Electronic Supplementary Information

Arylation of Indoles Using Cyclohexanones Dually-Catalyzed by Niobic Acid and Palladium-on-Carbons

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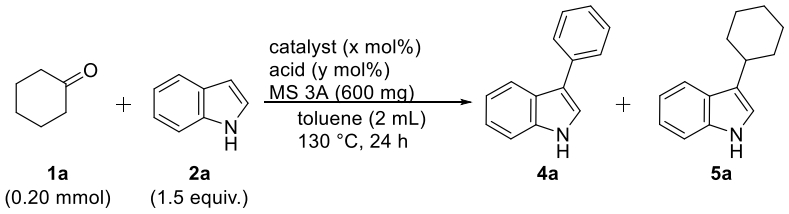
1. General information.

10% Pt/C, Pd/C, and Rh/C were supplied by the N. E. Chemcat Corporation (Tokyo, Japan). Toluene, DMF, DMSO, 1,4-dioxane, and water as solvents were purchased from commercial sources and used without further purification. Cyclohexanones (**1a**, **1b**, **1c**, **1e**, **1f**), indoles (**2a**, **2b**, **2c**, **2d**, **2e**, **2f**, **2g**) and pyrroles (**6a**, **6b**) were also purchased from commercial sources and used without further purification. Flash column chromatography was performed with Silica Gel 60 N (Kanto Chemical Co., Inc., 63―210 μm spherical, neutral). ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL AL 400, ECZ 400 or ECA 500 spectrometer at room temperature in $CDCl_3$ as a solvent and internal standard (^{1}H NMR: δ = 7.26 for $CDCl_3$, ^{13}C NMR: δ = 77.0 for $CDCl_3$) with tetramethylsilane as a further internal standard. IR spectra were recorded by a Brucker FT-IR ALPHA. ESI high-resolution mass spectra (HRMS) were measured by a Shimadzu hybrid IT-TOF mass spectrometer. Melting points were measured by a SANSYO SMP-300 melting point apparatus.

2. Detailed optimization.

Table S1. Further optimization.

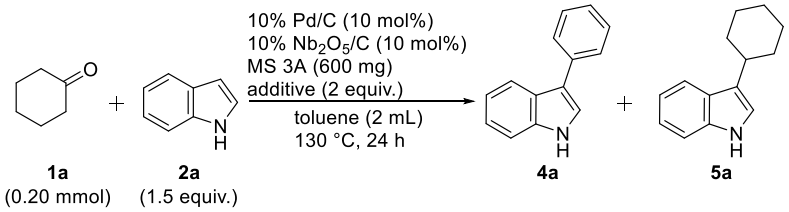


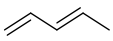
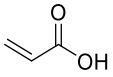
entry	transition metal cat. (x mol%)	acid (y mol%)	yield (%)	
			4a	**5a**
1[a)]	10% Pd/C (10)	10% Nb_2O_5/C (10)	18	54
2 [a)b)]	10% Pd/C (10)	10% Nb_2O_5/C (10)	22	18
3 [a)]	10% Pd/C (5)	10% Nb_2O_5/C (5)	13	41
4	10% Pd/C (10)	10% Nb_2O_5/C (10)	45	55
5 [c)]	10% Pd/C (10)	10% Nb_2O_5/C (10)	39	38
6 [d)]	10% Pd/C (10)	10% Nb_2O_5/C (10)	26	29
7 [e)]	10% Pd/C (10)	10% Nb_2O_5/C (10)	3	7
8 [f)]	10% Pd/C (10)	10% Nb_2O_5/C (10)	no reaction	
9 [g)]	10% Pd/C (10)	10% Nb_2O_5/C (10)	53	41
10 [a)h)]	10% Pd/C (10)	10% Nb_2O_5/C (10)	27	37
11	10% Pd/C (10)	10% Nb_2O_5/C (5)	45	51
12	10% Pd/C (10)	10% Nb_2O_5/C (1)	12	12
13	10% Pd/C (5) + 10% Pt/C (5)	10% Nb_2O_5/C (10)	43	53

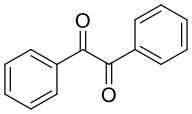
14 [i)]	10% Pd/C (10)	10% Nb_2O_5/C (10)	50	49
15 [j)]	10% Pd/C (10)	10% Nb_2O_5/C (10)	52	48
16	10% Ir/C (10)	10% Nb_2O_5/C (10)	19	36
17 [k)]	10% Pd/C (10)	10% Nb_2O_5/C (10)	50	50
18 [a)]	10% Pd/C (10)	Nb_2O_5 (10)	25	21
19	10% Pd/C (10)	Nb_2O_5 (20)	15	8
20 [l)]	10% Pd/C (10)	Nb_2O_5 (10)	11	7
21 [a)]	10% Pd/C (10)	conc. HCl (1.0 equiv.)	10	6

a) Without MS 3A. b) CH_3CN was used instead of toluene. c) **2a** (0.20 mmol) and **1a** (0.30 mmol; 1.5 equiv.) was used. d) At 100 °C. e) Toluene (1 mL) was used. f) 2-PrOH was used instead of toluene. g) *p*-Xylene was used instead of toluene. h) Neat conditions. i) The reaction was carried out in a sealed test tube. j) Under O_2 atmosphere. k) MS 5A was used instead of MS 4A. l) At 140 °C.

Table S2. Effect of hydrogen acceptor.



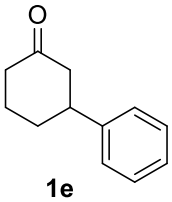
entry	additive	yield (%)	
		4a	**5a**
1		78	11
2 [a)]		42	11
3		22	18
4		24	9
5		59	27

6		39	-

a) **2a** (0.20 mmol) and **1a** (0.30 mmol; 1.5 equiv.) was used.

3. Preparation of Substrates.

3-Phenylcyclohexanone (1d)[1)]

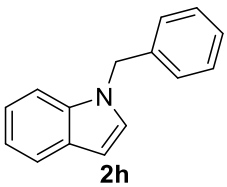


1e

To a solution of $Pd(OAc)_2$ (34 mg, 0.15 mmol, 5 mol %) and PPh_3 (79 mg, 0.30 mmol, 10 mol %), phenylboronic acid (732 mg, 6.00 mmol, 2 equiv.), 2-cyclohexenone (288 mg, 3.0 mmol), and Cs_2CO_3 (978 mg, 3.00 mmol, 3 equiv.) in anhydrous toluene (6 mL) was added chloroform (0.1 mL, 40 mol %) at room temperature under argon. After 48 h-stirring at 80 ºC, the reaction mixture was cooled down to room temperature and extracted with AcOEt (30 mL x 3). The organic layers were dried over with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified with silica-gel column chromatography (*n*-hex/EtOAc = 10/1), and 3-phenylcyclohexanone (**1e**; 157 mg, 0.9 mmol) was obtained in 30% yield.

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35—7.32 (m, 2H), 7.26—7.22 (m, 3H), 3.05—2.98 (m, 1H), 2.62—2.51 (m, 2H), 2.49—2.32 (m, 2H), 2.18—2.07 (m, 2H), 1.90—1.74 (m, 2H). ^{1}H NMR spectrum of the product was identical to that of the reference 2.

***N*-Benzylindole (2h)**



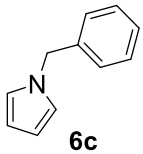
2h

To a solution of indole (590 mg, 5.04 mmol) and KOH (452 mg, 8.06 mmol, 1.6 equiv.) in anhydrous THF (10 mL) was added benzyl chloride (0.860 mL, 7.47 mmol, 1.5 equiv.) at 0 ºC under argon. After stirring 18 h-stirring at room temperature, the reaction mixture was cooled down to 0 ºC and extracted with AcOEt (30 mL x 3). The organic layers were dried over with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified with silica-gel column chromatography

(*n*-hex/EtOAc = 30/1), and *N*-benzylindole (**2h;** 1.03 g, 4.95 mmol) was obtained in 99% yield.

Pale red solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, 1H, J = 7.6 Hz), 7.32—7.25 (m, 5H), 7.19—7.05 (m, 4H), 7.56 (d, 1H, J = 3.2 Hz), 5.34 (s, 2H). ^{1}H NMR spectrum of the product was identical to that of the reference 3.

1-Benzyl-*1H*-pyrrole (6c)



6c

To a solution of pyrrole (350 mg, 5.22 mmol) and KOH (560 mg, 9.98 mmol, 1.9 equiv.) in anhydrous DMSO (10 mL) was added benzyl chloride (0.860 mL, 7.47 mmol, 1.4 equiv.) at 0 ^{o}C under argon. After 17 h-stirring at room temperature, the reaction mixture was cooled down to 0 ^{o}C, quenched with 1N HCl aq. (20 mL) and extracted with AcOEt (30 mL). The organic layer was washed with saturated $NaHCO_3$ aq. (30 mL) and Brine (30 mL), and dried over with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified with silica-gel column chromatography (*n*-hex/EtOAc = 100/1), and 1-benzyl-1*H*-pyrrole (**6c;** 728 mg, 4.63 mmol) was obtained in 89% yield.

Pale purple solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34—7.27 (m, 3H), 7.11 (d, 2H, J = 6.4 Hz), 6.69 (d, 2H, J = 1.6 Hz), 6.19 (t, 2H, J = 1.6 Hz), 5.07 (s, 2H). ^{1}H NMR spectrum of the product was identical to that of the reference 4.

4. General procedures (Tables 1-4 and Scheme 3).

Procedure A to synthesize 4 and 5:

To suspension of cyclohexanone (**1**; 0.20 mmol) and indole derivative (**2**; 0.30 mmol, 1.5 equiv.) in toluene (2 mL) were added MS3A (600 mg), 10% Pd/C (21.2 mg, 0.020 mmol, 10 mol %), 10% Nb_2O_5/C [including water (60% w/w), 130 mg, 0.020 mmol, 10 mol %][5] and 2,3-dimethyl-1,2-butadiene (45 μL, 0.40 mmol, 2 equiv.) under argon. After 24 h-stirring at 130 ^{o}C, the reaction mixture was cooled to room temperature and passed through a celite pad to remove catalysts and MA3A. The filtrate was concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding 3-arylindole derivative (**4**) and 3-cyclohexylindole derivative (**5**).

Procedure B to synthesize 4 and 5:

To suspension of cyclohexanone (**1**; 0.20 mmol) and indole derivative (**2**; 0.30 mmol, 1.5 equiv.) in

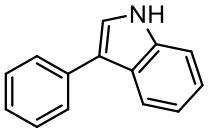
toluene (2 mL) were added MS3A (600 mg), 10% Pd/C (21.2 mg, 0.020 mmol, 10 mol %) and 10% Nb_2O_5/C [including water (60% w/w), 130 mg, 0.020 mmol, 10 mol %][5] under argon. After 24 h-stirring at 130 ºC, the reaction mixture was cooled to room temperature and passed through a celite pad to remove catalysts. The filtrate was concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding 3-arylindole derivative (**4**) and 3-cyclohexylindole derivative (**5**).

