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Supporting Information

Pd-Catalyzed Arylation/Aza-Michael Addition Cascade to C2-Spiroindolines and Azabicyclo[3.2.2]nonanones

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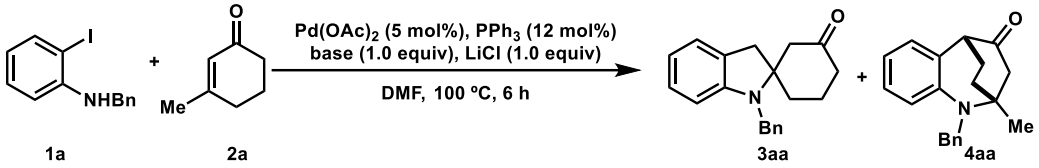
General Information and Materials

Unless otherwise stated, all reactions were carried out with oven-dried glassware using Schlenk manifolds under an atmosphere of dry argon. Reactions were monitored by thin-layer chromatography (TLC) or gas chromatography mass spectrometry (GC-MS). TLC was performed using Huanghai 8±0.2 μm precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, $KMnO_4$, *p*-anisaldehyde, or phosphomolybdic acid staining. Huanghai silica gel (particle size 300 – 400 or 200 – 300 mesh) was used for silica gel chromatography. ^1H NMR spectra were recorded at room temperature on a Bruker ADVANCE III 400 MHz spectrometer and were reported relative to $CDCl_3$ (δ 7.26 ppm), C_6D_6 (δ 7.16 ppm), or acetone-d_6 (δ 2.05 ppm). ^{13}C NMR spectra were recorded on a Bruker ADVANCE III 400 MHz spectrometer (100 MHz) and were reported relative to $CDCl_3$ (δ 77.16 ppm), C_6D_6 (δ 128.06 ppm), or acetone-d_6 (δ 29.84 ppm). ^{19}F NMR spectra were recorded on a Bruker ADVANCE III 400 MHz spectrometer (376 MHz) and were reported relative to $CFCl_3$ (δ 0.0 ppm). Data for ^1H NMR were reported as chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration) using standard abbreviations for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, and br s = broad signal. Data for ^{13}C NMR and ^{19}F NMR were reported in terms of chemical shifts (δ ppm). High resolution mass spectra (HRMS) were obtained by use of a Bruker Compact TOF mass spectrometer in an electrospray ionization mode (ESI+) or an atmospheric pressure chemical ionization (APCI+).

Petroleum ether (60 ~ 90 ºC) was used as eluent for silica gel chromatography. Dry solvents were purchased commercially or were dried by passage through an activated alumina column under argon. Other reagents were purchased commercially and used without further purification unless otherwise noted.

Optimization of Reaction Conditions for the synthesis of C2-Spiroindolines 3aa (Tables S1–S4)

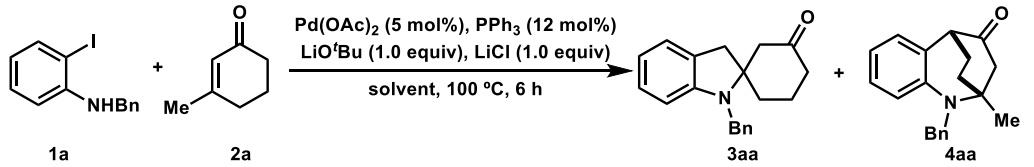
Table S1. Screening of bases.



entry[a]	base	yield of **3aa**/**4aa** (%)	entry	base	yield of **3aa**/**4aa** (%)
1	NaOMe	–	7	LiO^{t}Bu	62/5
2	NaOH	10/–	8	LiHMDS	31/–
3	NaH	6/–	9	KOTMS	29/–
4	NaHMDS	27/–	10	K_3PO_4	–
5	NaO^{t}Bu	37/–	11	Cs_2CO_3	–
6	KO^{t}Bu	43/8	12	TBD[b]	–

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (12 mol%), base (1.0 equiv), LiCl (1.0 equiv) in DMF (1 mL) at 100 °C for 6 h. [b] TBD = 1,5,7-triazabicyclo[4.4.0]dec-5-ene.

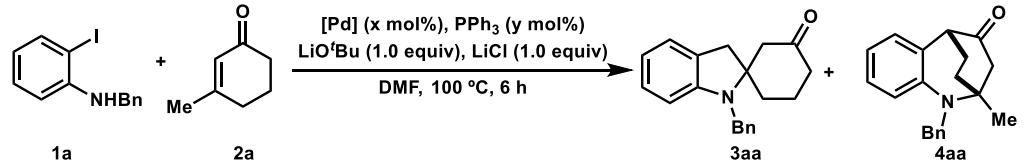
Table S2. Screening of solvents.



entry[a]	solvent	yield of **3aa**/**4aa** (%)	entry	solvent	yield of **3aa**/**4aa** (%)
1	THF	–	5	DMF	62/5
2	toluene	–	6	NMP	51/–
3	DME	–	7	DMSO	47/–
4	1,4-dioxane	–			

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (12 mol%), LiO^{t}Bu (1.0 equiv), LiCl (1.0 equiv) in solvent (1 mL) at 100 °C for 6 h.

Table S3. Screening of palladium precursors.

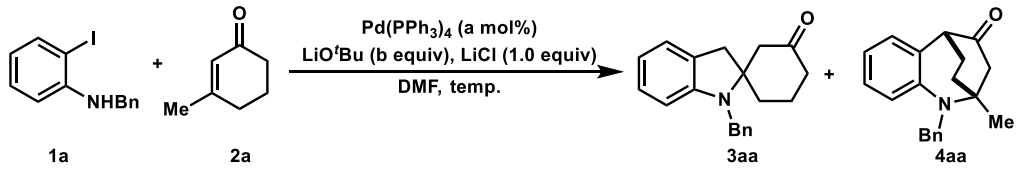


entry[a]	[Pd] (x mol%)	PPh_3 (y mol%)	yield of **3aa**/**4aa** (%)

1	$Pd(OAc)_2$ (5)	12	62/5
2	$Pd(PPh_3)_4$ (5)	0	71/–
3	$Pd_2(dba)_3$ (2.5)	12	68/6

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [Pd] (5 mol%), PPh_3 (12 mol%), LiO^tBu (1.0 equiv), LiCl (1.0 equiv) in DMF (1 mL) at 100 °C for 6 h.

Table S4. Screening of catalyst loading, amount of base, and temperature.



1a 2a 3aa 4aa

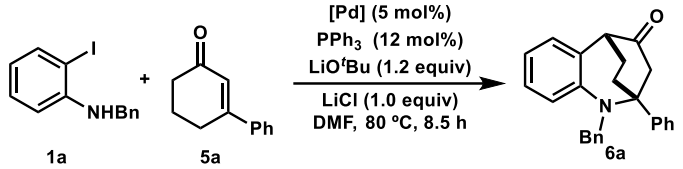
entry[a]	$Pd(PPh_3)_4$ (a mol%)	LiO^tBu (b equiv)	temp. (°C)	time (h)	yield of **3aa**/**4aa** (%)
1[b]	5	1.0	100	6	71/–
2	5	1.0	100	6	76/5
3	2	1.0	100	6	73/–
4	1	1.0	100	6	80/–
5	1	1.0	120	6	71/5
6	1	1.0	80	6	76/5
7	1	1.0	60	24	79/–
8	1	1.0	40	24	62/–
9	1	1.2	60	24	81(80)/–
10	1	1.5	60	24	67/13
11	0	1.2	60	24	–
12	1	0	60	24	–
13[c]	1	1.2	60	24	80/7

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $Pd(PPh_3)_4$ (a mol%), LiO^tBu (b equiv), LiCl (1.0 equiv) in DMF (2 mL, c = 0.1 mol/mL). [b] c = 0.2 mol/mL. [c] Without LiCl.

General procedure for condition optimizations (Tables S1–S4)*:* In an argon-filled glovebox, to a screw capped vial equipped with a magnetic stirring bar were added [Pd] (0.01 mmol, 5 mol%), PPh_3 (0.024 mmol, 12 mol%, if necessary), base (1.0 equiv), LiCl (1.0 equiv), **1a** (0.2 mmol), **2a** (0.4 mmol), and DMF (1 mL). After the vial was sealed, the contents were stirred at the indicated temperature for the indicated time. The vial was removed from the glovebox, diluted with EA (10 mL) and water (10 mL). The aqueous phase was extracted with EA (10 mL × 3) and the combined organic layers were washed with H_2O (10 mL × 3) and brine, then dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the yield was determined by ^1H NMR of the crude mixture using 1,3,5-trimethoxybenzene as an internal standard.

Optimization of Reaction Conditions for the synthesis of Azabicyclo[3.2.2]nonan-ones 6a (Tables S5–S8)

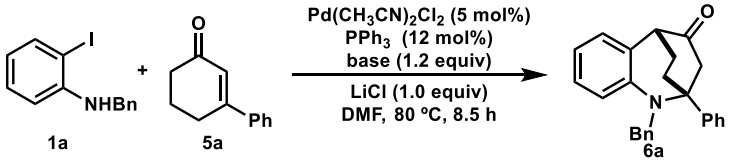
Table S5. Screening of palladium precursors.



entry[a]	[Pd]	yield (%)[b]
1[c]	$Pd(PPh_3)_4$	(49)[d]
2	$Pd(TFA)_2$	60
3	$Pd(OAc)_2$	51
4	$Pd(CH_3CN)_2Cl_2$	67 (65)[d]
5[e]	$Pd_2(dba)_3$	47

[a] Reaction conditions: **1a** (0.2 mmol), **5a** (0.4 mmol), [Pd] (5 mol%), PPh_3 (12 mol%), LiO^{t}Bu (1.2 equiv), LiCl (1.0 equiv) in DMF (2 mL) at 80 °C for 8.5 h. [b] Determined by GC analysis of the crude mixture using biphenyl as an internal standard. [c] Without PPh_3. [d] Isolated yield. [e] With $Pd_2(dba)_3$ (2.5 mol%).

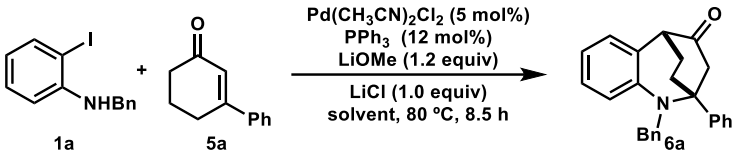
Table S6. Screening of bases.



entry[a]	base	yield (%)[b]
1	LiO^{t}Bu	85
2	NaO^{t}Bu	57
3	KO^{t}Bu	36
4	LiHMDS	75
5	LiOH	87(65)[c]
6	Li_2CO_3	–
7	LiOMe	88 (68)[c]
8	Cs_2CO_3	22
9	K_3PO_4	3

[a] Reaction conditions: **1a** (0.2 mmol), **5a** (0.4 mmol), $Pd(CH_3CN)_2Cl_2$ (5 mol%), PPh_3 (12 mol%), base (1.2 equiv), LiCl (1.0 equiv) in DMF (2 mL) at 80 °C for 8.5 h. [b] Determined by GC analysis of the crude mixture using biphenyl as an internal standard. [c] Isolated yield.

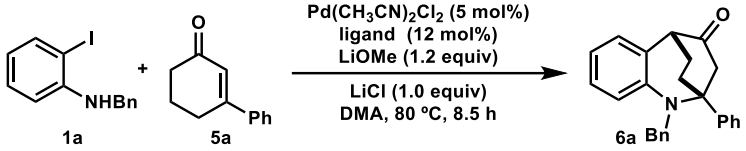
Table S7. Screening of solvents.



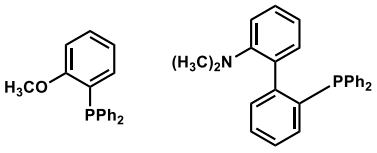
entry[a]	solvent	yield (%)[b]
1	DMF	88 (68)[c]
2	DMA	98 (75)[c]
3	DME	6
4	DCE	–
5	NMP	89
6	EA	–
7	DMSO	87
8	CH_3OH	13
9	1,4-dioxane	–
10	toluene	–

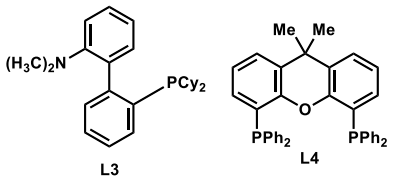
[a] Reaction conditions: **1a** (0.2 mmol), **5a** (0.4 mmol), $Pd(CH_3CN)_2Cl_2$ (5 mol%), PPh_3 (12 mol%), LiOMe (1.2 equiv), LiCl (1.0 equiv) in solvent (2 mL) at 80 °C for 8.5 h. [b] Determined by GC analysis of the crude mixture using biphenyl as an internal standard. [c] Isolated yield.

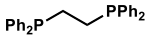
Table S8. Screening of ligands and ratio of substrates.



entry[a]	**1a**/**5a**	ligand	yield (%)[b]
1	1:2	PPh_3	98
2	1:2	PCy_3	89
3	1:2	P(2-furyl)$_3$	29
4	1:2	**L1**	70
5	1:2	**L2**	9
6	1:2	**L3**	19
7[c]	1:2	**L4**	11
8[c]	1:2	**L5**	trace
9	1:1.2	PPh_3	72
10	1.2:1	PPh_3	90
11	2:1	PPh_3	97(81)[c]







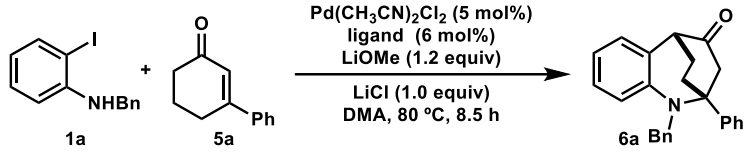
[a] Reaction conditions: **1a**, **5a**, $Pd(CH_3CN)_2Cl_2$ (5 mol%), ligand (12 mol%), LiOMe (1.2 equiv), LiCl (1.0 equiv) in DMA (2 mL) at 80 °C for 8.5 h. [b] Determined by GC analysis of the crude mixture using biphenyl as an internal standard. [c] Isolated yield.

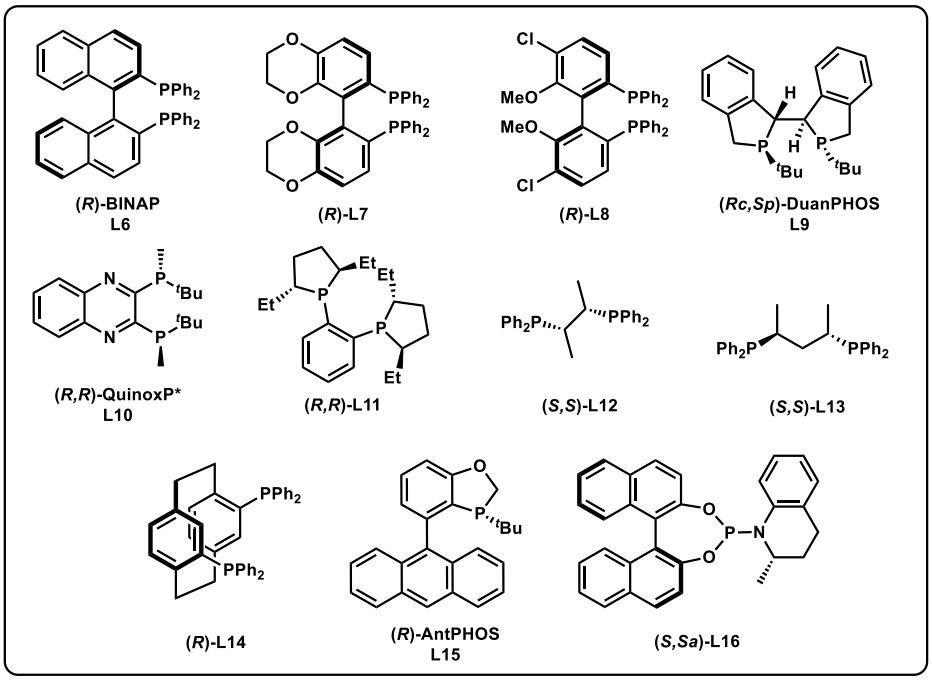
***General procedure for condition optimization (Tables S5–S8)*:** In an argon-filled glovebox, to a screw capped vial equipped with a magnetic stirring bar were added $Pd(CH_3CN)_2Cl_2$ (0.01 mmol, 5 mol%), PPh_3 (0.024 mmol, 12 mol%), LiOMe (0.24 mmol,

1.2 equiv), LiCl (0.2 mmol, 1.0 equiv), **1a** (0.2 mmol, 1.0 equiv), 3-arylcyclohex-2-en-1-one **5a** (0.4 mmol, 2.0 equiv), and DMA (2 mL). The vial was sealed and stirred at 80 °C for 8.5 h. After removed from the glove box, the mixture was diluted with water (10 mL), and extracted with EA (10 mL × 3). Then the combined organic layers were washed with H_2O (10 mL × 3) and brine, and then dried over anhydrous Na_2SO_4. Yield of **6a** was determined by GC analysis using biphenyl as an internal standard.

Asymmetric Evaluation to Azabicyclo[3.2.2]nonan-ones 6a (Tables S9)

Table S9. Evaluation of chiral phosphine ligands.

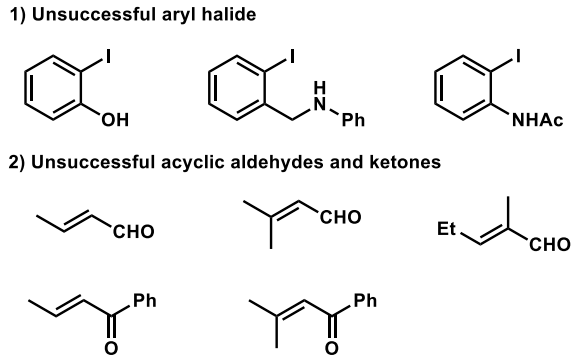




entry[a]	ligand	yield (%)[b]	ee (%)[c]	entry	ligand	yield (%)[b]	ee (%)[c]
1	**L6**	–	–	7	**L12**	67	<1
2	**L7**	30	<1	8	**L13**	45	4
3	**L8**	44	4	9	**L14**	29	5
4	**L9**	–	–	10	**L15**[d]	–	–
5	**L10**	–	–	11	**L16**[d]	11	8
6	**L11**	–	–				

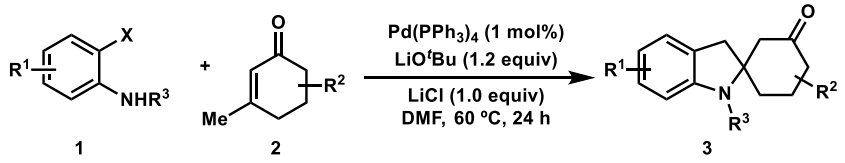
[a] Reaction conditions: **1a**, **5a**, $Pd(CH_3CN)_2Cl_2$ (5 mol%), ligand (6 mol%), LiOMe (1.2 equiv), LiCl (1.0 equiv) in DMA (2 mL) at 80 °C for 8.5 h. [b] Determined by GC analysis of the crude mixture using biphenyl as an internal standard. [c] Determined by HPLC analysis (Chiralpak IB). [d] 12 mol% of ligand.

Scheme S1. Unsuccessful Substrates

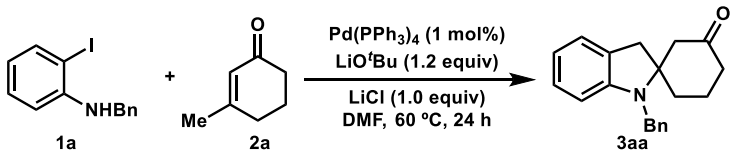


Substrates above were evaluated, either no reaction occurred, or an inseparable mixture was obtained.

General Procedure and Spectroscopic Data for Pd-Catalyzed Cascade Vinylogous Arylation/Aza-Michael Addition Reaction to Construct C2-Spiroindolines

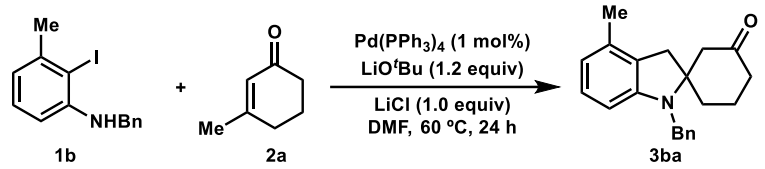


***General procedure*:** In an argon-filled glove box, $Pd(PPh_3)_4$ (0.002 mmol, 1 mol%), LiO^tBu (0.24 mmol, 1.2 equiv), LiCl (0.2 mmol, 1.0 equiv), **1** (0.2 mmol, 1.0 equiv), cyclohexenone **2** (0.4 mmol, 2.0 equiv), and DMF (2 mL) were added to a screw-capped vial equipped with a magnetic stirring bar. The vial was sealed and stirred at 60 °C for 24 h (or 100 °C for 2 h). After removed from the glove box, the mixture was diluted with water (10 mL), and extracted with EA (10 mL × 3). Then the combined organic layers were washed with H_2O (10 mL × 3) and brine, and then dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the crude mixture was purified by silica gel chromatography to provide the desired product **3**.

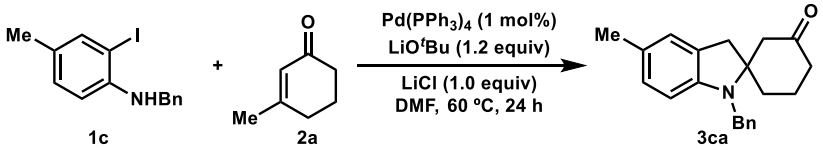


1'-Benzylspiro[cyclohexane-1,2'-indolin]-3-one 3aa: General procedure was followed. The reaction was performed with $Pd(PPh_3)_4$ (2.4 mg, 0.002 mmol, 1 mol%), LiO^tBu (19.9 mg, 0.24 mmol, 1.2 equiv), LiCl (8.6 mg, 0.2 mmol, 1 equiv), **1a** (62.1 mg, 0.2 mmol, 1 equiv), and 3-methylcyclohex-2-en-1-one **2a** (44 μL, 0.4 mmol, 2 equiv) in DMF (2 mL) at 60 °C for 24 h. The desired product **3aa** (46.3 mg, 80%) was obtained as a white solid

after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.5 (PE / EA = 5 / 1); mp: 138 – 142 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.25 – 7.17 (m, 4H), 7.11 (t, *J* = 6.9 Hz, 1H), 6.98 – 6.88 (m, 2H), 6.72 – 6.63 (m, 1H), 6.13 (d, *J* = 7.7 Hz, 1H), 3.86 (AB, *J* = 16.5 Hz, 1H), 3.74 (BA, *J* = 16.5 Hz, 1H), 2.65 (AB, *J* = 15.3 Hz, 1H), 2.46 (BA, *J* = 15.4 Hz, 1H), 2.34 (dt, *J* = 12.9, 2.3 Hz, 1H), 2.15 – 2.06 (m, 1H), 1.91 (d, *J* = 12.9 Hz, 1H), 1.63 (ddd, *J* = 16.5, 11.2, 6.5 Hz, 1H), 1.44 – 1.06 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ 207.0, 150.7, 140.0, 128.9, 128.2, 127.2, 126.9, 126.7, 124.8, 118.2, 107.3, 71.2, 48.8, 47.1, 40.6, 39.8, 33.9, 20.9; HRMS (ESI+): calc'd for $C_{20}H_{21}NNaO$ $[M+Na]^+$: 314.1515; found: 314.1520.

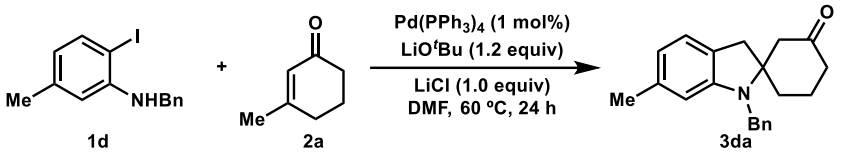


1'-Benzyl-4'-methylspiro[cyclohexane-1,2'-indolin]-3-one 3ba: General procedure was followed. The reaction was performed with $Pd(PPh_3)_4$ (1.2 mg, 0.001 mmol, 1 mol%), LiO^tBu (9.3 mg, 0.12 mmol, 1.2 equiv), LiCl (4.3 mg, 0.1 mmol, 1.0 equiv), **1b** (33.0 mg, 0.1 mmol, 1.0 equiv), and 3-methylcyclohex-2-en-1-one **2a** (22 μL, 0.2 mmol, 2.0 equiv) in DMF (1 mL) at 60 °C for 24 h. The desired product **3ba** (25.0 mg, 82%) was obtained as a yellow solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.5 (PE / EA = 5 / 1); mp: 104 – 106 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.26 (d, *J* = 7.1 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 7.1 Hz, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 6.03 (d, *J* = 7.8 Hz, 1H), 3.89 (AB, *J* = 16.5 Hz, 1H), 3.79 (BA, *J* = 16.5 Hz, 1H), 2.69 (AB, *J* = 15.3 Hz, 1H), 2.43 (BA, *J* = 15.4 Hz, 1H), 2.36 (dt, *J* = 12.8, 2.3 Hz, 1H), 2.18 – 2.08 (m, 1H), 2.01 (s, 3H), 1.95 (d, *J* = 12.8 Hz, 1H), 1.65 (td, *J* = 13.6, 6.3 Hz, 1H), 1.46 – 1.38 (m, 1H), 1.37 – 1.11 (m, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 207.2, 150.5, 140.2, 133.9, 128.9, 128.3, 127.2, 126.9, 125.0, 119.7, 104.9, 71.0, 49.2, 47.2, 40.6, 38.6, 34.1, 20.9, 18.6; HRMS (ESI+): calc'd for $C_{21}H_{23}NNaO$ $[M+Na]^+$: 328.1672; found: 328.1666.

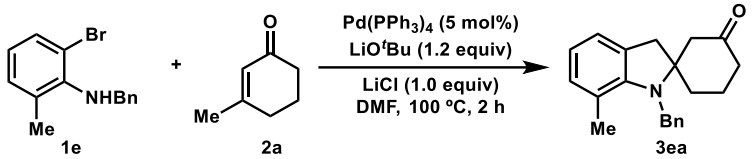


1'-Benzyl-5'-methylspiro[cyclohexane-1,2'-indolin]-3-one 3ca: General procedure was followed. The reaction was performed with $Pd(PPh_3)_4$ (2.2 mg, 0.002 mmol, 1 mol%), LiO^tBu (19.6 mg, 0.24 mmol, 1.2 equiv), LiCl (8.8 mg, 0.2 mmol, 1.0 equiv), **1c** (64.8 mg, 0.2 mmol, 1.0 equiv), and 3-methylcyclohex-2-en-1-one **2a** (44 μL, 0.4 mmol, 2.0 equiv) in DMF (2 mL) at 60 °C for 24 h. The desired product **3ca** (46.8 mg, 77%) was obtained as a white solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.5 (PE / EA = 5 / 1); mp: 92 – 93 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.27 (d, *J* = 7.1 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.78 – 6.71 (m, 2H), 6.08 (d, *J* = 8.3 Hz, 1H), 3.87 (AB, *J* = 16.4 Hz, 1H), 3.73 (BA, *J* = 16.4

Hz, 1H), 2.67 (AB, J = 15.2 Hz, 1H), 2.49 (BA, J = 15.3 Hz, 1H), 2.38 (dt, J = 12.8, 2.3 Hz, 1H), 2.17 (s, 3H), 2.16 – 2.10 (m, 1H), 1.92 (d, J = 12.8 Hz, 1H), 1.65 (td, J = 13.5, 6.3 Hz, 1H), 1.49 – 1.14 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ 207.2, 148.7, 140.2, 128.8, 128.2, 127.2, 127.02, 127.00, 126.9, 125.8, 107.1, 71.5, 48.5, 47.5, 40.6, 39.8, 33.9, 21.0, 20.9; HRMS (ESI+): calc'd for $C_{21}H_{23}NNaO$ $[M+Na]^+$: 328.1672; found: 328.1673.

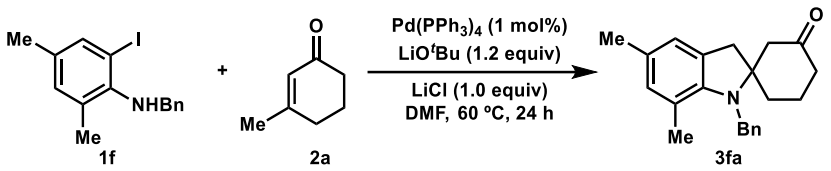


1'-Benzyl-6'-methylspiro[cyclohexane-1,2'-indolin]-3-one 3da: General procedure was followed. The reaction was performed with $Pd(PPh_3)_4$ (2.5 mg, 0.002 mmol, 1 mol%), LiO^tBu (19.3 mg, 0.24 mmol, 1.2 equiv), LiCl (8.7 mg, 0.2 mmol, 1.0 equiv), **1d** (64.8 mg, 0.2 mmol, 1.0 equiv), and 3-methylcyclohex-2-en-1-one **2a** (44 μL, 0.4 mmol, 2.0 equiv) in DMF (2 mL) at 60 °C for 24 h. The desired product **3da** (50.5 mg, 83%) was obtained as a white solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.6 (PE / EA = 5 / 1); mp: 89 – 91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 7.1 Hz, 2H), 7.20 (t, J = 7.5 Hz, 2H), 7.11 (t, J = 7.2 Hz, 1H), 6.89 (d, J = 7.3 Hz, 1H), 6.53 (d, J = 7.3 Hz, 1H), 6.06 (s, 1H), 3.90 (AB, J = 16.6 Hz, 1H), 3.80 (BA, J = 16.6 Hz, 1H), 2.66 (AB, J = 15.2 Hz, 1H), 2.47 (BA, J = 15.2 Hz, 1H), 2.38 (dt, J = 12.9, 2.3 Hz, 1H), 2.17 – 2.08 (m, 1H), 2.06 (s, 3H), 1.93 (d, J = 12.9 Hz, 1H), 1.64 (td, J = 13.6, 6.2 Hz, 1H), 1.46 – 1.08 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ 207.1, 151.0, 140.2, 137.6, 128.9, 127.2, 126.8, 124.7, 123.9, 118.8, 107.9, 71.5, 48.7, 47.0, 40.6, 39.5, 34.0, 21.8, 21.0; HRMS (ESI+): calc'd for $C_{21}H_{23}NNaO$ $[M+Na]^+$: 328.1672; found: 328.1674.

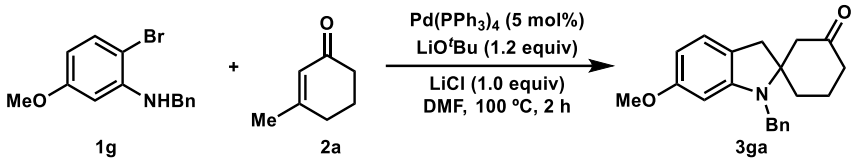


1'-Benzyl-7'-methylspiro[cyclohexane-1,2'-indolin]-3-one 3ea: General procedure was followed. General procedure was followed. The reaction was performed with $Pd(PPh_3)_4$ (11.8 mg, 0.01 mmol, 5 mol%), LiO^tBu (19.1 mg, 0.24 mmol, 1.2 equiv), LiCl (8.3 mg, 0.2 mmol, 1.0 equiv), **1e** (54.6 mg, 0.2 mmol, 1.0 equiv), and 3-methylcyclohex-2-en-1-one **2a** (44 μL, 0.4 mmol, 2.0 equiv) in DMF (2 mL) at 100 °C for 2 h. The desired product **3ea** (49.1 mg, 80%) was obtained as a white solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.5 (PE / EA = 5 / 1); mp: 103 – 105 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.24 – 7.13 (m, 4H), 7.09 (t, J = 6.8 Hz, 1H), 6.88 (d, J = 7.1 Hz, 1H), 6.79 (d, J = 7.1 Hz, 1H), 6.69 (t, J = 7.3 Hz, 1H), 4.35 (AB, J = 18.3 Hz, 1H), 4.07 (BA, J = 18.3 Hz, 1H), 2.66 (AB, J = 15.3 Hz, 1H), 2.45 (BA, J = 15.3 Hz, 1H), 2.40 (dt, J = 12.9, 2.3 Hz, 1H), 2.12 – 1.98 (m, 2H), 2.06 (s, 3H), 1.56 (td, J = 13.4, 6.3 Hz, 1H), 1.41 – 1.30 (m, 1H), 1.30 – 1.20 (m, 2H), 1.20 – 1.04 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 207.2, 148.5, 142.8, 132.3, 128.8, 127.1, 126.9, 126.3, 123.2, 118.4, 117.2, 70.4, 49.5, 47.2, 40.5, 40.1, 34.3, 20.9, 19.2; HRMS (ESI+): calc'd for

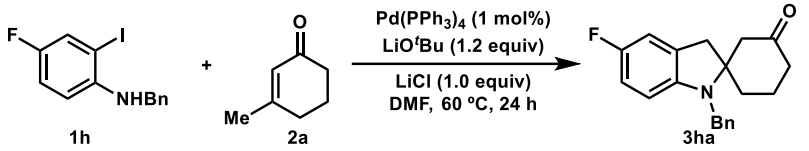
$C_{21}H_{23}NNaO$ $[M+Na]^+$: 328.1672; found: 328.1675.



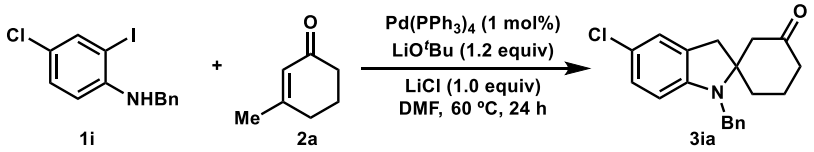
1'-Benzyl-5',7'-dimethylspiro[cyclohexane-1,2'-indolin]-3-one 3fa: General procedure was followed. The reaction was performed with $Pd(PPh_3)_4$ (2.7 mg, 0.002 mmol, 1 mol%), LiO^tBu (19.3 mg, 0.24 mmol, 1.2 equiv), LiCl (9.3 mg, 0.2 mmol, 1.0 equiv), **1f** (72.0 mg, 0.2 mmol, 1.0 equiv), and 3-methylcyclohex-2-en-1-one **2a** (44 μL, 0.4 mmol, 2.0 equiv) in DMF (2 mL) at 60 °C for 24 h. The desired product **3fa** (51.5 mg, 75%) was obtained as a white solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.5 (PE / EA = 5 / 1); mp: 119 – 121 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.25 (d, *J* = 7.1 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.67 (s, 1H), 6.59 (s, 1H), 4.33 (AB, *J* = 18.1 Hz, 1H), 4.06 (BA, *J* = 18.2 Hz, 1H), 2.67 (AB, *J* = 15.2 Hz, 1H), 2.54 – 2.40 (m, 2H), 2.20 (s, 3H), 2.12 – 1.97 (m, 5H), 1.58 (td, *J* = 13.4, 6.3 Hz, 1H), 1.45 – 1.07 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ 207.5, 146.8, 143.0, 132.6, 128.8, 127.6, 127.3, 126.9, 126.5, 124.0, 117.3, 70.7, 49.4, 47.6, 40.6, 40.2, 34.3, 21.0, 20.7, 19.0; HRMS (ESI+): calc'd for $C_{22}H_{25}NNaO$ $[M+Na]^+$: 342.1828; found: 342.1833.



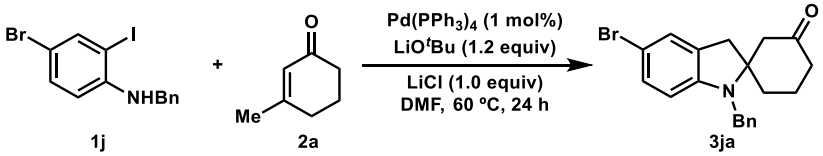
1'-Benzyl-6'-methoxyspiro[cyclohexane-1,2'-indolin]-3-one 3ga: General procedure was followed with slight modification. The reaction was performed with $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 5 mol%), LiO^tBu (18.8 mg, 0.24 mmol, 1.2 equiv), LiCl (8.4 mg, 0.2 mmol, 1.0 equiv), **1g** (63.1 mg, 0.2 mmol, 1.0 equiv), and 3-methylcyclohex-2-en-1-one **2a** (44 μL, 0.4 mmol, 2.0 equiv) in DMF (2 mL) at 100 °C for 2 h. The desired product **3ga** (52.3 mg, 81%) was obtained as a white solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.5 (PE / EA = 5 / 1); mp: 105 – 108 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.22 (d, *J* = 7.2 Hz, 2H), 7.19 – 7.14 (m, 2H), 7.09 (t, *J* = 7.1 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.21 (d, *J* = 7.9 Hz, 1H), 5.97 (s, 1H), 3.85 (AB, *J* = 16.5 Hz, 1H), 3.74 (BA, *J* = 16.4 Hz, 1H), 3.30 (s, 3H), 2.65 (AB, *J* = 14.9 Hz, 1H), 2.46 (BA, *J* = 14.9 Hz, 1H), 2.39 (dt, *J* = 12.8, 2.0 Hz, 1H), 2.17 – 2.07 (m, 1H), 1.92 (d, *J* = 12.8 Hz, 1H), 1.72 – 1.58 (m, 1H), 1.41 (d, *J* = 12.7 Hz, 1H), 1.37 – 1.11 (m, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 207.0, 161.2, 152.1, 139.9, 128.9, 127.2, 126.9, 124.9, 119.0, 101.7, 95.4, 71.9, 54.8, 48.8, 47.0, 40.6, 39.1, 34.0, 21.0; HRMS (ESI+): calc'd for $C_{21}H_{23}NNaO_2$ $[M+Na]^+$: 344.1621; found: 344.1618.



1'-Benzyl-5'-fluorospiro[cyclohexane-1,2'-indolin]-3-one 3ha: General procedure was followed. The reaction was performed with $Pd(PPh_3)_4$ (2.5 mg, 0.002 mmol, 1 mol%), LiO^tBu (19.5 mg, 0.24 mmol, 1.2 equiv), LiCl (8.4 mg, 0.2 mmol, 1.0 equiv), **1h** (64.6 mg, 0.2 mmol, 1.0 equiv), and 3-methylcyclohex-2-en-1-one **2a** (44 μL, 0.4 mmol, 2.0 equiv) in DMF (2 mL) at 60 °C for 24 h. The desired product **3ha** (45.6 mg, 74%) was obtained as yellow liquid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.5 (PE / EA = 5 / 1); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.42 (d, J = 7.1 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.25 (t, J = 7.3 Hz, 1H), 6.91 – 6.84 (m, 1H), 6.67 – 6.59 (m, 1H), 5.98 (dd, J = 8.5, 4.2 Hz, 1H), 4.52 (AB, J = 16.4 Hz, 1H), 4.18 (BA, J = 16.4 Hz, 1H), 2.93 (AB, J = 15.7 Hz, 1H), 2.79 (BA, J = 15.6 Hz, 1H), 2.83 (d, J = 12.6 Hz, 1H), 2.46 (td, J = 13.8, 6.6 Hz, 1H), 2.33 – 2.19 (m, 3H), 2.12 – 2.03 (m, 1H), 2.02 – 1.92 (m, 1H), 1.78 – 1.64 (m, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 208.8, 157.0 (d, J = 232.2 Hz), 148.0, 140.7, 129.6 (d, J = 8.4 Hz), 129.3, 127.6, 127.5, 113.5 (d, J = 22.9 Hz), 112.9 (d, J = 24.5 Hz), 107.1 (d, J = 8.2 Hz), 72.9, 49.0, 47.9, 41.0, 40.2, 34.2, 21.7; ^{19}F NMR (376 MHz, acetone-d_6) δ –129.5; HRMS (ESI+): calc'd for $C_{20}H_{20}FNNaO$ $[M+Na]^+$: 332.1421; found: 332.1428.

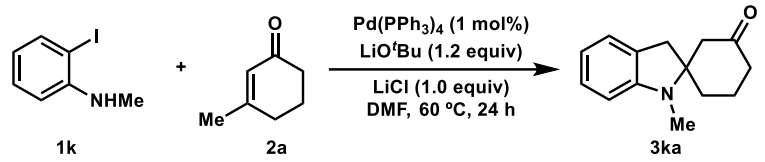


1'-Benzyl-5'-chlorospiro[cyclohexane-1,2'-indolin]-3-one 3ia: General procedure was followed. The reaction was performed with $Pd(PPh_3)_4$ (2.4 mg, 0.002 mmol, 1 mol%), LiO^tBu (19.5 mg, 0.24 mmol, 1.2 equiv), LiCl (8.4 mg, 0.2 mmol, 1.0 equiv), **1i** (69.0 mg, 0.2 mmol, 1.0 equiv), and 3-methylcyclohex-2-en-1-one **2a** (44 μL, 0.4 mmol, 2.0 equiv) in DMF (2 mL) at 60 °C for 24 h. The desired product **3ia** (43.9 mg, 68%) was obtained as a white solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.4 (PE / EA = 5 / 1); mp: 116 – 118 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.23 – 7.08 (m, 5H), 6.90 – 6.83 (m, 2H), 5.81 (d, J = 8.1 Hz, 1H), 3.75 (AB, J = 16.6 Hz, 1H), 3.60 (BA, J = 16.5 Hz, 1H), 2.44 (AB, J = 15.7 Hz, 1H), 2.28 – 2.21 (m, 2H), 2.04 – 2.14 (m, 1H), 1.84 (d, J = 12.9 Hz, 1H), 1.60 (td, J = 13.6, 6.5 Hz, 1H), 1.36 – 1.01 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ 206.6, 149.1, 139.3, 128.9, 128.7, 127.7, 127.4, 126.7, 125.2, 122.6, 107.6, 71.5, 48.7, 46.9, 40.5, 39.3, 33.7, 20.7; HRMS (ESI+): calc'd for $C_{20}H_{20}ClNNaO$ $[M+Na]^+$: 348.1126; found: 348.1120.

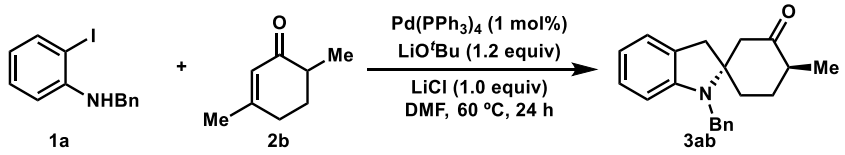


1'-Benzyl-5'-bromospiro[cyclohexane-1,2'-indolin]-3-one 3ja: General procedure was

followed. The reaction was performed with $Pd(PPh_3)_4$ (2.3 mg, 0.002 mmol, 1 mol%), LiO^{t}Bu (18.8 mg, 0.24 mmol, 1.2 equiv), LiCl (8.4 mg, 0.2 mmol, 1.0 equiv), **1j** (76.6 mg, 0.2 mmol, 1.0 equiv), and 3-methylcyclohex-2-en-1-one **2a** (44 μL, 0.4 mmol, 2.0 equiv) in DMF (2 mL) at 60 °C for 24 h. The desired product **3ja** (39.0 mg, 53%) was obtained as a white solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.5 (PE / EA = 5 / 1); mp: 128 – 130 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.22 – 7.15 (m, 2H), 7.14 – 7.08 (m, 3H), 7.03 – 6.95 (m, 2H), 5.76 (d, *J* = 8.2 Hz, 1H), 3.74 (AB, *J* = 16.6 Hz, 1H), 3.59 (BA, *J* = 16.6 Hz, 1H), 2.43 (AB, *J* = 15.7 Hz, 1H), 2.28 – 2.19 (m, 2H), 2.13 – 2.01 (m, 1H), 1.83 (d, *J* = 12.9 Hz, 1H), 1.59 (td, *J* = 13.6, 6.4 Hz, 1H), 1.34 – 0.98 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ 206.5, 149.5, 139.3, 130.6, 129.1, 128.9, 128.0, 127.4, 126.7, 109.6, 108.2, 71.4, 48.7, 46.8, 40.4, 39.3, 33.7, 20.7; HRMS (ESI+): calc'd for $C_{20}H_{20}BrNNaO$ $[M+Na]^+$: 392.0620; found: 392.0617.

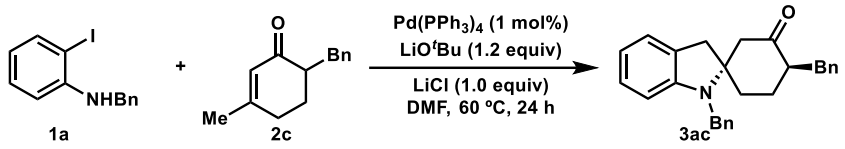


1'-Methylspiro[cyclohexane-1,2'-indolin]-3-one 3ka: General procedure was followed. The reaction was performed with $Pd(PPh_3)_4$ (2.4 mg, 0.002 mmol, 1 mol%), LiO^{t}Bu (20.2 mg, 0.24 mmol, 1.2 equiv), LiCl (8.4 mg, 0.2 mmol, 1.0 equiv), **1k** (48.2 mg, 0.2 mmol, 1.0 equiv), and 3-methylcyclohex-2-en-1-one **2a** (44 μL, 0.4 mmol, 2.0 equiv) in DMF (2 mL) at 60 °C for 24 h. The desired product **3ka** (40.2 mg, 93%) was obtained as a colorless liquid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.5 (PE / EA = 5 / 1); ^{1}H NMR (400 MHz, C_6D_6) δ 7.12 (t, *J* = 7.7 Hz, 1H), 6.92 (dd, *J* = 7.1, 0.7 Hz, 1H), 6.72 (td, *J* = 7.5, 0.8 Hz, 1H), 6.25 (d, *J* = 7.8 Hz, 1H), 2.55 (AB, *J* = 15.3 Hz, 1H), 2.36 (BA, *J* = 15.3 Hz, 1H), 2.23 (s, 3H), 2.21 – 2.15 (m, 1H), 2.15 – 2.06 (m, 1H), 1.94 (AB, *J* = 12.8 Hz, 1H), 1.65 (tdd, *J* = 13.7, 6.3, 0.7 Hz, 1H), 1.41 – 1.24 (m, 3H), 1.22 – 1.06 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 207.3, 151.5, 127.0, 124.8, 118.0, 106.4, 70.9, 47.5, 40.6, 39.4, 32.9, 28.0, 20.9; HRMS (ESI+): calc'd for $C_{14}H_{17}NNaO$ $[M+Na]^+$: 238.1202; found: 238.1203.

