Contents

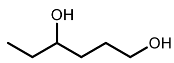
1. General Methods

NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{1}H 400 MHz, ^{13}C 101 MHz). The chemical shifts were recorded in ppm with the residual $CHCl_3$ signal referenced to 7.26 ppm and 77.16 ppm for ^{1}H and ^{13}C, respectively. When D_2O was used, the residual signal was referenced to 4.79 ppm for ^{1}H NMR. Coupling constants (*J*) are reported in Hz and refer to the observed peak multiplicities, where needed, 2D NMR was preformed to assign specific carbon atoms and stereochemistry of compounds. Thin layer chromatography was performed on Merck silica gel 60 F_{254} plates or Merck aluminium oxide 60 F_{254} neutral plates. Flash column chromatography was performed on silica gel (60 Å, 230-400 mesh) or Aluminium oxide 90 standardised.

Materials: Commercially available reagents, purchased from Sigma Aldrich or Acros, were used throughout without further purification. Anhydrous THF and CH_2Cl_2 were obtained from a Pure Solvent apparatus. Commercially available transaminases were purchased from Codexis® in the form of lyophilised cell extract.

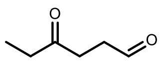
1.1. Preparation of aldehyde precursors

Hexane-1,4-diol (S1)



A solution of γ-caprolactone (1.6 mL, 14.3 mmol, 1.0 equiv.) in Et_2O (30 mL) was added dropwise to a suspension of $LiAlH_4$ (2.0 g, 57.2 mmol, 4.0 equiv.) in Et_2O (70 mL) at 0 °C. The reaction was stirred at rt for 19 h and quenched with the dropwise addition of sat. aq. Na_2SO_4 (4.5 mL) at 0 °C. The resulting white suspension was stirred vigorously for 30 min and then filtered through Celite. The filtrate was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The title product (0.783 g, 46%) was used directly in the next step without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.71 – 3.64 (m, 1H), 3.64 – 3.58 (m, 1H), 3.58 – 3.50 (m, 1H), 1.74 – 1.57 (m, 3H), 1.56 – 1.38 (m, 3H), 0.92 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 73.3, 63.0, 34.0, 30.4, 29.2, 10.1; **HRMS-ESI (m/z):** $C_6H_{15}O_2^+$ $[M+H]^+$ theoretical 119.1027, found 119.1042. Data is consistent with literature.[1]

4-Oxohexanal (S2)



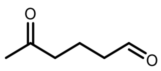
A solution of $(COCl)_2$ (2.2 mL, 25.2 mmol, 4.26 equiv.) in DCM (50 mL) was added a solution of DMSO (3.4 mL, 47.8 mmol, 8.07 equiv.) in DCM (3.4 mL) at -78 °C under nitrogen and stirred at this temperature for 10 min. The mixture was then dropwise added a solution of hexane-1,4-diol (0.700 g, 5.92 mmol, 1.0 equiv.) in DCM (25 mL) and stirred for 30 min at -78 °C. After this time the reaction was dropwise added Et_3N (12 mL, 86.1 mmol, 13.78 equiv.) and allowed to reach rt over 15 h. The reaction mixture was then added sat. aq. $NaHCO_3$ (20 mL) and extracted with EtOAc (50 mL x 4). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The title product was used in the next step without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.79 (1H, s), 2.78 – 2.66 (4H, m), 2.47 (2H, q, *J* = 7.3 Hz), 1.05 (3H, t, *J*

= 7.3 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.4, 200.7, 37.6, 36.0, 34.3, 7.9; **HRMS-ESI (m/z):** $C_6H_{11}O_2^+$ $[M+H]^+$ theoretical 115.0714, found 115.0754. Data is consistent with literature.[2]

General Procedure for the oxidative cleavage of 1-ethylcyclopent-1-ene, 1-methylcyclopentene and 6-methyl-5-hepten-2-one.

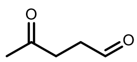
A stream of ozone was bubbled through a solution of the corresponding vinyl reagent (1 eq, 11.39 mmol) in CH_2Cl_2 (100 mL) at -78 °C for approx. 15 minutes until the solution turned a pale blue colour. Triphenylphosphine (1.1 eq, 3.286 g, 12.53 mmol) was then added, and the solution was left to react with stirring at r.t. for 16 h. The solution was concentrated *in vacuo* and the residue was purified by flash chromatography to provide the corresponding ketoaldehyde.

5-Oxohexanal (S3)



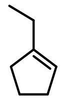
Derived from 1-methylcyclopentene. Colourless oil (0.870 g, 67 % yield) eluted in EtOAc / Cyclohexane (2:1) with an R_f = 0.42. **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.53 (1H, t, *J* = 1.4 Hz), 2.35-2.24 (4H, m), 1.92 (3H, s), 1.65 (2H, ap. quin, *J* = 7.1 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 207.8, 201.7, 42.5, 41.8, 29.4, 15.6; **HRMS-ESI** (m/z): $C_6H_{11}O_2^+$ $[M+H]^+$ theoretical 115.0754, found 115.0764.

4-Oxopentanal (S4)



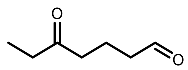
Derived from 6-methyl-5-hepten-2-one. Colourless oil (0.584 g, 43 %) eluted in EtOAc / Cyclohexane (1:9) with an R_f = 0.30. **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.66 (1H, s), 2.63 (4H, m), 2.08 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 206.5, 200.5, 37.3, 35.4, 29.6; **HRMS-ESI** (m/z): $C_5H_9O_2^+$ $[M+H]^+$ theoretical 101.0558, found 101.0539.

1-Ethylcyclopent-1-ene (S5)



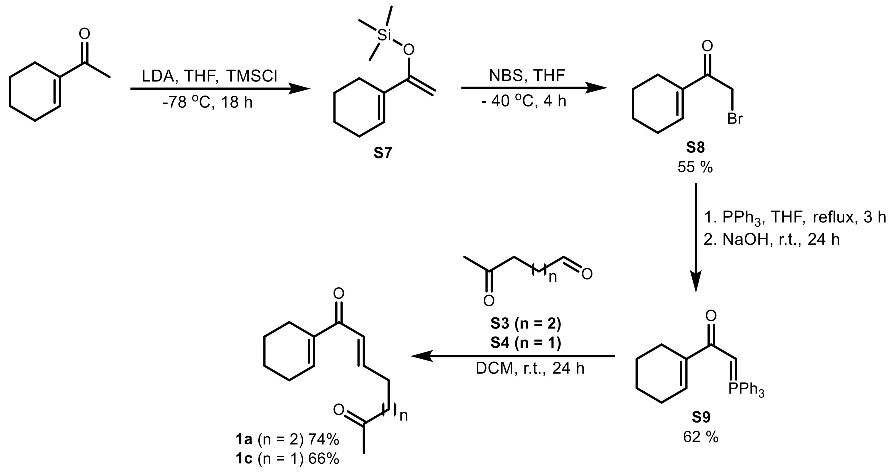
Ethyl magnesium bromide (16.0 mL, 3 M in Et_2O, 48.00 mmol, 1.2 equiv.) was added to cyclopentanone (3.54 mL, 40.00 mmol, 1.0 equiv.) in Et_2O (40 mL) under nitrogen at 0 °C. The mixture was then allowed to warm to room temperature and stirred for a further 2 h. The reaction mixture was then carefully quenched with cold water followed by sat. NH_4.Cl solution. The organic phase was separated, and the aqueous layer extracted with Et2O (2 × 50 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure to provide the crude 1-ethylcyclopentanol (3.884 g, 85% yield). To this crude, 85% wt. phosphoric acid (0.20 mL, 1.71 mmol, 0.05 equiv.) was added and the mixture was heated to 115 °C. The product was distilled off as it formed, and the biphasic solution was separated to provide crude 1-ethylcyclopentene as a colourless oil (1.042 g, 27% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 5.35-5.29 (1H, m), 2.35-2.26 (2H, m), 2.26-2.19 (2H, m), 2.11-2.02 (2H, m), 1.89-1.80 (2H, m), 1.04 (3H, t, J = 7.3 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 146.8, 122.1, 35.2, 32.5, 24.3, 23.6, 12.5; **HRMS-ESI (m/z):** $C_7H_{13}^+$ $[M+H]^+$ theoretical 97.0973, found 97.0999. Data is consistent with literature.[3]

5-Oxoheptanal (S6)



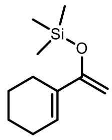
Derived from 1-Ethylcyclopent-1-ene. Colourless oil (0.666 g, 48 %) eluted in EtOAc / Cyclohexane (2:1) with an R_f = 0.60. **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.74 (1H, t, *J* = 1.45 Hz), 2.49-2.44 (4H, m), 2.40 (2H, q, *J* = 7.28 Hz), 1.88 (2H, quin, *J* = 7.09 Hz), 1.03 (3H, t, *J* = 7.40 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 210.8, 202.0, 43.1, 41.0, 36.0, 16.2, 7.9; **HRMS-ESI** (m/z): $C_7H_{13}O_2^+$ $[M+H]^+$ theoretical 129.0871, found 129.0892.

1.2. Substrate synthesis



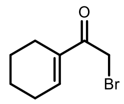
Scheme S1: *Synthesis of the bis-conjugated enone substrates **1a** and **1c** starting from 1-acetyl-1-cyclohexene.*

1-(1-Trimethylsilyloxy)vinyl-1-cyclohexene (S7)



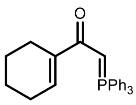
Lithium diisopropylamine (22.5 mL, 2M sol., 45.00 mmol, 1.45 equiv.) was dissolved in dry THF (20 mL) under inert conditions at -78 °C. 1-acetyl-1-cyclohexene (4.00 mL, 31.11 mmol, 1.0 equiv.) in dry THF (7 mL) was added dropwise and was stirred for 1 hr. Trimethylsilyl chloride (5.92 mL, 46.67 mmol, 1.5 equiv.) was then added, and the mixture was allowed to warm to r.t. overnight. The solution was then cooled to 0 °C, quenched with sat. ammonium chloride solution (25 mL) and extracted with ethyl acetate (3 x 15 mL). The organic fractions were combined and dried over $MgSO_4$ and concentrated *in vacuo* to give the crude title compound as an orange oil (R_f = 0.61 with EtOAc / Cyclohexane (1:9)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 6.23 - 6.17 (1H, m), 4.27 (2H, d, *J* = 63.7 Hz), 2.18 - 2.10 (4H, m), 1.72 - 1.53 (4H, m), 0.22 (9H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 156.7, 133.2, 125.4, 89.8, 25.6, 25.0, 22.9, 22.2, 0.1. Data is consistent with literature.[4]

1-Bromo-2-(cyclohex-1-enyl)ethan-one (S8)



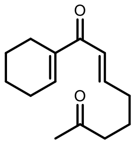
N-bromosuccinimide (6.092 g, 34.23 mmol, 1.1 equiv.) was added to a THF solution (45 mL) of the crude silyl enol ether **S7** at -40 °C and the mixture was stirred overnight at the same temperature. The mixture was then poured into sat. aq. $Na_2S_2O_3$ solution (60 mL) and the aqueous layer extracted with EtOAc (3 x 30 mL). The combined organic extracts were then washed with brine (2 ×60 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by column chromatography on silica gel (EtOAc / Cyclohexane (1:20)) to provide the title compound as an orange oil (3.49 g, 55 % yield). R_f 0.31 (EtOAc / Cyclohexane (1:9)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 6.99 - 6.95 (1H, m), 4.15 (2H, s), 2.31 - 2.22 (4H, m), 1.68 - 1.57 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 199.3, 142.9, 136.8, 30.2, 26.2, 23.2, 21.7, 21.3. Data is consistent with literature.[4]

1-Cyclohex-1-enyl-2-(triphenylphosphanylidene)ethenone (S9)



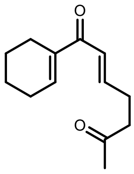
To 1-bromo-2-(cyclohex-1-enyl)ethan-2-one (**S8**) (3.490 g, 17.18 mmol, 1.0 equiv.) in THF (35 mL) was added triphenylphosphine (4.507 g, 17.18 mmol, 1.0 equiv.) and heated to reflux for 4 h. The reaction was allowed to cool to r.t. and the precipitate was collected by filtration. The residue was then suspended in MeOH:H_2O (1:1, 75 mL) and NaOH solution (1M) was added until the mixture became slightly basic and stirred for 24 h. The MeOH was removed under reduced pressure and the aqueous solution was extracted with DCM (3 x 50 mL). The combined organic extracts were then washed with brine (50 mL), dried with $MgSO_4$, filtered, and concentrated *in vacuo* to provide the title compound as a beige solid (4.128 g, 62 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.69 - 7.62 (6H, m), 7.55 - 7.49 (3H, m), 7.47 - 7.41 (6H, m), 6.64 (1H, m), 3.92 (1H,m), 2.42 - 2.36 (2H, m), 2.18 - 2.11 (2H, m), 1.71 - 1.63 (2H, m), 1.62 - 1.54 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 187.2,133.2 (3C), 133.1 (6C), 131.9 (3C), 128.8 (6C), 128.0, 127.1, 50.2 (d, J = 110 Hz), 25.8, 25.7, 23.0, 22.2; **HRMS-ESI (m/z):** $C_{26}H_{26}OP^+$ $[M+H]^+$ theoretical 385.1677, found 385.1721.

(2*E*)-1-(Cyclohex-1-en-1-yl)oct-2-ene-1,7-dione (1a)

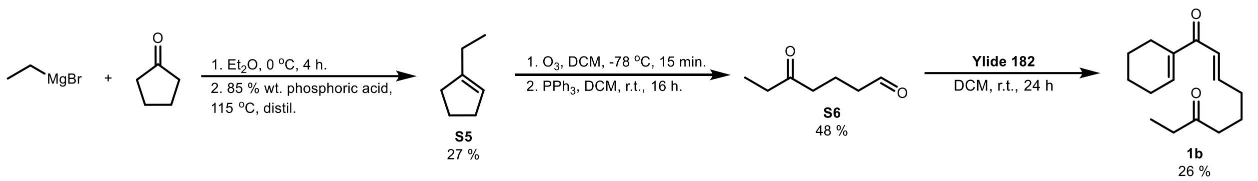


1-cyclohex-1-enyl-2-(triphenylphosphanylidene)ethenone (1.301 g, 3.38 mmol, 1.1 equiv.) was added to a solution of 5-oxohexanal (0.351 g, 3.07 mmol, 1.0 equiv.) in DCM (20 mL) and allowed to react at r.t. for 18 hrs. The DCM was removed under reduced pressure and purified via column chromatography on silica gel (EtOAc / Cyclohexane (1:19)) to provide the title compound as a yellow oil (0.503 g, 74 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 6.84-6.78 (1H, m), 6.75-6.66 (1H, dt, *J* = 15.31, 6.84 Hz), 6.60-6.53 (1H, d, *J* = 15.31 Hz), 2.38 (2H, t, *J* = 7.31 Hz), 2.21-2.11 (6H, m), 2.04 (3H, s), 1.67 (2H, quin, *J* = 5.89), 1.60-1.48 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 208.2, 191.0, 145.4, 140.1, 139.6, 125.4, 42.5, 31.6, 29.87, 26.0, 23.3, 22.1, 21.8, 21.5; **HRMS-ESI (m/z):** $C_{14}H_{21}O_2^+$ [M+H]$^+$ theoretical 221.1497, found 221.1537.

(2*E*)-1-(Cyclohex-1-en-1-yl)hept-2-ene-1,6-dione (1c)

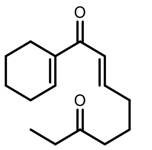


1-cyclohex-1-enyl-2-(triphenylphosphanylidene)ethenone (2.691 g, 6.99 mmol, 1.2 equiv.) was added to a solution of 4-oxopentanal (0.584 g, 5.833 mmol, 1.0 equiv.) in DCM (20 mL) and allowed to react at r.t. for 18 hrs. The DCM was removed under reduced pressure and purified via column chromatography on silica gel (EtOAc / Cyclohexane (1:9)) to provide the title compound as a yellow oil (0.793 g, 66 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 6.90-6.86 (1H, m), 6.77 (1H, dt, *J* = 15.2, 6.6 Hz), 6.69-6.62 (1H, d, J = 15.3 Hz), 2.64-2.57 (2H, m), 2.52-2.45 (2H, m), 2.30-2.22 (4H, m), 2.15 (3H, s), 1.68-1.57 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 207.2, 191.2, 144.5, 140.4, 139.9, 125.7, 41.9, 30.1, 26.6, 26.3, 23.5, 22.0, 21.7; **HRMS-ESI (m/z):** $C_{13}H_{19}O_2^+$ [M+H]$^+$ theoretical 207.1340, found 207.1381.

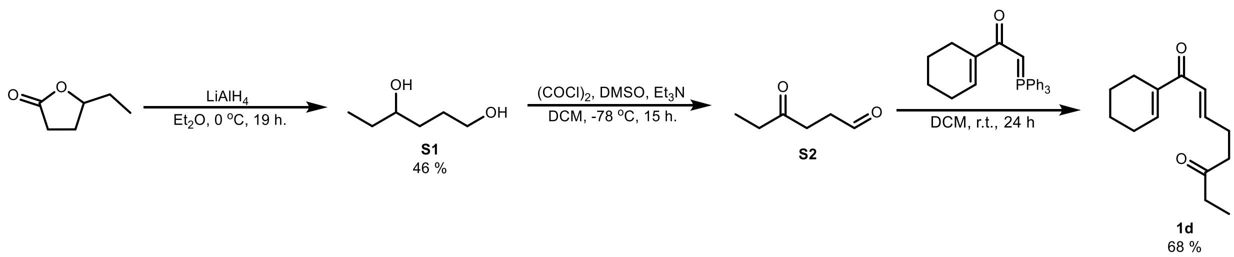


Scheme S2: *Synthesis of the bis-conjugated ethyl derivative substrate **193** starting from cyclopentanone **190**.*

(*E*)-1-(Cyclohex-1-en-1-yl)non-2-ene-1,7-dione (1b)

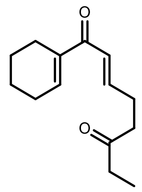


1-cyclohex-1-enyl-2-(triphenylphosphanylidene)ethenone (2.198 g, 5.72 mmol, 1.1 equiv.) was added to a solution of 5-oxoheptanal (0.666 g, 5.20 mmol, 1.0 eqiuv.) in DCM (20 mL) and allowed to react at r.t. for 18 hrs. The DCM was removed under reduced pressure and purified via column chromatography on silica gel (EtOAc / Cyclohexane (1:19)) to provide the title compound as a yellow oil (0.310 g, 26 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 6.90-6.86 (1H, m), 6.79 (1H, dt, *J* = 15.26, 6.84 Hz), 6.66-6.61 (1H, m), 2.46-2.37 (4H, m), 2.30-2.19 (6H, m), 1.76 (2H, quin, *J* = 7.37 Hz), 1.69-1.56 (4H, m), 1.04 (3H, t, *J* = 7.40 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 211.2, 191.3, 145.7, 140.3, 139.9, 125.6, 41.5, 36.1, 31.9, 26.3, 23.5, 22.4, 22.1, 21.7, 7.9; **HRMS-ESI (m/z):** $C_{15}H_{23}O_2^+$ $[M+H]^+$ theoretical 235.1653, found 235.1694.

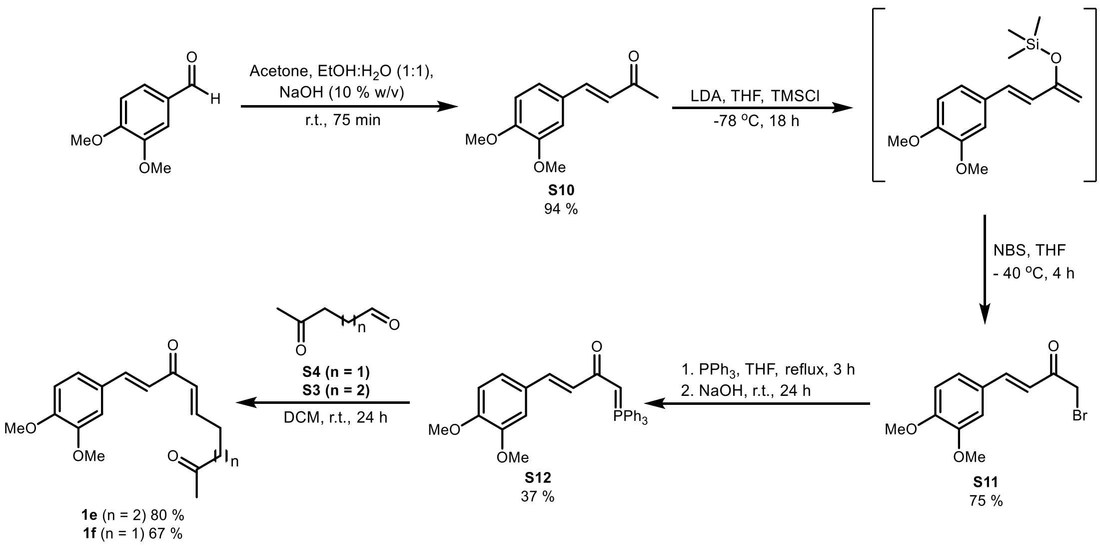


Scheme S3: *Synthesis of the bis-conjugated ethyl derivative substrate **1d** from 5-ethyldihydrofuran-2-one.*

(*E*)-1-(Cyclohex-1-en-1-yl)oct-2-ene-1,6-dione (1d)

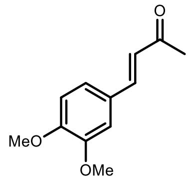


1-cyclohex-1-enyl-2-(triphenylphosphanylidene)ethenone (1.36 g, 3.54 mmol, 1.2 equiv.) was added to a solution of 4-Oxohexanal (0.336 g, 2.95 mmol, 1.0 equiv.) in DCM (10 mL) and allowed to react at r.t. for 18 hrs. The DCM was removed under reduced pressure and purified via column chromatography on silica gel (EtOAc / cyclohexane (1:7)) to provide the title compound (R_f = 0.5, EtOAc / Cyclohexane (1:2)) as a yellow oil (0.440 g, 68 % yield). **^{1}H NMR** (400 MHz, CDCl3) δ 6.87 (1H, t, *J* = 3.8 Hz), 6.77 (1H, dt, J = 15.3, 6.5 Hz), 6.65 (1H, d, *J* = 15.3 Hz), 2.62 – 2.53 (2H, m), 2.49 (2H, dt, J = 7.9, 6.6 Hz), 2.42 (2H, q, J = 7.3 Hz), 2.28-2.22 (4H, m), 1.67-1.57 (4H, m), 1.05 (3H, t, J = 7.3 Hz); **^{13}C NMR** (101 MHz, CDCl3) δ 209.9, 191.3, 144.8, 140.4, 139.9, 125.7, 40.6, 36.2, 26.7, 26.3, 23.5, 22.1, 21.7, 7.9; **HRMS-ESI (m/z):** $C_{14}H_{21}O_2^+$ [M+H]$^+$ theoretical 221.1497, found 221.1537.



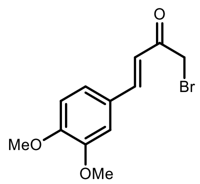
Scheme S4: *Synthesis of the bis-conjugated enone substrates **1e** and **1f** starting from 3,4-dimethoxybenzaldehyde.*

3,4-Dimethoxybenzylideneacetone (S10)



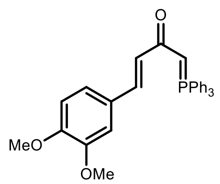
To a solution of 3,4-dimethoxybenzaldehyde (3.380 g, 20.4 mmol, 1.0 equiv.) dissolved in aq. ethanol (270 mL, 50 % v/v), acetone (7.56 mL, 102.0 mmol, 5.0 equiv.) and then NaOH solution (25 mL, 10% w/v) was added dropwise and left to react for 70 min. The reaction mixture was neutralised to pH 7.0 using 4M HCl, extracted with CH_2Cl_2, dried using $MgSO_4$ and concentrated *in vacuo*. The crude product was recrystalised diethyl ether: cyclohexane (1:1) to yield the product as a yellow crystal (3.96 g, 94 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.46 (1H, d, *J* = 12.95 Hz), 7.12 (1H, dd, *J* = 6.63, 1.58 Hz), 7.07 (1H, d, *J* = 1.62 Hz), 6.88 (1H, d, *J* = 6.62 Hz), 6.60 (1H, d, *J* = 12.82 Hz), 3.92 (6H, s), 2.37 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 198.5, 151.5, 149.4, 143.6, 127.5, 125.4, 123.15, 111.2, 109.7, 56.1, 56.0, 27.5; **HRMS-ESI (m/z):** $C_{12}H_{15}O_3^+$ $[M+H]^+$ theoretical 207.0976, found 207.1017. Data is consistent with literature.[5]

(*E*)-1-Bromo-4-(3,4-dimethoxyphenyl)but-3-en-2-one (S11)



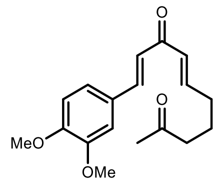
Lithium diisopropylamine (7.25 mL, 14.50 mmol, 1.45 equiv.) was dissolved in dry THF (10 mL) under inert conditions at -78 °C. 3,4-dimethoxybenzylideacetone (2.062 g, 10.00 mmol, 1.0 equiv.) in dry THF (5 mL) was added dropwise and was stirred for 1 hr. Trimethylsilyl chloride (1.903 mL, 15.00 mmol, 1.5 equiv.) was then added, and the mixture was allowed to warm to r.t. overnight. The solution was then cooled to 0 °C, quenched with sat. ammonium chloride solution (25 mL) and extracted with ethyl acetate (3 x 15 mL). The organic fractions were combined and dried over $MgSO_4$ and concentrated *in vacuo* to give the crude silyl enol ether as an orange oil. N-bromosuccinimide (1.958 g, 11.00 mmol, 1.1 equiv.) was added to a THF solution (15 mL) of the silyl enol ether at -40 °C and the mixture was stirred overnight at the same temperature. The mixture was then poured into sat. aq. $Na_2S_2O_3$ solution (30 mL) and the aqueous layer extracted with EtOAc (3 x 20 mL). The combined organic extracts were then washed with brine (30 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by column chromatography on silica gel (EtOAc / Cyclohexane (1:9)) to provide the title compound as a brown oil (2.148 g, 75 % yield). R_f 0.70 (EtOAc / Cyclohexane (1:9)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.63 (1H, d, J = 15.98 Hz), 7.16 (1H, dd, J = 8.31, 1.97 Hz), 7.07 (1H, d, J = 2.00 Hz), 6.87 (1H, d, J = 8.28 Hz), 6.79 (1H, d, J = 15.92 Hz), 4.07 (2H, s), 3.91-3.90 (6H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 191.0, 152.0, 149.4, 145.6, 126.9, 123.8, 120.2, 111.2, 110.0, 56.1, 56.0, 33.1.

(*E*)-4-(3,4-Dimethoxyphenyl)-1-(triphenylphosphaneylidene)but-3-en-2-one (S12)



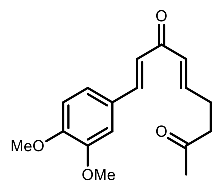
To 1-bromo-4-(3,4-dimethoxyphenyl)but-3-en-2-one (2.148 g, 7.533 mmol, 1.0 equiv.) in THF (15 mL) was added triphenylphosphine (2.173 g, 8.286 mmol, 1.1 equiv.) and heated to reflux for 4 h. The reaction was allowed to cool to r.t. and the precipitate was collected by filtration. The residue was then suspended in MeOH:H_2O (1:1, 40 mL) and NaOH solution (1M) was added until the mixture became slightly basic and stirred for 24 h. The MeOH was removed under reduced pressure and the aqueous solution was extracted with DCM (3 x 30 mL). The combined organic extracts were then washed with brine (30 mL), dried with $MgSO_4$, filtered, and concentrated *in vacuo* to provide the title compound as a beige solid (1.275 g, 37 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.69 (6H, m), 7.55 (3H, m), 7.47 (6H, m), 7.35 (1H, d, J = 15.61 Hz), 7.06 (2H, m), 6.79 (2H, m), 5.29 (1H, s), 3.88 (3H, s), 3.87 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 183.0, 149.3, 148.9, 133.8, 133.2 (6C), 132.1 (3C), 132.0 (3C), 128.9 (6C), 127.3, 126.4, 121.2, 111.0, 109.4, 55.8, 55.7, 53.4; **HRMS-ESI (m/z):** $C_{30}H_{28}O_3P^+$ $[M+H]^+$ theoretical 467.1731, found 467.1772.

(6*E*,9*E*)-10-(3,4-Dimethoxyphenyl)deca-6,9-diene-2,8-dione (1e)

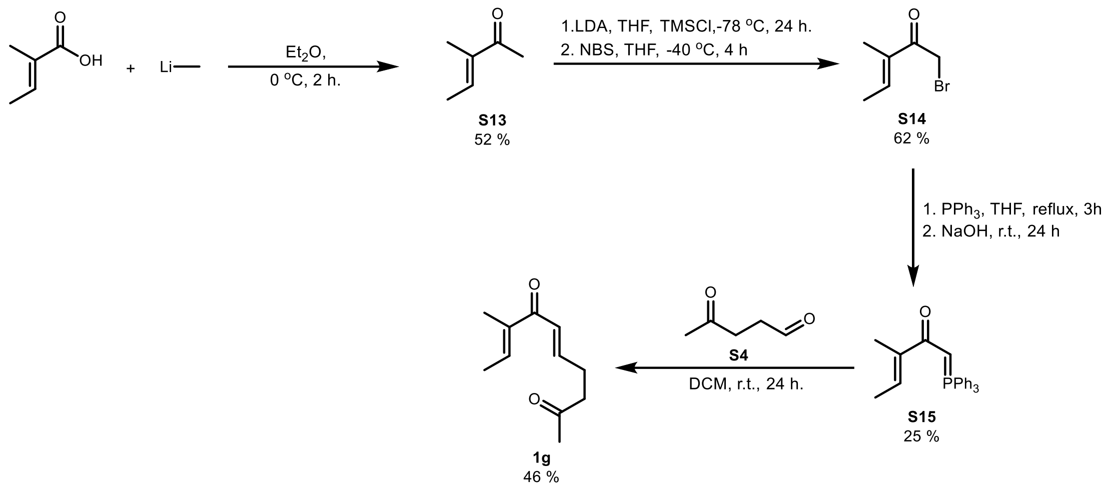


4-(3,4-dimethoxyphenyl)-1-(triphenylphosphanylidene)but-3-en-2-one (0.300 g, 0.64 mmol, 1.0 equiv.) was added to a solution of 4-oxopentanal (0.073 g, 0.64 mmol, 1.0 equiv.) in DCM (5 mL) and allowed to react at r.t. for 24 hrs. The DCM was removed under reduced pressure and purified via column chromatography on silica gel (EtOAc / Cyclohexane (1:4)) to provide the title compound as a yellow crystal (0.194 g, 80 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.60 (1H, d, *J* = 12.7 Hz), 7.16 (1H, dd, *J* = 6.6, 1.5 Hz), 7.10 (1H, d, *J* = 1.5 Hz), 6.94 (1H, dt, *J* = 12.5, 5.4 Hz), 6.88 (1H, d, *J* = 6.7), 6.82 (1H, d, *J* = 12.7 Hz), 6.46 (1H, dt, *J* = 12.5, 1.2 Hz), 3.93 (3H, s), 3.92 (3H, s), 2.49 (2H, t, *J* = 5.8 Hz), 2.32-2.26 (2H, m), 2.15 (3H, s), 1.81 (2H, quin, *J* = 5.9 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 208.4, 189.1, 151.5, 149.4, 146.5, 143.5, 129.7, 127.9, 123.2, 123.2, 111.3, 109.9, 56.1, 56.1, 42.8, 31.9, 30.2, 22.2; **HRMS-ESI (m/z):** $C_{18}H_{23}O_4^+$ $[M+H]^+$ theoretical 303.1552, found 303.1591.

(5*E*,8*E*)-9-(3,4-Dimethoxyphenyl)nona-5,8-diene-2,7-dione (1f)

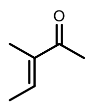


4-(3,4-dimethoxyphenyl)-1-(triphenylphosphanylidene)but-3-en-2-one (1.633 g, 3.50 mmol, 1.0 equiv.) was added to a solution of 4-oxopentanal (0.350 g, 3.50 mmol, 1.0 equiv.) in DCM (20 mL) and allowed to react at r.t. for 24 hrs. The DCM was removed under reduced pressure and purified via column chromatography on silica gel (EtOAc / Cyclohexane (1:9)) to provide the title compound as a yellow crystal (0.674 g, 67 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.59 (1H, d, *J* = 15.9 Hz), 7.16 (1H, dd, *J* = 8.4, 1.9 Hz), 7.09 (1H, d, *J* = 1.9 Hz), 6.94 (1H, dt, *J* = 15.6, 6.8 Hz), 6.87 (1H, d, J= 8.3 Hz), 6.81 (1H, d, *J* = 15.9 Hz), 6.46 (1H, dt, *J* = 15.6, 1.5 Hz), 3.93 (3H, s,), 3.92 (3H, s), 2.66 (2H, t, *J* = 6.6 Hz), 2.55 (2H, m), 2.18 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 207.1, 189.0, 151.5, 149.4, 145.5, 143.6, 129.8, 127.8, 123.2, 123.1, 111.2, 109.9, 56.1, 56.0, 41.8, 30.1, 26.5; **HRMS-ESI (m/z):** $C_{17}H_{21}O_4^+$ [M+H]$^+$ theoretical 289.1395, found 289.1434.



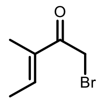
Scheme S5: *Synthesis of the bis-conjugated enone substrate **1g** starting from tiglic acid.*

(*E*)-3-Methylpent-3-en-2-one (S13)



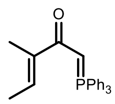
A solution of methyllithium (25 ml, 1.6 M in diethyl ether, 40 mmol, 2.0 equiv.) was added to a solution of tiglic acid (2.002 g, 20 mmol, 1.0 equiv.) in dry diethyl ether (46 ml) at 0 °C, and the mixture was stirred at the same temperature for 2 h. To the resulting mixture at 0 °C was gradually added 0.4 M hydrochloric acid (80 ml), and the mixture was extracted with diethyl ether. The extract was washed with brine, dried over $MgSO_4$, and concentrated. The residue was distilled under reduced pressure to give pentanone (0.773 g, 52 %) as an oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 6.73 (1H, qq, *J* = 6.9, 1.3 Hz), 2.29 (3H, s), 1.87 – 1.84 (3H, m), 1.77 – 1.75 (3H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 199.9, 139.9, 138.5, 25.5, 14.7, 10.9; Data is consistent with literature.[6]

(*E*)-1-Bromo-3-methylpent-3-en-2-one (S14)



The pentanone **165** (0.773 g, 7.47 mmol, 1.0 equiv.) was dissolved in dry THF (15 ml) and left to the side of LDA (5.415 ml, 2M in THF/hexanes, 10.83 mmol, 1.45 equiv.) at -78 °C. The enone solution was added dropwise to the LDA solution and left to react for 40 min. TMSCl (1.422 ml, 11.20 mmol, 1.5 equiv.) was then added to the mixture and the reaction was left to react for 18 h. The solution was cooled to 0 °C and quenched with sat. NH_4Cl (20 ml). The organic layer was collected and separated. The aqueous layer was extracted with ethyl acetate (3 x 15 ml) and the organic layers were combined and concentrated to yield an orange oil. This crude silyl enol ether was dissolved in dry THF (15 ml) and N-bromosuccinimide (1.462 g, 1.1 equiv., 8.21 mmol) was added at -40 °C and left to react o.n. The reaction was quenched with $Na_2S_2O_3$ and the organic layer was separated. The aqueous layer was extracted with diethyl ether (3 x 15 ml) and the organic layers were combined and concentrated *in vaccuo*. The crude product was purified by flash column chromatography (silica dry-load, cyclohexane: ethyl acetate (9:1)) as a yellow oil (0.858 g, 62 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 6.80 (1H, ap. qq, *J* = 6.9, 1.3 Hz), 4.15 (2H, s), 1.91 (3H, m), 1.83 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 192.7, 140.2, 135.8, 53.4, 15.0, 11.3; Data is consistent with literature.[7]

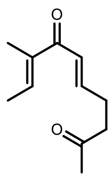
(*E*)-3-Methyl-1-(triphenylphosphaneylidene)pent-3-en-2-one (S15)



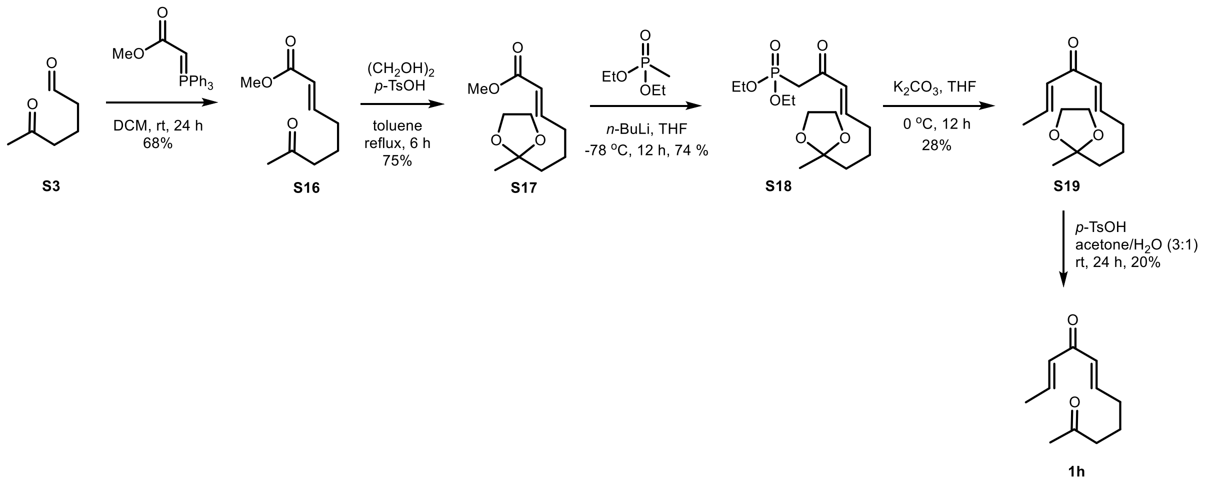
To 1-bromo-3-methylpent-3-en-2-one (0.858 g, 4.846 mmol, 1.0 equiv.) in THF (15 mL) was added triphenylphosphine (1.398 g, 5.331 mmol, 1.1 equiv.) and heated to reflux for 4 h. The reaction was allowed to cool to r.t. and the precipitate was collected by filtration. The residue was then suspended in MeOH:H_2O (1:1, 25 mL) and NaOH solution (1M) was added until the mixture became slightly basic and stirred for 24 h. The MeOH was removed under reduced pressure and the aqueous solution was extracted with DCM (3 x 20 mL). The combined organic extracts were then washed with brine (25 mL), dried with $MgSO_4$, filtered, and concentrated *in vacuo* to provide the title compound as a beige solid

(0.070 g, 25 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.70 - 7.62 (6H, m), 7.55 - 7.49 (3H, m), 7.47 - 7.41 (6H, m), 6.54-6.47 (1H, m), 3.98 (1H, br s), 1.91 (3H, s), 1.73-1.70 (3H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 187.8, 133.1, 133.0, 131.8 (3C),131.8 (3C), 128.8 (6C), 128.7 (6C), 50.7, 13.9, 13.4; **HRMS-ESI (m/z):** $C_{24}H_{24}OP^+$ $[M+H]^+$ theoretical 359.1520, found 359.1561. Data is consistent with literature.[7]

8-Methyldeca-5,8-diene-2,7-dione (1g)

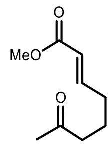


3-methyl-1-(triphenylphosphaneylidene)pent-3-en-2-one (0.070 g, 0.195 mmol, 1.0 equiv.) was added to a solution of 4-oxopentanal (0.020 g, 0.195 mmol, 1.0 equiv.) in DCM (2.5 mL) and allowed to react at r.t. for 18 hrs. The DCM was removed under reduced pressure and purified via column chromatography on silica gel (EtOAc / Cyclohexane (1:19)) to provide the title compound as a yellow oil (0.016 g, 46 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 6.74 (1H, dt, J = 12.3, 5.4 Hz), 6.71-6.66 (1H, m), 6.64 (1H, dt, J = 12.3, 1.0 Hz), 2.59 (2H, t, J = 5.8 Hz), 2.50-2.45 (2H, m), 2.14 (3H, s), 1.86-1.84 (3H, m), 1.81-1.79 (3H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 207.1, 191.9, 144.7, 138.9, 137.7, 126.0, 41.9, 30.1, 26.6, 14.9, 11.5; **HRMS-ESI (m/z):** $C_{11}H_{17}O_2$ $[M+H]^+$ theoretical 181.1184, found 181.1160.



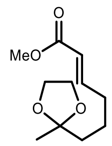
Scheme S6. *Synthesis of the bis-conjugated enone substrate* ***1h*** *starting from dicarbonyl* ***S3****.*

Methyl (2E)-7-oxooct-2-enoate (S16)[8]



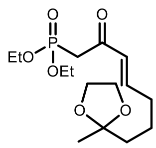
Methyl (triphenylphosphoranylidene)acetate (3.2 g, 9.60 mmol, 1.1 equiv.) was added to a solution of 5-oxohexanal (**S3**) (0.998 g, 8.73 mmol, 1.0 equiv.) in DCM (50 mL) and allowed to react at r.t. for 24 hrs. The DCM was removed under reduced pressure and purified via column chromatography on silica gel (EtOAc / Cyclohexane (1:4)) to provide the title compound as a colourless oil (1.01 g, 5.93 mmol, 68% yield). R.f. 0.42 (EtOAc/cyclohexane 1:1); 1H NMR (400 MHz, CDCl3): δ 6.91 (1H, dt, J = 15.6, 6.9 Hz, 3-H), 5.85-5.80 (1H, m, 2-H), 3.72 (3H, s, 1'-H), 2.45 (2H, t, J = 7.1 Hz, 6-H), 2.24-2.18 (2H, m, 4-H), 2.13 (3H, s, 8-H), 1.78-1.69 (2H, m, 5-H); 13C NMR (100 MHz, CDCl3): δ 208.1 (CO, C-7), 166.9 (CO, C-1), 148.3 (CH, C-3), 121.6 (CH, C-2), 51.4 (CH2, C-1'), 42.5 (CH2, C-6), 31.3 (CH2, C-4), 30.0 (CH3, C-8), 21.8 (CH2, C-5). The spectroscopic data was in accord with the previously reported data.[8]

Methyl (2E)-6-(2-methyl-1,3-dioxolan-2-yl)hex-2-enoate (S17)



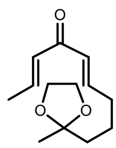
To compound 3g (1.0 eq, 5.29 mmol, 0.90 g) in toluene (50 mL) and pTsOH (0.10 eq, 0.53 mmol, 101 mg) and ethylene glycol (3.0 eq, 15.87 mmol, 0.89 mL) were added and the mixture was refluxed for a period of 6 h in a Dean-Stark apparatus, to remove water from the reaction mixture. The reaction mixture was then concentrated to remove the toluene and the resulting residue was diluted with Et2O (100 mL) and washed successively with sat. NaHCO3 solution, water, and brine (2 � 50 mL each). The organic layer was then dried over MgSO4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to provide the title compound as a colourless oil (760 mg, 75% yield). R.f. 0.31 (EtOAc/hexane 1:1); FTIR (neat) Vmax: 2984, 2949, 2876, 1720, 1656, 1436, 1376, 1270, 1197, 1171, 1039, 853 cm-1; 1H NMR (400 MHz, CDCl3): δ 6.95 (1H, dt, J = 15.7, 7.1 Hz, 3-H), 5.87-5.76 (1H, m, 2-H), 3.97-3.87 (4H, m, 1’’-H), 3.72 (3H, s, 1’-H), 2.26-2.17 (2H, m, 4-H), 1.68-1.62 (2H, m, 6-H), 1.60-1.52 (2H, m, 5-H), 1.30 (3H, s, 8-H); 13C NMR (100 MHz, $CDCl_3$): δ 167.1 (CO, C-1), 149.2 (CH, C3), 121.1 (CH, C-2), 109.8 (CO, C-7), 64.7 (CH2, C-1’’), 51.4 (CH2, C-1’), 38.5 (CH2, C-6), 32.2 (CH2, C-4), 23.8 (CH3, C-8), 22.4 (CH2, C-5); LC-MS (m/z): Calculated $C_{11}H_{19}O_4^+$ $[M+H]^+$: 215.1278, found: 215.1272.

Diethyl [(3E)-7-(2-methyl-1,3-dioxolan-2-yl)-2-oxohept-3-en-1-yl]phosphonate (S18)



To methyl diethylphosphonate (1.0 eq, 1.78 mmol, 0.26 mL) in THF (10 mL) at –78 °C was added n-BuLi (1.2 eq, 2.13 mmol, 0.79 mL) and the mixture stirred for 15 mins. Compound 22b (1.0 eq, 1.78 mmol, 381 mg) in a solution of THF (2 mL) was then added slowly and the mixture allowed to stir for 12 h. The reaction mixture was then quenched with sat. NH_4Cl (10 mL) and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by vacuum distillation and then eluted through a silica pad with MeOH/DCM (1:9) to provide the title compound as a pale yellow oil (384 mg, 74% yield). FTIR (neat) Vmax: 2981, 2939, 1730, 1665, 1625, 1376, 1247, 1018, 961, 856, 799 cm^{-1}; 1H NMR (400 MHz, $CDCl_3$): δ 6.97-6.86 (m, 1H), 6.27-6.18 (m, 1H), 4.19-4.00 (m, 4H), 3.99-3.85 (m, 4H), 3.19 (2H, d, J = 22.9 Hz, 1-H), 2.30-2.21 (2H, m, 5-H), 1.74-1.53 (4H, m, 6,7-H), 1.37-1.27 (9H, m); 13C NMR (101 MHz, $CDCl_3$) δ 208.2, 191.3, 149.3 (d, J = 23.9 Hz), 130.5, 109.9, 64.8, 62.7, 42.6, 40.3 (d, J = 128.4 Hz), 31.8, 23.9, 22.0 (d, J = 19.7 Hz), 16.4 (t, J = 6.2 Hz); LC-MS (m/z): Calculated $C_{15}H_{28}O_6P^+$ $[M+H]^+$: 335.1618, found: 335.1616.

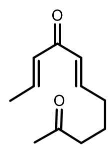
(2E,5E)-9-(2-methyl-1,3-dioxolan-2-yl)nona-2,5-dien-4-one (S19)



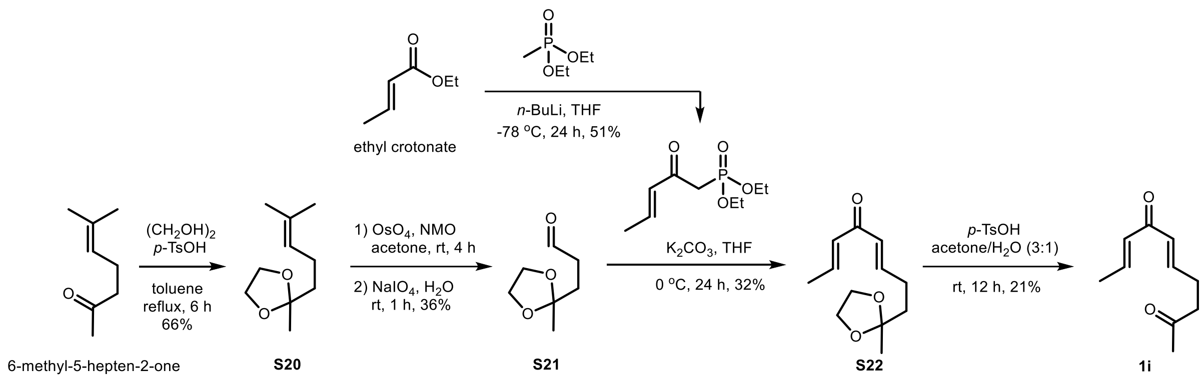
To compound 23b (1.0 eq, 3.11 mmol, 904 mg) dissolved in dry THF (10 mL) at 0 °C was added K_2CO_3 (5.0 eq, 15.57 mmol, 2.15 mg) and the mixture stirred for 15 mins.

Acetaldehyde (10 eq, 31.14 mmol, 1.74 mL) was then added and the mixture stirred for a further 12 h. The crude reaction mixture was filtered, concentrated under reduced pressure and purified by column chromatography on silica gel to provide the title compound as a colourless oil (195 mg, 28% yield). Rf 0.40 (EtOAc/hexane 1:1); FTIR (neat) Vmax: 2982, 2941, 2877, 1717, 1666, 1636, 1614, 1443, 1375, 1295, 1204, 1060, 976, 862 cm-1; 1H NMR (400 MHz, CDCl3): δ 7.01-6.78 (2H, m, 2,6-H), 6.43-6.22 (2H, m, 3,5-H), 4.03-3.82 (4H, m, 1',3'-H), 2.29-2.19 (2H, m, 7-H), 1.91 (3H, dd, J = 6.9, 1.4 Hz, 1-H), 1.70-1.62 (2H, m, 9-H), 1.62-1.52 (2H, m, 8-H), 1.30 (3H, s, 1''-H); 13C NMR (100 MHz, CDCl3): δ 189.4 (CO, C-4), 147.3 (CH, C-6), 143.0 (CH, C-2), 130.2 (CH, C-3), 128.8 (CH, C-5), 109.8 (C, C-2'), 64.6 (2CH2, C-1',3'), 38.6 (CH2, C-9), 32.6 (CH2, C-7), 23.8 (CH3, C-1''), 22.5 (CH2, C-8), 18.4 (CH3, C-1); LC-MS (m/z): Calculated C13H21O3+ [M+H]+: 225.1485, found: 225.1479.

(6*E*,9*E*)-undeca-6,9-diene-2,8-dione (1h)

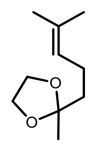


To 24a (1.0 eq, 0.83 mmol, 150 mg) dissolved in acetone:H2O (3:1, 8 mL) was added p-TsOH (0.05 eq, 0.042 mmol, 8.0 mg) and the mixture stirred for 24 h. The reaction mixture was diluted with brine (10 mL) and extracted with CH2Cl2 (3 x 10 mL). The combined organic layers were then washed with brine (10 mL), dried over MgSO4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to provide the title compound as a colourless oil (30 mg, 20% yield). Rf 0.31 (EtOAc/hexane 1:1); FTIR (neat) Vmax: 2937, 1711, 1665, 1636, 1612, 1440, 1357, 1294, 1204, 1161, 979, 746 cm-1; 1H NMR (400 MHz, CDCl3): δ 6.96-6.78 (2H, m, 6,10- H), 6.38-6.26 (2H, m, 7,9-H), 2.45 (2H, t, J = 7.3 Hz, 3-H), 2.29-2.18 (2H, m, 5-H), 2.12 (3H, s, 1-H), 1.91 (3H, dd, J = 6.9, 1.8 Hz, 11-H), 1.81-1.68 (2H, m, 4-H); 13C NMR (101 MHz, CDCl3) δ 189.6, 147.5, 143.2, 130.4, 128.9, 109.9, 64.8, 38.8, 32.7, 23.9, 22.7, 18.5; LC-MS (m/z): Calculated C10H15O2+ [M+H]+: 181.1223, found: 181.1217



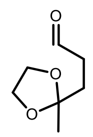
Scheme S7. *Synthesis of the bis-conjugated enone substrate **1i** starting from 6-methyl-5-hepten-2-one.*

2-methyl-2-(4-methylpent-3-en-1-yl)-1,3-dioxolane (S20)[9]



To 6-methyl-5-hepten-2-one (2.95 mL, 20 mmol) in toluene (20 mL), ethylene glycol (4.46 mL, 80 mmol) and p-TsOH (76 mg, 4.0 mmol) were added and the mixture was refluxed for a period of 6 h in a Dean-Stark apparatus, to remove water from the reaction mixture. The reaction mixture was then concentrated to remove the toluene and the resulting residue was diluted with Et2O (100 mL) and washed successively with sat. NaHCO3 solution, water and brine (2 x 50 mL each). The organic layer was then dried over MgSO4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to provide the title compound as a colourless oil (2.25 g, 66% yield). R.f. 0.31 (Et2O/Hexane 1:9); 1H NMR (400 MHz, CDCl3) δ 5.10 (1H, s, 3'- H), 3.99-3.87 (4H, m, 1,3-H), 2.14-1.99 (2H, m, 2'-H), 1.73-1.58 (8H, m, 1',5',1'''-H), 1.32 (3H, s, 1''-H); 13C NMR (100 MHz, CDCl3): δ 131.8 (C, C-4'), 124.2 (CH, C-3'), 110.1 (C, C-2), 64.8 (CH2, C-1,3), 39.2 (CH2, C-1'), 25.8 (CH3), 23.9 (CH3), 22.9 (CH2, C-2'), 17.7 (CH3).). The spectroscopic data was in full accord with the previously reported data.[9]

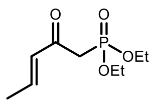
3-(2-methyl-1,3-dioxolan-2-yl)propanal (S21)[10]



2-methyl-2-(4-methylpent-3-en-1-yl)-1,3-dioxolane (**26**) (1 eq, 16.6 mmol) and OsO4 (4% w.t/v tBuOH, 0.01 eq, 0.17 mmol, 1.06 mL) were added to a solution of N-methylmorpholine N-oxide

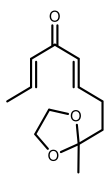
(2 eq, 33.2 mmol, 3.89 g) in acetone (20 mL). The mixture was stirred at room temperature for 4 h and then quenched with sat. aq. Na_2SO_3 solution (80 mL) and extracted with CH_2Cl_2 (3 � 60 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude material was dissolved in water (20 mL) and sodium periodate (2 eq, 33.2 mmol, 7.10 g) was added. The resulting mixture was stirred for 1 h at room temperature and then diluted with water (60 mL) and extracted with CH_2Cl_2 (3 x 30 mL). Next, the combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure to provide **27**, (1.03 g, 36% yield) as a pale, yellow oil which weas used in the next step without further purification. ^1H NMR (400 MHz, $CDCl_3$) δ 9.71 (1H, s, 3'-H), 3.98-3.83 (4H, m, 1,3-H), 2.51-2.42 (2H, m, 2'-H), 2.06 (2H, t, J = 7.1 Hz, 1'-H), 1.33 (3H, s, 1''-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.3 (CO, C3'), 109.2 (C, C-2), 64.9 (CH_2, C-1,3), 38.6 (CH_2, C-2'), 31.9 (CH_2, C-1'), 24.3 (CH_3, C-1''). The spectroscopic data was in full accord with the previously reported data.[10]

Diethyl [(3E)-2-oxopent-3-en-1-yl]phosphonate[11]



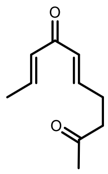
To diethyl methylphosphonate (1.0 eq, 20 mmol, 2.92 mL) in THF (80 mL) at -78 °C was added n-BuLi (1.2 eq, 24 mmol, 2.5 M, 9.60 mL) and the mixture stirred for 30 min. Ethyl crotonate (1.2 eq, 24 mmol, 2.98 mL) in THF (10 mL) was then added slowly and the mixture stirred for 24 h at -78 °C. The reaction mixture was then quenched with sat. NH_4Cl and extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by vacuum distillation to provide the title compound as a yellow oil (2.23 g, 51% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.06-6.86 (1H, m, 4-H), 6.34-6.16 (1H, m, 3-H), 4.26-3.96 (4H, m, 1'-H), 3.19 (2H, d, J = 22.9 Hz, 1-H), 1.97-1.90 (3H, m, 5-H), 1.36-1.27 (6H, m, 2'-H). The spectroscopic data was in full accord with the previously reported data.[11]

(2E,5E)-8-(2-methyl-1,3-dioxolan-2-yl)octa-2,5-dien-4-one (S22)



To a solution of **28** (2.0 eq, 2.0 mmol, 304 mg) and K_2CO_3 (5.0 eq, 5.0 mmol, 691 mg) in dry THF (20 mL) was added 27 (1.0 eq, 1.0 mmol 144 mg) and the mixture stirred at 0 °C for 24 h. The reaction mixture was then filtered, concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the title compound as a colourless oil (68 mg, 32% yield). FTIR (neat) Vmax: 2936, 1713, 1665, 1376, 1163, 1042, 973, 861 731 cm-1; 1H NMR (400 MHz, CDCl3) δ 6.98-6.82 (2H, m, 2,6-H), 6.38-6.27 (2H, m, 3,5-H), 3.99-3.85 (4H, m, 1',3'-H), 2.38-2.28 (2H, m, 7-H), 1.91 (3H, dd, J = 6.9, 1.4 Hz, 1'-H), 1.85-1.77 (2H, m, 8-H), 1.33 (3H, s, 1''-H); 13C NMR (100 MHz, CDCl3): δ 189.4 (CO, C-4), 147.4 (CH, C-6), 143.0 (CH, C-2), 130.2 (CH, C-3), 128.4 (CH, C-5), 109.4 (C, C-2'), 64.7 (2CH2, C-1',3'), 37.4 (CH2, C-8), 27.2 (CH2, C-7), 24.0 (CH3, C-1''), 18.4 (CH3, C-1); LC-MS (m/z): Calculated $C12H19O3^{+}$ $[M+H]^{+}$: 211.1329, found: 211.1326.

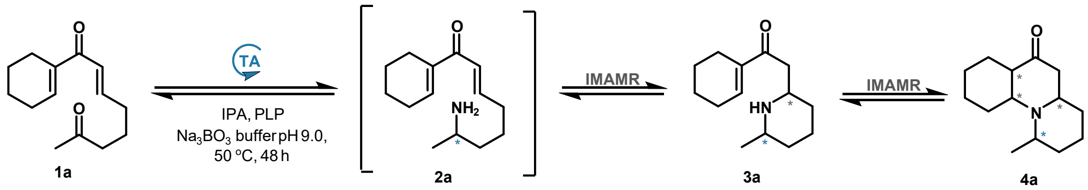
(5E,8E)-deca-5,8-diene-2,7-dione (1i)



To a solution of **24b** (1 eq, 0.32 mmol, 68 mg) in acetone:H2O (3:1, 4 mL) was added p-TsOH (0.05 eq, 0.016 mmol, 3 mg) and the mixture was stirred at r.t. for 12 h. The resulting mixture was diluted with brine (5 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were then washed with brine (20 mL), dried over MgSO4, filtered and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel to provide the title compound as a colourless oil (11 mg, 21% yield). R.f. 0.28 (EtOAc/hexane 1:1); FTIR (neat) Vmax: 2913, 1712, 1665, 1637, 1613, 1441, 1358, 1288, 1161, 977, 868 cm-1; 1H NMR (400 MHz, CDCl3): δ 7.00-6.73 (2H, m, 5,9-H), 6.40-6.22 (2H, m, 6,8-H), 2.65-2.56 (2H, m, 3-H), 2.52-2.44 (2H, m, 4-H), 2.15 (3H, s, 1-H), 1.90 (3H, dd, J = 6.9, 1.4 Hz, 10-H); 13C NMR (100 MHz, CDCl3): δ 206.9 (CO, C-2), 189.1 (CO, C-7), 145.4 (CH, C-5), 143.3 (CH, C-9), 130.2 (CH, C-8), 129.1 (CH, C-6), 41.6 (CH2, C-3), 29.9 (CH3, C-1), 26.3 (CH2, C-4), 18.4 (CH3, C-10); LCMS (m/z): Calculated $C10H15O2^{+}$ $[M+H]^{+}$: 167.1067, found: 161.1060

1.3. Optimisation of biotransformation conditions

Following the successful synthesis of target ketoenones, substrate **1a** was selected as a model substrate for optimisation of the biotransformation conditions due to its promising early results and the added complication of incomplete cyclisation, resulting in the co-formation of **3a**. Although having co-products in the model experiments may not seem a logical choice initially, the rationale was to determine if the conditions could be optimised to push the second aza-Michael reaction towards the formation of the quinolizidine target structures **4a** (Scheme S8).



Scheme S8: *The DIMAMR methodology carried out on substrate* ***1a,*** *which was used as the model reaction for optimisation of biotransformation conditions.*

Table S1: Optimisation of reaction conditions.

Entry	TA	Buffer	Temp. (°C)	Time (h)	pH	IPA (equiv.)	Conv. (%)*	Iso. Yield (%)**
1	ATA-113	HEPES	30	48	7.5	2	0	-
2	ATA-117	HEPES	30	48	7.5	2	0	-
3	ATA-256	HEPES	30	24	7.5	4	0	-
4	ATA-025	HEPES	30	24	7.5	4	0	-
5	ATA-256	HEPES	30	24	7.5	20	0	-
6	ATA-025	HEPES	30	24	7.5	20	0	-
7	ATA-256	HEPES	50	24	7.5	4	>99.9	69
8	ATA-025	HEPES	50	24	7.5	4	>99.9	52
9	ATA-256	HEPES	60	24	7.5	4	>99.9	20
10	ATA-256	HEPES	50	2	7.5	4	99	-
11	ATA-025	HEPES	50	2	7.5	4	37	-
12	ATA-256	HEPES	50	4	7.5	4	99	-
13	ATA-025	HEPES	50	4	7.5	4	92	-
14	ATA-256	HEPES	50	6	7.5	4	99	-
15	ATA-025	HEPES	50	6	7.5	4	93	-
16	ATA-256	HEPES	50	48	7.5	4	>99.9	72
17	ATA-025	HEPES	50	48	7.5	4	>99.9	57
18	ATA-256	HEPES	50	48	8.0	4	>99.9	65
19	ATA-256	HEPES	50	48	9.0	4	>99.9	72

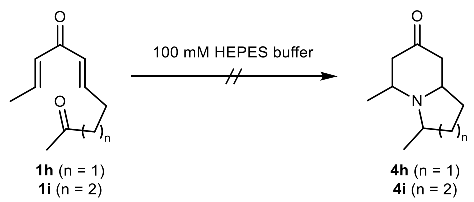
20	ATA-256	HEPES	50	48	10.0	4	>99.9	70
21	ATA-256	Na_3BO_3	50	48	9.0	4	>99.9	75
22	ATA-025	Na_3BO_3	50	48	9.0	4	>99.9	70
23	ATA-256	Na_3BO_3	50	72	9.0	4	>99.9	73

Highlighted optimised reaction conditions were used for all subsequent reactions when testing the methodology.

*By disappearance of starting substrate **1a** monitored using quantitative ^{1}H NMR.

** As a crude product mixture (both **3a** and **4a**).

For compounds **4a** and **4c** four diastereoisomers were observed in the crude reaction mixture extract. Upon attempted purification on silica (acidic) or basic alumina (pH 9.0) a mixture of three diastereoisomers were obtained. Although the R_f values of the isomers were distinct, the isomers could not readily be separated on silica or basic alumina due to observed interconversion. The same conversion (epimerisation) from four isomers to three isomers was observed when the crude reaction mixture was stirred in MeOH with potassium carbonate or with HCl at room temp. for 1 h. Therefore, compounds **4a** and **4c** were purified by column chromatography on neutral alumina.



Scheme S9: *Amination of substrates **1h** and **1i** was attempted under conditions presented in table S2.*

Table S2: Reaction conditions for the attempted amination of 1h and 1i

Entry	TA	Buffer	Temp. (°C)	Time (h)	pH	IPA (equiv.)	Conv.*
1	ATA-113	HEPES	30	24	7.5	2	decomp
2	ATA-117	HEPES	30	24	7.5	2	decomp
3	ATA-256	HEPES	50	24	7.5	2	decomp
4	ATA-025	HEPES	50	24	7.5	2	decomp
5	ATA-117	HEPES	30	24	7.5	20	decomp
6	ATA-256	HEPES	50	24	7.0	2	decomp
7	ATA-256	HEPES	50	24	9.0	2	decomp
8	-	HEPES	30	24	7.5	2	decomp

*No starting material or desired product was detected in any of the attempted biotransformations, including the no-enzyme control reaction. Decomposition products could not be isolated, and we suspect that this is due to formation of decomposition products that are either volatile or do not extract well from the aqueous buffer.

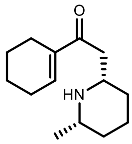
2. DIMAMR biotransformations

General procedure for biotransformations towards single and double IMAMR products

Commercially available (*S*)-selective ATA256 (50 mg) or (*R*)-selective ATA-025 (50 mg) was rehydrated in Na_3BO_3 buffer (8.5 mL, 100 mM, pH 9.0) containing PLP (2 mM) and isopropylamine (4 eq, 200 mM). The pH of the mixture was readjusted to 9.0, using aq. NaOH solution (1 M), and the total volume of the reaction was adjusted to 9 mL by addition of Na_3BO_3 buffer. The ketoenone substrate was added (50 mM, 1.0 mL from a 500 mM stock solution in DMSO) and the reaction mixture incubated at 50 °C, 220 rpm for 48 h. The reaction was basified to pH 10 and extracted using Et_2O (3 x 5 ml). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*.

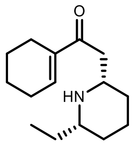
The crude material was purified by flash chromatography on neutral alumina using DCM. All isolated compounds were analysed by NMR.

1-(Cyclohex-1-en-1-yl)-2-[(2*S*, 6*S*)-6-methylpiperidin-2-yl]ethan-1-one ((*S*,*S*)-3a)



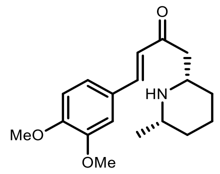
Yellow oil (0.062 g, 13 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 6.92-6.89 (1H, m), 3.08-3.01 (1H, m), 2.90 (1H, br s), 2.77-2.73 (2H, m), 2.72-2.68 (1H, m), 2.25 (4H, m), 1.78-1.72 (1H, m), 1.64-1.51 (6H, m), 1.43-1.32 (1H, m), 1.24-1.09 (2H, m), 1.06 (3H, d, J = 5.0 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 200.5, 140.6, 139.4, 53.2, 52.3, 43.6, 33.6, 31.7, 26.1, 24.5, 22.9, 22.7, 21.9, 21.5; **HRMS-ESI (m/z):** $C_{14}H_{24}NO^+$ $[M+H]^+$ theoretical 222.1813, found 222.1853; $[\alpha]_D^{20}$ = +40.0 (c=1.0, CH_3Cl); (*R*,*R*)-**3a**: $[\alpha]_D^{20}$ = -40.0 (c=1.0, CH_3Cl). The spectroscopic data for (*R*,*R*)-**3a** well in full accord with the reported data for (*S*,*S*)-**3a**.

1-(Cyclohex-1-en-1-yl)-2-((2*S*,6*S*)-6-ethylpiperidin-2-yl)ethan-1-one ((*S,S*)-3b)



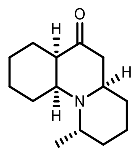
Yellow oil (0.017 g, 40 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 6.92-6.88 (1H, m), 3.03-2.95 (1H, m), 2.72 (1H, s), 2.70 (1H, d, J = 1.89 Hz), 2.48-2.40 (1H, m), 2.25-2.17 (4H, m), 1.79-1.72 (1H, m), 1.69-1.50 (6H, m), 1.41-1.29 (3H, m), 1.16 (1H, tdd, J = 12.84, 11.12, 3.87 Hz), 1.00 (1H, tdd, J = 12.87, 10.95, 3.90 Hz), 0.89 (3H, t, J = 7.5 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 200.8, 140.5, 139.6, 58.5, 53.3, 44.0, 32.7, 31.8, 30.1, 26.2, 24.7, 23.1, 22.0, 21.6, 10.5; **HRMS-ESI (m/z):** $C_{15}H_{26}NO^+$ $[M+H]^+$ theoretical 236.1970, found 236.2011.

(*E*)-4-(3,4-Dimethoxyphenyl)-1-((2*S*,6*S*)-6-methylpiperidin-2-yl)but-3-en-2-one ((*S*,*S*)-3e)



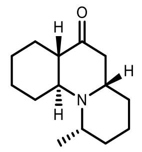
Yellow oil (0.045g, 36 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.50 (1H, d, *J* = 12.9 Hz), 7.10 (1H, dd, *J* = 6.3, 1.9 Hz), 7.04 (1H, d, *J* = 1.9 Hz), 6.86 (1H, d, *J* = 6.8 Hz), 6.59 (1H, d, *J* = 13.0 Hz), 3.90 (6H, s), 3.17 (1H, m), 2.84 (3H, m), 1.79 (1H, m), 1.64 (2H, m), 1.42 (1H, qt, *J* = 12.9, 3.6 Hz), 1.25 (2H, m), 1.12 (3H, d, *J* = 6.30 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 199.3, 151.6, 149.4, 143.5, 127.3, 124.6, 123.3, 111.2, 109.8, 56.1, 56.0, 53.5, 52.6, 46.8, 33.5, 31.6, 24.5, 22.7; **HRMS-ESI (m/z):** $C_{18}H_{26}NO_3^+$ $[M+H]^+$ theoretical 304.1868, found 304.1909. $[\alpha]_D^{22}$ = -10.0 (c=0.3, CH_2Cl_2); (*R*,*R*)-**3e**: $[\alpha]_D^{22}$ = +10.0 (c=0.3, CH_2Cl_2). The spectroscopic data for (*R*,*R*)-**3e** well in full accord with the reported data for (*S*,*S*)-**3e**.

(1*S*,4a*R*,6a*R*,10a*S*)-1-Methyldodecahydro-6H-pyrido[1,2-a]quinolin-6-one (1*S*,4a*R*,6a*R*,10a*S*-4a)



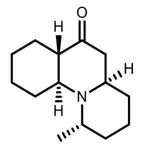
Yellow oil (0.007 g, 7 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 3.64-3.58 (1H, m), 3.47-3.42 (1H, m), 3.06-2.98 (1H, m), 2.75 (1H, t, *J* = 11.00 Hz), 2.72-2.69 (1H, m), 2.33-2.28 (1H, m), 1.94 (1H, dd, *J* = 11.29, 2.53 Hz), 1.89-1.81 (1H, m), 1.80-1.75 (1H, m), 1.72-1.66 (2H, m), 1.57-1.53 (2H, m), 1.47-1.35 (4H, m), 1.32-1.21 (2H, m), 1.16 (3H, d, J = 4.88 Hz), 1.13-1.07 (1H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 211.3, 59.6, 53.5, 52.3, 47.4, 44.0, 41.5, 35.4, 30.1, 26.5, 24.5, 22.2, 21.3, 19.4; **HRMS-ESI (m/z):** $C_{14}H_{24}NO^+$ $[M+H]^+$ theoretical 222.1813, found 222.1851.

(1*S*,4a*S*,6a*S*,10a*S*)-1-Methyldodecahydro-6H-pyrido[1,2-a]quinolin-6-one (1*S*,4a*S*,6a*S*,10a*S* -4a)



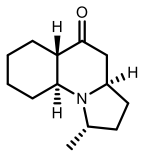
Yellow oil (0.008 g, 8 % yield, increased from NMR yield due to interconversion). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 3.04-3.00 (1H, m), 2.99-2.95 (1H, m), 2.95-2.91 (1H, m), 2.57-2.50 (1H, m), 2.35-2.30 (1H, m), 2.29 (1H, d, *J* = 2.29 Hz), 2.25 (1H, d, *J* = 9.11 Hz), 1.78-1.72 (1H, m), 1.69-1.66 (1H, m), 1.65-1.62 (1H, m), 1.62-1.58 (1H, m), 1.58-1.54 (1H, m), 1.46-1.40 (1H, m), 1.33-1.26 (3H, m), 1.23-1.17 (3H, m), 1.15 (3H, d, *J* = 4.90 Hz), 1.02 (1H, ap. q, *J* = 10.15 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 212.7, 58.8, 58.6, 55.6, 47.0, 46.2, 38.1, 36.1, 33.6, 25.5, 24.5, 24.4, 22.1, 21.7; **HRMS-ESI (m/z):** $C_{14}H_{24}NO^+$ $[M+H]^+$ theoretical 222.1813, found 222.1851.

(1*S*,4a*R*,6a*S*,10a*S*)-1-Methyldodecahydro-6H-pyrido[1,2-a]quinolin-6-one (1*S*,4a*R*,6a*S*,10a*S*-4a)



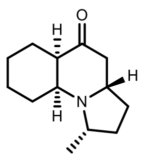
Yellow oil (0.003 g, 3 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 3.58-3.51 (1H, m), 2.69 (1H, tt, *J* = 8.36, 2.48 Hz), 2.29-2.20 (5H, m), 1.96-1.90 (1H, m), 1.82-1.72 (3H, m), 1.66-1.61 (2H, m), 1.57-1.49 (2H, m), 1.40-1.32 (1H, m), 1.26-1.63 (4H, m), 0.91 (3H, d, *J* = 5.33 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 210.0, 63.8, 54.7, 54.1, 49.6, 47.8, 35.5, 32.4, 30.2, 25.2, 24.7, 24.3, 18.3, 8.5; **HRMS-ESI (m/z):** $C_{14}H_{24}NO^+$ $[M+H]^+$ theoretical 222.1813, found 222.1852; $[\alpha]_D^{22}$ = -3.8 (c=0.4, CH_2Cl_2).

(1*S*,3a*R*,5a*S*,9a*S*)-1-Methyldecahydropyrrolo[1,2-a]quinolin-5(1H)-one (1*S*,3a*R*,5a*S*,9a*S*-4c)



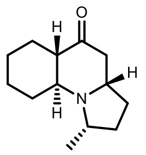
Yellow oil (0.015 g, 15 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 3.63 (1H, quin, *J* = 6.7 Hz), 2.87-2.80 (1H, m), 2.49 (1H, dd, *J* = 12.9, 3.2 Hz), 2.33 – 2.26 (2H, m), 2.20 – 2.10 (3H, m), 2.04 – 1.94 (2H, m), 1.77 (1H, d, *J* = 10.7 Hz), 1.55 – 1.49 (1H, m), 1.46 – 1.41 (1H, m), 1.39 – 1.30 (1H, m), 1.28 – 1.12 (4H, m), 0.89 (3H, d, *J* = 6.5 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 210.5, 60.8, 58.8, 53.8, 52.6, 48.2, 31.9, 30.3, 29.9, 25.2, 24.9, 23.9, 13.5; **HRMS-ESI (m/z):** $C_{13}H_{22}NO^+$ $[M+H]^+$ theoretical 208.1657, found 208.1697. $[\alpha]_D^{20}$ = +2.5 (c=2.2, CH_3Cl); (1*R*,3a*S*,5a*R*,9a*R*)-**4c**: $[\alpha]_D^{20}$ = -2.5 (c=2.2, CH_3Cl). The spectroscopic data for (1*R*,3a*S*,5a*R*,9a*R*)-**4c** well in full accord with the reported data for 1*S*,3a*R*,5a*S*,9a*S*)-**4c**.

(1*S*,3a*S*,5a*R*,9a*S*)-1-Methyldecahydropyrrolo[1,2-a]quinolin-5(1H)-one (1*S*,3a*S*,5a*R*,9a*S*-4c)



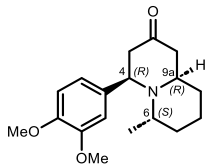
Yellow oil as a mixture with (1*S*,3a*S*,5a*S*,9a*S*)-**4c** (0.024 g, 23 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 3.34 (1H, m), 2.94 (1H, m), 2.84 (1H, m), 2.75 (1H, m), 2.44 (1H, dd, *J* = 13.66, 3.34 Hz), 2.31 – 2.23 (2H, m), 1.96-1.65 (4H, m), 1.51 – 1.39 (3H, m), 1.39 – 1.18 (3H, m), 1.14 (3H, d, *J* = 6.16 Hz), 1.04 (1H, qd, *J* = 12.49, 3.08 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 210.8, 56.7, 55.7, 52.4, 49.7, 47.9, 31.1, 29.7, 25.0, 24.9, 22.5, 19.9, 18.5; **HRMS-ESI (m/z):** $C_{13}H_{22}NO^+$ $[M+H]^+$ theoretical 208.1657, found 208.1696.

(1*S*,3a*S*,5a*S*,9a*S*)-1-Methyldecahydropyrrolo[1,2-a]quinolin-5(1H)-one (1*S*,3a*S*,5a*S*,9a*S*-4c)



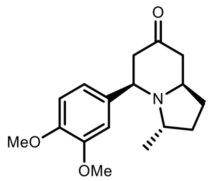
Yellow oil as a mixture with (1*S*,3a*S*,5a*R*,9a*S*)-**4c** (0.024 g, 23 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 3.74-3.68 (1H, m), 3.31-3.23 (2H, m), 2.80-2.75 (1H, m), 2.31-2.25 (2H, m), 2.23-2.17 (2H, m), 2.18-2.07 (2H, m), 1.80-1.74 (1H, m), 1.70-1.65 (1H, m), 1.56-1.42 (3H, m), 3.35-1.21 (3H, m), 1.16 (3H, d, *J* = 5.96 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 210.8, 58.9, 58.3, 52.7, 44.6, 44.0, 31.6, 30.6, 29.1, 26.2, 24.4, 21.7, 20.8; **HRMS-ESI (m/z):** $C_{13}H_{22}NO^+$ $[M+H]^+$ theoretical 208.1657, found 208.1696.

(4*R*,6*S*,9a*R*)-4-(3,4-Dimethoxyphenyl)-6-methyloctahydro-2H-quinolizin-2-one (4*R*,6*S*,9a*R*-4e)



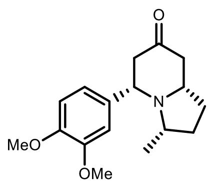
Yellow oil (0.018 g, 14 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 6.95 (1H, d, *J* = 1.86 Hz) , 6.86 (1H, dd, *J* = 8.10, 1.95 Hz), 6.81 (1H, d, *J* = 8.2 Hz), 3.90 (3H, s), 3.87 (3H, s), 3.60 (1H, dd, *J* = 11.8, 3.1 Hz), 3.04 (1H, m), 2.84 (1H, m), 2.61 (1H, m), 2.42-2.29 (3H, m), 1.75-1.64 (2H, m), 1.54-1.37 (4H, m), 0.83 (3H, d, *J* = 6.66 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 208.3, 134.9, 132.1, 132.0, 119.6, 111.1, 110.0, 56.1, 56.0, 53.7, 49.6, 49.0, 41.0, 35.3, 32.2, 29.8, 18.3, 8.3; **HRMS-ESI (m/z):** $C_{18}H_{26}NO_3^+$ $[M+H]^+$ theoretical 304.1868, found 304.1885. $[\alpha]_D^{22}$ = +62.5 (c=0.1, CH_2Cl_2); (4*S*,6*R*,9a*S*)-**4e**: $[\alpha]_D^{22}$ = -62.0 (c=0.1, CH_2Cl_2). The spectroscopic data for (4*R*,6*S*,9a*R*)-**4e** well in full accord with the reported data for (4*R*,6*S*,9a*R*)-**4e**.

(3*S*,5*R*,8a*R*)-5-(3,4-Dimethoxyphenyl)-3-methylhexahydroindolizin-7-one (3*S*,5*R*,8a*R*-4f)



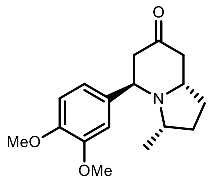
Yellow oil (0.040 g, 31 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 6.96 (1H, d, *J* = 1.30 Hz, Ar*H*), 6.89 (1H, dd, *J* = 5.45, 1.30 Hz, Ar*H*), 6.82 (1H, d, *J* = 5.44 Hz, Ar*H*), 3.89 (3H, s, -OMe), 3.87 (3H, s, -OMe), 3.66 (1H, dd, *J* = 7.26, 2.48 Hz), 3.33 (1H, m), 2.94 (1H, m), 2.56 (1H, dt, *J* = 8.87, 1.77 Hz), 2.43 (3H, m), 2.10 (2H, m), 1.60 (1H, m), 1.37 (1H, m), 0.74 (3H, d, *J* = 4.36); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 209.2, 149.4, 148.4, 134.9, 119.6, 111.1, 110.3, 60.9, 58.1, 56.2, 56.0, 53.5, 51.1, 48.5, 30.5, 30.3, 14.0; **HRMS-ESI (m/z):** $C_{17}H_{24}NO_3^+$ $[M+H]^+$ theoretical 290.1711, found 290.1750.

(3*S*,5*S*,8a*S*)-5-(3,4-Dimethoxyphenyl)-3-methylhexahydroindolizin-7-one (3*S*,5*S*,8a*S*-4f)



Yellow oil (0.037g, 29 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 6.90 (1H, d, *J* = 1.35 Hz, Ar*H*), 6.83 (1H, dd, *J* = 5.43, 1.28 Hz, Ar*H*), 6.77 (1H, d, *J* = 5.42 Hz, Ar*H*), 3.87 (3H, s, -OMe), 3.85 (3H, s, -OMe), 3.33 (1H, dd, *J* = 7.50, 2.42 Hz), 2.70 (1H, m), 2.52 (1H, m), 2.49 (3H, m), 2.41 (1H, m), 1.98 (1H, dq, *J* = 8.50, 5.98 Hz), 1.80 (1H, m), 1.57 (1H, m), 1.39 (1H, m), 0.44 (3H, d, *J* = 4.05 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 208.8, 149.0, 148.8, 135.3, 120.4, 111.1, 110.8, 67.7, 66.5, 59.5, 56.1, 55.9, 50.0, 47.4, 32.8, 29.6, 23.0; **HRMS-ESI (m/z):** $C_{17}H_{24}NO_3^+$ $[M+H]^+$ theoretical 290.1711, found 290.1750.

(3*S*,5*R*,8a*S*)-5-(3,4-Dimethoxyphenyl)-3-methylhexahydroindolizin-7-one (3*S*,5*R*,8a*S*-4f)



Yellow oil (0.020g, 16 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 6.78 (1H, d, *J* = 5.47 Hz), 6.58 (1H, dd, *J* = 5.49, 1.37 Hz), 6.53 (1H, d, *J* = 1.34 Hz), 4.48 (1H, dd, *J* = 4.77, 0.78 Hz), 3.84 (3H, s), 3.81 (3H, s), 2.94 (1H, dd, J = 10.34, 4.86 Hz), 2.82-2.77 (1H, m), 2.67-2.61 (2H, m), 2.41-2.36 (2H, m), 1.83-1.71 (2H, m), 1.47-1.40 (2H, m), 1.25 (3H, d, *J* = 3.97 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 211.1, 148.5, 148.4, 129.6, 121.5, 120.4, 112.4, 110.6, 56.2, 55.9, 54.9, 53.3, 48.6, 46.0, 30.9, 29.5, 18.7; **HRMS-ESI (m/z):** $C_{17}H_{24}NO_3^+$ $[M+H]^+$ theoretical 290.1711, found 290.1750.

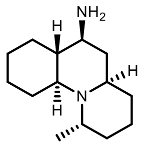
2.1. One-pot two enzyme biotransformations

General procedure for the one-pot two enzyme biotransformations towards double aminated indolizidine- or quinolizidine-containing structures.

(*S*)-selective ATA256 (50 mg) and ATA-234 (50 mg) were rehydrated in Na_3BO_3 buffer (8 mL, 25 mM, pH 9.0) containing PLP (1 mM) and isopropylamine (4 eq, 80 mM). The pH of the mixture was adjusted to 9.0, using aq. NaOH solution (1 M), and the total volume of the reaction was adjusted to 9 mL by addition of Na_3BO_3 buffer.

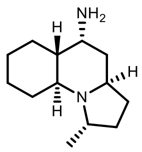
The ketoenone substrate was added (20 mM, 1.0 mL from a 200 mM stock solution in MeOH) and the reaction mixture incubated at 50 °C, 220 rpm for 48 h. The reaction was basified to pH 10 and extracted using Et_2O (3 x 5 ml). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography on neutral alumina (100% DCM to 0.5% MeOH), and the acid salt was formed from the product fractions using HCl (2M in diethyl ether).

(1*S*,3a*R*,5*S*,5a*R*,9a*S*)-1-methyldodecahydropyrrolo[1,2-a]quinolin-5-amine (5a)



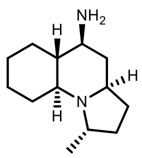
White crystalline salt (0.004 g, 10 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 3.97-3.89 (1H, m), 3.39 (1H, tt, *J* = 11.9, 3.1 Hz), 3.19 (1H, td, *J* = 11.6, 3.4 Hz), 3.03 (1H, td, *J* = 10.8, 4.0 Hz), 2.24-2.17 (2H, m), 1.95-1.36 (13H, m), 1.19 (3H, d, *J* = 7.0 Hz), 1.16-1.00 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 62.1, 54.5, 52.3, 49.9, 42.6, 34.8, 31.0, 29.2, 27.3, 25.8, 23.7, 23.2, 15.5, 9.4; **HRMS-ESI (m/z):** $C_{14}H_{27}N_2^+$ [M+H]$^+$ theoretical 223.2130, found 223.2153. $[\alpha]_D^{22}$ = +42.5 (c=0.2, H_2O)

(1*S*,3a*R*,5*R*,5a*R*,9a*S*)-1-Methyldodecahydropyrrolo[1,2-a]quinolin-5-amine ((5*R*)-5c)



White crystalline salt (0.004 g, 9 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 4.14 (1H, quin, *J* = 7.1 Hz), 3.78-3.74 (1H, m), 3.65-3.55 (1H, m), 3.29 (1H, td, *J* = 11.1, 3.7 Hz), 2.56-2.49 (1H, m), 2.46-2.37 (1H, m), 2.35-2.24 (2H, m), 2.17-2.02 (2H, m), 1.95-1.83 (4H, m), 1.79-1.69 (1H, m), 1.50-1.36 (3H, m), 1.33 (3H, d, *J* = 6.92 Hz), 1.31-1.23 (1H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 57.2, 56.0, 55.1, 48.2, 40.8, 31.2, 28.0, 27.2, 27.2, 26.5, 24.3, 23.5, 13.7; **HRMS-ESI (m/z):** $C_{13}H_{25}N_2^+$ [M+H]$^+$ theoretical 209.1973, found 209.2014. $[\alpha]_D^{22}$ = -15.0 (c=0.2, H_2O)

(1*S*,3a*R*,5*S*,5a*R*,9a*S*)-1-Methyldodecahydropyrrolo[1,2-a]quinolin-5-amine ((5*S*)-5c)



White crystalline salt (0.008 g, 19 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 4.12 (1H, quin, *J* = 7.08 Hz), 3.66 (1H, m), 3.37 (1H, td, *J* = 11.3, 3.9 Hz), 3.19-3.12 (1H, m), 2.64 (1H, dt, *J* = 13.7, 3.3 Hz), 2.45-2.21 (3H, m), 2.10-2.03 (1H, m), 1.95-1.69 (6H, m), 1.53-1.35 (3H, m), 1.29 (3H, d, J = 6.9 Hz), 1.27-1.17 (1H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 59.1, 58.8, 56.9, 50.5, 42.9, 32.2, 27.5, 27.3, 26.6, 26.1, 23.6, 23.3, 13.5; **HRMS-ESI (m/z):** $C_{13}H_{25}N_2^+$ $[M+H]^+$ theoretical 209.1973, found 209.2014. $[\alpha]_D^{22}$ = +27.5 (c=0.2, H_2O)

3. Additional selectivity

The apparent additional selectivity observed in many of the reactions leads to the formation of a reduced number of diastereoisomers. To rationalise this trend, the hypothesised transition states of the second IMAMR for one substrate, **1c**, will be discussed in detail. After transamination of the ketoenone **1c**, a reactive nitrogen nucleophile is stereoselectively generated in situ, which then undergoes two consecutive IMAMRs. Deconvolution of the crude reaction mixture via ^{1}H NMR spectroscopic analysis reveals that the initial IMAMR occurs at both faces of the C-3 prochiral aza-Michael acceptor, affording the pyrrolidine intermediates (*S*,*S*)-**3c** and (*S*,*R*)-**3c** (*re*- and *si*-addition, respectively). In contrast, the second aza-Michael reaction occurs with exclusively pro-(*S*) selectivity, proceeding *via* putative aminium enolate intermediates.