Procedure C to synthesize 7:

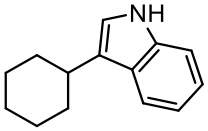
To suspension of cyclohexanone (**1a**; 0.20 mmol) and pyrrole derivative (**2**; 0.30 mmol, 1.5 equiv.) in toluene (2 mL) were added MS3A (600 mg), 10% Pd/C (21.2 mg, 0.020 mmol, 10 mol %) and 10% Nb_2O_5/C [including water (60% w/w), 130 mg, 0.020 mmol, 10 mol %][5] under argon. After 24 h-stirring at 130 ºC, the reaction mixture was cooled to room temperature and passed through a celite pad to remove catalysts. The filtrate was concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding 2 or 3-arylindole derivative (**7**).

5. Spectroscopic data of products.

3-Phenyl-1*H*-indole (4a) in Table 1, entry 1



3-Cyclohexyl-1*H*-indole (5a)



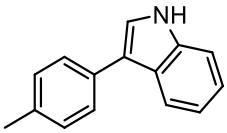
According to general procedure A (Table 2, entry 6), **1a** (19.6 mg, 0.20 mmol) and **2a** (35.1 mg, 0.30 mmol) were used as substrates. As a result, **4a** (30.1 mg, 0.16 mmol) was obtained in 78% yield, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

According to general procedure B (Table 1, entry 1), **1a** (19.6 mg, 0.20 mmol) and **2a** (35.1 mg, 0.30 mmol) were used as substrates. As a result, **4a** (17.4 mg, 0.090 mmol) and **5a** (21.9 mg, 0.11 mmol) were obtained in 45% and 55 % yield, respectively, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

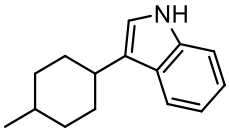
4a; Pale purple solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (brs, 1H), 7.95 (d, 1H, J = 8.0 Hz), 7.68 (d, 2H, J = 7.0 Hz), 7.47—7.40 (m, 3H), 7.38 (d, 1H, J = 2.0 Hz), 7.31—7.24 (m, 2H), 7.20 (t, 1H, J = 8.0 Hz). ^{1}H NMR spectrum of the product was identical to that of the reference 6.

5a; Pale purple solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (brs, 1H), 7.66 (d, 1H, J = 7.5 Hz), 7.35 (d, 1H, J = 8.0 Hz) , 7.17 (dt, 1H, J = 8.0, 1.0 Hz), 7.09 (dt, 1H, J = 7.5, 1.0 Hz), 6.95 (d, 1H, J = 2.0 Hz), 2.85—2.81 (m, 1H), 2.11—2.07 (m, 2H), 1.85—1.76 (m, 3H), 1.51—1.44 (m, 4H), 1.33—1.27 (m, 1H). ^{1}H NMR spectrum of the product was identical to that of the reference 6.

3-(4-Methylphenyl)-1*H*-indole (4b)



3-(4-Methylcyclohexyl)-1*H*-indole (5b)



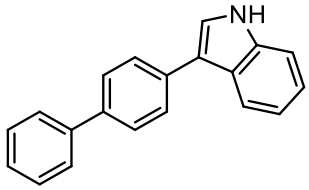
According to general procedure A (Table 3, entry 1), **1b** (22.4 mg, 0.20 mmol) and **2a** (35.1 mg, 0.30 mmol) were used as substrates. As a result, **4b** (21.1 mg, 0.10 mmol) was obtained in 51% yield, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

According to general procedure B (Table 3, entry 2), **1b** (22.4 mg, 0.20 mmol) and **2a** (35.1 mg, 0.30 mmol) were used as substrates. As a result, **4b** (18.2 mg, 0.088 mmol) and **5b** (19.6 mg, 0.092 mmol) were obtained in 44% and 46% yield, respectively, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

4b; Pale purple solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (brs, 1H), 7.93 (d, 1H, J = 7.6 Hz), 7.58 (d, 2H, J = 8.0 Hz), 7.43 (d, 1H, J = 8.4 Hz), 7.35 (d, 1H, J = 2.8 Hz), 7.28—7.25 (m, 4H), 2.41 (s, 3H). ^{1}H NMR spectrum of the product was identical to that of the reference 6.

5b; Colorless solid; Mixture of diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$, *trans* isomer): δ 7.89 (brs, 1H), 7.66 (d, 1H, J = 8.0 Hz), 7.36 (d, 1H, J = 8.4 Hz) , 7.18 (t, 1H, J = 7.6 Hz), 7.10 (t, 1H, J = 7.2 Hz), 6.95 (d, 1H, J = 2.4 Hz), 2.81—2.74 (m, 1H), 2.13—2.10 (m, 2H), 1.86-1.79 (m, 2H), 1.52—1.40(m, 3H), 1.15 (dq, 2H, J = 12.0, 3.2 Hz),0.96 (d, 3H, J = 6.4 Hz); ^{1}H NMR (400 MHz, $CDCl_3$, *cis* isomer): 7.89 (brs, 1H), 7.66 (d, 1H, J = 8.0 Hz), 7.36 (d, 1H, J = 8.4 Hz) , 7.18 (t, 1H, J = 7.6 Hz), 7.10 (t, 1H, J = 7.2 Hz), 7.02 (d, 1H, J = 2.4 Hz), 3.06-2.97 (m, 1H), 1.90—1.79 (m, 5H), 1.71—1.62 (m, 2H), 1.52—1.40 (m, 2H), 1.01 (d, 3H, J = 6.8 Hz). ^{1}H NMR spectrum of the product was identical to that of the reference 7.

3-([1-1'-Biphenyl]-4-yl)-1*H*-indole (4c)

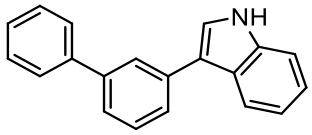


According to general procedure A (Table 3, entry 3), **1c** (34.8 mg, 0.20 mmol) and **2a** (35.1 mg, 0.30 mmol) were used as substrates. As a result, **4c** (34.5 mg, 0.13 mmol) was obtained in 64% yield, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

According to general procedure B (Table 3, entry 4), **1c** (34.8 mg, 0.20 mmol) and **2a** (35.1 mg, 0.30 mmol) were used as substrates. As a result, **4c** (21.6 mg, 0.080 mmol) was obtained in 40 % yield, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (brs, 1H), 8.00 (d, 1H, J = 7.6 Hz), 7.78—7.66 (m, 6H), 7.49—7.43 (m, 3H), 7.36 (t, 1H, J = 7.2 Hz), 7.30—7.21 (m, 3H). ^{1}H NMR spectrum of the product was identical to that of the reference 6.

3-([1-1'-Biphenyl]-3-yl)-1*H*-indole (4d)

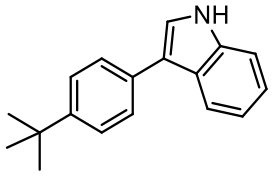


According to general procedure A (Table 3, entry 5), **1d** (34.8 mg, 0.20 mmol) and **2a** (35.1 mg, 0.30 mmol) were used as substrates. As a result, **4d** (32.3 mg, 0.12 mmol) was obtained in 60% yield, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

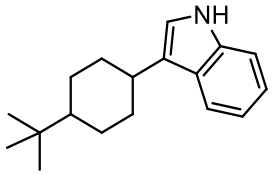
According to general procedure B (Table 3, entry 6), **1d** (34.8 mg, 0.20 mmol) and **2a** (35.1 mg, 0.30 mmol) were used as substrates. As a result, **4d** (25.8 mg, 0.096 mmol) was obtained in 48% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

Colorless solid; M.p. 92—94 ^{o}C; IR (ATR) cm^{-1}: 3404, 1594, 1454, 1427, 1235, 1104, 1014, 894, 794, 745, 694, 670, 666, 603, 580, 501, 463, 423; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (brs, 1H), 8.00 (d, 1H, J = 7.6 Hz), 7.90 (s, 1H), 7.69—7.65 (m, 3H), 7.53—7.52 (m, 2H), 7.49—7.44 (m, 4H), 7.38 (t, 1H, J = 7.2 Hz), 7.30—7.20 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 141.8, 141.4, 136.6, 136.0, 129.2, 128.8, 127.3, 126.4, 126.3, 125.7, 124.9, 122.5, 121.9, 120.4, 119.8, 118.3, 111.4; ESI-HRMS m/z: 269.1181 (M^+); $C_{20}H_{15}N$: 269.1199.

3-(4-*tert*-Butylphenyl)-1*H*-indole (4e)



3-(4-*tert*-Butylcyclohexyl)-1*H*-indole (5e)



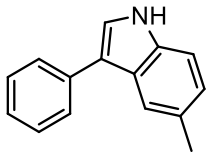
According to general procedure A (Table 3, entry 7), **1e** (30.9 mg, 0.20 mmol) and **2a** (35.1 mg, 0.30 mmol) were used as substrates. As a result, **4e** (20.4 mg, 0.082 mmol) was obtained in 41% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

According to general procedure B (Table 3, entry 8), **1e** (30.9 mg, 0.20 mmol) and **2a** (35.1 mg, 0.30 mmol) were used as substrates. As a result, **4e** (27.4 mg, 0.11 mmol) and **5e** (22.0 mg, 0.086 mmol) were obtained in 55% and 43% yield, respectively, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

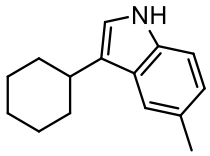
4e; Pale purple solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (brs, 1H), 7.96 (d, 1H, J = 8.4 Hz), 7.62 (d, 2H, J = 8.4 Hz), 7.48 (d, 2H, J = 8.4 Hz), 7.43 (d, 1H, J = 8.4 Hz), 7.36 (d, 1H, J = 2.4 Hz), 7.26—7.17 (m, 2H), 1.38 (s, 9H). ^{1}H NMR spectrum of the product was identical to that of the reference 8.

5e; Pale purple solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (brs, 1H), 7.66 (d, 1H, J = 8.0 Hz), 7.35 (d, 1H, J = 8.0 Hz) , 7.18 (t, 1H, J = 8.0 Hz), 7.10 (t, 1H, J = 8.0 Hz), 6.95 (d, 1H, J = 2.4 Hz), 2.80—2.73 (m, 1H), 2.19—2.16 (m, 2H), 1.92—1.89 (m, 2H), 1.55—1.46 (m, 2H), 1.28—1.05 (m, 3H), 0.90 (s, 9H). ^{1}H NMR spectrum of the product was identical to that of the reference 7.

5-Methyl-3-phenyl-1*H*-indole (4f)



5-Methyl-3-cyclohexyl-1*H*-indole (5f)



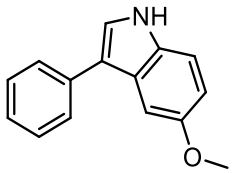
According to general procedure A (Table 4, entry 1), **1a** (19.6 mg, 0.20 mmol) and **2b** (39.4 mg, 0.30 mmol) were used as substrates. As a result, **4f** (20.7 mg, 0.10 mmol) and **5f** (6.40 mg, 0.030 mmol) were obtained in 50% and 15% yield, respectively, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

According to general procedure B (Table 4, entry 2), **1a** (19.6 mg, 0.20 mmol) and **2b** (39.4 mg, 0.30 mmol) were used as substrates. As a result, **4f** (18.6 mg, 0.090 mmol) and **5f** (21.3 mg, 0.10 mmol) were obtained in 45% and 51 % yield, respectively, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

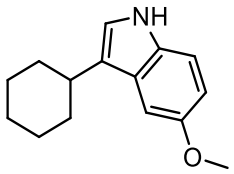
4f; Pale purple solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (brs, 1H), 7.73 (s, 1H), 7.67 (d, 2H, J = 8.0 Hz), 7.45 (t, 2H, J = 8.0 Hz), 7.34—7.27 (m, 3H), 7.08 (d, 1H, J = 8.0 Hz), 2.48 (s, 3H). ^{1}H NMR spectrum of the product was identical to that of the reference 6.