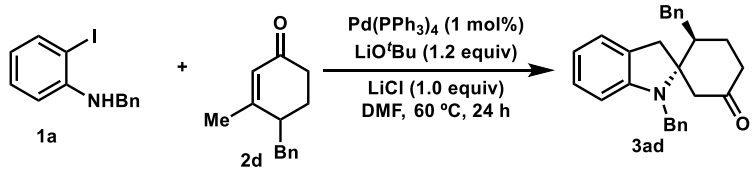


1'-Benzyl-4-methylspiro[cyclohexane-1,2'-indolin]-3-one 3ab: General procedure was followed. The reaction was performed with $Pd(PPh_3)_4$ (2.4 mg, 0.002 mmol, 1 mol%), LiO^{t}Bu (19.2 mg, 0.24 mmol, 1.2 equiv), LiCl (8.4 mg, 0.2 mmol, 1.0 equiv), **1a** (62.7 mg, 0.2 mmol, 1.0 equiv), and 3,6-dimethylcyclohex-2-en-1-one **2b** (49.5 mg, 0.4 mmol, 2.0 equiv) in DMF (2 mL) at 60 °C for 24 h. The desired product **3ab** (47.2 mg, 74%) was obtained as a white solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.5 (PE / EA = 5 / 1); mp: 125 – 127 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.28 – 7.17 (m, 4H), 7.12 (t, *J* = 7.1 Hz, 1H), 6.93 (t, *J* = 7.8 Hz, 2H), 6.69 (t, *J* = 6.9 Hz, 1H), 6.15 (d, *J* = 7.7 Hz, 1H), 3.92 (AB, *J* = 16.5 Hz, 1H), 3.79 (BA, *J* = 16.5

Hz, 1H), 2.66 (AB, J = 15.4 Hz, 1H), 2.44 (BA, J = 15.4 Hz, 1H), 2.36 (AB, J = 12.3 Hz, 1H), 1.96 (BA, J = 12.3 Hz, 1H), 1.77 – 1.63 (m, 1H), 1.54 – 1.31 (m, 3H), 1.01 (d, J = 6.5 Hz, 3H), 0.99 – 0.83 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 208.2, 150.7, 140.0, 128.9, 127.2, 126.9, 126.8, 124.9, 118.2, 107.1, 71.9, 48.6, 47.1, 44.1, 39.7, 34.5, 30.1, 14.4; HRMS (ESI+): calc'd for $C_{21}H_{23}NNaO$ $[M+Na]^+$: 328.1672; found: 328.1677.

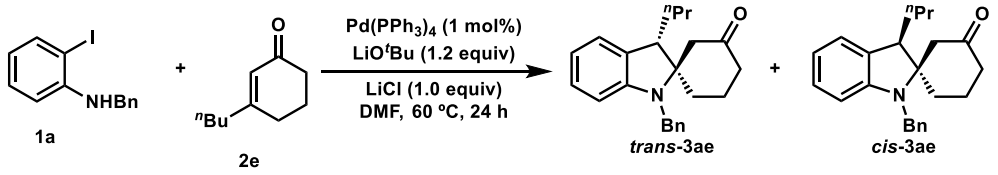


1',4-Dibenzylspiro[cyclohexane-1,2'-indolin]-3-one 3ac: General procedure was followed. The reaction was performed with $Pd(PPh_3)_4$ (2.4 mg, 0.002 mmol, 1 mol%), LiO^tBu (19.2 mg, 0.24 mmol, 1.2 equiv), LiCl (8.4 mg, 0.2 mmol, 1.0 equiv), **1a** (62.7 mg, 0.2 mmol, 1.0 equiv), and 6-benzyl-3-methylcyclohex-2-en-1-one **2c** (82.0 mg, 0.4 mmol, 2.0 equiv) in DMF (2 mL) at 60 °C for 24 h. The desired product **3ac** (61.7 mg, 81%) was obtained as a white solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.5 (PE / EA = 5 / 1); mp: 132 – 136 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.25 – 7.17 (m, 6H), 7.14 – 7.08 (m, 4H), 6.89 – 6.99 (m, 2H), 6.70 (t, J = 7.0 Hz, 1H), 6.14 (d, J = 7.8 Hz, 1H), 3.86 (AB, J = 16.6 Hz, 1H), 3.75 (BA, J = 16.6 Hz, 1H), 3.33 (dd, J = 13.9, 5.1 Hz, 1H), 2.73 (AB, J = 15.4 Hz, 1H), 2.45 (BA, J = 15.4 Hz, 1H), 2.40 – 2.32 (m, 2H), 2.09 – 1.94 (m, 1H), 1.90 (d, J = 12.2 Hz, 1H), 1.52 – 1.42 (m, 1H), 1.39 – 1.30 (m, 1H), 1.20 (td, J = 13.2, 4.2 Hz, 1H), 0.97 – 0.83 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 207.4, 150.7, 140.9, 140.0, 129.6, 128.9, 128.7, 127.9, 127.2, 126.8, 126.7, 126.4, 124.7, 118.2, 107.1, 72.0, 51.6, 48.9, 47.1, 39.7, 35.6, 34.4, 27.8; HRMS (ESI+): calc'd for $C_{27}H_{27}NNaO$ $[M+Na]^+$: 404.1985; found: 404.1989.



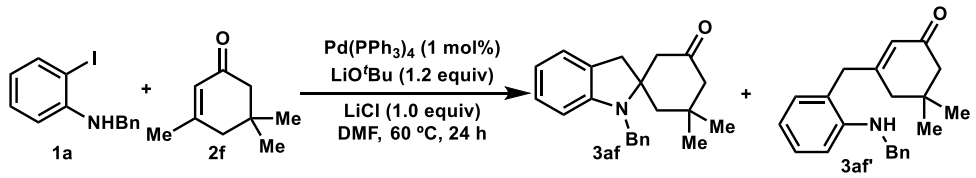
1',2-Dibenzylspiro[cyclohexane-1,2'-indolin]-5-one 3ad: General procedure was followed. The reaction was performed with $Pd(PPh_3)_4$ (2.3 mg, 0.002 mmol, 1 mol%), LiO^tBu (19.3 mg, 0.24 mmol, 1.2 equiv), LiCl (8.8 mg, 0.2 mmol, 1.0 equiv), **1a** (62.2 mg, 0.2 mmol, 1.0 equiv), and 4-benzyl-3-methylcyclohex-2-en-1-one **2d** (81.2 mg, 0.4 mmol, 2.0 equiv) in DMF (2 mL) at 60 °C for 24 h. The desired product **3ad** (56.1 mg, 74%) was obtained as a white solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.5 (PE / EA = 5 / 1); mp: 131 – 133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.3 Hz, 2H), 7.37 (t, J = 7.4 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 7.25 – 7.15 (m, 3H), 7.12 (d, J = 7.1 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 6.5 Hz, 2H), 6.69 (t, J = 7.3 Hz, 1H), 6.23 (d, J = 7.8 Hz, 1H), 4.58 (AB, J = 16.7 Hz, 1H), 4.37 (BA, J = 16.7 Hz, 1H), 3.22 (d, J = 12.1 Hz, 1H), 3.15 (AB, J = 15.8 Hz, 1H), 2.78 (BA, J = 15.8 Hz, 1H), 2.67 – 2.50 (m, 2H), 2.39 – 2.30 (m, 1H), 2.30 – 2.11 (m, 3H), 2.05 – 1.95 (m, 1H), 1.43 (ddd, J = 25.7, 13.7, 4.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 150.9, 140.6, 138.8, 129.2, 128.9, 128.5, 127.8, 127.2, 126.9, 126.3,

126.2, 124.7, 117.9, 107.0, 74.1, 50.2, 46.9, 44.6, 41.0, 36.5, 34.6, 26.0; HRMS (ESI+): calc'd for $C_{27}H_{27}NNaO$ $[M+Na]^+$: 404.1985; found: 404.1985.



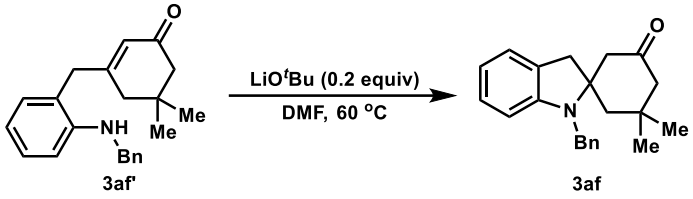
1'-Benzyl-3'-propylspiro[cyclohexane-1,2'-indolin]-3-one **3ae**: General procedure was followed. The reaction was performed with $Pd(PPh_3)_4$ (2.6 mg, 0.002 mmol, 1 mol%), LiO^tBu (19.4 mg, 0.24 mmol, 1.2 equiv), LiCl (8.6 mg, 0.2 mmol, 1.0 equiv), **1a** (62.1 mg, 0.2 mmol, 1.0 equiv), and 3-butylcyclohex-2-en-1-one **2e** (61.7 mg, 0.4 mmol, 2.0 equiv) in DMF (2 mL) at 60 °C for 24 h. A mixture of diastereoisomers were obtained after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). The stereochemistry was assigned by 2D-NOESY experiments.

The desired product cis-**3ae** (19.1 mg, 29%) and trans-**3ae** (21.9, 33%) was obtained. For cis-**3ae**: yellow liquid; R_f = 0.5 (PE / DCM = 1 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 4H), 7.28 – 7.18 (m, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.97 (td, *J* = 7.7, 1.3 Hz, 1H), 6.64 (td, *J* = 7.4, 1.0 Hz, 1H), 6.16 (dd, *J* = 7.8, 0.9 Hz, 1H), 4.45 (AB, *J* = 16.5 Hz, 1H), 4.11 (BA, *J* = 16.5 Hz, 1H), 2.94 – 2.80 (m, 2H), 2.56 (d, *J* = 13.9 Hz, 1H), 2.46 – 2.36 (m, 1H), 2.36 – 2.18 (m, 1H), 2.03 – 1.89 (m, 1H), 1.88 – 1.77 (m, 1H), 1.70 – 1.43 (m, 4H), 1.38 – 1.25 (m, 2H), 0.94 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 149.4, 139.5, 131.5, 128.8, 127.8, 127.1, 126.6, 125.4, 117.3, 107.2, 73.9, 47.4, 47.0, 46.8, 40.8, 32.2, 30.2, 20.5, 20.3, 14.3; HRMS (ESI+): calc'd for $C_{23}H_{28}NO$ $[M+H]^+$: 334.2165; found: 334.2155. For *trans*-**3ae**: colorless liquid; R_f = 0.3 (PE / DCM = 1 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 4H), 7.22 – 7.12 (m, 1H), 7.01 (dd, *J* = 7.2, 1.3 Hz, 1H), 6.89 (td, *J* = 7.7, 1.4 Hz, 1H), 6.57 (td, *J* = 7.4, 1.0 Hz, 1H), 6.10 (d, *J* = 8.0 Hz, 1H), 4.36 (AB, *J* = 16.3 Hz, 1H), 3.90 (BA, *J* = 16.3 Hz, 1H), 2.59 (dd, *J* = 10.9, 2.9 Hz, 1H), 2.45 – 2.22 (m, 4H), 2.21 – 2.11 (m, 1H), 2.10 – 1.971 (m, 1H), 1.89 (td, *J* = 13.6, 4.0 Hz, 1H), 1.71 – 1.53 (m, 1H), 1.53 – 1.31 (m, 3H), 1.30 – 1.12 (m, 1H), 0.84 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 149.7, 139.8, 131.6, 128.8, 127.8, 127.1, 126.7, 125.9, 117.7, 107.5, 74.1, 47.4, 47.2, 46.7, 41.3, 30.7, 29.2, 21.6, 20.0, 14.3; HRMS (ESI+): calc'd for $C_{23}H_{28}NO$ $[M+H]^+$: 334.2165; found: 334.2161.

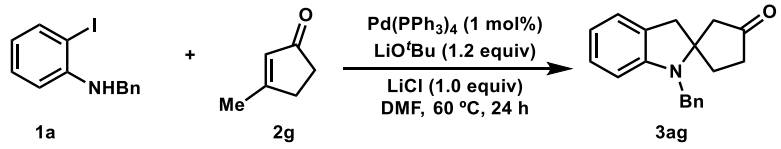


1'-Benzyl-3,3-dimethylspiro[cyclohexane-1,2'-indolin]-5-one 3af and 3-(2-(benzylamino)benzyl)-5,5-dimethylcyclohex-2-en-1-one 3af': General procedure was followed. The reaction was performed with $Pd(PPh_3)_4$ (2.4 mg, 0.002 mmol, 1 mol%), LiO^tBu (19.4 mg, 0.24 mmol, 1.2 equiv), LiCl (8.7 mg, 0.2 mmol, 1.0 equiv), **1a** (61.8 mg, 0.2 mmol, 1.0 equiv), and isophorone **2f** (56.3 mg, 0.4 mmol, 2.0 equiv) in DMF (2

mL) at 60 °C for 24 h. The desired products **3af** (29.1 mg, 46%) and **3af'** (26.5 mg, 42%) were obtained after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). For **3af**: white solid; R_f = 0.5 (PE / EA = 5 / 1); mp: 158 – 160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 4H), 7.27 (t, *J* = 7.0 Hz, 1H), 7.06 (d, *J* = 7.1 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.08 (d, *J* = 7.8 Hz, 1H), 4.49 (AB, *J* = 16.4 Hz, 1H), 4.08 (BA, *J* = 16.4 Hz, 1H), 3.03 (s, 2H), 2.55 – 2.40 (m, 2H), 2.34 (d, *J* = 12.8 Hz, 1H), 2.21 – 2.11 (m, 2H), 1.97 (d, *J* = 13.9 Hz, 1H), 1.15 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 149.7, 139.2, 128.8, 127.7, 127.2, 127.1, 126.5, 124.6, 117.7, 106.9, 71.6, 54.4, 47.9, 47.3, 46.8, 42.3, 33.9, 33.8, 27.5; HRMS (ESI+): calc'd for $C_{22}H_{25}NNaO$ $[M+Na]^+$: 342.1828; found: 342.1828. For **3af'**: colorless liquid; R_f = 0.3 (PE / EA = 5 / 1); ^{1}H NMR (400 MHz, C_6D_6) δ 7.18 (d, *J* = 4.4 Hz, 4H), 7.14 – 7.04 (m, 2H), 6.88 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.74 (td, *J* = 7.4, 1.1 Hz, 1H), 6.57 (d, *J* = 7.5 Hz, 1H), 5.94 (t, *J* = 1.4 Hz, 1H), 3.98 (s, 2H), 3.68 (br, 1H), 2.96 (s, 2H), 2.01 (s, 2H), 1.62 (s, 2H), 0.63 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 197.6, 159.5, 146.6, 139.6, 131.1, 129.0, 128.8, 127.7, 127.6, 126.3, 121.2, 117.9, 111.6, 51.2, 48.3, 43.0, 40.9, 33.2, 28.0; HRMS (ESI+): calc'd for $C_{22}H_{25}NNaO$ $[M+Na]^+$: 342.1828; found: 342.1833.

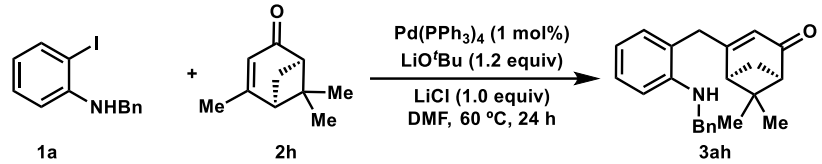


Procedure: In an argon-filled glovebox, to a screw capped vial equipped with a magnetic stirring bar were LiO^{t}Bu (1.2 equiv), intermediate **3af'** (0.1 mmol), and DMF (1 mL). After the vial was sealed, the contents were stirred at 60 °C for 24 h. The vial was removed from the glovebox, diluted with EA (10 mL) and water (10 mL). The aqueous phase was extracted with EA (10 mL × 3) and the combined organic layers were washed with H_2O (10 mL × 3) and brine, then dried over anhydrous Na_2SO_4. EA (1 mL) solution of 1,3,5-trimethoxybenzene (5.6 mg / mL) was added, and the solvents were removed under reduced pressure. Yield of **3af** was determined as 24% by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.



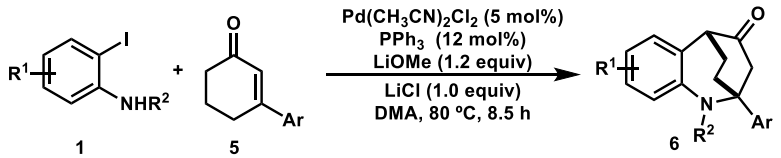
1'-Benzylspiro[cyclopentane-1,2'-indolin]-3-one 3ag: General procedure was followed. The reaction was performed with $Pd(PPh_3)_4$ (3.0 mg, 0.002 mmol, 1 mol%), LiO^{t}Bu (19.7 mg, 0.24 mmol, 1.2 equiv), LiCl (8.5 mg, 0.2 mmol, 1.0 equiv), **1a** (61.6 mg, 0.2 mmol, 1.0 equiv), and 3-methylcyclopent-2-en-1-one **2g** (38.6 mg, 0.4 mmol, 2.0 equiv) in DMF (2 mL) at 60 °C for 24 h. The desired product **3ag** (10.7 mg, 19%) was obtained as a colorless liquid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.3 (PE / EA = 10 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 7.09 (dd, *J* = 7.2, 0.7 Hz, 1H), 6.97 (t, *J* = 7.7 Hz, 1H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.17

(d, J = 7.8 Hz, 1H), 4.33 (AB, J = 16.6 Hz, 1H), 4.27 (BA, J = 16.6 Hz, 1H), 3.16 (AB, J = 15.2 Hz, 1H), 3.06 (BA, J = 15.2 Hz, 1H), 2.52 – 2.34 (m, 4H), 2.33 – 2.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.2, 151.2, 139.1, 128.8, 127.9, 127.2, 126.6, 126.3, 124.5, 117.7, 106.7, 72.2, 47.1, 47.0, 43.0, 37.5, 32.5. HRMS (ESI+): calc'd for $C_{19}H_{20}NO$ $[M+H]^+$: 278.1539; found: 278.1537.



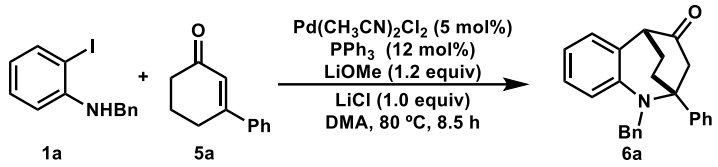
(1*R*,5*S*)-4-(2-(Benzylamino)benzyl)-6,6-dimethylbicyclo[3.1.1]hept-3-en-2-one 3ah: General procedure was followed. The reaction was performed with $Pd(PPh_3)_4$ (3.2 mg, 0.002 mmol, 1 mol%), LiO^tBu (20.4 mg, 0.24 mmol, 1.2 equiv), LiCl (9.2 mg, 0.2 mmol, 1.0 equiv), **1a** (61.8 mg, 0.2 mmol, 1.0 equiv), and cyclohexenone **2h** (61.2 mg, 0.4 mmol, 2.0 equiv) in DMF (2 mL) at 60 °C for 24 h. The desired product **3ah** (19.2 mg, 29%) was obtained as a colorless liquid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.3 (PE / EA = 5 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 7.17 (td, J = 8.0, 1.6 Hz, 1H), 7.01 (dd, J = 7.4, 1.5 Hz, 1H), 6.73 (td, J = 7.4, 0.9 Hz, 1H), 6.67 (d, J = 8.1 Hz, 1H), 5.61 (t, J = 1.6 Hz, 1H), 4.30 (s, 2H), 3.80 (br s, 1H), 3.49 (s, 2H), 2.78 (dt, J = 9.2, 5.5 Hz, 1H), 2.65 (td, J = 5.9, 1.7 Hz, 1H), 2.49 (t, J = 6.5 Hz, 1H), 2.02 (d, J = 9.2 Hz, 1H), 1.44 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 170.6, 146.3, 139.0, 131.1, 128.8, 128.7, 127.7, 127.5, 121.2, 120.2, 117.7, 111.3, 58.0, 54.1, 48.5, 48.2, 41.1, 39.9, 26.6, 22.1; HRMS (ESI+): calc'd for $C_{23}H_{26}NO$ $[M+H]^+$: 332.2009; found: 332.2008.

General Procedure and Spectroscopic Data for Pd-Catalyzed Cascade α'-Arylation/Aza-Michael Addition Reaction to Construct Azabicyclo[3.2.2]nonanones

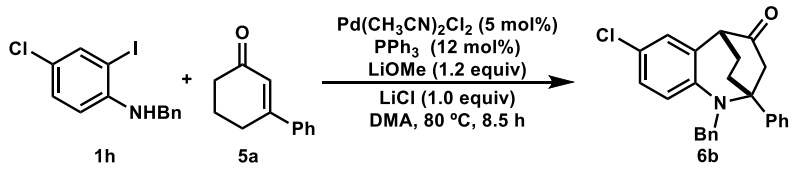


***General procedure*:** In an argon-filled glove box, $Pd(CH_3CN)_2Cl_2$ (0.01 mmol, 5 mol%), PPh_3 (0.024 mmol, 12 mol%), LiOMe (0.24 mmol, 1.2 equiv), LiCl (0.2 mmol, 1.0 equiv), **1** (0.4 mmol, 2.0 equiv), 3-arylcyclohex-2-en-1-one **5** (0.2 mmol, 1.0 equiv), and DMA (2 mL) were added to a screw-capped vial equipped with a magnetic stirring bar. The vial was sealed and stirred at 80 °C for 8.5 h. After removed from the glove box, the mixture was diluted with water (10 mL), and extracted with EA (10 mL × 3). Then the combined organic layers were washed with H_2O (10 mL × 3) and brine, and then dried over

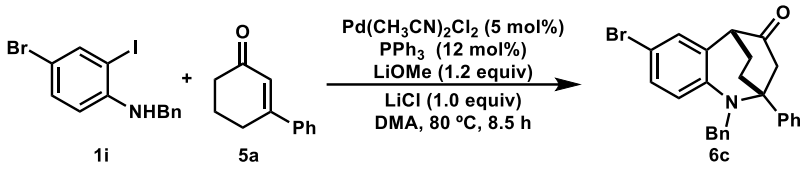
anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the crude mixture was purified by silica gel chromatography to provide the desired product.



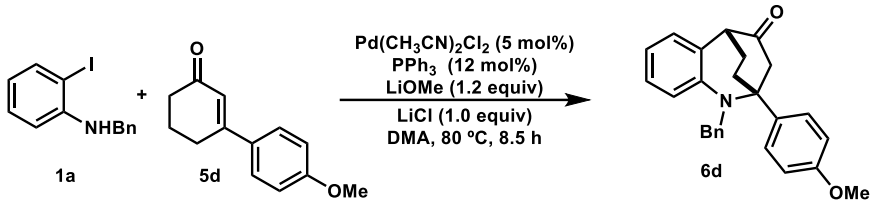
1-Benzyl-2-phenyl-2,3,4,5-tetrahydro-1*H*-2,5-ethanobenzo[*b*]azepin-10-one 6a: General procedure was followed. The reaction was performed with $Pd(CH_3CN)_2Cl_2$ (3.2 mg, 0.01 mmol, 5 mol%), PPh_3 (6.3 mg, 0.024 mmol, 12 mol%), LiOMe (9.5 mg, 0.24 mmol, 1.2 equiv), LiCl (9.0 mg, 0.2 mmol, 1.0 equiv), **1a** (123.1 mg, 0.4 mmol, 2.0 equiv), 3-phenylcyclohex-2-en-1-one **5a** (33.9 mg, 0.2 mmol, 1.0 equiv), and DMA (2 mL) at 80 °C for 8.5 h. The desired product **6a** (56.6 mg, 81%) was obtained as a yellow solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.5 (PE / EA = 5 / 1); mp: 178 – 180 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.50 – 7.42 (m, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.30 (d, J = 7.1 Hz, 1H), 7.28 – 7.24 (m, 4H), 7.20 (d, J = 7.3 Hz, 2H), 6.98 (t, J = 7.7 Hz, 1H), 6.73 (t, J = 7.4 Hz, 1H), 6.13 (d, J = 7.8 Hz, 1H), 4.03 (AB, J = 16.4 Hz, 1H), 3.96 (BA, J = 16.3 Hz, 1H), 3.67 (s, 1H), 3.29 (AB, J = 15.1 Hz, 1H), 2.94 (BA, J = 15.1 Hz, 1H), 2.39 – 2.19 (m, 4H); ^{13}C NMR (100 MHz, acetone-d_6) δ 210.0, 152.7, 145.8, 139.9, 131.7, 129.5, 129.2, 129.0, 128.5, 127.64, 127.55, 126.7, 124.4, 119.2, 108.4, 75.6, 51.1, 50.1, 45.0, 36.4, 26.3; HRMS (ESI+): calc'd for $C_{25}H_{24}NO$ $[M+H]^+$: 354.1852; found: 354.1849.



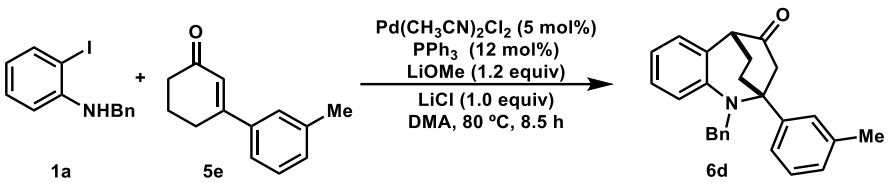
1-Benzyl-7-chloro-2-phenyl-2,3,4,5-tetrahydro-1*H*-2,5-ethanobenzo[*b*]azepin-10-one 6b: General procedure was followed. The reaction was performed with $Pd(CH_3CN)_2Cl_2$ (2.6 mg, 0.01 mmol, 5 mol%), PPh_3 (6.6 mg, 0.024 mmol, 12 mol%), LiOMe (10.1 mg, 0.24 mmol, 1.2 equiv), LiCl (9.2 mg, 0.2 mmol, 1.0 equiv), **1h** (135.2 mg, 0.4 mmol, 2.0 equiv), 3-phenylcyclohex-2-en-1-one **5a** (33.6 mg, 0.2 mmol, 1.0 equiv), and DMA (2 mL) at 80 °C for 8.5 h. The desired product **6b** (37.2 mg, 49%) was obtained as a yellow solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.6 (PE / EA = 5 / 1); mp: 162 – 163 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.45 (d, J = 7.4 Hz, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.34 – 7.18 (m, 7H), 6.99 (dd, J = 8.3, 2.1 Hz, 1H), 6.09 (d, J = 8.3 Hz, 1H), 4.05 (AB, J = 16.4 Hz, 1H), 3.97 (BA, J = 16.4 Hz, 1H), 3.71 (s, 1H), 3.32 (d, J = 15.2 Hz, 1H), 2.98 (BA, J = 15.2 Hz, 1H), 2.40 – 2.21 (m, 4H); ^{13}C NMR (100 MHz, acetone-d_6) δ 209.8, 151.6, 145.5, 139.5, 134.3, 129.7, 129.4, 128.7, 127.80, 127.75, 126.7, 124.9, 123.3, 109.2, 76.0, 51.0, 50.1, 45.0, 36.4, 26.3; HRMS (ESI+): calc'd for $C_{25}H_{23}ClNO$ $[M+H]^+$: 388.1463; found: 388.1451.



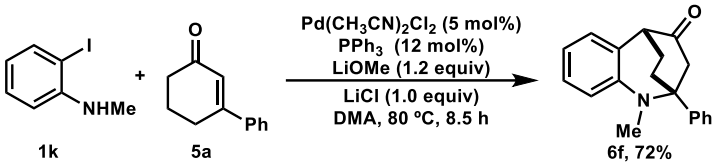
1-Benzyl-7-bromo-2-phenyl-2,3,4,5-tetrahydro-1*H*-2,5-ethanobenzo[*b*]azepin-10-one 6c: General procedure was followed. The reaction was performed with $Pd(CH_3CN)_2Cl_2$ (3.0 mg, 0.01 mmol, 5 mol%), PPh_3 (7.2 mg, 0.024 mmol, 12 mol%), LiOMe (9.7 mg, 0.24 mmol, 1.2 equiv), LiCl (8.7 mg, 0.2 mmol, 1.0 equiv), **1i** (168.1 mg, 0.4 mmol, 2.0 equiv), 3-phenylcyclohex-2-en-1-one **5a** (33.3 mg, 0.2 mmol, 1.0 equiv), and DMA (2 mL) at 80 °C for 8.5 h. The desired product **6c** (40.8 mg, 49%) was obtained as a yellow solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.6 (PE / EA = 5 / 1); mp: 165 – 166 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.48 – 7.42 (m, 2H), 7.41 – 7.18 (m, 9H), 7.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.05 (d, *J* = 8.3 Hz, 1H), 4.05 (AB, *J* = 16.4 Hz, 1H), 3.97 (BA, *J* = 16.4 Hz, 1H), 3.72 (s, 1H), 3.32 (AB, *J* = 15.2 Hz, 1H), 2.98 (BA, *J* = 15.2 Hz, 1H), 2.40 – 2.24 (m, 4H); ^{13}C NMR (100 MHz, acetone-d_6) δ 209.7, 151.9, 145.4, 139.3, 134.7, 131.6, 129.6, 129.3, 128.6, 127.7, 127.62, 127.55, 126.6, 110.1, 109.7, 75.8, 50.9, 49.9, 44.9, 36.3, 26.2; HRMS (ESI+): calc'd for $C_{25}H_{22}BrNNaO$ $[M+Na]^+$: 454.0777; found: 454.0778.



1-Benzyl-2-(4-methoxyphenyl)-2,3,4,5-tetrahydro-1*H*-2,5-ethanobenzo[*b*]azepin-10-one 6d: General procedure was followed. The reaction was performed with $Pd(CH_3CN)_2Cl_2$ (3.0 mg, 0.01 mmol, 5 mol%), PPh_3 (6.5 mg, 0.024 mmol, 12 mol%), LiOMe (9.6 mg, 0.24 mmol, 1.2 equiv), LiCl (8.8 mg, 0.2 mmol, 1.0 equiv), **1a** (124.0 mg, 0.4 mmol, 2.0 equiv), 4'-methoxy-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one **5d** (40.0 mg, 0.2 mmol, 1.0 equiv), and DMA (2 mL) at 80 °C for 8.5 h. The desired product **6d** (67.8 mg, 89%) was obtained as a yellow solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.4 (PE / EA = 5 / 1); mp: 58 – 60 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.43 – 7.37 (m, 2H), 7.30 – 7.24 (m, 4H), 7.24 – 7.17 (m, 2H), 6.97 (t, *J* = 7.7 Hz, 1H), 6.93 – 6.87 (m, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.12 (d, *J* = 7.8 Hz, 1H), 4.00 (AB, *J* = 16.2 Hz, 1H), 3.93 (BA, *J* = 16.3 Hz, 1H), 3.78 (s, 3H), 3.65 (s, 1H), 3.21 (AB, *J* = 15.0 Hz, 1H), 2.90 (BA, *J* = 15.0 Hz, 1H), 2.38 – 2.19 (m, 4H); ^{13}C NMR (100 MHz, acetone-d_6) δ 210.0, 160.0, 152.6, 140.0, 137.5, 131.8, 129.2, 128.9, 128.0, 127.6, 127.5, 124.3, 119.1, 114.7, 108.6, 75.6, 55.5, 51.0, 50.0, 45.1, 36.4, 26.0; HRMS (ESI+): calc'd for $C_{26}H_{26}NO_2$ $[M+H]^+$: 384.1958; found: 384.1945.

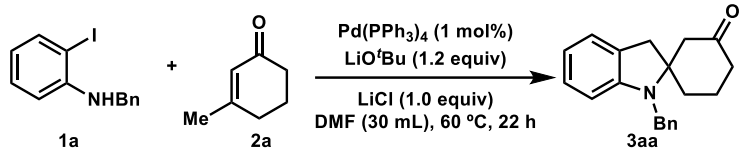


1-Benzyl-2-(m-tolyl)-2,3,4,5-tetrahydro-1*H*-2,5-ethanobenzo[*b*]azepin-10-one 6e: General procedure was followed. The reaction was performed with $Pd(CH_3CN)_2Cl_2$ (3.2 mg, 0.01 mmol, 5 mol%), PPh_3 (7.5 mg, 0.024 mmol, 12 mol%), LiOMe (9.6 mg, 0.24 mmol, 1.2 equiv), LiCl (9.4 mg, 0.2 mmol, 1.0 equiv), **1a** (126.2 mg, 0.4 mmol, 2.0 equiv), 3'-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one **5e** (37.0 mg, 0.2 mmol, 1.0 equiv), and DMA (2 mL) at 80 °C for 8.5 h. The desired product **6e** (57.3 mg, 79%) was obtained as a yellow solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.5 (PE / EA = 5 / 1); mp: 45 – 46 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.33 (s, 1H), 7.31 – 7.24 (m, 4H), 7.24 – 7.17 (m, 4H), 7.14 – 7.08 (m, 1H), 6.98 (t, J = 7.7 Hz, 1H), 6.73 (dd, J = 10.9, 3.9 Hz, 1H), 6.13 (d, J = 7.8 Hz, 1H), 4.02 (AB, J = 16.3 Hz, 1H), 3.96 (BA, J = 16.3 Hz, 1H), 3.67 (s, 1H), 3.26 (AB, J = 15.1 Hz, 1H), 2.91 (BA, J = 15.1 Hz, 1H), 2.32 – 2.21 (m, 7H); ^{13}C NMR (100 MHz, acetone-d_6) δ 210.1, 152.8, 145.9, 140.1, 139.0, 131.8, 129.5, 129.3, 129.2, 129.0, 127.8, 127.6, 127.5, 124.5, 124.0, 119.2, 108.5, 75.8, 51.1, 50.2, 45.1, 36.5, 26.2, 21.8; HRMS (ESI+): calc'd for $C_{26}H_{26}NO$ $[M+H]^+$: 368.2009; found: 368.1999.



1-Methyl-2-phenyl-2,3,4,5-tetrahydro-1*H*-2,5-ethanobenzo[*b*]azepin-10-one 6f: General procedure was followed. The reaction was performed with $Pd(CH_3CN)_2Cl_2$ (2.9 mg, 0.01 mmol, 5 mol%), PPh_3 (7.3 mg, 0.024 mmol, 12 mol%), LiOMe (9.8 mg, 0.24 mmol, 1.2 equiv), LiCl (8.2 mg, 0.2 mmol, 1.0 equiv), **1k** (95.3 mg, 0.4 mmol, 2.0 equiv), 5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one **5a** (34.4 mg, 0.2 mmol, 1.0 equiv), and DMA (2 mL) at 80 °C for 8.5 h. The desired product **6f** (39.7 mg, 72%) was obtained as a yellow liquid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA). R_f = 0.5 (PE / EA = 5 / 1); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.39 – 7.31 (m, 4H), 7.30 – 7.25 (m, 1H), 7.16 – 7.09 (m, 2H), 6.67 (t, J = 7.7 Hz, 1H), 6.45 (d, J = 8.0 Hz, 1H), 3.49 (d, J = 4.2 Hz, 1H), 3.31 (AB, J = 14.8 Hz, 1H), 2.81 (BA, J = 14.8 Hz, 1H), 2.52 (s, 3H), 2.42 – 2.27 (m, 1H), 2.23 – 2.08 (m, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 209.9, 153.0, 145.8, 130.9, 129.6, 129.4, 128.3, 126.5, 124.5, 118.4, 106.2, 74.6, 50.9, 44.2, 35.7, 28.9, 26.5; HRMS (ESI+): calc'd for $C_{19}H_{20}NO$ $[M+H]^+$: 278.1539; found: 278.1550.

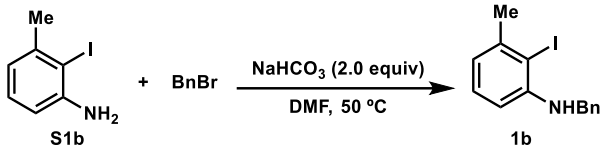
Gram Scale Synthesis of 3aa



1'-Benzylspiro[cyclohexane-1,2'-indolin]-3-one 3aa: In an argon-filled glove box, $Pd(PPh_3)_4$ (75.2 mg, 0.06 mmol, 1 mol%), LiO^{t}Bu (572.0 mg, 7.2 mmol, 1.2 equiv), LiCl (253.2 mg, 6 mmol, 1 equiv), **1a** (1.83 g, 6 mmol, 1 equiv), 3-methylcyclohex-2-en-1-one **2a** (1.34 mL, 12 mmol, 2 equiv), and DMF (30 mL) were added to a Schlenk flask equipped with a magnetic stirring bar. The vial was sealed and stirred at 60 °C for 24 h. After removed from the glove box, the mixture was diluted with water (100 mL), and extracted with EA (50 mL × 3). Then the combined organic layers were washed with H_2O (50 mL × 3) and brine, and then dried over anhydrous Na_2SO_4. The desired product **3aa** (1.43 g, 82%) was obtained as a white solid after purification by silica gel chromatography (PE / CH_2Cl_2 = 2 / 1 with 0.5% EA).

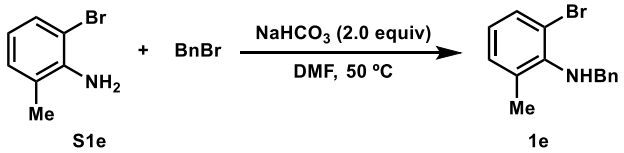
Preparation and Characterization of Substrates

2-Haloaniline derivatives (**1a**[1], **1c**[1], **1d**[1], **1f**[1], **1g**[1], **1h**[1], **1i**[1], and **1k**[2]) and cyclic enones (**2b**[3], **2c**[4], **2d**[4, 5], **5d**[6], and **5e**[6]) were prepared following the reported procedures and the spectroscopic data were found consistent with those reported in the literature.

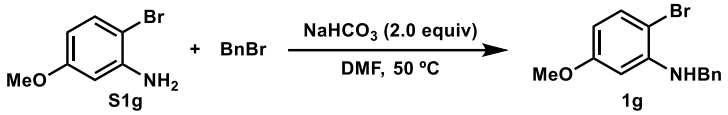


***N*-Benzyl-2-iodo-3-methylaniline 1b**: The reported procedure was followed.[1] To a dried two neck round-bottom flask, 2-iodo-3-methylaniline **S1b** (1.11g, 4.78 mmol, 1 equiv), and $NaHCO_3$ (0.82 g, 9.56 mmol, 2 equiv) were added, followed by the addition of DMF (10 mL) and BnBr (0.57 mL, 4.78 mmol, 1 equiv). The mixture was stirred at 50 °C overnight. Then the reaction was quenched by sat. NH_4Cl aq. (10 mL), diluted with water (20 mL), and extracted with EA (20 mL × 3). The combined organic layers were washed with H_2O (10 mL × 3) and brine, and then dried over anhydrous Na_2SO_4. The desired product **1b** (0.67 g, 42%) was obtained as a colorless liquid after purification by silica gel chromatography (PE / EA = 200 / 1). R_f = 0.5 (PE / EA = 200 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 7.05 (t, J = 7.7 Hz, 1H), 6.67 (d, J = 6.8 Hz, 1H), 6.40 (d, J = 8.0 Hz, 1H), 4.42 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 142.5, 138.6, 128.83, 128.82, 127.47, 127.46, 119.4, 108.9, 93.0, 49.0,

29.8; HRMS (ESI+): calc'd for $C_{14}H_{15}IN$ $[M+H]^+$: 324.0244; found: 324.0242.

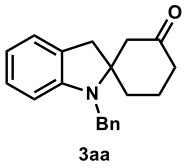


***N*-Benzyl-2-bromo-6-methylaniline 1e**: The reported procedure was followed.[1] To a dried two neck round-bottom flask, 2-bromo-6-methylaniline **S1e** (0.18 mL, 1.3 mmol, 1.3 equiv), and $NaHCO_3$ (0.17 mg, 2 mmol, 2 equiv) were added, followed by the addition of DMF (2.5 mL) and BnBr (0.19 g, 1 mmol, 1 equiv). The mixture was stirred at 50 °C overnight. Then the reaction was quenched by sat. NH_4Cl aq. (10 mL), diluted with water (20 mL), and extracted with EA (20 mL × 3). The combined organic layers were washed with H_2O (10 mL × 3) and brine, and then dried over anhydrous Na_2SO_4. The desired product **1e** (0.23 g, 84%) was obtained as a colorless liquid after purification by silica gel chromatography (PE / EA = 200 / 1). R_f = 0.5 (PE / EA = 200 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.40 – 7.27 (m, 4H), 7.13 – 7.07 (m, 1H), 6.79 (t, *J* = 7.7 Hz, 1H), 4.21 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 139.6, 132.2, 130.8, 130.6, 128.7, 128.2, 127.6, 123.5, 118.4, 52.6, 19.6; HRMS (ESI+): calc'd for $C_{14}H_{15}NBr$ $[M+H]^+$: 276.0382; found: 276.0385.



***N*-Benzyl-2-bromo-5-methoxyaniline 1g**: The reported procedure was followed.[1] To a dried two neck bottom flask, 2-bromo-5-methoxyaniline **S1g** (1.38 g, 6.5 mmol, 1.3 equiv), and $NaHCO_3$ (0.84 g, 10 mmol, 2 equiv) was added, followed by the addition of DMF (10 mL) and BnBr (0.57 mL, 5 mmol, 1 equiv). The mixture was stirred at 50 °C overnight. Then the reaction was quenched by sat. NH_4Cl aq. (10 mL), diluted with water (20 mL), and extracted with EA (20 mL × 3). The combined organic layers were washed with H_2O (10 mL × 3) and brine, and then dried over anhydrous Na_2SO_4. The desired product **1g** (1.29 g, 90%) was obtained as a colorless liquid after purification by silica gel chromatography (PE / EA = 100 / 1). R_f = 0.5 (PE / EA = 100 / 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 6H), 6.24 – 6.16 (m, 2H), 4.39 (s, 2H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 145.4, 138.4, 132.6, 128.9, 127.6, 127.5, 103.3, 101.2, 98.9, 55.4, 48.3; HRMS (ESI+): calc'd for $C_{14}H_{15}NOBr$ $[M+H]^+$: 292.0332; found: 292.0331.

X-Ray Crystallographic Data of 3aa and 3ac



3aa

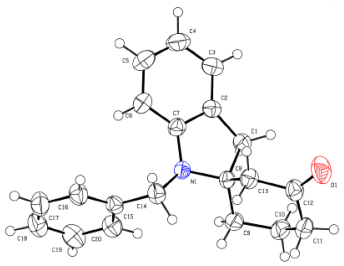


Table S9. Crystal data and structure refinement for 3aa.

Identification code	CCDC 1905674	
Empirical formula	$C_{20}H_{21}NO$	
Formula weight	291.38	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.162(15) Å	a = 90°.
	b = 19.10(3) Å	b = 109.780(18)°.
	c = 8.941(13) Å	g = 90°.
Volume	1633(4) $Å^3$	
Z	4	
Density (calculated)	1.185 Mg/m^3	
Absorption coefficient	0.072 mm^{-1}	
F(000)	624	
Crystal size	0.080 x 0.060 x 0.040 mm^3	
Theta range for data collection	4.265 to 29.342°.	
Index ranges	-11<=h<=13, -22<=k<=26, -11<=l<=12	
Reflections collected	11359	
Independent reflections	4432 [R(int) = 0.0185]	
Completeness to theta = 25.242°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7459 and 0.6455	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4432 / 0 / 283	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0484, wR2 = 0.1261	

R indices (all data)	R1 = 0.0581, wR2 = 0.1373
Extinction coefficient	n/a
Largest diff. peak and hole	0.280 and -0.202 e.Å^{-3}

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 3aa. U (eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	7497(1)	4753(1)	6738(1)	35(1)
O(1)	8144(1)	6566(1)	10670(1)	66(1)
C(1)	5746(1)	5372(1)	7425(1)	37(1)
C(2)	5731(1)	4602(1)	7804(1)	35(1)
C(3)	4863(1)	4215(1)	8413(1)	44(1)
C(6)	6962(2)	3539(1)	7503(2)	50(1)
C(5)	6074(2)	3156(1)	8119(2)	60(1)
C(4)	5041(2)	3484(1)	8566(2)	56(1)
C(7)	6775(1)	4267(1)	7348(1)	36(1)
C(8)	7206(1)	5473(1)	7220(1)	32(1)
C(9)	7153(1)	6022(1)	5950(1)	41(1)
C(10)	6789(2)	6750(1)	6439(2)	51(1)
C(11)	7833(2)	6985(1)	8041(2)	54(1)
C(12)	8094(1)	6430(1)	9319(1)	43(1)
C(13)	8318(1)	5688(1)	8829(1)	39(1)
C(14)	8877(1)	4576(1)	6640(1)	40(1)
C(15)	8772(1)	4144(1)	5169(1)	36(1)
C(16)	9457(1)	3501(1)	5297(2)	45(1)
C(17)	9338(2)	3101(1)	3944(2)	54(1)
C(18)	8538(2)	3345(1)	2453(2)	55(1)
C(19)	7875(1)	3993(1)	2304(2)	54(1)
C(20)	7991(1)	4391(1)	3659(2)	45(1)

Table S11. Bond lengths [Å] and angles [°] for 3aa.

