Supporting Information for

A Diastereodivergent Synthetic Strategy for the Syntheses of Communesin F and Perophoramidine.

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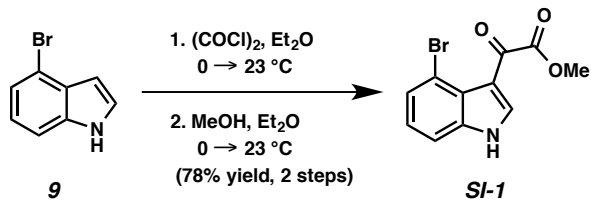
Materials and Methods.

Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Reaction progress was monitored by thin-layer chromatography (TLC). THF, Et_2O, CH_2Cl_2, toluene, benzene, CH_3CN, and dioxane were dried by passage through an activated alumina column under argon. Triethylamine was distilled over CaH_2 prior to use. Purified water was obtained using a Barnstead NANOpure Infinity UV/UF system. Brine solutions are saturated aqueous solutions of sodium chloride. Commercially available reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated. Reaction temperatures were controlled by an IKAmag temperature modulator unless otherwise indicated. Microwave-assisted reactions were performed in a Biotage Initiator 2.5 microwave reactor. Glove box manipulations were performed under a N_2 atmosphere. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, or PMA (phosphomolybdic acid) staining. Silicycle Silia*Flash* P60 Academic Silica gel (particle size 0.040-0.064 mm) was used for flash column chromatography. ^{1}H NMR spectra were recorded on a Varian Inova 500 MHz spectrometer and are reported relative to residual $CHCl_3$ (δ 7.26 ppm), or $(CD_3)_2CO$ (δ 2.05 ppm). ^{13}C NMR spectra are recorded on a Varian Inova 500 MHz spectrometer (125MHz) and are reported relative to $CHCl_3$ (δ 77.16 ppm), or $(CD_3)_2CO$ (δ 29.84 ppm). Data for ^{1}H NMR are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet, br d= broad doublet, app = apparent. Data for ^{13}C are reported in terms of chemical shifts (δ ppm). IR spectra were obtained using a Perkin Elmer Paragon 1000 spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). High resolution mass spectra (HRMS) were obtained from Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed ionization mode (MM: ESI-APCI+).

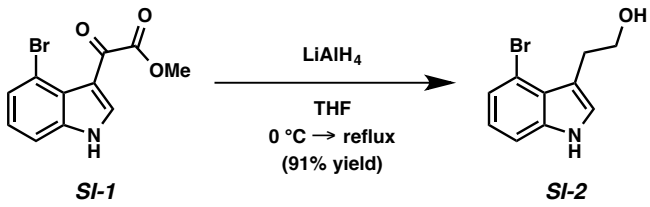
Experimental Procedures and Spectroscopic Data



Oxoacetate SI-1. To a solution of 4-bromoindole **9** (8.0 g, 40.8 mmol, 1.0 equiv) in Et_2O (204 mL) was added oxalyl chloride (9.25 mL, 102 mmol, 2.5 equiv) dropwise at 0 ^oC. The reaction mixture was stirred for 16 h at 23 ^oC. The resulting suspension was filtered and washed with cold ether. The filter cake was dried *in vacuo* to afford the oxoacetyl chloride, which was used without further purification.

To a solution of oxoacetyl chloride in Et_2O (204 mL) was added MeOH (10 mL) at 0 ^oC, and stirred for 2 h. The resulting mixture was concentrated *in vacuo* and purified by flash column chromatography (4:1 hexanes:EtOAc) on silica gel to give oxoacetate **SI-1** (9.0 g, 78% yield, 2 steps).

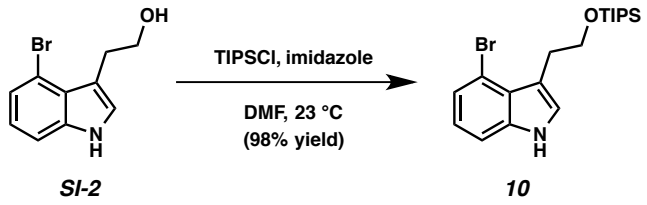
R_f = 0.23 (1:1 hexane:EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 9.01 (br, s, 1H), 8.27 (d, J = 3.2 Hz, 1H), 7.52 (dd, J = 7.6, 0.8 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.16 (t, J = 7.8Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.3, 164.0, 137.8, 136.2, 128.3, 125.3, 125.2, 115.3, 115.0, 111.0, 53.0; IR (Neat Film NaCl) 3206, 1656, 1500, 1410, 1306, 1252, 1196, 1139, 1104, 789, 770, 731 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{11}H_9BrNO_3$ $[M+H]^+$: 281.9760; found: 281.9760.



Alcohol SI-2. To a solution of oxoacetate **SI-1** (6.8 g, 24.1 mmol, 1.0 equiv) in THF (120 mL) was added $LiAlH_4$ (2.8 g, 72.3 mmol, 3.0 equiv) in portions at 0 ^oC. The reaction mixture was refluxed for 4 h. When the reaction was done, the solution was

cooled to 0 °C, and quenched by Fieser work-up.[1] The suspension was filtered and the filter cake was washed with EtOAc. The combined organic phases were concentrated *in vacuo*, and extracted with EtOAc (3 x 100 mL). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo.* The residue was purified by flash column chromatography (1:1 hexane:EtOAc) on silica gel to give alcohol **SI-2** (5.3 g, 91% yield).

R_f = 0.27 (1:1 hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (br, s, 1H), 7.31 (dd, J = 7.6, 0.8 Hz, 1H), 7.28 (dd, J = 7.6, 0.8 Hz, 1H), 7.12 (dd, J = 2.8Hz, 1H), 7.01 (t, J = 7.8 Hz, 1H), 3.97 (t, J = 6.4 Hz, 2H), 3.28 (dt, J = 6.4, 0.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 125.4, 124.1, 123.0, 114.4, 113.1, 110.6, 63.6, 29.5 ; IR (Neat Film NaCl) 3369, 2929, 1899, 1613, 1478, 1425, 1335, 1185, 1029, 913, 815, 770, 736 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{10}H_{11}BrNO$ $[M+H]^+$: 240.0019; found: 240.0021.



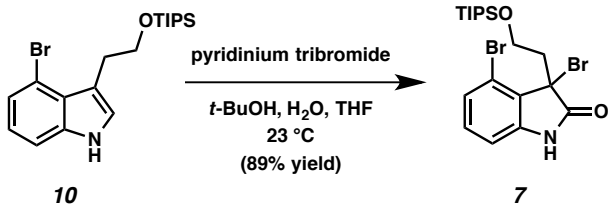
SI-2 *10*

Silyl ether 10. To a solution of alcohol **SI-2** (8.1 g, 33.7 mmol, 1.0 equiv) in DMF (112 mL) was added imidazole (5.0 g, 74.2 mmol, 2.2 equiv) and TIPSCl (10.7 mL, 50.6 mmol, 1.5 equiv). After stirring for 3 h at 23 °C, water (10 mL) was added. The aqueous phase was extracted with Et_2O (3 x 100 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography (9:1 hexanes:EtOAc) on silica gel to give silyl ether **10** (13.1 g, 98% yield).

R_f = 0.56 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (br, s, 1H), 7.30–7.25 (m, 2H), 7.12 (d, *J* = 2.4 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 4.00 (t, *J* = 7.1 Hz, 2H), 3.27 (t, *J* = 7.1 Hz, 2H), 1.05-1.07 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4, 125.7, 124.4, 123.9, 122.6, 114.3, 114.1, 110.4, 64.9, 29.9, 18.1, 12.0; IR (Neat Film NaCl) 3425, 3286, 2942, 1614, 1561, 1549, 1463, 1425, 1382, 1336, 1246,

[1] Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis* **1967**, 581-595.

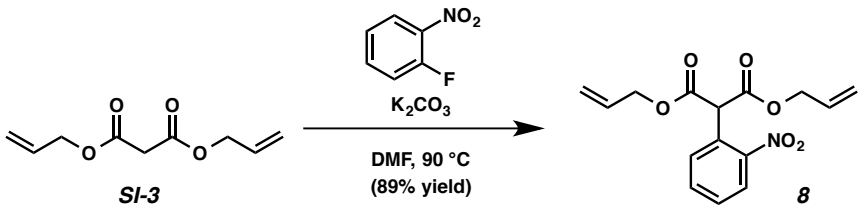
1184, 1102, 1064, 1013, 913, 883, 826, 772, 738 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{31}BrNOSi$ $[M+H]^+$: 396.1353; found: 396.1357.



10 *7*

3-Bromooxindole 7. To a solution of indole **10** (5.0 g, 12.6 mmol, 1.0 equiv) in *t*-BuOH (100 mL), THF (25 mL), and water (1.1 mL) was added pyridinium tribromide (7.9 g, 24.6 mmol, 1.95 equiv). The reaction mixture was stirred for 30 min and then diluted with EtOAc (50 mL) and water (80 mL). The aqueous phase was extracted with EtOAc (3 x 150 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography (4:1 hexanes:EtOAc) on silica gel to give 3-bromooxindole **7** (5.5 g, 89% yield).

R_f = 0.31 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (br, s, 1H), 7.19 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 1H), 6.86 (dd, *J* = 7.6, 1.0 Hz, 1H), 3.66 (ddd, *J* = 10.4, 5.5, 3.3 Hz, 1H), 3.46 (td, *J* = 10.5, 3.8 Hz, 1H), 3.08 (dt, *J* = 13.9, 3.5 Hz, 1H), 2.90 (ddd, *J* = 13.9, 10.6, 5.4 Hz, 1H), 0.87 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.8, 142.3, 131.2, 127.5, 127.0, 120.8, 109.5, 60.6, 56.1, 39.6, 17.8, 11.8; IR (Neat Film NaCl) 2941, 2864, 2109, 1728, 1613, 1583, 1312, 1102, 882, 744 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{30}Br_2NO_2Si$ $[M+H]^+$: 490.0407; found: 490.0340.

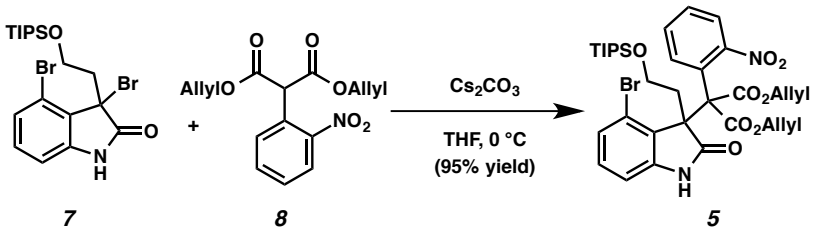


SI-3 *8*

Diallyl 2-(2-nitrophenyl)malonate 8. A 500 mL round-bottom flask with a magnetic stir bar was charged with diallyl malonate **SI-3** (22.0 g, 118 mmol, 1.0 equiv), 1-fluoro-2-nitrobenzene (13.7 mL, 129 mmol, 1.1 equiv), and K_2CO_3 (48.9 g, 354

mmol, 3.0 equiv). DMF (120 mL) was added and the brown suspension was heated to 90 °C for 16 h. The reaction mixture was cooled to ambient temperature and diluted with ice water (250 mL) and Et_2O (300 mL). The aqueous phase was extracted with Et_2O (3 x 300 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography (9:1 hexanes:EtOAc) on silica gel to give arylated malonate **8** (32.1 g, 89% yield).

R_f = 0.51 (1:1 hexane:Et_2O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.66 (td, *J* = 7.6, 1.4 Hz, 1H), 7.55–7.51 (m, 2H), 5.90 (ddt, *J* = 17.3, 10.4, 5.7 Hz, 2H), 5.38 (s, 1H), 5.34-5.23 (m, 4H), 4.70 (dt, *J* = 5.8, 1.4 Hz, 4H); ^{13}C NMR (125MHz, $CDCl_3$) δ 166.8, 148.7, 133.6, 131.4, 131.1, 129.3, 127.9, 125.3, 119.1, 66.8, 54.3; IR (Neat Film NaCl) 3086, 2950, 1738, 1611, 1530, 1447, 1350, 1154, 991, 937, 852, 787, 722 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{15}H_{16}NO_6$ $[M+H]^+$: 306.0972; found: 306.0930.

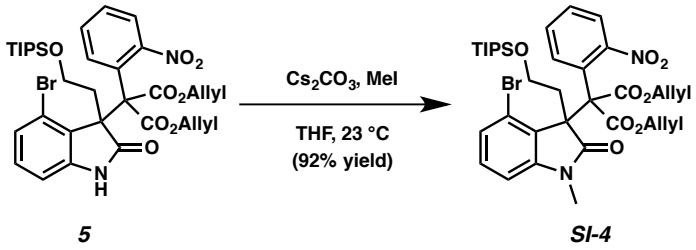


7 *8* *5*

Oxindole 5. To a solution of 3-bromooxindole **7** (5.6 g, 11.4 mmol, 1.0 equiv) and malonate **8** (5.2 g, 17.1 mmol, 1.5 equiv) in THF was added Cs_2CO_3 (7.4 g, 22.8 mmol, 2.0 equiv) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C. Solids were removed via a filtration through a celite plug and the resulting solution was concentrated under reduced pressure. The residue was purified by flash column chromatography (9:1 → 4:1 hexanes:EtOAc) on silica gel to give desired alkylated product **5** (5.4 g, 95% yield).

R_f= 0.18 (3:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.01 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.90 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.68 (ddd, *J* = 8.5, 7.4, 1.6 Hz, 1H), 7.55 (d, *J* = 5.3 Hz, 1H), 7.51 (td, *J* = 7.7, 1.2 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.93 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.78 (dd, *J* = 7.6, 1.0 Hz, 1H), 5.92–5.81 (m, 2H), 5.76–5.68 (m, 1H), 5.26–5.18 (m, 2H), 5.17–5.10 (m, 2H), 4.76-4.69 (m, 1H), 4.68-4.63 (m, 1H),

4.51–4.47 (m, 1H), 4.25–4.20 (m, 1H), 3.33–3.26 (m, 1H), 3.23–3.13 (m, 2H), 2.97-2.90 (m, 1H), 0.91 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 167.0, 166.0, 144.4, 133.8, 131.8, 131.3, 131.1, 129.8, 129.3, 128.3, 127.5, 126.9, 126.5, 121.82, 119.6, 119.0, 118.9, 108.5, 67.6, 66.6, 66.5, 59.5, 58.3, 32.9, 17.9, 11.9; IR (Neat Film NaCl) 3350, 3086, 2943, 1732, 1612, 1574, 1531, 1446, 1354, 1228, 1169, 1104, 992, 931, 789 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{34}H_{44}BrN_2O_8Si$ $[M+H]^+$: 715.2045; found 715.2055.

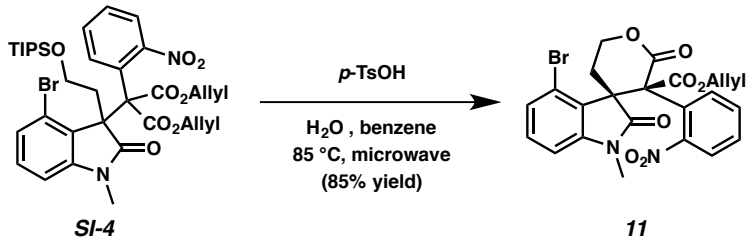


5 *SI-4*

Methyloxindole SI-4. To a solution of oxindole **5** (5.6 g, 11.2 mmol, 1.0 equiv) in THF (56 mL) was added Cs_2CO_3 (10.9 g, 33.6 mmol, 3.0 equiv) and MeI (4.3 mL, 67.2 mmol, 6.0 equiv) at 0 °C. Then, the reaction mixture was stirred for 12 h at 23 °C. After the reaction was done, sat. NH_4Cl was added. The aqueous phase was extracted with EtOAc (3 x 50 mL). The combined organic phases were washed with brine (50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography (7:1 hexanes:EtOAc) on silica gel to give methylated oxindole **SI-4** (7.5 g, 92% yield).

R_f = 0.38 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.01 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.91 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.69 (ddd, *J* = 8.5, 7.3, 1.6 Hz, 1H), 7.54–7.50 (m, 1H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.95 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.78 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.88 (ddt, *J* = 16.5, 10.4, 5.8 Hz, 1H), 5.71 (ddt, *J* = 16.7, 10.2, 6.3 Hz, 1H), 5.27–5.11 (m, 4H), 4.78 (ddt, *J* = 13.1, 6.0, 1.4 Hz, 1H), 4.68 (ddt, *J* = 13.1, 5.6, 1.5 Hz, 1H), 4.47 (ddt, *J* = 12.7, 6.3, 1.2 Hz, 1H), 4.21 (ddt, *J* = 12.8, 6.4, 1.2 Hz, 1H), 3.24 (s, 3H), 3.20–3.15 (m, 3H), 3.00–2.93 (m, 1H), 0.91 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.14, 167.03, 165.81, 152.74, 147.67, 147.67, 133.81, 131.78, 131.42, 131.19, 129.73, 129.21, 128.45, 126.99, 126.85, 126.54, 121.57, 119.44, 106.83, 67.43, 66.37, 65.91, 59.57, 57.96, 32.75, 26.77, 17.90, 11.85; IR (Neat Film NaCl) 2917, 2863, 1721, 1600, 1529, 1450, 1350, 1231, 1088, 923, 883, 852 cm^{-1};

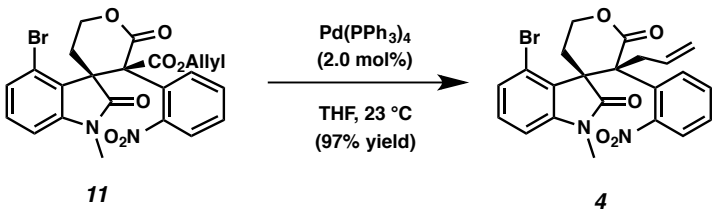
HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{35}H_{46}BrN_2O_8Si$ $[M+H]^+$: 729.2201; found: 729.2240.



SI-4 *11*

Lactone 11. To a 20 mL microwave vial with a magnetic stir bar were added oxindole **SI-4** (500 mg, 0.69 mmol, 1.0 equiv), *p*-TsOH (520 mg, 2.7 mmol, 4.0 equiv), and benzene (20 mL). The reaction was sealed with a microwave crimp cap and subjected to microwave irradiation in a Biotage Initiator microwave reactor (temperature: 85 ^oC, sensitivity: low) with a gradual temperature increase over 10 min (10 ^oC increments). After 20 min of stirring, the vial was cooled to ambient temperature and uncapped. The reaction was diluted with EtOAc (10 mL) and quenched by addition of sat. $NaHCO_3$. The phases were separated and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phases were dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (1:1 hexane:EtOAc) on silica gel to afford lactone **11** (300 mg, 85% yield).

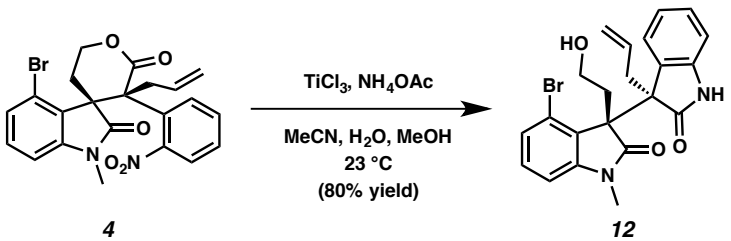
R_f = 0.23 (1:1 hexane:EtOAc); ^1H NMR (300 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.99 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.71 (dd, *J* = 9.1, 7.6 Hz, 1H), 7.59 (ddd, *J* = 8.1, 7.4, 1.3 Hz, 1H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.96 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.87 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.71 (ddt, *J* = 17.2, 10.4, 6.1 Hz, 1H), 5.18–5.07 (m, 3H), 4.71 (td, *J* = 11.0, 10.4, 7.4 Hz, 1H), 4.55 (ddt, *J* = 12.9, 5.9, 1.3 Hz, 1H), 4.26 (ddt, *J* = 12.9, 6.2, 1.3 Hz, 1H), 3.63 (ddd, *J* = 15.2, 13.1, 7.3 Hz, 1H), 3.34 (s, 3H), 1.67 (dd, *J* = 15.2, 5.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 165.3, 165.1, 152.1, 146.0, 133.4, 132.0, 131.0, 130.4, 130.1, 130.0, 127.7, 127.7, 127.5, 119.1, 107.8, 67.8, 67.0, 64.8, 60.4, 54.5, 27.0, 24.2; IR (Neat Film NaCl) 2929, 1742, 1713, 1601, 1532, 1456, 1353, 1192, 1112, 1058, 1033, 993, 936, 856, 767 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{23}H_{20}BrN_2O_7$ $[M+H]^+$: 515.0448; found: 515.0450.



11 *4*

Allyl 4. To a 250 mL round-bottom flask with a magnetic stir bar was added lactone **11** (2.5 g, 4.9 mmol, 1.0 equiv). The flask was brought into a N_2-filled glove box, and then $Pd(PPh_3)_4$ (0.1 g, 0.097 mmol, 0.02 equiv) was added. The reaction mixture was brought out from the glove box and treated with THF (97 mL). After 5 min stirring, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (1:1 hexane:EtOAc) on silica gel to afford allylated product **4** (2.0 g, 97% yield).

R_f = 0.24 (1:1 hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.20 (dd, *J* = 9.6, 6.5 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 6.48 (d, *J* = 8.1 Hz, 1H), 5.52 (ddt, *J* = 16.6, 12.0, 6.4 Hz, 1H), 5.43–5.35 (m, 1H), 4.79–4.72 (m, 3H), 4.32 (td, *J* = 13.7, 7.2 Hz, 1H), 3.31 (s, 3H), 3.13 (dd, *J* = 15.6, 5.0 Hz, 1H), 2.43–2.36 (m, 1H), 1.73 (dd, *J* = 14.7, 5.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.5, 169.8, 152.4, 146.0, 134.7, 134.3, 130.9, 130.7, 130.4, 128.5, 128.3, 126.0, 125.2, 124.0, 117.8, 107.6, 64.7, 56.7, 54.2, 42.9, 26.4, 23.8; IR (Neat Film NaCl) 3418, 2923, 1709, 1601, 1532, 1455, 1361, 1292, 1201, 1113, 1069, 986, 917, 777, 736 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{22}H_{20}BrN_2O_5$ $[M+H]^+$: 471.0550; found: 471.0552.

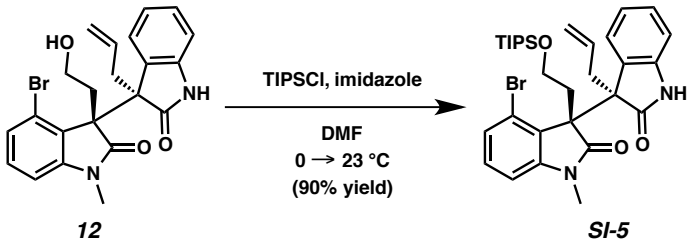


4 *12*

Bis-oxindole 12. To a solution of lactone **4** (2.4 g, 5.6 mmol, 1.0 equiv) in H_2O (282 mL) and MeOH (565 mL) were added NH_4OAc (43.5 g, 564 mmol, 100.0 equiv) and $TiCl_3$ (10% w/w, 70.3 mL, 56.4 mmol, 10.0 equiv). Then, the reaction was stirred for 12 h at 23 °C. The reaction mixture was diluted with EtOAc (500 mL) and then the phases were separated and the aqueous phase was extracted with EtOAc (3 x 300

mL). The combined organic phases were dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (1:1 hexane:EtOAc) on silica gel to afford bis-oxindole **12** (1.99 g, 80% yield).

R_f = 0.10 (1:1 hexane:EtOAc); ^{1}H NMR (500 MHz, DMSO) δ 10.33 (s, 1H), 6.98 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.96–6.87 (m, 2H), 6.77–6.67 (m, 2H), 6.58 (dd, *J* = 7.8, 1.0 Hz, 1H), 6.45 (d, *J* = 7.6 Hz, 1H), 4.96 (ddt, *J* = 16.7, 9.7, 6.9 Hz, 1H), 4.86 (dd, *J* = 17.0, 2.5 Hz, 1H), 4.74 (dd, *J* = 9.9, 2.6 Hz, 1H), 4.39 (t, *J* = 5.0 Hz, 1H), 3.41–3.32 (m, 2H), 3.22–3.13 (m, 1H), 3.03 (s, 3H), 2.86 (dtd, *J* = 10.3, 7.9, 5.5 Hz, 1H), 2.76 (dd, *J* = 13.5, 6.8 Hz, 1H), 2.24 (dt, *J* = 13.2, 7.9 Hz, 1H); ^{13}C NMR (125 MHz, DMSO) δ 177.5, 175.8, 146.5, 142.8, 133.4, 130.2, 128.5, 128.1, 126.9, 126.8, 123.5, 120.4, 119.3, 118.9, 108.9, 107.4, 58.4, 57.2, 56.0, 33.5, 28.9, 26.3; IR (Neat Film NaCl) 2917, 2356, 1697, 1599, 1574, 1455, 1349, 1184, 910, 752 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{22}H_{22}BrN_2O_3$ $[M+H]^+$: 441.0808; found 441.0812.

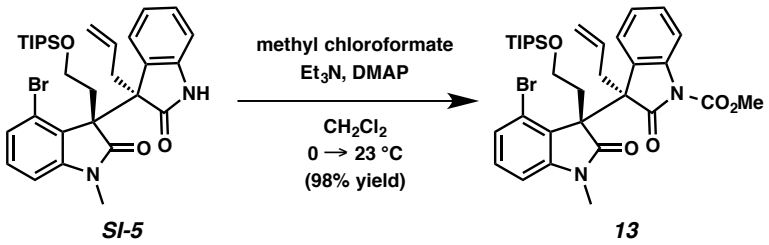


12 ***SI-5***

Silyl ether SI-5. Bis-oxindole **12** (1.66 g, 3.76 mmol, 1.0 equiv) was dissolved in DMF (18.8 mL) to which TIPSCl (1.61 mL, 7.52 mmol, 2.0 equiv) and imidazole (1.02 g, 15.0 mmol, 4.0 equiv) were added at 0 °C. The reaction was slowly warmed to 23 °C, and stirred for 12 h. The reaction mixture was extracted with EtOAc (3 x 40 mL), and washed with brine. The combined organic phases were dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (4:1 hexanes:EtOAc) on silica gel to afford TIPS protected compound **SI-5** (2.02 g, 90% yield).

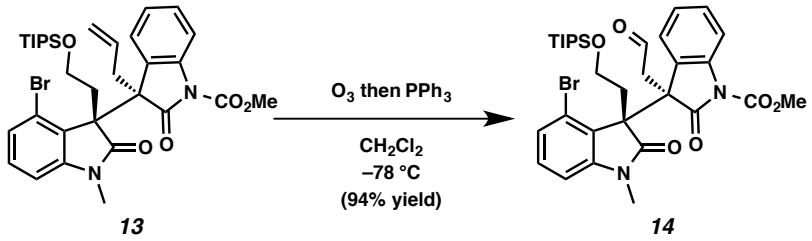
R_f = 0.20 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 6.97 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.94 (tt, *J* = 7.6, 1.1 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.84–6.80 (m, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.49 (d, *J* = 7.8 Hz, 1H), 6.28 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.10 (ddt, *J* = 16.9, 9.9, 7.1 Hz, 1H), 4.97 (dd, *J* = 17.1, 2.1 Hz, 1H), 4.77 (dd, *J* = 9.9, 2.2 Hz, 1H), 3.73 (ddd, *J* = 8.7, 5.7, 2.6 Hz, 1H), 3.57 (dd, *J* = 13.6, 7.1

Hz, 1H), 3.47–3.41 (m, 2H), 3.05 (s, 3H), 2.97 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.60 (ddd, *J* = 15.0, 11.5, 5.6 Hz, 1H), 0.87–0.82 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) d 178.1, 175.8, 146.3, 140.9, 132.6, 129.3, 128.2, 127.0, 126.8, 123.7, 120.6, 119.4, 119.1, 108.5, 106.2, 60.9, 57.7, 56.8, 33.0, 28.8, 25.9, 17.8, 17.8, 11.8; IR (Neat Film NaCl) 3191, 3081, 2942, 2865, 2251, 2699, 1602, 1471, 1337, 1236, 1108, 995, 920, 736 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{31}H_{42}BrN_2O_3Si$ $[M+H]^+$: 597.2143; found 597.2141.



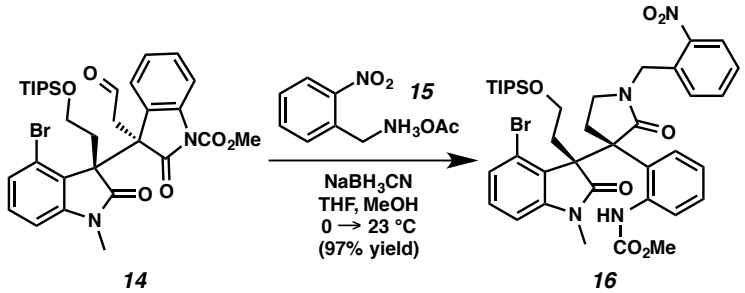
SI-5 *13*

Carbamate 13. To a stirred solution of bis-oxindole **SI-5** (350 mg, 0.59 mmol, 1.0 equiv) in CH_2Cl_2 (5.86 mL) were added DMAP (7 mg, 0.059 mmol, 0.1 equiv), Et_3N (0.812 mL, 5.9 mmol, 10.0 equiv), and methyl chloroformate (0.16 mL, 1.76 mmol, 3.0 equiv) at 0 ^{o}C. The reaction was slowly warmed to 23 ^{o}C, and stirred for 12 h. The solvent was concentrated *in vacuo*, and then the residue was purified by column chromatography (4:1 hexanes:EtOAc) to afford carbamate **13** (377 mg, 98% yield).
R_f = 0.61 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.05 (ddd, *J* = 8.1, 6.1, 2.9 Hz, 1H), 6.96 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.92–6.91 (m, 2H), 6.82 (t, *J* = 7.9 Hz, 1H), 6.25 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.06 (ddt, *J* = 16.6, 9.6, 6.9 Hz, 1H), 5.00 – 4.95 (m, 1H), 4.81–4.78 (m, 1H), 4.00 (s, 3H), 3.72 (ddd, *J* = 10.2, 5.7, 3.1 Hz, 1H), 3.61 (ddt, *J* = 13.8, 6.9, 1.0 Hz, 1H), 3.43 (td, *J* = 10.4, 3.9 Hz, 1H), 3.33–3.28 (m, 1H), 3.02 (m, 4H), 2.62 (ddd, *J* = 14.0, 10.6, 5.7 Hz, 1H), 0.87–0.81 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 174.2, 151.3, 146.1, 139.5, 132.0, 129.6, 128.6, 127.1, 126.5, 126.2, 123.2, 122.7, 119.9, 119.0, 113.9, 106.3, 60.7, 58.4, 57.3, 53.7, 33.4, 28.9, 26.0, 17.7, 11.8; IR (Neat Film NaCl) 2942, 2865, 2089, 1722, 1602, 1463, 1348, 1201, 1243, 1166, 1104, 1026, 920, 883, 736, 772 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{33}H_{44}BrN_2O_5Si$ $[M+H]^+$: 655.2197; found 655.2199.



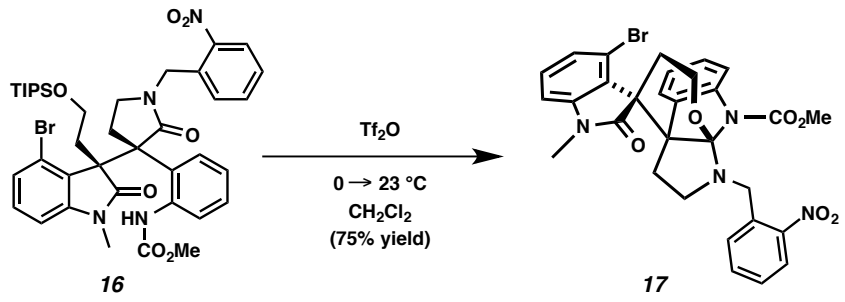
Aldehyde 14. To a 25 mL round bottom flask with magnetic stir bar was added alkene **13** (260 mg, 0.40 mmol, 1.0 equiv) and CH_2Cl_2 (2.0 mL). The flask was connected to an ozone generator, and purged with oxygen gas (flow: 0.5), for 5 min at –78 ^{o}C and then ozone gas (flow: 0.5) was bubbled through into the reaction solution for 10 min at –78 ^{o}C. After the reaction was done, oxygen gas was bubbled into the reaction mixture for 20 min and PPh_3 (313mg, 1.19 mmol, 3.0 equiv) was added. The reaction mixture was slowly warmed to ambient temperature, stirred for 16 h, and then concentrated under reduced pressure. The residue was purified by column chromatography (4:1 hexanes:EtOAc) to afford aldehyde **14** (245 mg, 94% yield).

R_f = 0.13 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.46 (d, *J*=1.0 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.06–7.01 (m, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.88–6.82 (m, 2H), 6.75 (d, *J* = 7.6 Hz, 1H), 6.23 (d, *J* = 7.8 Hz, 1H), 4.33 (d, *J* = 19.4 Hz, 1H), 4.02 (s, 3H), 3.72 (ddd, *J* = 9.3, 5.6, 2.7 Hz, 1H), 3.58 (dd, *J* = 19.3, 1.2 Hz, 1H), 3.42 (td, *J* = 10.3, 3.4 Hz, 1H), 3.23 (dt, *J* = 14.0, 3.4 Hz, 1H), 2.99 (s, 3H), 2.56–2.48 (m, 1H), 0.86–0.79 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.9, 175.4, 174.4, 151.3, 146.0, 140.0, 129.9, 128.8, 127.2, 126.5, 125.2, 122.6, 121.4, 119.3, 114.1, 106.5, 60.6, 58.2, 53.8, 52.8, 44.6, 28.9, 26.0, 17.7, 11.8; IR (Neat Film NaCl) 2942, 2865, 2255, 1773, 1718, 1603, 1576, 1459, 1351, 1295, 1245, 1163, 1108, 914, 883, 771, 732 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{32}H_{41}BrN_2O_6Si$ $[M+H]^+$: 657.1990; found: 657.1991.



Amide 16. To a solution of aldehyde **14** (100 mg, 0.13 mmol, 1.0 equiv) and *o*-nitrobenzylammonium acetate **15** (97 mg, 0.38 mmol, 3.0 equiv) in MeOH (7.6 mL) was added $NaBH_3CN$ (21 mg, 0.26 mmol, 2.0 equiv) in THF (3.8 mL) at 0 °C. The reaction mixture was slowly warmed to ambient temperature and stirred for 12 h. Then, H_2O (5 mL) was added and extracted with EtOAc (3 x 20 mL), and washed with brine. The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (4:1 hexanes:EtOAc) on silica gel to afford *o*-nitrobenzyl protected amide **16** (116 mg, 97% yield).