5f; Pale purple solid; M.p. 93—94 ^{o}C; IR (ATR) cm^{-1}: 3402, 2917, 2846, 1478, 1447, 1418, 1222, 1093, 871, 792, 762, 590, 502, 450, 423; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (brs, 1H), 7.43 (s, 1H), 7.24 (d, 1H, J = 6.4 Hz), 7.00 (d, 1H, J = 6.4 Hz) , 6.91 (d, 1H, J = 2.0 Hz), 2.82—2.78 (m, 1H), 2.46 (s, 3H), 2.13—2.09 (m, 2H), 1.85—1.76 (m, 3H), 1.51—1.40 (m, 4H), 1.32—1.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 134.6, 128.1, 126.9, 123.3, 122.7, 119.5, 118.9, 110.7, 35.4, 34.0, 26.9, 26.5, 21.5; ESI-HRMS m/z: 213.3231 (M^+); $C_{15}H_{19}N$: 213.3240.

5-Methoxy-3-phenyl-1*H*-indole (4g)



5-Methoxy-3-cyclohexyl-1*H*-indole (5g)



According to general procedure A (Table 4, entry 3), **1a** (19.6 mg, 0.20 mmol) and **2c** (26.6 mg, 0.30 mmol) were used as substrates. As a result, **4g** (19.6 mg, 0.084 mmol) and **5g** (6.00 mg, 0.026

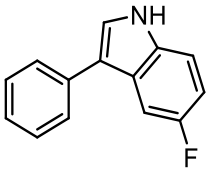
mmol) were obtained in 42% and 13% yield, respectively, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

According to general procedure B (Table 4, entry 4), **1a** (19.6 mg, 0.20 mmol) and **2c** (26.6 mg, 0.30 mmol) were used as substrates. As a result, **4g** (21.0 mg, 0.090 mmol) and **5g** (22.0 mg, 0.096 mmol) were obtained in 45% and 48 % yield, respectively, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

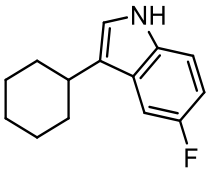
4g; Pale purple solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (brs, 1H), 7.67 (d, 2H, J = 6.4 Hz), 7.46 (t, 2H, J = 6.4 Hz), 7.39 (s, 1H), 7.34—7.25 (m, 3H), 6.92 (d, 1H, J = 8.4 Hz), 3.88 (s, 3H). ^{1}H NMR spectrum of the product was identical to that of the reference 6.

5g; Pale purple solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (brs, 1H), 7.22 (d, 1H, J = 9.2 Hz), 7.08 (d, 1H, J = 2.0 Hz), 6.91 (d, 1H, J = 2.8 Hz), 6.84 (dd, 1H, J = 9.2, 2.8 Hz), 2.81—2.75 (m, 1H), 2.10—2.08 (m, 2H), 1.87—1.75 (m, 3H), 1.52—1.26 (m, 5H). ^{1}H NMR spectrum of the product was identical to that of the reference 7.

5-Fluoro-3-phenyl-1*H*-indole (4h)



5-Fluoro-3-cyclohexyl-1*H*-indole (5h)



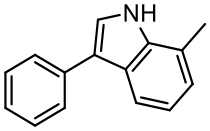
According to general procedure A (Table 4, entry 5), **1a** (19.6 mg, 0.20 mmol) and **2d** (40.5 mg, 0.30 mmol) were used as substrates. As a result, **4h** (19.6 mg, 0.084 mmol) was obtained in 32% yield, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

According to general procedure B (Table 4, entry 6), **1a** (19.6 mg, 0.20 mmol) and **2d** (40.5 mg, 0.30 mmol) were used as substrates. As a result, **4h** (19.0 mg, 0.090 mmol) and **5h** (22.6 mg, 0.10 mmol) were obtained in 45% and 52 % yield, respectively, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

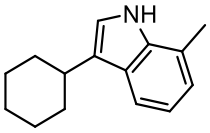
4h; Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (brs, 1H), 7.64—7.57 (m, 3H), 7.48—7.40 (m, 3H), 7.36—7.29 (m, 2H), 7.03—6.97 (m, 1H). ^{1}H NMR spectrum of the product was identical to that of the reference 6.

5h; Brown oil; IR (ATR) cm^{-1}: 3473, 3426, 2922, 2850, 1627, 1580, 1482, 1449, 1371, 1348, 1276, 1240, 1216, 1164, 1129, 1094, 1052, 994, 936, 905, 851, 827, 794, 749, 729, 647, 618, 591, 533, 469, 448, 425; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (brs, 1H), 7.30—7.23 (m, 2H), 6.98 (d, 1H, *J* = 2.4 Hz), 6.92 (dt, 1H, *J* = 9.2, 2.4 Hz), 2.79—2.72 (m, 1H), 2.08—2.07 (m, 2H), 1.85—1.76 (m, 3H), 1.51—1.22 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): 157.4 (d, *J* = 234.1 Hz), 132.8, 127.0 (d, *J* = 9.6 Hz), 123.3 (d, *J* = 4.8 Hz), 121.2, 111.6 (d, *J* = 9.6 Hz), 110.1 (d, *J* = 26.0 Hz), 104.2 (d, *J* = 23.1 Hz), 35.3, 33.8, 26.8, 26.4; ESI-HRMS m/z: 217.2868 (M^+); $C_{14}H_{16}FN$: 217.2874.

7-Methyl-3-phenyl-1*H*-indole (4j)



7-Methoxy-3-cyclohexyl-1*H*-indole (5j)



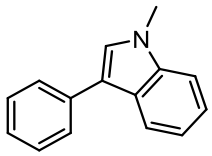
According to general procedure A (Table 4, entry 7), **1a** (19.6 mg, 0.20 mmol) and **2f** (39.4 mg, 0.30 mmol) were used as substrates. As a result, **4j** (13.3 mg, 0.064 mmol) was obtained in 32% yield, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

According to general procedure B (Table 4, entry 8), **1a** (19.6 mg, 0.20 mmol) and **2f** (39.4 mg, 0.300 mmol) were used as substrates. As a result, **4j** (18.7 mg, 0.090 mmol) and **5j** (23.5 mg, 0.11 mmol) were obtained in 45% and 55 % yield, respectively, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

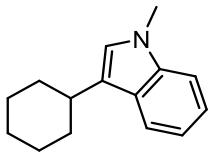
4j; Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (brs, 1H), 7.80 (d, 1H, *J* = 7.6 Hz), 7.67 (d, 2H, *J* = 7.6 Hz), 7.45 (t, 2H, *J* = 7.6 Hz), 7.35 (d, 1H, *J* = 2.8 Hz), 7.29 (t, 1H, *J* = 7.2 Hz), 7.13 (t, 1H, *J* = 7.6 Hz), 7.06 (d, 1H, *J* = 7.2 Hz), 2.51 (s, 3H). ^{1}H NMR spectrum of the product was identical to that of the reference 6.

5j; Colorless solid; M.p. 112—113 ^{o}C; IR (ATR) cm^{-1}: 3420, 2919, 2848, 1433, 1342, 1226, 1165, 1118, 1063, 987, 887, 803, 781, 743, 671, 666, 581, 532, 507, 468, 434; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (brs, 1H), 7.52 (d, 1H, *J* = 8.0 Hz), 7.05—6.96 (m, 3H), 2.83—2.82 (m, 1H), 2.11 (s, 3H), 1.85—1.76 (m, 3H), 1.52—1.21 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): 135.3, 126.2, 123.8, 122.3, 120.2, 119.2, 119.0, 117.1, 35.5, 34.0, 26.9, 26.5, 16.6; ESI-HRMS m/z: 213.3245 (M^+); $C_{15}H_{19}N$: 213.3240.

***N*-Methyl-3-phenyl-indole (4k)**



***N*-Methyl-3-cyclohexyl-indole (5k)**



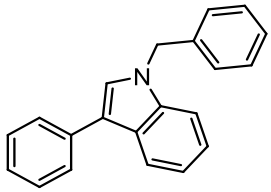
According to general procedure A (Table 4, entry 9), **1a** (19.6 mg, 0.20 mmol) and **2g** (39.4 mg, 0.30 mmol) were used as substrates. As a result, **4k** (29.4 mg, 0.14 mmol) and **5k** (6.00 mg, 0.026 mmol) were obtained in 72% and 13% yield, respectively, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

According to general procedure B (Table 4, entry 10), **1a** (19.6 mg, 0.20 mmol) and **2g** (39.4 mg, 0.30 mmol) were used as substrates. As a result, **4k** (19.2 mg, 0.094 mmol) and **5k** (17.9 mg, 0.084 mmol) were obtained in 47% and 42 % yield, respectively, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

4k; Pale purple solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, 1H, J = 7.6 Hz), 7.66 (d, 2H, J = 7.6 Hz), 7.43 (t, 2H, J = 7.6 Hz), 7.36 (d, 1H, J = 7.6 Hz), 7.30—7.25 (m, 2H), 7.22—7.17 (m, 2H), 3.82 (s, 3H). ^{1}H NMR spectrum of the product was identical to that of the reference 6.

5k; Pale purple solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, 1H, J = 8.0 Hz), 7.28 (d, 1H, J = 8.0 Hz), 7.20 (dt, 1H, J = 8.0, 1.0 Hz), 7.08 (dt, 1H, J = 8.0, 1.0 Hz), 6.80 (s. 1H), 3.74 (s, 3H), 2.85—2.79 (m, 1H), 2.10—2.08 (m, 2H), 1.85—1.75 (m, 3H), 1.48—1.25 (m, 5H). ^{1}H NMR spectrum of the product was identical to that of the reference 9.

***N*-Benzyl-3-phenyl-indole (4l)**



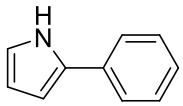
According to general procedure A (Table 4, entry 11), **1a** (19.6 mg, 0.20 mmol) and **2h** (62.2 mg, 0.30 mmol) were used as substrates. As a result, **4l** (15.3 mg, 0.054 mmol) was obtained in 27% yield after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

According to general procedure B (Table 4, entry 12), **1a** (19.6 mg, 0.20 mmol) and **2h** (62.2 mg,

0.30 mmol) were used as substrates. As a result, **4l** (17.0 mg, 0.060 mmol) was obtained in 30 % yield, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 5/1).

Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, 1H, J = 7.6 Hz), 7.67 (d, 2H, J = 7.6 Hz), 7.44 (t, 2H, J = 7.6 Hz), 7.35—7.17 (m, 10H), 5.37 (s, 2H). ^{1}H NMR spectrum of the product was identical to that of the reference 10.

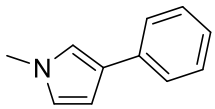
2-Phenyl-pyrrole (7a)



According to general procedure C, **1a** (19.6 mg, 0.20 mmol) and **6a** (20.8 μL, 0.30 mmol) were used as substrates. As a result, **7a** (8.0 mg, 0.056 mmol) was obtained in 28% yield, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 10/1).