N(1)-C(7)	1.4044(18)
N(1)-C(14)	1.474(2)
N(1)-C(8)	1.500(2)
O(1)-C(12)	1.219(2)

C(1)-C(2)	1.511(3)
C(1)-C(8)	1.567(3)
C(1)-H(18)	1.020(14)
C(1)-H(19)	0.976(15)
C(2)-C(3)	1.3938(19)
C(2)-C(7)	1.412(2)
C(3)-C(4)	1.410(3)
C(3)-H(1)	0.984(17)
C(6)-C(7)	1.403(3)
C(6)-C(5)	1.410(2)
C(6)-H(4)	0.972(17)
C(5)-C(4)	1.391(3)
C(5)-H(3)	1.01(2)
C(4)-H(2)	0.985(19)
C(8)-C(9)	1.533(2)
C(8)-C(13)	1.554(2)
C(9)-C(10)	1.539(2)
C(9)-H(16)	1.011(15)
C(9)-H(17)	1.007(16)
C(10)-C(11)	1.534(3)
C(10)-H(21)	0.982(19)
C(10)-H(20)	1.016(16)
C(11)-C(12)	1.515(2)
C(11)-H(14)	1.042(19)
C(11)-H(15)	0.970(19)
C(12)-C(13)	1.524(2)
C(13)-H(12)	0.988(17)
C(13)-H(13)	0.978(16)
C(14)-C(15)	1.526(2)
C(14)-H(10)	1.002(16)
C(14)-H(11)	0.992(16)
C(15)-C(20)	1.396(2)
C(15)-C(16)	1.399(2)
C(16)-C(17)	1.400(2)
C(16)-H(9)	0.973(18)
C(17)-C(18)	1.386(3)
C(17)-H(8)	0.98(2)
C(18)-C(19)	1.395(3)

C(18)-H(7)	1.00(2)
C(19)-C(20)	1.400(2)
C(19)-H(6)	0.978(18)
C(20)-H(5)	0.969(17)

C(7)-N(1)-C(14)	120.30(12)
C(7)-N(1)-C(8)	108.38(12)
C(14)-N(1)-C(8)	120.75(8)
C(2)-C(1)-C(8)	103.22(8)
C(2)-C(1)-H(18)	109.9(8)
C(8)-C(1)-H(18)	109.4(8)
C(2)-C(1)-H(19)	112.9(9)
C(8)-C(1)-H(19)	112.3(9)
H(18)-C(1)-H(19)	109.0(12)
C(3)-C(2)-C(7)	120.64(14)
C(3)-C(2)-C(1)	131.22(11)
C(7)-C(2)-C(1)	108.07(10)
C(2)-C(3)-C(4)	119.01(13)
C(2)-C(3)-H(1)	119.6(10)
C(4)-C(3)-H(1)	121.4(10)
C(7)-C(6)-C(5)	117.95(14)
C(7)-C(6)-H(4)	121.4(10)
C(5)-C(6)-H(4)	120.6(10)
C(4)-C(5)-C(6)	121.60(15)
C(4)-C(5)-H(3)	120.7(11)
C(6)-C(5)-H(3)	117.7(11)
C(5)-C(4)-C(3)	120.13(12)
C(5)-C(4)-H(2)	118.8(11)
C(3)-C(4)-H(2)	121.1(11)
C(6)-C(7)-N(1)	128.52(12)
C(6)-C(7)-C(2)	120.67(11)
N(1)-C(7)-C(2)	110.80(13)
N(1)-C(8)-C(9)	112.03(12)
N(1)-C(8)-C(13)	110.83(9)
C(9)-C(8)-C(13)	109.73(12)
N(1)-C(8)-C(1)	101.94(9)
C(9)-C(8)-C(1)	111.93(9)
C(13)-C(8)-C(1)	110.19(12)

C(8)-C(9)-C(10)	111.04(13)
C(8)-C(9)-H(16)	108.9(9)
C(10)-C(9)-H(16)	110.3(9)
C(8)-C(9)-H(17)	108.5(9)
C(10)-C(9)-H(17)	111.1(9)
H(16)-C(9)-H(17)	106.8(12)
C(11)-C(10)-C(9)	111.89(12)
C(11)-C(10)-H(21)	109.7(10)
C(9)-C(10)-H(21)	110.2(10)
C(11)-C(10)-H(20)	109.5(9)
C(9)-C(10)-H(20)	109.2(9)
H(21)-C(10)-H(20)	106.2(13)
C(12)-C(11)-C(10)	112.84(13)
C(12)-C(11)-H(14)	106.0(11)
C(10)-C(11)-H(14)	107.1(10)
C(12)-C(11)-H(15)	108.4(10)
C(10)-C(11)-H(15)	112.2(11)
H(14)-C(11)-H(15)	110.1(15)
O(1)-C(12)-C(11)	122.42(14)
O(1)-C(12)-C(13)	121.48(12)
C(11)-C(12)-C(13)	116.09(14)
C(12)-C(13)-C(8)	112.26(10)
C(12)-C(13)-H(12)	105.2(10)
C(8)-C(13)-H(12)	109.3(9)
C(12)-C(13)-H(13)	109.6(9)
C(8)-C(13)-H(13)	110.8(9)
H(12)-C(13)-H(13)	109.5(13)
N(1)-C(14)-C(15)	112.60(9)
N(1)-C(14)-H(10)	107.0(9)
C(15)-C(14)-H(10)	109.9(8)
N(1)-C(14)-H(11)	111.0(9)
C(15)-C(14)-H(11)	108.3(9)
H(10)-C(14)-H(11)	107.9(12)
C(20)-C(15)-C(16)	118.66(11)
C(20)-C(15)-C(14)	120.17(14)
C(16)-C(15)-C(14)	121.16(11)
C(15)-C(16)-C(17)	120.90(13)
C(15)-C(16)-H(9)	118.7(10)

C(17)-C(16)-H(9)	120.4(10)
C(18)-C(17)-C(16)	119.93(15)
C(18)-C(17)-H(8)	119.2(11)
C(16)-C(17)-H(8)	120.8(11)
C(17)-C(18)-C(19)	119.78(13)
C(17)-C(18)-H(7)	119.0(11)
C(19)-C(18)-H(7)	121.2(11)
C(18)-C(19)-C(20)	120.17(14)
C(18)-C(19)-H(6)	120.2(11)
C(20)-C(19)-H(6)	119.6(11)
C(15)-C(20)-C(19)	120.53(15)
C(15)-C(20)-H(5)	118.0(9)
C(19)-C(20)-H(5)	121.5(9)

Symmetry transformations used to generate equivalent atoms:

Table S12. Anisotropic displacement parameters ($Å^2$x 10^3) for 3aa. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	36(1)	31(1)	42(1)	-6(1)	17(1)	-3(1)
O(1)	89(1)	67(1)	42(1)	-15(1)	20(1)	6(1)
C(1)	35(1)	38(1)	38(1)	0(1)	14(1)	2(1)
C(2)	35(1)	39(1)	30(1)	-1(1)	9(1)	-4(1)
C(3)	41(1)	54(1)	37(1)	1(1)	14(1)	-8(1)
C(6)	60(1)	34(1)	59(1)	-2(1)	26(1)	-2(1)
C(5)	76(1)	37(1)	69(1)	3(1)	29(1)	-11(1)
C(4)	64(1)	52(1)	55(1)	3(1)	26(1)	-19(1)
C(7)	37(1)	34(1)	34(1)	-3(1)	11(1)	-5(1)
C(8)	34(1)	31(1)	30(1)	-3(1)	11(1)	-2(1)
C(9)	54(1)	37(1)	34(1)	1(1)	17(1)	-3(1)
C(10)	74(1)	35(1)	46(1)	7(1)	24(1)	5(1)
C(11)	77(1)	34(1)	54(1)	-9(1)	29(1)	-6(1)
C(12)	42(1)	45(1)	40(1)	-11(1)	12(1)	-4(1)
C(13)	40(1)	39(1)	34(1)	-4(1)	7(1)	-1(1)
C(14)	32(1)	44(1)	43(1)	-9(1)	12(1)	-1(1)
C(15)	30(1)	40(1)	38(1)	-4(1)	14(1)	-1(1)

C(16)	49(1)	45(1)	42(1)	1(1)	16(1)	10(1)
C(17)	64(1)	47(1)	55(1)	-7(1)	24(1)	10(1)
C(18)	58(1)	63(1)	47(1)	-16(1)	21(1)	-2(1)
C(19)	47(1)	72(1)	38(1)	0(1)	9(1)	5(1)
C(20)	39(1)	50(1)	45(1)	2(1)	12(1)	8(1)

Table S13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 3aa.

	x	y	z	U(eq)
H(1)	4152(18)	4458(9)	8743(19)	59(4)
H(2)	4442(19)	3195(10)	8990(20)	73(5)
H(3)	6220(20)	2635(11)	8240(20)	77(5)
H(6)	7330(20)	4174(10)	1250(20)	71(5)
H(5)	7520(17)	4837(9)	3585(18)	56(4)
H(4)	7667(17)	3302(9)	7177(18)	54(4)
H(7)	8450(20)	3050(10)	1500(20)	75(5)
H(8)	9798(19)	2643(11)	4040(20)	75(5)
H(9)	10025(18)	3335(9)	6350(20)	64(5)
H(10)	9367(16)	5030(8)	6618(17)	48(4)
H(11)	9449(16)	4311(8)	7594(18)	51(4)
H(12)	9252(18)	5693(9)	8716(18)	56(4)
H(13)	8320(15)	5360(8)	9671(18)	51(4)
H(14)	8790(20)	7065(10)	7880(20)	74(5)
H(15)	7537(18)	7412(10)	8430(20)	69(5)
H(16)	8090(16)	6035(8)	5787(17)	51(4)
H(17)	6444(17)	5868(8)	4912(19)	55(4)
H(18)	4974(15)	5480(7)	6376(17)	43(3)
H(19)	5630(15)	5672(8)	8254(17)	51(4)
H(21)	6760(18)	7096(9)	5620(20)	66(5)
H(20)	5810(17)	6737(8)	6505(18)	53(4)

Table S14. Torsion angles [°] for 3aa.

C(8)-C(1)-C(2)-C(3)	165.64(11)

C(8)-C(1)-C(2)-C(7)	-17.57(11)
C(7)-C(2)-C(3)-C(4)	-0.04(17)
C(1)-C(2)-C(3)-C(4)	176.41(12)
C(7)-C(6)-C(5)-C(4)	-0.1(2)
C(6)-C(5)-C(4)-C(3)	-0.2(2)
C(2)-C(3)-C(4)-C(5)	0.2(2)
C(5)-C(6)-C(7)-N(1)	-178.35(12)
C(5)-C(6)-C(7)-C(2)	0.22(19)
C(14)-N(1)-C(7)-C(6)	-19.91(17)
C(8)-N(1)-C(7)-C(6)	-164.80(12)
C(14)-N(1)-C(7)-C(2)	161.41(9)
C(8)-N(1)-C(7)-C(2)	16.52(12)
C(3)-C(2)-C(7)-C(6)	-0.17(16)
C(1)-C(2)-C(7)-C(6)	-177.37(11)
C(3)-C(2)-C(7)-N(1)	178.63(10)
C(1)-C(2)-C(7)-N(1)	1.43(12)
C(7)-N(1)-C(8)-C(9)	-146.12(10)
C(14)-N(1)-C(8)-C(9)	69.18(13)
C(7)-N(1)-C(8)-C(13)	90.95(15)
C(14)-N(1)-C(8)-C(13)	-53.75(14)
C(7)-N(1)-C(8)-C(1)	-26.30(11)
C(14)-N(1)-C(8)-C(1)	-171.00(9)
C(2)-C(1)-C(8)-N(1)	25.85(11)
C(2)-C(1)-C(8)-C(9)	145.75(9)
C(2)-C(1)-C(8)-C(13)	-91.86(11)
N(1)-C(8)-C(9)-C(10)	177.46(10)
C(13)-C(8)-C(9)-C(10)	-58.99(15)
C(1)-C(8)-C(9)-C(10)	63.67(13)
C(8)-C(9)-C(10)-C(11)	57.53(17)
C(9)-C(10)-C(11)-C(12)	-49.07(17)
C(10)-C(11)-C(12)-O(1)	-136.41(15)
C(10)-C(11)-C(12)-C(13)	44.71(18)
O(1)-C(12)-C(13)-C(8)	134.10(14)
C(11)-C(12)-C(13)-C(8)	-47.01(16)
N(1)-C(8)-C(13)-C(12)	177.37(9)
C(9)-C(8)-C(13)-C(12)	53.12(14)
C(1)-C(8)-C(13)-C(12)	-70.56(13)
C(7)-N(1)-C(14)-C(15)	82.03(15)

C(8)-N(1)-C(14)-C(15)	-137.40(10)
N(1)-C(14)-C(15)-C(20)	55.32(15)
N(1)-C(14)-C(15)-C(16)	-125.19(12)
C(20)-C(15)-C(16)-C(17)	-1.50(19)
C(14)-C(15)-C(16)-C(17)	179.01(12)
C(15)-C(16)-C(17)-C(18)	0.3(2)
C(16)-C(17)-C(18)-C(19)	1.1(2)
C(17)-C(18)-C(19)-C(20)	-1.4(2)
C(16)-C(15)-C(20)-C(19)	1.26(18)
C(14)-C(15)-C(20)-C(19)	-179.23(11)
C(18)-C(19)-C(20)-C(15)	0.1(2)

Symmetry transformations used to generate equivalent atoms:

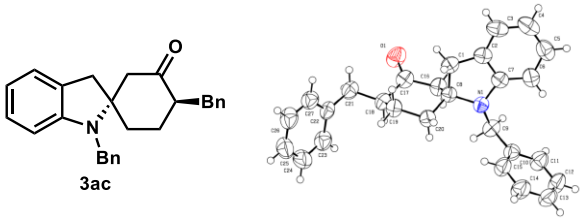


Table S15. Crystal data and structure refinement for 3ac.

Identification code	CCDC 1905675	
Empirical formula	$C_{27}H_27NO$	
Formula weight	381.49	
Temperature	296(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 13.7872(5) Å	a = 90°.
	b = 16.2182(8) Å	b = 96.759(3)°.
	c = 9.4765(4) Å	g = 90°.
Volume	2104.25(16) $Å^3$	
Z	4	
Density (calculated)	1.204 Mg/m^3	
Absorption coefficient	0.555 mm^{-1}	
F(000)	816	
Crystal size	0.120 x 0.060 x 0.040 mm^3	
Theta range for data collection	4.226 to 66.443°.	

Index ranges	-16<=h<=16, -19<=k<=15, -10<=l<=11
Reflections collected	5476
Independent reflections	2802 [R(int) = 0.0326]
Completeness to theta = 66.443°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.5648
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2802 / 2 / 262
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.1050
R indices (all data)	R1 = 0.0411, wR2 = 0.1063
Absolute structure parameter	-0.2(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.208 and -0.144 e.$Å^{-3}$

Table S16. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 3ac. U (eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4755(2)	5511(2)	9686(2)	76(1)
N(1)	2900(1)	6614(1)	5541(2)	49(1)
C(1)	3751(2)	7365(2)	7438(3)	58(1)
C(2)	2686(2)	7570(1)	7261(3)	55(1)
C(3)	2153(2)	8121(2)	7978(3)	70(1)
C(4)	1169(2)	8211(2)	7561(4)	78(1)
C(5)	712(2)	7758(2)	6437(4)	76(1)
C(6)	1243(2)	7196(2)	5709(3)	63(1)
C(7)	2225(2)	7111(1)	6131(2)	51(1)
C(8)	3810(2)	6570(1)	6549(2)	48(1)
C(9)	2557(2)	5895(2)	4701(3)	56(1)
C(10)	2212(2)	6092(1)	3161(3)	52(1)
C(11)	1334(2)	5808(2)	2507(3)	69(1)
C(12)	1042(2)	5966(2)	1091(4)	77(1)
C(13)	1622(2)	6426(2)	311(3)	72(1)
C(14)	2498(2)	6705(2)	947(3)	78(1)
C(15)	2793(2)	6546(2)	2363(3)	66(1)
C(16)	3804(2)	5794(2)	7493(3)	54(1)

C(17)	4745(2)	5665(1)	8437(3)	54(1)
C(18)	5675(2)	5715(2)	7705(3)	54(1)
C(19)	5652(2)	6498(2)	6795(3)	56(1)
C(20)	4715(2)	6556(2)	5761(2)	53(1)
C(21)	6585(2)	5645(2)	8781(3)	62(1)
C(22)	7531(2)	5721(2)	8140(3)	55(1)
C(23)	7773(2)	5163(2)	7126(4)	69(1)
C(24)	8634(2)	5230(2)	6540(4)	82(1)
C(25)	9288(2)	5846(2)	6978(4)	79(1)
C(26)	9055(2)	6403(2)	7984(4)	77(1)
C(27)	8193(2)	6341(2)	8546(3)	66(1)

Table S17. Bond lengths [Å] and angles [°] for 3ac.

O(1)-C(17)	1.208(3)
N(1)-C(7)	1.396(3)
N(1)-C(9)	1.460(3)
N(1)-C(8)	1.487(3)
C(1)-C(2)	1.496(4)
C(1)-C(8)	1.548(3)
C(1)-H(1A)	0.9700
C(1)-H(1AB)	0.9700
C(2)-C(3)	1.385(4)
C(2)-C(7)	1.395(4)
C(3)-C(4)	1.375(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.383(6)
C(4)-H(4)	0.9300
C(5)-C(6)	1.401(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.372(3)
C(6)-H(6)	0.9300
C(8)-C(20)	1.528(3)
C(8)-C(16)	1.544(3)
C(9)-C(10)	1.515(3)
C(9)-H(9A)	0.9700
C(9)-H(9AB)	0.9700

C(10)-C(11)	1.372(4)
C(10)-C(15)	1.378(4)
C(11)-C(12)	1.379(4)
C(11)-H(11)	0.9300
C(12)-C(13)	1.371(5)
C(12)-H(12)	0.9300
C(13)-C(14)	1.362(4)
C(13)-H(13)	0.9300
C(14)-C(15)	1.380(4)
C(14)-H(14)	0.9300
C(15)-H(15)	0.9300
C(16)-C(17)	1.502(3)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(17)-C(18)	1.530(3)
C(18)-C(21)	1.525(3)
C(18)-C(19)	1.534(3)
C(18)-H(18)	0.9800
C(19)-C(20)	1.530(3)
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(21)-C(22)	1.507(4)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-C(27)	1.383(4)
C(22)-C(23)	1.388(4)
C(23)-C(24)	1.373(5)
C(23)-H(23)	0.9300
C(24)-C(25)	1.377(5)
C(24)-H(24)	0.9300
C(25)-C(26)	1.377(5)
C(25)-H(25)	0.9300
C(26)-C(27)	1.362(5)
C(26)-H(26)	0.9300
C(27)-H(27)	0.9300

C(7)-N(1)-C(9)	119.41(18)
C(7)-N(1)-C(8)	108.82(19)
C(9)-N(1)-C(8)	120.38(17)
C(2)-C(1)-C(8)	103.78(19)
C(2)-C(1)-H(1A)	111.0
C(8)-C(1)-H(1A)	111.0
C(2)-C(1)-H(1AB)	111.0
C(8)-C(1)-H(1AB)	111.0
H(1A)-C(1)-H(1AB)	109.0
C(3)-C(2)-C(7)	120.1(2)
C(3)-C(2)-C(1)	131.3(3)
C(7)-C(2)-C(1)	108.6(2)
C(4)-C(3)-C(2)	119.3(3)
C(4)-C(3)-H(3)	120.3
C(2)-C(3)-H(3)	120.3
C(3)-C(4)-C(5)	120.7(3)
C(3)-C(4)-H(4)	119.7
C(5)-C(4)-H(4)	119.7
C(4)-C(5)-C(6)	120.5(3)
C(4)-C(5)-H(5)	119.8
C(6)-C(5)-H(5)	119.8
C(7)-C(6)-C(5)	118.5(3)
C(7)-C(6)-H(6)	120.7
C(5)-C(6)-H(6)	120.7
C(6)-C(7)-C(2)	121.0(2)
C(6)-C(7)-N(1)	128.5(2)
C(2)-C(7)-N(1)	110.53(19)
N(1)-C(8)-C(20)	111.26(18)
N(1)-C(8)-C(16)	110.52(17)
C(20)-C(8)-C(16)	109.38(17)
N(1)-C(8)-C(1)	102.39(17)
C(20)-C(8)-C(1)	112.06(18)
C(16)-C(8)-C(1)	111.09(19)
N(1)-C(9)-C(10)	113.62(19)
N(1)-C(9)-H(9A)	108.8
C(10)-C(9)-H(9A)	108.8
N(1)-C(9)-H(9AB)	108.8
C(10)-C(9)-H(9AB)	108.8

H(9A)-C(9)-H(9AB)	107.7
C(11)-C(10)-C(15)	118.0(2)
C(11)-C(10)-C(9)	121.6(2)
C(15)-C(10)-C(9)	120.3(2)
C(10)-C(11)-C(12)	121.2(3)
C(10)-C(11)-H(11)	119.4
C(12)-C(11)-H(11)	119.4
C(13)-C(12)-C(11)	120.3(3)
C(13)-C(12)-H(12)	119.9
C(11)-C(12)-H(12)	119.9
C(14)-C(13)-C(12)	119.0(3)
C(14)-C(13)-H(13)	120.5
C(12)-C(13)-H(13)	120.5
C(13)-C(14)-C(15)	120.9(3)
C(13)-C(14)-H(14)	119.6
C(15)-C(14)-H(14)	119.6
C(10)-C(15)-C(14)	120.6(2)
C(10)-C(15)-H(15)	119.7
C(14)-C(15)-H(15)	119.7
C(17)-C(16)-C(8)	113.32(17)
C(17)-C(16)-H(16A)	108.9
C(8)-C(16)-H(16A)	108.9
C(17)-C(16)-H(16B)	108.9
C(8)-C(16)-H(16B)	108.9
H(16A)-C(16)-H(16B)	107.7
O(1)-C(17)-C(16)	121.5(2)
O(1)-C(17)-C(18)	122.8(2)
C(16)-C(17)-C(18)	115.7(2)
C(21)-C(18)-C(17)	111.1(2)
C(21)-C(18)-C(19)	113.48(19)
C(17)-C(18)-C(19)	109.66(18)
C(21)-C(18)-H(18)	107.4
C(17)-C(18)-H(18)	107.4
C(19)-C(18)-H(18)	107.4
C(20)-C(19)-C(18)	111.77(18)
C(20)-C(19)-H(19A)	109.3
C(18)-C(19)-H(19A)	109.3
C(20)-C(19)-H(19B)	109.3

C(18)-C(19)-H(19B)	109.3
H(19A)-C(19)-H(19B)	107.9
C(8)-C(20)-C(19)	111.38(19)
C(8)-C(20)-H(20A)	109.4
C(19)-C(20)-H(20A)	109.4
C(8)-C(20)-H(20B)	109.4
C(19)-C(20)-H(20B)	109.4
H(20A)-C(20)-H(20B)	108.0
C(22)-C(21)-C(18)	114.0(2)
C(22)-C(21)-H(21A)	108.8
C(18)-C(21)-H(21A)	108.8
C(22)-C(21)-H(21B)	108.7
C(18)-C(21)-H(21B)	108.7
H(21A)-C(21)-H(21B)	107.6
C(27)-C(22)-C(23)	117.4(2)
C(27)-C(22)-C(21)	121.5(2)
C(23)-C(22)-C(21)	121.1(2)
C(24)-C(23)-C(22)	121.2(2)
C(24)-C(23)-H(23)	119.4
C(22)-C(23)-H(23)	119.4
C(23)-C(24)-C(25)	120.1(3)
C(23)-C(24)-H(24)	119.9
C(25)-C(24)-H(24)	119.9
C(24)-C(25)-C(26)	119.1(3)
C(24)-C(25)-H(25)	120.4
C(26)-C(25)-H(25)	120.4
C(27)-C(26)-C(25)	120.5(3)
C(27)-C(26)-H(26)	119.8
C(25)-C(26)-H(26)	119.8
C(26)-C(27)-C(22)	121.6(3)
C(26)-C(27)-H(27)	119.2
C(22)-C(27)-H(27)	119.2

Symmetry transformations used to generate equivalent atoms:

Table S18. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 3ac. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	78(1)	96(2)	52(1)	24(1)	4(1)	-11(1)
N(1)	49(1)	49(1)	49(1)	1(1)	2(1)	1(1)
C(1)	67(1)	53(1)	52(1)	0(1)	4(1)	-5(1)
C(2)	69(1)	47(1)	50(1)	7(1)	13(1)	1(1)
C(3)	94(2)	54(1)	65(2)	1(1)	26(1)	6(1)
C(4)	91(2)	66(2)	83(2)	13(2)	39(2)	20(1)
C(5)	67(1)	80(2)	83(2)	23(2)	22(1)	16(1)
C(6)	56(1)	69(1)	65(2)	15(1)	10(1)	4(1)
C(7)	58(1)	47(1)	49(1)	10(1)	11(1)	0(1)
C(8)	51(1)	48(1)	44(1)	7(1)	6(1)	-1(1)
C(9)	64(1)	49(1)	52(1)	2(1)	1(1)	-4(1)
C(10)	53(1)	50(1)	53(1)	-2(1)	4(1)	1(1)
C(11)	63(1)	76(2)	66(2)	3(1)	3(1)	-19(1)
C(12)	65(1)	92(2)	69(2)	-2(2)	-14(1)	-14(1)
C(13)	80(2)	84(2)	51(1)	2(1)	-4(1)	3(1)
C(14)	74(2)	102(2)	57(2)	12(1)	8(1)	-16(2)
C(15)	56(1)	85(2)	56(2)	6(1)	0(1)	-14(1)
C(16)	54(1)	55(1)	54(1)	14(1)	6(1)	-6(1)
C(17)	62(1)	48(1)	53(1)	12(1)	6(1)	-7(1)
C(18)	56(1)	54(1)	50(1)	5(1)	1(1)	0(1)
C(19)	50(1)	62(1)	56(1)	14(1)	5(1)	-5(1)
C(20)	53(1)	57(1)	48(1)	14(1)	8(1)	1(1)
C(21)	64(1)	66(1)	52(1)	4(1)	-4(1)	3(1)
C(22)	54(1)	52(1)	55(1)	2(1)	-11(1)	4(1)
C(23)	62(1)	56(1)	84(2)	-14(1)	-7(1)	-4(1)
C(24)	70(1)	78(2)	97(2)	-30(2)	7(1)	6(1)
C(25)	55(1)	80(2)	101(2)	-8(2)	5(1)	2(1)
C(26)	65(1)	62(2)	99(2)	-12(2)	-8(1)	-10(1)
C(27)	67(1)	59(1)	69(2)	-13(1)	-6(1)	2(1)

Table S19. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 3ac.

	x	y	z	U(eq)
H(1A)	3988	7268	8428	69

H(1AB)	4130	7806	7078	69
H(3)	2457	8427	8734	84
H(4)	808	8579	8040	93
H(5)	47	7828	6161	91
H(6)	938	6887	4958	76
H(9A)	2023	5643	5128	67
H(9AB)	3082	5495	4737	67
H(11)	928	5504	3028	82
H(12)	450	5760	663	93
H(13)	1420	6546	-638	87
H(14)	2902	7006	420	93
H(15)	3390	6747	2783	79
H(16A)	3275	5840	8079	65
H(16B)	3676	5314	6888	65
H(18)	5673	5242	7061	65
H(19A)	5700	6978	7411	67
H(19B)	6211	6500	6263	67
H(20A)	4731	7054	5197	63
H(20B)	4678	6088	5120	63
H(21A)	6563	6072	9493	74
H(21B)	6575	5117	9259	74
H(23)	7344	4736	6839	83
H(24)	8776	4859	5845	98
H(25)	9879	5886	6600	95
H(26)	9490	6824	8281	92
H(27)	8047	6724	9219	80

Table S20. Torsion angles [°] for 3ac.

C(8)-C(1)-C(2)-C(3)	167.4(2)
C(8)-C(1)-C(2)-C(7)	-14.6(2)
C(7)-C(2)-C(3)-C(4)	-0.2(4)
C(1)-C(2)-C(3)-C(4)	177.7(2)
C(2)-C(3)-C(4)-C(5)	-0.1(4)
C(3)-C(4)-C(5)-C(6)	0.5(4)
C(4)-C(5)-C(6)-C(7)	-0.6(4)
C(5)-C(6)-C(7)-C(2)	0.3(4)

C(5)-C(6)-C(7)-N(1)	-177.7(2)
C(3)-C(2)-C(7)-C(6)	0.1(3)
C(1)-C(2)-C(7)-C(6)	-178.2(2)
C(3)-C(2)-C(7)-N(1)	178.4(2)
C(1)-C(2)-C(7)-N(1)	0.1(2)
C(9)-N(1)-C(7)-C(6)	-22.7(3)
C(8)-N(1)-C(7)-C(6)	-166.4(2)
C(9)-N(1)-C(7)-C(2)	159.14(19)
C(8)-N(1)-C(7)-C(2)	15.5(2)
C(7)-N(1)-C(8)-C(20)	-143.38(18)
C(9)-N(1)-C(8)-C(20)	73.4(2)
C(7)-N(1)-C(8)-C(16)	94.9(2)
C(9)-N(1)-C(8)-C(16)	-48.3(3)
C(7)-N(1)-C(8)-C(1)	-23.5(2)
C(9)-N(1)-C(8)-C(1)	-166.75(19)
C(2)-C(1)-C(8)-N(1)	22.4(2)
C(2)-C(1)-C(8)-C(20)	141.72(19)
C(2)-C(1)-C(8)-C(16)	-95.6(2)
C(7)-N(1)-C(9)-C(10)	84.2(3)
C(8)-N(1)-C(9)-C(10)	-136.4(2)
N(1)-C(9)-C(10)-C(11)	-131.4(3)
N(1)-C(9)-C(10)-C(15)	50.6(3)
C(15)-C(10)-C(11)-C(12)	0.5(5)
C(9)-C(10)-C(11)-C(12)	-177.6(3)
C(10)-C(11)-C(12)-C(13)	-1.2(6)
C(11)-C(12)-C(13)-C(14)	1.7(6)
C(12)-C(13)-C(14)-C(15)	-1.5(6)
C(11)-C(10)-C(15)-C(14)	-0.3(5)
C(9)-C(10)-C(15)-C(14)	177.9(3)
C(13)-C(14)-C(15)-C(10)	0.8(6)
N(1)-C(8)-C(16)-C(17)	174.26(19)
C(20)-C(8)-C(16)-C(17)	51.4(3)
C(1)-C(8)-C(16)-C(17)	-72.8(3)
C(8)-C(16)-C(17)-O(1)	132.4(3)
C(8)-C(16)-C(17)-C(18)	-49.3(3)
O(1)-C(17)-C(18)-C(21)	-6.4(3)
C(16)-C(17)-C(18)-C(21)	175.4(2)
O(1)-C(17)-C(18)-C(19)	-132.7(3)

C(16)-C(17)-C(18)-C(19)	49.1(3)
C(21)-C(18)-C(19)-C(20)	-178.4(2)
C(17)-C(18)-C(19)-C(20)	-53.5(3)
N(1)-C(8)-C(20)-C(19)	-179.24(18)
C(16)-C(8)-C(20)-C(19)	-56.9(2)
C(1)-C(8)-C(20)-C(19)	66.8(2)
C(18)-C(19)-C(20)-C(8)	59.8(3)
C(17)-C(18)-C(21)-C(22)	-177.9(2)
C(19)-C(18)-C(21)-C(22)	-53.8(3)
C(18)-C(21)-C(22)-C(27)	119.6(3)
C(18)-C(21)-C(22)-C(23)	-61.1(3)
C(27)-C(22)-C(23)-C(24)	-0.6(5)
C(21)-C(22)-C(23)-C(24)	-180.0(3)
C(22)-C(23)-C(24)-C(25)	1.6(6)
C(23)-C(24)-C(25)-C(26)	-1.5(6)
C(24)-C(25)-C(26)-C(27)	0.5(6)
C(25)-C(26)-C(27)-C(22)	0.4(5)
C(23)-C(22)-C(27)-C(26)	-0.4(4)
C(21)-C(22)-C(27)-C(26)	179.0(3)

Symmetry transformations used to generate equivalent atoms:

Reference

1. H. Ren, Z. Chen, H. Li, G. Cao, J. Xu and M. Miao, *Synlett*, 2016, **28**, 504.
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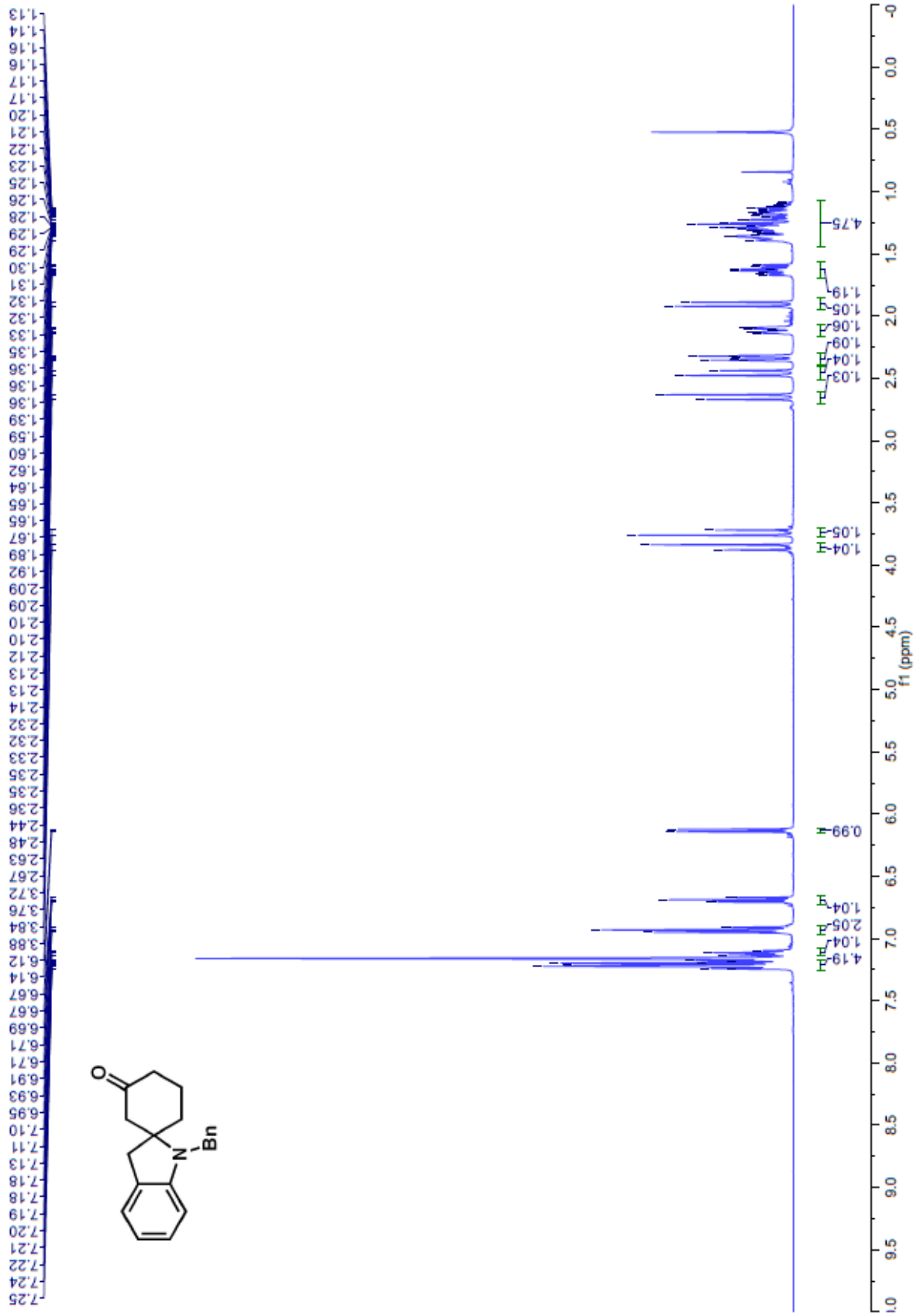
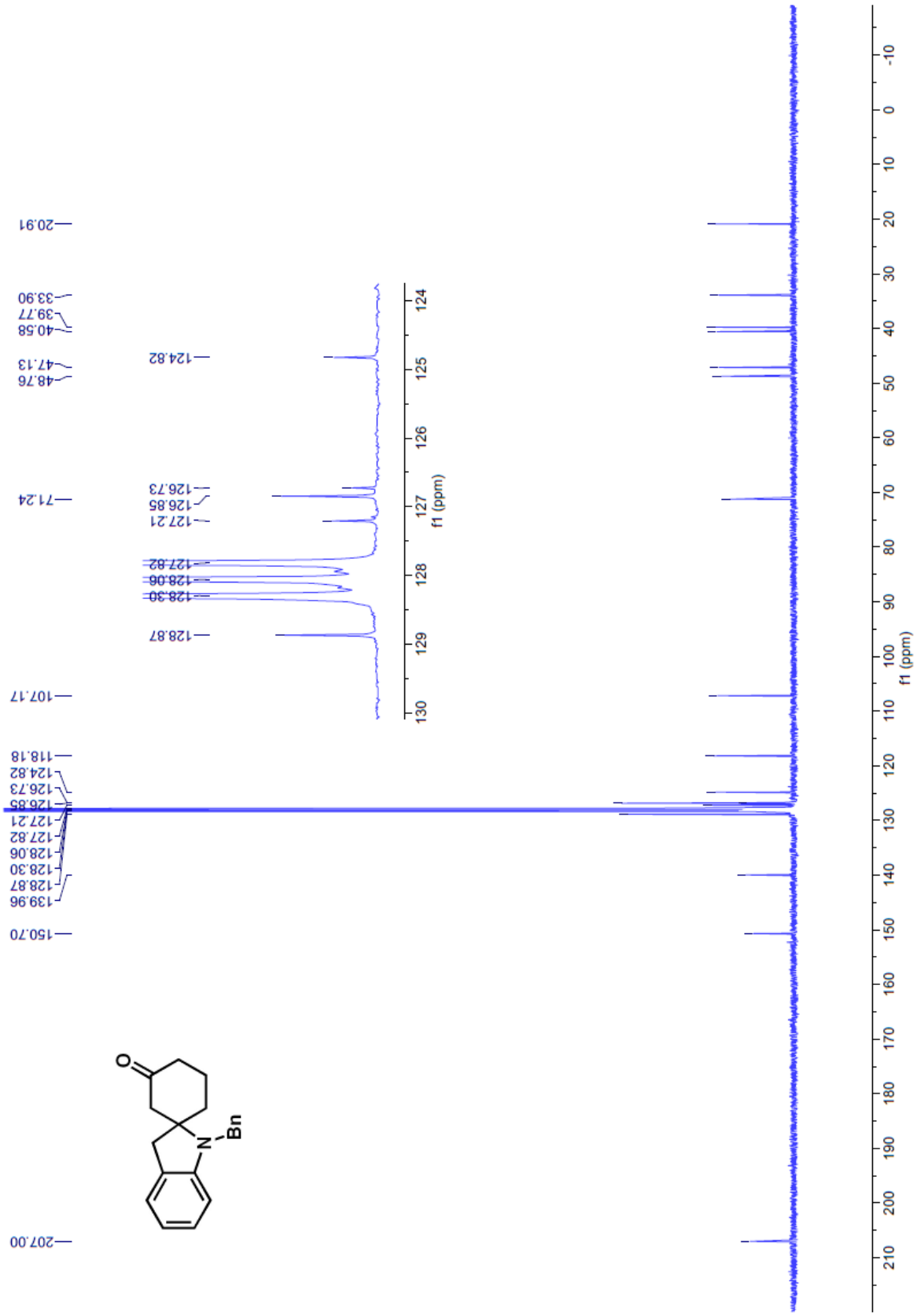
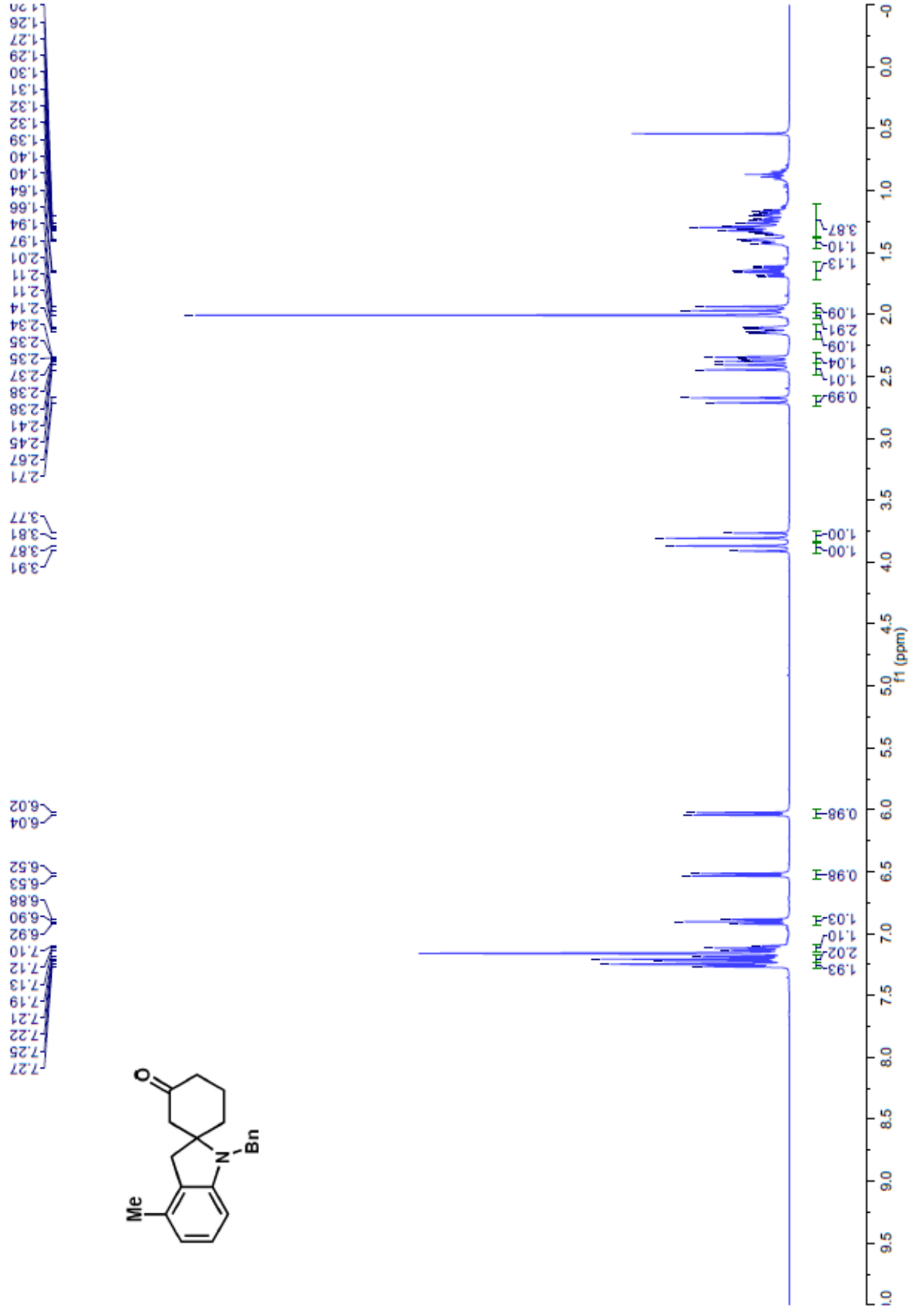
^{1}H NMR and ^{13}C NMR Spectra of New Compounds



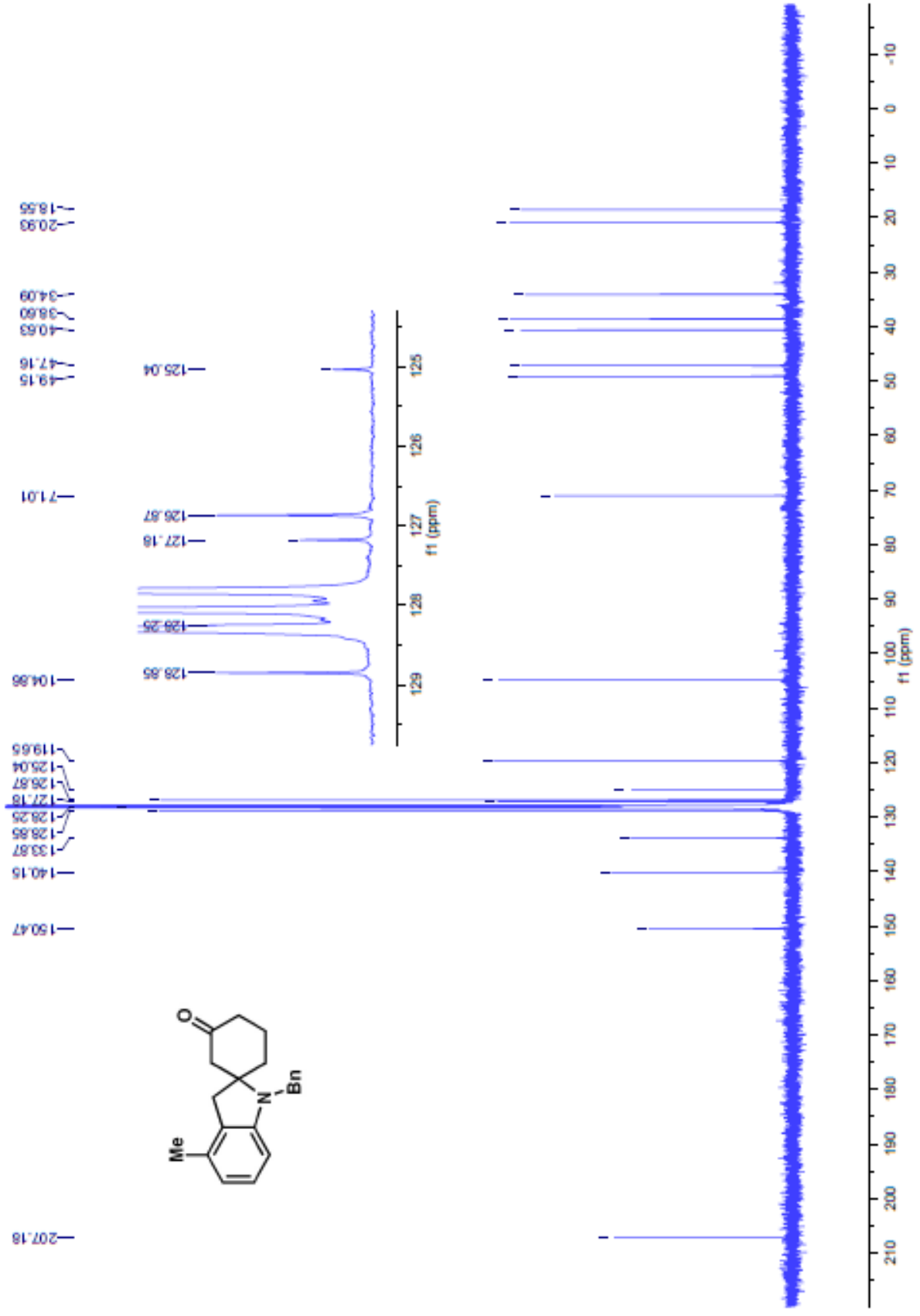
^{1}H NMR (400 MHz, C_6D_6) of ***3aa***



