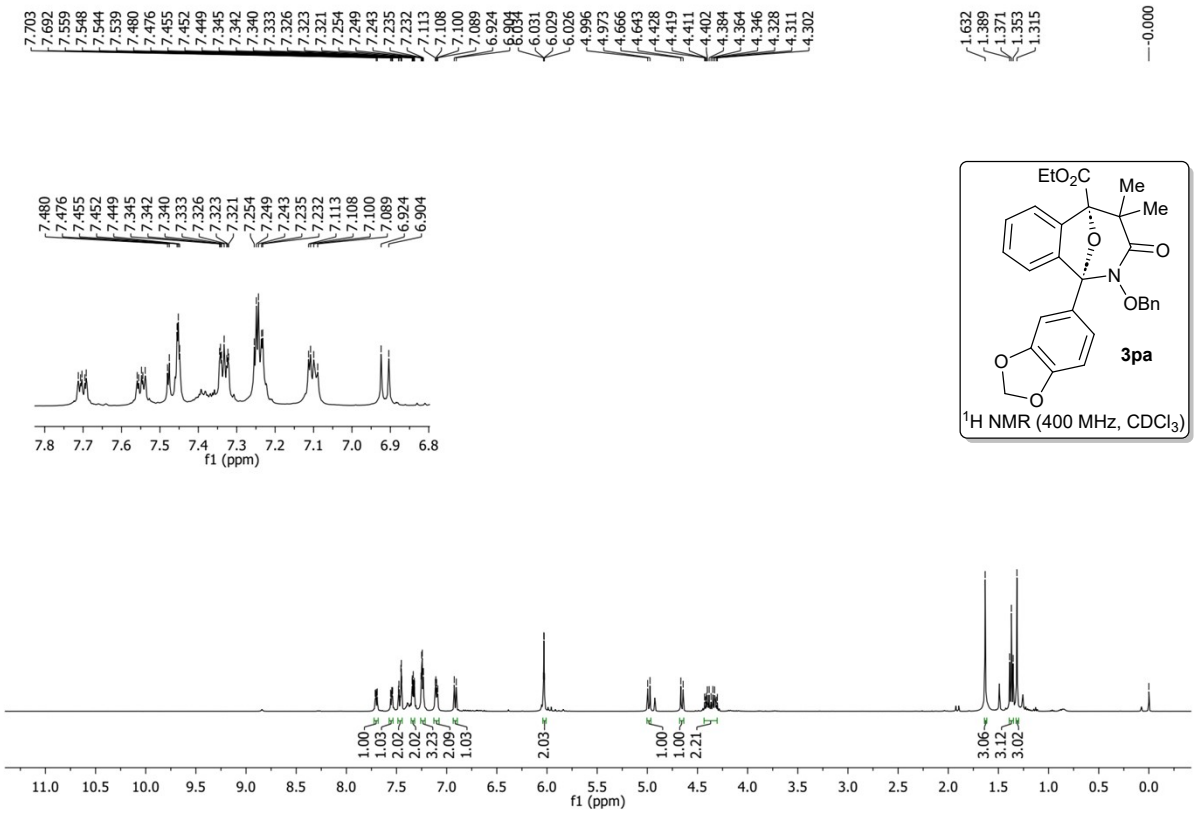
^{1}H NMR (400 MHz, $CDCl_3$)

KV-416-13C



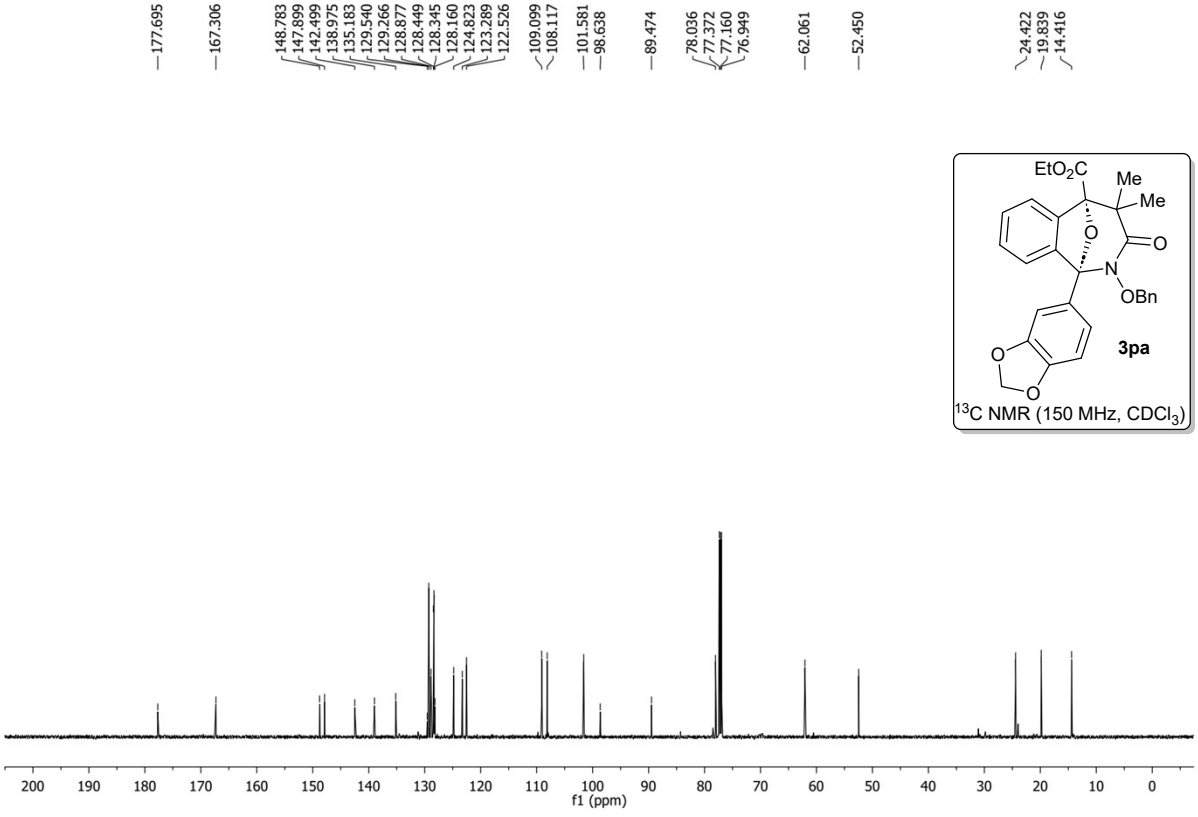
^{13}C NMR (150 MHz, $CDCl_3$)

KV-455-1H

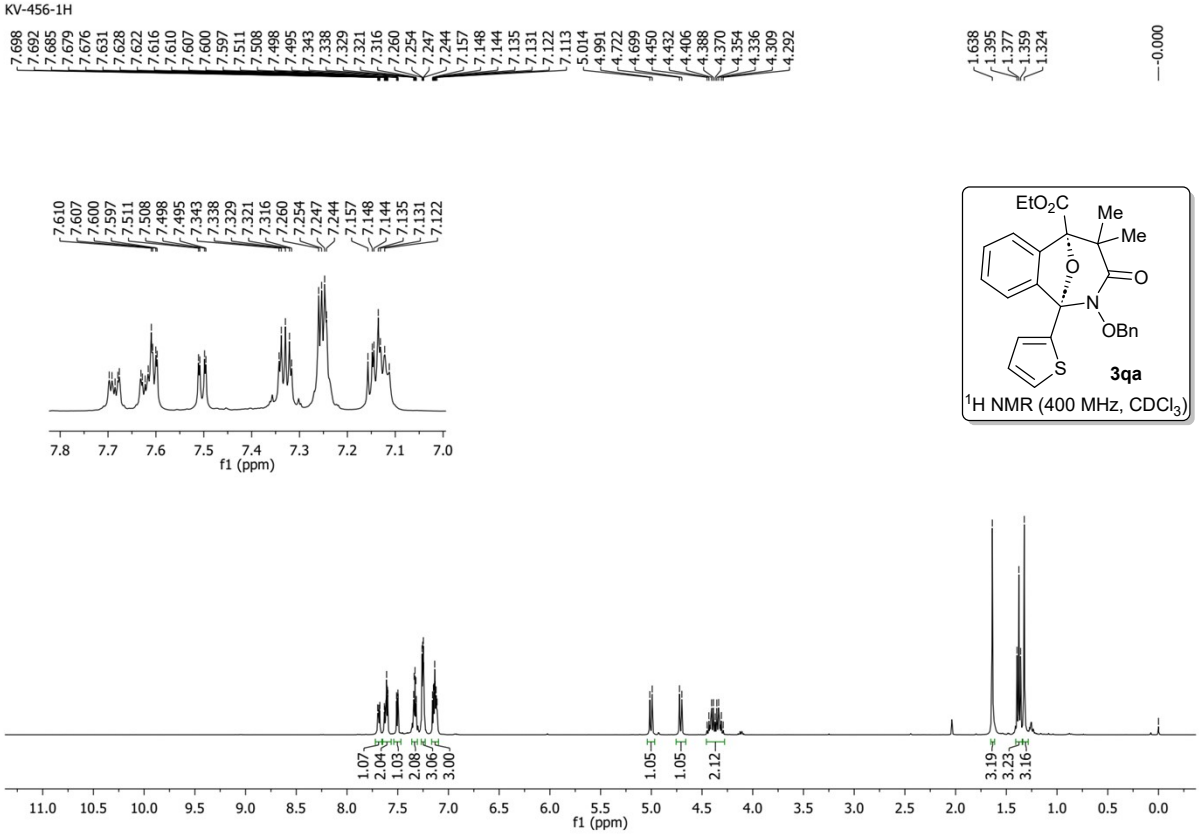


^{1}H NMR (400 MHz, $CDCl_3$)