Pale purple oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (brs, 1H), 7.49—7.48 (m, 2H), 7.37 (t, 2H, J = 8.0 Hz), 7.21 (t, 1H, J = 8.0 Hz), 6.88—6.87 (m, 1H), 6.54—6.53 (m, 1H), 6.32—6.30 (m, 1H). ^{1}H NMR spectrum of the product was identical to that of the reference 11.

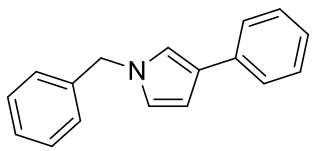
1-Methyl-3-phenyl-pyrrole (7b)



According to general procedure C, **1a** (19.6 mg, 0.20 mmol) and **6b** (27.0 μL, 0.30 mmol) were used as substrates. As a result, **7b** (3.2 mg, 0.020 mmol) was obtained in 10% yield, after purification by silica-gel column chromatography (*n*-hex/EtOAc = 50/1).

Pale purple oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, 2H, J = 8.0 Hz), 7.31 (t, 2H, J = 8.0 Hz), 7.14 (t, 1H, J = 8.0 Hz), 6.91—6.90 (m, 1H), 6.63—6.62 (m, 1H), 6.44—6.43 (m, 1H), 3.69 (s, 3H). ^{1}H NMR spectrum of the product was identical to that of the reference 12.

1-Benzyl-3-phenyl-pyrrole (7c)



According to general procedure C, **1a** (19.6 mg, 0.20 mmol) and **6c** (47.1 mg, 0.30 mmol) were used as substrates. As a result, **7c** (12.6 mg, 0.054 mmol) was obtained in 27% yield, after

purification by silica-gel column chromatography (*n*-hex/EtOAc = 50/1).

Pale purple oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51—7.49 (m, 2H), 7.34—7.29 (m, 5H), 7.18—7.14 (m, 3H), 7.00—6.99 (m, 1H), 6.72—6.71 (m, 1H), 6.50—6.49 (m, 1H), 5.09 (s, 2H). ^{1}H NMR spectrum of the product was identical to that of the reference 4.

6. References

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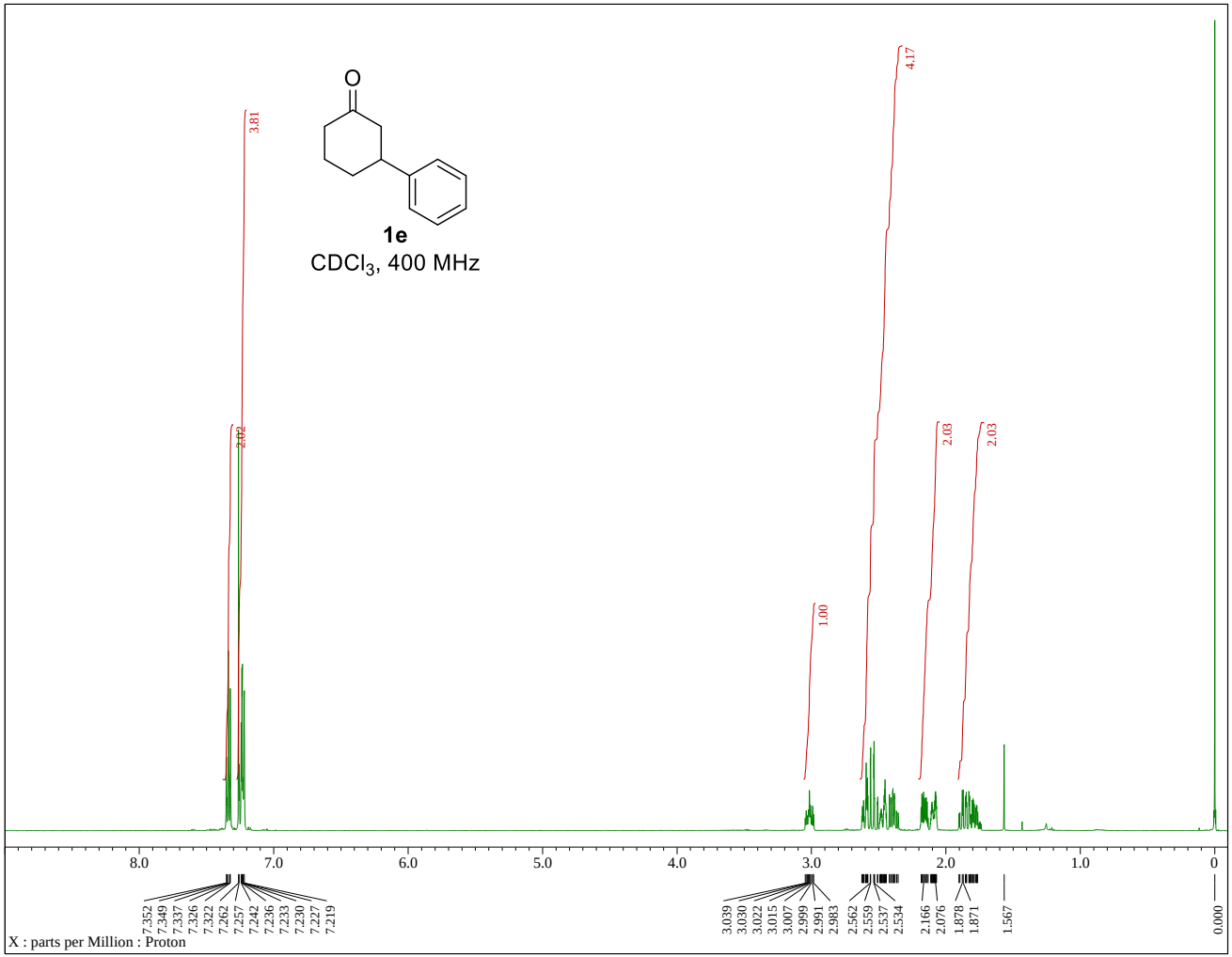
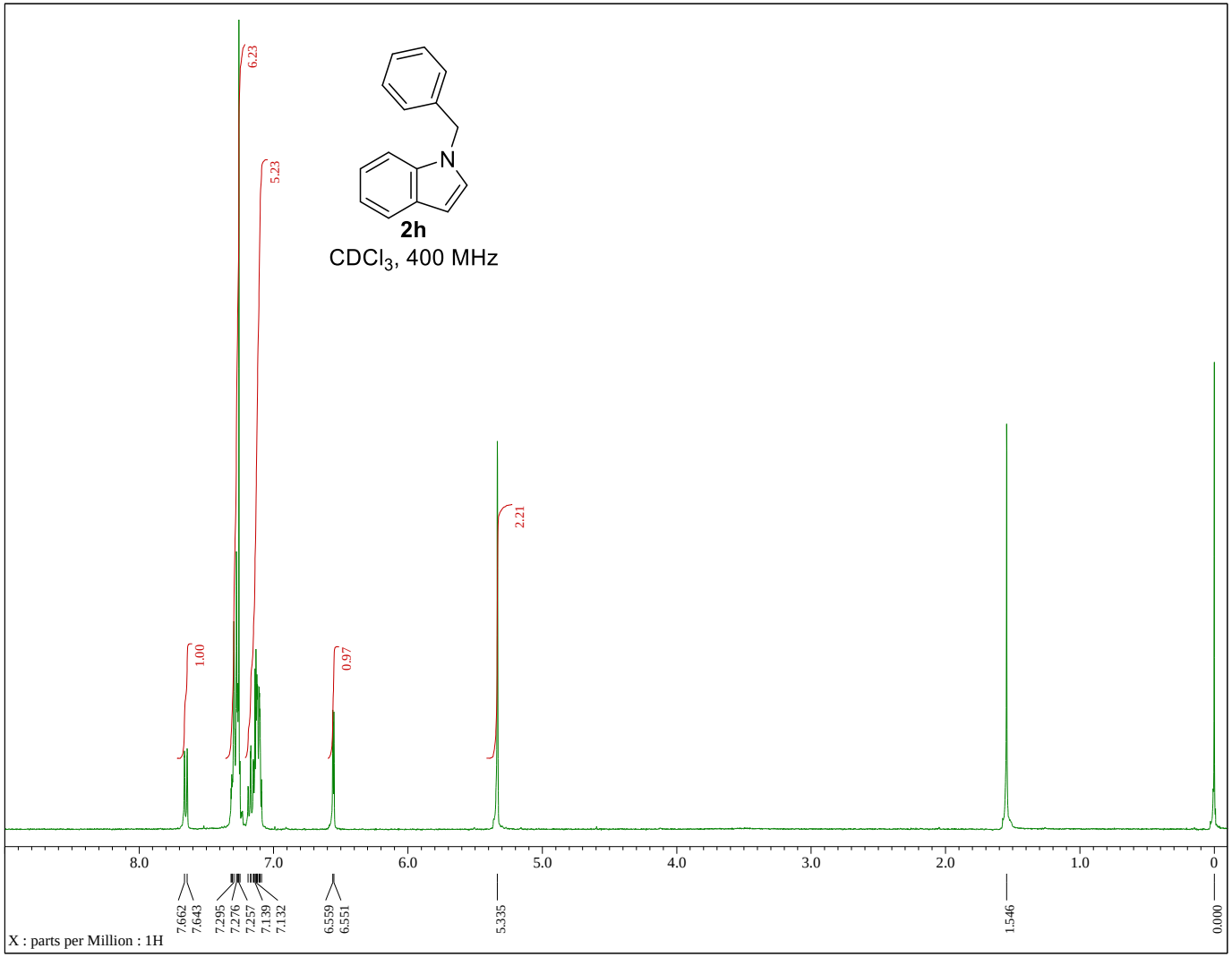
7. ^{1}H NMR and ^{13}C NMR spectra of products.