To rationalise this substrate-controlled selectivity, possible transition states **TS I-IV** and **TS A-D** were devised. **TS I-II** and **TS A-B** exhibit the incorrect angle of approach of the non-bonding electrons on the nitrogen (Michael donor) to the π* orbital of the enone (Michael acceptor), leading to disfavoured orbital overlap and discounting these transition states. Unfavourable steric interactions during pyramidalisation occur *via* **TS-III** and **D**, leading to the aminium enolate intermediates **S23** and **S26** and disfavouring their formation. Considering this, the transition states **TS IV** and **C** are favoured, leading to the aminium intermediates **S24** and **S25**, respectively, which correspond to the observed products (**4c**). Considering this hypothesised explanation of the additional selectivity is correct, the selectivity can be seen as analogous to organocatalytic approaches but relying purely on the enzyme-installed chiral centre to achieve it.

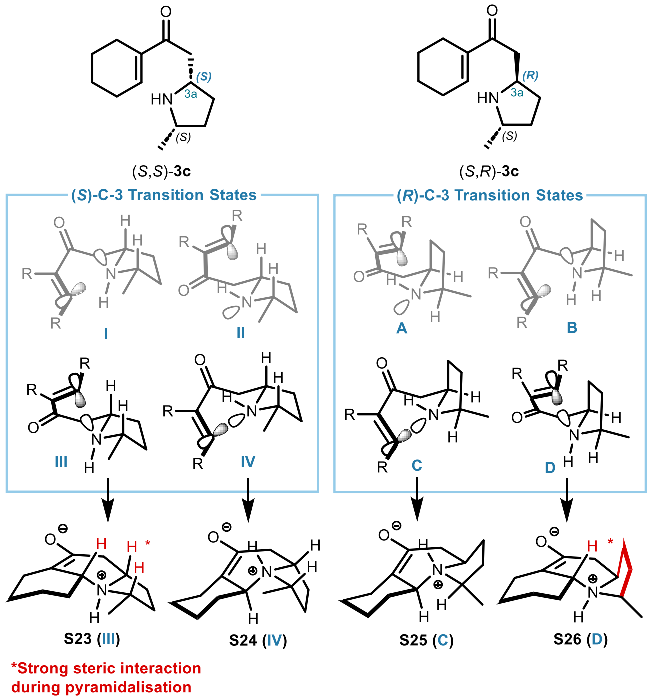
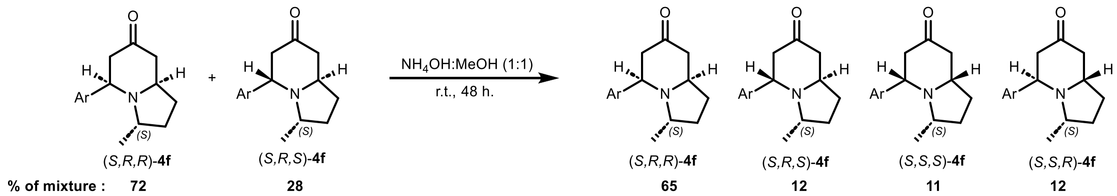


Figure S1. *Stereochemical model of the possible transition states corresponding to the second intramolecular aza-Michael reaction from the reactive intermediate (S,S)-**3c** or (S,R)-**3c**.*

4. Attempted epimerisation of 4f



Scheme S10: *Attempted epimerisation of a mixture of **4f** displaying a possible double retro-aza-Michael reaction process.*

A solution of 35% aq. NH_4OH/MeOH 1:1 (5 mL) was added a a mixture of (*S*,*R*,*R*)-**4f** and (*S*,*R*,*S*)-**4f** (18 mg, mmol) and stirred at room temperature for 48 h. The solution was then extracted with dichloromethane (10 mL x 3), dried over MgSO4, filtered, and concentrated under reduced pressure. The crude residue was dissolved in $CDCl_3$ and analysed by ^1H NMR.

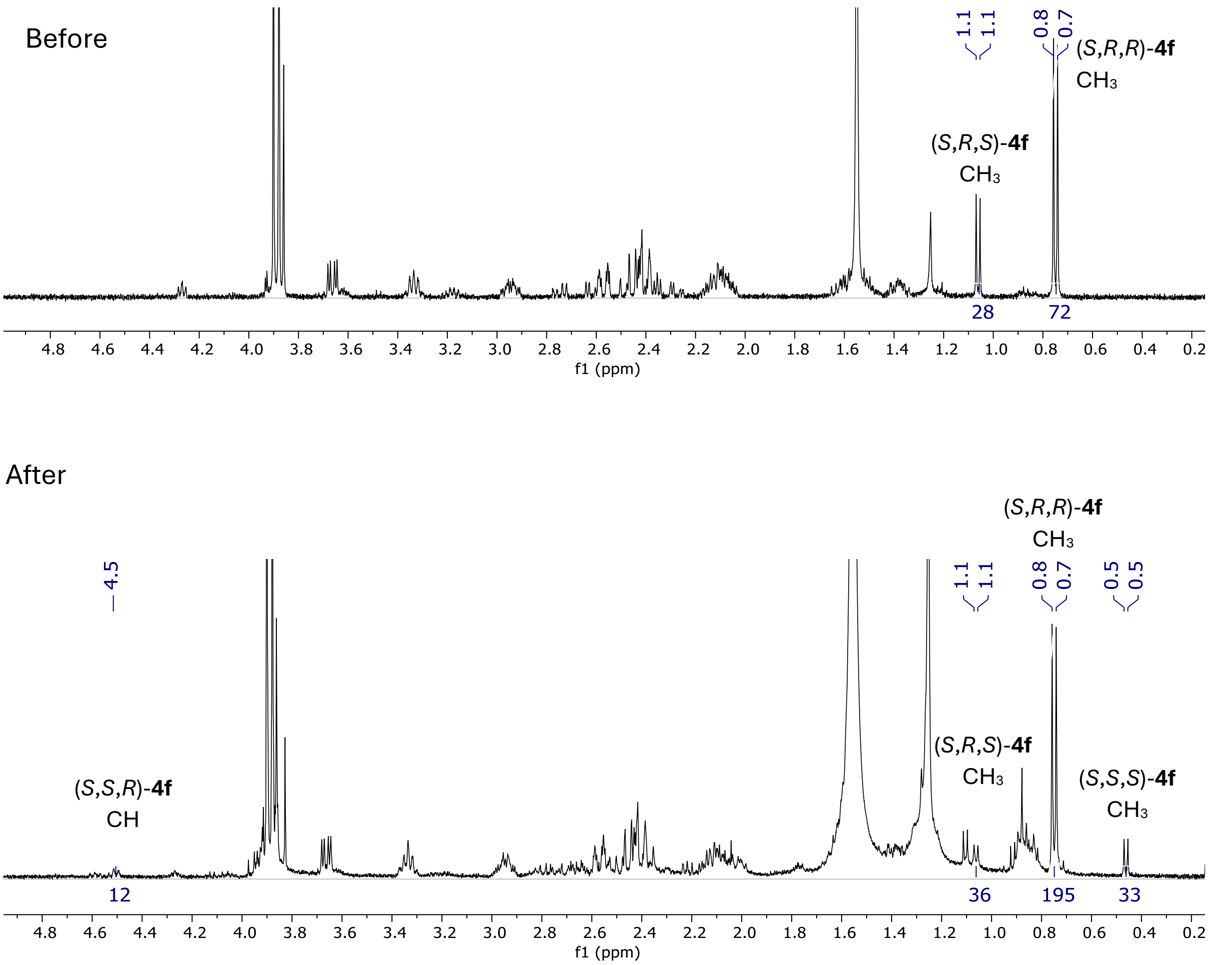


Figure S2: *[1]H NMR analysis before and after attempted epimerisation with NH_4OH in methanol.*

5. Enzyme screen for the formation of diamine 5c from 4c

The enzyme (5 mg) were rehydrated in Na_3BO_3 buffer (800 µL, 25 mM, pH 9.0) containing PLP (1 mM) and isopropylamine (4 eq, 80 mM). The pH of the mixture was adjusted to 9.0, using aq. NaOH solution (1 M), and the total volume of the reaction was adjusted to 900 µL by addition of Na_3BO_3 buffer. Indolizidine (1*S*)-**4c** was added (20 mM, 100 µL from a 200 mM stock solution in MeOH) and the reaction mixture incubated at 50 °C, 220 rpm for 48 h. The reaction was basified to pH 10 and extracted using Et_2O (3 x 2 ml). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was dissolved in $CDCl_3$ and analysed by ^{1}H NMR (Figure S3).

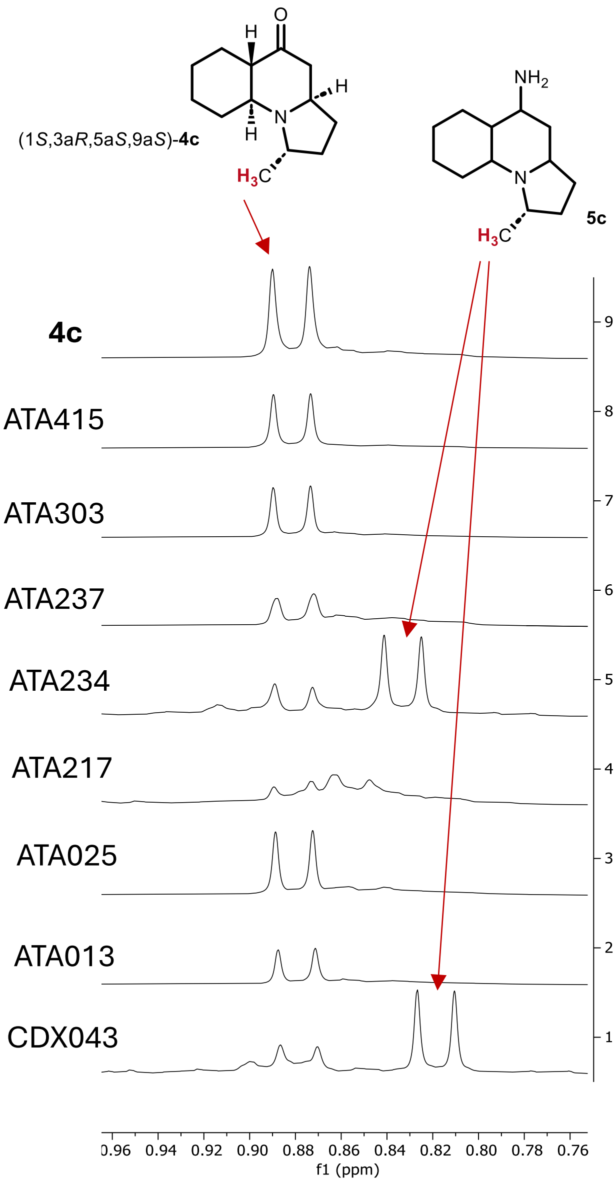


Figure S3. *[1]H NMR analysis of the enzyme screen for the transformation of indolizidine* ***4c*** *to diamine* ***5c****.*

6. Study of reaction conditions for the two-enzyme cascade

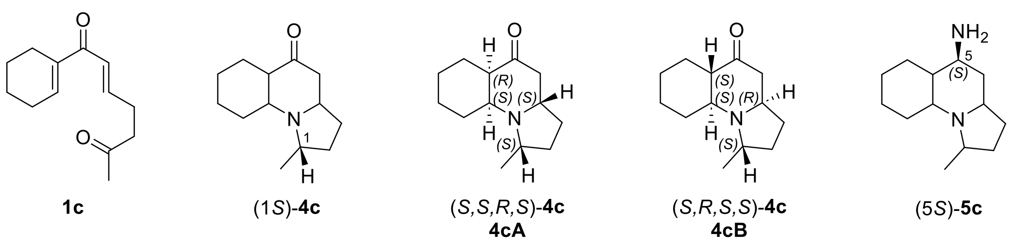


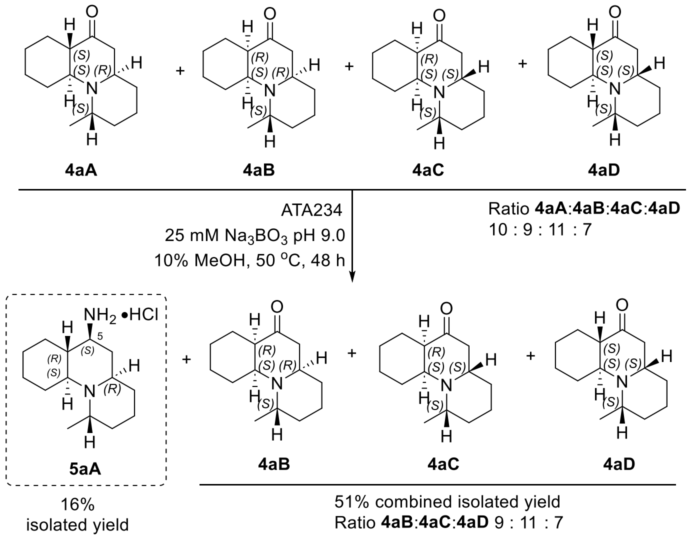
Figure S4: *Starting materials and target reaction products for the two-enzyme cascade.*

Table S3: Reaction conditions tested for the formation of diamine 5c

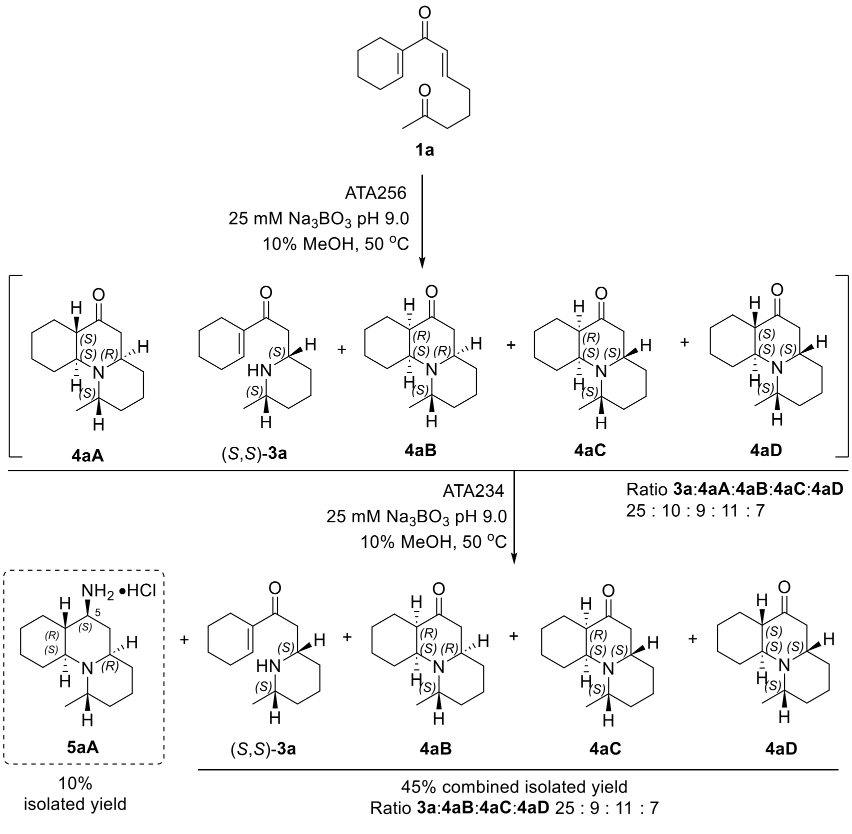
Entry	Starting material	Enzyme	Time	Buffer	IPA equiv.	Cosolvent	Reaction product(s)
1	**4c**	CDX043	48 h	100 mM HEPES pH 7.5	20	DMSO	**4c** (no reaction)
2	**4c**	CDX043	48 h	25 mM Na_3BO_3 pH 9.0	20	DMSO	**5c** 5*S*/5*R* 2:1.3 dr 39% isol. yield
3	**4c**	CDX043	48 h	25 mM Na_3BO_3 pH 9.0	20	MeOH	**5c** 5*S*/5*R* 2:1 dr 40% isol. yield
4	**4c**	ATA234	48 h	25 mM Na_3BO_3 pH 9.0	20	MeOH	**5c** 5*S*/5*R* 2:1 dr 40% isol. yield
5	**1c**	CDX043	48 h	25 mM Na_3BO_3 pH 9.0	20	MeOH	decomp.
6	**1c**	ATA234	48 h	25 mM Na_3BO_3 pH 9.0	20	MeOH	decomp.
7	**1c**	ATA256 +[a] CDX043	72 h	25 mM Na_3BO_3 pH 9.0	20	MeOH	**4c** (no amination) 72% isol. yield
8	**1c**	ATA256 then[b] ATA234	24h then[b] 24h	25 mM Na_3BO_3 pH 9.0	4 then[b] 16	MeOH	**4cA**:**4cB**:**5c** (1 : 0.4 : 0.96) 39% isol. yield
9	**1c**	ATA256 then[b] ATA234	24h then[b] 24h	25 mM Na_3BO_3 pH 9.0	4 then[b] 4	MeOH	**4cA**:**4cB**:**5c** (1 : 0.33 : 1.08) 43% isol. yield
10	**1c**	ATA256 then[b] ATA234	24h then[b] 24h	25 mM Na_3BO_3 pH 9.0	4	MeOH	**4cA**:**4cB**:**5c** (1 : 0.52 : 1.15) 51% isol. yield
11	**1c**	ATA256 +[a] ATA234	48 h	25 mM Na_3BO_3 pH 9.0	4	MeOH	**4cA**:**4cB**:**5c** (1 : 0.65 : 1.17) 47% isol. yield
12	**1c**	ATA256 then[b] ATA234	24h then[b] 48h	25 mM Na_3BO_3 pH 9.0	4	MeOH	**5c** 45% isol. yield
13	**1c**	ATA256 +[a] ATA234	65 h	25 mM Na_3BO_3 pH 9.0	4	MeOH	**4cA**:**5c** (0.66 : 1) 42% isol. yield
14	**1c**	ATA256 +[a] ATA234	72 h	25 mM Na_3BO_3 pH 9.0	4	MeOH	**5c** 42% isol. yield
15	(1*R*)-**4c**	ATA234	48 h	25 mM Na_3BO_3 pH 9.0	4	MeOH	(1*R*)-**4c** (no reaction)

Consistent reaction conditions: 6 mL reaction; 40 mM starting material, 5 mg/mL enzyme, 1 mM PLP, 10% cosolvent, 50 °C, 220 rpm. [a]One pot reaction, [b]Sequential reaction. Isolated yields are reported of the non-purified products.

The ATA234 catalysed amination of the crude isomeric mixture **4a**, gave products **5aA**, **4aB**, **4aC**, and **4aD** (Scheme S11). The isomeric ratio of the unreacted species **4a** were the same in the biotransformation product mixture as in the starting material. This indicates a kinetic resolution process without any dynamic interconversion present under the tested biotransformation conditions. The same product mixture was evident in the two-enzyme cascade (Scheme S12), where the partially cyclised piperidine (*S*,*S*)-**3a** was also present.



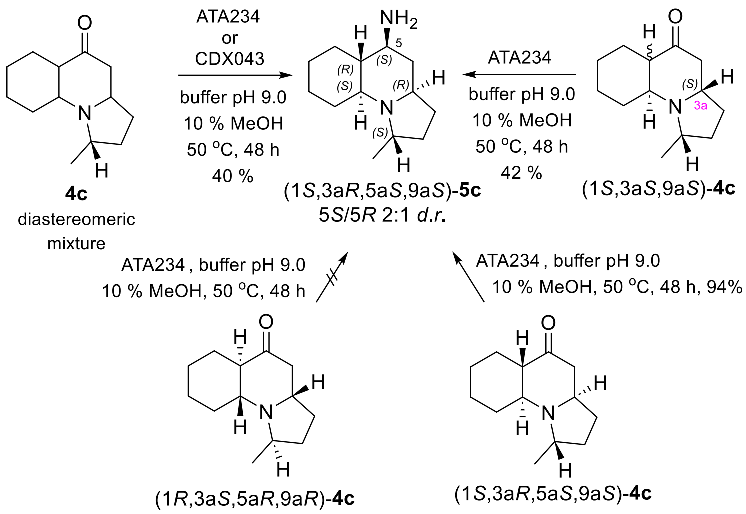
Scheme S11: *ATA234 catalysed kinetic resolution of the **4a** diastereomeric mixture.*



Scheme S12: *ATA234 catalysed kinetic resolution of the **4a** diastereomeric mixture in a one pot cascade from substrate **1a**.*

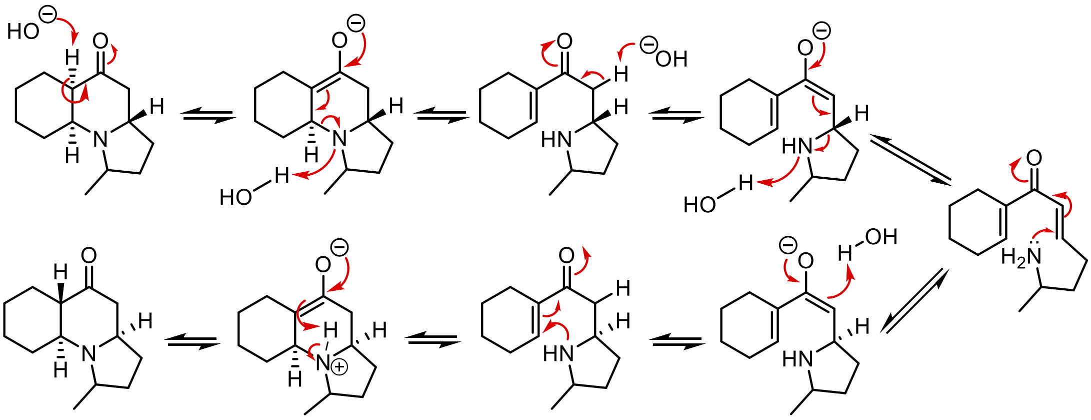
Full conversion of the indolizidine **4c** could be achieved, but the reaction yield from the two-enzyme cascade could not account for full mass balance. We therefore wanted to examine if the full conversion of starting material was due to a dynamic resolution or if the stereoisomers not accepted by the second ATA in the cascade were simply decomposing under biotransformation conditions.

First, the isolated yields presented in Table S3 (Entries 2-4 and 8-14) are approx 45% regardless of product distribution, which may indicate a dynamic process. Second, the retro aza Michael mechanism is supported by the observation presented in Scheme 4c (main text), in which epimerisation of the β-carbon of compound **4c** was observed under biotransformation conditions. Third, we obtain the same diamine stereoisomer **5c** regardless of the stereochemistry of the **4c** isomer starting material (Scheme S13). We ascribe the dynamic process which interconverts the α- and β- stereocentres to the double retro aza Michael reaction, depicted in Scheme S13. As shown in scheme 13 it is also possible that the reaction mechanism is a retro aza Michael/Mannich reaction.



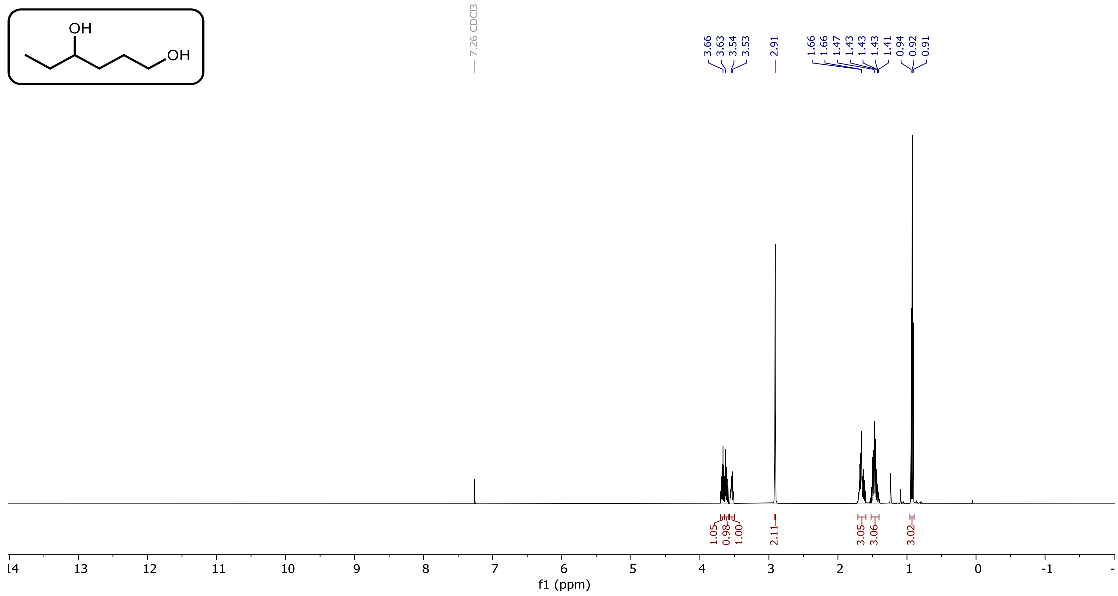
Scheme S13: *The same **5c** stereoisomer is produced in the ATA catalysed biotransformation regardless of the stereochemistry of the starting material.*

***Retro*-aza-Michael stereochemical scrambling**

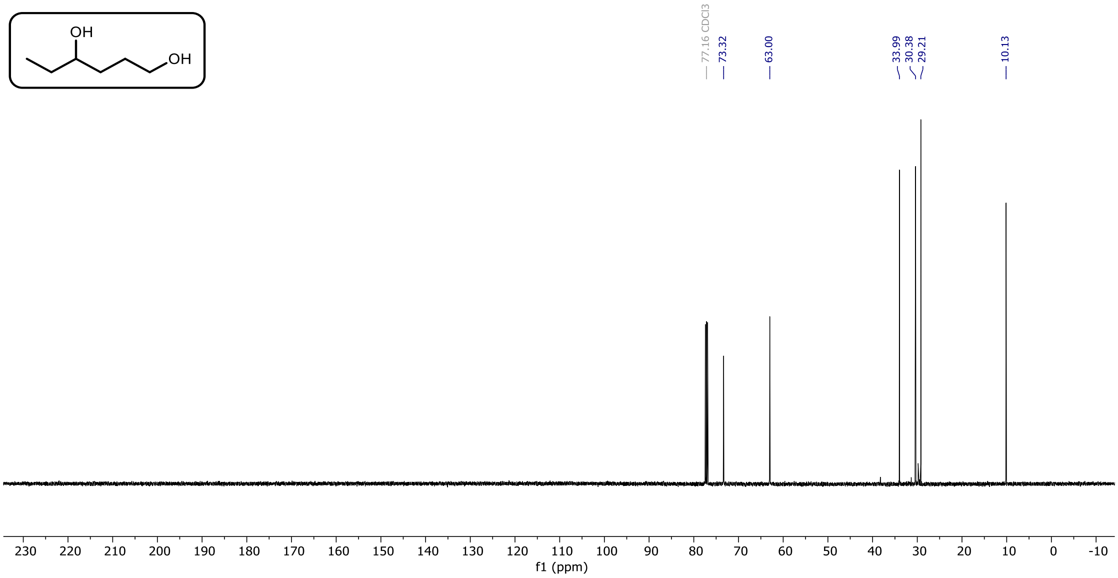


Scheme S14: *Scheme S13: Proposed mechanism for the stereochemical scrambling of stereocentres under basic conditions, via the double retro aza-Michael reaction. Other mechanisms are also possible.*[12]

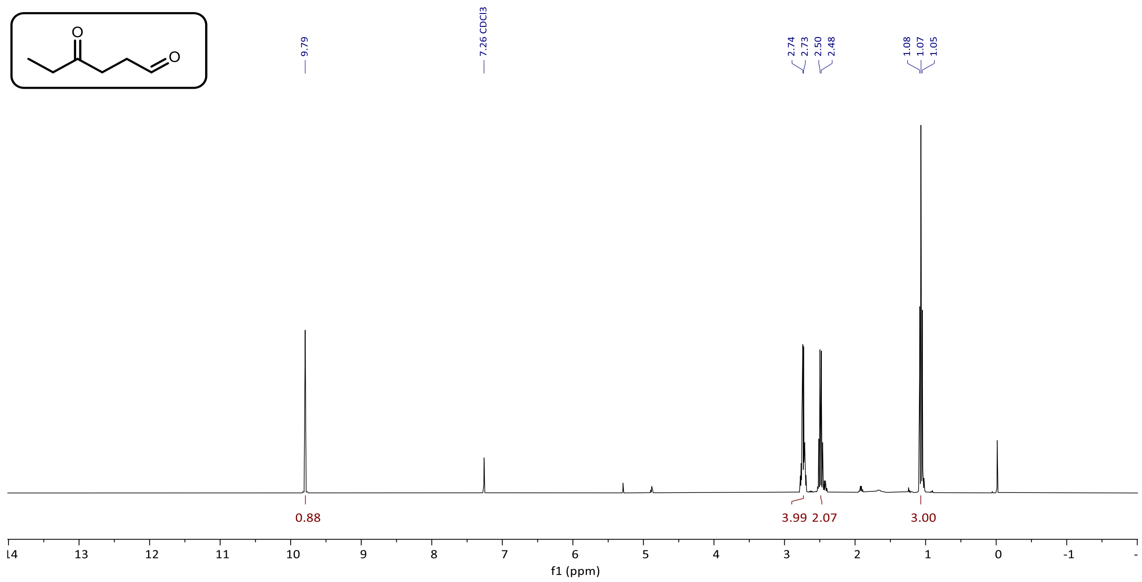
7. NMR Spectra



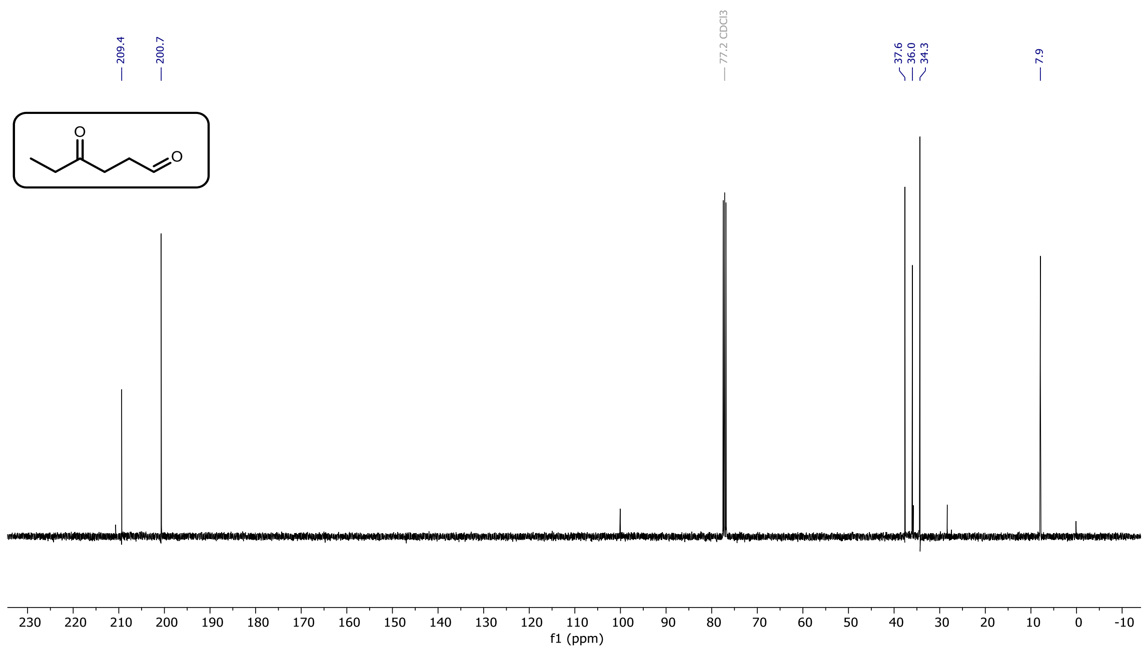
***A1:** ^{1}H NMR ($CDCl_3$) of compound **S1**.*



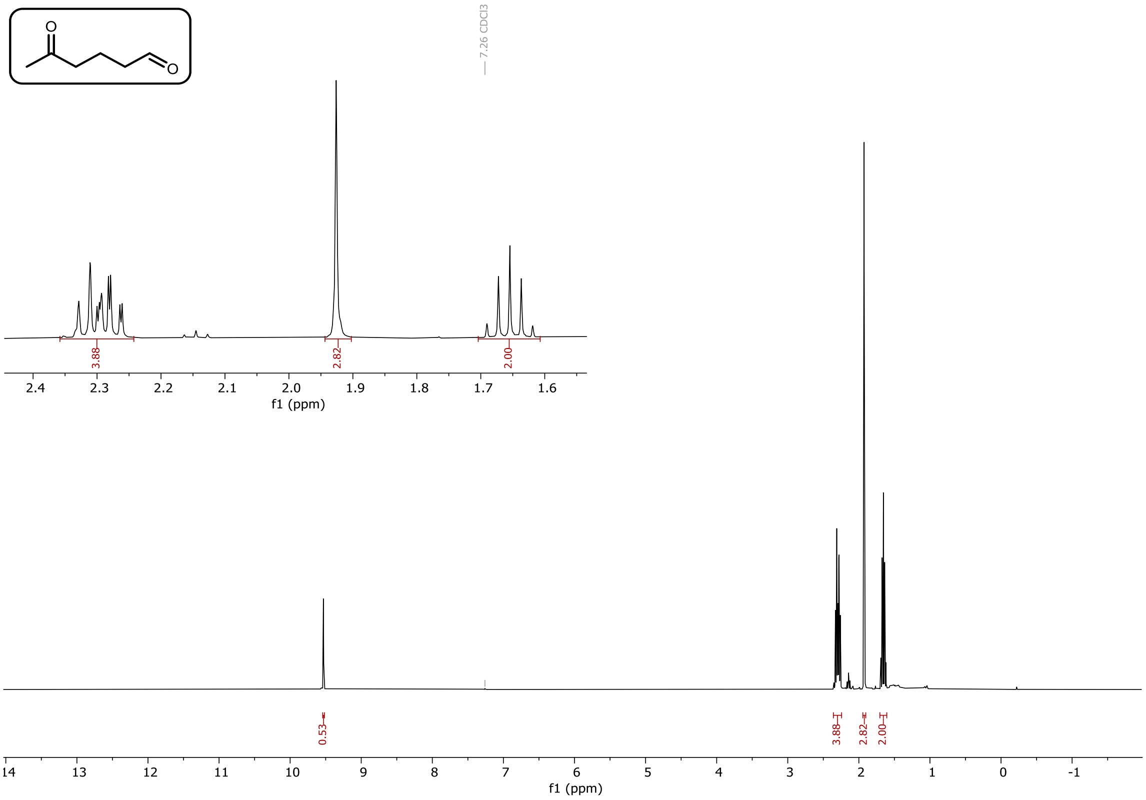
***A2:** ^{13}C NMR ($CDCl_3$) of compound **S1**.*



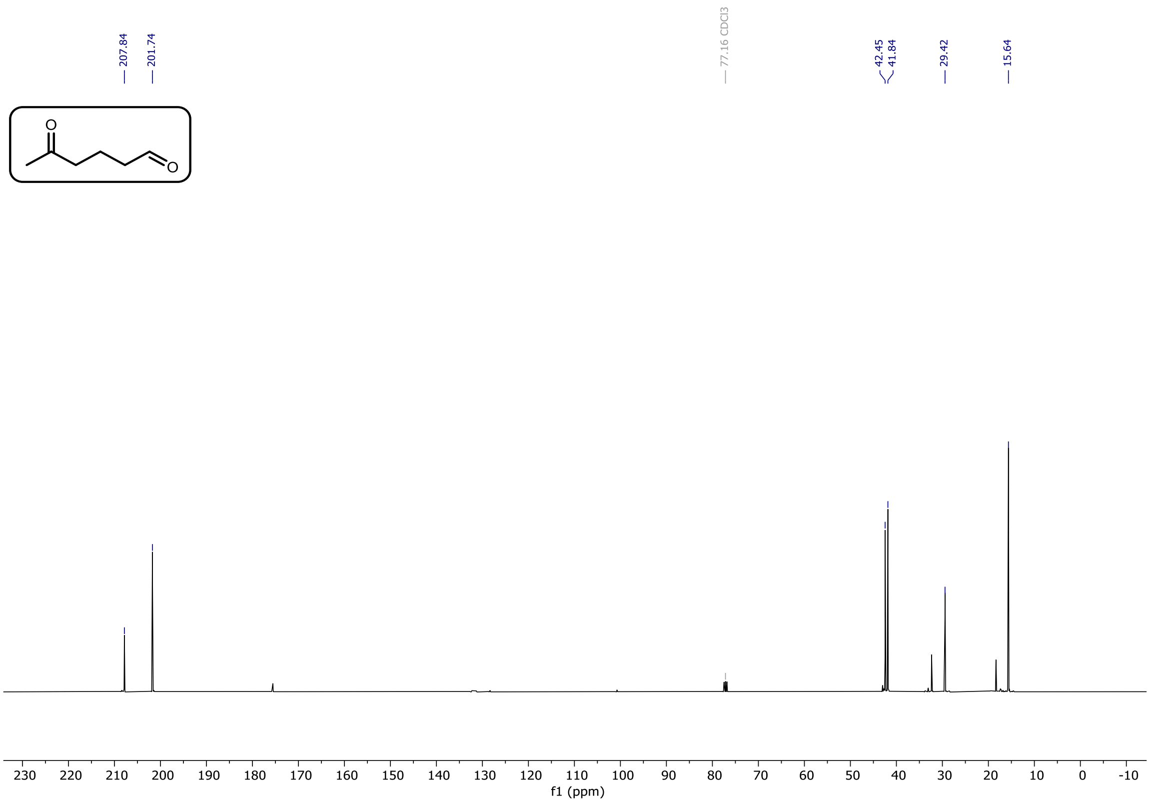
A3: *[1]H NMR ($CDCl_3$) of compound* ***S2****.*



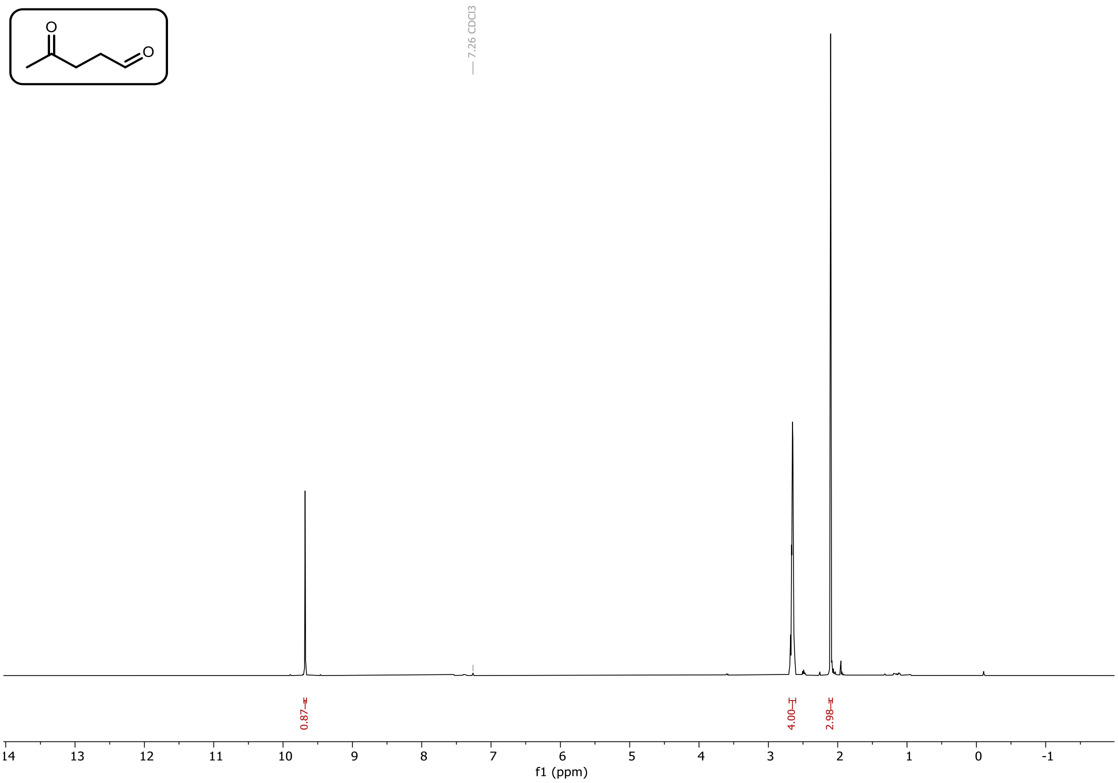
A4: *[13]C NMR ($CDCl_3$) of compound* ***S2****.*



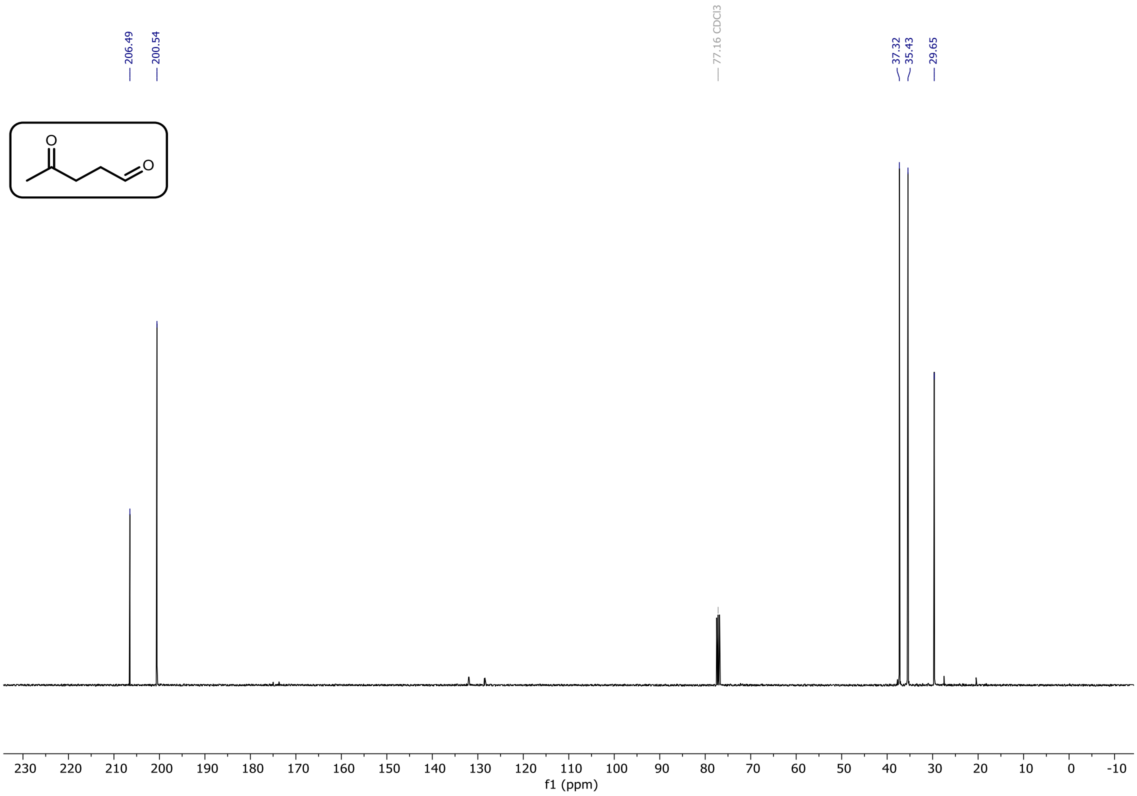
A5: *[1]H NMR (CDCl$_3$) of compound **S3**.*



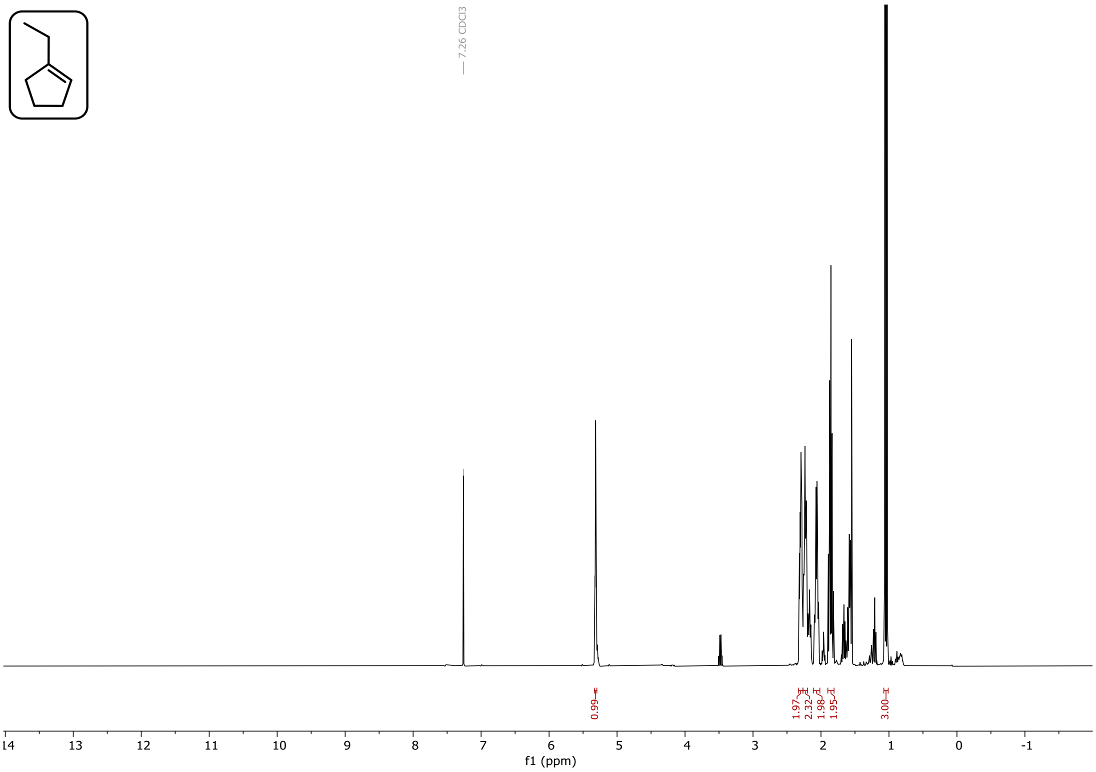
A6: *[13]C NMR (CDCl$_3$) of compound **S3**.*



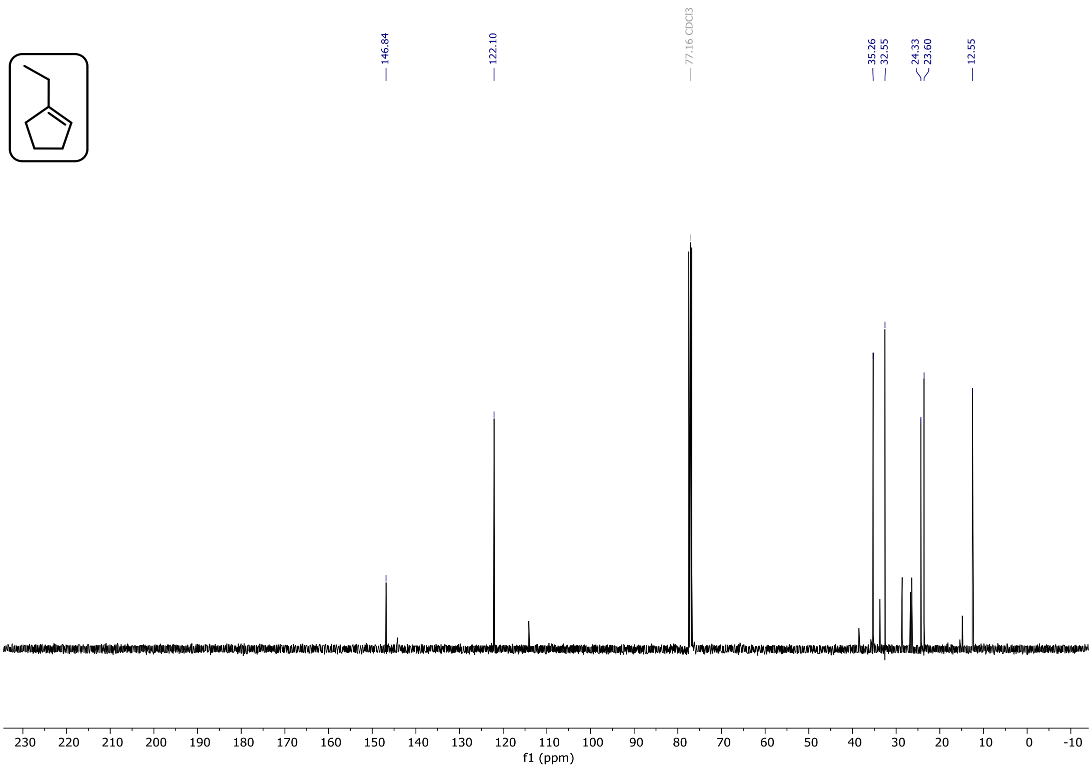
A7: *[1]H NMR (CDCl$_3$) of compound* ***S4****.*



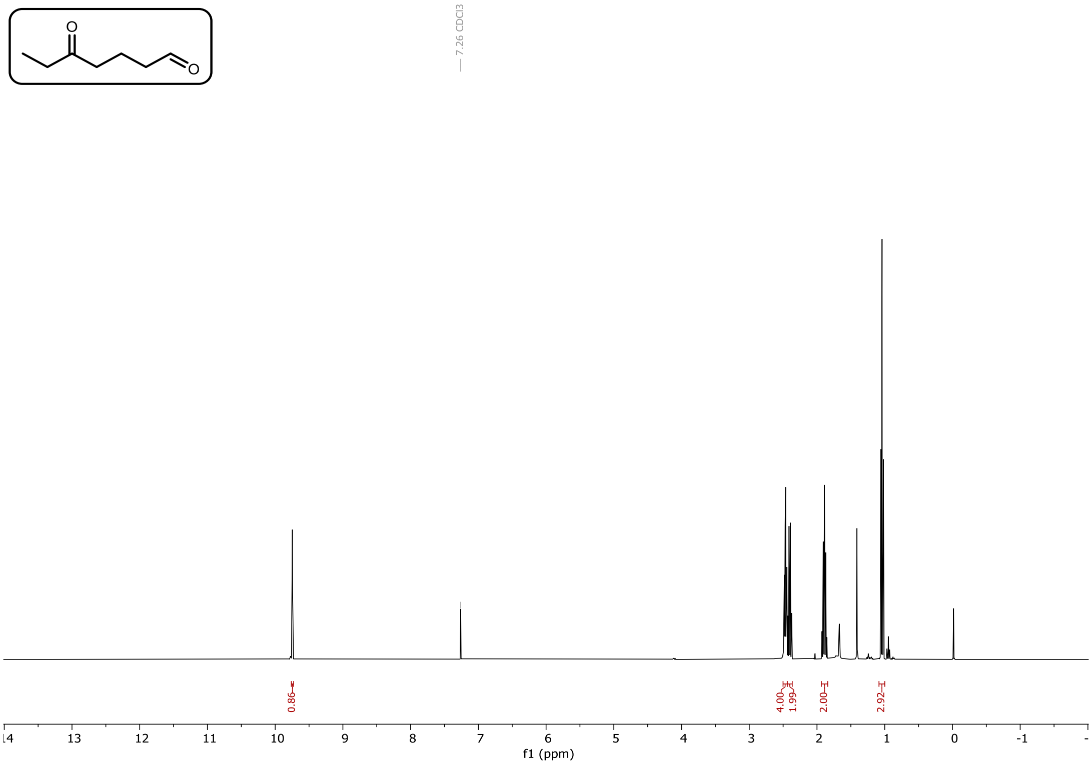
A8: *[13]C NMR (CDCl$_3$) of compound* ***S4****.*



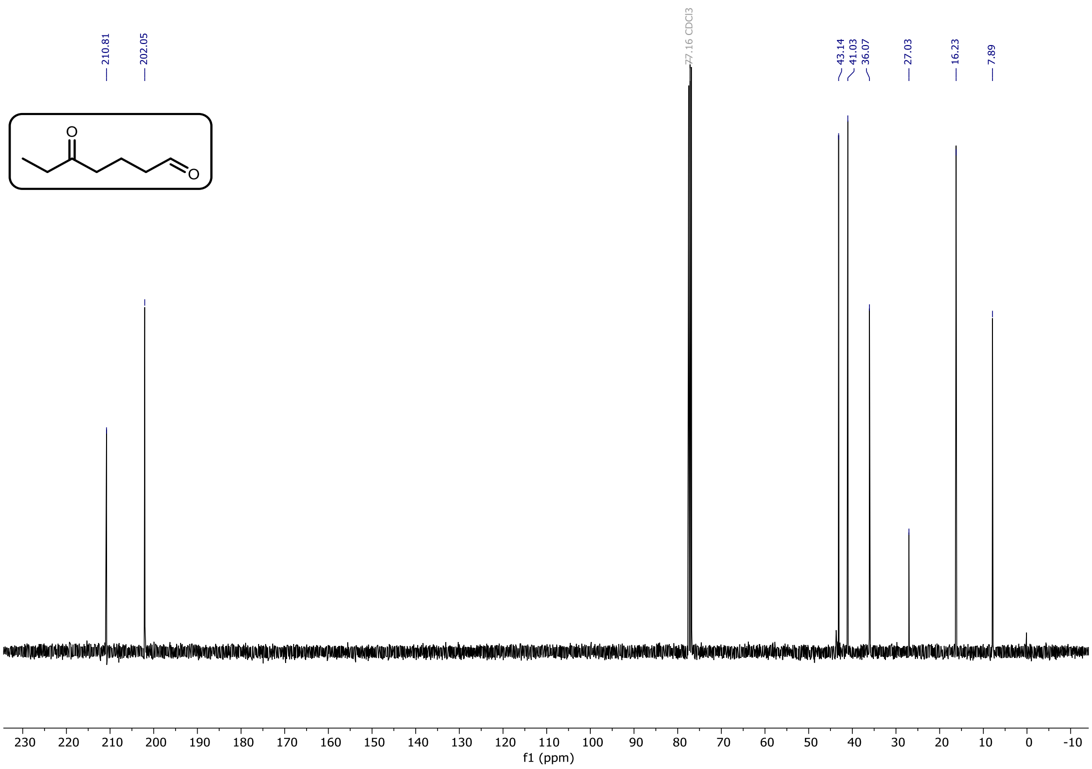
A9: ^{1}H *NMR* ($CDCl_3$) *of compound* ***S5***.



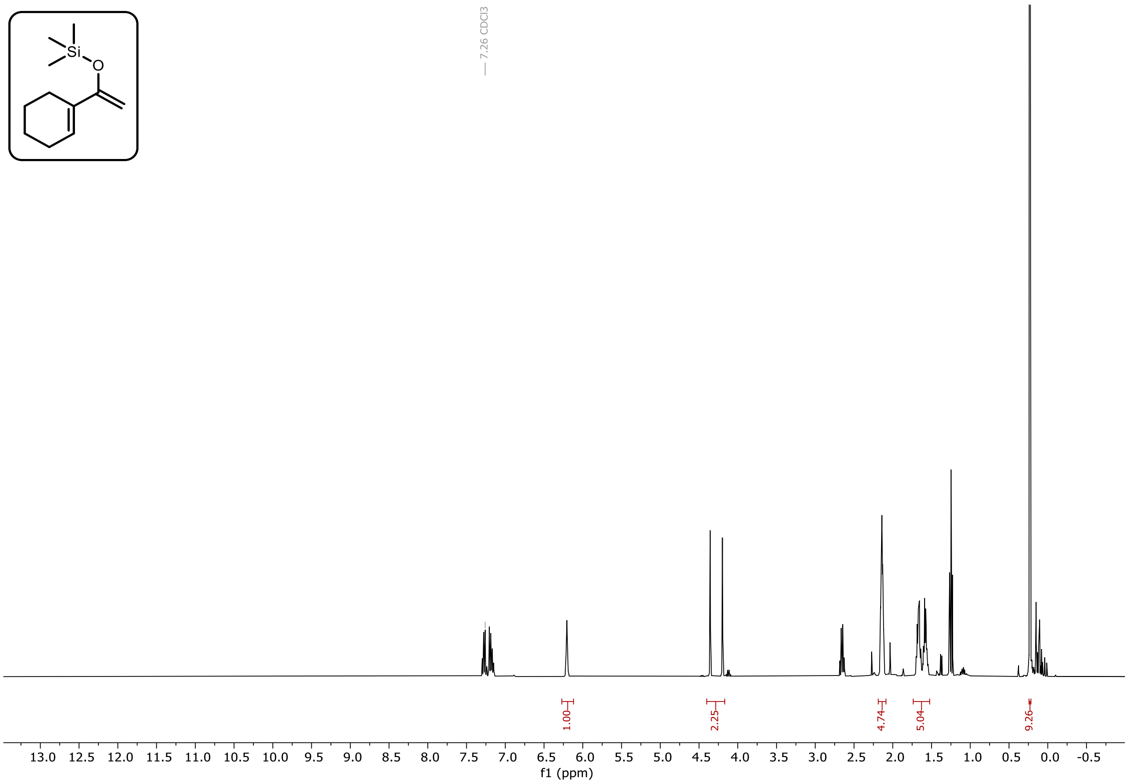
A10: ^{13}C *NMR* ($CDCl_3$) *of compound* ***S5***.



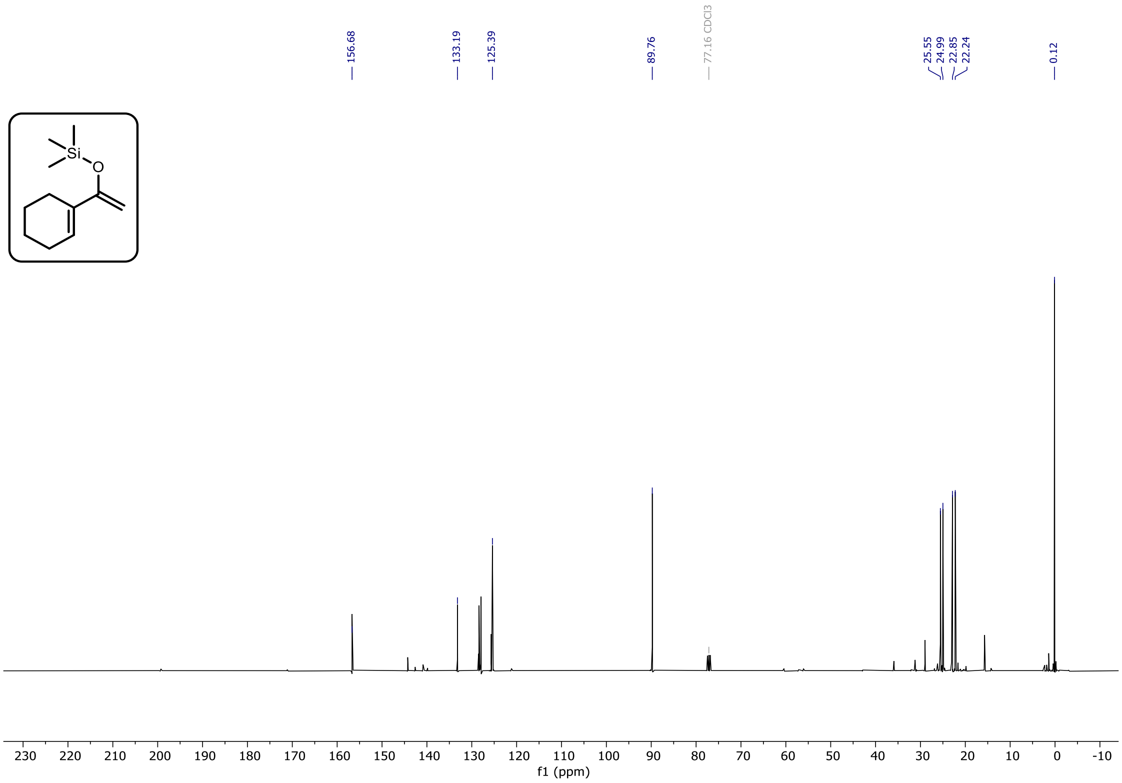
A11: *^{1}H NMR (CDCl$_3$) of compound **S6**.*



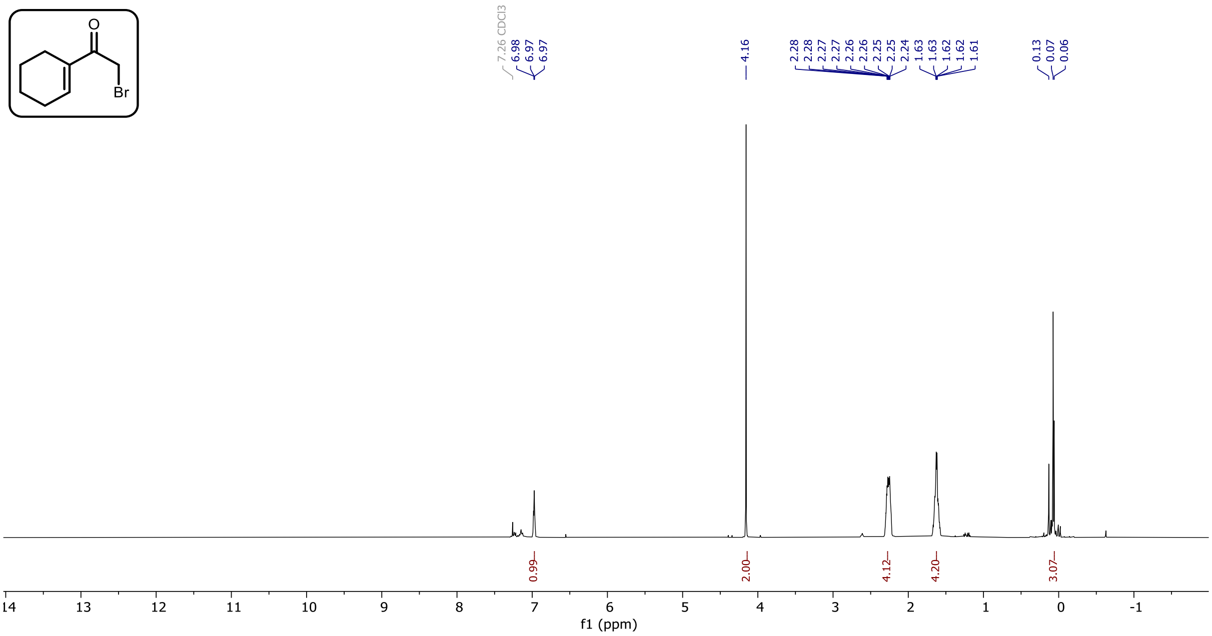
A12: *^{13}C NMR (CDCl$_3$) of compound **S6**.*



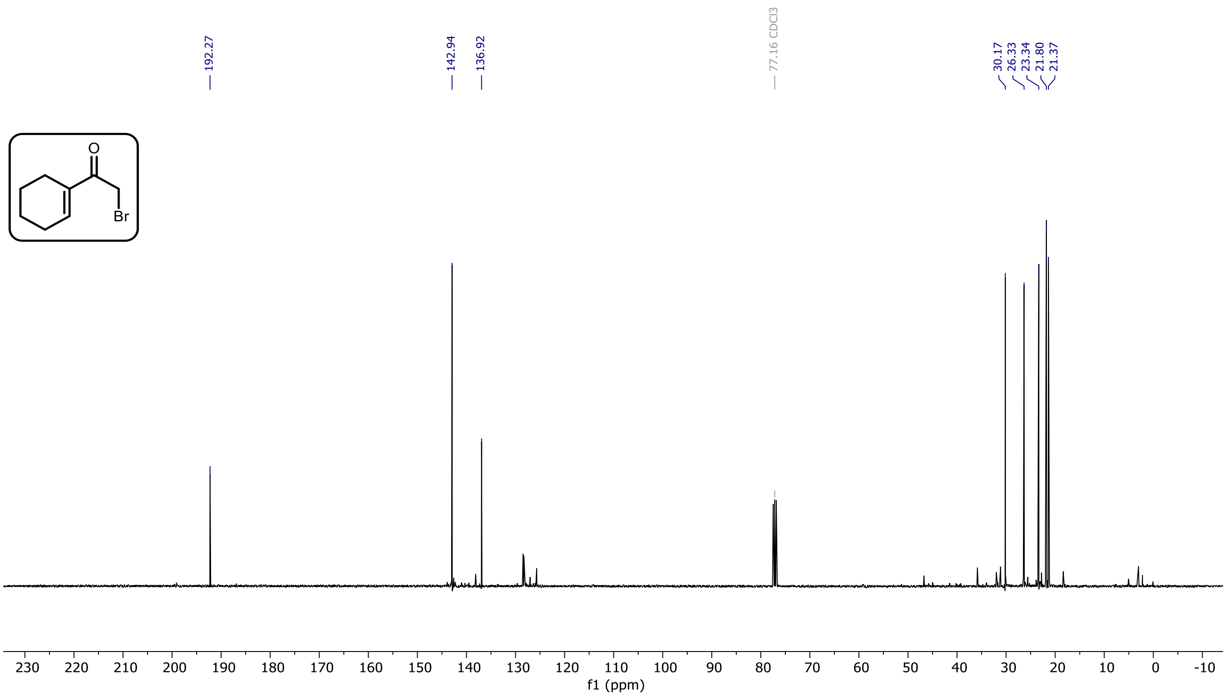
A13: *[1]H NMR ($CDCl_3$) of compound* ***S7***.



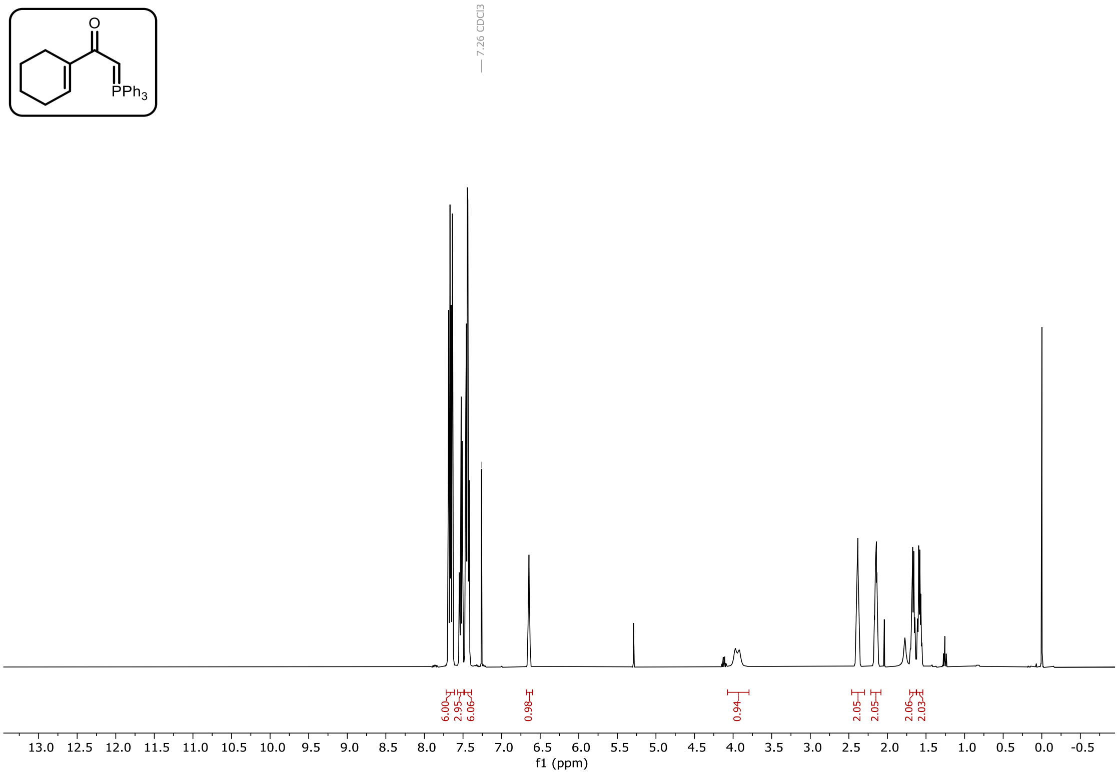
A14: *[13]C NMR ($CDCl_3$) of compound* ***S7***.



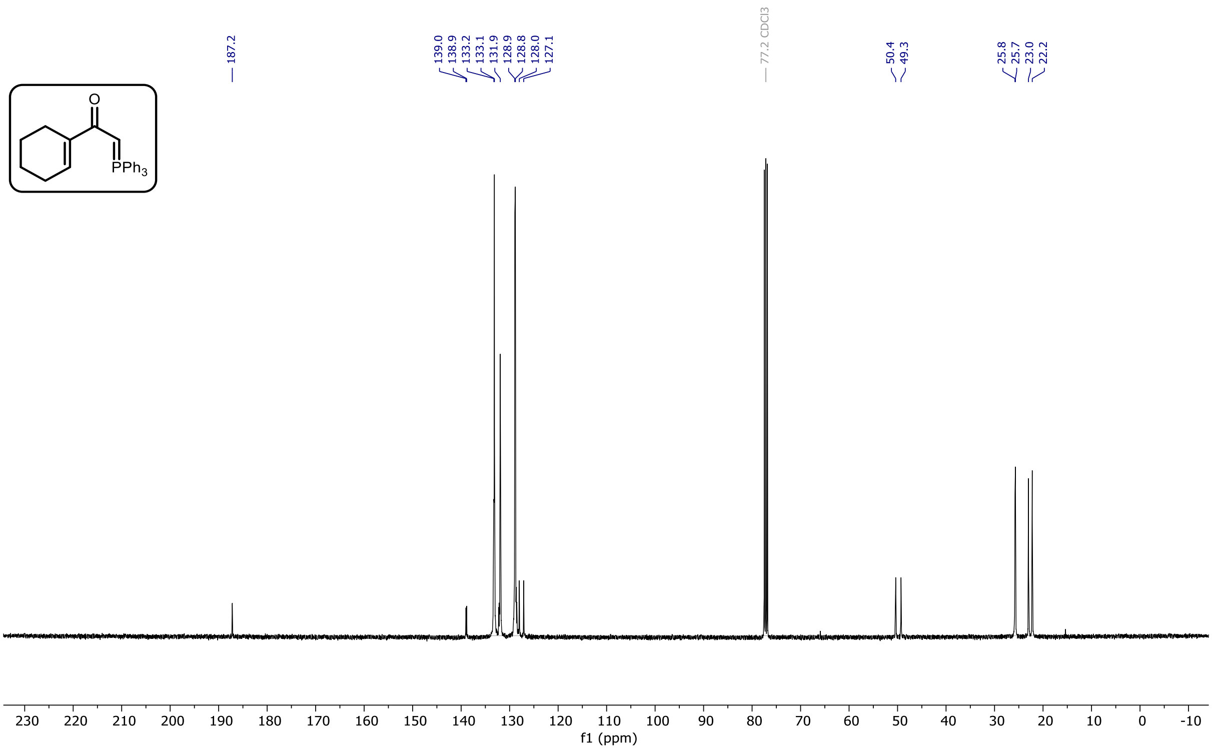
A15: *[1]H NMR (CDCl$_3$) of compound* ***S8***.



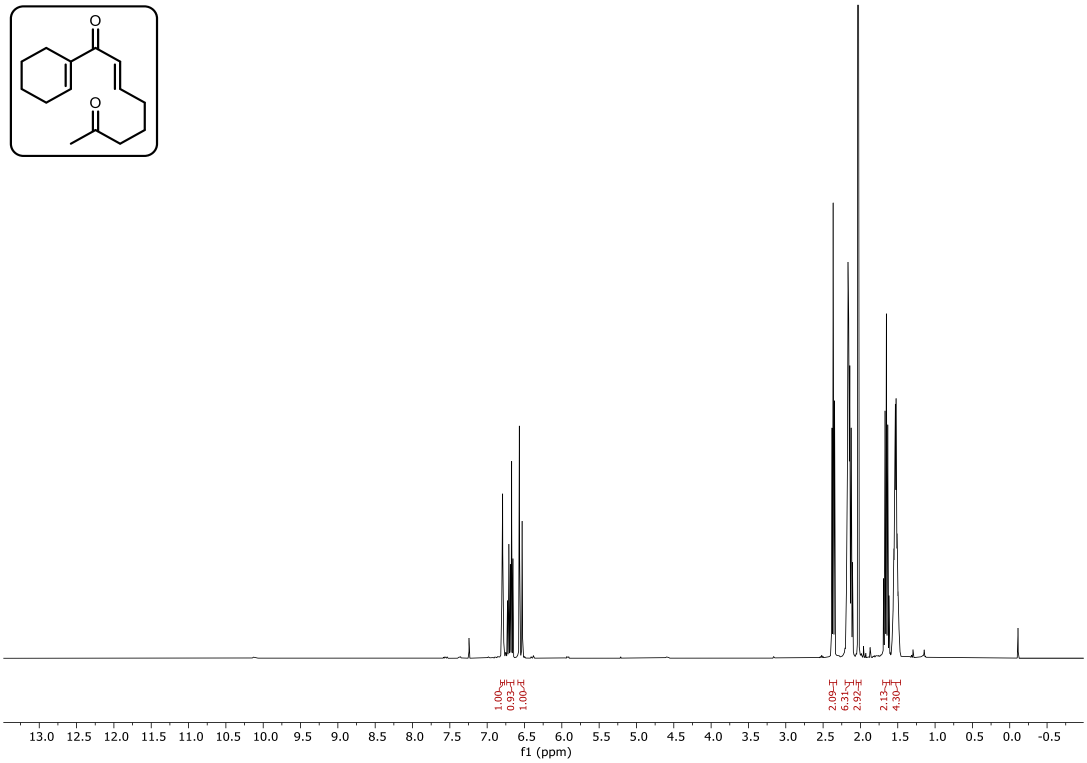
A16: *[13]C NMR (CDCl$_3$) of compound* ***S8***.



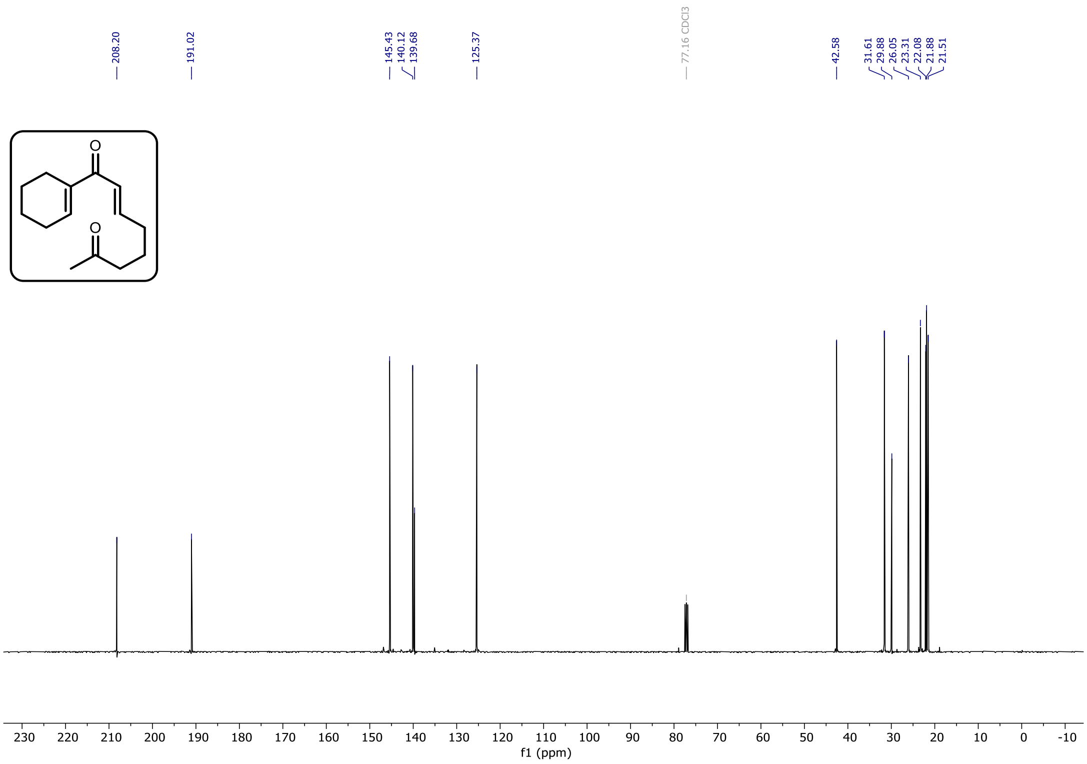
A17: *[1]H NMR (CDCl$_3$) of compound* ***S9****.*



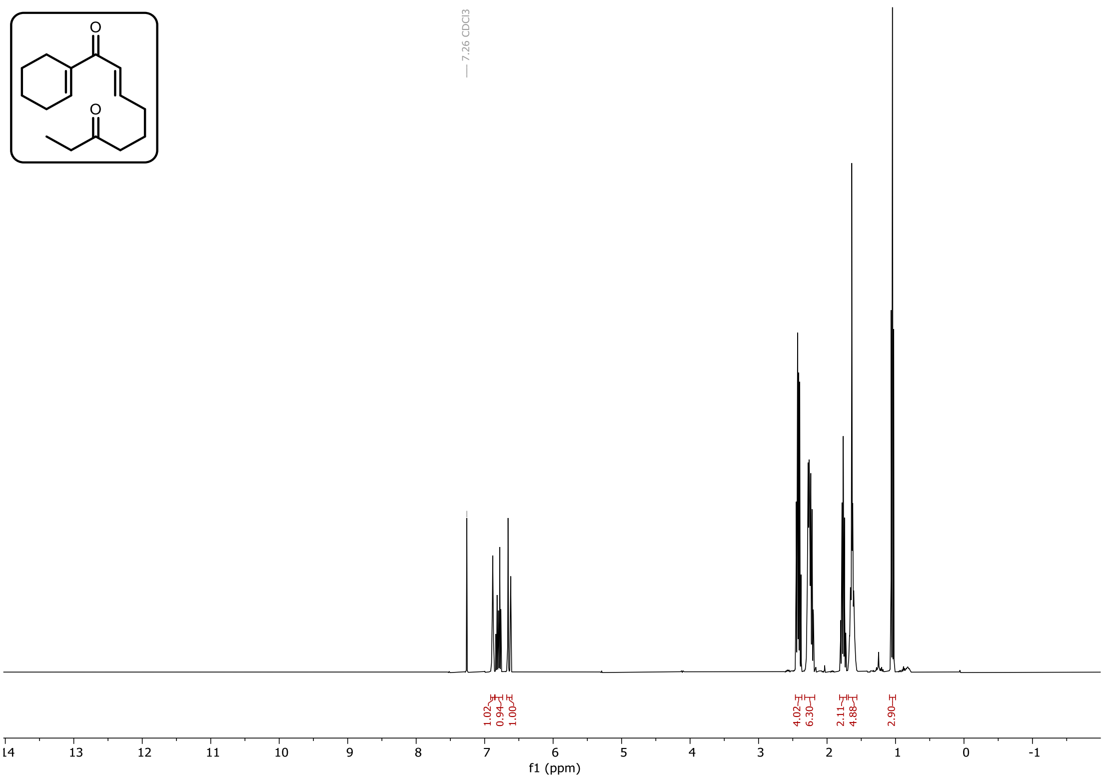
A18: *[13]C NMR (CDCl$_3$) of compound* ***S9****.*



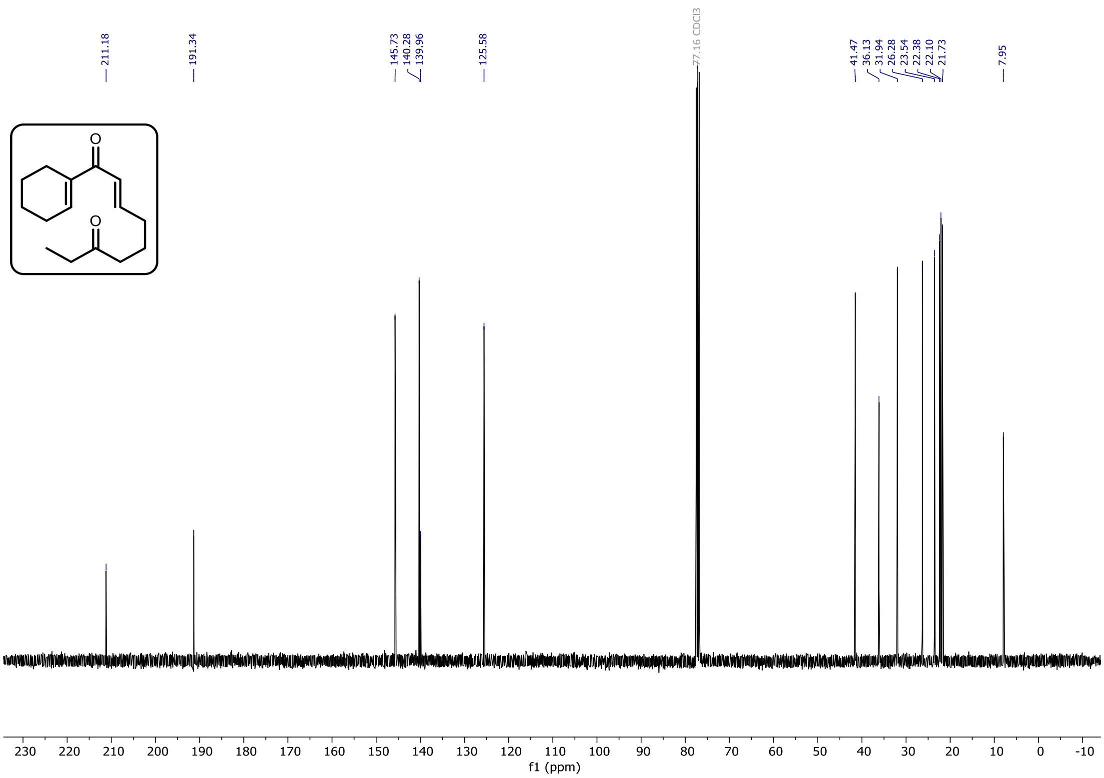
A19: *^{1}H NMR ($CDCl_3$) of compound* ***1a***.



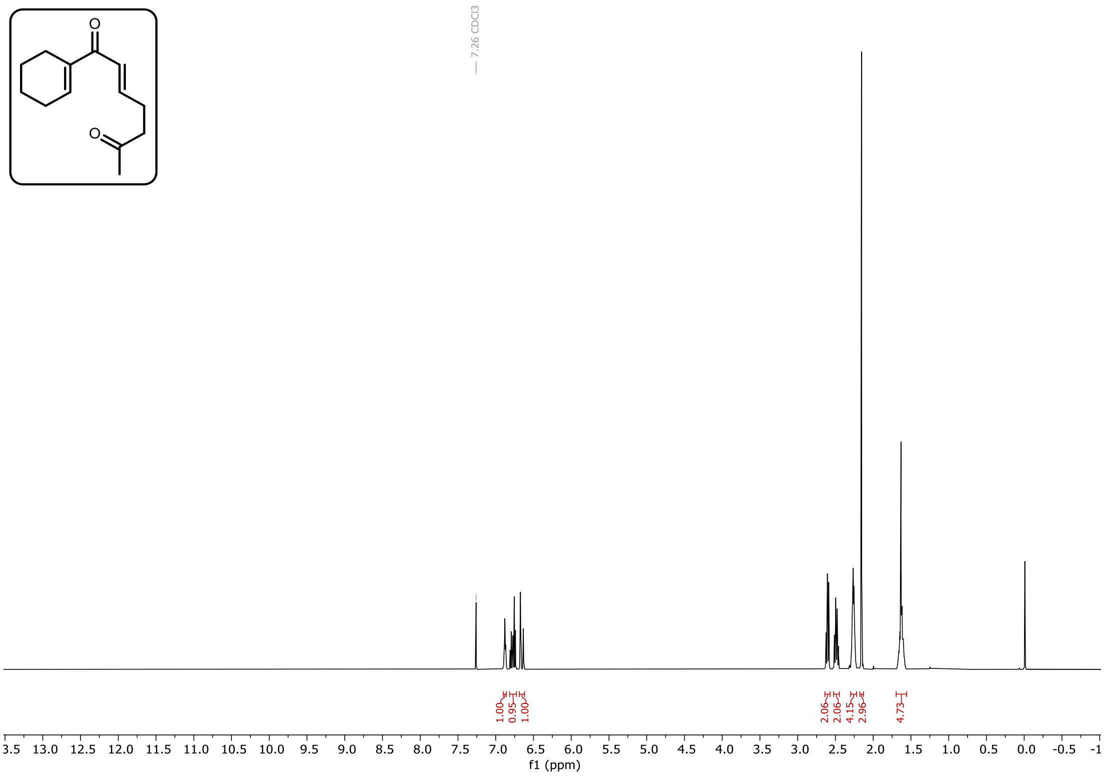
A20: *^{13}C NMR ($CDCl_3$) of compound* ***1a***.



