

Supporting information for

**C-H functionalization of 2-alkyl tryptamines: direct assembly of
azepino[4,5-*b*]indoles and total synthesis of ngouniensines**

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1. Materials and Methods

Unless stated otherwise, all solvents and commercially available reagents were used as received without further purification. Reaction temperatures were controlled using an IKA magnetic temperature modulator.

Thin layer chromatography (TLC) was conducted on plates (GF254) supplied by Yantai Chemicals (China) and visualized using UV (254nm). Silica gel (200-300 mesh) supplied by Tsingtao Haiyang Chemicals (China) was used for flash column chromatography.

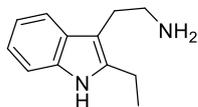
All NMR spectra were recorded on Bruker AVANCE III HD 400MHz instruments and are calibrated using residual undeuterated solvent (CHCl_3 at 7.26 ppm ^1H NMR, 77.16 ppm ^{13}C NMR; CH_3OH at 3.31 ppm ^1H NMR, 49.00 ppm ^{13}C NMR; DMSO at 2.50 ppm ^1H NMR, 39.52 ^{13}C NMR).

Data for ^1H NMR spectra were reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad. ^{13}C NMR spectra are reported in terms of chemical shift.

High resolution mass spectrometry (HRMS) data were obtained on a Xevo G2-XS QToF Quadrupole Time-of-Flight Mass Spectrometry by electrospray ionization (ESI) in the positive ion mode from Waters Corporation.

2. Synthesis of Tryptamine Derivatives 2

Compound **2k** and **2l** were prepared by following the literature procedure¹.



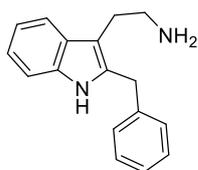
2-(2-ethyl-1H-indol-3-yl)ethan-1-amine (**2k**)

Light brown oil. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 (br, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.23 (m, 1H), 7.10 (m, 2H), 2.99 (s, 2H), 2.88 (t, *J* = 6.4 Hz, 2H), 2.78 (q, *J* = 7.6 Hz, 2H), 1.96 (br, 2H), 1.28 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 137.9, 135.4, 128.8, 121.2, 119.3, 118.3, 110.5, 108.2, 42.7, 28.1, 19.5, 14.6.

HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₁₂H₁₇N₂⁺, 189.1386, found 189.1382.



2-(2-benzyl-1H-indol-3-yl)ethan-1-amine (**2l**)

Brown solid. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.85 (br, 1H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.26 – 7.15 (m, 4H), 7.14 – 7.05 (m, 2H), 4.12 (s, 2H), 3.02 – 2.95 (m, 2H), 2.92 (dd, *J* = 10.0, 3.7 Hz, 2H), 1.40 (br, 2H).

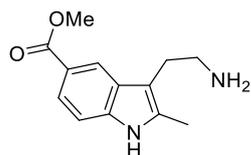
¹³C NMR (100 MHz, Chloroform-*d*) δ 138.9, 135.7, 134.2, 128.9, 128.8, 126.8, 121.5, 119.4, 118.6, 110.7, 110.2, 43.0, 32.5, 28.6.

HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₁₇H₁₉N₂⁺, 251.1543, found 251.1544.

Compound **2m-2r** were prepared by Fischer indolization by following the literature procedure².

¹ I. Fleming, J. Harley-Mason, *J. Chem. Soc. C.*, **1966**, 425-425.

² R. Amaradhi, A. Banik, S. Mohammed, V. Patro, A. Rojas, W. Wang, D. R. Motati, R. Dingedine, T. Ganesh, *J. Med. Chem.* **2020**, *63*, 1032–1050.



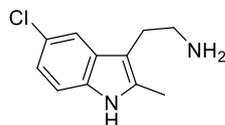
methyl 3-(2-aminoethyl)-2-methyl-1H-indole-5-carboxylate (2m)

Brown solid. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 8.68 (br, 1H), 8.26 (s, 1H), 7.81 (d, $J = 8.5$ Hz, 1H), 7.23 (d, $J = 8.5$ Hz, 1H), 3.91 (s, 3H), 2.97 (t, $J = 6.7$ Hz, 2H), 2.85 (t, $J = 6.7$ Hz, 2H), 2.37 (s, 3H), 1.55 (br, 2H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 168.6, 138.2, 133.5, 128.6, 122.6, 121.2, 120.9, 110.6, 110.0, 51.9, 42.8, 28.4, 11.8.

HRMS-ESI (m/z): $[M + H]^+$ calculated for $C_{13}H_{17}N_2O_2^+$, 233.1285, found 233.1296.



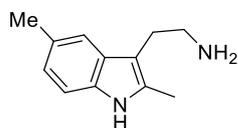
2-(5-chloro-2-methyl-1H-indol-3-yl)ethan-1-amine (2n)

Light yellow solid. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 9.07 (br, 1H), 7.45 (d, $J = 2.0$ Hz, 1H), 7.12 – 6.98 (m, 2H), 2.95 (t, $J = 6.7$ Hz, 2H), 2.79 (t, $J = 6.7$ Hz, 2H), 2.30 (s, 3H), 1.32 (br, 2H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 133.8, 129.9, 124.5, 120.8, 117.3, 111.3, 108.6, 108.5, 42.5, 28.1, 11.6.

HRMS-ESI (m/z): $[M + H]^+$ calculated for $C_{11}H_{14}N_2Cl^+$, 209.0840, found 209.0850.



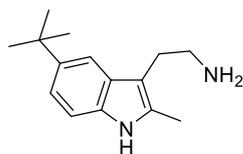
2-(2,5-dimethyl-1H-indol-3-yl)ethan-1-amine (2o)

Brown solid. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 8.08 (br, 1H), 7.31 (s, 1H), 7.14 (d, $J = 8.2$ Hz, 1H), 6.95 (d, $J = 8.1$ Hz, 1H), 2.98 (t, $J = 6.7$ Hz, 2H), 2.84 (t, $J = 6.7$ Hz, 2H), 2.46 (s, 3H), 2.36 (s, 3H), 1.29 (br, 2H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 133.8, 132.0, 129.2, 128.3, 122.5, 117.9, 110.0, 108.7, 42.8, 28.5, 21.6, 11.8.

HRMS-ESI (m/z): $[M + H]^+$ calculated for $C_{12}H_{17}N_2^+$, 189.1386, found 189.1382.



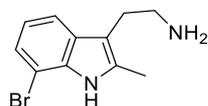
2-(5-(tert-butyl)-2-methyl-1H-indol-3-yl)ethan-1-amine (2p)

Brown solid. Characterization data:

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.98 (br, 1H), 7.50 (m, 1H), 7.21 (m, 2H), 3.00 (t, $J = 6.7$ Hz, 2H), 2.87 (t, $J = 6.7$ Hz, 2H), 2.37 (s, 3H), 1.40 (s, 9H).

$^{13}\text{C NMR}$ (100 MHz, Chloroform-*d*) δ 142.2, 133.6, 132.0, 128.6, 119.2, 113.9, 109.8, 109.2, 42.8, 34.7, 32.1, 28.5, 11.9.

HRMS-ESI (m/z): $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{23}\text{N}_2^+$, 231.1856, found 231.1863.



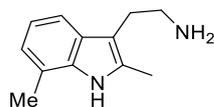
2-(7-bromo-2-methyl-1H-indol-3-yl)ethan-1-amine (2q)

Brown solid. Characterization data:

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.23 (br, 1H), 7.44 (d, $J = 7.8$ Hz, 1H), 7.24 (s, 1H), 6.95 (t, $J = 7.7$ Hz, 1H), 2.96 (t, $J = 6.6$ Hz, 2H), 2.82 (t, $J = 6.7$ Hz, 2H), 2.42 (s, 3H), 1.47 (br, 2H).

$^{13}\text{C NMR}$ (100 MHz, Chloroform-*d*) δ 134.1, 132.8, 130.2, 123.4, 120.5, 117.3, 110.7, 104.1, 42.8, 28.7, 11.9.

HRMS-ESI (m/z): $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{Br}^+$, 253.0335, found 253.0335.



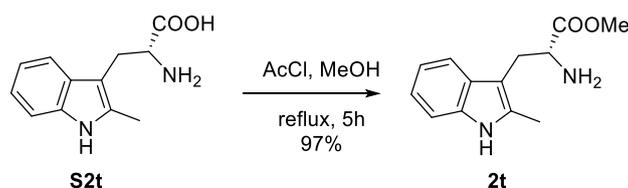
2-(2,7-dimethyl-1H-indol-3-yl)ethan-1-amine (2r)

Brown solid. Characterization data:

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.96 (br, 1H), 7.37 (d, $J = 7.8$ Hz, 1H), 7.01 (t, $J = 7.5$ Hz, 1H), 6.93 (d, $J = 7.1$ Hz, 1H), 2.98 (t, $J = 6.7$ Hz, 2H), 2.87 (t, $J = 6.7$ Hz, 2H), 2.47 (s, 3H), 2.42 (s, 3H), 1.96 (br, 2H).

$^{13}\text{C NMR}$ (100 MHz, Chloroform-*d*) δ 134.9, 131.6, 128.4, 121.8, 119.5, 115.9, 109.6, 42.7, 28.3, 16.7, 11.9.

HRMS-ESI (m/z): $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{12}\text{H}_{17}\text{N}_2^+$, 189.1386, found 189.1382.



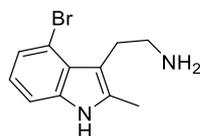
To a cooled solution (0 °C) of **S2t** (100 mg, 0.46 mmol) in MeOH (1.0 mL) was added acetyl chloride (125 μ L) dropwise over 15 mins. The mixture was heated to reflux for 5 hours and then cooled to room temperature. The mixture was concentrated under reduced pressure to afford the residue, which was basified with 3 mL NH_4OH and extracted with DCM (3 \times 10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure to give compound **2t** (103.1 mg, 97% yield) as a light brown oil. Characterization data:

^1H NMR (400 MHz, Chloroform-*d*) δ 8.05 (br, 1H), 7.52 (d, $J = 7.1$ Hz, 1H), 7.28 – 7.21 (m, 1H), 7.15 – 7.05 (m, 2H), 3.88 – 3.79 (m, 1H), 3.71 (s, 3H), 3.30 – 3.17 (m, 1H), 2.98 (dd, $J = 14.2, 8.0$ Hz, 1H), 2.36 (s, 3H), 1.53 (br, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 176.0, 135.4, 132.8, 128.9, 121.4, 119.5, 118.1, 110.4, 107.2, 55.5, 52.1, 30.2, 11.9.

HRMS-ESI (m/z): $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{13}\text{H}_{17}\text{N}_2\text{O}_2^+$, 233.1285, found 233.1296.

Compound **2u** and **2w** were prepared by following the literature procedure.³



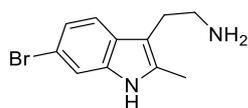
2-(4-bromo-2-methyl-1H-indol-3-yl)ethan-1-amine (**2u**)

Brown solid. Characterization data:

^1H NMR (400 MHz, Methanol-*d*₄) δ 7.21 (d, $J = 8.0$ Hz, 1H), 7.09 (d, $J = 7.6$ Hz, 1H), 6.84 (t, $J = 7.8$ Hz, 1H), 3.05 (t, $J = 7.4$ Hz, 2H), 2.89 (t, $J = 7.4$ Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, Methanol-*d*₄) δ 137.1, 134.1, 126.0, 122.7, 120.8, 112.2, 109.5, 108.0, 43.4, 27.0, 10.1.

HRMS-ESI (m/z): $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{Br}^+$, 253.0335, found 253.0335.



2-(6-bromo-2-methyl-1H-indol-3-yl)ethan-1-amine (**2w**)

³ M. Righi, F. Topi, S. Bartolucci, A. Bedini, G. Piersanti, G. Spadoni, *J. Org. Chem.* **2012**, *77*, 6351–6357.

Brown solid. Characterization data:

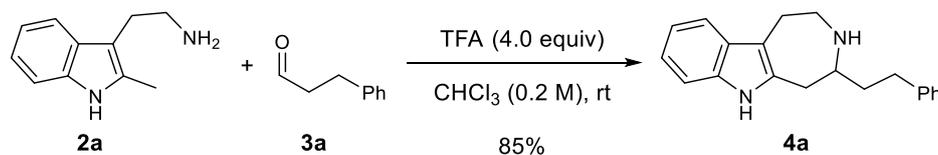
¹H NMR (400 MHz, Methanol-*d*₄) δ 7.43 – 7.39 (m, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.07 (dd, *J* = 8.4, 1.5 Hz, 1H), 2.95 – 2.85 (m, 4H), 2.38 (s, 3H).

¹³C NMR (100 MHz, Methanol-*d*₄) δ 136.6, 133.3, 127.4, 121.2, 118.3, 113.3, 112.9, 107.2, 41.3, 25.6, 10.0.

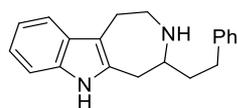
HRMS-ESI (*m/z*): [*M* + *H*]⁺ calculated for C₁₁H₁₄N₂Br, 253.0340, found 253.0335.

3. Synthesis of Azepino[4,5-*b*]indoles 4 and Alkene 5

General procedure:



To a stirred solution of amine **2a** (34.8 mg, 0.2 mmol, 1.0 equiv.) and aldehyde **3a** (53.6 mg, 0.4 mmol, 2.0 equiv.) in CHCl₃ (1.0 mL) was added TFA (91.2 mg, 0.8 mmol, 4.0 equiv.) in one portion at room temperature. The mixture was stirred at room temperature for 24 hours and quenched with 10% aqueous Na₂CO₃ (2 mL). The biphasic layers were separated, and the aqueous layer was extracted with DCM (3×10 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, DCM: MeOH = 100:3) to afford azepino[4,5-*b*]indoles **4a** (49.4 mg, 85% yield) as a light brown solid.



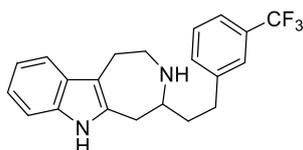
4-phenethyl-1,2,3,4,5,6-hexahydroazepino[4,5-*b*]indole (**4a**)

Light brown solid, 49.4 mg, 85% yield. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.77 (br, 1H), 7.48 (d, *J* = 6.8 Hz, 1H), 7.37 – 7.18 (m, 6H), 7.18 – 7.07 (m, 2H), 3.42 (m, 1H), 3.05 – 2.72 (m, 8H), 2.41 (br, 1H), 1.95 – 1.78 (m, 2H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 141.9, 134.8, 134.6, 129.2, 128.6, 128.5, 126.1, 121.1, 119.3, 117.7, 112.8, 110.4, 57.9, 49.1, 39.0, 37.9, 33.0, 27.5.

HRMS-ESI (*m/z*): [*M* + *H*]⁺ calculated for C₂₀H₂₃N₂⁺, 291.1856, found 291.1882.



4-(3-(trifluoromethyl)phenethyl)-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4b)

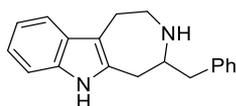
Brown solid, 50.9 mg, 71% yield. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.72 (br, 1H), 7.52 – 7.44 (m, 3H), 7.43 – 7.37 (m, 2H), 7.29 – 7.23 (m, 1H), 7.16 – 7.07 (m, 2H), 3.47 – 3.41 (m, 1H), 3.07 – 2.97 (m, 1H), 2.94 – 2.75 (m, 7H), 1.88 – 1.81 (m, 2H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 142.9, 134.6, 134.5, 131.8, 130.77 (q, $J = 31.9$ Hz), 129.1, 128.9, 125.11 (q, $J = 3.6$ Hz), 124.3 (q, $J = 270.7$ Hz), 122.88 (q, $J = 3.8$ Hz), 121.1, 119.3, 117.7, 112.9, 110.3, 57.6, 49.0, 38.9, 38.3, 32.7, 27.8.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -62.5.

HRMS-ESI (m/z): $[M + H]^+$ calculated for C₂₁H₂₂N₂F₃⁺, 359.1730, found 359.1735.



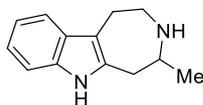
4-benzyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4c)

Brown solid, 27.8 mg, 50% yield. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.69 (br, 1H), 7.48 – 7.43 (m, 1H), 7.37 – 7.31 (m, 2H), 7.29 – 7.22 (m, 4H), 7.14 – 7.05 (m, 2H), 3.38 – 3.31 (m, 1H), 3.21 – 3.13 (m, 1H), 3.03 – 2.78 (m, 7H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 138.7, 134.6, 134.5, 129.4, 129.1, 128.9, 126.8, 121.2, 119.3, 117.8, 113.1, 110.4, 59.7, 49.5, 43.3, 36.9, 26.8.

HRMS-ESI (m/z): $[M + H]^+$ calculated for C₁₉H₂₁N₂⁺, 277.1699, found 277.1721.



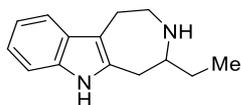
4-methyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4d)

Brown solid, 34.6 mg, 87% yield. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 (br, 1H), 7.47 (d, $J = 7.2$ Hz, 1H), 7.27 (d, $J = 7.5$ Hz, 1H), 7.15 – 7.07 (m, 2H), 3.43 – 3.36 (m, 1H), 3.09 – 2.97 (m, 2H), 2.96 – 2.74 (m, 4H), 2.16 (br, 1H), 1.26 (d, $J = 6.4$ Hz, 3H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 135.0, 134.7, 129.3, 121.1, 119.3, 117.7, 113.1, 110.4, 54.2, 49.6, 39.7, 27.5, 23.9.

HRMS-ESI (m/z): $[M + H]^+$ calculated for $C_{13}H_{17}N_2^+$, 201.1386, found 201.1405.



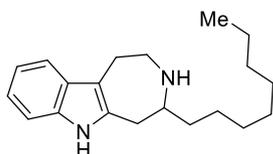
4-ethyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4e)

Brown solid, 40.5 mg, 95% yield. Characterization data:

1H NMR (400 MHz, Chloroform-*d*) δ 7.83 (br, 1H), 7.50 – 7.42 (m, 1H), 7.28 – 7.25 (m, 1H), 7.16 – 7.05 (m, 2H), 3.47 – 3.38 (m, 1H), 3.32 (br, 1H), 3.04 – 2.98 (m, 1H), 2.95 – 2.77 (m, 5H), 1.63 – 1.54 (m, 2H), 1.02 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 134.9, 134.7, 129.2, 121.1, 119.3, 117.7, 112.8, 110.4, 60.1, 49.2, 36.7, 29.9, 27.0, 11.1.

HRMS-ESI (m/z): $[M + H]^+$ calculated for $C_{14}H_{19}N_2^+$, 215.1543, found 215.1549.



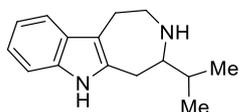
4-heptyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4f)

White solid, 51.8 mg, 87% yield. Characterization data:

1H NMR (400 MHz, Chloroform-*d*) δ 7.85 (br, 1H), 7.46 (d, $J = 7.2$ Hz, 1H), 7.31 – 7.22 (m, 1H), 7.15 – 7.07 (m, 2H), 3.91 – 3.55 (br, 1H), 3.51 – 3.40 (m, 1H), 3.06 – 3.00 (m, 1H), 2.98 – 2.83 (m, 5H), 1.62 – 1.54 (m, 2H), 1.46 – 1.37 (m, 2H), 1.36 – 1.24 (m, 10H), 0.90 (t, $J = 6.5$ Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 134.7, 129.1, 121.1, 119.3, 117.7, 112.7, 110.4, 58.6, 49.0, 36.8, 32.0, 29.8, 29.7, 29.4, 26.7, 26.6, 22.8, 14.2.

HRMS-ESI (m/z): $[M + H]^+$ calculated for $C_{20}H_{31}N_2^+$, 299.2482, found 299.2480.



4-isopropyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4g)

General procedure, with higher concentration and longer reaction time (0.25 mL $CHCl_3$, 48 hours).

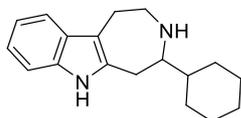
Brown solid, 25.6 mg, 56% yield. Characterization data:

1H NMR (400 MHz, Chloroform-*d*) δ 7.74 (br, 1H), 7.46 (dd, $J = 6.4, 2.4$ Hz, 1H), 7.32 – 7.23 (m, 1H), 7.16 – 7.05 (m, 2H), 3.46 – 3.40 (m, 1H), 3.04 – 2.74 (m, 5H),

2.72 – 2.66 (m, 1H), 2.03 (br, 1H), 1.86 – 1.75 (m, 1H), 1.02 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.4, 134.8, 129.4, 121.0, 119.3, 117.7, 112.7, 110.3, 64.1, 49.7, 34.2, 34.0, 27.6, 19.2, 19.0.

HRMS-ESI (*m/z*): $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{21}\text{N}_2^+$, 229.1699, found 229.1706.



4-cyclohexyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4h)

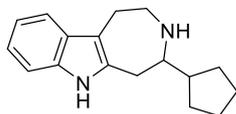
General procedure, with higher concentration and longer reaction time (0.25 mL CHCl_3 , 48 hours).

Brown solid, 36.6 mg, 68% yield. Characterization data:

^1H NMR (400 MHz, Chloroform-*d*) δ 7.75 (br, 1H), 7.51 – 7.40 (m, 1H), 7.32 – 7.21 (m, 2H), 7.17 – 7.04 (m, 2H), 3.48 – 3.38 (m, 1H), 3.04 – 2.76 (m, 5H), 2.73 – 2.67 (m, 1H), 2.30 (br, 1H), 1.85 – 1.76 (m, 4H), 1.74 – 1.66 (m, 1H), 1.52 – 1.42 (m, 1H), 1.33 – 1.07 (m, 5H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.5, 134.8, 129.4, 121.0, 119.3, 117.7, 112.7, 110.3, 63.5, 49.6, 44.3, 34.5, 29.8, 29.5, 27.6, 26.8, 26.7, 26.7.

HRMS-ESI (*m/z*): $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{25}\text{N}_2^+$, 269.2012, found 269.2027.



4-cyclopentyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4i)

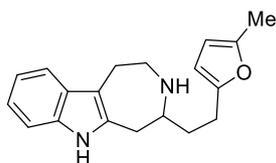
General procedure, with higher concentration and longer reaction time (0.25 mL CHCl_3 , 48 hours).

Light brown solid, 36.4 mg, 72% yield. Characterization data:

^1H NMR (400 MHz, Chloroform-*d*) δ 7.79 (br, 1H), 7.50 – 7.44 (m, 1H), 7.29 – 7.24 (m, 1H), 7.15 – 7.06 (m, 2H), 3.45 – 3.38 (m, 1H), 3.04 – 2.78 (m, 5H), 2.70 – 2.61 (m, 1H), 2.24 (br, 1H), 2.01 – 1.78 (m, 3H), 1.73 – 1.54 (m, 4H), 1.35 – 1.24 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.1, 134.7, 129.2, 121.0, 119.2, 117.7, 112.7, 110.3, 64.1, 49.3, 45.6, 36.2, 30.5, 30.0, 27.2, 25.8, 25.7.

HRMS-ESI (*m/z*): $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{23}\text{N}_2^+$, 255.1856, found 255.1872.



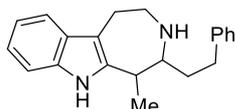
4-(2-(5-methylfuran-2-yl)ethyl)-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4j)

Brown oil, 41.8 mg, 71% yield. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.80 (br, 1H), 7.46 (dd, $J = 6.5, 1.9$ Hz, 1H), 7.30 – 7.23 (m, 1H), 7.16 – 7.06 (m, 2H), 5.90 (d, $J = 2.9$ Hz, 1H), 5.88 – 5.83 (m, 1H), 3.47 – 3.38 (m, 1H), 3.05 – 2.84 (m, 6H), 2.79 – 2.69 (m, 2H), 2.25 (s, 3H), 1.91 – 1.85 (m, 2H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 153.5, 150.6, 134.7, 134.5, 129.1, 121.2, 119.4, 117.7, 112.7, 110.4, 106.0, 106.0, 57.7, 48.7, 37.1, 35.1, 27.0, 25.2, 13.7.

HRMS-ESI (m/z): $[M + H]^+$ calculated for $C_{19}H_{23}N_2O^+$, 295.1805, found 295.1815.



5-methyl-4-phenethyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4k)

General procedure, with lower concentration and shorter reaction time (4.0 mL $CHCl_3$, 6 hours). This reaction was carried out strictly under N_2 .

Brown oil, 51.6 mg, 85% yield, dr = 1:1. Characterization data:

isomer 1:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.68 (br, 1H), 7.49 – 7.43 (m, 1H), 7.32 – 7.25 (m, 3H), 7.24 – 7.17 (m, 3H), 7.15 – 7.06 (m, 2H), 3.44 – 3.36 (m, 1H), 3.08 – 3.02 (m, 1H), 3.00 – 2.66 (m, 6H), 1.87 – 1.69 (m, 2H), 1.27 (d, $J = 7.1$ Hz, 3H).

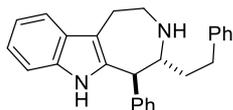
¹³C NMR (100 MHz, Chloroform-*d*) δ 142.1, 140.9, 134.6, 129.3, 128.6, 128.5, 126.1, 121.1, 119.3, 117.9, 111.5, 110.4, 61.0, 49.6, 40.1, 36.7, 33.6, 27.3, 13.4.

isomer 2:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.67 (br, 1H), 7.51 – 7.43 (m, 1H), 7.30 – 7.22 (m, 3H), 7.21 – 7.15 (m, 3H), 7.14 – 7.07 (m, 2H), 3.17 – 3.04 (m, 2H), 3.01 – 2.88 (m, 3H), 2.88 – 2.74 (m, 2H), 2.69 – 2.59 (m, 1H), 2.07 – 1.95 (m, 1H), 1.79 – 1.67 (m, 1H), 1.41 (d, $J = 7.1$ Hz, 3H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 142.4, 138.8, 134.8, 129.2, 128.5, 128.5, 125.9, 120.9, 119.3, 117.8, 110.7, 110.4, 58.9, 42.5, 40.9, 34.1, 33.2, 26.9, 18.9.

HRMS-ESI (m/z): $[M + H]^+$ calculated for $C_{21}H_{25}N_2^+$, 305.2012, found 305.2035.



4-phenethyl-5-phenyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4l)

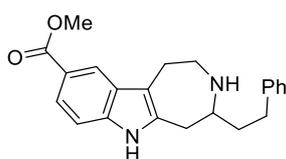
General procedure, with lower concentration and shorter reaction time (4.0 mL CHCl₃, 12 hours). This reaction was carried out strictly under N₂.

Brown solid, 54.9 mg, 75% yield, dr =10:1. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.51 (m, 1H), 7.41 – 7.30 (m, 4H), 7.29 – 7.22 (m, 2H), 7.22 – 7.05 (m, 8H), 4.09 (d, *J* = 7.7 Hz, 1H), 3.51 – 3.37 (m, 1H), 3.28 – 3.19 (m, 1H), 3.17 – 3.06 (m, 2H), 3.06 – 2.95 (m, 1H), 2.89 – 2.79 (m, 1H), 2.71 – 2.60 (m, 1H), 1.98 (br, 1H), 1.79 – 1.71 (m, 2H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 142.1, 141.3, 136.1, 134.9, 129.1, 129.0, 128.5, 128.4, 127.3, 125.9, 121.4, 119.2, 118.1, 112.5, 110.4, 62.1, 54.8, 46.9, 35.8, 32.6, 27.9.

HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₂₆H₂₇N₂⁺, 367.2169, found 367.2173.



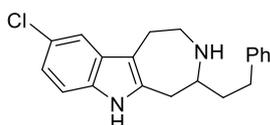
methyl 4-phenethyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole-9-carboxylate (4m)

Light brown solid, 59.0 mg, 85% yield. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 8.19 (br, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.33 – 7.14 (m, 6H), 3.92 (s, 3H), 3.46 – 3.34 (m, 1H), 3.06 – 2.96 (m, 1H), 2.94 – 2.79 (m, 5H), 2.79 – 2.68 (m, 2H), 2.61 (br, 1H), 1.88 – 1.79 (m, 2H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 168.6, 141.8, 137.4, 136.2, 128.9, 128.6, 128.5, 126.1, 122.6, 121.2, 120.8, 114.2, 110.0, 57.8, 51.9, 48.9, 38.8, 37.7, 32.9, 27.4.

HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₂₂H₂₅N₂O₂⁺, 349.1911, found 349.1914.



9-chloro-4-phenethyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4n)

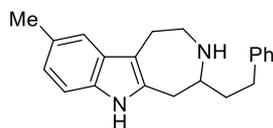
White solid, 56.2 mg, 87% yield. Characterization data:

¹H NMR (400 MHz, Methanol-*d*₄) δ 7.33 (d, *J* = 2.0 Hz, 1H), 7.29 – 7.12 (m, 6H), 6.96 (dd, *J* = 8.5, 2.0 Hz, 1H), 3.38 – 3.32 (m, 1H), 3.09 – 2.99 (m, 1H), 2.94 – 2.83

(m, 3H), 2.83 – 2.69 (m, 4H), 1.89 – 1.81 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.9, 136.5, 133.0, 130.5, 128.6, 128.5, 126.1, 125.1, 121.2, 117.4, 112.9, 111.3, 57.9, 49.1, 39.1, 38.3, 33.0, 27.7.

HRMS-ESI (*m/z*): $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{Cl}^+$, 325.1466, found 325.1483.



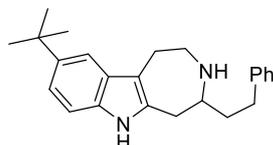
9-methyl-4-phenethyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4o)

White solid, 49.3 mg, 81% yield. Characterization data:

^1H NMR (400 MHz, Chloroform-*d*) δ 7.60 (br, 1H), 7.34 – 7.28 (m, 2H), 7.28 – 7.25 (m, 1H), 7.24 – 7.19 (m, 3H), 7.16 (d, $J = 8.2$ Hz, 1H), 6.95 (dd, $J = 8.2, 1.6$ Hz, 1H), 3.45 – 3.38 (m, 1H), 3.02 – 2.94 (m, 1H), 2.92 – 2.70 (m, 7H), 2.46 (s, 3H), 1.89 – 1.81 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.0, 135.0, 133.0, 129.5, 128.6, 128.6, 128.5, 128.5, 128.5, 126.1, 122.6, 117.5, 112.5, 110.0, 58.0, 49.3, 39.1, 38.2, 33.0, 27.7, 21.7.

HRMS-ESI (*m/z*): $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{25}\text{N}_2^+$, 305.2012, found 305.2035.



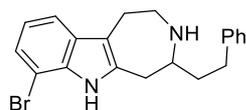
9-(tert-butyl)-4-phenethyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4p)

Brown oil, 49.4 mg, 71% yield. Characterization data:

^1H NMR (400 MHz, Chloroform-*d*) δ 7.65 (br, 1H), 7.45 (s, 1H), 7.33 – 7.27 (m, 2H), 7.25 – 7.16 (m, 5H), 3.48 – 3.38 (m, 1H), 3.23 (br, 1H), 3.08 – 2.99 (m, 1H), 2.98 – 2.69 (m, 7H), 1.95 – 1.80 (m, 2H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.3, 141.9, 134.8, 132.8, 128.8, 128.6, 128.5, 126.1, 119.4, 113.5, 112.8, 109.9, 57.8, 48.9, 38.6, 37.5, 34.7, 33.0, 32.1, 27.2.

HRMS-ESI (*m/z*): $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{31}\text{N}_2^+$, 347.2482, found 347.2499.



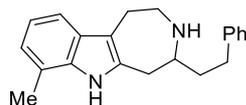
7-bromo-4-phenethyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4q)

Brown solid, 70.3 mg, 96% yield. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 (br, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.18 (m, 6H), 7.01 – 6.93 (m, 1H), 3.48 – 3.36 (m, 1H), 3.04 – 2.69 (m, 8H), 2.53 (br, 1H), 1.94 – 1.81 (m, 2H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 141.8, 135.7, 133.3, 130.4, 128.6, 128.5, 126.1, 123.4, 120.5, 117.0, 114.3, 104.0, 57.9, 49.0, 39.0, 38.0, 33.0, 27.8.

HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₂₀H₂₂N₂Br⁺, 369.0961, found 369.0959.



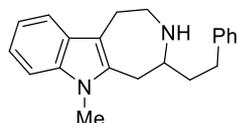
7-methyl-4-phenethyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4r)

Brown solid, 58.2 mg, 96% yield. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 (br, 1H), 7.40 – 7.30 (m, 3H), 7.28 – 7.21 (m, 3H), 7.12 – 7.03 (m, 1H), 7.01 – 6.94 (m, 1H), 3.55 (br, 1H), 3.49 – 3.42 (m, 1H), 3.08 – 2.73 (m, 8H), 2.49 (s, 3H), 1.98 – 1.85 (m, 2H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 141.8, 134.2, 134.2, 128.7, 128.6, 128.5, 126.1, 121.8, 119.6, 115.5, 113.2, 57.8, 48.8, 38.5, 37.3, 32.9, 27.2, 16.7.

HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₂₁H₂₅N₂⁺, 305.2012, found 305.2035.



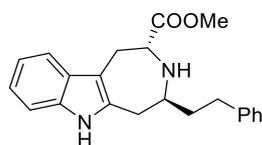
6-methyl-4-phenethyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4s)

Brown solid, 53.5 mg, 88% yield. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.29 – 7.23 (m, 3H), 7.23 – 7.17 (m, 1H), 7.16 – 7.10 (m, 1H), 3.66 (s, 3H), 3.46 – 3.40 (m, 1H), 3.14 – 3.04 (m, 2H), 3.01 – 2.76 (m, 6H), 2.52 (br, 1H), 1.98 – 1.90 (m, 2H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 141.9, 136.3, 136.2, 128.6, 128.6, 128.5, 128.5, 127.7, 126.1, 120.8, 118.9, 117.7, 112.4, 109.0, 57.4, 48.7, 39.1, 34.9, 33.0, 29.6, 27.3.

HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₂₁H₂₅N₂⁺, 305.2012, found 305.2035.



methyl (2R,4S)-4-phenethyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole-2-carboxylate (4t)

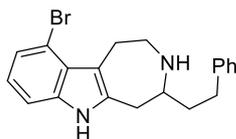
General procedure, with 1.2 equiv. of **3a** and shorter reaction time (12 hours). This reaction was carried out under N₂.

Light yellow solid, 79% yield, dr=7:1. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.72 (br, 1H), 7.54 – 7.48 (m, 1H), 7.33 – 7.24 (m, 3H), 7.23 – 7.17 (m, 3H), 7.16 – 7.08 (m, 2H), 3.99 (dd, *J* = 9.5, 2.8 Hz, 1H), 3.74 (s, 3H), 3.44 – 3.36 (m, 1H), 3.32 (dd, *J* = 15.3, 2.8 Hz, 1H), 3.13 (dd, *J* = 15.3, 9.6 Hz, 1H), 3.04 (dd, *J* = 15.6, 2.4 Hz, 1H), 2.88 – 2.65 (m, 3H), 2.33 (br, 1H), 1.97 – 1.85 (m, 1H), 1.84 – 1.72 (m, 1H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 174.6, 142.0, 134.9, 134.6, 129.0, 128.6, 128.5, 126.0, 121.2, 119.5, 117.7, 110.5, 109.7, 56.8, 52.5, 52.2, 36.8, 36.0, 32.9, 28.3.

HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₂₂H₂₅N₂O₂⁺, 349.1911, found 349.1914.



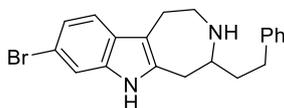
10-bromo-4-phenethyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4u)

Brown solid, 50.9 mg, 69% yield. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.34 – 7.29 (m, 2H), 7.26 – 7.17 (m, 5H), 6.92 (t, *J* = 7.8 Hz, 1H), 3.86 – 3.75 (m, 1H), 3.46 – 3.35 (m, 1H), 3.19 – 3.10 (m, 1H), 3.02 – 2.71 (m, 7H), 1.97 – 1.79 (m, 2H).

¹³C NMR (100 MHz, Methanol-*d*₄) δ 140.1, 136.6, 134.2, 128.3, 128.0, 126.1, 125.2, 123.6, 121.8, 112.5, 110.3, 110.1, 56.4, 45.0, 34.3, 31.2, 28.6, 22.2.

HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₂₀H₂₂N₂Br⁺, 369.0961, found 369.0959.



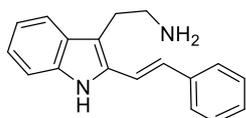
8-bromo-4-phenethyl-1,2,3,4,5,6-hexahydroazepino[4,5-b]indole (4w)

Brown solid, 40.3 mg, 55% yield. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.72 (s, 1H), 7.37 (d, *J* = 1.4 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.24 – 7.15 (m, 4H), 3.46 – 3.35 (m, 1H), 2.98 – 2.71 (m, 8H), 2.54 (s, 1H), 1.92 – 1.79 (m, 2H).

¹³C NMR (100 MHz, Methanol-*d*₄) δ 140.1, 136.0, 133.1, 128.3, 128.0, 126.9, 126.1, 121.9, 118.4, 114.2, 113.3, 109.8, 57.1, 45.9, 34.5, 31.2, 29.1, 21.0.

HRMS-ESI (m/z): $[M + H]^+$ calculated for $C_{20}H_{22}N_2Br$, 369.0966, found 369.0959.



(E)-2-(2-styryl-1H-indol-3-yl)ethan-1-amine (5)

General procedure, with 2.0 equiv. of TFA, higher concentration and temperature (0.5 mL, 80 °C). This reaction was carried out in a sealed tube, and purified by flash column chromatography (silica gel, DCM: MeOH = 20:1 to 10:1).

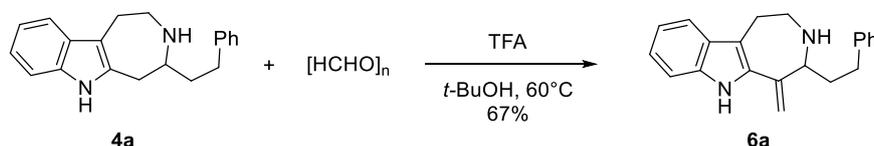
Brown solid, 41.9 mg, 80% yield. Characterization data:

1H NMR (400 MHz, Chloroform- d) δ 8.32 (br, 1H), 7.58 (d, $J = 7.9$ Hz, 1H), 7.53 – 7.48 (m, 2H), 7.41 – 7.17 (m, 6H), 7.13 – 7.07 (m, 1H), 6.83 (d, $J = 16.5$ Hz, 1H), 3.08 – 2.99 (m, 4H), 1.47 (br, 2H).

^{13}C NMR (100 MHz, Chloroform- d) δ 137.1, 136.8, 133.4, 129.2, 128.9, 127.8, 126.4, 123.4, 119.8, 119.1, 117.1, 114.7, 110.7, 43.2, 28.5.

HRMS-ESI (m/z): $[M + H]^+$ calculated for $C_{18}H_{19}N_2^+$, 263.1543, found 263.1535.

4. Synthesis of Exocyclic Alkenes 6 and Ngouniensines

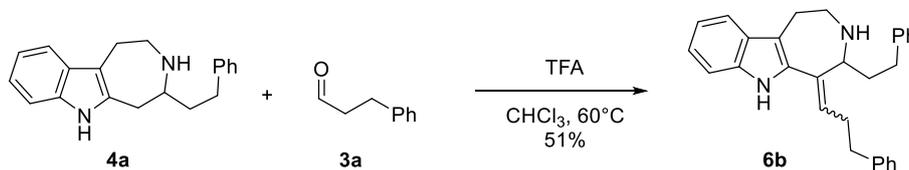


To a stirred solution of **4a** (58.0 mg, 0.2 mmol, 1.0 equiv.) and paraformaldehyde (6.6 mg, 0.22 mmol, 1.1 equiv.) in *t*-BuOH (1.0 mL) was added TFA (91.2 mg, 0.8 mmol, 4.0 equiv.) at room temperature. After being stirred at 60 °C for 3 hours, the reaction was cooled to room temperature and quenched with saturated aqueous $NaHCO_3$ (5 mL). The biphasic layers were separated, and the aqueous layer was extracted with DCM (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, DCM: MeOH = 100:3) to afford **6a** (40.7 mg, 67% yield) as a brown solid. Characterization data:

1H NMR (400 MHz, Chloroform- d) δ 7.86 (s, 1H), 7.51 (d, $J = 7.9$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.29 – 7.21 (m, 3H), 7.21 – 7.15 (m, 4H), 7.14 – 7.09 (m, 1H), 5.26 (s, 1H), 5.21 (s, 1H), 3.77 (t, $J = 7.0$ Hz, 1H), 3.37 (ddd, $J = 13.6, 7.1, 4.2$ Hz, 1H), 3.21 (ddd, $J = 13.7, 6.9, 4.3$ Hz, 1H), 2.82 – 2.65 (m, 2H), 2.80 – 2.66 (m, 2H), 2.05 – 1.95 (m, 2H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 146.0, 142.1, 135.9, 133.8, 129.1, 128.6, 128.5, 126.0, 122.7, 119.7, 118.8, 113.0, 112.2, 110.7, 62.2, 44.2, 36.3, 33.0, 28.1.

HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₂₁H₂₃N₂⁺, 303.1856, found 303.1853.



To a stirred solution of **4a** (58.0 mg, 0.2 mmol, 1.0 equiv.) and **3a** (53.6 mg, 0.4 mmol, 2.0 equiv.) in CHCl₃ (1.0 mL) was added TFA (91.2 mg, 0.8 mmol, 4.0 equiv.) at room temperature. After being stirred at 60 °C for 6 hours, the reaction was cooled to room temperature and quenched with saturated aqueous NaHCO₃ (5 mL). The biphasic layers were separated, and the aqueous layer was extracted with DCM (3×10 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, DCM: MeOH = 50:1) to afford **6b** (41.6 mg, 51% yield, Z/E = 3:1) as a brown solid. Characterization data:

Z-isomer:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.32 (m, 4H), 7.25 – 7.12 (m, 6H), 7.10 – 7.01 (m, 4H), 6.32 (s, 1H), 6.19 – 6.10 (m, 1H), 4.32 (dd, J = 9.9, 3.5 Hz, 1H), 3.57 – 3.45 (m, 1H), 3.41 – 3.29 (m, 1H), 3.22 – 3.07 (m, 2H), 2.96 – 2.85 (m, 1H), 2.79 – 2.55 (m, 3H), 2.55 – 2.37 (m, 2H), 2.32 – 2.19 (m, 1H), 1.91 – 1.74 (m, 1H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 141.5, 140.4, 138.4, 135.4, 129.8, 129.5, 129.1, 128.6, 128.6, 127.9, 127.4, 127.0, 126.3, 122.5, 119.9, 118.4, 111.1, 111.0, 63.8, 42.0, 35.0, 32.6, 32.4, 32.3, 22.2.

HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₂₉H₃₁N₂⁺, 407.2482, found 407.2495.

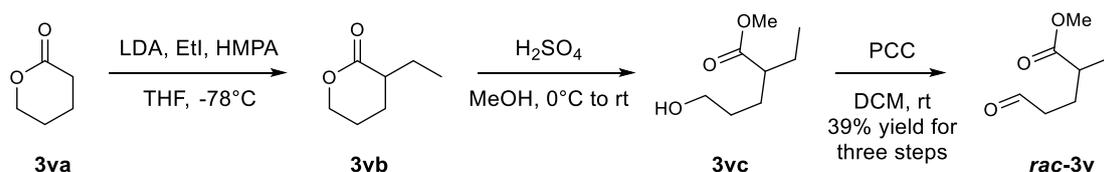
E-isomer:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.69 (s, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.34 – 7.08 (m, 13H), 5.73 (t, J = 7.4 Hz, 1H), 4.12 (t, J = 6.9 Hz, 1H), 3.31 – 3.23 (m, 1H), 3.05 – 2.64 (m, 6H), 2.63 – 2.50 (m, 2H), 2.49 – 2.36 (m, 1H), 1.99 – 1.87 (m, 1H), 1.83 – 1.71 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 141.9, 141.4, 137.9, 135.6, 134.2, 129.9, 129.1, 128.8, 128.6, 128.5, 128.4, 126.3, 126.0, 122.2, 119.6, 118.6, 111.2, 110.6, 56.9, 42.5, 36.1, 35.9, 32.7, 30.0, 28.2.

HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₂₉H₃₁N₂⁺, 407.2482, found 407.2495.

Synthesis of **3v**.⁴



To a solution of LDA (2.0 M in THF/heptane/ethylbenzene, 26.8 mL, 53.6 mmol) in THF (40 mL) was added a solution of δ -valerolactone (**3va**, 5.00 g, 50 mmol) in THF (75 mL) at -78 °C under N₂ atmosphere. After the reaction mixture was stirred for 0.5 hour at -78 °C, a solution of EtI (8 mL, 100 mmol) in HMPA (19.1 mL, 110 mmol) was added. The mixture was stirred for 18 hours at -78 °C, and quenched by adding saturated aqueous NH₄Cl. The aqueous layer was extracted three times with Et₂O (200 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue (**3vb**) was used for the next reaction without further purification.

To a solution of the above product **3vb** in MeOH (50 mL) was added H₂SO₄ (5 mL in 45 mL MeOH) at 0 °C. Then, the reaction mixture was allowed to warm to room temperature and stirred for 20 hours. The reaction was quenched by adding 1 M aqueous NaOH to pH=7. The aqueous layer was extracted three times with CHCl₃ (200 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue (**3vc**) was used for the next reaction without further purification.

To a solution of the above product **3vc** in DCM (250 mL), celite (27.3 g) and pyridinium chlorochromate (13.80 g, 64 mmol) were added. The mixture was stirred at room temperature for 3 hours. Hexane (200 mL) was added to dilute the mixture, which was then filtered through a pad of celite. The filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, PE: EtOAc = 5:1) to afford compound *rac*-**3v** (3.09g, 39% yield for three steps) as a colorless oil. Characterization data:

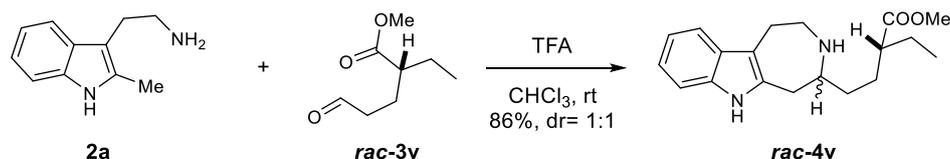
¹H NMR (400 MHz, Chloroform-*d*) δ 9.69 (s, 1H), 3.62 (s, 3H), 2.47 – 2.34 (m, 2H), 2.32 – 2.23 (m, 1H), 1.90 – 1.73 (m, 2H), 1.67 – 1.54 (m, 1H), 1.54 – 1.42 (m, 1H), 0.84 (t, $J = 7.4$ Hz, 3H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 201.5, 175.9, 51.5, 46.2, 41.6, 25.4, 23.9, 11.6.

HRMS-ESI (m/z): [M + H]⁺ calculated for C₈H₁₅O₃⁺, 159.1016, found 159.1011.

⁴ R. Tokuda, Y. Okamoto, T. Koyama, N. Kogure, M. Kitajima, H. Takayama, *Org. Lett.*, **2016**, *18*(14), 3490-3493.

Total synthesis of Ngouniensines.

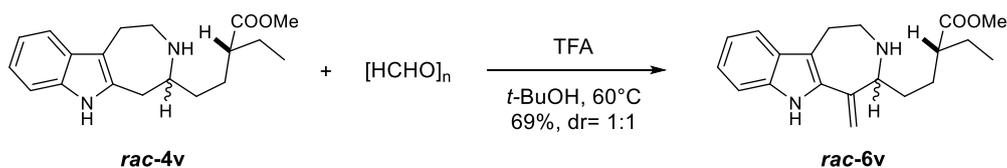


Compound *rac-4v* was obtained as a brown oil (267.6 mg, 86% yield, dr=1:1) by following the general procedure. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) mixture of diastereomers, δ 7.87 (br, 1H), 7.50 – 7.40 (m, 1H), 7.32 – 7.20 (m, 1H), 7.16 – 7.04 (m, 2H), 3.68 (s, 3H), 3.43 – 3.34 (m, 1H), 3.05 – 2.94 (m, 1H), 2.94 – 2.76 (m, 5H), 2.45 (br, 1H), 2.37 – 2.26 (m, 1H), 1.78 – 1.43 (m, 6H), 0.97 – 0.86 (m, 3H).

¹³C NMR (100 MHz, Chloroform-*d*) mixture of diastereomers, δ 176.8, 176.7, 134.7, 134.7, 129.2, 129.1, 121.0, 119.3, 117.7, 112.8, 112.8, 110.4, 110.4, 58.4, 51.6, 49.2, 49.0, 47.3, 47.2, 37.5, 37.3, 35.0, 35.0, 29.0, 28.8, 27.4, 27.3, 25.7, 25.6, 11.9.

HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₁₉H₂₇N₂O₂⁺, 315.2067, found 315.2076.



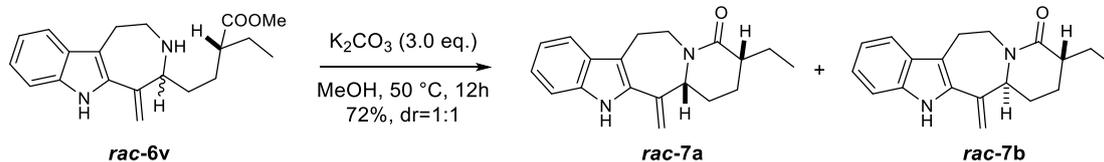
To a stirred solution of *rac-4v* (62.8 mg, 0.2 mmol, 1.0 equiv.) and paraformaldehyde (6.6 mg, 0.22 mmol, 1.1 equiv.) in *t*-BuOH (1.0 mL) was added TFA (91.2 mg, 0.8 mmol, 4.0 equiv.) at room temperature. After being stirred at 60 °C for 3 hours, the mixture was cooled to room temperature and quenched with saturated aqueous NaHCO₃ (5 mL). The biphasic layers were separated, and the aqueous layer was extracted with DCM (3×10 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, DCM: MeOH = 100:3) to afford *rac-6v* (43.3 mg, 69% yield, dr=1:1) as a brown solid. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) mixture of diastereomers, δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 5.24 (d, *J* = 5.9 Hz, 1H), 5.17 (d, *J* = 5.4 Hz, 1H), 3.72 – 3.66 (m, 1H), 3.64 (s, 1.5H), 3.59 (s, 1.5H), 3.35 – 3.26 (m, 1H), 3.21 – 3.11 (m, 1H), 3.01 – 2.95 (m, 2H), 2.32 – 2.23 (m, 1H), 1.80 – 1.45 (m, 7H), 0.87 (t, *J* = 8.0 Hz, 3H).

¹³C NMR (100 MHz, Chloroform-*d*) mixture of diastereomers, δ 176.8, 176.7, 146.2, 145.8, 135.9, 135.8, 133.7, 133.6, 129.0, 129.0, 122.6, 122.6, 119.6, 118.8, 118.8,

112.9, 112.8, 112.4, 112.0, 110.7, 110.7, 63.0, 62.8, 51.5, 51.5, 47.2, 47.2, 44.0, 44.0, 32.6, 32.6, 29.1, 29.1, 28.3, 28.2, 25.7, 25.6, 11.9, 11.9.

HRMS-ESI (m/z): $[M + H]^+$ calculated for $C_{20}H_{27}N_2O_2^+$, 327.2067, found 327.2052.



To a solution of *rac-6v* (47.2 mg, 0.145 mmol, 1.0 equiv.) in MeOH (1.4 mL) was added K_2CO_3 (59.9 mg, 0.434 mmol, 3.0 equiv.) at room temperature. The reaction was stirred at 50 °C for 12 hours, and quenched with saturated aqueous NH_4Cl (5 mL). The biphasic layers were separated and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, DCM: MeOH = 100:1) to afford compound *rac-7a* (15.3 mg, 36% yield) and *rac-7b* (15.3 mg, 36% yield) as a white solid. (*7a* and *7b* were separable in column chromatography). Characterization data:

***rac-7a*:**

1H NMR (400 MHz, $DMSO-d_6$) δ 10.84 (s, 1H), 7.40 (d, $J = 7.8$ Hz, 1H), 7.28 (d, $J = 8.1$ Hz, 1H), 7.08 (t, $J = 7.5$ Hz, 1H), 6.95 (t, $J = 7.4$ Hz, 1H), 5.43 (s, 1H), 5.37 (s, 1H), 4.65 – 4.57 (m, 1H), 4.39 – 4.32 (m, 1H), 3.19 – 3.08 (m, 2H), 2.82 – 2.74 (m, 1H), 2.20 – 2.12 (m, 1H), 2.03 – 1.77 (m, 3H), 1.60 – 1.50 (m, 2H), 1.26 – 1.18 (m, 1H), 0.69 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, $DMSO-d_6$) δ 171.5, 142.7, 136.1, 131.6, 128.0, 121.9, 118.5, 118.4, 113.8, 110.8, 110.7, 63.3, 43.9, 41.2, 28.9, 24.6, 24.1, 22.7, 11.3.

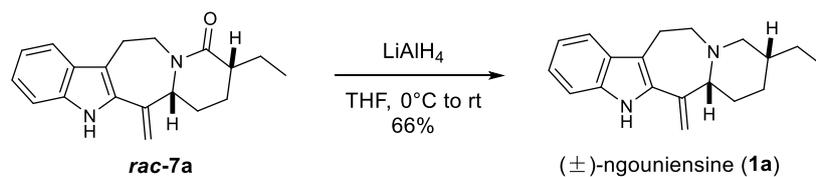
HRMS-ESI (m/z): $[M + H]^+$ calculated for $C_{19}H_{23}N_2O^+$, 295.1805, found 295.1805.