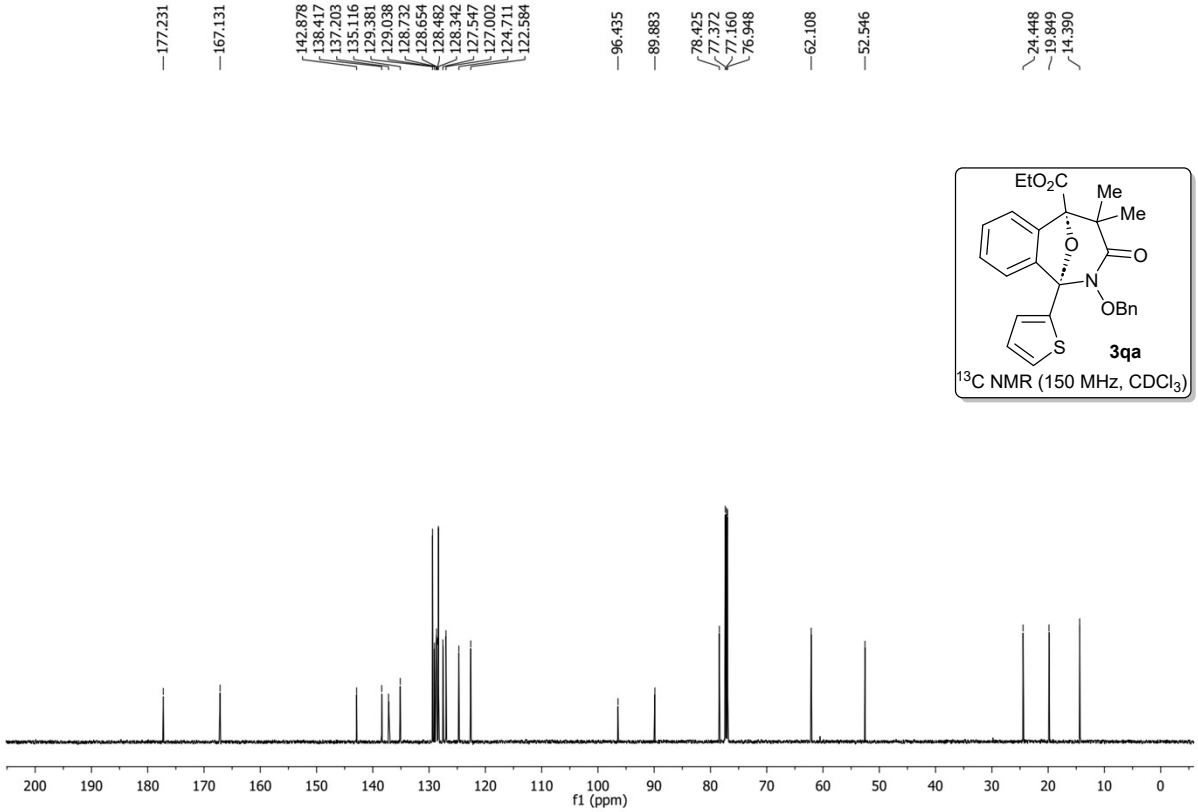
KV-455-13C



KV-456-1H



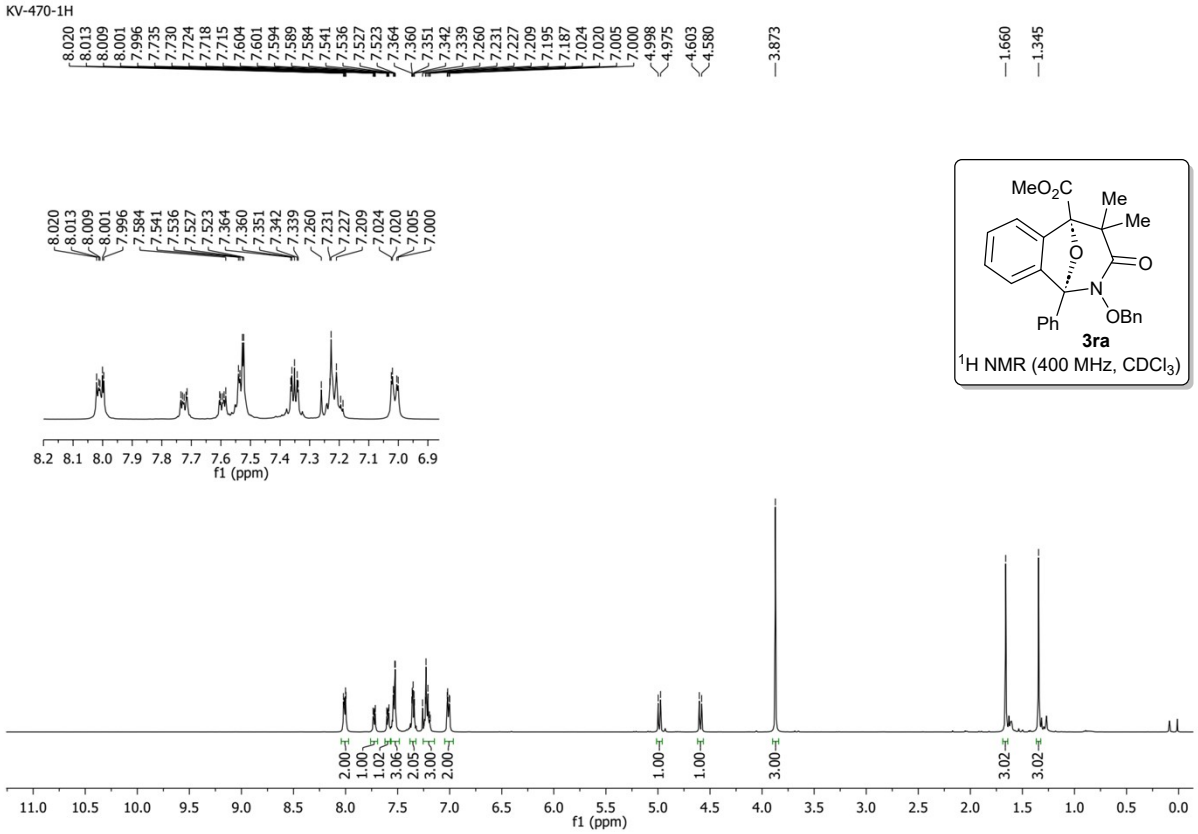
KV-456-13C



3qa

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

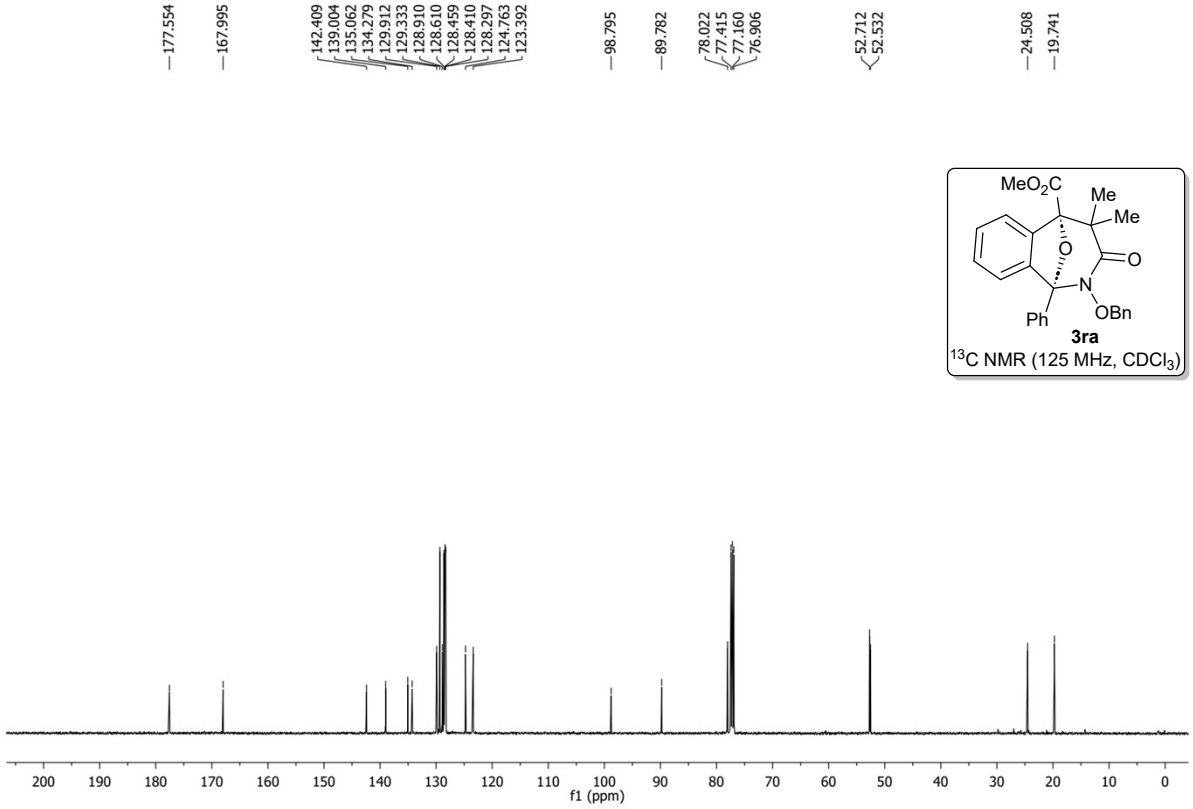
KV-470-1H



3ra

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

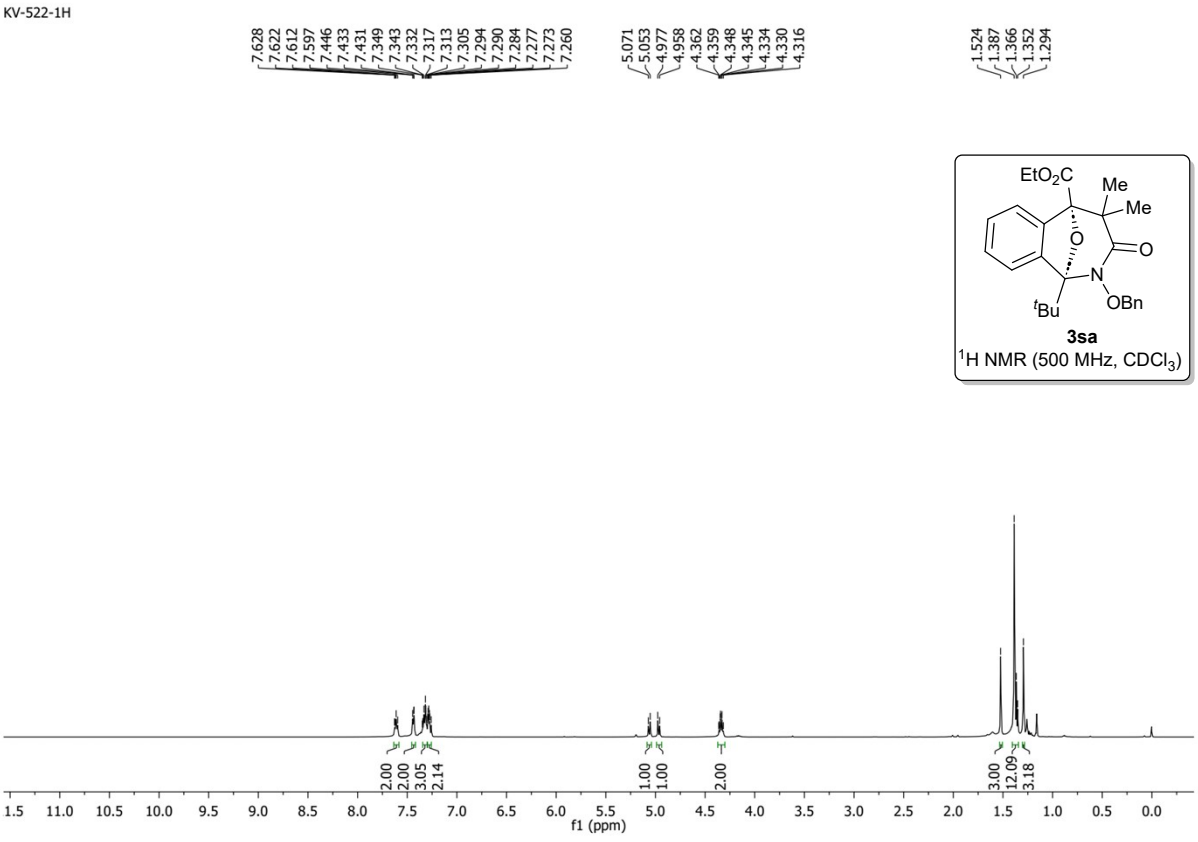
KV-470-13C



3ra

^{13}C NMR (125 MHz, $CDCl_3$)

