Supplementary Information for

$In(ONf)_3$-catalyzed 7-membered carbon-ring-forming annulation of heteroarylindoles with α,β-unsaturated carbonyl compounds

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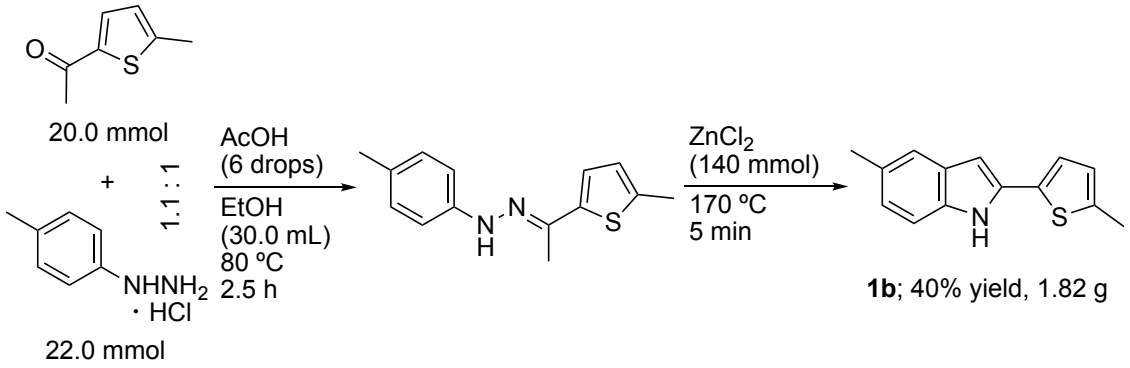
I. General Remarks

Unless otherwise noted, manipulations were conducted with a standard Schlenk technique under an argon atmosphere. Nuclear magnetic resonance (NMR) spectra were taken on a JEOL JMN-ECA 400 (^{1}H, 400 MHz; ^{13}C{^{1}H}, 100 MHz) or a JEOL JMN-ECA 500 (^{1}H, 500 MHz; ^{13}C{^{1}H}, 125 MHz) spectrometer, unless otherwise specified, using tetramethylsilane (^{1}H and ^{13}C{^{1}H}) as an internal standard. Analytical gas chromatography (GC) was performed on a Shimadzu model GC-2014 instrument equipped with a capillary column of InertCap 5 (5% diphenyl- and 95% dimethylpolysiloxane, 30 m × 0.25 mm × 0.25 μm) and with a FID detector, using nitrogen as carrier gas. Gas chromatography-mass spectrometry (GC-MS) analyses were performed with a Shimadzu model GCMS-QP2010 instrument equipped with a capillary column of InertCap 5 by electron ionization at 70 eV using helium as carrier gas. Preparative recycling high-performance liquid chromatography (HPLC) was performed with JAI LC-9104 equipped with JAIGEL-GS320 column using a mixture of hexane–ethyl acetate (EtOAc) as eluent. Preparative recycling gel permeation chromatography (GPC) was performed with JAI LC-9105 equipped with JAIGEL-1H and JAIGEL-2H columns using chloroform as eluent. High-resolution mass spectra (HRMS) were obtained with a JEOL JMS–T100GCV spectrometer. Elemental analyses were performed on a Vario EL III elemental analysis instrument. All melting points were measured with a Yanaco Micro Melting Point apparatus and are uncorrected. Under argon, methacrolein, acrolein, *trans*-crotonaldehyde, *trans*-cinnamaldehyde, methyl vinyl ketone, *trans*-2-hexenal, ethyl vinyl ketone and octylsilane were distilled as needed and stored in a Schlenk tube. As needed, 1,3-dibromo-5,5-dimethylhydantoin (DBH) was washed with cold deionized water or recrystallized from deionized water, and then dried at 90 °C in vacuo for 1 h. 1,4-Dioxane and dibutyl ether (Bu_2O) were distilled from sodium under argon just prior to use. Toluene (PhMe), dichloromethane (CH_2Cl_2), and chlorobenzene (PhCl) were distilled from calcium chloride under argon just prior to use. Propionitrile (EtCN) was distilled from P_2O_5 under argon just prior to use. EtOAc, butyl acetate (BuOAc), acetonitrile (MeCN), 1,2-dichloroethane (DCE), 1,2-dimethoxyethane (DME), 1,2-diethoxyethane (DEE), *p*-xylene, and nitromethane ($MeNO_2$) were stored over molecular sieves 4 Å (MS 4Å) under argon. The following substrates and indium salts were synthesized according to the respective literature methods: 2-(5-methylthien-2-yl)-1*H*-indole (**1a**), [1] 2-(thien-2-yl)-1*H*-indole (**1e**),[1] 2-(5-

[1] T. Tsuchimoto, H. Matsubayashi, M. Kaneko, Y. Nagase, T. Miyamura, E. Shirakawa, *J. Am. Chem. Soc.* **2008**, *130,* 15823, and related references therein.

methylfur-2-yl)-1*H*-indole (**1f**),[1] 2-(benzo[*b*]thien-2-yl)-1*H*-indole (**1g**),[1] 2-(benzo[*b*]fur-2-yl)-1*H*-indole (**1h**),[1] 2,2'-biindolyl (**1i**),[1] 1,1'-dimethyl-2,2'-biindolyl (**1j**),[1] 2-(thien-3-yl)-1*H*-indole (**1l**),[1] 2-(benzo[*b*]fur-3-yl)-1*H*-indole (**1m**),[1] 1,1'-dimethyl-3,3'-biindolyl (**1n**),[2] 2-[(4-methylphenyl)ethynyl]-2,3-dihydro-1*H*-naphtho[1,8-*de*]-1,3,2-diazaborine (**11b**),[3] $In(ONf)_3$ (Nf = $SO_2C_4F_9$),[1] and $In(NTf_2)_3$ (Tf = SO_2CF_3).[4] Unless otherwise noted, other substrates and reagents were commercially available and used as received without further purification.

II. Synthesis of Heteroarylindole Substrates



5-Methyl-2-(5-methylthien-2-yl)-1*H*-indole (1b). The title compound was synthesized according to the following modified literature procedure.[1] A 100 mL round-bottomed flask was charged with 4-methylphenylhydrazine hydrochloride (3.49 g, 22.0 mmol), 2-acetyl-5-methylthiophene (2.80 g, 20.0 mmol), acetic acid (6 drops), and EtOH (30.0 mL). The mixture was stirred at 80 ºC for 2.5 h. After evaporation of volatiles under reduced pressure, $ZnCl_2$ (19.1 g, 140 mmol) was added to the crude reaction mixture including the corresponding hydrazone intermediate, and the resulting mixture was stirred by hand with a spatula at 170 ºC for 5 min. After monitoring the consumption of the hydrazone intermediate by GC analysis (note: additional stirring would be performed if the intermediate should remain.), a concentrated HCl aqueous solution (ca. 12 N, 3.0 mL) diluted with water (50 mL) was added, and a solid stuck to the flask was removed with a spatula and stirred by hand. After filtration of the resulting mixture, a solid on the filter paper was washed with water (50 mL), a saturated $NaHCO_3$ aqueous solution (50 mL),

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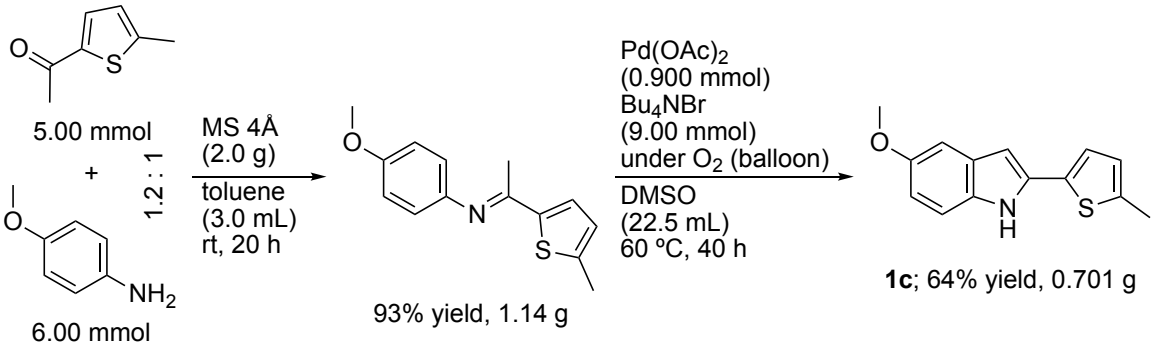
[2] a) Y. Nagase, H. Shirai, M. Kaneko, E. Shirakawa, T. Tsuchimoto, *Org. Biomol. Chem.* **2013**, *11*, 1456, and related references therein; for another procedure to prepare 3,3'-biindolyl, see: b) U. Berens, J. M. Brown, J. Long, R. Seike, *Tetrahedron: Asymmetry*, **1996**, *7*, 285.

[3] T. Tsuchimoto, H. Utsugi, T. Sugiura, S. Horio, *Adv. Synth. Catal.* **2015**, 357, 77.

[4] a) C. G. Frost, J. P. Hartley, D. Griffin, *Tetrahedron Lett.* **2002**, *43*, 4789; b) M. Nakamura, K. Endo, E. Nakamura, *Adv. Synth. Catal.* **2005**, *347*, 1681.

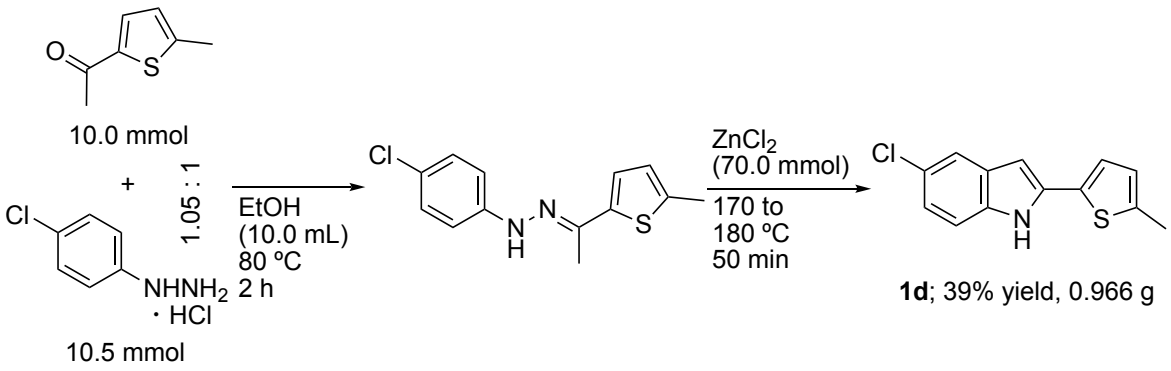
and water (50 mL) again. The remaining solid was collected by being dissolved in EtOAc (100 mL), and the solution was dried over anhydrous sodium sulfate (Na_2SO_4). Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 8/1) gave **1b** in 40% yield (1.82 g) as a beige solid, mp 180 ºC (decomp.). Compound **1b** was fully characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and HRMS, as follows: ^1H NMR (500 MHz, $CDCl_3$) δ 2.43 (s, 3 H), 2.51 (d, J = 1.1 Hz, 3 H), 6.56 (d, J = 1.1 Hz, 1 H), 6.72 (dq, J = 3.4, 1.2 Hz, 1 H), 6.99 (dd, J = 8.0, 1.1 Hz, 1 H), 7.02 (d, J = 3.4 Hz, 1 H), 7.24 (d, J = 8.1 Hz, 1 H), 7.35 (s, 1 H), 8.04 (br s, 1 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 15.4, 21.5, 99.3, 110.3, 120.0, 122.5, 123.8, 126.0, 129.4, 129.5, 132.7, 133.4, 134.7, 139.3. HRMS (FD) Calcd for $C_{14}H_{13}NS$: M^+, 227.07632. Found: *m/z* 227.07903.



5-Methoxy-2-(5-methylthien-2-yl)-1*H*-indole (1c). The title compound was synthesized according to the following modified literature procedure.[5] Under an argon atmosphere, a flame-dried 50 mL Schlenk tube was charged with 2-acetyl-5-methylthiophene (0.701 g, 5.00 mmol), *p*-anisidine (0.739 g, 6.00 mmol), MS 4Å (2.0 g) and toluene (3.0 mL), and the mixture was stirred at room temperature for 20 h. Filtration, rinse with EtOAc, and evaporation followed by simple purification through a pad of silica gel (hexane/EtOAc = 10/1) gave *N*-[1-(5-methylthien-2-yl)ethylidene]-4-methoxybenzenamine in 93% yield (1.14 g), the structure of which was confirmed by measuring ^1H NMR and GC-MS, as follows: ^1H NMR (500 MHz, $CDCl_3$) δ 2.20 (s, 3 H), 2.51 (s, 3 H), 3.81 (s, 3 H), 6.73−6.78 (m, 3 H), 6.88 (dt, J = 6.0, 3.8 Hz, 2 H), 7.25 (d, J = 4.0 Hz, 1 H). MS (GC-MS, EI) Calcd for $C_{14}H_{15}NOS$: M^+, 245. Found: *m/z* (relative intensity) 245 (62) [M^+], 230 (100), 189 (12), 161 (13), 123 (10), 92 (27), 77 (40), 64 (30), 53 (11), 45 (13). For the next step, a 200 mL Schlenk tube was charged with the imine (1.10 g, 4.50 mmol) prepared

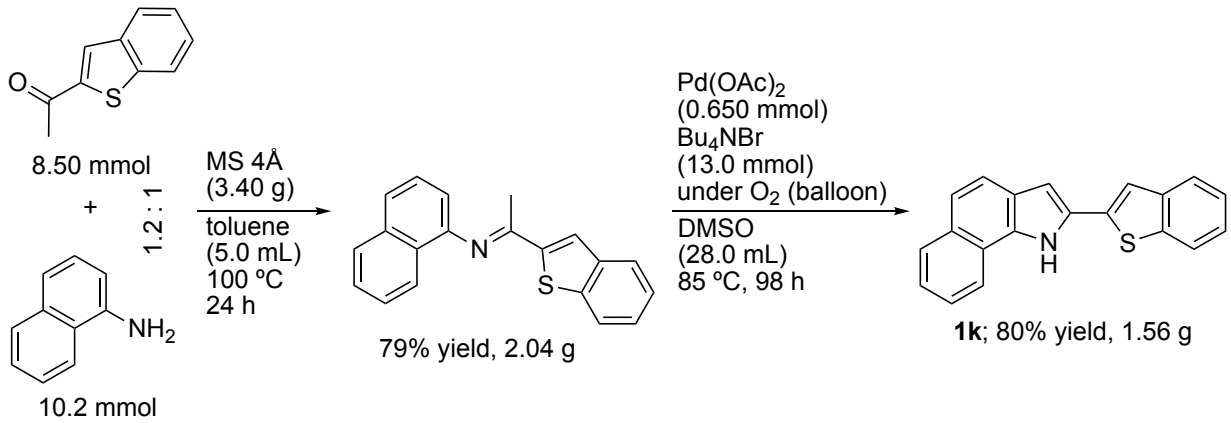
[5] a) N. Mršić, A. J. Minnaard, B. L. Feringa, J. G. de Vries, *J. Am. Chem. Soc.* **2009**, *131,* 8358; b) Y. Wei, I. Deb, N. Yoshikai, *J. Am. Chem. Soc.* **2012**, *134,* 9098.

above, $Pd(OAc)_2$ (0.101 g, 0.450 mmol) and Bu_4NBr (2.90 g, 9.00 mmol), followed by addition of dimethyl sulfoxide (DMSO) (22.5 mL). The tube was quickly evacuated and then filled with oxygen using an oxygen balloon. The resulting mixture was stirred at 60 °C for 20 h, and monitoring the reaction progress by GC analysis showed that the imine had remained unconsumed. Additional $Pd(OAc)_2$ (0.101 g, 0.450 mmol) was added accordingly, and the resulting mixture was stirred further for 20 h. After cooling to room temperature, the mixture was diluted with EtOAc (100 mL), followed by filtration through a pad of silica gel. The filtrate was washed with water (20 mL × 5) and brine (20 mL), and then dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 5/1) gave **1c** in 64% yield (0.701 g) as a white solid, mp 159–160 ºC. Compound **1c** was fully characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and HRMS, as follows: ^1H NMR (400 MHz, $CDCl_3$) δ 2.52 (d, J = 0.9 Hz, 3 H), 3.85 (s, 3 H), 6.57 (d, J = 1.4 Hz, 1 H), 6.71–6.74 (m, 1 H), 6.87 (dd, J = 8.7, 2.3 Hz, 1 H), 7.02–7.04 (m, 2 H), 7.24 (d, J = 8.7 Hz, 1 H), 8.03 (br s, 1 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 15.4, 55.8, 99.6, 102.1, 111.3, 112.4, 122.6, 126.0, 129.7, 131.5, 133.35, 133.39, 139.4, 154.6. HRMS (FD) Calcd for $C_{14}H_{13}NOS$: M^+, 243.07124. Found: *m/z* 243.07023.



5-Chloro-2-(5-methylthien-2-yl)-1*H*-indole (1d). The title compound was synthesized according to the following modified literature procedure.[1] A 100 mL round-bottomed flask was charged with 4-chlorophenylhydrazine hydrochloride (1.89 g, 10.5 mmol), 2-acetyl-5-methylthiophene (1.40 g, 10.0 mmol) and EtOH (10.0 mL). The mixture was stirred at 80 ºC for 2 h. After evaporation of volatiles under reduced pressure, $ZnCl_2$ (9.54 g, 70.0 mmol) was added to the crude reaction mixture including the corresponding hydrazone intermediate, and the mixture was stirred by hand with a spatula at 170 ºC for 30 min and then at 180 ºC for 20 min. After monitoring the consumption of the hydrazone intermediate by GC analysis (note: additional

stirring would be performed if the intermediate should remain.), a concentrated HCl aqueous solution (ca. 12 N, 1.5 mL) diluted with water (25 mL) was added, and a solid stuck to the flask was removed with a spatula and stirred by hand. After filtration of the resulting mixture, a solid on the filter paper was washed with water (25 mL), a saturated $NaHCO_3$ aqueous solution (25 mL), and water (25 mL) again. The remaining solid was collected by being dissolved in EtOAc (50 mL), and the solution was dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 5/1) gave **1d** in 39% yield (0.966 g) as a white solid, mp 194–195 ºC (decomp.). Compound **1d** was fully characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and HRMS, as follows: ^1H NMR (400 MHz, $CDCl_3$) δ 2.52 (d, J = 0.9 Hz, 3 H), 6.57 (d, J = 1.4 Hz, 1 H), 6.72–6.76 (m, 1 H), 7.06 (d, J = 3.2 Hz, 1 H), 7.11 (dd, J = 8.5, 2.1 Hz, 1 H), 7.25 (d, J = 8.7 Hz, 1 H), 7.52 (d, J = 1.8 Hz, 1 H), 8.16 (br s, 1 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 15.4, 99.2, 111.6, 119.7, 122.5, 123.2, 125.9, 126.1, 130.3, 132.6, 134.1, 134.7, 140.1. HRMS (FD) Calcd for $C_{13}H_{10}ClNS$: M^+, 247.02170. Found: *m/z* 247.02424.

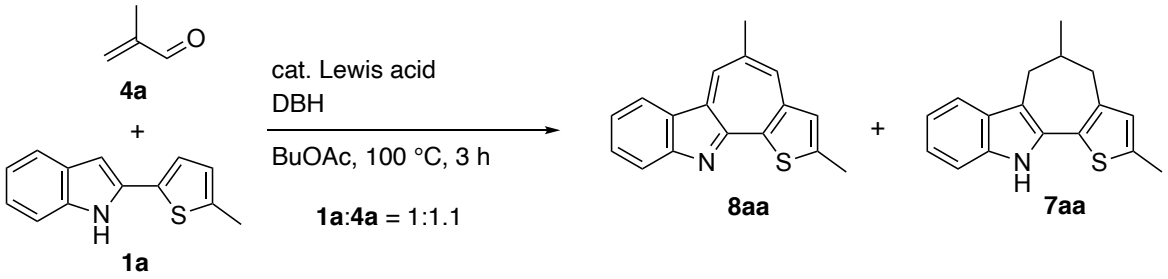


2-(Benzo[*b*]thien-2-yl)-1*H*-benzo[*g*]indole (1k). The title compound was synthesized according to the following modified literature procedure.[5] Under an argon atmosphere, a flame-dried 50 mL Schlenk tube was charged with 2-acetylbenzothiophene (1.50 g, 8.50 mmol), 1-naphthylamine (1.46 g, 10.2 mmol), MS 4Å (3.40 g) and toluene (5.0 mL), and the mixture was stirred at 100 ºC for 24 h. Filtration, rinse with EtOAc, and evaporation gave a crude product as a yellow solid, which was filtered by simply washing with EtOAc to give *N*-[1-(benzo[*b*]thien-2-yl)ethylidene]-4-naphthalenamine (1.36 g) as a pure form. The remaining filtrate was concentrated, and the resulting solid was further washed with a mixture of hexane/EtOAc, providing an additional imine (0.68 g) as a pure form. As a result, the imine was obtained in

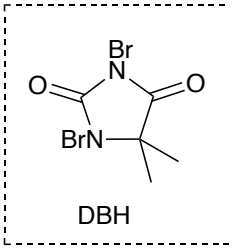
79% yield [2.04 g (= 1.36 g + 0.68 g)] in total. The formation of the imine was confirmed by measuring ^{1}H NMR and GC-MS, as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3 H), 6.84 (dd, *J* = 7.1, 1,1 Hz, 1 H), 7.36–7.53 (m, 5 H), 7.63 (d, *J* = 8.7 Hz, 1 H), 7.77 (s, 1 H), 7.86 (m, 4 H). MS (GC-MS, EI) Calcd for $C_{20}H_{15}NS$: M^+, 301. Found: *m/z* (relative intensity) 301 (62) [M^+], 286 (64), 127 (100), 115 (12), 101 (13), 89 (13), 77 (27). For the next step, a flame-dried 200 mL Schlenk tube was charged with the imine (1.96 g, 6.50 mol) prepared above, $Pd(OAc)_2$ (0.146 g, 0.650 mol), Bu_4NBr (4.19 g, 13.0 mmol) and DMSO (28.0 mL). The tube was quickly evacuated and then filled with oxygen using an oxygen balloon. The resulting mixture was stirred at 85 °C for 98 h. After cooling to room temperature, the mixture was diluted with EtOAc (100 mL), followed by filtration through a pad of silica gel. The filtrate was washed with water (20 mL × 5) and brine (20 mL), and then dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 10/1) gave **1k** in 80% yield (1.56 g) as a white solid, mp 230–232 ºC. Compound **1k** was fully characterized by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy and HRMS, as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 2.3 Hz, 1 H), 7.33 (td, *J* = 7.4, 1.2 Hz, 1 H), 7.38 (td, *J* = 7.4, 1.1 Hz, 1 H), 7.46 (t, *J* = 7.3 Hz, 1 H), 7.51–7.59 (m, 3 H), 7.69 (d, *J* = 8.2 Hz, 1 H), 7.79 (d, *J* = 7.3 Hz, 1 H), 7.84 (d, *J* = 7.8 Hz, 1 H), 7.93 (d, *J* = 8.2 Hz, 1 H), 8.08 (d, *J* = 8.2 Hz, 1 H), 9.02 (br s, 1 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 103.8, 118.2, 119.5, 120.5, 121.4, 121.6, 122.3, 123.4, 124.4, 124.5, 124.8, 125.1, 125.8, 129.1, 130.5, 130.9, 131.7, 135.5, 138.9, 140.4. HRMS (FD) Calcd for $C_{20}H_{13}NS$: M^+, 299.07632. Found: *m/z* 299.07505.

III. Indium-Catalyzed 7-Membered Carbon-Ring-Forming Annulation of 2-(5-Methylthien-2-yl)indole (1a) with Methacrolein (4a) in the Presence of DBH: Examination of Suitable Reaction Conditions

Table S1. Effect of Lewis acids[a]

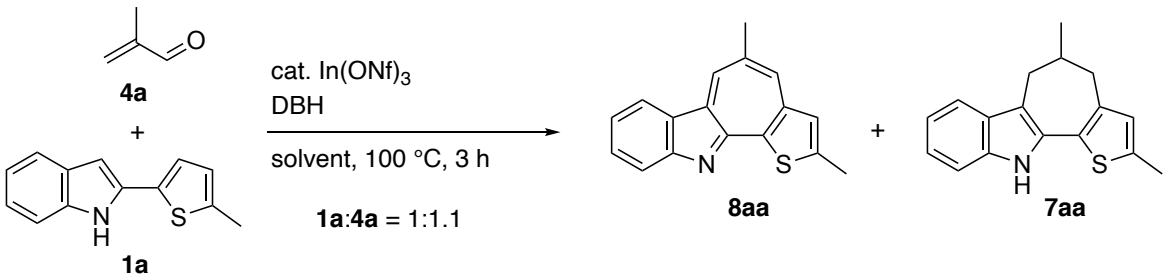


Lewis acid	conv. (%) of **1a**[b]	yield (%) of **8aa** and **7aa**[c]	**8aa**/**7aa**[b]
$In(ONf)_3$	**>99**	**67 (66)**[d]	**>99:1**
$In(OTf)_3$	>99	58	>99:1
$In(NTf_2)_3$	>99	44	>99:1
$Bi(OTf)_3$	>99	43	>99:1
$Cu(OTf)_2$	>99	60	98:2
AgOTf	>99	55	>99:1
$Sc(OTf)_3$	97	18	97:3



[a] Reagents: **1a** (0.20 mmol), **4a** (0.22 mmol), Lewis acid (6.0 μmol, 3 mol%), DBH (0.11 mmol), BuOAc (5.0 mL). [b] Determined by GC. [c] Determined by ^{1}H NMR. [d] Isolated yield.

Table S2. Effect of Solvents[a]

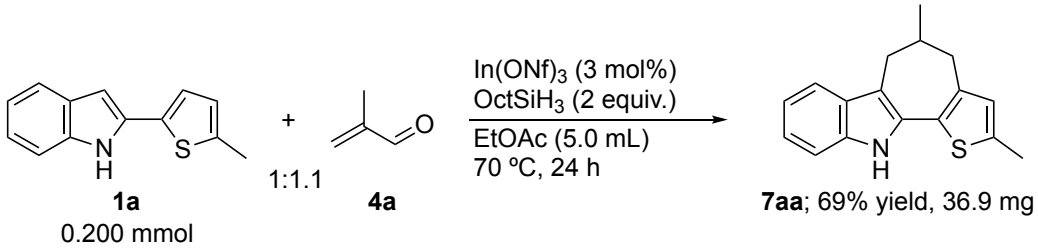


solvent	conv. (%) of **1a**[b]	yield (%) of **8aa** and **7aa**[c]	**8aa**/**7aa**[b]
BuOAc	**>99**	**67 (66)**[d]	**>99:1**
EtCN	>99	57	>99:1
1,4-dioxane	>99	60	>99:1
DEE	>99	55	>99:1
Bu_2O	96	40	97:3
$MeNO_2$	>99	29	99:1
PhMe	98	53	>99:1
p-xylene	>99	49	>99:1
PhCl	>99	60	>99:1

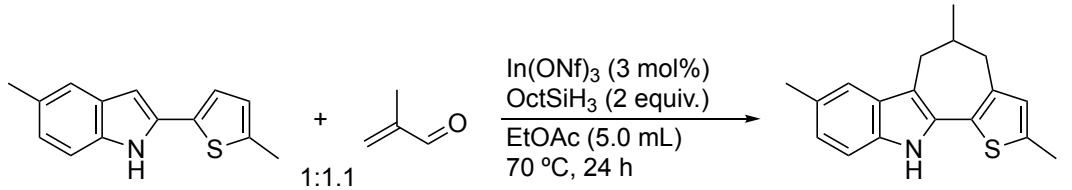
[a] Reagents: **1a** (0.20 mmol), **4a** (0.22 mmol), $In(ONf)_3$ (6.0 μmol, 3 mol%), DBH (0.11 mmol), solvent (5.0 mL). [b] Determined by GC. [c] Determined by ^1H NMR. [d] Isolated yield.

IV. Indium-Catalyzed 7-Membered Carbon-Ring-Forming Annulation in the Presence of Octylsilane: A General Procedure for Table 3

$In(ONf)_3$ [(6.07 mg, 6.00 μmol), (10.1 mg, 10.0 μmol) or (20.2 mg, 20.0 μmol)] was placed in a 20 or 50 mL Schlenk tube, which was heated at 150 ºC in vacuo for 2 h. The tube was cooled down to room temperature, and filled with argon. EtOAc (5.0–10.0 mL) or BuOAc (5.0–10.0 mL) was added to the tube, and the mixture was stirred for 10 min at room temperature. To this were added heteroarylindole **1** (0.200 mmol), α,β-unsaturated carbonyl compound **4** (0.220, 0.240 or 0.300 mmol), and octylsilane [(57.7 mg, 0.400 mmol) or (72.2 mg, 0.500 mmol)], and the resulting mixture was stirred at 70, 85 or 100 °C for 5–72 h. The mixture diluted with EtOAc (10 mL) was washed with a saturated $NaHCO_3$ aqueous solution (1 mL) and brine (1 mL), and then dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvent followed by purification gave product **7**. Unless otherwise noted, products **7** synthesized in this section were fully characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and HRMS.



2,5-Dimethyl-4,5,6,11-tetrahydrothieno[2',3':7,6]cyclohepta[1,2-*b*]indole (7aa). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc/Et_3N = 200/5/6). A white solid, mp 73–74 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (d, *J* = 6.9 Hz, 3 H), 2.21–2.35 (m, 1 H), 2.47 (d, *J* = 0.9 Hz, 3 H), 2.72–2.86 (m, 2 H), 2.92 (dt, *J* = 16.0, 1.8 Hz, 1 H), 3.13 (ddd, *J* = 16.6, 3.1, 1.7 Hz, 1 H), 6.51 (d, *J* = 1.4 Hz, 1 H), 7.09 (td, *J* = 7.4, 1.1 Hz, 1 H), 7.15 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.29 (dt, *J* = 8.1, 1.0 Hz, 1 H), 7.47 (d, *J* = 7.8 Hz, 1 H), 7.77 (br s, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 15.2, 22.4, 29.0, 34.0, 38.9, 110.3, 111.2, 118.1, 119.6, 122.1, 126.9, 129.2, 129.8, 130.0, 135.7, 135.8, 138.1. HRMS (FD) Calcd for $C_{17}H_{17}NS$: M^+, 267.10762. Found: *m/z* 267.11036.

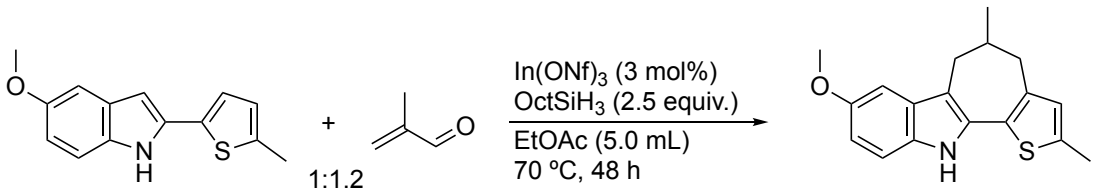


1b
0.200 mmol

4a

7ba; 69% yield, 38.8 mg

2,5,8-Trimethyl-4,5,6,11-tetrahydrothieno[2',3':7,6]cyclohepta[1,2-*b*]indole (7ba). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc/Et_3N = 200/5/6). A white solid, mp 64–65 ºC. ^{1}H NMR (400 MHz, acetone-d_6) δ 1.16 (d, J = 6.9 Hz, 3 H), 2.19–2.27 (m, 1 H), 2.38 (s, 3 H), 2.43 (d, J = 0.9 Hz, 3 H), 2.71–2.80 (m, 2 H), 2.95 (dt, J = 16.0, 1.8 Hz, 1 H), 3.11 (ddd, J = 16.5, 3.4, 1.8 Hz, 1 H), 6.57 (d, J = 0.9 Hz, 1 H), 6.89 (dd, J = 8.2, 1.4 Hz, 1 H), 7.18 (d, J = 8.2 Hz, 1 H), 7.20–7.22 (m, 1 H), 9.79 (br s, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 15.2, 21.5, 22.4, 29.0, 34.0, 38.9, 110.0, 110.9, 117.8, 123.6, 127.1, 128.9, 129.4, 130.0, 130.1, 134.1, 135.5, 137.8. HRMS (FD) Calcd for $C_{18}H_{19}NS$: M^+, 281.12327. Found: *m/z* 281.12592.

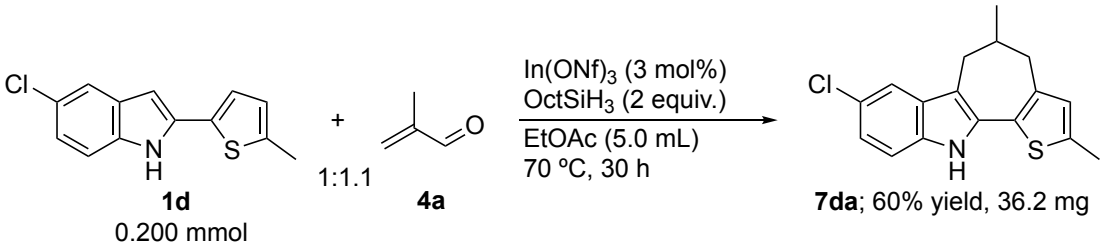


1c
0.200 mmol

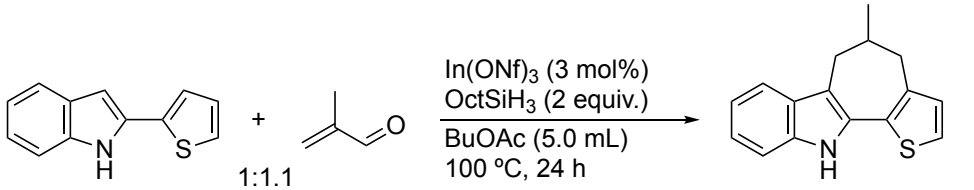
4a

7ca; 31% yield, 18.4 mg

8-Methoxy-2,5-dimethyl-4,5,6,11-tetrahydrothieno[2',3':7,6]cyclohepta[1,2-*b*]indole (7ca). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc/Et_3N = 100/10/3). A white solid, mp 58–61 ºC. ^{1}H NMR (500 MHz, acetone-d_6) δ 1.16 (d, J = 6.9 Hz, 3 H), 2.18–2.26 (m, 1 H), 2.42 (s, 3 H), 2.71–2.80 (m, 2 H), 2.94 (dt, J = 15.8, 2.0 Hz, 1 H), 3.10 (ddd, J = 16.5, 3.0, 1.9 Hz, 1 H), 3.81 (s, 3 H), 6.56 (d, J = 1.1 Hz, 1 H), 6.71 (dd, J = 8.9, 2.6 Hz, 1 H), 6.93 (d, J = 2.3 Hz, 1 H), 7.19 (d, J = 8.6 Hz, 1 H), 9.78 (br s, 1 H); ^{13}C{^{1}H} NMR (125 MHz, acetone-d_6) δ 15.1, 22.7, 34.9, 39.6, 55.8, 100.5, 111.1, 112.18, 112.23, 112.5, 128.5, 130.9, 131.0, 132.5, 136.4, 138.4, 155.1 (One carbon signal is missing due to overlapping). HRMS (FD) Calcd for $C_{18}H_{19}NOS$: M^+, 297.11819. Found: *m/z* 297.11940.

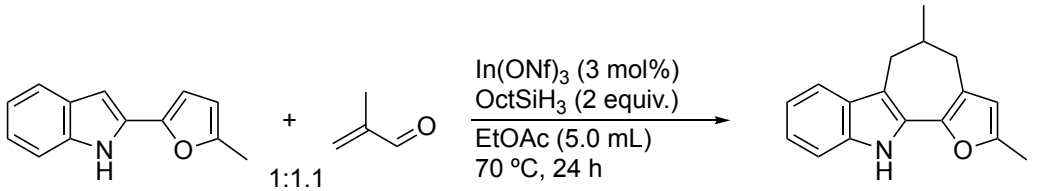


8-Chloro-2,5-dimethyl-4,5,6,11-tetrahydrothieno[2',3':7,6]cyclohepta[1,2-*b*]indole (7da). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc/Et_3N = 200/5/6). A white solid, mp 79–80 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15 (d, *J* = 6.9 Hz, 3 H), 2.20–2.32 (m, 1 H), 2.46 (d, *J* = 0.9 Hz, 3 H), 2.72–2.79 (m, 2 H), 2.92 (dt, *J* = 16.0, 1.9 Hz, 1 H), 3.05 (ddd, *J* = 16.6, 1.7, 0.9 Hz, 1 H), 6.51 (d, *J* = 0.9 Hz, 1 H), 7.08 (dd, *J* = 8.3, 2.0 Hz, 1 H), 7.19 (d, *J* = 8.6 Hz, 1 H), 7.41 (d, *J* = 2.0 Hz, 1 H), 7.78 (br s, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 15.3, 22.3, 28.9, 33.9, 38.9, 110.8, 111.3, 117.6, 122.1, 125.3, 126.3, 130.1, 130.7, 131.0, 134.1, 136.3, 138.7. HRMS (FD) Calcd for $C_{17}H_{16}ClNS$: M^+, 301.06865. Found: *m/z* 301.07084.

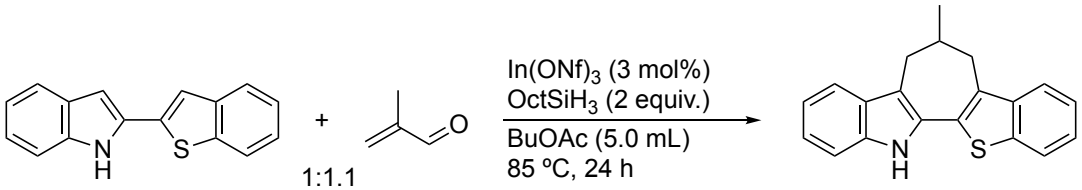


5-Methyl-4,5,6,11-tetrahydrothieno[2',3':7,6]cyclohepta[1,2-*b*]indole (7ea). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc/Et_3N = 200/5/6). A white solid, mp 127–130 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17 (d, *J* = 6.7 Hz, 3 H), 2.26–2.35 (m, 1 H), 2.83 (t, *J* = 9.1 Hz, 1 H), 2.86 (t, *J* = 9.5 Hz, 1 H), 3.02 (dt, *J* = 15.8, 2.3 Hz, 1 H), 3.16 (d, *J* = 16.6 Hz, 1 H), 6.84 (d, *J* = 5.0 Hz, 1 H), 7.06–7.12 (m, 2 H), 7.17 (td, *J* = 8.0, 1.2 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 1 H), 7.49 (d, *J* = 7.9 Hz, 1 H), 7.86 (br s, 1 H); ^{13}C{^{1}H} NMR (125 MHz, acetone-d_6) δ 22.7, 34.8, 39.4, 111.6, 111.8, 118.8, 120.0, 122.4, 122.8, 129.9, 130.5, 130.6, 132.3, 137.5, 138.6 (The chemical shifts were referenced to the solvent signal at 29.84 ppm.[6] One carbon signal is missing due to overlapping). HRMS (FD) Calcd for $C_{16}H_{15}NS$: M^+, 253.09197. Found: *m/z* 253.09301.

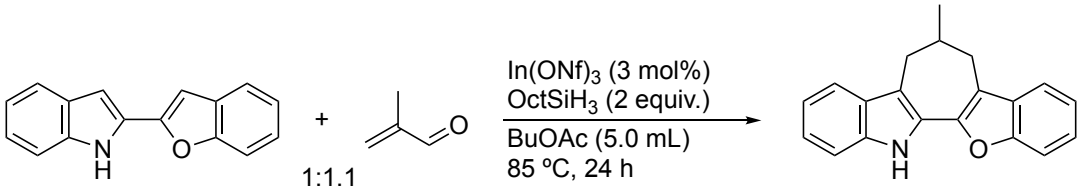
[6] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176.



2,5-Dimethyl-4,5,6,11-tetrahydrofuro[2',3':7,6]cyclohepta[1,2-*b*]indole (7fa). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc/Et_3N = 200/5/6). A white solid, mp 132–133 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (d, *J* = 6.9 Hz, 3 H), 2.20–2.30 (m, 1 H), 2.33 (d, *J* = 0.9 Hz, 3 H), 2.61 (dd, *J* = 16.5, 9.2 Hz, 1 H), 2.73–2.83 (m, 2 H), 3.09 (dt, *J* = 16.3, 2.1 Hz, 1 H), 5.90 (d, *J* = 0.9 Hz, 1 H), 7.06–7.15 (m, 2 H), 7.31 (dd, *J* = 7.3, 1.4 Hz, 1 H), 7.46–7.49 (m, 1 H), 8.26 (br s, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 13.6, 22.3, 28.6, 33.0, 34.6, 109.2, 110.4, 110.5, 117.9, 119.4, 121.0, 121.4, 126.8, 129.2, 135.4, 141.9, 150.2. HRMS (FD) Calcd for $C_{17}H_{17}NO$: M^+, 251.13047. Found: *m/z* 251.13208.



6-Methyl-5,6,7,12-tetrahydrobenzo[4',5']thieno[2',3':7,6]cyclohepta[1,2-*b*]indole (7ga). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc/Et_3N = 200/5/6). A white solid, mp 170–171 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (d, *J* = 6.9 Hz, 3 H), 2.36–2.48 (m, 1 H), 2.93 (dd, *J* = 9.5, 2.4 Hz, 1 H), 2.96 (dd, *J* = 9.5, 2.6 Hz, 1 H), 3.21–3.29 (m, 2 H), 7.13 (ddd, *J* = 7.9, 7.0, 0.9 Hz, 1 H), 7.21 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1 H), 7.32 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1 H), 7.36 (dt, *J* = 8.0, 0.9 Hz, 1 H), 7.40 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1 H), 7.55 (ddd, *J* = 7.9, 1.8, 0.9 Hz, 1 H), 7.70 (dt, *J* = 8.0, 1.0 Hz, 1 H), 7.81 (dt, *J* = 8.0, 0.9 Hz, 1 H), 8.00 (br s, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 22.7, 29.0, 33.8, 36.1, 110.7, 114.3, 118.5, 119.9, 121.5, 122.3, 122.9, 124.2, 124.5, 128.9, 129.1, 129.5, 131.3, 136.2, 137.3, 141.1. HRMS (FD) Calcd for $C_{20}H_{17}NS$: M^+, 303.10762. Found: *m/z* 303.11033.

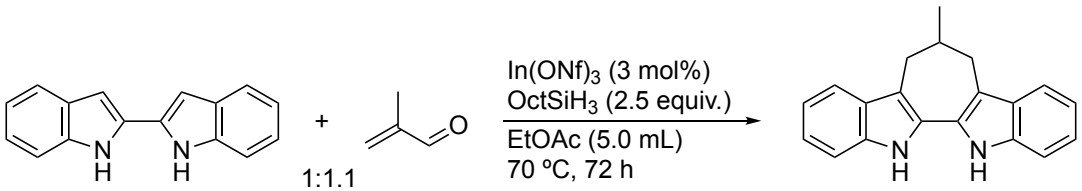


1h
0.200 mmol

4a

7ha; 71% yield, 40.8 mg

6-Methyl-5,6,7,12-tetrahydrobenzo[4',5']furo[2',3':7,6]cyclohepta[1,2-*b*]indole (7ha). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc/Et_3N = 200/5/6). A white solid, mp 159–160 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (d, *J* = 6.8 Hz, 3 H), 2.36–2.45 (m, 1 H), 2.83 (dd, *J* = 16.7, 9.2 Hz, 1 H), 2.94 (dd, *J* = 16.4, 9.2 Hz, 1 H), 3.08 (dt, *J* = 16.7, 2.4 Hz, 1 H), 3.22 (dt, *J* = 16.4, 2.2 Hz, 1 H), 7.13 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1 H), 7.21 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1 H), 7.23–7.29 (m, 2 H), 7.38 (dt, *J* = 8.0, 0.9 Hz, 1 H), 7.43–7.50 (m, 2 H), 7.56 (dd, *J* = 7.9, 0.9 Hz, 1 H), 8.54 (br s, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 22.4, 28.2, 32.2, 33.0, 110.8, 110.9, 113.4, 114.4, 118.4, 118.7, 119.8, 122.6, 122.8, 123.9, 125.9, 128.9, 130.4, 135.8, 145.2, 153.8. HRMS (FD) Calcd for $C_{20}H_{17}NO$: M^+, 287.13047. Found: *m/z* 287.13234.

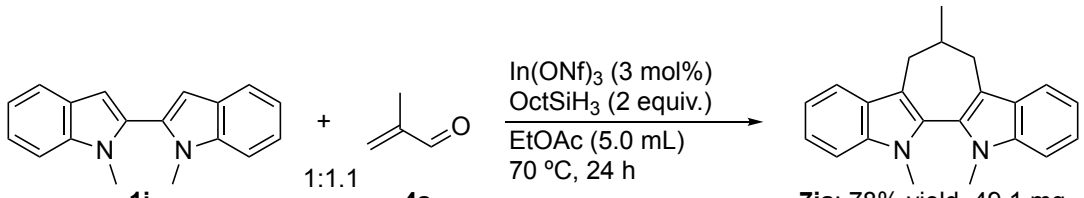


1i
0.200 mmol

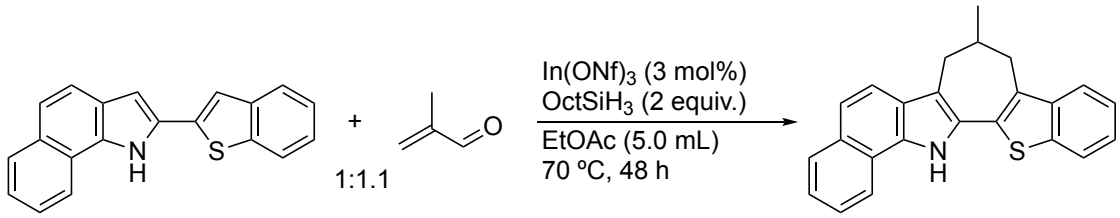
4a

7ia; 57% yield, 32.6 mg

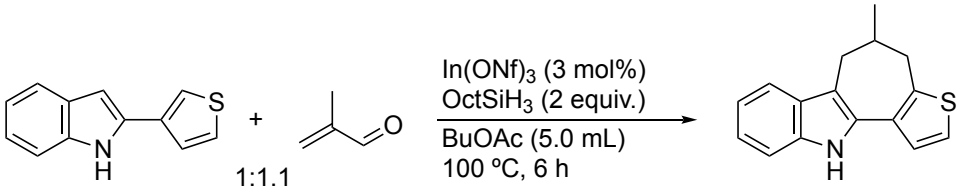
6-Methyl-6,7,12,13-tetrahydro-5*H*-cyclohepta[2,1-*b*:3,4-*b*']diindole (7ia). The title compound was produced as a 94:6 mixture of **7ia** and **8ia** before purification, and was isolated by column chromatography on silica gel (hexane/EtOAc/Et_3N = 100/20/3). A white solid, mp 93–94 ºC. ^{1}H NMR (500 MHz, acetone-d_6) δ 1.26 (d, *J* = 6.9 Hz, 3 H), 2.31–2.41 (m, 1 H), 2.93 (dd, *J* = 15.8, 9.5 Hz, 2 H), 3.25 (dd, *J* = 15.5, 2.3 Hz, 2 H), 7.04 (td, *J* = 7.4, 1.1 Hz, 2 H), 7.10 (td, *J* = 7.4, 1.1 Hz, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.52 (d, *J* = 8.0 Hz, 2 H), 10.20 (br s, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 22.7, 29.2, 33.5, 110.7, 114.1, 118.3, 120.0, 122.4, 127.4, 129.8, 136.3. HRMS (FD) Calcd for $C_{20}H_{18}N_2$: M^+, 286.14645. Found: *m/z* 286.14743.



6,12,13-Trimethyl-6,7-dihydro-5*H*-cyclohepta[2,1-*b*:3,4-*b*']diindole (7ja). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc/Et_3N = 200/5/6). A white solid, mp 174–175 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (d, *J* = 6.9 Hz, 3 H), 1.97 (dd, *J* = 14.0, 11.2 Hz, 1 H), 2.58 (dd, *J* = 14.7, 6.9 Hz, 1 H), 2.65–2.78 (m, 2 H), 3.00 (dd, *J* = 14.2, 6.0 Hz, 1 H), 3.82 (s, 6 H), 7.19 (t, *J* = 7.3 Hz, 2 H), 7.26–7.32 (m, 2 H), 7.40 (d, *J* = 8.2 Hz, 2 H), 7.67 (t, *J* = 7.3 Hz, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 22.4, 29.1, 29.9, 32.2, 42.1, 109.6, 109.7, 116.5, 118.3, 118.4, 118.7, 119.5, 119.6, 121.88, 121.94, 127.7, 129.3, 130.9, 138.49, 138.53 (Two carbon signals are missing due to overlapping). HRMS (FD) Calcd for $C_{22}H_{22}N_2$: M^+, 314.17775. Found: *m/z* 314.17952.

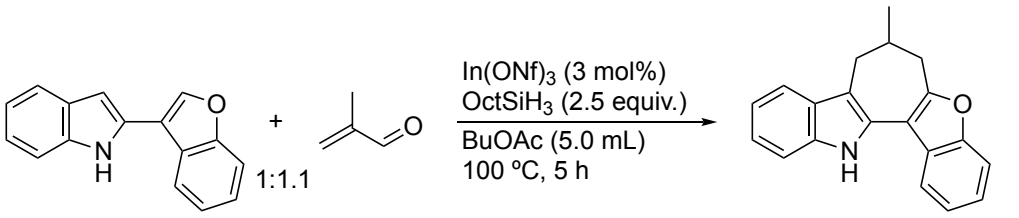


6-Methyl-5,6,7,14-tetrahydrobenzo[*g*]benzo[4',5']thieno[2',3':7,6]cyclohepta[1,2-*b*]indole (7ka). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc = 40/1). A white solid, mp 169–172 ºC. ^{1}H NMR (400 MHz, acetone-d_6) δ 1.29 (d, *J* = 6.9 Hz, 3 H), 2.37–2.49 (m, 1 H), 2.95–3.06 (m, 2 H), 3.33 (d, *J* = 2.4 Hz, 1 H), 3.37 (d, *J* = 2.5 Hz, 1 H), 7.33 (dt, *J* = 10.3, 3.8 Hz, 1 H), 7.39–7.44 (m, 2 H), 7.49–7.55 (m, 2 H), 7.68 (d, *J* = 8.6 Hz, 1 H), 7.79 (d, *J* = 8.0 Hz, 1 H), 7.89 (dd, *J* = 7.8, 0.6 Hz, 1 H), 7.93 (d, *J* = 7.7 Hz, 1 H), 8.54 (d, *J* = 8.2 Hz, 1 H), 10.86 (br s, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 21.7, 28.0, 32.9, 35.2, 115.0, 117.4, 118.7, 119.9, 120.3, 120.4, 121.3, 123.1, 123.2, 123.5, 124.2, 124.6, 126.5, 128.0, 128.2, 129.4, 129.79, 129.85, 136.0, 140.3. HRMS (FD) Calcd for $C_{24}H_{19}NS$: M^+, 353.12327. Found: *m/z* 353.12223.



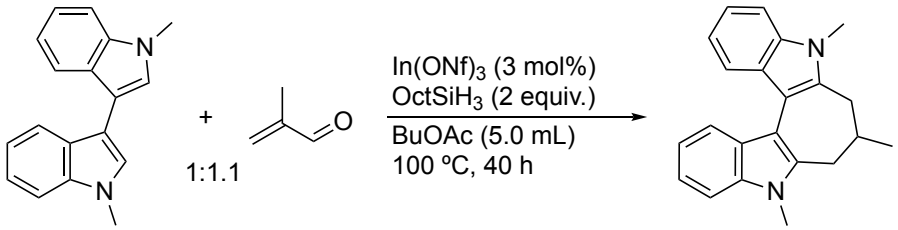
1l 0.200 mmol **4a** **7la**; 64% yield, 32.4 mg

5-Methyl-4,5,6,11-tetrahydrothieno[2',3':6,7]cyclohepta[1,2-*b*]indole (7la). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc/Et_3N = 300/5/9). A white solid, mp 132–134 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 1.19 (d, J = 6.9 Hz, 3 H), 2.28–2.40 (m, 1 H), 2.89 (dd, J = 16.8, 9.6 Hz, 1 H), 3.00 (dd, J = 16.1, 9.1 Hz, 1 H), 3.14 (dt, J = 16.0, 1.8 Hz, 1 H), 3.20 (ddd, J = 16.6, 3.4, 1.6 Hz, 1 H), 7.00 (t, J = 7.4 Hz, 1 H), 7.08 (t, J = 7.5 Hz, 1 H), 7.25 (d, J = 5.4 Hz, 1 H), 7.30 (d, J = 8.0 Hz, 1 H), 7.46 (d, J = 7.9 Hz, 1 H), 7.53 (d, J = 5.4 Hz, 1 H), 10.21 (br s, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 22.1, 29.9, 34.2, 37.5, 110.5, 111.3, 118.2, 119.5, 122.2, 122.3, 124.3, 129.6, 129.79, 129.81, 135.5, 138.3. HRMS (FD) Calcd for $C_{16}H_{15}NS$: M^+, 253.09197. Found: *m/z* 253.09305.



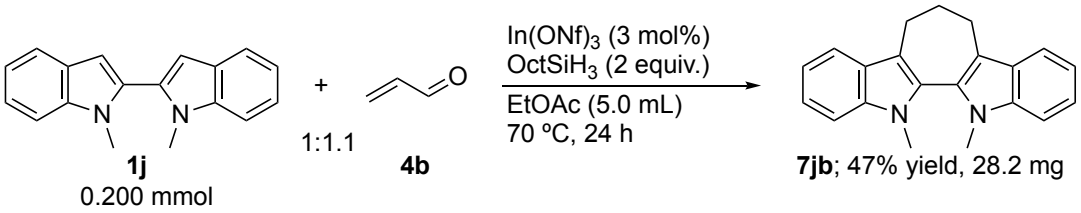
1m 0.200 mmol **4a** **7ma**; 80% yield, 46.0 mg

7-Methyl-6,7,8,13-tetrahydrobenzo[4',5']furo[2',3':6,7]cyclohepta[1,2-*b*]indole (7ma). The title compound was isolated by column chromatography on alumina (hexane/EtOAc = 60/1). A white solid, mp 77–81 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 1.23 (d, J = 6.9 Hz, 3 H), 2.34–2.46 (m, 1 H), 2.90 (dd, J = 16.0, 9.2 Hz, 1 H), 3.10 (dd, J = 17.6, 9.4 Hz, 1 H), 3.20 (dt, J = 16.0, 2.1 Hz, 1 H), 3.31 (ddd, J = 17.9, 3.7, 1.8 Hz, 1 H), 7.05 (td, J = 7.3, 1.2 Hz, 1 H), 7.10 (td, J = 7.4, 1.2 Hz, 1 H), 7.30–7.36 (m, 2 H), 7.47–7.55 (m, 3 H), 8.21–8.26 (m, 1 H), 10.26 (br s, 1 H); ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6) δ 22.3, 28.9, 33.0, 38.2, 110.2, 111.77, 111.84, 112.1, 118.3, 120.0, 121.0, 122.0, 123.7, 124.8, 127.3, 127.9, 129.7, 137.7, 155.0, 156.1 (The chemical shifts were referenced to the solvent signal at 29.84 ppm).[6] HRMS (FD) Calcd for $C_{20}H_{17}NO$: M^+, 287.13047. Found: *m/z* 287.12859.



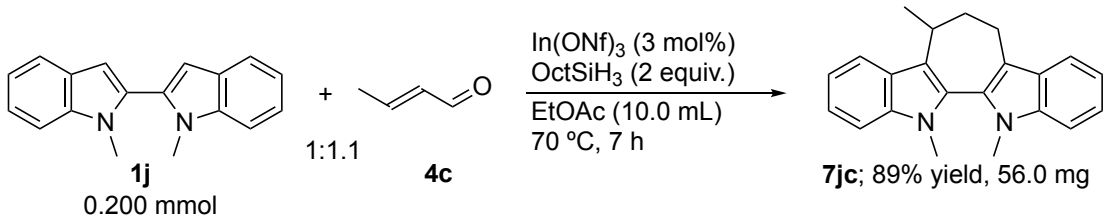
1n 0.200 mmol **4a** **7na**; 86% yield, 54.1 mg

5,7,9-Trimethyl-7,8-dihydro-6*H*-cyclohepta[1,2-*b*:4,3-*b*']diindole (7na). The title compound was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 3/1). A white solid, mp 239–243 ºC. ^{1}H NMR (400 MHz, acetone-d_6) δ 1.20 (d, J = 6.4 Hz, 3 H), 2.58–2.72 (m, 3 H), 3.00 (dd, J = 14.4, 4.8 Hz, 2 H), 3.83 (s, 6 H), 7.07 (ddd, J = 8.0, 7.0, 1.0 Hz, 2 H), 7.16 (ddd, J = 8.0, 7.0, 1.0 Hz, 2 H), 7.43 (d, J = 8.2 Hz, 2 H), 7.79 (d, J = 7.8 Hz, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 22.5, 29.7, 32.0, 39.9, 108.7, 109.2, 119.1, 120.68, 120.72, 126.4, 136.9, 137.2 (The chemical shifts were referenced to the solvent signal at 77.16 ppm).[6] HRMS (FD) Calcd for $C_{22}H_{22}N_2$: M^+, 314.17775. Found: *m/z* 314.17951.



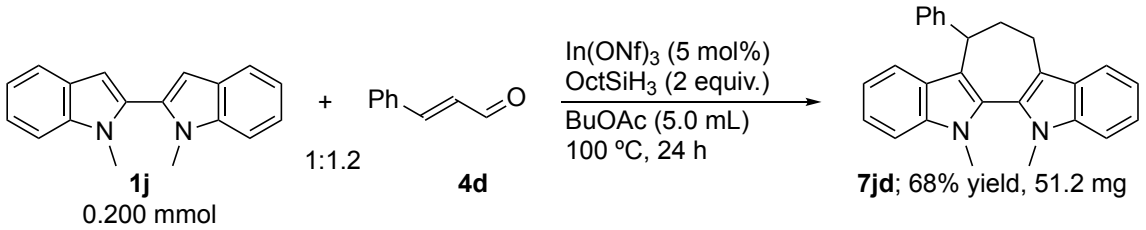
1j 0.200 mmol **4b** **7jb**; 47% yield, 28.2 mg

12,13-Dimethyl-6,7-dihydro-5*H*-cyclohepta[2,1-*b*:3,4-*b*']diindole (7jb). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc/Et_3N = 200/5/6). A white solid, mp 192–194 ºC. ^{1}H NMR (400 MHz, acetone-d_6) δ 2.26–2.33 (m, 2 H), 2.36–2.45 (m, 2 H), 3.07 (dt, J = 9.5, 4.8 Hz, 2 H), 3.87 (s, 6 H), 7.13 (t, J = 7.4 Hz, 2 H), 7.24 (t, J = 7.7 Hz, 2 H), 7.48 (d, J = 8.6 Hz, 2 H), 7.65 (d, J = 8.0 Hz, 2 H); ^{13}C{^{1}H} NMR (125 MHz, acetone-d_6) δ 21.9, 32.6, 34.6, 110.8, 118.2, 118.9, 120.2, 122.7, 128.9, 131.6, 139.7. HRMS (FD) Calcd for $C_{21}H_{20}N_2$: M^+, 300.16210. Found: *m/z* 300.16506.



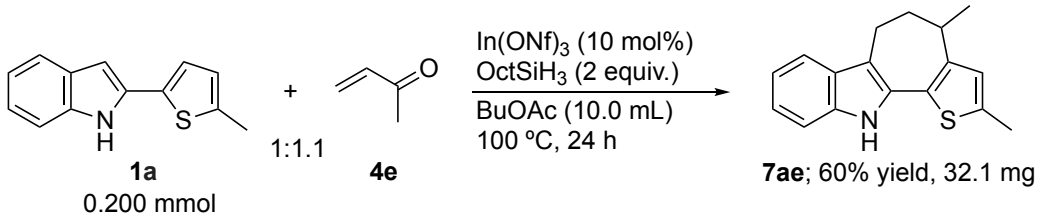
1j 0.200 mmol **4c** **7jc**; 89% yield, 56.0 mg

5,12,13-Trimethyl-6,7-dihydro-5*H*-cyclohepta[2,1-*b*:3,4-*b*']diindole (7jc). The title compound was isolated as a 56:44 mixture of diastereomers by column chromatography on silica gel (hexane/EtOAc/Et_3N = 100/5/3). A separation of the diastereomeric mixture was conducted by recycling HPLC, but could not be achieved. A white solid, mp 77–78 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12 (d, *J* = 7.2 Hz, 0.56 × 3 H), 1.69 (d, *J* = 7.4 Hz, 0.44 × 3 H), 1.81–1.89 (m, 0.56 × 1 H), 2.09–2.18 (m, 0.44 × 1 H), 2.31–2.45 (m, 0.44 × 2 H), 2.51–2.58 (m, 0.56 × 1 H), 2.63 (ddd, *J* = 14.7, 11.1, 3.6 Hz, 0.56 × 1 H), 2.88–2.94 (m, 0.44 × 1 H), 2.95–3.00 (m, 0.44 × 1 H), 3.04 (ddd, *J* = 14.9, 5.7, 3.7 Hz, 0.56 × 1 H), 3.57–3.66 (m, 0.56 × 1 H), 3.76 (s, 0.56 × 3 H), 3.78 (s, 0.44 × 3 H), 3.79 (s, 0.44 × 3 H), 3.81 (s, 0.56 × 3 H), 7.13–7.22 (m, 2 H), 7.26–7.31 (m, 2 H), 7.38–7.42 (m, 2 H), 7.60–7.68 (m, 0.44 × 1 H + 0.56 × 2 H), 7.96 (d, *J* = 8.0 Hz, 0.44 × 1 H); ^{13}C{^{1}H} NMR (125 MHz, acetone-d_6) δ 20.2, 21.2, 22.1, 23.8, 30.6, 32.39, 32.42, 32.6, 32.7, 32.8, 41.0, 45.5, 110.8, 110.9, 118.7, 118.9, 119.0, 119.5, 120.1, 120.2, 120.3, 120.4, 121.2, 122.2, 122.5, 122.7, 122.9, 128.2, 128.5, 128.6, 129.5, 129.6, 131.3, 131.4, 139.6, 139.8, 140.2, 140.3 (**7jc** has 22 carbon atoms, and 44 carbon signals are thus supposed to be observed in the ^{13}C{^{1}H} NMR spectrum of the diastereomeric mixture of **7jc**. However, 6 carbon signals were missing, due probably to overlapping). Due to the inseparable diastereomeric mixture, elemental analysis was performed to evaluate the purity of **7jc** isolated. Elemental Analysis Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.66; H, 6.95; N, 8.53. HRMS (FD) Calcd for $C_{22}H_{22}N_2$: M^+, 314.17775. Found: *m/z* 314.17836.