***rac-7b*:**

1H NMR (400 MHz, $DMSO-d_6$) δ 10.87 (s, 1H), 7.39 (d, $J = 7.8$ Hz, 1H), 7.29 (d, $J = 8.1$ Hz, 1H), 7.08 (t, $J = 7.3$ Hz, 1H), 6.96 (t, $J = 7.3$ Hz, 1H), 5.37 (s, 1H), 5.34 (s, 1H), 4.63 – 4.56 (m, 1H), 4.33 – 4.25 (m, 1H), 3.28 – 3.11 (m, 2H), 2.77 – 2.69 (m, 1H), 2.05 – 1.95 (m, 2H), 1.89 – 1.73 (m, 2H), 1.65 – 1.50 (m, 2H), 1.44 – 1.35 (m, 1H), 0.83 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, $DMSO-d_6$) δ 170.8, 143.3, 136.1, 131.0, 127.9, 121.8, 118.5, 118.3, 114.2, 110.9, 110.5, 65.2, 43.2, 41.8, 31.9, 24.8, 24.2, 24.1, 11.0.

HRMS-ESI (m/z): $[M + H]^+$ calculated for $C_{19}H_{23}N_2O^+$, 295.1805, found 295.1808.



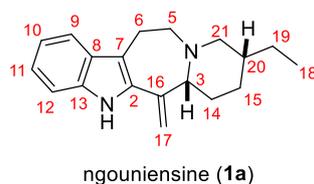
To a solution of *rac-7a* (39.0 mg, 0.133 mmol, 1.0 equiv.) in THF (2.7 mL) was added LiAlH₄ (25.2 mg, 0.663 mmol, 5.0 equiv.) at 0 °C. The resulting suspension was stirred for 10 min at 0 °C and then warmed to room temperature for 2 hours. The mixture was cooled to 0 °C again and quenched with 25 μL of water, followed by 25 μL of a 15% aqueous NaOH solution and finally an additional 75 μL of water. The resulting suspension was stirred vigorously for 1 hour at room temperature. Then anhydrous MgSO₄ was added, and the mixture was stirred for another 30 minutes. The inorganic salts were removed by filtration, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, PE: EA = 1:1) to afford (±)-ngouniensiene (**1a**, 24.4 mg, 66% yield) as a yellow solid. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.3 Hz, 1H), 5.46 (s, 1H), 5.30 (s, 1H), 3.73 (t, *J* = 4.9 Hz, 1H), 3.33 – 3.23 (m, 1H), 3.08 – 2.97 (m, 2H), 2.95 – 2.85 (m, 1H), 2.75 (dd, *J* = 11.5, 3.3 Hz, 1H), 2.49 (dd, *J* = 11.4, 7.6 Hz, 1H), 2.12 – 2.02 (m, 1H), 1.87 – 1.77 (m, 1H), 1.73 – 1.64 (m, 1H), 1.63 – 1.54 (m, 1H), 1.54 – 1.44 (m, 1H), 1.44 – 1.30 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 142.4, 135.8, 135.6, 128.9, 122.7, 119.6, 118.8, 115.4, 112.1, 110.6, 62.3, 56.6, 55.2, 37.9, 29.2, 28.0, 26.2, 22.6, 11.9.

HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₁₉H₂₅N₂⁺, 281.2012, found 281.2011.

NMR Spectral Comparison of Ngouniensiene.

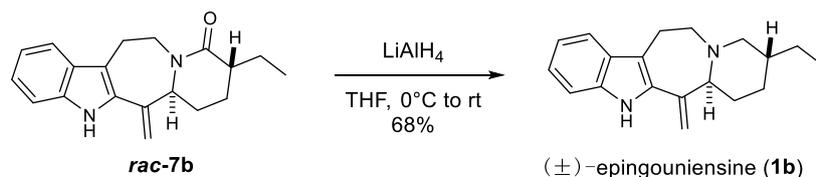


Position	¹ H NMR (δ ppm)	
	Isolated ⁵	This work

⁵ G. Massiot, M. Zeches, P. Thepenier, M.-J. Jacquier, L. Le Men-Olivier, C. Delaude. *J. Chem. Soc. Chem. Commun.* 1982, 768.

N-H	7.97 (s)	7.89 (s, -0.08)
H-3 β	3.72 (t)	3.73 (t, +0.01)
H-5	3.28, 3.00	3.28 (m, 0), 3.02 (m, +0.02)
H-6	(2H), 2.91	3.02 (m, +0.02), 2.89 (m, -0.02)
H-14 α	2.05 (m)	2.06 (m, +0.01)
H-14 β	1.82 (m)	1.82 (m,0)
H-15 α	1.46 (m)	1.48 (m, +0.02)
H-15 β	1.67 (m)	1.68 (m, +0.01)
H-17	5.47 (s)	5.46 (s, -0.01)
H-17'	5.31 (s)	5.30 (s, -0.01)
H-18	0.90 (t)	0.91 (t, +0.01)
H-19	1.38 (m)	1.40 (m, +0.02)
H-19'	1.32 (m)	1.33 (m, +0.01)
H-20 β	1.58 (m)	1.59 (m,+0.01)
H-21 α	2.48 (dd)	2.49 (dd, +0.01)
H-21 β	2.75 (dd)	2.75 (dd,0)

Position	¹³ C NMR (δ ppm)	
	Isolated	This work
2	142.2	142.4 (+0.2)
3	62.3	62.3 (0)
5	56.4	56.6 (+0.2)
6	22.5	22.6 (+0.1)
7	115.2	115.4 (+0.2)
8	128.9	128.9 (0)
9	118.7	118.8 (+0.1)
10	122.5	122.7 (+0.2)
11	119.4	119.6 (+0.2)
12	110.7	110.6 (-0.1)
13	135.7	135.6 (-0.1)
14	27.8	28.0 (+0.2)
15	26.0	26.2 (+0.2)
16	135.7	135.8 (+0.1)
17	112.1	112.1 (0)
18	11.7	11.9 (+0.2)
19	29.1	29.2 (+0.1)
20	37.7	37.9 (+0.2)
21	55.2	55.2 (0)



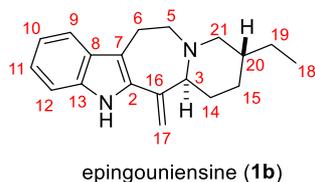
(±)-Epingouniensiene (**1b**) was obtained as a yellow solid (25.4mg, 68% yield) by following the above procedure. Characterization data:

¹H NMR (400 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.36 (s, 1H), 5.31 (s, 1H), 3.26 – 3.18 (m, 1H), 3.17 – 3.07 (m, 2H), 3.01 – 2.85 (m, 3H), 2.31 (t, *J* = 10.9 Hz, 1H), 1.95 – 1.85 (m, 1H), 1.82 – 1.72 (m, 2H), 1.68 – 1.53 (m, 1H), 1.33 – 1.18 (m, 2H), 1.05 – 0.97 (m, 1H), 0.93 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 143.6, 135.7, 135.6, 128.9, 122.5, 119.5, 118.8, 114.7, 111.9, 110.7, 67.8, 62.0, 56.1, 38.4, 33.0, 31.3, 27.4, 22.2, 11.6.

HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₁₉H₂₅N₂⁺, 281.2012, found 281.2023.

NMR Spectral Comparison of Epingouniensiene.

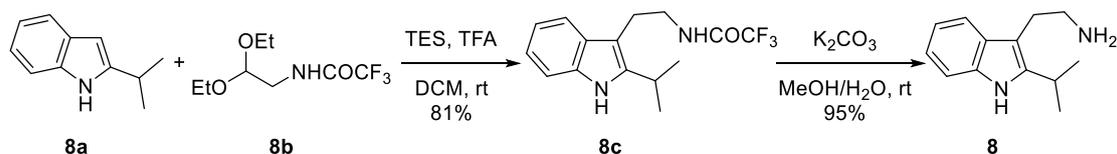


Position	¹³ C NMR (δ ppm)	
	Isolated ⁶	This work
2	143.2	143.6 (+0.4)
3	67.8	67.8 (0)
5	55.8	56.1 (+0.3)
6	22.2	22.2(0)
7	114.3	114.7 (+0.4)
8	128.8	128.9 (+0.1)
9	118.5	118.8(+0.3)
10	122.3	122.5 (+0.2)
11	119.3	119.5 (+0.2)
12	110.7	110.7 (0)
13	135.7	135.7 (0)
14	31.0	31.3 (+0.3)

⁶ G. Massiot, P. Thepenier, M.-J. Jacquier, J. Lounkokobi, C. Mirand, M. Zeches, L. Le Men-Olivier. *Tetrahedron*, **1983**, 39, 3645.

15	27.1	27.4 (+0.3)
16	135.7	135.6(-0.1)
17	112.0	111.9 (-0.1)
18	11.3	11.6 (+0.3)
19	32.7	33.0 (+0.3)
20	38.1	38.4 (+0.3)
21	61.8	62.0 (+0.2)

5. Synthesis of Tryptamine Derivative **8**⁷ and Oxindole **9**



A solution of **8a**⁸ (318 mg, 2.0 mmol) and **8b** (504 mg, 2.2 mmol) in DCM (4.0 mL) were added to a solution of trifluoroacetic acid (1140 mg, 10.0 mmol) and triethylsilane (698 mg, 6.0 mmol) in DCM (4.0 mL). The resulting mixture was stirred at room temperature for 3 hours. The reaction was cooled to 0 °C and carefully neutralized with saturated aqueous NaHCO₃ and diluted with DCM. The two phases were separated, and the aqueous layer was extracted three times with DCM (30 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, PE: EtOAc = 5:1) to afford **8c** (480 mg, 81% yield).

A solution of **8c** (480 mg, 1.61 mmol) and potassium carbonate (1104 mg, 8 mmol) in MeOH (32 mL)/H₂O (2.4 mL) was heated to reflux for 2 hours. After removal of volatiles under reduced pressure, to the residue was added water (20 mL) and the mixture extracted three times with DCM (20 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (DCM:MeOH = 10:1) to afford **8** as a light yellow oil (310 mg, 95% yield). Characterization data:

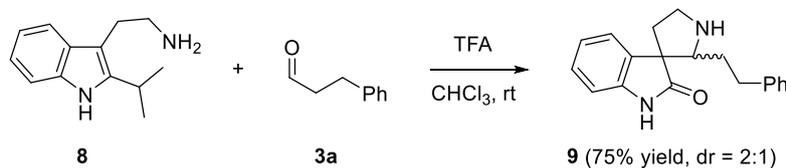
¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 (br, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.18 – 7.06 (m, 2H), 3.35 – 3.23 (m, 1H), 3.01 (t, *J* = 6.9 Hz, 2H), 2.90 (t, *J* = 6.6 Hz, 2H), 1.79 (br, 2H), 1.34 (s, 3H), 1.32 (s, 3H).

⁷ M. Righi, F. Topi, S. Bartolucci, A. Bedini, G. Piersanti, G. Spadoni, *J. Org. Chem.* **2012**, *77*, 6351–6357.

⁸ N. German, J.-S. Kim, A. Jain, M. Dukat, A. Pandya, Y. Ma, M. Weltzin, M. K. Schulte, R. A. Glennon, *J. Med. Chem.*, **2011**, *54*, 7259–7267.

¹³C NMR (100 MHz, Chloroform-*d*) δ 141.8, 135.3, 128.8, 121.1, 119.2, 118.3, 110.6, 107.2, 42.9, 28.2, 25.6, 23.0.

HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₁₃H₁₉N₂⁺, 203.1543, found 203.1521.



Oxindole **9** was obtained as a colorless oil (43.1 mg, 75% yield, dr=2:1) by following the general procedure. Characterization data:

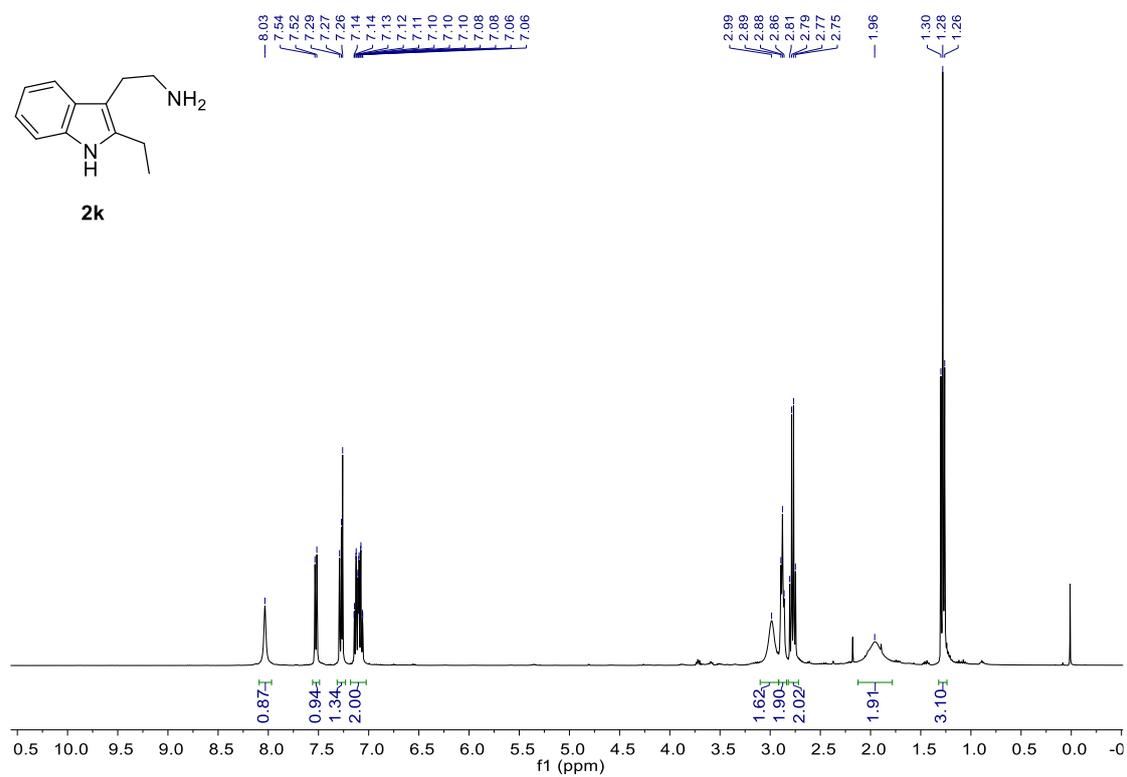
¹H NMR (400 MHz, Chloroform-*d*) mixture of diastereomers. δ 9.42 (br, 0.3H), 9.18 (br, 0.6H), 7.29 – 7.01 (m, 6H), 7.00 – 6.89 (m, 3H), 3.53 – 3.44 (m, 1H), 3.43 – 3.30 (m, 1H), 3.29 – 3.19 (m, 1H), 2.79 – 2.69 (m, 1H), 2.67 – 2.59 (m, 1H), 2.57 – 2.34 (m, 2H), 2.27 – 2.18 (m, 0.7H), 2.15 – 2.04 (m, 0.4H), 1.83 – 1.71 (m, 0.7H), 1.59 – 1.38 (m, 2H).

¹³C NMR (100 MHz, Chloroform-*d*) mixture of diastereomers. δ 182.5, 182.3, 141.8, 141.6, 141.4, 140.7, 132.5, 132.0, 128.4, 128.3, 128.3, 127.9, 127.9, 125.9, 125.9, 124.1, 122.7, 122.5, 110.1, 109.9, 71.0, 68.6, 58.3, 58.2, 46.6, 46.1, 38.8, 38.4, 34.0, 33.7, 33.3, 31.3.

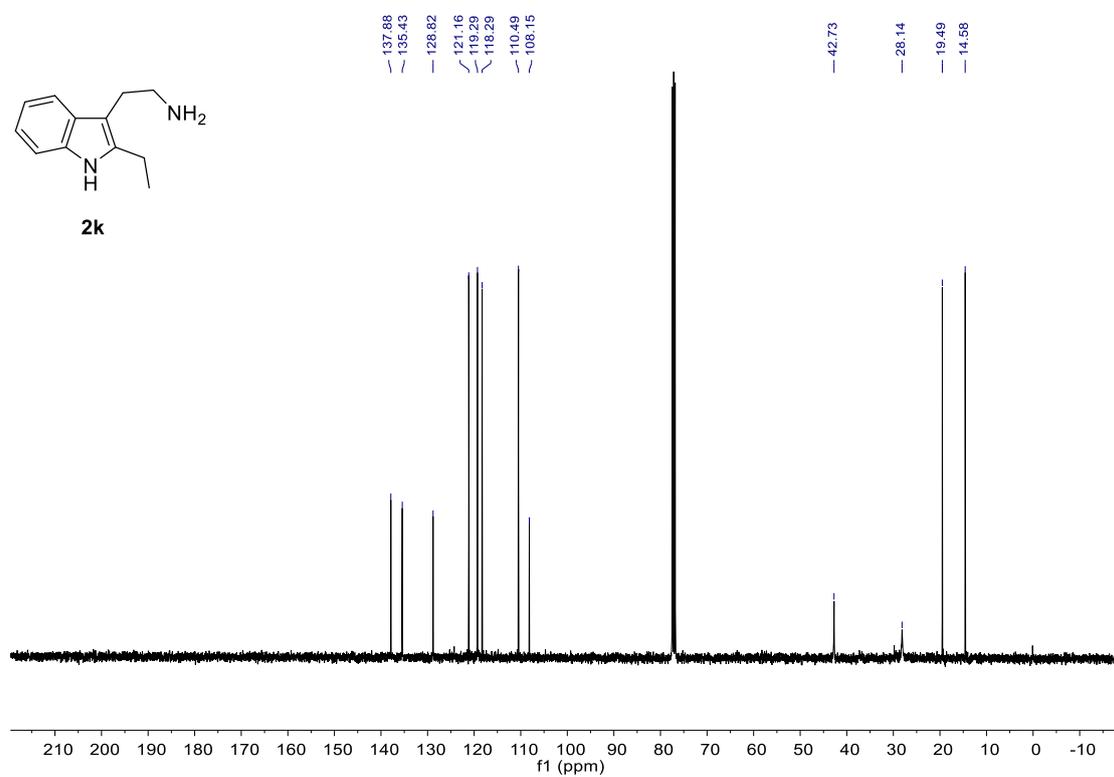
HRMS-ESI (*m/z*): [M + H]⁺ calculated for C₁₉H₂₁N₂O⁺, 293.1648, found 293.1653.

6. NMR Spectra

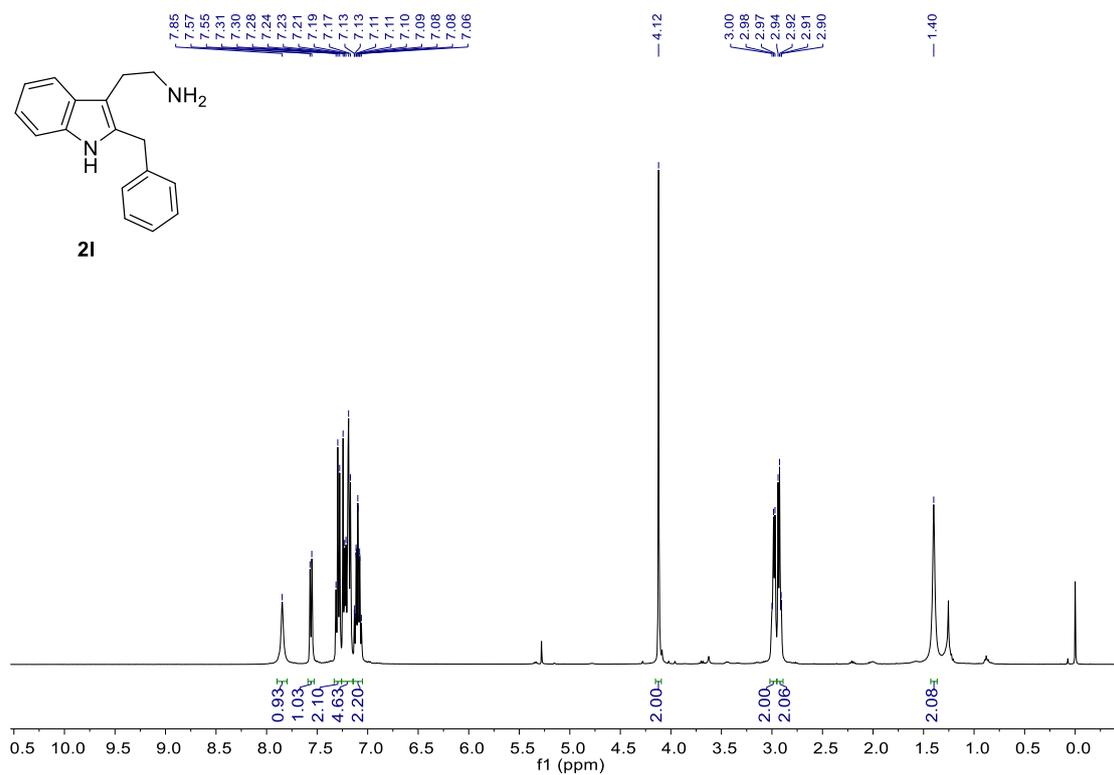
^1H NMR (400 MHz, CDCl_3 , compound **2k**)



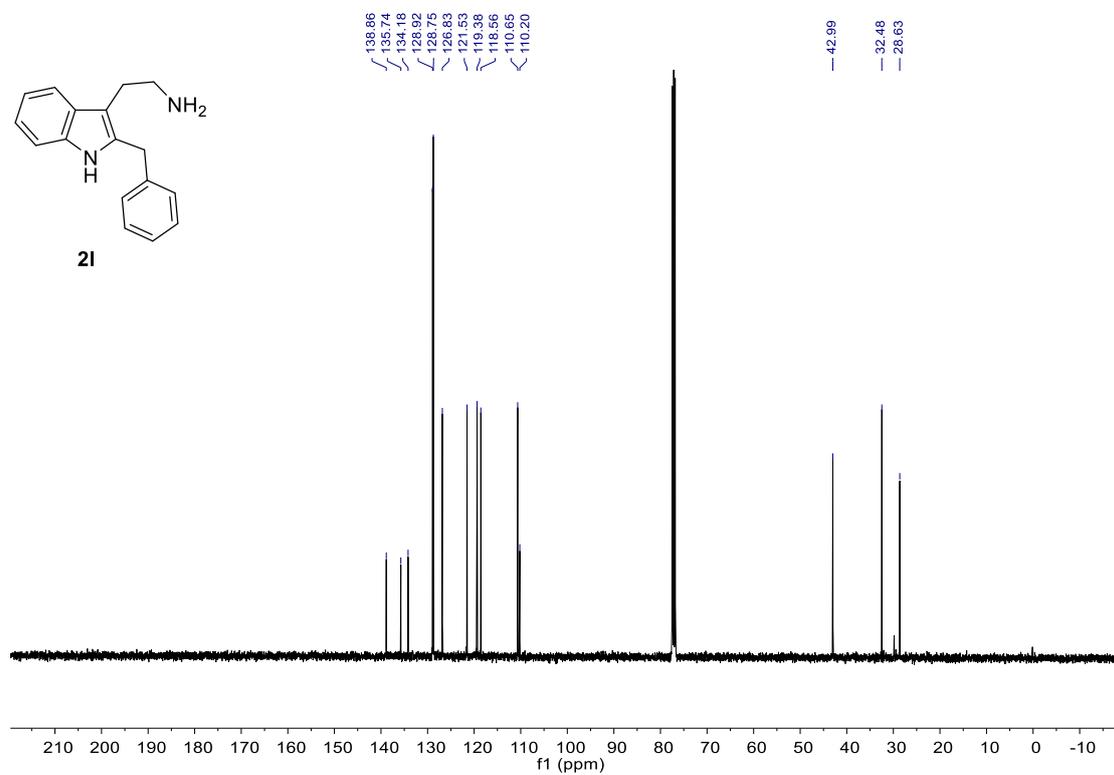
^{13}C NMR (100 MHz, CDCl_3 , compound **2k**)



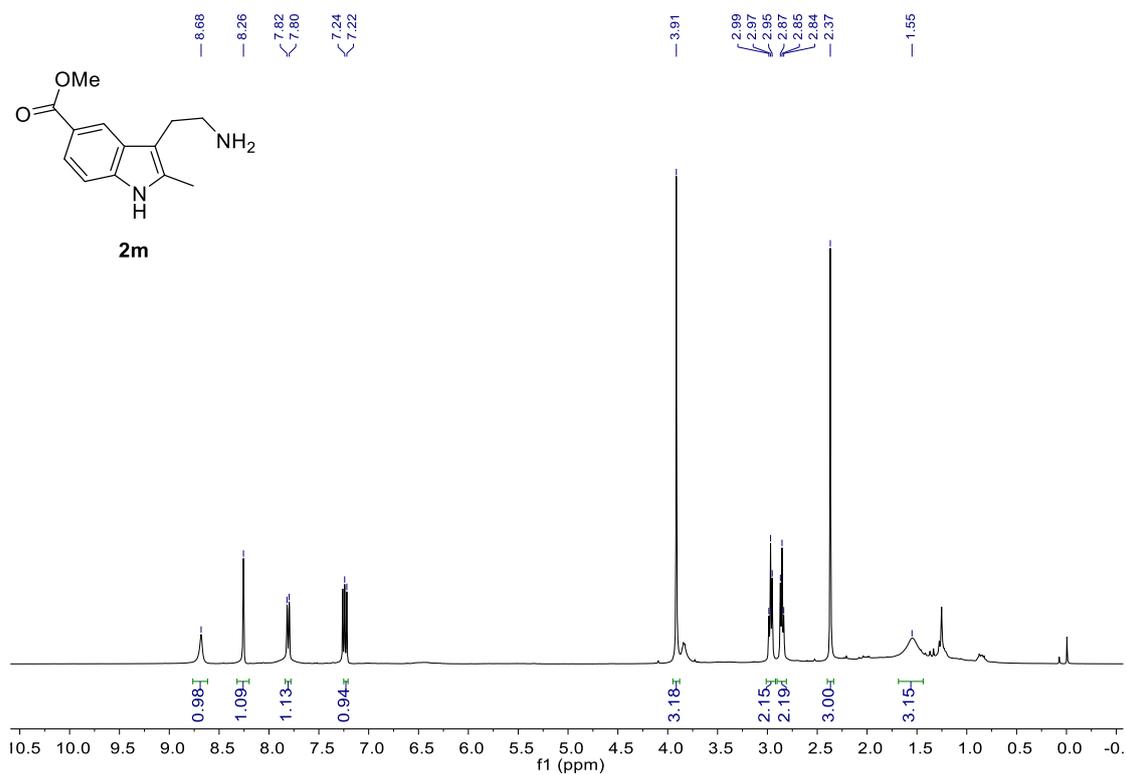
¹H NMR (400 MHz, CDCl₃, compound 2I)



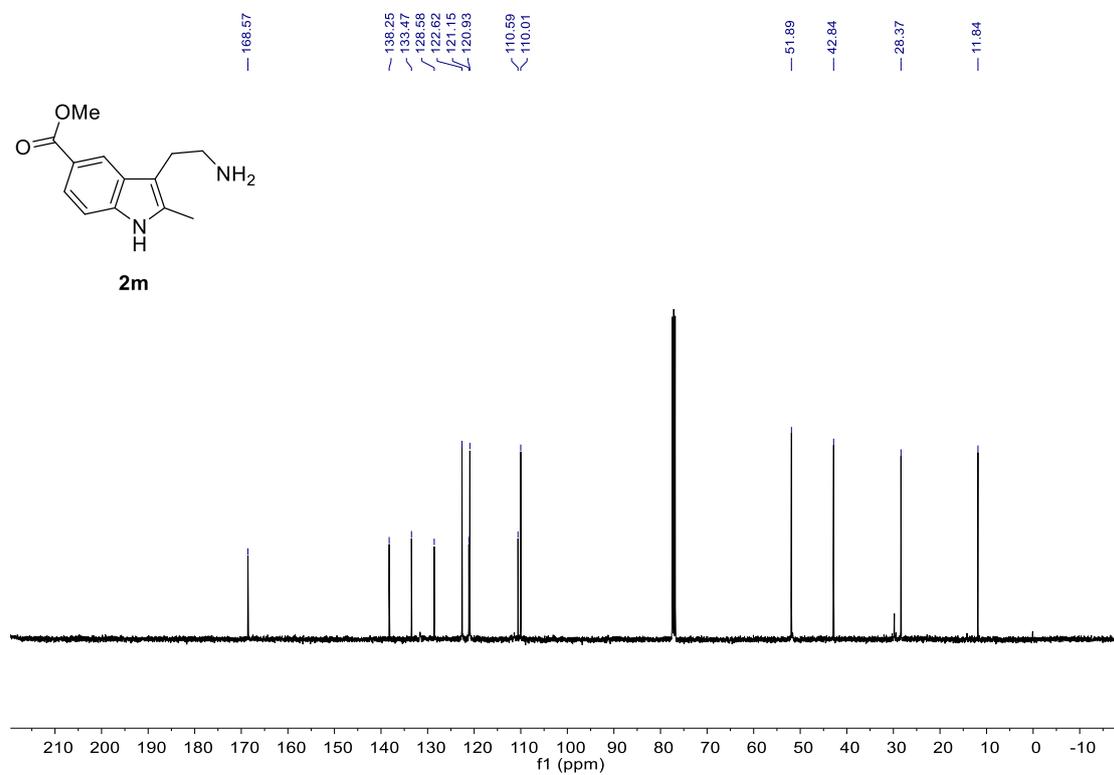
¹³C NMR (100 MHz, CDCl₃, compound 2I)



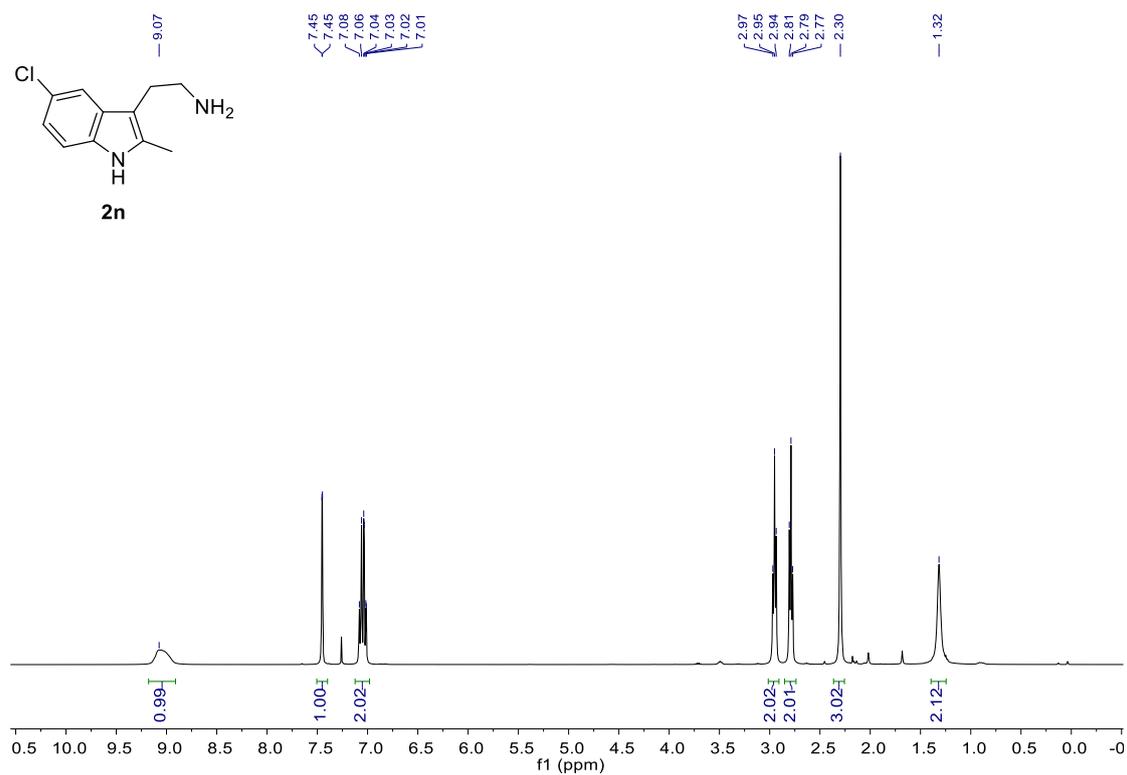
¹H NMR (400 MHz, CDCl₃, compound **2m)**



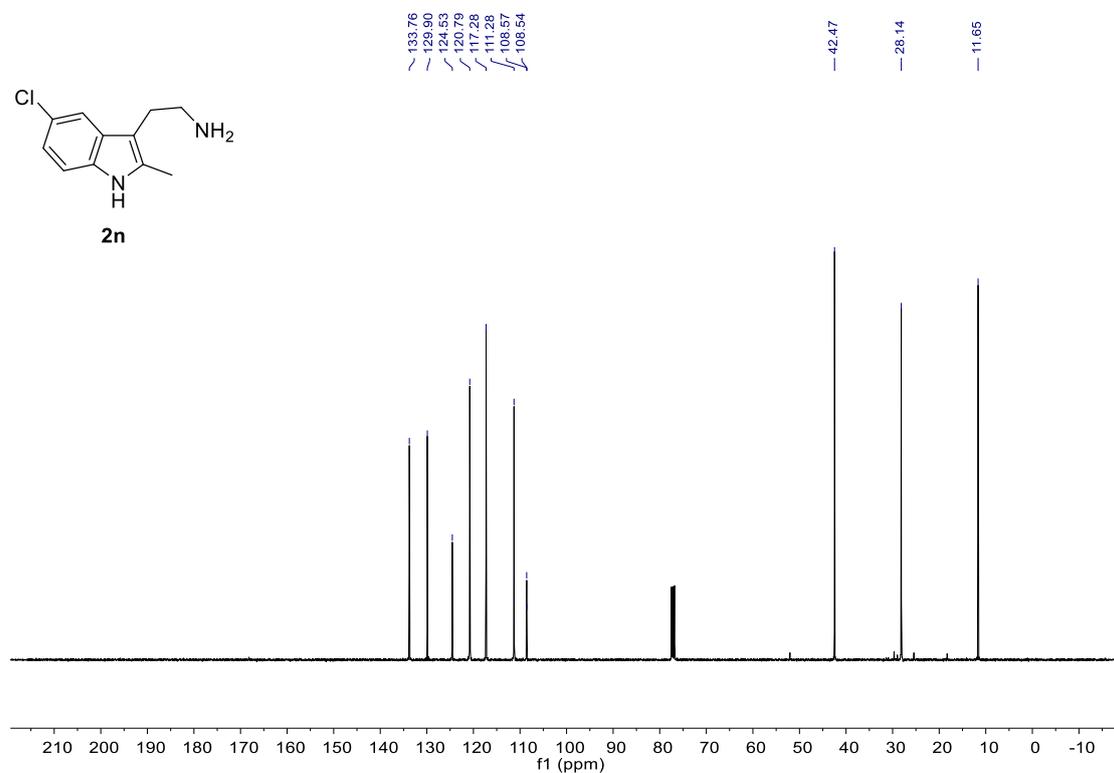
¹³C NMR (100 MHz, CDCl₃, compound **2m)**



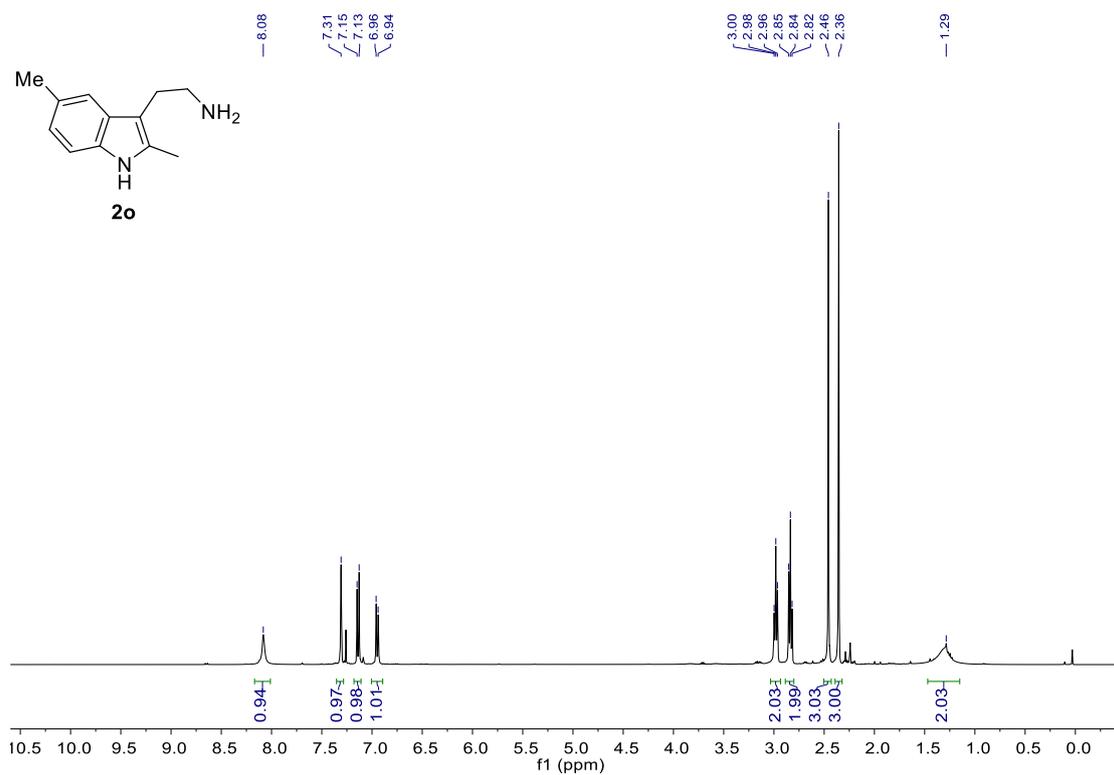
¹H NMR (400 MHz, CDCl₃, compound 2n)



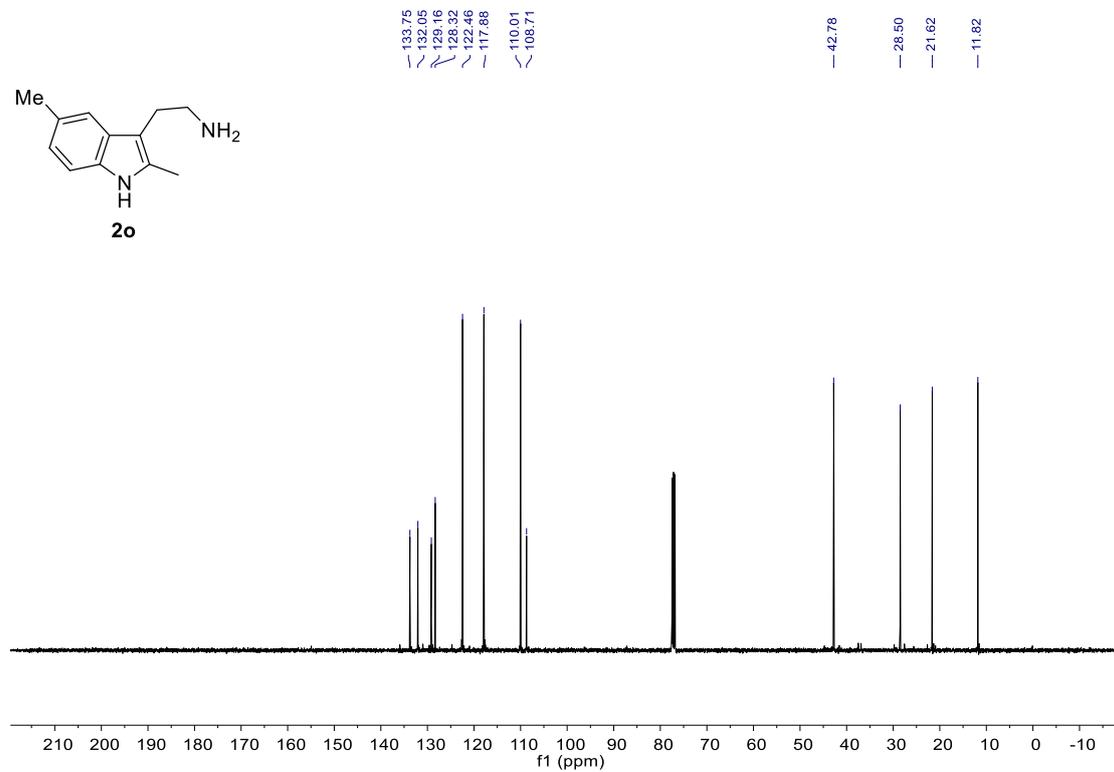
¹³C NMR (100 MHz, CDCl₃, compound 2n)



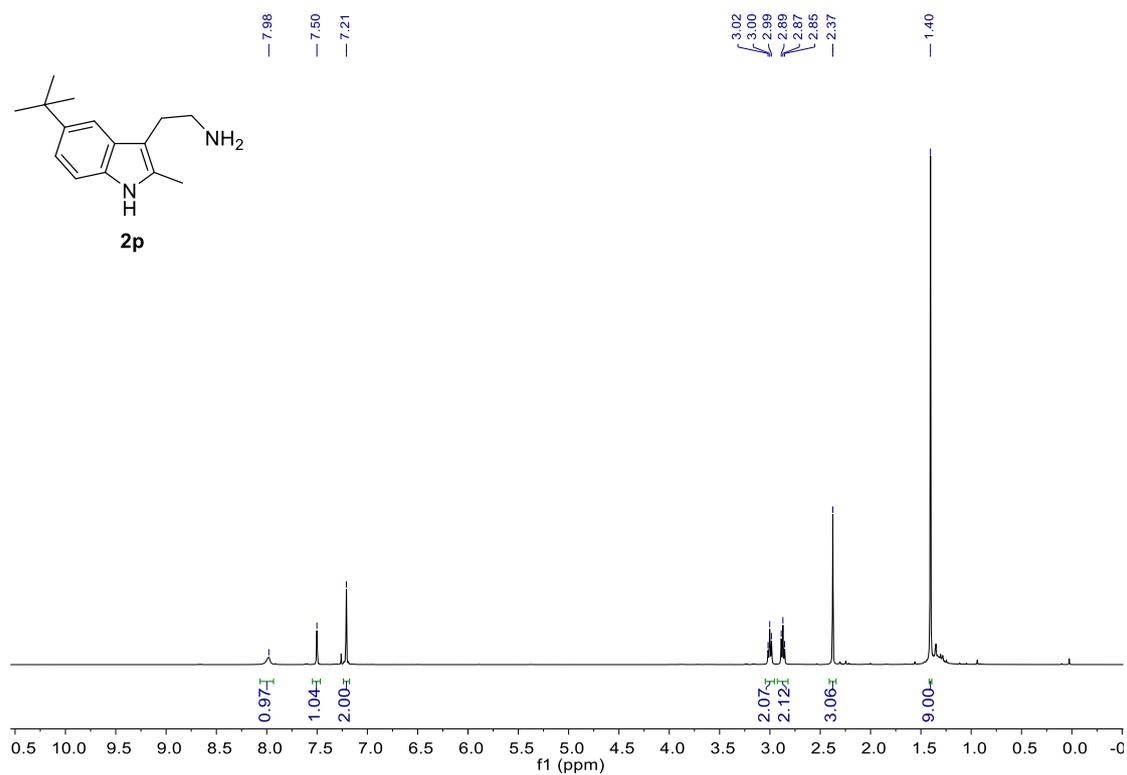
¹H NMR (400 MHz, CDCl₃, compound 2o)



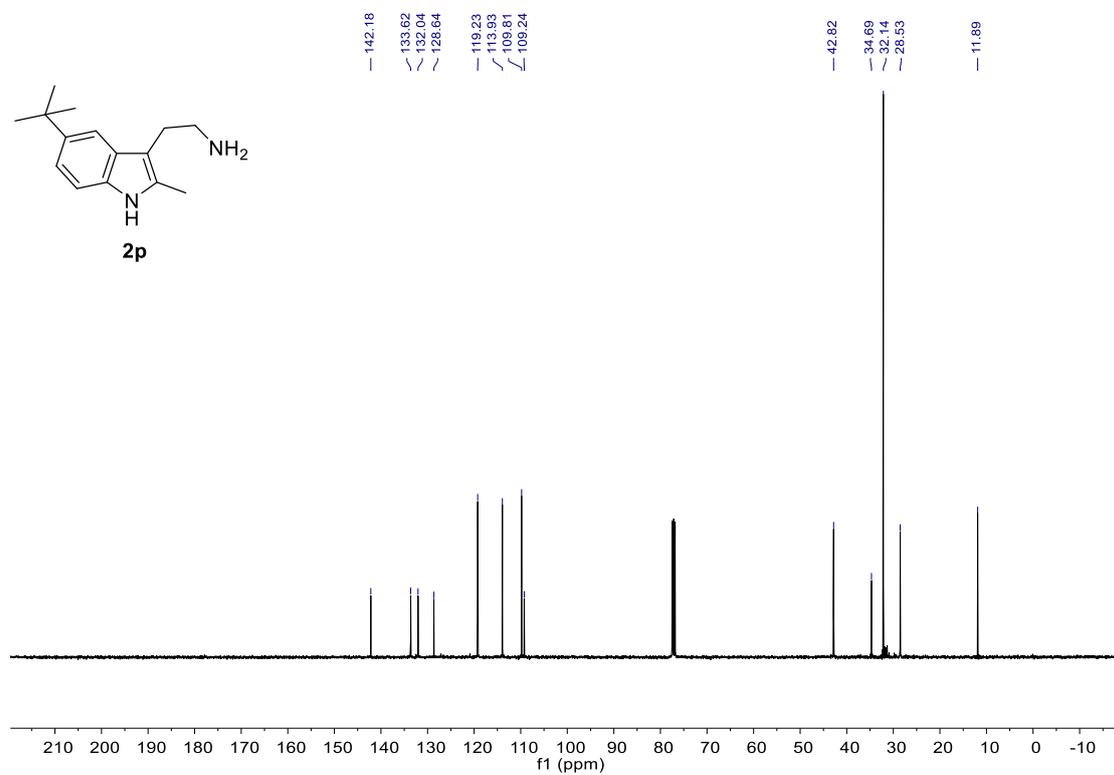
¹³C NMR (100 MHz, CDCl₃, compound 2o)



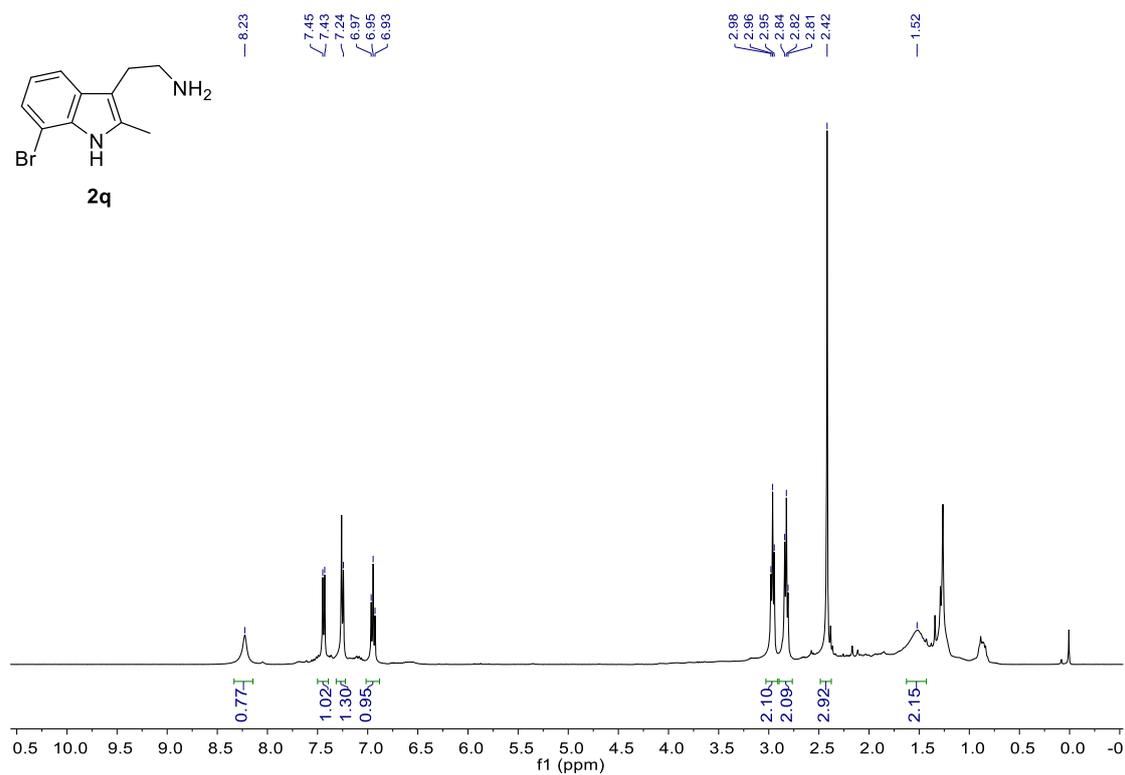
¹H NMR (400 MHz, CDCl₃, compound 2p)



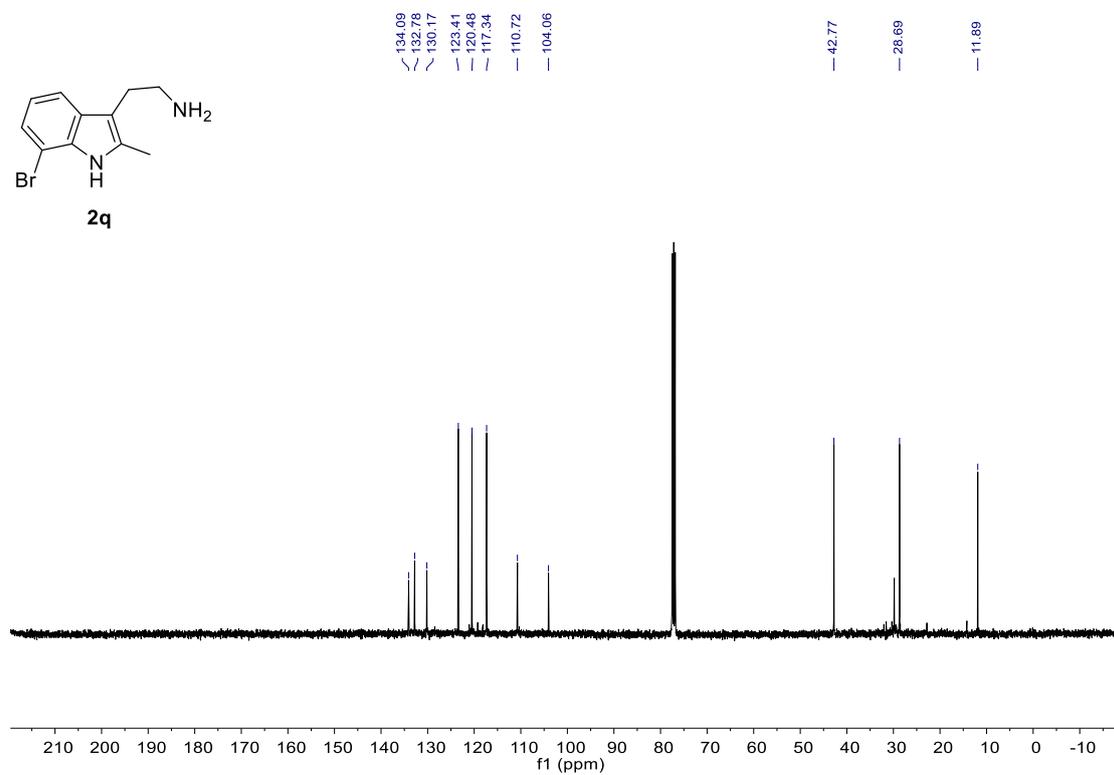
¹³C NMR (100 MHz, CDCl₃, compound 2p)