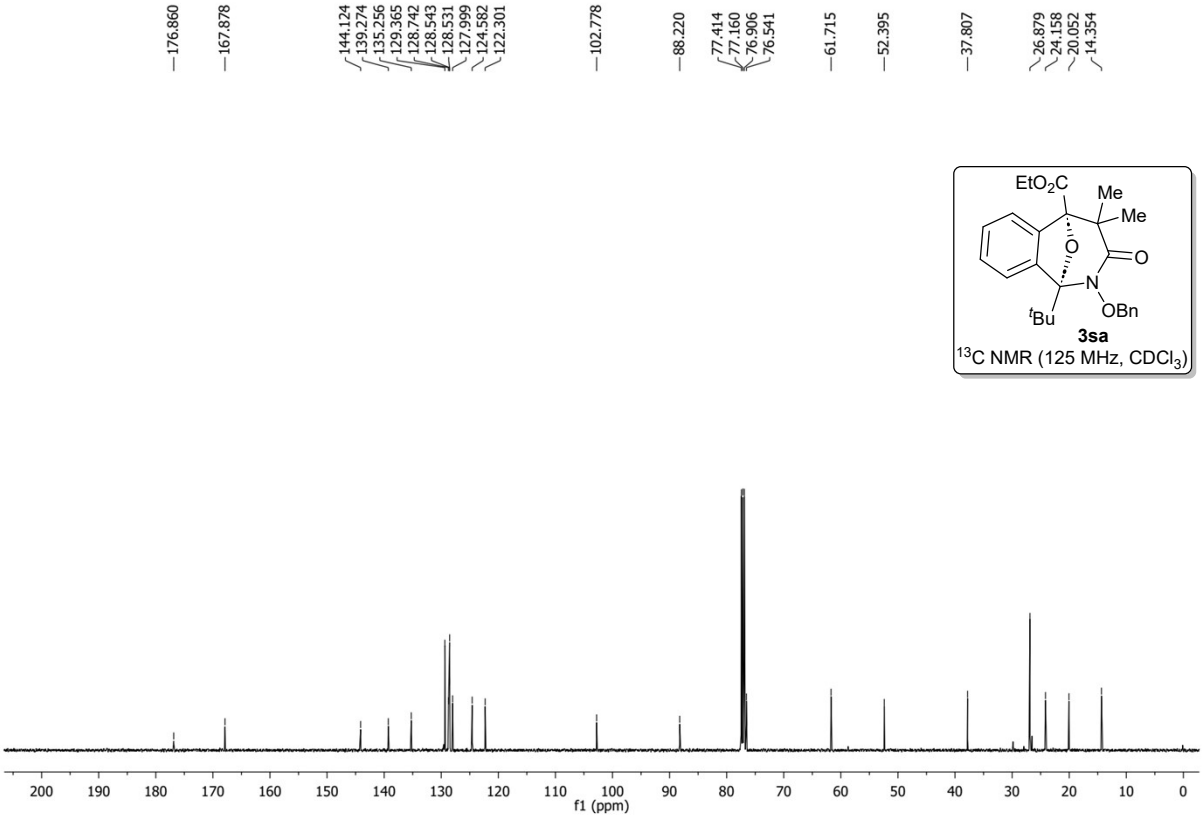
KV-522-1H



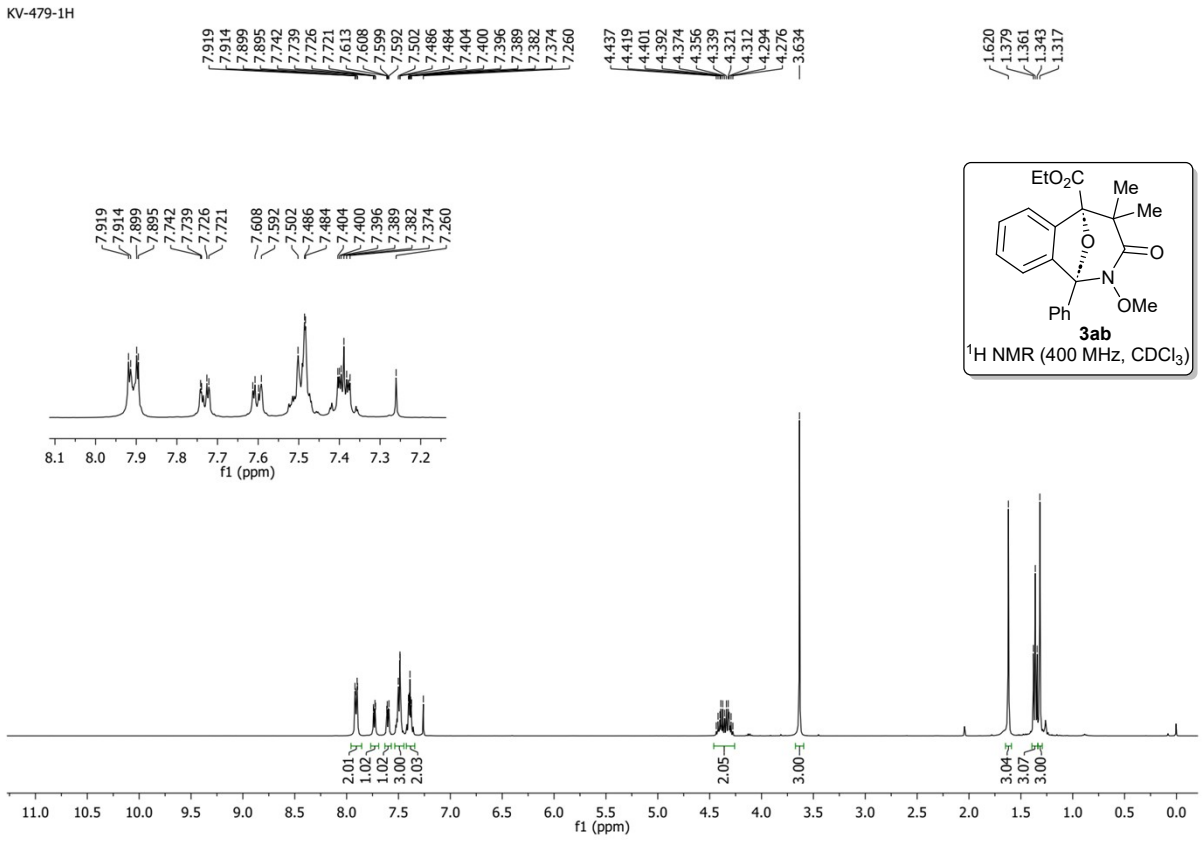
3sa

^{1}H NMR (500 MHz, $CDCl_3$)

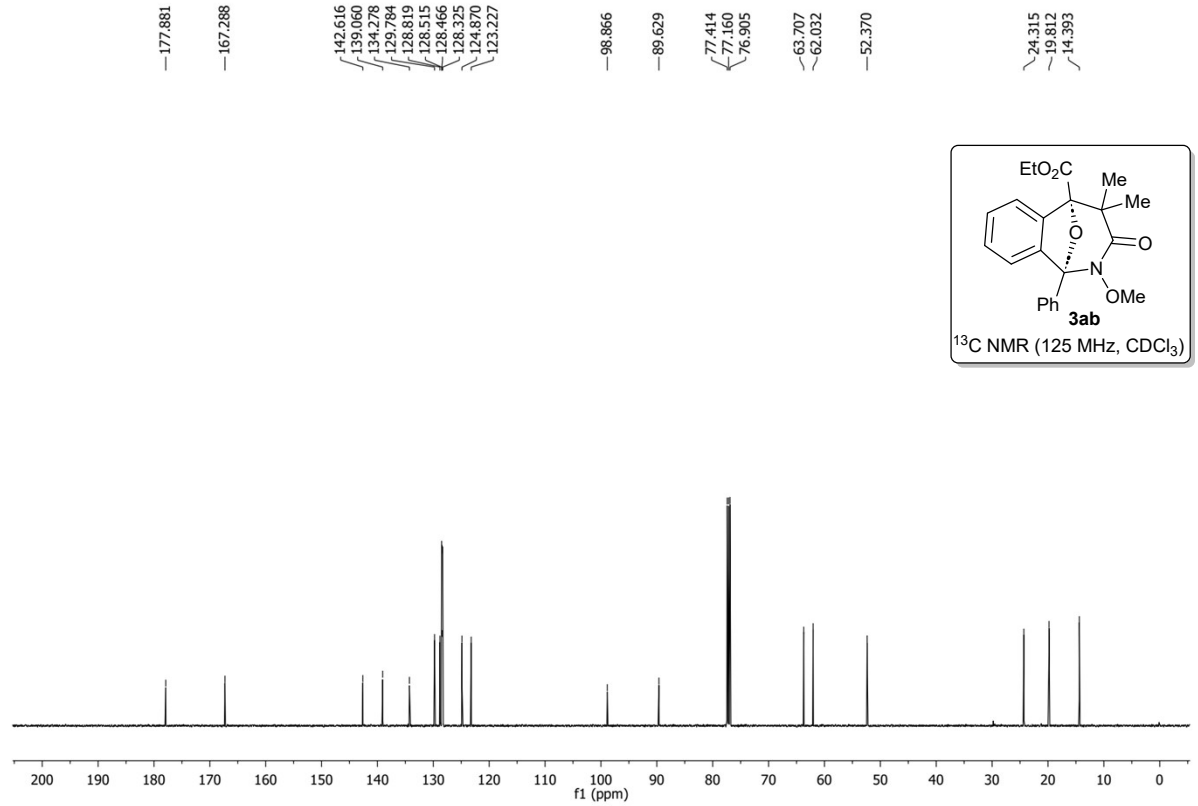
KV-522-13C



KV-479-1H



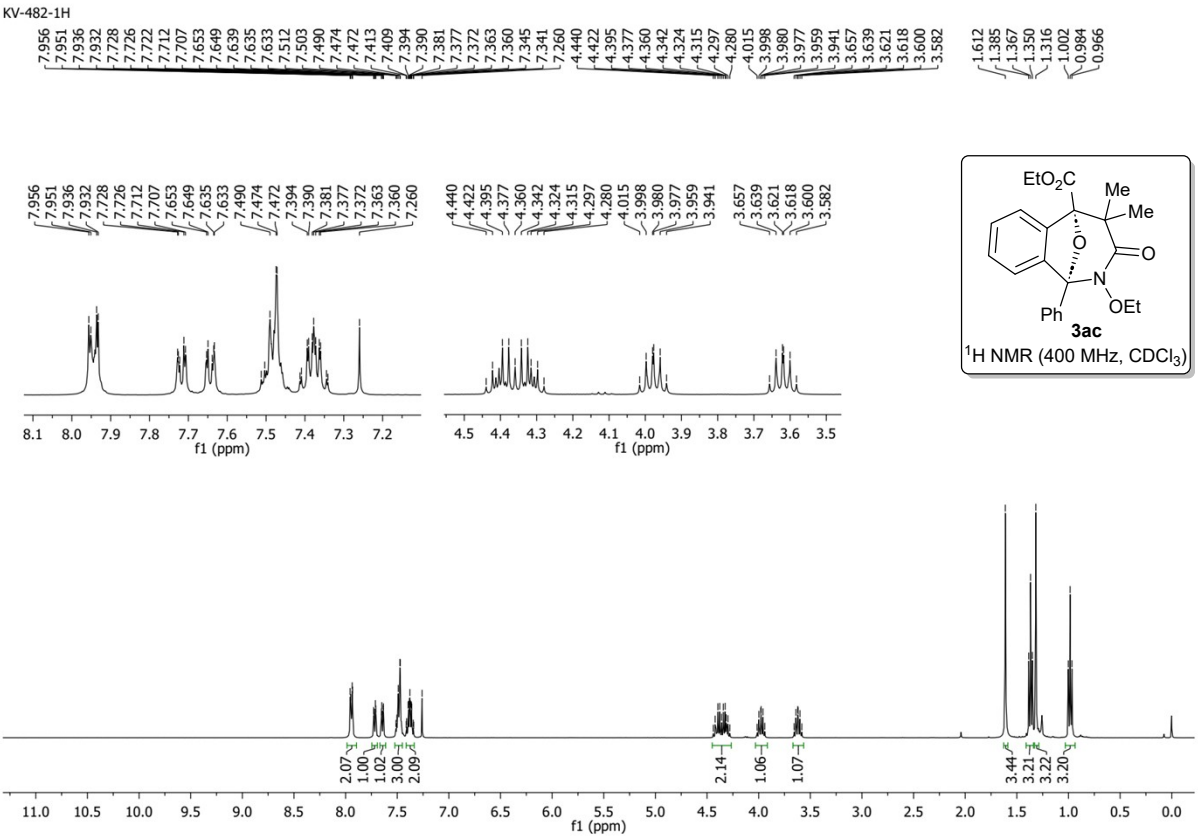
KV-479-13C



3ab

^{13}C NMR (125 MHz, $CDCl_3$)

