Synthesis of Cycloheptatriene-containing Azetidine Lactones Supporting Information

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1 Materials and methods

Reactions were performed on scales ranging from several milligrams to grams in suitable containers: 1-dram vials for small scale, round-bottom flasks for larger scale. All air- and moisture-sensitive reactions were carried out under an inert atmosphere of nitrogen. The reactions were initially monitored by thin-layer chromatography (TLC). Concentration under reduced pressure was performed by rotary evaporation at 25-40 ℃ at an appropriate pressure to avoid uncontrolled evaporation. Residual solvent was further removed under high vacuum. Yields refer to purified and spectroscopically pure compounds, unless otherwise stated.

Solvents Solvents were passed through drying columns[1] and used with additional drying on 3 Å molecular sieves for 24 h. Solvents for photochemical reactions were purged of dissolved gases by bubbling nitrogen for 15-60 minutes depending on volume. All deuterated solvents were purchased from Cambridge Isotope Laboratories.

Chromatography Thin layer chromatography (TLC) was performed using EMD TLC plates pre-coated with 250 µm thickness silica gel 60 F_{254} and neutral alumina plates. Upon elution, spots were visualized under weak UV light at 254 nm, or by staining with ninhydrin solution (for compounds containing free amines), potassium permanganate solution (for compounds containing oxidizable groups), or with Seebach stain. Flash chromatography was performed using 4-24 g column from Teledyne ISCO.

UV-vis spectroscopy Ultraviolet and visible (UV-vis) spectrum absorptions of key substrates were recorded in open-top UV quartz macro cell (pathlength 10 mm, volume 3.0 ml, 5061-3387) on an Agilent Cary50 Bio spectrophotometer with a range of absorptions from 200-800 nm at a rate of 4800 nm/min and with subtracted solvent absorptions.

NMR spectroscopy Nuclear magnetic resonance (NMR) spectra were obtained on Bruker instruments at Larmor frequency of 400 MHz or 500 MHz for proton nuclei, and 126 MHz for carbon. Chemical shifts are reported in ppm with the solvent residual peak as the internal standard. For ^{1}H NMR: $CDCl_3$, δ 7.26; methanol-d_4, δ 3.31; For ^{13}C NMR: $CDCl_3$, δ 77.2; methanol-d_4, δ 49.0. Data is reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sept = septet, m = multiplet, bs = broad singlet; coupling constants in Hz; integration.
Assigment of the compounds were performed on the basis of complete 2D-NMR (^{1}H, ^{13}C {^{1}H }, DEPT, gCOSY, gHSQC, gHMBC, and NOESY) spectral characterization.

TLC-MS/ASAP (Atmospheric Solid Analysis Probe) Reactions were monitored using Advion expression^s compact mass spectrometer (CMS) via TLC-MS and ASAP module. For TLC-MS 5% water-acetonitrile mixture was used to extract the analyte from TLC plate matrix and carry it to the mass spectrometer. High-resolution mass spectra were obtained using Q-Tof-2^{TM}.

High Performance Liquid Chromatography Analytical assessment of the yields were determined using LC-6AD Shimadzu Liquid Chromatograph with SPD-20A prominence UV-vis detector. InertSustain C18 column (particle size: 5 µm, internal diameter: 4.6 mm, length: 100 mm) from G.L. Sciences was used for the analytical characterization. InertSustain ODS, Prep, 250 x 10.0mm (particle size: 5 µm, internal diameter: 10 mm, length: 250 mm) was used for the preparative purification of the compounds. Mixture of HPLC-grade acetonitrile and 0.1% ammonium acetate in de-ionized water (pH= 6.98) or mixture of HPLC-grade acetonitrile and 1% ammonium acetate with 0.12% concentrated ammonium hydroxide (29.4%, 14.8 N) in de-ionized MilliQ-treated water (final pH=8.00) was used for chromatographic separation. 5-10 µL of analyte (0.312 mM to 5 mM) was injected for analytical assessment. For preparative purification 250-300 µL of analyte was injected.

HRMS-LCT Premier ESI Electrospray ionization spectra were acquired on a LCT Premier (Waters Corp., Milford MA) time-of-flight mass spectrometer. The instrument was operated at 10,000 resolution (W mode) with dynamic range enhancement that attenuates large intensity signals. The cone voltage was 60 eV. Spectra were acquired covering the mass range 100 to 1500 u and accumulating data for 2 seconds per cycle. Mass correction for exact mass determinations were made automatically with the lock mass feature in the MassLynx data system. A reference compound in an auxiliary sprayer is sampled every third cycle by toggling a "shutter" between the analysis and reference needles. The reference mass is used for a linear mass correction of the analytical cycles. Samples are presented in acetonitrile as a 100 µL loop injection using an auto injector (LC PAL, CTC Analytics AG, Zwingen, Switzerland).

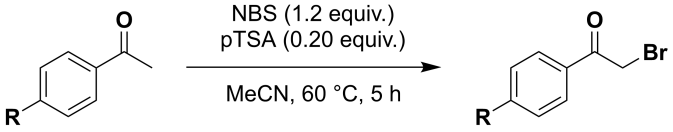
Crystallization All crystals reported in the manuscript were grown using vapor diffusion technique[2] in combination with dichloromethane and pentane/hexanes. The compound was dissolved in minimum amount of mixture of dichloromethane and hexanes (1:10), or only dichloromethane, and placed in a larger container containing pentane, and this container was then sealed.

2 Synthesis of starting materials

2.1 General procedure for synthesis of 2-bromo-1-phenylethan-1-ones

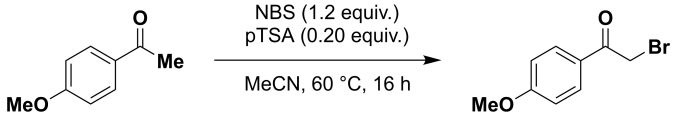
Following a modified procedure,[3] to a 500 mL pear-shaped flask, acetonitrile (final concentration of the limiting reagent 200 mM) was added, followed by acetophenone (1 eq), *N*-bromosuccinimide (NBS) (1.2 eq), and *p*-toluenesulfonic acid monohydrate (0.20 eq). The reaction was heated to 60 ℃ using oil bath and stirred for 16-22 h. Reaction was monitored by TLC in 10% ethyl acetate/hexanes, showing consumption of the starting material and two new product spots (monobrominated and dibrominated acetophenone). Reaction was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Crude product was purified via flash chromatography (0-20% ethyl acetate/hexanes gradient). Product was concentrated under reduced pressure and dried under vacuum, yielding a white solid. Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments.

2.1.1 2-Bromo-1-phenylethan-1-one



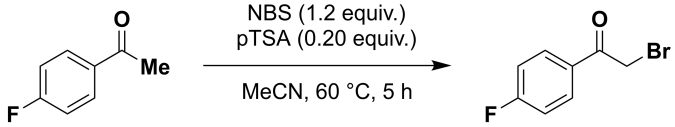
Following the general procedure, to a 500 mL pear-shaped flask, acetonitrile (208 mL) was added, followed by acetophenone (4.9 mL, 42 mmol, 1 eq) and NBS (3.9 g, 50 mmol, 1.2 eq). The reaction was heated to 60 ℃ using an oil bath, *p*-toluenesulfonic acid monohydrate (1.6 g, 8.3 mmol, 0.20 eq) was added, and the reaction was stirred for 22 h. Reaction was monitored by TLC in 10% ethyl acetate/hexanes, showing consumption of starting material and two new product spots. Reaction was quenched with saturated sodium bicarbonate solution (25 mL) and extracted with ethyl acetate (2 x 35 mL). The organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Crude product was separated into 2 portions purified via flash chromatography (0-0.5% ethyl acetate/hexanes). Product was concentrated under reduced pressure, giving white solid in 47% yield (3.91 g).
^{1}H (500 MHz, Chloroform-d) δ 8.03 - 7.92 (2H, m), 7.67 - 7.57 (1H, m), 7.55 - 7.45 (2H, m), 4.46 (2H, s)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 191.4, 134.1, 129.1, 128.7, 46.1, 31.1

2.1.2 2-Bromo-1-(4-methoxyphenyl)ethan-1-one



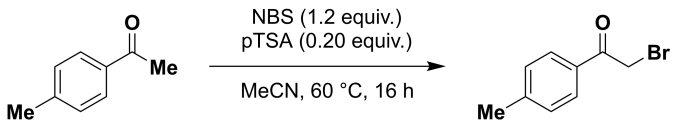
Following the general procedure, to a 50 mL round bottom flask, acetonitrile (6.7 mL) was added, followed by 4-methoxyacetophenone (200 mg, 1.3 mmol, 1 eq) and NBS (284 g, 1.6 mmol, 1.2 eq). The reaction was heated to 60 ℃ using an oil bath, *p*-toluenesulfonic acid monohydrate (50 mg, 0.27 mmol, 0.20 eq) was added, and the reaction was stirred for 22 h. Reaction was monitored by TLC in 5% ethyl acetate/hexanes. Reaction was quenched with saturated sodium bicarbonate solution (10 mL) and extracted with ethyl acetate (2 x 35 mL). The organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Crude product was purified via flash chromatography (0 - 20% ethyl acetate/hexanes). Pure product was concentrated under reduced pressure, giving white solid in 49.8% yield (152 mg).
^{1}H (500 MHz, Chloroform-d) δ 7.97 (2H, d, *J*=8.8 Hz), 6.96 (2H, d, *J*=8.9 Hz), 4.40 (2H, s), 3.89 (3H, s)
^{13}C {^{1}H } was not acquired because proton spectrum matched the previously published one.[4]

2.1.3 2-Bromo-1-(4-fluorophenyl)ethan-1-one



Following the general procedure, to a 500 mL pear-shaped flask, acetonitrile (362 mL) was added, followed by 4-fluoroacetophenone (8.8 mL, 72 mmol, 1 eq) and NBS (15 g, 87 mmol, 1.2 eq). The reaction was heated to 60 ℃ using an oil bath, *p*-toluenesulfonic acid monohydrate (2.8 g, 14 mmol, 0.20 eq) was added, and the reaction was stirred for 16 h. Reaction was monitored by TLC in 10% ethyl acetate/hexanes, showing consumption of starting material and two new product spots. Reaction was quenched with saturated sodium bicarbonate solution (75 mL) and extracted with ethyl acetate (2 x 150 mL). The organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Crude product was purified via flash chromatography (0 - 20% ethyl acetate/hexanes). Product was concentrated under reduced pressure, giving white solid in 51.0% yield (8.0 g).
^{1}H (500 MHz, Chloroform-d) δ 8.07 - 7.98 (1H, m), 7.20 - 7.10 (1H, m), 4.41 (1H, s)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 189.9, 167.6, 164.0, 131.9, 131.8, 116.1, 116.35, 30.6

2.1.4 2-Bromo-1-*p*-tolylethan-1-one



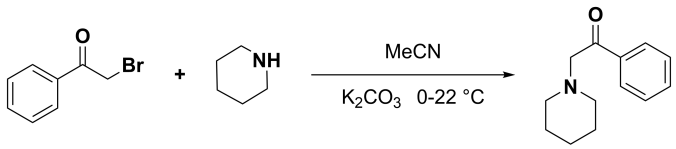
Following the general procedure, to a 500 mL pear-shaped flask, acetonitrile (373 mL) was added, followed by 4-methylacetophenone (9.9 mL, 75 mmol, 1 eq) and NBS (16 g, 89 mmol, 1.2 eq). The reaction was heated to 60 ℃ usng an oil bath, *p*-toluenesulfonic acid monohydrate (2.8 g, 15 mmol, 0.20 eq) was added, and the reaction was stirred for 16 h. Reaction was monitored by TLC in 10% ethyl acetate/hexanes, showing consumption of starting material and two new product spots. ASAP mass spectrometry also confirmed complete disappearance of

the starting material molecular ion peak. Reaction was quenched with saturated sodium bicarbonate solution (75 mL) and extracted with ethyl acetate (2 x 150 mL). The organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Crude product was purified via flash chromatography (0 - 20% ethyl acetate/hexanes). Product was concentrated under reduced pressure, giving white solid in 53.5% yield (8.5 g).
^{1}H (500 MHz, Chloroform-d) δ 7.98 - 7.79 (2H, m), 7.33 - 7.19 (2H, m), 4.43 (2H, s), 2.43 (3H, s)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 191.1, 145.2, 131.5, 129.7, 129.2, 31.1, 21.9

2.2 General procedure for synthesis of phenacylpiperidines

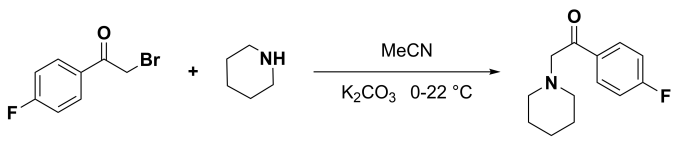
Following a modified procedure,[5] to a round bottom flask with stir bar, 2-bromophenylethanone (1 eq) was added, followed by potassium carbonate (2.0 eq). Acetonitrile (200 mM) was added and the suspension was cooled to 0 ℃. Subsequently, piperidine (1.05 eq) was added dropwise over 15 minutes, under nitrogen environment. The reaction was then stirred at room temperature for 16 h. Reaction was monitored by TLC in 20% ethyl acetate/hexanes and 5% methanol/DCM, showing consumption of starting material and appearance of the product. Reaction was filtered and solid was washed with ethyl acetate. Filtrate was concentrated under reduced pressure.The resulting residue was purified on a silica column (0-20% MeOH/DCM) to give pure product.Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments.

2.2.1 1-Phenyl-2-(piperidin-1-yl)ethan-1-one (6)



Following the general procedure, to a 250 mL round botttom flask with stir bar, 2-bromo-1-phenylethan-1-one (3.0 g, 15 mmol, 1 eq) was added, followed by potassium carbonate (4.2 g, 30.1 mmol, 2.0 eq). Acetonitrile (75 mL) was added and the suspension was cooled to 0 ℃. Subsequently, piperidine (1.6 mL, 16 mmol, 1.05 eq) was added slowly over 15 minutes, under nitrogen atmosphere. The reaction was then stirred at room temperature for 48 h. Reaction was monitored by TLC in 20% ethyl acetate in hexanes and 5% MeOH in DCM, showing consumption of starting material. Reaction was filtered and solid was washed with ethyl acetate (15 mL). Filtrate was concentrated under reduced pressure. The crude product was purified on a silica column (0-20% MeOH/DCM), giving pure product as yellow oil in 66% yield (2.03 g).
^{1}H (500 MHz, Chloroform-d) δ 8.05 - 7.98 (2H, m, 4, 6), 7.60 - 7.51 (1H, m, 2), 7.49 - 7.40 (2H, m, 1, 3), 3.78 (2H, s, 8), 2.57 - 2.50 (4H, m, 11, 15), 1.65 (4H, p, *J*=5.6 Hz, 12, 14), 1.51 - 1.40 (2H, m, 13)
^{13}C {^{1}H } was not acquired because the ^{1}H NMR matched with the reported spectrum.[6]

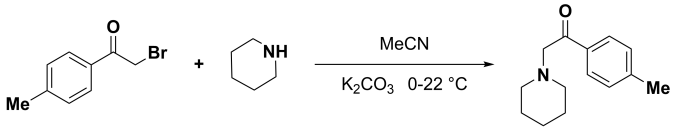
2.2.2 1-(4-Fluorophenyl)-2-(piperidin-1-yl)ethan-1-one



Following the general procedure, to a 25 mL round bottom flask with stir bar, 2-bromo-1-(4-fluorophenyl)ethan-1-one (3.0 g, 14 mmol, 1 eq) was added, followed by potassium carbonate (3.8 g, 28 mmol, 2.0 eq). Acetonitrile

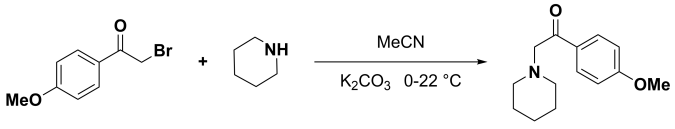
(69 mL) was added and the suspension cooled to 0 °C. Subsequently, piperidine (1.5 mL, 15 mmol, 1.05 eq) was added slowly over 15 minutes, under nitrogen atmosphere. The reaction was then stirred at room temperature for 16 h. Reaction was monitored by TLC in 20% ethyl acetate/hexanes and 5% MeOH/DCM, showing consumption of starting material. Reaction was filtered and solid was washed with ethyl acetate (20 mL). Filtrate was concentrated under reduced pressure. The resulting residue was purified on a silica column (0-20% MeOH/DCM), giving pure product as yellow oil in 75.2% yield (2.3 g).
^{1}H (500 MHz, Chloroform-d) δ 8.20 - 7.96 (2H, m, 4, 6), 7.16 - 6.94 (2H, m, 1, 3), 3.70 (2H, s, 8), 2.66 - 2.42 (4H, m, 11, 15), 1.84 - 1.48 (4H, m, 12, 14), 1.50 - 1.40 (2H, m, 13)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 195.5, 165.7 (d, *J* = 254.6 Hz), 132.6 (d, *J* = 3.1 Hz), 131.0 (d, *J* = 9.2 Hz), 115.5 (d, *J* = 22.0 Hz), 65.5, 54.8, 25.8, 23.9

2.2.3 2-(Piperidin-1-yl)-1-(p-tolyl)ethan-1-one



Following the general procedure, to a 250 mL round bottom flask with stir bar, 2-bromo-1-(p-tolyl)ethan-1-one (3 g, 14 mmol, 1 eq) was added, followed by potassium carbonate (3.9 g, 28 mmol, 2.0 eq). Acetonitrile (70.4 mL) was added and the suspension was cooled to 0 °C. Subsequently, piperidine (1.5 mL, 15 mmol, 1.05 eq) was added slowly over 15 minutes, under nitrogen atmosphere. The reaction was then stirred at room temperature for 16 h. Reaction was monitored by TLC in 20% ethyl acetate/hexanes and 5% MeOH/DCM, showing consumption of starting material. Reaction was filtered and solid was washed with ethyl acetate (20 mL). Filtrate was concentrated under reduced pressure. The resulting residue was purified on a silica column (0-20% MeOH/DCM), giving pure product as oil in 61% yield (1.86 g).
^{1}H (500 MHz, Chloroform-d) δ 7.90 (2H, d, *J*=8.3 Hz, 4, 6), 7.25 - 7.20 (2H, m, 1, 3), 3.74 (2H, s, 8), 2.57 - 2.46 (4H, m, 11, 15), 2.39 (3H, s, 16), 1.68 - 1.55 (4H, m, 12, 14), 1.53 - 1.36 (2H, m, 13)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 196.5, 143.9, 133.8, 129.2, 128.3, 65.2, 54.9, 25.8, 24.0, 21.7

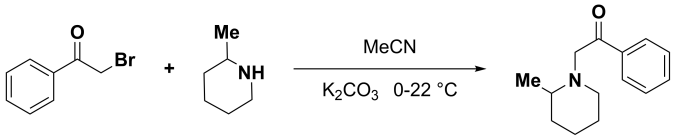
2.2.4 1-(4-Methoxyphenyl)-2-(piperidin-1-yl)ethan-1-one (20)



Following the general procedure, to a 250 mL round bottom flask with stir bar, 2-bromo-1-(4-methoxyphenyl)ethan-1-one (152 mg, 0.66 mmol, 1 eq) was added, followed by potassium carbonate (183 mg, 1.3 mmol, 2.0 eq). Acetonitrile (1.7 mL) was added and the suspension was cooled to 0 °C. Subsequently, piperidine (0.069 mL, 0.70 mmol, 1.05 eq) was added slowly over 15 minutes, under nitrogen atmosphere. The reaction was then stirred at room temperature for 16 h. Reaction was monitored by TLC in 20% ethyl acetate/hexanes and 5% MeOH/DCM, showing consumption of starting material. Reaction was filtered and solid was washed with ethyl acetate (10 mL). Filtrate was concentrated under reduced pressure. The resulting residue was purified on a silica column (0-20% MeOH/DCM), giving pure product in 60.2% yield (93.2 mg).
^{1}H (500 MHz, Chloroform-d) δ 8.02 (2H, d, *J*=9.0 Hz), 6.92 (2H, d, *J*=8.9 Hz), 3.87 (3H, s), 3.73 (2H, s), 2.59 - 2.50 (4H, m), 1.64 (4H, p, *J*=5.7 Hz), 1.53 - 1.41 (2H, m)

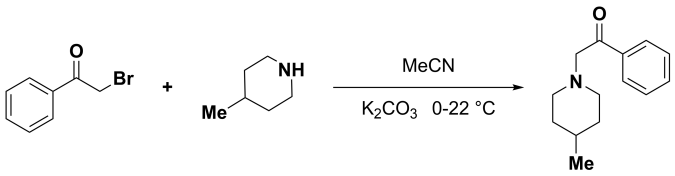
^{13}C {^{1}H } (126 MHz, Chloroform-d) 195.5, 163.5, 130.6, 129.4, 113.7, 65.2, 55.5, 54.9, 25.8, 24.1

2.2.5 2-(2-Methylpiperidin-1-yl)-1-phenylethan-1-one



Following the general procedure, to a 50 mL round bottom flask with stir bar, 2-bromo-1-phenylethan-1-one (500 mg, 2.5 mmol, 1 eq) was added, followed by potassium carbonate (694 mg, 5.0 mmol, 2.0 eq). Acetonitrile (12.5 mL) was added and the suspension was cooled to 0 ℃. Subsequently, 2-methylpiperidine (0.31 mL, 2.6 mmol, 1.05 eq) was added slowly over 15 minutes, under nitrogen atmosphere. The reaction was then stirred at room temperature for 16 h. Reaction was monitored by TLC in 20% ethyl acetate in hexanes and 5% MeOH/DCM, showing consumption of starting material. Reaction was filtered and solid was washed with ethyl acetate (10 mL). Filtrate was concentrated under reduced pressure. The resulting residue was purified on a silica column (0-20% MeOH/DCM), giving pure product as oil in 86% yield (470 mg).
^{1}H (500 MHz, Chloroform-d) δ 8.06 - 8.00 (2H, m, 1, 3), 7.59 - 7.52 (1H, m, 2), 7.50 - 7.40 (2H, m, 4, 6), 4.13 (1H, d, *J*=16.7 Hz, 8"), 3.75 (1H, d, *J*=16.7 Hz, 8'), 2.92 - 2.83 (1H, m, 11), 2.68 - 2.56 (1H, m, 15"), 2.50 - 2.37 (1H, m, 15'), 1.75 - 1.62 (2H, m, 12), 1.63 - 1.53 (2H, m, 14), 1.44 - 1.32 (2H, m, 13'), 1.11 (3H, d, *J*=6.3 Hz, 16)

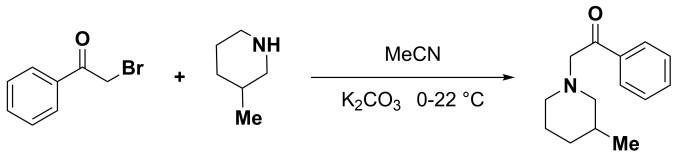
2.2.6 2-(4-Methylpiperidin-1-yl)-1-phenylethan-1-one



Following the general procedure, to a 250 mL round bottom flask with stir bar, 2-bromo-1-phenylethan-1-one (3.0 g, 15 mmol, 1 eq) was added, followed by potassium carbonate (4.2 g, 30 mmol, 2.0 eq). Acetonitrile (75 mL) was added and the suspension was cooled to 0 ℃. Subsequently, 4-methylpiperidine (1.9 mL, 16 mmol, 1.05 eq) was added slowly over 15 minutes, under nitrogen atmosphere. The reaction was then stirred at room temperature for 16 h. Reaction was monitored by TLC in 20% ethyl acetate/hexanes and 5% MeOH/DCM, showing consumption of starting material. Reaction was filtered and solid was washed with ethyl acetate (25 mL). Filtrate was concentrated under reduced pressure. The resulting residue was purified on a silica column (0-20% MeOH/DCM), giving pure product as oil in 76% yield (2.5 g).
^{1}H (500 MHz, Chloroform-d) δ 8.04 - 7.95 (2H, m), 7.59 - 7.50 (1H, m), 7.48 - 7.36 (2H, m), 3.77 (2H, s), 2.99 - 2.90 (2H, m), 2.17 - 2.04 (2H, m), 1.66 - 1.53 (2H, m), 1.43 - 1.29 (3H, m), 0.92 (3H, d, *J*=5.8 Hz)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 196.9, 136.3, 133.1, 128.5, 128.2, 65.1, 54.4, 34.2, 30.4, 21.9

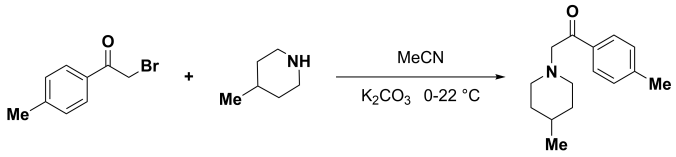
2.2.7 2-(3-Methylpiperidin-1-yl)-1-phenylethan-1-one

Following the general procedure, to a 25 mL round bottom flask with stir bar, 2-bromo-1-phenylethan-1-one (200 mg, 1.0 mmol, 1 eq) was added, followed by potassium carbonate (277 mg, 2.0 mmol, 2.0 eq). Acetonitrile (5.0 mL) was added and the suspension was cooled to 0 ℃. Subsequently, 3-methylpiperidine (0.12 mL, 1.1 mmol, 1.05 eq)



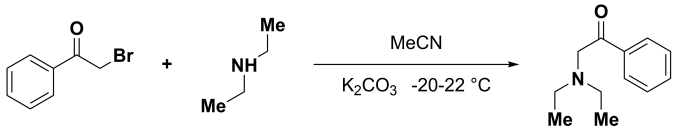
was added slowly over 15 minutes, under nitrogen atmosphere. The reaction was then stirred at room temperature for 16 h. Reaction was monitored by TLC in 20% ethyl acetate/hexanes and 5% MeOH/DCM, showing consumption of starting material. Reaction was filtered and solid was washed with ethyl acetate (5 mL). Filtrate was concentrated under reduced pressure. The resulting residue was purified on a silica column (0-20% MeOH/DCM), giving pure product as oil in 62.15% yield (136 mg).
^{1}H (500 MHz, Chloroform-d) δ 8.03 - 7.96 (2H, m), 7.59 - 7.51 (1H, m), 7.47 - 7.39 (2H, m), 3.76 (2H, s), 2.96 - 2.84 (2H, m), 2.11 - 1.98 (1H, m), 1.82 - 1.57 (6H, m), 0.85 (3H, d, *J*=6.1 Hz)
^{13}C{^{1}H } (126 MHz, Chloroform-d) δ 197.0, 136.3, 133.1, 128.5, 65.3, 62.3, 54.4, 32.6, 31.0, 25.4, 19.6

2.2.8 2-(4-Methylpiperidin-1-yl)-1-(p-tolyl)ethan-1-one



Following the general procedure, to a 25 mL round bottom flask with stir bar, 2-bromo-1-(p-tolyl)ethan-1-one (300 mg, 1.4 mmol, 1 eq) was added, followed by potassium carbonate (389 mg, 2.8 mmol, 2.0 eq). Acetonitrile (7.0 mL) was added and the suspension was cooled to 0 ℃. Subsequently, 4-methylpiperidine (0.21 mL, 1.5 mmol, 1.05 eq) was added slowly over 15 minutes, under nitrogen atmosphere. The reaction was then stirred at room temperature for 16 h. Reaction was monitored by TLC in 20% ethyl acetate/hexanes and 5% MeOH/DCM, showing consumption of starting material. Reaction was filtered and solid was washed with ethyl acetate (5.0 mL). Filtrate was concentrated under reduced pressure. The resulting residue was purified on a silica column (0-20% MeOH/DCM), giving pure product as oil in 79% yield (256 mg).
^{1}H (500 MHz, Chloroform-d) δ 7.92-7.90 (m, 2H), 7.23-7.21 (m, 2H), 3.75 (s, 2H), 2.98-2.95 (m, 2H), 2.39 (s, 3H), 2.14-2.10 (m, 2H), 1.64-1.58 (m, 2H), 1.38-1.34 (m, 3H), 0.92 (d, *J*=5.50 Hz, 3H)
^{13}C{^{1}H } (126 MHz, Chloroform-d) δ 196.6, 143.9, 133.9, 129.3, 128.4, 65.1, 54.4, 34.3, 30.5, 21.9, 21.8

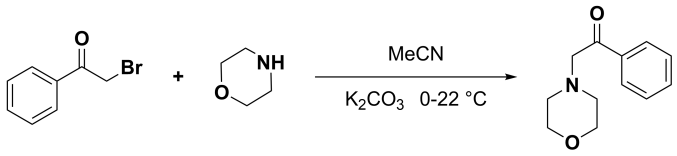
2.2.9 2-(Diethylamino)-1-phenylethan-1-one



Following the general procedure, to a 100 mL round bottom flask with stir bar, 2-bromo-1-(p-tolyl)ethan-1-one (500 mg, 2.5 mmol, 1 eq) was added, followed by potassium carbonate (694 mg, 5.0 mmol, 2.0 eq). Acetonitrile (13 mL) was added and the suspension was **cooled to -20 ℃**. Subsequently, diethylamine (0.31 mL, 3.0 mmol, 1.05 eq) was added slowly over 15 minutes, under nitrogen atmosphere. The reaction was stirred for 16 h and allowed to warm to room temperature. Reaction was monitored by TLC in 20% ethyl acetate/hexanes and 5% MeOH/DCM, showing consumption of starting material. Reaction was filtered and solid was washed with ethyl acetate (5.0 mL).

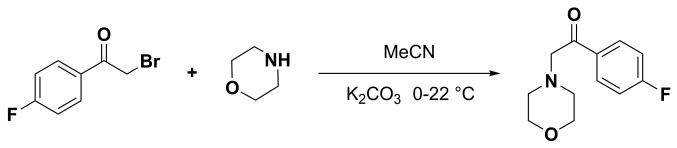
Filtrate was concentrated under reduced pressure and resulting residue was dried in vacuo, giving product as oil in 40% yield (194 mg). **This product was used in the next step without further purification**.
^{1}H (500 MHz, Chloroform-d) δ 8.04 - 7.99 (2H, m, 4, 6), 7.59 - 7.53 (1H, m, 2), 7.48 - 7.41 (2H, m, 1, 3), 3.94 (2H, s, 8), 2.73 (4H, q, *J*=7.2 Hz, 11, 12), 1.09 (6H, t, *J*=7.2 Hz, 13, 14)
^{13}C{^{1}H } was not acquired because the ^{1}H NMR matched the reported spectrum.[7]

2.2.10 2-Morpholino-1-phenylethan-1-one (18)



Following the general procedure, to a 25 mL round bottom flask with stir bar, 2-bromo-1-phenylethan-1-one (300 mg, 1.5 mmol, 1 eq) was added, followed by potassium carbonate (417 mg, 3.0 mmol, 2.0 eq). Acetonitrile (7.5 mL) was added and the suspension was cooled to 0 ℃. Subsequently, morpholine (0.14 mL, 1.6 mmol, 1.05 eq) was added slowly over 15 minutes, under nitrogen atmosphere. The reaction was then stirred at room temperature for 16 h. Reaction was monitored by TLC in 20% ethyl acetate/hexanes and 5% MeOH/DCM, showing consumption of starting material. Reaction was filtered and solid was washed with ethyl acetate (15 mL). Filtrate was concentrated under reduced pressure. The resulting residue was purified on a silica column (0-20% MeOH/DCM), giving pure product as oil in 49% yield (151 mg).
^{1}H (500 MHz, Chloroform-d) δ 8.01 - 7.95 (2H, m), 7.60 - 7.54 (1H, m), 7.49 - 7.42 (2H, m), 3.83 (2H, s), 3.81 - 3.75 (4H, m), 2.68 - 2.57 (4H, m)
^{13}C{^{1}H } (126 MHz, Chloroform-d) δ 195.9, 135.9, 133.4, 128.6, 128.1, 66.8, 64.6, 53.8

2.2.11 1-(4-Fluorophenyl)-2-morpholinoethan-1-one

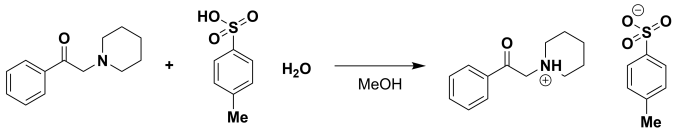


Following the general procedure, to a 50 mL round bottom flask with stir bar, 2-bromo-1-(4-fluorophenyl)ethan-1-one (500 mg, 2.3 mmol, 1 eq) was added, followed by potassium carbonate (637 mg, 4.6 mmol, 2.0 eq). Acetonitrile (12 mL) was added and the suspension was cooled to 0 ℃. Subsequently, morpholine (0.24 mL, 2.3 mmol, 1.05 eq) was added slowly over 15 minutes, under nitrogen atmosphere. The reaction was then stirred at room temperature for 16 h. Reaction was monitored by TLC in 20% ethyl acetate/hexanes and 5% MeOH/DCM, showing consumption of starting material. Reaction was filtered and solid was washed with ethyl acetate (10 mL). Filtrate was concentrated under reduced pressure. The resulting residue was purified on a silica column (0-20% MeOH/DCM), giving pure product as oil in 80% yield (412 mg).
^{1}H (500 MHz, Chloroform-d) δ 8.10 - 7.98 (2H, m), 7.13 (1H, t, *J*=8.6 Hz), 3.80 (6H, dd, *J*=9.2, 4.5 Hz), 2.75 - 2.59 (4H, m)
^{13}C{^{1}H } (126 MHz, Chloroform-d) δ 132.2, 130.9, 130.8, 115.9, 115.7, 66.6, 64.5, 53.7

2.3 General procedure for preparation of piperidinium salts of phenacylpiperidines

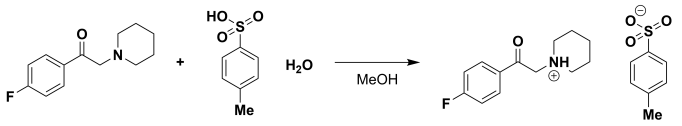
To a 250 mL round bottom flask, phenacylpiperidine (1 eq) was added and dissolved in a minimal amount of methanol. *p*-Toluenesulfonic acid monohydrate (1 eq) was added and the resulting residue was washed with toluene. This was concentrated under reduced pressure and remaining residue was dissolved in a minimal amount of DCM. Subsequently, hexanes were added and the salt precipitated. Residue was concentrated under reduced pressure and dried in vacuum, giving the product.Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments.

2.3.1 1-(2-Oxo-2-phenylethyl)piperidin-1-ium 4-methylbenzenesulfonate (6H$^+$OTs$^-$)

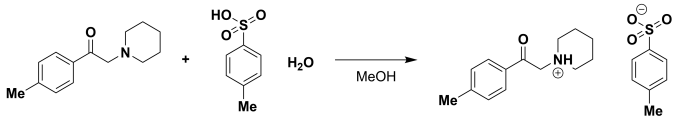


Following the general procedure, phenacylpiperidine (2.0 g, 10.0 mmol, 1 eq) was taken into 250 mL round bottom flask, and dissolved in methanol (6 mL). *p*-Toluenesulfonic acid monohydrate (1.9 g, 10.0 mmol, 1 eq) was then added and salt formed within 3 min. Toluene (6.0 mL) was added and residue was concentrated under reduced pressure. Product was dissolved in DCM (5.0 mL) and hexanes (25 mL) was added. This was concentrated under reduced pressure and dried in vacuum, giving product as light yellow solid in 96% yield (3.6 g).
^{1}H (500 MHz, Methanol-d4) δ 8.05 -7.98 (2H, m), 7.70 (3H, d, *J*=8.0 Hz), 7.57 (2H, t, *J*=7.8 Hz), 7.21 (2H, d, *J*=7.9 Hz), 4.91 (2H, s), 3.64 - 3.55 (2H, m), 3.11 (2H, td, *J*=11.8, 4.3 Hz), 2.35 (3H, s), 2.04 - 1.75 (5H, m), 1.64 - 1.49 (1H, m)
^{13}C{^{1}H } (126 MHz, Methanol-d4) δ 192.0, 141.7, 135.9, 135.0, 130.2, 129.8, 129.5, 126.9, 62.6, 55.6, 23.9, 22.5, 21.3

2.3.2 1-(2-(4-Fluorophenyl)-2-oxoethyl)piperidin-1-ium 4-methylbenzenesulfonate



Following the general procedure, 4-fluorophenacylpiperidine (1.7 g, 7.6 mmol, 1 eq) was taken into 250 mL round bottom flask, and dissolved in methanol (6 mL). *p*-Toluenesulfonic acid monohydrate (1.5 g, 7.6 mmol, 1 eq) was then added and salt formed within 3 min. Toluene (6.0 mL) was added and residue was concentrated under reduced pressure. Product was dissolved in DCM (5.0 mL) and hexanes (25 mL) was added. This was concentrated under reduced pressure and dried in vacuum, giving product in 97% yield (2.9 g).
^{1}H (500 MHz, Methanol-d4) δ 8.10 (2H, dd, *J*=8.8, 5.4 Hz), 7.69 (2H, d, *J*=8.2 Hz), 7.31 (2H, t, *J*=8.7 Hz), 7.22 (2H, d, *J*=7.9 Hz), 4.89 (2H, s), 3.65 - 3.55 (2H, m), 3.14 - 3.05 (2H, m), 2.36 (3H, s), 2.02 - 1.78 (5H, m), 1.64 - 1.51 (1H, m)
^{13}C{^{1}H } (126 MHz, Methanol-d4) δ 190.6, 168.1 (d, *J*=256.0 Hz), 143.5, 141.7, 132.5 (d, *J*=9.9 Hz), 131.7 (d, *J*=2.9 Hz), 129.8, 126.9, 117.3 (d, *J*=22.7 Hz), 62.4, 55.6, 23.9, 22.5, 21.3

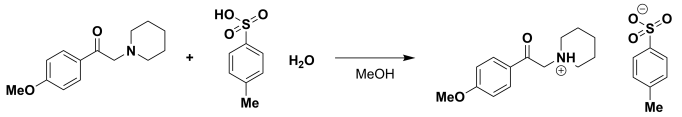


2.3.3 1-(2-Oxo-2-(p-tolyl)ethyl)piperidin-1-ium 4-methylbenzenesulfonate

Following the general procedure, 4-methylphenacylpiperidine (1.0 g, 4.7 mmol, 1 eq) was taken into 250 mL round bottom flask, and dissolved in methanol (6 mL). *p*-Toluenesulfonic acid monohydrate (884 mg, 4.7 mmol, 1 eq) was then added and salt formed within 3 min. Toluene (6.0 mL) was added and residue was concentrated under reduced pressure. Product was dissolved in DCM (5.0 mL) and hexanes (25 mL) was added. This was concentrated under reduced pressure and dried in vacuum, giving product in 88% yield (1.6 g).
^{1}H (500 MHz, Methanol-d4) δ 7.92 (2H, d, *J*=8.2 Hz), 7.70 (2H, d, *J*=8.1 Hz), 7.39 (2H, d, *J*=8.0 Hz), 7.22 (2H, d, *J*=7.9 Hz), 4.88 – 4.83 (2H, m, merged with methanol residual water peak) 3.64 – 3.54 (2H, m), 3.09 (2H, td, *J*=12.1, 3.5 Hz), 2.45 (3H, s), 2.36 (3H, s), 2.01 – 1.83 (5H, m), 1.64 – 1.50 (1H, m)

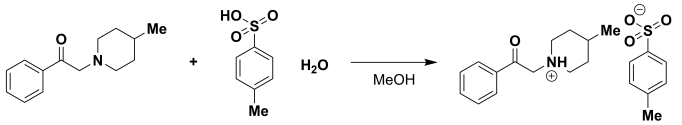
^{13}C{^{1}H } (126 MHz, Methanol-d4) δ 190.0, 146.3, 142.2, 140.3, 131.2, 129.4, 128.4, 128.1, 125.6, 61.0, 54.2, 22.5, 21.2, 20.4, 19.9

2.3.4 1-(2-(4-Methoxyphenyl)-2-oxoethyl)piperidin-1-ium 4-methylbenzenesulfonate (20H^{+}OTs^{-})



Following the general procedure, 4-methoxyphenacylpiperidine (62 mg, 0.27 mmol, 1 eq) was taken into 50 mL round bottom flask, and dissolved in methanol (6 mL). *p*-Toluenesulfonic acid monohydrate (51 mg, 0.27 mmol, 1 eq) was then added. Toluene (6.0 mL) was added and residue was concentrated under reduced pressure. Product was dissolved in DCM (5.0 mL) and hexanes (25 mL) was added. This was concentrated under reduced pressure and dried in vacuum, giving product in 99.9% yield (107 mg).
^{1}H (500 MHz, Methanol-d4) δ 8.00 (2H, d, *J*=8.9 Hz, 11, 15), 7.70 (2H, d, *J*=8.2 Hz, 18, 22), 7.22 (2H, d, *J*=8.0 Hz, 12, 14), 7.07 (2H, d, *J*=8.9 Hz, 19, 21), 4.83 (2H, s, 7), 3.90 (3H, s, 17), 3.58 (2H, dt, *J*=12.1, 3.9 Hz), 3.09 (2H, td, *J*=12.2, 3.6 Hz), 2.36 (3H, s), 2.01 - 1.82 (6H, m, 3, 4, 5), 1.65 - 1.48 (1H, m)
^{13}C{^{1}H } (126 MHz, Methanol-d4) δ 188.7, 165.2, 142.3, 142.2, 130.5, 128.4, 126.5, 125.6, 114.0, 60.8, 54.8, 54.2, 22.5, 21.12, 19.9

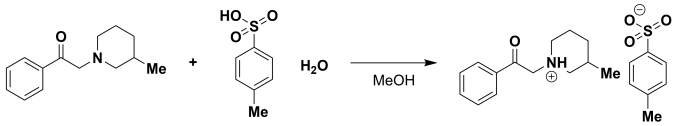
2.3.5 4-Methyl-1-(2-oxo-2-phenylethyl)piperidin-1-ium 4-methylbenzenesulfonate



Following the general procedure, 4-methylphenacylpiperidine (1.4 g, 6.3 mmol, 1 eq) was taken into 250 mL round bottom flask, and dissolved in methanol (6 mL). *p*-Toluenesulfonic acid monohydrate (1.2 g, 6.3 mmol, 1 eq) was then added and salt formed within 3 min. Toluene (6.0 mL) was added and residue was concentrated under reduced pressure. Product was dissolved in DCM (5.0 mL) and hexanes (25 mL) was added. This was concentrated under reduced pressure and dried in vacuum, giving product in 95% yield (2.3 g).

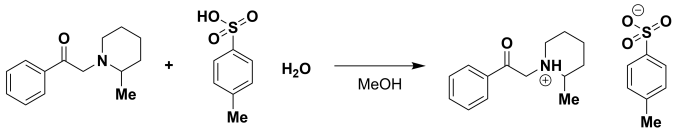
^{1}H (500 MHz, Methanol-d4) δ 8.04 - 8.00 (2H, m), 7.76 - 7.67 (3H, m), 7.62 - 7.54 (2H, m), 7.25 - 7.20 (2H, m), 4.91 (2H, s), 3.69 - 3.61 (2H, m), 3.17 - 3.07 (2H, m), 2.36 (3H, s), 2.00 - 1.87 (2H, m), 1.79 - 1.68 (1H, m), 1.65 - 1.53 (2H, m), 1.05 (3H, d, *J*=6.5 Hz)
^{13}C{^{1}H } (126 MHz, Methanol-d4) δ 192.4, 143.6, 141.6, 136.1, 135.0, 130.2, 129.8, 129.5, 129.3, 126.9

2.3.6 3-Methyl-1-(2-oxo-2-phenylethyl)piperidin-1-ium 4-methylbenzenesulfonate



Following the general procedure, 3-methylphenacylpiperidine (20 mg, 0.093 mmol, 1 eq) was taken into 50 mL round bottom flask, and dissolved in methanol (2.0 mL). *p*-Toluenesulfonic acid monohydrate (18 mg, 0.093 mmol, 1 eq) was then added and salt formed within 3 min. Toluene (4.0 mL) was added and residue was concentrated under reduced pressure. Product was dissolved in DCM (2.0 mL) and hexanes (10.0 mL) was added. This was concentrated under reduced pressure and dried in vacuum, giving product in 99% yield (36 mg).
^{1}H (500 MHz, Chloroform-d) δ 7.88 (2H, d, *J*=7.6 Hz, 4, 6), 7.71 (2H, d, *J*=7.9 Hz, 17, 21), 7.62 (1H, t, *J*=7.4 Hz, 2), 7.46 (2H, t, *J*=7.6 Hz, 1, 3), 7.12 (2H, d, *J*=7.8 Hz, 18, 20), 4.84 - 4.74 (2H, m, 8), 3.74 - 3.51 (2H, m, 15), 3.24 (1H, q, *J*=11.4 Hz, 11"), 2.91 (1H, q, *J*=11.1 Hz, 11'), 2.58 (2H, s, 10), 2.33 (3H, s, 23), 2.28 - 2.12 (1H, m), 1.92 - 1.79 (2H, m), 1.18 - 1.05 (1H, m), 0.92 (3H, d, *J*=6.6 Hz, 16)
^{13}C{^{1}H } (126 MHz, Chloroform-d) δ 190.3, 141.6, 140.2, 134.8, 133.9, 129.0, 128.8, 128.2, 126.1, 60.6, 59.1, 53.1, 30.4, 29.4, 23.1, 21.4, 18.7

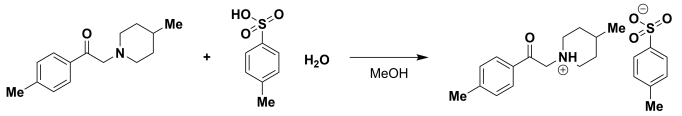
2.3.7 2-Methyl-1-(2-oxo-2-phenylethyl)piperidin-1-ium 4-methylbenzenesulfonate



Following the general procedure, 2-methylphenacylpiperidine (423 mg, 2.0 mmol, 1 eq) was taken into 100 mL round bottom flask, and dissolved in methanol (5.0 mL). *p*-Toluenesulfonic acid monohydrate (371 mg, 2.0 mmol, 1 eq) was then added and salt formed within 3 min. Toluene (7.0 mL) was added and residue was concentrated under reduced pressure. Product was dissolved in DCM (2.0 mL) and hexanes (15 mL) was added. This was concentrated under reduced pressure and dried in vacuum, giving product in 99% yield (as rotamers) (758 mg).
^{1}H (500 MHz, Methanol-d4) δ 8.12 – 8.09 (1H, m), 8.08 - 8.05 (1H, m), 7.79 - 7.72 (1H, m), 7.70 (2H, d, *J*=8.0 Hz), 7.63 - 7.55 (2H, m), 7.23 (2H, d, *J*=8.0 Hz), 5.12 (1H, d, *J*=18.1 Hz, 7"), 3.75 - 3.61 (1H, m), 3.49 - 3.42 (1H, m, 2), 3.15 - 3.05 (1H, m), 2.37 (3H, s), 2.10 - 2.00 (1H, m), 1.98 - 1.73 (3H, m), 1.69 - 1.58 (1H, m), 1.40 (1H, d, *J*=6.4 Hz), 1.34 (1H, d, *J*=6.8 Hz)
^{13}C{^{1}H } (126 MHz, Methanol-d4) δ 192.3, 143.6, 141.6, 136.2, 136.1, 135.0, 134.8, 130.2, 129.8, 129.6, 126.9, 56.2, 52.6, 31.9, 28.6, 23.9, 22.7, 21.6, 21.3, 20.6, 18.1

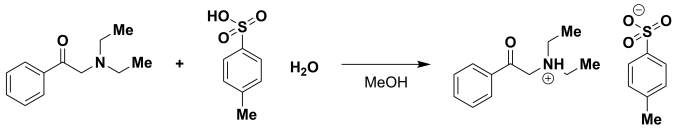
2.3.8 4-Methyl-1-(2-oxo-2-(p-tolyl)ethyl)piperidin-1-ium 4-methylbenzenesulfonate

Following the general procedure, 4-methylphenacyl-4-methylpiperidine (99 mg, 0.43 mmol, 1 eq) was taken into 25 mL round bottom flask, and dissolved in methanol (3 mL). *p*-Toluenesulfonic acid monohydrate (81 mg, 0.43 mmol,



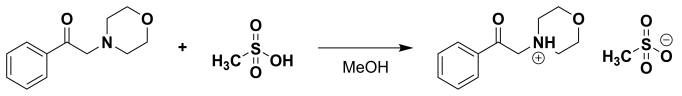
1 eq) was then added and salt formed within 3 min. Toluene (5.0 mL) was added and residue was concentrated under reduced pressure. Product was dissolved in DCM (2.0 mL) and hexanes (15 mL) was added. This was concentrated under reduced pressure and dried in vacuo, giving product in 99% yield (170 mg). (note: 1.08 equivalents of *p*-toluenesulfonic acid monohydrate was added instead of 1 equivalent, leading to improper integration of tosylate peaks in the ^{1}H spectrum. Corrected tosylate peak integrations are listed.)
^{1}H (500 MHz, Methanol-d4) δ 7.90 (2H, d, *J*=8.3 Hz), 7.72 - 7.65 (2H, m), 7.41 - 7.34 (2H, m), 7.26 - 7.19 (2H, m), 4.91 (2H, s), 3.68 - 3.52 (2H, m), 3.19 - 3.04 (2H, m), 2.68 (1H, s), 2.44 (3H, s), 2.36 (3H, s), 2.03 - 1.87 (3H, m), 1.76 - 1.68 (1H, m), 1.64 - 1.51 (2H, m), 1.03 (3H, d, *J*=6.4 Hz).
^{13}C {^{1}H } (126 MHz, Methanol-d4) δ 191.5, 147.5, 143.4, 141.7, 132.6, 130.8, 129.8, 129.5, 126.9, 62.6, 55.5, 32.4, 30.6, 29.7, 21.8, 21.4, 21.3

2.3.9 *N,N*-Diethyl-2-oxo-2-phenylethan-1-aminium 4-methylbenzenesulfonate



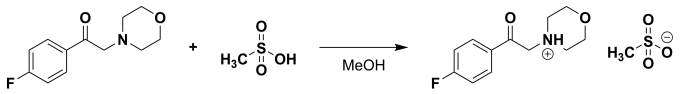
Following the general procedure, phenacyldiethylamine (194 mg, 1.0 mmol, 1 eq) was taken into 25 mL round bottom flask, and dissolved in methanol (5.0 mL). *p*-Toluenesulfonic acid monohydrate (193 mg, 1.0 mmol, 1 eq) was then added and salt formed within 3 min. Toluene (5.0 mL) was added and residue was concentrated under reduced pressure. Product was dissolved in DCM (4.0 mL) and hexanes (20.0 mL) was added. This was concentrated under reduced pressure and dried in vacuum, giving product in 99.2% yield (366 mg). A sample (50 mg) was taken for purification on a silica column (0-13% MeOH/DCM) and pure product (26.5 mg) was isolated.
^{1}H (500 MHz, Methanol-d4) δ 8.08 - 8.02 (2H, m), 7.75 - 7.66 (3H, m), 7.57 (2H, t, *J*=7.9 Hz), 7.21 (2H, d, *J*=7.9 Hz), 4.94 (2H, s), 3.37 - 3.27 (4H, m, merged with residual methanol peak of CD_3OD), 2.35 (3H, s), 1.34 (6H, t, *J*=7.3 Hz)
^{13}C {^{1}H } (126 MHz, Methanol-d4) δ 192.6, 143.5, 141.6, 136.1, 134.7, 130.2, 129.8, 129.5, 126.9, 59.4, 50.9, 21.9, 11.5, 9.5

2.3.10 4-(2-Oxo-2-phenylethyl)morpholin-4-ium methanesulfonate (18H$^+$OTs$^-$)



Following the general procedure, phenacylmorpholine (71 mg, 0.35 mmol, 1 eq) was taken into 20 mL vial. Methanesulfonic acid (22 µL, 0.35 mmol, 1 eq) was then added in glove box and salt formed within 3 min. The mixture was removed from glove box and methanol (5.0 mL) was added. This was concentrated under reduced pressure and dried in vacuum, giving product in 98.9% yield (103 mg).
^{1}H (500 MHz, Methanol-d4) δ 8.09 - 8.01 (2H, m), 7.79 - 7.70 (1H, m), 7.65 - 7.55 (2H, m), 5.03 (2H, s), 4.13 - 4.05 (2H, m), 3.94 (2H, ddd, *J*=13.4, 11.3, 2.2 Hz), 3.65 - 3.57 (2H, m), 3.40 - 3.33 (2H, m), 2.69 (3H, s)
^{13}C {^{1}H } (126 MHz, Methanol-d4) δ 190.4, 134.7, 133.5, 128.8, 127.9, 63.3, 61.2, 52.9, 38.0

2.3.11 4-(2-(4-Fluorophenyl)-2-oxoethyl)morpholin-4-ium methanesulfonate

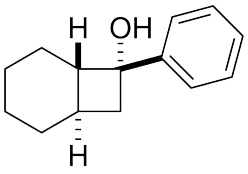


Following the general procedure, 4-fluorophenacylmorpholine (412 mg, 1.9 mmol, 1 eq) was taken into 20 mL vial. Methanesulfonic acid (120 µL, 1.9 mmol, 1 eq) was then added in glove box and salt formed within 3 min. The mixture was removed from glove box and methanol (5.0 mL) was added to fully dissolve mixture. This was concentrated under reduced pressure and dried in vacuo, giving product in 94.8% yield (559 mg).
^{1}H (500 MHz, Methanol-d4) δ 8.18 - 8.08 (2H, m), 7.38 - 7.29 (2H, m), 5.01 (2H, s), 4.13 - 4.04 (2H, m), 4.00 - 3.89 (2H, m), 3.66 - 3.57 (2H, m), 3.40 - 3.32 (2H, m), 2.69 (3H, s)
^{13}C {^{1}H } (126 MHz, Methanol-d4) δ 190.4, 169.4, 166.9, 132.6, 132.5, 131.6, 117.4, 117.2, 64.7, 62.6, 54.3, 39.5

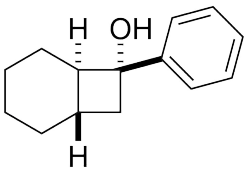
3 Norrish-Yang/Aza-Yang cyclization

3.1 Experimental procedure for Norrish-Yang cyclization

3.1.1 Synthesis of 2 and 3



Compound 2



Compound 3

In a 250 mL round bottom flask (Pyrex®), 2-cyclohexyl-1-phenylethan-1-one (1.2 mmol) was dissolved in 123.6 mL acetonitrile (10 mM). Solution was purged with nitrogen for 10 min. Flask was irradiated under nitrogen with Hg-Xe lamp at 200 W for 2 h through a longpass (LP) filter ($\lambda \geq 305$ nm). The reaction was monitored in 10% ethyl acetate in hexanes. Four spots were observed on TLC at R_f = 0.72, 0.68, 0.60, and 0.58. Spots at 0.72 and 0.60 were UV active, while spots at 0.68 and 0.58 were $KMnO_4$ active. UV-active spots correspond to acetophenone (R_f= 0.72) and 1,4-diphenylbutane-1,4-dione (R_f= 0.60) respectively. Non UV-active spots were the compound **2** (R_f= 0.68) and compound **3** (R_f= 0.58). After complete conversion of the starting material, solvent was evaporated. Crude was purified on silica column through flash column chromatography to yield acetophenone (20%), compound **2** (40%), 1,4-diphenylbutane-1,4-dione (10%), and compound **3** (20%).

Compound 2 ^{1}H (500 MHz, Chloroform-d) δ 7.40 - 7.31 (m, 4H, 4, 6, 1, 3), 7.26 (m, 4.6 Hz, 1H), 2.30 (dd, *J*=9.8, 6.2 Hz, 1H, 8'), 2.25 - 2.14 (m, 1H, 17), 2.11 (t, *J*=10.1 Hz, 1H, 8"), 1.85 (ddq, *J*=10.8, 7.0, 3.5 Hz, 3H, 11', 13', 16), 1.77 (ddt, *J*=15.0, 11.9, 3.1 Hz, 2H), 1.64 (qd, *J*=11.7, 3.9 Hz, 1H, 11"), 1.48 - 1.35 (m, 2H), 1.29 (qd, *J*=11.6, 3.6 Hz, 1H, 13")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 146.9 (5), 128.6, 127.4, 125.8, 125.3, 82.1(7), 53.3 (14), 42.0 (8), 38.4 (9), 31.7 (13) 26.8 (10), 26.3 (11), 26.2 (12)

Compound 3 ^{1}H (500 MHz, Chloroform-d) δ 7.52 - 7.44 (2H, m), 7.38 (2H, dd, *J*=8.5, 6.8 Hz), 7.36 - 7.27 (1H, m), 2.89 (1H, dd, *J*=10.6, 6.6 Hz), 1.96 - 1.87 (2H, m), 1.86 - 1.76 (2H, m), 1.74 - 1.63 (2H, m), 1.38 - 1.21 (2H, m), 1.19 - 1.07 (1H, m), 1.05 - 0.92 (1H, m), 0.93 - 0.82 (1H, m)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 141.7, 128.4, 127.6, 127.4, 79.8, 57.1, 41.6, 33.1, 31.9, 28.7, 26.7, 26.1

3.2 General experimental procedure for Aza-Yang cyclization

Salt of the corresponding phenacyl piperidine (Table 1) was suspended in acetonitrile or acetone (10 mM) in a Pyrex® glass flask. Suspension was purged with nitrogen for 10 min. Suspension was irradiated under nitrogen with Hg-Xe lamp at 300 W for 8-16 h through a longpass (LP) filter ($\lambda \geq 305$ nm).The reaction was monitored in 10% methanol in dichloromethane on silica TLC plates, and in 5% methanol in dichloromethane on neutral alumina plate. Spots were visualized using iodine, $KMnO_4$ and ninhydrin stains. After complete conversion of the starting material, solvent was evaporated. Crude reaction mixture was purified on silica or neutral alumina or basic alumina columns. Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments.

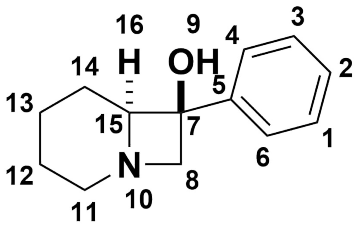
Note:

- Azetidinols are difficult to visualize on TLC. Combination of different staining methods (iodine, $KMnO_4$, ninhydrin, Seebach) is helpful to confirm the presence of product on the TLC.
- Silica columns were used for the purification of cyclobutanols. Azetidinols can be purified on either silica or neutral/basic alumina column. However, through silica columns azetidinols elute as salts with corresponding counter anion.

salt	azetidinol (%)	acetophenone (%)
perchlorate	18	50
tosylate	55	30
camphor sulfonate	25	40
mesylate	46	35

Table S1: Salt counterion has effect on the isolated yield of azetidinol and acetophenone.

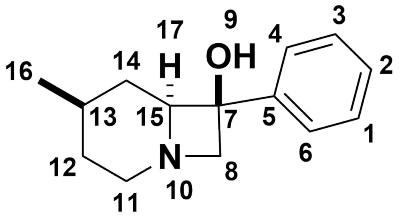
3.2.1 Synthesis of 7



Compound 7

Following the general procedure, tosylate salt of phenacyl piperidine (3.9 mmol) was suspended in 400 mL (10 mM) acetone in a 500 mL round bottom flask. Flask was purged with nitrogen for 15 min, and then irradiated with Hg-Xe lamp at 300 W for 16 h through a longpass (LP) filter ($\lambda \geq 305$ nm).The reaction was monitored in 10% methanol in dichloromethane on silica TLC plates, and in 5% methanol in dichloromethane on neutral alumina plate. Spots were visualized using iodine, $KMnO_4$ and ninhydrin stains (R_f= 0.4). After complete consumption of the starting material, solvent was evaporated. Crude was purified on neutral alumina or basic alumina columns through flash column chromatography to yield compound **7** (55 $\pm$ 7%, based on 3 reactions).
^{1}H (MeOD, 500 MHz) δ 7.64 - 7.59 (m, 2H, 4, 6), 7.39 (t, *J*=7.6 Hz, 2H, 1, 3), 7.30 (t, *J*=7.4 Hz, 1H, 2), 3.93 (dd, *J*=11.1, 6.0 Hz, 1H, 16), 3.79 - 3.69 (m, 2H, 8', 8"), 2.68 (dtd, *J*=22.8, 13.2, 4.5 Hz, 2H, 11', 11"), 2.28 (tdd, *J*=13.3, 11.0, 4.7 Hz, 1H, 14'), 1.87 (dq, *J*=13.8, 4.5 Hz, 1H), 1.74 (dtt, *J*=14.4, 9.7, 4.9 Hz, 1H, 13', 14"), 1.63 (ddd, *J*=14.0, 6.7, 4.2 Hz, 1H, 12'), 1.44 (ddtd, *J*=31.1, 13.5, 9.6, 4.9 Hz, 2H, 12", 13")
^{13}C {^{1}H }(MeOD, 126 MHz) δ 146.3 (5), 129.4 (1, 3), 128.5 (2), 126.9 (4, 6), 74.2 (7), 69.0 (15), 63.9 (8), 47.9 (11), 21.5 (14), 21.4 (12), 20.5 (13)
HRMS-ESI Calc M+H = $C_{13}H_{18}NO$ = 204.1388, Found Mass = 204.1380, 3.9 ppm

3.2.2 Synthesis of 8

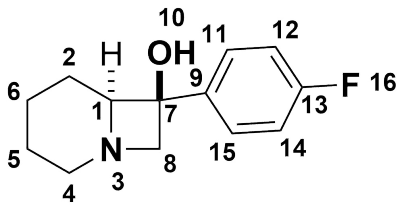


Compound 8

Following the general procedure, tosylate salt of phenacyl 4-methylpiperidine (6.7 mmol) was suspended in 673 mL

(10 mM) acetone in a 1 L round bottom flask. Flask was purged with nitrogen for 15 min, and then irradiated with Hg-Xe lamp at 300 W for 16 h through a longpass (LP) filter ($\lambda \geq 305$ nm). The reaction was monitored in 10% methanol in dichloromethane on silica TLC plates, and in 5% methanol in dichloromethane on neutral alumina plate. Spots were visualized using iodine, $KMnO_4$ and ninhydrin stains (R_f= 0.4). After complete conversion of the starting material, solvent was evaporated. Crude was purified on neutral alumina or basic alumina columns through flash column chromatography to yield compound **8** (42 $\pm$ 3%, based on 3 reactions).
^{1}H (500 MHz, Chloroform-d) δ 7.65 (d, *J*=7.4 Hz, 2H, 4, 6), 7.39 (t, *J*=7.6 Hz, 2H, 1, 3), 7.30 (t, *J*=7.4 Hz, 1H, 2), 3.82 (dd, *J*=11.3, 5.8 Hz, 1H, 17), 3.69 (d, *J*=6.7 Hz, 1H, 8'), 3.61 (d, *J*=6.7 Hz, 1H, 8"), 2.82 - 2.67 (m, 2H, 11), 1.78 (q, *J*=12.2 Hz, 1H, 14'), 1.55 (ddd, *J*=11.7, 6.2, 3.4 Hz, 1H, 14"), 1.48 (dtt, *J*=12.4, 6.4, 3.3 Hz, 1H, 13), 1.42 (dt, *J*=15.6, 3.2 Hz, 1H, 12'), 1.37 - 1.27 (m, 1H, 12"), 1.03 (d, *J*=6.4 Hz, 3H, 16)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 145.0 (5), 128.7 (1, 3), 127.7 (2), 125.4 (4, 6), 73.3 (7), 68.9 (15), 62.5 (8), 47.2 (11), 29.9 (14), 29.6 (12), 27.3 (13), 23.3 (16)
HRMS-ESI Calc M+H = $C_{14}H_{20}NO$ = 218.1545, Found Mass = 218.1491, 24.8 ppm

3.2.3 Synthesis of 9

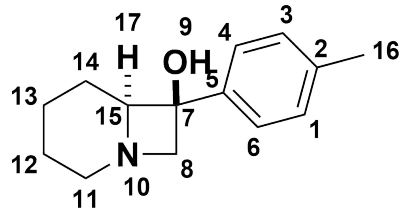


Compound 9

Following the general procedure, tosylate salt of 4-fluorophenacylpiperidine (3.8 mmol) was suspended in 381 mL (10 mM) acetone in a 500 mL round bottom flask. Flask was purged with nitrogen for 15 min, and then irradiated with Hg-Xe lamp at 300 W for 16 h through a longpass (LP) filter ($\lambda \geq 305$ nm).The reaction was monitored in 10% methanol in dichloromethane on silica TLC plates, and in 5% methanol in dichloromethane on neutral alumina plate. Spots were visualized using iodine, $KMnO_4$ and ninhydrin stains (R_f = 0.4). After complete conversion of the starting material, solvent was evaporated. Crudereaction mixture was purified on neutral alumina or basic alumina columns to yield compound **9** (40 $\pm$ 4%, based on 3 reactions).
^{1}H (500 MHz, Chloroform-d) δ 7.62 (2H, dd, *J*=8.5, 5.4 Hz, 11, 15), 7.06 (2H, t, *J*=8.6 Hz, 12, 14), 3.76 - 3.67 (2H, m, 1, 8'), 3.59 (1H, d, *J*=6.9 Hz, 8"), 2.79 - 2.70 (1H, m, 4'), 2.69 - 2.63 (1H, m, 4"), 2.09 (1H, qd, *J*=13.4, 4.4 Hz, 5'), 1.86 (1H, dp, *J*=13.1, 4.3 Hz, 2'), 1.72 - 1.54 (2H, m, 2", 5"), 1.49 – 1.30 (2H, m, 6')
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 162.4 (d, *J*=246.0 Hz, (13)), 140.8 (9), 127.2 (d, *J*=8.1 Hz,(11, 15)), 115.4 (d, *J*=21.6 Hz, (12, 14)), 73.5 (7), 68.8 (1), 63.6 (8), 47.3 (4), 21.0 (5), 21.0 (2), 20.4 (6)
HRMS-ESI Calc M+H = $C_{13}H_{17}FNO$ = 222.1294, Found Mass = 222.1282, 5.4 ppm

3.2.4 Synthesis of 10

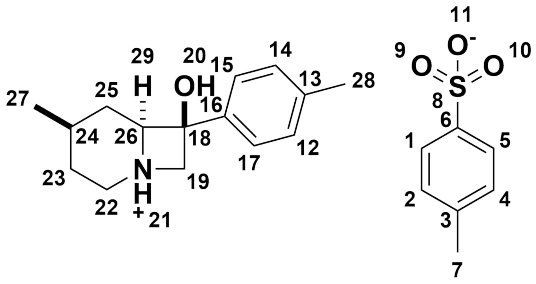
Following the general procedure, tosylate salt of 4-methylphenacylpiperidine (4.1 mmol) was suspended in 411 mL (10 mM) acetone in a 500 mL round bottom flask. Flask was purged with nitrogen for 15 min, and then irradiated with Hg-Xe lamp at 300 W for 16 h through a longpass (LP) filter ($\lambda \geq 305$ nm).The reaction was monitored in 10% methanol in dichloromethane on silica TLC plates, and in 5% methanol in dichloromethane on neutral alumina plate. Spots were visualized using iodine, $KMnO_4$ and ninhydrin stains (R_f= 0.4). After complete conversion of the starting material, solvent was evaporated. Crude was purified on neutral alumina or basic alumina columns to yield compound **10** (37 $\pm$ 2%, based on 2 reactions).



Compound 10

^{1}H (500 MHz, Chloroform-d) δ 7.51 (d, *J*=8.0 Hz, 2H, 4, 6), 7.19 (d, *J*=7.9 Hz, 2H, 1, 3), 3.78 (dd, *J*=11.1, 5.8 Hz, 1H, 17), 3.72 - 3.63 (m, 2H, 8), 2.81 - 2.64 (m, 2H, 11), 2.35 (s, 3H, 16), 2.13 (tdd, *J*=13.1, 10.7, 4.4 Hz, 1H, 14'), 1.86 (dp, *J*=13.2, 4.4 Hz, 1H, 13'), 1.67 (dtd, *J*=17.6, 10.7, 5.3 Hz, 1H, 14"), 1.61 - 1.52 (m, 1H, 12'), 1.48 - 1.34 (m, 2H, 12", 13")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 141.8 (5), 137.3 (2), 129.3 (1, 3), 125.1 (4, 6), 73.8 (7), 68.6 (15), 63.3 (8), 47.3 (11), 21.1 (16), 20.9 (14), 20.9 (12), 20.3 (13)
HRMS-ESI Calc M+H = $C_{14}H_{20}NO$ = 218.1545, Found Mass = 218.1503, 19.3 ppm

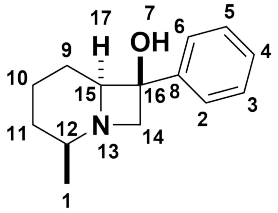
3.2.5 Synthesis of 11



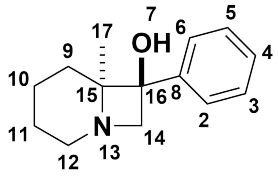
Compound 11

Following the general procedure, tosylate salt of 4-methylphenacyl 4-methylpiperidine (0.37 mmol) was suspended in 37.4 mL (10 mM) acetone in a 100 mL round bottom flask. Flask was purged with nitrogen for 15 min, and then irradiated with Hg-Xe lamp at 300 W for 8 h through a longpass (LP) filter ($\lambda \geq$ 305 nm).The reaction was monitored in 10% methanol in dichloromethane on silica TLC plates, and in 5% methanol in dichloromethane on neutral alumina plate. Spots were visualized using iodine, $KMnO_4$ and ninhydrin stains (R_f= 0.4). After complete conversion of the starting material, solvent was evaporated. Crude was purified on silica columns through flash column chromatography to yield compound **11** (51.6%, as a tosylate salt).
^{1}H (MeOD, 500 MHz) δ 7.69 (d, *J*=7.9 Hz, 2H, 1, 5), 7.41 (d, *J*=7.9 Hz, 2H, 15, 17), 7.28 (d, *J*=8.0 Hz, 2H, 12, 14), 7.23 (d, *J*=7.9 Hz, 3H, 2, 4), 4.92 - 4.78 (1H, m, 29, merged with methanol water residual peak), 4.51 (dd, *J*=11.0, 2.5 Hz, 1H, 19'), 4.14 (d, *J*=10.9 Hz, 1H, 19"), 3.23 (ddd, *J*=13.3, 8.1, 5.6 Hz, 1H, 22"), 2.37 (s, 3H, 7), 2.36 (s, 3H, 28), 2.25 - 2.12 (m, 1H, 23'), 1.95 - 1.86 (m, 2H, 23", 25"), 1.71 (qt, *J*=8.8, 6.2, 2.9 Hz, 1H, 24), 1.55 (dtd, *J*=14.4, 8.8, 5.4 Hz, 1H, 25'), 1.14 (d, *J*=6.5 Hz, 2H, 27)
^{13}C {^{1}H }(MeOD, 126 MHz) δ 143.5 (6), 141.7 (3), 139.9 (13), 139.4 (16), 130.6 (12, 14), 129.8 (2, 4), 126.9 (15, 17), 126.9 (1, 5), 73.8 (18), 72.6 (26), 64.2 (19), 46.6 (22), 27.8 (25), 27.5 , (23), 24.5 (24), 22.5 (27), 21.3 (7), 21.2 (28)
HRMS-ESI Calc M+H = $C_{15}H_{22}NO$ = 232.1701, Found Mass = 232.1660, 17.7 ppm

3.2.6 Synthesis of 12 and 13



Compound 12



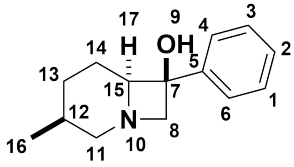
Compound 13

Following the general procedure, tosylate salt of phenacyl 2-methylpiperidine (1.9 mmol) was suspended in 197 mL (10 mM) acetone in a 100 mL round bottom flask. Flask was purged with nitrogen for 15 min, and then irradiated with Hg-Xe lamp at 300 W for 16 h through a longpass (LP) filter ($\lambda \geq 305$ nm).The reaction was monitored in 10% methanol in dichloromethane on silica TLC plates, and in 5% methanol in dichloromethane on neutral alumina plate. Spots were visualized using iodine, $KMnO_4$ and ninhydrin stains (R_f= 0.4). After complete conversion of the starting material, solvent was evaporated. Crude was purified on basic alumina column to afford the regiosomers in 2:1 ratio (Compound **12** (20%), Compound **13** (10%)).
Note: Product spots trail on TLC plates. All spots appear same with minor differences in R_f. For product characterization, each fraction was collected individually and characterized by NMR. **Compound 12**
^{1}H (500 MHz, Chloroform-d) δ 7.61 (dd, *J*=7.4, 1.7 Hz, 2H, 2, 6), 7.39 (td, *J*=7.7, 1.6 Hz, 2H, 3, 5), 7.33 - 7.27 (m, 1H, 4), 3.71 - 3.60 (m, 2H, 14', 17), 3.49 (d, *J*=6.5 Hz, 1H, 14"), 2.75 - 2.65 (m, 1H, 12), 2.03 - 1.84 (m, 2H, 10', 11'), 1.64 - 1.54 (m, 1H, 10"), 1.50 - 1.23 (m, 3H, 9', 9", 11"), 0.96 (dd, *J*=6.8, 1.7 Hz, 3H, 1)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 144.4 (8), 128.7 (3, 5), 127.8 (4), 125.6 (2, 6), 74.7 (16), 70.2 (15), 58.7 (14), 52.4 (12), 29.8 (11), 22.7 (9), 21.9 (10), 18.6 (1)

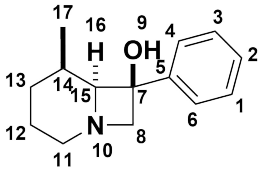
HRMS-ESI Calc M+H = $C_{14}H_{20}NO$ = 218.1545, Found Mass = 218.1505, 18.3 ppm

Compound 13
^{1}H (500 MHz, Chloroform-d) δ 7.39 - 7.28 (3H, m, 1, 3, 5), 7.22 - 7.16 (2H, m, 2, 4), 4.14 (1H, d, *J*=7.7 Hz, 13"), 3.29 (1H, d, *J*=7.7 Hz, 13'), 2.88 - 2.74 (1H, m, 11"), 2.69 - 2.56 (1H, m, 11'), 1.58 - 1.49 (1H, m, 8'), 1.43 (2H, s, 16), 1.40 - 1.25 (2H, m, 9', 10'), 1.19 - 1.15 (1H, m, 8"), 1.10 - 0.95 (2H, m, 9", 10")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 140.7 (C-7), 128.3 (C-2, C-4), 127.6 (C-3), 126.6 (C-1, C-5), 79.6 (C-15), 68.8 (d, *J* = 86.1 Hz, C-14), 56.5 (C-16), 44.4 (C-11), 29.9, 19.7 (C-8), 19.6 (C-10), 19.1 (C-9)

3.2.7 Synthesis of 14 and 15



Compound 14



Compound 15

Following the general procedure, tosylate salt of phenacyl 3-methylpiperidine (0.52 mmol) was suspended in 52 mL (10 mM) acetone in a 100 mL round bottom flask. Flask was purged with nitrogen for 15 min, and then irradiated with Hg-Xe lamp at 300 W for 16 h through a longpass (LP) filter ($\lambda \geq 305$ nm).The reaction was monitored in 10% methanol in dichloromethane on silica TLC plates, and in 5% methanol in dichloromethane on neutral alumina plate.

Spots were visualized using iodine, $KMnO_4$ and ninhydrin stains (R_f= 0.4). After complete conversion of the starting material, solvent was evaporated. Crude was purified on neutral alumina column to afford the regioisomers in 1:1 ratio (Combined yield 39%)).

Note:

- Both the regioisomers eluted together from neutral alumina column.
- Crystal structure showed the H-bonding between the two regioisomers, which may explain co-elution through column.
- Reported NMR is the mixture of regioisomers.

^{1}H (500 MHz, Chloroform-d) δ 7.68 - 7.60 (2H, m), 7.44 - 7.36 (2H, m), 7.33 - 7.27 (1H, m), 3.75 - 3.68 (1H, m), 3.67 (1H, s), 3.60 (1H, dd, *J* = 6.4, 1.8 Hz), 3.27 (1H, d, *J* = 10.0 Hz), 2.75 - 2.58 (2H, m), 2.29 - 2.09 (2H, m), 1.85 - 1.65 (2H, m), 1.65 - 1.57 (1H, m), 0.93 (2H, d, *J* = 6.0 Hz), 0.83 (2H, d, *J* = 6.5 Hz)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 145.2, 145.1, 128.7, 128.7, 127.74, 127.71, 125.5, 125.4, 75.6, 73.9, 73.3, 67.7, 62.8, 54.9, 46.7, 29.9, 26.6, 26.3, 21.8, 21.3, 20.5, 19.8
HRMS-ESI Calc M+H = $C_{14}H_{20}NO$ = 218.1545, Found Mass = 218.1503, 19.3 ppm

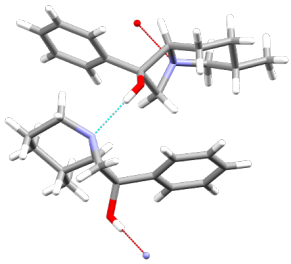
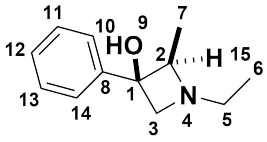


Figure S1: Crystal structure of the co-crystallized compounds 14 and 15 (CCDC2101761)

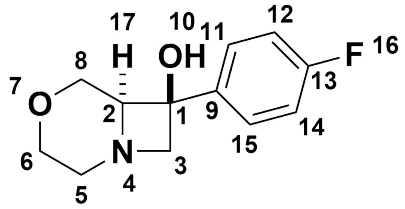
3.2.8 Synthesis of 16



Following the general procedure, tosylate salt of phenacyl diethylamine (0.20 mmol) was suspended in 20 mL (10 mM) acetone in a 50 mL round bottom flask. Flask was purged with nitrogen for 15 min, and then irradiated with Hg-Xe lamp at 300 W for 16 h through a longpass (LP) filter ($\lambda \geq$ 305 nm).The reaction was monitored in 10% methanol in dichloromethane on silica TLC plates, and in 5% methanol in dichloromethane on neutral alumina plate. Spots were visualized using iodine, $KMnO_4$ and ninhydrin stains (R_f= 0.3). After complete conversion of the starting material, solvent was evaporated. Crude reaction mixture was purified on neutral alumina column to afford compound **16** in 9% isolated yield (NMR yield using internal standard 1,3,5-trimethoxybenzene was 27%).

^{1}H (500 MHz, Chloroform-d) δ 7.45 - 7.32 (4H, m, 10, 14), 7.32 - 7.22 (1H, m, 12, merged with chloroform-d), 3.75 (1H, d, *J*=8.6 Hz, 3”), 3.53 (1H, q, *J*=6.5 Hz, 15), 3.31 (1H, d, *J*=8.5 Hz, 3’), 2.82 (1H, dq, *J*=14.3, 7.4 Hz, 5’), 2.51 (1H, dq, *J*=14.0, 7.2 Hz, 5”), 1.35 (3H, dd, *J*=6.5, 1.5 Hz, 7), 1.11 (3H, td, *J*=7.3, 1.6 Hz, 6)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 142.7 (C-8), 128.6 (C-10, C-14), 127.7, 125.5 (C-11, C-13), 74.9 (C-1), 72.1, 65.3 (C-3), 51.7 (C-5), 13.7 (C-7), 12.7 (C-6)
HRMS-ESI Calc M+H = $C_{12}H_{18}NO$ = 192.1388, Found Mass = 192.1346, 21.9 ppm

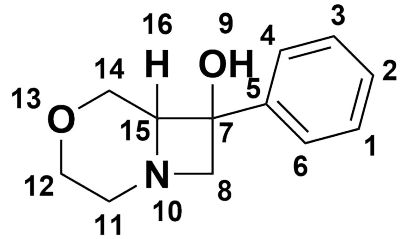
3.2.9 Synthesis of 17



Compound 17

Following the general procedure, mesylate salt of 4-fluorophenacyl morpholine (1.69 mmol) was suspended in 170 mL (10 mM) acetone in a 250 mL round bottom flask. Flask was purged with nitrogen for 15 min, and then irradiated with Hg-Xe lamp at 300 W for 16 h through a longpass (LP) filter ($\lambda \geq$ 305 nm).The reaction was monitored in 10% methanol in dichloromethane on silica TLC plates, and in 5% methanol in dichloromethane on neutral alumina plate. Spots were visualized using iodine, $KMnO_4$ and ninhydrin stains (R_f= 0.4). After complete conversion of the starting material, solvent was evaporated. Crude was purified on neutral alumina column to afford compound **17** in 46% NMR yield with 1,3,5-trimethoxybenzene as a standard (10% isolated yield)
^{1}H (500 MHz, Chloroform-d) δ 7.62 (2H, dd, *J*=8.3, 5.4 Hz, 11, 15), 7.06 (2H, t, *J*=8.6 Hz, 12, 14), 4.18 (1H, q, *J*=6.5 Hz, 8’), 4.09 (1H, td, *J*=11.1, 5.5 Hz, 8”), 3.93 (1H, d, *J*=8.1 Hz, 3’), 3.90 - 3.82 (2H, m, 6’, 17), 3.82 - 3.72 (2H, m, 3”, 6”), 3.23 - 3.05 (1H, m, 5’), 2.65 (1H, dd, *J*=14.6, 5.5 Hz, 5”)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ162.2 (d, *J* = 246.0 Hz, C-13), 140.1 (d, *J* = 3.4 Hz, C-9), 126.5 (d, *J* = 8.2 Hz, C-11, C-15), 115.2 (d, *J* = 21.6 Hz, C-12, C-14), 73.3 (C-1), 68.0 (C-2), 65.3 (C-3), 61.9 (C-8), 61.8 (C-6), 43.1 (C-5)
HRMS-ESI Calc M+H = $C_{12}H_{15}FNO_2$ = 224.1087, Found Mass = 224.1059, 12.5 ppm

3.2.10 Synthesis of 19



Compound 19

Following the general procedure, mesylate salt of phenacyl morpholine (0.07 mmol) was suspended in 6.7 mL (10 mM) acetone in a 10 mL round bottom flask. Flask was purged with nitrogen for 15 min, and then irradiated with Hg-

Xe lamp at 300 W for 16 h through a longpass (LP) filter ($\lambda \geq 305$ nm).The reaction was monitored in 10% methanol in dichloromethane on silica TLC plates, and in 5% methanol in dichloromethane on neutral alumina plate. Spots were visualized using iodine, $KMnO_4$ and ninhydrin stains (R_f= 0.4). After complete consumption of the starting material, solvent was evaporated. Crude was purified on neutral alumina column to afford compound **19** in 25.2% yield.
^{1}H (500 MHz, Chloroform-d) δ 7.68 - 7.62 (m, 2H, 4, 6), 7.45 - 7.37 (m, 2H, 1, 3), 7.32 (dd, *J*=8.2, 6.6 Hz, 1H, 2), 4.25 (dd, *J*=13.0, 4.2 Hz, 1H, 14'), 4.15 (td, *J*=10.6, 5.5 Hz, 1H, 12'), 4.12 - 4.01 (m, 2H, 8", 15), 3.99 - 3.91 (m, 2H, 8', 14"), 3.84 (dt, *J*=10.8, 4.3 Hz, 1H, 12"), 3.36 - 3.20 (m, 1H, 11'), 2.87 (d, *J*=14.5 Hz, 1H, 11")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 128.8 (1, 3), 127.9 (2), 124.7 (4, 6), 74.5 (7), 67.7 (15), 65.9 (8), 62.1 (12, 14), 43.8 (11)

HRMS-ESI Calc M+H = $C_{12}H_{16}NO_2$ = 206.1181, Found Mass = 206.1134, 22.8 ppm

3.3 Origin of diastereoselectivity

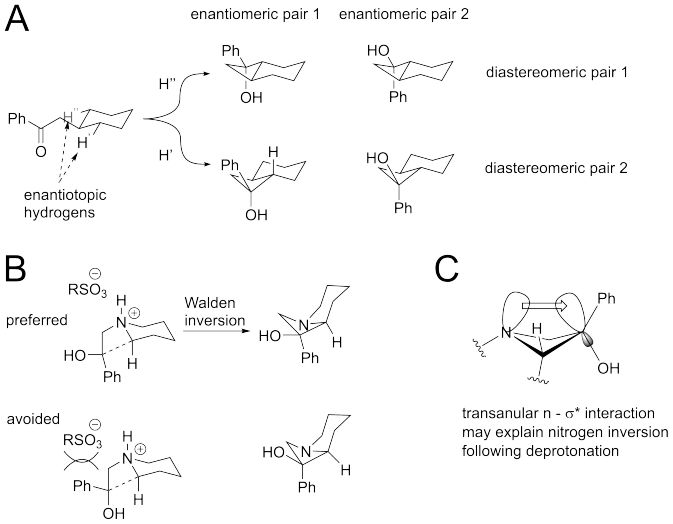


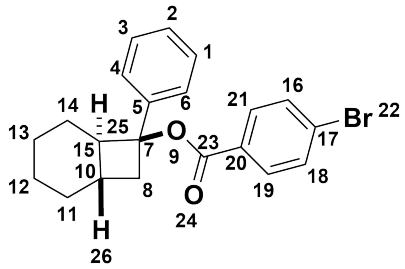
Figure S2: A. Abstraction of enantiotopic hydrogen in phenacyl cyclohexane leads to the generation of diastereomeric pairs. **B**. Formation of salt in phenacyl piperidine lock the conformation in which phenyl and tosyl group prefers to avoid steric clash. **C**. Desalting leads to the Walden inversion of the amine favoring transannular n-σ^* interaction

4 Esterification

4.1 General experimental procedure for esterification

In a round bottom flask, alcohol (1 eq), acid (1.5 eq), 4-dimethylaminopyridine (DMAP) (0.2 eq), and dicyclohexyl carbodiimide (DCC) (1.5 eq) were dissolved in anhydrous dichloromethane (100 mM), and reaction was allowed to proceed for 3 h. Progress of the reaction was monitored in 5% methanol in dichloromethane on neutral alumina for the disappearance of azetidinol, and on silica for spotting the product ester. Azetidinol disappearance (R_f 0.4-0.5) was monitored on neutral alumina plate, followed by ninhydrin staining. Ester product elutes at 0.5 R_f in 5% methanol in dichloromethane, followed by $KMnO_4$ staining. Often, running of the TLC multiple times in the same solvent system helps in the separation of the overlapping spots. After complete disappearance of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. This will precipitate out most of the dicyclohexylurea by-product from the reaction. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column. Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments.