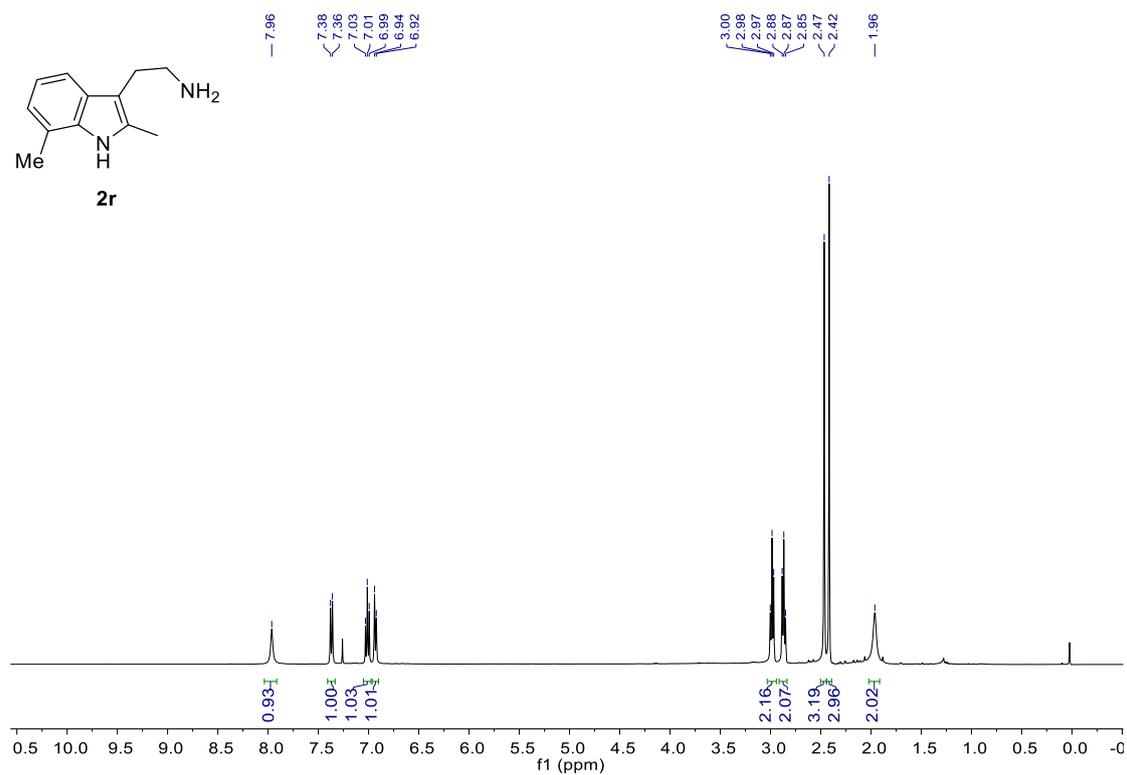
¹H NMR (400 MHz, CDCl₃, compound **2q**)



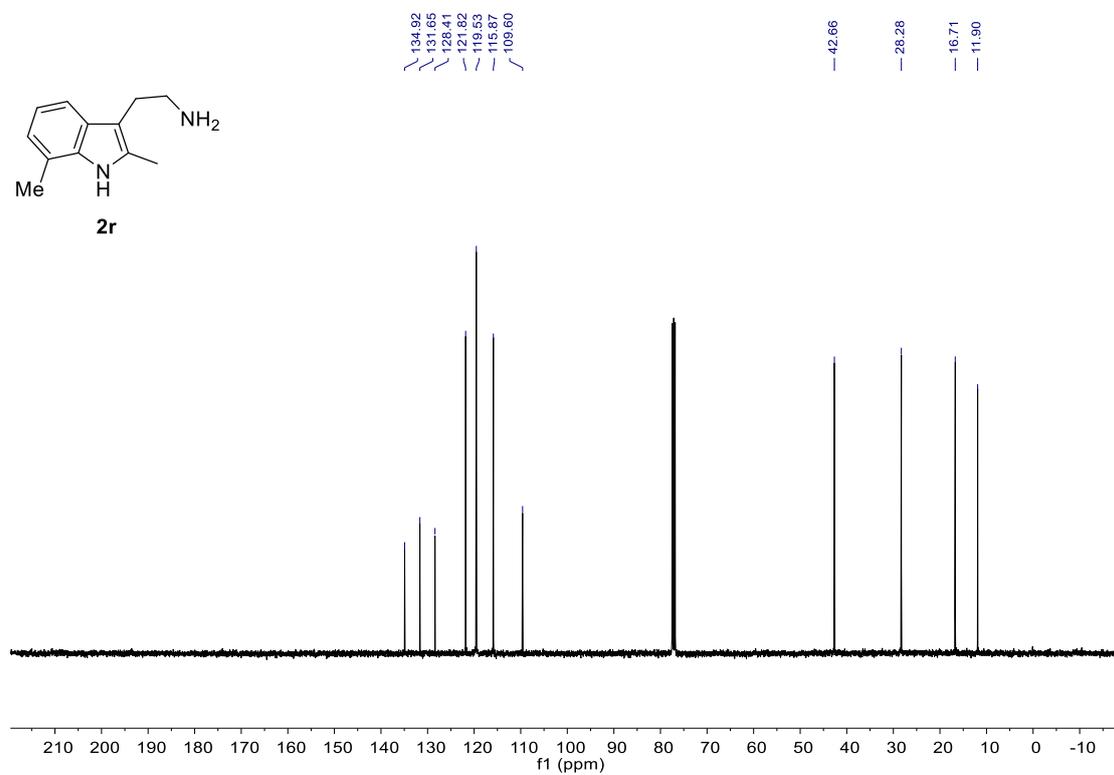
¹³C NMR (100 MHz, CDCl₃, compound **2q**)



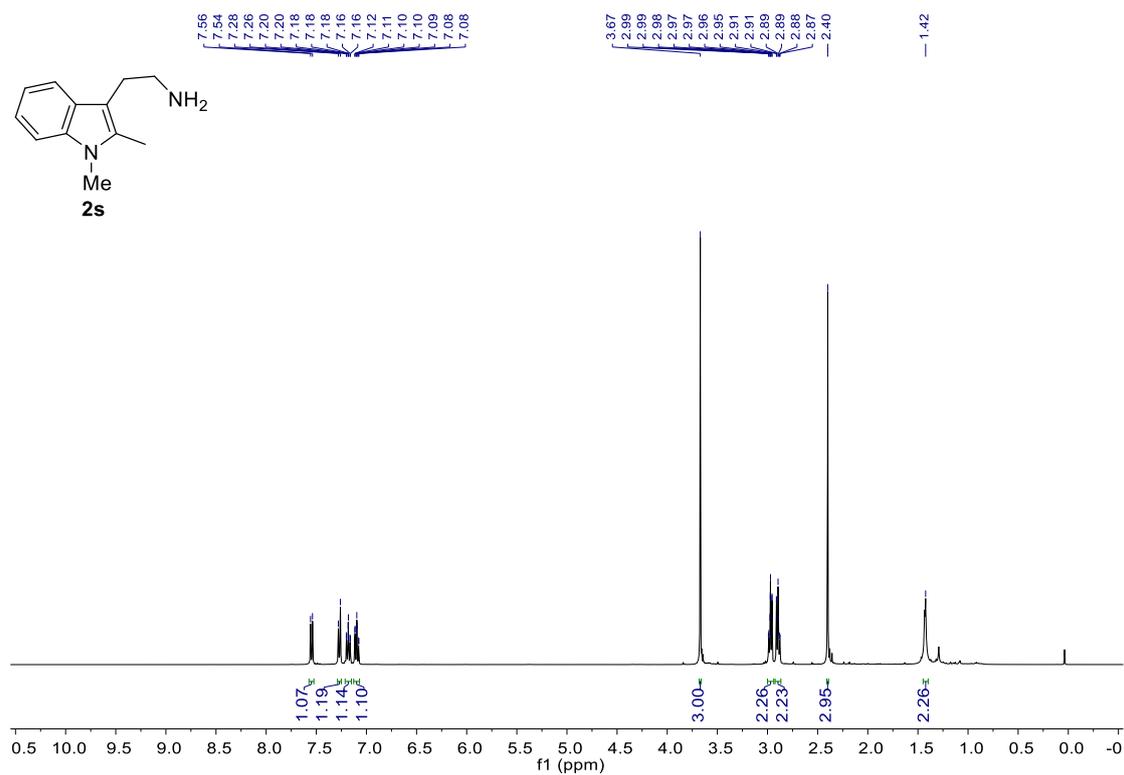
¹H NMR (400 MHz, CDCl₃, compound **2r**)



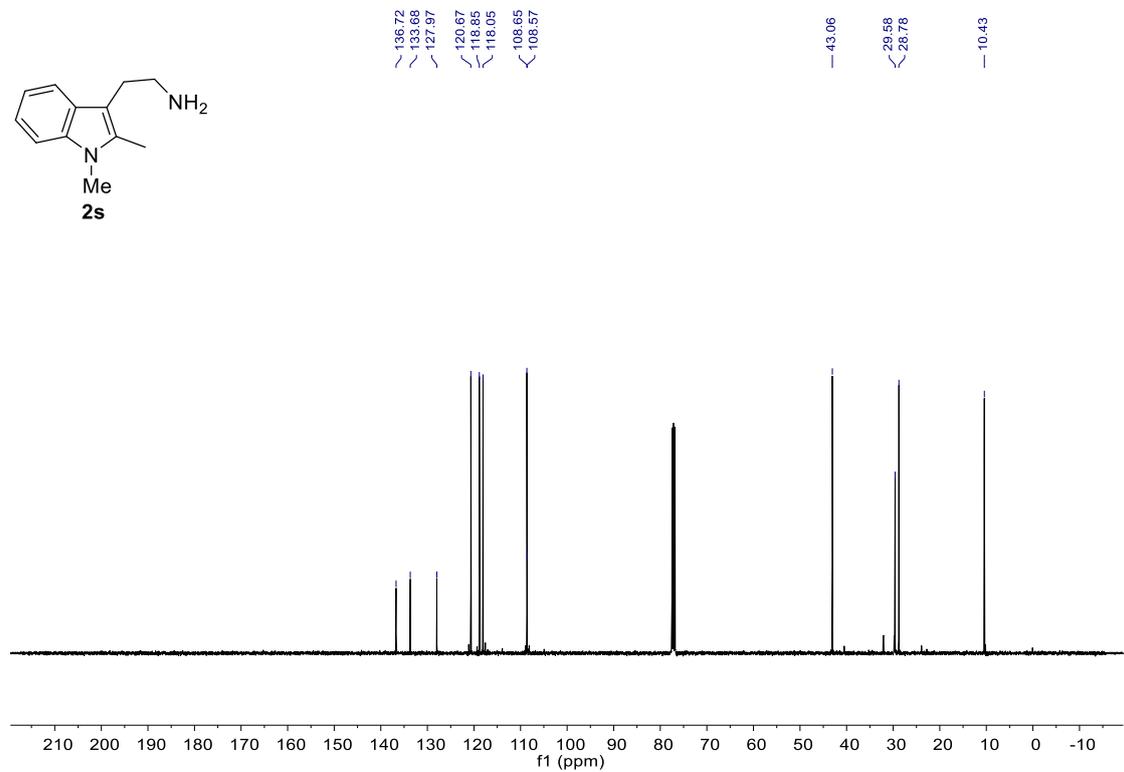
¹³C NMR (100 MHz, CDCl₃, compound **2r**)



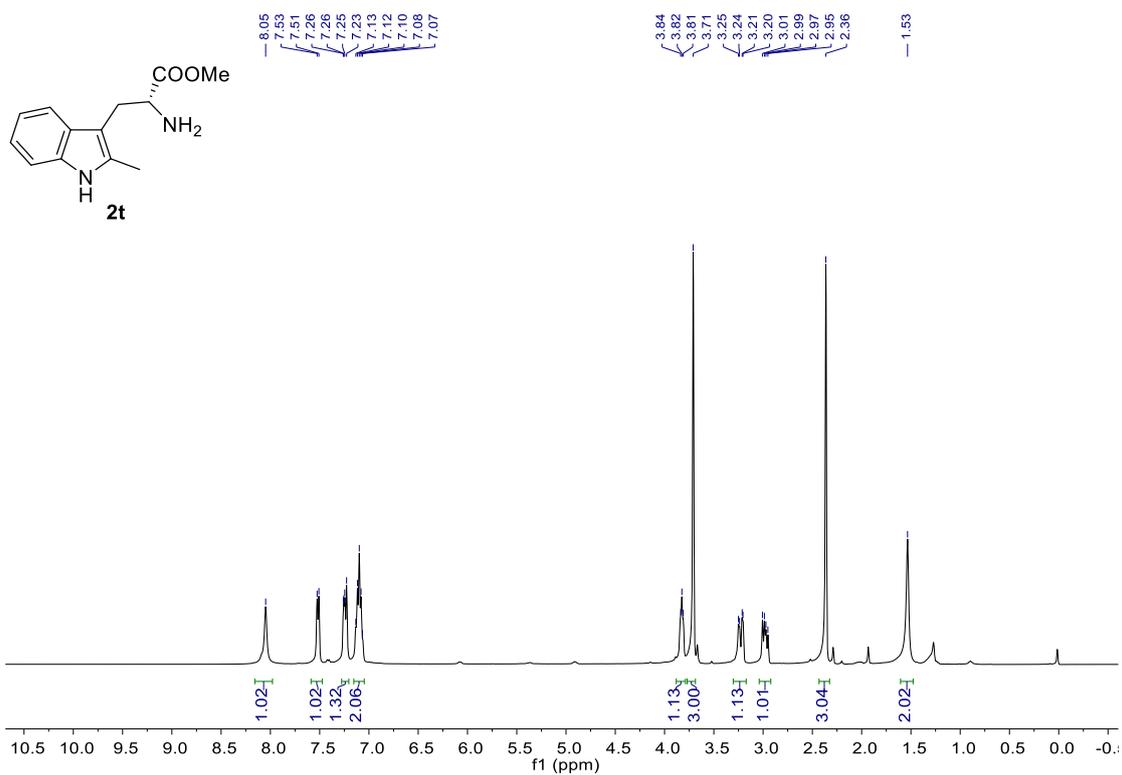
¹H NMR (400 MHz, CDCl₃, compound 2s)



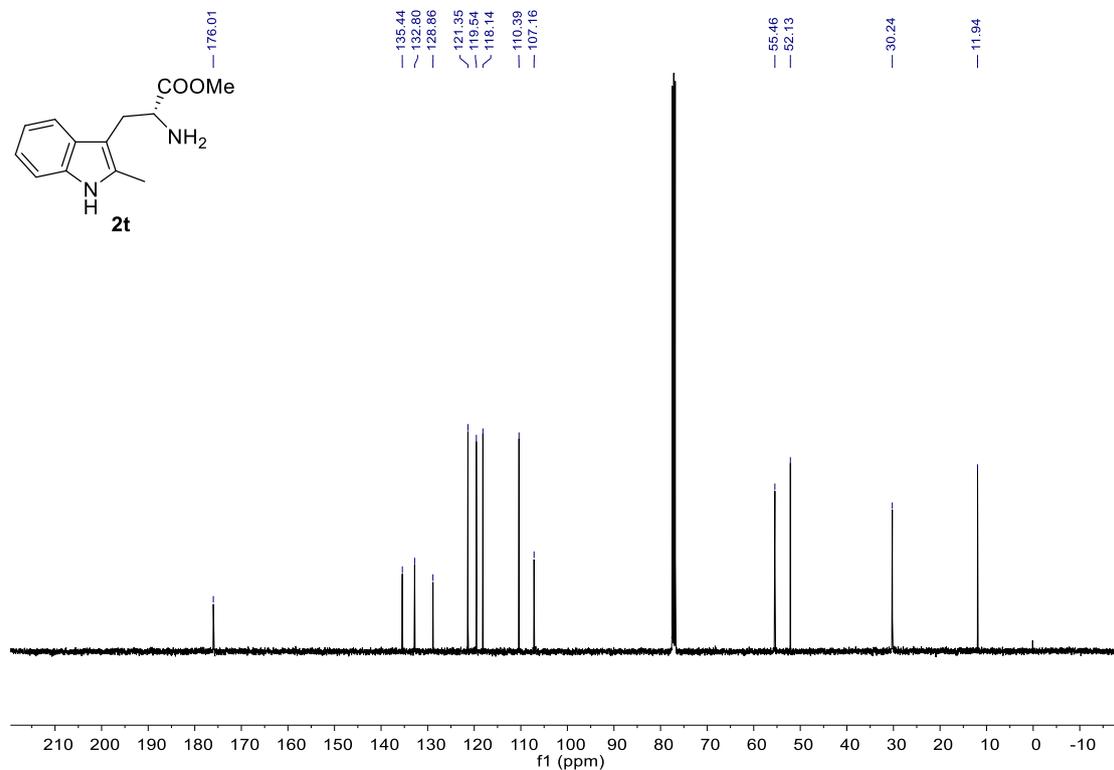
¹³C NMR (100 MHz, CDCl₃, compound 2s)



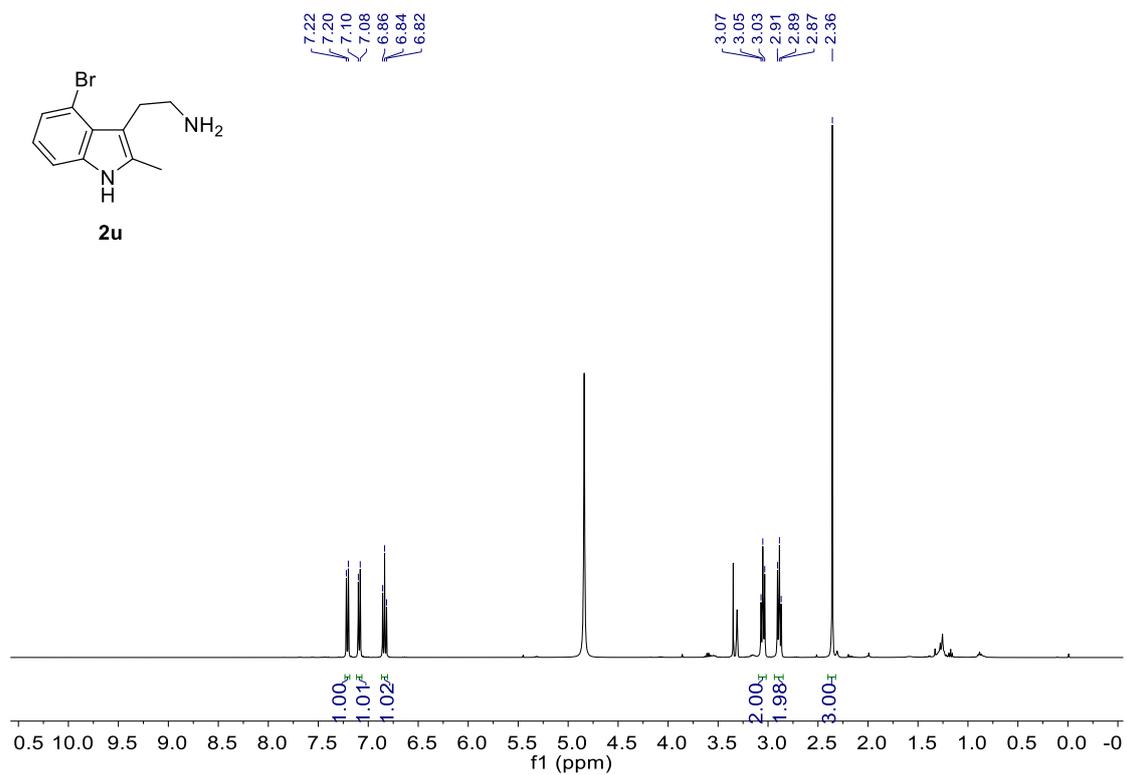
¹H NMR (400 MHz, CDCl₃, compound 2t)



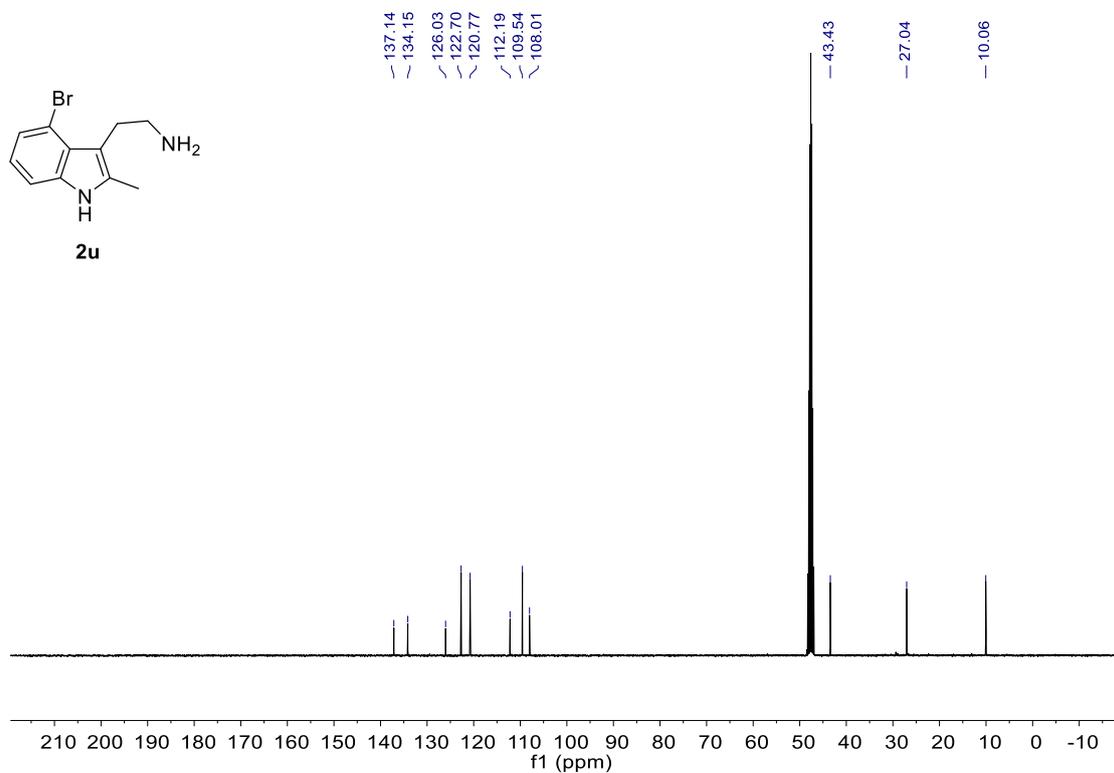
¹³C NMR (100 MHz, CDCl₃, compound 2t)



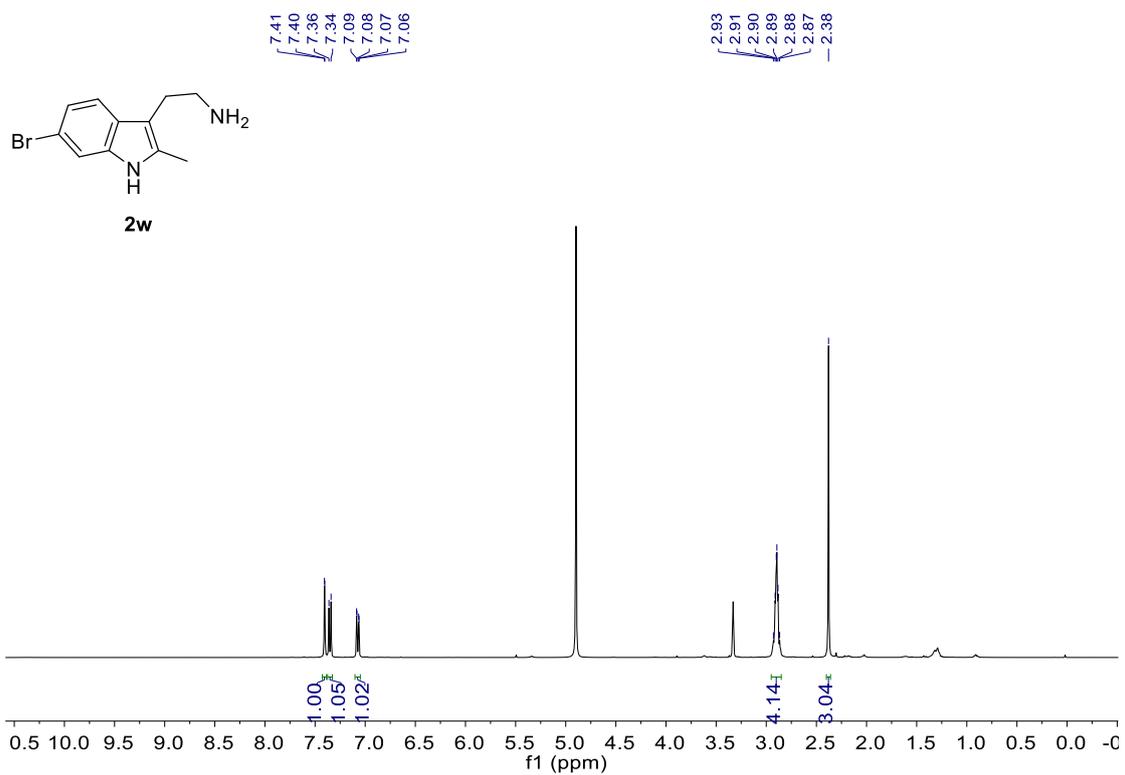
¹H NMR (400 MHz, Methanol-*d*₄, compound **2u)**



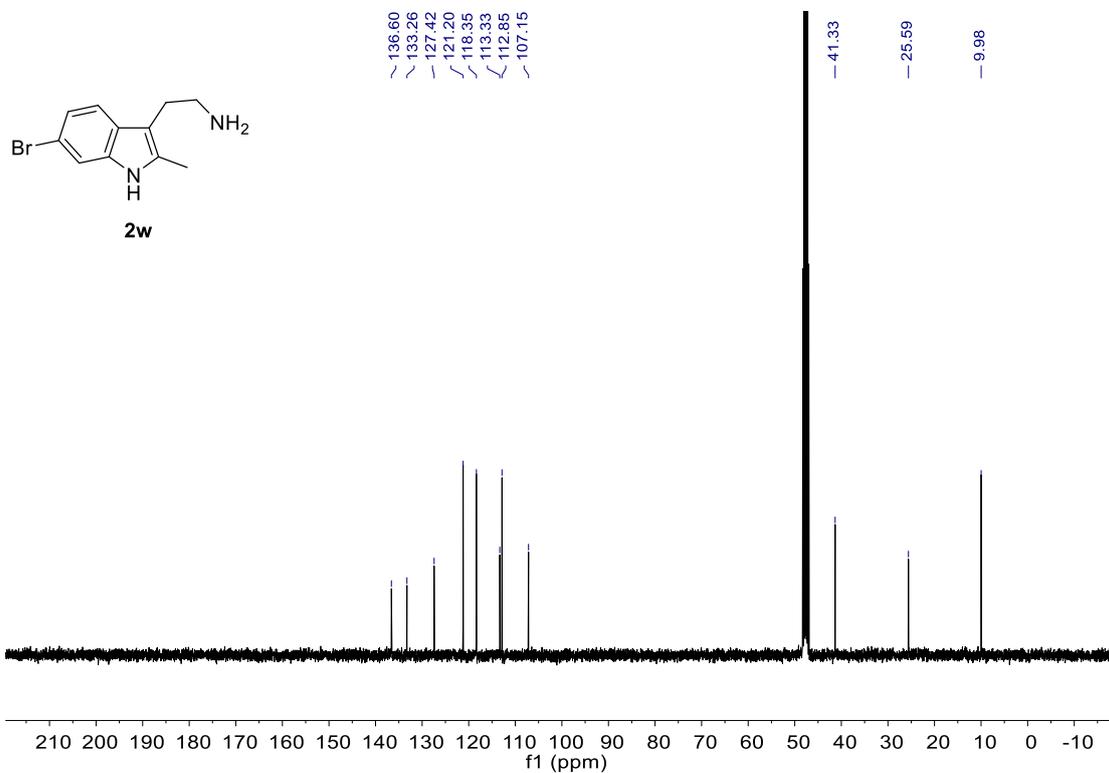
¹³C NMR (100 MHz, Methanol-*d*₄, compound **2u)**



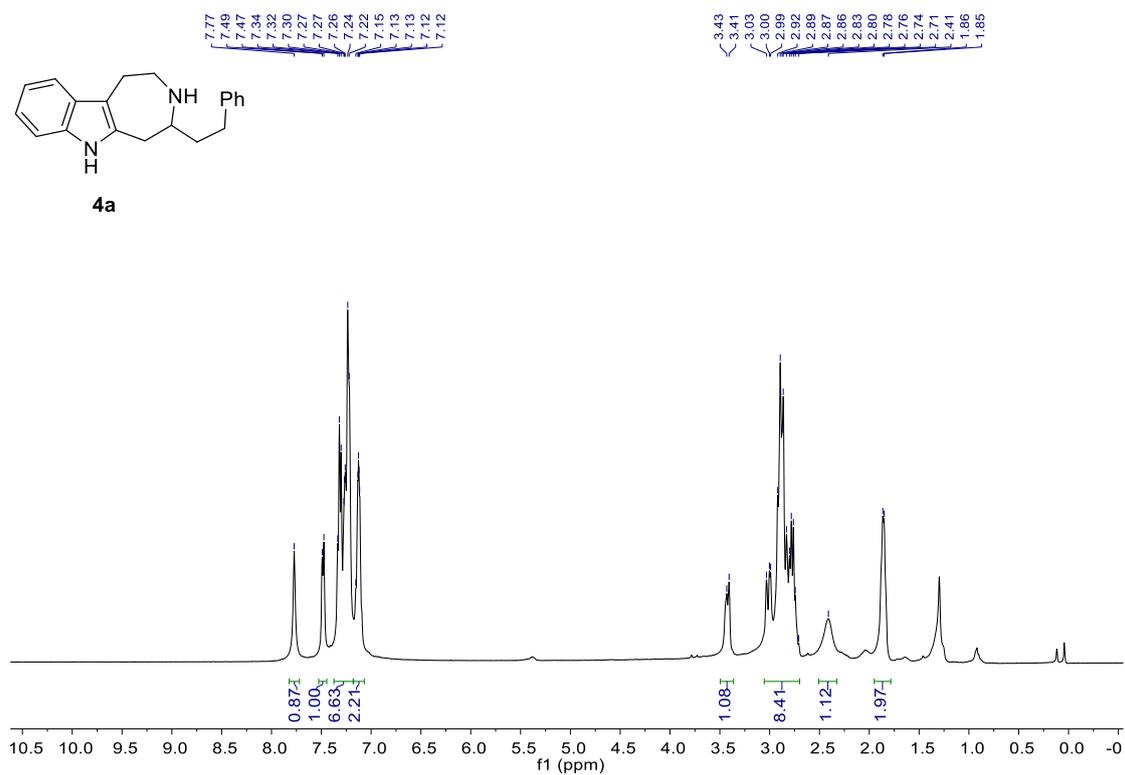
¹H NMR (400 MHz, Methanol-d₄, compound 2w)



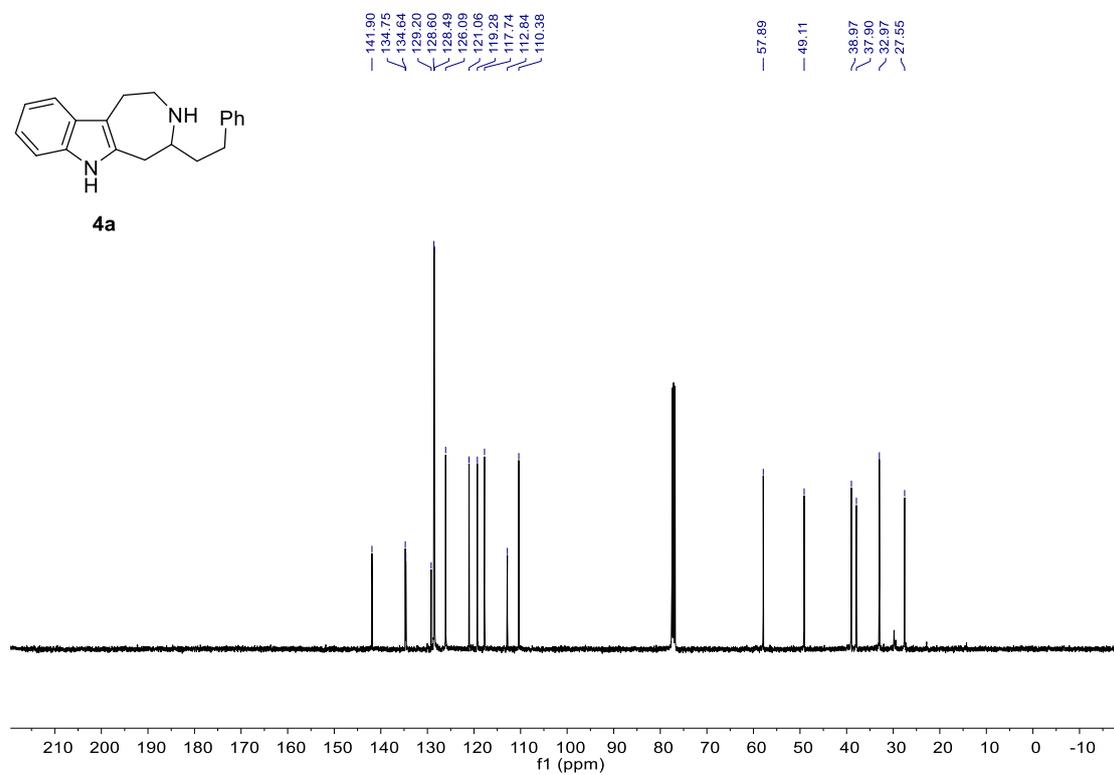
¹³C NMR (100 MHz, Methanol-d₄, compound 2w)



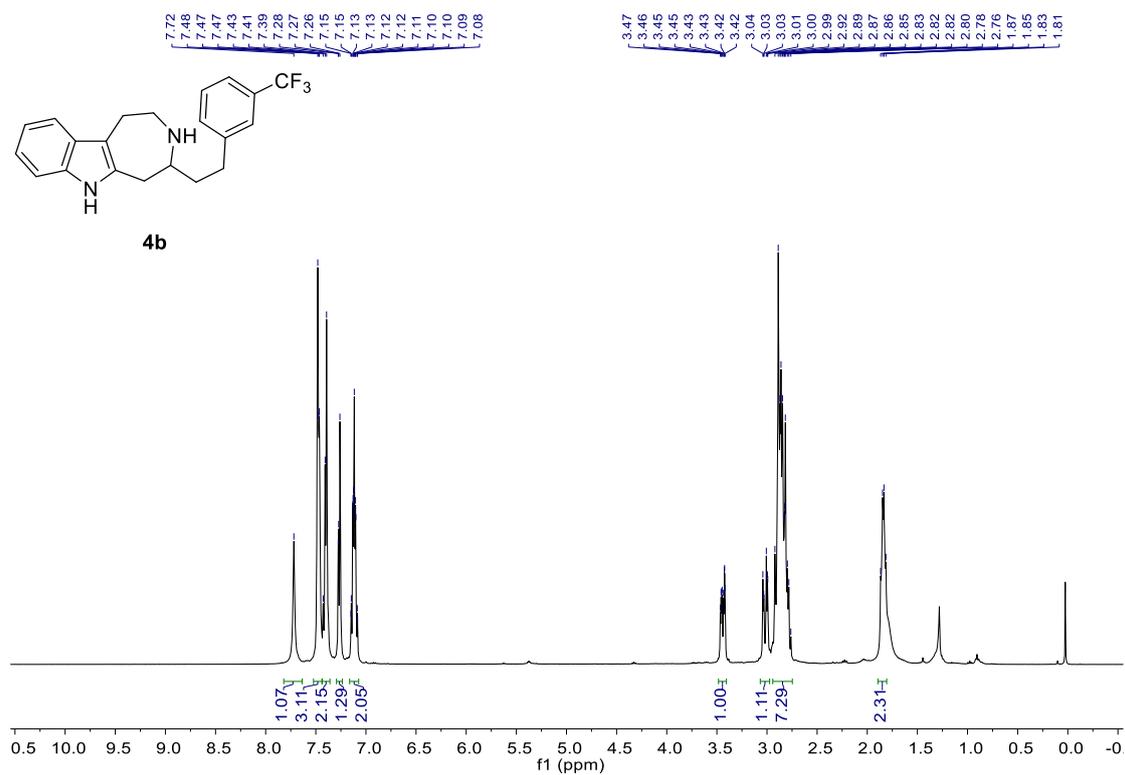
^1H NMR (400 MHz, CDCl_3 , compound **4a)**



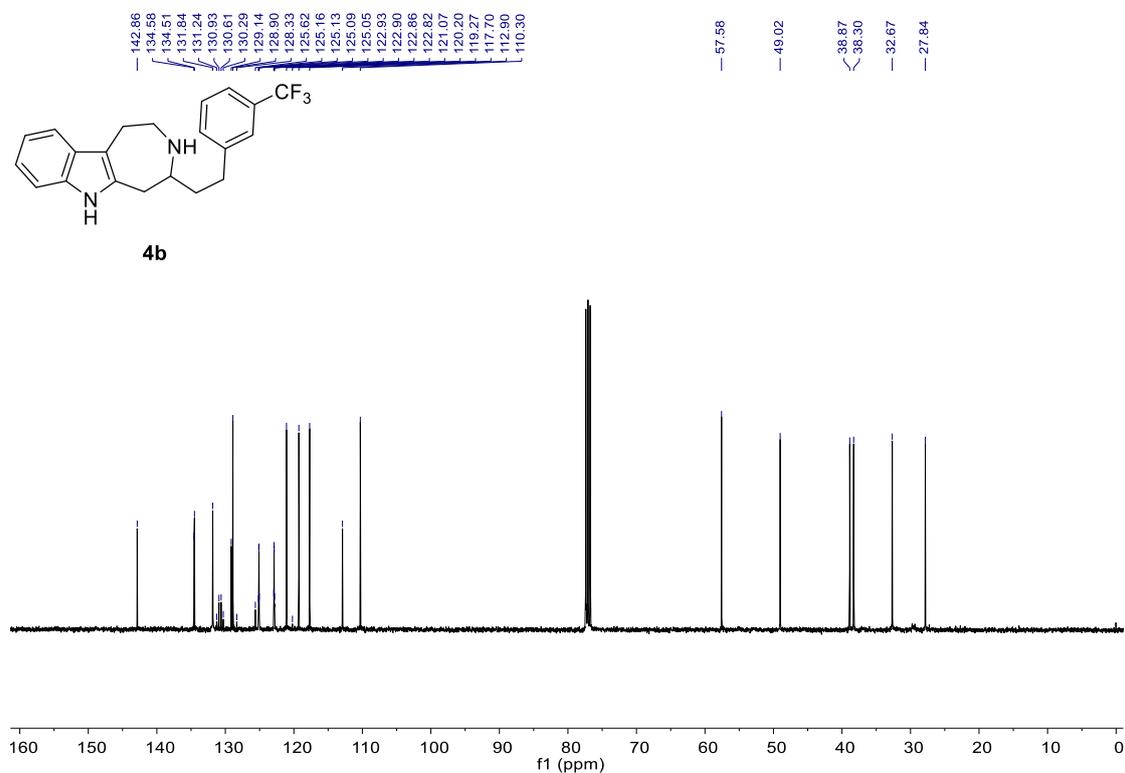
^{13}C NMR (100 MHz, CDCl_3 , compound **4a)**



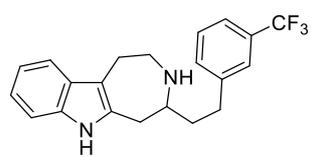
¹H NMR (400 MHz, CDCl₃, compound 4b)



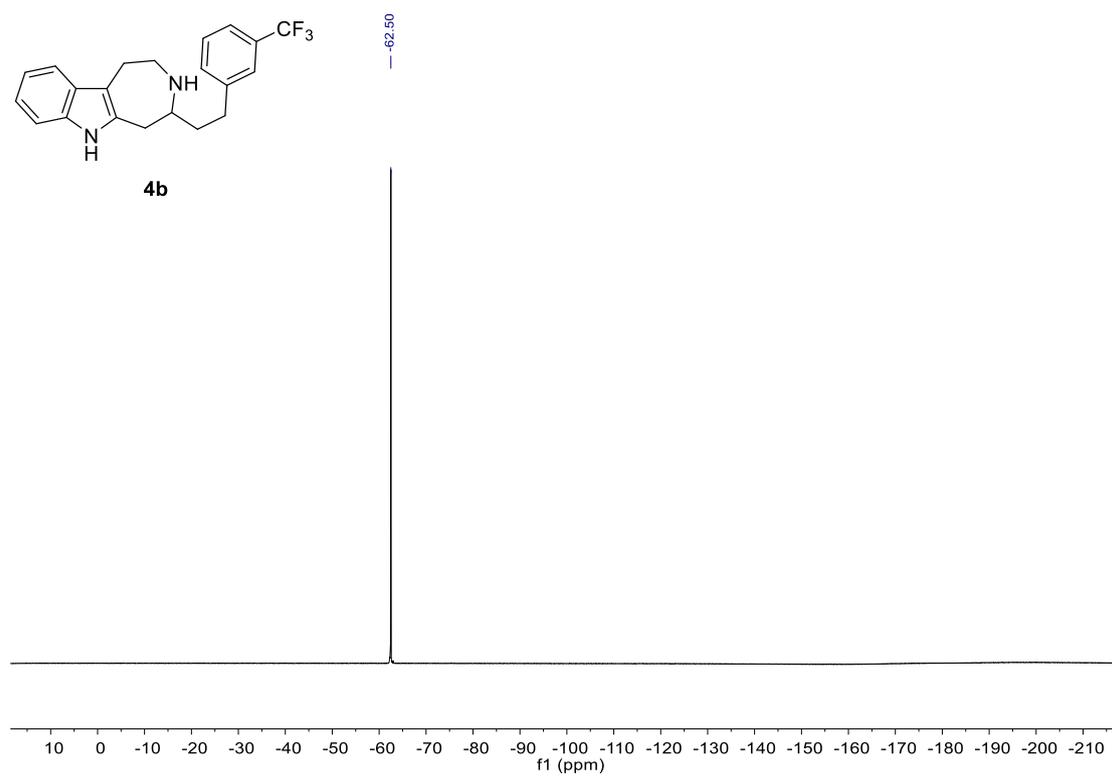
¹³C NMR (100 MHz, CDCl₃, compound 4b)



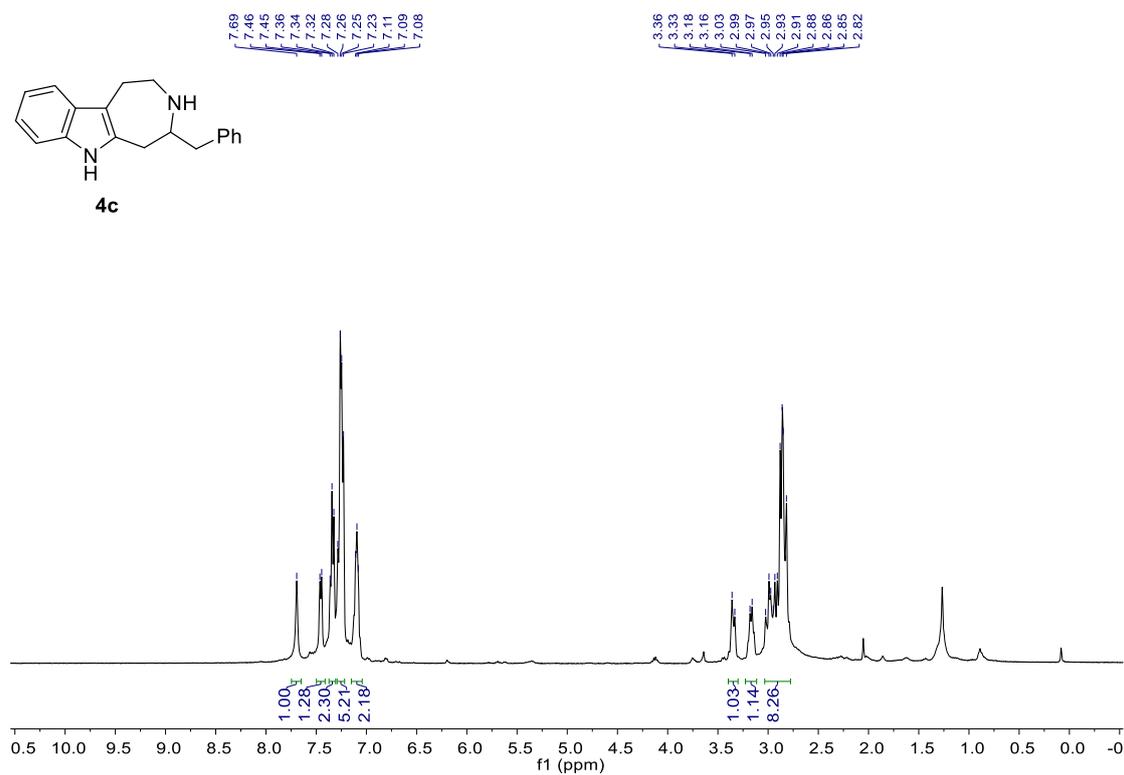
¹⁹F NMR (376 MHz, CDCl₃, compound 4b)



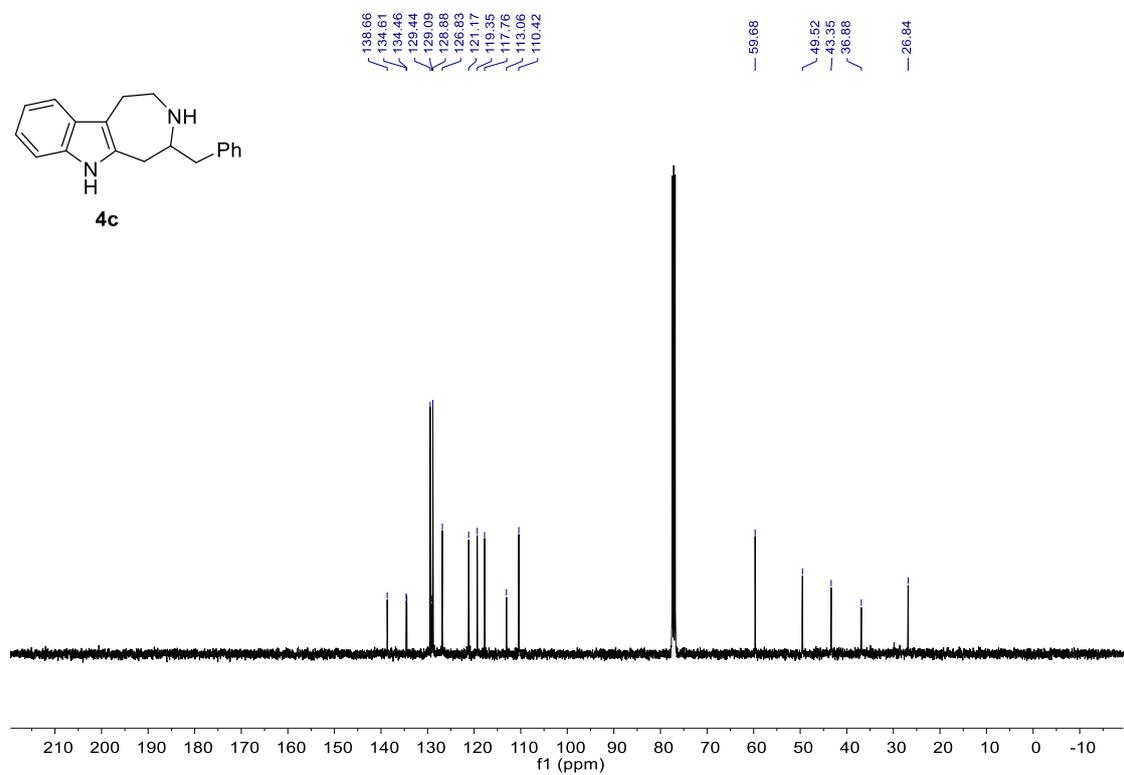
4b



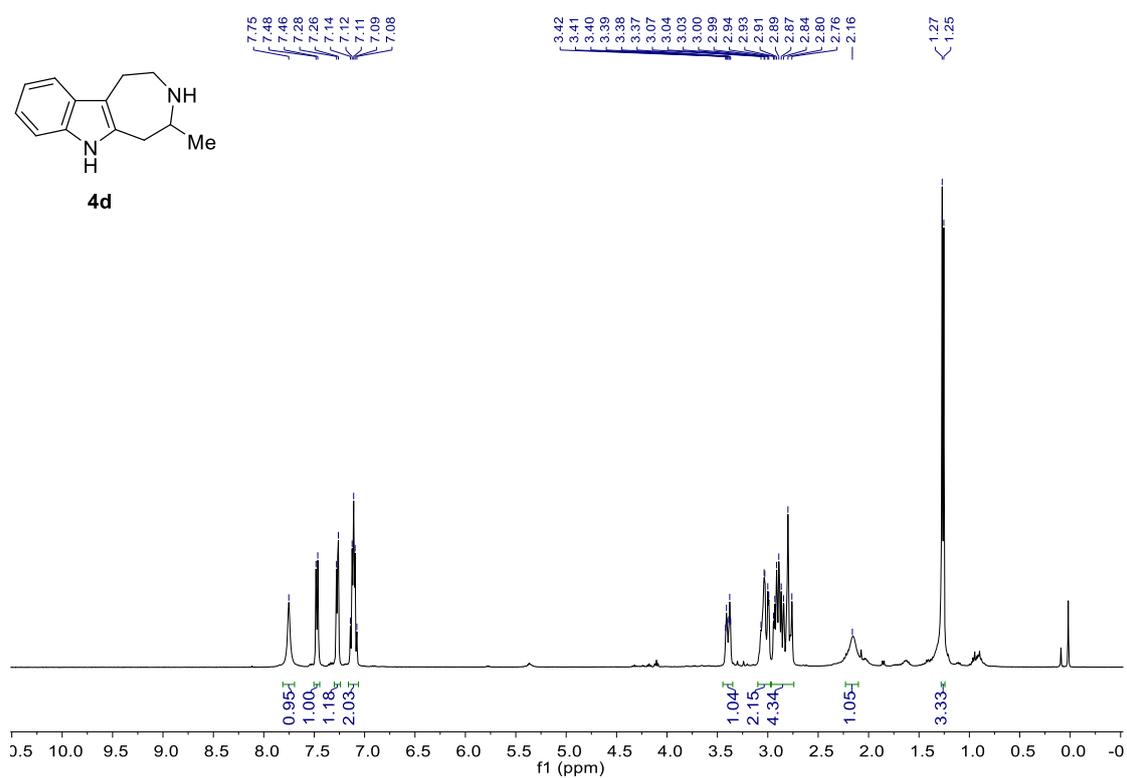
¹H NMR (400 MHz, CDCl₃, compound 4c)



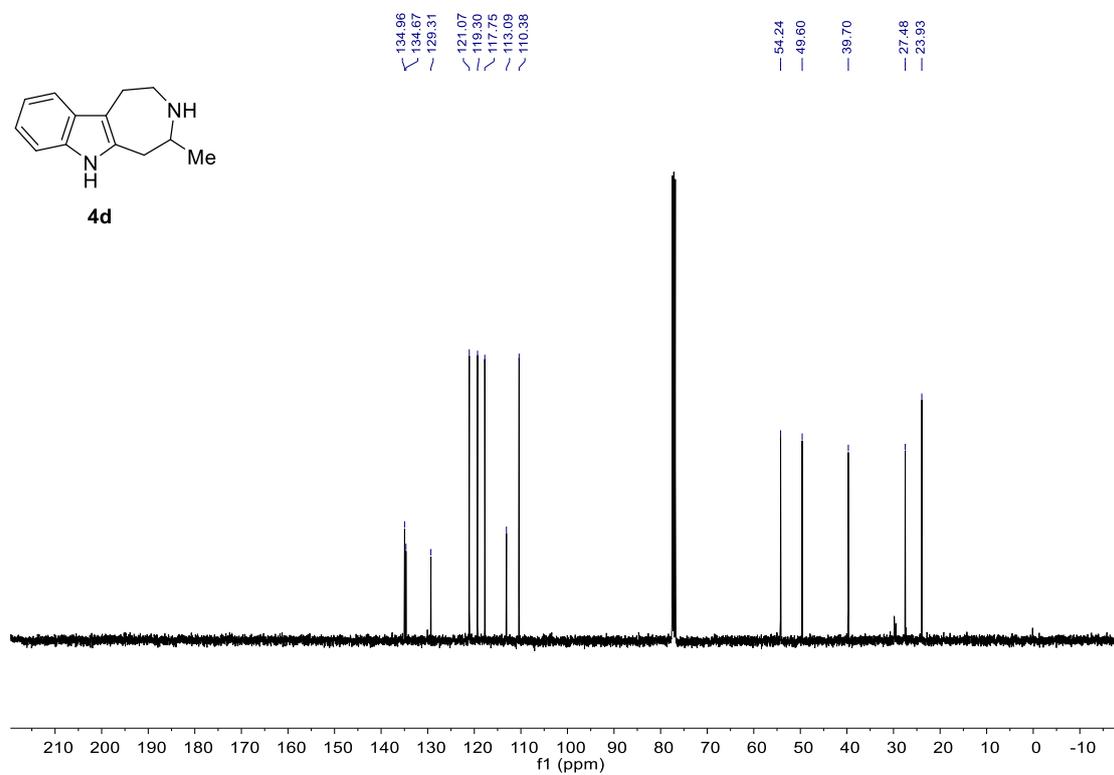
¹³C NMR (100 MHz, CDCl₃, compound 4c)