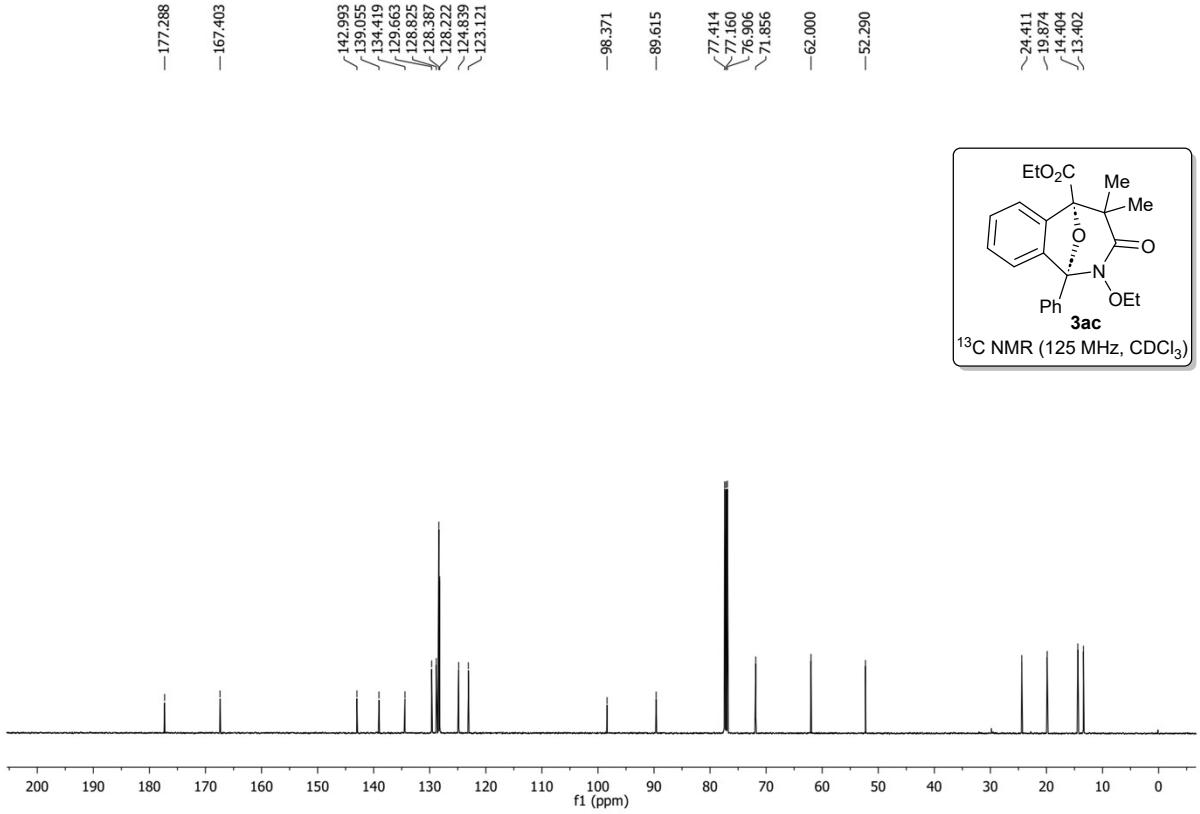
KV-482-1H



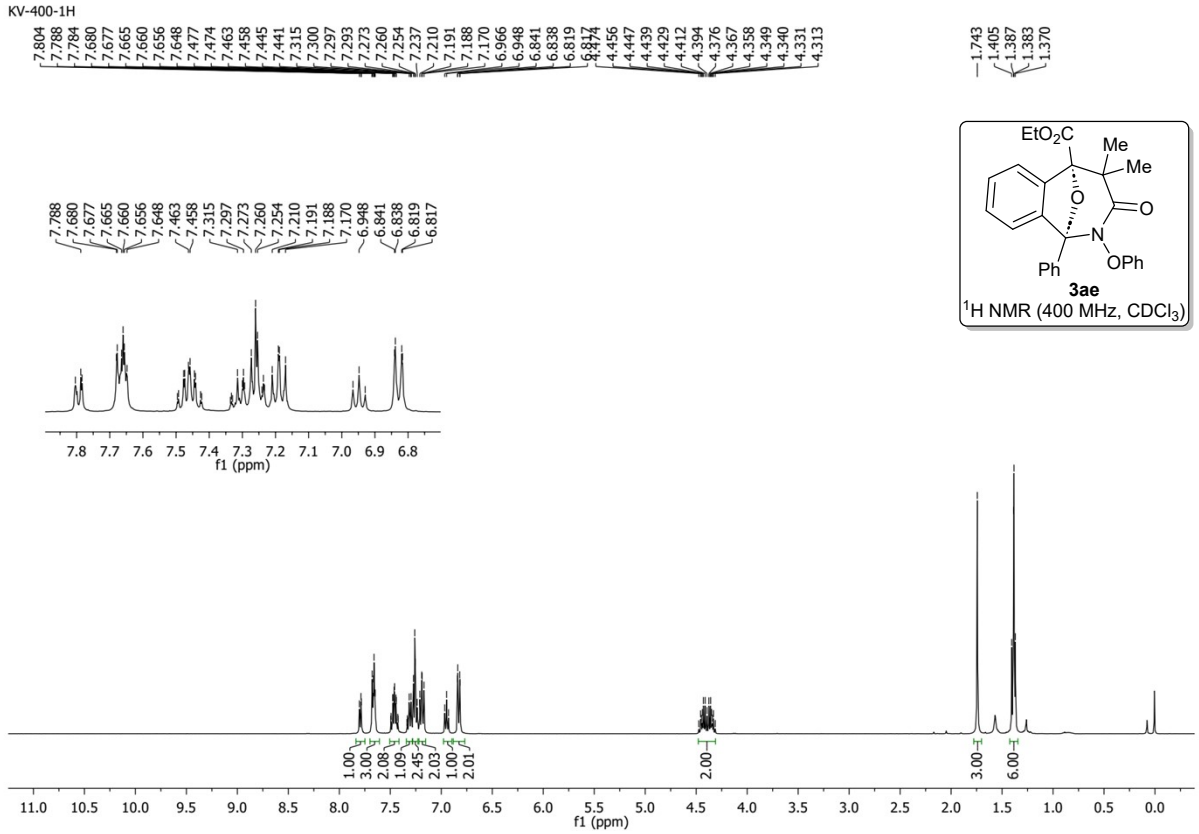
3ac

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

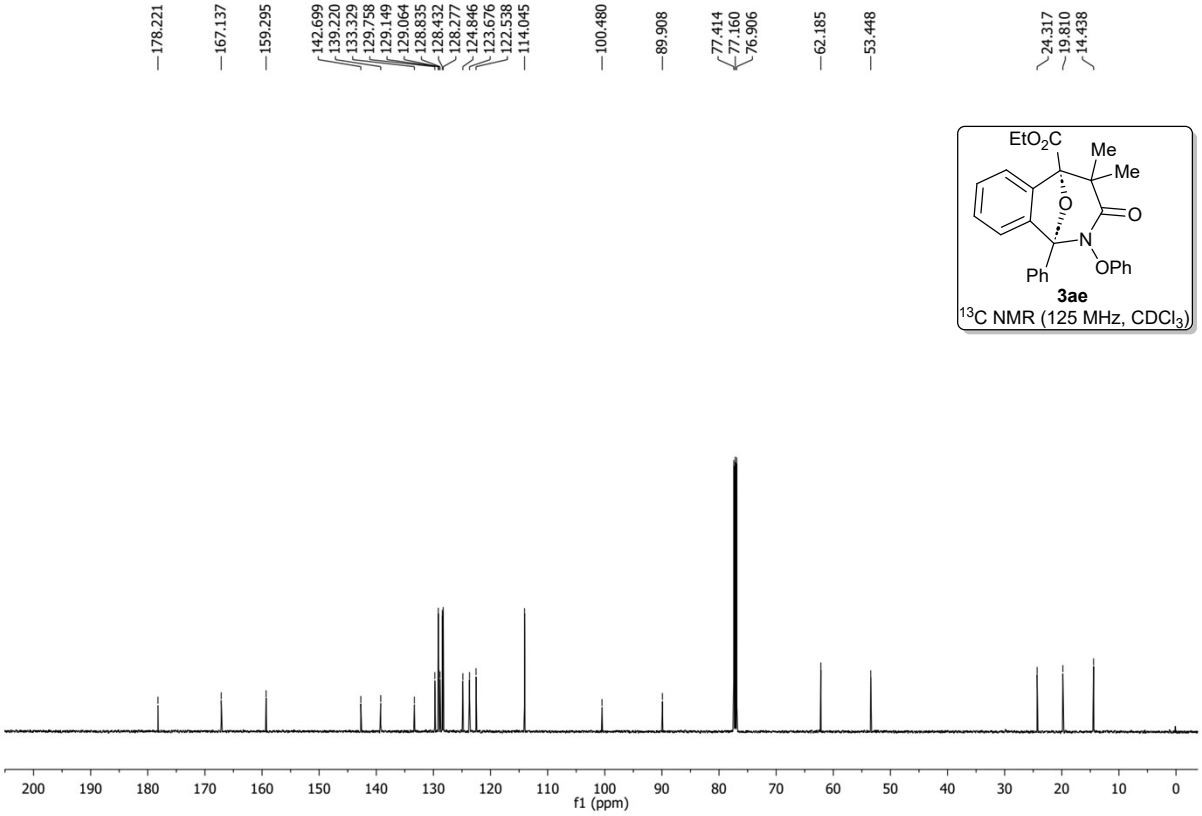
KV-482-13C



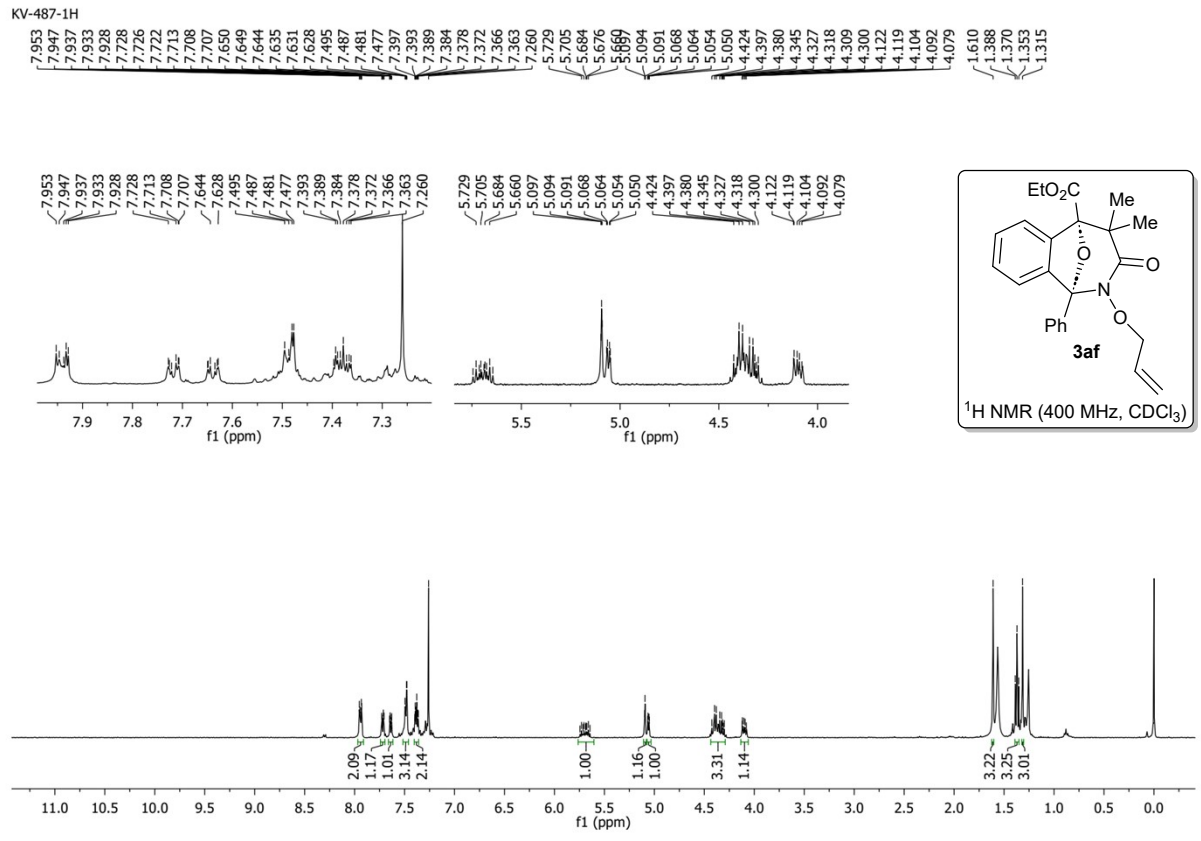
KV-400-1H



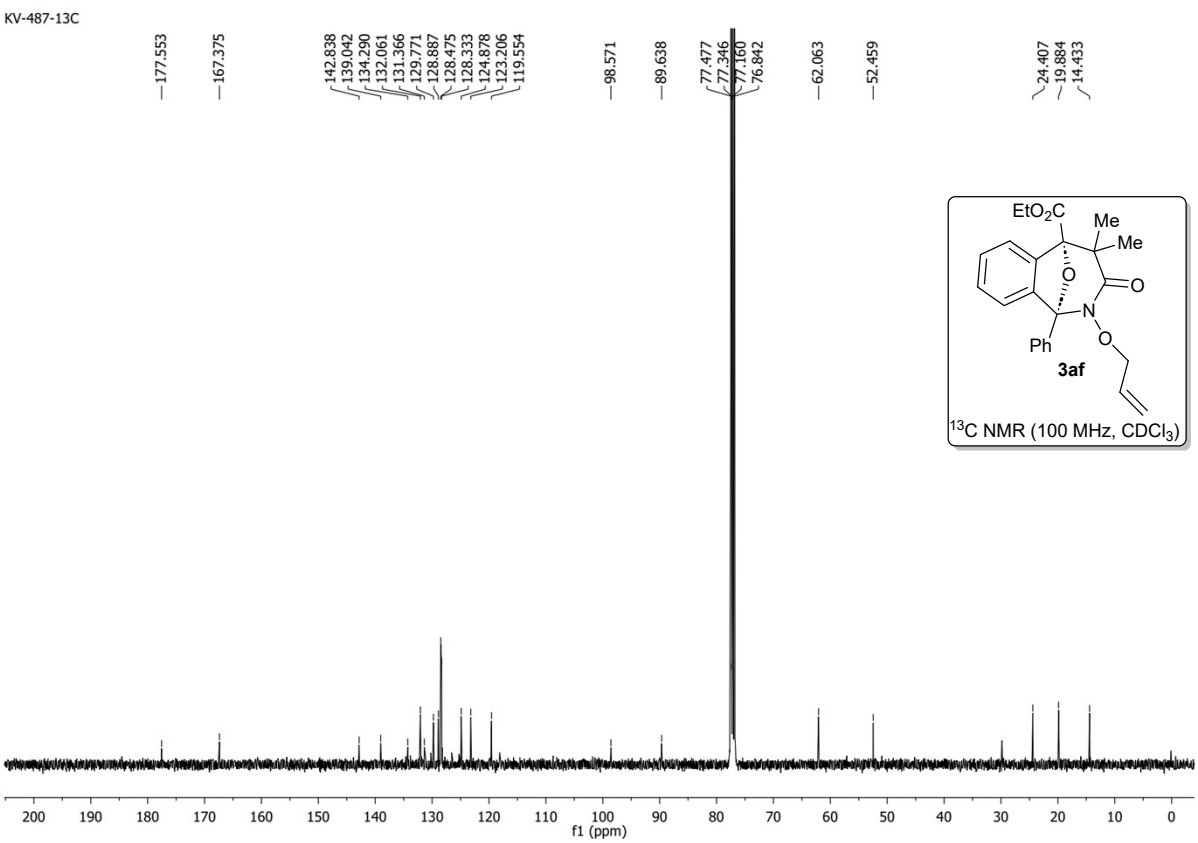