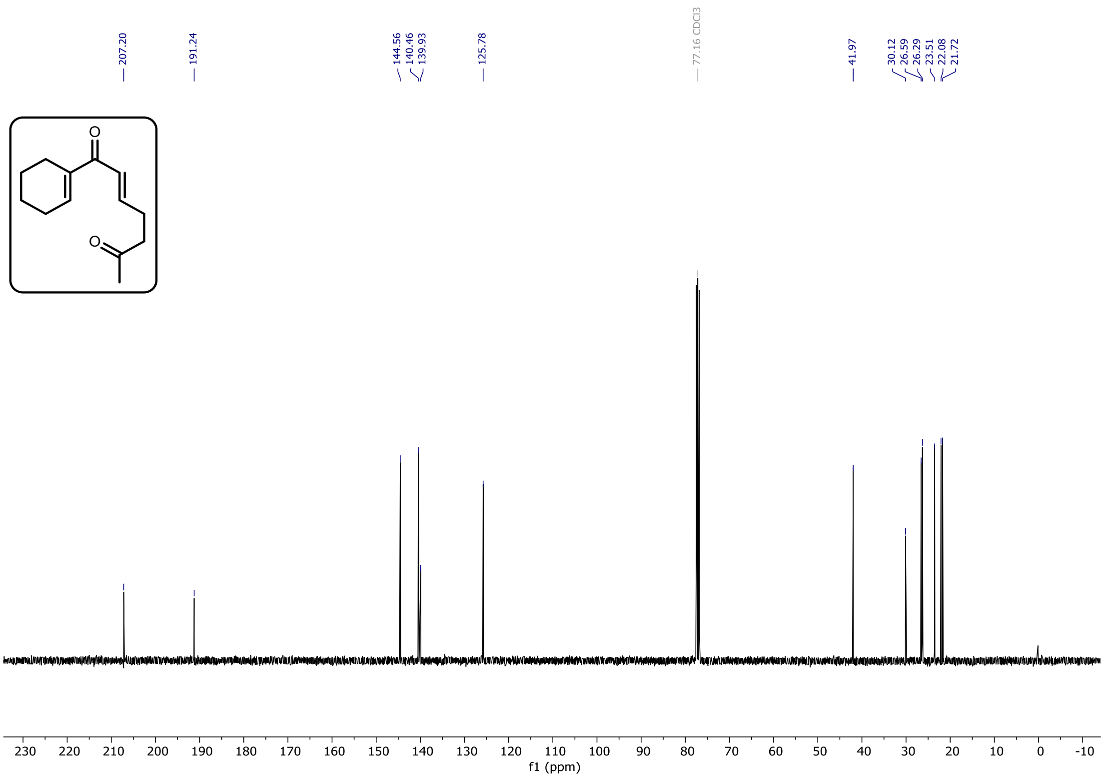
***A21:** ¹H NMR (CDCl₃) of compound **1b**.*



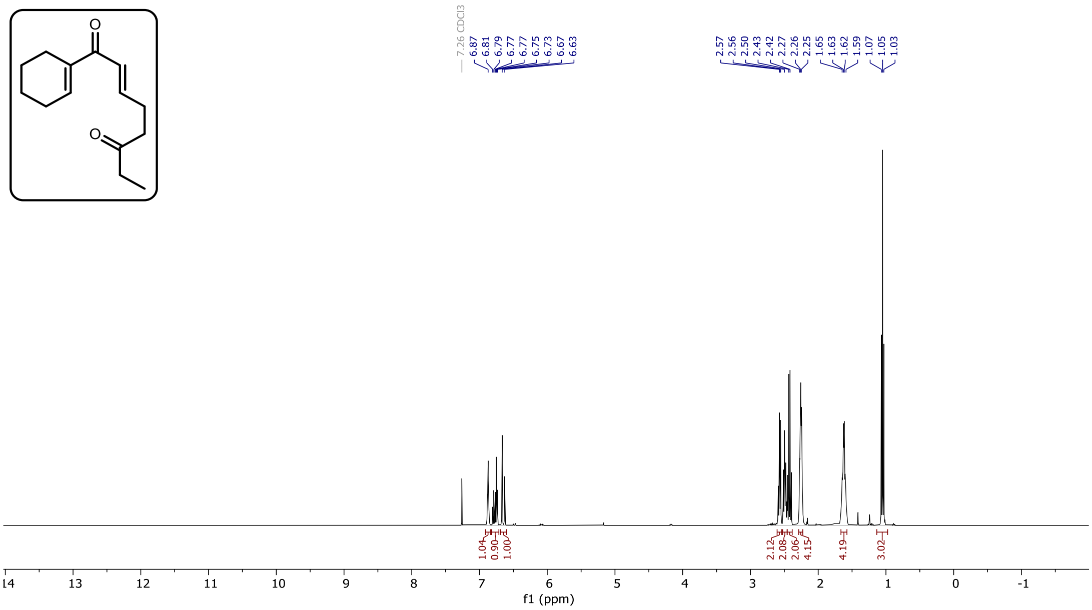
***A22:** ¹³C NMR (CDCl₃) of compound **1b**.*



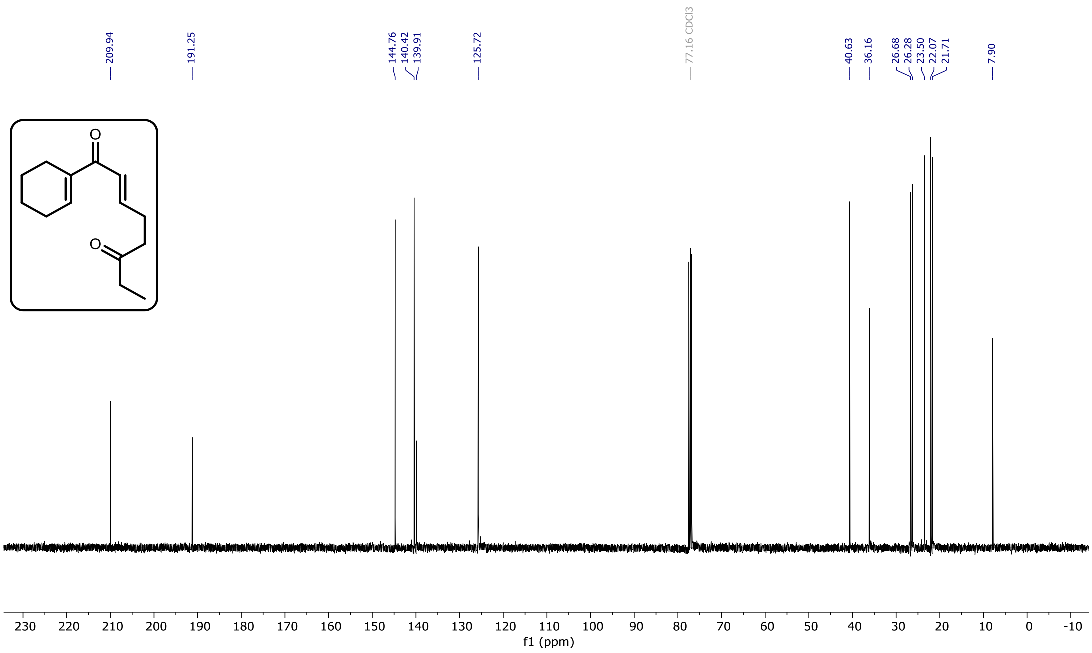
A23: *[1]H NMR ($CDCl_3$) of compound **1c**.*



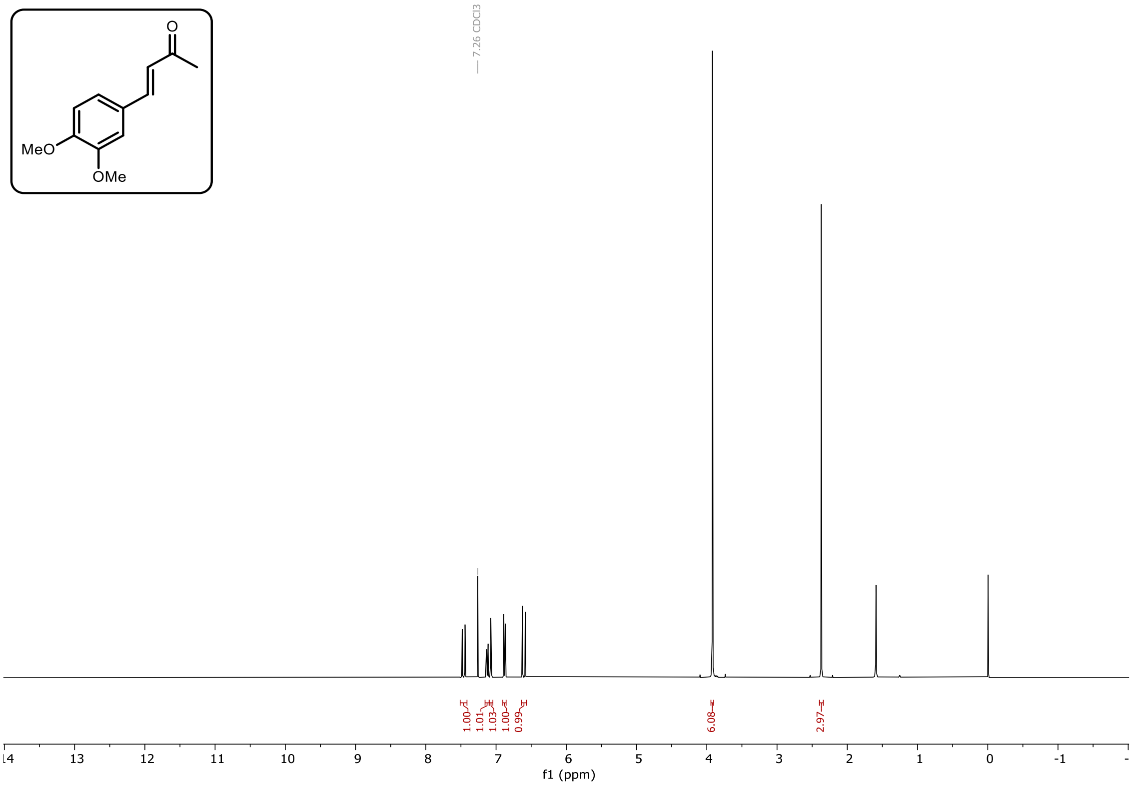
A24: *[13]C NMR ($CDCl_3$) of compound **1c**.*



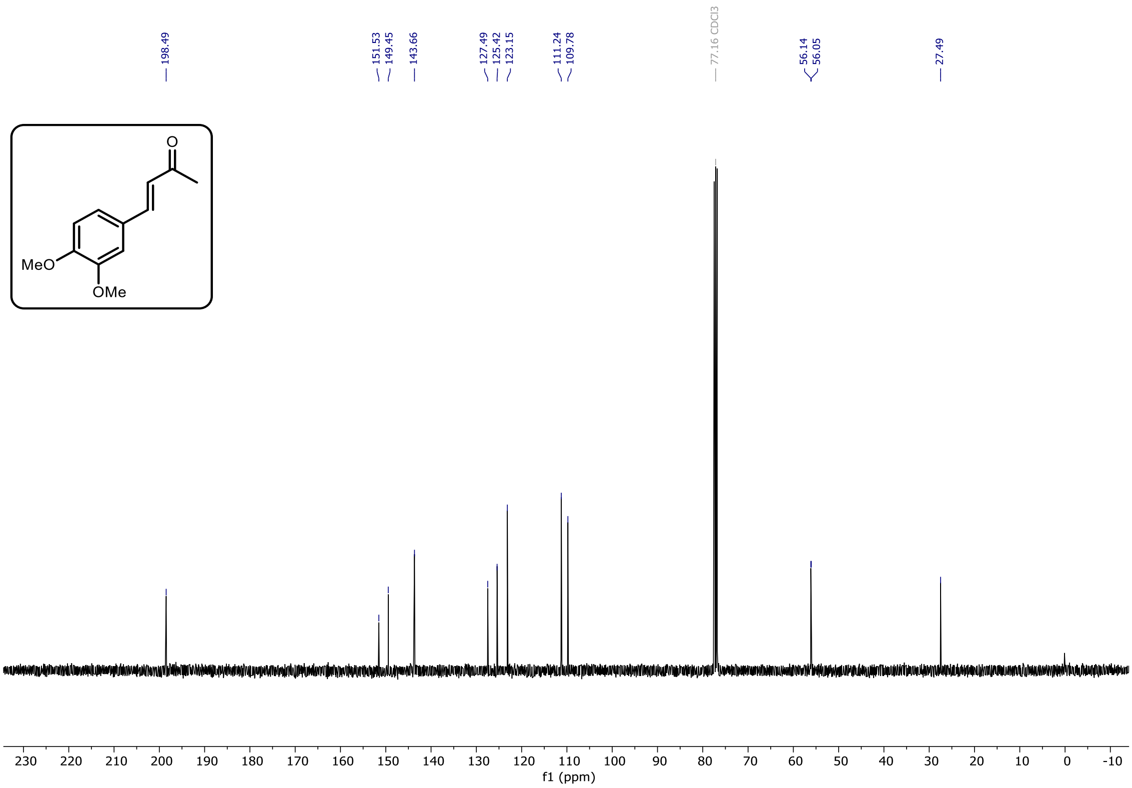
A25: *^{1}H NMR ($CDCl_3$) of compound* ***1d****.*



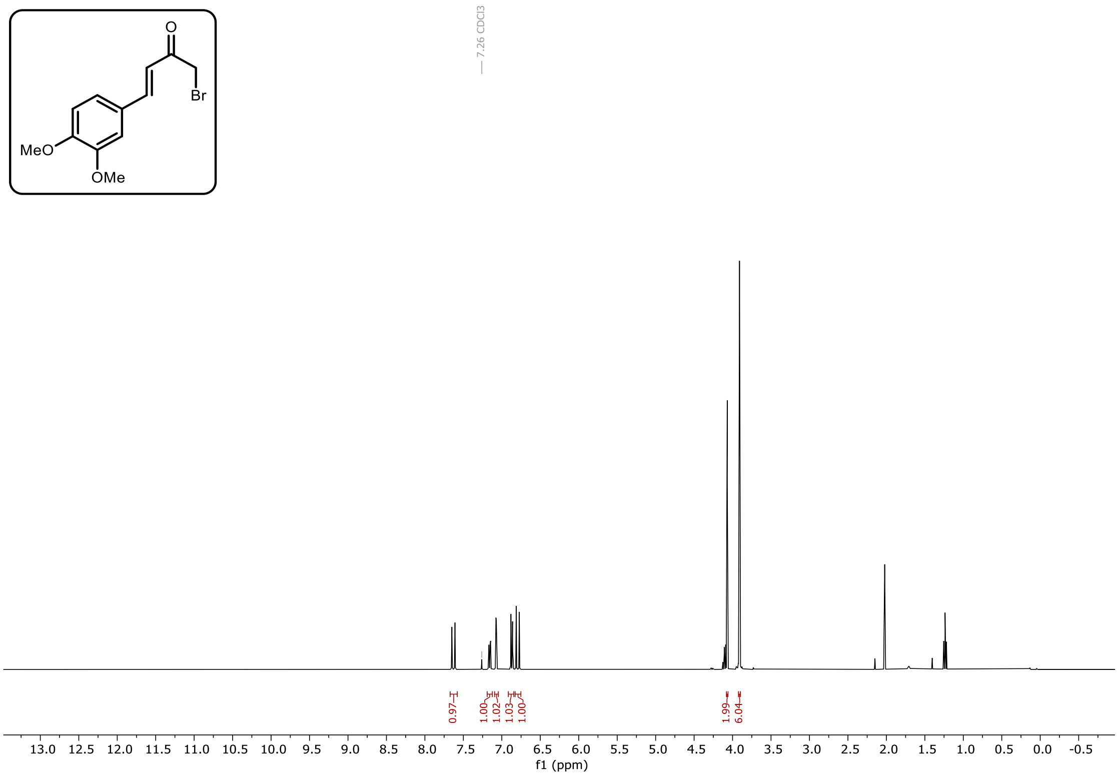
A26: *^{13}C NMR ($CDCl_3$) of compound* ***1d****.*



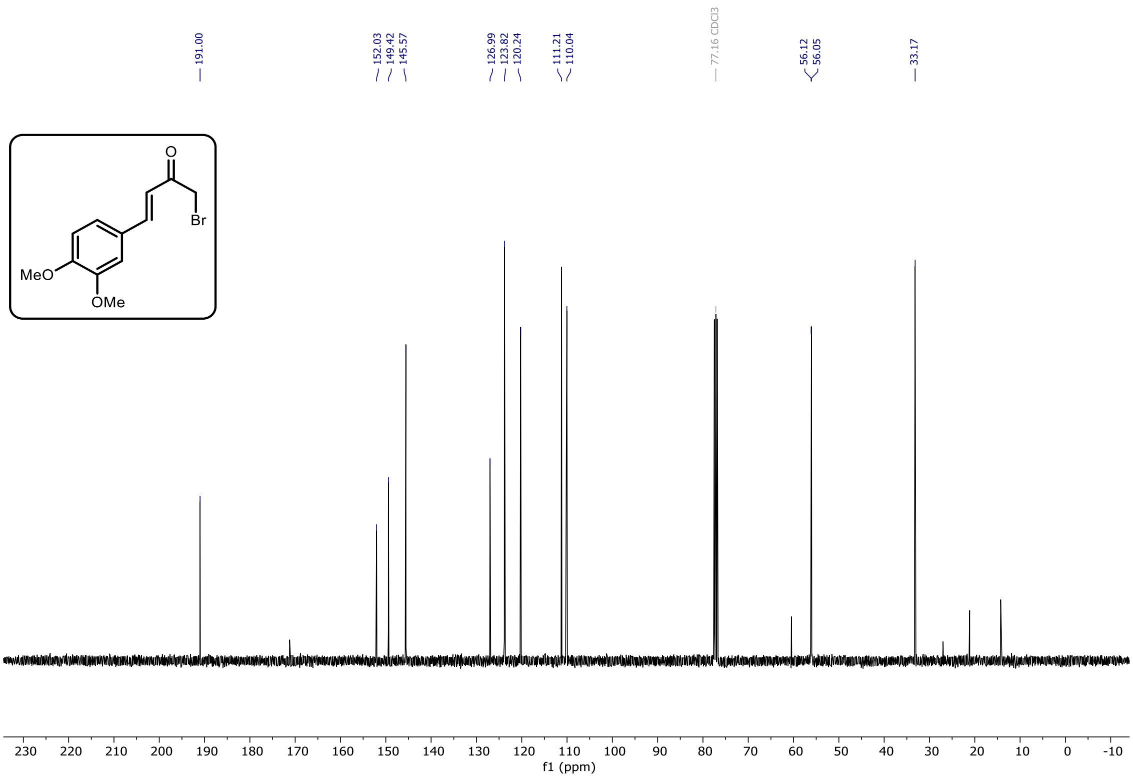
***A27:** ^{1}H NMR ($CDCl_3$) of compound **S10**.*



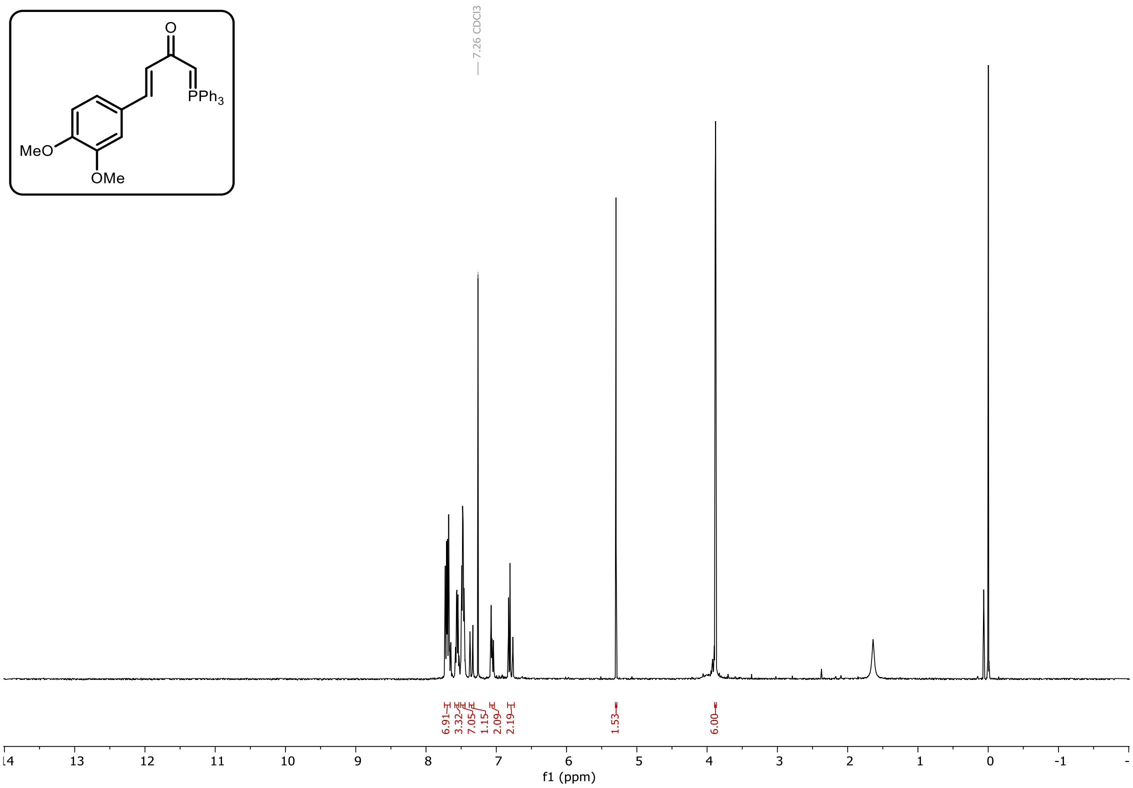
***A28:** ^{13}C NMR ($CDCl_3$) of compound **S10**.*



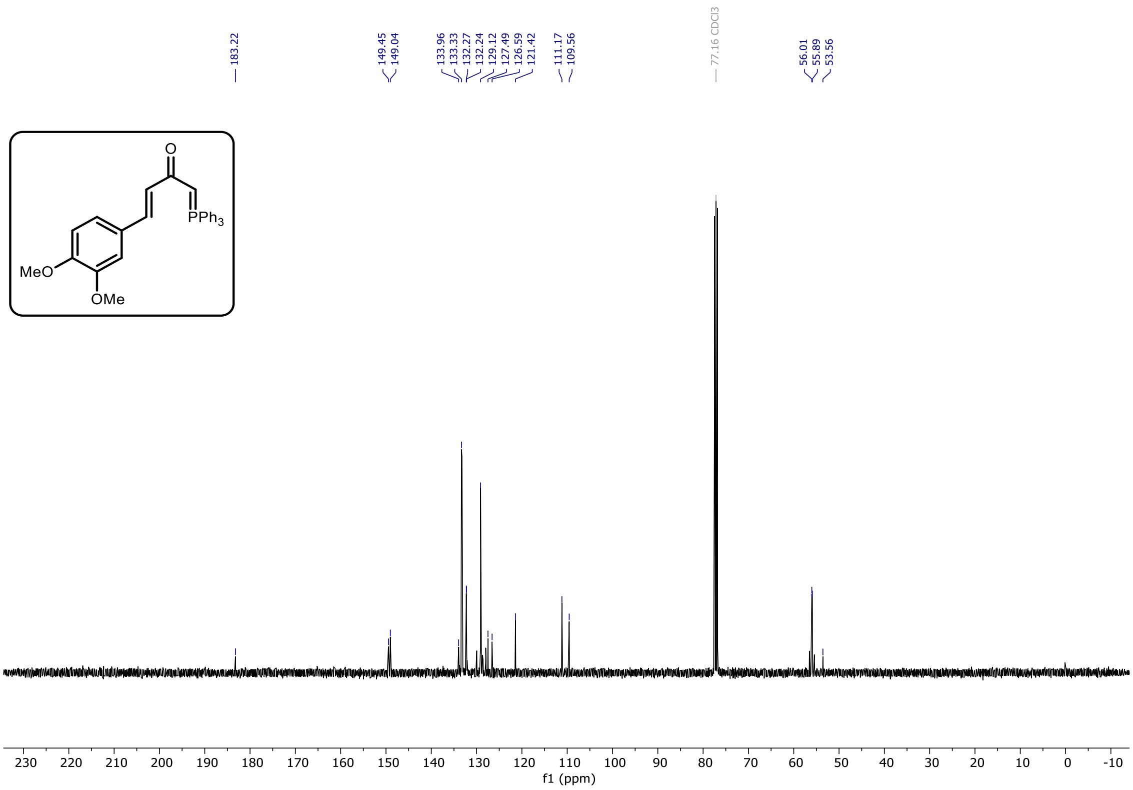
A29: *^{1}H NMR ($CDCl_3$) of compound* ***S11***.



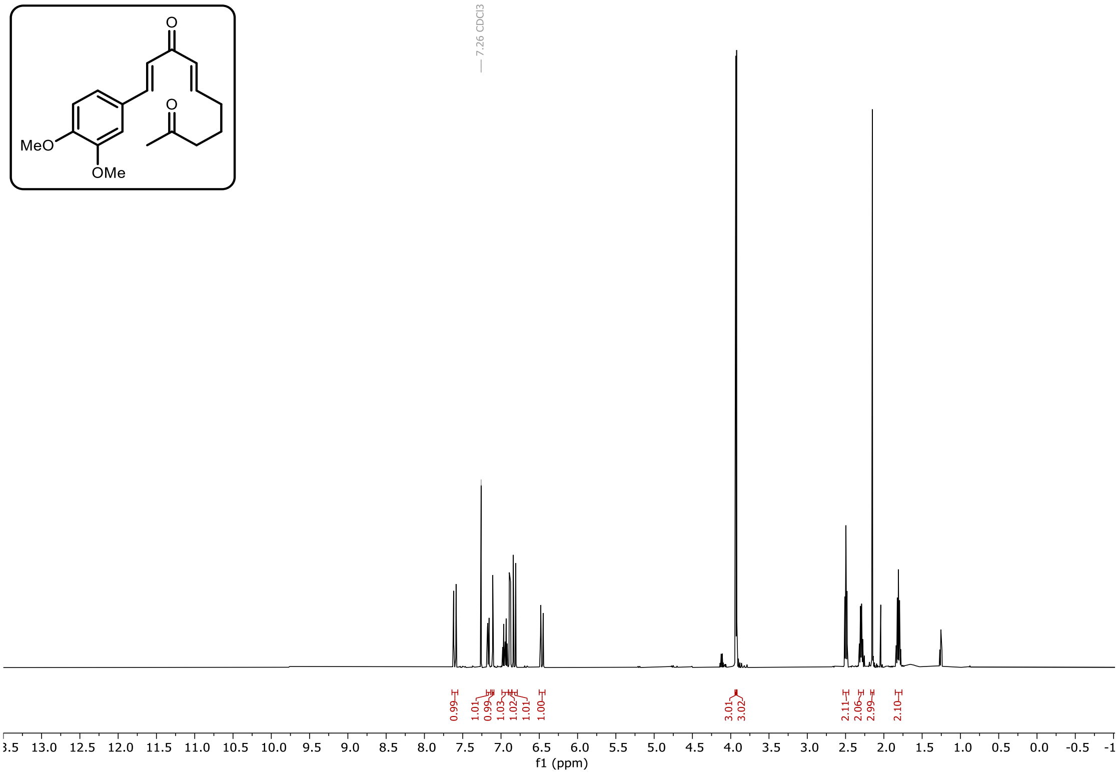
A30: *^{13}C NMR ($CDCl_3$) of compound* ***S11***.



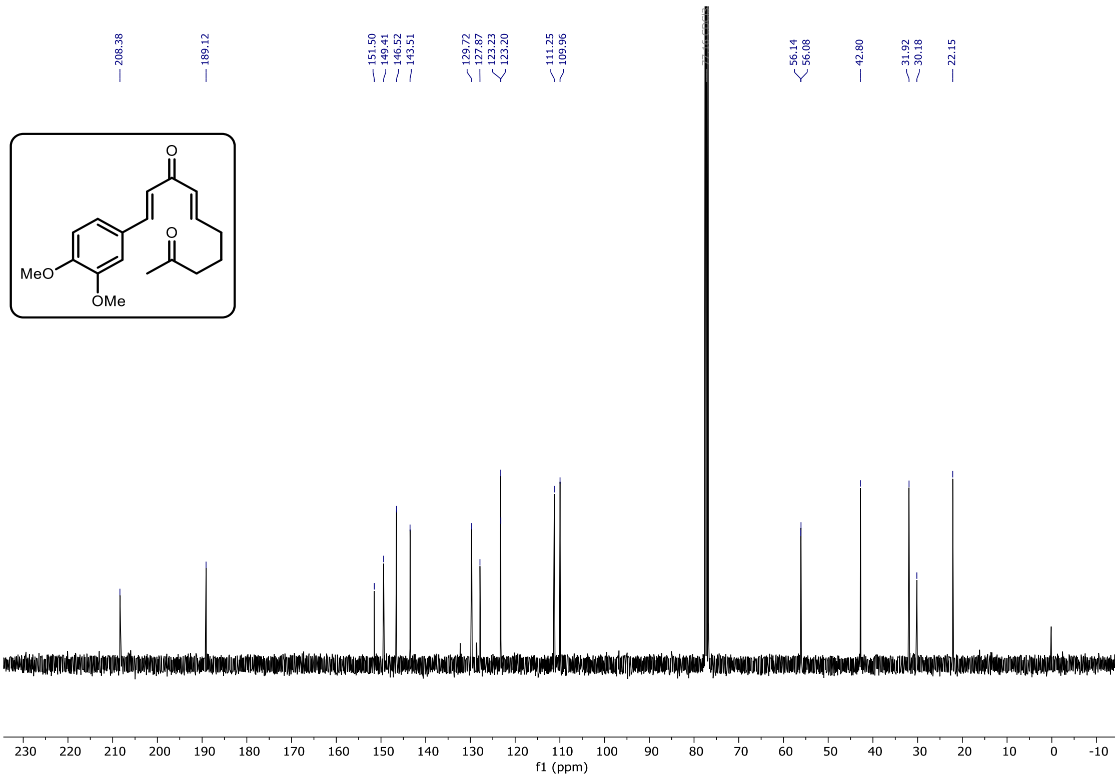
A31: *[1]H NMR (CDCl$_3$) of compound* ***S12***.



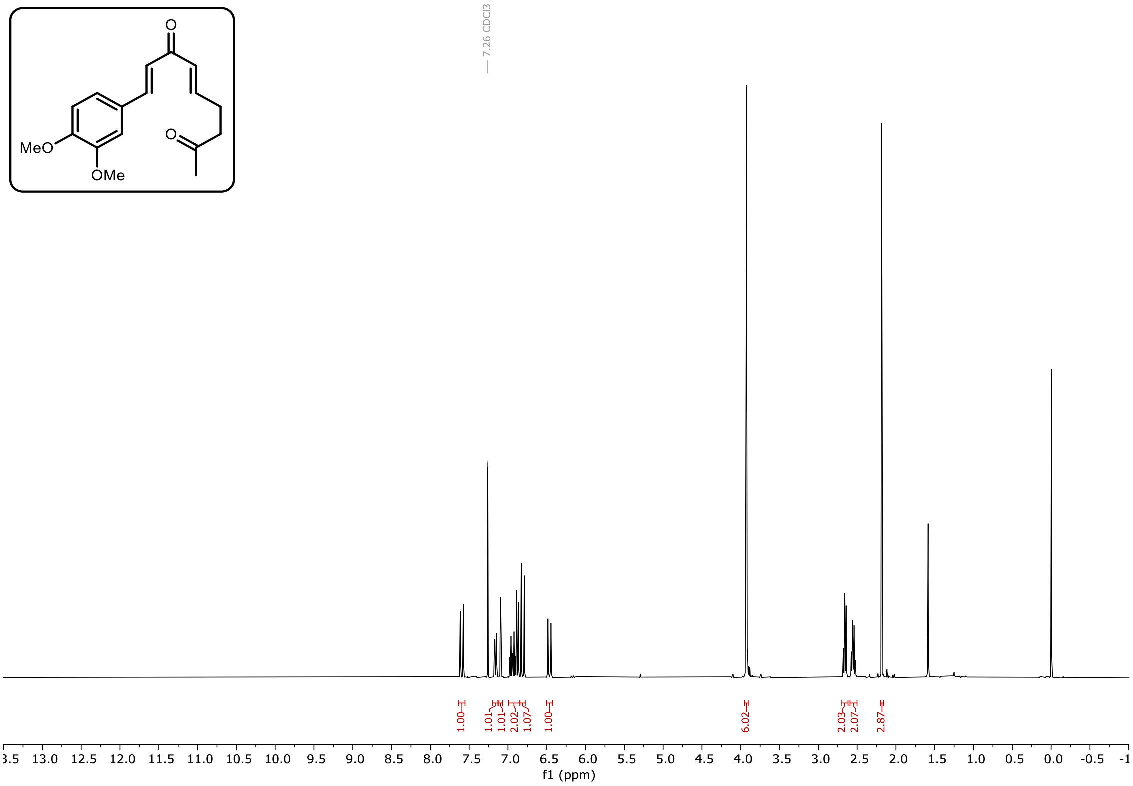
A32: *[13]C NMR (CDCl$_3$) of compound* ***S12***.



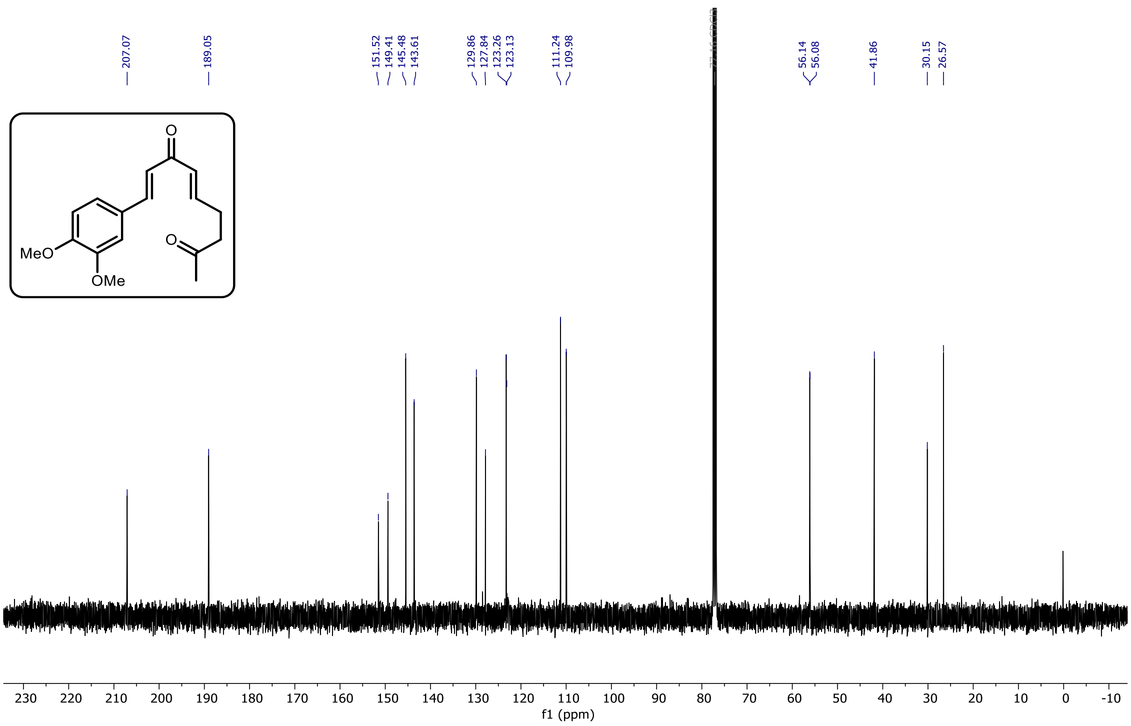
A33: *^{1}H NMR ($CDCl_3$) of compound **1e**.*



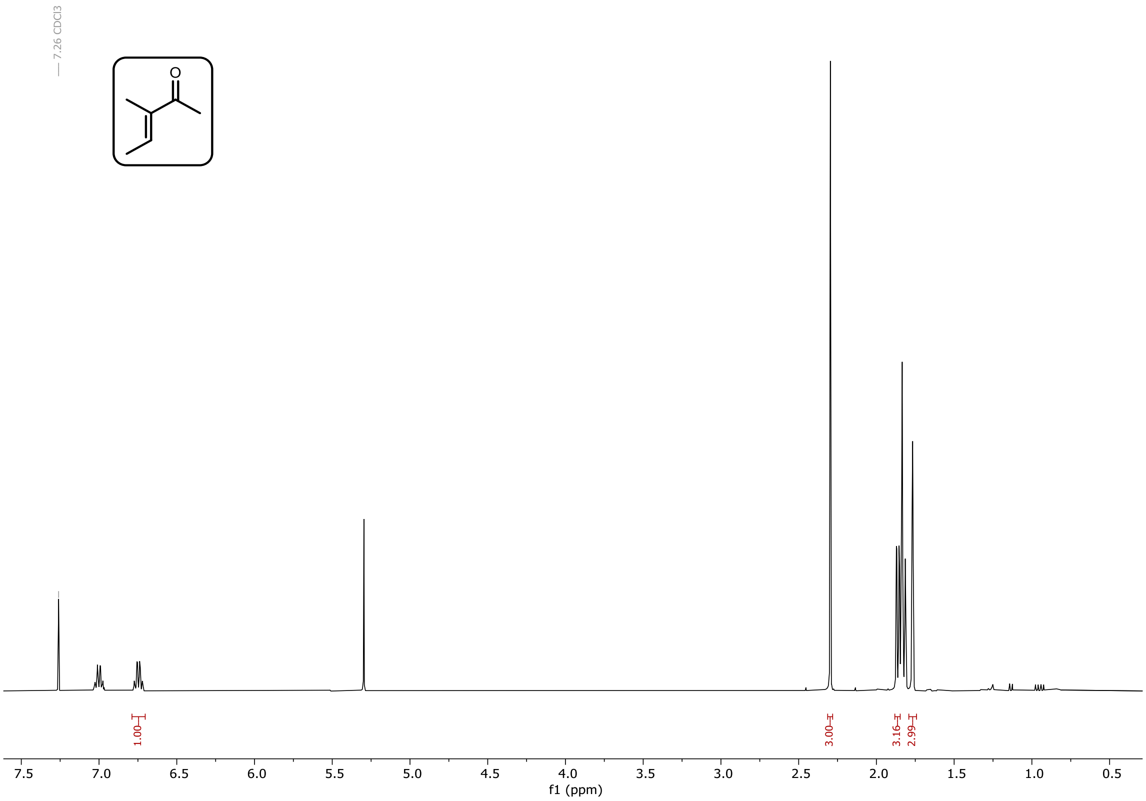
A34: *^{13}C NMR ($CDCl_3$) of compound **1e**.*



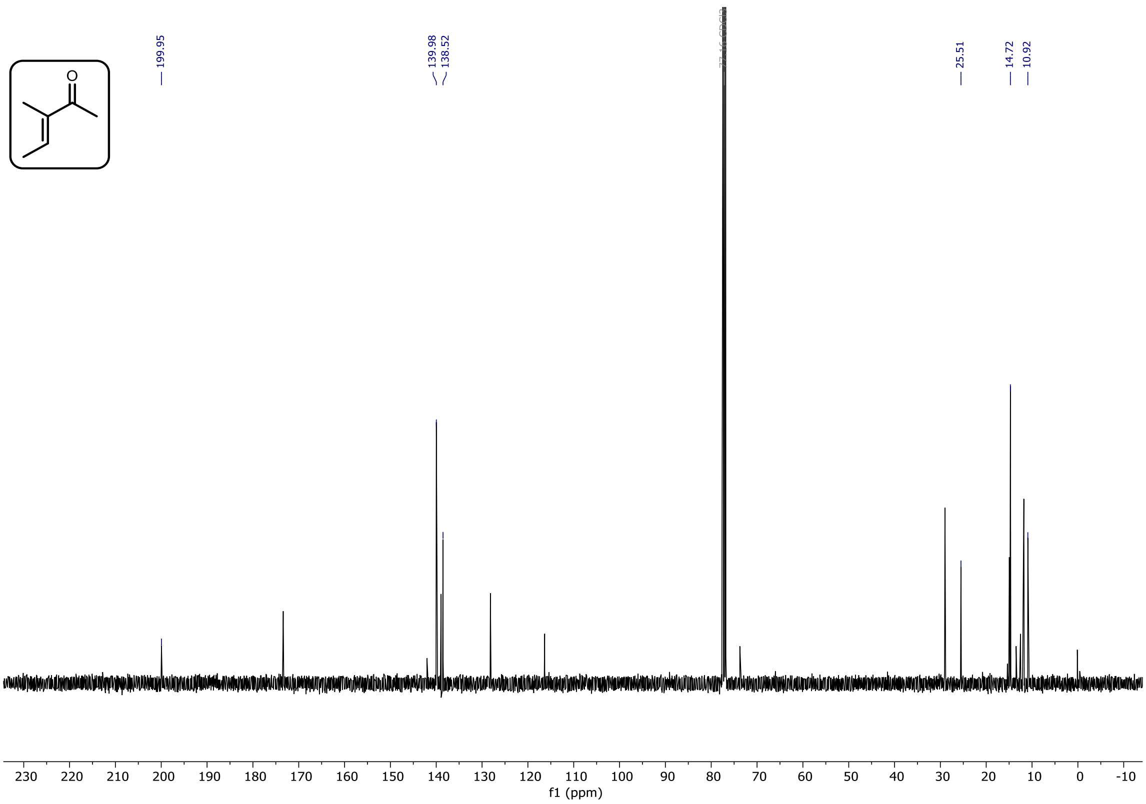
A35: *^{1}H NMR ($CDCl_3$) of compound **1f**.*



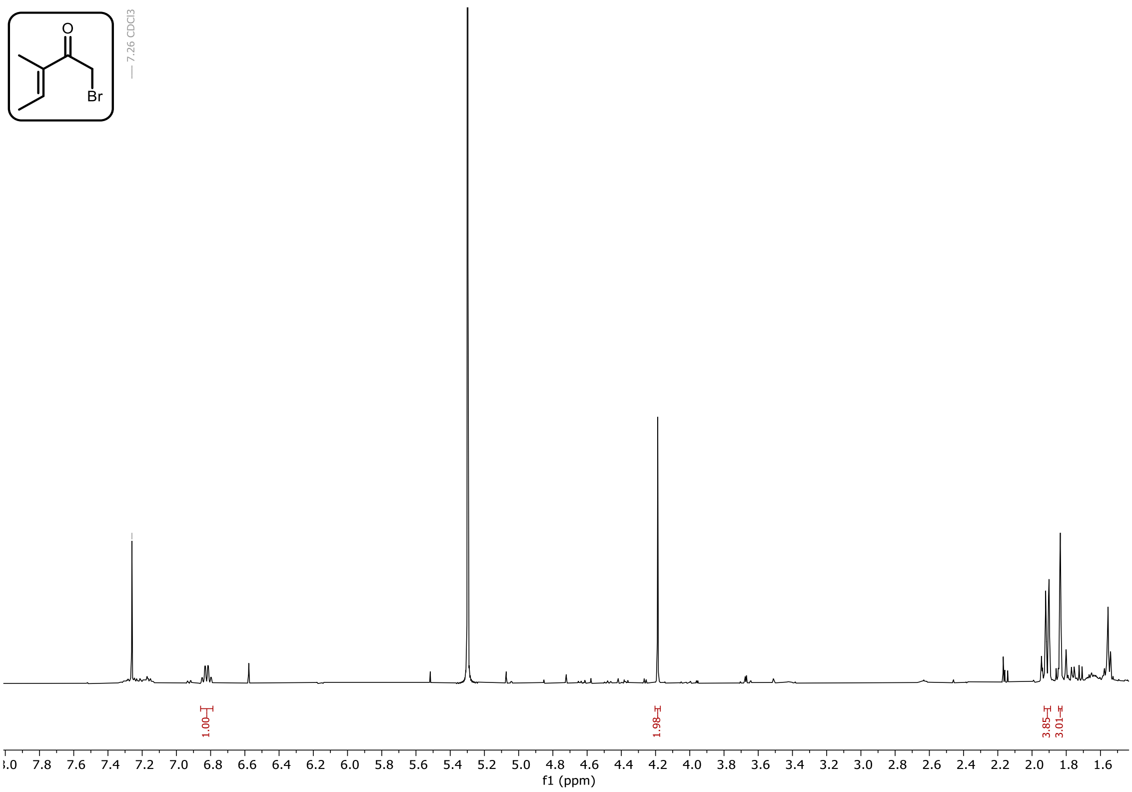
A36: *^{13}C NMR ($CDCl_3$) of compound **1f**.*



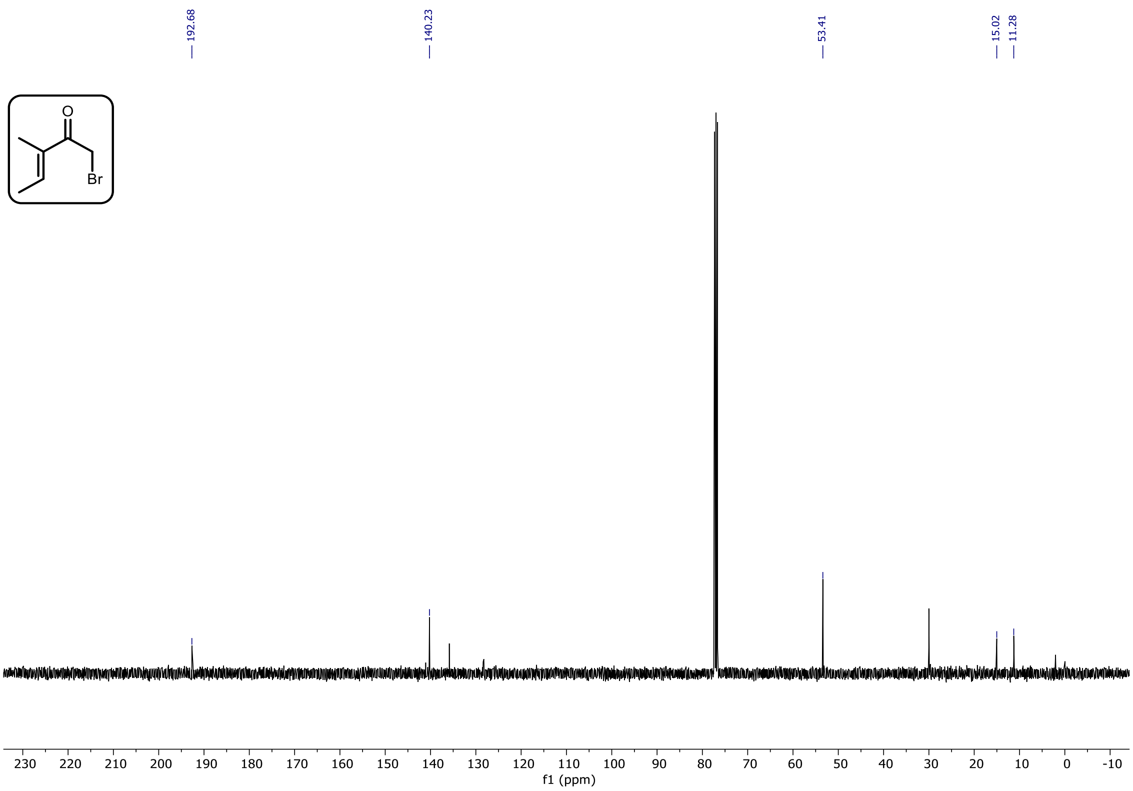
A37: *[1]H NMR (CDCl$_3$) of compound* ***S13****.*



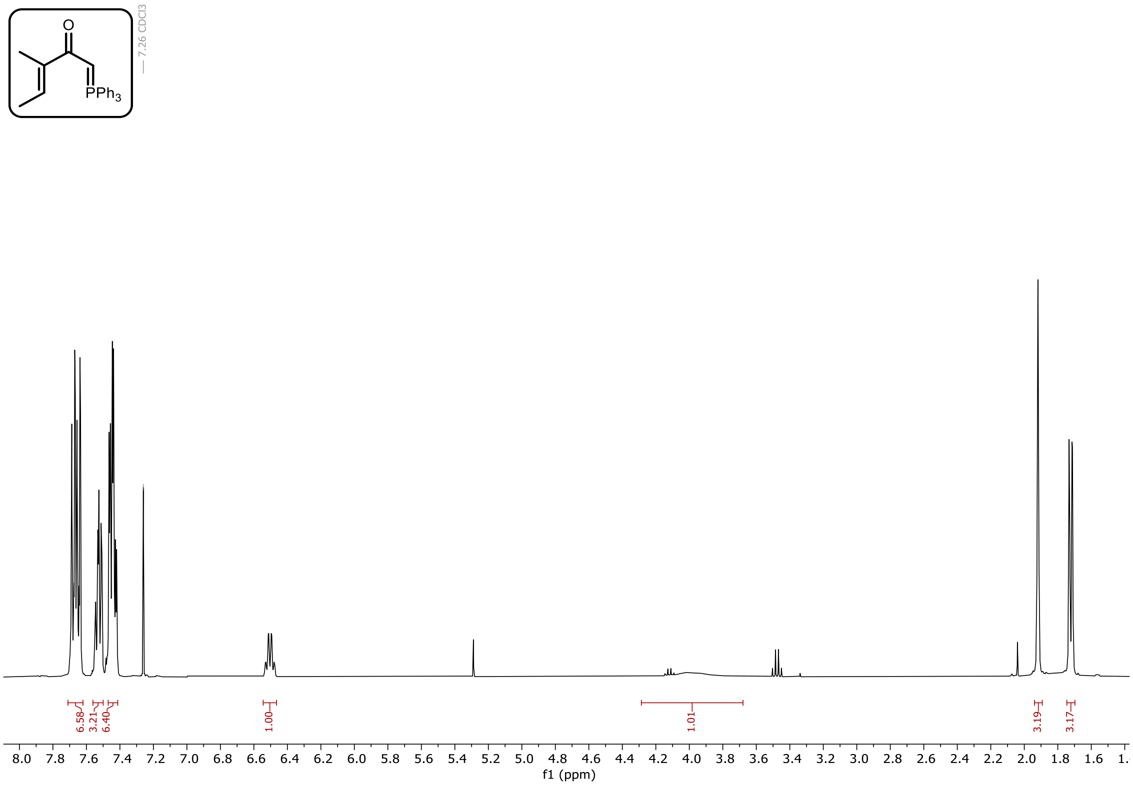
A38: *[13]C NMR (CDCl$_3$) of compound* ***S13****.*



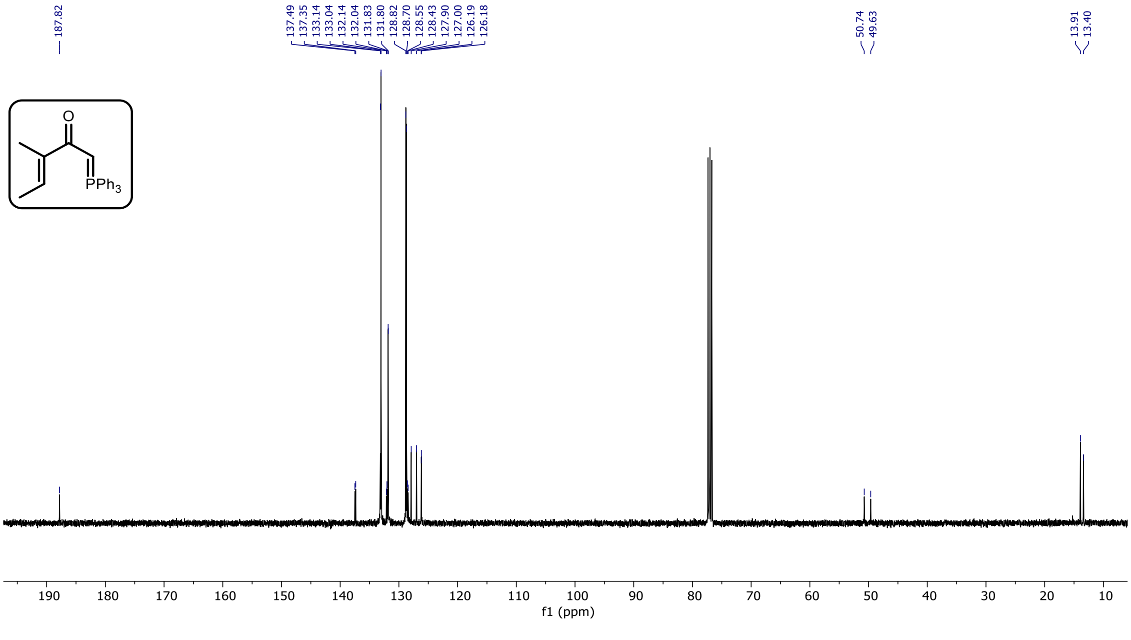
A39: ^{1}H *NMR* ($CDCl_3$) *of compound* ***S14***.



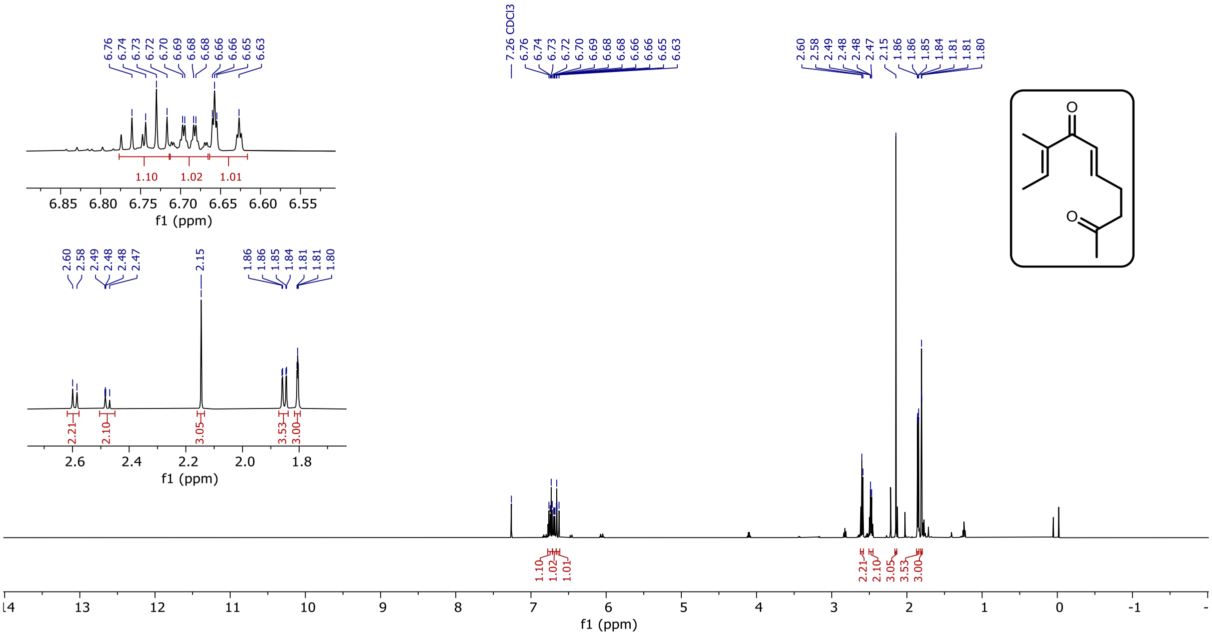
A40: ^{13}C *NMR* ($CDCl_3$) *of compound* ***S14***.



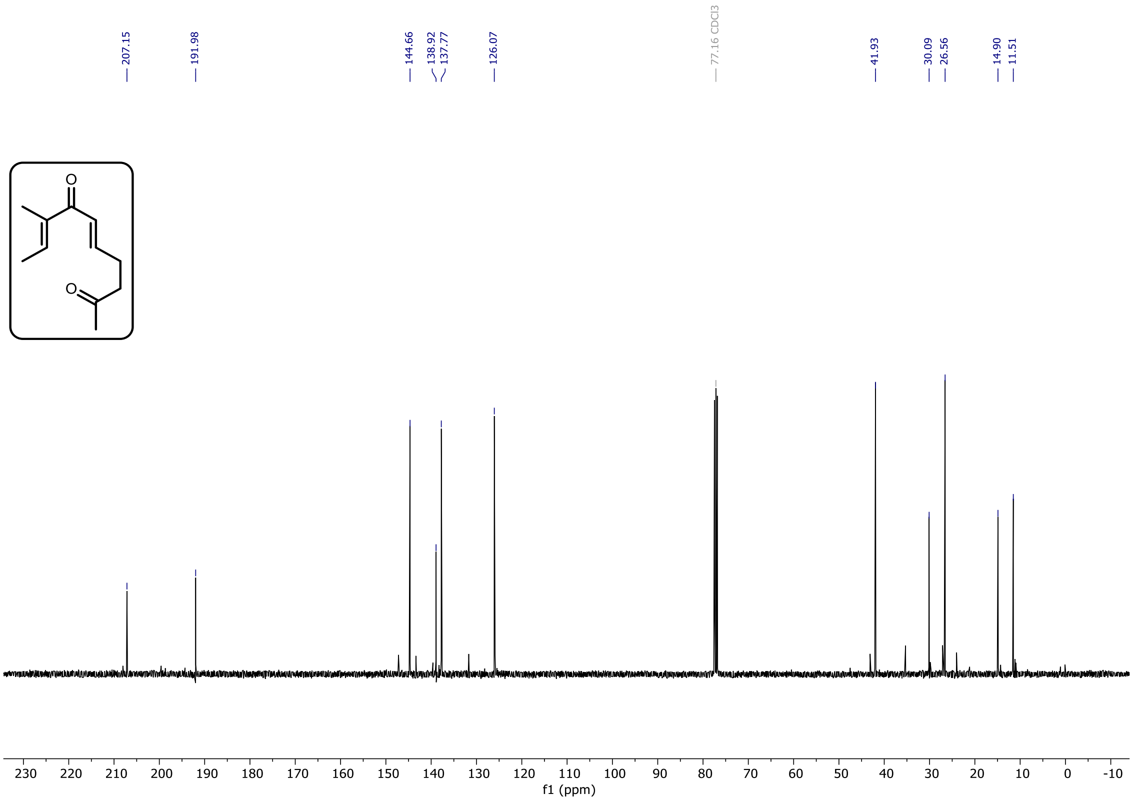
A41: *^{1}H NMR ($CDCl_3$) of compound* ***S15***.



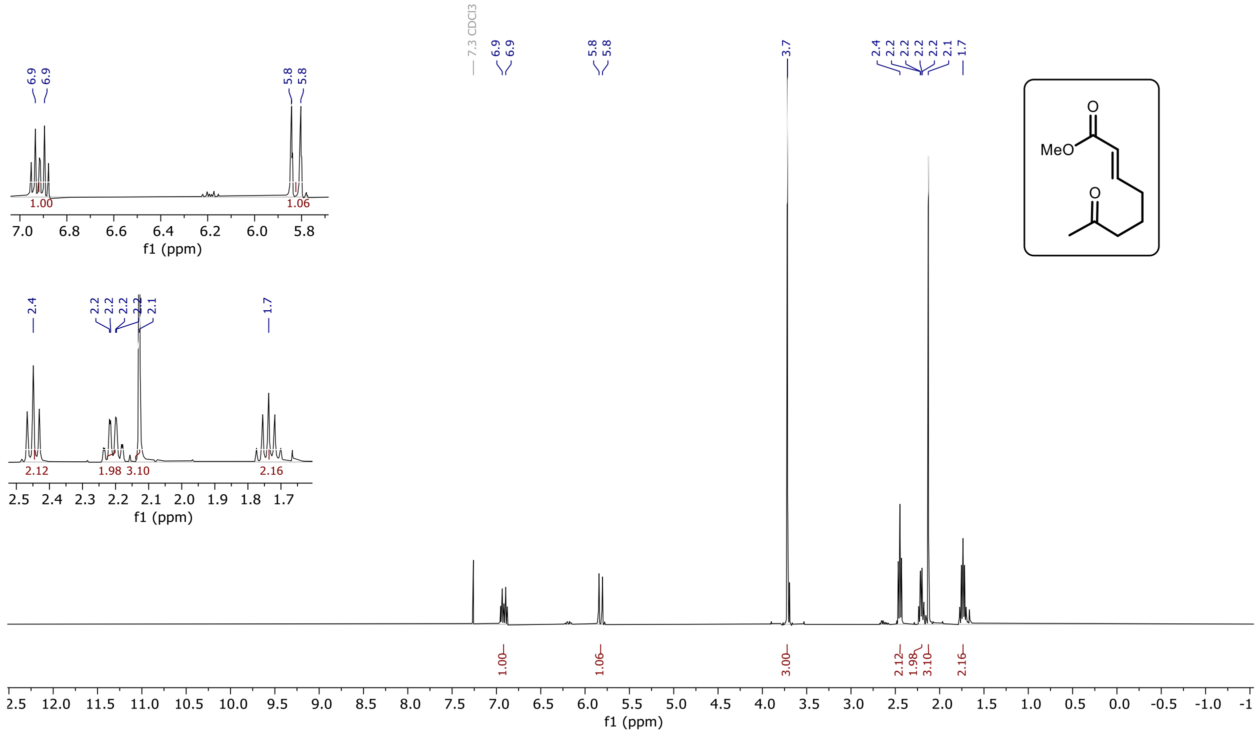
A42: *^{13}C NMR ($CDCl_3$) of compound* ***S15***.



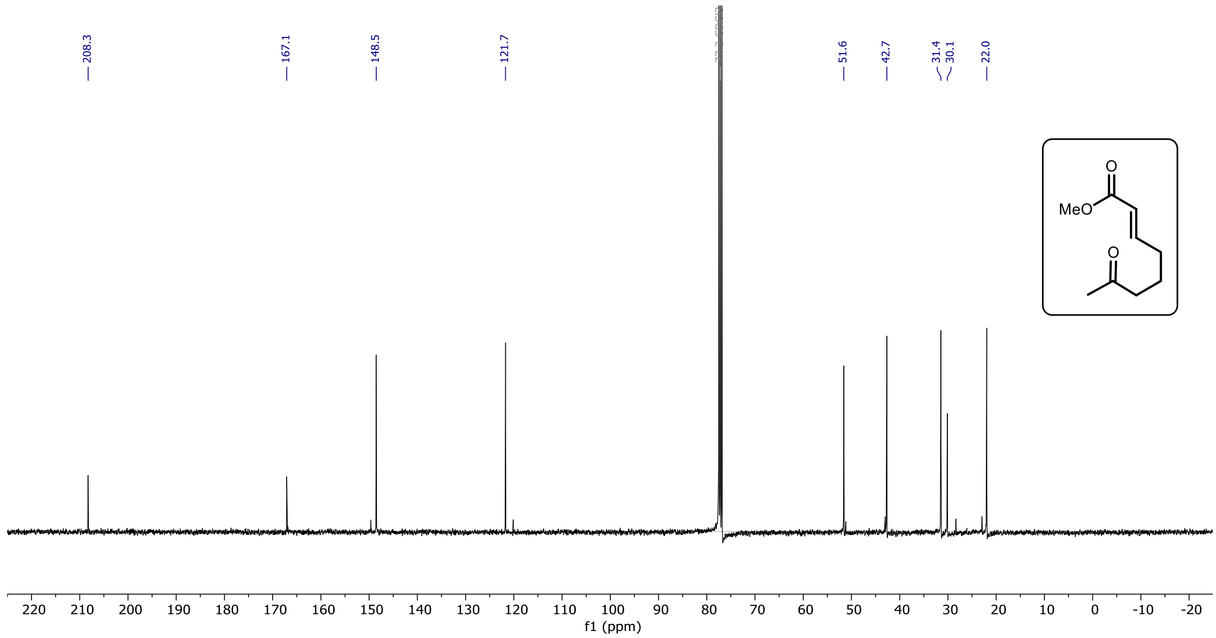
A43: *[1]H NMR ($CDCl_3$) of compound **1g**.*



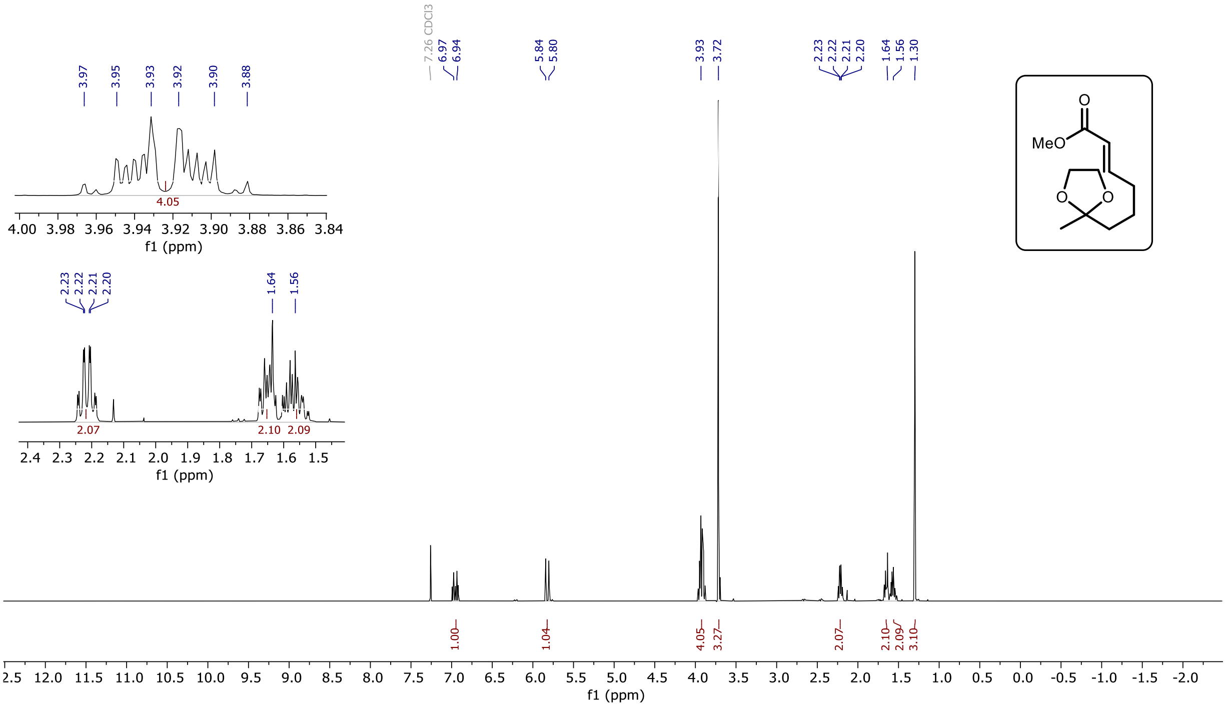
A44: *[13]C NMR ($CDCl_3$) of compound **1g**.*



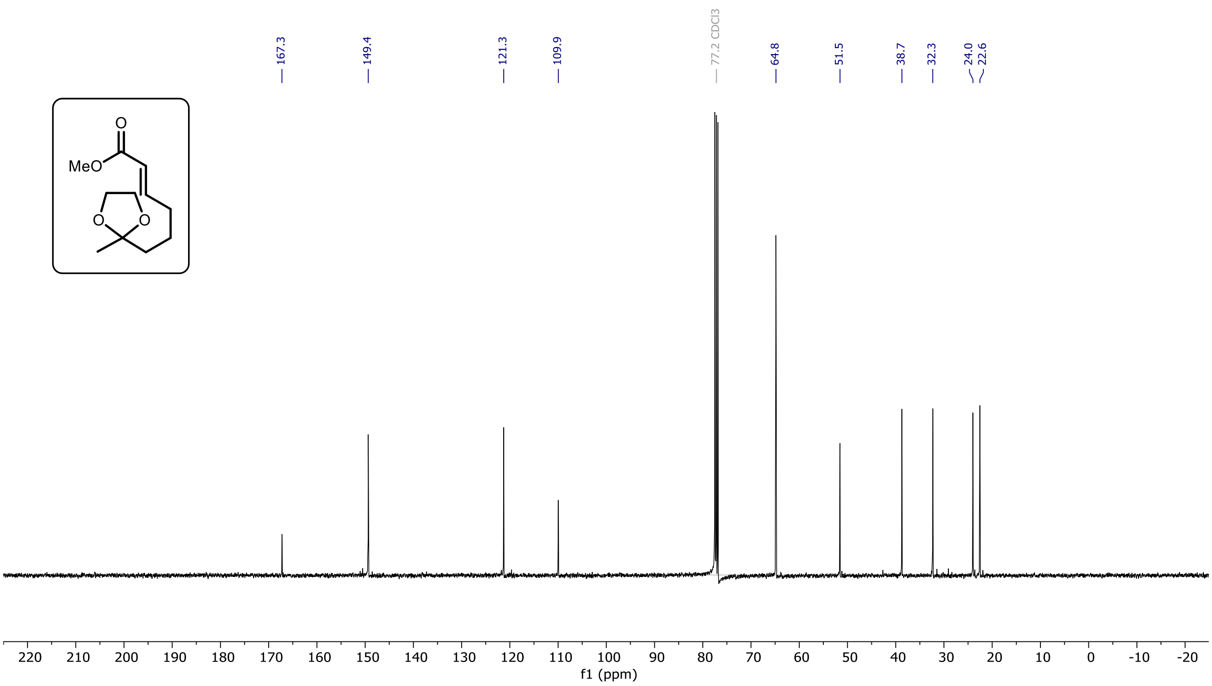
A45: *[1]H NMR ($CDCl_3$) of compound* ***S16.***



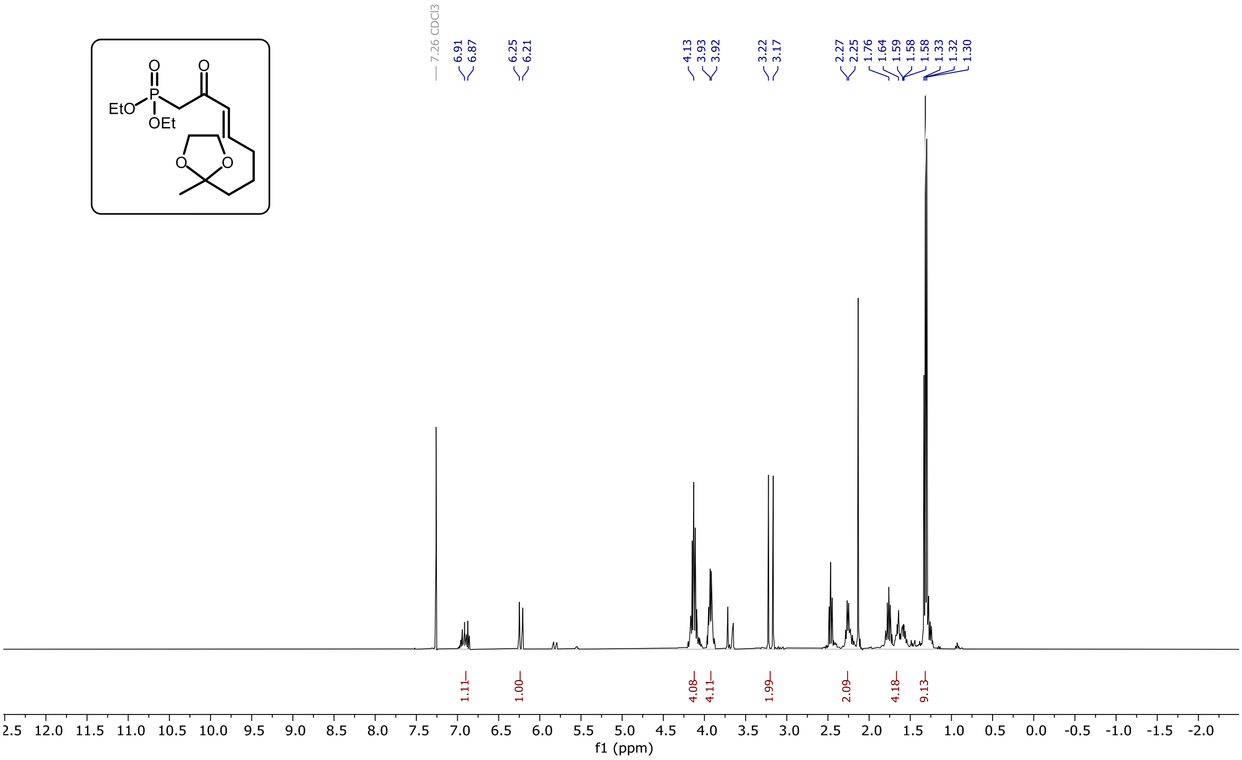
A46: *[13]C NMR ($CDCl_3$) of compound* ***S16.***



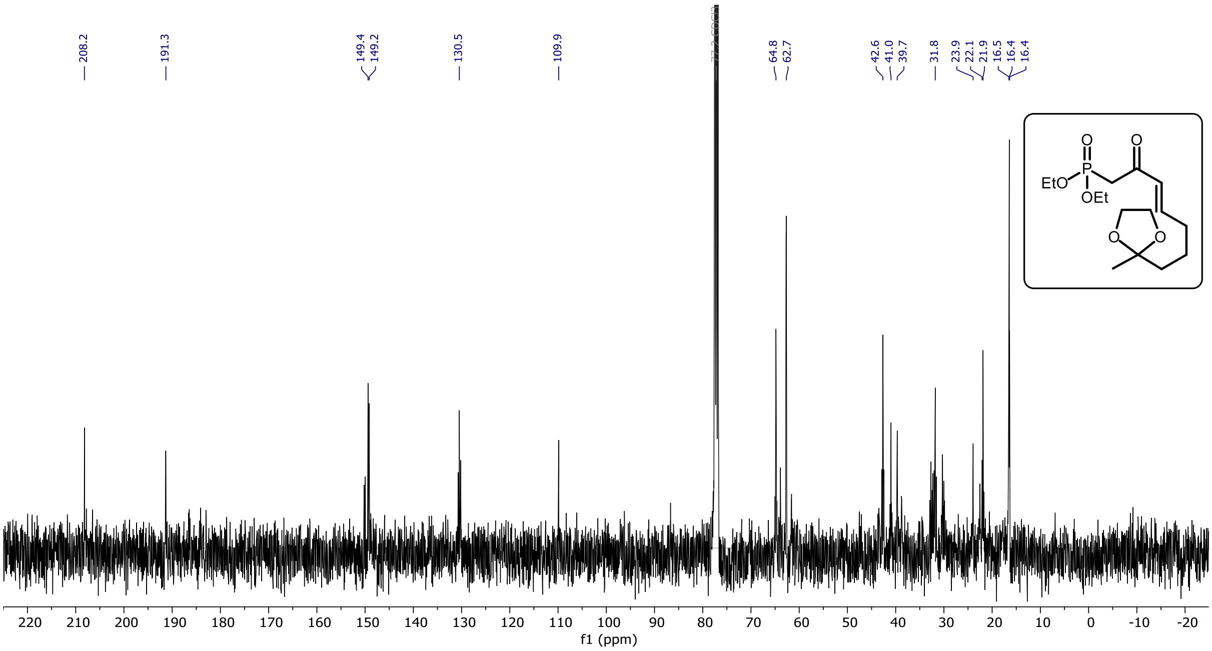
A47: *^1H NMR ($CDCl_3$) of compound* ***S17*****.**



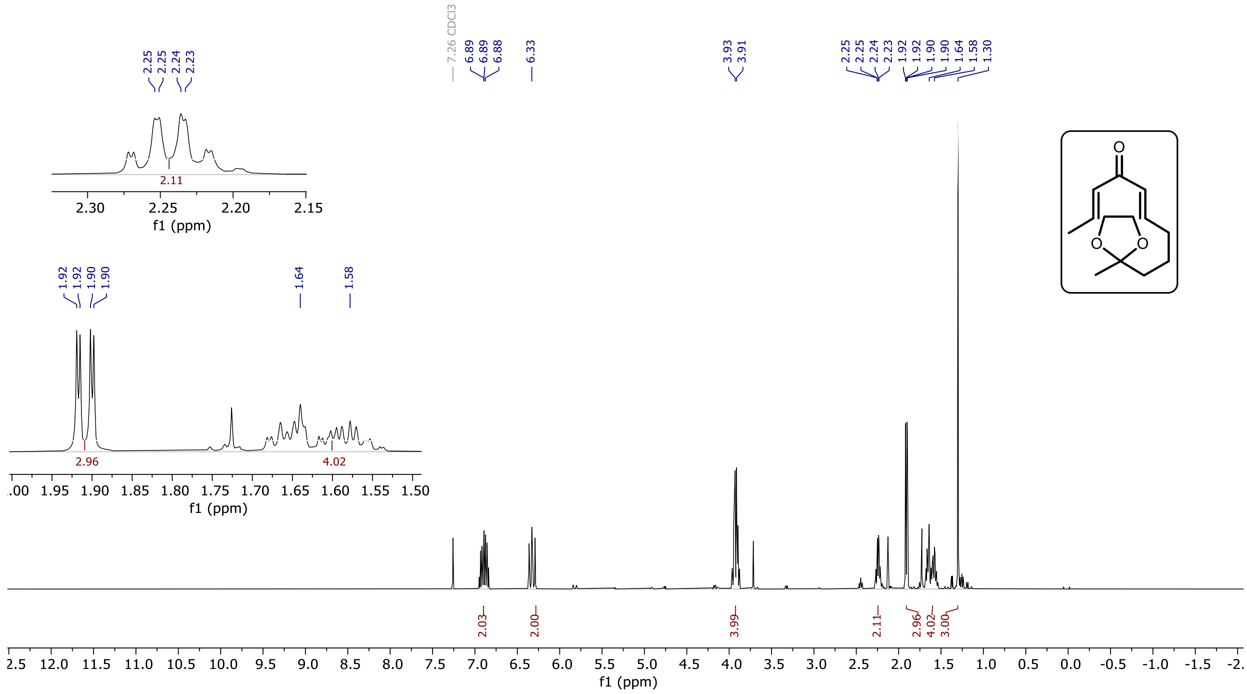
A48: ^{13}C NMR ($CDCl_3$) of compound **S17**.



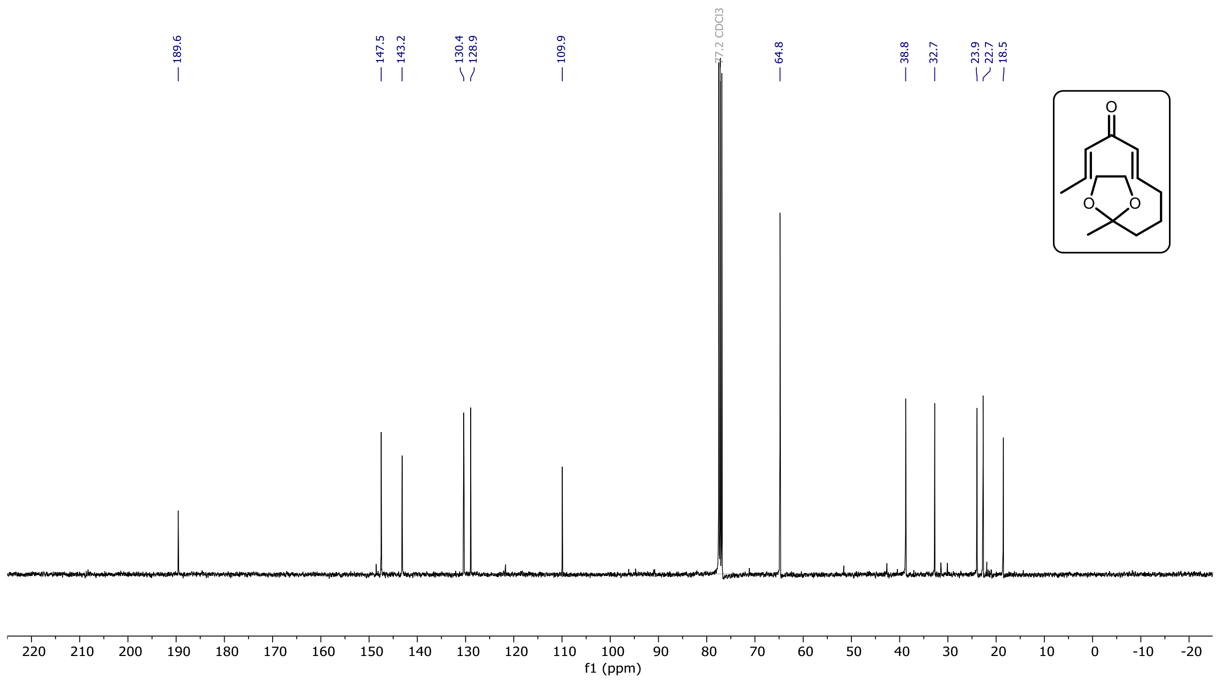
A49: *[1]H NMR (CDCl$_3$) of compound* ***S18.***



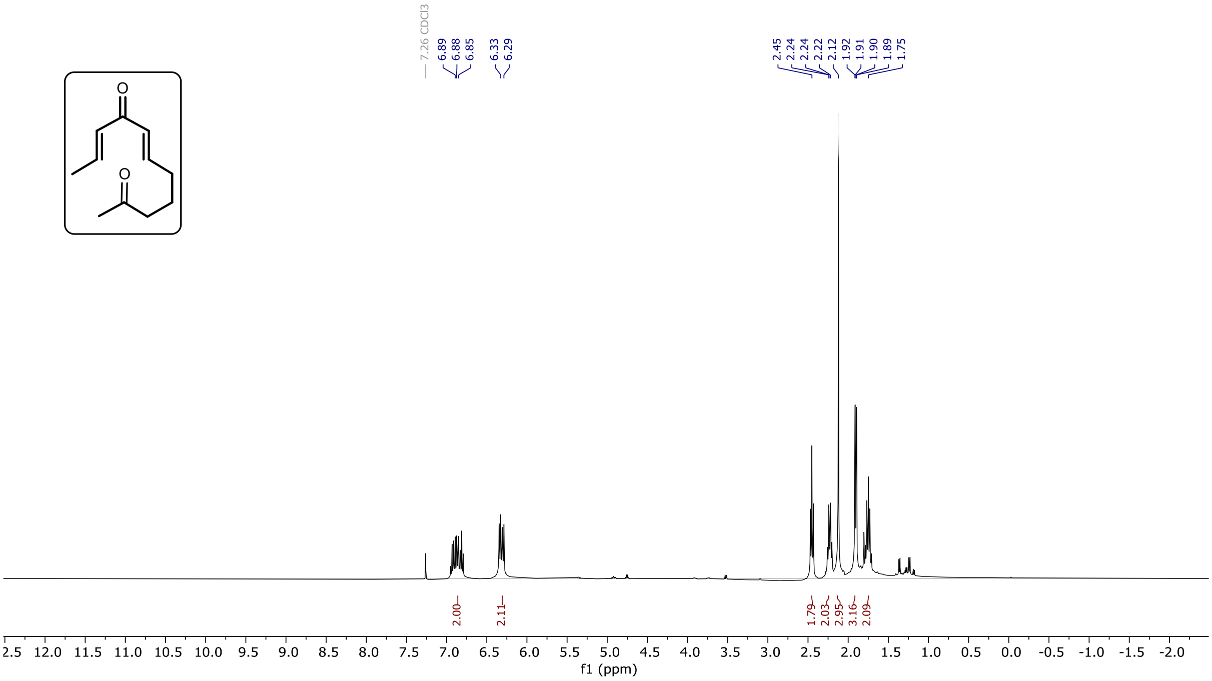
A50: ^{13}C NMR (CDCl$_3$) of compound **S18**.



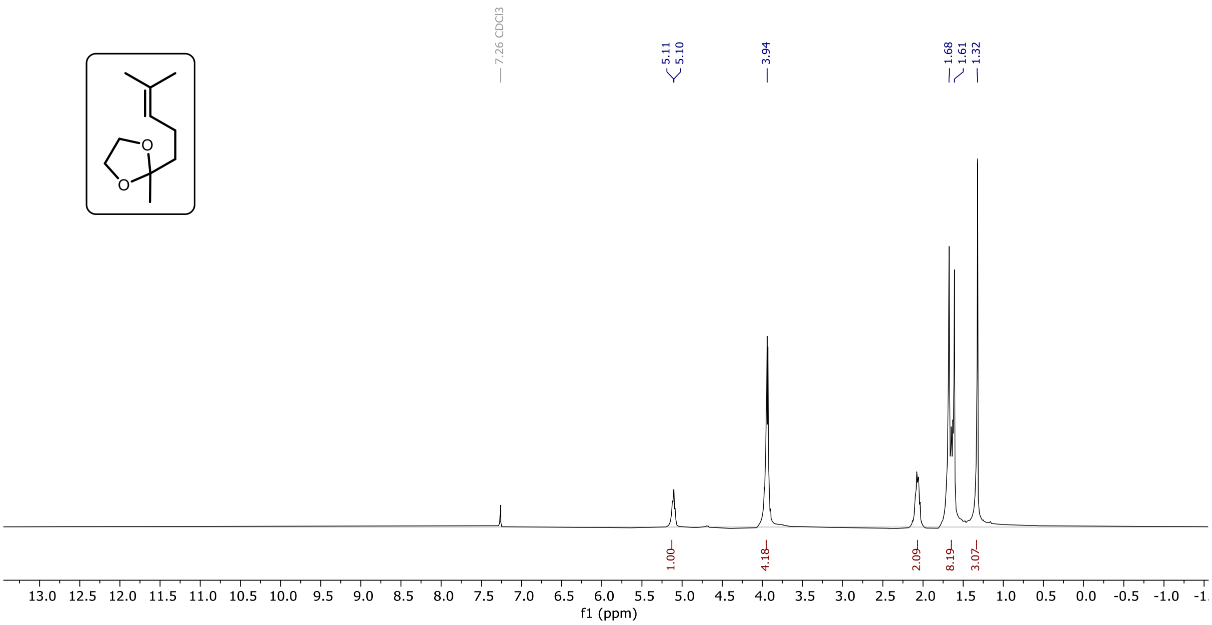
A51:** [1]H NMR ($CDCl_3$) of compound **S19.



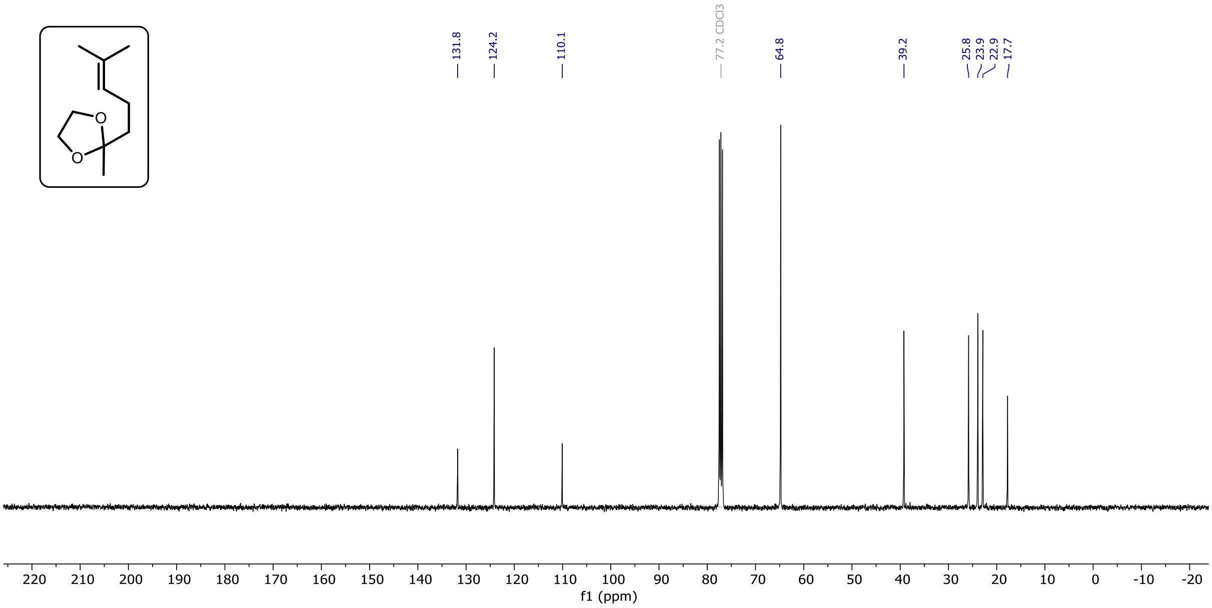
A52: ^{13}C NMR ($CDCl_3$) of compound **S19**.