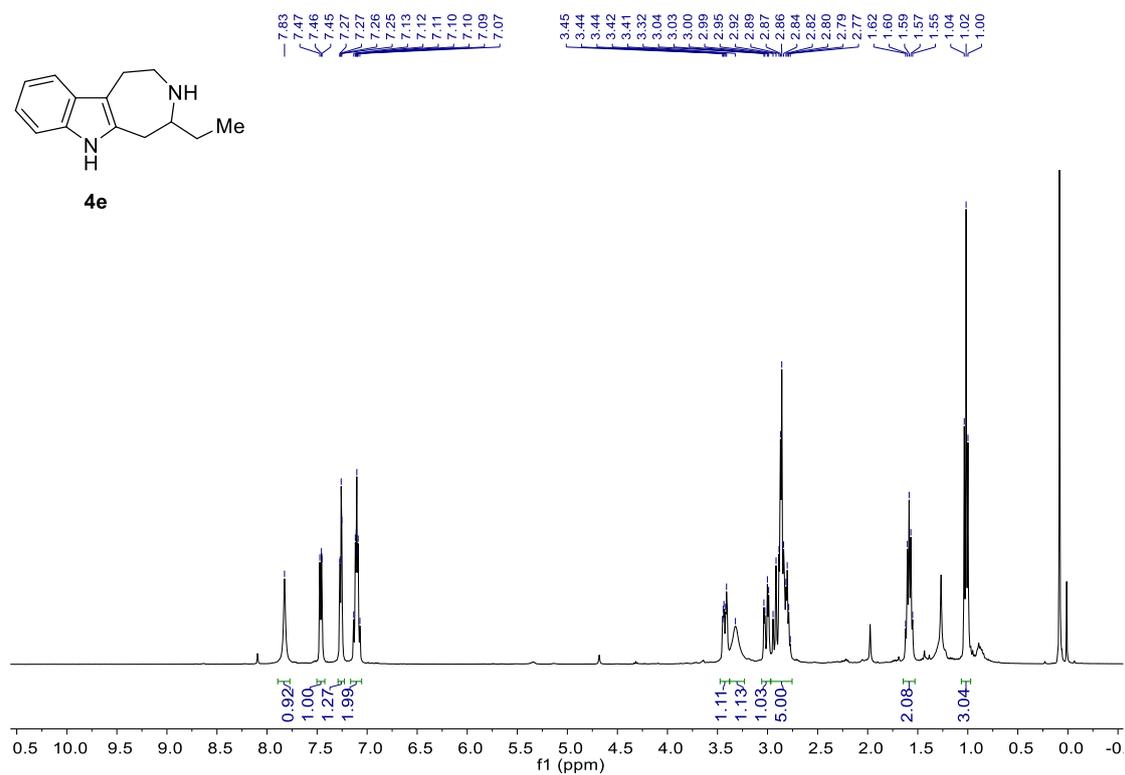
¹H NMR (400 MHz, CDCl₃, compound 4d)



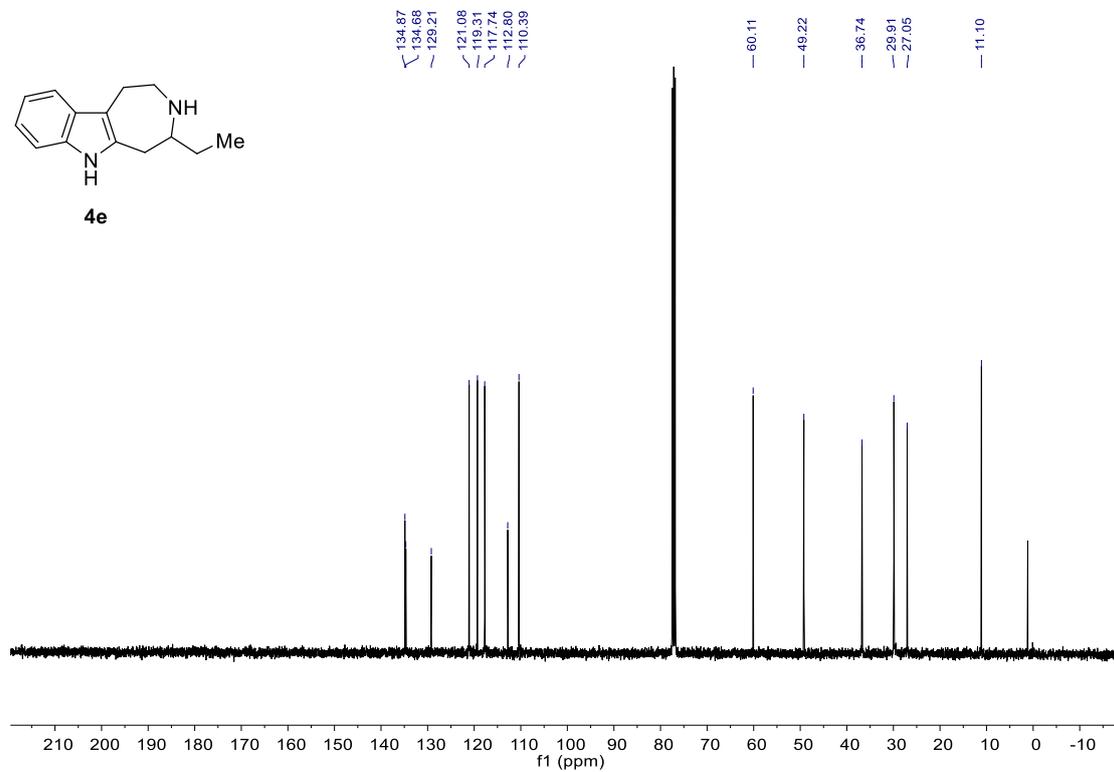
¹³C NMR (100 MHz, CDCl₃, compound 4d)



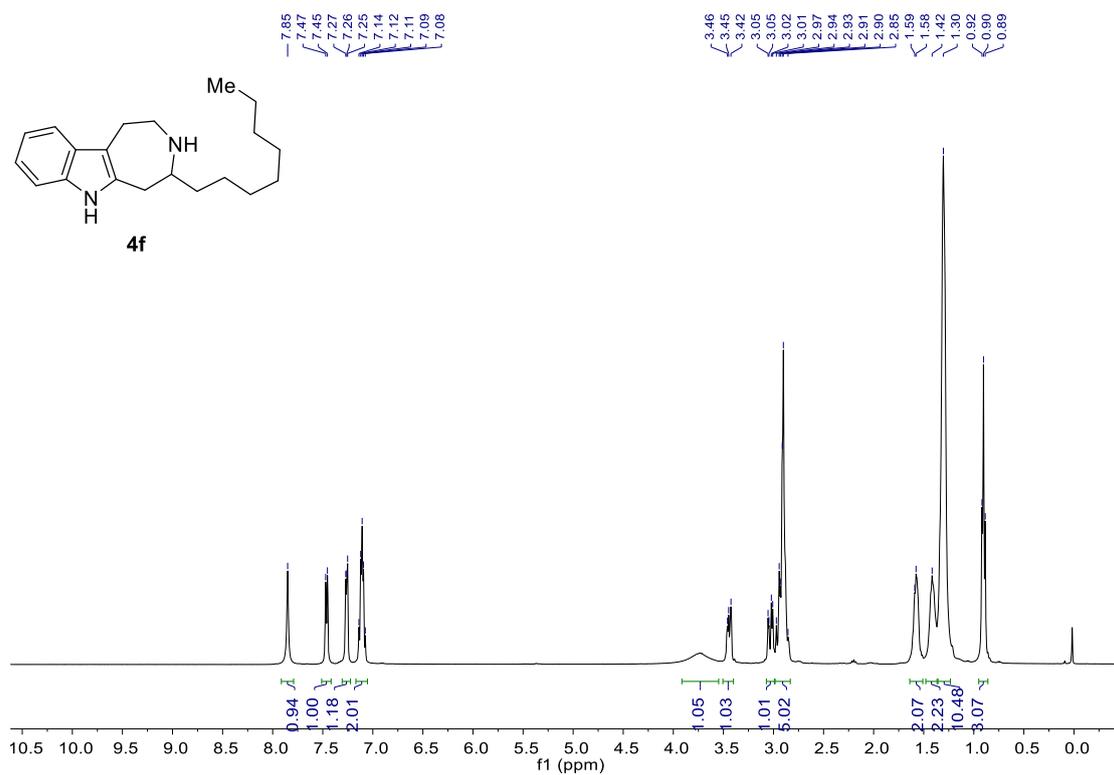
¹H NMR (400 MHz, CDCl₃, compound 4e)



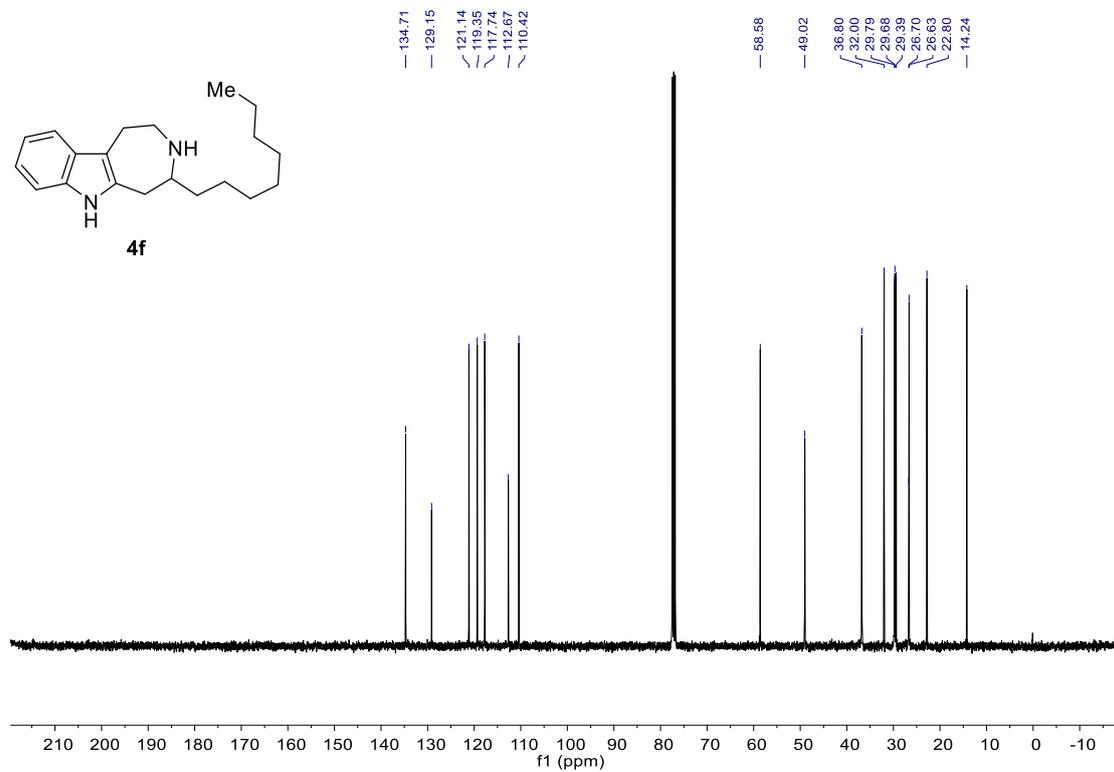
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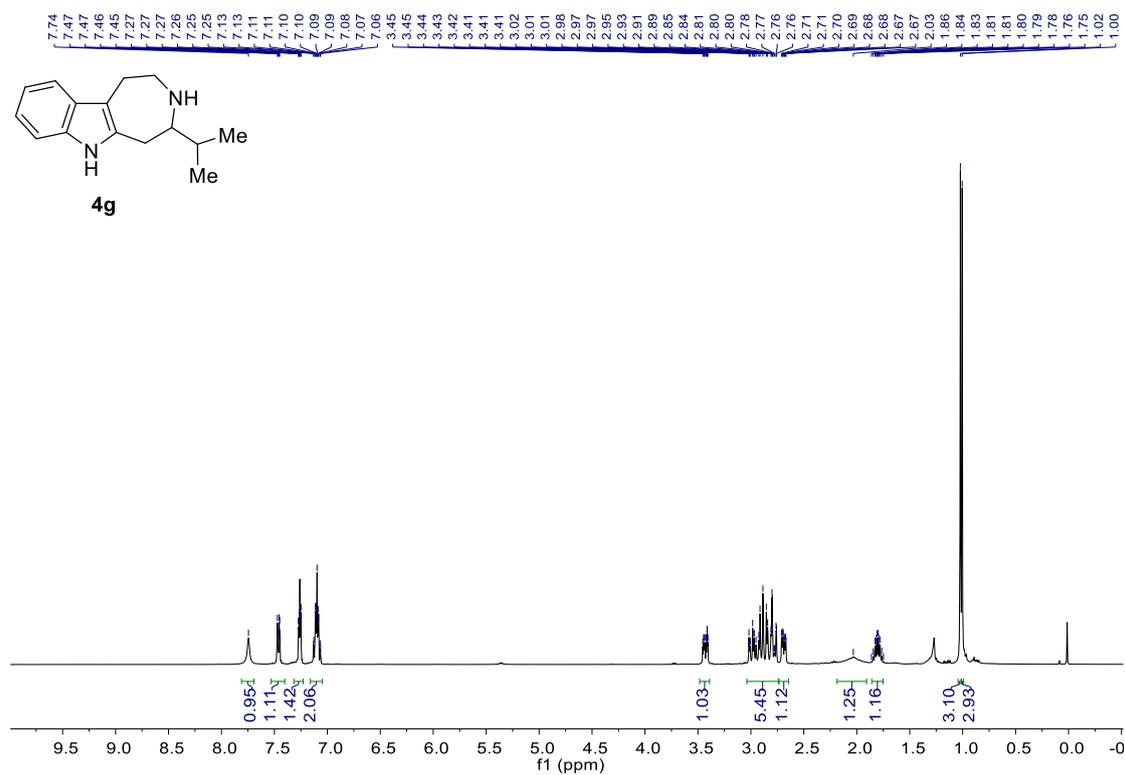
¹H NMR (400 MHz, CDCl₃, compound 4f)



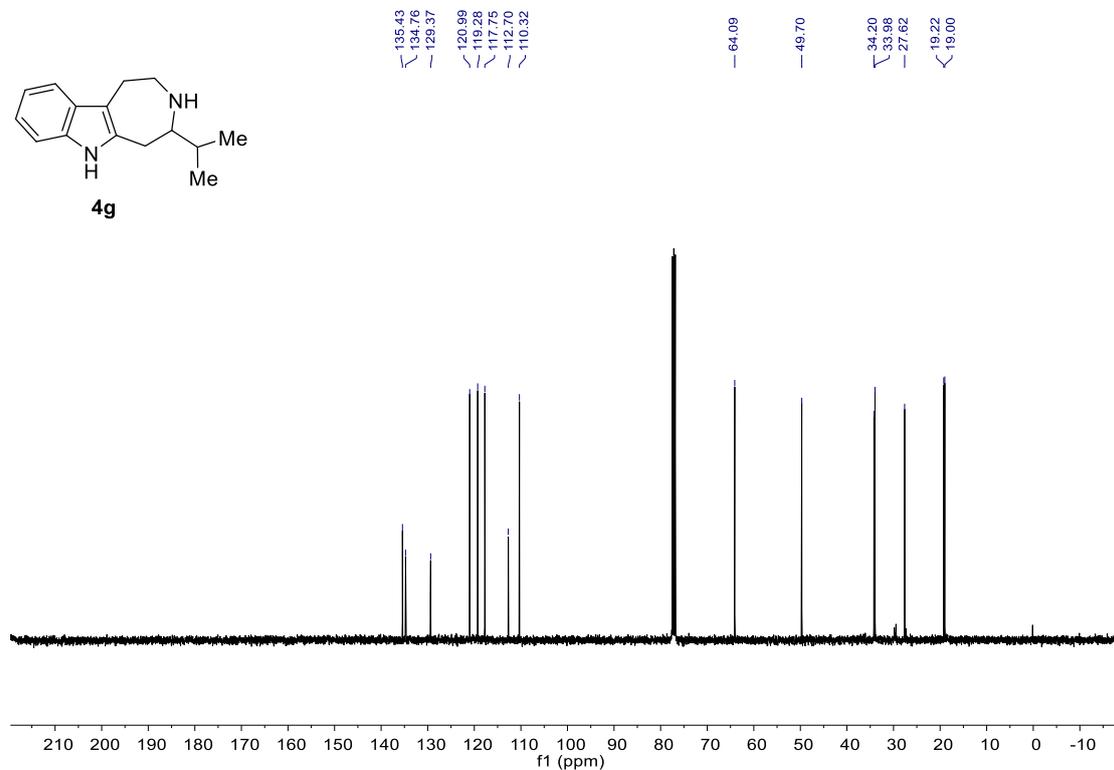
¹³C NMR (100 MHz, CDCl₃, compound 4f)



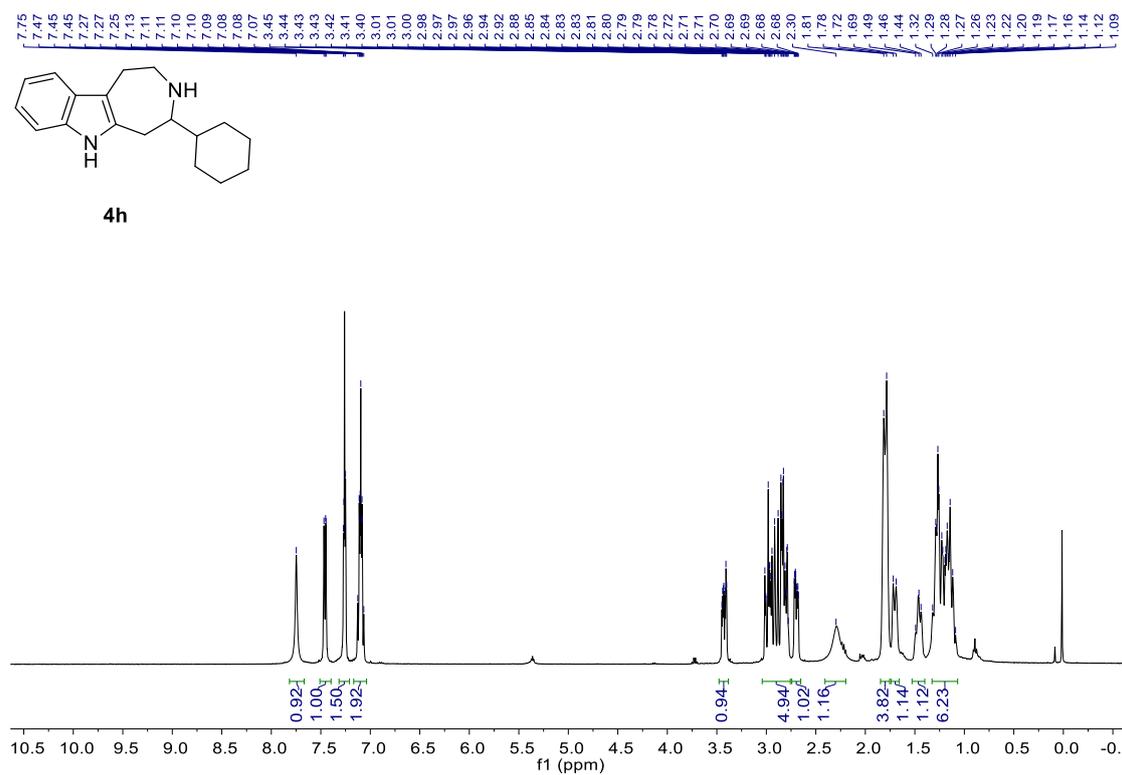
¹H NMR (400 MHz, CDCl₃, compound **4g**)



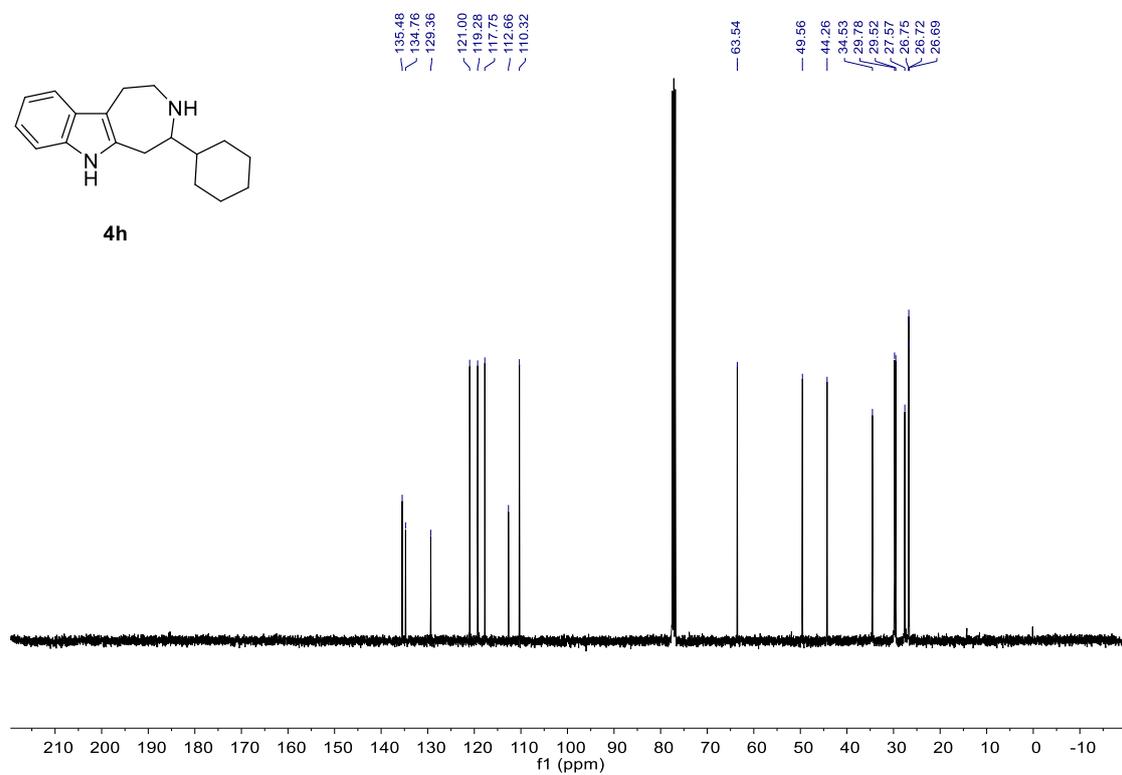
¹³C NMR (100 MHz, CDCl₃, compound **4g**)



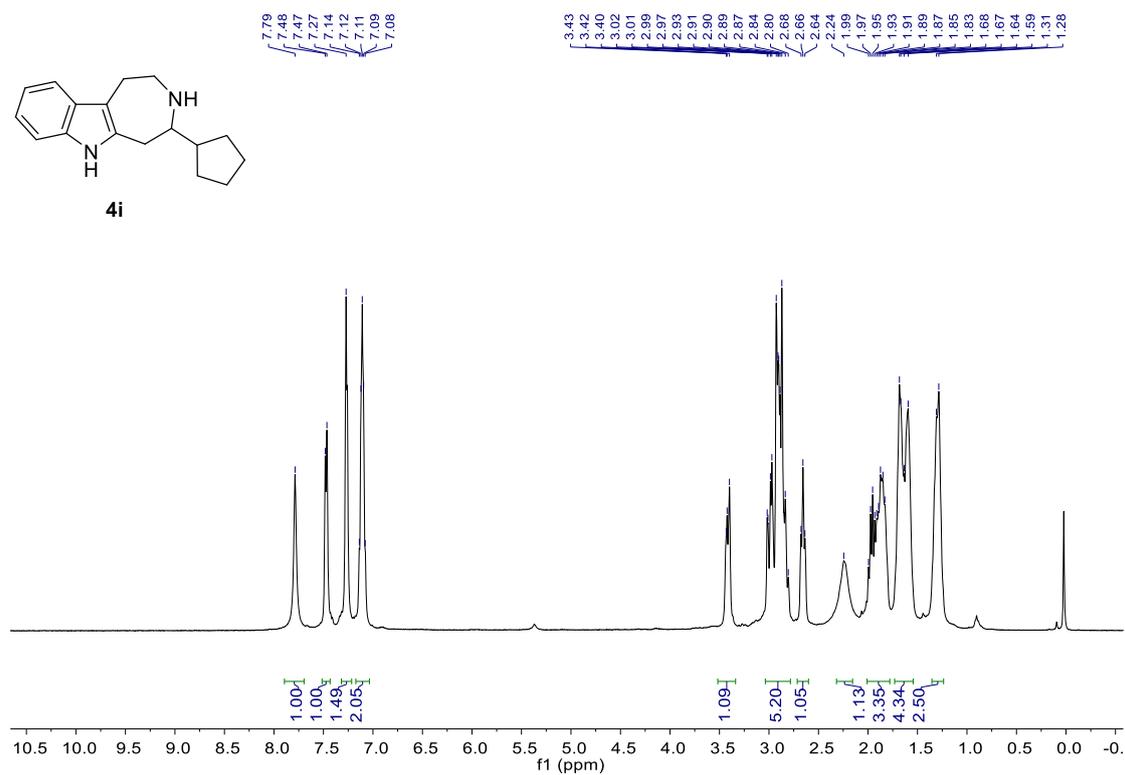
¹H NMR (400 MHz, CDCl₃, compound 4h)



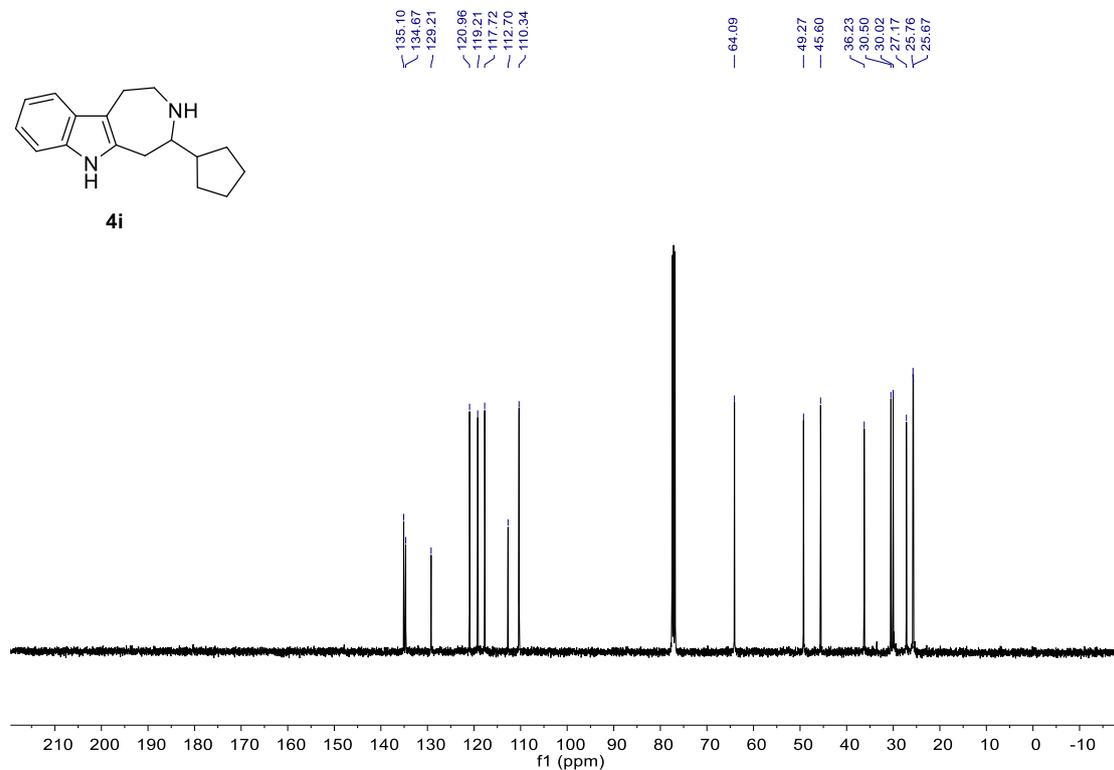
¹³C NMR (100 MHz, CDCl₃, compound 4h)



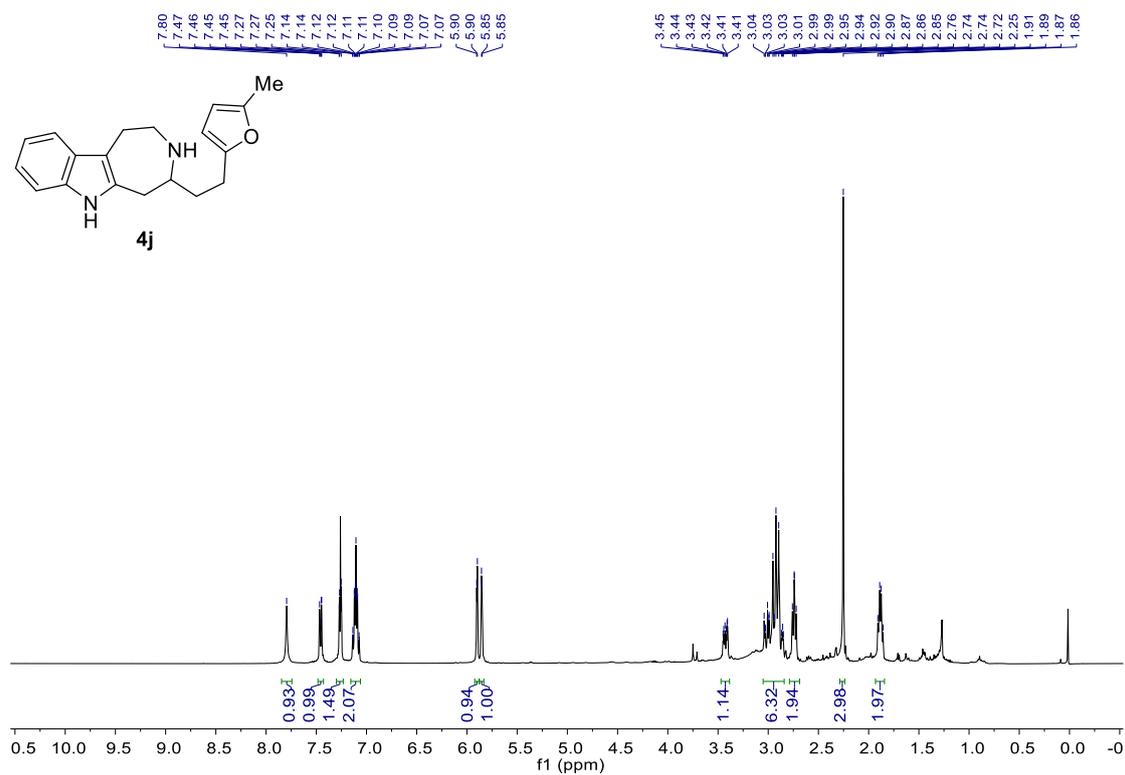
¹H NMR (400 MHz, CDCl₃, compound 4i)



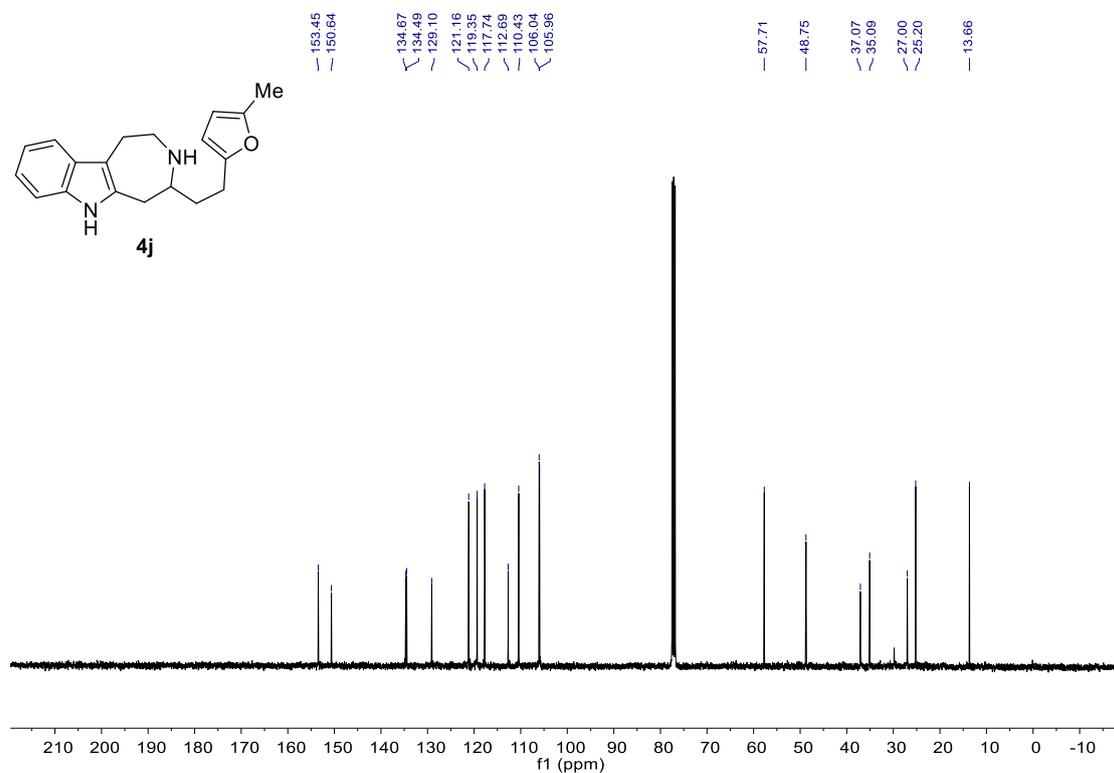
¹³C NMR (100 MHz, CDCl₃, compound 4i)



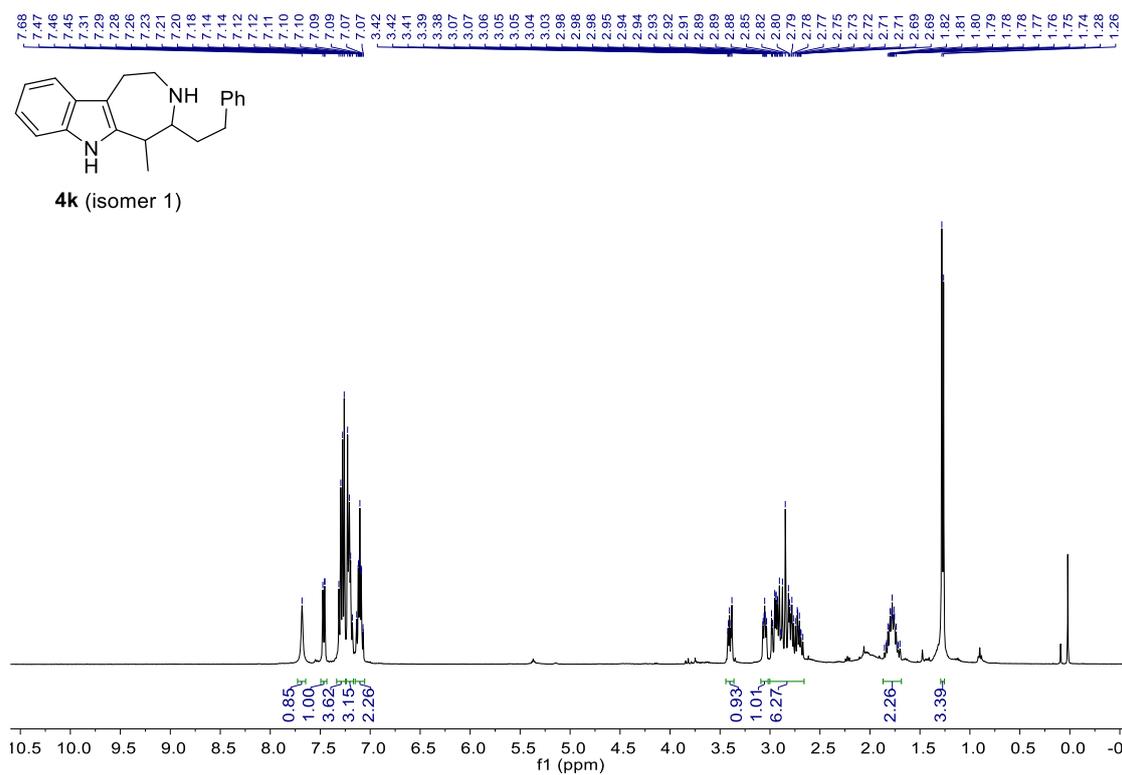
¹H NMR (400 MHz, CDCl₃, compound 4j)



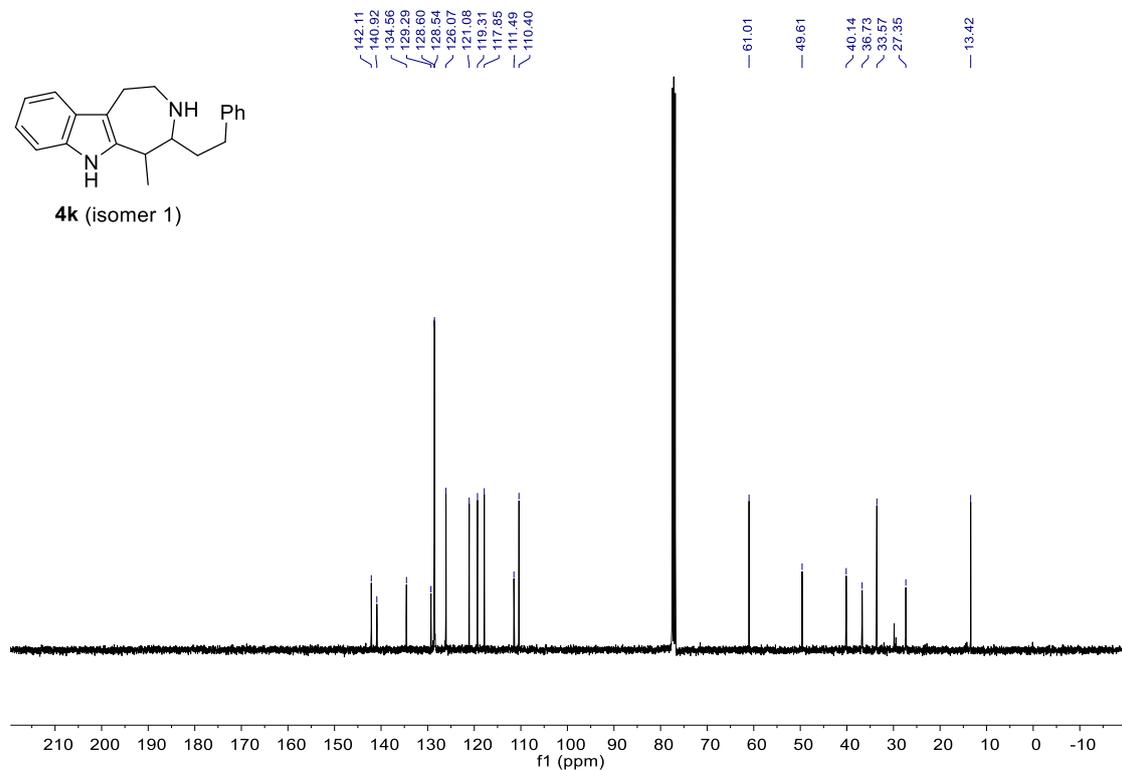
¹³C NMR (100 MHz, CDCl₃, compound 4j)



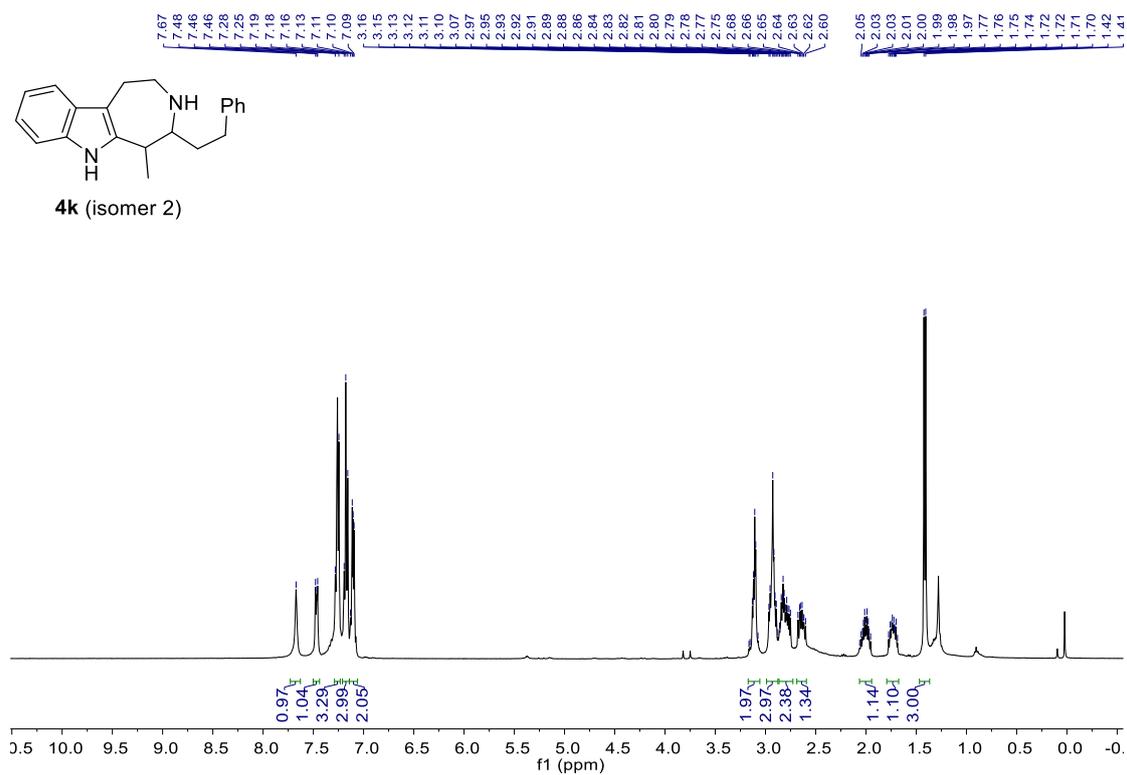
¹H NMR (400 MHz, CDCl₃, compound **4k**, isomer 1)



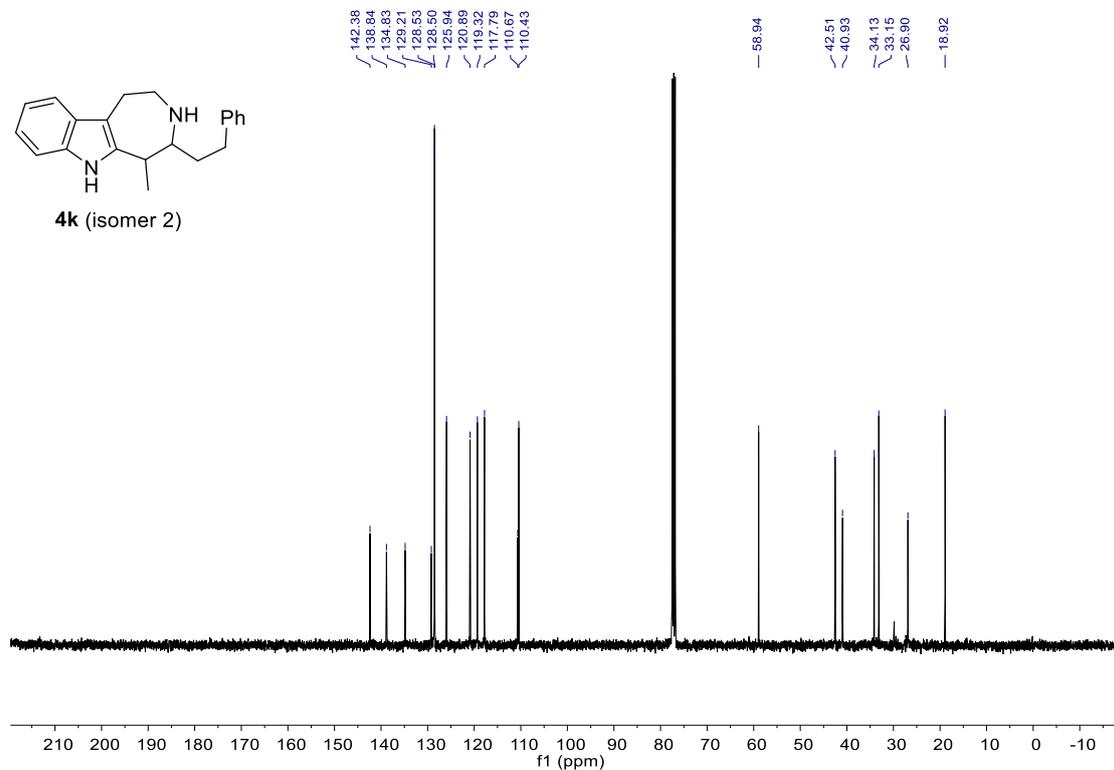
¹³C NMR (100 MHz, CDCl₃, compound **4k**, isomer 1)



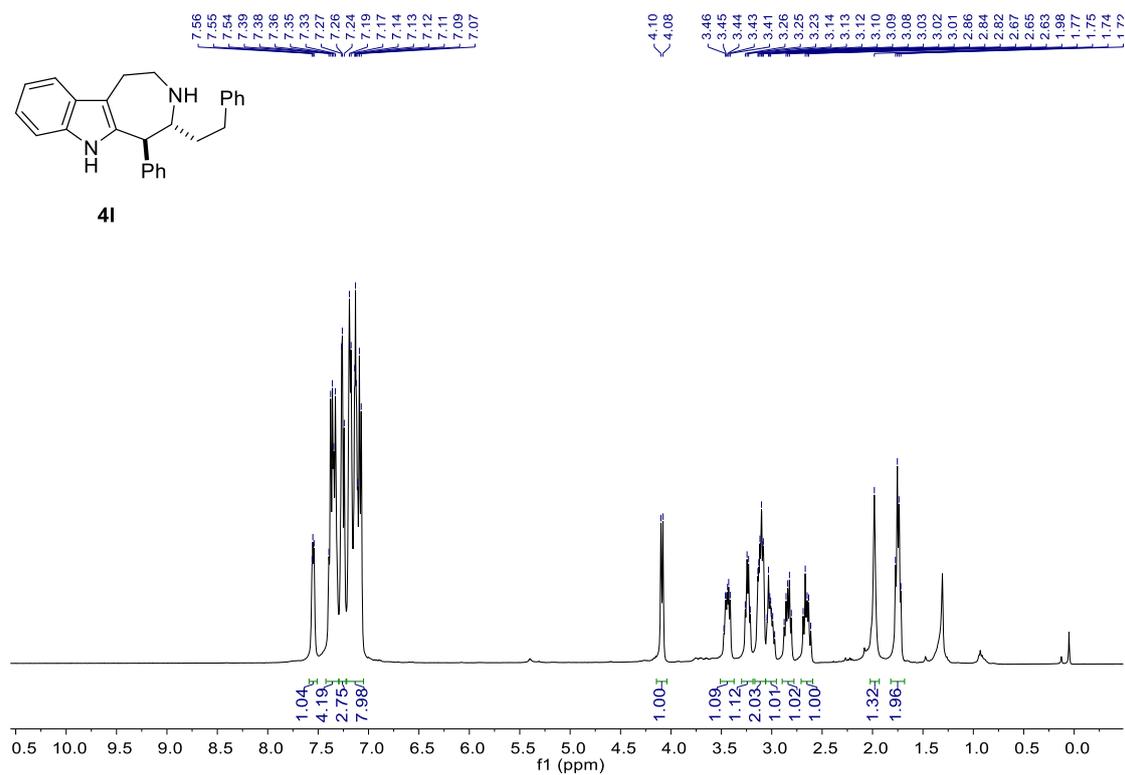
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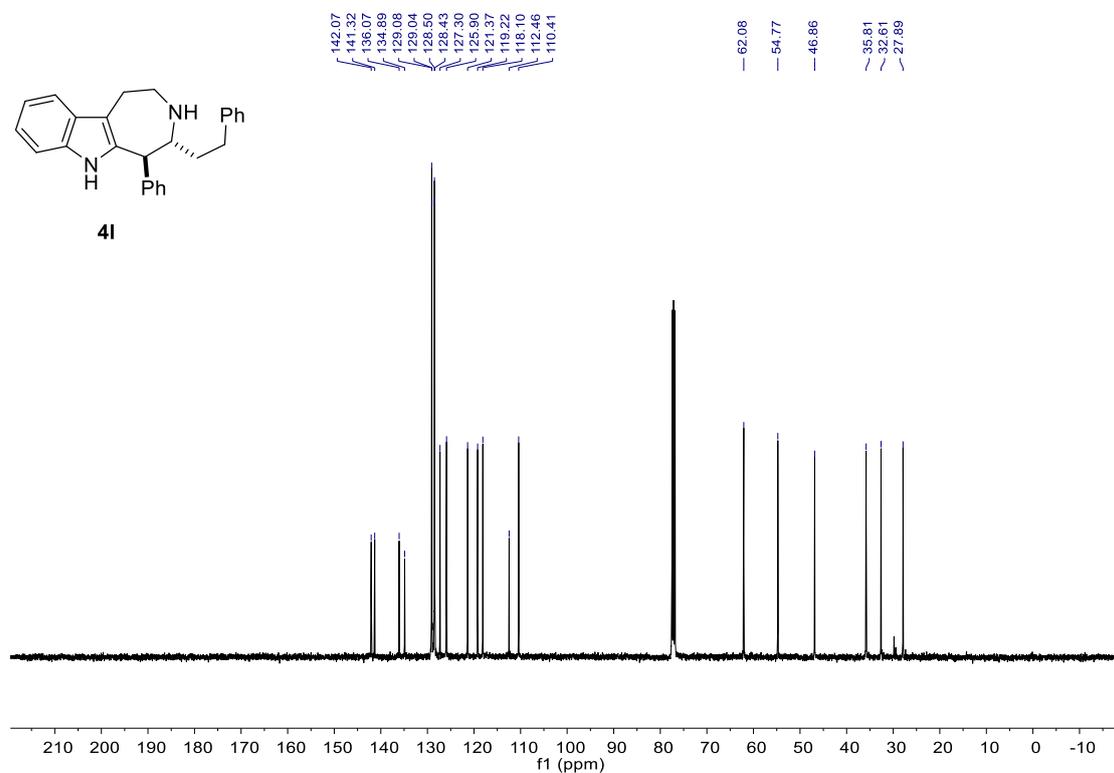
¹³C NMR (100 MHz, CDCl₃, compound **4k**, isomer 2)