KV-400-13C



KV-487-1H

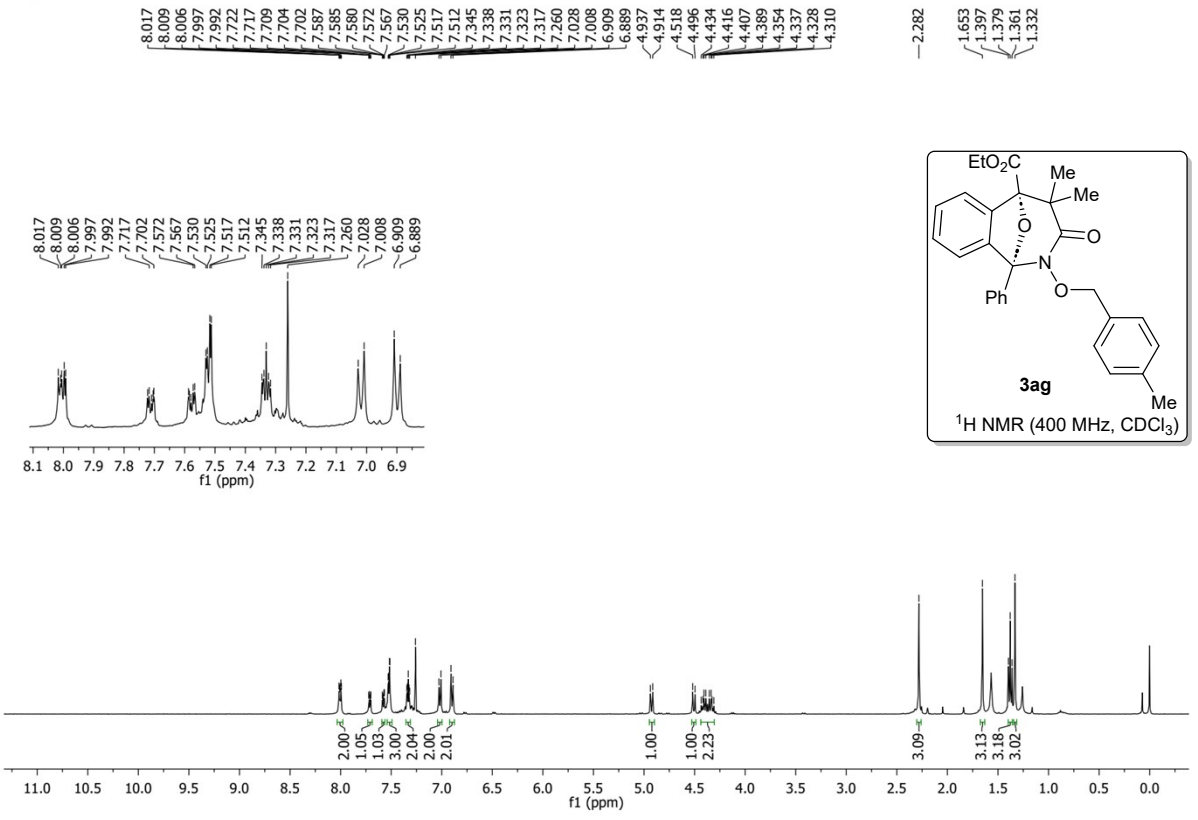


KV-487-13C



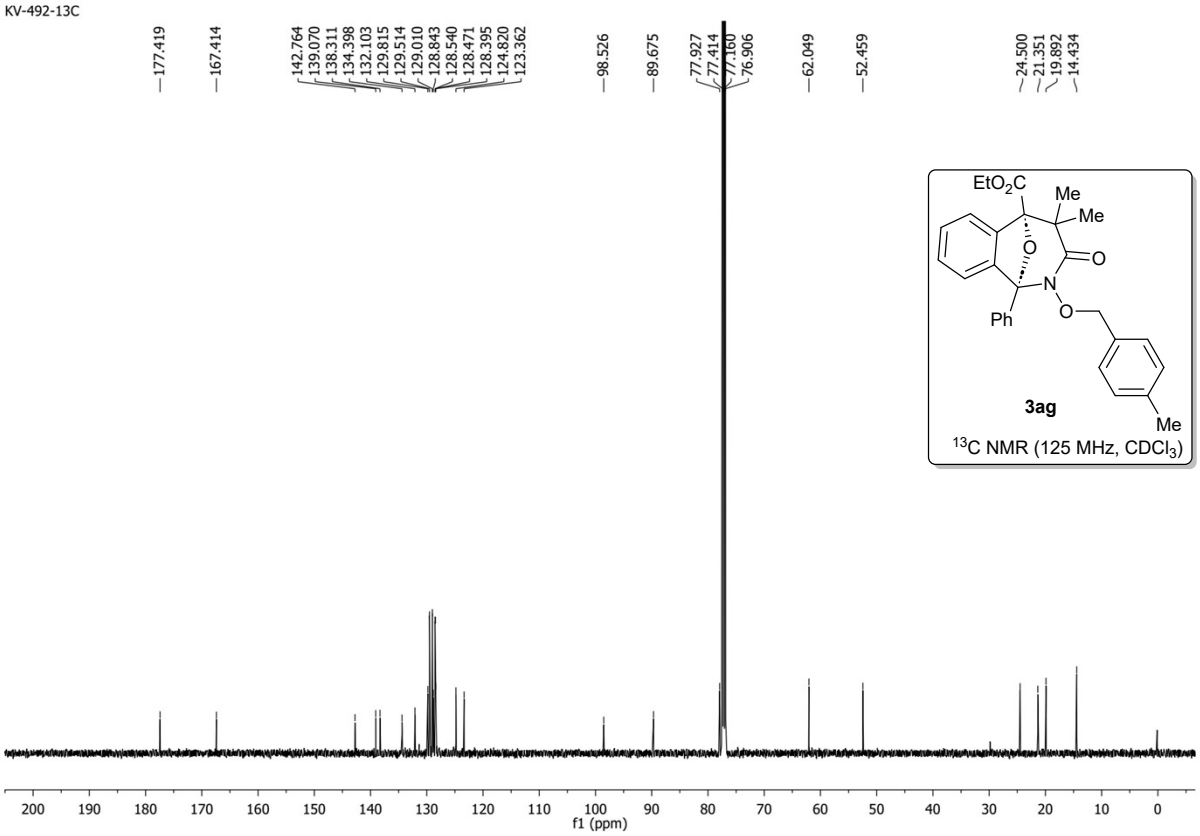
^{13}C NMR (100 MHz, $CDCl_3$)

KV-492-1H



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

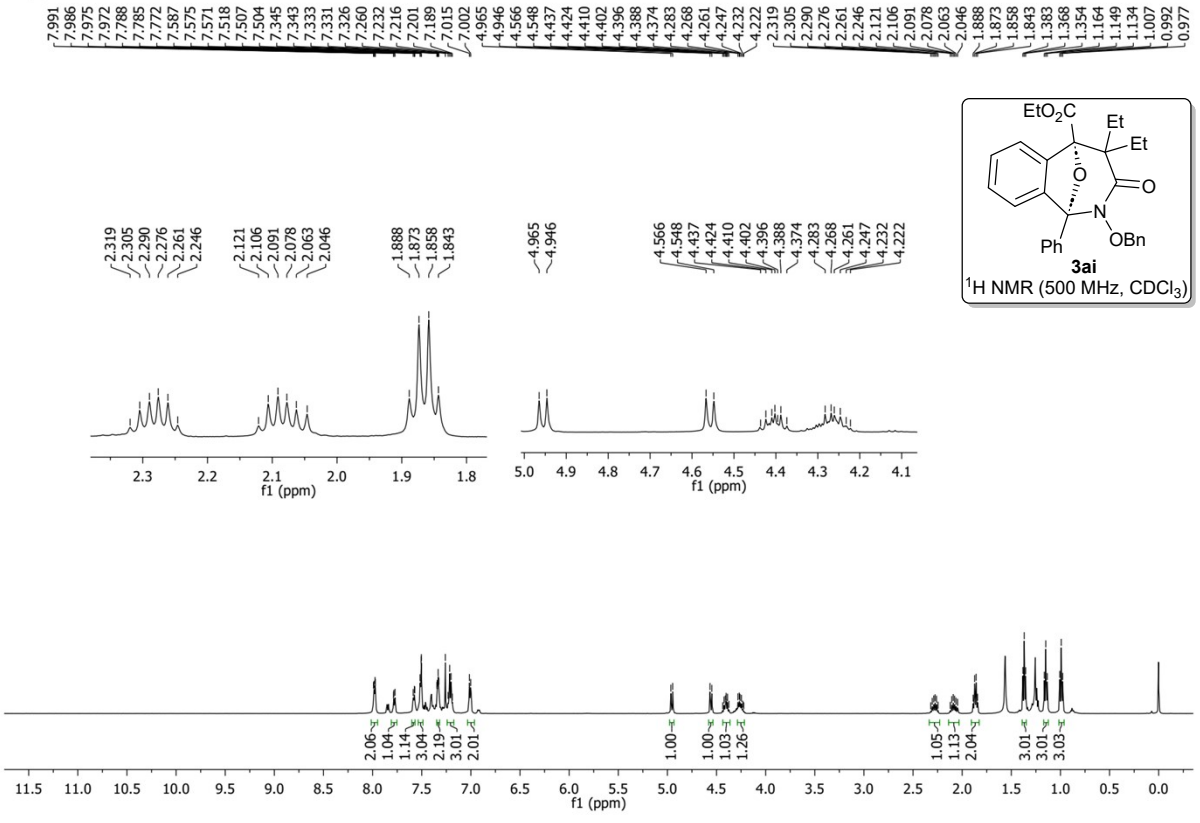
KV-492-13C



3ag

^{13}C NMR (125 MHz, $CDCl_3$)

