Supporting Information

Total Synthesis of Aspidostomide G from a Brominated Tryptamine

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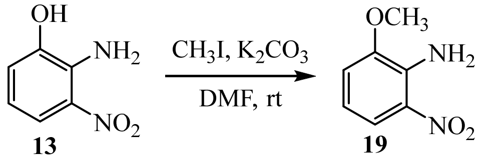
A. General Information

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol-400 MHz spectrometer. Chloroform-*d* (δ = 7.24) or DMSO-d_6 (δ = 2.49) or acetone-d_6 (δ = 2.05) was used as internal standard in ^{1}H NMR spectra. The center peak of chloroform-*d* (δ = 77.0) or DMSO-d_6 (δ = 39.5) or acetone-d_6 (δ = 29.9) was used as internal standard in ^{13}C NMR spectra. High-resolution mass spectrometry (HRMS) analyses were determined on a Thermo Scientific Orbitrap LTQ XL mass spectrometer. Melting points were measured on a melting point apparatus with a capillary melting point tube. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light at 254 nm and/or immersion in a staining solution (phosphomolybdic acid, potassium permanganate, ninhydrin, or *p*-anisaldehyde) followed by heating on a hot plate. Flash chromatography was carried out utilizing silica gel 60, 70-230 mesh ASTM.

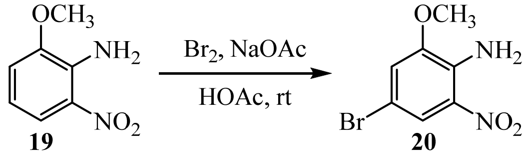
B. Experimental section



Compound 19.[S1]

To the flask was added 2-amino-3-nitrophenol (**13**) (15.4 g, 100 mmol), potassium carbonate (27.6 g, 200 mmol, 2 equiv) and DMF (100 mL). The mixture was then stirred at room temperature for 3 h. Once the reaction was complete (monitored by TLC), ice water (500 mL) was poured into the mixture and the product was precipitated. The solid was collected by filtration through a Büchner funnel to give the title compound as a yellow solid (15.3 g, 91%).

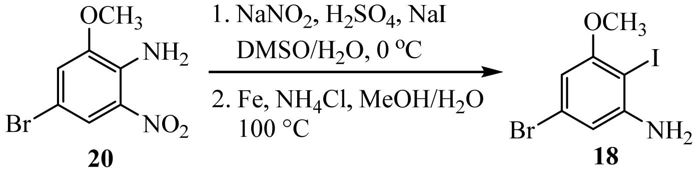
R*f*: 0.2 (hexanes/EtOAc = 3:1). M.p. 62.5–63.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.9, 1.2 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.53 (dd, *J* = 8.9, 7.7 Hz, 1H), 6.40 (s, 2H), 3.85 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 148.0, 136.9, 131.3, 117.0, 114.4, 113.1, 56.1. HRMS (EI): calculated for $C_7H_8N_2O_3$ (M^+), 168.0535, found 168.0543.



Compound 20.[S2]

To the flask was added compound **19** (16.8 g, 100 mmol), sodium acetate (16.4 g, 200 mmol, 2 equiv) and acetic acid (100 mL). The mixture was stirred for 10 min until all solids were dissolved. A solution of bromine (5.1 mL, 100 mmol, 1 equiv) in acetic acid (100 mL) was added dropwise into the previous mixture in an ice-water bath. The reaction was warmed to room temperature and stirred for an additional hour. Ice water (500 mL) was poured into the mixture and the product precipitated. The solid was collected by filtration through a Büchner funnel to give the title compound as a red solid (23.6 g, 96%).

R*f*: 0.45 (hexanes/EtOAc = 3:1). M.p. 126–127.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.1 Hz, 1H), 6.90 (d, *J* = 1.9 Hz, 1H), 6.43 (s, 2H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.6, 136.3, 131.4, 119.3, 116.5, 106.1, 56.6. HRMS (EI): calculated for $C_7H_7BrN_2O_3$ (M^+), 245.9640, found 245.9639.

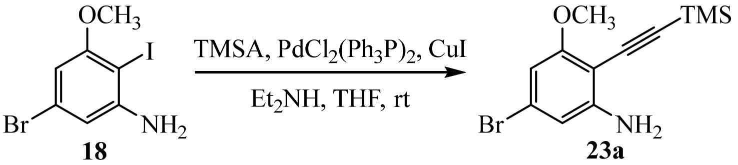


Compound 18.

Compound **20** (37.1 g, 150 mmol) was added to a mixture of DMSO (300 mL) and H_2SO_4 (240 mL, 30% aqueous solution). The resulting mixture was stirred in an ice-water bath for 5 min. The mixture was then treated with a solution of sodium nitrite (31.0 g, 450 mmol, 3 equiv) in water (40 mL). The reaction was stirred at 0 °C for 1.5 h and then treated, in one portion, with a solution of sodium iodide (67.5 g, 450 mmol, 3 equiv) in water (40 mL). After the completion of the reaction by TLC analysis (another 1.5 h), the mixture was then extracted with Et_2O (500 mL × 3). The collected organic layers were washed with saturated aqueous sodium thiosulfate, brine then dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give the crude iodide **21** as an orange-brown solid.

Without any purification, the crude iodide was dissolved in $MeOH/H_2O$ (500 mL, 1/1 v/v) and iron (41.9 g, 750 mmol, 5 equiv) and ammonium chloride (40.1 g, 750 mmol, 5 equiv) were added respectively. After stirring under refluxing for 12 h, the reaction mixture was filtered and the filtrate was concentrated. After the dilution of the residue with EtOAc (500 mL), the mixture was washed with brine. The separated aqueous layer was further extracted with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography [silica gel, hexanes/ethyl acetate = 40/1] to afford the title compound (38.9 g, 79% over 2 steps) as a pale yellow solid.

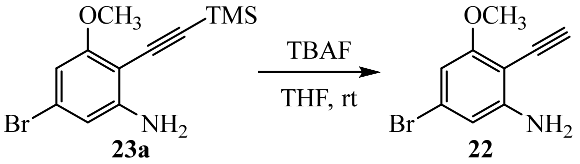
R*f*: 0.7 (hexanes/EtOAc = 3:1). M.p. 85.9–87.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (d, *J* = 1.9 Hz, 1H), 6.33 (d, *J* = 1.9 Hz, 1H), 4.26 (s, 2H), 3.82 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.0, 148.8, 123.1, 110.2, 103.9, 73.9, 56.5. HRMS (EI): calculated for C_7H_7BrINO (M^+), 326.8756, found 326.8752.



Compound 23a.

A mixture of $PdCl_2(PPh_3)_2$ (970 mg, 1.38 mmol, 0.069 equiv) and CuI (520 mg, 2.8 mmol, 0.14 equiv) in a flask was vacuumed and then charged with an atmosphere of nitrogen. To this flask were sequentially added anhydrous THF (15 mL), Et_2NH (15 mL), and compound **18** (6.54 g, 20 mmol). The mixture was stirred for 10 min, followed by the addition of TMSA (trimethylsilylacetylene, 3.4 mL, 24 mmol, 1.2 equiv), and then stirred for 16 h under a mixed atmosphere of nitrogen and hydrogen [4/1 (v/v)]. The resulting mixture was filtrated, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography [silica gel, hexanes/ethyl acetate 30/1] to afford the title compound (5.55 g, 93%) as a yellow oil.

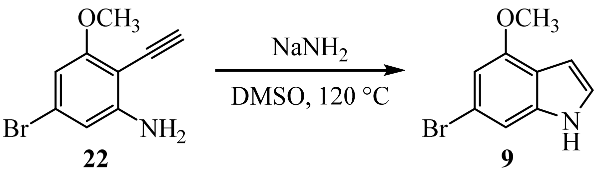
R_f: 0.75 (hexanes/EtOAc = 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ 6.49 (d, J = 1.5 Hz, 1H), 6.35 (d, J = 1.4 Hz, 1H), 4.34 (s, 2H), 3.81 (s, 3H), 0.26 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.3, 150.4, 123.8, 110.0, 105.1, 103.7, 97.3, 96.2, 56.0, 0.2. HRMS (EI): calculated for $C_{12}H_{16}BrNOSi$ (M^+), 297.0185, found 297.0190.



Compound 22.

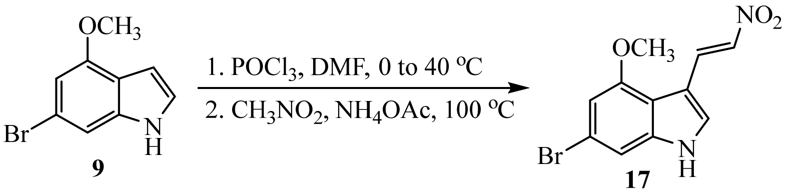
Compound **23a** (5.55 g, 18.6 mmol) was dissolved in THF (85 mL) and TBAF (1M solution in THF, 19 mL, 18.6 mmol, 1 equiv) was added. After stirring at room temperature for 0.5 h, the mixture was concentrated and the residue was purified by column chromatography [silica gel, hexanes/ethyl acetate 40/1] to afford the title compound (3.99 g, 95%) as a brown solid.

R_f: 0.6 (hexanes/EtOAc = 3:1). M.p. 83.2–84.6 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 6.51 (d, J = 1.6 Hz, 1H), 6.39 (d, J = 1.6 Hz, 1H), 4.34 (s, 2H), 3.84 (s, 3H), 3.64 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.7, 150.6, 124.1, 110.1, 103.7, 94.9, 87.3, 76.4, 56.0. HRMS (EI): calculated for C_9H_8BrNO (M^+), 224.9789, found 224.9797.



Compound 9.[S3]

To a solution of compound **22** (5.94 g, 26.3 mmol) in anhydrous DMSO (53 mL) was added sodium amide (5.12 g, 131 mmol, 5 equiv). The reaction mixture was stirred at 120 °C for 16 h. After cooling to room temperature, the reaction mixture was then poured into water (50 mL) and extracted with Et_2O (100 mL × 3). The combined organic layers were washed with saturated aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to afford the title compound (5.23 g, 88%) as a white solid. R*f*: 0.6 (hexanes/EtOAc = 3:1). M.p. 85.3–87.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.11 (t, *J* = 1.0 Hz, 1H), 7.00 (dd, *J* = 3.2, 2.5 Hz, 1H), 6.69 (d, *J* = 1.2 Hz, 1H), 6.64 (t, *J* = 2.3 Hz, 1H), 3.93 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.3, 137.2, 123.1, 117.4, 115.5, 107.5, 103.7, 99.8, 55.4. HRMS (EI): calculated for C_9H_8BrNO (M^+), 224.9789, found 224.9783.

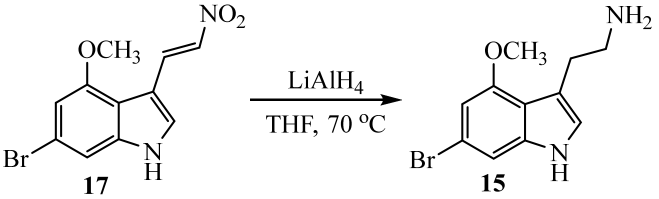


Compound 17.[S3b]

A solution of $POCl_3$ (1.24 mL, 13.3 mmol, 1.3 equiv) in anhydrous DMF (12 mL) was stirred in an ice-water bath for 30 min. Then a solution of compound **9** (2.3 g, 10.2 mmol) in anhydrous DMF (12 mL) was added dropwise over a period of 10 min to the above mixture. The resulting mixture was stirred for 30 min at the same temperature, then heated to 40 °C for 1 h. The reaction mixture was then chilled in an ice-water bath, and 1N aqueous NaOH solution (24 mL) was added until the mixture became basic. The mixture was placed at low temperature (5 °C) for 20 min. 1N aqueous HCl solution (24 mL) was added until the mixture became acidic, and then was extracted with EtOAc (50 mL × 3). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to afford the crude product, which was purified by column chromatography [silica gel, hexanes/ethyl acetate 40/1] to afford the aldehyde (2.33 g, 90%) as white solid.

To a solution of the aldehyde intermediate (3.64 g, 14.3 mmol) in nitromethane (29 mL) was added ammonium acetate (1.10 g, 14.3 mmol, 1 equiv) at room temperature. The reaction mixture was then heated to 100 °C for 2 h, then chilled in an ice-water bath for 12 h. The precipitate was filtered, and the solid was washed with toluene (10 mL). The combined organic layers were concentrated to give the title compound quantitatively (4.25 g) as a brown solid.

R*f*: 0.3 (hexanes/EtOAc = 3:1). M.p. 226.3–227.9 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.49 (d, *J* = 13.3 Hz, 1H), 8.25 (s, 1H), 8.07 (d, *J* = 13.3 Hz, 1H), 7.28 (d, *J* = 1.4 Hz, 1H), 6.86 (d, *J* = 1.2 Hz, 1H), 3.96 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 154.1, 139.0, 134.7, 132.9, 132.4, 116.2, 114.4, 108.7, 107.9, 106.0, 56.0. HRMS (EI): calculated for $C_{11}H_9O_3N_2Br$ (M^+), 294.9797, found 294.9793.

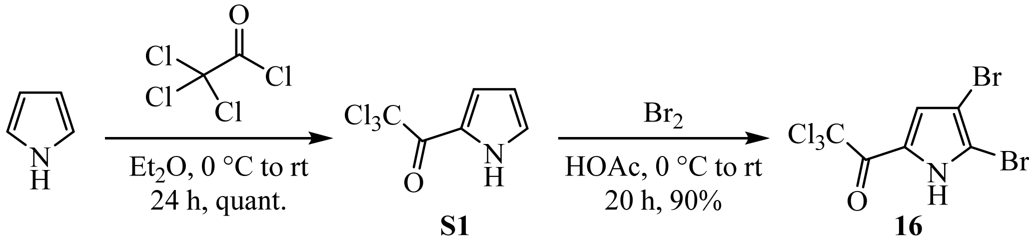


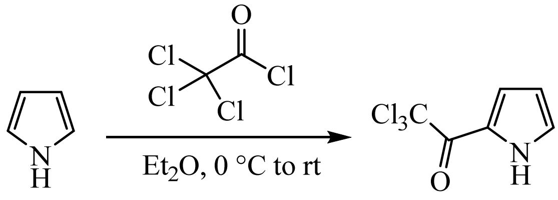
Compound 15.[S3b]

To a solution of compound **17** (1.54 g, 5.19 mmol) in THF (45 mL) in an ice-water bath was slowly added LiAlH4 (1.18 g, 31.1 mmol, 6 equiv). The reaction mixture was then heated to 70 °C for 3.5 h. After the reaction, the resulting mixture was chilled in an ice-water bath, and excess LiAlH4 was quenched by the dropwise addition of water (1 mL), 6N aqueous KOH solution (1 mL) and water (2 mL) until no further gas evolution was observed. The mixture was diluted with EtOAc (150 mL), filtered through Celite, dried over anhydrous MgSO4 and concentrated to afford the title compound quantitatively (1.40 g) as a brown oil.

R*f*: 0.1 (DCM/MeOH = 10:1). ^{1}H NMR (400 MHz, DMSO-*d*6) δ 10.90 (s, 1H), 7.09 (d, *J* = 1.5 Hz, 1H), 6.97 (s, 1H), 6.54 (d, *J* = 1.5 Hz, 1H), 3.84 (s, 3H), 2.85–2.75 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*6) δ 154.6, 138.2, 122.3, 115.9, 113.8, 112.7, 107.5, 102.4, 55.4, 42.7, 30.0. HRMS (EI): calculated for $C_{11}H_{13}BrN_2O$ (M$^+$), 268.0211, found 268.0201.

Scheme S1. Synthetic route of the trichloromethyl ketone **16**



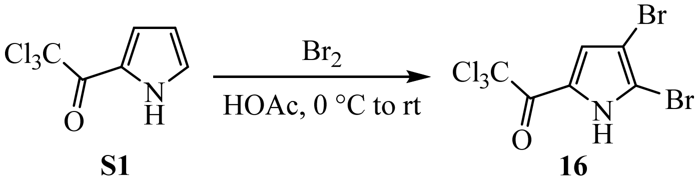


Compound S1.[S4]

To a solution of pyrrole (3 mL, 43.2 mmol) in anhydrous ether (50 mL) in an ice-water bath was added a solution of trichloroacetyl chloride (5.3 mL, 47.6 mmol, 1.1 equiv) in anhydrous ether (20 mL). The reaction mixture was then stirred at room temperature for 24 h. After the reaction, the reaction mixture was treated with saturated aqueous sodium bicarbonate solution (200 mL). The mixture was extracted with EtOAc (200 mL × 2). The combined organic layers were washed with brine (200 mL), dried over anhydrous

$MgSO_4$, and concentrated under reduced pressure to afford the title compound quantitatively (10.0 g) as a black solid.

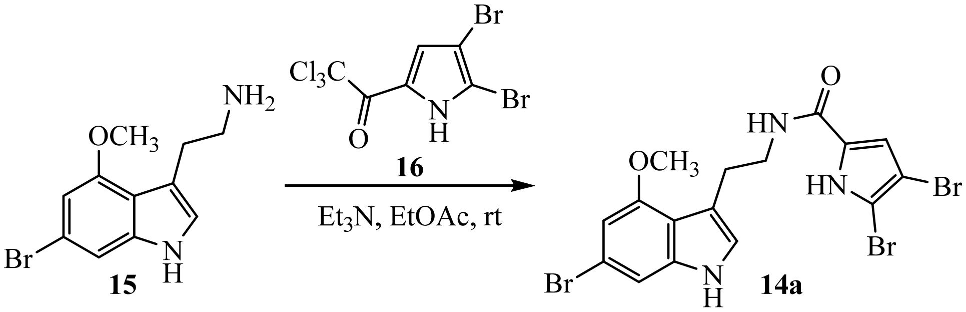
R*f*: 0.5 (hexanes/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.37 (s, 1H), 7.15 (s, 1H), 6.38–6.36 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.3, 127.4, 122.9, 121.3, 111.8, 94.9. HRMS (APCI) *m/z*: $[M - H]^+$ calculated for $C_6H_3ONCl_3$ 209.9275, found 209.9282.



Compound 16.[S5]

To a solution of compound **S1** (10.0 g, 47.1 mmol) in acetic acid (50 mL) in an ice-water bath was slowly added bromine (5.6 mL, 109 mmol, 2.3 equiv). After addition, the reaction mixture was then stirred at room temperature for 20 h. The reaction was quenched with saturated aqueous sodium hyposulfite solution (100 mL). The resulting mixture was extracted with EtOAc (200 mL × 2). The combined organic layers were washed with saturated aqueous sodium bicarbonate solution (200 mL) and brine (200 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude mixture was purified by column chromatography [silica gel, hexanes/ethyl acetate 30/1 (v/v)] to afford the title compound (15.8 g, 90%) as a white solid.

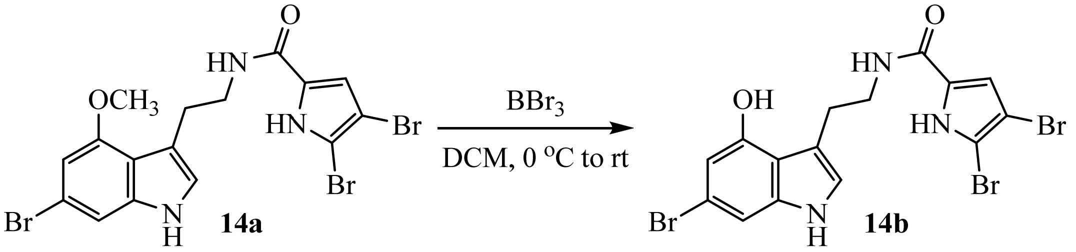
R*f* : 0.7 (hexanes/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.31 (d, J = 2.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.0, 123.8, 123.1, 113.3, 102.4, 93.8. HRMS (APCI) *m/z*: $[M - H]^+$ calculated for $C_6HONBr_2Cl_3$ 365.7485, found 365.7483.



Compound 14a.

To a solution of compound **15** (1.09 g, 4.06 mmol) and compound **16** (1.5 g, 4.87 mmol, 1.2 equiv) in EtOAc (9 mL) was added Et_3N (1.41 mL, 10.2 mmol, 2.5 equiv) dropwise. The mixture was stirred at room temperature for 12 h. The volatiles were removed under reduced pressure. The residue was purified by column chromatography [silica gel, hexanes/ethyl acetate 10/1] to afford the title compound (1.25 g, 59%) as a pale yellow solid.

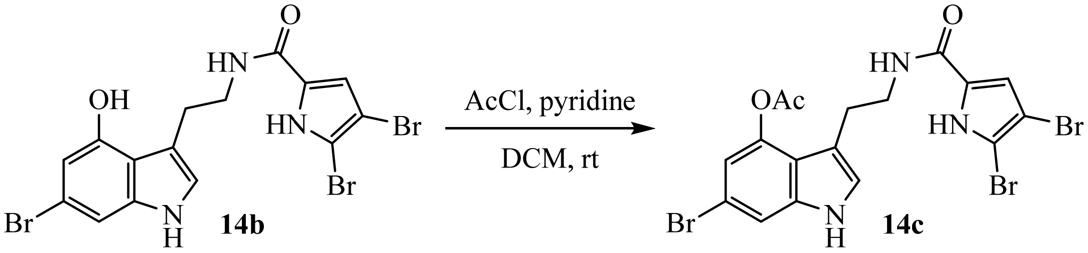
R*f*: 0.6 (hexanes/EtOAc = 1:1). M.p. 184.1–185.7 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.93 (s, 1H), 8.02 (s, 1H), 7.16 (s, 1H), 6.88 (s, 1H), 6.65 (s, 1H), 6.30 (s, 1H), 6.10 (s, 1H), 3.92 (s, 3H), 3.71–3.67 (m, 2H), 3.11 (t, J = 6.3 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 159.3, 154.4, 138.3, 127.3, 121.6, 116.3, 116.0, 113.6, 111.3, 107.9, 104.9, 104.1, 99.5, 55.6, 41.0, 26.2. HRMS (ESI) *m/z*: [M + H]$^+$ calculated for $C_{16}H_{15}O_2N_3Br_3$ 517.8709, found 517.8697.



Compound 14b.

To a solution of compound **14a** (950 mg, 1.83 mmol) in DCM (18 mL) in an ice-water bath was added dropwise of BBr_3 (1M solution in DCM, 18 mL, 10 equiv). After addition, the mixture was then stirred at room temperature for 12 h. After the reaction was completed by TLC analysis, the mixture was extracted with DCM (50 mL) and EtOAc (50 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography [silica gel, hexanes/ethyl acetate 3/1 (v/v)] to afford the title compound (674 mg, 73%) as a dark green solid.

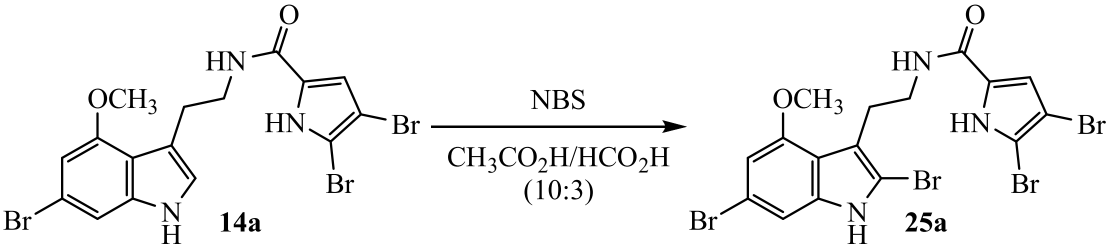
R*f*: 0.4 (hexanes/EtOAc = 1:1). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 12.60 (s, 1H), 10.75 (s, 1H), 9.84 (s, 1H), 8.09 (t, J = 5.4 Hz, 1H), 6.93 (s, 2H), 6.89 (d, J = 2.6 Hz, 1H), 6.45 (d, J = 1.2 Hz, 1H), 3.48 (dd, J = 12.8, 6.8 Hz, 2H), 2.98 (t, J = 7.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 158.7, 152.5, 138.9, 128.4, 121.8, 115.7, 113.6, 112.4, 112.3, 105.9, 105.6, 104.2, 97.7, 40.1, 26.3. HRMS (EI): calculated for $C_{15}H_{12}Br_3N_3O_2$ (M$^+$) 502.8480, found 502.8470.



Compound 14c.

To a solution of compound **14b** (200 mg, 390 μmol) in DCM (790 μL) was added acetyl chloride (34 μL, 468 μmol, 1.2 equiv) and pyridine (48 μL, 585 μmol, 1.5 equiv). The mixture was stirred at room temperature for 3 h. The volatiles were removed under reduced pressure. The residue was purified by column chromatography [silica gel, hexanes/ethyl acetate 3/1 (v/v)] to afford the title compound (187 mg, 87%) as a white solid.

R_f: 0.4 (hexanes/EtOAc = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.65 (d, J = 2.1 Hz, 1H), 11.19 (d, J = 1.6 Hz, 1H), 8.16 (t, J = 5.4 Hz, 1H), 7.42 (d, J = 1.6 Hz, 1H), 7.17 (d, J = 2.5 Hz, 1H), 6.91 (d, J = 1.6 Hz, 1H), 6.89 (d, J = 2.7 Hz, 1H), 3.43 (q, J = 6.8 Hz, 2H), 2.83 (t, J = 7.2 Hz, 2H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 169.5, 158.9, 143.9, 139.0, 128.4, 124.9, 119.0, 114.8, 112.5, 112.4, 112.0, 110.9, 104.5, 97.7, 40.3, 26.0, 20.8, HRMS (EI): calculated for $C_{17}H_{14}Br_3N_3O_3$ (M^+) 544.8585, found 544.8592.



Compound 25a.