12,13-Dimethyl-5-phenyl-6,7-dihydro-5*H*-cyclohepta[2,1-*b*:3,4-*b*']diindole (7jd). The title compound was isolated as a 79:21 mixture of diastereomers by column chromatography on silica gel (hexane/EtOAc/Et_3N = 100/5/3). A white solid, mp 108–114 ºC. ^{1}H NMR (500 MHz, acetone-d_6) δ 1.88–1.97 (m, 1 H), 2.47–2.59 (m, 0.21 × 2 H), 2.71–2.82 (m, 0.79 × 2 H), 3.14–3.20 (m, 1 H), 3.85 (s, 0.79 × 3 H), 3.89 (s, 0.21 × 3 H), 3.93 (s, 0.21 × 3 H), 3.95 (s, 0.79 × 3 H), 4.21 (dd, *J* = 10.6, 4.3 Hz, 0.21 × 1 H), 4.86 (t, *J* = 8.9 Hz, 0.79 × 1 H), 6.28 (d, *J* = 8.6 Hz, 0.21 × 1 H), 6.71 (t, *J* = 7.7 Hz, 0.21 × 1 H), 6.97–7.04 (m, 0.79 × 2 H), 7.08–7.54 (m, 10 H), 7.61 (d,

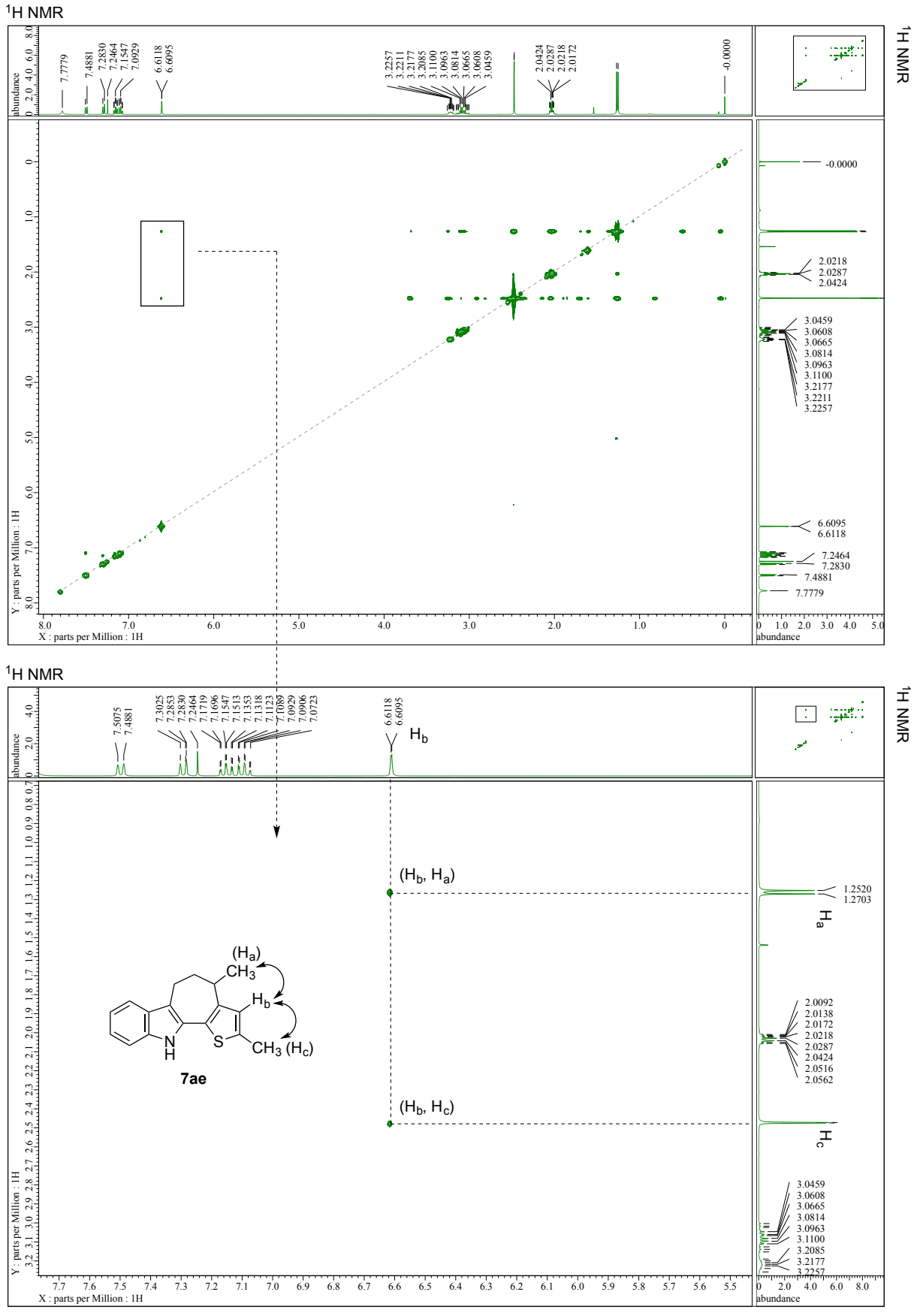
J = 7.4 Hz, 0.79 × 1 H), 7.68 (d, J = 7.4 Hz, 0.21 × 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ 14.5, 20.8, 22.4, 33.0, 33.1, 42.0, 44.1, 60.5, 110.7, 110.9, 111.1, 119.0, 119.07, 119.13, 119.7, 119.8 120.3, 120.4, 120.5, 120.9, 122.3, 122.8, 123.1, 126.4, 127.1, 128.3, 128.4, 129.0, 129.8, 130.2, 130.9, 131.1, 140.6, 140.7, 148.1 (The chemical shifts were referenced to the solvent signal at 29.84 ppm.[6] **7jd** has 27 carbon atoms, among which 2 carbon atoms in the phenyl ring are symmetric. Thus, 50 [= (27–2) x 2] carbon signals are supposed to be observed in the $^{13}C\{^1H\}$ NMR spectrum of the diastereomeric mixture of **7jd**. However, 15 carbon signals were missing, due probably to overlapping). Due to the inseparable diastereomeric mixture, elemental analysis was performed to evaluate the purity of **7jd** isolated. Elemental Analysis Calcd for $C_{27}H_{24}N_2$: C, 86.13; H, 6.43; N, 7.44. Found: C, 86.26; H, 6.09; N, 7.29. HRMS (FD) Calcd for $C_{27}H_{24}N_2$: M^+, 376.19340. Found: *m/z* 376.19383.

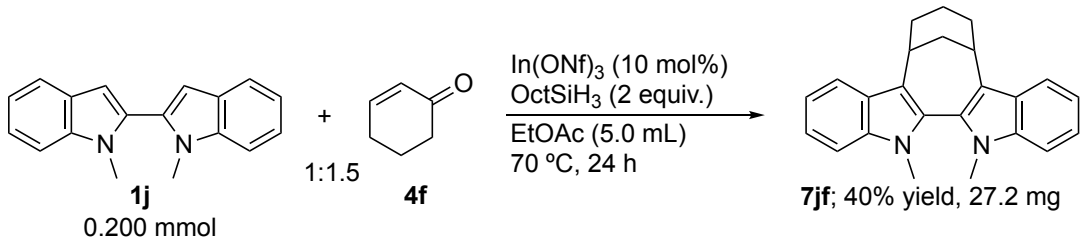


2,4-Dimethyl-4,5,6,11-tetrahydrothieno[2',3':7,6]cyclohepta[1,2-*b*]indole (7ae). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc = 40/1). A white solid, mp 135–136 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (d, J = 7.3 Hz, 3 H), 2.00–2.07 (m, 2 H), 2.47 (d, J = 0.9 Hz, 3 H), 3.00–3.16 (m, 2 H), 3.18–3.26 (m, 1 H), 6.61 (d, J = 0.9 Hz, 1 H), 7.09 (td, J = 7.3, 1.2 Hz, 1 H), 7.15 (td, J = 7.4, 1.2 Hz, 1 H), 7.29 (d, J = 7.8 Hz, 1 H), 7.50 (d, J = 7.8 Hz, 1 H), 7.78 (br s, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 15.3, 20.6, 21.6, 30.0, 34.9, 110.4, 112.9, 118.2, 119.6, 122.2, 126.3, 128.8, 129.4, 129.6, 135.5, 135.8, 144.8. HRMS (FD) Calcd for $C_{17}H_{17}NS$: M^+, 267.10762. Found: *m/z* 267.11054.

The position of the methyl group in **7ae** was determined by a ^1H–^1H NOESY NMR technique.

^1H–^1H NOESY NMR Spectrum of 7ae:


1H NMR
1H NMR
7.7779
7.4881
7.2830
7.2464
7.1547
7.0929
6.6118
6.6095
3.2257
3.2211
3.2177
3.2085
3.1100
3.0963
3.0814
3.0665
3.0608
3.0459
2.0424
2.0287
2.0218
2.0172
-0.0000
Y : parts per Million : 1H
X : parts per Million : 1H
abundance
1H NMR
1H NMR
7.5075
7.4881
7.3025
7.2853
7.2830
7.2464
7.1719
7.1696
7.1547
7.1513
7.1333
7.1318
7.1123
7.1089
7.0929
7.0906
7.0723
6.6118
6.6095
Hb
(Hb, Ha)
(Hb, Hc)
(Ha)
CH3
Hb
N
H
S
CH3 (Hc)
7ae
Ha
Hc
1.2520
1.2703
2.0092
2.0138
2.0172
2.0218
2.0287
2.0424
2.0516
2.0562
3.0459
3.0608
3.0665
3.0814
3.0963
3.1100
3.2085
3.2177
3.2257
Y : parts per Million : 1H
X : parts per Million : 1H
abundance



14,15-Dimethyl-6,7,8,9-tetrahydro-5*H*-5,9-methanocyclonona[2,1-*b*:3,4-*b'*]diindole (7jf). The title compound was isolated by recycling GPC after column chromatography on silica gel (hexane/acetone = 50/1). A pale yellow solid, mp 245–247 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (qt, *J* = 13.3, 3.5 Hz, 1 H), 1.23–1.32 (m, 1 H), 1.71–2.10 (m, 5 H), 2.33 (dt, *J* = 8.9, 4.4 Hz, 1 H), 3.75 (br s, 2 H), 3.82 (s, 6 H), 7.17 (ddd, *J* = 7.8, 6.9, 0.9 Hz, 2 H), 7.27 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 2 H), 7.40 (d, *J* = 7.8 Hz, 2 H), 7.58 (d, *J* = 7.8 Hz, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 18.7, 30.2, 31.0, 33.3, 34.7, 110.6, 118.4, 120.1, 122.3, 124.7, 129.3, 132.8, 141.6. HRMS (FD) Calcd for $C_{24}H_{24}N_2$: M^+, 340.19340. Found: *m/z* 340.19404.

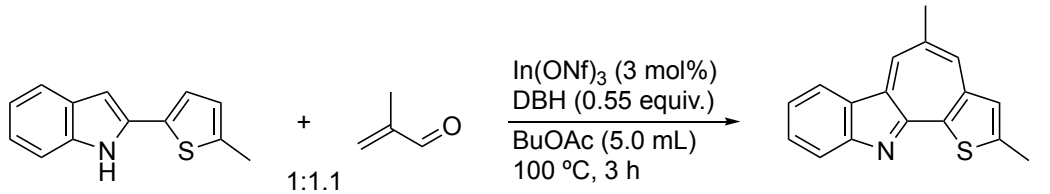
V. Indium-Catalyzed 7-Membered Carbon-Ring-Forming Annulation in the Presence of DBH: General Procedures for Methods A and B in Table 4

Method A: In(ONf)$_3$ [(6.07 mg, 6.00 μmol), (14.2 mg, 14.0 μmol) or (40.5 mg, 40.0 μmol)] was placed in a 20 or 50 mL Schlenk tube, which was heated at 150 ºC in vacuo for 2 h. The tube was cooled down to room temperature and filled with argon. BuOAc (5.0 or 10.0 mL) was added to the tube, and the mixture was stirred for 10 min at room temperature. To this were added 2-heteroarylindole **1** (0.200 mmol), α,β-unsaturated carbonyl compound **4** (0.220 mmol) and DBH [(31.5 mg, 0.110 mmol) or (34.3 mg, 0.120 mmol)], and the resulting mixture was stirred at 90 or 100 °C for 3, 5 or 24 h. A saturated $NaHCO_3$ aqueous solution (0.5 mL) was added, and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvent followed by purification gave product **8**.

Method B: In(ONf)$_3$ [(6.07 mg, 6.00 μmol), (20.2 mg, 20.0 μmol) or (40.4 mg, 40.0 μmol)] was placed in a 20 or 50 mL Schlenk tube, which was heated at 150 ºC in vacuo for 2 h. The tube was cooled down to room temperature and filled with argon. BuOAc (5.0–10.0 mL) was added to the tube, and the mixture was stirred for 10 min at room temperature. To this were

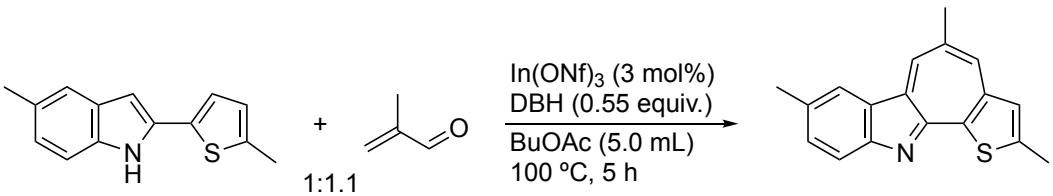
added 2-heteroarylindole **1** (0.200 mmol) and α,β-unsaturated carbonyl compound **4** (0.220 mmol), and the resulting mixture was stirred at room temperature or 100 °C for 0.25, 1, 3, 13, 24 or 48 h. To this was added DBH [(31.5 mg, 0.110 mmol) or (34.3 mg, 0.120 mmol)], and the resulting mixture was stirred further at 100 °C for 1, 3, 8, 12 or 24 h. A saturated $NaHCO_3$ aqueous solution (0.5 mL) was added, and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvent followed by purification gave product **8**.

Unless otherwise noted, products **8** synthesized in this section were fully characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and HRMS.



1a 0.200 mmol **4a** **8aa**; 66% yield, 34.8 mg

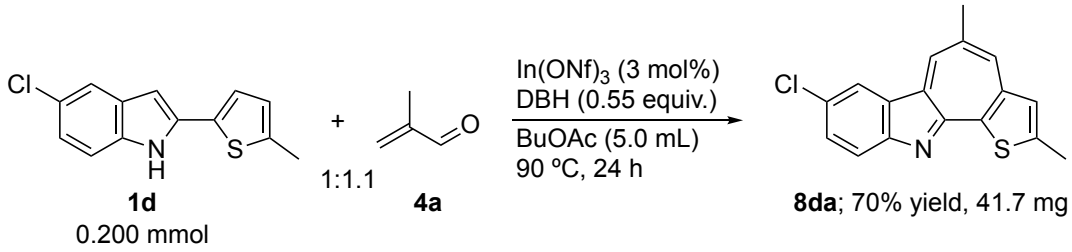
2,5-Dimethylthieno[2',3':7,6]cyclohepta[1,2-*b*]indole (8aa). The title compound was synthesized by method A, and isolated by column chromatography on silica gel ($CHCl_3$/EtOAc = 5/1). A brown solid, mp 192–194 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 2.68 (d, *J* = 1.1 Hz, 3 H), 2.74 (d, *J* = 0.9 Hz, 3 H), 7.16 (q, *J* = 1.2 Hz, 1 H), 7.39 (ddd, *J* = 7.9, 7.0, 0.8 Hz, 1 H), 7.68 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1 H), 7.88 (t, *J* = 1.4 Hz, 1 H), 8.00 (dt, *J* = 8.0, 0.8 Hz, 1 H), 8.18 (dt, *J* = 7.7, 0.9 Hz, 1 H), 8.46 (d, *J* = 1.6 Hz, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 16.1, 27.0, 119.4, 120.4, 121.7, 128.0, 128.9, 130.1, 132.2, 132.6, 134.0, 136.8, 140.8, 142.3, 144.3, 155.7, 156.1. HRMS (FD) Calcd for $C_{17}H_{13}NS$: M^+, 263.07632. Found: *m/z* 263.07918.



1b 0.200 mmol **4a** **8ba**; 63% yield, 35.0 mg

2,5,8-Trimethylthieno[2',3':7,6]cyclohepta[1,2-*b*]indole (8ba). The title compound was synthesized by method A, and isolated by column chromatography on silica gel ($CHCl_3$/EtOAc = 5/1). A brown solid, mp 226–229 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 2.58 (s,

3 H), 2.67 (d, J = 1.4 Hz, 3 H), 2.73 (s, 3 H), 7.14 (d, J = 1.4 Hz, 1 H), 7.50 (dd, J = 8.2, 1.4 Hz, 1 H), 7.84 (t, J = 1.4 Hz, 1 H), 7.88 (d, J = 8.2 Hz, 1 H), 7.97 (t, J = 0.9 Hz, 1 H), 8.41 (d, J = 1.4 Hz, 1 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 16.1, 21.7, 27.0, 119.0, 120.4, 128.0, 128.8, 131.3, 131.5, 132.0, 132.4, 133.7, 136.7, 140.5, 142.3, 143.9, 154.3, 155.4. HRMS (FD) Calcd for $C_{18}H_{15}NS$: M^+, 277.09197. Found: *m/z* 277.09281.

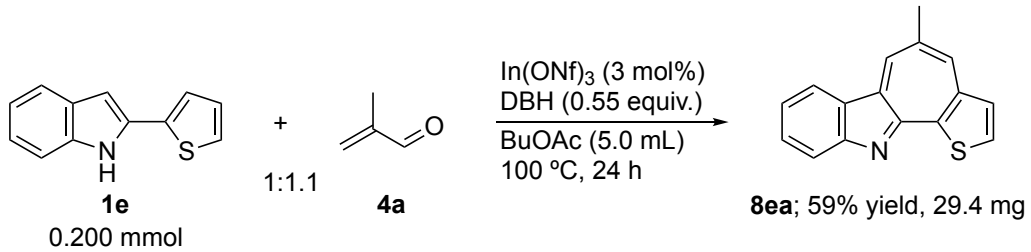


1d
0.200 mmol

4a

8da; 70% yield, 41.7 mg

8-Chloro-2,5-dimethylthieno[2',3':7,6]cyclohepta[1,2-*b*]indole (8da). The title compound was synthesized by method A using DBH washed with cold deionized water, and isolated by column chromatography on silica gel ($CHCl_3$/EtOAc/MeOH = 60/5/1). A brown solid, mp 226–228 ºC (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.70 (d, J = 0.9 Hz, 3 H), 2.73 (s, 3 H), 7.17 (d, J = 0.9 Hz, 1 H), 7.60 (dd, J = 8.5, 2.1 Hz, 1 H), 7.87–7.91 (m, 2 H), 8.07 (d, J = 1.8 Hz, 1 H), 8.37 (d, J = 1.8 Hz, 1 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 16.2, 27.0, 120.2, 120.3, 127.2, 129.0, 129.1, 130.1, 133.1, 133.6, 134.1, 135.9, 141.1, 142.8, 144.7, 154.3, 156.0. HRMS (FD) Calcd for $C_{17}H_{12}ClNS$: M^+, 297.03735. Found: *m/z* 297.03935.



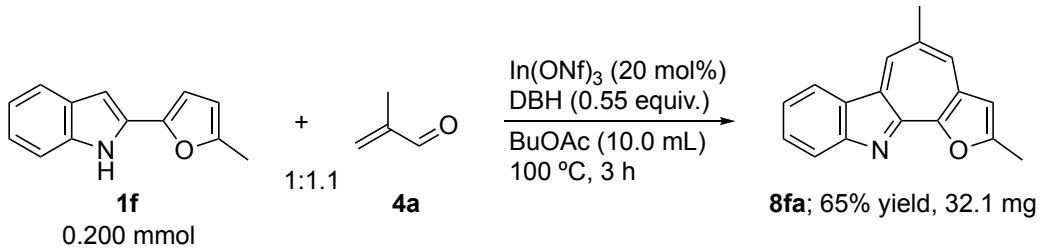
1e
0.200 mmol

4a

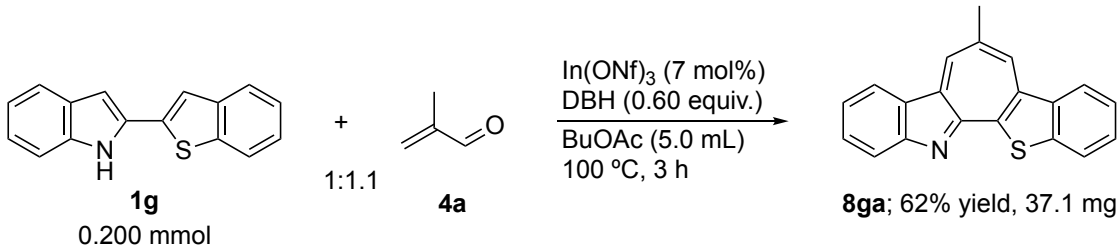
8ea; 59% yield, 29.4 mg

5-Methylthieno[2',3':7,6]cyclohepta[1,2-*b*]indole (8ea). The title compound was synthesized by method A, and isolated by column chromatography on silica gel ($CHCl_3$/EtOAc = 20/1). A brown solid, mp 191–196 ºC (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.80 (d, J = 1.0 Hz, 3 H), 7.43 (ddd, J = 7.9, 7.0, 0.9 Hz, 1 H), 7.54 (d, J = 5.3 Hz, 1 H), 7.70 (ddd, J = 8.2, 7.1, 1.0 Hz, 1 H), 7.73 (d, J = 5.3 Hz, 1 H), 8.03 (dt, J = 8.0, 0.9 Hz, 1 H), 8.05 (t, J = 1.4 Hz, 1 H), 8.22 (dt, J = 7.7, 0.9 Hz, 1 H), 8.54 (d, J = 1.6 Hz, 1 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ

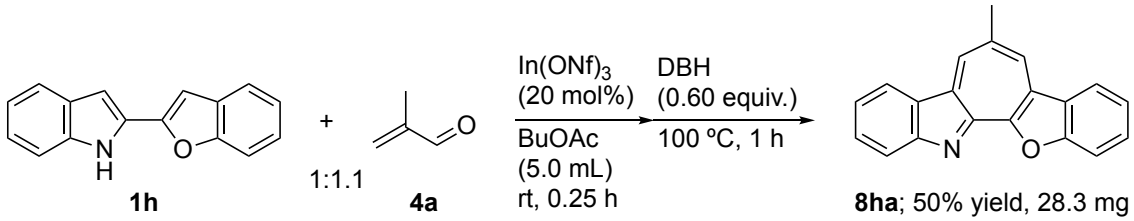
27.0, 119.6, 120.5, 122.1, 128.0, 129.4, 130.2, 131.2, 132.6, 133.2, 133.9, 136.8, 140.0, 142.9, 155.9, 156.0. HRMS (FD) Calcd for $C_{16}H_{11}NS$: M^+, 249.06067. Found: *m/z* 249.06231.



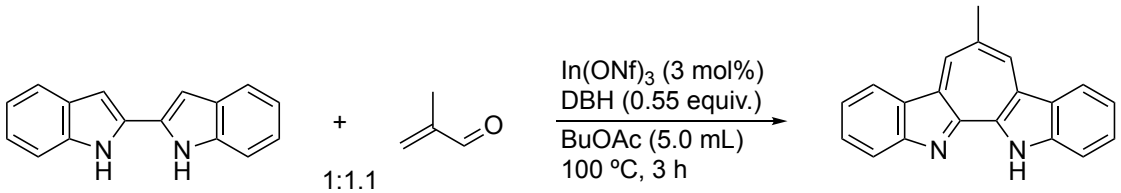
2,5-Dimethylfuro[2',3':7,6]cyclohepta[1,2-*b*]indole (8fa). The title compound was synthesized by method A using DBH washed with cold deionized water, and isolated by column chromatography on silica gel ($CHCl_3$/EtOAc/MeOH = 20/5/1). A red solid, mp 155–158 ºC (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (s, 3 H), 2.82 (s, 3 H), 6.67 (s, 1 H), 7.43 (t, *J* = 7.4 Hz, 1 H), 7.72 (t, *J* = 7.6 Hz, 1 H), 7.87 (s, 1 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 8.27 (d, *J* = 7.7 Hz, 1 H), 8.62 (s, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 14.2, 27.0, 108.6, 120.0, 120.3, 121.6, 127.1, 129.3, 130.3, 131.2, 132.1, 134.3, 140.7, 148.7, 150.8, 156.8, 157.9. HRMS (FD) Calcd for $C_{17}H_{13}NO$: M^+, 247.09917. Found: *m/z* 247.10106.



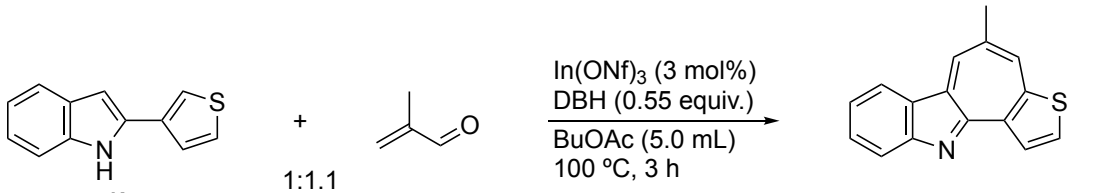
6-Methylbenzo[4',5']thieno[2',3':7,6]cyclohepta[1,2-*b*]indole (8ga). The title compound was synthesized by method A, and isolated by column chromatography on silica gel ($CHCl_3$/MeOH = 40/1). A red solid, mp 266–269 ºC (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.84 (d, *J* = 1.1 Hz, 3 H), 7.43 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 7.52 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 7.57 (td, *J* = 7.4, 1.1 Hz, 1 H), 7.72 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 7.98 (d, *J* = 7.4 Hz, 1 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 8.18–8.22 (m, 2 H), 8.37 (s, 1 H), 8.50 (d, *J* = 1.7 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 27.5, 119.9, 120.6, 122.1, 122.3, 122.9, 125.1, 127.8, 128.2, 128.6, 130.3, 132.9, 134.5, 134.7, 136.6, 138.4, 139.5, 145.1, 155.5, 156.0. HRMS (FD) Calcd for $C_{20}H_{13}NS$: M^+, 299.07632. Found: *m/z* 299.07847.



6-Methylbenzo[4',5']furo[2',3':7,6]cyclohepta[1,2-*b*]indole (8ha). The title compound was synthesized by method B, and isolated by column chromatography on silica gel twice (first: $CHCl_3$/MeOH = 40/1; second: $CHCl_3$/EtOAc = 3/1). A red solid, mp 232–234 ºC (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.89 (d, *J* = 0.8 Hz, 3 H), 7.48 (ddd, *J* = 7.9, 7.1, 0.8 Hz, 2 H), 7.61 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1 H), 7.78 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1 H), 7.84 (dt, *J* = 8.3, 0.7 Hz, 1 H), 8.07 (ddd, *J* = 7.8, 1.2, 0.7 Hz, 1 H), 8.17 (dt, *J* = 8.1, 0.8 Hz, 1 H), 8.26–8.31 (m, 2 H), 8.66 (d, *J* = 1.6 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 27.2, 112.6, 120.2, 120.5, 120.6, 122.4, 124.0, 124.5, 126.2, 126.9, 127.5, 128.8, 130.6, 132.9, 134.8, 140.8, 148.9, 153.1, 155.7, 156.7. HRMS (FD) Calcd for $C_{20}H_{13}NO$: M^+, 283.09917. Found: *m/z* 283.10114.



6-Methyl-12*H*-cyclohepta[2,1-*b*:3,4-*b*']diindole (8ia). The title compound was synthesized by method A, and isolated by column chromatography on silica gel ($CHCl_3$/MeOH = 15/1). A red solid, mp 266–268 ºC (decomp.). ^{1}H NMR (500 MHz, DMSO-d_6, 50 ºC) δ 2.92 (s, 3 H), 7.44 (t, *J* = 7.2 Hz, 2 H), 7.66 (t, *J* = 7.2 Hz, 2 H), 7.87 (d, *J* = 8.0 Hz, 2 H), 8.51 (d, *J* = 8.0 Hz, 2 H), 9.00 (s, 2 H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6, 50 ºC) δ 25.9, 115.3, 120.6, 121.1, 126.8, 128.0, 129.0, 131.2, 132.6, 143.1, 146.4. Note: due to the low solubility of **8ia** to DMSO-d_6, NMR spectra were measured at 50 °C. HRMS (FD) Calcd for $C_{20}H_{14}N_2$: M^+, 282.11515. Found: *m/z* 282.11527.

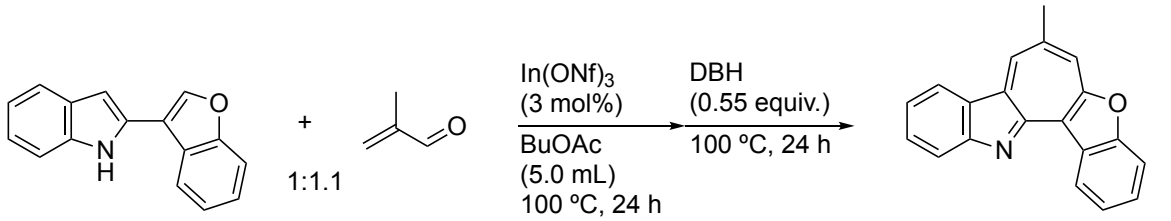


1l
0.200 mmol

4a

8la; 51% yield, 38.1 mg

5-Methylthieno[2',3':6,7]cyclohepta[1,2-*b*]indole (8la). The title compound was synthesized by method A, and isolated by column chromatography on silica gel ($CHCl_3$/EtOAc = 20/1). A red solid, mp 226–234 ºC (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.78 (d, J = 1.0 Hz, 3 H), 7.45 (ddd, J = 7.9, 7.1, 0.8 Hz, 1 H), 7.72 (ddd, J = 8.2, 7.1, 1.1 Hz, 1 H), 7.88 (d, J = 5.4 Hz, 1 H), 8.03 (dt, J = 8.0, 0.8 Hz, 1 H), 8.06 (s, 1 H), 8.23 (dt, J = 7.8, 0.9 Hz, 1 H), 8.52 (d, J = 1.6 Hz, 1 H), 8.62 (dd, J = 5.5, 0.6 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 26.7, 119.6, 120.2, 122.2, 127.9, 128.9, 130.1, 130.6, 131.4, 132.1, 133.2, 138.9, 139.5, 143.3, 155.5, 156.8. HRMS (FD) Calcd for $C_{16}H_{11}NS$: M^+, 249.06067. Found: *m/z* 249.06000.

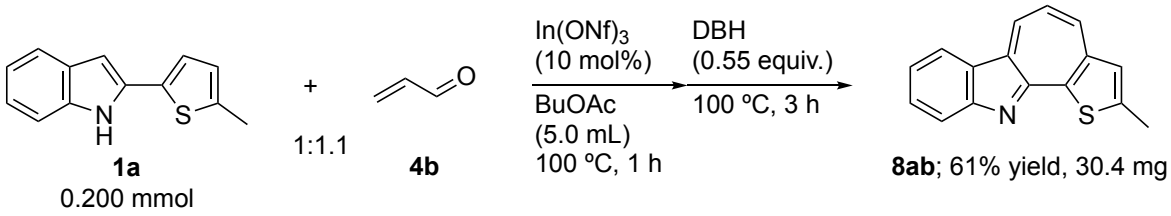


1m
0.200 mmol

4a

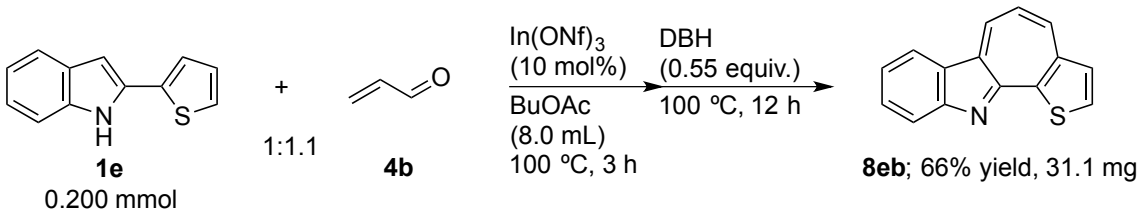
8ma; 43% yield, 24.4 mg

7-Methylbenzo[4',5']furo[2',3':6,7]cyclohepta[1,2-*b*]indole (8ma). The title compound was synthesized by method B, and isolated by column chromatography on silica gel ($CHCl_3$/EtOAc = 5/1). A red solid, mp 215–217 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.88 (d, J = 0.9 Hz, 3 H), 7.46 (ddd, J = 7.9, 7.1, 0.8 Hz, 1 H), 7.61 (ddd, J = 8.0, 6.6, 1.4 Hz, 1 H), 7.66 (dt, J = 7.5, 1.4 Hz, 1 H), 7.69 (ddd, J = 8.2, 1.4, 0.8 Hz, 1 H), 7.77 (ddd, J = 8.1, 7.1, 1.0 Hz, 1 H), 8.11 (dd, J = 1.4, 1.0 Hz, 1 H), 8.13 (dt, J = 8.1, 0.8 Hz, 1 H), 8.29 (dt, J = 7.7, 0.9 Hz, 1 H), 8.60 (d, J = 1.7 Hz, 1 H), 9.32 (ddd, J = 7.7, 1.5, 0.8 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 27.1, 110.9, 119.7, 120.6, 121.8, 123.0, 123.9, 124.2, 126.0, 126.8, 127.1, 129.0, 130.5, 130.7, 136.1, 141.9, 154.4, 155.7, 155.9, 157.5. HRMS (FD) Calcd for $C_{20}H_{13}NO$: M^+, 283.09917. Found: *m/z* 283.09941.



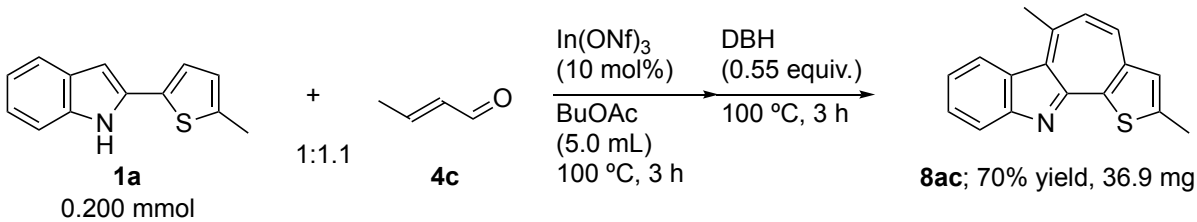
1a 0.200 mmol + **4b** → **8ab**; 61% yield, 30.4 mg

2-Methylthieno[2',3':7,6]cyclohepta[1,2-*b*]indole (8ab). The title compound was synthesized by method B using DBH recrystallized from deionized water, and isolated by column chromatography on silica gel ($CHCl_3$/EtOAc = 5/1). A red solid, mp 66–68 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.70 (d, *J* = 1.0 Hz, 3 H), 7.25 (d, *J* = 1.0 Hz, 1 H), 7.41–7.46 (m, 2 H), 7.71 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1 H), 8.00 (d, *J* = 10.9 Hz, 1 H), 8.04 (d, *J* = 8.0 Hz, 1 H), 8.22 (d, *J* = 7.7 Hz, 1 H), 8.56 (d, *J* = 8.9 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 16.1, 119.5, 120.6, 122.0, 124.2, 128.0, 128.8, 129.5, 130.1, 132.9, 137.9, 141.1, 144.5, 156.0, 155.95, 156.02. HRMS (FD) Calcd for $C_{16}H_{11}NS$: M^+, 249.06067. Found: *m/z* 249.06252.



1e 0.200 mmol + **4b** → **8eb**; 66% yield, 31.1 mg

Thieno[2',3':7,6]cyclohepta[1,2-*b*]indole (8eb). The title compound was synthesized by method B using DBH recrystallized from deionized water, and isolated by column chromatography on silica gel ($CHCl_3$). A red solid, mp 68–69 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.51 (m, 2 H), 7.59 (d, *J* = 5.5 Hz, 1 H), 7.71 (dd, *J* = 8.2, 0.9 Hz, 1 H), 7.74 (d, *J* = 5.5 Hz, 1 H), 8.05 (d, *J* = 7.8 Hz, 1 H), 8.12 (d, *J* = 11.0 Hz, 1 H), 8.23 (d, *J* = 7.8 Hz, 1 H), 8.59 (d, *J* = 9.2 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 119.6, 120.6, 122.4, 124.1, 128.0, 129.6, 130.0, 130.2, 131.1, 133.4, 137.8, 140.2, 145.0, 155.7, 156.2. HRMS (FD) Calcd for $C_{15}H_9NS$: M^+, 235.04502. Found: *m/z* 235.04423.

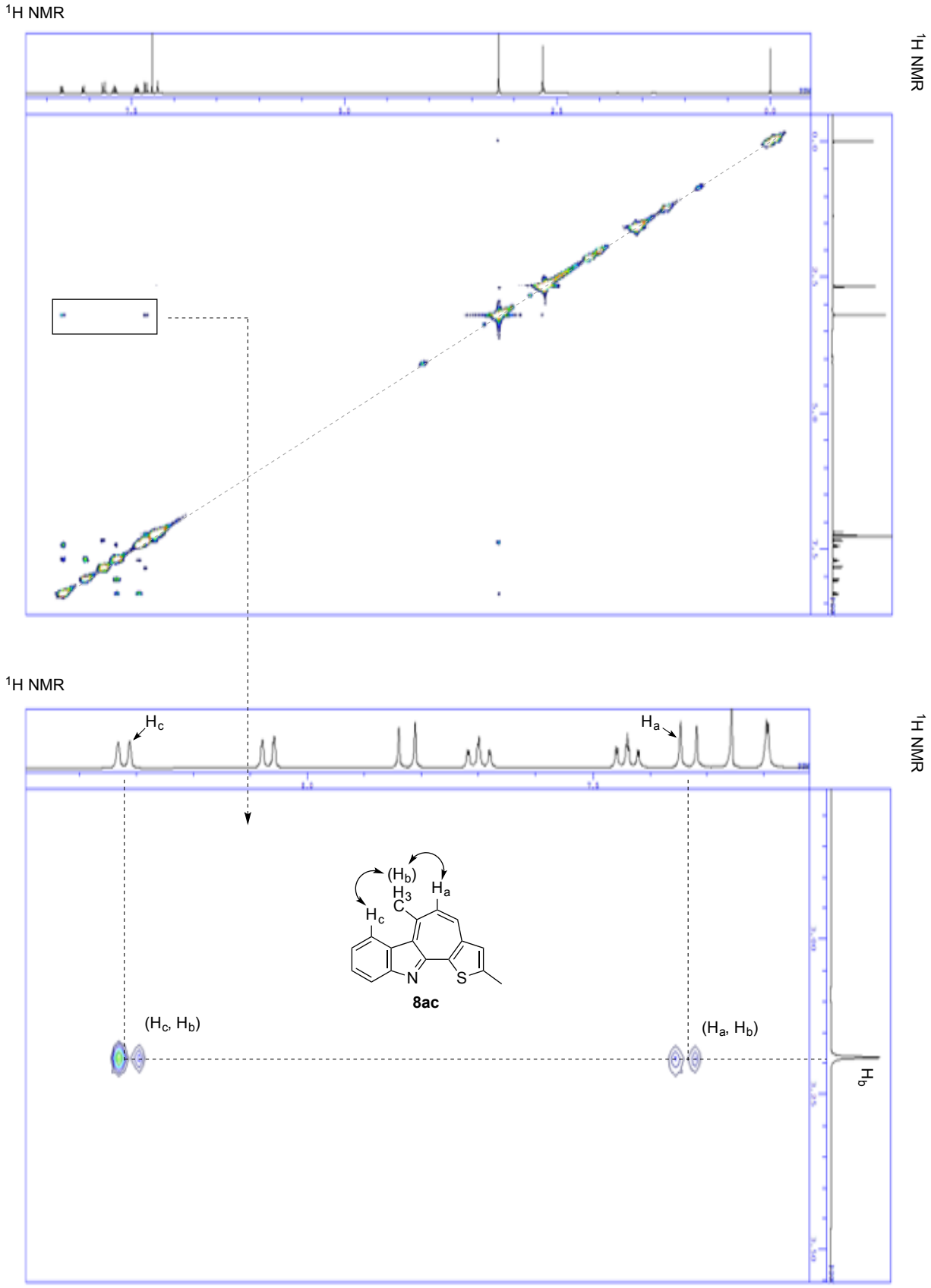


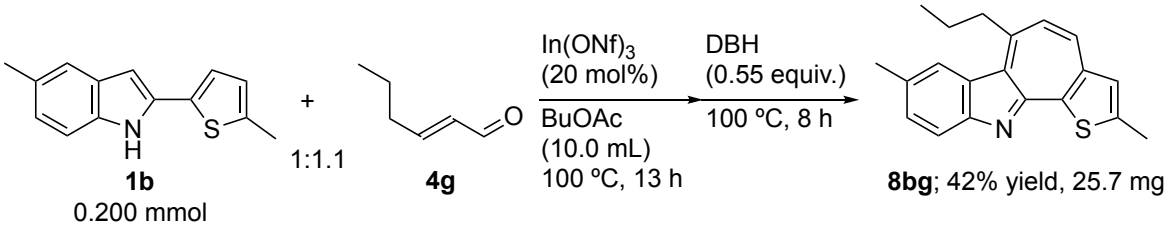
1a 0.200 mmol + **4c** → **8ac**; 70% yield, 36.9 mg

2,6-Dimethylthieno[2',3':7,6]cyclohepta[1,2-*b*]indole (8ac). The title compound was synthesized by method B using DBH recrystallized from deionized water, and isolated by column chromatography on silica gel ($CHCl_3$). A brown solid, mp 149–151 ºC (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (d, *J* = 1.1 Hz, 3 H), 3.19 (s, 3 H), 7.20 (q, *J* = 1.2 Hz, 1 H), 7.33 (d, *J* = 11.4 Hz, 1 H), 7.44 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1 H), 7.70 (ddd, *J* = 8.3, 7.2, 1.1 Hz, 1 H), 7.83 (d, *J* = 11.4 Hz, 1 H), 8.07 (dt, *J* = 8.1, 0.9 Hz, 1 H), 8.32 (d, *J* = 8.1 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 16.1, 27.5, 119.7, 121.9, 125.4, 128.0, 128.3, 129.1, 130.7, 131.0, 135.1, 139.6, 144.4, 145.2, 146.2, 155.5, 156.0. HRMS (FD) Calcd for $C_{17}H_{13}NS$: M^+, 263.07632. Found: *m/z* 263.07504.

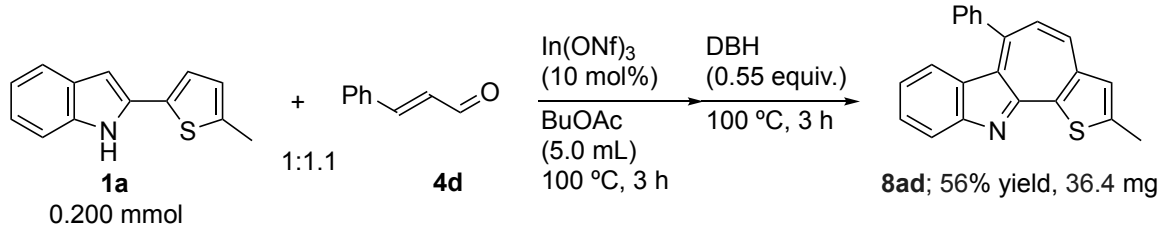
Some NMR techniques involving ^{1}H–^{1}H COSY, ^{1}H–^{1}H NOESY, ^{1}H–^{13}C HMQC, and HMBC experiments were utilized to determine the position of the methyl group in **8ac**. The result of the ^{1}H–^{1}H NOESY NMR experiment is provided here as the representative.

^{1}H–^{1}H NOESY NMR Spectrum of 8ac:

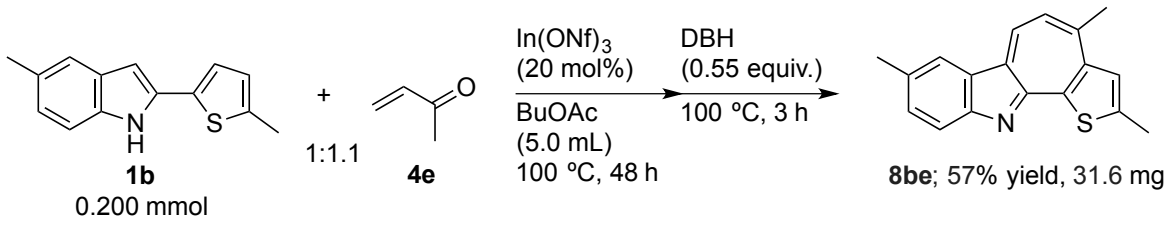

^{1}H NMR
^{1}H NMR
^{1}H NMR
^{1}H NMR
H_c
H_a
(H_b)
H_3C
H_a
H_c
N
S
8ac
(H_c, H_b)
(H_a, H_b)
H_b



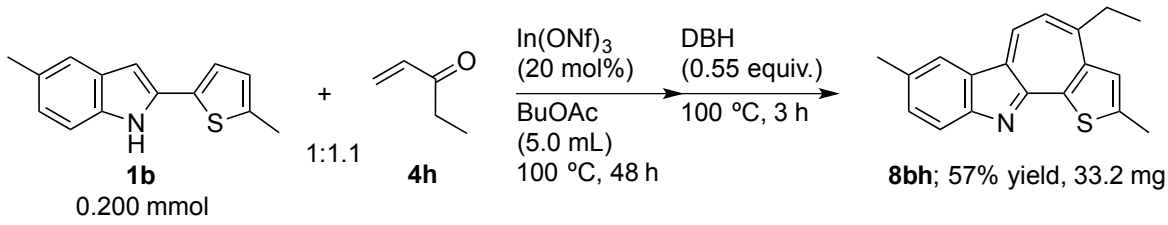
2,8-Dimethyl-6-propylthieno[2',3':6,7]cyclohepta[1,2-*b*]indole (8bg). The title compound was synthesized by method B, and isolated by column chromatography on silica gel ($CHCl_3$/EtOAc = 10/1). A red solid, mp 128–130 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (t, *J* = 7.4 Hz, 3 H), 1.95 (sext, *J* = 7.6 Hz, 2 H), 2.61 (s, 3 H), 2.65 (d, *J* = 0.9 Hz, 3 H), 3.39–3.43 (m, 2 H), 7.15 (d, *J* = 1.0 Hz, 1 H), 7.26 (d, *J* = 11.5 Hz, 1 H), 7.51 (dd, *J* = 8.2, 1.0 Hz, 1 H), 7.78 (d, *J* = 11.4 Hz, 1 H), 7.95 (d, *J* = 8.1 Hz, 1 H), 7.98 (s, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.4, 16.0, 22.3, 23.1, 41.5, 119.4, 124.9, 127.2, 127.8, 130.1, 130.5, 131.0, 131.4, 134.6, 139.1, 144.0, 145.2, 150.9, 154.1, 155.5. HRMS (FD) Calcd for $C_{20}H_{19}NS$: M^+, 305.12327. Found: *m/z* 305.12377.



2-Methyl-6-phenylthieno[2',3':6,7]cyclohepta[1,2-*b*]indole (8ad). The title compound was synthesized by method B, and isolated by column chromatography on silica gel ($CHCl_3$/EtOAc = 10/1). A red solid, mp 197–199 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.73 (d, *J* = 1.1 Hz, 3 H), 6.58 (d, *J* = 8.0 Hz, 1 H), 7.00 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1 H), 7.29 (d, *J* = 1.0 Hz, 1 H), 7.35 (d, *J* = 11.3 Hz, 1 H), 7.47–7.49 (m, 2 H), 7.53–7.61 (m, 4 H), 7.92 (d, *J* = 11.3 Hz, 1 H), 7.98 (d, *J* = 8.1 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 16.2, 119.4, 121.6, 124.6, 127.78, 127.84, 128.2, 128.5, 129.2, 129.5, 130.7, 135.0, 139.8, 143.2, 144.7, 145.3, 148.2, 156.2, 156.4 (One carbon signal is missing due to overlapping). HRMS (FD) Calcd for $C_{22}H_{15}NS$: M^+, 325.09197. Found: *m/z* 325.09297.



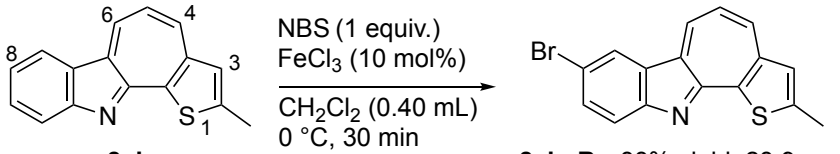
2,4,8-Trimethylthieno[2',3':7,6]cyclohepta[1,2-*b*]indole (8be). The title compound was synthesized by method B, and isolated by column chromatography on silica gel ($CHCl_3$/EtOAc = 5/1). A brown solid, mp 217–219 ºC (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.59 (s, 3 H), 2.72 (d, J = 1.1 Hz, 3 H), 2.90 (d, J = 0.7 Hz, 3 H), 7.39–7.42 (m, 2 H), 7.50 (dd, J = 8.2, 1.1 Hz, 1 H), 7.91 (d, J = 8.2 Hz, 1 H), 7.99 (t, J = 0.8 Hz, 1 H), 8.41 (d, J = 9.3 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 16.3, 21.7, 27.7, 119.0, 120.2, 125.5, 126.3, 128.1, 128.9, 131.1, 131.3, 135.6, 140.5, 143.0, 143.8, 144.5, 153.8, 155.8. HRMS (FD) Calcd for $C_{18}H_{15}NS$: M^+, 277.09197. Found: *m/z* 277.09086.



4-Ethyl-2,8-dimethylthieno[2',3':6,7]cyclohepta[1,2-*b*]indole (8bh). The title compound was synthesized by method B, and isolated by column chromatography on silica gel ($CHCl_3$/EtOAc = 20/1). A red solid, mp 92–94 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (t, J = 7.5 Hz, 3 H), 2.59 (s, 3 H), 2.72 (d, J = 1.0 Hz, 3 H), 3.19 (q, J = 7.5 Hz, 2 H), 7.41 (d, J = 9.5 Hz, 1 H), 7.44 (d, J = 1.0 Hz, 1 H), 7.50 (dd, J = 8.4, 1.3 Hz, 1 H), 7.91 (d, J = 8.1 Hz, 1 H), 7.99–8.01 (m, 1 H), 8.45 (d, J = 9.4 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 15.9, 16.4, 21.7, 33.9, 118.9, 120.2, 124.4, 125.9, 128.1, 129.2, 131.1, 131.2, 135.4, 139.8, 143.7, 145.1, 149.1, 153.8, 155.7. HRMS (FD) Calcd for $C_{19}H_{17}NS$: M^+, 291.10762. Found: *m/z* 291.10851.

VI. Bromination of 8

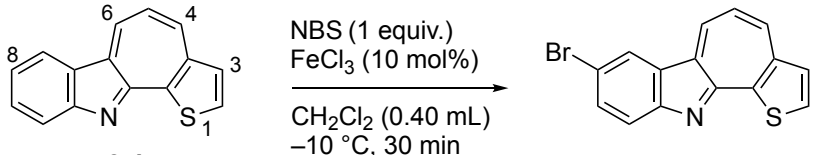
Experimental procedures for the synthesis of **8ab–Br** and **8eb–Br** in Scheme 4, and their spectroscopic and analytical data are provided in this section.



8ab
0.100 mmol

8ab–Br; 88% yield, 28.9 mg

8-Bromo-2-methylthieno[2',3':7,6]cyclohepta[1,2-*b*]indole (8ab–Br). The title compound was synthesized according to the following procedure: $FeCl_3$ (1.62 mg, 10.0 μmol) was placed in a 20 mL Schlenk tube, which was heated at 80 ºC in vacuo for 15 min. The tube was cooled down to room temperature and filled with argon. CH_2Cl_2 (0.40 mL) and *N*-bromosuccinimide (NBS) (17.8 mg, 0.100 mmol) were added to the tube, and the mixture was stirred at 0 ºC for 10 min. To this was added **8ab** (24.9 mg, 0.100 mmol), and the resulting mixture was stirred further at 0 °C for 30 min. A saturated $NaHCO_3$ aqueous solution (1 mL) was added to the mixture, and the aqueous phase was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed with brine (5 mL), and then dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvent followed by column chromatography on silica gel ($CHCl_3$) gave **8ab–Br** in 88% yield (28.9 mg) as a dark red solid [mp 159–160 ºC (decomp.)]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.73 (d, *J* = 1.1 Hz, 3 H), 7.31 (d, *J* = 1.1 Hz, 1 H), 7.51 (dd, *J* = 10.9, 9.2 Hz, 1 H), 7.78 (dd, *J* = 8.6, 1.7 Hz, 1 H), 7.90 (d, *J* = 8.6 Hz, 1 H), 8.09 (d, *J* = 10.9 Hz, 1 H), 8.33 (d, *J* = 1.7 Hz, 1 H), 8.56 (d, *J* = 8.0 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 16.2, 115.1, 120.9, 123.4, 124.3, 128.9, 129.7, 130.5, 132.9, 133.9, 136.8, 141.4, 144.9, 145.1, 154.4, 156.1. HRMS (FD) Calcd for $C_{16}H_{10}BrNS$: M^+, 326.97118. Found: *m/z* 326.97319.



8eb
0.100 mmol

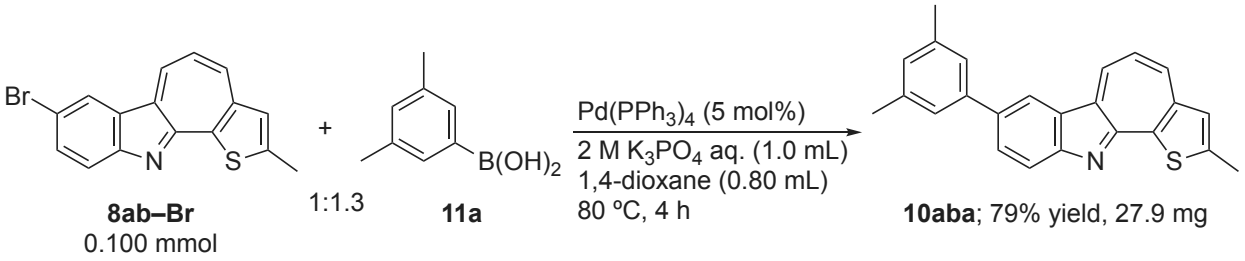
8eb–Br; 94% yield, 29.5 mg

8-Bromothieno[2',3':7,6]cyclohepta[1,2-*b*]indole (8eb–Br). The title compound was synthesized according to the following procedure: $FeCl_3$ (1.62 mg, 10.0 μmol) was placed in a 20 mL Schlenk tube, which was heated at 80 ºC in vacuo for 15 min. The tube was cooled down to room temperature and filled with argon. CH_2Cl_2 (0.40 mL) and NBS (17.8 mg, 0.100 mmol) were added to the tube, and the mixture was stirred at –10 ºC for 10 min. To this was added **8eb** (23.5 mg, 0.100 mmol), and the resulting mixture was stirred further at –10 °C for 30 min. A

saturated $NaHCO_3$ aqueous solution (1 mL) was added to the mixture, and the aqueous phase was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed with brine (5 mL), and then dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvent followed by column chromatography on silica gel ($CHCl_3$) gave **8eb–Br** in 94% yield (29.5 mg) as a dark red solid [mp 209–210 ºC (decomp.)]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.54 (m, 1 H), 7.63 (d, *J* = 5.2 Hz, 1 H), 7.77–7.81 (m, 2 H), 7.91 (d, *J* = 8.6 Hz, 1 H), 8.18 (d, *J* = 10.9 Hz, 1 H), 8.31 (d, *J* = 2.6 Hz, 1 H), 8.56 (d, *J* = 9.2 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 115.5, 121.0, 123.5, 124.2, 129.7, 130.0, 131.0, 131.3, 133.0, 134.4, 136.7, 140.5, 145.4, 154.2, 156.4. HRMS (FD) Calcd for $C_{15}H_8BrNS$: M^+, 312.95553. Found: *m/z* 312.95689.

VII. Suzuki–Miyaura Cross-Coupling Reaction of 8ab–Br

Experimental procedures for the synthesis of **10aba** and **10abb** in Scheme 5, and their spectroscopic and analytical data are provided in this section.



8ab–Br
0.100 mmol

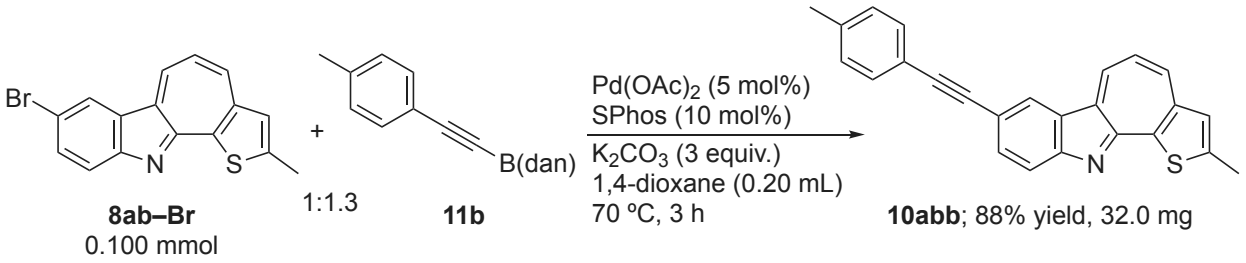
1:1.3

11a

10aba; 79% yield, 27.9 mg

2-Methyl-8-(3,5-dimethylphenyl)thieno[2',3':7,6]cyclohepta[1,2-*b*]indole (10aba). The title compound was synthesized according to the following procedure: under an argon atmosphere, a 20 mL Schlenk tube was charged with **8ab–Br** (32.8 mg, 0.100 mmol), **11a** (19.5 mg, 0.130 mmol), a 2 M K_3PO_4 aqueous solution (1.0 mL, 2.00 mmol of K_3PO_4), and 1,4-dioxane (0.80 mL). After degassing by three freeze-pump-thaw cycles, to this was added $Pd(PPh_3)_4$ (5.78 mg, 5.00 μmol), and the resulting mixture was stirred at 80 ºC for 4 h. H_2O (0.5 mL) was added to the mixture, and the aqueous phase was extracted with Et_2O (5 mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvent followed by column chromatography on silica gel ($CHCl_3$/acetone = 100/1) gave **10aba** in 79% yield (27.9 mg) as a dark red solid (mp 63–65 ºC). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (s, 6 H), 2.72 (d, *J* = 1.1 Hz, 3 H), 7.03 (s, 1 H), 7.30 (d, *J* = 1.1 Hz, 1 H), 7.37 (s, 2 H), 7.54 (t, *J* = 9.7 Hz, 1 H), 7.96 (dd, *J* = 8.0, 1.7 Hz, 1 H), 8.09 (d, *J* = 8.6 Hz, 2 H), 8.41 (d, *J* = 1.1 Hz, 1 H), 8.71 (d, *J* = 8.6 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 16.2, 21.5,

119.0, 119.6, 124.2, 125.3, 128.5, 128.8, 129.7, 129.8, 131.8, 133.1, 135.5, 136.3, 138.0, 138.3, 141.1, 141.7, 144.6, 155.3, 156.3. HRMS (FD) Calcd for $C_{24}H_{19}NS$: M^+, 353.12327. Found: *m/z* 353.12123.