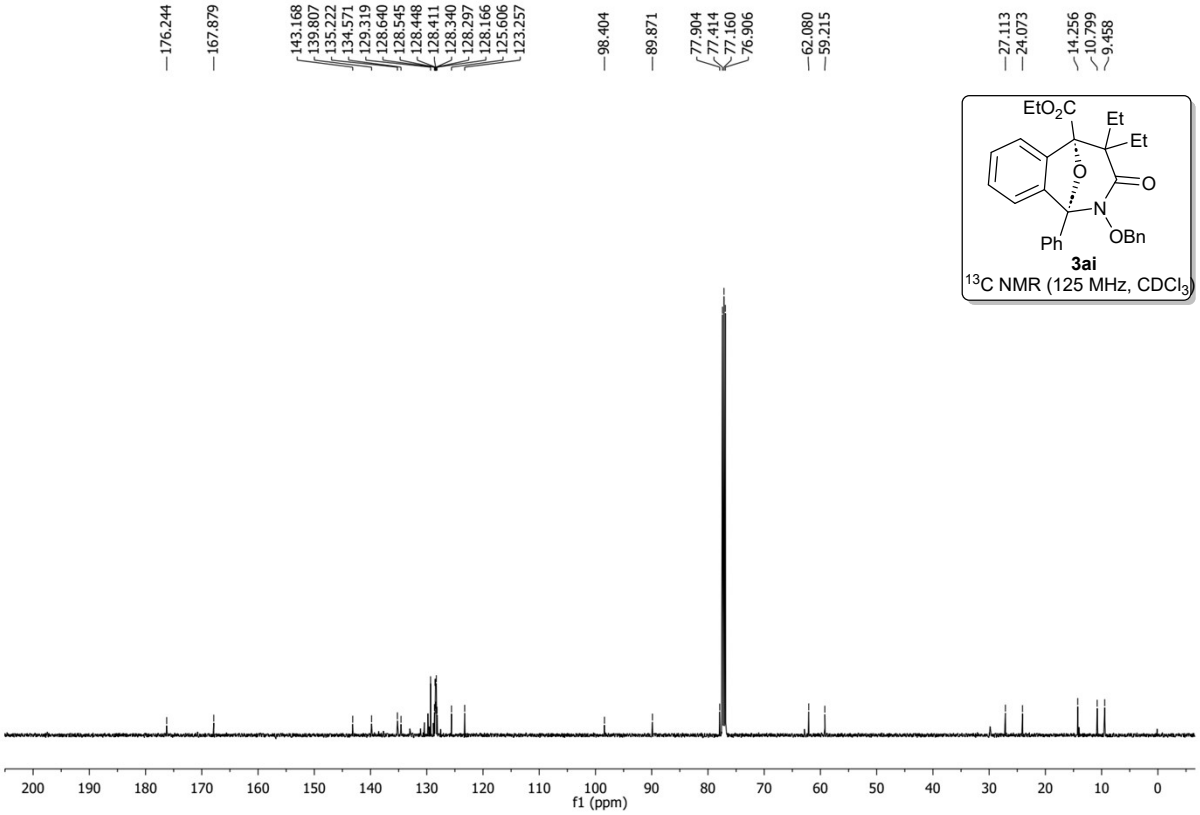
KV-516-1H



3ai

^{1}H NMR (500 MHz, $CDCl_3$)

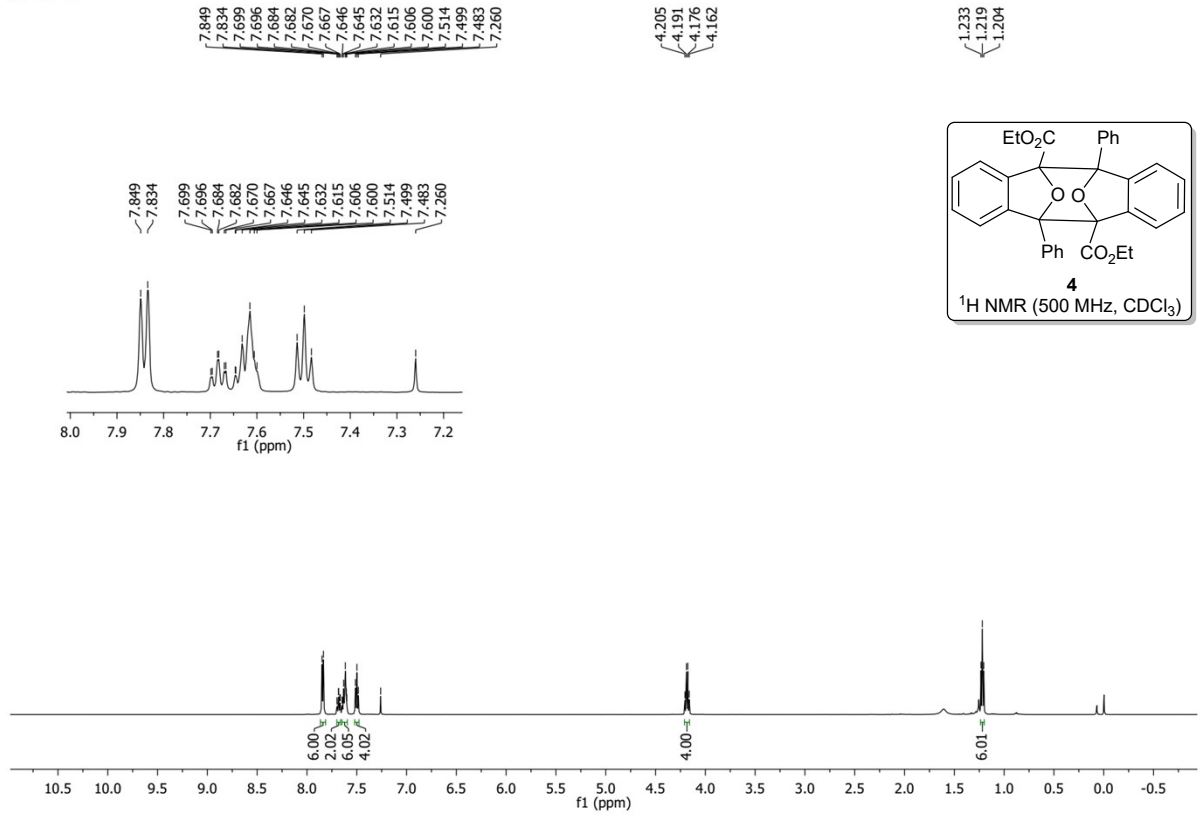
KV-516-13C



3ai

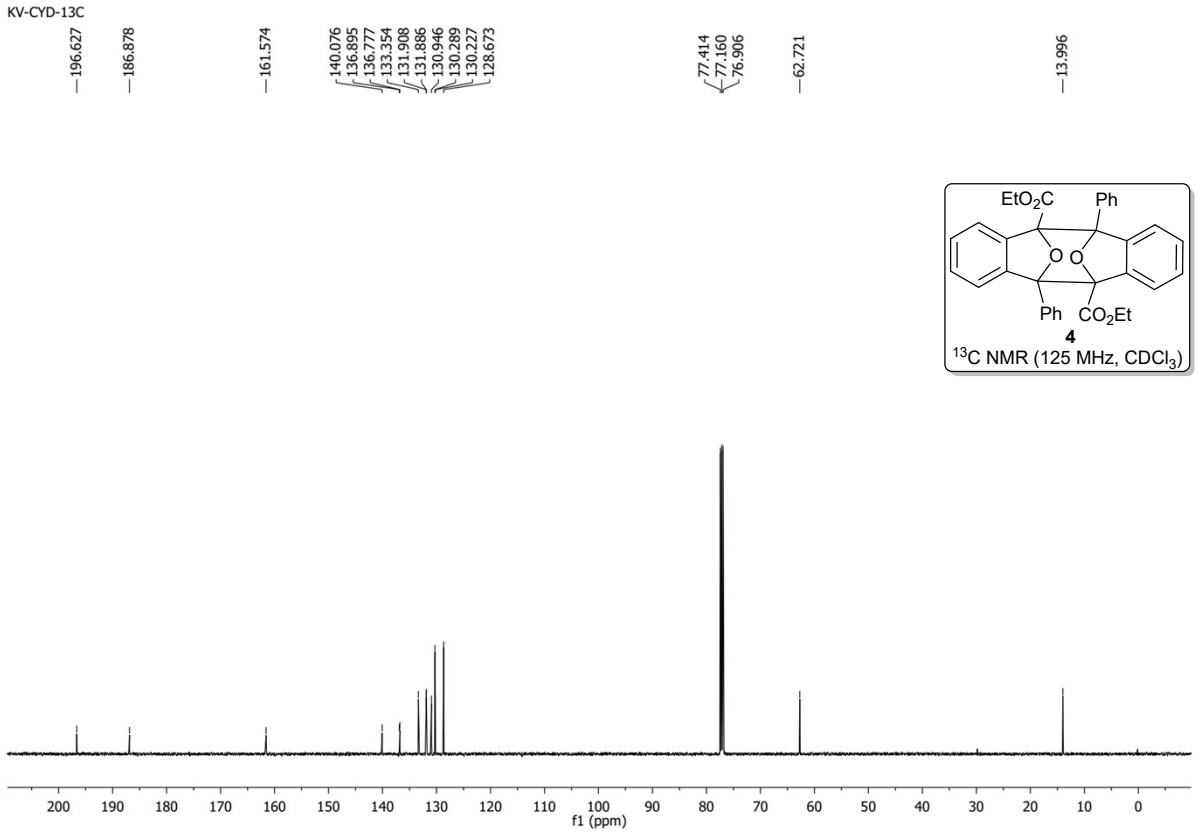
^{13}C NMR (125 MHz, $CDCl_3$)