To a solution of compound **14a** (200 mg, 385 µmol) in acetic acid (3.9 mL) and formic acid (1.17 mL). Then NBS (69 mg, 385 µmol, 1 equiv) was added in the resulting mixture and stirred at room temperature for 20 min. The volatiles were removed under reduced pressure. The residue was purified by column chromatography [silica gel, hexanes/ethyl acetate 10/1] and then by TLC plate [dichloromethane/hexanes 15/1] for four developments to afford the title compound (99 mg, 43%) as a colorless solid.

R_f = 0.65 (hexanes/EtOAc = 1:1). M.p. 178.3–179.2 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.98 (s, 1H), 8.14 (s, 1H), 7.07 (d, J = 1.2 Hz, 1H), 6.64 (d, J = 1.2 Hz, 1H), 6.27 (s, 1H), 6.09–6.05 (m, 1H), 3.88 (s, 3H), 3.65 (q, J = 6.0 Hz, 2H), 3.06 (t, J = 6.1 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 159.4, 153.2, 137.7, 127.3, 116.4, 116.2, 112.8, 111.4, 107.6, 107.3, 104.9, 99.5, 55.8, 40.5, 29.7, 25.5. HRMS (ESI) *m/z*: [M − H]$^+$ calculated for $C_{16}H_{12}O_2N_3Br_4$ 593.7658, found 593.7676.

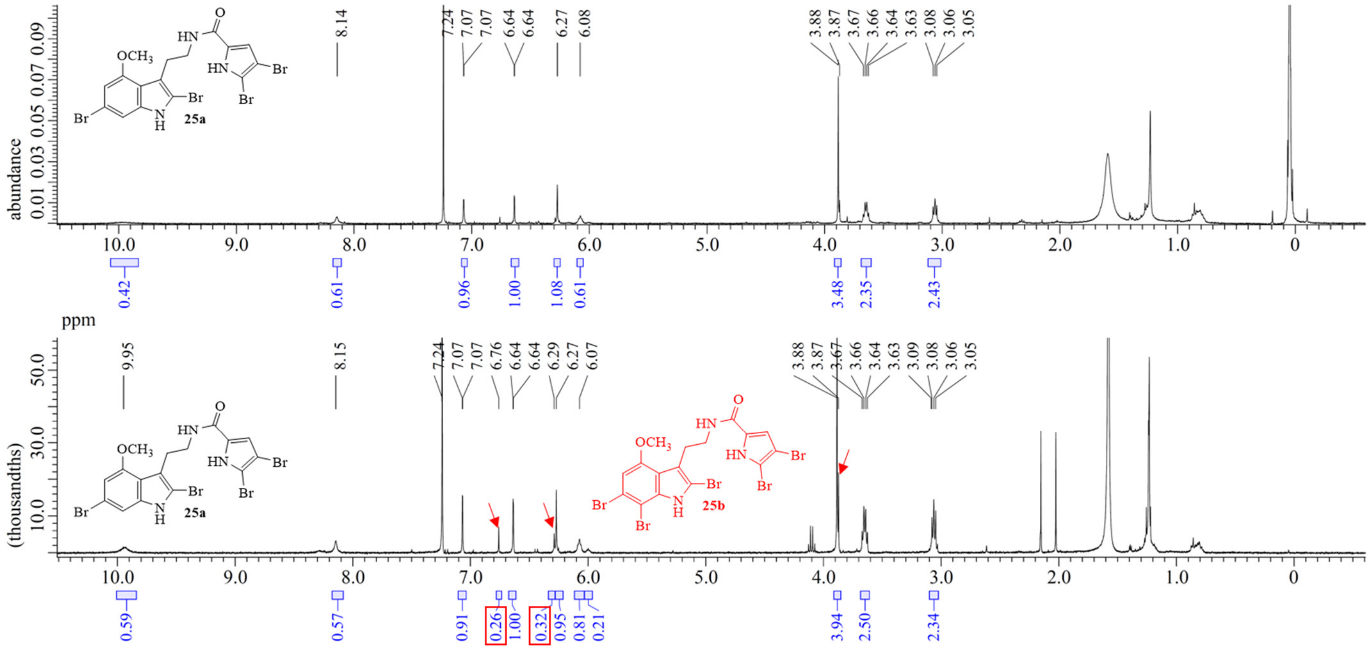
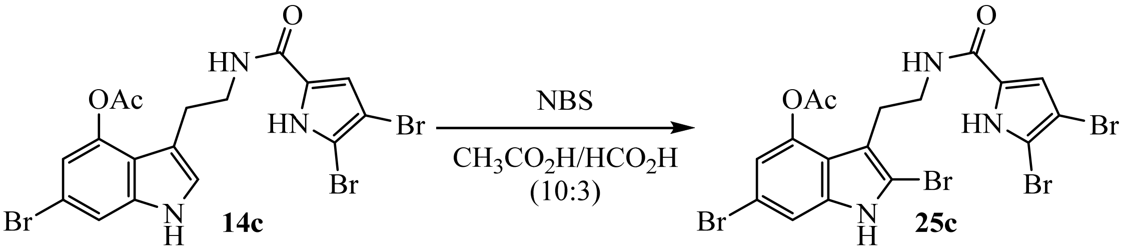


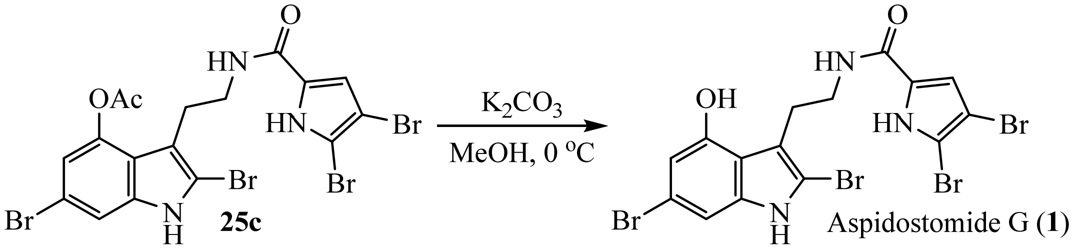
Figure S1. Comparing the clean proton NMR spectrum of **25a** with the mixed NMR spectrum of **25a** and **25b**



Compound 25c.

To a solution of compound **14c** (180 mg, 328 μmol) in acetic acid (3.3 mL) and formic acid (0.99 mL). Then NBS (59 mg, 328 μmol, 1 equiv) was added in the resulting mixture and stirred at room temperature for 3 h. The volatiles were removed under reduced pressure. The residue was purified by column chromatography [silica gel, hexanes/ethyl acetate 4/1 (v/v)] to afford the title compound (48 mg, 55%) as a white solid.

R*f* = 0.6 (hexanes/EtOAc = 1:1). ^{1}H NMR (400 MHz, DMSO-*d*6) δ 12.63 (d, *J* = 2.2 Hz, 1H), 12.12 (s, 1H), 8.20 (t, *J* = 5.8 Hz, 1H), 7.34 (d, *J* = 1.6 Hz, 1H), 7.00 (d, *J* = 1.5 Hz, 1H), 6.86 (d, *J* = 2.7 Hz, 1H), 2.78 (t, *J* = 7.0 Hz, 2H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*6) δ 170.0 159.4, 143.3, 139.0, 128.8, 119.4, 116.4, 113.5, 113.0, 112.1, 111.8, 110.7, 104.8, 98.2, 40.2, 29.5, 26.3. HRMS (EI): calculated for $C_{17}H_{13}Br_4N_3O_3$ (M$^+$) 622.7690, found 622.7698.

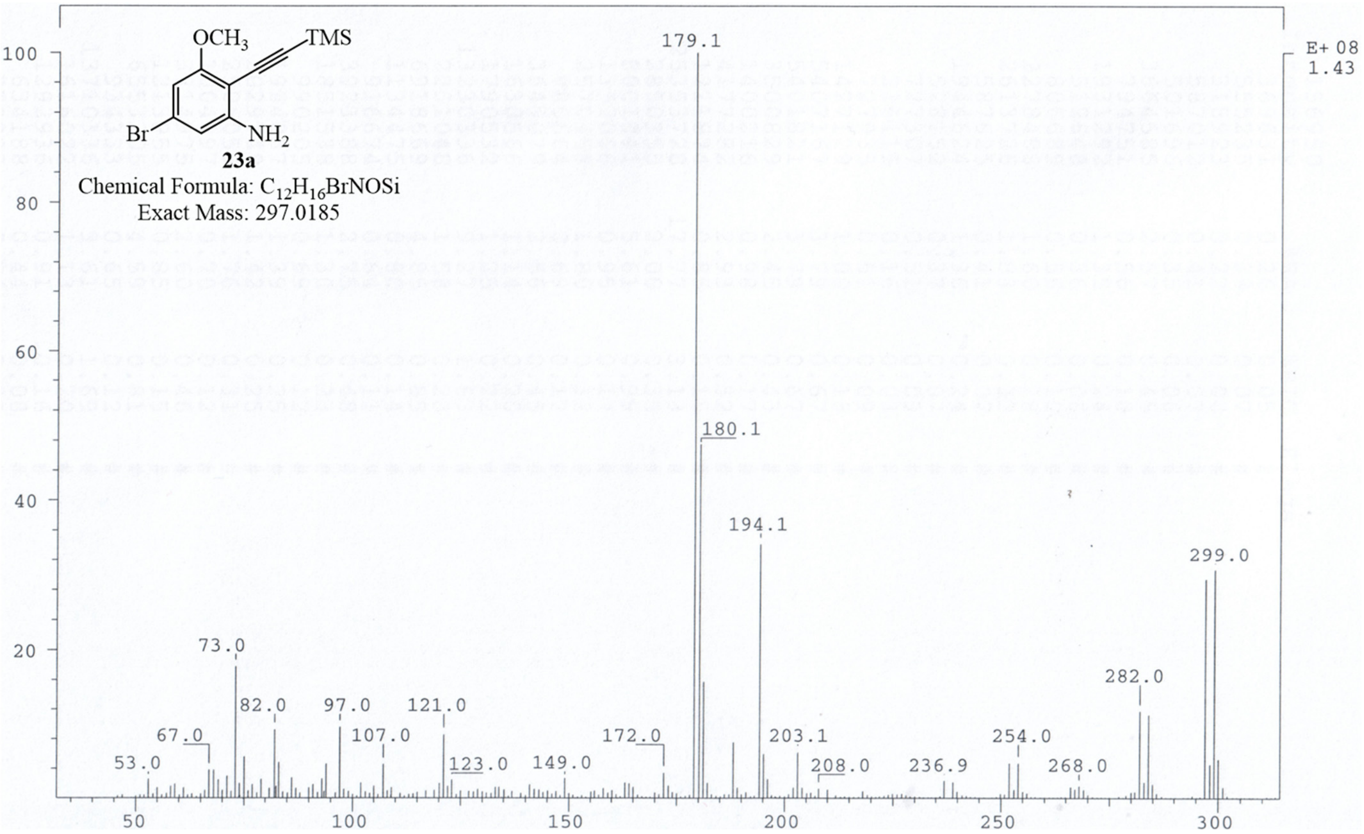


Aspidostomide G (1).[S6]

To a solution of compound **25c** (46 mg, 73 μmol) in dry MeOH (730 μL) was added K_2CO_3 (25 mg, 183 μmol, 2.5 equiv). After stirring at 0 °C for 5 h, the reaction was quenched with a mixed solution of saturated aqueous $Na_2S_2O_3$/saturated aqueous $NaHCO_3$ (5 mL, 1/1 v/v). The resulting mixture was extracted with EtOAc (5 mL × 3). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography [silica gel, hexanes/ethyl acetate 4/1 (v/v)] to afford the title compound (33 mg, 77%) as a pale yellow solid.

R*f* = 0.6 (hexanes/EtOAc = 1:1). ^{1}H NMR (400 MHz, acetone-*d*6) δ 11.63 (s, 1H), 10.54 (s, 1H), 9.07 (s, 1H), 6.90 (d, *J* = 1.5 Hz, 1H), 6.68 (s, 1H), 6.53 (d, *J* = 1.5 Hz, 1H), 3.52 (dd, *J* = 12.4, 6.5 Hz, 2H), 2.95 (t, *J* = 6.5 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, acetone-*d*6) δ 159.2, 151.1, 138.9, 128.6, 116.1, 114.9, 112.3, 112.0, 107.8, 107.5, 105.8, 104.1, 98.5, 40.2, 25.8. HRMS (EI): calculated for $C_{15}H_{11}Br_4N_3O_2$ (M$^+$) 580.7585, found 580.7593.

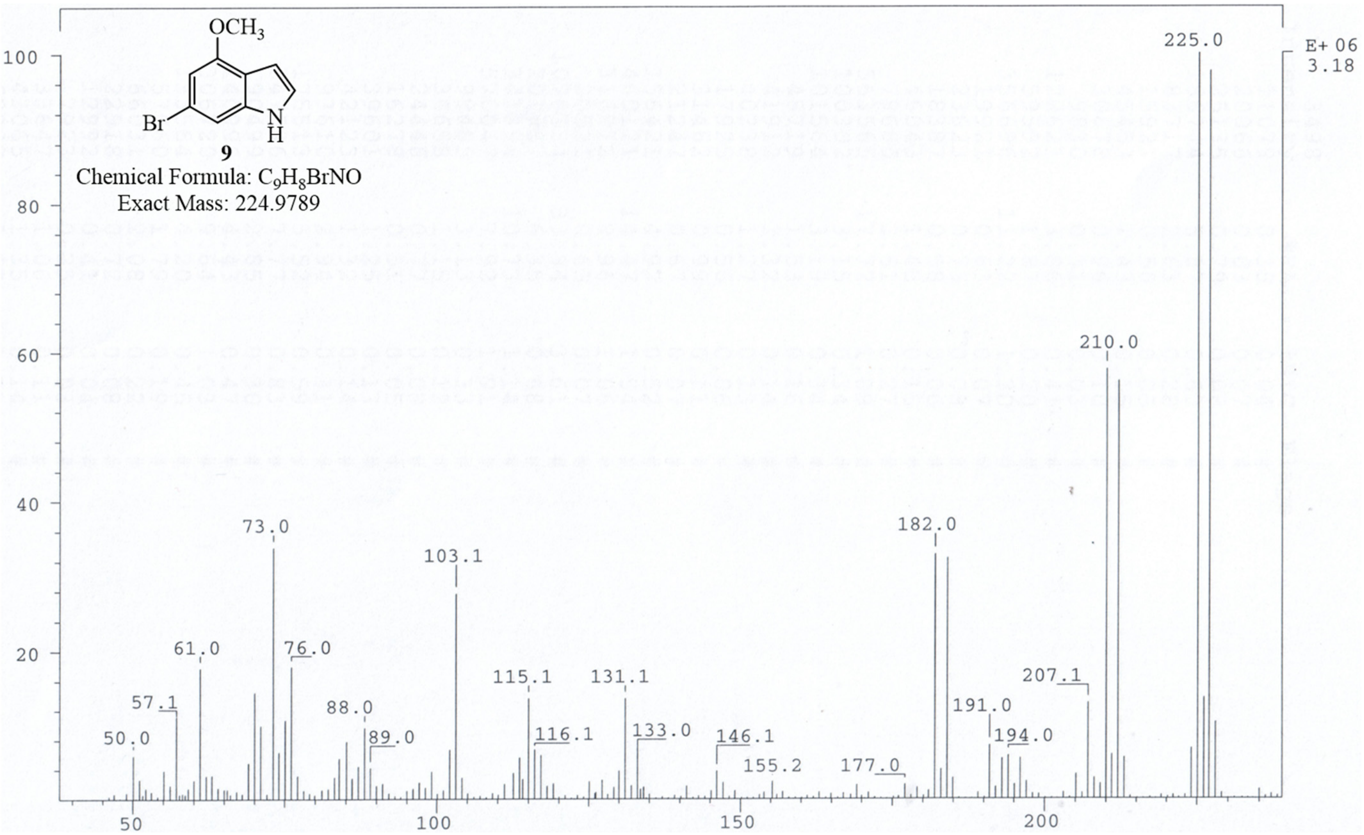
C. LRMS Spectra for brominated compounds