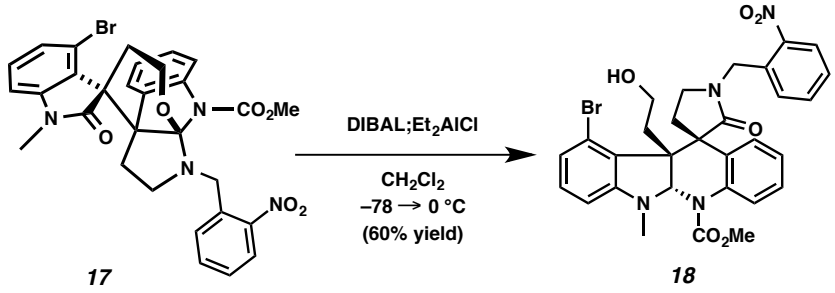
R_f = 0.35 (2:1 hexanes:EtOAc); (Due to the distinct presence of rotameric isomers, the ^1H NMR and ^{13}C NMR contained extra peaks. See the attached spectrum), ^1H NMR (500 MHz, $CDCl_3$) δ 11.63 (s, 1H), 8.06–7.97 (m, 2H), 7.51 (td, *J* = 7.6, 1.5 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.25–7.18 (m, 2H), 7.13 (dd, *J* = 14.1, 8.2 Hz, 2H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.97–6.90 (m, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 5.32 (d, *J* = 16.5 Hz, 1H), 4.71 (dd, *J* = 16.4, 6.5 Hz, 1H), 3.70–3.63 (m, 2H), 3.57 (td, *J* = 6.3, 2.9 Hz, 1H), 3.55–3.51 (m, 1H), 3.35–3.26 (m, 2H), 2.92 (ddd, *J* = 13.1, 5.4, 3.3 Hz, 1H), 2.84 (s, 1H), 2.69 (ddd, *J* = 19.4, 8.7, 5.3 Hz, 2H), 2.63 (s, 3H), 0.85 (t, *J* = 4.1 Hz, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 175.4, 154.4, 148.7, 147.1, 139.7, 134.1, 132.1, 131.2, 130.0, 129.4, 128.8, 128.7, 127.6, 126.6, 126.0, 125.3, 122.1, 121.8, 121.3, 107.3, 60.9, 60.6, 60.4, 51.6, 46.0, 45.1, 31.8, 31.6, 25.9, 17.9, 11.9; IR (Neat Film NaCl) 3418, 2943, 2865, 2251, 1717, 1601, 1527, 1456, 1338, 1313, 1282, 1227, 1113, 1069, 911, 883, 857, 730 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{39}H_{50}BrN_4O_7Si$ $[M+H]^+$: 793.2627; found: 793.2658.



Propellane hexacycle 17. To a solution of amide **16** (54.1 mg, 0.087 mmol, 1.0 equiv) in CH_2Cl_2 (6.82 mL), was added Tf_2O (34 mL, 0.26 mmol, 3.0 equiv) dropwise at 0 °C. The reaction mixture was slowly warmed to 23 °C, and stirred for 2 h. After the reaction was done, the solution was brought to pH 10.5-11.0 by addition of sat.

$NaHCO_3$. The reaction mixture was extracted with EtOAc (3 x 6 mL) and washed with brine. The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (2:1 hexanes:EtOAc) on silica gel to afford propellane hexacycle **17** (39.6 mg, 75% yield).

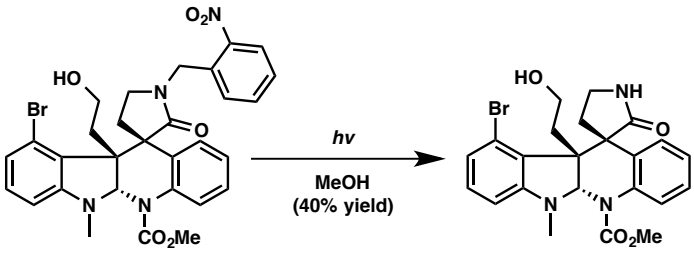
R_f = 0.46 (1:1 hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.72–7.58 (m, 1H), 7.46–7.40 (m, 2H), 7.30 (ddd, *J* = 8.0, 6.7, 2.2 Hz, 1H), 7.21–7.14 (m, 1H), 6.99–6.93 (m, 2H), 6.81–6.76 (m, 1H), 6.64 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.36 (dd, *J* = 7.7, 1.3 Hz, 1H), 4.61 (d, *J* = 16.6 Hz, 1H), 4.54 (d, *J* = 18.2 Hz, 1H), 4.45 (td, *J* = 11.4, 6.5 Hz, 1H), 4.18–4.11 (m, 1H), 3.72 (d, *J* = 9.4 Hz, 3H), 3.21 (s, 3H), 3.11–3.02 (m, 1H), 2.96–2.87 (m, 1H), 2.51 (dt, *J* = 14.4, 9.0 Hz, 2H), 1.94–1.81 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6, 153.5, 148.9, 145.8, 144.4, 142.1, 136.2, 132.9, 131.0, 130.0, 129.6, 129.1, 128.1, 127.3, 125.1, 124.3, 123.1, 116.1, 111.9, 106.8, 64.5, 58.4, 56.5, 54.5, 52.6, 50.0, 47.9, 33.9, 26.5, 22.8; IR (Neat Film NaCl) 2953, 2360, 1721, 1599, 1573, 1524, 1483, 1455, 1367, 1242, 1134, 1088, 1134, 1088, 947, 856, 761, 733 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{30}H_{28}BrN_4O_6$ $[M+H]^+$: 619.1187; found: 619.1188.



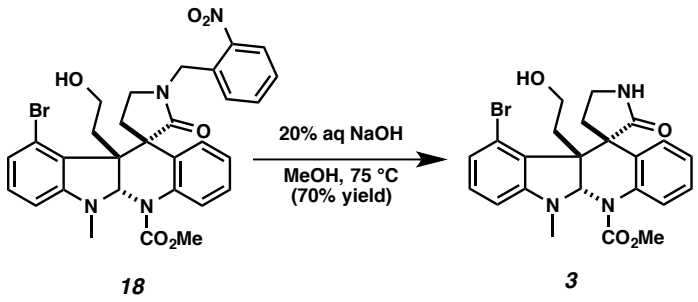
Aminal 18. To a solution of propellane hexacyclic oxindole **17** (14.6 mg, 0.024 mmol, 1.0 equiv) in CH_2Cl_2 (2.4 mL) was added DIBAL (1.0 M in THF; 0.12 mL, 0.12 mmol, 5 equiv) dropwise at –78 °C. After the reaction mixture was stirred for 1 h at –78 °C, the solution was warmed to 0 °C and DIBAL (1.0 M in THF; 24 mL, 0.024 mmol, 1.0 equiv) was added dropwise. The mixture was stirred for 1 h at 0 °C, and more DIBAL (1.0 M in THF; 24 mL, 0.024 mmol, 1.0 equiv) was added dropwise. The reaction mixture was stirred for 1 h at 0 °C, and warmed to 23 °C. To the reaction mixture was added Et_2AlCl (1.0 M in hexanes; 48 mL, 0.048 mmol, 2.0 equiv) dropwise. The reaction was stirred for 30 min and quenched with aq. NH_4Cl (1 mL) and aq. potassium sodium tartrate (1 mL). The reaction mixture was washed

with EtOAc (3 x 3 mL), and brine. The combined organic phases were dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (1:1 hexane:EtOAc) on silica gel to afford aminal **18** (8.9 mg, 60% yield).

R_f = 0.12 (1:1 hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.58 (td, *J* = 7.6, 1.3 Hz, 1H), 7.50–7.48 (m, 1H), 7.44 (ddd, *J* = 8.6, 7.4, 1.5 Hz, 1H), 7.37–7.34 (m, 1H), 7.23–7.19 (m, 1H), 7.09–7.05 (m, 1H), 6.81 (t, *J* = 7.9 Hz, 1H), 6.69 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.26 (s, 1H), 6.01 (dd, *J* = 7.9, 0.9 Hz, 1H), 5.41 (d, *J* = 16.3 Hz, 1H), 4.56 (d, *J* = 16.2 Hz, 1H), 3.86 (s, 3H), 3.73–3.64 (m, 2H), 3.56 (td, *J* = 9.5, 7.4 Hz, 1H), 3.24–3.18 (m, 1H), 3.09 (ddd, *J* = 13.6, 8.6, 5.3 Hz, 1H), 2.95 (ddd, *J* = 14.2, 7.4, 1.7 Hz, 1H), 2.48 (s, 3H), 2.35 (ddd, *J* = 13.2, 8.5, 6.2 Hz, 1H), 1.78 (dt, *J* = 14.2, 9.4 Hz, 1H), 1.74 (br, s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 171.3 152.6, 148.9, 138.8, 136.3, 133.7, 132.1, 130.4, 129.7, 128.4, 126.9, 126.2, 126.0, 125.0, 124.8, 122.7, 122.2, 104.6, 83.2, 64.4, 60.7, 60.4, 53.3, 53.1, 45.3, 44.5, 35.2, 33.0, 31.0; IR (Neat Film NaCl) 2955, 2357, 1694, 1595, 1524, 1444, 1335, 1281, 1073, 1032, 911, 857, 835, 730 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{30}H_{30}BrN_4O_6$ $[M+H]^+$: 621.1343; found: 621.1286.



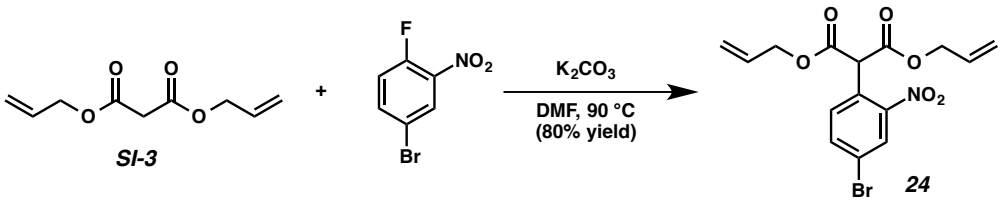
Amide 3. A solution of aminal **18** (21.5 mg, 0.035 mmol, 1.0 equiv) in anhydrous MeOH (3.5 mL) in a Pyrex flask was purged with N_2 for 5 min. The reaction mixture was irradiated in a cylindrical photoreactor with 254 nm lamps under N_2 for 3 h and concentrated. The residue was purified by column chromatography (4:1 CH_2Cl_2:acetone) on silica gel to afford aminal **3** (6.7 mg, 40% yield). See below for characterization data.



18 *3*

Amide 3. To a solution of *o*-nitrobenzyl protected aminal **18** (10.8 mg, 0.017 mmol, 1.0 equiv) in MeOH (0.8 mL) was added 20% aq NaOH (0.2 mL) and the mixture was stirred for 4 h at 75 °C. After the reaction mixture was cooled to 23 °C, it was diluted with water and extracted with EtOAc (3 x 2 mL). The organic layer was washed with brine, dried over $MgSO_4$, concentrated *in vacuo.* The residue was purified by column chromatography (4:1 CH_2Cl_2:acetone) to afford compound **3** (5.9 mg, 70% yield).

R_f = 0.18 (4:1 CH_2Cl_2:acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.45 (m, 1H), 7.19 (td, *J* = 7.6, 1.4 Hz, 1H), 7.05 (td, *J* = 7.7, 1.4 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.69 (dt, *J* = 8.0, 1.0 Hz, 1H), 6.60 (br, s, 1H), 6.25 (br, s, 1H), 5.99 (dd, *J* = 7.9, 0.9 Hz, 1H), 3.87 (s, 3H), 3.74–3.63 (m, 2H), 3.55 (td, *J* = 9.4, 7.3 Hz, 1H), 3.33 (ddd, *J* = 9.8, 8.8, 1.5 Hz, 1H), 3.17 (ddd, *J* = 13.6, 8.4, 5.6 Hz, 1H), 3.03–2.96 (m, 1H), 2.49 (s, 3H), 2.36 (ddd, *J* = 13.2, 8.2, 6.3 Hz, 1H), 1.92 (dt, *J* = 14.0, 9.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.8, 155.4, 152.9, 138.6, 136.4, 130.4, 126.9, 126.6, 126.1, 125.0, 123.4, 122.5, 104.6, 83.2, 76.9, 60.9, 60.6, 53.5, 52.3, 40.4, 35.8, 35.2, 31.1; IR (Neat Film NaCl) 3418, 2955, 2357, 1693, 1593, 1446, 1335, 1282, 1032, 836, 754 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{23}H_{25}BrN_3O_4$ $[M+H]^+$: 486.1023; found: 486.1004.

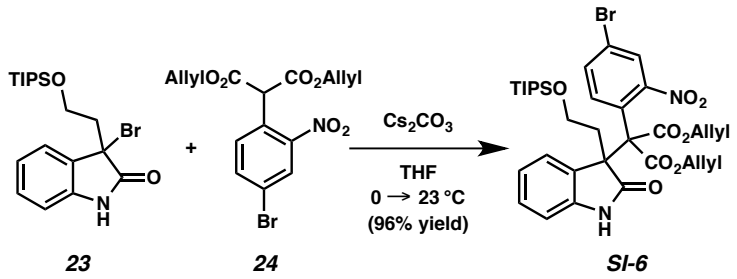


SI-3 *24*

Diallyl 2-(4-bromo-2-nitrophenyl)malonate 24. A 500 mL round-bottom flask with a magnetic stir bar was charged with diallyl malonate **SI-3** (15.0 g, 81.5 mmol, 1.0 equiv), 4-bromo-1-fluoro-2-nitrobenzene (11.0 mL, 89.7 mmol, 1.1 equiv), and

K_2CO_3 (33.8 g, 245 mmol, 3.0 equiv). DMF (163 mL) was added and the brown suspension was heated to 90 °C for 16 h. The reaction mixture was cooled to ambient temperature and diluted with ice water (250 mL) and Et_2O (300 mL). The aqueous phase was extracted with Et_2O (3 x 300 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography (9:1 hexanes:EtOAc) on silica gel to give arylated malonate **24** (32.1 g, 80% yield).

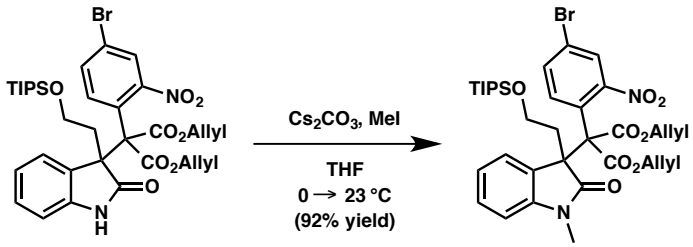
R_f = 0.69 (1:1 hexane:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 2.1 Hz, 1H), 7.77 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 5.94–5.84 (m, 2H), 5.37–5.24 (m, 5H), 4.70 (dt, *J* = 5.9, 1.3 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 149.1, 136.5, 132.8, 131.0, 128.2, 126.8, 122.8, 119.3, 66.9, 53.8; IR (Neat Film NaCl) 3085, 2986, 2951, 1733, 1649, 1538, 1348, 1283, 1218, 1148, 989, 936 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{15}H_{15}BrNO_6$ $[M+H]^+$: 384.0077; found: 384.0072.



Oxindole SI-6. To a solution of 3-bromooxindole **23** (2.0 g, 4.85 mmol, 1.0 equiv) and malonate **24** (3.7 g, 9.70 mmol, 2.0 equiv) in THF (49 mL) was added Cs_2CO_3 (3.2 g, 9.70 mmol, 2.0 equiv) at 0 °C. The reaction mixture was warmed to 23 °C and stirred overnight. Solids were removed via a filtration through a celite plug and the resulting solution was concentrated under reduced pressure. The residue was purified by flash column chromatography (9:1 → 4:1 hexanes:EtOAc) on silica gel to give desired alkylated product **SI-6** (3.3g, 96% yield).

R_f = 0.33 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (br, s, 1H), 7.95 (d, *J* = 8.9 Hz, 1H), 7.86 (d, *J* = 2.3 Hz, 1H), 7.53 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.43–7.39 (m, 1H), 7.16 (td, *J* = 7.7, 1.2 Hz, 1H), 6.92 (td, *J* = 7.7, 1.1 Hz, 1H), 6.75–6.72 (m, 1H), 5.79 (dddt, *J* = 33.6, 17.2, 10.4, 5.9 Hz, 2H), 5.26–5.14 (m, 4H), 4.66 (qdt, *J* = 13.2, 5.9, 1.4 Hz, 2H), 4.55–4.42 (m, 2H), 3.32 (dt, *J* = 9.7, 7.5 Hz, 1H), 3.09 (ddd, *J*

= 9.8, 8.5, 4.5 Hz, 1H), 2.89–2.82 (m, 1H), 2.63 (ddd, *J* = 12.7, 8.1, 4.5 Hz, 1H), 0.89 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.0, 166.6, 166.2, 150.9, 140.9, 134.3, 134.1, 131.3, 130.8, 129.0, 129.0, 128.6, 128.3, 127.2, 122.7, 122.2, 119.6, 119.0, 109.5, 67.2, 67.1, 66.9, 59.7, 57.0, 38.4, 18.0, 11.9; IR (Neat Film NaCl) 3203, 2943, 2865, 1716, 1619, 1538, 1471, 1357, 1229, 1111, 992, 935, 753, 735 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{34}H_{44}BrN_2O_8Si$ $[M+H]^+$: 715.2045; found: 715.2090.

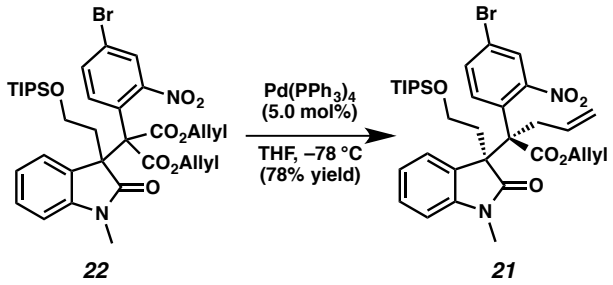


SI-6 ***22***

Methyloxindole 22. To a solution of oxindole **SI-6** (14.1 g, 0.0197 mol, 1.0 equiv) in THF (106 mL) was added Cs_2CO_3 (19.3 g, 0.0591 mol, 3.0 equiv) and MeI (7.40 mL, 0.118 mol, 6.0 equiv) at 0 °C. Then, the reaction mixture was stirred for 12 h at 23 °C. After the reaction was done, sat. NH_4Cl was added. The aqueous phase was extracted with EtOAc (3 x 100 mL). The combined organic phases were washed with brine (50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography (7:1 hexanes:EtOAc) on silica gel to give methylated oxindole **22** (13.2 g, 92% yield).

R_f = 0.40 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 1H), 7.76 (d, *J* = 2.3 Hz, 1H), 7.53–7.48 (m, 2H), 7.21 (td, *J* = 7.7, 1.2 Hz, 1H), 6.95 (td, *J* = 7.6, 1.1 Hz, 1H), 6.69–6.66 (m, 1H), 5.85 (ddt, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.74 (ddt, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.26–5.20 (m, 2H), 5.18 (ddt, *J* = 10.4, 2.2, 1.2 Hz, 2H), 4.72–4.63 (m, 2H), 4.54 (ddt, *J* = 13.1, 6.0, 1.4 Hz, 1H), 4.40 (ddt, *J* = 13.0, 6.0, 1.3 Hz, 1H), 3.18–3.13 (m, 1H), 3.13 (s, 3H), 3.05 (ddd, *J* = 9.9, 7.9, 4.7 Hz, 1H), 2.82 (dt, *J* = 13.0, 7.6 Hz, 1H), 2.71 (ddd, *J* = 12.8, 7.6, 4.7 Hz, 1H), 0.90–0.84 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 166.3, 166.2, 150.8, 143.7, 134.4, 133.4, 131.1, 130.8, 128.8, 128.1, 128.0, 127.0, 122.5, 122.1, 119.4, 119.0, 107.6, 67.0, 66.9, 66.9, 59.6, 56.8, 37.9, 26.3, 17.8, 17.8, 11.8; IR (Neat Film NaCl) 2943, 2865, 1747,

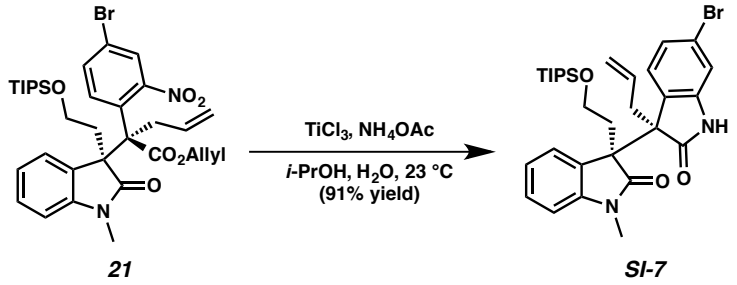
1713, 1611, 1538, 1471, 1357, 1223, 1103, 993, 935, 882, 752 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{35}H_{46}BrN_2O_8Si$ $[M+H]^+$: 729.2201; found: 729.2253.



22 ***21***

Allyl 21. To a 500 mL round-bottom flask with a magnetic stir bar was added malonate **22** (11.1 g, 15.2 mmol, 1.0 equiv). The flask was brought into a N_2-filled glove box and then $Pd(PPh_3)_4$ (0.88 g, 0.761 mol, 0.05 equiv) was added. The reaction mixture was brought out from the glove box and treated with THF (152 mL). After 1 h stirring, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (1:1 hexane:EtOAc) on silica gel to afford allylated product **21** (8.1 g, 78% yield).

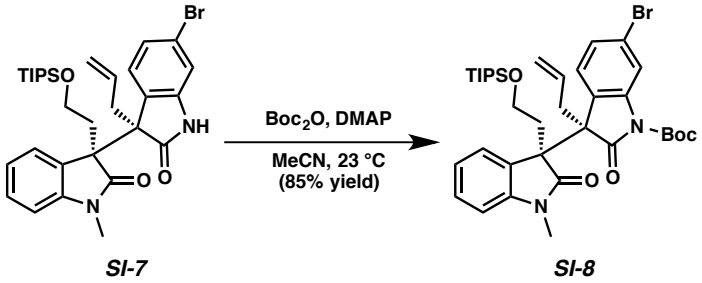
R_f = 0.45 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.7 Hz, 1H), 7.97 (d, *J* = 2.3 Hz, 1H), 7.80 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.22 (td, *J* = 7.7, 1.1 Hz, 1H), 6.83–6.77 (m, 2H), 6.33 (d, *J* = 7.5 Hz, 1H), 5.66 (ddt, *J* = 16.9, 10.3, 6.2 Hz, 1H), 5.56 (ddt, *J* = 17.0, 10.1, 6.9 Hz, 1H), 5.16–5.09 (m, 2H), 4.91 (dq, *J* = 17.1, 1.5 Hz, 1H), 4.84 (ddd, *J* = 10.2, 1.9, 1.1 Hz, 1H), 4.38–4.26 (m, 2H), 3.37 (dd, *J* = 15.3, 7.0 Hz, 1H), 3.23 (s, 3H), 3.21–3.10 (m, 2H), 2.90 (ddd, *J* = 9.5, 8.5, 4.2 Hz, 1H), 2.59–2.51 (m, 1H), 2.16 (ddd, *J* = 12.5, 8.1, 4.3 Hz, 1H), 0.92–0.80 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.7, 169.6, 152.1, 144.3, 134.8, 134.5, 133.7, 131.3, 131.1, 128.9, 128.8, 128.70, 125.13, 121.9, 121.8, 119.5, 118.2, 108.1, 65.7, 60.7, 59.5, 55.5, 39.0, 36.6, 26.5, 18.0, 11.9; IR (Neat Film NaCl) 2942, 2865, 1713, 1610, 1538, 1495, 1471, 1353, 1106, 995, 918, 882, 750, 732 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{34}H_{46}BrN_2O_6Si$ $[M+H]^+$: 685.2303; found: 685.2294.



21 *SI-7*

Bis-oxindole SI-7. To a solution of oxindole **21** (7.65 g, 11.2 mmol, 1.0 equiv) in H_2O (187 mL) and *i*-PrOH (373 mL) were added NH_4OAc (43.2 g, 0.560 mol, 50 equiv) and $TiCl_3$ (20% w/w, 69.2 mL, 0.11 mol, 10 equiv). Then, the reaction was stirred for 12 h at 23 ^oC. The reaction mixture was diluted with EtOAc (200 mL) and then the phases were separated and the aqueous phase was extracted with EtOAc (3 x 300 mL). The combined organic phases were dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (2:1 hexanes:EtOAc) on silica gel to afford bis-oxindole **SI-7** (6.10 g, 91% yield).

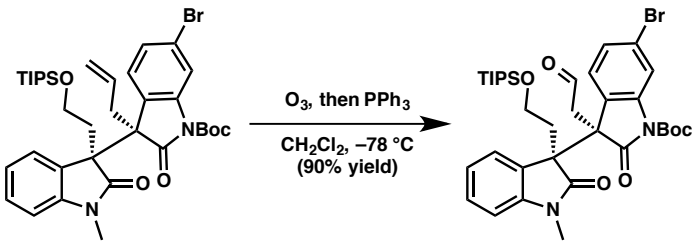
R_f = 0.68 (1:1 hexane:EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (br, s, 1H), 7.31–7.26 (m, 1H), 6.98–6.90 (m, 2H), 6.88 (dd, *J* = 2.7, 1.5 Hz, 1H), 6.82 (s, 1H), 6.73–6.69 (m, 1H), 6.21 (br, s, 1H), 5.14 (ddt, *J* = 17.1, 10.0, 7.1 Hz, 1H), 4.96 (ddd, *J* = 17.1, 2.0, 0.9 Hz, 1H), 4.86–4.80 (m, 1H), 3.42–3.31 (m, 2H), 3.25 (ddd, *J* = 9.9, 7.5, 4.7 Hz, 1H), 3.05 (dt, *J* = 14.5, 7.4 Hz, 1H), 2.90 (s, 3H), 2.79 (dd, *J* = 13.0, 6.9 Hz, 1H), 2.34 (ddd, *J* = 13.4, 6.8, 4.7 Hz, 1H), 0.92–0.81 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.14, 176.05, 144.65, 142.73, 131.37, 128.80, 127.92, 127.73, 125.58, 124.41, 124.20, 121.97, 121.73, 119.88, 112.70, 108.15, 59.61, 56.86, 54.80, 35.16, 32.66, 25.91, 17.82, 11.77; IR (Neat Film NaCl) 3270, 2942, 2865, 1716, 1611, 1471, 1377, 1241, 1105, 916, 883, 791, 734 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{31}H_{42}BrN_2O_3Si$ $[M+H]^+$: 597.2143; found: 597.2187.



SI-7 *SI-8*

Carbamate SI-8. To a stirred solution of bis-oxindole **SI-7** (2.63 g, 4.40 mmol, 1.0 equiv) in MeCN (44 mL) were added DMAP (1.08, 8.80 mmol, 2.0 equiv) and Boc_2O (1.92 g, 8.80 mmol, 2.0 equiv) at 0 °C. The reaction was slowly warmed to 23 °C, and stirred for 12 h. The solvent was concentrated *in vacuo* and then the residue was purified by column chromatography (4:1 hexanes:EtOAc) to afford protected compound **SI-8** (2.6 g, 85% yield).

R_f = 0.52 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.9 Hz, 1H), 7.25 (td, *J* = 7.7, 1.3 Hz, 1H), 7.14–7.09 (m, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.71–6.67 (m, 1H), 6.62–6.53 (m, 1H), 6.47 (s, 1H), 5.10 (ddt, *J* = 17.0, 9.9, 7.1 Hz, 1H), 4.99–4.92 (m, 1H), 4.83 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.43 (dd, *J* = 13.3, 7.3 Hz, 1H), 3.35 (dt, *J* = 9.9, 7.2 Hz, 1H), 3.20 (ddd, *J* = 9.9, 7.7, 4.8 Hz, 1H), 2.94 (s, 3H), 2.90 (dd, *J* = 13.9, 8.0 Hz, 1H), 2.81–2.75 (m, 1H), 2.30 (ddd, *J* = 13.2, 7.2, 4.8 Hz, 1H), 1.51 (s, 9H), 0.89–0.84 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.60, 173.73, 148.46, 144.52, 141.67, 131.26, 128.95, 127.19, 126.28, 126.06, 125.32, 124.15, 122.43, 121.69, 120.23, 118.24, 108.06, 84.08, 59.56, 57.36, 55.29, 34.77, 32.70, 27.92, 25.97, 17.82, 11.76; IR (Neat Film NaCl) 2941, 2866, 1770, 1716, 1610, 1471, 1420, 1370, 1342, 1287, 1246, 1153, 1105, 1067, 1023, 919, 882, 845, 752, 733 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{31}H_{42}BrN_2O_3Si$ $[M+H-Boc]^+$: 597.2143 found: 597.2181.

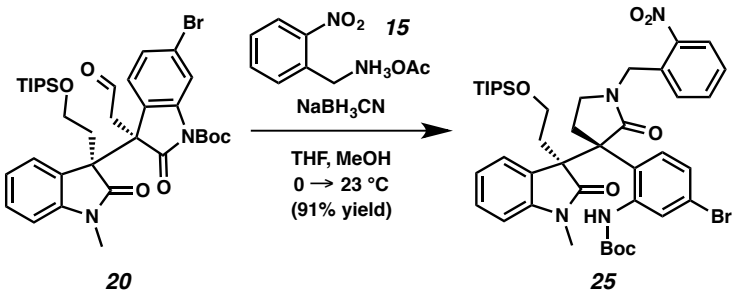


SI-8 ***20***

Aldehyde 20. To a 100 mL round bottom flask with magnetic stir bar was added alkene **SI-8** (2.61 g, 0.00374 mol, 1.0 equiv) in CH_2Cl_2 (18.7 mL). The flask was connected to an ozone generator and purged with oxygen gas (flow: 0.5) for 5 min at –78 °C. Then, ozone gas (flow: 0.5) was bubbled through into the reaction solution for 30 min at –78 °C. After the reaction was done, oxygen gas was bubbled into the reaction mixture for 20 min and PPh_3 (2.95 g, 0.0112 mol, 3.0 equiv) was added. The reaction mixture was slowly warmed to ambient temperature, stirred for 16 h, and

then concentrated under reduced pressure. The residue was purified by column chromatography (4:1 hexanes:EtOAc) to afford aldehyde **20** (2.4 g, 90% yield).

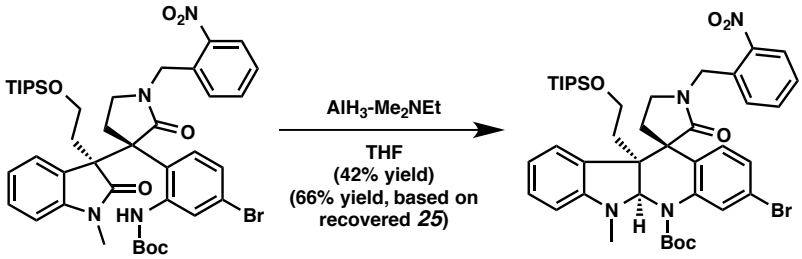
R_f = 0.23 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.00 (d, *J* = 1.8 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.21 (td, *J* = 7.8, 1.2 Hz, 1H), 6.93 (br, s, 1H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 5.99 (br, s, 1H), 4.43 (d, *J* = 19.1 Hz, 1H), 3.39 (dd, *J* = 19.2, 1.1 Hz, 1H), 3.31 (dt, *J* = 9.9, 7.3 Hz, 1H), 3.15 (ddd, *J* = 9.9, 8.0, 4.7 Hz, 1H), 3.10 (s, 3H), 2.64 (dt, *J* = 12.8, 7.6 Hz, 1H), 2.20 (ddd, *J* = 12.6, 7.5, 4.7 Hz, 1H), 1.43 (s, 9H), 0.91–0.82 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.38, 175.36, 173.47, 148.07, 144.01, 142.38, 129.18, 126.57, 126.04, 125.73, 124.51, 123.59, 122.99, 121.72, 118.74, 108.14, 83.83, 59.25, 53.78, 53.64, 44.47, 33.42, 27.83, 26.20, 17.80, 11.74; IR (Neat Film NaCl) 1941, 2865, 1771, 1722, 1609, 1471, 1422, 1370, 1345, 1291, 1245, 1152, 1109, 1070, 1015, 882, 845, 793, 749 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{30}H_{40}BrN_2O_4Si$ $[M+H-Boc]^+$: 599.1935 found: 597.1971.



Amide 25. To a solution of aldehyde **20** (200 mg, 0.29 mmol, 1.0 equiv) and *o*-nitrobenzylammonium acetate **15** (182 mg, 0.86 mmol, 3.0 equiv) in MeOH (14.3 mL) was added $NaBH_3CN$ (39 mg, 0.57 mmol, 2.0 equiv) in THF (7.2 mL) at 0 ^oC. The reaction mixture was slowly warmed to ambient temperature, and stirred for 12 h. Then, H_2O (10 mL) was added. The mixture was extracted with EtOAc (3 x 20 mL) and washed with brine. The combined organic phases were dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (4:1 hexanes:EtOAc) on silica gel to afford *o*-nitrobenzyl protected amide **25** (221 mg, 91% yield).

R_f = 0.22 (4:1 hexanes:EtOAc); (Due to the distinct presence of rotameric isomers, the ^{1}H NMR and ^{13}C NMR contained extra peaks. See attached the spectrum behind); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.9 Hz, 1H), 8.36 (d, *J* = 2.3 Hz, 1H), 8.09 (s,

1H), 8.06–7.96 (m, 2H), 7.83 (s, 1H), 7.62 (d, *J* = 7.1 Hz, 2H), 7.46 (t, *J* = 8.5 Hz, 1H), 7.42–7.30 (m, 6H), 7.23 (d, *J* = 8.3 Hz, 3H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.93–6.86 (m, 2H), 6.81 (d, *J* = 7.5 Hz, 2H), 6.10 (d, *J* = 7.6 Hz, 1H), 5.00 (d, *J* = 16.9 Hz, 1H), 4.91 (d, *J* = 17.3 Hz, 1H), 4.58 (d, *J* = 17.3 Hz, 1H), 4.27 (s, 1H), 3.75 (s, 1H), 3.37 (t, *J* = 7.4 Hz, 1H), 3.28 (s, 3H), 3.23 (d, *J* = 4.9 Hz, 1H), 3.18 (d, *J* = 7.2 Hz, 4H), 3.14–3.06 (m, 3H), 2.99 (dt, *J* = 9.2, 4.7 Hz, 2H), 2.80 (dd, *J* = 13.3, 9.4 Hz, 3H), 2.43 (t, *J* = 7.8 Hz, 1H), 2.25–2.13 (m, 1H), 2.06 (d, *J* = 8.9 Hz, 2H), 1.45 (s, 9H), 1.30 (s, 9H), 0.87 (d, *J* = 1.9 Hz, 21H), 0.80 (d, *J* = 2.7 Hz, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.3, 176.9, 174.6, 152.9, 148.3, 148.1, 145.0, 144.7, 141.9, 134.5, 134.1, 131.8, 131.0, 129.1, 128.8, 128.8, 128.5, 128.4, 128.4, 128.2, 127.0, 125.3, 125.2, 125.1, 124.9, 123.2, 122.9, 122.1, 121.7, 108.4, 107.9, 79.9, 59.9, 59.2, 59.1, 52.9, 44.6, 44.2, 44.1, 36.4, 34.6, 31.3, 31.1, 28.6, 28.3, 26.5, 26.3, 18.2, 18.0, 17.9, 12.2, 12.1, 11.9; IR (Neat Film NaCl) 3329, 2941, 2866, 1701, 1612, 1531, 1496, 1473, 1344, 1280, 1159, 1103, 1072, 1024, 914, 885, 753, 731, 688 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{42}H_{56}BrN_4O_7Si$ $[M+H]^+$: 835.3096; found: 835.3105.

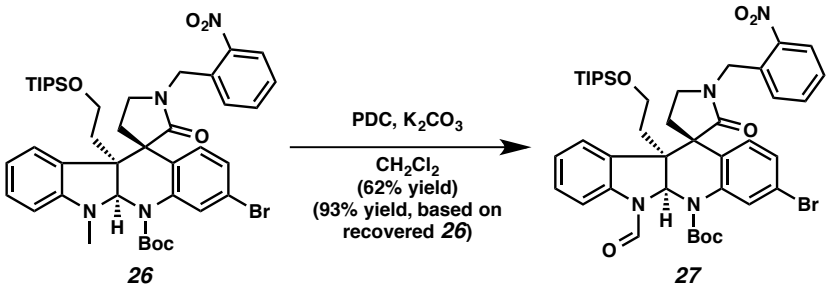


25 ***26***

Aminal 26. Oxindole **25** (20 mg, 0.0239 mmol, 1.0 equiv) was dissolved in THF (2.39 mL) and cooled to 0 °C. AlH_3-Me_2NEt (0.5 M in toluene; 0.096 mL, 0.0478 mmol, 2.0 equiv) was added dropwise at 0 °C. The solution was stirred for 2 h and quenched with MeOH. The solution was concentrated under reduced pressure and purified by column chromatography (4:1 hexanes:EtOAc) on silica gel to afford cyclized compound **26** (8.23 mg, 42% yield; 66% yield, based on recovered starting material).