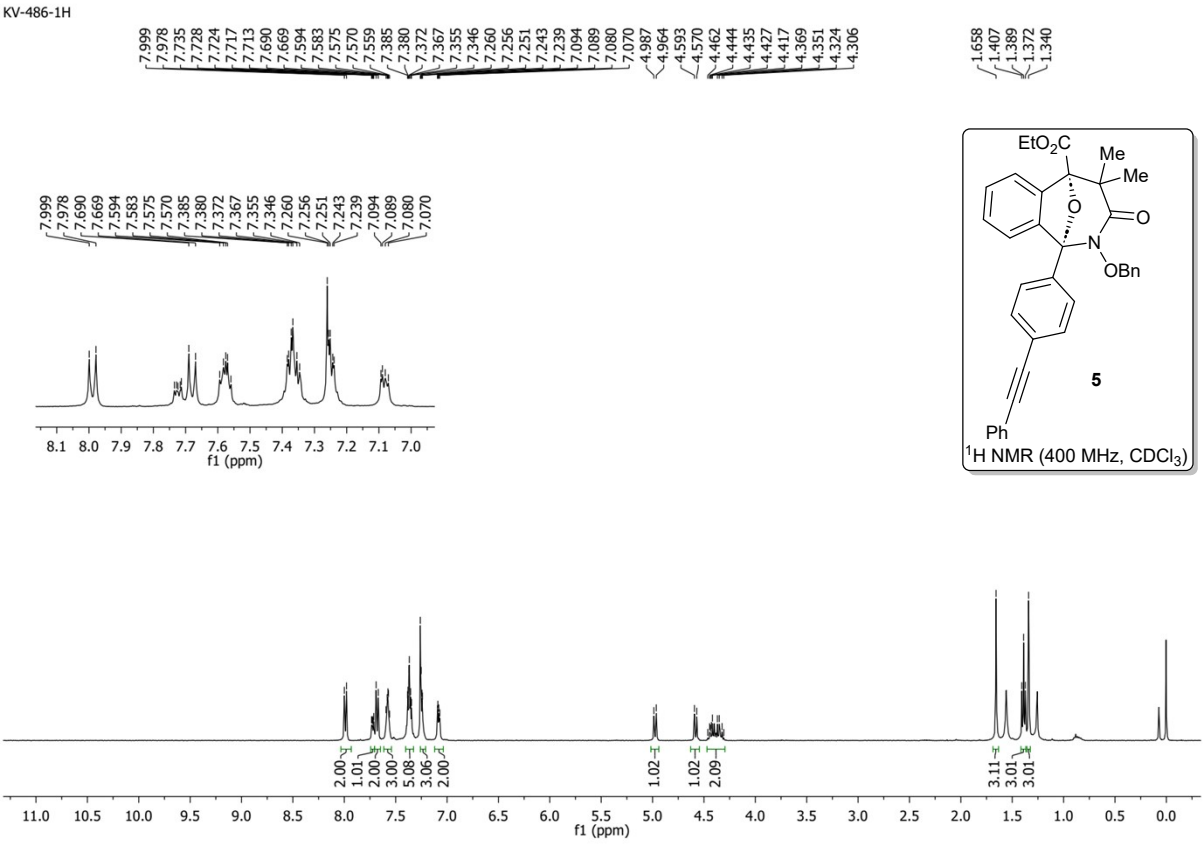
KV-CYD-1H



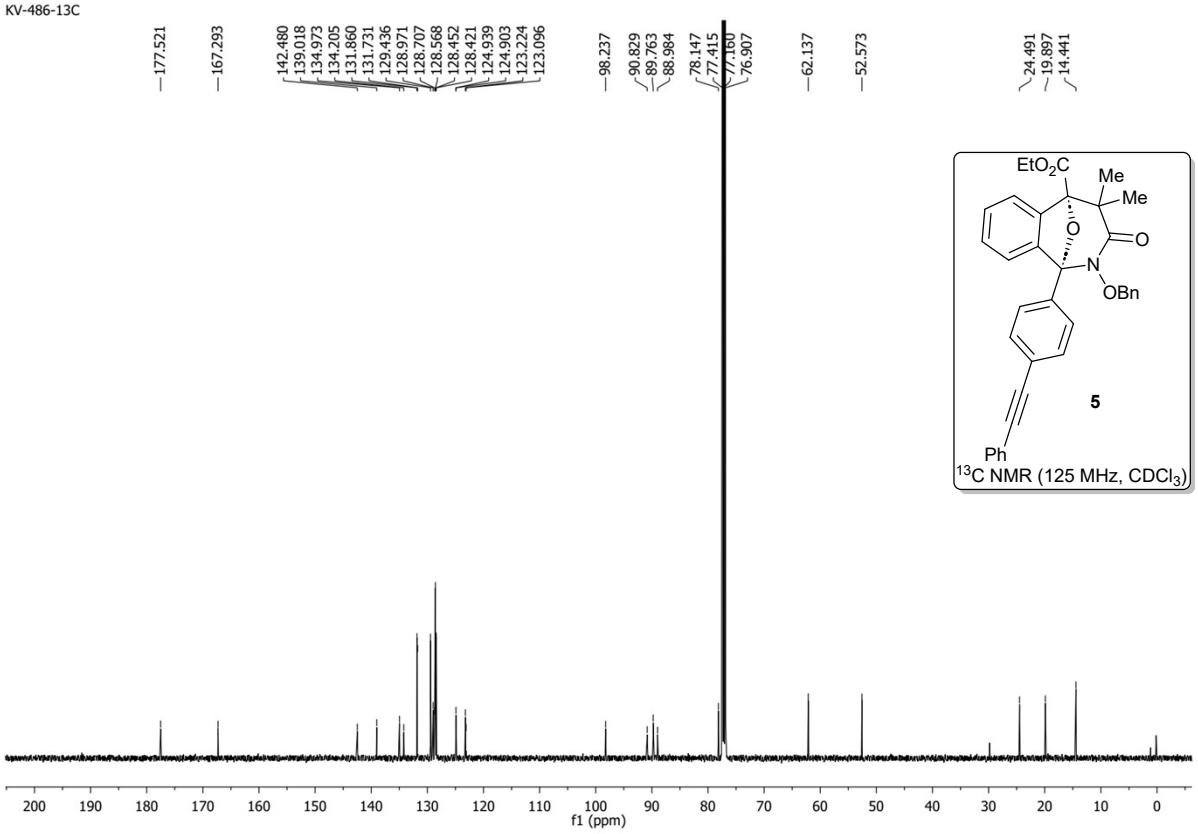
4

^{1}H NMR (500 MHz, $CDCl_3$)


KV-CYD-13C
196.627
186.878
161.574
140.076
136.895
136.777
133.354
131.908
131.886
130.946
130.289
130.227
128.673
77.414
77.160
76.906
62.721
13.996
EtO2C
Ph
O
O
Ph
CO2Et
4
13C NMR (125 MHz, CDCl3)
f1 (ppm)

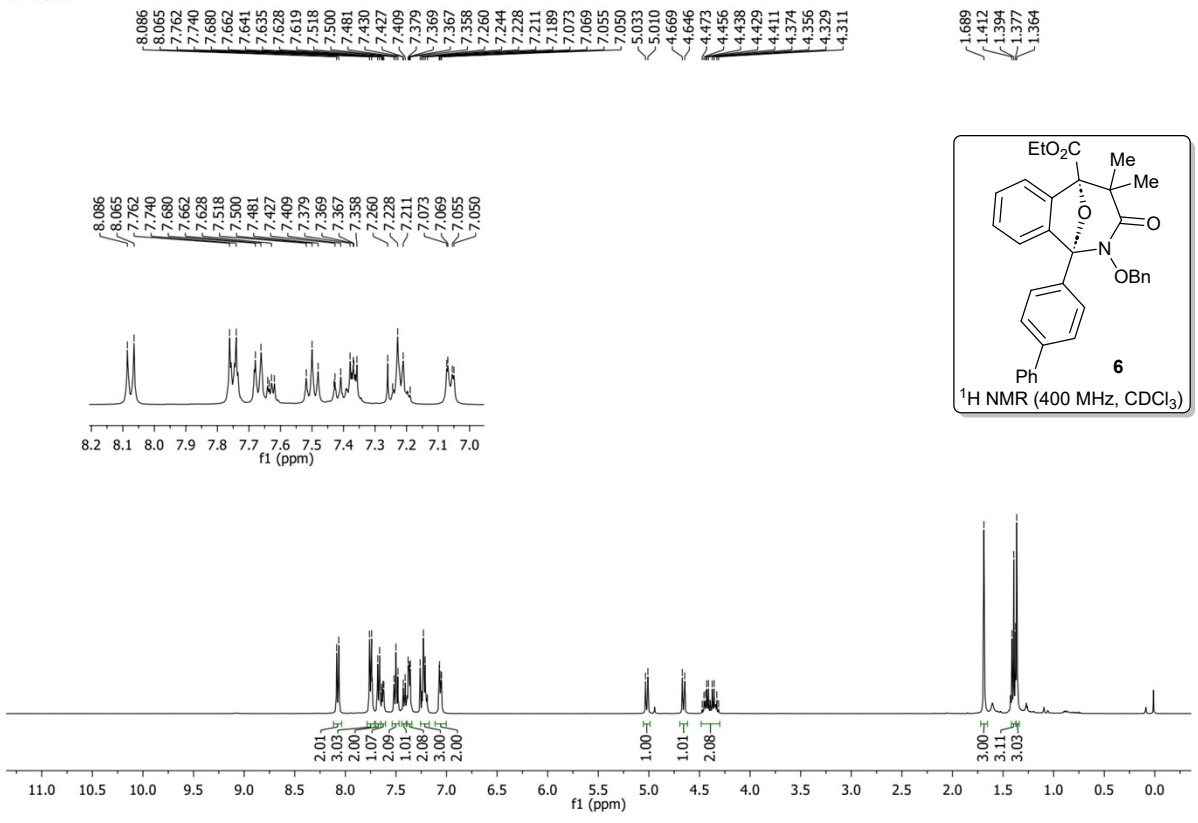

KV-486-1H
7.999
7.978
7.735
7.728
7.724
7.717
7.713
7.690
7.669
7.594
7.583
7.575
7.570
7.559
7.385
7.380
7.372
7.367
7.355
7.346
7.260
7.256
7.251
7.243
7.239
7.094
7.089
7.080
7.070
4.987
4.964
4.593
4.570
4.462
4.444
4.435
4.427
4.417
4.369
4.351
4.324
4.306
1.658
1.407
1.389
1.372
1.340
EtO2C
Me
Me
O
O
N
OBn
5
Ph
1H NMR (400 MHz, CDCl3)
2.00
1.01
2.00
3.00
5.08
3.06
2.00
1.02
1.02
2.09
3.11
3.01
3.01
f1 (ppm)

KV-486-13C



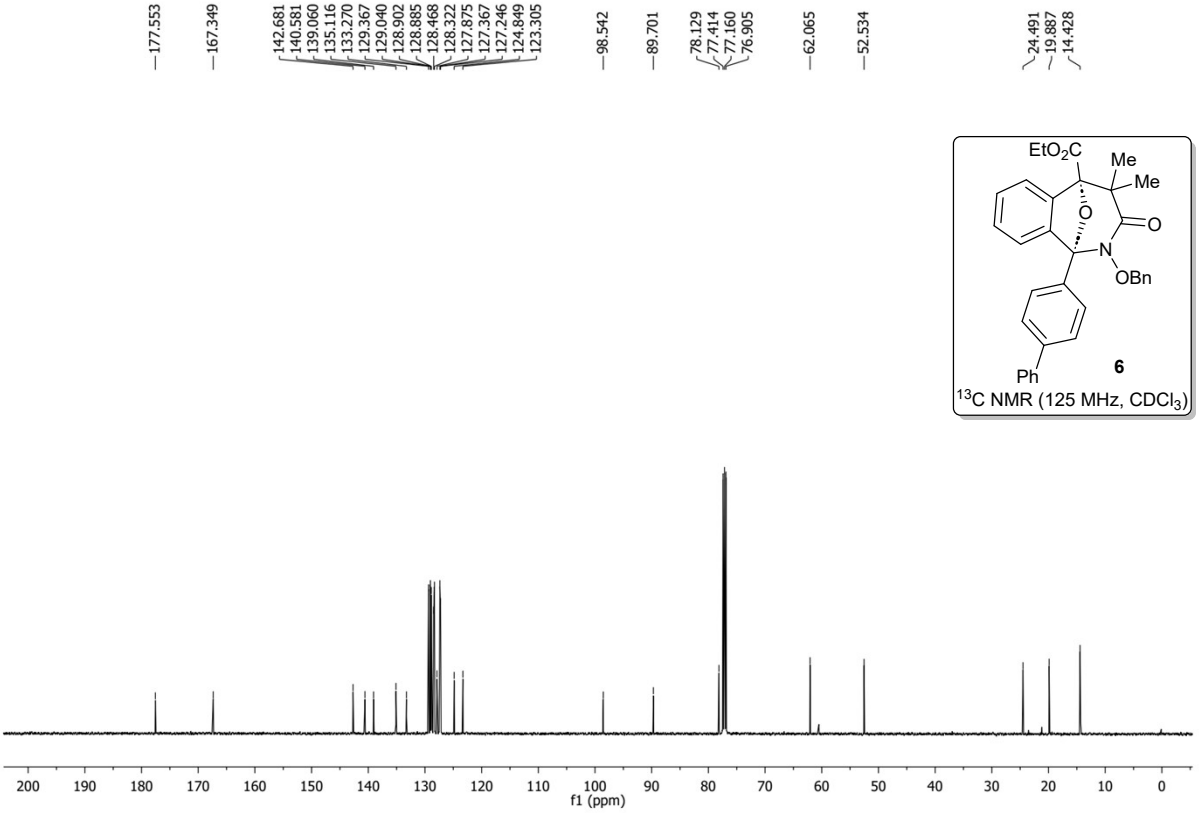
^{13}C NMR (125 MHz, $CDCl_3$)