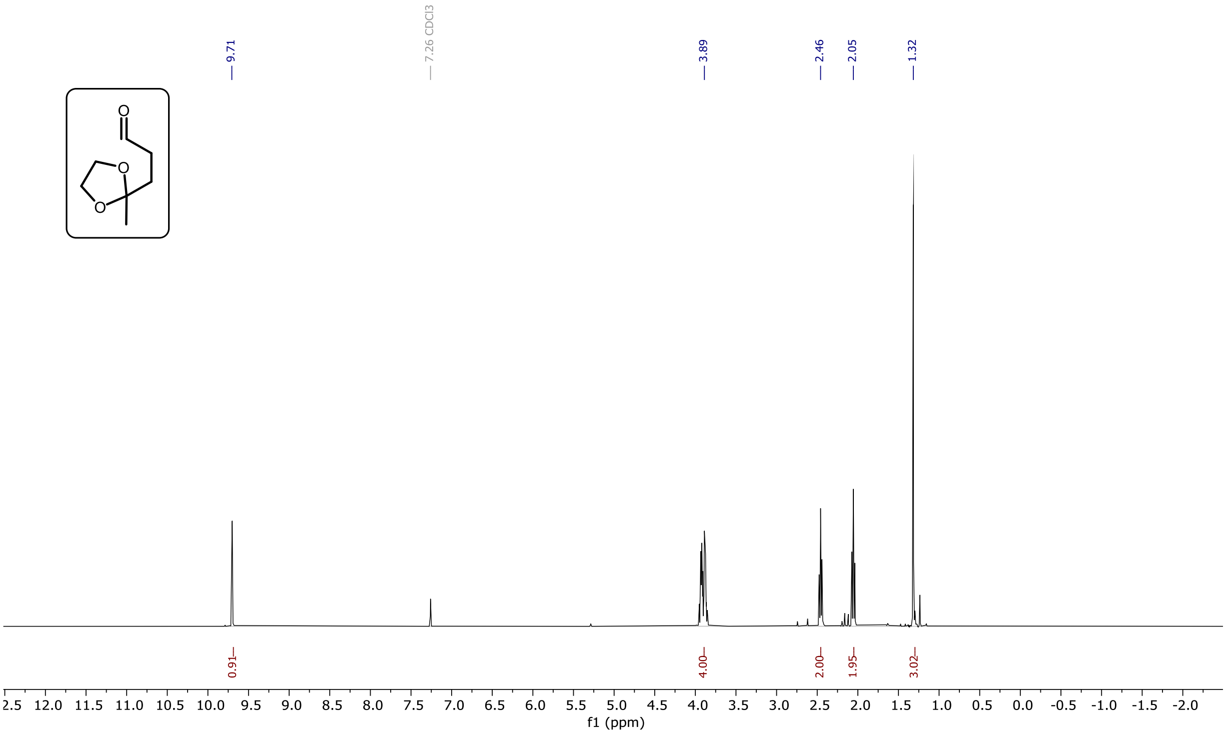
A53: *[1]H NMR ($CDCl_3$) of compound* ***1h.***



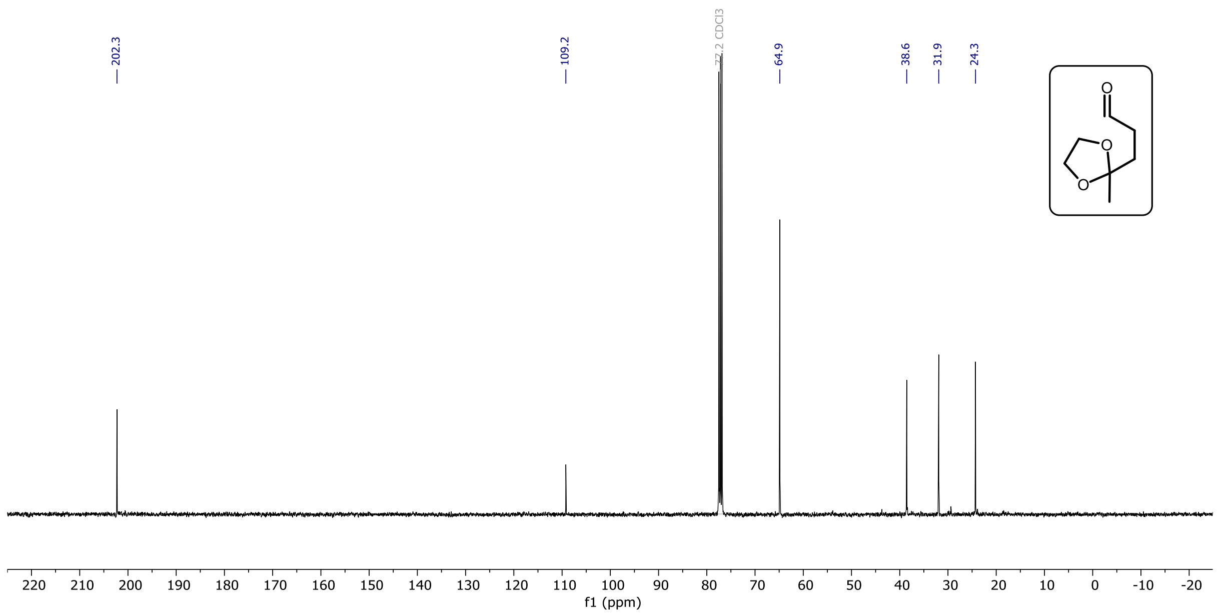
A54: *[1]H NMR ($CDCl_3$) of compound* ***S20.***



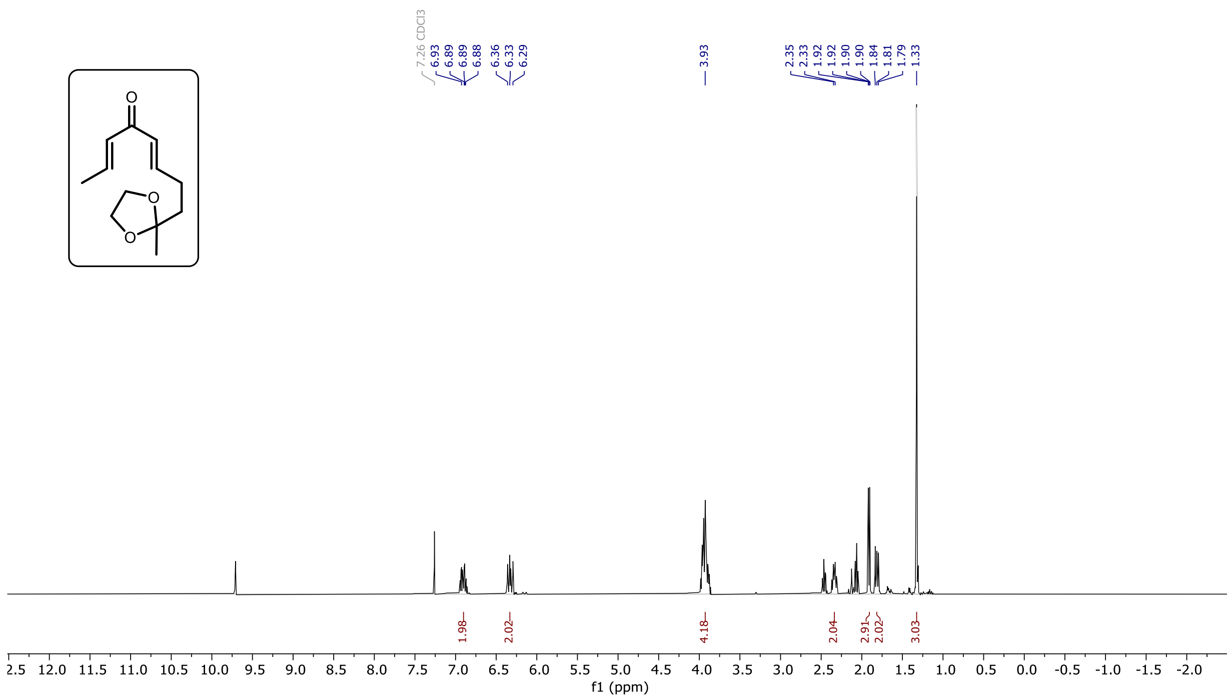
A55: ^{13}C NMR ($CDCl_3$) of compound **S20**.



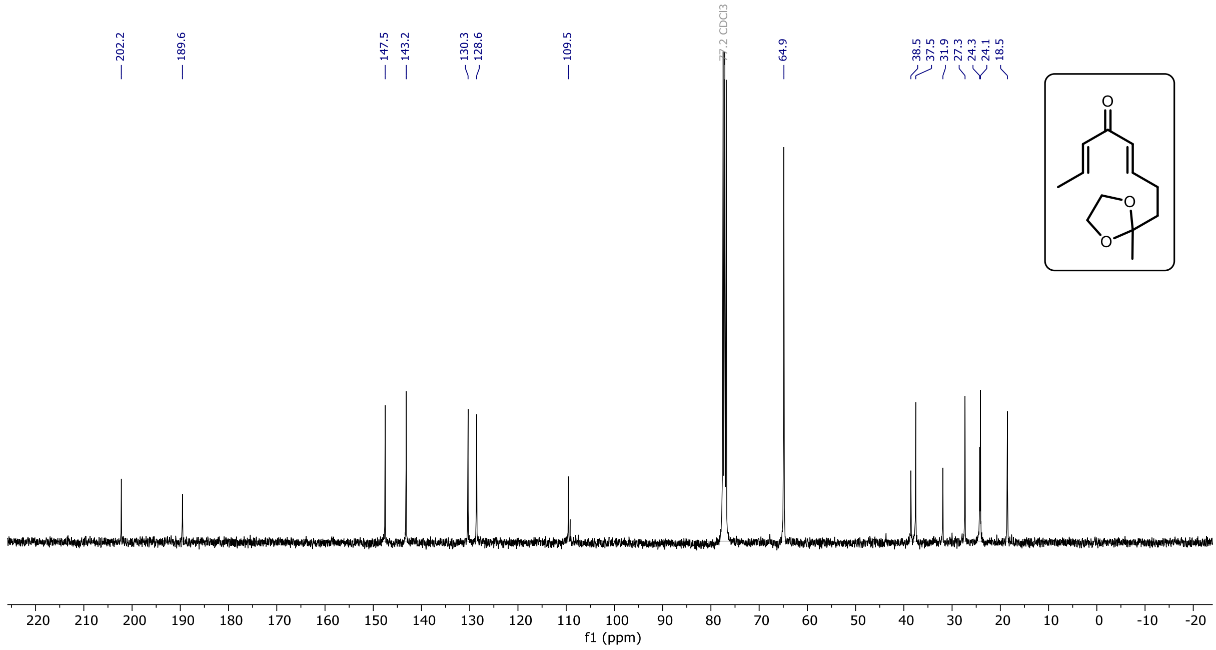
A56: *^{1}H NMR ($CDCl_3$) of compound* ***S21*****.**



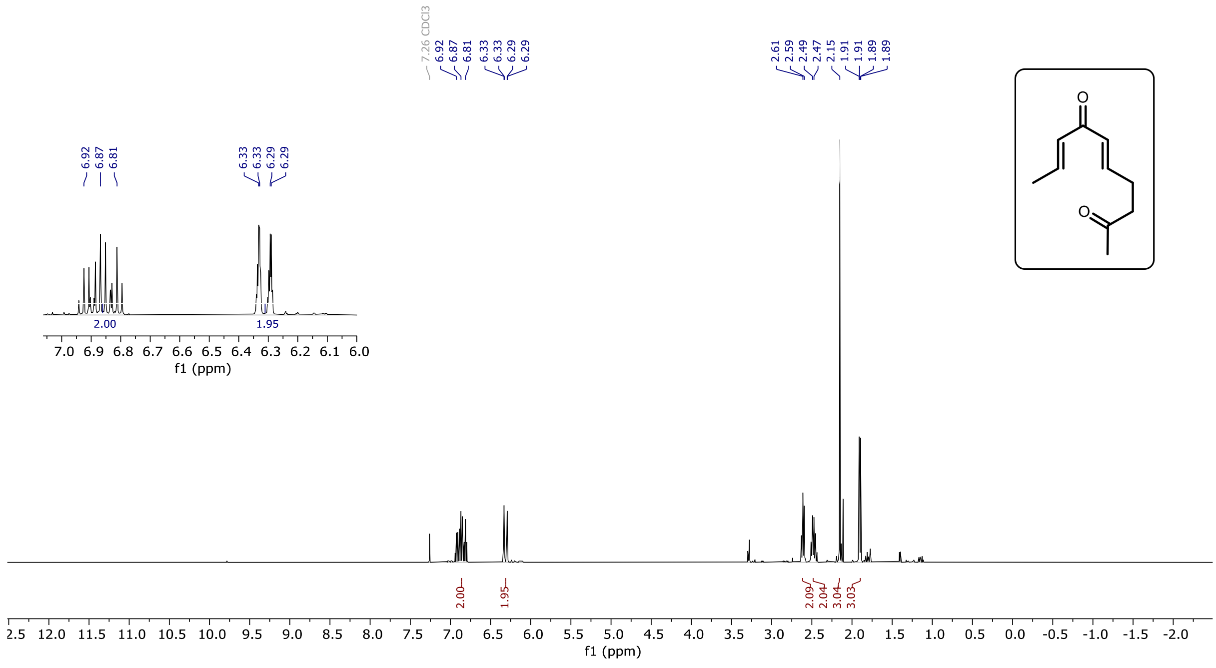
A57: ^{13}C NMR ($CDCl_3$) of compound **S21**.



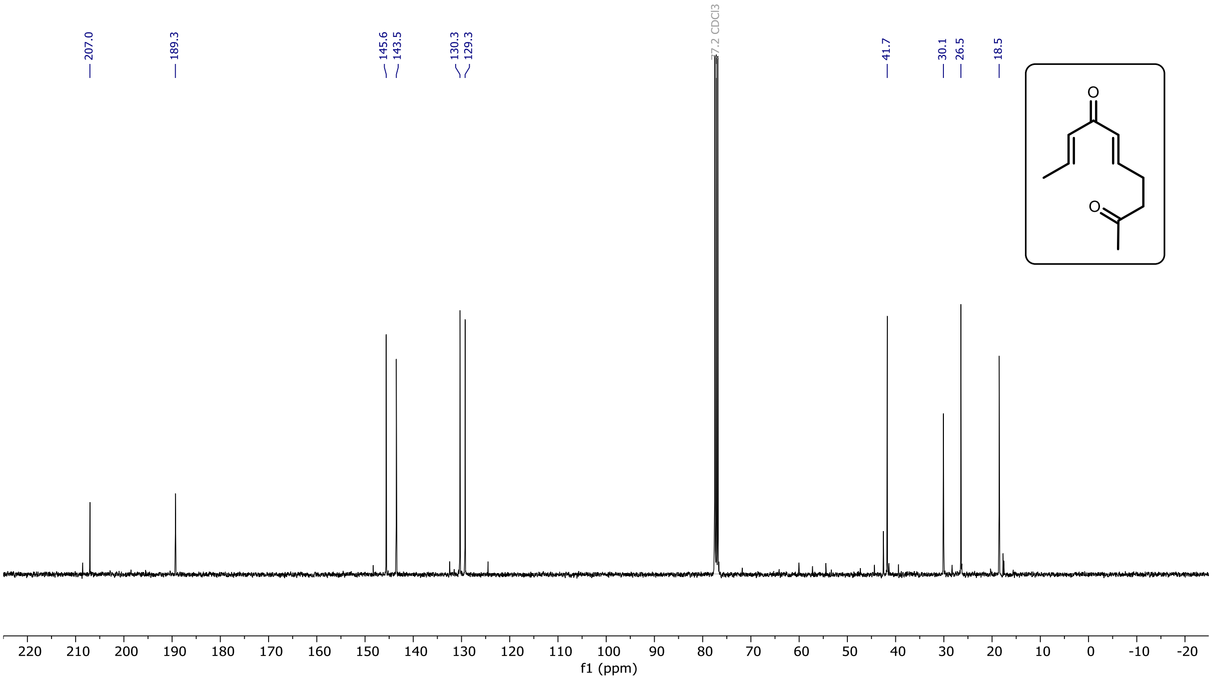
A58: *^{1}H NMR ($CDCl_3$) of compound* ***S22.***



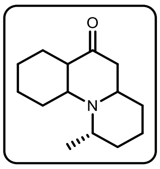
A59: ^{13}C NMR ($CDCl_3$) of compound **S22**.



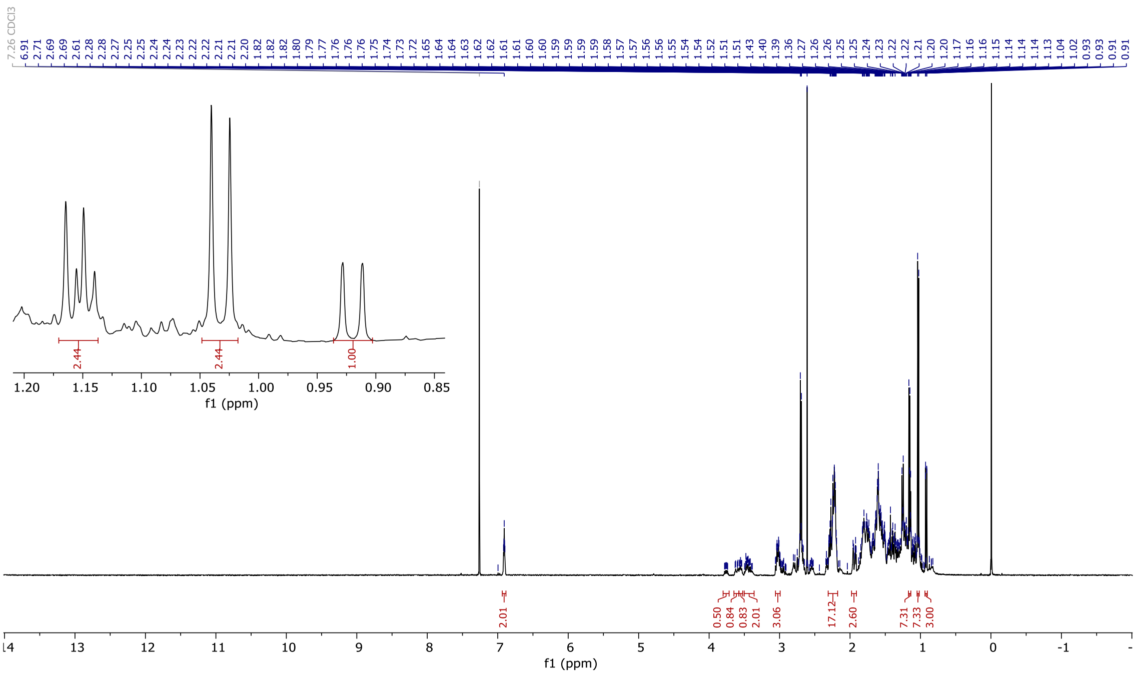
A60: *^1H NMR ($CDCl_3$) of compound* ***1i.***



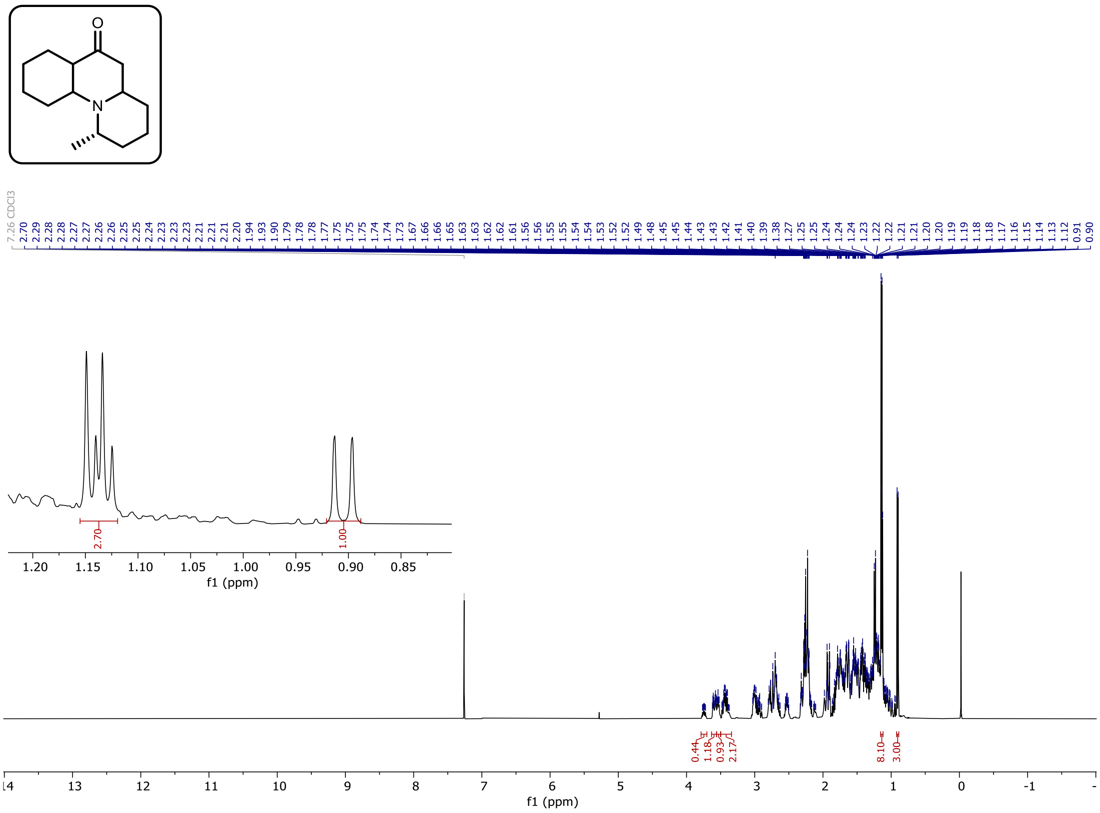
A61: ^{13}C NMR ($CDCl_3$) of compound **1i**.



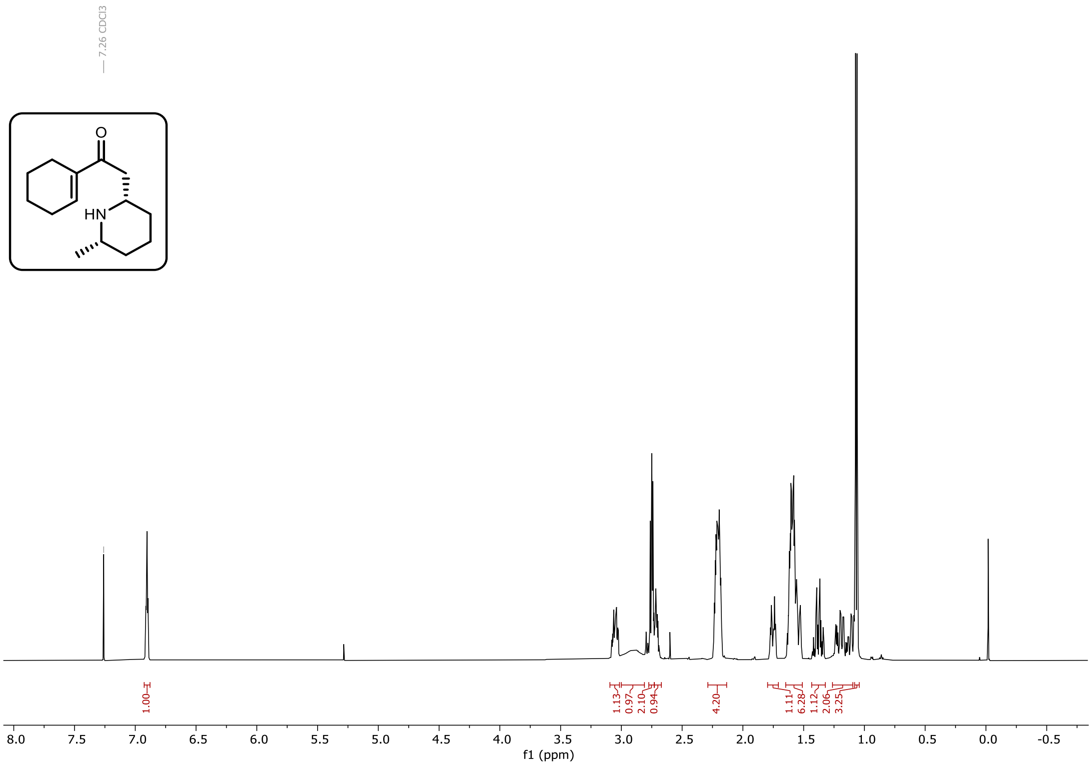
Crude reaction mixture: 4 stereoisomers



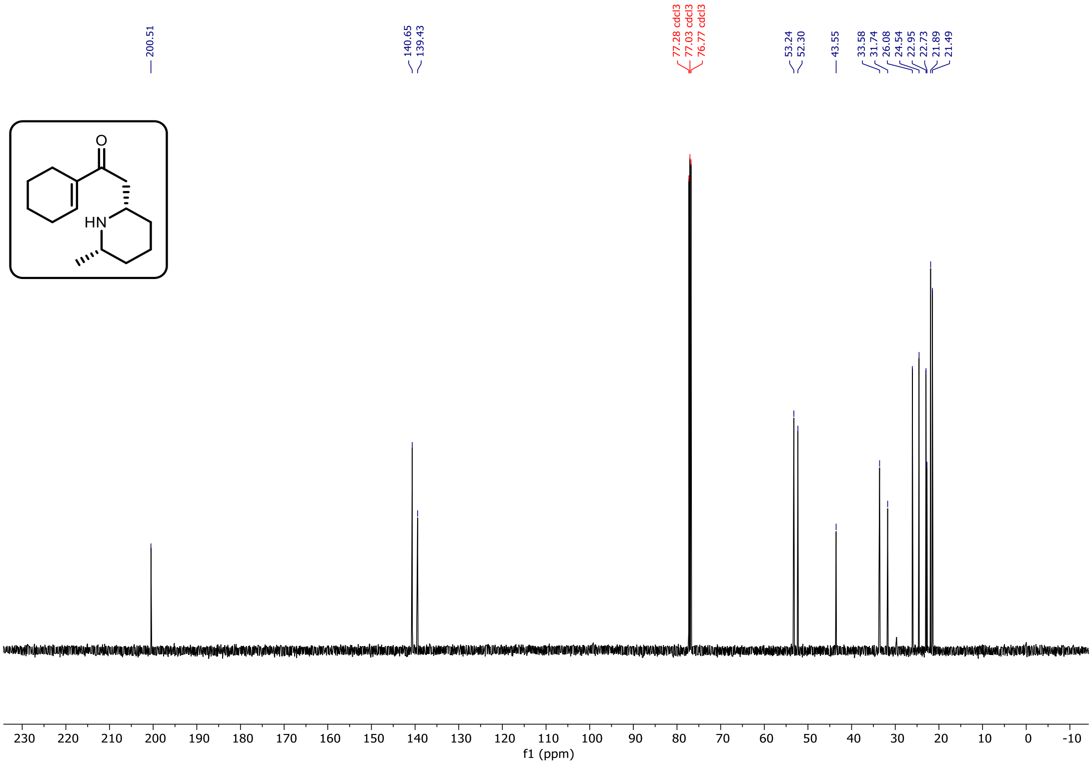
***A62:** ^{1}H NMR ($CDCl_3$) of compounds (S,S)-**3a** and (1S)-**4a**.*



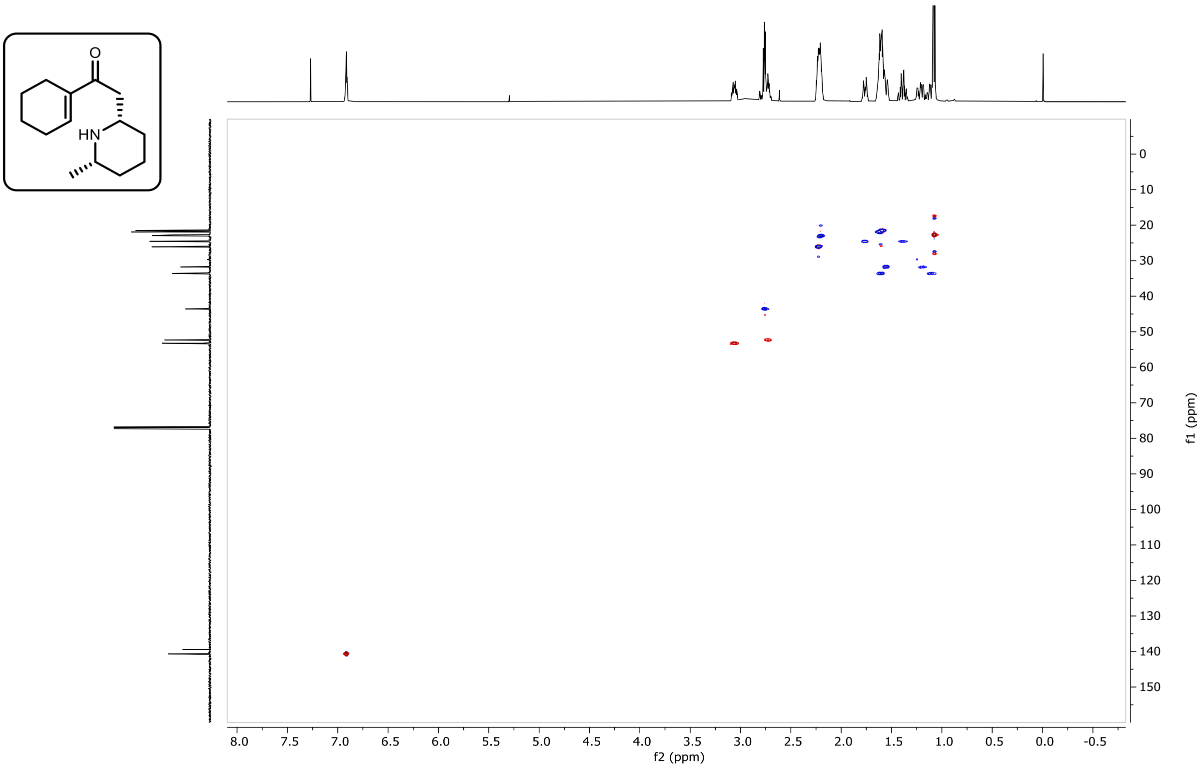
A63: *[1]H NMR ($CDCl_3$) of compounds* ***(1S)-4a*** *(single IMAMR product removed).*



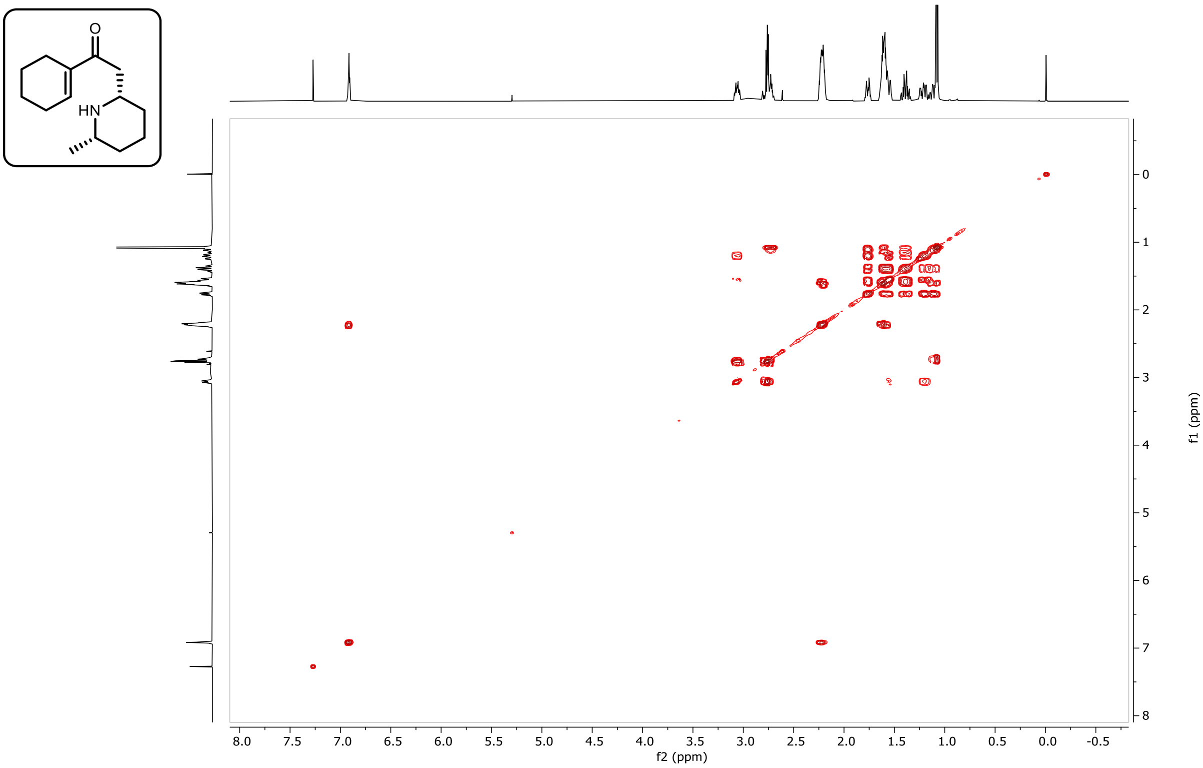
A64: *[1]H NMR ($CDCl_3$) of compound* **(*S*,*S*)-3a**.



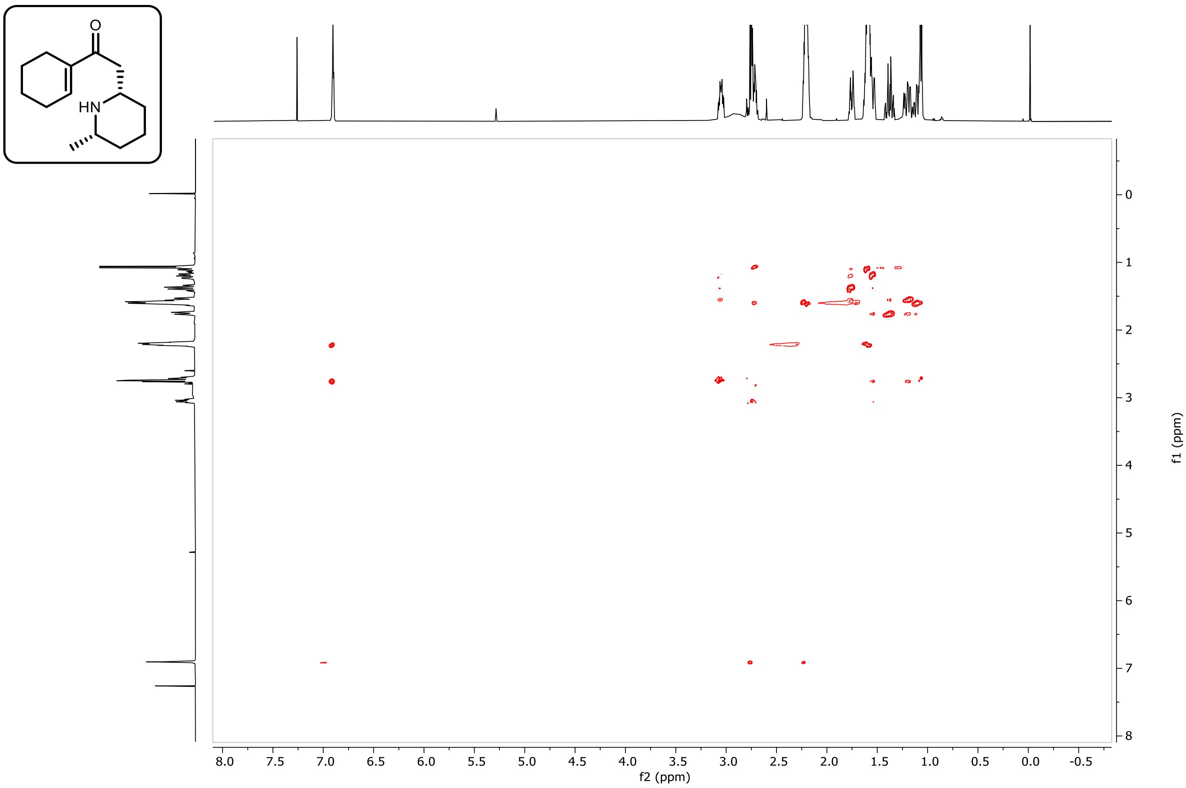
***A65:** ^{13}C NMR (CDCl$_3$) of compound* **(*S*,*S*)-3a**.



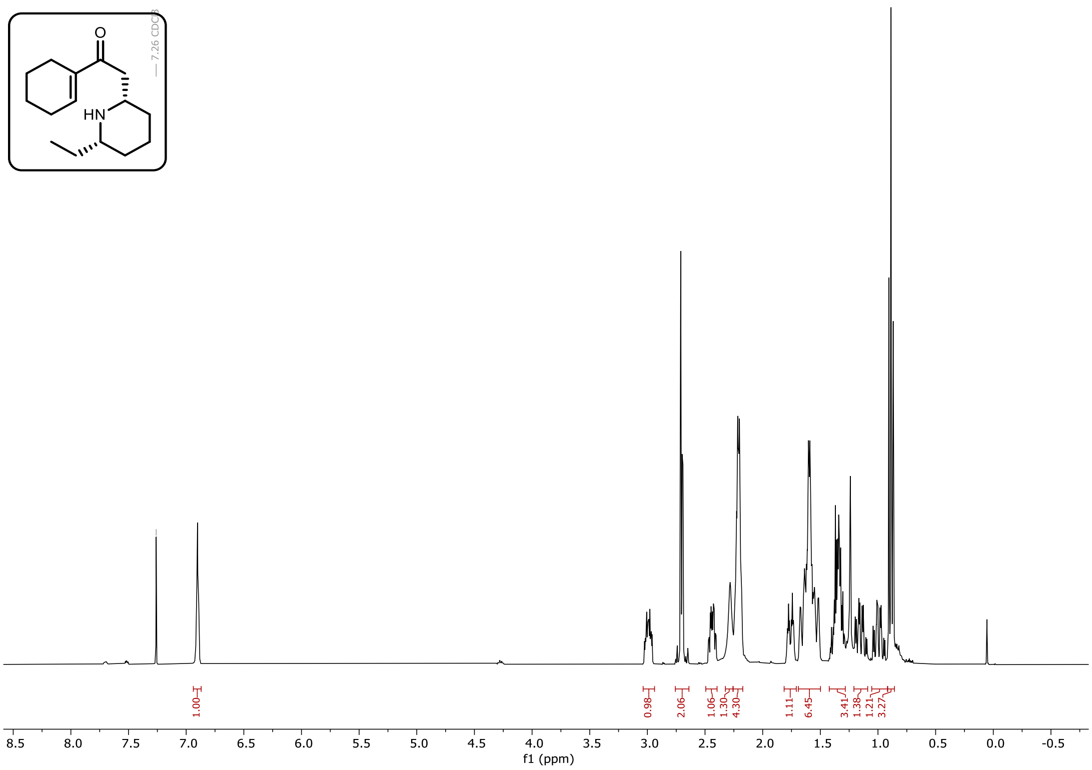
***A66:** HSQC (CDCl$_3$) of compound* **(*S*,*S*)-3a**.



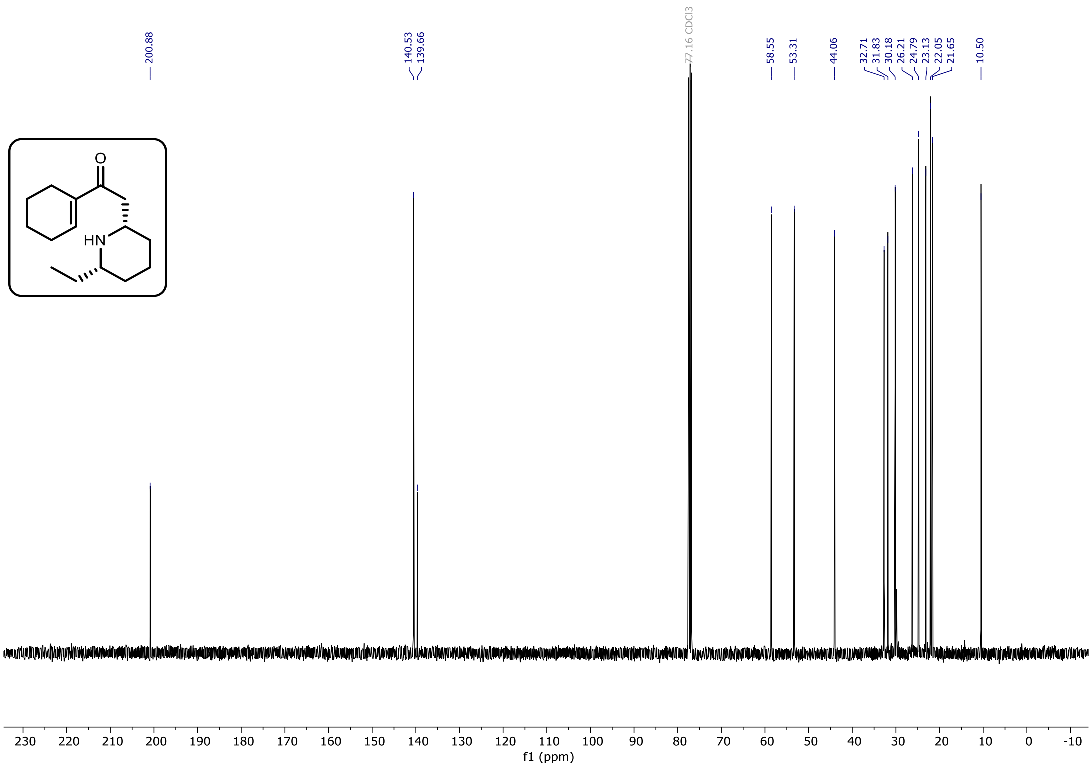
A67: *COSY (CDCl$_3$) of compound* ***(S,S)*-3a**.



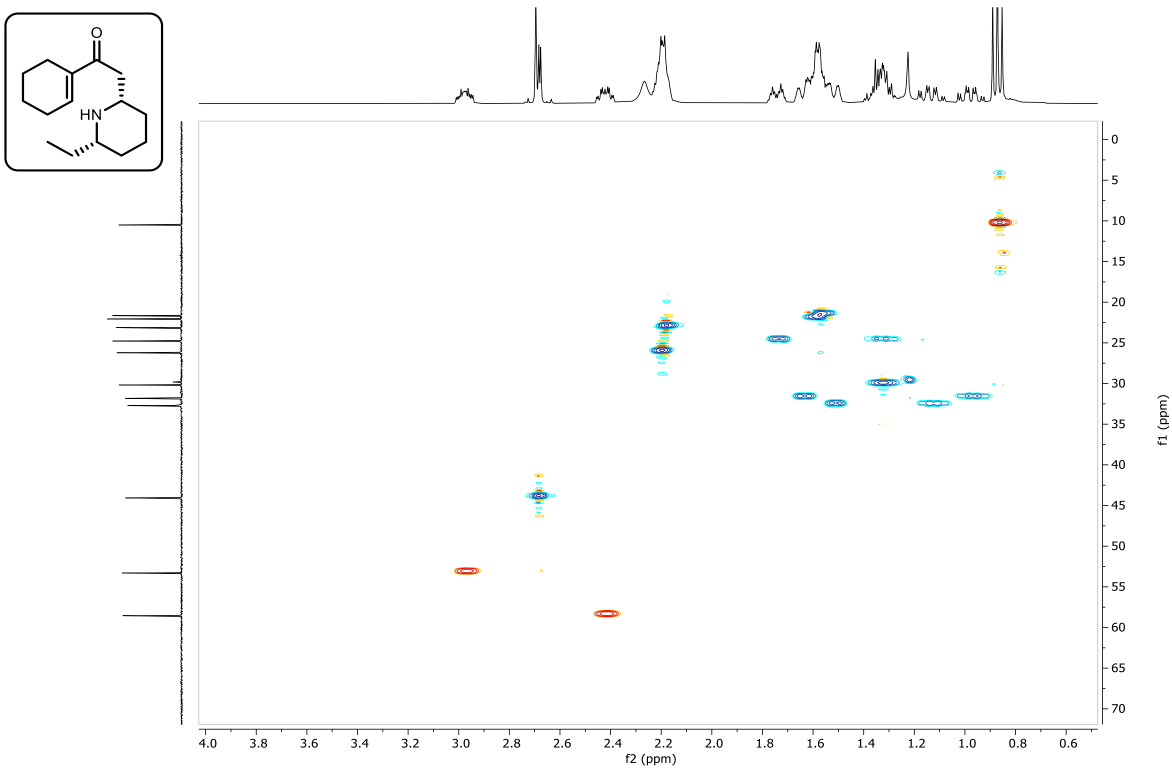
A68: *NOESY (CDCl$_3$) of compound* ***(S,S)*-3a**.



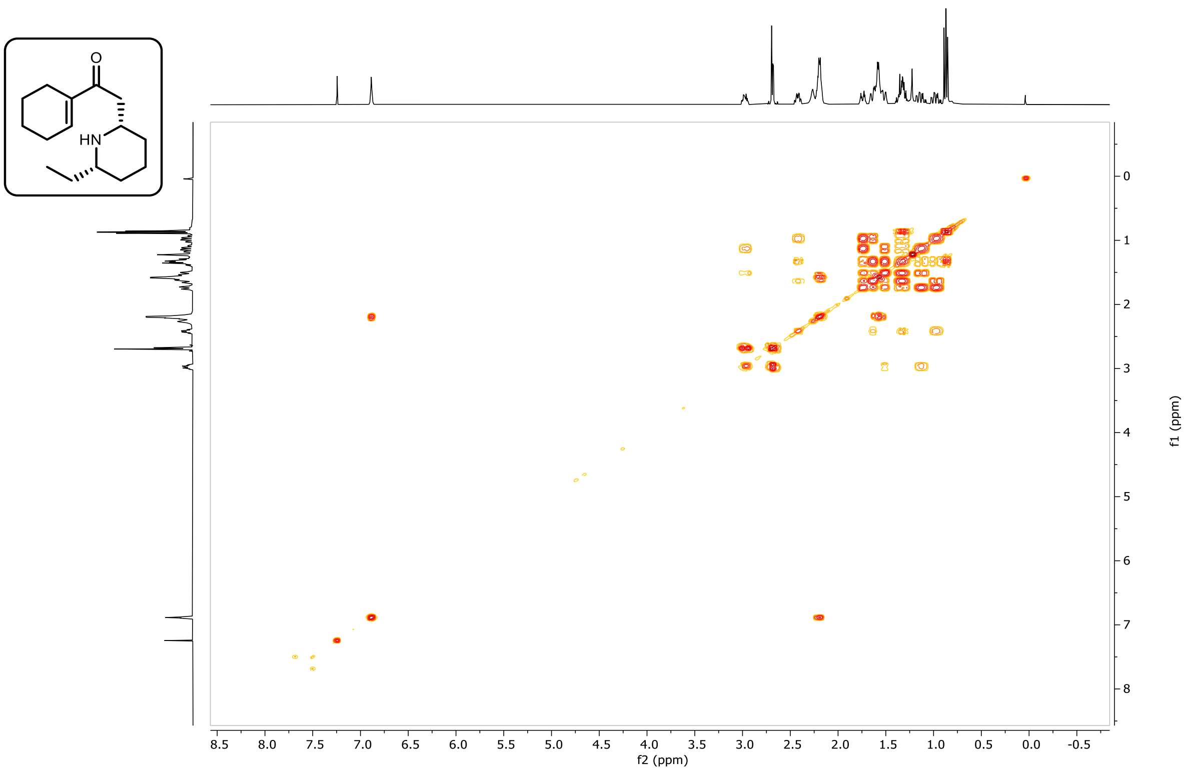
***A69:** ^{1}H NMR (CDCl$_3$) of compound* **(S,S)-3b**.



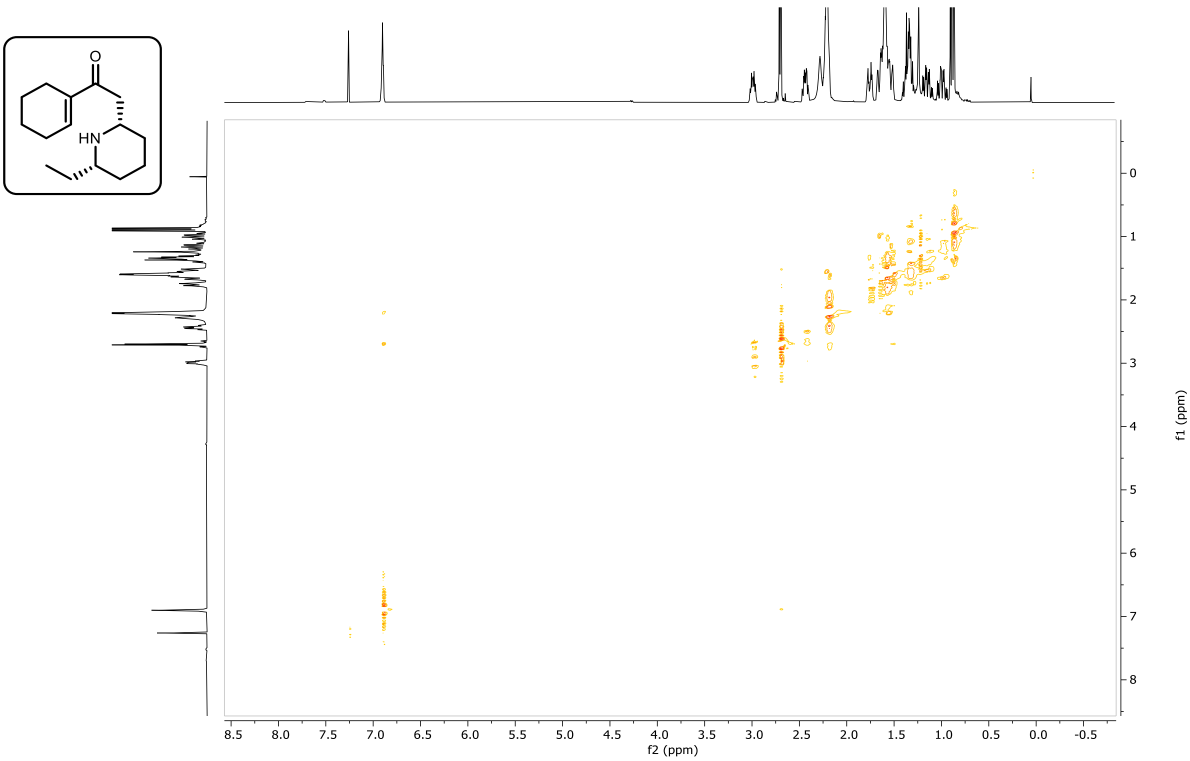
***A70:** ^{13}C NMR (CDCl$_3$) of compound* **(S,S)-3b**.



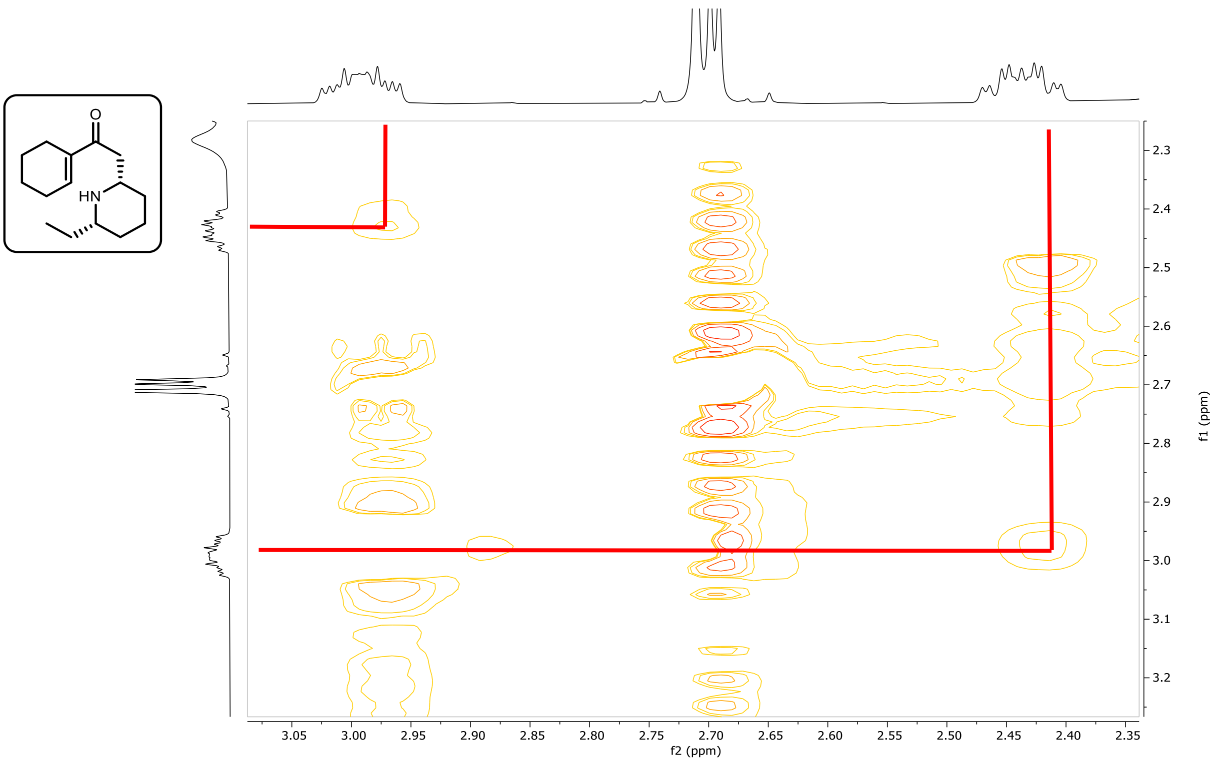
***A71:** H91SQC (CDCl$_3$) of compound* **(S,S)-3b**.



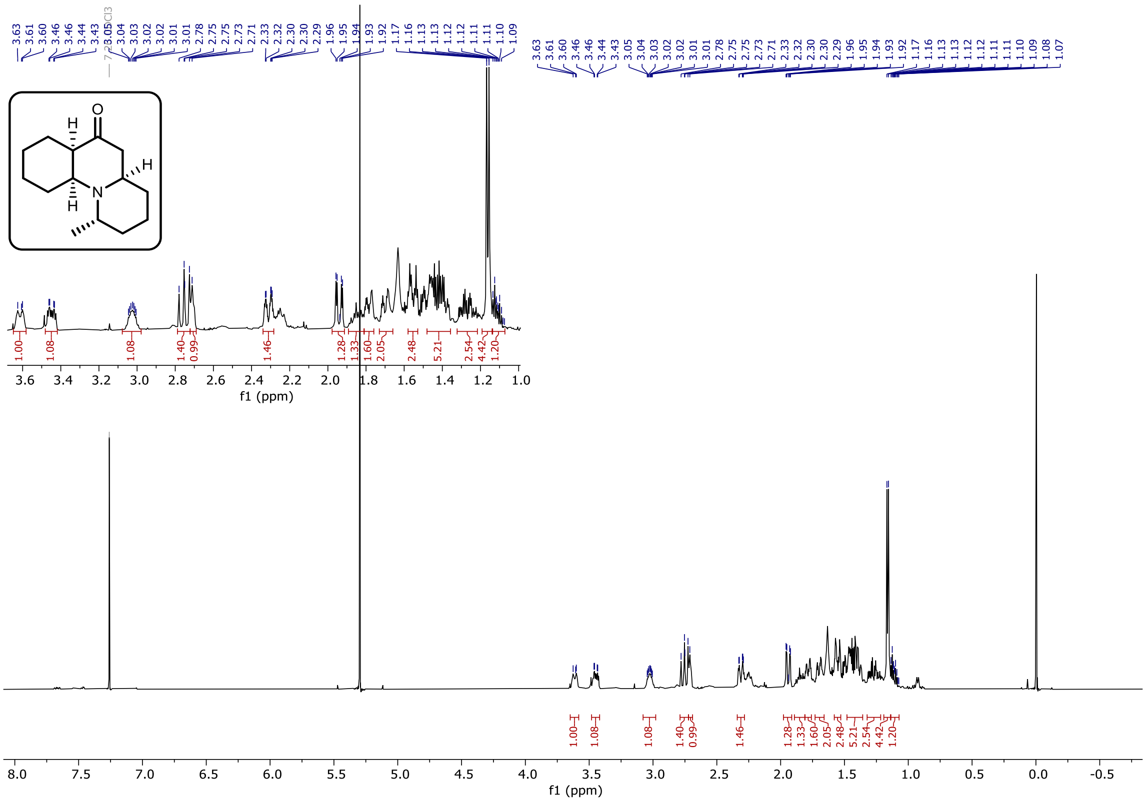
***A72:** COSY (CDCl$_3$) of compound* **(S,S)-3b**.



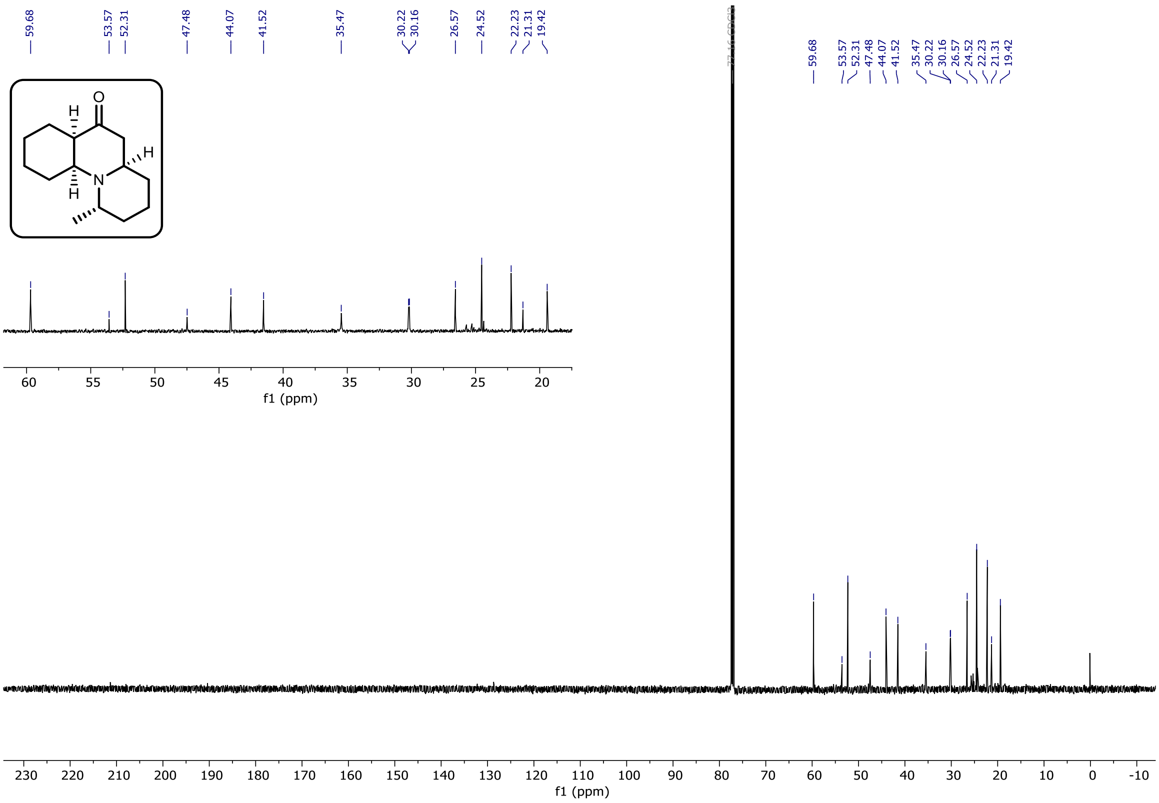
***A73:** NOESY (CDCl$_3$) of compound* **(S,S)-3b**.



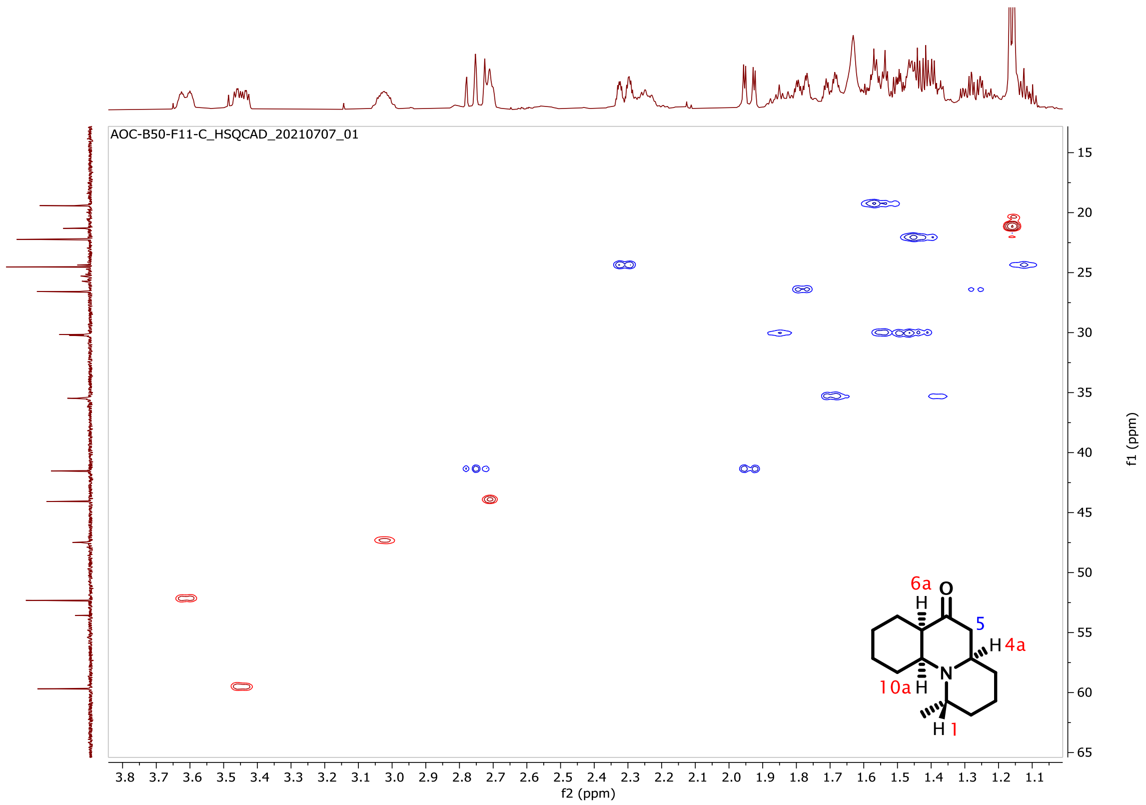
***A74:** NOESY zoomed (CDCl$_3$) of compound* **(S,S)-3b**.



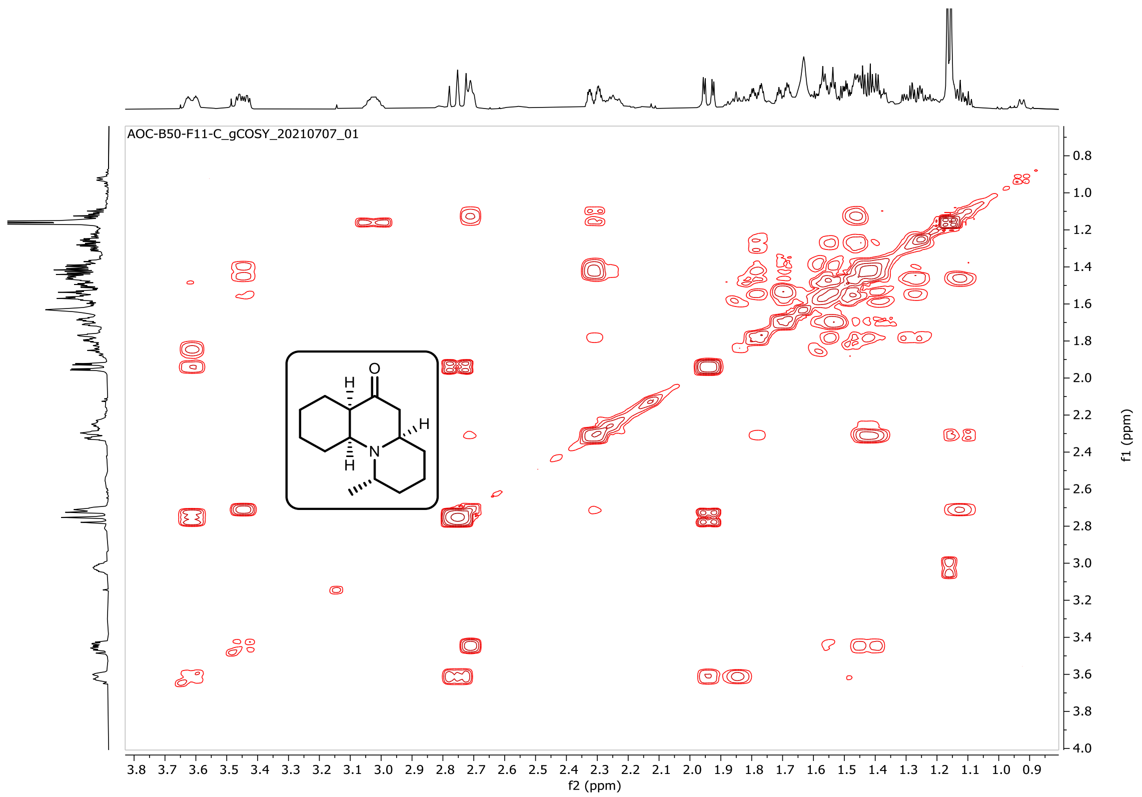
A75: *^{1}H NMR ($CDCl_3$) of compound 1S,4aR,6aR,10aS-**4a**.*



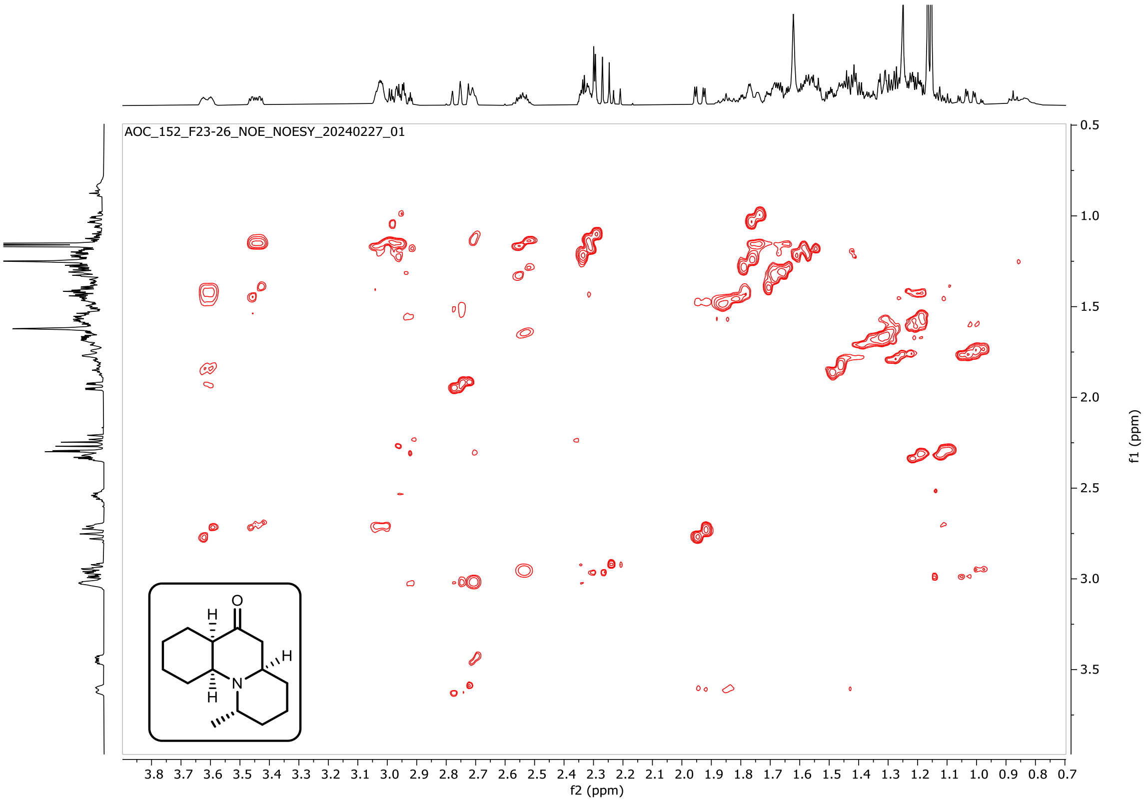
A76: *^{13}C NMR ($CDCl_3$) of compound 1S,4aR,6aR,10aS-**4a**.*



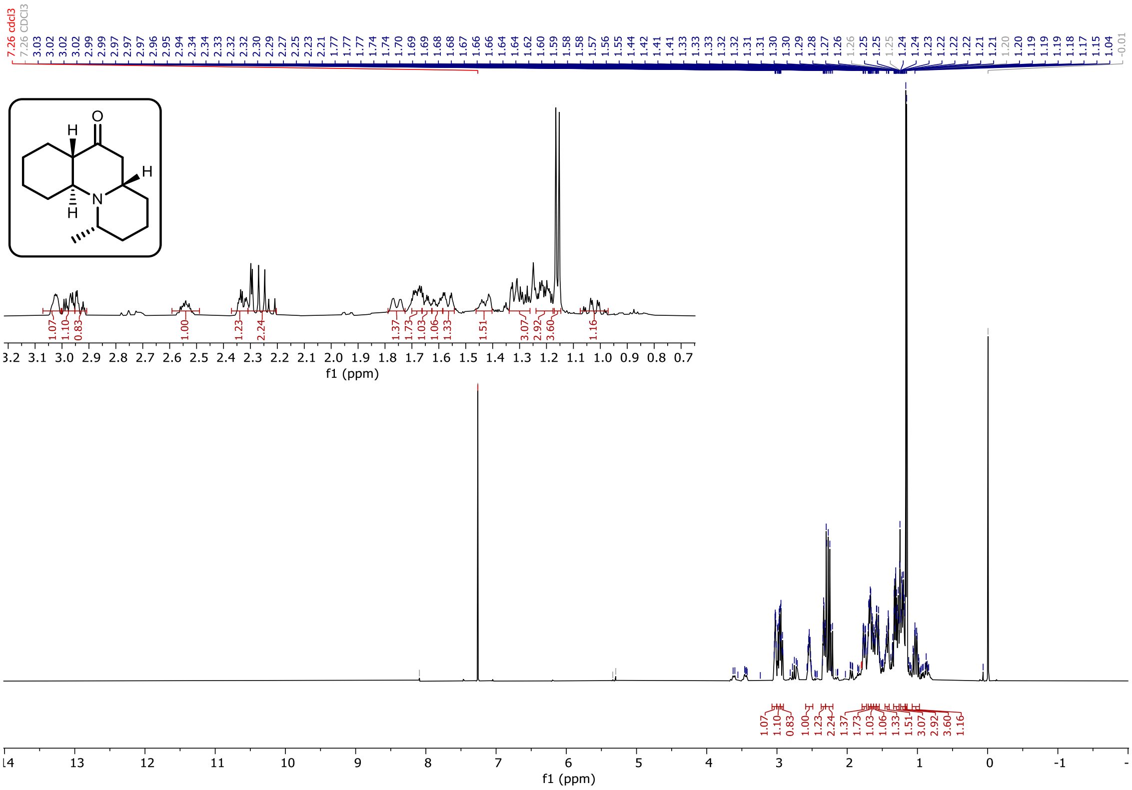
***A77:** HSQC ($CDCl_3$) of compound 1S,4aR,6aR,10aS-**4a**.*



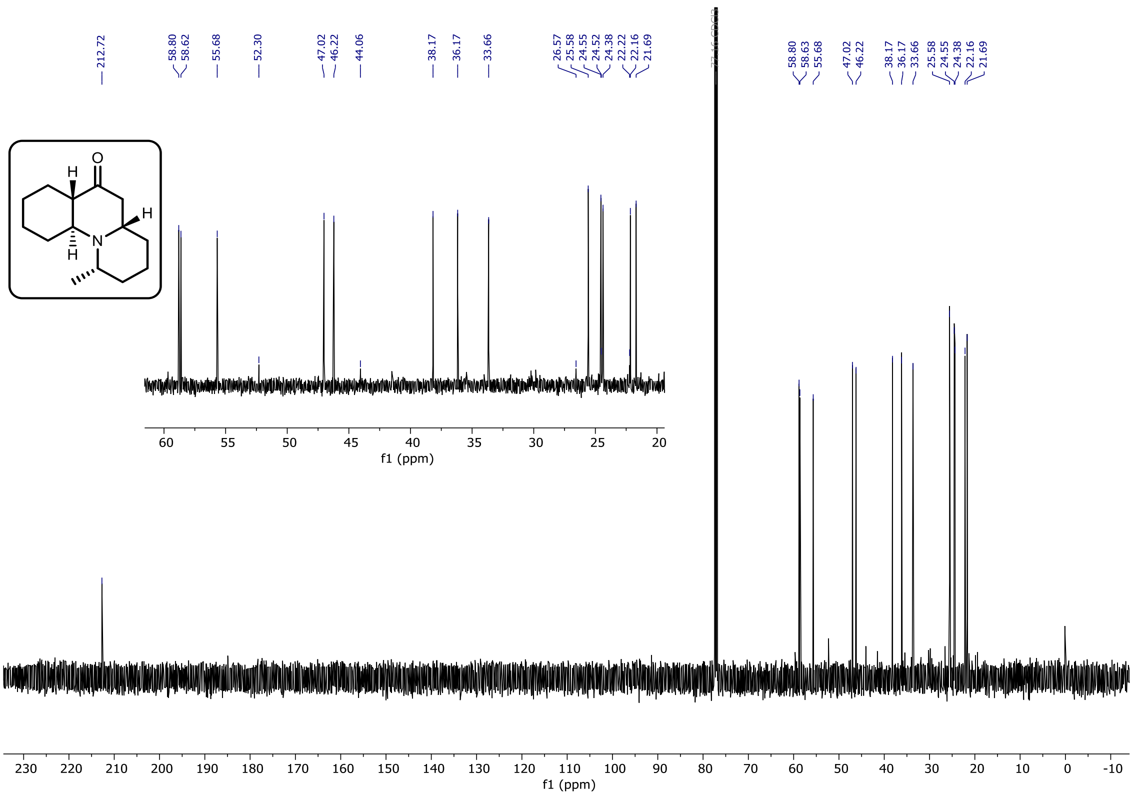
***A78:** COSY NMR ($CDCl_3$) of compound 1S,4aR,6aR,10aS-**4a**.*



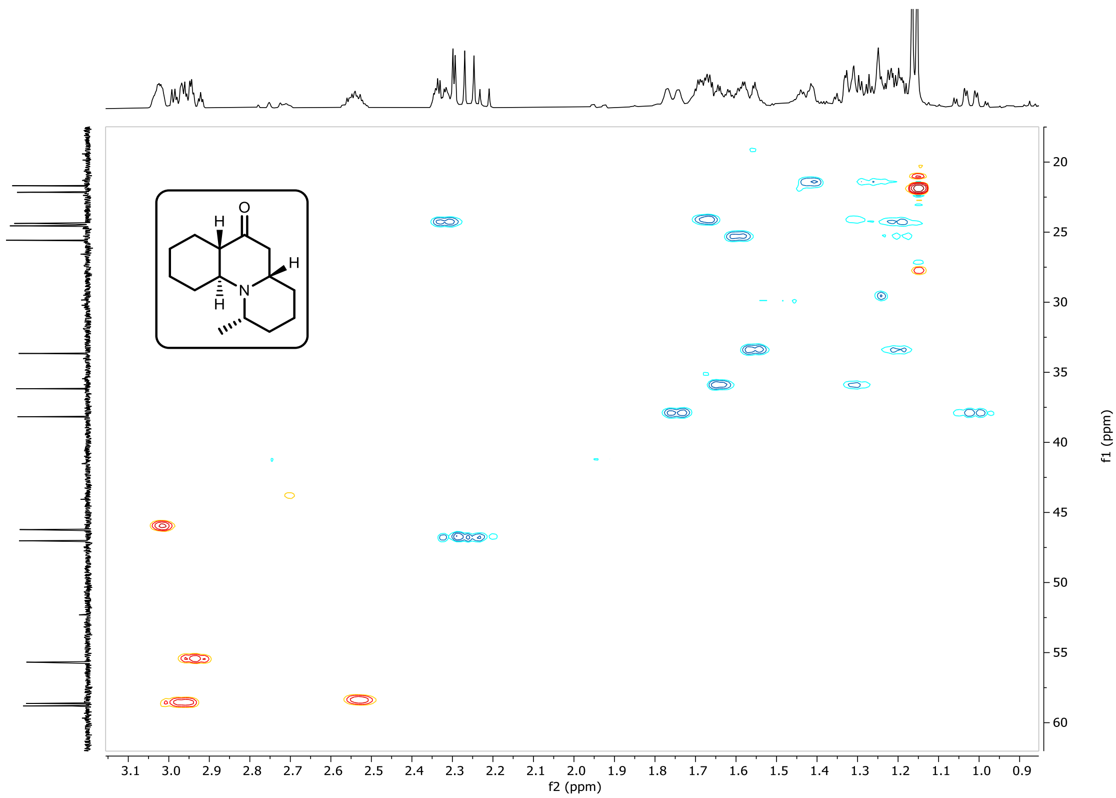
***A79:** NOESY ($CDCl_3$) of compound 1S,4aR,6aR,10aS-**4a**.*



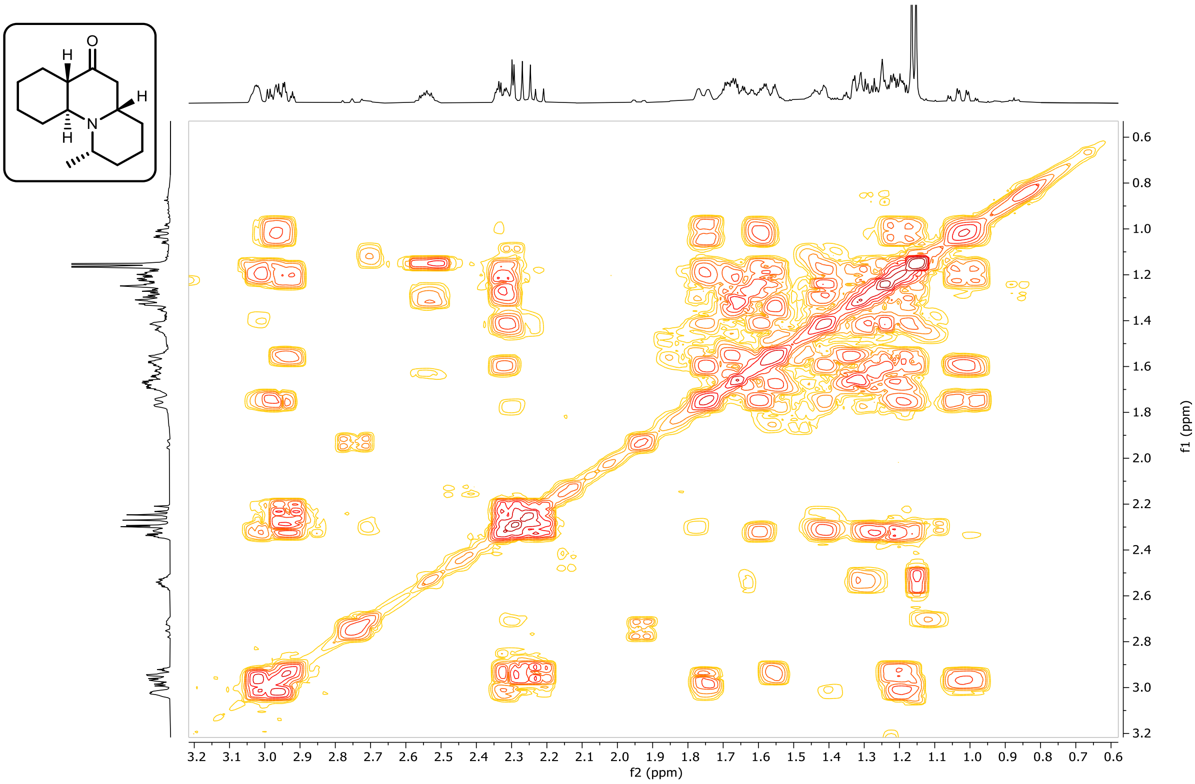
***A80:** ^1H NMR ($CDCl_3$) of compound 1S,4aS,6aS,10aS -**4a**.*



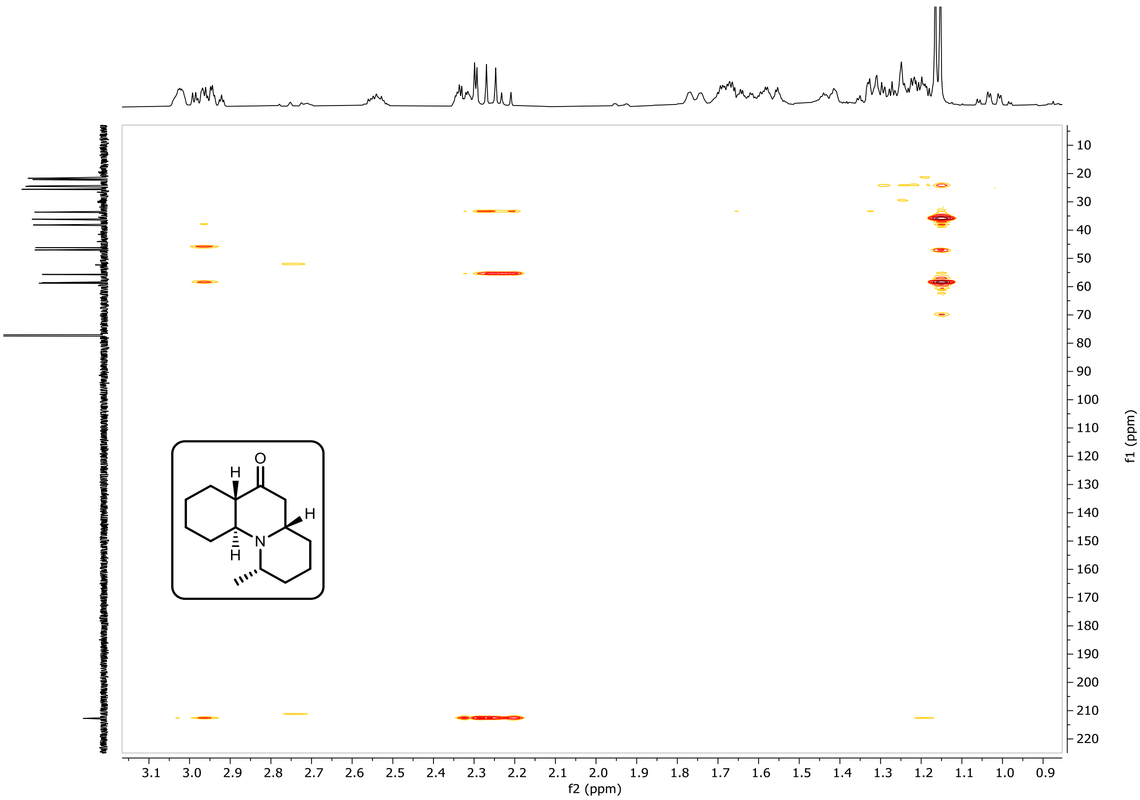
A81: *^{13}C NMR (CDCl$_3$) of compound 1S,4aS,6aS,10aS -**4a**.*



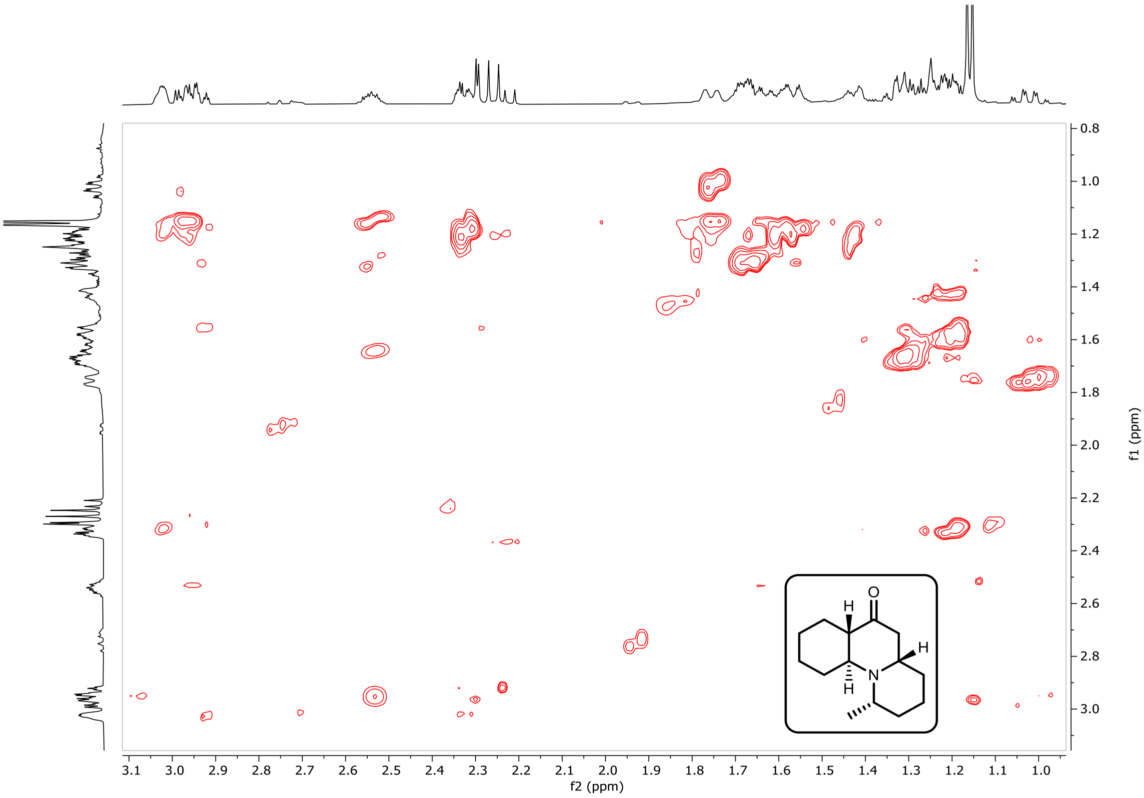
A82: *HSQC (CDCl$_3$) of compound 1S,4aS,6aS,10aS -**4a**.*