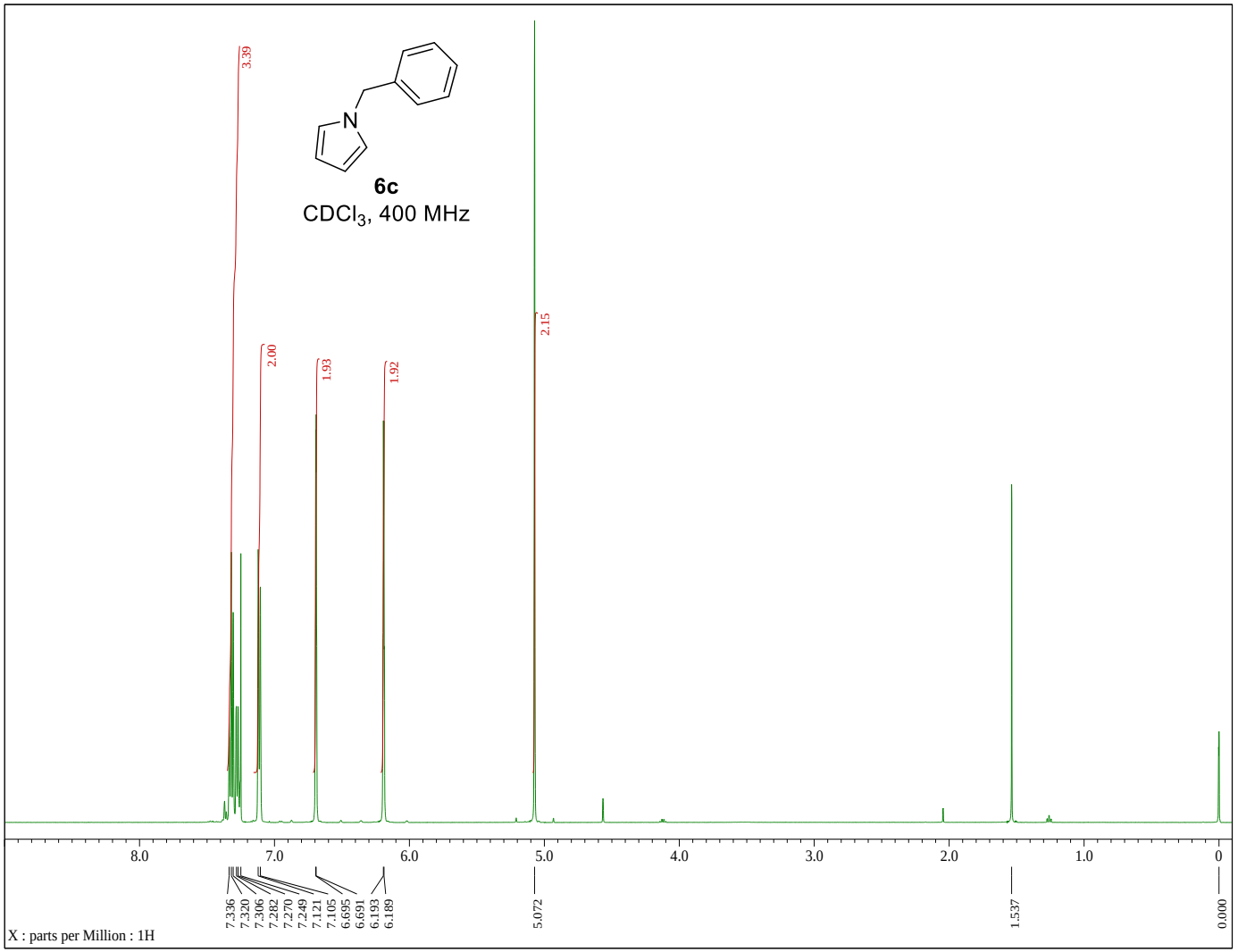
^{1}H NMR of 3-phenylcyclohexanone (1d)



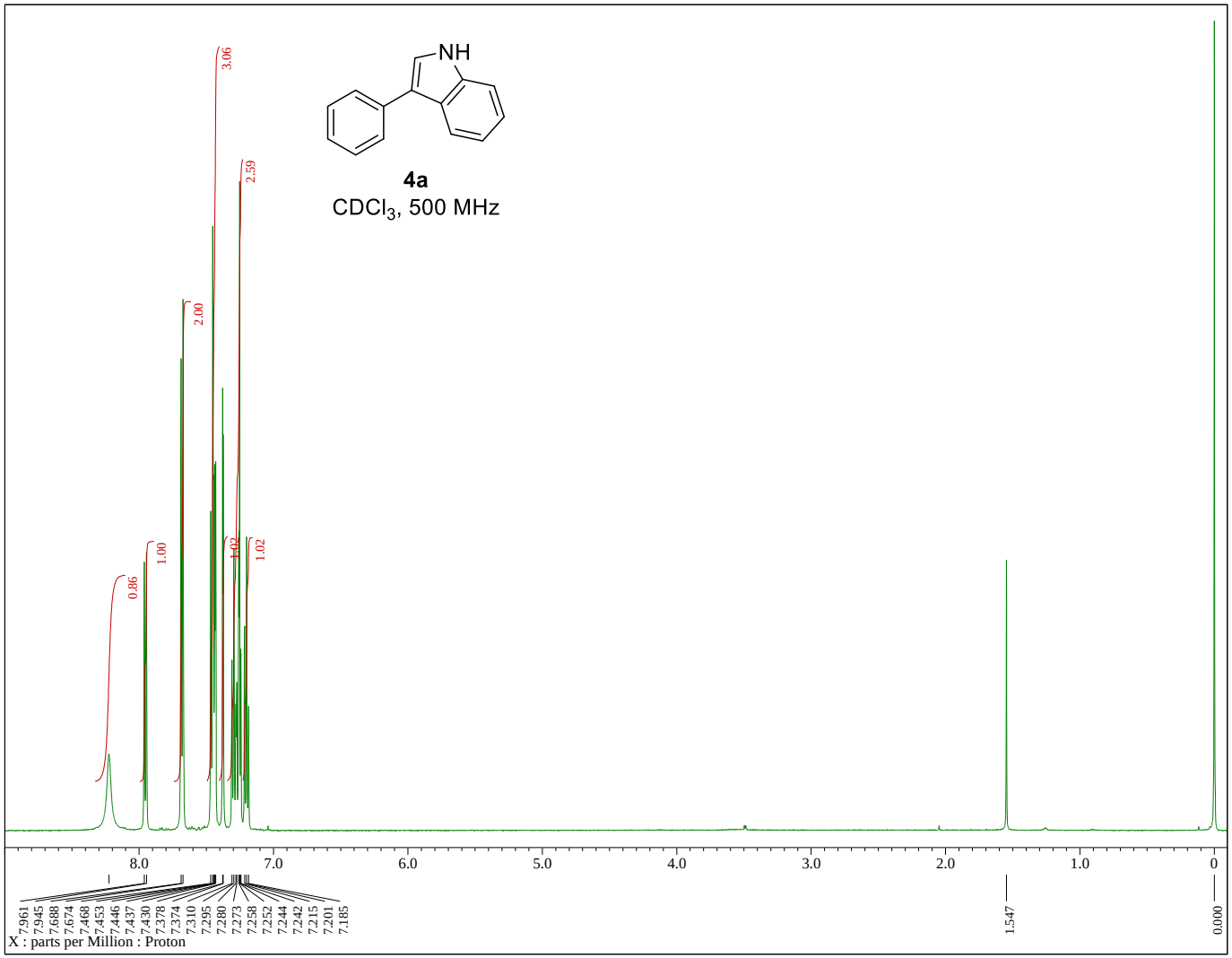
^{1}H NMR of *N*-benzylindole (2h)



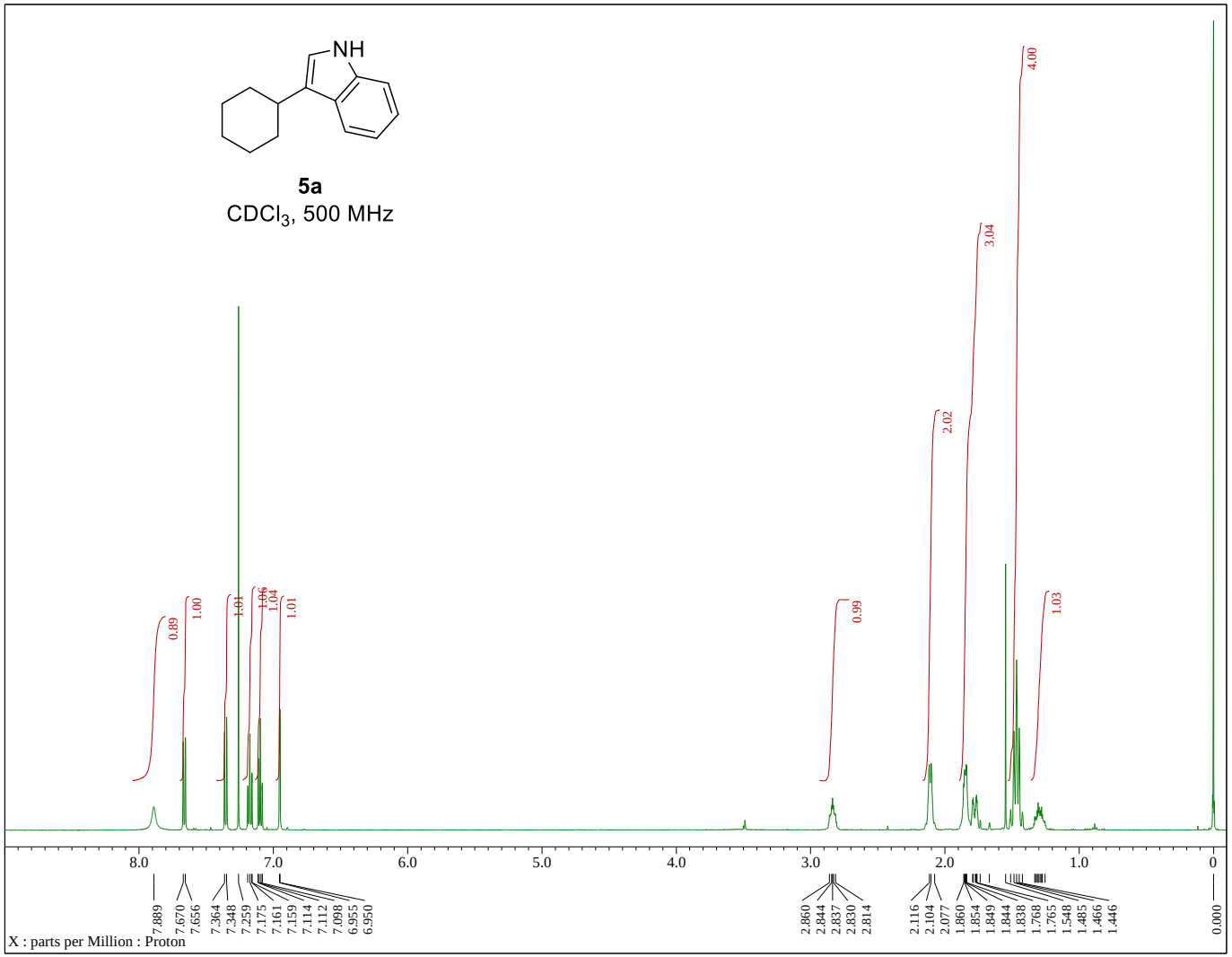
^{1}H NMR of 1-benzyl-pyrrole (6c)