4.2 Synthesis of 4

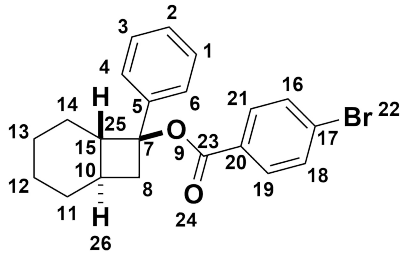


Following the general procedure, compound **2** (0.05 mmol, 1 eq), 4-bromobenzoic acid (0.5 mmol, 1.0 eq), DCC (0.06 mmol, 1.2 eq), DMAP (0.5 mmol, 1 eq) was dissolved in 0.5 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 10% ethyl acetate in hexanes. After completion of the starting material, reaction was diluted with water and extracted with ethyl acetate.The water layer was washed with ethyl acetate, and combined organic layer was washed with brine. The organic layer was concentrated and column purification was done in 0-20% ethyl acetate in hexanes to yield 52.9% of compound **4**.
^{1}H (400 MHz, Chloroform-d) δ 7.94 – 7.88 (2H, m, 19, 21), 7.59 – 7.55 (2H, m, 16, 18), 7.43 – 7.38 (2H, m), 7.35 – 7.29 (2H, m), 7.27 – 7.21 (1H, m), 2.84 (1H, dd, *J*=11.5, 6.6 Hz, 25), 2.38 (1H, t, *J*=10.9 Hz), 2.18 – 2.06 (1H, m), 2.06 – 1.96 (2H, m), 1.90 – 1.82 (2H, m), 1.81 – 1.66 (1H, m), 1.45 – 1.23 (4H, m)

^{13}C {^{1}H } (101 MHz, Chloroform-d) δ 165.0 (C-23), 143.1 (C-5), 131.7, 131.2, 130.2 (C-20), 128.3, 127.9 (C-17), 127.6, 126.2, 89.7 (C-7), 54.4 (C-15), 39.3 (C-8), 38.6 (C-10), 31.7 (C-11), 27.8 (C-14), 26.6 (C-13), 26.4 (C-12)

4.3 Synthesis of 5

Following the general procedure, compound **3** (0.05 mmol, 1 eq), 4-bromobenzoic acid (0.5 mmol, 1.0 eq), DCC (0.06 mmol, 1.2 eq), DMAP (0.5 mmol, 1 eq) was dissolved in 0.5 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 10% ethyl acetate in hexanes. After completion of the starting material, reaction was diluted with water and extracted with ethyl acetate.The water layer was washed with ethyl acetate, and combined organic layer was washed with brine. The organic layer was concentrated and column purification was done

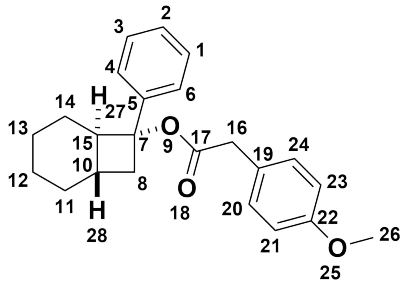


in 0-20% ethyl acetate in hexanes to yield 76.1% of compound **5**.
^{1}H (400 MHz, Chloroform-d) δ 7.88 - 7.82 (2H, m), 7.56 - 7.49 (4H, m), 7.39 - 7.33 (2H, m), 7.31 - 7.26 (1H, m), 3.34 (1H, dd, *J*=11.3, 6.3 Hz, 25), 2.23 - 2.10 (2H, m), 1.98 - 1.82 (2H, m), 1.79 - 1.67 (2H, m), 1.45 - 1.31 (2H, m), 1.31 - 1.10 (1H, m), 1.04 - 0.87 (1H, m)
^{13}C {^{1}H } (101 MHz, Chloroform-d) δ 164.4 (C-23), 138.3 (C-5), 131.7, 131.2, 130.0, 128.2, 127.8, 127.8, 85.1 (C-7), 54.8 (C-15), 40.4 (C-8), 34.8 (C-10), 31.9 (C-14), 28.5 (C-11), 26.5 (C-13), 26.0 (C-12)

4.4 Synthesis of E1

Code	Compound
ArAA-1	4-Methoxyphenylacetic acid
ArAA-2	Phenylacetic acid
ArAA-3	Indole-3-acetic acid
ArAA-4	3-Thiopheneacetic acid

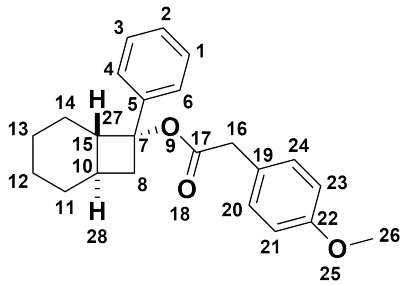
Table S2: Codes of phenylacetic acids used for esterification, and progressed for complete compound collection synthesis.



Following the general procedure, compound **3** (0.15 mmol, 1 eq), ArAA-1 (0.22 mmol, 1.5 eq), DCC (0.22 mmol, 1.5 eq), DMAP (0.03 mmol, 0.2 eq) was dissolved in 1.5 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 10% ethyl acetate in hexanes. After completion of the starting material, reaction was diluted with water and extracted with ethyl acetate.The water layer was washed with ethyl acetate, and combined organic layer was washed with brine. The organic layer was concentrated and column purification was done in 0-20% ethyl acetate in hexanes to yield **E1** in 61.2%.
^{1}H (500 MHz, Chloroform-d) δ 7.38 (dd, *J*=8.2, 1.5 Hz, 2H, 4, 6), 7.31 (dd, *J*=8.3, 6.6 Hz, 2H, 1, 3), 7.24 (m, 1H, 2), 7.11 - 7.05 (m, 2H, 20, 24), 6.84 - 6.78 (m, 2H, 21, 23), 3.78 (s, 3H, 26), 3.49 - 3.37 (m, 2H, 16', 16"), 3.20 (dd, *J*=11.3, 6.4 Hz, 1H, 8'), 2.05 - 1.96 (m, 2H, 8", 27), 1.80 (dt, *J*=11.5, 3.3 Hz, 2H, 11', 14'), 1.68 (dp, *J*=9.3, 3.1 Hz, 2H, 12", 13'), 1.56 (s, 1H), 1.39 - 1.22 (m, 3H, 12', 13", 14"), 1.21 - 1.05 (m, 1H, 28), 0.93 - 0.75 (m, 1H, 11")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 170.3 (17), 158.6 (22), 138.3 (5), 130.4 (20, 24), 128.0 (4, 6), 127.7 (1, 3),

127.6 (2), 126.3 (19), 113.9 (21, 23), 84.6 (7), 55.4 (26), 54.6 (15), 40.8 (16), 40.3 (8), 34.8 (10), 31.8 (14), 28.3 (11), 26.4 (13), 25.9 (12)

4.5 Synthesis of E2

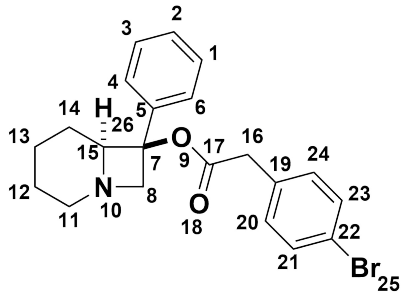


Following the general procedure, compound **2** (0.15 mmol, 1 eq), ArAA-1 (0.22 mmol, 1.5 eq), DCC (0.22 mmol, 1.5 eq), DMAP (0.03 mmol, 0.2 eq) was dissolved in 1.5 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 10% ethyl acetate in hexanes. After completion of the starting material, reaction was diluted with water and extracted with ethyl acetate.The water layer was washed with ethyl acetate, and combined organic layer was washed with brine. The organic layer was concentrated and column purification was done in 0-20% ethyl acetate in hexanes to yield **E2**in 47.7%.

^{1}H (500 MHz, Chloroform-d) δ 7.27 (m, 4H, 1, 3, 4, 6), 7.21 (m, 1H, 2), 7.17 (d, *J*=8.5 Hz, 2H, 20, 24), 6.85 (d, *J*=8.6 Hz, 2H, 21, 23), 3.80 (s, 3H, 26), 3.52 (s, 2H, 16), 2.63 (dd, *J*=11.3, 6.0 Hz, 1H, 8'), 2.28 - 2.15 (m, 1H, 8"), 1.95 - 1.82 (m, 3H, 11', 27, 28), 1.80 - 1.70 (m, 2H, 11", 12'), 1.62 - 1.44 (m, 2H, 13', 14'), 1.40 - 1.16 (m, 2H, 13", 14")

^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 171.0 (17), 158.6 (22) , 143.3 (5), 130.5 (20, 24), 128.1 (4, 6) , 127.3 (2), 126.5 (19), 126.2 (1, 3), 113.9 (21, 23), 89.0 (7), 55.4 (26), 53.9 (15), 41.4 (16), 39.3 (8), 38.3 (10), 31.7 (14), 27.6 (11), 26.6 (13), 26.3 (12)

4.6 Synthesis of E4

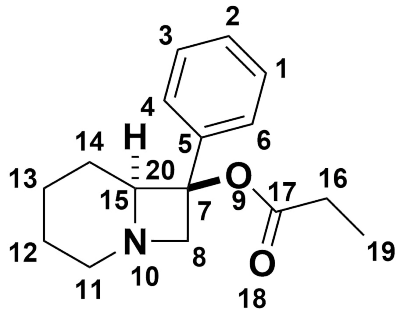


Following the general procedure, Compound **7** (0.25 mmol, 1 eq), 4-bromophenylacetic acid (0.38 mmol, 1.5 eq), DCC (0.38 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.6 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E4** in 65.4%.

^{1}H (500 MHz, Chloroform-d) δ 7.50 - 7.46 (m, 2H, 4, 6), 7.45 - 7.42 (m, 2H, 21, 23), 7.36 - 7.30 (m, 2H, 1, 3), 7.29

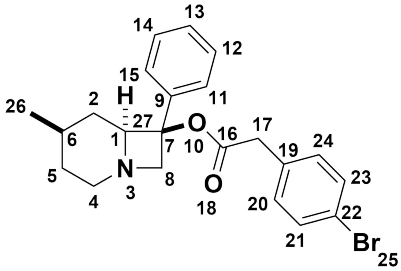
- 7.24 (m, 1H, 2), 7.13 - 7.08 (m, 2H, 20, 24), 3.95 (ddd, *J*=11.0, 5.8, 1.4 Hz, 1H, 26), 3.88 - 3.82 (m, 2H, 8'), 3.56 (s, 2H, 16'), 2.78 (ddd, *J*=13.8, 11.3, 4.0 Hz, 1H, 11'), 2.71 - 2.61 (m, 1H, 11"), 1.97 - 1.73 (m, 2H, 13', 14'), 1.66 - 1.53 (m, 2H, 12', 14"), 1.46 - 1.23 (m, 2H, 12", 13")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 169.4 (17), 141.3 (5), 132.7 (19), 131.7 (21, 23), 131.1 (20, 24), 128.5 (1, 3), 127.7 (2), 125.6 (4, 6), 121.3 (22), 78.5 (7), 67.2 (15), 60.6 (8), 46.6 (11), 41.0 (16), 20.8 (14), 20.5 (12), 20.3 (13)

4.7 Synthesis of E7



Following the general procedure, compound **7** (0.42 mmol, 1 eq), propionic acid (0.63 mmol, 1.5 eq), DCC (0.63 mmol, 1.5 eq), DMAP (0.08 mmol, 0.2 eq) was dissolved in 4.2 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E7** in 57.7%.
^{1}H (500 MHz, Chloroform-d) δ 7.57 (d, *J*=7.8 Hz, 2H, 4, 6), 7.35 (t, *J*=7.6 Hz, 2H, 1, 3), 7.26 (m, 1H, 2), 3.97 (dd, *J*=11.0, 5.8 Hz, 1H, 20), 3.92 - 3.83 (m, 2H, 8), 2.80 (ddd, *J*=14.9, 11.4, 4.0 Hz, 1H, 11'), 2.72 - 2.61 (m, 1H, 11"), 2.33 (q, *J*=7.6 Hz, 2H, 16', 16"), 2.06 - 1.91 (m, 1H, 12'), 1.82 (dt, *J*=13.1, 4.2 Hz, 1H, 13'), 1.65 (m, 2H, 14', 13"), 1.50 - 1.27 (m, 2H, 12", 14"), 1.10 (t, *J*=7.6 Hz, 3H, 19)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 172.9 (17), 141.9 (5), 128.5 (1, 3), 127.6 (2), 125.5 (4, 6), 77.8 (7), 67.3 (15), 60.8 (8), 46.7 (11), 27.8 (16), 20.8 (12), 20.5 (14), 20.4 (13), 9.1 (19))

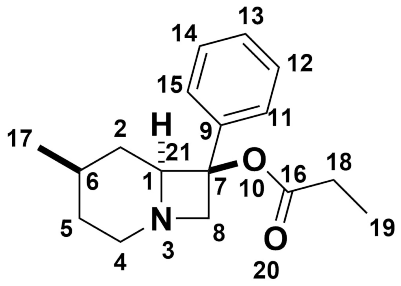
4.8 Synthesis of E12



Following the general procedure, compound **8** (0.23 mmol, 1 eq), 4-bromophenylacetic acid (0.35 mmol, 1.5 eq), DCC (0.35 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.3 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and

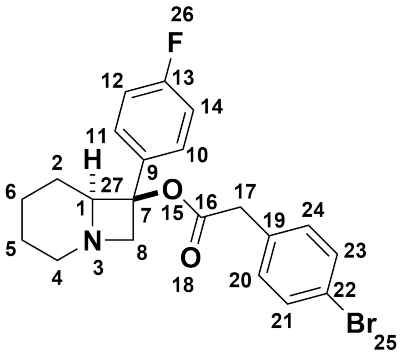
purified in 5% methanol in dichloromethane on silica column to yield **E12** in 62.6%.
^{1}H (500 MHz, Chloroform-d) δ 7.52 - 7.47 (m, 2H, 11, 15), 7.44 (dd, *J*=8.3, 1.4 Hz, 2H, 21, 23), 7.35 - 7.29 (m, 2H, 12, 14), 7.28 - 7.23 (m, 1H, 13), 7.14 - 7.08 (m, 2H, 20, 24), 4.00 - 3.90 (m, 1H, 27), 3.77 (s, 2H, 8), 3.55 (s, 2H, 17', 17"), 2.82 - 2.72 (m, 1H, 4'), 2.71 - 2.61 (m, 1H, 4"), 1.53 - 1.46 (m, 1H, 2'), 1.43 - 1.31 (m, 3H, 2", 5", 6), 1.27 - 1.15 (m, 1H, 5'), 0.97 - 0.91 (m, 3H, 26)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 169.4 (16), 141.4 (9), 132.8 (19), 131.8 (21, 23), 131.2 , (20, 24), 128.5 (12, 14), 127.8 (13), 125.6 (11, 15), 121.4 (22), 78.1 (7), 67.7 (1), 60.2 (8), 46.8 (4), 41.3 (17), 29.7 (2), 29.1 (5), 27.1 (6), 23.2 (26)

4.9 Synthesis of E13



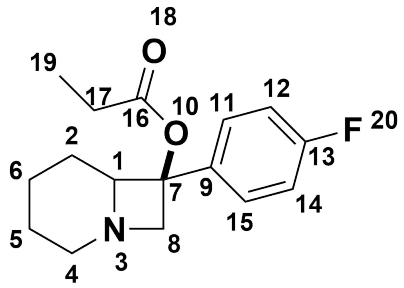
Following the general procedure, compound **8** (0.23 mmol, 1 eq), propionic acid (0.35 mmol, 1.5 eq), DCC (0.35 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.3 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E13** in 83.8%.
^{1}H (500 MHz, Chloroform-d) δ 7.48 (d, *J*=7.7 Hz, 2H, 11, 15), 7.26 (t, *J*=7.6 Hz, 2H, 12, 14), 7.20 - 7.13 (m, 1H, 13), 4.01 - 3.92 (m, 1H, 21), 3.88 - 3.72 (m, 2H, 8), 2.73 (td, *J*=13.0, 11.7, 4.0 Hz, 1H, 4'), 2.63 (dt, *J*=14.2, 3.7 Hz, 1H, 4"), 2.23 (q, *J*=7.6 Hz, 2H, 18'), 1.60 - 1.50 (m, 2H, 2), 1.44 - 1.31 (m, 2H, 5', 6), 1.24 - 1.13 (m, 1H, 5"), 1.00 (td, *J*=7.6, 1.3 Hz, 3H, 17), 0.92 (d, *J*=6.5 Hz, 3H, 19)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 172.9 (16), 141.7 (9), 128.5 (12, 14), 127.7 (13), 125.7 (11 , 15), 77.4 (7), 67.7 (1), 60.3 (8), 46.7 (4), 29.7 (2), 29.1 (5), 27.8 (18), 27.0 (6), 23.2 (19), 9.0 (17)

4.10 Synthesis of E15



Following the general procedure, ccompound **9** (0.23 mmol, 1 eq), 4-bromophenylacetic acid (0.34 mmol, 1.5 eq), DCC (0.34 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.3 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E15** in 75.1%.
^{1}H (500 MHz, Chloroform-d) δ 7.36 (d, *J*=7.5 Hz, 4H), 7.00 (d, *J*=8.0 Hz, 2H), 6.91 (t, *J*=8.5 Hz, 2H), 3.89 - 3.81 (m, 1H), 3.78 - 3.71 (m, 2H, 8), 3.46 (s, 2H, 17', 17"), 2.77 - 2.62 (m, 1H, 4'), 2.61 - 2.50 (m, 1H, 4"), 1.89 - 1.42 (m, 4H, 2', 2", 6), 1.39 - 1.13 (m, 2H, 5', 5"))
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 169.4 (16), 162.3 (d, *J*=246.2 Hz, 13), 137.5 (9), 132.6 (19), 131.8 (21, 23), 131.1 (20, 24), 127.6 (d, *J*=8.2 Hz, 11, 15), 121.4 (22), 115.4 (d, *J*=21.1 Hz, 12, 14), 78.2 (7), 67.5 (1), 60.6 (8), 46.6 (4), 41.1 (17), 20.7 (2), 20.4 (5), 20.2 (6)

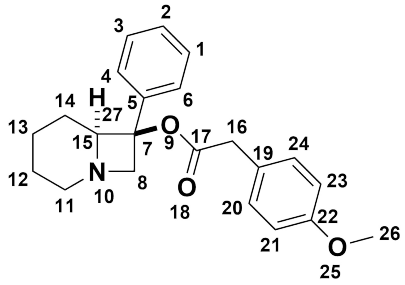
4.11 Synthesis of E18



Following the general procedure, compound **9** (0.24 mmol, 1 eq), propionic acid (0.35 mmol, 1.5 eq), DCC (0.35 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.3 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E18** in 86.1%.
^{1}H (500 MHz, Chloroform-d) δ 7.61 - 7.49 (m, 2H, 11, 15), 7.03 (t, *J*=8.7 Hz, 2H, 12, 14), 3.92 (ddd, *J*=11.8, 6.1, 2.3 Hz, 1H, 1), 3.88 (d, *J*=7.2 Hz, 1H, 8'), 3.77 (dd, *J*=7.1, 2.0 Hz, 1H, 8"), 2.81 - 2.70 (m, 1H, 4'), 2.71 - 2.61 (m, 1H, 4"), 2.32 (q, *J*=7.6 Hz, 2H, 17), 2.04 - 1.92 (m, 1H, 5"), 1.88 - 1.76 (m, 1H, 2"), 1.70 - 1.56 (m, 2H, 2', 5'), 1.46 - 1.38 (m, 1H, 6"), 1.35 - 1.30 (m, 1H, 6'), 1.09 (t, *J*=7.5 Hz, 3H, 19)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 172.9 (16), 162.2 (d, *J*=246.1 Hz, 13), 137.9 (d, *J*=3.5 Hz, 9), 127.6 (d, *J*=8.2 Hz, 11, 15), 115.3 (d, *J*=21.0 Hz, 12, 14), 77.3 (7), 67.3 (1), 60.8 (8), 46.7 (4), 27.9 (17), 20.9 (5), 20.6 (2), 20.5 (6), 9.1 (19)

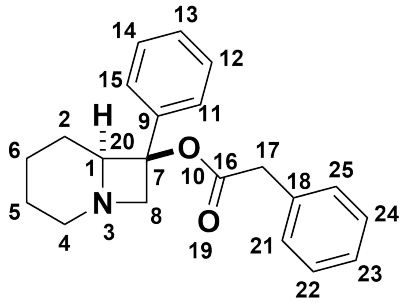
4.12 Synthesis of E-1-1-1

Following the general procedure, compound **7** (0.33 mmol, 1 eq), ArAA-1 (0.50 mmol, 1.5 eq), DCC (0.50 mmol, 1.5 eq), DMAP (0.06 mmol, 0.2 eq) was dissolved in 3.3 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E-1-1-1** in 45.8%.
^{1}H (500 MHz, Chloroform-d) δ 7.50 - 7.45 (m, 2H, 4, 6), 7.34 - 7.28 (m, 2H, 1, 3), 7.27 - 7.22 (m, 1H, 2), 7.17 - 7.12 (m, 2H, 20, 24), 6.89 - 6.81 (m, 2H, 21, 23), 3.90 (s, 1H, 27), 3.82 (s, 2H, 8', 8"), 3.80 (s, 3H, 26), 3.55 (s, 2H, 16',



16”), 2.82 (t, *J*=12.2 Hz, 1H, 11), 2.63 (dt, *J*=14.2, 4.1 Hz, 1H, 11), 1.91 (tdd, *J*=13.2, 10.6, 4.3 Hz, 1H, 12’), 1.76 (dt, *J*=13.1, 4.3 Hz, 1H, 13’, 13”), 1.60 (m, 2H, 12”, 14”), 1.50 - 1.28 (m, 1H, 14’)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 170.2 (17), 158.9 (22), 140.8 (5), 130.5 (20, 24), 128.5 (1, 3), 127.7 (2), 125.8 (19), 125.5 (4, 6), 114.1 (21, 23), 67.4 (15), 60.9 (8), 55.4 (26), 46.7 (11), 40.9 (16), 20.7 (12), 20.5 (14), 20.0 (13)

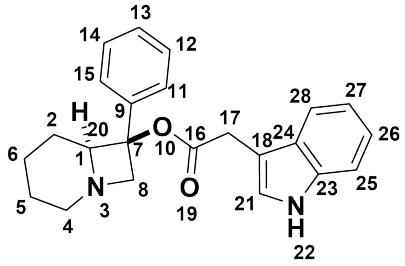
4.13 Synthesis of E-1-1-2



Following the general procedure, compound **7** (0.25 mmol, 1 eq), ArAA-2 (0.37 mmol, 1.5 eq), DCC (0.37 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.5 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E-1-1-2** in 62.0%.
^{1}H (500 MHz, Chloroform-d) δ 7.43 - 7.38 (m, 2H, 11, 15), 7.26 - 7.19 (m, 4H, 12, 14, 22, 24), 7.19 - 7.11 (m, 4H, 13, 21, 23, 25), 3.81 (dd, *J*=11.2, 5.7 Hz, 1H, 20), 3.78 - 3.70 (m, 2H, 8), 3.52 (s, 2H, 17), 2.74 - 2.62 (m, 1H, 4”), 2.61 - 2.49 (m, 1H, 4’), 1.84 - 1.72 (m, 1H, 2”), 1.72 - 1.62 (m, 1H, 5”), 1.56 - 1.45 (m, 2H, 2’), 1.34 - 1.26 (m, 1H, 6”), 1.24 - 1.15 (m, 1H, 6’)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 169.8 (16), 141.6 (9), 133.7 (18), 129.3 (21, 25), 128.5 , (12, 14), 128.3 (22, 24), 127.5 (13), 127.1 (23), 125.4 (11, 15), 78.2 (7), 67.3 (1), 60.7 (8), 46.6 (4), 41.7 (17), 20.7 (2), 20.4 (5), 20.3 (6)

4.14 Synthesis of E-1-1-3

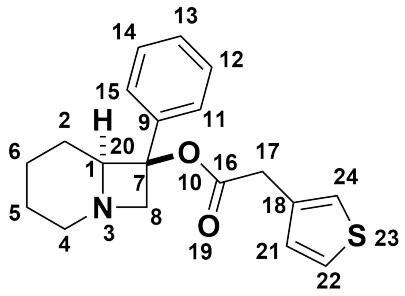
Following the general procedure, compound **7** (0.13 mmol, 1 eq), ArAA-3 (0.18 mmol, 1.5 eq), DCC (0.18 mmol, 1.5 eq), DMAP (0.02 mmol, 0.2 eq) was dissolved in 1.2 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E-1-1-3** in 96.1%.



^{1}H (500 MHz, Chloroform-d) δ 8.28 (1H, s, 22), 7.60 - 7.51 (1H, m, 28), 7.51 - 7.42 (2H, m, 11, 15), 7.36 - 7.32 (1H, m, 25), 7.32 - 7.26 (2H, m, 12, 14), 7.26 - 7.16 (2H, m, 26, 27), 7.14 - 7.09 (1H, m, 13), 7.08 - 7.04 (1H, m, 21), 4.13 - 3.93 (2H, m, 8', 20), 3.86 - 3.80 (1H, m, 8"), 3.78 (2H, s, 17"), 2.93 - 2.69 (1H, m, 4"), 2.62 - 2.33 (1H, m, 4'), 2.04 - 1.78 (1H, m, 2'), 1.74 - 1.51 (2H, m, 2", 6'), 1.52 - 0.90 (3H, m, 5, 6")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 170.4 (C-16), 136.2 (C-9), 128.6 (C-11, C-15), 127.9 (C-24), 127.2 (C-23), 125.5 (C-12, C-14), 123.2 (C-26), 122.4 (C-27), 119.8 (C-28), 118.8 (C-25), 111.4 (C-13), 108.1 (C-18), 78.8 (C-7), 67.4 (C-1), 60.8 (C-8), 46.7 (C-17), 31.8 (C-4), 20.5 (C-2), 20.4 (C-5), 20.2 (C-6)

Boc protection on E-1-1-3 To a stirred solution of **E-1-1-3** (0.29 mmol, 1 eq) in THF (2.9 mL, 100 mM) was added Boc-anhydride (1.7 mmol, 6 eq), DMAP (0.20 mmol, 0.7 eq), and Et_3N (0.20 mmol, 0.7 eq). Solution was heated at 50 ℃ for 1 h. After complete conversion of the starting material, solvent was evaporated and crude was purified in 5% methanol in dichloromethane, to obtain the compound in 81.9% yield.
^{1}H (500 MHz, Chloroform-d) δ 7.56 - 7.46 (3H, m, 11, 13, 15), 7.46 - 7.41 (1H, m, 25), 7.38 - 7.17 (5H, m, 12, 14, 21, 26, 27), 4.09 - 3.82 (3H, m, 8', 20), 3.71 (2H, s, 17), 2.84 - 2.73 (1H, m, 4"), 2.66 - 2.56 (1H, m, 4'), 1.96 - 1.82 (1H, m, 2'), 1.66 (11H, s, 5', 6", 33, 34, 35), 1.63 - 1.49 (1H, m, 6'), 1.48 - 1.22 (2H, m, 2", 5")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 169.3 (C-16), 149.6 (C-29), 129.9 (C-9), 128.4 (C-11, C-15), 127.7, 125.5 (C-12, C-14), 124.6, 122.6, 118.9, 115.3, 112.8 (C-18), 83.7 (C-32), 78.6 (C-7), 67.2 (C-1), 60.6 (C-8), 53.5 (C-17), 46.6 (C-4), 31.4, 28.2 (C-33, C-34, C-35), 27.8, 20.6 (C-2), 20.3 (C-5), 20.0 (C-6)

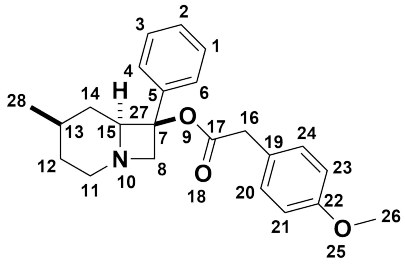
4.15 Synthesis of E-1-1-4



Following the general procedure, compound **7** (0.25 mmol, 1 eq), ArAA-4 (0.37 mmol, 1.5 eq), DCC (0.37 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.5 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E-1-1-4** in 79.7%.
^{1}H (500 MHz, Chloroform-d) δ 7.51 - 7.43 (2H, m, 11, 15), 7.37 - 7.31 (2H, m, 12, 14), 7.31 - 7.21 (2H, m, 13, 22), 7.14 - 7.07 (1H, m, 24), 7.02 - 6.95 (1H, m, 21), 4.08 - 3.91 (2H, m, 20, 8'), 3.89 - 3.81 (1H, m, 8"), 3.66 (2H, s, 17',

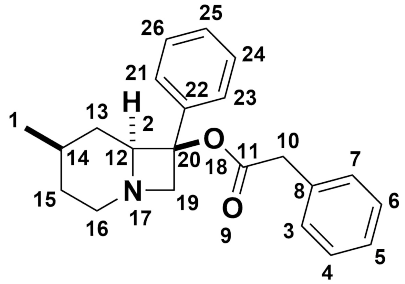
17”), 2.91 - 2.78 (1H, m, 4’), 2.70 - 2.59 (1H, m, 4”), 2.00 - 1.88 (1H, m, 2’), 1.82 - 1.72 (1H, m, 6’), 1.67 - 1.56 (2H, m, 5’, 2”), 1.51 - 1.39 (1H, m, 5”), 1.38 - 1.29 (1H, m, 6”)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 169.4 (C-16), 141.3 (C-9) 133.2 (C-18), 128.6 (C-12, C-14), 128.6 (C-21), 127.9 (C-13), 125.9 (C-22), 125.5 (C-11, C-15), 123.2 (C-24), 78.5 (C-7), 67.4 (C-1), 60.8 (C-8), 46.8 (C-4), 36.3 (C-17), 20.6 (C-2), 20.4 (C-5), 19.9 (C-6)

4.16 Synthesis of E-1-2-1



Following the general procedure, compound **8** (0.38 mmol, 1 eq), ArAA-1 (0.57 mmol, 1.5 eq), DCC (0.57 mmol, 1.5 eq), DMAP (0.08 mmol, 0.2 eq) was dissolved in 3.8 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E-1-2-1** in 52.5%.
^{1}H (500 MHz, Chloroform-d) δ 7.54 - 7.47 (m, 2H, 4, 6), 7.31 (m, 2H, 1, 3), 7.24 (m, 1H, 2), 7.16 (m, 2H, 20, 24), 6.85 (m, 2H, 21, 23), 3.95 (m, 1H, 27), 3.80 (s, 3H, 26), 3.77 (m, 2H, 8’, 8”), 3.54 (s, 2H, 16’), 2.77 (m, 1H, 11’), 2.67 (m, 1H, 11”), 1.52 - 1.47 (m, 1H, 14”), 1.38 (m, 4H, 12, 13), 1.27 - 1.15 (m, 1H, 14’), 0.93 (d, *J*=5.8 Hz, 3H, 28))
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 170.2 (17), 158.9 (22), 141.7 (5), 130.5 (20, 24), 128.5 (1, 3), 127.6 (2), 126.0 (19), 125.6 (4, 6), 114.1 (21, 23), 77.8 (7), 67.8 (15), 60.4 (8), 55.4 (26), 46.8 (11), 41.0 (16), 29.6 (12), 29.2 (14), 27.1 (13), 23.2 (28)

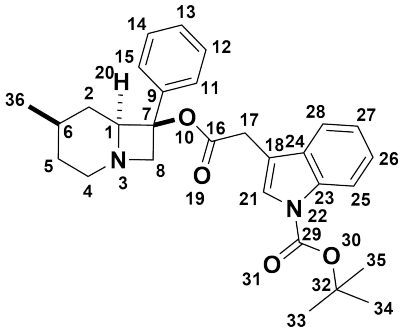
4.17 Synthesis of E-1-2-2



Following the general procedure, Ccompound **8** (0.23 mmol, 1 eq), ArAA-2 (0.35 mmol, 1.5 eq), DCC (0.35 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.3 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E-1-2-2** in 72.3%.

^{1}H (500 MHz, Chloroform-d) δ 7.52 - 7.46 (m, 2H, 21, 23), 7.35 - 7.28 (m, 3H, 5, 24, 26), 7.25 - 7.21 (m, 3H, 4, 6, 25), 4.09 - 3.92 (m, 1H, 2), 3.89 - 3.73 (m, 2H, 19', 19"), 3.60 (s, 2H, 10), 2.84 - 2.62 (m, 2H, 16', 16"), 2.01 - 1.86 (m, 1H, 13'), 1.55 - 1.46 (m, 1H, 15'), 1.45 - 1.28 (m, 1H, 14), 1.27 - 1.13 (m, 1H, 15"), 1.13 - 1.00 (m, 1H, 13"), 0.91 (d, *J*=5.2 Hz, 3H, 1)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 169.8 (11), 141.4 (22), 133.8 (8), 129.5 (3, 7), 128.7 (24, 26), 128.5 (4, 6), 127.7 (25), 127.3 (5), 125.6 (21, 23), 77.9 (20), 67.8 (12), 60.2 (19), 46.7 (16), 41.9 (10), 34.1 (13), 29.5 (15), 26.9 (14), 23.1 (1)

4.18 Synthesis of E-1-2-3

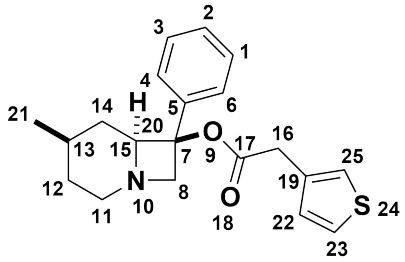


Following the general procedure, compound **8** (0.23 mmol, 1 eq), ArAA-3 (0.35 mmol, 1.5 eq), DCC (0.35 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.3 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and carried forward for Boc protection without purification.

Boc protection on E-1-2-3 To a stirred solution of **E-1-2-3** (0.23 mmol, 1 eq) in THF (2.3 mL, 100 mM) was added Boc-anhydride (1.4 mmol, 6 eq), DMAP (0.16 mmol, 0.7 eq), and Et_3N (0.16 mmol, 0.7 eq). Solution was heated at 50 ℃ for 1 h. After complete conversion of the starting material, solvent was evaporated and crude was purified in 5% methanol in dichlormethane, to obtain the compound in 81.4% yield.
^{1}H (500 MHz, Chloroform-d) δ 8.27 - 8.03 (1H, m, 28), 7.64 - 7.40 (4H, m, 11, 13, 15, 25), 7.37 - 7.29 (3H, m, 12, 14, 27), 7.28 - 7.26 (1H, m, 26), 7.25 - 7.21 (1H, m, 21), 4.23 - 3.90 (2H, m, 8', 20), 3.79 (1H, d, *J*=8.0 Hz, 8"), 3.71 (2H, s, 17), 2.87 - 2.70 (1H, m, 4'), 2.68 - 2.48 (1H, m, 4"), 1.66 (9H, s, 33, 34, 35), 1.56 - 1.44 (1H, m, 2'), 1.43 - 1.23 (3H, m, 2", 5", 6), 1.18 - 1.03 (1H, m, 5'), 0.84 (3H, d, *J*=5.8 Hz, 36)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ169.3 (C-16), 149.7 (C-29), 130.1, 128.6, 128.0, 125.6, 124.8, 124.6, 122.8, 119.1, 83.9 (C-32), 78.3 (C-7), 68.1 (C-1), 60.3 (C-8), 46.5 (C-4), 34.1, 31.7 (C-17), 28.3, 22.9

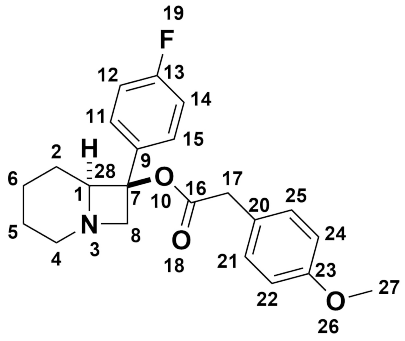
4.19 Synthesis of E-1-2-4

Following the general procedure, compound **8** (0.23 mmol, 1 eq), ArAA-4 (0.35 mmol, 1.5 eq), DCC (0.35 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.3 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E-1-2-4** in 76.4%.



^{1}H (500 MHz, Chloroform-d) δ 7.52 (d, *J*=7.9 Hz, 2H, 4, 6), 7.37 - 7.31 (m, 2H), 7.30 - 7.23 (m, 3H, 1, 3, 23), 7.13 - 7.08 (m, 1H), 7.00 (d, *J*=4.9 Hz, 1H), 4.03 - 3.92 (m, 1H, 20), 3.81 (s, 2H, 8), 3.65 (s, 2H, 16), 2.83 - 2.73 (m, 1H, 11'), 2.73 - 2.65 (m, 1H, 11"), 1.62 - 1.52 (m, 1H, 12'), 1.52 - 1.34 (m, 3H, 12", 13, 14'), 1.29 - 1.15 (m, 1H, 14"), 0.96 (d, *J*=5.9 Hz, 3H, 21))
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 169.5 (17), 141.5 (5), 133.4 (19), 128.6 (22), 128.5 (1, 3), 127.7 (23), 125.8 (2), 125.6 (4, 6), 123.1 (25), 77.9 (7), 67.8 (15), 60.3 (8), 46.8 (11), 36.3 (16), 29.7 (12), 29.2 (14), 27.1 (13), 23.2 (21)

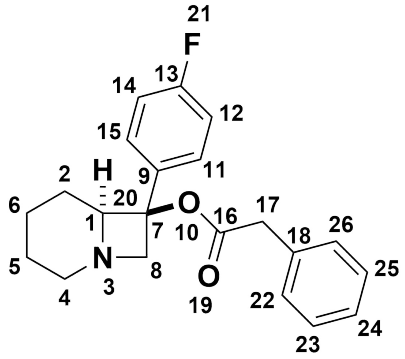
4.20 Synthesis of E-2-1-1



Following the general procedure, compound **9** (0.23 mmol, 1 eq), ArAA-1 (0.34 mmol, 1.5 eq), DCC (0.34 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.3 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 °C for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E-2-1-1** in 83.8%.
^{1}H (500 MHz, Chloroform-d) δ 7.48 - 7.41 (m, 2H, 11, 15), 7.13 (d, *J*=8.5 Hz, 2H, 21, 25), 6.97 (t, *J*=8.7 Hz, 2H, 12, 14), 6.88 - 6.79 (m, 2H, 22, 24), 3.93 - 3.86 (m, 1H), 3.83 (d, J=7.3 Hz, 1H, 8"), 3.80 (s, 3H, 27), 3.78 (d, *J*=7.8 Hz, 1H, 8'), 3.53 (s, 2H, 17), 2.81 - 2.72 (m, 1H, 4'), 2.69 - 2.57 (m, 1H, 4"), 1.93 - 1.82 (m, 1H, 5'), 1.81 - 1.71 (m, 1H, 2"), 1.66 - 1.49 (m, 2H, 2', 5"), 1.44 - 1.37 (m, 1H, 6"), 1.36 - 1.23 (m, 1H, 6')
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 170.3 (16), 162.3 (d, *J*=246.1 Hz, 13), 158.9 (23), 137.5 (9) 130.4 (21, 25), 127.5 (d, *J*=8.2 Hz, 11, 15), 125.7 (20), 115.3 (d, *J*=21.1 Hz, 12, 14), 114.1 (22, 24), 77.8 (7), 67.3 (1), 60.8 (8), 55.4 (27), 46.6 (4), 40.8 (17), 20.8 (5), 20.5 (2), 20.3 (6)

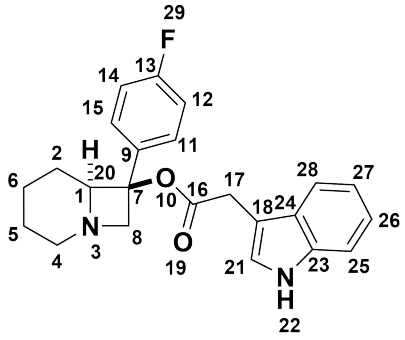
4.21 Synthesis of E-2-1-2

Following the general procedure, compound **9** (0.24 mmol, 1 eq), ArAA-2 (0.35 mmol, 1.5 eq), DCC (0.35 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.3 mL dichloromethane (100 mM). Reaction was stopped



after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E-2-1-2** in 57.8%.
^{1}H (500 MHz, Chloroform-d) δ 7.46 - 7.40 (m, 2H, 11, 15), 7.37 - 7.27 (m, 3H, 23, 24, 25), 7.24 - 7.18 (m, 2H, 22, 26), 6.96 (t, *J*=8.7 Hz, 2H, 12, 14), 3.94 (dd, *J*=10.9, 5.9 Hz, 1H, 20), 3.87 - 3.81 (m, 2H, 8), 3.59 (s, 2H, 17', 17"), 2.78 (ddd, *J*=14.9, 11.2, 4.0 Hz, 1H, 4'), 2.62 (dt, *J*=13.8, 4.2 Hz, 1H, 4"), 1.92 - 1.81 (m, 1H, 2'), 1.79 - 1.72 (m, 1H, 6'), 1.65 - 1.53 (m, 2H, 2", 5'), 1.46 - 1.36 (m, 1H, 5"), 1.35 - 1.24 (m, 1H, 6")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 169.8 (16), 162.2 (d, *J*=246.1 Hz, 13), 137.0 (9), 133.5 (18), 129.3 (22, 26), 128.6 (23, 25), 127.5 (d, *J*=8.1 Hz, 11, 15), 127.2 (24), 115.1 (d, *J*=21.7 Hz, 12, 14), 77.9 (7), 67.1 (1), 60.5 (8), 46.4 (4), 41.7 (17), 20.6 (2), 20.3 (5), 19.9 (6)

4.22 Synthesis of E-2-1-3

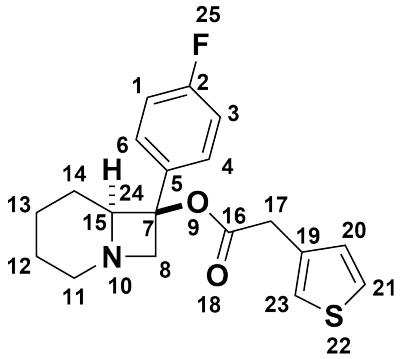


Following the general procedure, compound **9** (0.23 mmol, 1 eq), ArAA-3 (0.35 mmol, 1.5 eq), DCC (0.35 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.3 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E-2-1-3** in 87.7%.
^{1}H (500 MHz, Chloroform-d) δ 8.18 (1H, s, 22), 7.53 (1H, d, *J*=7.9 Hz, 28), 7.46 - 7.39 (2H, m, 11, 15), 7.36 (1H, d, *J*=8.1 Hz, 25), 7.21 (1H, t, *J*=7.6 Hz, 26), 7.13 (1H, t, *J*=7.5 Hz, 27), 7.09 (1H, d, *J*=2.4 Hz, 21), 7.01 - 6.91 (2H, m, 12, 14), 4.03 (2H, s), 3.85 (2H, d, *J*=8.3 Hz, 8', 20), 3.78 (2H, s, 17'), 2.89 - 2.72 (1H, m, 4'), 2.60 - 2.48 (1H, m, 4"), 1.96 - 1.81 (1H, m, 2'), 1.77 - 1.55 (2H, m, 2", 5"), 1.55 - 1.46 (1H, m, 6"), 1.45 - 1.37 (1H, m, 6'), 1.36 - 1.23 (1H, m, 5')
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 170.3 (C-16), 162.4 (d, *J* = 246.5 Hz, C-13), 136.6 (C-9), 136.2 (C-23), 127.6

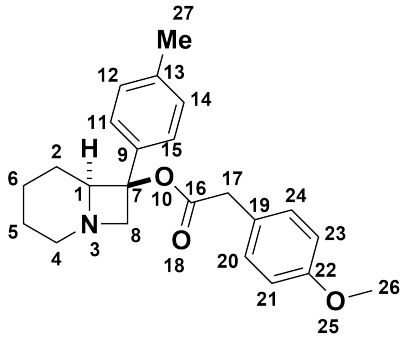
(d, *J* = 8.2 Hz, C-11, C-15), 127.2 (C-24), 123.2 (C-21), 122.6 (C-26), 119.9 (C-27), 118.8 (C-28), 115.4 (d, *J* = 21.5 Hz, C-12, C-14), 111.4 (C-25), 108.1 (C-18), 78.4 (C-7), 67.4 (C-1), 60.8 (C-8), 46.6 (C-4), 31.8 (C-17), 20.4 (C-2), 20.2 (C-6), 19.5 (C-5)

Boc protection on E-2-1-3 To a stirred solution of **E-2-1-3** (0.19 mmol, 1 eq) in THF (1.9 mL, 100 mM) was added Boc-anhydride (1.2 mmol, 6 eq), DMAP (0.14 mmol, 0.7 eq), and Et_3N (0.14 mmol, 0.7 eq). Solution was heated at 50 ℃ for 1 h. After complete conversion of the starting material, solvent was evaporated and crude was purified in 5% methanol in dichlormethane, to obtain the compound in 70.4% yield.
^{1}H (500 MHz, Chloroform-d) δ 8.14 (1H, d, *J*=8.0 Hz), 7.52 - 7.39 (4H, m), 7.33 (1H, ddd, *J*=8.4, 7.2, 1.3 Hz), 7.22 (1H, ddd, *J*=8.1, 7.2, 1.0 Hz), 7.01 - 6.90 (2H, m), 3.99 - 3.90 (1H, m), 3.90 - 3.80 (2H, m), 3.69 (2H, d, *J*=1.0 Hz), 2.85 - 2.71 (1H, m), 2.69 - 2.53 (1H, m), 1.96 - 1.79 (1H, m), 1.78 - 1.70 (1H, m), 1.66 (9H, s), 1.61 - 1.49 (2H, m), 1.46 - 1.36 (1H, m), 1.33 - 1.21 (1H, m)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 169.4 (C-16), 162.2 (d, *J* = 246.5 Hz, C-13), 149.6 (C-29), 135.4 (C-9), 129.9, 127.6, 124.6 (d, *J* = 18.8 Hz, C-11, C-15), 122.6, 118.9, 115.2 (d, *J* = 22.3 Hz, C-12, C-14), 112.7 (C-18), 83.8 (C-32), 78.1 (C-7), 67.2 (C-1), 60.5 (C-8), 46.5 (C-4), 31.4 (C-17), 28.2 (C-33, C-34, C-35), 20.6 (C-2), 20.3 (C-5), 20.1 (C-6)

4.23 Synthesis of E-2-1-4



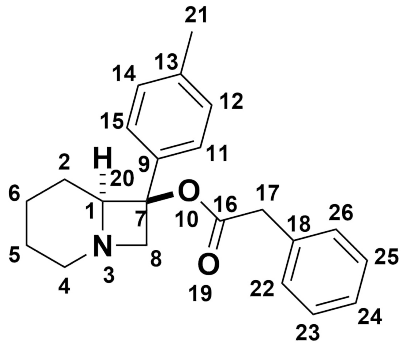
Following the general procedure, compound **9** (0.24 mmol, 1 eq), ArAA-4 (0.35 mmol, 1.5 eq), DCC (0.35 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.3 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E-2-1-4** in 64.1%.
^{1}H (500 MHz, Chloroform-d) δ 7.47 - 7.40 (m, 2H, 4, 6), 7.31 - 7.27 (m, 1H, 21), 7.12 - 7.07 (m, 1H, 23), 7.03 - 6.95 (m, 3H, 1, 3, 20), 4.12 - 3.95 (m, 2H, 8', 24), 3.90 - 3.82 (m, 1H, 8"), 3.64 (s, 2H, 17), 2.96 - 2.81 (m, 1H, 11'), 2.73 - 2.57 (m, 1H, 11"), 2.02 - 1.88 (m, 1H, 14'), 1.86 - 1.75 (m, 1H, 12'), 1.71 - 1.55 (m, 2H, 14", 12"), 1.53 - 1.42 (m, 1H, 13"), 1.42 - 1.31 (m, 1H, 13')
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 169.4 (16), 162.4 (d, *J*=246.5 Hz, 2), 136.6 (5), 133.0 (19), 128.5 (20), 127.6 (d, *J*=8.2 Hz, 4, 6), 126.13 (21), 123.3 (23), 115.4 (d, *J*=21.7 Hz, 1, 3), 78.4 (7), 67.3 (15), 60.7 (8), 46.6 (11), 36.3 (17), 20.5 (14), 20.3 (12), 19.7 (13)



4.24 Synthesis of E-3-1-1

Following the general procedure, compound **10** (0.24 mmol, 1 eq), ArAA-1 (0.35 mmol, 1.5 eq), DCC (0.35 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.3 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E-3-1-1** in 88.1%.
^{1}H (500 MHz, Chloroform-d) δ 7.35 (d, *J*=7.8 Hz, 2H, 11, 15), 7.15 (d, *J*=8.2 Hz, 2H, 20, 24), 7.12 (d, *J*=7.9 Hz, 2H, 12, 14), 6.85 (d, *J*=8.3 Hz, 2H, 21, 23), 4.09 - 3.89 (m, 2H, 1), 3.84 - 3.78 (m, 4H, 8', 8", 26), 3.54 (s, 2H, 17), 2.91 - 2.76 (m, 1H, 4'), 2.67 - 2.57 (m, 1H, 4"), 2.31 (s, 3H, 27), 1.96 - 1.83 (m, 1H, 2'), 1.80 - 1.68 (m, 1H, 5'), 1.66 - 1.53 (m, 2H, 2", 5"), 1.49 - 1.40 (m, 1H, 6'), 1.39 - 1.27 (m, 1H, 6")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 170.2 (16), 158.9 (22), 138.1 (9), 137.5 (13), 130.5 (20, 24), 129.2 (12, 14), 125.8 (19), 125.5 (11, 15), 114.1 (21,23), 78.8 (7), 67.5 (1), 60.9 (8), 55.5 (26), 46.8 (4), 40.9 (17), 21.2 (27), 20.6 (2), 20.4 (6), 19.8 (5)

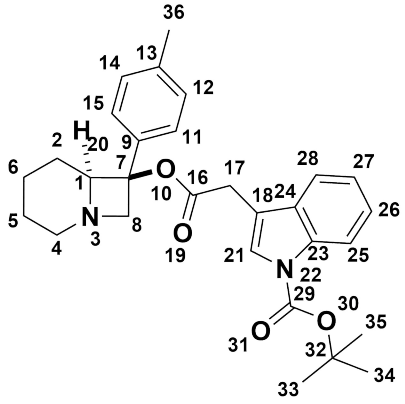
4.25 Synthesis of E-3-1-2



Following the general procedure, compound **10** (0.27 mmol, 1 eq), ArAA-2 (0.41 mmol, 1.5 eq), DCC (0.41 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.7 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5% methanol in dichloromethane on silica column to yield **E-3-1-2** in 74.6%.
^{1}H (500 MHz, Chloroform-d) δ 7.37 (d, *J*=7.8 Hz, 2H, 11, 15), 7.34 - 7.29 (m, 2H, 23, 25), 7.29 - 7.21 (m, 3H, 22, 24, 26), 7.11 (d, *J*=7.8 Hz, 2H, 12, 14), 3.87 (dd, *J*=11.3, 5.7 Hz, 1H, 20), 3.84 - 3.73 (m, 2H, 8', 8"), 3.59 (s, 2H, 17), 2.81 - 2.69 (m, 1H, 4'), 2.67 - 2.58 (m, 1H, 4"), 2.31 (s, 3H, 21), 1.95 - 1.81 (m, 1H, 2'), 1.79 - 1.69 (m, 1H, 5'),

1.64 - 1.49 (m, 2H, 2”, 5”), 1.46 - 1.34 (m, 1H, 6’), 1.33 - 1.22 (m, 1H, 6”)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 169.9 (16), 138.8 (9), 137.2 (13), 133.9 (18), 129.5 (22, 26), 129.2 (12, 14), 128.6 (23, 25), 127.2 (24), 125.5 (11, 15), 78.3 (7), 67.5 (1), 60.9 (8), 46.7 (4), 41.8 (17), 21.2 (21), 20.8 (2), 20.6 (5), 20.5 (6)

4.26 Synthesis of E-3-1-3

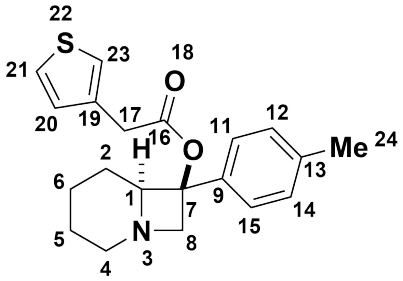


Following the general procedure, compound **10** (0.35 mmol, 1 eq), ArAA-3 (0.52 mmol, 1.5 eq), DCC (0.52 mmol, 1.5 eq), DMAP (0.07 mmol, 0.2 eq) was dissolved in 3.5 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and carried forward for boc protection without purification.

Boc protection on E-3-1-3 To a stirred solution of **E-3-1-3** (0.33 mmol, 1 eq) in THF (3.3mL, 100 mM) was added Boc-anhydride (1.9 mmol, 6 eq), DMAP (0.23 mmol, 0.7 eq), and Et_3N (0.23 mmol, 0.7 eq). Solution was heated at 50 ℃ for 1 h. After complete conversion of the starting material, solvent was evaporated and crude was purified in 5% methanol in dichlormethane, to obtain the compound in 51.8% yield.
^{1}H (500 MHz, Chloroform-d) δ 8.20 - 8.08 (1H, m, 25), 7.52 (1H, s, 21), 7.48 - 7.41 (1H, m, 28), 7.41 - 7.35 (2H, m, 11, 15), 7.35 - 7.29 (1H, m, 26), 7.24 - 7.18 (1H, m, 27), 7.14 - 7.04 (2H, m, 12, 14), 3.98 - 3.81 (3H, m, 8’, 20), 3.69 (2H, s, 17’), 2.83 - 2.69 (1H, m, 4’), 2.66 - 2.55 (1H, m, 4”), 2.31 (3H, s, 36), 1.99 (1H, s), 1.94 - 1.82 (1H, m, 2’), 1.76 - 1.63 (10H, m, 5’, 33, 34, 35), 1.61 - 1.50 (2H, m, 2”, 6’), 1.49 - 1.24 (2H, m, 5”, 6’)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 167.5 (C-16), 147.8 (C-29), 135.5 (C-13), 133.5 (C-23), 128.1 (C-24), 127.2 (C-12, C-14), 123.6 (C-11, C-15), 122.7 (C-21), 122.6 (C-26), 120.7 (C-27), 117.1 (C-28), 113.4 (C-25), 110.9 (C-18), 81.8 (C-32), 76.7 (C-7), 65.4 (C-1), 58.8 (C-8), 44.7 (C-4), 29.5 (C-17), 26.3 (C-33, C-34, C-35), 19.2 (C-2), 18.7 (C-5), 18.4 (C-6)

4.27 Synthesis of E-3-1-4

Following the general procedure, compound **10** (0.27 mmol, 1 eq), ArAA-4 (0.41 mmol, 1.5 eq), DCC (0.41 mmol, 1.5 eq), DMAP (0.05 mmol, 0.2 eq) was dissolved in 2.7 mL dichloromethane (100 mM). Reaction was stopped after 3 h, and monitored in 5% methanol in dichloromethane. After complete consumption of the azetidinol, reaction was quenched by addition of acetonitrile, and cooling the reaction at 0 ℃ for few hours. Reaction was filtered and the solid was washed with cold acetonitrile. The filtrate was collected, evaporated to dryness, and purified in 5%



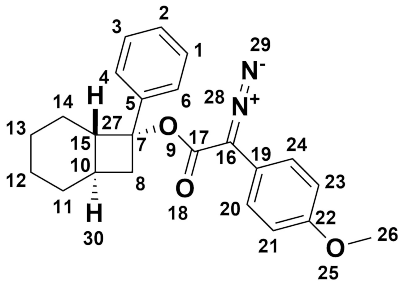
methanol in dichloromethane on silica column to yield **E-3-1-4** in 63.3%.
^{1}H (500 MHz, Chloroform-d) δ 7.33 (d, *J*=7.8 Hz, 2H, 11, 15), 7.30 (dd, *J*=4.9, 3.1 Hz, 1H, 21), 7.15 - 7.11 (m, 3H, 23, 12, 14), 7.00 (d, *J*=5.1 Hz, 1H, 20), 4.31 - 3.99 (m, 2H, 1, 8'), 3.85 (d, *J*=8.8 Hz, 1H, 8"), 3.66 (s, 2H, 17), 3.05 - 2.86 (m, 1H, 4'), 2.72 - 2.57 (m, 1H, 4"), 2.32 (s, 3H, 24), 2.04 - 1.86 (m, 1H, 2'), 1.81 - 1.58 (m, 3H, 5, 2"), 1.57 - 1.45 (m, 1H, 6'), 1.46 - 1.32 (m, 1H, 6")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 169.3 (16), 133.1 (19), 129.3 (12, 14), 128.5 (20), 126.1 (21), 125.5 (11, 15), 123.3 (23), 67.4 (1), 60.9 (8), 46.9 (4), 36.4 (17), 21.3 (24), 20.2 (2, 5, 6)

5 Diazo formation

5.1 General experimental procedure for diazo formation

To a round bottom flask equipped with a magnetic stir bar, ester (1 eq) was dissolved in acetonitrile (100 mM). Solution was cooled to -10 ℃. *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (1.2 eq) was added to the flask, followed by slow addition of diazabicycloundecane (DBU) (2 eq). The reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 5% methanol in dichloromethane, and in 50% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filtrate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-20% methanol in dichloromethane or in 0-70% ethyl acetate in hexanes.Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments.

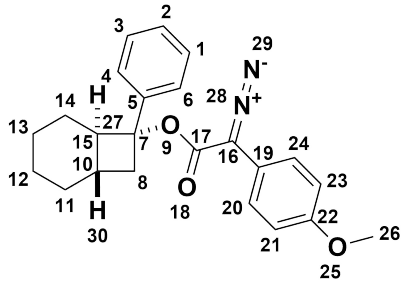
5.2 Synthesis of D1



Following the general procedure, to solution of compound **E2** (0.05 mmol, 1 eq) in acetonitrile (0.460 mL, 100 mM), *p*-ABSA (0.06 mmol, 1.2 eq) was added at -10 ℃. DBU (13.6 µL, 2 eq) was added slowly to the solution. The reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 10% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The

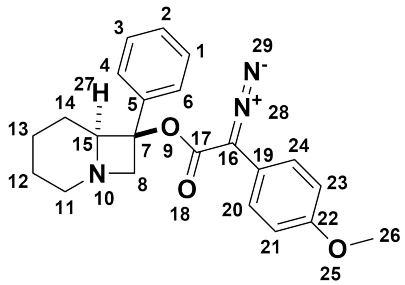
crude was purified by flash column chromatography in 0-20% ethyl acetate in hexanes to yield **D1** in 41.9%
^{1}H (500 MHz, Chloroform-d) δ 7.44 - 7.37 (m, 2H, 4, 6), 7.36 - 7.30 (m, 4H, 1, 3, 20, 24), 7.28 - 7.22 (m, 2H, 2, merged with chloroform), 6.94 - 6.87 (m, 2H, 21, 23), 3.79 (s, 3H, 26), 2.79 (dd, *J*=11.4, 6.7 Hz, 1H, 8"), 2.35 (t, *J*=11.0 Hz, 1H, 8'), 2.14 - 2.03 (m, 1H, 30), 1.98 - 1.88 (m, 2H, 11', 27), 1.88 - 1.81 (m, 2H, 13', 14'), 1.66 - 1.57 (m, 1H, 11"), 1.45 - 1.22 (m, 4H, 12', 12", 13", 14")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 164.7 (17), 157.9 (22), 143.3 (5), 128.3 (1, 3), 127.5 (2), 126.2 (4, 6), 125.8 (20, 24), 117.2 (19), 114.6 (21, 23), 89.7 (7), 63.1 (16), 55.5 (26), 54.5 (15), 39.1 (8), 38.5 (10), 31.7 (14), 27.6 (11), 26.6 (12), 26.3 (13)

5.3 Synthesis of D2



Following the general procedure, to solution of compound **E1** (0.07 mmol, 1 eq) in acetonitrile (0.710 mL, 100 mM), *p*-ABSA (0.09 mmol, 1.2 eq) was added at -10 °C. DBU (13.6 µL, 2 eq) was added slowly to the solution. The reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 10% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-20% ethyl acetate in hexanes to yield **D2** in 50.3%
^{1}H (500 MHz, Chloroform-d) δ 7.50 (d, *J*=7.6 Hz, 2H, 4, 6), 7.38 (t, *J*=7.6 Hz, 2H, 1, 3), 7.34 - 7.28 (m, 3H, 20, 24, 2), 6.91 - 6.85 (m, 2H, 21, 23), 3.78 (s, 3H, 26), 3.28 (dd, *J*=11.3, 6.4 Hz, 1H, 8'), 2.18 (t, *J*=11.3 Hz, 1H, 8"), 2.09 (td, *J*=11.9, 3.0 Hz, 1H, 27), 1.89 - 1.81 (m, 2H, 11", 14"), 1.75 - 1.67 (m, 2H, 13', 12"), 1.42 - 1.31 (m, 2H, 13", 14'), 1.28 - 1.08 (m, 2H, 12', 30), 1.00 - 0.80 (m, 1H, 11')
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 164.3 (17), 157.9 (22), 138.4 (5), 128.2 (1, 3), 127.8 (4, 6), 127.8 (2), 125.8 (20, 24), 117.1 (19), 114.6 (21, 23), 85.0 (7), 62.6 (16), 55.5 (26), 54.7 (15), 40.6 (8), 34.9 (10), 31.9 (14), 28.4 (11), 26.5 (12), 25.9 (13)

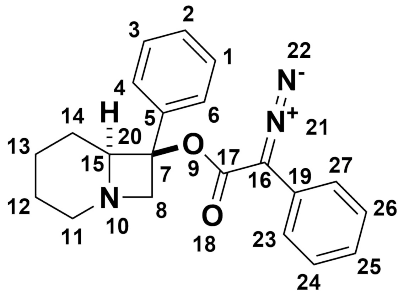
5.4 Synthesis of D-1-1-1



Following the general procedure, to solution of **E-1-1-1** (0.14 mmol, 1 eq) in acetonitrile (1.4 mL, 100 mM), *p*-ABSA (0.17 mmol, 1.2 eq) was added at -10 °C. DBU (42.5 µL, 2 eq, 0.28 mmol) was added slowly to the solution. The

reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-20% methanol in dichloromethane to yield **D-1-1-1** in 59.6%.
^{1}H (500 MHz, Chloroform-d) δ 7.65 - 7.54 (m, 2H, 4, 6), 7.36 (t, *J*=7.7 Hz, 2H, 1, 3), 7.29 (d, *J*=8.8 Hz, 2H, 20, 24), 7.25 (d, *J*=14.0 Hz, 1H, 2), 6.87 (d, *J*=9.0 Hz, 2H, 21, 23), 4.00 - 3.93 (m, 3H, 8', 27), 3.76 (s, 3H, 26), 2.87 - 2.75 (m, 1H, 11'), 2.74 - 2.63 (m, 1H, 11"), 2.14 - 1.97 (m, 1H, 14'), 1.86 - 1.75 (m, 1H, 13'), 1.74 - 1.62 (m, 1H, 14"), 1.48 - 1.25 (m, 3H, 12, 13")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 164.0 (C-17), 158.2 (C-22), 141.5 (C-5), 128.7 (C-1, C-3), 127.8 (C-2), 125.8 (C-20, C-24), 125.6 (C-4, C-6), 116.6 (C-19), 114.7 (C-21, C-23), 78.7 (C-7), 62.3 (C-16), 67.7 (C-15), 60.9 (C-8), 55.5 (C-26), 46.8 (C-11), 21.0 (C-14), 20.6 (C-12), 20.3 (C-13)
Characteristic IR vibrations (cm^{-1}): 2079 (diazo), 1701 (ester)

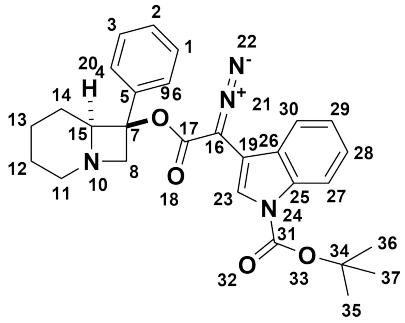
5.5 Synthesis of D-1-1-2



Following the general procedure, to solution of **E-1-1-2** (0.12 mmol, 1 eq) in acetonitrile (1.2 mL, 100 mM), *p*-ABSA (0.15 mmol, 1.2 eq) was added at -10 ℃. DBU (37.1 µL, 2 eq, 0.25 mmol) was added slowly to the solution. The reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 50% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-20% methanol in dichloromethane to yield **D-1-1-2** in 64.8%.
^{1}H (500 MHz, Chloroform-d) δ 7.62 (d, *J*=7.7, 2H, 4, 6), 7.43 - 7.28 (m, 7H, 1, 3, 23, 24, 26, 27, 2), 7.24 - 7.12 (m, 1H, 25), 4.20 - 4.04 (m, 2H, 20, 8'), 4.03 - 3.97 (m, 1H, 8"), 3.00 - 2.79 (m, 1H, 11'), 2.78 - 2.68 (m, 1H, 11"), 2.34 - 2.01 (m, 1H, 14'), 1.94 - 1.63 (m, 3H, 12", 13', 14"), 1.56 - 1.32 (m, 2H, 12', 13")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 163.5 (C-17), 141.3 (C-5), 129.5 (C-2), 129.1 (C-1, C-3), 128.7 (C-24, C-26), 126.1 (C-25), 125.6 (C-4, C-6), 125.2 (C-19), 124.0 (C-23, C-27), 79.1 (C-7), 64.1 (C-16), 67.6 (C-15), 60.9 (C-8), 46.7 (C-11), 20.9 (C-14), 20.5 (C-12), 20.0 (C-13))
Characteristic IR vibrations (cm^{-1}): 2081 (diazo), 1701 (ester)

5.6 Synthesis of D-1-1-3

Following the general procedure, to solution of **E-1-1-3** (0.91 mmol, 1 eq) in acetonitrile (0.9 mL, 100 mM), *p*-ABSA (0.11 mmol, 1.2 eq) was added at -10 ℃. DBU (17.7 µL, 1.3 eq, 0.12 mmol) was added slowly to the solution. The reaction was left to warm to room temperature and stir for 4 h. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 50% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was



collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-20% methanol in dichloromethane to yield **D-1-1-3** in 51.2%

Note: Diazo products of indole tend to decompose quickly under ambient conditions.

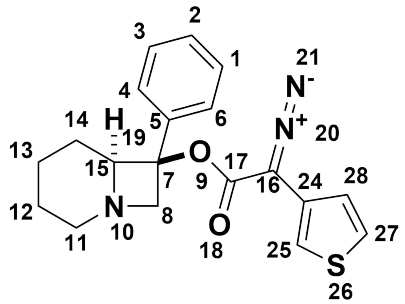
^{1}H (500 MHz, Chloroform-d) δ 8.22 (1H, d, *J* = 8.4 Hz), 7.81 (1H, s), 7.70 - 7.61 (2H, m), 7.50 - 7.45 (1H, m), 7.43 - 7.27 (5H, m), 4.18 - 3.89 (3H, m), 2.92 - 2.78 (1H, m), 2.74 - 2.68 (1H, m), 2.20 - 2.03 (1H, m), 1.85 (1H, dt, *J* = 13.0, 4.1 Hz), 1.65 (11H, s), 1.52 - 1.32 (2H, m)

^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 149.6, 141.5, 135.2, 128.6, 127.8, 125.5, 125.0, 123.6, 122.9, 118.4, 115.7, 84.2, 67.7, 60.9, 46.6, 28.2, 21.0, 20.5, 20.2

Characteristic IR vibrations (cm^{-1}): 2083 (diazo), 1734 (carbamate), 1705 (ester)

Note: C-17, C-7 and C-16 and several other peaks were weak and difficult to observe in ^{13}C {^{1}H }

5.7 Synthesis of D-1-1-4



Following the general procedure, to solution of **E-1-1-4** (0.18 mmol, 1 eq) in acetonitrile (1.8 mL, 100 mM), *p*-ABSA (0.21 mmol, 1.2 eq) was added at -10 ℃. DBU (52.8 µL, 2 eq, 0.35 mmol) was added slowly to the solution. The reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 50% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-20% methanol in dichloromethane to yield **D-1-1-4** in 90.2%

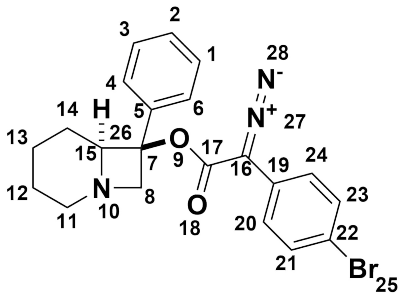
^{1}H (500 MHz, Chloroform-d) δ 7.68 - 7.58 (2H, m, 4, 6), 7.42 - 7.31 (4H, m, 1, 3, 25, 27), 7.32 - 7.27 (1H, m, 2), 7.03 - 6.95 (1H, m, 28), 4.09 - 3.92 (3H, m, 8, 19), 2.91 - 2.77 (1H, m, 11'), 2.77 - 2.64 (1H, m, 11"), 2.16 - 1.98 (1H, m, 14'), 1.91 - 1.81 (1H, m, 12'), 1.80 - 1.61 (2H, m, 13', 14"), 1.53 - 1.31 (2H, m, 12", 13")

^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 141.9 (C-5), 128.7 (C-1, C-3), 127.9 (C-2), 126.6 (C-27), 125.5 (C-4, C-6), 118.1 (C-25), 78.9 (C-7), 67.8 (C-15), 62.7 (C-16) 61.0 (C-8), 46.7 (C-11), 21.0 (C-14), 20.5 (C-12), 20.2 (C-13)

Note: C-17 and C-24 peaks were not observed in ^{13}C {^{1}H }

Characteristic IR vibrations (cm^{-1}): 2077 (diazo), 1699 (ester)

5.8 Synthesis of D7



Following the general procedure, to solution of **E4** (0.10 mmol, 1 eq) in acetonitrile (2.1 mL, 100 mM), *p*-ABSA (0.18 mmol, 1.7 eq) was added at -10 ℃. DBU (47 µL, 3 eq, 0.31 mmol) was added slowly to the solution. The reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 50% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-30% methanol in dichloromethane to yield **D7** in 85.2%

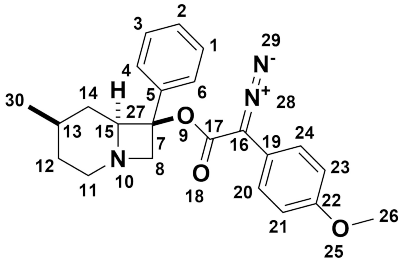
^{1}H (500 MHz, Chloroform-d) δ 7.61 (2H, d, *J*=7.7 Hz, 4, 6), 7.46 (2H, d, *J*=8.4 Hz, 20, 24), 7.39 (2H, t, *J*=7.6 Hz, 1, 3), 7.34 - 7.28 (3H, m, 2, 21, 23), 4.17 - 3.98 (3H, m, 8', 26), 3.00 - 2.79 (1H, m, 11"), 2.81 - 2.67 (1H, m, 11'), 2.17 - 2.06 (1H, m, 14'), 1.89 - 1.80 (1H, m, 12'), 1.80 - 1.64 (2H, m, 13", 14"), 1.58 - 1.45 (1H, m, 13'), 1.45 - 1.32 (1H, m, 12")

^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 163.1 (C-17), 132.2 (C-4, C-6), 128.8 (C-1, C-3), 128.2 (C-2), 125.6 (C-20, C-24), 125.4 (C-21, C-23), 124.3 (C-22), 119.7 (C-19), 79.4 (C-7), 67.8 (C-15), 60.9 (C-16), 60.5 (C-8), 46.8 (C-11), 20.8 (C-14), 20.4 (C-12), 19.9 (C-13)

Note: C-5 peak was not observed in ^{13}C {^{1}H }

Characteristic IR vibrations (cm^{-1}): 2083 (diazo), 1701 (ester)

5.9 Synthesis of D-1-2-1

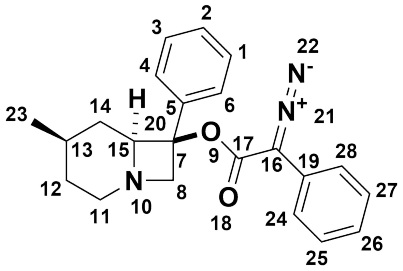


Following the general procedure, to solution of **E-1-2-1** (0.17 mmol, 1 eq) in acetonitrile (1.7 mL, 100 mM), *p*-ABSA (0.21 mmol, 1.2 eq) was added at -10 ℃. DBU (76.5 µL, 3 eq, 0.51 mmol) was added slowly to the solution. The reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 50% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-70% ethyl acetate in hexanes to yield **D-1-2-1** in 76.5%

^{1}H (500 MHz, Chloroform-d) δ 7.73 - 7.59 (2H, m, 21, 23), 7.42 - 7.36 (2H, m, 1, 3), 7.35 - 7.31 (2H, m, 4, 6), 7.31 - 7.26 (1H, m, 2), 6.94 - 6.81 (2H, m, 20, 24), 4.06 - 3.99 (1H, m, 27), 3.96 (1H, d, *J*=7.1 Hz, 8"), 3.87 (1H, dd, *J*=7.1,

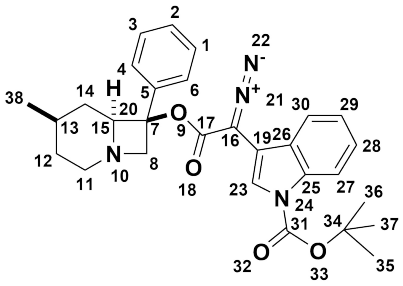
2.0 Hz, 8'), 3.79 (3H, s, 26), 2.89 - 2.68 (2H, m, 11), 1.74 - 1.61 (2H, m, 14", 14'), 1.54 - 1.20 (3H, m, 12", 13), 1.02 (3H, d, J=6.4 Hz, 30)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 158.2(C-22), 141.8 (C-5), 128.6 (C-1, C-3), 127.8 (C-2), 125.8 (C-20, C-24), 125.6 (C-4, C-6), 116.6 (C-19), 114.7 (C-21, C-23), 78.3 (C-7), 62.9 (C-16), 68.2 (C-15), 60.4 (C-8), 55.5 (C-26), 46.8 (C-11), 29.9 (C-14), 29.3 (C-12), 27.3 (C-13), 23.3 (C-30)
Note: Ester peak was not observed in ^{13}C {^{1}H }
Characteristic IR vibrations (cm^{-1}): 2079 (diazo), 1701 (ester)

5.10 Synthesis of D-1-2-2



Following the general procedure, to solution of **E-1-2-2** (0.11 mmol, 1 eq) in acetonitrile (1.1 mL, 100 mM), *p*-ABSA (0.13 mmol, 1.2 eq) was added at -10 ℃. DBU (32.5 µL, 2 eq, 0.22 mmol) was added slowly to the solution. The reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 50% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-70% ethyl acetate in hexanes to yield **D-1-2-2** in 62.8%
^{1}H (500 MHz, Chloroform-d) δ 7.65 (2H, d, *J*=8.0 Hz, 4, 6), 7.46 - 7.41 (2H, m, 24, 28), 7.41 - 7.32 (4H, m, 1, 3, 25, 27), 7.32 - 7.27 (1H, m, 2), 7.19 - 7.13 (1H, m, 26), 4.09 - 4.02 (1H, m, 20), 3.98 (1H, d, *J*=7.2 Hz, 8"), 3.92 (1H, s, 8'), 2.92 - 2.70 (2H, m, 11), 1.77 - 1.60 (2H, m, 12", 14'), 1.56 - 1.40 (2H, m, 12', 13), 1.39 - 1.29 (1H, m, 14"), 1.02 (3H, dd, *J*=6.4, 1.3 Hz, 23)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 163.5 (C-17), 141.6 (C-5), 129.1, 128.7, 127.9, 126.0, 125.6, 125.3, 123.9, 78.4 (C-7), 68.2 (C-15), 60.4 (C-8), 46.8 (C-11), 29.8 (C-13), 29.3 (C-14), 27.2 (C-12), 23.3 (C-23)
Characteristic IR vibrations (cm^{-1}): 2083 (diazo), 1701 (ester)

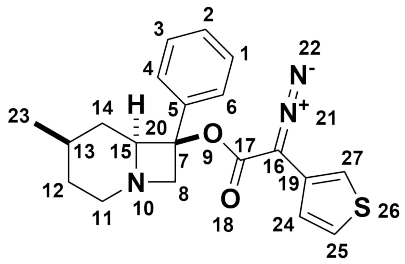
5.11 Synthesis of D-1-2-3



Following the general procedure, to solution of **E-1-2-3** (0.12 mmol, 1 eq) in acetonitrile (1.2 mL, 100 mM), *p*-ABSA (0.15 mmol, 1.2 eq) was added at -10 ℃. DBU (24.0 µL, 1.3 eq, 0.16 mmol) was added slowly to the solution.

The reaction was left to warm to room temperature and stir for 4 h. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 70% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-70% ethyl acetate in hexanes to yield **D-1-2-3** in 55.6%
Note: Diazo products of indole tend to decompose quickly at ambinet conditions.
^{1}H (500 MHz, Chloroform-d) δ 8.21 (1H, d, *J* = 8.4 Hz), 7.81 (1H, s), 7.67 (2H, dd, *J* = 7.7, 1.7 Hz), 7.54 - 7.44 (1H, m), 7.44 - 7.26 (4H, m), 7.24 (1H, d, *J* = 7.2 Hz), 4.16 - 3.89 (3H, m), 2.97 - 2.70 (2H, m), 1.67 (11H, m), 1.55 - 1.27 (3H, m), 1.03 (3H, d, *J* = 6.3 Hz)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 149.4, 135.3, 128.7, 127.9, 125.6, 125.1, 123.0, 118.5, 115.7, 84.3, 78.6, 68.3, 60.5, 46.8, 29.8, 29.3, 28.3, 27.2, 23.3
Note: C-17 and C-16 were not observed in ^{13}C {^{1}H }.
Characteristic IR vibrations (cm^{-1}): 2039 (diazo), 1732 (carbamate), 1705 (ester)

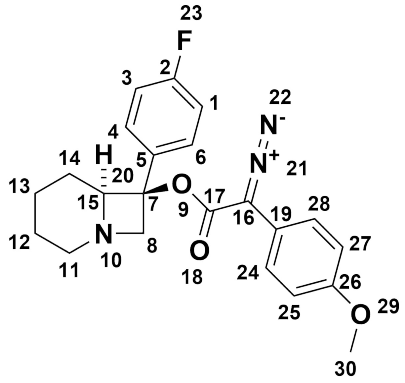
5.12 Synthesis of D-1-2-4



Following the general procedure, to solution of **E-1-2-4** (0.13 mmol, 1 eq) in acetonitrile (1.3 mL, 100 mM), *p*-ABSA (0.16 mmol, 1.2 eq) was added at -10 ℃. DBU (40.2 µL, 2 eq, 0.27 mmol) was added slowly to the solution. The reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 50% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-70% ethyl acetate in hexanes to yield **D-1-2-4** in 89.3%
^{1}H (500 MHz, Chloroform-d) δ 7.64 (2H, d, *J*=7.7 Hz, 4, 6), 7.43 - 7.34 (4H, m, 1, 3, 24, 25), 7.29 (1H, t, *J*=7.4 Hz, 2), 7.00 (1H, dd, *J*=5.0, 1.5 Hz, 27), 4.08 - 4.00 (1H, m, 20), 3.97 (1H, d, *J*=7.2 Hz, 8"), 3.89 (1H, d, *J*=7.2 Hz, 8'), 2.87 - 2.69 (2H, m, 11', 11"), 1.71 - 1.64 (2H, m, 14', 12"), 1.50 - 1.39 (2H, m, 13, 14"), 1.38 - 1.23 (1H, m, 12'), 1.01 (3H, d, *J*=6.4 Hz, 23)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 141.6 (C-5), 128.7 (C-24), 127.9 (C-1, C-3), 126.6 (C-2), 125.6 (C-4, C-6), 123.6 (C-27), 118.0 (C-25), 78.5 (C-7), 68.2 (C-15), 60.5 (C-8), 46.9 (C-11), 29.9, 29.3 (C-12), 27.3, 23.3 (C-23)
Note: C-16, C-17, and C-19 peaks were not observed in ^{13}C {^{1}H }. Characteristic IR vibrations (cm^{-1}): 2071 (diazo), 1701 (ester)

5.13 Synthesis of D-2-1-1

Following the general procedure, to solution of **E-2-1-1** (0.17 mmol, 1 eq) in acetonitrile (1.7 mL, 100 mM), *p*-ABSA (0.20 mmol, 1.2 eq) was added at -10 ℃. DBU (50.7 µL, 2 eq, 0.34 mmol) was added slowly to the solution. The reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 50% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was



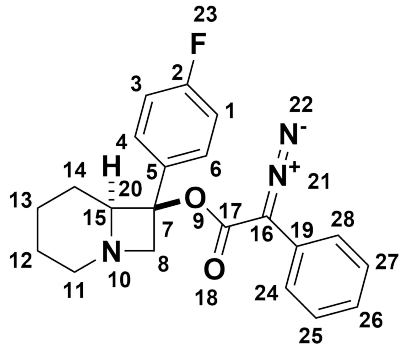
collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-70% ethyl acetate in hexanes to yield **D-2-1-1** in 72.3%

^{1}H (500 MHz, Chloroform-d) δ 7.62 (2H, dd, *J*=8.7, 5.4 Hz, 4, 6), 7.31 (2H, d, *J*=8.7 Hz, 24, 28), 7.06 (2H, t, *J*=8.6 Hz, 1, 3), 6.91 (2H, d, *J*=8.7 Hz, 25, 27), 3.99 (1H, d, *J*=7.5 Hz, 8'), 3.98 - 3.93 (1H, m, 20), 3.90 (1H, d, J=7.4 Hz, 8"), 3.79 (3H, s, 30), 2.86 - 2.77 (1H, m, 11'), 2.74 - 2.64 (1H, m, 11"), 2.13 - 2.01 (1H, m, 14'), 1.90 - 1.80 (1H, m, 12'), 1.76 - 1.61 (2H, m, 12", 14"), 1.48 - 1.41 (1H, m, 13'), 1.39 - 1.30 (1H, m, 13")

^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 164.0 (C-17), 162.4 (d, *J* = 246.3 Hz, C-2), 158.3 (C-26), 137.6 (d, *J* = 3.2 Hz, C-5), 127.6 (d, *J* = 8.2 Hz, C-4, C-6), 125.9 (C-24, C-28), 116.5 (C-19), 115.5 (d, *J* = 21.7 Hz, C-1, C-3), 114.7 (C-25, C-27), 78.3 (C-7), 67.8 (C-15), 63.1 (C-16), 60.9 (C-8), 55.5 (C-30), 46.6 (C-11), 21.0 (C-14), 20.5 (C-13), 20.3 (C-12)

Characteristic IR vibrations (cm^{-1}): 2083 (diazo), 1701 (ester)

5.14 Synthesis of D-2-1-2

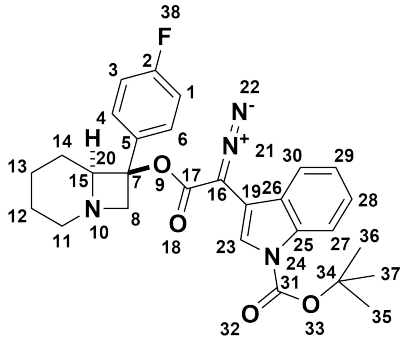


Following the general procedure, to solution of **E-2-1-2** (0.12 mmol, 1 eq) in acetonitrile (1.2 mL, 100 mM), *p*-ABSA (0.15 mmol, 1.2 eq) was added at -10 ℃. DBU (36.9 µL, 2 eq, 0.25 mmol) was added slowly to the solution. The reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 50% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-10% methanol in dichloromethane to yield **D-2-1-2** in 82.0%

^{1}H (500 MHz, Chloroform-d) δ 7.62 (2H, dd, *J*=8.4, 5.3 Hz, 4, 6), 7.41 (2H, d, *J*=7.9 Hz, 24, 28), 7.35 (2H, t, *J*=7.7 Hz, 25, 27), 7.17 (1H, t, *J*=7.4 Hz, 26), 7.06 (2H, t, *J*=8.5 Hz, 1, 3), 4.06 - 3.94 (2H, m, 8', 20), 3.95 - 3.83 (1H, m, 8"), 2.88 - 2.76 (1H, m, 11'), 2.74 - 2.60 (1H, m, 11"), 2.21 - 1.97 (1H, m, 14'), 1.88 - 1.80 (1H, m, 13'), 1.73 - 1.69 (2H, m, 12", 14"), 1.50 - 1.42 (1H, m, 12'), 1.41 - 1.32 (1H, m, 13")

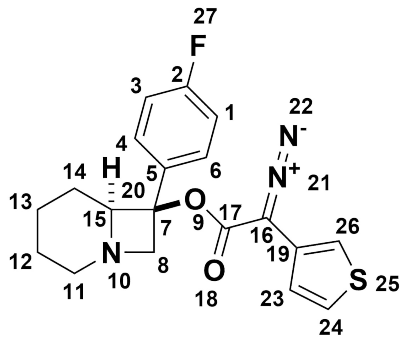
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 162.4 (d, *J* = 246.3 Hz, C-2), 137.5 (C-5), 129.1 (C-25, C-27), 127.6 (d, *J* = 8.2 Hz, C-4, C-6), 126.1 (C-26), 125.1 (C-19), 123.9 (C-24, C-28), 115.5 (d, *J* = 21.2 Hz, C-1, C-3), 78.4 (C-7), 67.8 (C-15), 63.8 (C-16), 60.9 (C-8), 46.7 (C-11), 21.1 (C-14), 20.5 (C-12), 20.3 (C-13)
Note: C-17 peak was not observed in ^{13}C {^{1}H } Characteristic IR vibrations (cm^{-1}): 2079 (diazo), 1701 (ester)

5.15 Synthesis of D-2-1-3



Following the general procedure, to solution of **E-2-1-3** (0.16 mmol, 1 eq) in acetonitrile (1.6 mL, 100 mM), *p*-ABSA (0.19 mmol, 1.2 eq) was added at -10 ℃. DBU (31.6 µL, 1.3 eq, 0.21 mmol) was added slowly to the solution. The reaction was left to warm to room temperature and stir for 4 h. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 50% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-70% ethyl acetate in hexanes to yield **D-2-1-3** in 44.1%
Note: Diazo products of indole tend to decompose quickly when left under ambient conditions.
^{1}H (500 MHz, Chloroform-d) δ 8.21 (1H, d, *J* = 8.4 Hz), 7.80 (1H, s), 7.66 - 7.58 (2H, m), 7.48 - 7.43 (1H, m)), 7.39 - 7.33 (1H, m), 7.29 - 7.22 (2H, m, merged with chloroform-d), 7.12 - 7.04 (2H, m), 4.06 - 4.02 (3H, m), 2.92 - 2.79 (1H, m), 2.78 - 2.63 (1H, m), 1.92 - 1.80 (1H, m), 1.68 - 1.63 (12H, m), 1.52 - 1.22 (2H, m)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 149.2 (C-31), 135.2 (C-5), 127.5 (d, *J* = 8.0 Hz, C-4, C-6), 125.1, 123.8, 122.9, 118.3, 115.6 (d, *J* = 14.4 Hz, C-1, C-3), 115.3, 84.3 (C-34), 67.7 (C-15), 60.9 (C-8), 46.6 (C-11), 41.4, 28.2 (C-35, C-36, C-37), 20.8 (C-14), 20.3 (C-12), 19.9 (C-13)
Note: C-17, C-7, and C-16 and several other peaks were not observed in ^{13}C {^{1}H }.
Characteristic IR vibrations (cm^{-1}): 2083 (diazo), 1734 (carbamate), 1707 (ester)

5.16 Synthesis of D-2-1-4



Following the general procedure, to solution of **E-2-1-4** (0.13 mmol, 1 eq) in acetonitrile (1.3 mL, 100 mM), *p*-ABSA (0.15 mmol, 1.2 eq) was added at -10 ℃. DBU (38.0 µL, 2 eq, 0.25 mmol) was added slowly to the solution. The reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 50% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filtrate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-5% methanol in dichloromethane to yield **D-2-1-4** in 68.5%

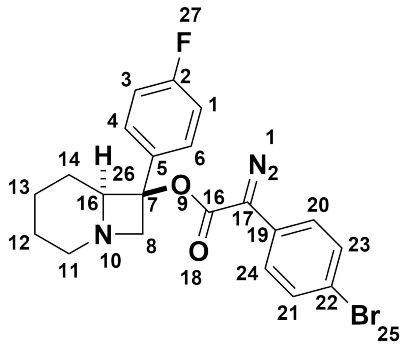
^{1}H (500 MHz, Chloroform-d) δ 7.62 (2H, dd, *J*=8.5, 5.3 Hz, 4, 6), 7.39 - 7.31 (2H, m, 23, 24), 7.06 (2H, t, *J*=8.6 Hz, 1, 3), 6.99 (1H, d, *J*=5.1 Hz, 26), 4.00 (1H, d, *J*=7.4 Hz, 8'), 3.96 (1H, dd, *J*=11.2, 5.7 Hz, 20), 3.89 (1H, d, *J*=7.4 Hz, 8"), 2.87 - 2.76 (1H, m, 11'), 2.74 - 2.65 (1H, m, 11"), 2.12 - 1.99 (2H, m, 12', 14'), 1.90 - 1.79 (1H, m), 1.76 - 1.58 (2H, m, 12", 14"), 1.47 - 1.40 (1H, m, 13")

^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 162.4 (d, *J* = 246.2 Hz, C-2), 137.6 (d, *J* = 3.2 Hz, C-5), 127.5 (d, *J* = 8.2 Hz, C-4, C-6), 126.6 (C-24), 123.6 (C-26), 123.4 (C-19), 118.1 (C-23), 115.5 (d, *J* = 21.1 Hz, C-1, C-3), 78.4 (C-7), 67.8 (C-15), 60.9 (C-8), 46.6 (C-11), 21.1 (C-14), 20.5 (C-13), 20.4 (C-12)

Note: C-17 and C-16 peaks were not observed in ^{13}C {^{1}H }.