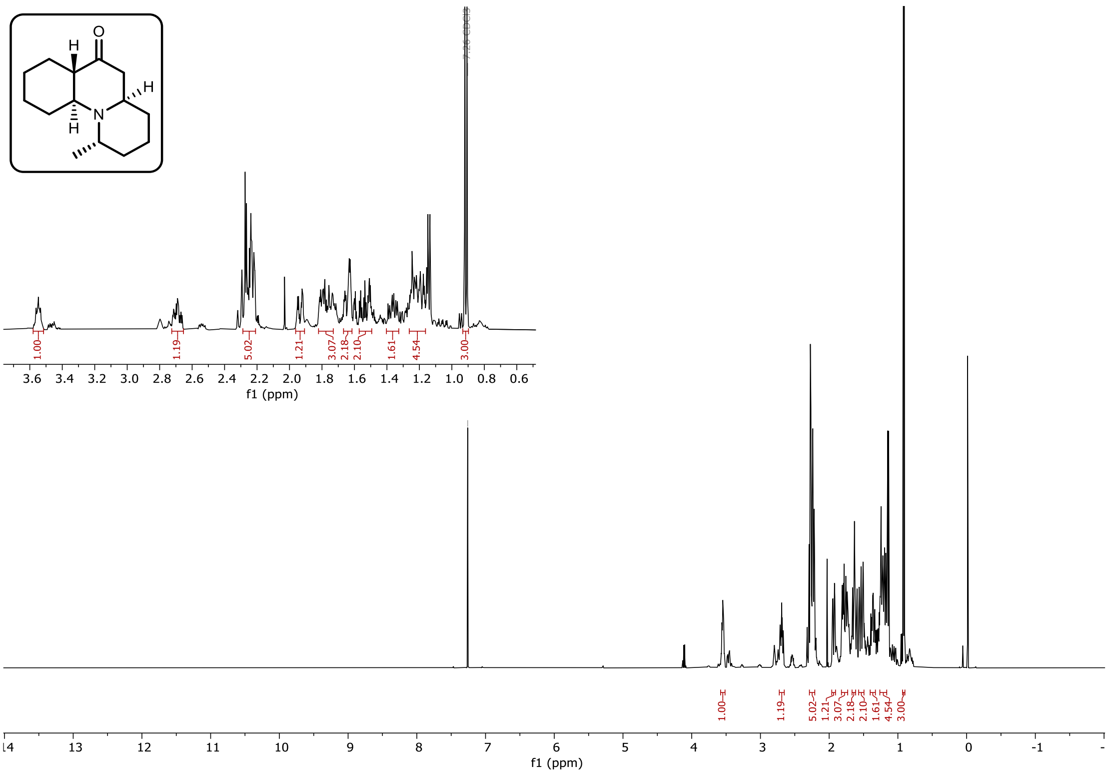
***A83:** COSY NMR (CDCl$_3$) of compound 1S,4aS,6aS,10aS -**4a**.*



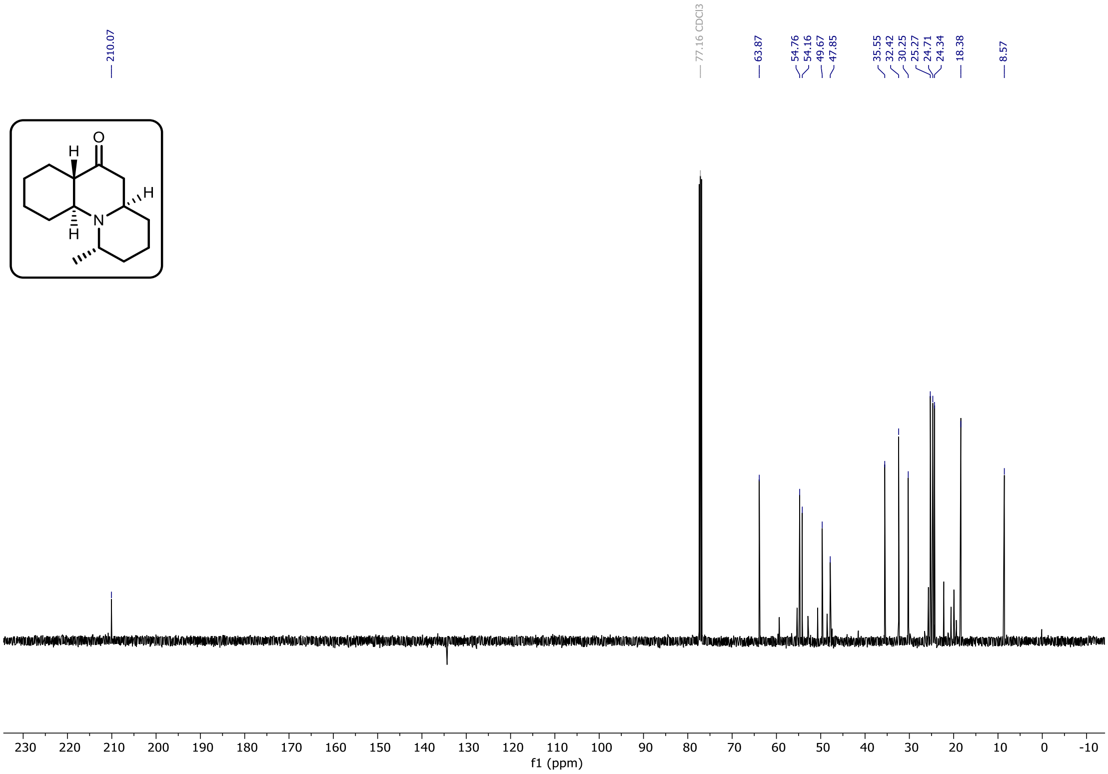
***A84:** HMBC (CDCl$_3$) of compound 1S,4aS,6aS,10aS -**4a**.*



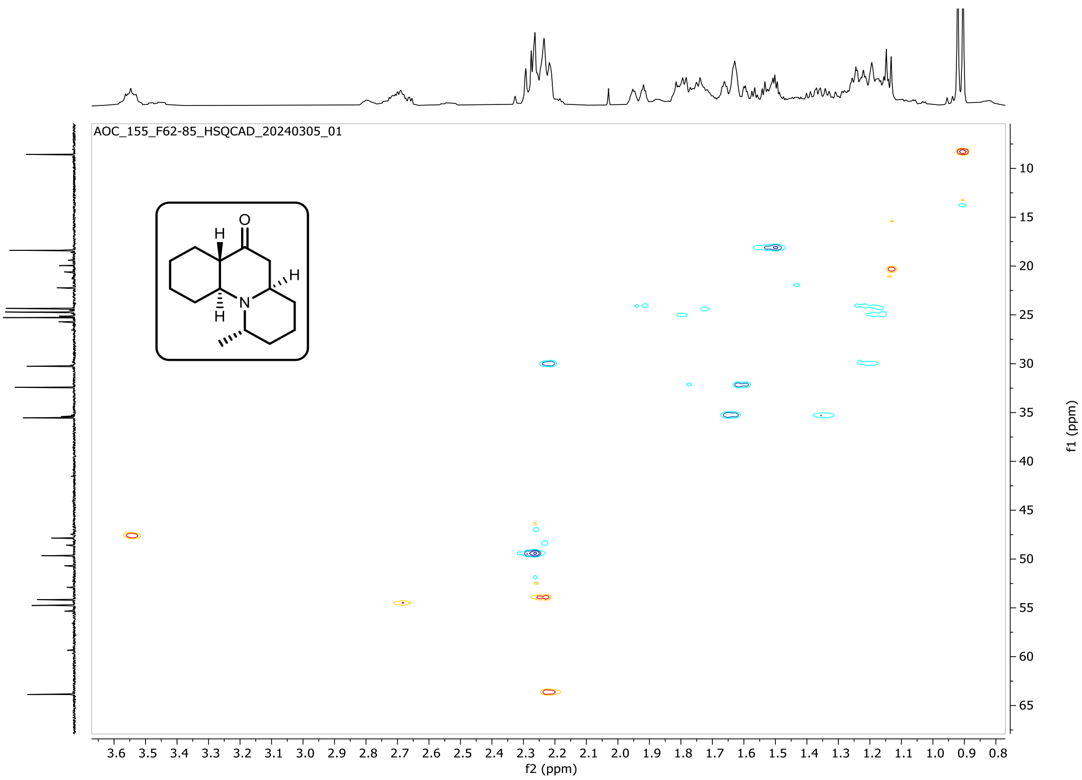
A85: *NOESY ($CDCl_3$) of compound 1S,4aS,6aS,10aS -**4a**.*



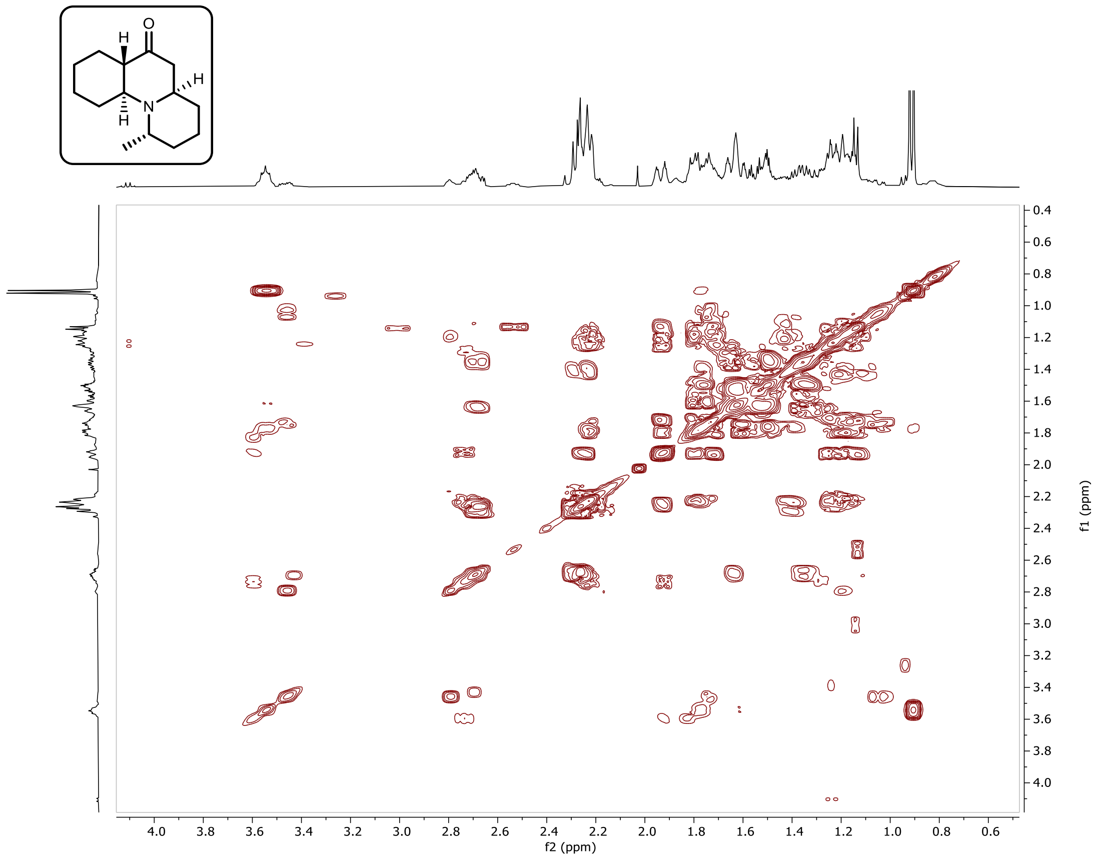
A86: *[1]H NMR ($CDCl_3$) of compound 1S,4aR,6aS,10aS-**4a**.*



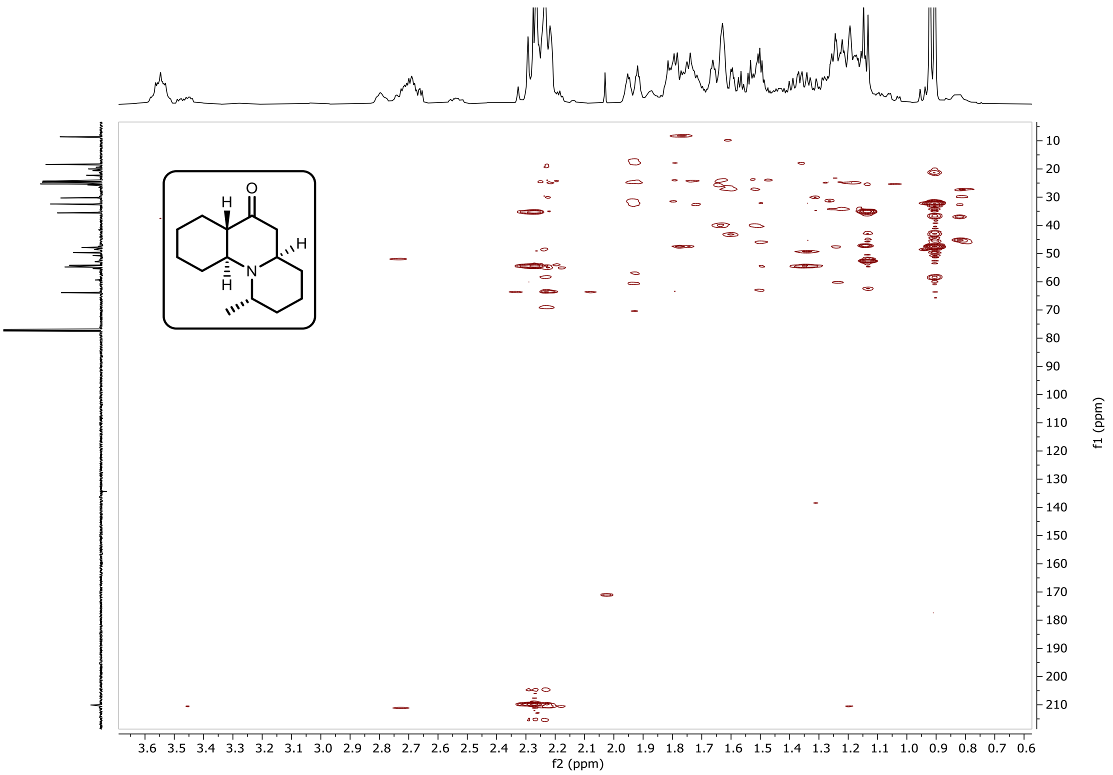
A87: *^{13}C NMR ($CDCl_3$) of compound 1S,4aR,6aS,10aS-**4a**.*



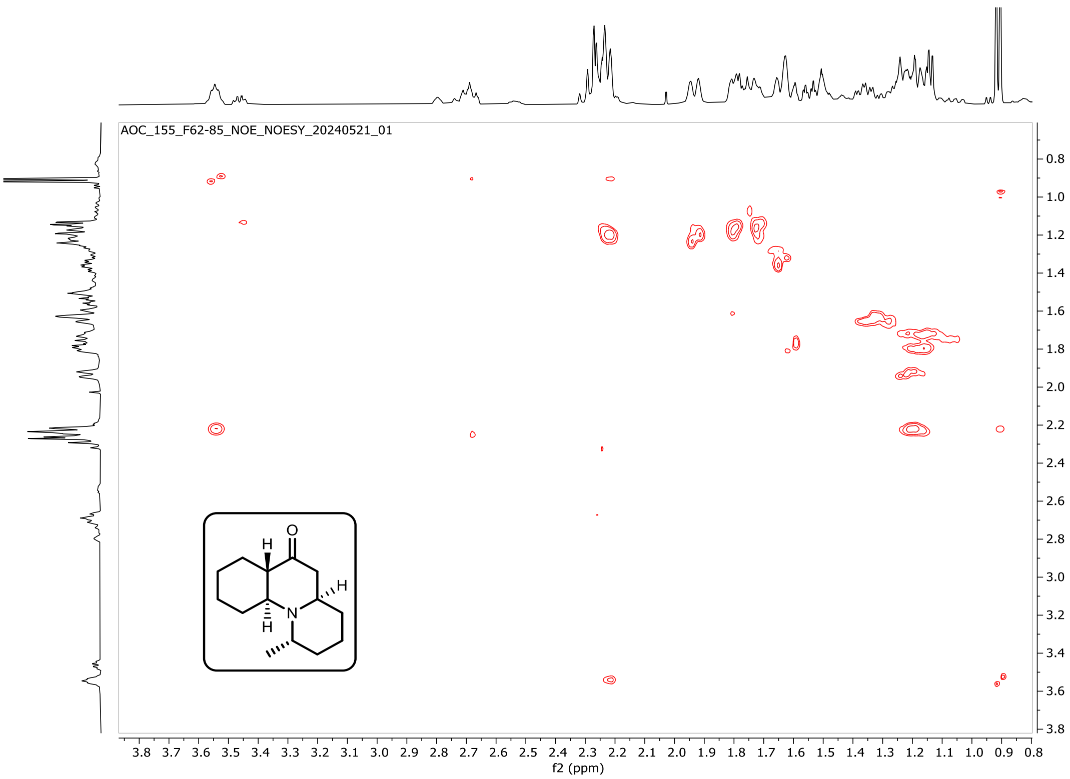
A88: *HSQC ($CDCl_3$) of compound 1S,4aR,6aS,10aS-**4a**.*



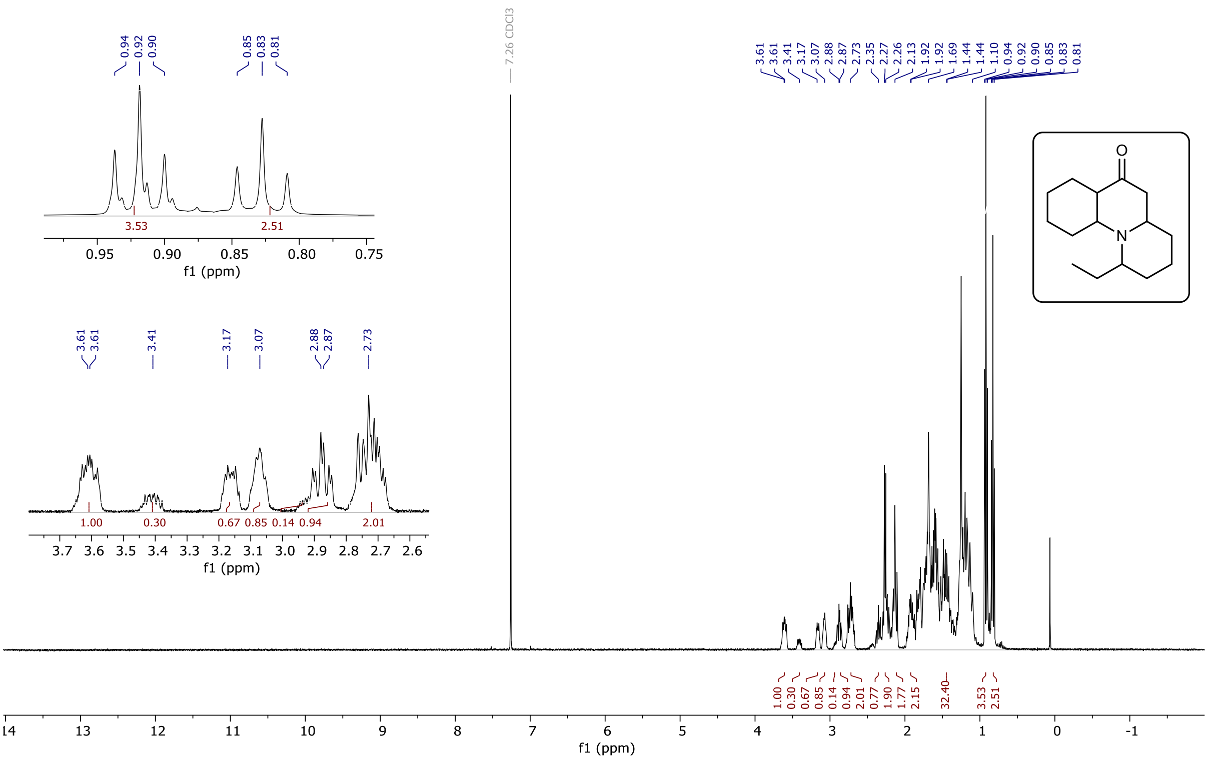
A89: *COSY NMR (CDCl$_3$) of compound 1S,4aR,6aS,10aS-**4a**.*



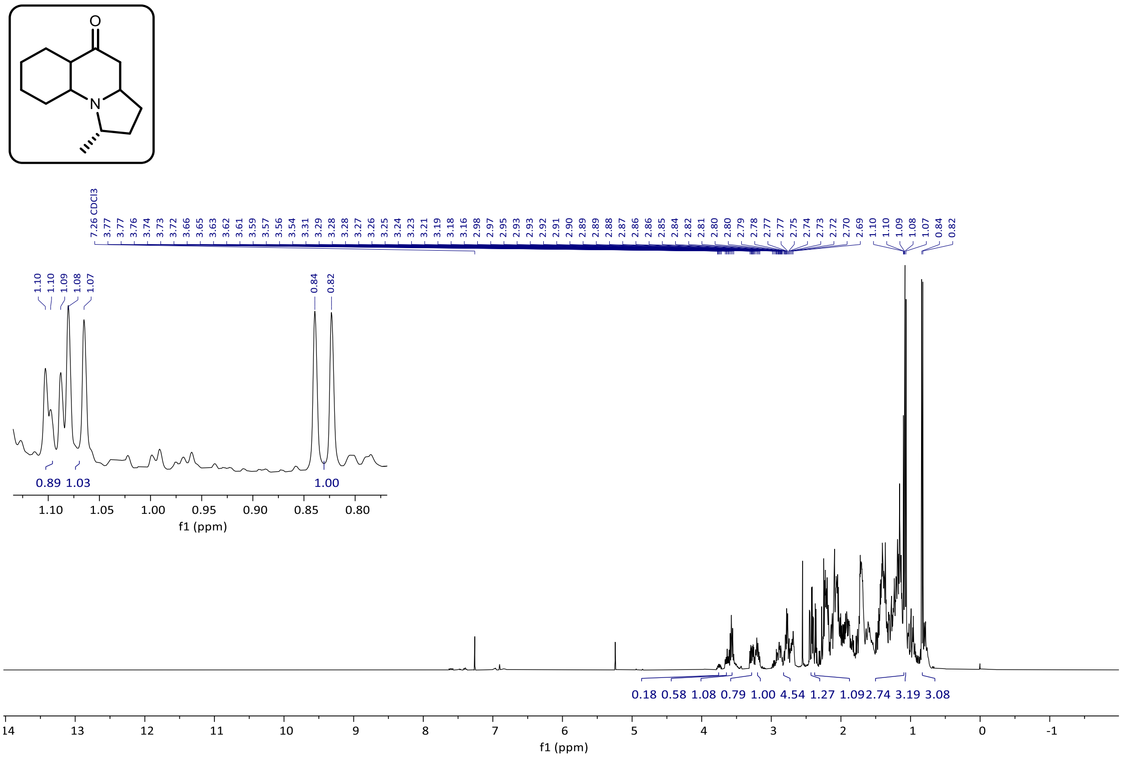
A90: *HMBC (CDCl$_3$) of compound 1S,4aR,6aS,10aS-**4a**.*



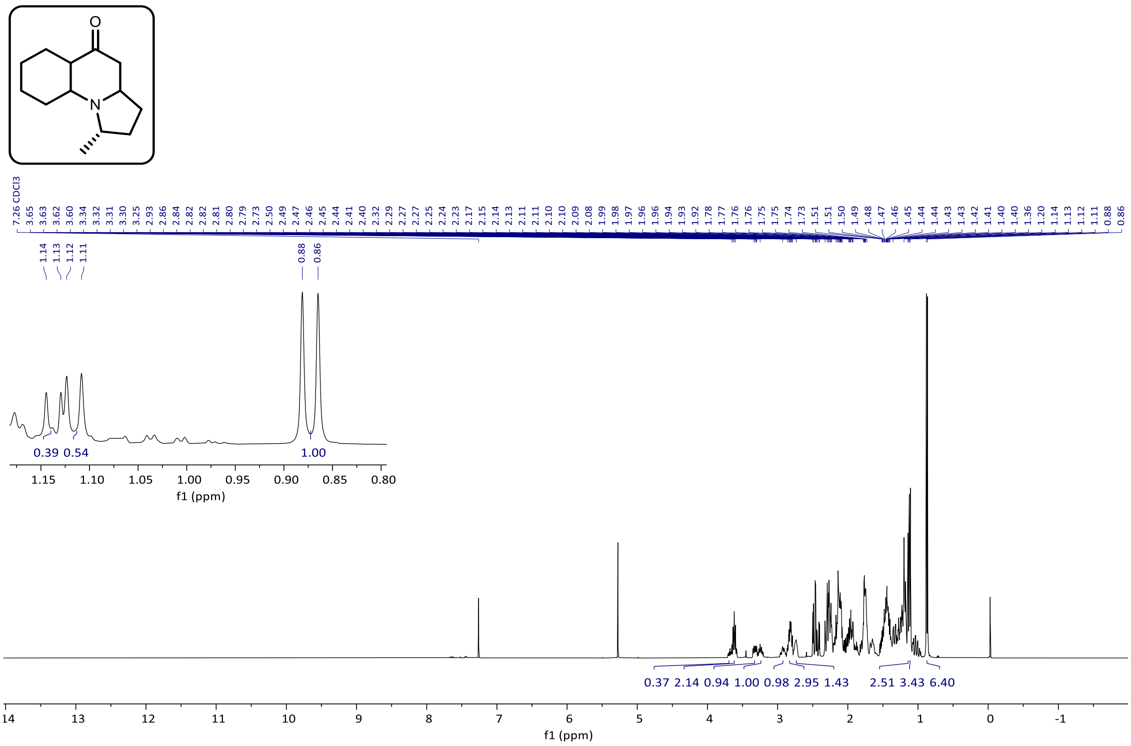
***A91:** NOESY ($CDCl_3$) of compound 1S,4aR,6aS,10aS-**4a**.*



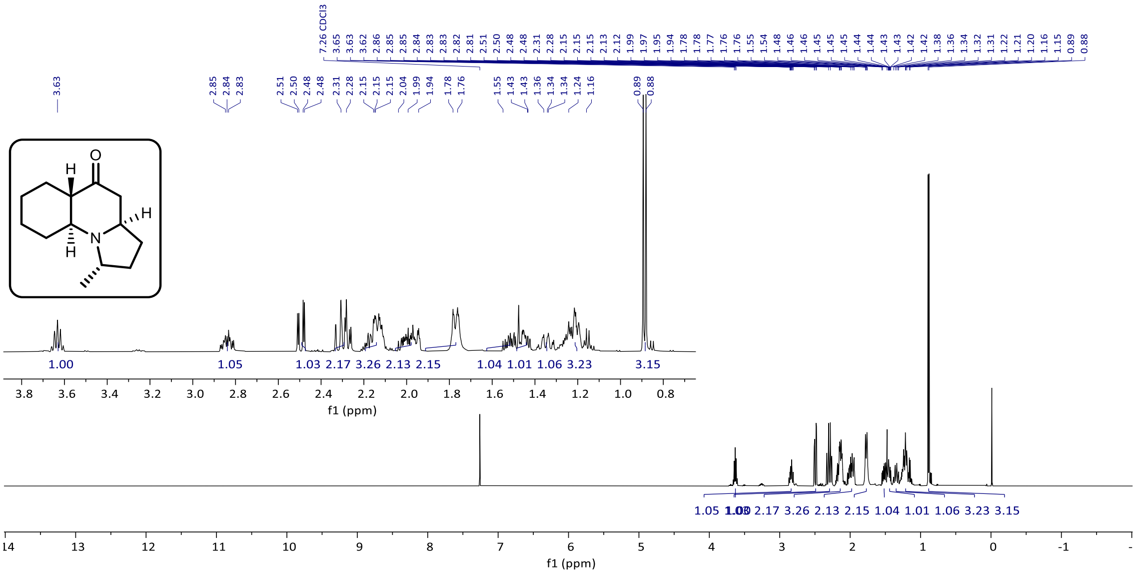
***A92:** ^1H NMR ($CDCl_3$) of compounds **4b**.*



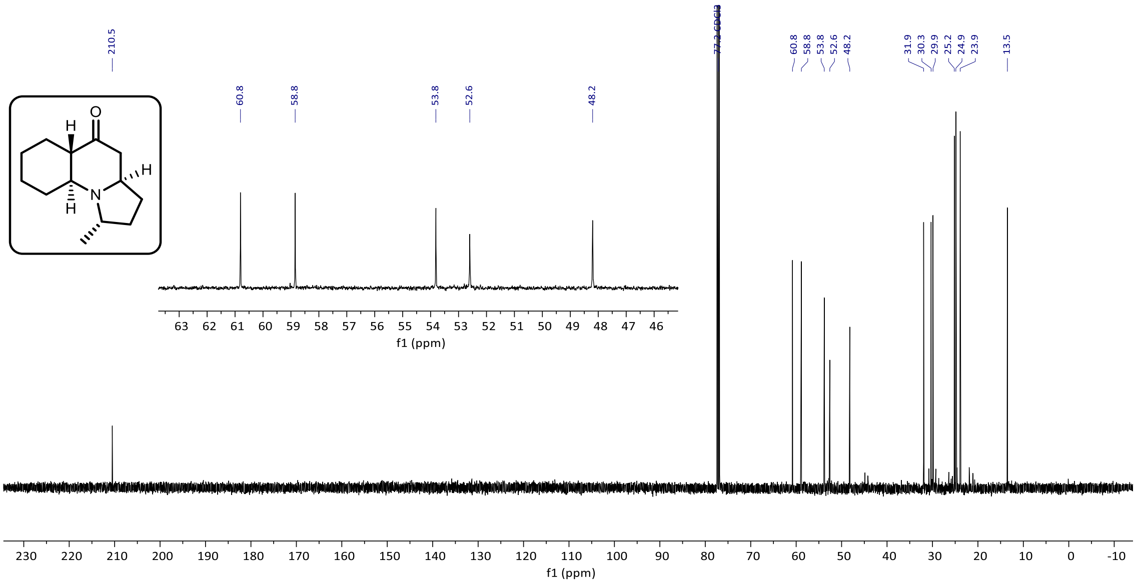
A93: *^{1}H NMR ($CDCl_3$) of compounds* **(1*S*)-4c**.



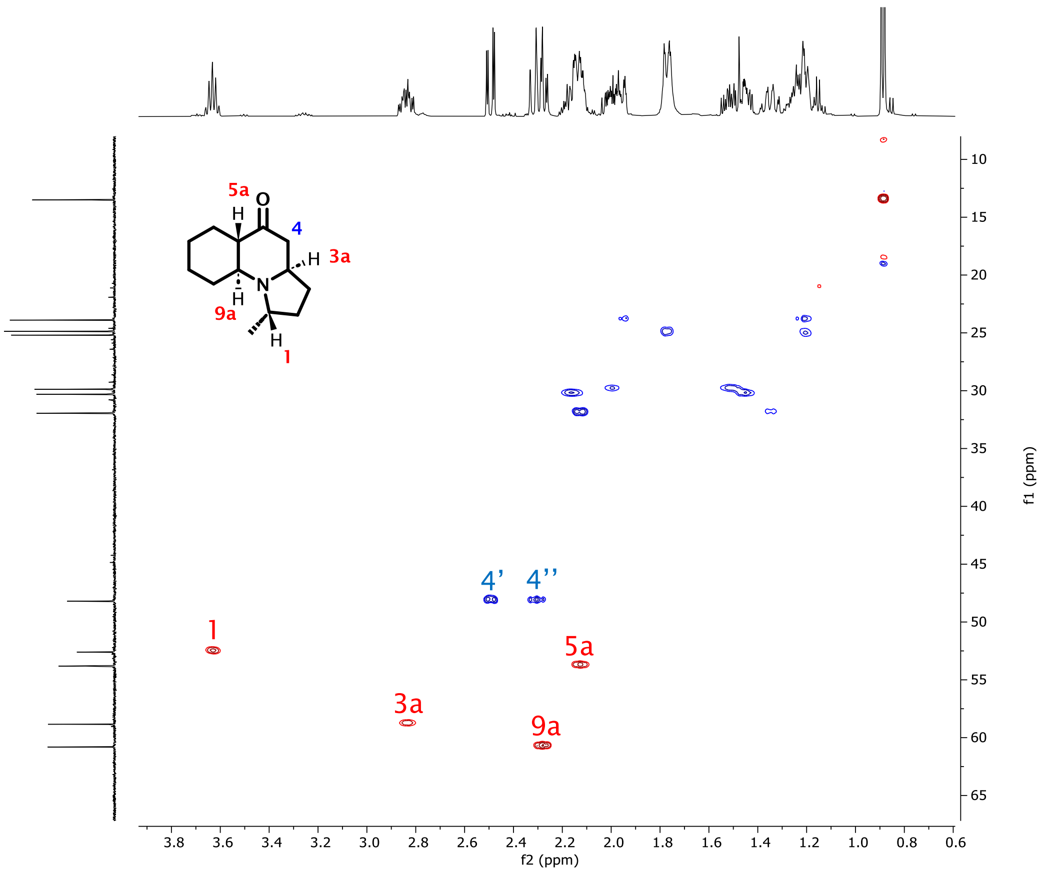
A94: *^{1}H NMR ($CDCl_3$) of compounds* **(1*S*)-4c** *after silica plug.*



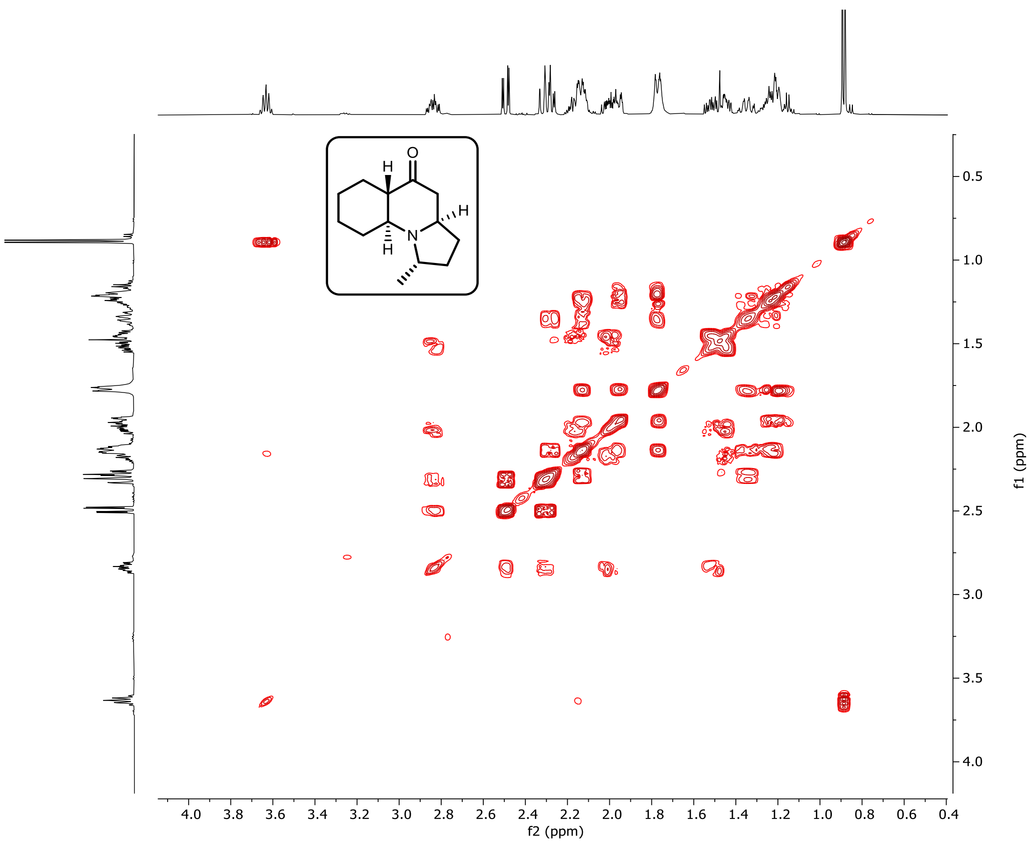
A95: *[1]H NMR ($CDCl_3$) of compound 1S,3aR,5aS,9aS-**4c**.*



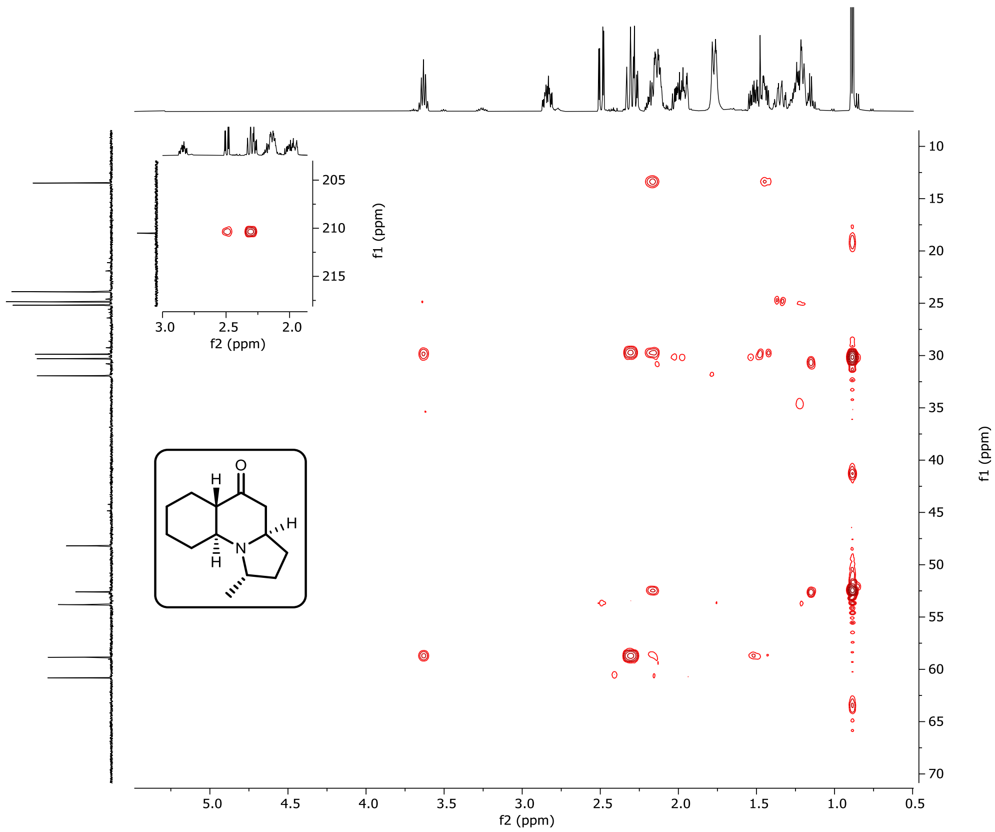
A96: *[13]C NMR ($CDCl_3$) of compound 1S,3aR,5aS,9aS-**4c**.*



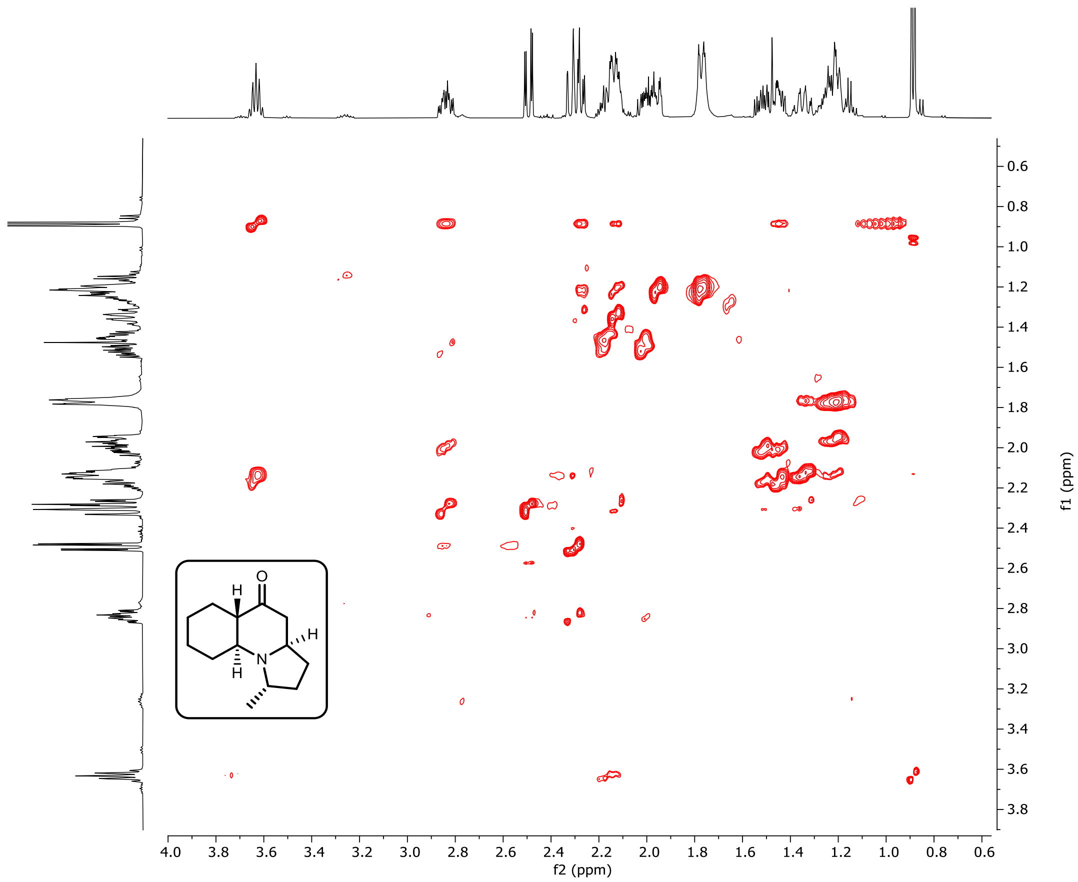
A97: *HSQC ($CDCl_3$) of compound 1S,3aR,5aS,9aS-**4c**.*



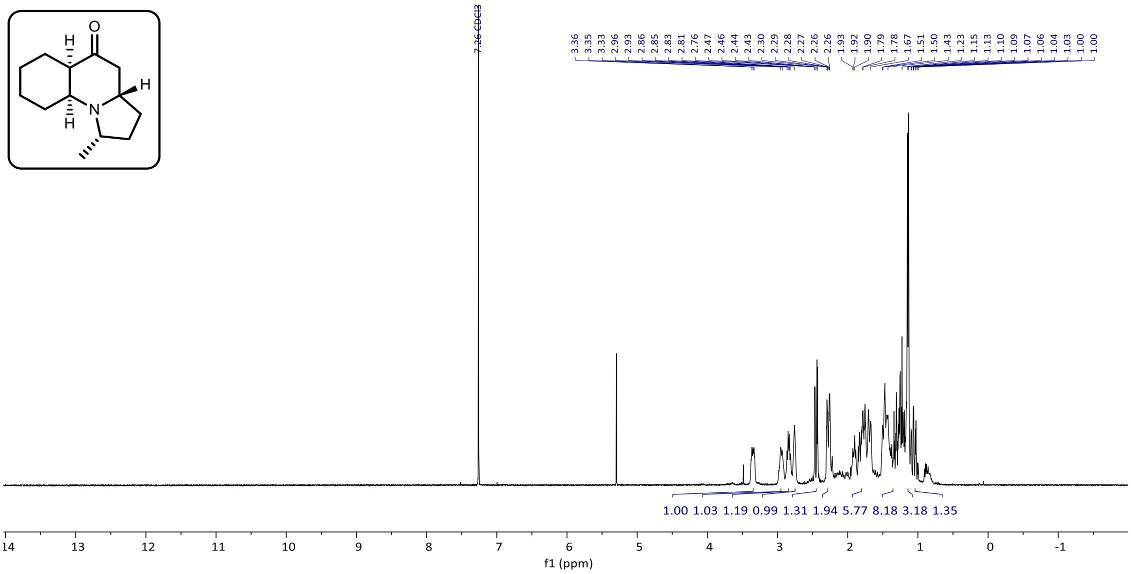
A98: *COSY NMR ($CDCl_3$) of compound 1S,3aR,5aS,9aS-**4c**.*



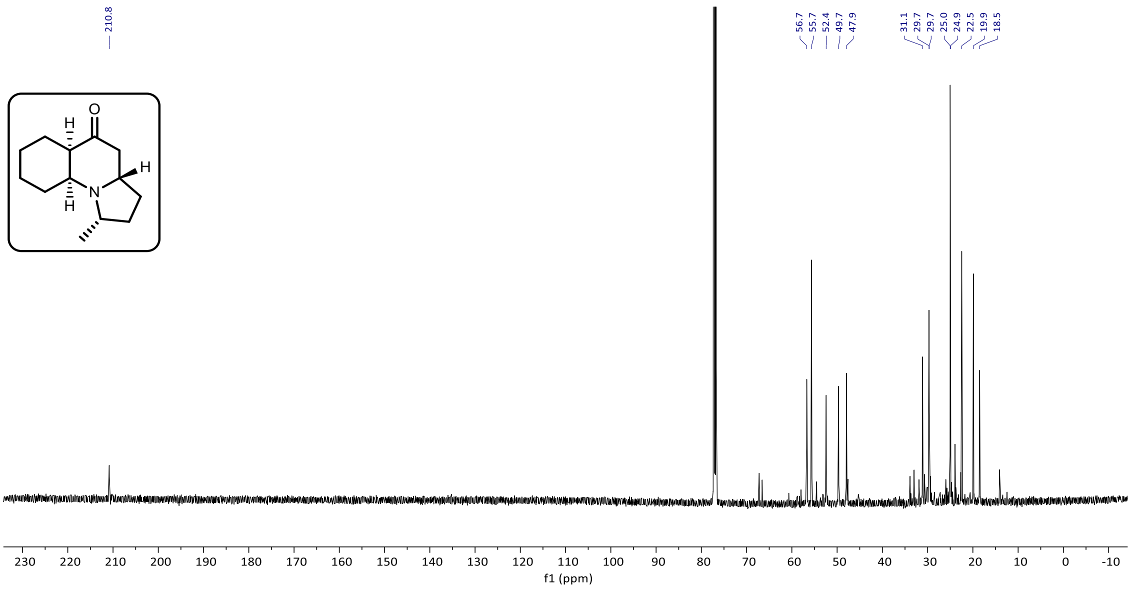
***A99:** HMBC ($CDCl_3$) of compound 1S,3aR,5aS,9aS-**4c**.*



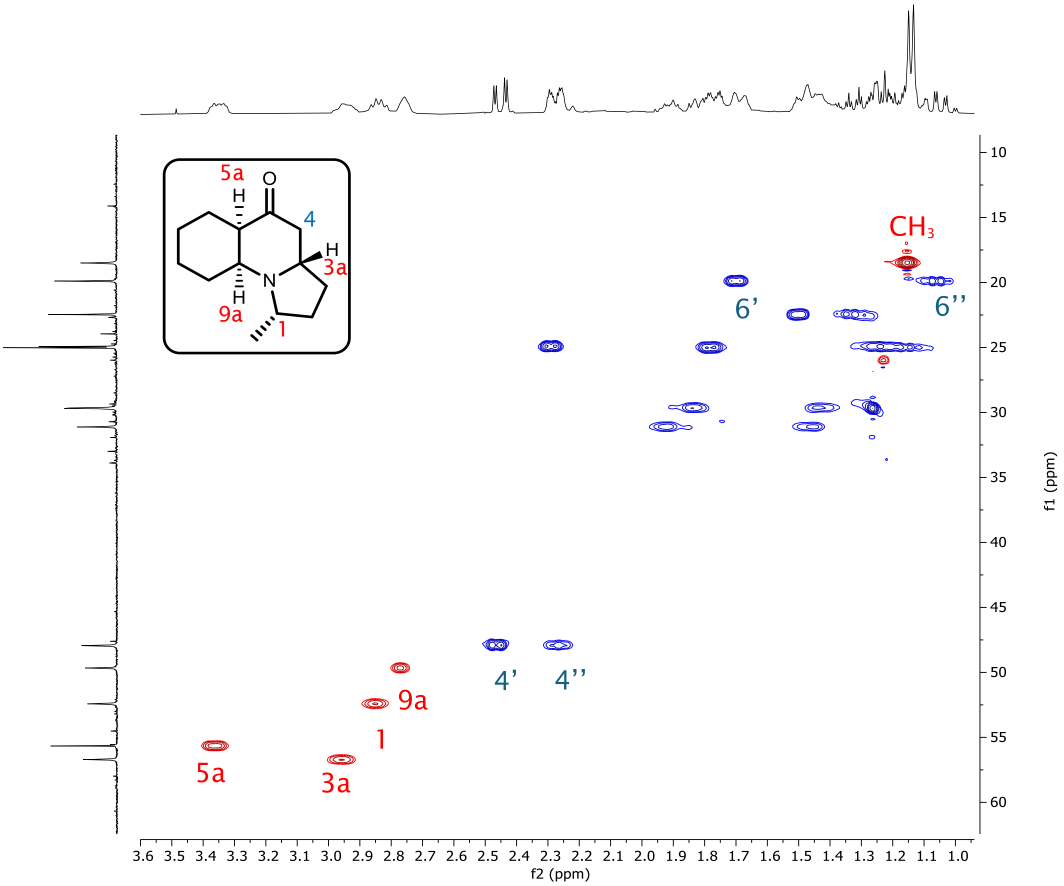
***A100:** NOESY ($CDCl_3$) of compound 1S,3aR,5aS,9aS-**4c**.*



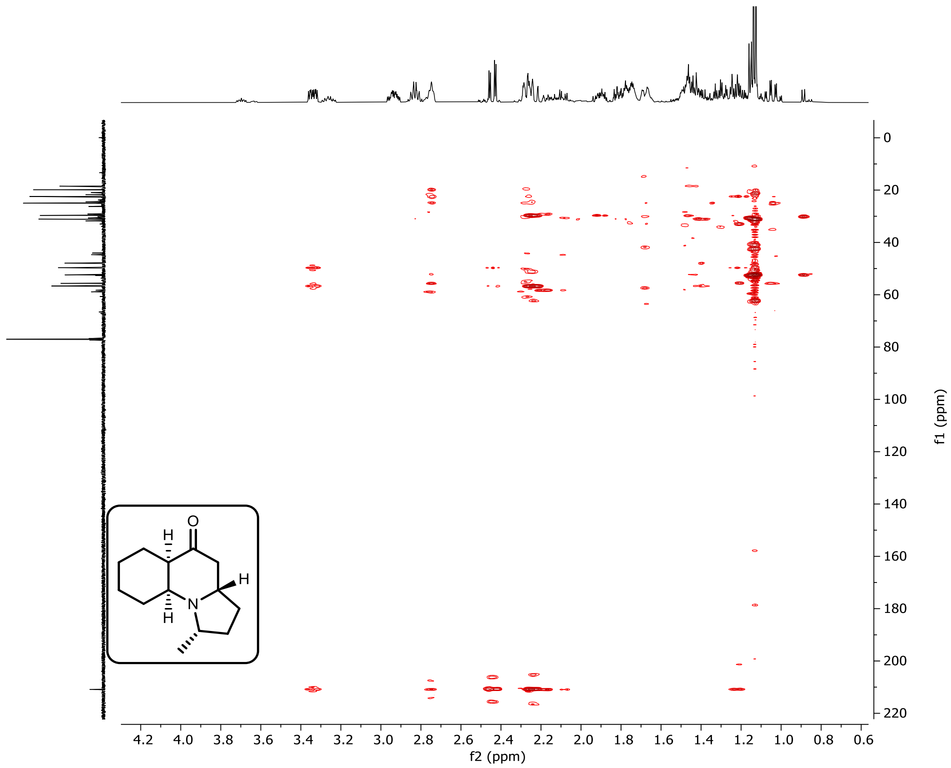
A101: *[1]H NMR ($CDCl_3$) of compound 1S,3aS,5aR,9aS-**4c**.*



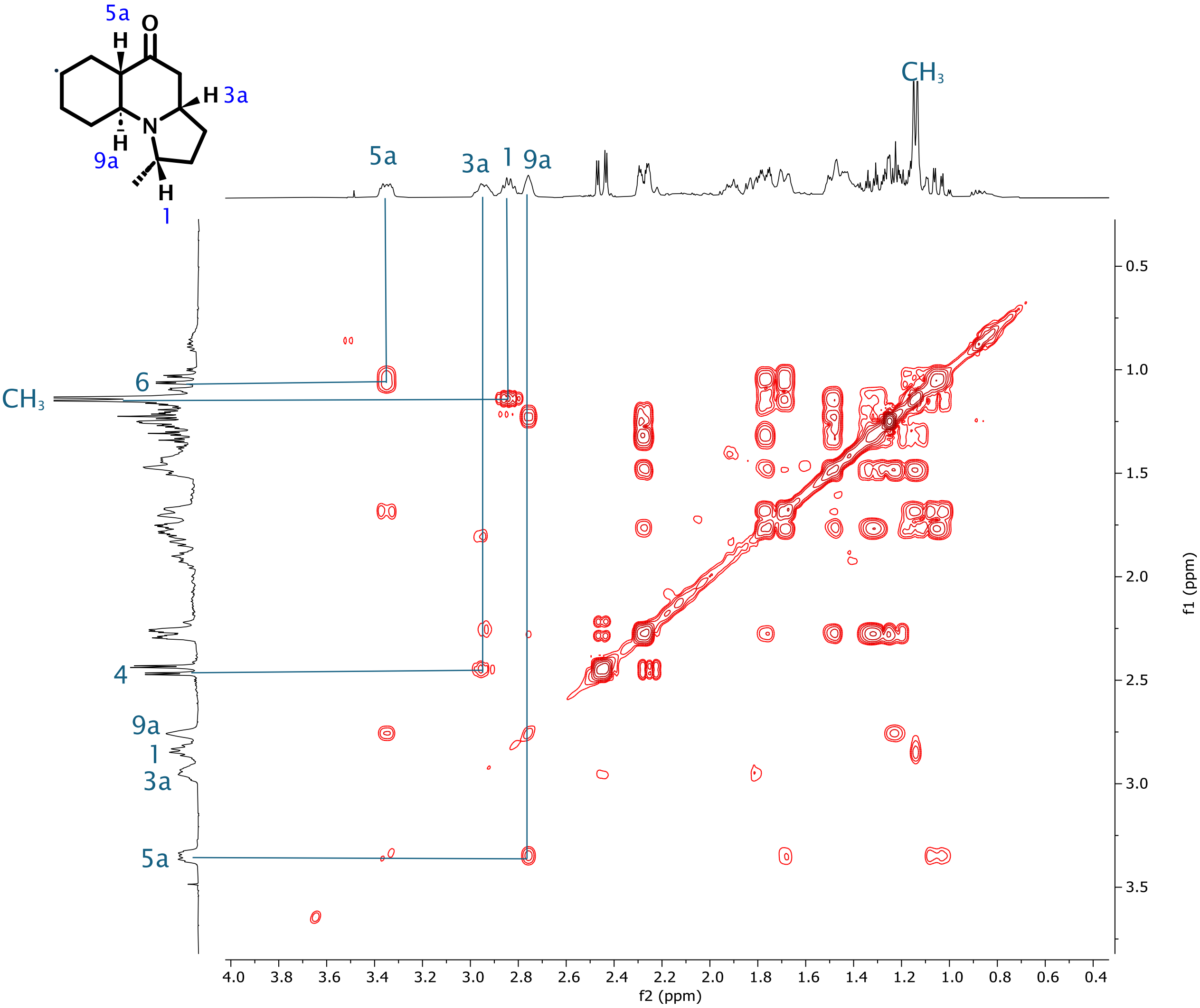
A102: *[13]C NMR ($CDCl_3$) of compound 1S,3aS,5aR,9aS-**4c**.*



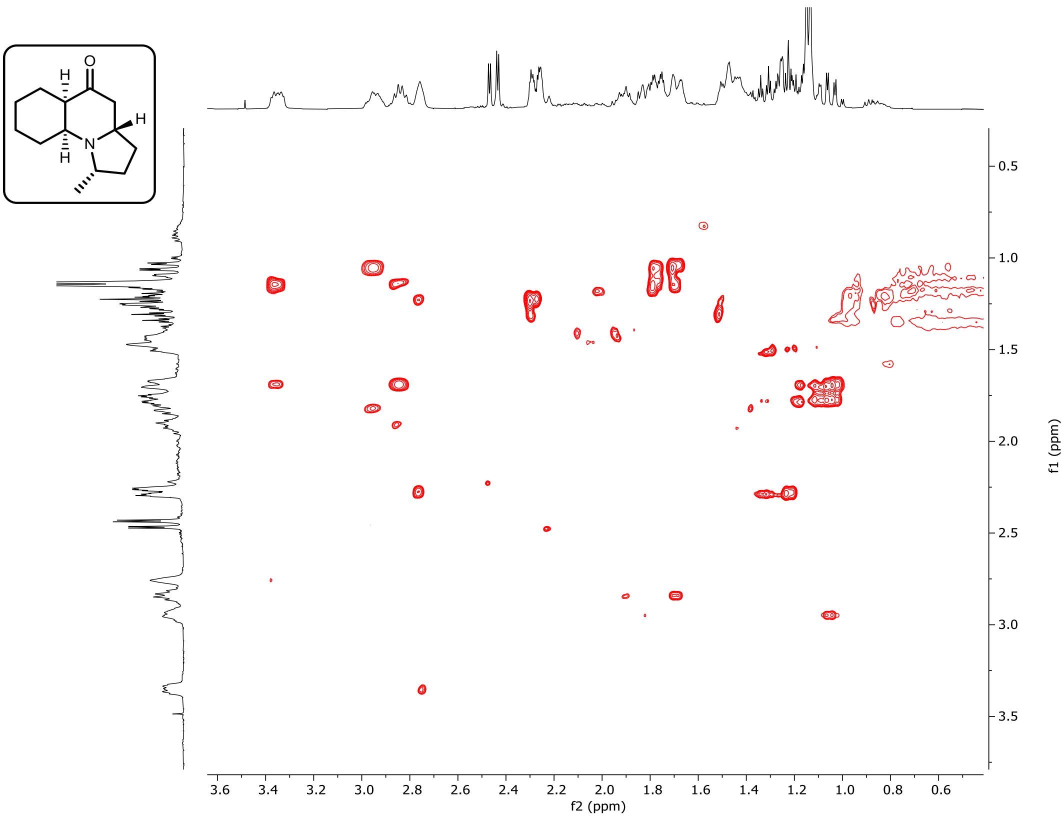
A103: *HSQC (CDCl$_3$) of compound 1S,3aS,5aR,9aS-**4c**.*



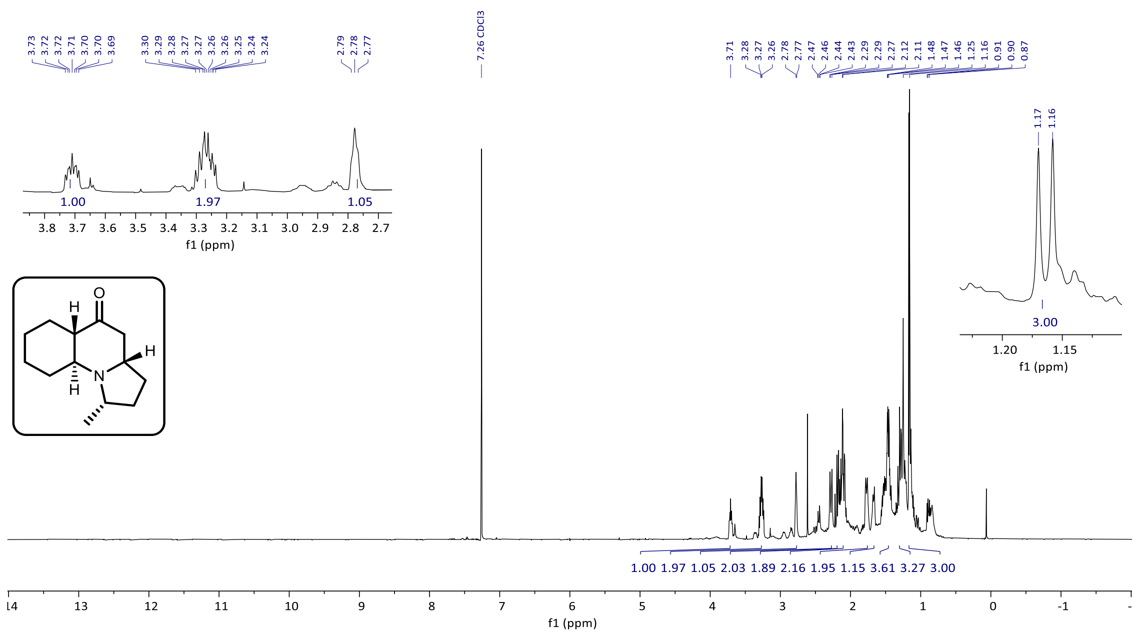
A104: *HMBC (CDCl$_3$) of compound 1S,3aS,5aR,9aS-**4c**.*



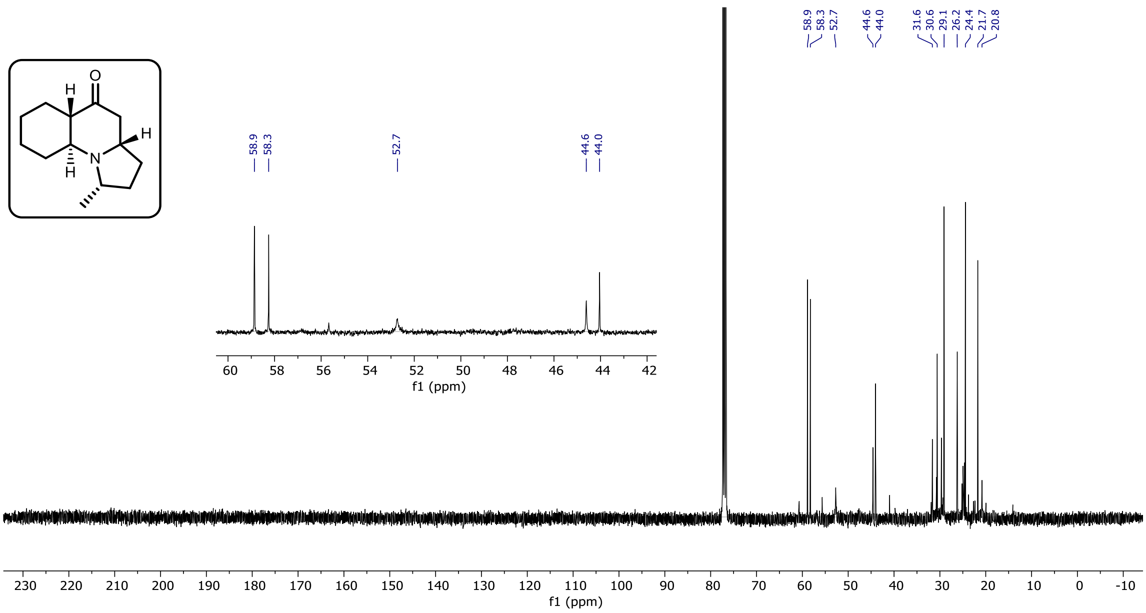
***A105:** COSY ($CDCl_3$) of compound 1S,3aS,5aR,9aS-**4c**.*



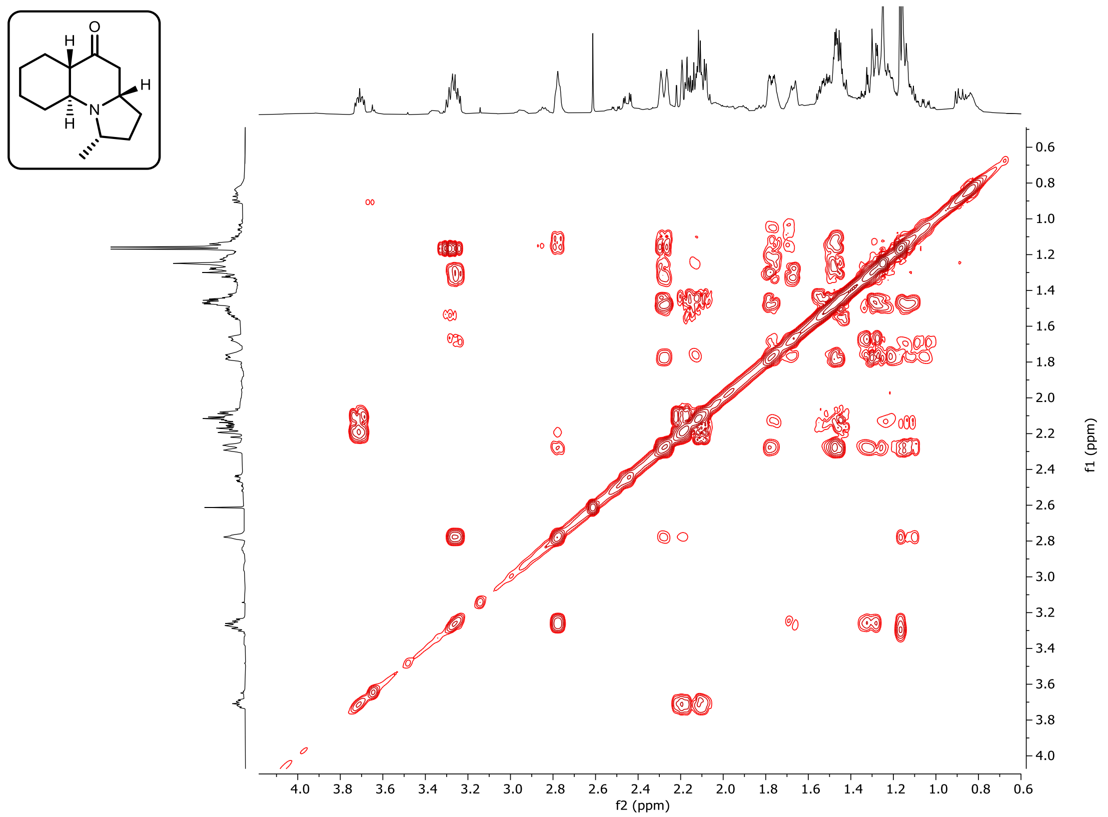
A106: *NOESY ($CDCl_3$) of compound 1S,3aS,5aR,9aS-**4c**.*



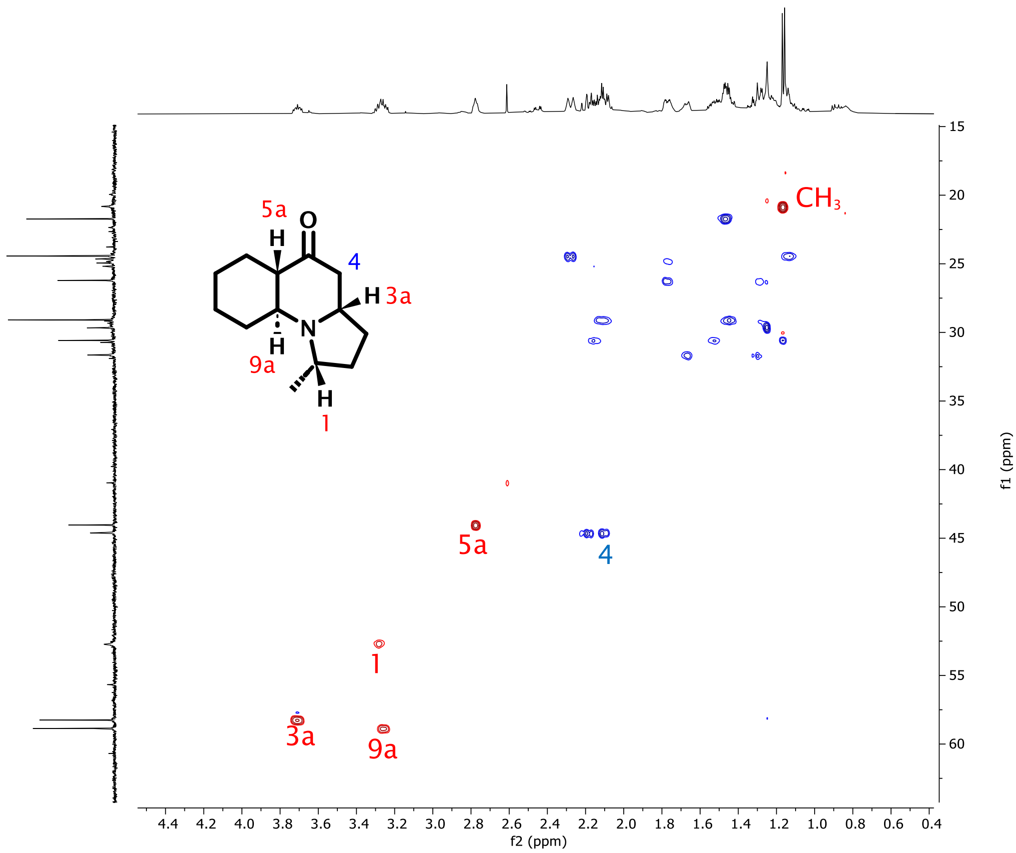
A107: *^1H NMR ($CDCl_3$) of compound 1S,3aS,5aS,9aS-**4c**.*



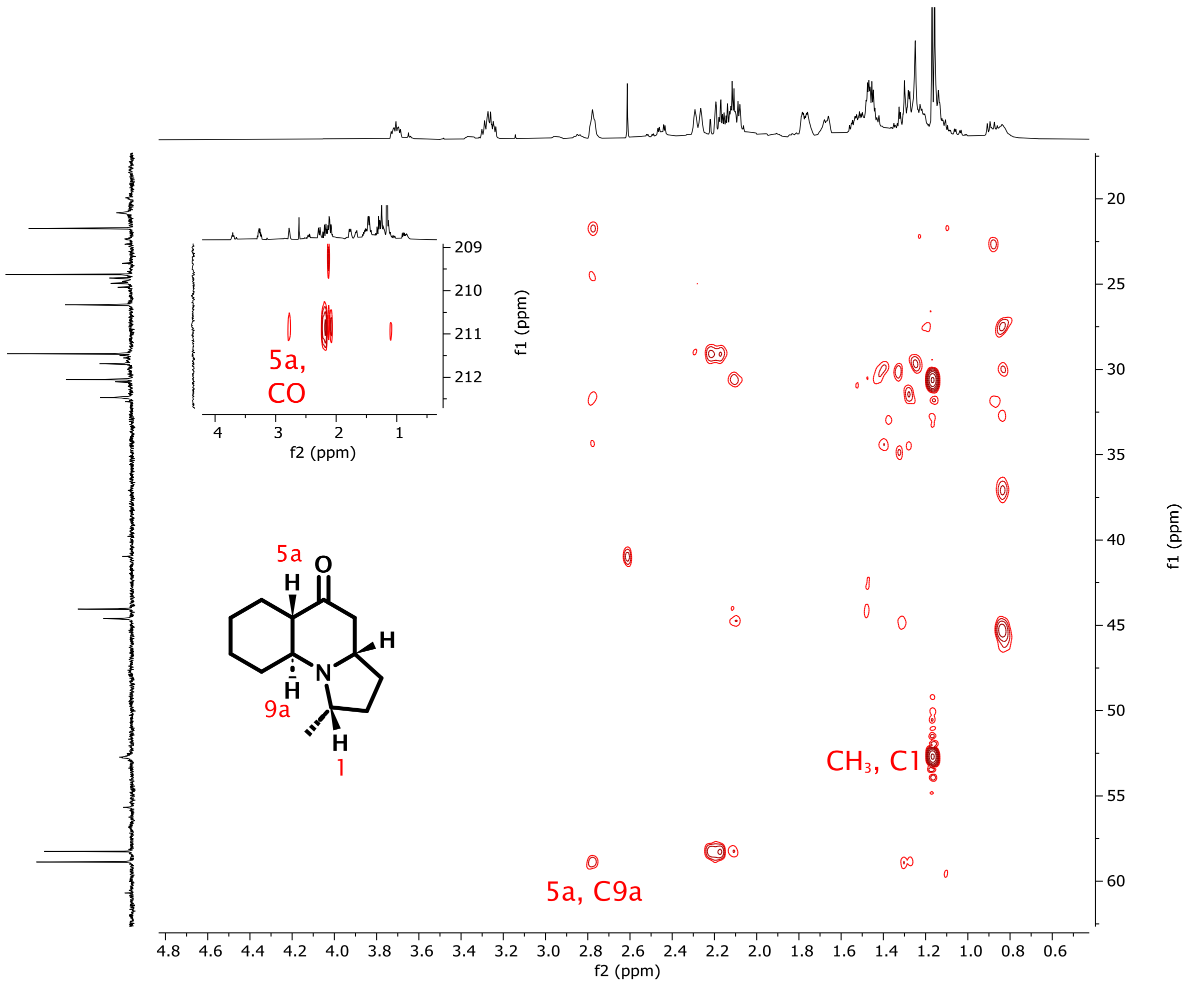
A108: *^{13}C NMR (CDCl$_3$) of compound 1S,3aS,5aS,9aS-**4c**.*



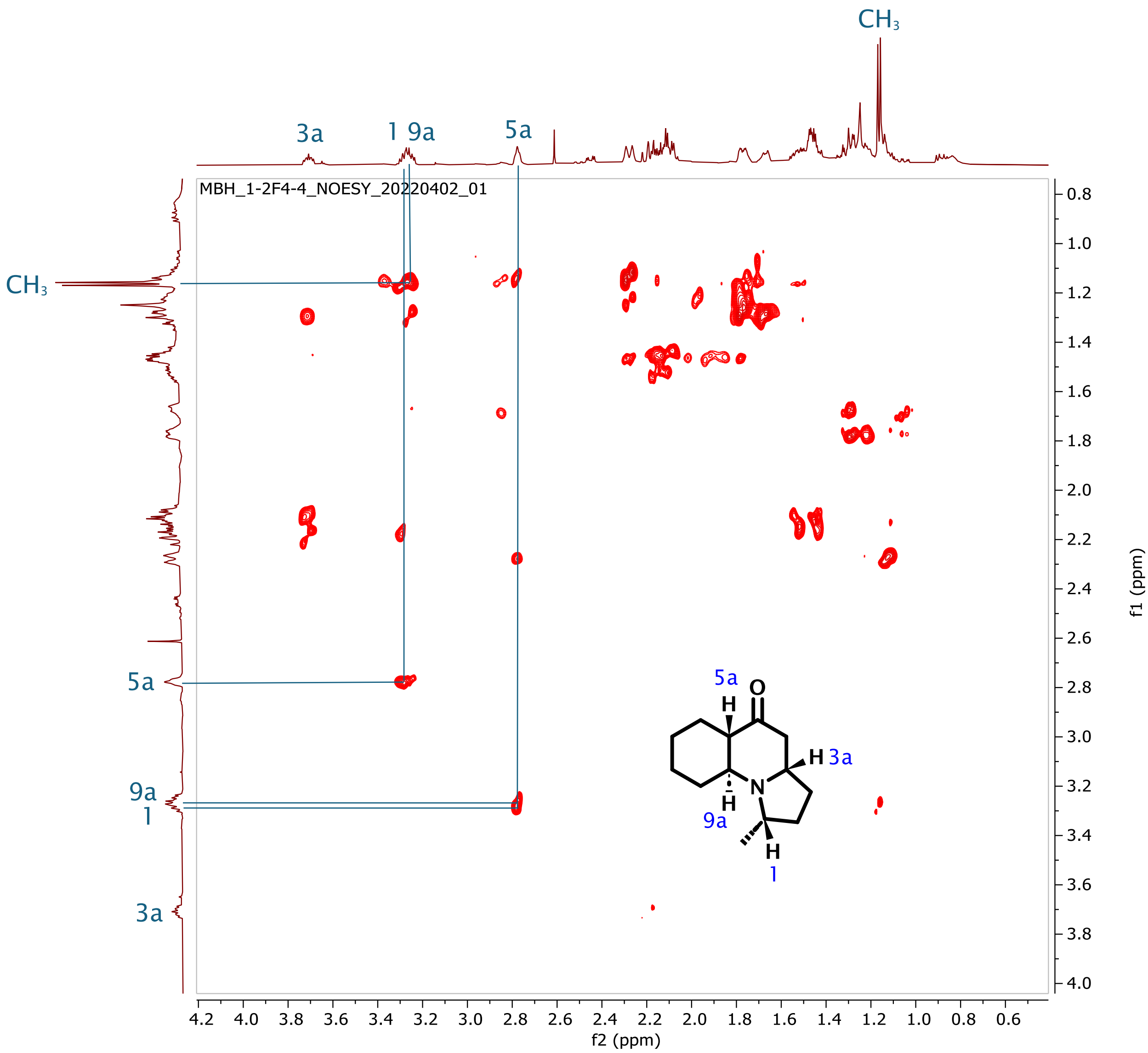
A109: *COSY (CDCl$_3$) of compound 1S,3aS,5aS,9aS-**4c**.*



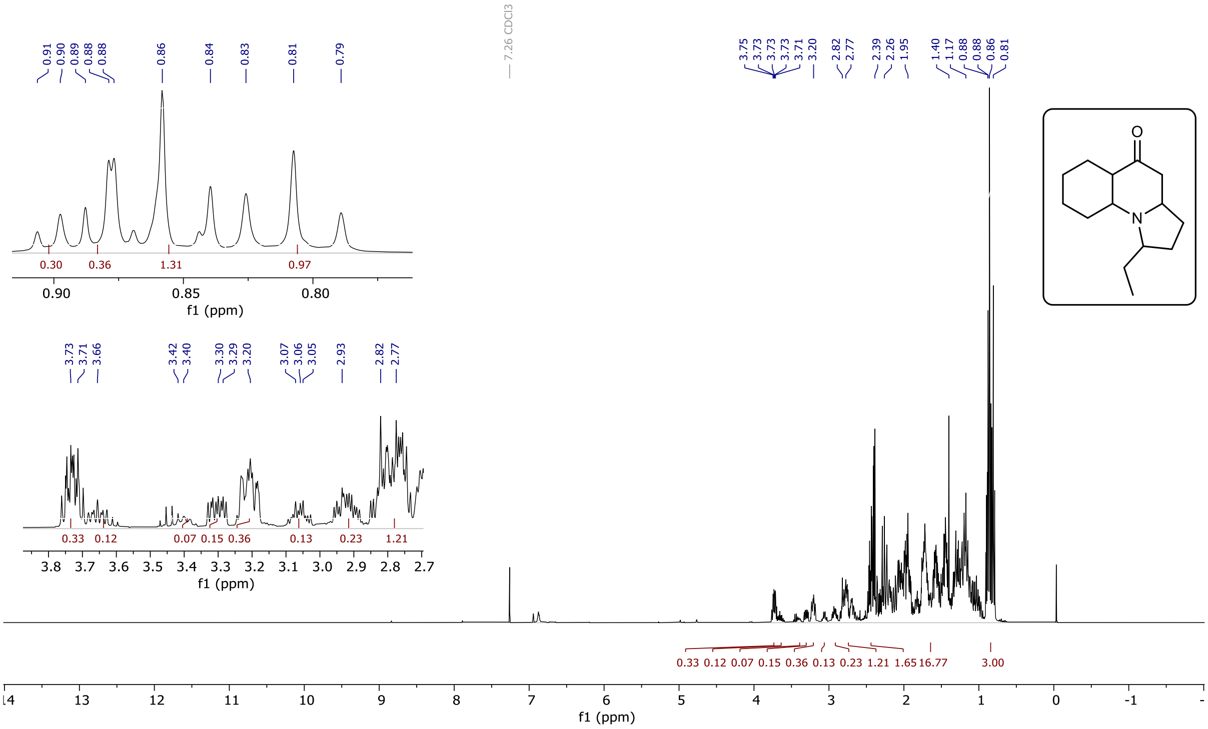
***A110:** HSQC ($CDCl_3$) of compound 1S,3aS,5aS,9aS-**4c**.*



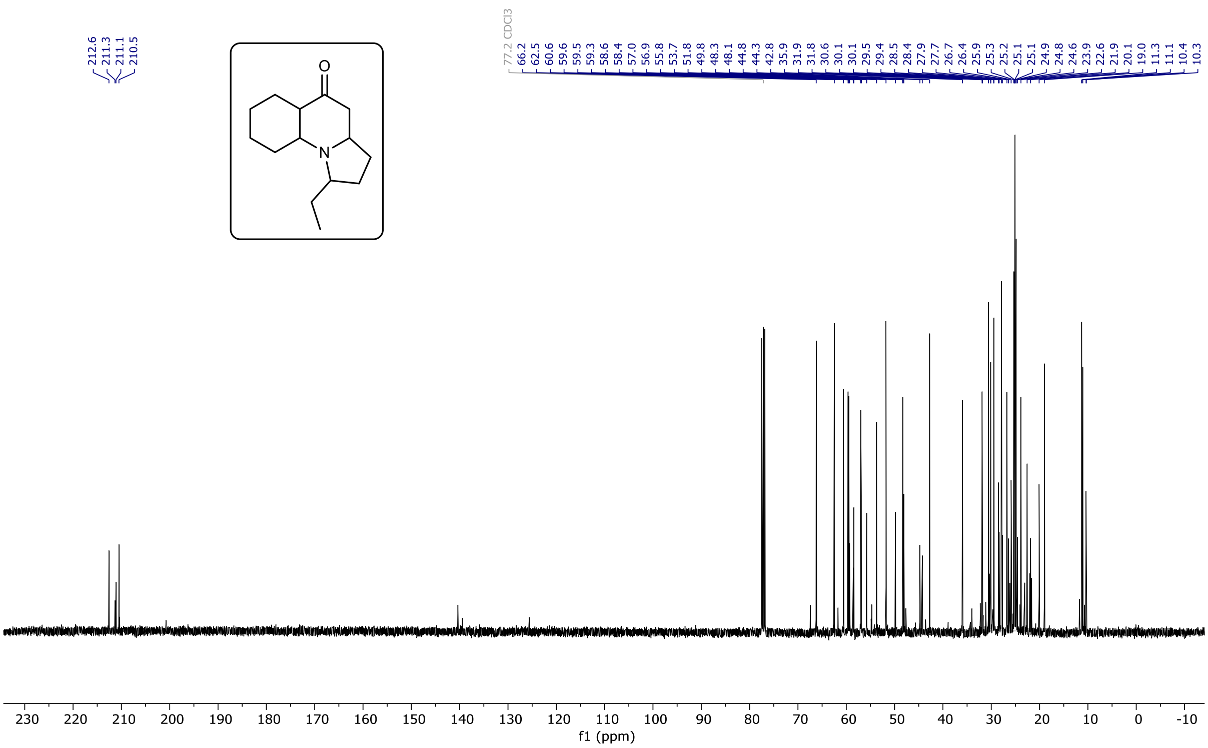
***A111:** HMBC (CDCl$_3$) of compound 1S,3aS,5aS,9aS-**4c**.*



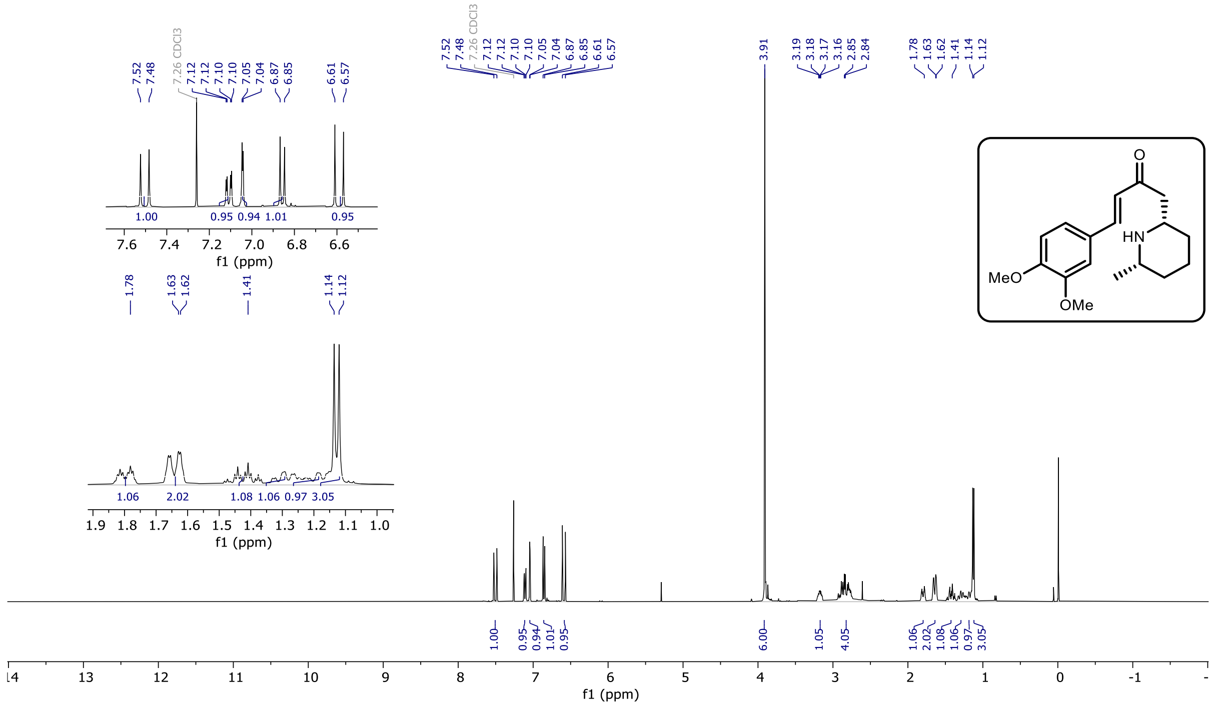
A112: *NOESY ($CDCl_3$) of compound (1S,3aS,5aS,9aS)-**4c**.*



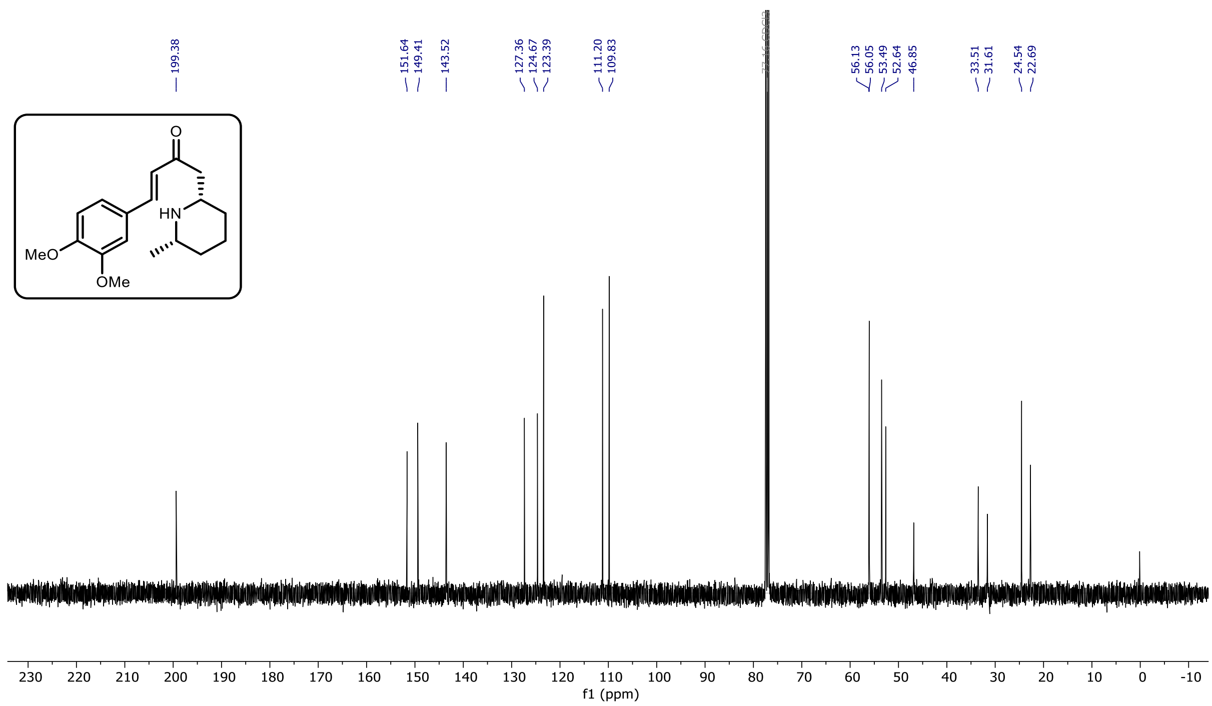
A113: ^{1}H *NMR ($CDCl_3$) of compound* ***4d.***



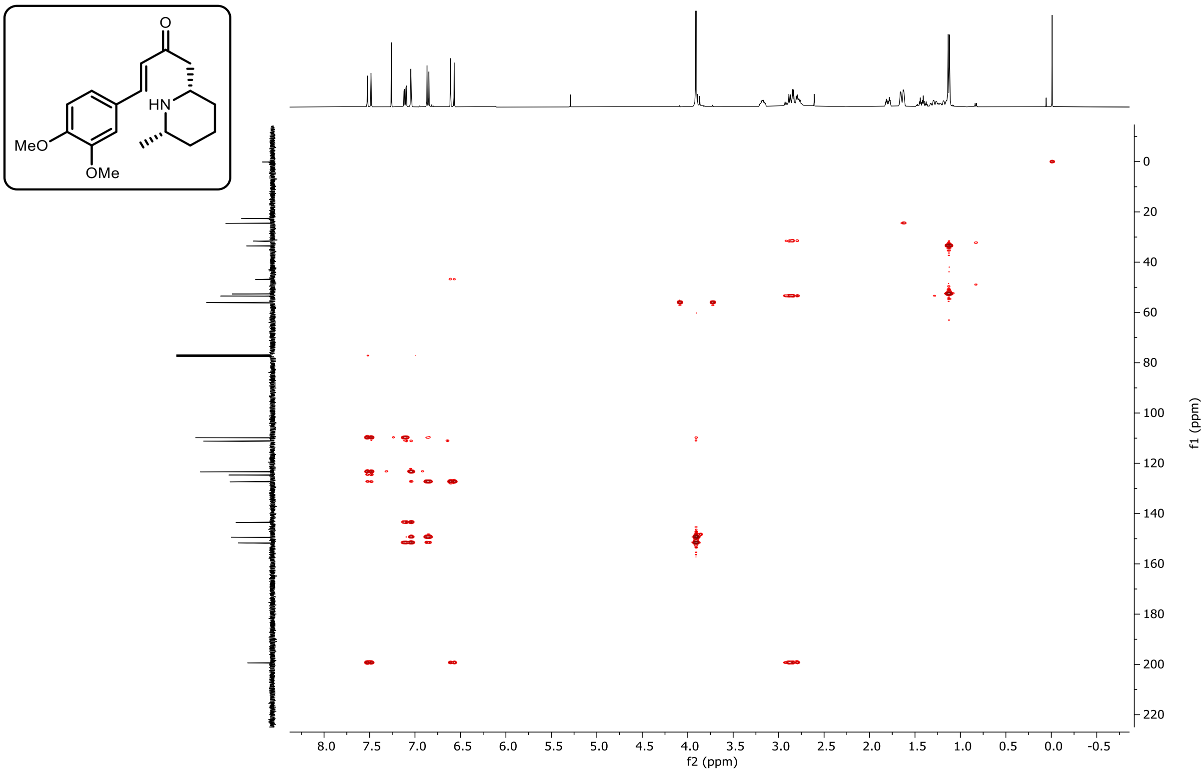
A114: ^{13}C *NMR ($CDCl_3$) of compound* ***4d.***



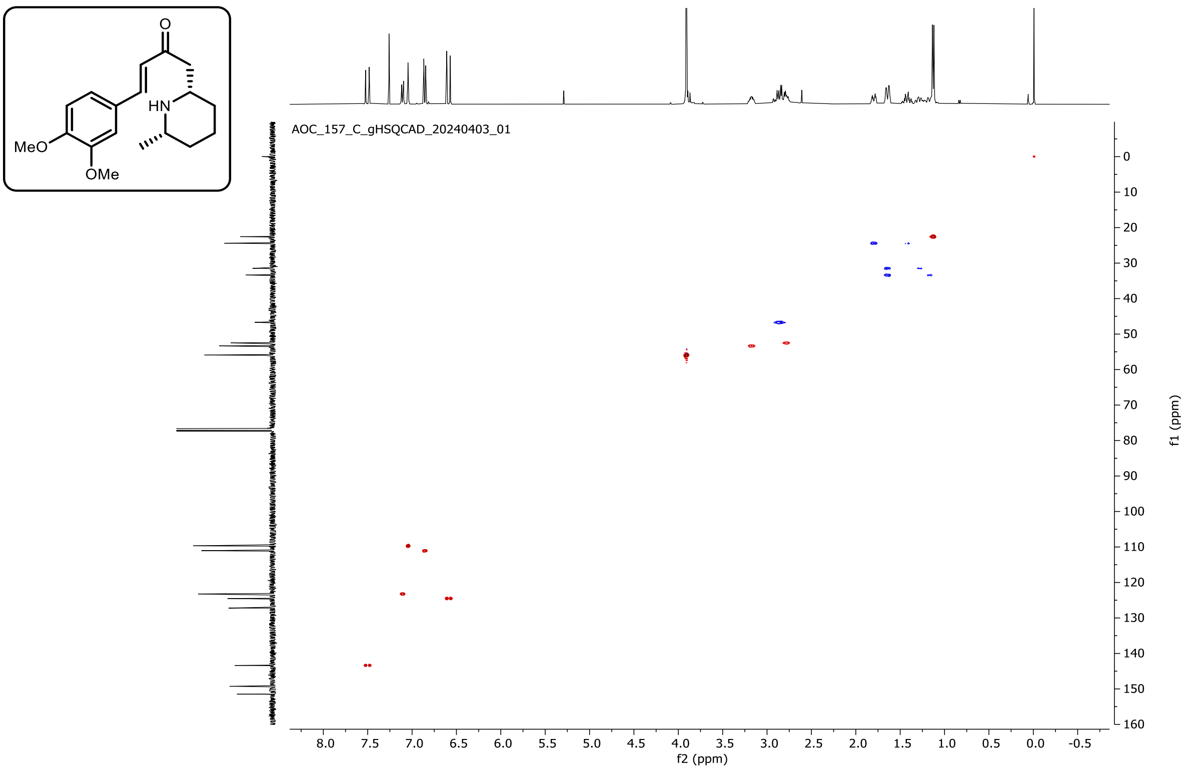
A115: *[1]H NMR (CDCl$_3$) of compound (S,S)-**3e**.*



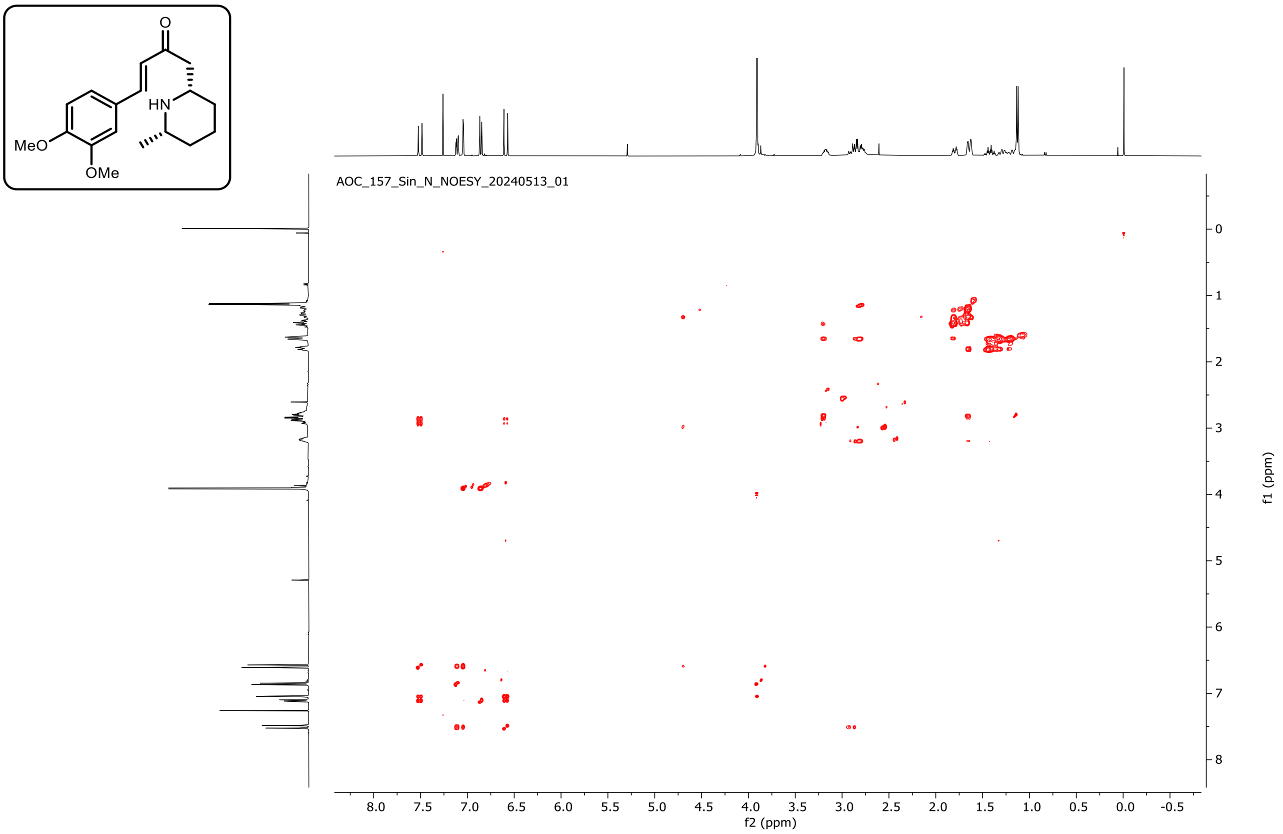
A116: *[13]C NMR (CDCl$_3$) of compound (S,S)-**3e**.*



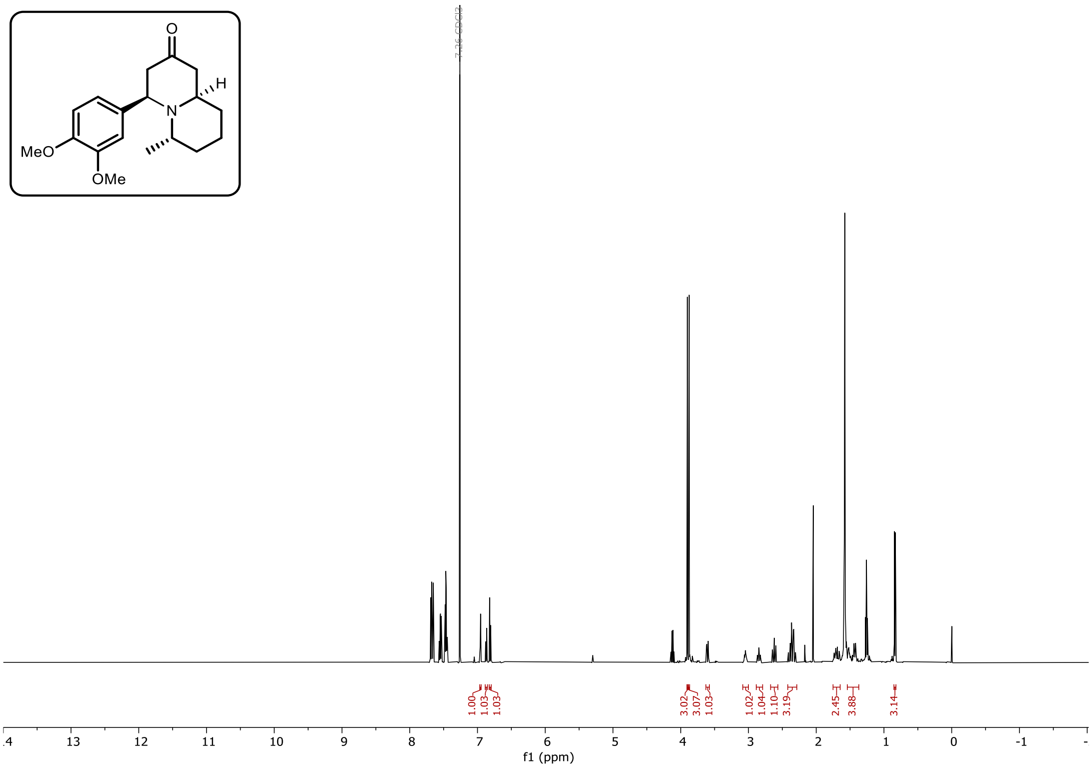
A117:** HMBC (CDCl$_3$) of compound (S,S)-**3e.