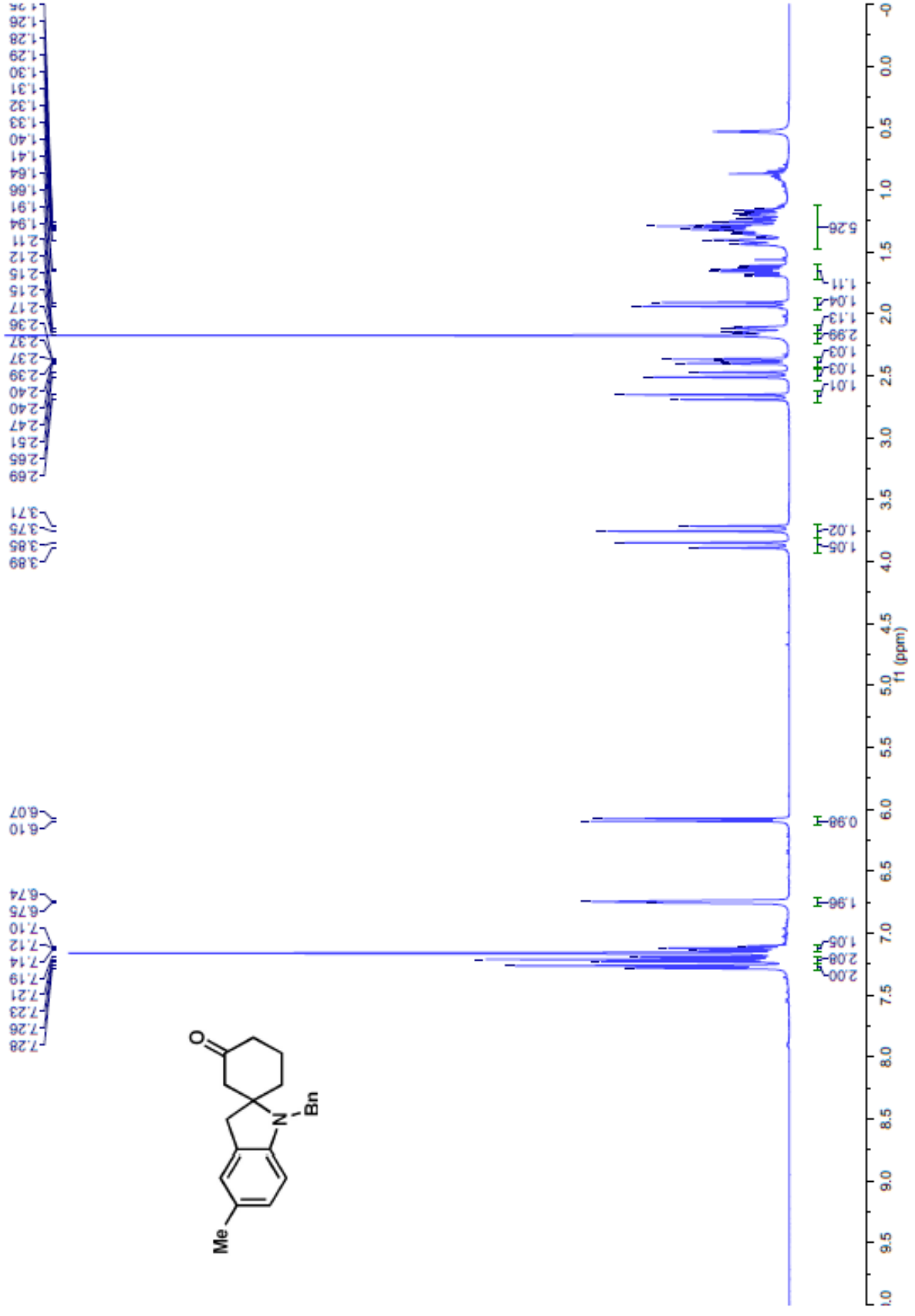
^{13}C NMR (100 MHz, C_6D_6) of ***3aa***



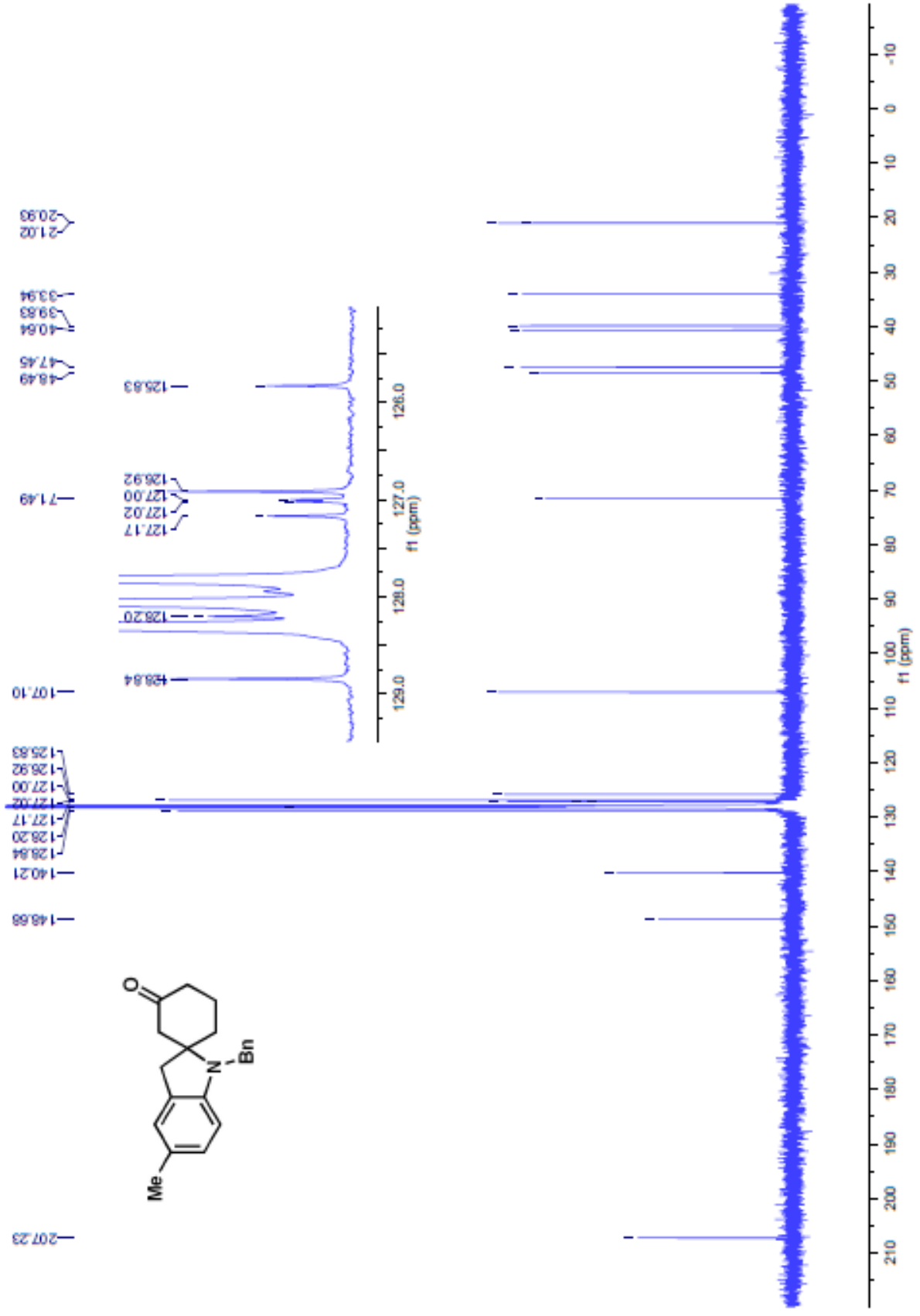
^{1}H NMR (400 MHz, C_6D_6) of ***3ba***



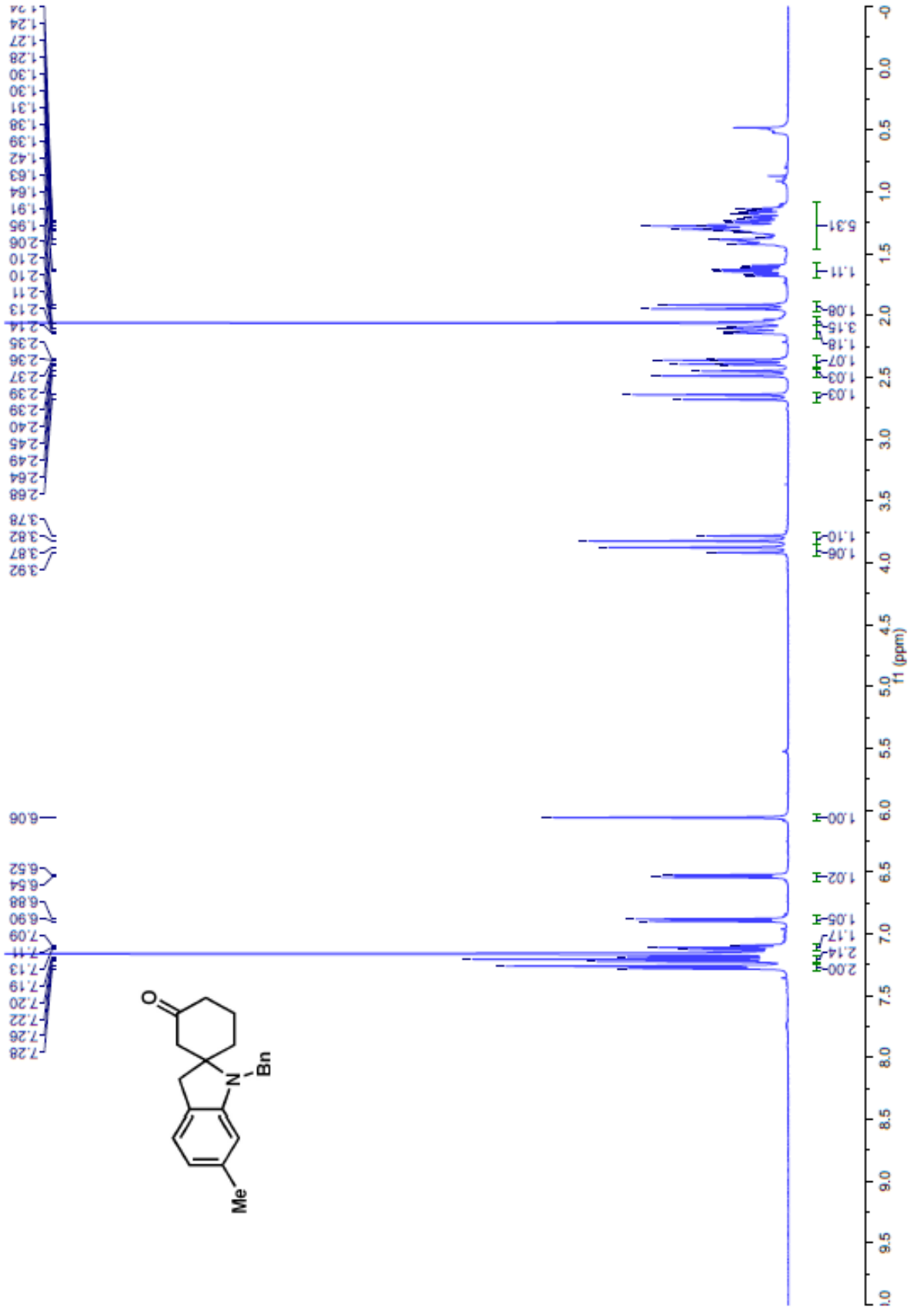
^{13}C NMR (100 MHz, C_6D_6) of ***3ba***



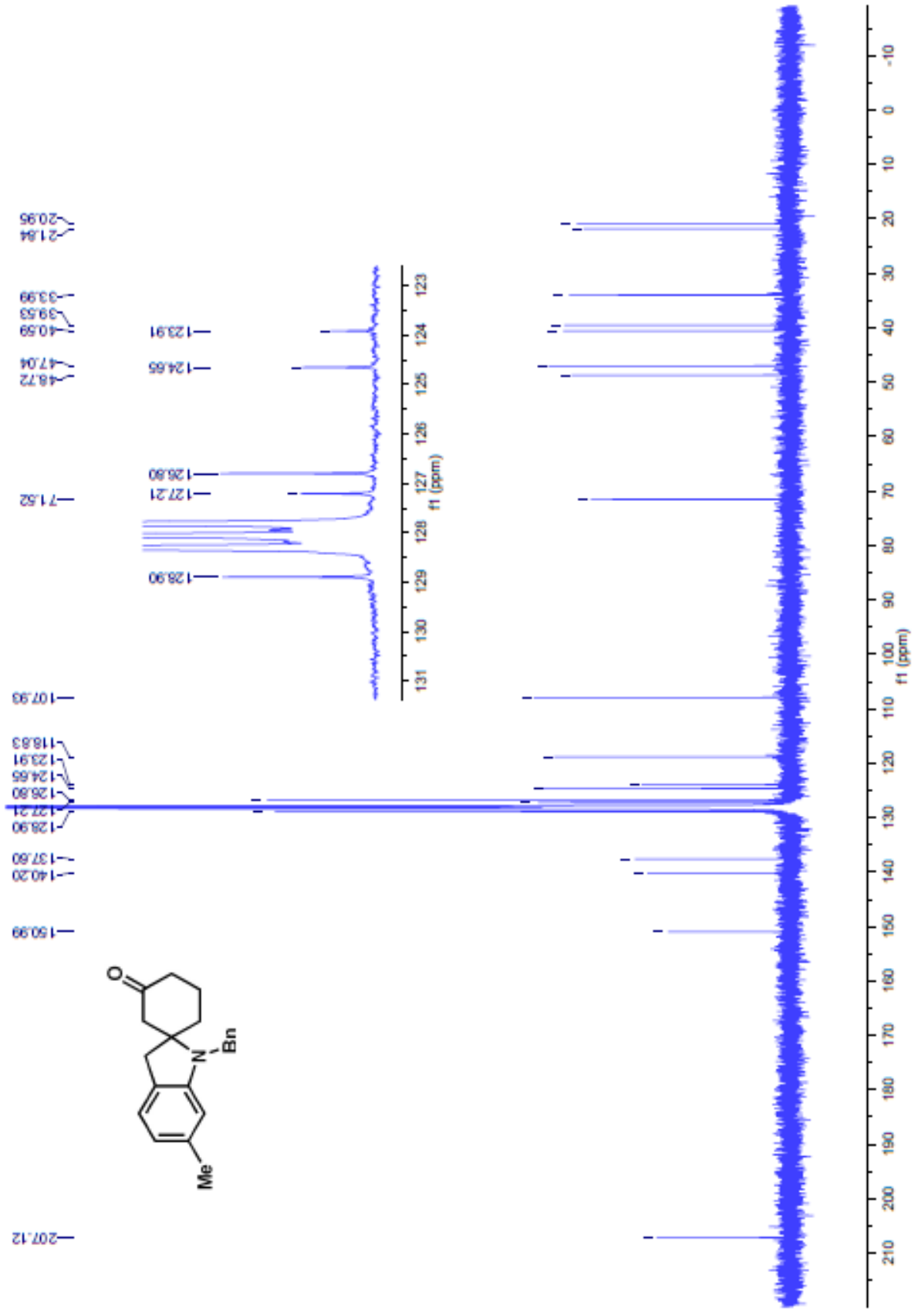
^{1}H NMR (400 MHz, C_6D_6) of ***3ca***



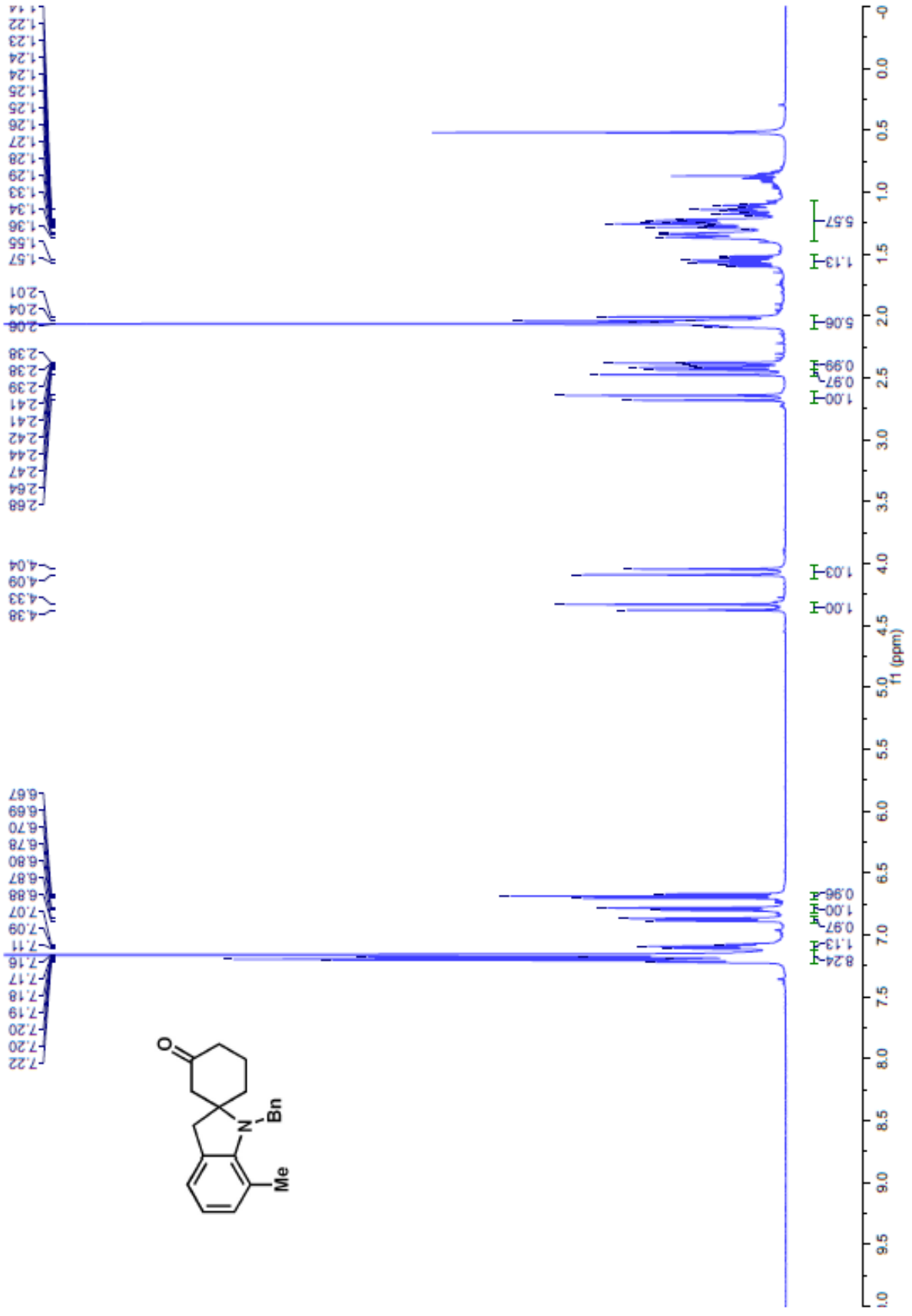
^{13}C NMR (100 MHz, C_6D_6) of ***3ca***



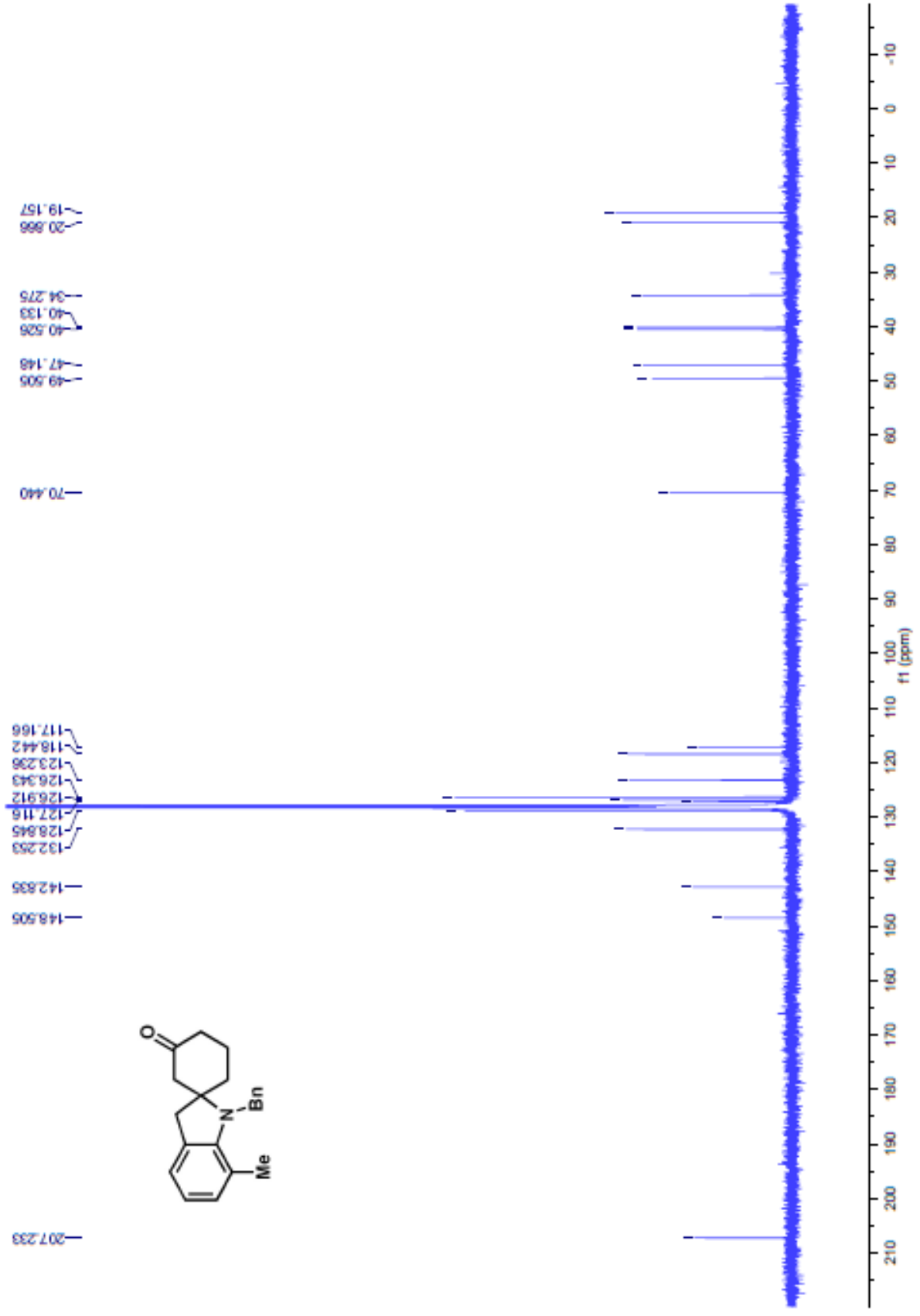
^{1}H NMR (400 MHz, $CDCl_3$) of ***3da***



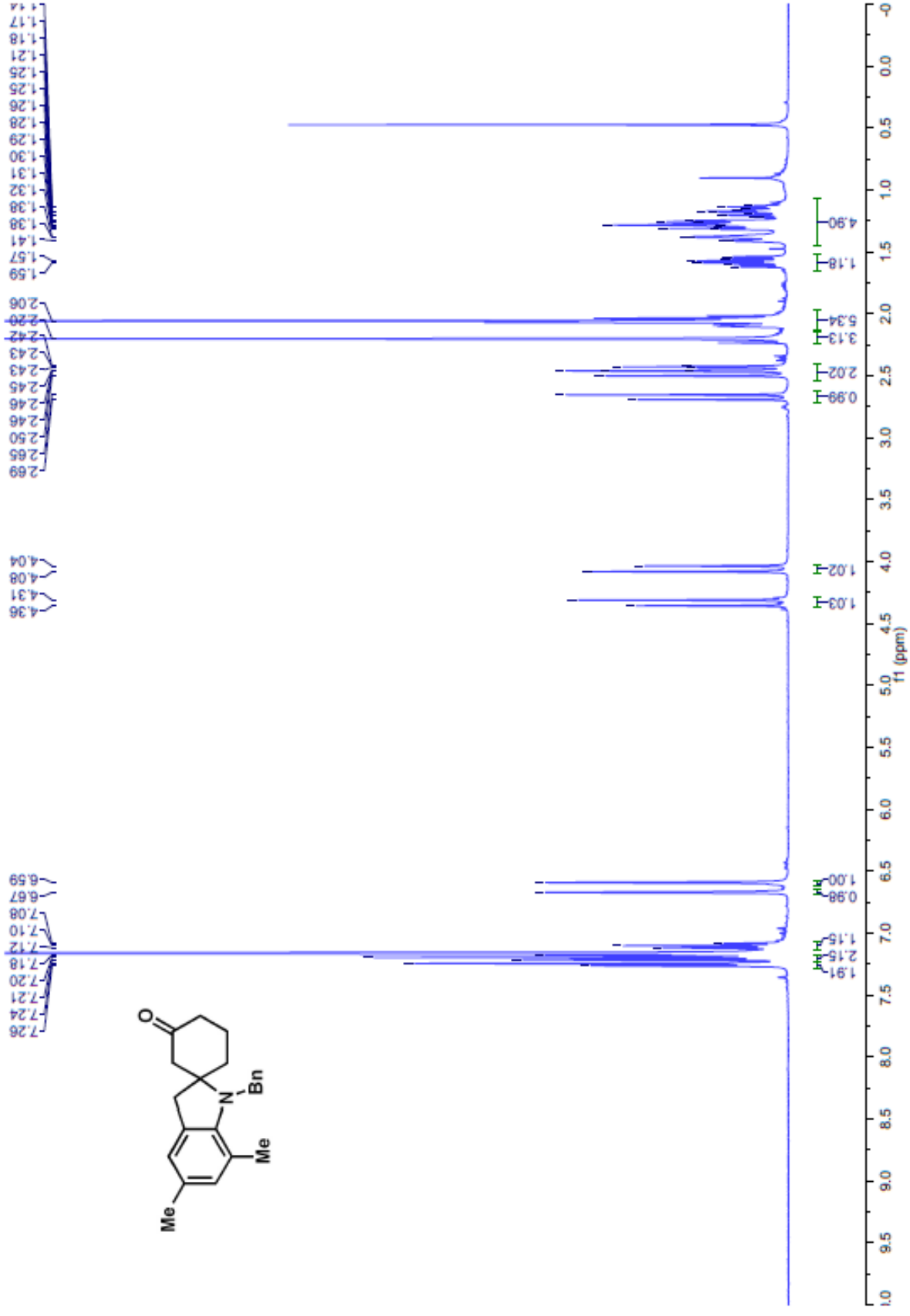
^{13}C NMR (100 MHz, C_6D_6) of ***3da***



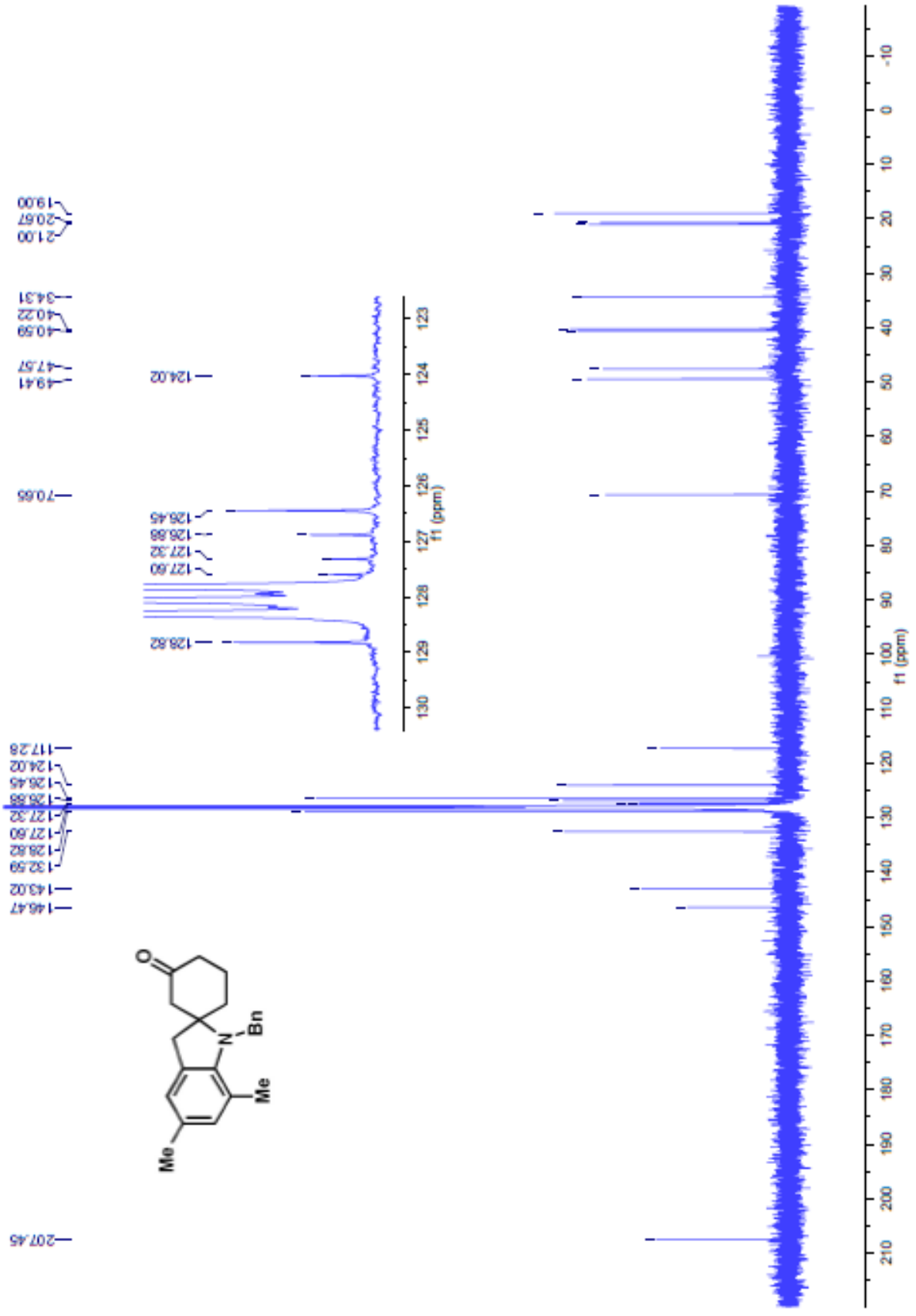
^{1}H NMR (400 MHz, C_6D_6) of ***3ea***



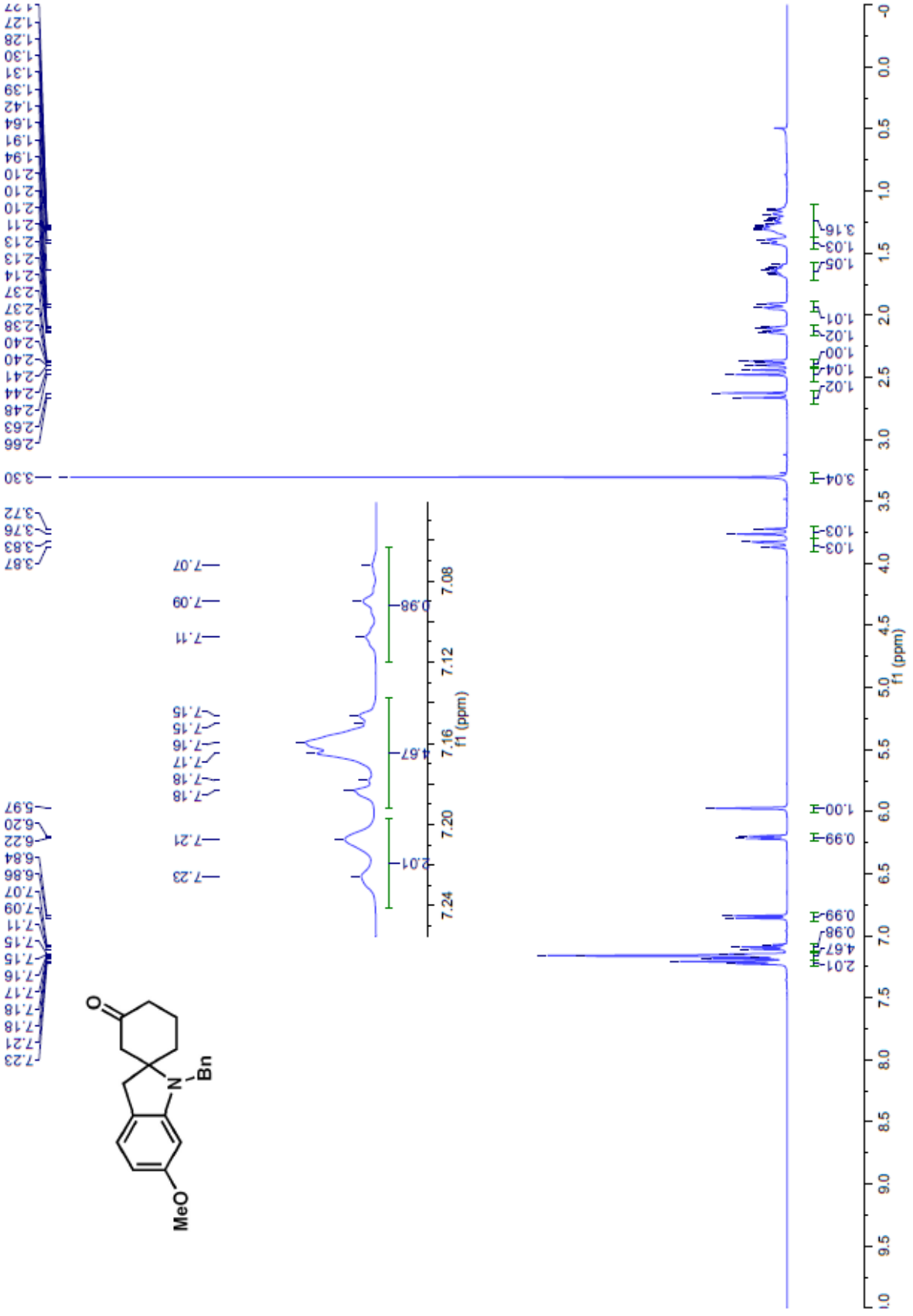
^{13}C NMR (100 MHz, C_6D_6) of ***3ea***



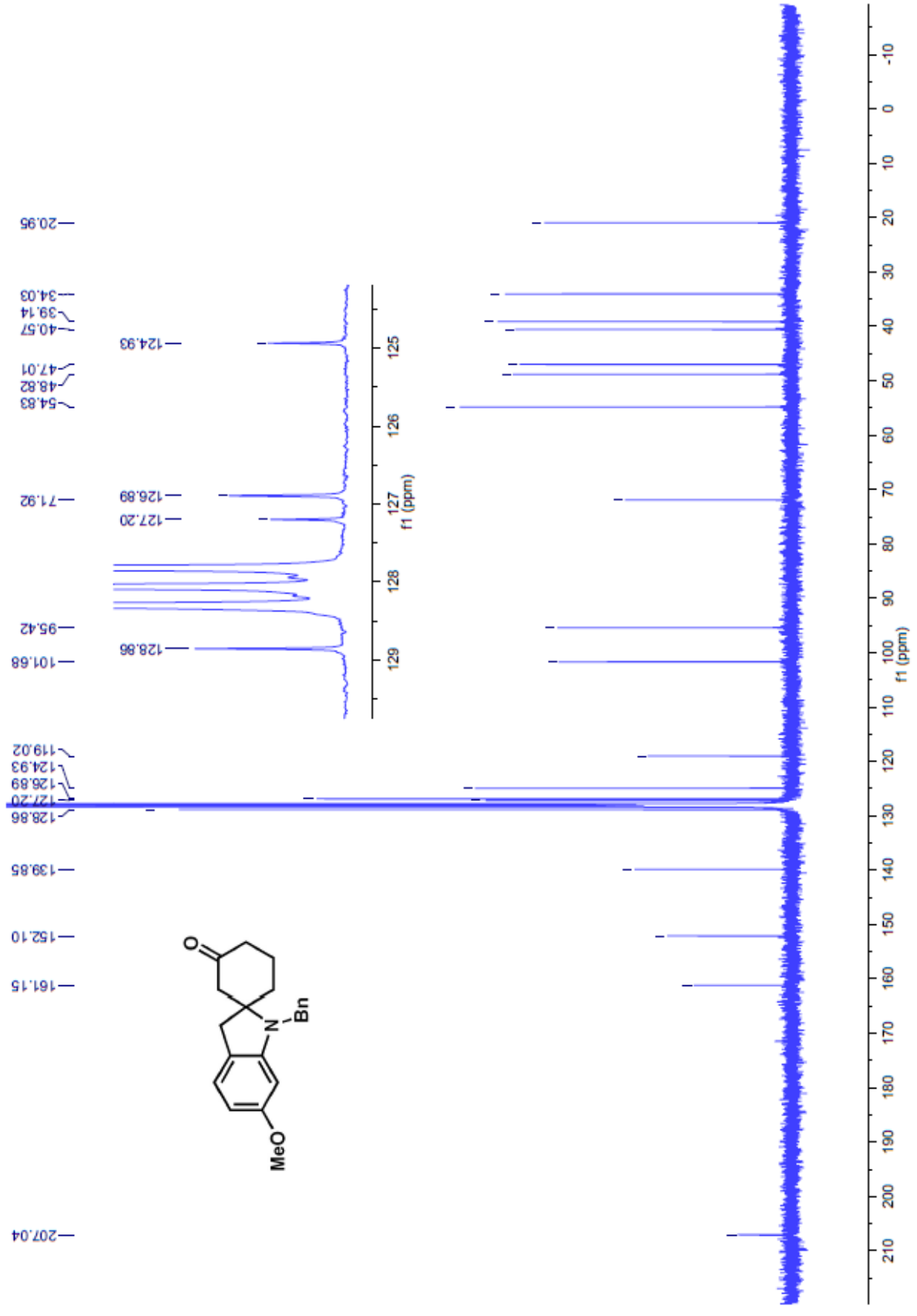
^{1}H NMR (400 MHz, C_6D_6) of ***3fa***



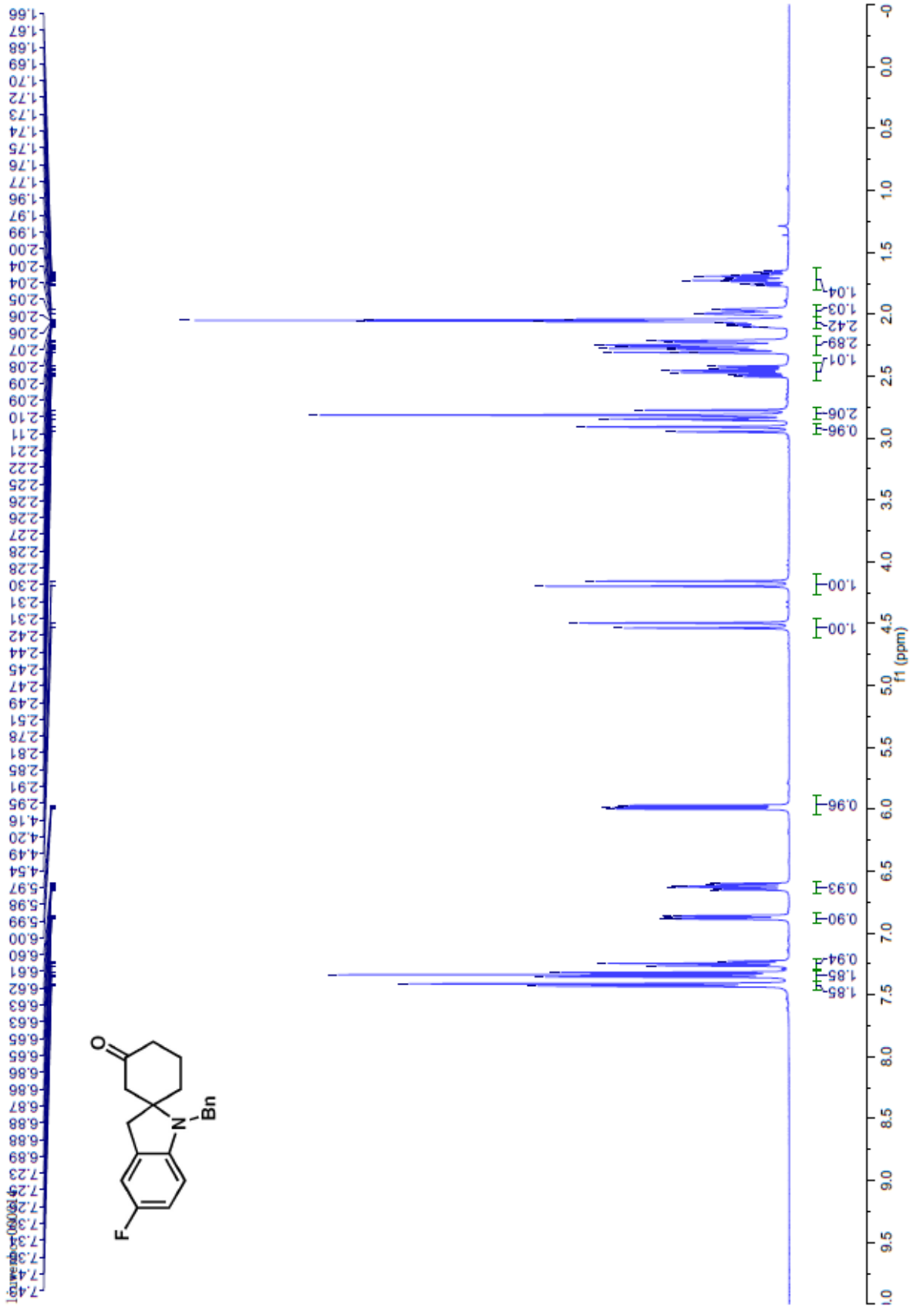
^{13}C NMR (100 MHz, C_6D_6) of ***3fa***



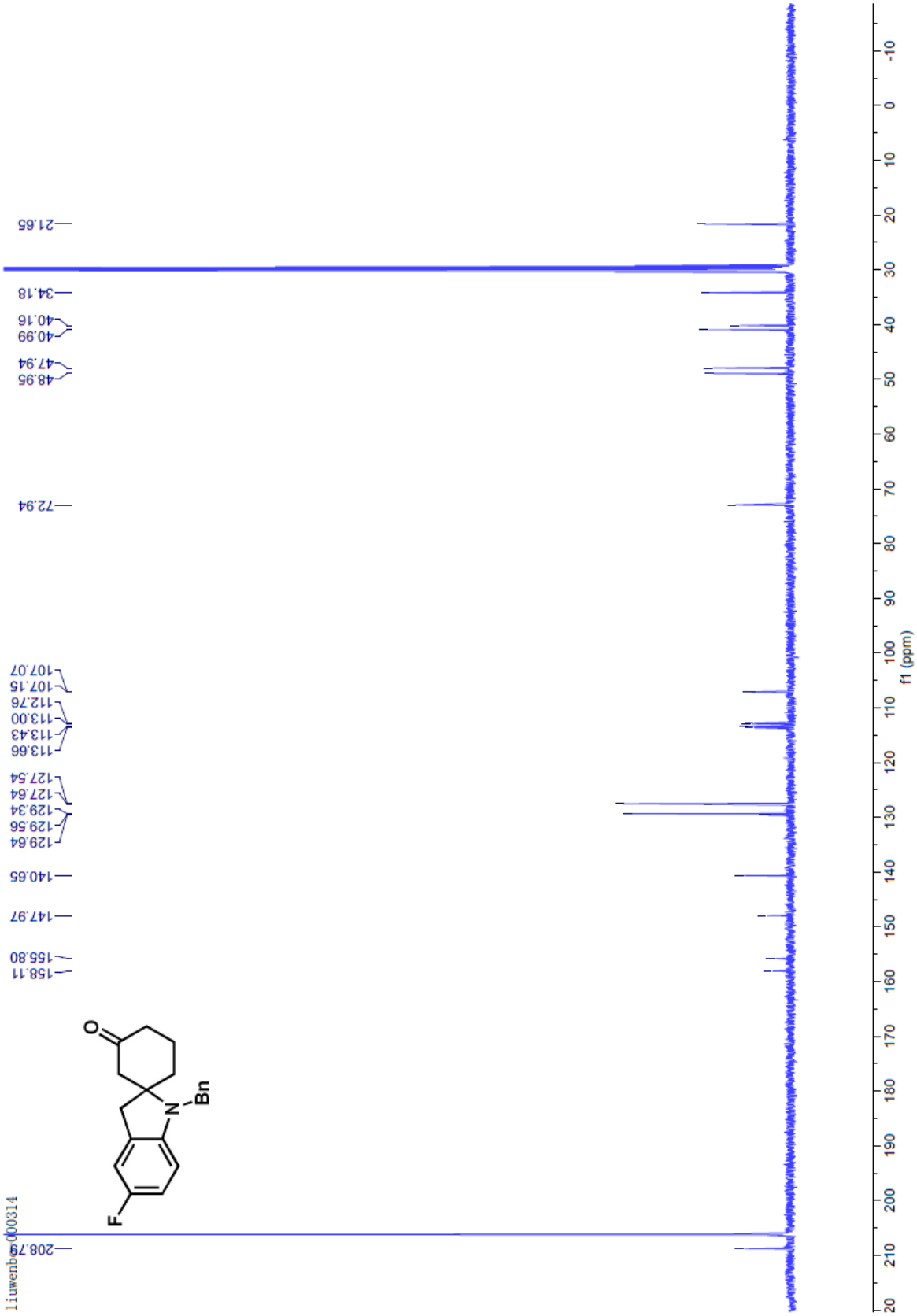
^{1}H NMR (400 MHz, C_6D_6) of ***3ga***