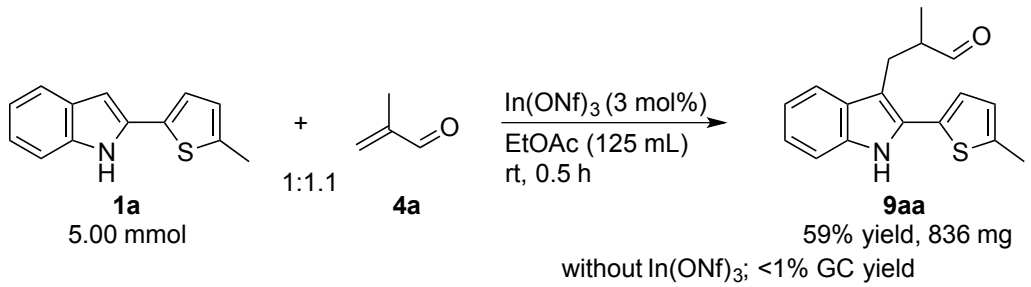


2-Methyl-8-[2-(4-methylphenyl)ethynyl]thieno[2',3':7,6]cyclohepta[1,2-*b*]indole (10abb). The title compound was synthesized according to the following procedure: under an argon atmosphere, a flame-dried 20 mL Schlenk tube was charged with **8ab–Br** (32.8 mg, 0.100 mmol), **11b** (36.7 mg, 0.130 mmol), K_2CO_3 (41.5 mg, 0.300 mmol), and 1,4-dioxane (0.20 mL). After degassing by three freeze-pump-thaw cycles, to this was added $Pd(OAc)_2$ (1.12 mg, 5.00 μmol) and SPhos (4.11 mg, 10.0 μmol), and the resulting mixture was stirred at 70 ºC for 3 h. H_2O (0.5 mL) was added to the mixture, and the aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvent followed by column chromatography on silica gel ($CHCl_3$/EtOAc = 50/1) gave **10abb** in 88% yield (32.0 mg) as a dark red solid (mp 221–223 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 3 H), 2.67 (d, *J* = 1.1 Hz, 3 H), 7.16–7.20 (m, 3 H), 7.36 (dd, *J* = 10.9, 8.6 Hz, 1 H), 7.48 (d, *J* = 8.0 Hz, 2 H), 7.82 (dd, *J* = 8.0, 1.7 Hz, 1 H), 7.91–7.96 (m, 2 H), 8.28 (s, 1 H), 8.44 (d, *J* = 8.6 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 16.2, 21.5, 89.0, 89.9, 116.5, 119.4, 120.5, 123.9, 124.4, 128.0, 128.9, 129.1, 130.1, 131.4, 133.4, 133.5, 137.0, 138.1, 141.4, 144.7, 145.0, 155.4, 156.6. HRMS (FD) Calcd for $C_{25}H_{17}NS$: M^+, 363.10762. Found: *m/z* 363.10824.

VIII. Control Experiments for Mechanistic Studies

Experimental procedures for Scheme 6 are described in this section.

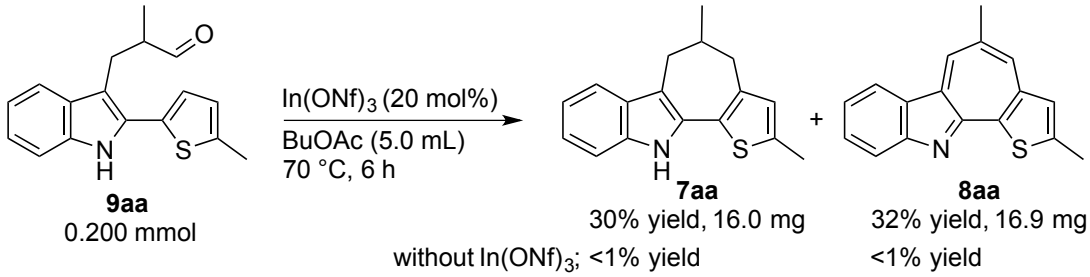
Control Experiments for Scheme 6-(a)



$In(ONf)_3$ (152 mg, 0.150 mmol) was placed in a 300 mL Schlenk tube, which was heated at 150 ºC in vacuo for 2 h. The tube was cooled down to room temperature, and filled with argon. EtOAc (125 mL) was added to the tube, and the mixture was stirred for 10 min at room temperature. To this were added **1a** (1.07 g, 5.00 mmol) and **4a** (386 mg, 5.50 mmol), and the resulting mixture was stirred at room temperature for 0.5 h. The mixture diluted with EtOAc (200 mL) was washed with a saturated $NaHCO_3$ aqueous solution (25 mL) and brine (25 mL), and then dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 6/1) gave 2-methyl-3-[2-(5-methylthien-2-yl)-1*H*-indol-3-yl]propanal (**9aa**) in 59% yield (836 mg) as a beige solid (mp 80–81 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (d, J = 6.9 Hz, 3 H), 2.53 (d, J = 1.4 Hz, 3 H), 2.79–2.89 (m, 1 H), 2.99 (dd, J = 14.4, 8.5 Hz, 1 H), 3.36 (dd, J = 14.7, 6.4 Hz, 1 H), 6.76–6.78 (m, 1 H), 7.01 (d, J = 3.7 Hz, 1 H), 7.12 (ddd, J = 8.0, 7.0, 1.0 Hz, 1 H), 7.19 (ddd, J = 8.2, 7.1, 1.1 Hz, 1 H), 7.33 (dt, J = 7.8, 0.9 Hz, 1 H), 7.53 (d, J = 6.9 Hz, 1 H), 8.07 (s, 1 H), 9.75 (d, J = 1.4 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6) δ 13.9, 15.1, 26.5, 48.1, 110.4, 111.8, 119.5, 120.2, 123.0, 125.7, 126.8, 130.1, 130.4, 133.4, 137.2, 140.5, 204.9 (The chemical shifts were referenced to the solvent signal at 29.84 ppm).[6] HRMS (FD) Calcd for $C_{17}H_{17}NOS$: M^+, 283.10253. Found: *m/z* 283.10012.

The reaction in the absence of $In(ONf)_3$ was conducted by simply mixing **1a**, **4a**, and EtOAc in a flame-dried 300 mL Schlenk tube and stirring at room temperature for 0.5 h. The yield of **9aa** was determined by GC using *o*-dichlorobenzene as an internal standard.

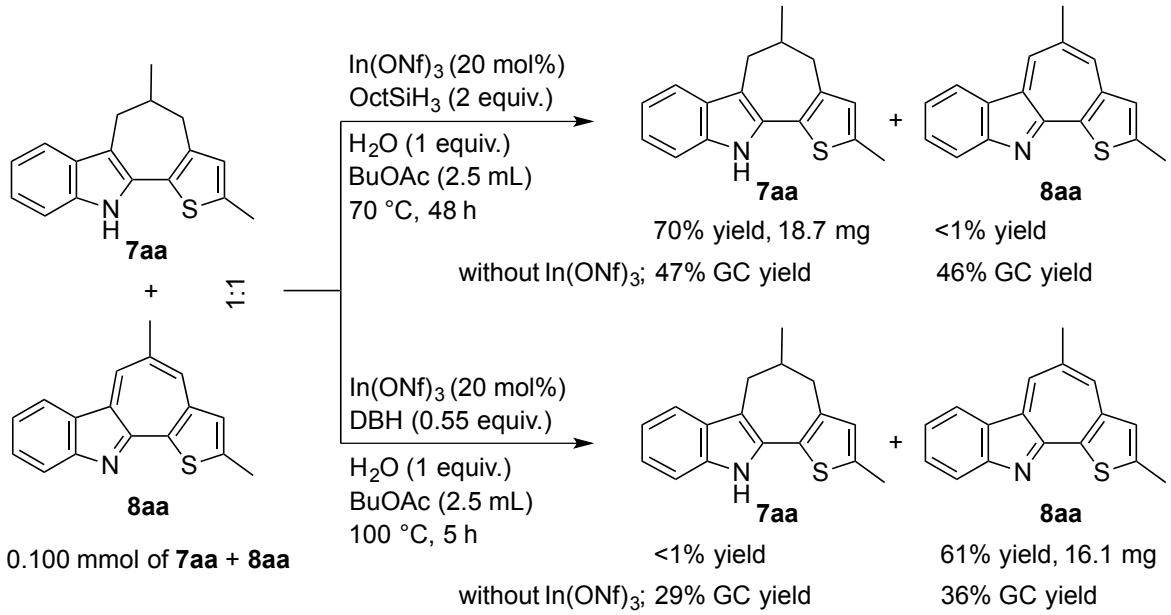
Control Experiments for Scheme 6-(b)



$In(ONf)_3$ (40.5 mg, 40.0 μmol) was placed in a 20 mL Schlenk tube, which was heated at 150 ºC in vacuo for 2 h. The tube was cooled down to room temperature, and filled with argon. BuOAc (5.0 mL) was added to the tube, and the mixture was stirred at room temperature for 10 min. To this was added **9aa** (56.7 mg, 0.200 mmol), and the resulting mixture was stirred at 70 °C for 6 h. The mixture diluted with EtOAc (10 mL) was washed with a saturated $NaHCO_3$ aqueous solution (1 mL) and brine (1 mL), and then dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the crude product was purified by column chromatography on silica gel: **7aa** was isolated in 30% yield (16.0 mg) by elution with hexane/EtOAc/Et_3N (100/5/3), and, following on this, **8aa** was isolated in 32% yield (16.9 mg) by changing the eluent to hexane/EtOAc/Et_3N (50/50/3). For spectral and analytical data of **7aa**, refer to Section **IV**. For spectral and analytical data of **8aa**, refer to Section **V**.

The reaction in the absence of $In(ONf)_3$ was carried out by simply mixing **9aa** and BuOAc in a flame-dried 20 mL Schlenk tube and stirring at 70 °C for 6 h. The yields of **7aa** and **8aa** were determined by GC using *o*-dichlorobenzene as an internal standard.

Control Experiments for Scheme 6-(c)



A procedure performed in the presence of octylsilane: $In(ONf)_3$ (20.2 mg, 20.0 μmol) was placed in a 20 mL Schlenk tube, which was heated at 150 ºC in vacuo for 2 h. The tube was cooled down to room temperature, and filled with argon. BuOAc (2.5 mL) and H_2O (1.80 mg, 0.100 mmol) were added to the tube, and the mixture was stirred at room temperature for 10 min. To this were added **7aa** (13.4 mg, 50.0 μmol), **8aa** (13.2 mg, 50.0 μmol), and octylsilane (28.9 mg, 0.200 mmol), and the resulting mixture was stirred at 70 °C for 48 h. The mixture diluted with EtOAc (5 mL) was washed with a saturated $NaHCO_3$ aqueous solution (1 mL) and brine (1 mL), and then dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc/Et_3N = 200/5/6) gave **7aa** in 70% yield (18.7 mg).

The reaction without using $In(ONf)_3$ was carried out by simply mixing BuOAc, H_2O, **7aa**, **8aa**, and octylsilane in a flame-dried 20 mL Schlenk tube and stirring at 70 °C for 48 h. The yields of **7aa** and **8aa** were determined by GC using *o*-dichlorobenzene as an internal standard.

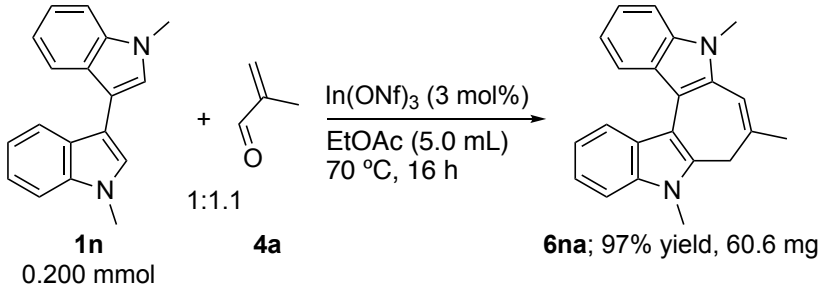
A procedure performed in the presence of DBH: $In(ONf)_3$ (20.2 mg, 20.0 μmol) was placed in a 20 mL Schlenk tube, which was heated at 150 ºC in vacuo for 2 h. The tube was cooled down to room temperature, and filled with argon. BuOAc (2.5 mL) and H_2O (1.80 mg, 0.100 mmol) were added to the tube, and the mixture was stirred at room temperature for 10 min. To this were added **7aa** (13.4 mg, 50.0 μmol), **8aa** (13.2 mg, 50.0 μmol), and DBH (15.7 mg, 55.0 μmol), and the resulting mixture was stirred at 100 °C for 5 h. A saturated $NaHCO_3$ aqueous solution (0.5 mL) was added to the mixture, and the aqueous phase was extracted with EtOAc (5

mL × 3). The combined organic layer was washed with brine (1 mL) and then dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvent followed by column chromatography on silica gel ($CHCl_3$/EtOAc = 5/1) gave **8aa** in 61% yield (16.1 mg).

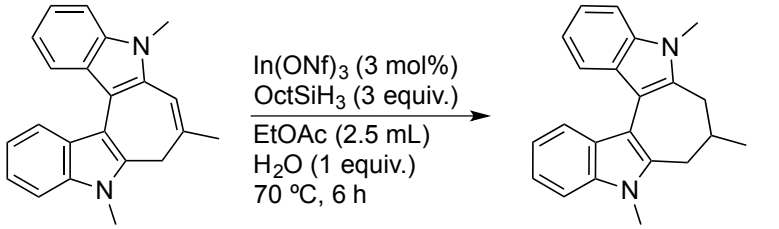
The reaction without using $In(ONf)_3$ was carried out by simply mixing BuOAc, H_2O, **7aa**, **8aa**, and DBH in a flame-dried 20 mL Schlenk tube and stirring at 100 °C for 5 h. The yields of **7aa** and **8aa** were determined by GC using *o*-dichlorobenzene as an internal standard.

IX. Confirmation of and Ensuing Reduction of 6na

Experimental procedures for Scheme 8 are described in this section.



5,7,9-Trimethyl-6*H*-cyclohepta[1,2-*b*:4,3-*b*']diindole (6na). The title compound was synthesized in a manner similar to that described for Section **IV** except for using no octylsilane, and isolated as a white solid (mp 198–199 °C) by column chromatography on silica gel (hexane/$CHCl_3$/NEt_3 = 75/25/3). Reagents used are as follows: $In(ONf)_3$ (6.07 mg, 6.00 μmol), **1n** (52.1 mg, 0.200 mmol), **4a** (15.4 mg, 0.220 mmol), EtOAc (5.0 mL). ^{1}H NMR (400 MHz, acetone-d_6) δ 2.24 (d, J = 1.6 Hz, 3 H), 3.78 (s, 2 H), 3.83 (s, 3 H), 3.94 (s, 3 H), 6.56 (q, J = 1.5 Hz, 1 H), 7.08 (ddd, J = 8.0, 7.0, 1.0 Hz, 1 H), 7.12–7.21 (m, 2 H), 7.27 (ddd, J = 8.3, 6.9. 1.4 Hz, 1 H), 7.44–7.49 (m, 2 H), 7.92 (d, J = 7.8 Hz, 1 H), 8.03 (d, J = 7.8 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, acetone-d_6) δ 25.2, 29.8, 30.1, 30.2, 108.8, 110.1, 110.6, 112.3, 115.2, 119.4, 119.6, 120.4, 121.5, 121.8, 122.8, 126.3, 126.7, 133.1, 135.2, 135.8, 138.0, 139.0 (The chemical shifts were referenced to the solvent signal at 29.84 ppm).[6] HRMS (FD) Calcd for $C_{22}H_{20}N_2$: M^+, 312.16210. Found: *m/z* 312.16142.



6na
0.100 mmol

7na; 90% yield, 28.3 mg

$In(ONf)_3$ (3.04 mg, 3.00 μmol) was placed in a 20 mL Schlenk tube, which was heated at 150 ºC in vacuo for 2 h. The tube was cooled down to room temperature, and filled with argon. EtOAc (2.5 mL) and H_2O (1.80 mg, 0.100 mmol) were added to the tube, and the mixture was stirred at room temperature for 10 min. To this were added **6na** (31.2 mg, 0.100 mmol) and octylsilane (43.3 mg, 0.300 mmol), and the resulting mixture was stirred at 70 °C for 6 h. The mixture diluted with EtOAc (5 mL) was washed with a saturated $NaHCO_3$ aqueous solution (1 mL) and brine (1 mL), and then dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/$CHCl_3$/NEt_3 = 75/25/3) gave **7na** in 90% yield (28.3 mg). For spectral and analytical data of **7na**, refer to Section **IV**.

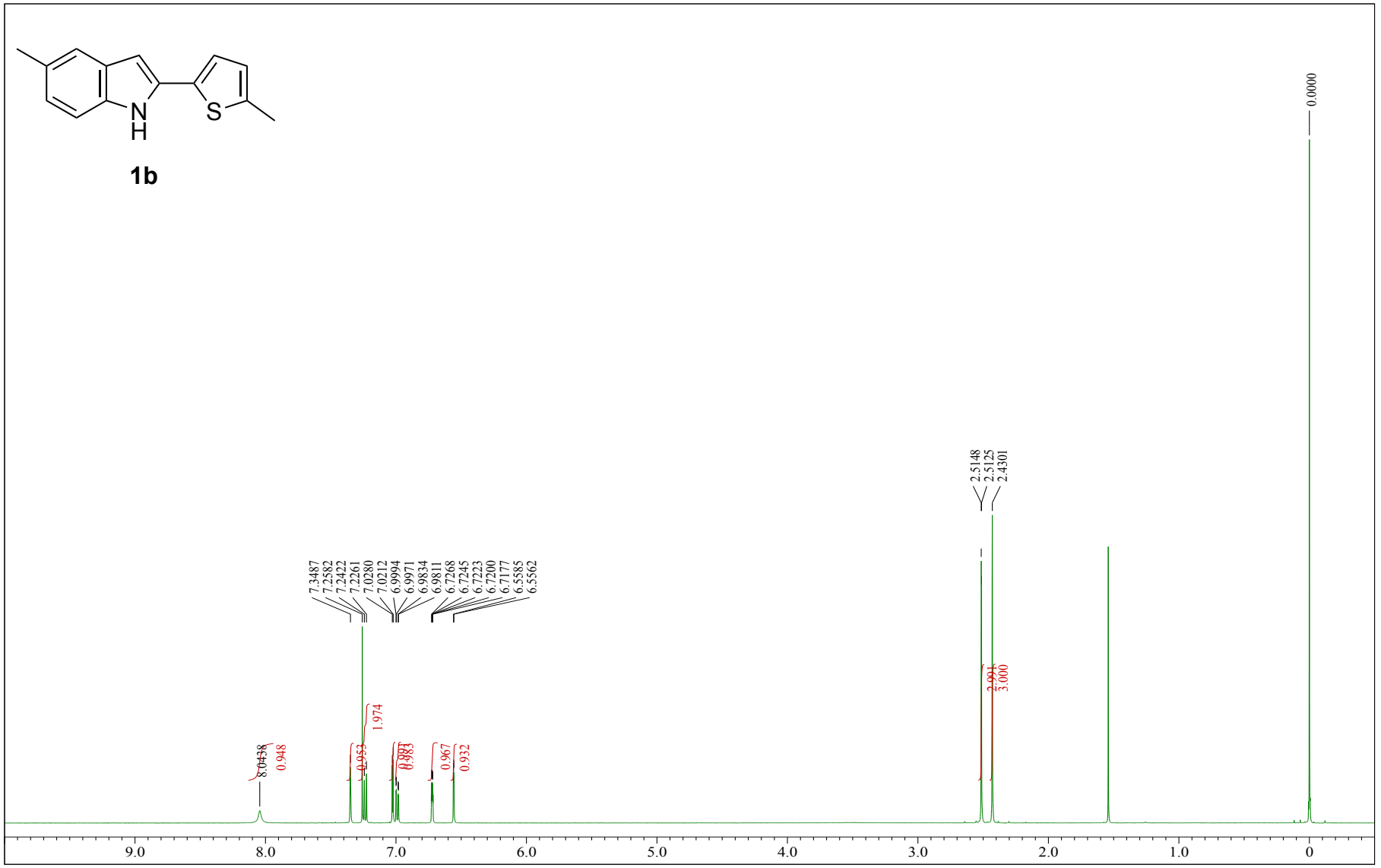


Figure S1. ^{1}H NMR spectrum of compound **1b** in $CDCl_3$.

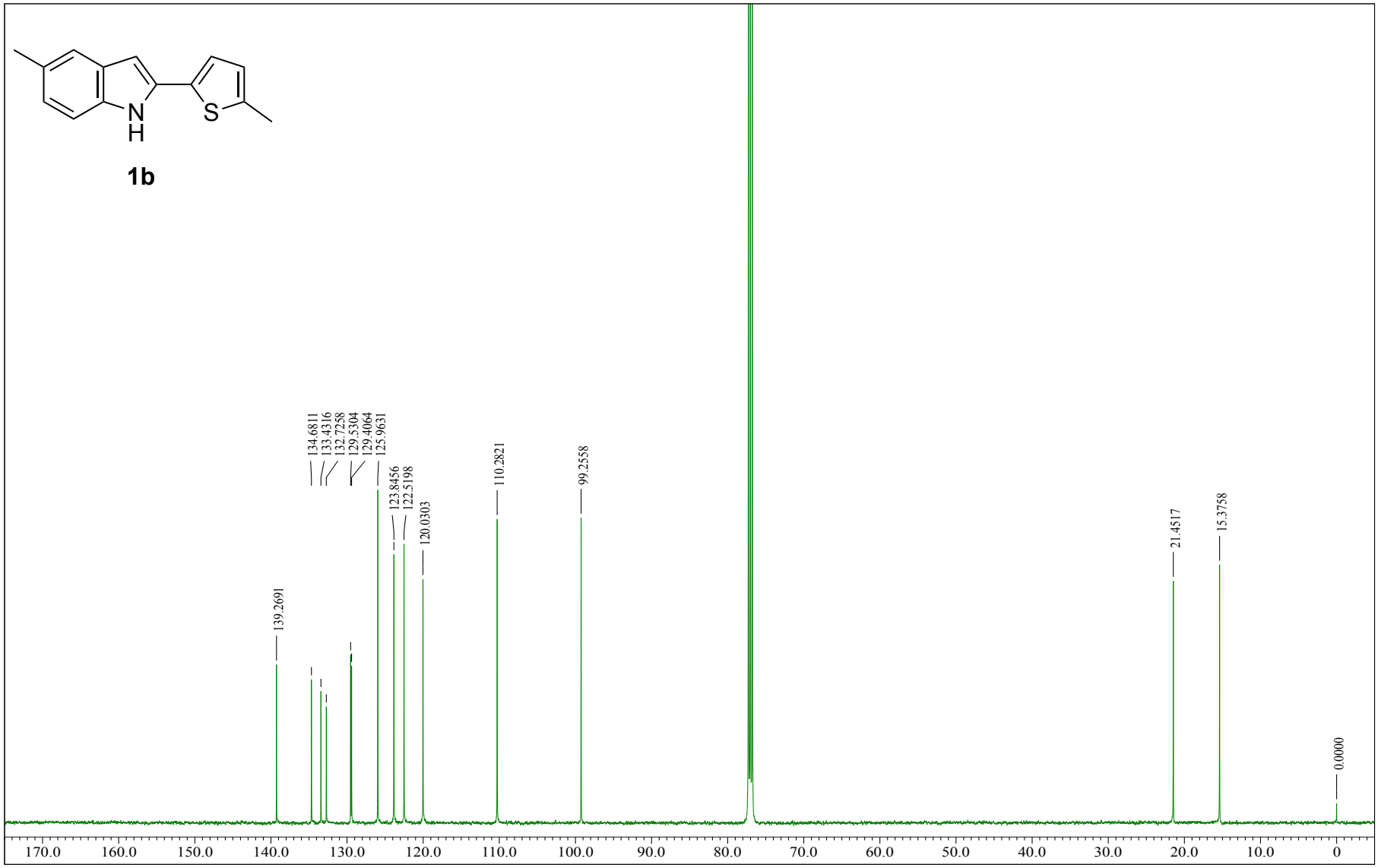


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1b** in $CDCl_3$.

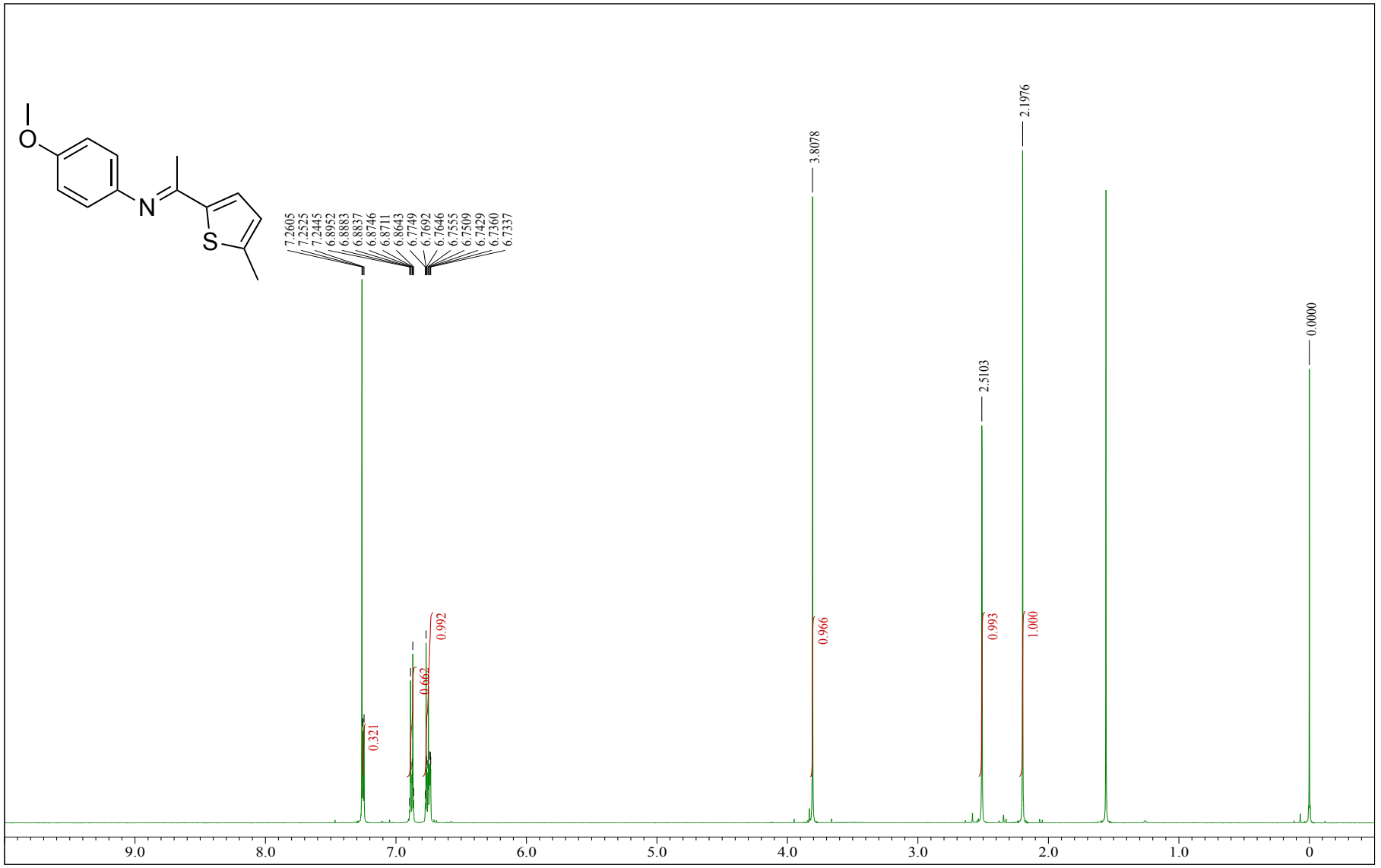


Figure S3. ^{1}H NMR spectrum of compound *N*-[1-(5-methylthien-2-yl)ethylidene]-4-methoxybenzenamine in $CDCl_3$.

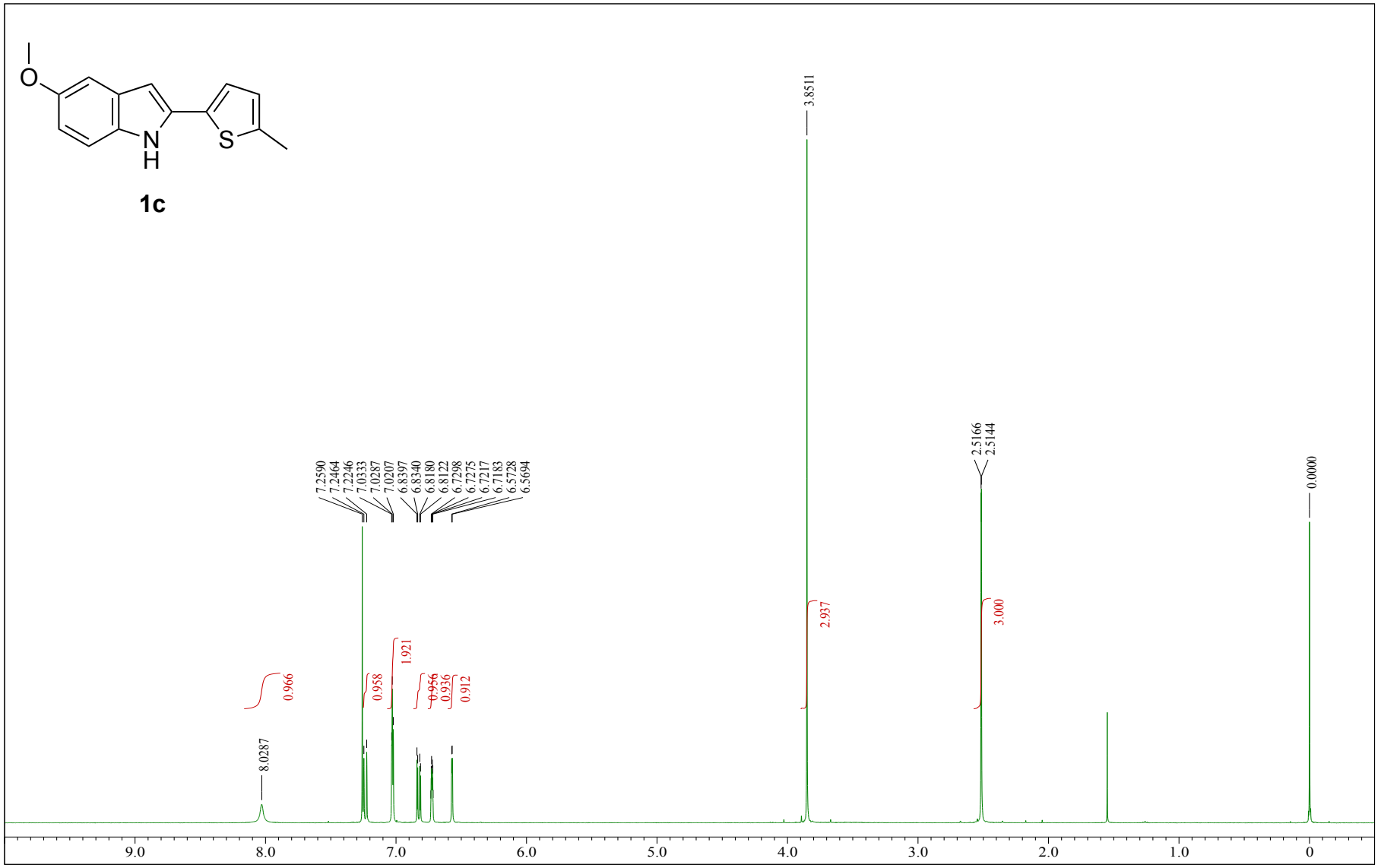


Figure S4. ^{1}H NMR spectrum of compound **1c** in $CDCl_3$.

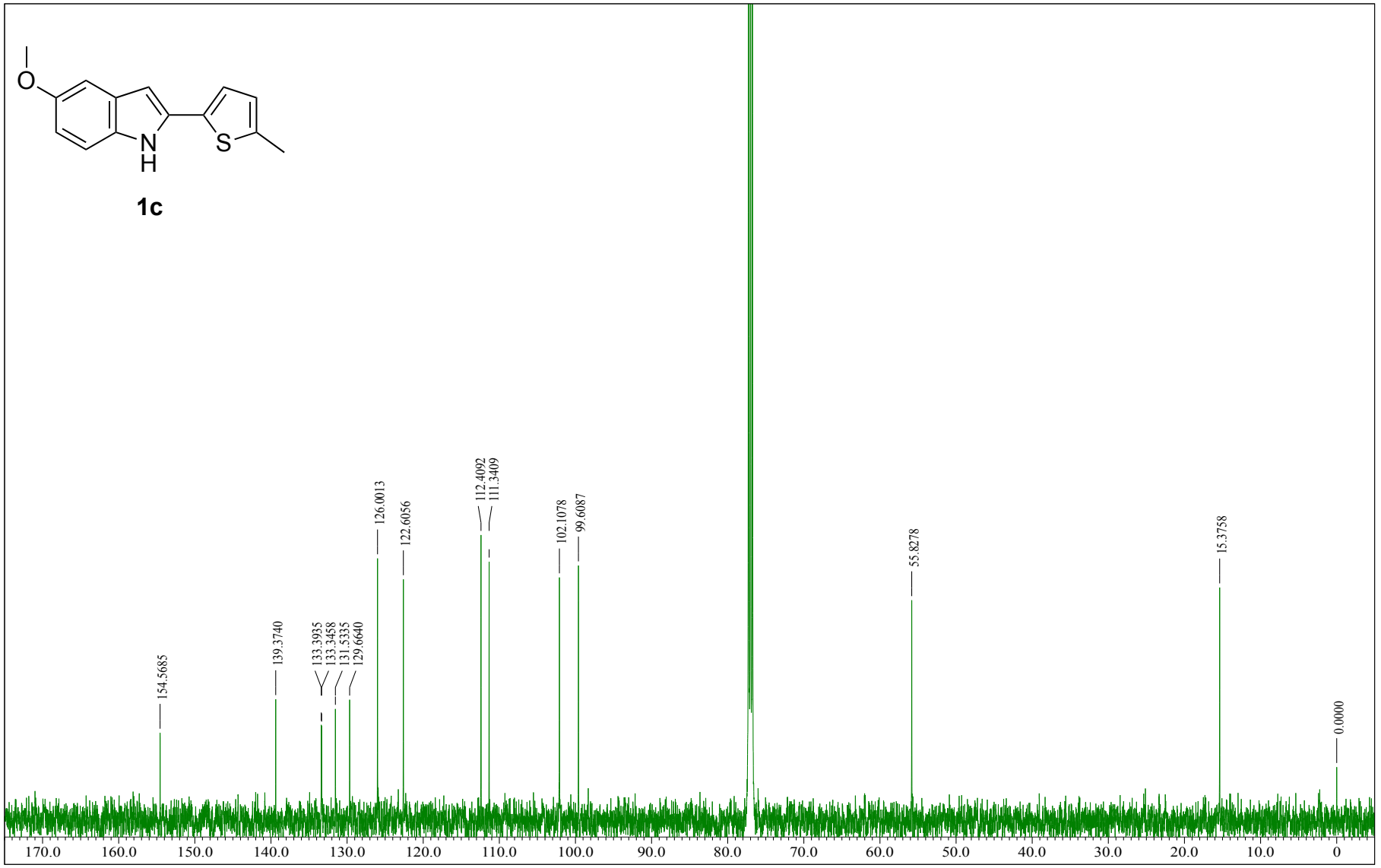


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1c** in $CDCl_3$.

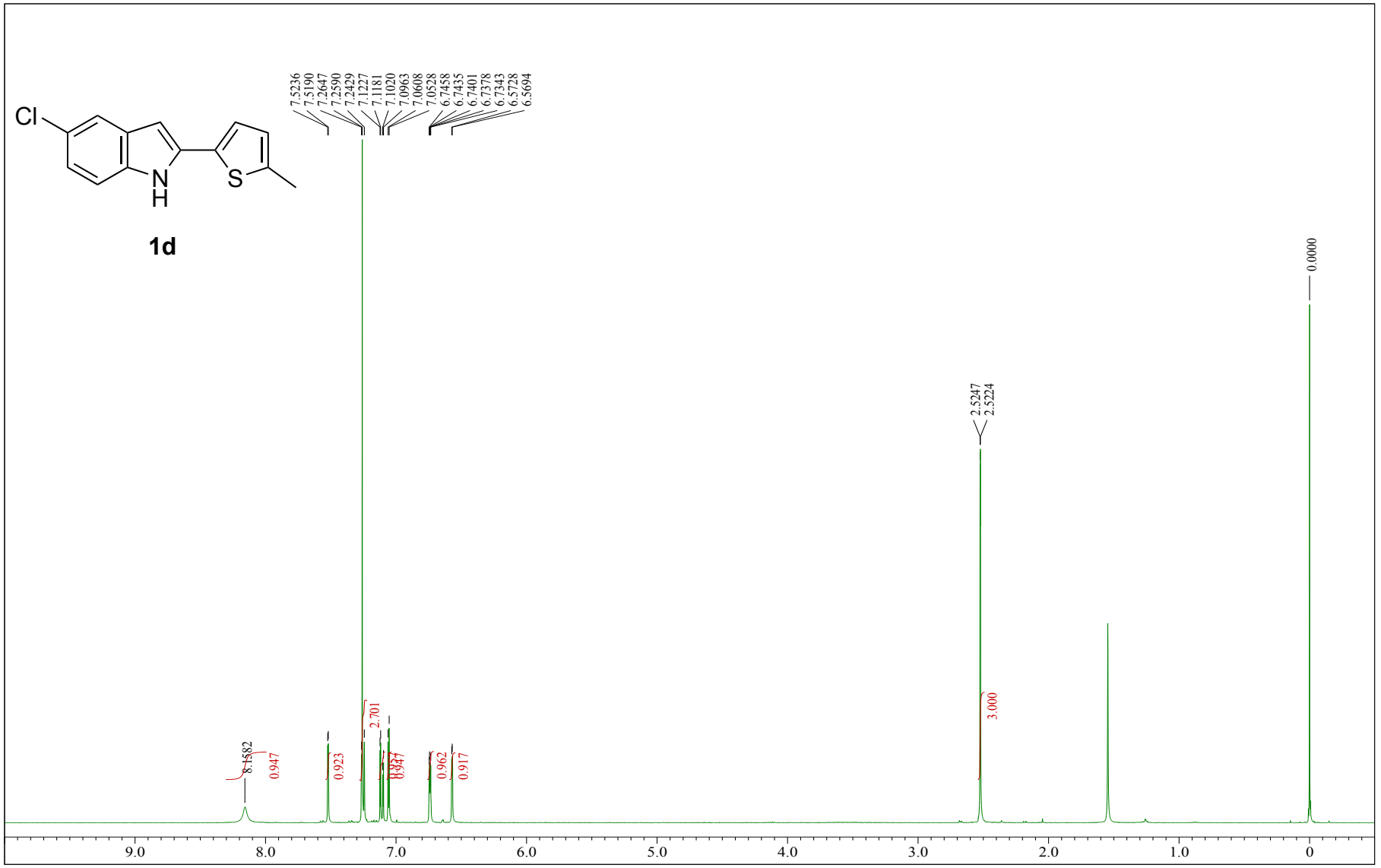


Figure S6. ^{1}H NMR spectrum of compound **1d** in $CDCl_3$.

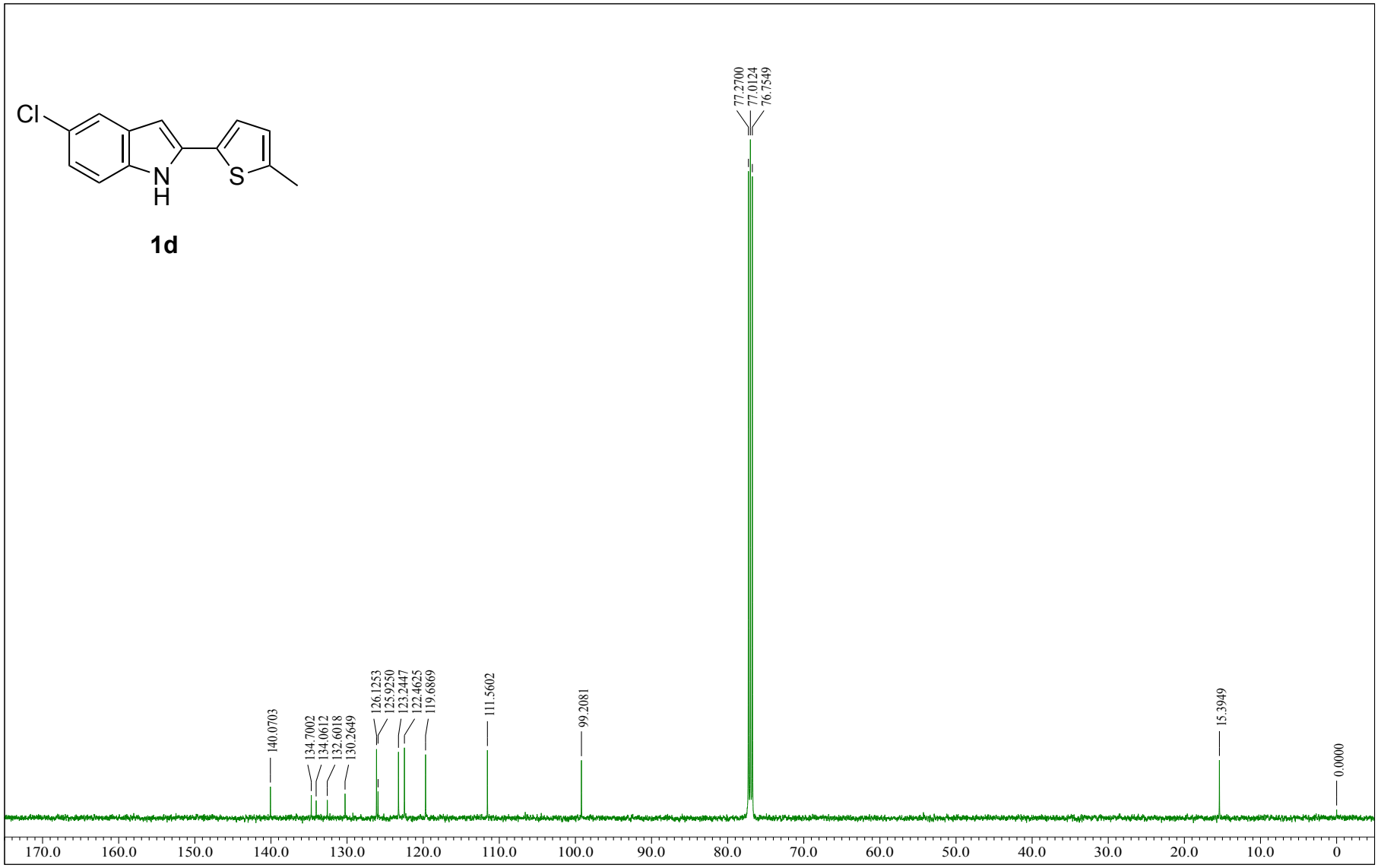


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1d** in $CDCl_3$.

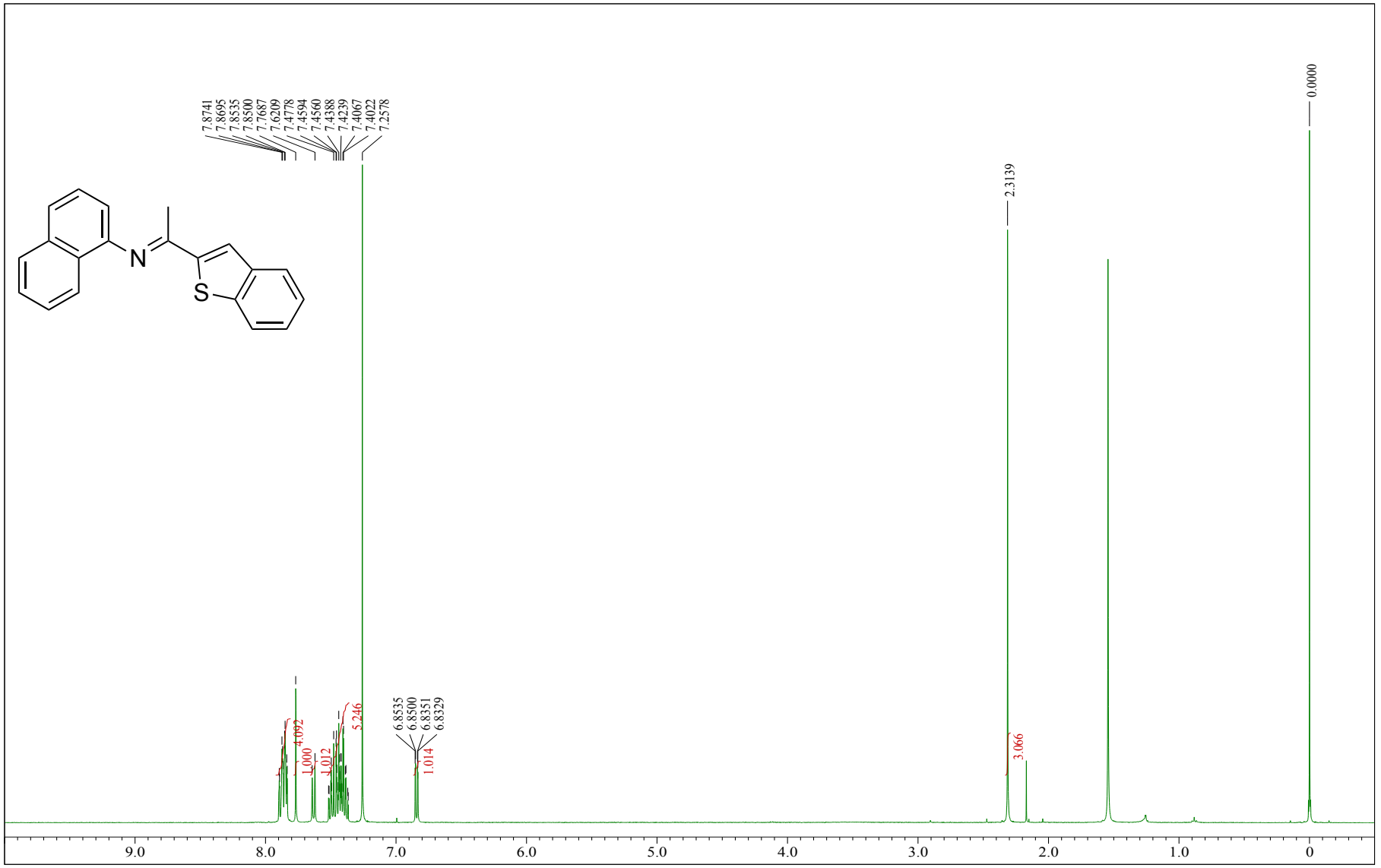


Figure S8. ^{1}H NMR spectrum of compound *N*-[1-(benzo[*b*]thien-2-yl)ethylidene]-4-naphthalenamine in $CDCl_3$.

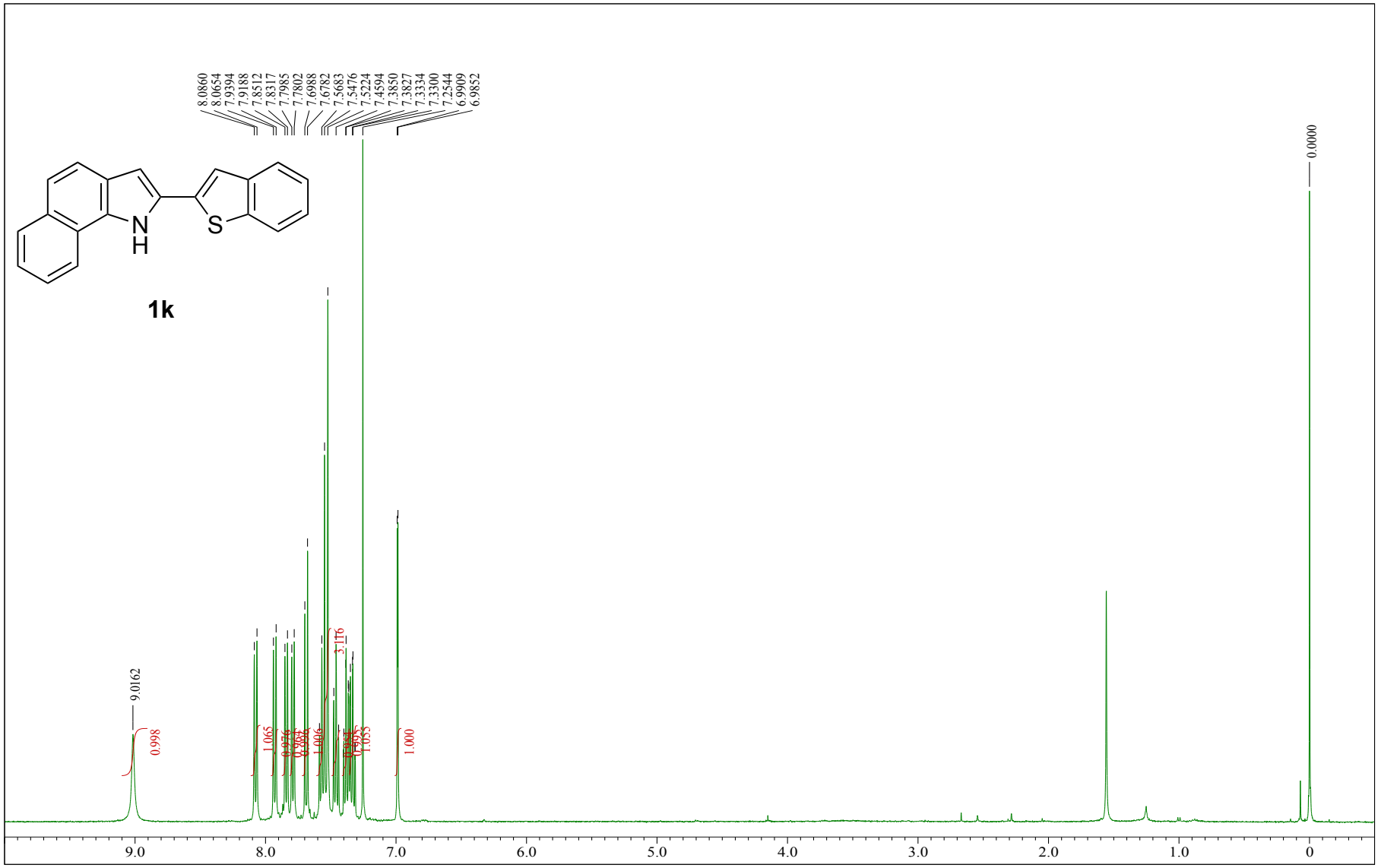


Figure S9. ^{1}H NMR spectrum of compound **1k** in $CDCl_3$.

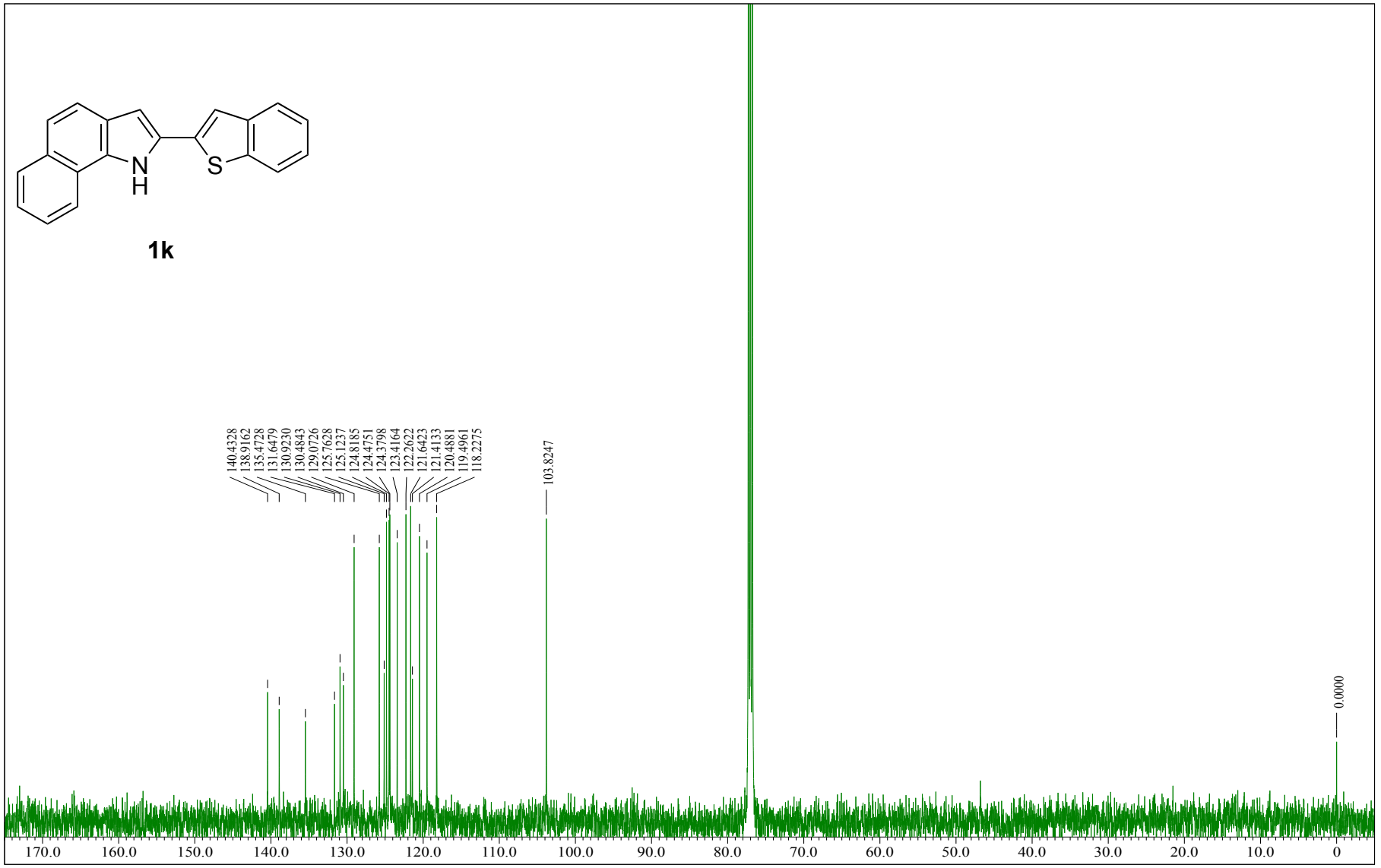


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1k** in $CDCl_3$.

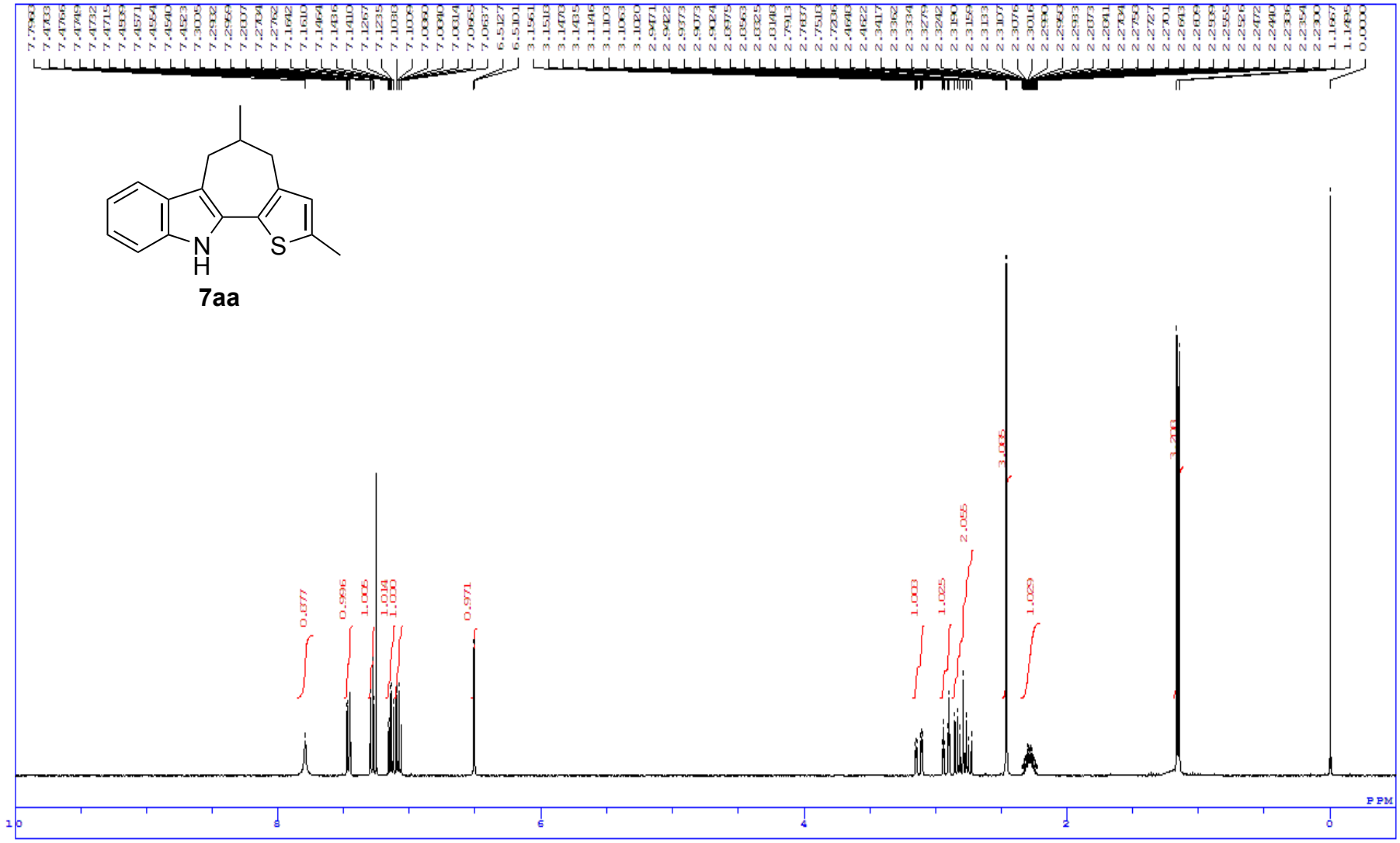


Figure S11. ^{1}H NMR spectrum of compound **7aa** in $CDCl_3$.

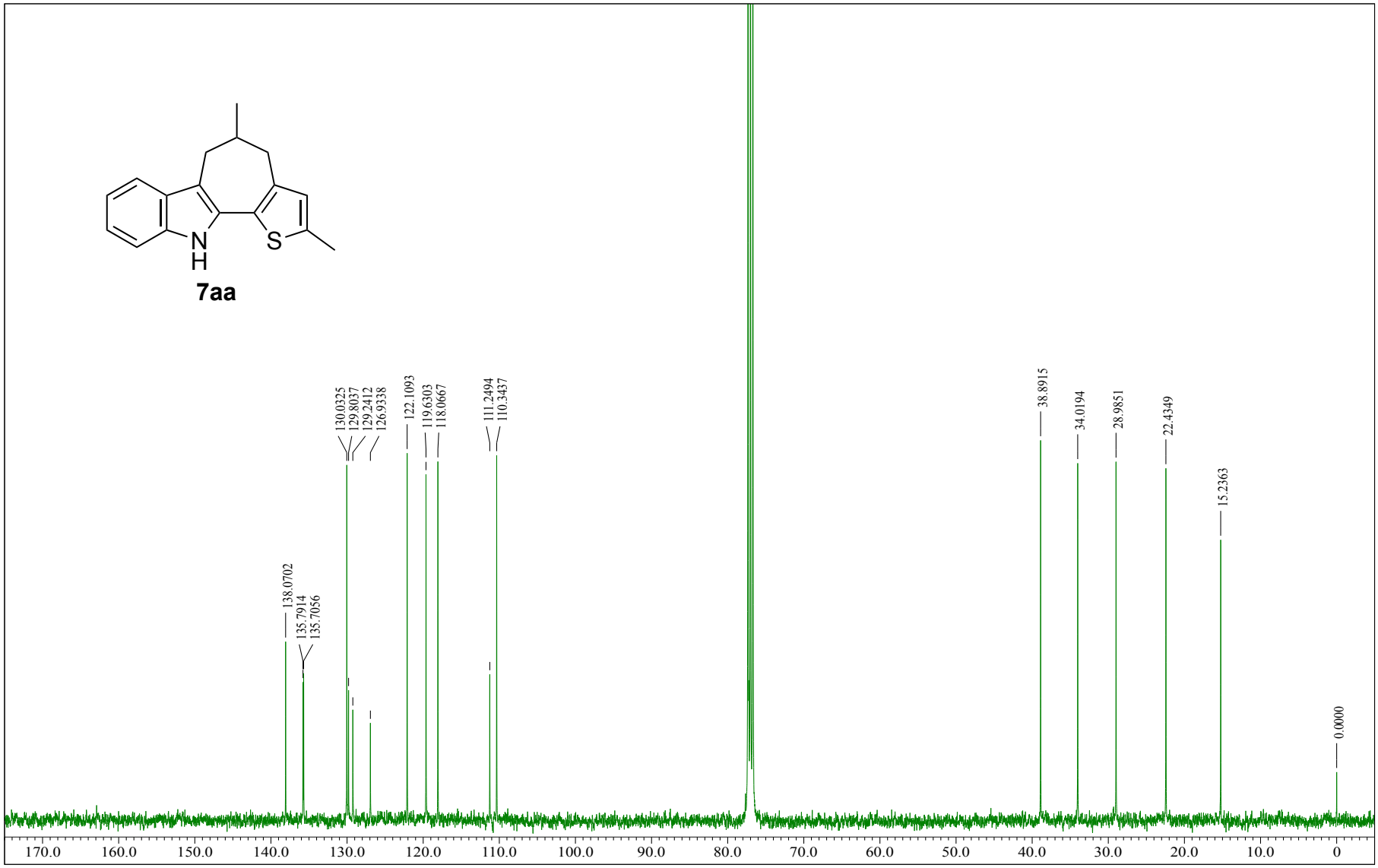


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7aa** in $CDCl_3$.