R_f = 0.33 (4:1 hexanes:EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.9 Hz, 1H), 7.40 (s, 1H), 7.35 (dt, *J* = 19.0, 7.4 Hz, 2H), 7.06–7.03 (m, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.93–6.91 (m, 2H), 6.90–6.86 (m, 1H), 6.40 (t, *J* = 7.4 Hz, 1H), 6.20 (s, 1H), 6.12 (d, *J* = 7.8 Hz, 1H), 4.75 (q, *J* = 16.8, 16.1 Hz, 2H), 3.78 (td, *J* = 10.7, 10.3, 6.0

Hz, 1H), 3.53 (q, *J* = 8.8 Hz, 1H), 3.46 (t, *J* = 9.3 Hz, 1H), 3.16–3.07 (m, 2H), 2.84(s, 3H), 2.75 (dd, *J* = 13.4, 6.0 Hz, 1H), 2.50 (td, *J* = 11.4, 5.6 Hz, 1H), 2.23–2.16 (m, 1H), 1.47 (s, 9H), 0.95 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 153.6, 150.9, 148.7, 139.9, 133.5, 132.2, 131.0, 130.6, 128.9, 128.5, 128.2, 127.8, 125.2, 124.8, 123.2, 120.6, 116.2, 104.3, 80.9, 79.6, 59.9, 56.9, 54.12, 44.49, 43.5, 39.5, 31.0, 29.6, 28.2, 26.3, 17.9, 11.9; IR (Neat Film NaCl) 2941, 2865, 1697, 1603, 1528, 1491, 1333, 1302, 1168, 1100, 992, 882, 739 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{42}H_{56}BrN_4O_6Si$ $[M+H]^+$: 819.3147; found: 819.3153.

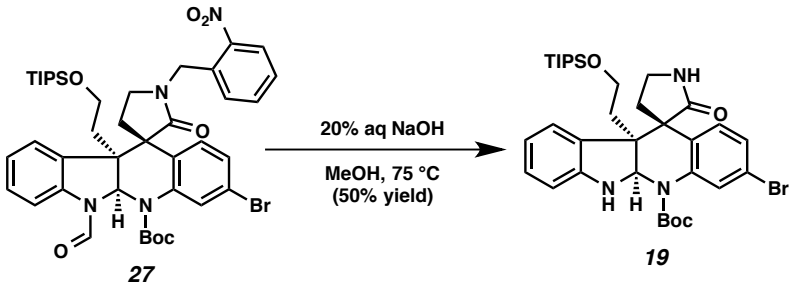


26 *27*

Formyl 27. To a solution of methyl protected compound **26** (11 mg, 0.0161 mmol, 1.0 equiv) in CH_2Cl_2 (1.61 mL) was added PDC (9.1 mg, 0.0241 mmol, 1.5 equiv) at 23 °C. After being stirred at 23 °C for 12 h, the reaction mixture was quenched with water. The reaction mixture was washed with CH_2Cl_2 (3 x 2 mL), and brine. The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (4:1 hexanes:EtOAc) on silica gel to afford aldehyde **27** (7.0 mg, 62% yield; 93% yield, based on recovered starting material).

R_f = 0.55 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.96 (dd, *J* = 7.8, 2.5 Hz, 2H), 7.38 (q, *J* = 8.5, 8.0 Hz, 2H), 7.33 (s, br, 1H), 7.14–6.99 (m, 4H), 6.96–6.87 (m, 3H), 4.83 (s, br, 1H), 4.70 (d, 15Hz, 1H), 3.64–3.54 (m, 2H), 3.51 (t, *J* = 9.4 Hz, 1H), 3.26 (q, *J* = 10.0, 7.4 Hz, 1H), 3.11 (q, *J* = 10.9 Hz, 1H), 2.79 (dd, *J* = 13.2, 5.8 Hz, 1H), 2.58 (dt, *J* = 13.1, 7.8 Hz, 1H), 2.19 (ddd, *J* = 12.9, 7.9, 4.7 Hz, 1H), 1.44 (s, br, 9H), 0.98–0.76 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 161.4, 153.1, 148.7, 141.3, 138.3, 133.5, 131.8, 131.5, 131.2, 129.3, 128.7, 128.4, 125.1, 124.9, 124.2, 123.5, 121.1, 116.0, 81.9, 75.1, 59.4, 57.2, 54.1, 44.6, 43.6, 39.6, 29.7, 28.1, 26.3, 17.9, 17.9, 11.8; IR (Neat Film NaCl) 2942, 2866, 1683, 1591, 1527,

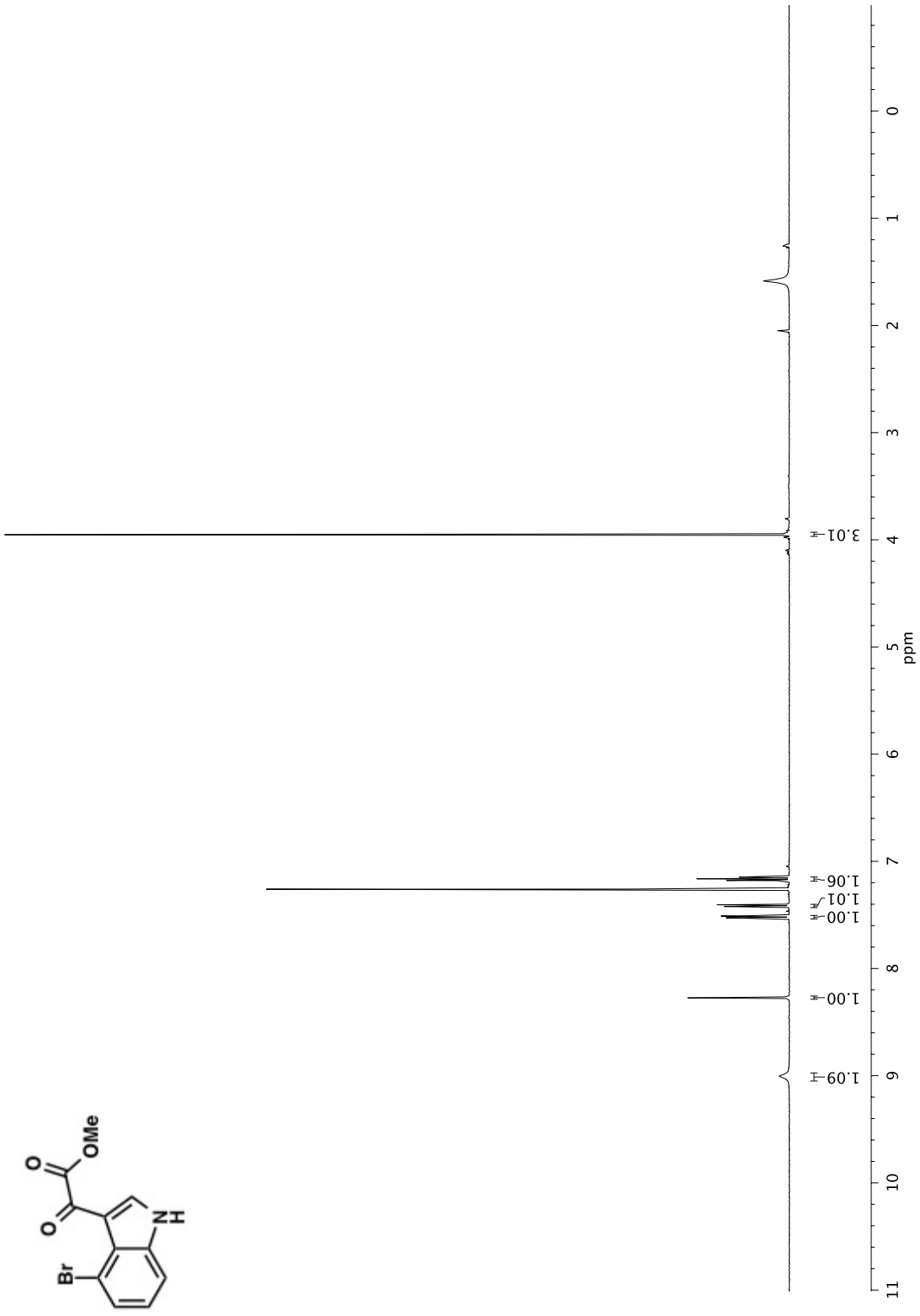
1489, 1393, 1323, 1280, 1155, 1096, 911, 733 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{42}H_{54}BrN_4O_7Si$ $[M+H]^+$: 833.2940; found: 833.2960.



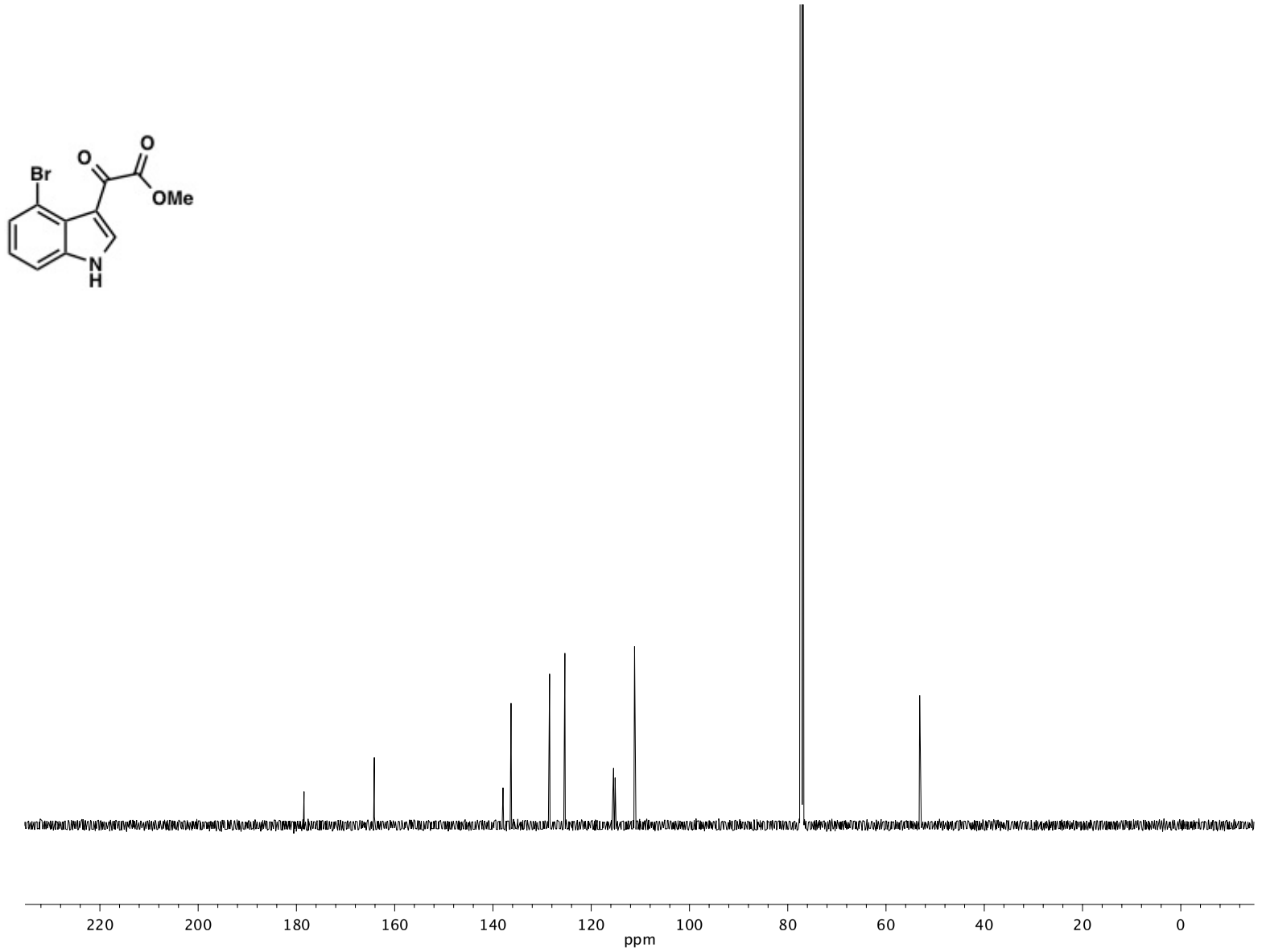
27 *19*

Amide 19. To a solution of aldehyde **27** (14.8 mg, 0.0177 mmol, 1.0 equiv) in MeOH (0.4 mL) was added 20% aq NaOH (0.2 mL) and the reaction mixture was stirred for 4 h at 75 °C. The reaction mixture was diluted with EtOAc (1 mL) and the aqueous phase was extracted with EtOAc (3 x 1 mL). The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (4:1 hexanes:EtOAc) on silica gel to afford desired amide **19** (5.9 mg, 50% yield).

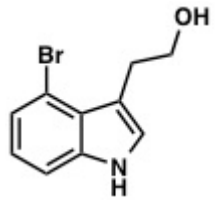
R_f = 0.21 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.14 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.06 (dt, *J* = 7.7, 3.7 Hz, 3H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 7.7 Hz, 1H), 6.17 (s, 1H), 5.72 (s, 1H), 3.69–3.61 (m, 1H), 3.48 (dt, *J* = 10.8, 5.6 Hz, 1H), 3.07 (m, 1H), 2.85 (m, 1H), 2.77 (m, 2H), 2.33 (d, *J* = 7.9 Hz, 1H), 1.59 (s, 9H), 0.91 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.2, 153.9, 149.2, 138.2, 130.4, 128.9, 127.1, 126.8, 126.5, 124.4, 120.6, 119.5, 109.4, 82.5, 60.3, 55.6, 53.4, 38.9, 35.7, 31.2, 28.6, 18.4, 11.9; IR (Neat Film NaCl) 3401, 2941, 2865, 1696, 1487, 1465, 1314, 1163, 1094, 882, 740 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{34}H_{49}BrN_3O_4Si$ $[M+H]^+$: 670.2670; found: 670.2679.

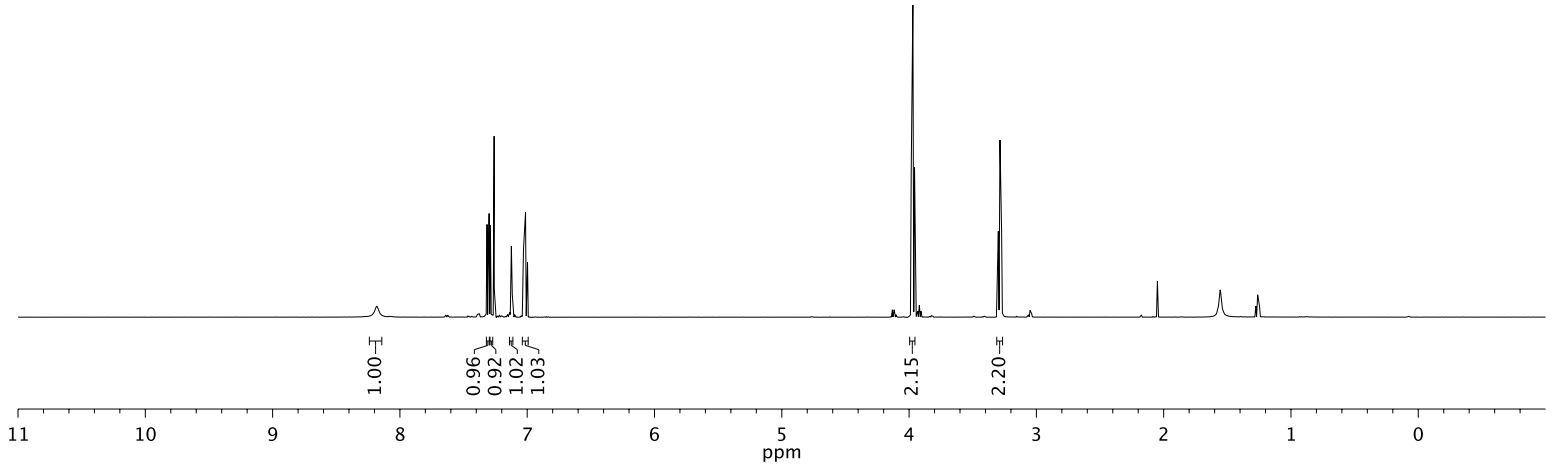


^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-1**.

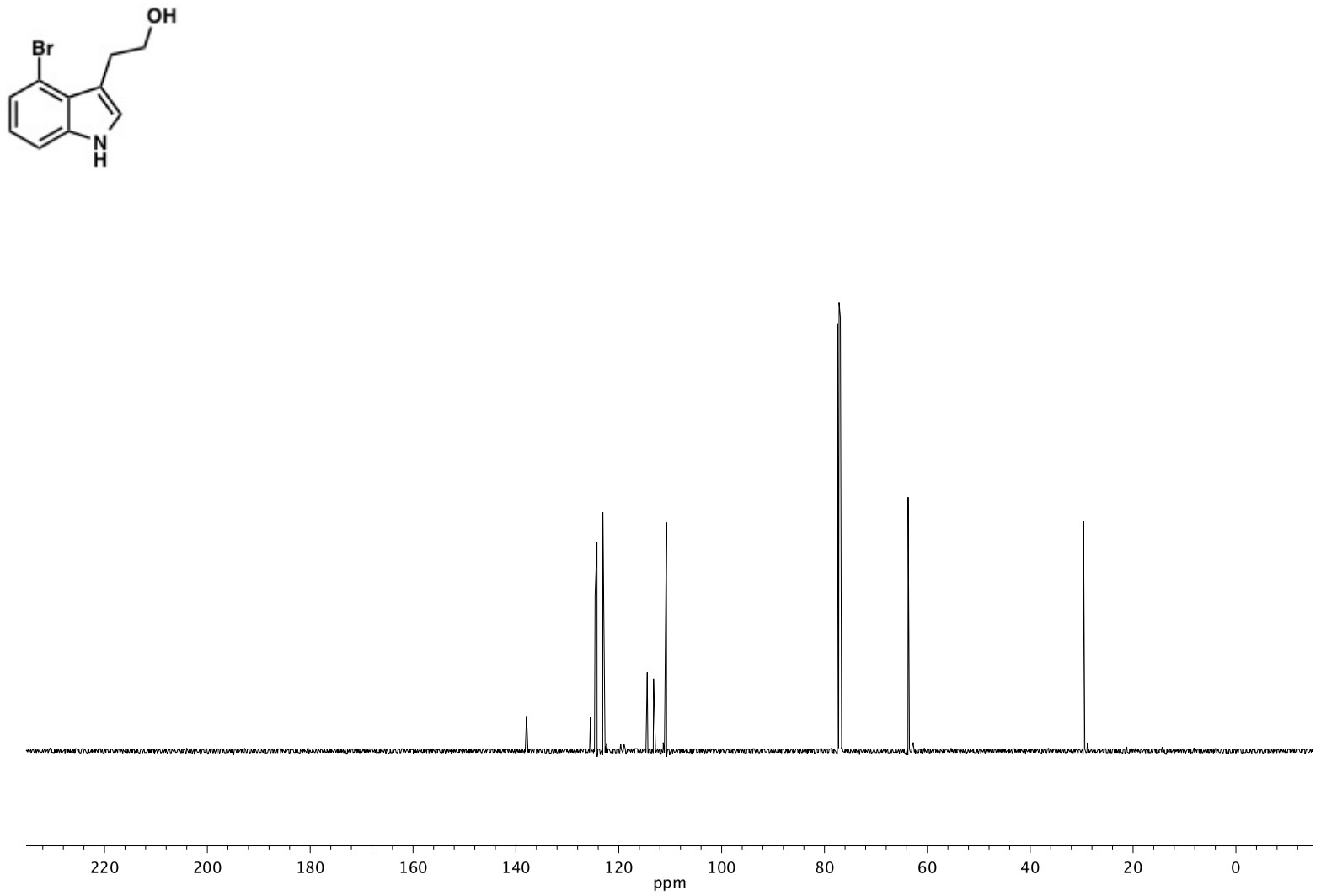


^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-1**.

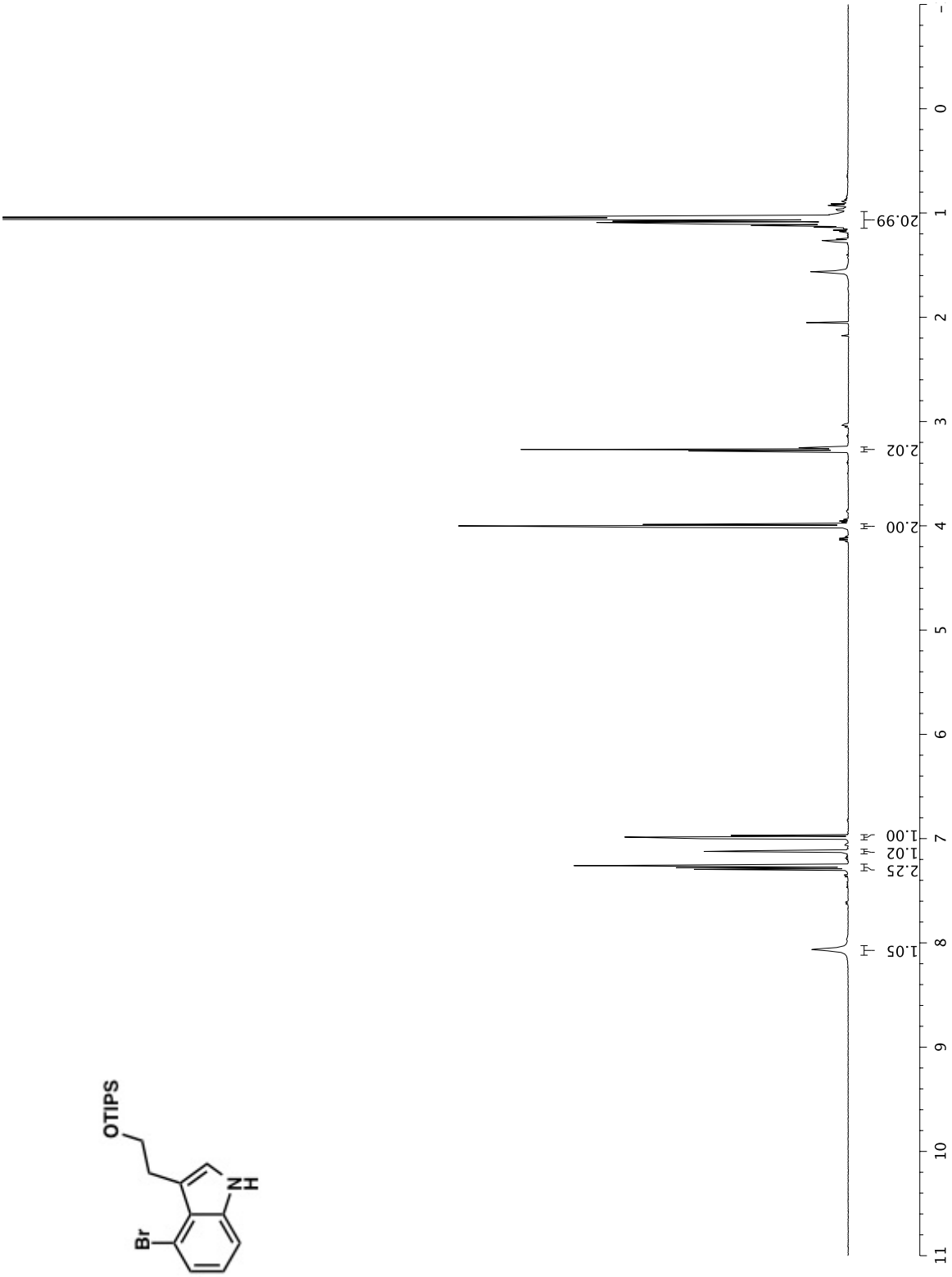




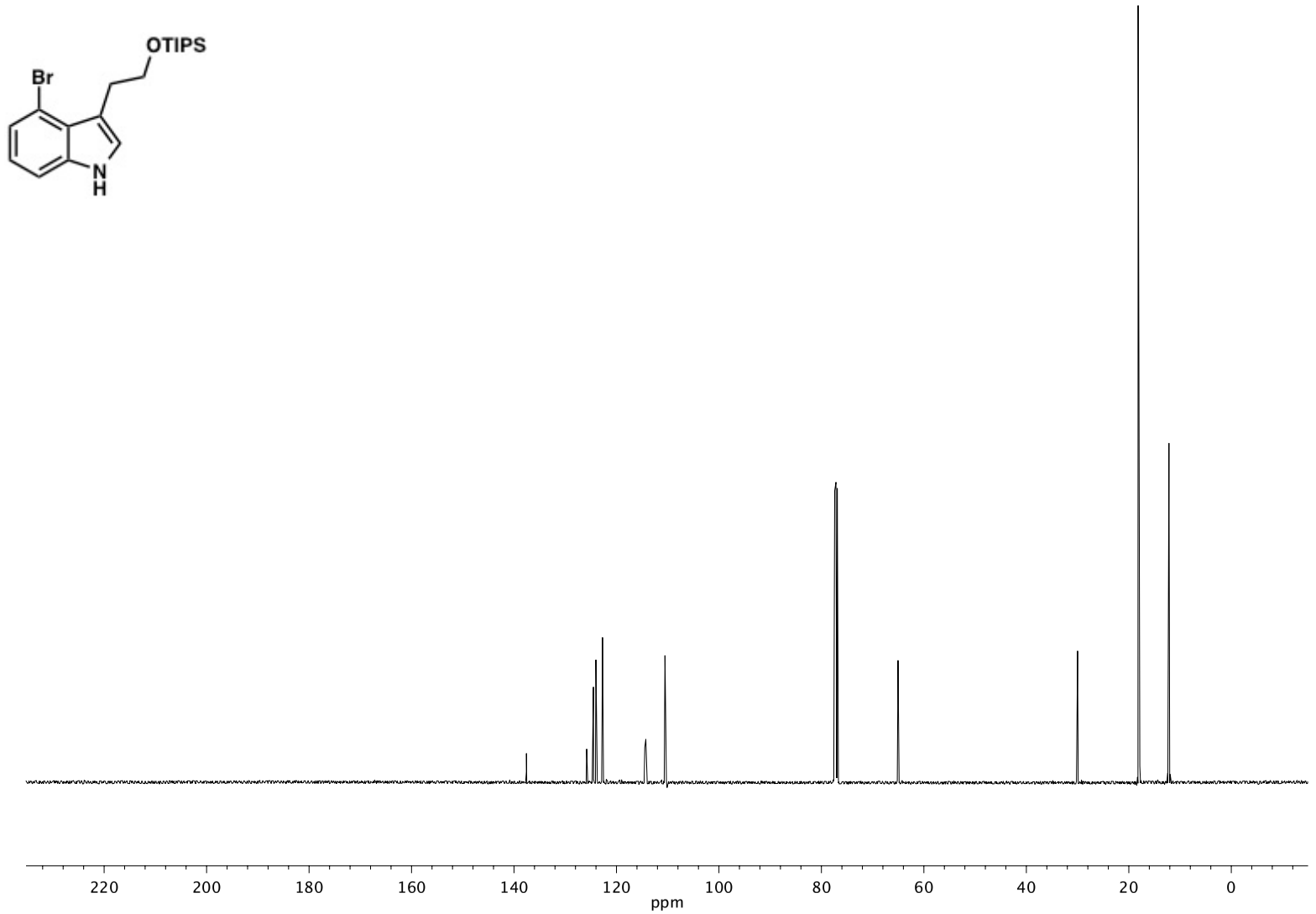
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-2**.



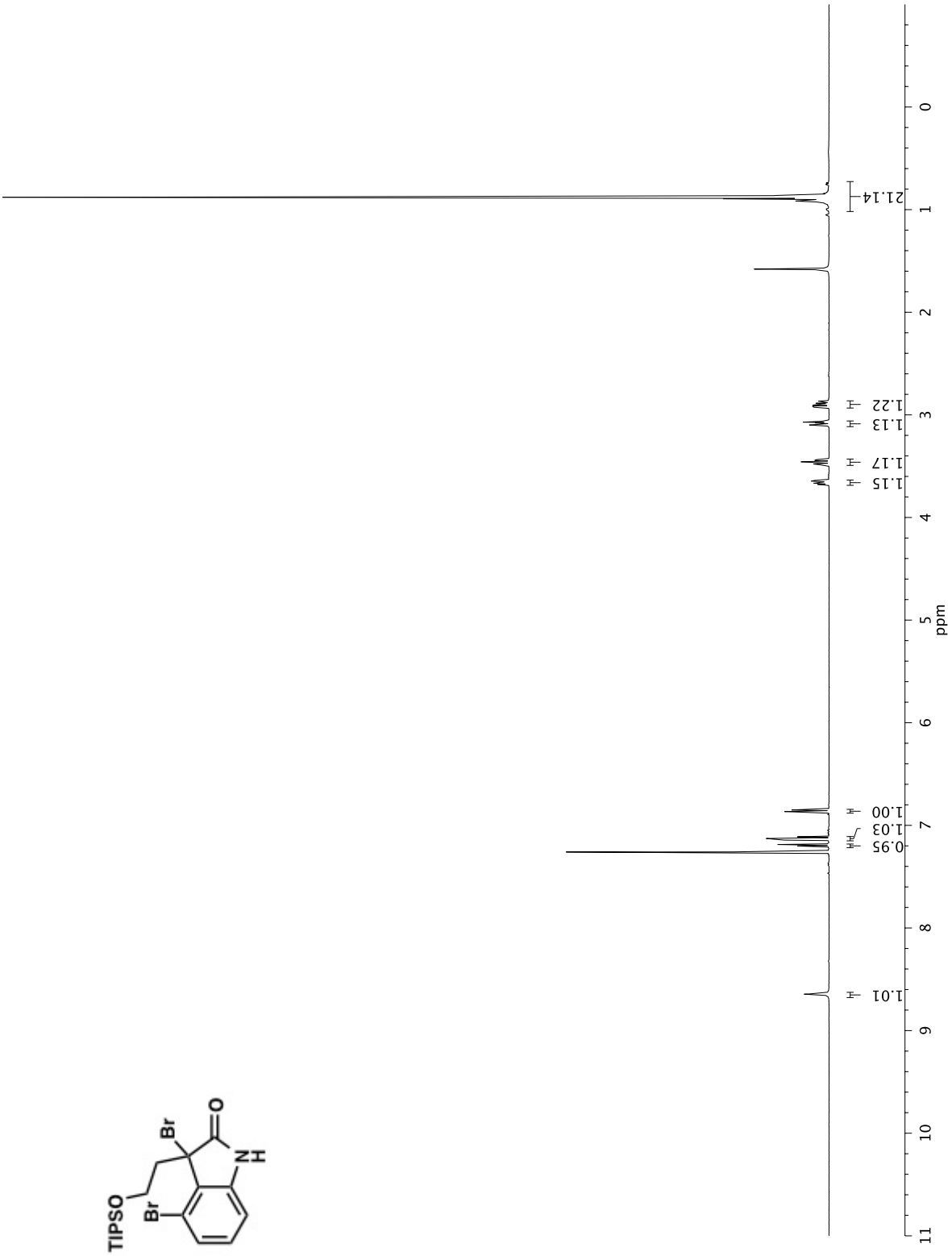
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-2**.



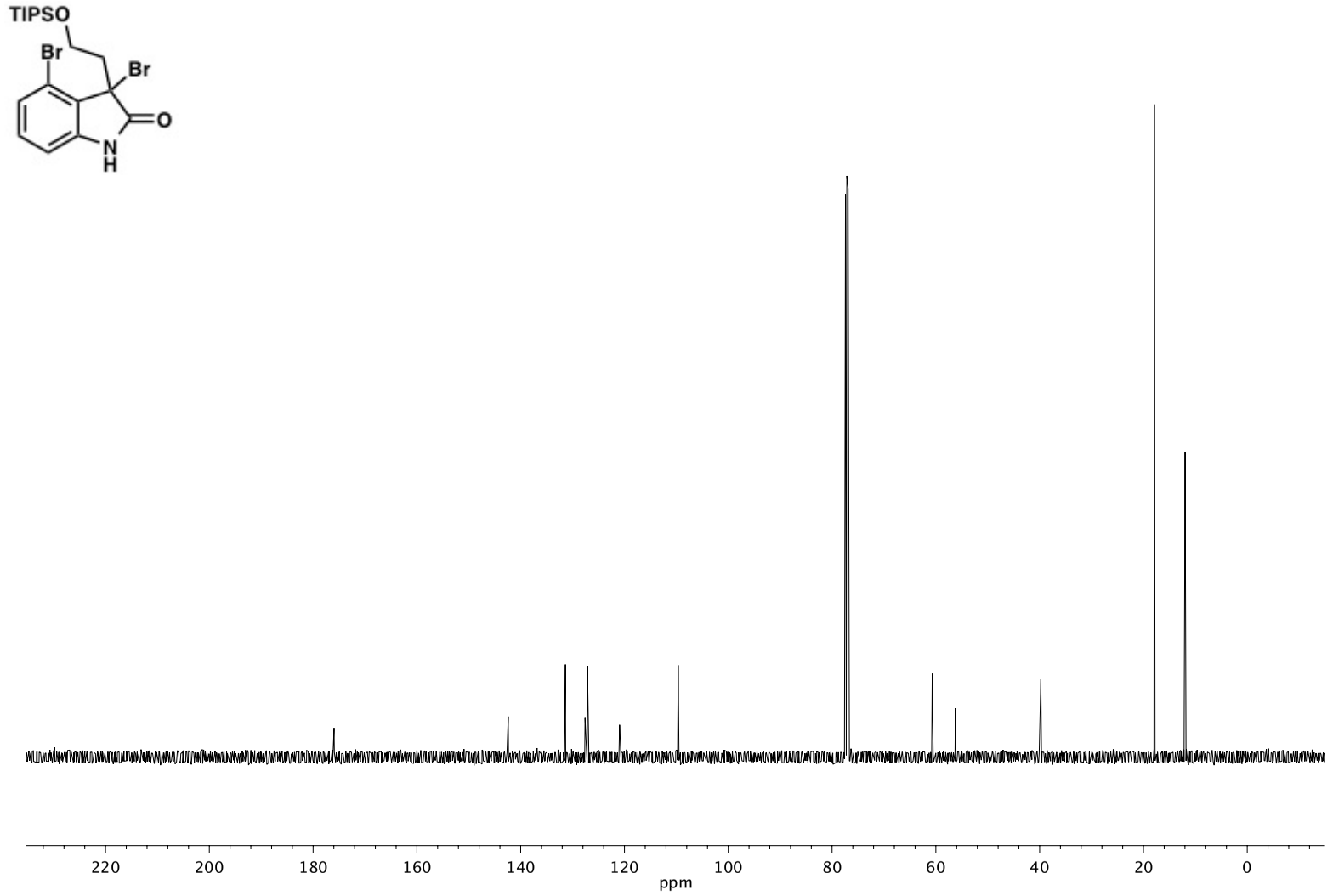
^{1}H NMR (500 MHz, $CDCl_3$) of compound **10**.