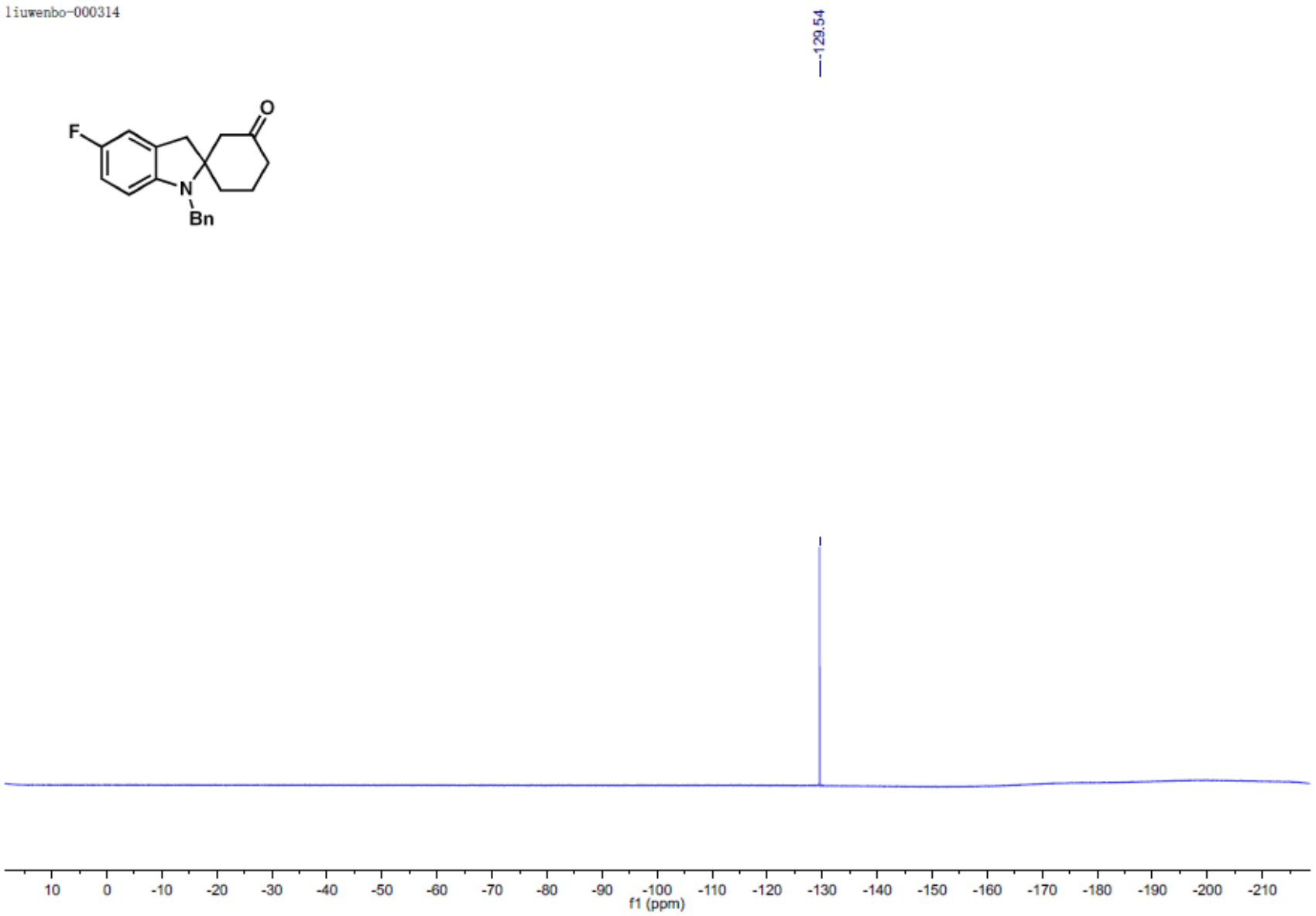
^{13}C NMR (100 MHz, C_6D_6) of ***3ga***



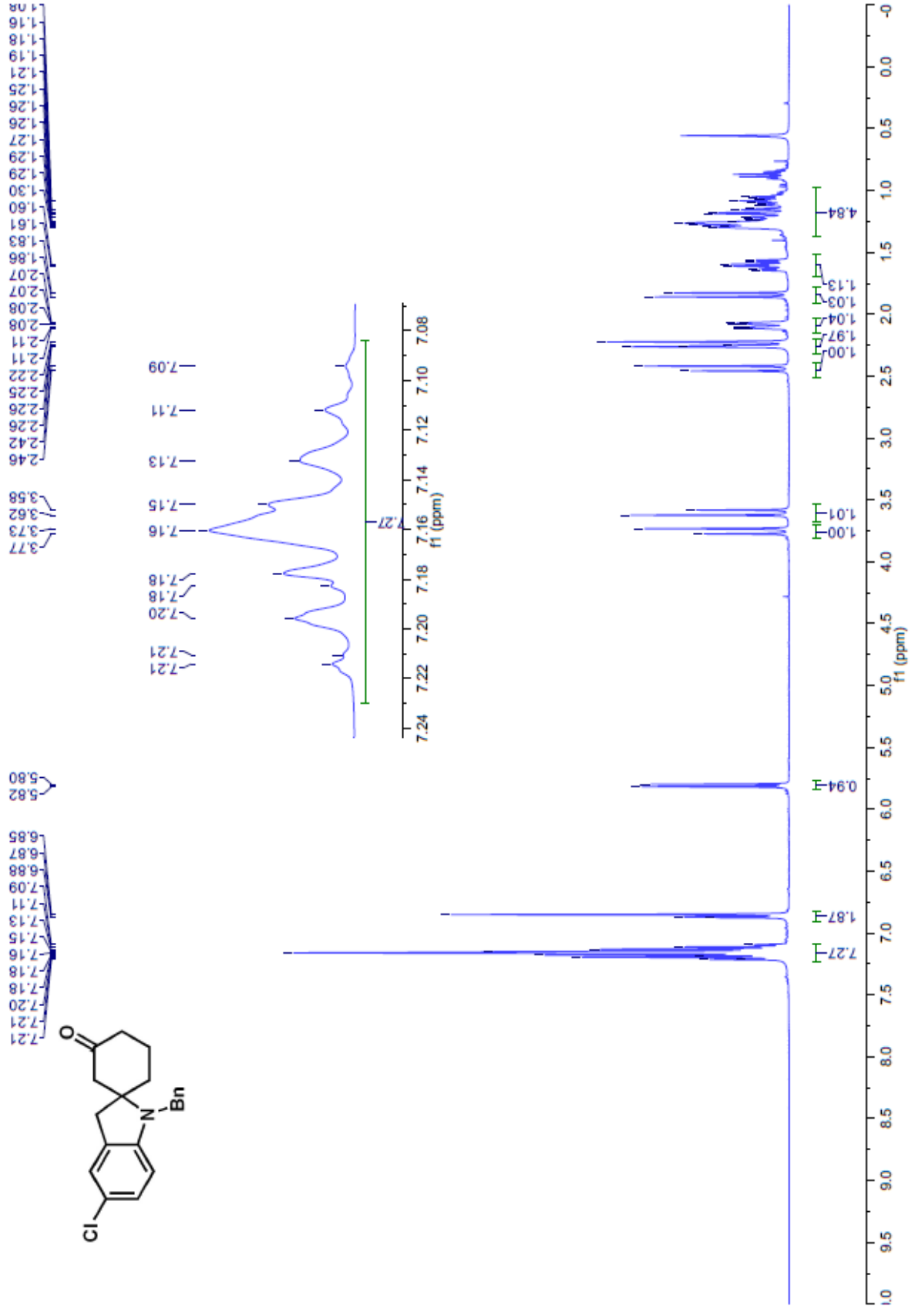
^{1}H NMR (400 MHz, acetone-d_6) of ***3ha***



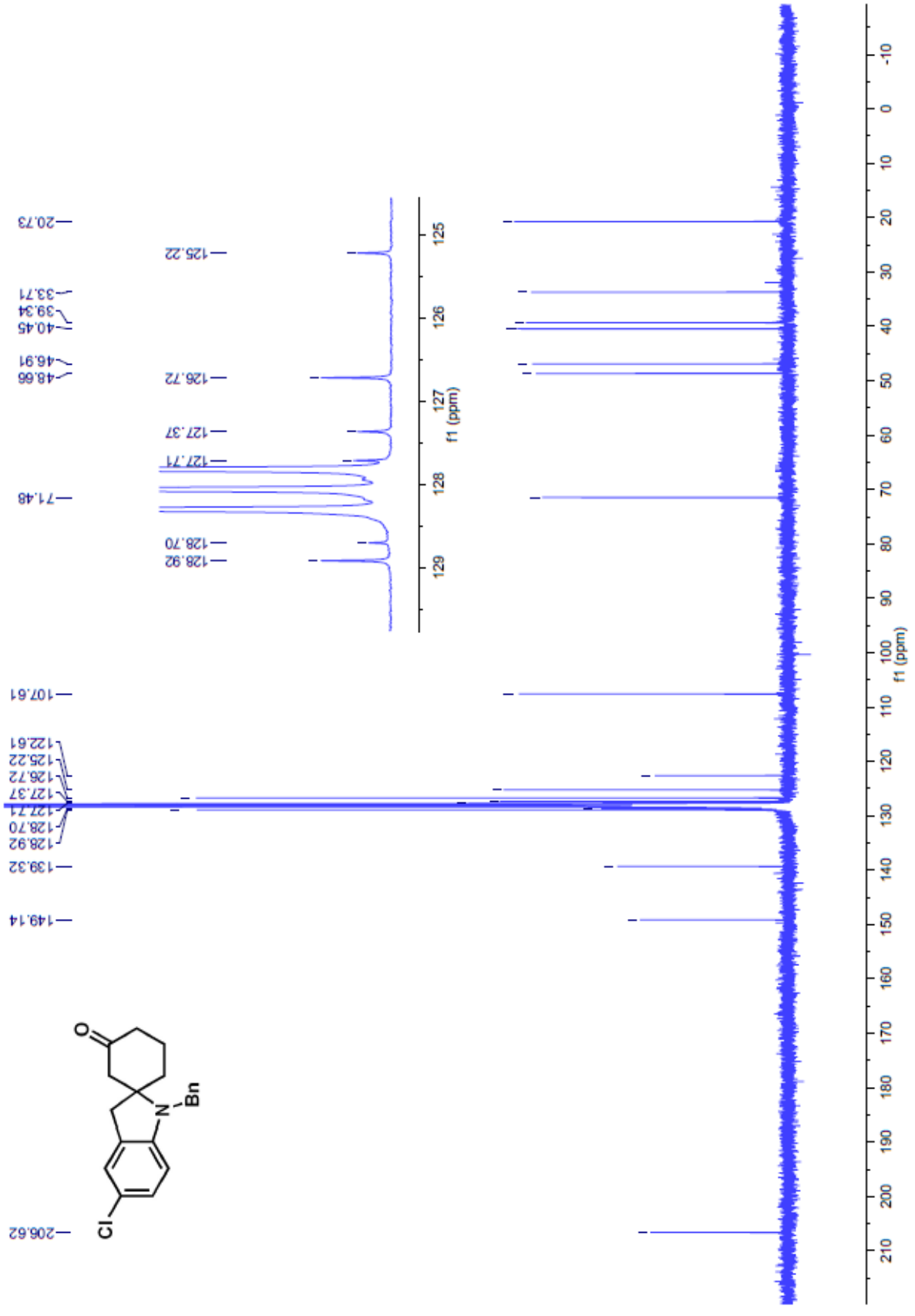
^{13}C NMR (100 MHz, acetone-d_6) of ***3ha***



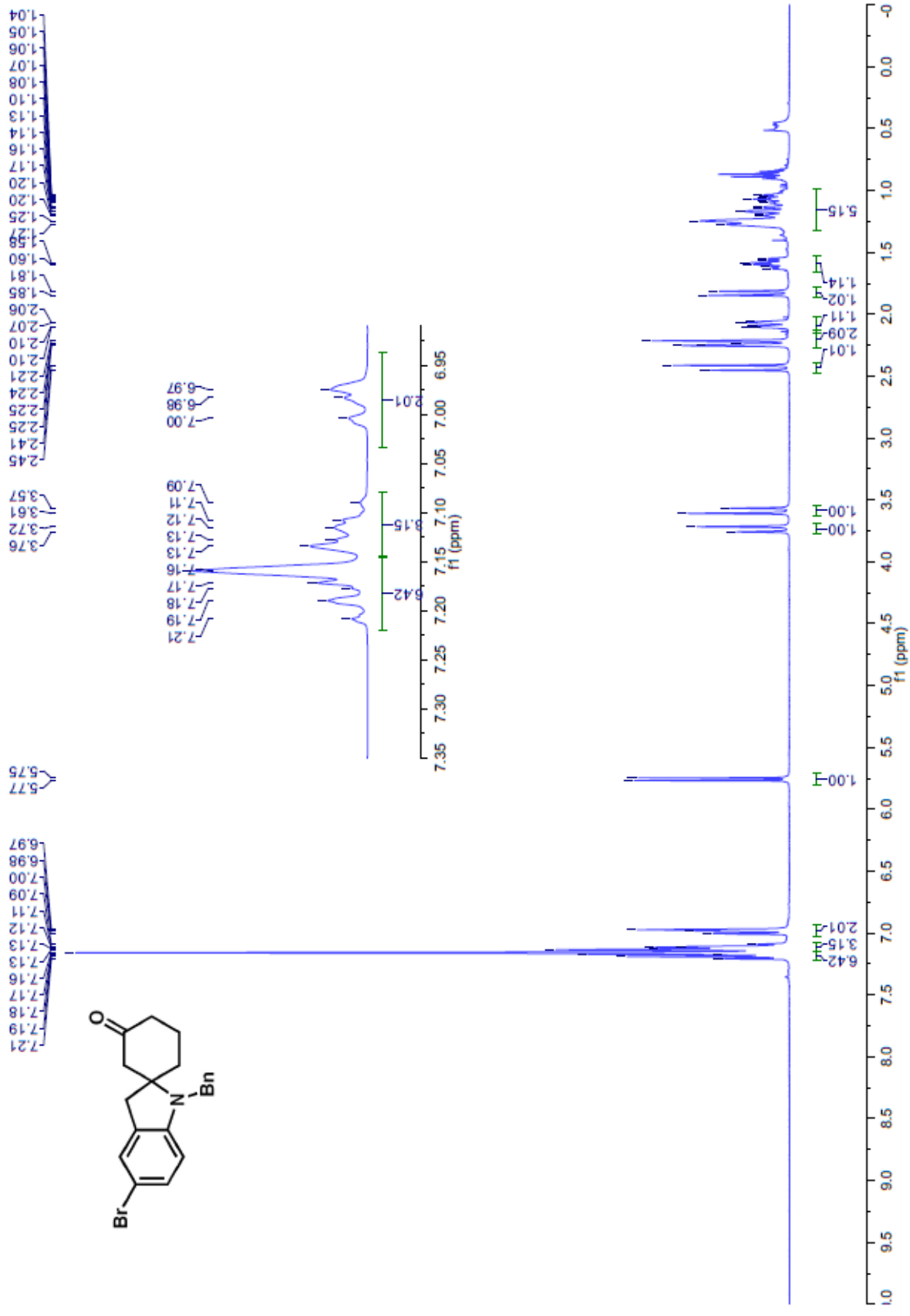
^{19}F NMR (376 MHz, acetone-d_6) of ***3ha***



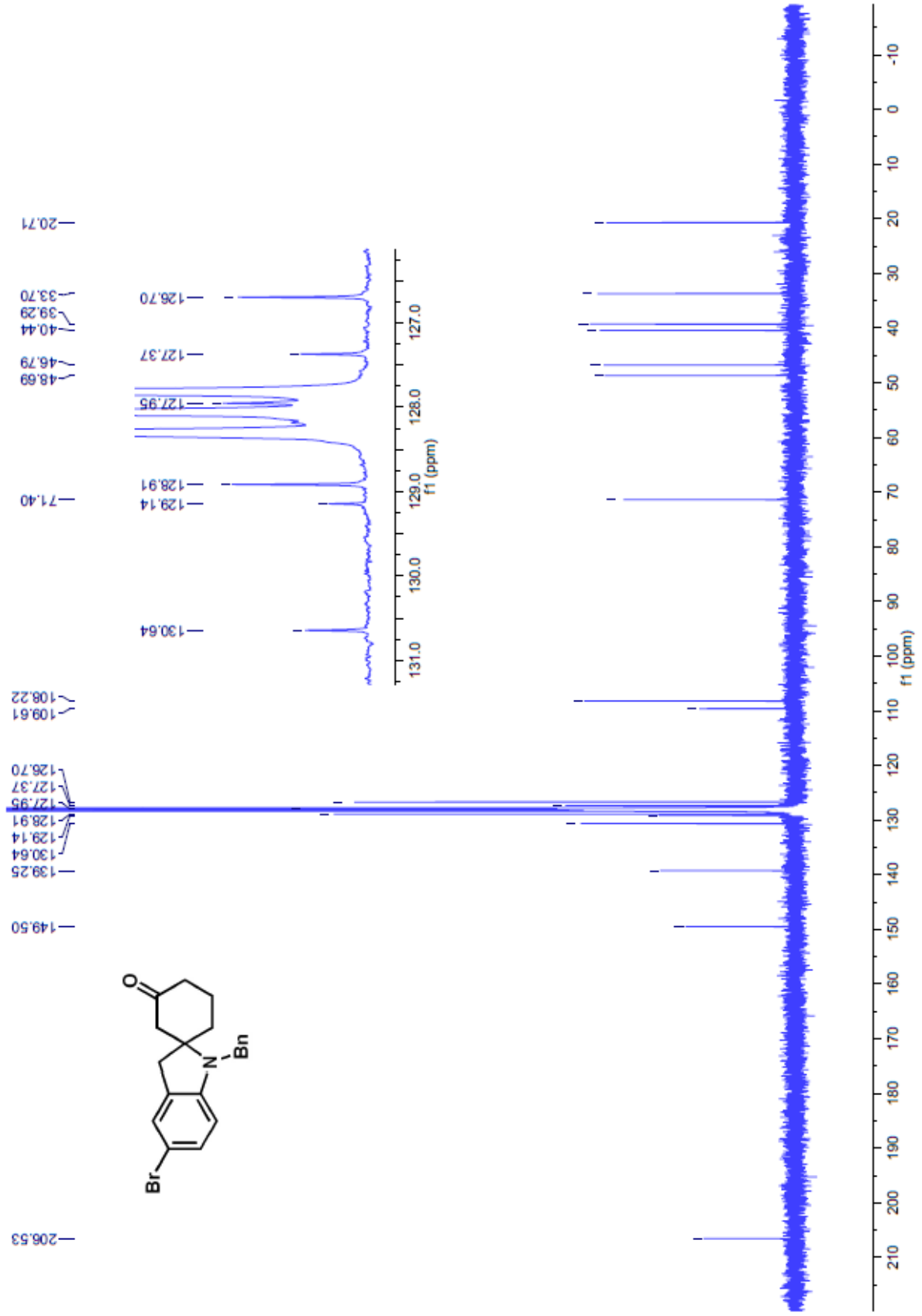
^{1}H NMR (400 MHz, C_6D_6) of ***3ia***



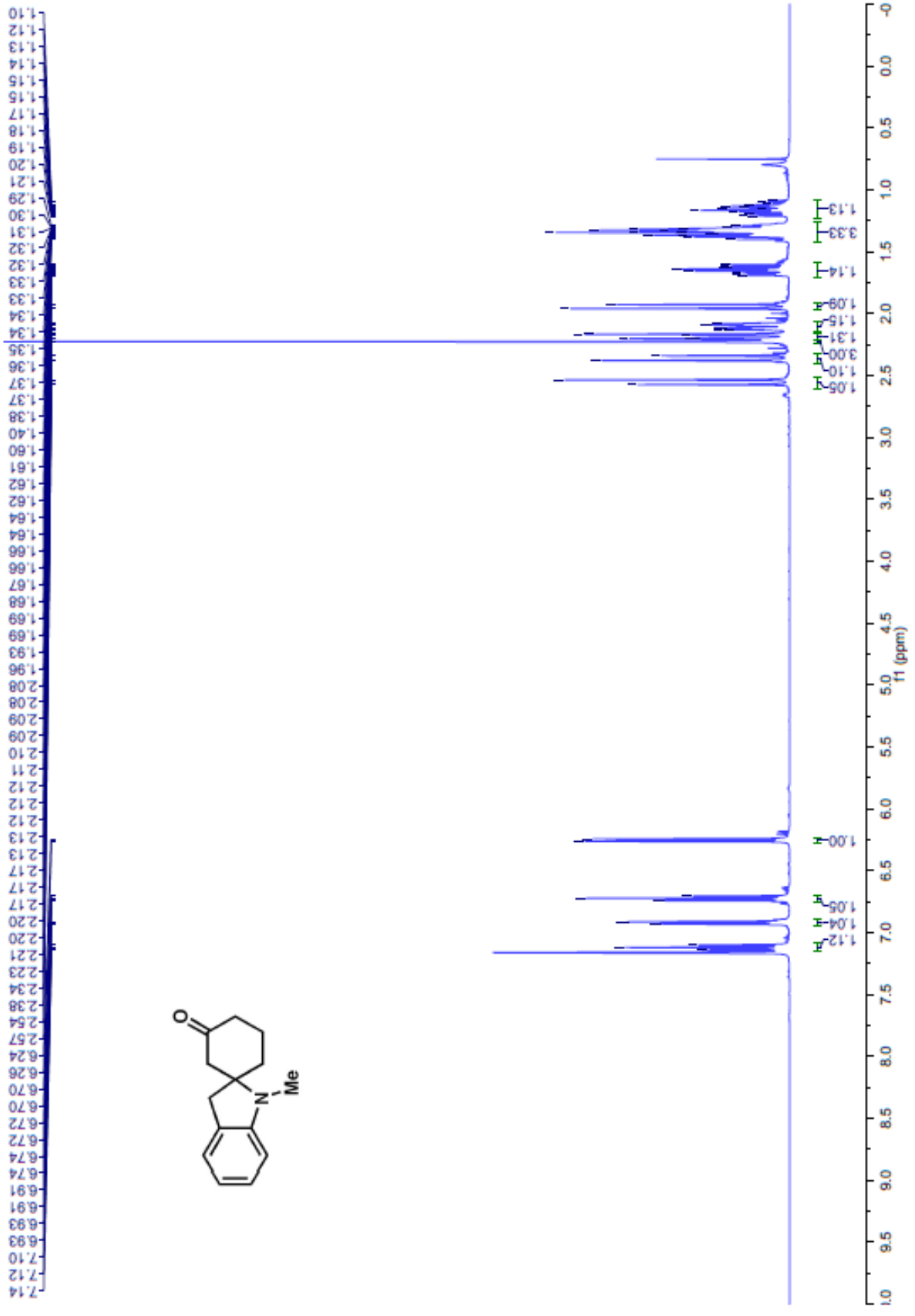
^{13}C NMR (100 MHz, C_6D_6) of ***3iu***



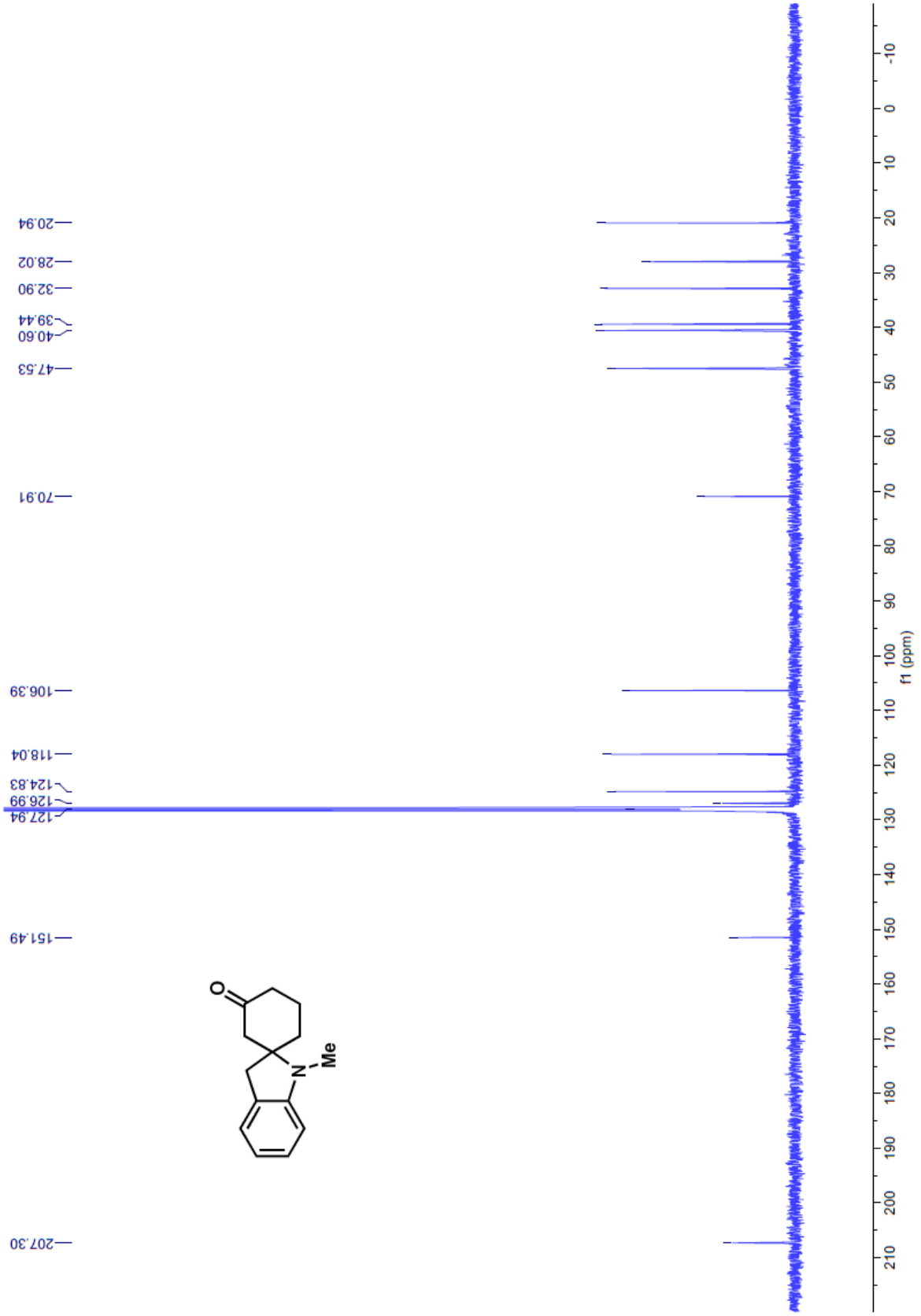
^{1}H NMR (400 MHz, C_6D_6) of ***3ja***



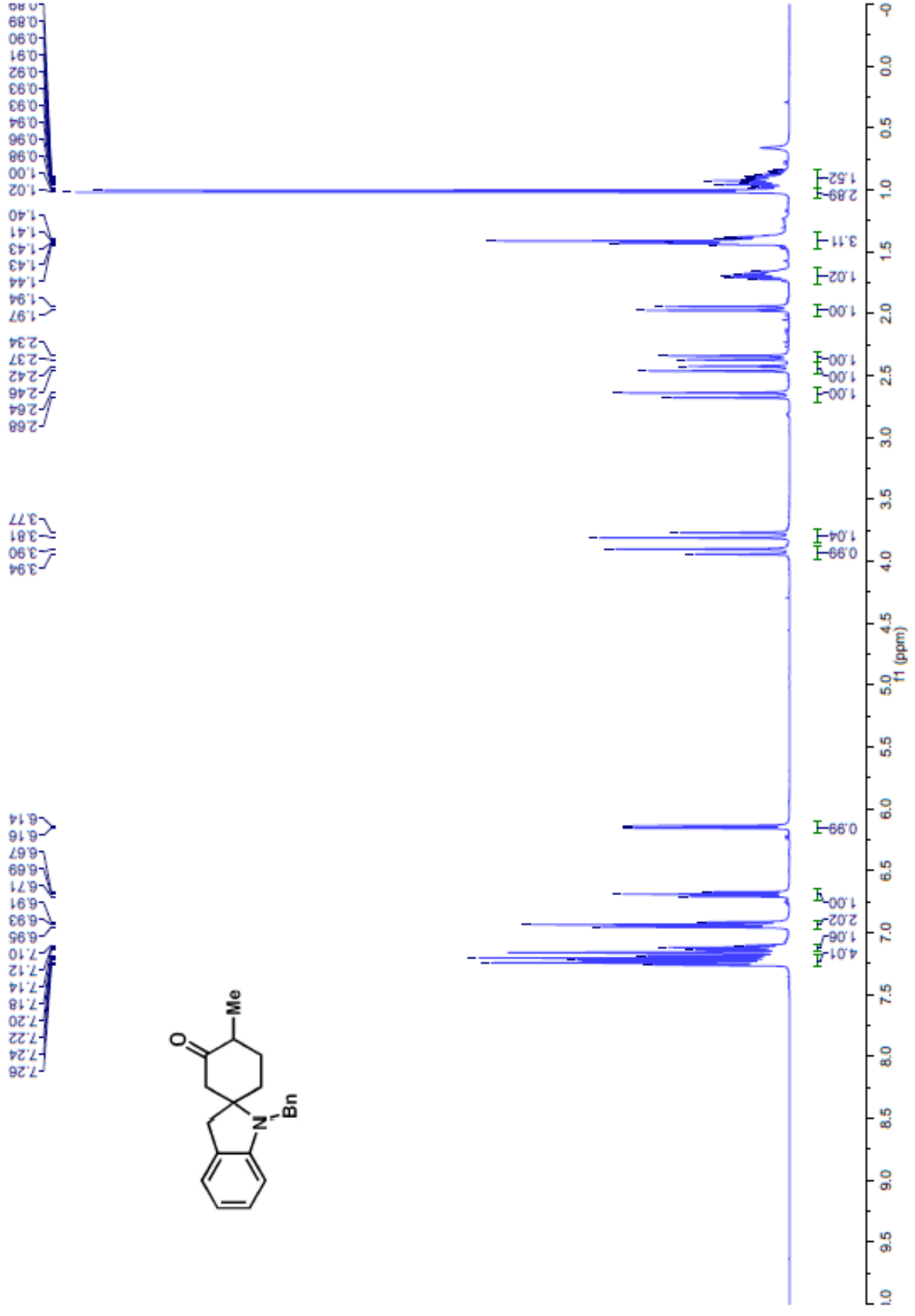
^{13}C NMR (100 MHz, C_6D_6) of ***3ju***



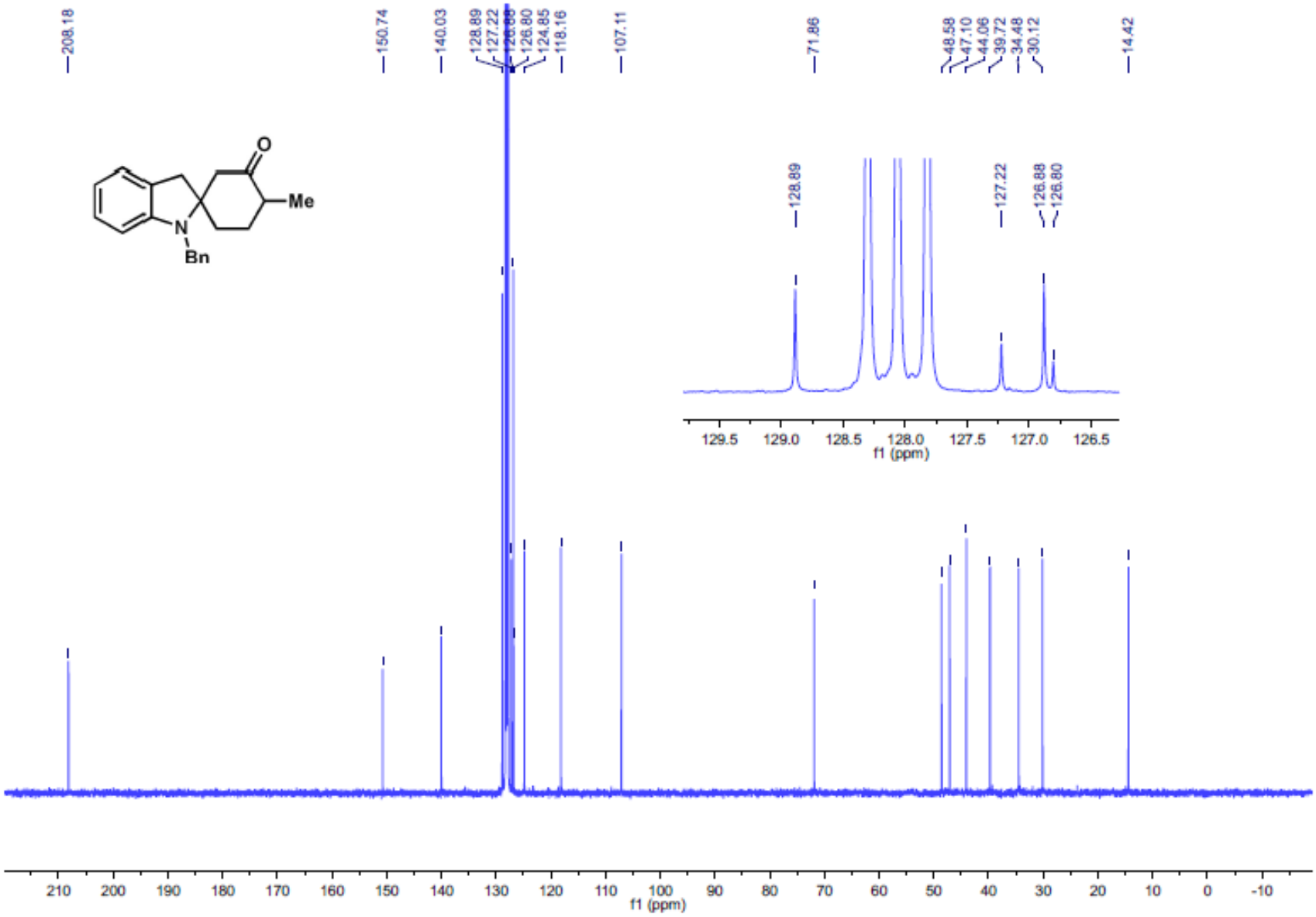
^{1}H NMR (400 MHz, C_6D_6) of ***3ka***



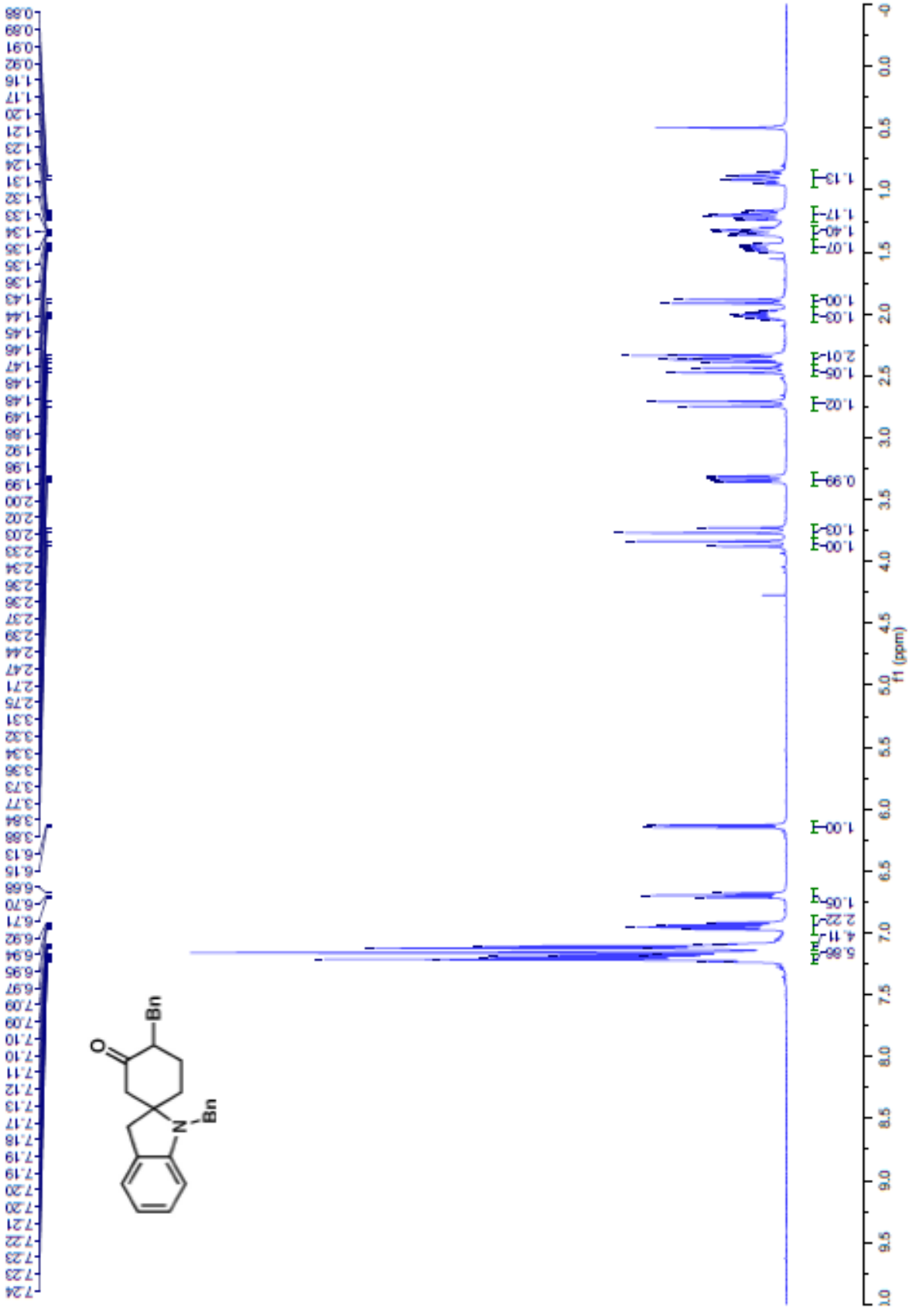
^{13}C NMR (100 MHz, C_6D_6) of ***3ka***



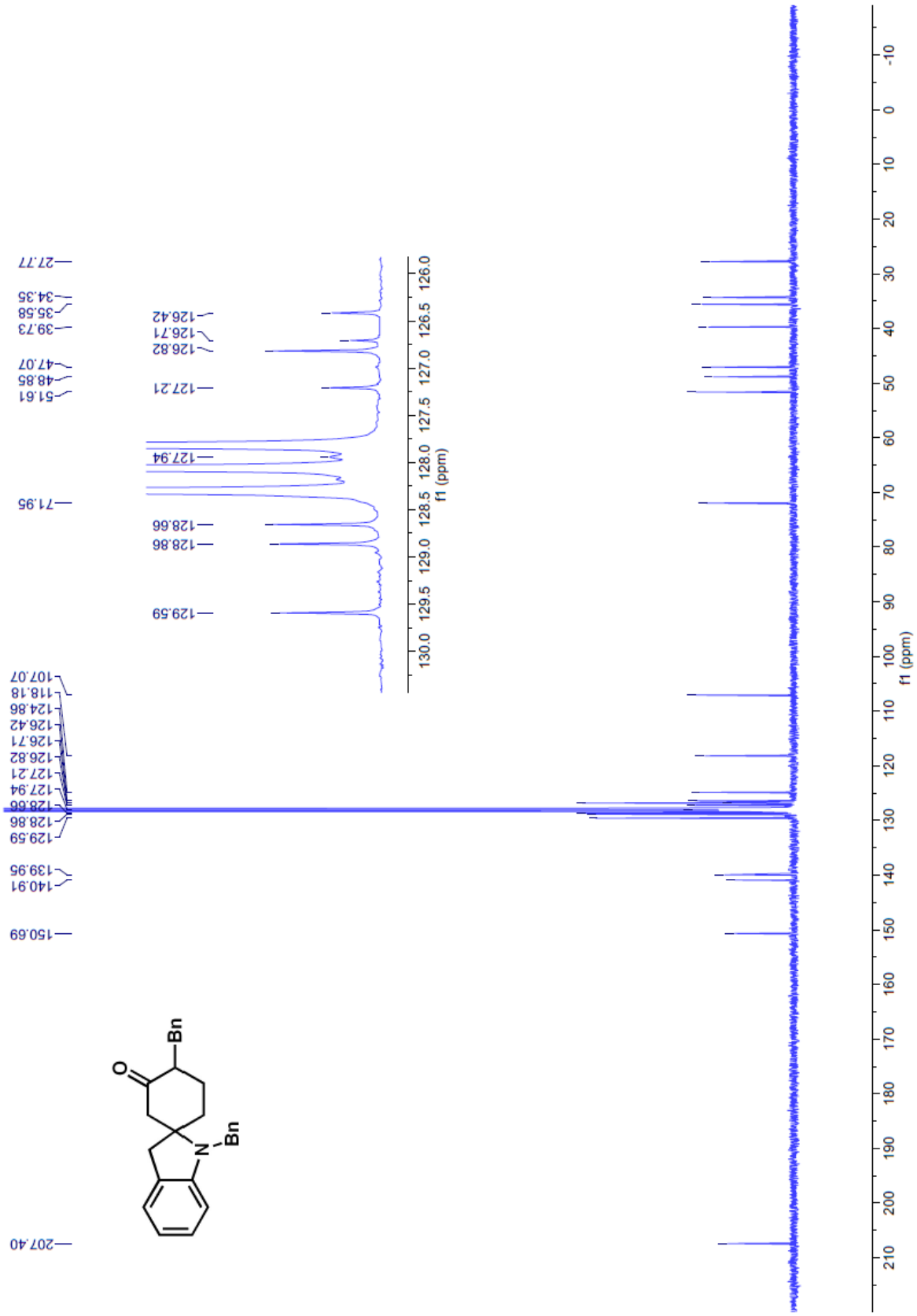
^{1}H NMR (400 MHz, C_6D_6) of ***3ab***



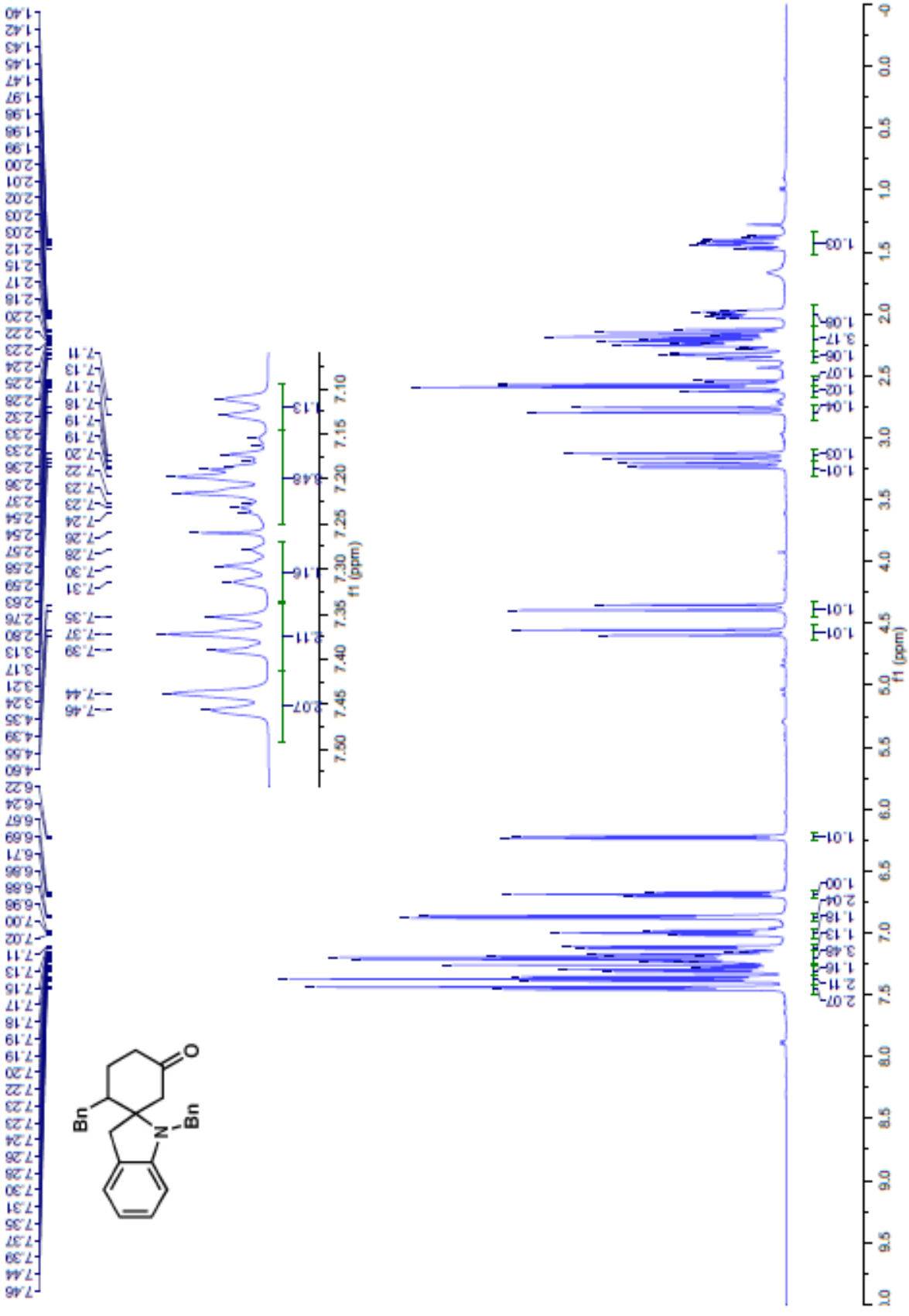
^{13}C NMR (100 MHz, C_6D_6) of ***3ab***