23a

Chemical Formula: $C_{12}H_{16}BrNOSi$

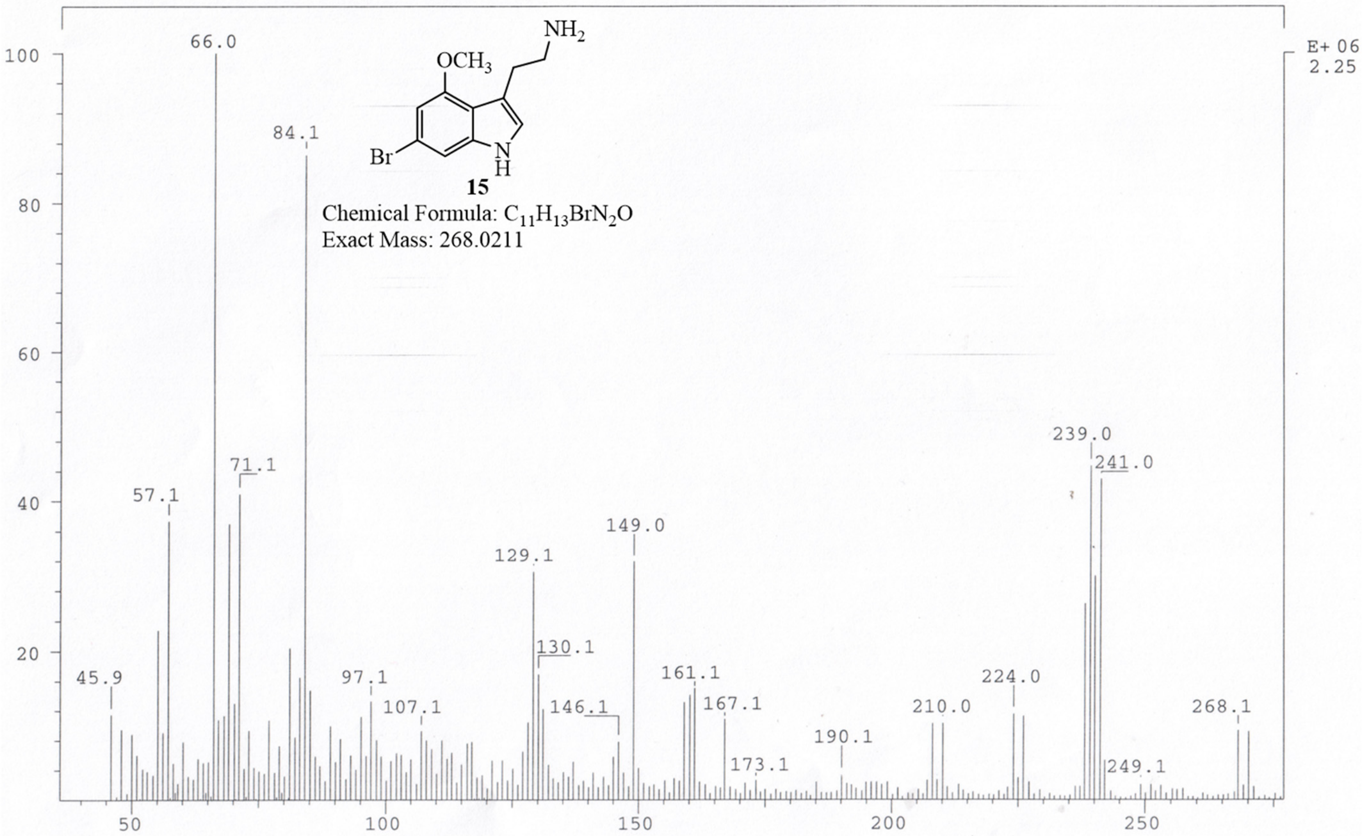
Exact Mass: 297.0185

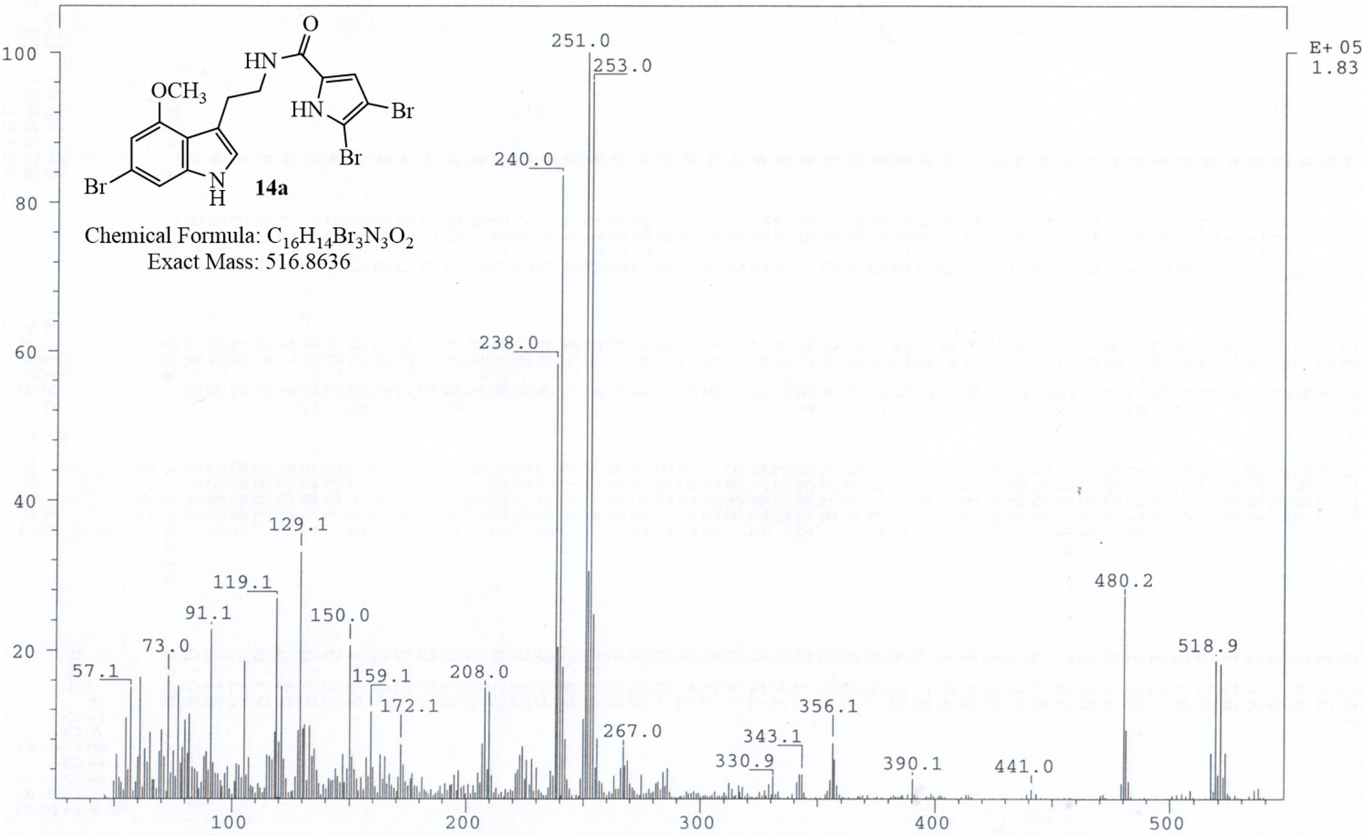


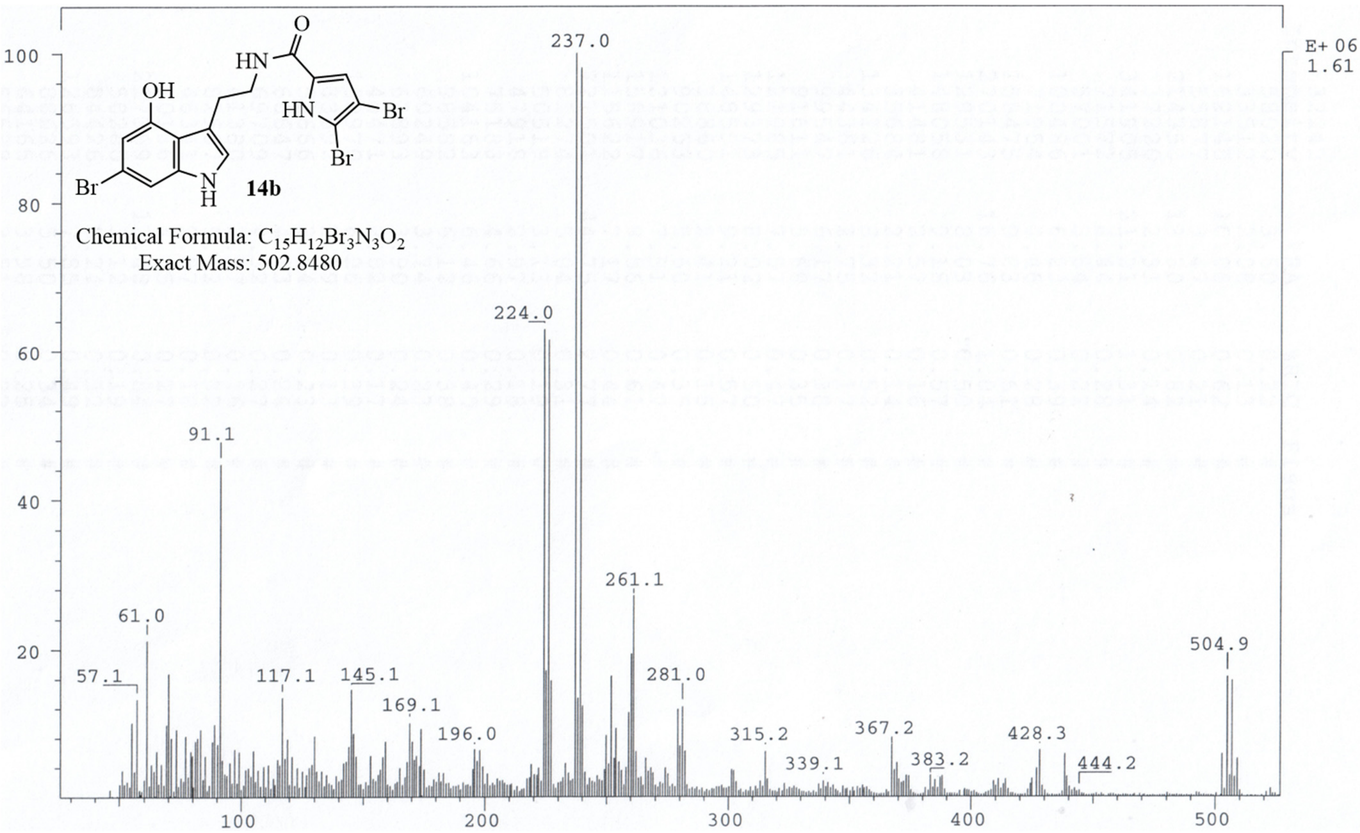
9

Chemical Formula: C_9H_8BrNO

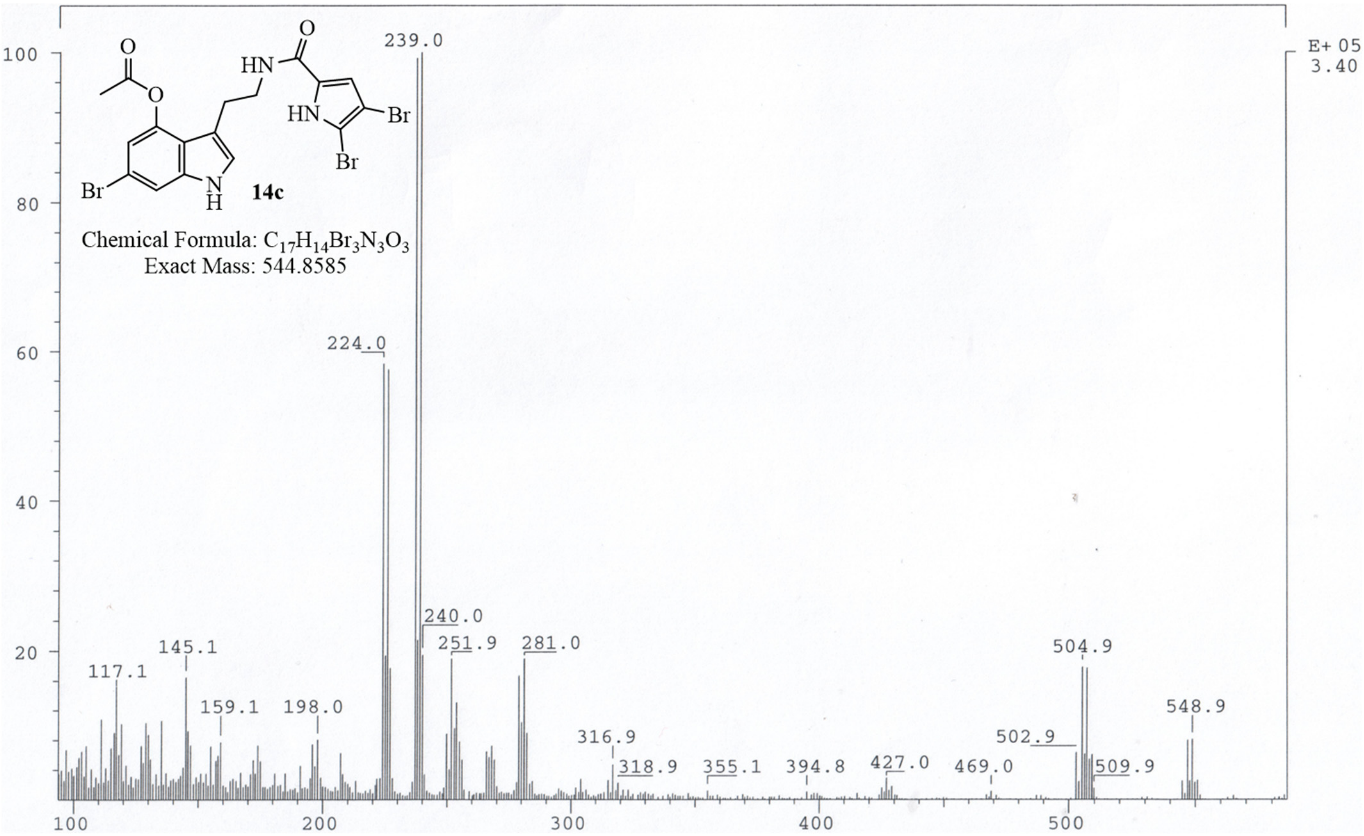
Exact Mass: 224.9789


NH$_2$
OCH$_3$
Br
N
H
15
Chemical Formula: $C_{11}H_{13}BrN_2O$
Exact Mass: 268.0211
E+ 06
2.25
100
80
60
40
20
66.0
84.1
57.1
71.1
45.9
97.1
107.1
129.1
130.1
146.1
149.0
161.1
167.1
173.1
190.1
210.0
224.0
239.0
241.0
249.1
268.1
50
100
150
200
250

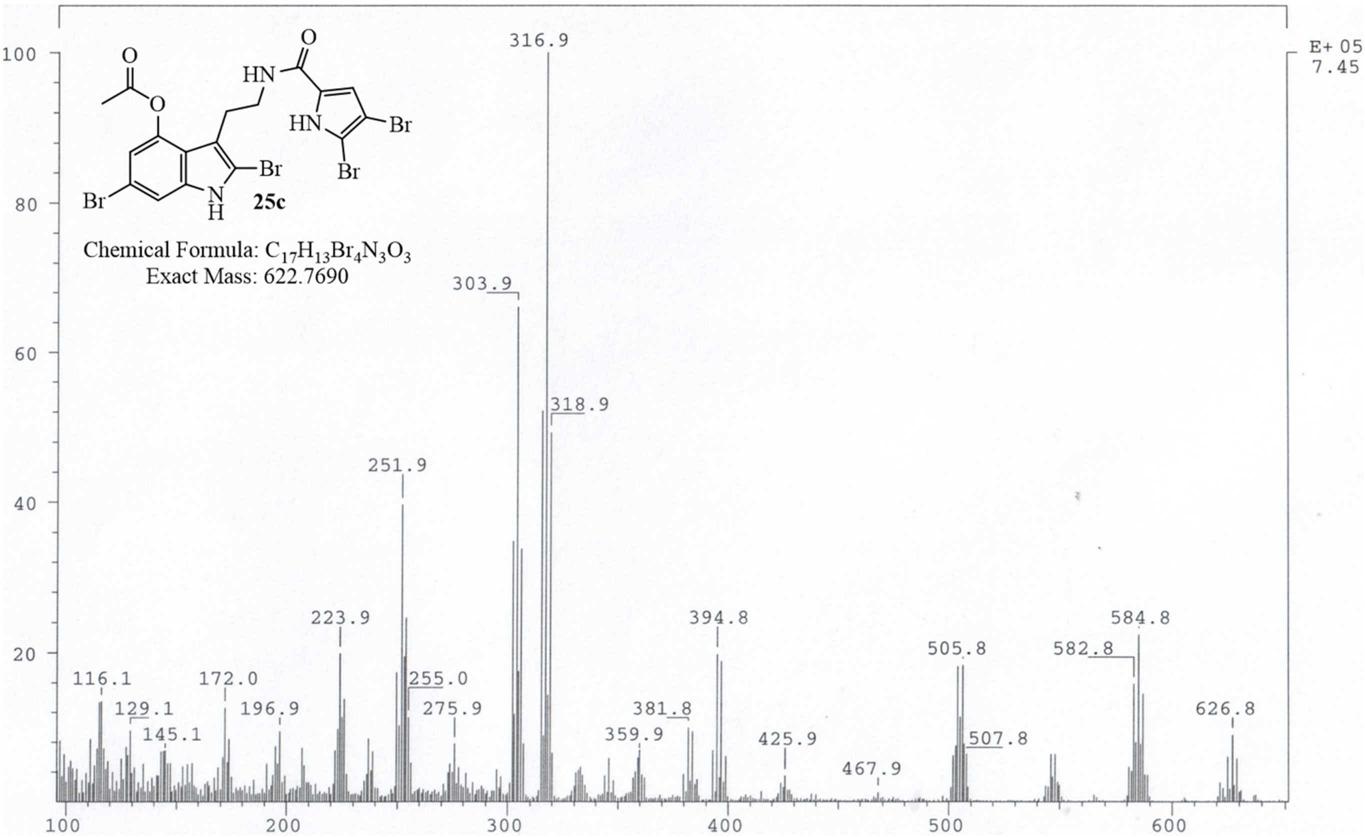

O
HN
OCH$_3$
HN
Br
Br
Br
N
H
14a
Chemical Formula: $C_{16}H_{14}Br_3N_3O_2$
Exact Mass: 516.8636
E+ 05
1.83
100
80
60
40
20
251.0
253.0
240.0
238.0
129.1
119.1
91.1
73.0
57.1
150.0
159.1
172.1
208.0
267.0
330.9
343.1
356.1
390.1
441.0
480.2
518.9
100
200
300
400
500


14b

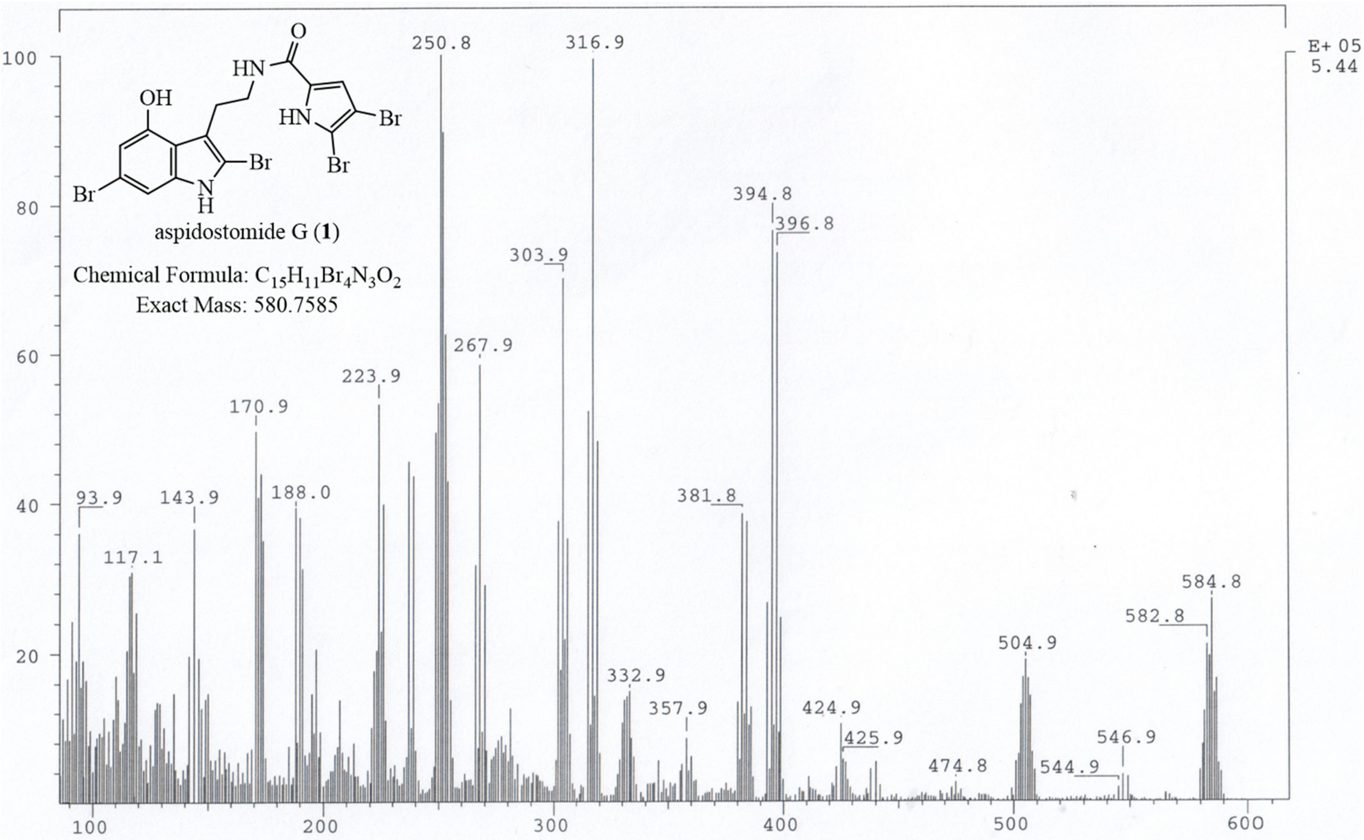
Chemical Formula: $C_{15}H_{12}Br_3N_3O_2$
Exact Mass: 502.8480


14c

Chemical Formula: $C_{17}H_{14}Br_3N_3O_3$
Exact Mass: 544.8585

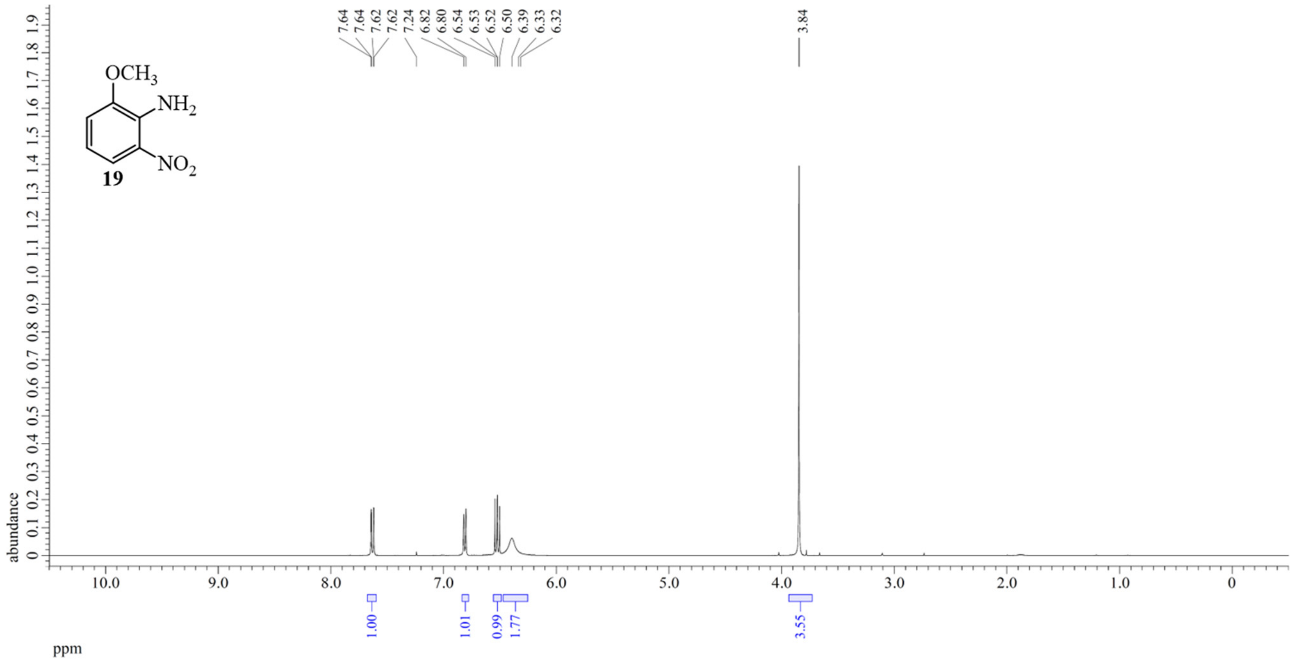

25c

Chemical Formula: $C_{17}H_{13}Br_4N_3O_3$
Exact Mass: 622.7690


aspidostomide G (**1**)