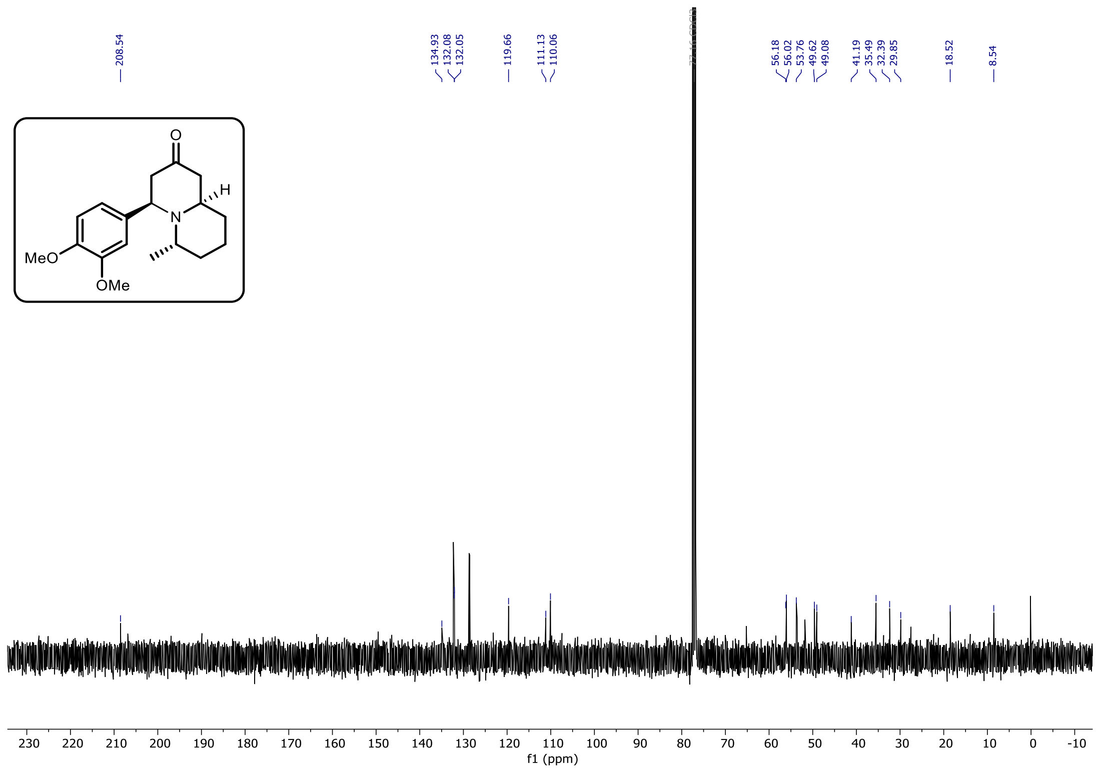
A118:** HSQC (CDCl$_3$) of compound (S,S)-**3e.



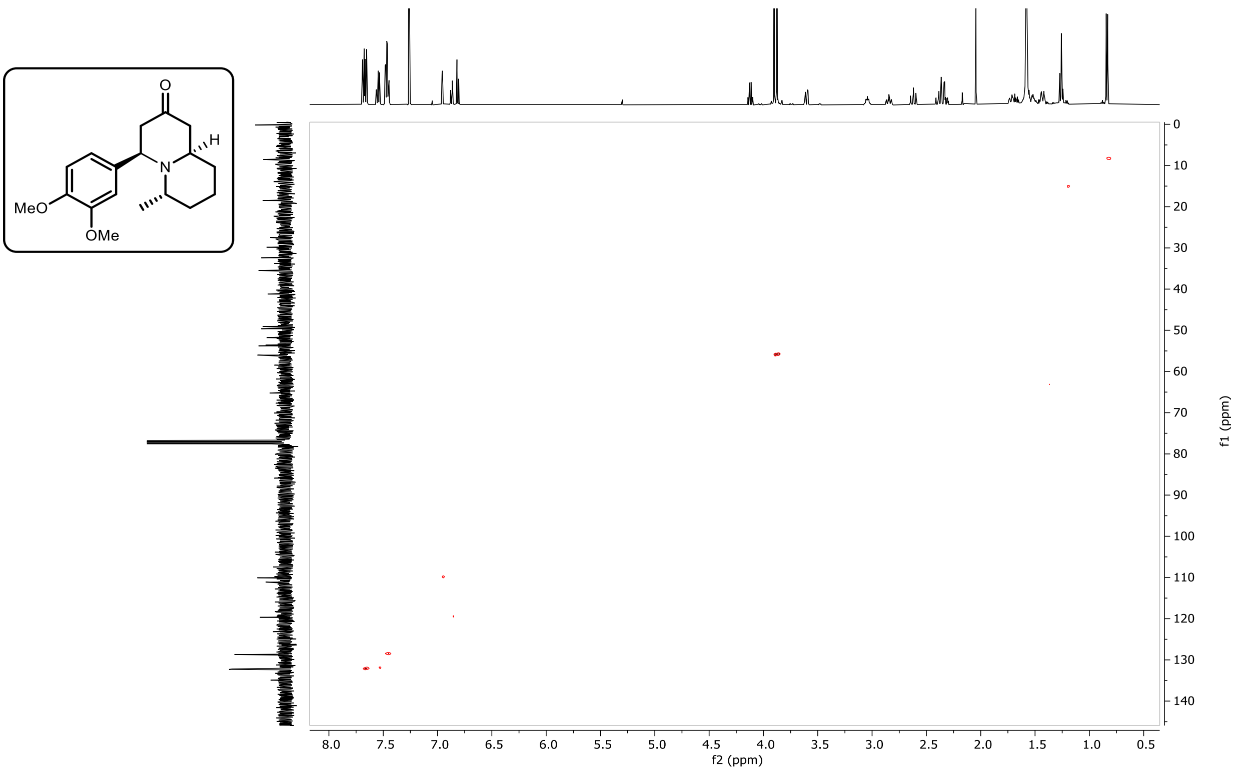
A119: *NOESY ($CDCl_3$) of compound (S,S)-**3e**.*



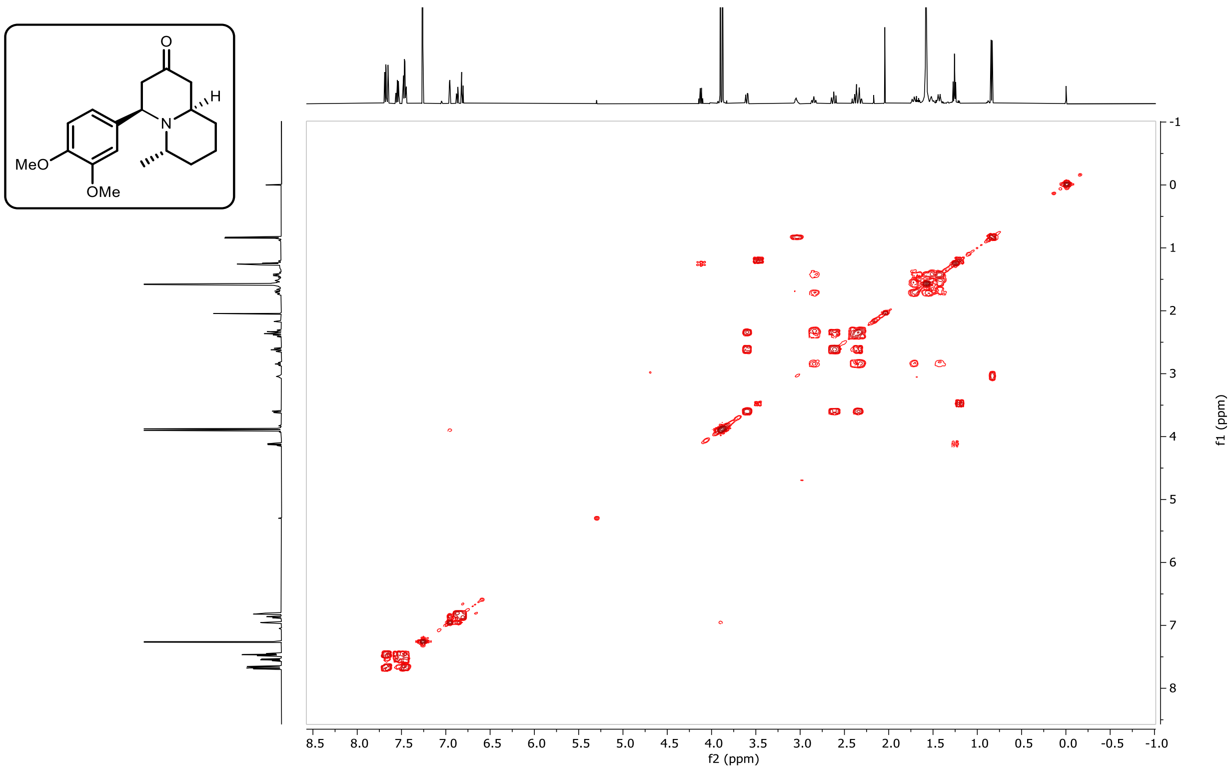
A120: *[1]H NMR ($CDCl_3$) of compound (4R,6S,9aR)-**4e**.*



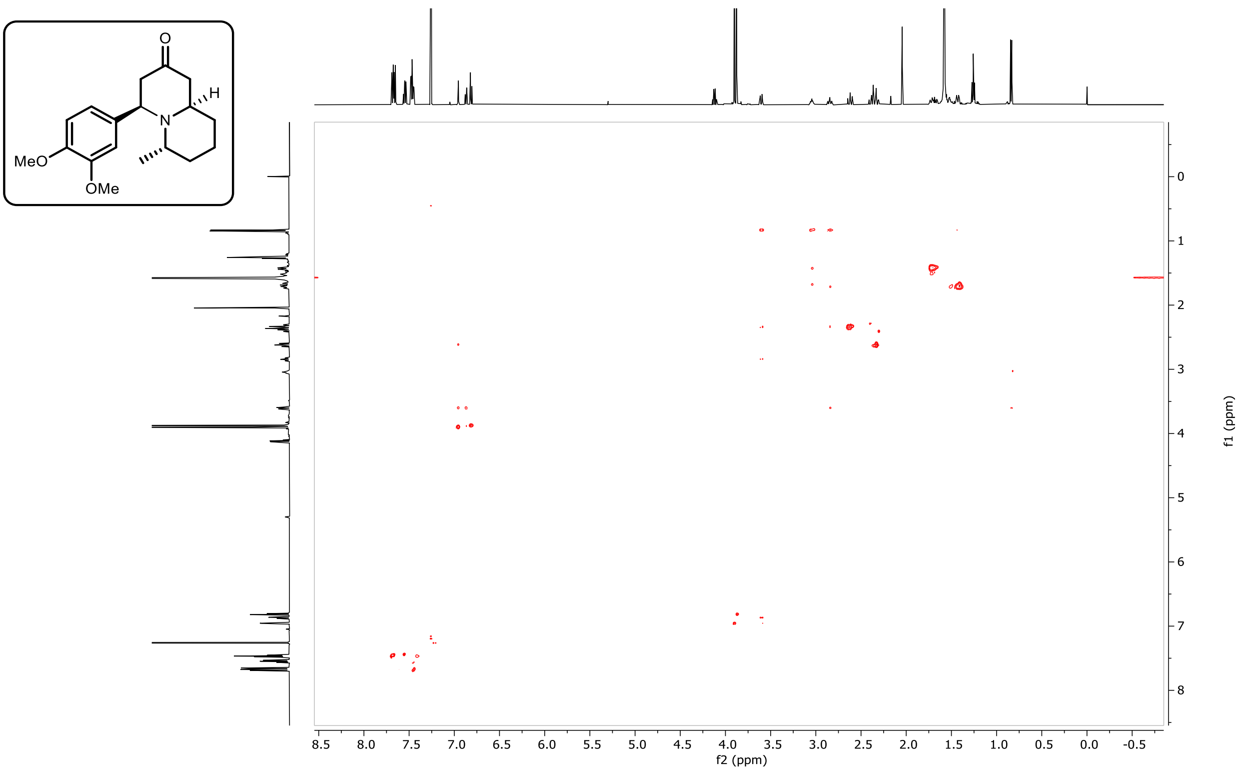
A121: *^{13}C NMR (CDCl$_3$) of compound* 4*R*,6*S*,9a*R*-**4e**.



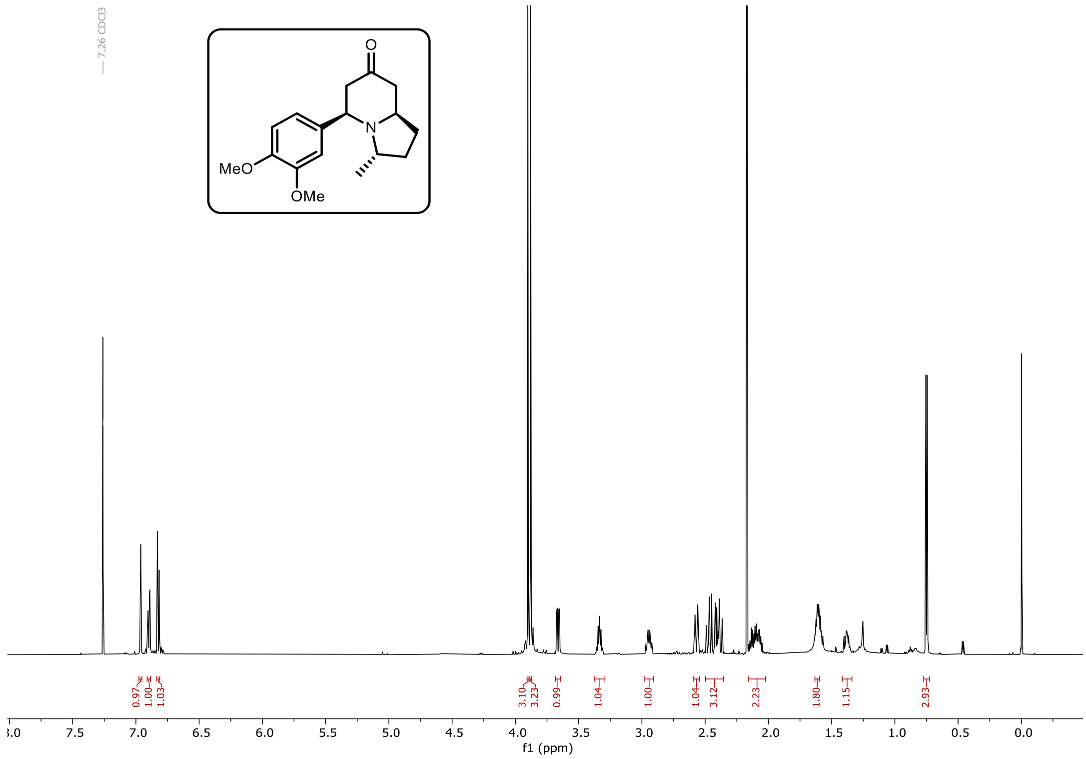
A122: *HSQC (CDCl$_3$) of compound* 4*R*,6*S*,9a*R*-**4e**.



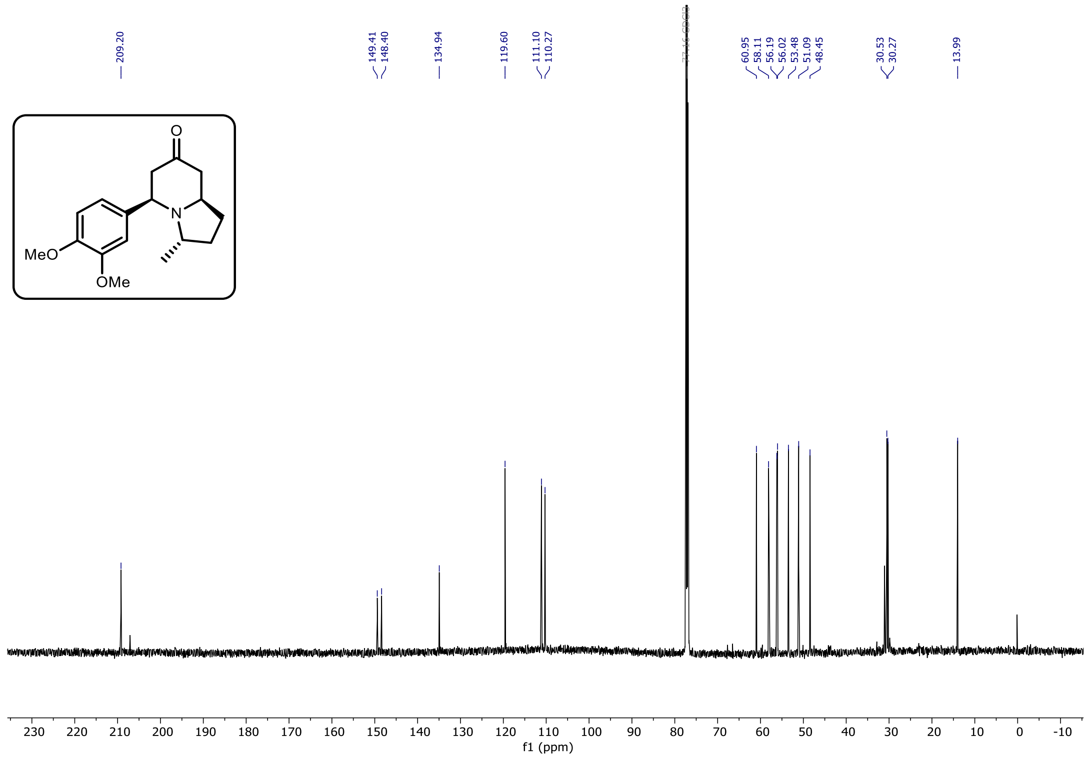
***A123**: COSY NMR (CDCl$_3$) of compound* 4*R*,6*S*,9a*R*-**4e**.



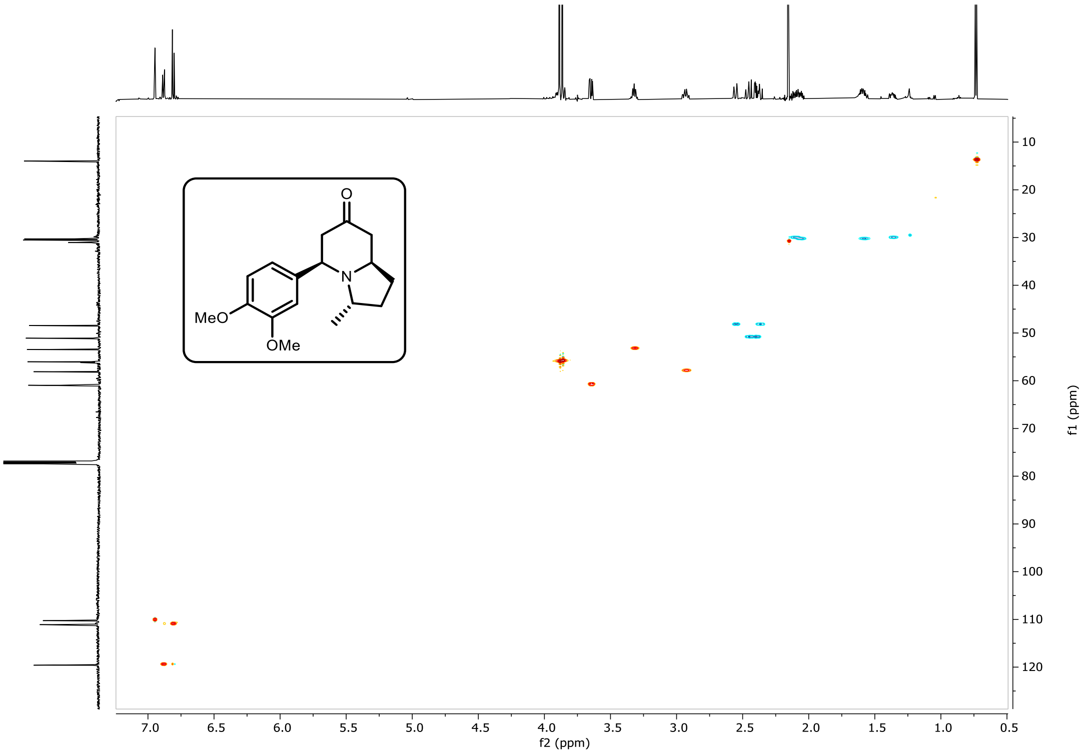
***A124**: NOESY (CDCl$_3$) of compound* 4*R*,6*S*,9a*R*-**4e**.



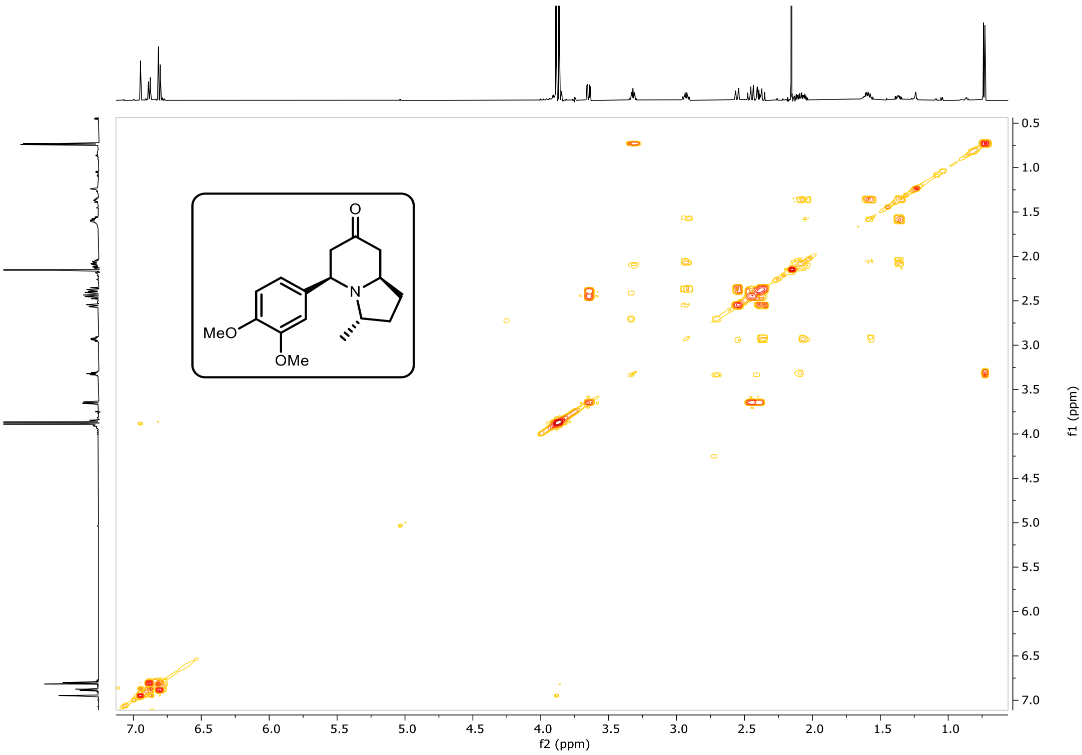
A125: *[1]H NMR (CDCl$_3$) of compound 3S,5R,8aR-**4f**.*



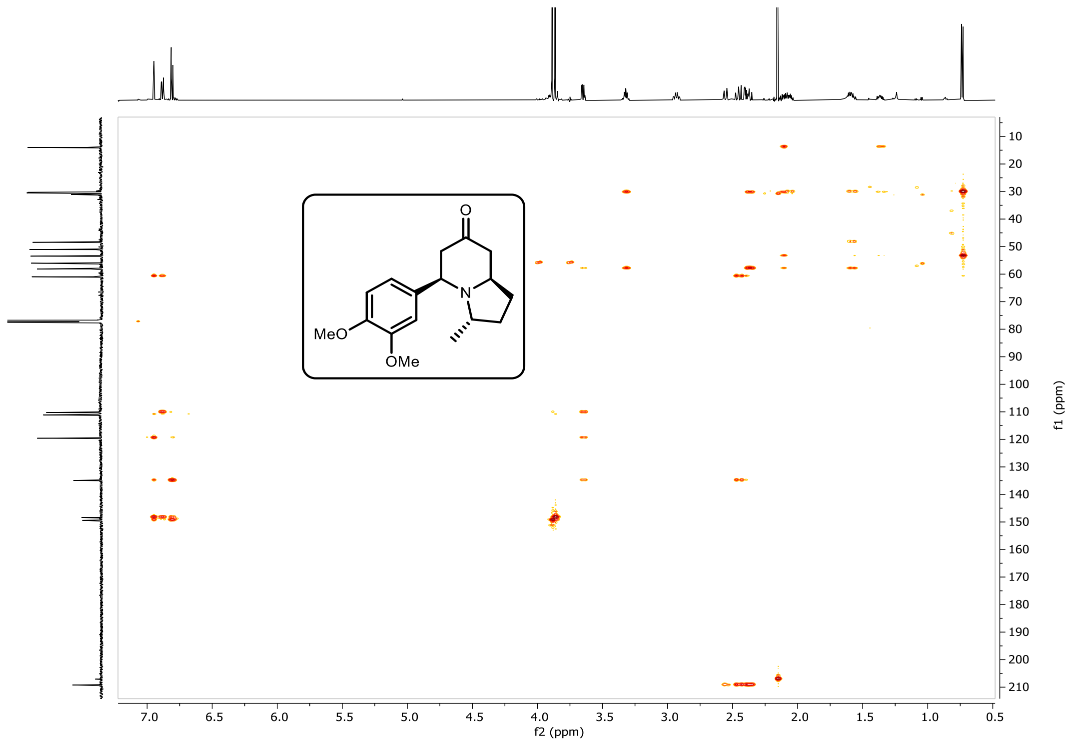
A126: *[13]C NMR (CDCl$_3$) of compound 3S,5R,8aR-**4f**.*



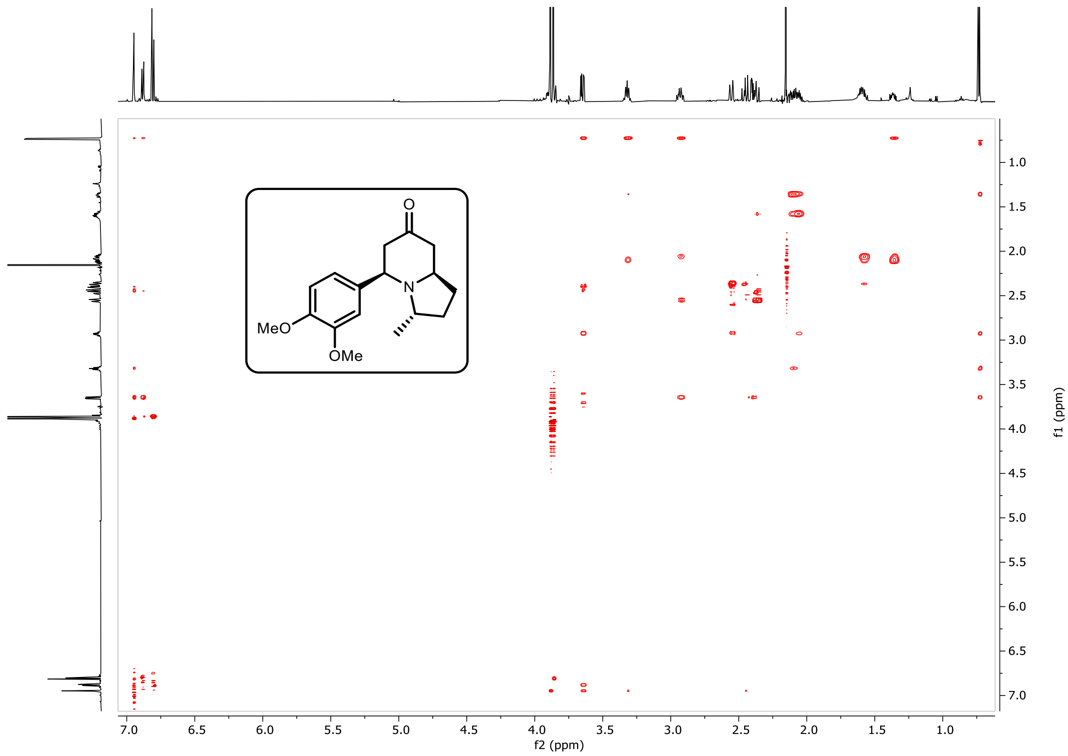
A127: *HSQC ($CDCl_3$) of compound 3S,5R,8aR-**4f**.*



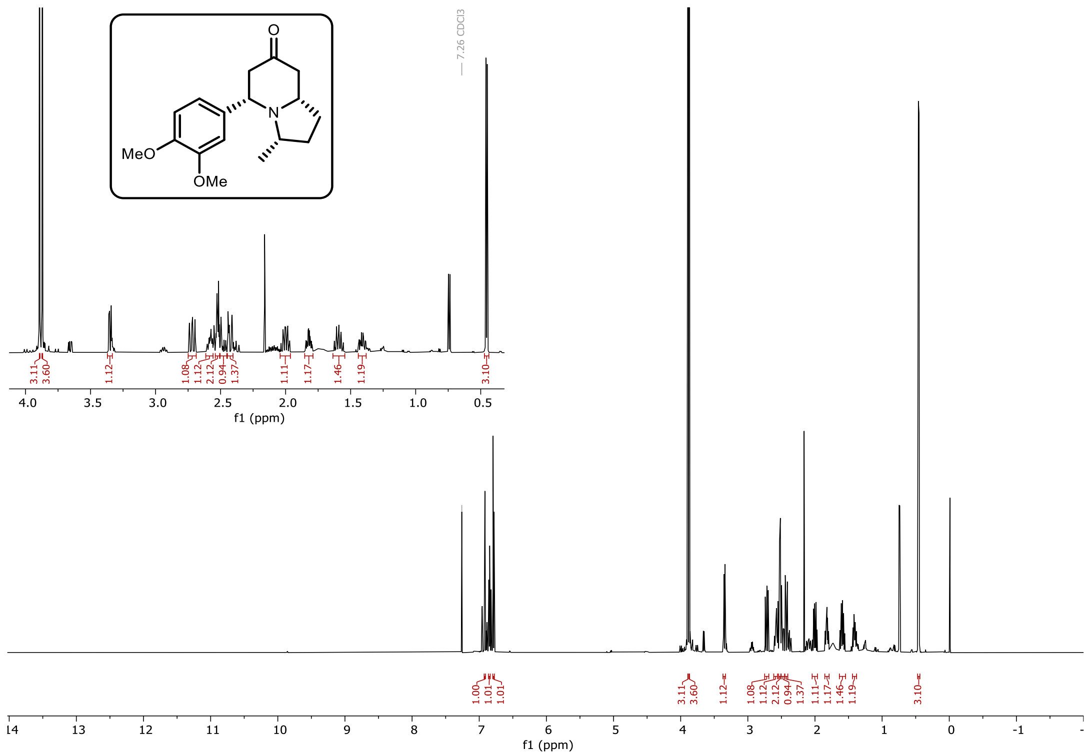
A128: *COSY NMR ($CDCl_3$) of compound 3S,5R,8aR-**4f**.*



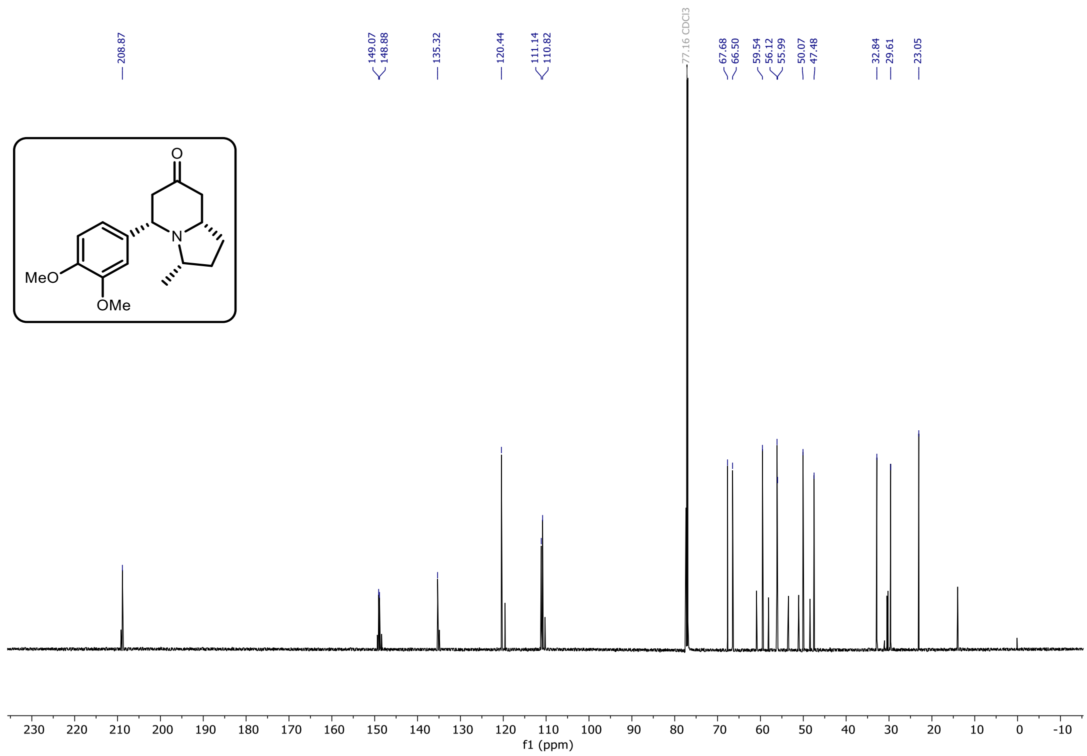
A129: *HMBC (CDCl$_3$) of compound 3S,5R,8aR-**4f**.*



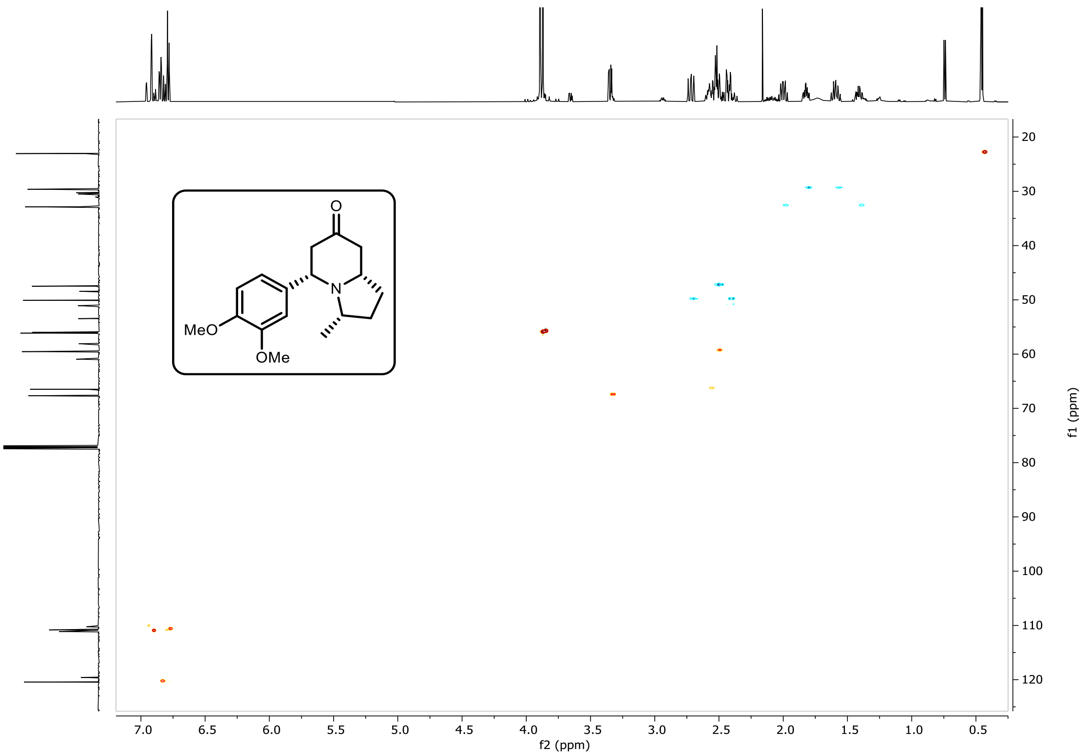
A130: *NOESY (CDCl$_3$) of compound 3S,5R,8aR-**4f**.*



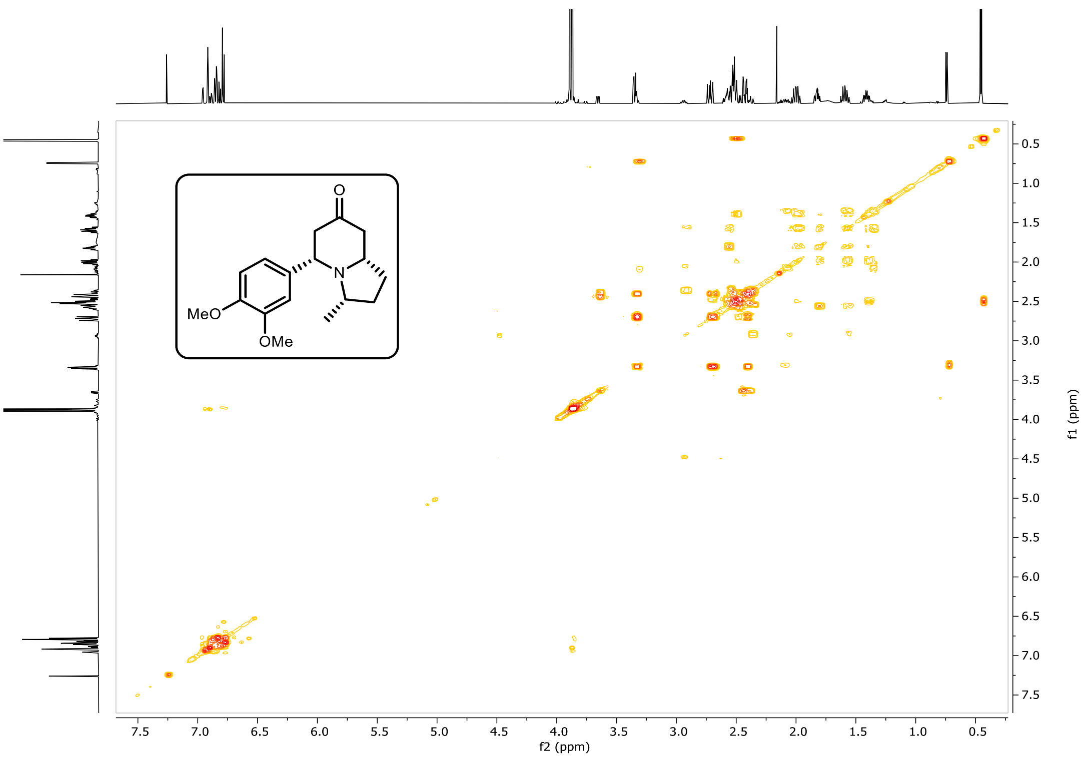
A131: *[1]H NMR (CDCl$_3$) of compound 3S,5S,8aS-**4f**.*



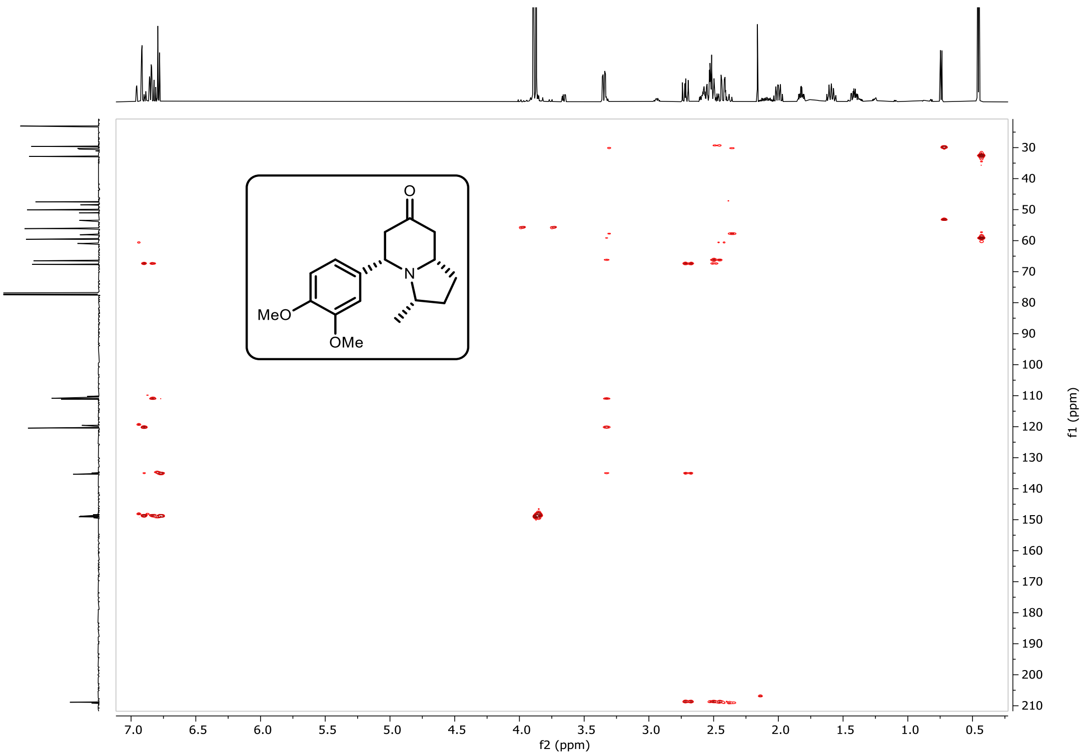
A132: *[13]C NMR (CDCl$_3$) of compound 3S,5S,8aS-**4f**.*



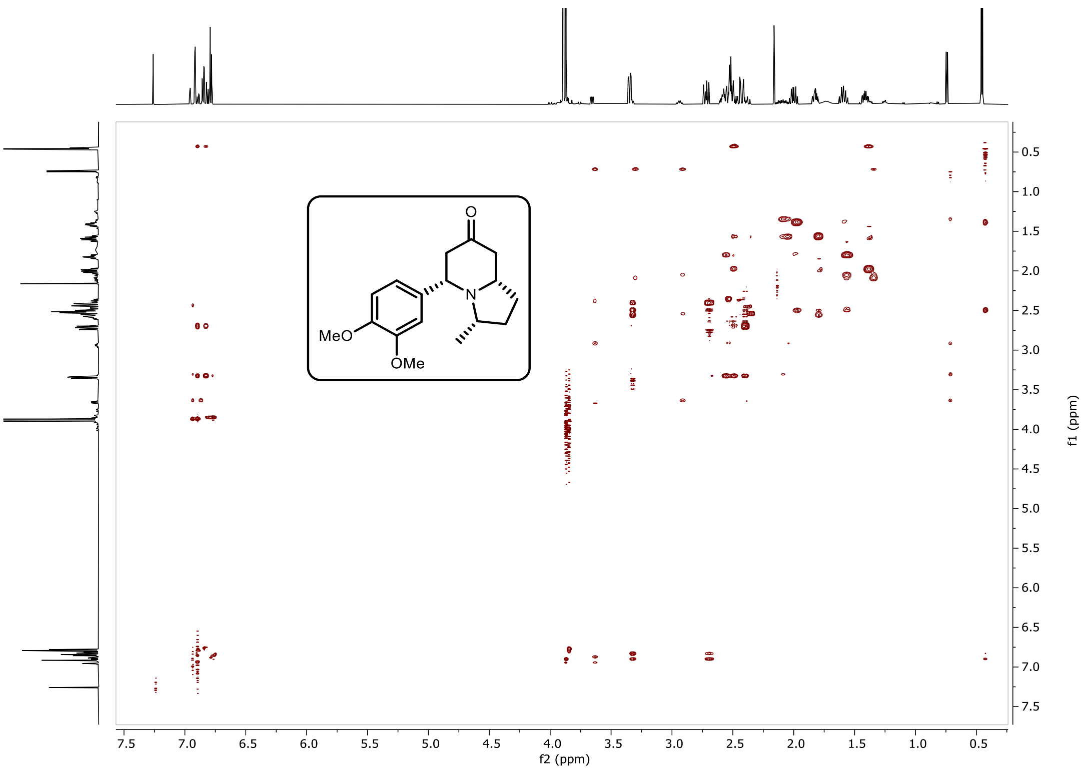
***A133:** HSQC ($CDCl_3$) of compound 3S,5S,8aS-**4f**.*



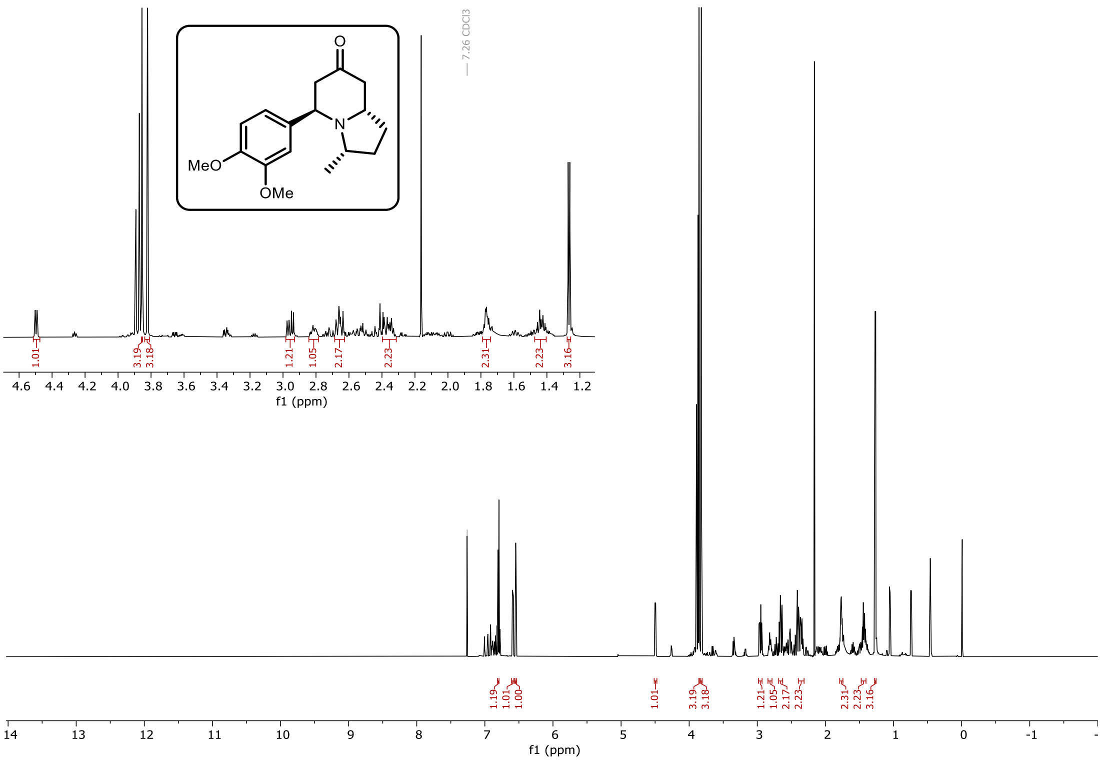
***A134:** COSY NMR ($CDCl_3$) of compound 3S,5S,8aS-**4f**.*



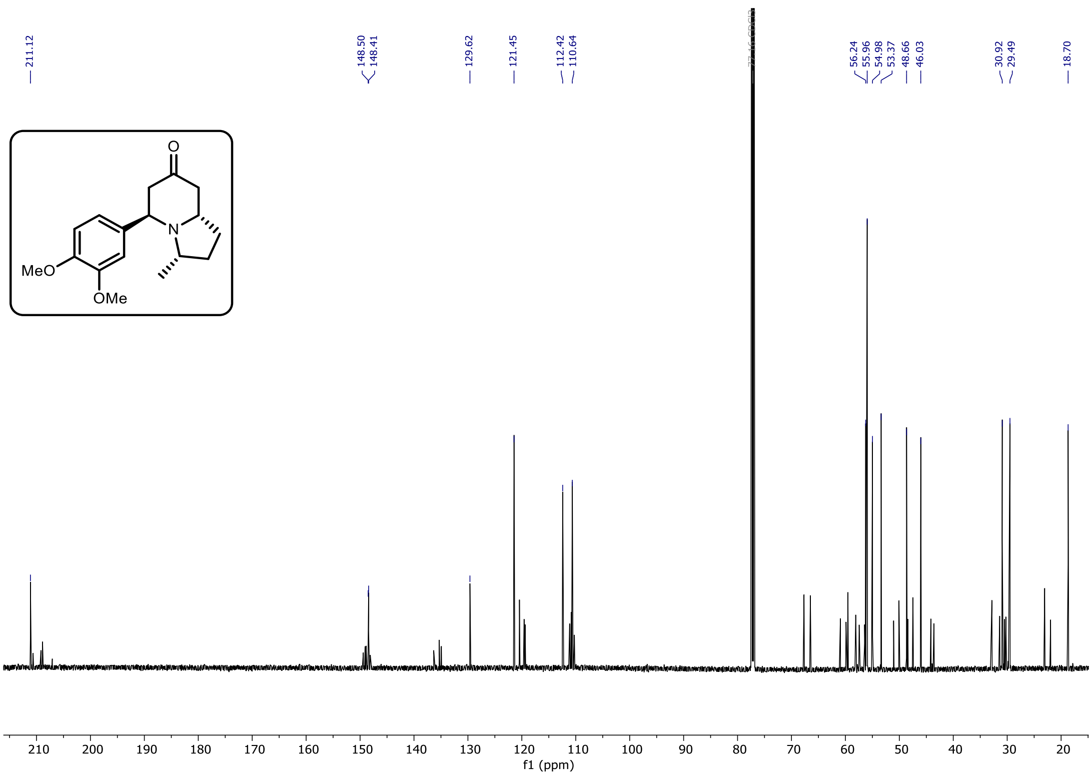
***A135:** HMBC (CDCl$_3$) of compound 3S,5S,8aS-**4f**.*



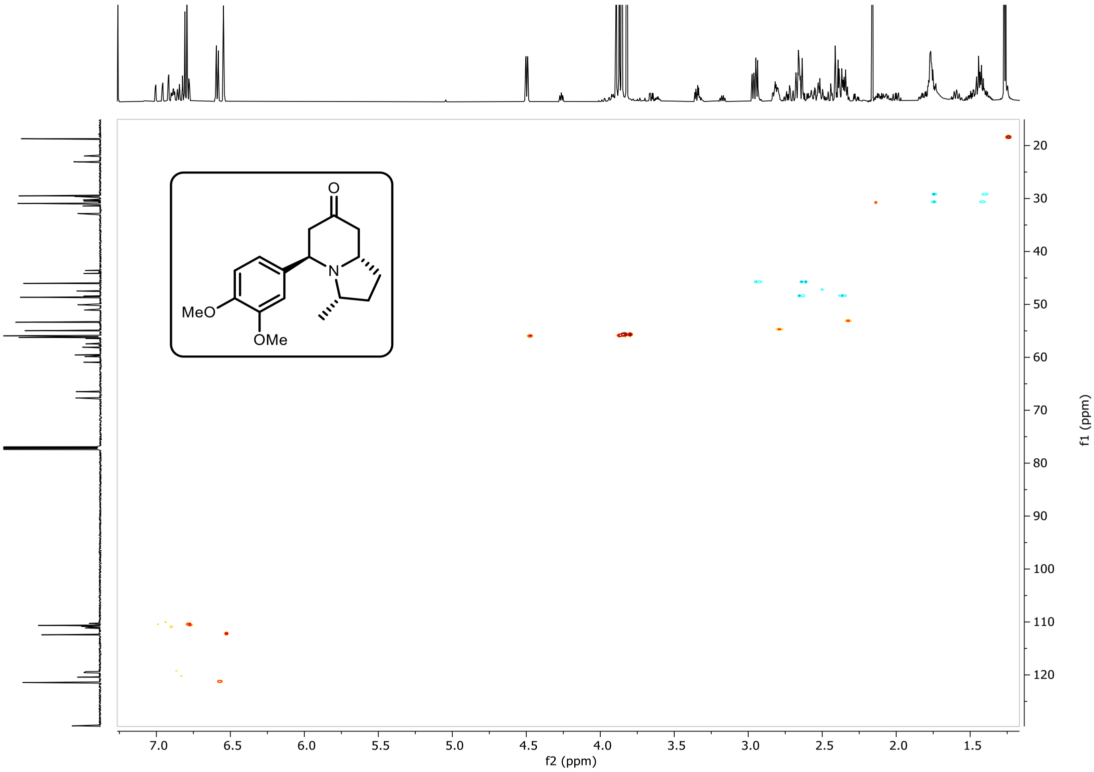
***A136:** NOESY (CDCl$_3$) of compound 3S,5S,8aS-**4f**.*



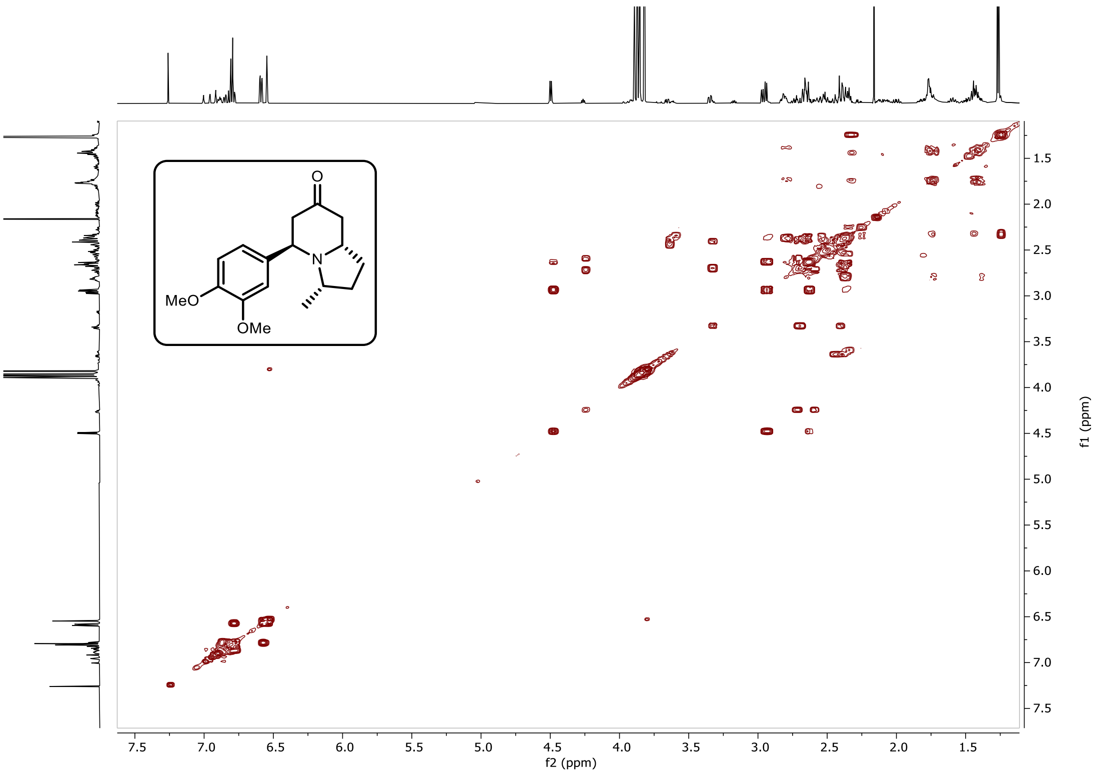
A137: *[1]H NMR (CDCl$_3$) of compound 3S,5R,8aS-**4f** (enriched).*



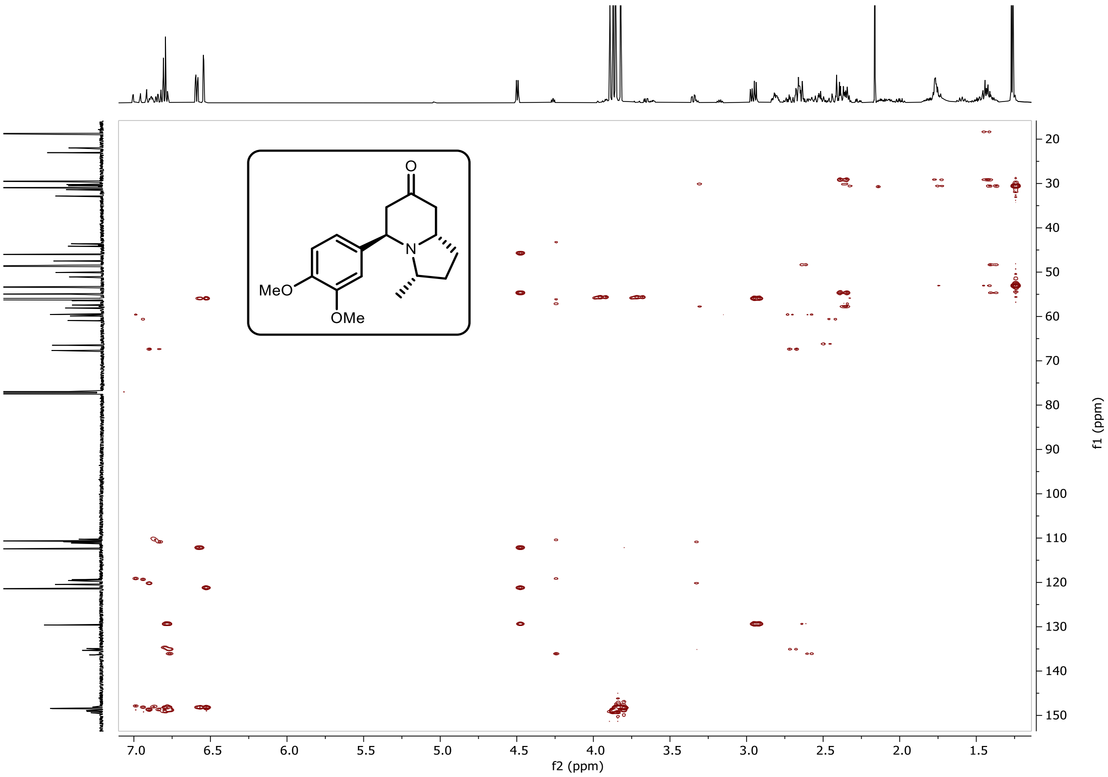
A138: *[13]C NMR (CDCl$_3$) of compound 3S,5R,8aS-**4f** (enriched).*



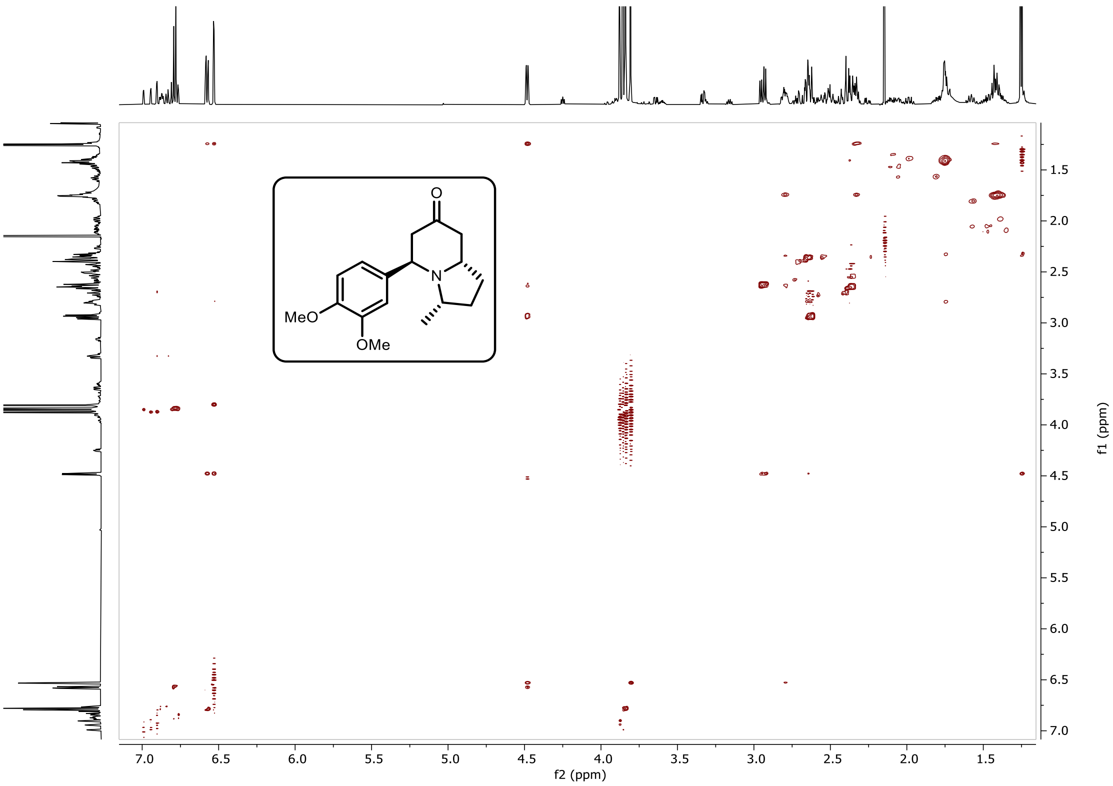
A139: *HSQC (CDCl$_3$) of compound 3S,5R,8aS-**4f** (enriched).*



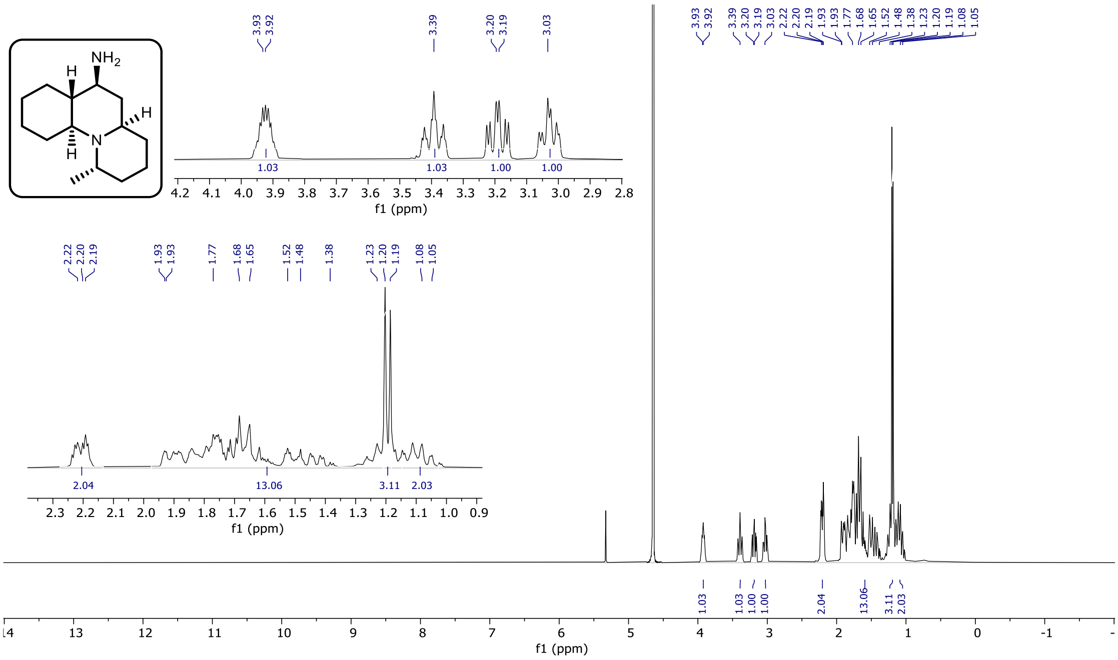
A140: *COSY NMR (CDCl$_3$) of compound 3S,5R,8aS-**4f** (enriched).*



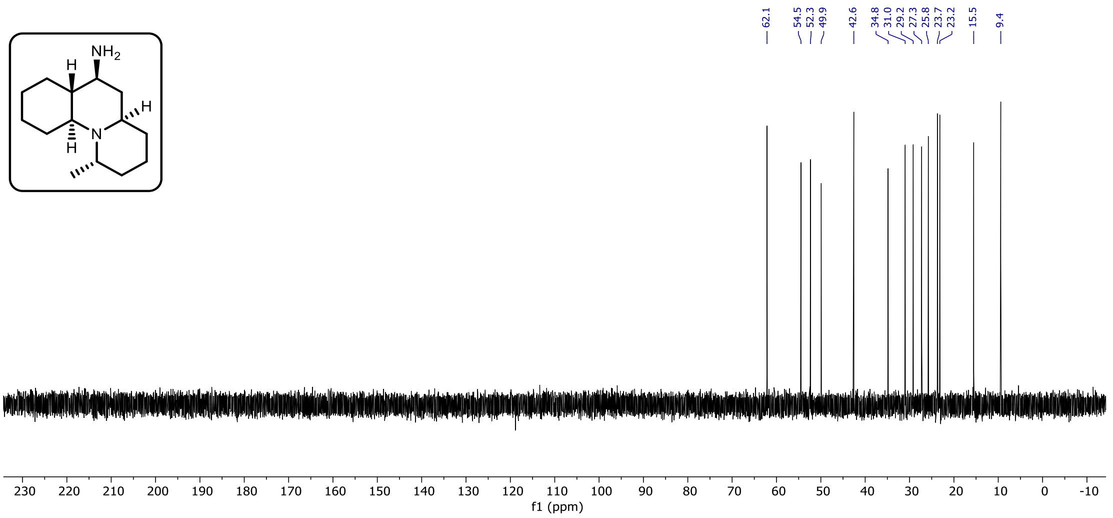
A141: *HMBC (CDCl₃) of compound 3S,5R,8aS-**4f** (enriched).*



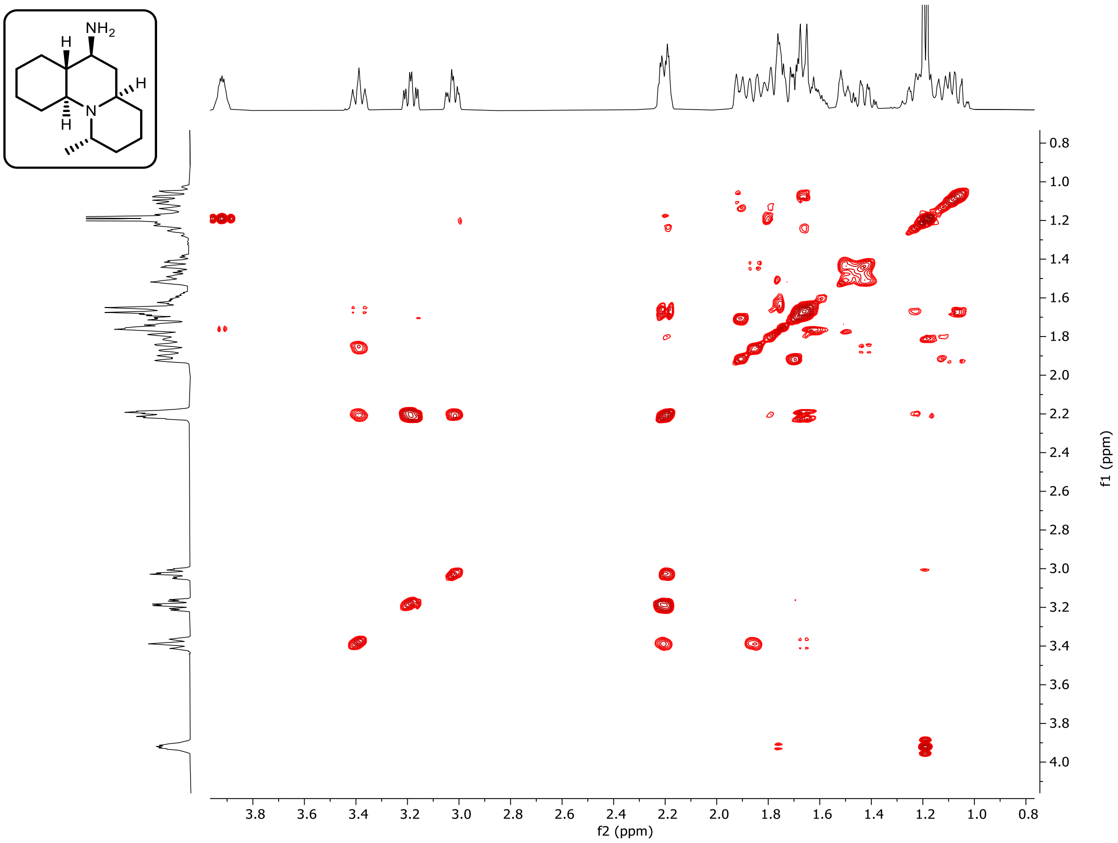
A142: *NOESY (CDCl₃) of compound 3S,5R,8aS-**4f** (enriched).*



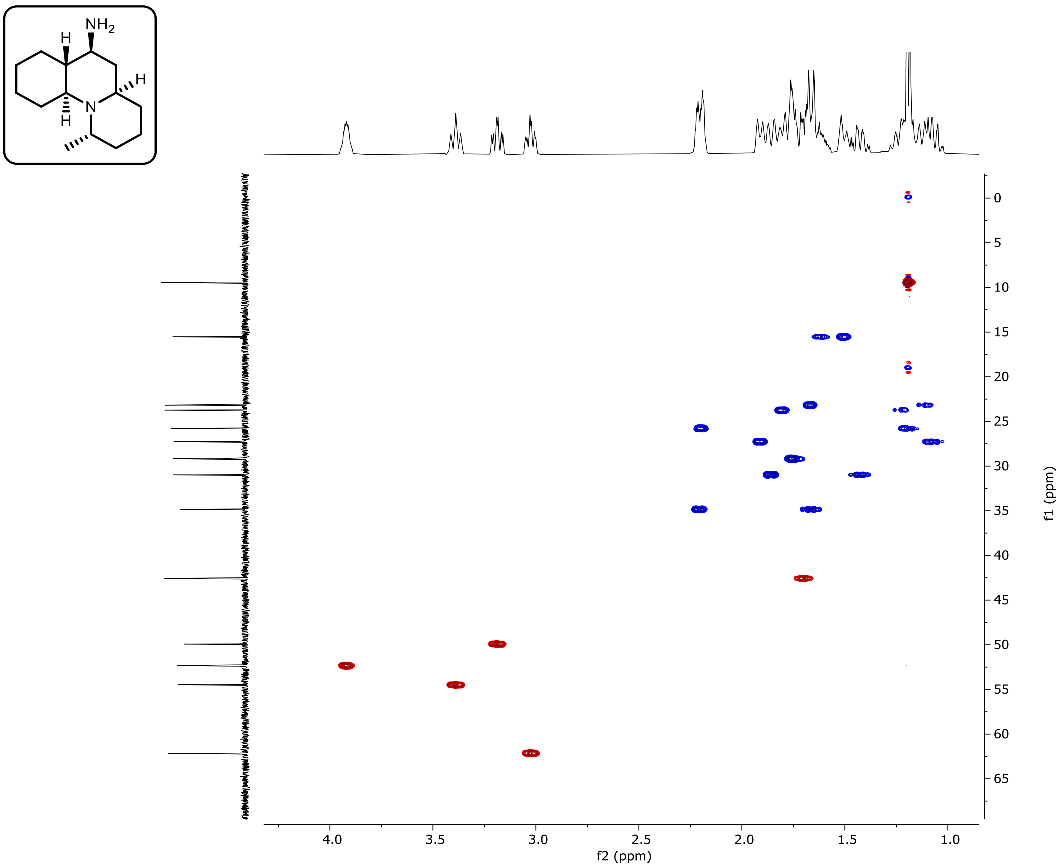
***A143:** ¹H NMR (D₂O) of compound **5a**.*



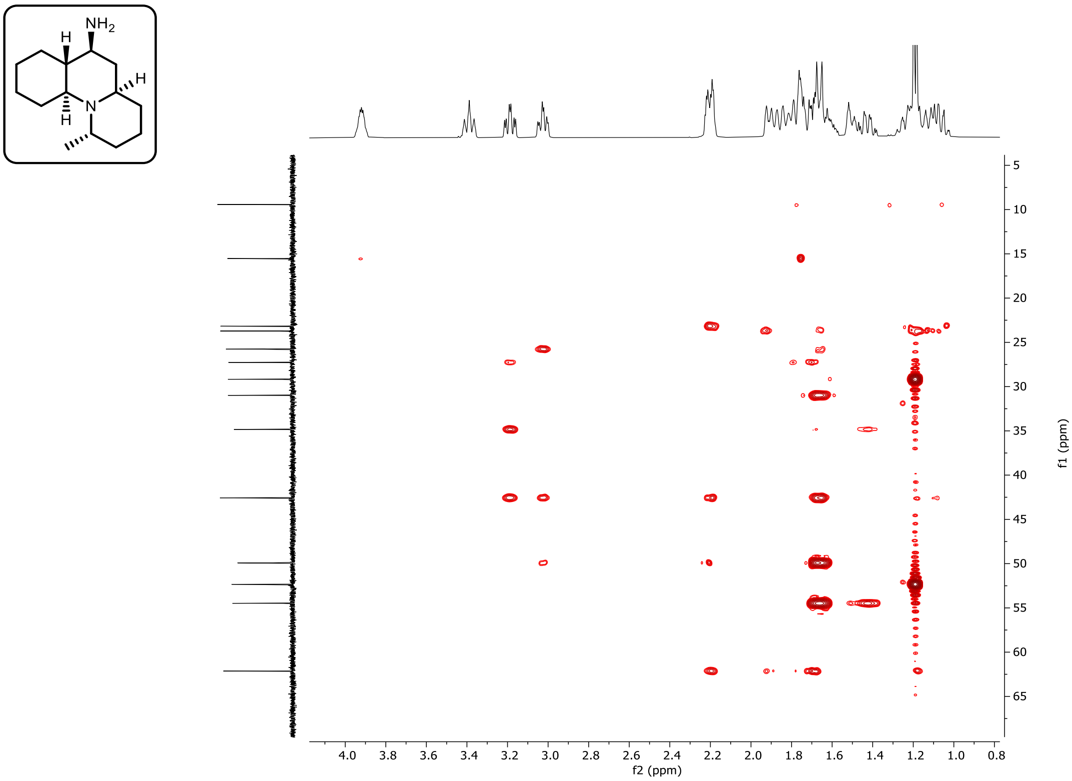
***A144:** ¹³C NMR (D₂O) of compound **5a**.*



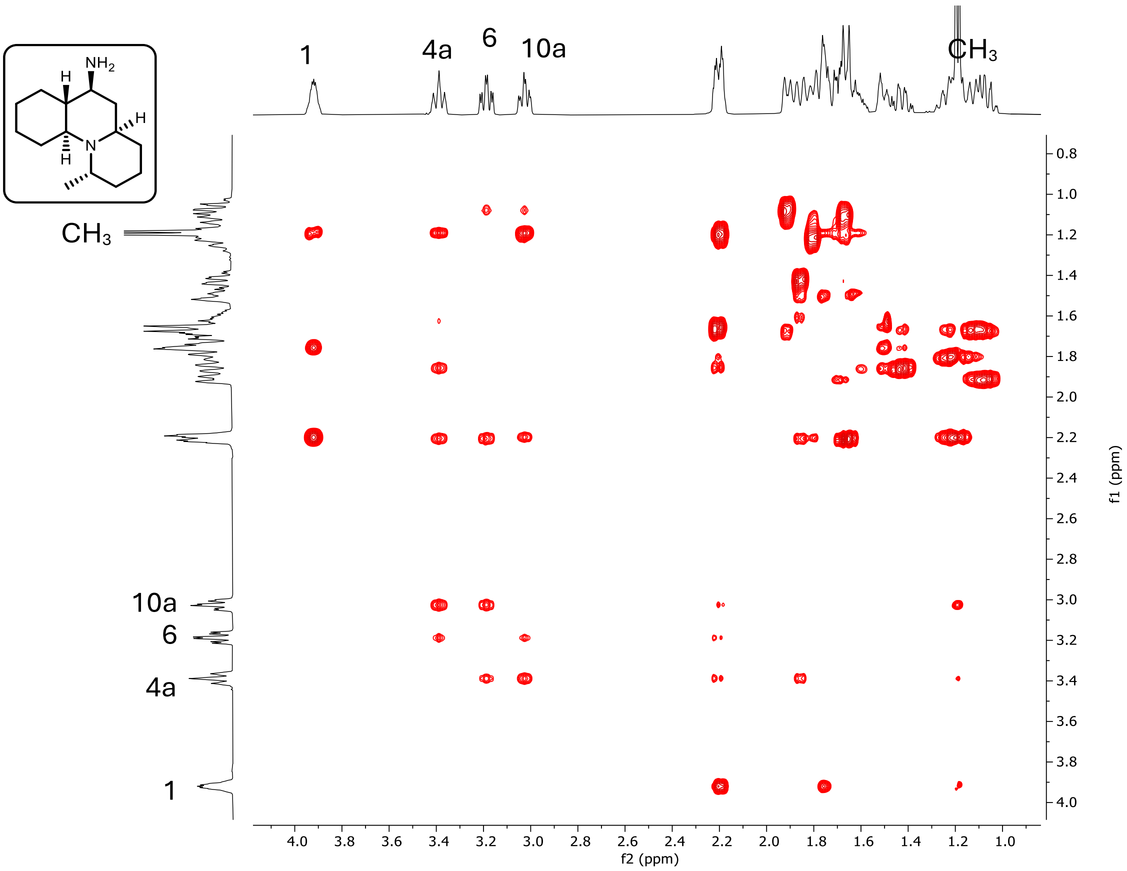
***A145:** COSY NMR (D_2O) of compound **5a**.*



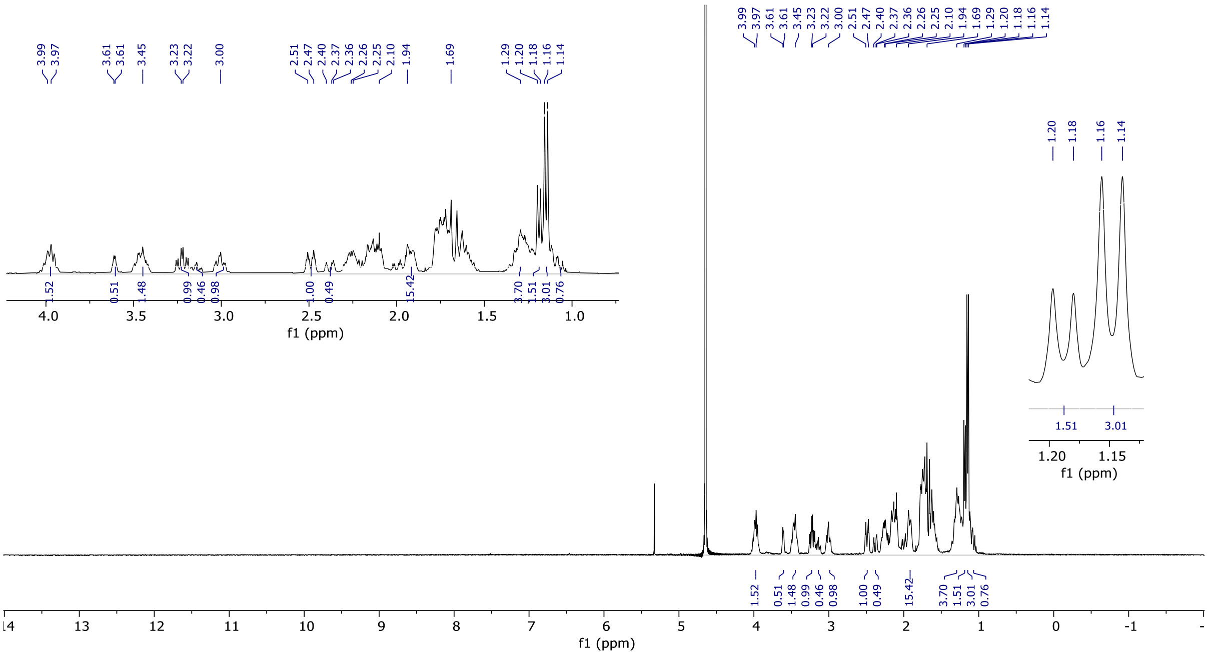
***A146:** HSQC (D_2O) of compound **5a**.*



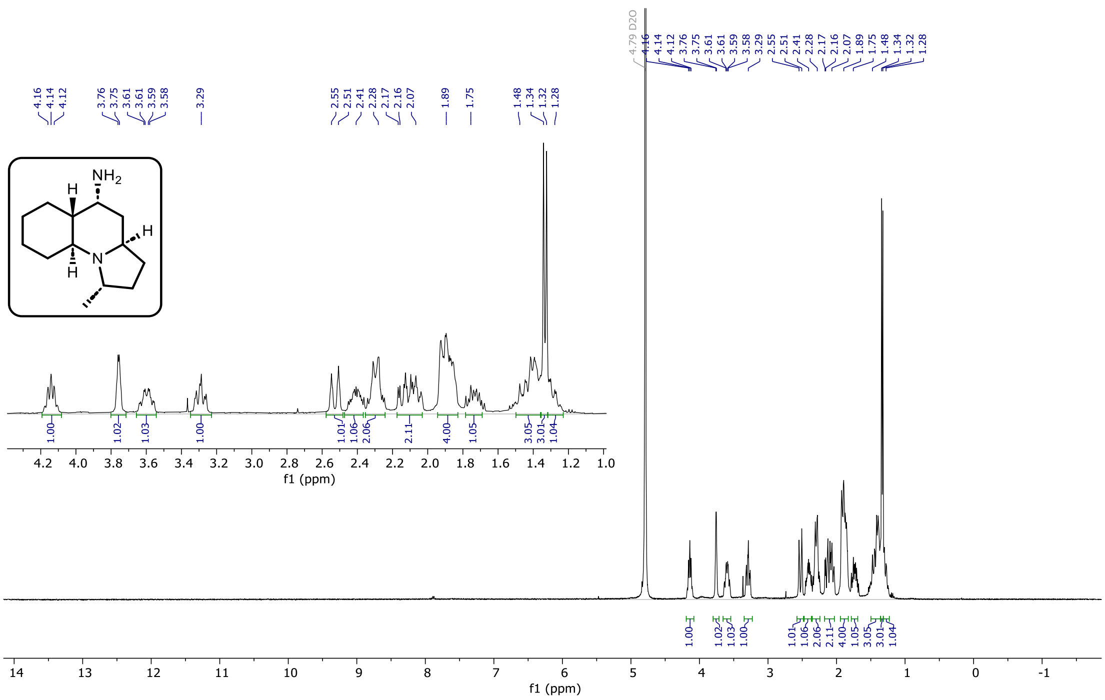
***A147:** HMBC (D_2O) of compound **5a**.*



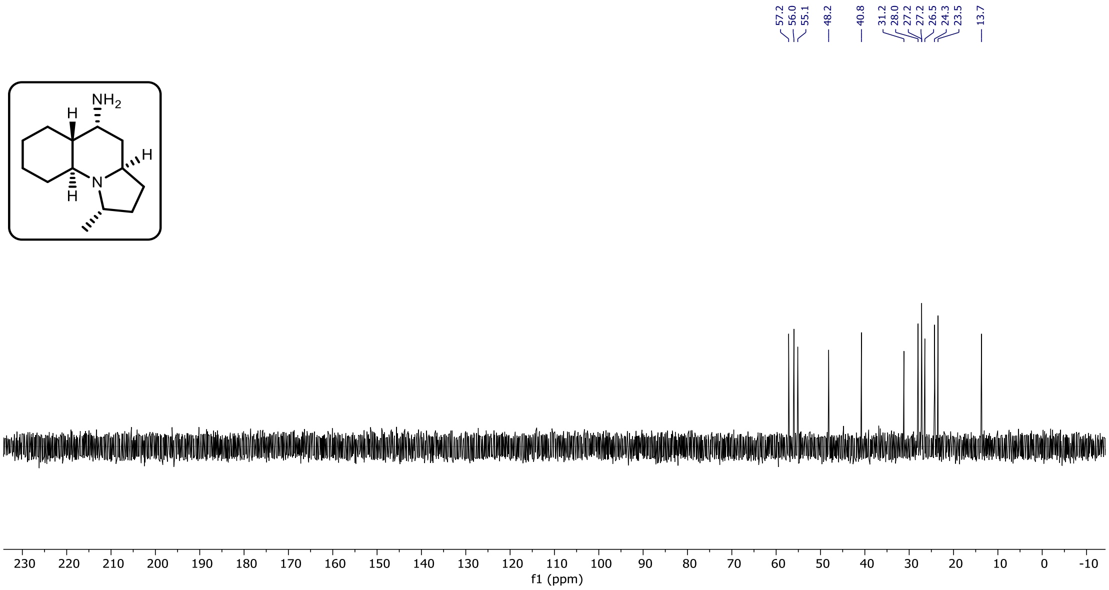
***A148:** NOESY (D_2O) of compound **5a**.*



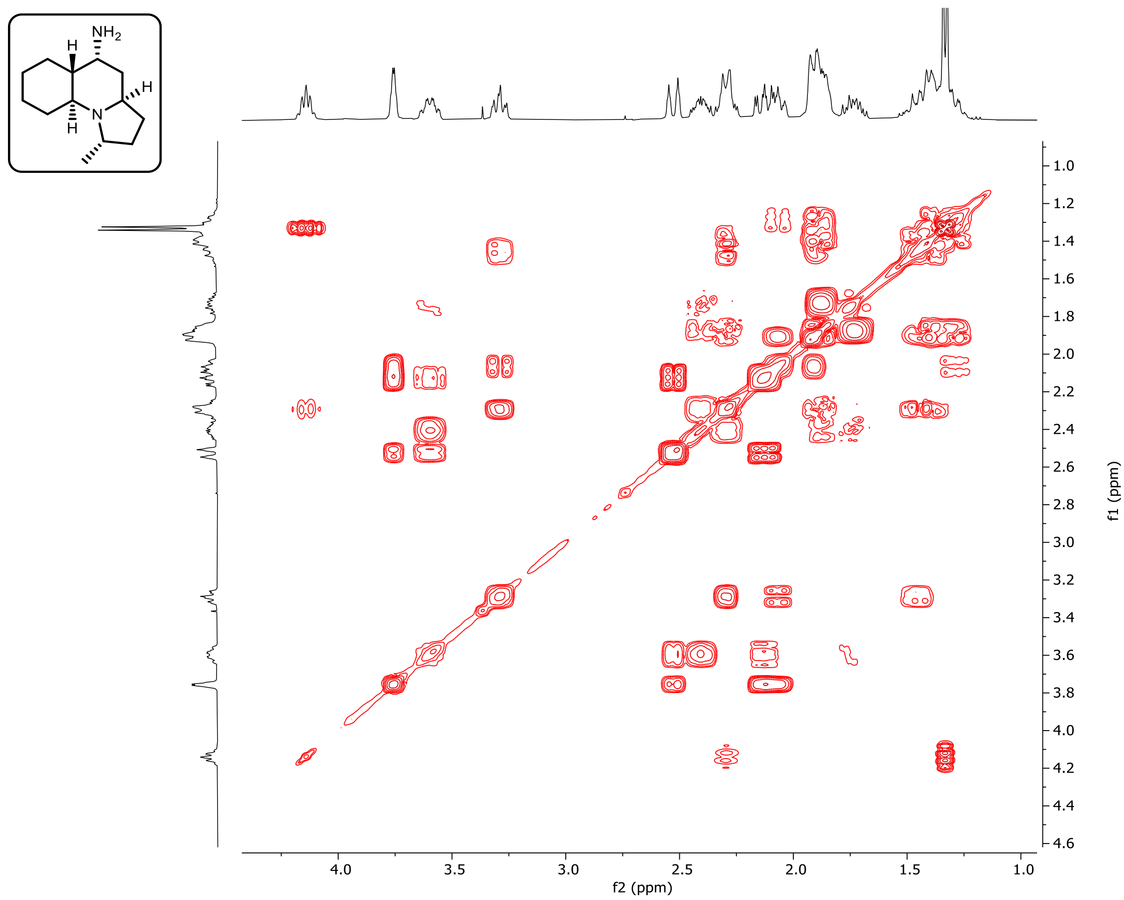
A149: ^{1}H NMR (D_2O) of compound (5*S*/5*R*)-**5c** in a 2:1 ratio from the transaminase catalysed biotransformation of **4c**.