Characteristic IR vibrations (cm^{-1}): 2083 (diazo), 1701 (ester)

5.17 Synthesis of D17

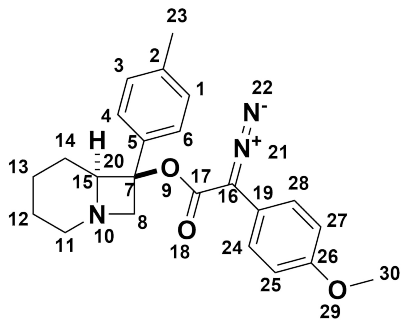


Following the general procedure, to solution of **E15** (0.14 mmol, 1 eq) in acetonitrile (1.4 mL, 100 mM), *p*-ABSA (0.17 mmol, 1.2 eq) was added at -10 ℃. DBU (42.0 µL, 2 eq, 0.29 mmol) was added slowly to the solution. The reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 50% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-5% methanol in dichloromethane to yield **D17** in 87.7%

^{1}H (500 MHz, Chloroform-d) δ 7.68 - 7.59 (2H, m, 4, 6), 7.52 - 7.44 (2H, m, 20, 24), 7.36 - 7.24 (2H, m, 21, 23), 7.14 - 7.00 (2H, m, 1, 3), 4.06 - 3.87 (3H, m, 8', 26), 2.87 - 2.77 (1H, m, 11"), 2.74 - 2.66 (1H, m, 11'), 2.15 - 1.99 (1H, m, 14'), 1.94 - 1.80 (1H, m, 12'), 1.77 - 1.59 (2H, m, 12", 14"), 1.51 - 1.24 (2H, m, 13)

^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 162.4 (d, *J* = 246.5 Hz, C-2), 137.4 (C-5), 132.2, 127.6 (d, *J* = 8.1 Hz, C-4, C-6), 125.5 (C-21, C-23), 124.4 (C-22), 119.6 (C-19), 115.5 (d, *J* = 21.3 Hz, C-1, C-3), 78.5 (C-7), 67.7 (C-15), 60.8 (C-8), 46.6 (C-11), 21.1 (C-14), 20.5 (C-12), 20.4 (C-13))

Note: C-17 and C-16 peaks were not observed in ^{13}C {^{1}H }. Characteristic IR vibrations (cm^{-1}): 2083 (diazo), 1703 (ester)



5.18 Synthesis of D-3-1-1

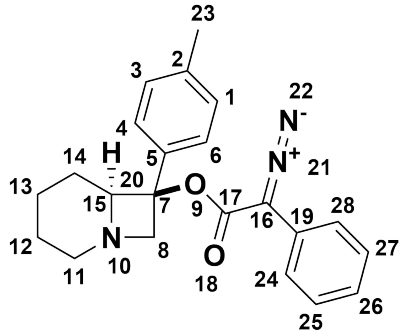
Following the general procedure, to solution of **E-3-1-1** (0.12 mmol, 1 eq) in acetonitrile (1.3 mL, 100 mM), *p*-ABSA (0.15 mmol, 1.2 eq) was added at -10 ℃. DBU (37.6 µL, 2 eq, 0.25 mmol) was added slowly to the solution. The reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 50% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-5% methanol in dichloromethane to yield **D-3-1-1** in 71.0%

^{1}H (500 MHz, Chloroform-d) δ 7.52 (2H, d, *J*=7.8 Hz, 4, 6), 7.32 (2H, d, *J*=8.5 Hz, 24, 28), 7.19 (2H, d, *J*=7.8 Hz, 1, 3), 6.90 (2H, d, *J*=8.5 Hz, 25, 27), 4.03 - 3.91 (3H, m, 8, 20), 3.79 (3H, s, 30), 2.90 - 2.78 (1H, m, 11'), 2.76 - 2.63 (1H, m, 11"), 2.33 (3H, s, 23), 2.13 - 2.02 (1H, m, 14'), 1.94 - 1.79 (1H, m, 12'), 1.75 - 1.64 (2H, m, 12", 14"), 1.49 - 1.40 (1H, m, 13'), 1.40 - 1.33 (1H, m, 13")

^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 164.1 (C-17), 158.2 (C-26), 138.7 (C-5), 137.5 (C-2), 129.3 (C-1, C-3), 125.9 (C-24, C-28), 125.6 (C-4, C-6), 116.7 (C-19), 114.7 (C-25, C-27), 78.8 (C-7), 67.8 (C-15), 61.0 (C-8), 60.5 (C-16), 55.5 (C-30), 46.8 (C-11), 21.5 (C-23), 21.0 (C-14), 20.6 (C-13), 20.3 (C-12)

Characteristic IR vibrations (cm^{-1}): 2075 (diazo), 1701 (ester)

5.19 Synthesis of D-3-1-2

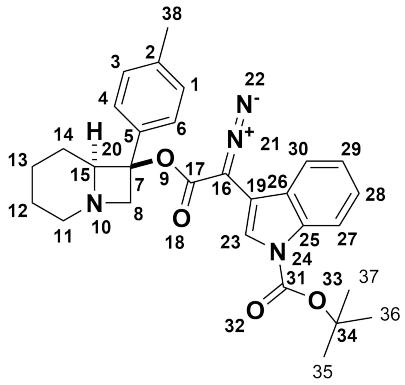


Following the general procedure, to solution of **E-3-1-2** (0.15 mmol, 1 eq) in acetonitrile (1.6 mL, 100 mM), *p*-ABSA (0.19 mmol, 1.2 eq) was added at -10 ℃. DBU (46.5 µL, 2 eq, 0.31 mmol) was added slowly to the solution. The reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 50% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-5% methanol in dichloromethane to yield **D-3-1-2** in 80.5%

^{1}H (500 MHz, Chloroform-d) δ 7.52 - 7.48 (2H, m, 4, 6), 7.41 (2H, d, *J*=8.2 Hz, 24, 28), 7.37 - 7.31 (2H, m, 25, 27),

7.21 - 7.12 (3H, m, 1, 3, 26), 4.15 - 4.04 (2H, m, 8', 20), 4.04 - 3.93 (1H, m, 8"), 2.96 - 2.82 (1H, m, 11'), 2.79 - 2.65 (1H, m, 11"), 2.33 (3H, s, 23), 2.16 - 2.03 (1H, m, 14'), 1.90 - 1.81 (1H, m, 13'), 1.80 - 1.59 (2H, m, 12', 14"), 1.52 - 1.45 (1H, m, 12"), 1.45 - 1.32 (1H, m, 13")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 163.5 (C-17), 138.2 (C-5), 137.8 (C-2), 129.4 (C-19), 129.4 (C-26), 129.1 (C-25, C-27), 128.4, 126.1 (C-1, C-3), 125.6 (C-4, C-6), 124.0 (C-24, C-28), 79.1 (C-7), 67.7 (C-15), 63.6 (C-16), 60.9 (C-8), 46.8 (C-11), 21.23 (C-23), 20.9 (C-14), 20.5 (C-12), 19.9 (C-13)
Characteristic IR vibrations (cm^{-1}): 2081 (diazo), 1703 (ester)

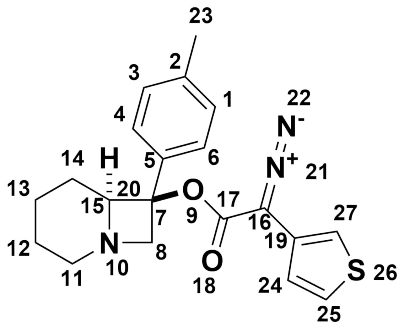
5.20 Synthesis of D-3-1-3



Following the general procedure, to solution of **E-3-1-3** (0.17 mmol, 1 eq) in acetonitrile (1.7 mL, 100 mM), *p*-ABSA (0.20 mmol, 1.2 eq) was added at -10 °C. DBU (32.7 µL, 1.3 eq, 0.22 mmol) was added slowly to the solution. The reaction was left to warm to room temperature and stir for 4 h. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 70% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-70% ethyl acetate in hexanes to yield **D-3-1-3** in 27.3%
^{1}H (500 MHz, Chloroform-d) δ 8.21 (1H, d, *J* = 8.3 Hz), 7.81 (1H, s), 7.56 - 7.51 (3H, m), 7.49 - 7.44 (1H, m), 7.40 - 7.31 (1H, m), 7.25 - 7.16 (2H, m), 4.01 (3H, s), 2.94 - 2.78 (1H, m), 2.77 - 2.66 (1H, m), 2.34 (3H, s), 2.16 - 2.04 (1H, m), 1.94 - 1.75 (1H, m), 1.73 - 1.61 (11H, m), 1.50 - 1.31 (2H, m)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 149.3 (C-31), 129.3, 125.5, 124.5, 122.9, 118.3, 115.6, 84.2 (C-34), 67.8 (C-15), 60.9 (C-8), 46.7 (C-11), 28.2 (C-35, C-36, C-37), 22.7 (C-38), 21.1 (C-14), 20.9 (C-12), 20.4 (C-13)
Note: C-17, C-7, C-16 and several other peaks were not observed in ^{13}C {^{1}H }. Characteristic IR vibrations (cm^{-1}): 2079 (diazo), 1734 (carbamate) 1707 (ester)

5.21 Synthesis of D-3-1-4

Following the general procedure, to solution of **E-3-1-4** (0.14 mmol, 1 eq) in acetonitrile (1.4 mL, 100 mM), *p*-ABSA (0.17 mmol, 1.2 eq) was added at -10 °C. DBU (42.0 µL, 2 eq, 0.28 mmol) was added slowly to the solution. The reaction was left to warm to room temperature and stir over night. Progress of the reaction was monitored in 5% methanol in dichloromethane on silica plate, and in 50% ethyl acetate in hexanes on silica plate. The reaction was quenched by the addition of solid ammonium chloride, followed by filtration of the reaction. The filterate was collected, and concentrated under reduced pressure. The crude was purified by flash column chromatography in 0-5% methanol in dichloromethane to yield **D-3-1-4** in 67.8%
^{1}H (500 MHz, Chloroform-d) δ 7.50 (2H, d, *J*=7.8 Hz, 4, 6), 7.39 - 7.35 (1H, m, 25), 7.35 - 7.32 (1H, m, 27), 7.19 (2H, d, *J*=7.8 Hz, 1, 3), 7.02 - 6.96 (1H, m, 24), 4.13 - 4.03 (2H, m, 20), 4.03 - 3.96 (1H, m, 8), 2.97 - 2.80 (1H, m,



11'), 2.77 - 2.67 (1H, m, 11"), 2.33 (3H, s, 23), 2.16 - 2.00 (1H, m, 14'), 1.89 - 1.80 (1H, m, 12"), 1.79 - 1.61 (2H, m, 14"), 1.54 - 1.44 (1H, m, 13'), 1.40-1.36 (1H, m, 13")

^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 137.8 (C-2), 129.4 (C-1, C-3), 126.6 (C-25), 125.5 (C-4, C-6), 123.7 (C-24), 118.1 (C-27), 79.2 (C-7), 67.8 (C-15), 61.1 (C-8), 46.8 (C-11), 21.3 (C-23), 20.9 (C-14), 20.5 (C-13), 20.0 (C-12))

Note: C-17, C-16, and C-19 peaks were not observed in ^{13}C {^{1}H }.

Characteristic IR vibrations (cm^{-1}): 2075 (diazo), 1701 (ester)

6 Buchner ring expansion

6.1 General experimental procedure for Buchner ring expansion

Following the procedure,[8] in a round bottom flask equipped with a magnetic stir bar, diazo compound (1 eq) was dissolved in anhydrous dichloromethane (5 mM). Solution was purged with nitrogen for 10 min. Flask was irradiated under nitrogen with Hg-Xe lamp at 200 W for 6 to 16 h through a longpass (LP) filter ($\lambda \geq 400$ nm). The reaction was monitored in 50% ethyl acetate in hexanes, 5% methanol in dichloromethane, 60% acetone in dichloromethane, 10% methanol in ethyl acetate. After complete conversion of the starting material, solvent was evaporated and crude was pre-purified on silica column. After pre-purification, mixture of isomers were purified through preprative HPLC to obtain the major isomer (Table 3).Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments.

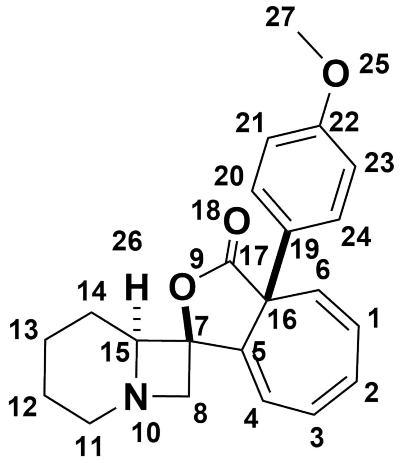
Compound code	Combined yield (%)	yield after prep HPLC (%)	NMR-dr	HPLC-dr
1-1-1	63.5	16.2	2:1	2.7:1
1-1-2	34.4	4.5	2:1	nd
1-1-3	nd	58.9	nd	2:1
1-1-4	53.9	19.3	nd	nd
1-2-1	81.2	42.9	4:1	nd
1-2-2	52.3	12.0	8:1	6:1
1-2-3	57.9	13.0	2:1	3.8:1
1-2-4	43.7	19.1	2.4:1	2.5:1
2-1-1	35.9	18.0	2:1	2:1
2-1-2	39.6	17.0	nd	nd
2-1-3	48.6	21.7	nd	4:1
2-1-4	45.5	10.5	nd	2:1
3-1-1	53.8	mixture	2:1	2.8:1
3-1-2	58.6	40.8	2:1	nd
3-1-3	53.1	mixture	nd	2:1
3-1-4	35.4	15.7	2:1	3.3:1

nd: not determined (because of no separation on HPLC or no characteristic peak in crude NMR)
mixture: isolated as diastereomeric mixture

Table S3: Diastereomeric ratio determined by NMR and HPLC and yields of the synthesized compounds.

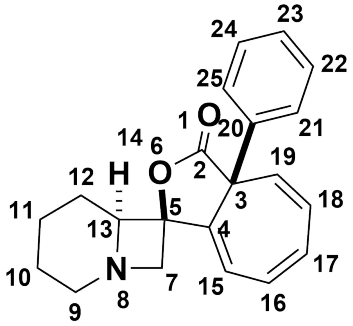
6.2 Synthesis of 1-1-1

Following the general procedure, a 5 mM solution of **D-1-1-1** (34 mg, 0.09 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 6 h through a longpass (LP) filter ($\lambda \geq 400$ nm). After completion of the reaction, solvent was evaporated, and crude was pre-purified in 5% methanol in dichloromethane to obtain the mixture of isomers in 63.5% (20 mg, 2:1). This mixture was subjected to prep-purification on HPLC to yield 16.2% (3.8 mg as ammonium acetate salt) of major diastereomer.
^{1}H (500 MHz, Chloroform-d) δ 7.32 (1H, d, *J*=6.4 Hz, 4), 7.08 (2H, d, *J*=8.5 Hz, 20, 24), 6.73 (2H, d, *J*=8.5 Hz, 21, 23), 6.54 - 6.47 (1H, m, 3), 6.40 - 6.30 (2H, m, 1, 2), 5.86 - 5.80 (1H, m, 6), 4.55 - 4.44 (2H, m, 8', 26), 3.93 (1H, d, *J*=9.6 Hz, 8"), 3.73 (3H, s, 27), 3.32 - 3.22 (1H, m, 11'), 2.99 - 2.90 (1H, m, 11"), 2.08 (3H, s, acetate), 2.06 - 2.01



(1H, m, 14'), 1.92 - 1.84 (1H, m, 13'), 1.83 - 1.76 (1H, m, 14"), 1.75 - 1.68 (1H, m, 12"), 1.68 - 1.60 (1H, m, 13"), 1.58 - 1.46 (1H, m, 12')
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 176.6 (C-17), 176.3 (acetate), 159.4 (C-22), 135.3 (C-5), 130.9 (C-2), 129.4 (C-3), 128.3 (C-19), 127.8 (C-1), 127.7 (C-20, C-24), 124.8 (C-6), 122.0 (C-4), 113.6 (C-21, C-23), 83.9 (C-7), 69.1 (C-15), 64.6 (C-8), 55.3 (C-27), 53.7 (C-16), 47.0 (C-11), 19.9 (C-14), 19.3 (C-12), 17.8 (C-13)
Characteristic IR vibrations (cm^{-1}): 1780 (lactone), 1653
HRMS-ESI Calc M+H = $C_{22}H_{24}NO_3$ = 350.1756, Found Mass = 350.1725, 8.9 ppm

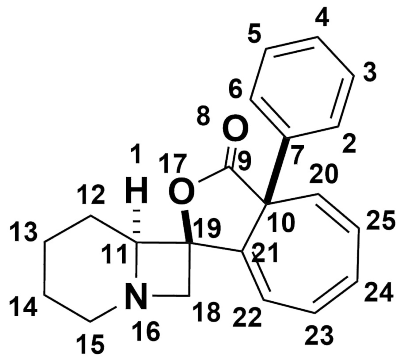
6.3 Synthesis of 1-1-2



may be chloride salt

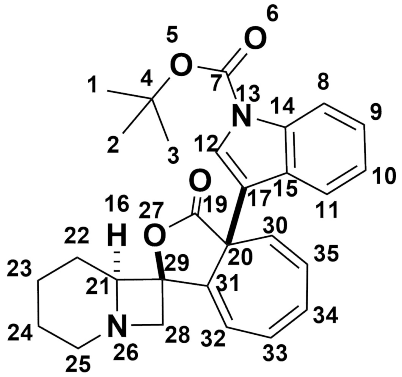
Following the general procedure, a 5 mM solution of **D-1-1-2** (48 mg, 0.14 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 6 h through a longpass (LP) filter ($\lambda \geq$ 400 nm). After completion of the reaction, solvent was evaporated, and crude was pre-purified in 5% methanol in dichloromethane to obtain the mixture of isomers in 34.4% (15.2 mg). This mixture was further subjected for the prep-purification on HPLC, which yielded 9.0% (4 mg, 2:1 ratio) of mixture of diastereomers, and 4.5% (2 mg) as one single diastereomer.
^{1}H (500 MHz, Chloroform-d) δ 7.48 (1H, d, *J*=6.4 Hz, 15), 7.27 - 7.20 (3H, m, 22, 23, 24), 7.17 - 7.10 (2H, m, 21, 25), 6.58 (1H, dd, *J*=11.3, 6.3 Hz, 16), 6.47 - 6.38 (2H, m, 17, 18), 5.96 - 5.89 (1H, m, 19), 5.24 - 5.00 (2H, m, 7', 14), 4.05 (1H, d, *J*=11.9 Hz, 7"), 3.85 - 3.67 (1H, m, 9'), 3.30 - 3.10 (1H, m, 9"), 2.20 - 2.11 (2H, m, 12"), 2.03 - 1.87 (4H, m, 10', 10", 11', 12'), 1.81 - 1.72 (1H, m, 11")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 175.4 (C-2), 135.7 (C-20), 132.4 (C-4), 132.1 (C-17), 129.3 (C-16), 128.5 (C-18), 128.5 (C-23), 128.5 (C-22, C-24), 126.3 (C-21, C-25), 125.6 (C-19), 124.9 (C-15), 83.8 (C-5), 69.8 (C-13), 66.1 (C-7), 54.1 (C-3), 47.1 (C-9), 18.8 (C-12), 17.6 (C-10), 15.6 (C-11)

NMR as mixture of isomers ^{1}H (500 MHz, Chloroform-d) δ 7.42 - 7.32 (2H, m, 22), 7.23 - 7.16 (7H, m, 2, 3, 4, 5,



6), 6.53 - 6.44 (1H, m, 24), 6.42 - 6.27 (3H, m, 23, 25), 5.84 (1H, d, *J*=9.6 Hz, 20), 4.32 - 4.08 (2H, m, 1, 18"), 4.05 (1H, d, *J*=8.3 Hz, 18'), 3.19 - 3.02 (2H, m, 15'), 2.97 - 2.76 (2H, m, 15"), 2.16 - 2.03 (2H, m, 12'), 1.92 - 1.83 (2H, m, 13", 14"), 1.81 - 1.72 (1H, m), 1.70 - 1.63 (1H, m), 1.61 - 1.51 (1H, m, 14'), 1.53 - 1.35 (2H, m, 13')
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 176.6 (C-9), 136.6 (C-7), 130.6, 129.6 (C-24), 128.2, 128.2 (C-3, C-5), 128.0 (C-25), 127.8 (C-4), 126.7 (C-2, C-6), 126.5 (C-21), 124.6 (C-20), 82.7 (C-19), 70.1 (C-11), 64.2 (C-18), 54.7 (C-10), 46.7 (C-15), 20.0 (C-14), 18.6 (C-13)
HRMS-ESI Calc M+H = $C_{21}H_{22}NO_2$ = 320.1651, Found Mass = 320.1618, 10.3 ppm

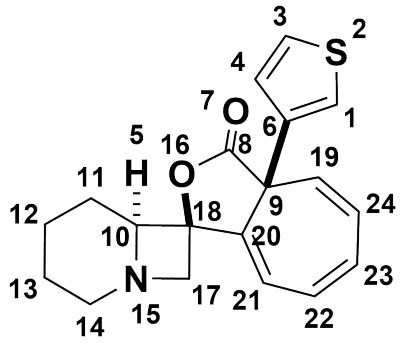
6.4 Synthesis of 1-1-3



Following the general procedure, a 5 mM solution of **D-1-1-3** (18 mg, 0.37 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 16 h through a longpass (LP) filter ($\lambda \geq$ 400 nm). After completion of the reaction, solvent was evaporated, and crude was subjected for the prep-purification on HPLC, which yielded 58.9% (10 mg) of major diastereomer as acetate salt.
^{1}H (500 MHz, Chloroform-d) δ 7.99 (1H, d, *J*=8.1 Hz, 8), 7.78 - 7.65 (1H, m, 11), 7.25 - 7.17 (3H, m, 9, 10, 32), 7.11 (1H, s, 12), 6.57 - 6.48 (1H, m, 33), 6.42 - 6.28 (2H, m, 34, 35), 5.80 - 5.63 (1H, m, 30), 4.32 (1H, d, *J*=8.8 Hz, 28'), 4.23 (1H, t, *J*=7.9 Hz, 16), 4.02 (1H, d, *J*=8.8 Hz, 28"), 3.17 - 3.06 (1H, m, 25'), 2.93 - 2.83 (1H, m, 25"), 2.14 - 2.03 (3H, m, acetate), 1.90 - 1.81 (1H, m, 23), 1.81 - 1.73 (1H, m), 1.63 (11H, s, 1, 2, 3, 24, 22'), 1.60 - 1.52 (1H, m, 22"), 1.52 - 1.40 (1H, m)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 175.7 (C-19), 149.6 (C-7), 136.2 (C-14), 130.3 (C-34), 129.1 (C-33), 128.0 (C-35), 127.6 (C-15), 125.8 (C-12), 124.5 (C-9), 122.7 (C-10), 121.5 (C-11), 120.9 (C-32), 118.5 (C-30), 115.5 (C-8), 113.5 (C-17), 84.2 (C-4), 83.7 (C-29), 69.5 (C-21), 63.8 (C-28), 48.6 (C-20), 46.9 (C-25), 28.3 (C-1, C-2, C-3), 20.2 (C-22), 19.9 (C-24), 18.6 (C-23)

HRMS-ESI Calc M+H = $C_{28}H_{31}N_2O_4$ = 459.2284, Found Mass = 459.2259, 5.4 ppm

6.5 Synthesis of 1-1-4



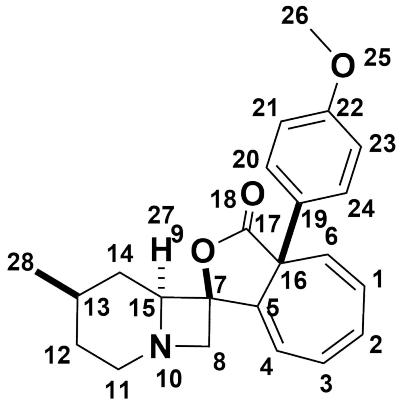
Following the general procedure, a 5 mM solution of **D-1-1-4** (54 mg, 0.15 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 16 h through a longpass (LP) filter ($\lambda \geq 400$ nm). After completion of the reaction, solvent was evaporated, and crude was pre-purified in 5% methanol in dichloromethane to obtain the mixture of isomers in 53.9% (26.8 mg). This mixture was further subjected for the prep-purification on HPLC, which yielded 19.3% (9.6 mg) of one single diastereomer.

^{1}H (500 MHz, Chloroform-d) δ 7.28 - 7.24 (1H, m, 21), 7.17 (1H, dd, *J*=5.1, 3.0 Hz, 3), 6.97 (1H, dd, *J*=5.1, 1.4 Hz, 4), 6.93 (1H, dd, *J*=3.0, 1.3 Hz, 1), 6.52 - 6.45 (1H, m, 22), 6.36 - 6.26 (2H, m, 23, 24), 5.84 - 5.76 (1H, m, 19), 4.07 (1H, dd, *J*=6.8, 0.8 Hz, 17'), 3.85 - 3.75 (1H, m, 5), 3.72 (1H, d, *J*=6.8 Hz, 17"), 2.86 (1H, ddd, *J*=14.7, 11.0, 4.0 Hz, 14'), 2.71 (1H, dt, *J*=13.6, 3.9 Hz, 14"), 2.19 - 2.02 (1H, m, 11'), 1.88 - 1.75 (1H, m, 12'), 1.74 - 1.55 (2H, m, 11", 13'), 1.51 - 1.41 (1H, m, 13"), 1.39 - 1.23 (1H, m, 12")

^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 176.4 (C-8), 139.6 (C-20), 136.6 (C-6), 130.1 (C-23), 129.5 (C-22), 127.6 (C-24), 126.2 (C-4), 125.9 (C-3), 124.7 (C-19), 122.7 (C-1), 119.3 (C-21), 81.5 (C-18), 70.3 (C-10), 63.7 (C-17), 52.6 (C-9), 46.5, 20.8 (C-11), 20.4 (C-13), 19.8 (C-12)

HRMS-ESI Calc M+H = $C_{19}H_{20}NO_2S$ = 326.1215, Found Mass = 326.1187, 8.6 ppm

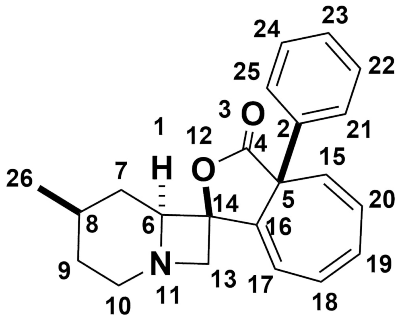
6.6 Synthesis of 1-2-1



Following the general procedure, a 5 mM solution of **D-1-2-1** (18.4 mg, 0.05 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 16 h through a longpass (LP) filter ($\lambda \geq 400$ nm). After completion of the reaction, solvent was evaporated, and crude was pre-purified in 5% methanol in dichloromethane

to obtain the mixture of isomers in 81.2% (14 mg, 4:1). 8 mg of this mixture was further subjected for the prep-purification on HPLC, which yielded 42.9% (4 mg, with ammonium acetate)) of major diastereomer and 32.2% (3 mg, with ammonium acetate) as minor isomer.
^{1}H (500 MHz, Chloroform-d) δ 7.36 (1H, d, *J*=6.5 Hz, 4), 7.18 - 7.13 (2H, m, 20, 24), 6.73 (2H, d, *J*=8.5 Hz, 21, 23), 6.46 (1H, dd, *J*=10.7, 6.6 Hz, 3), 6.39 - 6.24 (2H, m, 1, 2), 5.79 (1H, d, *J*=9.3 Hz, 6), 4.06 (1H, d, *J*=6.9 Hz, 8'), 3.92 - 3.80 (2H, m, 27, 8"), 3.73 (3H, s, 26), 2.93 - 2.86 (1H, m, 11'), 2.85 - 2.75 (1H, m, 11"), 1.83 - 1.73 (1H, m, 14'), 1.63 - 1.51 (1H, m, 14"), 1.49 - 1.39 (2H, m, 12', 13'), 1.34 - 1.20 (1H, m, 13"), 0.99 (3H, d, J=6.2 Hz, 28)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 177.3 (C-17), 159.2 (C-22), 138.1 (C-5), 130.1 (C-2), 129.6 (C-3), 127.9 (C-20, C-24), 127.3 (C-1), 123.9 (C-6), 119.4 (C-4), 113.5 (C-21, C-23), 81.2 (C-7), 71.0 (C-15), 62.8 (C-8), 55.3 (C-26), 54.2 (C-16), 46.6 (C-11), 29.6 (C-14), 28.9 (C-13), 26.7 (C-12), 23.1 (C-28)
HRMS-ESI Calc M+H = $C_{23}H_{26}NO_3$ = 364.1913, Found Mass = 364.1940, 7.4 ppm

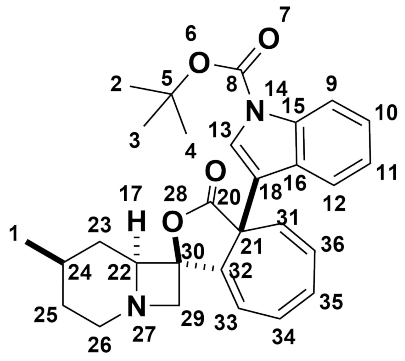
6.7 Synthesis of 1-2-2



Following the general procedure, a 5 mM solution of **D-1-2-2** (45 mg, 0.12 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 16 h through a longpass (LP) filter ($\lambda \geq 400$ nm). After completion of the reaction, solvent was evaporated, and crude was pre-purified in 5% methanol in dichloromethane to obtain the mixture of isomers in 52.3% (21.7 mg, 8:1). This mixture was further subjected for the prep-purification on HPLC, which yielded 12.0% (5 mg) of major diastereomer.
^{1}H (500 MHz, Chloroform-d) δ 7.38 (1H, d, *J*=6.5 Hz, 17), 7.25 - 7.17 (5H, m, 21, 22, 23, 24, 25), 6.47 (1H, dd, *J*=11.0, 6.4 Hz, 18), 6.36 (1H, dd, *J*=9.7, 6.5 Hz, 20), 6.30 (1H, dd, *J*=11.0, 6.4 Hz, 19), 5.82 (1H, d, *J*=9.6 Hz, 15), 4.07 (1H, d, *J*=6.9 Hz, 13'), 3.95 - 3.74 (2H, m, 1, 13"), 2.94 - 2.74 (2H, m, 10), 1.82 - 1.71 (1H, m, 7'), 1.63 - 1.53 (1H, m, 7"), 1.52 - 1.39 (2H, m, 8, 9'), 1.38 - 1.25 (1H, m, 9"), 1.00 (3H, d, *J*=6.1 Hz, 26)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 177.0 (C-4), 139.0 (C-16), 136.8 (C-2), 130.2 (C-19), 129.7 (C-18), 128.1 (C-22, C-24), 127.8 (C-23), 127.6 (C-20), 126.8 (C-21, C-25), 124.2 (C-15), 119.4 (C-17), 81.3 (C-14), 71.1 (C-6), 62.9 (C-13), 55.0 (C-5), 46.6 (C-10), 29.6 (C-7), 28.9 (C-9), 26.7 (C-8), 23.1 (C-26)
HRMS-ESI Calc M+H = $C_{22}H_{24}NO_2$ = 334.1807, Found Mass = 334.1796, 3.3 ppm

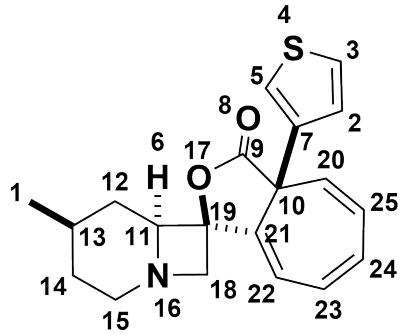
6.8 Synthesis of 1-2-3

Following the general procedure, a 5 mM solution of **D-1-2-3** (34 mg, 0.07 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 6 h through a longpass (LP) filter ($\lambda \geq 400$ nm). After completion of the reaction, solvent was evaporated, and crude was pre-purified in 5% methanol in dichloromethane to obtain the mixture of isomers in 57.9% (18.6 mg, 2:1). This mixture was subjected to prep-purification on HPLC to yield 23.0% (7.4 mg) of major diastereomer
^{1}H (500 MHz, Chloroform-d) δ 7.99 (1H, s, 9), 7.82 - 7.72 (1H, m, 12), 7.31 - 7.26 (1H, m, 33), 7.26 - 7.13 (3H, m, 10, 11, 13), 6.58 - 6.42 (1H, m, 34), 6.42 - 6.26 (2H, m, 35, 36), 5.76 - 5.66 (1H, m, 31), 4.13 (1H, d, *J*=6.8 Hz, 29'), 3.95 - 3.68 (2H, m, 17, 29"), 2.95 - 2.69 (2H, m, 26')), 1.87 - 1.70 (1H, m, 23'), 1.68 - 1.66 (1H, m, 25"), 1.63 (11H,

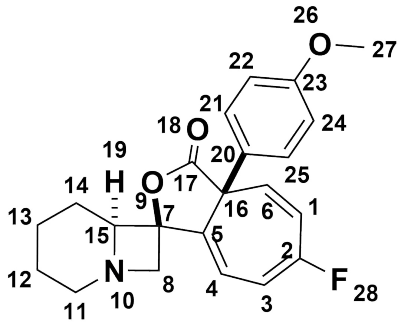


s, 2, 3, 4, 23”), 1.50 - 1.28 (1H, m, 24, 25’), 1.01 (3H, d, *J*=6.2 Hz, 1)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 175.9 (C-20), 149.5 (C-8), 136.1 (C-15), 132.1 (C-32), 129.6 (C-35), 127.6 (C-36), 125.8 (C-13), 124.3 (C-10), 122.5 (C-11), 121.5 (C-12), 118.8 (C-33), 117.3 (C-31), 115.3 (C-9), 113.5 (C-18), 83.9 (C-5), 81.1 (C-30), 71.1 (C-22), 62.4 (C-29), 48.4 (C-21), 46.5 (C-26), 29.7 (C-23), 28.8 (C-25), 28.2 (C-2, C-3, C-4), 26.8 (C-24), 22.9 (C-1)
HRMS-ESI Calc M+H = $C_{29}H_{33}N_2O_4$ = 473.2440, Found Mass = 473.2453, 2.7 ppm

6.9 Synthesis of 1-2-4



Following the general procedure, a 5 mM solution of **D-1-2-4** (26 mg, 0.07 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 16 h through a longpass (LP) filter ($\lambda \geq$ 400 nm). After completion of the reaction, solvent was evaporated, and crude was pre-purified in 5% methanol in dichloromethane to obtain the mixture of isomers in 43.7% (10.5 mg, 2.4:1). This mixture was further subjected for the prep-purification on HPLC, which yielded 19.1% (4.6 mg) of major diastereomer.
^{1}H (500 MHz, Chloroform-d) δ 7.31 (1H, d, *J*=6.5 Hz, 22), 7.18 (1H, dd, *J*=5.0, 3.0 Hz, 3), 6.97 (1H, dd, *J*=5.1, 1.4 Hz, 2), 6.93 (1H, dd, *J*=3.0, 1.4 Hz, 5), 6.53 - 6.44 (1H, m, 23), 6.37 - 6.25 (2H, m, 24, 25), 5.84 - 5.74 (1H, m, 20), 4.04 (1H, d, *J*=6.8 Hz, 18’), 3.95 - 3.56 (2H, m, 6, 18”), 2.95 - 2.68 (2H, m, 15’, 15”), 1.83 - 1.67 (1H, m, 12’), 1.67 - 1.53 (1H, m, 12”), 1.44 (2H, s, 13, 14’), 1.38 - 1.23 (1H, m, 14”), 1.00 (3H, d, *J*=6.2 Hz, 1)
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 176.3 (C-9), 139.3 (C-21), 136.6 (C-7), 130.1 (C-24), 129.6 (C-23), 127.6 (C-25), 126.2 (C-2), 125.9 (C-3), 124.7 (C-20), 122.7 (C-5), 119.3 (C-22), 81.0 (C-19), 70.9 (C-11), 63.1 (C-18), 52.6 (C-10), 46.6 (C-15), 29.6 (C-12), 28.9 (C-14), 26.8 (C-13), 23.1 (C-1)
HRMS-ESI Calc M+H = $C_{20}H_{22}NO_2S$ = 340.1371, Found Mass = 340.1348, 6.8 ppm



6.10 Synthesis of 2-1-1

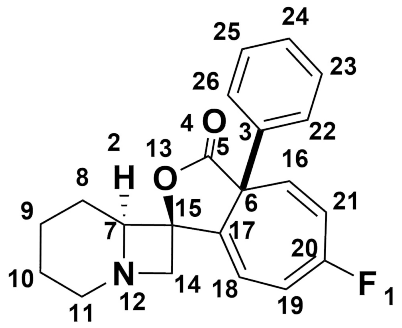
Following the general procedure, a 5 mM solution of **D-2-1-1** (30 mg, 0.07 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 16 h through a longpass (LP) filter ($\lambda \geq 400$ nm). After completion of the reaction, solvent was evaporated, and crude was pre-purified in 5% methanol in dichloromethane to obtain the major diasteromer in 17.9% (5 mg) yield, and mixture of isomers in 35.9% (10 mg, 2:1). The mixture was further subjected for the prep-purification on HPLC, which yielded 35.2% (4.1 mg, with ammonium acetate) as major diastereomer, and 28.4% (3.3 mg, with ammonium acetate) as mixture of isomers.

^{1}H (400 MHz, MeOD) δ 7.23 (1H, dd, *J*=7.5, 5.7 Hz, 4), 7.17 - 7.10 (2H, m, 21, 25), 6.83 - 6.74 (2H, m, 22, 24), 6.41 (1H, ddd, *J*=10.8, 8.9, 2.1 Hz, 1), 6.26 (1H, ddd, *J*=16.9, 7.5, 2.1 Hz, 3), 5.99 (1H, dd, *J*=10.5, 5.0 Hz, 6), 4.09 (1H, d, *J*=7.7 Hz), 3.89 (1H, dd, *J*=7.7, 1.4 Hz, 8"), 3.80 - 3.75 (1H, m, 19), 3.74 (3H, s, 27), 2.95 - 2.82 (1H, m, 11'), 2.82 - 2.72 (1H, m, 11"), 2.16 - 1.99 (1H, m, 14"), 1.88 - 1.80 (1H, m, 13"), 1.79 - 1.68 (1H, m, 12'), 1.64 - 1.55 (1H, m, 12"), 1.53 - 1.33 (2H, m, 13', 14')

^{13}C {^{1}H } (126 MHz, MeOD) δ 177.94 (C-17), 162.62 (d, *J* = 245.2 Hz, C-2), 160.99 (C-23), 137.52 (C-5), 129.72 (C-20), 128.80 (C-21, C-25), 128.72 - 128.45 (m, C-6), 122.73 (d, *J* = 36.4 Hz, C-1), 117.84 (d, *J* = 11.5 Hz, C-4), 114.58 (C-22, C-24), 111.63 (d, *J* = 28.4 Hz, C-3), 83.81 (C-7), 71.95 (C-15), 64.82 (C-8), 55.72, 55.62 (C-16), 47.64 (C-11), 21.39 (C-12), 21.22 (C-14), 20.19 (C-13)

HRMS-ESI Calc M+H = $C_{22}H_{23}FNO_3$ = 368.1662, Found Mass = 368.1632, 8.1 ppm

6.11 Synthesis of 2-1-2

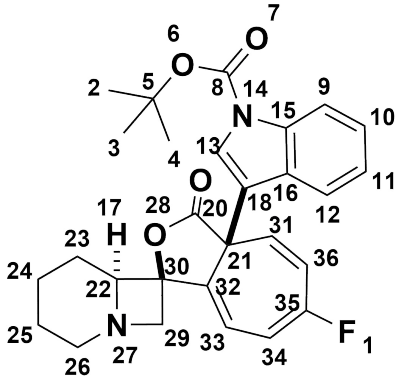


Following the general procedure, a 5 mM solution of **D-2-1-2** (57.4 mg, 0.16 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 16 h through a longpass (LP) filter ($\lambda \geq 400$ nm). After completion of the reaction, solvent was evaporated, and crude was purified in 5% methanol in dichloromethane to obtain the major diasteromer in 17.0% (9 mg) yield.

^{1}H (500 MHz, Chloroform-d) δ 7.37 - 7.30 (1H, m, 18), 7.25 - 7.19 (5H, m, 22, 23, 24, 25, 26), 6.41 - 6.29 (1H, m, 19), 6.27 - 6.16 (1H, m, 21), 6.09 - 5.99 (1H, m, 16), 4.08 (1H, d, *J*=7.0 Hz, 14'), 3.90 - 3.78 (2H, m, 2, 14"), 2.95 - 2.84 (1H, m, 11'), 2.81 - 2.69 (1H, m, 11"), 2.15 - 1.99 (1H, m, 8'), 1.91 - 1.79 (1H, m, 9'), 1.74 - 1.64 (1H, m, 8"),

1.64 - 1.53 (1H, m, 10'), 1.51 - 1.41 (1H, m, 10"), 1.41 - 1.29 (1H, m, 9")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 176.3 (C-5), 161.2 (d, *J* = 246.2 Hz, C-20), 136.5 (C-17), 128.4 (C-22, C-26), 128.3 (C-24), 128.1 (d, *J* = 13.5 Hz, C-16), 126.5 (C-23, C-25), 122.3 (d, *J* = 37.0 Hz, C-21), 116.8 (C-18), 110.7 (d, *J* = 28.1 Hz, C-19), 82.1 (C-15), 70.4 (C-7), 63.4 (C-14), 55.2 (C-6), 46.5 (C-11), 20.7 (C-8), 20.3 (C-10), 19.7 (C-9)
HRMS-ESI Calc M+H = $C_{21}H_{21}FNO_2$ = 338.1556, Found Mass = 338.1538, 5.3 ppm

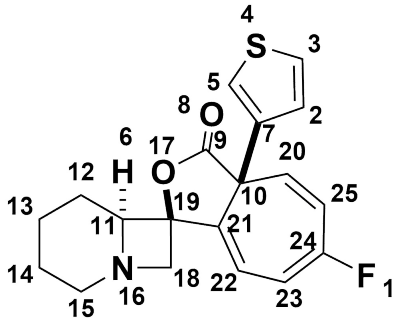
6.12 Synthesis of 2-1-3



Following the general procedure, a 5 mM solution of **D-2-1-3** (37 mg, 0.07 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 12 h through a longpass (LP) filter ($\lambda \geq$ 400 nm). After completion of the reaction, solvent was evaporated, and crude was purified in 5% methanol in dichloromethane to obtain the mixture of isomer in 48.6% (17 mg) yield. This mixture was further subjected to prep-purification on HPLC to yield 21.7% (7.6 mg) of major diastereomer.
^{1}H (500 MHz, Chloroform-d) δ 8.02 (1H, s, 9), 7.79 (1H, d, *J*=7.8 Hz, 12), 7.29 - 7.14 (4H, m, 10, 11, 13, 33, mix with chloroform peak), 6.35 - 6.23 (2H, m, 36, 34), 6.06 (1H, dd, *J*=10.5, 4.9 Hz, 31), 4.13 (1H, d, *J*=6.8 Hz, 29'), 3.87 - 3.72 (2H, m, 17, 29"), 2.93 - 2.78 (1H, m, 26'), 2.77 - 2.68 (1H, m, 26"), 2.16 - 2.04 (1H, m, 23'), 1.91 - 1.79 (1H, m, 24'), 1.64 (10H, s, 2, 3, 4, 23"), 1.51 - 1.41 (1H, m, 25"), 1.39 - 1.28 (1H, m, 25')
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 175.3 (C-20), 160.6 (d, *J* = 246.1 Hz, C-35), 149.6 (C-8), 136.4 (C-15), 133.7 (C-32), 127.3 (C-16), 125.4 (C-11), 124.6 (C-13), 124.6 (C-31), 122.7 (C-10), 122.3 (d, *J* = 36.5 Hz, C-36), 121.7 (C-12), 116.7 (C-33), 115.5 (C-9), 113.6 (C-18), 110.6 (d, *J* = 28.3 Hz, C-34), 84.3 (C-5), 81.9 (C-30), 70.7 (C-22), 63.3 (C-29), 50.1 (C-21), 46.5 (C-26), 28.3 (C-2, C-3, C-4), 20.9 (C-23), 20.3 (C-25), 19.8 (C-24)
HRMS-ESI Calc M+H = $C_{28}H_{30}FN_2O_4$ = 477.2190, Found Mass = 477.2192, 0.4 ppm

6.13 Synthesis of 2-1-4

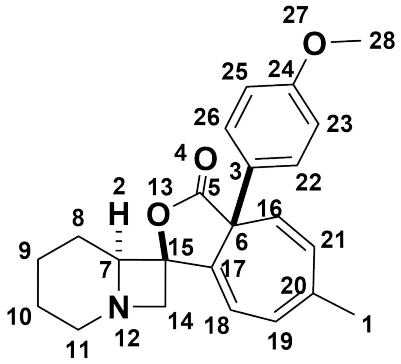
Following the general procedure, a 5 mM solution of **D-2-1-4** (27.7 mg, 0.07 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 16 h through a longpass (LP) filter ($\lambda \geq$ 400 nm). After completion of the reaction, solvent was evaporated, and crude was pre-purified in 10% methanol in ethyl acetate to obtain the mixture of isomer in 45.5% (11.7 mg) yield. This mixture was further subjected for the prep-purification on HPLC, which yielded major diastereomer in 10.5% yield.
^{1}H (500 MHz, Chloroform-d) δ 7.25 - 7.19 (2H, m, 3, 22), 7.01 - 6.93 (2H, m, 2, 5), 6.32 - 6.27 (1H, m, 25), 6.26 - 6.19 (1H, m, 23), 6.00 (1H, dd, *J*=10.8, 4.9 Hz, 20), 4.05 (1H, d, *J*=7.0 Hz, 18'), 3.93 - 3.69 (2H, m, 6, 18"), 2.94 - 2.84 (1H, m, 15'), 2.78 - 2.68 (1H, m, 15"), 2.12 - 1.99 (1H, m, 12'), 1.90 - 1.78 (1H, m, 13'), 1.76 - 1.67 (1H, m, 14'), 1.67 - 1.57 (1H, m, 12"), 1.54 - 1.43 (1H, m, 14"), 1.43 - 1.30 (1H, m, 13")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 175.6 (C-9), 160.9 (d, *J* = 246.2 Hz, C-24), 137.5 (C-21), 136.1 (C-7), 127.8



(d, *J* = 13.6 Hz, C-20), 126.5 (C-3), 125.8 (C-2), 122.9 (C-5), 122.5 (d, *J* = 37.2 Hz, C-25), 116.6 (C-22), 110.3 (d, *J* = 28.2 Hz, C-23), 81.9 (C-19), 70.2 (C-11), 63.6 (C-18), 52.6 (C-10), 46.5 (C-15), 20.7 (C-12), 20.3 (C-14), 19.6 (C-13)

HRMS-ESI Calc M+H = $C_{19}H_{19}FNO_2S$ = 344.1121, Found Mass = 344.1121, 3.2 ppm

6.14 Synthesis of 3-1-1



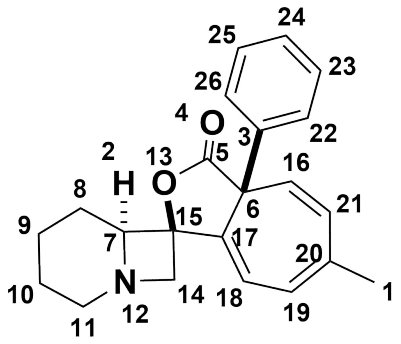
Following the general procedure, a 5 mM solution of **D-3-1-1** (30 mg, 0.08 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 6 h through a longpass (LP) filter ($\lambda \geq$ 400 nm). After completion of the reaction, solvent was evaporated, and crude was pre-purified in 0-40% methanol in ethyl acetate to obtain the mixture of isomer in 53.8% (15 mg, 2:1) yield.

^{1}H (500 MHz, Chloroform-d) δ 7.17 - 7.07 (5H, m, 18, 22, 26, mix with minor isomer), 6.72 (3H, d, *J*=8.3 Hz, 23, 25, mix with minor isomer), 6.21 (2H, d, *J*=6.9 Hz, 19), 6.16 (1H, dd, *J*=9.9, 6.4 Hz, 21), 5.72 (0.4 H, d, *J*=9.9 Hz, minor isomer), 5.62 (1H, d, *J*=9.7 Hz, 16), 4.04 (1H, d, *J*=7.3 Hz, 14'), 3.98 (0.4H, d, *J*=7.5 Hz, minor isomer), 3.94 - 3.80 (2H, m, 2, 14"), 3.73 (4H, s, 28, mix with minor isomer), 2.97 - 2.84 (2H, m, 11'), 2.81 - 2.65 (2H, m, 11"), 2.19 - 2.02 (2H, m, 8', mix with minor isomer), 1.90 - 1.79 (6H, m, 1, 9', mix with minor isomer), 1.76 - 1.65 (1H, m), 1.63 - 1.53 (2H, m, 8", 10"), 1.51 - 1.44 (1H, m, 10'), 1.41 - 1.30 (3H, m, 9", mix with minor isomer)

^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 177.4 (C-5), 159.1 (C-24), 139.2 (minor isomer), 139.2 (C-20), 132.4 (C-17), 130.4, 130.0 (C-21), 129.2 (minor isomer), 128.9 (C-3), 127.9 (C-22, C-26), 127.7 (minor isomer), 126.7 (C-19), 126.5 (minor isomer), 122.3 (minor isomer), 119.9 (C-16), 119.4 (C-18), 113.6 (minor isomer), 113.5 (C-23, C-25), 82.3 (minor isomer), 82.1 (C-15), 70.6 (minor isomer), 70.2 (C-7), 63.4 (C-14), 63.3 (minor isomer), 53.6 (minor isomer), 53.3 (minor isomer), 55.3 (C-28), 52.8 (C-6), 46.6 (C-11), 24.6 (minor isomer), 24.4 (C-1), 20.9 (minor isomer), 20.7 (C-8), 20.4 (C-10), 20.2 (minor isomer), 19.5 (C-9)

HRMS-ESI Calc M+H = $C_{23}H_{26}NO_3$ = 364.1913, Found Mass = 364.1886, 7.4 ppm

6.15 Synthesis of 3-1-2



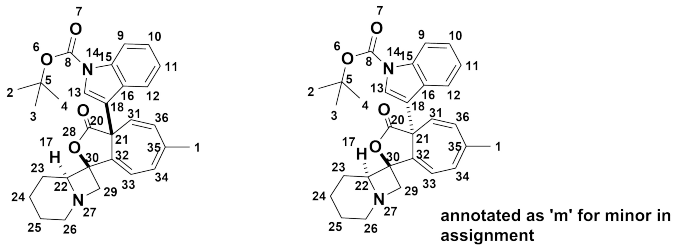
Following the general procedure, a 5 mM solution of **D-3-1-2** (37 mg, 0.10 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 6.5 h through a longpass (LP) filter ($\lambda \geq 400$ nm). After completion of the reaction, solvent was evaporated, and crude was pre-purified in 0-40% methanol in ethyl acetate to obtain the mixture of isomer in 58.6% (16.6 mg, 2:1) yield. This mixture was subjected to prep-purification on HPLC to yield 40.8% (8 mg, as acetate salt, 0.2:1)of mixture of isomers.

^{1}H (500 MHz, Chloroform-d) δ 7.23 - 7.19 (4H, m, 22, 23, 25, 26), 7.19 - 7.16 (1H, m, 18), 7.15 - 7.10 (1H, m, 24), 6.27 (1H, d, *J*=6.7 Hz, 19), 6.22 (1H, d, *J*=9.9 Hz, 21), 5.83 (0.15H, d, J=10.0 Hz, minor isomer), 5.76 (1H, d, *J*=9.9 Hz, 16), 4.64 - 4.51 (2H, m, 2, 14'), 3.95 (1H, d, *J*=10.0 Hz, 14"), 3.85 (0.2H, d, *J*=10.1 Hz, minor isomer), 3.40 - 3.24 (1H, m, 11'), 3.13 - 2.93 (1H, m, 11"), 2.08 (4H, s, 10' and acetate), 1.85 (4H, s, 1, 8"), 1.83 - 1.77 (1H, m, 10"), 1.77 - 1.62 (2H, m, 8', 9"), 1.61 - 1.49 (1H, m, 9')

^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 176.4 (C-5), 175.6 (acetate), 140.5 (C-20), 136.6 (C-3), 131.3 (C-17), 131.1 (C-21), 128.3 (C-22, C-26), 128.1 (C-24), 126.6 (C-19), 126.5 (C-23, C-25), 126.4, 122.4 (C-16, C-18), 84.1 (C-15), 69.3 (C-7), 64.8 (C-14), 53.6 (C-6), 47.1 (C-11), 46.8, 24.7, 24.5 (C-1), 21.5 (acetate), 19.8 (C-8), 19.1 (C-10), 17.5 (C-9)

HRMS-ESI Calc M+H = $C_{22}H_{24}NO_2$ = 334.1807, Found Mass = 334.1804, 0.9 ppm

6.16 Synthesis of 3-1-3



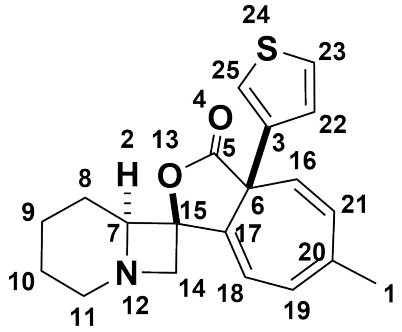
Following the general procedure, a 5 mM solution of D-3-1-3 (23 mg, 0.05 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 6 h through a longpass (LP) filter ($\lambda \geq 400$ nm). After completion of the reaction, solvent was evaporated, and crude was subjected to prep-purification on HPLC to yield 53.1% (13.2 mg, as acetate salt, 2:1)of mixture of isomers.

NMR reported as mixture of diastereomers, where peaks from minor isomer are annotated with 'm'.

^{1}H (500 MHz, Chloroform-d) δ 8.01 (2H, s, 9m, 9), 7.76 (0.5H, d, *J*=7.8 Hz, 12m), 7.57 (1H, d, *J*=7.8 Hz, 12), 7.25 - 7.22 (1.5H, m, 11m, 11), 7.22 - 7.16 (1.5H, m, 10m, 10), 7.13 - 7.06 (2H, m, 13m, 33m, 13), 7.02 (1H, d, *J*=6.9 Hz, 33), 6.32 - 6.24 (2H, m, 34m, 34), 6.18 (2H, dd, *J*=13.3, 9.4 Hz, 36m, 36), 5.70 (0.5H, d, J=9.8 Hz, 31m), 5.53 (1H, d, *J*=9.6 Hz, 31), 4.62 (0.5H, t, J=7.7 Hz, 17), 4.44 (1H, d, *J*=9.3 Hz, 29'), 4.33 (1H, t, *J*=7.6 Hz, 17), 4.08 (0.5H, d,

J=9.2 Hz, 29m'), 3.99 (1H, d, *J*=9.3 Hz, 29"), 3.84 (0.5H, d, *J*=9.3 Hz, 29m"), 3.26 - 3.10 (2H, m, 26m', 26'), 2.91 (1H, dtd, *J*=12.9, 8.3, 3.8 Hz, 26m", 26"), 2.06 (7H, s, 23m', 23', mix with acetate), 1.90 (3H, s, 1), 1.87 (2H, s, 1m,), 1.86 - 1.67 (2H, m), 1.63 (14H, m , 2', 3', 4', 2, 3, 4), 1.60 - 1.45 (3H, m, 24m", 25m", 24")
^{13}C {^{1}H } (126 MHz, Chloroform-d) δ 176.5 (C-20), 175.9 (20m), 175.8 (acetate), 149.5 (8m, C-8), 139.5 (C-35), 139.3 (35m), 136.3 (C-16), 130.5 (36m), 130.3 (C-36), 127.7 (15m, C-15), 126.6 (C-34), 126.5 (34m), 126.1 (C-13), 125.4 (13m), 124.5 (11m), 124.5 (C-11), 124.1 (C-32), 122.7 (C-10), 122.6 (10m), 121.5 (33m), 121.3 (C-33), 120.8 (12m, C-12), 116.8 (31m), 115.5 (C-9), 115.4 (9m), 113.4 (C-31), 84.4 (C-5), 84.2 (C-30), 69.1 (C-22), 68.9 (22m), 63.8, 63.7 (C-29), 47.0 (C-26), 46.8 (26m), 28.3 (C-2, C-3, C-4), 24.6 (1m), 24.3 (C-1), 22.1, 20.3 (25m), 20.2 (C-25), 20.0, 19.7 (23m), 18.4 (24m), 18.2 (C-24)
HRMS-ESI Calc M+H = $C_{29}H_{33}N_2O_4$ = 473.2440, Found Mass = 473.2415, 5.3 ppm

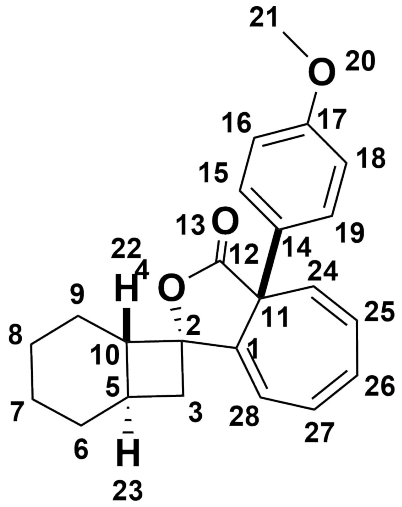
6.17 Synthesis of 3-1-4



Following the general procedure, a 5 mM solution of **D-3-1-4** (22 mg, 0.06 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 7 h through a longpass (LP) filter ($\lambda \geq 400$ nm). After completion of the reaction, solvent was evaporated, and crude was pre-purified in 0-5% methanol in dichloromethane to obtain the mixture of isomer in 35.4% (7.2 mg, 2:1) yield. This mixture was subjected to prep-purification on HPLC to yield 15.7% (3.2 mg) of major diastereomer.
^{1}H (500 MHz, Chloroform-d) δ 7.17 (1H, dd, *J*=5.0, 3.1 Hz, 23), 7.08 (1H, d, *J*=6.7 Hz, 18), 6.94 - 6.91 (2H, m, 22, 25), 6.25 (1H, dq, *J*=6.9, 1.2 Hz, 19), 6.14 (1H, dd, *J*=10.0, 1.2 Hz, 21), 5.70 (1H, d, *J*=10.0 Hz, 16), 4.04 (1H, d, *J*=7.1 Hz, 14'), 3.92 - 3.75 (2H, m, 2, 14"), 2.97 - 2.82 (1H, m, 11'), 2.82 - 2.64 (1H, m, 11"), 2.17 - 2.01 (1H, m, 8'), 1.90 (3H, s, 1), 1.88 - 1.75 (1H, m, 9'), 1.75 - 1.55 (1H, m, 8", 10'), 1.54 - 1.42 (1H, m, 10"), 1.40 - 1.22 (1H, m, 9")
^{13}C{^{1}H } (126 MHz, Chloroform-d) δ 176.5 (C-5), 139.2 (C-20), 136.8 (C-3), 135.8 (C-17), 130.6 (C-21), 126.4 (C-19), 126.1 (C-22), 125.8 (C-23), 122.6 (C-25), 122.1 (C-16), 119.3 (C-18), 81.8 (C-15), 70.2 (C-7), 63.7 (C-14), 51.6 (C-6), 46.6 (C-11), 24.7 (C-1), 20.7 (C-8), 20.3 (C-10), 19.6 (C-9)
HRMS-ESI Calc M+H = $C_{20}H_{22}NO_2S$ = 340.1371, Found Mass = 340.1337, 10.0 ppm

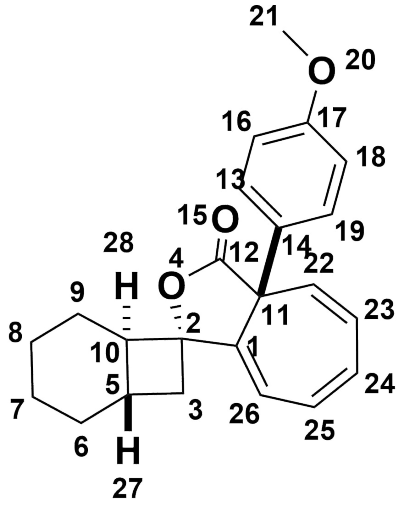
6.18 Synthesis of *cis*-1-cyclohexane-1

Following the general procedure, a 5 mM solution of **D1** (5 mg, 0.01 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 4 h through a longpass (LP) filter ($\lambda \geq 400$ nm). After completion of the reaction, solvent was evaporated, and crude was pre-purified in 0-5% methanol in dichloromethane to obtain the mixture of isomer in 71.5% (3.3 mg, 4:1) yield.
^{1}H (500 MHz, Chloroform-d) δ 7.13 - 7.08 (2H, m), 6.74 - 6.69 (2H, m), 6.58 (1H, d, *J*=6.3 Hz), 6.43 (1H, dd, *J*=11.0, 6.3 Hz), 6.37 (1H, dd, *J*=9.7, 6.4 Hz), 6.35 - 6.28 (1H, m), 5.82 (1H, d, *J*=9.5 Hz), 3.72 (3H, s), 2.65 (1H, dd, *J*=11.0, 6.7 Hz), 2.40 - 2.32 (1H, m), 2.21 - 2.08 (1H, m), 1.96 - 1.85 (2H, m), 1.84 - 1.74 (2H, m), 1.54 - 1.43 (1H, m), 1.42 - 1.33 (2H, m), 1.33 - 1.23 (2H, m)
^{13}C{^{1}H } (126 MHz, Chloroform-d) δ 177.8 (C-12), 159.1 (C-17), 138.4 (C-1), 130.1 (C-26), 129.3 (C-14), 128.9



(C-27), 127.9 (C-15, C-19), 127.8, 127.4 (C-25), 127.2, 126.1, 124.3 (C-24), 119.9, 119.4 (C-28), 113.3 (C-16, C-18), 93.4 (C-2), 57.6, 55.8 (C-10), 55.3 (C-21), 54.6 (C-11), 44.8 (C-3), 43.8, 37.5 (C-5), 31.7 (C-9), 26.5 (C-7), 25.8 (C-8), 25.2 (C-6)

6.19 Synthesis of compound *trans*-1-cyclohexane-1

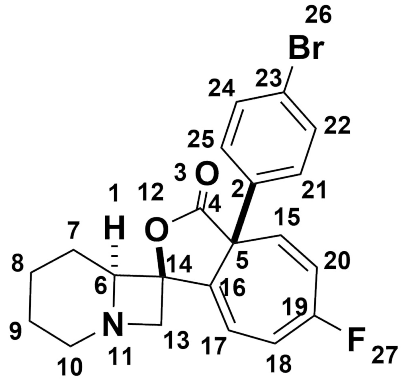


Following the general procedure, a 5 mM solution of **D2** (10 mg, 0.03 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 4 h through a longpass (LP) filter ($\lambda \geq 400$ nm). After completion of the reaction, solvent was evaporated, and crude was pre-purified in 0-5% methanol in dichloromethane to obtain the single diastereomer in 57.4% (5.3 mg) yield.

^{1}H (500 MHz, Chloroform-d) δ 7.10 (2H, d, *J*=8.8 Hz), 6.71 (3H, dd, *J*=8.0, 3.3 Hz), 6.42 - 6.36 (1H, m), 6.35 - 6.32 (1H, m), 6.29 (1H, dd, *J*=10.3, 6.6 Hz), 5.33 - 5.25 (1H, m), 3.72 (3H, s), 2.82 (1H, dd, *J*=10.8, 7.1 Hz), 2.56 (1H, t, *J*=11.1 Hz), 2.29 - 2.17 (1H, m), 1.95 - 1.90 (1H, m), 1.84 - 1.69 (2H, m), 1.63 - 1.53 (2H, m), 1.47 - 1.42 (1H, m), 1.38 - 1.22 (3H, m), 1.20 - 1.05 (1H, m)

^{13}C{^{1}H } (126 MHz, Chloroform-d) δ 177.3, 159.0, 129.5, 128.9, 128.5, 127.8, 126.8, 118.1, 113.2, 111.1, 100.1, 88.3, 55.8, 55.3, 51.6, 43.2, 34.5, 32.4, 26.8, 26.2, 25.6

6.20 Synthesis of compound 2-1-*p*-bromophenylacetic acid



Following the general procedure, a 5 mM solution of **D17** (45 mg, 0.10 mmol) in anhydrous dichloromethane was irradiated under nitrogen with Hg-Xe lamp at 200 W for 6 h through a longpass (LP) filter ($\lambda \geq 400$ nm). After completion of the reaction, solvent was evaporated, and crude was pre-purified in 0-5% methanol in dichloromethane to obtain the mixture of isomers in 31.5% (13.3 mg) yield. This mixture was subjected to prep-purification on HPLC to yield 1.6 mg of major diastereomer (CCDC 2126589).

^{1}H (500 MHz, Chloroform-d) δ 7.48 - 7.41 (1H, m, 17), 7.40 - 7.32 (2H, m, 22, 24), 7.11 - 7.04 (2H, m, 21, 25), 6.37 (1H, ddd, *J*=10.7, 8.8, 2.1 Hz, 18), 6.28 (1H, ddd, *J*=16.4, 7.5, 2.1 Hz, 20), 6.03 (1H, dd, *J*=10.5, 4.9 Hz, 15), 4.30 (2H, s, 1, 13'), 4.05 (1H, d, *J*=9.1 Hz, 13"), 3.31 - 3.08 (1H, m, 10'), 2.98 - 2.84 (1H, m, 10"), 2.17 - 2.00 (2H, m, 7', 9'), 1.95 - 1.83 (1H, m, 8"), 1.83 - 1.58 (2H, m, 7", 9", mix with ammonium peak), 1.48 (1H, s, 8')

^{13}C{^{1}H } (126 MHz, Chloroform-d) δ 162.6, 151.3, 131.7, 128.1, 123.2, 122.8 (d, *J*=5.2 Hz), 110.9 (d, *J*=28.8 Hz), 83.4, 69.8, 46.7, 29.8, 19.5

6.21 Structural assignment and stereochemistry

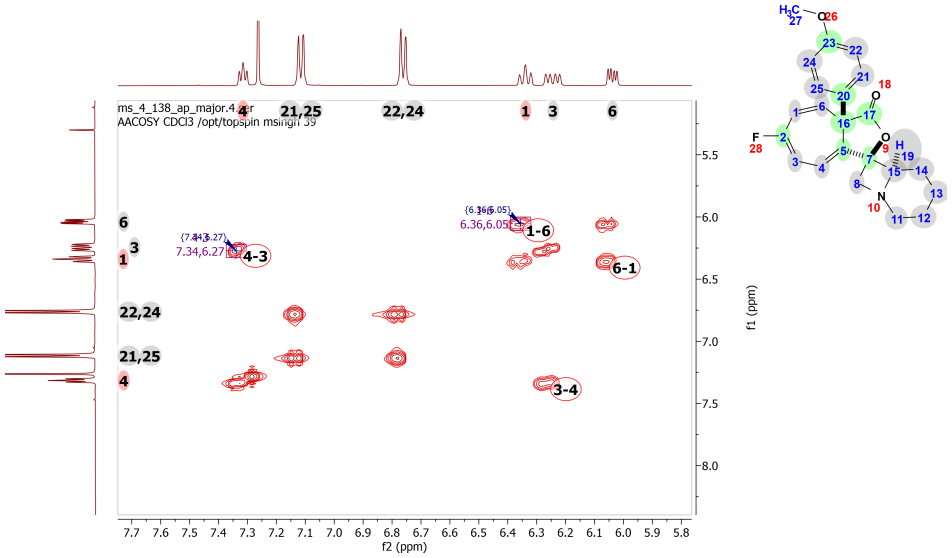


Figure S3: COSY assignment of the cycloheptatriene protons

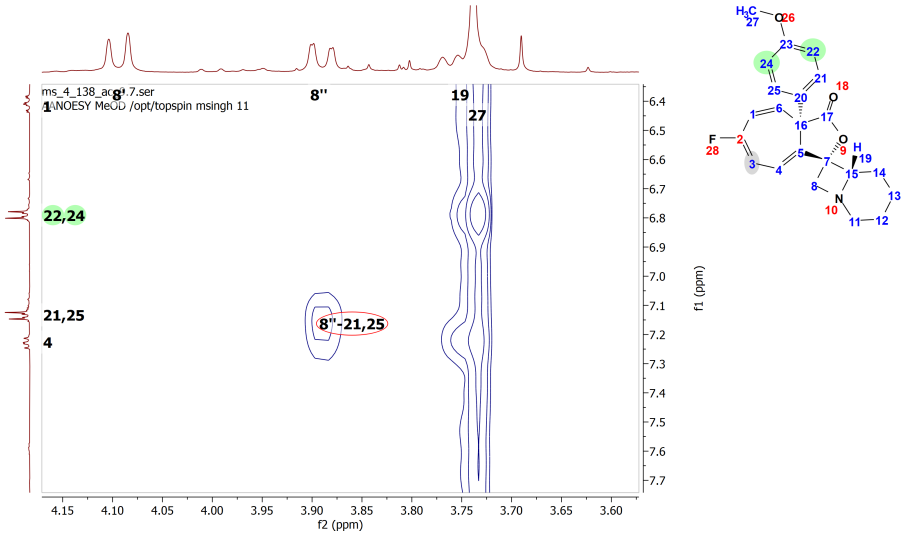


Figure S4: NOE assignment to establish stereochemistry: interactions between *exo* methylene proton on azetidine and *ortho* protons on the aromatic ring

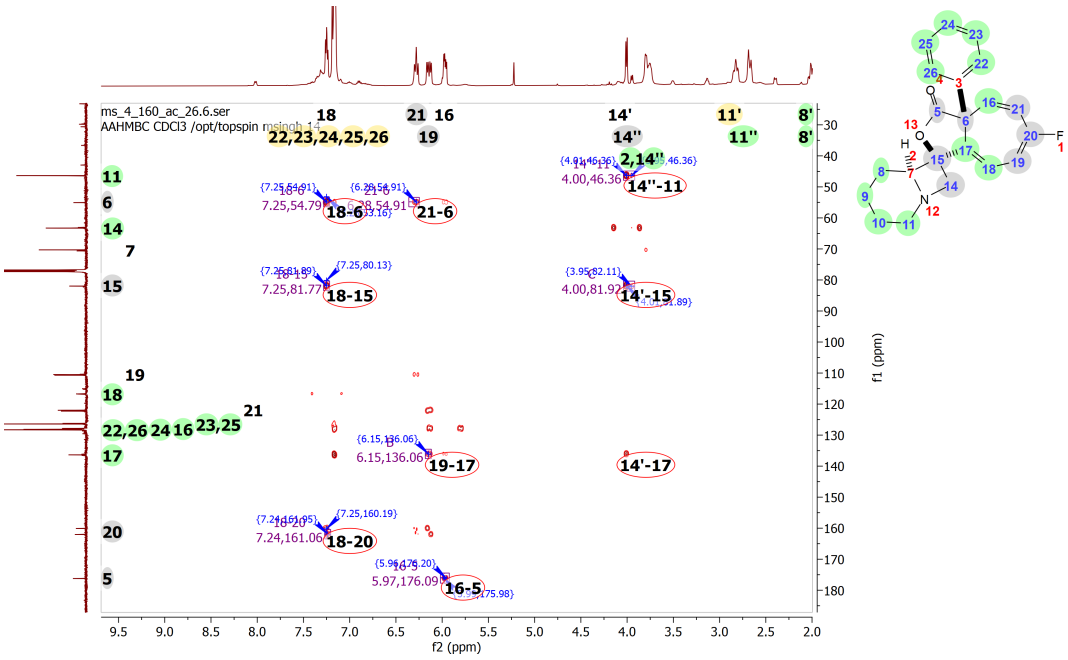


Figure S5: HMBC assignment of the key through-bond correlations.

7 Actinometry

7.1 General procedure for the determination of number of photons

Following the procedure,[9] 6 mM (3 mL) solution of potassium ferrioxalate was exposed to light for different time periods. 1 mL of each of the solution after exposure for a given time period was transferred to a 10 mL Erlenmyer flask (kept under red light).After completing acquisition of all time points, 4 mL solution of 0.1% phenanthroline was added to the flask, followed by the addition of 0.5 mL of sodium acetate buffer. Final volume was made up to 10 mL by adding 4.5 mL of distilled water.Flask was kept protected from light (in red-light) for 1 h, for complete complexation of Fe(II) with phenantroline. After an hour, sample was taken out from the flask and UV absorbance of the samples were measured at wavelength 510 nm.

7.2 Determination of photon flux without filter

Power: 100 Watt
Time points: 10 s, 30 s, 60 s, 120 s, 240 s
6 mM solution (3 mL) of potassium ferrioxalate was exposed to light (Hg-Xe lamp, no filter, 100 W) for 10s, 30s, 60s, 120s and 240s. 1 mL of each of the solution after exposure was transferred to a 10 mL erlenmyer flask (kept under red light).After completion of all the time points, 4 mL solution of 0.1% phenanthroline was added to the flask, followed by the addition of 0.5 mL of sodium acetate buffer. Final volume was made up to 10 mL by adding 4.5 mL of distilled water. Flask was kept under dark (red-light) for 1 h, for complete complexation or conversion of Fe (III) to Fe(II). After an hour, 600 µL of the sample was taken out from the flask and diluted to 3 mL (5x dilution) to give a concentration of 120 µM. UV absorbance of the samples were taken (510 nm).

7.3 Determination of photon flux with 280 nm longpass filter

Power: 100 Watt
Time points: 2s, 4 s, 8 s, 16 s, 32 s, 64 s
6 mM (3 mL) solution of potassium ferrioxalate was exposed to light (Hg-Xe lamp, 280 nm longpass, 100 W) for 2s, 4 s, 8 s, 16 s, 32 s, 64 s . 1 mL of each of the solution after exposure was transferred to a 10 mL erlenmyer flask (kept under red light).After completion of all the time points, 4 mL solution of 0.1% phenanthroline was added to the flask, followed by the addition of 0.5 mL of sodium acetate buffer. Final volume was made up to 10 mL by adding 4.5 mL of distilled water.Flask was kept under dark (red-light) for 1 h, for complete complexation or conversion of Fe (III) to Fe(II). After an hour, sample was taken out from the flask and UV absorbance of the samples were taken (conc. 600 µM, wavelength= 510 nm).

7.4 Determination of photon flux with 305 nm longpass filter

Power: 100 Watt
Time points: 2s, 4 s, 8 s, 16 s, 32 s, 64 s
6 mM (3 mL) solution of potassium ferrioxalate was exposed to light (Hg-Xe lamp, 305 nm longpass, 100 W) for 2s, 4 s, 8 s, 16 s, 32 s, 64 s . 1 mL of each of the solution after exposure was transferred to a 10 mL erlenmyer flask (kept under red light).After completion of all the time points, 4 mL solution of 0.1% phenanthroline was added to the flask, followed by the addition of 0.5 mL of sodium acetate buffer. Final volume was made up to 10 mL by adding 4.5 mL of distilled water.Flask was kept under dark (red-light) for 1 h, for complete complexation or conversion of Fe (III) to Fe(II). After an hour, sample was taken out from the flask and UV absorbance of the samples were taken (conc. 600 µM, wavelength= 510 nm).

7.5 Determination of photon flux with 280 nm bandpass filter

Power: 100 Watt
Time points: 60 s, 600 s, 1200 s
6 mM (3 mL) solution of potassium ferrioxalate was exposed to light (Hg-Xe lamp, 280 nm bandpass, 100 W) for 60 s, 600 s, 1200 s. 1 mL of each of the solution after exposure was transferred to a 10 mL erlenmyer flask (kept under red light).After completion of all the time points, 4 mL solution of 0.1% phenanthroline was added to the flask, followed by the addition of 0.5 mL of sodium acetate buffer. Final volume was made up to 10 mL by adding 4.5 mL of distilled water.Flask was kept under dark (red-light) for 1 h, for complete complexation or conversion of Fe (III) to Fe(II). After an hour, sample was taken out from the flask and UV absorbance of the samples were taken (conc. 600 µM, wavelength= 510 nm).

7.6 Calculation of number of photons

Refer to the MatLab file on the https://github.com/boskovicgroup/aza_yang_buchner

filter	photons [nmol/s]	C [µM/s]
none	58	19
280-nm bandpass	0.18	0.06
280-nm longpass	42	14
305-nm longpass	36	12

Table S4: Actinometric determination of the number of photons that reach reaction cell from the light source (at 100 W) passing through filters used in the aza-Yang reaction. Amount of photons per second was divided with the reactor volume (3 mL) to give the concentration of photons in solution.

8 Study of reaction kinetics

We studied the initial rates of the aza-Yang cyclization under four different conditions: 1) variable concentration of the substrate, keeping the nominal power output of the light source at 300W, and using a high pass, cut-off filter at 305 nm; 2) as for 1, but with the high pass filter at 280 nm; 3) as for 1, but with a band pass filter centered at 280 nm (with a 10 nm half-width); and 4) variable nominal power output with the concentration of the substrate constant at 200 µM and with the cut-off filter at 305 nm (Table 5).

8.1 280 nm bandpass filter

Five concentrations (200, 150, 100, 75, and 50 µM) of the phenacylpiperidinium tosylate in acetonitrile were prepared, and 3-mL aliquots in quartz vial were exposed to Hg-Xe lamp at 300 W for 1 min interval for first 20 minutes. This was followed by 10 min interval till 60 minutes, and then 60 minute interval till 180 minutes (Figures 6 - 10). Each time the solution was removed from the light path, the spectrum of the reaction mixture was acquired on Agilent Cary 50 UV-vis spectrophotometer. This data formed the basis for quantitative assessment of reaction progress, and with the use of standard mixtures provided concentration of the starting material and tosylate-containing products in the mixture as a function of time.

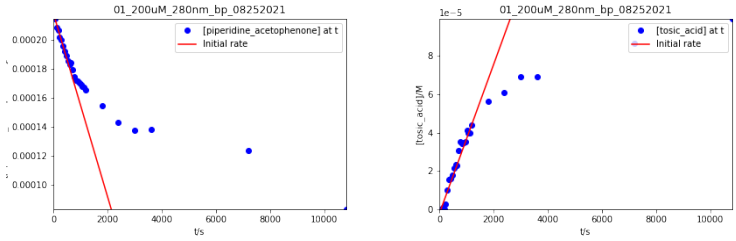


Figure S6: Rate of Aza-Yang reaction at 200 µM concentration with 280 nm bandpass filter.

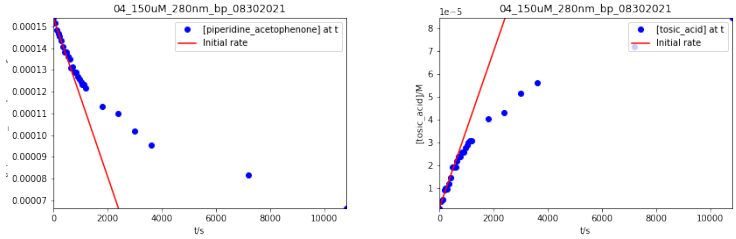


Figure S7: Rate of Aza-Yang reaction at 150 µM concentration with 280 nm bandpass filter

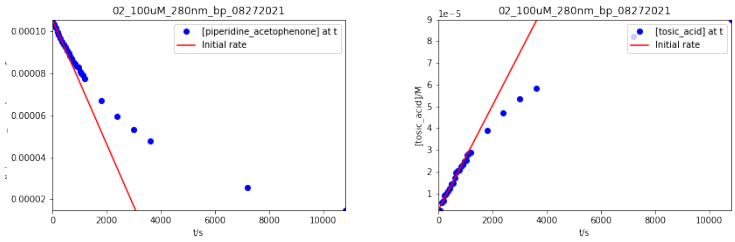


Figure S8: Rate of Aza-Yang reaction at 100 µM concentration with 280 nm bandpass filter

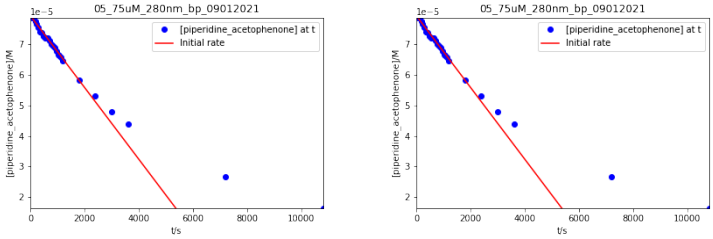


Figure S9: Rate of Aza-Yang reaction at 75 µM concentration with 280 nm bandpass filter

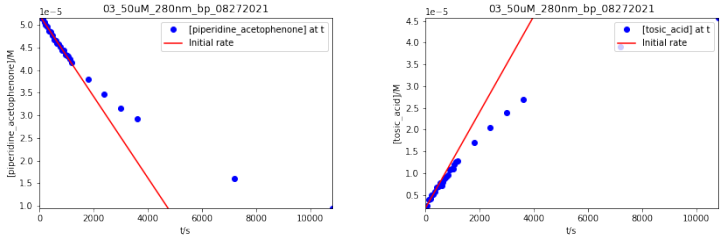


Figure S10: Rate of Aza-Yang reaction at 50 µM concentration with 280 nm bandpass filter

8.2 280 nm longpass filter

Five concentrations (200, 150, 100, 75, and 50 µM) of the phenacylpiperidinium tosylate in acetonitrile were prepared, and 3-mL aliquots in quartz vial were exposed to Hg-Xe lamp at 300 W for 1 min interval for first 20 minutes. This was followed by 10 min interval till 60 minutes, and then 60 minute interval till 180 minutes (Figures 11 - 15). Each time the solution was removed from the light path, the spectrum of the reaction mixture was acquired on Agilent Cary 50 UV-vis spectrophotometer. This data formed the basis for quantitative assessment of reaction progress, and with the use of standard mixtures provided concentration of the starting material and tosylate-containing products in the mixture as a function of time.

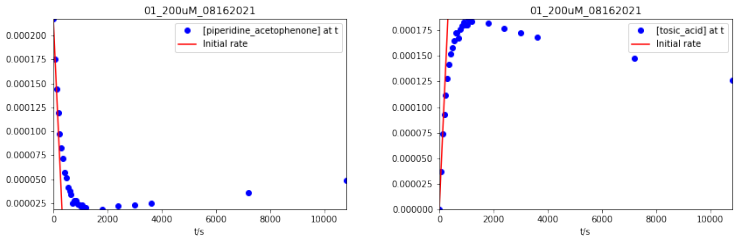


Figure S11: Rate of Aza-Yang reaction at 200 µM concentration with 280 nm longpass filter

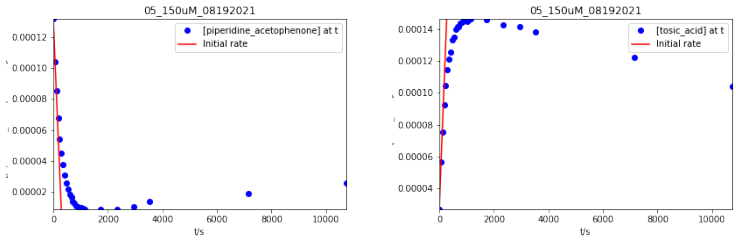


Figure S12: Rate of Aza-Yang reaction at 150 µM concentration with 280 nm longpass filter

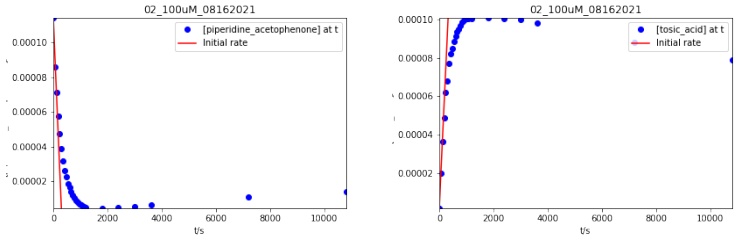


Figure S13: Rate of Aza-Yang reaction at 100 µM concentration with 280 nm longpass filter

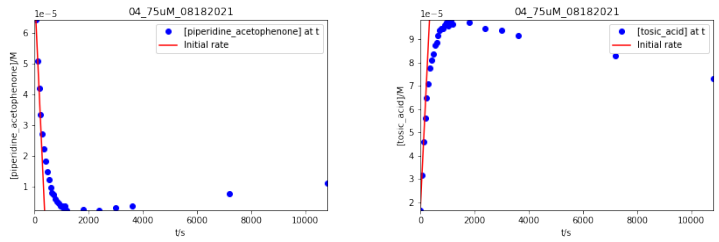


Figure S14: Rate of Aza-Yang reaction at 75 µM concentration with 280 nm longpass filter

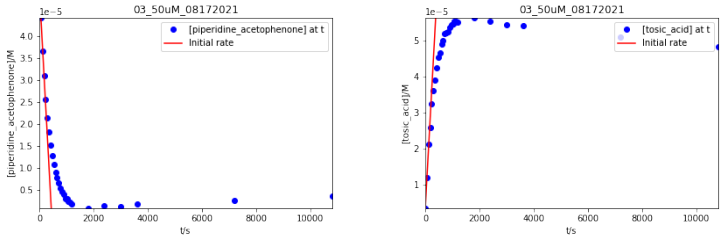


Figure S15: Rate of Aza-Yang reaction at 50 µM concentration with 280 nm longpass filter

8.3 305 nm longpass filter

Five concentrations (200, 150, 100, 75, and 50 µM) of the phenacylpiperidinium tosylate in acetonitrile were prepared, and 3-mL aliquots in quartz vial were exposed to Hg-Xe lamp at 300 W for 1 min interval for first 20 minutes. This was followed by 10 min interval till 60 minutes, and then 60 minute interval till 180 minutes (Figures 16 - 20). Each time the solution was removed from the light path, the spectrum of the reaction mixture was acquired on Agilent Cary 50 UV-vis spectrophotometer. This data formed the basis for quantitative assessment of reaction progress, and with the use of standard mixtures provided concentration of the starting material and tosylate-containing products in the mixture as a function of time.