Chemical Formula: $C_{15}H_{11}Br_4N_3O_2$
Exact Mass: 580.7585

D. NMR Spectra for the synthesized compounds



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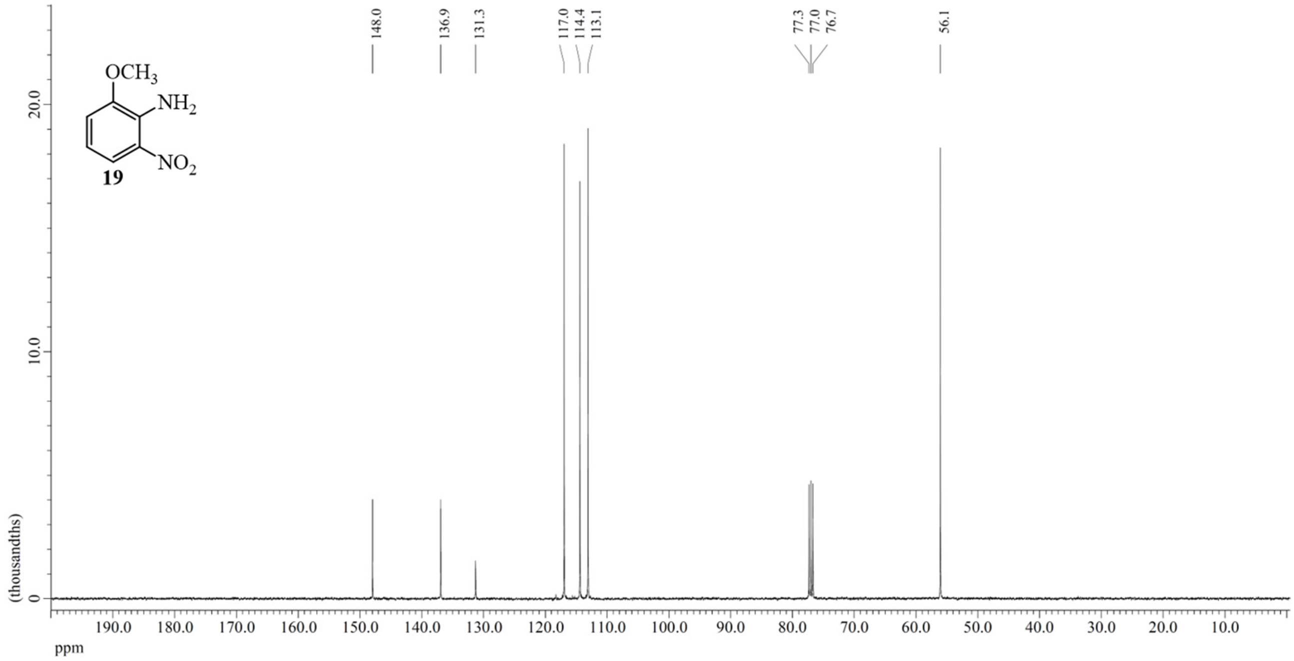
Author             = nmr                 Field_Strength   = 9.389766[T] (400[MHz]   Blanking            = 2[us]
Experiment         = proton_auto.jxp     X_Acq_Duration   = 2.44288[s]           Clipped             = FALSE
Sample_Id          = 20220509-new1       X_Domain         = Proton               Scans               = 2
Solvent            = CHLOROFORM-D        X_Freq           = 399.78219838[MHz]    Total_Scans         = 2
Actual_Start_Time  =  9-MAY-2022 06:34:06 X_Offset        = 6[ppm]
Revision_Time      = 29-JUN-2022 15:23:06 X_Points        = 22000                Relaxation_Delay    = 2[s]
                                         X_Prescans       = 1                    Recvr_Gain          = 36
Data_Format        = 1D COMPLEX          X_Resolution     = 0.40935289[Hz]       Temp_Get            = 22[dC]
Dim_Size           = 52429               X_Sweep          = 9.00576369[kHz]      X_90_Width          = 7.36[us]
X_Domain           = Proton              X_Sweep_Clipped  = 7.20461095[kHz]      X_Acq_Time          = 2.44288[s]
Dim_Title          = Proton              Irr_Domain       = Proton               X_Angle             = 45[deg]
Dim_Units          = [ppm]               Irr_Freq         = 399.78219838[MHz]    X_Atn               = 4[dB]
Dimensions         = X                   Irr_Offset       = 5[ppm]               X_Pulse             = 3.68[us]
Site               = NCHU                Tri_Domain       = Proton               Irr_Mode            = Off
Spectrometer       = JNM-ECZ400S/L1      Tri_Freq         = 399.78219838[MHz]    Tri_Mode            = Off
```

^{1}H NMR spectrum of compound **19** (400 MHz, CDCl$_3$)



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Filename           = 20220509-new1carbo                                   Scans                        = 345
Author             = nmr                  Field_Strength   = 9.389766[T] (400[M   Total_Scans                  = 345
Experiment         = carbon_auto.jxp      X_Acq_Duration   = 0.6336[s]
Sample_Id          = 20220509-new1carbo   X_Domain         = Carbon13             Relaxation_Delay             = 2[s]
Solvent            = CHLOROFORM-D         X_Freq           = 100.52530333[MHz]    Recvr_Gain                   = 50
Actual_Start_Time  =  9-MAY-2022 06:38:   X_Offset         = 100[ppm]             Temp_Get                     = 22[dC]
Revision_Time      =  2-JUL-2022 22:57:   X_Points         = 20000                X_90_Width                   = 10.35[us]
                                          X_Prescans       = 4                    X_Acq_Time                   = 0.6336[s]
Data_Format        = 1D COMPLEX           X_Resolution     = 1.57828283[Hz]       X_Angle                      = 40[deg]
Dim_Size           = 52429                X_Sweep          = 31.56565657[kHz]     X_Atn                        = 7.8[dB]
X_Domain           = Carbon13             X_Sweep_Clipped  = 25.25252525[kHz]     X_Pulse                      = 4.6[us]
Dim_Title          = Carbon13             Irr_Domain       = Proton               Irr_Atn_Dec                  = 27.876[dB]
Dim_Units          = [ppm]                Irr_Freq         = 399.78219838[MHz]    Irr_Atn_Dec_Calc             = 27.876[dB]
Dimensions         = X                    Irr_Offset       = 5[ppm]               Irr_Atn_Dec_Default_Calc     = 27.876[dB]
Site               = NCHU                 Blanking         = 5[us]                Irr_Atn_Noe                  = 27.876[dB]
Spectrometer       = JNM-ECZ400S/L1       Clipped          = FALSE                Irr_Dec_Bandwidth_Hz         = 4.7826087[kHz]
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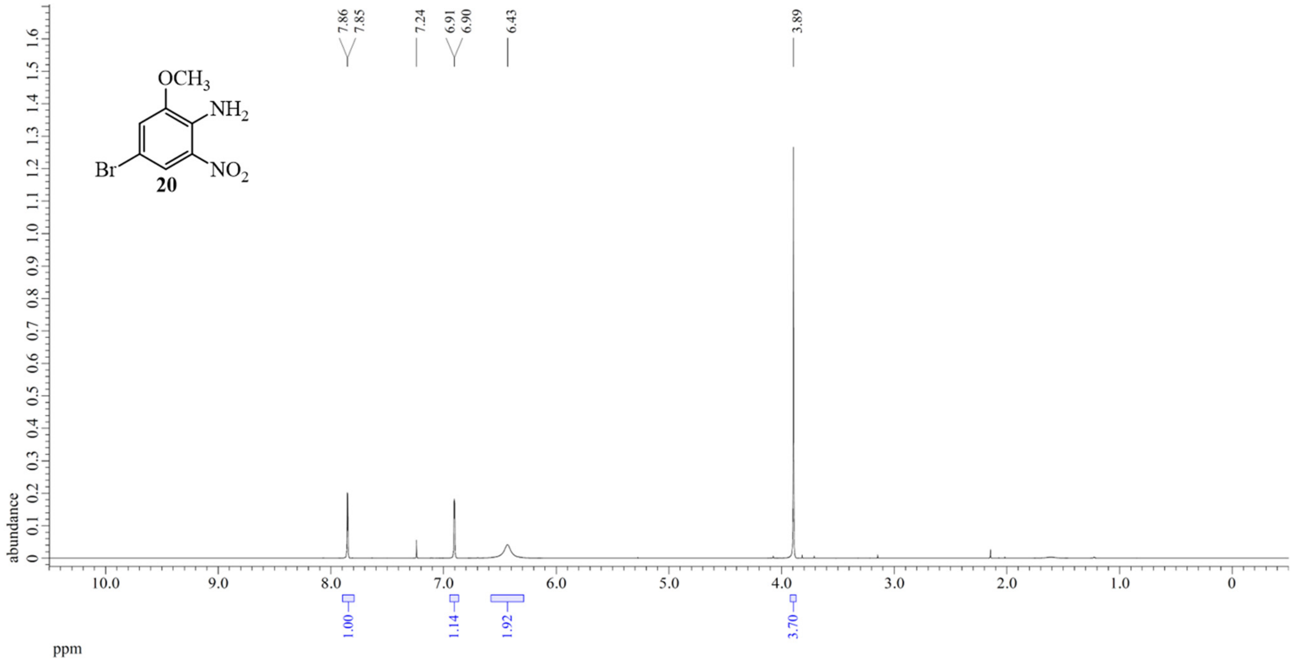
^{13}C NMR spectrum of compound **19** (100 MHz, CDCl$_3$)



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Filename           = 20220522-new2_Proton-                                                  Tri_Offset          = 5[ppm]
Author             = nmr                   Field_Strength     = 9.389766[T] (400[MHz]       Blanking            = 2[us]
Experiment         = proton_auto.jxp       X_Acq_Duration     = 2.44288[s]                  Clipped             = FALSE
Sample_Id          = 20220522-new2         X_Domain           = Proton                      Scans               = 2
Solvent            = CHLOROFORM-D          X_Freq             = 399.78219838[MHz]           Total_Scans         = 2
Actual_Start_Time  = 22-MAY-2022 01:48:56  X_Offset           = 6[ppm]
Revision_Time      = 29-JUN-2022 15:25:34  X_Points           = 22000                       Relaxation_Delay    = 2[s]
                                           X_Prescans         = 1                           Recvr_Gain          = 46
Data_Format        = 1D COMPLEX            X_Resolution       = 0.40935289[Hz]              Temp_Get            = 21.9[dC]
Dim_Size           = 52429                 X_Sweep            = 9.00576369[kHz]             X_90_Width          = 7.36[us]
X_Domain           = Proton                X_Sweep_Clipped    = 7.20461095[kHz]             X_Acq_Time          = 2.44288[s]
Dim_Title          = Proton                Irr_Domain         = Proton                      X_Angle             = 45[deg]
Dim_Units          = [ppm]                 Irr_Freq           = 399.78219838[MHz]           X_Atn               = 4[dB]
Dimensions         = X                     Irr_Offset         = 5[ppm]                      X_Pulse             = 3.68[us]
Site               = NCHU                  Tri_Domain         = Proton                      Irr_Mode            = Off
Spectrometer       = JNM-ECZ400S/L1        Tri_Freq           = 399.78219838[MHz]           Tri_Mode            = Off
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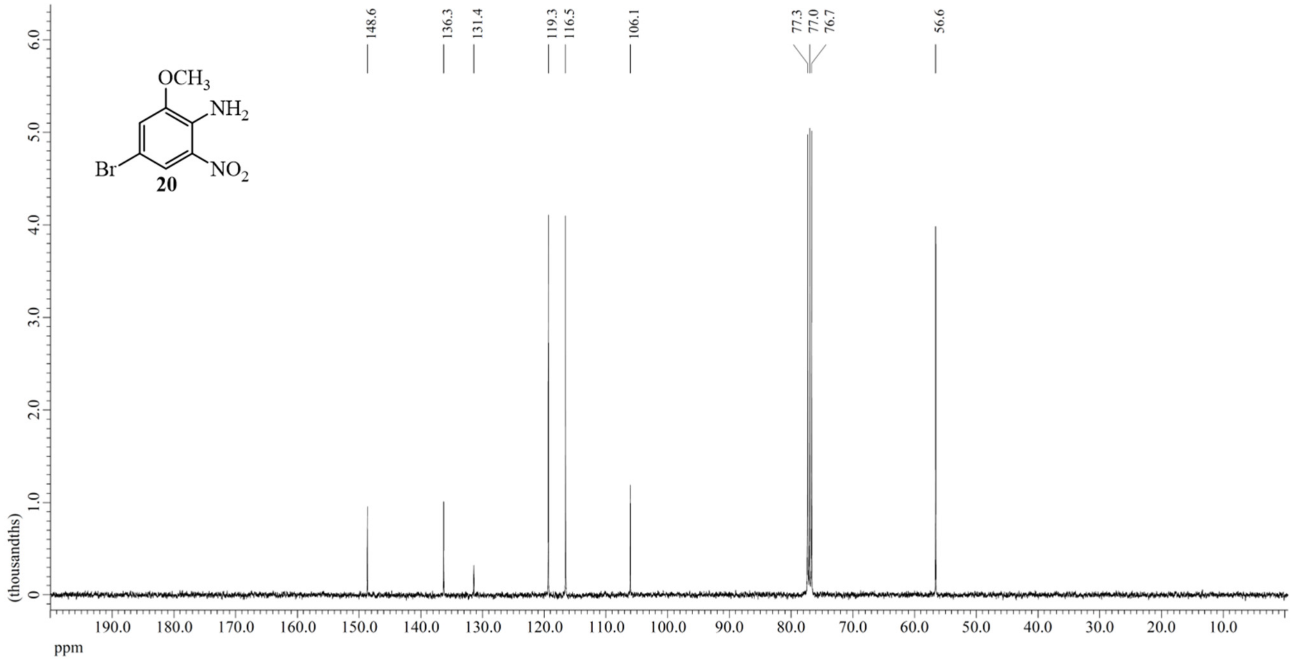
^{1}H NMR spectrum of compound **20** (400 MHz, CDCl$_3$)



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Author             = nmr                   Field_Strength     = 9.389766[T] (400[M         Total_Scans                 = 716
Experiment         = carbon_auto.jxp       X_Acq_Duration     = 0.6336[s]
Sample_Id          = 20220522-new2-carb    X_Domain           = Carbon13                   Relaxation_Delay            = 2[s]
Solvent            = CHLOROFORM-D          X_Freq             = 100.52530333[MHz]          Recvr_Gain                  = 50
Actual_Start_Time  = 22-MAY-2022 01:51:    X_Offset           = 100[ppm]                   Temp_Get                    = 21.9[dC]
Revision_Time      =  3-JUL-2022 23:23:    X_Points           = 20000                      X_90_Width                  = 10.35[us]
                                           X_Prescans         = 4                          X_Acq_Time                  = 0.6336[s]
Data_Format        = 1D COMPLEX            X_Resolution       = 1.57828283[Hz]             X_Angle                     = 40[deg]
Dim_Size           = 52429                 X_Sweep            = 31.56565657[kHz]           X_Atn                       = 7.8[dB]
X_Domain           = Carbon13              X_Sweep_Clipped    = 25.25252525[kHz]           X_Pulse                     = 4.6[us]
Dim_Title          = Carbon13              Irr_Domain         = Proton                     Irr_Atn_Dec                 = 27.876[dB]
Dim_Units          = [ppm]                 Irr_Freq           = 399.78219838[MHz]          Irr_Atn_Dec_Calc            = 27.876[dB]
Dimensions         = X                     Irr_Offset         = 5[ppm]                     Irr_Atn_Dec_Default_Calc = 27.876[dB]
Site               = NCHU                  Blanking           = 5[us]                      Irr_Atn_Noe                 = 27.876[dB]
Spectrometer       = JNM-ECZ400S/L1        Clipped            = FALSE                      Irr_Dec_Bandwidth_Hz        = 4.7826087[kHz]
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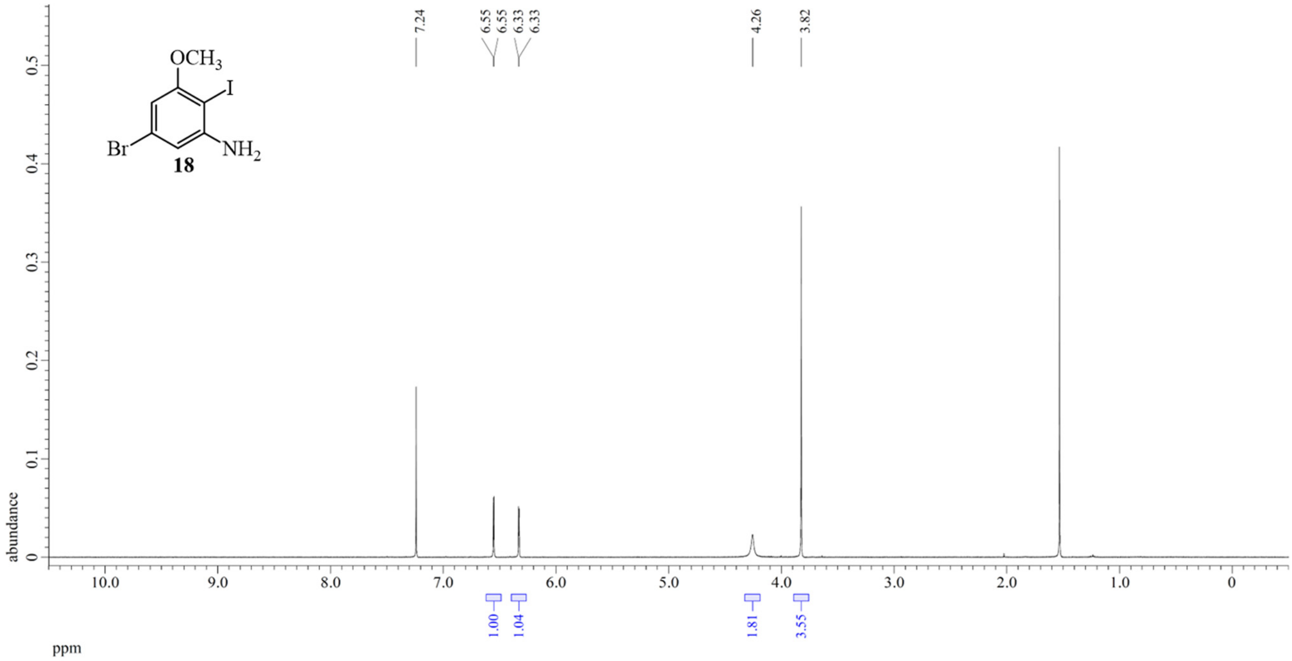
^{13}C NMR spectrum of compound **20** (100 MHz, CDCl$_3$)



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Experiment          = proton_auto.jxp          X_Acq_Duration     = 2.44288[s]              Clipped            = FALSE
Sample_Id           = 20220423-4column         X_Domain           = Proton                  Scans              = 2
Solvent             = CHLOROFORM-D             X_Freq             = 399.78219838[MHz]       Total_Scans        = 2
Actual_Start_Time   = 23-APR-2022 03:54:55     X_Offset           = 6[ppm]
Revision_Time       = 29-JUN-2022 15:33:43     X_Points           = 22000                   Relaxation_Delay   = 2[s]
                                               X_Prescans         = 1                       Recvr_Gain         = 56
Data_Format         = 1D COMPLEX               X_Resolution       = 0.40935289[Hz]          Temp_Get           = 23.5[dC]
Dim_Size            = 52429                    X_Sweep            = 9.00576369[kHz]         X_90_Width         = 7.36[us]
X_Domain            = Proton                   X_Sweep_Clipped    = 7.20461095[kHz]         X_Acq_Time         = 2.44288[s]
Dim_Title           = Proton                   Irr_Domain         = Proton                  X_Angle            = 45[deg]
Dim_Units           = [ppm]                    Irr_Freq           = 399.78219838[MHz]       X_Atn              = 4[dB]
Dimensions          = X                        Irr_Offset         = 5[ppm]                  X_Pulse            = 3.68[us]
Site                = NCHU                     Tri_Domain         = Proton                  Irr_Mode           = Off
Spectrometer        = JNM-ECZ400S/L1           Tri_Freq           = 399.78219838[MHz]       Tri_Mode           = Off
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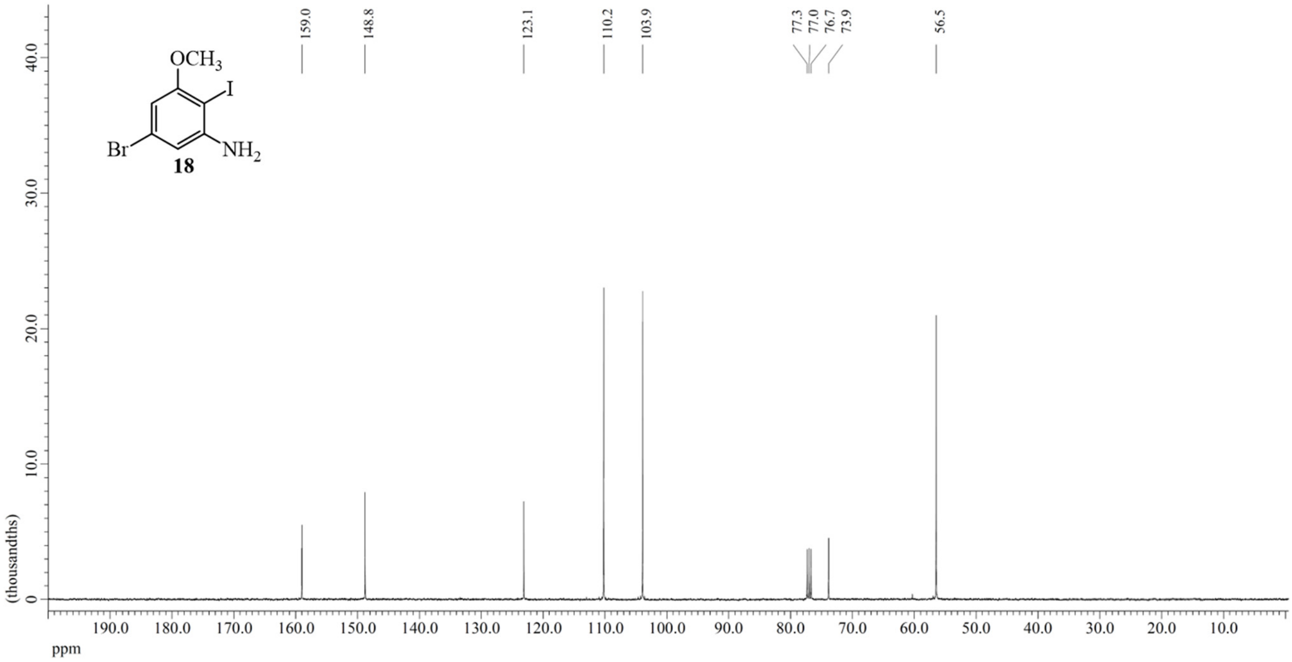
^{1}H NMR spectrum of compound **18** (400 MHz, CDCl$_3$)



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Author              = nmr                      Field_Strength     = 9.389766[T] (400[M    Total_Scans                = 180
Experiment          = carbon_auto.jxp          X_Acq_Duration     = 0.6336[s]
Sample_Id           = 20220509-4carbon         X_Domain           = Carbon13              Relaxation_Delay           = 2[s]
Solvent             = CHLOROFORM-D             X_Freq             = 100.52530333[MHz]     Recvr_Gain                 = 50
Actual_Start_Time   =  9-MAY-2022 06:56:       X_Offset           = 100[ppm]              Temp_Get                   = 22.1[dC]
Revision_Time       =  2-JUL-2022 23:00:       X_Points           = 20000                 X_90_Width                 = 10.35[us]
                                               X_Prescans         = 4                     X_Acq_Time                 = 0.6336[s]
Data_Format         = 1D COMPLEX               X_Resolution       = 1.57828283[Hz]        X_Angle                    = 40[deg]
Dim_Size            = 52429                    X_Sweep            = 31.56565657[kHz]      X_Atn                      = 7.8[dB]
X_Domain            = Carbon13                 X_Sweep_Clipped    = 25.25252525[kHz]      X_Pulse                    = 4.6[us]
Dim_Title           = Carbon13                 Irr_Domain         = Proton                Irr_Atn_Dec                = 27.876[dB]
Dim_Units           = [ppm]                    Irr_Freq           = 399.78219838[MHz]     Irr_Atn_Dec_Calc           = 27.876[dB]
Dimensions          = X                        Irr_Offset         = 5[ppm]                Irr_Atn_Dec_Default_Calc = 27.876[dB]
Site                = NCHU                     Blanking           = 5[us]                 Irr_Atn_Noe                = 27.876[dB]
Spectrometer        = JNM-ECZ400S/L1           Clipped            = FALSE                 Irr_Dec_Bandwidth_Hz       = 4.7826087[kHz]
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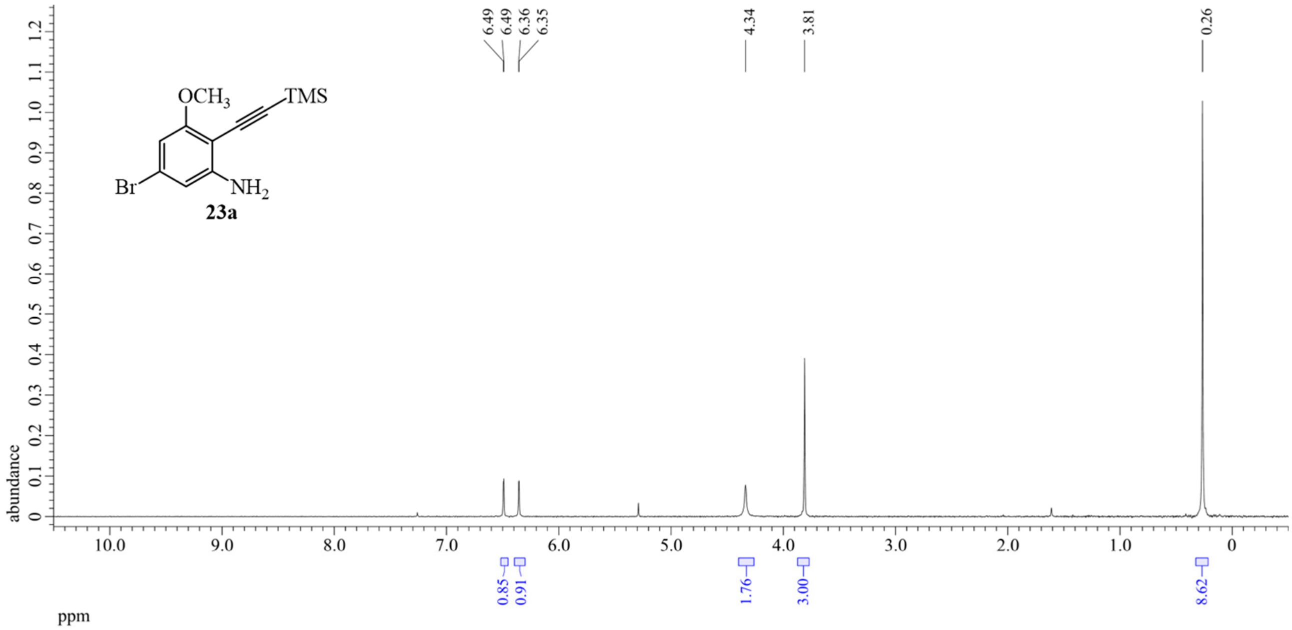
^{13}C NMR spectrum of compound **18** (100 MHz, CDCl$_3$)



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Filename           = H5-column-2-p372_protDim_Units         = [ppm]              X_Resolution       = 0.4173344[Hz]
Author             = nmr                  Dimensions        = X                  X_Sweep            = 10.01602564[kHz]
Experiment         = proton.jxp           Site              = NCHU               X_Sweep_Clipped    = 8.01282051[kHz]
Sample_Id          = H5-column-2-p372     Spectrometer      = JNM-ECZ400S/L1     Irr_Domain         = Proton
Solvent            = CHLOROFORM-D                                                Irr_Freq           = 399.78219838[MHz]
Actual_Start_Time  = 17-FEB-2023 12:53:09 Field_Strength    = 9.389766[T]  (400[MHz]Irr_Offset      = 5[ppm]
Revision_Time      = 18-FEB-2023 02:53:54 X_Acq_Duration    = 2.39616[s]         Tri_Domain         = Proton
                                          X_Domain          = Proton             Tri_Freq           = 399.78219838[MHz]
Data_Format        = 1D COMPLEX           X_Freq            = 399.78219838[MHz]  Tri_Offset         = 5[ppm]
Dim_Size           = 52429                X_Offset          = 5[ppm]             Blanking           = 2[us]
X_Domain           = Proton               X_Points          = 24000              Clipped            = FALSE
Dim_Title          = Proton               X_Prescans        = 1                  Scans              = 2
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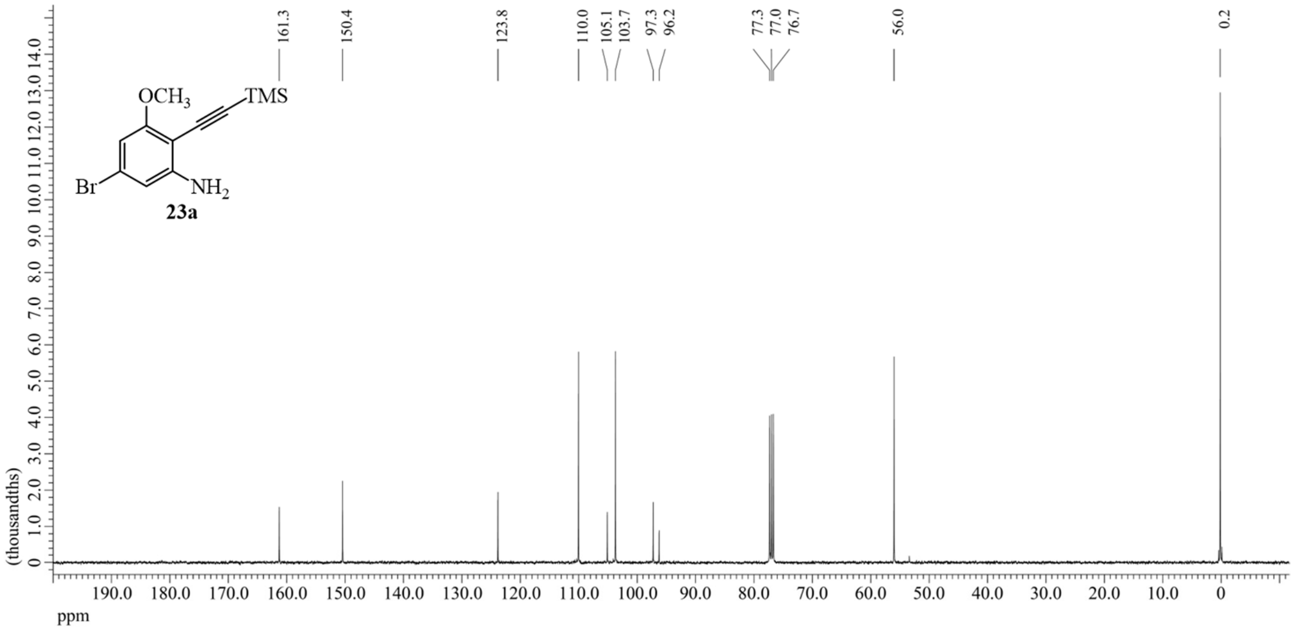
^{1}H NMR spectrum of compound **23a** (400 MHz, $CDCl_3$)



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Filename           = H5-column-2-p372-cDim_Units              = [ppm]              X_Resolution       = 1.57828283[Hz]
Author             = nmr                  Dimensions           = X                  X_Sweep            = 31.56565657[kHz]
Experiment         = carbon.jxp           Site                 = NCHU               X_Sweep_Clipped    = 25.25252525[kHz]
Sample_Id          = H5-column-2-p372-cSpectrometer            = JNM-ECZ400S/L1     Irr_Domain         = Proton
Solvent            = CHLOROFORM-D                                                   Irr_Freq           = 399.78219838[MHz]
Actual_Start_Time  = 17-FEB-2023 14:57:Field_Strength          = 9.389766[T]  (400[MIrr_Offset         = 5[ppm]
Revision_Time      = 18-FEB-2023 02:59:X_Acq_Duration          = 0.6336[s]          Blanking           = 5[us]
                                          X_Domain             = Carbon13           Clipped            = FALSE
Data_Format        = 1D COMPLEX           X_Freq               = 100.52530333[MHz]  Scans              = 542
Dim_Size           = 52429                X_Offset             = 100[ppm]           Total_Scans        = 542
X_Domain           = Carbon13             X_Points             = 20000
Dim_Title          = Carbon13             X_Prescans           = 4                  Relaxation_Delay   = 2[s]
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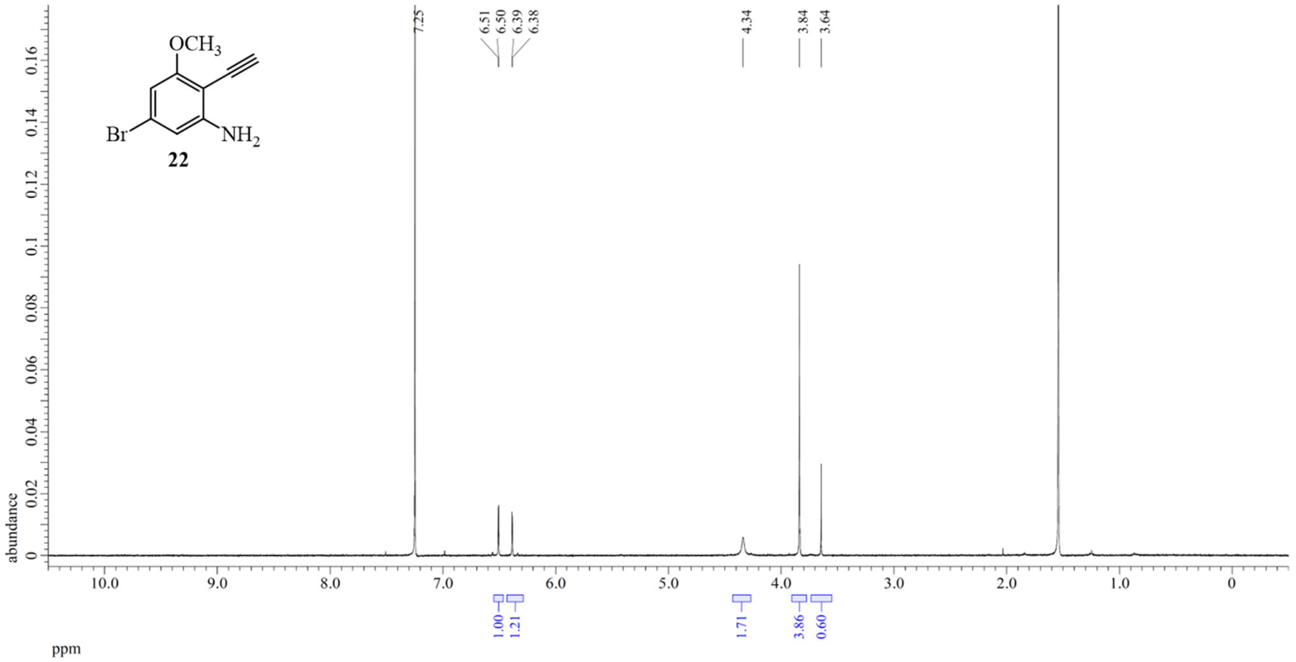
^{13}C NMR spectrum of compound **23a** (100 MHz, $CDCl_3$)



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Author              = nmr                   Field_Strength      = 9.389766[T] (400[MHz]  Blanking            = 2[us]
Experiment          = proton_auto.jxp       X_Acq_Duration      = 2.44288[s]             Clipped             = FALSE
Sample_Id           = 20220602-6column      X_Domain            = Proton                 Scans               = 2
Solvent             = CHLOROFORM-D          X_Freq              = 399.78219838[MHz]      Total_Scans         = 2
Actual_Start_Time   =  2-JUN-2022 06:58:20  X_Offset            = 6[ppm]
Revision_Time       = 29-JUN-2022 15:36:50  X_Points            = 22000                  Relaxation_Delay    = 2[s]
                                            X_Prescans          = 1                      Recvr_Gain          = 56
Data_Format         = 1D COMPLEX            X_Resolution        = 0.40935289[Hz]         Temp_Get            = 22.4[dC]
Dim_Size            = 52429                 X_Sweep             = 9.00576369[kHz]        X_90_Width          = 7.36[us]
X_Domain            = Proton                X_Sweep_Clipped     = 7.20461095[kHz]        X_Acq_Time          = 2.44288[s]
Dim_Title           = Proton                Irr_Domain          = Proton                 X_Angle             = 45[deg]
Dim_Units           = [ppm]                 Irr_Freq            = 399.78219838[MHz]      X_Atn               = 4[dB]
Dimensions          = X                     Irr_Offset          = 5[ppm]                 X_Pulse             = 3.68[us]
Site                = NCHU                  Tri_Domain          = Proton                 Irr_Mode            = Off
Spectrometer        = JNM-ECZ400S/L1        Tri_Freq            = 399.78219838[MHz]      Tri_Mode            = Off
```
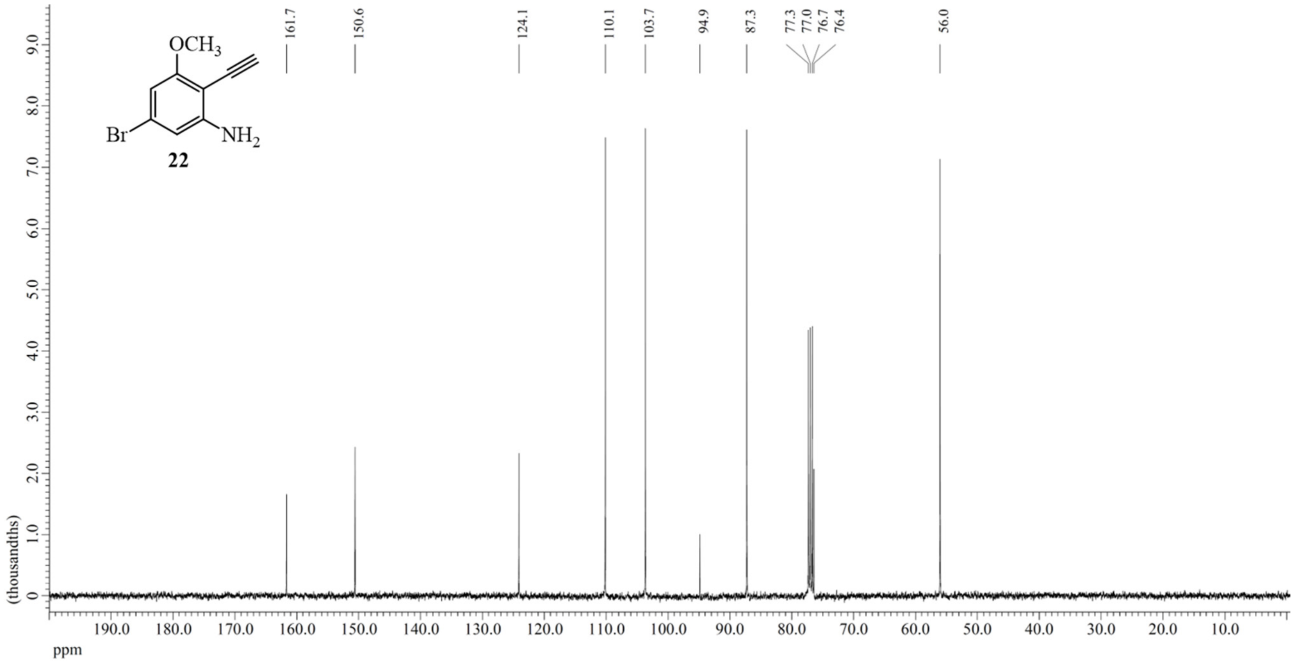