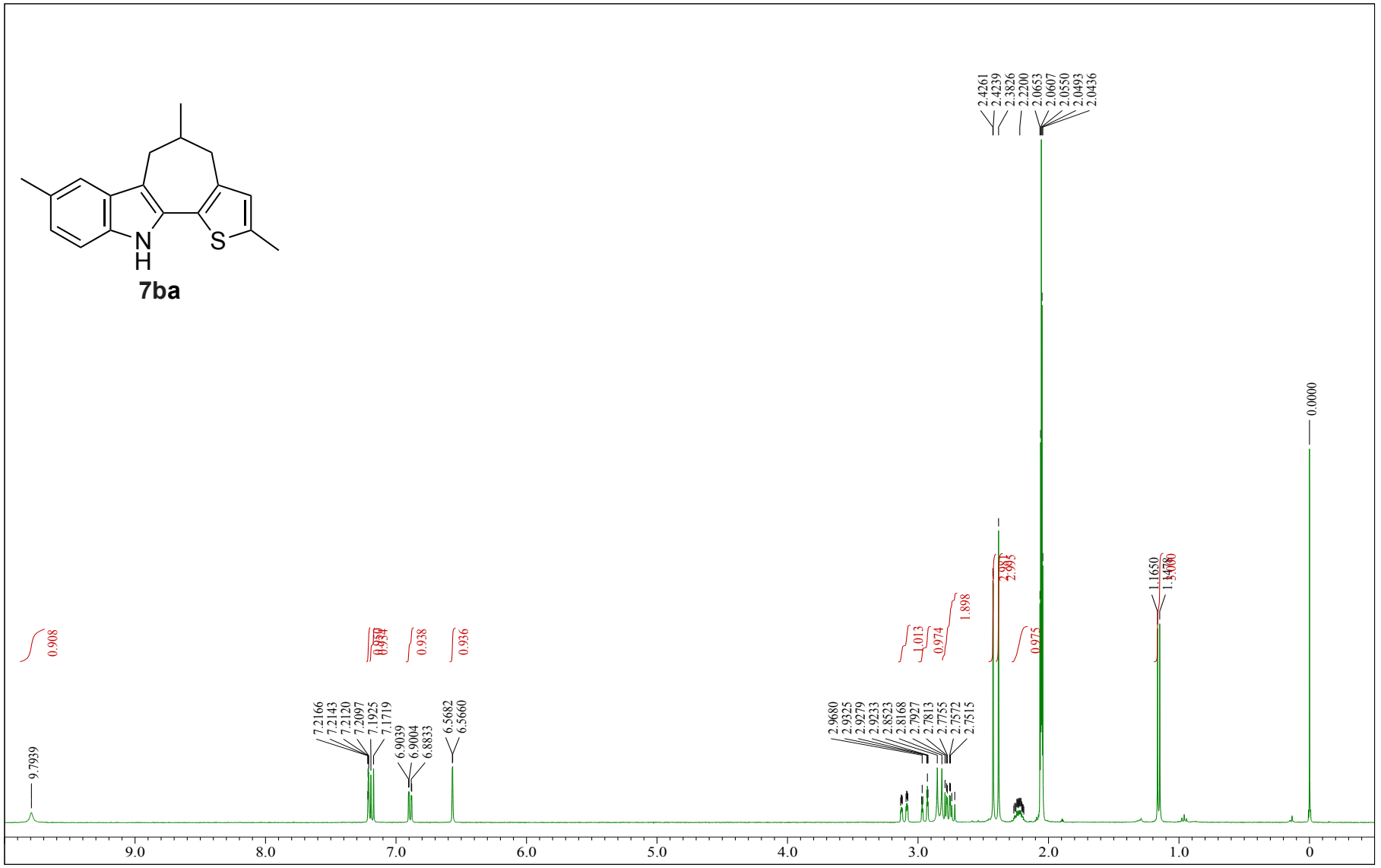


Figure S13. ^{1}H NMR spectrum of compound **7ba** in acetone-d_6.

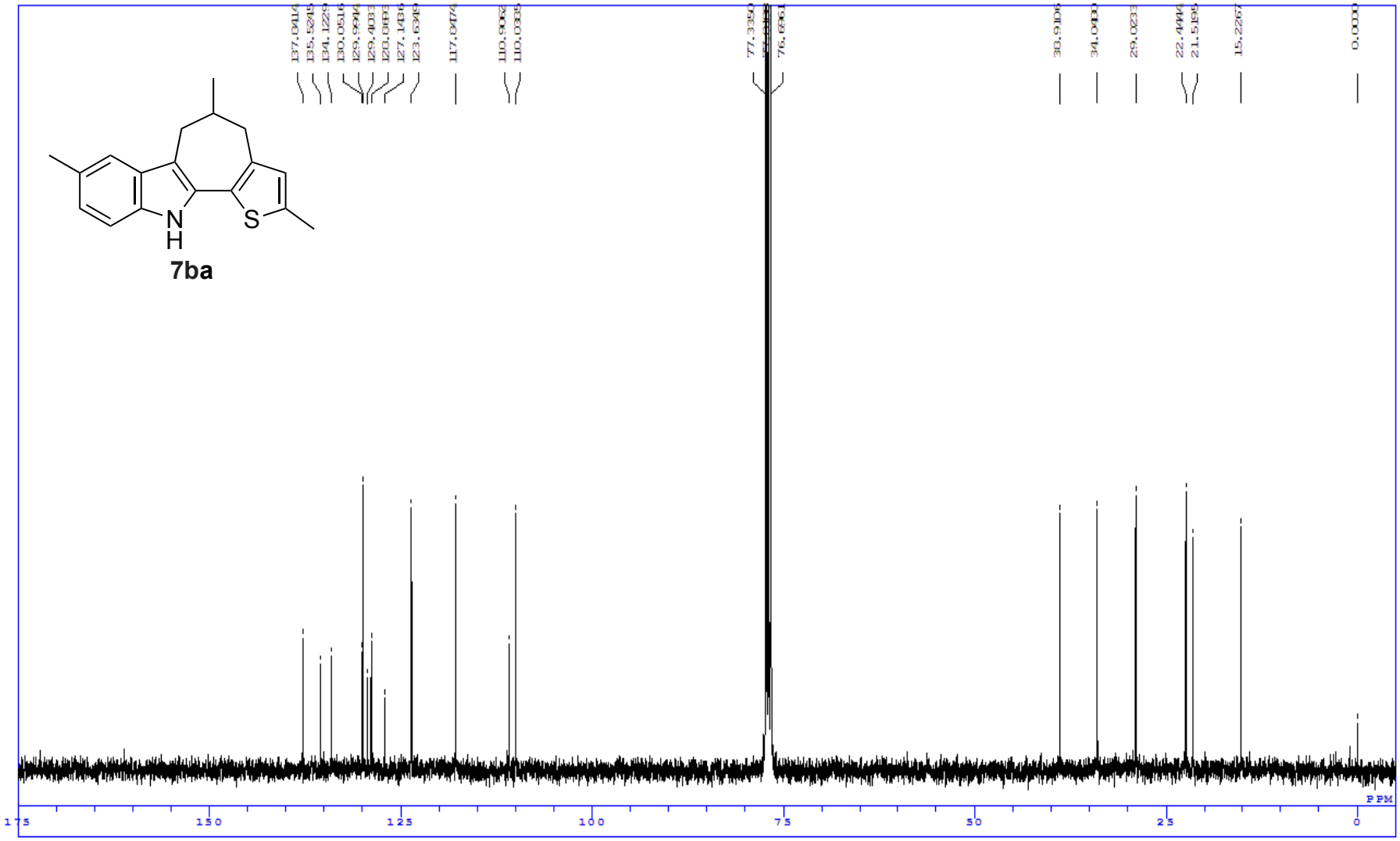


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7ba** in $CDCl_3$.

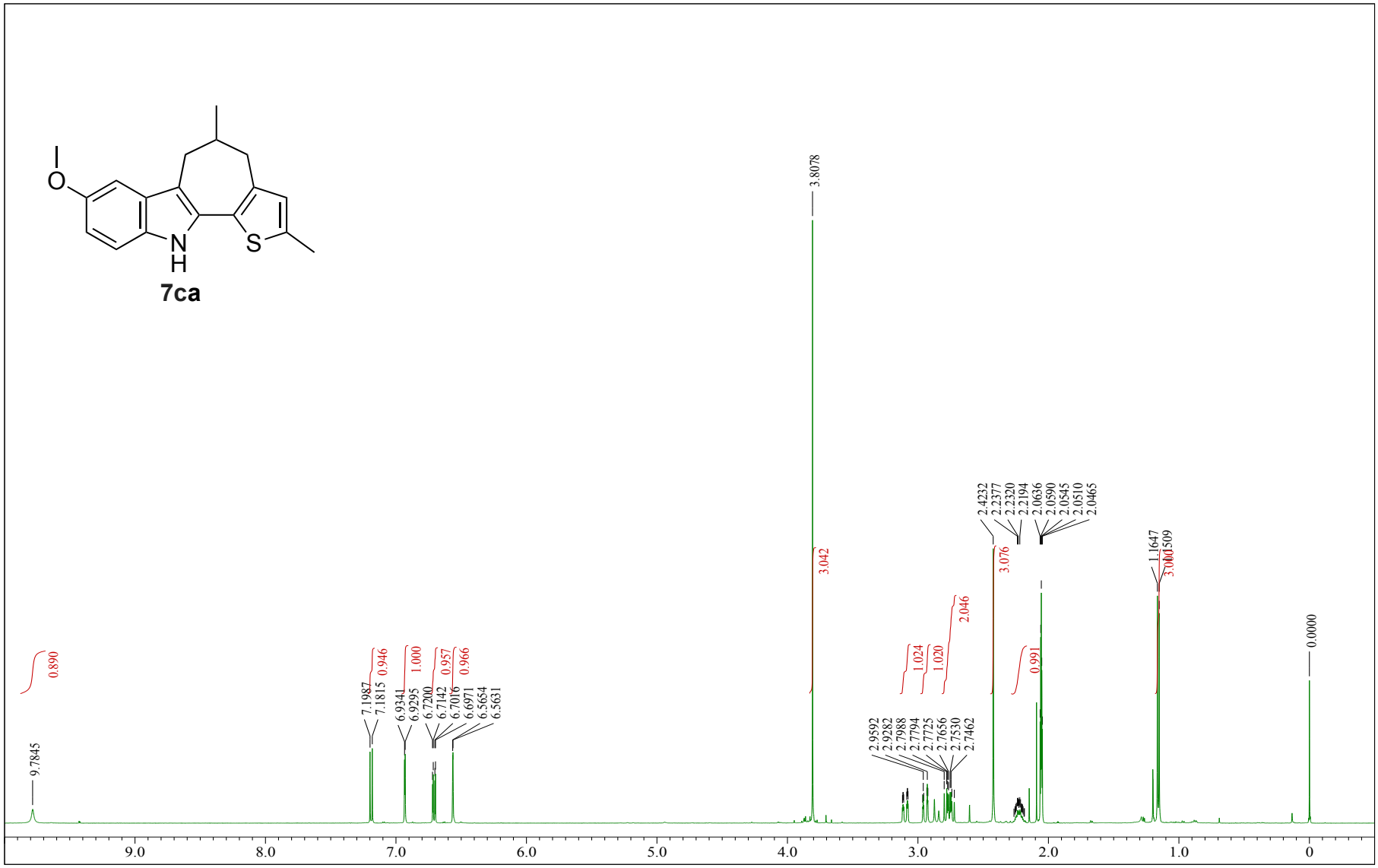


Figure S15. ^{1}H NMR spectrum of compound **7ca** in acetone-d_6.

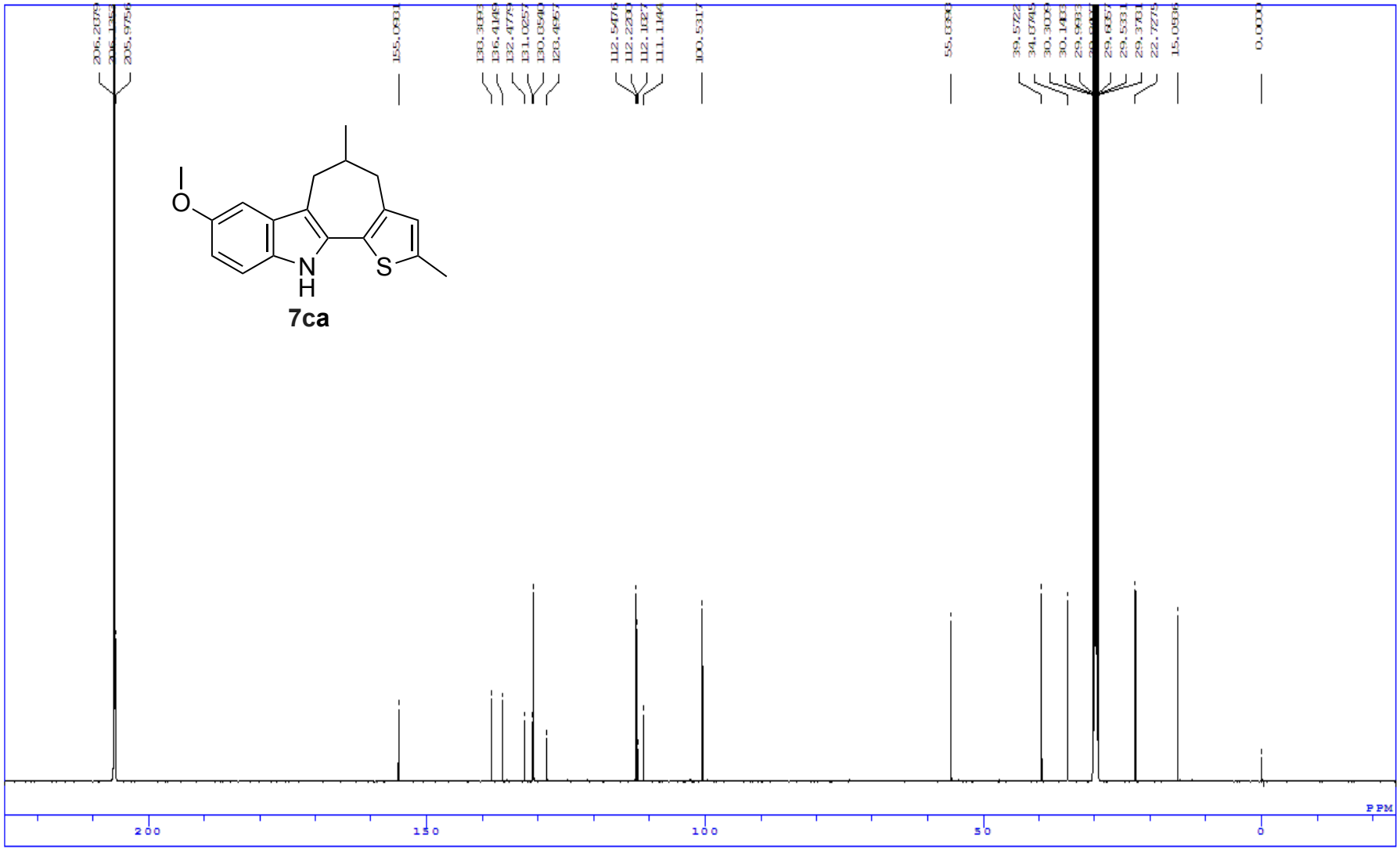


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7ca** in acetone-d_6.

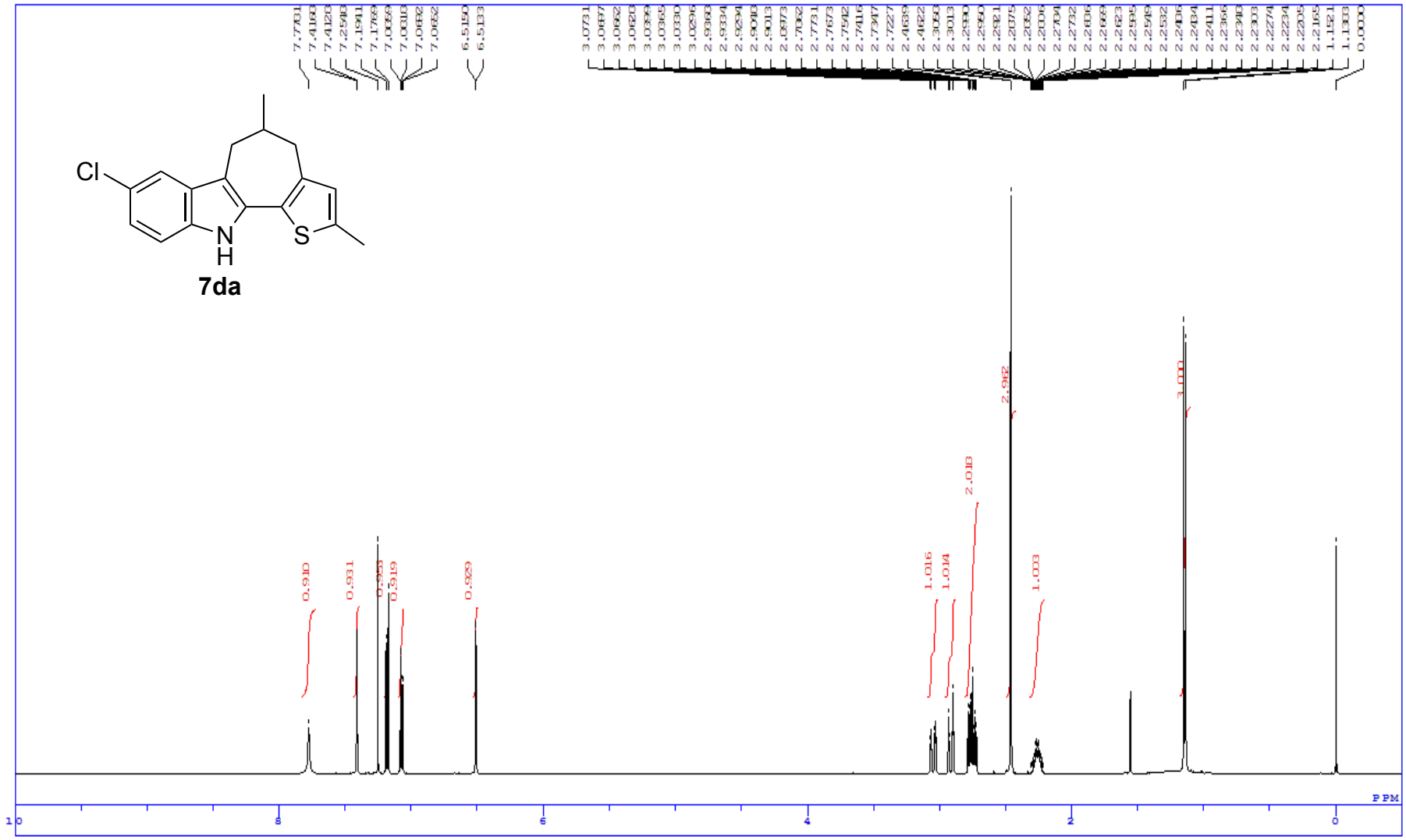


Figure S17. ^{1}H NMR spectrum of compound **7da** in $CDCl_3$.

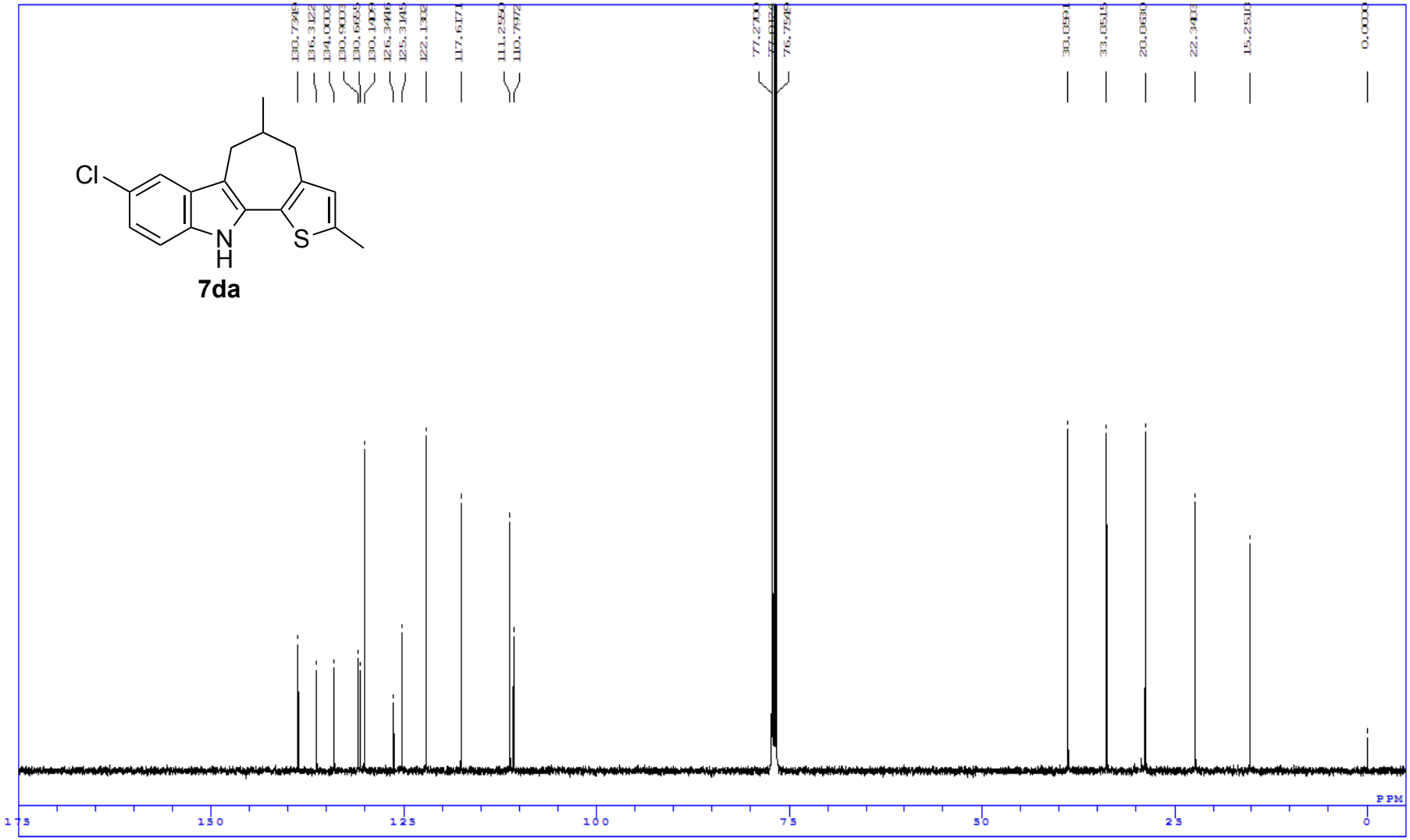


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7da** in $CDCl_3$.

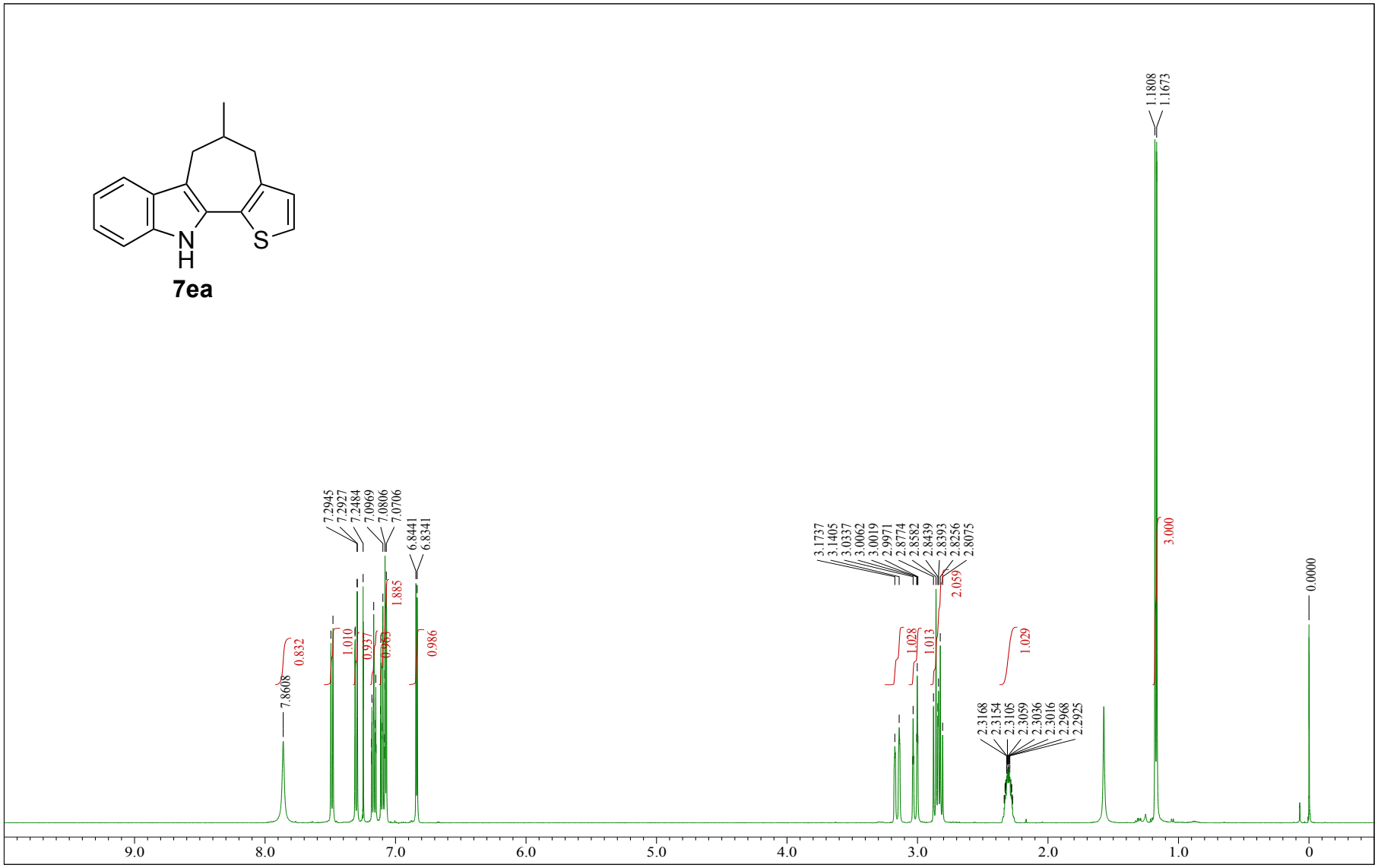


Figure S19. ^{1}H NMR spectrum of compound **7ea** in $CDCl_3$.

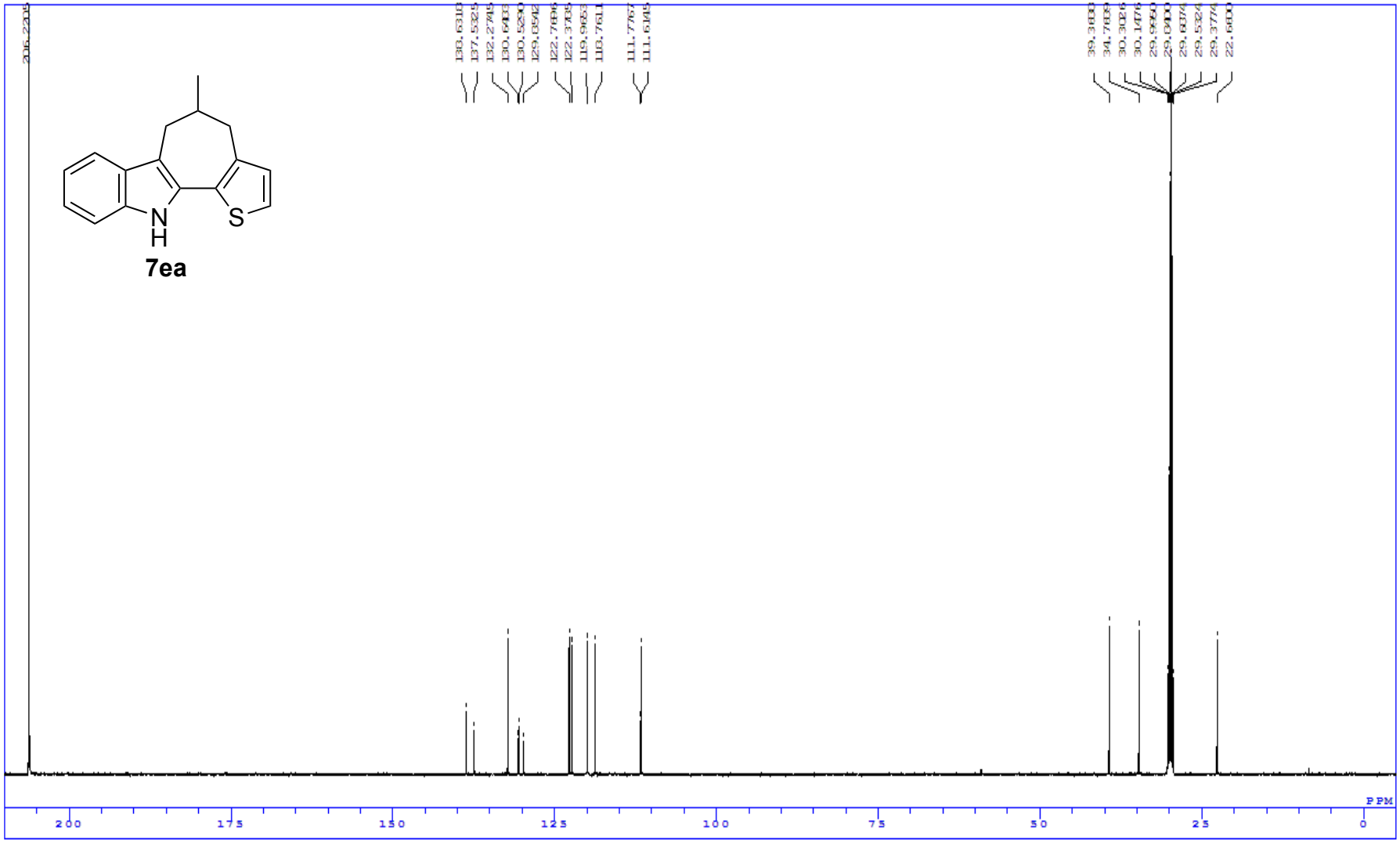


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7ea** in acetone-d_6.

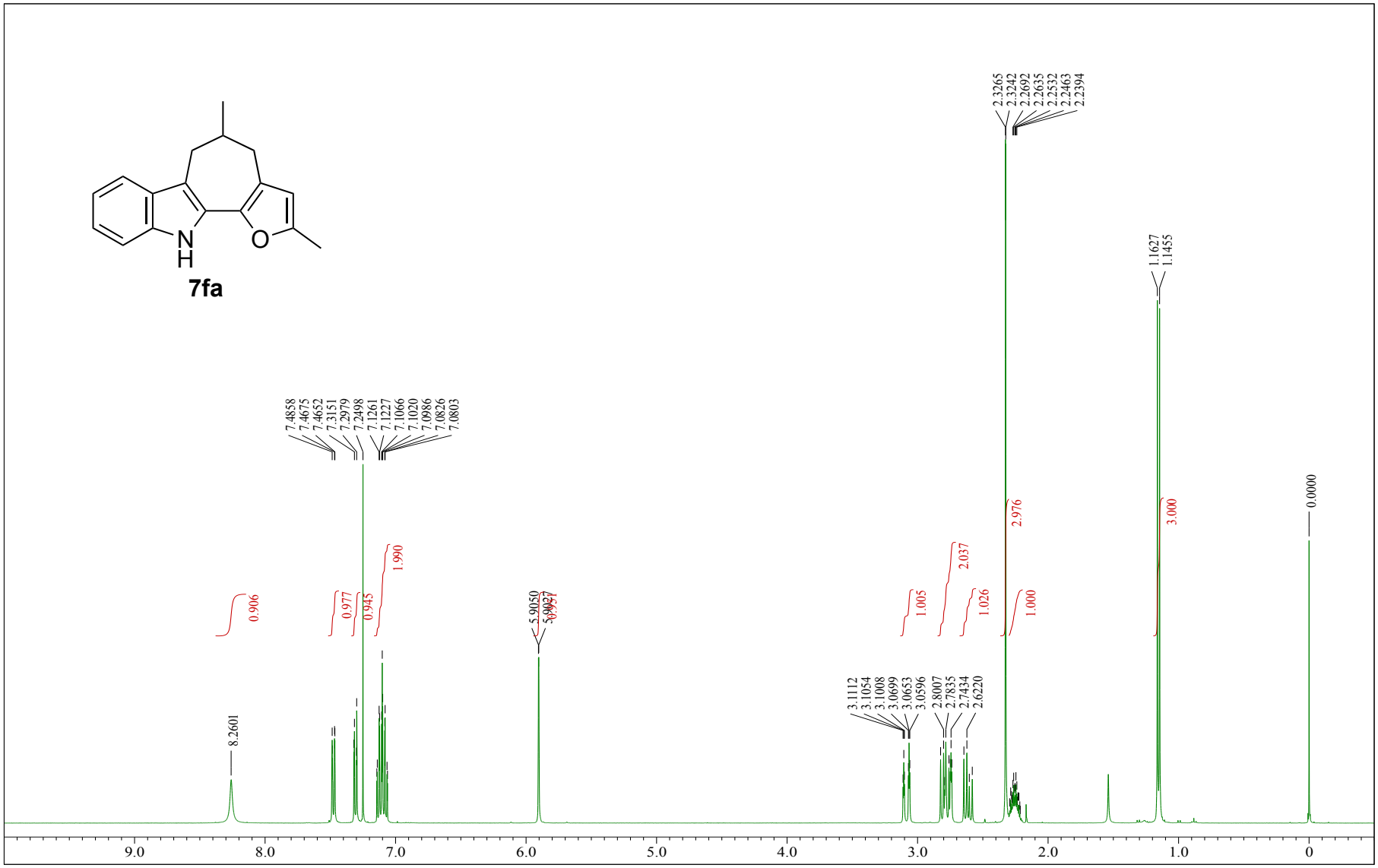


Figure S21. ^{1}H NMR spectrum of compound **7fa** in $CDCl_3$.

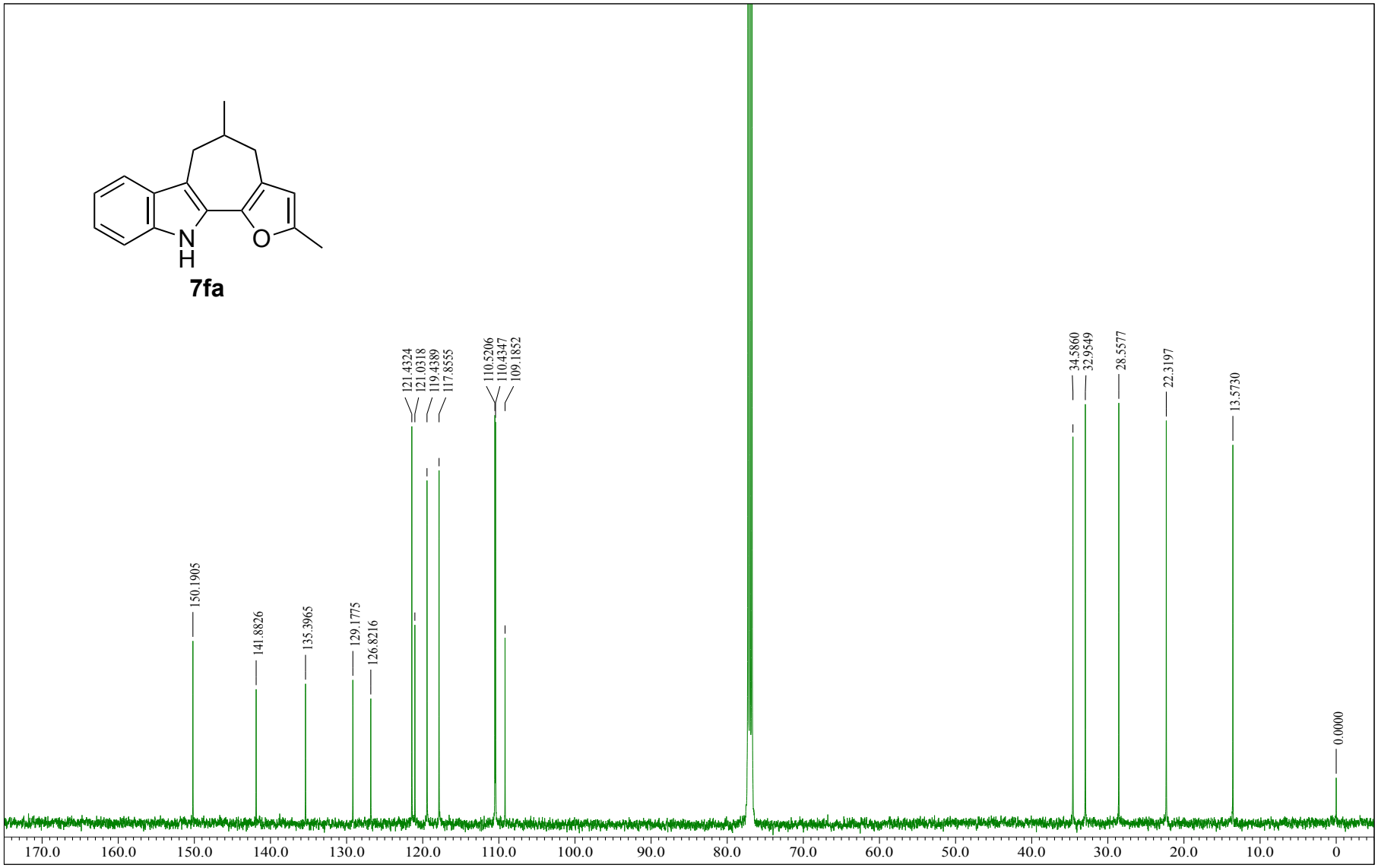


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7fa** in $CDCl_3$.

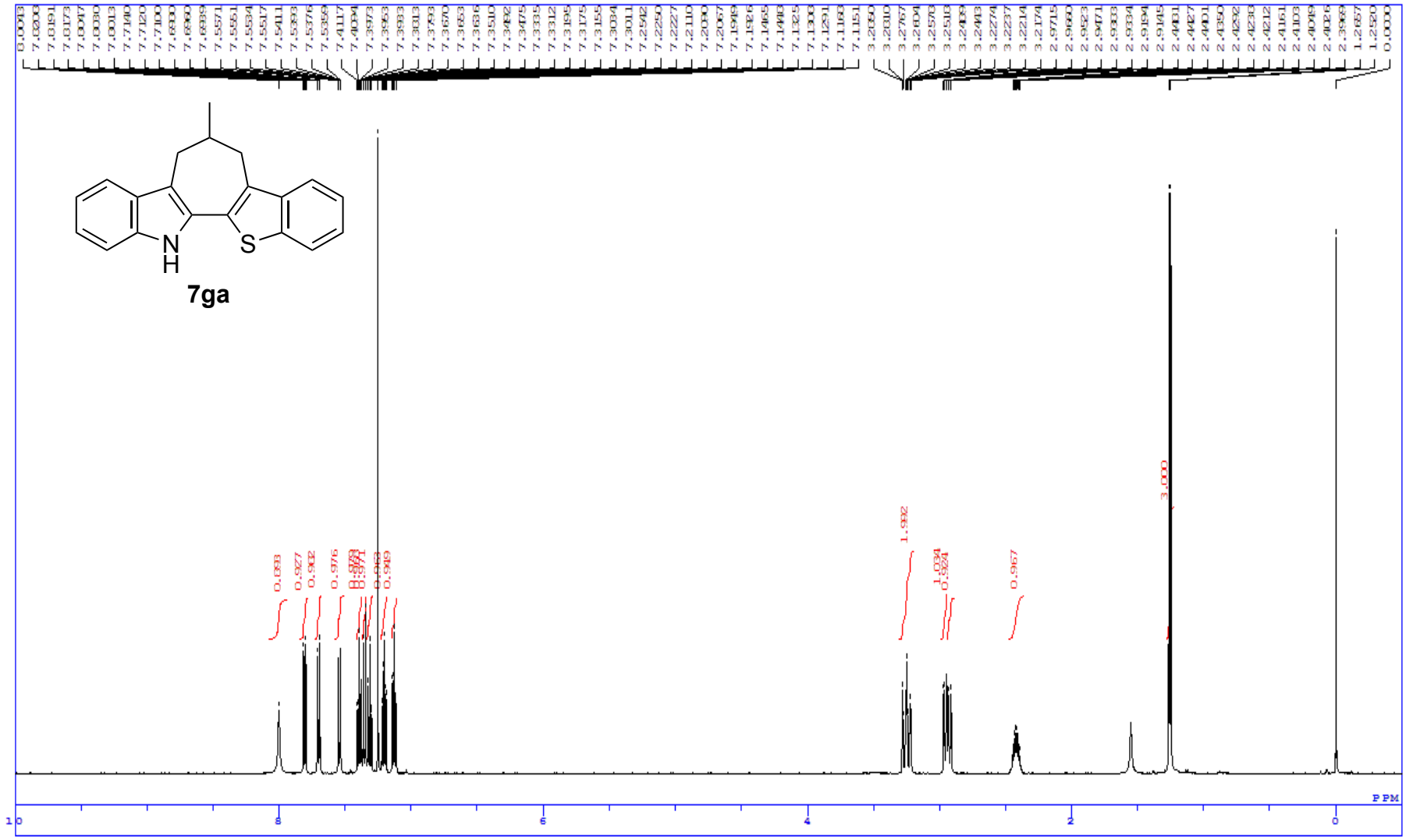


Figure S23. ^{1}H NMR spectrum of compound **7ga** in $CDCl_3$.

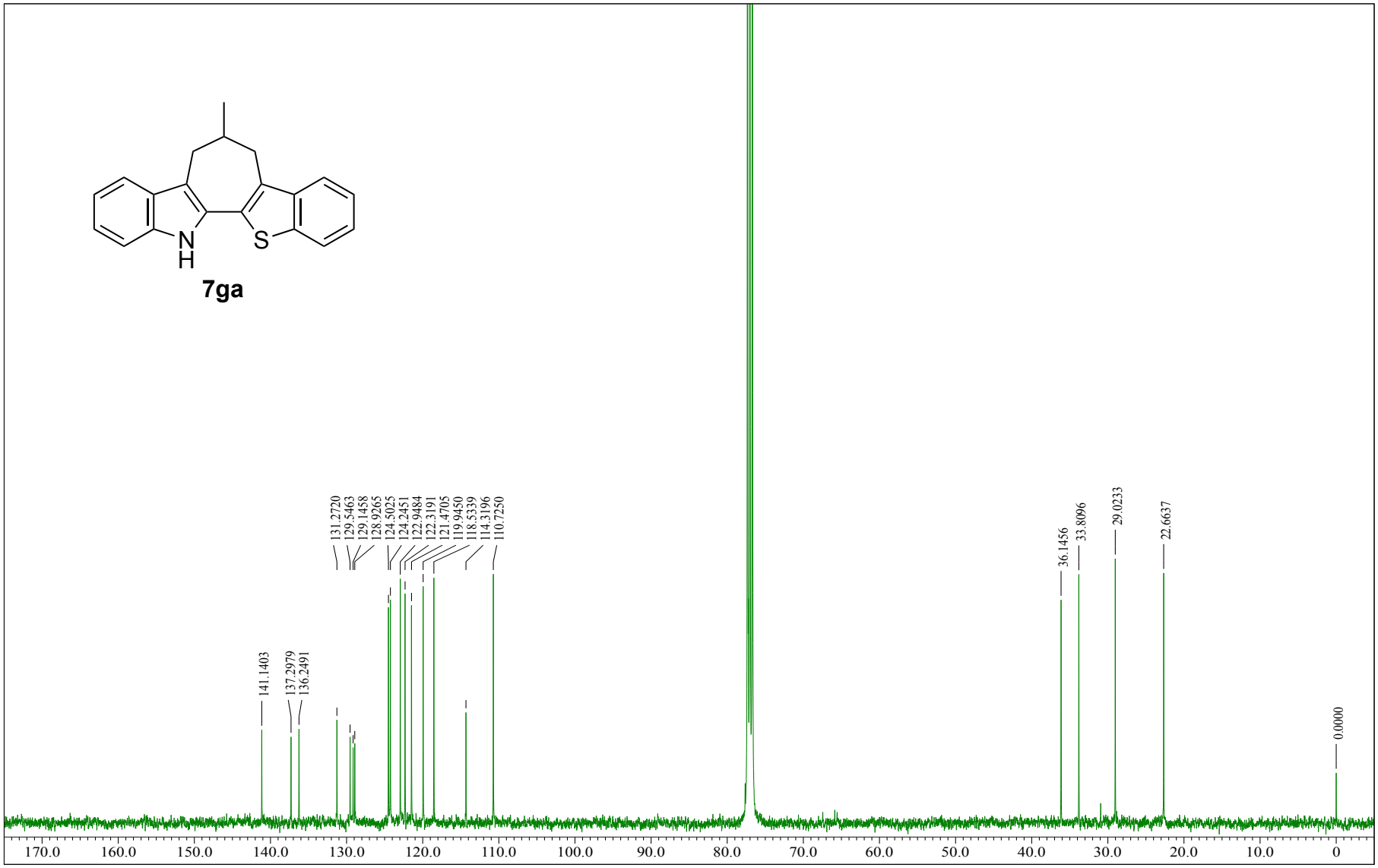


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7ga** in $CDCl_3$.

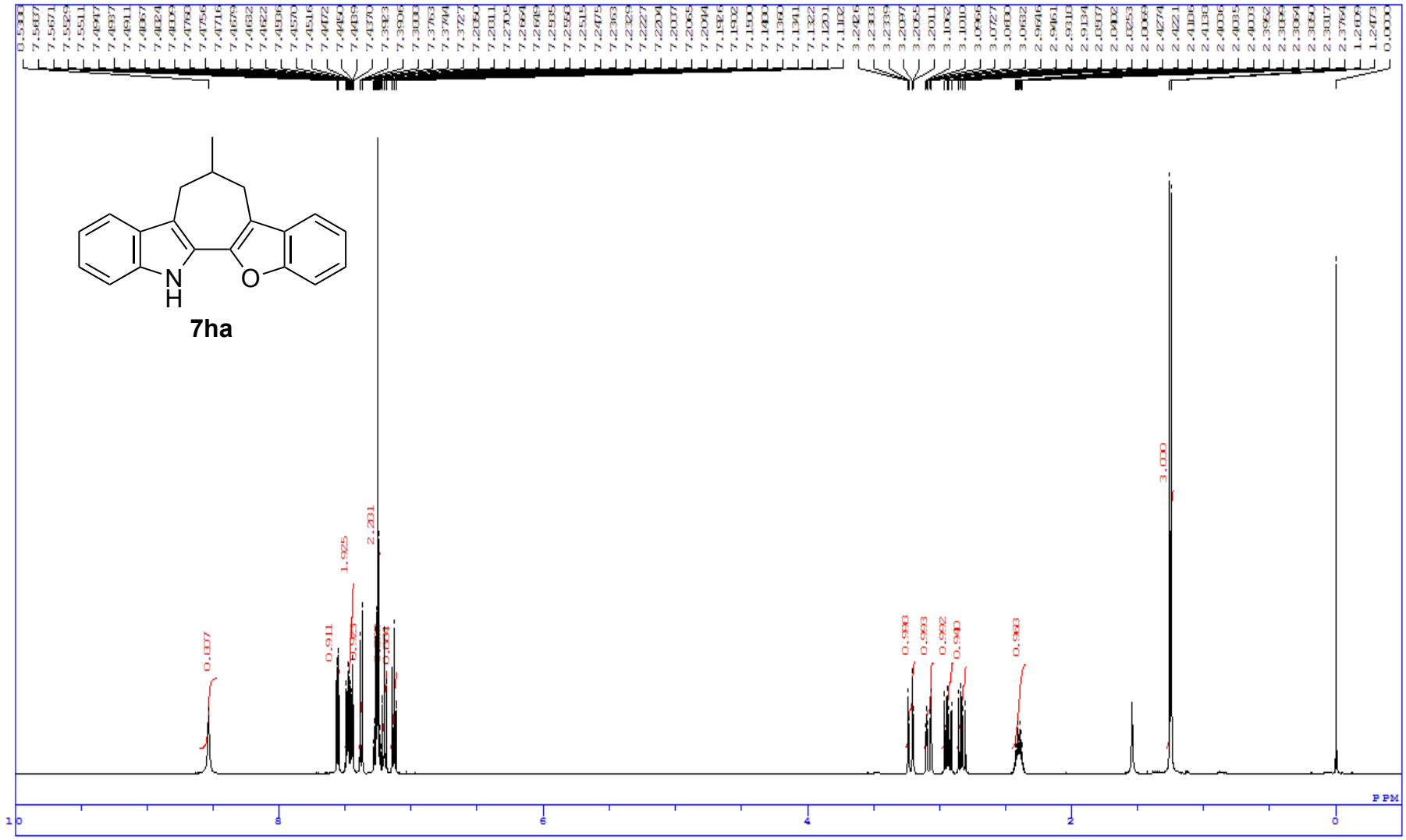


Figure S25. ^{1}H NMR spectrum of compound **7ha** in $CDCl_3$.

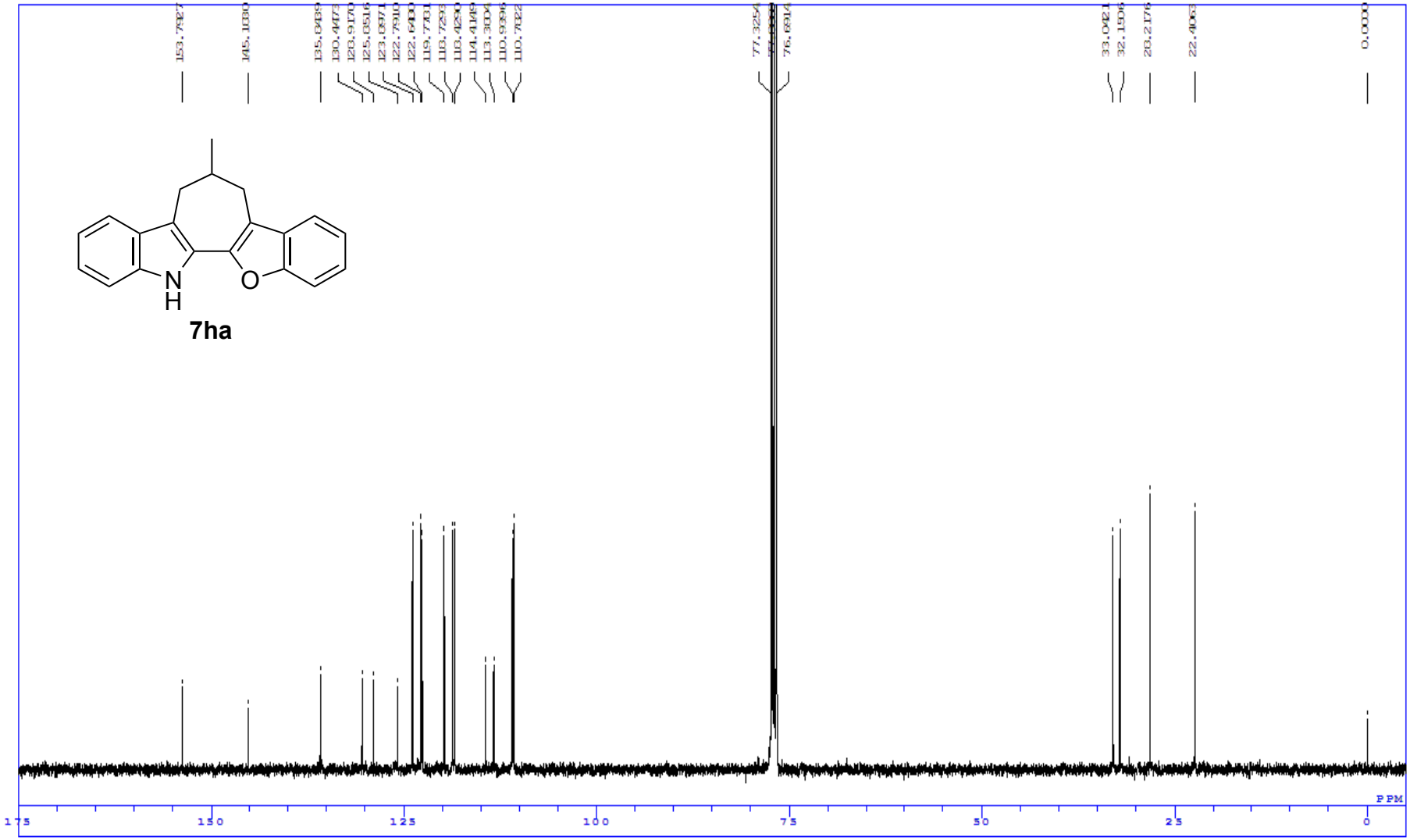


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7ha** in $CDCl_3$.

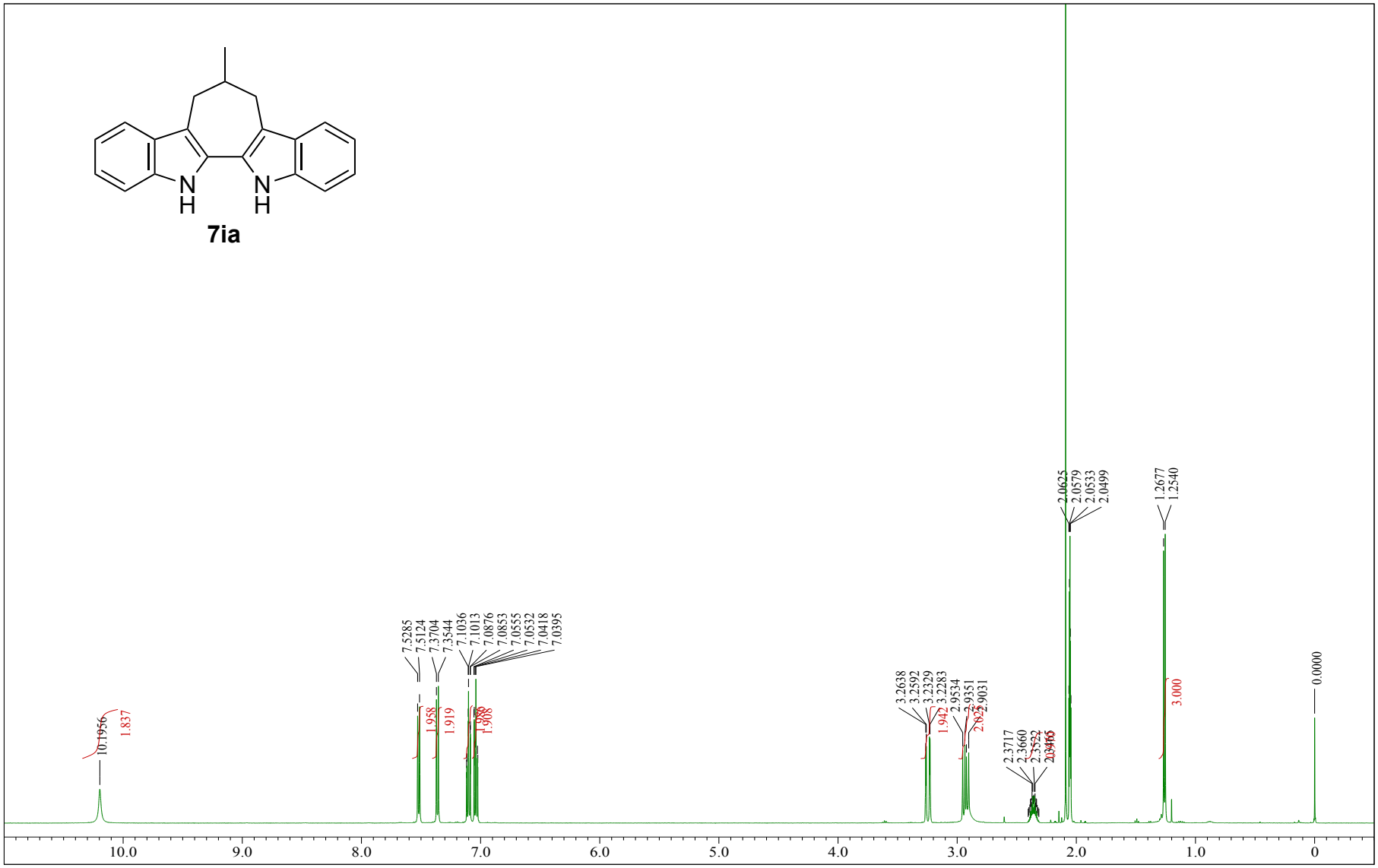


Figure S27. ^{1}H NMR spectrum of compound **7ia** in acetone-d_6.

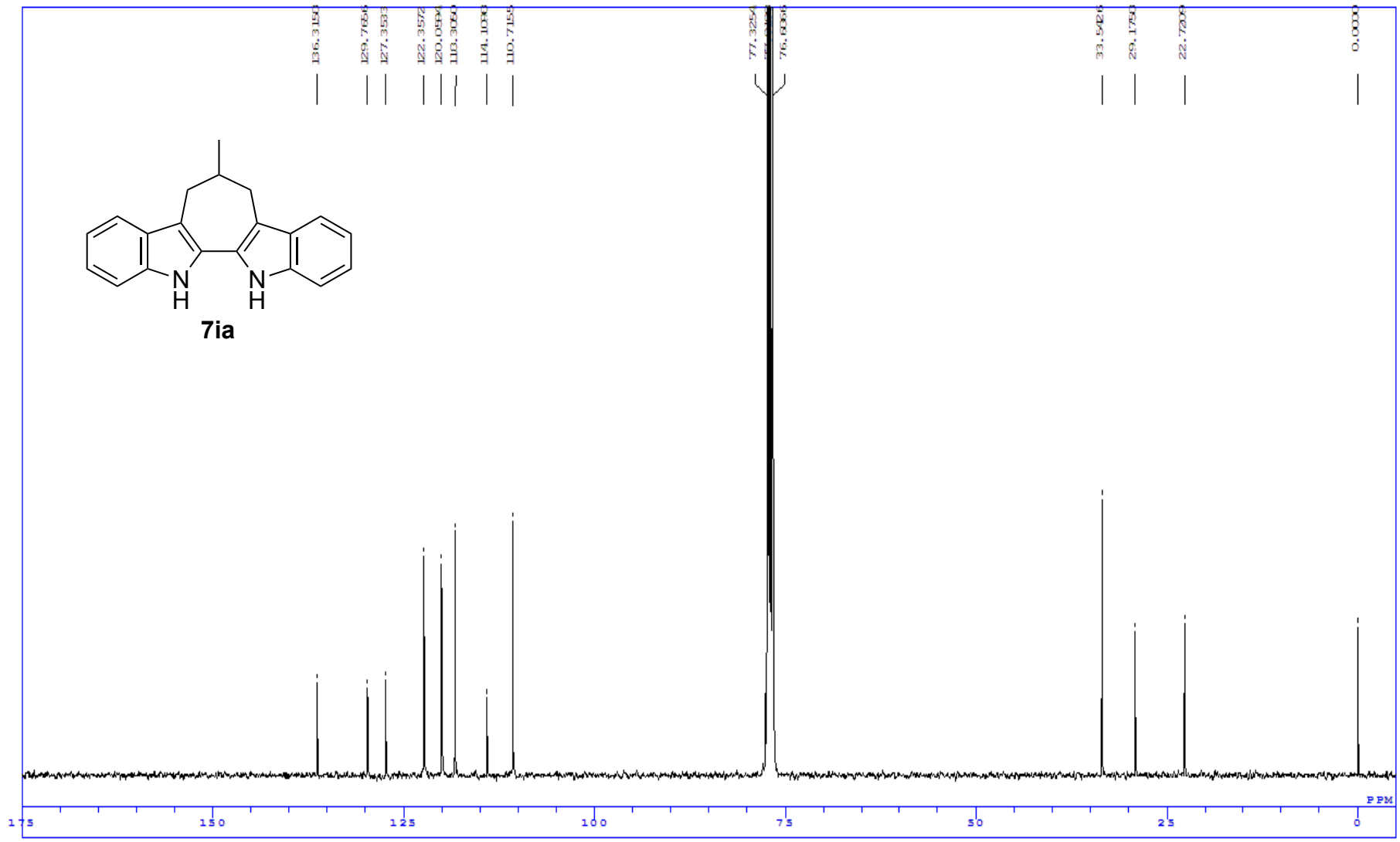


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7ia** in $CDCl_3$.

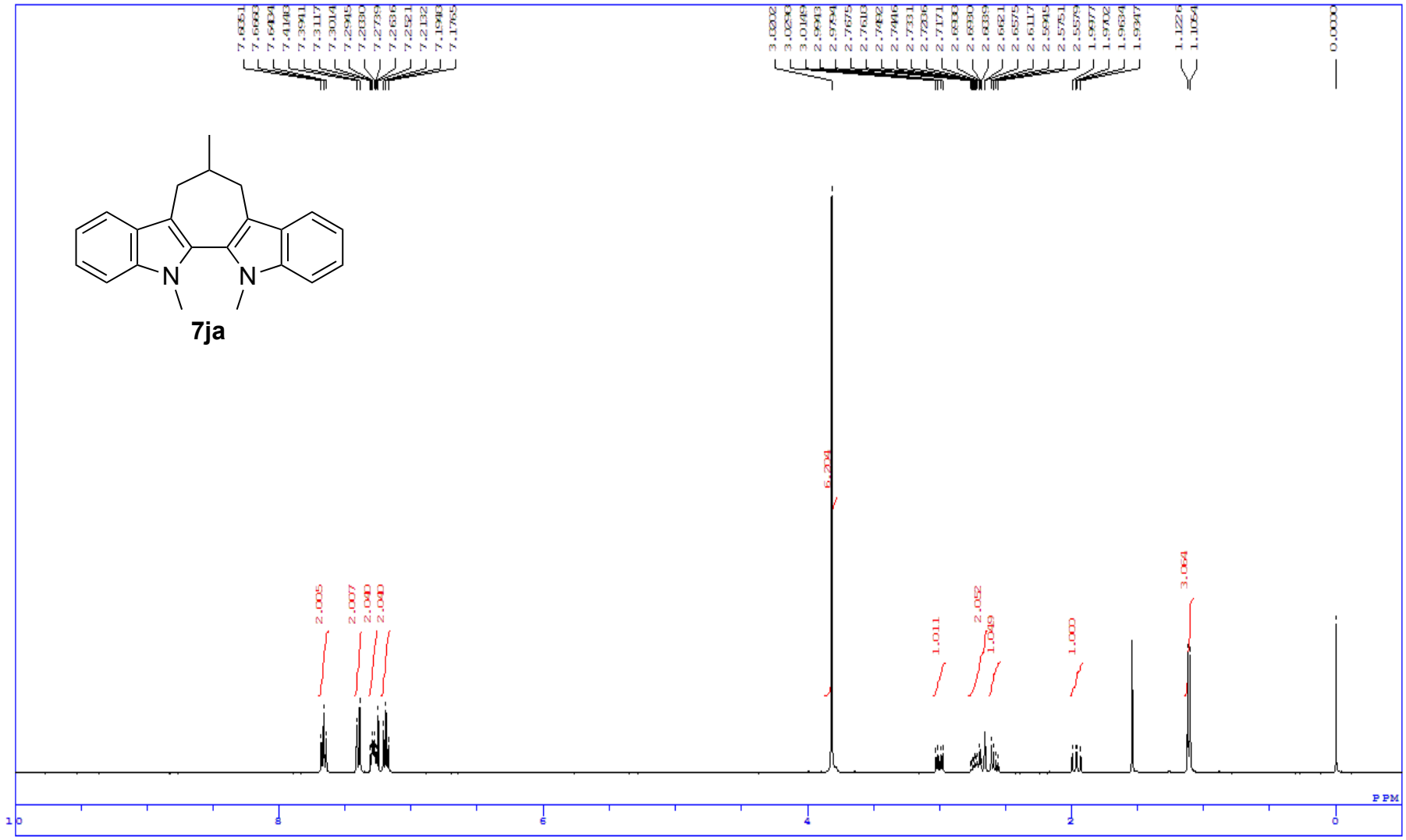


Figure S29. ^{1}H NMR spectrum of compound **7ja** in $CDCl_3$.