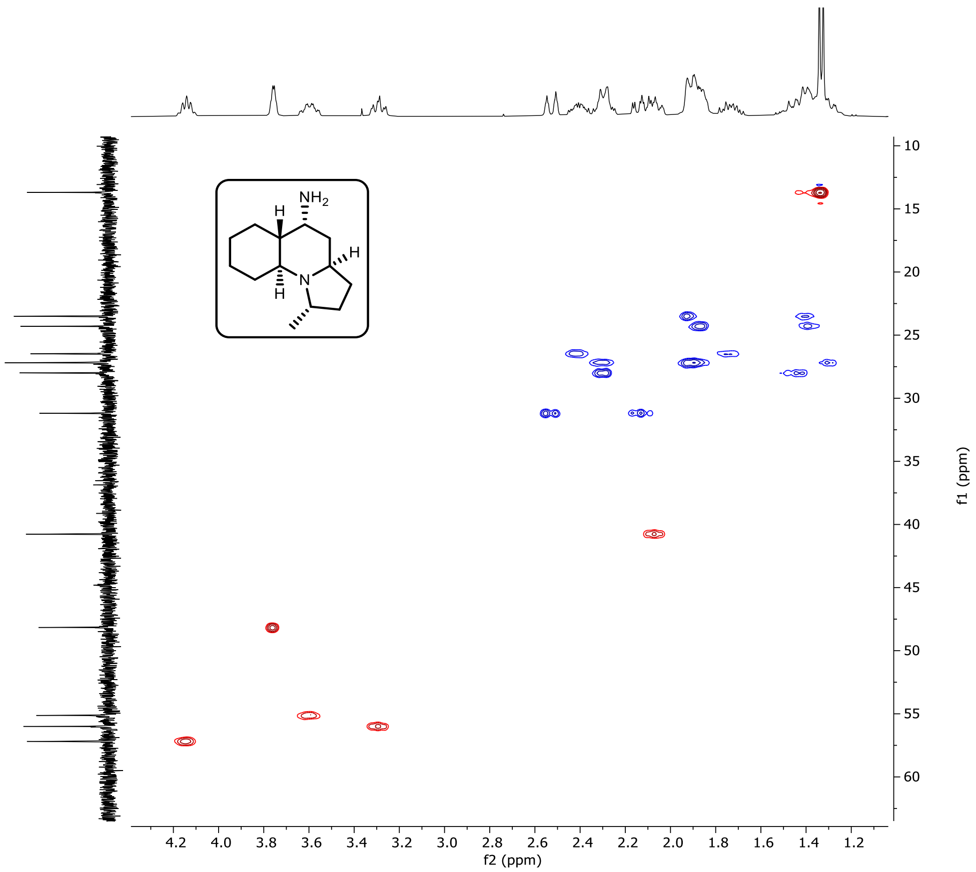
***A150:** ^{1}H NMR (D_2O) of compound 5R-**5c**.*



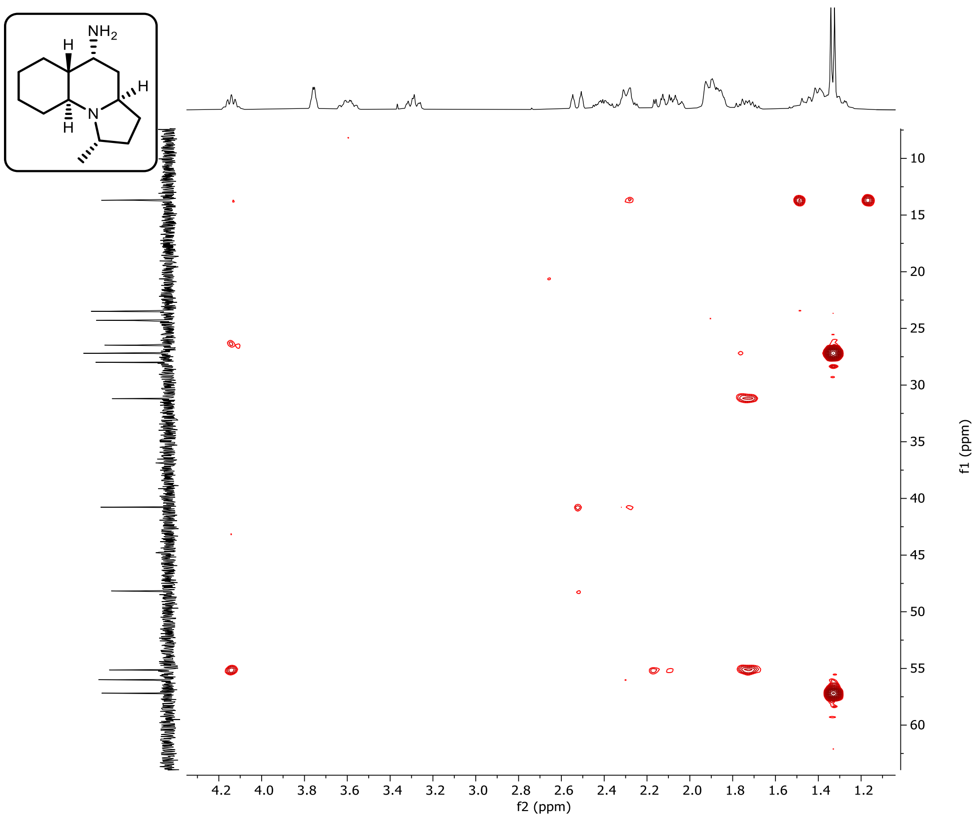
A151: *^{13}C NMR (D_2O) of compound 5R-**5c**.*



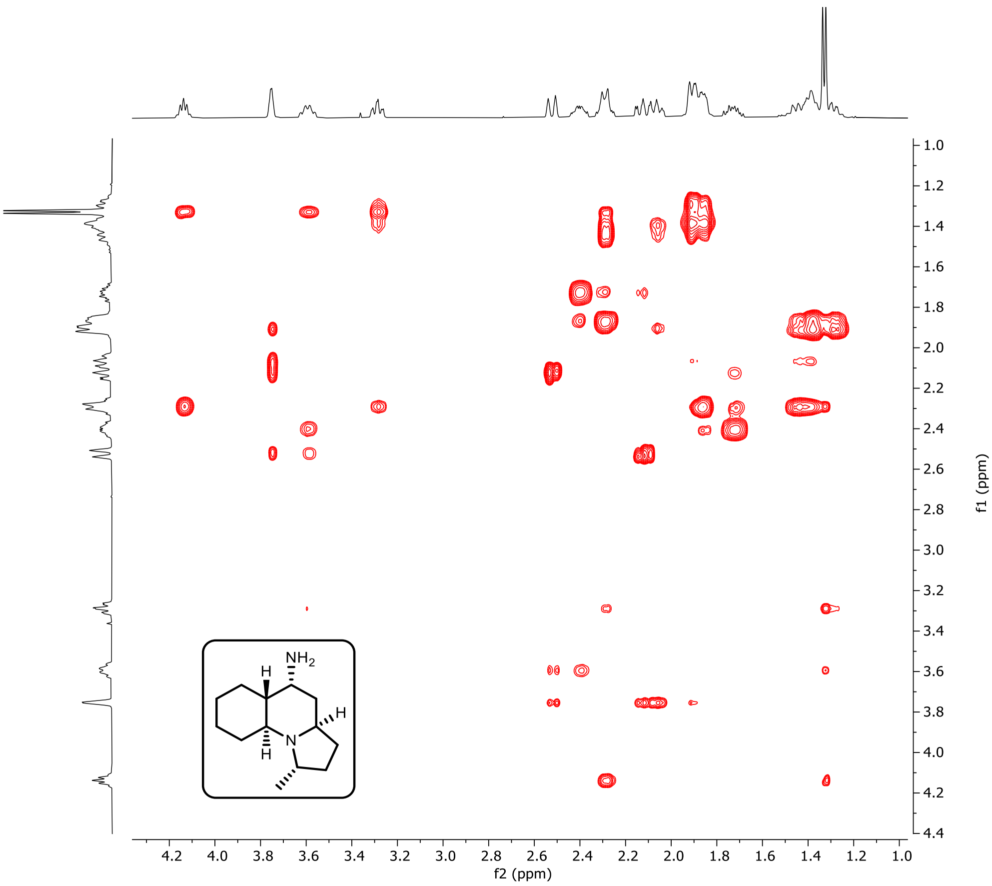
A152: *COSY NMR (D_2O) of compound 5R-**5c**.*



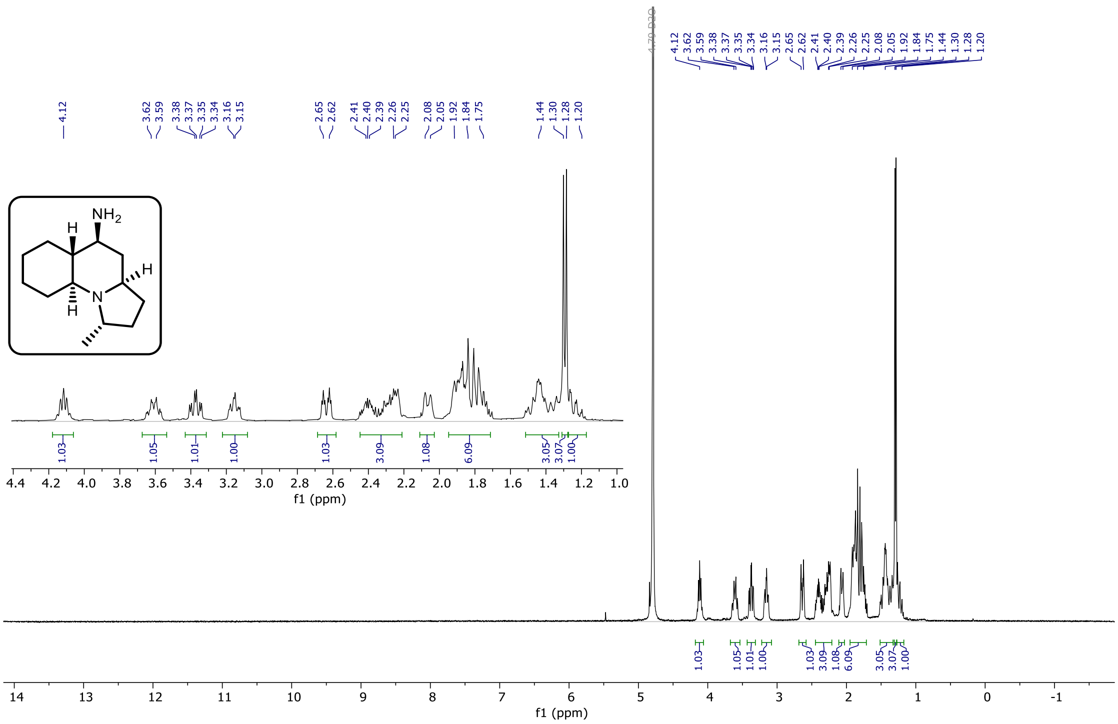
A153: *HSQC (D_2O) of compound 5R-**5c***



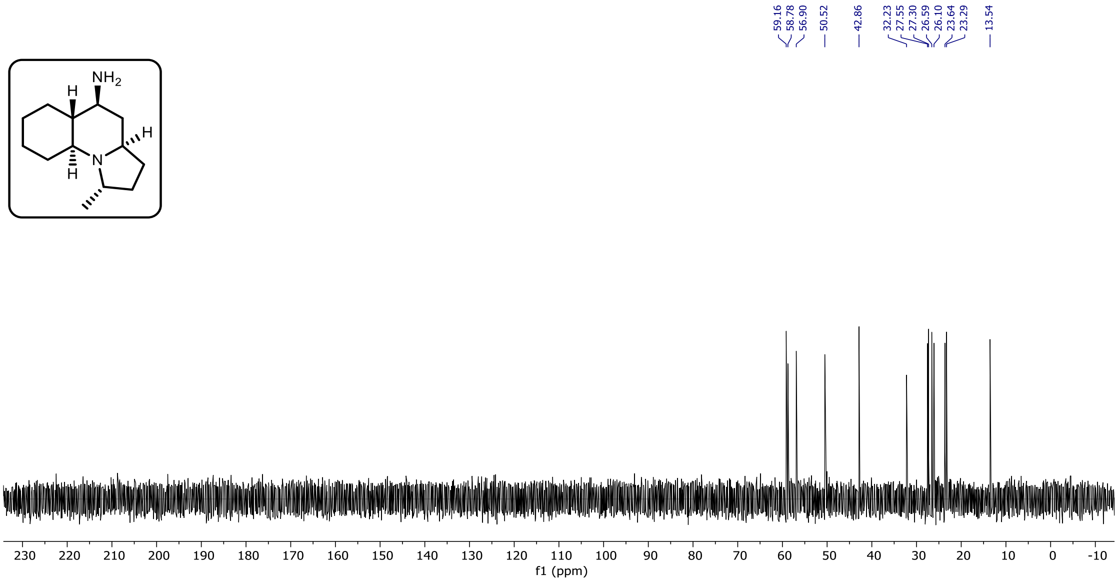
A154: *HMBC (D_2O) of compound 5R-**5c**.*



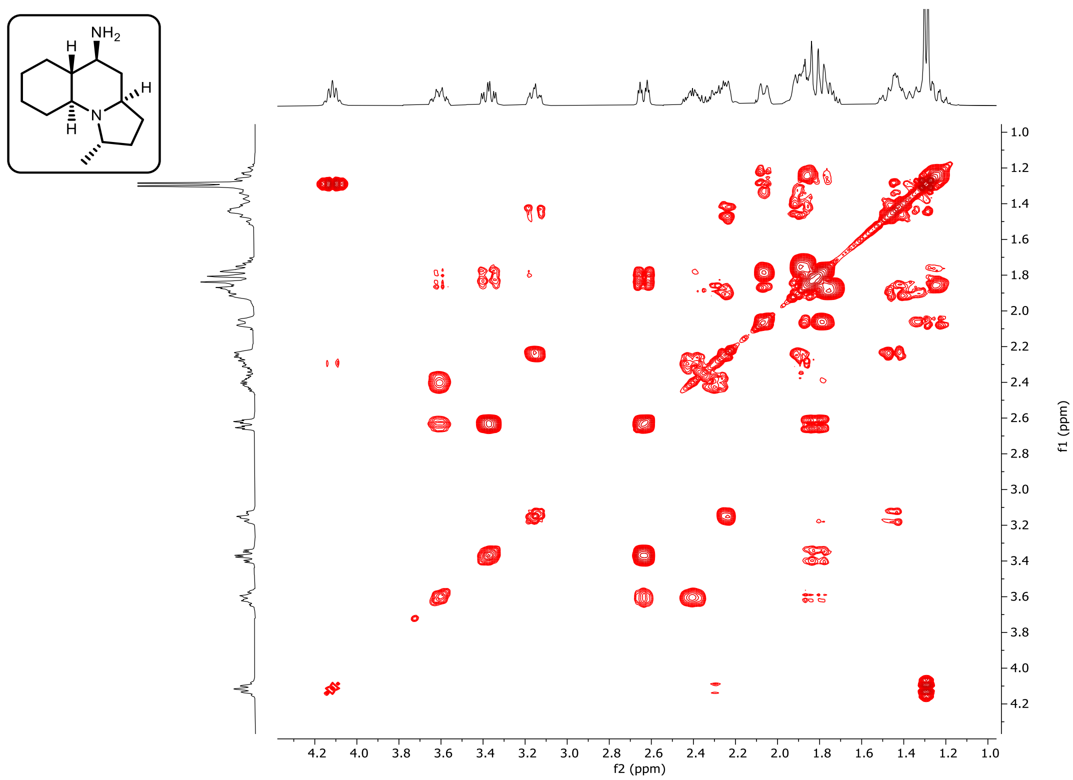
A155: *NOESY (D_2O) of compound 5R-**5c**.*



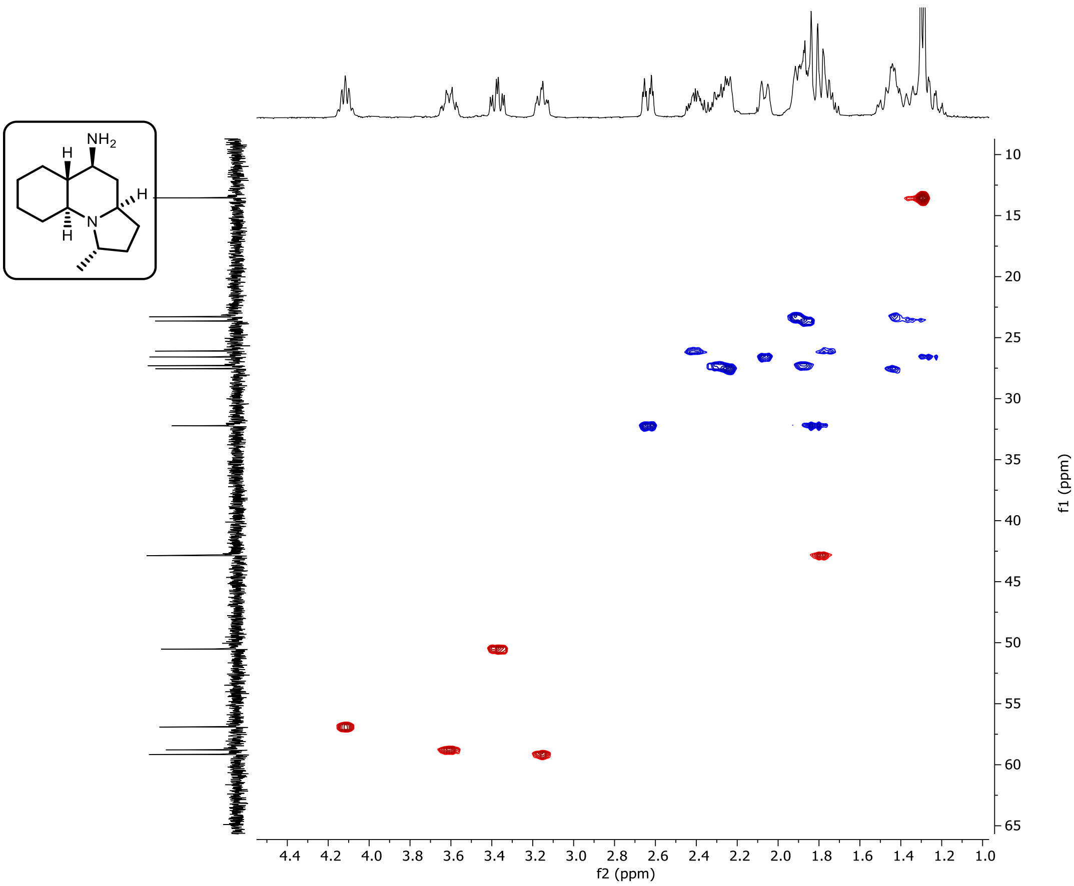
A156: *^1H NMR (D_2O) of compound 5S-**5c**.*



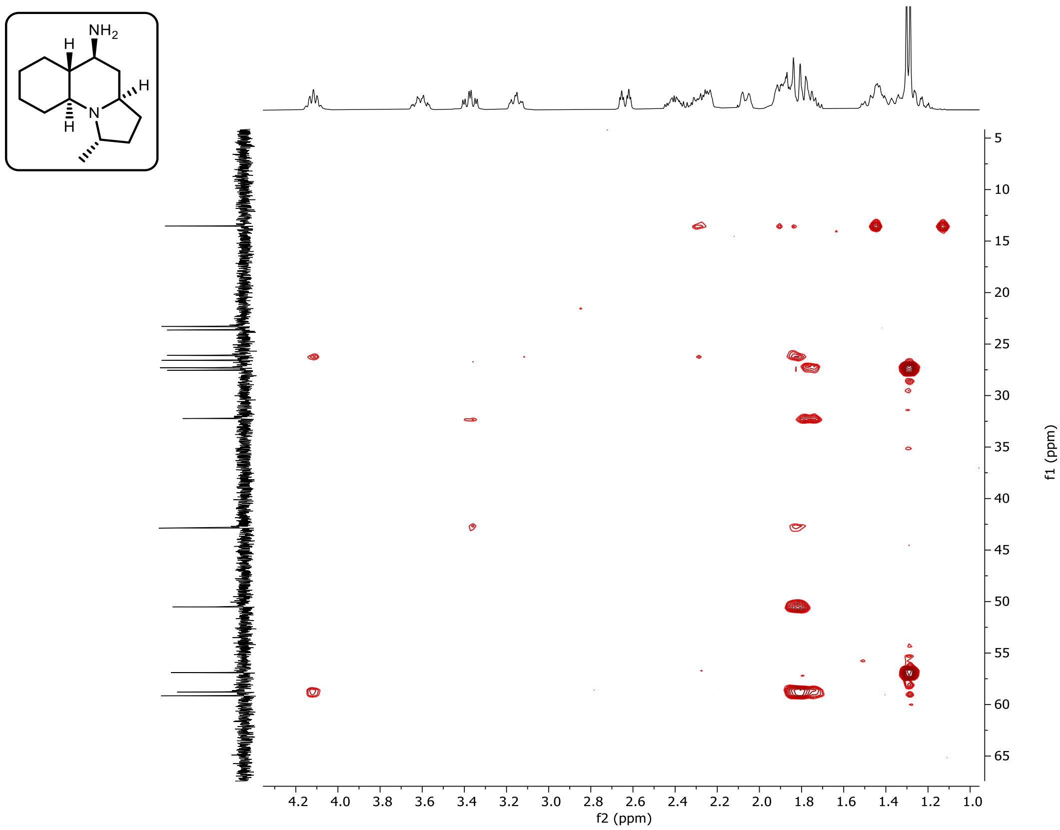
A157: *^{13}C NMR (D_2O) of compound 5S-**5c**.*



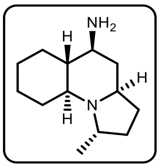
A158: *COSY NMR (D_2O) of compound 5S-**5c**.*

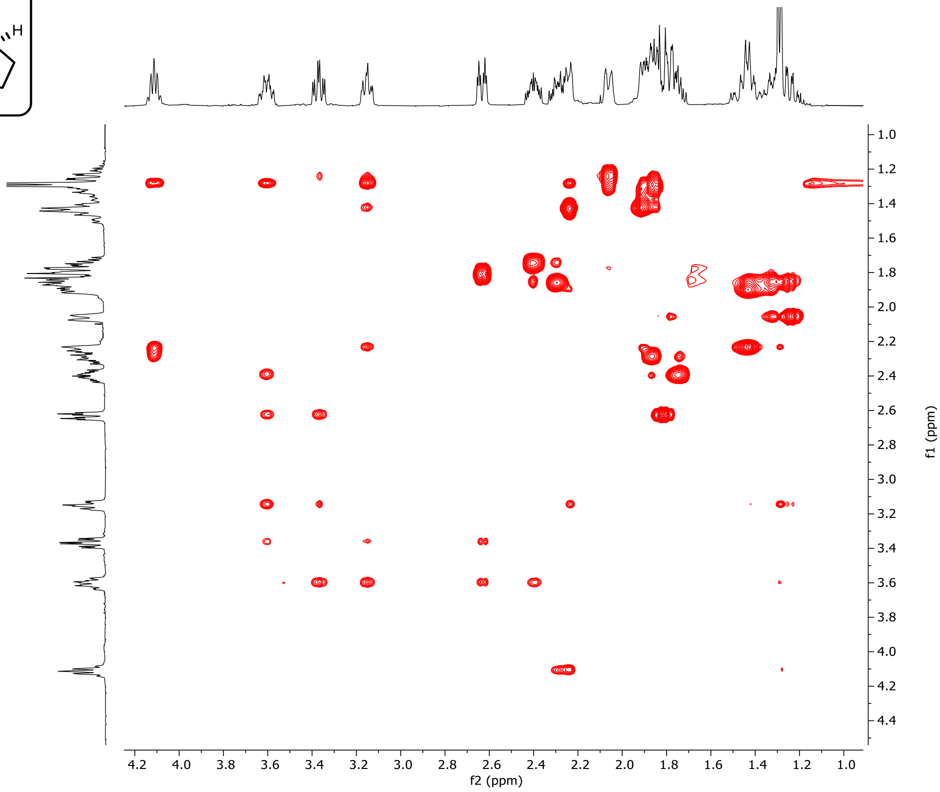


***A159:** HSQC (D_2O) of compound 5S-**5c**.*



***A160:** HMBC (D_2O) of compound 5S-**5c**.*





A161: *NOESY (D_2O) of compound 5S-**5c**.*

8. Chiral GC-MS Chromatograms

e.e. determination of compounds **3a** was carried out in an Agilent 5977B MSD combined to an Agilent 7890B GC system equipped with a Cyclosil-β chiral column (30 m long, 0.25 mm diam. narrowbore, 0.25 μm film).

Isothermic method, 130 °C, 10 psi. Helium used as carrier gas.

Cyclosil-β, 30 m long, 0.25 mm diam. narrowbore, 0.25 μm film

Isothermic 120 °C, 10 psi

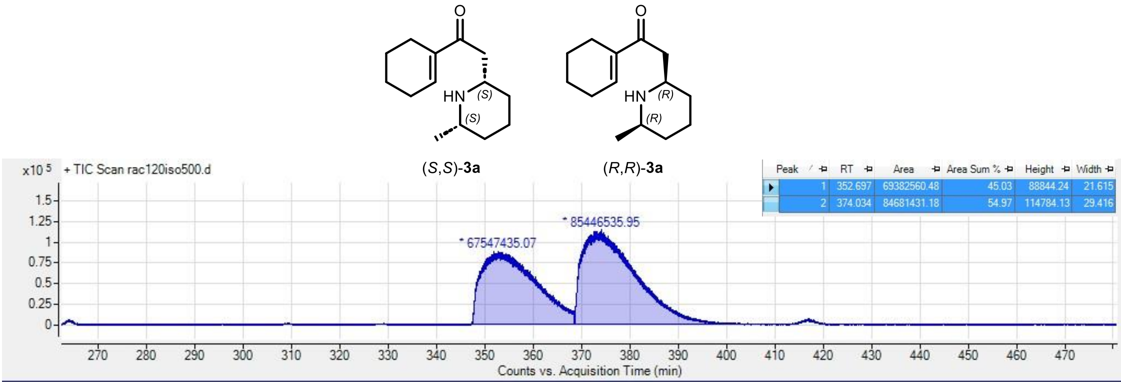


Figure S5: *Racemic sample – prepared by combined equal amounts of samples* (*S*,*S*)-***3a*** *and* (*R*,*R*)-***3a***.

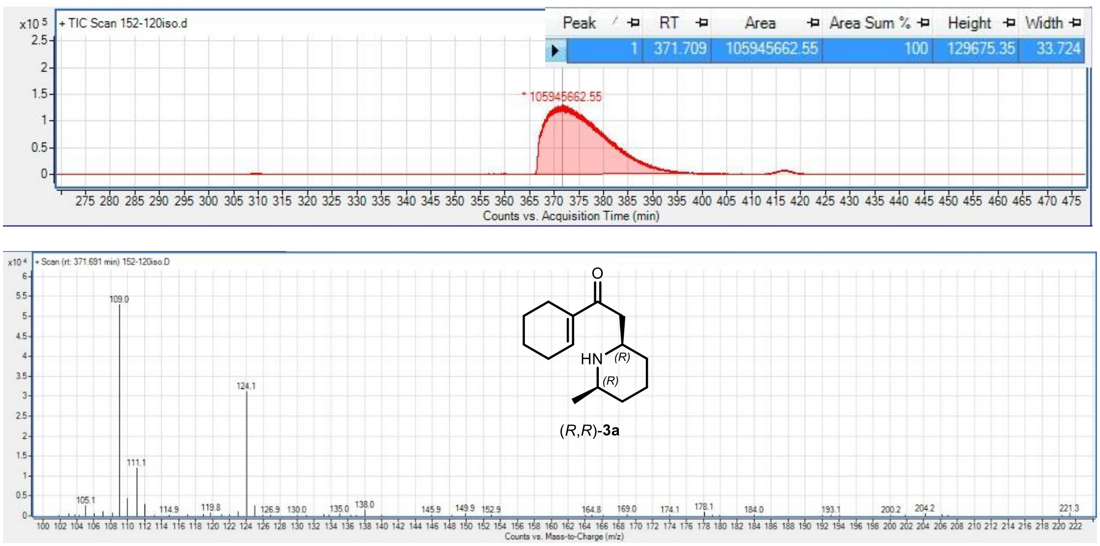


Figure S6: *GC-MS chromatograms of* (*R*,*R*)-***3a***.

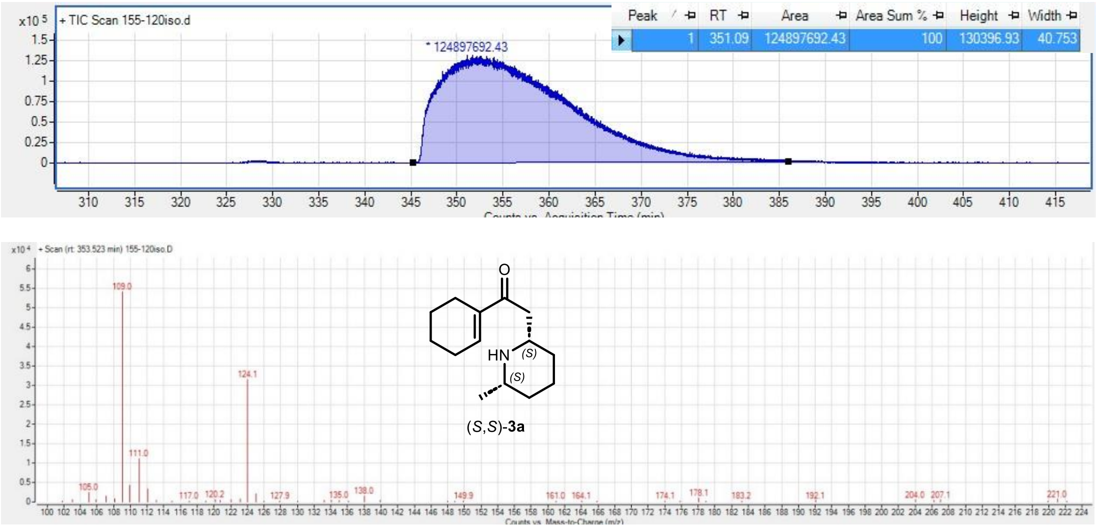
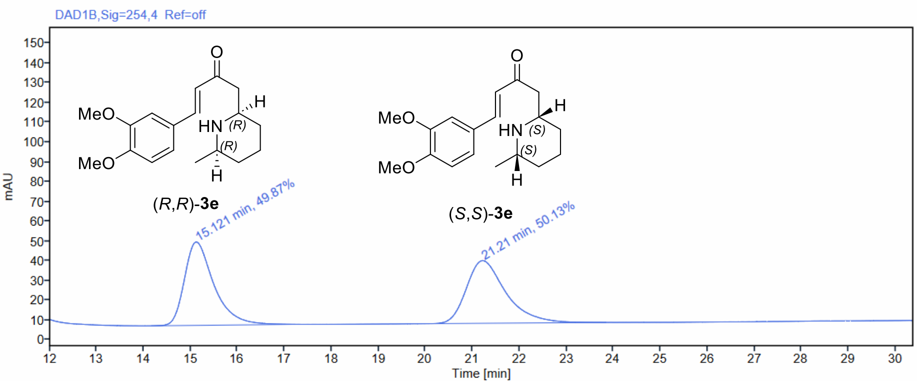


Figure S7: *GC-MS chromatograms of* (*S*,*S*)-***3a***.

9. Chiral HPLC Chromatograms

Chiral HPLC analysis of compound **3e** was performed using an Agilent Technologies 1200 series equipped with a binary pump (G1312A) and automated liquid sampler (G1329A); OJ-H, 1.0 mL/min, 95:5 Heptane/isopropanol.



Peak Results (Area Percent at least 1%)

RT (min)	Signal Description	Width (min)	Area	Height	Area%
15.121	DAD1B,Sig=254,4 Ref=off	3.097	1840.8	42.2	49.87
21.210	DAD1B,Sig=254,4 Ref=off	3.708	1850.2	31.7	50.13
	Sum DAD1B		3691.0		

Figure S8: *Racemic sample – prepared by combined equal amounts of samples* (*S*,*S*)-***3e*** *and* (*R*,*R*)-***3e***.

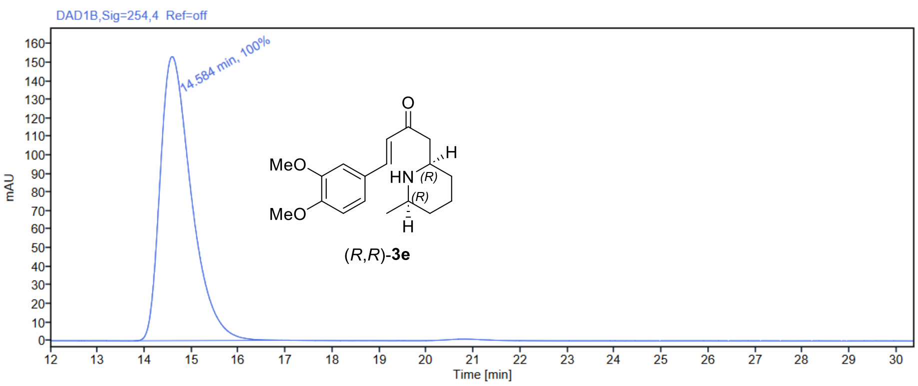


Figure S9: *HPLC chromatograms of* (*R*,*R*)-***3e***.

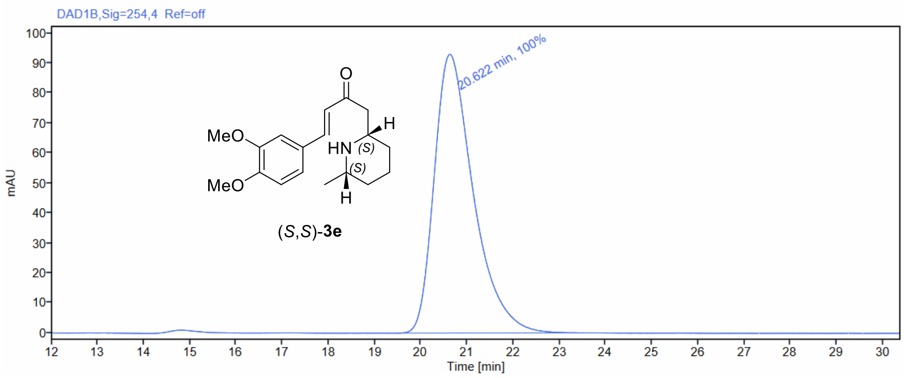


Figure S10: *HPLC chromatograms of* (*S*,*S*)-***3e***.

10. Energy calculations

All structures were constructed in ChemDraw and geometry-optimized (HF/6-31G*) in Gaussian16.[13] Hydrogen-hydrogen distances were calculated from the optimized structures using a TCL script (available upon request).

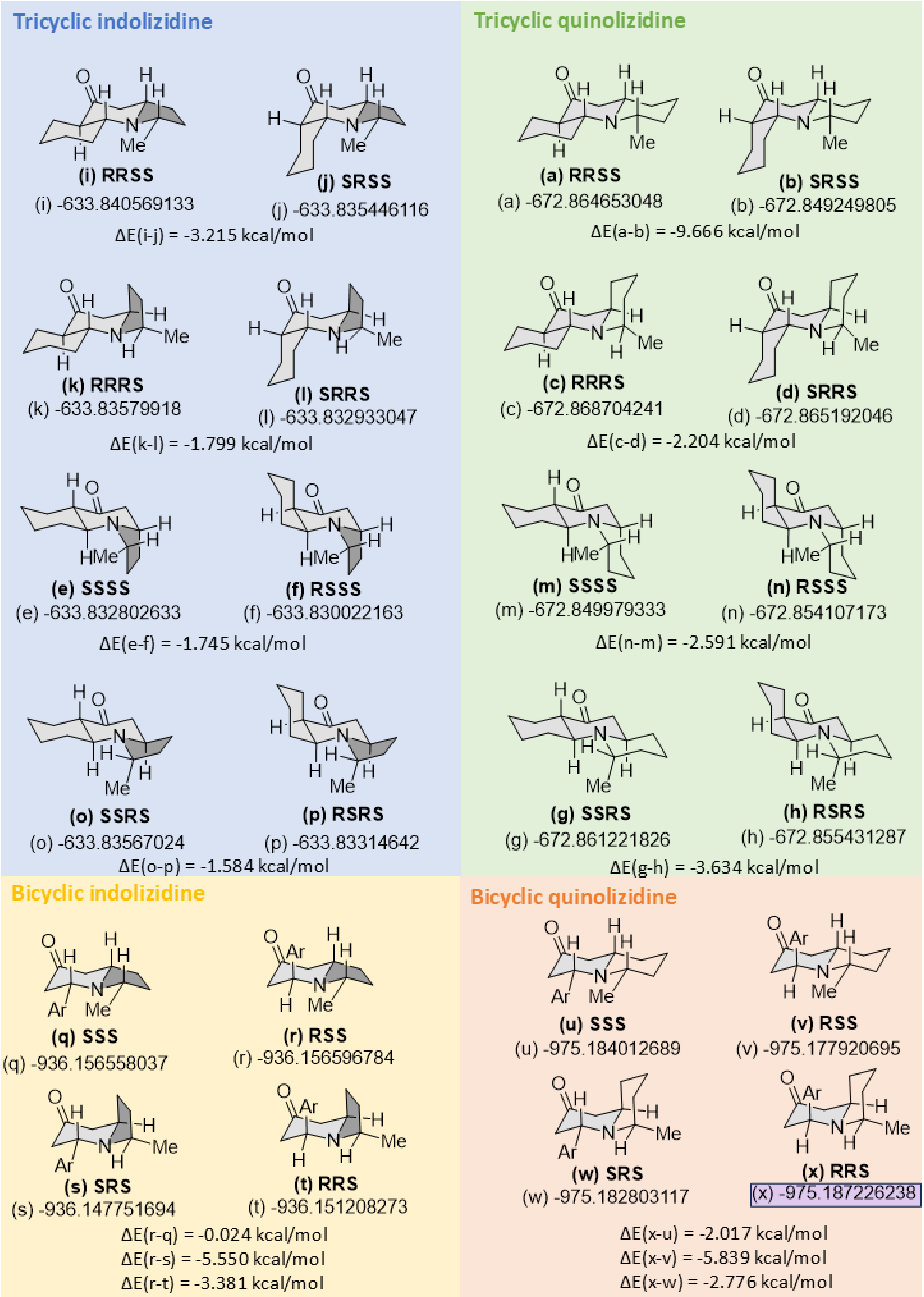
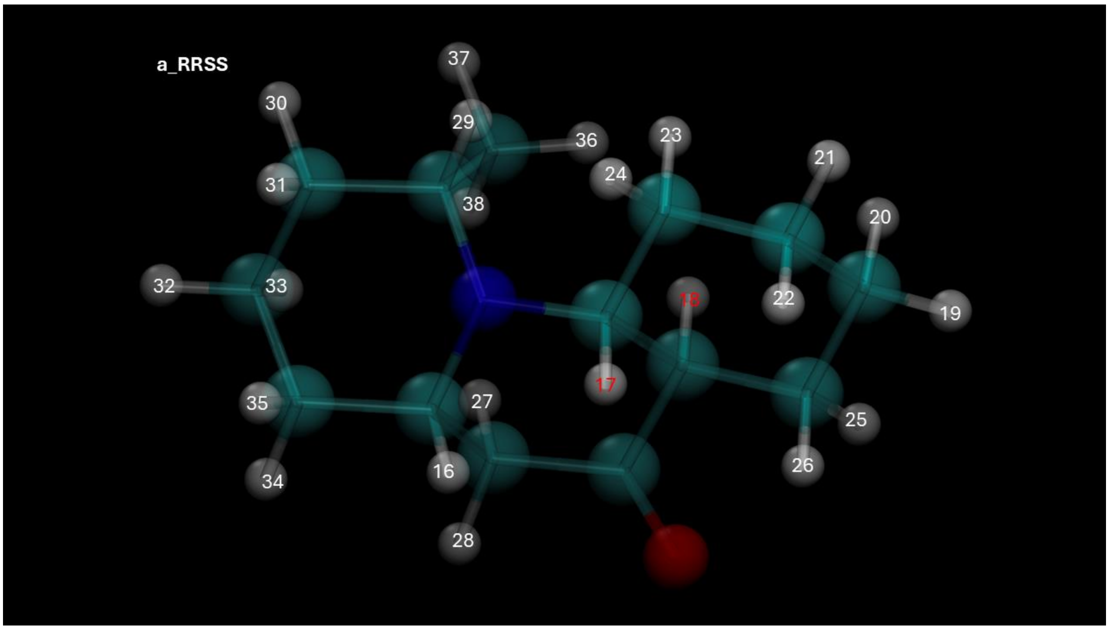
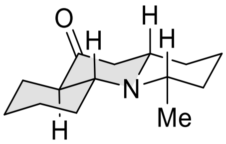


Figure S11. *Energy calculation for the quinolizidines **4a** and **4e**, and indolizidines **4c** and **4f**. Absolute energies are given in Hartree. ΔE is given in kcal/mol. 1 Hartree = 627.503 kcal/mol*

11. H-H proximity calculation





(a) RRSS

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#H17
H17 H18 3.0224008560180664
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H17 H25 3.7103166580200195
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H17 H28 3.961921453475952
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H29 H32 4.245436191558838
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H29 H36 2.465608596801758
H29 H37 2.4173264503479004
H29 H38 3.0478222370147705
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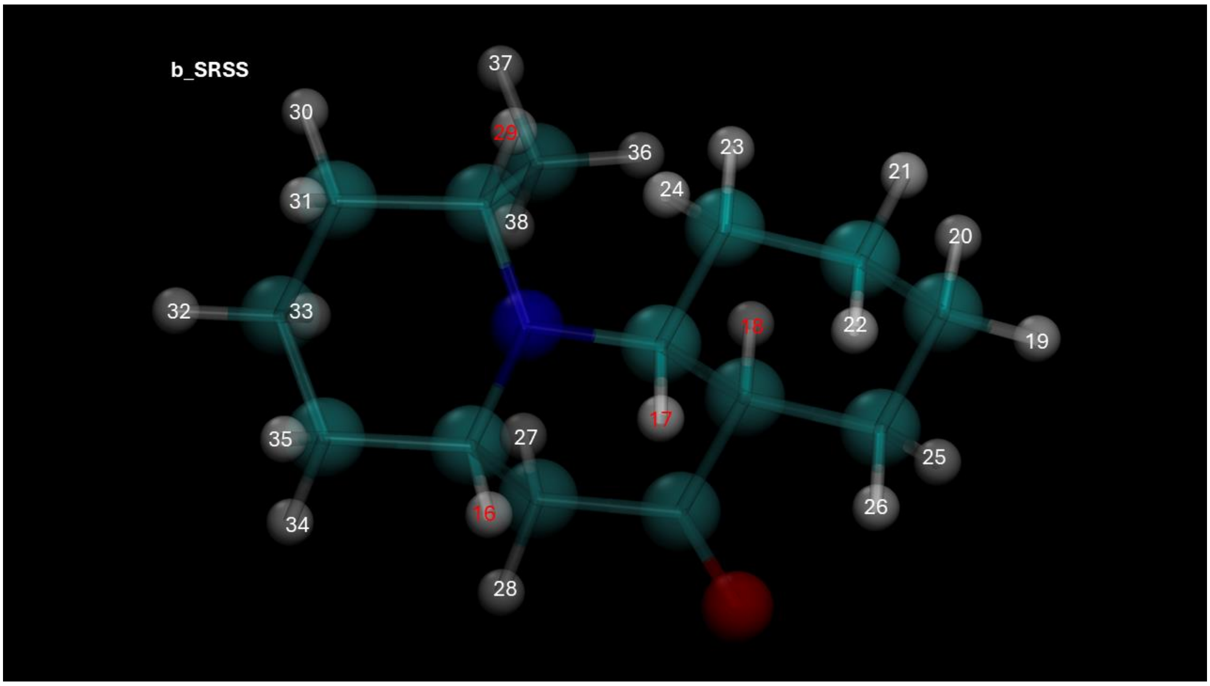

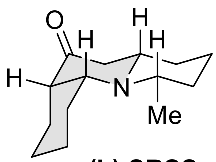

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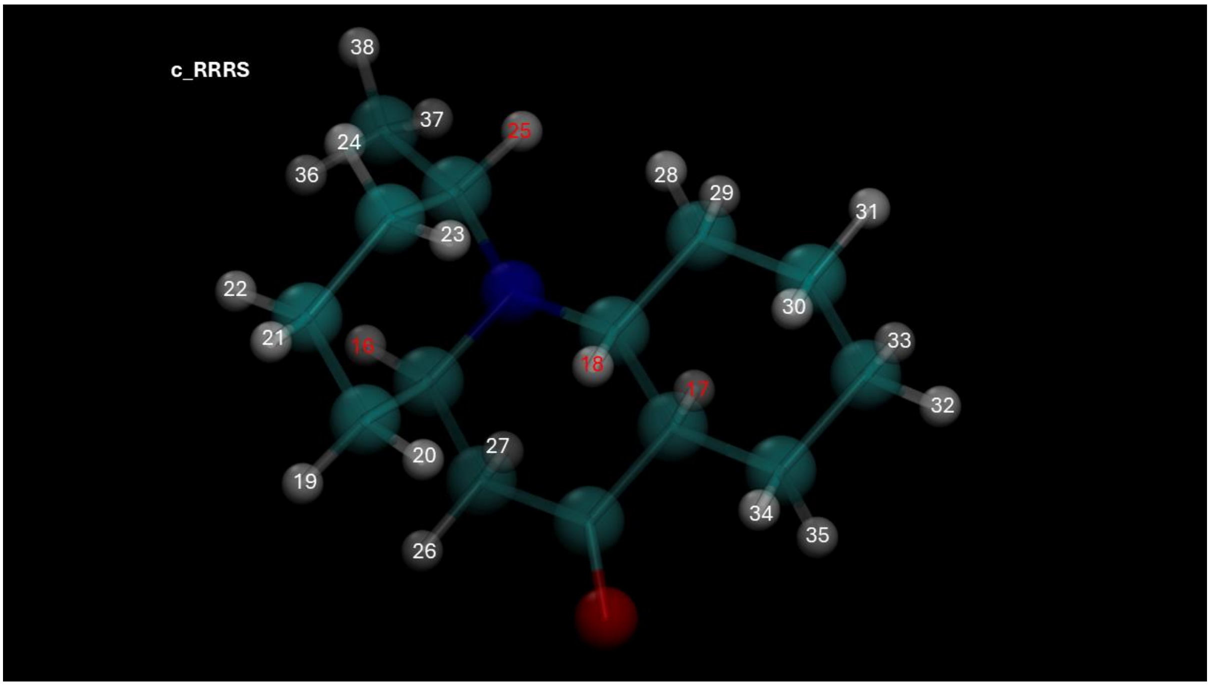

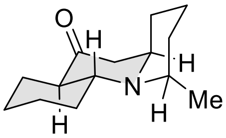

(c) RRRS

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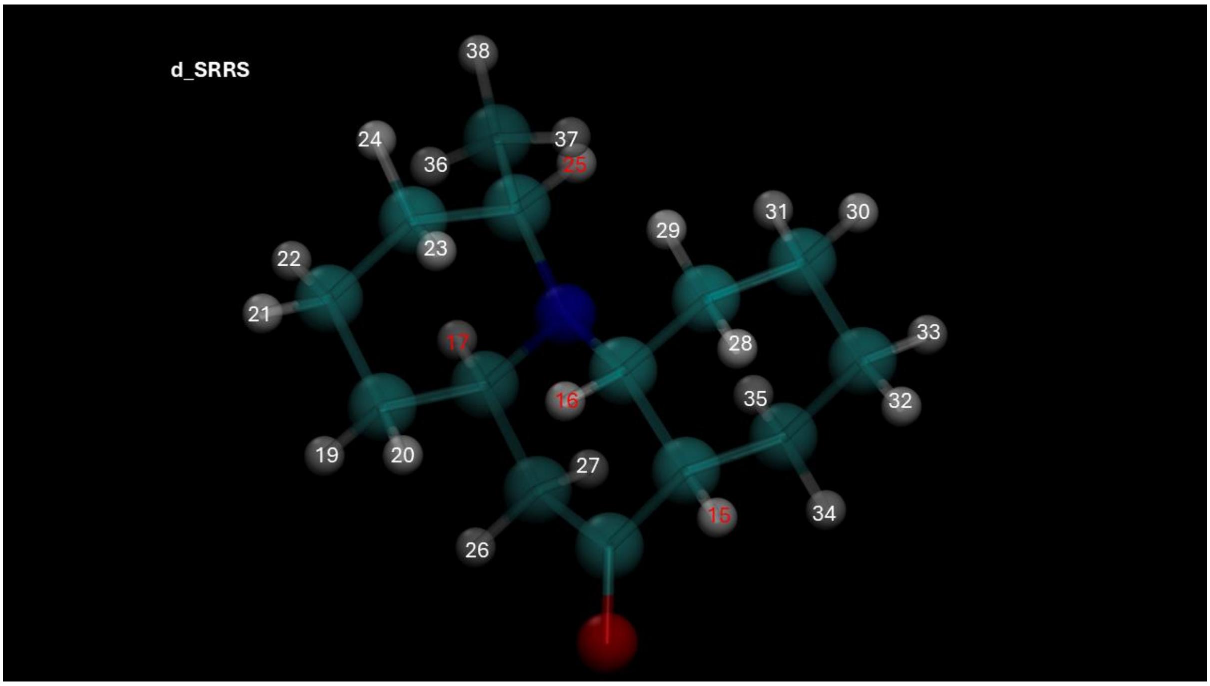

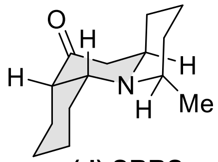

(d) SRRS

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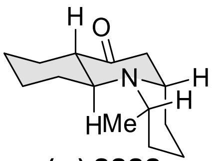

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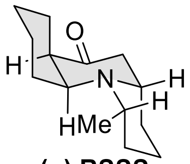
H29 H37 2.4352598190307617
H29 H38 2.442859411239624



(n) RSSS

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#H-H distances (n)
#H16
H16 H17 2.410846710205078
H16 H18 4.049373149871826
H16 H19 2.8937673568725586
H16 H20 3.923755645751953
H16 H21 3.84234356880188
H16 H34 3.876873254776001
H16 H35 4.382880687713623
#H17
H17 H16 2.410846710205078
H17 H18 3.7947001457214355
H17 H19 4.16529655456543
H17 H20 4.975197792053223
H17 H21 2.3642148971557617
H17 H23 4.29379940032959
H17 H34 2.2190282344818115
H17 H35 2.661545991897583
H17 H36 2.465543270111084
H17 H37 3.779594898223877
H17 H38 3.68558931350708
#H18
H18 H16 4.049373149871826
H18 H17 3.7947001457214355
H18 H19 3.0748443603515625
H18 H20 2.4219725131988525
H18 H21 4.1768412590026855
H18 H26 2.5001330375671387
H18 H27 2.3393492698669434
#H21
H21 H16 3.84234356880188
H21 H17 2.3642148971557617
H21 H18 4.1768412590026855
H21 H19 4.1768412590026855
H21 H20 4.2479071617126465
H21 H22 5.340999603271484
H21 H23 2.384725570678711
H21 H24 4.278432369232178
H21 H25 3.846802234649658
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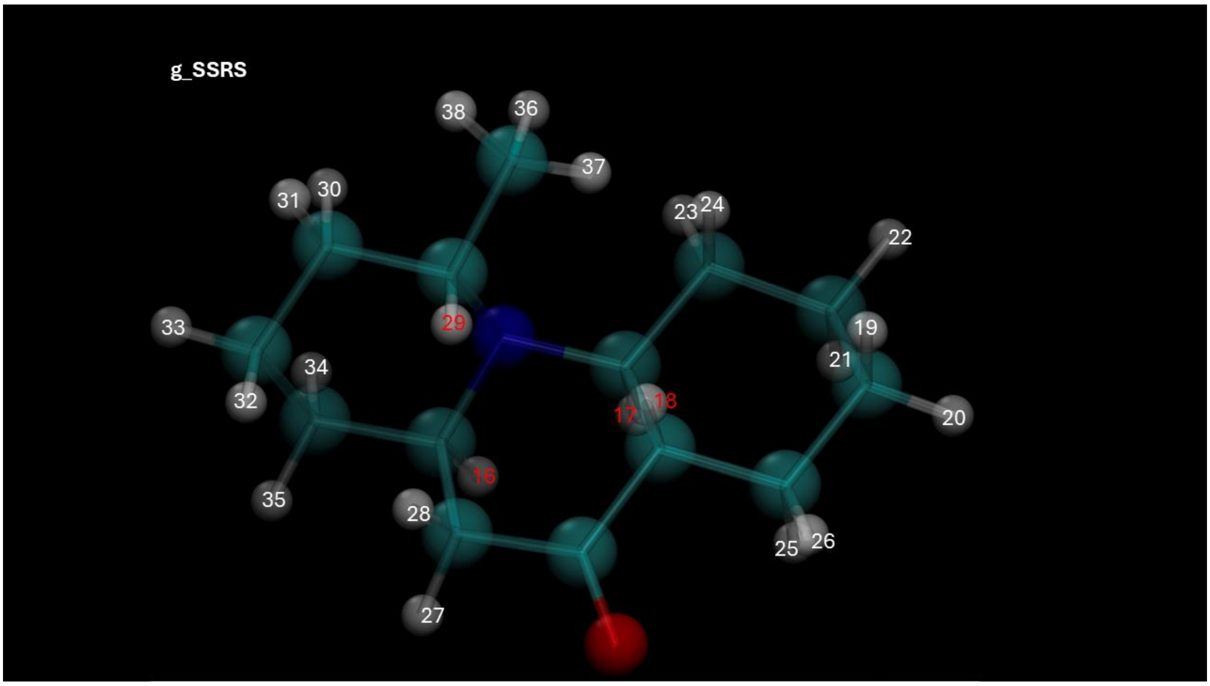