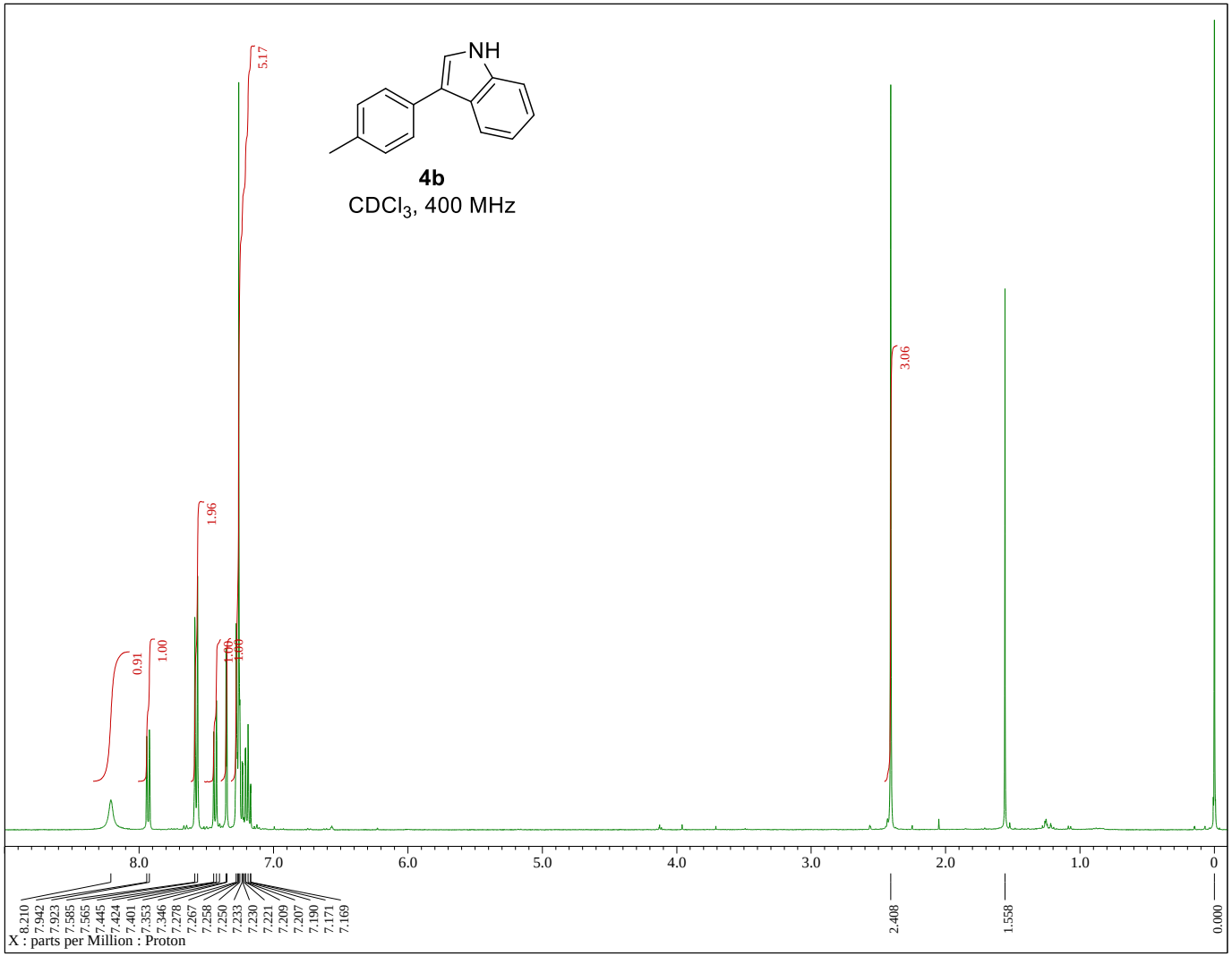
^{1}H NMR of 3-phenyl-1*H*-indole (4a)



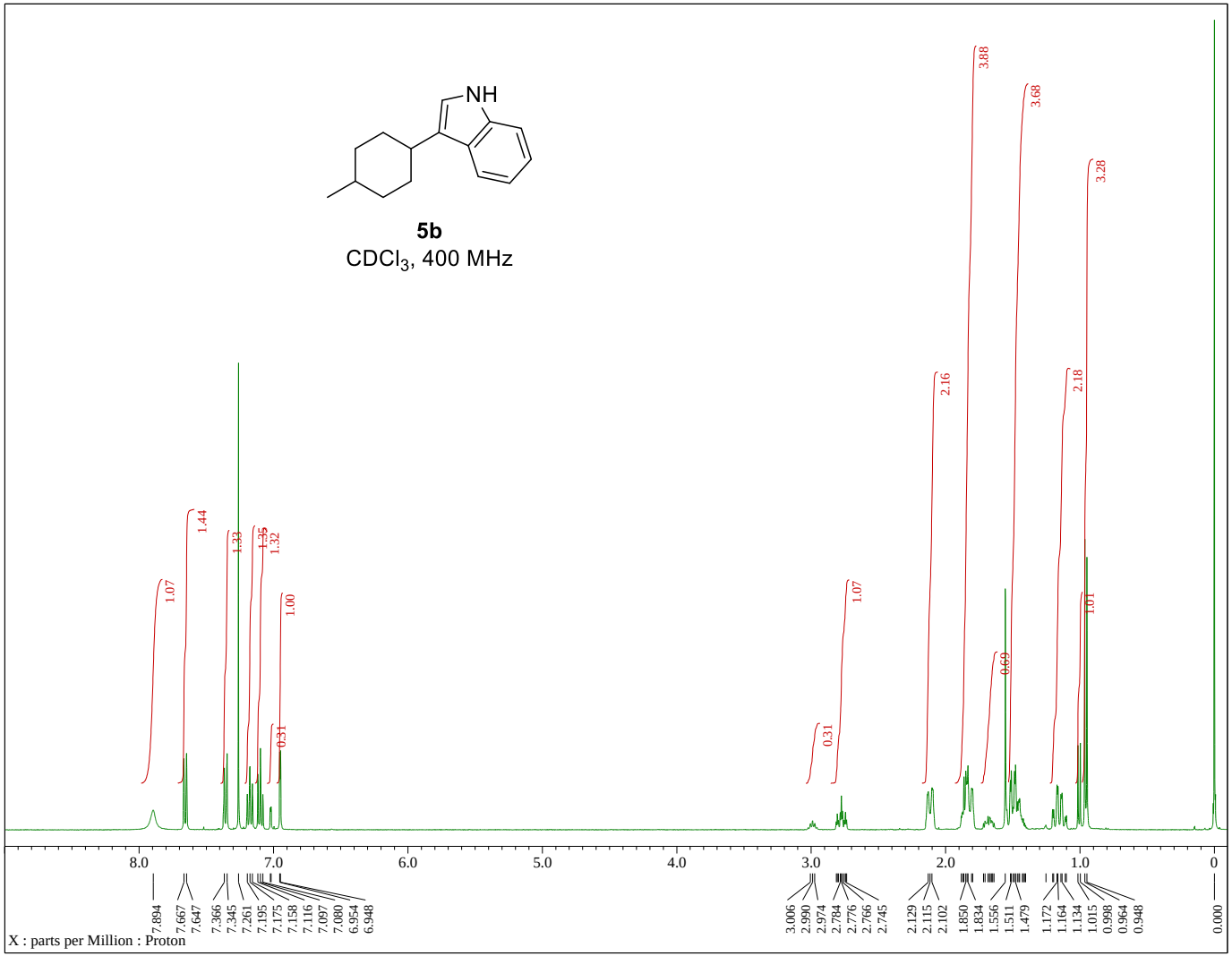
^{1}H NMR of 3-cyclohexyl-1*H*-indole (5a)



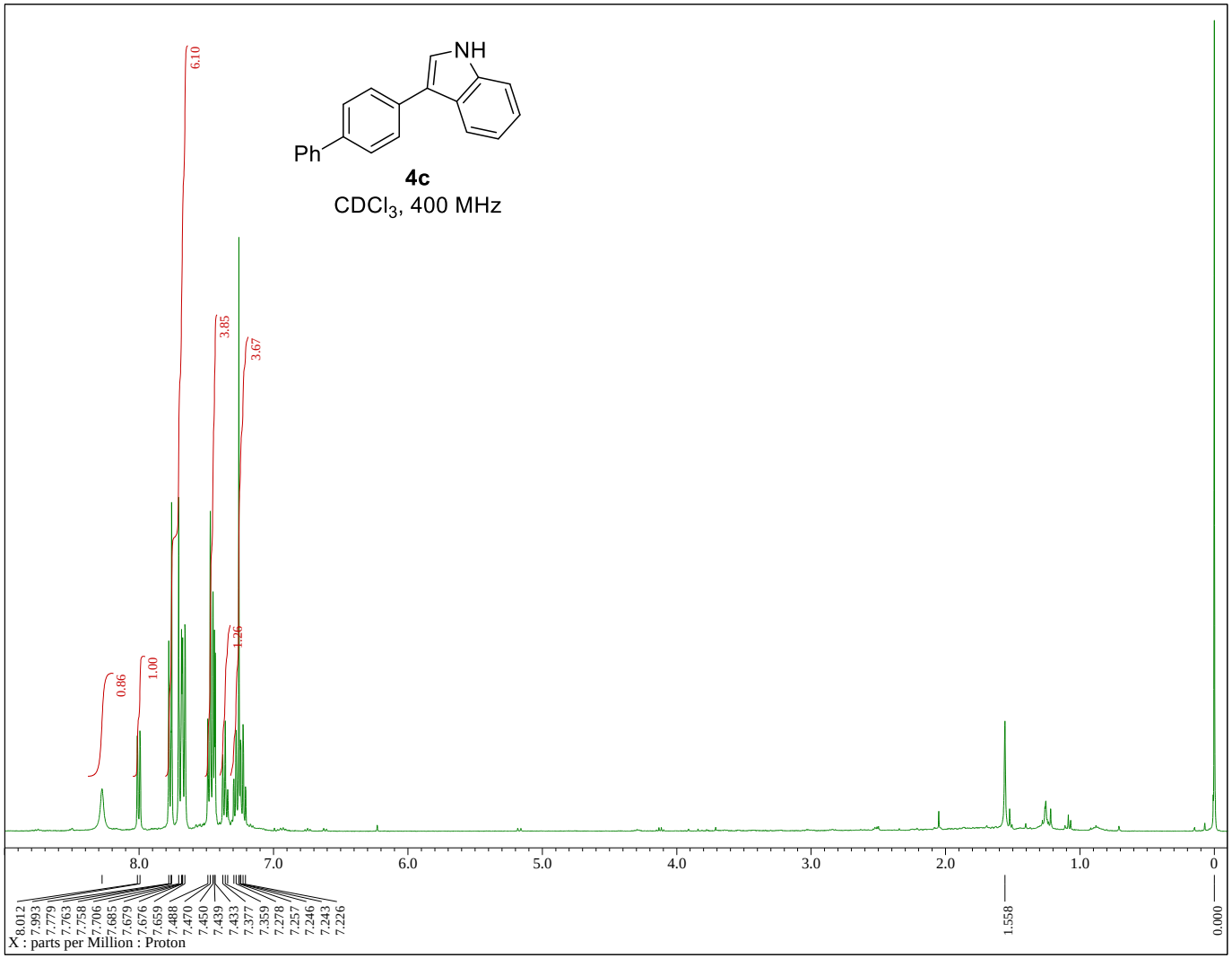
^{1}H NMR of 3-(4-methylphenyl)-1*H*-indole (4b)