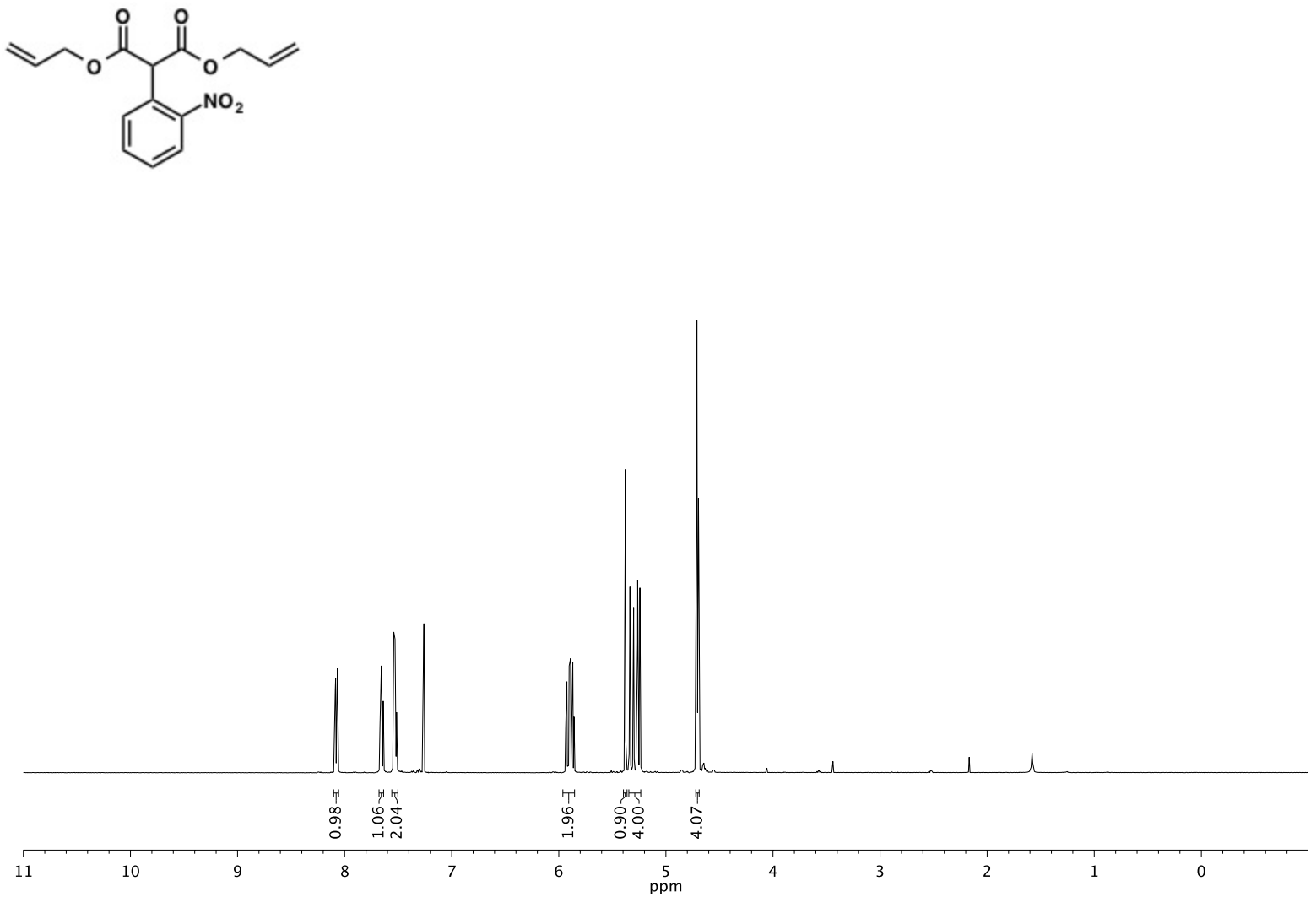
^{13}C NMR (125 MHz, $CDCl_3$) of compound **10.**



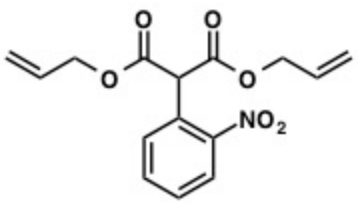
^{1}HNMR (500 MHz, $CDCl_3$) of compound **7.**

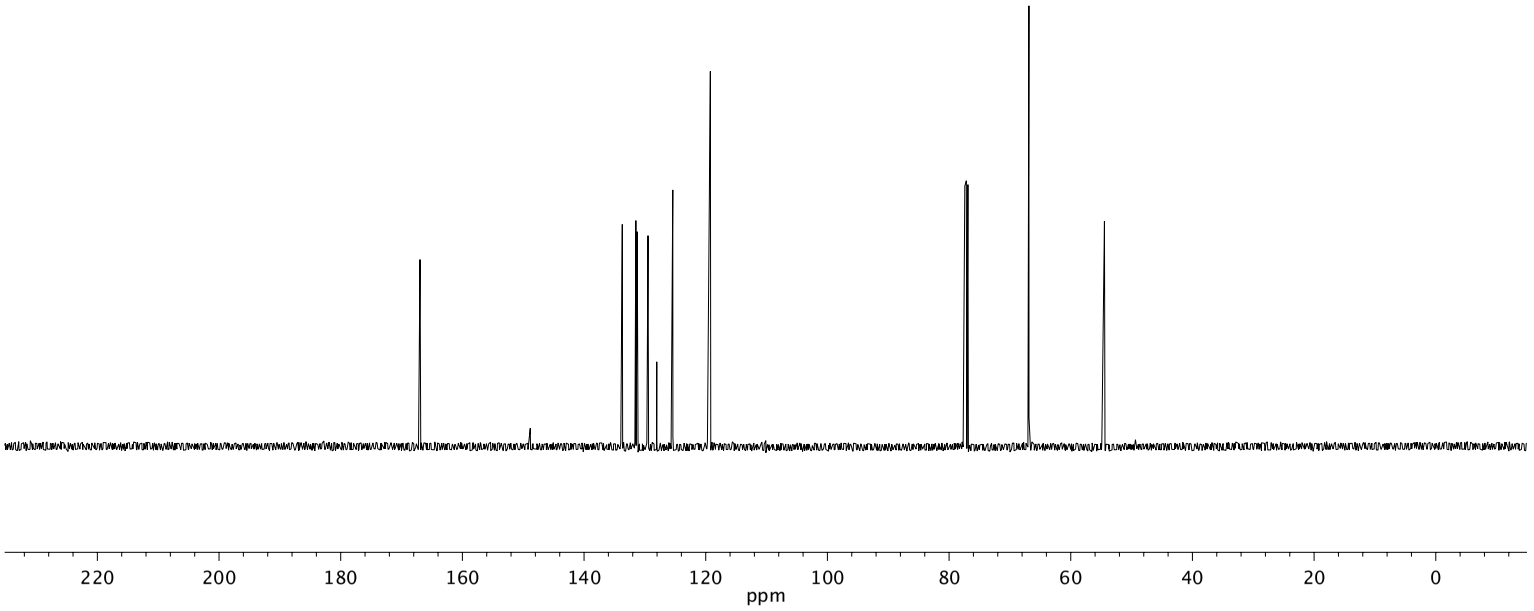


^{13}C NMR (125 MHz, $CDCl_3$) of compound **7.**

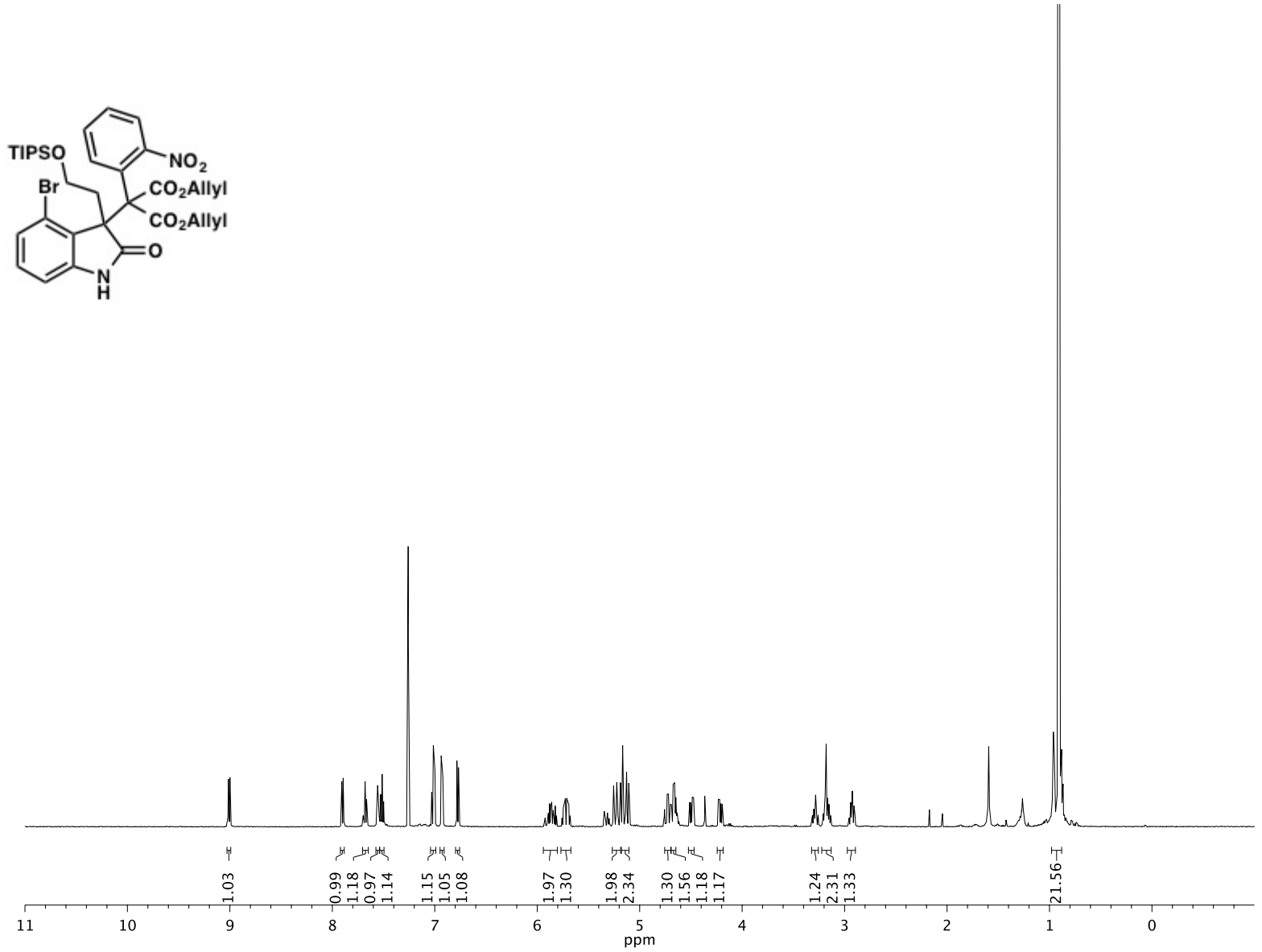


^{1}H NMR (500 MHz, $CDCl_3$) of compound **8**.

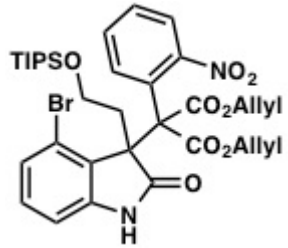


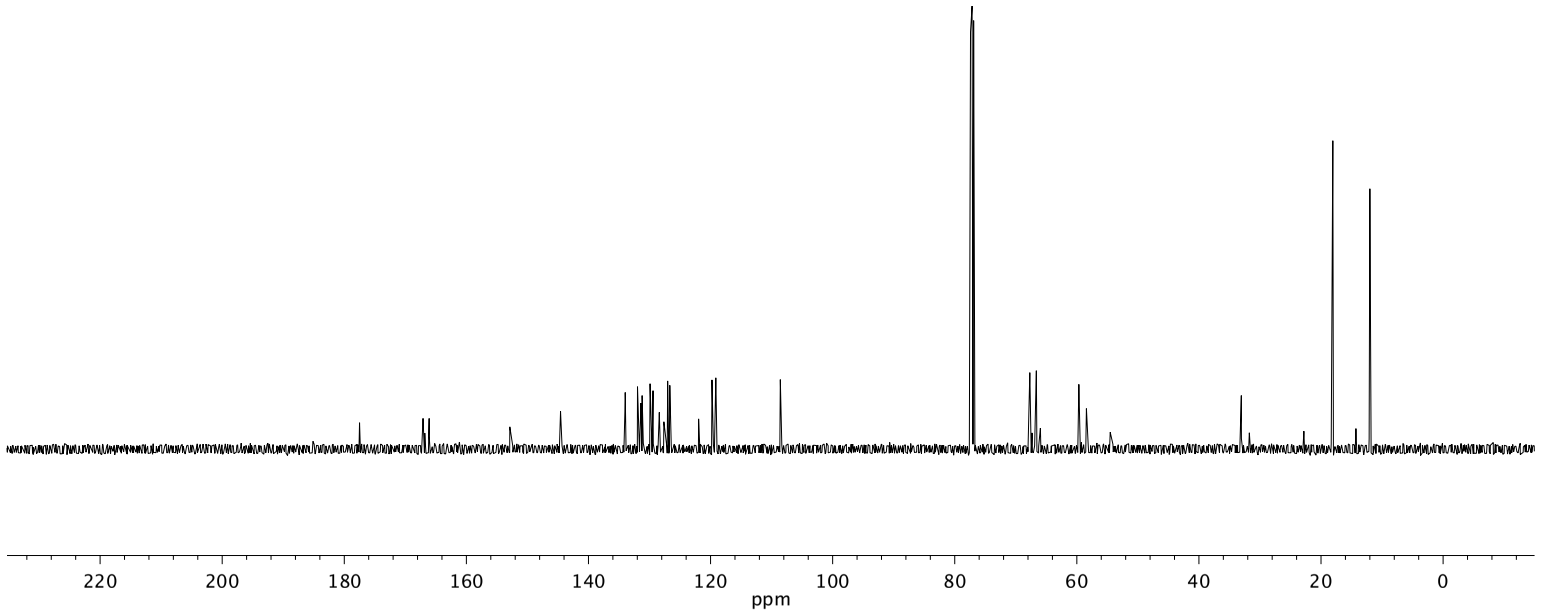


^{13}C NMR (125 MHz, $CDCl_3$) of compound **8**.

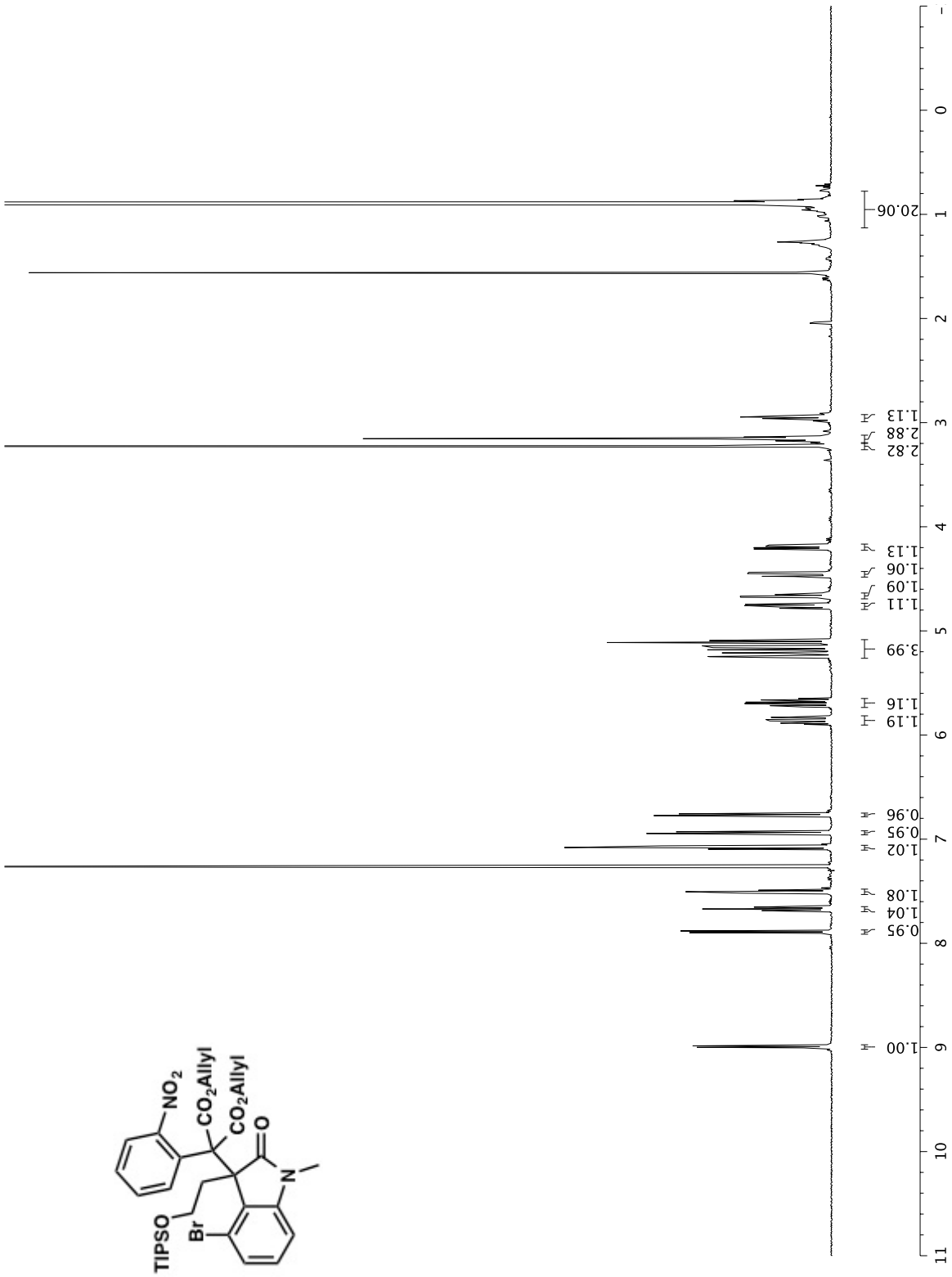


^{1}H NMR (500 MHz, $CDCl_3$) of compound **5.**

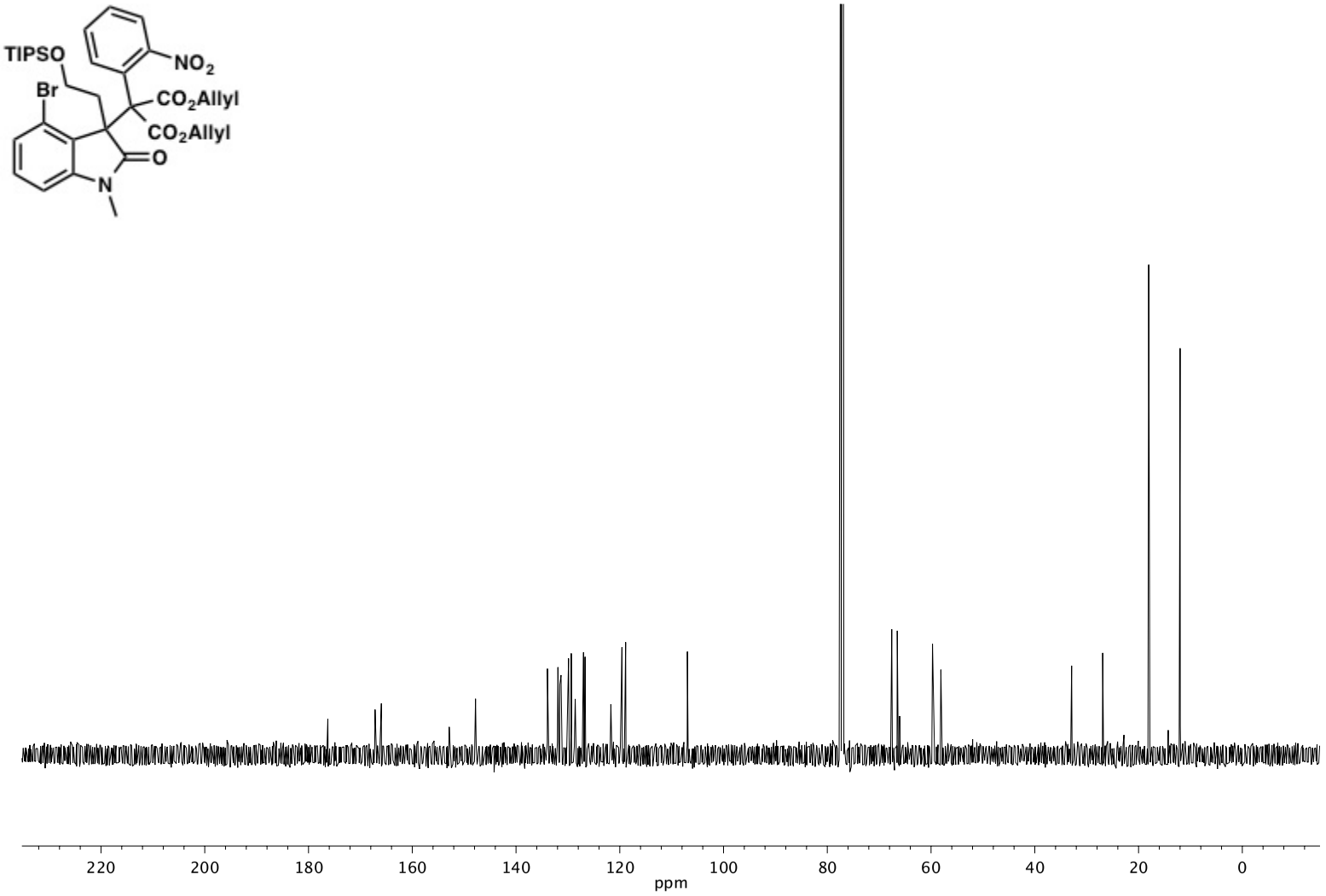




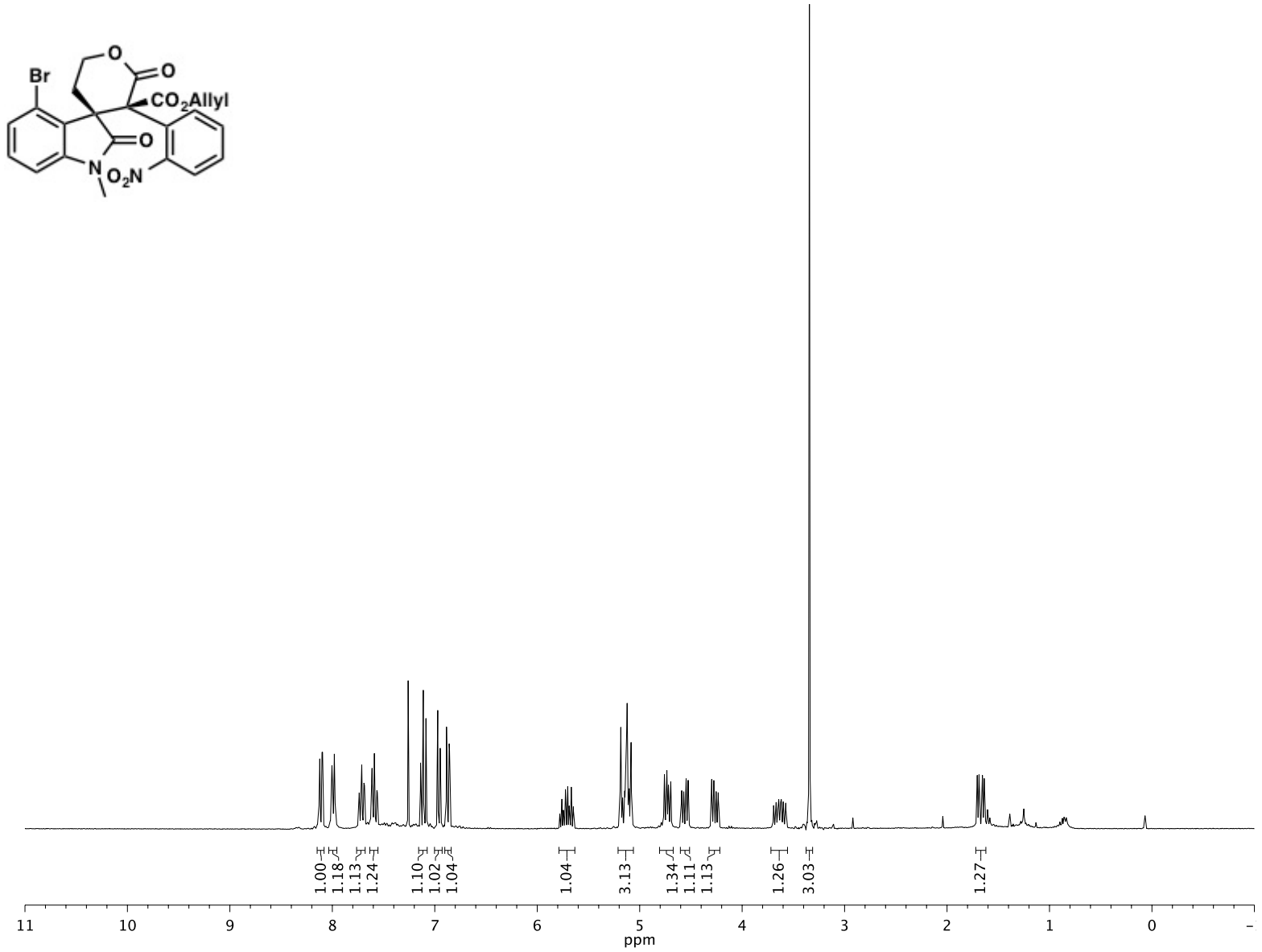
^{13}C NMR (125 MHz, $CDCl_3$) of compound **5.**



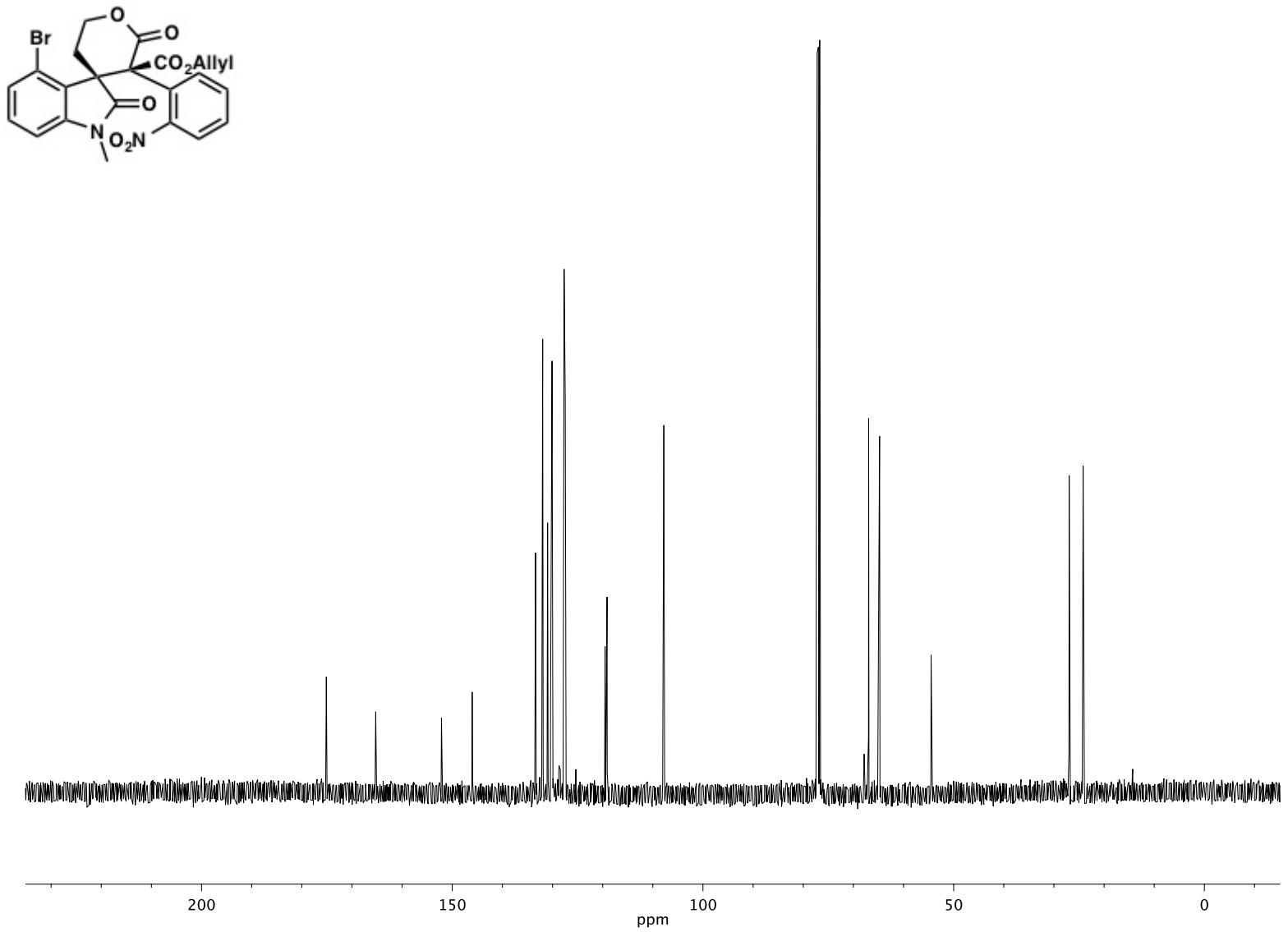
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-4.**



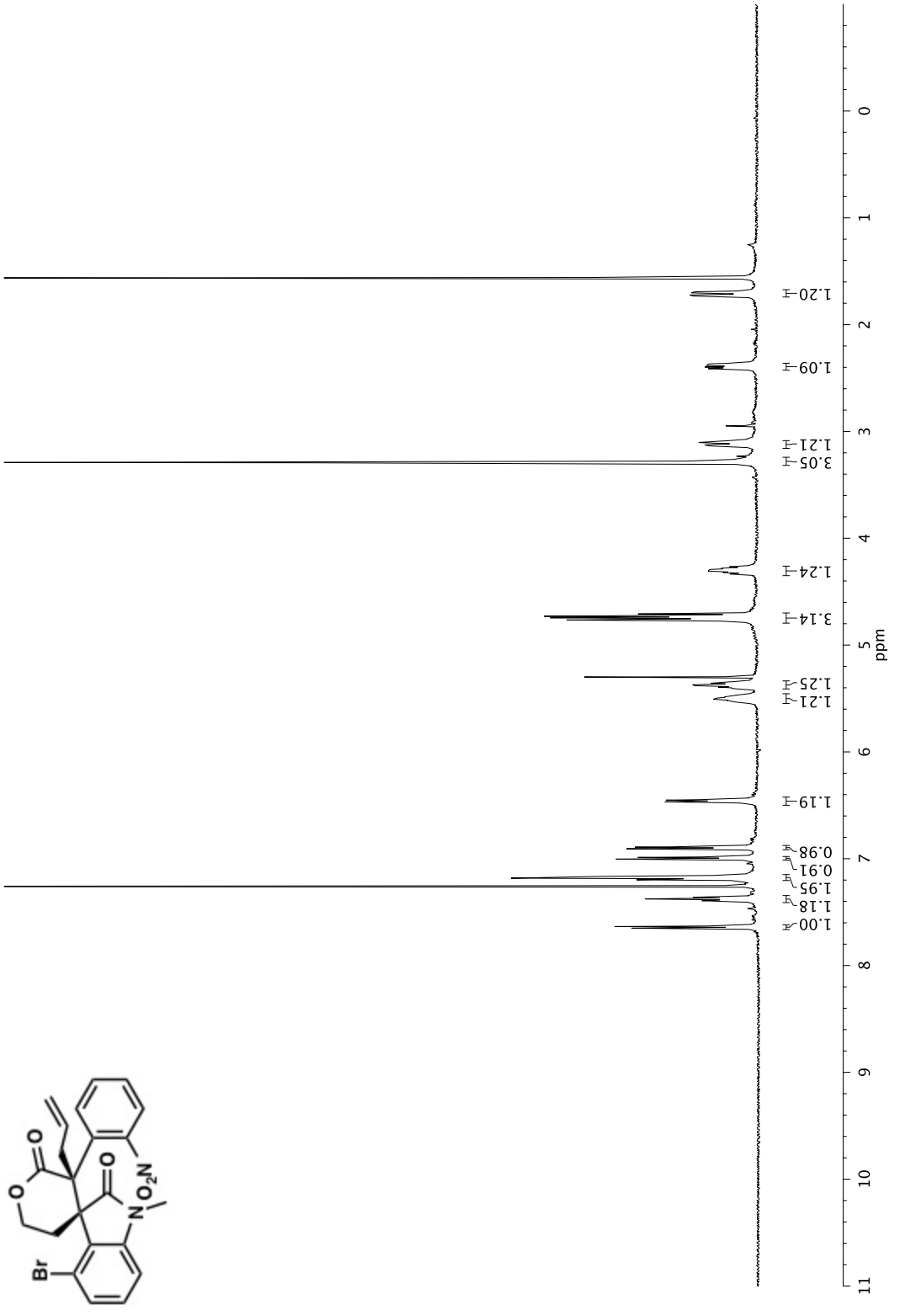
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-4.**



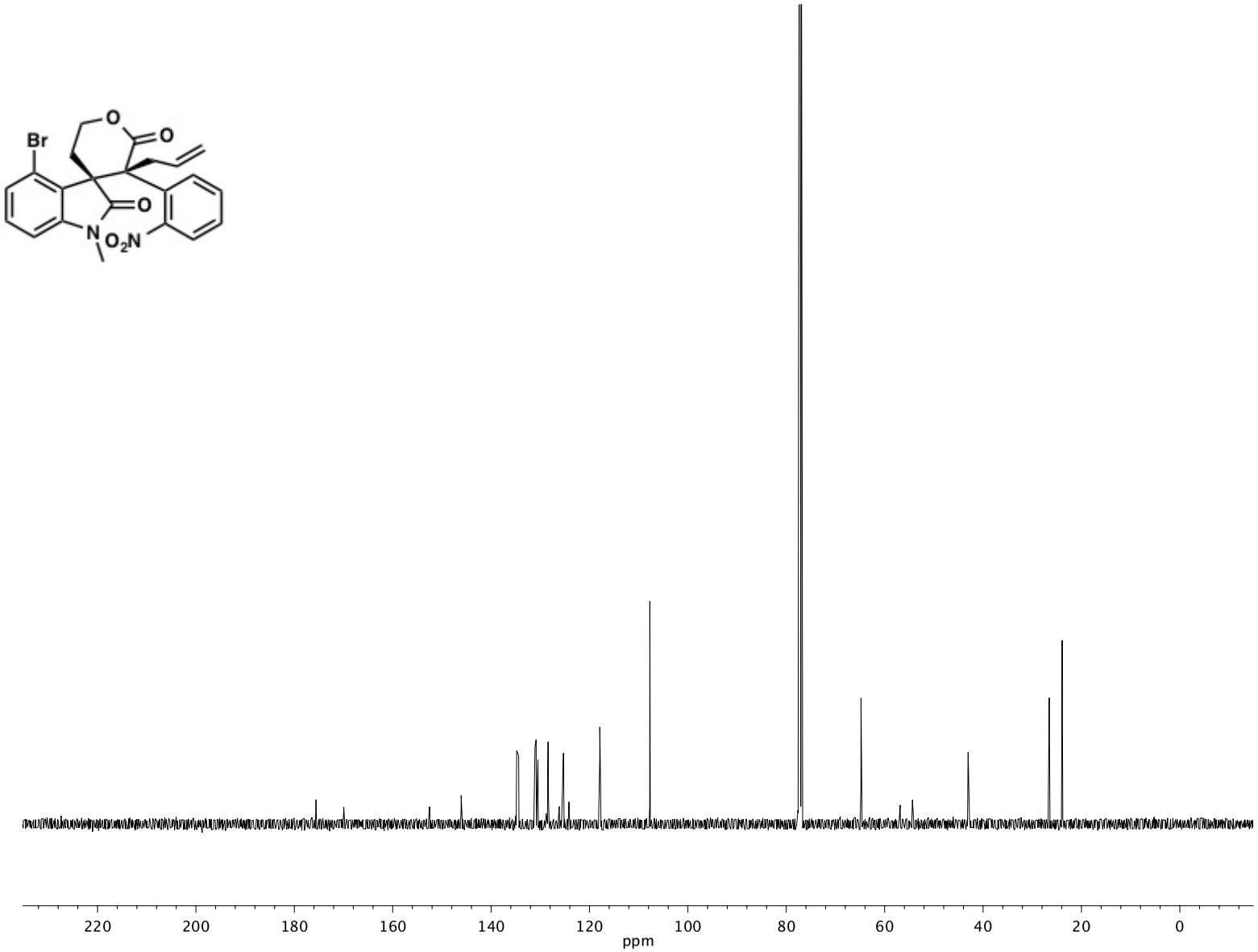
^{1}H NMR (300 MHz, $CDCl_3$) of compound **11.**