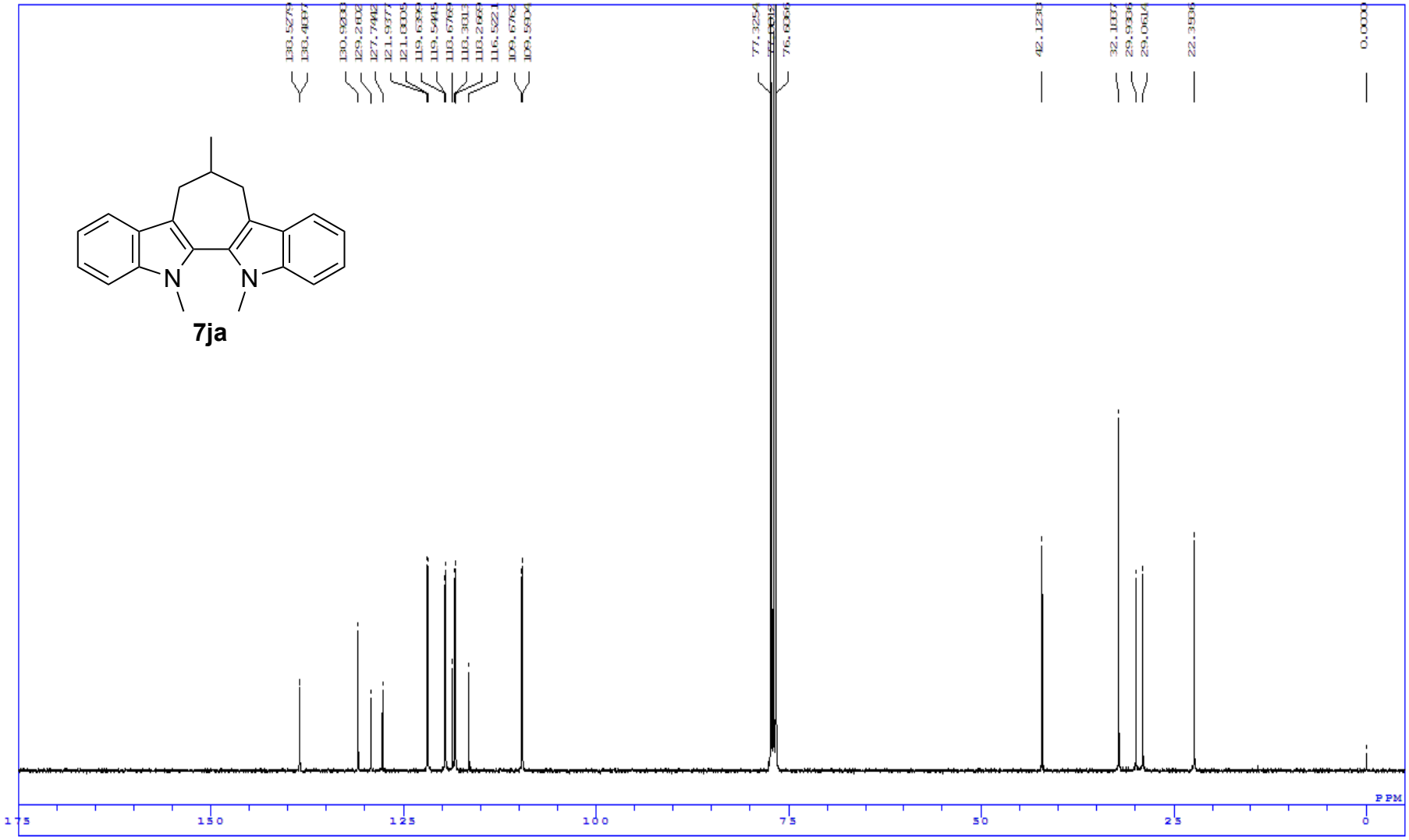


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7ja** in $CDCl_3$.

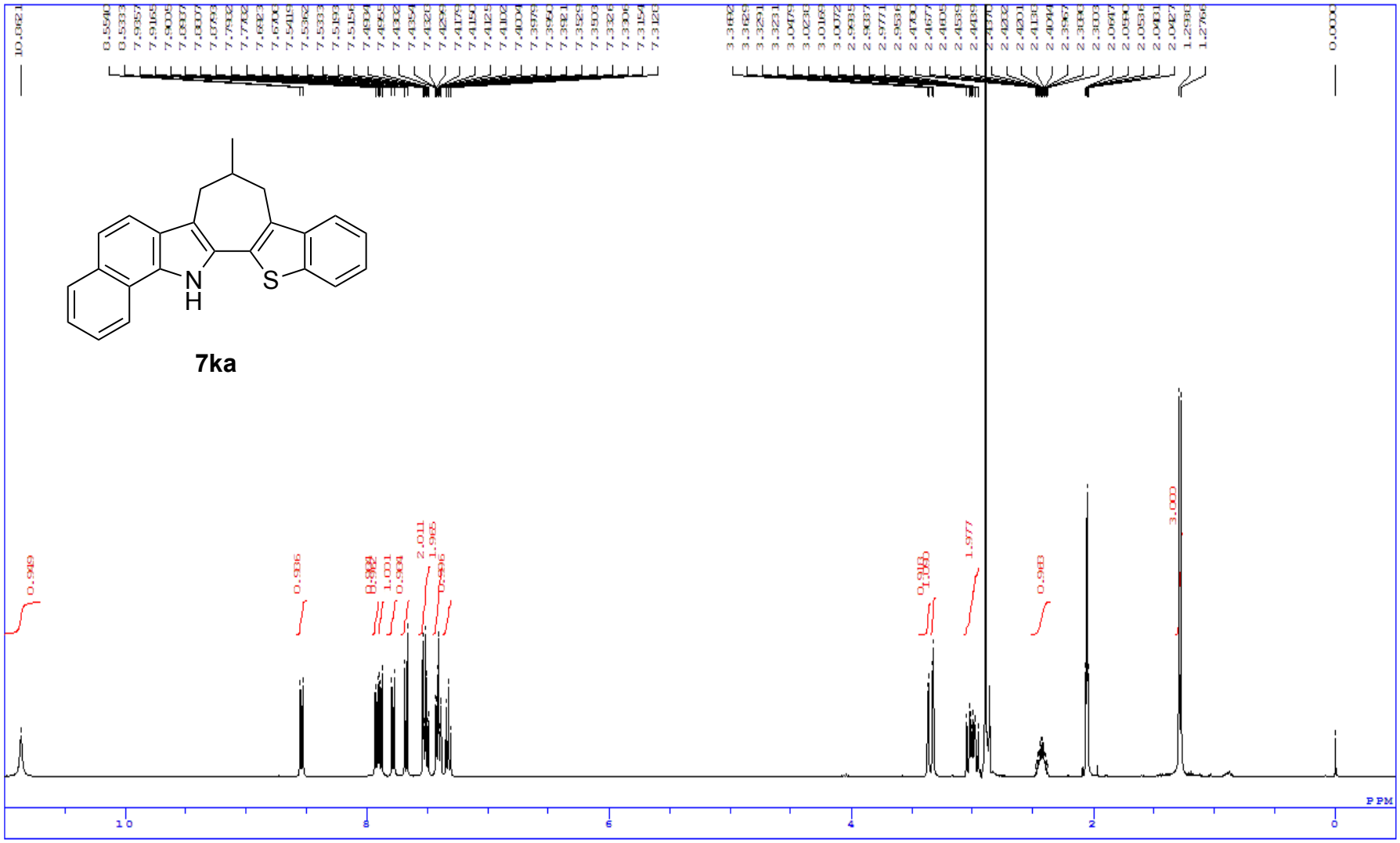


Figure S31. ^{1}H NMR spectrum of compound **7ka** in acetone-d_6.

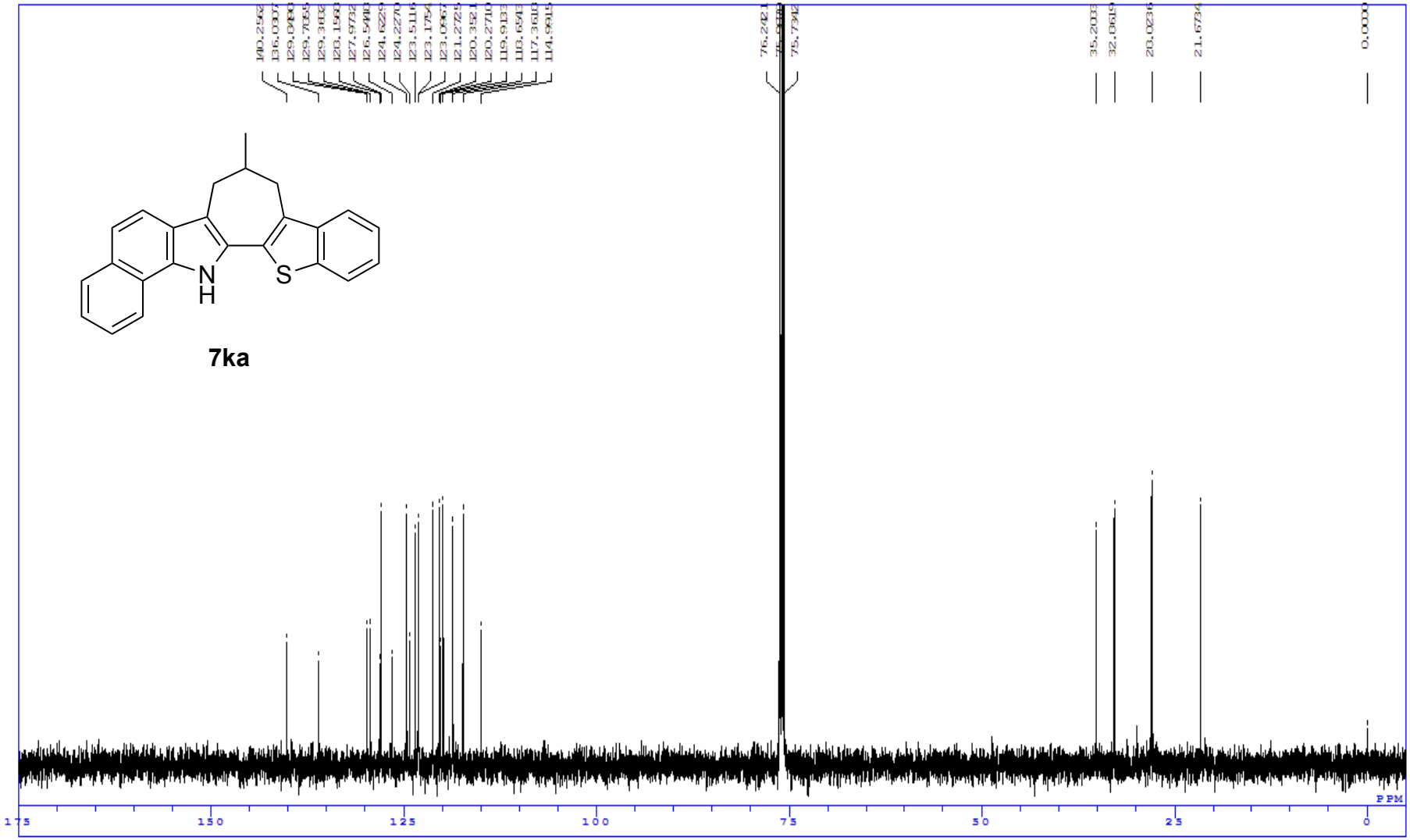


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7ka** in $CDCl_3$.

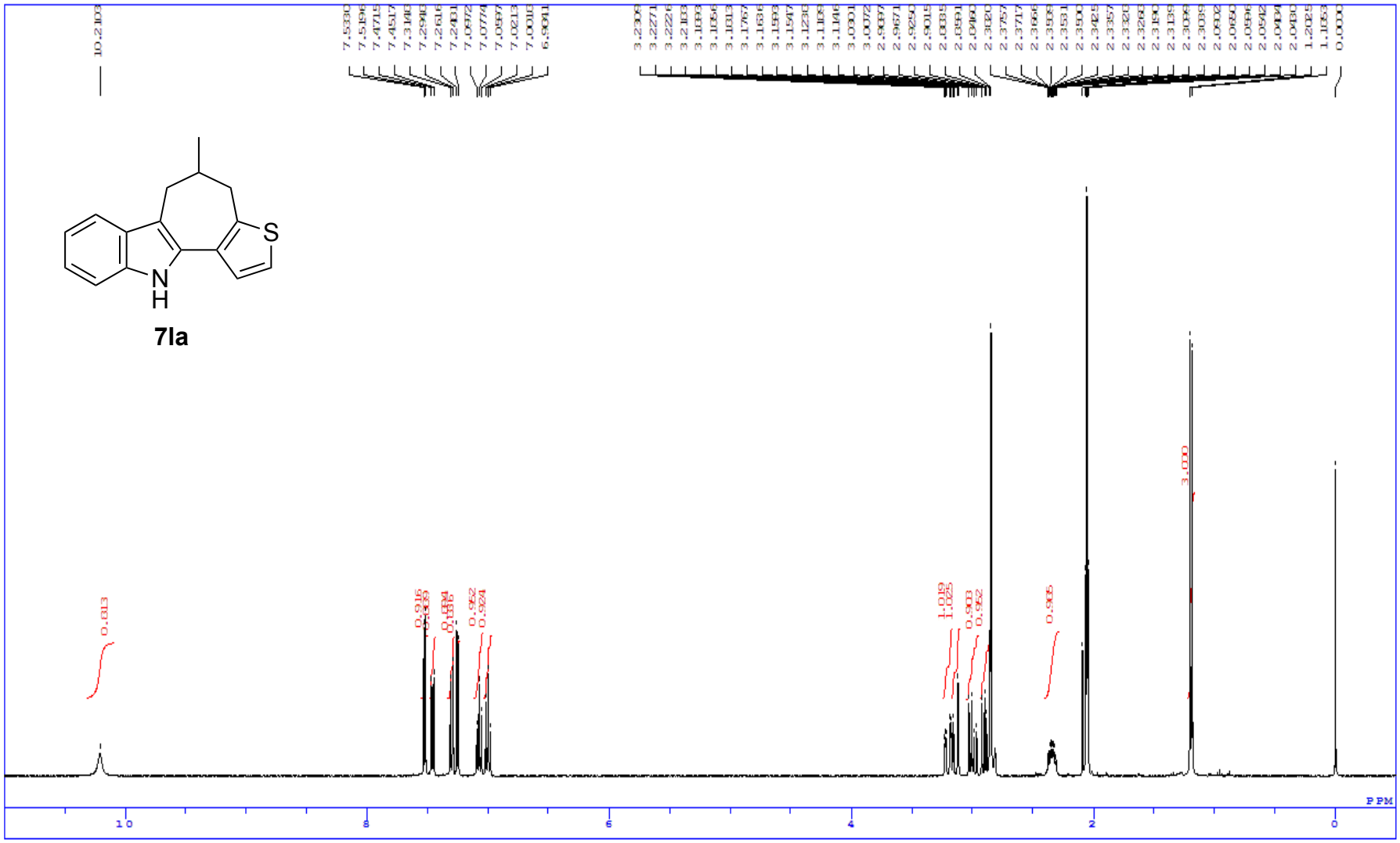


Figure S33. ^{1}H NMR spectrum of compound **7la** in acetone-d_6.

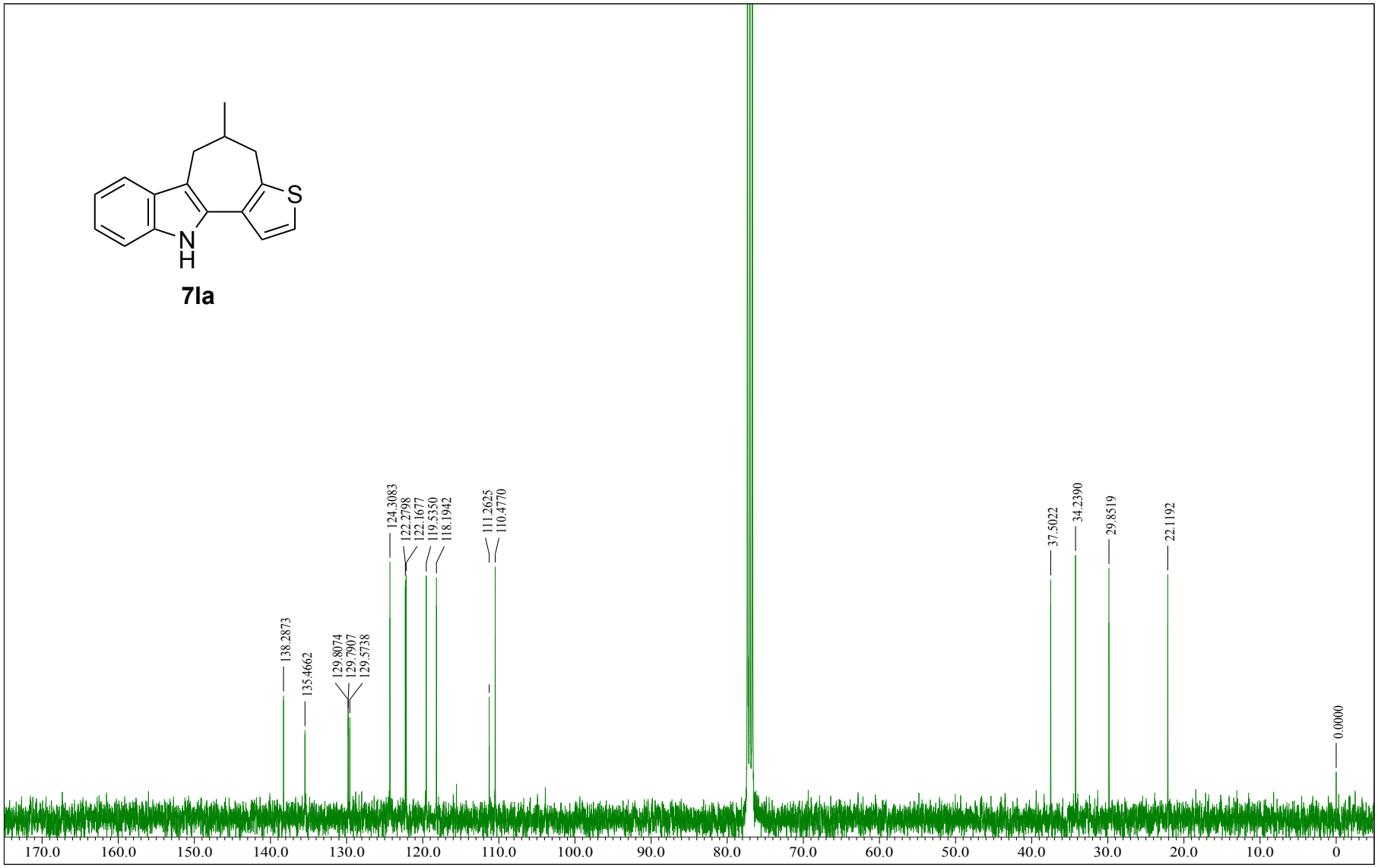


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7la** in $CDCl_3$.

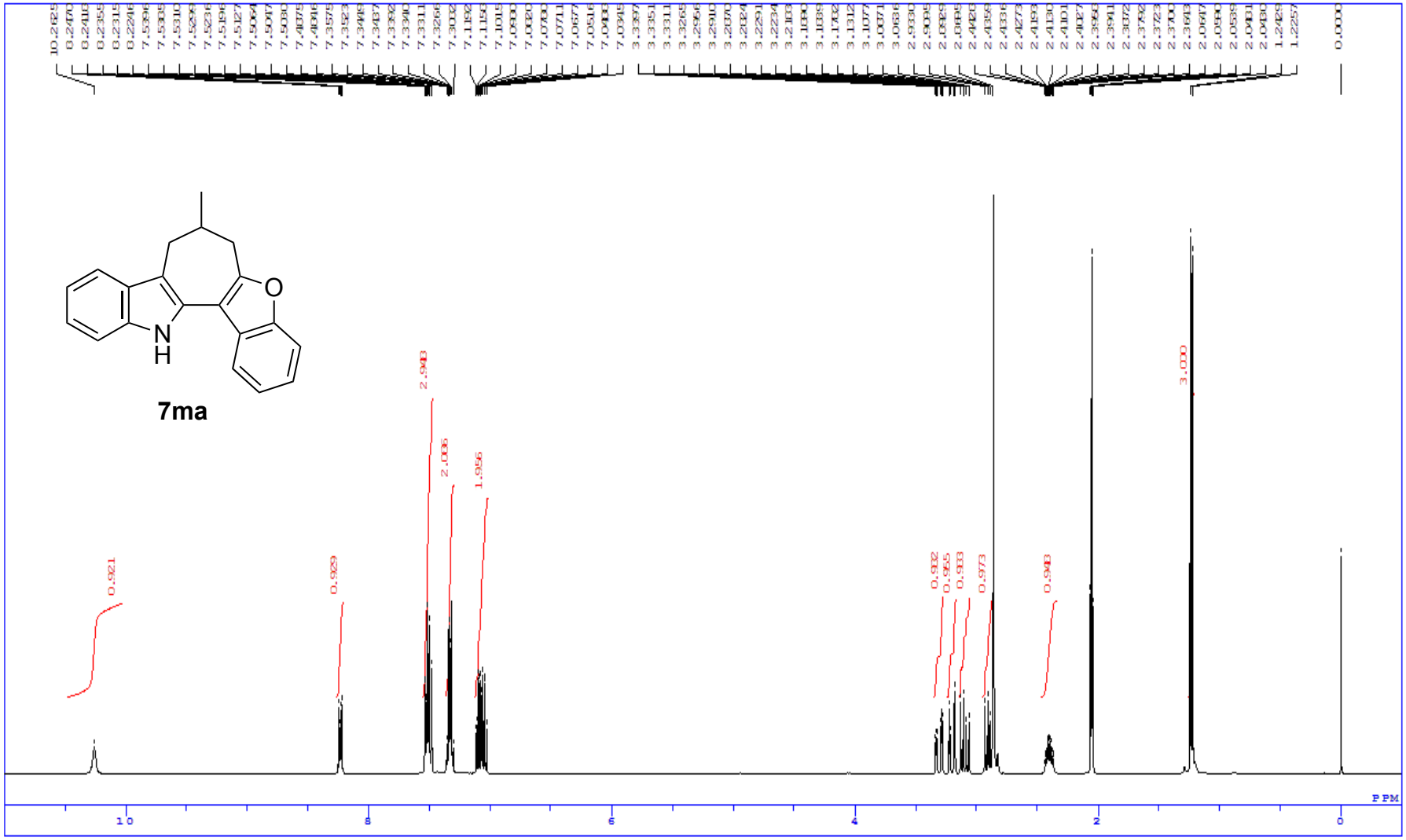


Figure S35. ^{1}H NMR spectrum of compound **7ma** in acetone-d_6.

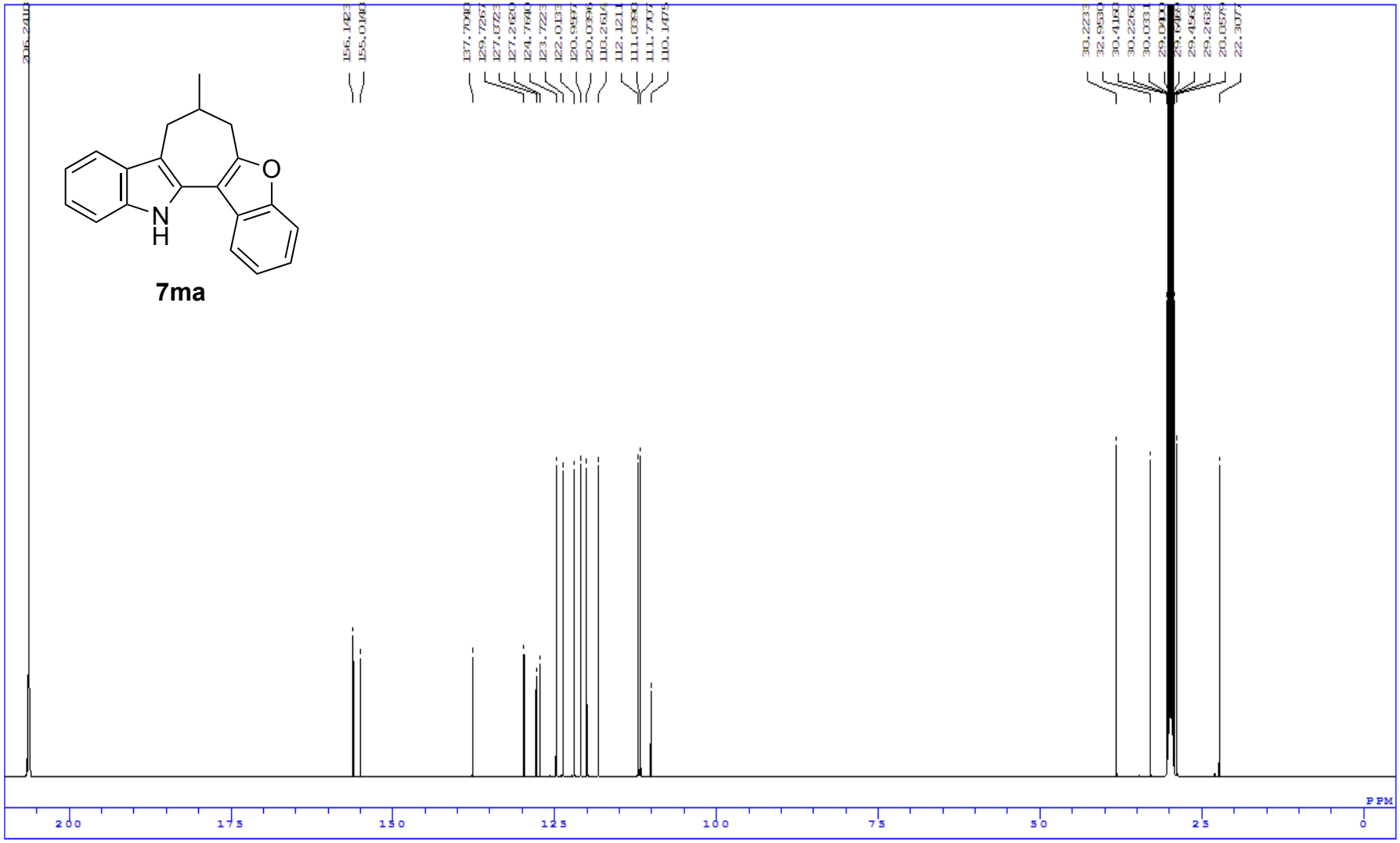


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7ma** in acetone-d_6.

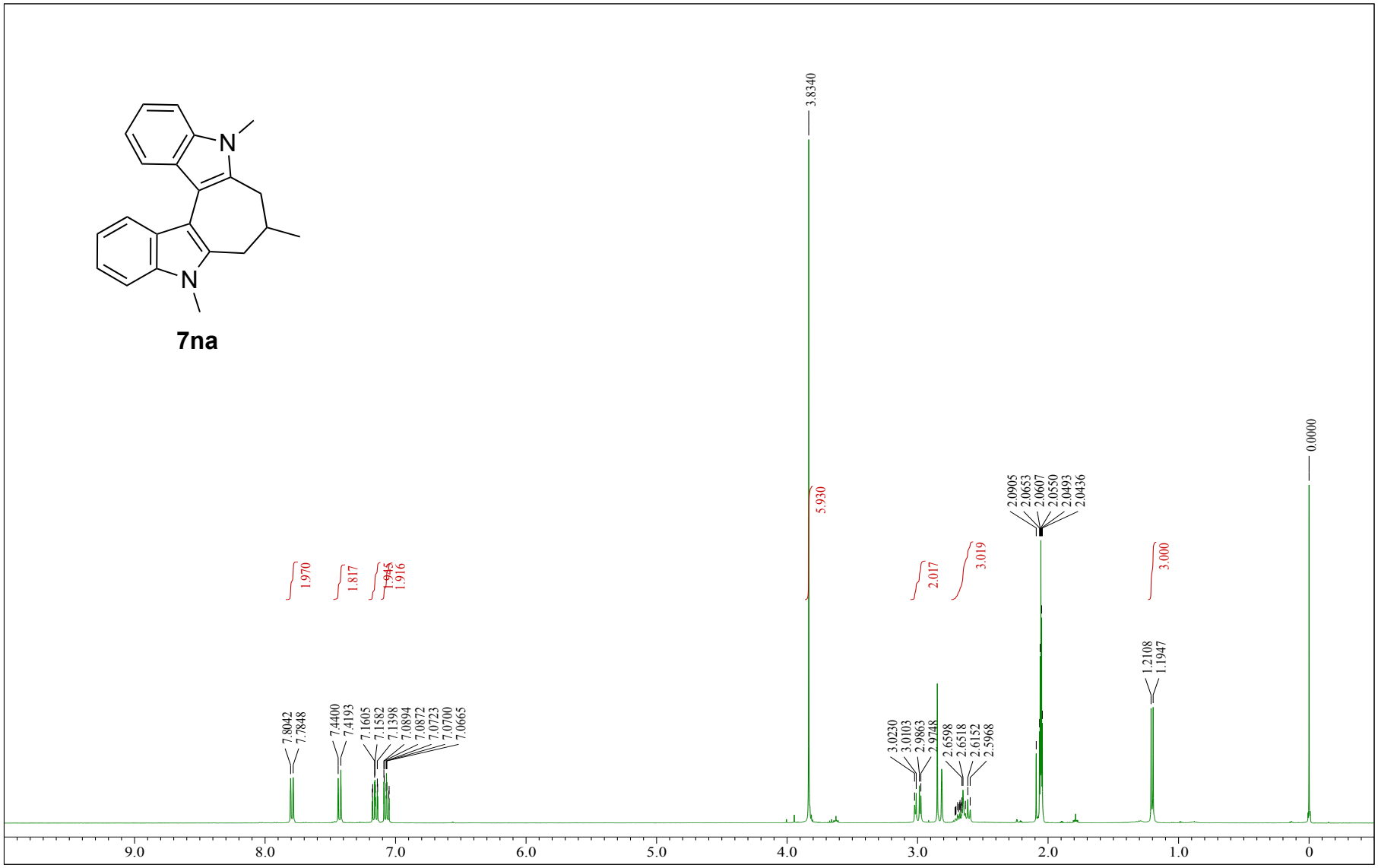


Figure S37. ^{1}H NMR spectrum of compound **7na** in acetone-d_6.

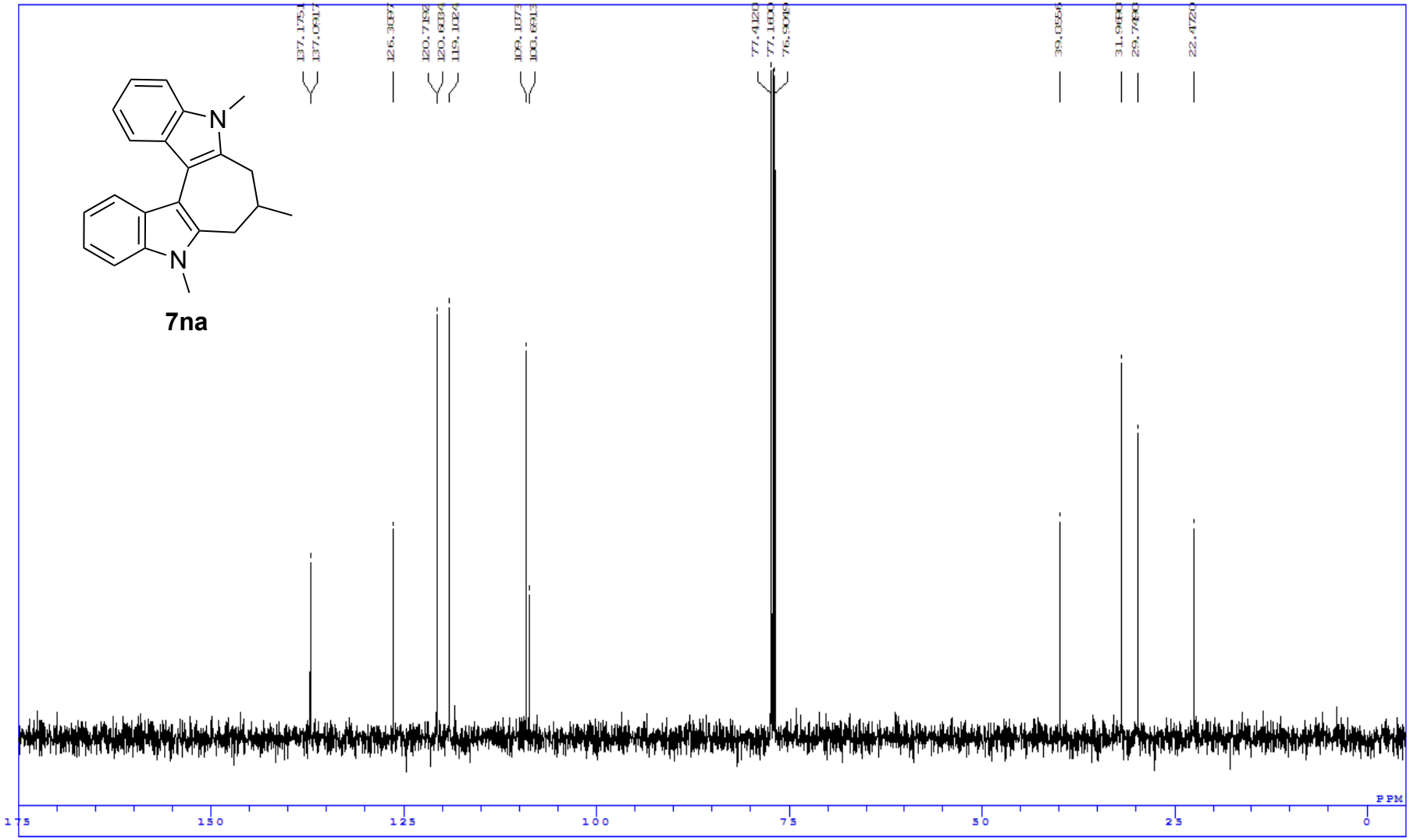


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7na** in $CDCl_3$.

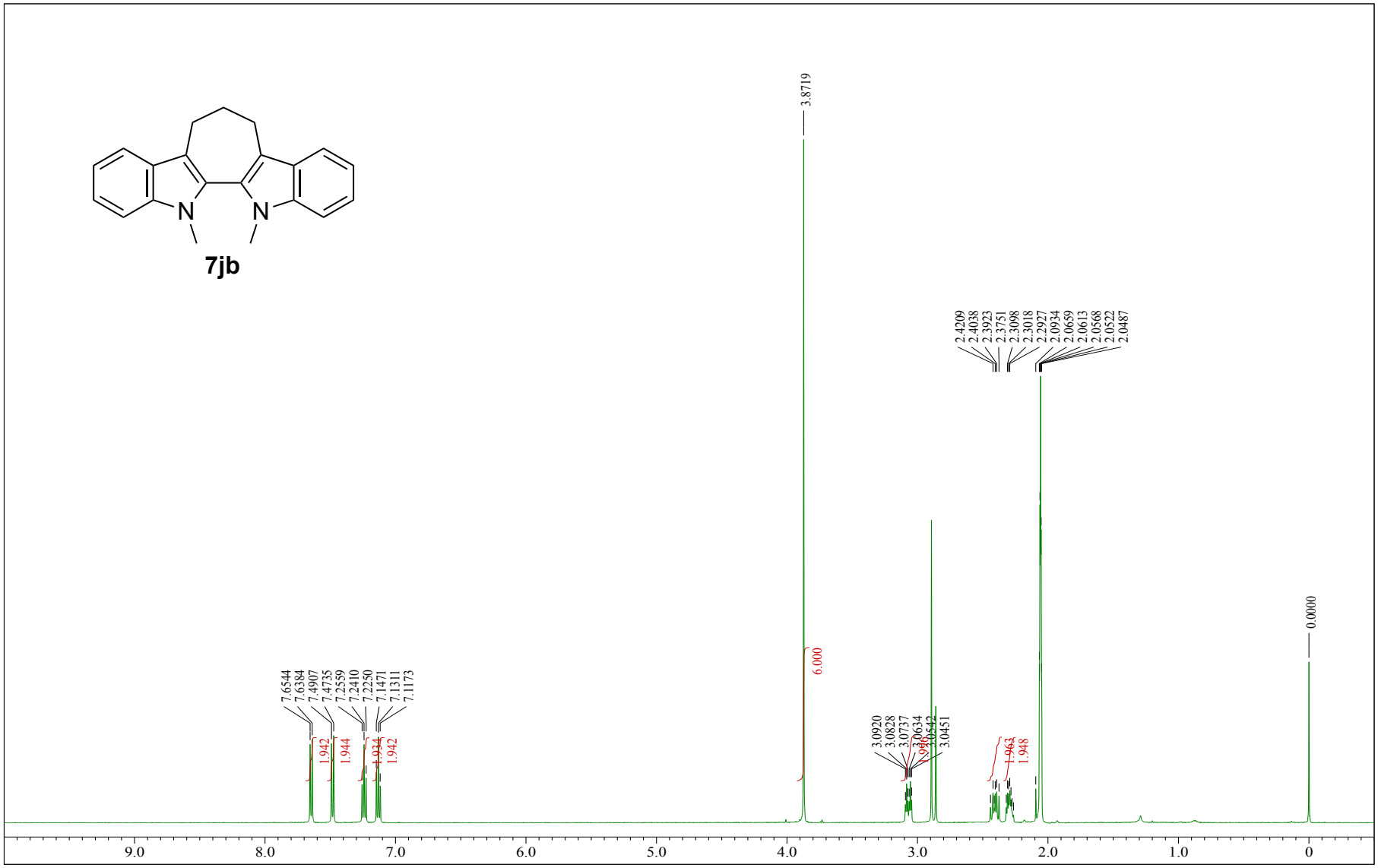


Figure S39. ^{1}H NMR spectrum of compound **7jb** in acetone-d_6.

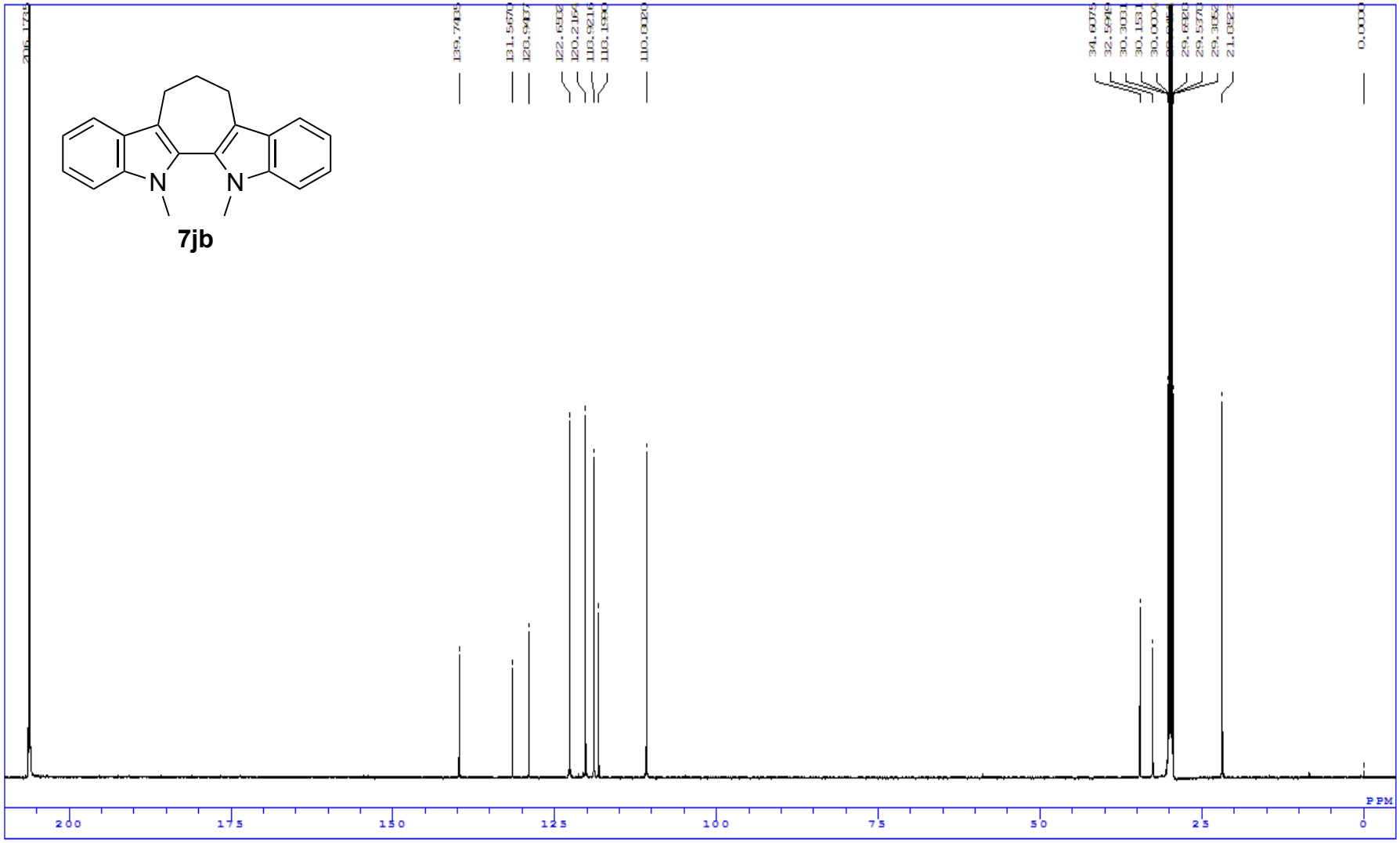


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7jb** in acetone-d_6.

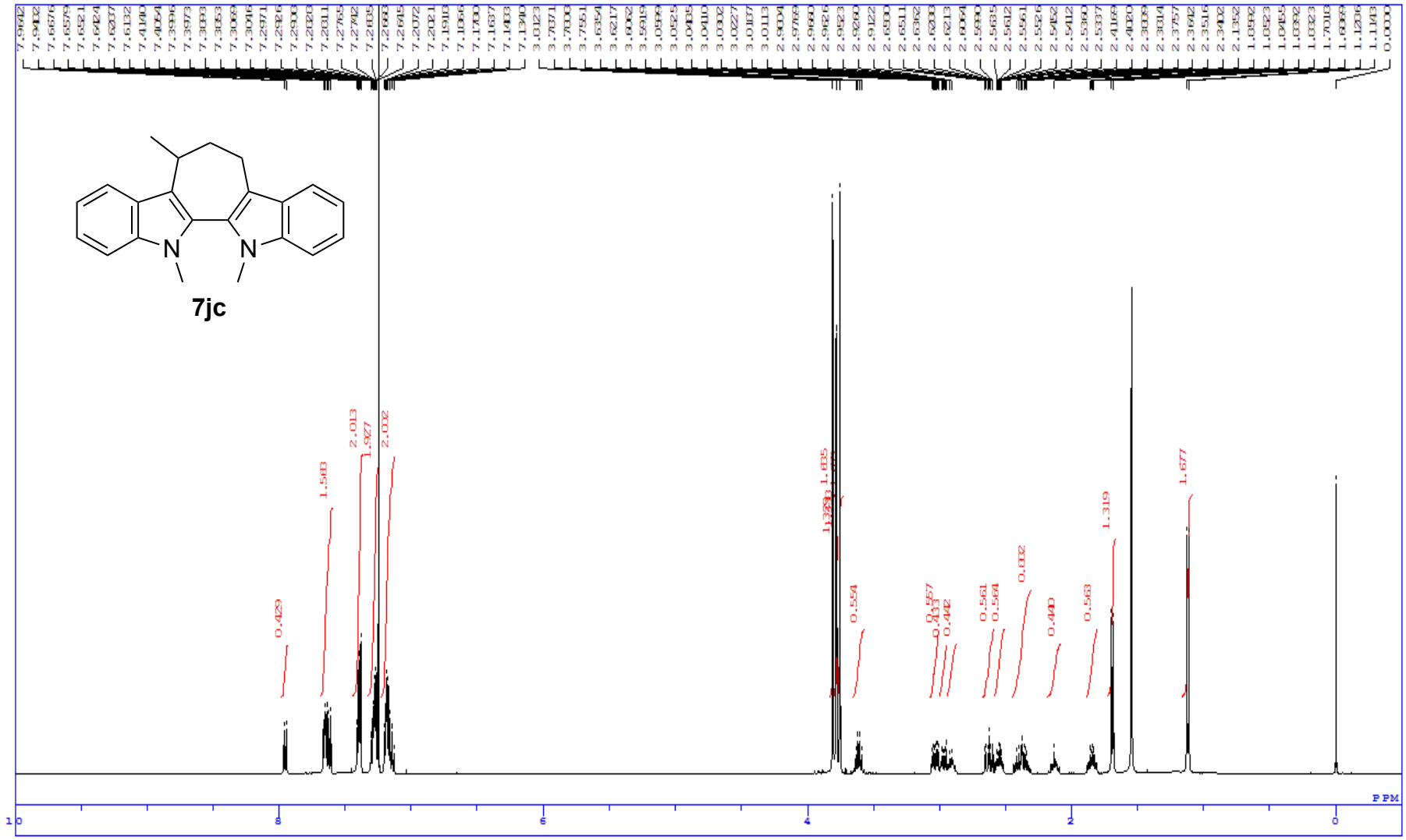


Figure S41. ^{1}H NMR spectrum of compound **7jc** in $CDCl_3$.

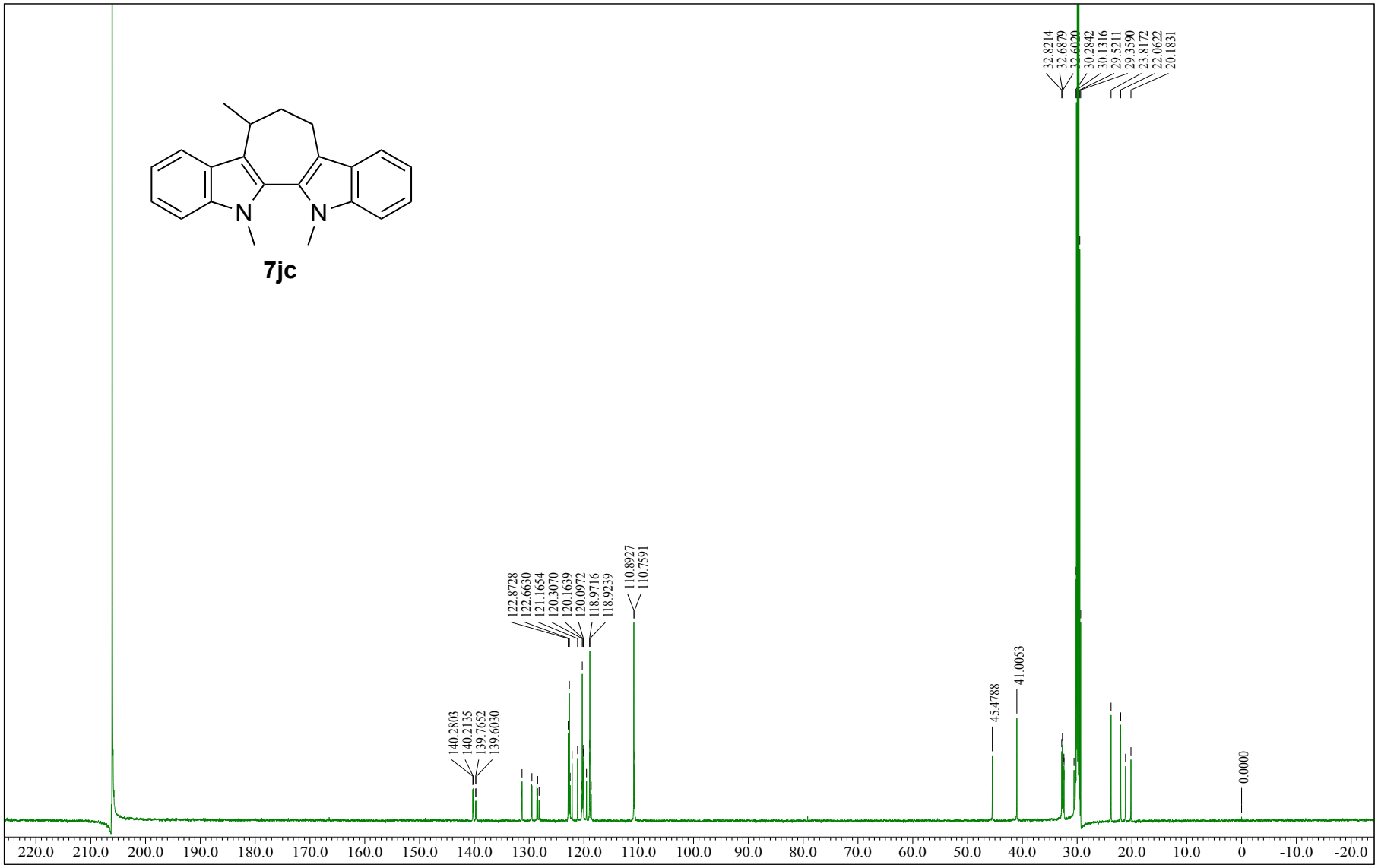


Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7jc** in acetone-d_6.

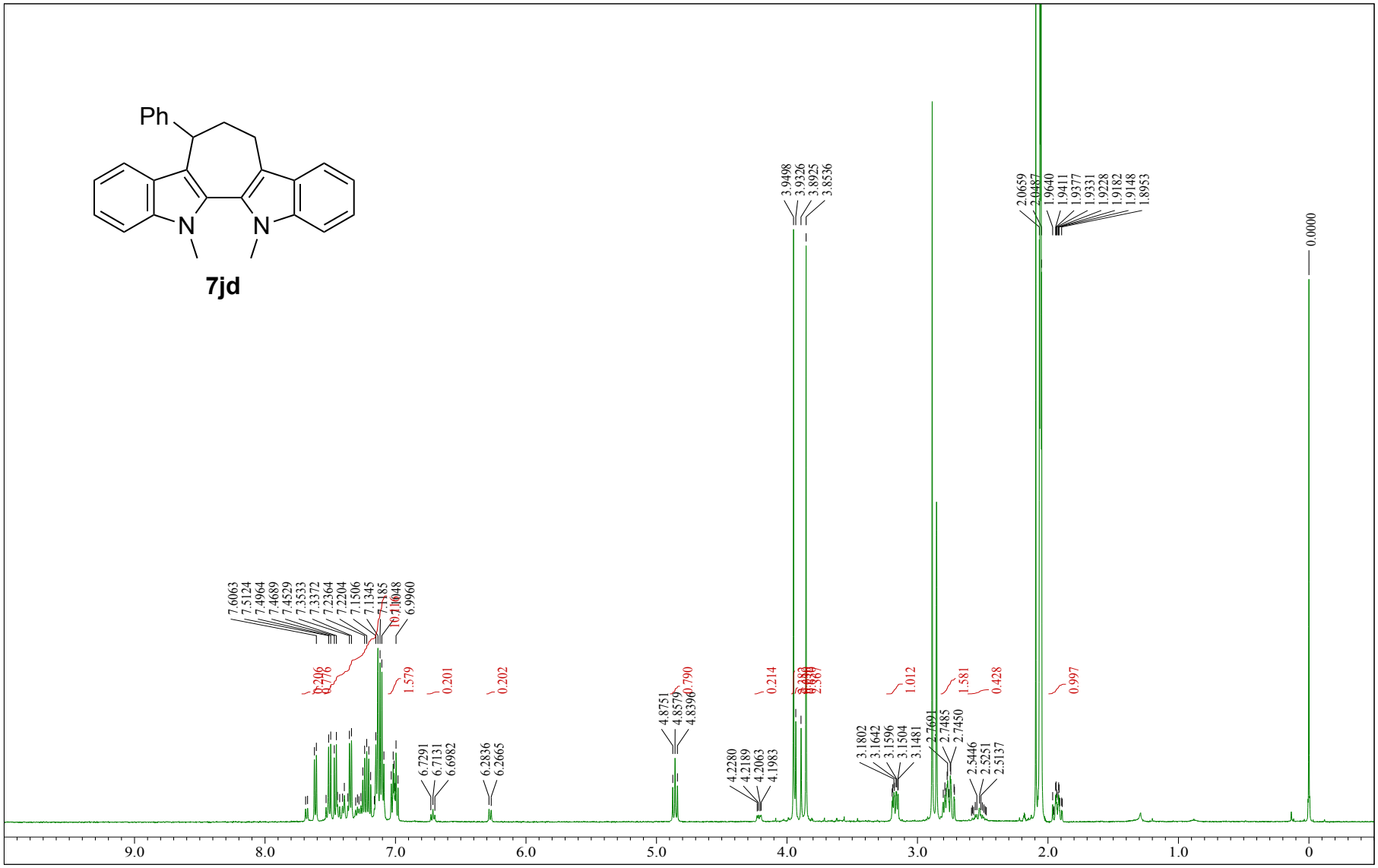


Figure S43. ^{1}H NMR spectrum of compound **7jd** in acetone-d_6.

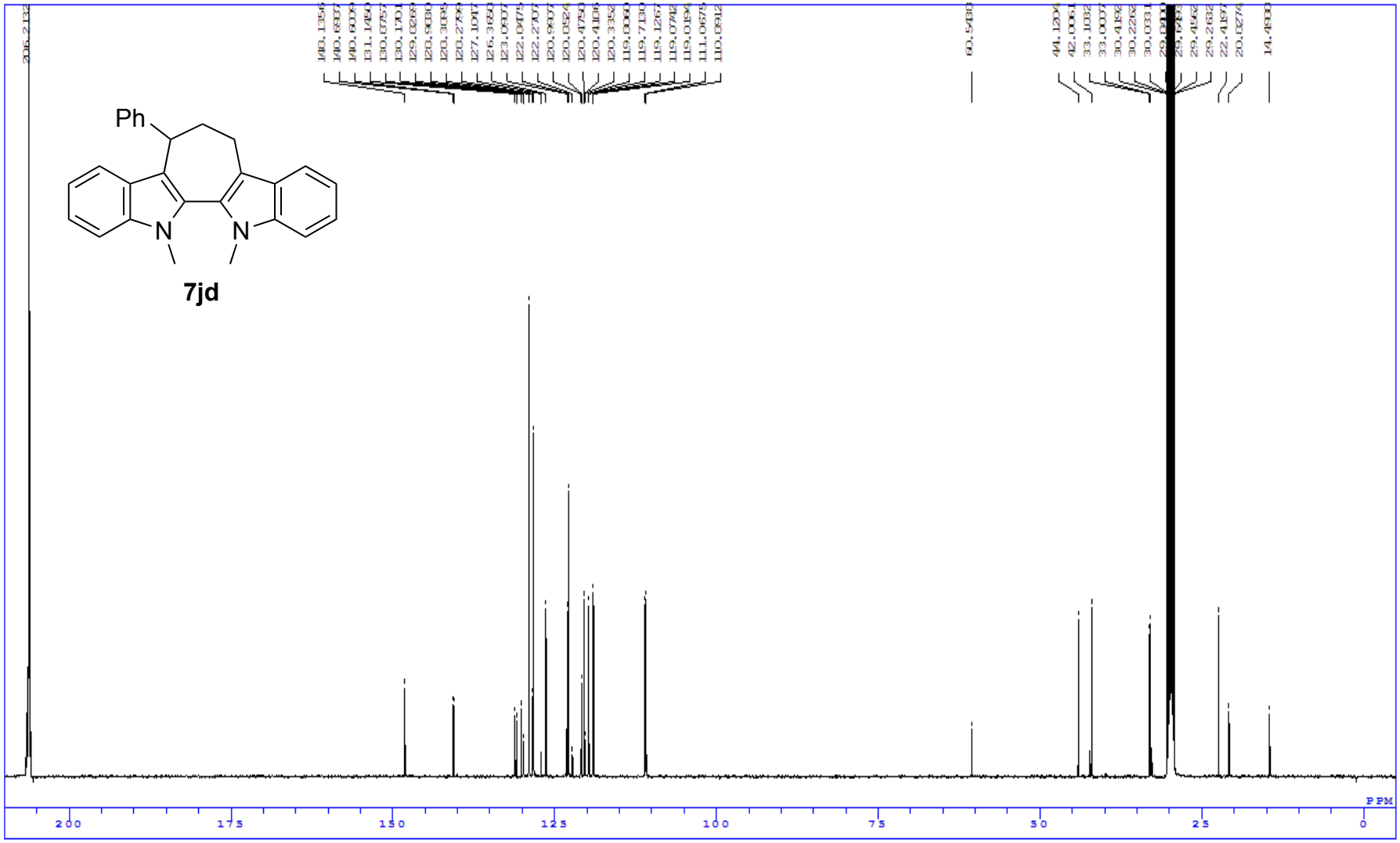


Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7jd** in acetone-d_6.

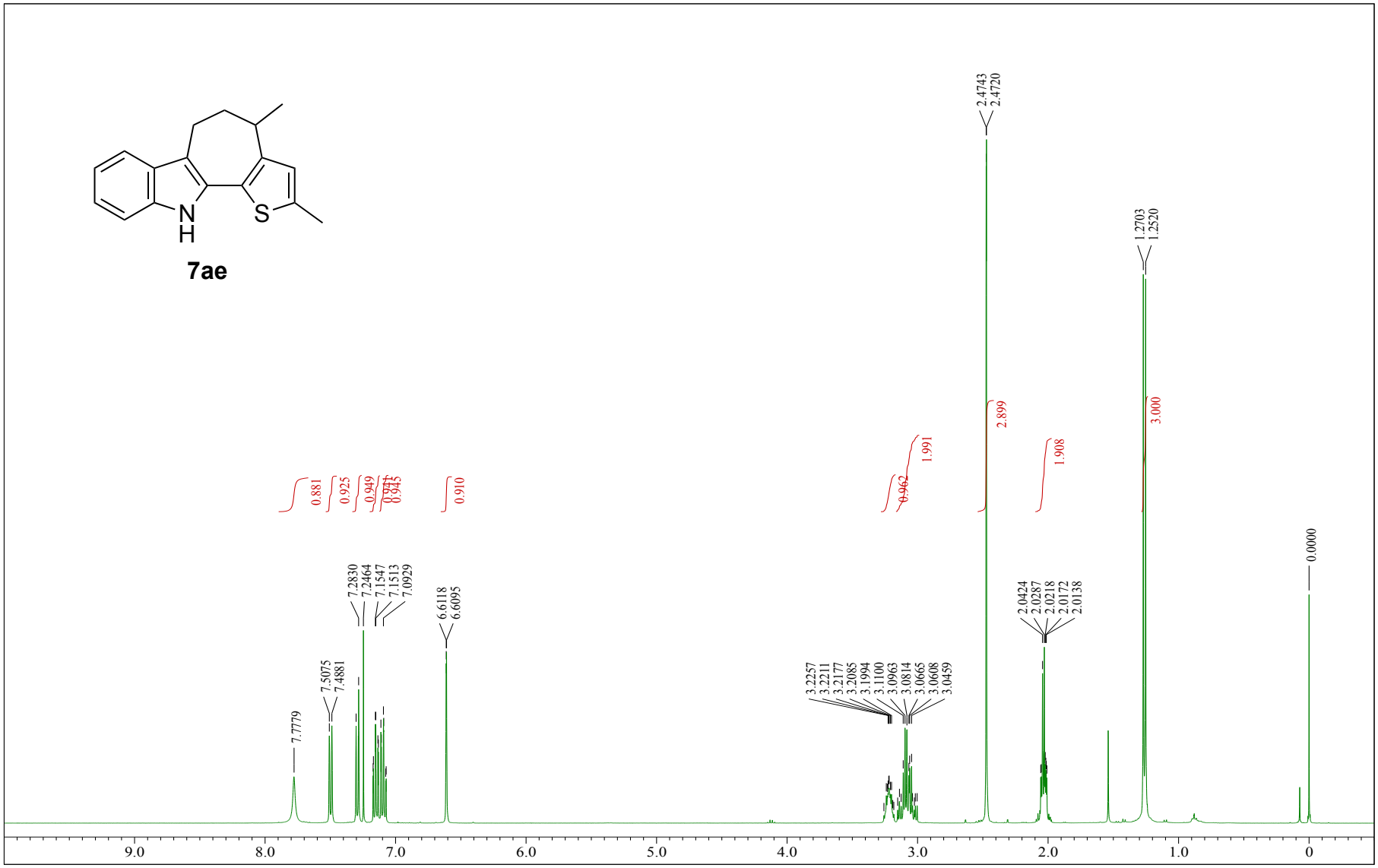


Figure S45. ^{1}H NMR spectrum of compound **7ae** in $CDCl_3$.