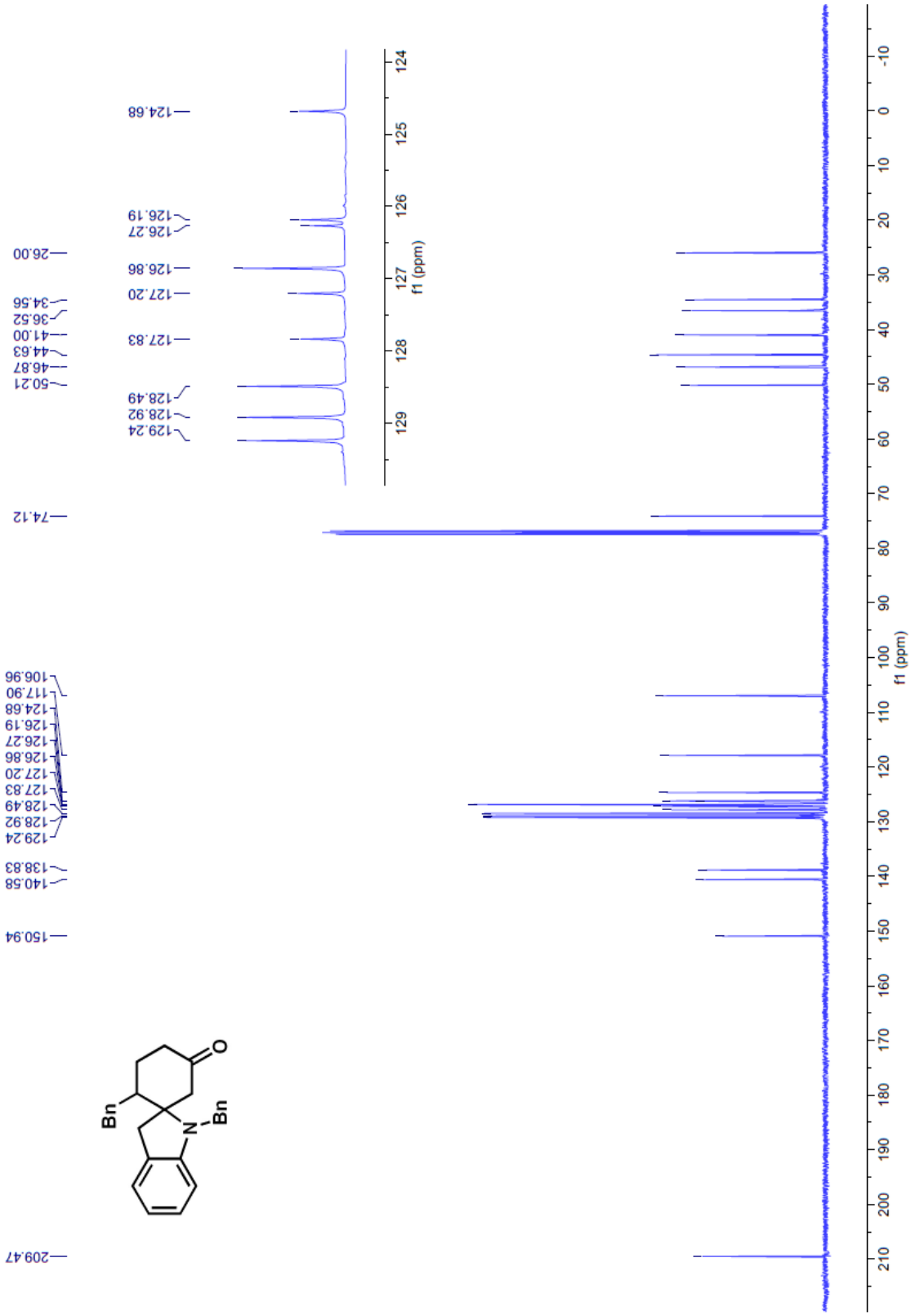
^{1}H NMR (400 MHz, C_6D_6) of ***3ac***



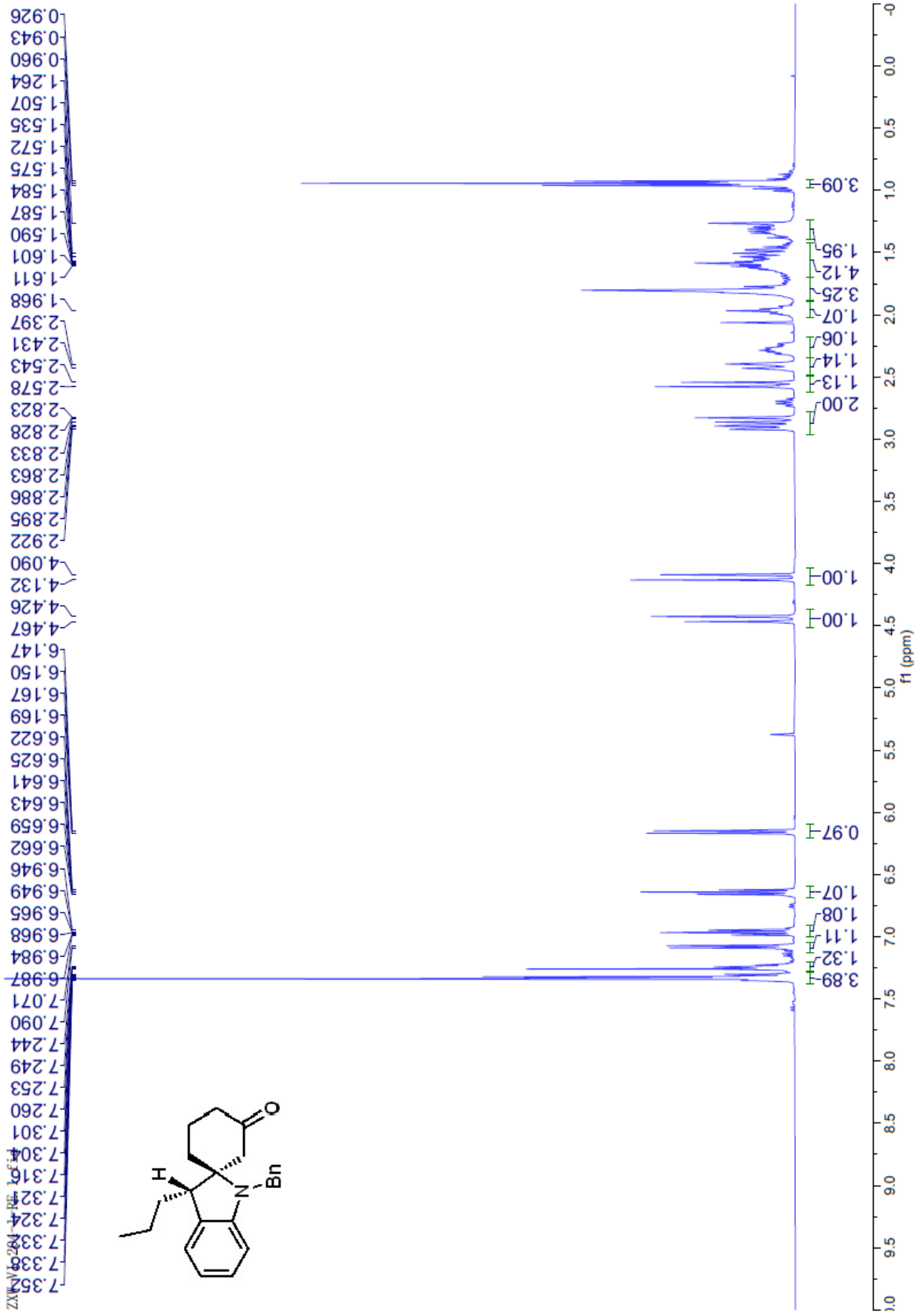
^{13}C NMR (100 MHz, C_6D_6) of ***3ac***



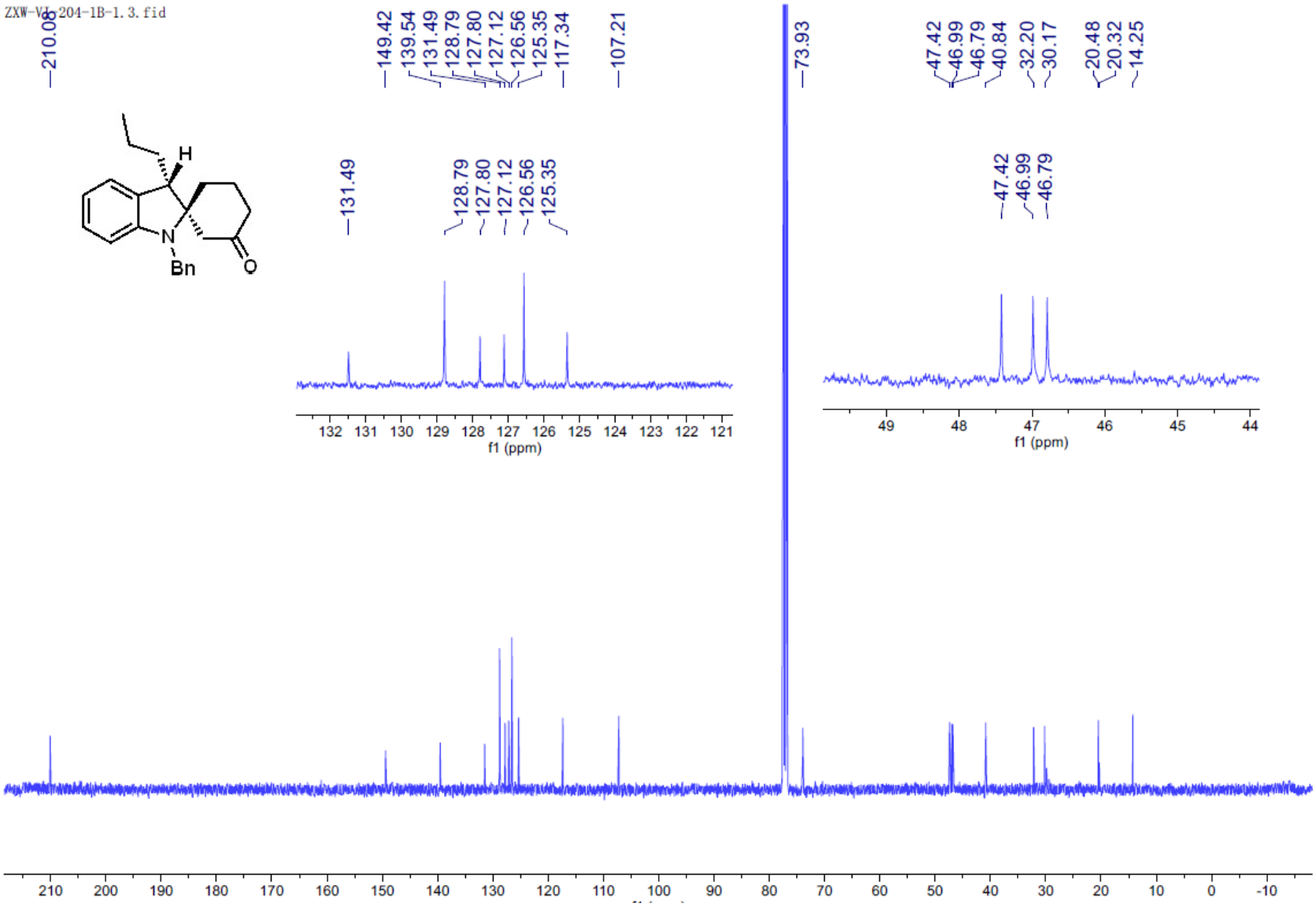
^{1}H NMR (400 MHz, $CDCl_3$) of ***3ad***



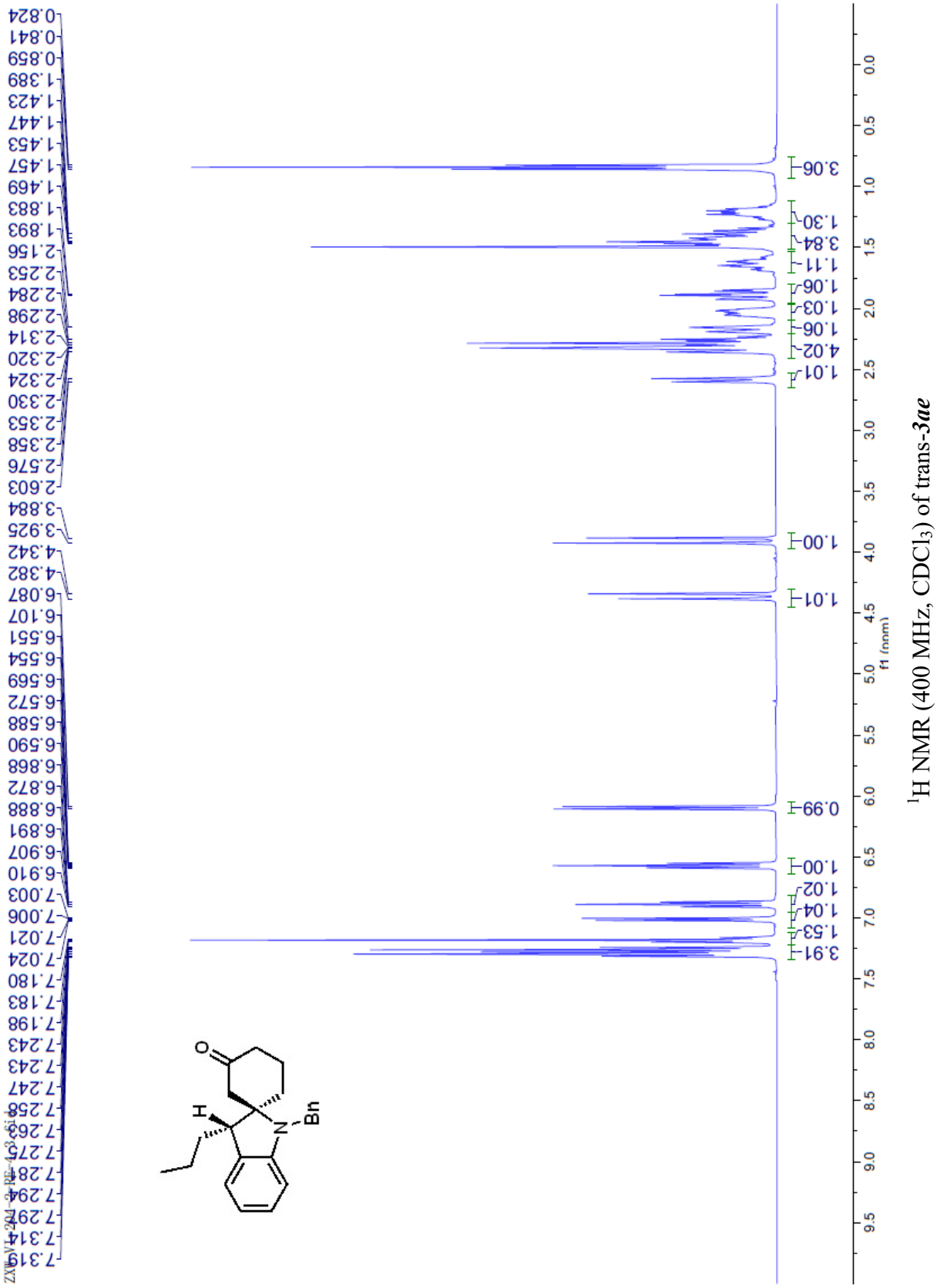
^{13}C NMR (100 MHz, $CDCl_3$) of ***3ad***



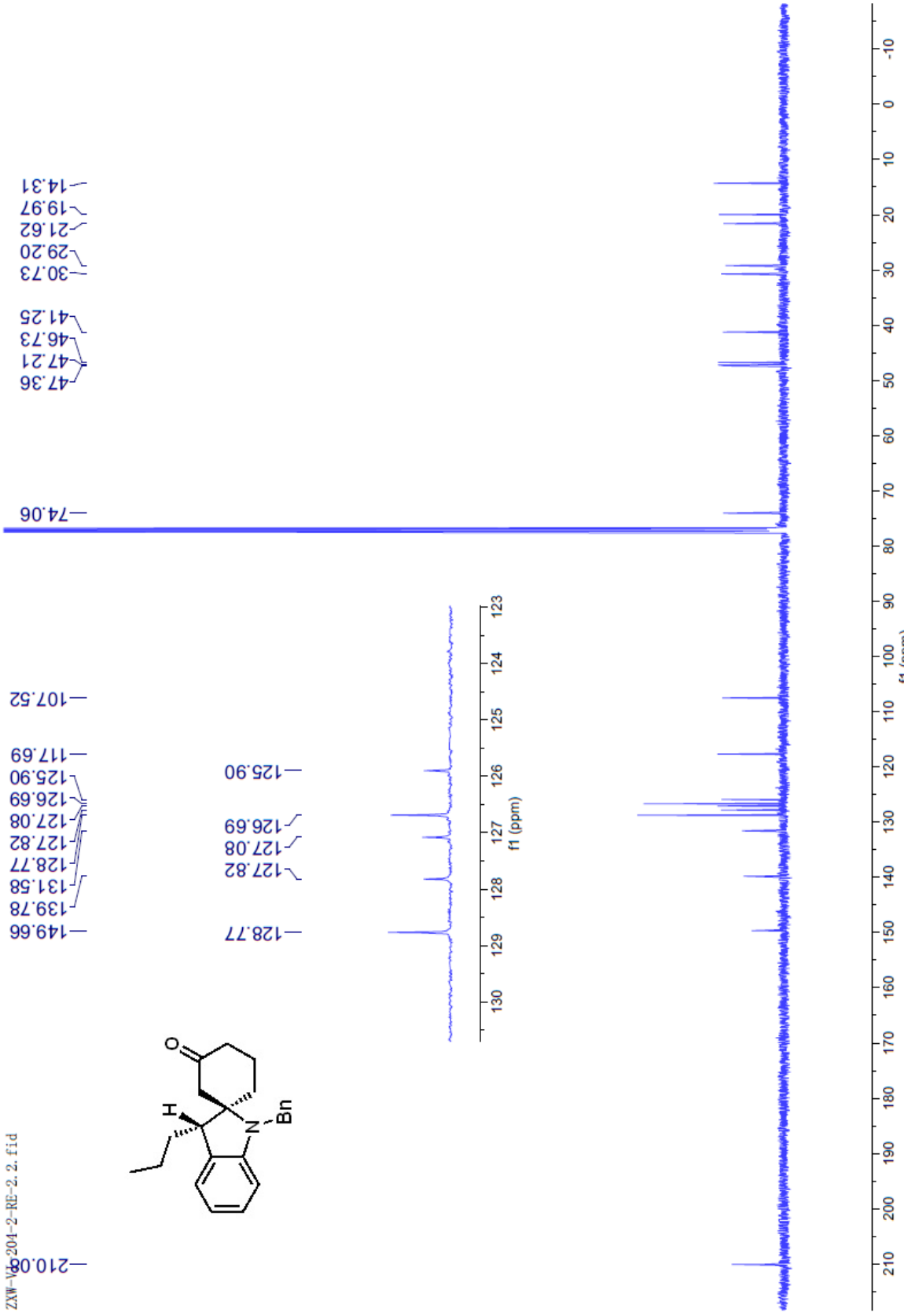
^{1}H NMR (400 MHz, $CDCl_3$) of cis-***3ae***



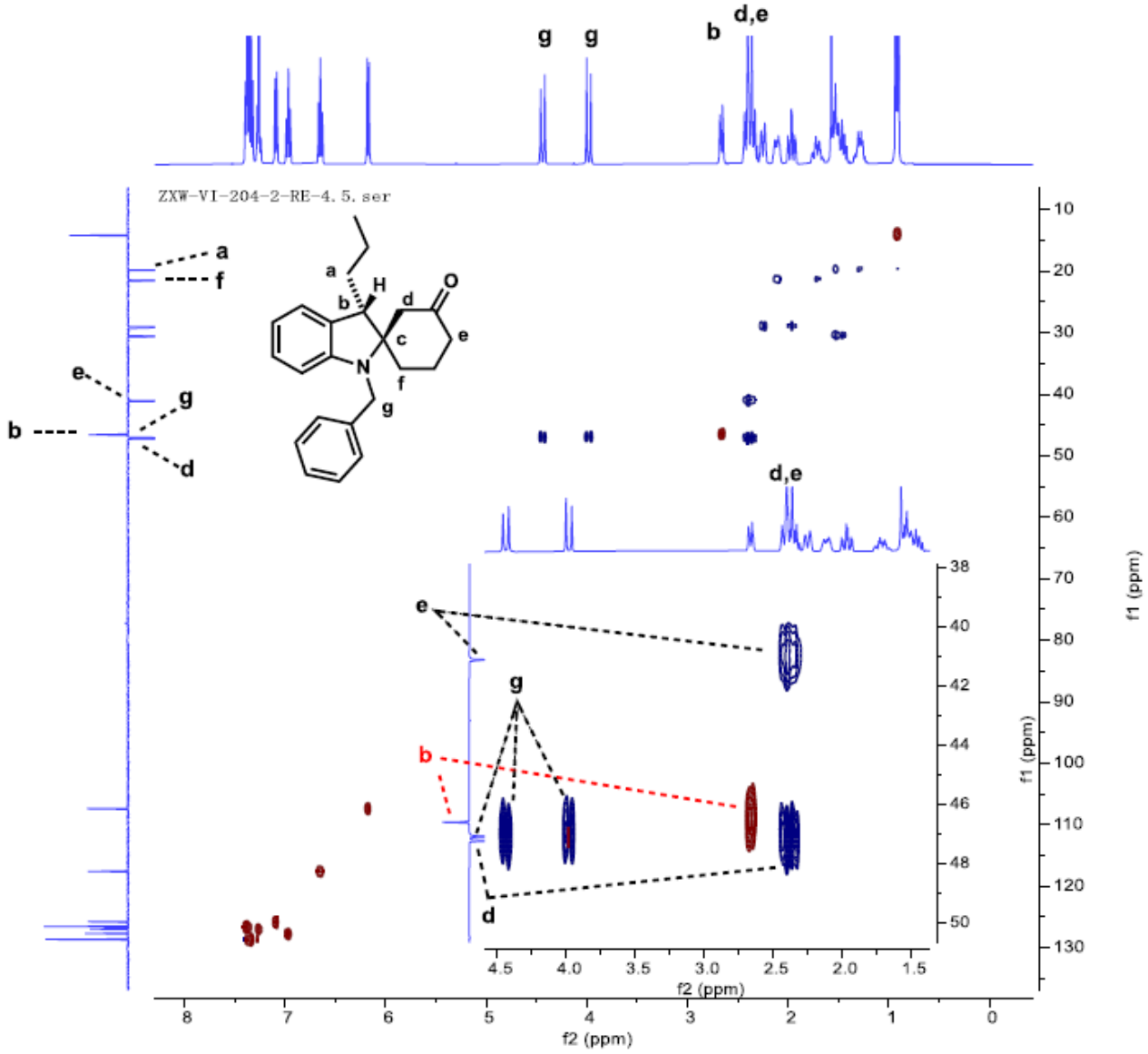
^{13}C NMR (100 MHz, $CDCl_3$) of cis-***3ae***



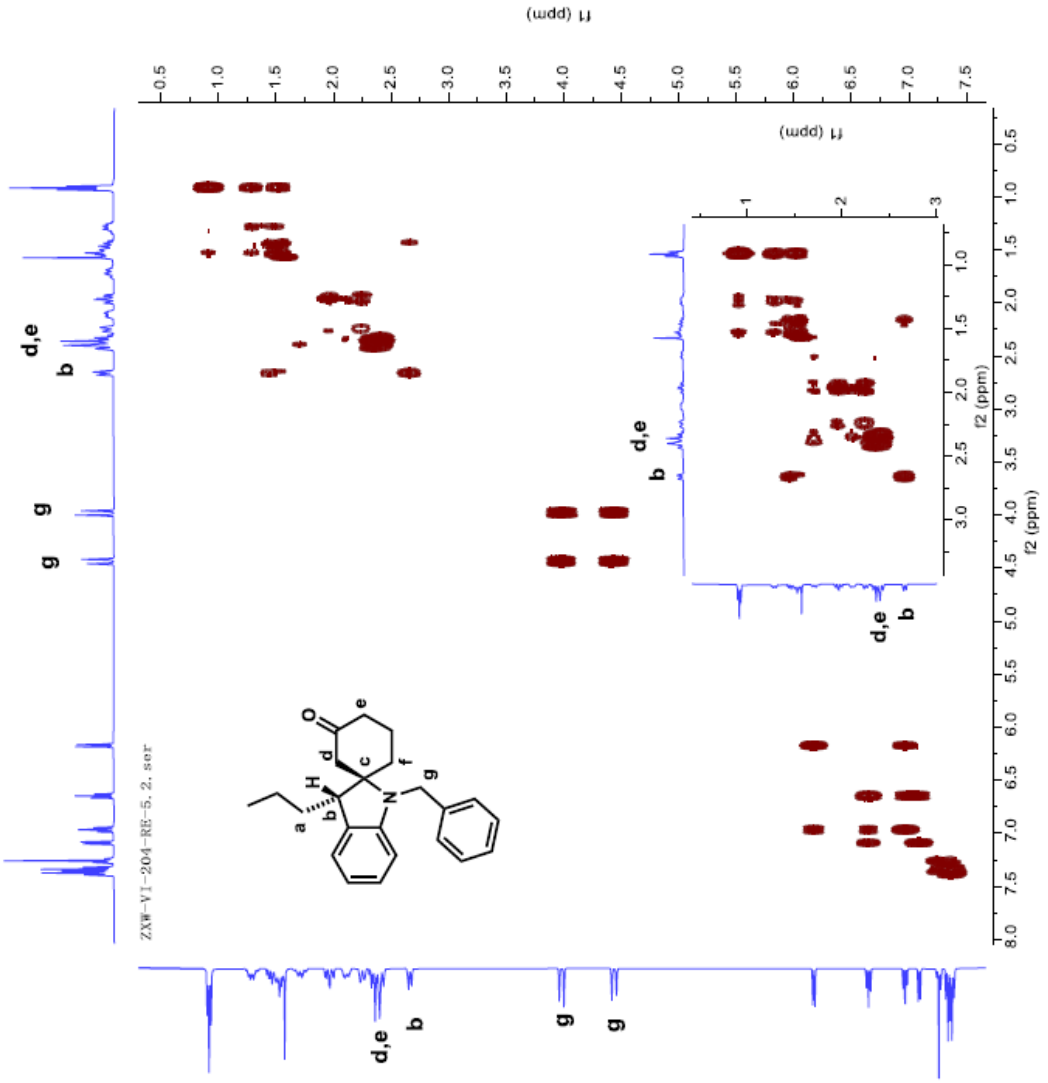
^{1}H NMR (400 MHz, $CDCl_3$) of trans-***3ae***



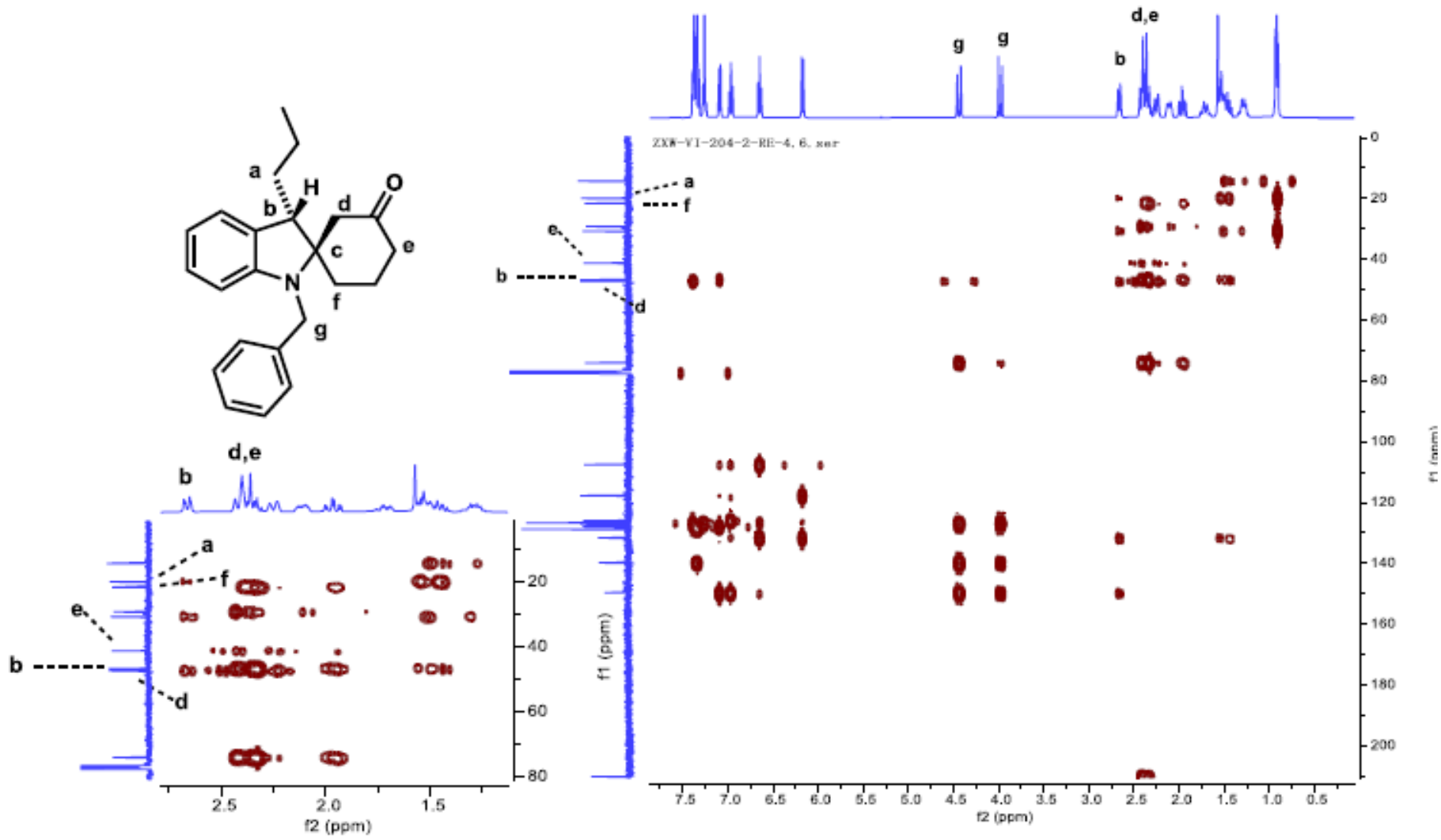
^{13}C NMR (100 MHz, $CDCl_3$) of trans-***3ae***



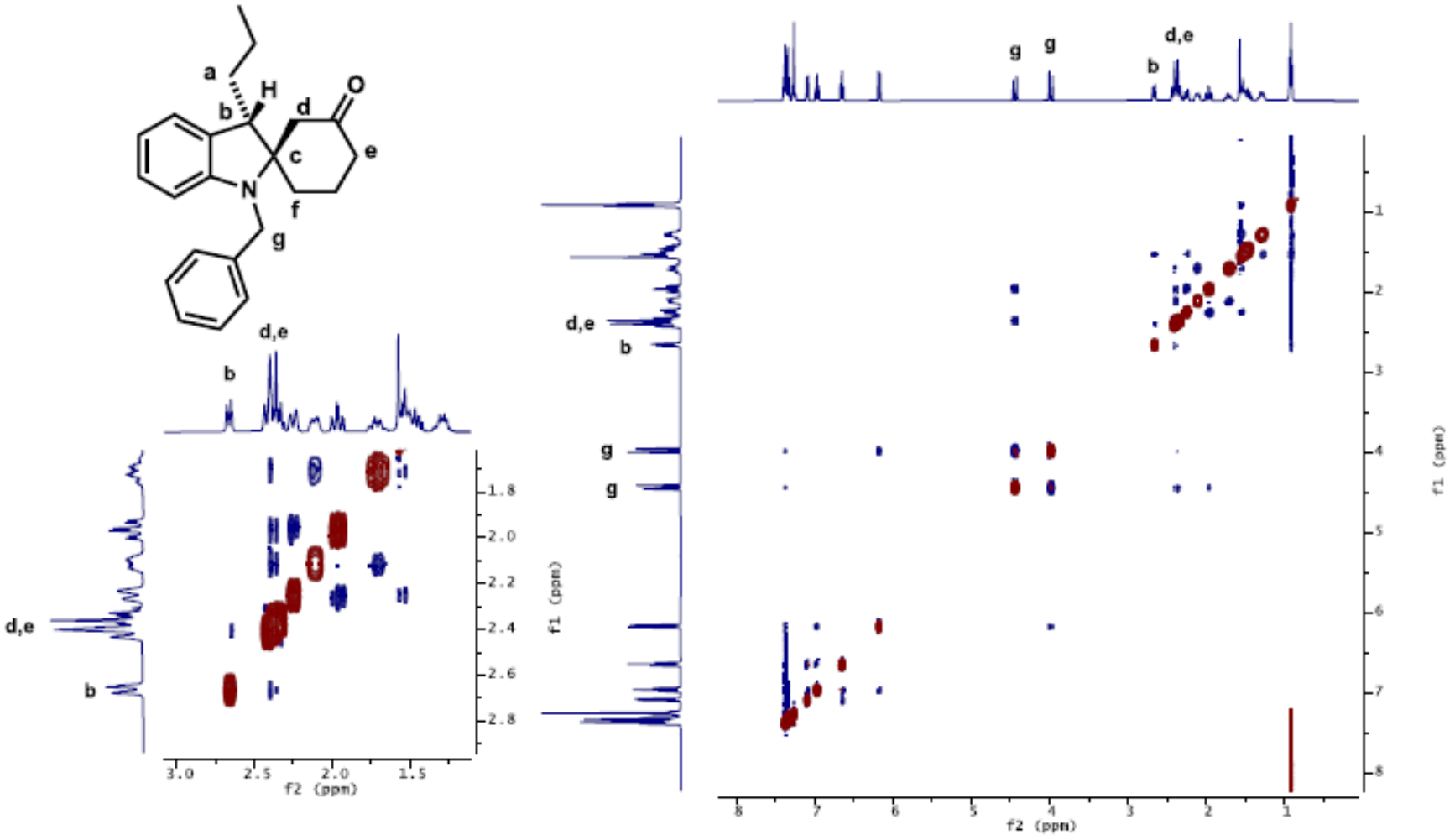
HSQC (400 MHz, $CDCl_3$) of trans-***3ae***



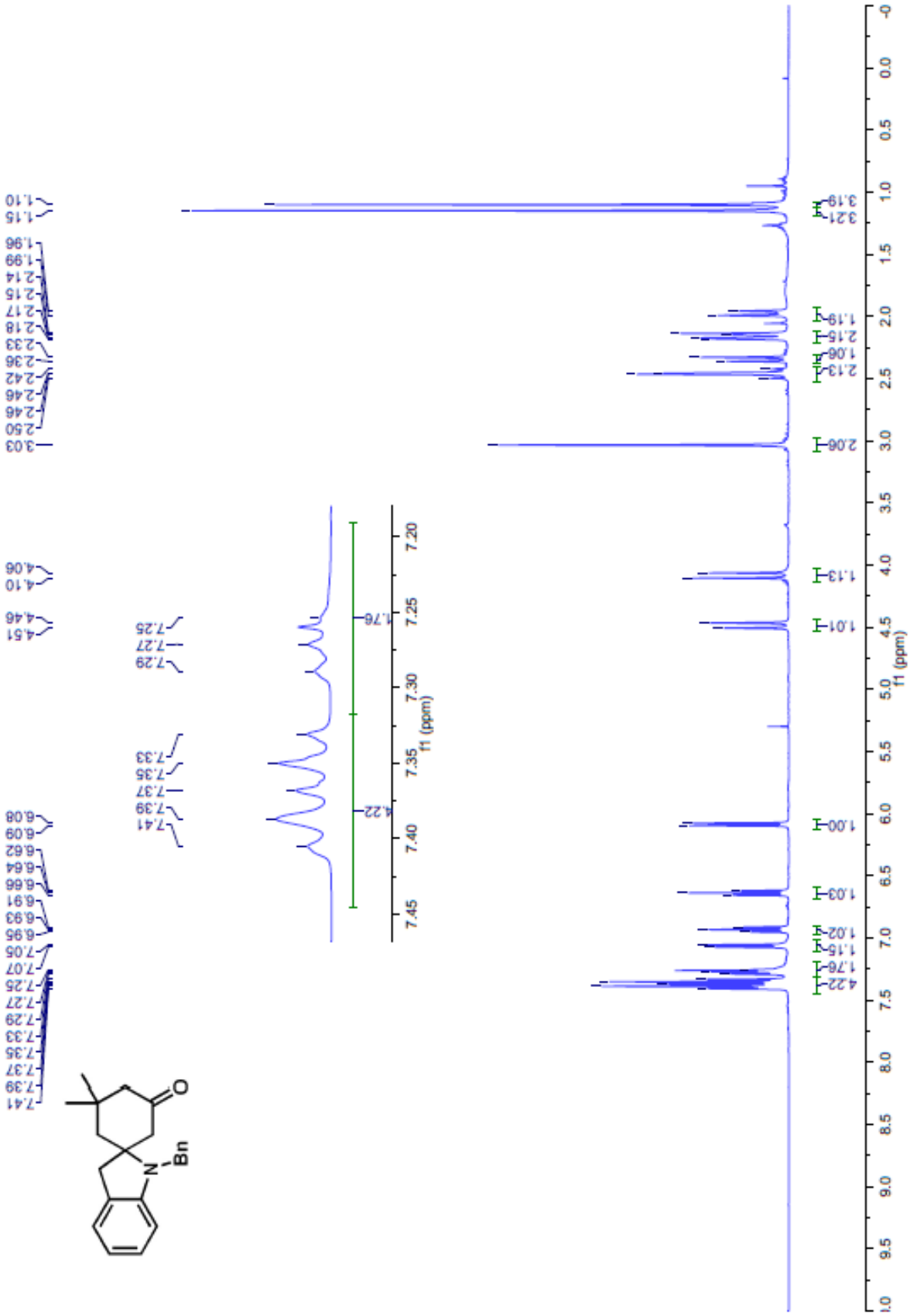
COESY (400 MHz, $CDCl_3$) of trans-***3ae***



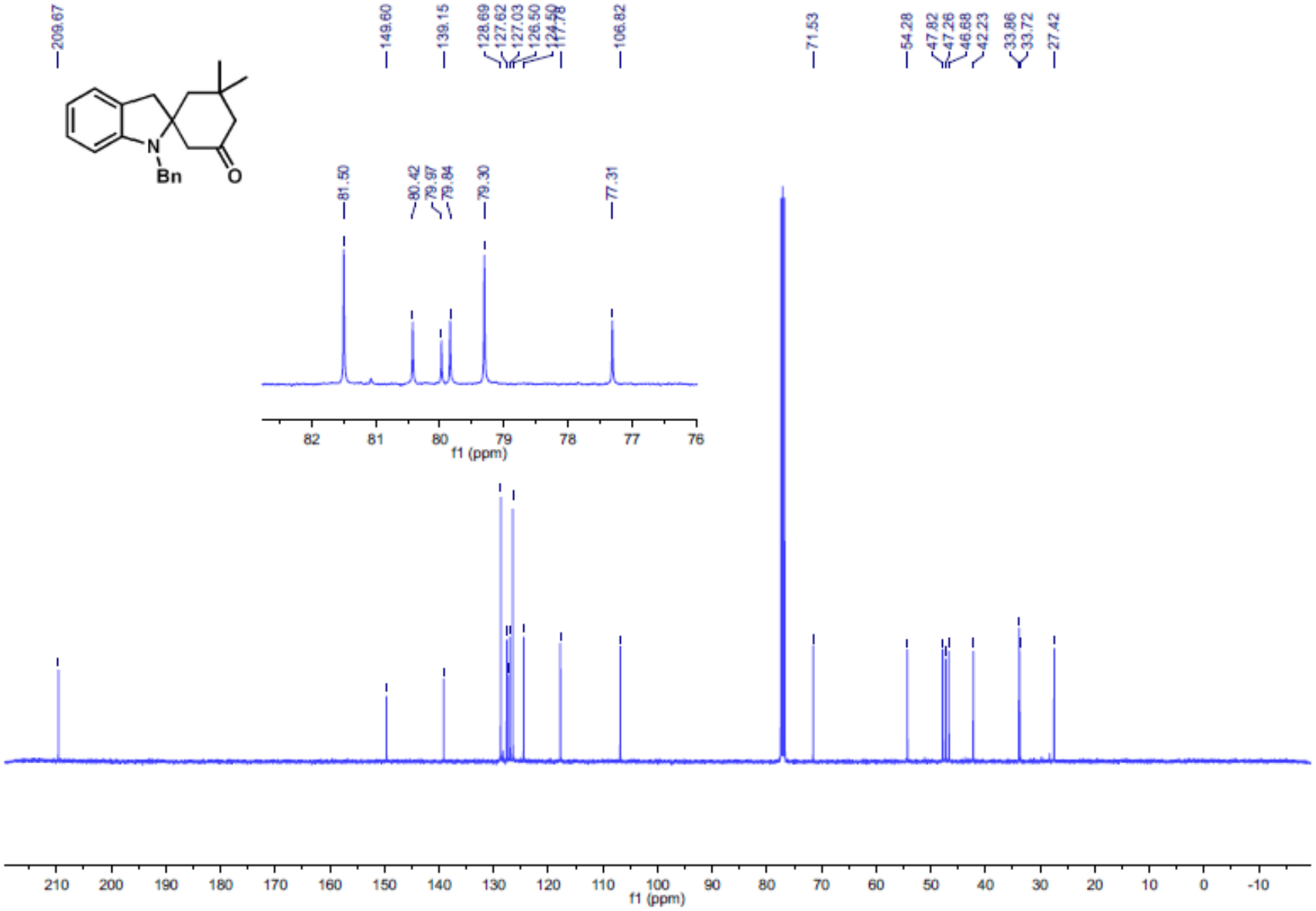
HMBC (400 MHz, $CDCl_3$) of trans-***3ae***



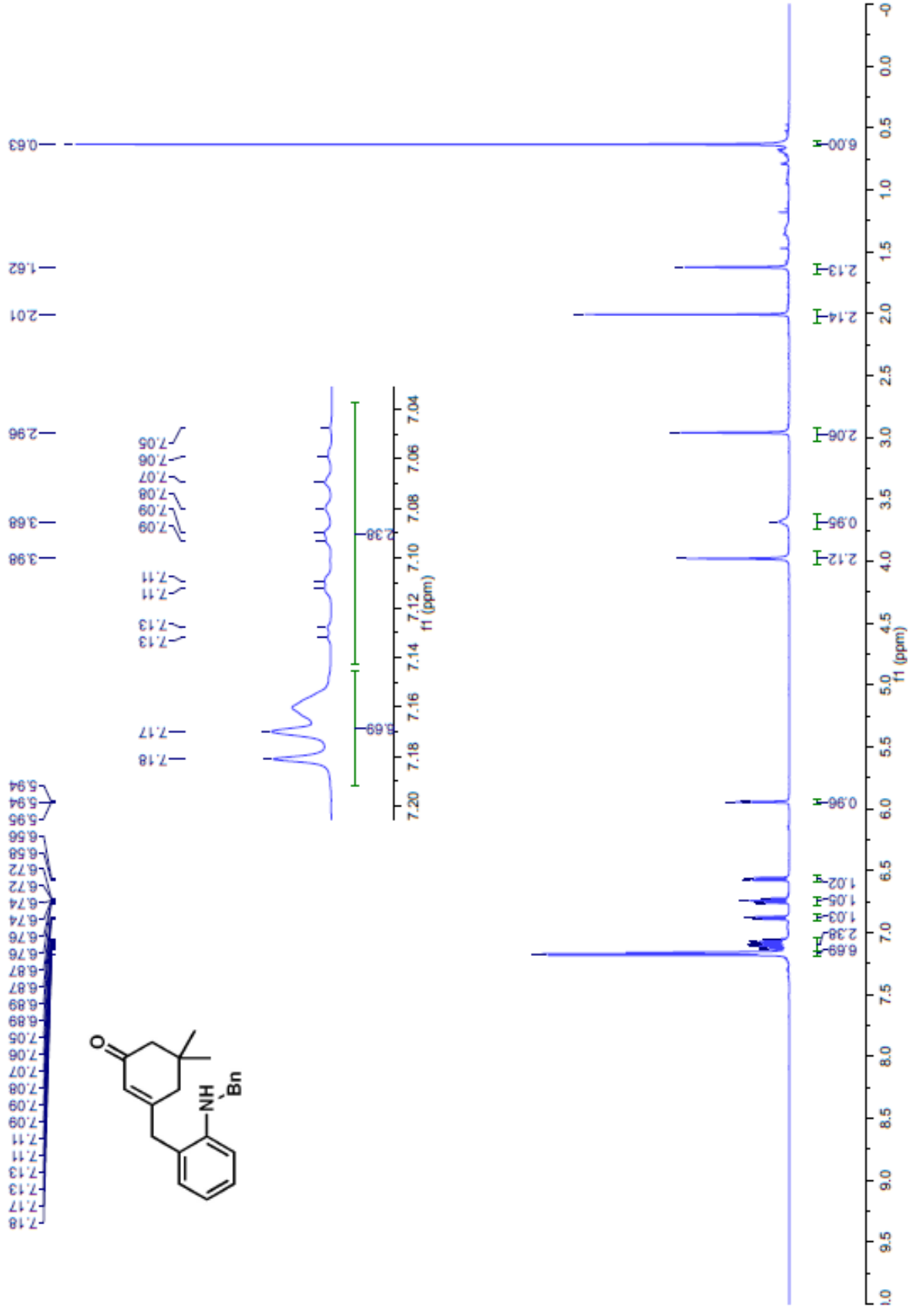
NOESY (400 MHz, $CDCl_3$) of trans-***3ae***