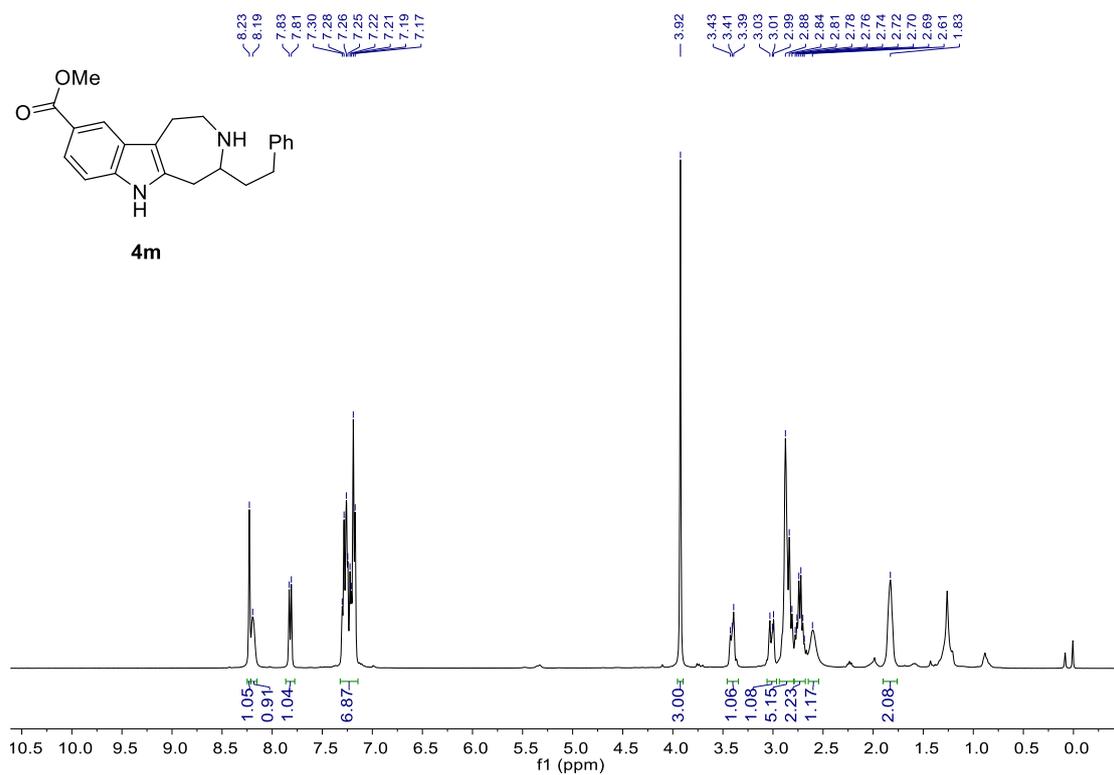
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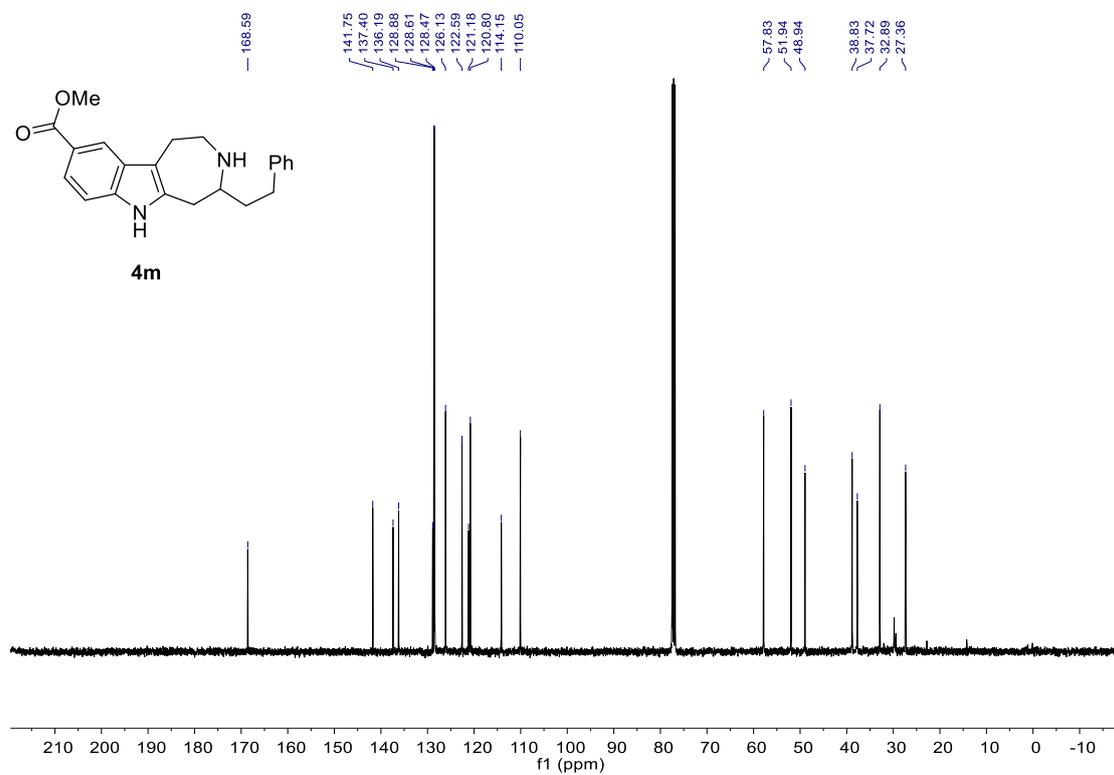
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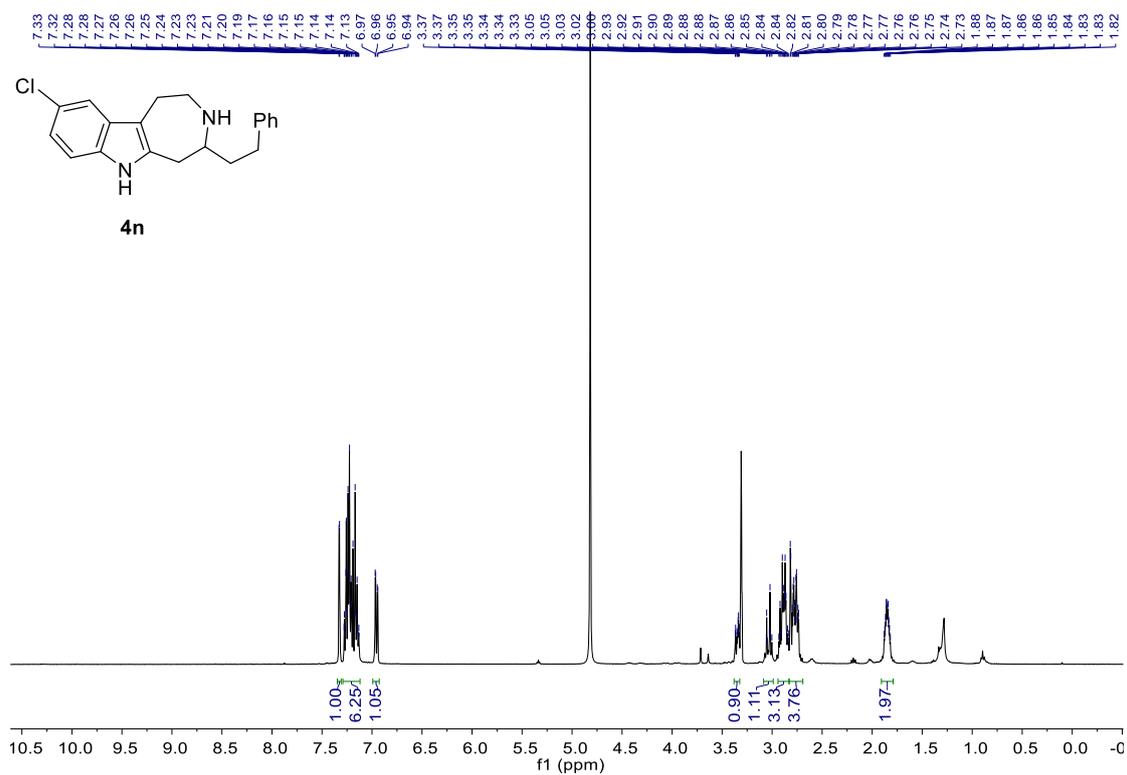
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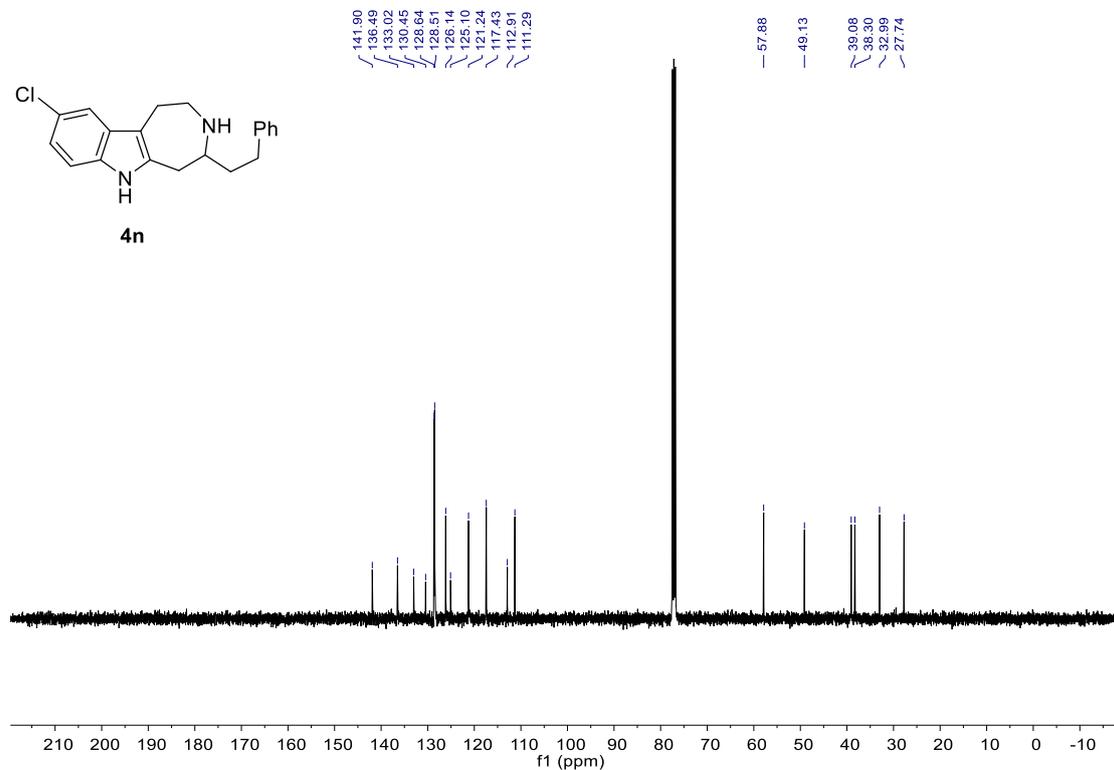
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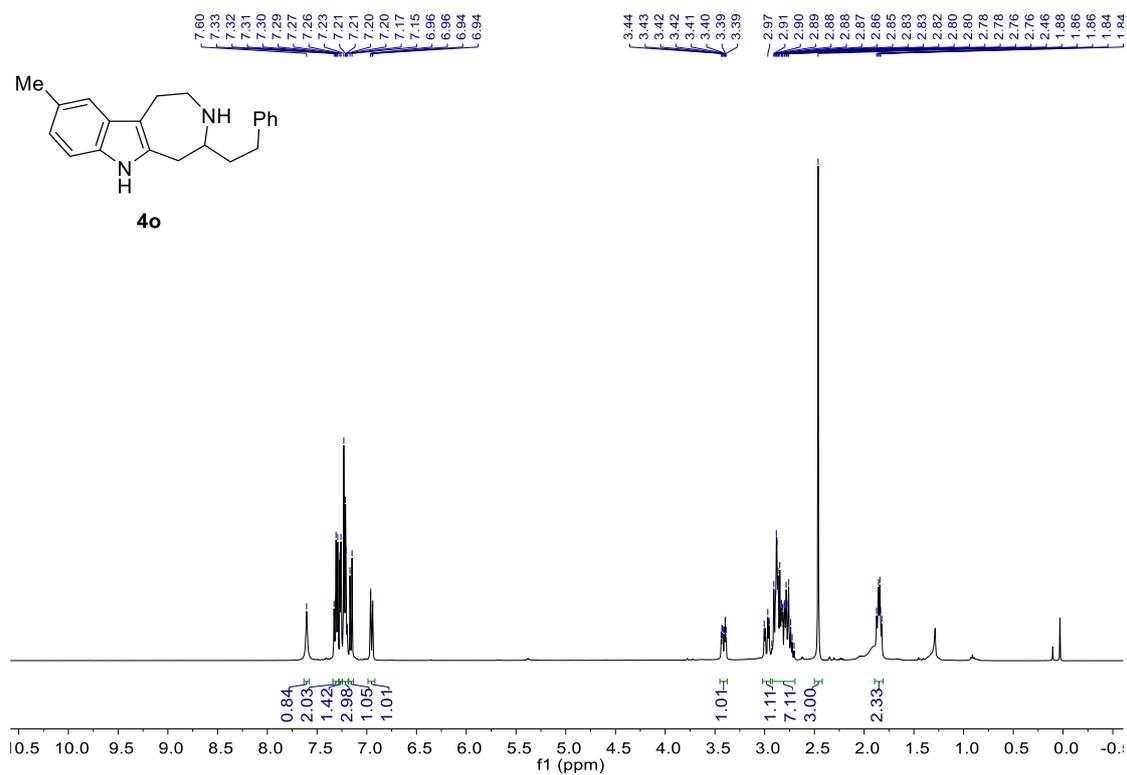
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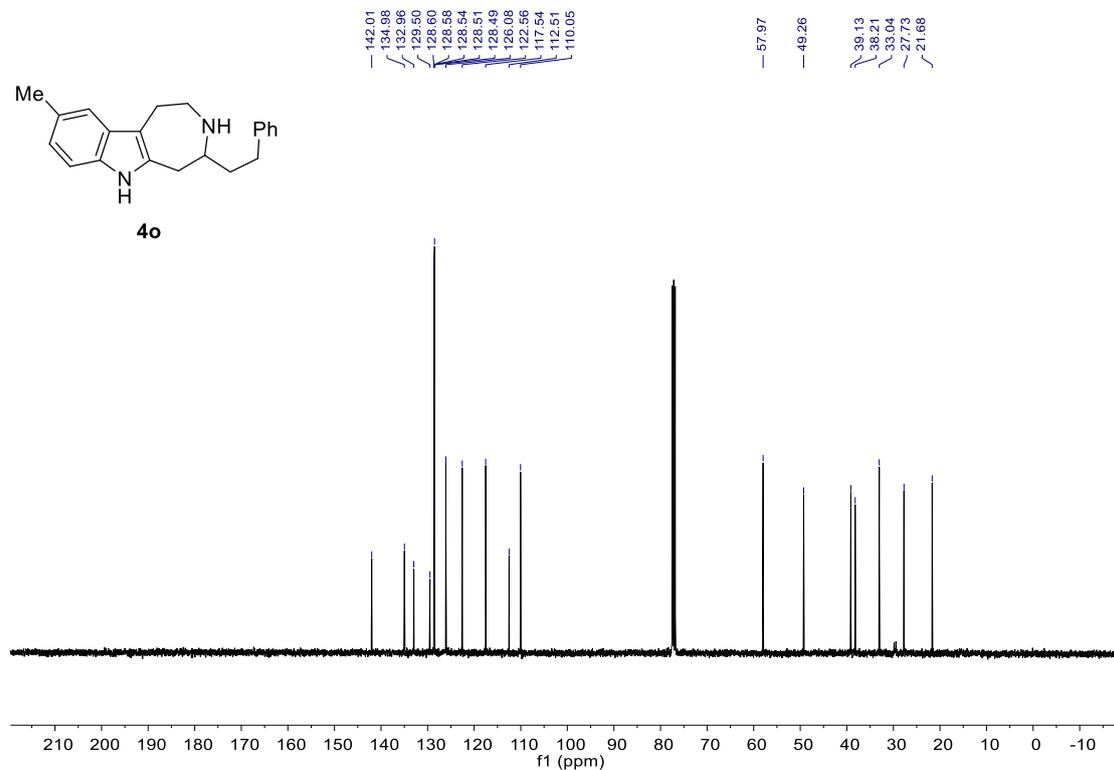
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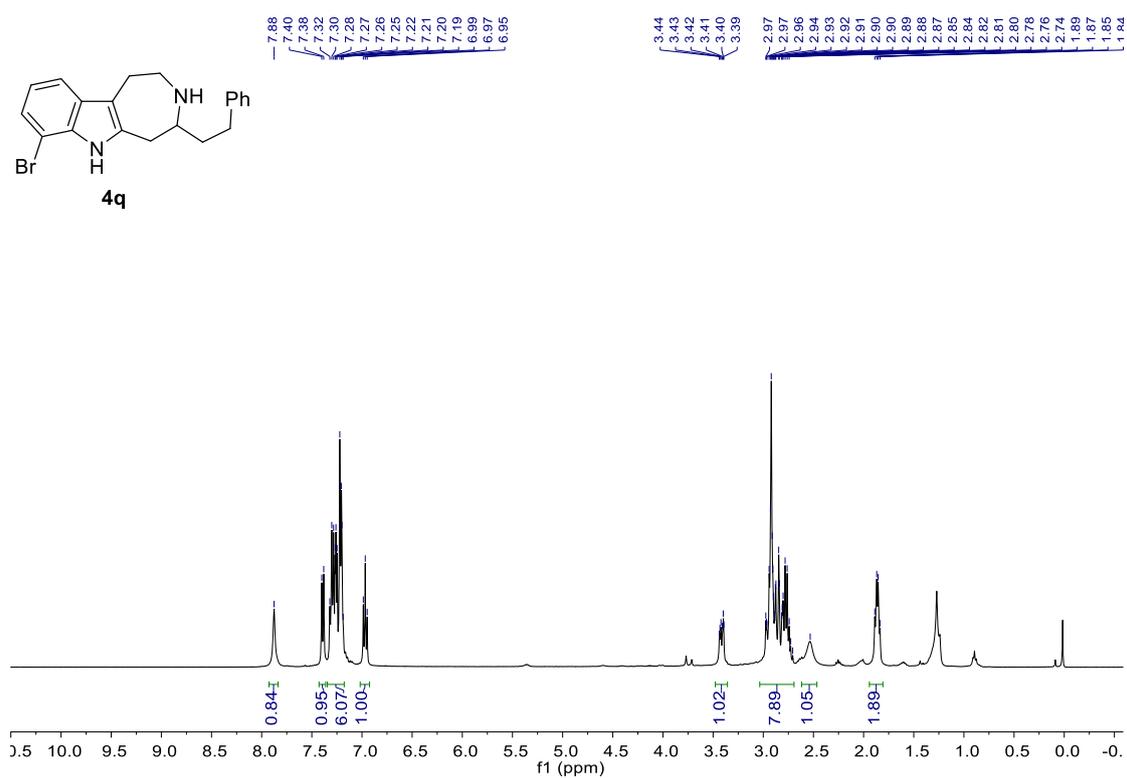
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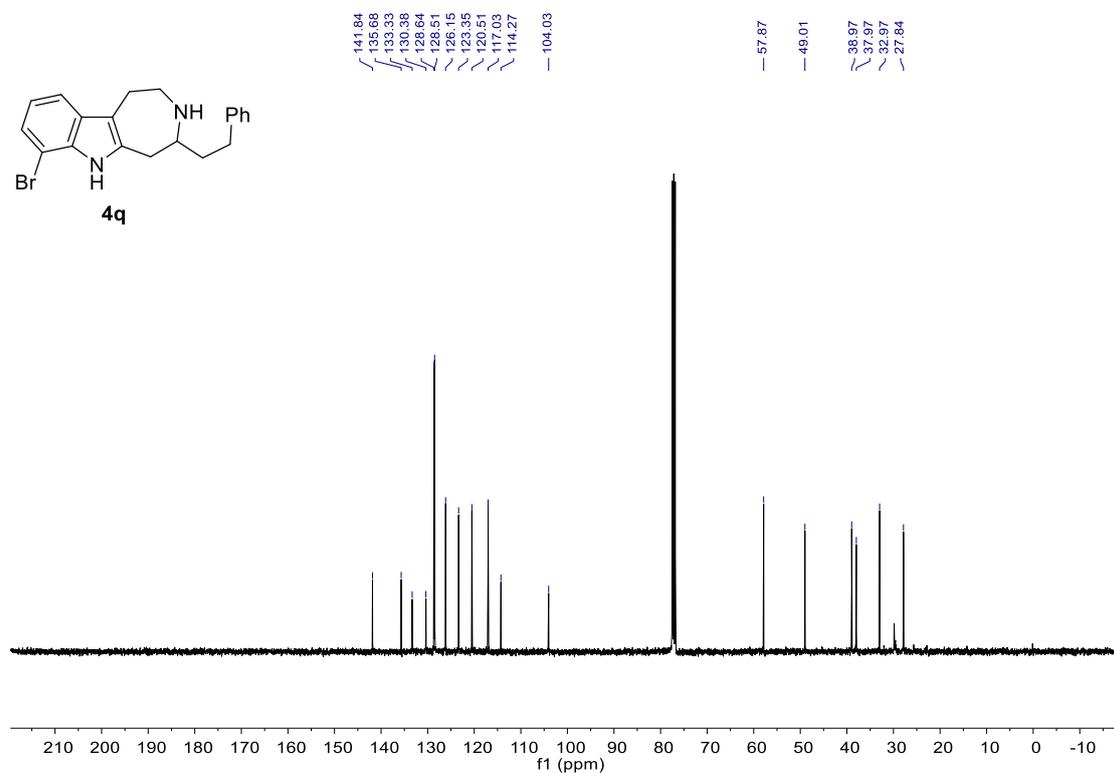
¹³C NMR (100 MHz, CDCl₃, compound 4o)



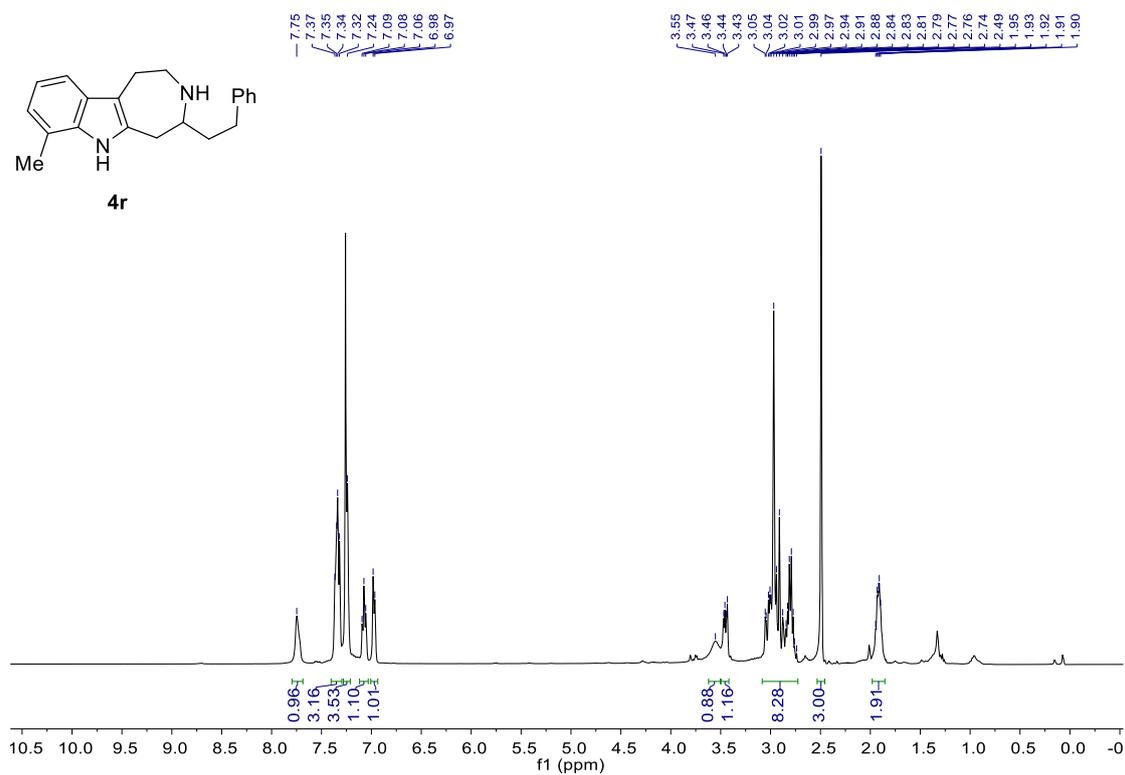
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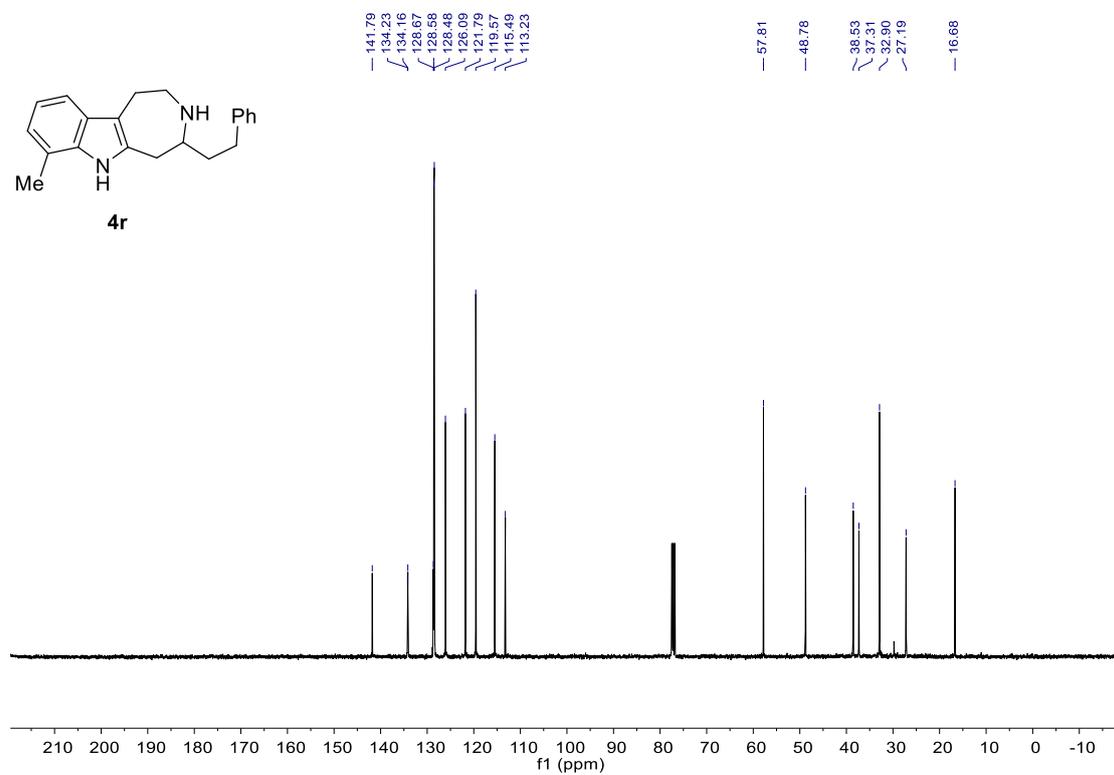
¹³C NMR (100 MHz, CDCl₃, compound 4q)



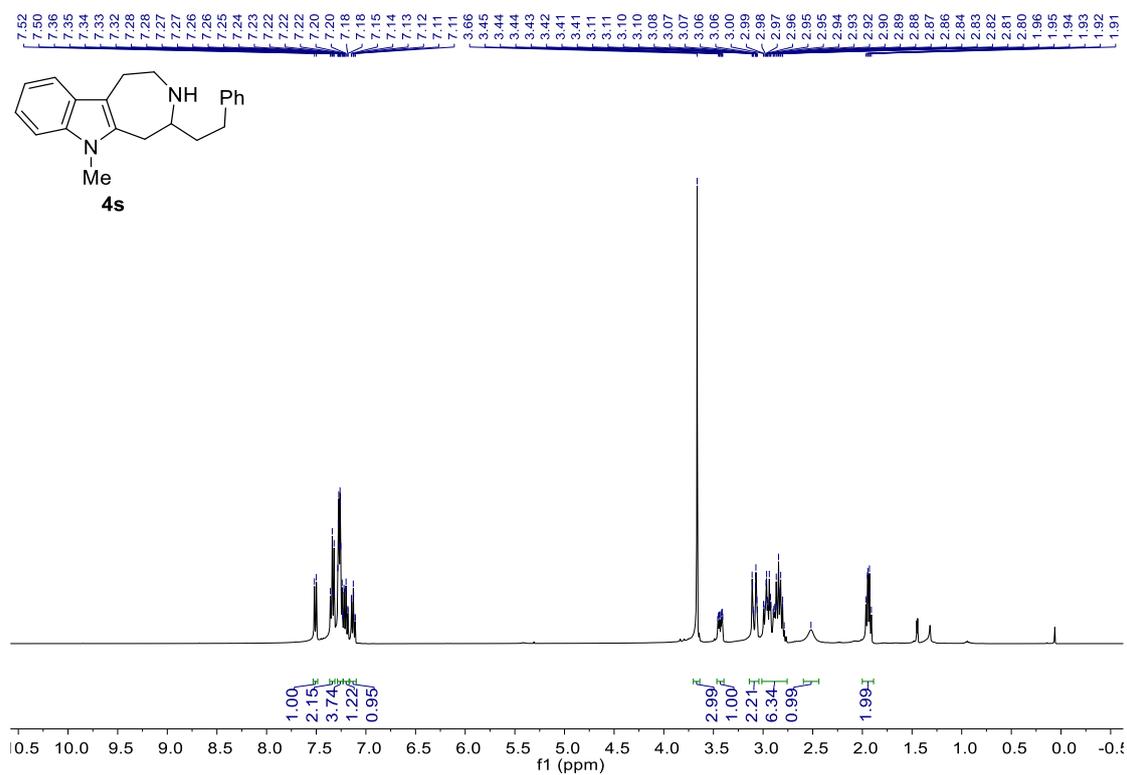
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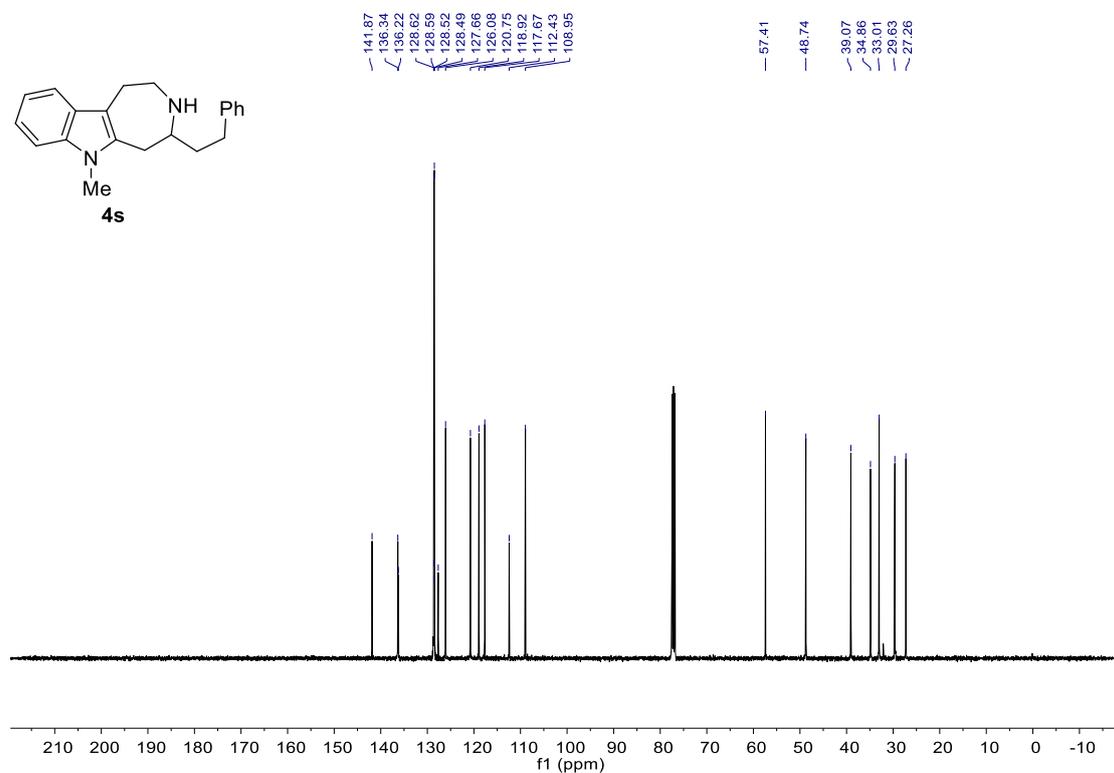
¹³C NMR (100 MHz, CDCl₃, compound **4r**)



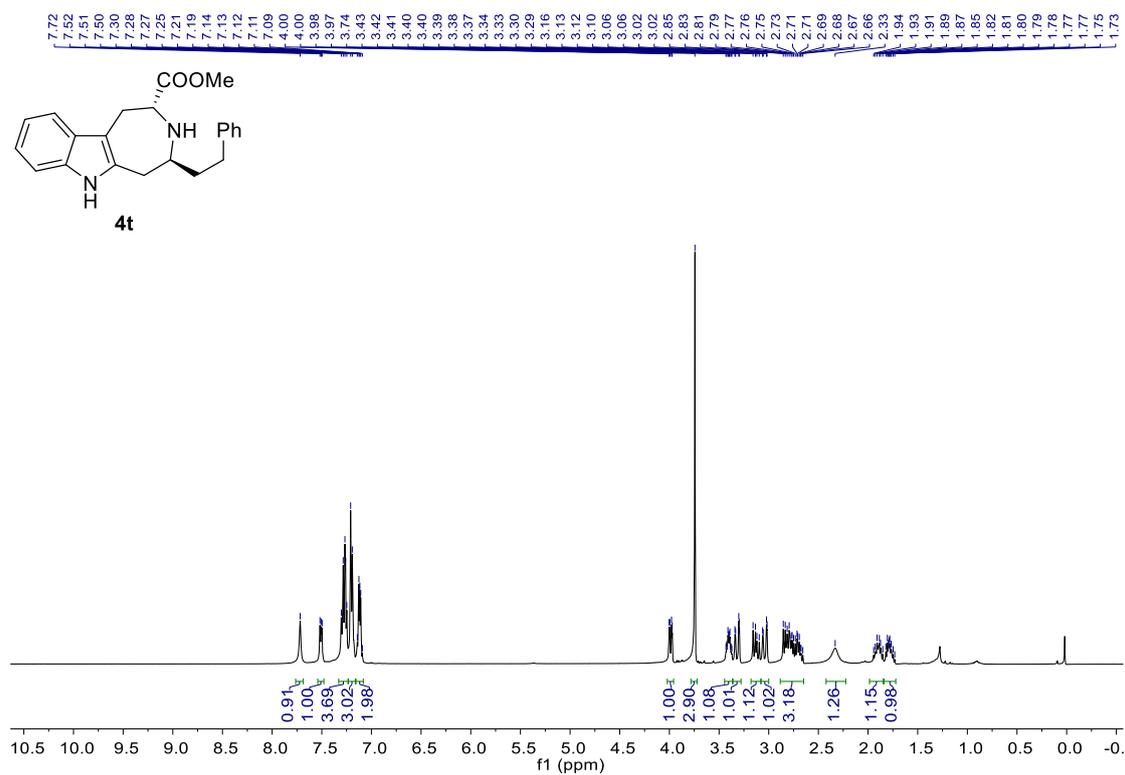
¹H NMR (400 MHz, CDCl₃, compound 4s)



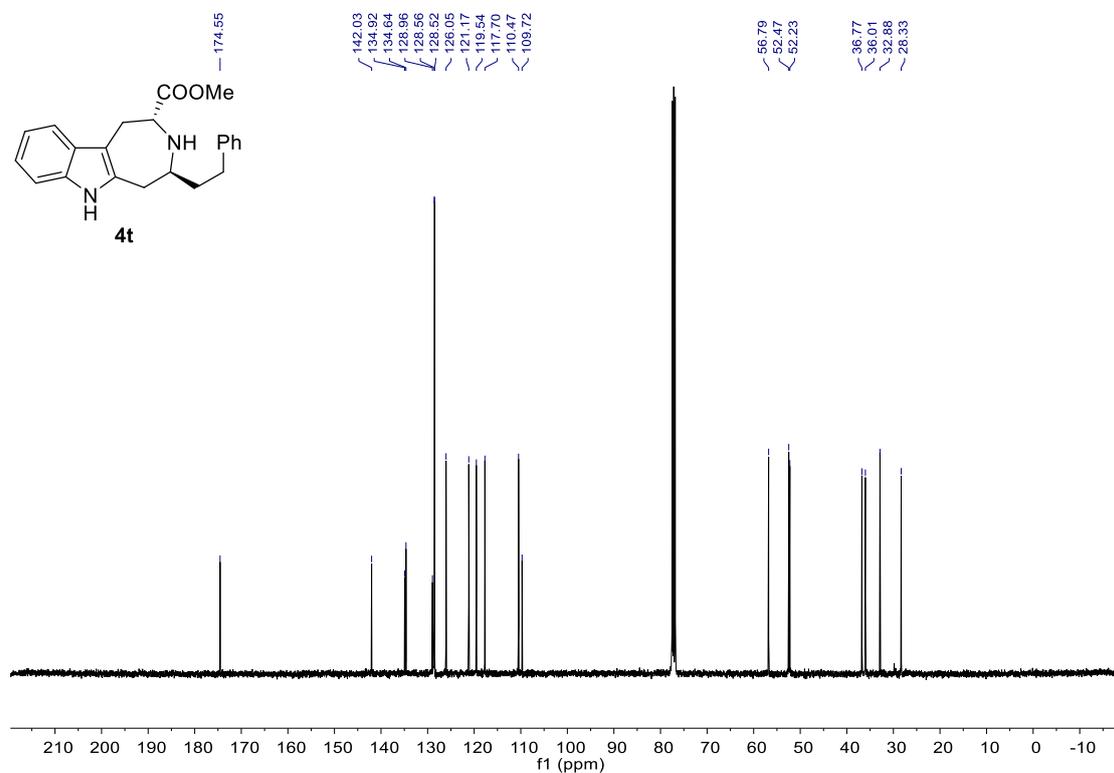
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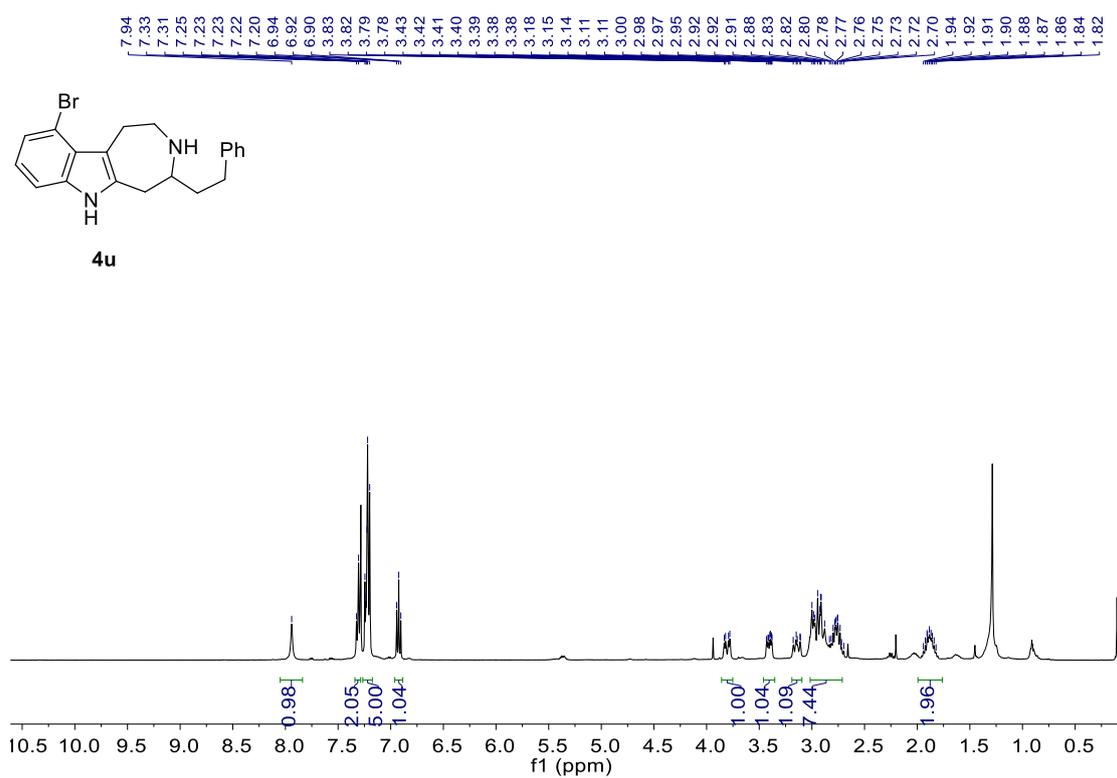
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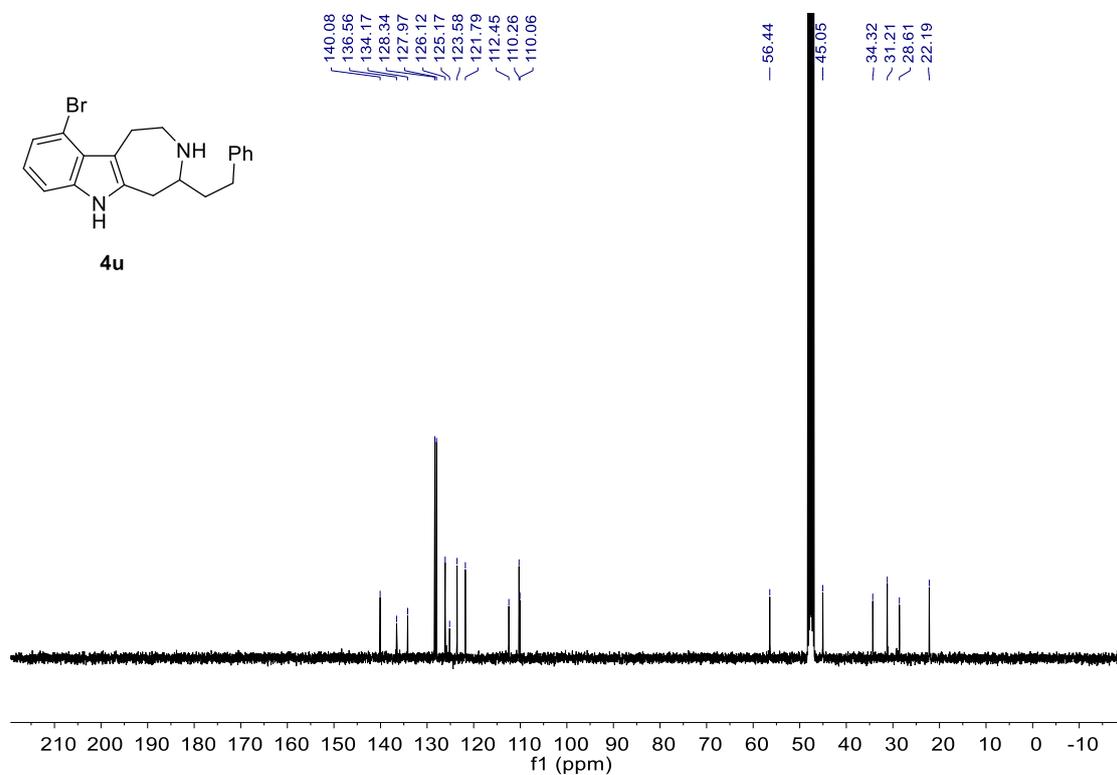
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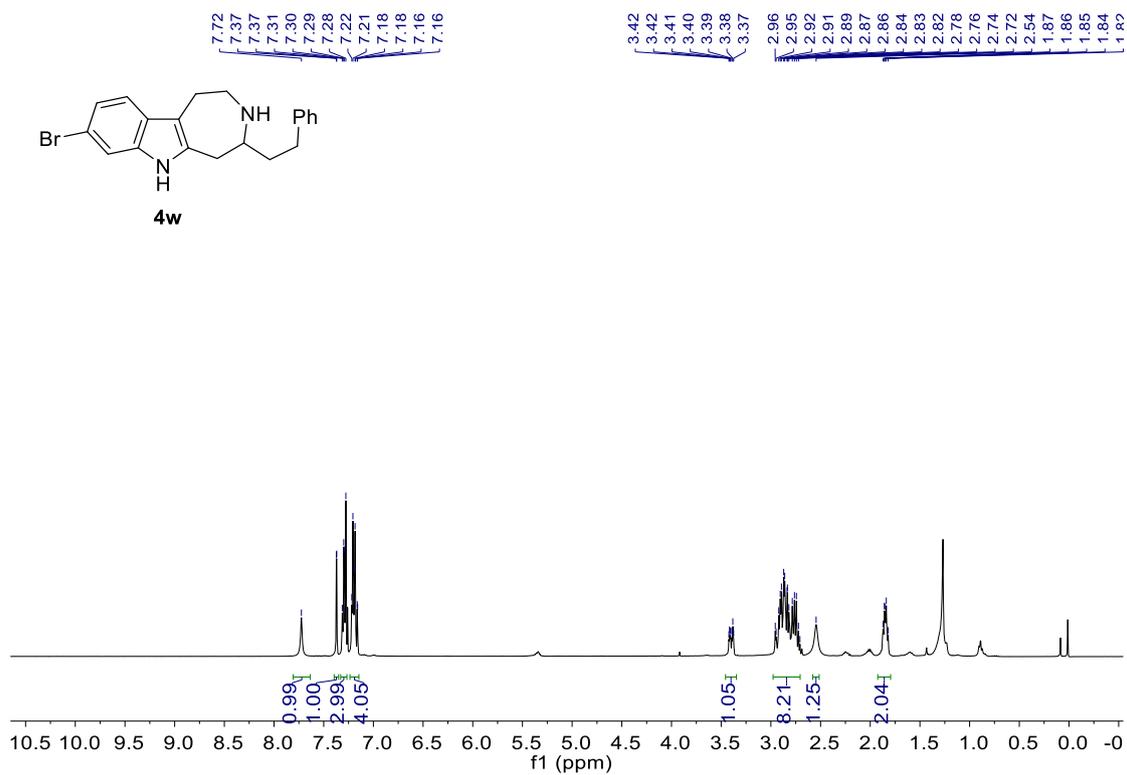
¹H NMR (400 MHz, CDCl₃, compound 4u)



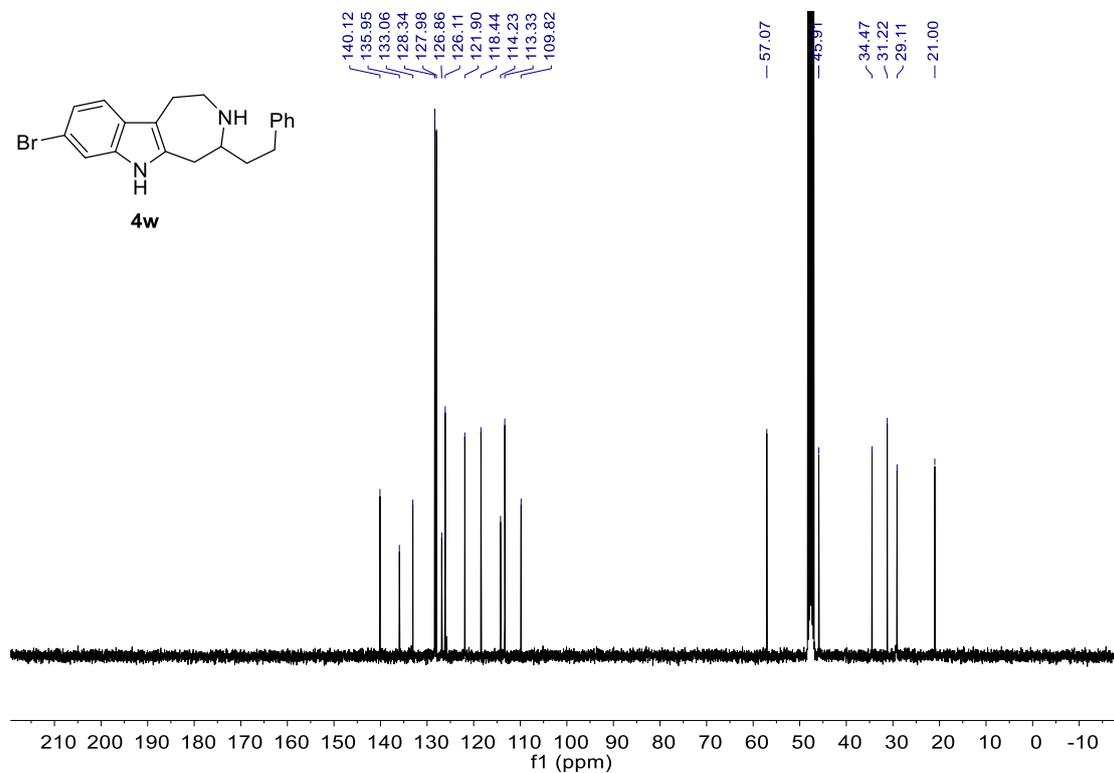
¹³C NMR (100 MHz, Methanol-d₄, compound 4u)



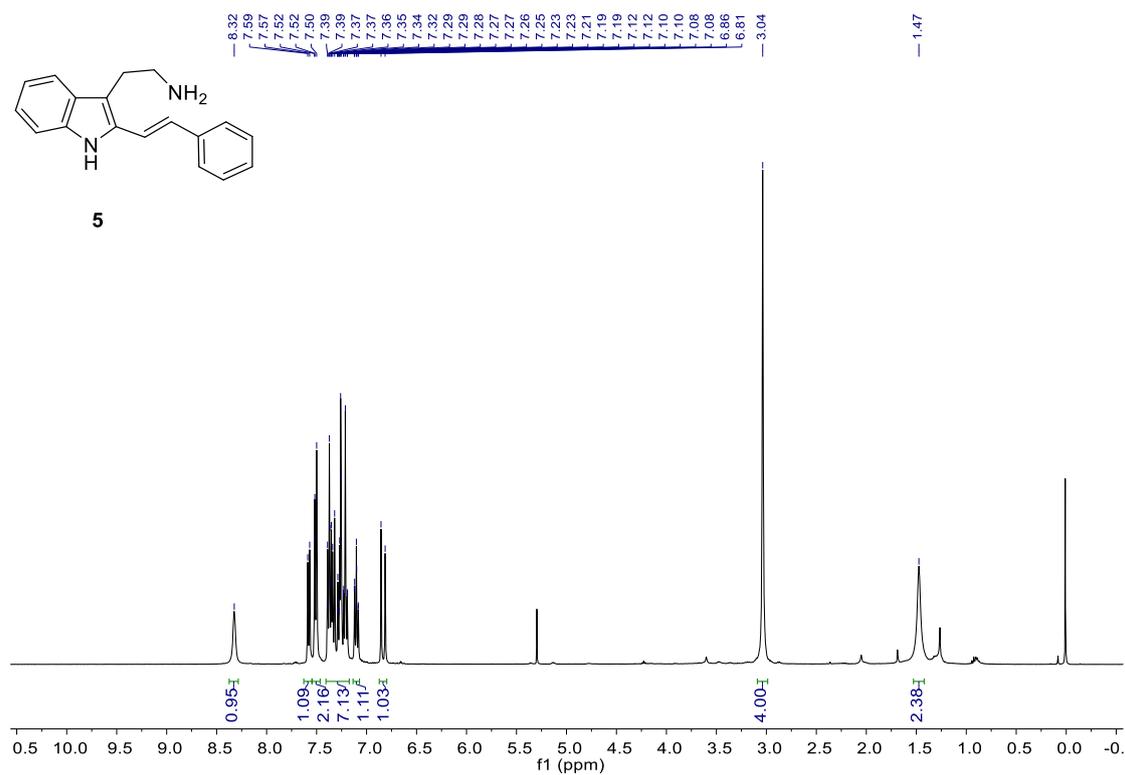
^1H NMR (400 MHz, CDCl_3 , compound **4w)**



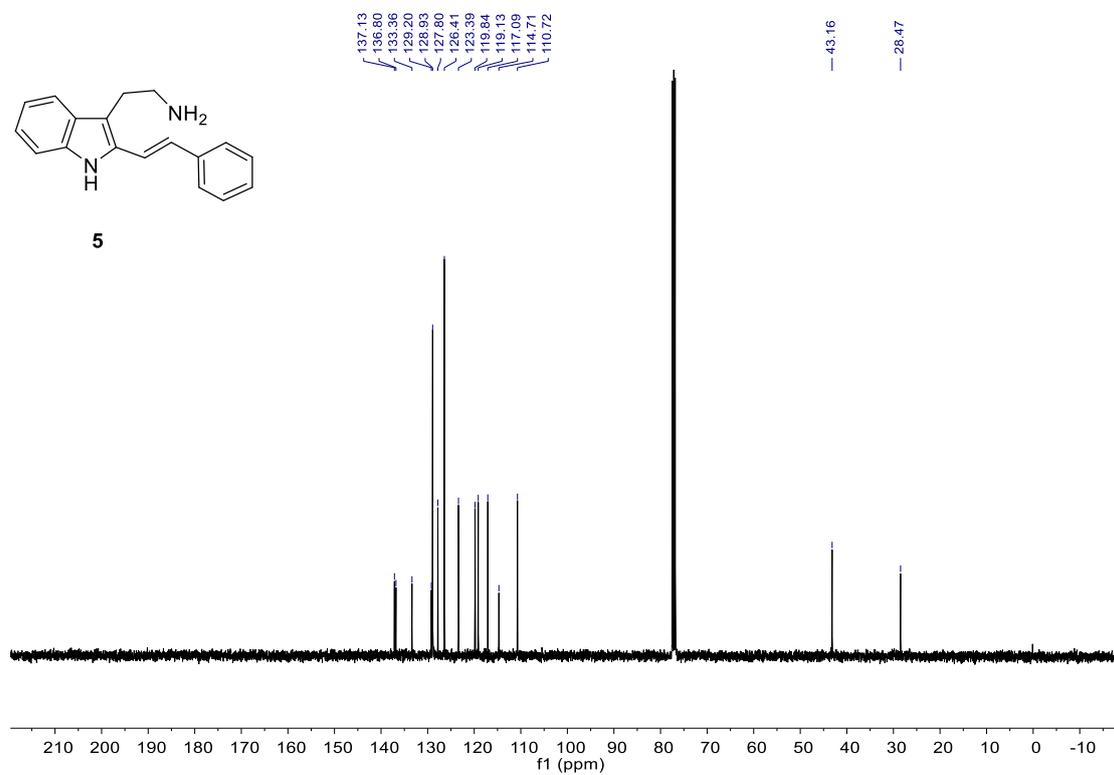
^{13}C NMR (100 MHz, $\text{Methanol-}d_4$, compound **4w)**



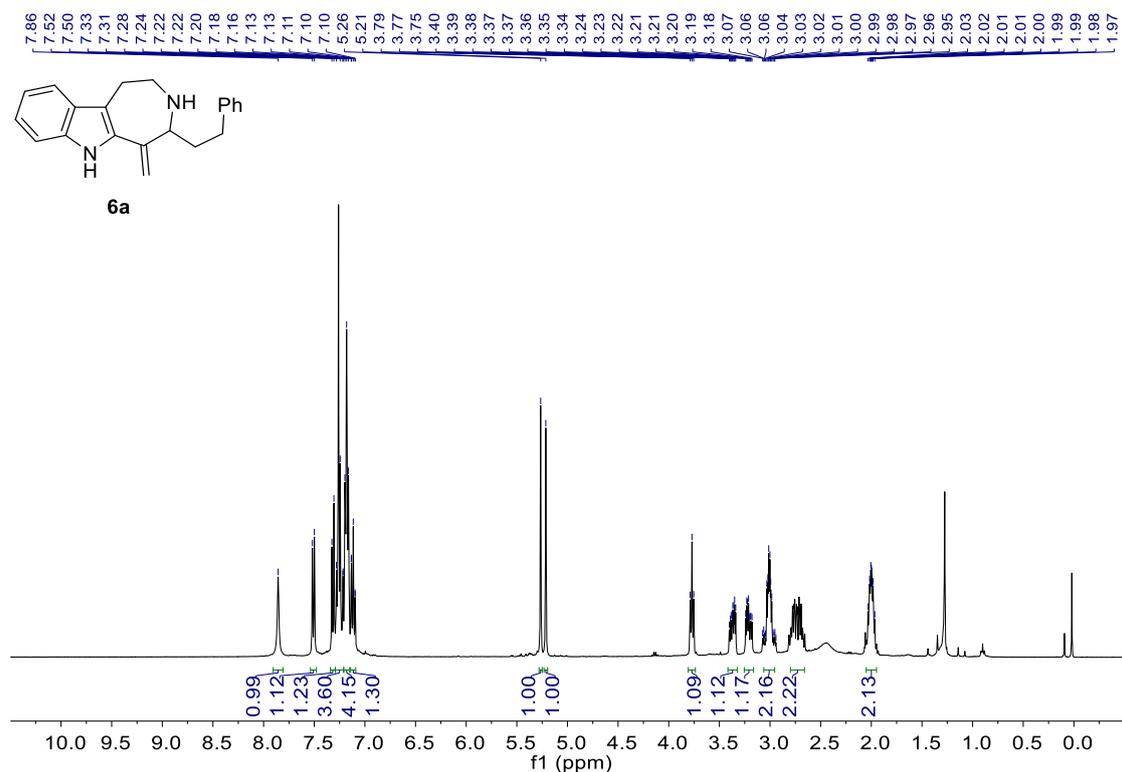
¹H NMR (400 MHz, CDCl₃, compound 5)