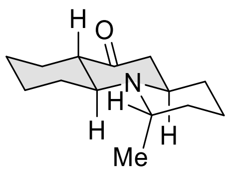

(g) SSRS

```
#H-H distances (g)
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H16 H17 2.0152759552001953
H16 H18 3.941641092300415
H16 H27 2.4418652057647705
H16 H28 3.0411219596862793
H16 H29 3.7156567573547363
H16 H30 3.9745357036590576
H16 H31 4.835440158843994
H16 H34 2.32846736907959
H16 H35 2.4687793254852295
H16 H36 4.6831159591674805
H16 H37 4.9798102378845215
H16 H38 5.425002574920654
#H17
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H17 H16 2.0152759552001953
H17 H18 3.020108461380005
H17 H23 2.3959810733795166
H17 H24 3.008091926574707
H17 H25 2.633697509765625
H17 H26 3.7554614543914795
H17 H27 3.7225165367126465
H17 H28 3.8765671253204346
H17 H29 3.8155646324157715
#H18
H18 H16 3.941641092300415
H18 H17 3.020108461380005
H18 H23 3.8283536434173584
H18 H24 2.7457363605499268
H18 H25 3.0372090339660645
H18 H26 2.436363458633423
H18 H27 3.950187921524048
H18 H28 3.0290799140930176
H18 H29 2.475264310836792
#H29
H29 H16 3.7156567573547363
H29 H17 3.8155646324157715
H29 H18 2.475264310836792
H29 H27 3.7548623085021973
H29 H28 2.234041929244995
H29 H30 3.024094820022583
H29 H31 2.4340503215789795
H29 H36 3.034071922302246
H29 H37 2.4089198112487793
H29 H38 2.5002710819244385
#H30
H30 H29 3.024094820022583
H30 H31 1.7497085332870483
H30 H18 5.017143726348877
H30 H19 6.799642086029053
H30 H23 4.285325527191162
H30 H24 4.560378074645996
H30 H36 2.6227376461029053
H30 H37 3.7365031242370605
H30 H38 2.8135030269622803
#H31
H31 H17 5.408580780029297
H31 H18 4.849887371063232
H31 H29 2.4340503215789795
H31 H30 1.7497085332870483
H31 H32 2.4459807872772217
H31 H33 2.5091631412506104
H31 H36 3.1588633060455322
H31 H37 3.557534694671631
H31 H38 2.25711989402771
#H34
H34 H15 4.559057712554932
H34 H17 3.8901147842407227
H34 H18 5.374241352081299
H34 H21 6.170171737670898
H34 H22 7.034179210662842
H34 H31 3.7662551403045654
H34 H33 2.432619333267212
H34 H35 1.7482794523239136
#H35
H35 H15 5.374346733093262
H35 H17 4.393375873565674
H35 H18 5.378992557525635
H35 H21 6.841216087341309
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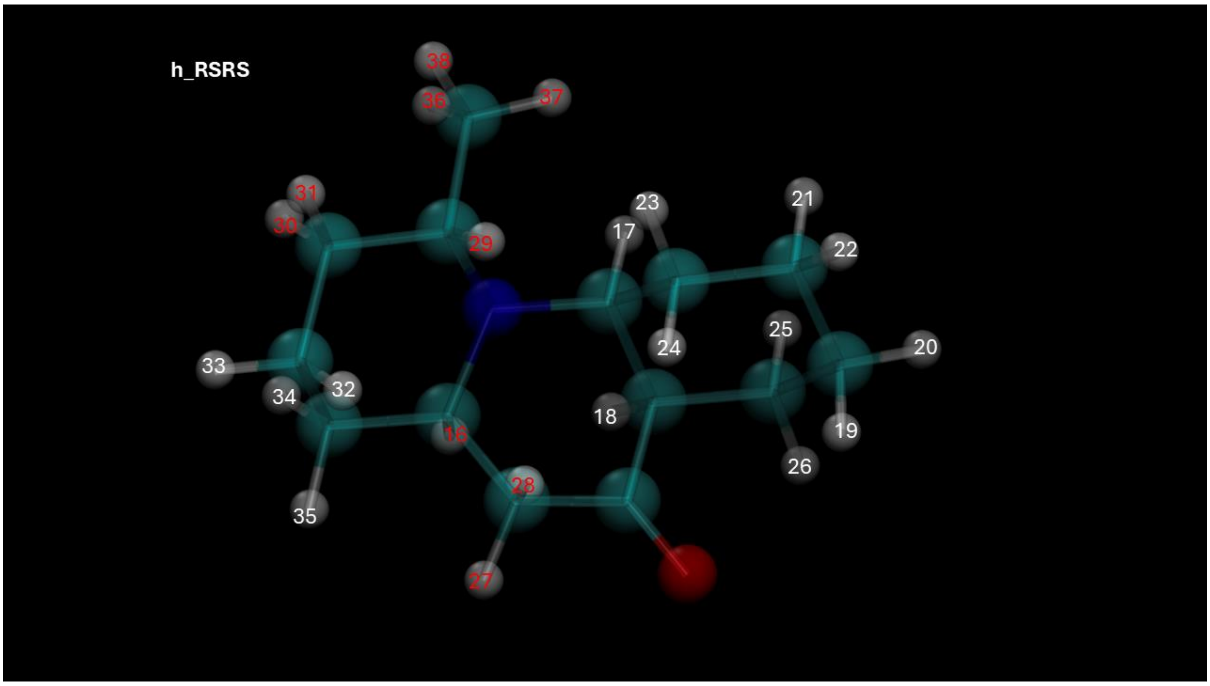
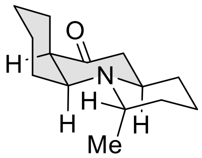
H35 H31 4.278370380401611
H35 H33 2.539233684539795
H35 H34 1.7482794523239136





(h) RSRS

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#H-H distances (h)
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H16 H17 3.350390672683716
H16 H26 4.430899620056152
H16 H27 2.481499195098877
H16 H28 3.02990460395813
H16 H29 3.9941322803497314
H16 H30 3.741410255432129
H16 H31 4.771738052368164
H16 H32 3.8388314247131348
H16 H33 4.204478740692139
H16 H34 2.2537310123443604
H16 H35 2.5174591541290283
H16 H36 4.204206943511963
H16 H37 4.699637413024902
H16 H38 5.267868995666504
#H17
H17 H18 2.4282784461975098
H17 H21 2.4975643157958984
H17 H22 3.6885666847229004
H17 H23 2.5021302700042725
H17 H24 3.040989398956299
H17 H25 2.555913209915161
H17 H26 3.7217040061950684
H17 H27 4.84902811050415
H17 H28 4.185085296630859
#H18
H18 H17 2.4282784461975098
H18 H19 3.8419253826141357
H18 H20 4.263055324554443
H18 H21 4.112231731414795
H18 H22 4.93388032913208
H18 H23 4.289885520935059
H18 H24 3.770322799682617
H18 H25 2.382896661758423
H18 H26 2.4691481590270996
#H19
H19 H18 3.8419253826141357
H19 H20 1.7430168390274048
H19 H21 3.0451788902282715
H19 H22 2.457620859146118
H19 H23 3.789581537246704
H19 H24 2.6678597927093506
H19 H25 3.039156198501587
H19 H26 2.4396767616271973
#H29
H29 H16 3.9941322803497314
H29 H17 3.2968966960906982
H29 H27 4.498043060302734
H29 H28 3.1058058738708496
H29 H30 3.0078704357147217
H29 H31 2.330488681793213
H29 H36 3.042652130126953
H29 H37 2.5143191814422607
H29 H38 2.473994016647339

#H30
H30 H16 3.741410255432129
H30 H29 3.0078704357147217
H30 H31 1.7470238208770752
H30 H32 3.0455105304718018
H30 H33 2.4895401000976562
H30 H36 2.465907096862793
H30 H37 3.6824421882629395
H30 H38 2.8523879051208496

#H31
H31 H16 4.771738052368164
H31 H29 2.330488681793213
H31 H30 1.7470238208770752
H31 H32 2.521040439605713
H31 H33 2.494533061981201
H31 H36 3.1670281887054443
H31 H37 3.6934494972229004
H31 H38 2.460721254348755

#H36
H36 H16 4.204206943511963
H36 H17 2.9347081184387207
H36 H18 4.650691032409668
H36 H29 3.042652130126953

#H37
H37 H16 4.699637413024902
H37 H17 2.311356782913208
H37 H18 4.582381725311279
H37 H29 2.5143191814422607

#H38
H38 H16 5.267868995666504
H38 H17 3.82857084274292
H38 H18 5.779983043670654
H38 H29 2.473994016647339
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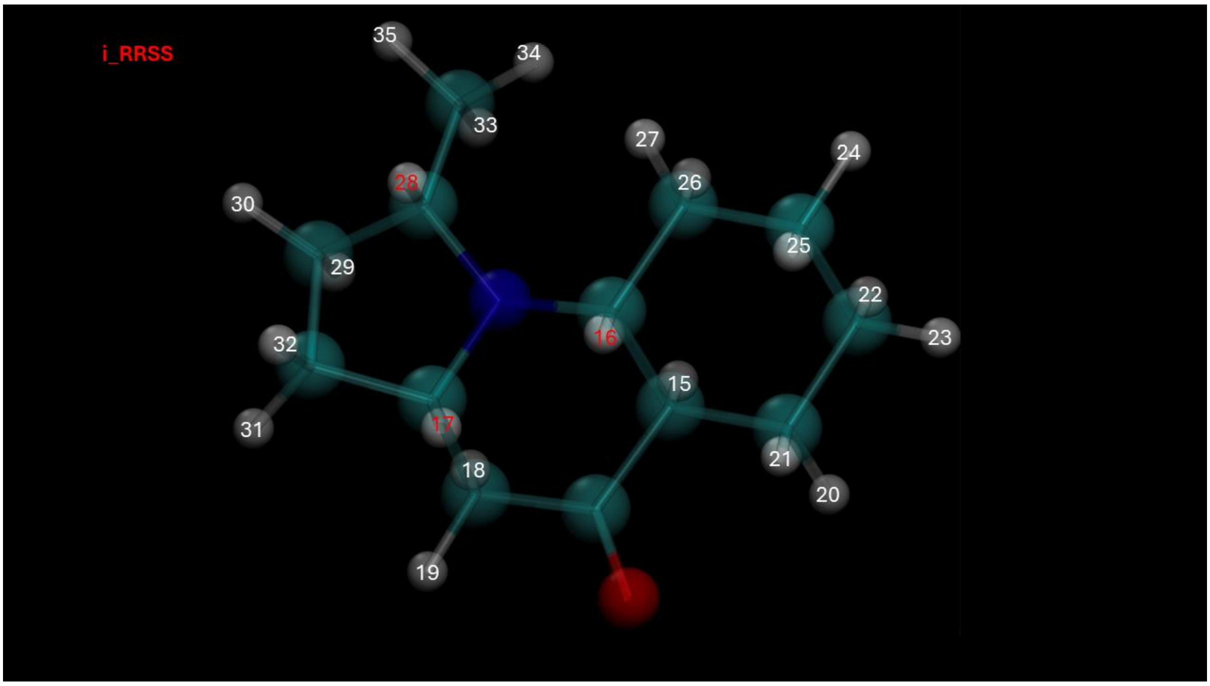

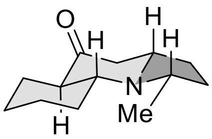

(i) RRSS

#H-H distances (i)
#H16
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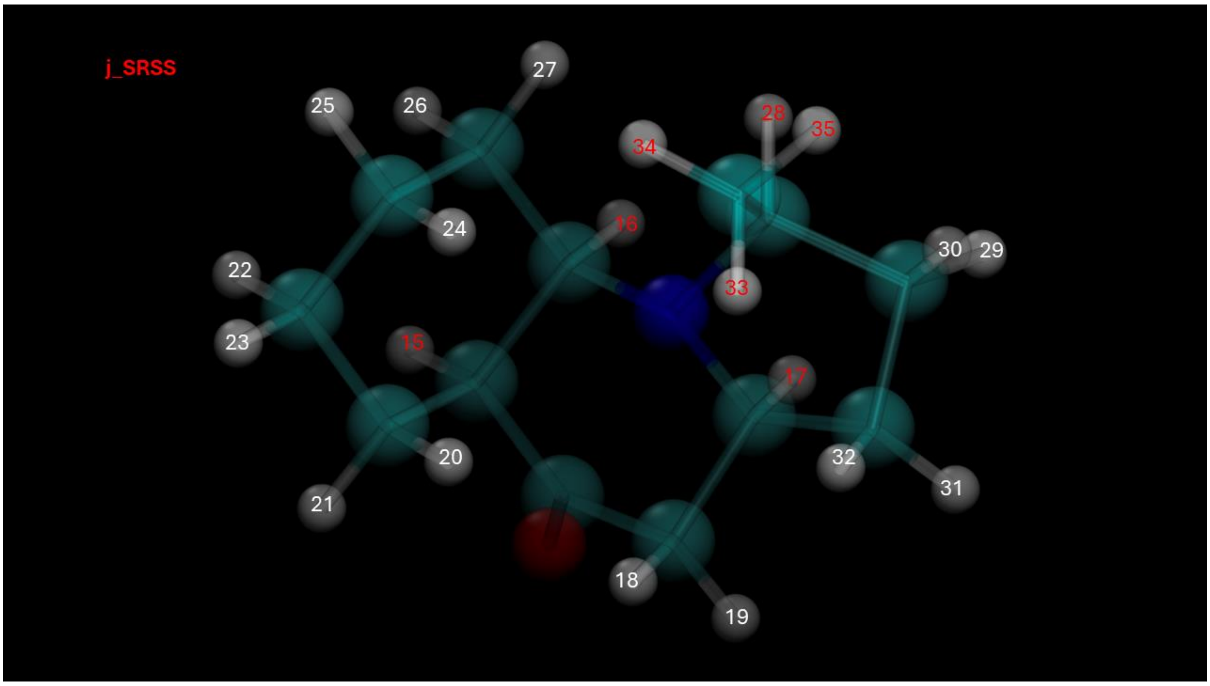
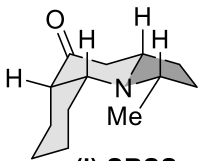
H16 H17 2.284801959991455
H16 H18 4.041592597961426
H16 H19 4.1367974281311035
H16 H26 3.083815336227417
H16 H27 2.4589176177978516
H16 H28 3.033634901046753
H16 H33 4.527142524719238
H16 H34 3.925123929977417
H16 H35 4.977095127105713
#H17
H17 H15 3.9123947620391846
H17 H16 2.284801959991455
H17 H18 3.0781548023223877
H17 H19 2.494049072265625
H17 H29 3.7662999629974365
H17 H30 4.054847717285156
H17 H31 2.8022119998931885
H17 H32 2.2085933685302734
#H18
H18 H15 2.749983310699463
H18 H16 4.041592597961426
H18 H17 3.0781548023223877
H18 H19 1.8120825290679932
H18 H31 2.982492446899414
H18 H32 3.9380390644073486
#H28
H28 H16 3.033634901046753
H28 H17 2.989964723587036
H28 H29 3.104753017425537
H28 H30 2.5715372562408447
H28 H33 3.120378017425537
H28 H34 2.552609443664551
H28 H35 2.5420279502868652
#H33
H33 H26 2.917091131210327
H33 H27 3.5501701831817627
H33 H28 3.120378017425537
H33 H29 2.447922945022583
H33 H30 3.2515313625335693
H33 H34 1.7993377447128296
H33 H35 1.805186152458191
#H34
H34 H26 2.360694408416748
H34 H27 2.180738925933838
H34 H28 2.552609443664551
H34 H29 3.7174317836761475
H34 H30 3.8920042514801025
H34 H33 1.7993377447128296
H34 H35 1.7698321342468262
#H35
H35 H26 3.958726406097412
H35 H27 3.759351968765259
H35 H28 2.5420279502868652
H35 H29 3.0004727840423584
H35 H30 2.6653265953063965
H35 H33 1.805186152458191
H35 H34 1.7698321342468262





(j) SRSS

#H-H distances (j)
#H15
H15 H16 2.495083808898926
H15 H17 3.896345853805542
H15 H18 3.935655355453491
H15 H19 4.321197032928467
H15 H20 3.097569704055786
H15 H21 2.4777820110321045
H15 H21 2.4777820110321045
H15 H22 3.756240129470825
H15 H23 2.530355215072632
H15 H24 4.022121906280518
H15 H25 4.166080474853516
H15 H26 2.6069321632385254
H15 H27 3.8363447189331055
#H16
H16 H15 2.495083808898926
H16 H17 2.342231512069702
H16 H18 4.075924873352051
H16 H19 4.162993431091309
H16 H24 3.8745460510253906
H16 H25 4.322678565979004
H16 H26 2.4304158687591553
H16 H27 2.5368871688842773
H16 H28 2.650919198989868
H16 H33 4.6613688468933105
H16 H34 4.133923053741455
H16 H35 4.876774787902832
#H17
H17 H16 2.342231512069702
H17 H18 3.077601671218872
H17 H19 2.4791226387023926
H17 H28 3.1384966373443604
H17 H29 3.6087145805358887
H17 H30 2.2808046340942383
H17 H31 3.0709896087646484
H17 H32 2.4896132946014404
H17 H33 4.356574535369873
H17 H34 4.738417148590088
H17 H35 4.839174747467041
#H28
H28 H16 2.650919198989868
H28 H17 3.1384966373443604
H28 H29 2.776123285293579
H28 H30 2.3304359912872314
H28 H31 3.7946059703826904
H28 H32 4.190736293792725
H28 H33 3.0968177318573
H28 H34 2.4897682666778564
H28 H35 2.492147207260132
#H33
H33 H16 4.6613688468933105
H33 H17 4.356574535369873
H33 H28 3.0968177318573
H33 H29 2.8791604042053223
H33 H30 3.849177122116089
H33 H31 2.45281982421875
H33 H32 4.025505542755127
H33 H34 1.8063668012619019
H33 H35 1.8062231540679932
#H34
H34 H16 4.133923053741455
H34 H17 4.738417148590088
H34 H28 2.4897682666778564
H34 H29 3.734097480773926
H34 H30 4.271815776824951
H34 H31 3.9282071590423584

H34 H32 5.226253986358643
H34 H33 1.8063668012619019
H34 H35 1.779442548751831
#H35
H35 H16 4.876774787902832
H35 H17 4.839174747467041
H35 H28 2.492147207260132
H35 H29 2.4771957397460938
H35 H30 3.5719871520996094
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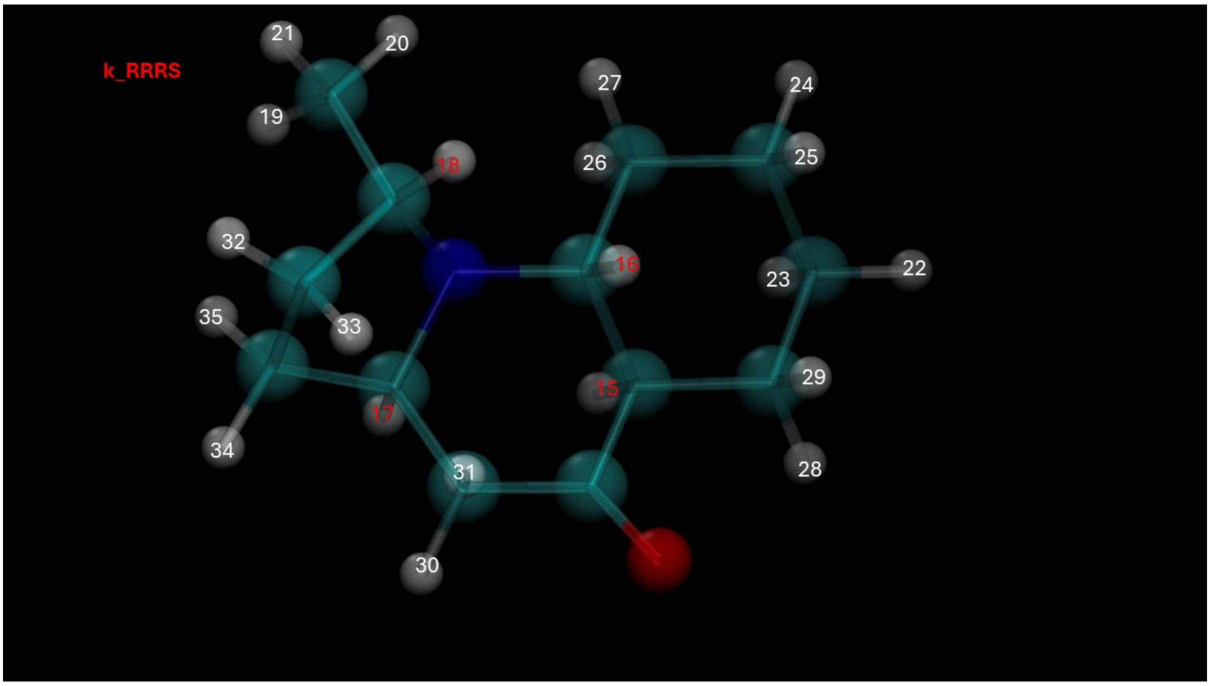
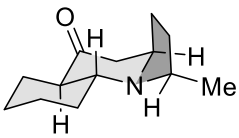
H35 H34 1.779442548751831





(k) RRRS

#H-H distances (k)
#H15
H15 H16 3.085693836212158
H15 H17 2.487208604812622
H15 H18 4.622262001037598
H15 H28 2.503389596939087
H15 H29 3.1006827354431152
H15 H30 3.526456356048584
H15 H31 3.8381845951080322
#H16
H16 H15 3.085693836212158
H16 H17 3.8341176509857178
H16 H19 4.527358055114746
H16 H20 3.8066647052764893
H16 H21 4.573228359222412
H16 H18 2.318532943725586
H16 H22 4.2001051902771
H16 H23 4.0356268882751465
H16 H24 3.8044886589050293
H16 H25 2.594539165496826
H16 H26 3.0972535610198975
H16 H27 2.50309419631958
H16 H28 3.8173515796661377
H16 H29 2.6132278442382812
#H17
H17 H15 2.487208604812622
H17 H16 3.8341176509857178
H17 H18 4.170382499694824
H17 H19 3.5988948345184326
H17 H20 4.401975631713867
H17 H21 4.905324935913086
H17 H30 2.4023351669311523
H17 H31 3.0921688079833984
H17 H32 4.2598676681518555
H17 H33 3.7365002632141113
H17 H34 2.7131595611572266
H17 H35 2.3970746994018555
#H18
H18 H16 2.318532943725586
H18 H17 4.170382499694824
H18 H19 3.0946826934814453
H18 H20 2.481955051422119
H18 H21 2.472580671310425
H18 H26 3.913487195968628
H18 H27 2.7869133949279785
H18 H32 2.72515869140625
H18 H33 2.373492956161499
H18 H34 4.256747722625732
H18 H35 3.756169319152832
#H19
H19 H18 3.0946826934814453

H19 H20 1.7930903434753418
H19 H21 1.8040953874588013
H19 H26 3.9446728229522705
H19 H27 3.788252830505371
H19 H32 2.9685420989990234
H19 H33 3.87245774269104
H19 H34 3.9036874771118164
H19 H35 2.2627968788146973
#H20
H20 H18 2.481955051422119
H20 H19 1.7930903434753418
H20 H21 1.7959100008010864
H20 H26 3.118790626525879
H20 H27 2.3467459678649902
H20 H32 3.783447027206421
H20 H33 4.297637939453125
H20 H34 5.144302845001221
H20 H35 3.7709269523620605
#H21
H21 H18 2.472580671310425
H21 H19 1.8040953874588013
H21 H20 1.7959100008010864
H21 H26 4.757336139678955
H21 H27 3.863662004470825
H21 H32 2.5485825538635254
H21 H33 3.665628671646118
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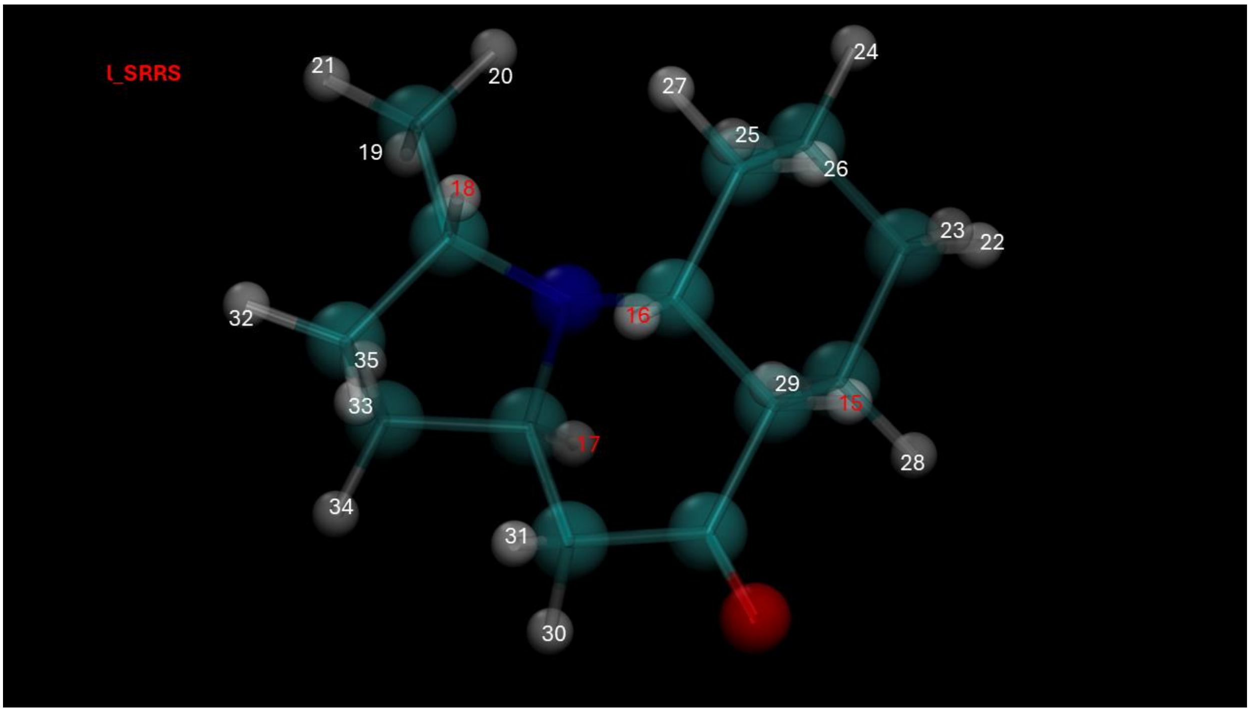
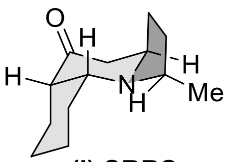
H21 H35 3.427595853805542





(l) SRRS

#H-H distances (l)
#H15
H15 H16 2.4585139751434326
H15 H17 4.171119689941406
H15 H18 4.629546165466309
H15 H28 3.095231533050537
H15 H29 2.477414608001709
H15 H30 4.2763991355896
H15 H31 3.81459379196167
#H16
H16 H15 2.4585139751434326
H16 H17 3.8265459537506104
H16 H18 2.30694317817688
H16 H22 4.138825416564941
H16 H23 5.011595249176025
H16 H24 3.8325140476226807
H16 H25 4.3307623863220215
H16 H26 2.5412354469299316
H16 H27 2.4663708209991455
H16 H28 3.8752453327178955
H16 H29 4.33194637298584
#H17
H17 H15 4.171119689941406
H17 H16 3.8265459537506104
H17 H18 4.173085689544678
H17 H19 3.493023633956909
H17 H20 4.333494186401367
H17 H21 4.8263678550720215
H17 H30 2.3852808475494385
H17 H31 3.0869362354278564
H17 H32 4.22971010208l299
H17 H33 3.717257022857666

H17 H34 2.3629543781280518
H17 H35 2.6942803859710693
#H18
H18 H16 2.30694317817688
H18 H17 4.173085689544678
H18 H19 3.0901830196380615
H18 H20 2.4651987552642822
H18 H21 2.461366653442383
H18 H24 4.022594928741455
H18 H25 4.838090896606445
H18 H26 2.536687135696411
H18 H27 3.7707443237304688
H18 H32 2.699371814727783
H18 H33 2.383004903793335
H18 H34 3.7398605346679688
H18 H35 4.259425163269043
#H19
H19 H18 3.0901830196380615
H19 H20 1.7919995784759521
H19 H21 1.8045034408569336
H19 H26 3.901251792907715
H19 H27 5.368136405944824
H19 H32 3.0204923152923584
H19 H33 3.893623113632202
H19 H34 2.232694387435913
H19 H35 3.8847174644470215
#H20
H20 H18 2.4651987552642822
H20 H19 1.7919995784759521
H20 H21 1.7982237339019775
H20 H26 2.452756881713867
H20 H27 4.152398586273193
H20 H32 3.8007736206054688
H20 H33 4.301331996917725
H20 H34 3.747098684310913
H20 H35 5.125955581665039
#H21
H21 H18 2.461366653442383
H21 H19 1.8045034408569336
H21 H20 1.7982237339019775
H21 H26 3.8341431617736816
H21 H27 5.517261981964111
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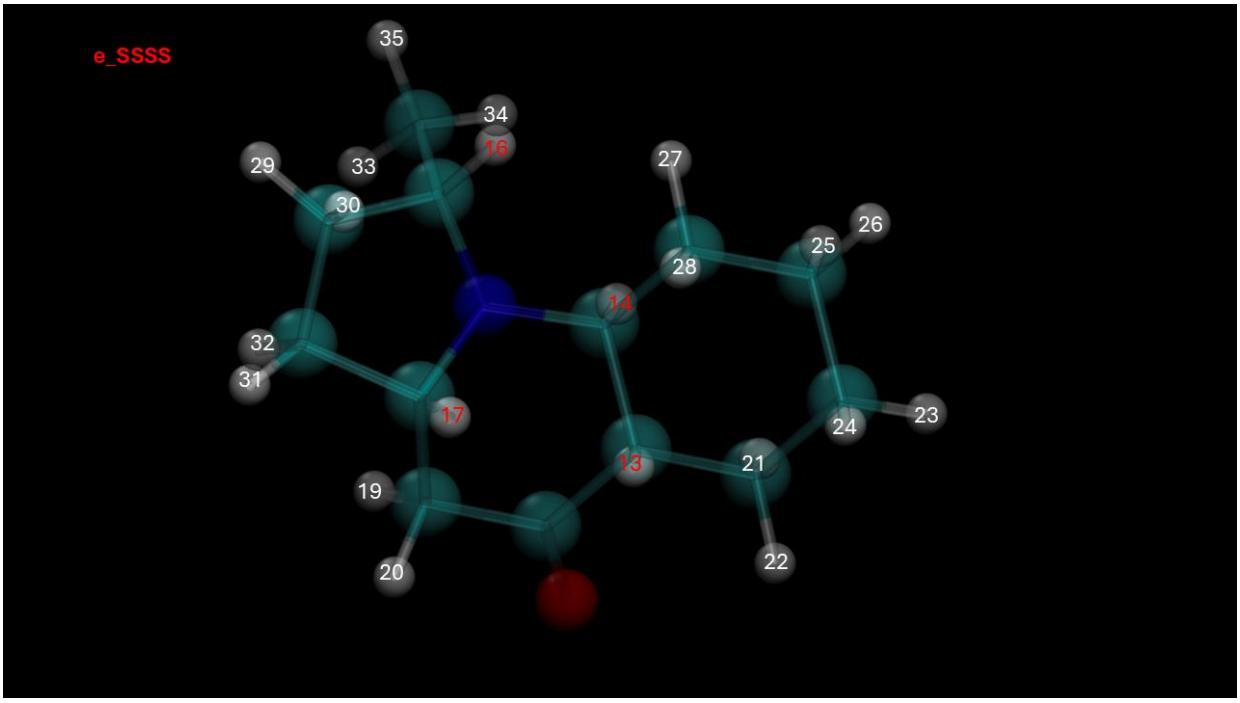
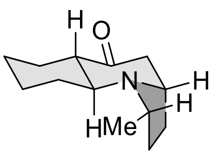
H21 H33 3.6968696117401123
H21 H34 3.369710683822632
H21 H35 4.607275009155273





(e) SSSS

#H-H distances (e)
#H13
H13 H14 3.0170278549194336
H13 H17 2.3418188095092773
H13 H21 3.036106824874878
H13 H22 2.4799468517303467
H13 H27 3.678208827972412
H13 H28 2.4737913608551025
#H14
H14 H13 3.0170278549194336
H14 H16 3.2962803840637207
H14 H17 3.825310707092285

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H14 H27 2.477142810821533
H14 H28 3.0314104557037354
H14 H33 3.4569246768951416
H14 H34 2.6364147663116455
H14 H35 4.158455848693848
#H16
H16 H14 3.2962803840637207
H16 H17 3.3161733150482178
H16 H27 2.1678738594055176
H16 H28 2.683210611343384
H16 H29 2.7782106399536133
H16 H30 2.2871384620666504
H16 H33 3.0405633449554443
H16 H34 2.507309675216675
H16 H35 2.443206787109375
#H17
H17 H13 2.3418188095092773
H17 H14 3.825310707092285
H17 H16 3.3161733150482178
H17 H19 3.0389602184295654
H17 H20 2.4148738384246826
H17 H29 3.8314990997314453
H17 H30 2.779426097869873
H17 H31 2.3972535133361816
H17 H32 3.021347761154175
#H19
H19 H13 3.7167749404907227
H19 H17 3.0389602184295654
H19 H20 1.7494990825653076
H19 H31 3.2642266750335693
H19 H32 2.3504457473754883
#H20
H20 H13 3.181819200515747
H20 H17 2.4148738384246826
H20 H19 1.7494990825653076
H20 H31 3.087502956390381
H20 H32 3.161036252975464
#H33
H33 H14 3.4569246768951416
H33 H16 3.0405633449554443
H33 H17 4.516113758087158
H33 H29 2.6942074298858643
H33 H30 3.8009583950042725
H33 H34 1.7537988424301147
H33 H35 1.7637031078338623
#H34
H34 H14 2.6364147663116455
H34 H16 2.507309675216675
H34 H17 4.796438217163086
H34 H29 3.6941585540771484
H34 H30 4.255570411682129
H34 H33 1.7537988424301147
H34 H35 1.7543723583221436
#H35
H35 H14 4.158455848693848
H35 H16 2.443206787109375
H35 H17 5.08101749420166
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H35 H34 1.7543723583221436
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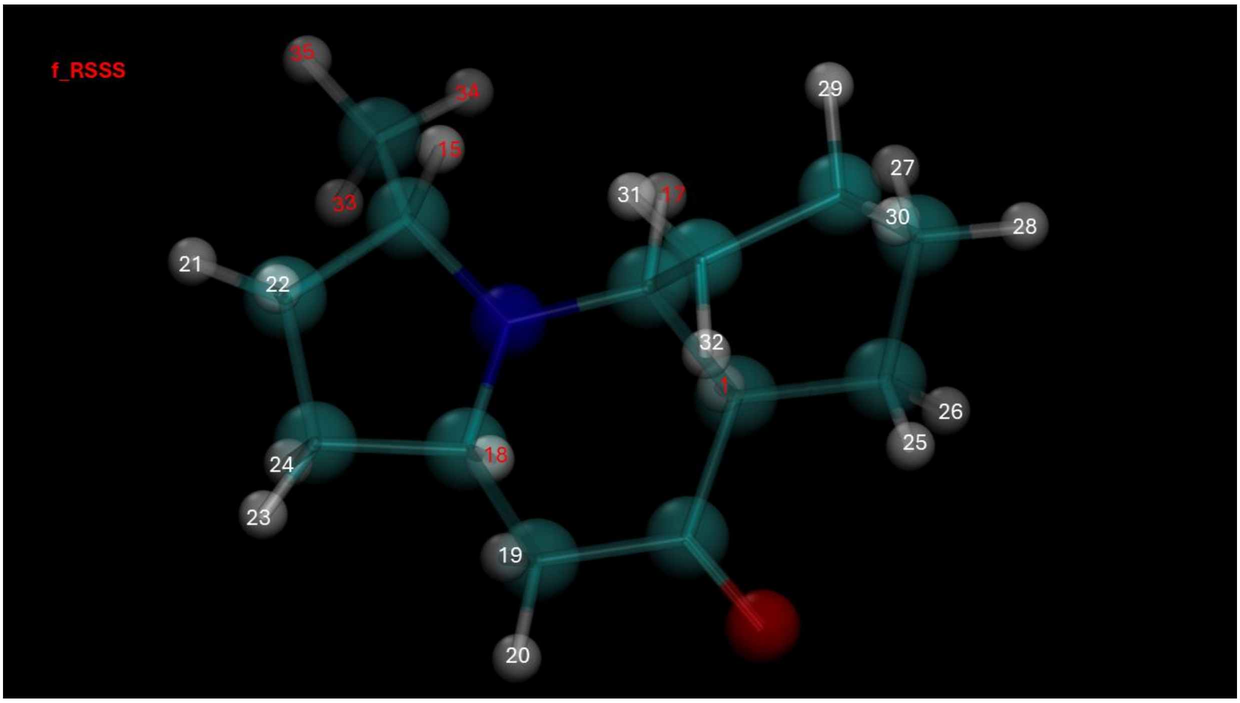

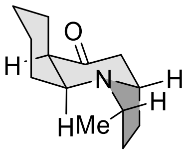

(f) RSSS

#H-H distances (f)
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H1 H18 4.020094871520996
H1 H19 2.7779102325439453
H1 H20 3.8382232189178467
H1 H25 2.991110324859619
H1 H26 2.3345465660095215
H1 H31 4.262908458709717
H1 H32 3.725621223449707
#H15
H15 H17 2.7013819217681885
H15 H18 3.1970043182373047
H15 H18 3.1970043182373047
H15 H21 2.8101143836975098
H15 H22 2.2970542907714844
H15 H23 4.0644426345825195
H15 H24 3.865967035293579
H15 H33 3.041111707687378
H15 H34 2.509404420852661
H15 H35 2.4456374645233154
#H17
H17 H1 2.3129048347473145
H17 H15 2.7013819217681885
H17 H18 3.7525882720947266
H17 H31 2.562046527862549
H17 H29 2.791614055633545
H17 H30 3.668734550476074
H17 H32 3.025036334991455
H17 H33 3.5101168155670166
H17 H34 2.4005305767059326
H17 H35 3.8300156593322754
#H18
H18 H1 4.020094871520996
H18 H15 3.1970043182373047
H18 H17 3.7525882720947266
H18 H19 3.0326104164123535
H18 H20 2.4628570079803467
H18 H21 3.7981488704681396
H18 H22 2.7431766986846924
H18 H23 2.4123756885528564
H18 H24 3.0266263484954834
H18 H33 4.519864082336426
H18 H34 4.75467586517334
H18 H35 5.0253825187683105
#H19
H19 H1 2.7779102325439453
H19 H18 3.0326104164123535
H19 H20 1.7652992010116577
H19 H23 3.3458595275878906
H19 H24 2.443786144256592
#H20
H20 H1 3.8382232189178467
H20 H18 2.4628570079803467
H20 H19 1.7652992010116577
H20 H23 3.0342538356781006
H20 H24 3.124263048171997
H20 H25 4.502316951751709
H20 H26 5.103431701660156
#H33
H33 H15 3.041111707687378
H33 H17 3.5101168155670166
H33 H18 4.519864082336426
H33 H21 2.650505304336548
H33 H22 3.7817606925964355
H33 H31 4.8817620277404785
H33 H34 1.754231333732605
H33 H35 1.7633055448532104
#H34
H34 H15 2.509404420852661
H34 H17 2.4005305767059326
H34 H18 4.75467586517334
H34 H21 3.683234930038452
H34 H22 4.249947547912598
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H34 H33 1.754231333732605
H34 H35 1.7541545629501343
#H35
H35 H15 2.4456374645233154
H35 H17 3.8300156593322754
H35 H18 5.0253825187683105
H35 H21 2.5953474044799805
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H35 H31 4.587160587310791
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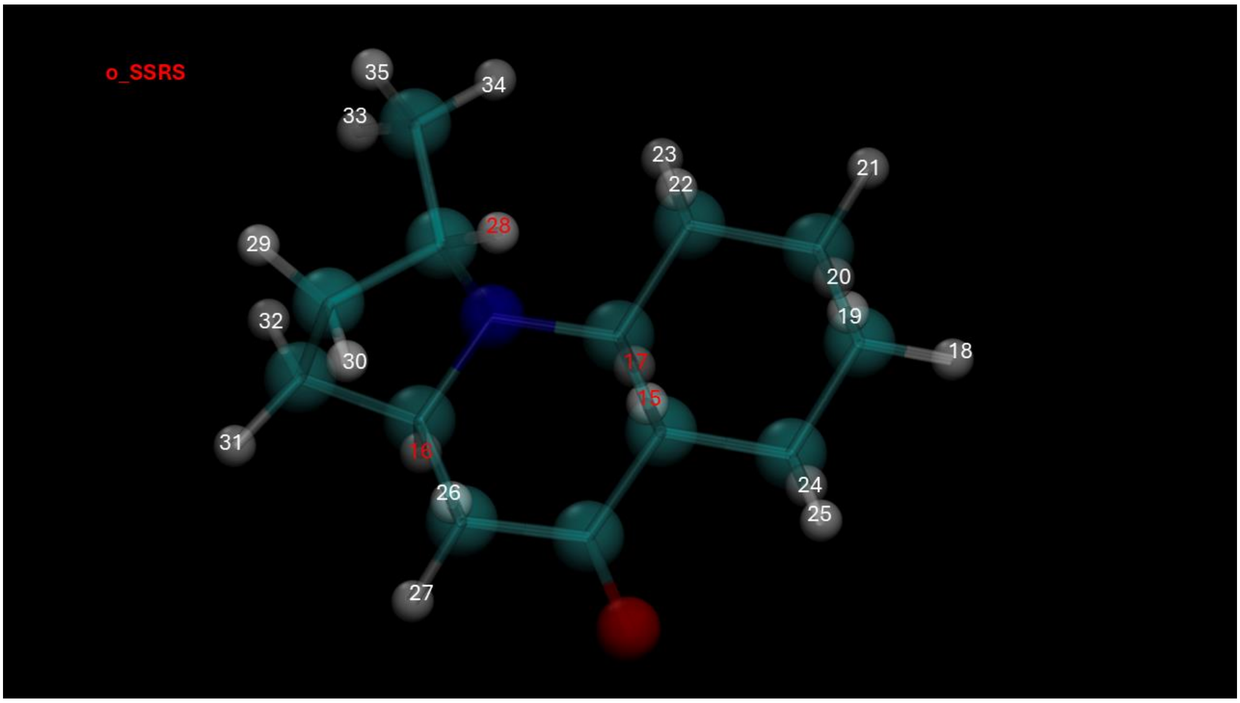
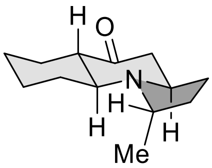
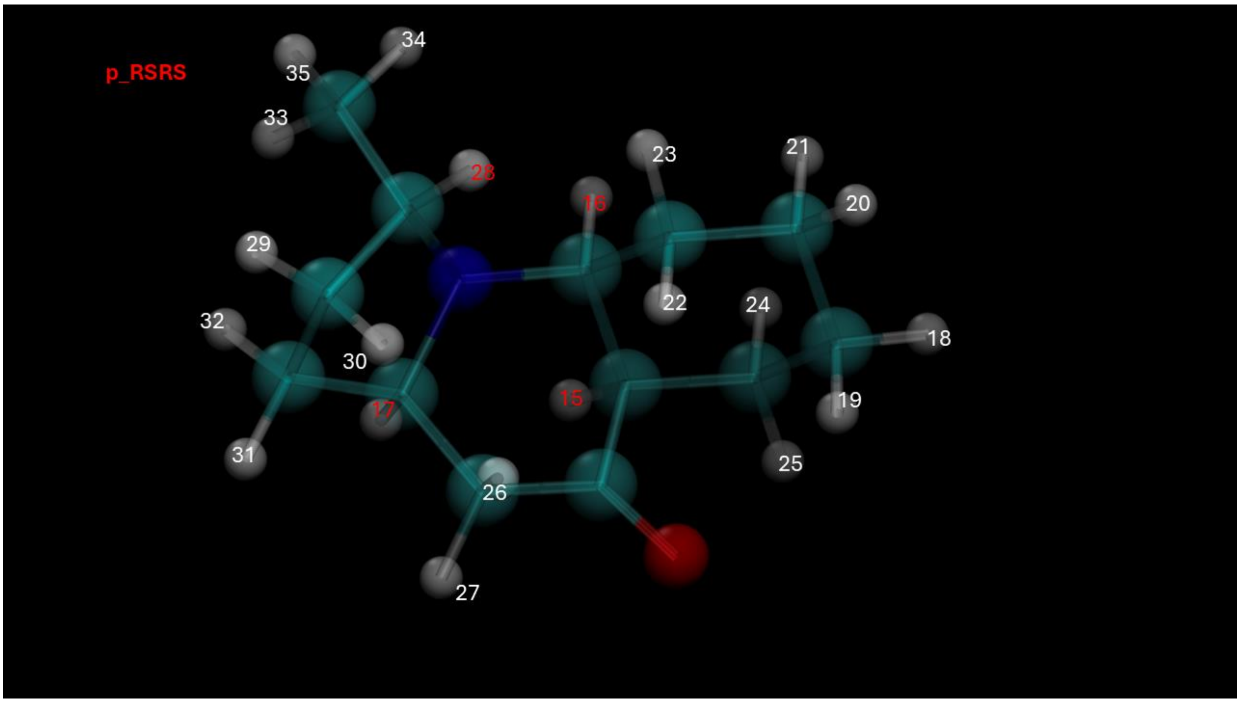


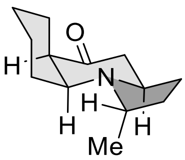


(o) SSRS

#H-H distances (o)
#H15
H15 H16 4.088494777679443
H15 H17 3.0854458808898926
H15 H18 2.5609021186828613
H15 H19 3.7810637950897217
H15 H22 3.830350160598755
H15 H23 2.6344478130340576
H15 H24 3.098076105117798
H15 H25 2.4952094554901123
H15 H26 3.8041324615478516
H15 H27 2.547654628753662
H15 H33 5.158360958099365
H15 H34 4.4919633865356445
H15 H35 5.061049938201904
#H16
H16 H15 4.088494777679443
H16 H17 2.6723804473876953
H16 H26 2.457061767578125
H16 H27 3.1132326126098633
H16 H28 4.133126258850098
H16 H29 4.286613464355469
H16 H30 3.7701027393341064
H16 H31 2.4294681549072266
H16 H32 2.701629161834717
H16 H33 3.8762779235839844
H16 H34 4.606853485107422
H16 H35 5.088926315307617
#H17
H17 H15 3.0854458808898926
H17 H16 2.6723804473876953
H17 H19 4.125362873077393
H17 H22 2.475929021835327
H17 H23 3.0856380462646484
H17 H24 2.5437567234039307
H17 H25 3.7647597789764404
H17 H26 4.123026371002197
H17 H27 4.008006572723389
H17 H28 3.814561367034912
H17 H33 4.2830095291137695
H17 H34 3.925229549407959
H17 H35 5.183022499084473
#H28
H28 H15 2.629917621612549
H28 H16 4.133126258850098
H28 H17 3.814561367034912
H28 H29 2.7859625816345215
H28 H30 2.331979990005493
H28 H31 3.781179428100586
H28 H32 4.209290504455566
H28 H33 3.101209878921509
H28 H34 2.5152978897094727
H28 H35 2.4944443702697754
#H33
H33 H22 3.5590481758117676
H33 H23 4.051008224487305
H33 H28 3.101209878921509
H33 H29 2.8443870544433594
H33 H30 3.8305044174194336
H33 H34 1.7990068197250366
H33 H35 1.8054871559143066
#H34
H34 H22 2.3016841411590576

H34 H23 2.6235876083374023
H34 H28 2.5152978897094727
H34 H29 3.740640163421631
H34 H30 4.278548240661621
H34 H35 1.7898082733154297
#H35
H35 H22 4.0069732666015625
H35 H23 3.7968342304229736
H35 H28 2.4944443702697754
H35 H29 2.4996337890625
H35 H30 3.567727565765381
H35 H34 1.7898082733154297





(p) RSRS

#H-H distances (p)
#H15
H15 H16 2.4710044860839844
H15 H17 2.3540866374969482
H15 H18 3.8630640506744385
H15 H19 4.317279815673828
H15 H22 4.349453449249268
H15 H23 3.861372947692871
H15 H24 2.439171552658081
H15 H25 2.522521734237671
H15 H26 3.4504435062408447
H15 H27 3.8187146186828613
#H16
H16 H15 2.4710044860839844
H16 H17 3.4939305782318115
H16 H26 4.917600154876709
H16 H27 4.387388706207275
H16 H28 3.2910819053649902
H16 H29 5.287528991699219
H16 H30 4.724786281585693
H16 H31 4.619485855102539
H16 H32 5.442877769470215
#H17
H17 H15 2.3540866374969482
H17 H16 3.4939305782318115
H17 H19 6.318894386291504
H17 H22 4.877645015716553
H17 H23 4.378373146057129
H17 H24 4.688466548919678
H17 H25 4.701684951782227
H17 H26 2.4232780933380127
H17 H27 3.094139814376831
H17 H28 4.180204391479492
#H28
H28 H15 4.754049301147461
H28 H16 3.2910819053649902
H28 H17 4.180204391479492
H28 H29 2.688046932220459
H28 H30 2.3461854457855225
H28 H31 3.7424983978271484
H28 H32 4.238032817840576
H28 H33 3.0876715183258057
H28 H34 2.478321075439453
H28 H35 2.4635419845581055
#H33
H33 H22 4.516806602478027
H33 H23 5.191020488739014
H33 H28 3.0876715183258057

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H33 H29 3.00779390335083                H33 H30 3.887315511703491
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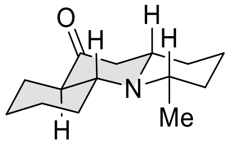
12. Atomic coordinates



(a) RRSS

(a) RRSS

C	1.9382000000	-0.4002000000	-1.1740000000
C	1.8362000000	1.0707000000	-0.7443000000
C	0.4565000000	1.6441000000	-1.0991000000
C	-0.6599000000	0.8074000000	-0.4337000000
C	-0.5495000000	-0.6938000000	-0.8351000000
C	0.8517000000	-1.2362000000	-0.4825000000
N	-2.0334000000	1.3550000000	-0.6508000000
C	-3.0633000000	0.5531000000	0.0801000000
C	-3.0576000000	-0.9300000000	-0.3450000000
C	-1.6623000000	-1.4423000000	-0.1468000000
C	-2.4053000000	1.9160000000	-1.9936000000
C	-3.8048000000	2.5605000000	-1.9405000000
C	-4.8516000000	1.5828000000	-1.4029000000
C	-4.4560000000	1.2043000000	0.0206000000
O	-1.4441000000	-2.3805000000	0.6063000000
C	-2.3094000000	0.9470000000	-3.1921000000
H	-2.7964000000	0.5442000000	1.1629000000
H	-0.4704000000	0.8642000000	0.6641000000
H	-0.6914000000	-0.8217000000	-1.9211000000
H	2.9397000000	-0.7967000000	-0.9010000000
H	1.8227000000	-0.4761000000	-2.2778000000
H	2.6268000000	1.6648000000	-1.2510000000
H	1.9984000000	1.1451000000	0.3537000000
H	0.3545000000	1.6358000000	-2.2026000000

H	0.3977000000	2.6974000000	-0.7494000000
H	0.9401000000	-2.2967000000	-0.8043000000
H	1.0091000000	-1.1908000000	0.6184000000
H	-3.3568000000	-1.0630000000	-1.3956000000
H	-3.7725000000	-1.5123000000	0.2769000000
H	-1.7095000000	2.7484000000	-2.2338000000
H	-4.0995000000	2.9359000000	-2.9447000000
H	-3.7689000000	3.4416000000	-1.2612000000
H	-5.8428000000	2.0849000000	-1.3805000000
H	-4.9392000000	0.6840000000	-2.0474000000
H	-5.2166000000	0.5412000000	0.4866000000
H	-4.4267000000	2.1424000000	0.6193000000
H	-1.2765000000	0.6038000000	-3.3675000000
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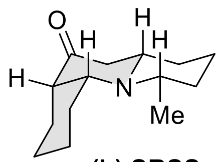
H	-2.9844000000	0.0808000000	-3.1226000000



(b) SRSS

(b) SRSS

C	2.5818000000	-1.6546000000	1.1264000000
C	3.0597000000	-0.5968000000	0.1202000000
C	2.1428000000	0.6259000000	0.1933000000
C	0.6566000000	0.2871000000	-0.0524000000
C	0.1490000000	-0.9457000000	0.7667000000
C	1.1575000000	-2.1189000000	0.7985000000
N	0.1864000000	0.3343000000	-1.4620000000
C	-1.2965000000	0.3207000000	-1.4979000000
C	-1.8665000000	-1.0129000000	-1.0013000000
C	-1.1969000000	-1.4805000000	0.2772000000
C	0.9420000000	-0.1657000000	-2.6522000000

C	0.3352000000	0.4413000000	-3.9361000000
C	-1.1700000000	0.1570000000	-4.0334000000
C	-1.8575000000	0.8158000000	-2.8425000000
O	-1.7069000000	-2.4145000000	0.8785000000
C	1.0213000000	-1.6954000000	-2.8125000000
H	-1.6788000000	1.0635000000	-0.7588000000
H	0.1428000000	1.1646000000	0.4057000000
H	0.0625000000	-0.5979000000	1.8212000000
H	2.6035000000	-1.2254000000	2.1526000000
H	3.2677000000	-2.5286000000	1.1048000000
H	3.0948000000	-1.0131000000	-0.9010000000
H	4.0941000000	-0.2868000000	0.3827000000
H	2.4773000000	1.4430000000	-0.4810000000
H	2.2344000000	1.0072000000	1.2361000000
H	1.1614000000	-2.6612000000	-0.1522000000
H	0.8360000000	-2.8655000000	1.5575000000
H	-1.7867000000	-1.8212000000	-1.7509000000
H	-2.9516000000	-0.8561000000	-0.8133000000
H	1.9880000000	0.2042000000	-2.6041000000
H	0.8606000000	0.0545000000	-4.8365000000
H	0.4862000000	1.5438000000	-3.9202000000
H	-1.5677000000	0.6027000000	-4.9705000000
H	-1.3808000000	-0.9313000000	-4.0620000000
H	-2.9605000000	0.6854000000	-2.8822000000
H	-1.6525000000	1.9079000000	-2.9162000000
H	1.6448000000	-2.1579000000	-2.0493000000
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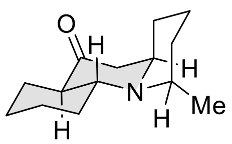
H	0.0388000000	-2.1925000000	-2.8447000000



(c) RRRS

(c) RRRS

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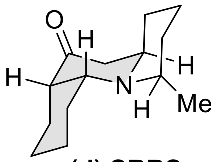
C	1.0258169363	-1.7011584291	2.8559992147
C	2.4471673127	-1.2406701107	2.4487672950
N	2.6573500462	-1.3444576576	0.9699831155
C	1.6073143888	-0.5555888751	0.2379387067
C	2.7860815074	-2.7585039094	0.4574361844
C	3.0673304593	-2.7546658778	-1.0747965857
C	2.0017565328	-1.9462588314	-1.7517945949
C	1.8594216164	-0.5459377275	-1.2768425079
C	3.9277862281	-3.5621127563	1.1466995818
C	4.0336098305	-4.9847051376	0.5750828586
C	4.2869836970	-4.9508624388	-0.9319983519
C	3.1621616272	-4.1885565695	-1.6341794398
O	1.2740420788	-2.4006619107	-2.6228780594
C	2.7781624286	0.1719118620	2.9711334014
H	1.6634879971	0.5129424488	0.5284973002
H	4.0390491893	-2.2426910580	-1.2611910126
H	1.8407781693	-3.3133783058	0.6329807757
H	-0.5775623877	-0.4214677504	0.0597824476
H	0.0258508717	-2.0931458270	0.2694558370
H	-1.0588372456	-1.3065360143	2.3603926622
H	-0.0158850939	0.1500020923	2.3897319694
H	0.9099312277	-2.7804335672	2.6233905325
H	0.8795032599	-1.5864744237	3.9517717987
H	3.1745521969	-1.8651651375	2.9933062788
H	1.0496662824	-0.0047998430	-1.8139420228
H	2.8184321804	-0.0202522925	-1.4782383543
H	3.7476220837	-3.6965774140	2.2293193234
H	4.8946564764	-3.0304441855	1.0068003372

H	3.0879085242	-5.5347884145	0.7779326710
H	4.8635389983	-5.5274106811	1.0768541621
H	4.3402813847	-5.9881306132	-1.3268175687
H	5.2599949725	-4.4508103341	-1.1339533386
H	2.1976235439	-4.7216924096	-1.4786318905
H	3.3750972888	-4.1582415495	-2.7250904718
H	2.1084746144	0.9625757177	2.5858588426
H	3.8216114332	0.4348771863	2.6960710325
H	2.6987818048	0.1893169148	4.0792752735

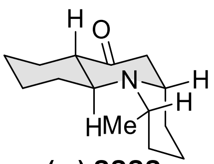


(d) SRRS

(d) SRRS

C	1.2205000000	0.8265000000	1.4478000000
C	1.0037000000	2.2632000000	0.9661000000
C	2.1376000000	3.1614000000	1.4684000000
C	3.5218000000	2.6139000000	1.0410000000
N	3.7205000000	1.2022000000	1.4955000000
C	2.6099000000	0.3243000000	0.9813000000
C	3.9280000000	1.0554000000	2.9846000000
C	4.2232000000	-0.4256000000	3.3475000000
C	3.1098000000	-1.2646000000	2.7987000000
C	2.8348000000	-1.1560000000	1.3377000000
C	5.0874000000	1.9144000000	3.5674000000
C	6.4445000000	1.4912000000	2.9922000000
C	6.7146000000	0.0194000000	3.3286000000
C	5.5942000000	-0.8664000000	2.7763000000
O	2.4144000000	-1.9569000000	3.5261000000
H	4.2594000000	-0.5422000000	4.4550000000
H	3.0092000000	1.3645000000	3.5233000000

H	2.5953000000	0.3383000000	-0.1273000000
C	3.7692000000	2.7606000000	-0.4734000000
H	0.4191000000	0.1830000000	1.0237000000
H	1.1277000000	0.7819000000	2.5519000000
H	0.0256000000	2.6430000000	1.3316000000
H	0.9750000000	2.2793000000	-0.1438000000
H	2.0878000000	3.2065000000	2.5766000000
H	1.9977000000	4.1984000000	1.0935000000
H	4.2952000000	3.2742000000	1.4687000000
H	1.9674000000	-1.7797000000	1.0290000000
H	3.7189000000	-1.5309000000	0.7831000000
H	5.1165000000	1.7736000000	4.6712000000
H	4.9253000000	2.9989000000	3.4267000000
H	7.2489000000	2.1179000000	3.4336000000
H	6.4502000000	1.6418000000	1.8904000000
H	6.7700000000	-0.1037000000	4.4330000000
H	7.6898000000	-0.2926000000	2.8969000000
H	5.7947000000	-1.9254000000	3.0489000000
H	5.6127000000	-0.7826000000	1.6693000000
H	3.0471000000	2.2079000000	-1.1021000000
H	4.7914000000	2.4018000000	-0.7191000000
H	3.7008000000	3.8316000000	-0.7617000000



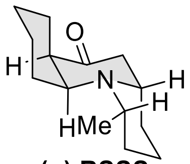
(m) SSSS

(m) SSSS - Geph-6Mem

C	1.7019000000	-2.2265000000	-1.0553000000
C	2.8555000000	-2.5626000000	-1.9931000000
C	3.8042000000	-1.3385000000	-2.1164000000
C	3.9017000000	-0.4843000000	-0.8126000000

C	3.6901000000	-1.4088000000	0.4021000000
C	2.2408000000	-1.9815000000	0.3799000000
N	5.1780000000	0.2953000000	-0.7632000000
C	5.6366000000	0.7037000000	0.6130000000
C	4.4954000000	0.7053000000	1.6415000000
C	3.9821000000	-0.7023000000	1.6964000000
C	5.3018000000	1.3423000000	-1.8178000000
C	6.7371000000	1.9443000000	-1.8495000000
C	7.4524000000	1.9734000000	-0.4878000000
C	6.4484000000	2.0248000000	0.6501000000
O	3.9217000000	-1.3023000000	2.7592000000
C	4.2123000000	2.4418000000	-1.7099000000
H	3.0381000000	0.2108000000	-0.7546000000
H	4.4231000000	-2.2415000000	0.3028000000
H	6.3594000000	-0.0823000000	0.9352000000
H	0.9189000000	-3.0139000000	-1.0271000000
H	1.2321000000	-1.2994000000	-1.4534000000
H	2.5158000000	-2.8691000000	-3.0053000000
H	3.3935000000	-3.4269000000	-1.5435000000
H	3.4488000000	-0.6579000000	-2.9196000000
H	4.7958000000	-1.7402000000	-2.4186000000
H	1.5111000000	-1.3019000000	0.8734000000
H	2.2685000000	-2.9280000000	0.9628000000
H	3.6993000000	1.4050000000	1.3085000000
H	4.8478000000	1.0179000000	2.6492000000
H	5.1450000000	0.9054000000	-2.8270000000
H	6.6806000000	2.9633000000	-2.2906000000
H	7.3967000000	1.3563000000	-2.5252000000
H	8.1885000000	2.8051000000	-0.4633000000
H	8.0265000000	1.0277000000	-0.3576000000
H	5.8316000000	2.9360000000	0.5597000000

H	6.9737000000	2.0964000000	1.6275000000
H	4.1924000000	2.9690000000	-0.7430000000
H	3.2008000000	2.0263000000	-1.8814000000
H	4.3615000000	3.1974000000	-2.5101000000

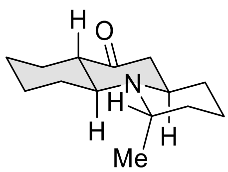


(n) RSSS

(n) RSSS - Geph-6Mem

C	2.6489999099	-0.0179128786	-0.7993792931
C	2.3377696412	-1.5189650841	-0.8880700284
C	0.9770169255	-1.7768428076	-0.3157044998
C	0.6521395677	-1.1934655797	1.0441089957
C	1.1781506035	0.2852544948	1.2098055900
N	2.5145205877	0.5037271864	0.5887720283
C	3.6856296194	0.3712898122	1.5123023331
C	4.9947063380	0.7685564220	0.8042962509
C	5.1750985110	0.0041121830	-0.5081243270
C	4.0060479331	0.3562010248	-1.4238308573
C	-0.8620454188	-1.2013262564	1.3136362256
C	-1.6392440428	-0.3634349349	0.2649911235
C	-0.8229437444	0.8206840530	-0.3058574013
C	0.1451524025	1.3656203250	0.7442563161
C	3.8271574627	-0.9993596880	2.2045711271
O	0.3718645758	-2.7674034819	-0.6996998748
H	1.1545999179	-1.8478334238	1.7811907214
H	1.2672468676	0.5042410427	2.2985150822
H	1.9013042167	0.4858473279	-1.4427769975
H	3.0776414866	-2.1411991900	-0.3612146834
H	2.3568964313	-1.8373964260	-1.9538056756

H	3.5548080103	1.0994724685	2.3434408442
H	5.8655117180	0.6087444941	1.4763262433
H	4.9578168251	1.8559259412	0.5696183685
H	6.1229414443	0.3273144509	-0.9903059310
H	5.2357031317	-1.0901243734	-0.3358089819
H	4.1204505564	-0.1208006023	-2.4215123978
H	4.0244963599	1.4579376679	-1.5827783459
H	-0.9948171564	-0.7362088543	2.3162646909
H	-1.2963303098	-2.2223669054	1.3748298577
H	-2.5664886655	-0.0109476936	0.7669031141
H	-1.9472518340	-0.9843958442	-0.6040094639
H	-1.5175718726	1.5969652730	-0.6916782172
H	-0.2309468843	0.4730140701	-1.1709504174
H	-0.4997408627	1.6540327652	1.6055935005
H	0.6696194902	2.2888949465	0.4165958095
H	2.9475655544	-1.2178212171	2.8368964306
H	4.6958256423	-0.9698350986	2.8963339626
H	4.0058412579	-1.8323735555	1.5086062779



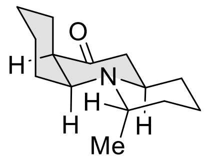
(g) SSRS

(g) SSRS

C	-1.8340000000	0.1926000000	1.2608000000
C	-1.6573000000	-1.2720000000	0.8296000000
C	-0.2775000000	-1.8018000000	1.2587000000
C	0.8263000000	-0.8929000000	0.6686000000
C	0.6620000000	0.5801000000	1.0892000000
C	-0.7319000000	1.0775000000	0.6504000000
N	2.2293000000	-1.3763000000	0.8306000000

C	3.0263000000	-0.6925000000	-0.2281000000
C	3.0658000000	0.8512000000	-0.0290000000
C	1.7838000000	1.4408000000	0.5327000000
C	2.9245000000	-1.2740000000	2.1579000000
C	4.2991000000	-1.9777000000	2.0501000000
C	5.1641000000	-1.3209000000	0.9727000000
C	4.4194000000	-1.3347000000	-0.3629000000
O	1.7385000000	2.6491000000	0.7096000000
C	2.1616000000	-1.9111000000	3.3244000000
H	2.5399000000	-0.8645000000	-1.2160000000
H	0.5927000000	-0.9406000000	-0.4223000000
H	0.7194000000	0.6620000000	2.1969000000
H	-1.7920000000	0.2597000000	2.3703000000
H	-2.8291000000	0.5586000000	0.9285000000
H	-1.7543000000	-1.3369000000	-0.2768000000
H	-2.4563000000	-1.8997000000	1.2796000000
H	-0.1541000000	-2.8403000000	0.8829000000
H	-0.2782000000	-1.8336000000	2.3563000000
H	-0.8108000000	1.0549000000	-0.4594000000
H	-0.8849000000	2.1260000000	0.9863000000
H	3.3417000000	1.3283000000	-0.9942000000
H	3.8422000000	1.1370000000	0.7062000000
H	3.0996000000	-0.2133000000	2.4399000000
H	4.1439000000	-3.0502000000	1.7959000000
H	4.8459000000	-1.9239000000	3.0171000000
H	5.4044000000	-0.2818000000	1.2765000000
H	6.1273000000	-1.8660000000	0.8732000000
H	4.2826000000	-2.3957000000	-0.6694000000
H	5.0165000000	-0.8248000000	-1.1495000000
H	1.8837000000	-2.9619000000	3.0948000000
H	1.2814000000	-1.3026000000	3.5951000000

H	2.7912000000	-1.9031000000	4.2401000000

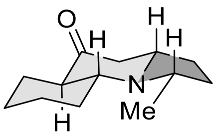


(h) RSRS

(h) RSRS

C	2.8161211422	1.1287868919	0.6076854662
C	3.2910945564	-0.0955975143	-0.1734921204
C	2.1826053321	-0.6191107004	-1.1004945906
C	0.9128226918	-1.0416827356	-0.2745119720
C	0.4328032323	0.2148870326	0.5182009249
C	1.5556827475	0.7872153257	1.4138159183
N	-0.2154277289	-1.6537009901	-1.0880069176
C	-1.4327955221	-0.7808065640	-1.2154937633
C	-1.0722926331	0.6790081219	-1.5448006474
C	-0.1147078129	1.1965232128	-0.5079122902
C	0.2157142885	-2.4011056596	-2.3125849324
C	-0.9603975452	-2.9040921857	-3.1754106447
C	-1.9463936669	-1.7875103972	-3.4739021052
C	-2.5221942105	-1.3443960228	-2.1422987546
O	0.2583965766	2.3587825285	-0.5580939232
C	1.0379912813	-3.6511041657	-1.9236121580
H	-1.9365011069	-0.7399012122	-0.2241041889
H	1.2411998540	-1.8121067803	0.4574041231
H	-0.3960010029	-0.0831993103	1.1954016183
H	2.6151954684	1.9540047916	-0.1051970946
H	3.6185974528	1.4716991593	1.2954989678
H	3.5865989896	-0.9001960114	0.5357942102
H	4.1844976573	0.1800023988	-0.7746031392
H	2.6332977626	-1.4580957233	-1.6568993194

H	1.9238944322	0.1610077007	-1.8485051181
H	1.8233048628	0.0187947183	2.1725012318
H	1.1957031439	1.6876889797	1.9568968921
H	-1.9950989220	1.2985983599	-1.5225980462
H	-0.6049012834	0.7595011992	-2.5488958836
H	0.8024975837	-1.7226005553	-2.9676024242
H	-1.5049050442	-3.7209043265	-2.6484950774
H	-0.5701034829	-3.3233014782	-4.1289952542
H	-1.4580979663	-0.9468980106	-4.0121010484
H	-2.7657001093	-2.1858999071	-4.1106015904
H	-2.9849029014	-2.2330005983	-1.6555999245
H	-3.3334012502	-0.5975955716	-2.2844020773
H	0.4116014584	-4.3455973276	-1.3233976612
H	1.9298040467	-3.4284979336	-1.3115960292
H	1.3830976280	-4.1832987392	-2.8359906564

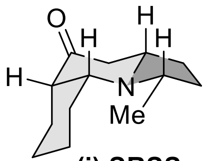


(i) RRSS

(i) RRSS - Geph-6Mem

C	-0.0261045148	-0.6277346179	-0.1163794872
C	-0.3074400433	0.9041626875	-0.2228261252
N	-1.7664965982	1.0333144479	-0.4458446446
C	-2.5076651744	0.6119228383	0.7623677743
C	-2.4284829212	-0.9135230053	0.8255295098
C	-0.9517898864	-1.2266515902	0.9329048444
C	1.4664703028	-0.8901696655	0.1609665725
C	2.3249580627	-0.2653662548	-0.9469232315
C	2.0537557215	1.2412690874	-1.0516808081
C	0.5670129907	1.5068535445	-1.3365479576
C	-2.5022367098	2.1777897683	-0.9958420905

C	-3.9510458420	1.7348142143	-0.7623927126
C	-3.8943890599	1.2557469499	0.6678424803
C	-2.2879199310	2.4084257586	-2.4992889500
O	-0.5205896001	-1.8614823292	1.8843571336
H	-0.2952879213	-1.0979131604	-1.0896890042
H	-0.0259996228	1.4133524810	0.7288214520
H	-2.0510911540	1.0038718534	1.7043432734
H	-2.8491752605	-1.3563620774	-0.1031631750
H	-2.9845089404	-1.3088668661	1.7031555266
H	1.6608467708	-1.9839536108	0.2006844831
H	1.7495919883	-0.4458535317	1.1410669675
H	2.0867989065	-0.7510972381	-1.9190389775
H	3.4004289568	-0.4377031813	-0.7274788564
H	2.6717896628	1.6743380209	-1.8672218164
H	2.3433519218	1.7356558512	-0.0979149100
H	0.2998232252	1.0538312070	-2.3165798854
H	0.4206225747	2.6060781306	-1.3746346136
H	-2.2722661397	3.1009053022	-0.4154807864
H	-4.1688004070	0.8513028695	-1.4064681560
H	-4.7191478959	2.5160677441	-0.9484191826
H	-4.7475471737	0.6446559779	1.0314473283
H	-3.8659557576	2.1883100738	1.2785667221
H	-2.4862495694	1.4763329114	-3.0710121302
H	-1.2726818465	2.7629187877	-2.7397591051
H	-2.9845284544	3.1976658293	-2.8537934201



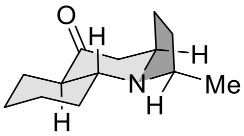
(j) SRSS

(j) SRSS - Geph-6Mem

C	1.4866239403	0.4311651320	0.8665116296

C	1.2834685863	-0.8098124250	-0.0684254592
N	1.5027788286	-0.3913234660	-1.4790695757
C	2.8784193605	0.1104487907	-1.6627271081
C	3.0889138289	1.4201991014	-0.9088353022
C	2.8087364822	1.0842370522	0.5331707686
C	0.3428046930	1.4552931685	0.6937475028
C	-1.0068921839	0.8034510767	0.9998962145
C	-1.2420372551	-0.3671504072	0.0438783159
C	-0.1220746751	-1.4110702413	0.1852155519
C	1.3262171373	-1.3943504614	-2.5609623296
C	2.5732678133	-1.2731290437	-3.4609942247
C	3.0643447982	0.1328850931	-3.1645225981
C	0.0688130632	-1.0586271004	-3.3708553953
O	3.6668793045	1.2358942317	1.3891011438
H	1.4822751877	0.1031153523	1.9308593479
H	2.0352035134	-1.5923523898	0.1859307227
H	3.6155871028	-0.6254865130	-1.2471149461
H	2.3856905514	2.1955492953	-1.2777281474
H	4.1287378920	1.7910454295	-1.0389815231
H	0.3143489202	1.8502365506	-0.3447235111
H	0.5000083738	2.3114542755	1.3855048829
H	-1.8191929547	1.5518242598	0.8769849886
H	-1.0222267372	0.4428688480	2.0521694191
H	-1.2820266735	0.0281206034	-0.9897775583
H	-2.2207740918	-0.8410246320	0.2720006874
H	-0.1512231239	-1.8025117603	1.2262751424
H	-0.3144164102	-2.2704672584	-0.4888801732
H	1.2378254800	-2.4412448609	-2.1954872628
H	2.4270198245	-1.5293423264	-4.5323923569
H	3.3475623902	-1.9731215492	-3.0675943420
H	2.3817182606	0.8850104037	-3.6191564653

H	4.1075324899	0.3220161846	-3.4961735016
H	0.1044691714	-0.0165007361	-3.7532586708
H	-0.8402561163	-1.1899993396	-2.7566649178
H	-0.0218169538	-1.7532801391	-4.2329435588

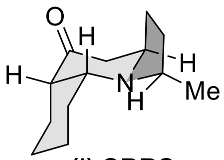


(k) RRRS

(k) RRRS - Geph-6Mem

C	2.8314824951	-1.8887565795	0.6716770196
C	-0.7528134634	-6.1680915832	-1.7355521107
C	-0.8143368210	-5.2672081155	-0.4959397188
C	0.4950547849	-4.4836440530	-0.3389962861
C	0.7842986337	-3.6252960404	-1.5864278688
C	0.7997564614	-4.5181137679	-2.8550597863
C	-0.5119318133	-5.3212465178	-2.9894732229
N	2.0939663114	-2.9410271256	-1.4173468368
C	2.9307669182	-2.7398735809	-2.6250092584
C	2.0922518163	-2.5384954873	-3.9145132012
C	1.0287544802	-3.5921352762	-4.0274784342
C	2.0886514305	-1.6741057007	-0.6551332873
C	2.8135982109	-0.6544405874	-1.5446096071
C	3.8000362690	-1.5280299813	-2.2990552075
O	0.2826973257	-3.5921858457	-4.9961861815
H	1.6519982363	-5.2300677377	-2.7743312556
H	-0.0323801754	-2.8750928878	-1.7073903059
H	3.5633813896	-3.6388143394	-2.7970610100
H	1.0689429737	-1.3035682732	-0.4061564229
H	3.8644697243	-2.2603646410	0.5136720557
H	2.2940655045	-2.6312479435	1.2956805126
H	2.8787025251	-0.9340623343	1.2374764032

H	-1.7094385415	-6.7236111328	-1.8401057135
H	0.0693572739	-6.9085445363	-1.6202297350
H	-0.9841009358	-5.8904913116	0.4081646764
H	-1.6643554756	-4.5561795052	-0.5929235666
H	1.3305849238	-5.2020458351	-0.1839753726
H	0.4197813696	-3.8361168623	0.5591835797
H	-0.4632598312	-5.9833888380	-3.8810846697
H	-1.3692013763	-4.6226717926	-3.1173347573
H	2.7705796457	-2.5647521861	-4.7943600902
H	1.5594652618	-1.5670911089	-3.9169467291
H	3.2510520884	0.2140985731	-1.0071223765
H	2.0833416621	-0.2480443343	-2.2743534670
H	4.2934914728	-1.0530154569	-3.1737449692
H	4.5932735187	-1.8436681959	-1.5876460506

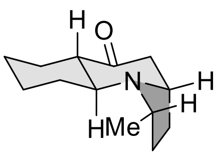


(l) SRRS

(l) SRRS - Geph-6Mem

C	0.5857601969	2.1264734317	-0.6169605617
C	2.6884506719	6.8872570672	-1.5120103028
C	1.5768888582	6.0842238445	-0.8174291380
C	2.1457178968	5.3218893083	0.3914875621
C	3.2740337574	4.3635665547	-0.0441868089
C	4.3817586082	5.1770495274	-0.7612439354
C	3.8221948844	5.9585134900	-1.9700922402
N	2.7282794765	3.2867081465	-0.9154129880
C	3.6726436511	2.6485125854	-1.8717297389
C	5.1581781447	2.7970970655	-1.4608773961
C	5.4921835659	4.2283464233	-1.1369325820

C	2.0561692251	2.1918558808	-0.1779422236
C	2.8250282255	0.9149778875	-0.5346229590
C	3.2389371338	1.1871629339	-1.9639403393
O	6.6473358284	4.5161306112	-0.8620676013
H	4.7901181955	5.9287431128	-0.0465931859
H	3.7298659999	3.9066251713	0.8651906778
H	3.5784830086	3.1125988120	-2.8750026676
H	2.0503552859	2.3263192530	0.9277840503
H	0.4792592420	1.9967365334	-1.7127127655
H	0.0673271337	3.0668304013	-0.3356343609
H	0.0747217962	1.2833702754	-0.1053037781
H	3.0937092465	7.6411574989	-0.8014940604
H	2.2712093902	7.4282848149	-2.3883674618
H	1.1261691075	5.3670713519	-1.5381291122
H	0.7786472128	6.7779190107	-0.4767671485
H	1.3366715654	4.7604157016	0.9038699528
H	2.5520716922	6.0585611507	1.1194694491
H	3.4214166828	5.2790867285	-2.7456539274
H	4.6302742932	6.5629709283	-2.4361423184
H	5.7916359872	2.4342652152	-2.2991029861
H	5.4046817768	2.1991199786	-0.5598715407
H	2.2681436711	-0.0318174791	-0.3677794801
H	3.7438123478	0.8748032391	0.0886154127
H	2.3317521838	1.1238732422	-2.6022783114
H	3.9981257956	0.4959681671	-2.3887412910

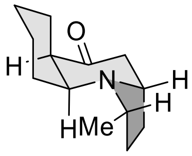


(e) SSSS

(e) SSSS

C	1.5369000000	0.0201000000	0.1472000000
C	0.0949000000	0.5054000000	-0.1368000000
N	-0.9692000000	-0.4069000000	0.4046000000
C	-0.7095000000	-1.8757000000	0.3105000000
C	0.7548000000	-2.3349000000	0.3957000000
C	1.6393000000	-1.3935000000	-0.3257000000
C	2.5618000000	0.9663000000	-0.5123000000
C	2.3988000000	2.3803000000	0.0603000000
C	0.9679000000	2.8872000000	-0.1565000000
C	-0.0532000000	1.9237000000	0.4701000000
C	-2.3292000000	-0.2406000000	-0.2405000000
C	-2.8075000000	-1.6572000000	-0.5907000000
C	-1.4949000000	-2.3516000000	-0.8963000000
H	1.7307000000	0.0190000000	1.2447000000
H	0.0303000000	0.5486000000	-1.2422000000
O	2.4031000000	-1.7595000000	-1.2068000000
H	-3.0365000000	0.2391000000	0.4701000000
H	-1.1926000000	-2.3689000000	1.1893000000
C	-2.4093000000	0.5941000000	-1.5529000000
H	0.8677000000	-3.3919000000	0.0704000000
H	1.0701000000	-2.2803000000	1.4615000000
H	2.4093000000	0.9889000000	-1.6145000000
H	3.5953000000	0.6106000000	-0.3090000000
H	3.1209000000	3.0703000000	-0.4266000000
H	2.6184000000	2.3622000000	1.1508000000
H	0.7669000000	2.9739000000	-1.2472000000
H	0.8598000000	3.8957000000	0.2972000000
H	-1.0661000000	2.3381000000	0.3137000000
H	0.1020000000	1.8729000000	1.5706000000
H	-3.5851000000	-1.7260000000	-1.3825000000
H	-3.2419000000	-2.1262000000	0.3234000000

H	-1.5919000000	-3.4566000000	-0.9601000000
H	-1.0379000000	-1.9645000000	-1.8333000000
H	-1.8031000000	0.1565000000	-2.3731000000
H	-2.1199000000	1.6501000000	-1.4147000000
H	-3.4619000000	0.6165000000	-1.9086000000



(f) RSSS

(f) RSSS

C	1.4903000000	-0.9682000000	0.4867000000
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N	-0.3874000000	0.6699000000	0.6701000000
C	0.3128000000	1.6527000000	-0.1524000000
C	1.8041000000	1.5976000000	0.1612000000
C	2.2351000000	0.1959000000	-0.1679000000
C	-1.7837000000	1.1134000000	0.8125000000
C	-1.8397000000	2.4711000000	0.0883000000
C	-0.3979000000	2.9554000000	0.1766000000
C	1.9316000000	-2.3295000000	-0.1490000000
C	0.8047000000	-3.3490000000	-0.0437000000
C	-0.4160000000	-2.8700000000	-0.8818000000
C	-0.6047000000	-1.3255000000	-0.8941000000
C	-0.0708000000	-0.7506000000	0.4229000000
O	3.1028000000	0.0153000000	-1.0104000000
H	-2.5279000000	0.4138000000	0.3757000000
C	-2.0953000000	1.2573000000	2.3049000000
H	-0.5616000000	-1.3387000000	1.2315000000
H	0.1502000000	1.4295000000	-1.2346000000
H	1.9782000000	1.7975000000	1.2407000000

H	2.3626000000	2.3456000000	-0.4427000000
H	-2.6209000000	3.1743000000	0.4484000000
H	-2.0416000000	2.2732000000	-0.9902000000
H	-0.1527000000	3.7964000000	-0.5062000000
H	-0.1728000000	3.2541000000	1.2247000000
H	2.1150000000	-2.2272000000	-1.2422000000
H	2.8776000000	-2.6721000000	0.3221000000
H	0.5351000000	-3.4195000000	1.0335000000
H	1.1069000000	-4.3640000000	-0.3791000000
H	-1.3051000000	-3.3772000000	-0.4483000000
H	-0.3317000000	-3.1891000000	-1.9431000000
H	-1.6721000000	-1.1025000000	-1.0968000000
H	-0.0060000000	-0.8762000000	-1.7163000000
H	-1.3876000000	1.9547000000	2.8006000000
H	-2.0186000000	0.2664000000	2.8005000000
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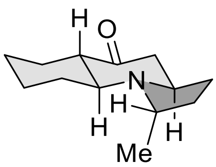
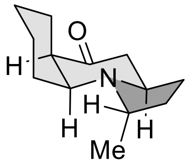


(o) SSRS

(o) SSRS - Geph-6Mem

C	-1.9049017287	-0.1239024995	0.6682743469
C	-1.5010007748	-1.5566145807	0.2954185730
C	-0.0386926488	-1.8244727633	0.6806826295
C	0.8972404800	-0.8048546545	-0.0042572643
C	0.4790463325	0.6423159622	0.3440228382
C	-0.9945680141	0.8858201604	-0.0431984019
N	2.3369639804	-1.0515960283	0.2788566564
C	3.2811109573	-0.0879079858	-0.3195963764
C	2.8748733969	1.3880891695	-0.0369183564

C	1.4329220345	1.5644025904	-0.3694410762
C	2.8280177434	-1.3853020534	1.6356541067
C	4.1845644644	-0.6689768133	1.7809171283
C	4.6099044350	-0.4555472317	0.3343909893
O	1.0651854108	2.3932449297	-1.1892830637
C	3.0253690713	-2.9040992434	1.7323466899
H	0.5876629916	0.8034870913	1.4402726636
H	3.3196286321	-0.2226166470	-1.4232364053
H	0.7634420872	-0.9335129305	-1.1037180430
H	-1.8254802635	0.0120695293	1.7694794850
H	-2.9606664034	0.0538698405	0.3709829125
H	-1.6279953781	-1.7007683261	-0.8003804980
H	-2.1622022066	-2.2806765701	0.8181489805
H	0.2272412135	-2.8546423332	0.3633111626
H	0.0537049373	-1.7531403668	1.7852258127
H	-1.1215648124	0.7740990503	-1.1434012837
H	-1.2948775747	1.9179070957	0.2403062539
H	3.5272318397	2.0853085655	-0.6060626748
H	2.9533413264	1.6565045919	1.0318285688
H	2.1444914718	-1.0602883016	2.4497872979
H	4.9281369313	-1.1740177175	2.4345531434
H	4.0113634602	0.3216895840	2.2427128791
H	4.9338771411	-1.4383723544	-0.0748468625
H	5.4314024411	0.2773125077	0.1858992408
H	3.7144902207	-3.2686969026	0.9412552501
H	2.0602452738	-3.4361220753	1.6280840670
H	3.4493686066	-3.1683521920	2.7244240051

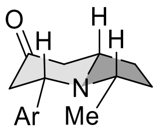


(p) RSRS

(p) RSRS - Geph-6Mem

C	2.6075664079	0.6779215150	0.7362971070
C	2.9072703910	-0.5679230577	-0.1020914917
C	1.7487925122	-0.8762156229	-1.0638758413
C	0.4283373332	-1.1011808915	-0.2778875907
C	0.1174695253	0.1457327923	0.6038504469
C	1.3066243673	0.4819706769	1.5307767134
N	-0.7455233147	-1.4113992543	-1.1476145202
C	-1.8537602871	-0.4413431138	-1.2447248701
C	-1.3129979162	0.9981335405	-1.3970601424
C	-0.2991839586	1.2805059565	-0.3195533515
C	-0.6458895371	-2.1530641672	-2.4207129420
C	-1.6073524293	-1.4275672303	-3.3732727624
C	-2.6846852548	-0.9201738563	-2.4334456467
O	0.2232337011	2.3835237695	-0.2601784007
C	-1.0503721073	-3.6106532991	-2.1754113517
H	-0.7586642783	-0.0902584101	1.2468506414
H	0.5939556654	-1.9733980079	0.3924778858
H	-2.4744284988	-0.4624614265	-0.3214164720
H	2.5292083169	1.5579483867	0.0652271662
H	3.4470554090	0.8651519378	1.4397238566
H	3.0648700782	-1.4372123955	0.5742894266
H	3.8418800330	-0.4083265275	-0.6817415819
H	2.0356300334	-1.7918058456	-1.6191517939
H	1.6298378896	-0.0398789171	-1.7866882953
H	1.4536500090	-0.3655244100	2.2363904311
H	1.0825632287	1.3881560760	2.1339244583

H	-2.1603196885	1.7144839215	-1.3383572695
H	-0.7962760496	1.1405768152	-2.3678043593
H	0.3578712861	-2.1599074856	-2.8848326038
H	-1.9626416656	-2.0314580193	-4.2355289629
H	-1.0809200206	-0.5410034089	-3.7867850526
H	-3.2853692770	-1.7976059223	-2.1092695725
H	-3.3812365360	-0.1650558992	-2.8559637980
H	-2.0622526976	-3.6884395913	-1.7271794037
H	-0.3252541663	-4.0837059277	-1.4797410296
H	-1.0380612070	-4.1746067993	-3.1321808011



(q) SSS

(q) SSS - Dimeth-5Mem

C	-1.6902342120	0.2412633273	-1.3233032302
C	-0.8601941898	-0.9339670926	-0.7342494974
N	0.4492449820	-0.3999200146	-0.2880454930
C	0.2769360716	0.6052835247	0.7736461054
C	-0.4007699558	1.8538410664	0.2141639679
C	-1.7201329542	1.3724981011	-0.3293235580
C	1.4788920676	-1.3355997141	0.2198286694
C	1.9900405499	-0.7175372023	1.5367399813
C	1.6647788346	0.7583305389	1.3601874551
O	-2.7771887692	1.8245949128	0.0827849565
C	-0.7025929616	-2.0290314341	-1.7739928457
C	-1.2158199466	-3.3099477973	-1.5256691563
C	-1.0815622443	-4.3243080277	-2.4742450894
C	-0.4260920675	-4.0787764330	-3.6967973985
C	0.0948994464	-2.8007982051	-3.9570204812
C	-0.0490204647	-1.7817613097	-2.9935459467

O	-0.2758936507	-5.0415415333	-4.6448200441
O	0.7278143763	-2.5924069787	-5.1422323479
C	1.3082198324	-1.4111426101	-5.5551091252
C	-0.7294804129	-6.3412051580	-4.5586210779
C	2.6232471731	-1.4195449268	-0.7985442883
H	-0.3838520976	0.2008478008	1.5834617478
H	-1.4059183320	-1.3394567344	0.1495140460
H	-2.7168914674	-0.0905522585	-1.5922913017
H	-1.1963544127	0.6314783950	-2.2378811517
H	0.2115568892	2.2841521247	-0.6073730161
H	-0.5449332440	2.6210398208	1.0053376244
H	1.0969016269	-2.3650235182	0.4012996260
H	3.0389033760	-0.9617399802	1.8104633628
H	1.3436222592	-1.0927817177	2.3642162548
H	2.3452662982	1.2148546368	0.6076778923
H	1.7025815781	1.3447244131	2.3027113466
H	-1.7244181556	-3.5278974614	-0.5947192224
H	-1.4921985615	-5.2983861324	-2.2453972131
H	0.3523056470	-0.7957567161	-3.1824591875
H	1.7445378337	-1.5557722810	-6.5645439819
H	2.1211339994	-1.1185493008	-4.8569624281
H	0.5444778781	-0.6067078440	-5.6118319807
H	-0.4564870428	-6.8820100451	-5.4878021994
H	-1.8351417147	-6.3554372387	-4.4529499839
H	-0.2560025257	-6.8570923920	-3.6965808299
H	3.0427640414	-0.4149869228	-1.0163160520
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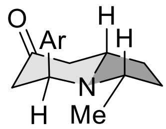
H	3.4342980119	-2.0672857429	-0.4031388554

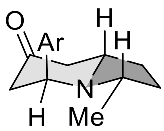


(r) RSS

(r) RSS - Dimeth-5Mem

C	-2.2874024305	-0.3042717372	-0.6992641693
C	-1.0051281764	-1.0367604689	-0.2318857688
N	0.1237223696	-0.0696974627	-0.2594328474
C	-0.0602624349	1.1449981154	0.5451728969
C	-1.2714600095	1.9412470126	0.0516967070
C	-2.4435817529	0.9929331578	0.0537552472
C	1.4752748825	-0.5015031645	0.0977143771
C	2.2437250353	0.8077483252	-0.0540933811
C	1.2978471460	1.8633795152	0.5297419214
O	-3.4589157853	1.2404944353	0.6859008652
C	-1.1815564180	-1.8071989690	1.0876612924
C	-0.8916595699	-3.1839933636	1.0988669548
C	-1.0423613265	-3.9450433196	2.2575172317
C	-1.4989674604	-3.3520066236	3.4473232812
C	-1.8063576495	-1.9840665877	3.4599048208
C	-1.6489105895	-1.2216285566	2.2831324739
O	-1.6632813235	-4.0618197934	4.5954490201
O	-2.2575889919	-1.4397471563	4.6219858925
C	-2.6144787275	-0.1217408135	4.8194150942
C	-1.4255353324	-5.4112698864	4.7553432331
C	2.0258516601	-1.5988930137	-0.8182702027
H	-0.2132118573	0.8490565643	1.6012037126
H	-0.7981850431	-1.7933788396	-1.0195758686
H	-3.1817323087	-0.9601239080	-0.6218316365
H	-2.1551026993	-0.0274584101	-1.7680357682
H	-1.0883187976	2.2792867445	-0.9910262262

H	-1.4577326996	2.8291218285	0.6935439189
H	1.5060825244	-0.8431806382	1.1593653883
H	2.2841640104	1.0087043007	-1.1505059704
H	3.2850071202	0.8348756013	0.3308104656
H	1.3368067520	2.7773916260	-0.1027161613
H	1.5670850514	2.1257338258	1.5770877308
H	-0.5413724236	-3.6823200290	0.2038660279
H	-0.8022357207	-4.9988707725	2.2144534755
H	-1.9130037560	-0.1821099024	2.3127018046
H	-2.9402047763	0.0112675202	5.8713807723
H	-3.4586149436	0.1519932390	4.1511392275
H	-1.7453363288	0.5441356294	4.6311432867
H	-1.6528797677	-5.6973894933	5.8025791941
H	-0.3584296155	-5.6407890442	4.5491056925
H	-2.0811506190	-5.9991790318	4.0780086676
H	1.9834205335	-1.2815977026	-1.8821657428
H	1.4410641653	-2.5327448541	-0.7015945538
H	3.0806080851	-1.8181838989	-0.5484723775



(r) RSS

(s) SRS – Dimeth-5Mem

C	-1.4923379848	-0.8070191073	0.8234676177
C	-0.2662233917	-1.5377550092	0.2242180379
N	0.7696561206	-0.5301224541	-0.1062818260
C	0.4129428697	0.6399971922	-0.9120303799
C	-0.7591522973	1.3958102845	-0.2767416760
C	-1.8507771973	0.3911989097	-0.0184464580
C	2.2109123716	-0.7914177450	-0.2675193545
C	2.6784402147	0.2658720941	-1.2812545472

C	1.7200861682	1.4155476495	-1.0033369942
O	-2.9674979449	0.5254649675	-0.4941512436
C	-0.6368958739	-2.4552236946	-0.9469406298
C	-1.2689095588	-1.9964936295	-2.1178058917
C	-1.5903291170	-2.8771841145	-3.1510179224
C	-1.2934947372	-4.2476399457	-3.0442373372
C	-0.6733585547	-4.7283580068	-1.8823741803
C	-0.3540924928	-3.8315752987	-0.8424103125
O	-1.5919439307	-5.1338036605	-4.0313657526
O	-0.4013315440	-6.0583860394	-1.8023097430
C	0.2039899865	-6.7014080721	-0.7424998803
C	-2.2020841503	-4.8343238996	-5.2318117204
C	2.5792804295	-2.2104313561	-0.7075626193
H	0.1457345843	0.3120372658	-1.9369531615
H	0.1334849276	-2.1765073942	1.0422746777
H	-2.3453960312	-1.5043885376	0.9720200176
H	-1.2017973065	-0.4057715048	1.8190726933
H	-1.0969513977	2.2286466096	-0.9303611277
H	-0.4443586260	1.8141823327	0.7039397943
H	2.6841140647	-0.5764321093	0.7160202560
H	2.4613681033	-0.0915501530	-2.3151774976
H	3.7592913082	0.5138596184	-1.2193434722
H	1.7242073636	2.2183519809	-1.7709889591
H	1.9684238212	1.8521117091	-0.0089233808
H	-1.5371547052	-0.9640783541	-2.2539305955
H	-2.0755765759	-2.4785655246	-4.0318151203
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H	0.2880435751	-7.7826348201	-0.9753645414
H	-0.4072622527	-6.5845203114	0.1776869134
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H	-2.3098685638	-5.7651930660	-5.8253205802

H	-1.5817984636	-4.1161245297	-5.8092655438
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H	2.1091266057	-2.4539836342	-1.6836314445
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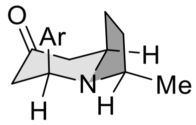
H	3.6814880697	-2.2943908079	-0.8139229210



(t) RRS

(t) RRS – Dimeth-5Mem

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C	0.1949139825	0.7645866970	-0.2078823998
C	-1.0033814300	1.0870240122	0.6973142933
C	-2.1909335705	0.3932784075	0.0895366655
C	1.8067160269	-0.9937487850	-0.3829915868
C	2.4797589811	0.3742981988	-0.5474896414
C	1.5571184750	1.2635946338	0.2729662155
O	-3.2050607912	1.0226670699	-0.1689636061
C	-0.6315345205	-2.0900344468	1.4843865147
C	0.2099535830	-1.5473926215	2.4728512204
C	0.1846027473	-2.0230735119	3.7843340700
C	-0.6819203284	-3.0666725985	4.1522935433
C	-1.5261433476	-3.6296198563	3.1862419228
C	-1.4948694294	-3.1382934080	1.8652715931
O	-0.7317497090	-3.5566343675	5.4196637732
O	-2.3508540789	-4.6426507392	3.5645742736
C	-3.2341412463	-5.3189895329	2.7487658576
C	0.0254594586	-3.1206618480	6.4871824946
C	2.2305821431	-1.9887690732	-1.4621293319
H	0.0057851492	1.2174174201	-1.2090704414

H	-0.5424313515	-2.5790599024	-0.5756890699
H	-2.8947358880	-1.6657803610	0.0606742752
H	-2.1665829924	-1.0456418902	-1.4540015081
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H	2.4010071842	0.6999184677	-1.6109274048
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H	1.7135739809	2.3549908090	0.1391942763
H	1.7086438679	1.0219885396	1.3437826009
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H	0.8478133703	-1.5678407068	4.5076652999
H	-2.1410042272	-3.5789196817	1.1181198601
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H	-2.6857612803	-5.8253169476	1.9258723626
H	-3.9873234724	-4.6169291021	2.3318778861
H	-0.2405320566	-3.7138743404	7.3859262723
H	-0.1845514876	-2.0498148619	6.6949786236
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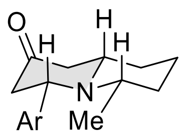

(u) SSS

(u) SSS – Dimeth-6Mem

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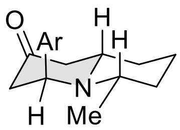
C	1.3279195207	-1.4858115808	-0.5611715099
C	2.4821357130	-0.5438317052	-0.4736887764
O	3.5490428789	-0.8798719209	0.0169537870
C	0.7315798626	2.8158132896	-0.7822338380
C	0.8375321476	3.9475821907	0.0390679870
C	0.5755716208	5.2201873355	-0.4690367679
C	0.1983602675	5.3895220484	-1.8156892106
C	0.0867422718	4.2638922512	-2.6488393577
C	0.3559693468	2.9822720311	-2.1262402788
O	-0.0660512549	6.6136443222	-2.3452830721
O	-0.2834520411	4.4544578749	-3.9433229197
C	-0.4509385162	3.4674510098	-4.8926452626
C	-0.0050905440	7.8173620399	-1.6739162008
H	0.4961865892	-0.7728038342	1.2864027427
H	1.2826242661	1.5242158795	0.8670254521
C	-1.4533257984	1.0848137467	0.1581059820
C	-2.0189267880	0.3065931530	1.3591797063
C	-2.1996155055	-1.1907405460	1.0548117864
C	-1.0746633674	-1.7454743480	0.1603058524
C	-2.4669443469	1.1406106466	-0.9930026077
H	3.1429559938	1.4849224757	-0.7968801165
H	2.0419483419	0.7875935580	-2.0443913220
H	1.0423280133	-1.6160484276	-1.6279420461
H	1.5953875910	-2.4781641030	-0.1359224193
H	1.1241850313	3.8475194161	1.0785638710
H	0.6688746845	6.0675563937	0.1966872671
H	0.2686551911	2.1084560271	-2.7571323951
H	-0.7566360696	3.9348765078	-5.8510068821
H	-1.2464069416	2.7599366733	-4.5747917252
H	0.5036713092	2.9227189485	-5.0536585508
H	-0.2744474517	8.6357639348	-2.3725524523

H	1.0252648962	7.9968715858	-1.2995639247
H	-0.7255806739	7.8228469410	-0.8284005089
H	-1.3244338436	2.1295601939	0.5141508652
H	-2.9621635712	0.7406375424	1.7557525306
H	-1.2608489838	0.4083551947	2.1673019435
H	-3.1679414117	-1.4057240913	0.5532402604
H	-2.2126105673	-1.7055826175	2.0402563365
H	-1.4051613760	-1.7340097246	-0.9012884894
H	-0.8796200405	-2.8058342208	0.4312121887
H	-2.6828506942	0.1330986129	-1.4004334659
H	-2.0778099949	1.7681001008	-1.8192613851
H	-3.4195210312	1.5905637153	-0.6407090671



(v) RSS

(v) RSS – Dimeth-6Mem

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N	-0.1083486772	0.7354388113	0.2075250083
C	0.0106902902	-0.7579475723	0.2670058060
C	1.1917151456	-1.3021729790	-0.5585212575
C	2.4123390127	-0.5020618119	-0.2424781524
O	3.4302998795	-1.0215733655	0.1885332046
C	1.4782519403	1.7626025783	1.8284815079
C	1.4017251284	3.0632165293	2.3586945790
C	1.7023787101	3.3135189675	3.6972786607
C	2.0938698115	2.2657783525	4.5497542681
C	2.1825256037	0.9614290272	4.0414819055
C	1.8753871586	0.7179006530	2.6863348861
O	2.3946199734	2.4705662859	5.8598719903

O	2.5683634338	-0.0317710672	4.8869019621
C	2.7101854271	-1.3656238732	4.5638185388
C	2.3592807606	3.6815903021	6.5195526451
H	0.1801071562	-1.0041378631	1.3336585316
H	0.9568580086	2.5606463697	-0.0726050093
C	-1.1887446188	1.3013077307	-0.6297456875
C	-2.5632316249	0.6866806627	-0.2312702430
C	-2.4654265595	-0.6940370697	0.4517499587
C	-1.3033103873	-1.4840415121	-0.1251014826
C	-0.8815122494	1.1486424101	-2.1322994226
H	3.2585747008	1.5049842080	-0.2250442073
H	2.1118269646	1.1118988501	-1.5451181779
H	0.9843981417	-1.1800894245	-1.6420028956
H	1.3475752811	-2.3837139358	-0.3529304954
H	1.1030541920	3.8974647241	1.7359491600
H	1.6262230659	4.3300717114	4.0589904598
H	1.9591333366	-0.2845071472	2.3126079427
H	3.0360484113	-1.9237722312	5.4651984648
H	3.4808885596	-1.4897280518	3.7733360845
H	1.7394735406	-1.7832011797	4.2208046917
H	2.6556128215	3.5265933561	7.5771306918
H	1.3306996582	4.1006611908	6.4980380949
H	3.0724279667	4.3941256810	6.0529772090
H	-1.2784776387	2.3987551440	-0.4663349032
H	-3.2044067561	0.6396747253	-1.1384850654
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H	-3.4374959312	-1.2233361801	0.3558971607
H	-2.2602323915	-0.5640915553	1.5385817556
H	-1.4508914591	-1.5588604606	-1.2208281078
H	-1.2760368080	-2.5221346549	0.2719014928
H	-0.7876546687	0.0978804265	-2.4552943274

H	0.0574619493	1.6784869678	-2.3870675896
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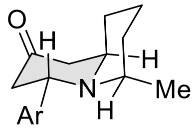

(w) SRS

(w) SRS

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N	0.1412067459	0.6610869212	-0.3565765023
C	-0.1631948035	-0.4926206993	0.5459328682
C	-1.5531245622	-1.1010426105	0.2350692565
C	-2.5742398551	-0.0231693176	0.1172696667
O	-3.5864429583	-0.0107807963	0.8008635833
C	-1.0906543399	2.6838443884	0.6451459899
C	-0.8685056607	4.0528149244	0.4040240578
C	-1.0038607264	4.9944334159	1.4234103999
C	-1.3720986182	4.5952434068	2.7205147501
C	-1.6068903440	3.2374848818	2.9826139600
C	-1.4674605992	2.2915891796	1.9455772242
O	-1.5129230811	5.4836914840	3.7400918327
O	-1.9662978631	2.8807865879	4.2450049669
C	-2.2348372313	1.6003377303	4.6831234757
C	-1.3201224838	6.8472498738	3.6589922185
H	-0.1258683855	-0.1527841728	1.5989119598
H	-0.6604604528	2.3011451158	-1.4210341057
C	1.5395439440	1.1787089163	-0.2529581289
C	2.5315076187	0.0236605955	-0.4979410502
C	2.3058343050	-1.1169227922	0.4987939742
C	0.8754603151	-1.6234148968	0.3517963278
C	1.8737894644	1.8836197743	1.0850077637
H	-2.1922046855	0.5602787712	-1.8719394663

H	-3.0854357334	1.8095543388	-0.9342069039
H	-1.8344681246	-1.8586234609	0.9989105124
H	-1.5231018915	-1.6023775015	-0.7577381957
H	-0.5828269021	4.4006200555	-0.5809493062
H	-0.8185343452	6.0340773147	1.1895619879
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H	-2.4985873962	1.6340283796	5.7599604592
H	-1.3386173767	0.9557134371	4.5583162741
H	-3.0938456841	1.1743903719	4.1219302228
H	-1.5093983040	7.2994965522	4.6539920176
H	-2.0277409223	7.2924596625	2.9275075020
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H	3.5793997705	0.3887201538	-0.4295851371
H	2.3799137493	-0.3667546163	-1.5289402879
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H	3.0152835382	-1.9454254958	0.2860545381
H	0.6914273934	-2.4478886477	1.0747960254
H	0.7755148040	-2.0390854325	-0.6764489968
H	1.6807450491	1.2446331590	1.9680345697
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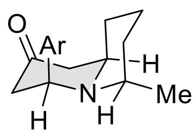

(x) RRS

(x) RRS – Dimeth-6Mem

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N	0.6221705199	0.2291058647	-0.2353326139
C	0.5268418158	-0.9972328844	0.6149788138

C	-0.7423868548	-1.8155901425	0.2716579380
C	-1.9541855005	-0.9319917796	0.2344822751
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C	-0.9650317599	1.3202774926	-1.7777726472
C	-0.9987071382	2.6327929376	-2.2785688718
C	-1.3194614228	2.8812408371	-3.6131676612
C	-1.6142848848	1.8184275832	-4.4873322271
C	-1.5815441639	0.5006473213	-4.0056567174
C	-1.2555912664	0.2604130933	-2.6547227523
O	-1.9307615950	2.0207928027	-5.7940679105
O	-1.8677943840	-0.5079319896	-4.8719374141
C	-1.8866806966	-1.8546381447	-4.5725388472
C	-2.0052285422	3.2429041906	-6.4296339026
H	0.4694496607	-0.6960896209	1.6836510739
H	-0.4250061530	2.0836254137	0.1286198503
C	1.8759492834	1.0075411030	-0.0277913634
C	3.0954363253	0.0963791161	-0.2729692666
C	3.0597679986	-1.1345544591	0.6393981079
C	1.7605934223	-1.9006256067	0.3989795262
C	1.9630853541	1.6859458299	1.3640717122
H	-2.7131482868	1.1054133935	0.3707257443
H	-1.5014751089	0.6072956374	1.5930598330
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H	-0.7764818028	3.4751520909	-1.6351701734
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H	-1.2243005797	-0.7504021695	-2.2936513925
H	-2.1555441739	-2.4247194472	-5.4852376875
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H	-2.2850432946	3.0826170838	-7.4909468767

H	-1.0191301616	3.7534063375	-6.3969259148
H	-2.7808390651	3.8781118847	-5.9511519994
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H	4.0407095383	0.6608941231	-0.1198791300
H	3.0745512570	-0.2468637949	-1.3312633300
H	3.1341753578	-0.8384369285	1.7057678097
H	3.9267807025	-1.7925198521	0.4153962516
H	1.7169810052	-2.7853028028	1.0708206458
H	1.7659774982	-2.2637968756	-0.6533903381
H	1.9218862940	0.9618902412	2.1995463843
H	1.1540371662	2.4224593998	1.5264112138
H	2.9196549820	2.2447910870	1.4433480204

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