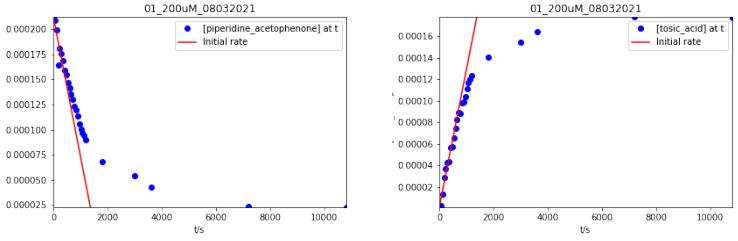


Figure S16: Rate of Aza-Yang reaction at 200 µM concentration with 305 nm longpass filter

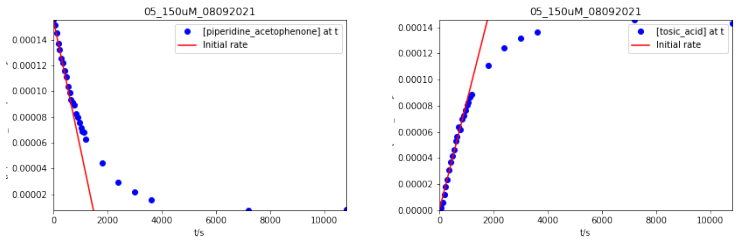


Figure S17: Rate of Aza-Yang reaction at 150 µM concentration with 305 nm longpass filter

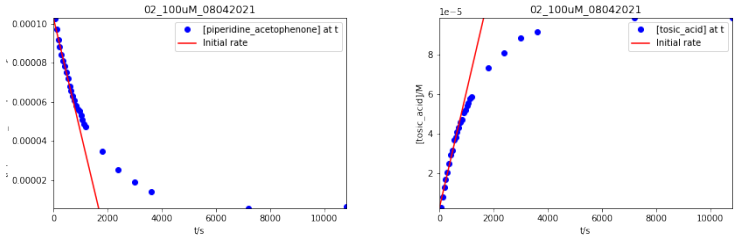


Figure S18: Rate of Aza-Yang reaction at 100 µM concentration with 305 nm longpass filter

rate [M/s]			
concentration [µM]	280nm-bandpass	280-nm longpass	305-nm longpass
200	6.37 x 10^{-8}	6.19 x 10^{-7}	1.39 x 10^{-7}
150	3.65 x 10^{-8}	4.19 x 10^{-7}	10.0 x 10^{-8}
100	2.96 x 10^{-8}	3.69 x 10^{-7}	5.84 x 10^{-8}
75	1.17 x 10^{-8}	1.94 x 10^{-7}	3.70 x 10^{-8}
50	9.00 x 10^{-9}	1.13 x 10^{-7}	2.48 x 10^{-8}

Table S5: Effect of filter on the initial rate of disappearance of starting material.

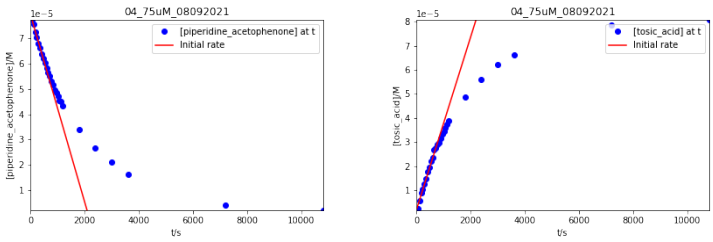


Figure S19: Rate of Aza-Yang reaction at 75 µM concentration with 305 nm longpass filter

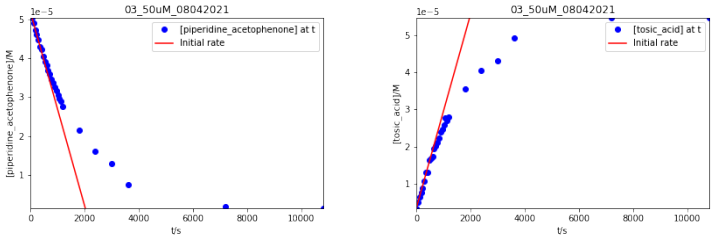


Figure S20: Rate of Aza-Yang reaction at 50 µM concentration with 305 nm longpass filter

8.4 Power variation

A solution of phenacylpiperidinium tosylate (200 µM) in acetonitrile was irradiated with Hg-Xe lamp (305 nm longpass filter), at variable powers from 450, 375, 300, 225, to 150 Watt. Absorbance of the reaction mixture was taken at time points 1-20 min each minute, then at 30, 40, 50, 60, 120, and 180 min. Table 6 summarizes the initial rates obtained in this experiment.

rate [M/s]		
Power (W)	disappearance of starting material	appearance of tosic acid
450	2.89×10^{-7}	2.83×10^{-7}
375	1.91×10^{-7}	2.10×10^{-7}
300	1.39×10^{-7}	1.28×10^{-7}
225	1.07×10^{-7}	9.04×10^{-8}
150	4.84×10^{-8}	4.06×10^{-8}

Table S6: Effect of variation of power on the initial rate of aza-Yang reaction

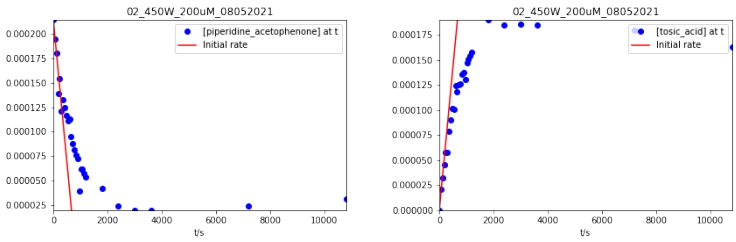


Figure S21: Rate of Aza-Yang reaction at 200 µM concentration with 305 nm longpass filter at 450 W

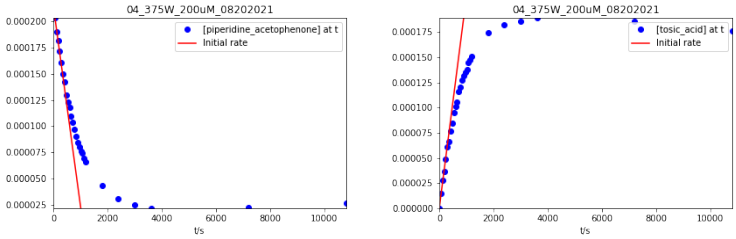


Figure S22: Rate of Aza-Yang reaction at 200 µM concentration with 305 nm longpass filter at 375 W

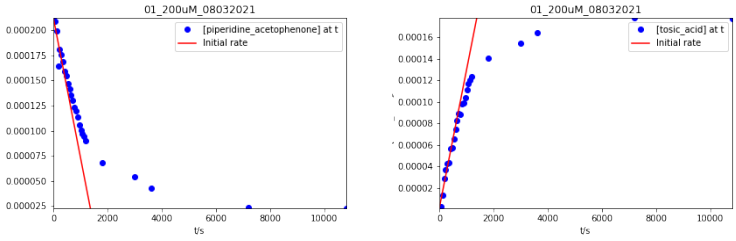


Figure S23: Rate of Aza-Yang reaction at 200 µM concentration with 305 nm longpass filter at 300 W

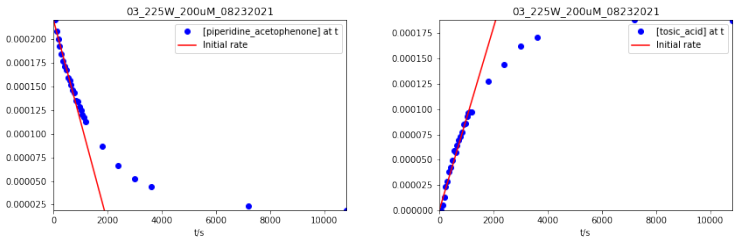


Figure S24: Rate of Aza-Yang reaction at 200 µM concentration with 305 nm longpass filter at 225 W

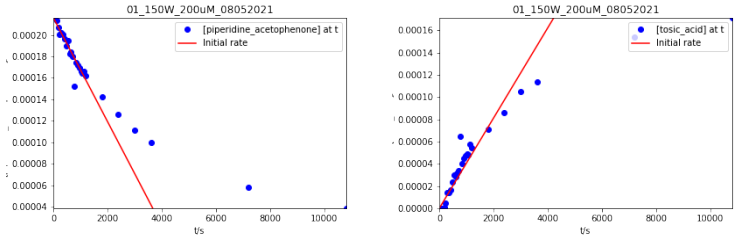


Figure S25: Rate of Aza-Yang reaction at 200 µM concentration with 305 nm longpass filter at 150 W

9 Ultrafast spectroscopy

Transient absorption spectra were measured with an amplified Ti:Sapphire laser at 1 kHz repetition rate for a 4 mM solution of the substrate in acetonitrile. The pump beam at 280 nm was generated via nonlinear frequency conversion and had 1 µJ pulse energy and < 100 fs pulse duration at the sample. The white-light probe beam was generated by focusing 800 nm fundamental laser light into a circularly translating CaF_2 substrate. The pump and probe beams were focused and overlapped in the sample and the probe beam was dispersed with spectrograph onto a 256-pixel photodiode array. The relative pump-probe delay was set by adjusting the probe path length with a delay stage and a synchronized chopper blocked the pump beam at 500 Hz for active background subtraction.[10]

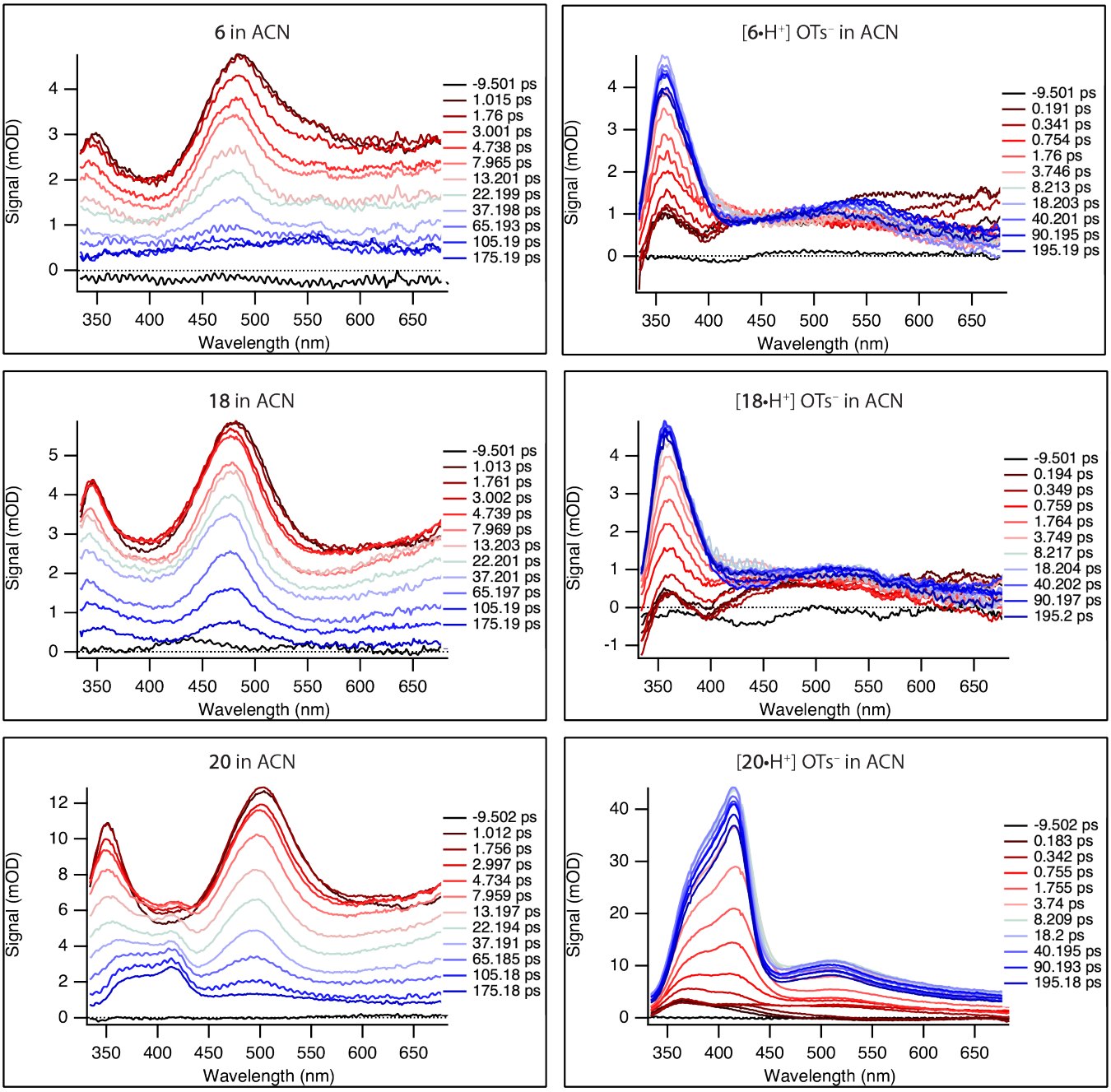


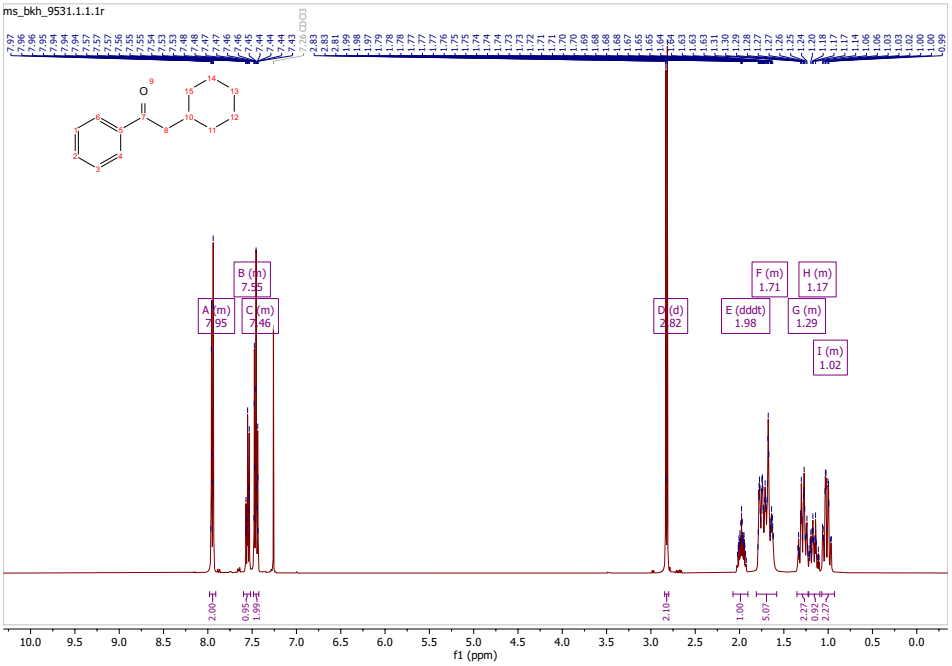
Figure S26: Time evolution of absorption spectra of the excited states of **6**, **18**, and **20**, and the corresponding tosylate salts.

10 Compound characterization

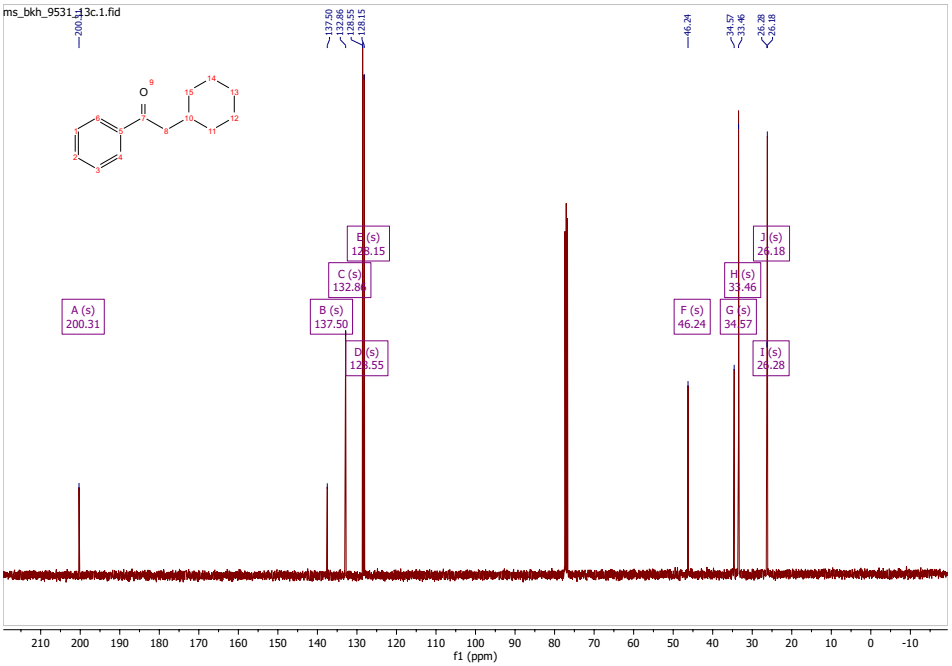
10.1 Starting materials: phenacyl bromide

10.1.1 Compound 1

^{1}H NMR spectrum (400 MHz, Chloroform-d) of cyclohexyl acetophenone, Compound 1

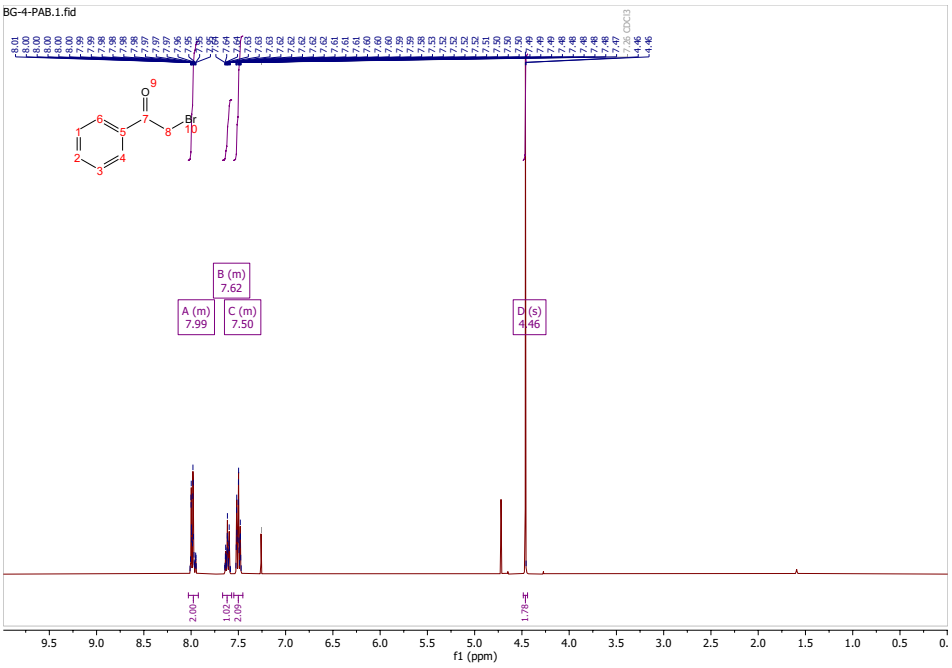


^{13}C {^{1}H } NMR spectrum (100 MHz, Chloroform-d) of cyclohexyl acetophenone, Compound 1

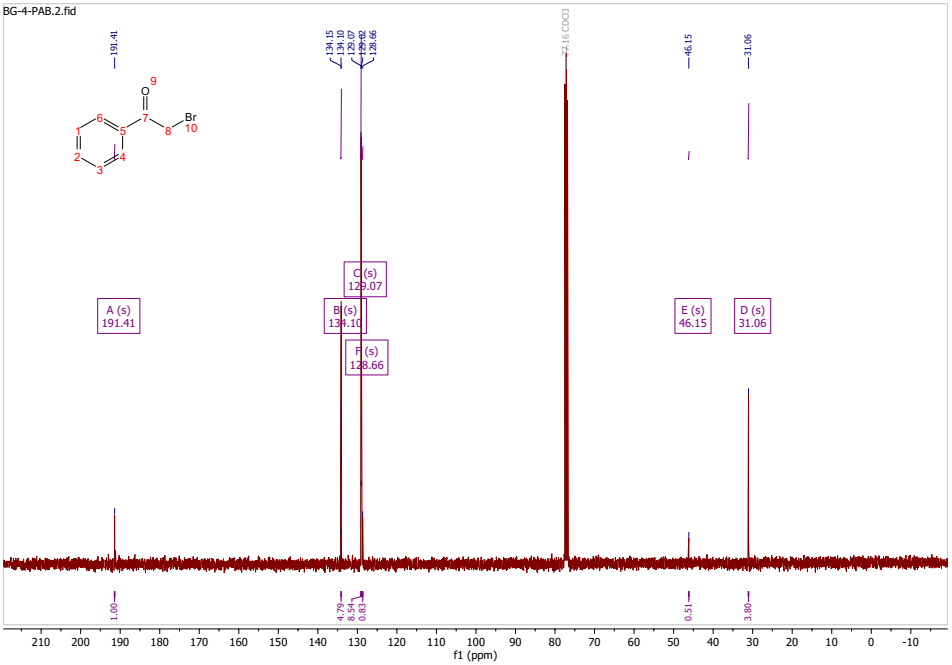


10.1.2 2-bromo-1-phenylethan-1-one

^{1}H NMR spectrum (400 MHz, Chloroform-d) of 2-bromo-1-phenylethan-1-one

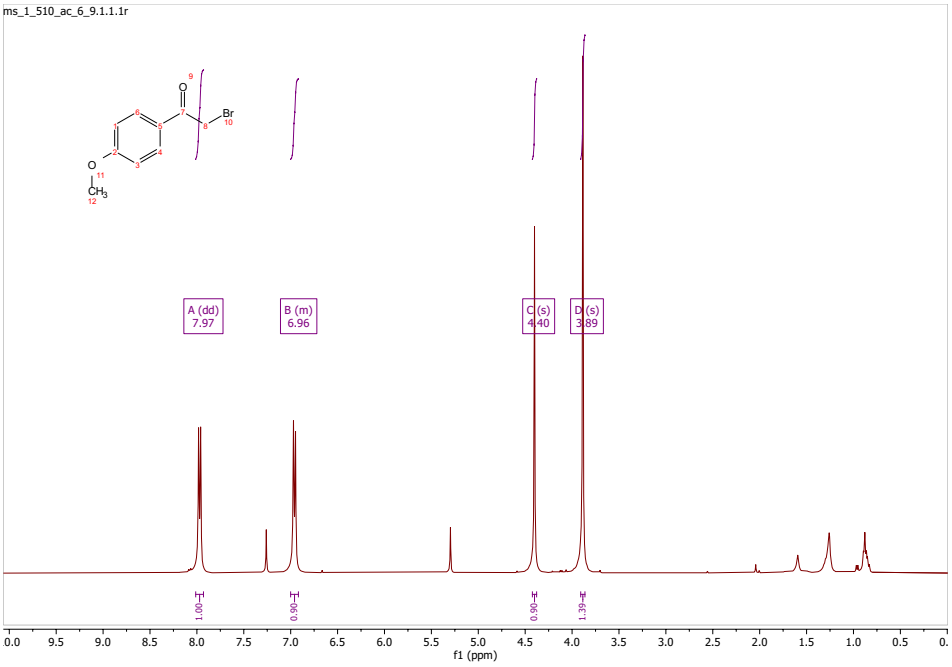


^{13}C {^{1}H } NMR spectrum (100 MHz, Chloroform-d) of 2-bromo-1-phenylethan-1-one



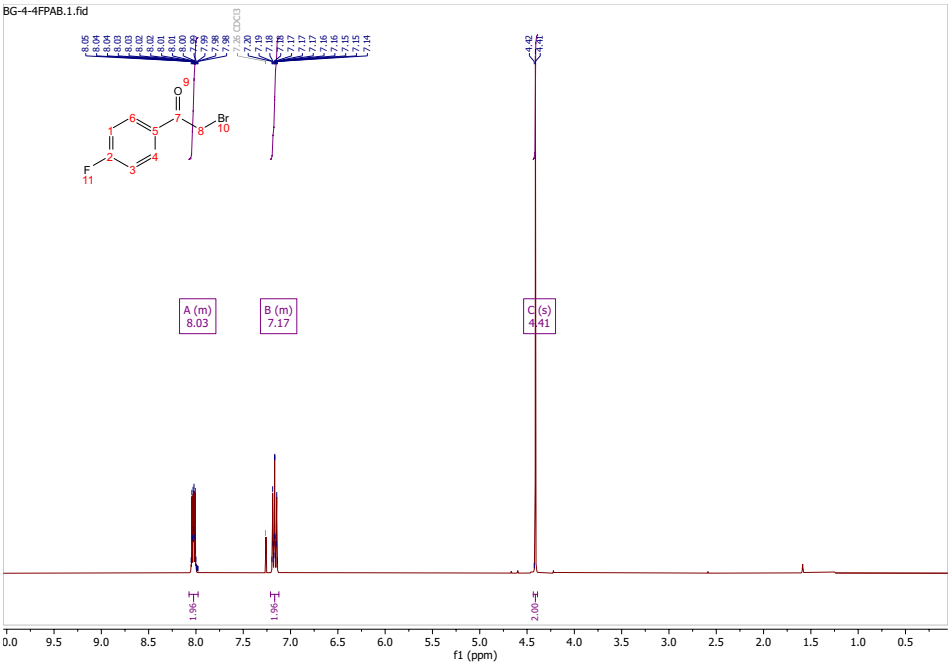
10.1.3 2-bromo-1-(4-methoxyphenyl)ethan-1-one

^{1}H NMR spectrum (400 MHz, Chloroform-d) 2-bromo-1-(4-methoxyphenyl)ethan-1-one

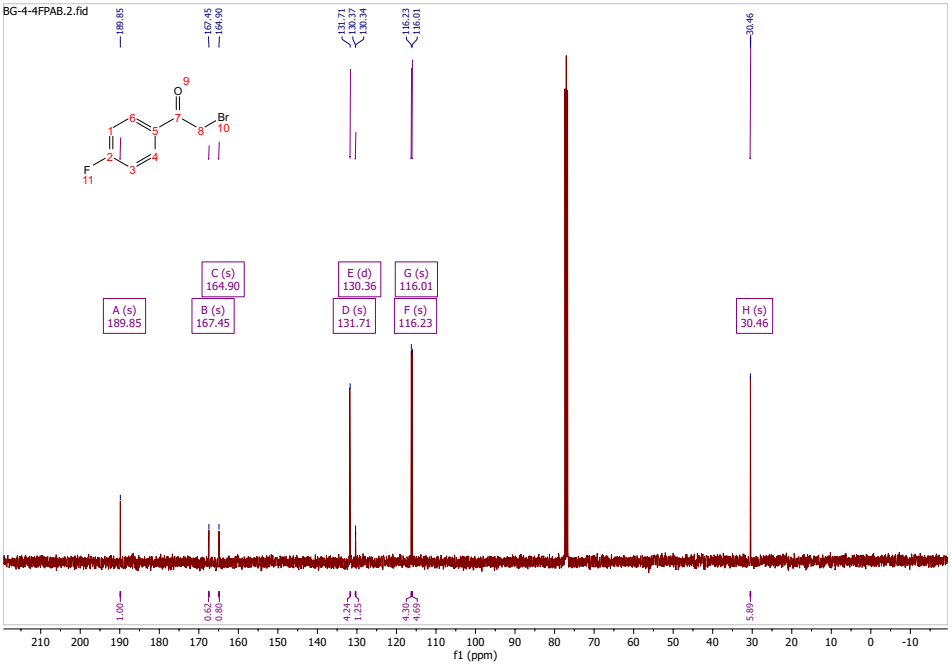


10.1.4 2-bromo-1-(4-fluorophenyl)ethan-1-one

^{1}H NMR spectrum (400 MHz, Chloroform-d) 2-bromo-1-(4-fluorophenyl)ethan-1-one

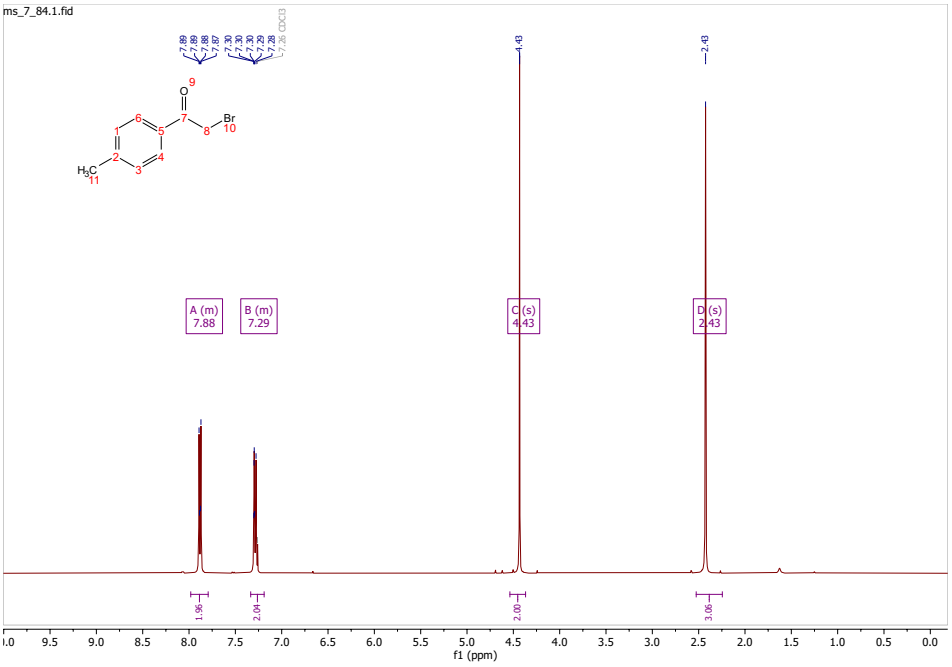


^{13}C {^{1}H } NMR spectrum (100 MHz, Chloroform-d) 2-bromo-1-(4-fluorophenyl)ethan-1-one

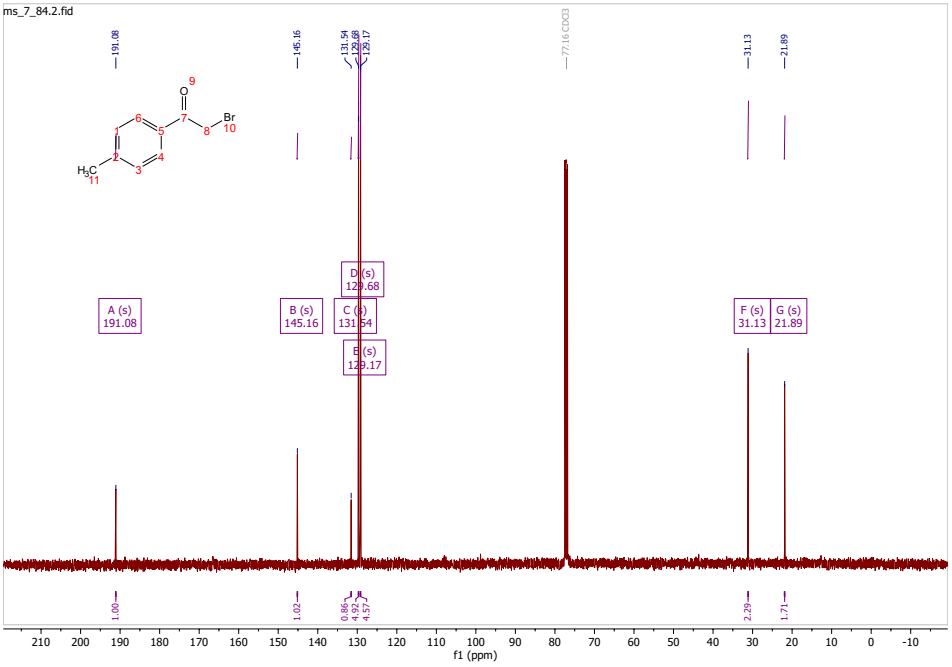


10.1.5 2-bromo-1-(p-tolyl)ethan-1-one

^{1}H NMR spectrum (400 MHz, Chloroform-d) 2-bromo-1-(p-tolyl)ethan-1-one



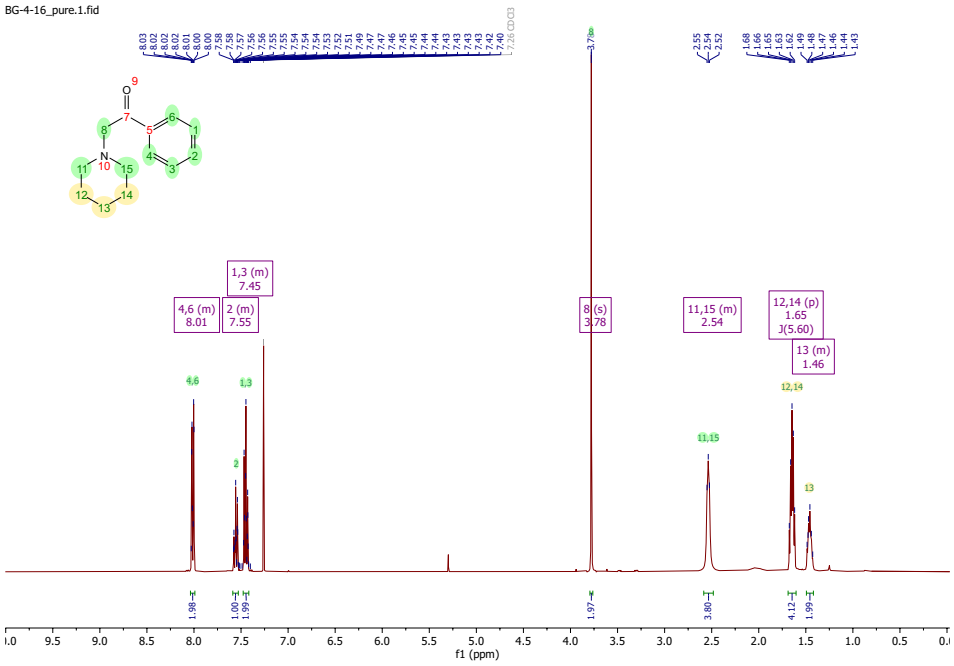
^{13}C {^{1}H } NMR spectrum (100 MHz, Chloroform-d) 2-bromo-1-(p-tolyl)ethan-1-one



10.2 Starting materials: phenacyl piperidines

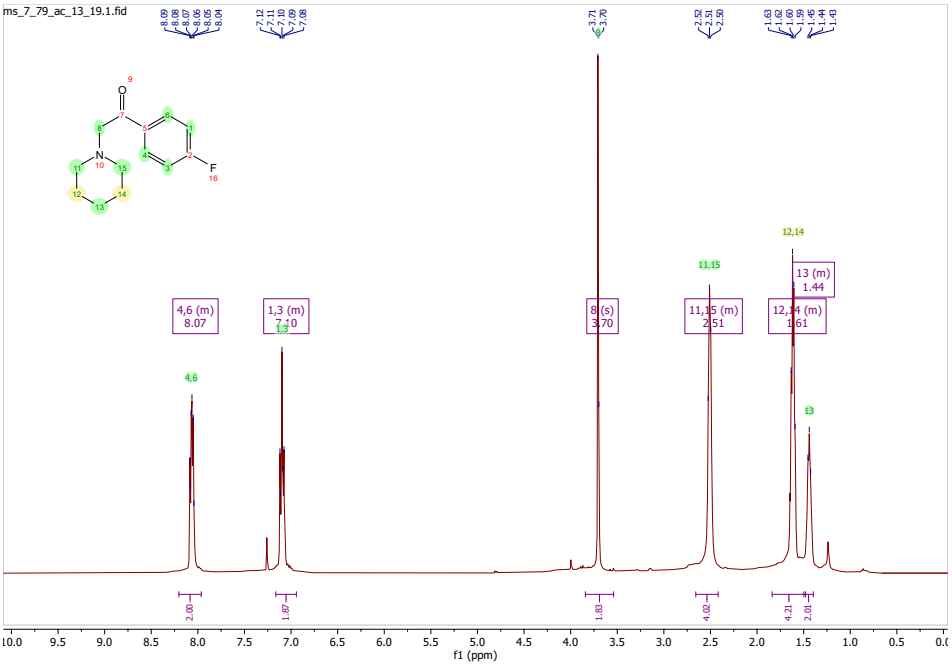
10.2.1 1-phenyl-2-(piperidin-1-yl)ethan-1-one(6)

^{1}H NMR spectrum (400 MHz, Chloroform-d) 1-phenyl-2-(piperidin-1-yl)ethan-1-one (6)

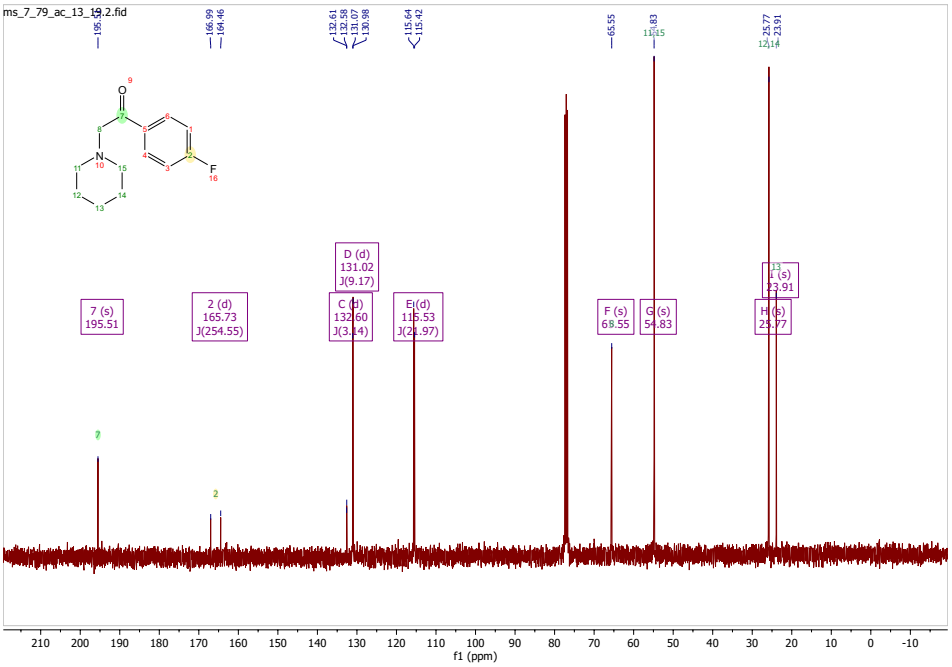


10.2.2 1-(4-fluorophenyl)-2-(piperidin-1-yl)ethan-1-one

^{1}H NMR spectrum (400 MHz, Chloroform-d) 1-(4-fluorophenyl)-2-(piperidin-1-yl)ethan-1-one

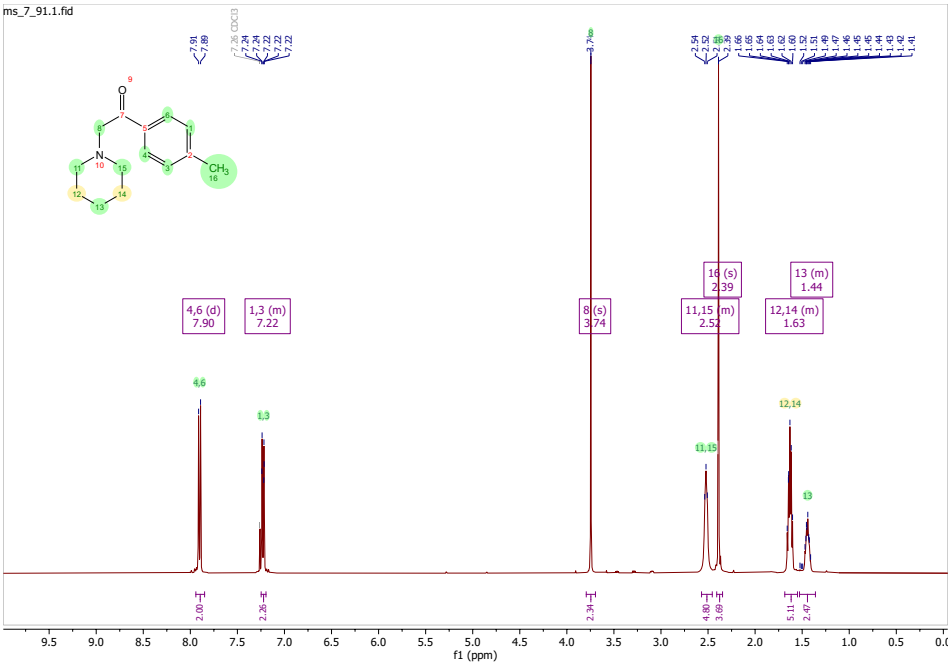


^{13}C {^{1}H } NMR spectrum (100 MHz, Chloroform-d) 1-(4-fluorophenyl)-2-(piperidin-1-yl)ethan-1-one

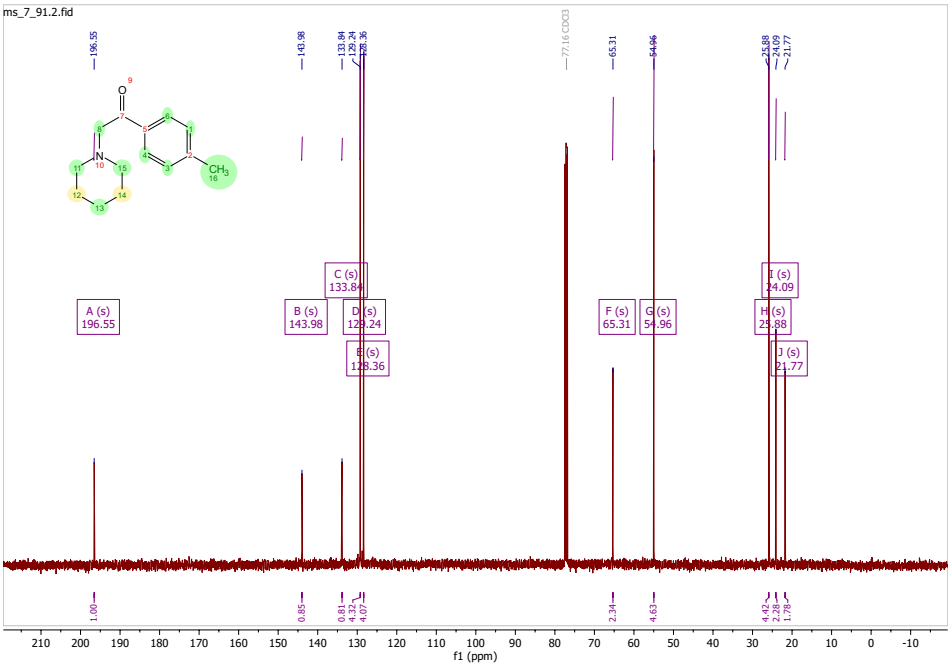


10.2.3 2-(piperidin-1-yl)-1-(p-tolyl)ethan-1-one

^{1}H NMR spectrum (400 MHz, Chloroform-d)

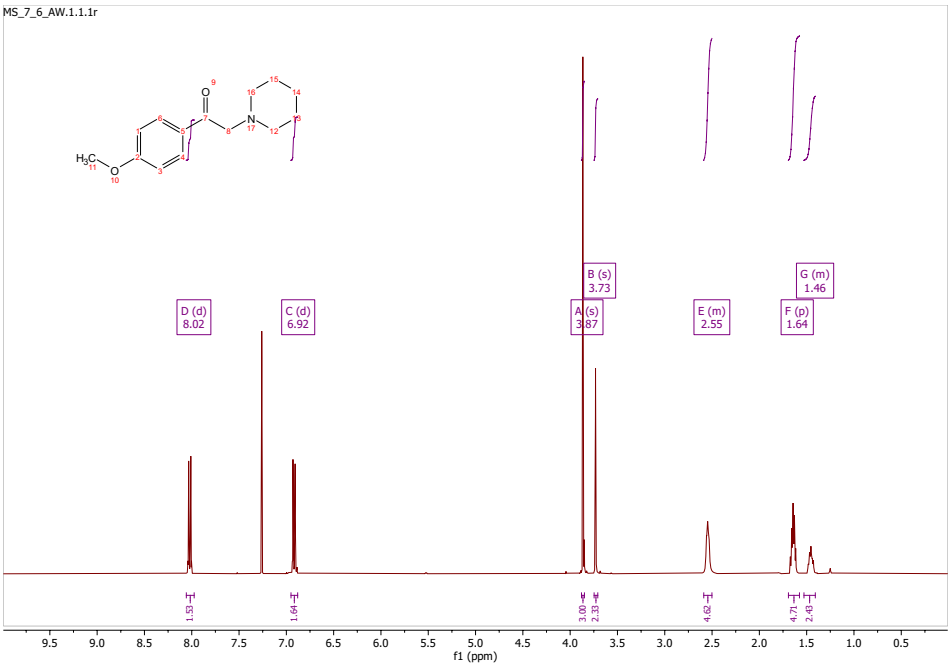


^{13}C {^{1}H } NMR spectrum (100 MHz, Chloroform-d 2-(piperidin-1-yl)-1-(p-tolyl)ethan-1-one



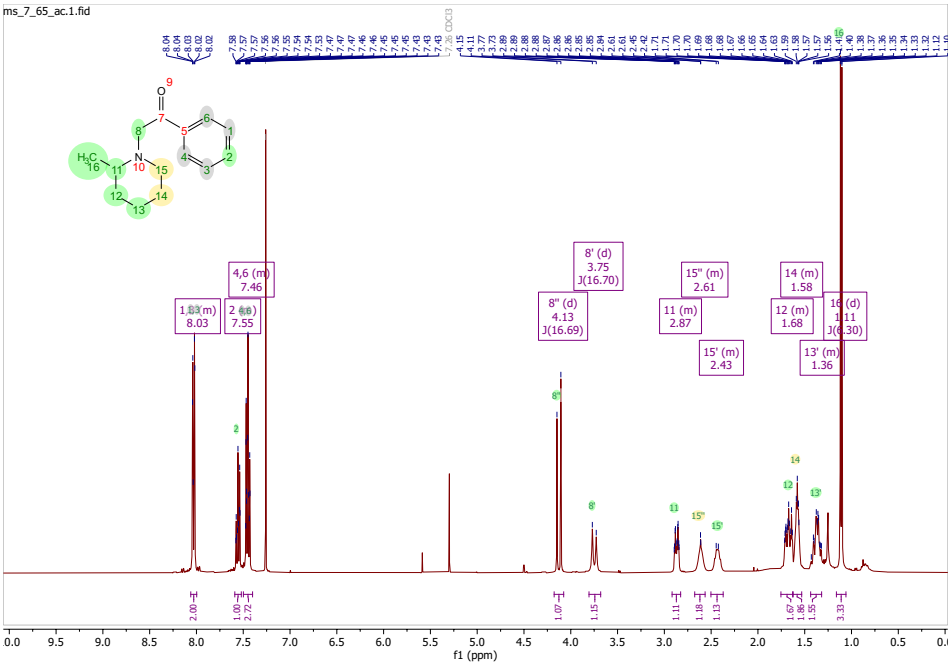
10.2.4 1-(4-methoxyphenyl)-2-(piperidin-1-yl)ethan-1-one (20)

^{1}H NMR spectrum (400 MHz, Chloroform-d) 1-(4-methoxyphenyl)-2-(piperidin-1-yl)ethan-1-one (20)



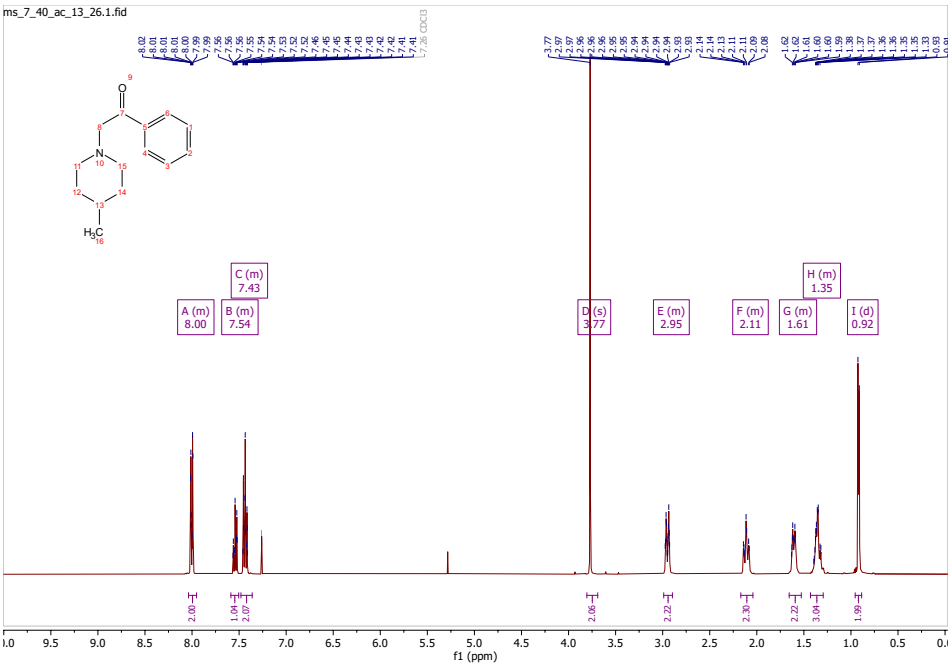
10.2.5 2-(2-methylpiperidin-1-yl)-1-phenylethan-1-one

^{1}H NMR spectrum (400 MHz, Chloroform-d) 2-(2-methylpiperidin-1-yl)-1-phenylethan-1-one

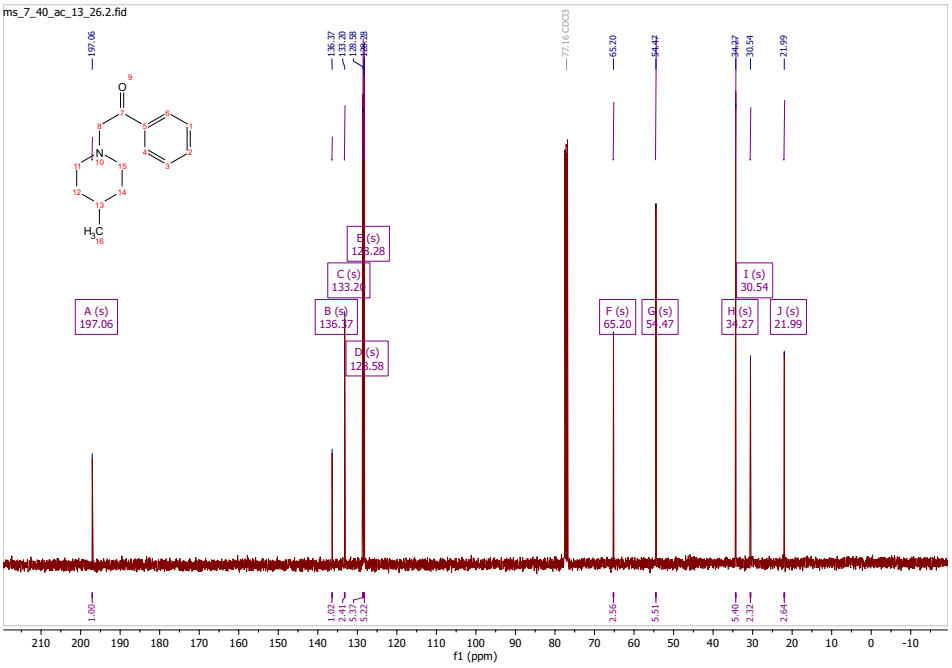


10.2.6 2-(4-methylpiperidin-1-yl)-1-phenylethan-1-one

^{1}H NMR spectrum (400 MHz, Chloroform-d) 2-(4-methylpiperidin-1-yl)-1-phenylethan-1-one



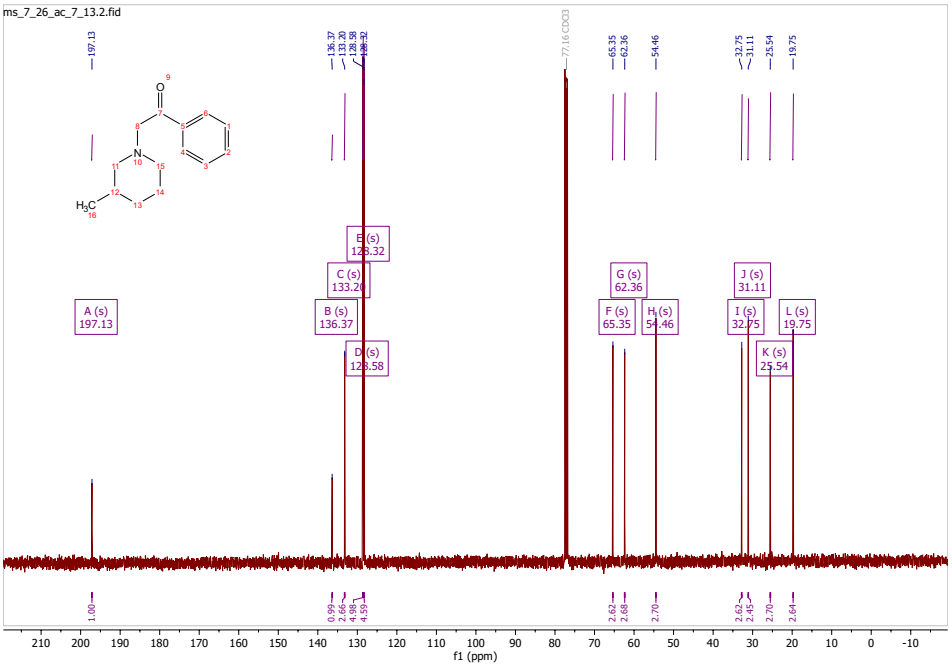
^{13}C {^{1}H } NMR spectrum (100 MHz, Chloroform-d) 2-(4-methylpiperidin-1-yl)-1-phenylethan-1-one



10.2.7 2-(3-methylpiperidin-1-yl)-1-phenylethan-1-one

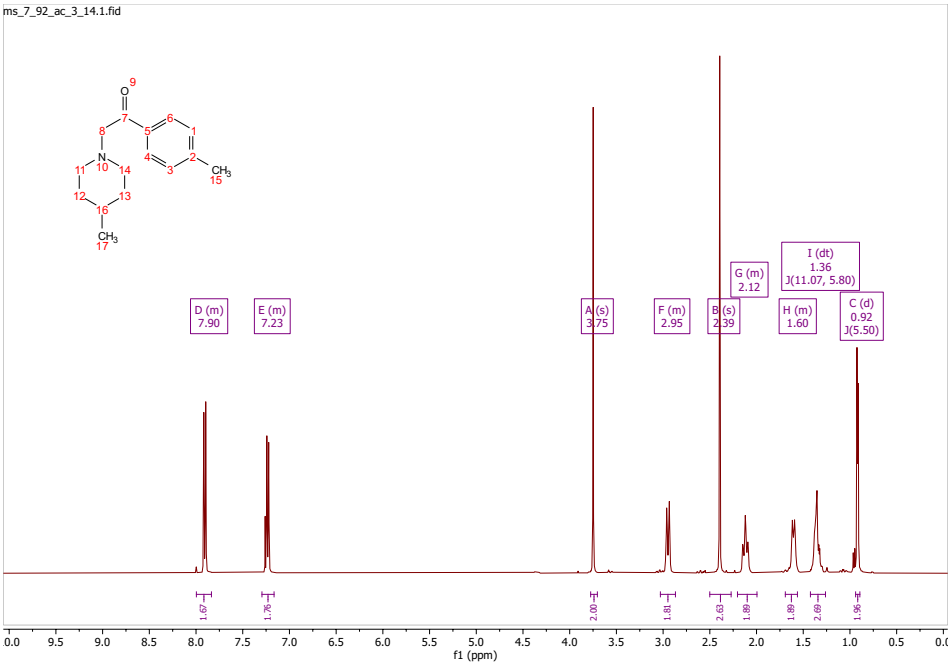
^{1}H NMR spectrum (400 MHz, Chloroform-d) 2-(3-methylpiperidin-1-yl)-1-phenylethan-1-one

^{13}C {^{1}H } NMR spectrum (100 MHz, Chloroform-d) 2-(3-methylpiperidin-1-yl)-1-phenylethan-1-one

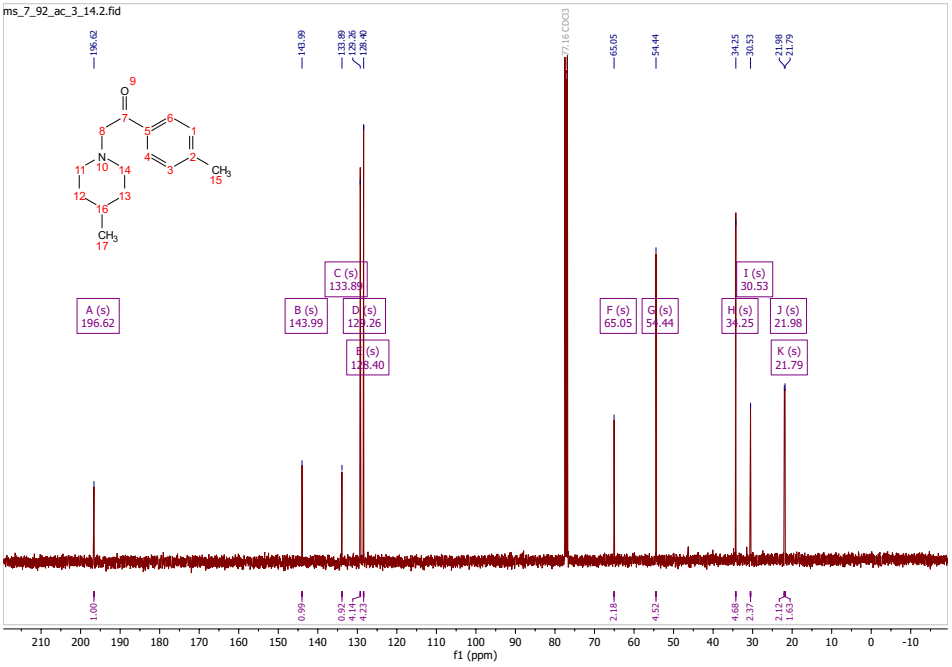


10.2.8 2-(4-methylpiperidin-1-yl)-1-(p-tolyl)ethan-1-one

^{1}H NMR spectrum (400 MHz, Chloroform-d) 2-(4-methylpiperidin-1-yl)-1-(p-tolyl)ethan-1-one

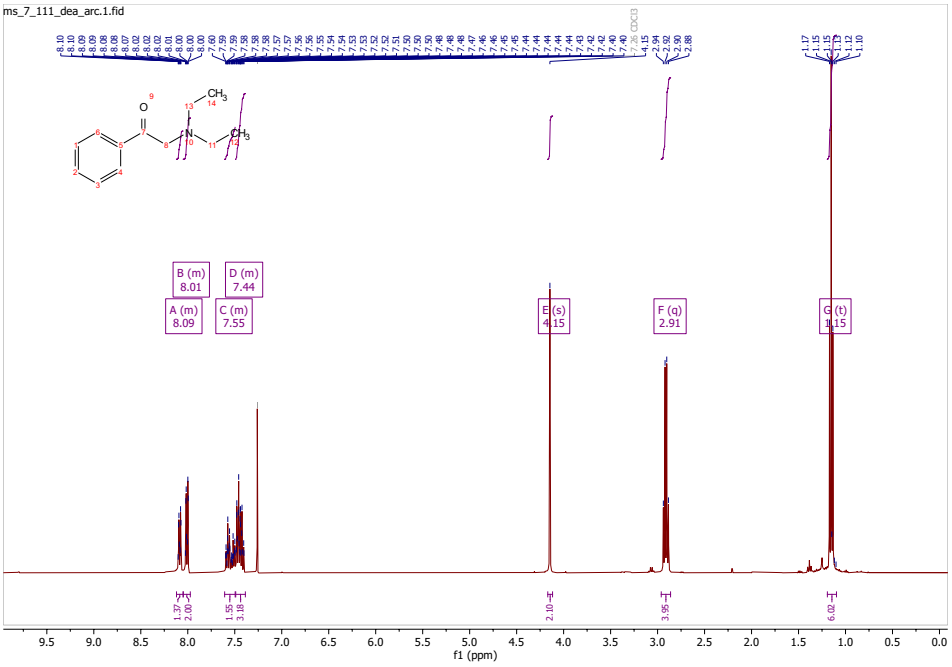


^{13}C {^{1}H } NMR spectrum (100 MHz, Chloroform-d) 2-(4-methylpiperidin-1-yl)-1-(p-tolyl)ethan-1-one



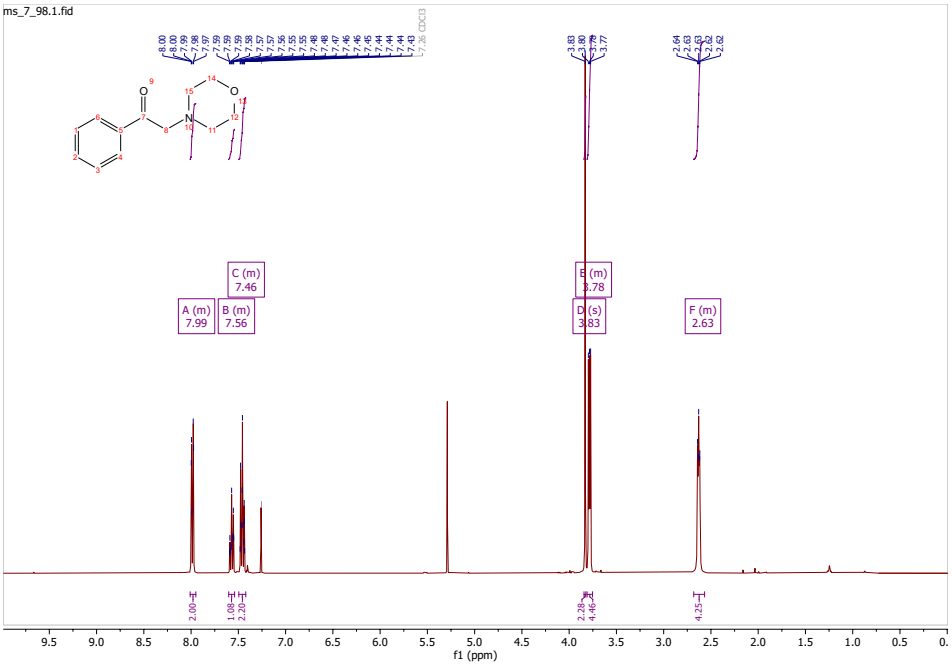
10.2.9 2-(diethylamino)-1-phenylethan-1-one

^{1}H NMR spectrum (400 MHz, Chloroform-d) 2-(diethylamino)-1-phenylethan-1-one

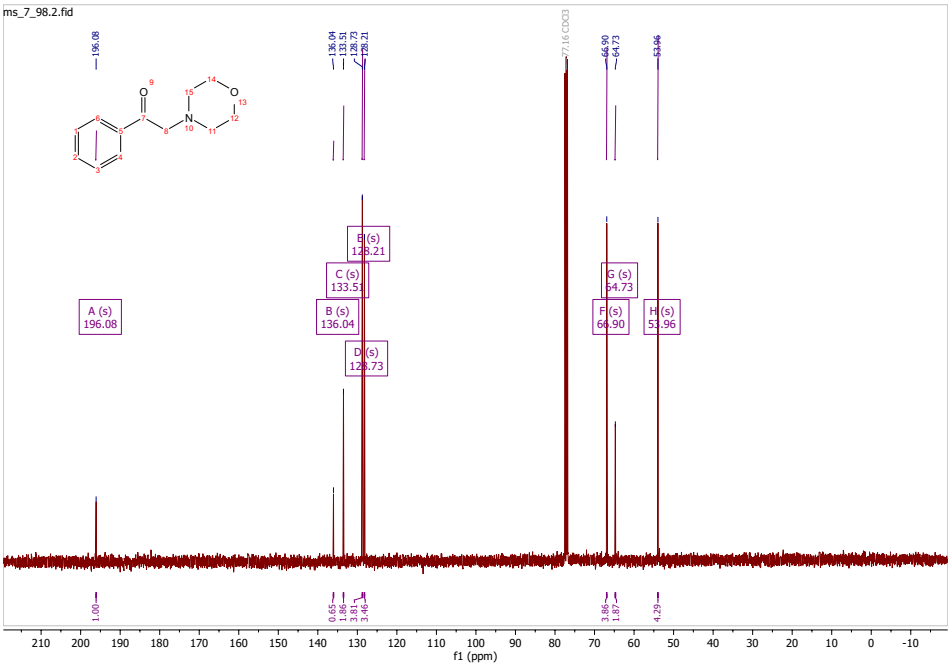


10.2.10 2-morpholino-1-phenylethan-1-one (18)

^{1}H NMR spectrum (400 MHz, Chloroform-d) 2-morpholino-1-phenylethan-1-one (18)

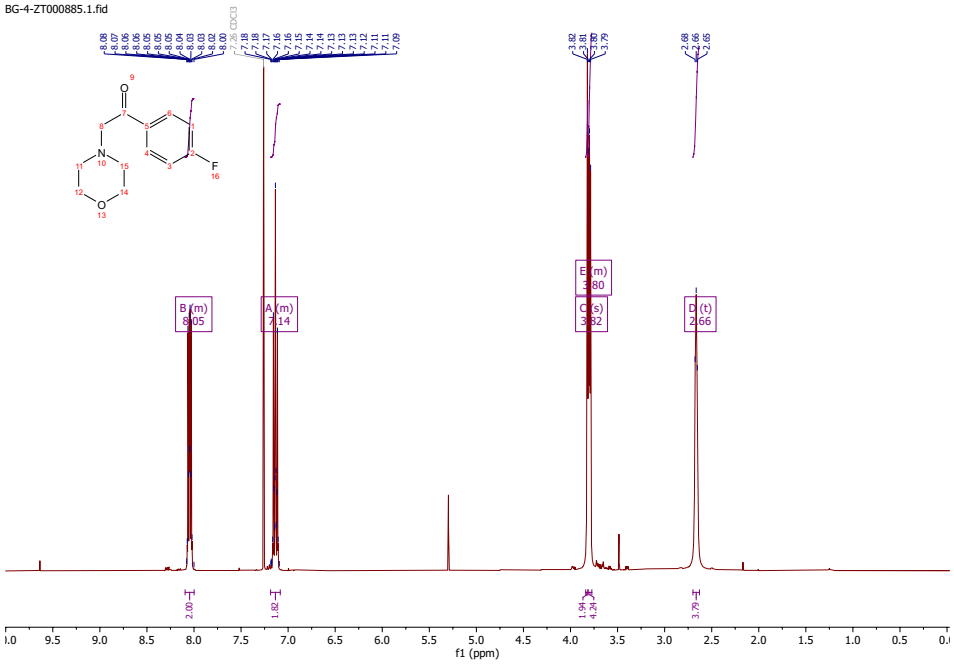


^{13}C {^{1}H } NMR spectrum (100 MHz, Chloroform-d) 2-morpholino-1-phenylethan-1-one (18)

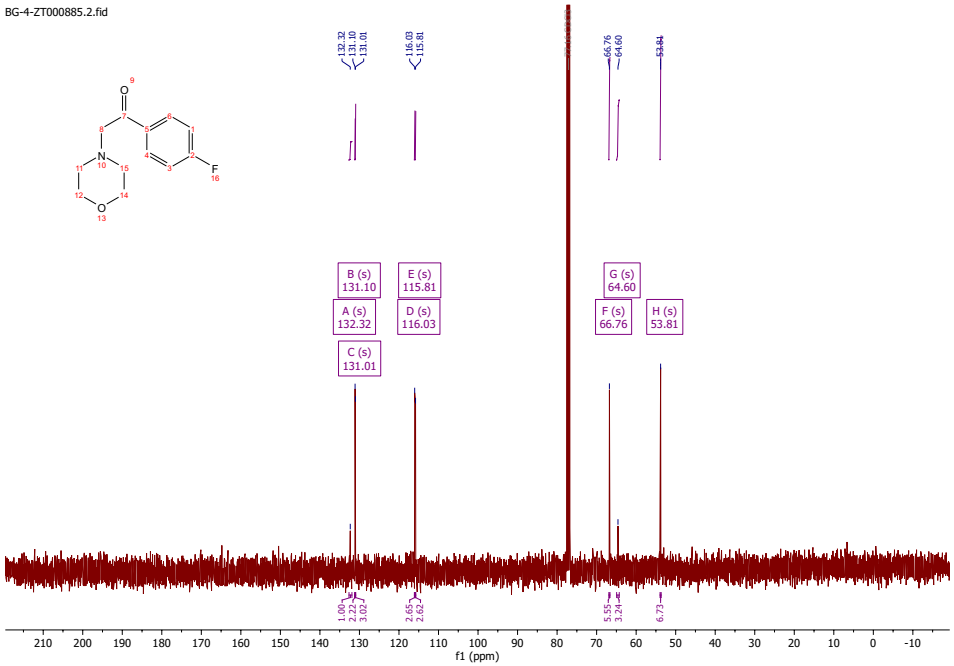


10.2.11 1-(4-fluorophenyl)-2-morpholinoethan-1-one

^{1}H NMR spectrum (400 MHz, Chloroform-d) 1-(4-fluorophenyl)-2-morpholinoethan-1-one



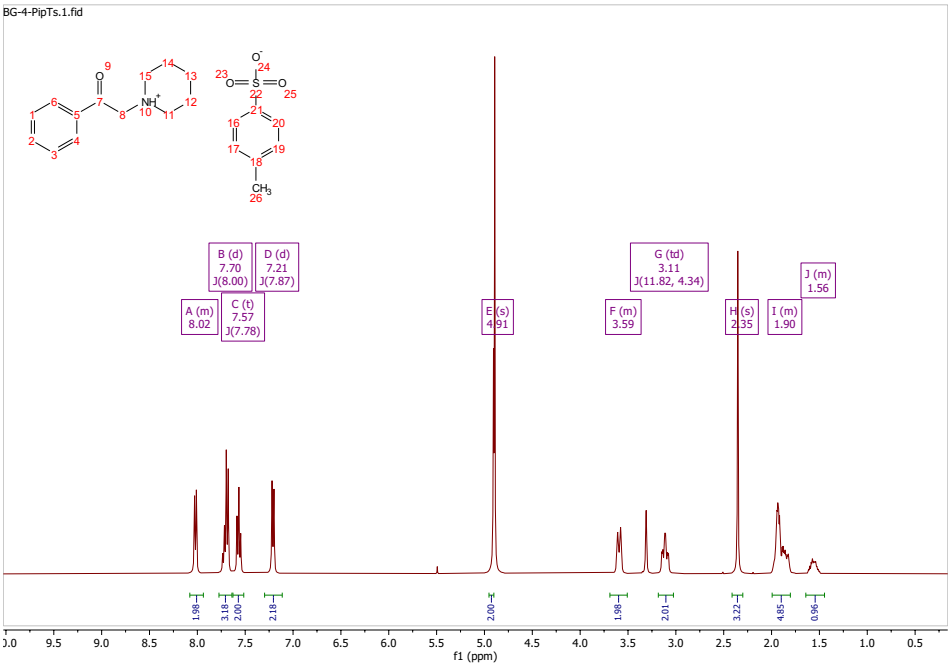
^{13}C {^{1}H } NMR spectrum (100 MHz, Chloroform-d) 1-(4-fluorophenyl)-2-morpholinoethan-1-one



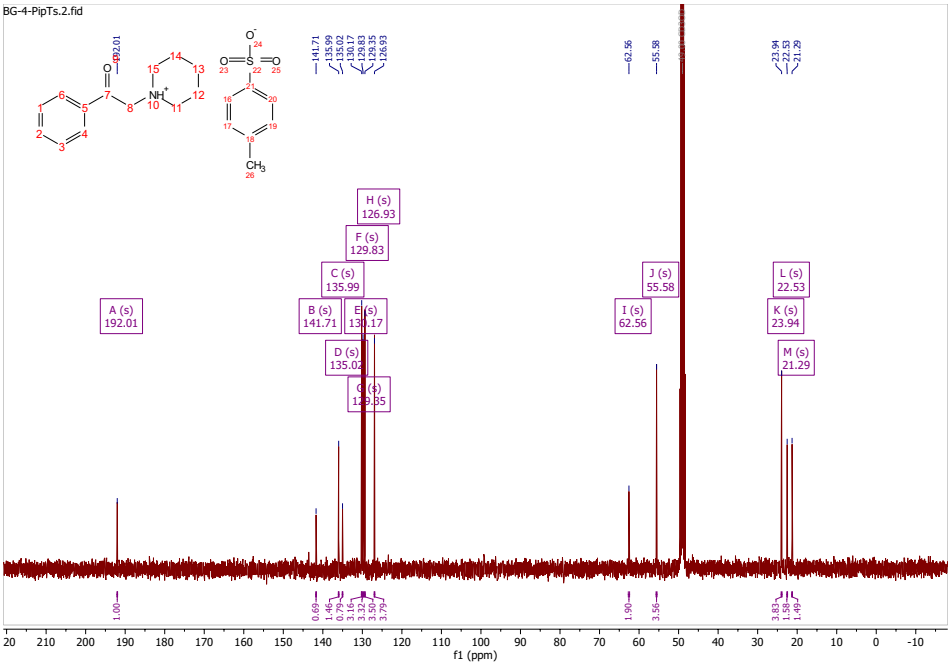
10.3 Starting materials: phenacyl piperidinium salts

10.3.1 1-(2-oxo-2-phenylethyl)piperidin-1-ium 4-methylbenzenesulfonate (6H+OTs-)

^{1}H NMR spectrum (500 MHz, MeOD) 1-(2-oxo-2-phenylethyl)piperidin-1-ium 4-methylbenzenesulfonate

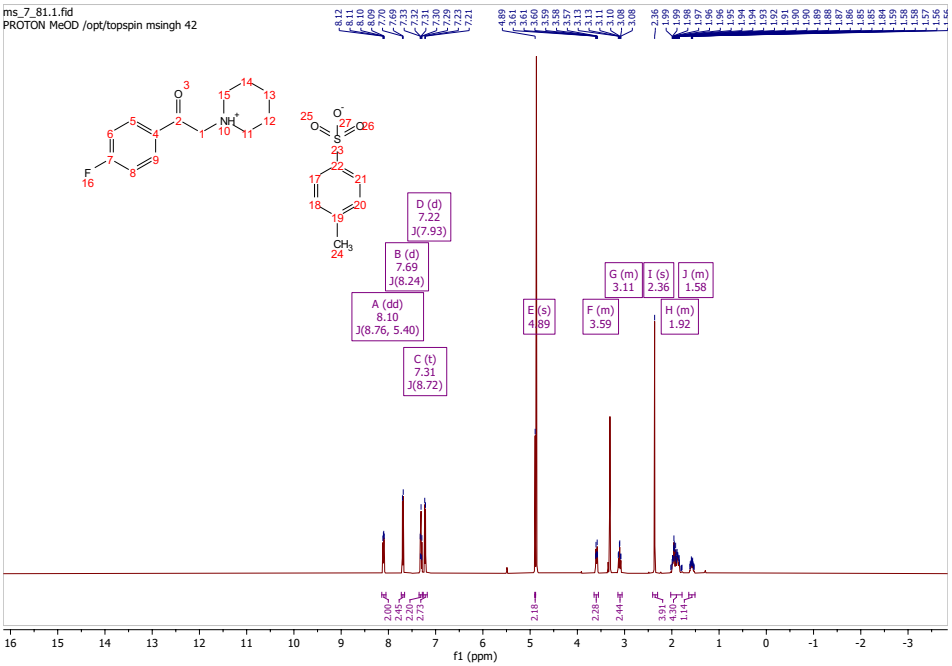


^{13}C {^{1}H } NMR spectrum (126 MHz, MeOD) 1-(2-oxo-2-phenylethyl)piperidin-1-ium 4-methylbenzenesulfonate (6H+OTs-)

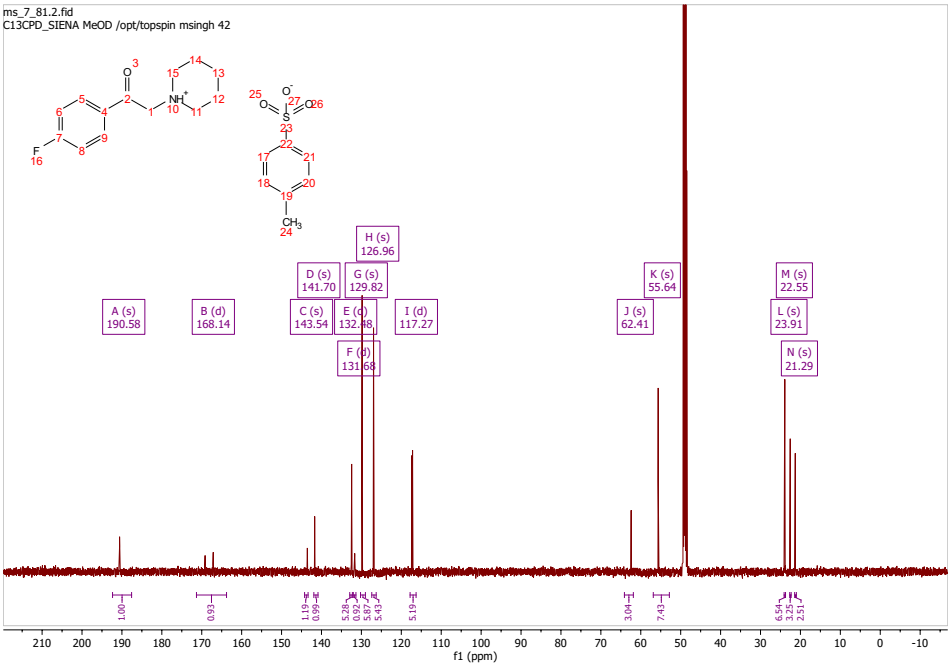


10.3.2 1-(2-(4-fluorophenyl)2-oxoethyl)piperidin-1-ium 4-methylbenzenesulfonate

^{1}H NMR spectrum (500 MHz, MeOD) 1-(2-(4-fluorophenyl)2-oxoethyl)piperidin-1-ium 4-methylbenzenesulfonate

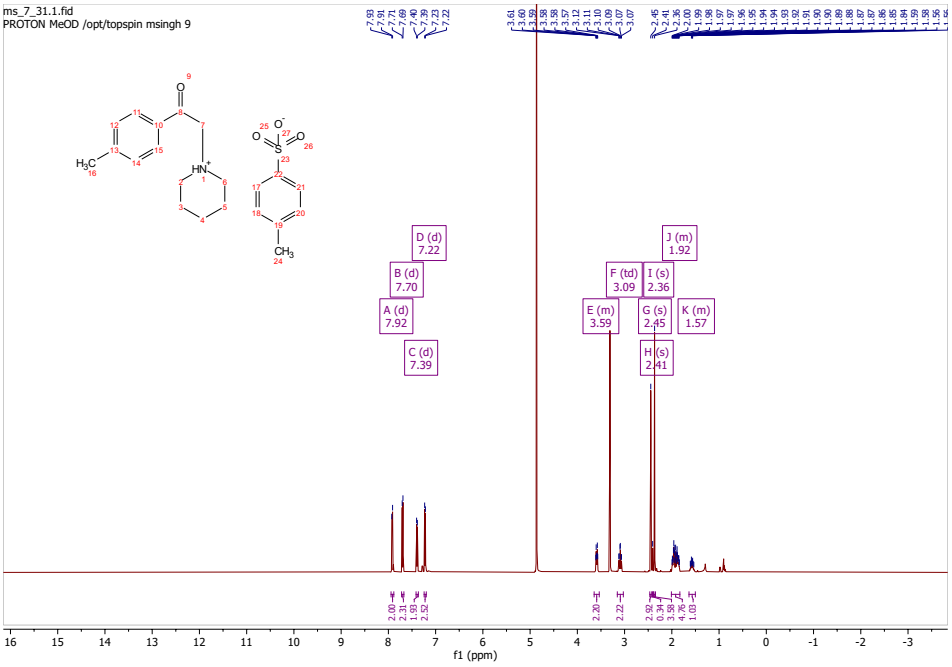


^{13}C {^{1}H } NMR spectrum (126 MHz, MeOD) 1-(2-(4-fluorophenyl)2-oxoethyl)piperidin-1-ium 4-methylbenzenesulfonate

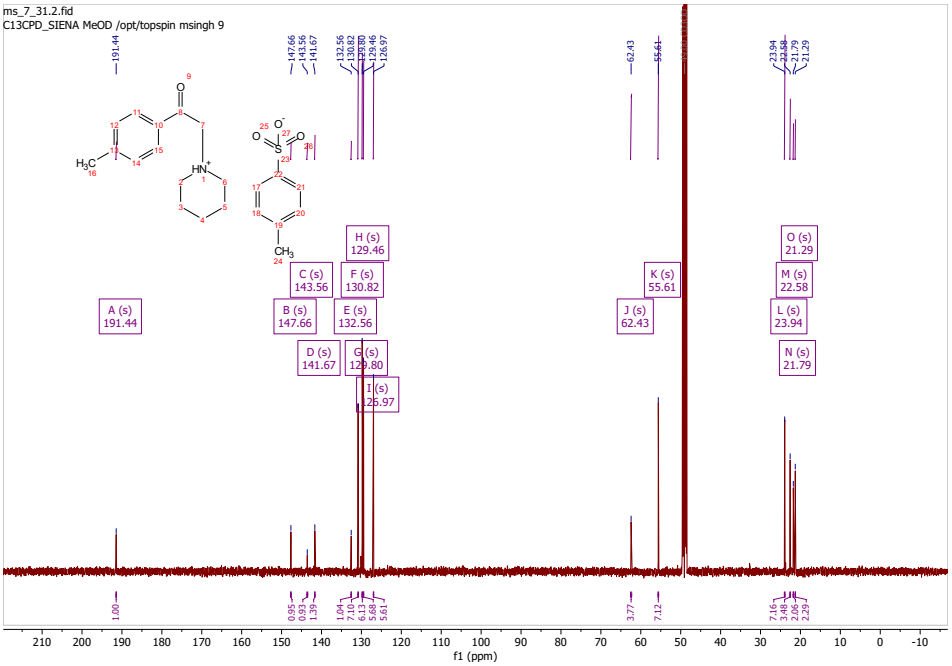


10.3.3 1-(2-oxo-2-(p-tolyl)ethyl)piperidin-1-ium 4-methylbenzenesulfonate

^{1}H NMR spectrum (500 MHz, MeOD) 1-(2-oxo-2-(p-tolyl)ethyl)piperidin-1-ium 4-methylbenzenesulfonate

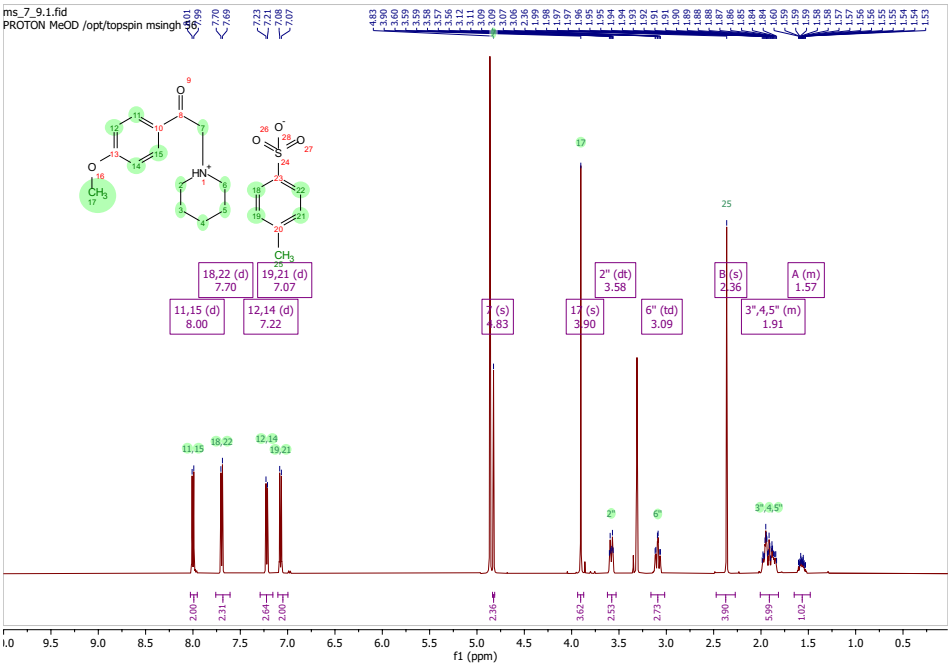


^{13}C {^{1}H } NMR spectrum (126 MHz, MeOD) 1-(2-oxo-2-(p-tolyl)ethyl)piperidin-1-ium 4-methylbenzenesulfonate

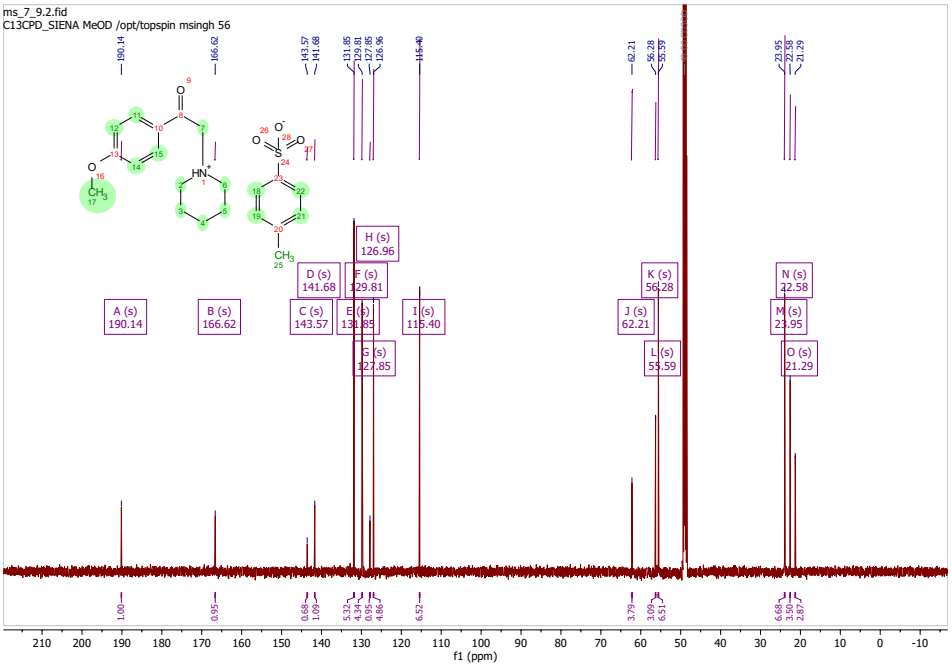


10.3.4 1-(2-(4-methoxyphenyl)-2-oxoethyl)piperidin-1-ium 4-methylbenzenesulfonate (20H+OTs-)

^{1}H NMR spectrum (500 MHz, MeOD) 1-(2-(4-methoxyphenyl)-2-oxoethyl)piperidin-1-ium 4-methylbenzenesulfonate (20H+OTs-)

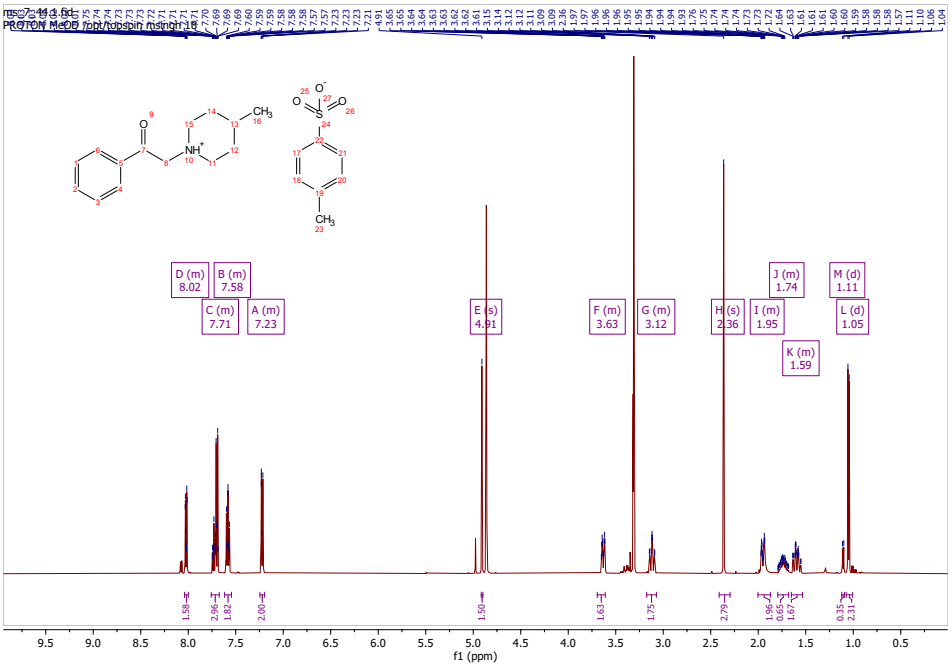


^{13}C {^{1}H } NMR spectrum (126 MHz, MeOD) 1-(2-(4-methoxyphenyl)-2-oxoethyl)piperidin-1-ium 4-methylbenzenesulfonate (20H+OTs-)