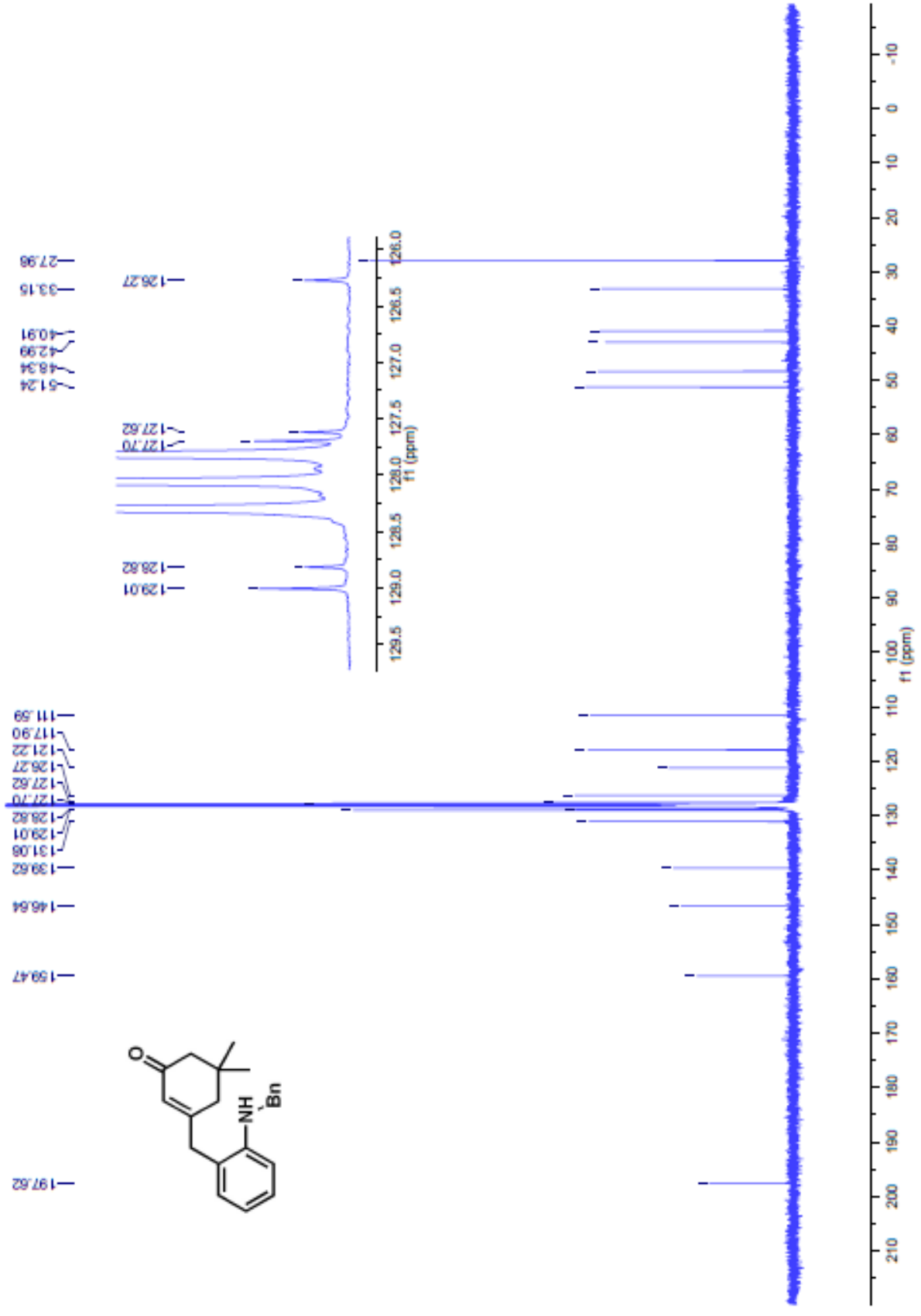
^{1}H NMR (400 MHz, $CDCl_3$) of ***3af***



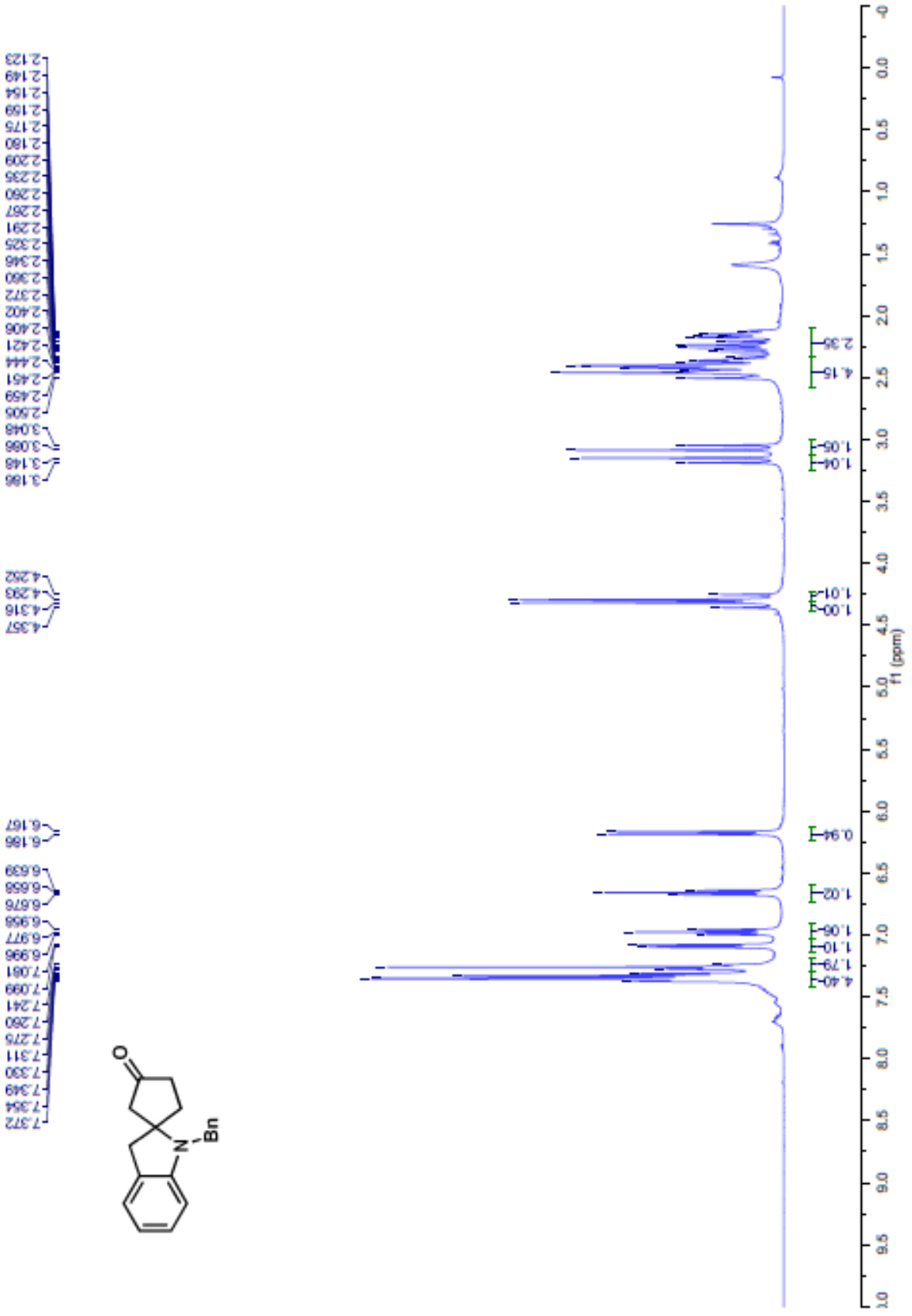
^{13}C NMR (100 MHz, $CDCl_3$) of ***3af***



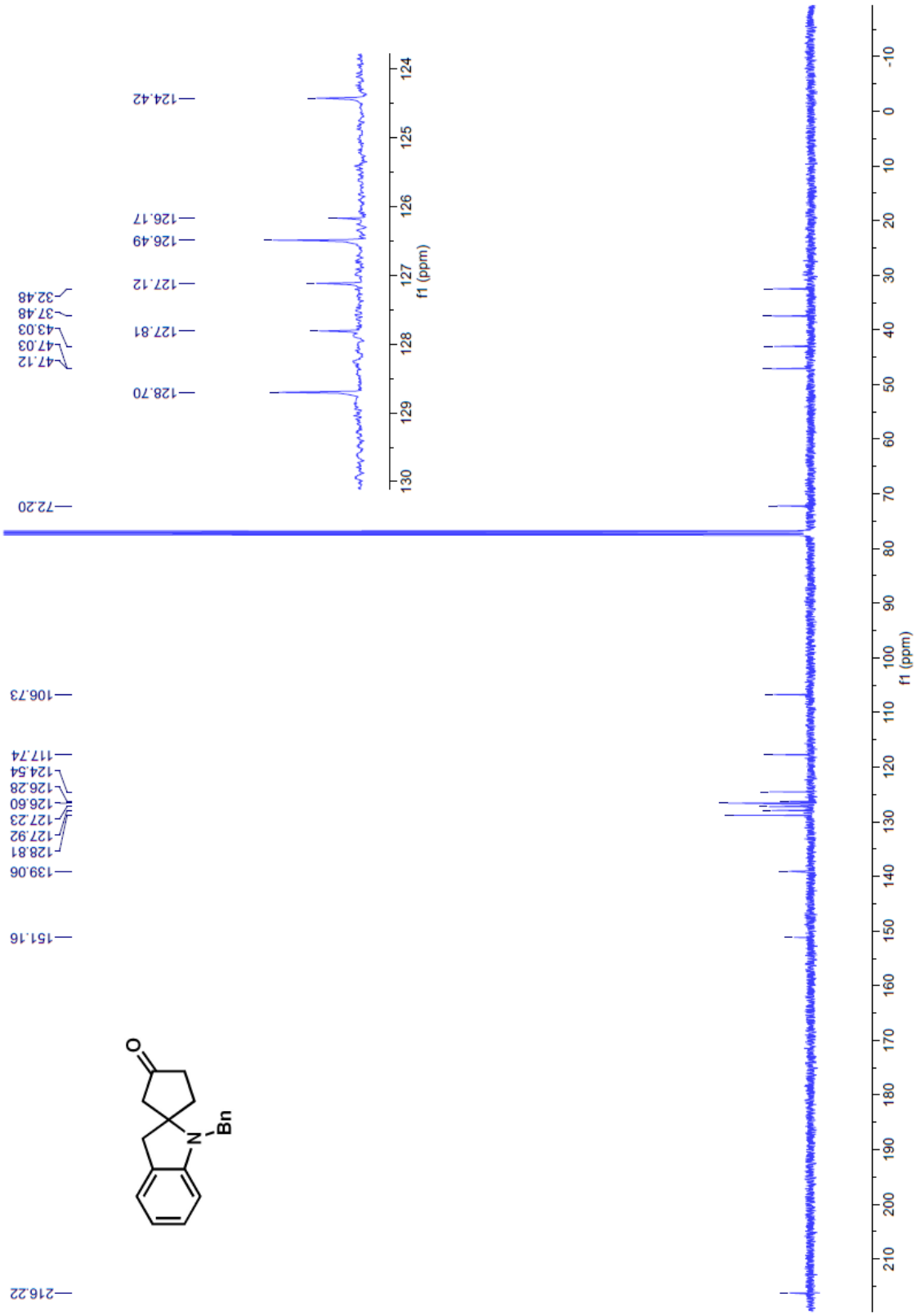
^{1}H NMR (400 MHz, C_6D_6) of ***3af'***



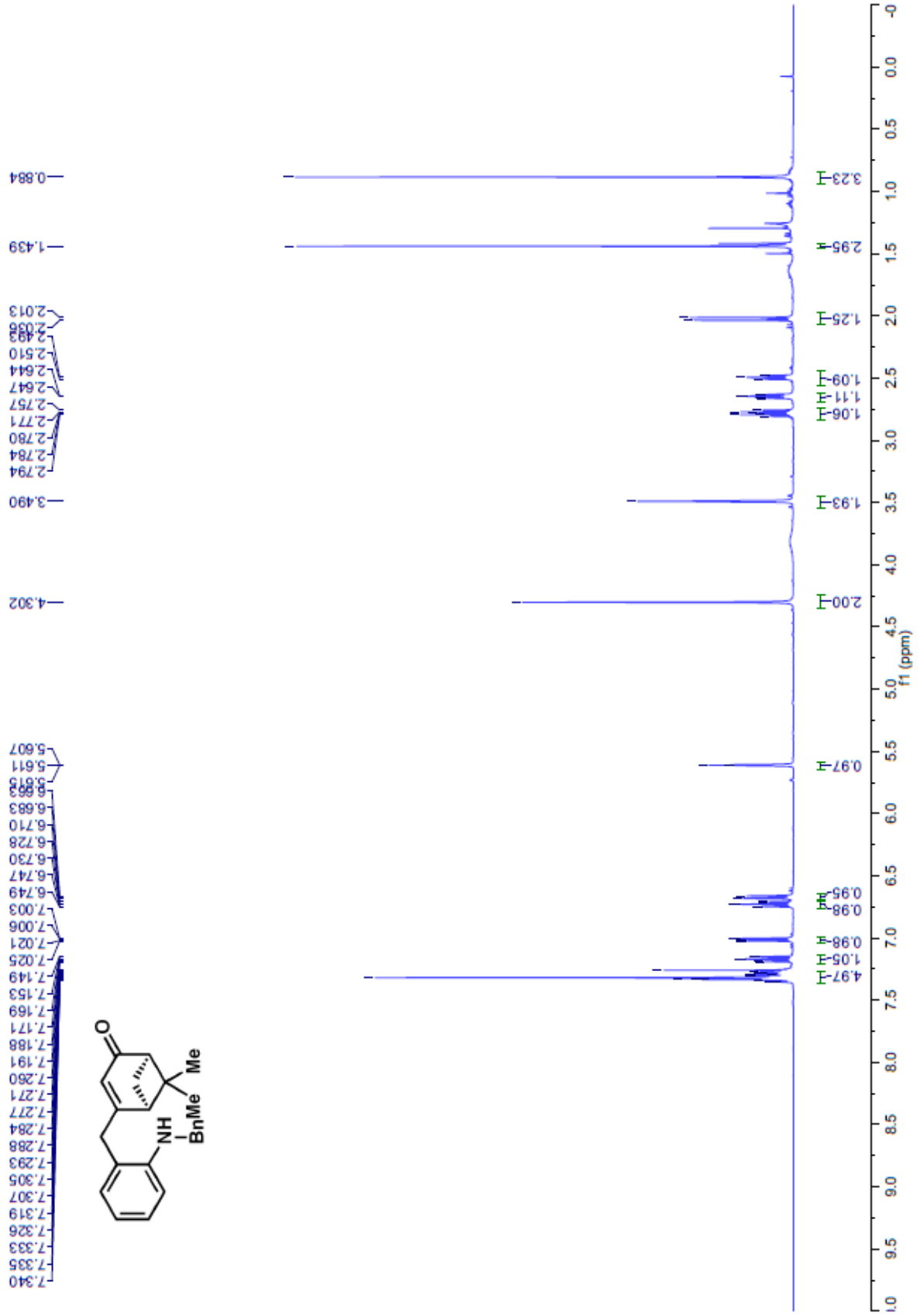
^{13}C NMR (100 MHz, C_6D_6) of ***3af'***



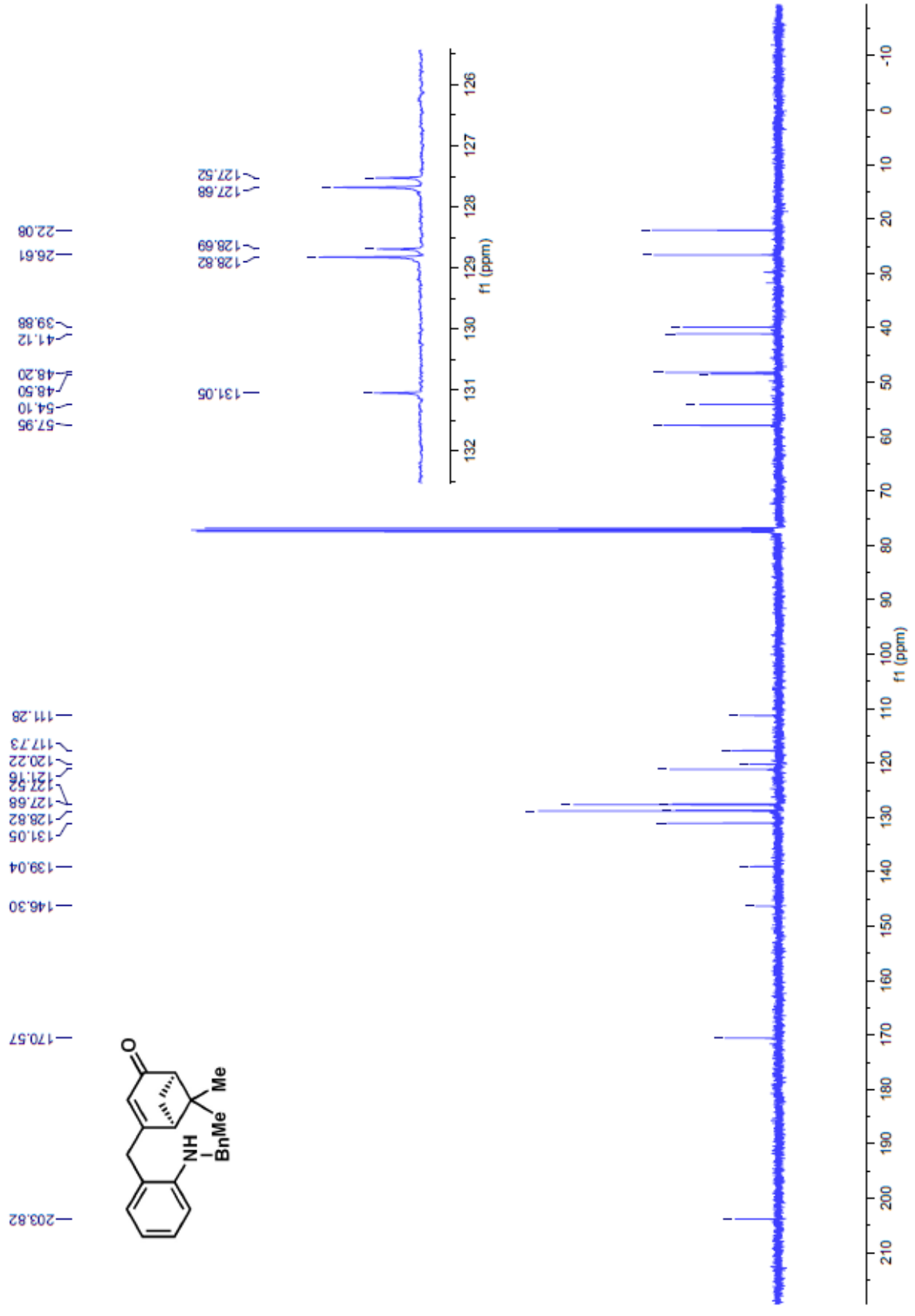
^{1}H NMR (400 MHz, $CDCl_3$) of ***3ag***



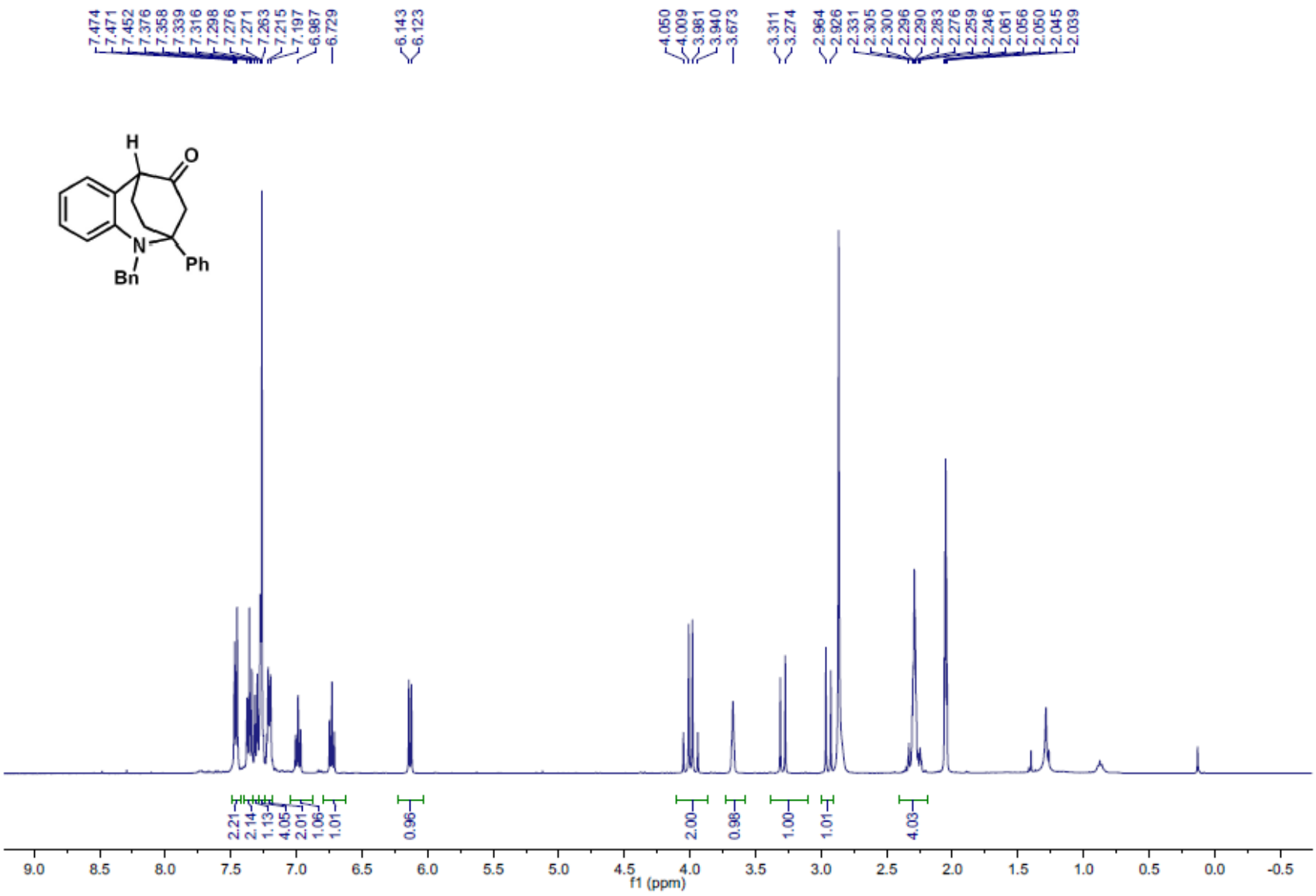
^{13}C NMR (100 MHz, $CDCl_3$) of ***3ag***



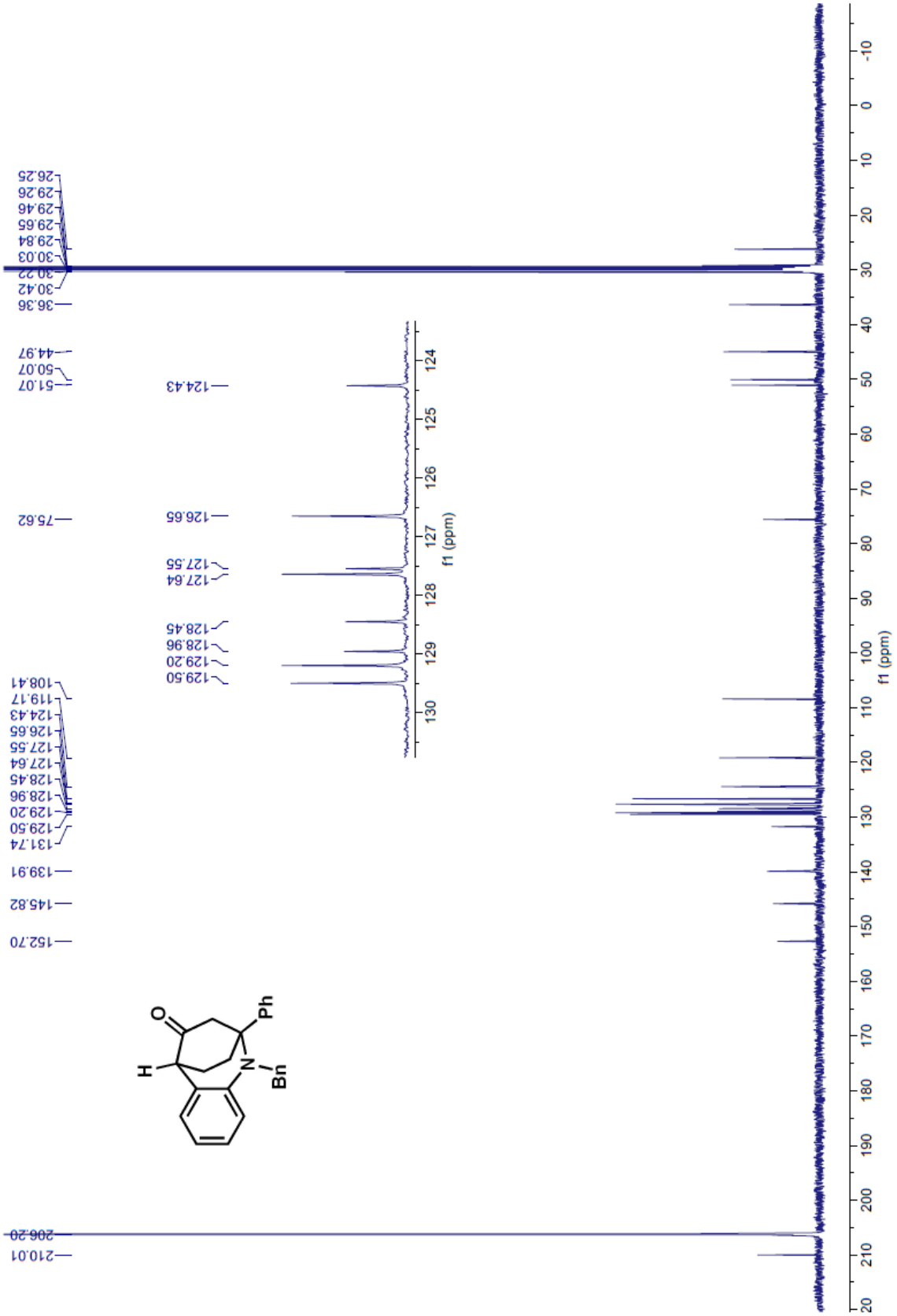
^{1}H NMR (400 MHz, $CDCl_3$) of ***3ah***



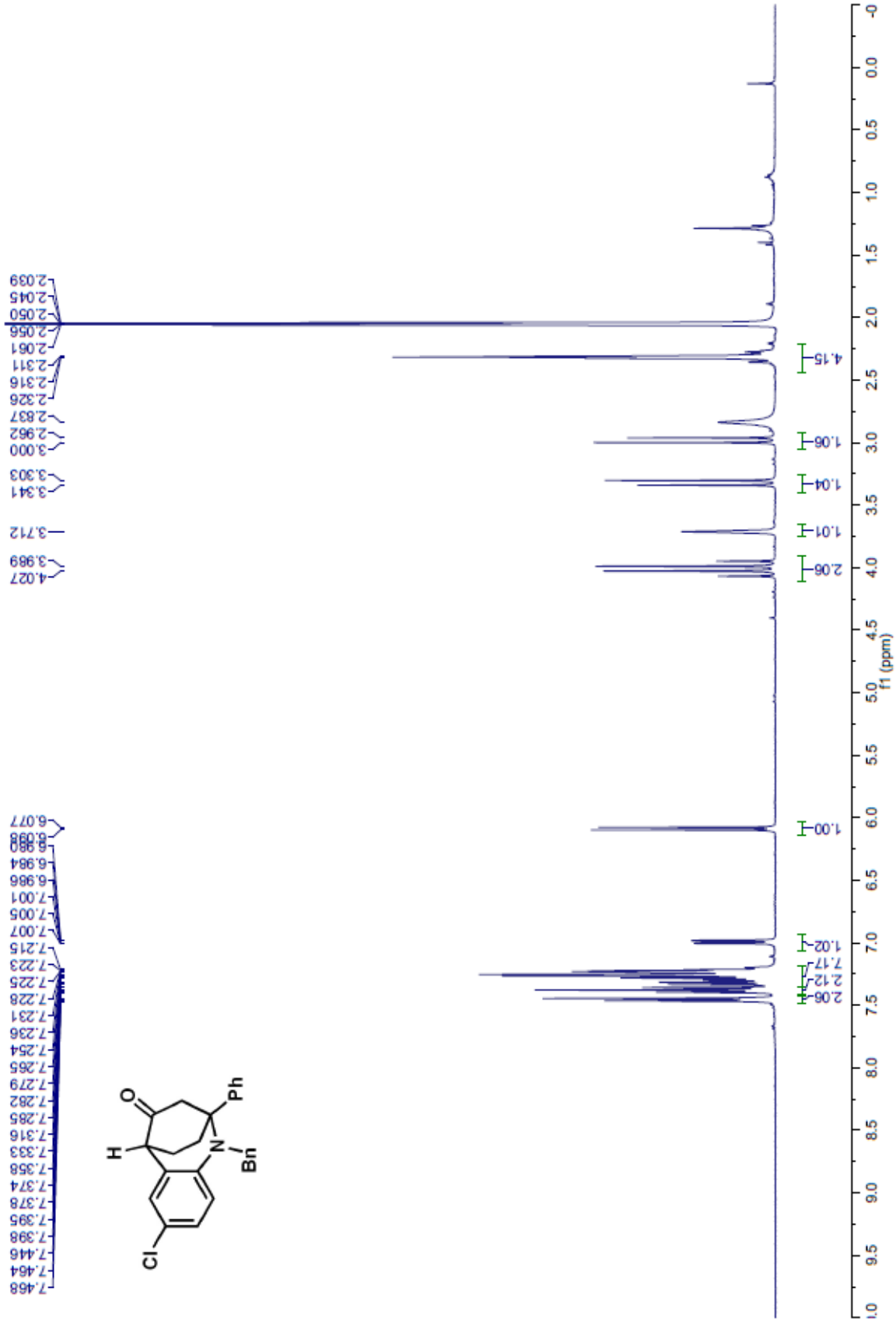
^{13}C NMR (100 MHz, $CDCl_3$) of ***3ah***



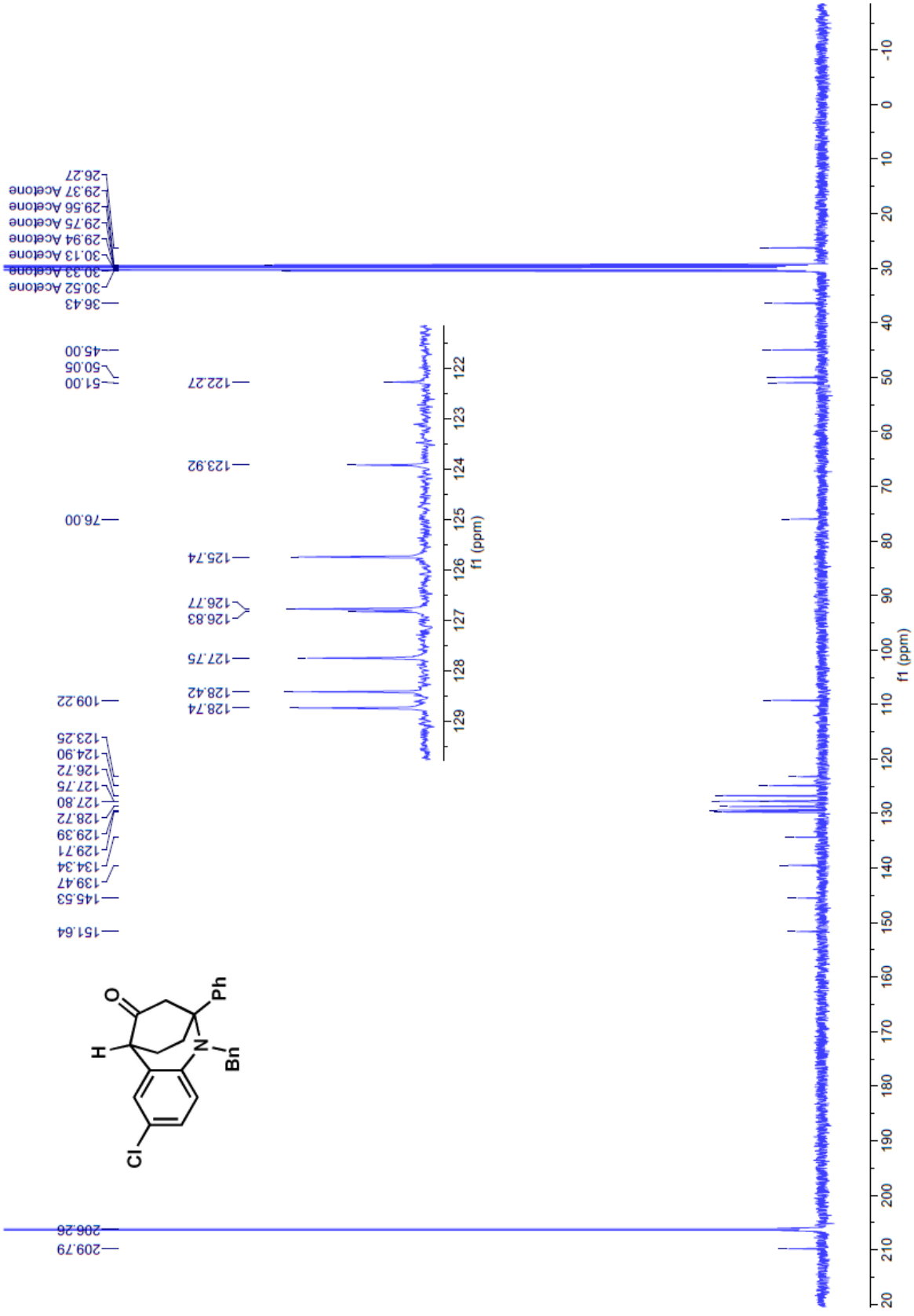
^{1}H NMR (400 MHz, acetone-d_6) of ***6a***



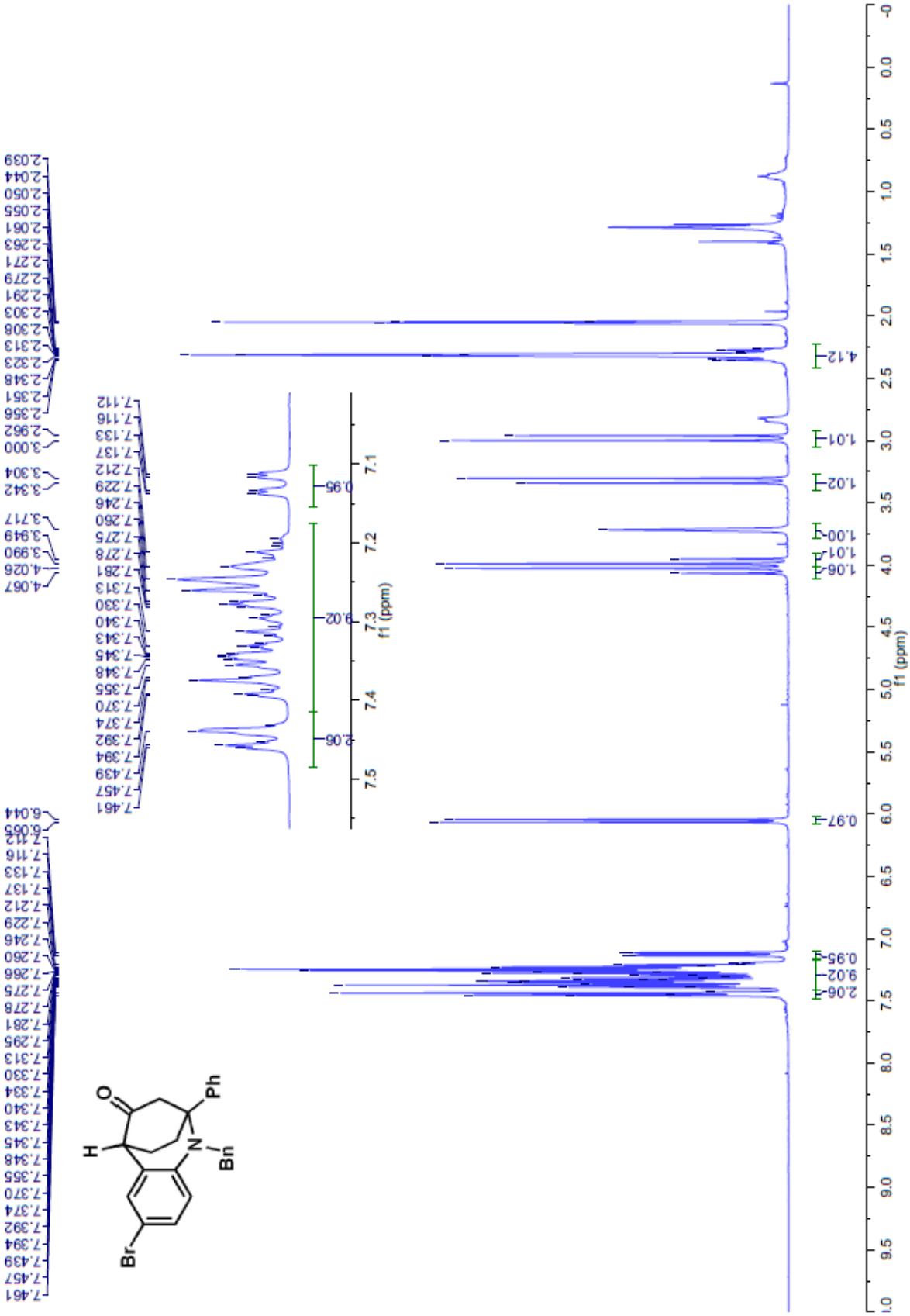
^{13}C NMR (100 MHz, acetone-d_6) of ***6a***



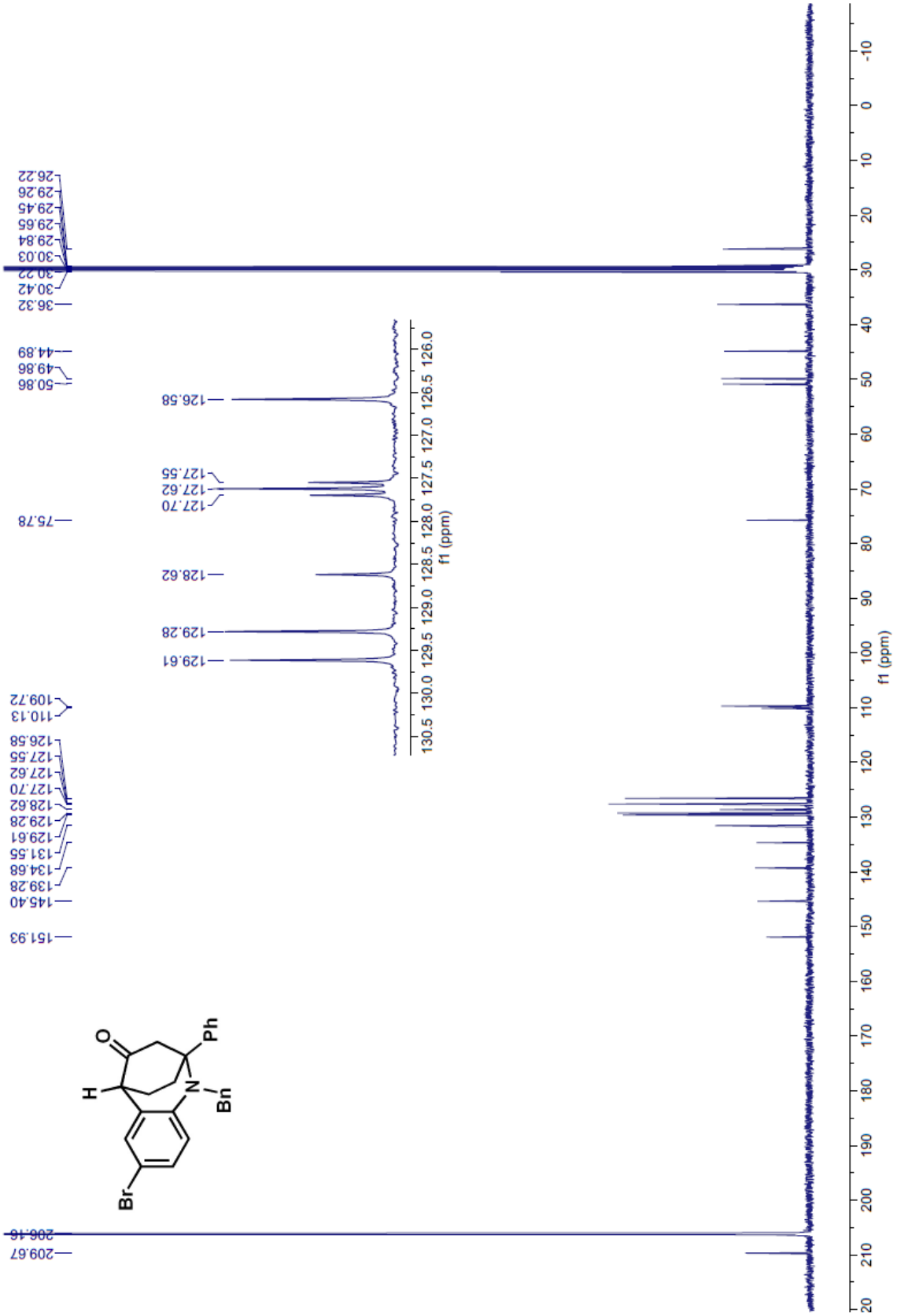
^{1}H NMR (400 MHz, acetone-d_6) of ***6b***



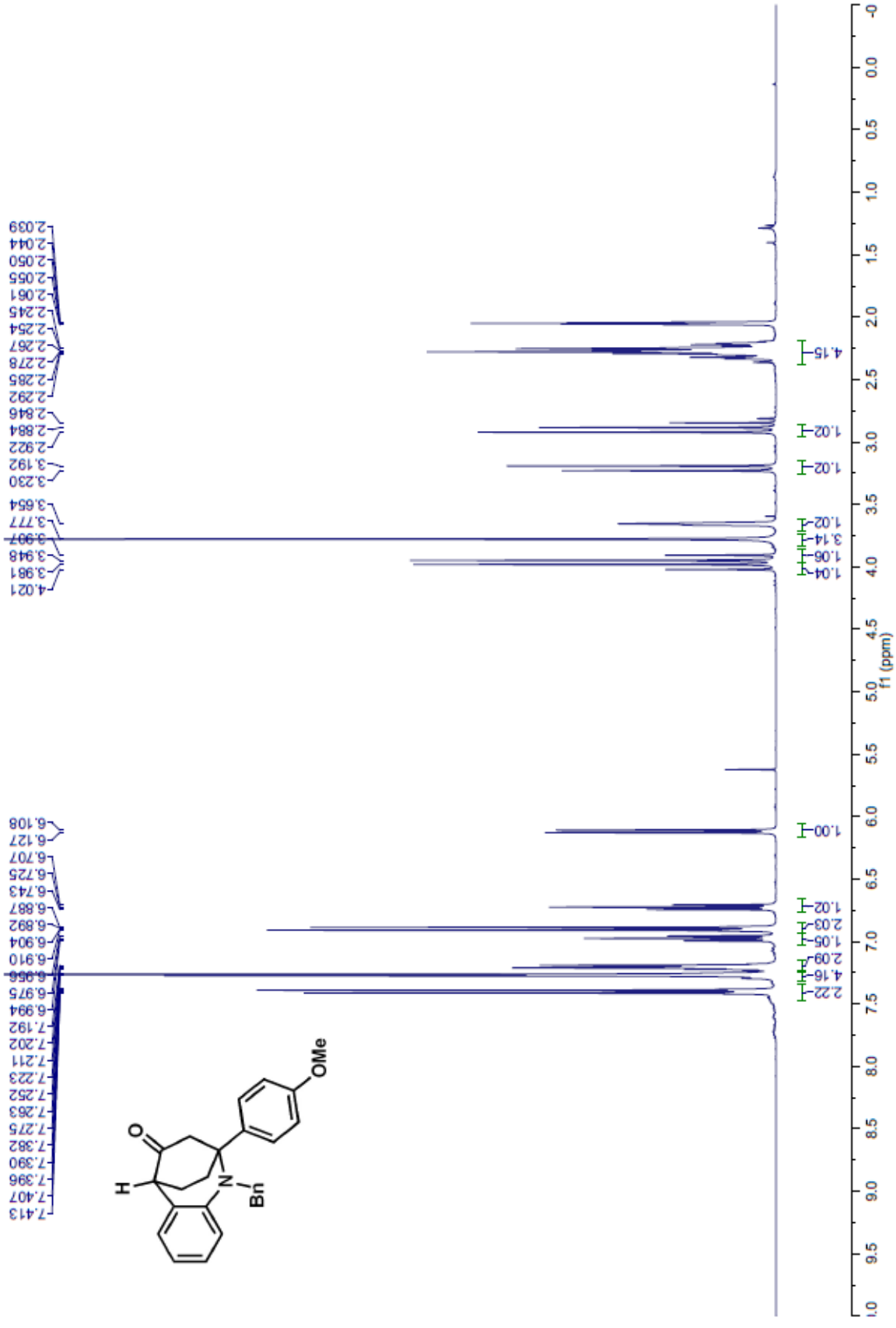
^{13}C NMR (100 MHz, acetone-d_6) of ***6b***