^{1}H NMR spectrum of compound **22** (400 MHz, $CDCl_3$)



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Filename            = 6-column_Carbon-1-                                           Scans                      = 242
Author              = nmr                   Field_Strength      = 9.389766[T] (400[M   Total_Scans                = 242
Experiment          = carbon_auto.jxp       X_Acq_Duration      = 0.6336[s]
Sample_Id           = 6-column              X_Domain            = Carbon13             Relaxation_Delay           = 2[s]
Solvent             = CHLOROFORM-D          X_Freq              = 100.52530333[MHz]    Recvr_Gain                 = 50
Actual_Start_Time   = 14-JUN-2022 06:05:    X_Offset            = 100[ppm]             Temp_Get                   = 22.9[dC]
Revision_Time       =  2-JUL-2022 23:13:    X_Points            = 20000                X_90_Width                 = 10.35[us]
                                            X_Prescans          = 4                    X_Acq_Time                 = 0.6336[s]
Data_Format         = 1D COMPLEX            X_Resolution        = 1.57828283[Hz]       X_Angle                    = 40[deg]
Dim_Size            = 52429                 X_Sweep             = 31.56565657[kHz]     X_Atn                      = 7.8[dB]
X_Domain            = Carbon13              X_Sweep_Clipped     = 25.25252525[kHz]     X_Pulse                    = 4.6[us]
Dim_Title           = Carbon13              Irr_Domain          = Proton               Irr_Atn_Dec                = 27.876[dB]
Dim_Units           = [ppm]                 Irr_Freq            = 399.78219838[MHz]    Irr_Atn_Dec_Calc           = 27.876[dB]
Dimensions          = X                     Irr_Offset          = 5[ppm]               Irr_Atn_Dec_Default_Calc = 27.876[dB]
Site                = NCHU                  Blanking            = 5[us]                Irr_Atn_Noe                = 27.876[dB]
Spectrometer        = JNM-ECZ400S/L1        Clipped             = FALSE                Irr_Dec_Bandwidth_Hz       = 4.7826087[kHz]
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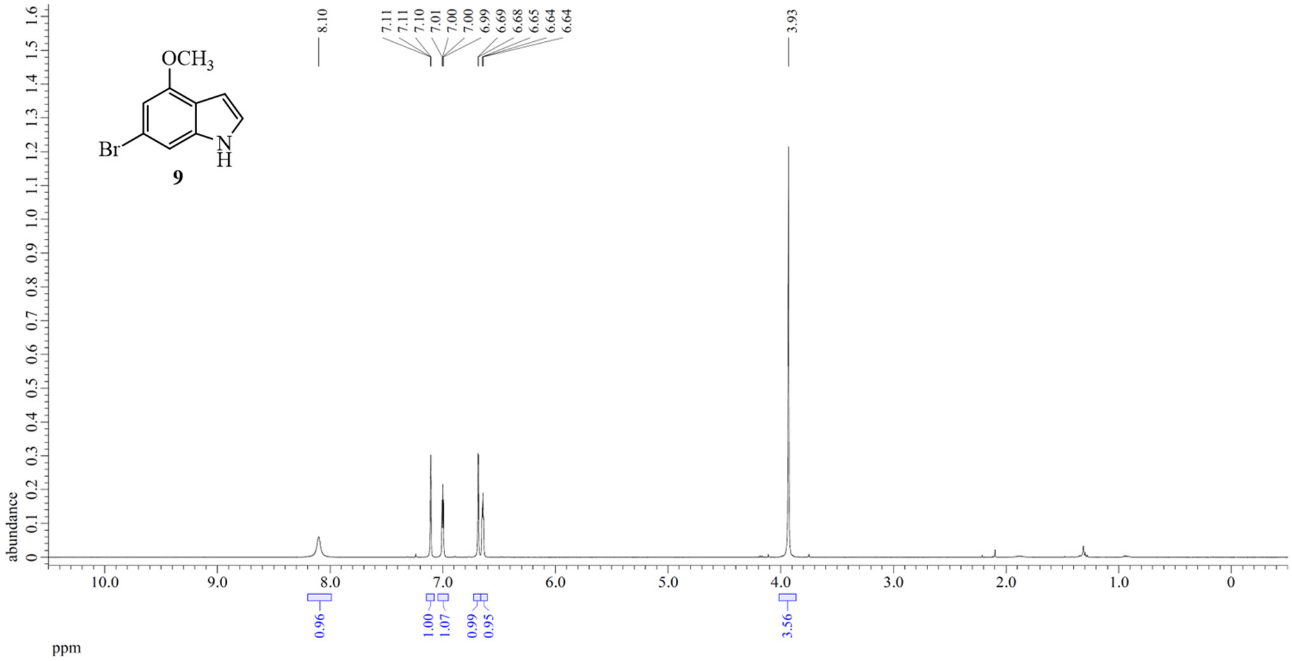
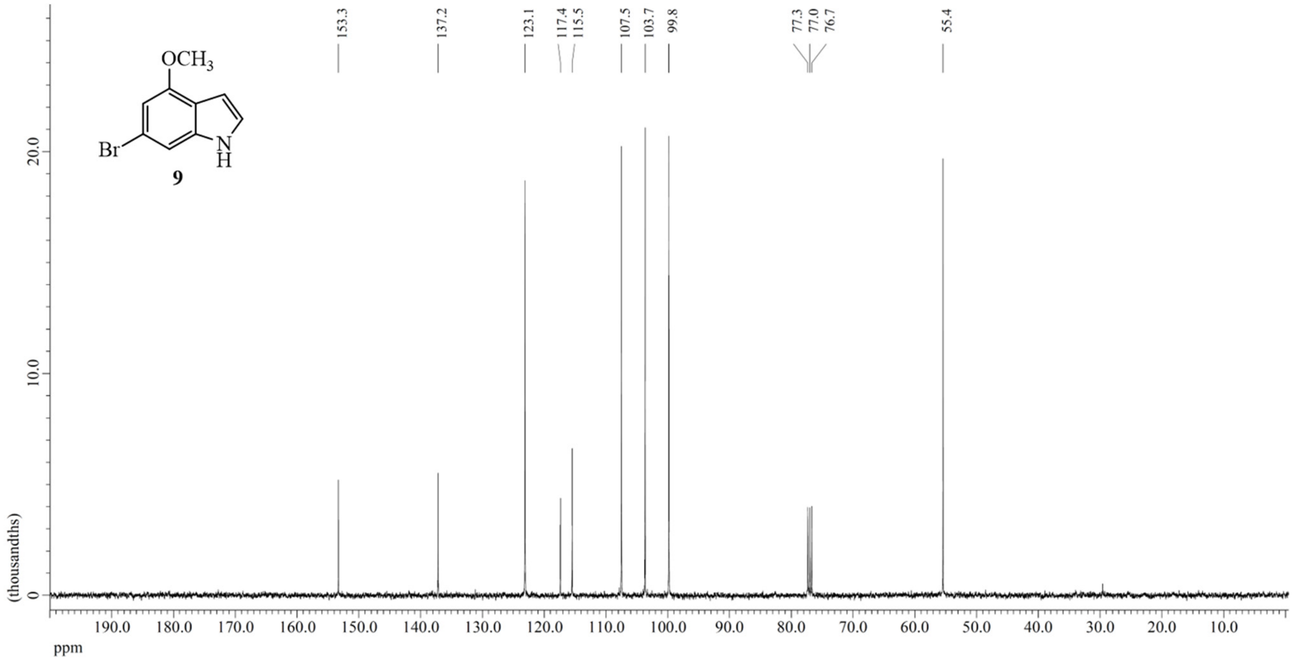
^{13}C NMR spectrum of compound **22** (100 MHz, $CDCl_3$)



```
Filename           = 7 CNMR column_Proton-                                            Tri_Offset          = 5[ppm]
Author             = nmr                   Field_Strength     = 9.389766[T] (400[MHz]  Blanking            = 2[us]
Experiment         = proton_auto.jxp       X_Acq_Duration     = 2.44288[s]             Clipped             = FALSE
Sample_Id          = 7 CNMR column         X_Domain           = Proton                 Scans               = 2
Solvent            = CHLOROFORM-D          X_Freq             = 399.78219838[MHz]      Total_Scans         = 2
Actual_Start_Time  = 17-MAY-2022 03:59:05  X_Offset           = 6[ppm]
Revision_Time      = 29-JUN-2022 15:43:26  X_Points           = 22000                  Relaxation_Delay    = 2[s]
                                           X_Prescans         = 1                      Recvr_Gain          = 36
Data_Format        = 1D COMPLEX            X_Resolution       = 0.40935289[Hz]         Temp_Get            = 20.2[dC]
Dim_Size           = 52429                 X_Sweep            = 9.00576369[kHz]        X_90_Width          = 7.36[us]
X_Domain           = Proton                X_Sweep_Clipped    = 7.20461095[kHz]        X_Acq_Time          = 2.44288[s]
Dim_Title          = Proton                Irr_Domain         = Proton                 X_Angle             = 45[deg]
Dim_Units          = [ppm]                 Irr_Freq           = 399.78219838[MHz]      X_Atn               = 4[dB]
Dimensions         = X                     Irr_Offset         = 5[ppm]                 X_Pulse             = 3.68[us]
Site               = NCHU                  Tri_Domain         = Proton                 Irr_Mode            = Off
Spectrometer       = JNM-ECZ400S/L1        Tri_Freq           = 399.78219838[MHz]      Tri_Mode            = Off
```

^{1}H NMR spectrum of compound **9** (400 MHz, CDCl$_3$)



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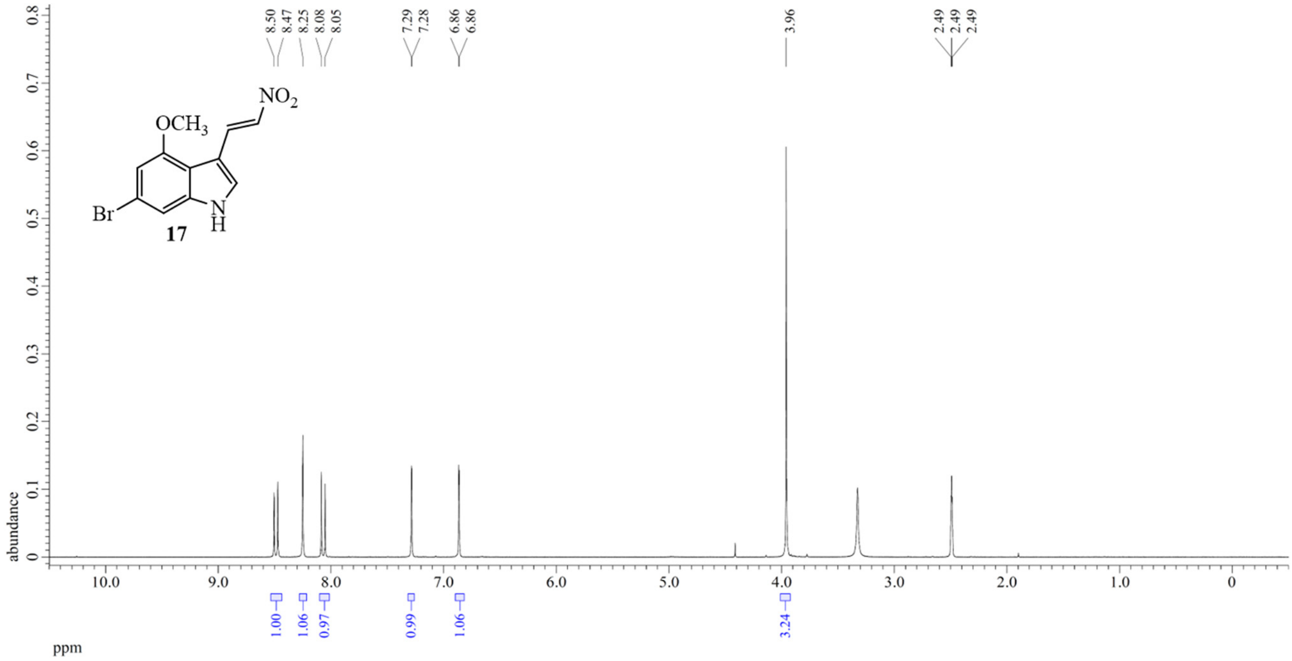
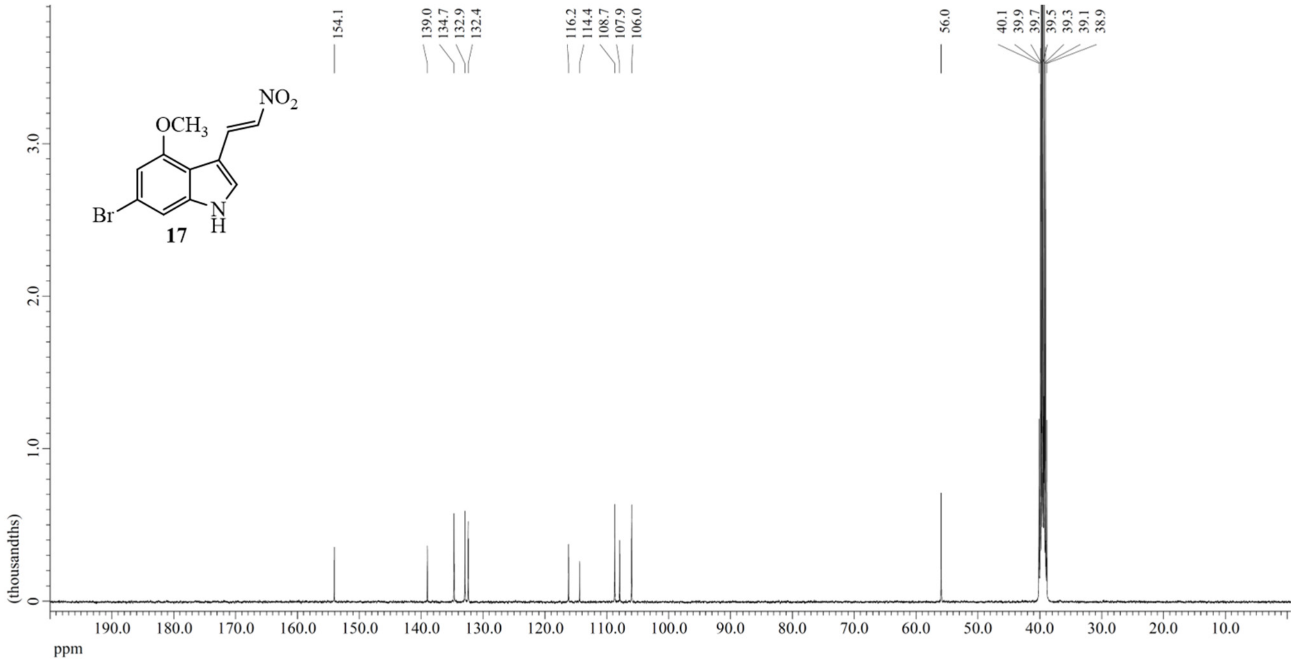
Filename           = 7 CNMR column_Carb                                              Scans                          = 43
Author             = nmr                  Field_Strength     = 9.389766[T] (400[M    Total_Scans                    = 43
Experiment         = carbon_auto.jxp      X_Acq_Duration     = 0.6336[s]
Sample_Id          = 7 CNMR column        X_Domain           = Carbon13              Relaxation_Delay               = 2[s]
Solvent            = CHLOROFORM-D         X_Freq             = 100.52530333[MHz]     Recvr_Gain                     = 50
Actual_Start_Time  = 17-MAY-2022 03:59:   X_Offset           = 100[ppm]              Temp_Get                       = 20.2[dC]
Revision_Time      =  2-JUL-2022 23:05:   X_Points           = 20000                 X_90_Width                     = 10.35[us]
                                          X_Prescans         = 4                     X_Acq_Time                     = 0.6336[s]
Data_Format        = 1D COMPLEX           X_Resolution       = 1.57828283[Hz]        X_Angle                        = 40[deg]
Dim_Size           = 52429                X_Sweep            = 31.56565657[kHz]      X_Atn                          = 7.8[dB]
X_Domain           = Carbon13             X_Sweep_Clipped    = 25.25252525[kHz]      X_Pulse                        = 4.6[us]
Dim_Title          = Carbon13             Irr_Domain         = Proton                Irr_Atn_Dec                    = 27.876[dB]
Dim_Units          = [ppm]                Irr_Freq           = 399.78219838[MHz]     Irr_Atn_Dec_Calc               = 27.876[dB]
Dimensions         = X                    Irr_Offset         = 5[ppm]                Irr_Atn_Dec_Default_Calc       = 27.876[dB]
Site               = NCHU                 Blanking           = 5[us]                 Irr_Atn_Noe                    = 27.876[dB]
Spectrometer       = JNM-ECZ400S/L1       Clipped            = FALSE                 Irr_Dec_Bandwidth_Hz           = 4.7826087[kHz]
```

^{13}C NMR spectrum of compound **9** (100 MHz, CDCl$_3$)



```
Filename          = 20220618-9_Proton-3-2                                        Tri_Offset        = 5[ppm]
Author            = nmr                    Field_Strength    = 9.389766[T] (400[MHz] Blanking          = 2[us]
Experiment        = proton_auto.jxp        X_Acq_Duration    = 2.44288[s]          Clipped           = FALSE
Sample_Id         = 20220618-9             X_Domain          = Proton              Scans             = 2
Solvent           = DMSO-D6                X_Freq            = 399.78219838[MHz]   Total_Scans       = 2
Actual_Start_Time = 18-JUN-2022 05:02:13   X_Offset          = 6[ppm]
Revision_Time     = 29-JUN-2022 15:54:53   X_Points          = 22000               Relaxation_Delay  = 2[s]
                                           X_Prescans        = 1                   Recvr_Gain        = 56
Data_Format       = 1D COMPLEX             X_Resolution      = 0.40935289[Hz]      Temp_Get          = 22.5[dC]
Dim_Size          = 52429                  X_Sweep           = 9.00576369[kHz]     X_90_Width        = 7.36[us]
X_Domain          = Proton                 X_Sweep_Clipped   = 7.20461095[kHz]     X_Acq_Time        = 2.44288[s]
Dim_Title         = Proton                 Irr_Domain        = Proton              X_Angle           = 45[deg]
Dim_Units         = [ppm]                  Irr_Freq          = 399.78219838[MHz]   X_Atn             = 4[dB]
Dimensions        = X                      Irr_Offset        = 5[ppm]              X_Pulse           = 3.68[us]
Site              = NCHU                   Tri_Domain        = Proton              Irr_Mode          = Off
Spectrometer      = JNM-ECZ400S/L1         Tri_Freq          = 399.78219838[MHz]   Tri_Mode          = Off
```

^{1}H NMR spectrum of compound **17** (400 MHz, DMSO-d_6)



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Filename          = 20220618-9carbon_C                                           Scans                      = 11255
Author            = nmr                    Field_Strength    = 9.389766[T] (400[M  Total_Scans                = 11255
Experiment        = carbon_auto.jxp        X_Acq_Duration    = 0.6336[s]
Sample_Id         = 20220618-9carbon       X_Domain          = Carbon13            Relaxation_Delay           = 2[s]
Solvent           = DMSO-D6                X_Freq            = 100.52530333[MHz]   Recvr_Gain                 = 50
Actual_Start_Time = 18-JUN-2022 10:19:     X_Offset          = 100[ppm]            Temp_Get                   = 22.4[dC]
Revision_Time     =  2-JUL-2022 23:19:     X_Points          = 20000               X_90_Width                 = 10.35[us]
                                           X_Prescans        = 4                   X_Acq_Time                 = 0.6336[s]
Data_Format       = 1D COMPLEX             X_Resolution      = 1.57828283[Hz]      X_Angle                    = 40[deg]
Dim_Size          = 52429                  X_Sweep           = 31.56565657[kHz]    X_Atn                      = 7.8[dB]
X_Domain          = Carbon13               X_Sweep_Clipped   = 25.25252525[kHz]    X_Pulse                    = 4.6[us]
Dim_Title         = Carbon13               Irr_Domain        = Proton              Irr_Atn_Dec                = 27.876[dB]
Dim_Units         = [ppm]                  Irr_Freq          = 399.78219838[MHz]   Irr_Atn_Dec_Calc           = 27.876[dB]
Dimensions        = X                      Irr_Offset        = 5[ppm]              Irr_Atn_Dec_Default_Calc   = 27.876[dB]
Site              = NCHU                   Blanking          = 5[us]               Irr_Atn_Noe                = 27.876[dB]
Spectrometer      = JNM-ECZ400S/L1         Clipped           = FALSE               Irr_Dec_Bandwidth_Hz       = 4.7826087[kHz]
```
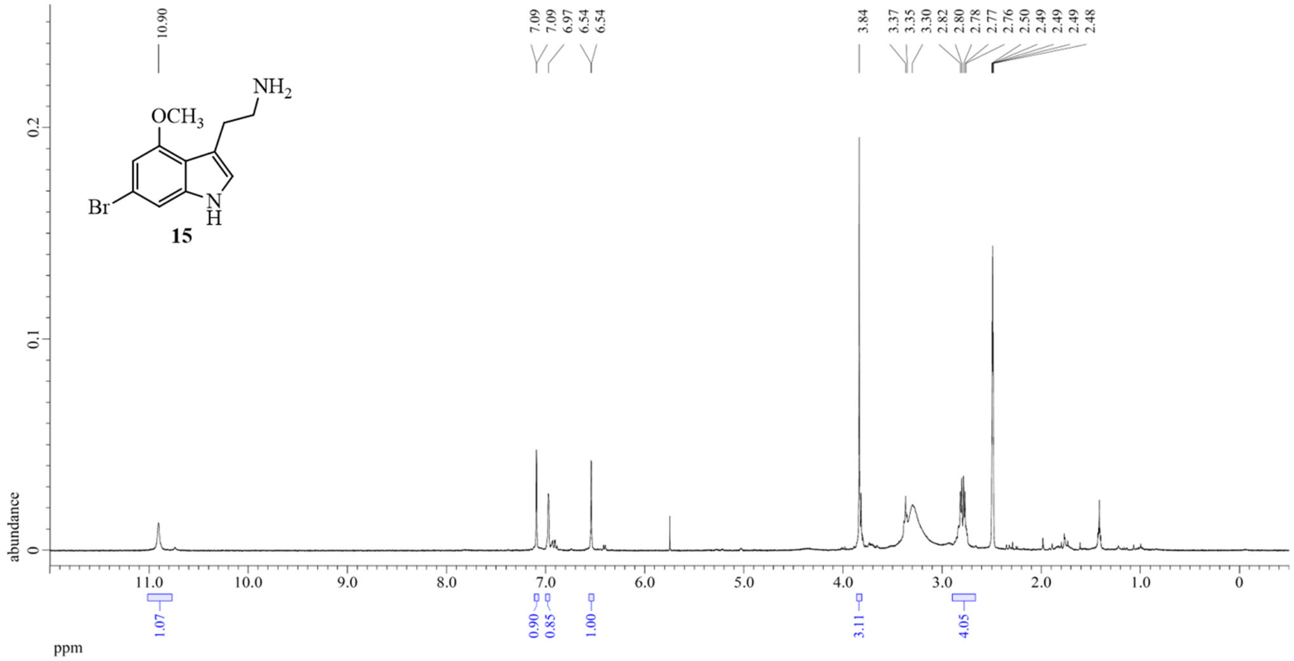
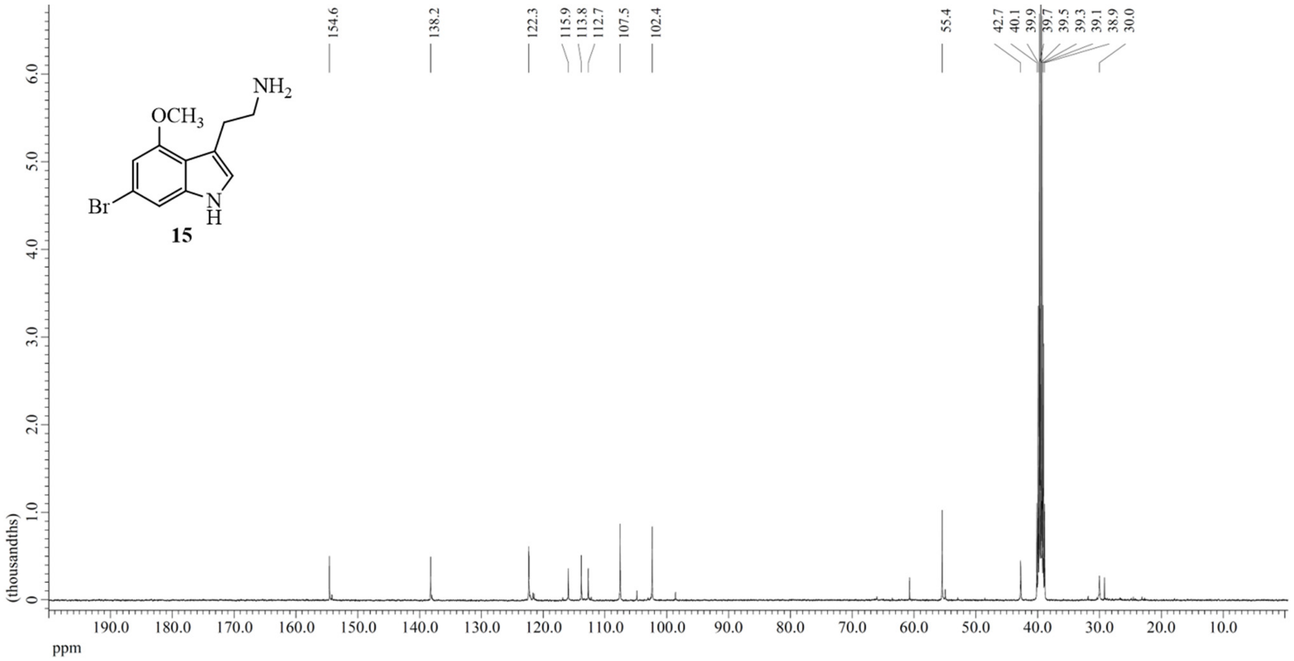