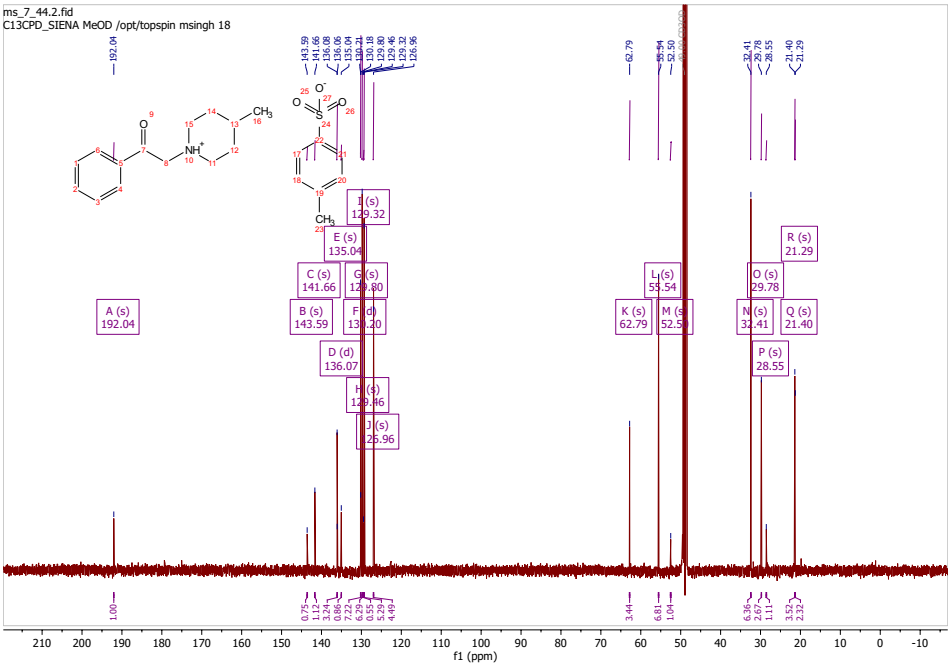


10.3.5 4-methyl-1-(2-oxo-2-phenylethyl)piperidin-1-ium 4-methylbenzenesulfonate

^{1}H NMR spectrum (500 MHz, MeOD) 4-methyl-1-(2-oxo-2-phenylethyl)piperidin-1-ium 4-methylbenzenesulfonate

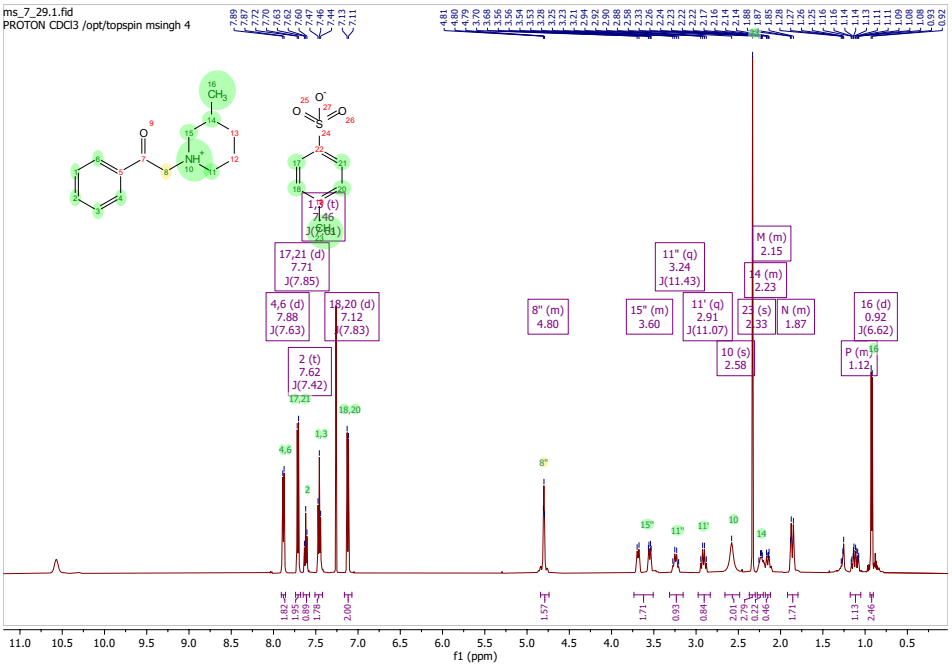


^{13}C {^{1}H } NMR spectrum (126 MHz, MeOD) 4-methyl-1-(2-oxo-2-phenylethyl)piperidin-1-ium 4-methylbenzenesulfonate

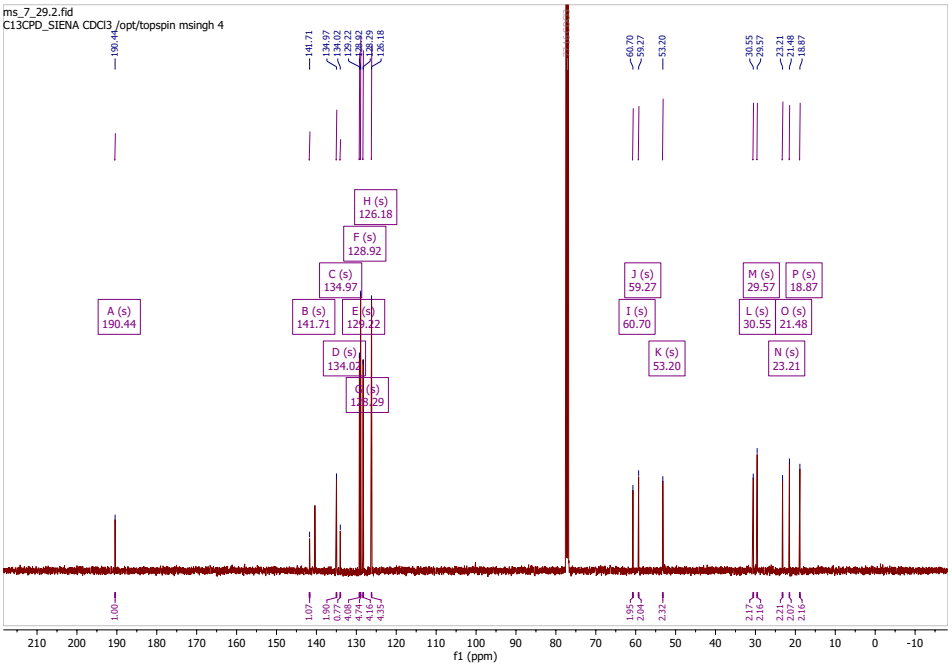


10.3.6 3-methyl-1-(2-oxo-2-phenylethyl)piperidin-1-ium 4-methylbenzenesulfonate

^{1}H NMR spectrum (500 MHz, Chloroform-d) 3-methyl-1-(2-oxo-2-phenylethyl)piperidin-1-ium 4-methylbenzenesulfonate

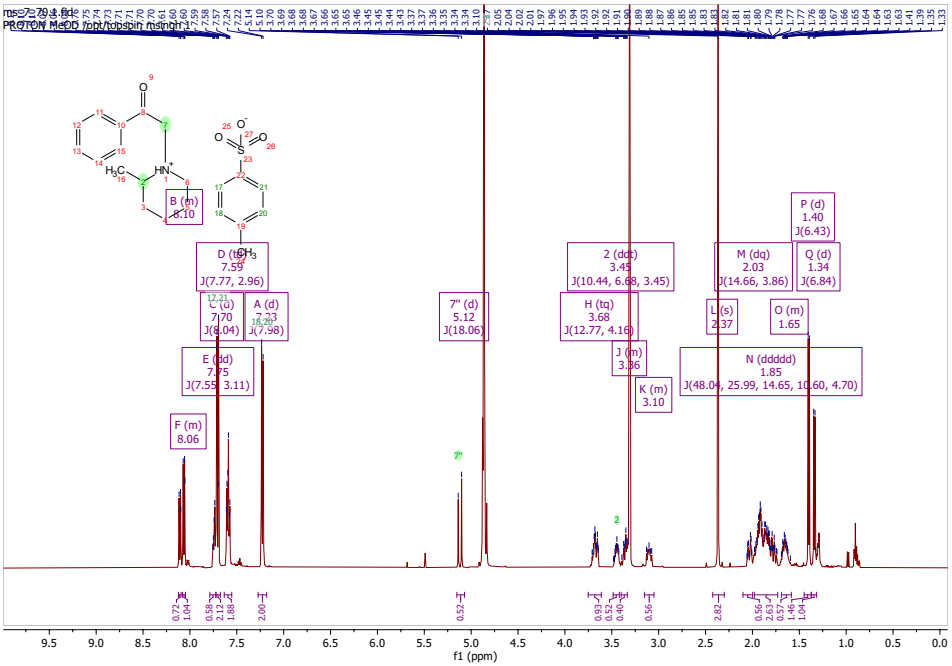


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) 3-methyl-1-(2-oxo-2-phenylethyl)piperidin-1-ium 4-methylbenzenesulfonate

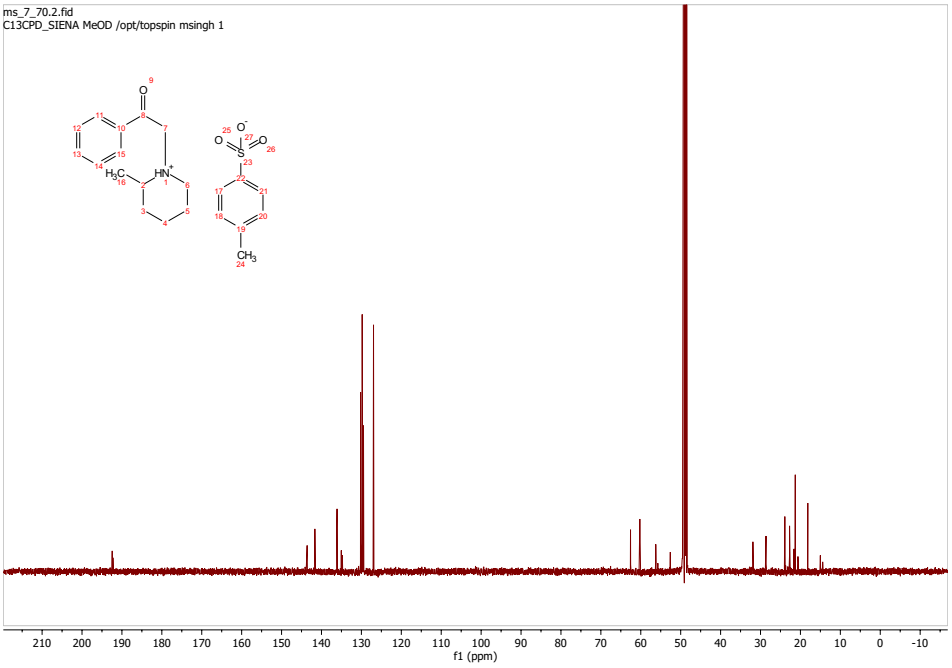


10.3.7 2-methyl-1-(2-oxo-2-phenylethyl)piperidin-1-ium 4-methylbenzenesulfonate

^{1}H NMR spectrum (500 MHz, MeOD) 2-methyl-1-(2-oxo-2-phenylethyl)piperidin-1-ium 4-methylbenzenesulfonate

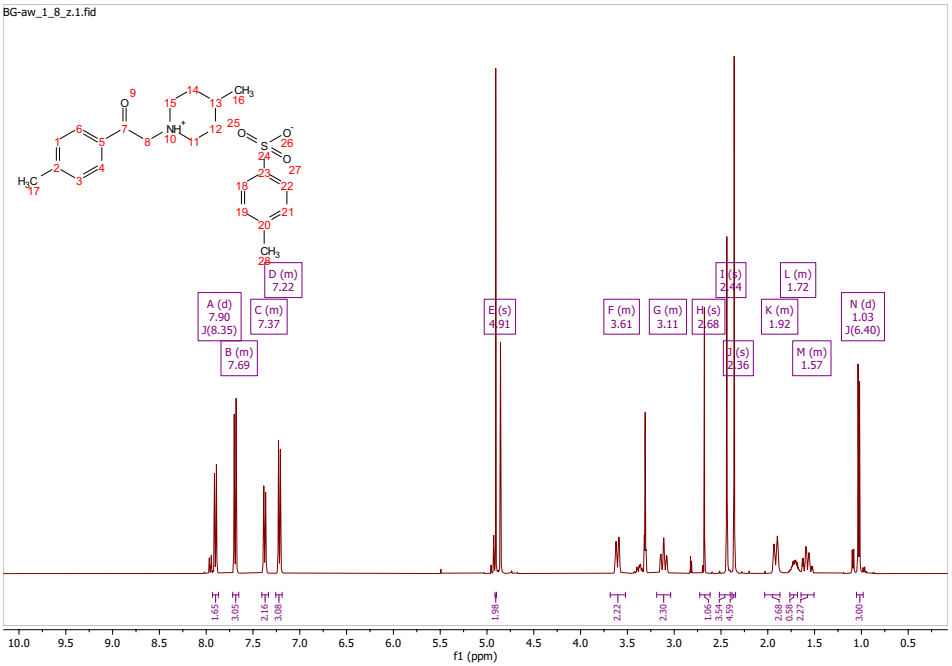


^{13}C {^{1}H } NMR spectrum (126 MHz, MeOD) 2-methyl-1-(2-oxo-2-phenylethyl)piperidin-1-ium 4-methylbenzenesulfonate

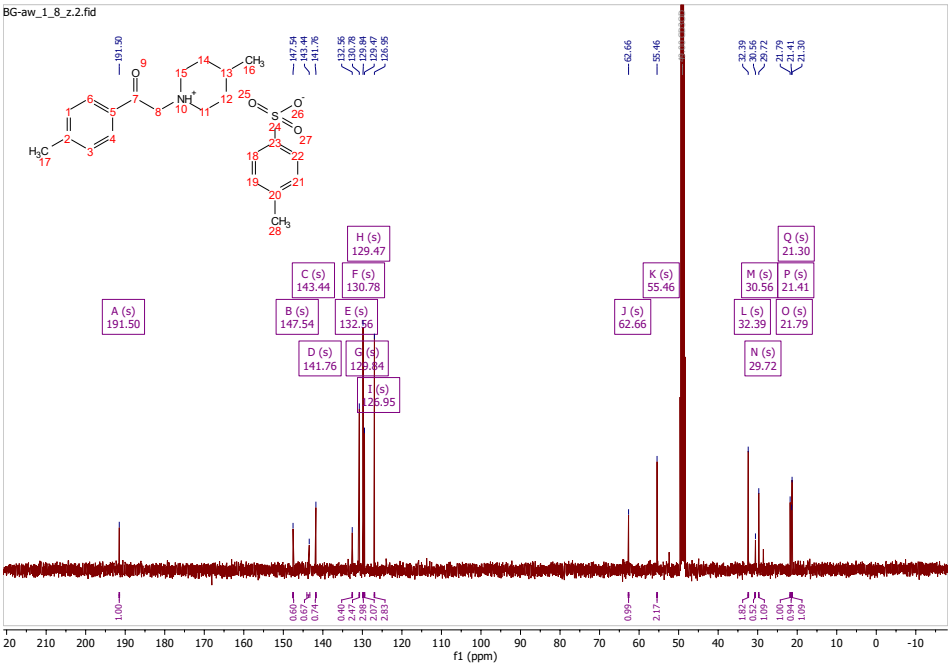


10.3.8 4-methyl-1-(2-oxo-2-(p-tolyl)ethyl)piperidin-1-ium 4-methylbenzenesulfonate

^{1}H NMR spectrum (500 MHz, MeOD) 4-methyl-1-(2-oxo-2-(p-tolyl)ethyl)piperidin-1-ium 4-methylbenzenesulfonate

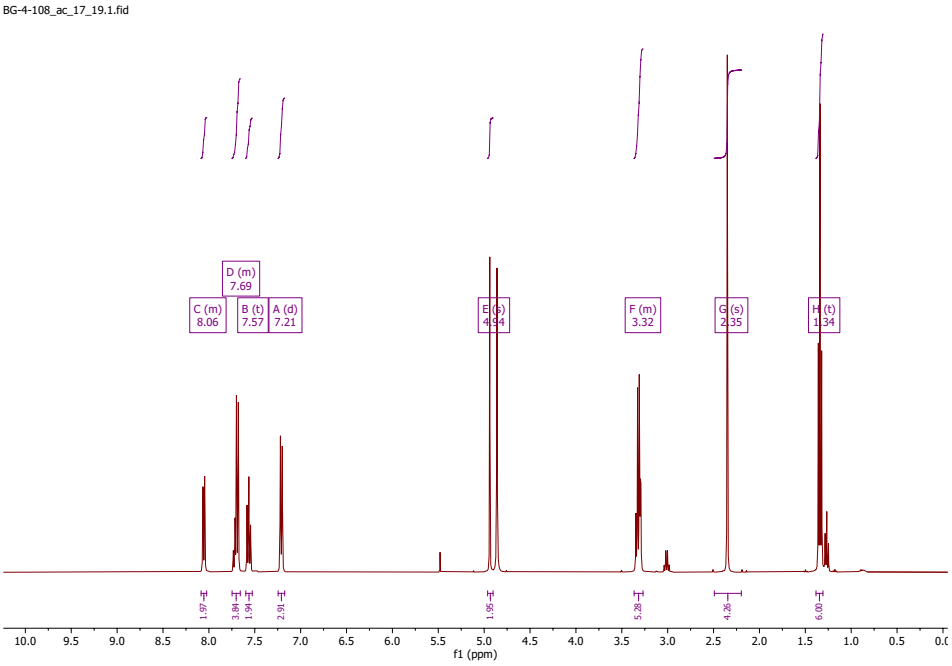


^{13}C {^{1}H } NMR spectrum (126 MHz, MeOD) 4-methyl-1-(2-oxo-2-(p-tolyl)ethyl)piperidin-1-ium 4-methylbenzenesulfonate

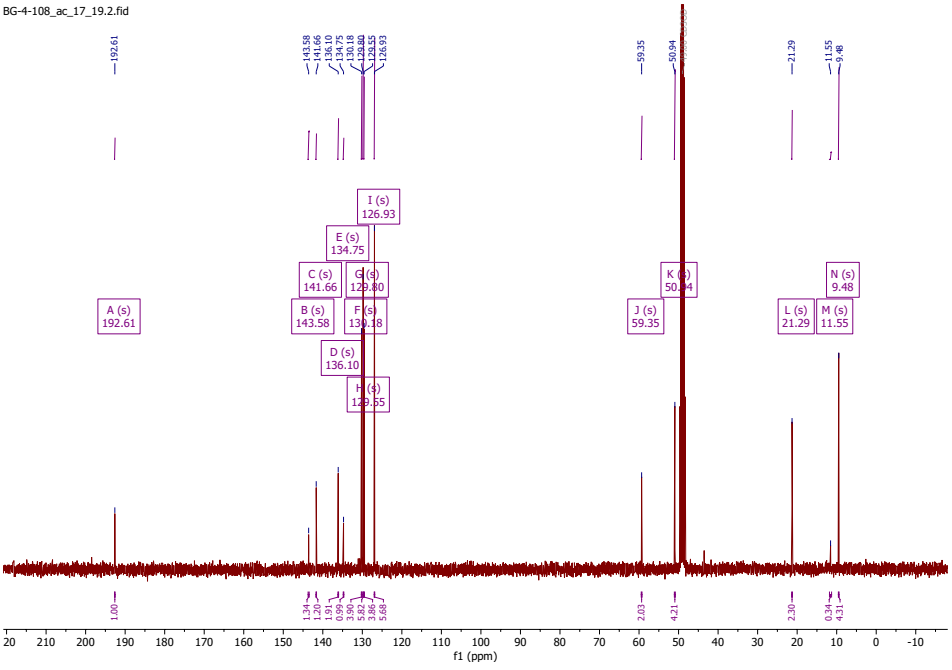


10.3.9 N,N-diethyl-2-oxo-2-phenylethan-1-aminium 4-methylbenzenesulfonate

^{1}H NMR spectrum (500 MHz, MeOD) N,N-diethyl-2-oxo-2-phenylethan-1-aminium 4-methylbenzenesulfonate

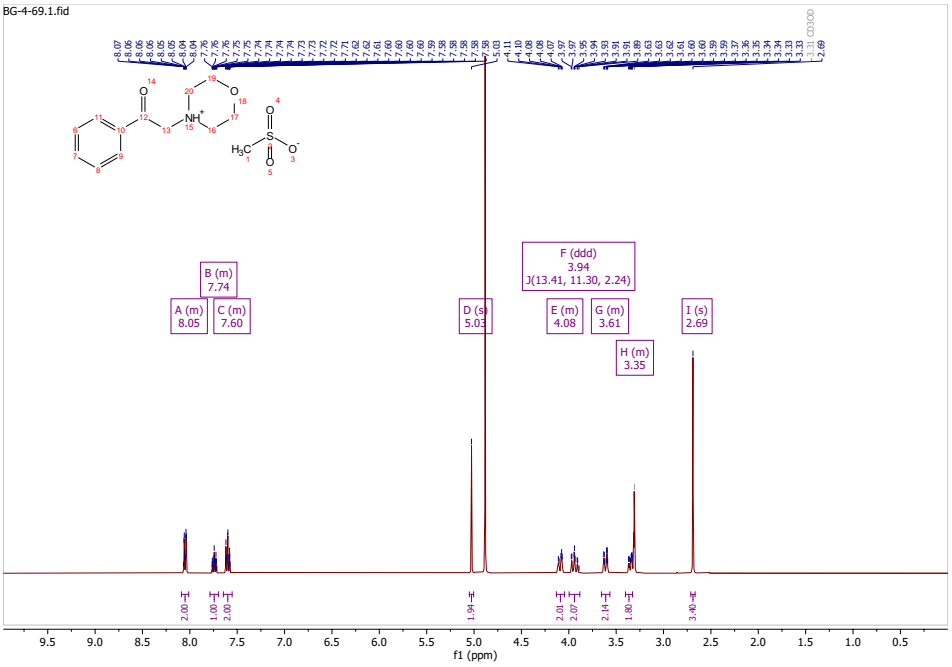


^{13}C {^{1}H } NMR spectrum (126 MHz, MeOD) N,N-diethyl-2-oxo-2-phenylethan-1-aminium 4-methylbenzenesulfonate

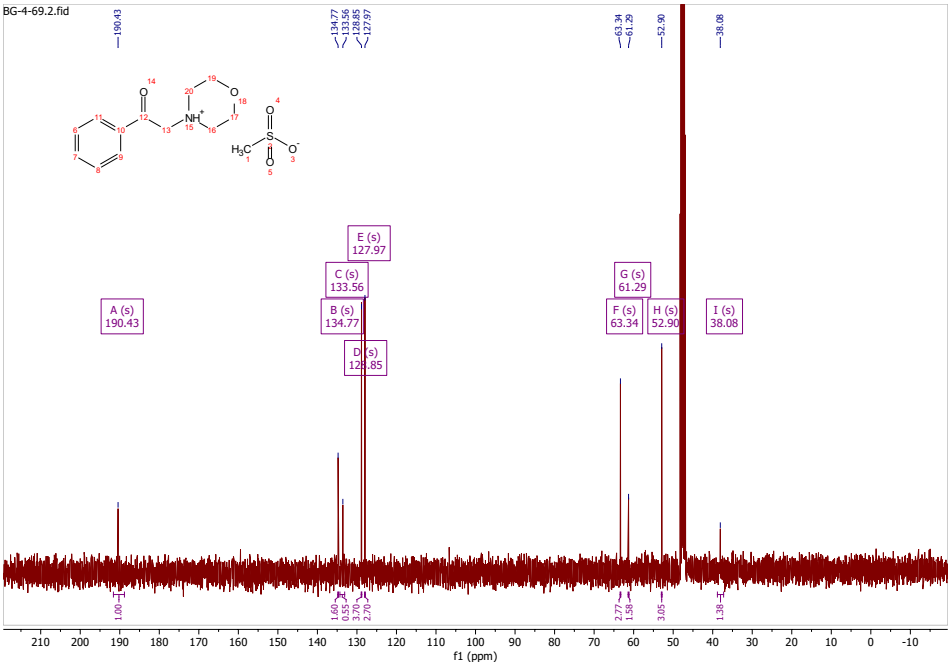


10.3.10 4-(2-oxo-2-phenylethyl)morpholin-4-ium methanesulfonate (18H+OTs-)

^{1}H NMR spectrum (500 MHz, MeOD) 4-(2-oxo-2-phenylethyl)morpholin-4-ium methanesulfonate (18H+OTs-)

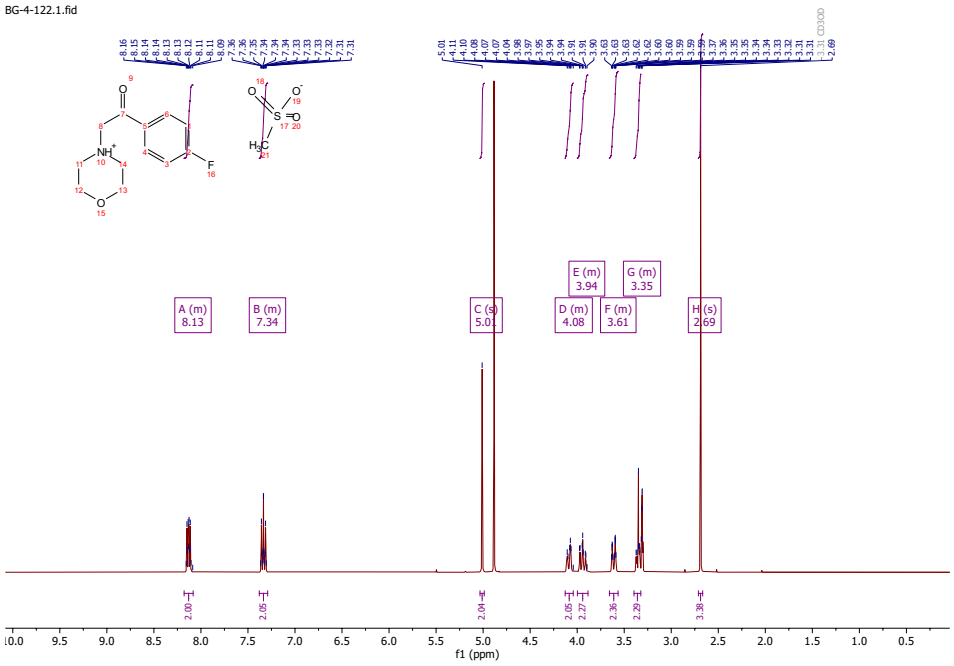


^{13}C {^{1}H } NMR spectrum (126 MHz, MeOD) 4-(2-oxo-2-phenylethyl)morpholin-4-ium methanesulfonate (18H+OTs-)

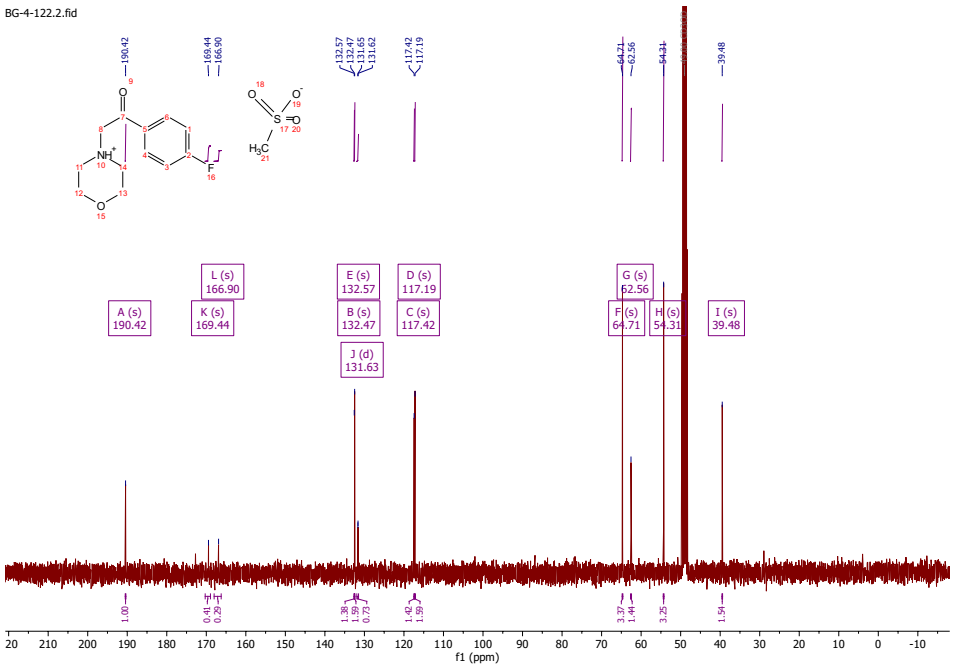


10.3.11 4-(2-(4-fluorophenyl)-2-oxoethyl)morpholin-4-ium methanesulfonate

^{1}H NMR spectrum (500 MHz, MeOD) 4-(2-(4-fluorophenyl)-2-oxoethyl)morpholin-4-ium methanesulfonate



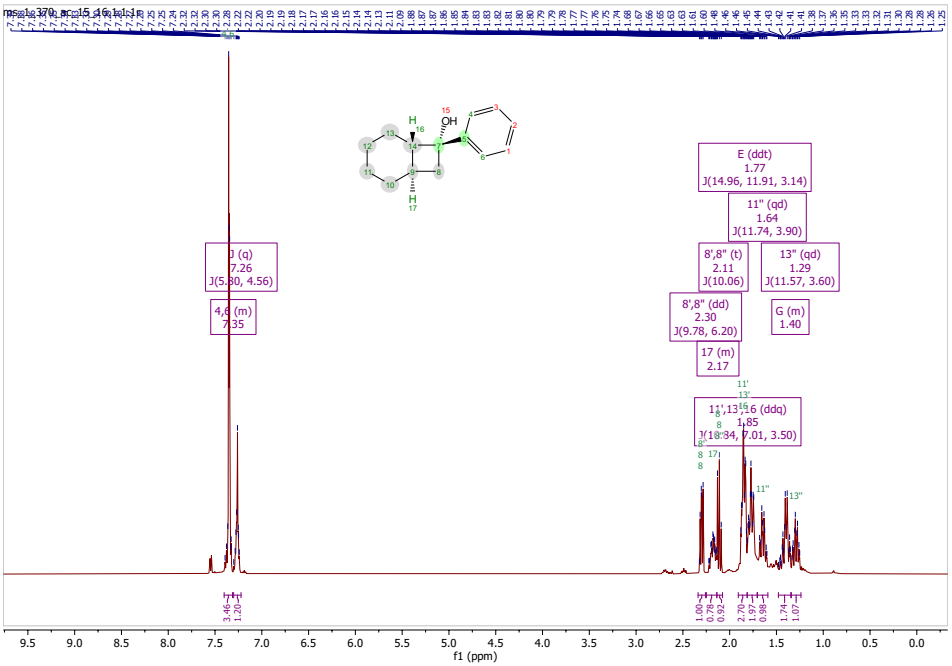
^{13}C {^{1}H } NMR spectrum (126 MHz, MeOD) 4-(2-(4-fluorophenyl)-2-oxoethyl)morpholin-4-ium methanesulfonate



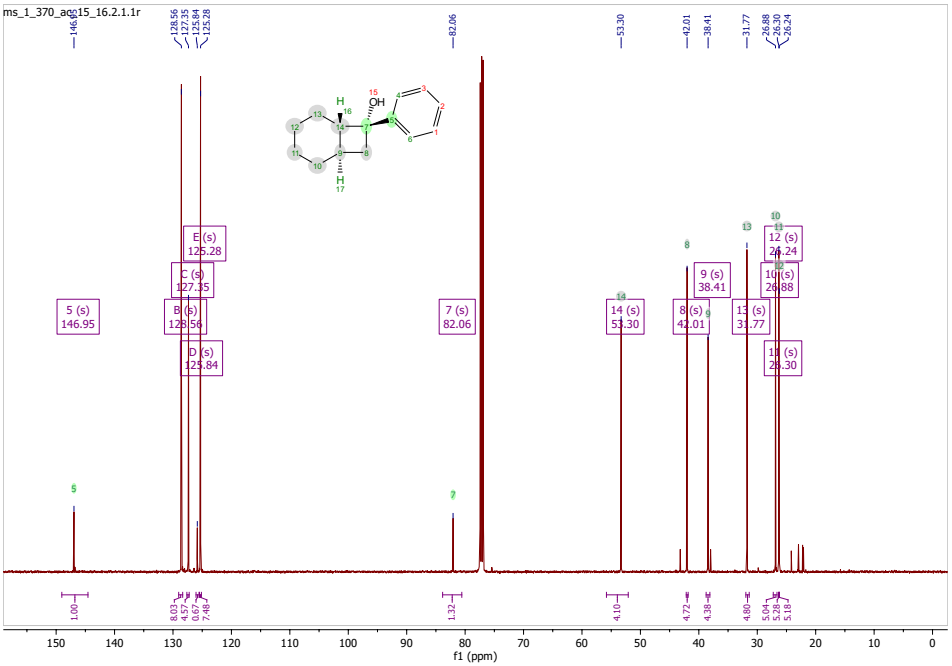
10.4 Azetidinols

10.4.1 Compound 2

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 2

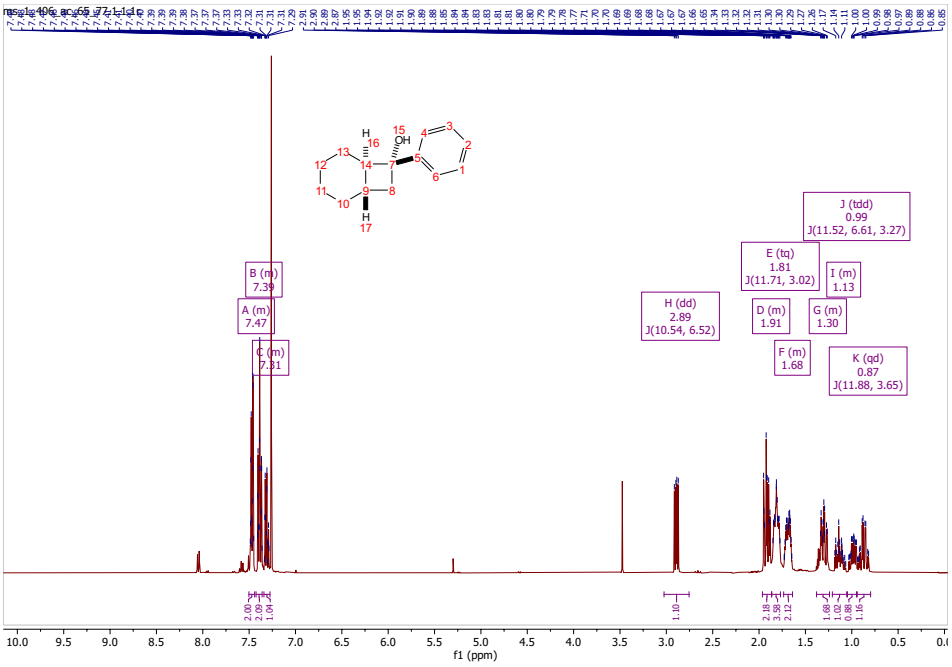


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 2

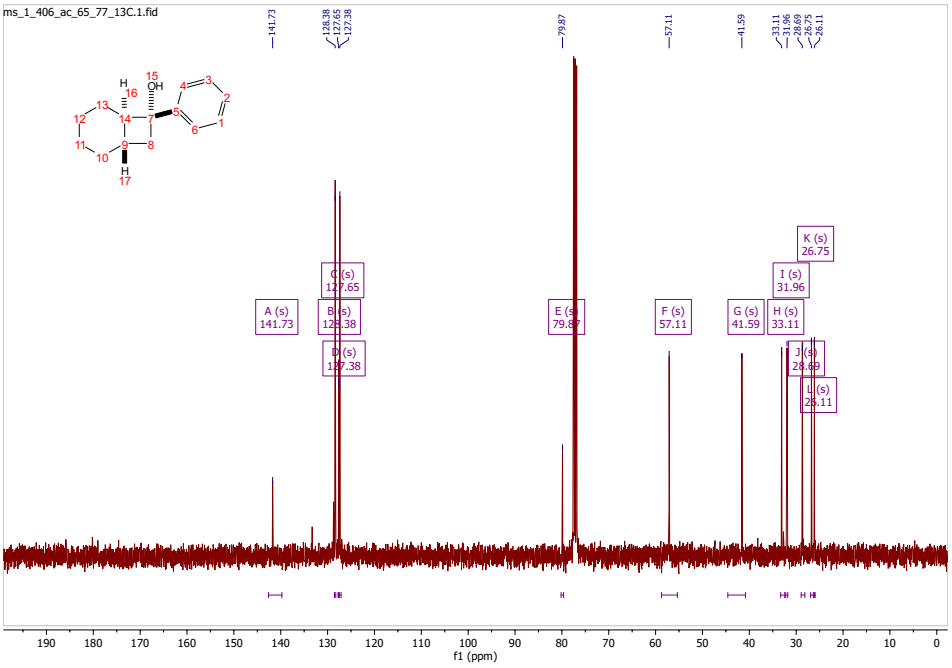


10.4.2 Compound 3

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 3

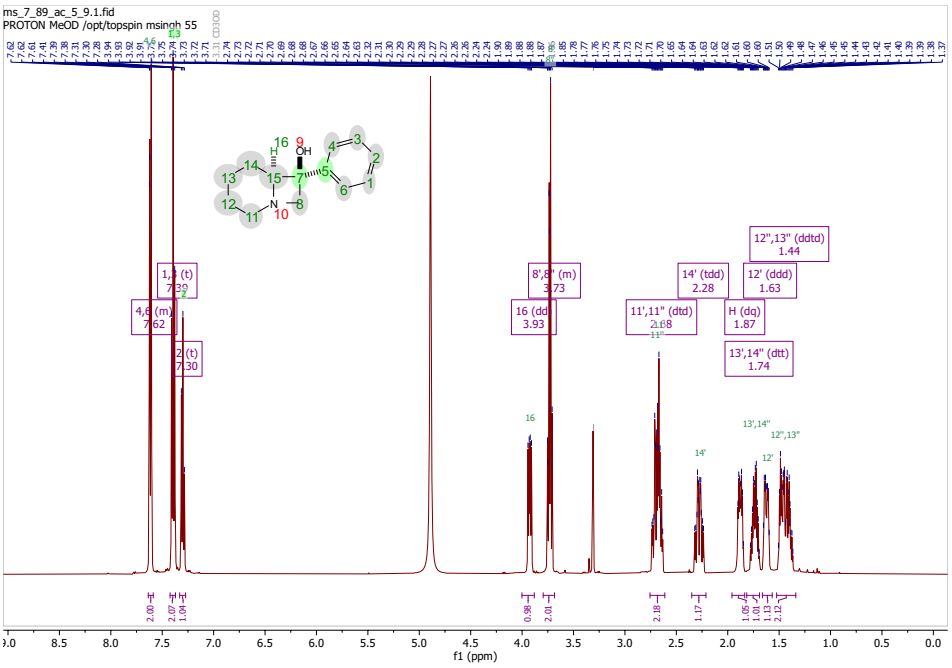


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 3

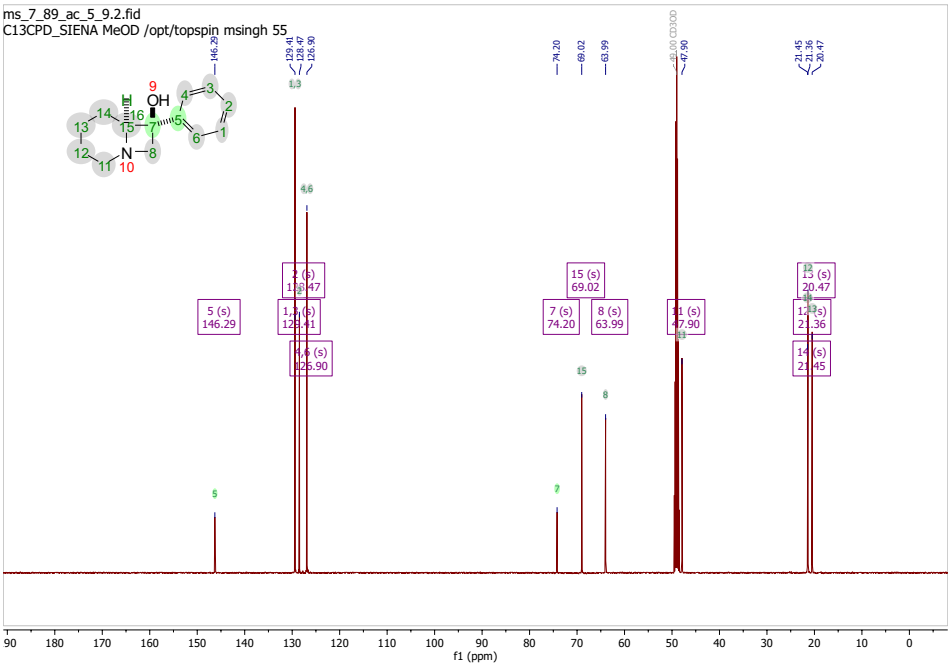


10.4.3 Compound 7

^{1}H NMR spectrum (500 MHz, MeOD) of Compound 7

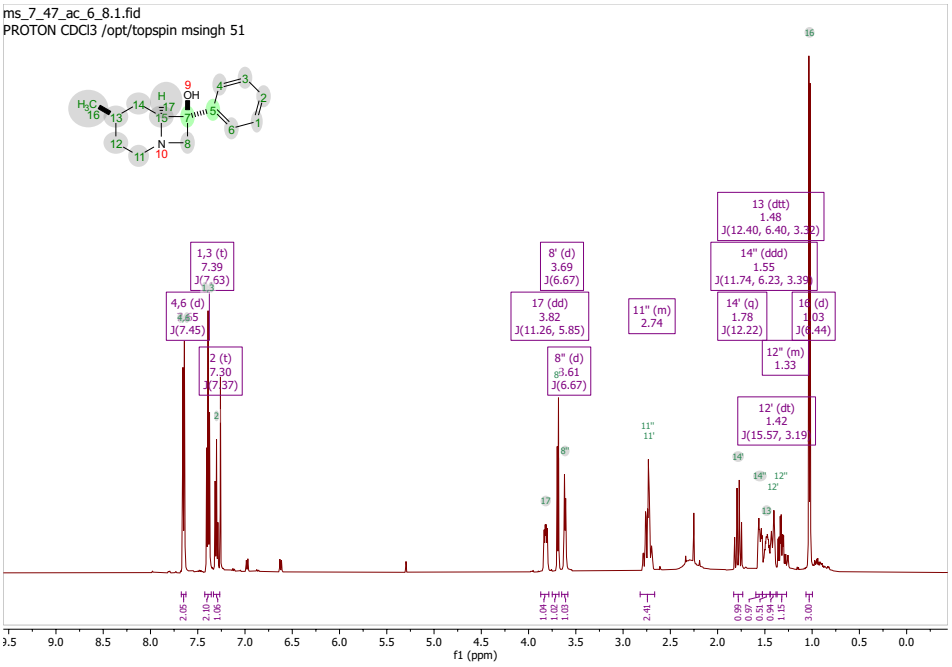


^{13}C {^{1}H } NMR spectrum (126 MHz, MeOD) of Compound 7

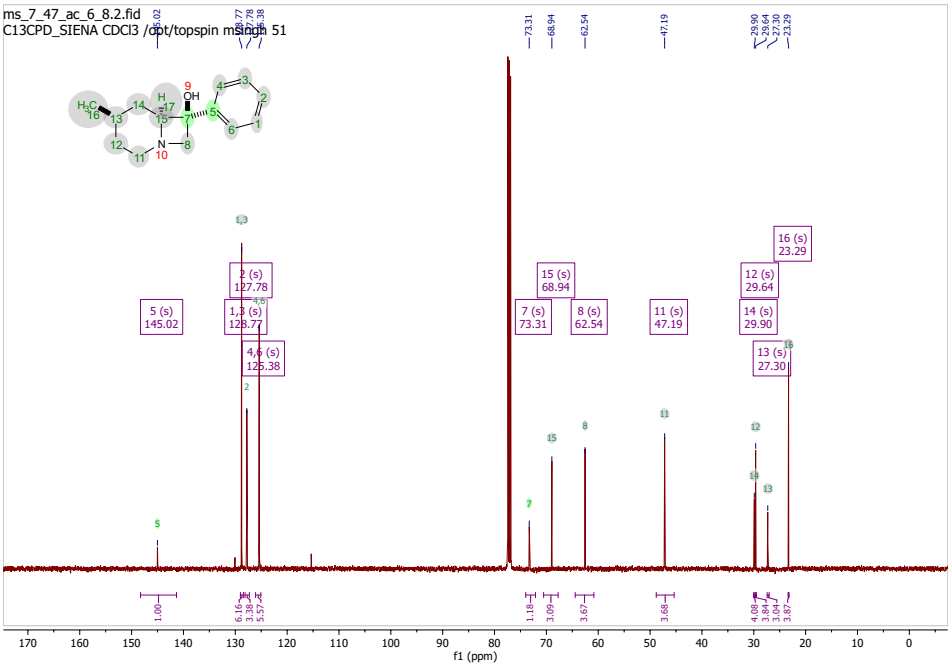


10.4.4 Compound 8

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 8

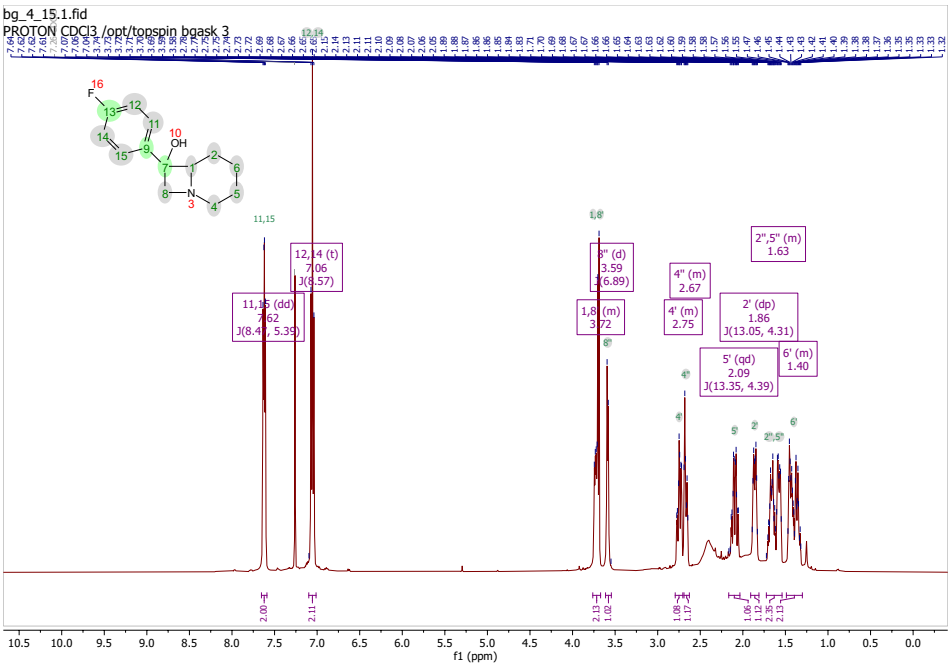


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 8

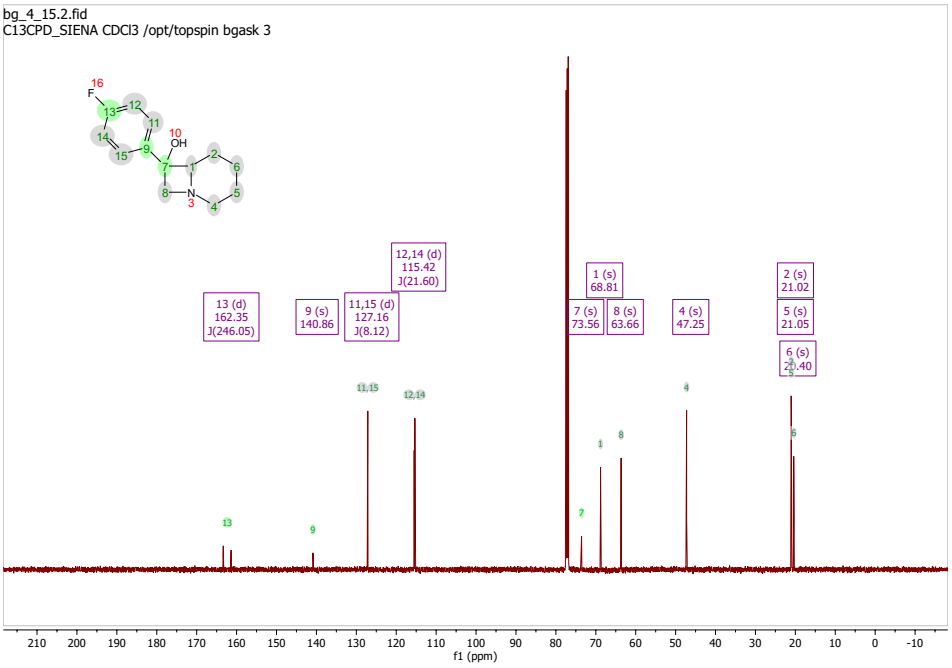


10.4.5 Compound 9

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 9

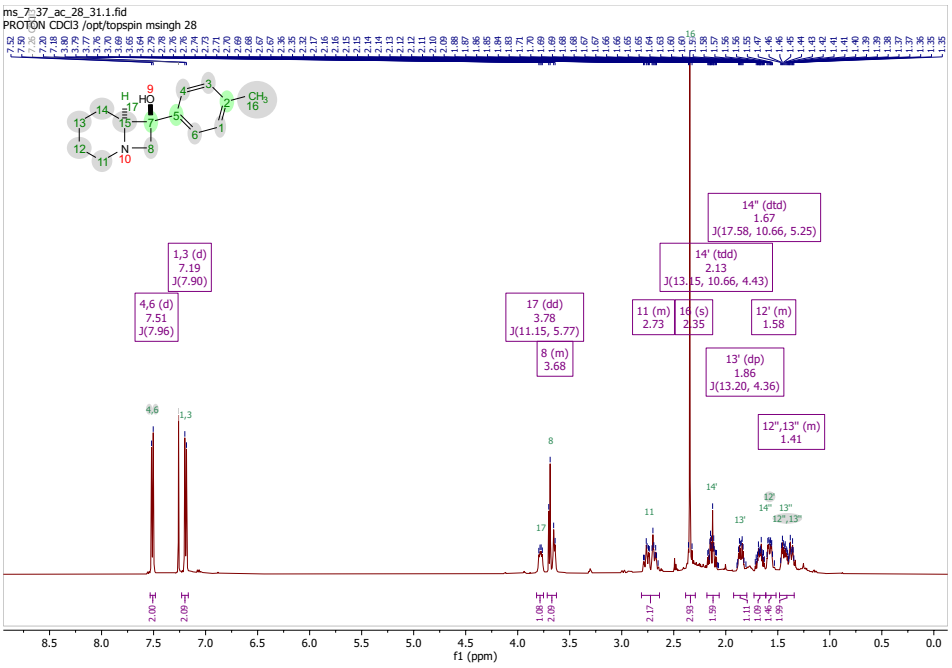


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 9

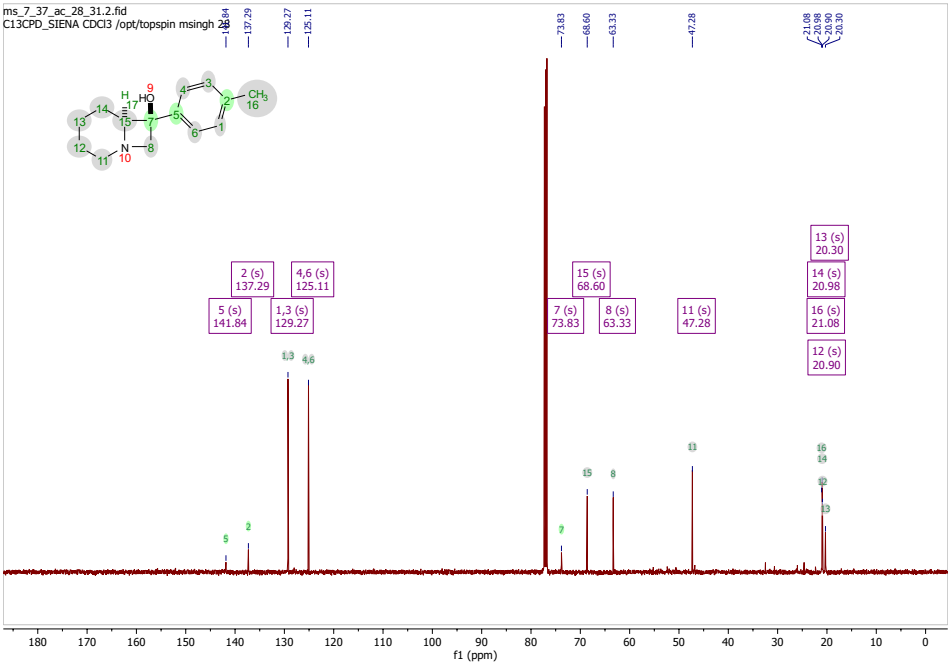


10.4.6 Compound 10

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 10

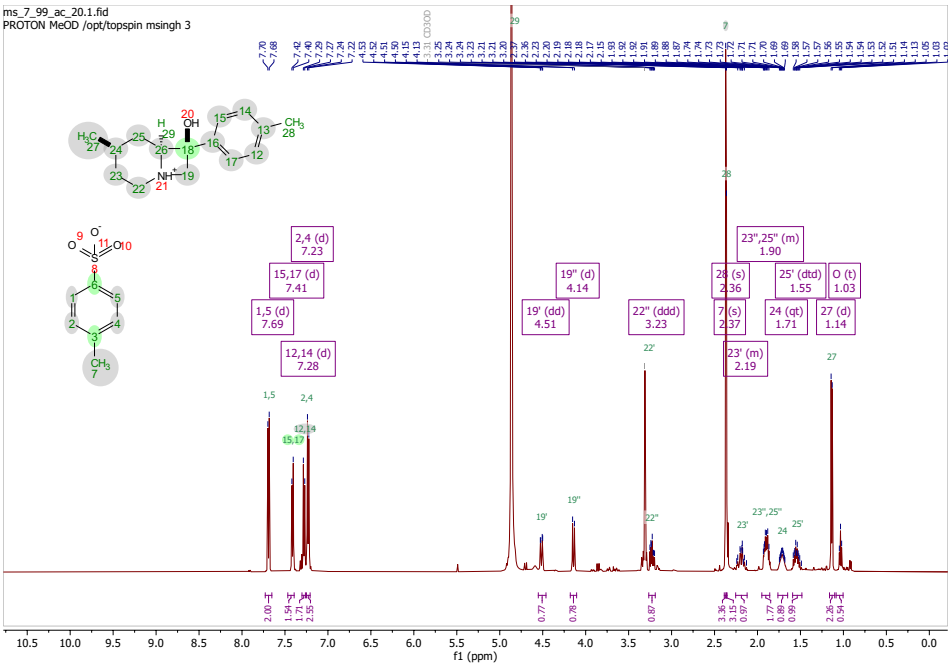


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 10

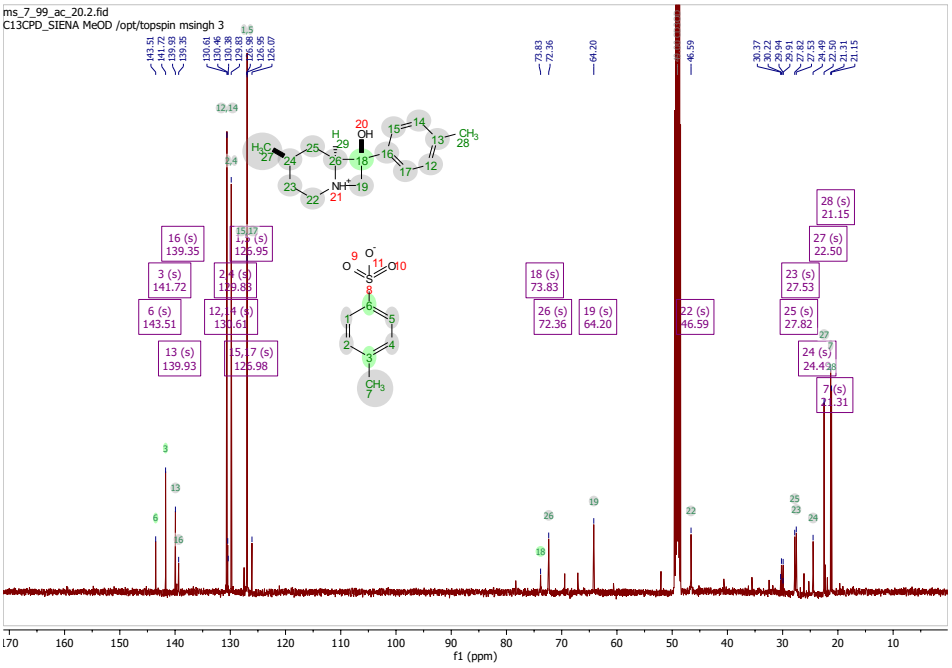


10.4.7 Compound 11

^{1}H NMR spectrum (500 MHz, MeOD) of Compound 11

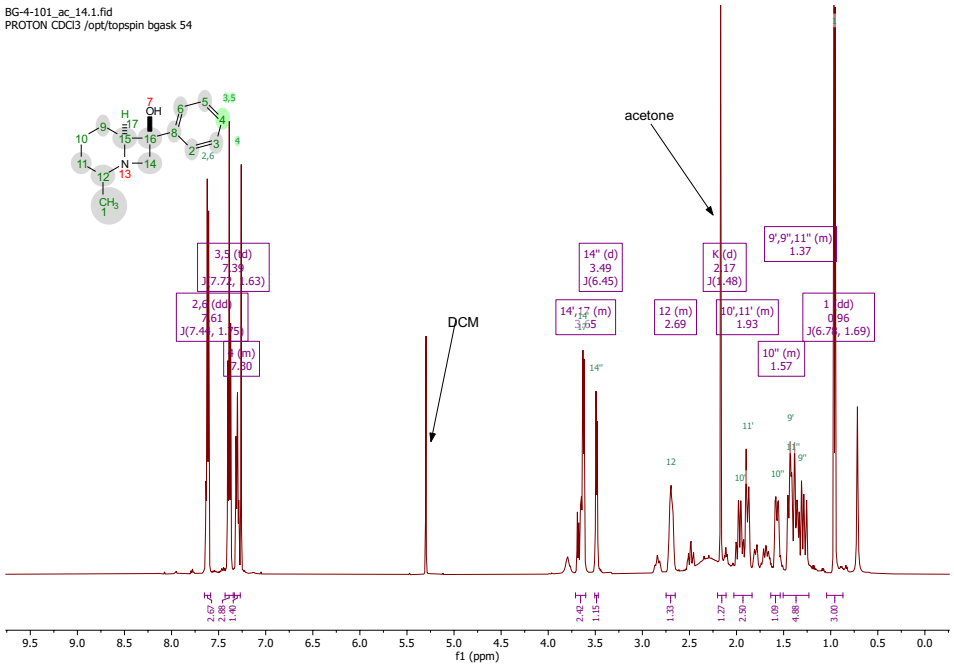


^{13}C {^{1}H } NMR spectrum (126 MHz, MeOD) of Compound 11

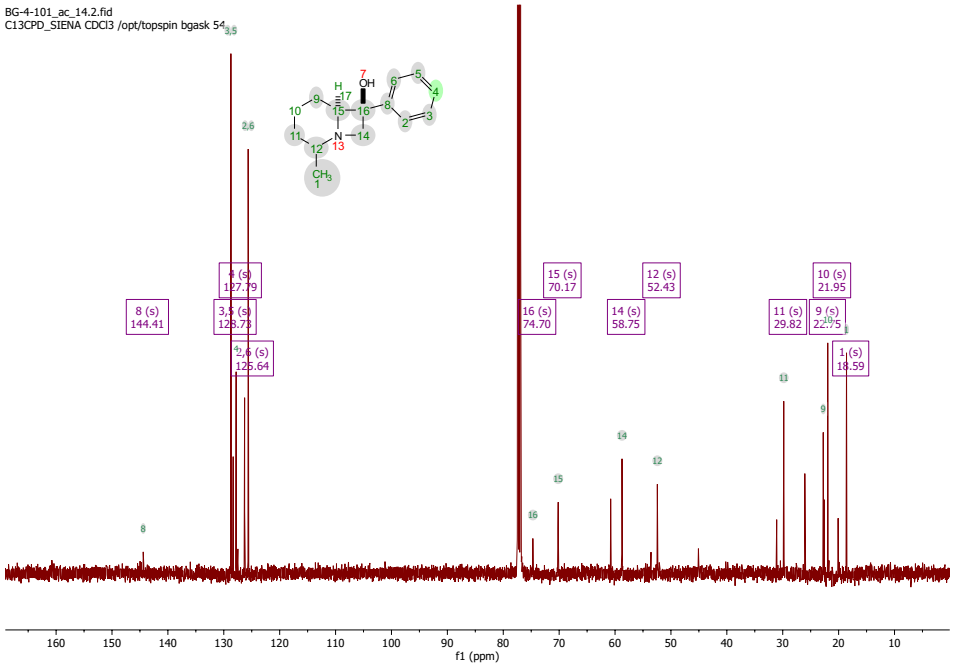


10.4.8 Compound 12

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 12

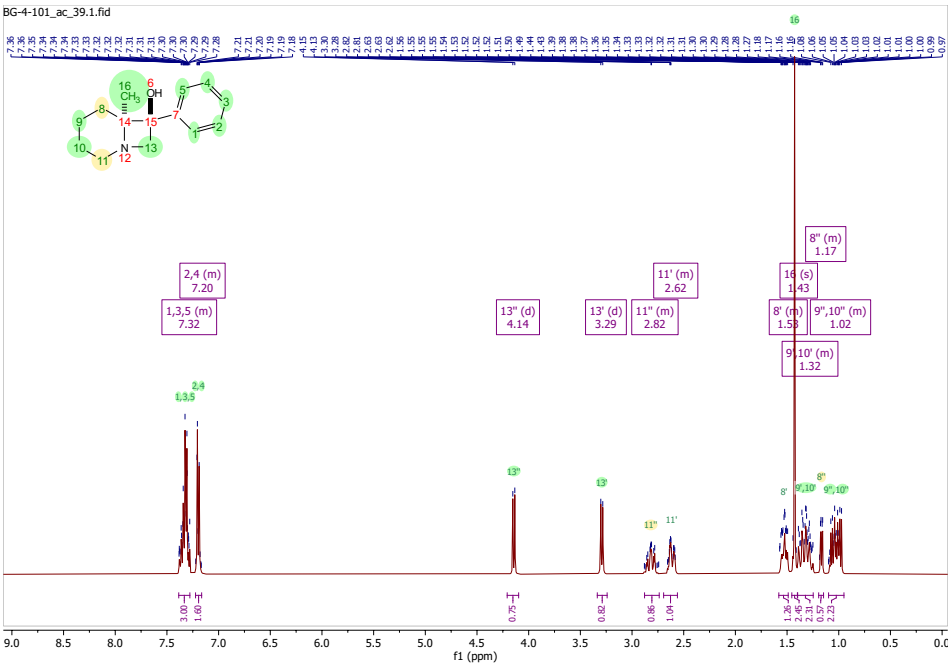


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 12

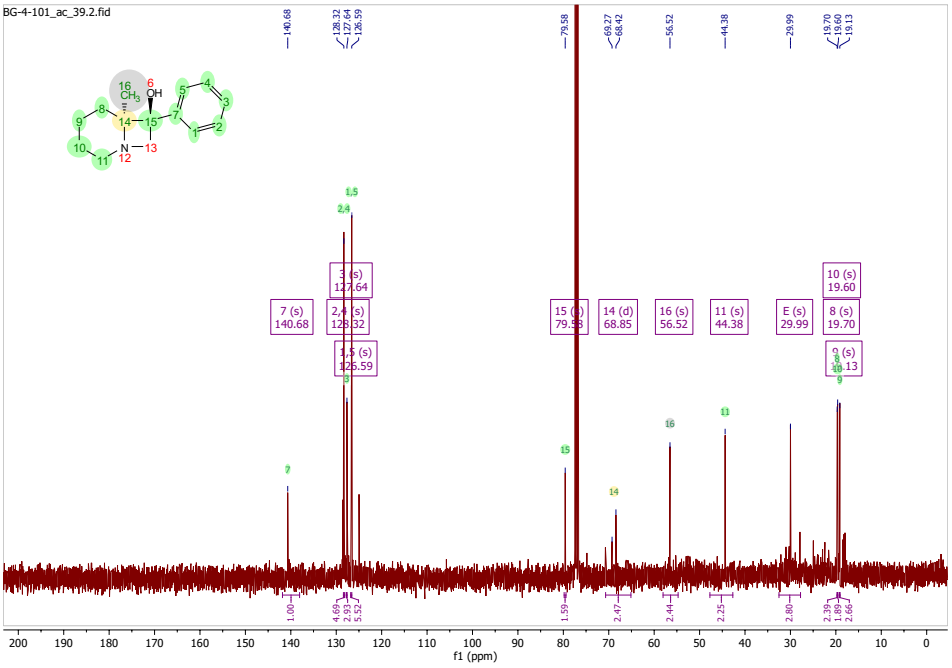


10.4.9 Compound 13

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 13

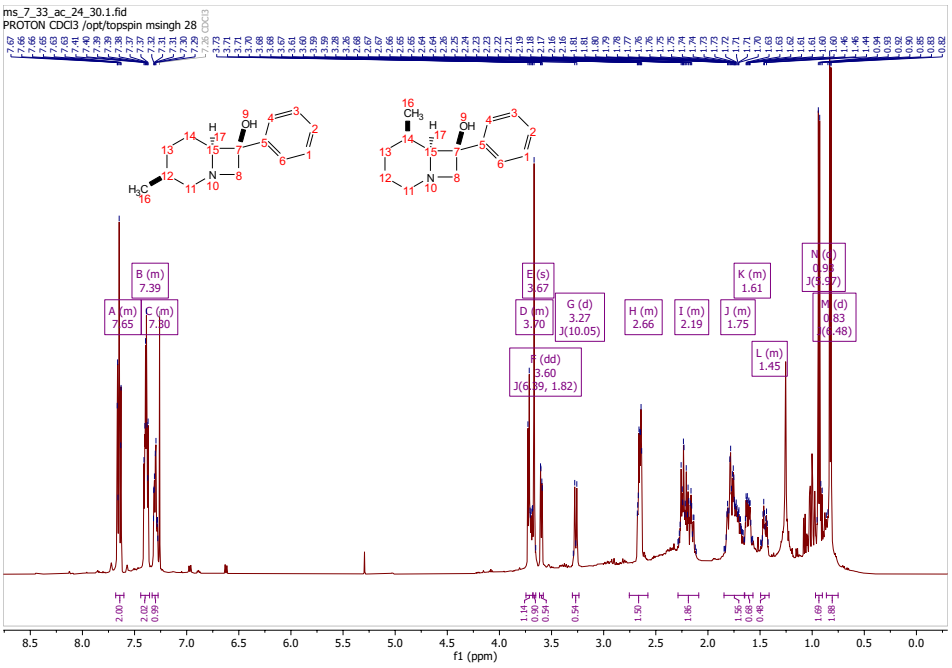


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 13

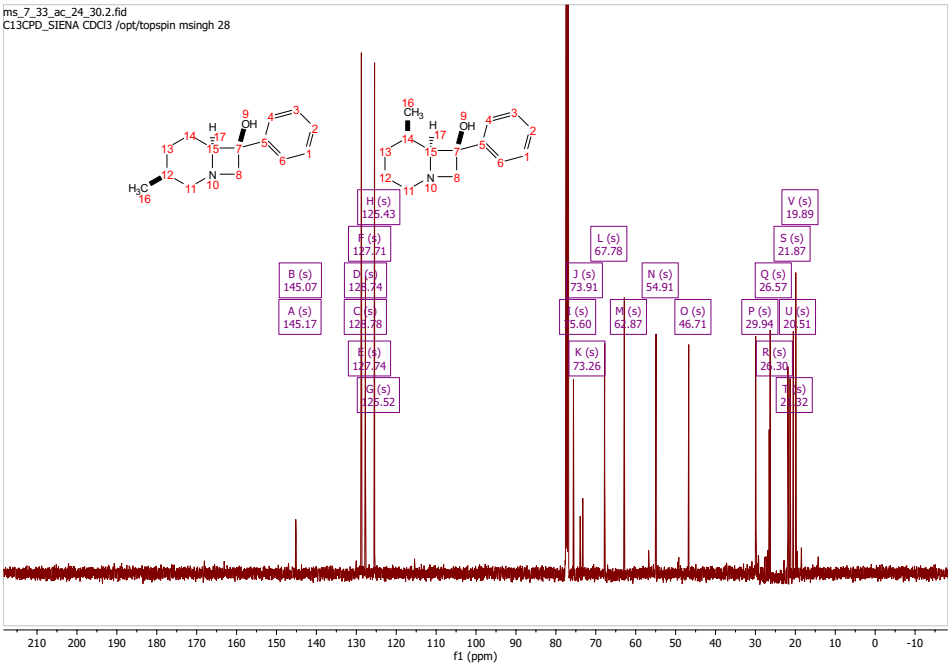


10.4.10 Compound 14 and 15

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 14 and 15

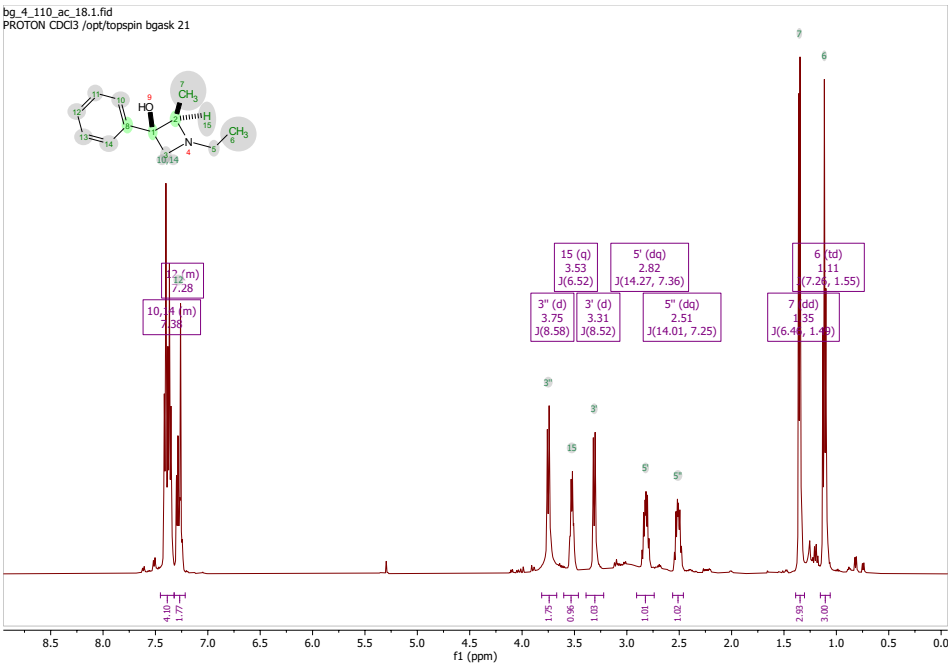


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of compound 14 and 15

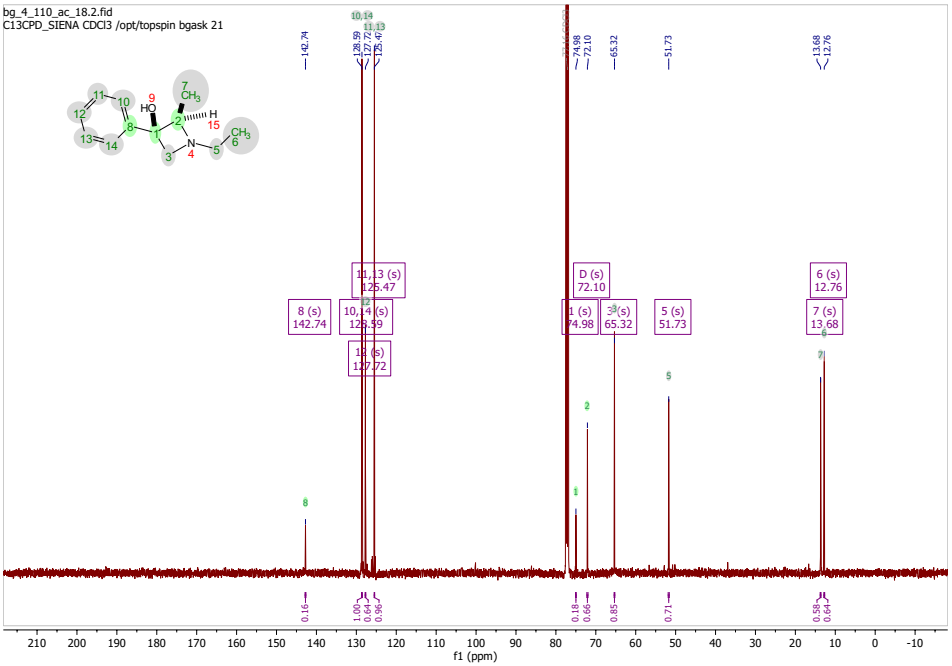


10.4.11 Compound 16

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 16

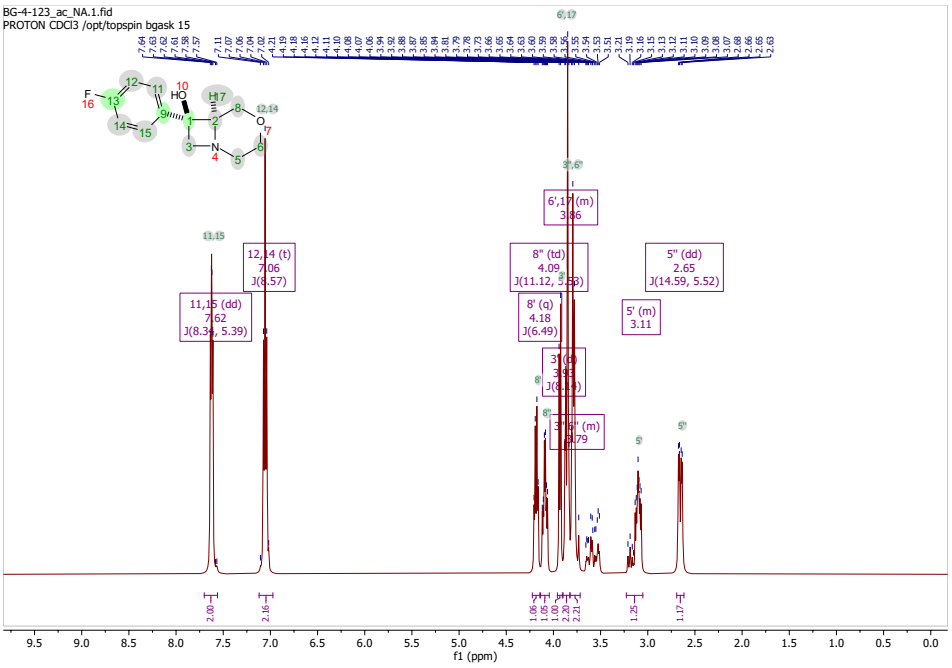


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 16

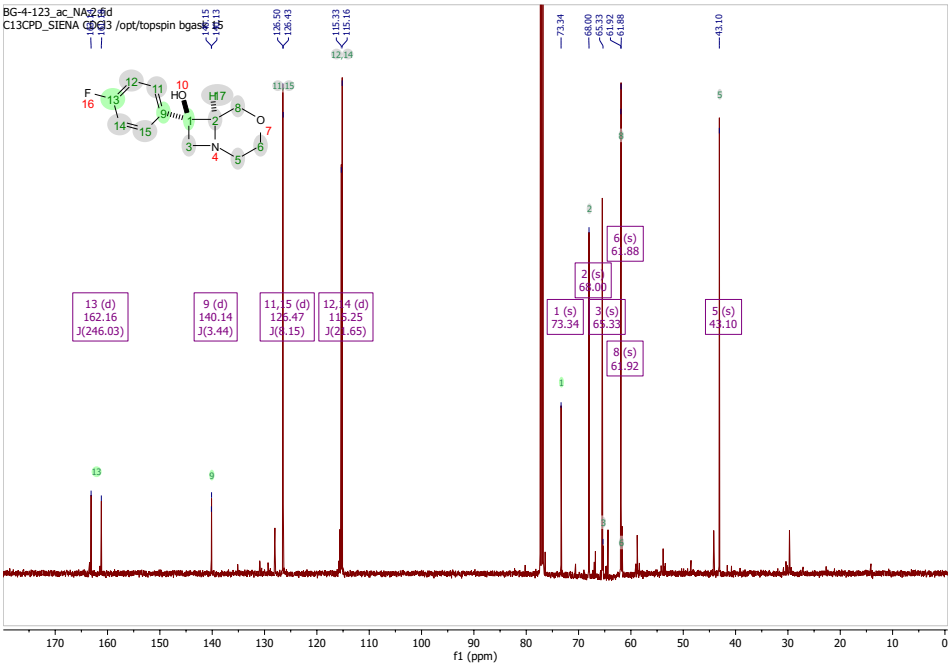


10.4.12 Compound 17

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 17

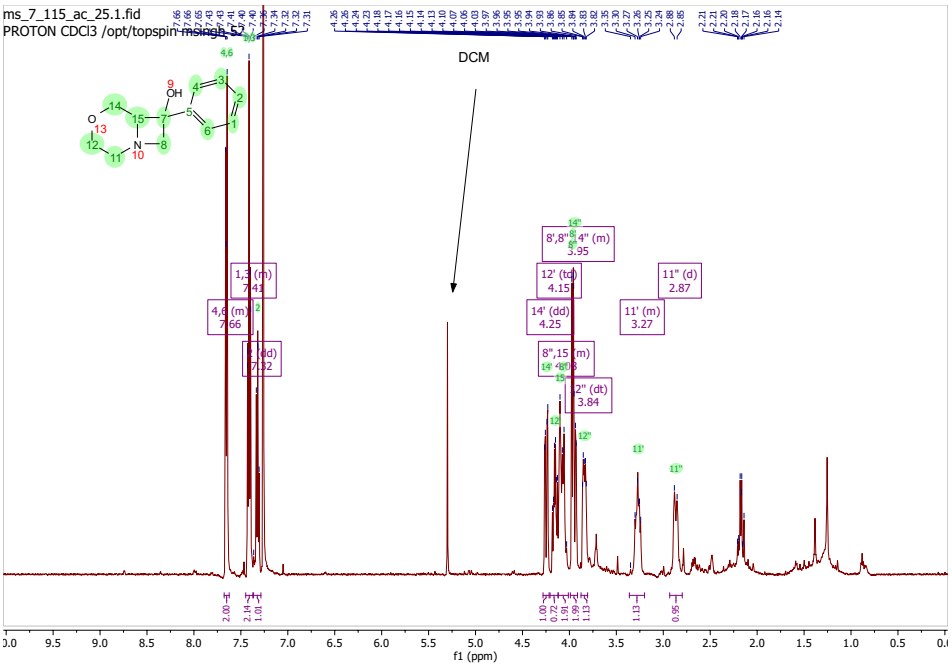


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 17

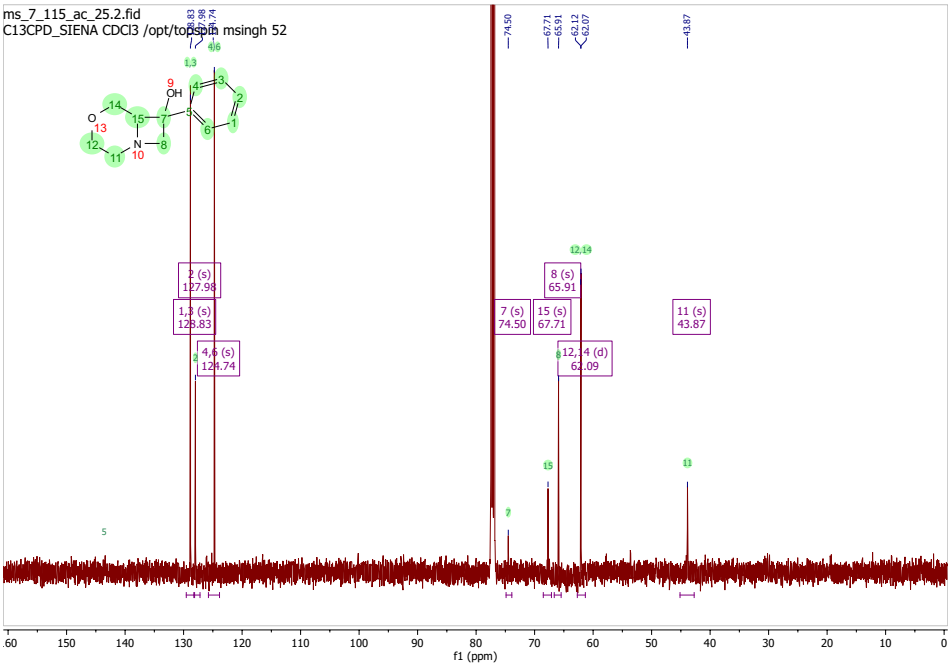


10.4.13 Compound 19

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 19



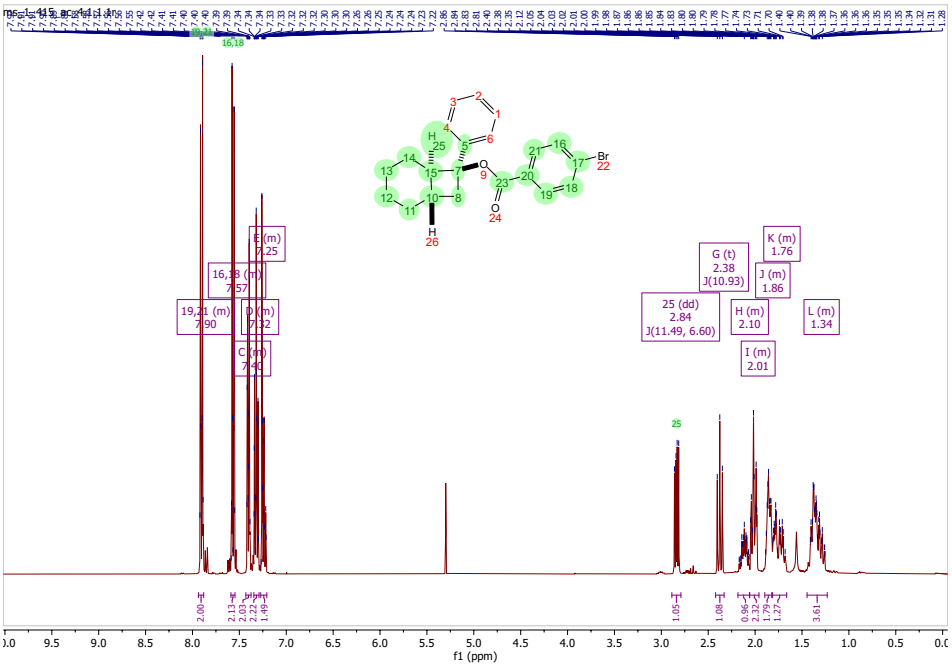
^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 19