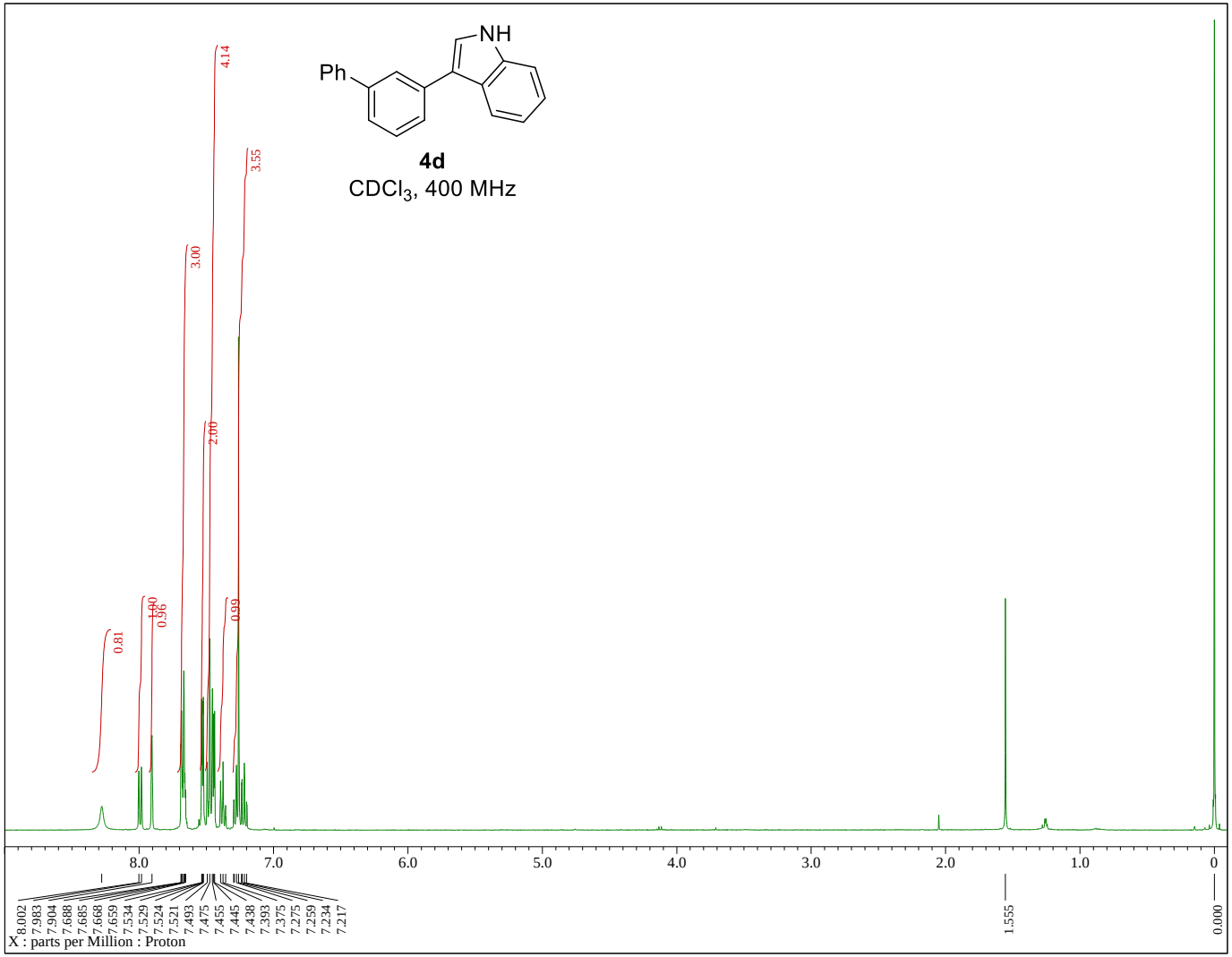
^{1}H NMR of 3-(4-methylcyclohexyl)-1*H*-indole (5b)



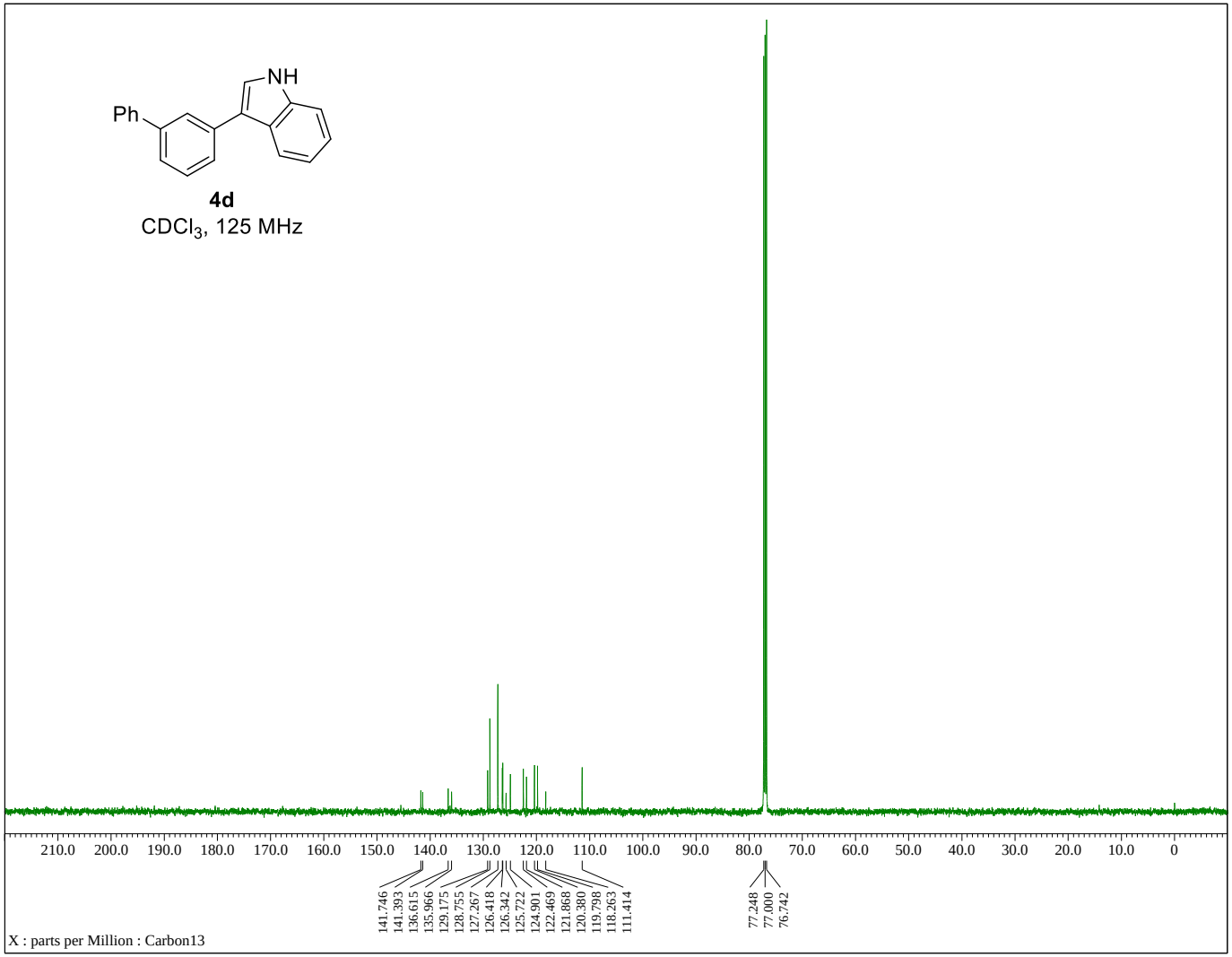
^{1}H NMR of 3-([1-1'-biphenyl]-4-yl)-1*H*-indole (4c)



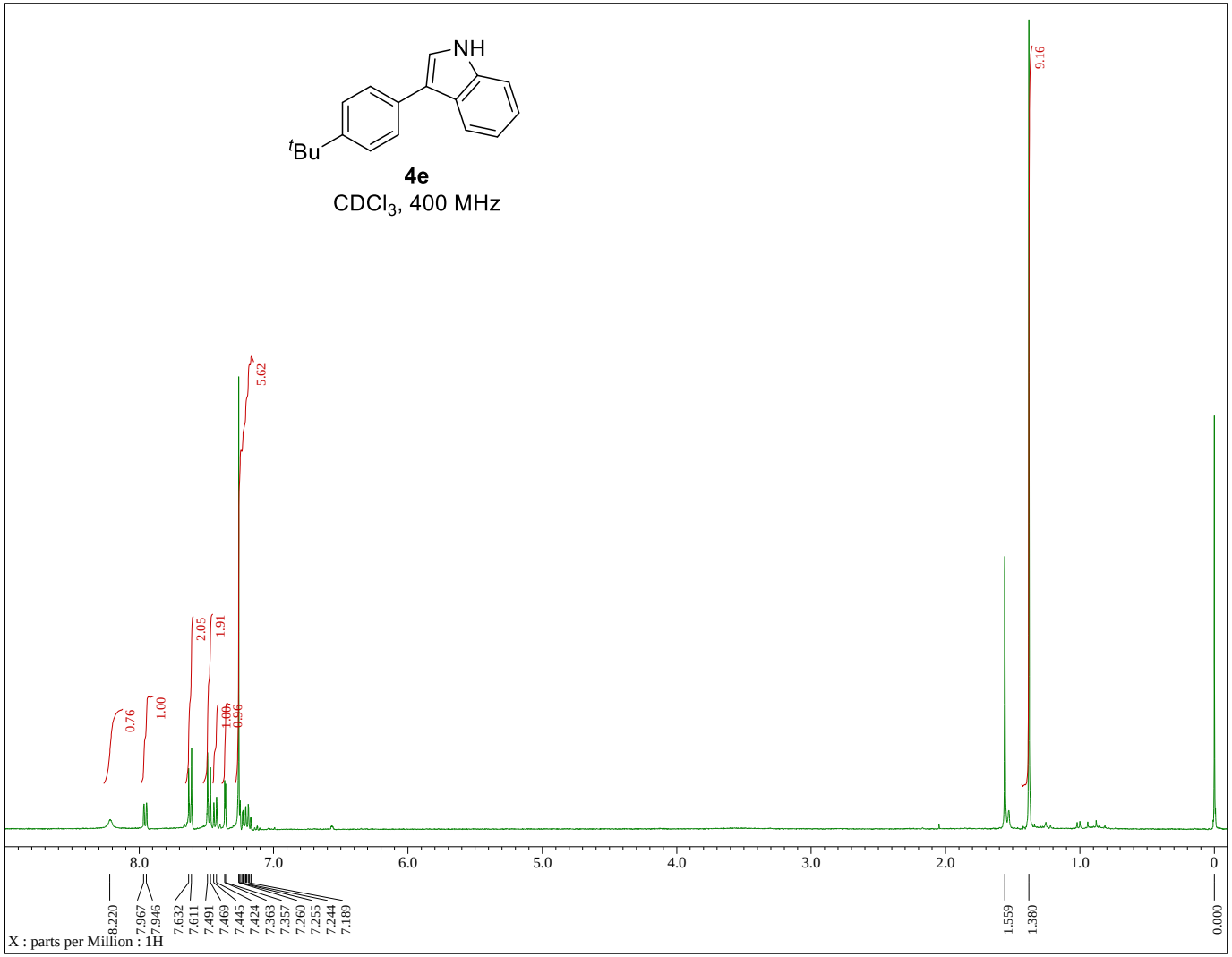
^{1}H NMR of 3-([1-1'-biphenyl]-3-yl)-1*H*-indole (4d)