KV-478-1H

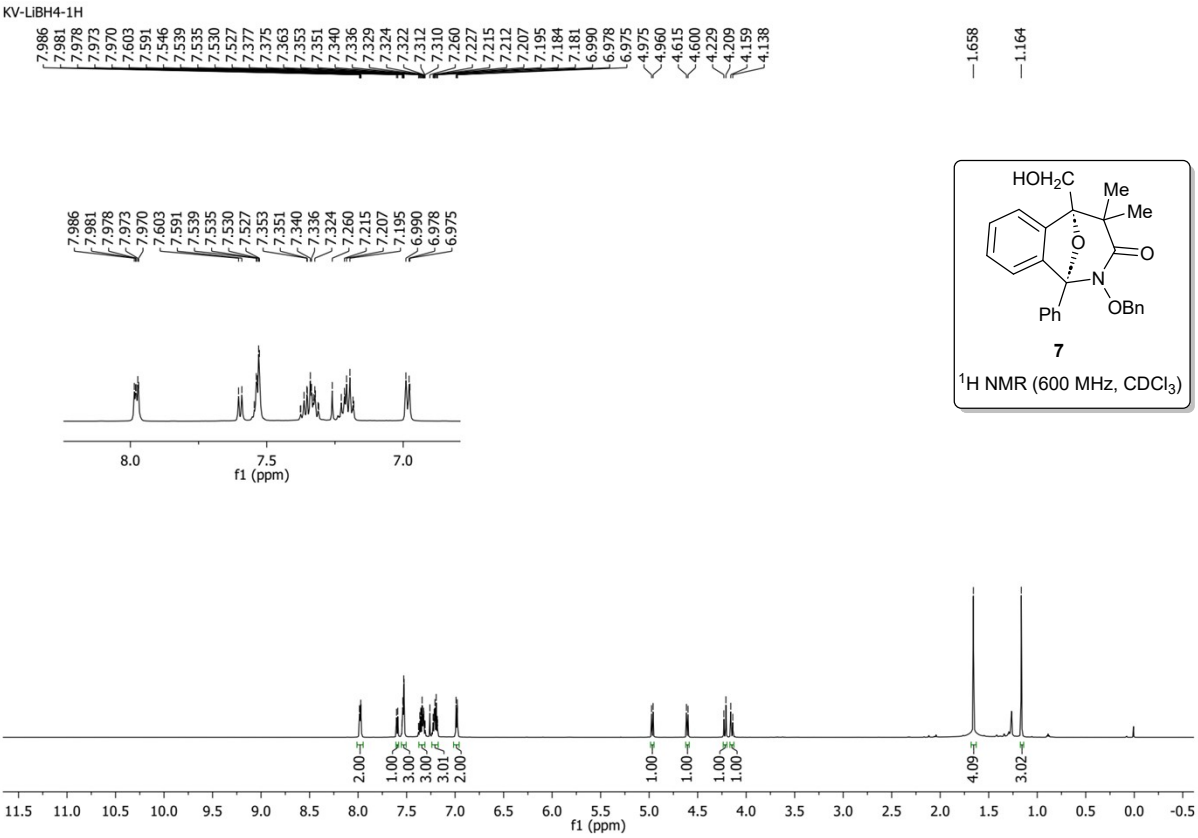


^{1}H NMR (400 MHz, $CDCl_3$)

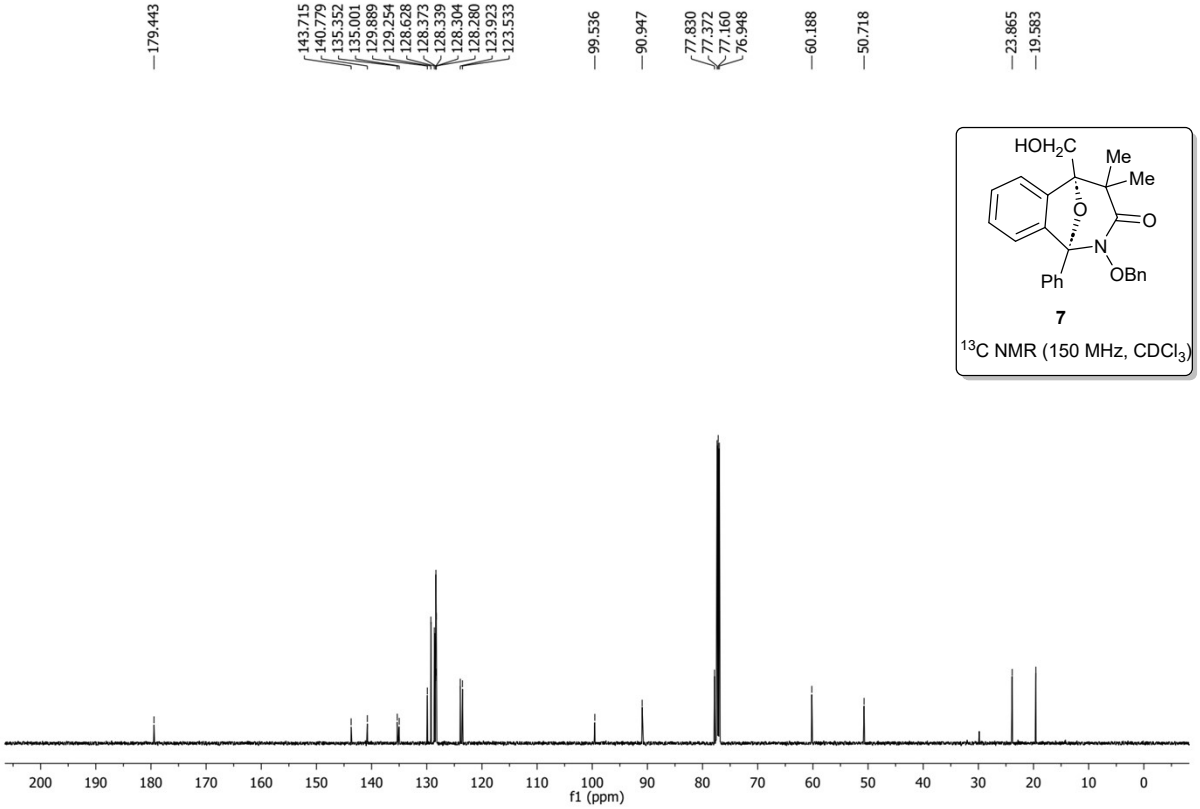
KV-478-13C



KV-LiBH4-1H



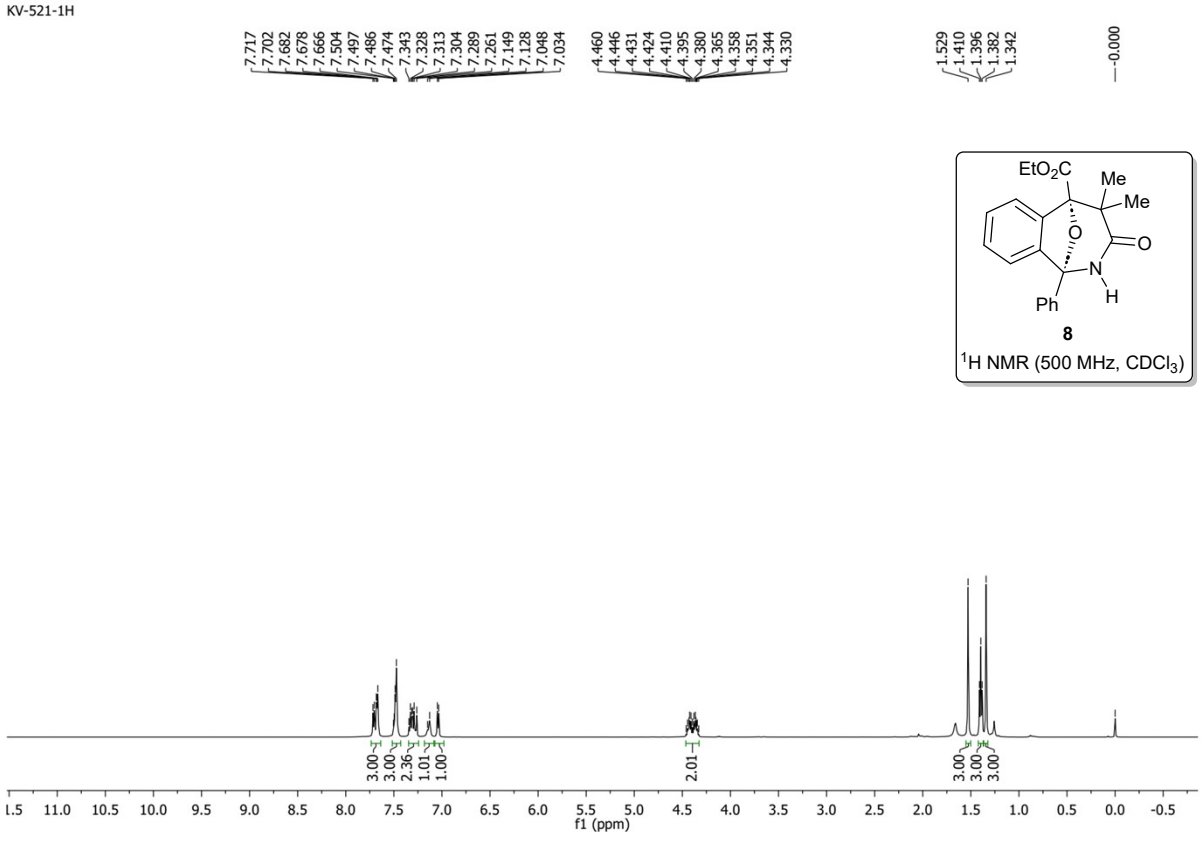
KV-LiBH4-13C



7

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

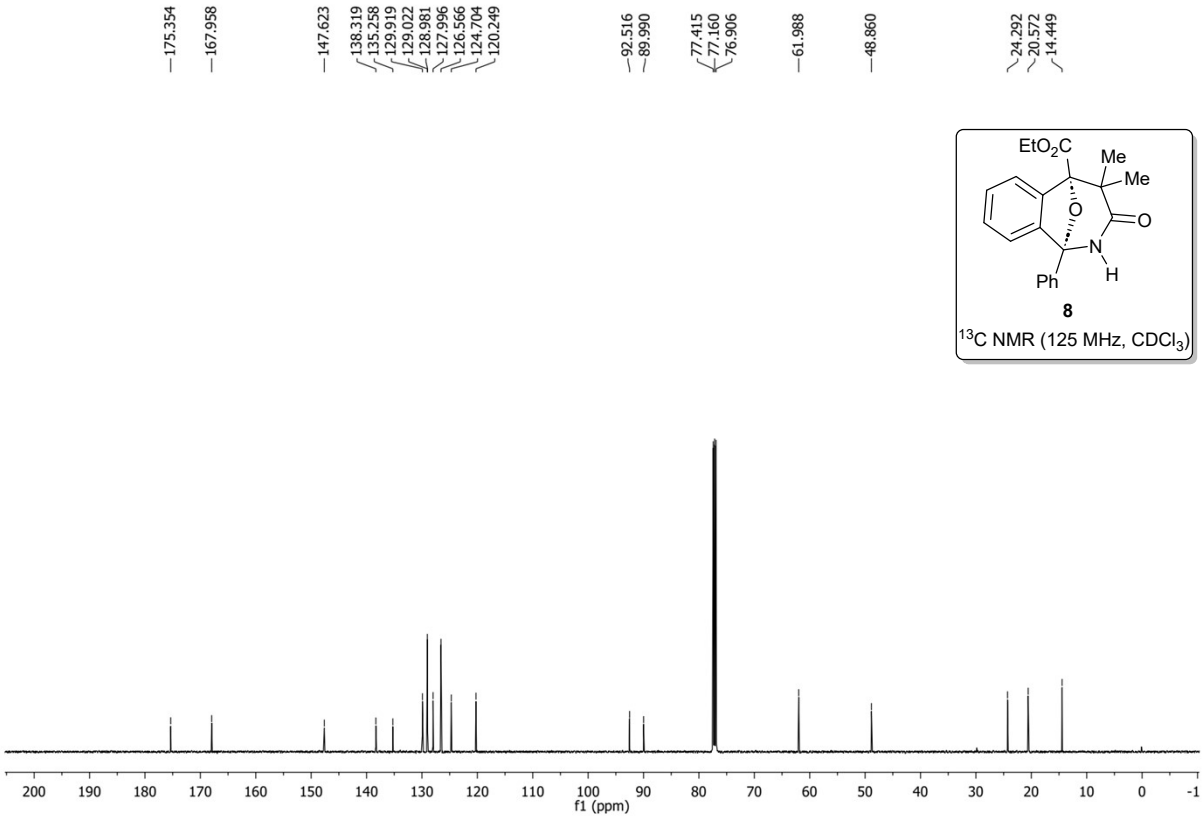
KV-521-1H



8

^{1}H NMR (500 MHz, $CDCl_3$)

KV-521-13C


175.354
167.958
147.623
138.319
135.258
129.919
129.022
128.981
127.996
126.566
124.704
120.249
92.516
89.990
77.415
77.160
76.906
61.988
48.860
24.292
20.572
14.449
EtO2C
Me
Me
O
O
N
H
Ph
8
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)