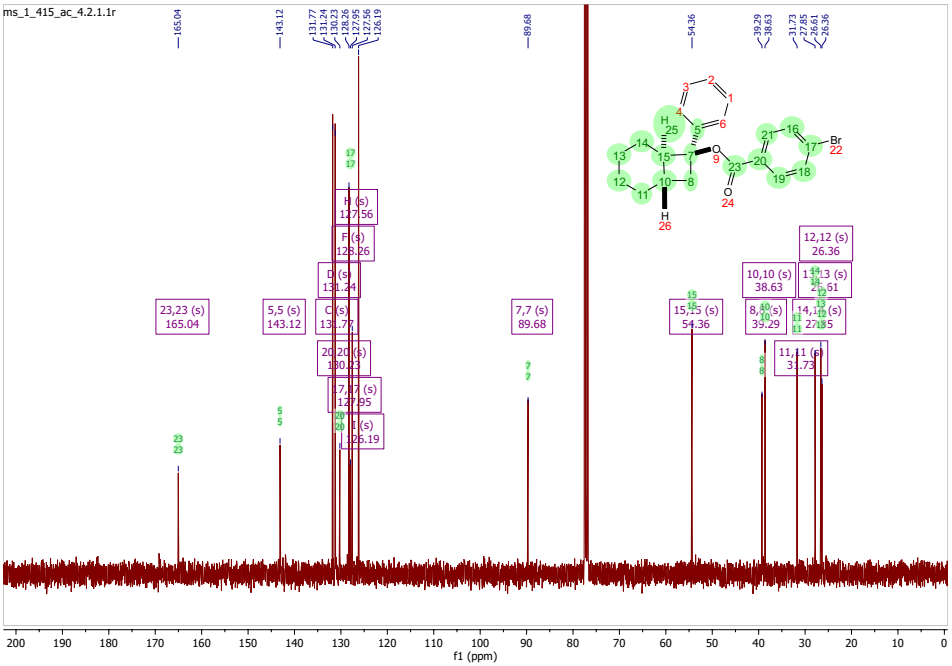
10.5 Esters

10.5.1 Compound 4

^{1}H NMR spectrum (400 MHz, Chloroform-d) of Compound 4

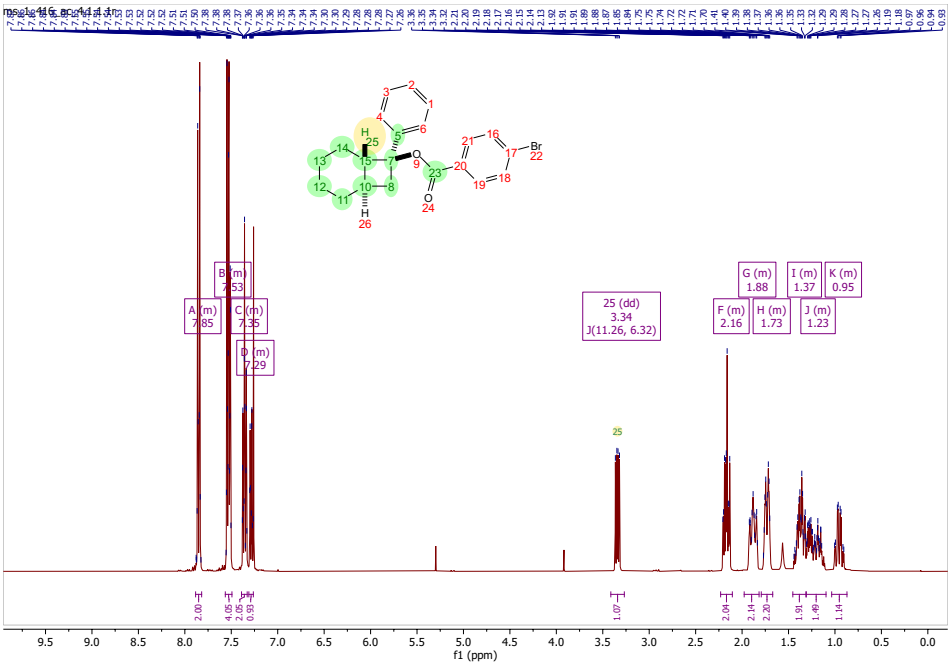


^{13}C {^{1}H } NMR spectrum (101 MHz, Chloroform-d) of Compound 4

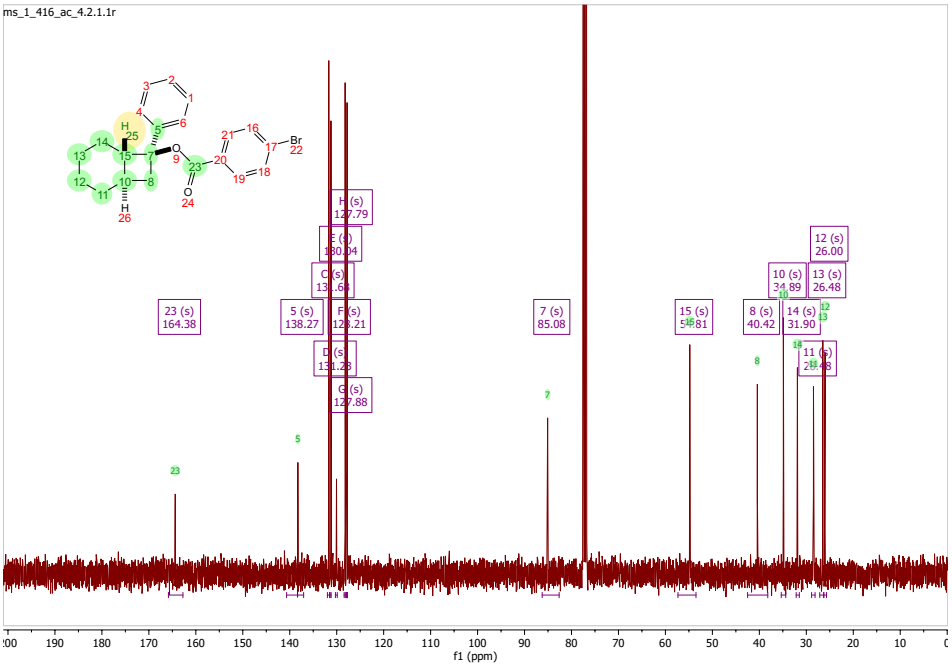


10.5.2 Compound 5

^{1}H NMR spectrum (400 MHz, Chloroform-d) of Compound 5

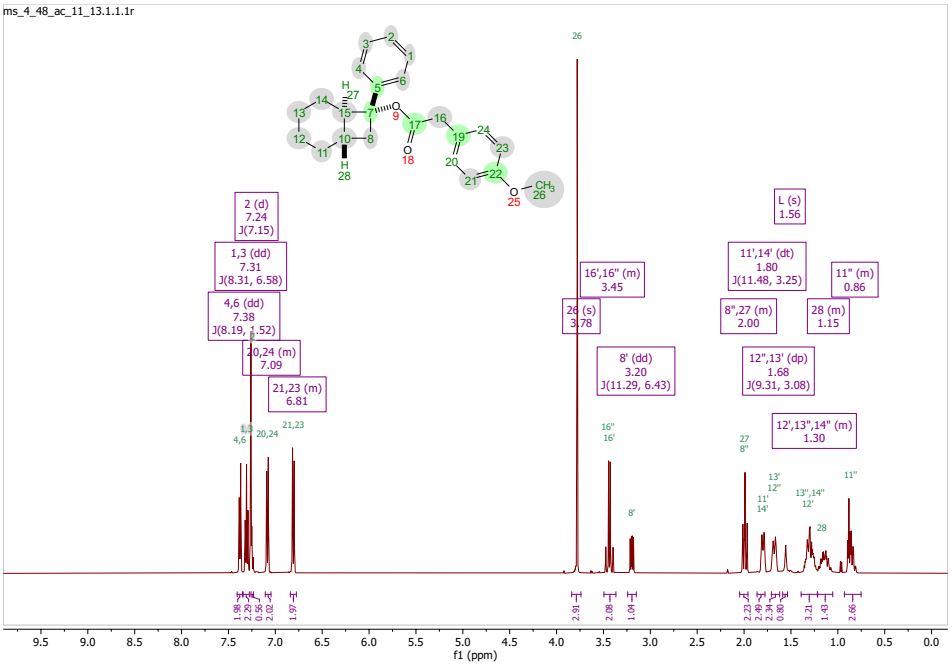


^{13}C {^{1}H } NMR spectrum (101 MHz, Chloroform-d) of Compound 5

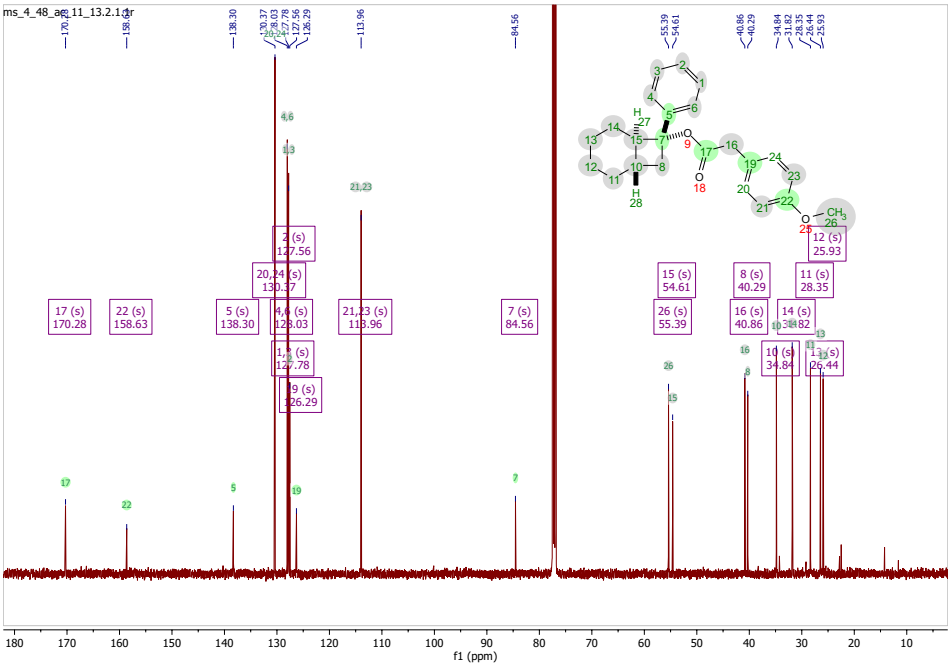


10.5.3 Compound E1

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E1

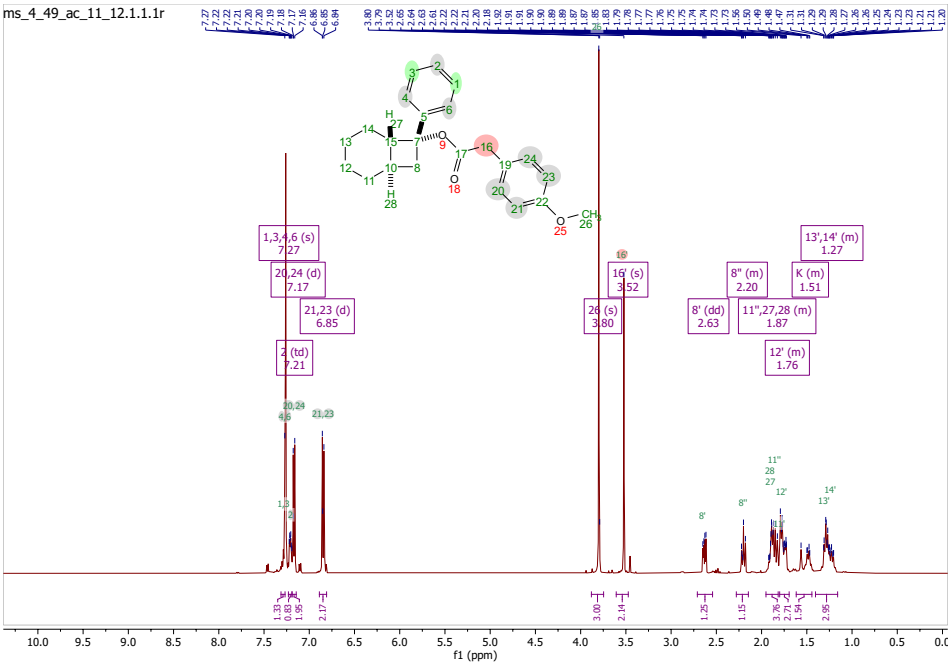


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E1

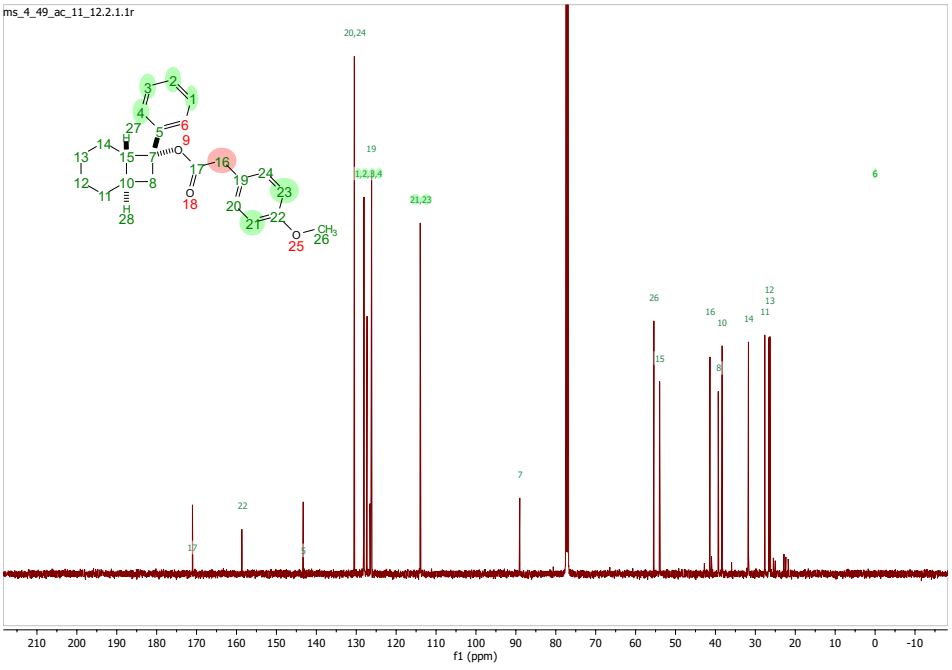


10.5.4 Compound E2

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E2

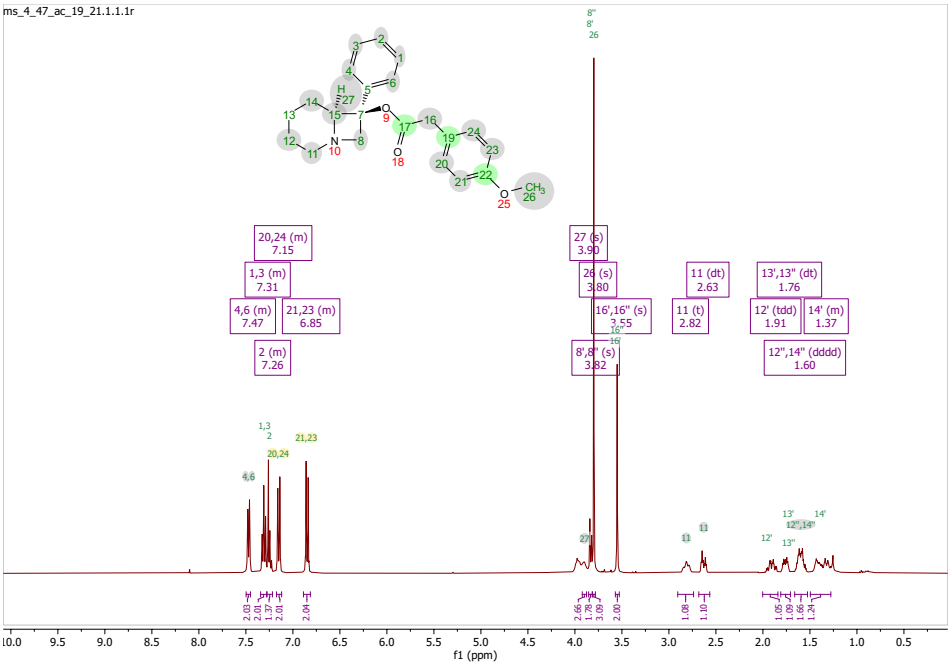


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E2

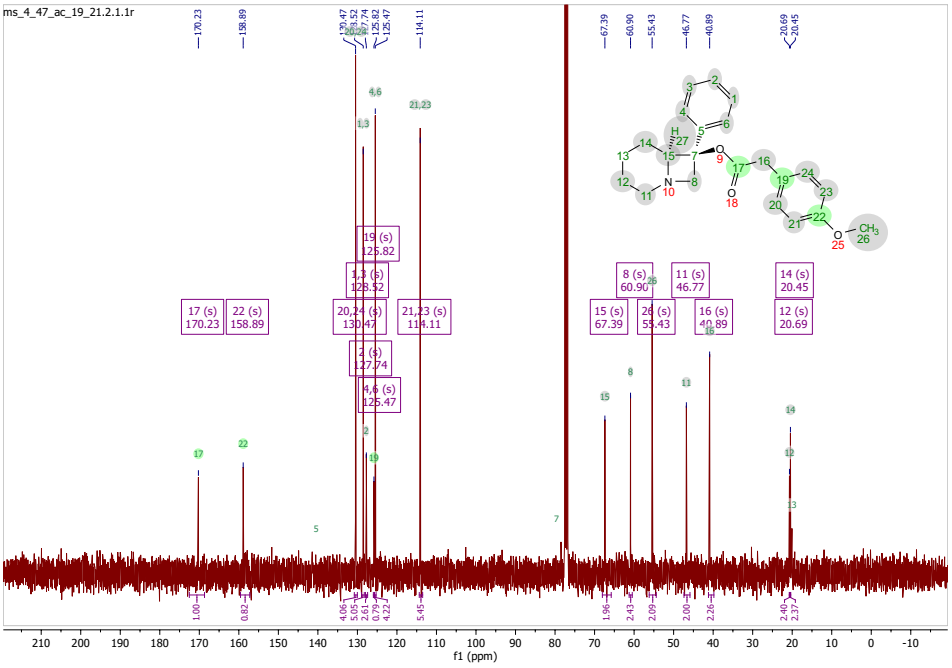


10.5.5 Compound E-1-1

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E-1-1

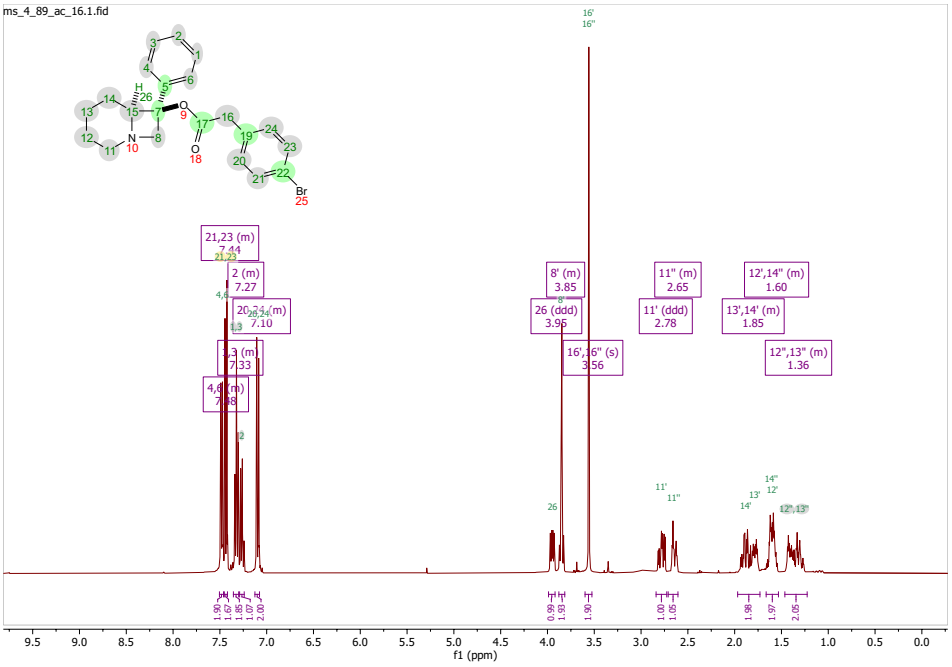


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E-1-1

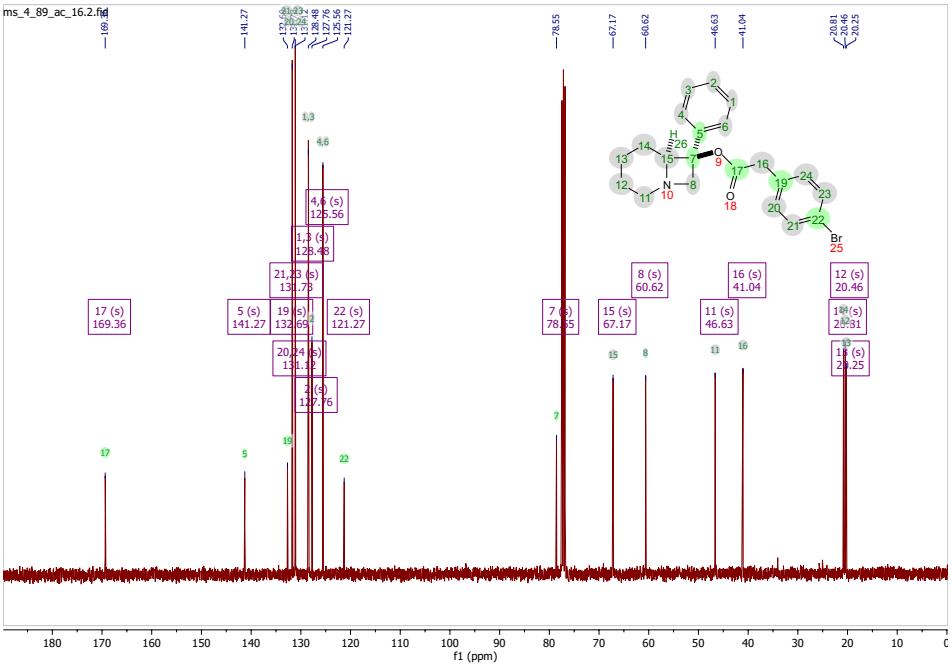


10.5.6 Compound E4

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E4

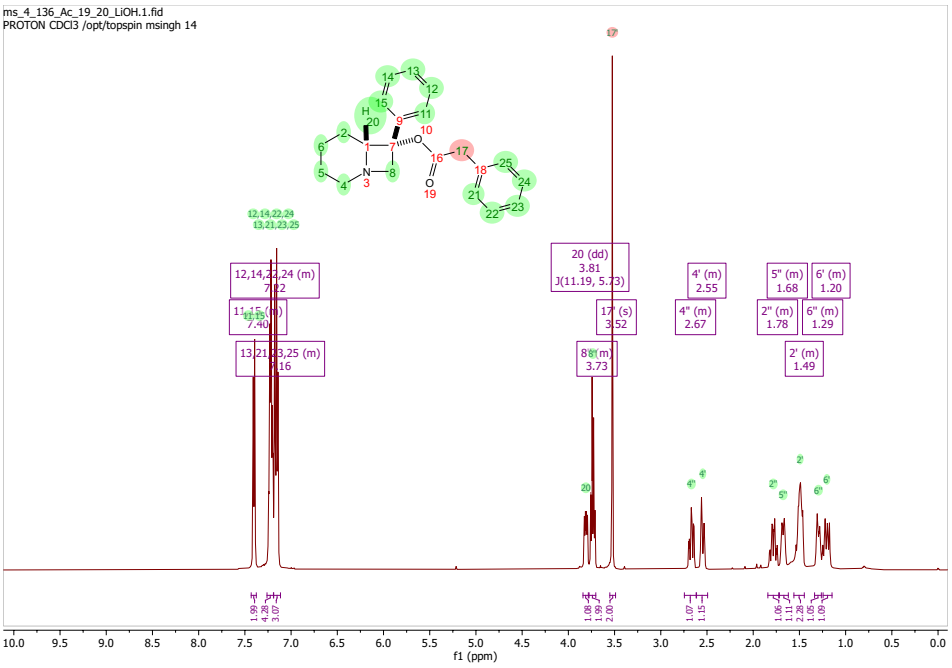


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of compound E4

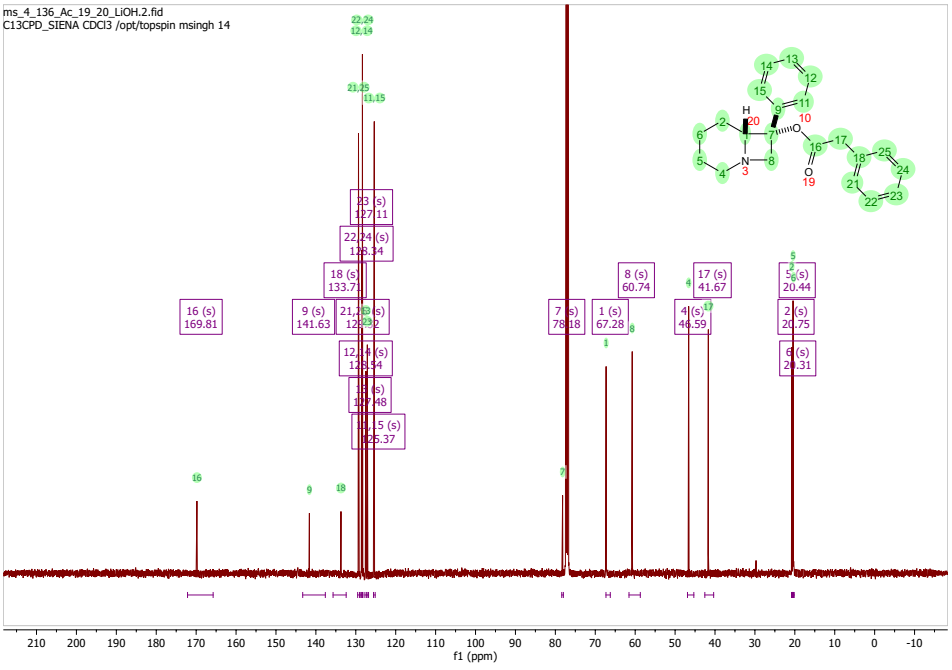


10.5.7 Compound E-1-1-2

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E-1-1-2

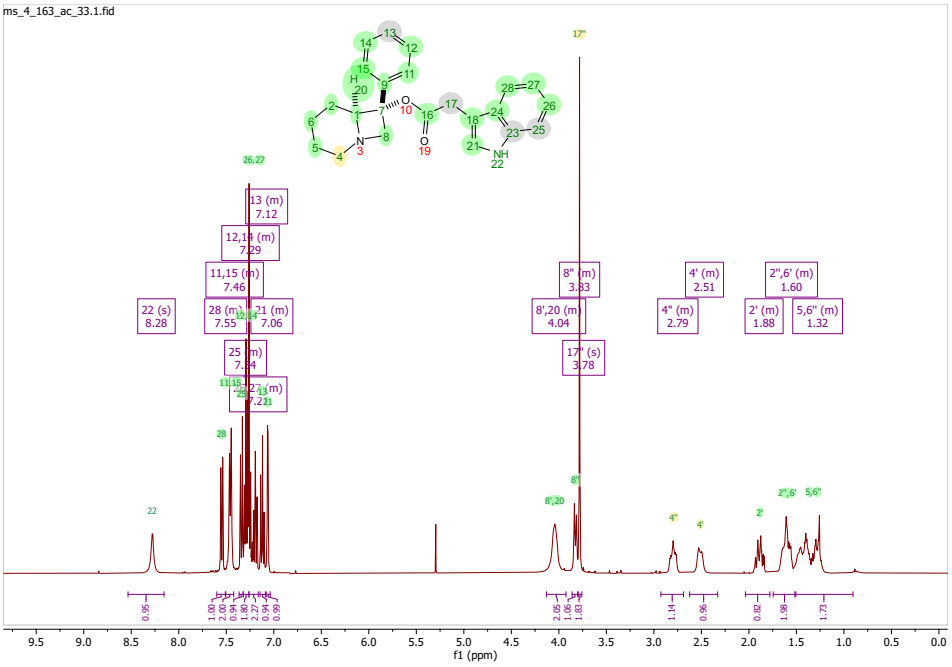


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of compound E-1-1-2

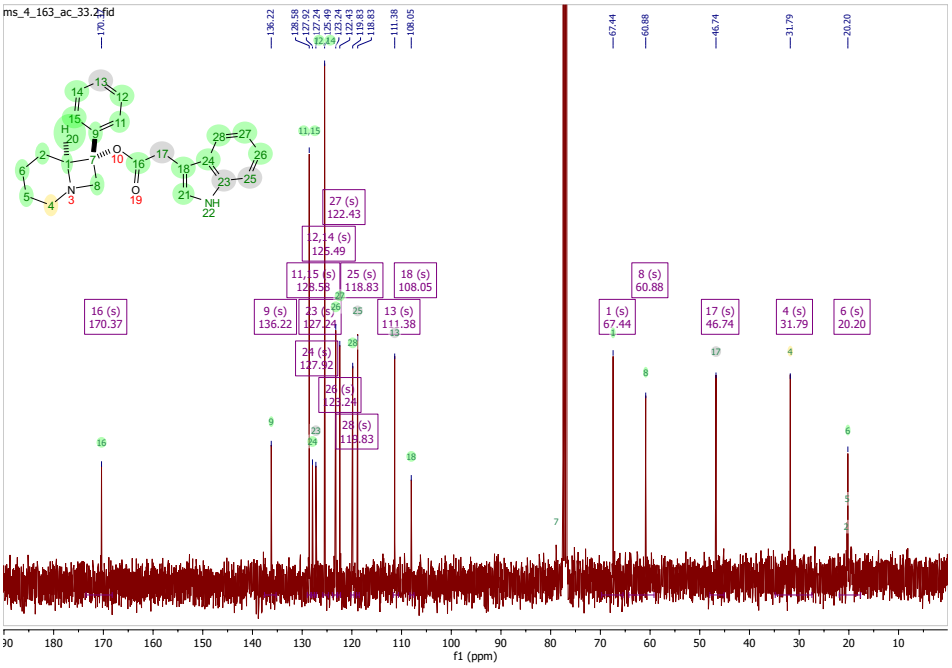


10.5.8 Compound E-1-1-3

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E-1-1-3

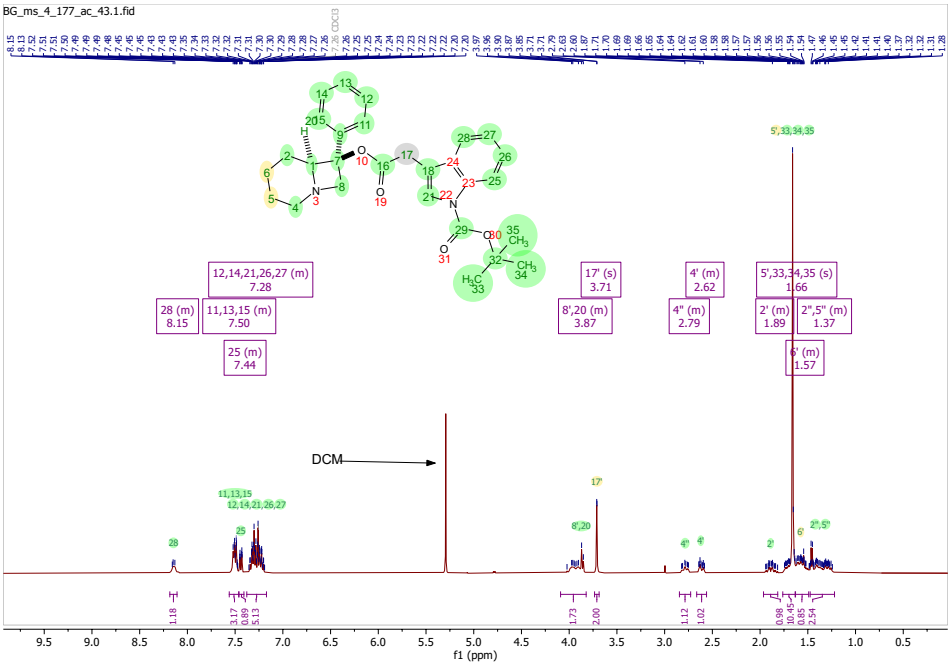


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E-1-1-3

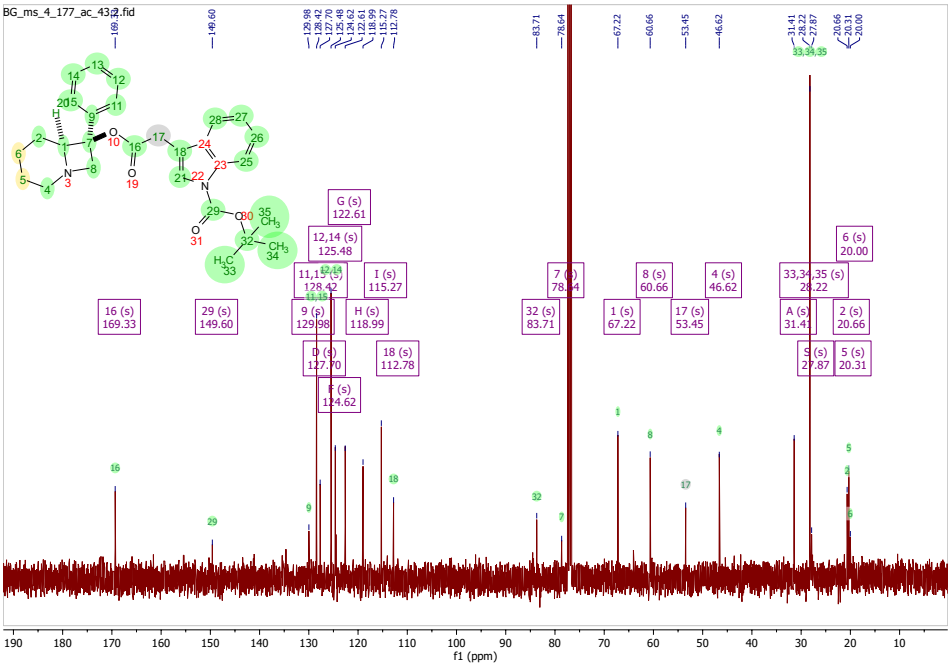


10.5.9 Compound E-1-1-3-Boc

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E-1-1-3-Boc

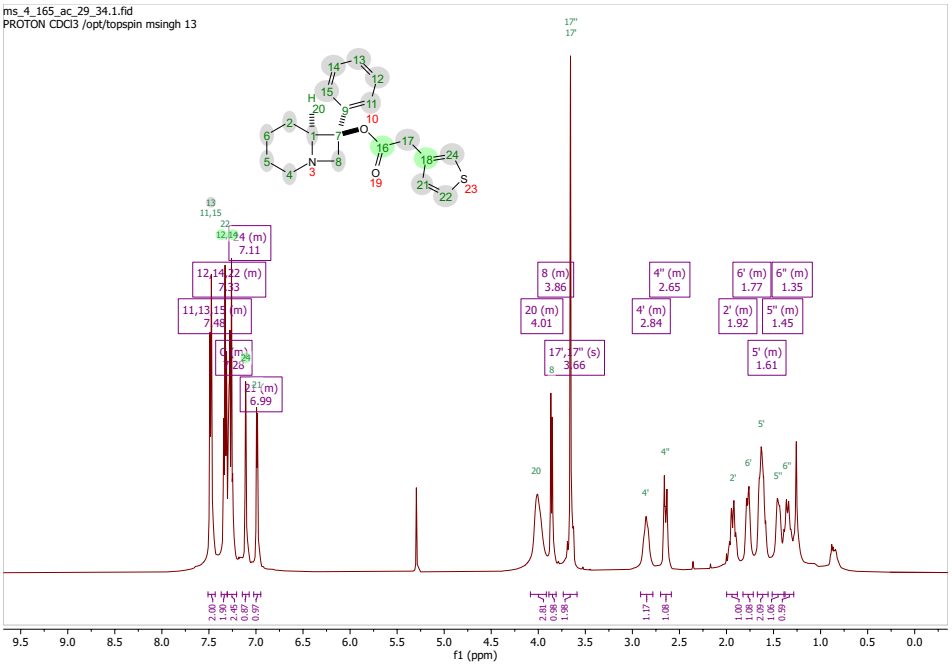


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E-1-1-3-Boc

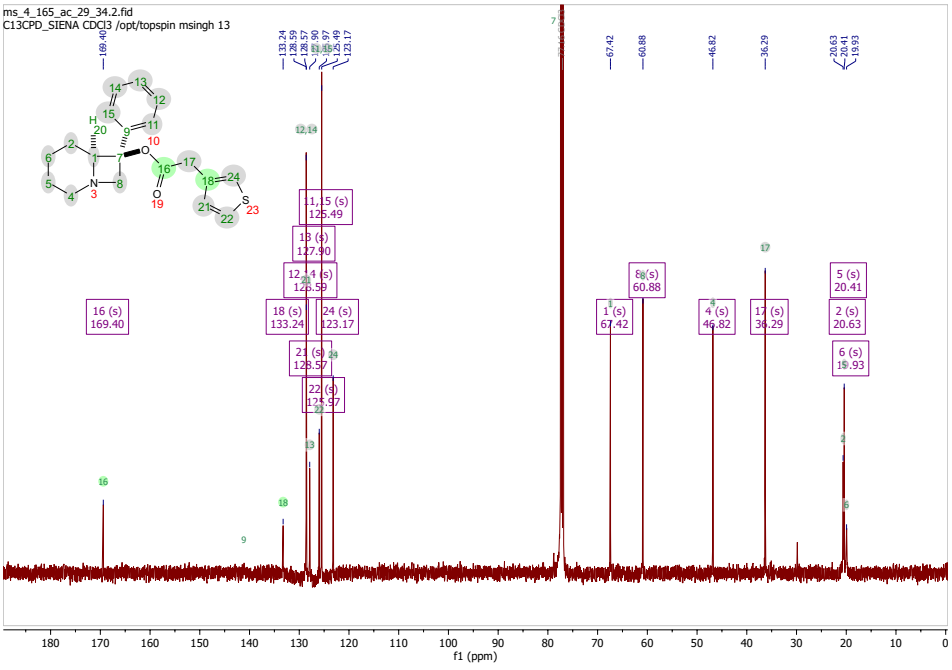


10.5.10 Compound E-1-1-4

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E-1-1-4

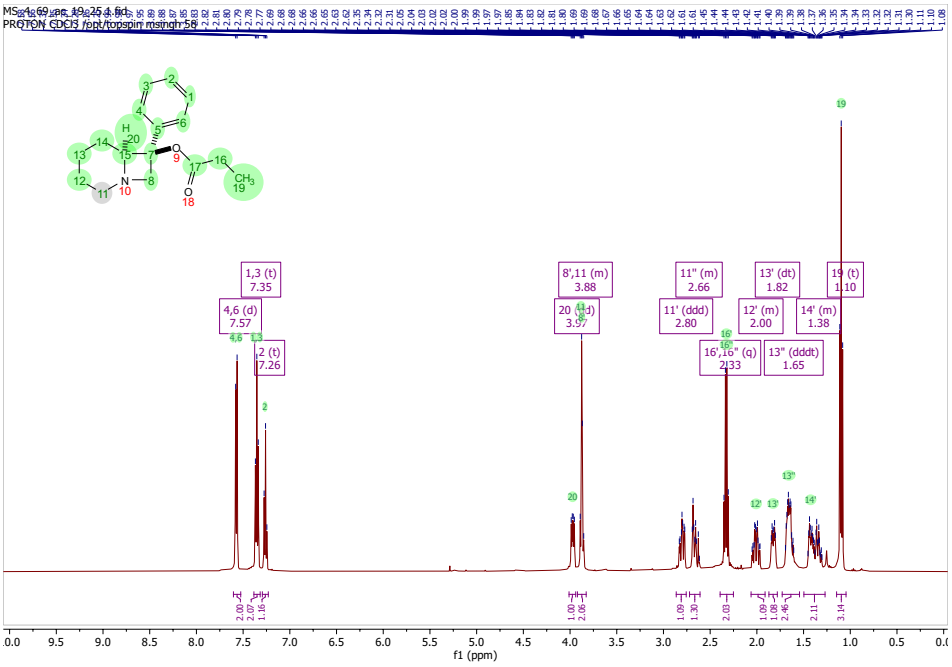


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of compound E-1-1-4

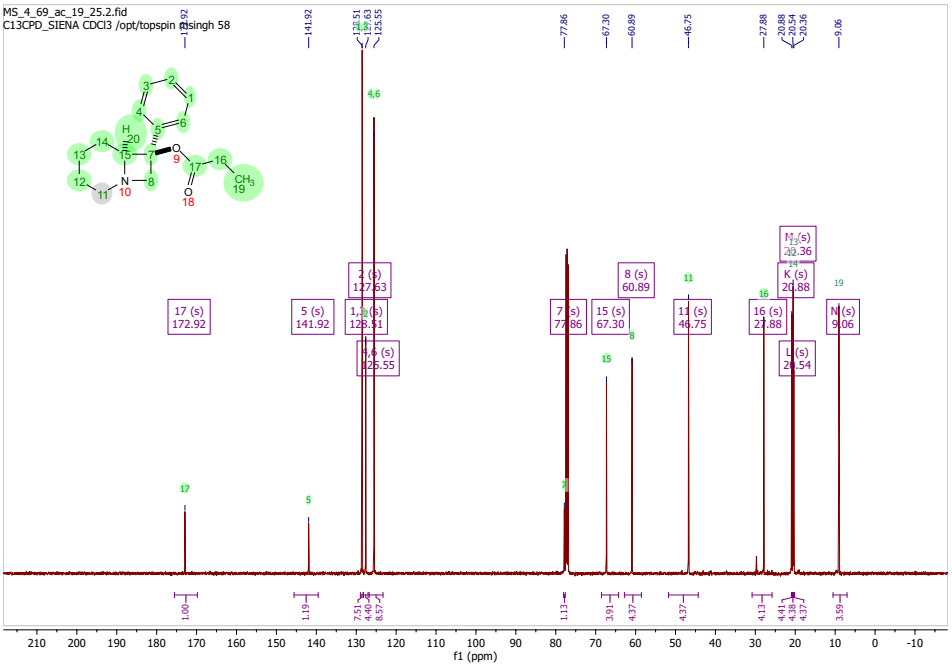


10.5.11 Compound E7

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E7

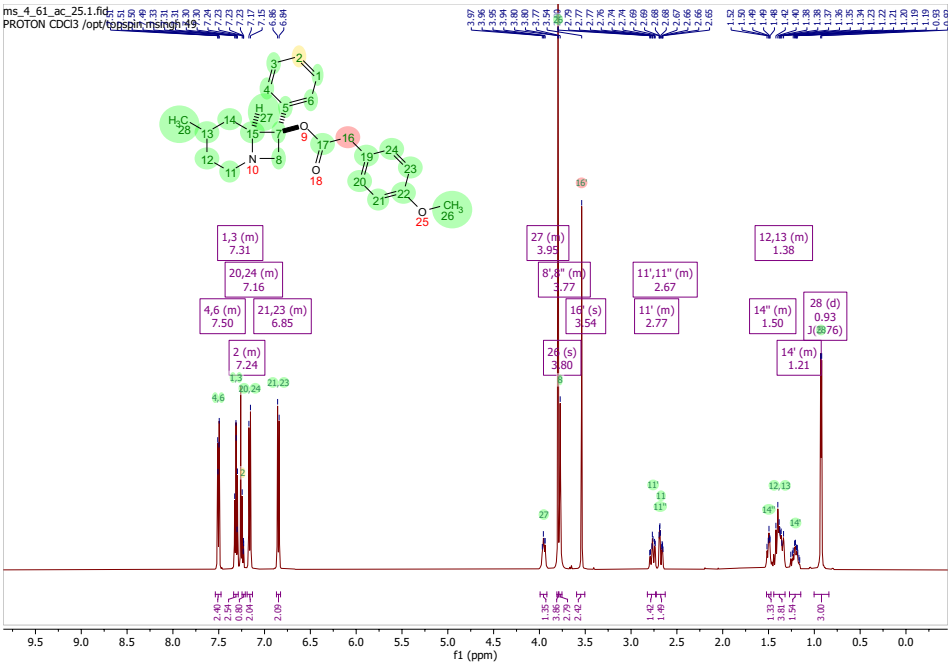


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E7

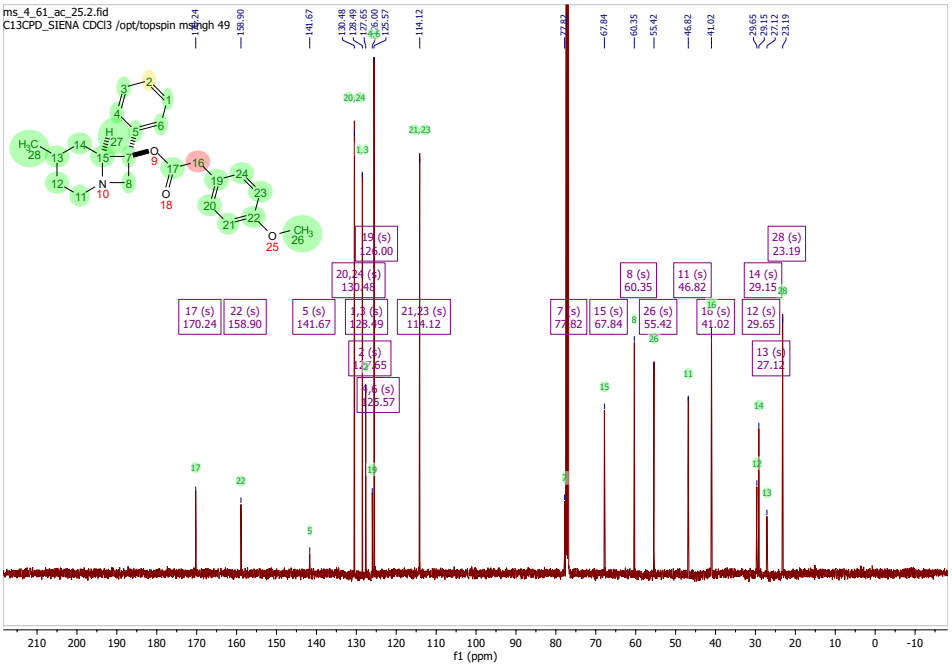


10.5.12 Compound E-1-2-1

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E-1-2-1

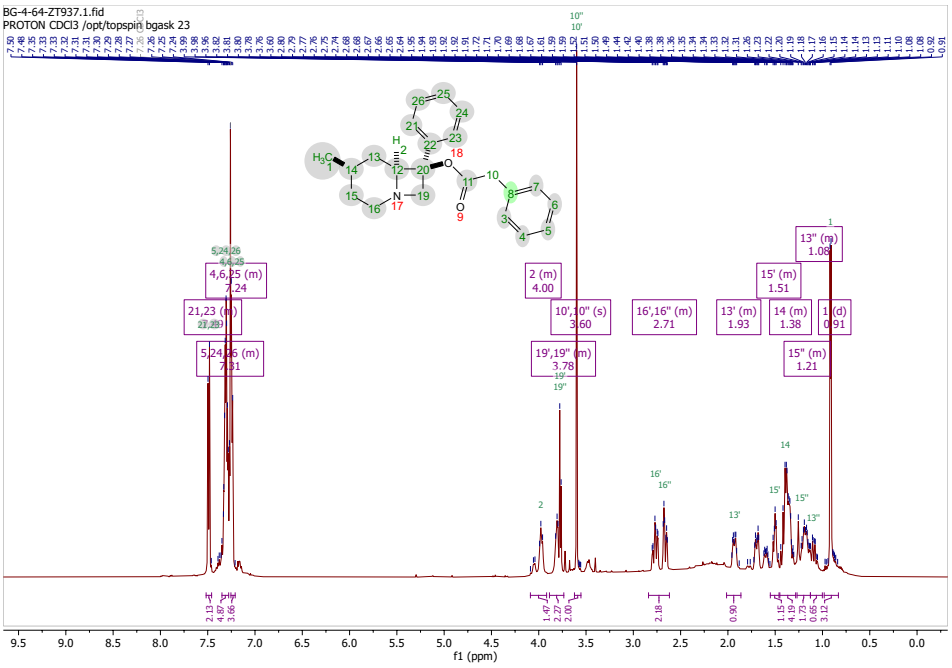


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E-1-2-1

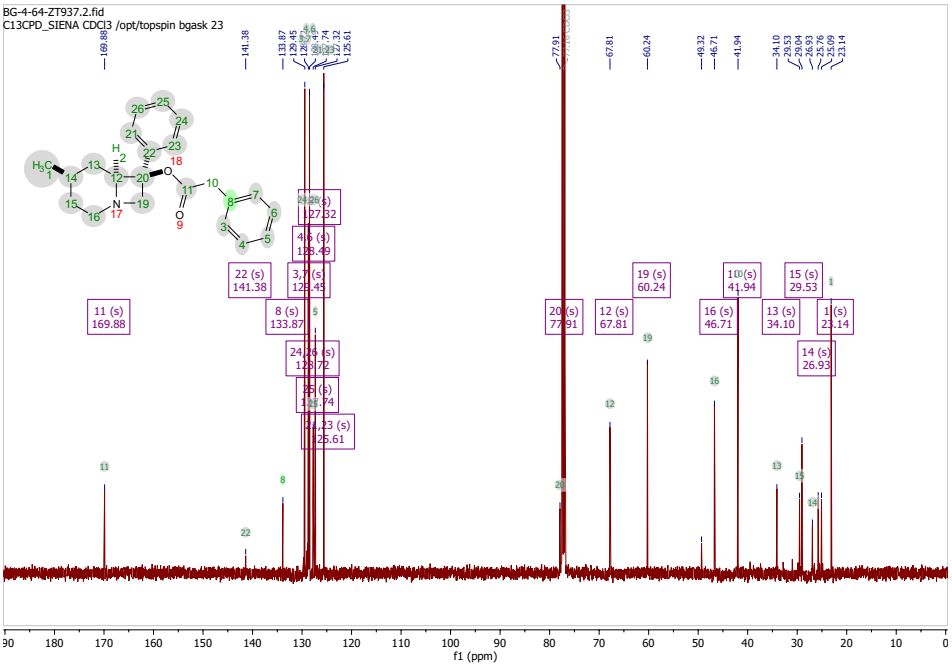


10.5.13 Compound E-1-2-2

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E-1-2-2

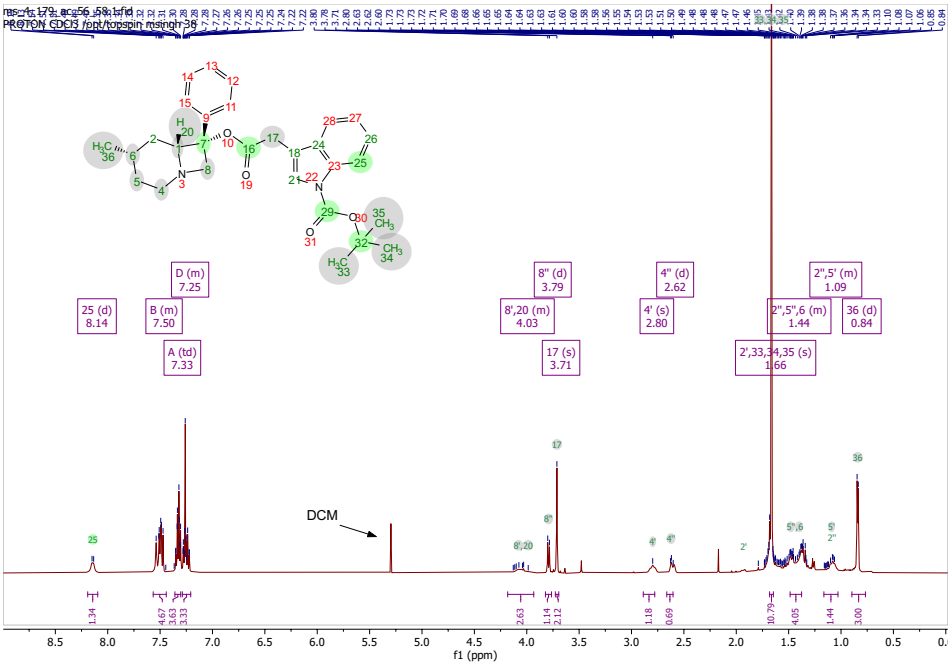


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E-1-2-2

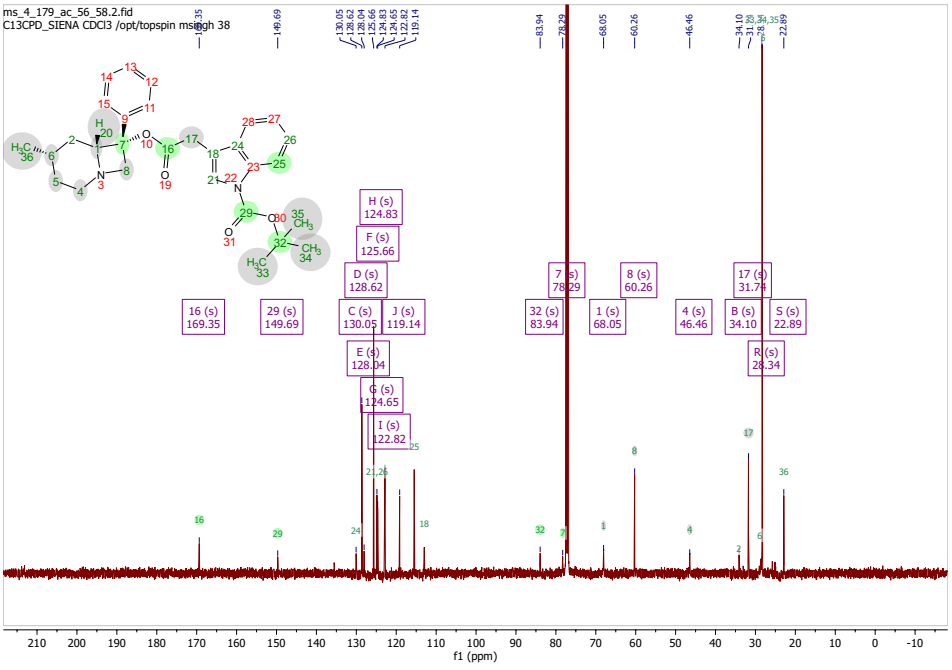


10.5.14 Compound E-1-2-3

^{1}H NMR spectrum (500 MHz, Chloroform-d) of compound E-1-2-3

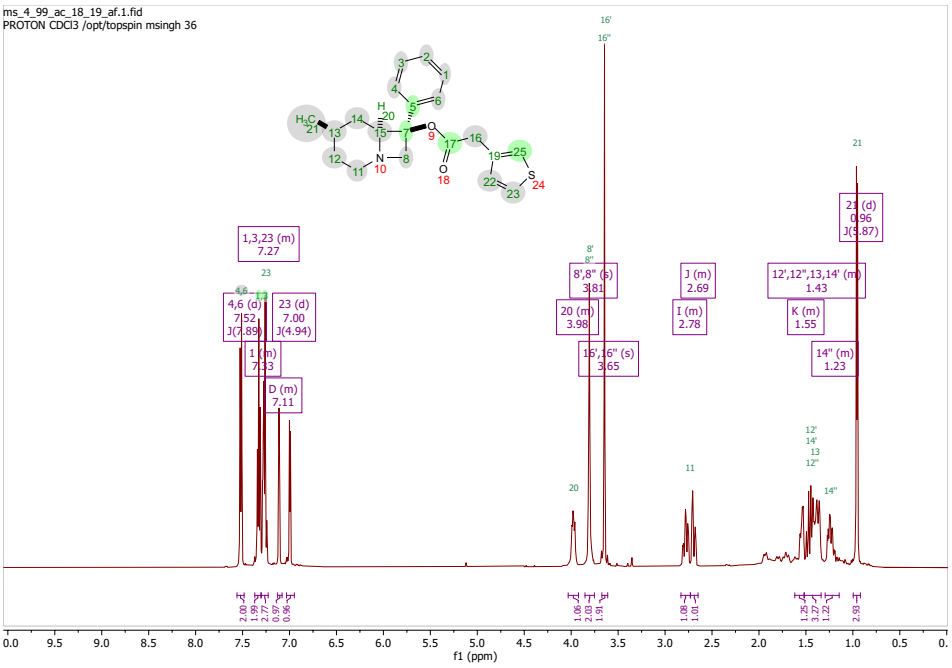


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E-1-2-3

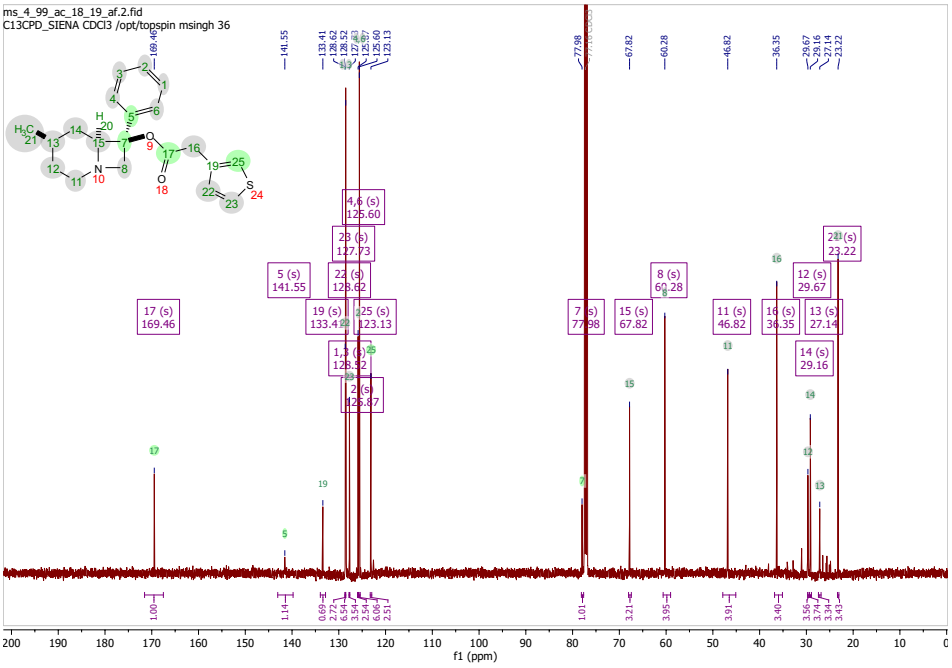


10.5.15 Compound E-1-2-4

^{1}H NMR spectrum (500 MHz, Chloroform-d) of compound E-1-2-4

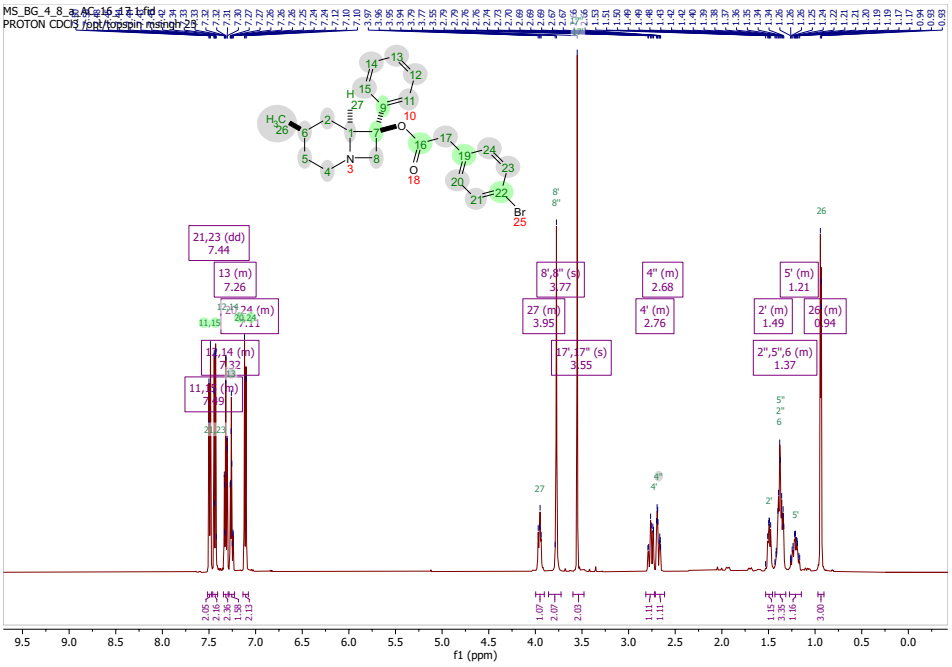


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E-1-2-4

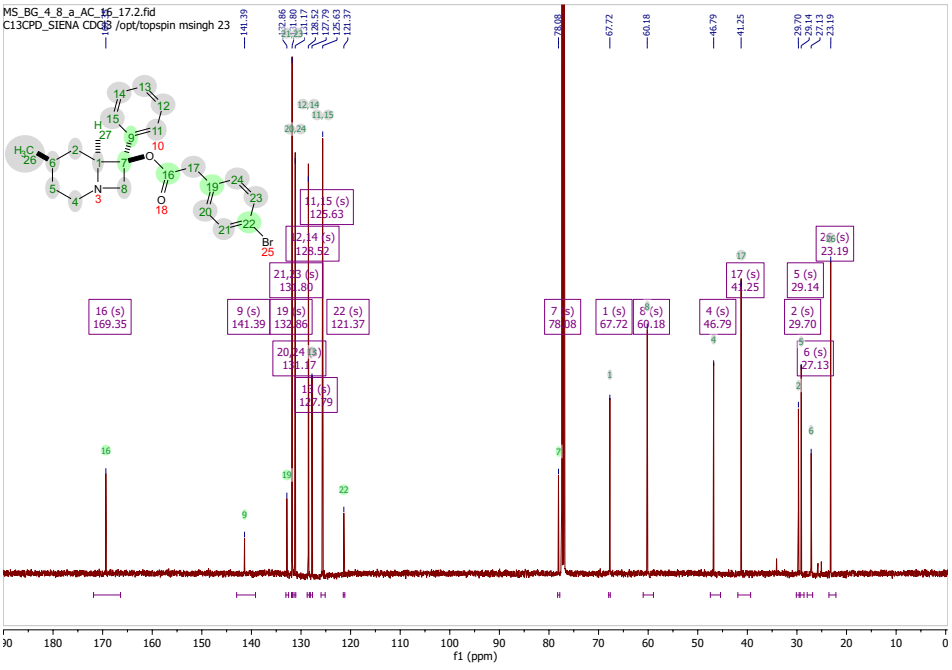


10.5.16 Compound E12

^{1}H NMR spectrum (500 MHz, Chloroform-d) of compound E12

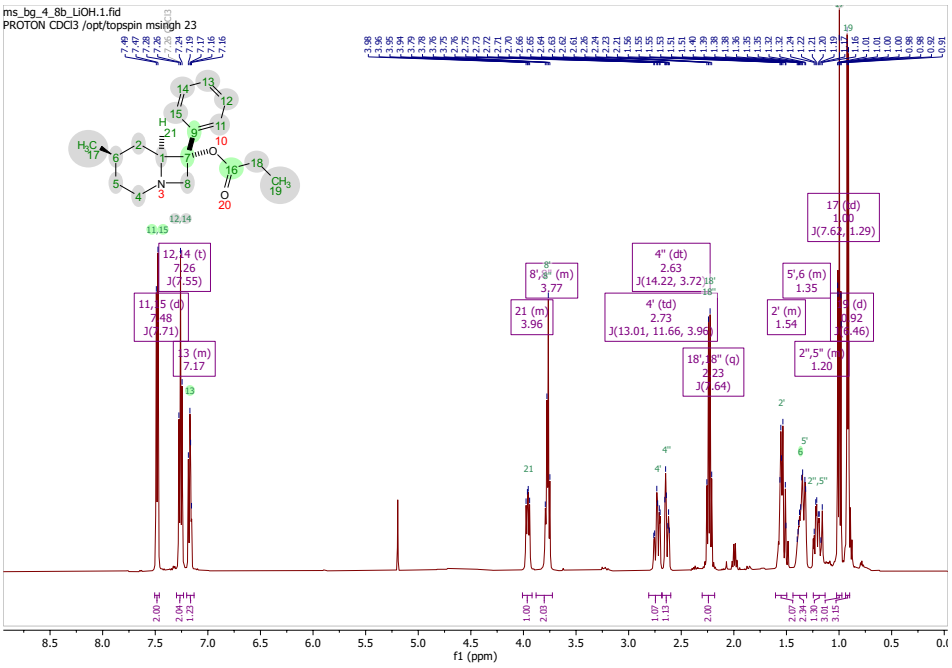


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E12

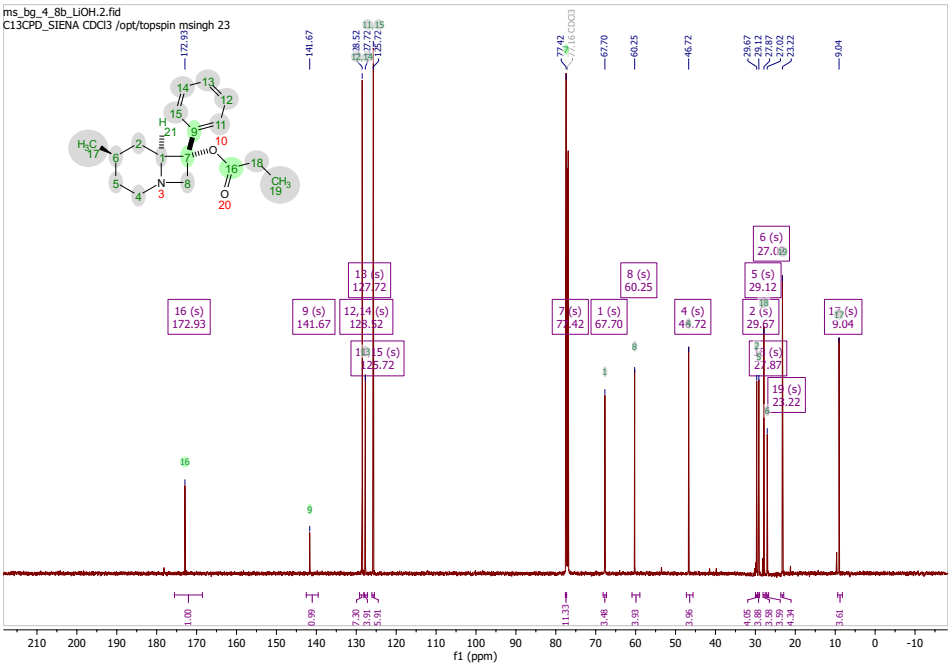


10.5.17 Compound E13

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E13

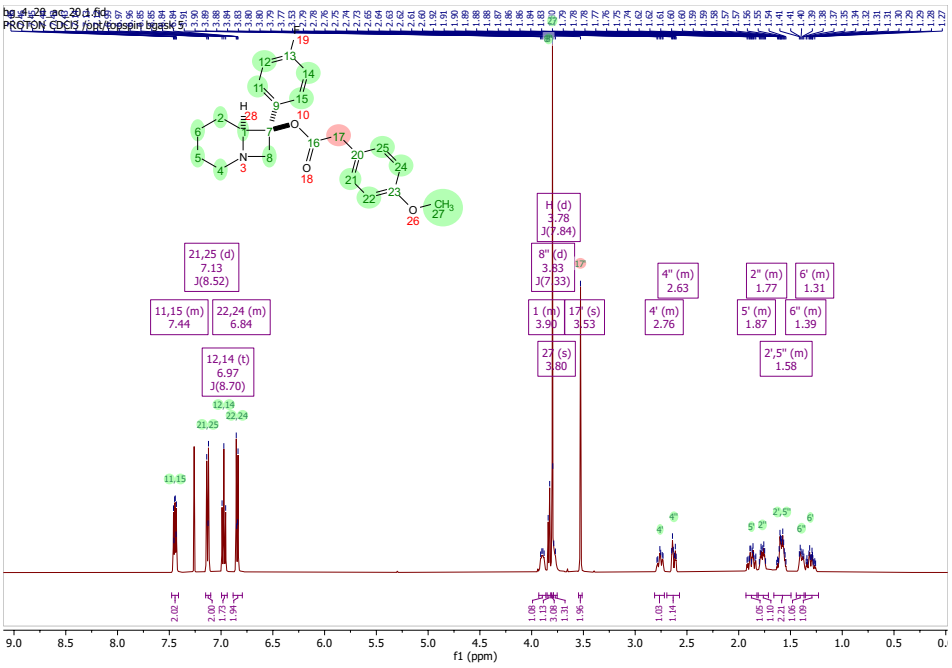


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E13

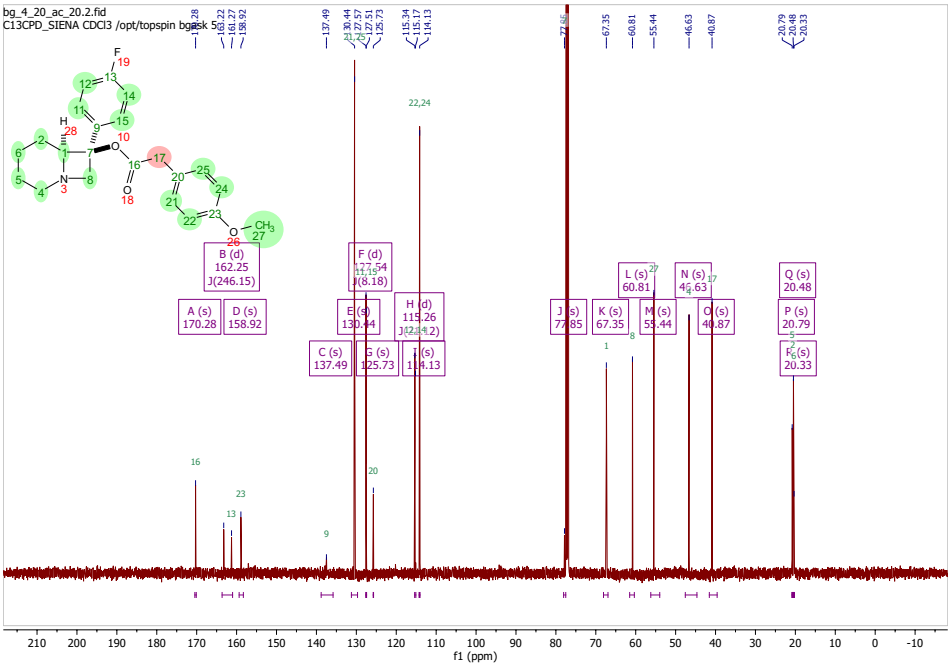


10.5.18 Compound E-2-1-1

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E-2-1-1

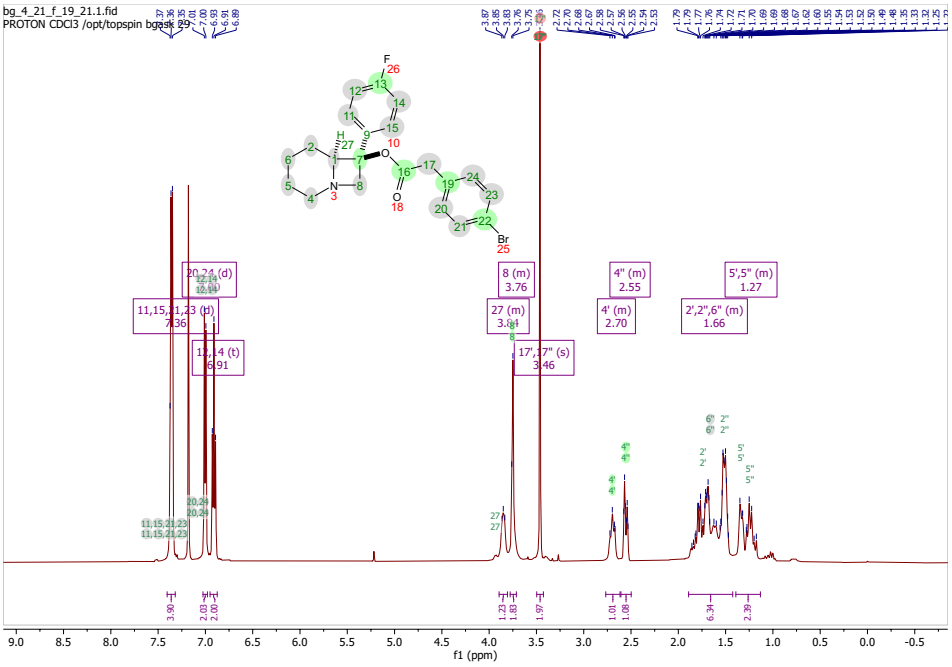


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E-2-1-1

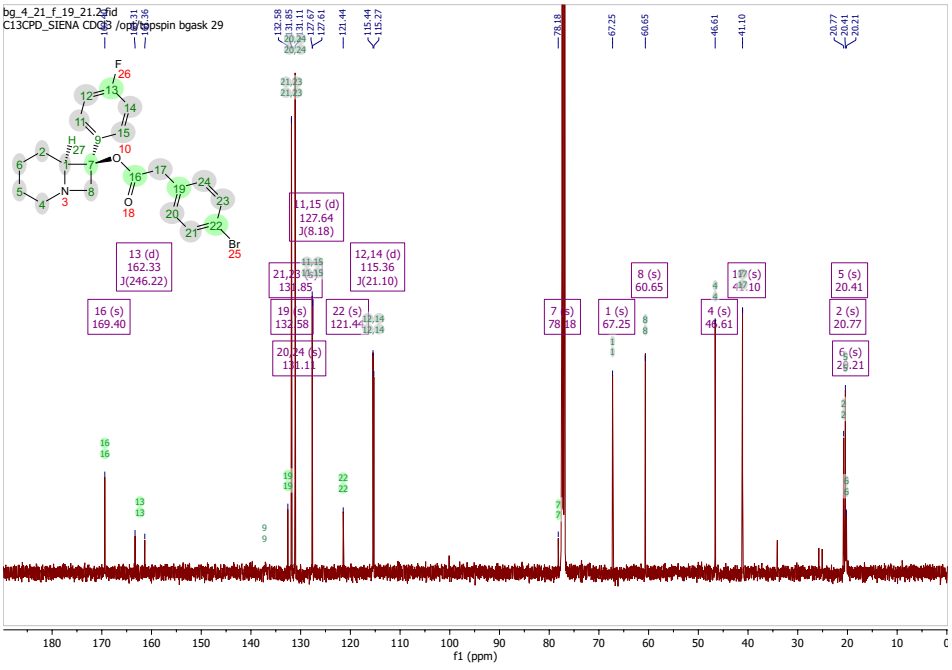


10.5.19 Compound E15

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E15

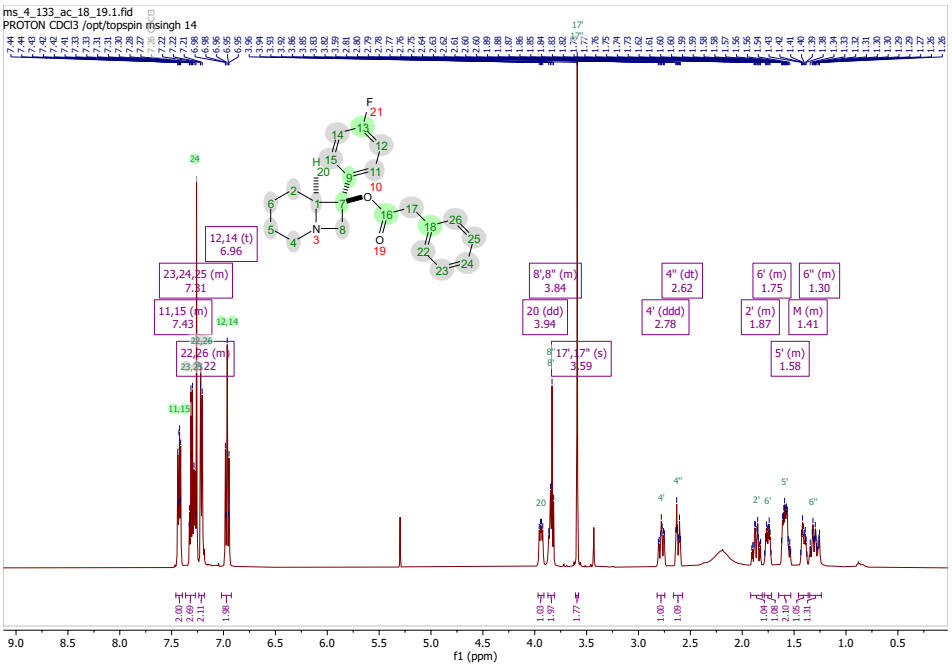


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E15

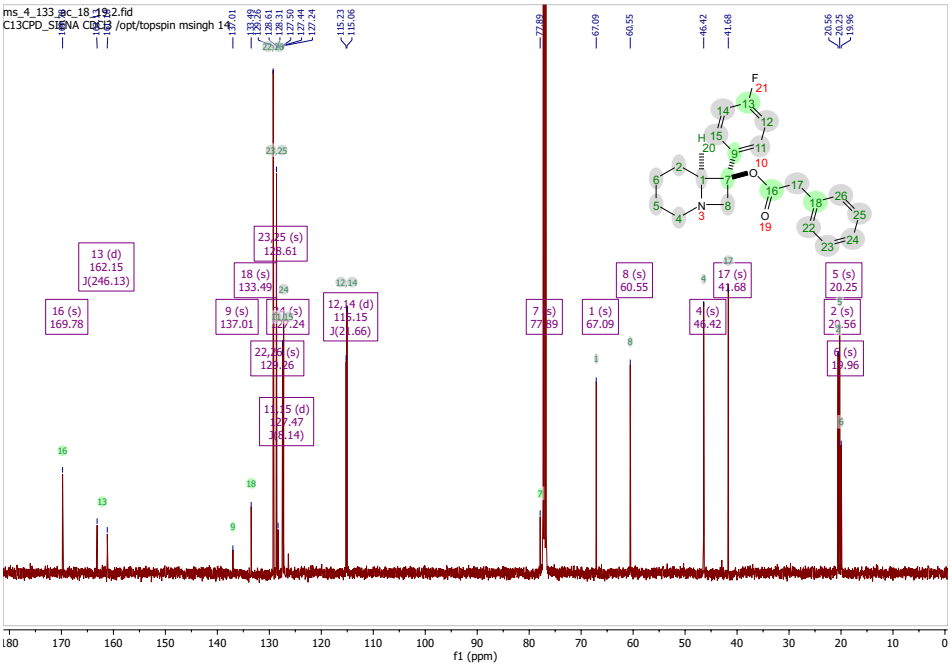


10.5.20 Compound E-2-1-2

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E-2-1-2

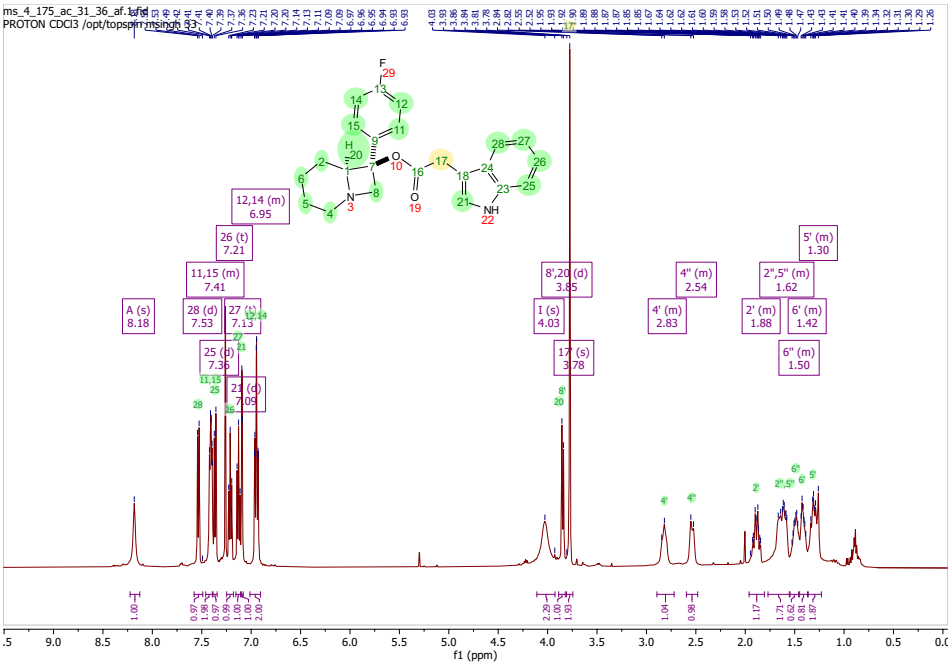


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E-2-1-2

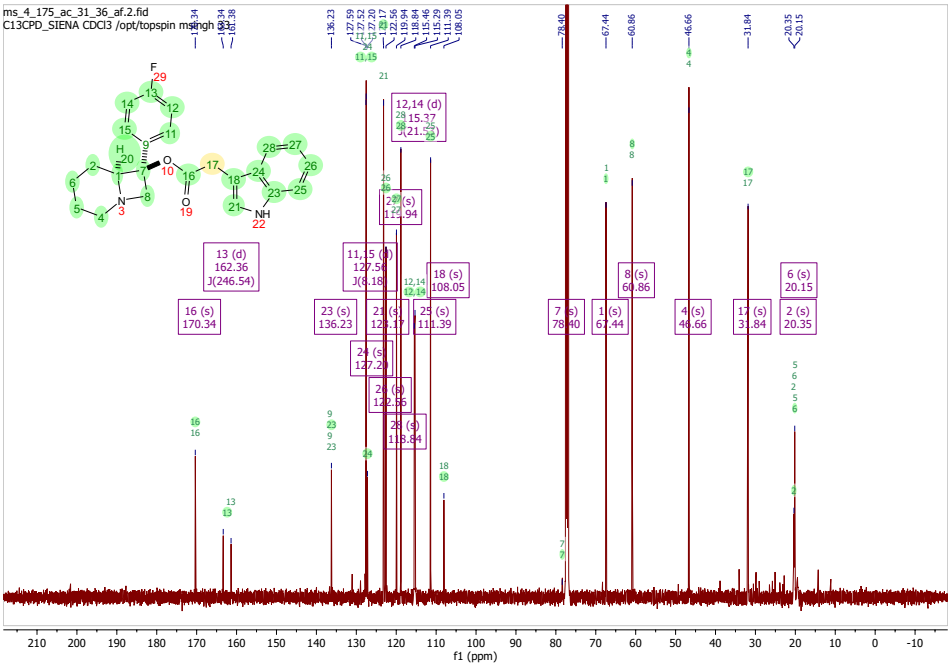


10.5.21 Compound E-2-1-3

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E-2-1-3

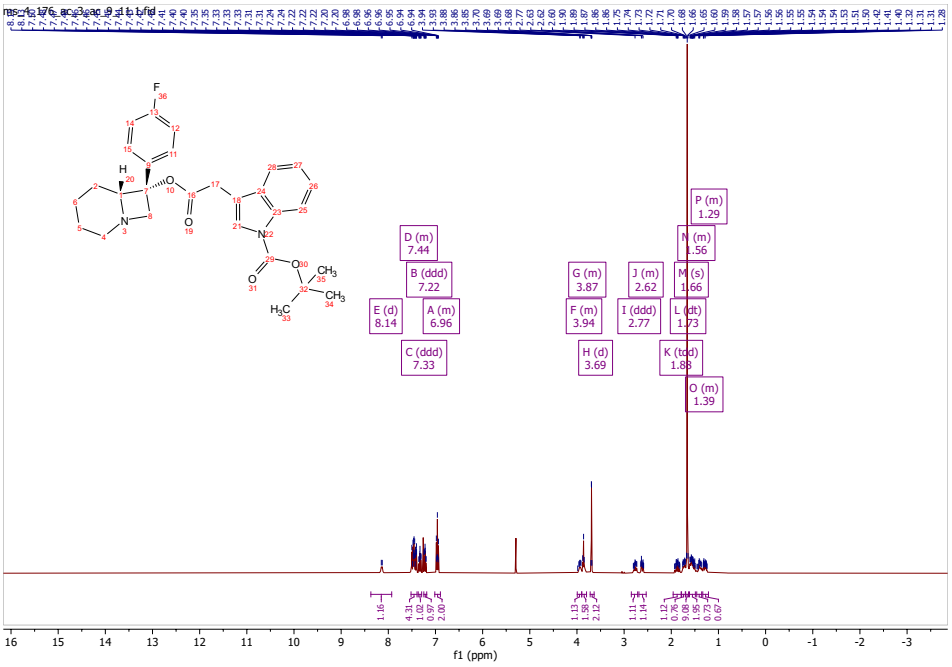


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E-2-1-3

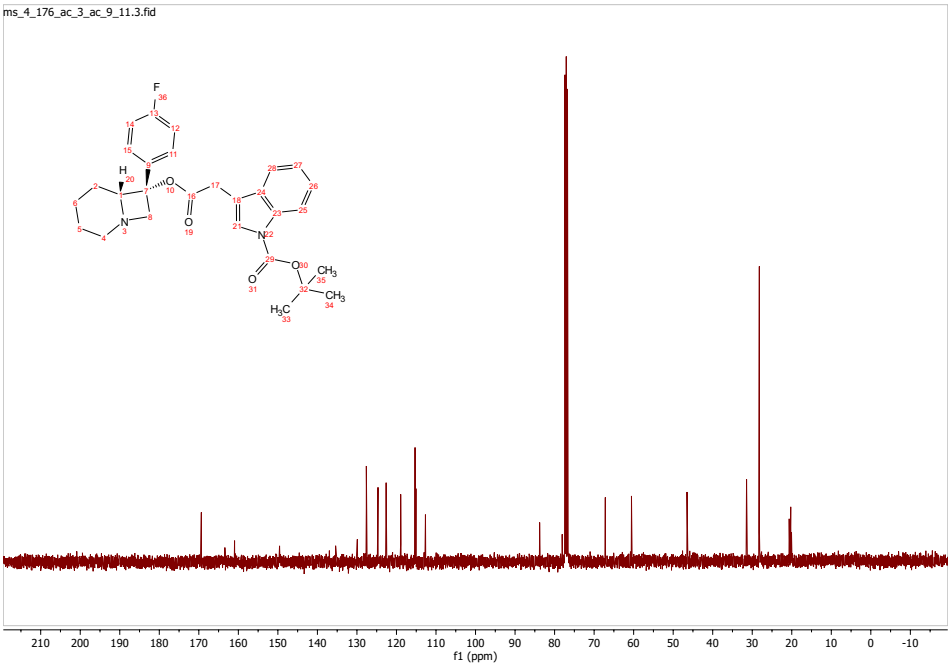


10.5.22 Compound E-2-1-3-Boc