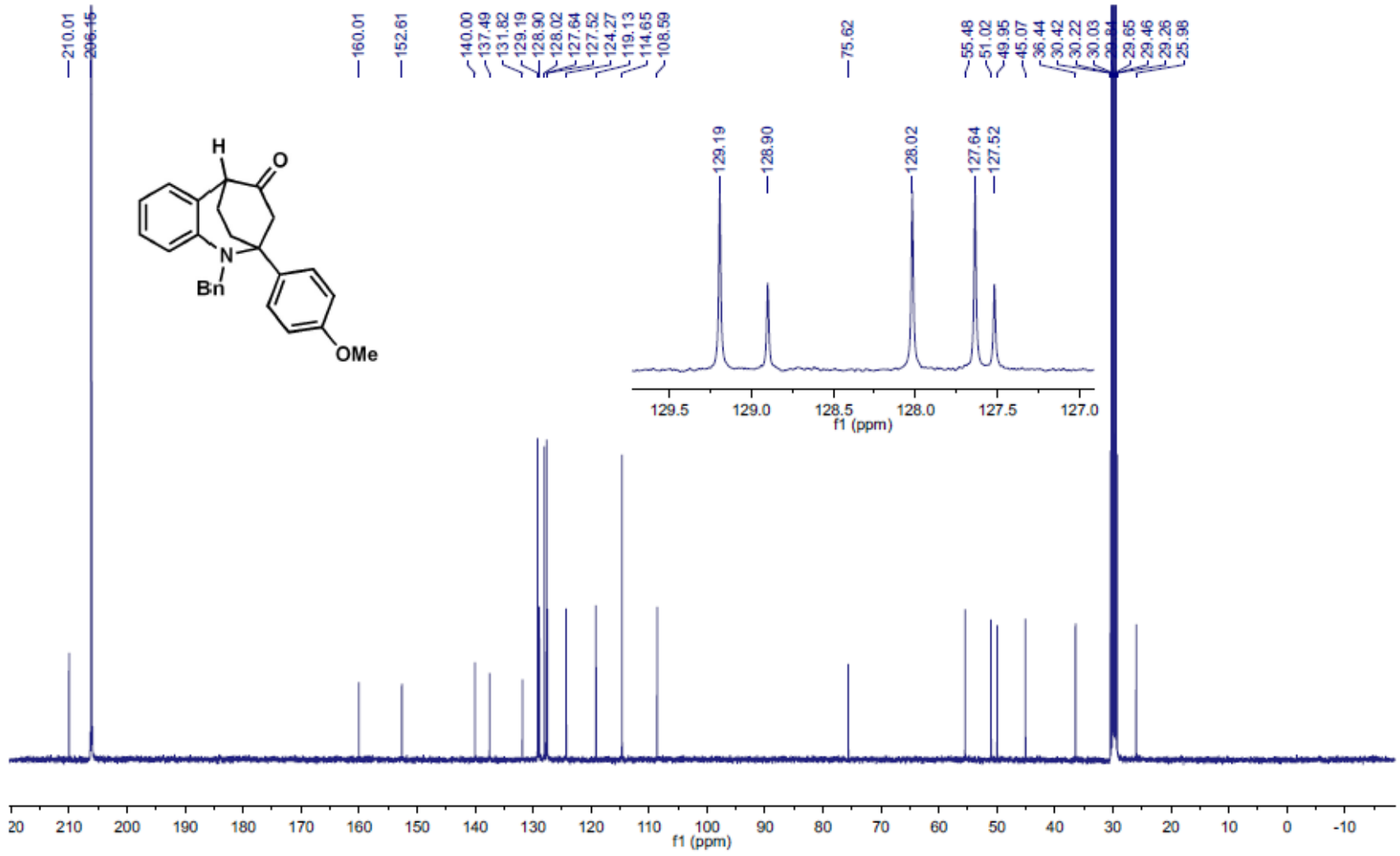
^{1}H NMR (400 MHz, acetone-d_6) of ***6c***



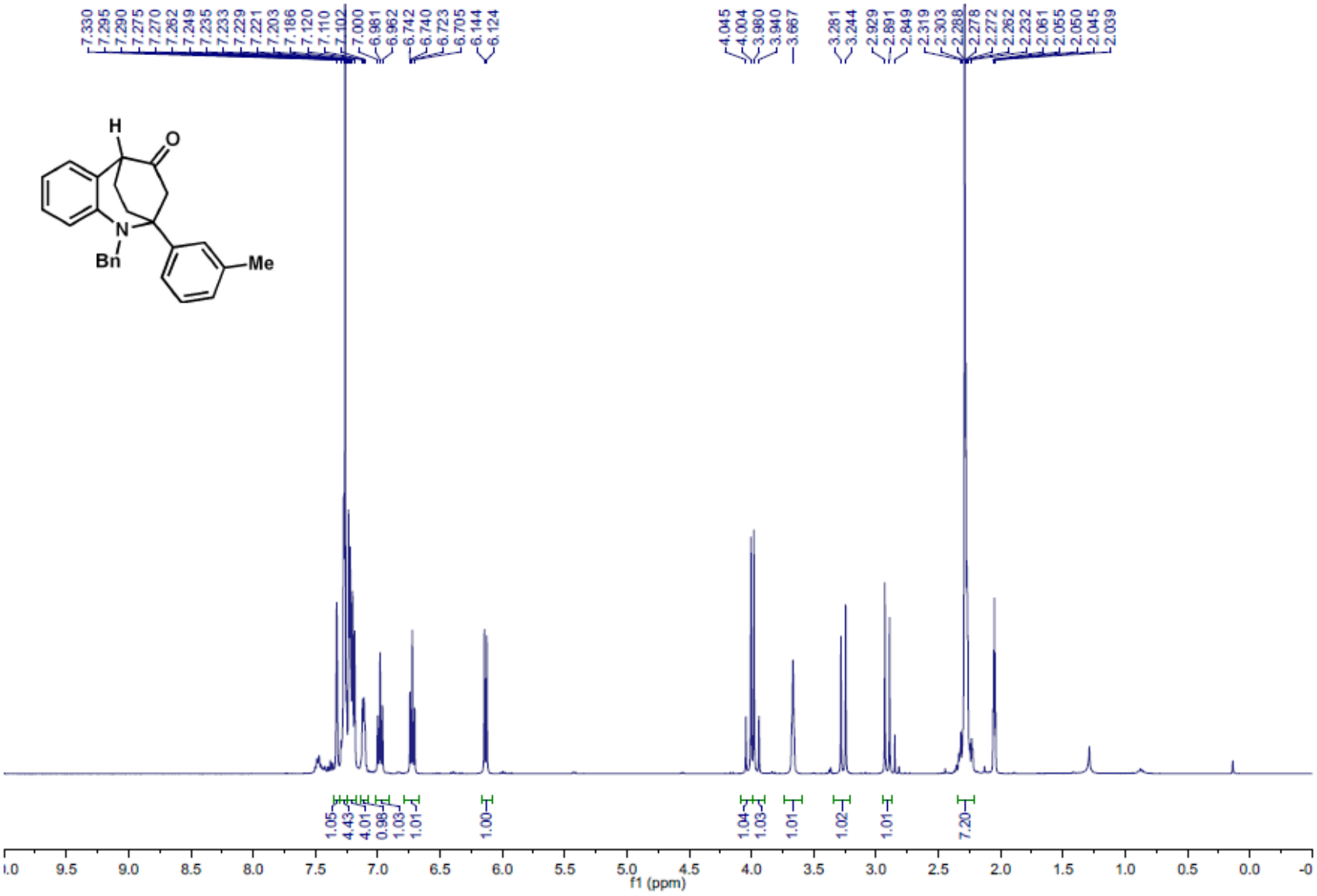
^{13}C NMR (100 MHz, acetone-d_6) of ***6c***



^{1}H NMR (400 MHz, acetone-d_6) of ***6d***

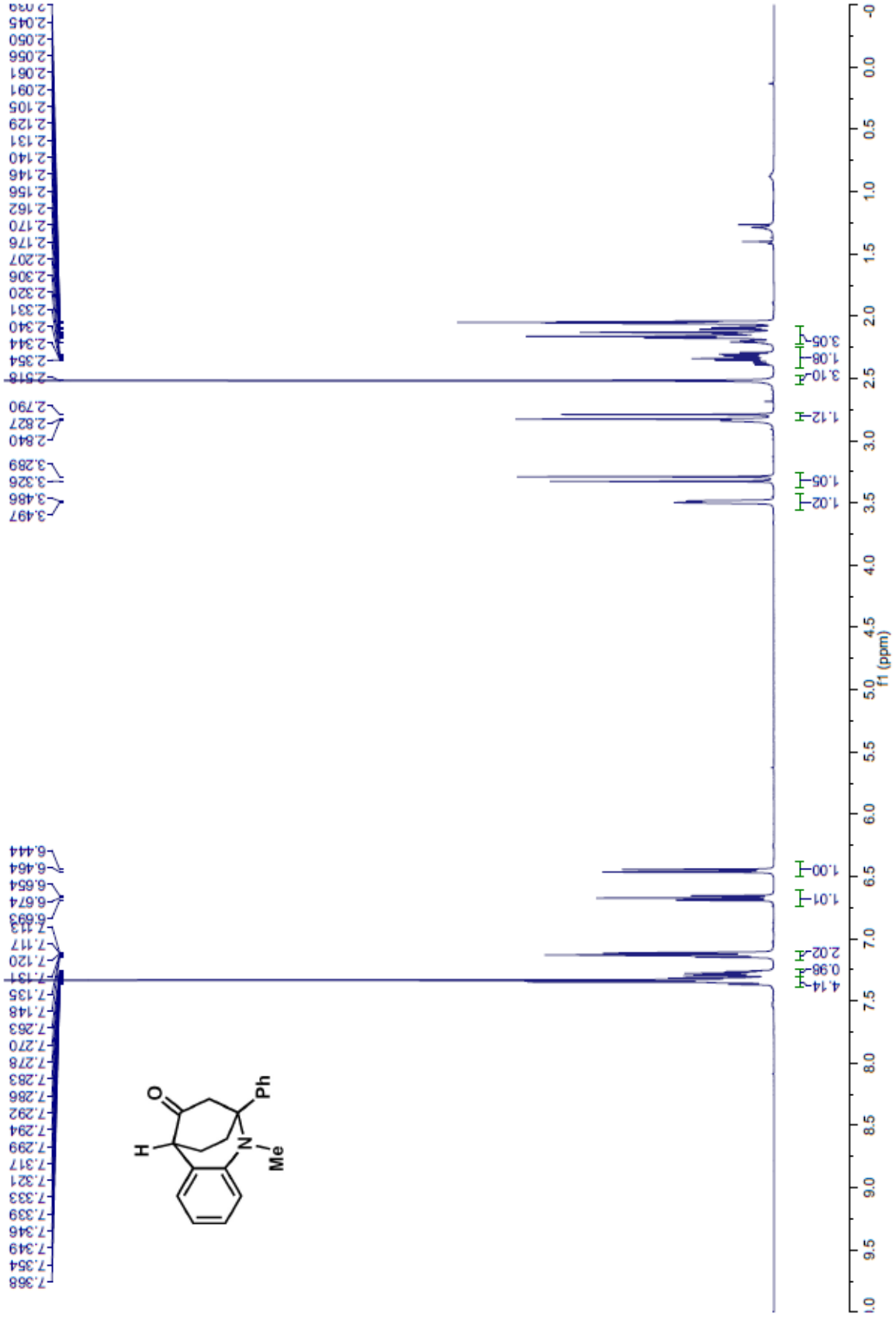


^{13}C NMR (100 MHz, acetone-d_6) of ***6d***

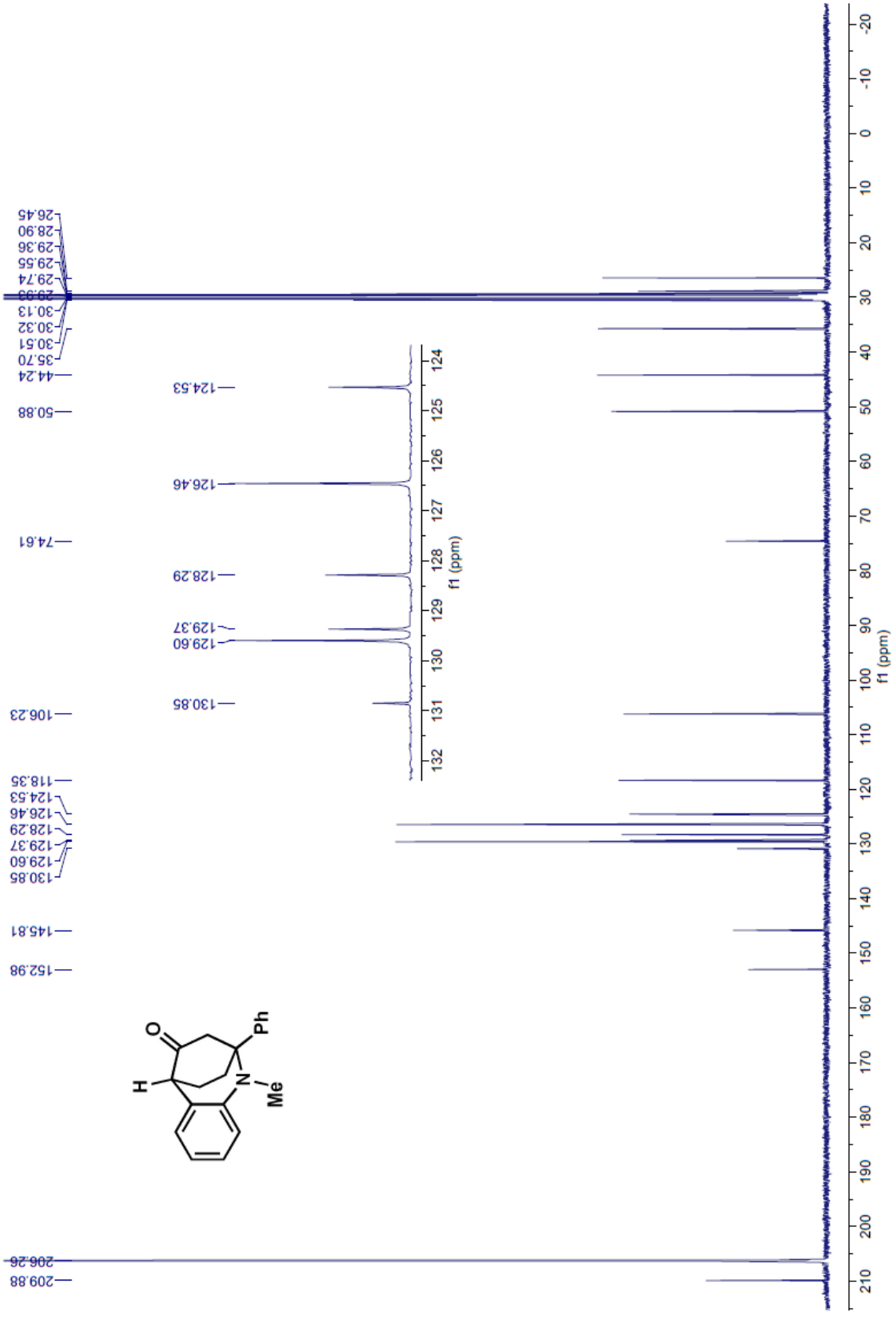


^{1}H NMR (400 MHz, acetone-d_6) of ***6e***

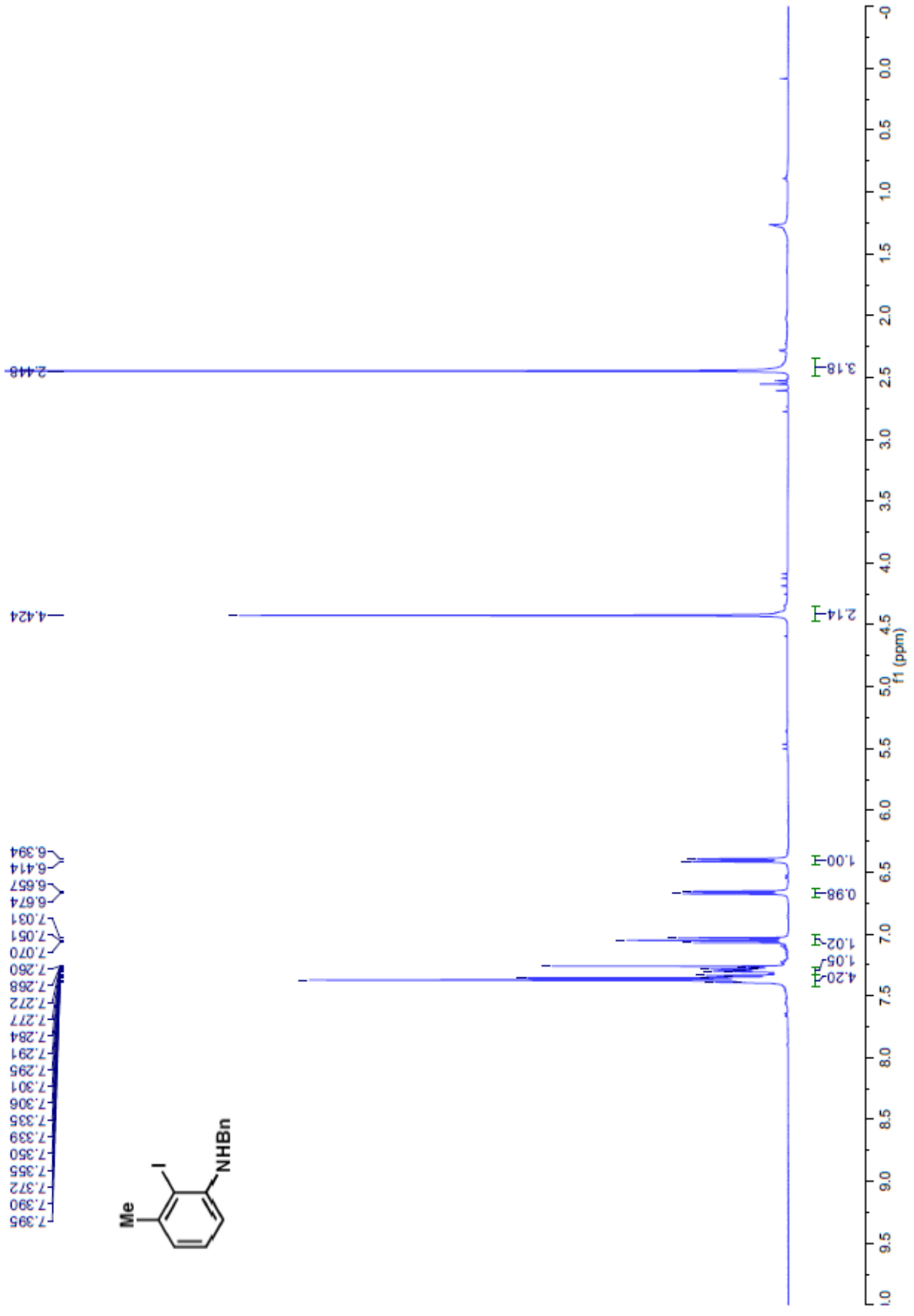
^{13}C NMR (100 MHz, acetone-d_6) of ***6e***



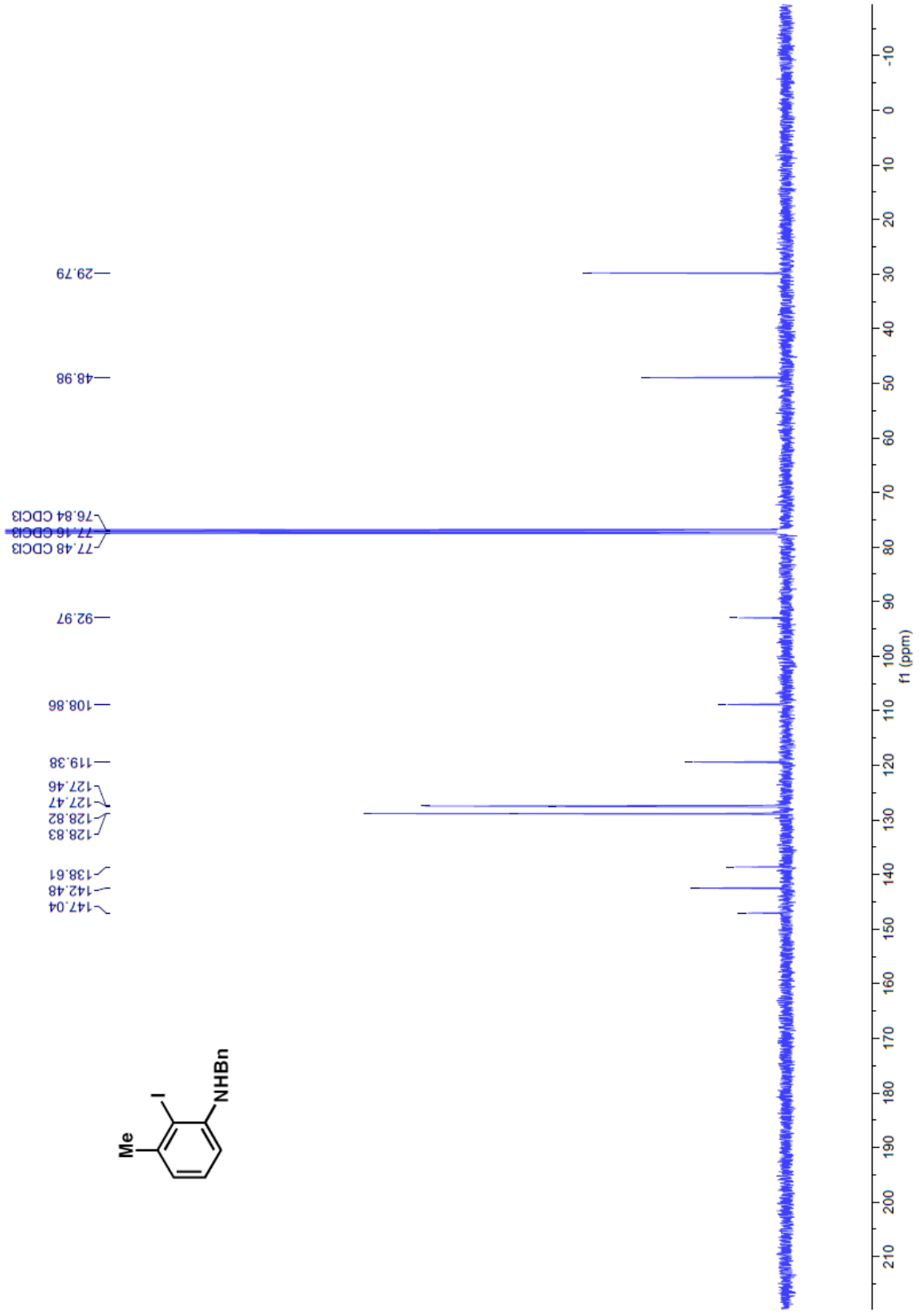
^{1}H NMR (400 MHz, acetone-d_6) of ***6f***



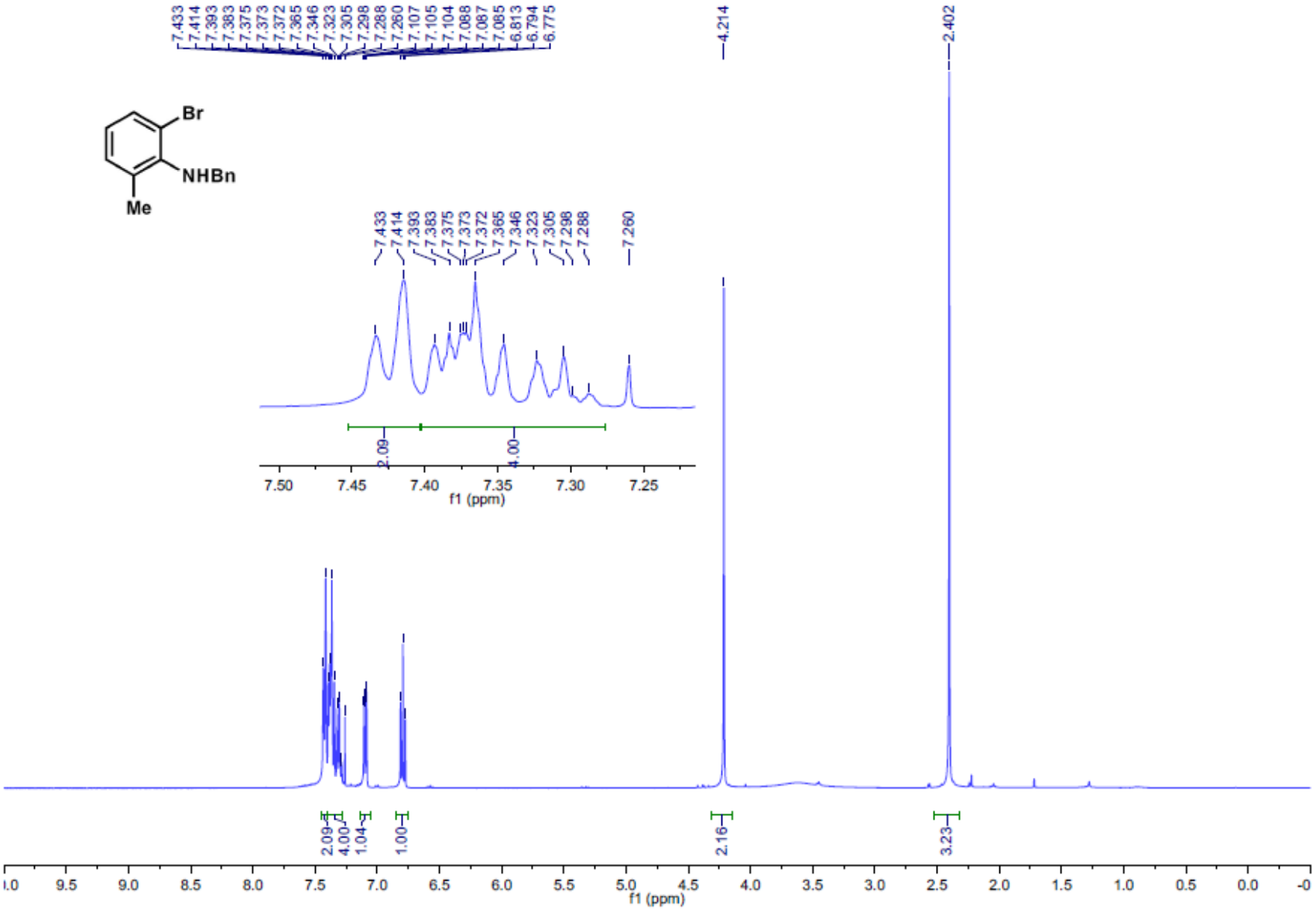
^{13}C NMR (100 MHz, acetone-d_6) of ***6f***



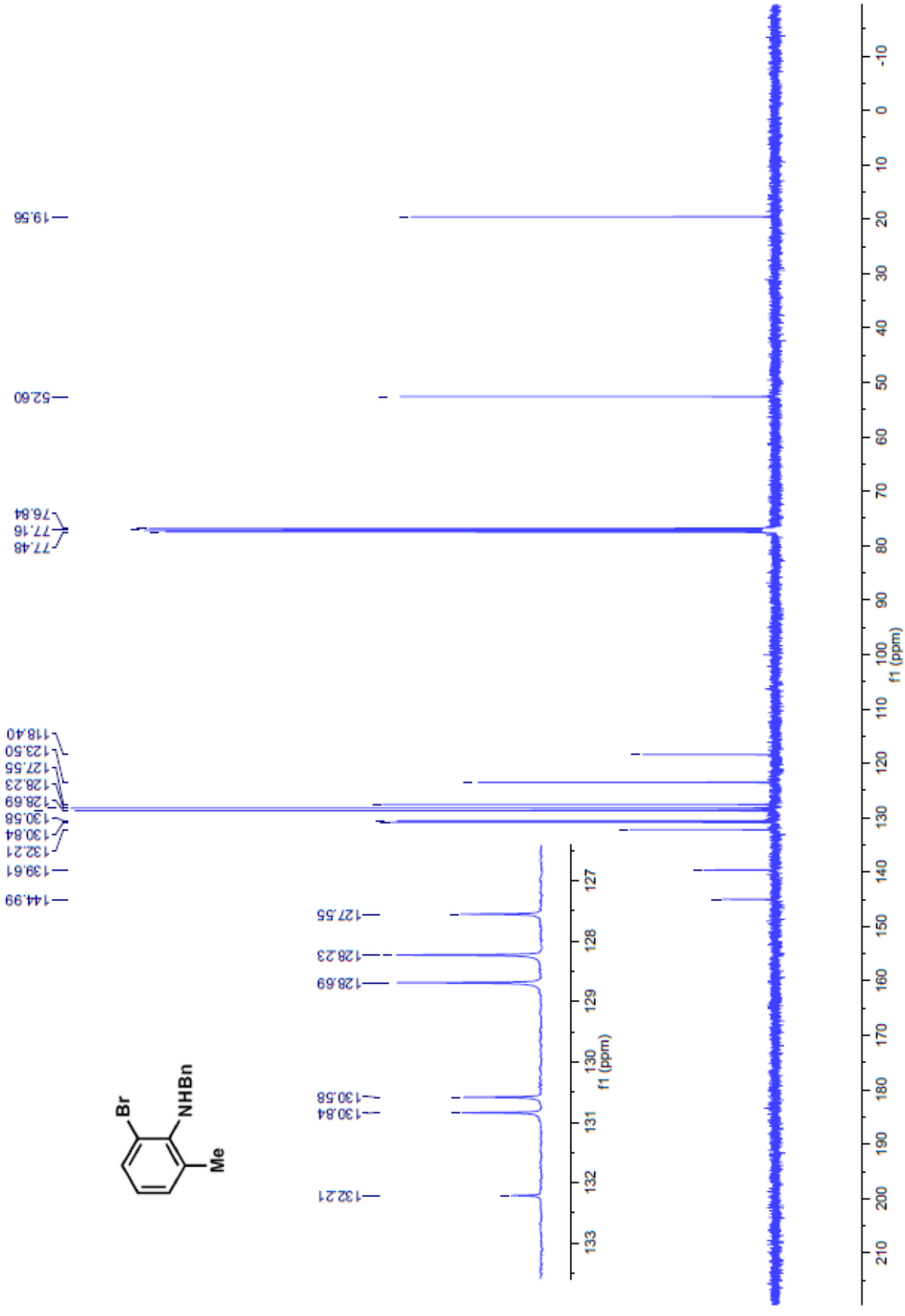
^{1}H NMR (400 MHz, $CDCl_3$) of ***1b***



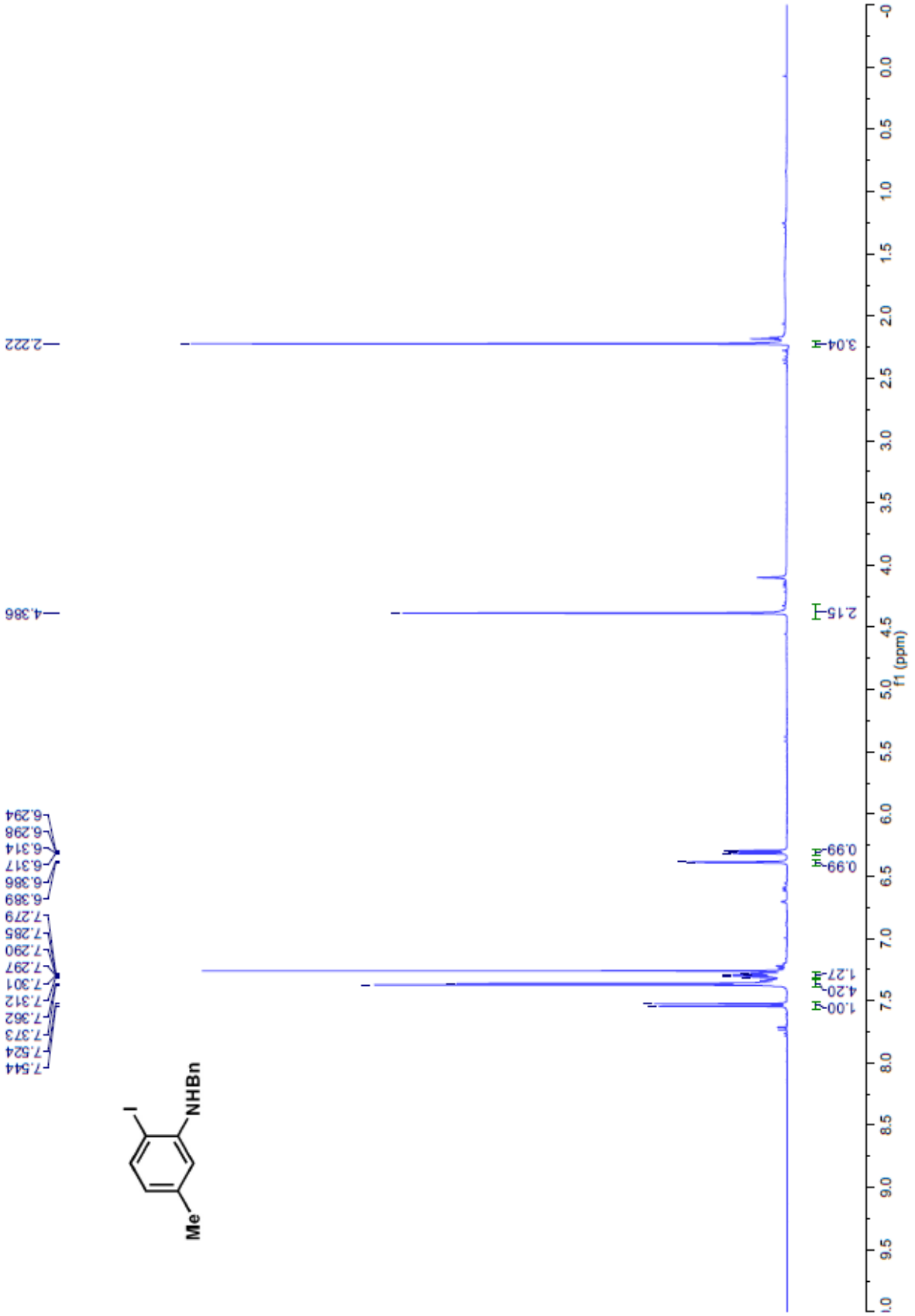
^{13}C NMR (100 MHz, $CDCl_3$) of ***1b***



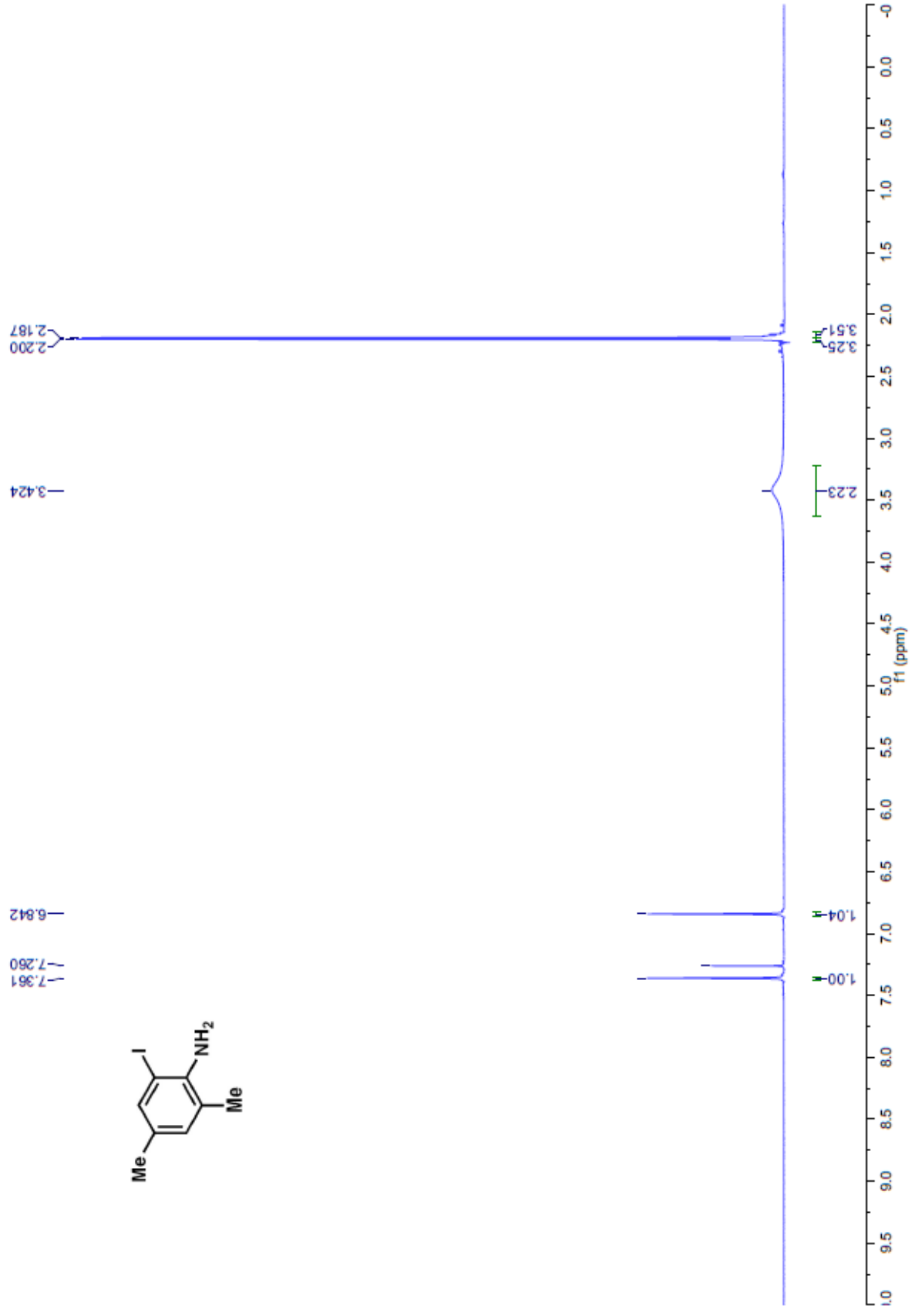
^{1}H NMR (400 MHz, $CDCl_3$) of ***1e***



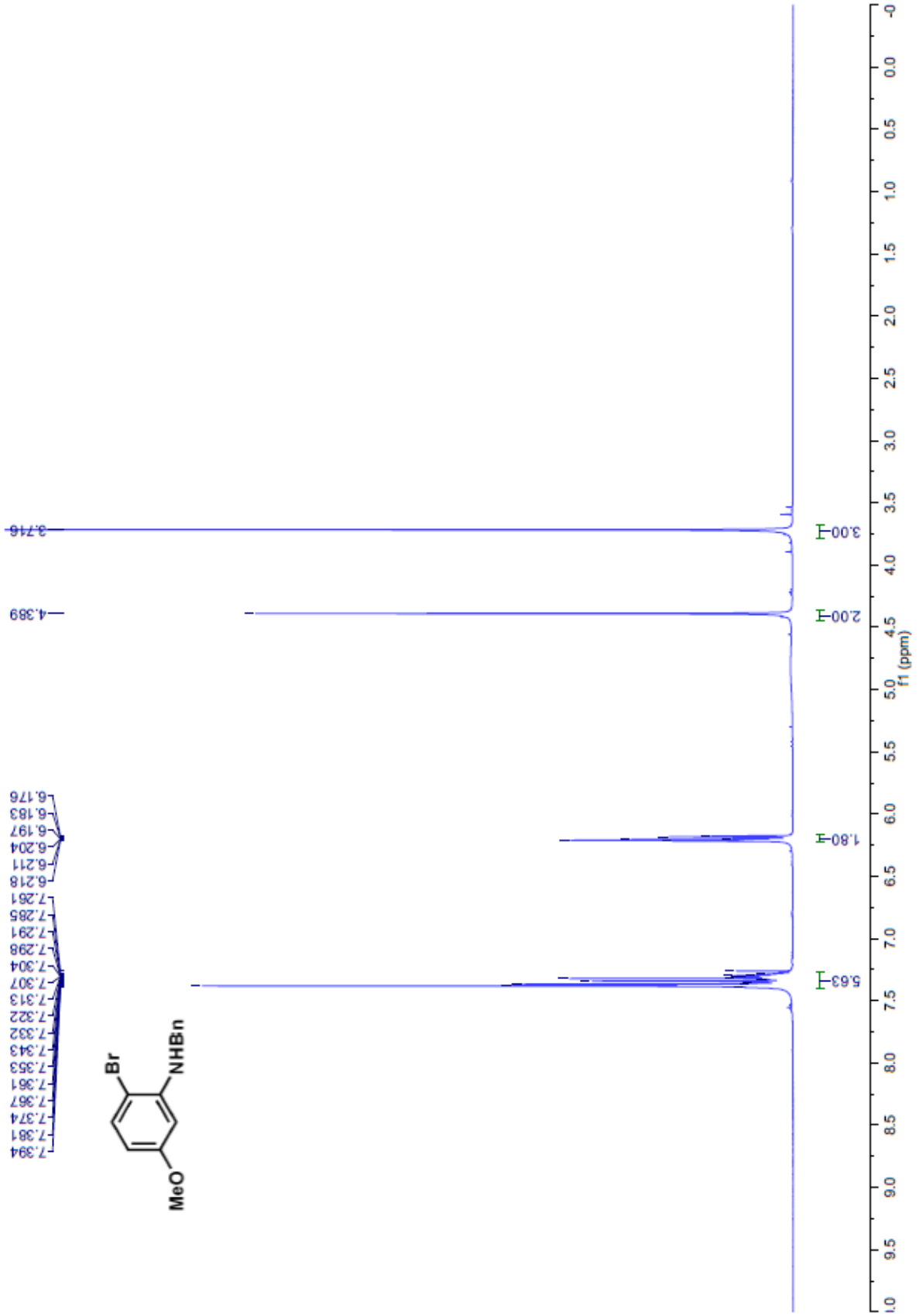
^{13}C NMR (100 MHz, $CDCl_3$) of ***1e***



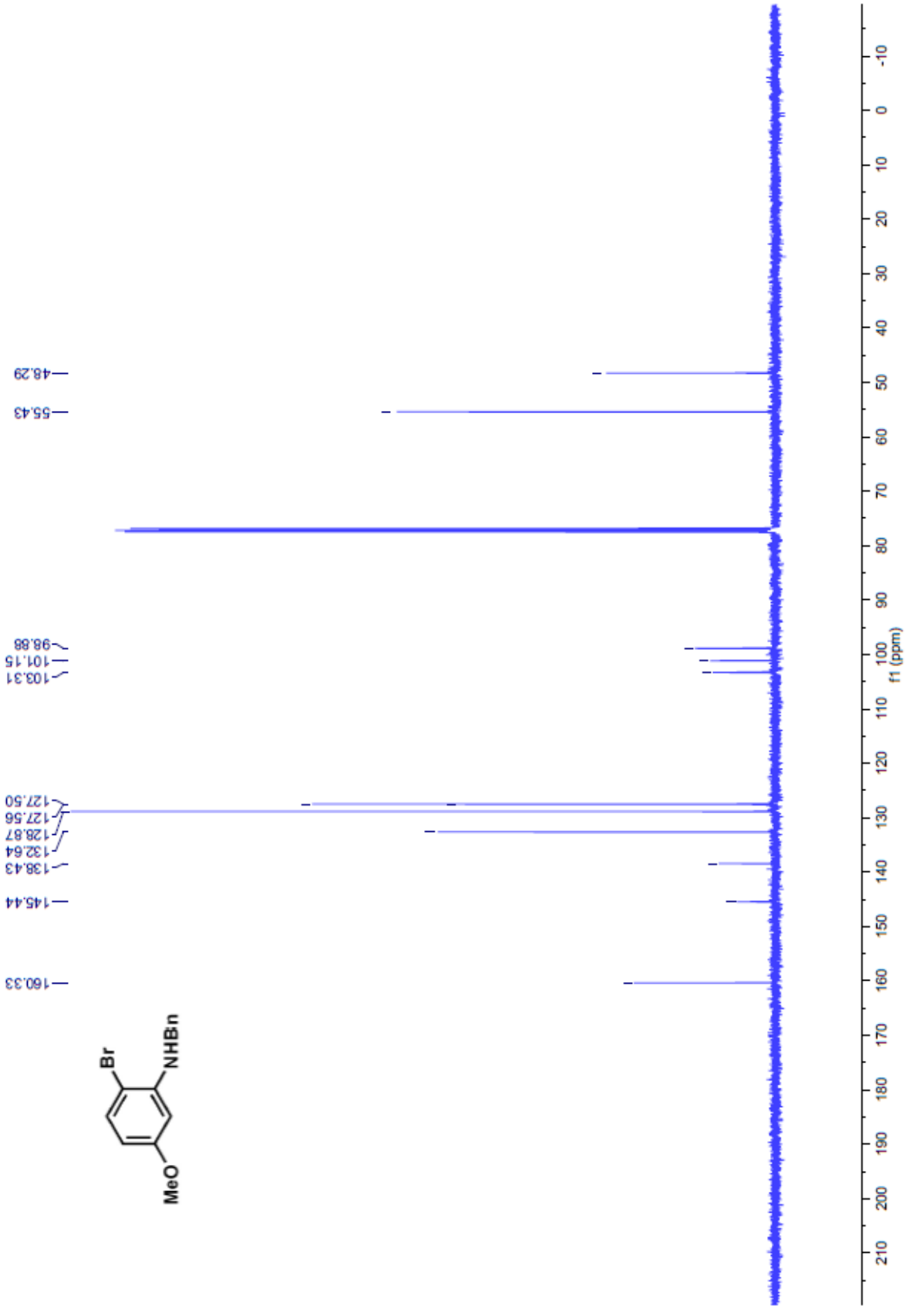
^{1}H NMR (400 MHz, $CDCl_3$) of ***1d***



^{1}H NMR (600 MHz, $CDCl_3$) of ***SIf***



^{1}H NMR (400 MHz, $CDCl_3$) of ***1g***



^{13}C NMR (100 MHz, $CDCl_3$) of ***1g***