^{13}C NMR spectrum of compound **17** (100 MHz, DMSO-d_6)



15

```
Filename           = tryptamine4_Proton-1-                                            Tri_Offset         = 5[ppm]
Author             = nmr                    Field_Strength    = 9.389766[T] (400[MHz]   Blanking           = 2[us]
Experiment         = proton_auto.jxp        X_Acq_Duration    = 2.44288[s]              Clipped            = FALSE
Sample_Id          = tryptamine4            X_Domain          = Proton                  Scans              = 2
Solvent            = DMSO-D6                X_Freq            = 399.78219838[MHz]       Total_Scans        = 2
Actual_Start_Time  = 17-JUN-2022 05:52:59   X_Offset          = 6[ppm]
Revision_Time      = 29-JUN-2022 16:09:06   X_Points          = 22000                   Relaxation_Delay   = 2[s]
                                            X_Prescans        = 1                       Recvr_Gain         = 56
Data_Format        = 1D COMPLEX             X_Resolution      = 0.40935289[Hz]          Temp_Get           = 22.8[dC]
Dim_Size           = 52429                  X_Sweep           = 9.00576369[kHz]         X_90_Width         = 7.36[us]
X_Domain           = Proton                 X_Sweep_Clipped   = 7.20461095[kHz]         X_Acq_Time         = 2.44288[s]
Dim_Title          = Proton                 Irr_Domain        = Proton                  X_Angle            = 45[deg]
Dim_Units          = [ppm]                  Irr_Freq          = 399.78219838[MHz]       X_Atn              = 4[dB]
Dimensions         = X                      Irr_Offset        = 5[ppm]                  X_Pulse            = 3.68[us]
Site               = NCHU                   Tri_Domain        = Proton                  Irr_Mode           = Off
Spectrometer       = JNM-ECZ400S/L1         Tri_Freq          = 399.78219838[MHz]       Tri_Mode           = Off
```

^{1}H NMR spectrum of compound **15** (400 MHz, DMSO-d_6)



15

```
Filename           = tryptamine4carbon_                                               Scans                       = 13921
Author             = nmr                    Field_Strength    = 9.389766[T] (400[M    Total_Scans                 = 13921
Experiment         = carbon_auto.jxp        X_Acq_Duration    = 0.6336[s]
Sample_Id          = tryptamine4carbon      X_Domain          = Carbon13              Relaxation_Delay            = 2[s]
Solvent            = DMSO-D6                X_Freq            = 100.52530333[MHz]     Recvr_Gain                  = 50
Actual_Start_Time  = 23-JUN-2022 08:42:     X_Offset          = 100[ppm]              Temp_Get                    = 22.3[dC]
Revision_Time      =  2-JUL-2022 23:28:     X_Points          = 20000                 X_90_Width                  = 10.35[us]
                                            X_Prescans        = 4                     X_Acq_Time                  = 0.6336[s]
Data_Format        = 1D COMPLEX             X_Resolution      = 1.57828283[Hz]        X_Angle                     = 40[deg]
Dim_Size           = 52429                  X_Sweep           = 31.56565657[kHz]      X_Atn                       = 7.8[dB]
X_Domain           = Carbon13               X_Sweep_Clipped   = 25.25252525[kHz]      X_Pulse                     = 4.6[us]
Dim_Title          = Carbon13               Irr_Domain        = Proton                Irr_Atn_Dec                 = 27.876[dB]
Dim_Units          = [ppm]                  Irr_Freq          = 399.78219838[MHz]     Irr_Atn_Dec_Calc            = 27.876[dB]
Dimensions         = X                      Irr_Offset        = 5[ppm]                Irr_Atn_Dec_Default_Calc = 27.876[dB]
Site               = NCHU                   Blanking          = 5[us]                 Irr_Atn_Noe                 = 27.876[dB]
Spectrometer       = JNM-ECZ400S/L1         Clipped           = FALSE                 Irr_Dec_Bandwidth_Hz        = 4.7826087[kHz]
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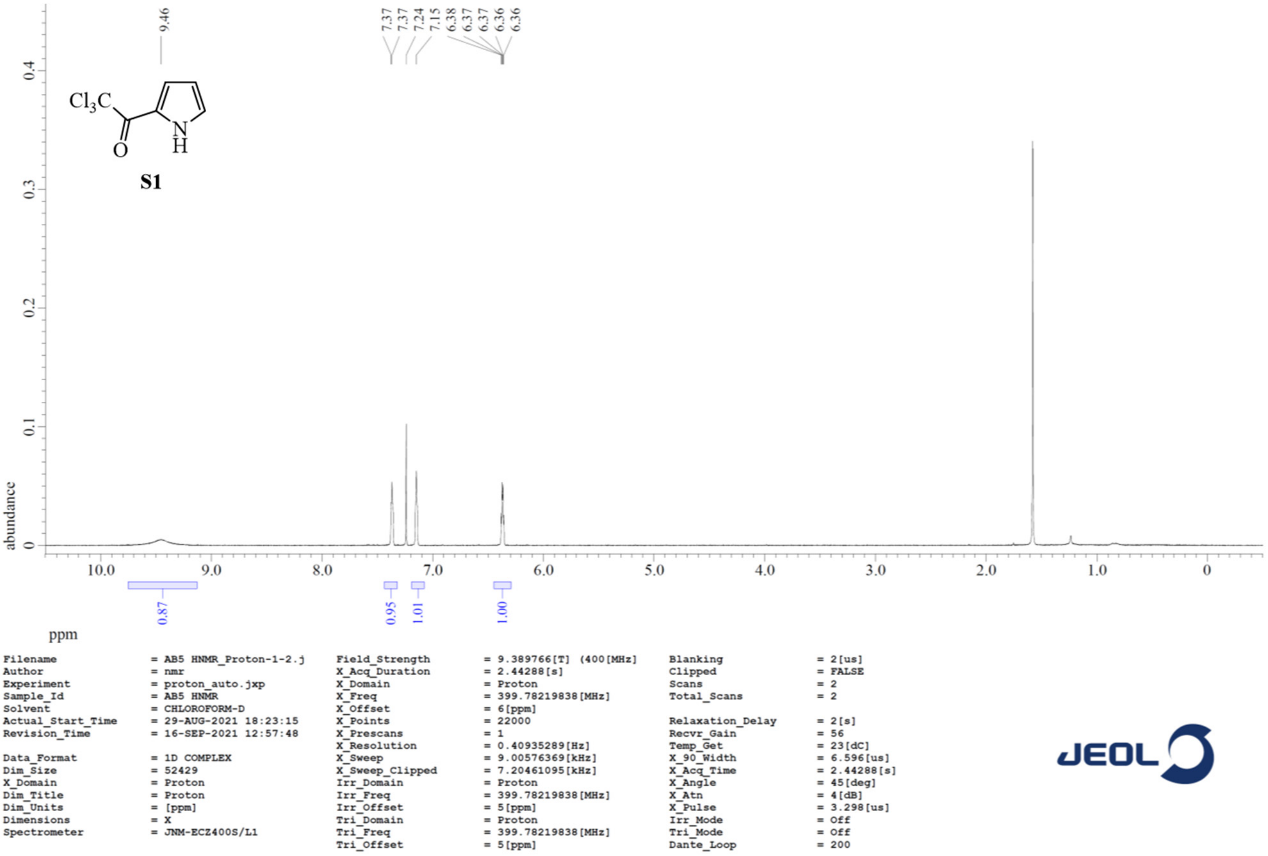
^{13}C NMR spectrum of compound **15** (100 MHz, DMSO-d_6)



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Filename              = AB5 HNMR_Proton-1-2.j   Field_Strength      = 9.389766[T] (400[MHz]   Blanking            = 2[us]
Author                = nmr                     X_Acq_Duration      = 2.44288[s]              Clipped             = FALSE
Experiment            = proton_auto.jxp         X_Domain            = Proton                  Scans               = 2
Sample_Id             = AB5 HNMR                X_Freq              = 399.78219838[MHz]       Total_Scans         = 2
Solvent               = CHLOROFORM-D            X_Offset            = 6[ppm]
Actual_Start_Time     = 29-AUG-2021 18:23:15    X_Points            = 22000                   Relaxation_Delay    = 2[s]
Revision_Time         = 16-SEP-2021 12:57:48    X_Prescans          = 1                       Recvr_Gain          = 56
                                                X_Resolution        = 0.40935289[Hz]          Temp_Get            = 23[dC]
Data_Format           = 1D COMPLEX              X_Sweep             = 9.00576369[kHz]         X_90_Width          = 6.596[us]
Dim_Size              = 52429                   X_Sweep_Clipped     = 7.20461095[kHz]         X_Acq_Time          = 2.44288[s]
X_Domain              = Proton                  Irr_Domain          = Proton                  X_Angle             = 45[deg]
Dim_Title             = Proton                  Irr_Freq            = 399.78219838[MHz]       X_Atn               = 4[dB]
Dim_Units             = [ppm]                   Irr_Offset          = 5[ppm]                  X_Pulse             = 3.298[us]
Dimensions            = X                       Tri_Domain          = Proton                  Irr_Mode            = Off
Spectrometer          = JNM-ECZ400S/L1          Tri_Freq            = 399.78219838[MHz]       Tri_Mode            = Off
                                                Tri_Offset          = 5[ppm]                  Dante_Loop          = 200
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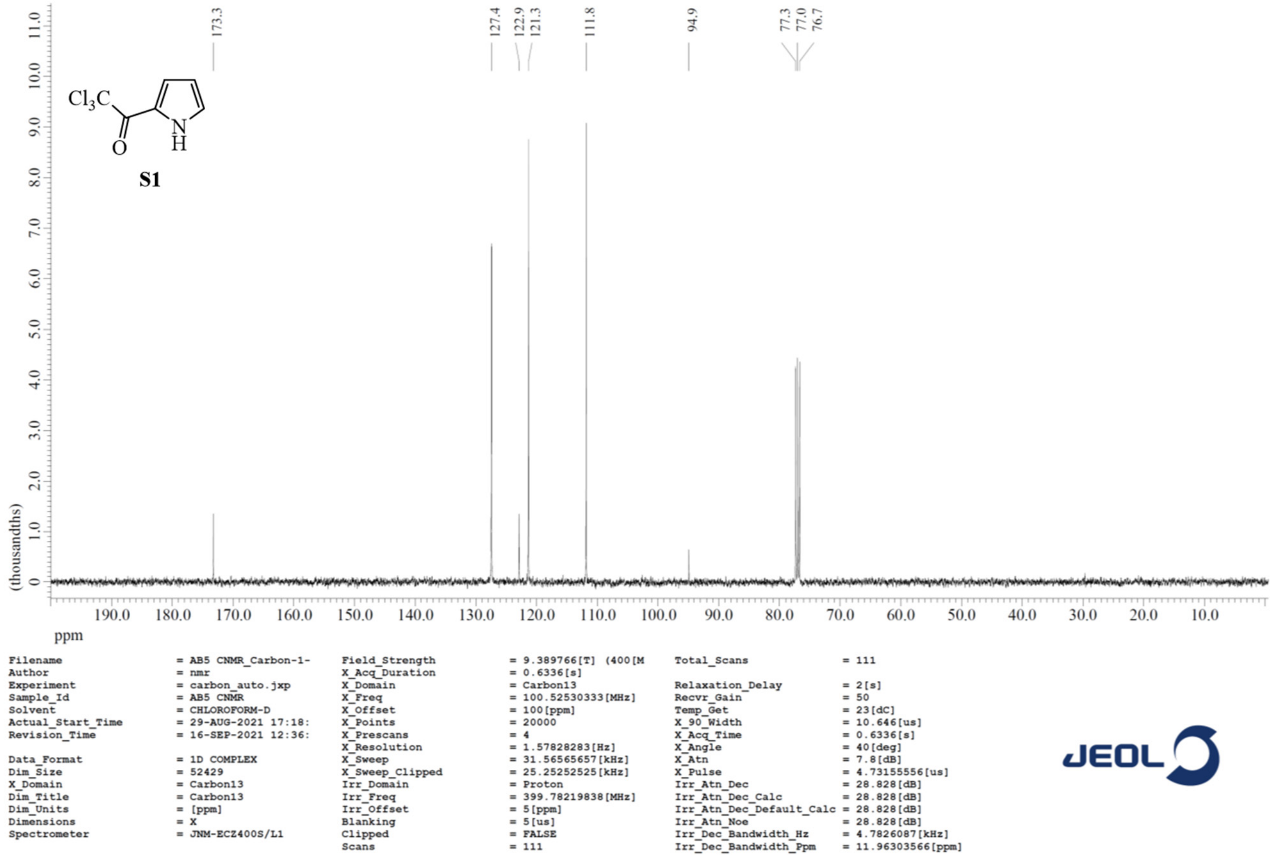
^{1}H NMR spectrum of compound **S1** (400 MHz, CDCl₃)



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Filename              = AB5 CNMR_Carbon-1-      Field_Strength      = 9.389766[T] (400[M      Total_Scans                  = 111
Author                = nmr                     X_Acq_Duration      = 0.6336[s]
Experiment            = carbon_auto.jxp         X_Domain            = Carbon13                Relaxation_Delay             = 2[s]
Sample_Id             = AB5 CNMR                X_Freq              = 100.52530333[MHz]       Recvr_Gain                   = 50
Solvent               = CHLOROFORM-D            X_Offset            = 100[ppm]                Temp_Get                     = 23[dC]
Actual_Start_Time     = 29-AUG-2021 17:18:      X_Points            = 20000                   X_90_Width                   = 10.646[us]
Revision_Time         = 16-SEP-2021 12:36:      X_Prescans          = 4                       X_Acq_Time                   = 0.6336[s]
                                                X_Resolution        = 1.57828283[Hz]          X_Angle                      = 40[deg]
Data_Format           = 1D COMPLEX              X_Sweep             = 31.56565657[kHz]        X_Atn                        = 7.8[dB]
Dim_Size              = 52429                   X_Sweep_Clipped     = 25.25252525[kHz]        X_Pulse                      = 4.73155556[us]
X_Domain              = Carbon13                Irr_Domain          = Proton                  Irr_Atn_Dec                  = 28.828[dB]
Dim_Title             = Carbon13                Irr_Freq            = 399.78219838[MHz]       Irr_Atn_Dec_Calc             = 28.828[dB]
Dim_Units             = [ppm]                   Irr_Offset          = 5[ppm]                  Irr_Atn_Dec_Default_Calc = 28.828[dB]
Dimensions            = X                       Blanking            = 5[us]                   Irr_Atn_Noe                  = 28.828[dB]
Spectrometer          = JNM-ECZ400S/L1          Clipped             = FALSE                   Irr_Dec_Bandwidth_Hz         = 4.7826087[kHz]
                                                Scans               = 111                     Irr_Dec_Bandwidth_Ppm        = 11.96303566[ppm]
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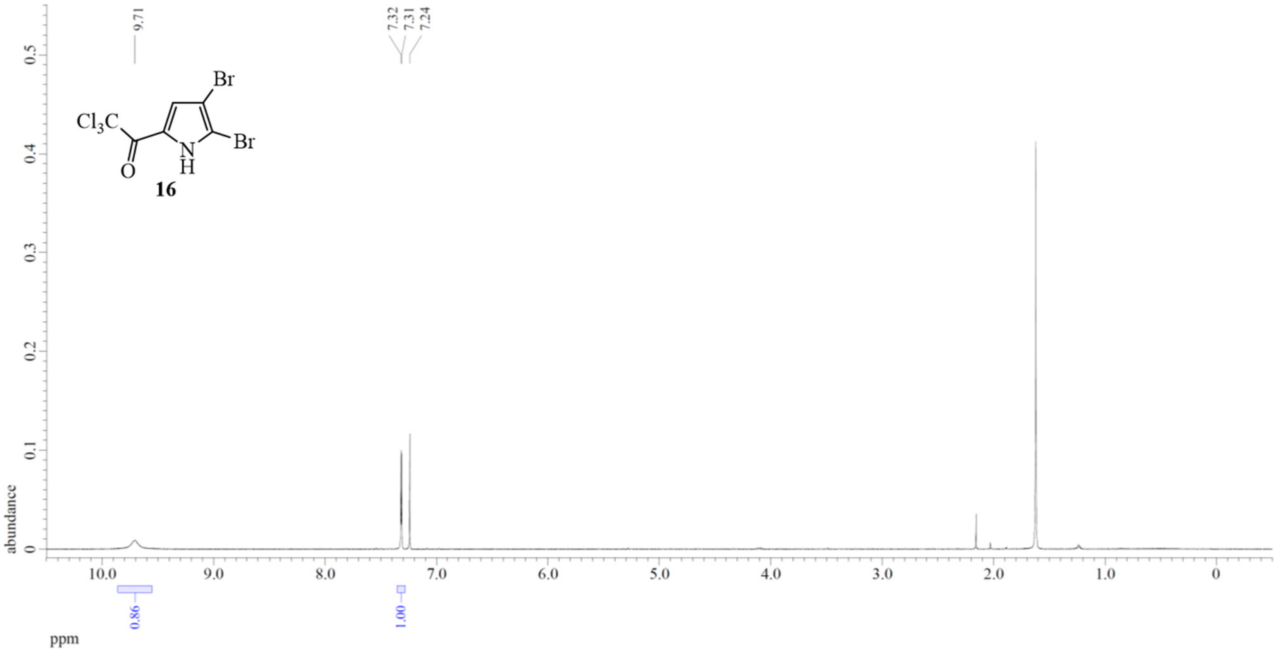
^{13}C NMR spectrum of compound **S1** (100 MHz, CDCl₃)



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Filename              = AB6 HNMR_Proton-1-2.j   Field_Strength      = 9.389766[T] (400[MHz]   Blanking            = 2[us]
Author                = nmr                     X_Acq_Duration      = 2.44288[s]              Clipped             = FALSE
Experiment            = proton_auto.jxp         X_Domain            = Proton                  Scans               = 2
Sample_Id             = AB6 HNMR                X_Freq              = 399.78219838[MHz]       Total_Scans         = 2
Solvent               = CHLOROFORM-D            X_Offset            = 6[ppm]
Actual_Start_Time     = 29-AUG-2021 18:29:45    X_Points            = 22000                   Relaxation_Delay    = 2[s]
Revision_Time         = 16-SEP-2021 13:02:09    X_Prescans          = 1                       Recvr_Gain          = 56
                                                X_Resolution        = 0.40935289[Hz]          Temp_Get            = 23[dC]
Data_Format           = 1D COMPLEX              X_Sweep             = 9.00576369[kHz]         X_90_Width          = 6.596[us]
Dim_Size              = 52429                   X_Sweep_Clipped     = 7.20461095[kHz]         X_Acq_Time          = 2.44288[s]
X_Domain              = Proton                  Irr_Domain          = Proton                  X_Angle             = 45[deg]
Dim_Title             = Proton                  Irr_Freq            = 399.78219838[MHz]       X_Atn               = 4[dB]
Dim_Units             = [ppm]                   Irr_Offset          = 5[ppm]                  X_Pulse             = 3.298[us]
Dimensions            = X                       Tri_Domain          = Proton                  Irr_Mode            = Off
Spectrometer          = JNM-ECZ400S/L1          Tri_Freq            = 399.78219838[MHz]       Tri_Mode            = Off
                                                Tri_Offset          = 5[ppm]                  Dante_Loop          = 200
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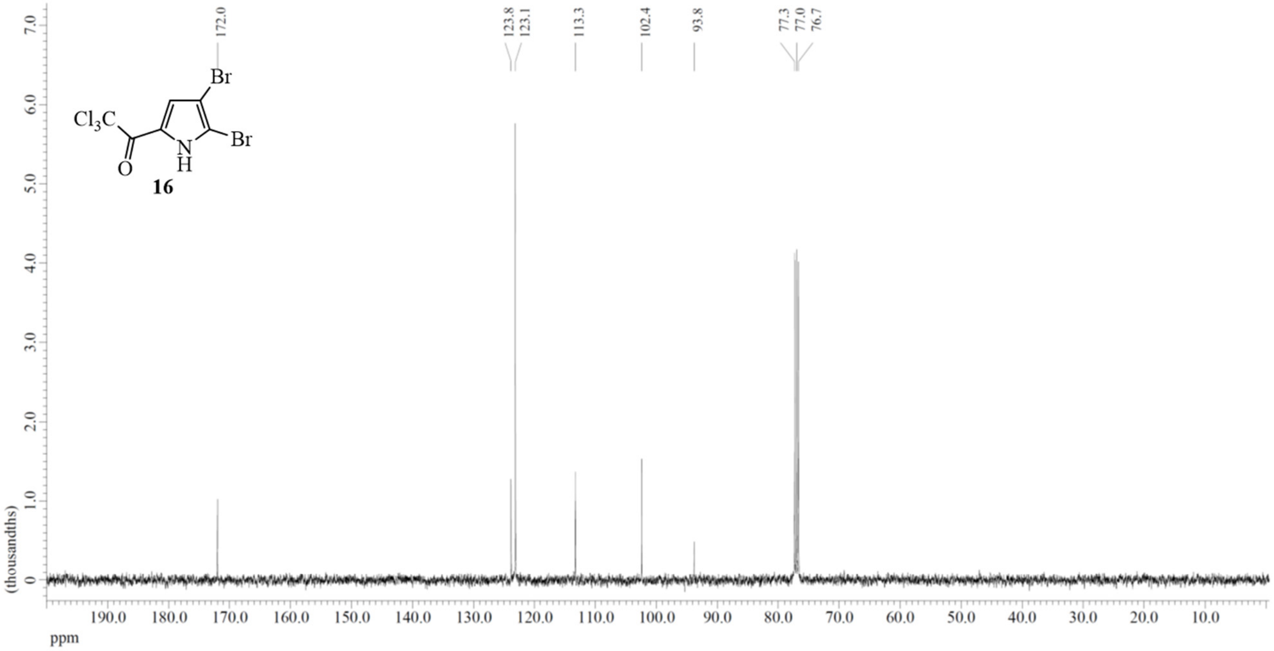
^{1}H NMR spectrum of compound **16** (400 MHz, $CDCl_3$)



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Filename              = AB6 CNMR_Carbon-1-      Field_Strength      = 9.389766[T] (400[M      Total_Scans                 = 135
Author                = nmr                     X_Acq_Duration      = 0.6336[s]
Experiment            = carbon_auto.jxp         X_Domain            = Carbon13                Relaxation_Delay            = 2[s]
Sample_Id             = AB6 CNMR                X_Freq              = 100.52530333[MHz]       Recvr_Gain                  = 50
Solvent               = CHLOROFORM-D            X_Offset            = 100[ppm]                Temp_Get                    = 22.9[dC]
Actual_Start_Time     = 29-AUG-2021 17:27:      X_Points            = 20000                   X_90_Width                  = 10.646[us]
Revision_Time         = 16-SEP-2021 12:37:      X_Prescans          = 4                       X_Acq_Time                  = 0.6336[s]
                                                X_Resolution        = 1.57828283[Hz]          X_Angle                     = 40[deg]
Data_Format           = 1D COMPLEX              X_Sweep             = 31.56565657[kHz]        X_Atn                       = 7.8[dB]
Dim_Size              = 52429                   X_Sweep_Clipped     = 25.25252525[kHz]        X_Pulse                     = 4.73155556[us]
X_Domain              = Carbon13                Irr_Domain          = Proton                  Irr_Atn_Dec                 = 28.828[dB]
Dim_Title             = Carbon13                Irr_Freq            = 399.78219838[MHz]       Irr_Atn_Dec_Calc            = 28.828[dB]
Dim_Units             = [ppm]                   Irr_Offset          = 5[ppm]                  Irr_Atn_Dec_Default_Calc    = 28.828[dB]
Dimensions            = X                       Blanking            = 5[us]                   Irr_Atn_Noe                 = 28.828[dB]
Spectrometer          = JNM-ECZ400S/L1          Clipped             = FALSE                   Irr_Dec_Bandwidth_Hz        = 4.7826087[kHz]
                                                Scans               = 135                     Irr_Dec_Bandwidth_Ppm       = 11.96303566[ppm]
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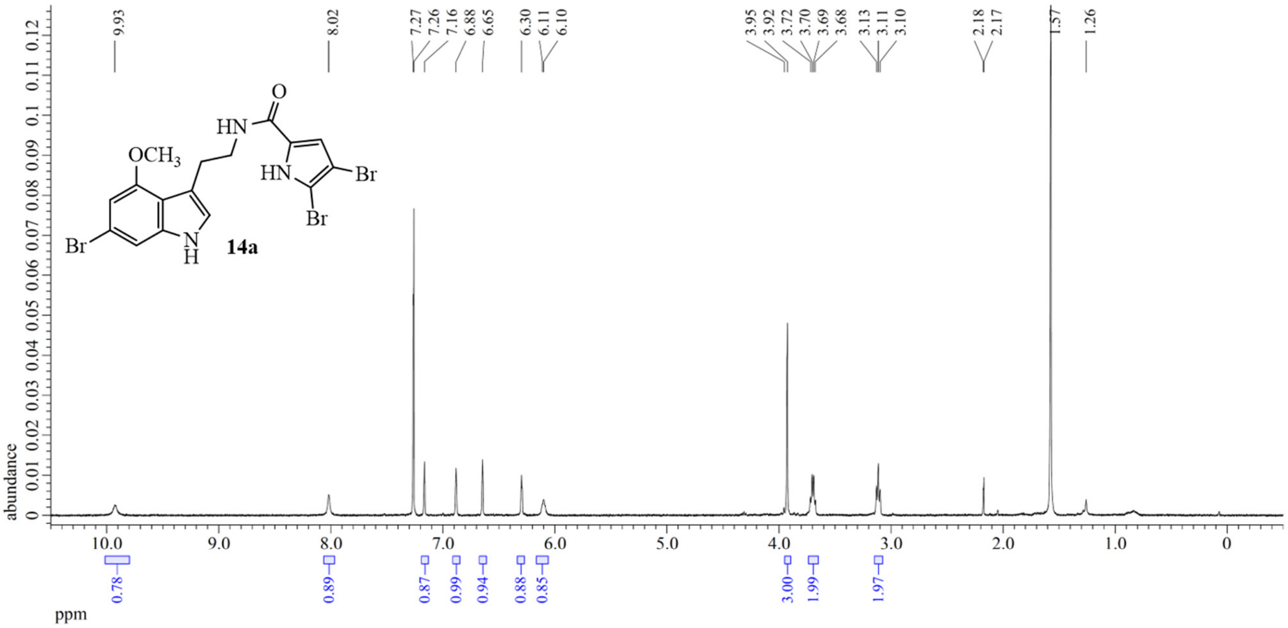
^{13}C NMR spectrum of compound **16** (100 MHz, $CDCl_3$)



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Filename          = H11-clean-p235_ProtonDim_Units          = [ppm]                 X_Resolution      = 0.40935289[Hz]
Author            = nmr                 Dimensions          = X                     X_Sweep           = 9.00576369[kHz]
Experiment        = proton_auto.jxp     Site                = NCHU                  X_Sweep_Clipped   = 7.20461095[kHz]
Sample_Id         = H11-clean-p235      Spectrometer        = JNM-ECZ400S/L1        Irr_Domain        = Proton
Solvent           = CHLOROFORM-D                                                    Irr_Freq          = 399.78219838[MHz]
Actual_Start_Time = 25-AUG-2022 15:08:33 Field_Strength     = 9.389766[T] (400[MHz]Irr_Offset        = 5[ppm]
Revision_Time     = 11-JAN-2023 11:32:17 X_Acq_Duration     = 2.44288[s]            Tri_Domain        = Proton
                                        X_Domain            = Proton                Tri_Freq          = 399.78219838[MHz]
Data_Format       = 1D COMPLEX          X_Freq              = 399.78219838[MHz]     Tri_Offset        = 5[ppm]
Dim_Size          = 52429               X_Offset            = 6[ppm]                Blanking          = 2[us]
X_Domain          = Proton              X_Points            = 22000                 Clipped           = FALSE
Dim_Title         = Proton              X_Prescans          = 1                     Scans             = 2
```
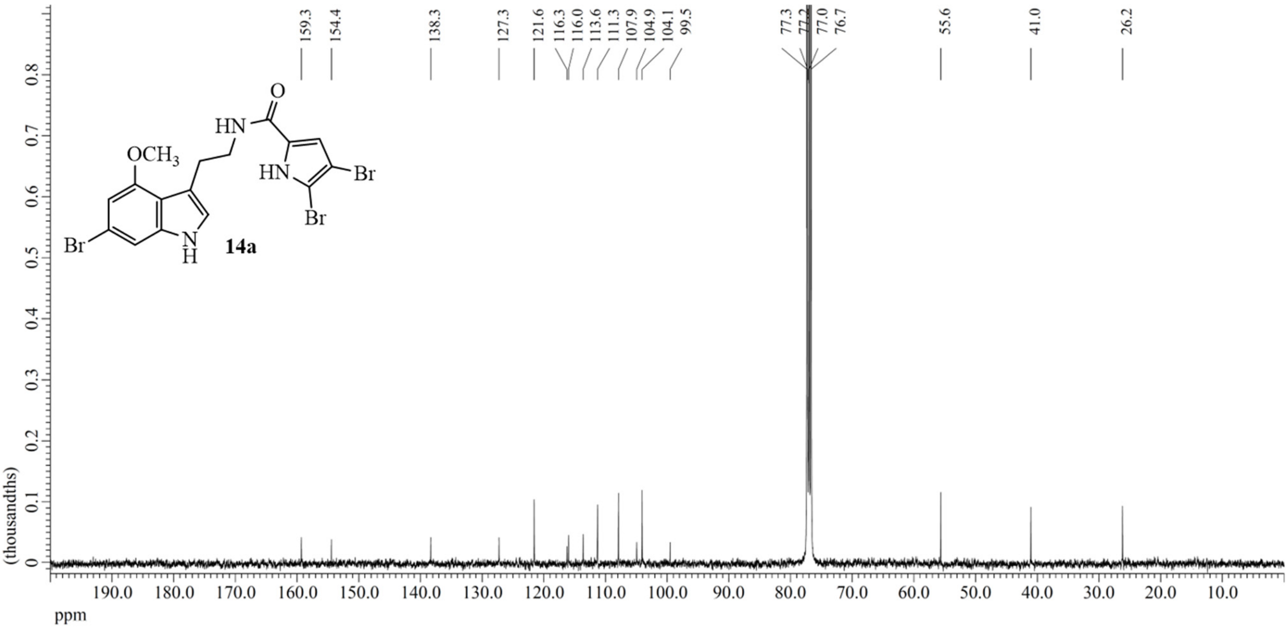
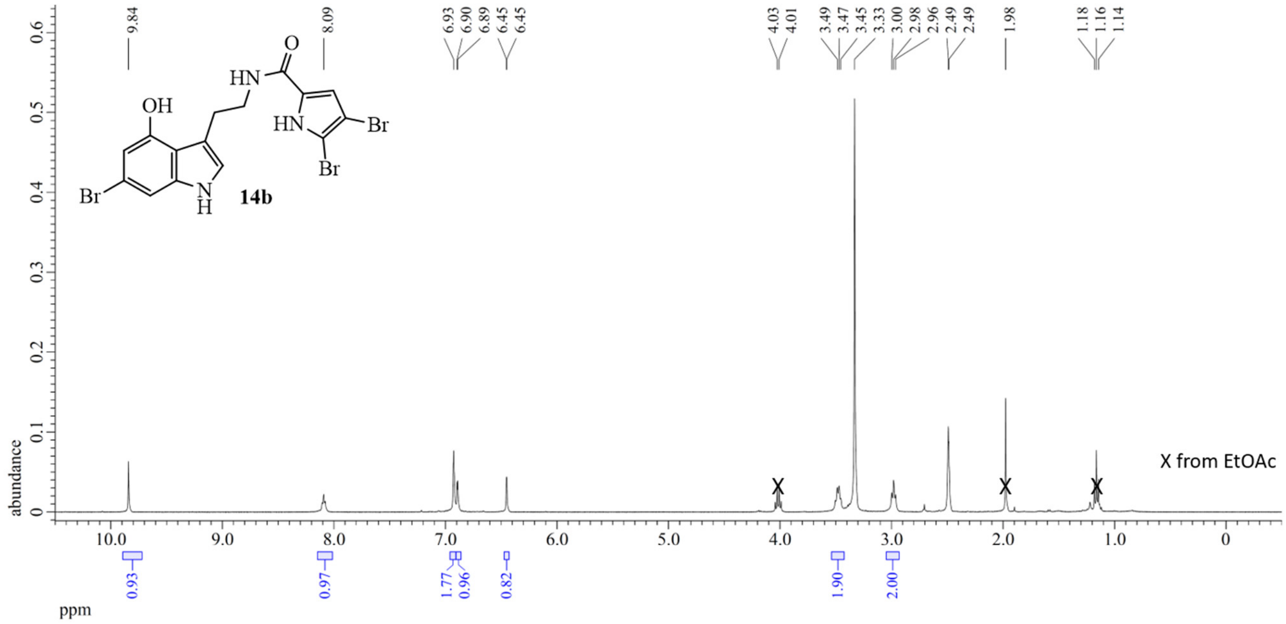