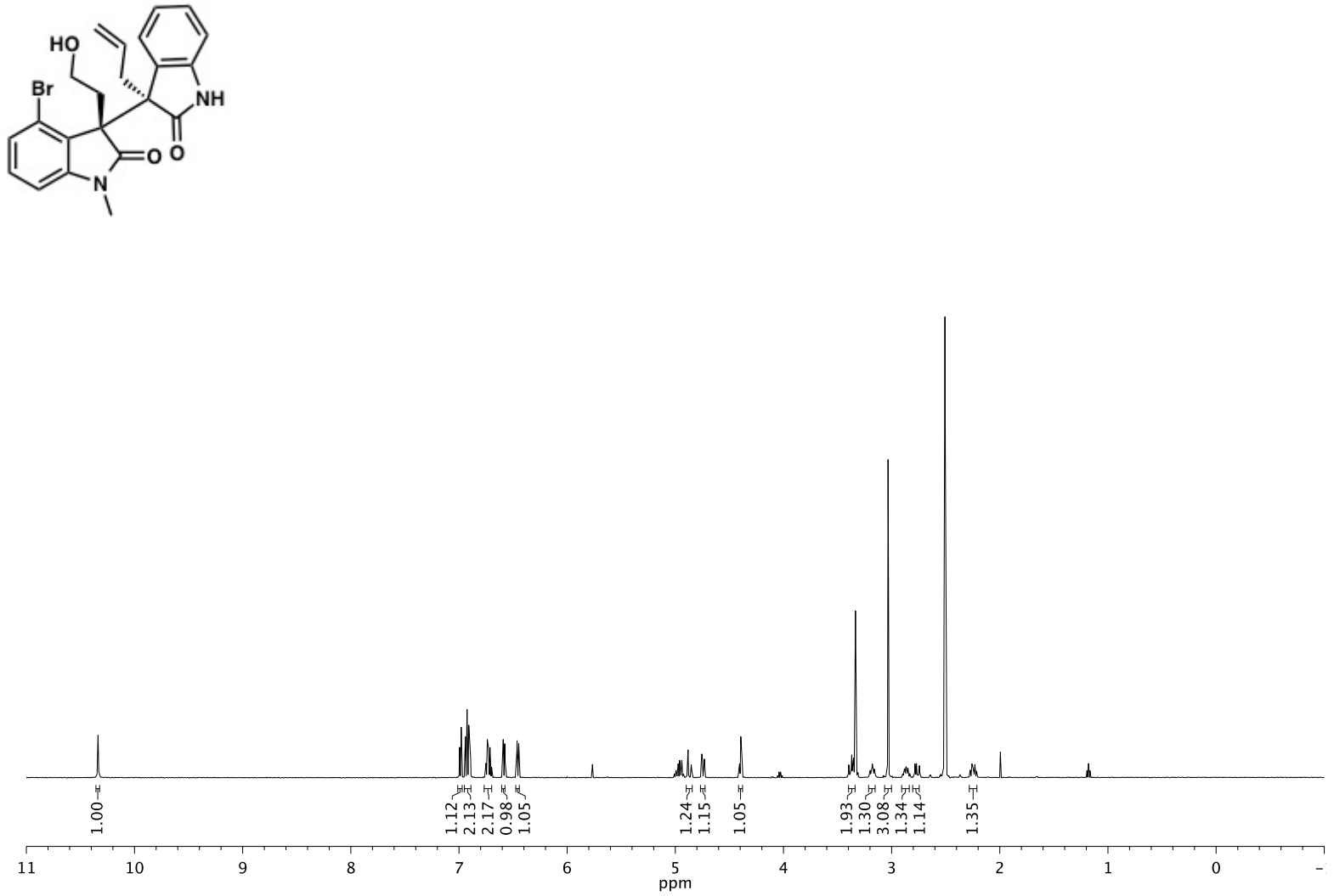
^{13}C NMR (125 MHz, $CDCl_3$) of compound **11.**



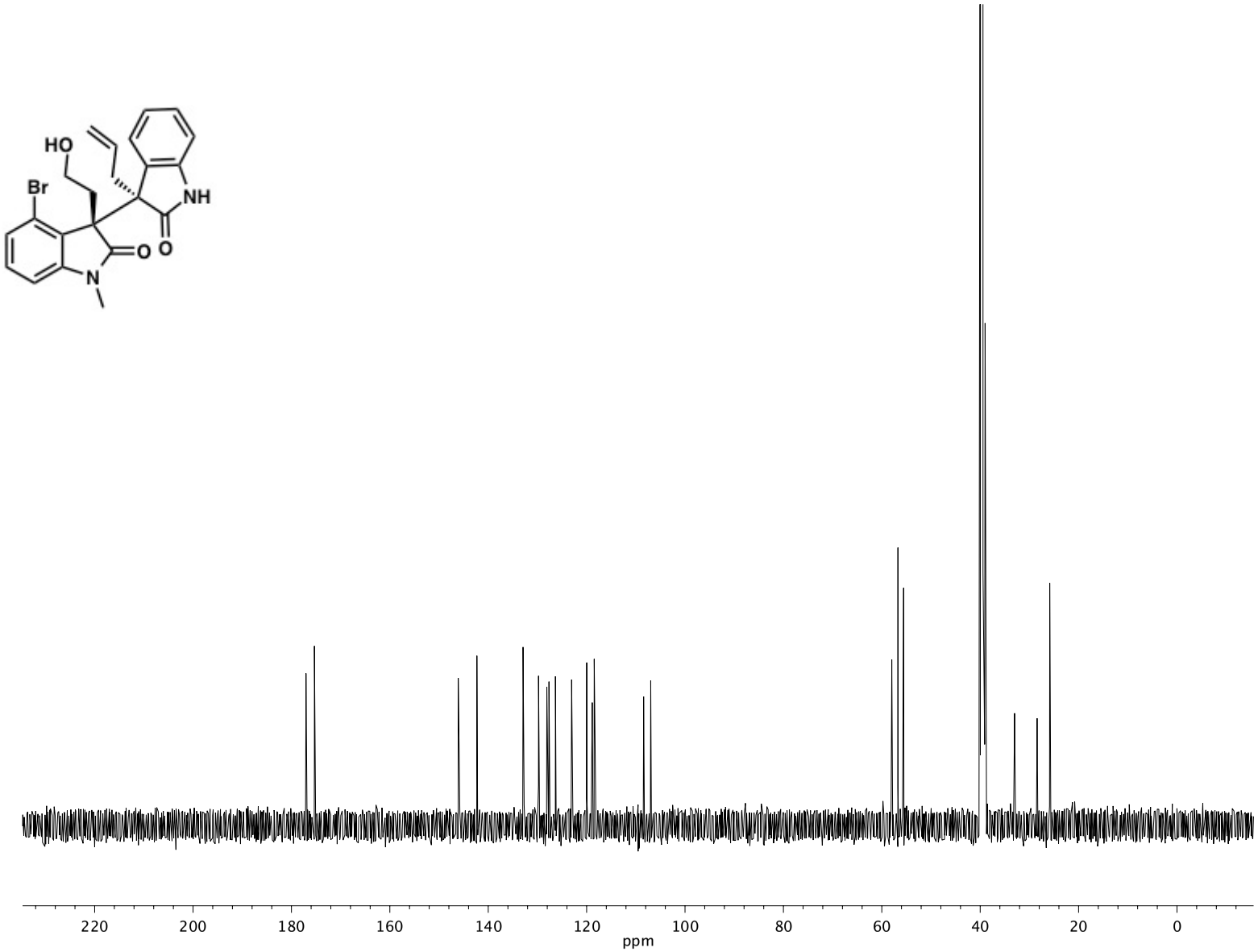
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4.**



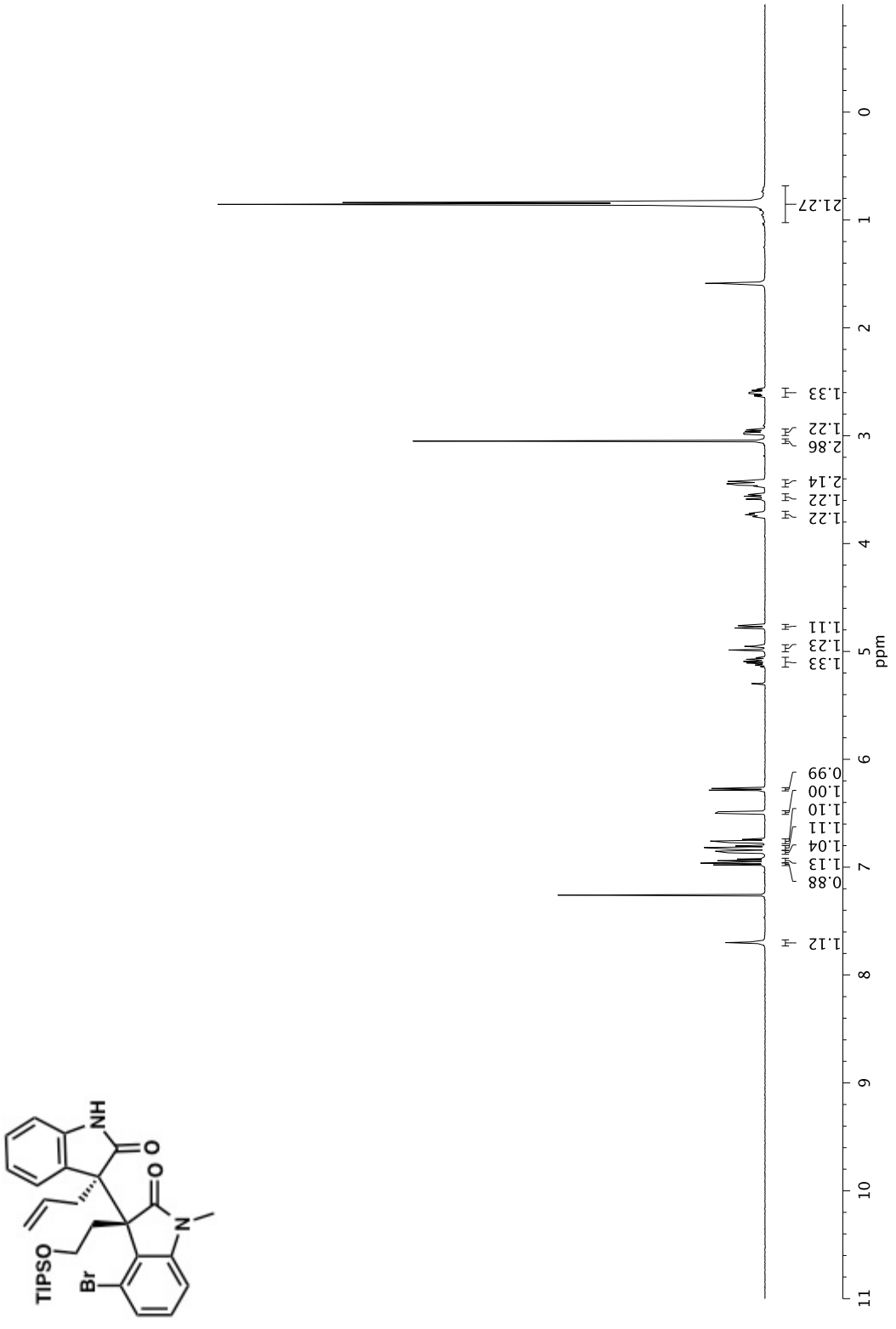
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4.**



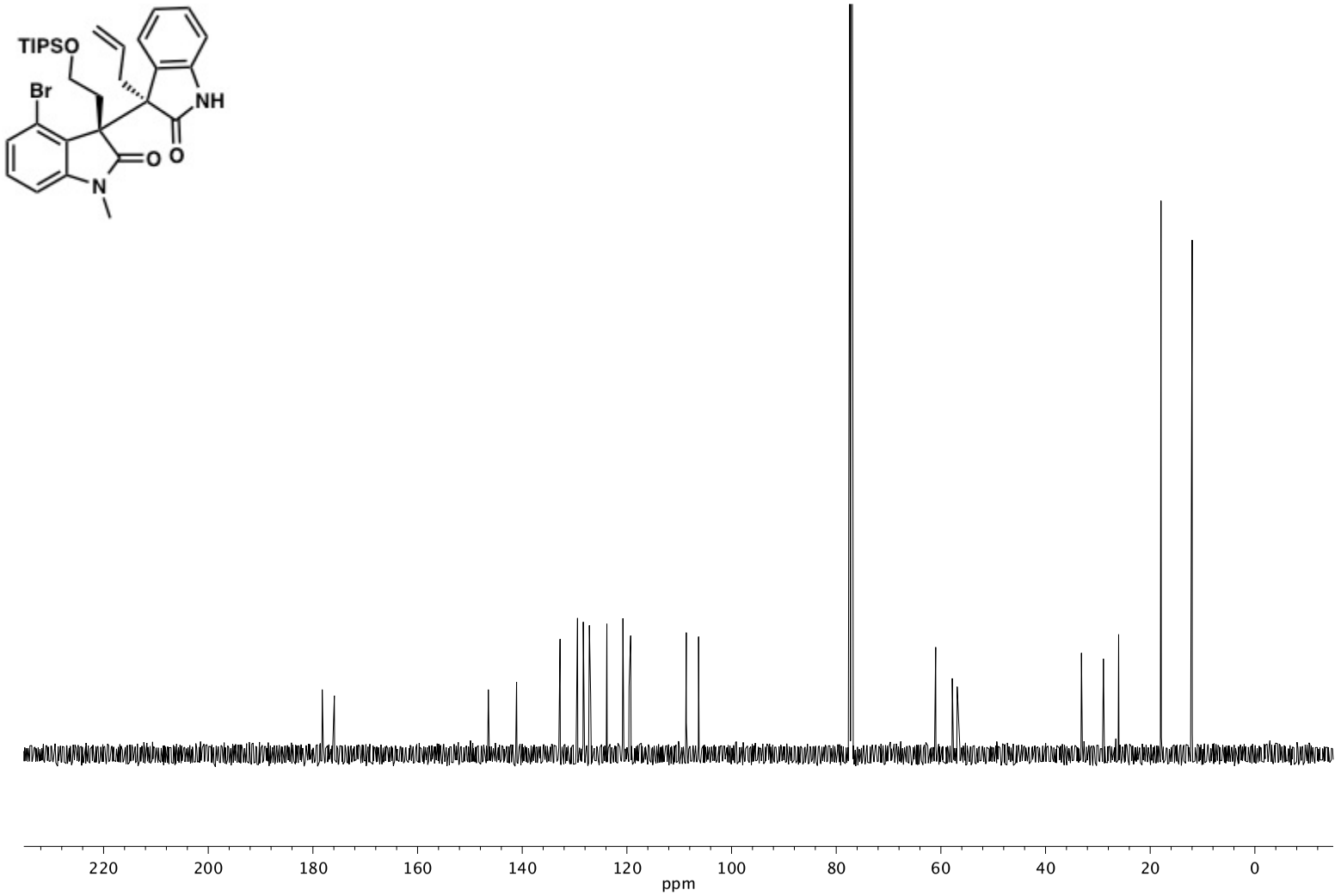
^{1}H NMR (500 MHz, DMSO) of compound **12.**



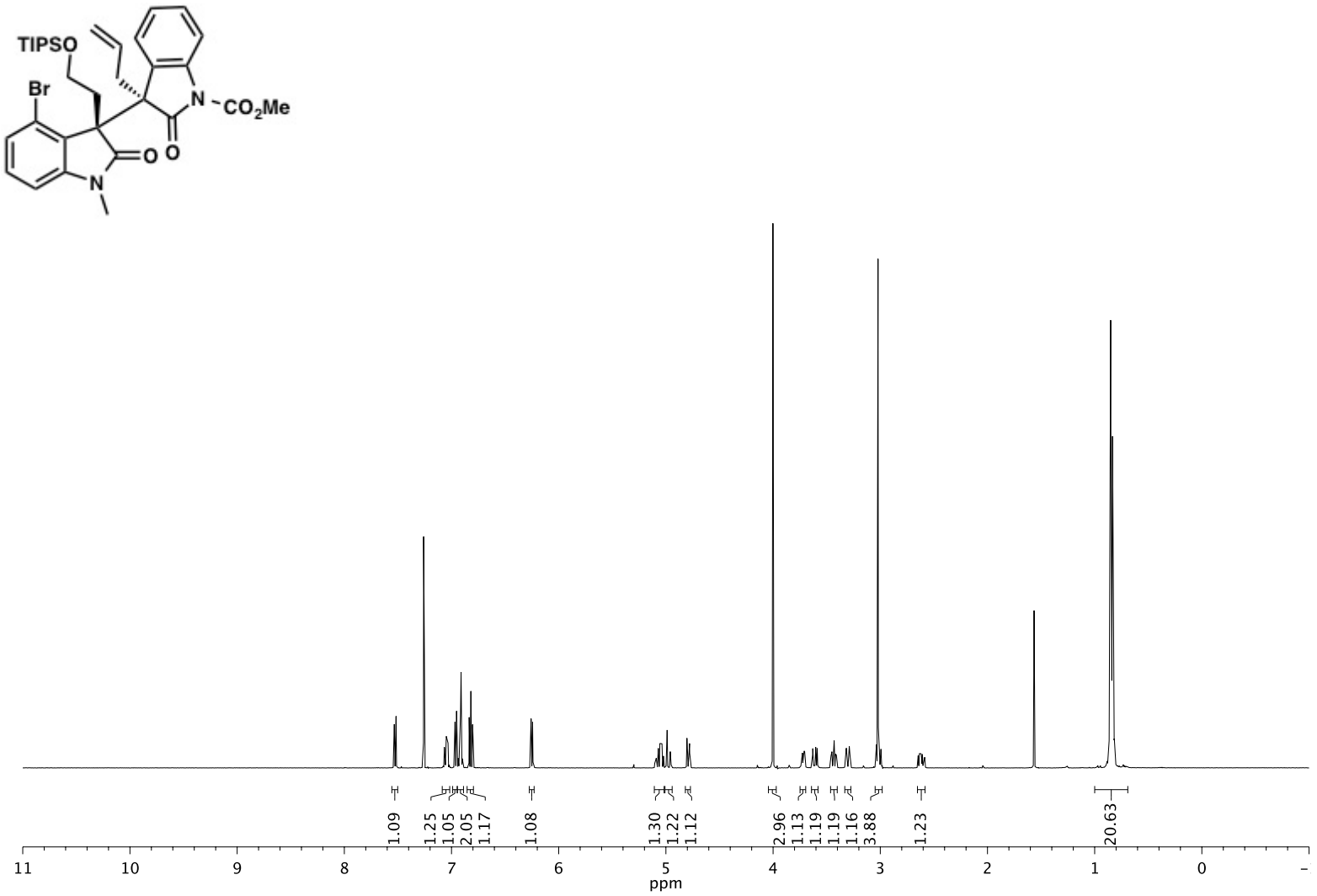
^{13}C NMR (125 MHz, DMSO) of compound **12.**



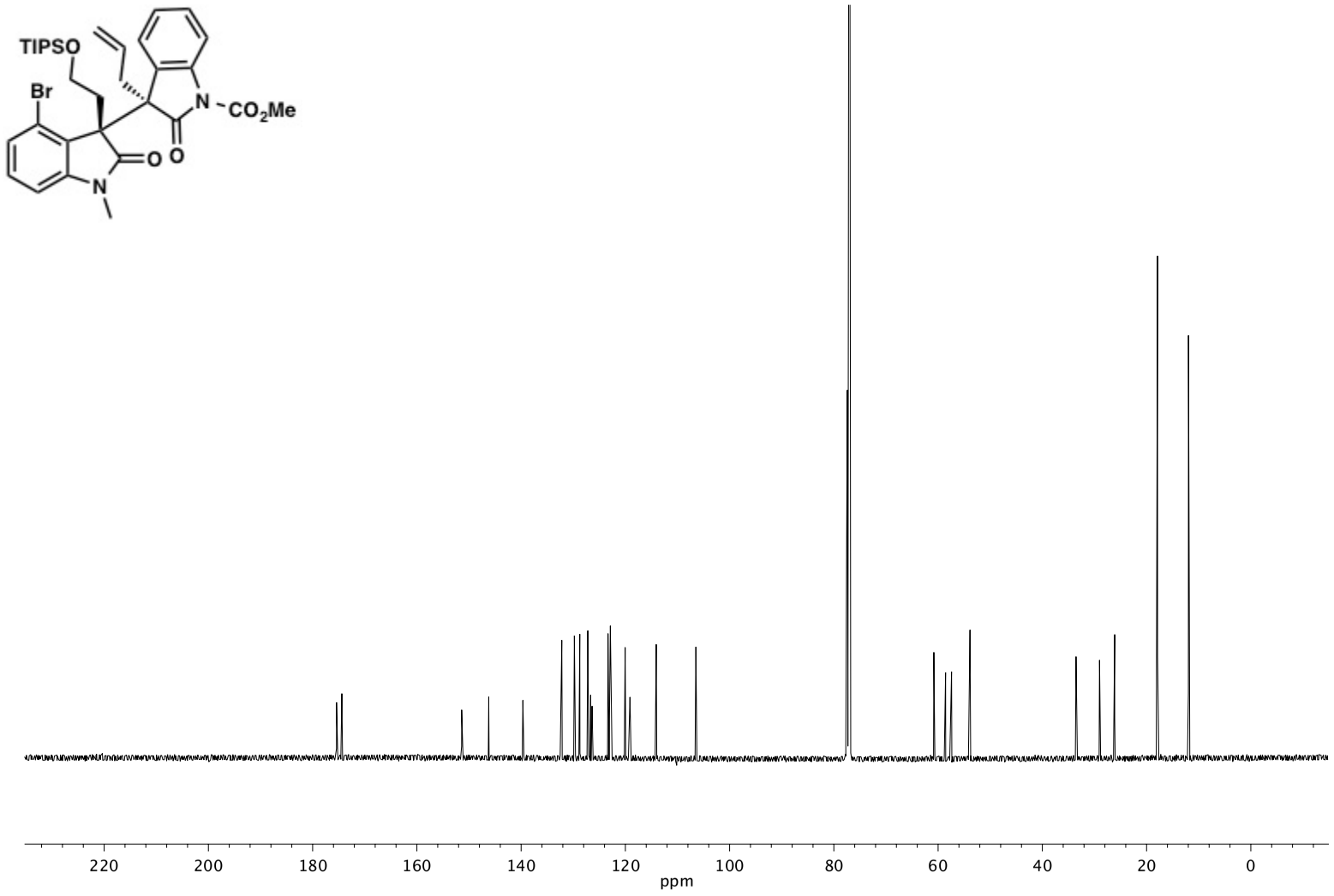
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-5.**



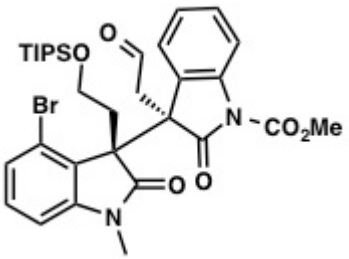
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-5.**

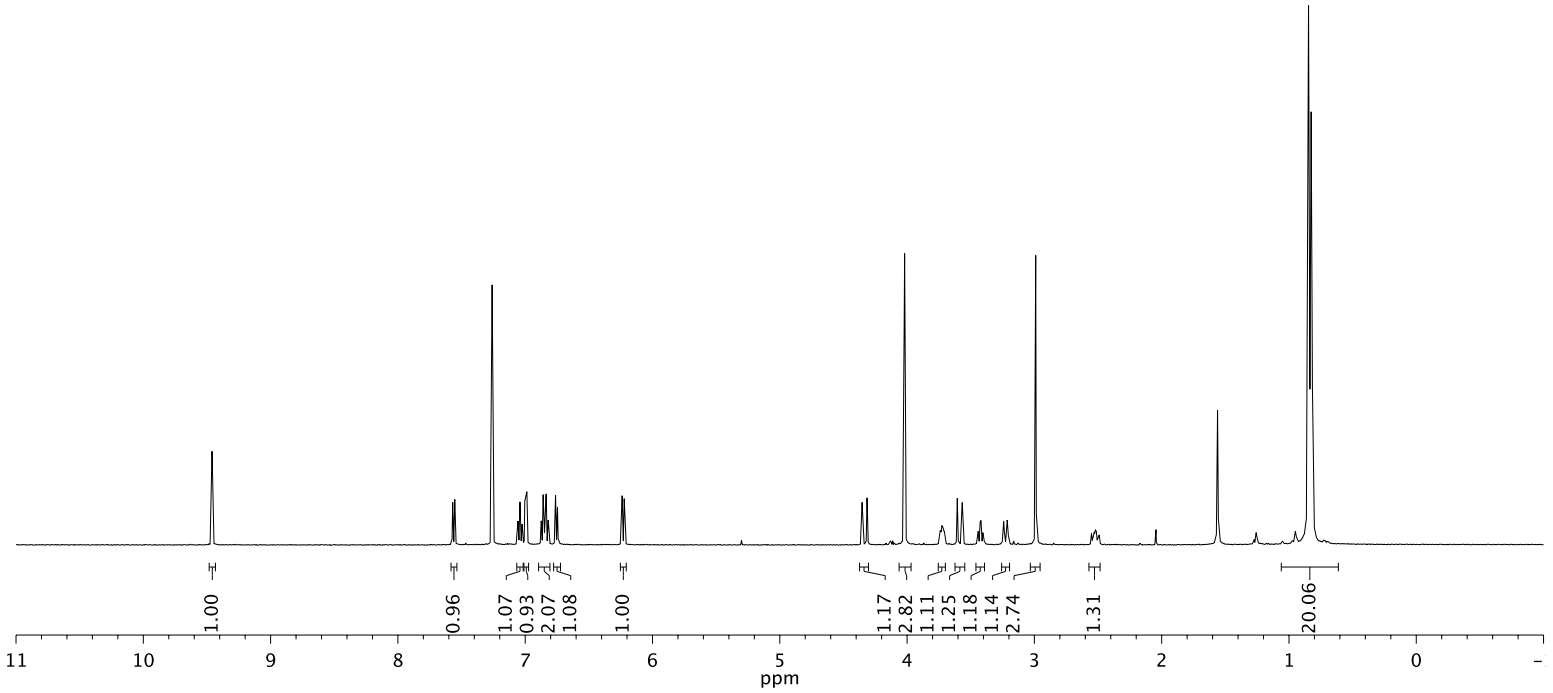


^{1}H NMR (500 MHz, $CDCl_3$) of compound **13.**

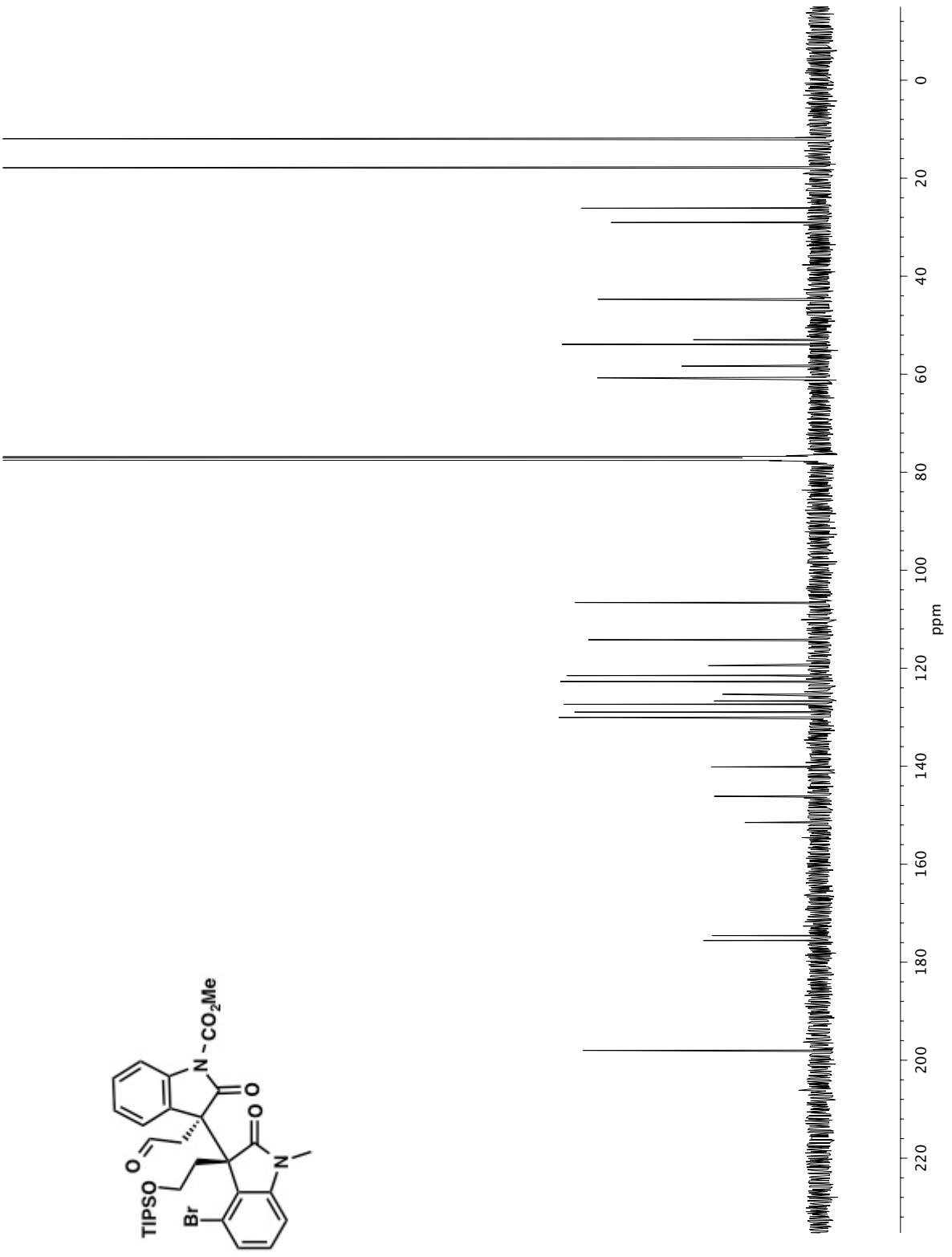


^{13}C NMR (125 MHz, $CDCl_3$) of compound **13.**

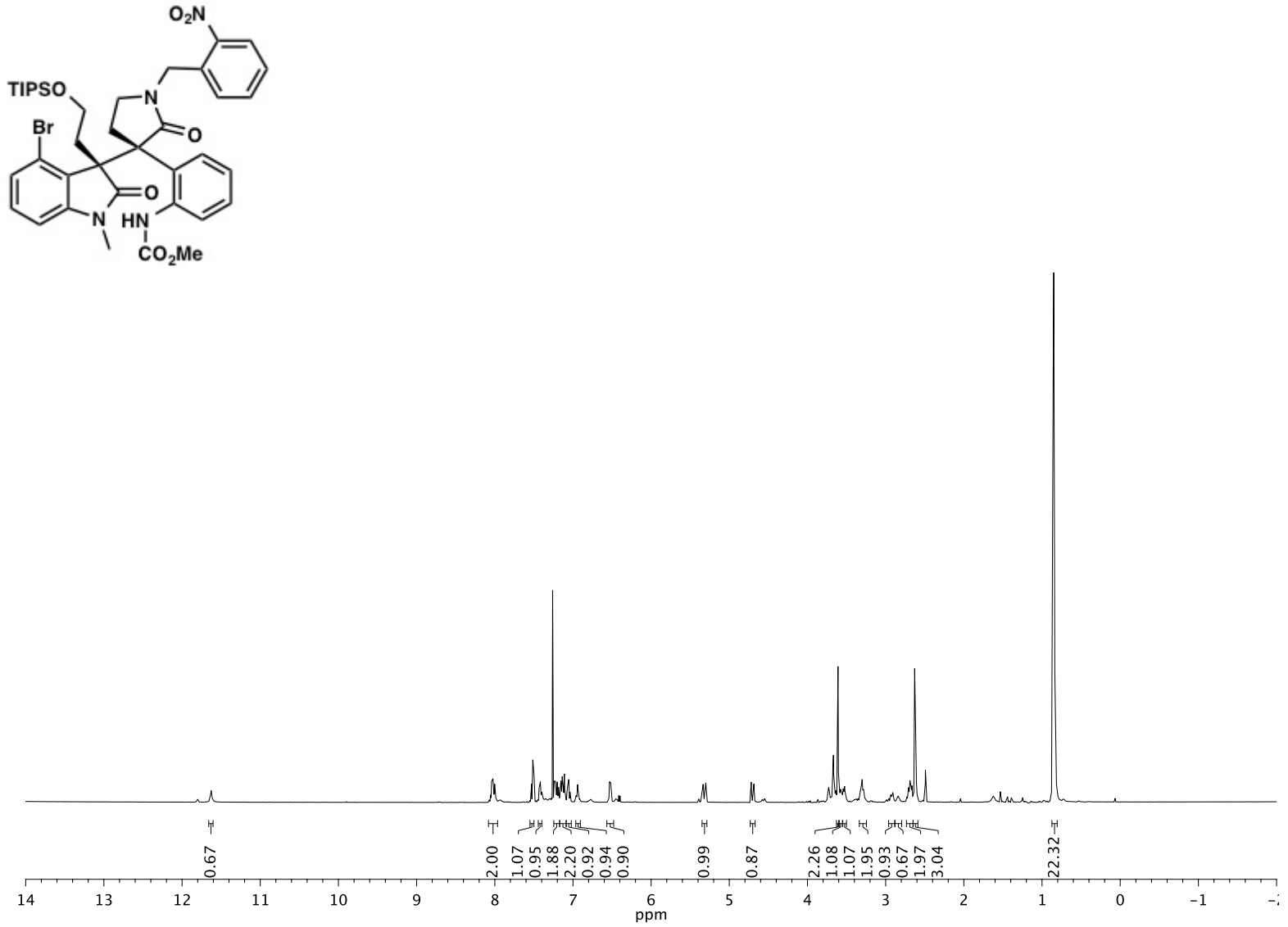




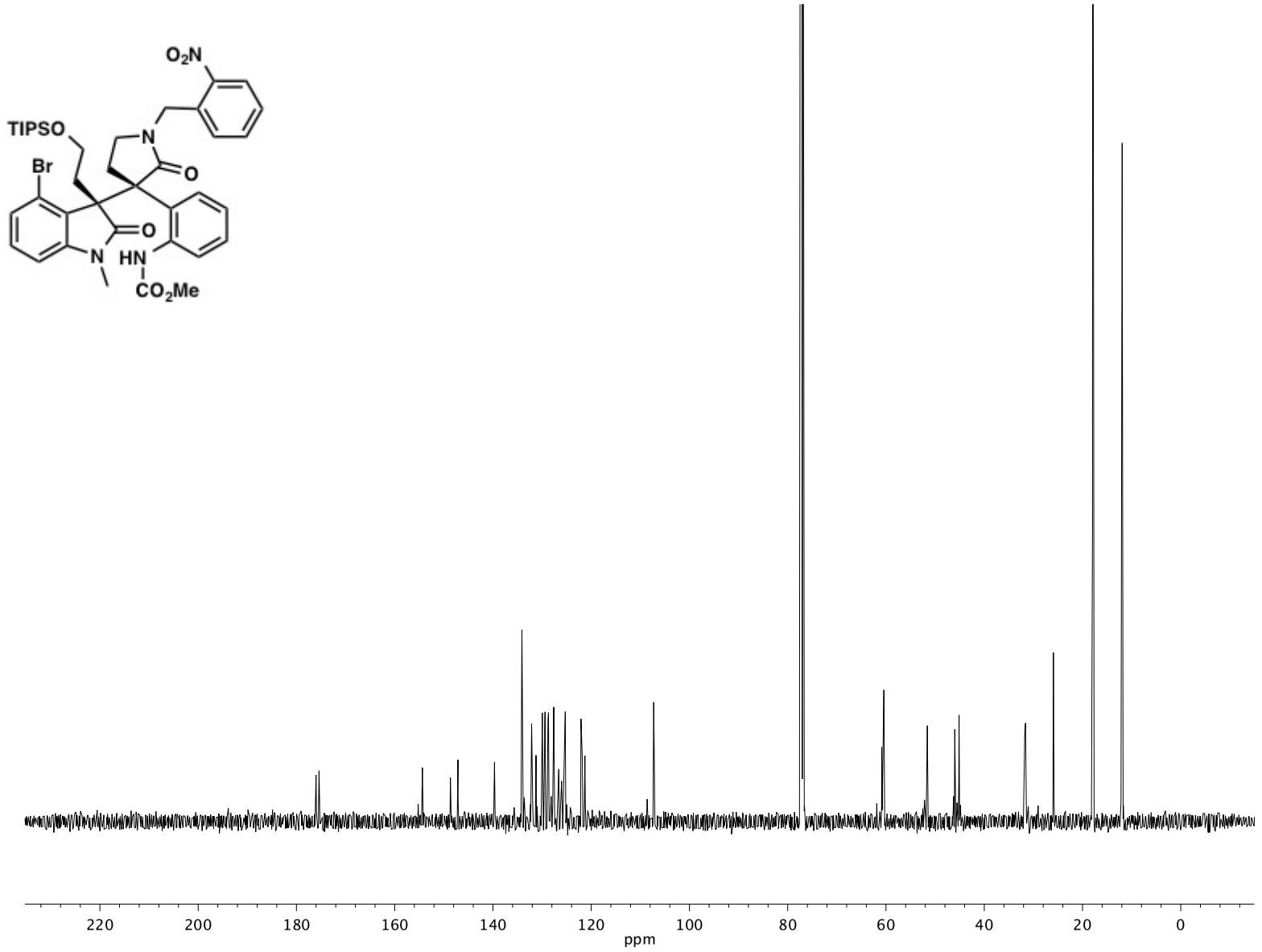
^{1}H NMR (500 MHz, $CDCl_3$) of compound **14.**