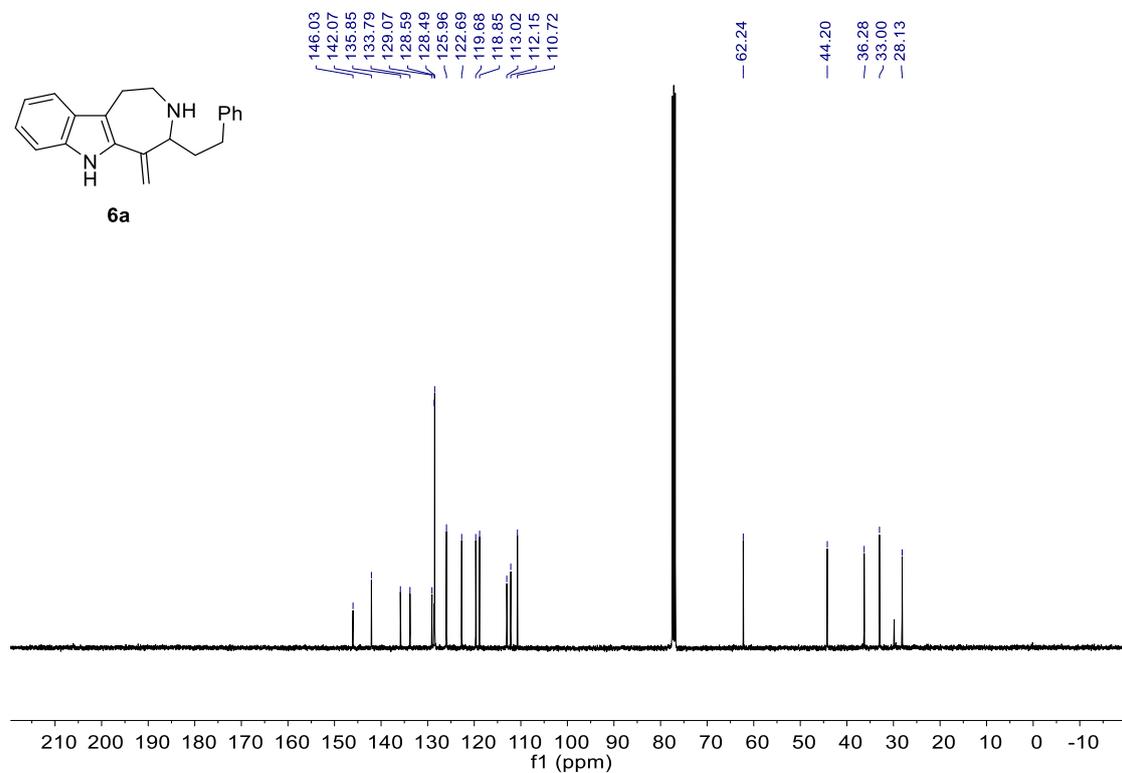
¹³C NMR (100 MHz, CDCl₃, compound 5)



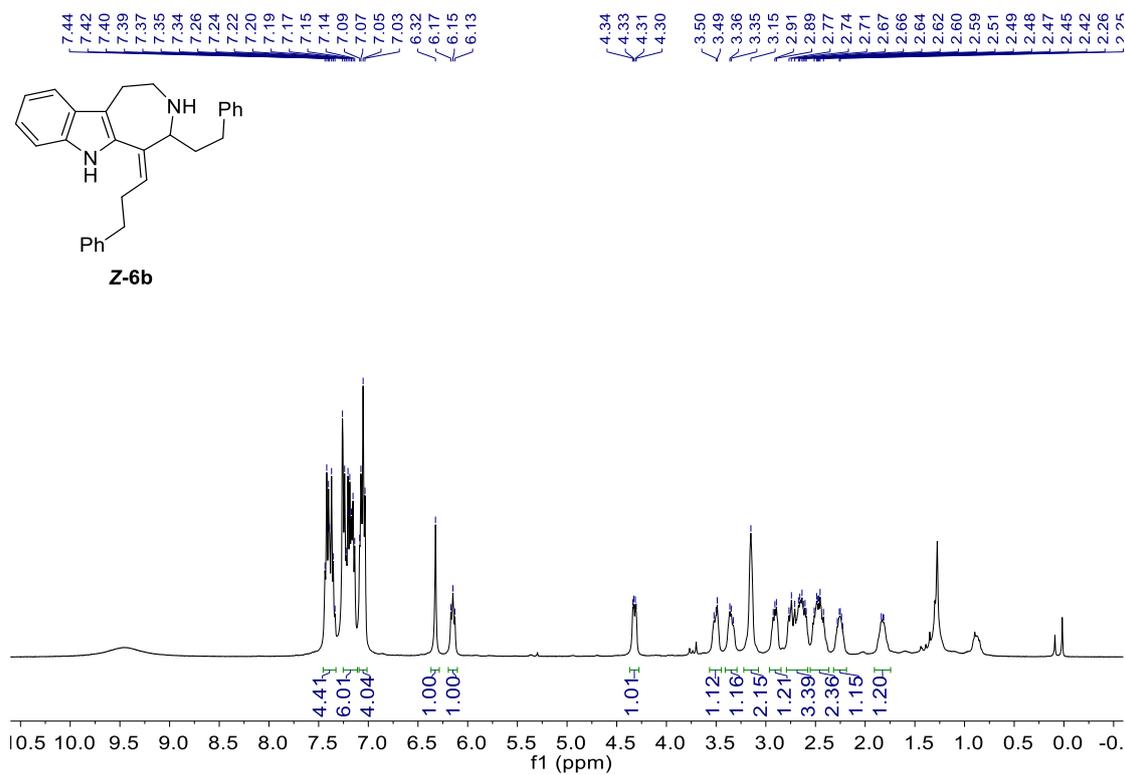
¹H NMR (400 MHz, CDCl₃, compound **6a**)



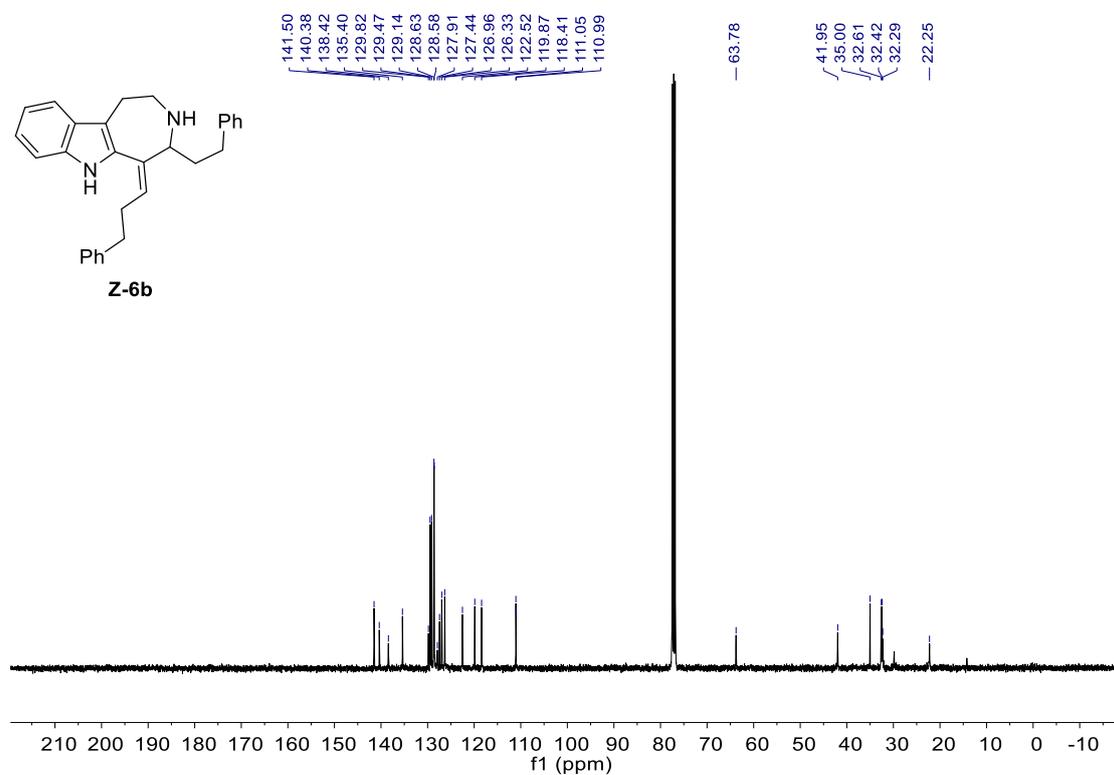
¹³C NMR (100 MHz, CDCl₃, compound **6a**)



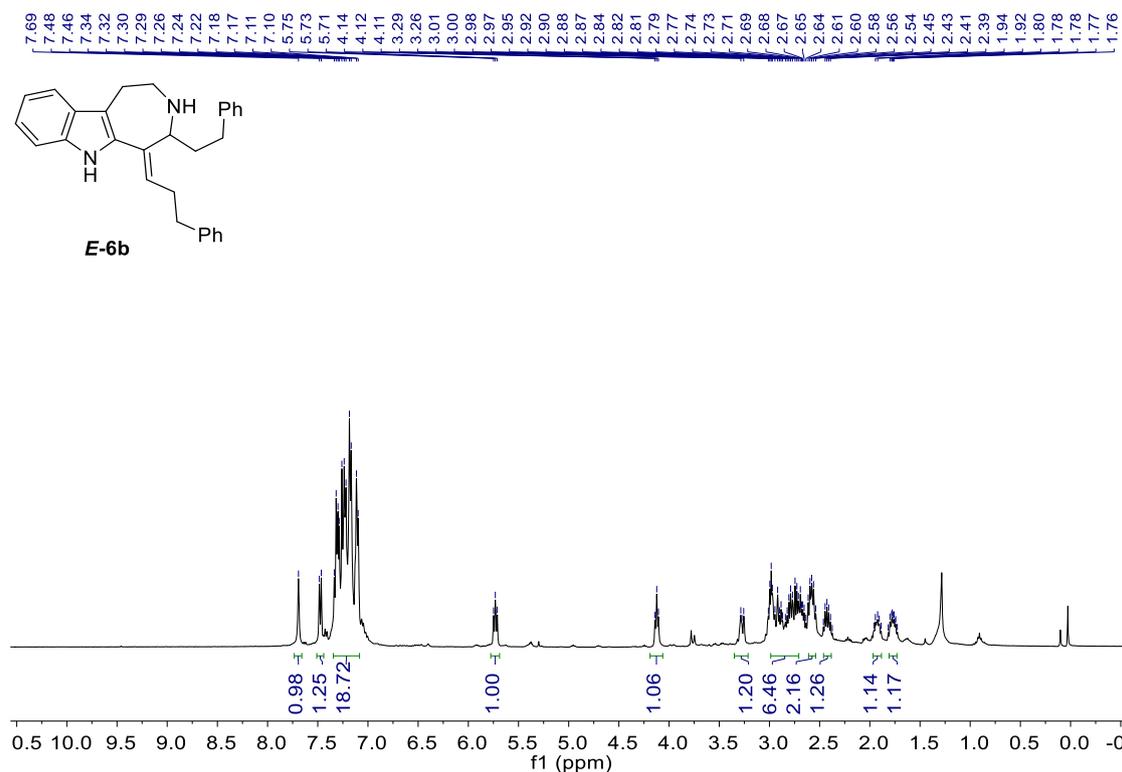
¹H NMR (400 MHz, CDCl₃, compound Z-6b)



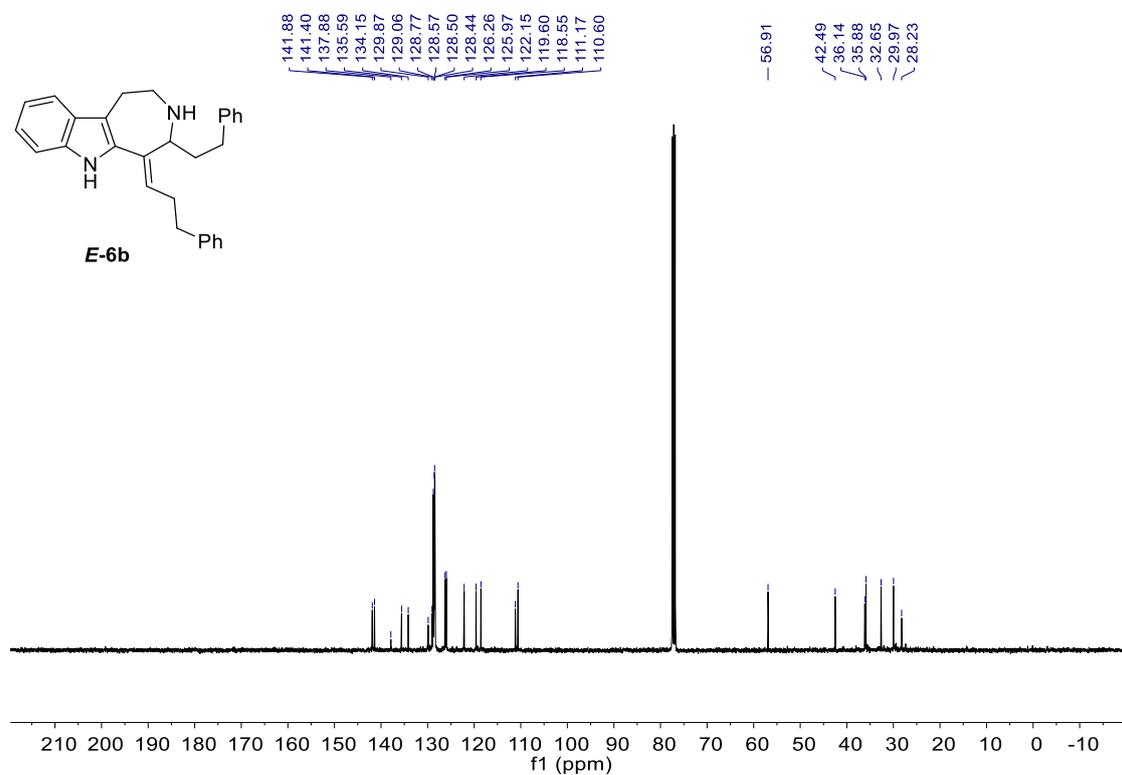
¹³C NMR (100 MHz, CDCl₃, compound Z-6b)



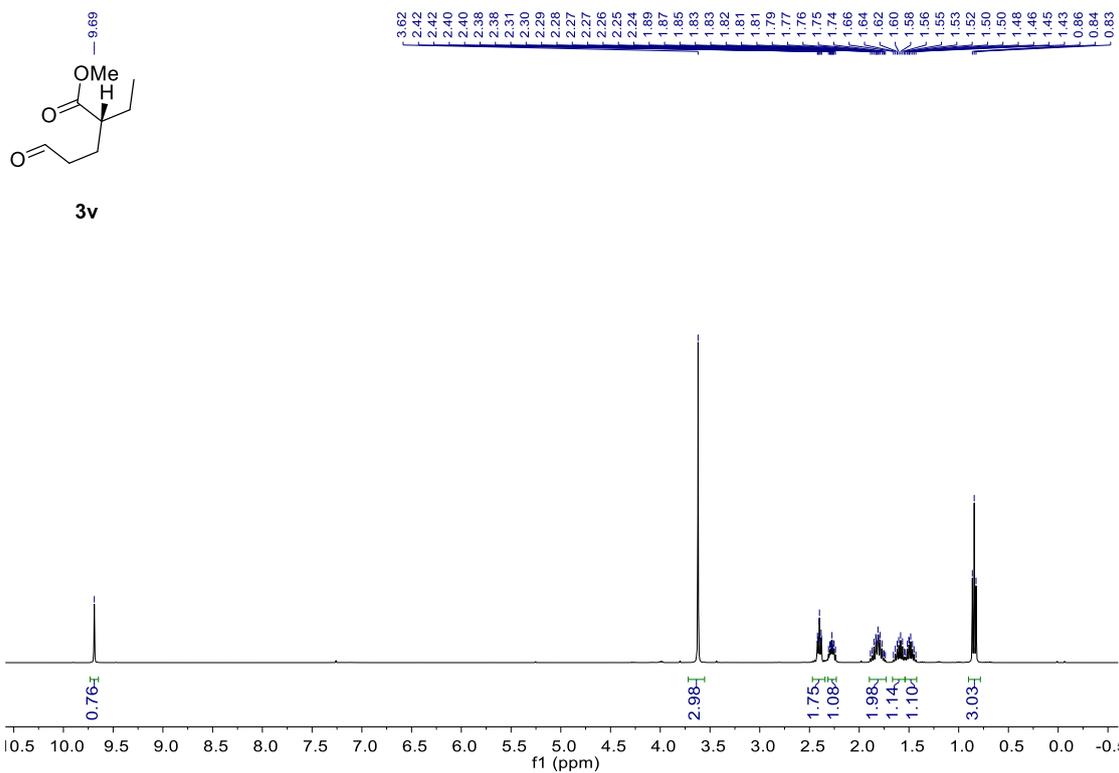
¹H NMR (400 MHz, CDCl₃, compound *E-6b*)



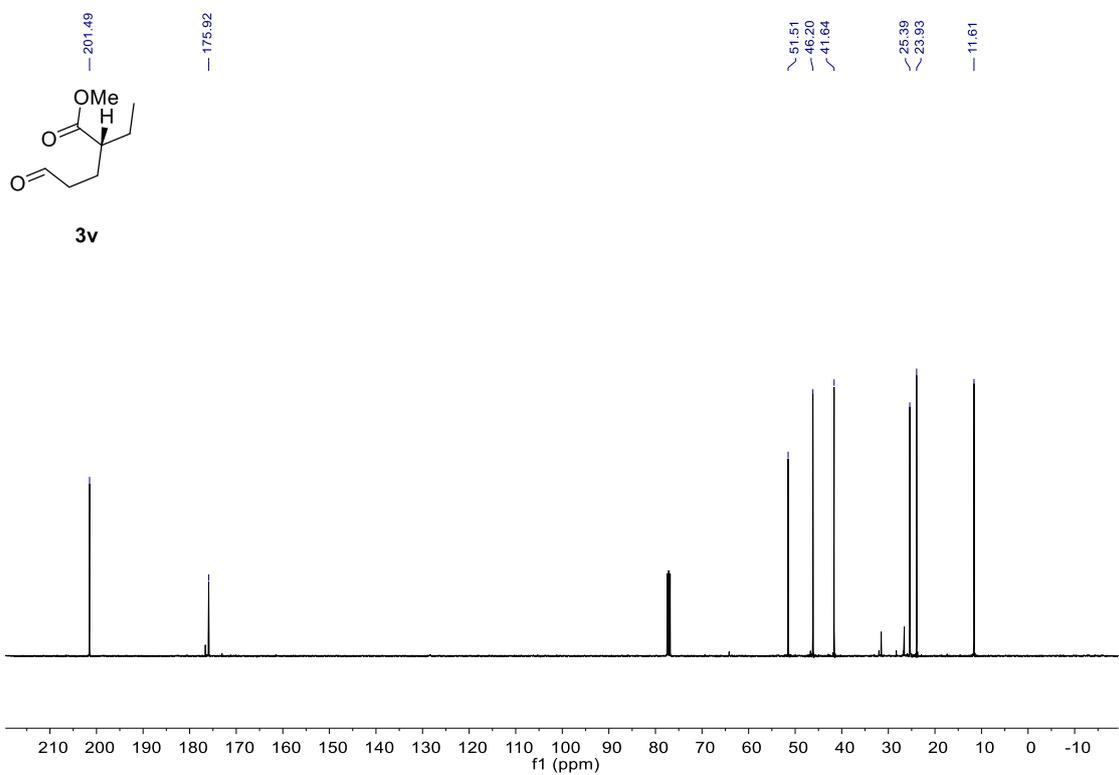
¹³C NMR (100 MHz, CDCl₃, compound *E-6b*)



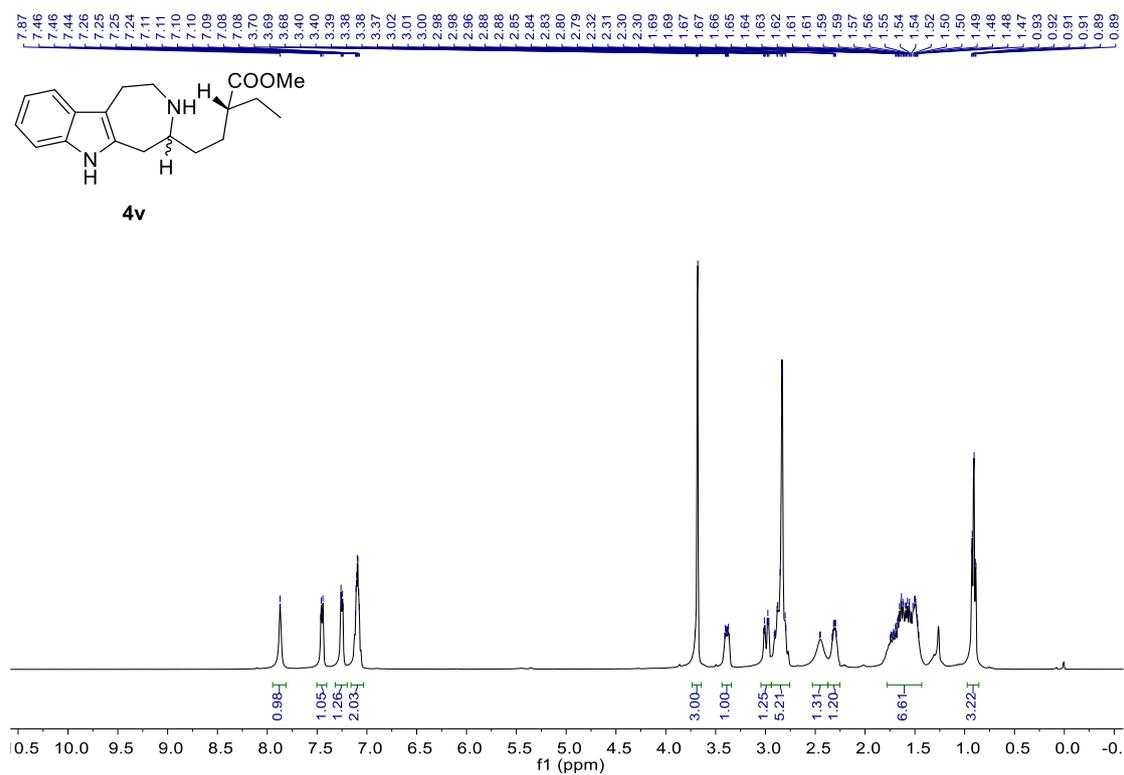
¹H NMR (400 MHz, CDCl₃, compound **3v**)



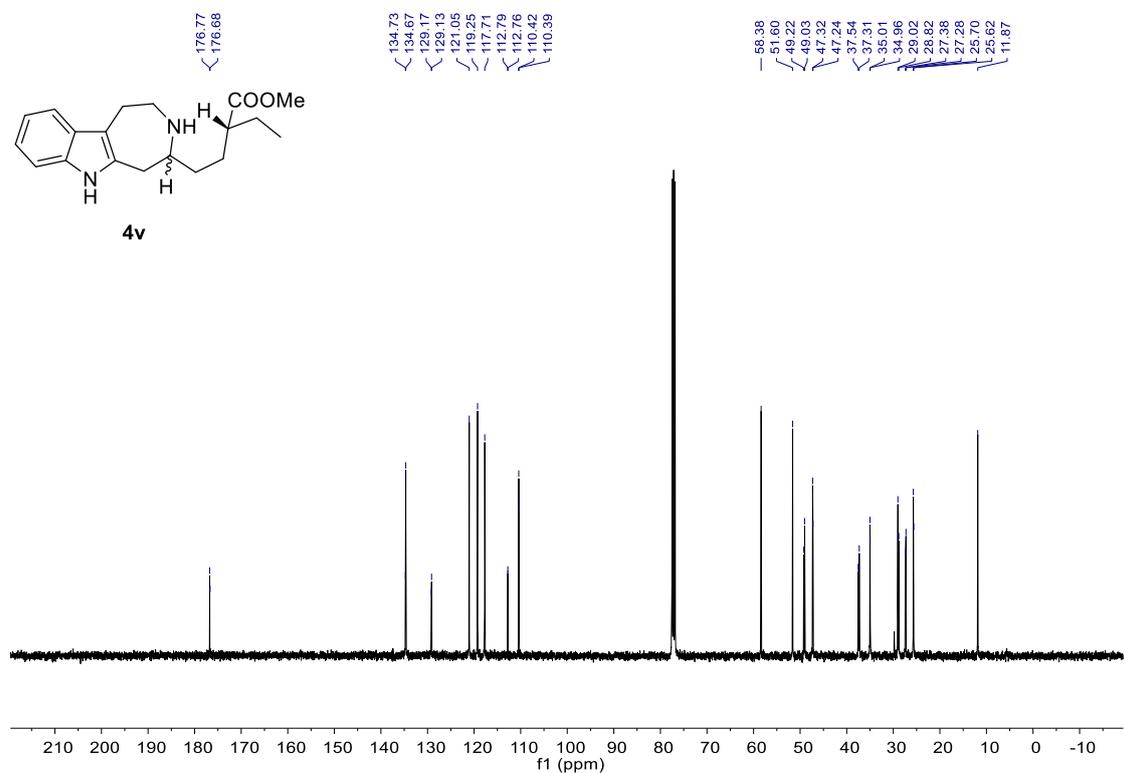
¹³C NMR (100 MHz, CDCl₃, compound **3v**)



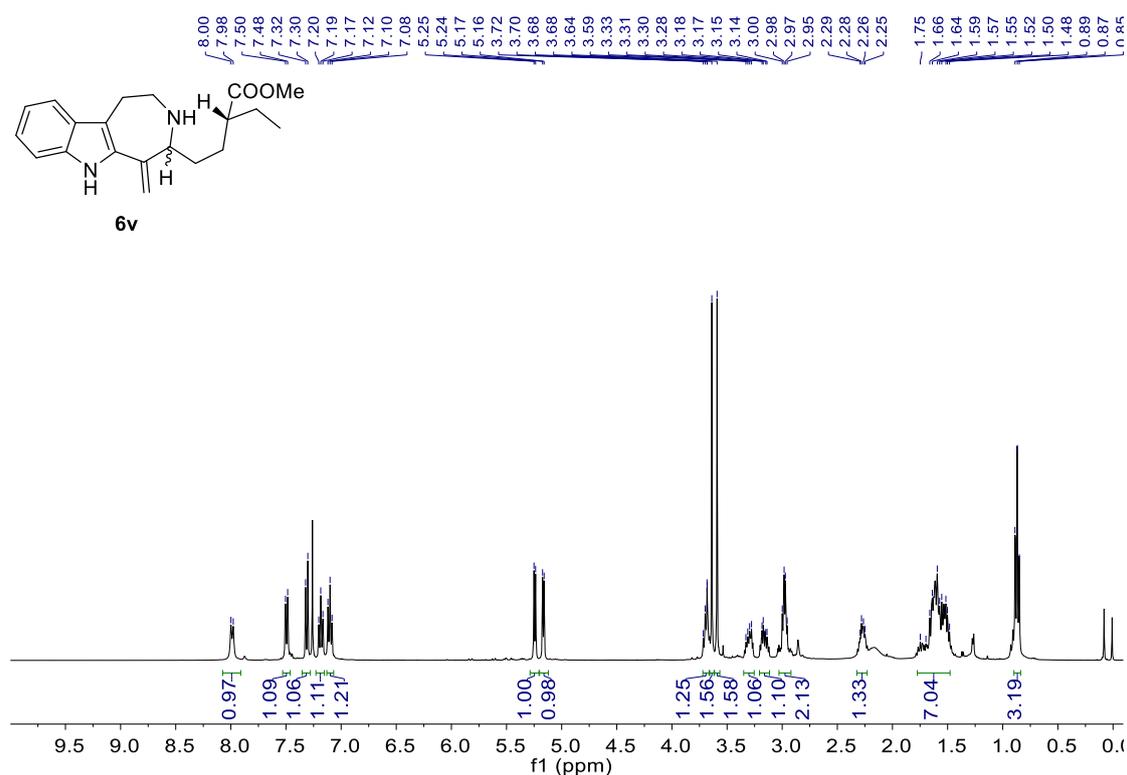
¹H NMR (400 MHz, CDCl₃, compound **4v**, mixture of diastereomers)



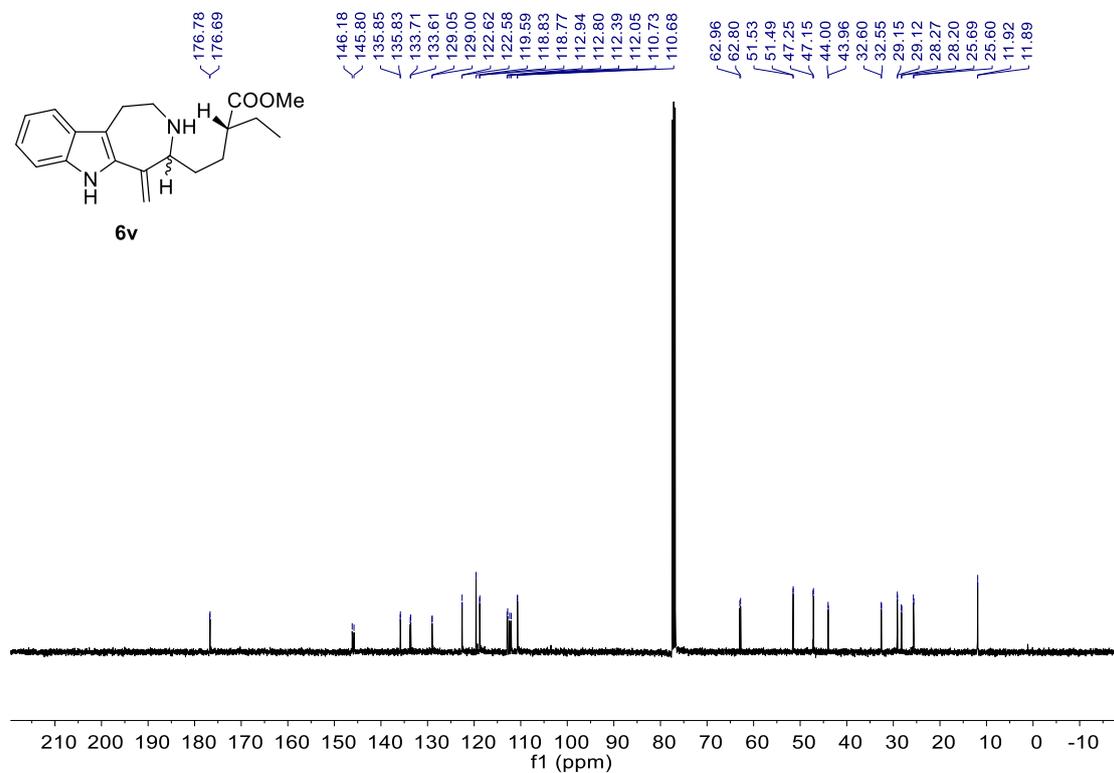
¹³C NMR (100 MHz, CDCl₃, compound **4v**, mixture of diastereomers)



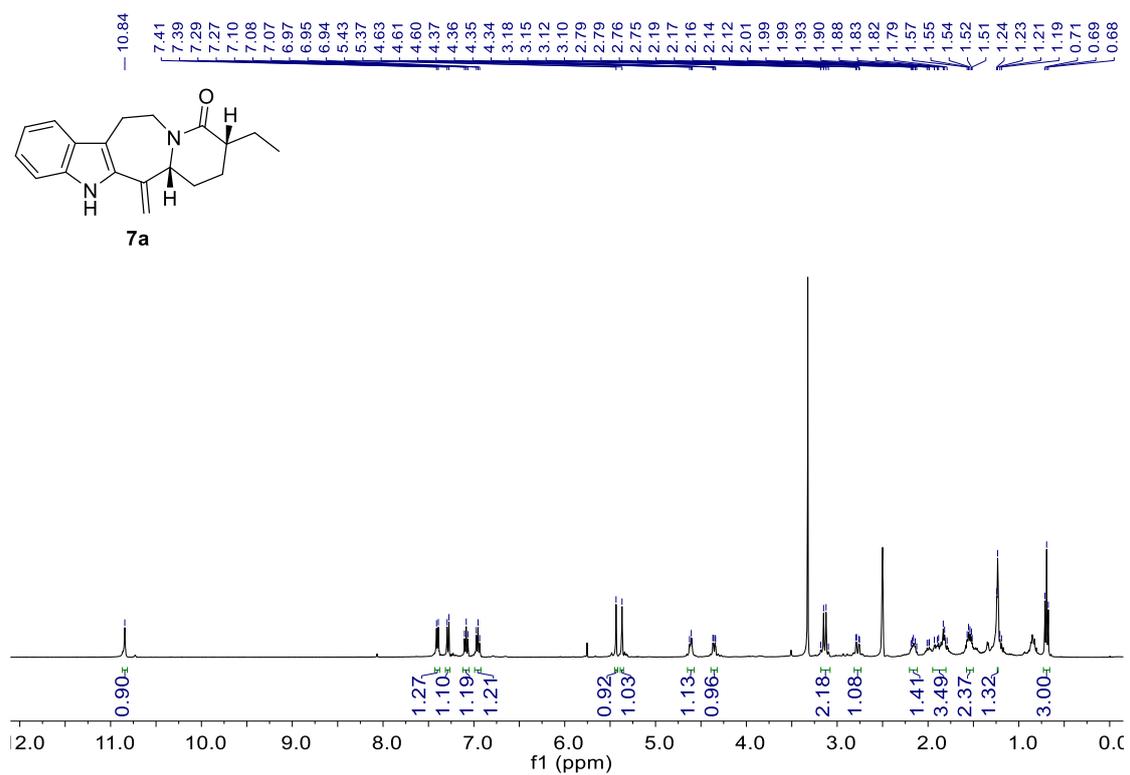
¹H NMR (400 MHz, CDCl₃, compound **6v**, mixture of diastereomers)



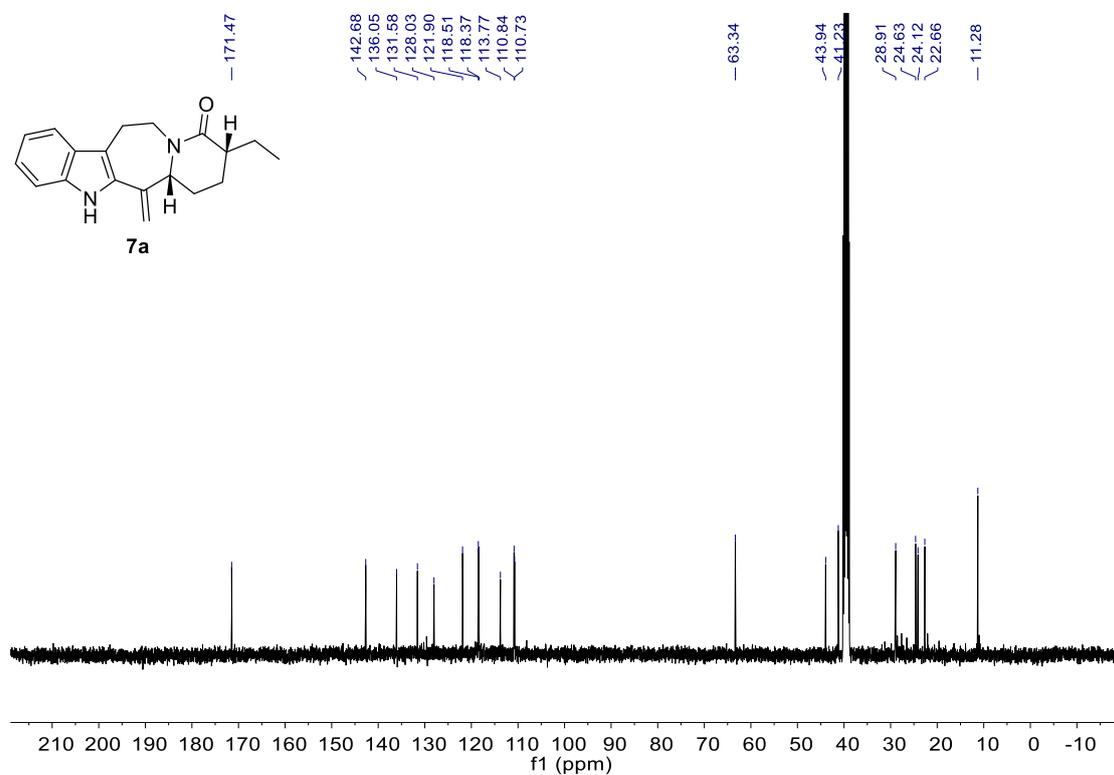
¹³C NMR (100 MHz, CDCl₃, compound **6v**, mixture of diastereomers)



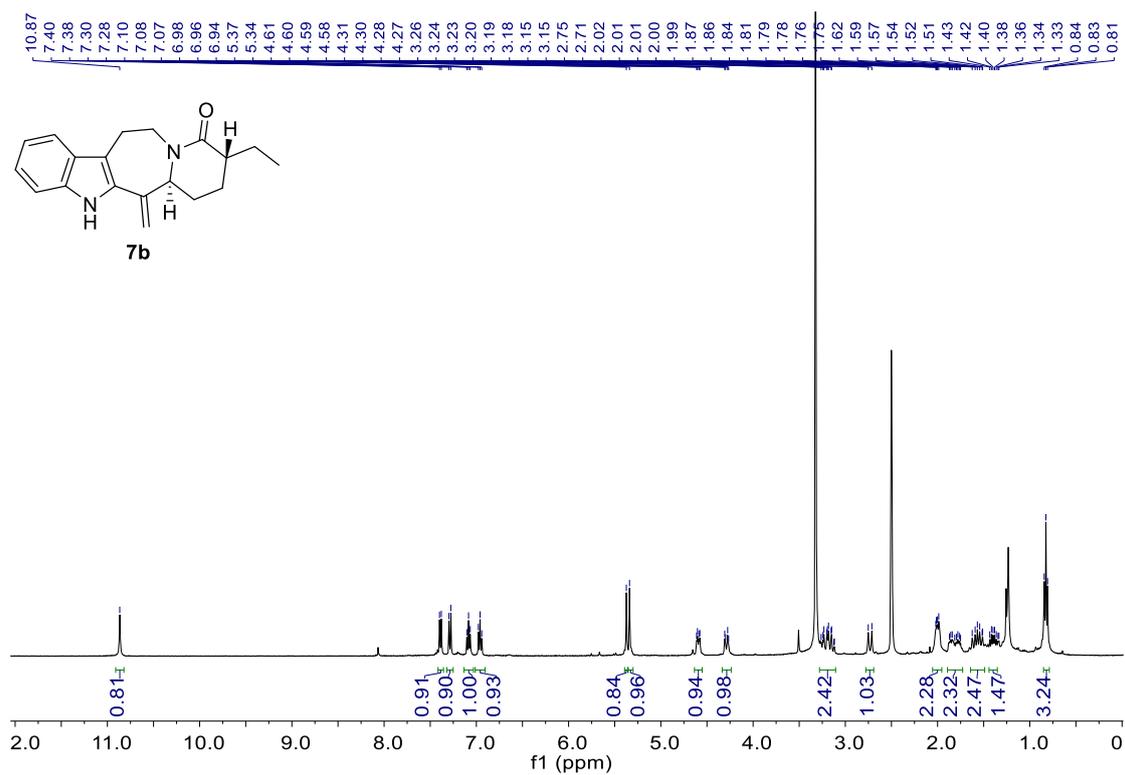
¹H NMR (400 MHz, DMSO-*d*₆, compound 7a)



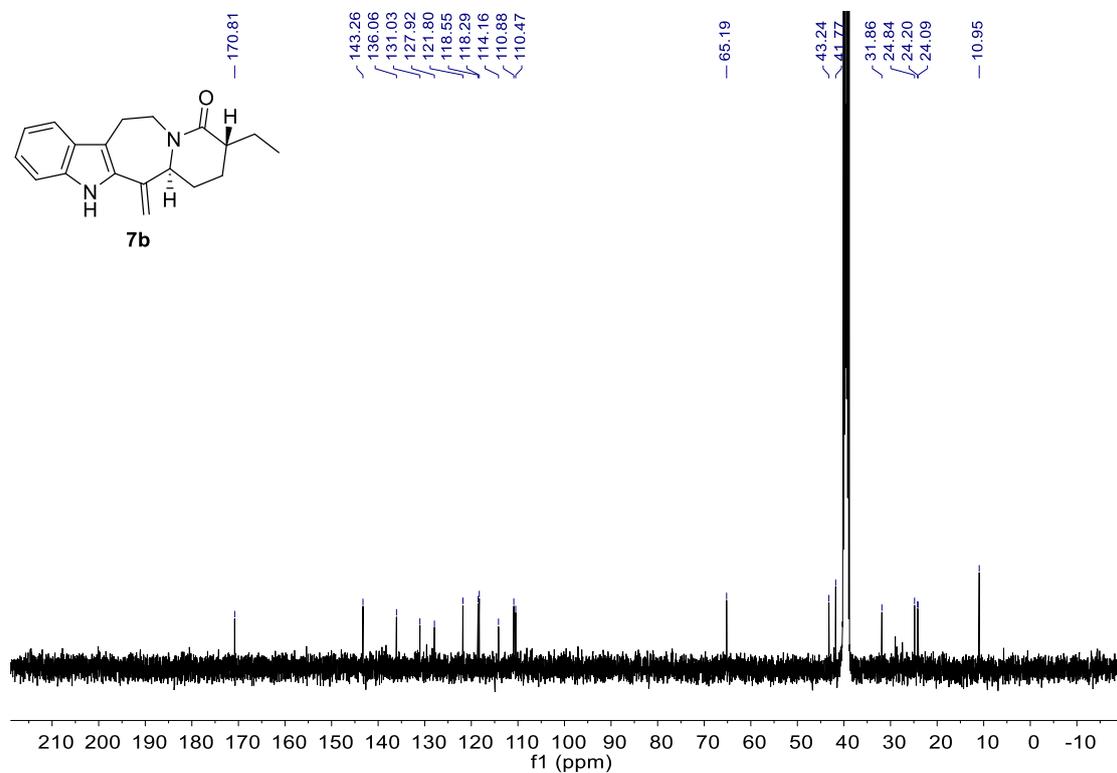
¹³C NMR (100 MHz, DMSO-*d*₆, compound 7a)



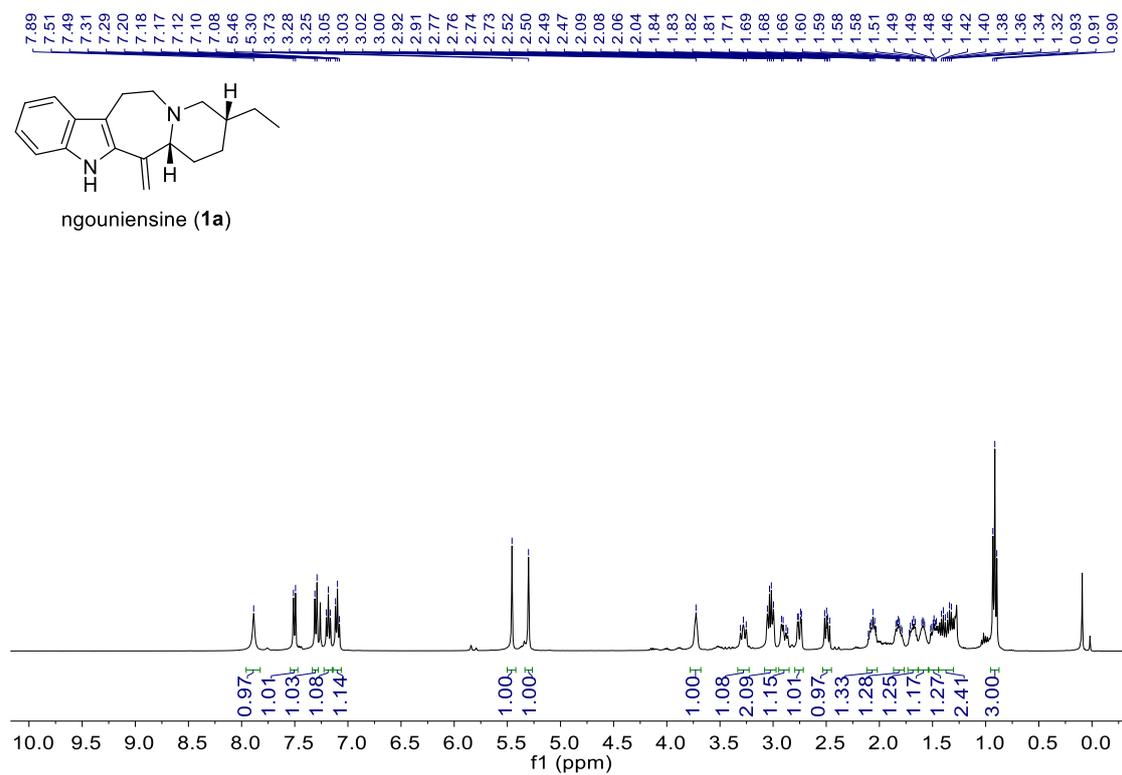
¹H NMR (400 MHz, DMSO-d₆, compound **7b**)



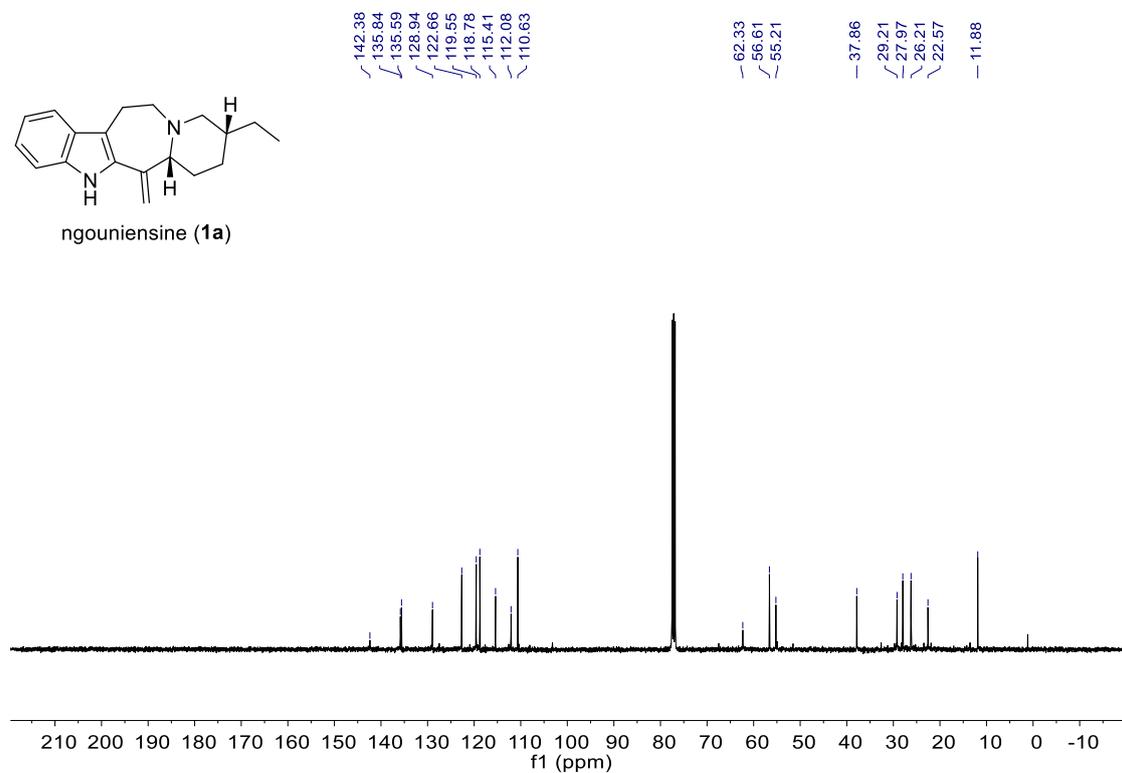
¹³C NMR (100 MHz, DMSO-d₆, compound **7b**)



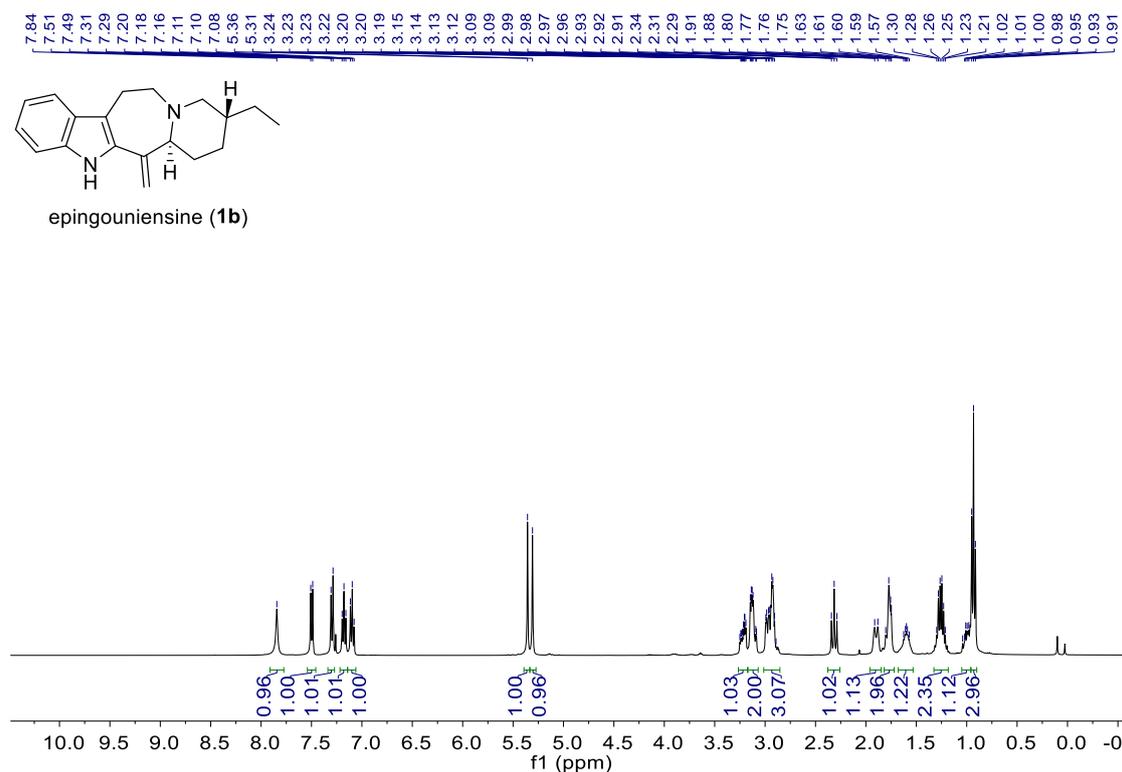
¹H NMR (400 MHz, CDCl₃, ngouniensine, **1a**)



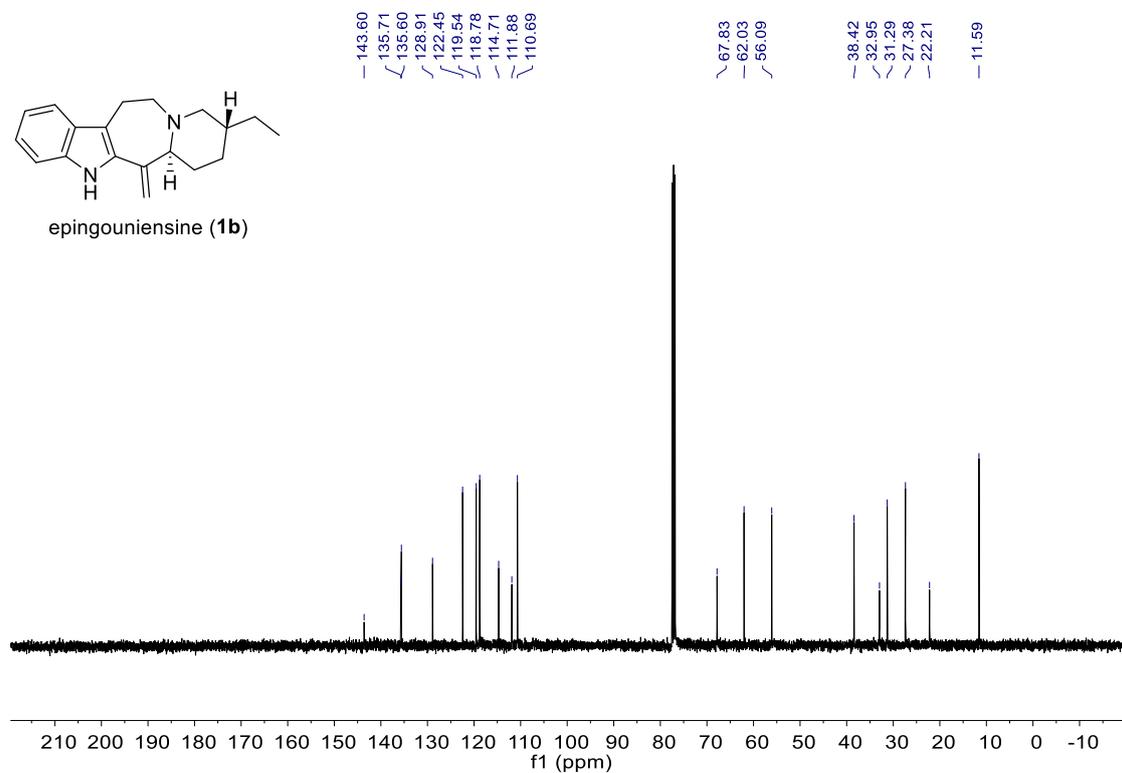
¹³C NMR (100 MHz, CDCl₃, ngouniensine, **1a**)