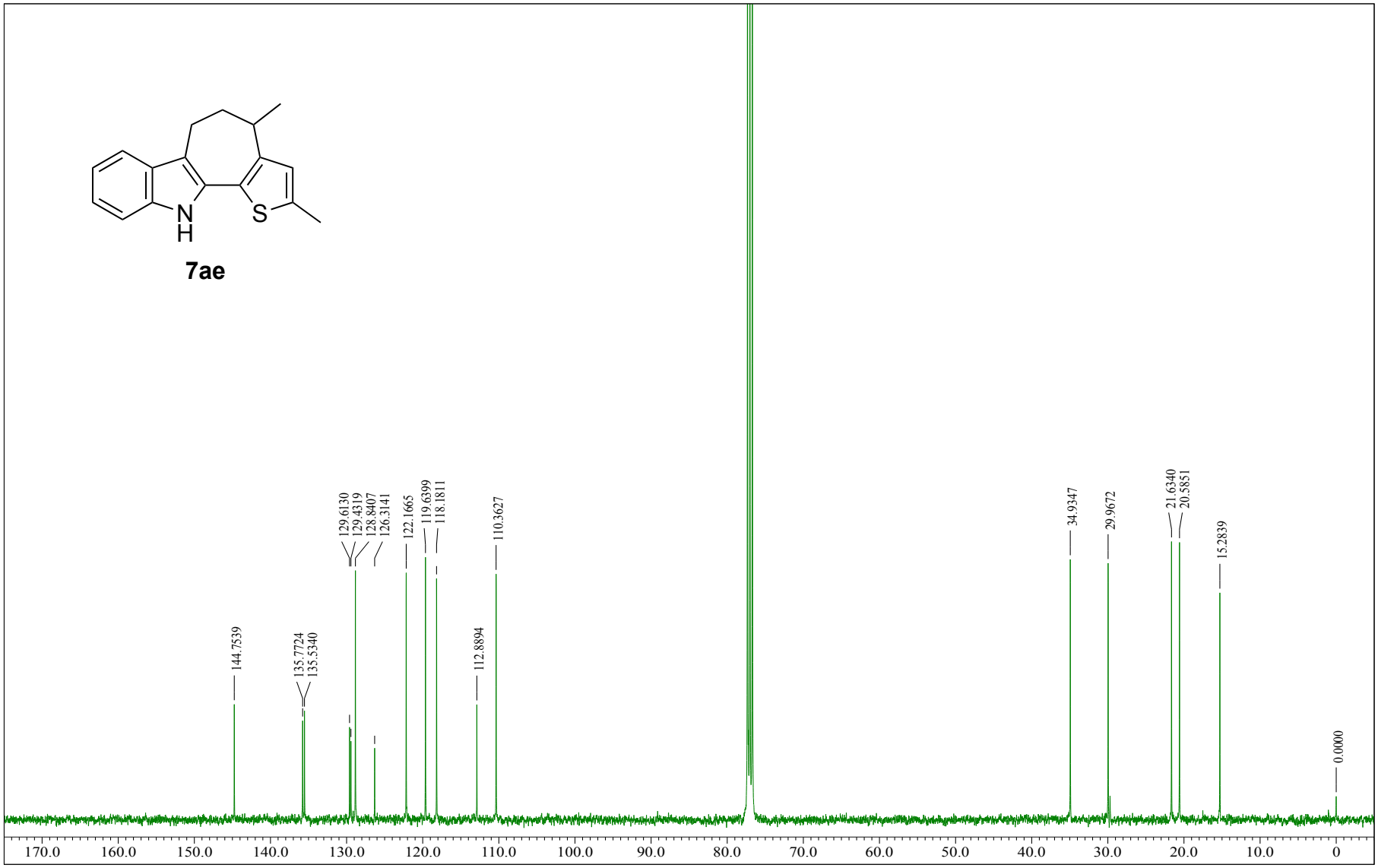


Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7ae** in $CDCl_3$.

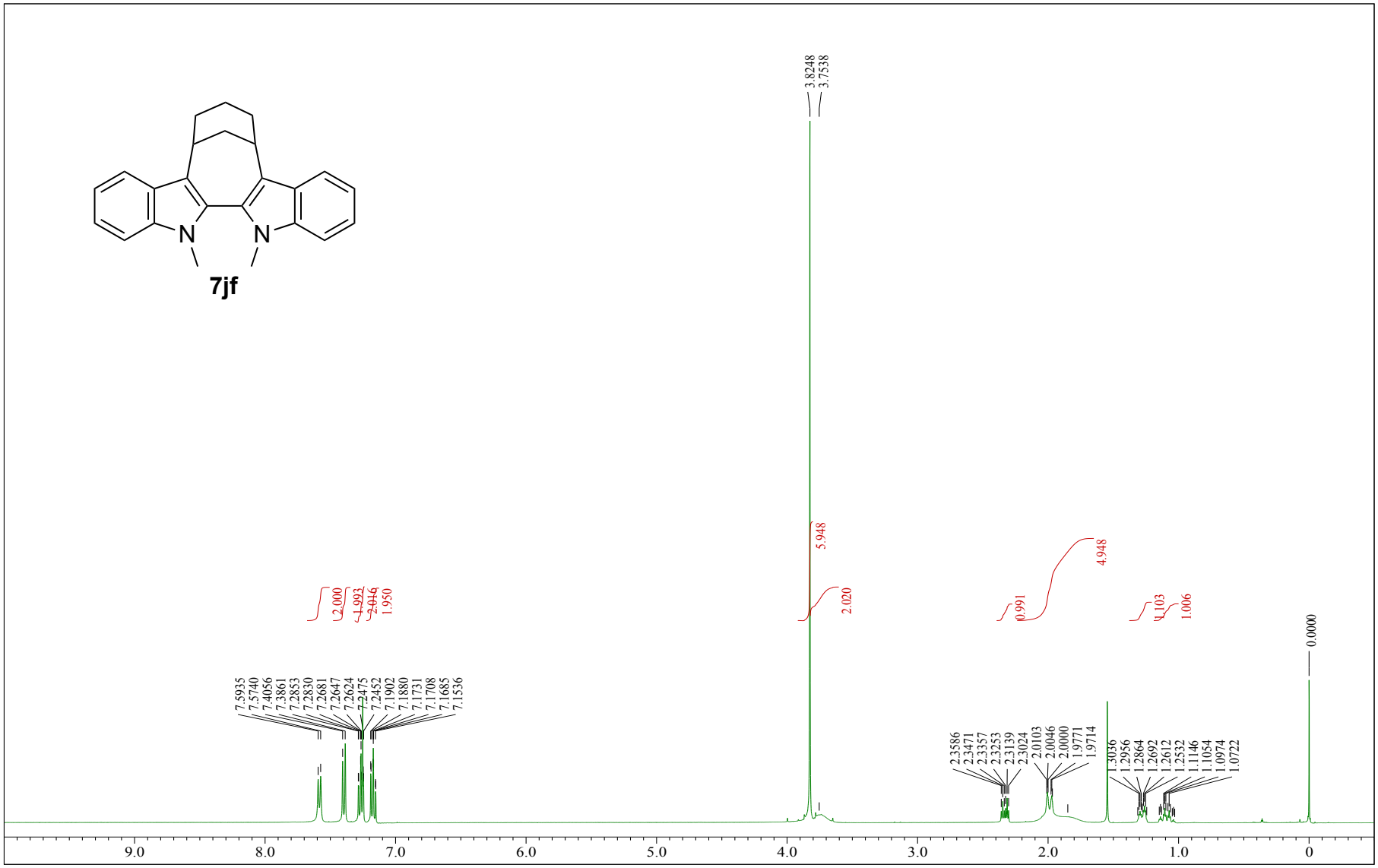


Figure S47. ^{1}H NMR spectrum of compound **7jf** in $CDCl_3$.

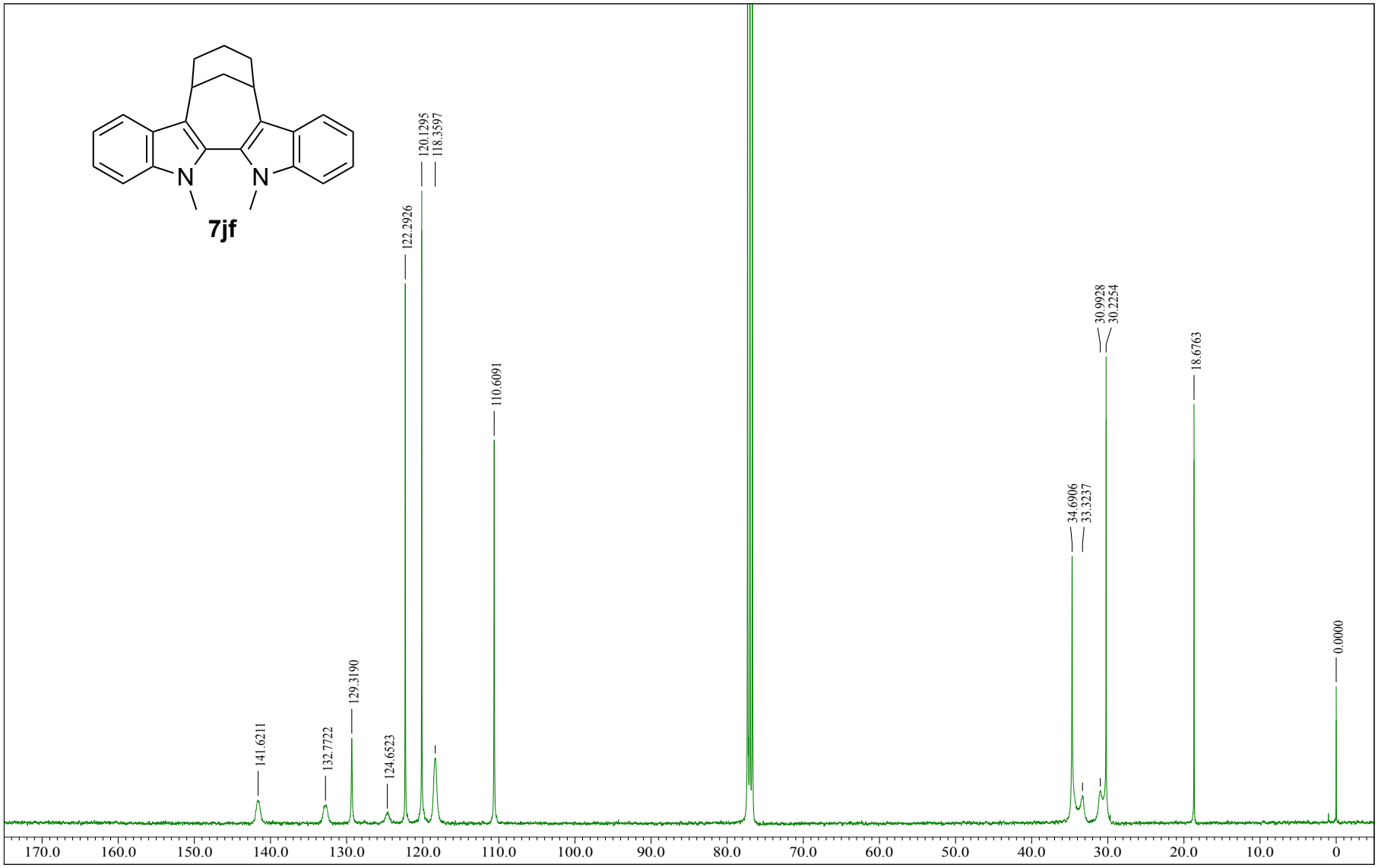


Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7jf** in $CDCl_3$.

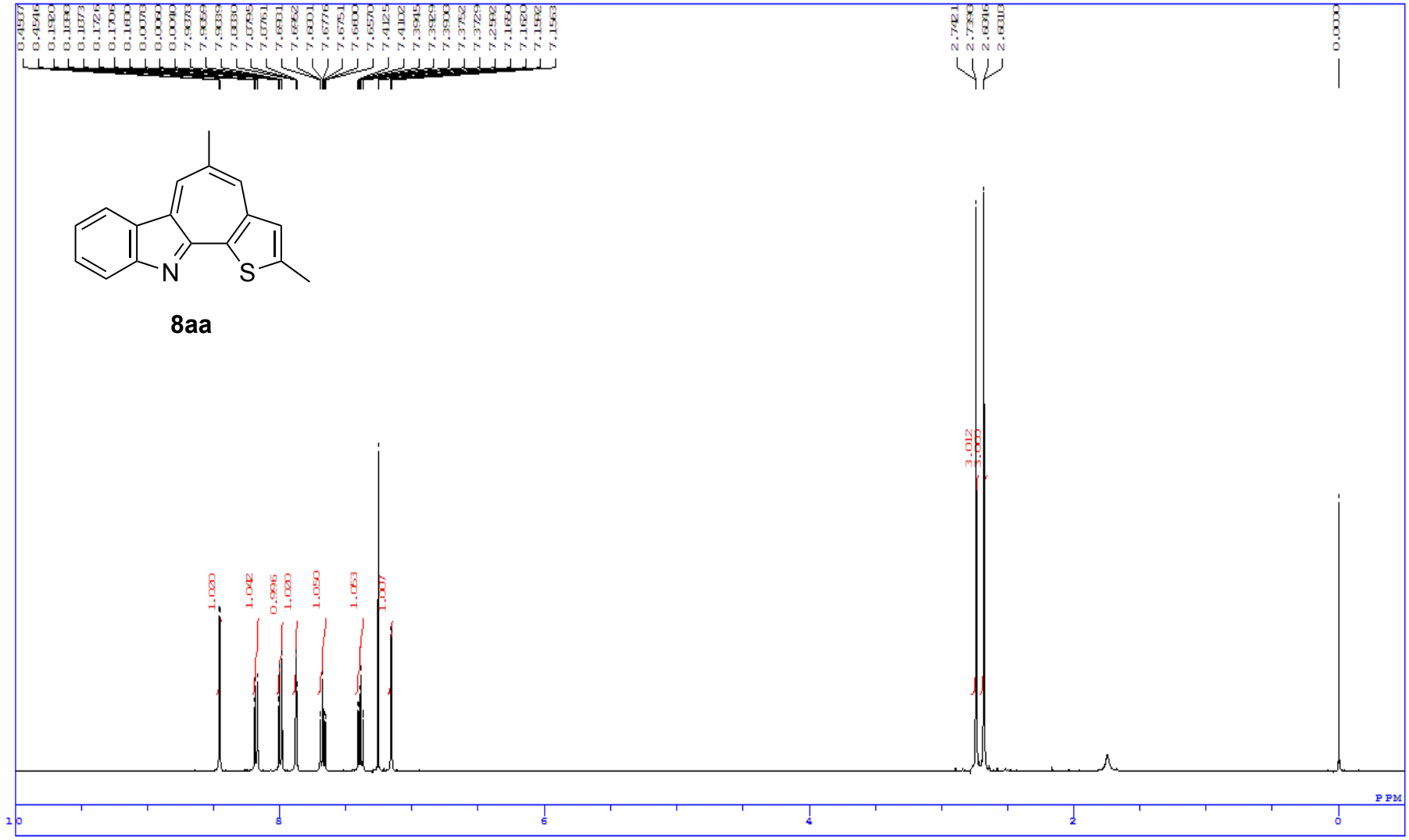


Figure S49. ^{1}H NMR spectrum of compound **8aa** in $CDCl_3$.

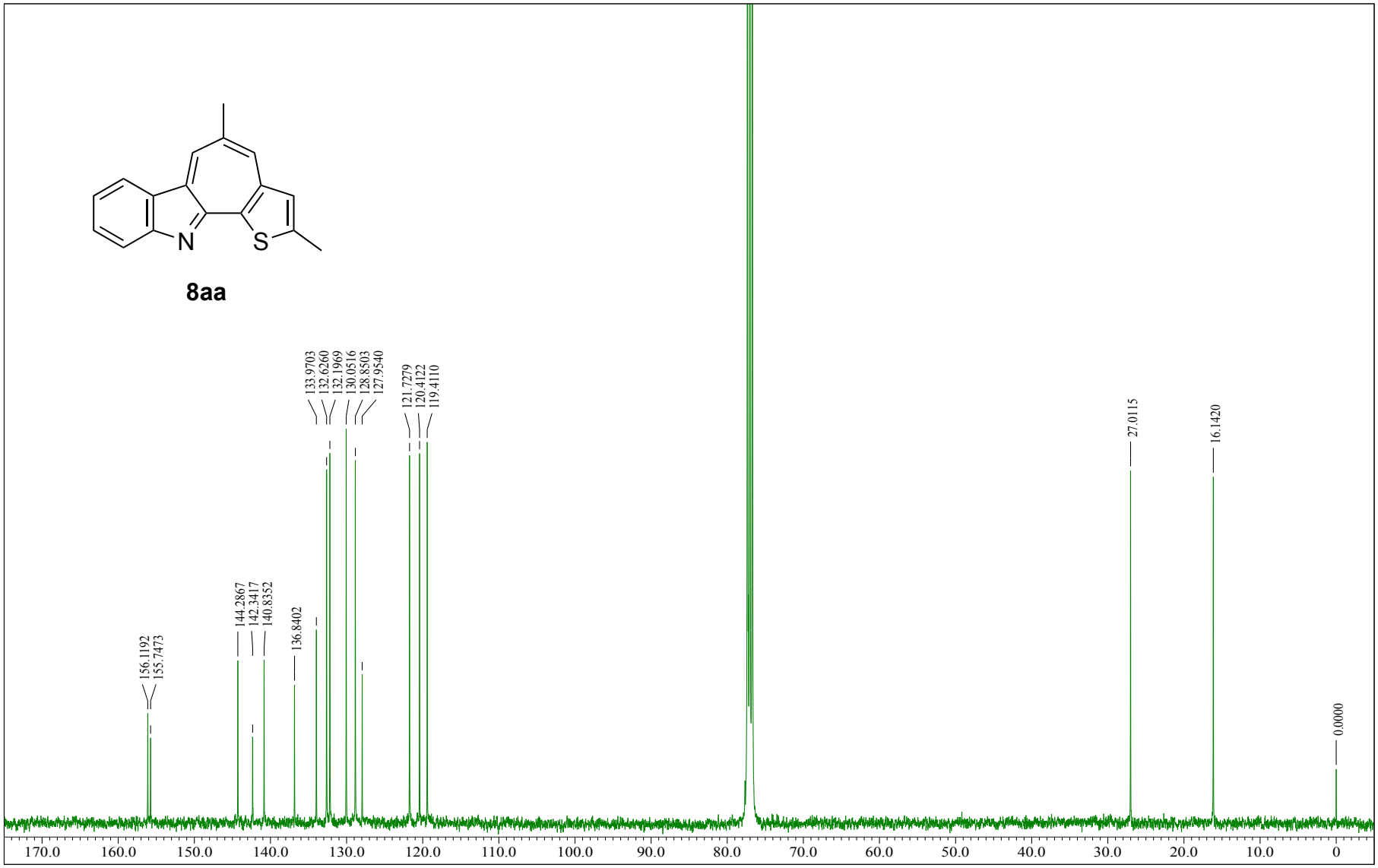


Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8aa** in $CDCl_3$.

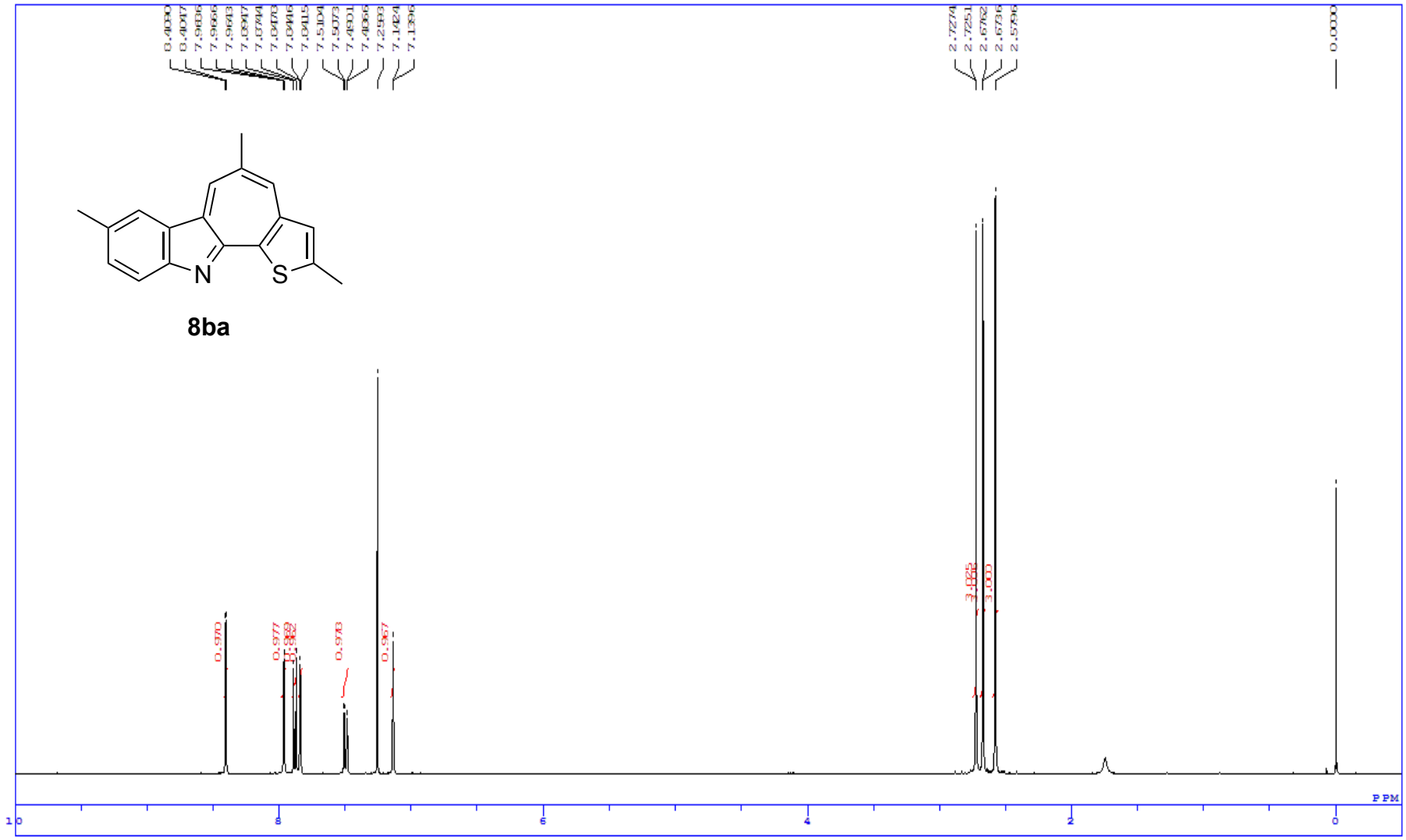


Figure S51. ^{1}H NMR spectrum of compound **8ba** in $CDCl_3$.

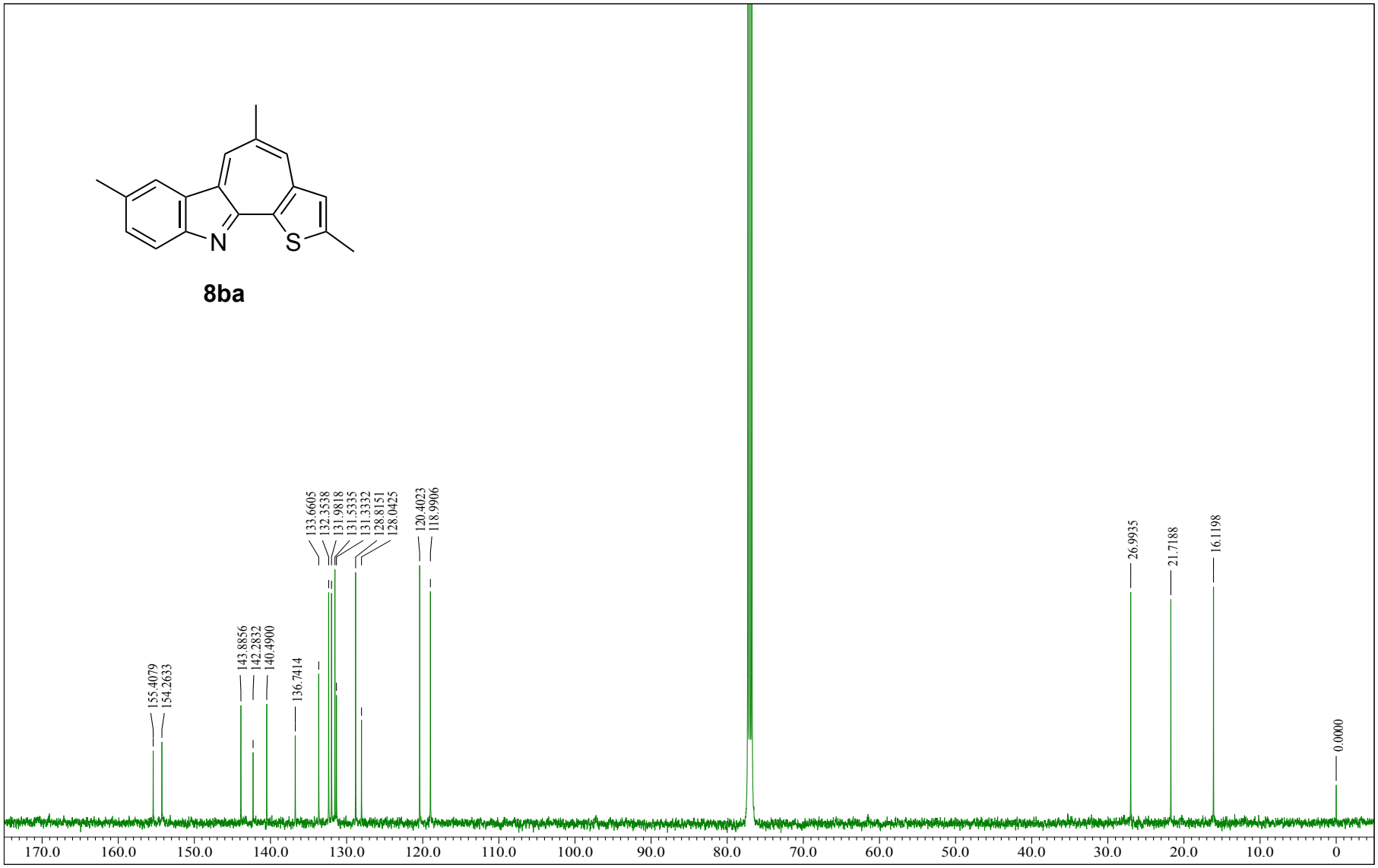


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8ba** in $CDCl_3$.

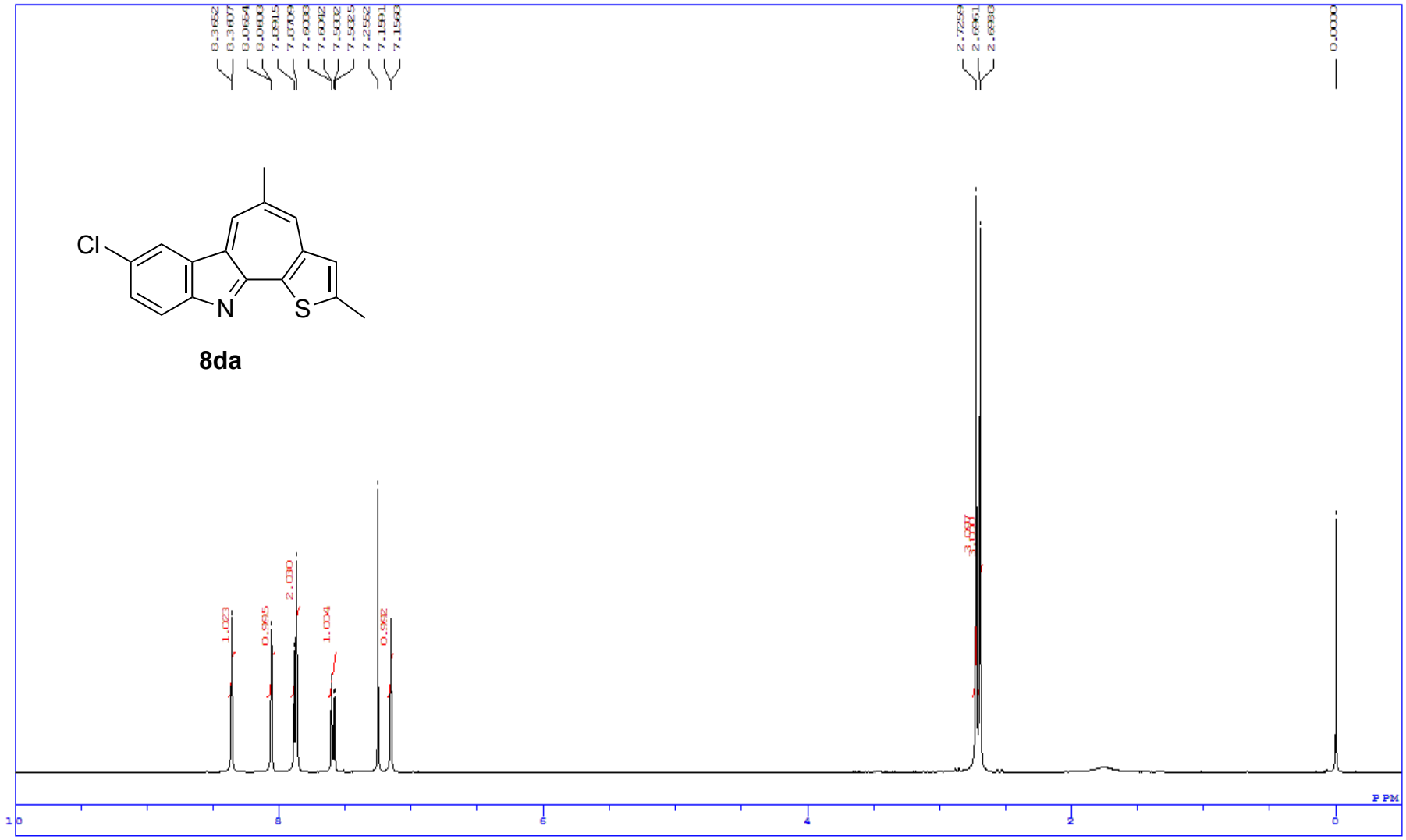


Figure S53. ^{1}H NMR spectrum of compound **8da** in $CDCl_3$.

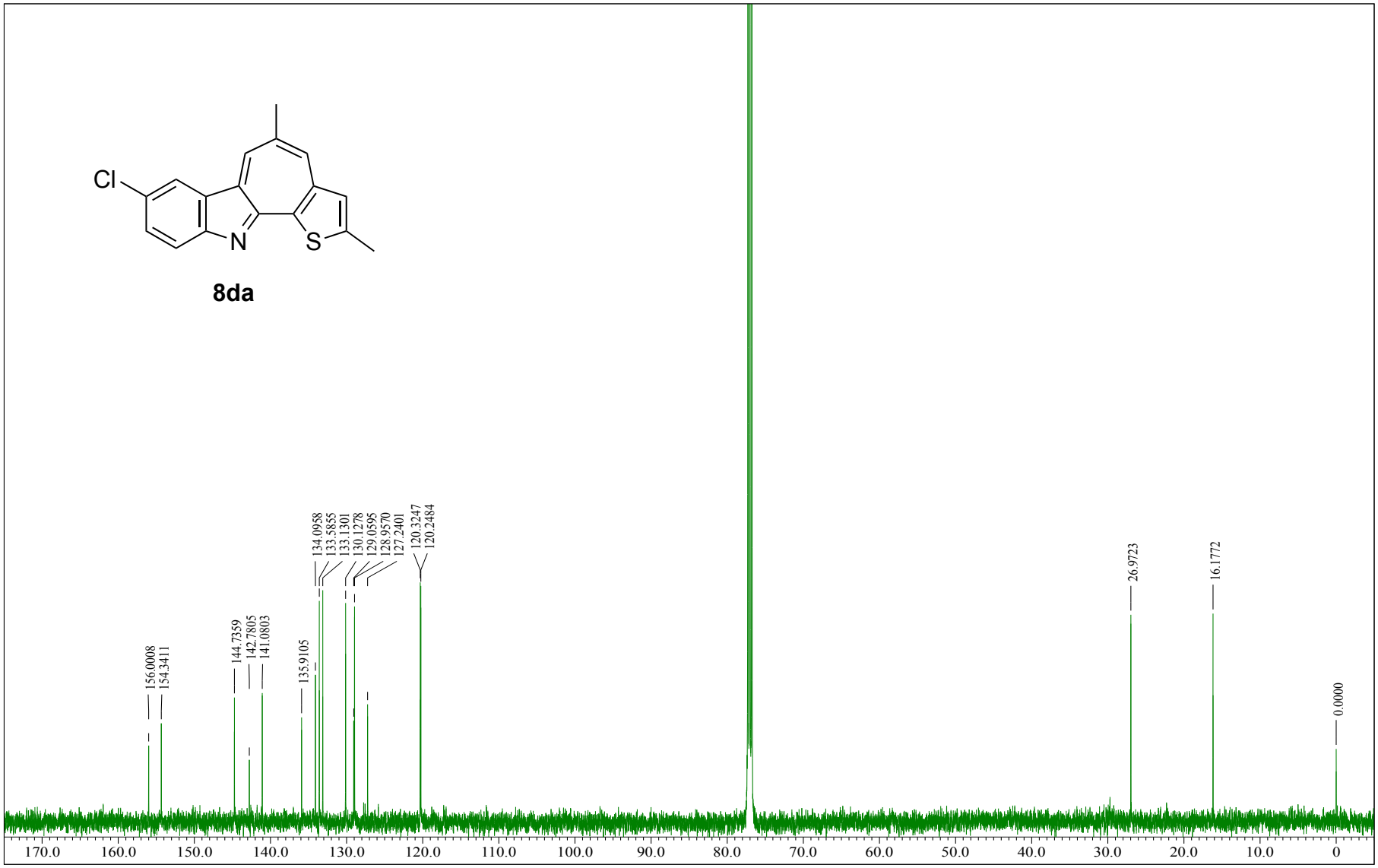


Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8da** in $CDCl_3$.

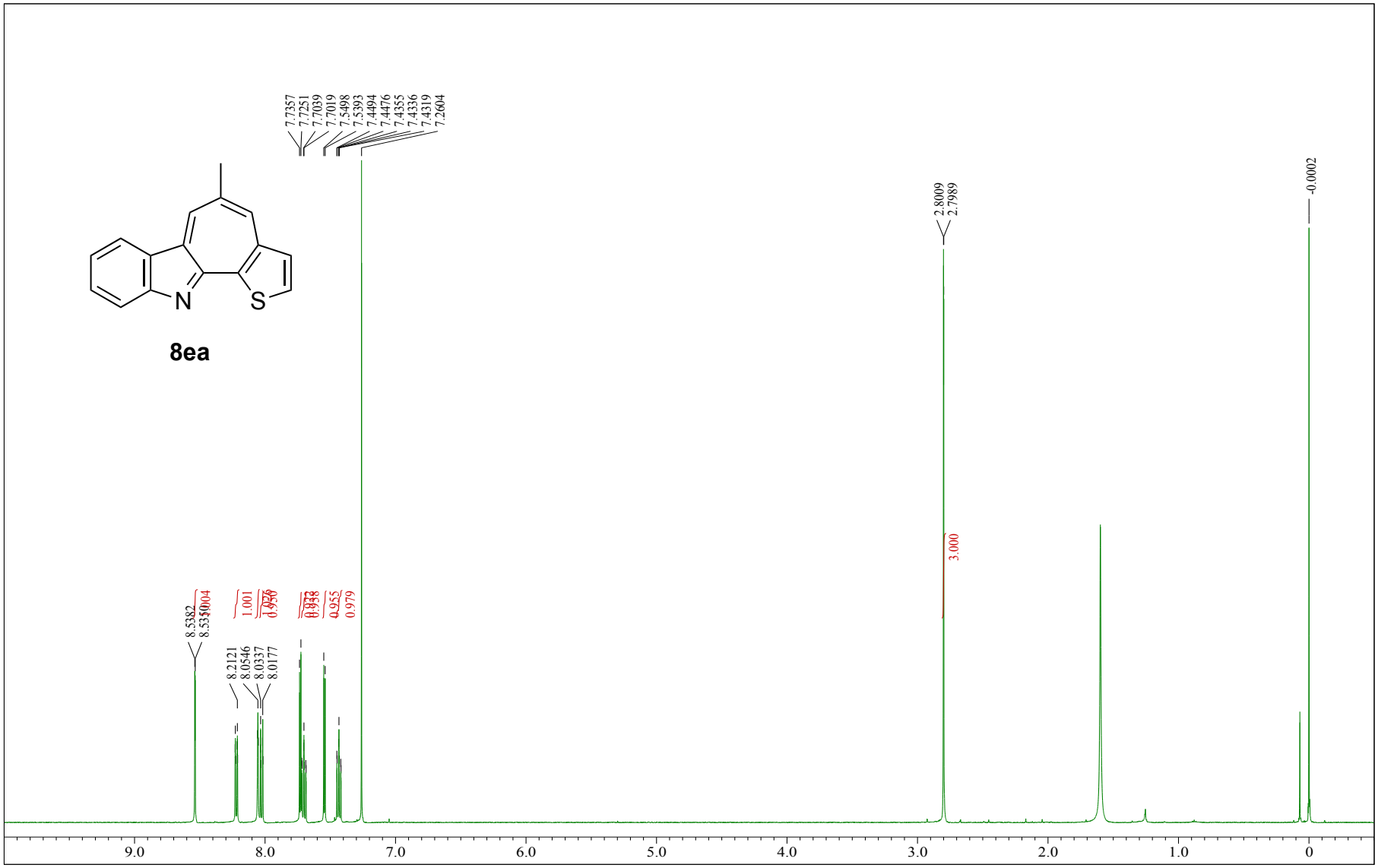


Figure S55. ^{1}H NMR spectrum of compound **8ea** in $CDCl_3$.

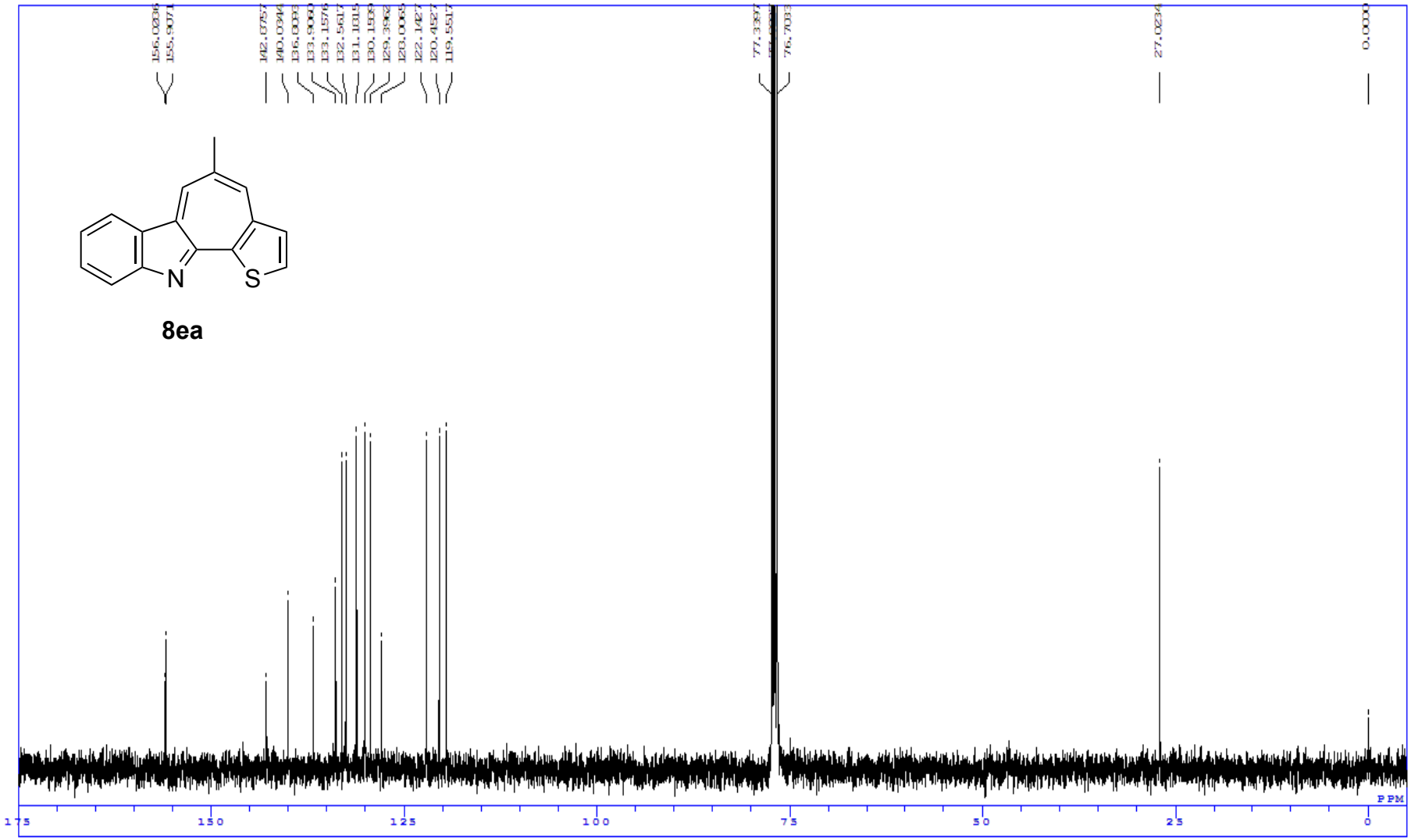


Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8ea** in $CDCl_3$.

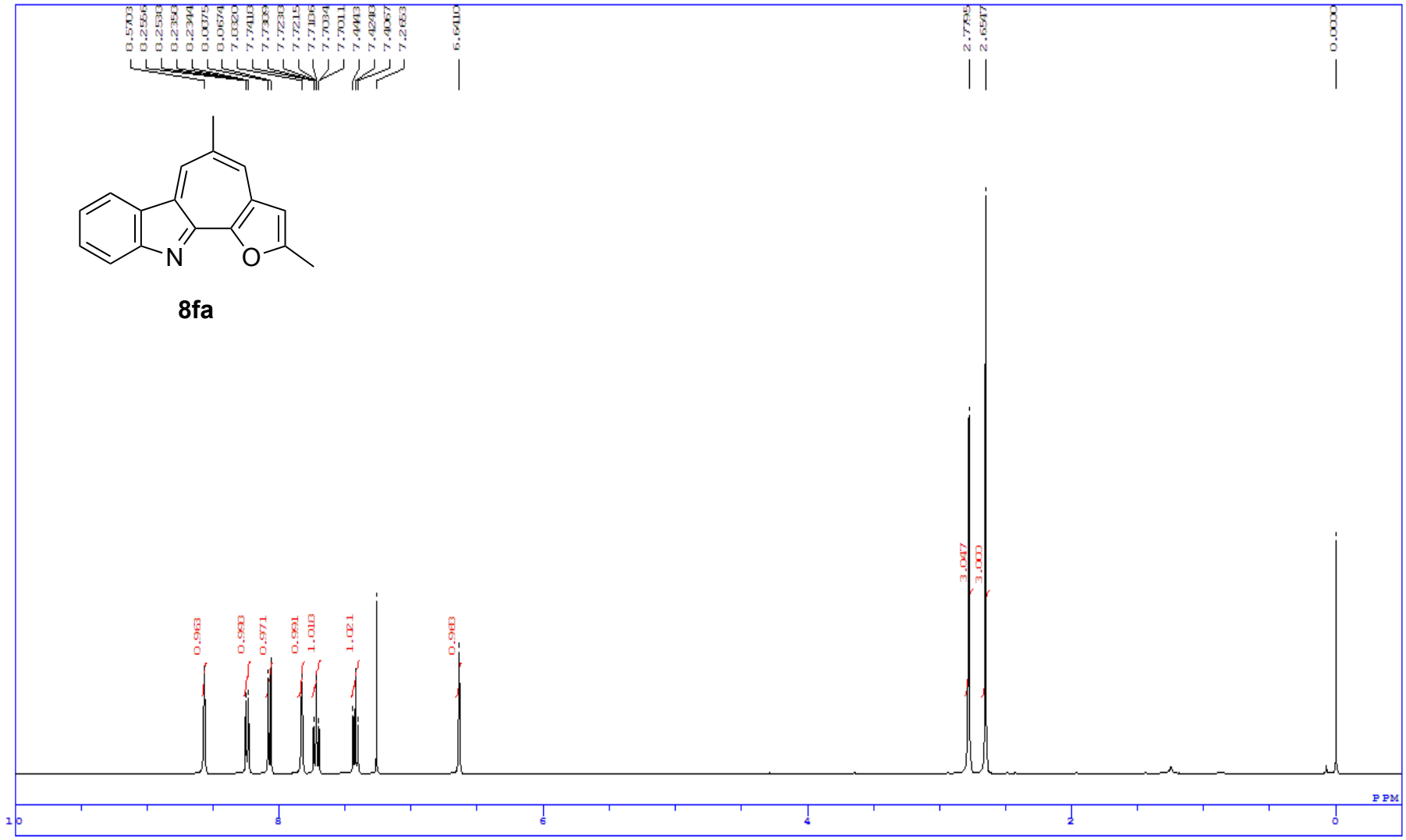


Figure S57. ^{1}H NMR spectrum of compound **8fa** in $CDCl_3$.

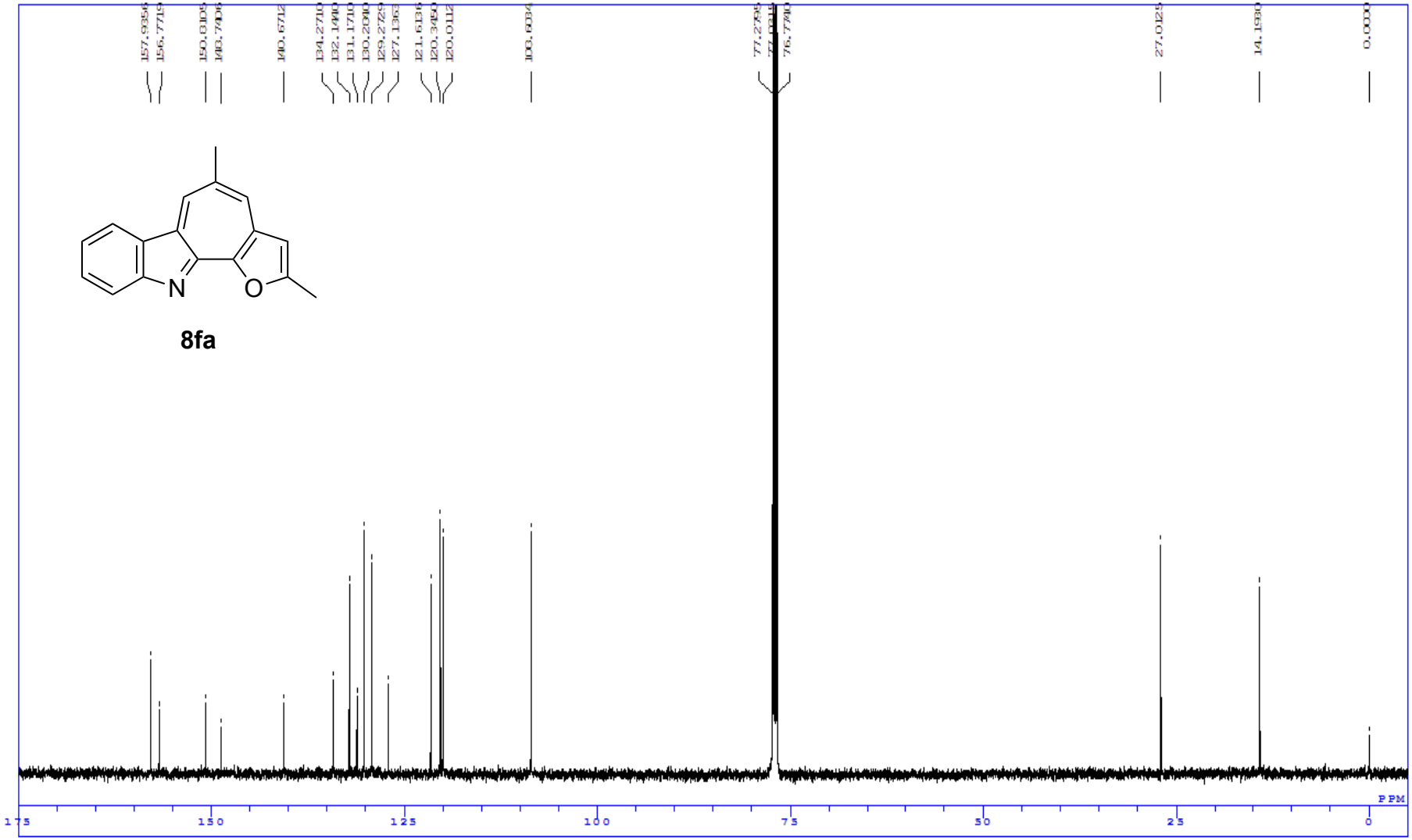


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8fa** in $CDCl_3$.

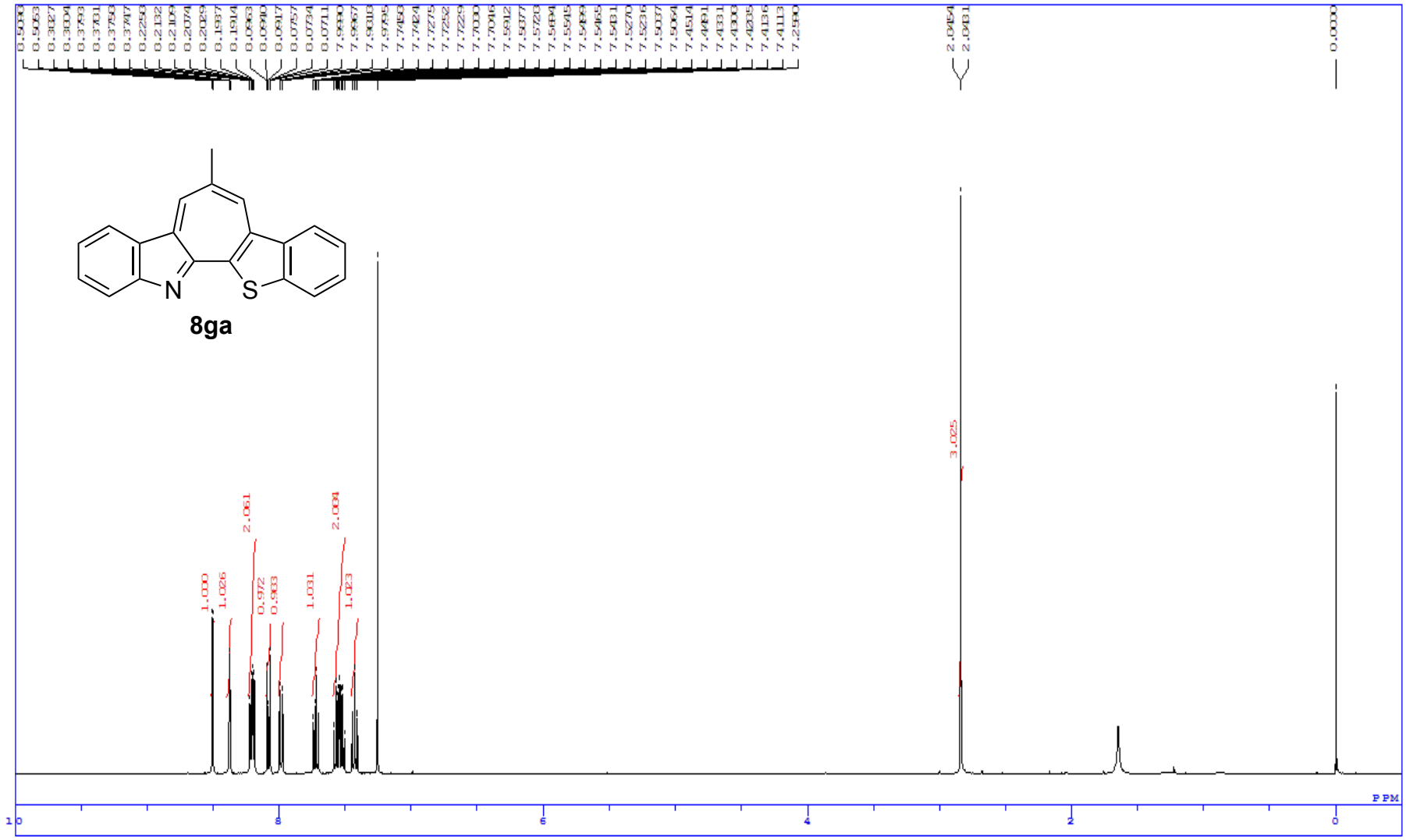


Figure S59. ^{1}H NMR spectrum of compound **8ga** in $CDCl_3$.

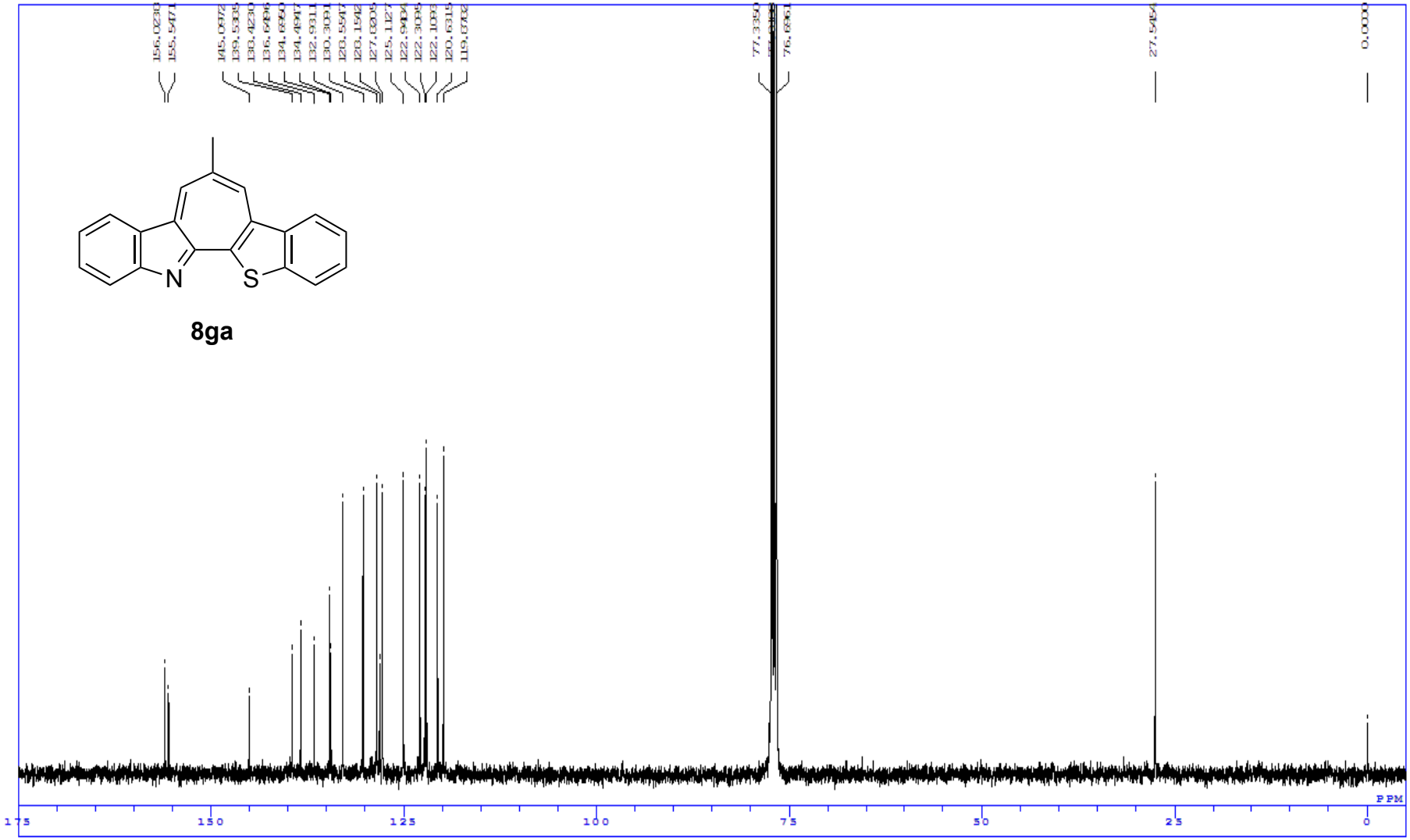


Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8ga** in $CDCl_3$.

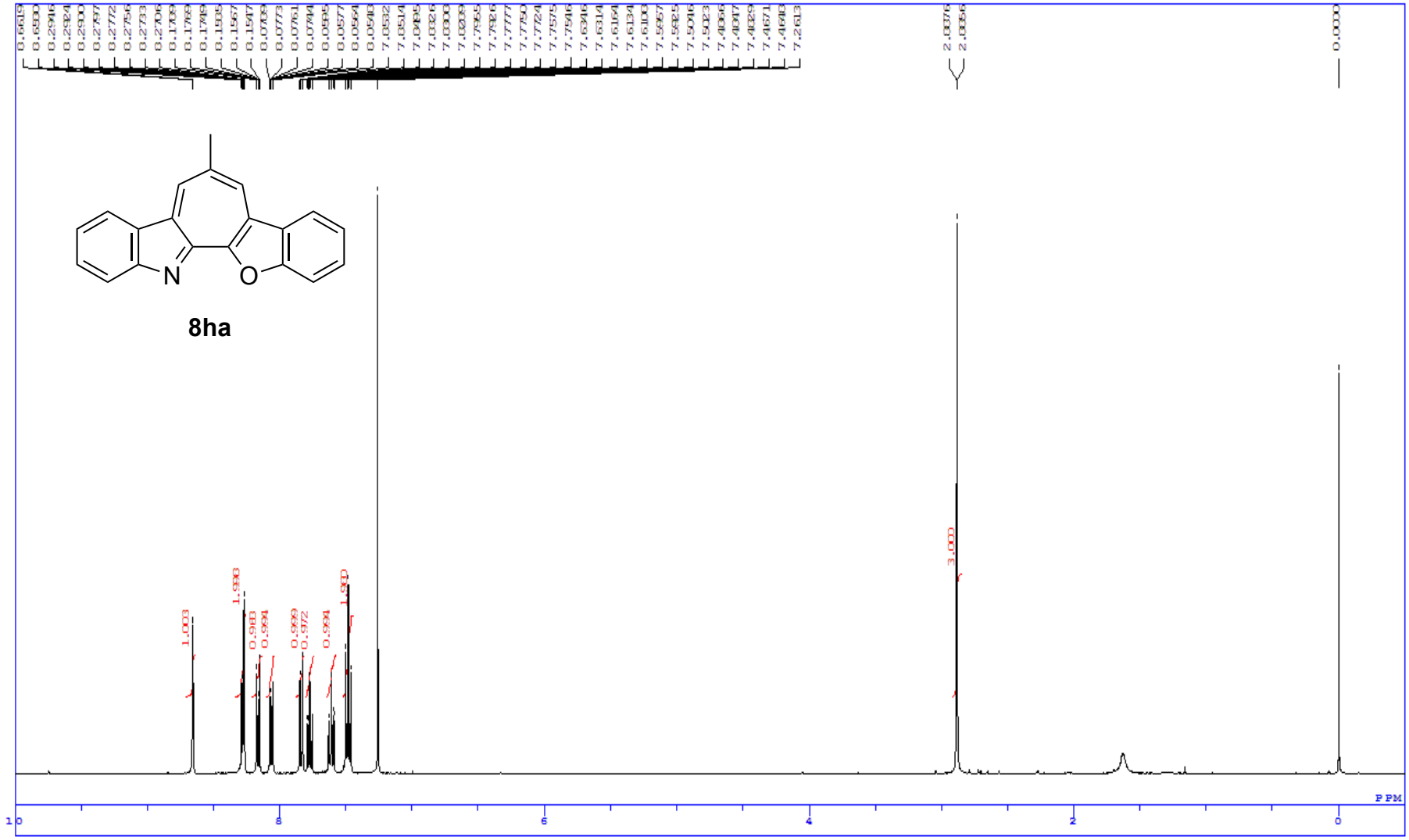


Figure S61. ^{1}H NMR spectrum of compound **8ha** in $CDCl_3$.