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E-2-1-3-Boc

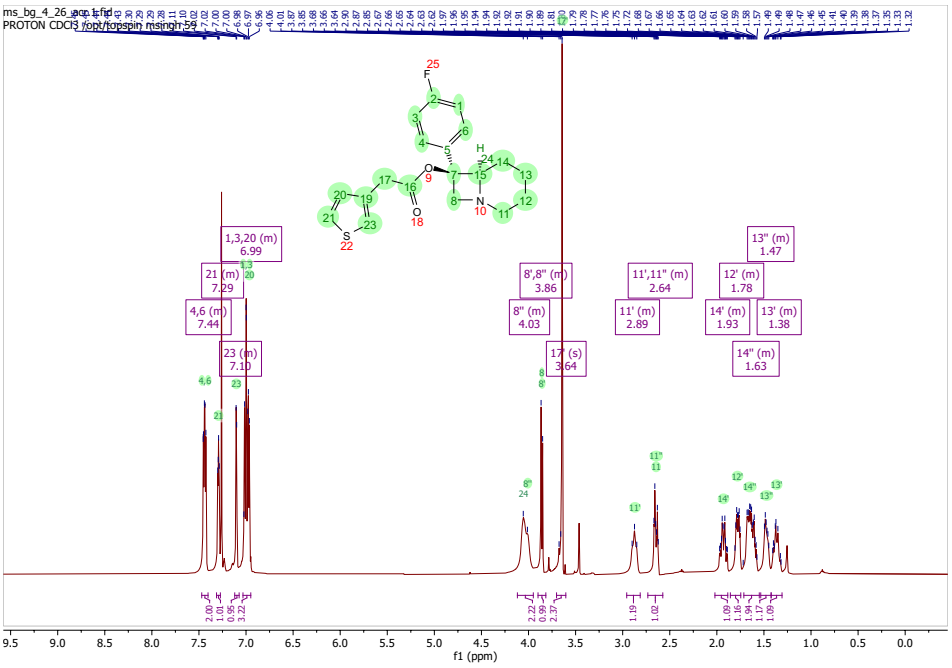


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E-2-1-3-Boc

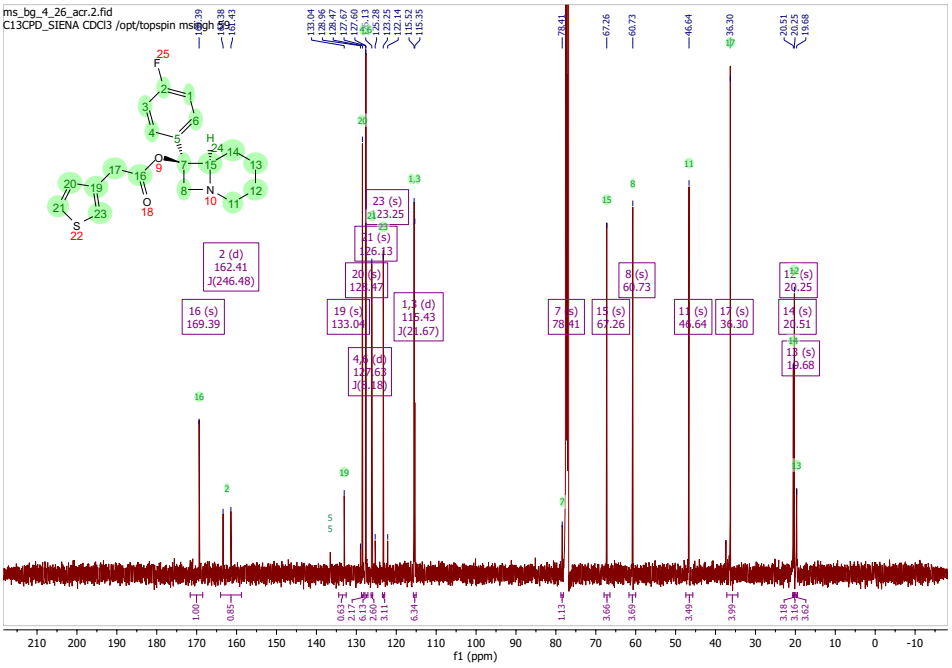


10.5.23 Compound E-2-1-4

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E-2-1-4

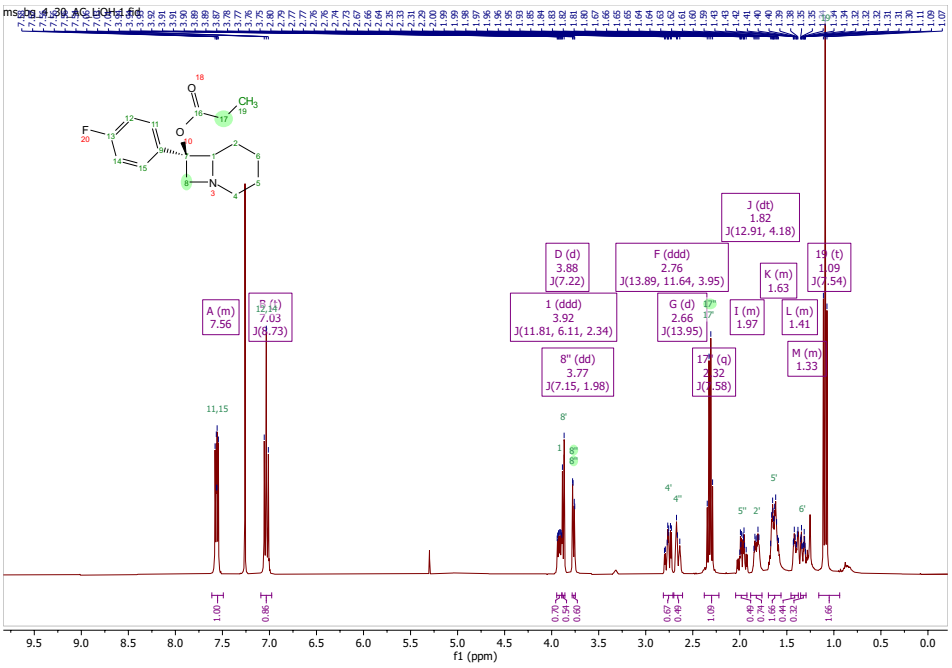


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E-2-1-4

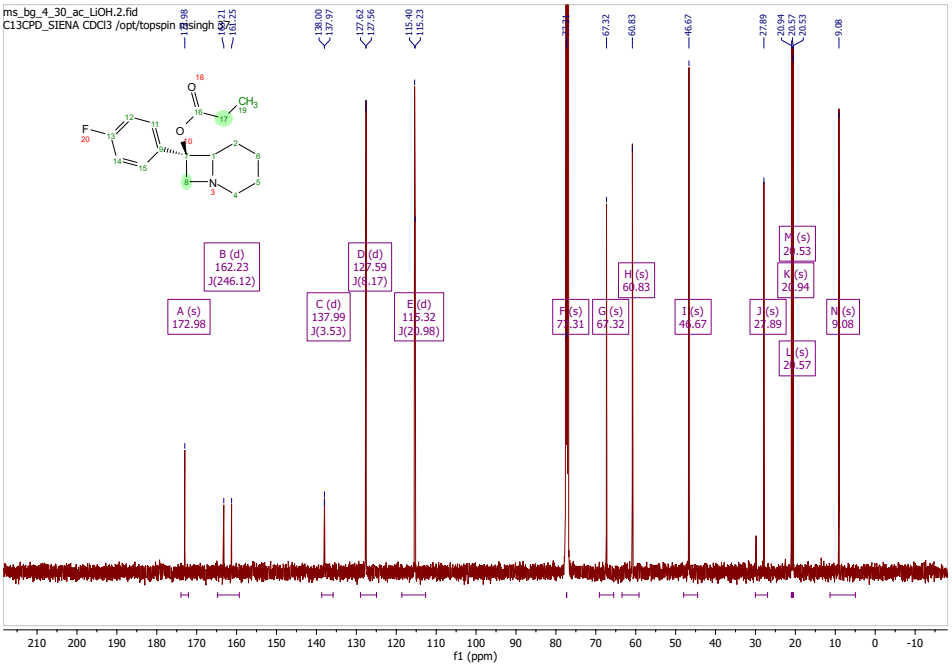


10.5.24 Compound E18

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E18

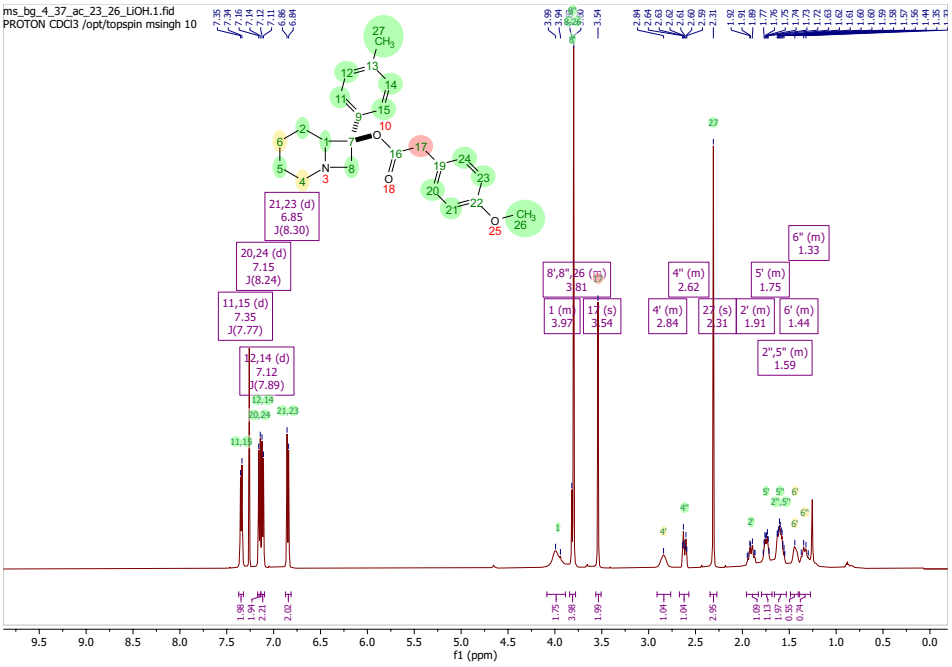


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E18

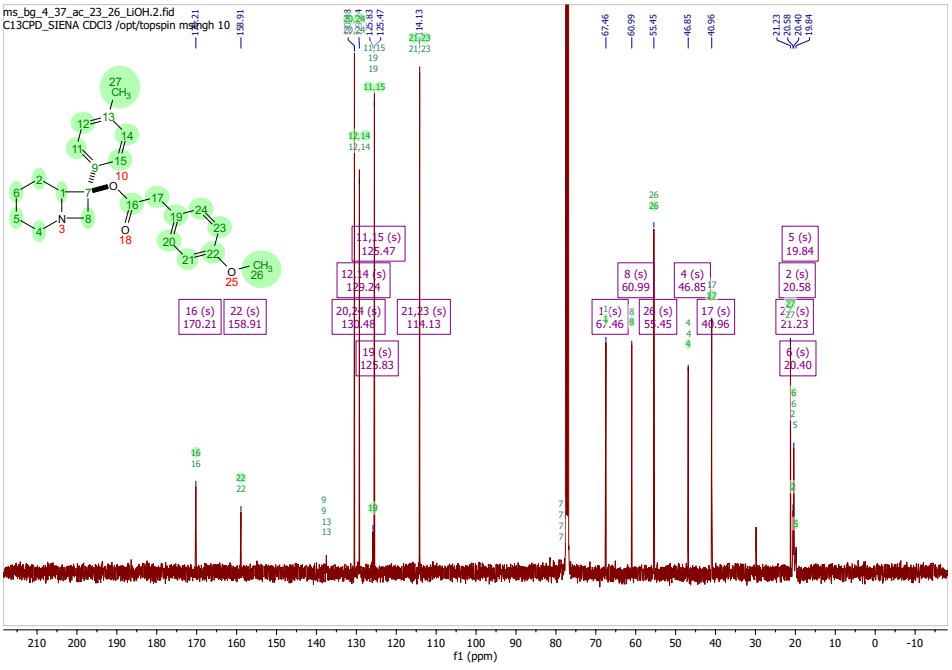


10.5.25 Compound E-3-1-1

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E-3-1-1

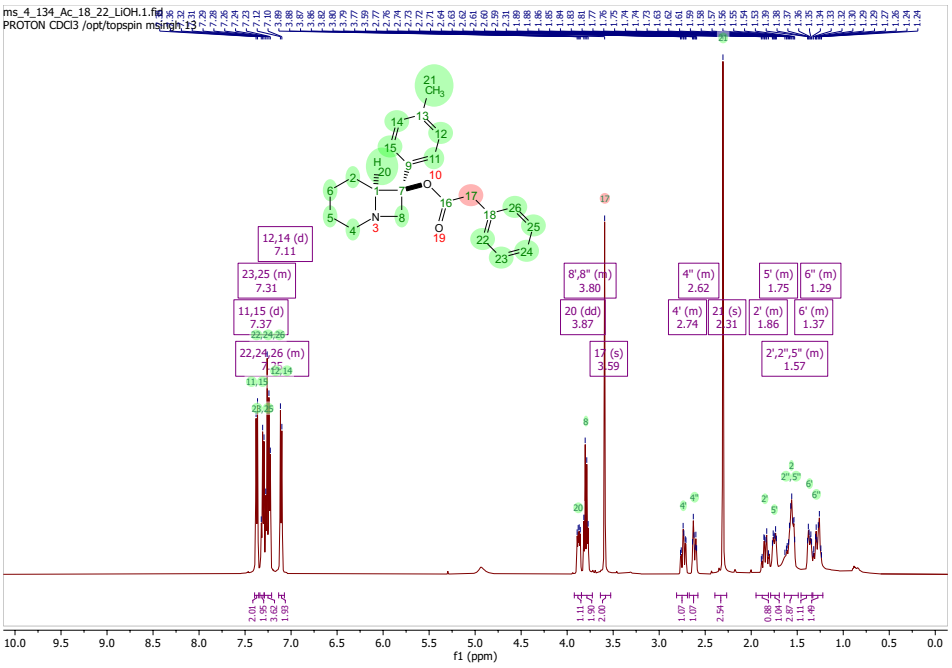


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E-3-1-1

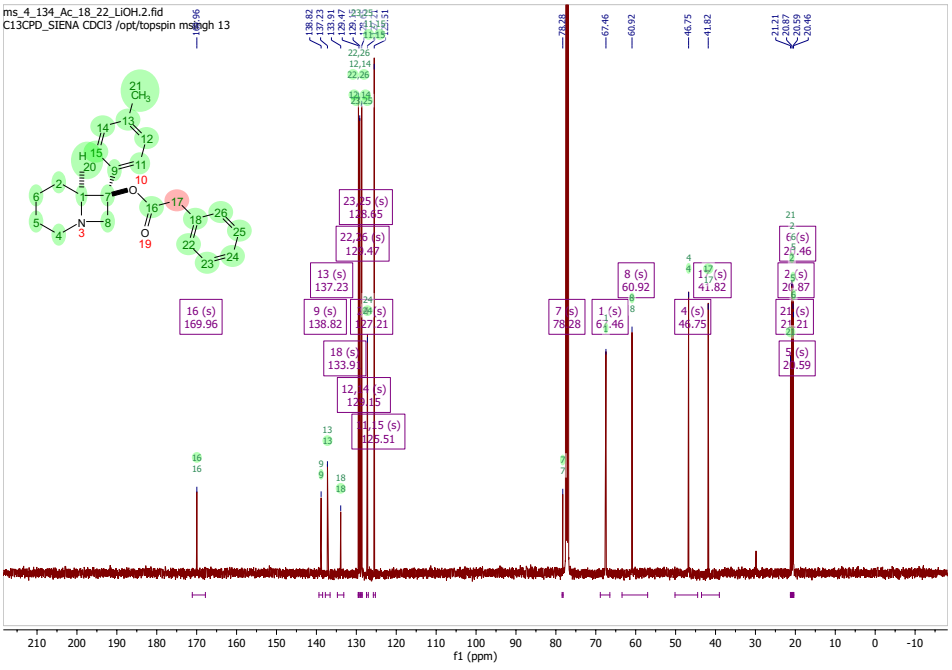


10.5.26 Compound E-3-1-2

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E-3-1-2

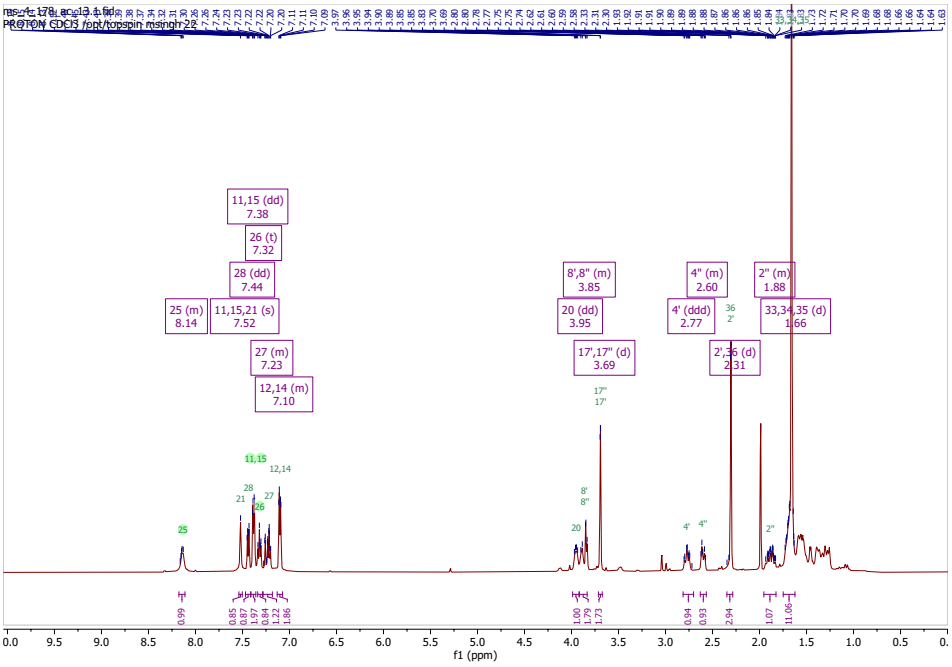


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E-3-1-2

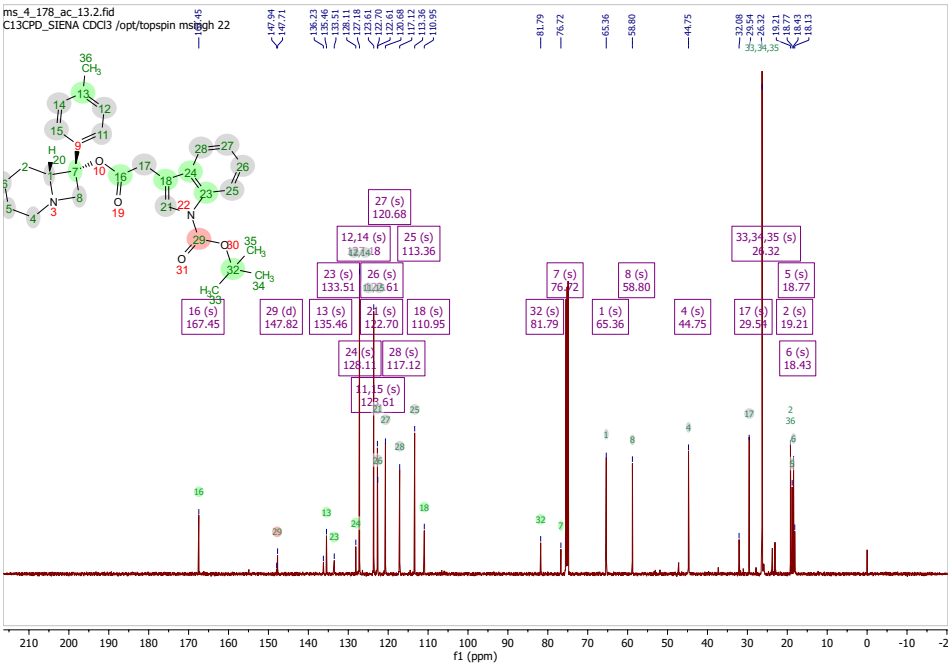


10.5.27 Compound E-3-1-3

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E-3-1-3

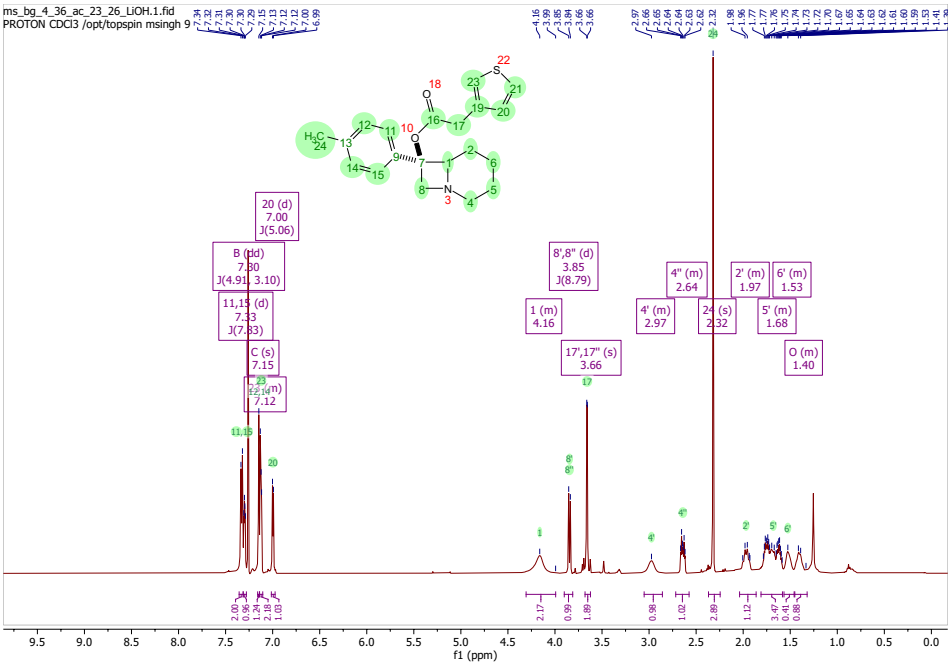


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E-3-1-3

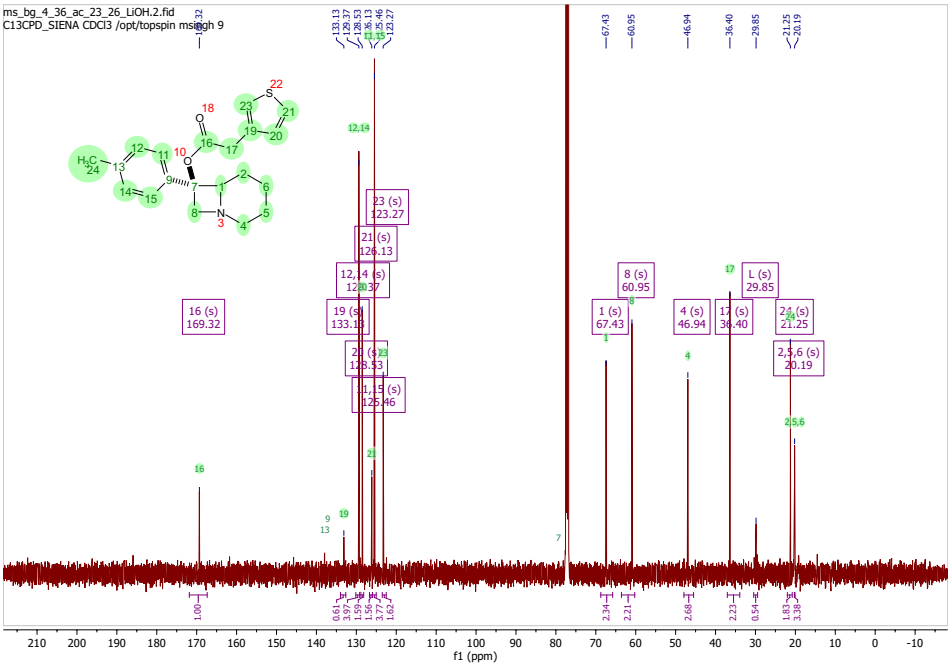


10.5.28 Compound E-3-1-4

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound E-3-1-4



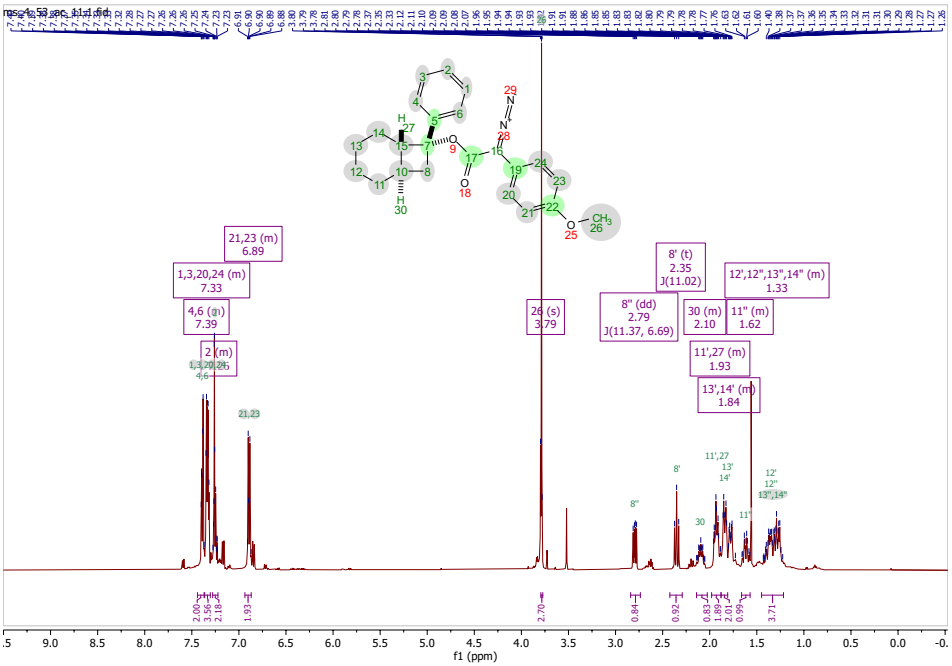
^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound E-3-1-4



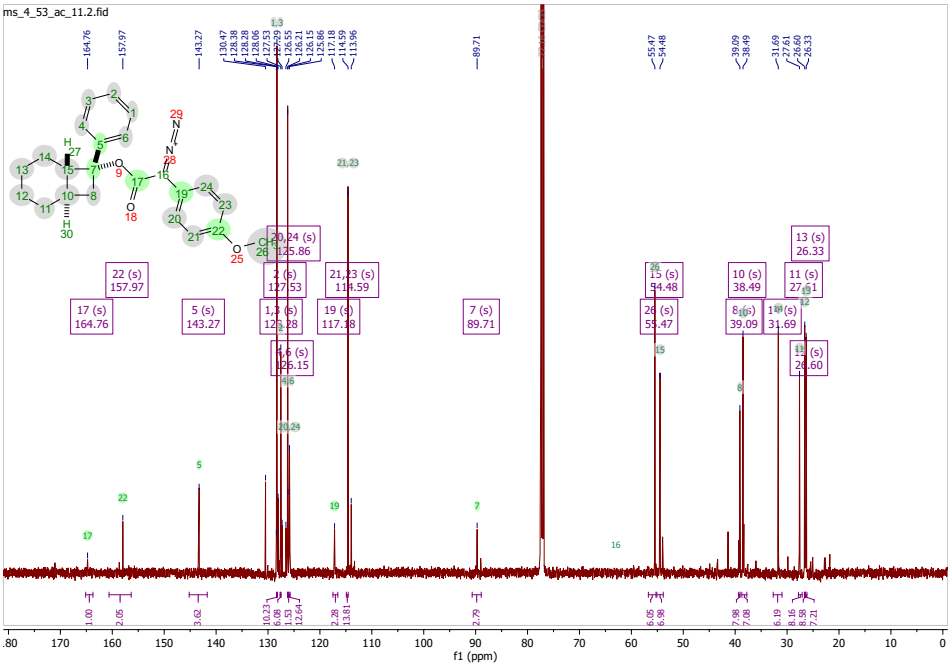
10.6 Diazo

10.6.1 Compound D1

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D1

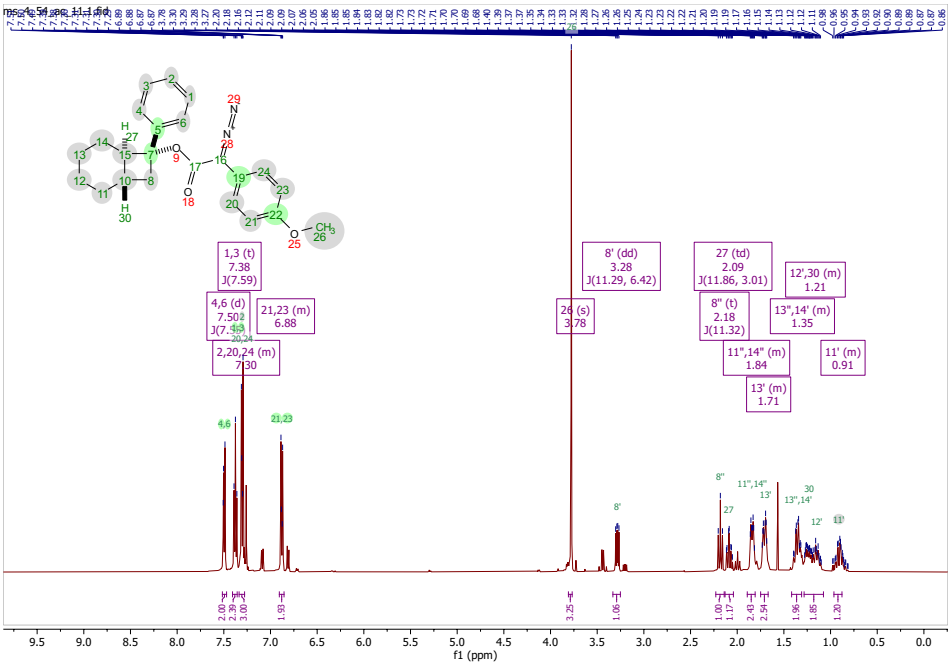


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D1

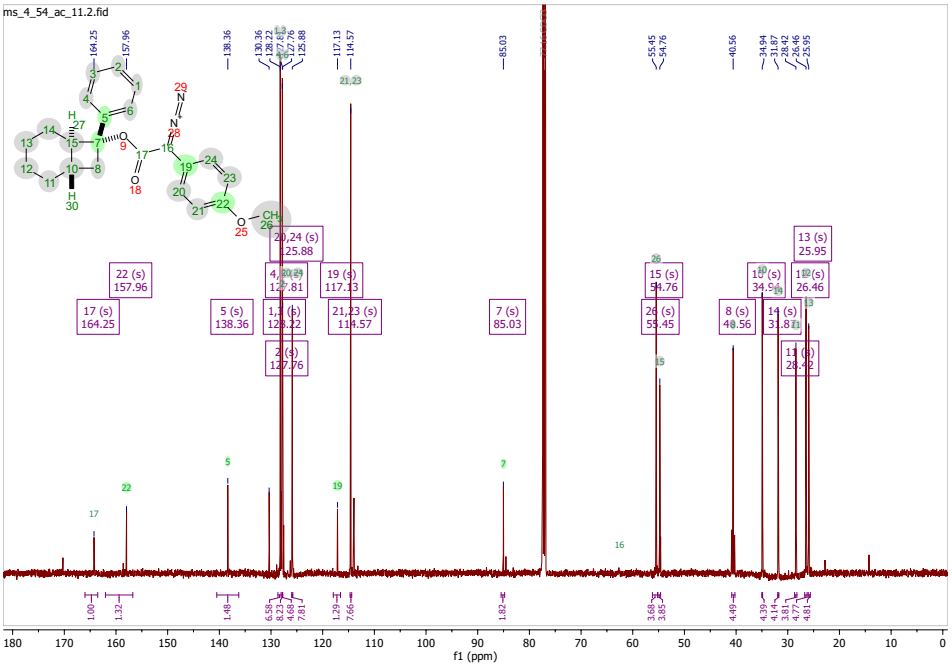


10.6.2 Compound D2

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D2

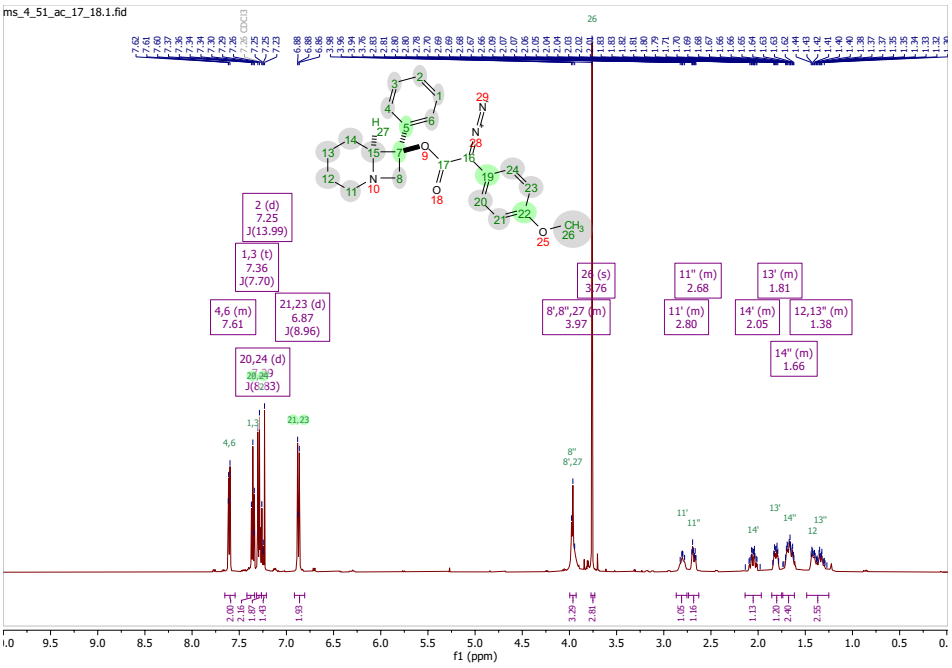


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D2

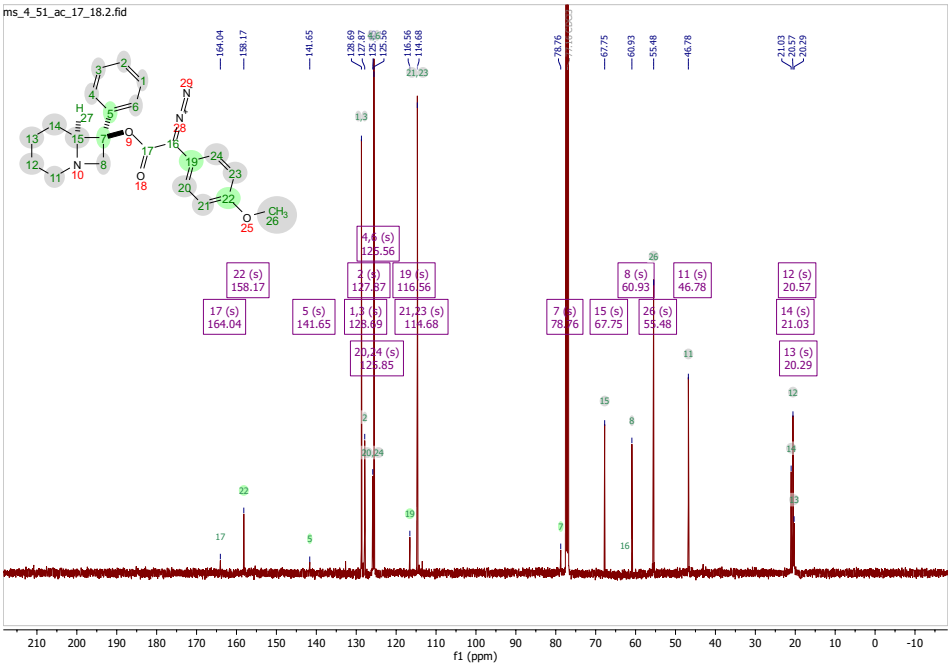


10.6.3 Compound D-1-1-1

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D-1-1-1

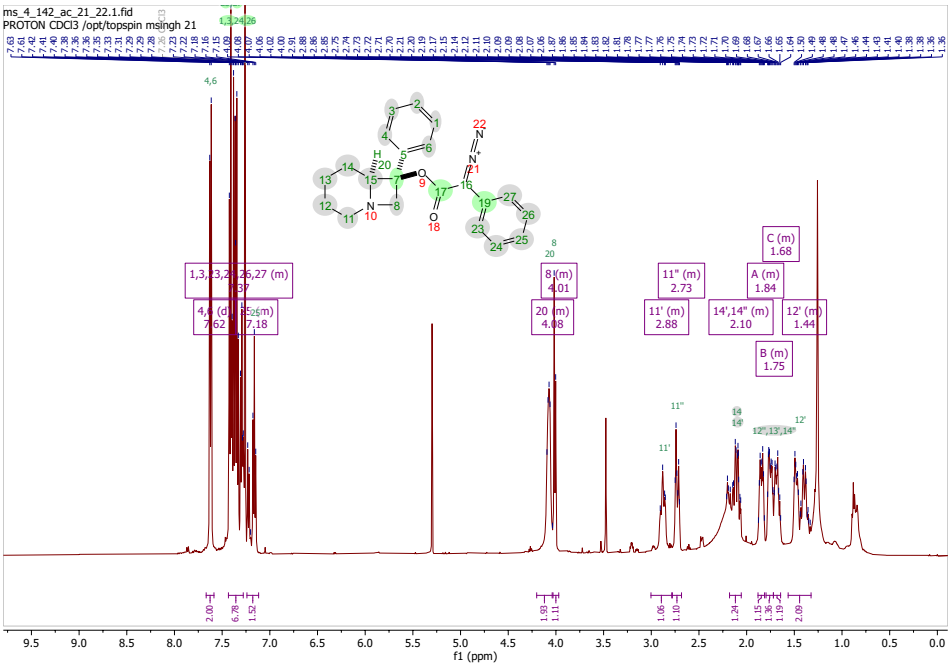


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D-1-1-1

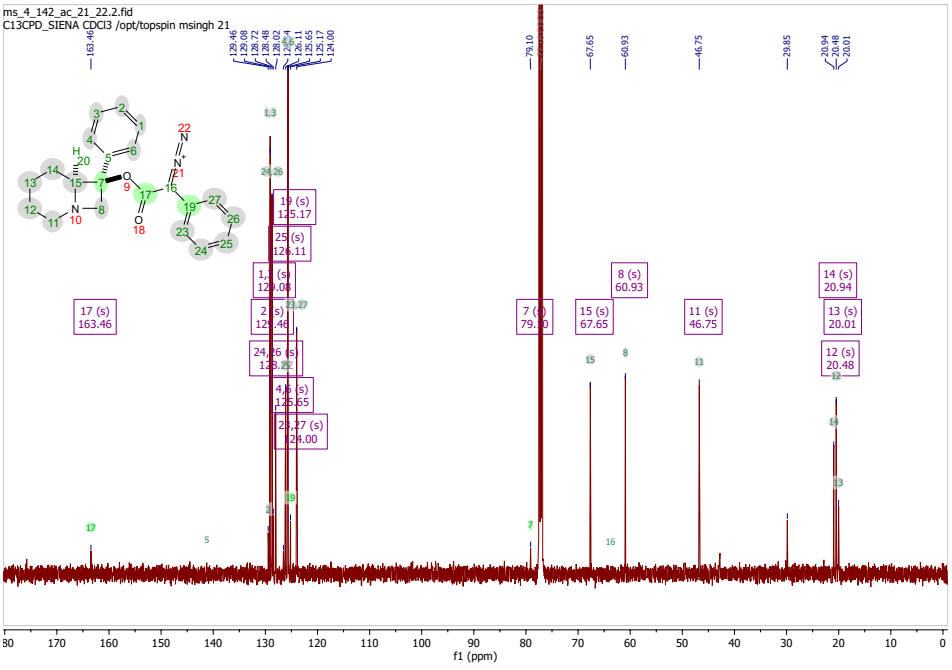


10.6.4 Compound D-1-1-2

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D-1-1-2

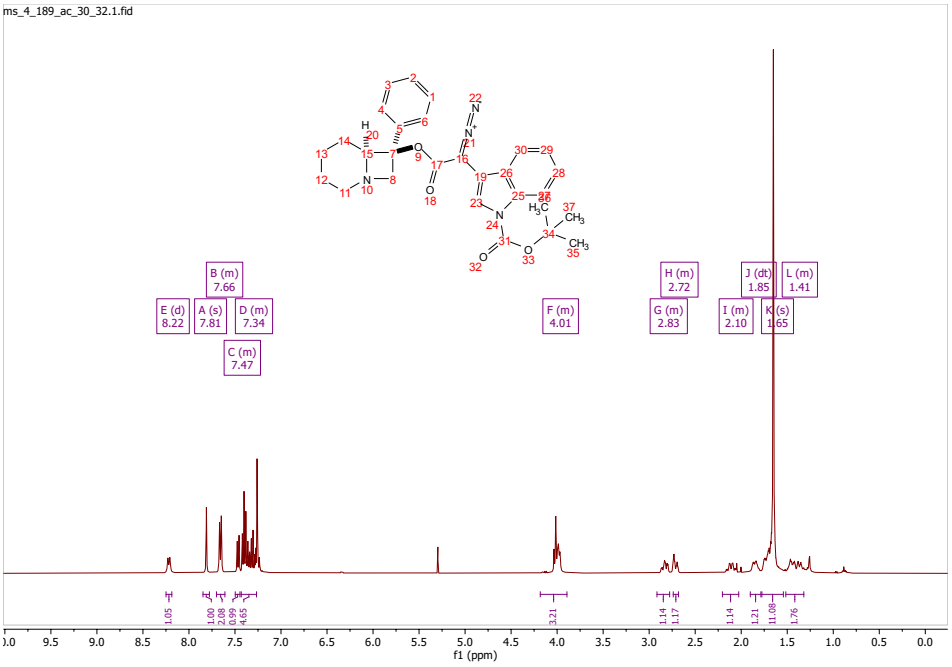


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D-1-1-2

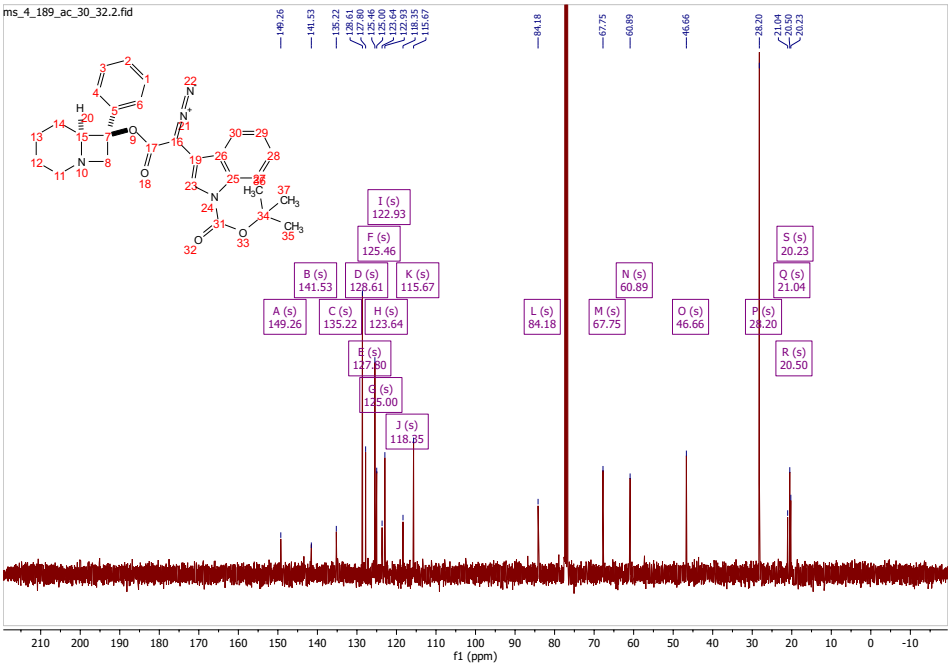


10.6.5 Compound D-1-1-3

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D-1-1-3

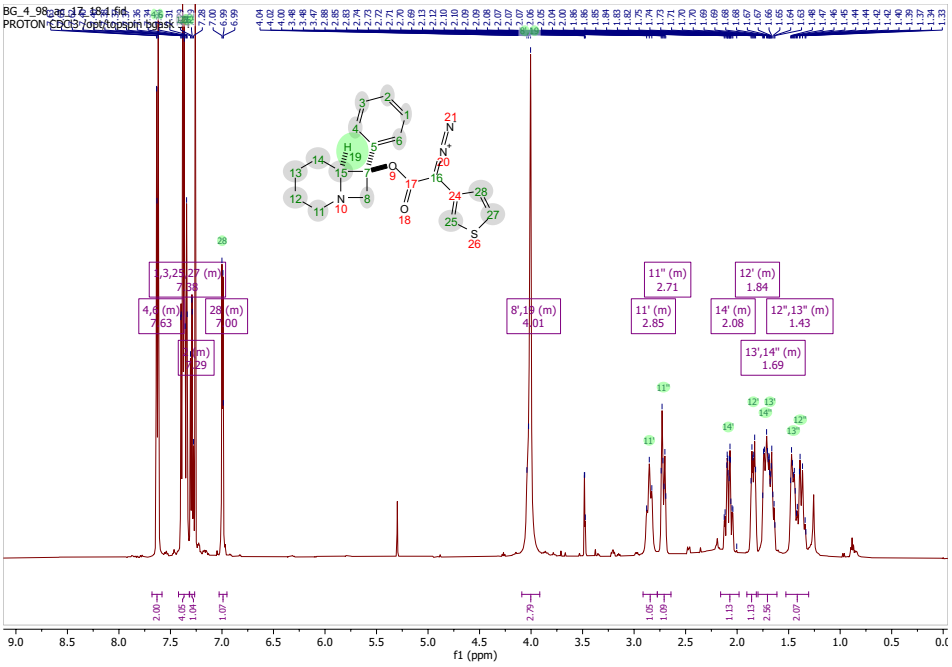


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D-1-1-3

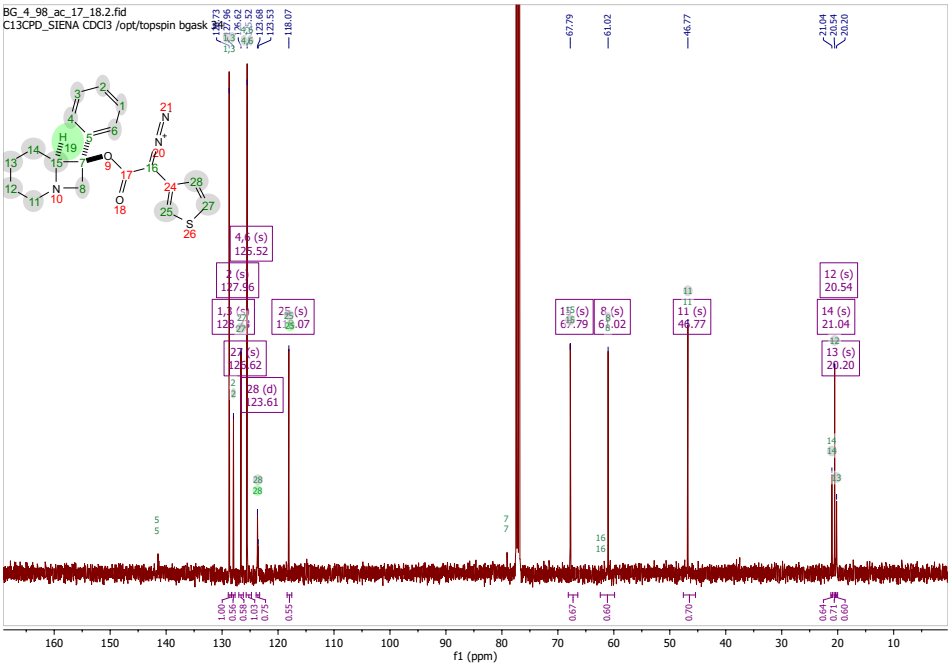


10.6.6 Compound D-1-1-4

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D-1-1-4

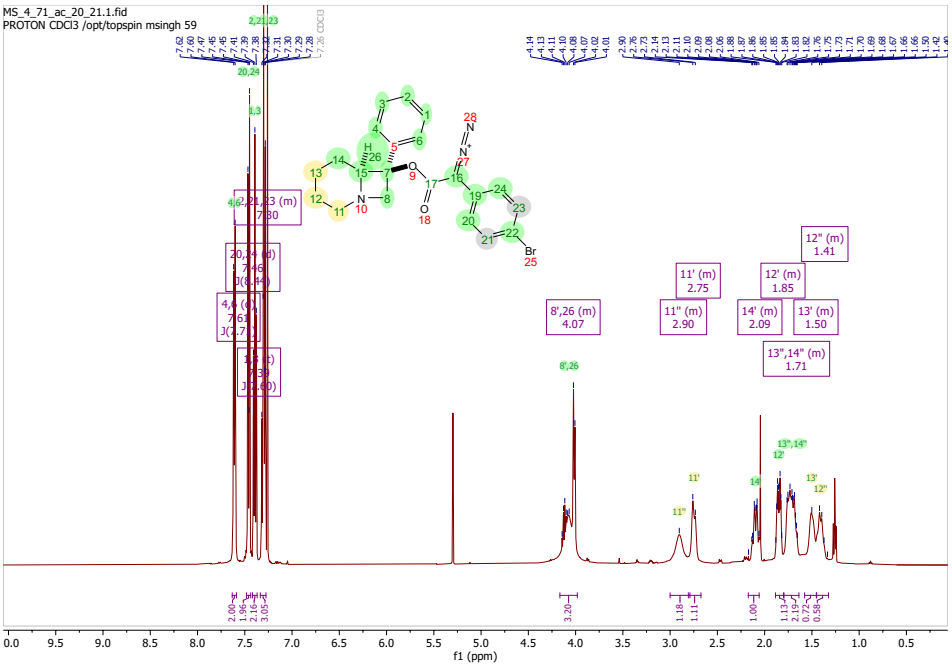


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D-1-1-4

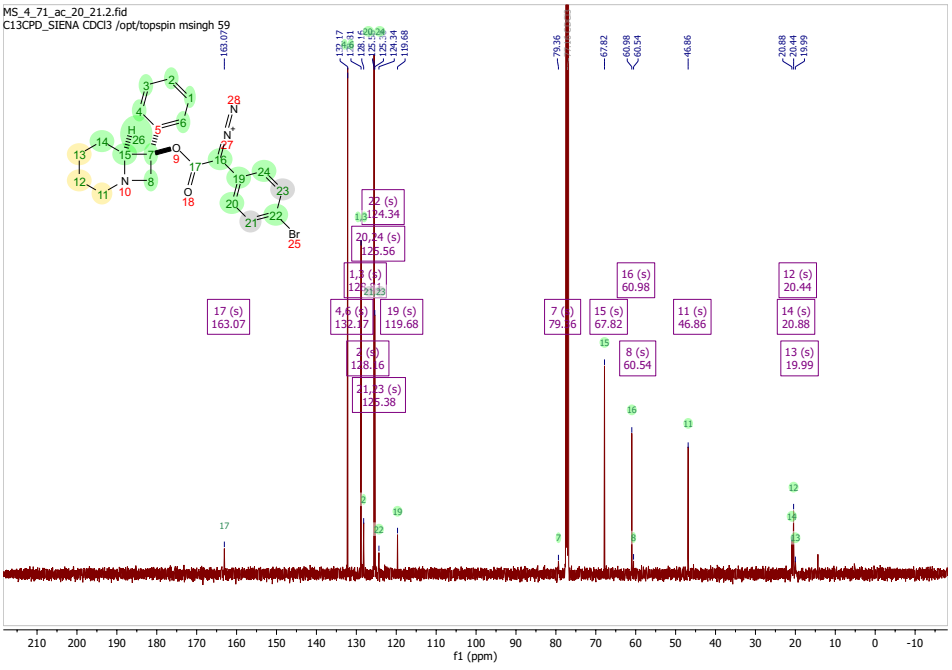


10.6.7 Compound D7

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D7

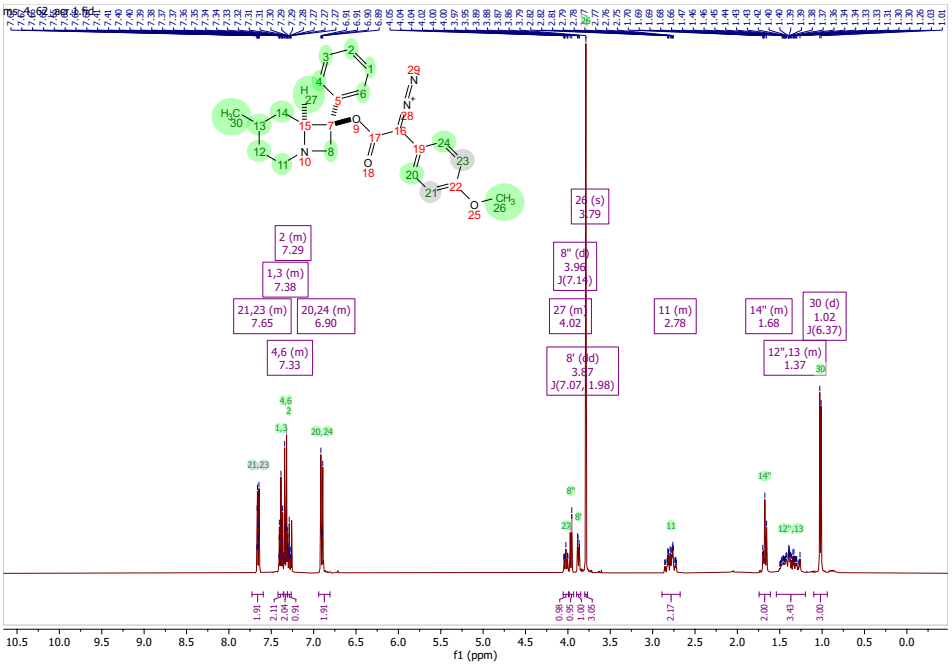


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D7

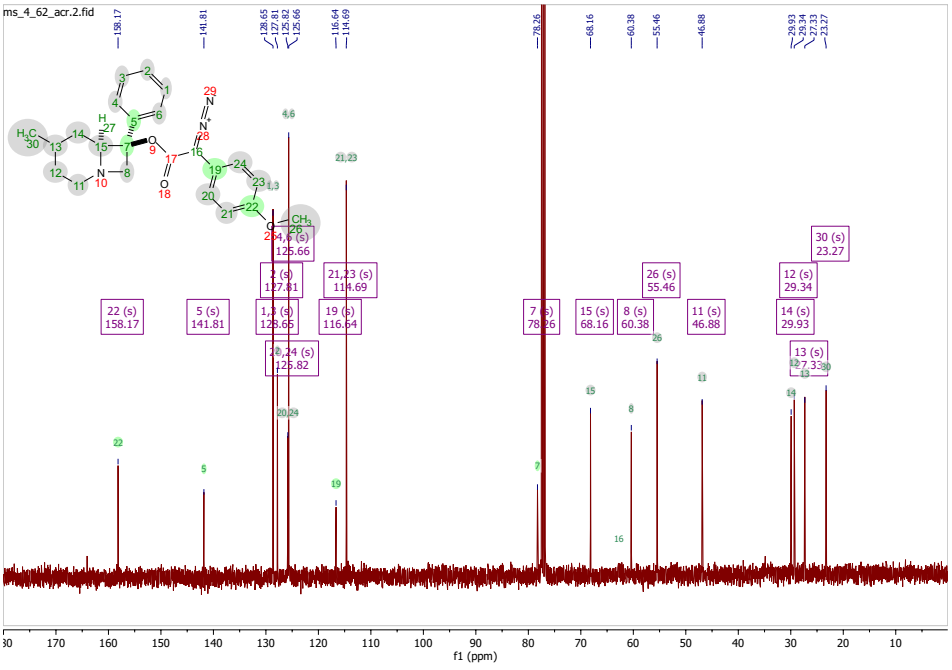


10.6.8 Compound D-1-2-1

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D-1-2-1

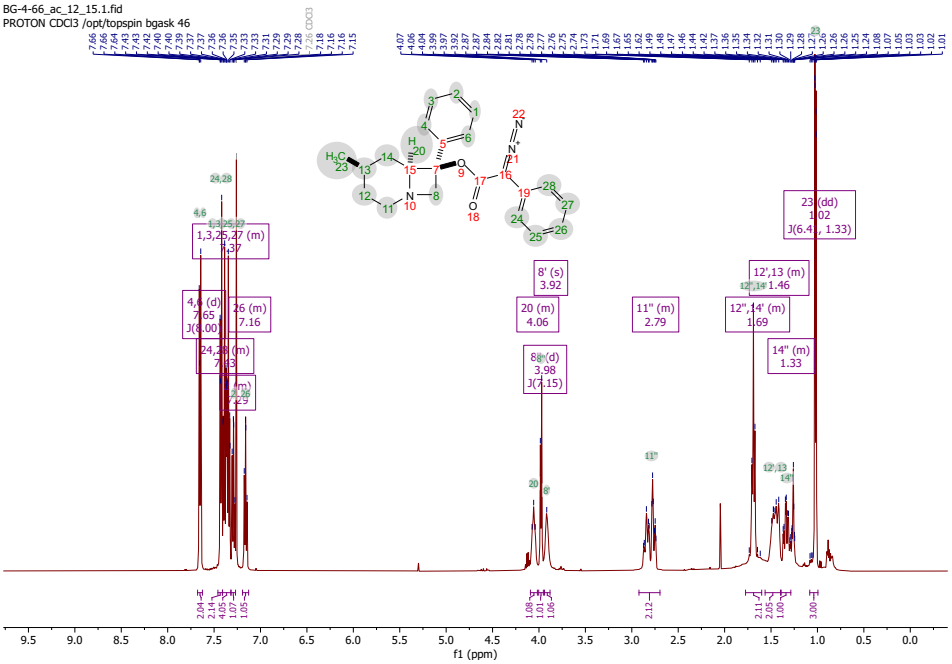


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D-1-2-1

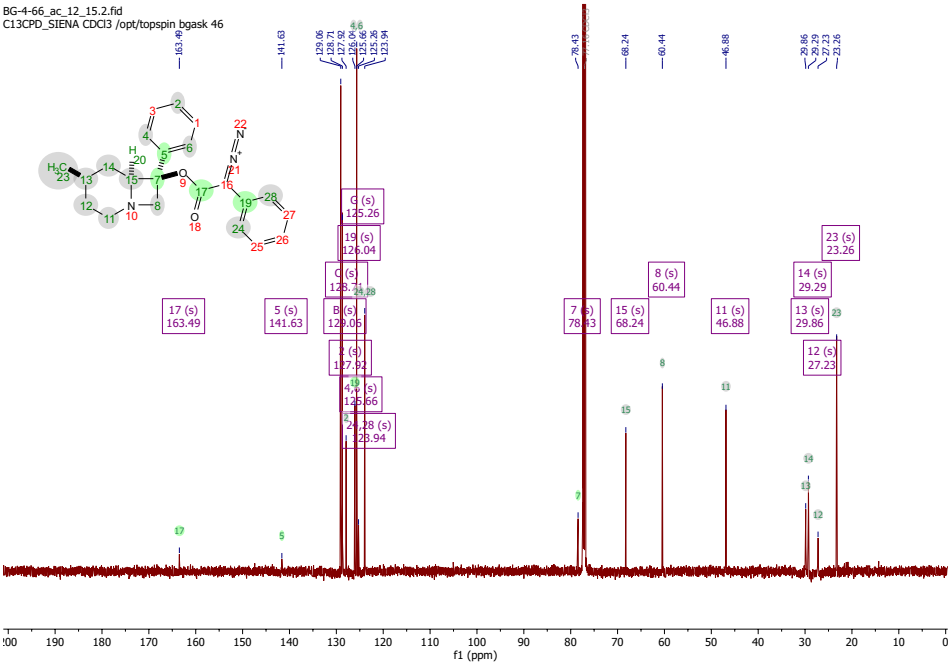


10.6.9 Compound D-1-2-2

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D-1-2-2

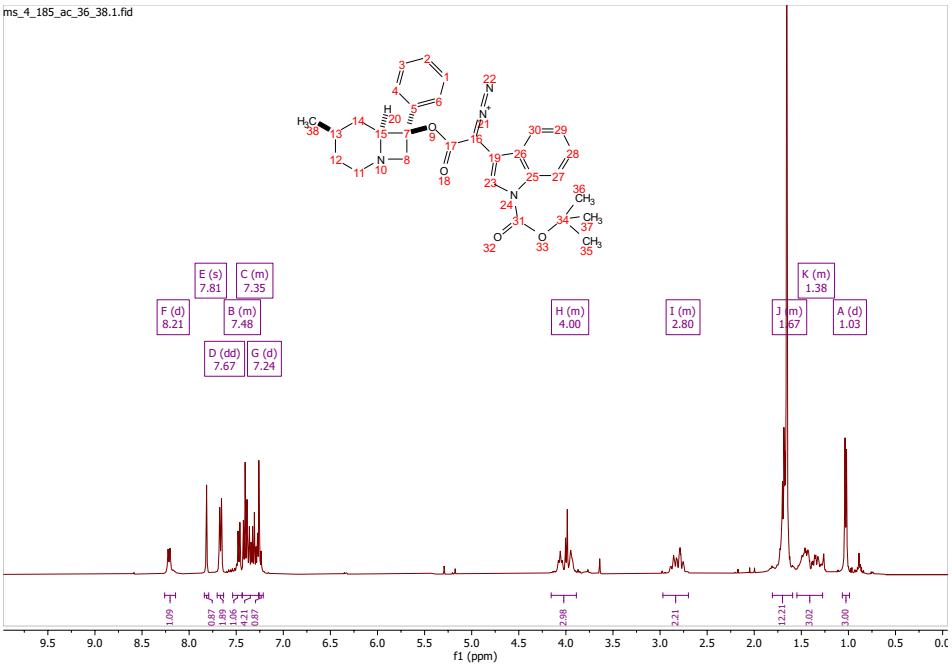


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D-1-2-2

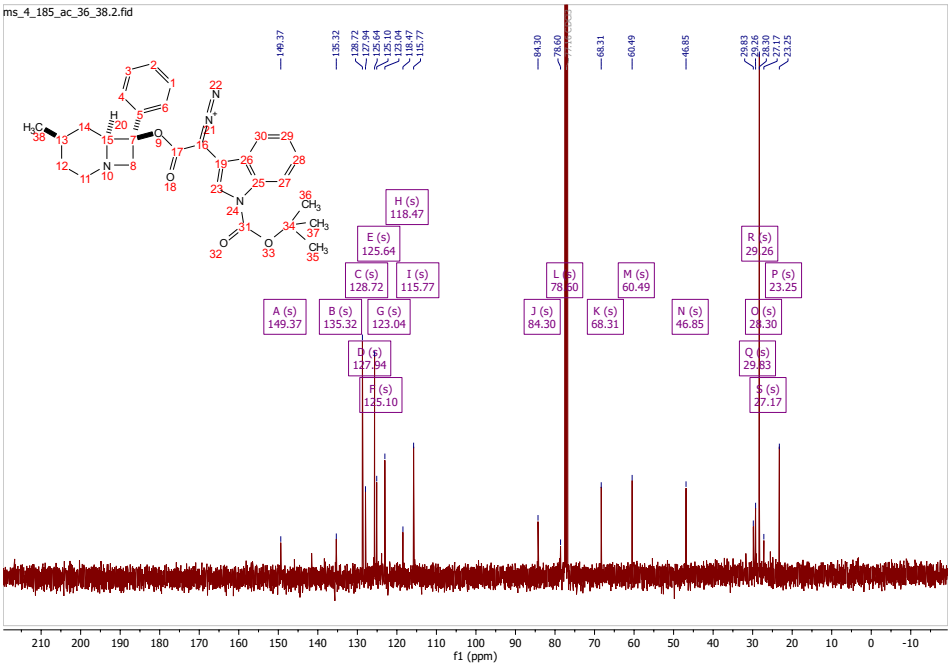


10.6.10 Compound D-1-2-3

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D-1-2-3

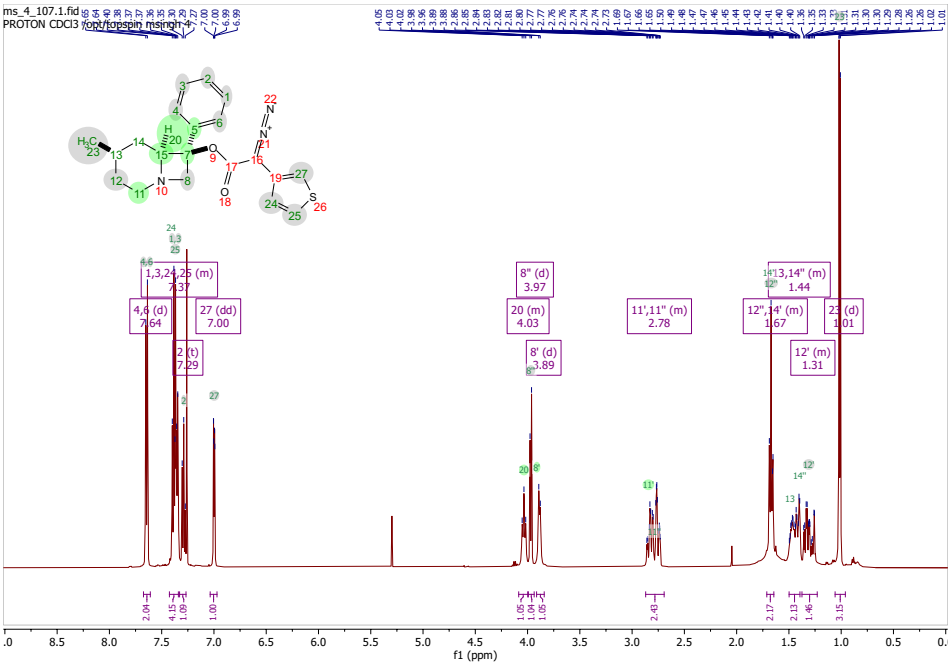


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D-1-2-3

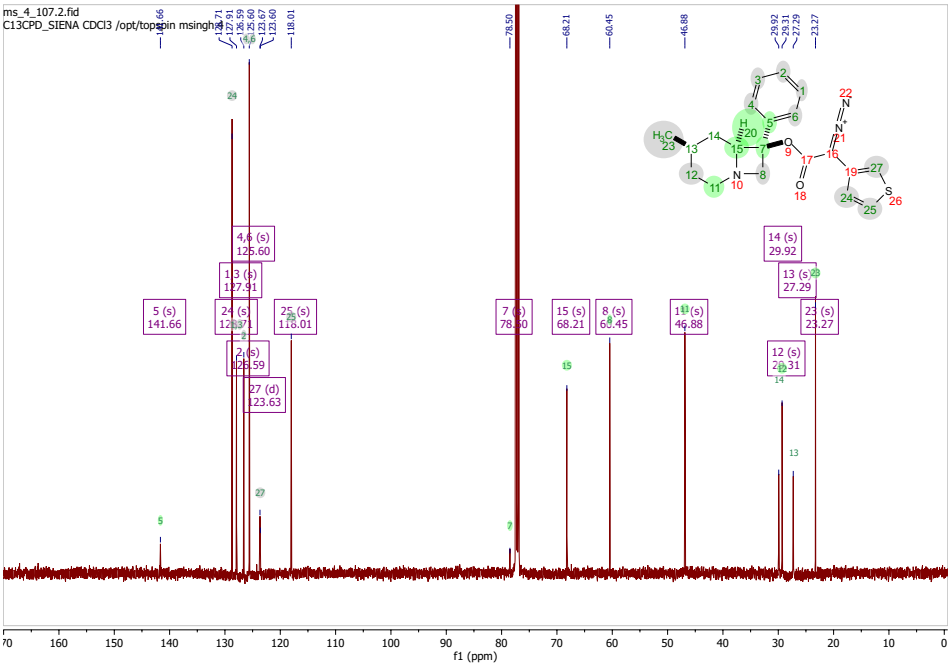


10.6.11 Compound D-1-2-4

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D-1-2-4

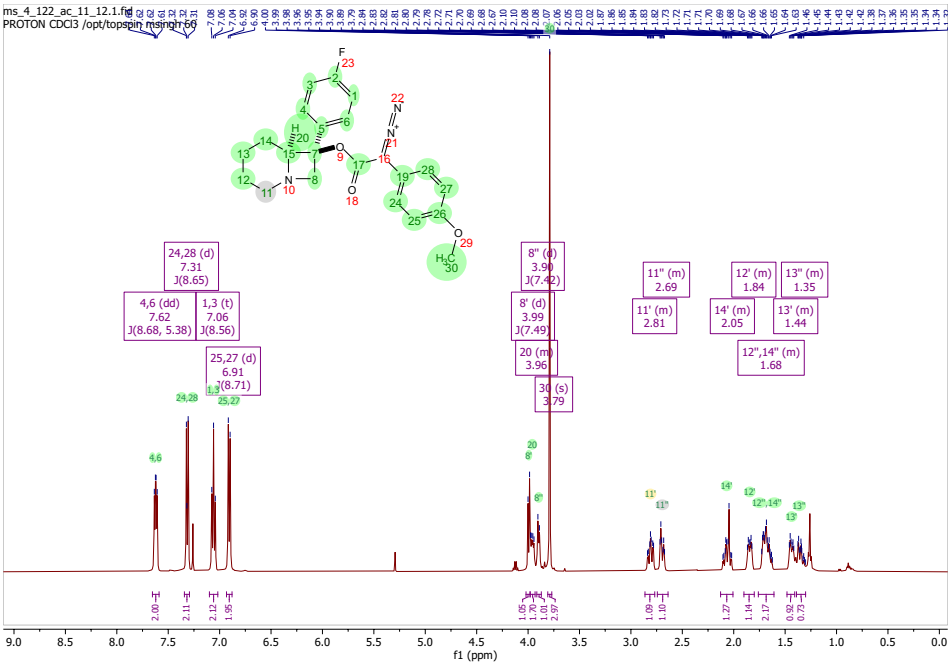


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D-1-2-4

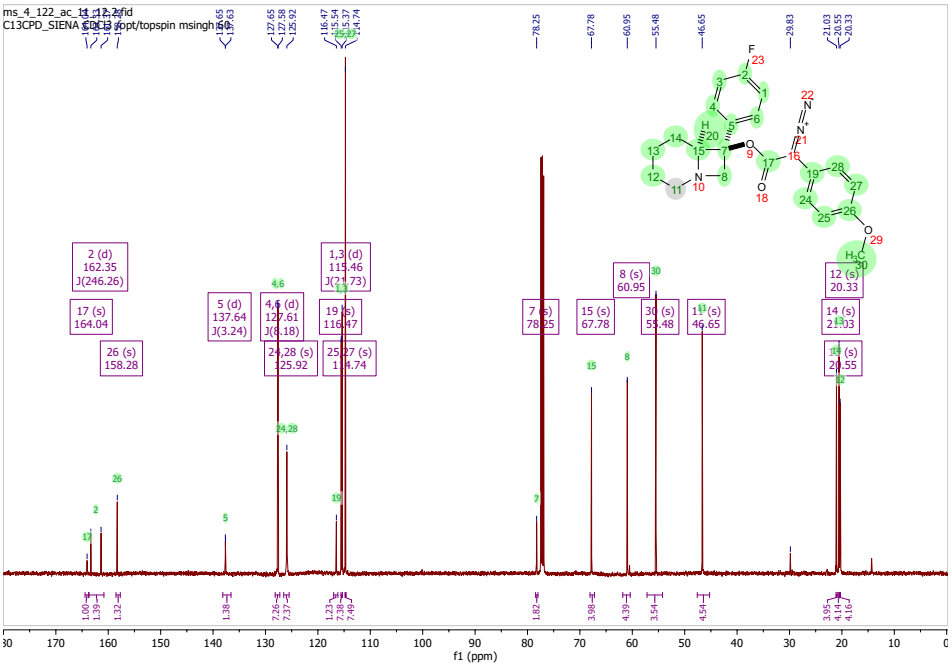


10.6.12 Compound D-2-1-1

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D-2-1-1

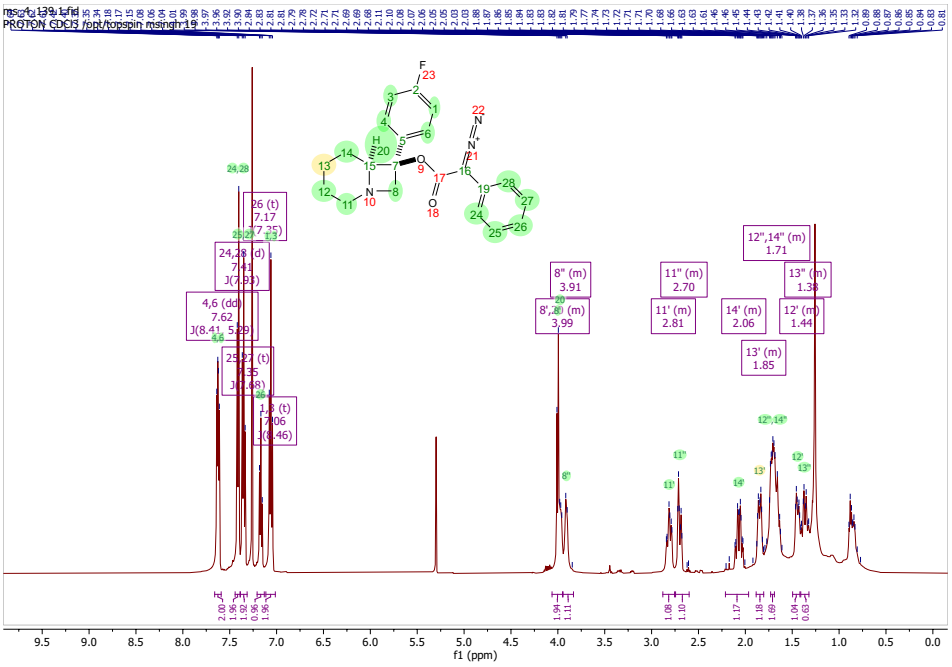


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D-2-1-1

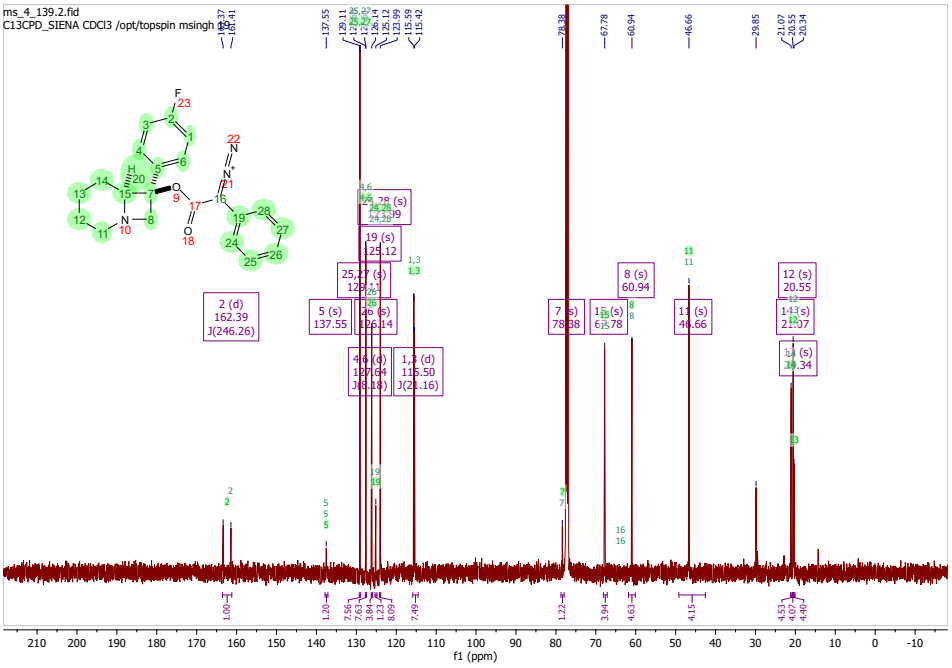


10.6.13 Compound D-2-1-2

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D-2-1-2

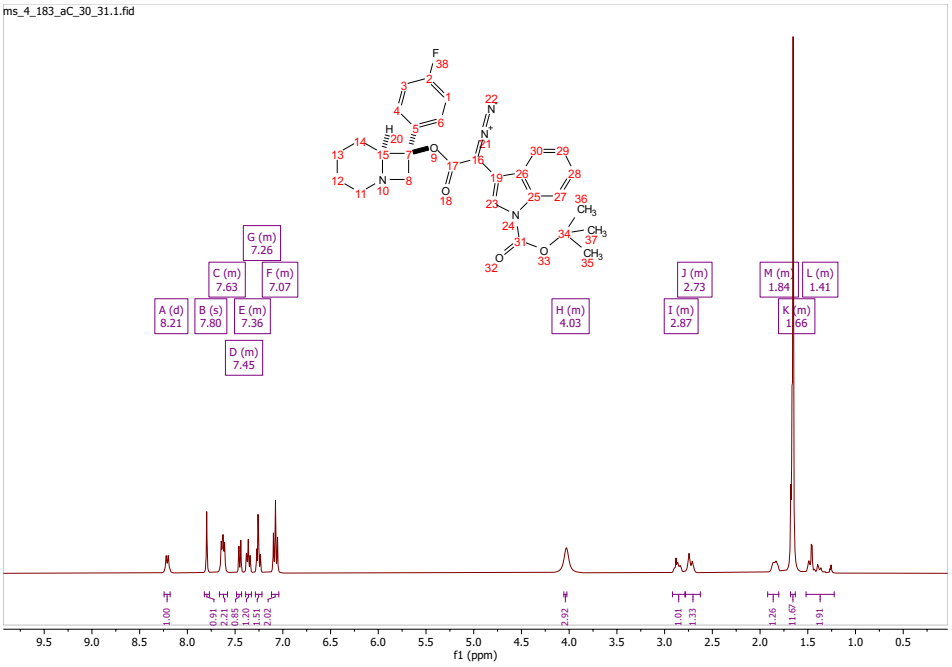


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D-2-1-2

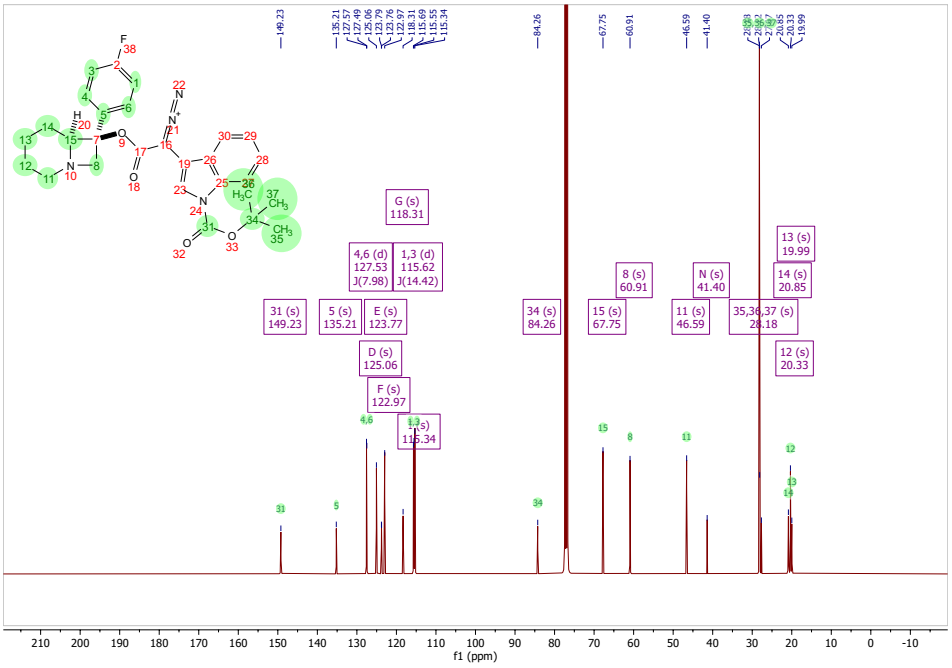


10.6.14 Compound D-2-1-3

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D-2-1-3



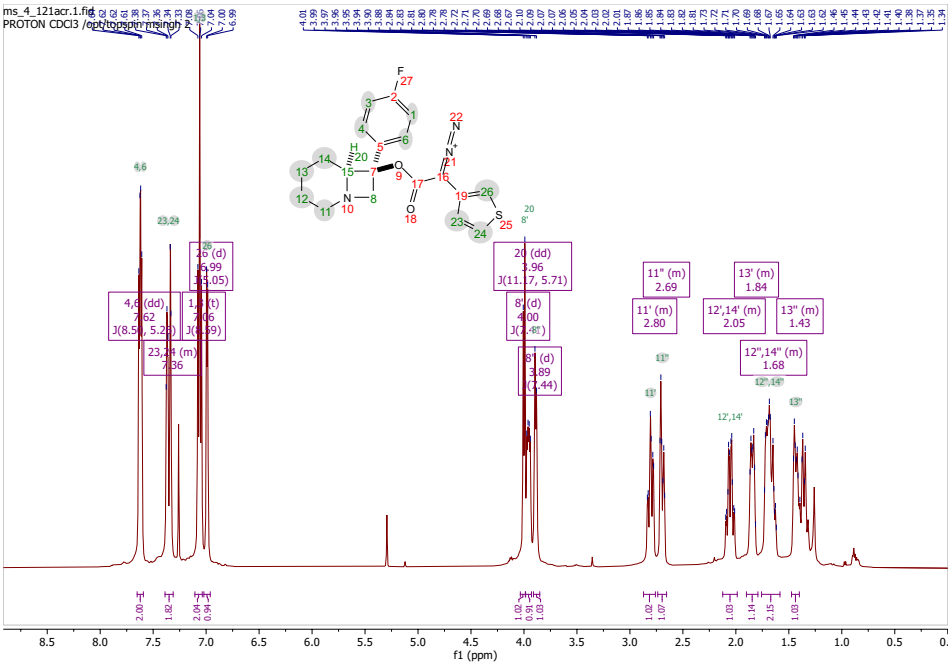
^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D-2-1-3



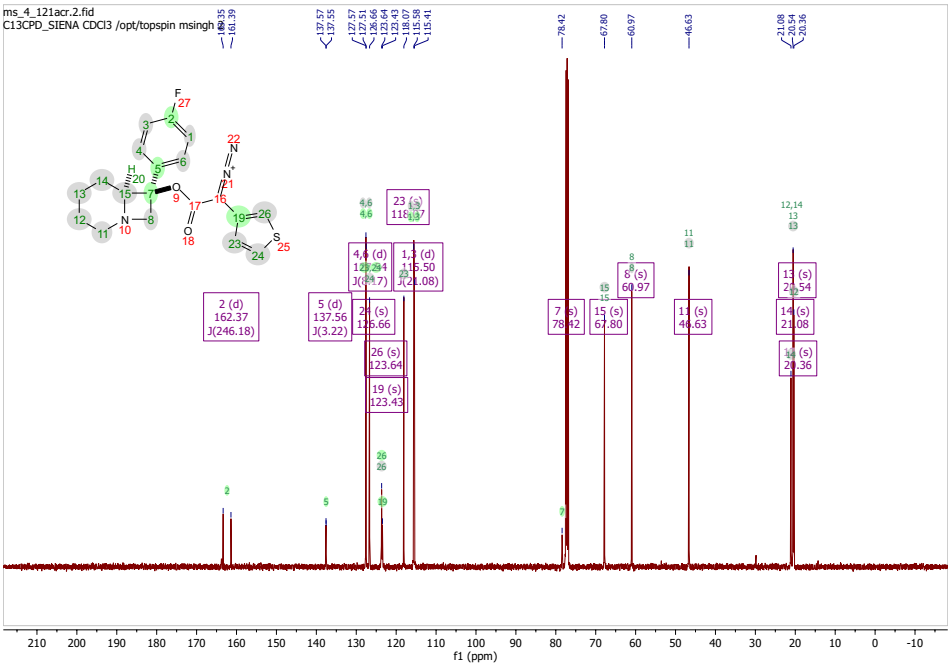
^{1}H NMR spectrum (500 MHz, Chloroform-d) of compound D-2-1-3