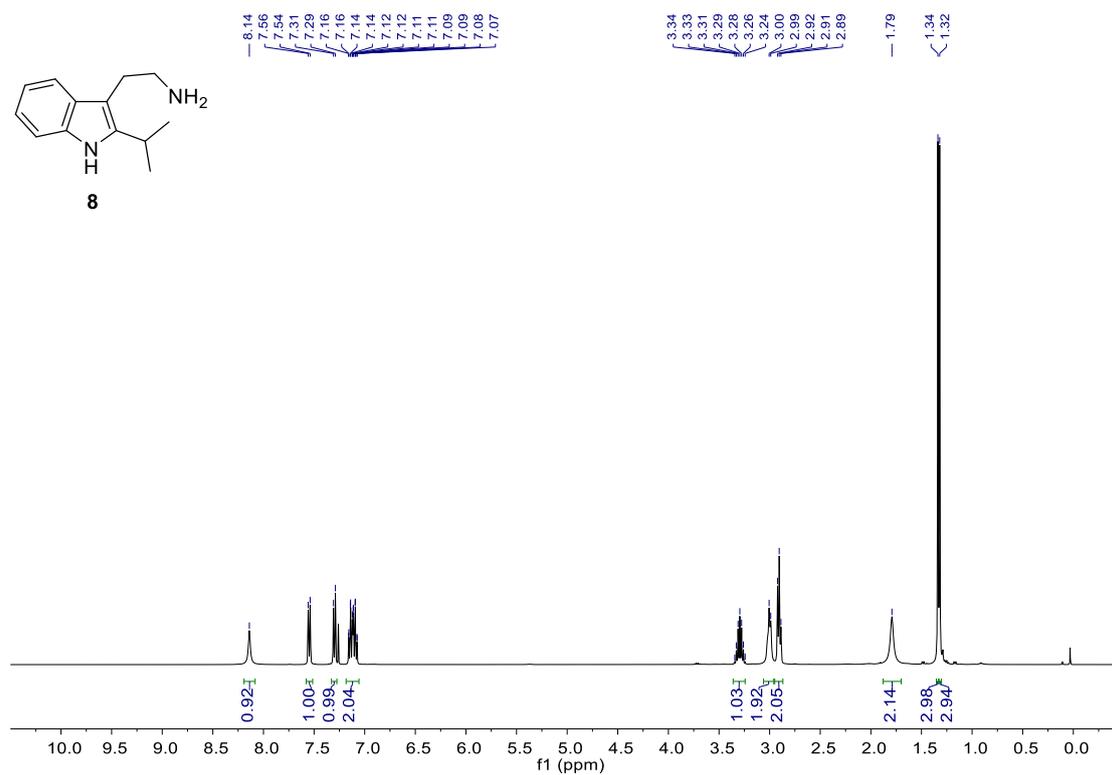
¹H NMR (400 MHz, CDCl₃, epingouniense, **1b**)



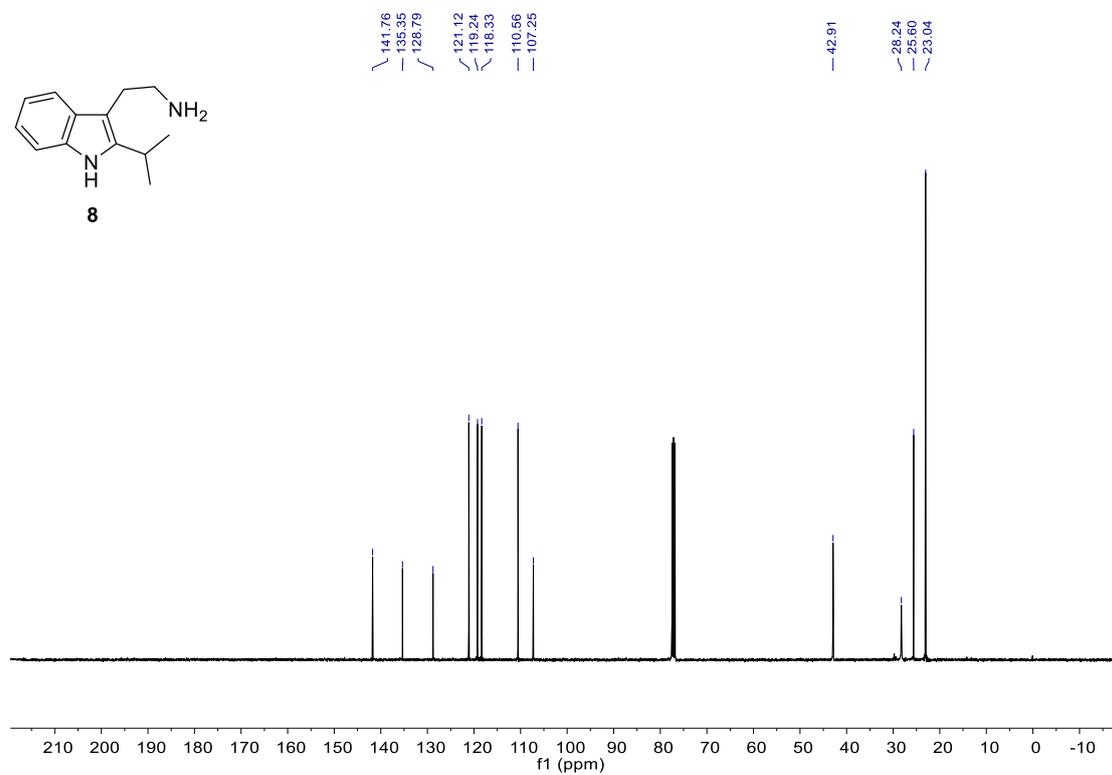
¹³C NMR (100 MHz, CDCl₃, epingouniense, **1b**)



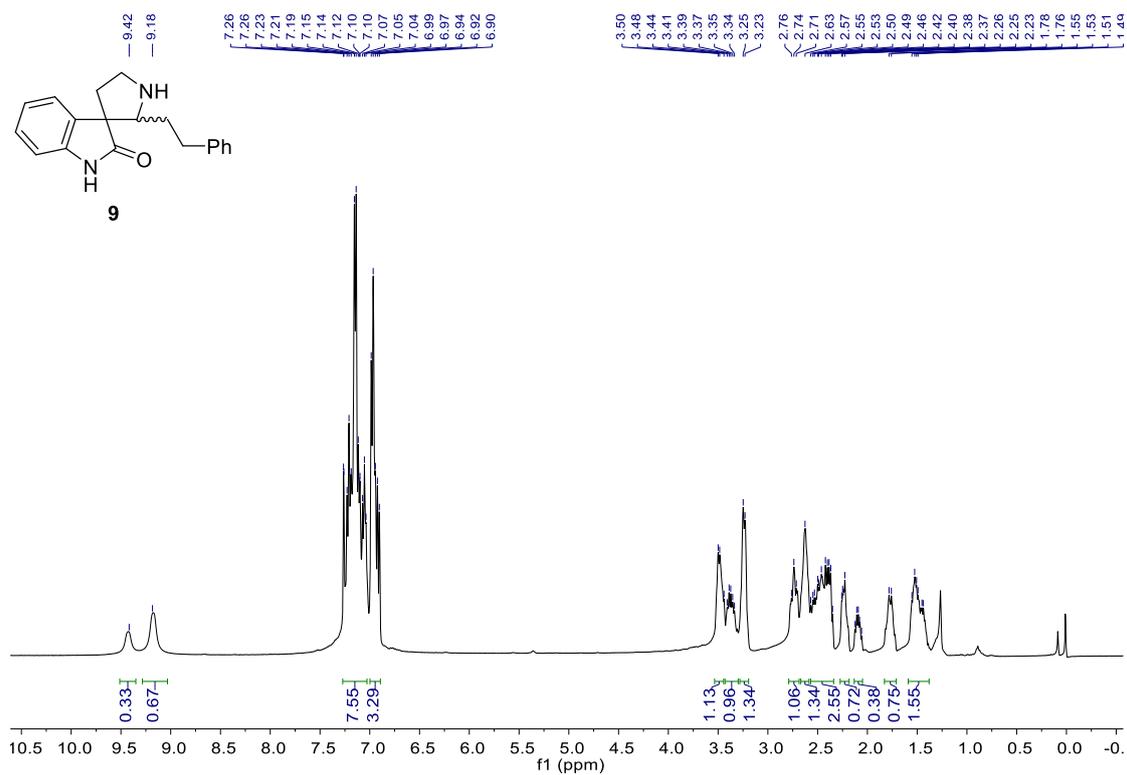
¹H NMR (400 MHz, CDCl₃, compound 8)



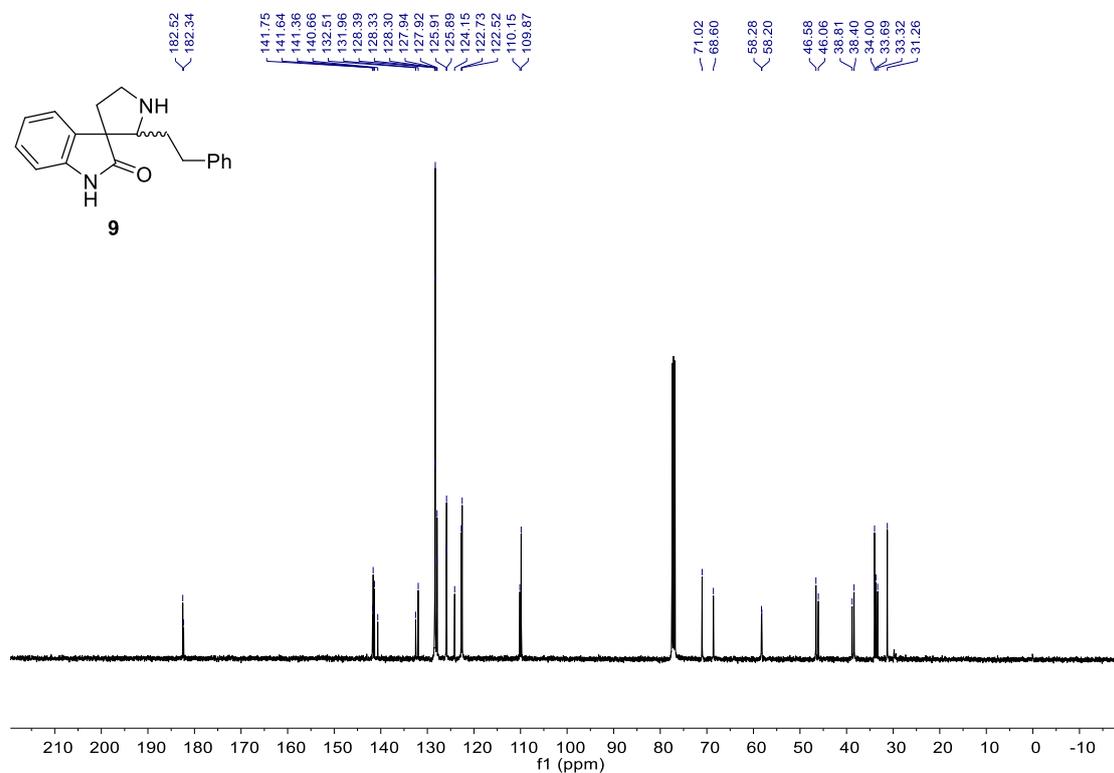
¹³C NMR (100 MHz, CDCl₃, compound 8)



¹H NMR (400 MHz, CDCl₃, compound **9**, mixture of diastereomers)



¹³C NMR (100 MHz, CDCl₃, compound **9**, mixture of diastereomers)



7. X-Ray Structures of 4a and Derivatives of 4l and 4t

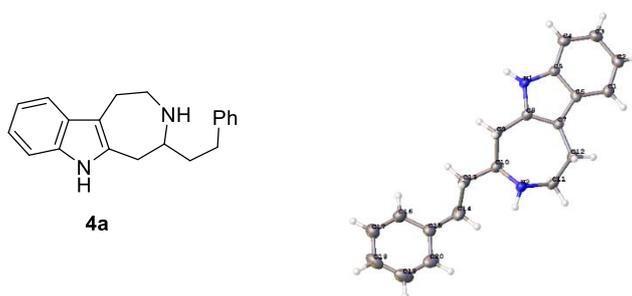


Table S1: Crystal data and structure refinement for compound **4a**

Identification code	exp_7889
Empirical formula	C ₂₀ H ₂₂ N ₂
Formula weight	290.40
Temperature / K	111.60(14)
Crystal system	monoclinic
Space group	P2 ₁
a / Å, b / Å, c / Å	6.8833(11), 7.8177(10), 14.677(4)
α /°, β /°, γ /°	90.00, 99.67(2), 90.00
Volume / Å ³	778.6(3)
Z	2
ρ_{calc} / mg mm ⁻³	1.239
μ / mm ⁻¹	0.073
F(000)	312
Crystal size / mm ³	0.41 × 0.37 × 0.16
2 θ range for data collection	6 to 51.98°
Index ranges	-8 ≤ h ≤ 8, -9 ≤ k ≤ 9, -17 ≤ l ≤ 18
Reflections collected	6324
Independent reflections	2965[R(int) = 0.0469 (inf-0.9Å)]
Data/restraints/parameters	2965/1/199
Goodness-of-fit on F ²	1.059
Final R indexes [I > 2 σ (I) i.e. F _o > 4 σ (F _o)]	R ₁ = 0.0573, wR ₂ = 0.1181
Final R indexes [all data]	R ₁ = 0.0725, wR ₂ = 0.1337
Largest diff. peak/hole / e Å ⁻³	0.351/-0.210
Flack Parameters	-2(4)
Completeness	0.9967

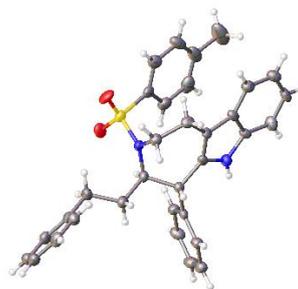
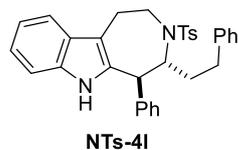


Table S2: Crystal data and structure refinement for **NTs-4I**

Identification code	exp_8244
Empirical formula	C ₃₃ H ₃₂ N ₂ O ₂ S
Formula weight	520.67
Temperature / K	115.00(14)
Crystal system	orthorhombic
Space group	Pbca
a / Å, b / Å, c / Å	12.115(3), 20.818(4), 21.153(3)
α/°, β/°, γ/°	90.00, 90.00, 90.00
Volume / Å ³	5334.8(19)
Z	8
ρ _{calc} / mg mm ⁻³	1.297
μ / mm ⁻¹	0.155
F(000)	2208
Crystal size / mm ³	0.37 × 0.28 × 0.05
2θ range for data collection	6.44 to 52°
Index ranges	-14 ≤ h ≤ 11, -25 ≤ k ≤ 23, -26 ≤ l ≤ 25
Reflections collected	20010
Independent reflections	5213[R(int) = 0.1344 (inf-0.9Å)]
Data/restraints/parameters	5213/0/344
Goodness-of-fit on F ²	1.029
Final R indexes [I > 2σ (I) i.e. F _o > 4σ (F _o)]	R ₁ = 0.0783, wR ₂ = 0.1267
Final R indexes [all data]	R ₁ = 0.1700, wR ₂ = 0.1670
Largest diff. peak/hole / e Å ⁻³	0.378/-0.309
Flack Parameters	N
Completeness	0.9968

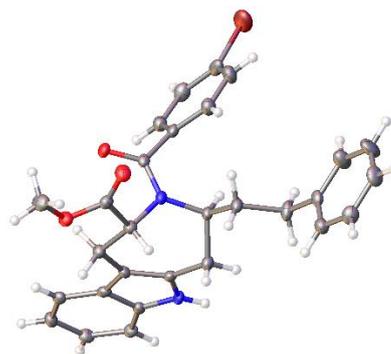
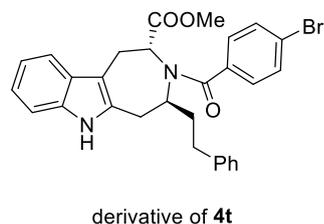


Table S3: Crystal data and structure refinement for derivative of **4t**

Identification code	exp_8216
Empirical formula	C ₂₉ H ₂₇ BrN ₂ O ₃
Formula weight	531.43
Temperature / K	116.5(3)
Crystal system	triclinic
Space group	P1
a / Å, b / Å, c / Å	7.1378(8), 8.1657(5), 11.6045(11)
α/°, β/°, γ/°	85.389(6), 79.331(9), 68.354(8)
Volume / Å ³	617.75(11)
Z	1
ρ _{calc} / mg mm ⁻³	1.429
μ / mm ⁻¹	2.539
F(000)	274
Crystal size / mm ³	0.350 × 0.060 × 0.015
2θ range for data collection	7.754 to 142.214°
Index ranges	-8 ≤ h ≤ 8, -9 ≤ k ≤ 9, -13 ≤ l ≤ 14
Reflections collected	8110
Independent reflections	4161[R(int) = 0.0405 (inf-0.9Å)]
Data/restraints/parameters	4161/3/317
Goodness-of-fit on F ²	1.055
Final R indexes [I > 2σ (I) i.e. F _o > 4σ (F _o)]	R ₁ = 0.0367, wR ₂ = 0.0888
Final R indexes [all data]	R ₁ = 0.0390, wR ₂ = 0.0911
Largest diff. peak/hole / e Å ⁻³	0.543/-0.285
Flack Parameters	-0.017(14)
Completeness	0.9991

8. Computational Studies

8.1 Computational Methods

DFT calculations were performed with Gaussian 09.¹ Geometry optimizations of all the stationary points were carried out using the PBE0 functional,² which performs well in previous mechanistic study of Pictet-Spengler Reactions.³ The D3(BJ) version of Grimme's dispersion⁴ was added due to the existence of hydrogen bonding in the reaction system. The 6-31+G(d,p) basis set⁵ was used for all atoms. The SMD⁶ implicit solvation model was used to account for solvation effects of CHCl₃. On the basis of the optimized structures, single-point energies were computed at the SMD(CHCl₃)/PBE0-D3(BJ)/6-311+G(d,p) level. All the discussed energy differences were based on Gibbs energies at 298 K. Reference states for solutes in CHCl₃ solution are the hypothetical states at 1 mol/L, respectively.

8.2 Mechanism of the reaction between tryptamine derivatives and aromatic aldehydes

We have also computed the free energy profile of the reaction between tryptamine derivatives and aromatic aldehydes (**Figure S1**). For **5a** is the simplest product in **Scheme 2**, the reaction between substrate **2a** and benzaldehyde was chosen as the model reaction. Substrate **2a-TFA** will first react with benzaldehyde to form imine intermediate **Int7**. Subsequently, the intramolecular Pictet-Spengler type cyclization (via **TS5**) gives the spiroindolenine **Int8**. This step has an activation free energy of 13.6 kcal/mol. The tautomerization of imine to enamine **Int9** has an activation free energy of 16.1 kcal/mol. With excess benzaldehyde, iminium ion **Int10** can be generated and then undergoes a Mannich-type cyclization via **TS7** to give **Int11**, which requires an activation free energy of 5.5 kcal/mol.

Int11 might undergo two different reaction pathways (**Figure S1b**). The first pathway is similar to the transformation of **Int5** to **4d-TFA**, which involves a retro-Mannich reaction, following with the hydrolysis of iminium ion **Int12** to generate the 7-membered ring product **5a'-TFA**. The second pathway gives the elimination product **5a-TFA**, which was obtained in experiment. Firstly, imine/enamine tautomerization of **Int11** will form **Int13**, with an activation free energy of 18.3 kcal/mol. **Int13** will be protonated by TFA to give **Int14**, and then undergo a formal retro-Diels-Alder reaction to generate **Int16**, which is a step-wise process rather than a concerted reaction. The 6-membered ring in **Int14** could open via **TS10**, generating imine **Int15**, with an activation free energy of 25.4 kcal/mol. This step could be regarded as a retro-Michael addition. Subsequently, a retro-Pictet-Spengler type

reaction will take place via **TS11**, giving **Int16** as a product. This step has an activation free energy of 5.7 kcal/mol. Finally, the hydrolysis of **Int16** generates the alkene product **5a-TFA**.

Although the second pathway has a higher energy barrier than the first one (24.8 kcal/mol vs. 6.7 kcal/mol), alkene product **5a** was obtained as the only product. This could be explained thermodynamically, namely, **Int16** is thermodynamically more stable than the kinetically favored product **5a'-TFA**. Thus, **5a'-TFA** can return to **Int11** through a Mannich-type cyclization, then the second pathway can take place to generate **Int16**.

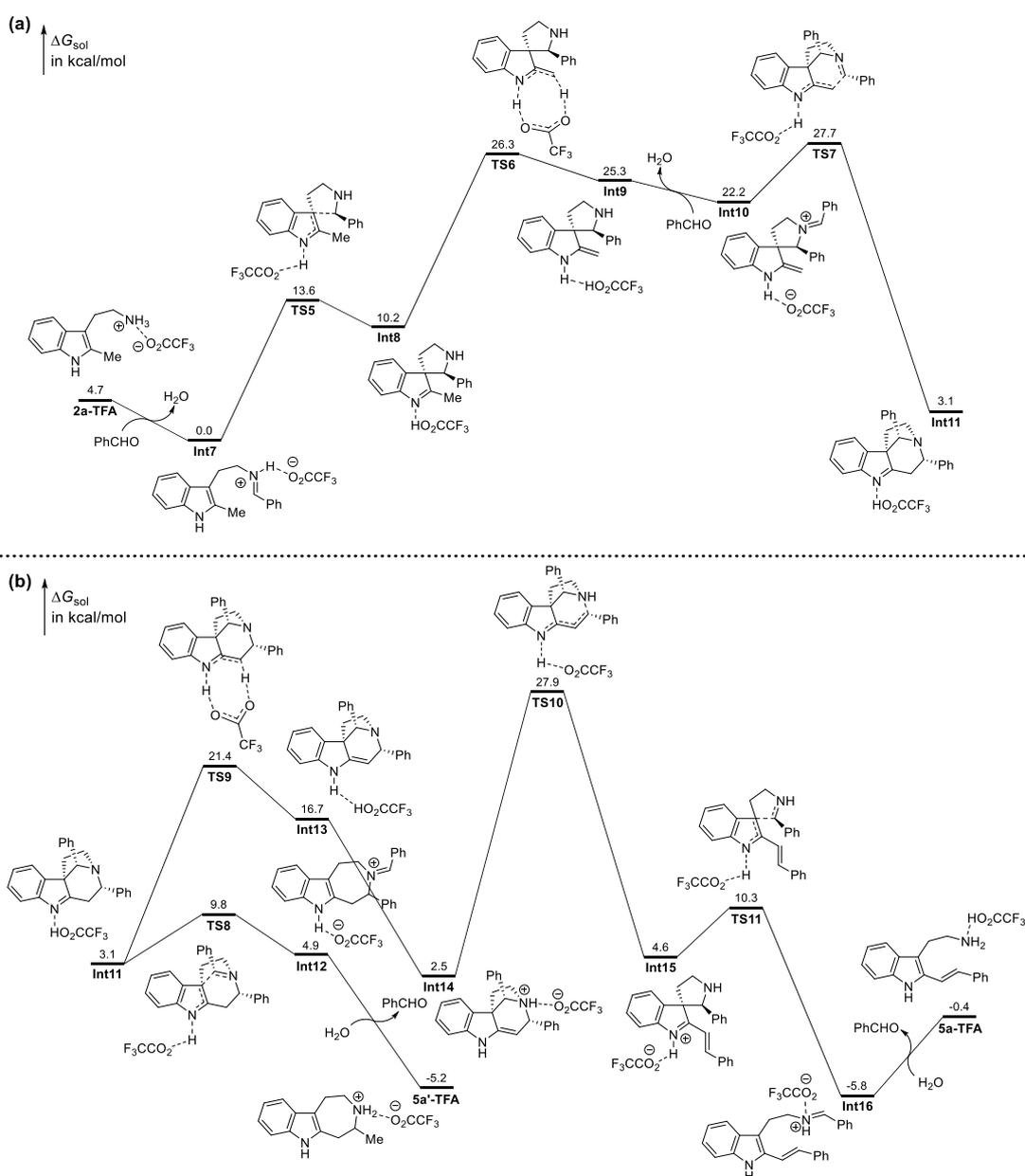


Figure S1. Gibbs energy profile for the reaction between substrate **2a** and benzaldehyde. Computed at the SMD(CHCl₃)/PBE0-D3BJ/6-311+G(d,p)//PBE0-D3BJ/6-31+G(d,p) level.

Computed Energies for the Stationary Points:

Table S4. Thermal corrections to Gibbs free energies (TCGs), single-point energies (SPEs) and Gibbs free energies(Gs).

Entry	TCG / Hartree ^a	SPE / Hartree ^b	G / Hartree
H₂O	0.003989	-76.3796294	-76.3756404
CH₃CHO	0.030849	-153.7056147	-153.6747657
PhCHO	0.080084	-345.2796423	-345.1995583
2a-TFA	0.223849	-1063.147872	-1062.924023
Int1	0.249699	-1140.484076	-1140.234377
TS1	0.254921	-1140.46557	-1140.210649
Int2	0.25599	-1140.475912	-1140.219922
TS2	0.254366	-1140.452562	-1140.198196
Int3	0.257062	-1140.456442	-1140.19938
Int4	0.289077	-1217.792918	-1217.503841
TS3	0.291507	-1217.789241	-1217.497734
Int5	0.290944	-1217.828776	-1217.537832
TS4	0.292509	-1217.817771	-1217.525262
Int6	0.290474	-1217.822038	-1217.531564
4d-TFA	0.259896	-1140.505433	-1140.245537
Int7	0.301514	-1332.060826	-1331.759312
TS5	0.3054	-1332.043077	-1331.737677
Int8	0.30359	-1332.046684	-1331.743094
TS6	0.304013	-1332.021422	-1331.717409
Int9	0.306609	-1332.025554	-1331.718945
Int10	0.386544	-1600.934342	-1600.547798
TS7	0.389199	-1600.928301	-1600.539102
Int11	0.388473	-1600.966689	-1600.578216
TS8	0.389458	-1600.957144	-1600.567686
Int12	0.388481	-1600.963875	-1600.575394
5a'-TFA	0.306541	-1332.074098	-1331.767557
TS9	0.386376	-1600.935549	-1600.549173
Int13	0.389131	-1600.945671	-1600.55654
Int14	0.390199	-1600.969462	-1600.579263
TS10	0.3867	-1600.925407	-1600.538707
Int15	0.382376	-1600.958233	-1600.575857
TS11	0.38532	-1600.952062	-1600.566742
Int16	0.383997	-1600.976458	-1600.592461
5a-TFA	0.301189	-1332.06115	-1331.759961

^aComputed at the PBE0-D3BJ/6-31+G(d,p) level.

^bComputed at the SMD(CHCl₃)/PBE0-D3BJ/6-311+G(d,p) level.

Cartesian coordinates for the stationary points:

H₂O			H	-1.07218900	0.06240200	2.28065100	
O	0.00000000	0.00000000	0.11609800	C	1.66542800	0.99222900	0.88980400
H	0.00000000	0.76584000	-0.46439000	C	1.42434100	2.45336200	0.69076100
H	0.00000000	-0.76584000	-0.46439000	C	0.17127400	2.73466800	-0.14539300
CH₃CHO			H	2.29765000	2.89663600	0.19688800	
C	1.16425400	-0.14908300	0.00000500	H	1.31784400	2.98426000	1.64373300
H	1.70413400	0.22241000	-0.87927400	H	0.18019300	3.75656600	-0.53738900
H	1.70397700	0.22199400	0.87956000	H	-0.73399100	2.61199800	0.45610600
H	1.15255400	-1.24033800	-0.00024000	O	-2.70591700	1.12503200	-1.46269100
C	-0.22958900	0.39871400	0.00003600	H	0.99299500	-1.96801800	1.89555400
H	-0.30623700	1.50846400	0.00014600	C	-2.39382500	0.15765200	-0.76824400
O	-1.23280200	-0.27628900	-0.00005500	O	-1.23108200	-0.19634100	-0.38459100
PhCHO			C	-3.51357500	-0.76368300	-0.22278000	
C	0.57849000	-2.14906600	0.00000000	F	-3.25525900	-2.05730300	-0.47593900
C	1.61933800	-1.22206000	0.00000000	F	-3.60299600	-0.62772200	1.12031900
C	1.32854700	0.13904100	0.00000000	F	-4.71030600	-0.47743400	-0.73629900
C	0.00000000	0.57190800	0.00000000	N	0.04350400	1.76738300	-1.25776700
C	-1.04256200	-0.36223400	0.00000000	H	-0.69636000	2.04962700	-1.90501400
C	-0.75144700	-1.71963600	0.00000000	H	0.92010800	1.61787500	-1.75429700
H	0.80233600	-3.21211100	0.00000000	H	-0.40069600	0.77163200	-0.84695700
H	2.65106000	-1.56056200	0.00000000	Int1			
H	2.13168400	0.87306700	0.00000000	C	3.04467000	-0.10731600	-0.58698100
H	-2.06619500	0.00067400	0.00000000	C	3.53330200	1.02623900	0.11006400
H	-1.55625600	-2.44880200	0.00000000	C	4.85060900	1.11674800	0.55796000
C	-0.28998100	2.01943100	0.00000000	C	5.68921200	0.03874500	0.30293100
H	0.60909300	2.67367400	0.00000000	C	5.22674800	-1.09805100	-0.38325200
O	-1.40325500	2.50122000	0.00000000	C	3.91495000	-1.17990300	-0.83050100
2a-TFA			C	1.35457100	1.38593500	-0.37427600	
C	2.55001100	0.18707100	0.09312100	H	5.21176900	1.99509400	1.08570600
C	2.36162600	-1.15971000	0.49594500	H	6.72152700	0.07677500	0.63747100
C	3.05842900	-2.21557900	-0.08898300	H	5.91070300	-1.92054400	-0.57004800
C	3.95666400	-1.90952100	-1.10374600	H	3.57469600	-2.05765100	-1.37402400
C	4.16358300	-0.58187200	-1.51739300	N	2.48413700	1.90845600	0.22448700
C	3.47230400	0.46756000	-0.92660500	C	0.08216000	2.15456000	-0.39092500
C	0.98255800	0.13437900	1.72289700	H	-0.21245400	2.45864600	0.62122100
H	2.90120500	-3.24224400	0.22909800	H	0.17663500	3.06639100	-0.99287100
H	4.51016600	-2.71050000	-1.58426300	H	-0.73180800	1.55753200	-0.80852900
H	4.88039800	-0.37674300	-2.30700500	C	1.65958800	0.14302800	-0.89127300
H	3.66105900	1.49144600	-1.24325200	C	0.42933700	-1.04077000	1.57277700
N	1.42448100	-1.14914000	1.49981800	C	0.72041700	-0.80968200	-1.54456000
C	-0.11319800	0.40264800	2.68892900	C	0.34334300	-1.97934300	-0.60859900
H	0.05650700	-0.10818100	3.64296500	H	1.17409900	-1.24787700	-2.44186500
H	-0.19146400	1.47291700	2.89445500	H	-0.20265900	-0.31131000	-1.85219200

H	1.23416500	-2.55879100	-0.34226400	O	-2.23933800	0.88926100	-0.99162600
H	-0.37431500	-2.63932800	-1.10190800	H	-0.75867900	0.83416200	-1.24925400
N	-0.27557300	-1.46478600	0.59560400	C	-2.56103500	0.05740900	-0.10008800
H	-1.43783400	-1.26109200	0.59393700	O	-1.85872100	-0.78365900	0.47999700
O	-2.71983300	-0.98701900	0.67764300	C	-4.06999500	0.08513200	0.27005900
H	2.54166700	2.83214400	0.62016400	F	-4.31415900	-0.47359800	1.46433900
C	-3.11067000	-0.24953400	-0.28735000	F	-4.56549500	1.33214900	0.30385400
O	-2.47552600	0.13531600	-1.26396200	F	-4.78118000	-0.60633000	-0.64780300
C	-4.58044300	0.21646100	-0.12303000	C	0.81836900	-0.30199900	2.04002500
F	-4.67681400	1.07559100	0.91459700	H	1.67594400	0.28110000	2.38592600
F	-5.03733600	0.84560800	-1.20870000	H	0.11525400	0.33333600	1.49778200
F	-5.40345100	-0.81411800	0.12947700	H	0.26180400	-0.69802200	2.89869600
H	1.51246500	-1.18634900	1.54091800	H	0.40010300	-1.98049800	0.70572500
C	-0.16666300	-0.36629900	2.75037800	Int2			
H	-1.25047600	-0.27366500	2.65923400	C	2.21050600	0.76792900	-0.17309000
H	0.08339500	-0.91887100	3.66279000	C	0.99251300	1.36299600	-0.52682300
H	0.28296100	0.62819000	2.85363800	C	0.75877500	2.72138500	-0.37046300
TS1				C	1.79581400	3.49712700	0.15136200
C	2.40524900	0.64094900	-0.36726600	C	3.02208500	2.92192700	0.48929300
C	1.27203600	1.43654500	-0.64578900	C	3.24201600	1.54954200	0.32583100
C	1.21583900	2.78755000	-0.31844400	H	-0.19430000	3.16043100	-0.64894500
C	2.33669000	3.34284500	0.29200900	H	1.64963300	4.56442300	0.28738600
C	3.47674400	2.57113400	0.56438700	H	3.81783400	3.54873700	0.88052700
C	3.52246400	1.21758500	0.24024600	H	4.20954500	1.12281800	0.57643800
C	0.76758500	-0.61843100	-1.34035900	C	2.07701300	-0.70085900	-0.44697300
H	0.32987700	3.37858900	-0.52815200	C	3.23993400	-1.33003300	-1.22613000
H	2.33042700	4.39511600	0.55938200	C	4.22470000	-1.81120600	-0.12406400
H	4.33731100	3.04062600	1.03163900	H	3.69124400	-0.61877000	-1.92260100
H	4.41505300	0.63211800	0.44884600	H	2.88047200	-2.18262500	-1.81142800
N	0.30911000	0.63409900	-1.24017100	H	5.13990000	-1.21132500	-0.09992900
C	-0.05830600	-1.70790800	-1.91318500	H	4.52599800	-2.84668800	-0.31803900
H	0.53969500	-2.60287600	-2.09998500	N	3.52558900	-1.72038400	1.15754900
H	-0.87466300	-1.94586200	-1.21808800	H	3.84414300	-0.91910800	1.69214500
H	-0.51756000	-1.38812600	-2.85224100	N	0.10369000	0.40342600	-1.05369200
C	2.05789900	-0.71432500	-0.74947500	C	0.69962000	-0.74763700	-1.05683600
C	1.21333600	-1.43455100	1.17771000	C	0.01285500	-1.99270600	-1.47963000
C	3.02042800	-1.85093600	-0.87166200	H	-0.80620400	-1.76664900	-2.16484700
C	2.79832800	-2.88479700	0.27560600	H	0.70188400	-2.69413200	-1.95728600
H	4.04293500	-1.46302600	-0.81749700	H	-1.42149300	0.53161600	-1.03326600
H	2.92653600	-2.35645100	-1.83836400	O	-2.46140300	0.59656400	-0.91766100
H	3.70336200	-3.44402900	0.52107900	C	-2.86472500	-0.18932100	0.04005800
H	2.02348600	-3.60227700	-0.01155700	C	-4.39397700	-0.07261700	0.23965900
N	2.32554500	-2.15329500	1.42793500	O	-2.20328200	-0.94440500	0.71851000
H	3.04472100	-1.65154300	1.93858700	F	-4.74964400	1.19690700	0.48863500

F	-5.04208200	-0.47396100	-0.86685800	C	0.85461500	-1.00785600	1.94419000
F	-4.80603000	-0.82656500	1.25693300	H	-0.15282500	-0.73035100	1.62148000
C	2.11523600	-1.57648100	0.86934200	H	0.75752700	-1.70994900	2.77661800
H	1.72861700	-2.56473100	0.57851000	H	1.36459700	-0.10745400	2.30285400
C	1.30741000	-1.05477600	2.03682000	H	-1.29290900	-1.40173500	-0.74395800
H	0.25097200	-0.95557300	1.76859700	Int3			
H	1.38385100	-1.74822300	2.87863400	C	2.24478800	0.65120600	-0.09459500
H	1.67012300	-0.07332100	2.36030700	C	1.27934000	1.51154000	-0.63274200
H	-0.41855100	-2.48449100	-0.59850700	C	1.31988800	2.88513800	-0.43852700
TS2				C	2.37808300	3.39919100	0.31540400
C	2.28556800	0.64035600	-0.12286500	C	3.36275600	2.56370500	0.83905800
C	1.28277000	1.50921200	-0.56471300	C	3.30032100	1.18002200	0.63137500
C	1.33361000	2.87928200	-0.36667300	H	0.56227500	3.53821300	-0.86086500
C	2.45280000	3.38480300	0.29949900	H	2.43645600	4.47028000	0.48489400
C	3.47680400	2.54117200	0.72854200	H	4.18439000	2.98673600	1.40840100
C	3.40097000	1.15957700	0.51668500	H	4.08077700	0.53961900	1.03253200
H	0.53978400	3.53210100	-0.71553900	C	1.87728800	-0.76809400	-0.45299100
H	2.52852100	4.45348100	0.47521800	C	3.01619900	-1.56923300	-1.10208200
H	4.34383300	2.96028200	1.22952500	C	3.76692800	-2.20971600	0.09051300
H	4.21347900	0.51705600	0.84380200	H	3.65741800	-0.93666600	-1.72162600
C	1.87244100	-0.76680800	-0.46418400	H	2.58848400	-2.34150500	-1.74923000
C	2.94497200	-1.60483700	-1.17366800	H	4.72549500	-1.71528700	0.28182900
C	3.72918000	-2.28129800	-0.01784400	H	3.98806500	-3.26203800	-0.12135100
H	3.57878400	-0.99119300	-1.81913400	N	2.89374300	-2.09452200	1.26209000
H	2.45996400	-2.35779600	-1.80278200	H	3.26084300	-1.42407000	1.92791900
H	4.72758400	-1.84986700	0.10743600	N	0.36702600	0.76548500	-1.37065900
H	3.86597900	-3.34717700	-0.23162700	C	0.64464400	-0.57464300	-1.32146400
N	2.94263800	-2.10279900	1.20267800	C	-0.10608700	-1.55052200	-1.89707800
H	3.36707000	-1.42003600	1.82058600	H	-0.88222500	-1.30212900	-2.61537100
N	0.30382300	0.75947600	-1.22907900	H	0.22057100	-2.58292600	-1.84943200
C	0.59007700	-0.54743200	-1.22433300	H	-0.52637000	1.11091800	-1.69689800
C	-0.29761600	-1.52711600	-1.68828700	O	-2.56548600	0.70353700	-1.24618400
H	-0.92254000	-1.24412700	-2.53528400	C	-2.90168200	-0.10131600	-0.40820800
H	0.08200000	-2.54459300	-1.73386200	C	-4.18973400	0.08894200	0.42383100
H	-0.65712100	1.06890500	-1.42052600	O	-2.28996900	-1.20551200	-0.06114800
O	-2.44677800	0.83646200	-1.04837400	F	-4.80697700	1.21752400	0.08851700
C	-2.84113100	-0.06431100	-0.31036000	F	-5.03304700	-0.93249800	0.22256000
C	-4.22577700	0.08705100	0.36800400	F	-3.89584400	0.13877100	1.73103500
O	-2.26977800	-1.16729800	-0.01042600	C	1.58822500	-1.66216900	0.80352700
F	-4.72964000	1.31129100	0.20281100	H	1.04545200	-2.54018500	0.42126100
F	-5.09540300	-0.79291600	-0.15770500	C	0.76842500	-1.02493300	1.90502300
F	-4.14588100	-0.15101600	1.68652600	H	-0.22085500	-0.73400600	1.54172500
C	1.62193400	-1.66056000	0.81580100	H	0.62951300	-1.73588700	2.72419900
H	1.05452500	-2.53123000	0.45696000	H	1.26221200	-0.12949000	2.29737700

H	-1.46772400	-1.35139700	-0.63199100	H	-0.24004100	0.30907800	1.18637200
Int4				TS3			
C	-2.69738000	-0.19241900	-0.24457300	C	-2.66440600	-0.34171200	-0.24859300
C	-2.16003300	-1.48218700	-0.40911000	C	-1.95999200	-1.53829300	-0.47499700
C	-2.89908600	-2.60975700	-0.06279400	C	-2.53750900	-2.77492300	-0.20195800
C	-4.19877800	-2.41965600	0.40987300	C	-3.85221600	-2.78763800	0.26382000
C	-4.75545700	-1.14549500	0.53222200	C	-4.57447300	-1.60681100	0.45273000
C	-3.99117700	-0.01702700	0.21400500	C	-3.97168600	-0.36895600	0.20778300
H	-2.48127700	-3.60514700	-0.17415000	H	-1.98539600	-3.69563300	-0.36009700
H	-4.79489200	-3.28869500	0.67383000	H	-4.32795600	-3.74164800	0.47230100
H	-5.77666500	-1.02936600	0.88085000	H	-5.60303900	-1.65007300	0.79641600
H	-4.41138500	0.97883900	0.33510200	H	-4.52441100	0.55182000	0.37784200
C	-1.57867400	0.78201300	-0.50398600	C	-1.68426400	0.77731500	-0.44814200
C	-1.84854600	2.16137300	-1.11316700	C	-2.09993300	2.15498200	-0.97415900
C	-0.73281400	3.07794200	-0.56445600	C	-1.12289600	3.15651600	-0.30116600
H	-2.83112800	2.53129400	-0.80884300	H	-3.13292100	2.37974300	-0.69585600
H	-1.82861600	2.11520300	-2.20431000	H	-2.03119600	2.19533000	-2.06425500
H	-1.12586200	3.93595200	-0.01183800	H	-1.64039400	3.85979400	0.35566200
H	-0.06343200	3.44406400	-1.34269000	H	-0.53661600	3.73139600	-1.01664700
N	0.01858100	2.21424800	0.36572800	N	-0.24030500	2.30140300	0.50653100
N	-0.90171800	-1.41164500	-0.97875400	N	-0.71914600	-1.26442200	-1.01992400
C	-0.58581300	-0.08985300	-1.26878000	C	-0.56501600	0.08499800	-1.20933000
C	0.43339900	0.31591500	-2.04064900	C	0.46107700	0.69108600	-1.85560300
H	1.10433200	-0.40125200	-2.49971400	H	1.26426300	0.10652900	-2.29026100
H	0.60600300	1.36726000	-2.24130900	H	0.39912900	1.73854600	-2.12430600
C	-0.86805800	1.13913900	0.84045200	C	-1.01759800	1.14271100	0.93821500
C	1.29350600	2.16091500	0.52443900	C	1.03983000	2.14084600	0.30057900
H	1.65697500	1.29548300	1.09674200	H	1.48112300	1.25981800	0.78178600
C	2.26817100	3.10969600	-0.04310900	C	1.94454800	3.13491700	-0.31486900
H	1.83176900	3.96932400	-0.55123900	H	1.46002300	3.84888300	-0.98221300
H	2.92530600	3.45626100	0.76172600	H	2.42626000	3.69594600	0.49757500
H	2.91275100	2.54870400	-0.73037900	H	2.73947100	2.60659800	-0.84491000
H	-0.12789000	-2.05763800	-0.76609100	H	0.12687800	-1.86334300	-0.93433200
O	1.59209600	-2.33025000	-0.22849300	O	1.78356400	-2.15737200	-0.54318000
C	2.08266800	-1.40169700	0.43145400	C	2.18600600	-1.32564300	0.29254500
C	3.59150800	-1.10327700	0.17165200	C	3.70752100	-0.99506300	0.24451800
O	1.56878100	-0.63769100	1.28083000	O	1.56059400	-0.66277500	1.14667900
F	4.10707800	-1.76732500	-0.86600900	F	4.39888900	-1.72186200	-0.63674700
F	4.34702100	-1.38255800	1.24926800	F	4.29654700	-1.14128300	1.44309700
F	3.77481100	0.22575600	-0.09173600	F	3.87339700	0.31371400	-0.11276700
C	-1.77311200	1.64638800	1.94847200	C	-1.99414900	1.48711800	2.04525600
H	-2.42100600	2.47008800	1.63005000	H	-2.73682000	2.23360400	1.74610200
H	-2.41136600	0.82761500	2.28594500	H	-2.52842700	0.58337200	2.34402100
H	-1.17077300	1.98332500	2.79706300	H	-1.44860900	1.86600500	2.91395500

H	-0.32704000	0.35180700	1.25096000	H	1.86811700	-0.71248000	1.79065500
Int5				TS4			
C	2.12589900	1.50852200	-0.15140200	C	-2.59983500	-0.85741600	-0.30439200
C	0.76143500	1.83692000	-0.20564800	C	-1.51211900	-1.71045900	-0.62249200
C	0.31181800	3.14534800	-0.09451900	C	-1.57425900	-3.08928500	-0.42688600
C	1.27361400	4.14413200	0.06448300	C	-2.75865700	-3.61054500	0.07829800
C	2.63506500	3.83346300	0.10577900	C	-3.85386700	-2.78213500	0.38069900
C	3.07374800	2.51024500	-0.00138800	C	-3.78621400	-1.40747200	0.19426600
H	-0.74797000	3.37761700	-0.13503400	H	-0.72596100	-3.72504000	-0.65992600
H	0.95872500	5.17971500	0.15138700	H	-2.84183900	-4.68090300	0.24085000
H	3.36256200	4.63135300	0.22109300	H	-4.76648400	-3.22751200	0.76536100
H	4.13534300	2.28053300	0.02786600	H	-4.63907700	-0.77627800	0.43044100
C	2.21747800	0.02335100	-0.26994400	C	-2.13992300	0.48598100	-0.54847600
C	3.12261800	-0.61884400	-1.33204900	C	-2.88861700	1.77700100	-0.58417900
C	3.33342000	-2.06393800	-0.79657100	C	-2.14460900	2.89661300	0.24002000
H	4.06583000	-0.06892000	-1.40451000	H	-3.90250200	1.63798700	-0.19685500
H	2.65906600	-0.59657100	-2.32307700	H	-2.99377400	2.12187900	-1.61947400
H	4.39641800	-2.26227700	-0.62951300	H	-2.74355800	3.19653200	1.10198700
H	2.97714500	-2.82470600	-1.49387700	H	-1.97296800	3.79214800	-0.35589800
N	2.61386100	-2.16615600	0.48231900	N	-0.86864800	2.37425800	0.69963500
N	-0.03112700	0.68042700	-0.39317200	N	-0.46748000	-0.94329000	-1.10262900
C	0.76676300	-0.33591800	-0.47099400	C	-0.82983100	0.34974800	-1.07012900
C	0.39426700	-1.75780700	-0.63903800	C	0.01966800	1.50029200	-1.44988200
H	-0.67912200	-1.90460300	-0.49337400	H	0.98338400	1.16796000	-1.84272300
H	0.64598300	-2.05908700	-1.66728900	H	-0.48966800	2.07129500	-2.23854200
C	2.62823600	-0.80710900	1.00701600	C	-0.97282100	1.16908300	1.27947500
C	1.22721500	-2.63128600	0.34248600	C	0.26869100	2.44728400	-0.22820100
H	0.78248300	-2.51349200	1.33812600	H	1.11210200	2.02307900	0.32209500
C	1.14627700	-4.10210600	-0.02422700	C	0.60970300	3.85890500	-0.65913600
H	1.54489800	-4.29979300	-1.02495600	H	-0.15950800	4.30716300	-1.29678500
H	1.70953200	-4.70255100	0.69473200	H	0.77010300	4.50497200	0.20811000
H	0.10275800	-4.43084400	-0.01632500	H	1.53682800	3.83578900	-1.23875900
H	-1.55774900	0.69749200	-0.37602700	H	0.56381600	-1.22619500	-1.12915600
O	-2.60202100	0.82157500	-0.34659400	O	2.10687500	-1.37651500	-0.95912200
C	-3.21496800	-0.25539100	0.04634200	C	2.50568800	-0.71846000	0.03270700
C	-4.74229900	-0.02122000	0.12224600	C	4.04231500	-0.73153100	0.26437100
O	-2.73680800	-1.33168800	0.33281000	O	1.85946400	-0.01595000	0.82978600
F	-5.02763100	0.96203600	0.99155200	F	4.66851800	-1.72687400	-0.37380800
F	-5.38063000	-1.12123800	0.51734000	F	4.35261100	-0.83002300	1.56713700
F	-5.22882600	0.33531100	-1.07758300	F	4.57423500	0.43043100	-0.18587500
C	3.97354900	-0.40439800	1.58455600	C	-2.00132000	0.83062900	2.29789400
H	4.77273900	-0.42780400	0.83770300	H	-2.98184600	1.27345500	2.11813400
H	3.92288200	0.60636300	1.99773700	H	-2.11314700	-0.25393200	2.35565800
H	4.24083700	-1.09771700	2.38638000	H	-1.63239400	1.17863900	3.27241900

H	-0.04355200	0.59069900	1.30788100	H	0.38881900	0.73646000	1.41306200
Int6				4d-TFA			
C	-2.73893500	-0.78424000	-0.40162300	C	-3.66970100	-0.65625400	0.08464700
C	-1.64384900	-1.67926700	-0.59034000	C	-4.33625400	0.58807200	0.21419500
C	-1.75638200	-3.04694600	-0.32351900	C	-5.72735400	0.69652700	0.19836400
C	-2.97823100	-3.51464200	0.13597100	C	-6.45681200	-0.47463600	0.05221200
C	-4.07240500	-2.64637400	0.32584400	C	-5.81720500	-1.72188300	-0.07599400
C	-3.96541600	-1.29022700	0.06071000	C	-4.43473700	-1.82324800	-0.06095300
H	-0.91188900	-3.71335800	-0.47002500	H	-6.22310700	1.65802600	0.29808700
H	-3.09606900	-4.57222300	0.35245700	H	-7.54150000	-0.42781500	0.03737100
H	-5.01507000	-3.05140600	0.68214500	H	-6.42024100	-2.61800000	-0.18691800
H	-4.81915600	-0.63224400	0.20417500	H	-3.95506300	-2.79357200	-0.15727800
C	-2.24723200	0.51768300	-0.72646800	C	-2.25925700	-0.38829600	0.13730200
C	-2.84671200	1.87291200	-0.59897500	C	-1.15400600	-1.39104300	0.06083500
C	-2.16922700	2.71962900	0.53802300	C	-0.03302200	-1.02048000	-0.89684600
H	-3.91926000	1.82369700	-0.38996200	H	-1.56173400	-2.34985900	-0.27689600
H	-2.73416800	2.42660200	-1.53956600	H	-0.72287600	-1.58654200	1.05403200
H	-2.73497900	2.63879100	1.46513000	H	-0.42732700	-0.80310000	-1.89409600
H	-2.12622600	3.77579200	0.27095400	H	0.67804300	-1.84780100	-0.98473300
N	-0.81839100	2.23930700	0.78369900	N	0.77242700	0.14657100	-0.47208200
N	-0.55900300	-0.95764700	-1.02175800	N	-3.36629100	1.55317900	0.33803900
C	-0.91474700	0.35525800	-1.08888800	C	-2.11702500	0.97004100	0.29308000
C	-0.00533600	1.47672800	-1.44122000	C	-0.87889700	1.78883300	0.43312900
H	0.97316500	1.10163500	-1.74918200	H	-1.13512900	2.85206700	0.36191400
H	-0.43554000	2.02799200	-2.28771100	H	-0.43704900	1.65281400	1.43182200
C	-0.61423100	1.17726600	1.51042300	C	0.20144500	1.51168000	-0.61281800
C	0.21004700	2.48072800	-0.25523000	H	-0.24535200	1.55446300	-1.61288000
H	1.15486200	2.20774300	0.21929700	H	-3.53667000	2.53962800	0.43965900
C	0.26069900	3.92309100	-0.71354300	H	1.13835500	0.00178300	0.48864800
H	-0.62990100	4.21572800	-1.27954000	H	1.75861600	0.08126800	-0.96508800
H	0.39400100	4.61065600	0.12669000	O	3.21759300	-0.15260400	-1.11424500
H	1.11910600	4.04064000	-1.38066300	C	3.61368700	-0.29466900	0.07948300
H	0.44720800	-1.25687400	-1.01475200	C	5.14892300	-0.46113400	0.21408000
O	2.08060300	-1.40770300	-0.83965900	O	2.93872100	-0.29468800	1.12148400
C	2.60312700	-0.65306100	0.00599200	F	5.60645300	-1.43024700	-0.59616200
C	4.14724300	-0.76096100	0.15401400	F	5.77070600	0.68431800	-0.13178000
O	2.08084500	0.21184300	0.74081000	F	5.52537500	-0.76353700	1.45987100
F	4.67811600	-1.78487600	-0.52315000	C	1.34170800	2.51563200	-0.50602000
F	4.50905400	-0.90090800	1.44279200	H	2.11386100	2.32104400	-1.25429600
F	4.73357100	0.36881200	-0.30431200	H	0.95957900	3.52879600	-0.65610700
C	-1.55014400	0.53543700	2.44795400	H	1.81234100	2.46722300	0.48160900
H	-2.50269700	1.04254200	2.59261500	Int7			
H	-1.75461900	-0.47259300	2.05957700	C	-3.01321700	-1.36174900	0.12580800
H	-1.04369200	0.40032700	3.40979900	C	-3.52078300	-0.33240700	0.95866300