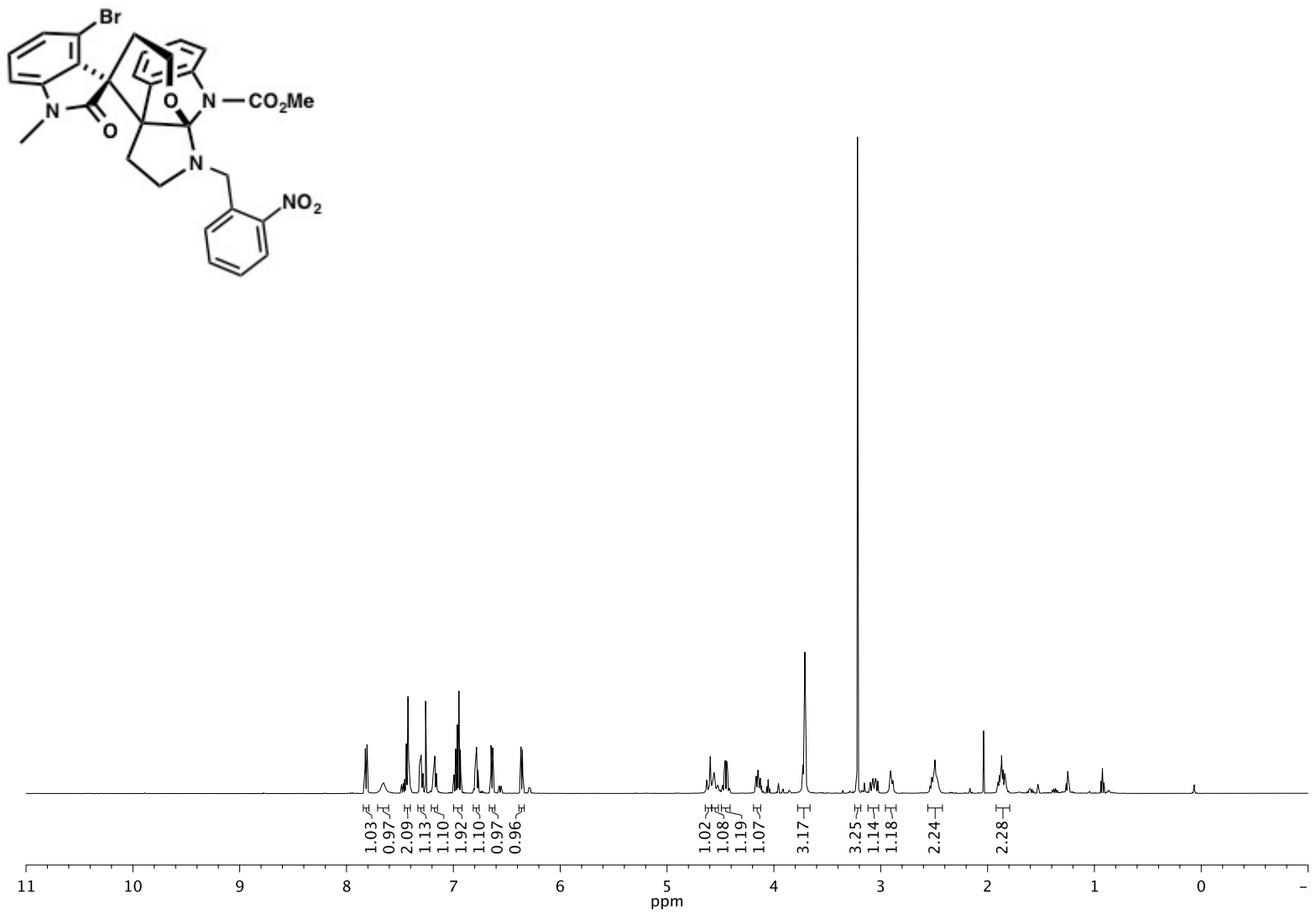
^{13}C NMR (125 MHz, $CDCl_3$) of compound **14.**



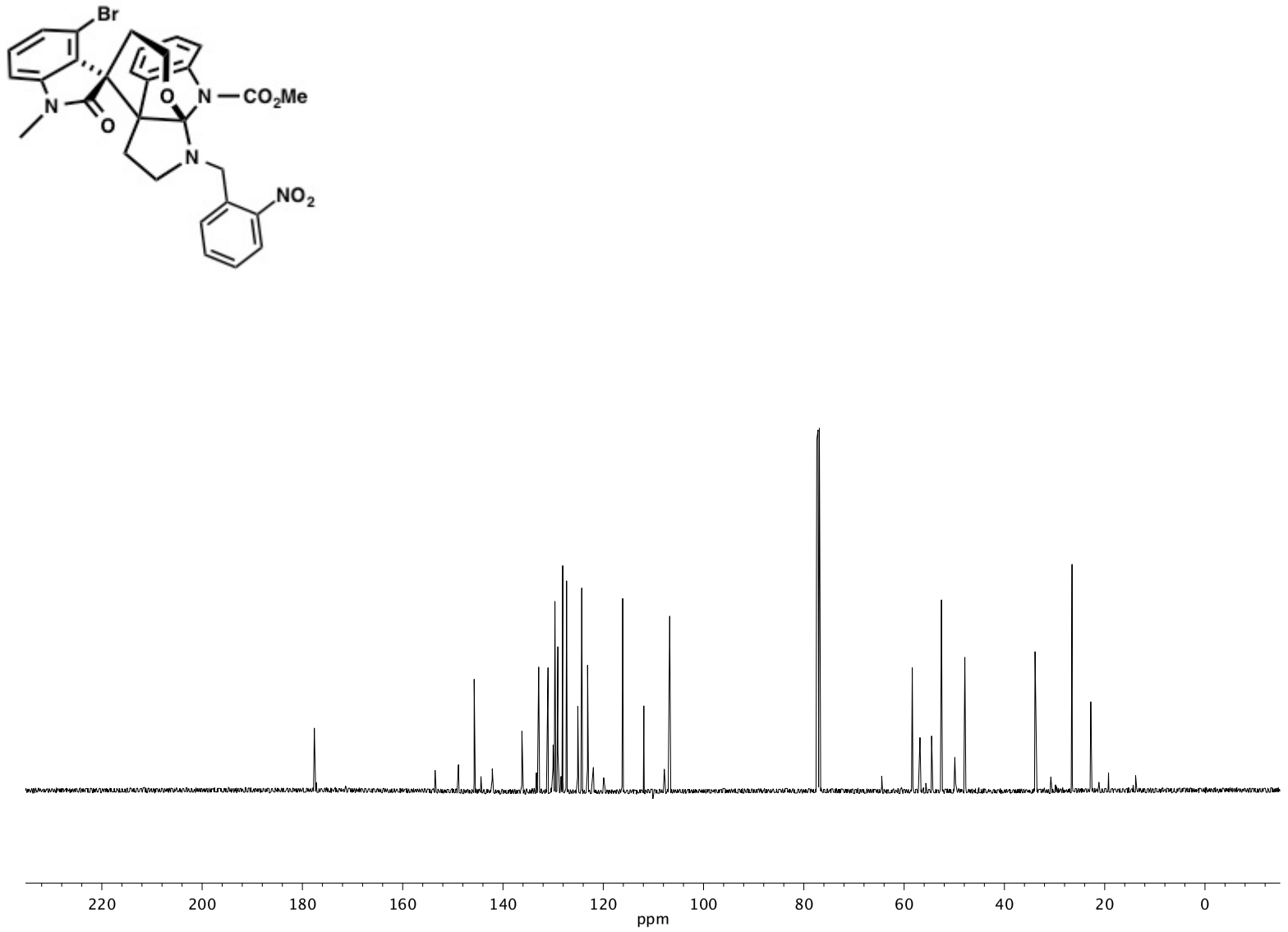
^{1}H NMR (500 MHz, $CDCl_3$) of compound **16.**



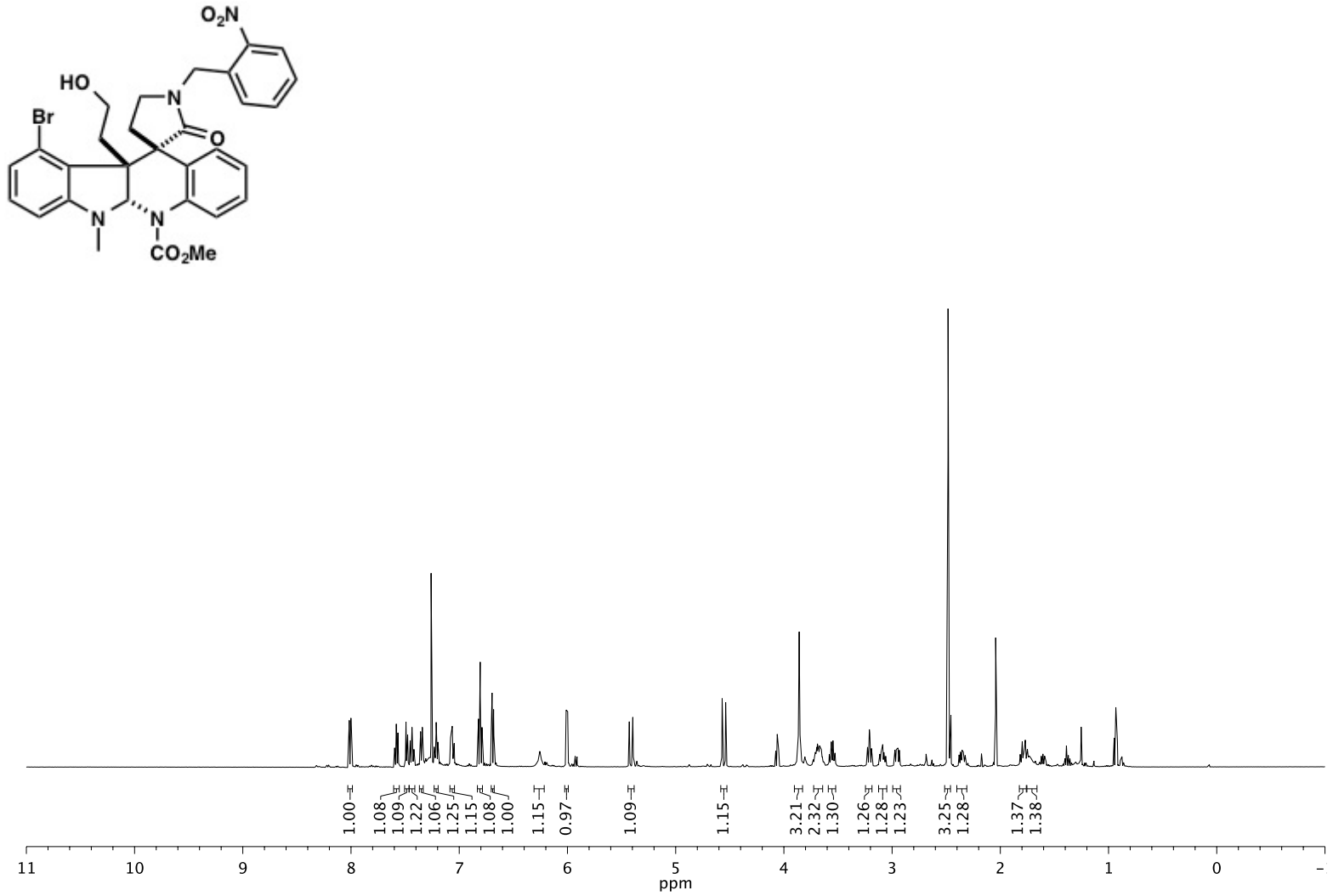
^{13}C NMR (125 MHz, $CDCl_3$) of compound **16.**



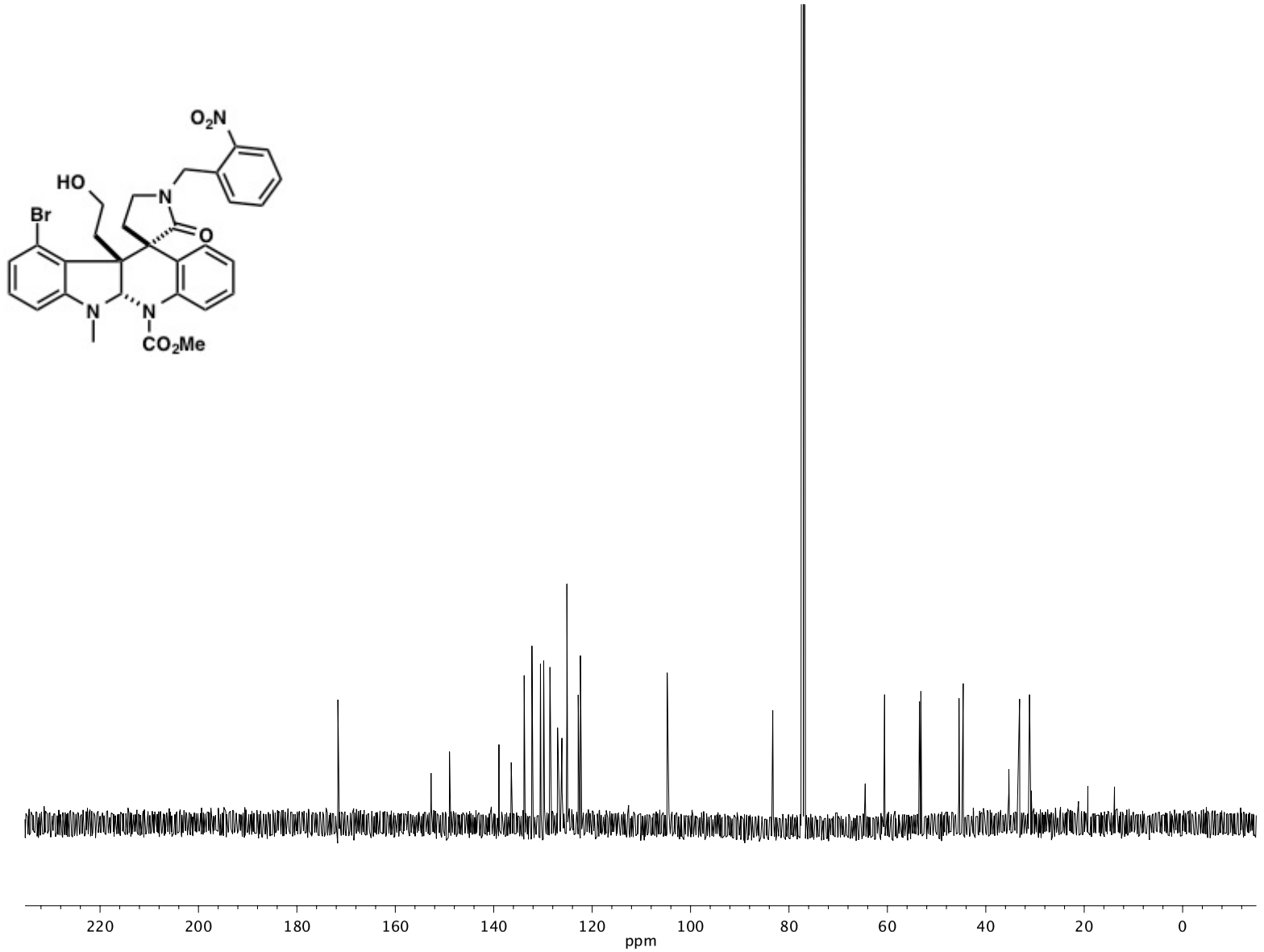
^{1}H NMR (500 MHz, $CDCl_3$) of compound **17.**



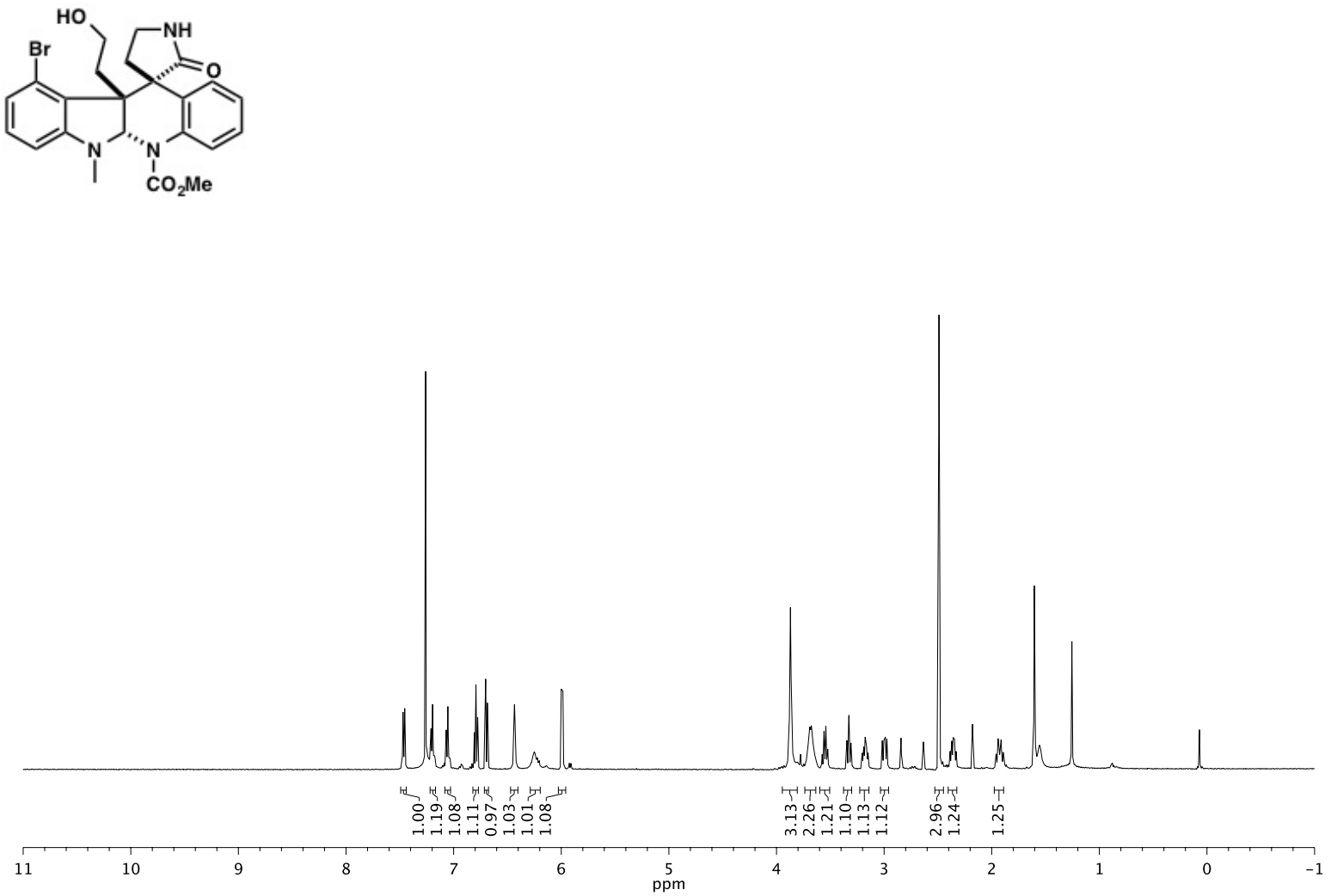
^{13}C NMR (125 MHz, $CDCl_3$) of compound **17.**



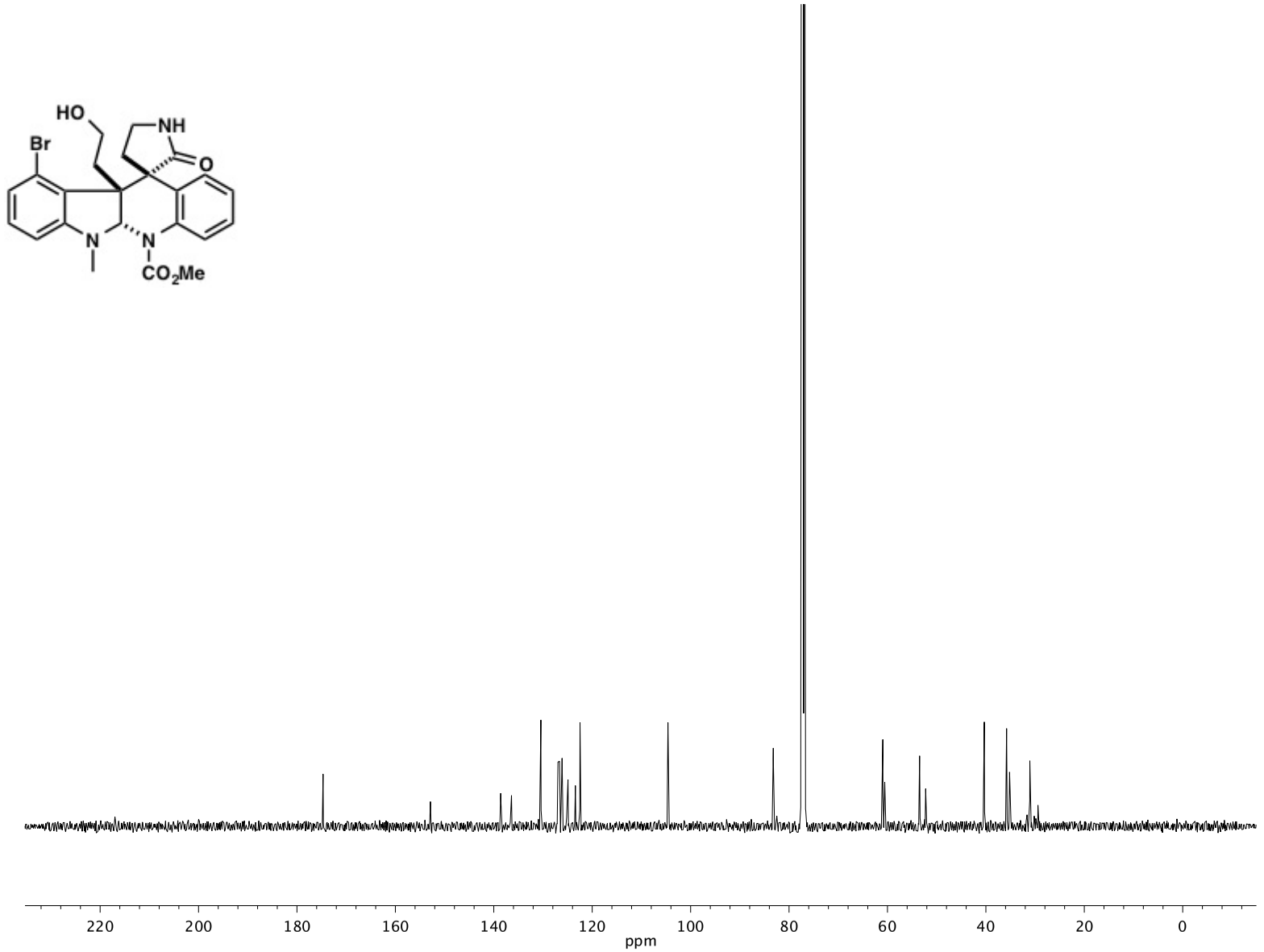
^{1}H NMR (500 MHz, $CDCl_3$) of compound **18.**



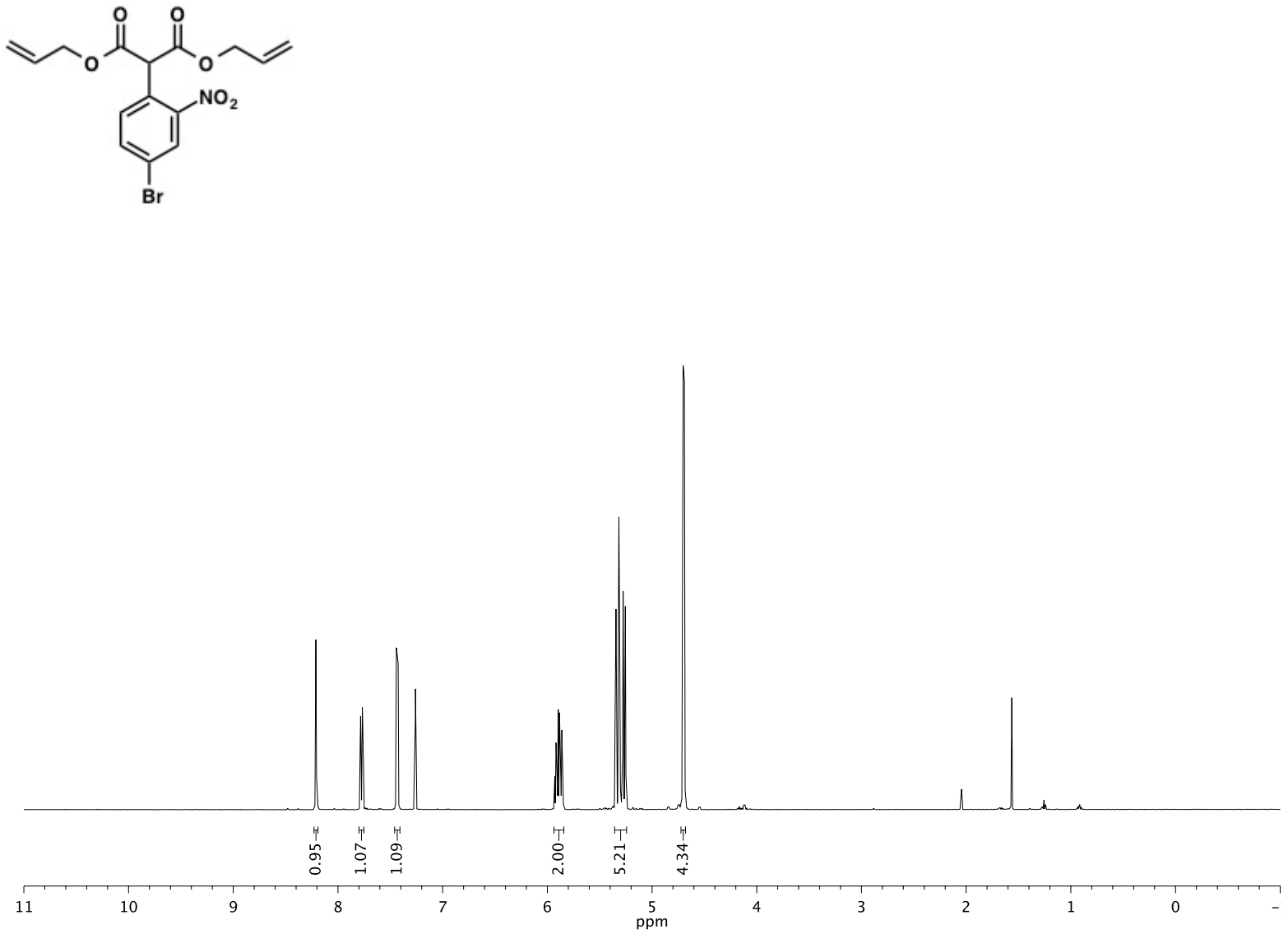
^{13}C NMR (125 MHz, $CDCl_3$) of compound **18.**



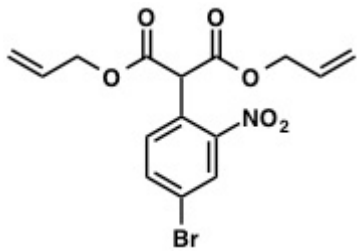
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3.**

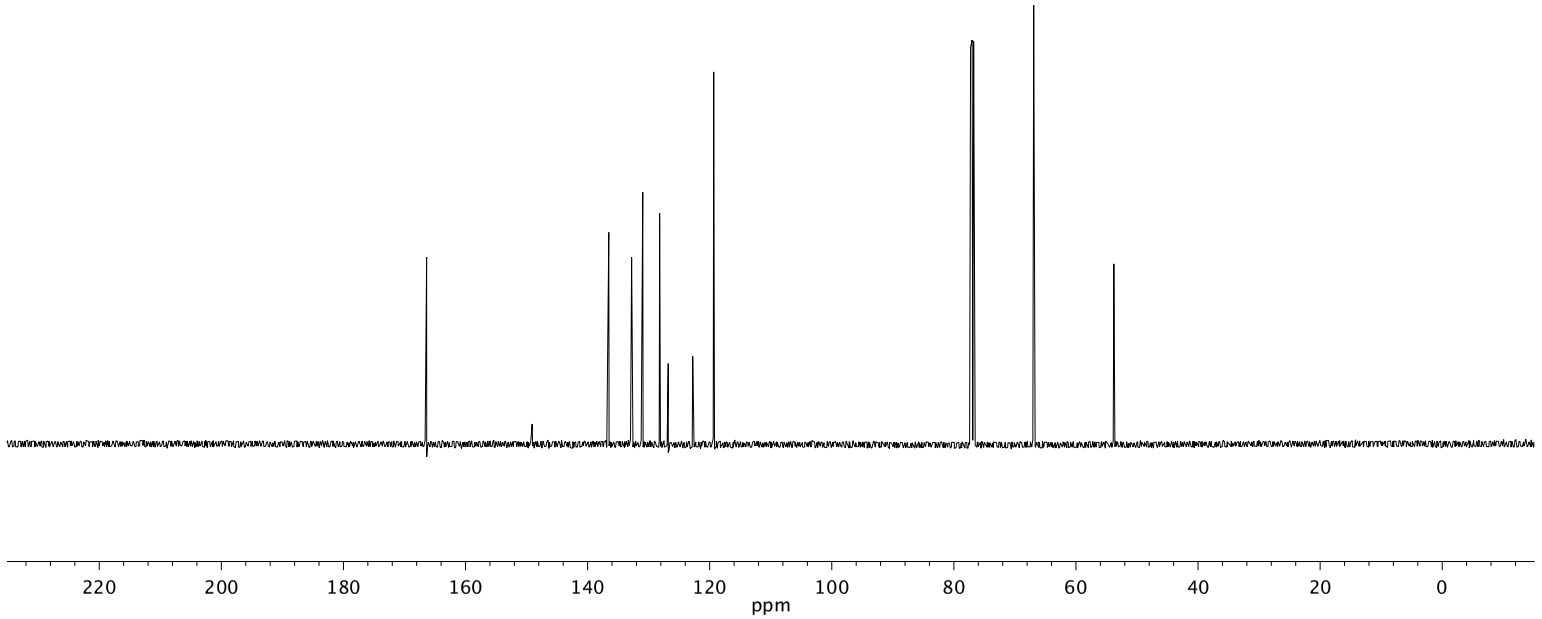


^{13}C NMR (125 MHz, $CDCl_3$) of compound **3.**

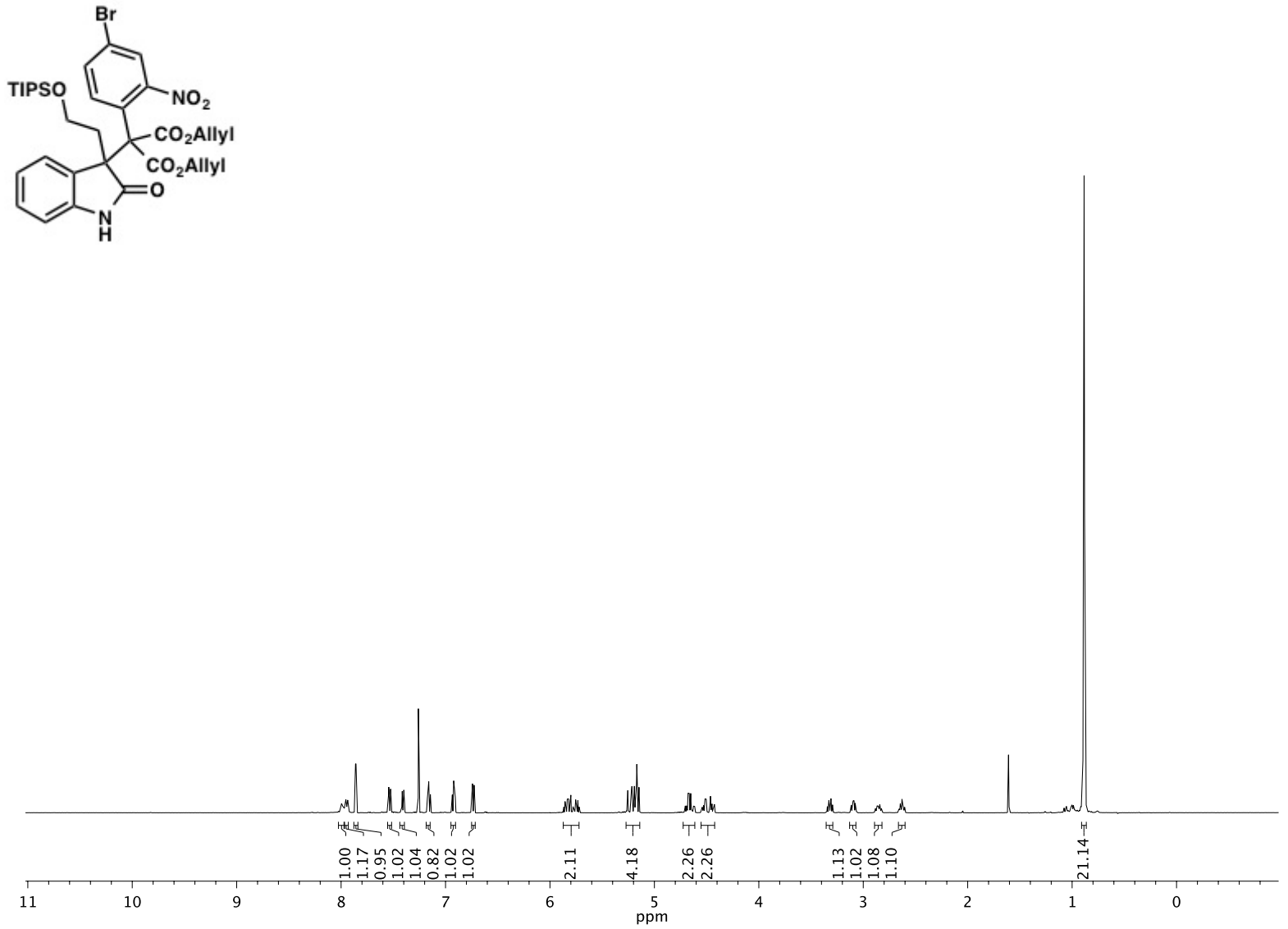


^{1}H NMR (500 MHz, $CDCl_3$) of compound **24**.