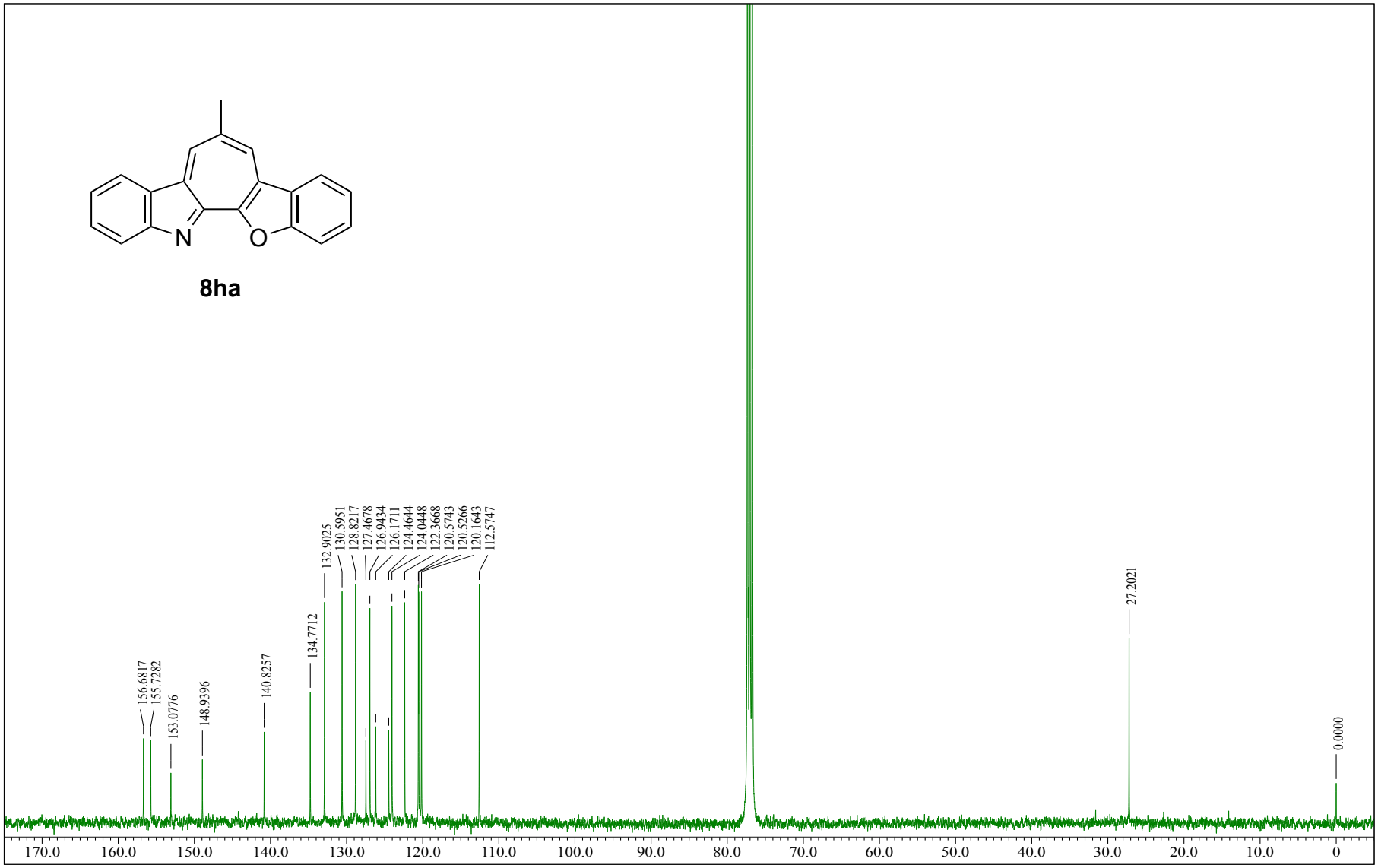


Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8ha** in $CDCl_3$.

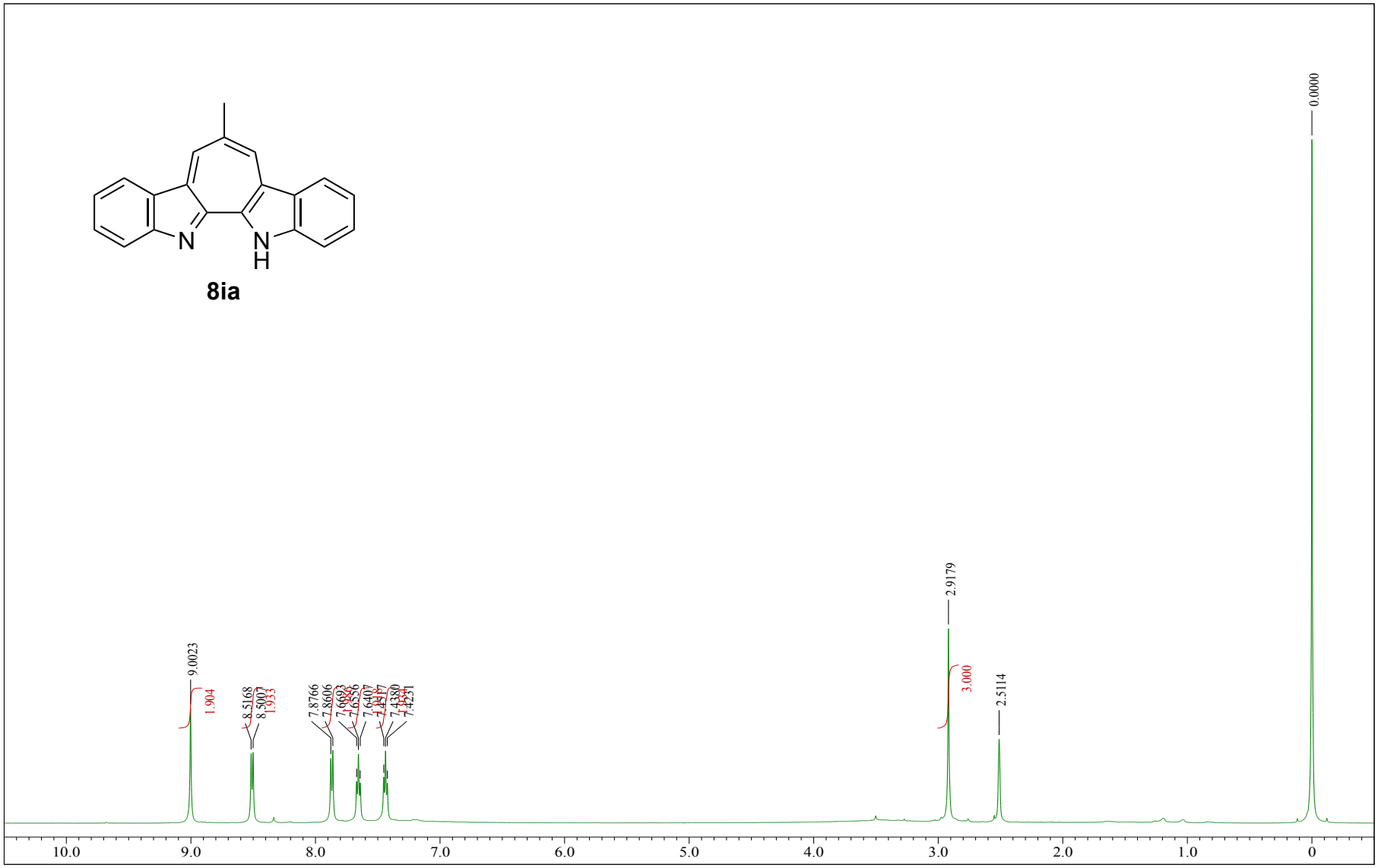


Figure S63. ^{1}H NMR spectrum of compound **8ia** in DMSO-d_6.

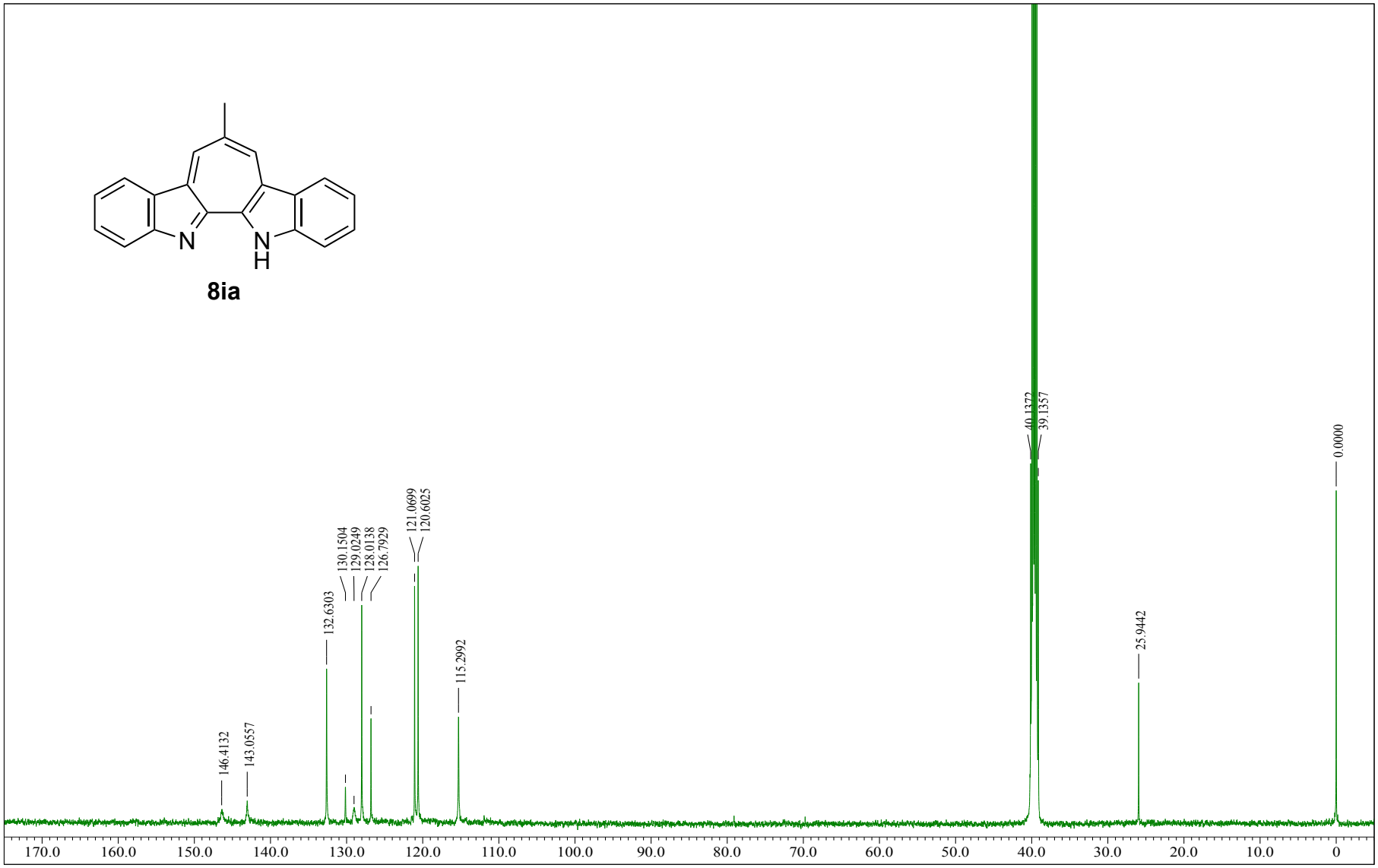


Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8ia** in DMSO-d_6.

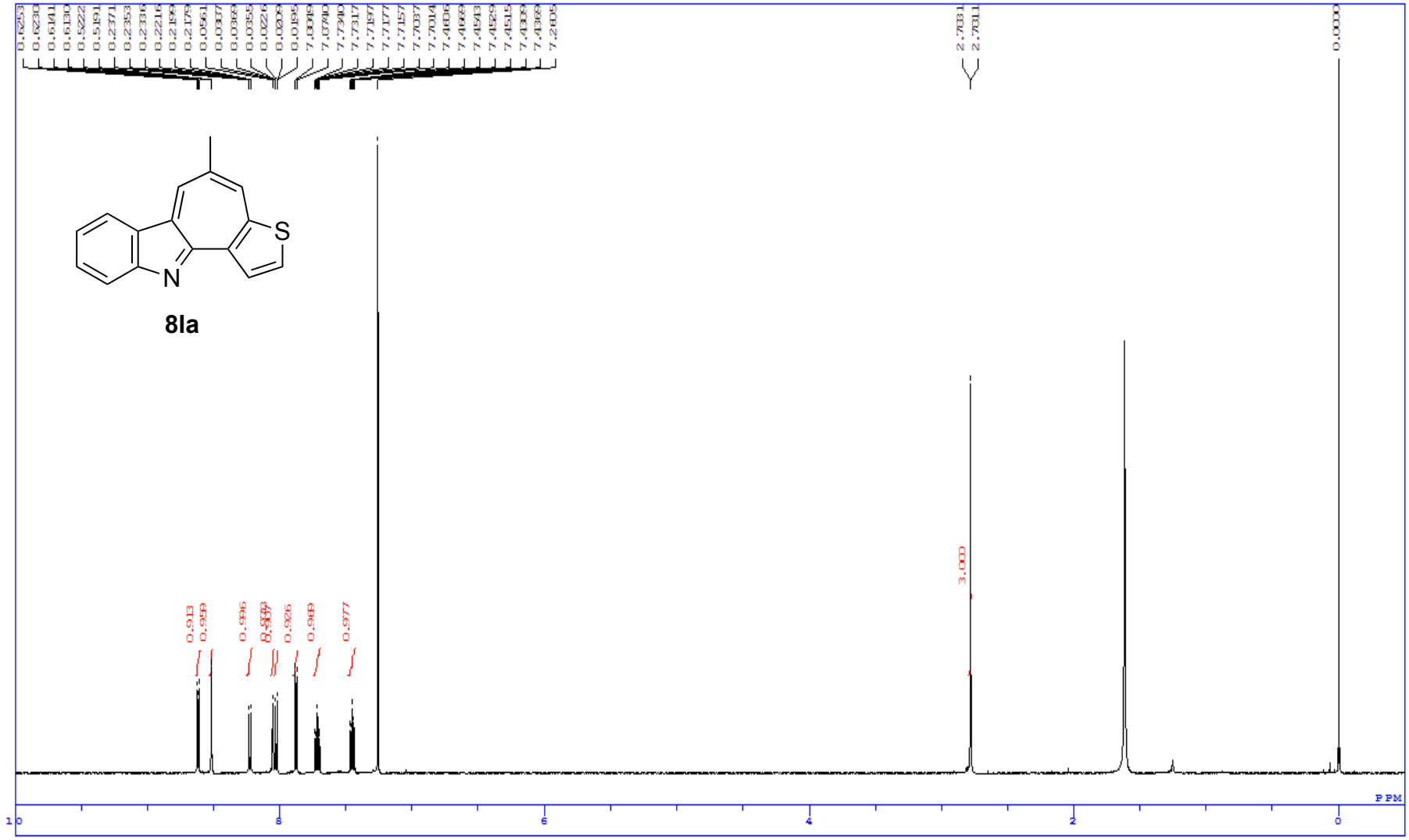


Figure S65. ^{1}H NMR spectrum of compound **8la** in $CDCl_3$.

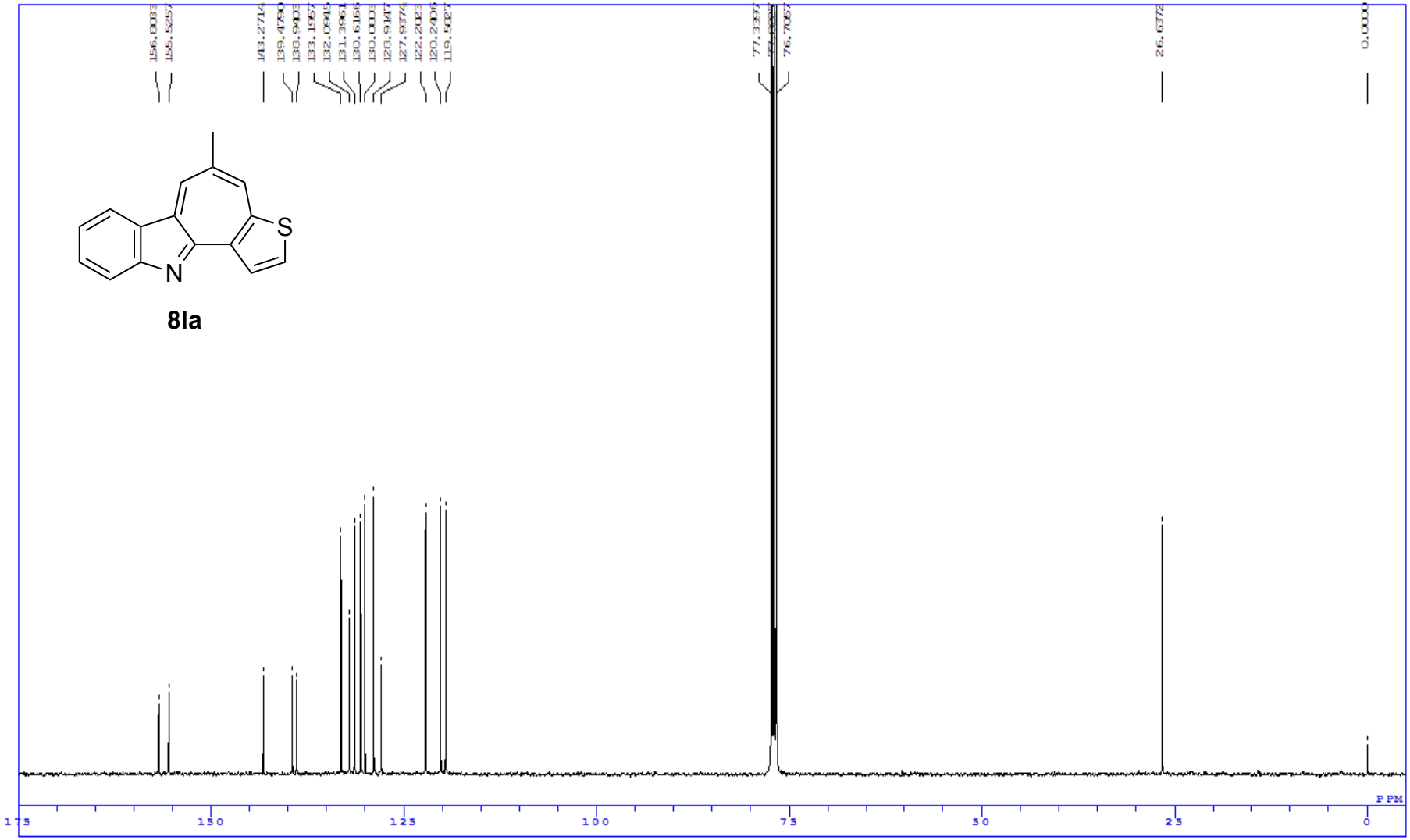


Figure S66. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8ia** in $CDCl_3$.

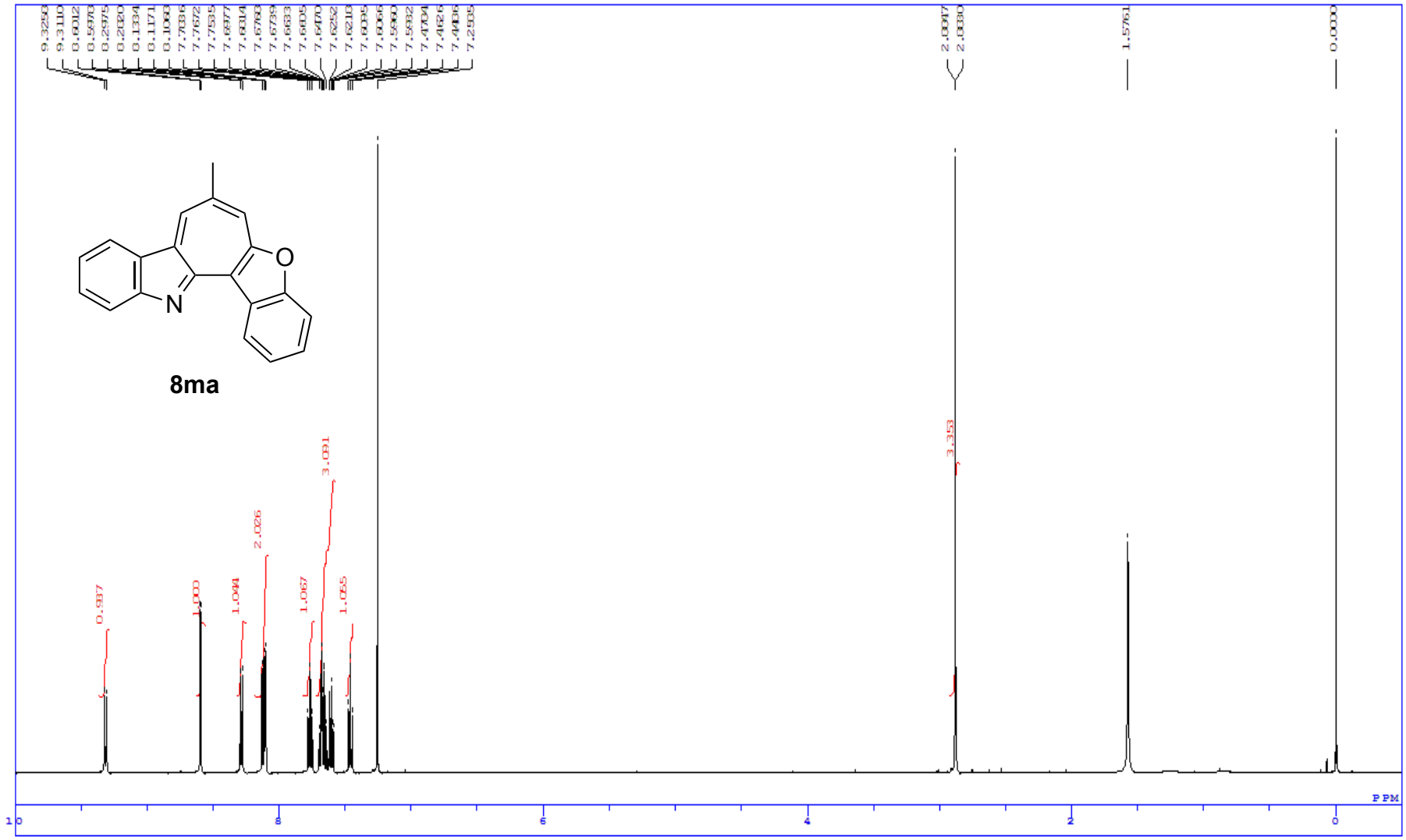


Figure S67. ^{1}H NMR spectrum of compound **8ma** in $CDCl_3$.

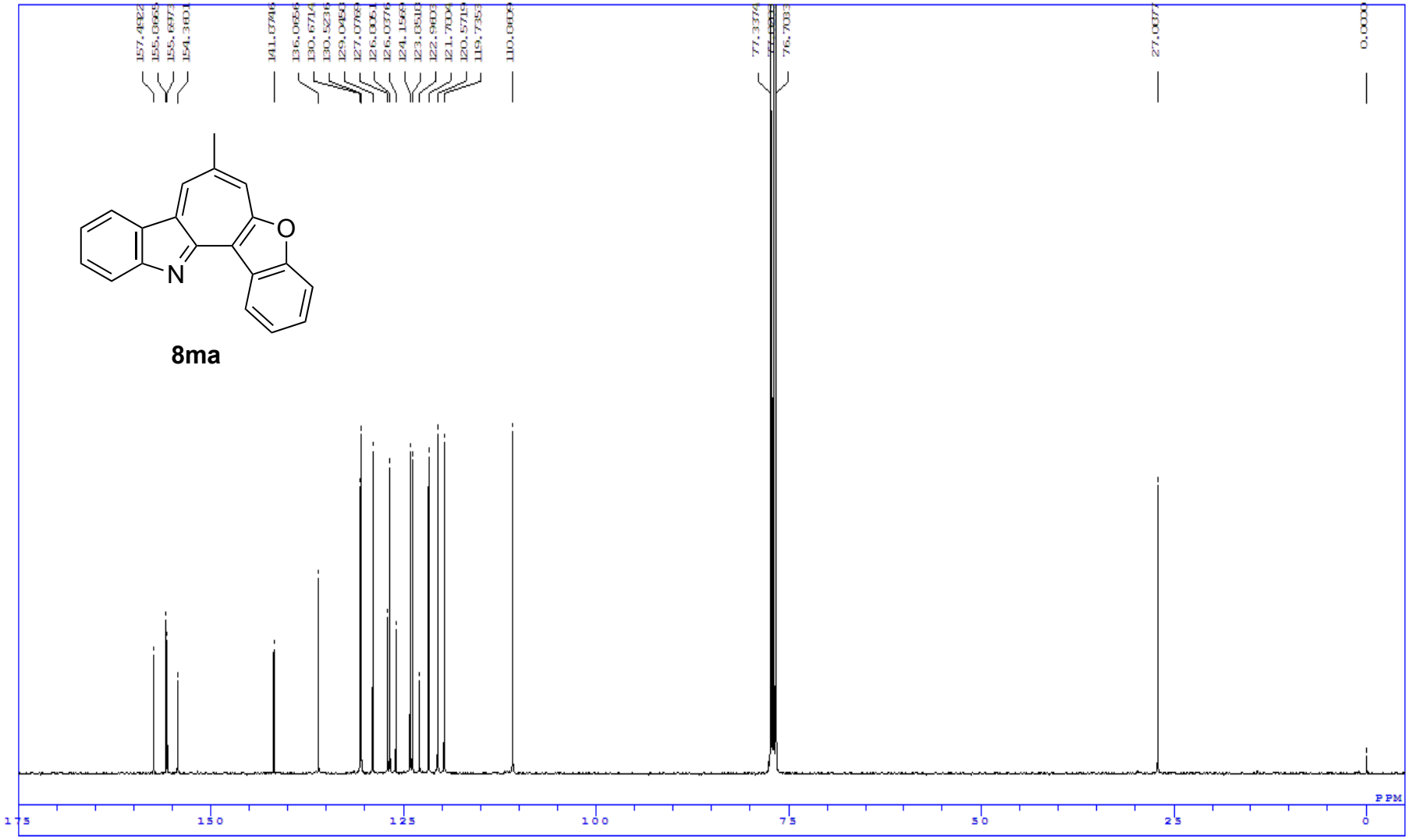


Figure S68. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8ma** in $CDCl_3$.

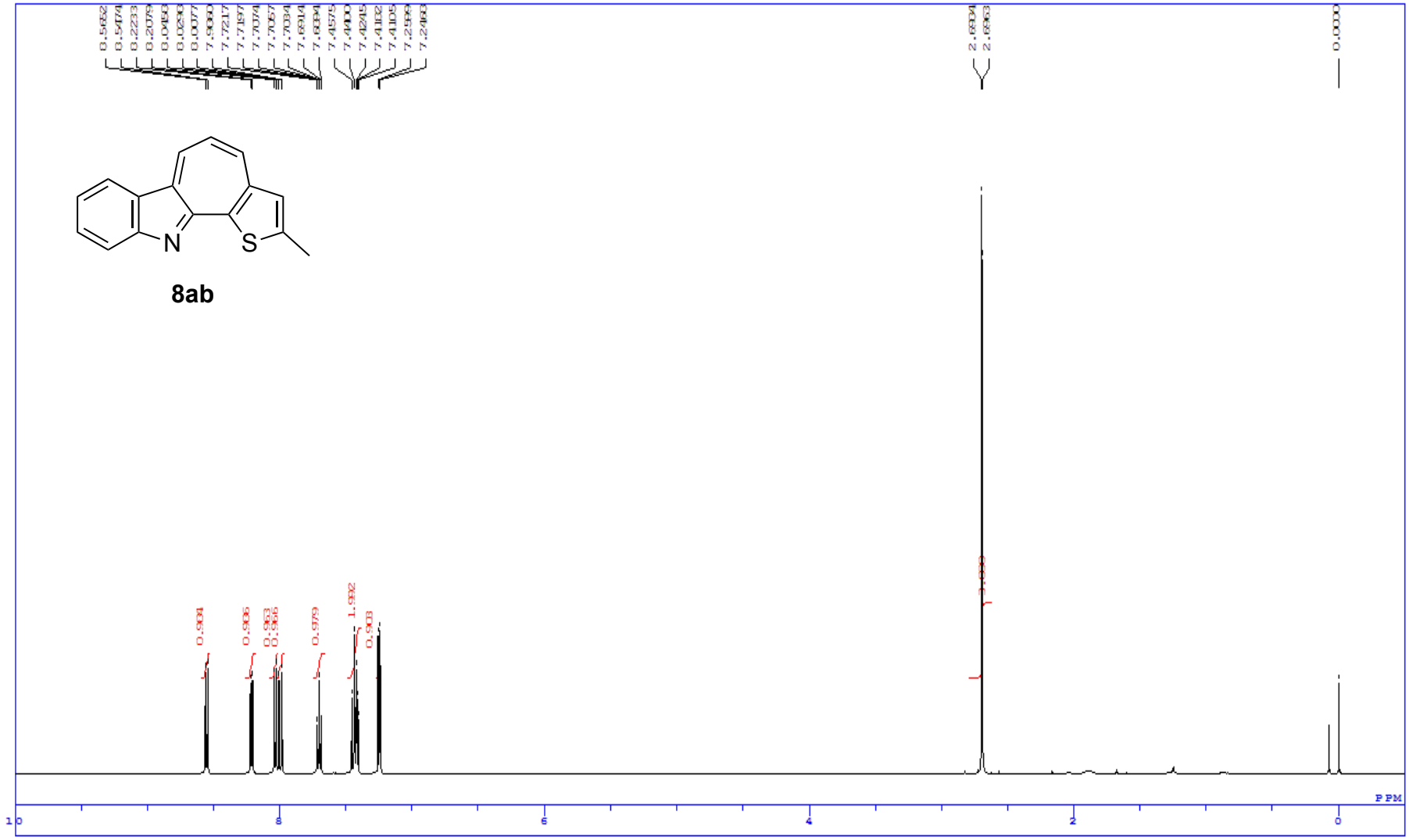


Figure S69. ^{1}H NMR spectrum of compound **8ab** in $CDCl_3$.

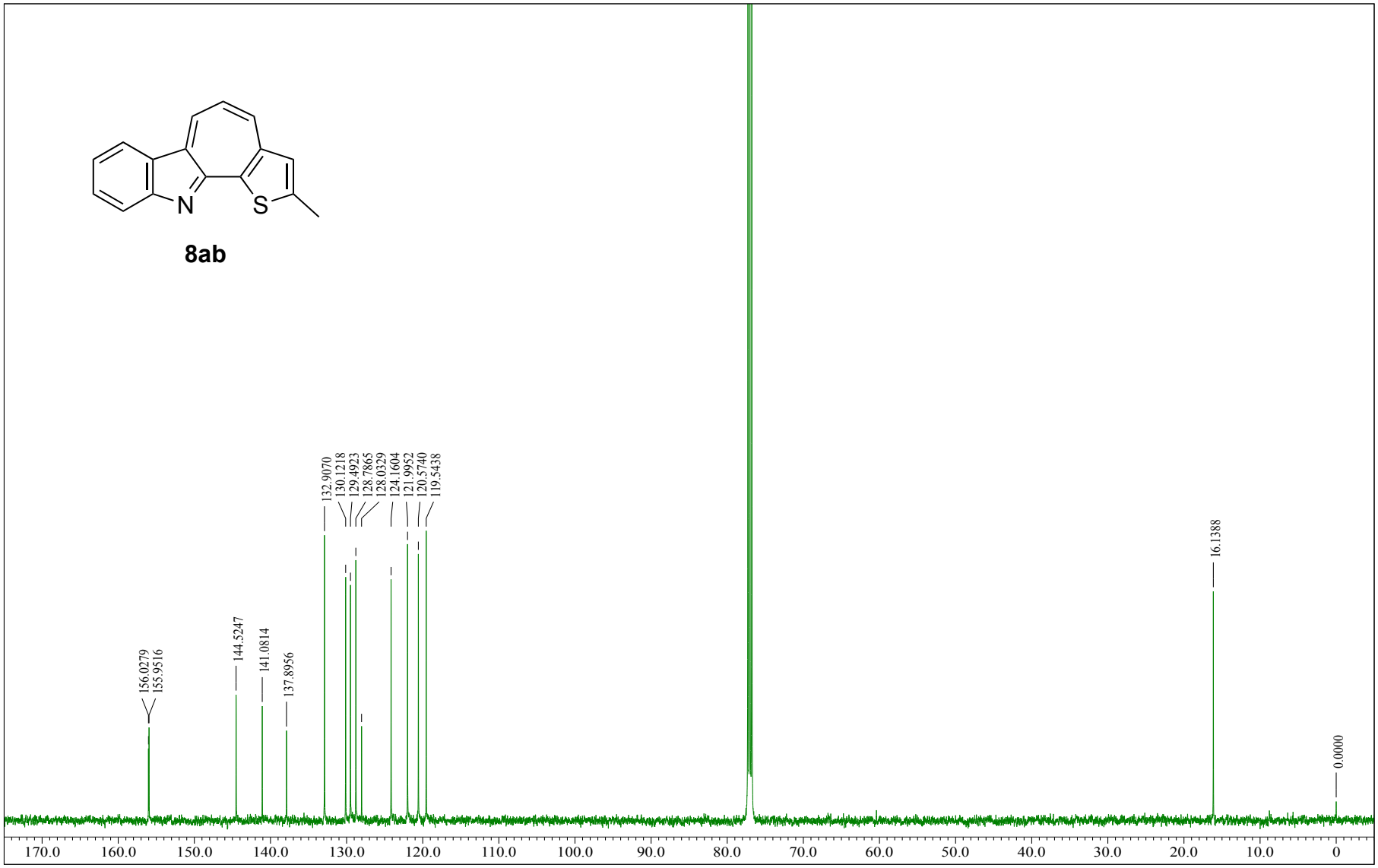


Figure S70. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8ab** in $CDCl_3$.

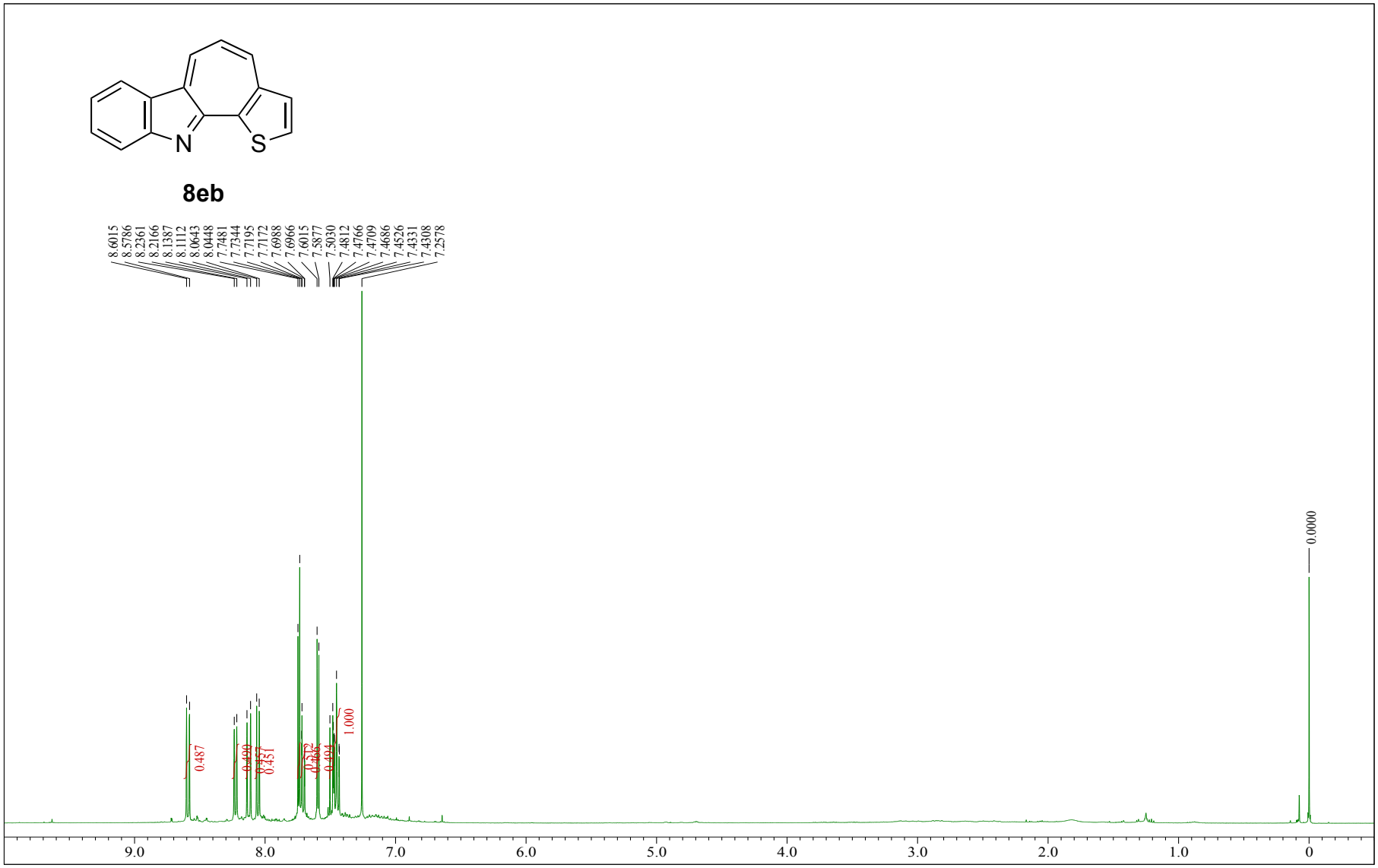


Figure S71. ^{1}H NMR spectrum of compound **8eb** in $CDCl_3$.

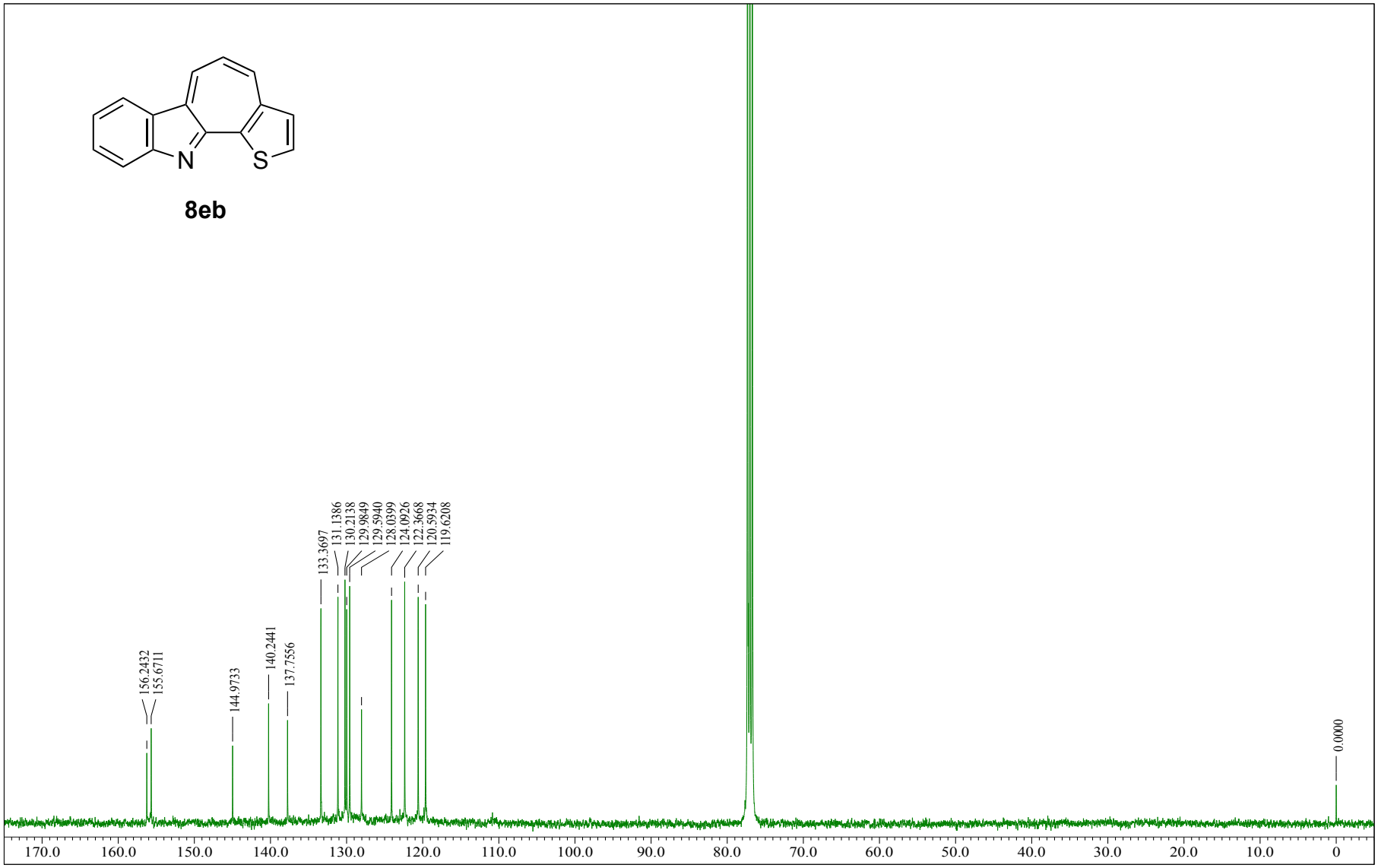


Figure S72. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8eb** in $CDCl_3$.

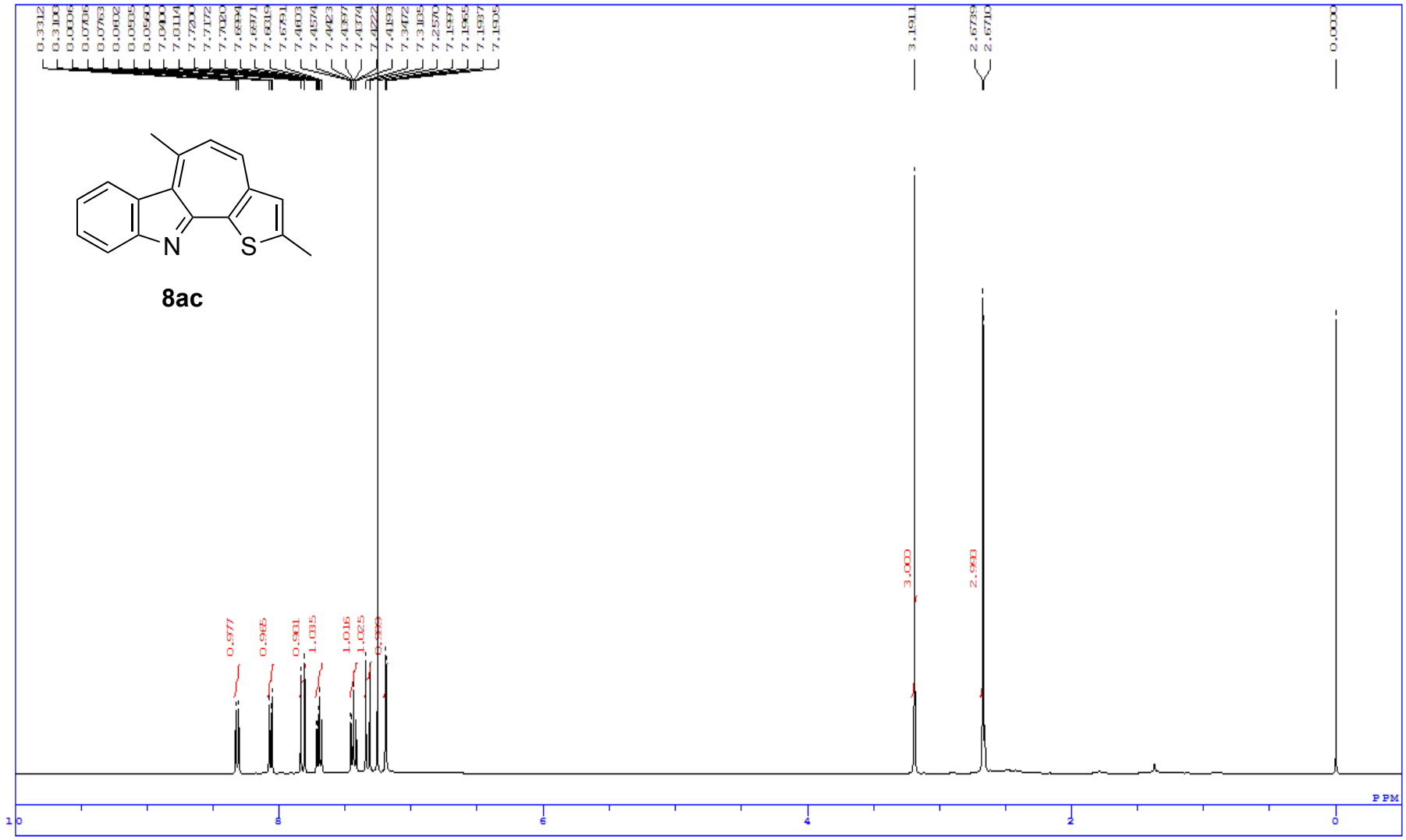


Figure S73. ^{1}H NMR spectrum of compound **8ac** in $CDCl_3$.

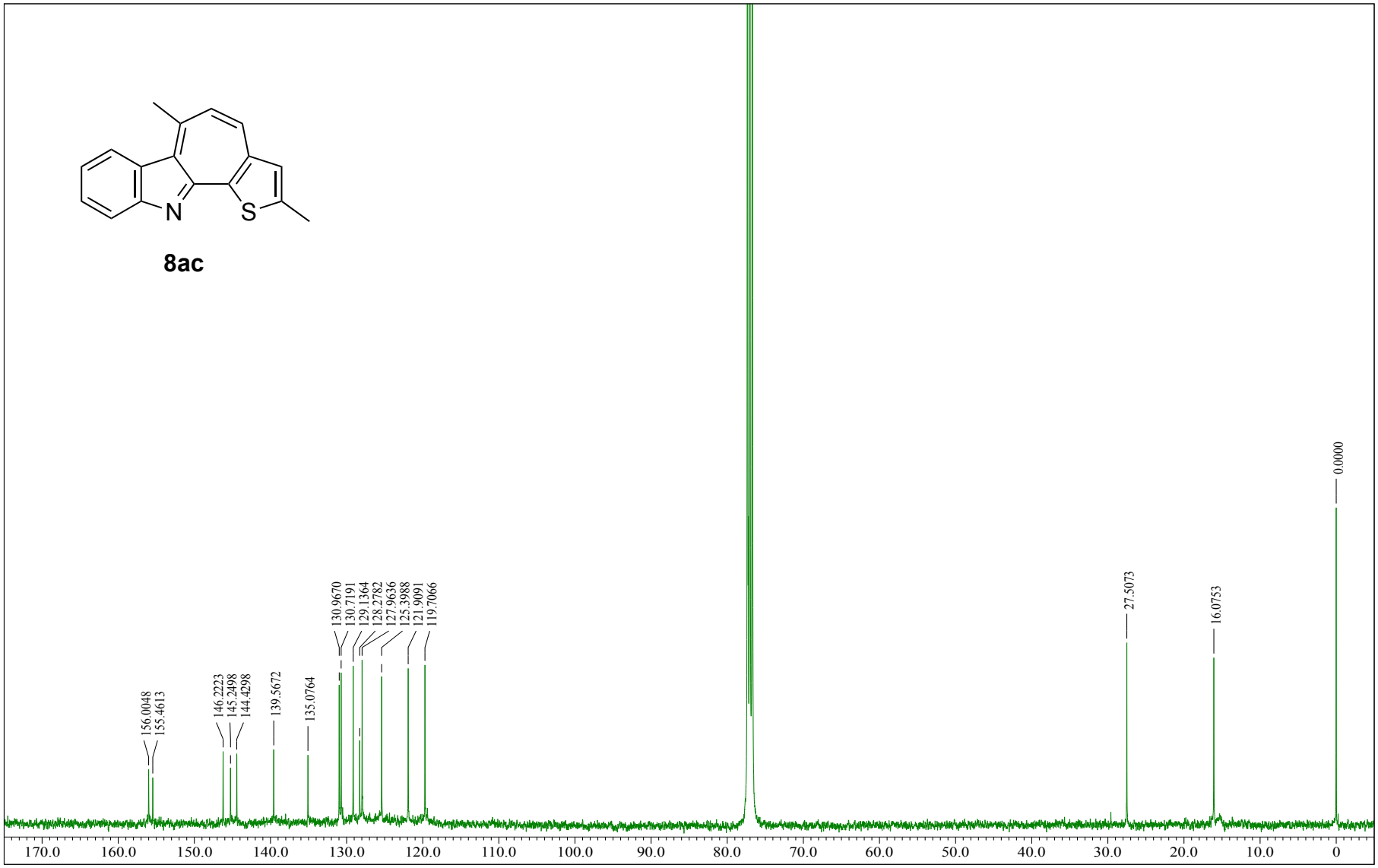


Figure S74. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8ac** in $CDCl_3$.

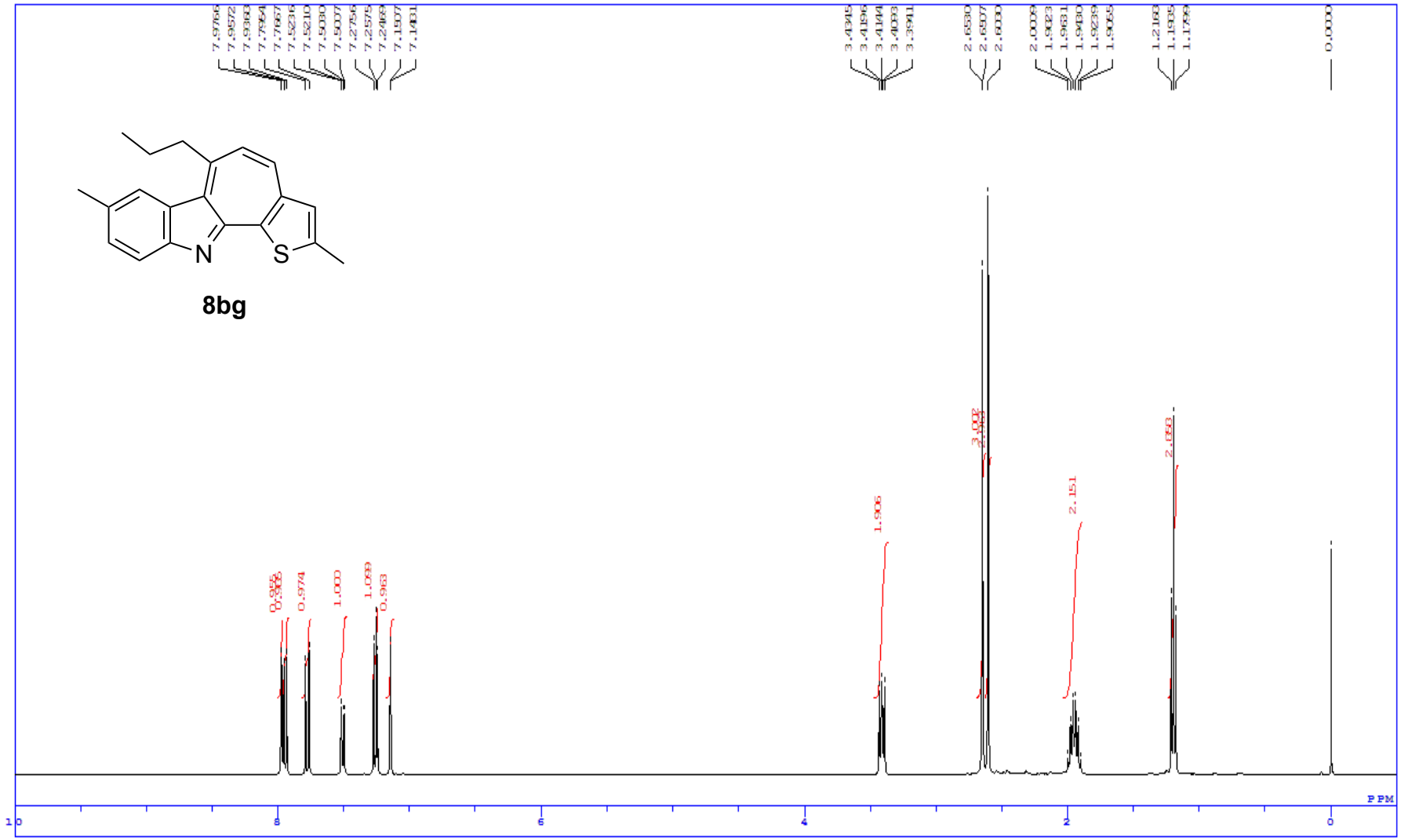


Figure S75. ^{1}H NMR spectrum of compound **8bg** in $CDCl_3$.

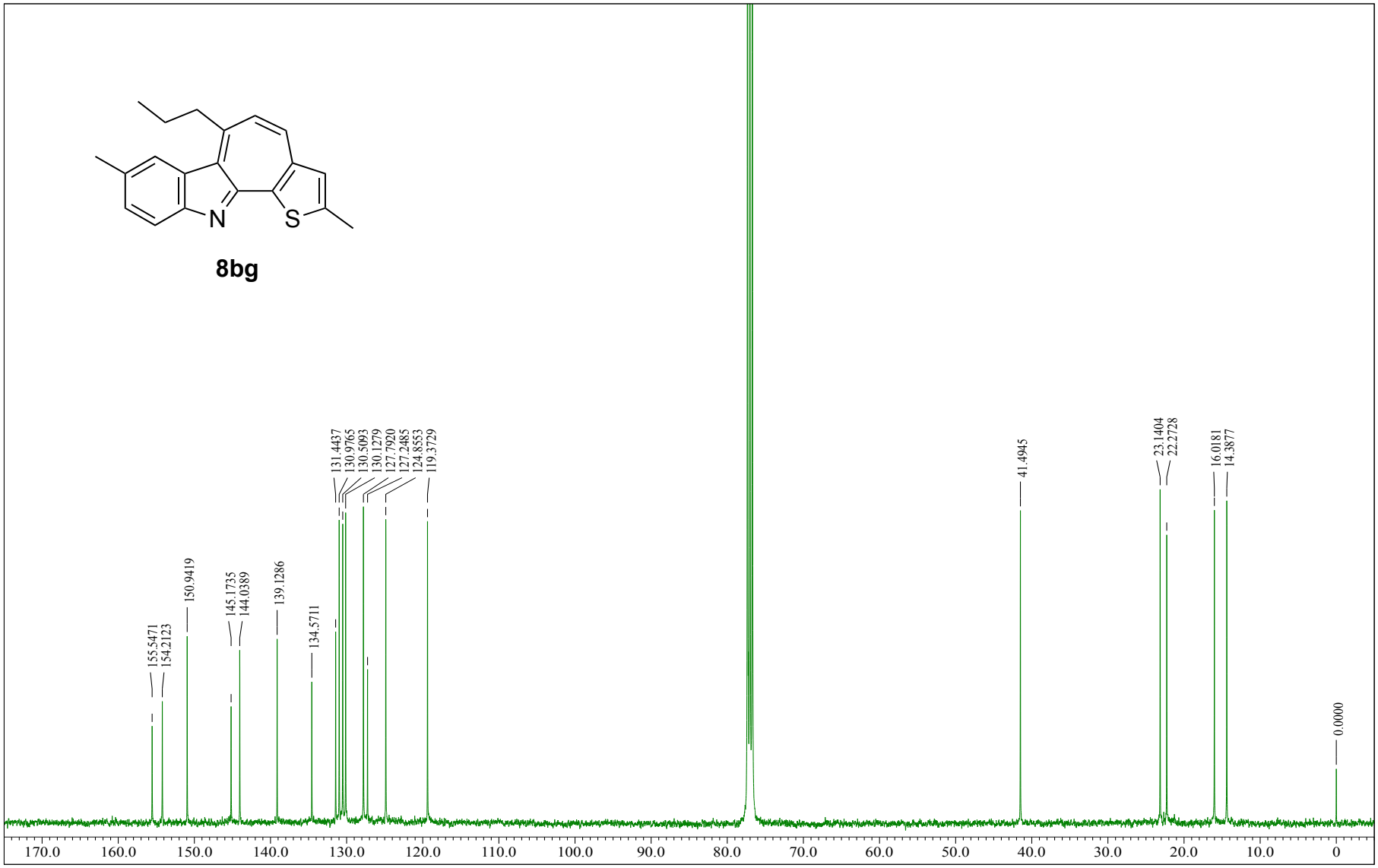


Figure S76. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8bg** in $CDCl_3$.

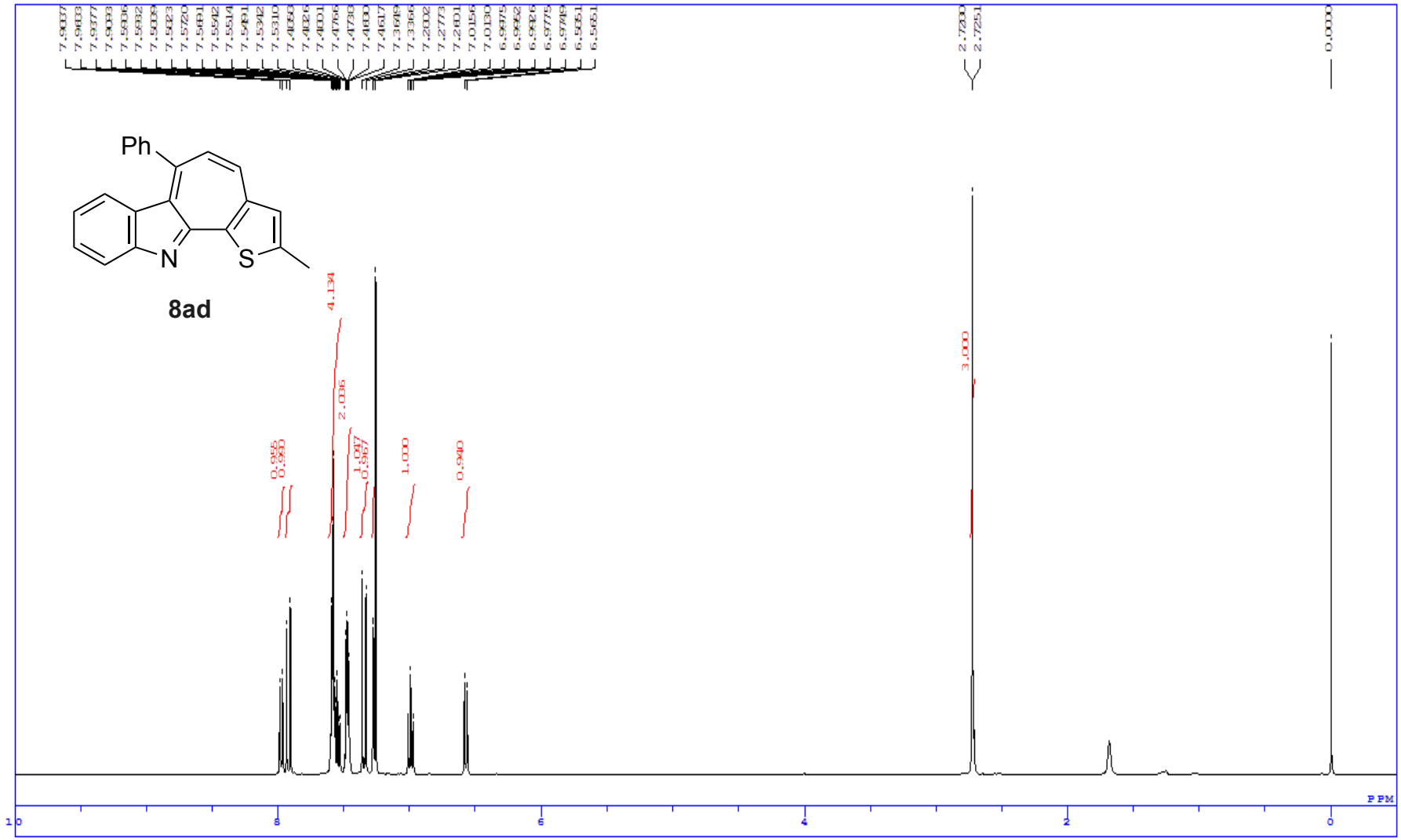


Figure S77. ^{1}H NMR spectrum of compound **8ad** in $CDCl_3$.

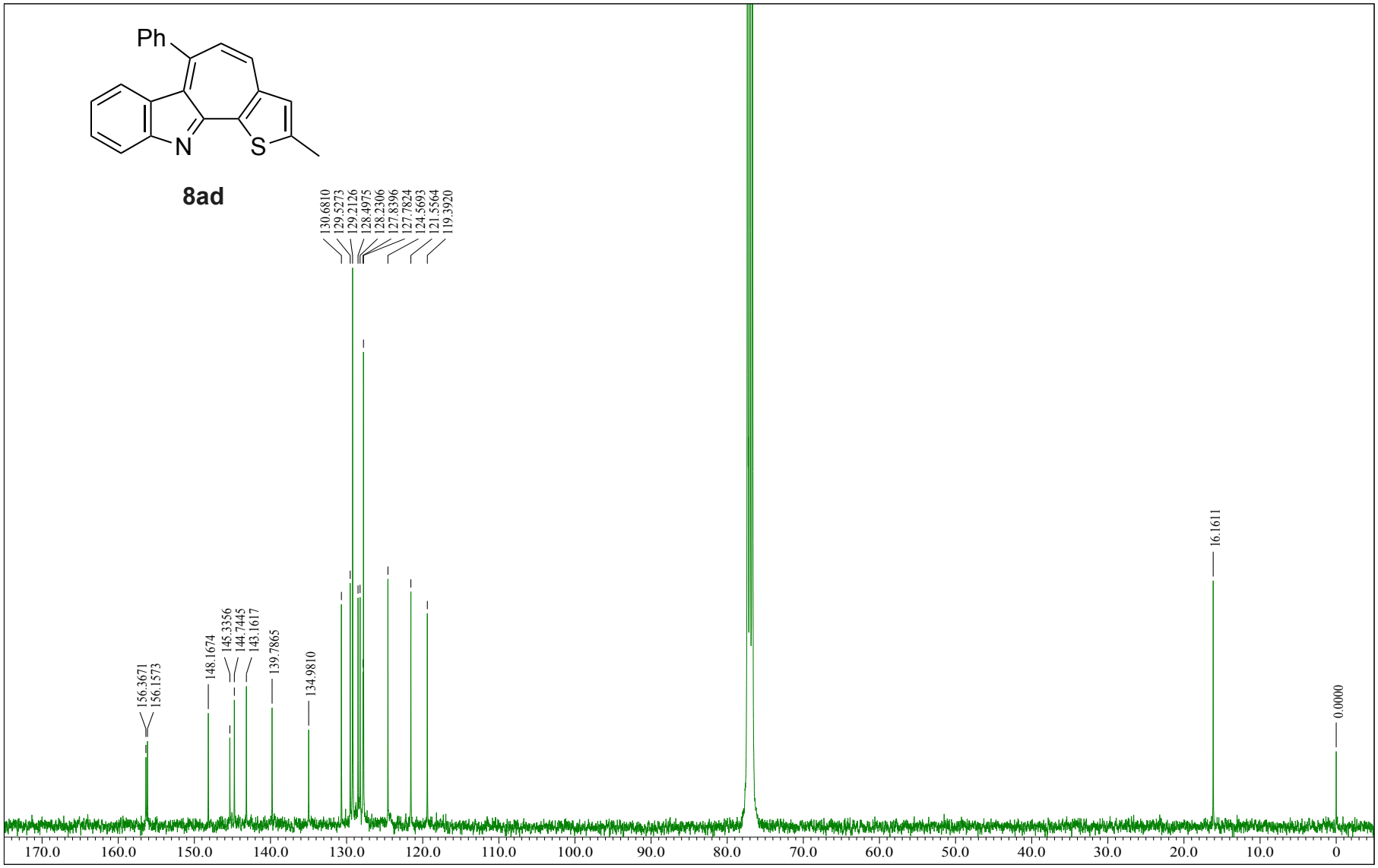


Figure S78. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8ad** in $CDCl_3$.