C	-4.85032400	0.08388900	0.90380700	TS5			
C	-5.68046000	-0.54511900	-0.01649100	C	-2.25696600	-0.02761900	1.14885000
C	-5.19850100	-1.56423000	-0.85663400	C	-0.97050500	0.41663000	1.50806700
C	-3.87456400	-1.97812600	-0.79296300	C	-0.72589200	1.70261200	1.96908000
C	-1.32270600	-0.58264400	1.41944400	C	-1.82582500	2.54962300	2.09318500
H	-5.22699000	0.86859900	1.55411000	C	-3.11766900	2.11827400	1.76638900
H	-6.72175500	-0.24506200	-0.08541400	C	-3.34615900	0.82886600	1.28501200
H	-5.87612200	-2.03588800	-1.56190900	C	-0.70829000	-1.68599000	0.82344400
H	-3.51539100	-2.77492700	-1.43927000	H	0.27964200	2.02716700	2.21665200
N	-2.47315700	0.10864600	1.73332800	H	-1.67876700	3.56199500	2.45681500
C	-0.03948700	-0.26714300	2.09750700	H	-3.95382500	2.79989000	1.89147900
H	0.21779200	0.79223700	1.97293800	H	-4.35452000	0.50412600	1.03762900
H	-0.09748800	-0.47287900	3.17282700	N	-0.07026900	-0.62586400	1.29819100
H	0.77837700	-0.86133700	1.68266200	C	-0.00608400	-2.95238600	0.51009800
C	-1.61553600	-1.51248700	0.43706600	H	-0.63593900	-3.61587100	-0.08729000
C	-0.59381400	0.51515200	-1.27385200	H	0.93264600	-2.73743400	-0.01798600
C	-0.64255800	-2.38103900	-0.27672700	H	0.25098800	-3.47667200	1.43752100
C	-0.25123300	-1.79064800	-1.65836700	C	-2.09011700	-1.36068200	0.58521400
H	-1.06623300	-3.37541500	-0.46051100	C	-1.88419400	-0.93131300	-1.42626100
H	0.27652000	-2.51117400	0.30011400	C	-3.22014400	-2.33359800	0.41358400
H	-1.12012500	-1.77648200	-2.32531100	C	-3.65461900	-2.38108100	-1.08661200
H	0.53918100	-2.39114700	-2.11331300	H	-4.06166100	-2.01179800	1.03512900
N	0.24379000	-0.44225600	-1.48685800	H	-2.94099000	-3.33541900	0.75411700
H	1.33931600	-0.34700000	-1.30102700	H	-4.73295200	-2.49718500	-1.21246000
O	2.74762200	-0.25531100	-1.07314000	H	-3.17016300	-3.22819400	-1.58391300
H	-2.52537400	0.83680400	2.42625800	N	-3.20171600	-1.16718800	-1.72924800
C	3.14165800	-1.00150700	-0.12337300	H	-3.80831300	-0.37007100	-1.57452900
O	2.50392900	-1.82911500	0.52546300	O	2.44925000	-0.26390100	1.32123900
C	4.63048700	-0.76577700	0.24535000	H	1.03059600	-0.52208700	1.35058800
F	4.78958900	0.47942400	0.74856000	C	3.00487200	-0.68328900	0.26729300
F	5.07638200	-1.62671600	1.16437900	O	2.55205700	-1.41562500	-0.61974200
F	5.43051800	-0.86774900	-0.82979900	C	4.43934900	-0.12772700	0.05539900
H	-1.64944900	0.29965000	-1.44490300	F	5.16537900	-0.88202000	-0.77769600
C	-0.27862000	1.86248500	-0.83928800	F	4.36329200	1.11169300	-0.49091600
C	-1.36952400	2.71134400	-0.59188900	F	5.12604900	-0.01450100	1.20099400
C	1.03005700	2.32542000	-0.61950700	H	-1.24423400	-1.77910500	-1.66817600
C	-1.16148500	4.00514400	-0.13024100	C	-1.25116300	0.37199500	-1.59218900
H	-2.37967800	2.34347200	-0.75544900	C	0.15005700	0.41924100	-1.61158200
C	1.22754500	3.62124500	-0.16186600	C	-1.97905600	1.57137500	-1.63704300
H	1.88224500	1.67532300	-0.80151900	C	0.81164700	1.64196700	-1.65605500
C	0.13869300	4.46037500	0.08361200	H	0.73748500	-0.49486000	-1.56190900
H	-2.00837400	4.65755800	0.05919900	C	-1.31535000	2.78781500	-1.68836700
H	2.23879700	3.97838600	0.00654100	H	-3.06472200	1.56738500	-1.61578100
H	0.30574200	5.47224800	0.44148800	C	0.08087000	2.82599200	-1.68805500

H	1.89699200	1.66171900	-1.65153000	C	-1.16488600	3.11142500	-1.41522500
H	-1.88567600	3.71127200	-1.71525800	H	-3.02372800	2.12038900	-1.06221700
H	0.59580300	3.78193400	-1.71381900	C	0.18440700	2.97941400	-1.73507400
Int8				H	1.76130400	1.59050300	-2.22863300
C	-2.16025200	-0.21639000	1.13235500	H	-1.58790000	4.09457900	-1.23040300
C	-0.86111200	-0.09102300	1.64033000	H	0.81914400	3.85831000	-1.79935000
C	-0.53315400	0.84653500	2.60786800	TS6			
C	-1.56033800	1.66423300	3.08367600	C	-2.38677400	-0.38628500	0.84101300
C	-2.86578100	1.53007000	2.60788000	C	-1.36654200	-0.25228000	1.78749700
C	-3.17824700	0.58556400	1.62377200	C	-1.48780700	0.54731000	2.91174200
H	0.48306800	0.93600600	2.97902700	C	-2.70126600	1.21725200	3.08823900
H	-1.34221300	2.40834900	3.84373900	C	-3.74739700	1.06631200	2.17850900
H	-3.64972900	2.16536200	3.00929700	C	-3.59587100	0.25920900	1.04522800
H	-4.20289900	0.48339500	1.27460100	H	-0.67821300	0.64485900	3.62790700
C	-2.10110800	-1.24633600	0.04786600	H	-2.83450000	1.85274000	3.95841900
C	-3.24037400	-2.26632000	-0.01341900	H	-4.68906600	1.57773200	2.35236200
C	-4.28052400	-1.63942600	-0.98672000	H	-4.42055200	0.14359000	0.34735100
H	-3.65118500	-2.46009900	0.98082900	C	-1.87607700	-1.25245900	-0.27606100
H	-2.87343000	-3.21917500	-0.40883600	C	-2.84547100	-2.32892300	-0.77042900
H	-5.22684100	-1.40291200	-0.49182200	C	-3.68668800	-1.62002500	-1.86322000
H	-4.50739400	-2.34411900	-1.79440800	H	-3.45572400	-2.72858000	0.04364500
N	-3.69236500	-0.42447600	-1.54679400	H	-2.27925000	-3.16097800	-1.20014500
H	-4.02968400	0.39295100	-1.05220700	H	-4.70408300	-1.40423500	-1.52066700
N	-0.00078300	-1.03862700	1.04579700	H	-3.77658100	-2.26524700	-2.74432700
C	-0.68828000	-1.74134600	0.20050300	N	-2.99440800	-0.37871500	-2.20904500
C	-0.10435200	-2.86456200	-0.57393300	H	-3.49968500	0.43782600	-1.88999700
H	0.96824200	-2.71465000	-0.71586300	N	-0.29864300	-1.07171700	1.40615100
H	-0.26297700	-3.80661500	-0.03459300	C	-0.54758900	-1.71967500	0.26247200
H	1.51209400	-0.87813400	1.12384800	C	0.37748200	-2.57723900	-0.35007300
O	2.52803200	-0.61301000	1.19241400	H	0.96090900	-3.19399300	0.33485800
C	3.12351400	-0.69067700	0.04000200	H	0.02693300	-3.11319900	-1.22869600
C	4.55936200	-0.12175200	0.11858000	H	0.66000100	-1.03177800	1.77417600
O	2.68377000	-1.11660200	-1.00665100	O	2.45167800	-0.80950200	1.48332800
F	4.51571300	1.20883100	0.31004200	C	2.97293700	-0.74347700	0.37341900
F	5.24569400	-0.66255800	1.13510800	C	4.37586500	-0.09768500	0.24832800
F	5.23202900	-0.35413200	-1.00761300	O	2.52527200	-1.14352600	-0.75473700
C	-2.26541500	-0.54583000	-1.38849700	F	4.83171000	0.33495600	1.42386700
H	-1.90866300	-1.28636800	-2.11781700	F	5.26174900	-0.97921300	-0.24171100
H	-0.58463700	-2.96844100	-1.55122700	F	4.33721700	0.95399800	-0.59029300
C	-1.45812700	0.71042800	-1.55692000	C	-1.67297900	-0.42987400	-1.63104900
C	-0.10630400	0.59158400	-1.89340000	H	-1.04393100	-1.07754200	-2.25713900
C	-1.97859700	1.98546600	-1.32375300	H	1.47375300	-1.76444400	-0.64044800
C	0.71244900	1.71346700	-1.97568600	C	-0.97168600	0.89320200	-1.48912500
H	0.32684500	-0.38712900	-2.08213900	C	0.38940500	0.96599100	-1.79344500

C	-1.61298300	2.04360500	-1.01745000	H	1.63788300	-0.76423400	-1.51415400
C	1.10378400	2.14690000	-1.60984300	C	-0.84568600	1.64830600	-0.53016300
H	0.90578200	0.08672100	-2.16549300	C	0.46740200	1.97697700	-0.87504000
C	-0.90570700	3.22962500	-0.84545600	C	-1.34257300	2.10104400	0.69786600
H	-2.66723000	2.02408300	-0.75914200	C	1.27725800	2.71296700	-0.01368000
C	0.45668000	3.28373300	-1.13422300	H	0.86261500	1.65401200	-1.83403600
H	2.16498100	2.17121500	-1.83768200	C	-0.53969200	2.84376300	1.55829900
H	-1.42077200	4.11167400	-0.47601900	H	-2.35564400	1.86187400	1.00407300
H	1.00900900	4.20782500	-0.99062500	C	0.77524500	3.14668100	1.20991200

Int9

C	-2.47723900	-0.77857100	0.37883000
C	-1.50279900	-1.39930700	1.16990200
C	-1.65797900	-1.55978300	2.53970600
C	-2.84691200	-1.10095300	3.11273400
C	-3.84926300	-0.52387400	2.33447000
C	-3.66679800	-0.36344600	0.95529300
H	-0.88979600	-2.03282200	3.14361200
H	-2.99676300	-1.21485100	4.18236400
H	-4.77567800	-0.19991900	2.79826300
H	-4.45464600	0.08342300	0.35482100
C	-1.95498600	-0.68437200	-1.03130600
C	-2.97508600	-1.06757200	-2.10741900
C	-3.73939000	0.24911500	-2.39824300
H	-3.63049100	-1.87666100	-1.77473200
H	-2.44965500	-1.41411200	-3.00282700
H	-4.74626700	0.24156300	-1.96752100
H	-3.85684800	0.38805400	-3.47893800
N	-2.95094800	1.34669600	-1.82959800
H	-3.40053700	1.75176800	-1.01764900
N	-0.46200100	-1.82343900	0.35469800
C	-0.67969400	-1.50602100	-0.96012500
C	0.14311100	-1.83360300	-1.99066600
H	0.92082700	-2.58054200	-1.85801700
H	-0.13477400	-1.58077100	-3.00728000
H	0.44458700	-2.13232400	0.68344300
O	2.45440400	-1.68118100	0.55584300
C	2.99266600	-0.87929100	-0.17215900
C	4.39367000	-0.31295000	0.15072100
O	2.54298000	-0.38104900	-1.29495000
F	4.83705600	-0.78410300	1.31150600
F	5.26516900	-0.65697600	-0.80840300
F	4.35907300	1.02514000	0.22193500
C	-1.65519600	0.80558700	-1.47754300
H	-1.06801400	0.69925700	-2.40127300

Int10

C	2.71698100	0.32329300	-1.26816100
C	2.42674000	1.69803300	-1.31743200
C	3.42494600	2.64325900	-1.09678400
C	4.72245700	2.18092000	-0.86719300
C	5.02401600	0.81806500	-0.85533300
C	4.00613100	-0.12376900	-1.03955400
H	3.20067300	3.70494800	-1.11783800
H	5.51716100	2.90382200	-0.70440300
H	6.04380000	0.48823900	-0.68446200
H	4.22514300	-1.18670600	-0.97522000
C	1.40094500	-0.40287200	-1.31514400
C	1.28852200	-1.77787700	-1.96848100
C	0.07406700	-2.44611000	-1.30142100
H	2.19637500	-2.35605300	-1.77490000
H	1.15507200	-1.69571100	-3.04962000
H	0.28448400	-3.46618500	-0.96823100
H	-0.80613700	-2.47569800	-1.94789200
N	-0.23280200	-1.58295800	-0.14499300
N	1.09468300	1.90293700	-1.63197000
C	0.46748600	0.68055300	-1.85104500
C	-0.75716000	0.53019600	-2.37680500
H	-1.33942300	1.39635100	-2.67038800
H	-1.20231200	-0.44573800	-2.52645200
C	0.89363100	-0.68516100	0.14700600
C	-1.41143900	-1.29069900	0.30918500
H	-1.44740800	-0.40505300	0.95208900
H	0.52192000	2.65828800	-1.21984900
O	-0.81599100	3.34261800	-0.26080700
C	-1.39033100	2.60204200	0.55326000
C	-2.80539200	3.06674100	1.01249600
O	-1.03572700	1.51652800	1.06693400

F	-3.16439300	4.26362400	0.54298900	N	-0.04669900	-1.72063000	0.03239800
F	-2.90992200	3.11035000	2.35315500	N	0.69834800	1.78648800	-1.54224700
F	-3.74805100	2.17912700	0.58004900	C	0.24594900	0.50652200	-1.67557700
H	0.47942000	0.23859400	0.57174700	C	-1.03499100	0.13725900	-1.95995300
C	1.90912800	-1.26927300	1.08981200	H	-1.79918300	0.89263200	-2.10829500
C	2.64629300	-0.36314200	1.85846500	H	-1.25679800	-0.86609000	-2.29785300
C	2.18422600	-2.63339900	1.20784500	C	1.01150400	-0.74619600	0.25236100
C	3.64887400	-0.80913500	2.71203800	C	-1.27958900	-1.24939600	0.16280400
H	2.43425700	0.69918900	1.77383200	H	-1.36845100	-0.31312700	0.72054600
C	3.18496100	-3.08228100	2.06766200	H	0.03408300	2.53870400	-1.23612200
H	1.61703400	-3.36643200	0.64244800	O	-1.22150700	3.26037800	-0.42384300
C	3.92402300	-2.17109900	2.81737300	C	-1.58024800	2.57019200	0.55418200
H	4.21497500	-0.08983300	3.29601700	C	-2.97932800	2.93462200	1.13089400
H	3.38371700	-4.14682100	2.15180700	O	-1.02735200	1.59705200	1.10267900
H	4.70485100	-2.52152400	3.48583400	F	-3.34415000	4.19922600	0.90030900
C	-2.66355100	-1.94031300	-0.00273400	F	-3.06933200	2.72148800	2.45145800
C	-3.81109900	-1.14750500	0.18129600	F	-3.91916500	2.13780200	0.54231900
C	-2.79993000	-3.27082800	-0.43678600	H	0.57148400	0.14787300	0.70864500
C	-5.06590400	-1.66101200	-0.11686700	C	2.16325100	-1.21569400	1.09619500
H	-3.70100100	-0.12494000	0.53164800	C	2.95761300	-0.22898400	1.69068700
C	-4.06095500	-3.78336000	-0.70593100	C	2.48270800	-2.55691400	1.31580900
H	-1.93307400	-3.91654900	-0.52089900	C	4.06026000	-0.57494100	2.46336200
C	-5.19123300	-2.97666800	-0.56021900	H	2.70659900	0.81788500	1.54251000
H	-5.94535500	-1.03725000	0.00635700	C	3.58700400	-2.90522800	2.09149700
H	-4.16672900	-4.81531900	-1.02548200	H	1.86042200	-3.34642600	0.90893300
H	-6.17414800	-3.38213800	-0.78144700	C	4.38349500	-1.91592900	2.66134500
TS7				H	4.66453500	0.20634900	2.91441000
C	2.56731900	0.48750800	-1.33275600	H	3.81727500	-3.95377900	2.25669000
C	2.06933900	1.80208600	-1.35633500	H	5.24258500	-2.18827800	3.26730400
C	2.91872800	2.89822000	-1.23678500	C	-2.50376000	-1.97831300	-0.11846800
C	4.28692800	2.64451300	-1.13519300	C	-3.68888700	-1.22431100	-0.18079200
C	4.79443700	1.34258500	-1.14813100	C	-2.57295400	-3.37624600	-0.23536500
C	3.92736200	0.24924200	-1.22966100	C	-4.90521600	-1.85068900	-0.40773500
H	2.52832900	3.91071000	-1.23432100	H	-3.64082200	-0.14635800	-0.05596200
H	4.97330200	3.48247700	-1.05283900	C	-3.79756300	-3.99822300	-0.44876700
H	5.86512000	1.17915700	-1.07807000	H	-1.68143800	-3.98211100	-0.11173800
H	4.31566000	-0.76486500	-1.19074900	C	-4.96170800	-3.23806700	-0.54902000
C	1.37989600	-0.41988600	-1.27104000	H	-5.81243400	-1.25739100	-0.46397100
C	1.39311400	-1.81602500	-1.87937700	H	-3.84519600	-5.08021800	-0.52489000
C	0.32280200	-2.60579800	-1.09369400	H	-5.91564200	-3.72831000	-0.71928000
H	2.38057900	-2.26677800	-1.74480700	Int11			
H	1.17001700	-1.79473600	-2.94952100	C	-1.07139700	-2.25744200	-0.82351100
H	0.69782700	-3.56571600	-0.73190400	C	0.29113400	-2.53808800	-0.63722400
H	-0.56949900	-2.80017200	-1.69015800	C	0.78072800	-3.83659500	-0.60277300

C	-0.13711500	-4.87251800	-0.78260200	C	-1.55703400	4.14045900	0.28075200
C	-1.49191100	-4.60612000	-0.99776300	C	0.75052300	3.99511400	-0.38375500
C	-1.97218700	-3.29369100	-1.02293900	C	-1.51600400	5.52272300	0.12627100
H	1.83796200	-4.03240300	-0.45238600	H	-2.46913300	3.64632400	0.60070600
H	0.20939700	-5.90152500	-0.76587100	C	0.79275200	5.38023800	-0.53448400
H	-2.18182500	-5.43102000	-1.14862700	H	1.65063800	3.41839200	-0.57395500
H	-3.02758600	-3.09607400	-1.18468400	C	-0.34034000	6.14888800	-0.28401500
C	-1.21696600	-0.77220400	-0.79077900	H	-2.40559600	6.11296400	0.32791400
C	-1.94249100	-0.07423600	-1.94443400	H	1.71723100	5.85639900	-0.84815600
C	-2.20619500	1.34777700	-1.39921900	H	-0.30740200	7.22773100	-0.40511200
H	-2.87805200	-0.60368600	-2.15040000	TS8			
H	-1.34750400	-0.07710200	-2.86276100	C	2.45027800	-0.12703100	-1.51679100
H	-3.25825300	1.62023800	-1.51977000	C	2.08687800	1.23409300	-1.64188800
H	-1.62457000	2.11482900	-1.91642100	C	3.03037700	2.25656300	-1.64193600
N	-1.83603000	1.33748400	0.03036700	C	4.36788100	1.88717900	-1.53384800
N	1.04293600	-1.34511400	-0.52269000	C	4.74793000	0.54013000	-1.42705600
C	0.22737400	-0.34883600	-0.65236100	C	3.79824800	-0.47614900	-1.41314400
C	0.57988200	1.08845400	-0.59065900	H	2.73004300	3.29678300	-1.71796600
H	1.59252500	1.21299100	-0.19919700	H	5.13316700	2.65753700	-1.53262100
H	0.56648300	1.48357600	-1.61739300	H	5.80153000	0.28997900	-1.34644000
C	-1.89194000	-0.05359600	0.45298200	H	4.10098800	-1.51417600	-1.30963200
C	-0.48092800	1.86104900	0.24345900	C	1.21486100	-0.87199500	-1.42994000
H	-0.25694800	1.68067900	1.30360900	C	1.00572600	-2.34531600	-1.56717500
H	2.55108000	-1.34059000	-0.23640700	C	-0.18951100	-2.80161500	-0.67981000
O	3.57414200	-1.47056700	-0.04170600	H	1.92299600	-2.86312100	-1.26862700
C	4.15194900	-0.37277600	0.34669800	H	0.80538500	-2.62156500	-2.60902400
C	5.65016600	-0.61674500	0.64485400	H	0.05141400	-3.72573700	-0.15248900
O	3.66285700	0.72763000	0.48475500	H	-1.08241700	-3.01083300	-1.27301300
F	5.79507400	-1.52553200	1.62275500	N	-0.53247400	-1.72099600	0.25287900
F	6.25422900	0.50586300	1.02918400	N	0.70453900	1.32326800	-1.71719500
F	6.28225700	-1.07967000	-0.44551400	C	0.18220100	0.09948800	-1.61237600
H	-1.26213600	-0.18569600	1.34033000	C	-1.26511000	-0.20252600	-1.56735900
C	-3.27173400	-0.55855300	0.79871900	H	-1.85129800	0.71019200	-1.69625800
C	-3.40462500	-1.82091700	1.38770300	H	-1.50742200	-0.88812400	-2.38981800
C	-4.41777900	0.21349700	0.60263700	C	0.53435400	-0.95344900	0.61664600
C	-4.65788200	-2.31738800	1.73134000	C	-1.64612500	-0.88749300	-0.21240000
H	-2.51866300	-2.41825800	1.58362600	H	-1.74682200	-0.07822700	0.51870300
C	-5.67452600	-0.28301300	0.94429400	H	0.12155500	2.19973700	-1.47387500
H	-4.32127200	1.22127000	0.21450100	O	-0.75394200	3.27298400	-0.84595600
C	-5.80061000	-1.55323200	1.49994700	C	-1.02985200	2.93999700	0.33547800
H	-4.74046900	-3.29916800	2.18875200	C	-1.84375300	3.97900100	1.15489300
H	-6.55573000	0.33193000	0.78499000	O	-0.76221600	1.88882600	0.94047800
H	-6.77994700	-1.93870200	1.76804500	F	-2.04086700	5.13290500	0.50684000
C	-0.42594500	3.35905700	0.02231500	F	-1.22562900	4.26903200	2.31430200

F	-3.05944900	3.47852200	1.46197200	C	-0.79658400	-1.19285500	-1.62841400
H	0.27956200	0.08263000	0.85722200	C	0.63602800	-0.89925700	-1.92912300
C	-2.94113100	-1.66392700	-0.26094200	H	0.89475000	-1.13914700	-2.96835100
C	-3.20437100	-2.62694800	0.72003600	H	0.79062400	0.17694800	-1.79644900
C	-3.91889900	-1.40435900	-1.22373300	C	1.00571800	-0.60108900	1.04920700
C	-4.40960500	-3.32107900	0.72916700	C	1.59151500	-1.67696200	-1.01716700
H	-2.45388500	-2.82583600	1.47964700	H	1.60835200	-2.72587700	-1.31759600
C	-5.12971600	-2.09522200	-1.21152000	H	-1.52067000	0.71053100	-2.14458300
H	-3.75294100	-0.65048300	-1.98698900	O	0.69975400	1.96483300	-0.39067900
C	-5.37777300	-3.05862900	-0.23884000	C	-0.16776700	2.63685700	-0.99746200
H	-4.59506000	-4.06624900	1.49744700	C	-0.39086400	4.04980700	-0.38297600
H	-5.87939500	-1.87578800	-1.96605600	O	-0.86053900	2.34626400	-1.98562400
H	-6.31996200	-3.59854300	-0.23125200	F	-0.72257100	3.94402300	0.92936800
C	1.73649200	-1.45692300	1.28294900	F	-1.36315900	4.74724000	-0.97576700
C	2.73275700	-0.51792600	1.59577000	F	0.73299300	4.79069700	-0.44244400
C	1.92267700	-2.79284500	1.66565300	H	1.37311500	0.27869200	0.52085800
C	3.89682100	-0.91021500	2.24341000	C	0.49804500	-0.35471600	2.38112800
H	2.58480900	0.52320100	1.32288600	C	0.04341300	0.95835200	2.60246700
C	3.08671000	-3.18046200	2.31990100	C	0.48564600	-1.28610400	3.43498300
H	1.14141600	-3.52470000	1.49661800	C	-0.48714100	1.30754600	3.83759600
C	4.08084100	-2.24437600	2.60177300	H	0.10157500	1.67874100	1.78885300
H	4.65847500	-0.17105900	2.47131200	C	-0.01685700	-0.91555300	4.67355600
H	3.21236800	-4.21582800	2.62256300	H	0.91205700	-2.27529800	3.30576900
H	4.98868300	-2.55209400	3.11217200	C	-0.52069700	0.37256100	4.86986500
Int12				H	-0.86079500	2.31438000	3.99388400
C	-2.76909000	-2.00090400	-0.88695500	H	-0.01127100	-1.62814100	5.49239600
C	-2.97268100	-0.72377000	-1.47670200	H	-0.92360500	0.65003000	5.83957000
C	-4.23113800	-0.12113200	-1.52318200	C	3.02276300	-1.19133600	-1.02270600
C	-5.29770000	-0.81866600	-0.97417500	C	3.35446100	0.16538500	-1.09730300
C	-5.11938000	-2.08997500	-0.39549600	C	4.04686500	-2.13933500	-0.93305700
C	-3.86807500	-2.68635100	-0.34744600	C	4.69130700	0.55711400	-1.06885000
H	-4.36406900	0.85958700	-1.96996400	H	2.58008300	0.92702600	-1.16497200
H	-6.28958100	-0.37673000	-0.99276400	C	5.38144000	-1.74613900	-0.90806900
H	-5.97846700	-2.61015300	0.01841600	H	3.79672200	-3.19755300	-0.88978100
H	-3.74733300	-3.67013500	0.10029300	C	5.70556900	-0.39259400	-0.97416100
C	-1.36535400	-2.27909800	-0.99234000	H	4.93563400	1.61369500	-1.12437200
C	-0.60532500	-3.41674000	-0.39186100	H	6.16558900	-2.49470700	-0.84314000
C	0.31131100	-2.93368000	0.74692700	H	6.74552700	-0.07998600	-0.95742600
H	-0.03111500	-3.97691000	-1.13963000	5a'-TFA			
H	-1.29518800	-4.14204700	0.05239800	C	3.84694600	-0.69900200	0.11647700
H	1.05043500	-3.69548000	1.02434200	C	4.34869800	0.34609400	-0.69990900
H	-0.30021000	-2.69766100	1.61706900	C	5.70293400	0.46436200	-1.01488400
N	1.02220300	-1.70363100	0.37025900	C	6.56439600	-0.49278300	-0.49789400
N	-1.75989200	-0.26985400	-1.93090600	C	6.08912500	-1.54072500	0.31270000

C	4.74265300	-1.65247000	0.62321000	C	1.56248500	-3.18509000	-2.30420200
H	6.07145100	1.27133000	-1.64201500	C	0.92009400	-4.42500000	-2.28612400
H	7.62461900	-0.43284700	-0.72452300	C	-0.37788900	-4.55635400	-1.79116900
H	6.79170100	-2.27379900	0.69751800	C	-1.06649000	-3.45055000	-1.28305300
H	4.38957100	-2.47018400	1.24573600	H	2.56475600	-3.07135400	-2.70481800
C	2.42785700	-0.50531000	0.22941000	H	1.43809300	-5.29689800	-2.67380900
C	1.46119400	-1.37698200	0.96424700	H	-0.86039500	-5.52875600	-1.80153700
C	0.47969900	-0.63105800	1.85430500	H	-2.07786900	-3.55834400	-0.90448700
H	2.01827100	-2.06194300	1.61212900	C	-0.88954400	-0.84562000	-0.86386600
H	0.89301600	-2.01085000	0.26975100	C	-2.07515800	-0.34654100	-1.70939200
H	1.00588100	0.01894400	2.56237200	C	-2.53145600	0.91966800	-0.96630500
H	-0.12916400	-1.34616400	2.41449400	H	-2.84654100	-1.12326600	-1.70667500
N	-0.49541000	0.18846800	1.09046200	H	-1.78783400	-0.16338200	-2.74884500
N	3.27691800	1.12850800	-1.05499000	H	-3.60695400	0.88666600	-0.76901000
C	2.12098100	0.61730200	-0.50152500	H	-2.34387200	1.82767800	-1.54094800
C	0.80067900	1.26459000	-0.74489800	N	-1.78447600	0.97046400	0.30395100
H	0.94860400	2.24746100	-1.20472500	N	1.27394500	-0.76053700	-1.72219300
H	0.20309300	0.67898000	-1.45689800	C	0.34488100	-0.01142700	-1.12787100
C	-0.02968700	1.48582500	0.52464300	C	0.55280400	1.25554000	-0.55866900
H	0.60299900	1.96579000	1.28123700	H	1.47208300	0.84030300	0.30460600
H	3.32074700	1.94729000	-1.63812500	H	1.23662800	1.93174900	-1.07182800
H	-0.97442500	-0.48410600	0.29602100	C	-1.34327100	-0.39936300	0.57349500
H	-1.30072800	0.35762000	1.69836500	C	-0.60415200	1.86290300	0.24347900
O	-2.80938500	-1.43509200	1.45858000	H	-0.26312000	1.94394300	1.28568700
C	-2.66468700	-1.69818700	0.26513700	H	2.26149500	-0.46013700	-1.68962900
C	-3.74907200	-2.53963000	-0.45263400	O	3.67473100	0.10512500	-0.74758500
O	-1.71660000	-1.33434400	-0.50750800	C	3.51683300	0.28449100	0.46166500
F	-4.67150500	-3.00973200	0.38957200	C	4.76412700	0.24951000	1.38006100
F	-4.38441700	-1.78326000	-1.37258900	O	2.44078400	0.51868300	1.10181600
F	-3.20898400	-3.58832900	-1.09613600	F	5.85883100	-0.13936600	0.72366200
C	-1.22754800	2.36524000	0.25507700	F	4.57934700	-0.59410000	2.40792000
C	-1.29485200	3.63652000	0.82856300	F	4.99923000	1.47182900	1.88808200
C	-2.26568400	1.93356200	-0.57838400	H	-0.47584200	-0.37080000	1.24316800
C	-2.38101100	4.47082500	0.57351900	C	-2.38600600	-1.27890800	1.21784300
H	-0.49319500	3.97642100	1.48051400	C	-2.02106200	-2.55949400	1.64757400
C	-3.35408600	2.76518900	-0.82509200	C	-3.68814300	-0.83656200	1.45297400
H	-2.23543600	0.94180100	-1.02356900	C	-2.94951000	-3.39593200	2.25881000
C	-3.41332300	4.03495500	-0.25332200	H	-0.99875100	-2.90120400	1.50882100
H	-2.42270600	5.45696400	1.02649700	C	-4.62074200	-1.67428800	2.06272300
H	-4.15944600	2.41545500	-1.46393300	H	-3.95718100	0.18092900	1.19074500
H	-4.26464400	4.68048100	-0.44782700	C	-4.25851400	-2.95905600	2.45827700
TS9				H	-2.64749200	-4.38587400	2.58877100
C	-0.42537100	-2.22077400	-1.25522700	H	-5.63069600	-1.31501200	2.23897700
C	0.86431100	-2.10589700	-1.78727000	H	-4.98503600	-3.61000400	2.93583900

C	-1.01868800	3.26124500	-0.16270200	F	4.25916700	-1.53121800	-1.98360400
C	-1.81066800	3.99514500	0.72678100	H	-0.12793900	0.45079300	-1.15115900
C	-0.67254500	3.83977700	-1.38388900	C	-0.88704600	2.41645700	-1.14532700
C	-2.24439300	5.27587000	0.40474000	C	0.28095300	3.05708600	-1.57423300
H	-2.09117800	3.54436900	1.67540600	C	-2.11438800	3.04059600	-1.37039000
C	-1.10428600	5.12559900	-1.71075200	C	0.22715000	4.31040900	-2.17534600
H	-0.06719000	3.28569000	-2.09563400	H	1.24129900	2.56660500	-1.43705100
C	-1.89041600	5.84706200	-0.81814600	C	-2.17110400	4.29792500	-1.96998800
H	-2.85591700	5.83254100	1.10915000	H	-3.02977600	2.52327900	-1.10496300
H	-0.82352300	5.56078100	-2.66561300	C	-1.00157100	4.94120600	-2.36616000
H	-2.22410700	6.84942900	-1.07017300	H	1.14482700	4.79093600	-2.50276300
Int13				H	-3.13524600	4.76994100	-2.13712600
C	1.06144900	1.68894400	1.40519600	H	-1.04698100	5.91946800	-2.83596300
C	1.85131300	0.71627900	2.03578000	C	-3.09766800	-1.83986800	0.01158800
C	3.07843800	1.02066900	2.60860400	C	-4.12904800	-1.73141600	-0.92720900
C	3.50750200	2.34885100	2.55065400	C	-3.30393300	-2.61666600	1.15097200
C	2.71853600	3.33603300	1.96193800	C	-5.33924000	-2.38614700	-0.73088900
C	1.48073600	3.01069400	1.39654500	H	-3.97433200	-1.11404700	-1.80845300
H	3.68173500	0.25600400	3.08864800	C	-4.51694400	-3.27722900	1.35022700
H	4.46751400	2.61452900	2.98353700	H	-2.51658500	-2.69894400	1.89511600
H	3.06471200	4.36470300	1.94294200	C	-5.53683600	-3.16450100	0.41080500
H	0.86515900	3.78312900	0.94626500	H	-6.13090400	-2.29200900	-1.46893900
C	-0.21973600	1.03821800	0.95718300	H	-4.66228300	-3.87800600	2.24363500
C	-1.45737500	1.51764100	1.73144000	H	-6.48111200	-3.67881900	0.56454900
C	-2.61593500	0.87780000	0.94907600	H	1.70294600	-1.39135600	2.08351400
H	-1.49335000	2.61165600	1.69501800	Int14			
H	-1.42444700	1.21334000	2.78129500	C	-3.29561200	0.34553200	-0.00064700
H	-3.40538000	1.60622300	0.74084400	C	-3.93212200	1.34603400	-0.74965200
H	-3.07903600	0.05896800	1.50209500	C	-5.28182400	1.26829900	-1.06664700
N	-2.05053100	0.36108700	-0.31749500	C	-5.99003100	0.15128200	-0.61530000
N	1.19344000	-0.51885000	2.01748400	C	-5.37185500	-0.84410600	0.13991200
C	0.05742500	-0.43509700	1.24504900	C	-4.01358500	-0.74518100	0.46110600
C	-0.66291900	-1.43669700	0.68793700	H	-5.77391600	2.04486400	-1.64474800
H	-0.43628800	-2.47994300	0.90135200	H	-7.04512100	0.06298900	-0.85759400
C	-0.77127600	1.05680300	-0.50343500	H	-5.94522200	-1.70090100	0.47895900
C	-1.80394000	-1.09447100	-0.25297300	H	-3.52655800	-1.51864700	1.04737300
H	-1.50363100	-1.38096300	-1.27467700	C	-1.86933300	0.76232300	0.22161200
H	0.89094000	-1.54986500	-0.47816100	C	-1.53104700	1.12932900	1.67679600
O	1.64315900	-1.72349500	-1.11555000	C	-0.00591600	1.27392700	1.65668900
C	2.60921000	-2.36750900	-0.50242600	H	-1.85481100	0.31887100	2.33709500
C	3.76453900	-2.67073900	-1.48145900	H	-2.03501700	2.04703300	1.98902900
O	2.64969900	-2.70243200	0.65732300	H	0.49534100	0.73398700	2.46186400
F	3.32866500	-3.42420800	-2.49978200	H	0.32120000	2.31186000	1.70749600
F	4.74496600	-3.32073900	-0.86357100	N	0.43866300	0.70034100	0.34733700

N	-3.02215000	2.36208900	-1.05902700	C	2.54160300	-4.25870700	0.23069400
C	-1.74044500	1.97516500	-0.69283300	C	2.68984900	-2.86655000	0.26598200
C	-0.55357100	2.44508800	-1.09875900	H	-0.82159500	-4.48746200	-0.37630100
H	-0.47292500	3.25670400	-1.81612300	H	1.19354400	-5.91426300	-0.01277500
C	-0.69172300	-0.15572500	-0.15524300	H	3.40626100	-4.89504300	0.39131300
C	0.72786100	1.77363400	-0.68124400	H	3.65994700	-2.42300800	0.46867400
H	1.14878600	1.20430400	-1.52247900	C	1.33408100	-0.59625100	0.14464900
H	1.36848000	0.04980700	0.43875400	C	1.29184300	-0.16584900	1.63291900
O	1.82858900	-1.09725400	-1.69359600	C	1.22038500	1.35811900	1.56832800
C	2.43219000	-1.42924200	-0.67323400	H	2.20911400	-0.51372700	2.11836500
C	3.32103300	-2.69776300	-0.71354100	H	0.43781600	-0.60476900	2.15346500
O	2.42600700	-0.86119300	0.46491800	H	1.84716000	1.85723600	2.31260600
F	3.34017500	-3.27258600	-1.92000400	H	0.19041500	1.71199600	1.69456600
F	2.87756300	-3.61607800	0.16608800	N	1.65327200	1.68506800	0.19830400
F	4.59429200	-2.40482000	-0.38413800	N	-0.64582900	-1.68970900	-0.40687300
H	-0.57734200	-0.22253800	-1.23792500	C	-0.09736000	-0.46712000	-0.38284800
C	-0.74461300	-1.56000400	0.38247300	C	-0.72625300	0.73560300	-0.60368200
C	-1.25106100	-2.53404000	-0.48427800	H	-1.81323700	0.75609100	-0.50715600
C	-0.37236100	-1.94388400	1.67275300	C	2.24161400	0.49228000	-0.45855100
C	-1.40614500	-3.85176900	-0.06881900	C	-0.00109900	1.93590800	-0.86250300
H	-1.51840800	-2.25405500	-1.49949400	H	0.65054300	1.99082500	-1.73806900
C	-0.51770100	-3.26483500	2.08855800	H	2.22987000	2.51874600	0.12500500
H	0.07062400	-1.23303900	2.35988500	O	-3.19521300	-2.04210800	-0.57137500
C	-1.04231700	-4.22117800	1.22396400	C	-3.89393200	-1.09994900	-0.11042400
H	-1.79634000	-4.59182800	-0.76099100	C	-5.40601900	-1.43289500	0.03851500
H	-0.20421300	-3.54696400	3.08910800	O	-3.55624500	0.02834600	0.27062900
H	-1.14829600	-5.25176100	1.54925400	F	-5.80831500	-2.44314300	-0.74644400
C	1.80236700	2.71612100	-0.17871900	F	-6.18341000	-0.37447500	-0.24680400
C	3.12864500	2.27583500	-0.11939000	F	-5.67365300	-1.79030800	1.31548000
C	1.50129700	4.01853800	0.22704500	H	2.05933500	0.57018500	-1.53617200
C	4.13006100	3.12025000	0.34906900	C	3.72473200	0.30998500	-0.26131400
H	3.37179600	1.26240000	-0.42408900	C	4.44420000	-0.34835900	-1.26387700
C	2.50451700	4.86618500	0.69272800	C	4.40365100	0.74064700	0.88116400
H	0.47355300	4.36915100	0.17491200	C	5.80630800	-0.58962200	-1.12088200
C	3.82122500	4.41759300	0.75601200	H	3.92544700	-0.68807500	-2.15707700
H	5.15467200	2.76324500	0.39376200	C	5.77013500	0.50642500	1.02360700
H	2.25614600	5.87691700	1.00372500	H	3.87433300	1.26267200	1.67263800
H	4.60521800	5.07686600	1.11726500	C	6.47365300	-0.16372400	0.02662200
H	-3.17587400	2.98820800	-1.83374100	H	6.34742700	-1.10781600	-1.90690300
TS10				H	6.28334100	0.84710100	1.91796200
C	1.57686800	-2.07575500	0.03536000	H	7.53759500	-0.34849600	0.13991100
C	0.32050200	-2.66716200	-0.19211700	C	-0.59183100	3.23256500	-0.50754700
C	0.15535900	-4.04653200	-0.20647900	C	-0.02405100	4.41092800	-1.01507500
C	1.29048600	-4.83256300	0.00155200	C	-1.68820100	3.32082500	0.36420200

C	-0.53407100	5.65316500	-0.66024200	C	2.40028300	-0.83469500	1.52017400
H	0.81750500	4.34448100	-1.70230000	C	1.40969900	-0.08116000	2.15834300
C	-2.20255900	4.56566600	0.71037700	C	3.73803900	-0.58424300	1.83095500
H	-2.15436900	2.41514700	0.74403400	C	1.74763600	0.92065700	3.06256800
C	-1.62552300	5.73043400	0.20593200	H	0.36196600	-0.27872000	1.94462400
H	-0.09063200	6.55930300	-1.06203400	C	4.07865000	0.41069300	2.74332400
H	-3.06175100	4.62486900	1.37139600	H	4.53212300	-1.16385700	1.36978100
H	-2.03093300	6.69980700	0.48109900	C	3.08596700	1.17234000	3.35489900
H	-1.71537800	-1.85095600	-0.53256600	H	0.96371500	1.50160700	3.53903900
Int15				H	5.12436800	0.59181900	2.97409200
C	2.58402200	-0.08296900	-1.27128900	H	3.35358600	1.95295900	4.06075500
C	1.87030000	1.11755600	-1.19544400	C	-2.64723500	-2.75049600	-0.11914800
C	2.46548500	2.36057600	-1.36179000	C	-2.84524200	-4.13748000	-0.01930200
C	3.83427100	2.37261300	-1.62748600	C	-3.74045800	-1.89030500	0.09857600
C	4.56012900	1.18295300	-1.73281200	C	-4.09732800	-4.65949800	0.28208100
C	3.93936400	-0.05803100	-1.55860600	H	-2.00370300	-4.80721900	-0.18154800
H	1.88343100	3.27377800	-1.28991700	C	-4.98811200	-2.41707500	0.40027100
H	4.34204800	3.32208600	-1.76597900	H	-3.61647300	-0.81240500	0.03885500
H	5.62165800	1.22337400	-1.95737100	C	-5.17261900	-3.79854500	0.49239700
H	4.51670200	-0.97361500	-1.65945600	H	-4.23441200	-5.73421000	0.35502800
C	1.63336900	-1.20011200	-0.95536700	H	-5.82387900	-1.74452400	0.56799700
C	1.74188400	-2.42741400	-1.88410700	H	-6.15298100	-4.20100900	0.73026400
C	2.35772600	-3.54299600	-0.99770800	H	-0.28792600	1.68356000	-0.79683200
H	2.39344100	-2.18380900	-2.72760200	TS11			
H	0.77389400	-2.71306000	-2.30354700	C	2.37153200	-1.51326400	-1.13470000
H	3.12972300	-4.12074600	-1.51158600	C	2.16672800	-0.14770400	-1.41523300
H	1.57849800	-4.24945500	-0.68529800	C	3.21665600	0.73659800	-1.63895300
N	2.89831100	-2.90548100	0.19342200	C	4.50447100	0.21122000	-1.59451700
N	0.52346000	0.84069200	-0.95364100	C	4.72890300	-1.14948400	-1.33894100
C	0.32498500	-0.45712700	-0.86627400	C	3.66856700	-2.02329300	-1.10430500
C	-0.98760900	-0.95496800	-0.59910200	H	3.02940900	1.78811800	-1.83097400
H	-1.74802300	-0.17970600	-0.49731400	H	5.35273600	0.86679400	-1.76618600
C	1.97747900	-1.84094600	0.48973100	H	5.74721500	-1.52670100	-1.32605300
C	-1.31709600	-2.25911500	-0.43644900	H	3.85749700	-3.07724900	-0.91289000
H	-0.55569500	-3.03027000	-0.53934300	C	1.07085700	-2.07973300	-0.81913700
H	3.82673700	-2.53812500	0.01033300	C	0.84678100	-3.56515500	-0.80106600
O	-1.05377300	2.73177500	-0.61501600	C	0.77104900	-4.07910200	0.67172100
C	-2.26379400	2.54543700	-0.26955700	H	1.68902900	-4.04540100	-1.30930000
C	-3.01732100	3.87914800	-0.02329000	H	-0.05096300	-3.85192700	-1.35538900
O	-2.87507100	1.49177000	-0.10728300	H	1.20826400	-5.07218700	0.79281100
F	-2.97708900	4.66706300	-1.11286300	H	-0.27413000	-4.13557400	0.99559300
F	-2.45131900	4.56184700	0.99099700	N	1.44739900	-3.12416200	1.52262400
F	-4.30238900	3.68673200	0.28885500	N	0.80828100	0.10251800	-1.38921400
H	1.04189900	-2.30286600	0.82854100	C	0.13046900	-1.01569400	-1.09505700

C	-1.29136300	-0.93314600	-0.91656100	H	-5.41831300	2.14446200	-1.08278800
H	-1.69587400	0.06845500	-1.03389100	H	-7.34844900	0.69638100	-0.50220900
C	1.00827200	-1.85643800	1.25938100	H	-7.04119900	-1.71323400	-0.05596900
C	-2.10582600	-1.93249300	-0.51050900	H	-4.79940400	-2.75588700	-0.19894800
H	-1.71701800	-2.94256200	-0.39764600	C	-2.41719900	-1.15428300	-0.87976800
H	2.45496100	-3.22740200	1.55234500	C	-1.72805500	-2.44089600	-0.59848400
O	-0.06522300	2.51736700	-1.34415200	C	-1.53335900	-2.66191900	0.92499100
C	-0.95426700	2.75059100	-0.48135300	H	-0.74251800	-2.48565800	-1.07073000
C	-1.16003500	4.25924500	-0.17213500	H	-2.31766900	-3.28499000	-0.97498200
O	-1.63711000	1.95693400	0.17854200	H	-0.99455000	-3.59493900	1.10421900
F	-0.90341800	5.05168700	-1.22113000	H	-2.50438800	-2.70460500	1.42990500
F	-0.31679200	4.63079200	0.82453800	N	-0.75001400	-1.57596200	1.47067600
F	-2.40436900	4.53048700	0.24334700	N	-2.78639100	1.04187300	-1.21795500
H	-0.07818200	-1.77120200	1.29274300	C	-1.81063200	0.06300200	-1.18237200
C	1.73253900	-0.65406900	1.64435800	C	-0.40855400	0.34230900	-1.35313400
C	1.02979800	0.56114500	1.63785000	H	0.23157100	-0.53435500	-1.42687600
C	3.10906600	-0.65063600	1.91866100	C	-1.30560300	-0.43808000	1.72102600
C	1.69437100	1.75697300	1.88772700	C	0.13233400	1.57910800	-1.32592600
H	-0.03433800	0.58328800	1.41233600	H	-0.51850300	2.44135300	-1.17354500
C	3.76656200	0.54398100	2.17015100	H	0.34427100	-1.71734500	1.41454900
H	3.67975700	-1.57466000	1.91763600	O	1.58196200	-2.23869800	-0.89117400
C	3.06213200	1.74973400	2.14741600	C	2.20759300	-2.16917000	0.16864600
H	1.14223800	2.69101200	1.86329200	C	3.75151800	-2.32861100	0.11001500
H	4.83339200	0.53978900	2.37160000	O	1.77230200	-1.98809400	1.34409900
H	3.58365900	2.68442600	2.33170300	F	4.22727200	-2.22427300	-1.13901900
C	-3.52014400	-1.76987800	-0.20044000	F	4.12033800	-3.53421000	0.58328100
C	-4.33612900	-2.90840400	-0.11195800	F	4.37453000	-1.39536700	0.85229000
C	-4.08961300	-0.50537300	0.03558500	H	-2.39614800	-0.40599900	1.70653400
C	-5.69236300	-2.79267900	0.17059400	C	-0.62221700	0.80675200	1.99827800
H	-3.89994000	-3.89064500	-0.28035200	C	-1.42334700	1.95310900	2.11713000
C	-5.44402300	-0.39607100	0.32170800	C	0.77690800	0.92269800	2.06222600
H	-3.46658000	0.38607000	0.02830000	C	-0.83806800	3.20082500	2.29372200
C	-6.25067500	-1.53381600	0.38466000	H	-2.50459600	1.85844100	2.05247500
H	-6.31260200	-3.68245600	0.22650800	C	1.35245400	2.17189400	2.24040100
H	-5.87109600	0.58459800	0.50929700	H	1.40807800	0.04437200	1.95759800
H	-7.30867900	-1.43900800	0.61119400	C	0.55061600	3.30884800	2.35463500
H	0.37547800	1.10648300	-1.41214000	H	-1.46084100	4.08570300	2.38360900
Int16				H	2.43351100	2.26229300	2.27091000
C	-3.81815800	-0.89215900	-0.71676300	H	1.01220600	4.28328000	2.48654600
C	-4.01706300	0.49308600	-0.95219500	C	1.55081200	1.90545100	-1.40133500
C	-5.27808600	1.08490900	-0.88805100	C	2.54426600	0.94120400	-1.64307900
C	-6.35294400	0.26693700	-0.56201600	C	1.94926200	3.23336800	-1.18266100
C	-6.17753100	-1.10561100	-0.30850600	C	3.88626900	1.29721700	-1.64142700
C	-4.92228700	-1.69184100	-0.38355300	H	2.27026100	-0.09376800	-1.82460800

C	3.29383900	3.58978200	-1.18835000	H	0.56728700	-1.66058500	1.11581700
H	1.19003600	3.98960700	-0.99513200	H	-0.74274500	-2.51689100	2.36082300
C	4.26907600	2.62049600	-1.41295000	O	1.57931900	-1.43971700	0.73464600
H	4.63783100	0.53334100	-1.81659200	H	-1.26134700	-1.07582300	1.76196800
H	3.58030900	4.62357700	-1.01592300	C	2.15629100	-2.52105000	0.30321600
H	5.32064600	2.89222900	-1.41387100	C	3.55196400	-2.21034900	-0.28685400
H	-2.63174600	1.98280300	-1.53858600	F	3.42097900	-1.47404700	-1.40655100
5a-TFA				F	4.21360800	-3.32170600	-0.59660700
C	-3.75041900	-0.30604300	-0.32876400	F	4.30007600	-1.50419800	0.57740200
C	-4.02147600	1.04759200	-0.00114300	O	1.71711900	-3.65130600	0.30258800
C	-5.31915600	1.51839000	0.20041600				
C	-6.35805100	0.60678600	0.06757700				
C	-6.11347200	-0.73962600	-0.26193600				
C	-4.82210300	-1.20296600	-0.46165400				
H	-5.51325200	2.55781900	0.44934400				
H	-7.38032200	0.94070700	0.21785300				
H	-6.95204300	-1.42200500	-0.36266000				
H	-4.64460200	-2.24309700	-0.72190700				
C	-2.32916700	-0.43303600	-0.46377900				
C	-1.59261900	-1.69572100	-0.77493400				
C	-1.47837800	-2.62563700	0.43489500				
H	-0.58957600	-1.47509100	-1.15467000				
H	-2.10953600	-2.24056700	-1.57387700				
H	-0.89419600	-3.51298300	0.17469400				
H	-2.47714300	-2.94151800	0.75983000				
N	-0.76827300	-1.93675200	1.52668700				
N	-2.81714000	1.70053700	0.05915500				
C	-1.78455000	0.82098000	-0.21302200				
C	-0.39701100	1.20607400	-0.20914700				
H	0.30283000	0.39530700	-0.38841700				
C	0.08769400	2.44866000	-0.00173900				
H	-0.60428800	3.27971100	0.14052200				
H	-2.69774400	2.67248800	0.28632100				
C	1.49885800	2.82046700	0.03153100				
C	1.84842100	4.17927200	-0.00454700				
C	2.53039900	1.86845900	0.10631200				
C	3.18112100	4.57776900	0.00980200				
H	1.06182900	4.92903200	-0.05337900				
C	3.85986700	2.26798800	0.11973600				
H	2.29459500	0.81159000	0.17764700				
C	4.19352700	3.62260800	0.06834700				
H	3.42892500	5.63485400	-0.02452900				
H	4.64013800	1.51481400	0.18017300				
H	5.23516800	3.92979700	0.08160100				

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