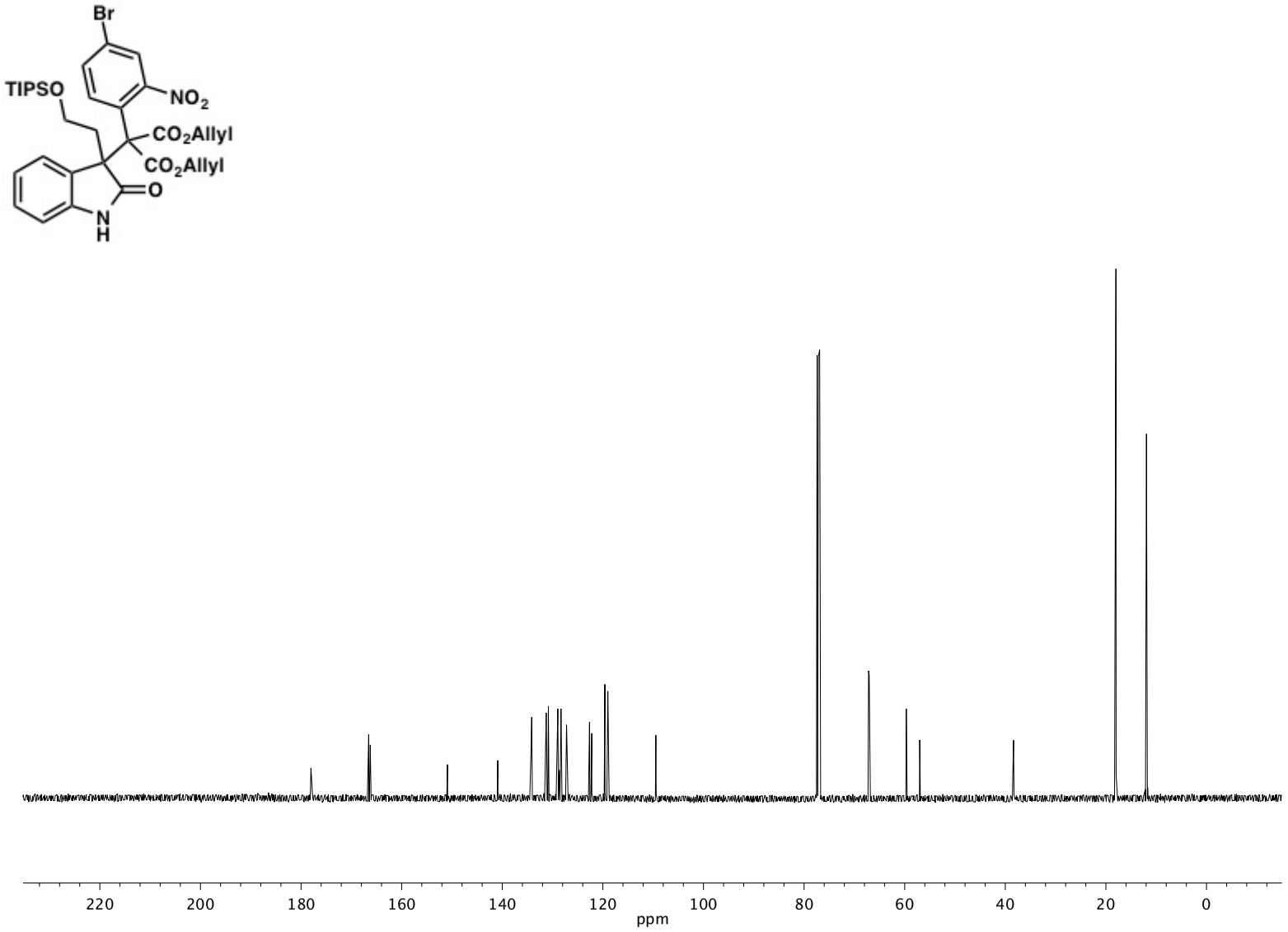




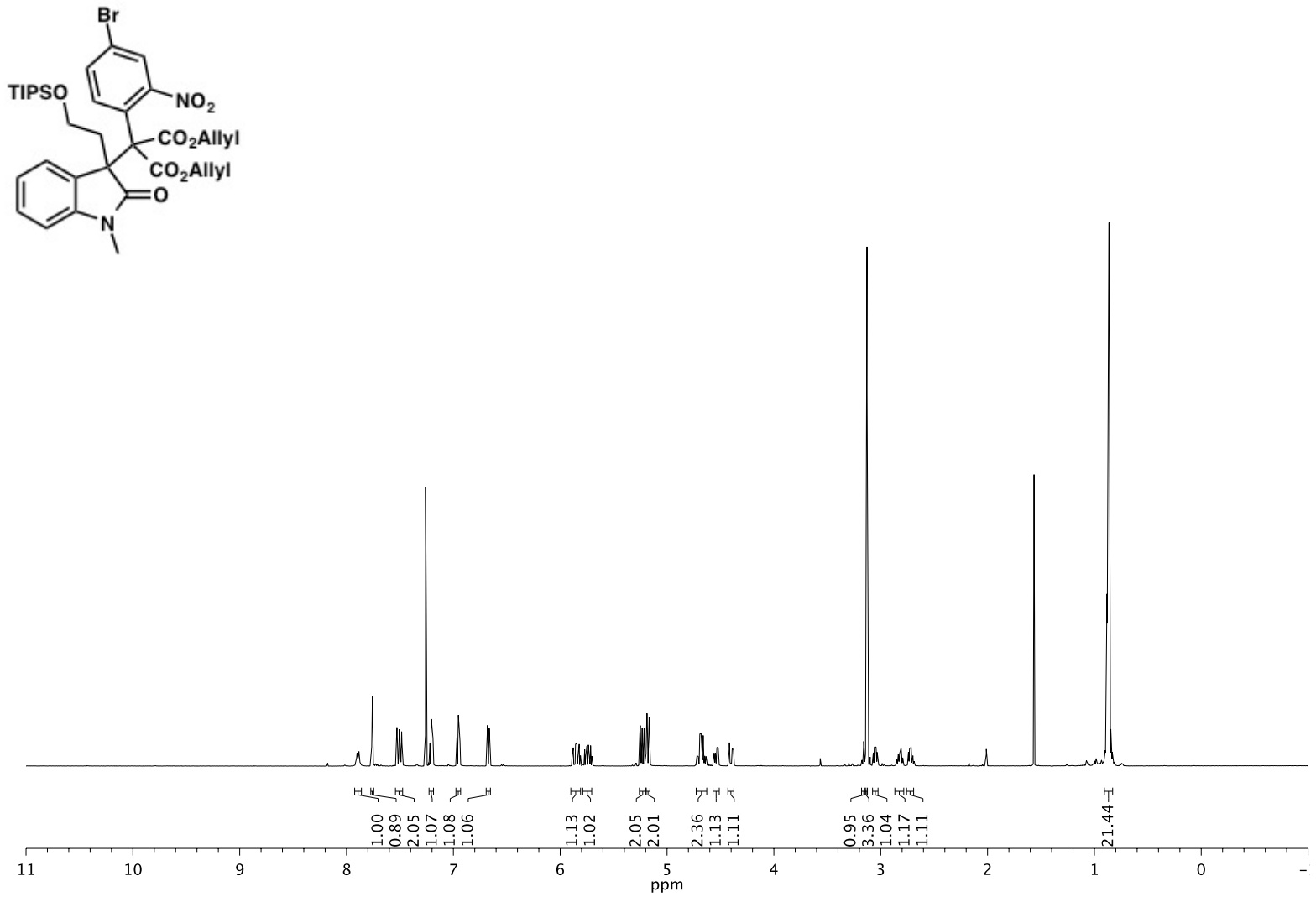
^{13}C NMR (125 MHz, $CDCl_3$) of compound **24**.



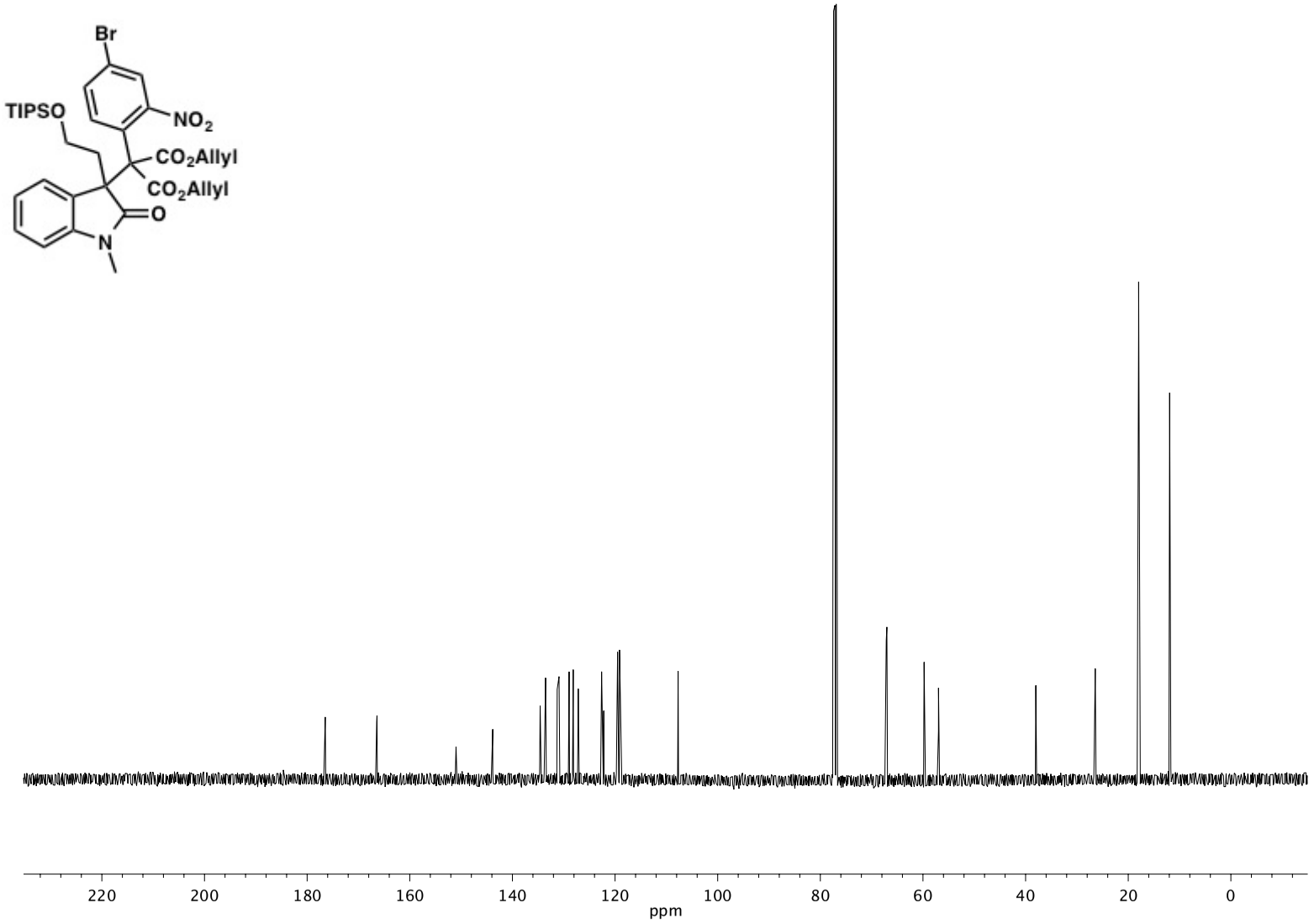
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-6**.



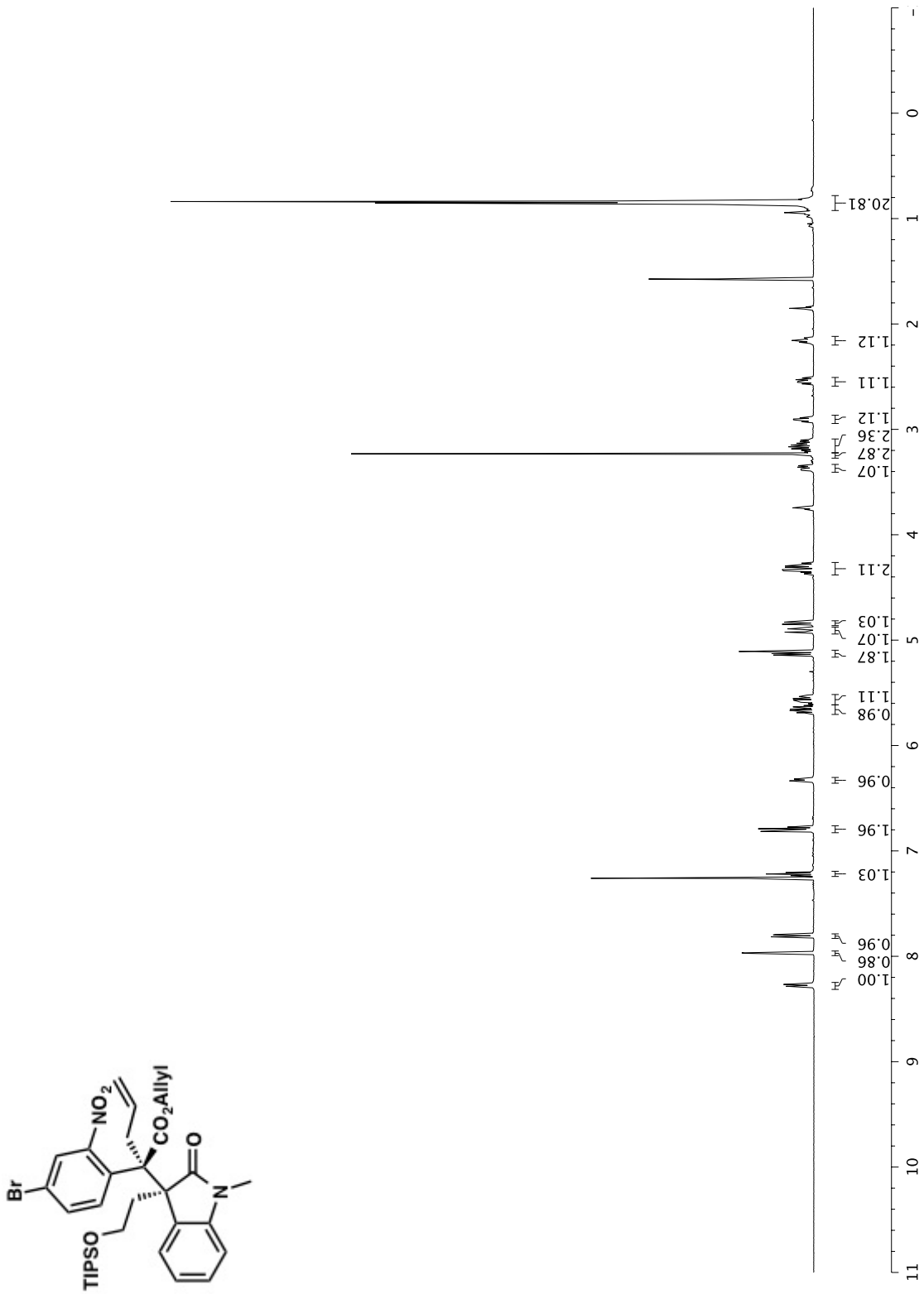
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-6**.



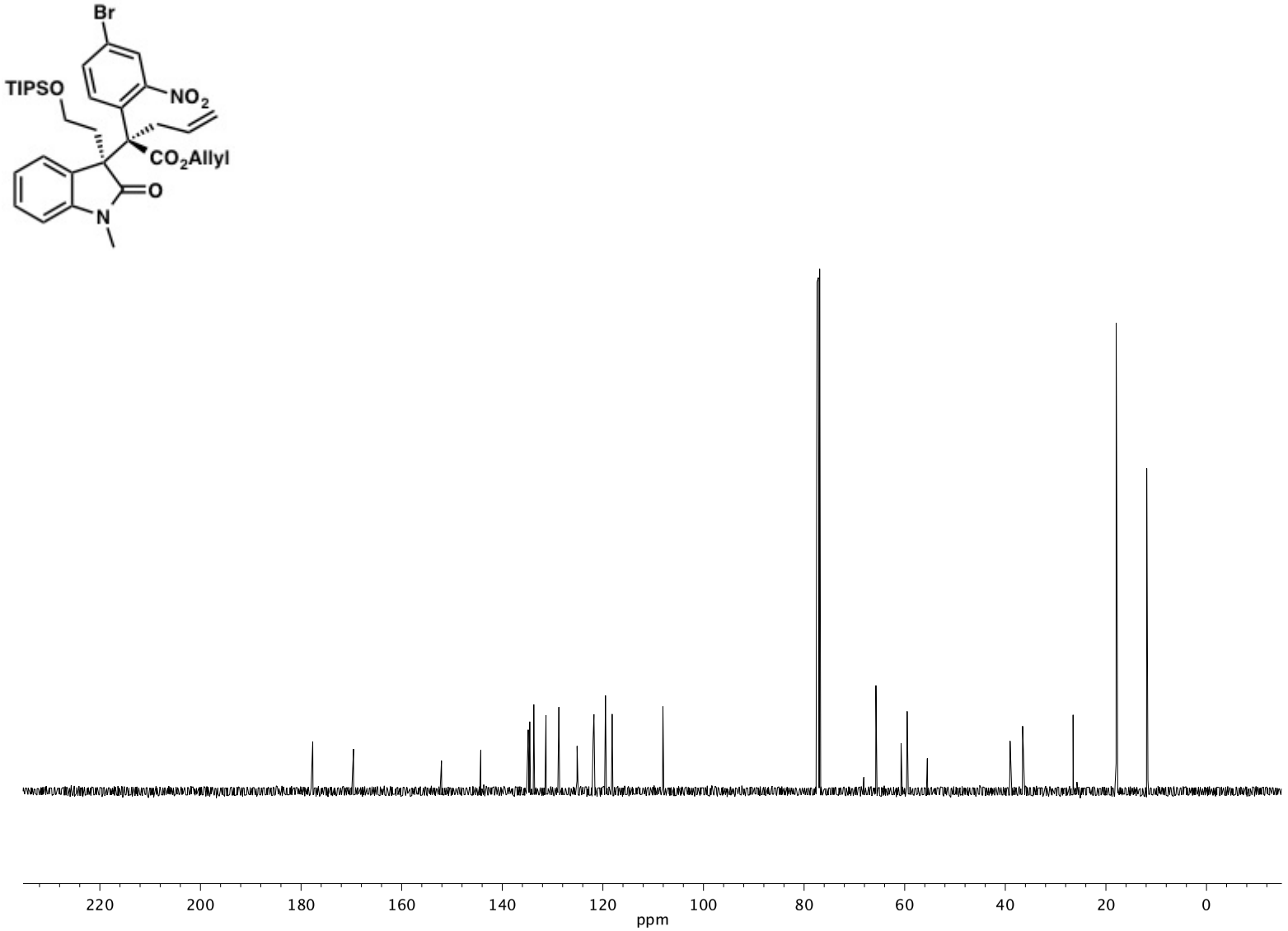
^{1}H NMR (500 MHz, $CDCl_3$) of compound **22**.



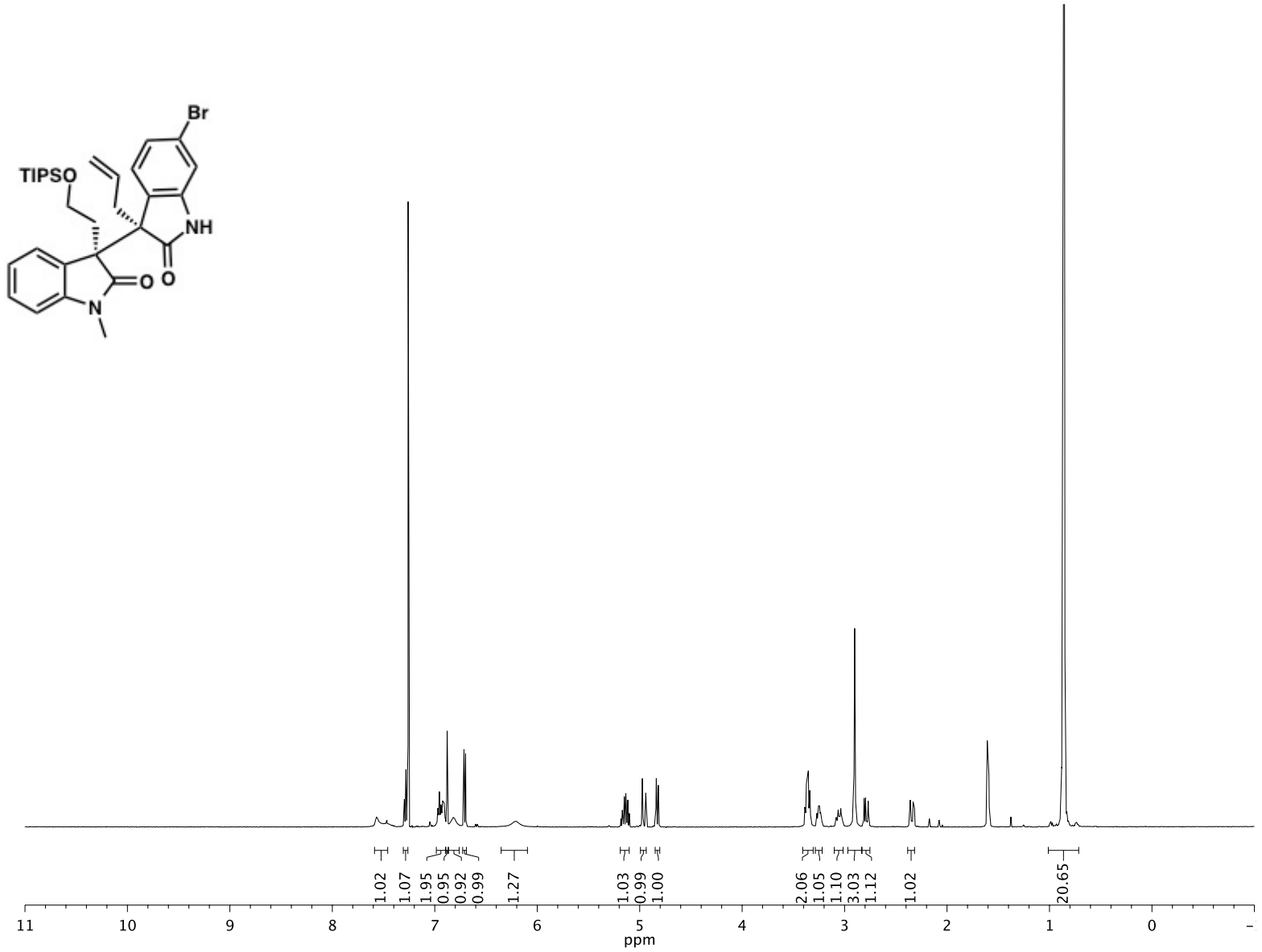
^{13}C NMR (125 MHz, $CDCl_3$) of compound **22**.



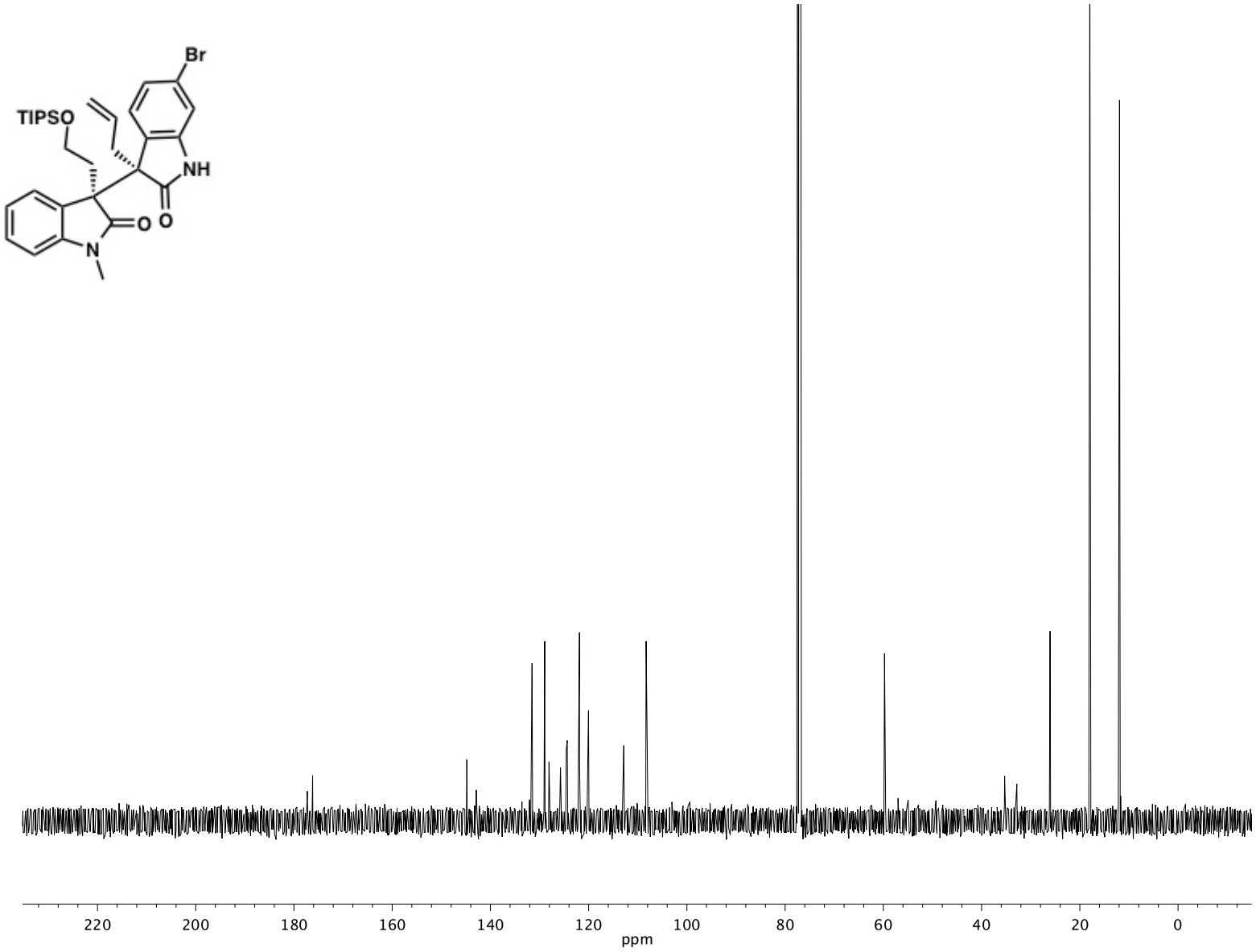
^{1}H NMR (500 MHz, $CDCl_3$) of compound **21**.



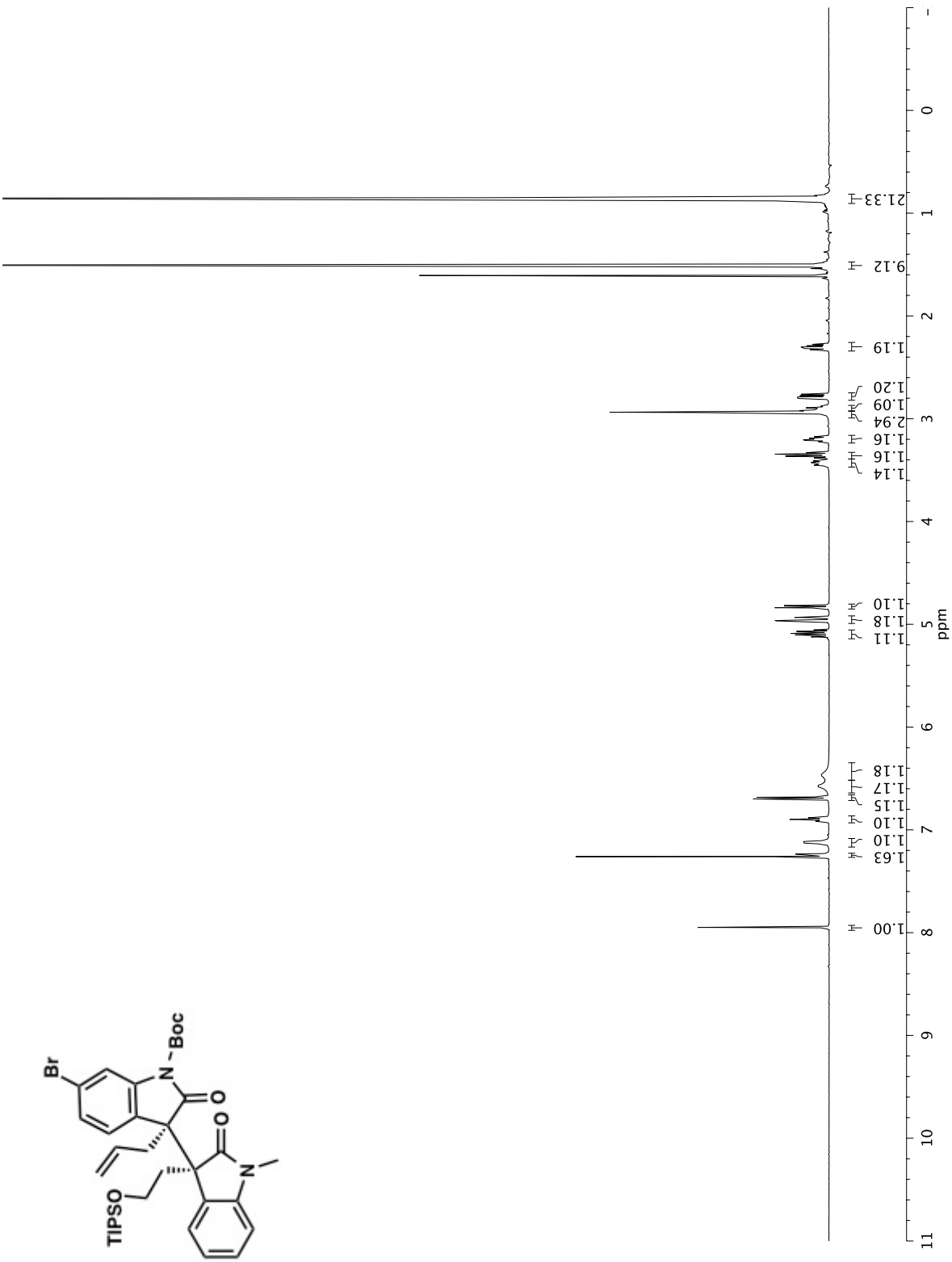
^{13}C NMR (125 MHz, $CDCl_3$) of compound **21**.



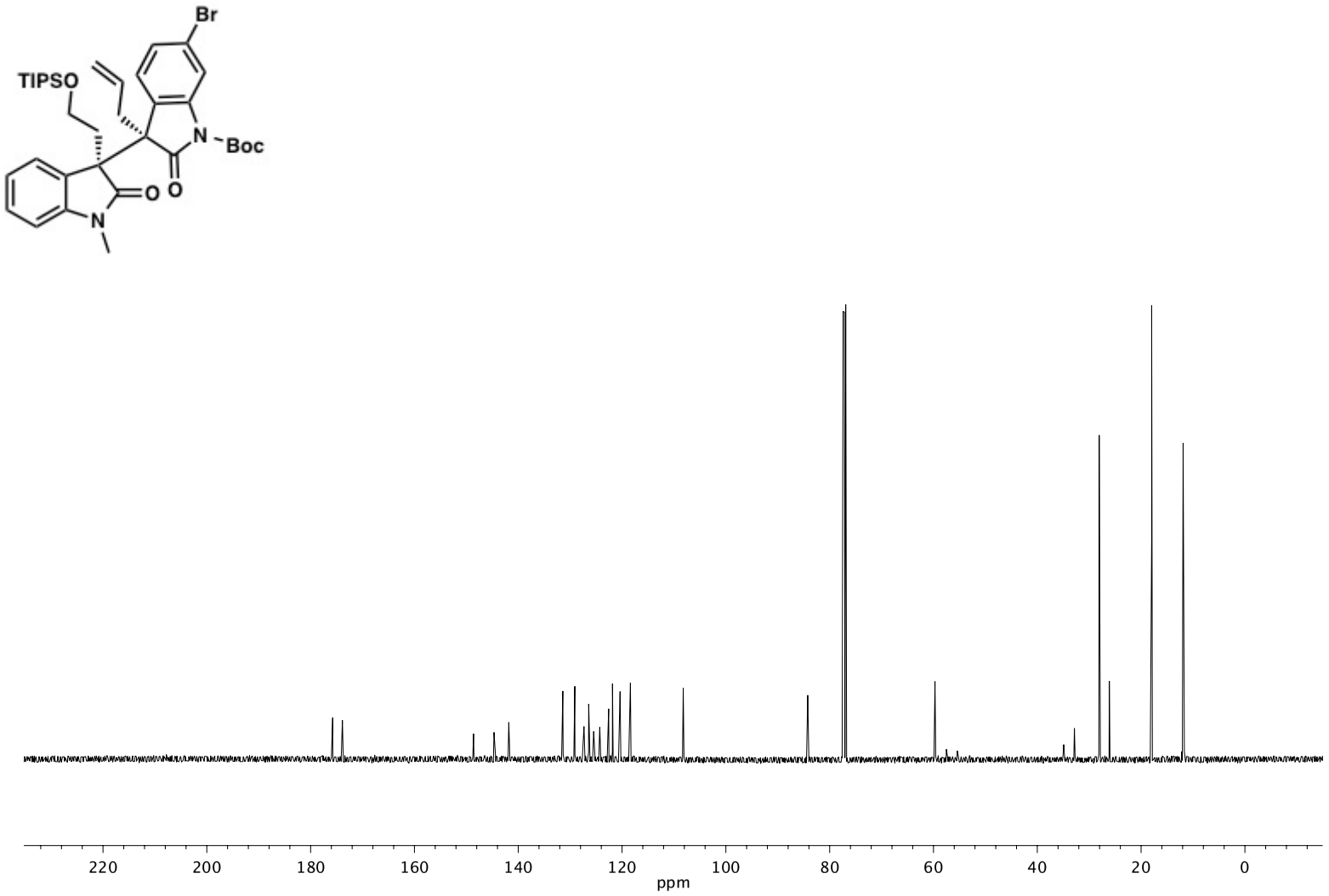
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-7**.



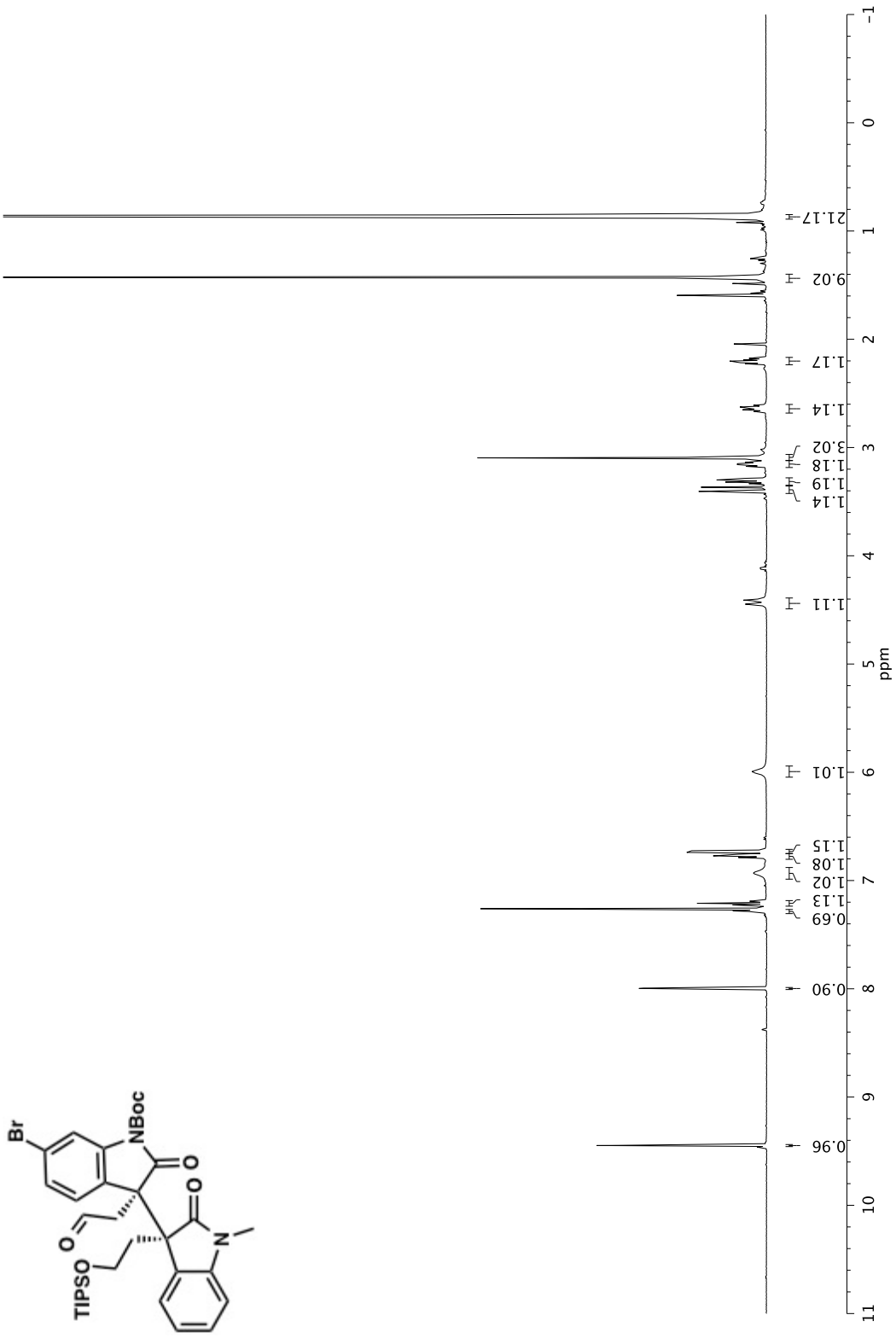
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-7**.