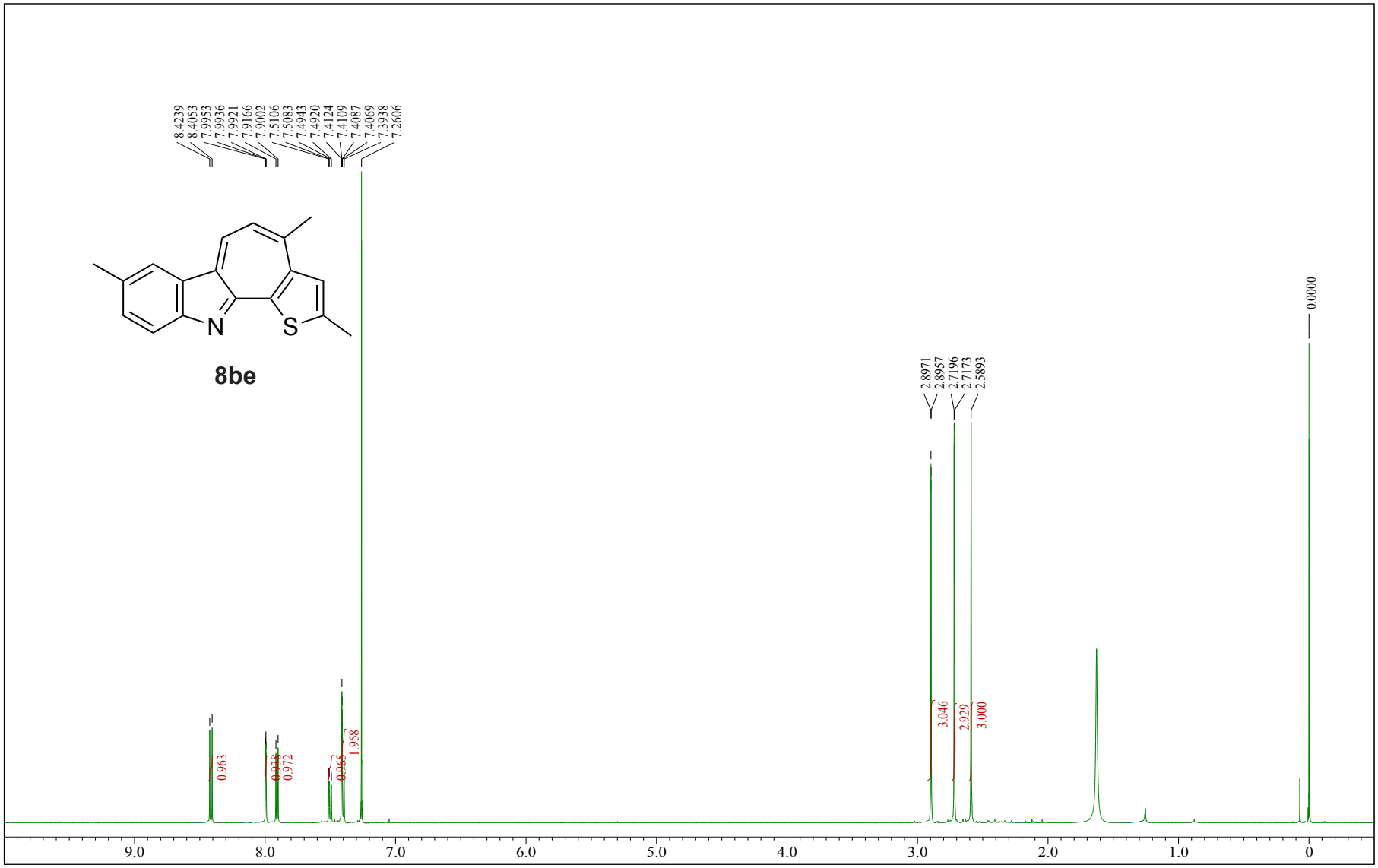


Figure S79. ^{1}H NMR spectrum of compound **8be** in $CDCl_3$.

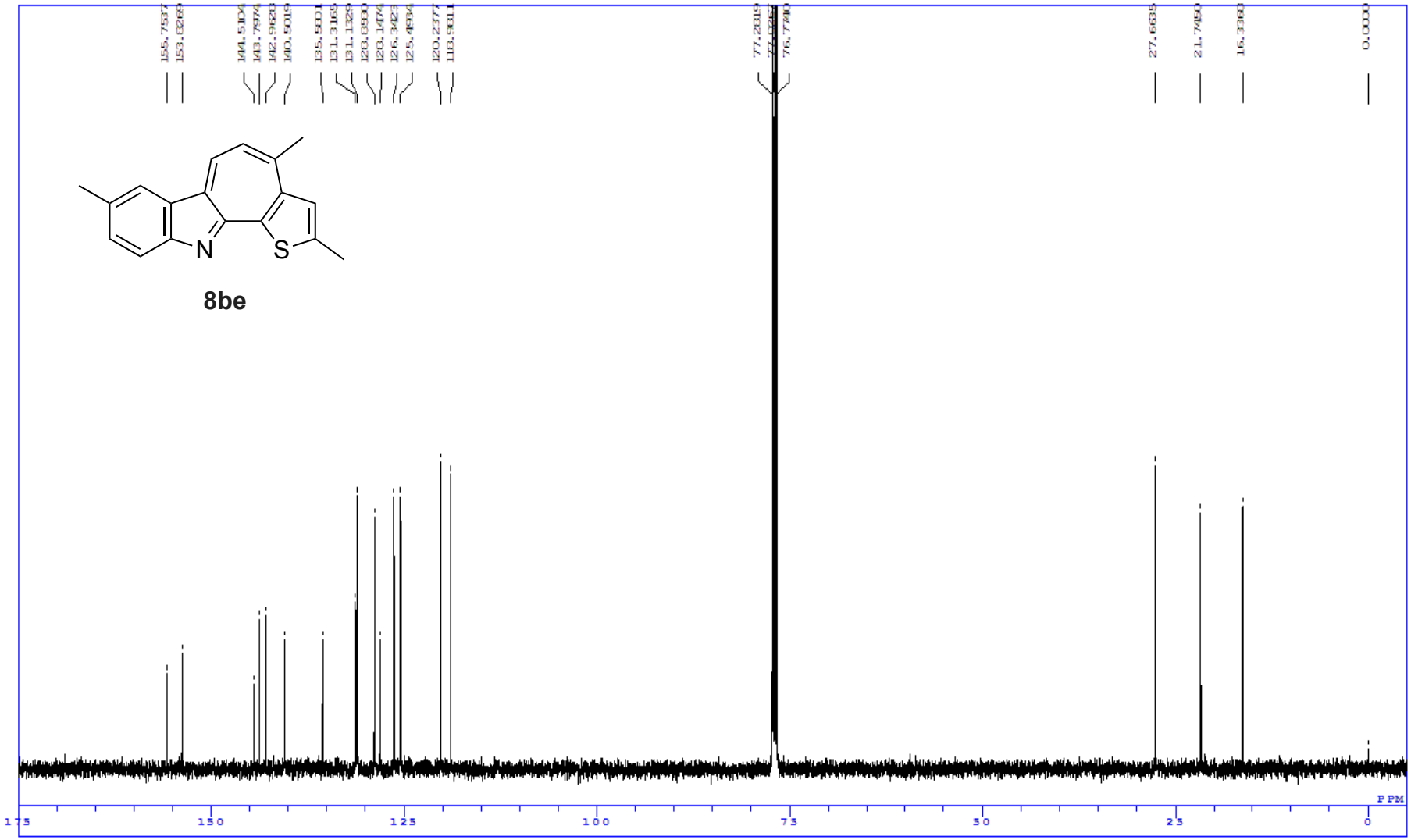


Figure S80. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8be** in $CDCl_3$.

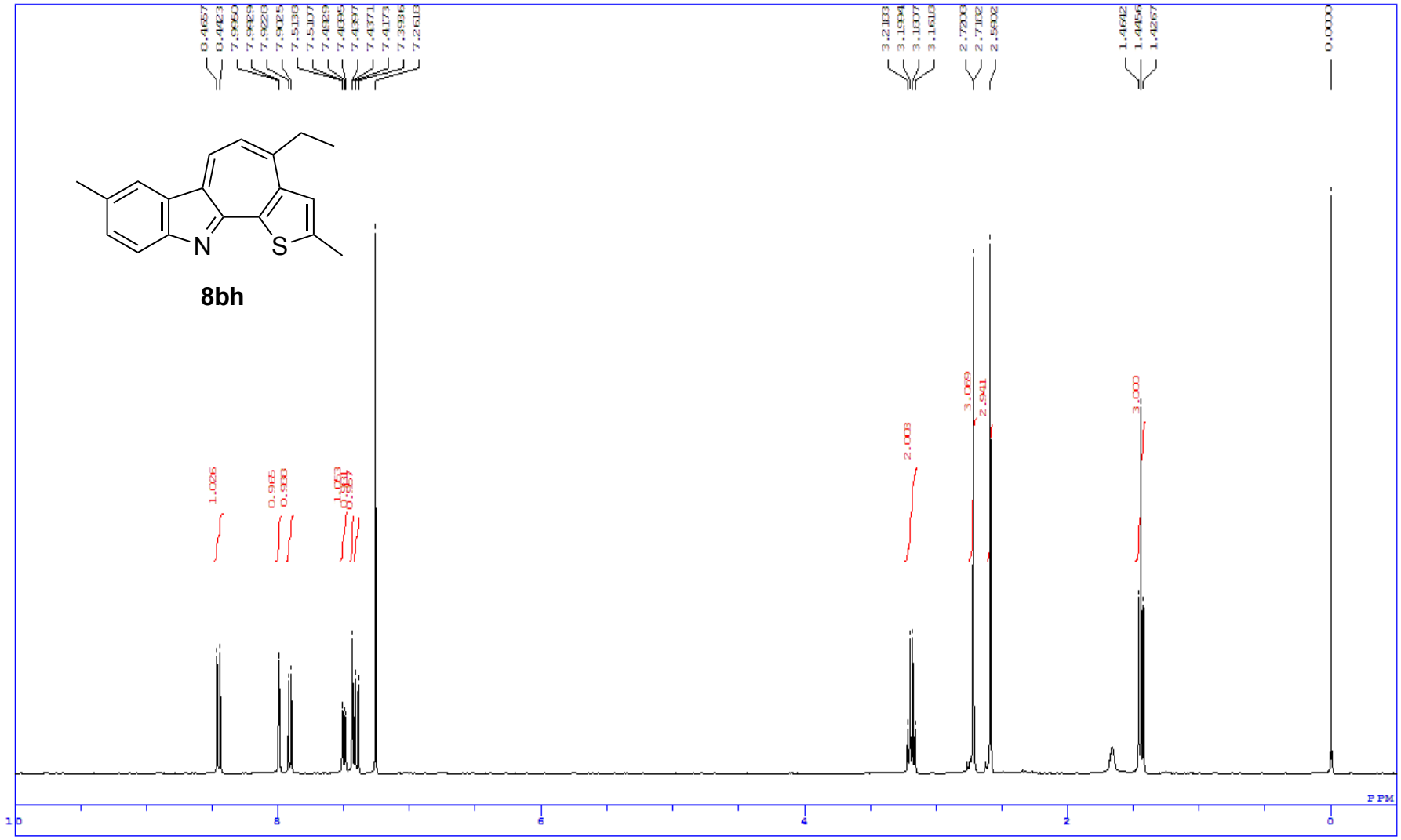


Figure S81. ^{1}H NMR spectrum of compound **8bh** in $CDCl_3$.

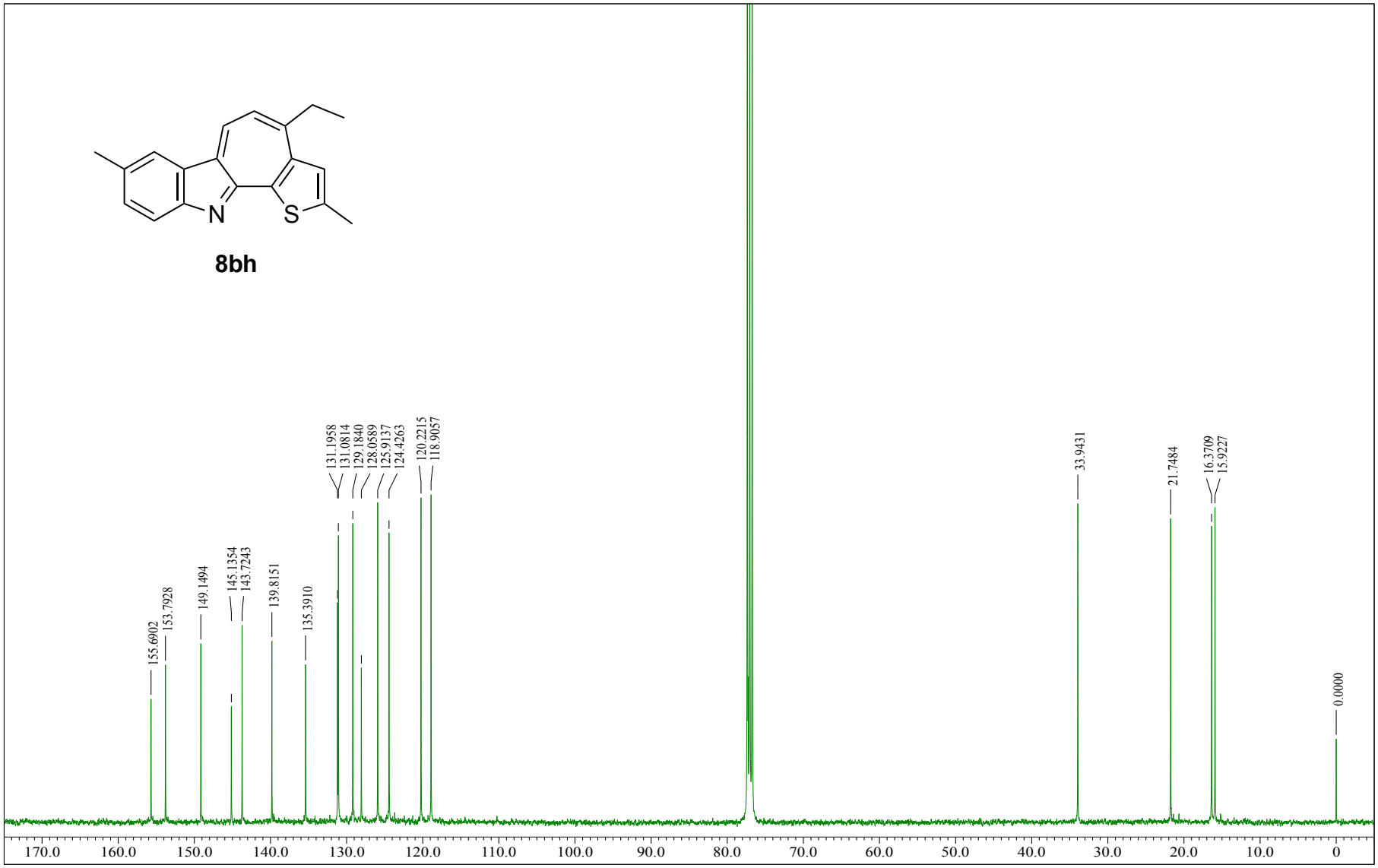


Figure S82. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8bh** in $CDCl_3$.

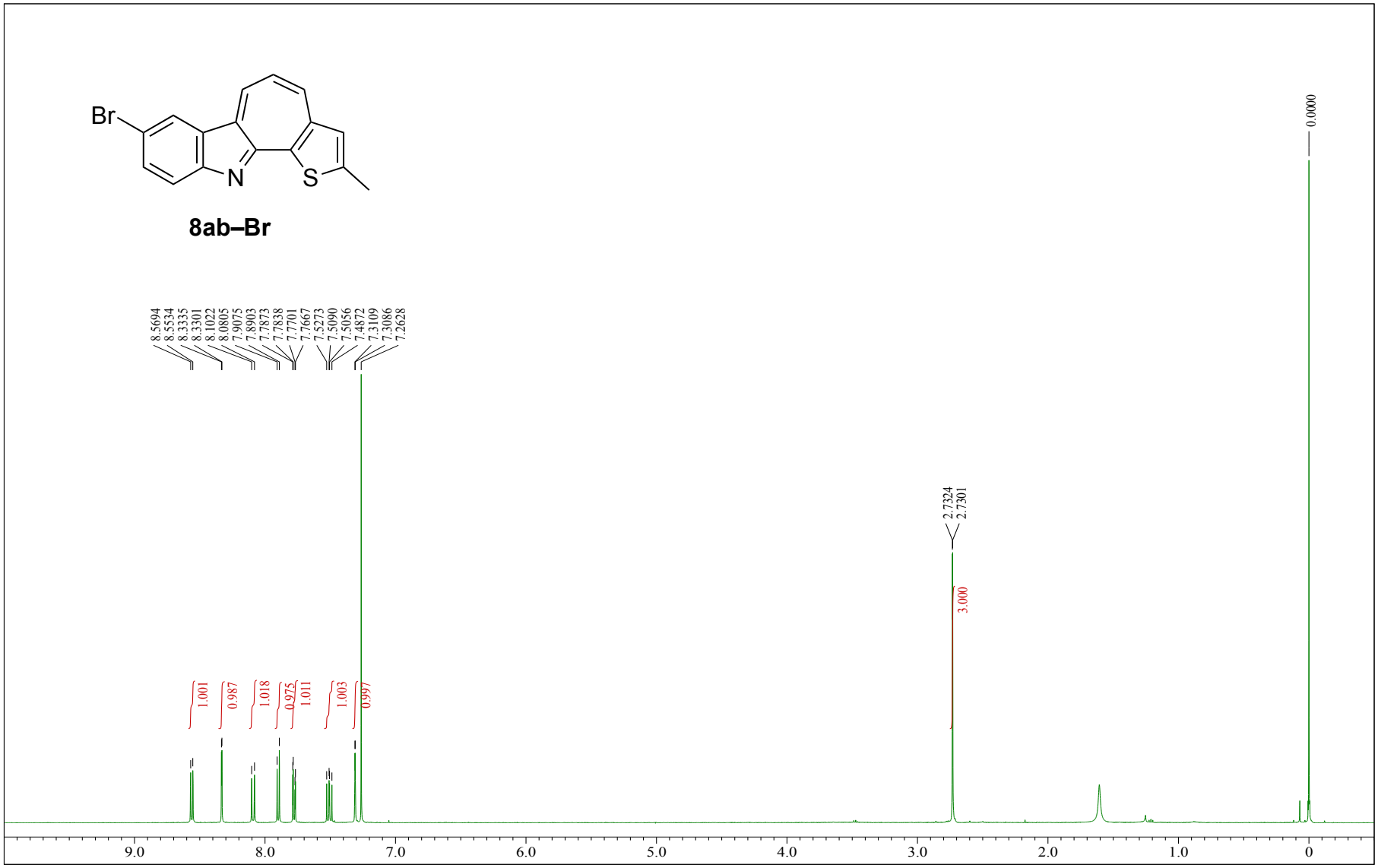


Figure S83. ^{1}H NMR spectrum of compound **8ab–Br** in $CDCl_3$.

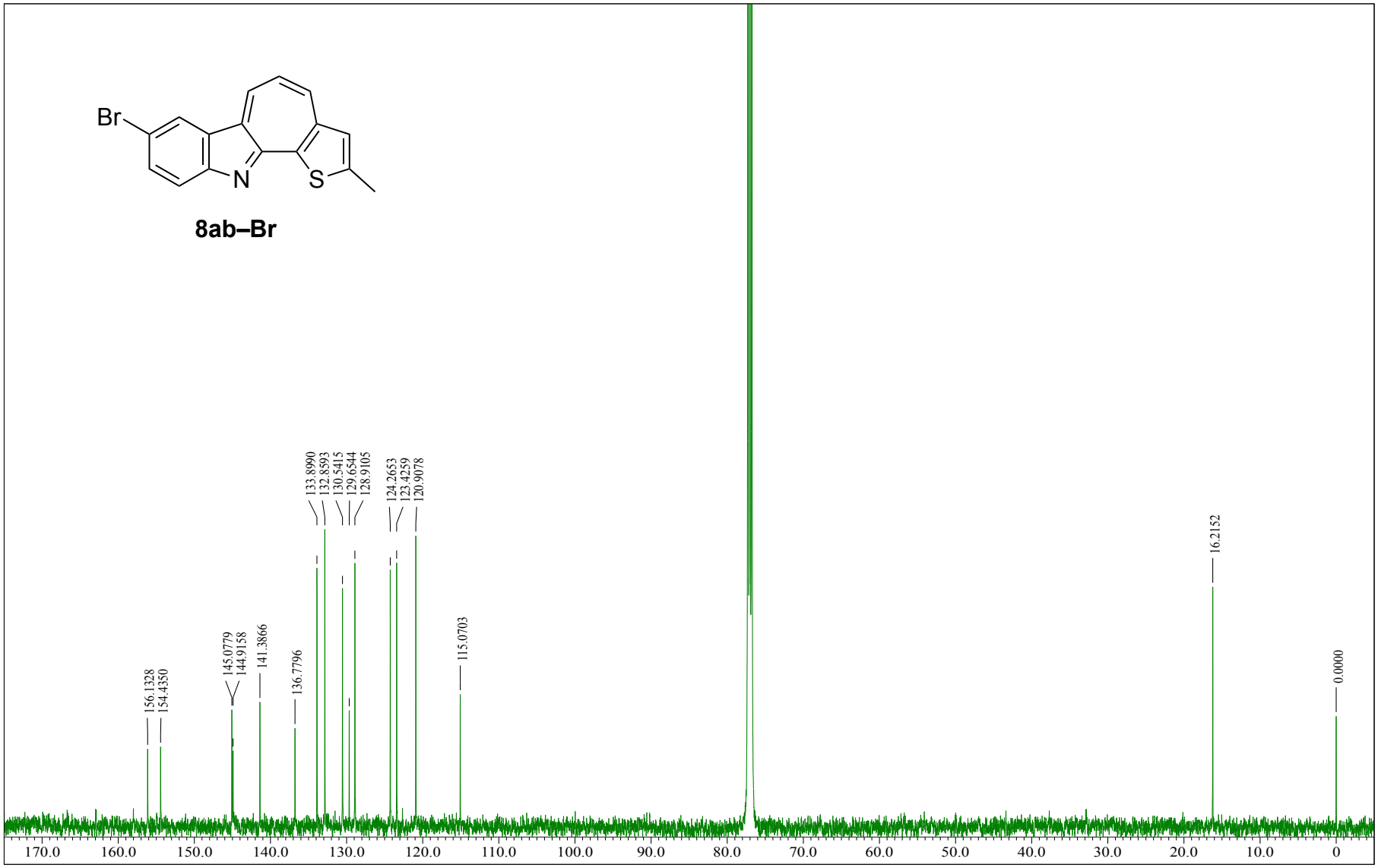


Figure S84. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8ab–Br** in $CDCl_3$.

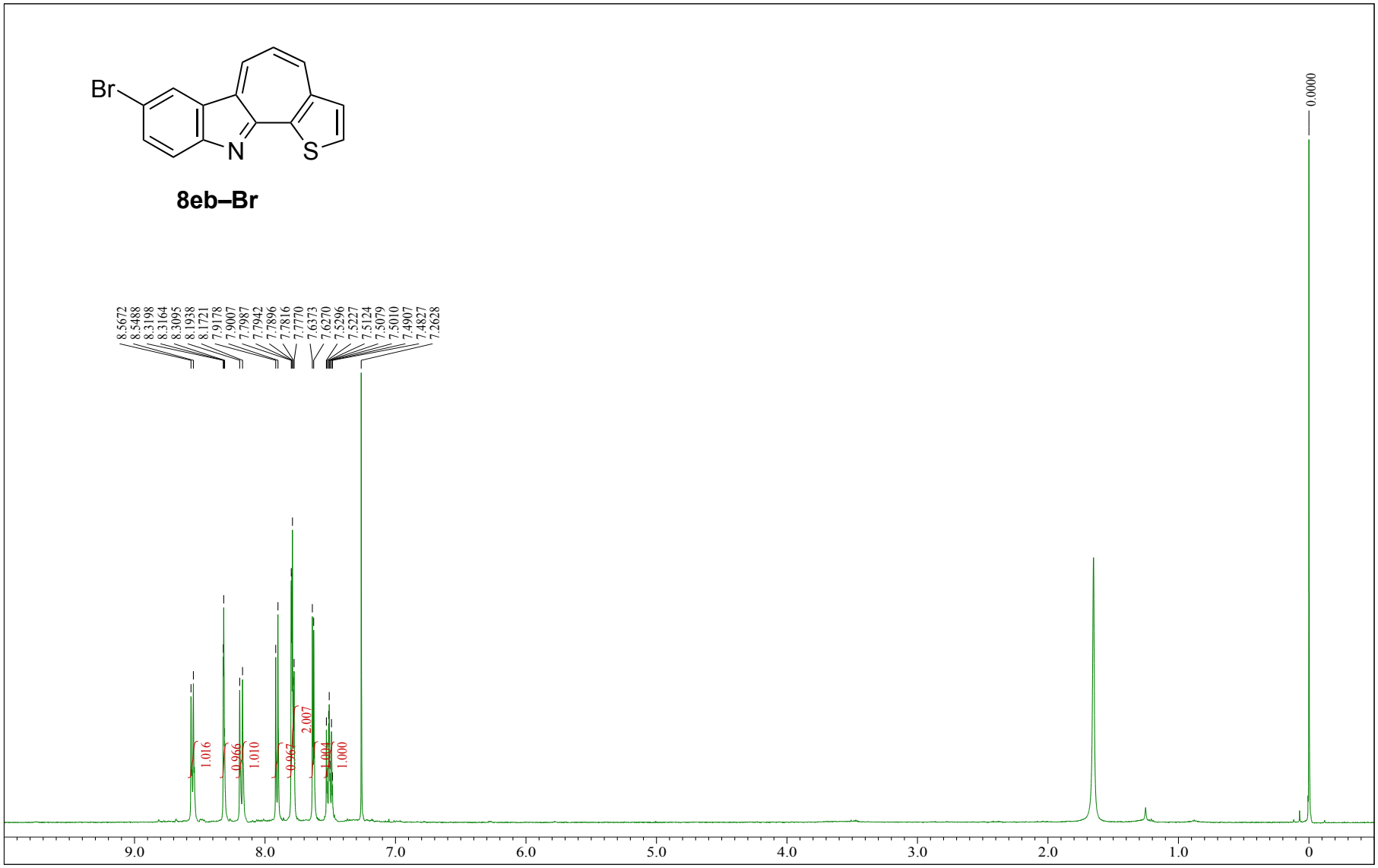


Figure S85. ^{1}H NMR spectrum of compound **8eb–Br** in $CDCl_3$.

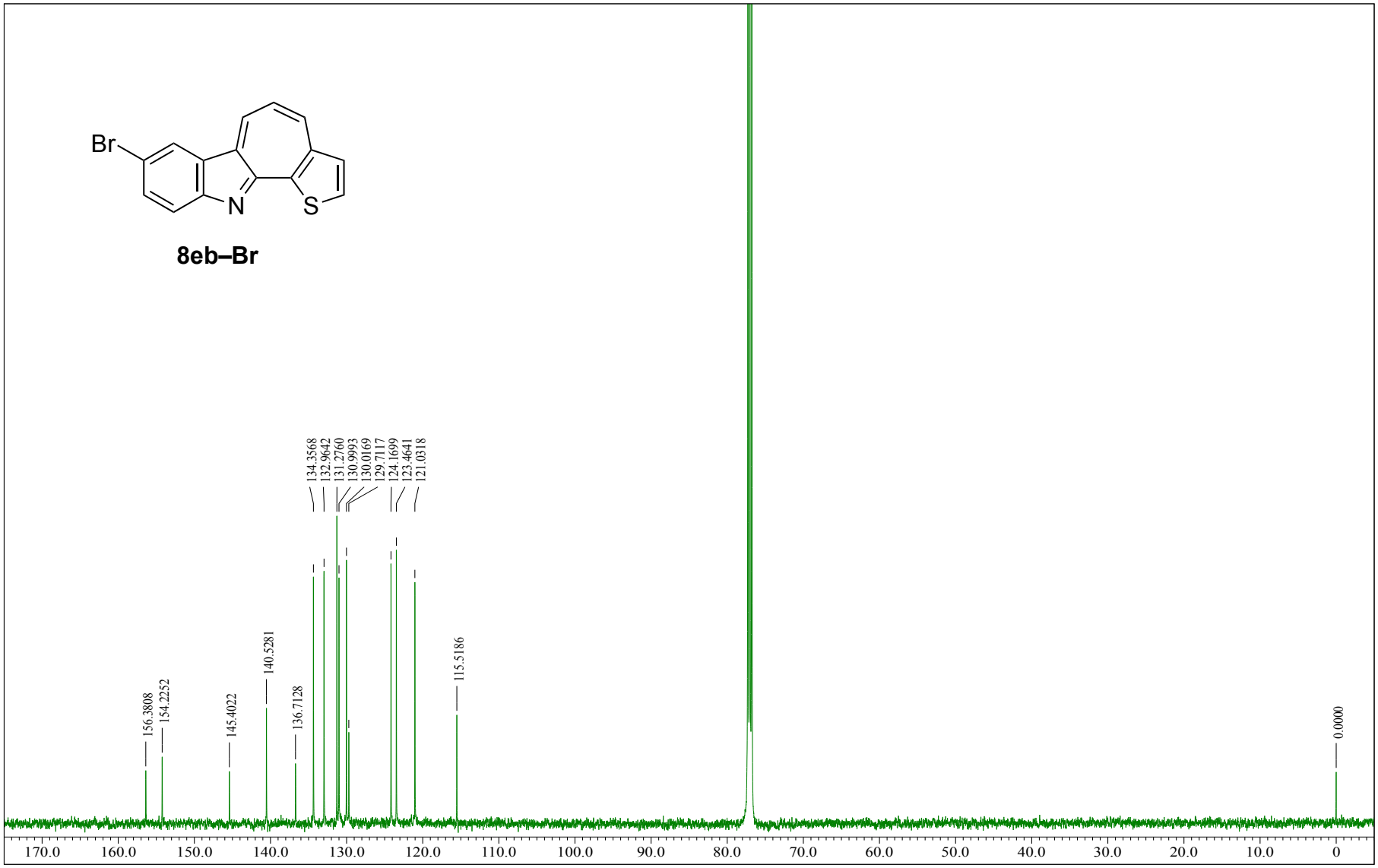


Figure S86. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8eb–Br** in $CDCl_3$.

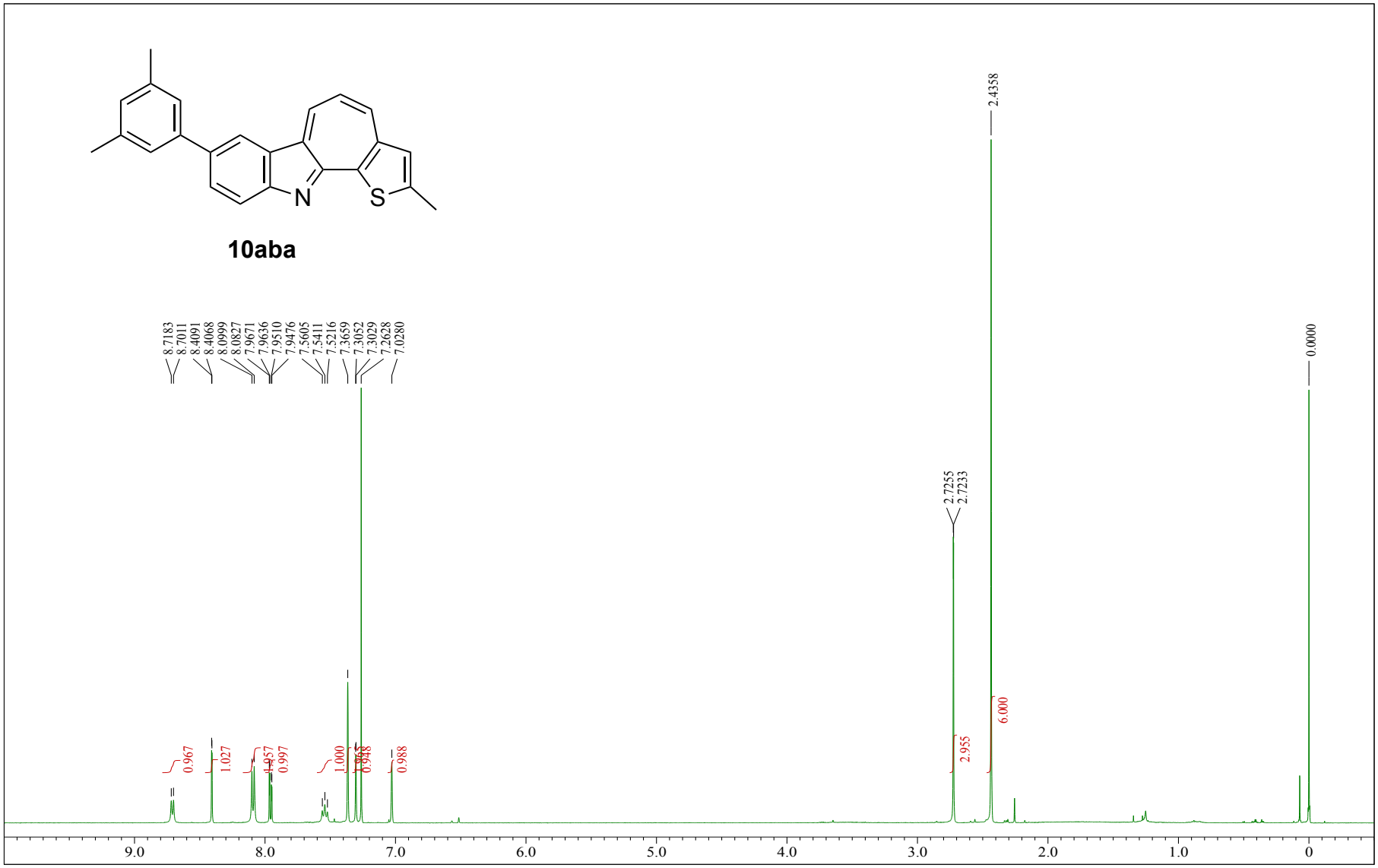


Figure S87. ^{1}H NMR spectrum of compound **10aba** in $CDCl_3$.

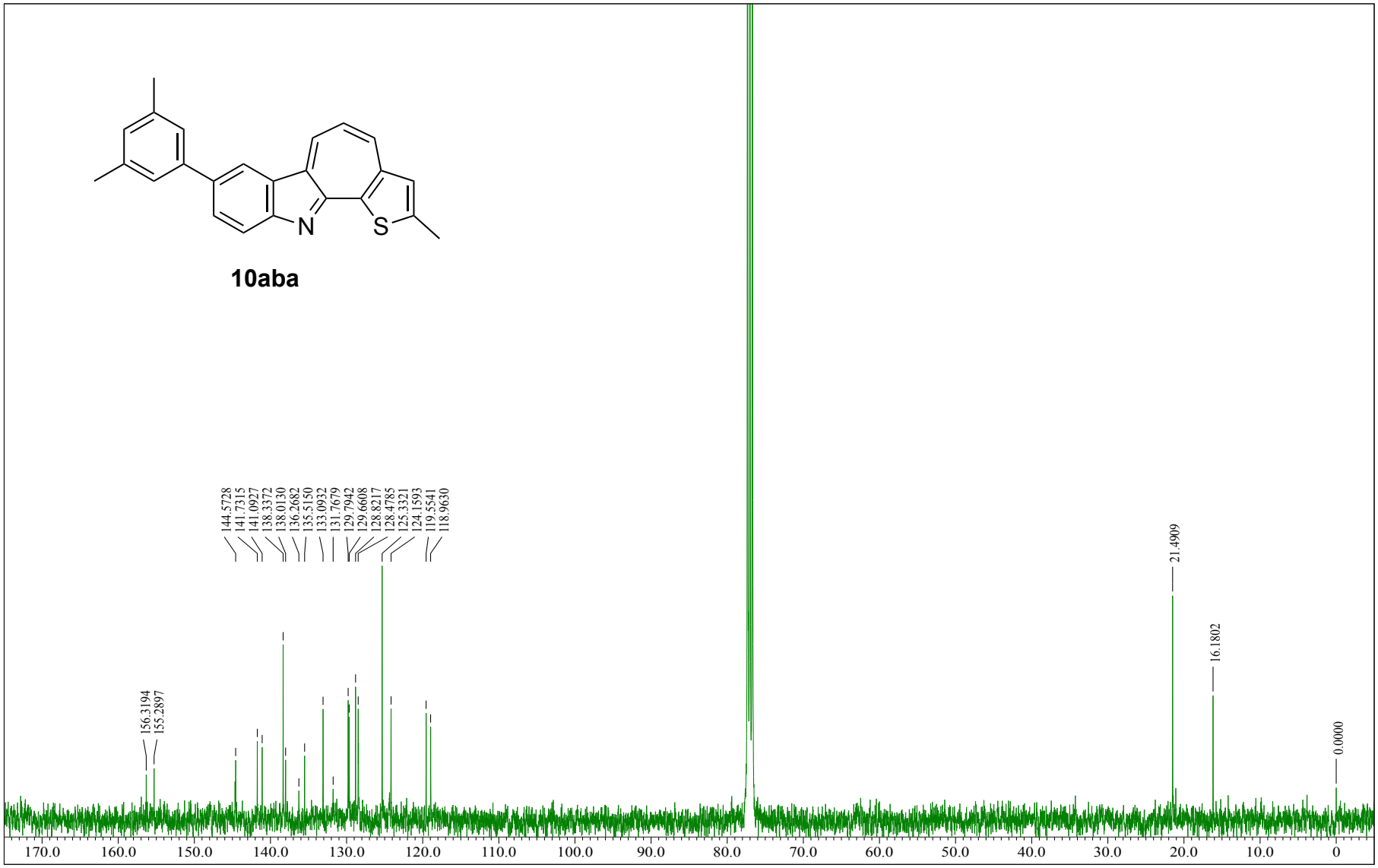


Figure S88. $^{13}C\{^{1}H\}$ NMR spectrum of compound **10aba** in $CDCl_3$.

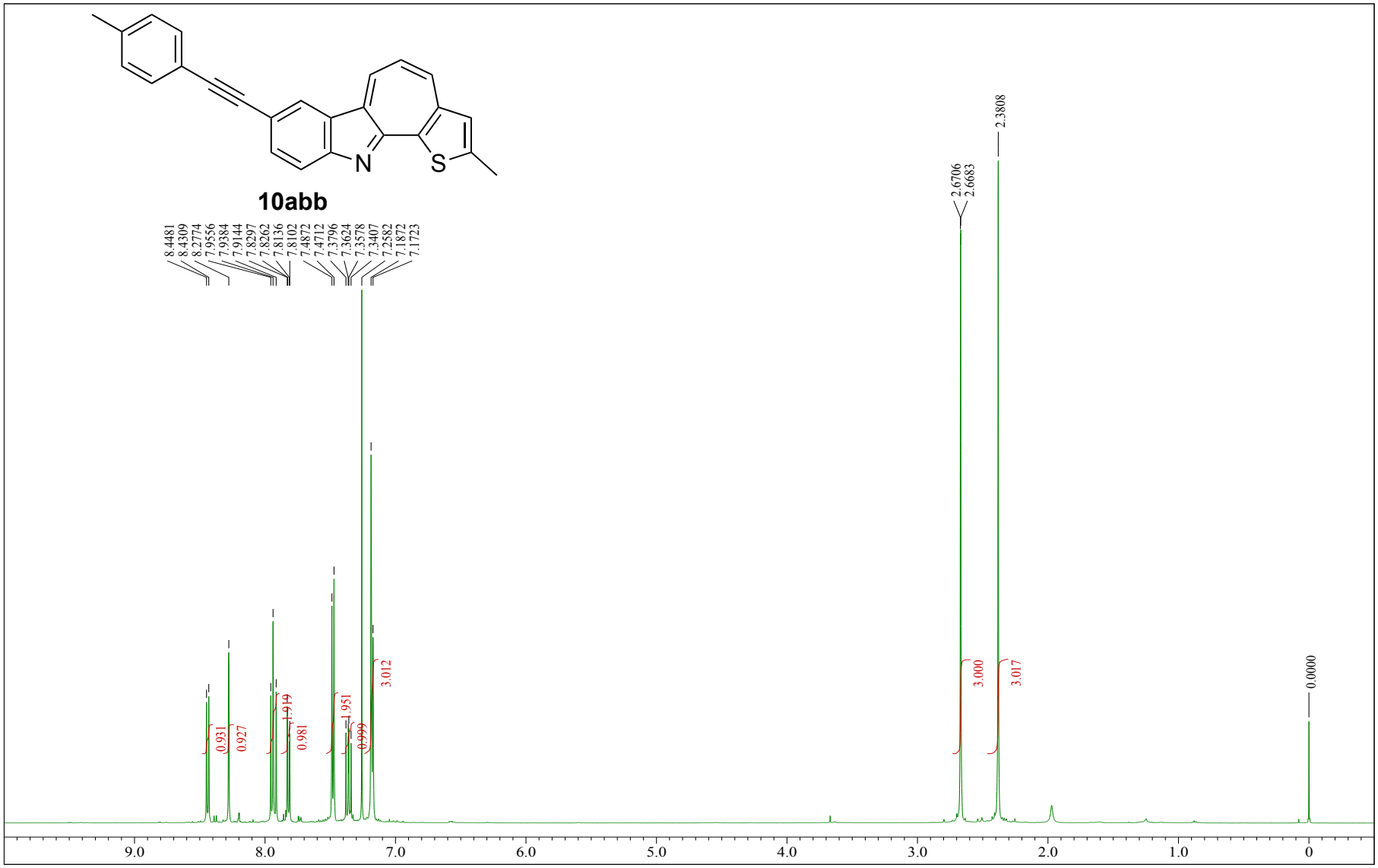


Figure S89. ^{1}H NMR spectrum of compound **10abb** in $CDCl_3$.

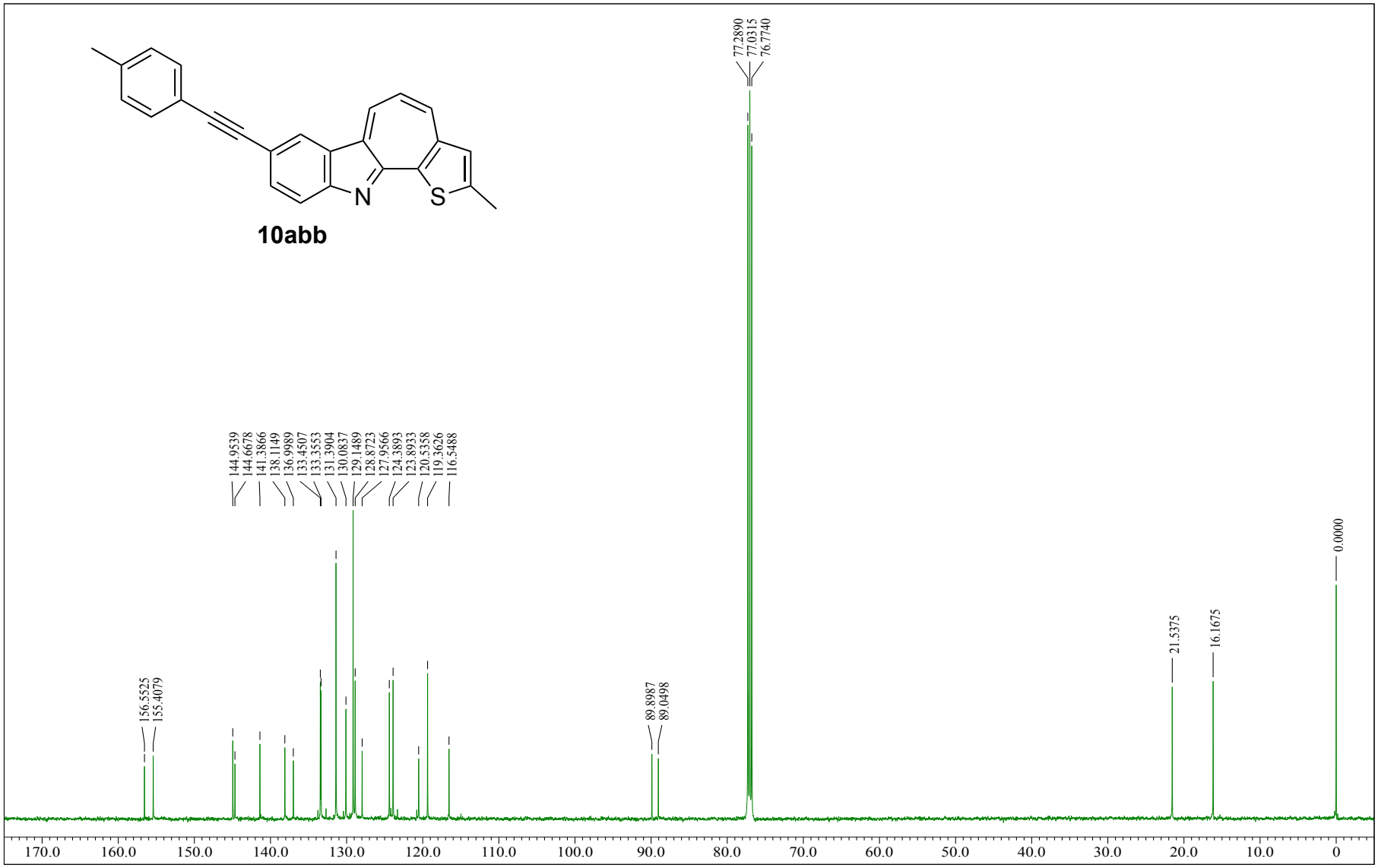


Figure S90. $^{13}C\{^{1}H\}$ NMR spectrum of compound **10abb** in $CDCl_3$.

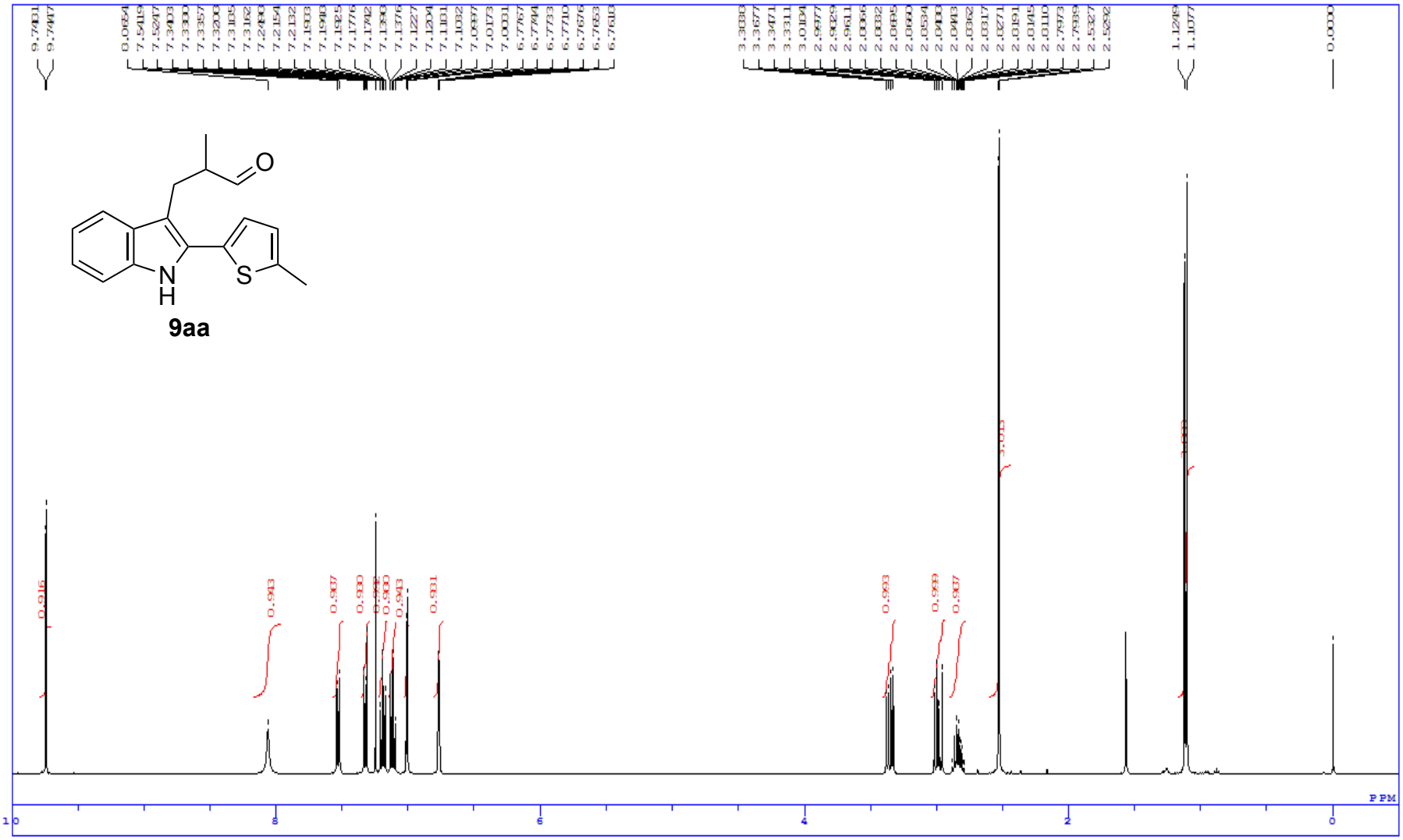


Figure S91. ^{1}H NMR spectrum of compound **9aa** in $CDCl_3$.

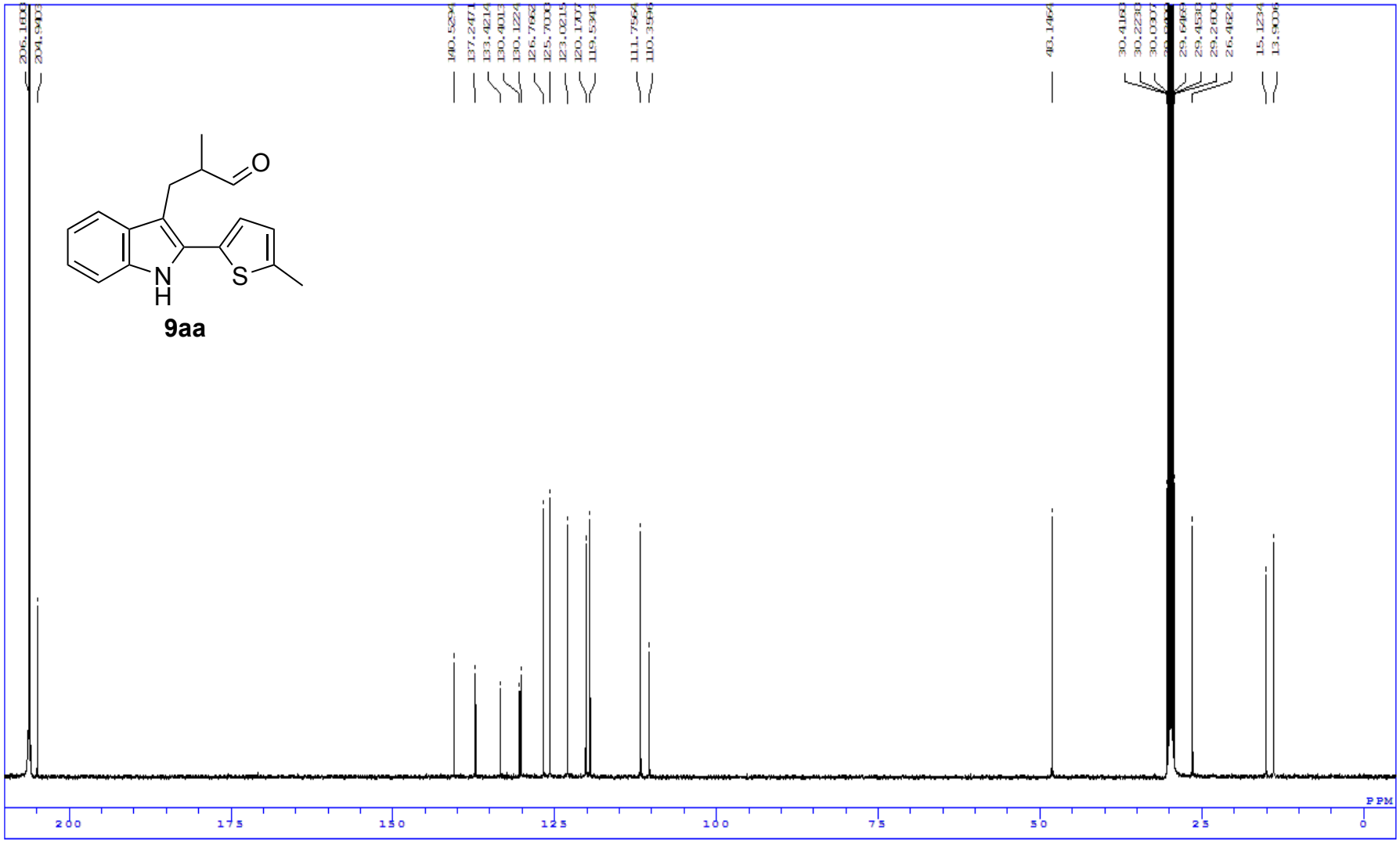


Figure S92. $^{13}C\{^{1}H\}$ NMR spectrum of compound **9aa** in acetone-d_6.

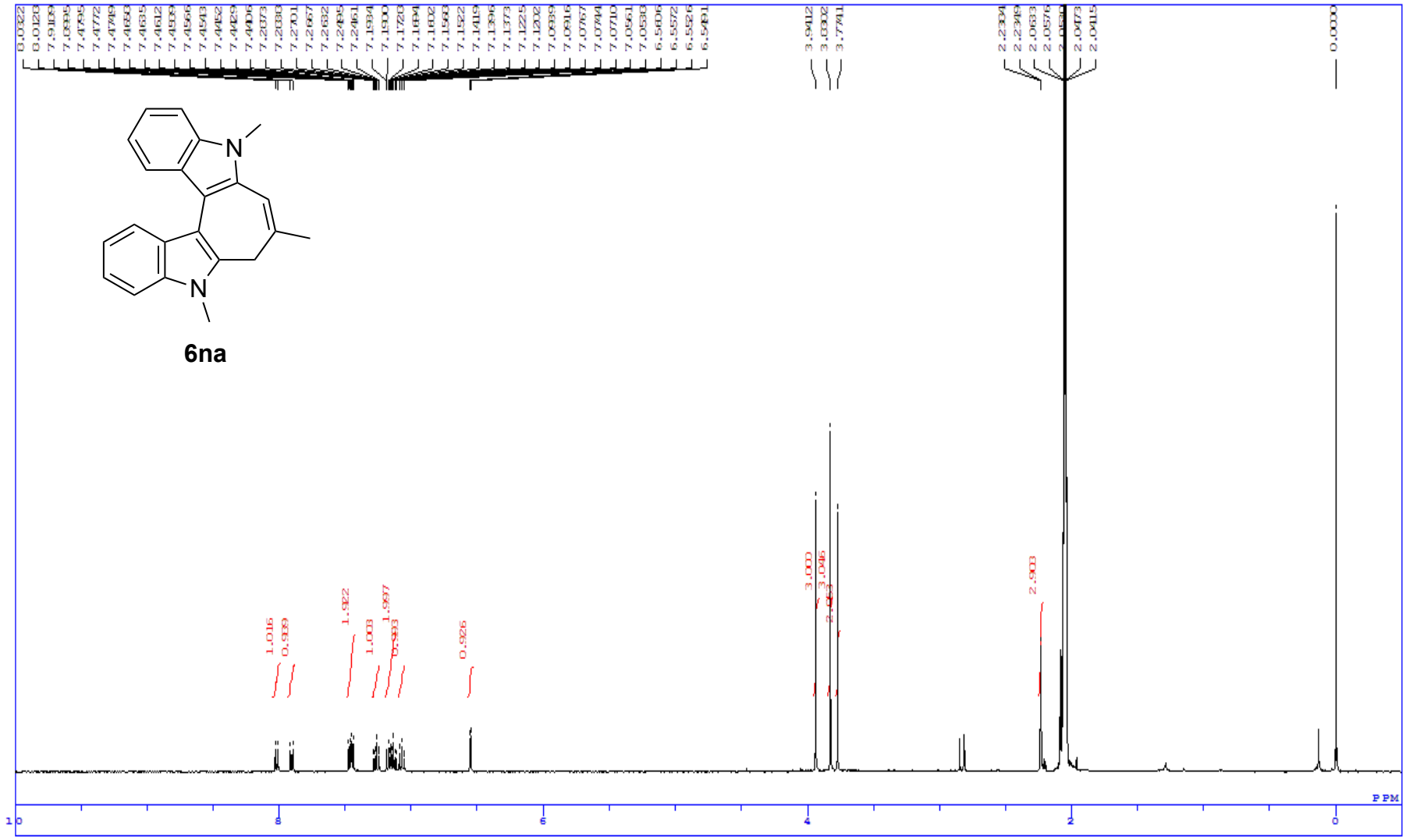


Figure S93. ^{1}H NMR spectrum of compound **6na** in acetone-d_6.

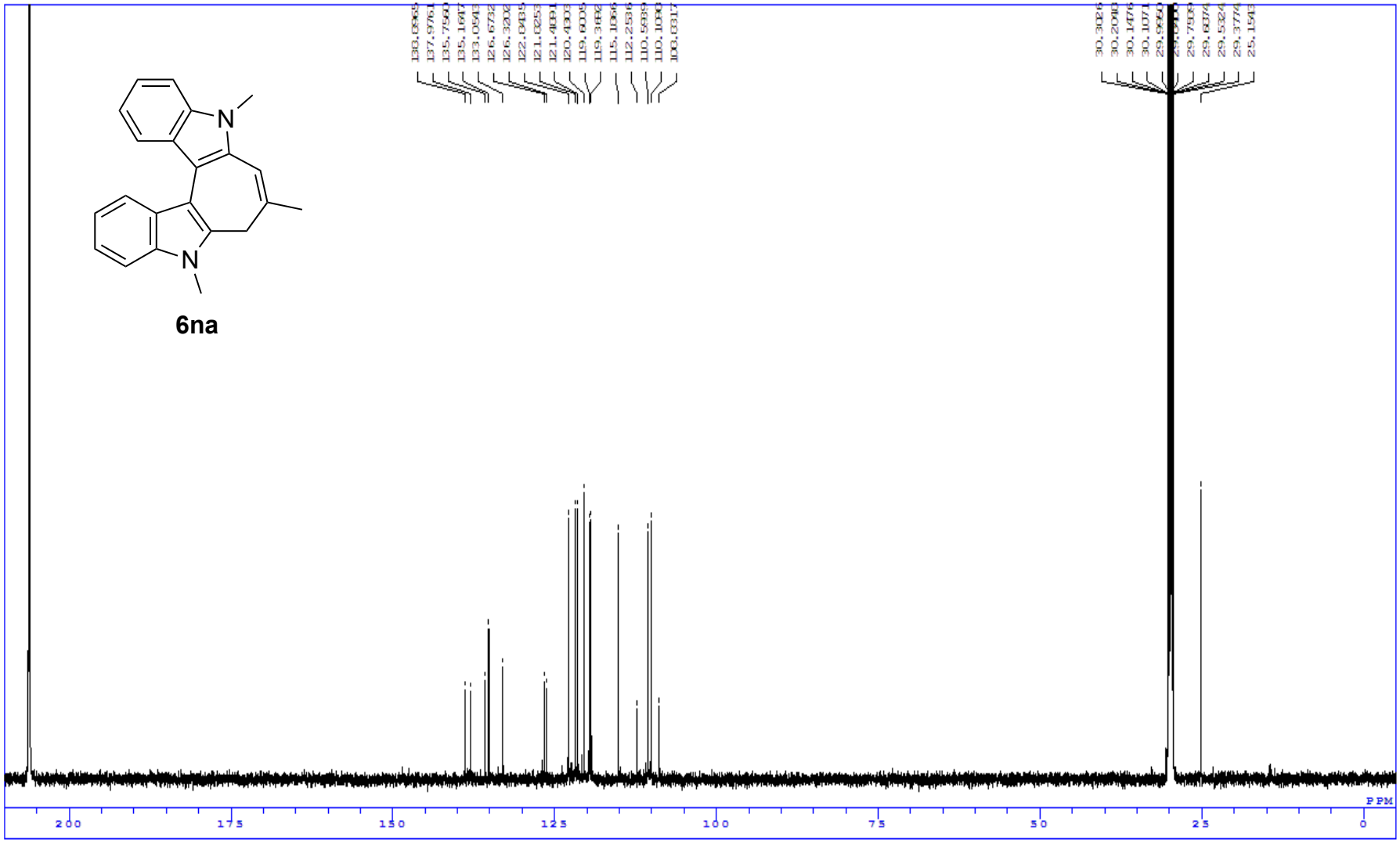


Figure S94. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6na** in acetone-d_6.