10.6.15 Compound D-2-1-4

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D-2-1-4

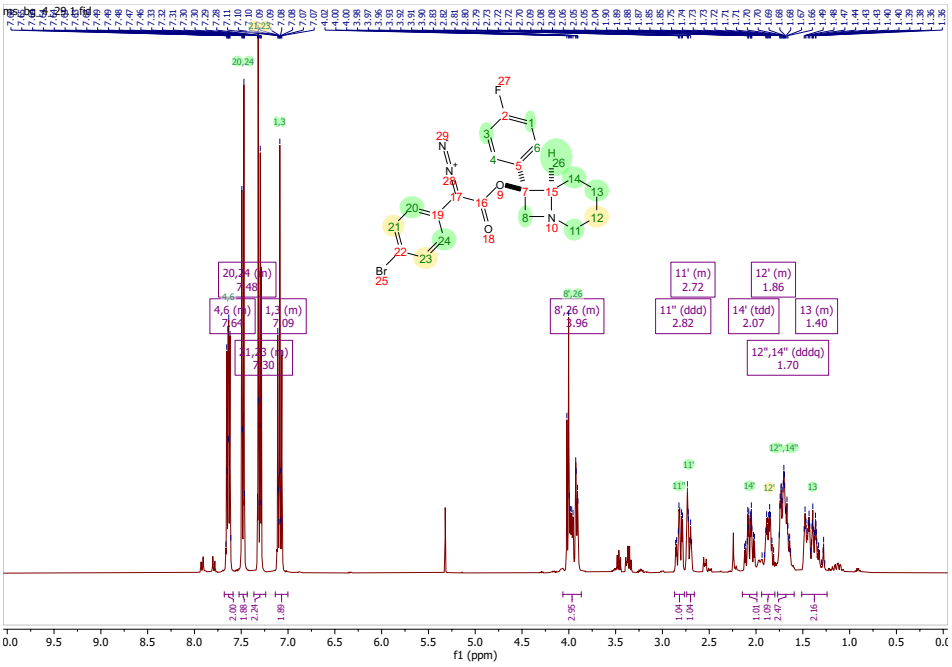


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D-2-1-4

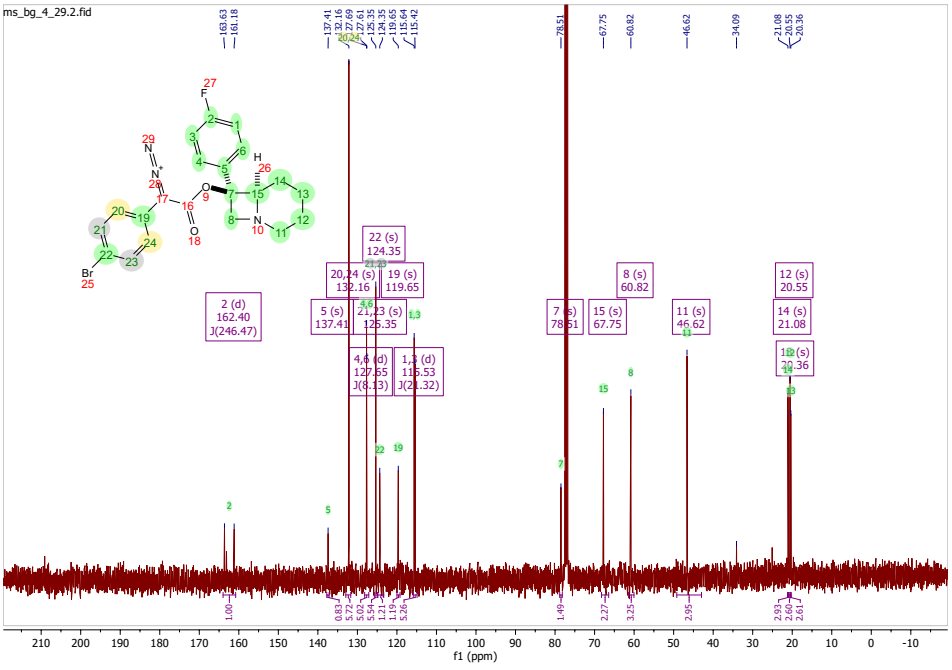


10.6.16 Compound D17

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D17

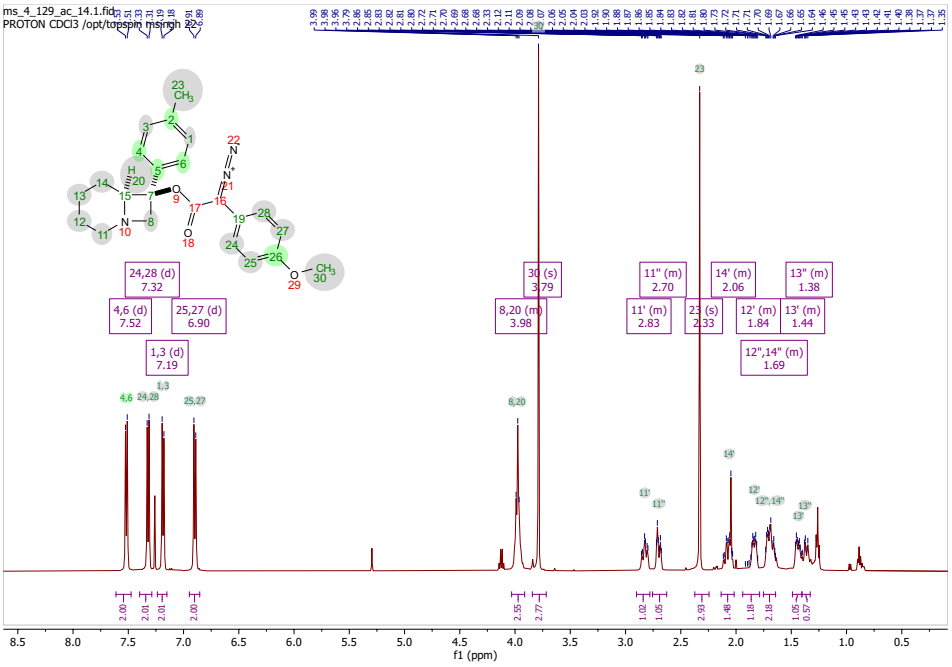


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D17

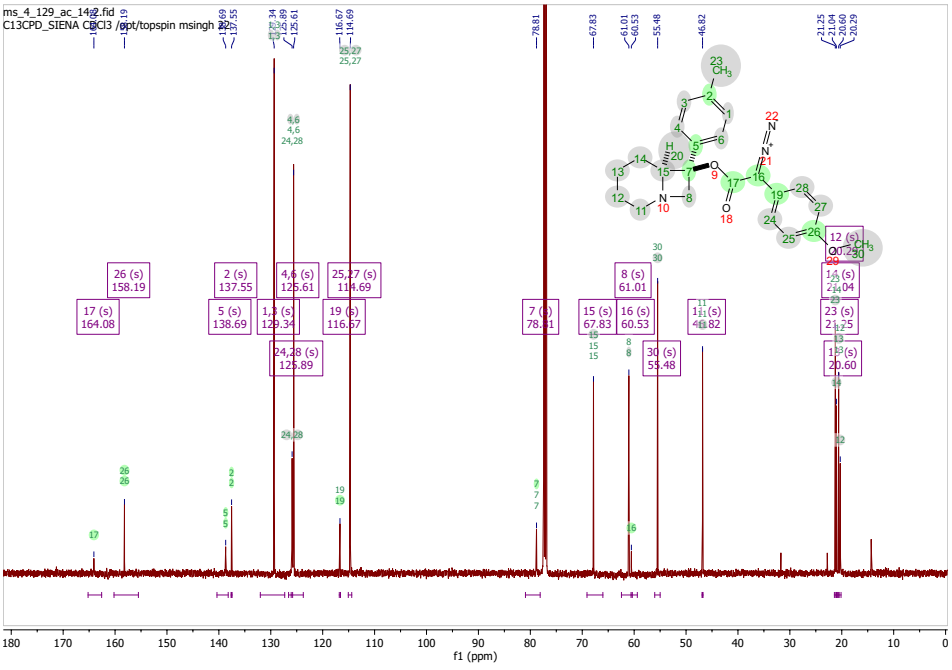


10.6.17 Compound D-3-1-1

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D-3-1-1

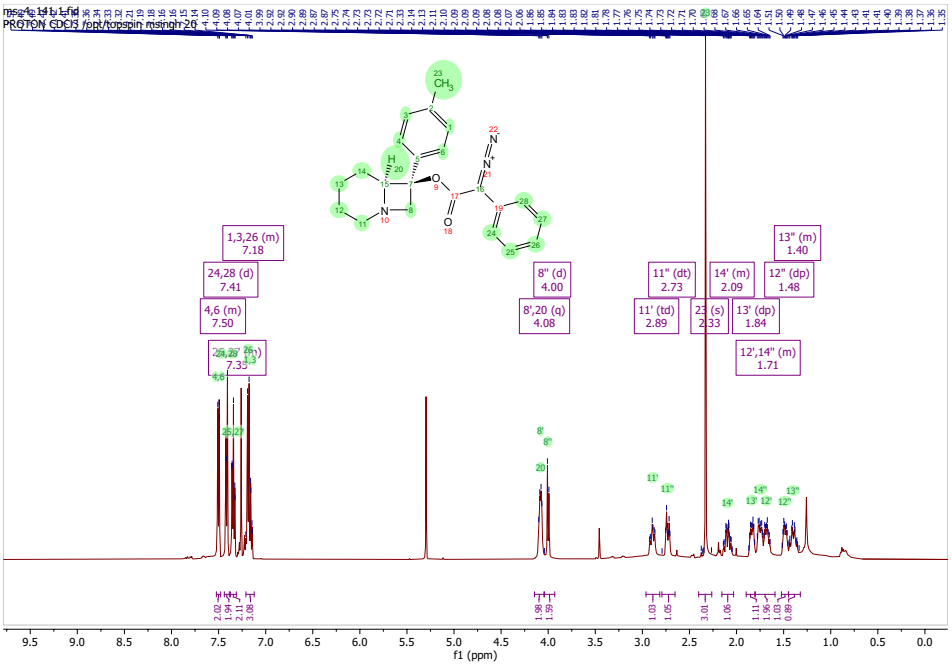


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D-3-1-1

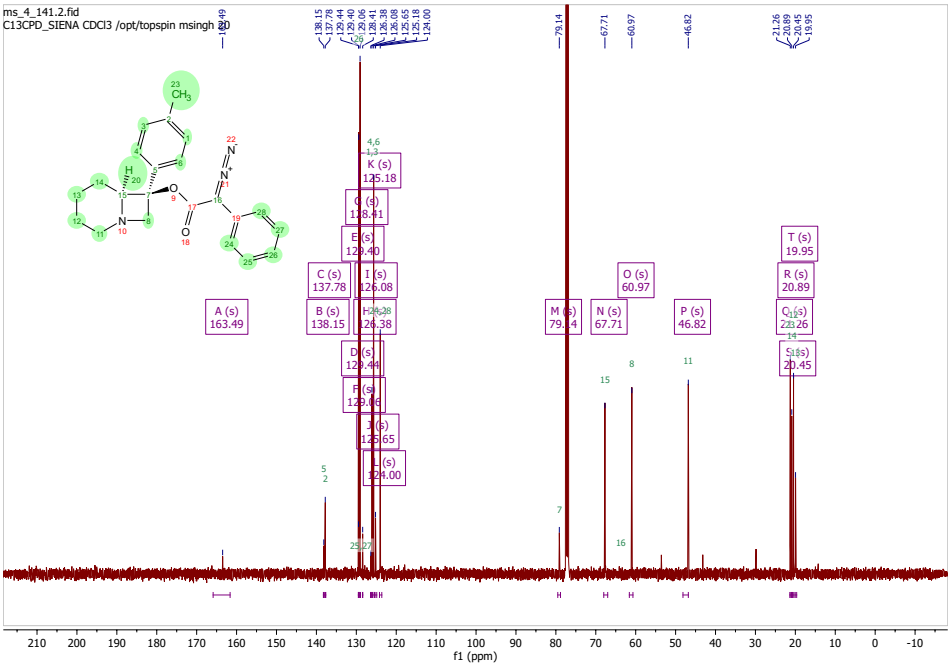


10.6.18 Compound D-3-1-2

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D-3-1-2

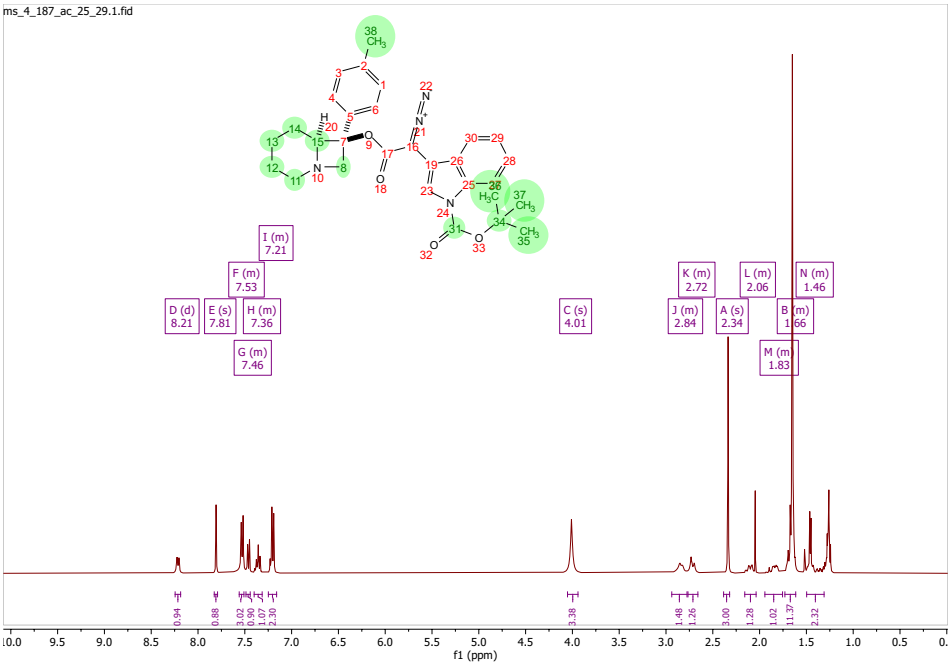


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D-3-1-2

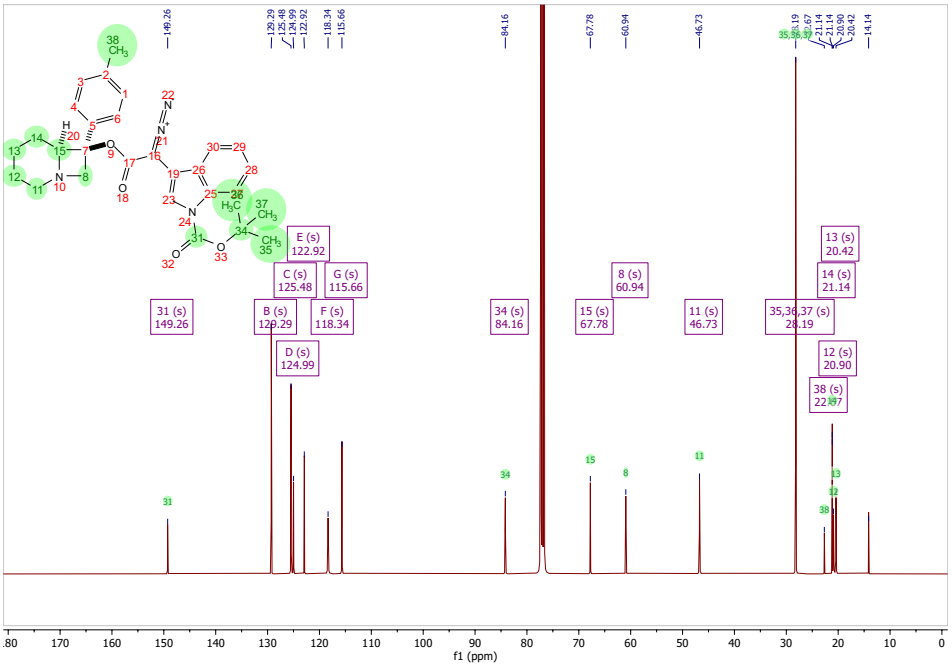


10.6.19 Compound D-3-1-3

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D-3-1-3

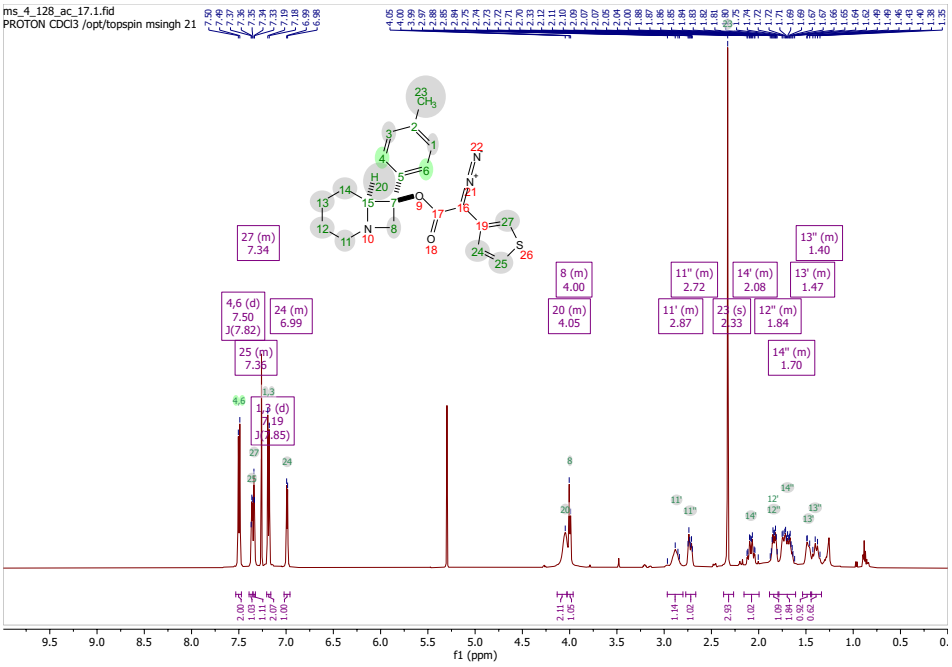


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D-3-1-3

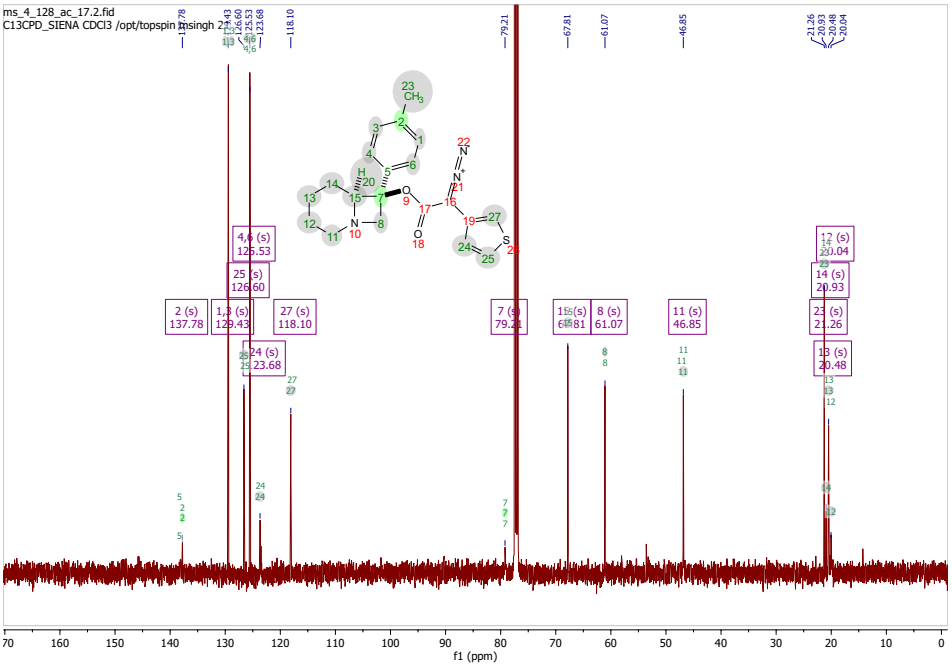


10.6.20 Compound D-3-1-4

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound D-3-1-4



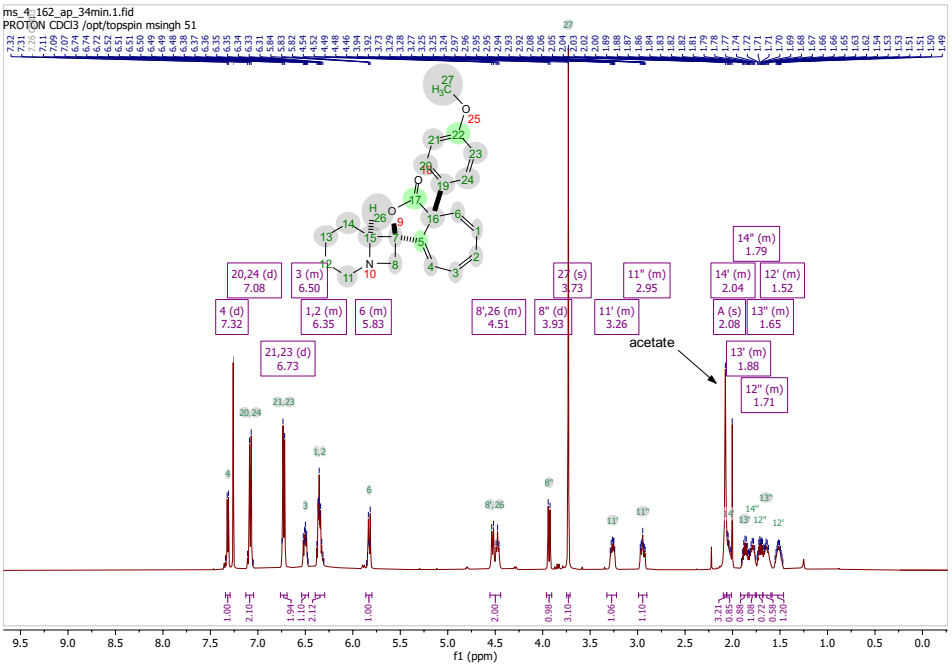
^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound D-3-1-4



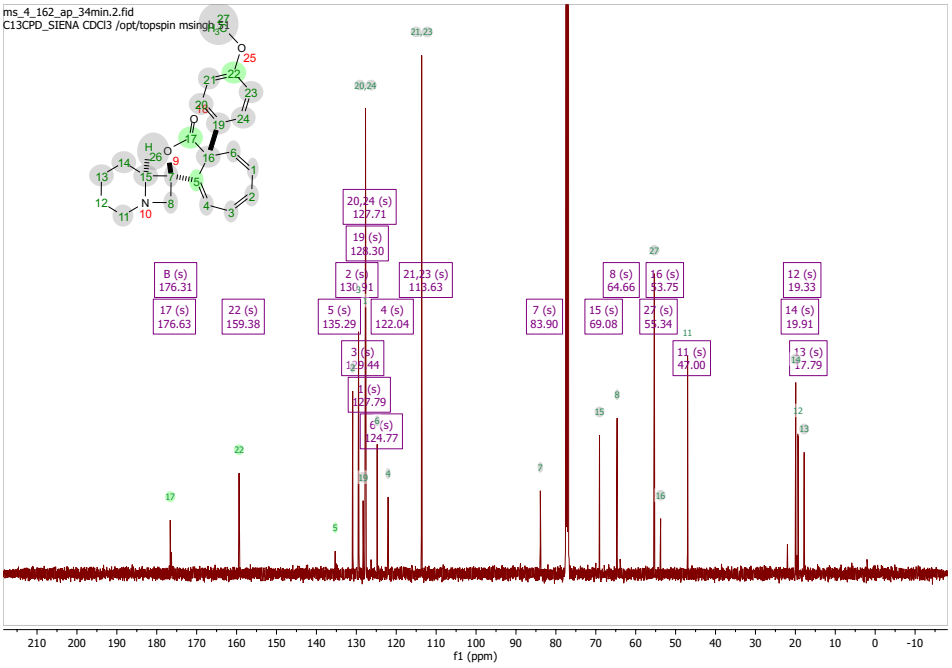
10.7 Buchner ring expansion

10.7.1 Compound 1-1-1

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 1-1-1

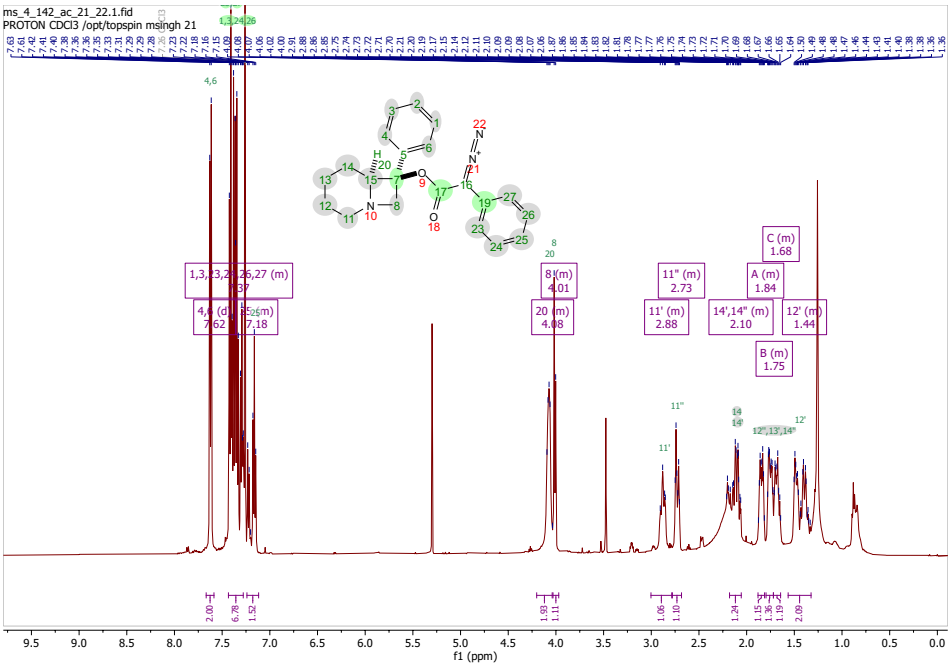


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 1-1-1

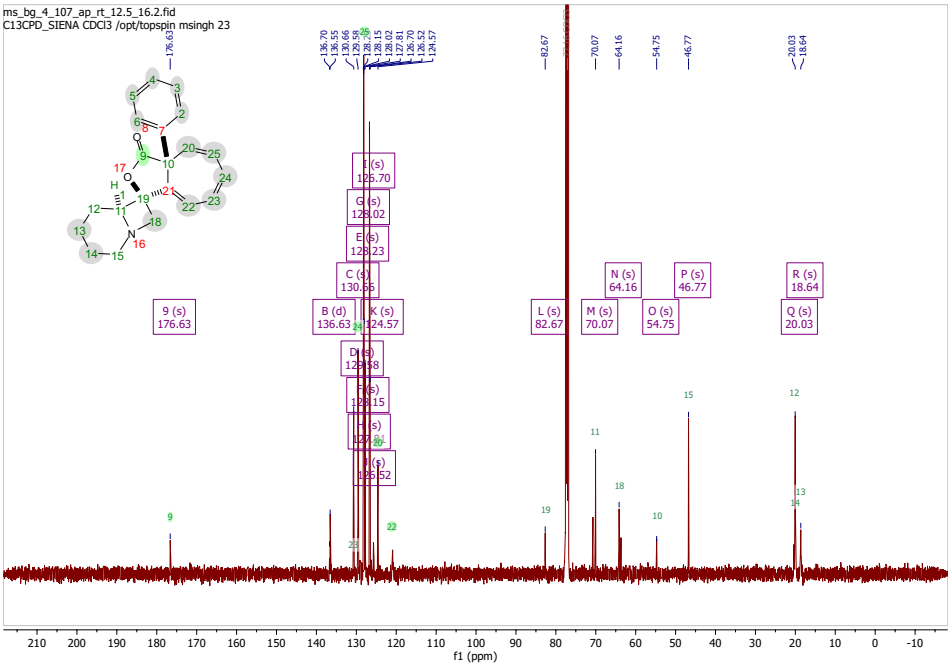


10.7.2 Compound 1-1-2

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 1-1-2

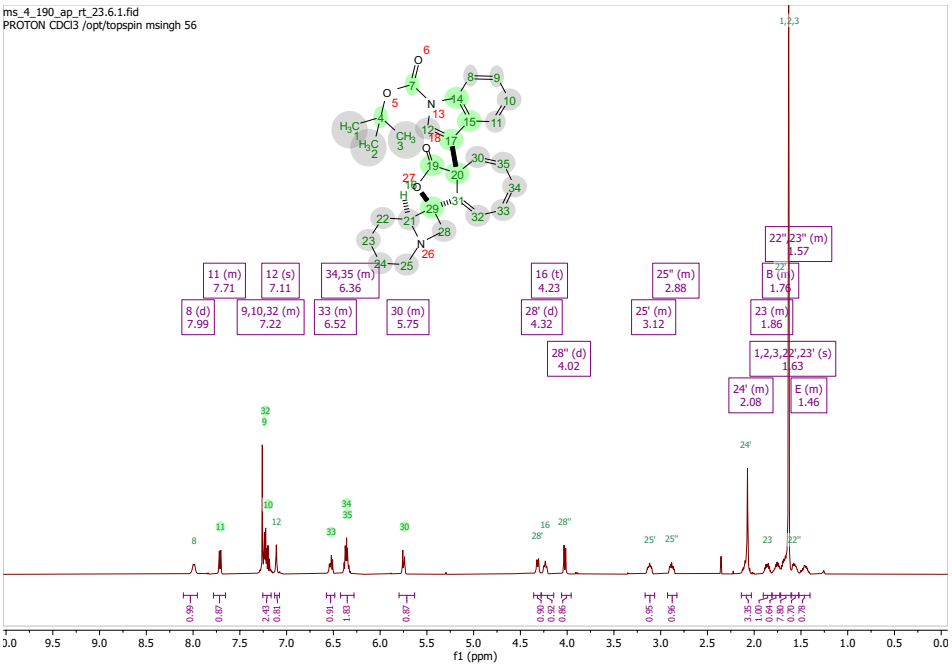


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 1-1-2

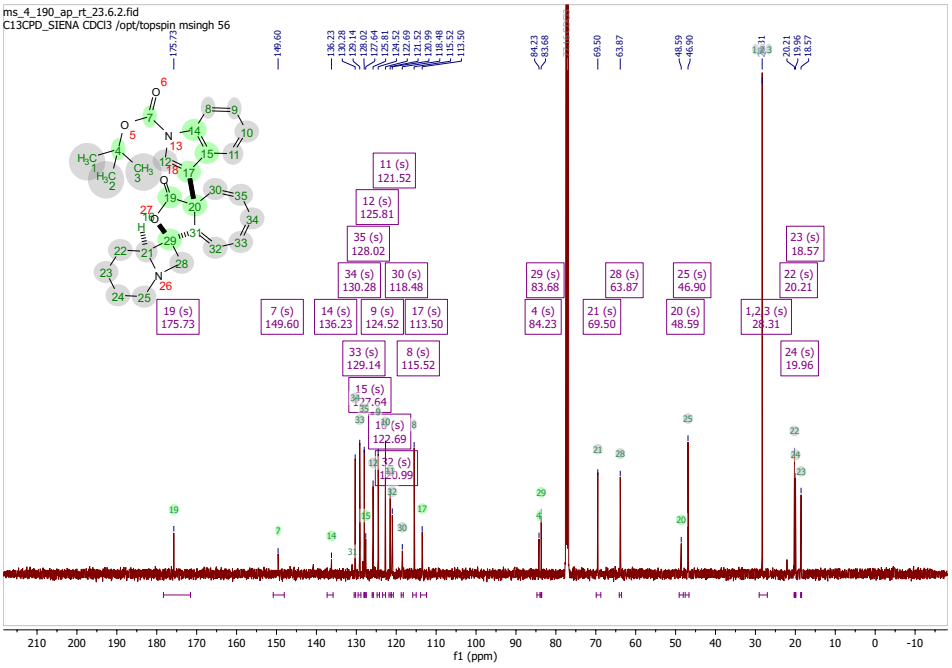


10.7.3 Compound 1-1-3

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 1-1-3

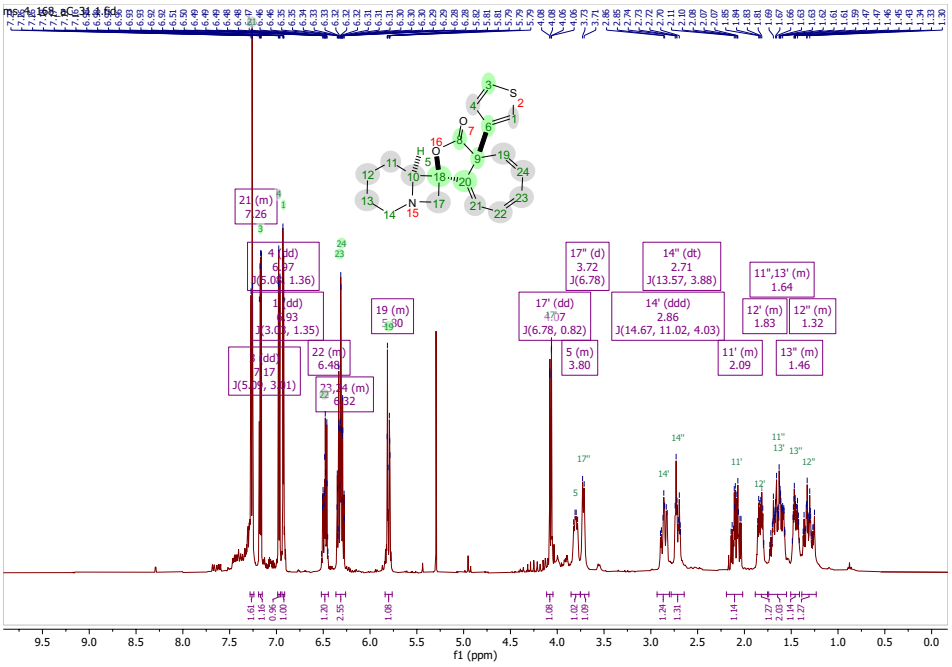


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 1-1-3

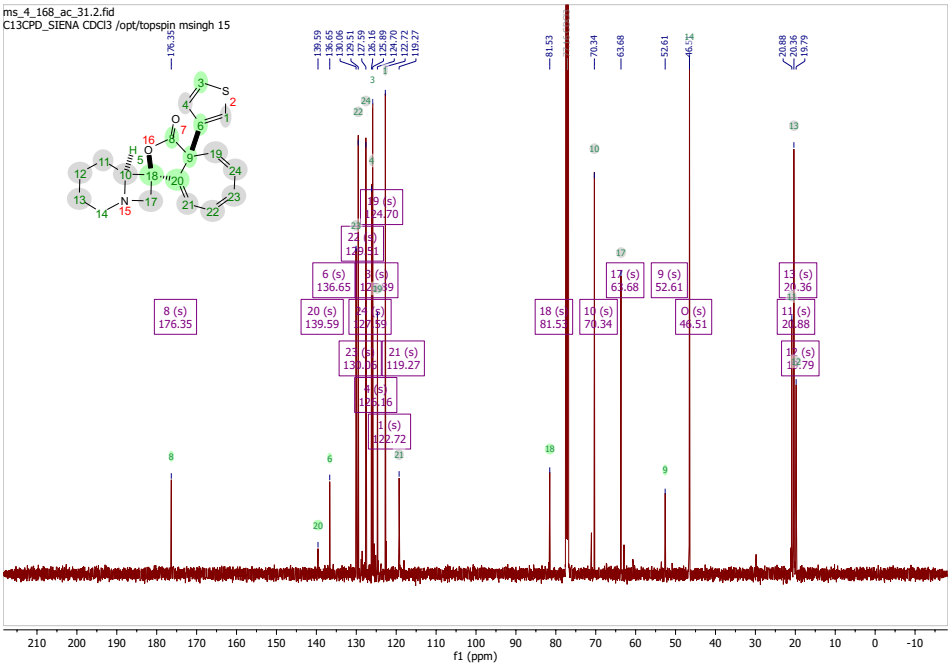


10.7.4 Compound 1-1-4

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 1-1-4

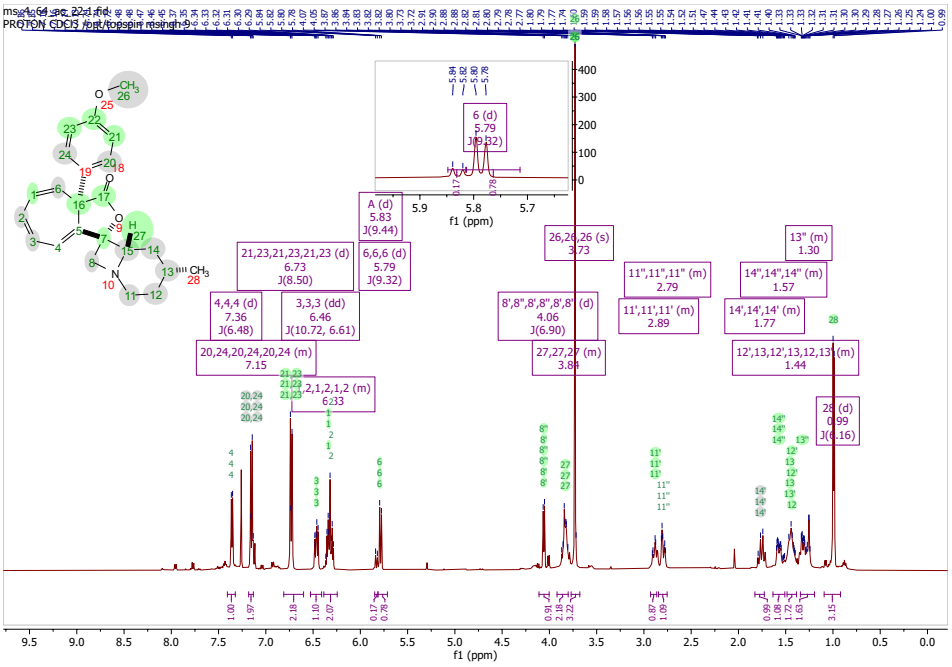


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 1-1-4

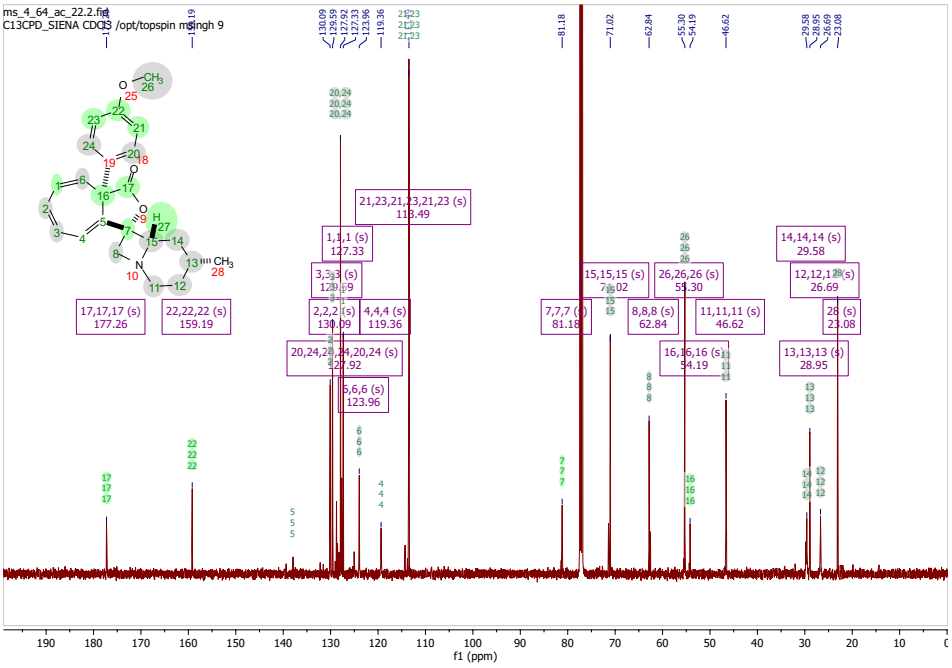


10.7.5 Compound 1-2-1

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 1-2-1

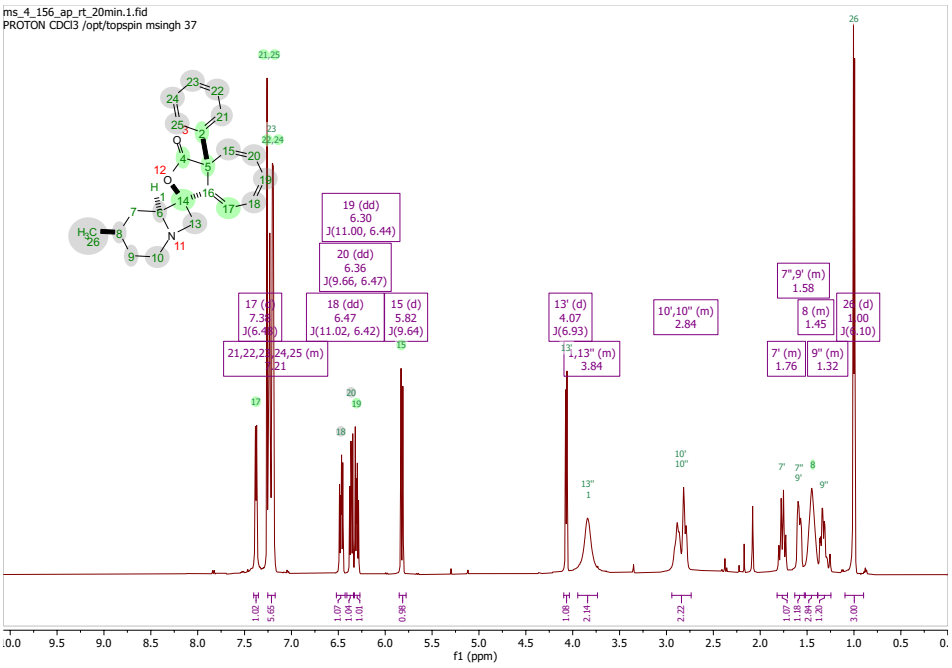


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 1-2-1

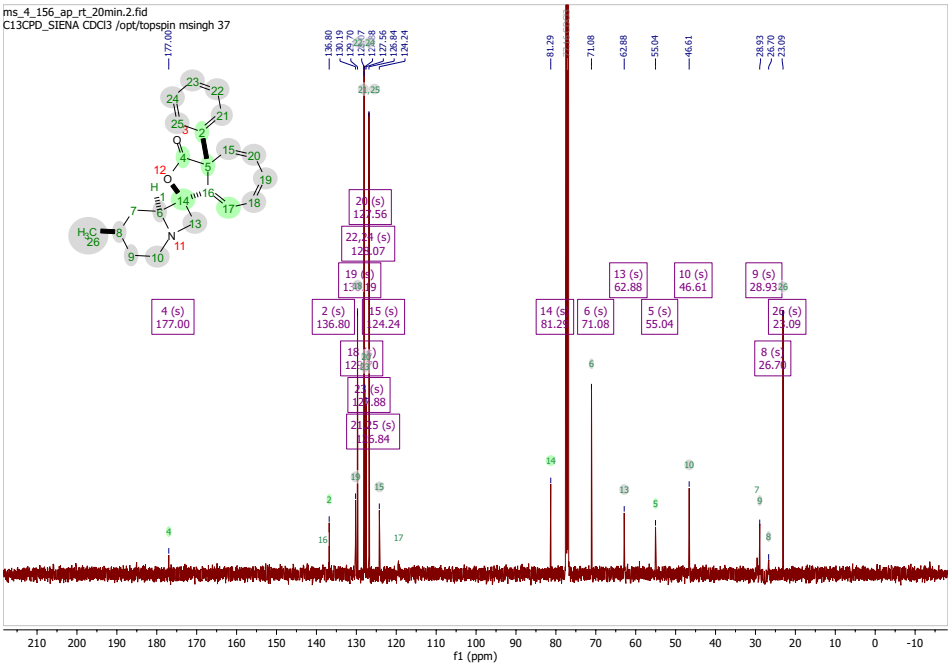


10.7.6 Compound 1-2-2

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 1-2-2

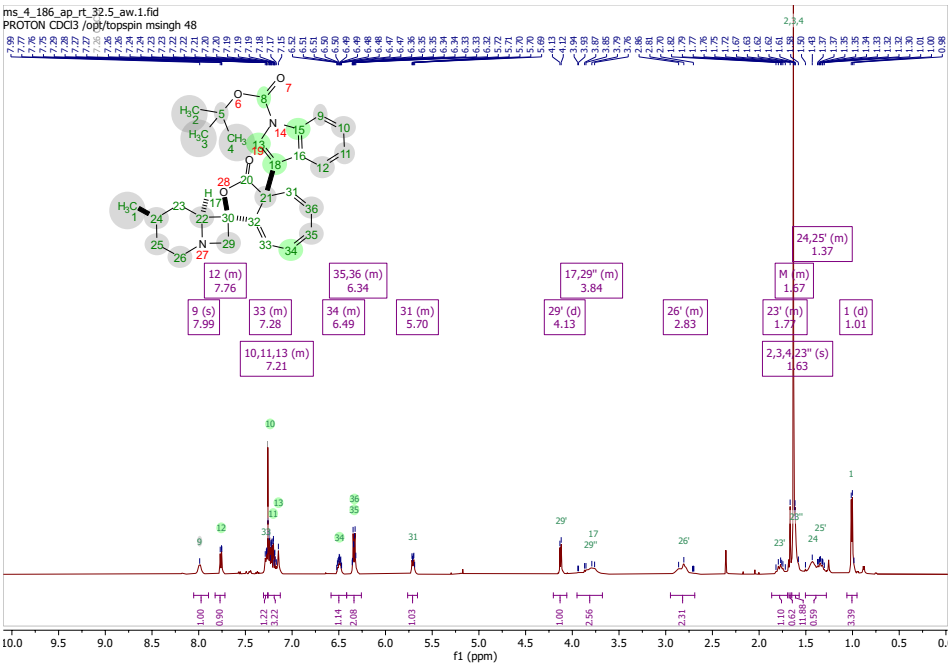


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 1-2-2

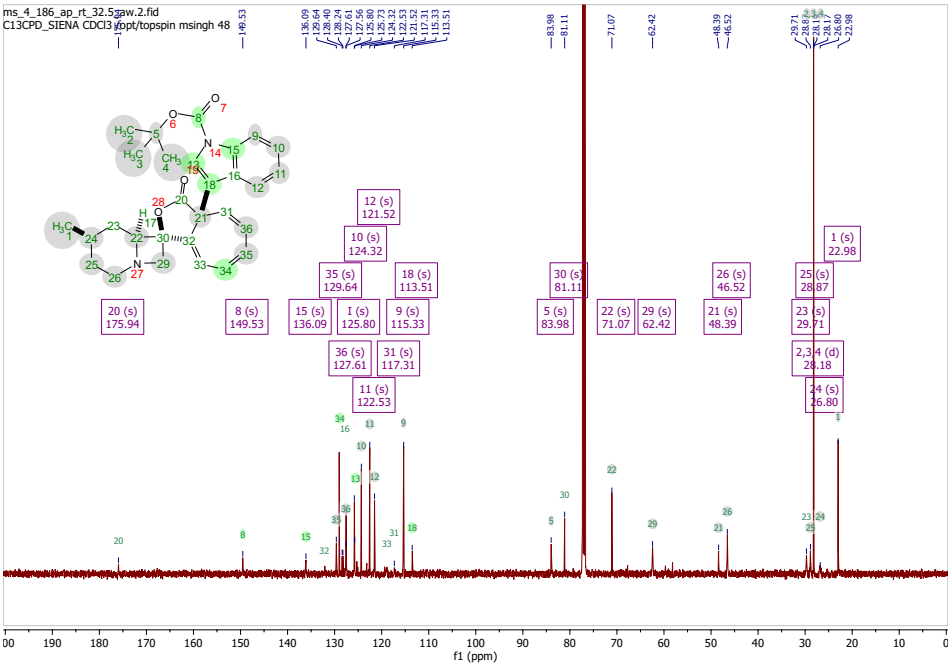


10.7.7 Compound 1-2-3

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 1-2-3

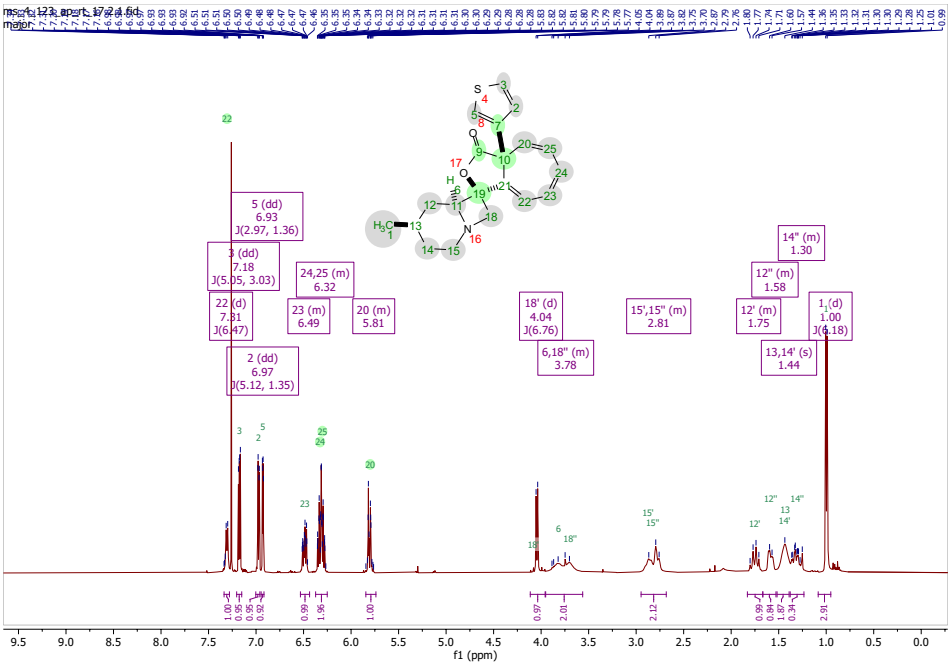


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 1-2-3

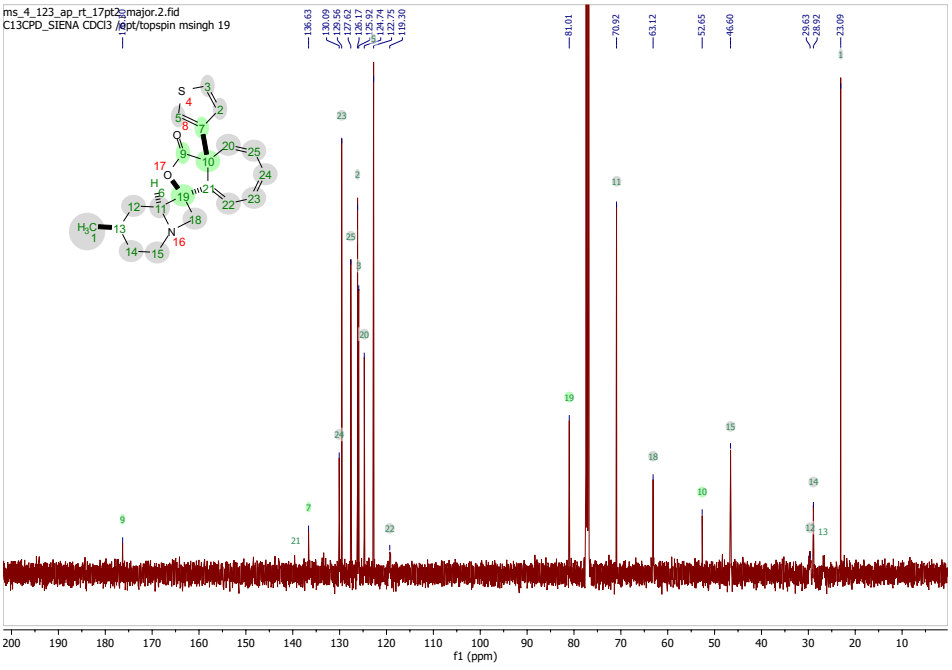


10.7.8 Compound 1-2-4

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 1-2-4

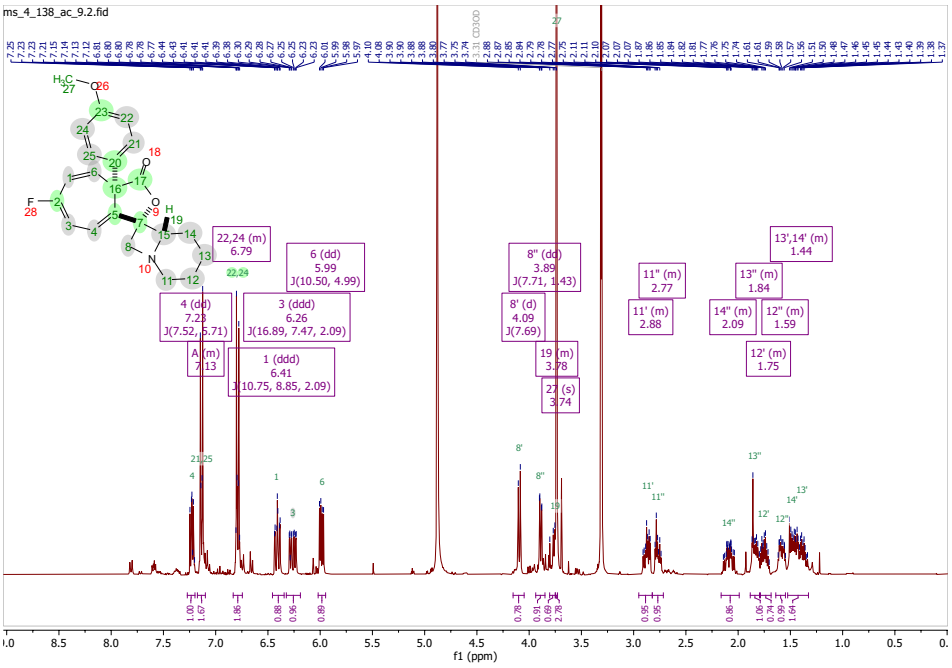


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 1-2-4

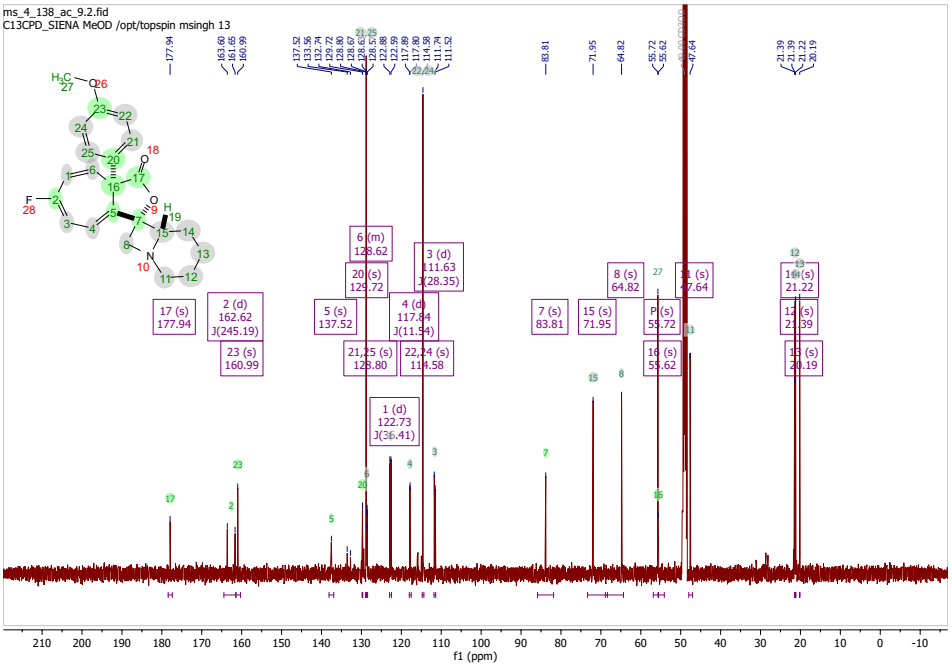


10.7.9 Compound 2-1-1

^{1}H NMR spectrum (500 MHz, MeOD) of Compound 2-1-1

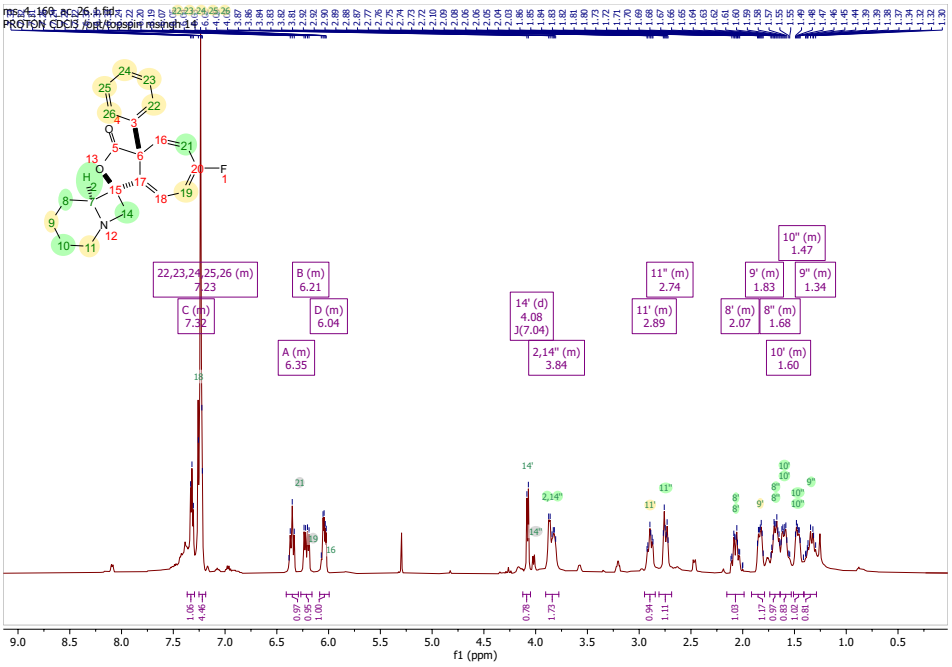


^{13}C {^{1}H } NMR spectrum (126 MHz, MeOD) of Compound 2-1-1

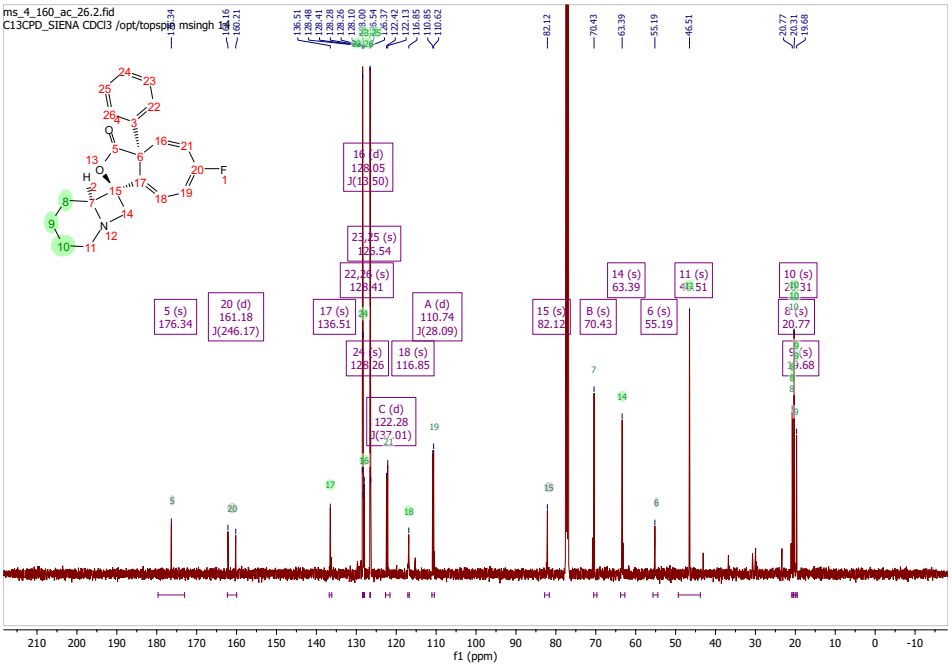


10.7.10 Compound 2-1-2

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 2-1-2

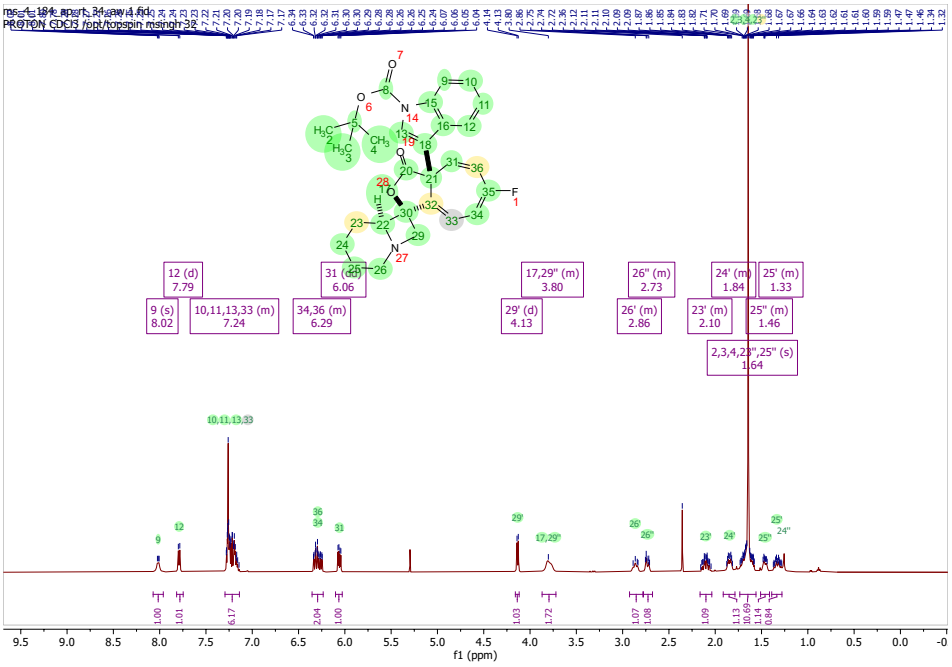


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 2-1-2

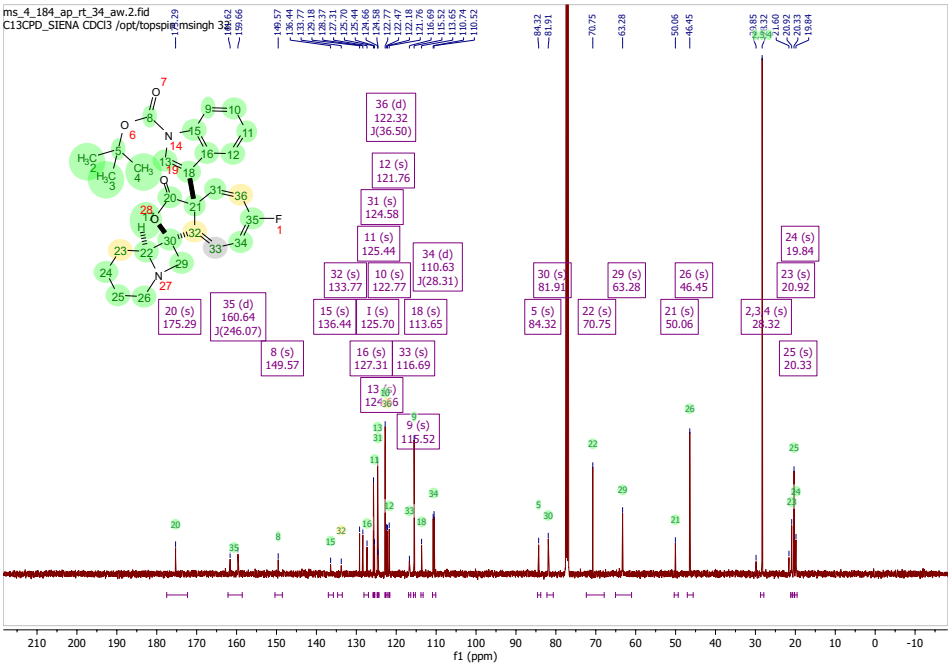


10.7.11 Compound 2-1-3

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 2-1-3

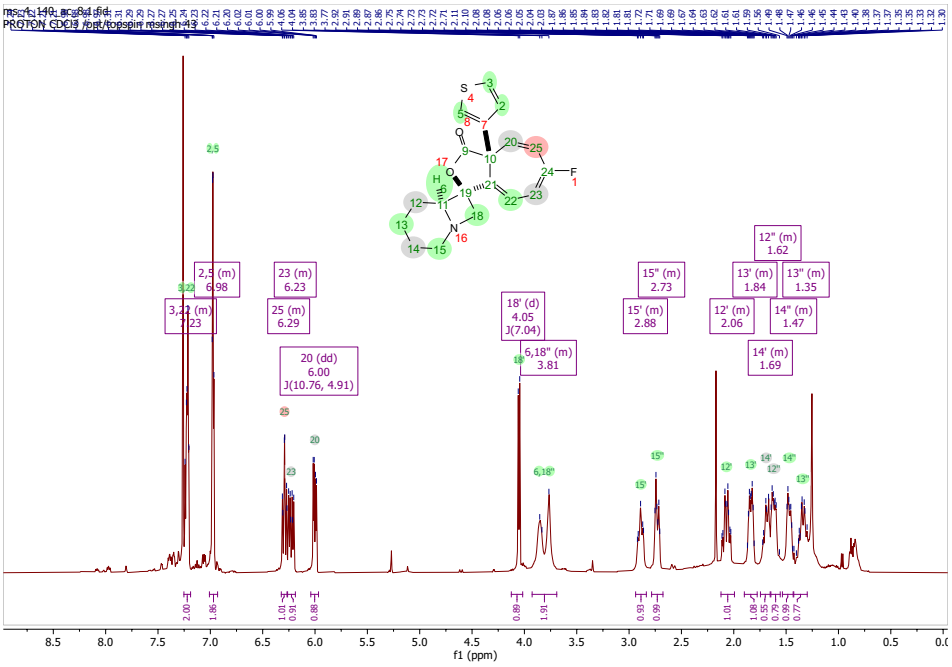


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 2-1-3

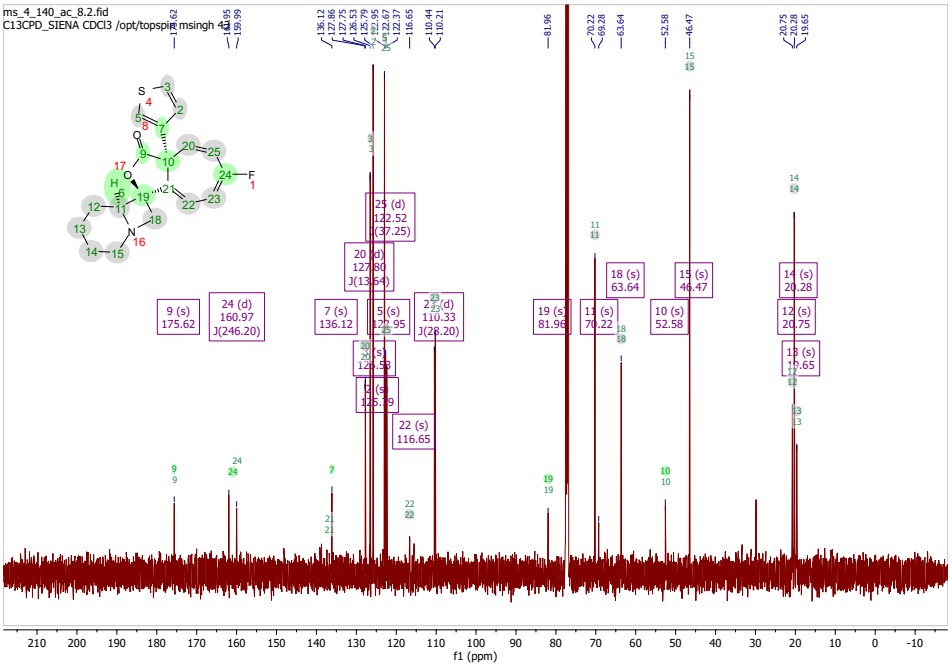


10.7.12 Compound 2-1-4

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 2-1-4

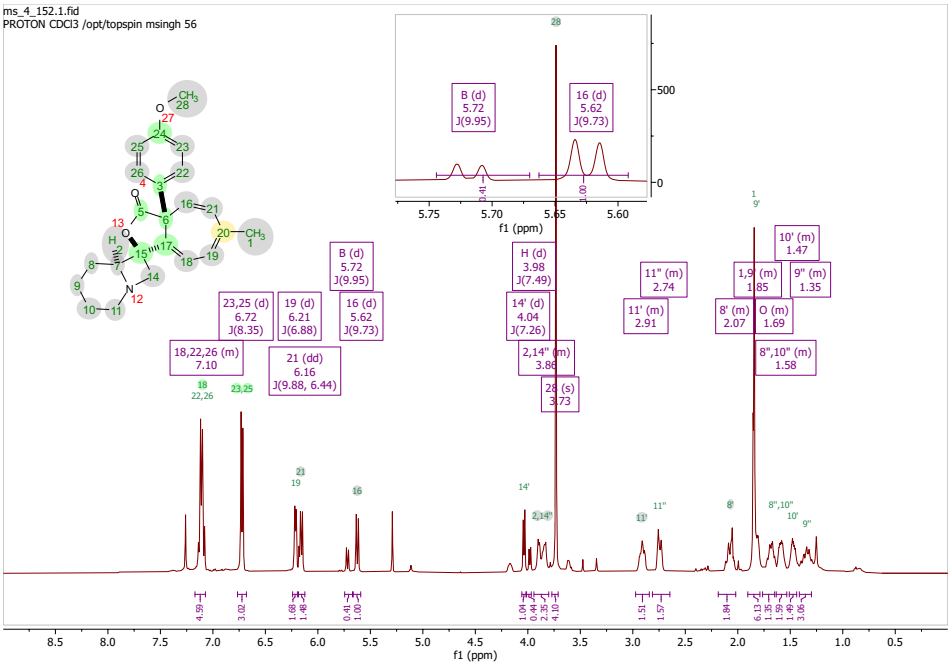


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 2-1-4

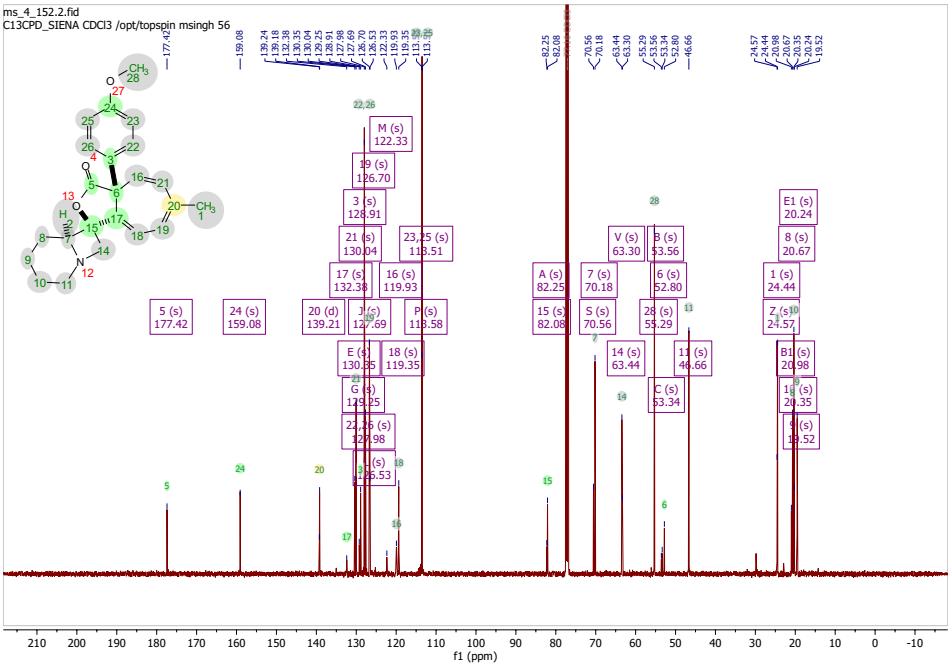


10.7.13 Compound 3-1-1

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 3-1-1

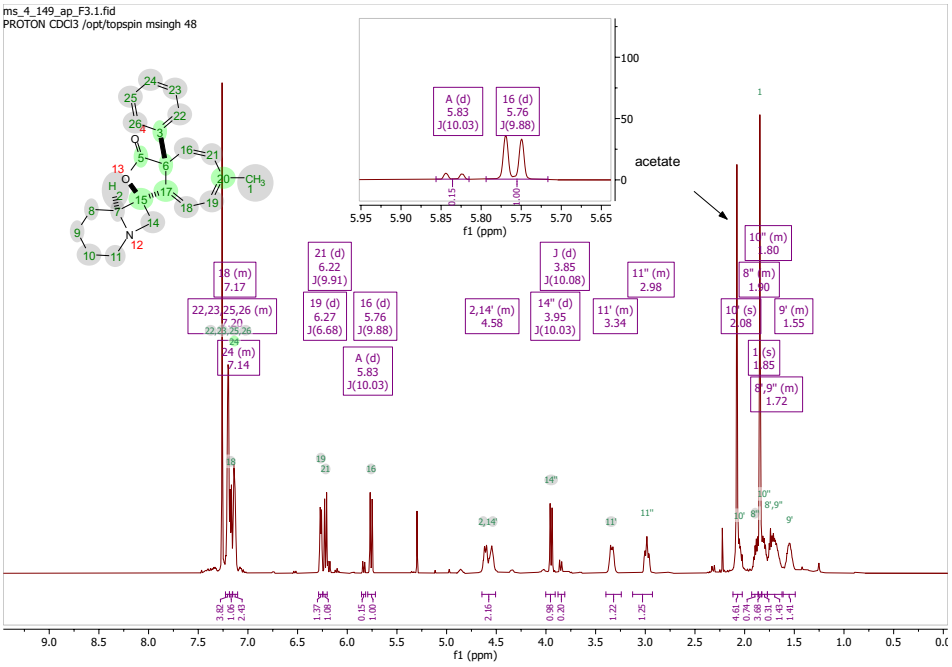


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 3-1-1

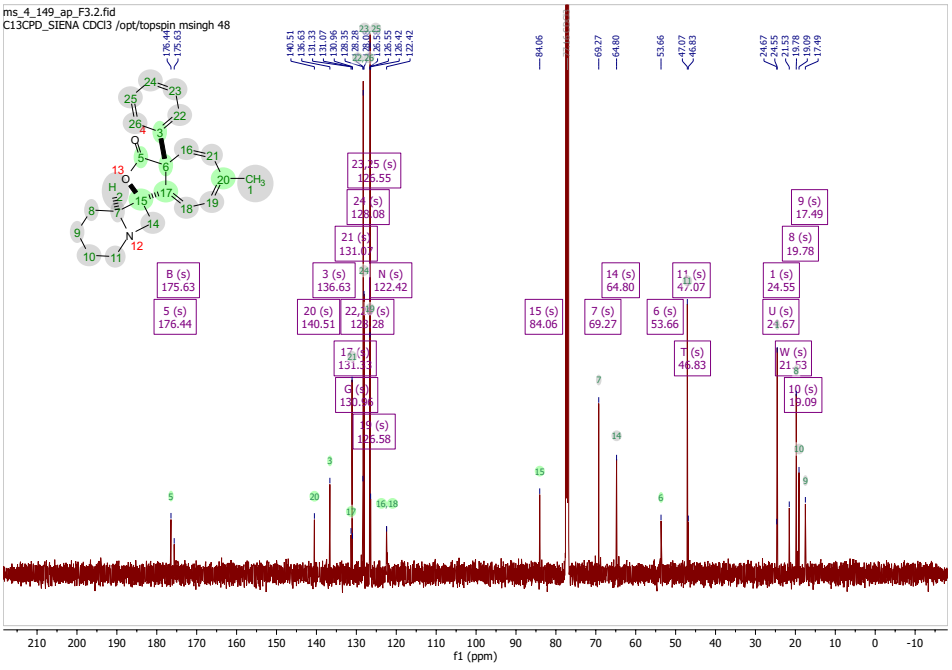


10.7.14 Compound 3-1-2

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 3-1-2

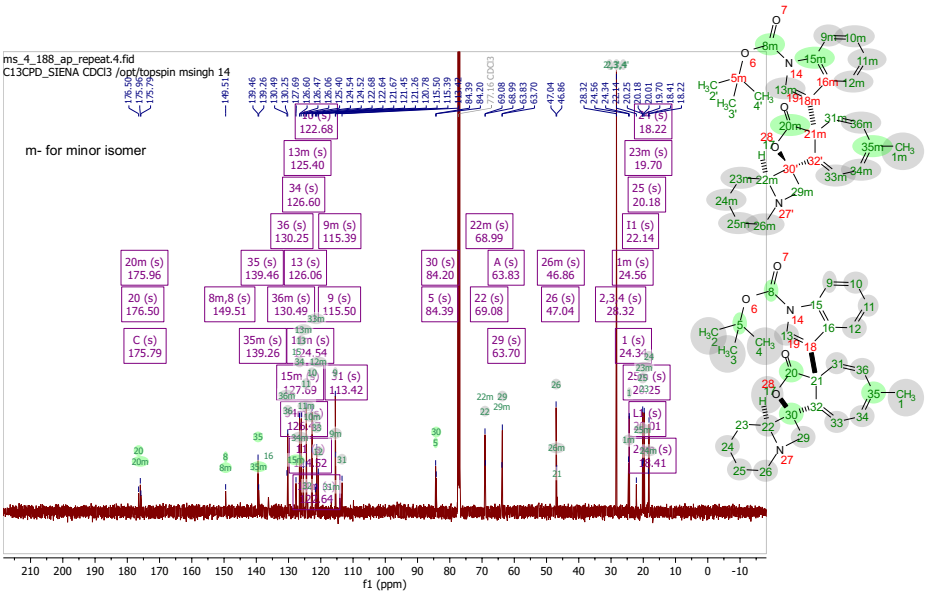


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 3-1-2

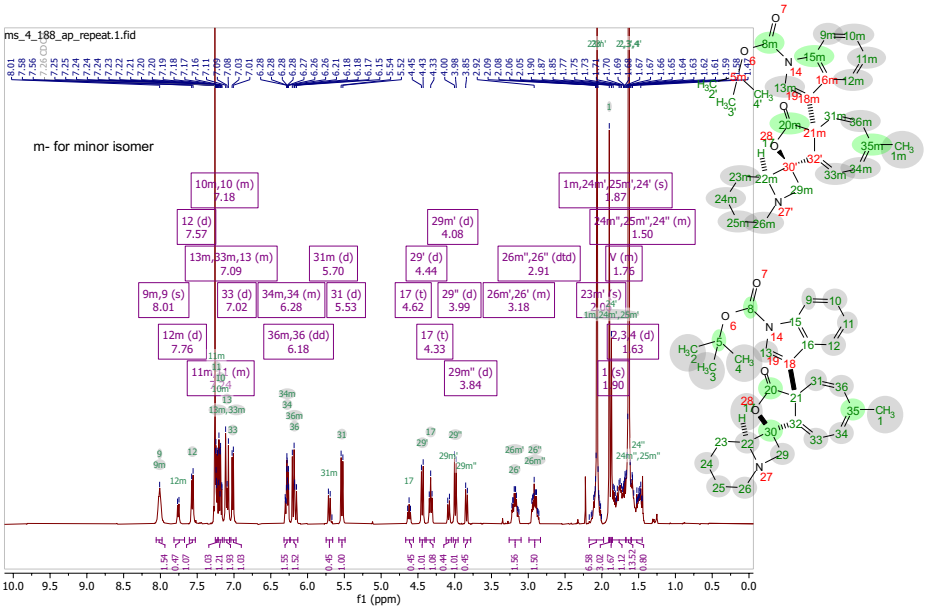


10.7.15 Compound 3-1-3

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 3-1-3

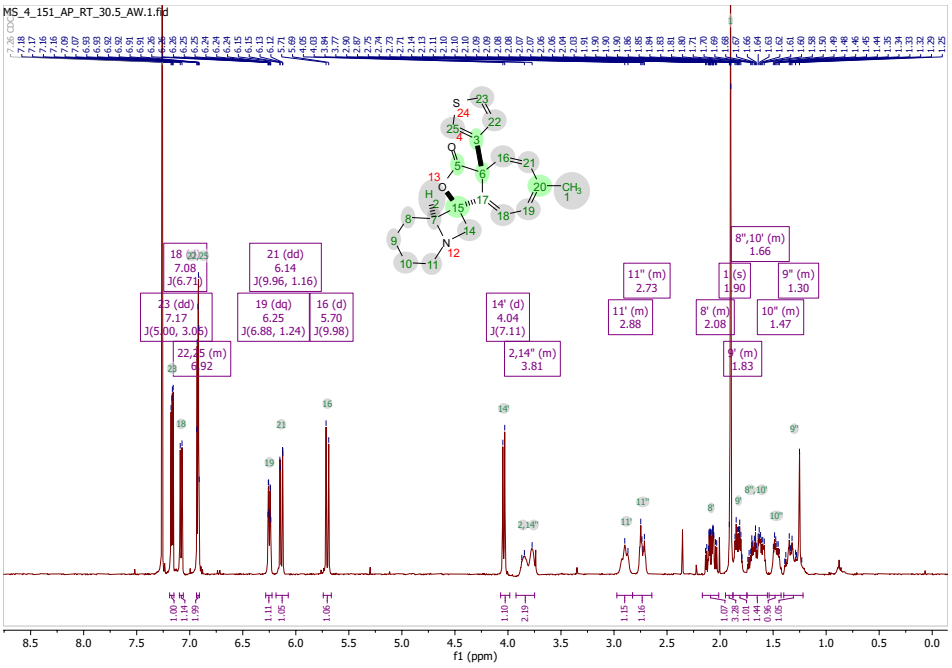


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 3-1-3

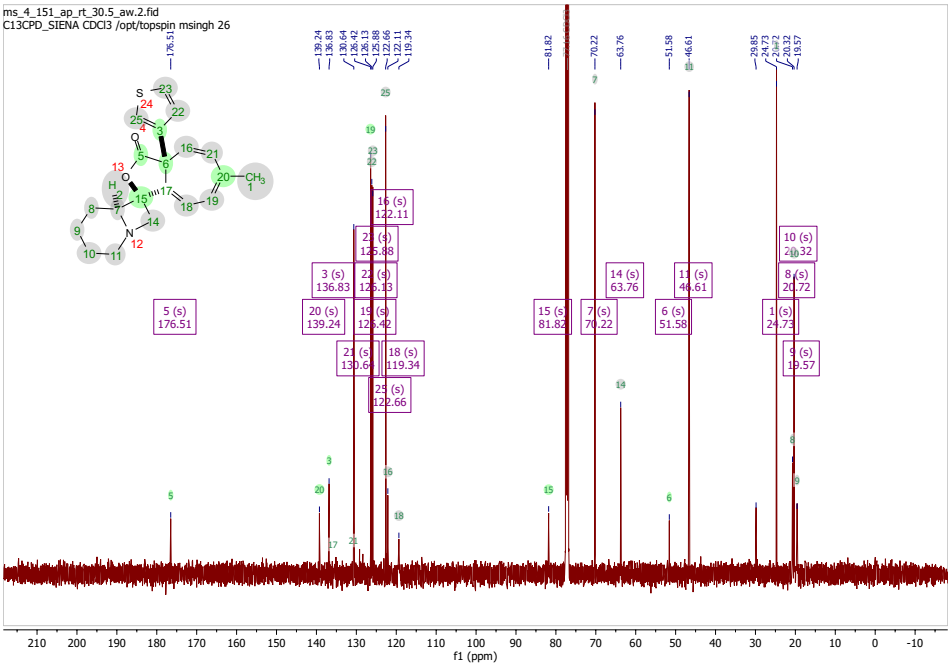


10.7.16 Compound 3-1-4

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 3-1-4

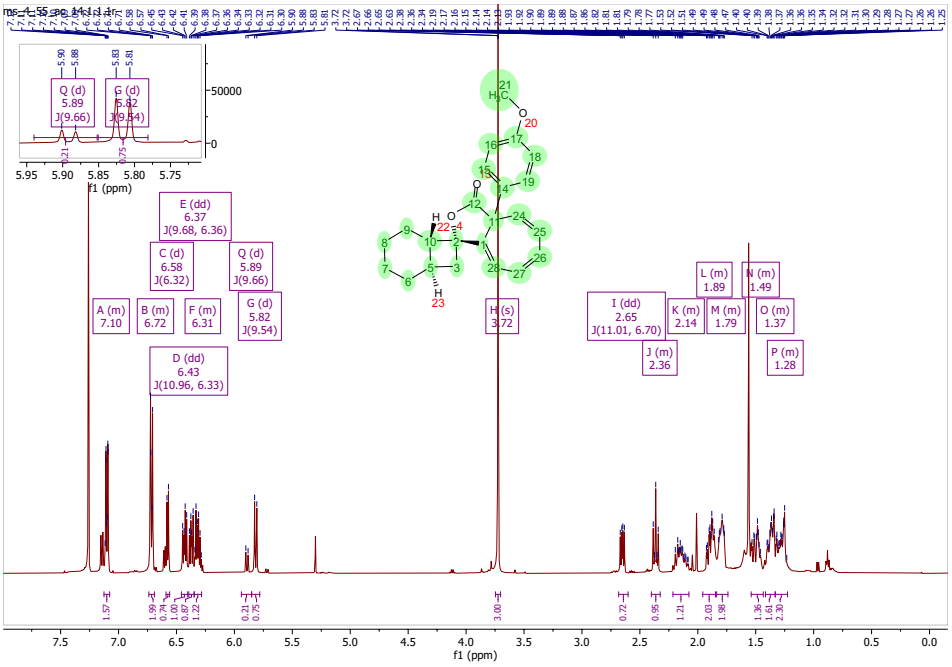


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 3-1-4

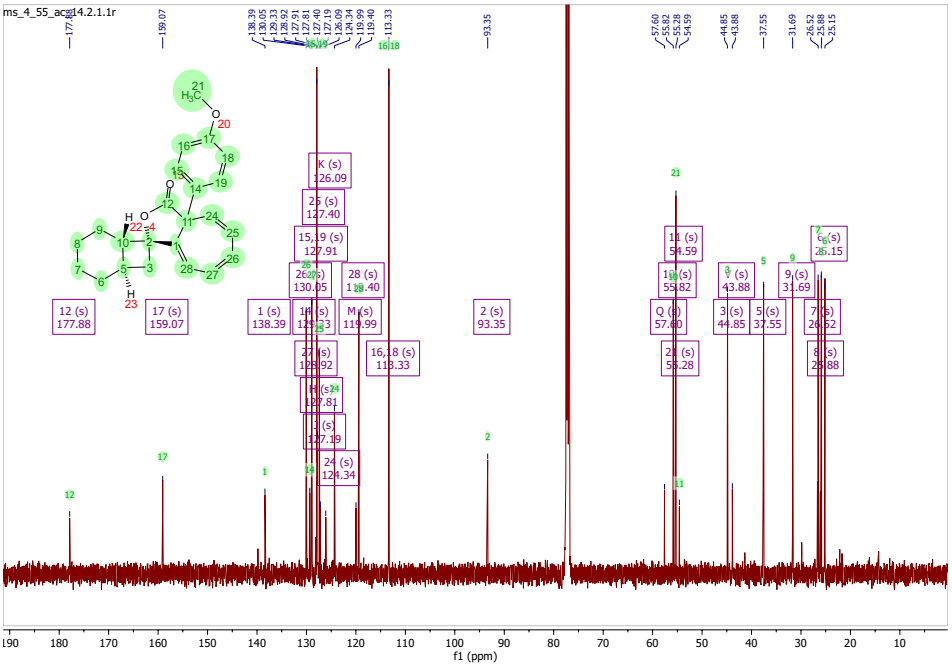


10.7.17 Compound 2-1-1 (CH)

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 2-1-1 (CH)

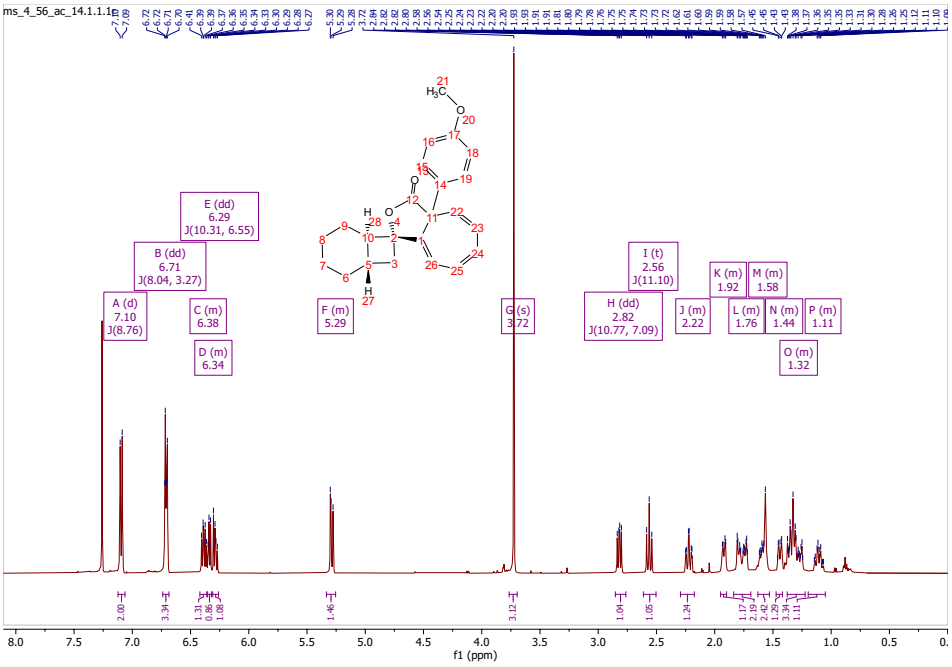


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 2-1-1 (CH)

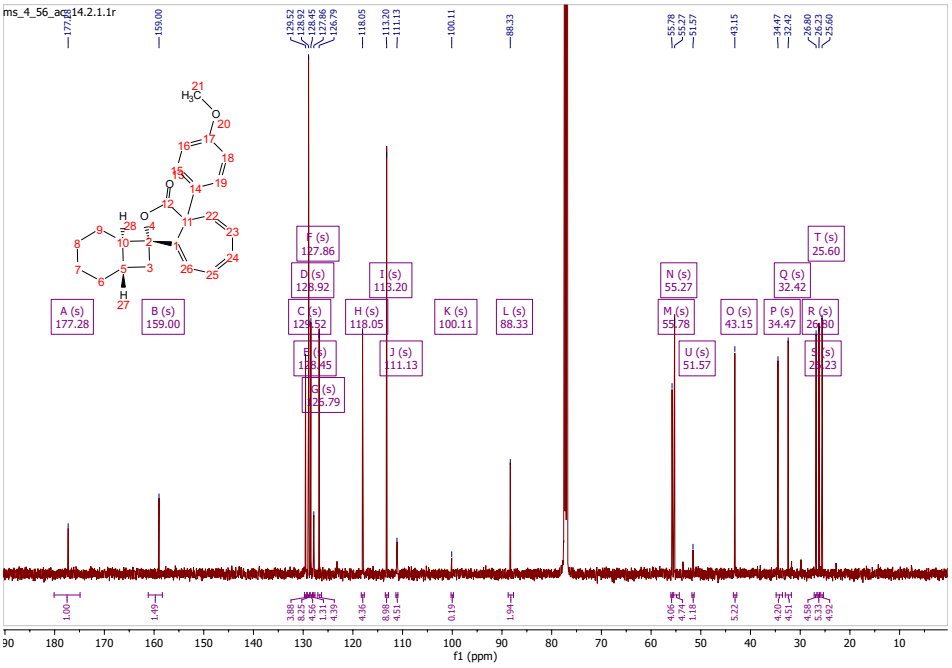


10.7.18 Compound 3-1-1 (CH

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 3-1-1 (CH)

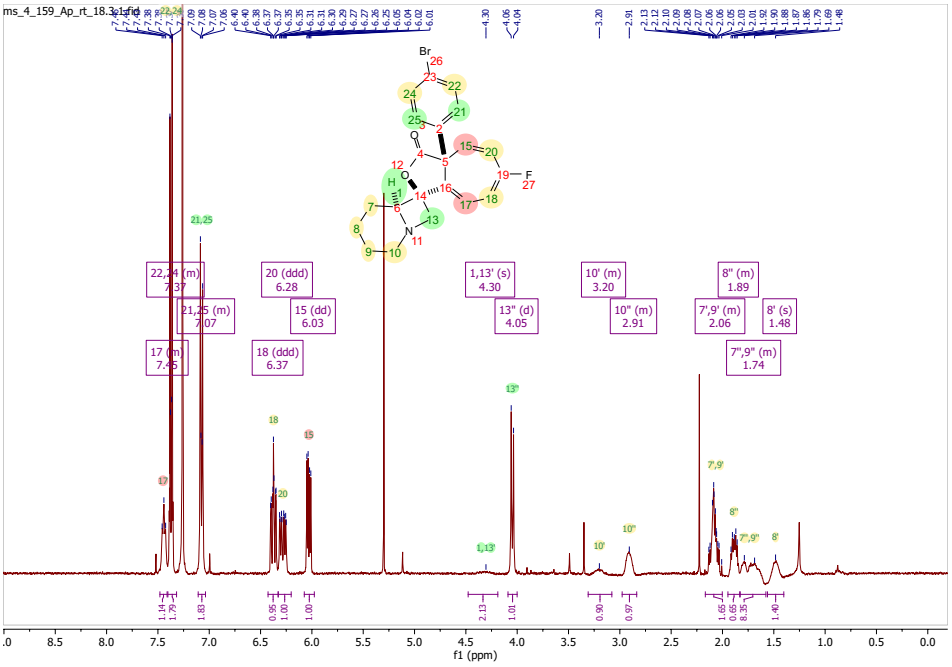


^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 3-1-1 (CH)

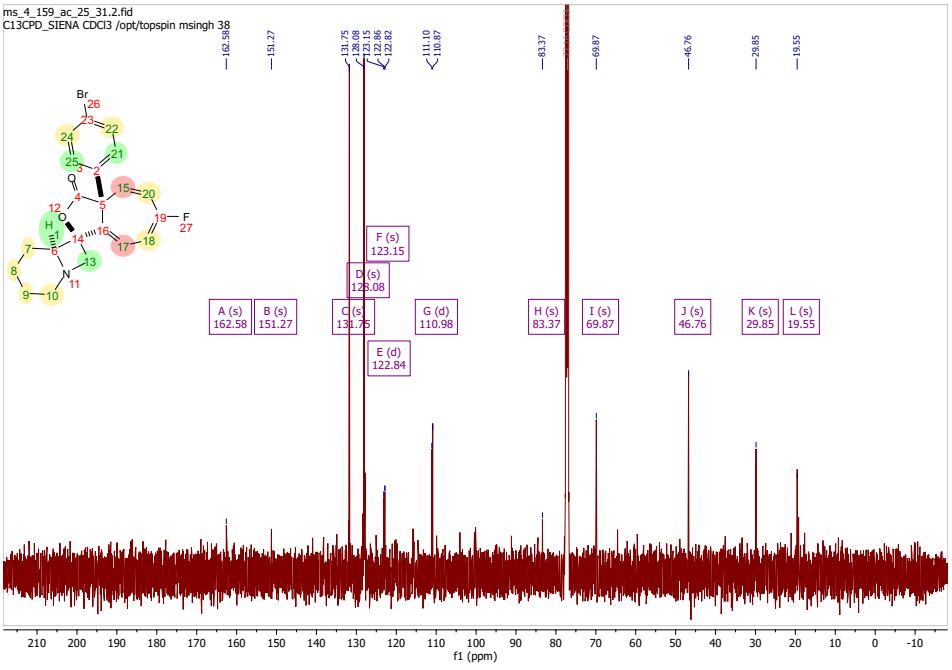


10.7.19 Compound 2-1-*p*-bromophenylacetic acid

^{1}H NMR spectrum (500 MHz, Chloroform-d) of Compound 2-1-*p*-bromophenylacetic acid



^{13}C {^{1}H } NMR spectrum (126 MHz, Chloroform-d) of Compound 2-1-*p*-bromophenylacetic acid



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