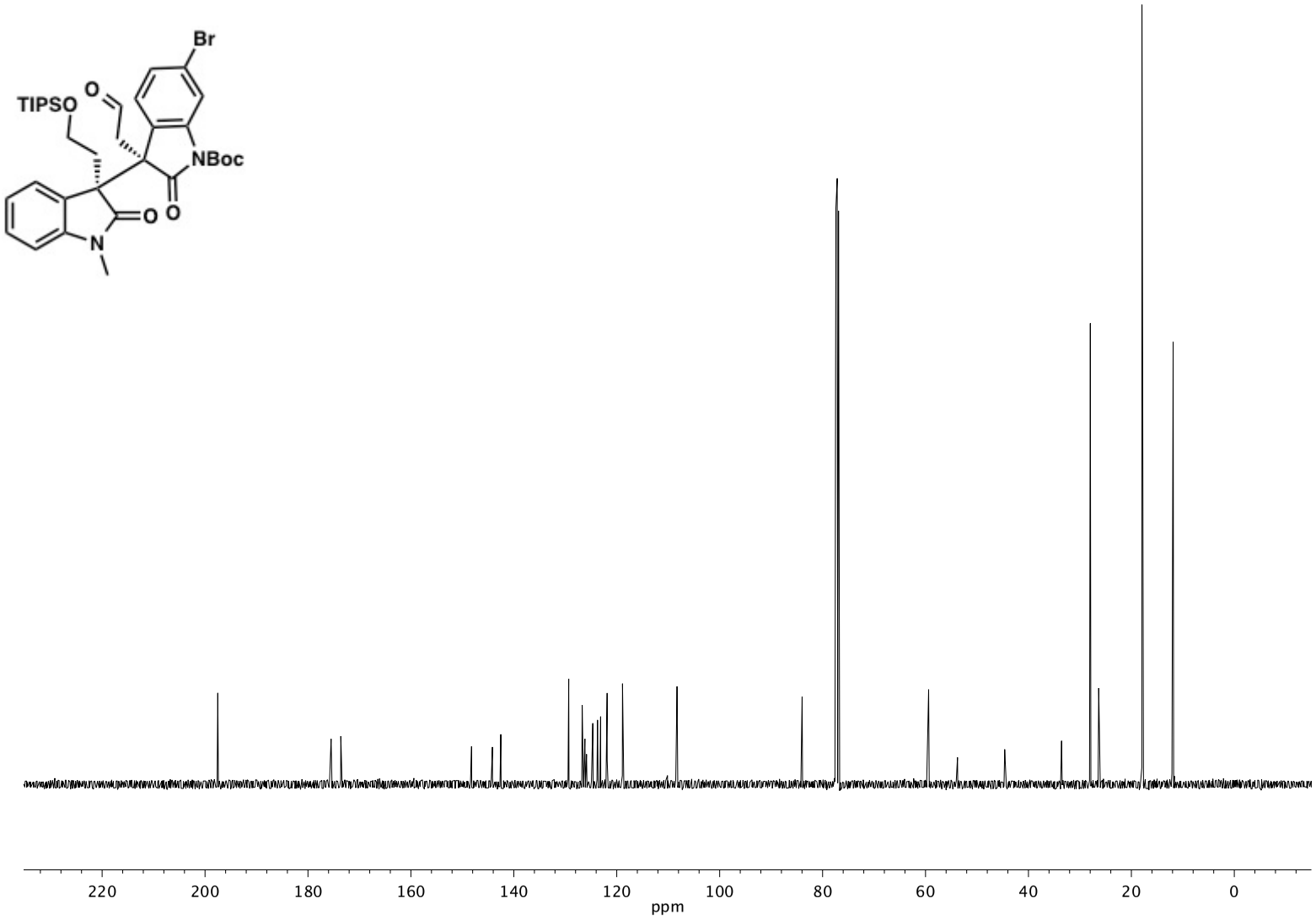
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-8**.



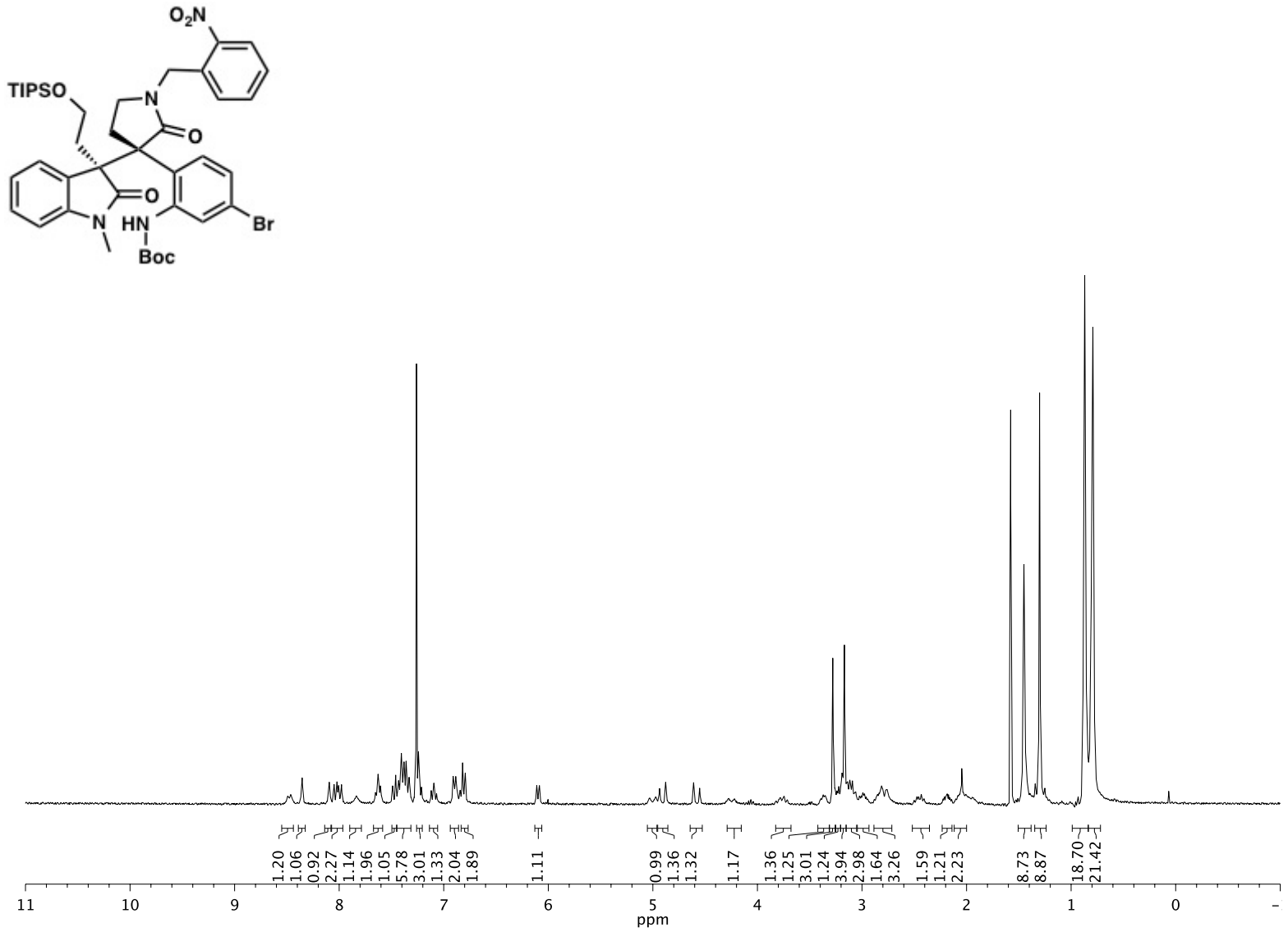
^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-8**.



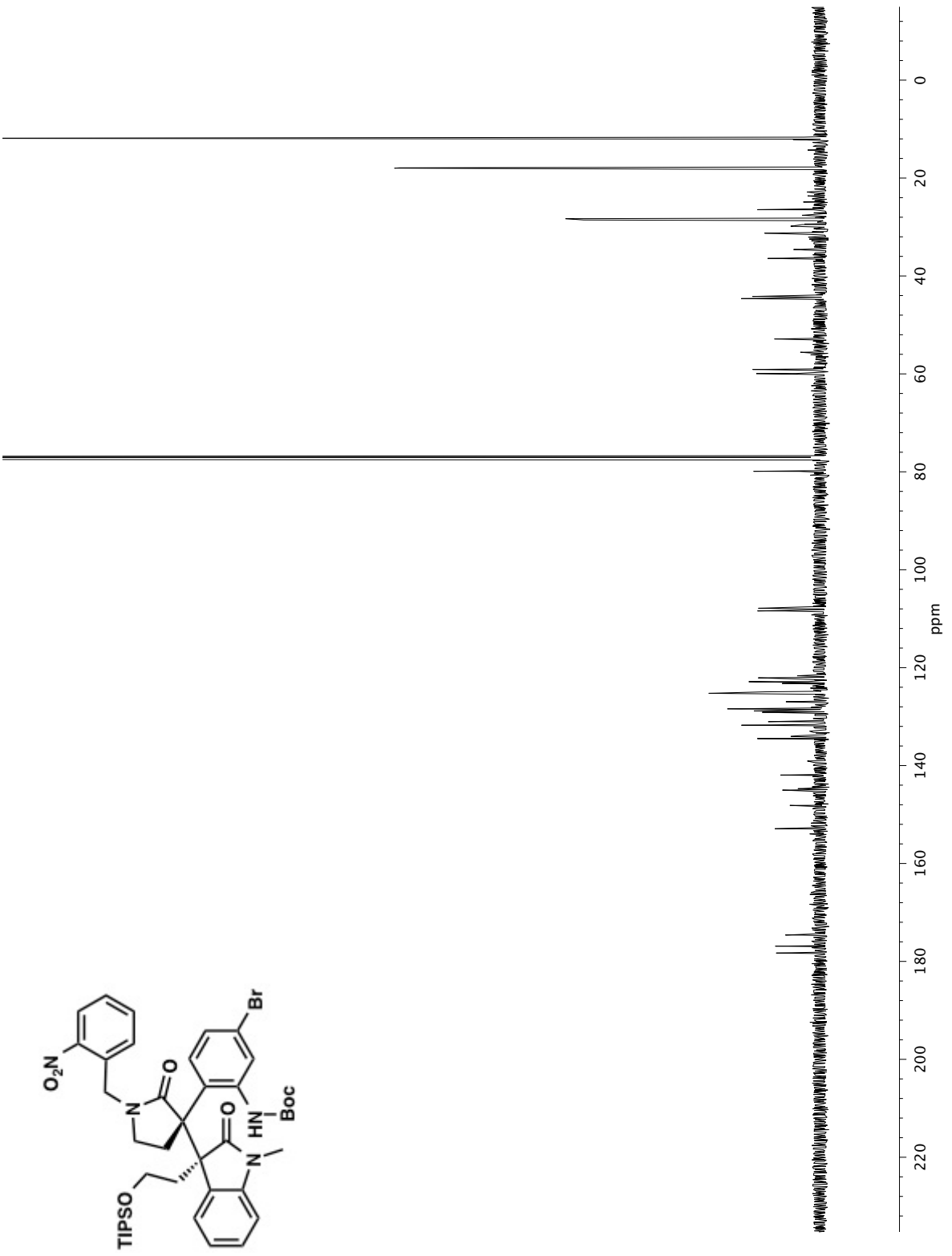
^{1}H NMR (500 MHz, $CDCl_3$) of compound **20**.



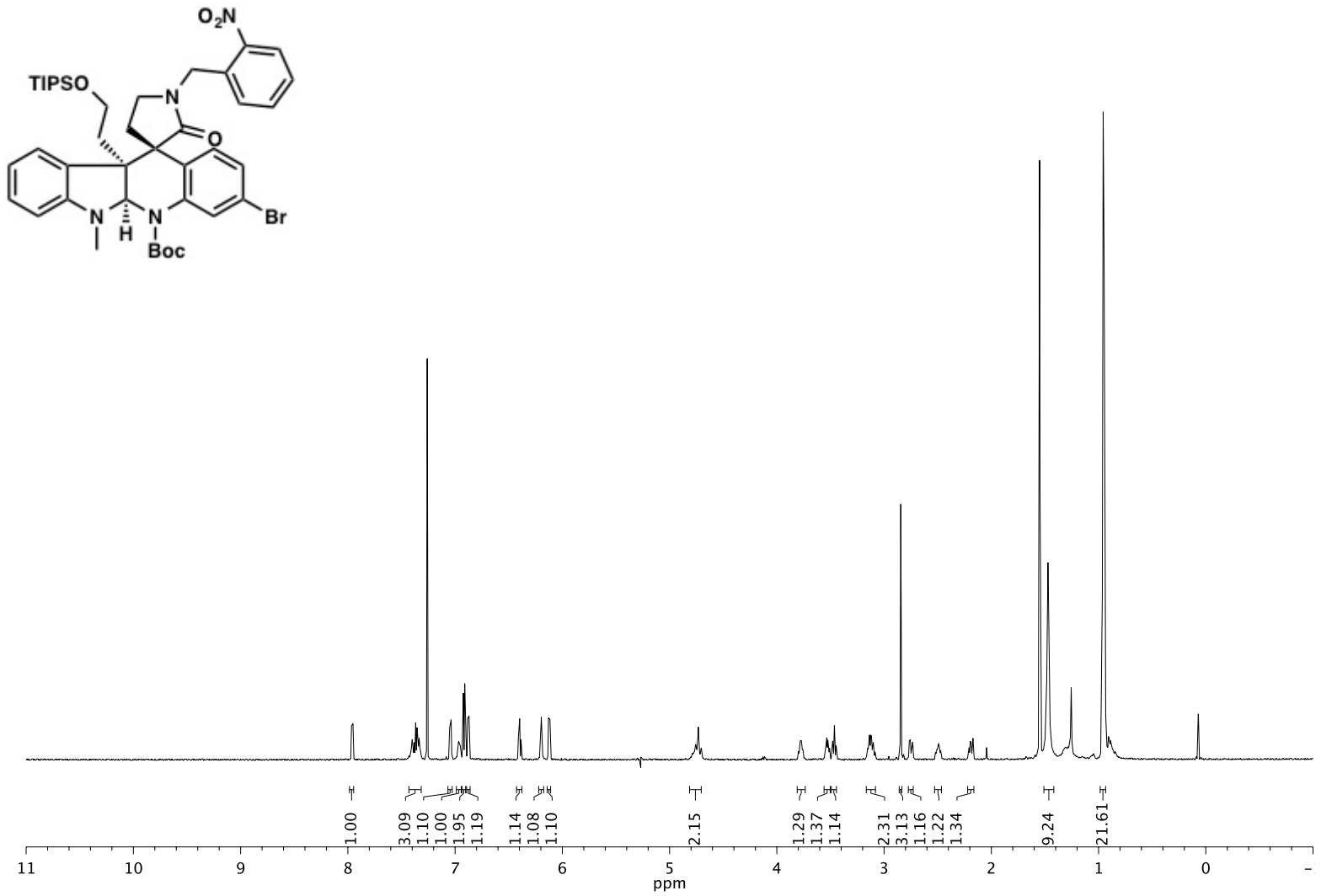
^{13}C NMR (125 MHz, $CDCl_3$) of compound **20**.



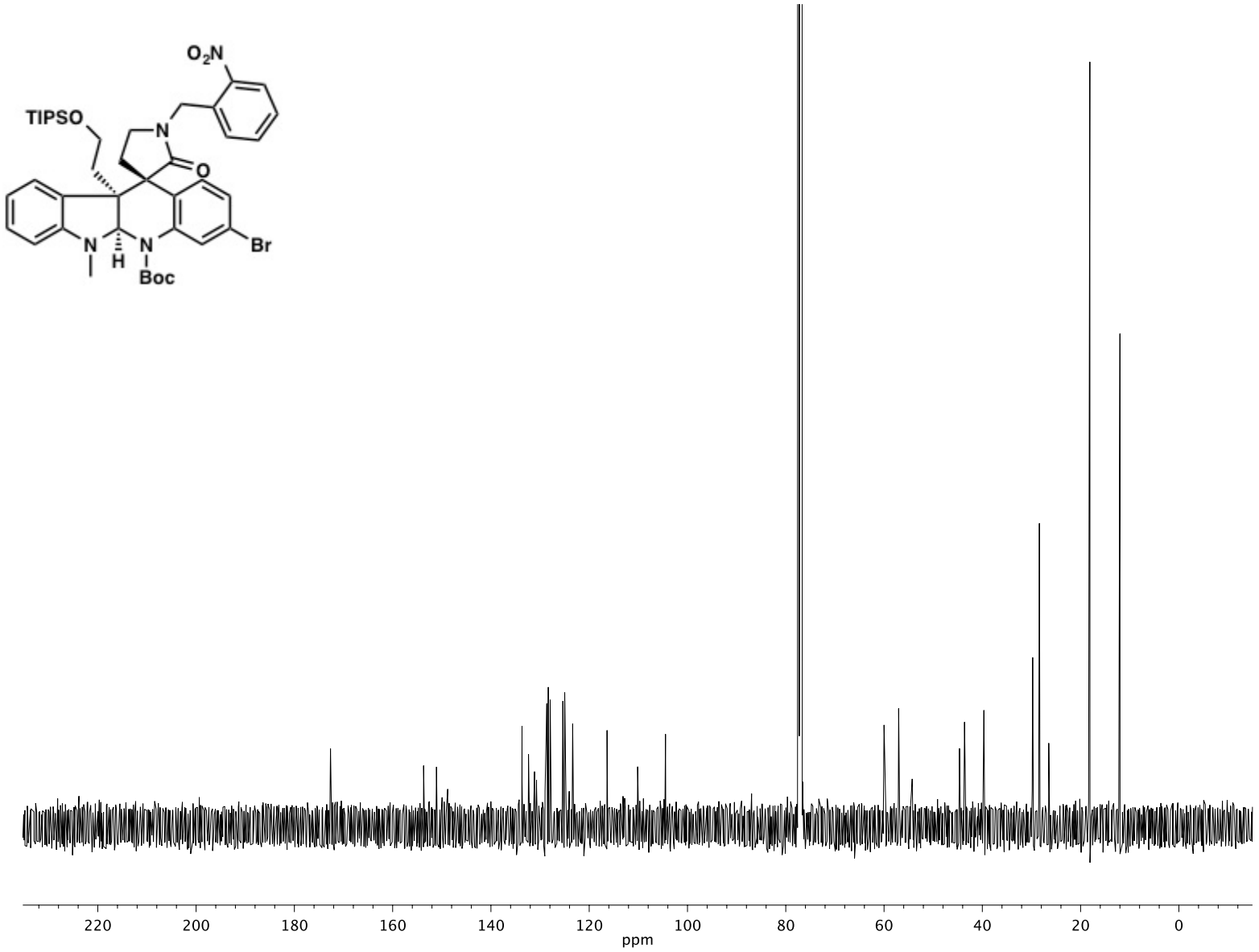
^{1}H NMR (300 MHz, $CDCl_3$) of compound **25**.



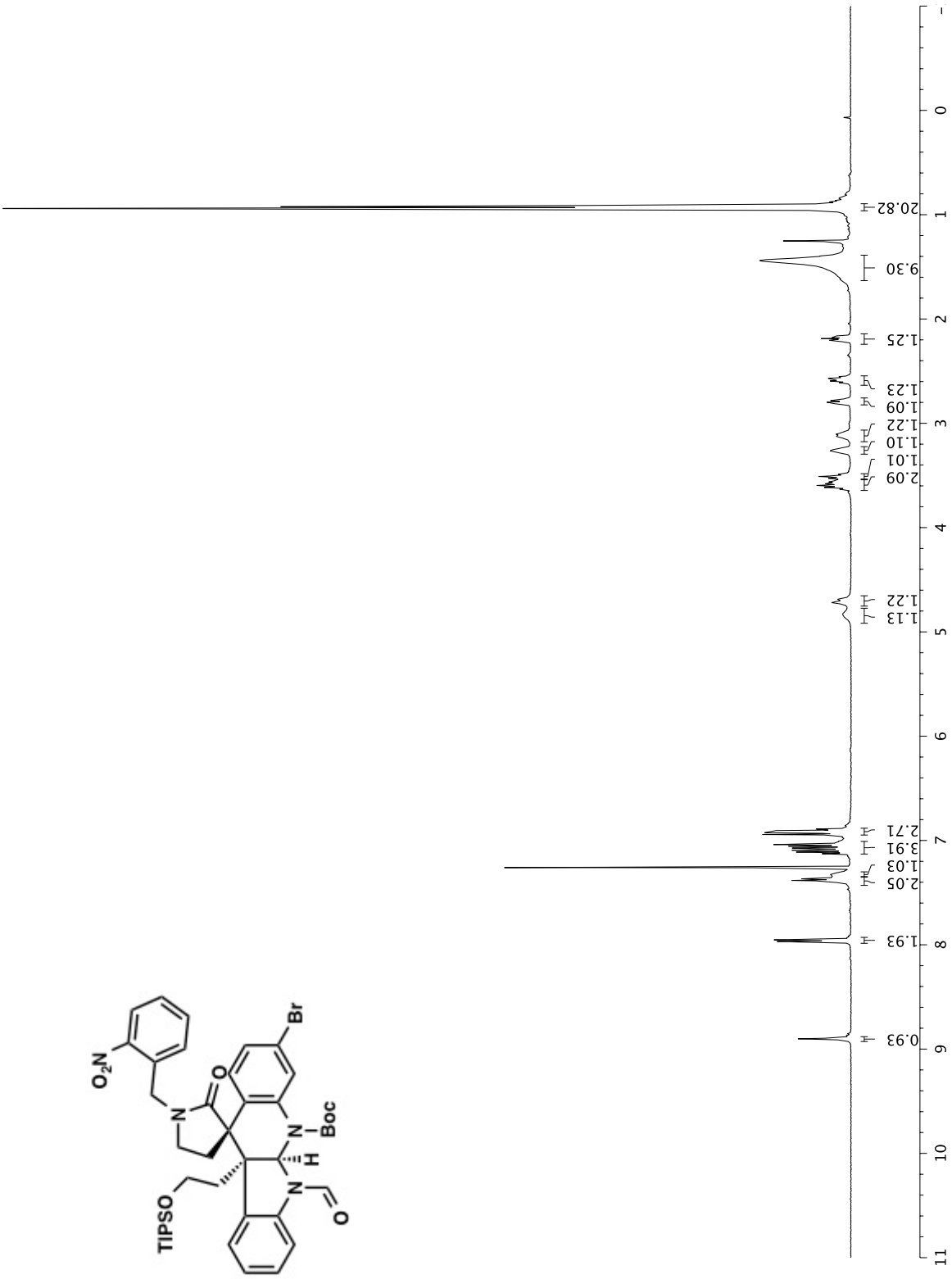
^{13}C NMR (125 MHz, $CDCl_3$) of compound **25**.



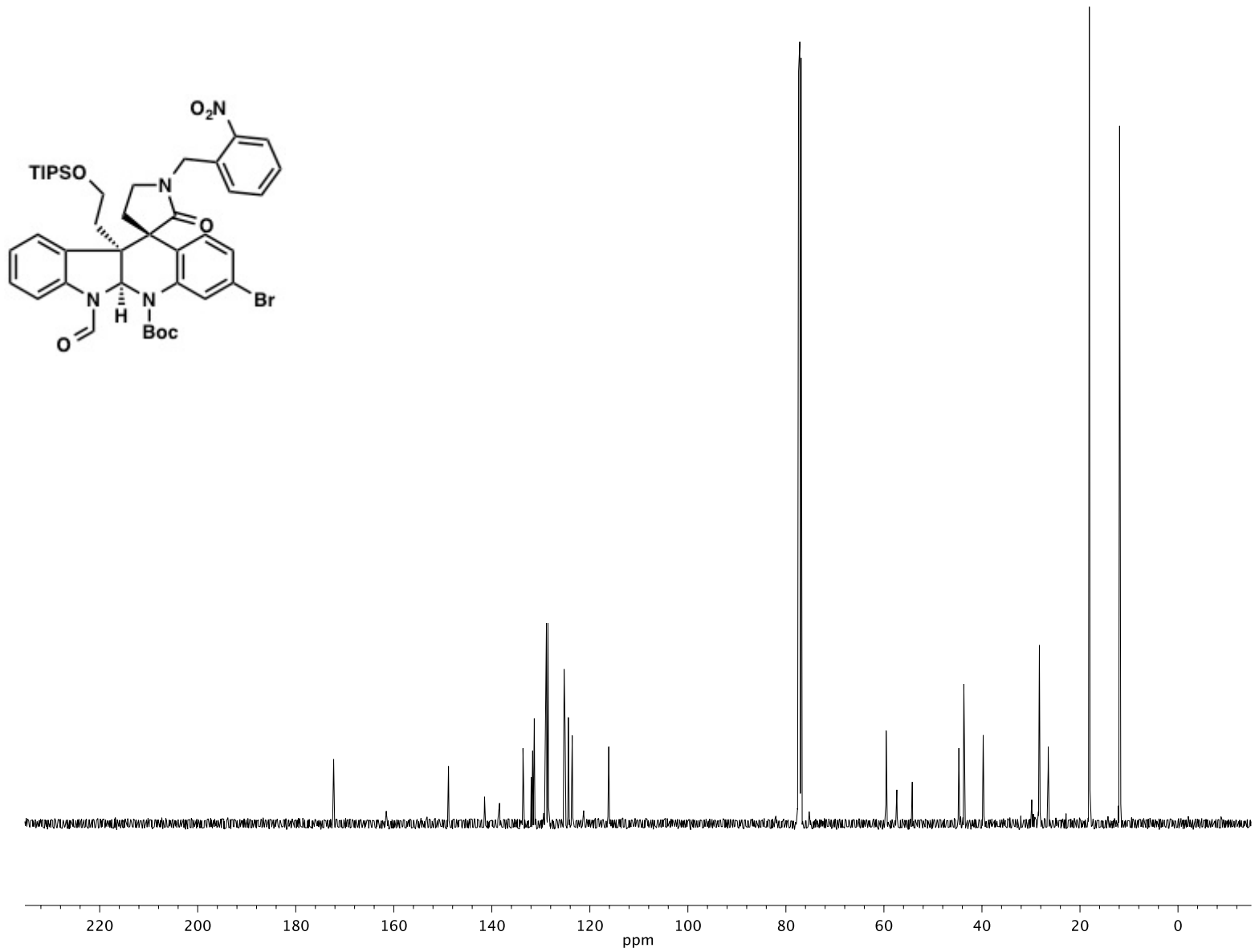
^{1}H NMR (600 MHz, $CDCl_3$) of compound **26**.



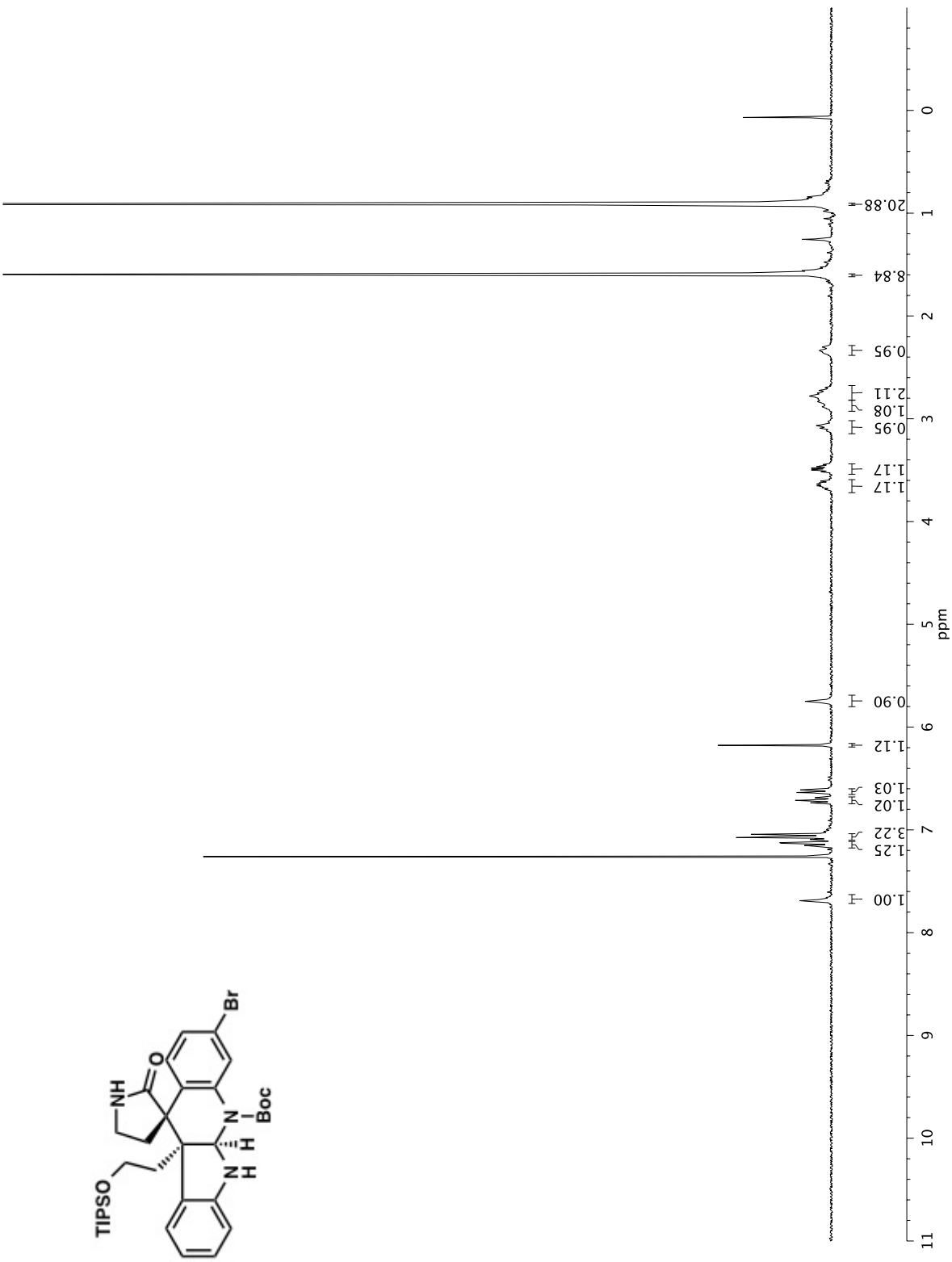
^{13}C NMR (125 MHz, $CDCl_3$) of compound **26**.



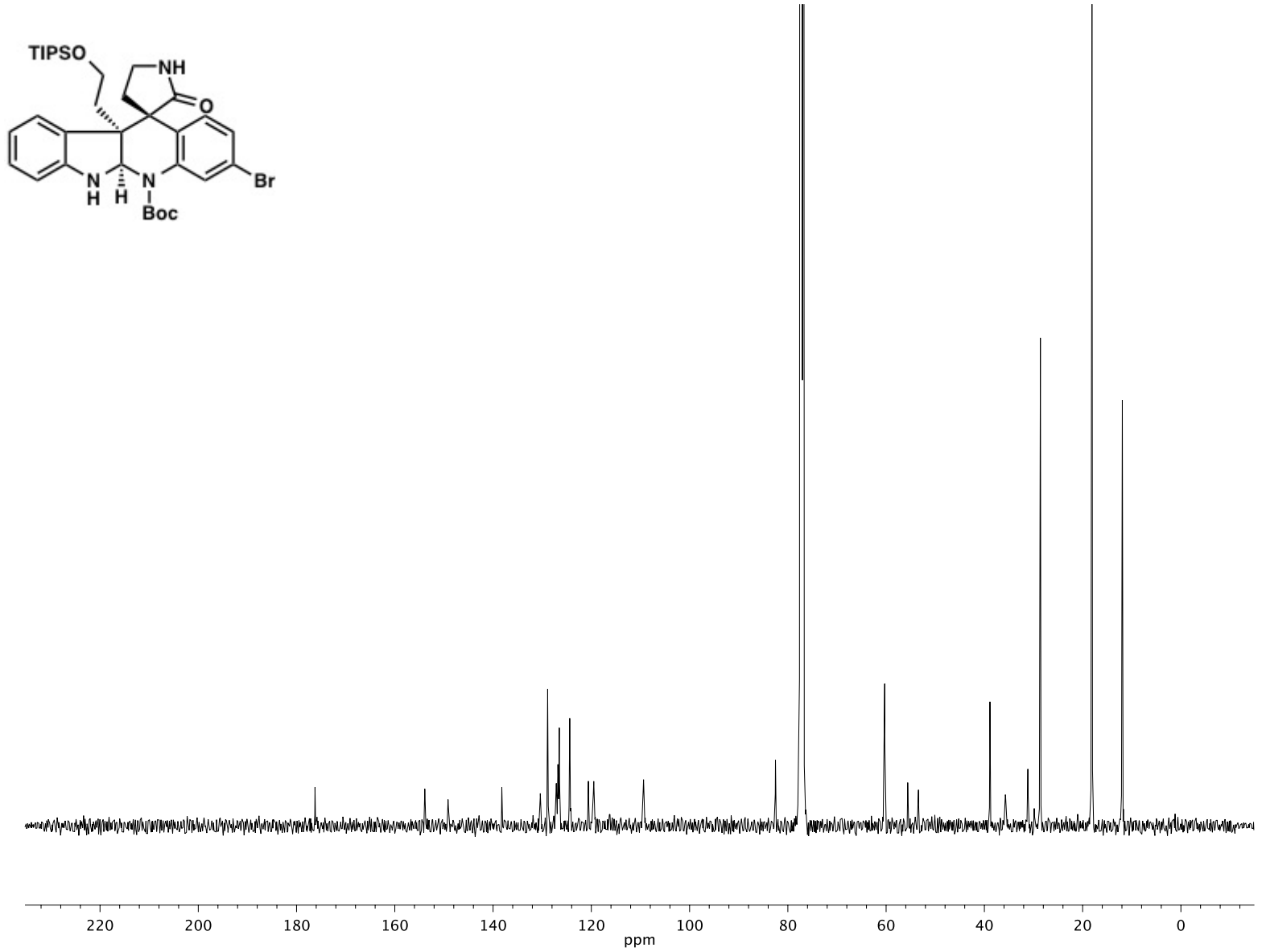
^{1}H NMR (500 MHz, $CDCl_3$) of compound **27**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **27**.



^{1}H NMR (500 MHz, $CDCl_3$) of compound **19**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **19**.