^{1}H NMR spectrum of compound **14a** (400 MHz, CDCl$_3$)



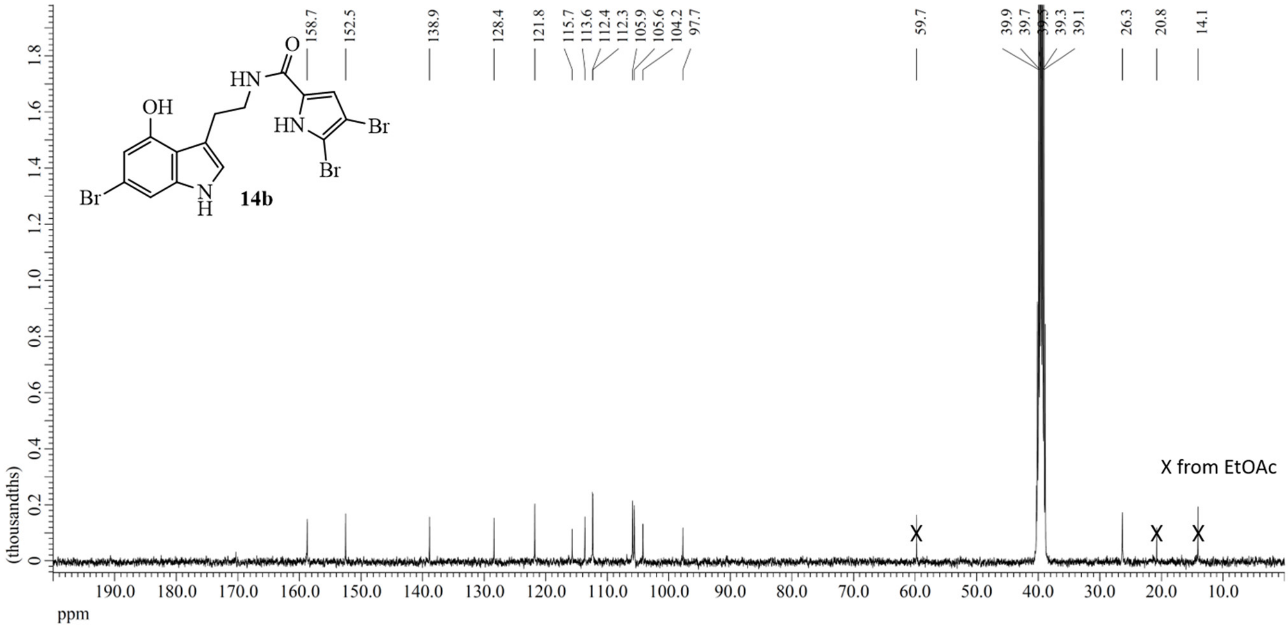
```
Filename          = H11-column-clean-cDim_Units          = [ppm]                X_Resolution      = 1.57828283[Hz]
Author            = nmr                 Dimensions       = X                    X_Sweep           = 31.56565657[kHz]
Experiment        = carbon_auto.jxp     Site             = NCHU                 X_Sweep_Clipped   = 25.25252525[kHz]
Sample_Id         = H11-column-clean-cSpectrometer       = JNM-ECZ400S/L1       Irr_Domain        = Proton
Solvent           = CHLOROFORM-D                                                Irr_Freq          = 399.78219838[MHz]
Actual_Start_Time = 24-AUG-2022 23:02:Field_Strength     = 9.389766[T] (400[MIrr_Offset         = 5[ppm]
Revision_Time     = 21-FEB-2023 10:51:X_Acq_Duration     = 0.6336[s]            Tri_Domain        = 5[us]
                                      X_Domain           = Carbon13             Clipped           = FALSE
Data_Format       = 1D COMPLEX        X_Freq             = 100.52530333[MHz]    Scans             = 14153
Dim_Size          = 52429             X_Offset           = 100[ppm]             Total_Scans       = 14153
X_Domain          = Carbon13          X_Points           = 20000
Dim_Title         = Carbon13          X_Prescans         = 4                    Relaxation_Delay  = 2[s]
```

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



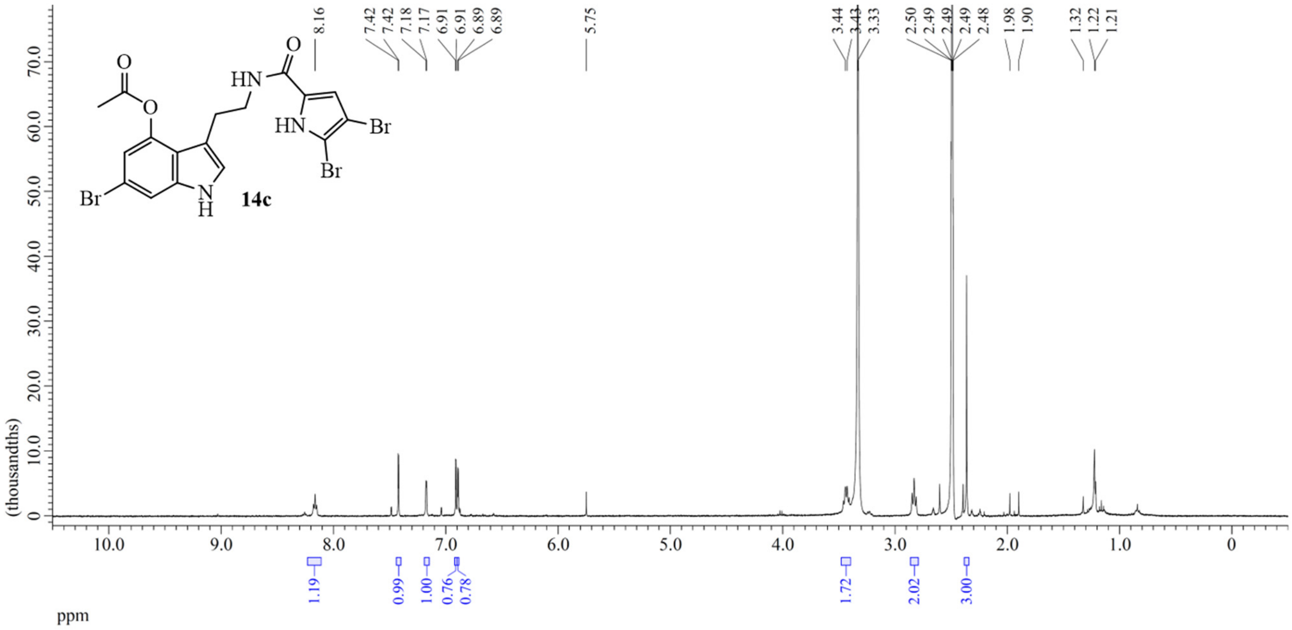
```
Filename          = H12--p242_Proton-1-3.Dim_Units          = [ppm]               X_Resolution      = 0.40935289[Hz]
Author            = nmr                  Dimensions         = X                   X_Sweep           = 9.00576369[kHz]
Experiment        = proton_auto.jxp      Site               = NCHU                X_Sweep_Clipped   = 7.20461095[kHz]
Sample_Id         = H12--p242            Spectrometer       = JNM-ECZ400S/L1      Irr_Domain        = Proton
Solvent           = DMSO-D6                                                       Irr_Freq          = 399.78219838[MHz]
Actual_Start_Time = 23-SEP-2022 04:18:22 Field_Strength     = 9.389766[T] (400[MHz]Irr_Offset       = 5[ppm]
Revision_Time     = 22-DEC-2022 23:05:09 X_Acq_Duration     = 2.44288[s]          Tri_Domain        = Proton
                                         X_Domain           = Proton              Tri_Freq          = 399.78219838[MHz]
Data_Format       = 1D COMPLEX           X_Freq             = 399.78219838[MHz]   Tri_Offset        = 5[ppm]
Dim_Size          = 52429                X_Offset           = 6[ppm]              Blanking          = 2[us]
X_Domain          = Proton               X_Points           = 22000               Clipped           = FALSE
Dim_Title         = Proton               X_Prescans         = 1                   Scans             = 2
```

^{1}H NMR spectrum of compound **14b** (400 MHz, DMSO-d_6)



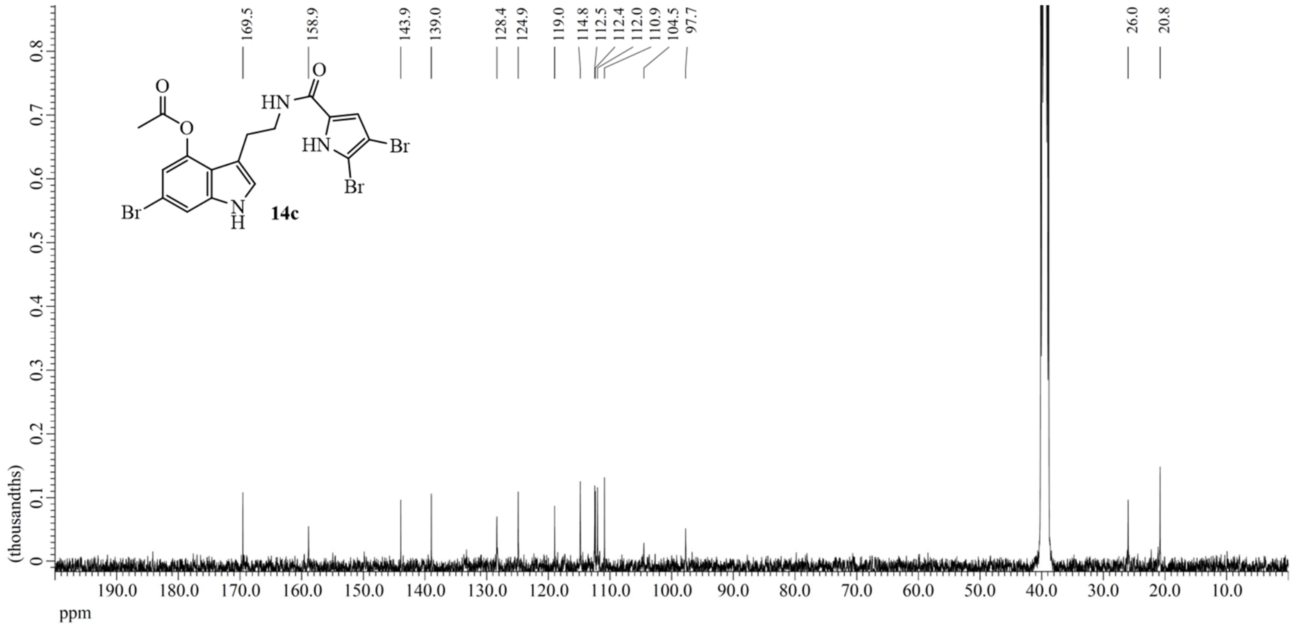
```
Filename          = H12-p242-carbon_CaDim_Units          = [ppm]               X_Resolution      = 1.57828283[Hz]
Author            = nmr               Dimensions         = X                   X_Sweep           = 31.56565657[kHz]
Experiment        = carbon_auto.jxp   Site               = NCHU                X_Sweep_Clipped   = 25.25252525[kHz]
Sample_Id         = H12-p242-carbon   Spectrometer       = JNM-ECZ400S/L1      Irr_Domain        = Proton
Solvent           = DMSO-D6                                                    Irr_Freq          = 399.78219838[MHz]
Actual_Start_Time = 23-SEP-2022 04:27:Field_Strength     = 9.389766[T] (400[MIrr_Offset          = 5[ppm]
Revision_Time     = 17-OCT-2022 22:03:X_Acq_Duration     = 0.6336[s]           Blanking          = 5[us]
                                      X_Domain           = Carbon13            Clipped           = FALSE
Data_Format       = 1D COMPLEX        X_Freq             = 100.52530333[MHz]   Scans             = 3027
Dim_Size          = 52429             X_Offset           = 100[ppm]            Total_Scans       = 3027
X_Domain          = Carbon13          X_Points           = 20000
Dim_Title         = Carbon13          X_Prescans         = 4                   Relaxation_Delay  = 2[s]
```

^{13}C NMR spectrum of compound **14b** (100 MHz, DMSO-d_6)



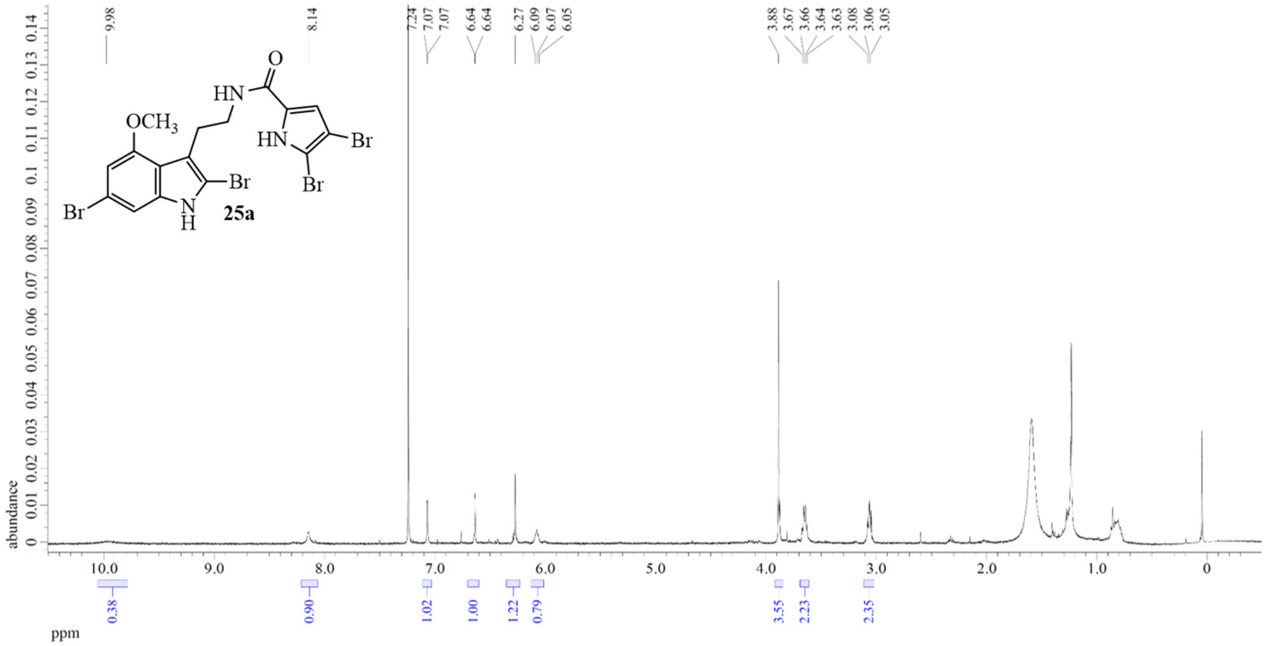
```
Filename            = H31-column-1-p322-DMSDim_Units            = [ppm]               X_Resolution          = 0.40935289[Hz]
Author              = nmr                  Dimensions           = X                   X_Sweep               = 9.00576369[kHz]
Experiment          = proton_auto.jxp      Site                 = NCHU                X_Sweep_Clipped       = 7.20461095[kHz]
Sample_Id           = H31-column-1-p322-DMSSpectrometer         = JNM-ECZ400S/L1      Irr_Domain            = Proton
Solvent             = DMSO-D6                                                         Irr_Freq              = 399.78219838[MHz]
Actual_Start_Time   = 14-DEC-2022 00:35:47 Field_Strength       = 9.389766[T]  (400[MHz]Irr_Offset          = 5[ppm]
Revision_Time       = 22-DEC-2022 22:54:22 X_Acq_Duration       = 2.44288[s]          Tri_Domain            = Proton
                                           X_Domain             = Proton              Tri_Freq              = 399.78219838[MHz]
Data_Format         = 1D COMPLEX           X_Freq               = 399.78219838[MHz]   Tri_Offset            = 5[ppm]
Dim_Size            = 52429                X_Offset             = 6[ppm]              Blanking              = 2[us]
X_Domain            = Proton               X_Points             = 22000               Clipped               = FALSE
Dim_Title           = Proton               X_Prescans           = 1                   Scans                 = 8
```

^{1}H NMR spectrum of compound **14c** (400 MHz, DMSO-d_6)



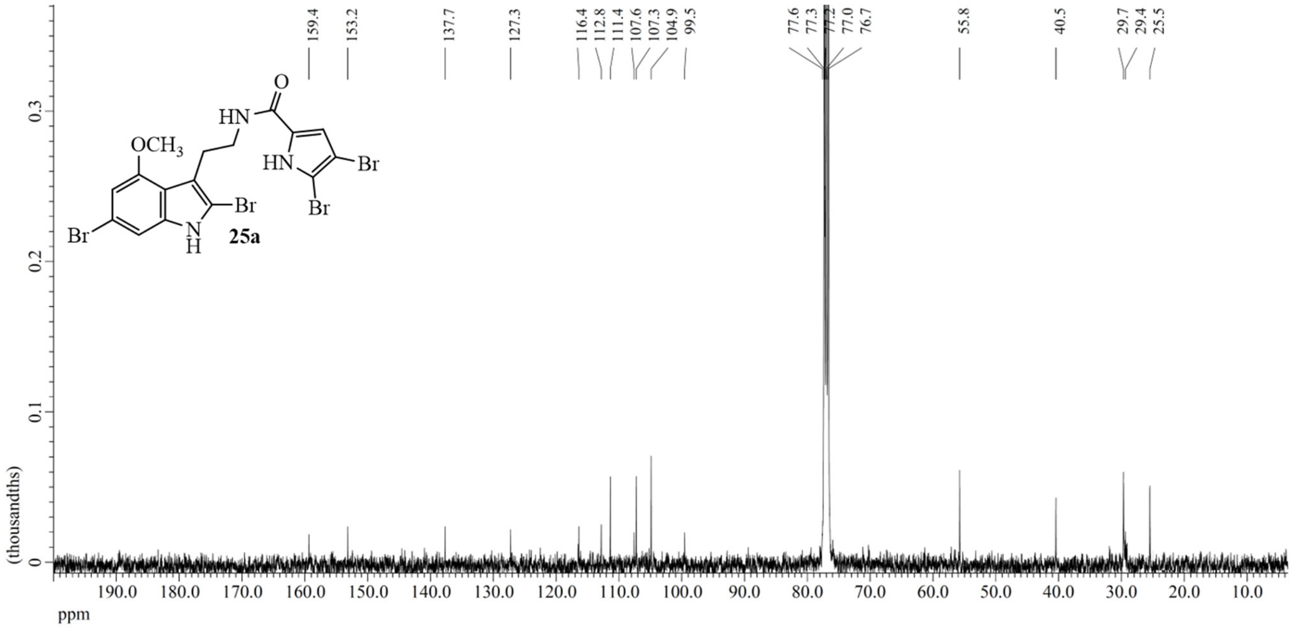
```
Filename            = H31-p322-carbon-04Dim_Units            = [ppm]               X_Resolution          = 1.26262626[Hz]
Author              = nmr               Dimensions           = X                   X_Sweep               = 31.56565657[kHz]
Experiment          = carbon.jxp        Site                 = NCHU                X_Sweep_Clipped       = 25.25252525[kHz]
Sample_Id           = H31-p322-carbon-04Spectrometer         = JNM-ECZ400S/L1      Irr_Domain            = Proton
Solvent             = DMSO-D6                                                      Irr_Freq              = 399.78219838[MHz]
Actual_Start_Time   = 30-APR-2023 01:36:Field_Strength       = 9.389766[T]  (400[MIrr_Offset            = 5[ppm]
Revision_Time       =  1-MAY-2023 11:01:X_Acq_Duration       = 0.792[s]            Blanking              = 5[us]
                                        X_Domain             = Carbon13            Clipped               = TRUE
Data_Format         = 1D COMPLEX        X_Freq               = 100.52530333[MHz]   Scans                 = 12008
Dim_Size            = 52429             X_Offset             = 100[ppm]            Total_Scans           = 12008
X_Domain            = Carbon13          X_Points             = 25000
Dim_Title           = Carbon13          X_Prescans           = 4                   Relaxation_Delay      = 2[s]
```

^{13}C NMR spectrum of compound **14c** (100 MHz, DMSO-d_6)



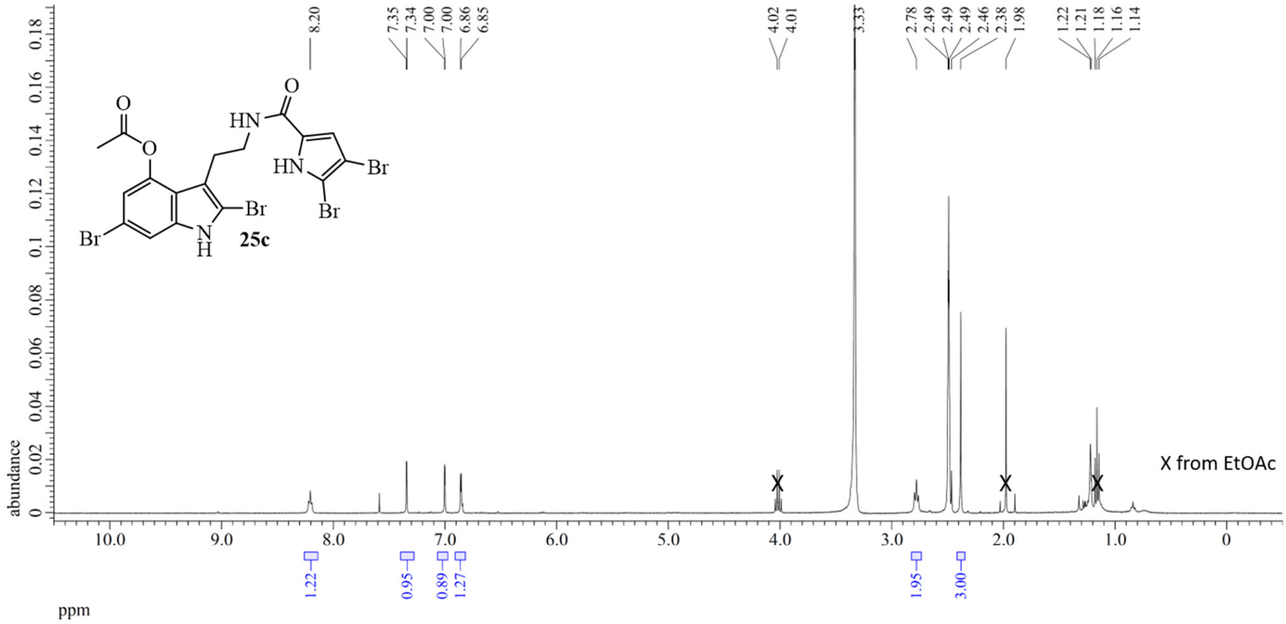
```
Filename            = 20220708-AGdown sec_P                                                         Tri_Offset          = 5[ppm]
Author              = nmr                    Field_Strength        = 9.389766[T] (400[MHz]         Blanking            = 2[us]
Experiment          = proton_auto.jxp        X_Acq_Duration        = 2.44288[s]                    Clipped             = FALSE
Sample_Id           = 20220708-AGdown sec    X_Domain              = Proton                        Scans               = 2
Solvent             = CHLOROFORM-D           X_Freq                = 399.78219838[MHz]             Total_Scans         = 2
Actual_Start_Time   =  8-JUL-2022 23:39:28   X_Offset              = 6[ppm]
Revision_Time       = 18-JUL-2022 09:02:32   X_Points              = 22000                         Relaxation_Delay    = 2[s]
                                             X_Prescans            = 1                             Recvr_Gain          = 56
Data_Format         = 1D COMPLEX             X_Resolution          = 0.40935289[Hz]                Temp_Get            = 23.6[dC]
Dim_Size            = 52429                  X_Sweep               = 9.00576369[kHz]               X_90_Width          = 7.36[us]
X_Domain            = Proton                 X_Sweep_Clipped       = 7.20461095[kHz]               X_Acq_Time          = 2.44288[s]
Dim_Title           = Proton                 Irr_Domain            = Proton                        X_Angle             = 45[deg]
Dim_Units           = [ppm]                  Irr_Freq              = 399.78219838[MHz]             X_Atn               = 4[dB]
Dimensions          = X                      Irr_Offset            = 5[ppm]                        X_Pulse             = 3.68[us]
Site                = NCHU                   Tri_Domain            = Proton                        Irr_Mode            = Off
Spectrometer        = JNM-ECZ400S/L1         Tri_Freq              = 399.78219838[MHz]             Tri_Mode            = Off
```

^{1}H NMR spectrum of compound **25a** (400 MHz, $CDCl_3$)



```
Filename            = 20220708-AGdown seDim_Units              = [ppm]                X_Resolution          = 1.57828283[Hz]
Author              = nmr               Dimensions             = X                    X_Sweep               = 31.56565657[kHz]
Experiment          = carbon_auto.jxp   Site                   = NCHU                 X_Sweep_Clipped       = 25.25252525[kHz]
Sample_Id           = 20220708-AGdown seSpectrometer           = JNM-ECZ400S/L1       Irr_Domain            = Proton
Solvent             = CHLOROFORM-D                                                    Irr_Freq              = 399.78219838[MHz]
Actual_Start_Time   =  8-JUL-2022 23:42:Field_Strength         = 9.389766[T] (400[MIrr_Offset            = 5[ppm]
Revision_Time       = 11-JAN-2023 11:57:X_Acq_Duration         = 0.6336[s]            Blanking              = 5[us]
                                        X_Domain               = Carbon13             Clipped               = FALSE
Data_Format         = 1D COMPLEX        X_Freq                 = 100.52530333[MHz]    Scans                 = 14419
Dim_Size            = 52429             X_Offset               = 100[ppm]             Total_Scans           = 14419
X_Domain            = Carbon13          X_Points               = 20000
Dim_Title           = Carbon13          X_Prescans             = 4                    Relaxation_Delay      = 2[s]
```

^{13}C NMR spectrum of compound **25a** (100 MHz, $CDCl_3$)



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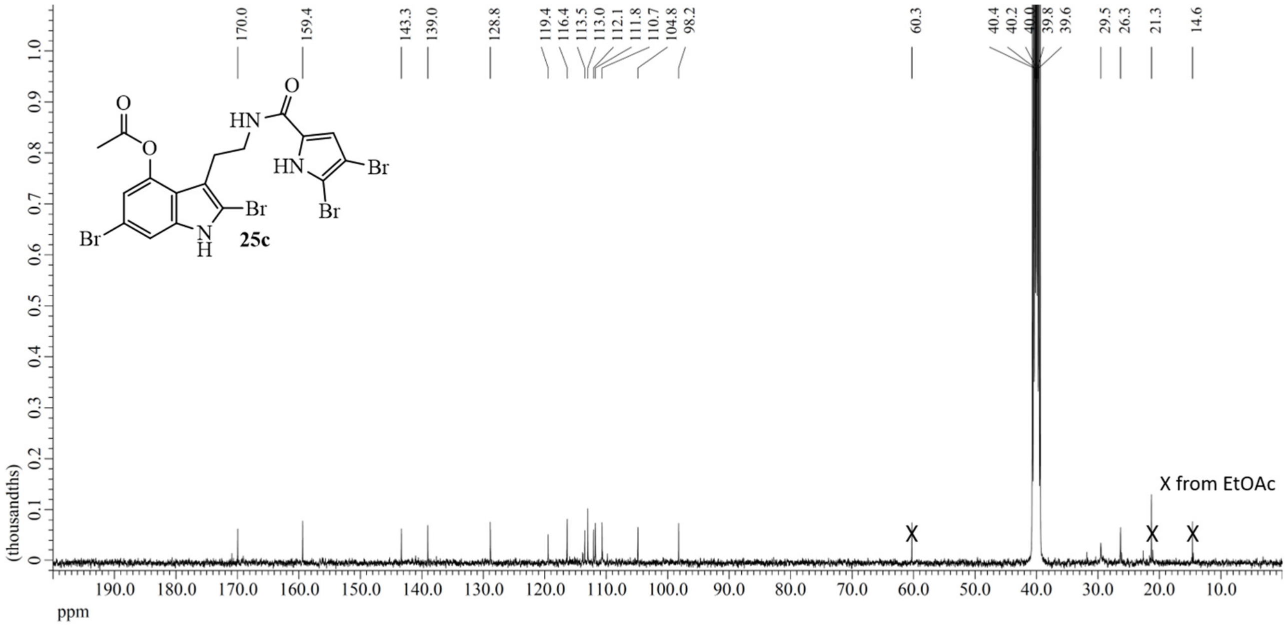
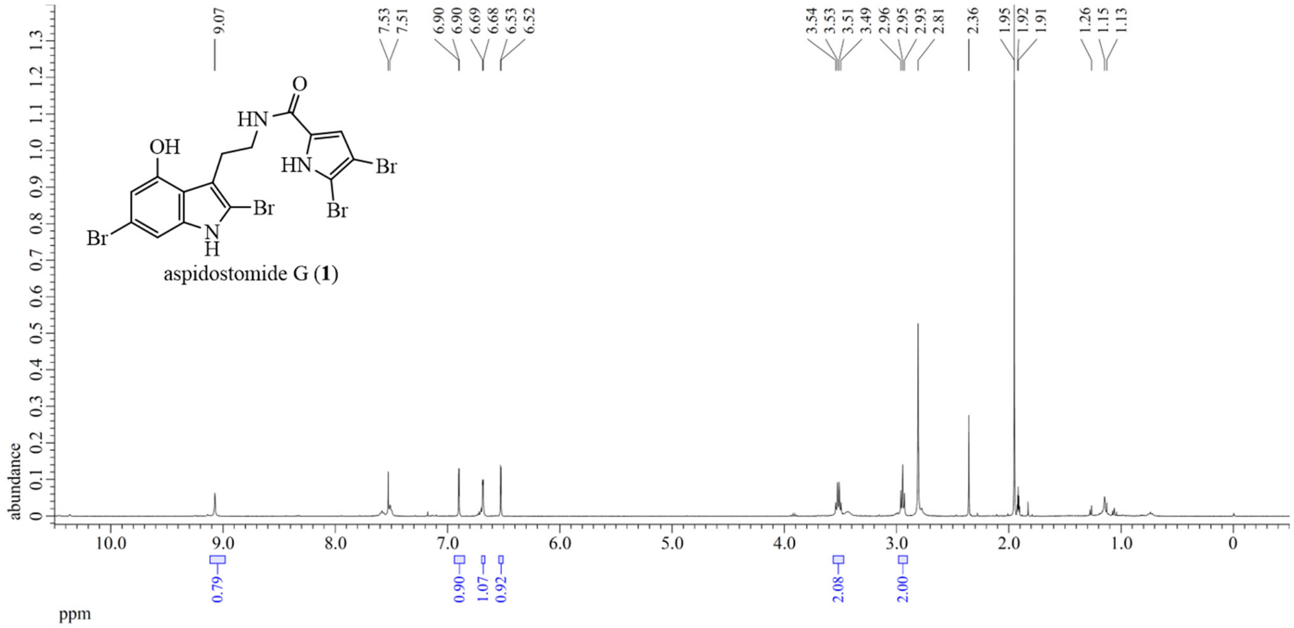
Filename            = H32-column-1-p319-DMSDim_Units          = [ppm]              X_Resolution        = 0.40935289[Hz]
Author              = nmr                  Dimensions         = X                  X_Sweep             = 9.00576369[kHz]
Experiment          = proton_auto.jxp      Site               = NCHU               X_Sweep_Clipped     = 7.20461095[kHz]
Sample_Id           = H32-column-1-p319-DMSSpectrometer       = JNM-ECZ400S/L1     Irr_Domain          = Proton
Solvent             = DMSO-D6                                                      Irr_Freq            = 399.78219838[MHz]
Actual_Start_Time   =  9-DEC-2022 16:26:38 Field_Strength     = 9.389766[T] (400[MHz]Irr_Offset        = 5[ppm]
Revision_Time       = 22-DEC-2022 23:15:24 X_Acq_Duration     = 2.44288[s]         Tri_Domain          = Proton
                                           X_Domain           = Proton             Tri_Freq            = 399.78219838[MHz]
Data_Format         = 1D COMPLEX           X_Freq             = 399.78219838[MHz]  Tri_Offset          = 5[ppm]
Dim_Size            = 52429                X_Offset           = 6[ppm]             Blanking            = 2[us]
X_Domain            = Proton               X_Points           = 22000              Clipped             = FALSE
Dim_Title           = Proton               X_Prescans         = 1                  Scans               = 8
```

^{1}H NMR spectrum of compound **25c** (400 MHz, DMSO-d_6)



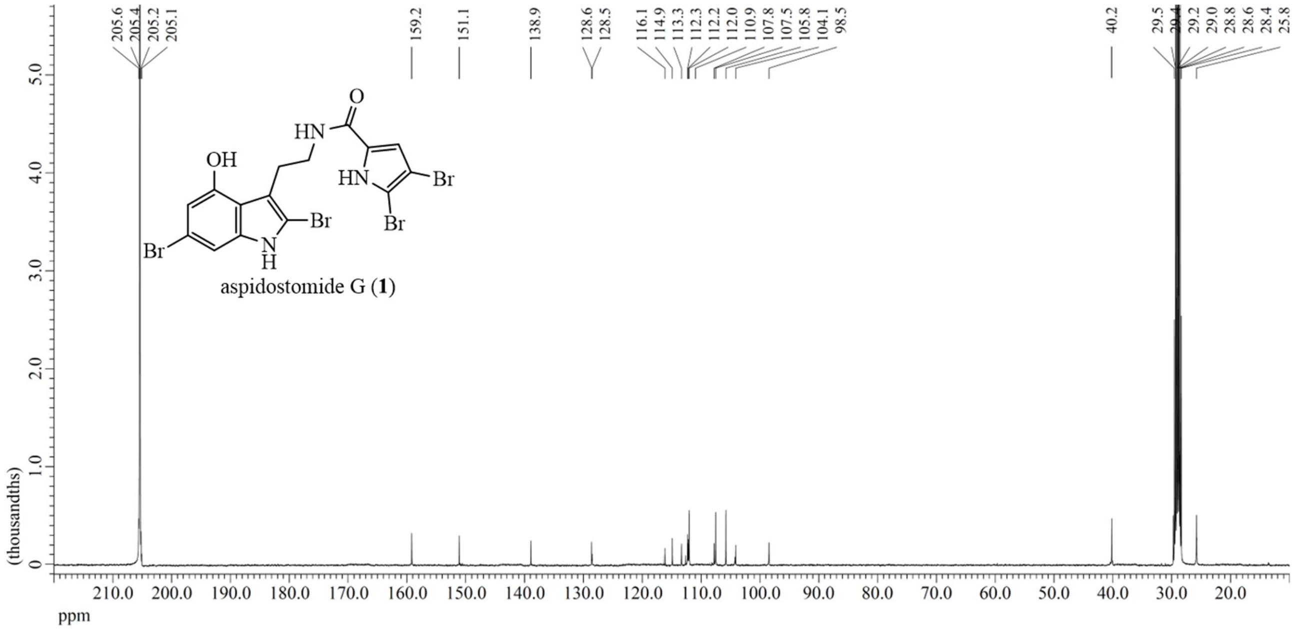
```
Filename            = H32-column-1-p319-Dim_Units             = [ppm]              X_Resolution        = 1.57828283[Hz]
Author              = nmr                  Dimensions         = X                  X_Sweep             = 31.56565657[kHz]
Experiment          = carbon_auto.jxp      Site               = NCHU               X_Sweep_Clipped     = 25.25252525[kHz]
Sample_Id           = H32-column-1-p319-Spectrometer          = JNM-ECZ400S/L1     Irr_Domain          = Proton
Solvent             = DMSO-D6                                                      Irr_Freq            = 399.78219838[MHz]
Actual_Start_Time   = 13-DEC-2022 00:50:Field_Strength        = 9.389766[T] (400[MIrr_Offset           = 5[ppm]
Revision_Time       = 22-DEC-2022 23:26:X_Acq_Duration        = 0.6336[s]          Blanking            = 5[us]
                                        X_Domain              = Carbon13           Clipped             = FALSE
Data_Format         = 1D COMPLEX        X_Freq                = 100.52530333[MHz]  Scans               = 13420
Dim_Size            = 52429             X_Offset              = 100[ppm]           Total_Scans         = 13420
X_Domain            = Carbon13          X_Points              = 20000
Dim_Title           = Carbon13          X_Prescans            = 4                  Relaxation_Delay    = 2[s]
```

^{13}C NMR spectrum of compound **25c** (100 MHz, DMSO-d_6)



```
Filename          = H33-column-1-p324-aceDim_Units          = [ppm]               X_Resolution      = 0.40935289[Hz]
Author            = nmr                 Dimensions          = X                   X_Sweep           = 9.00576369[kHz]
Experiment        = proton_auto.jxp     Site                = NCHU                X_Sweep_Clipped   = 7.20461095[kHz]
Sample_Id         = H33-column-1-p324-aceSpectrometer       = JNM-ECZ400S/L1      Irr_Domain        = Proton
Solvent           = ACETONE-D6                                                    Irr_Freq          = 399.78219838[MHz]
Actual_Start_Time = 16-DEC-2022 20:06:19 Field_Strength     = 9.389766[T]  (400[MHz]Irr_Offset      = 5[ppm]
Revision_Time     = 22-DEC-2022 23:22:10 X_Acq_Duration     = 2.44288[s]          Tri_Domain        = Proton
                                        X_Domain            = Proton              Tri_Freq          = 399.78219838[MHz]
Data_Format       = 1D COMPLEX          X_Freq              = 399.78219838[MHz]   Tri_Offset        = 5[ppm]
Dim_Size          = 52429               X_Offset            = 6[ppm]              Blanking          = 2[us]
X_Domain          = Proton              X_Points            = 22000               Clipped           = FALSE
Dim_Title         = Proton              X_Prescans          = 1                   Scans             = 8
```

^{1}H NMR spectrum of aspidostomide G (**1**) (400 MHz, acetone-d_6)



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Filename          = H33-column-1-p324-Dim_Units             = [ppm]               X_Resolution      = 1.57828283[Hz]
Author            = nmr                 Dimensions          = X                   X_Sweep           = 31.56565657[kHz]
Experiment        = carbon_auto.jxp     Site                = NCHU                X_Sweep_Clipped   = 25.25252525[kHz]
Sample_Id         = H33-column-1-p324-Spectrometer          = JNM-ECZ400S/L1      Irr_Domain        = Proton
Solvent           = ACETONE-D6                                                    Irr_Freq          = 399.78219838[MHz]
Actual_Start_Time = 22-DEC-2022 01:16:Field_Strength        = 9.389766[T]  (400[MIrr_Offset         = 5[ppm]
Revision_Time     =  3-JAN-2023 18:59:X_Acq_Duration        = 0.6336[s]           Blanking          = 5[us]
                                      X_Domain              = Carbon13            Clipped           = TRUE
Data_Format       = 1D COMPLEX        X_Freq                = 100.52530333[MHz]   Scans             = 13412
Dim_Size          = 52429             X_Offset              = 100[ppm]            Total_Scans       = 13412
X_Domain          = Carbon13          X_Points              = 20000
Dim_Title         = Carbon13          X_Prescans            = 4                   Relaxation_Delay  = 2[s]
```

^{13}C NMR spectrum of aspidostomide G (**1**) (100 MHz, acetone-d_6)

References and Notes:

1. G. G. Pawar, A. Brahmanandan and M. Kapur, *Org. Lett.*, 2016, **18**, 448.
2. K. T. Tran, J. S. Pallesen, S. M. Ø. Solbak, D. Narayanan, A. Baig, J. Zang, A. Aguayo-Orozco, R. M. C. Carmona, A. D. Garcia and A. Bach, *J. Med. Chem.*, 2019, **62**, 8028.
3. (a) S. K. Pandey, Y. Guttormsen, B. E. Haug, C. Hedberg and A. Bayer, *Org. Lett.*, 2015, **17**, 122; (b) A. H. Khan and J. S. Chen, *Org. Lett.*, 2015, **17**, 3718.
4. N. M. Hewlett and J. J. Tepe, *Org. Lett.*, 2011, **13**, 3718.
5. M. van Rensburg, B. R. Copp and D. Barker, *Eur. J. Org. Chem.*, 2018, 3065.
6. L. P. Patiño C, C. Muniain, M. E. Knott, L. Puricelli and J. A. Palermo, *J. Nat. Prod.*, 2014, **77**, 1170.