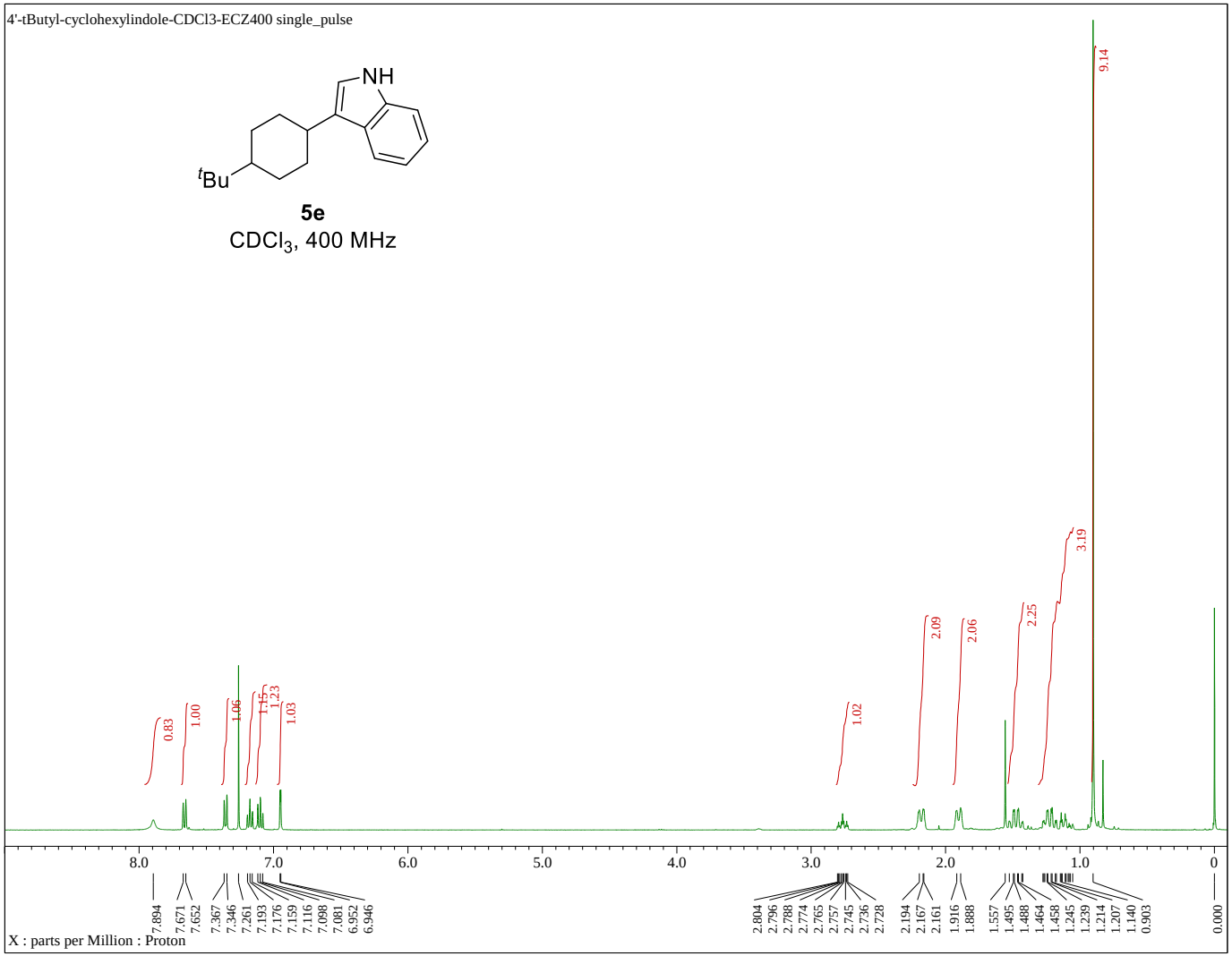
^{13}C NMR of 3-([1-1'-biphenyl]-3-yl)-1*H*-indole (4d)



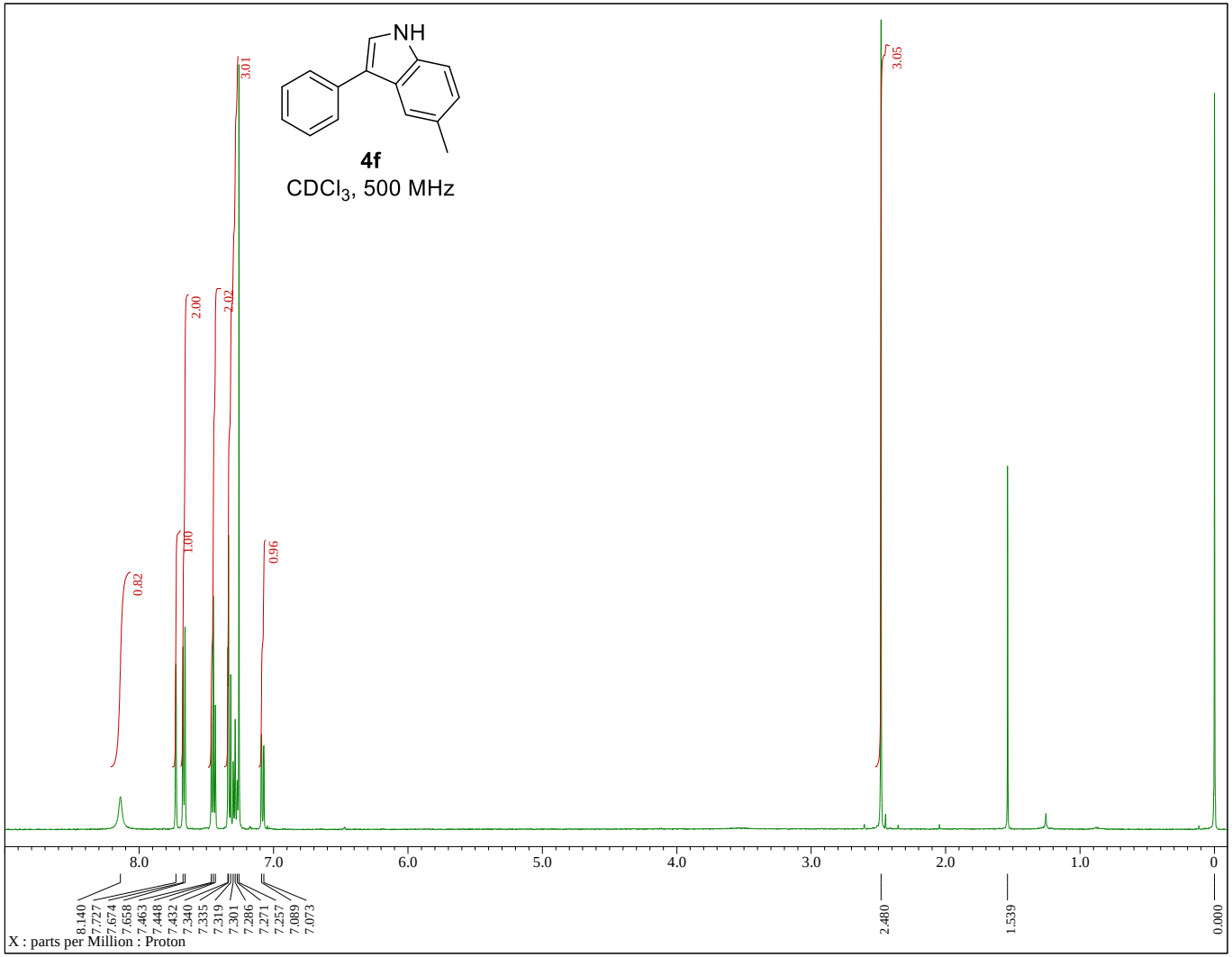
^{1}H NMR of 3-(4-*tert*-butylphenyl)-1*H*-indole (4e) in Table 2



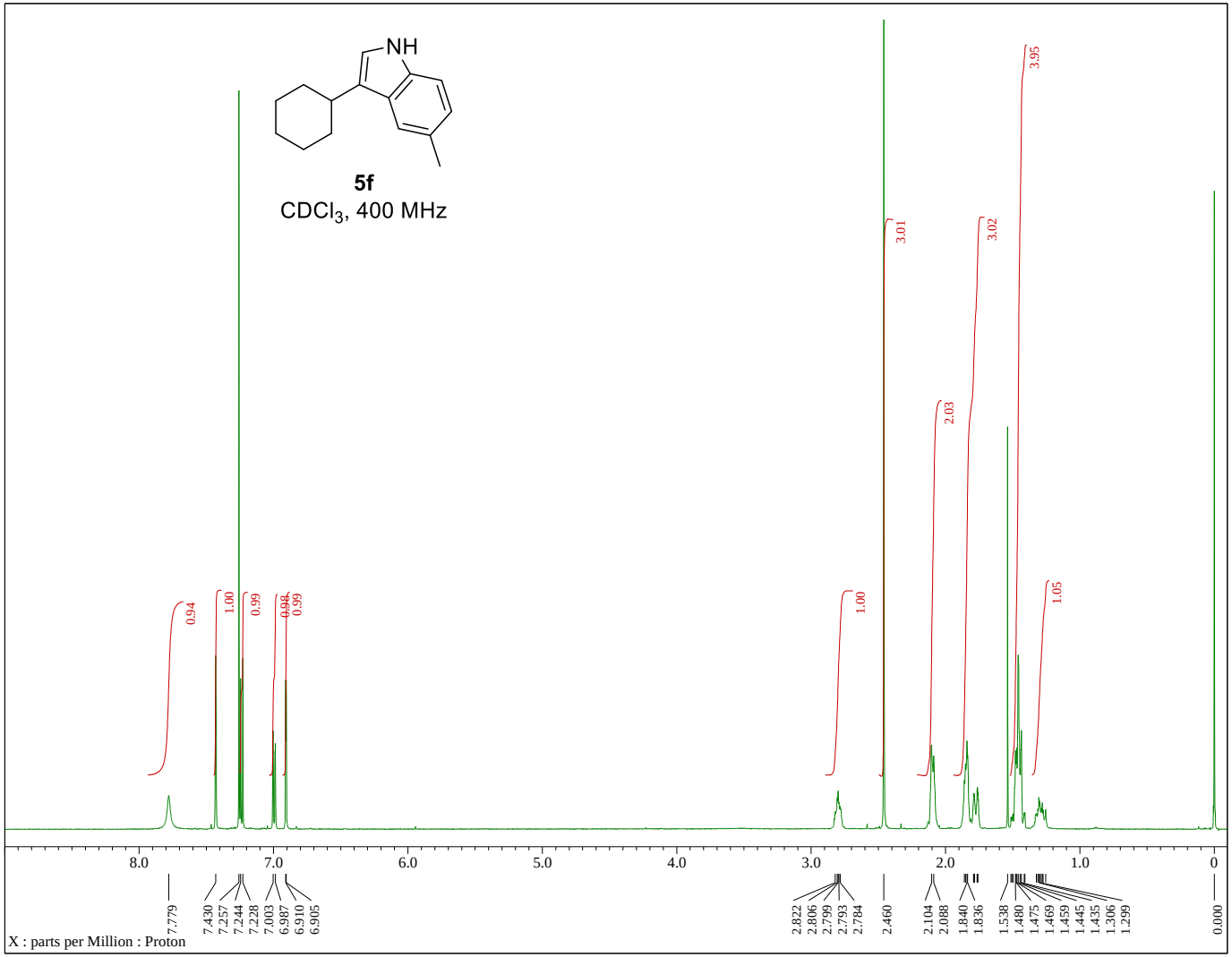
^{1}H NMR of 3-(4-*tert*-butylcyclohexyl)-1*H*-indole (5e)



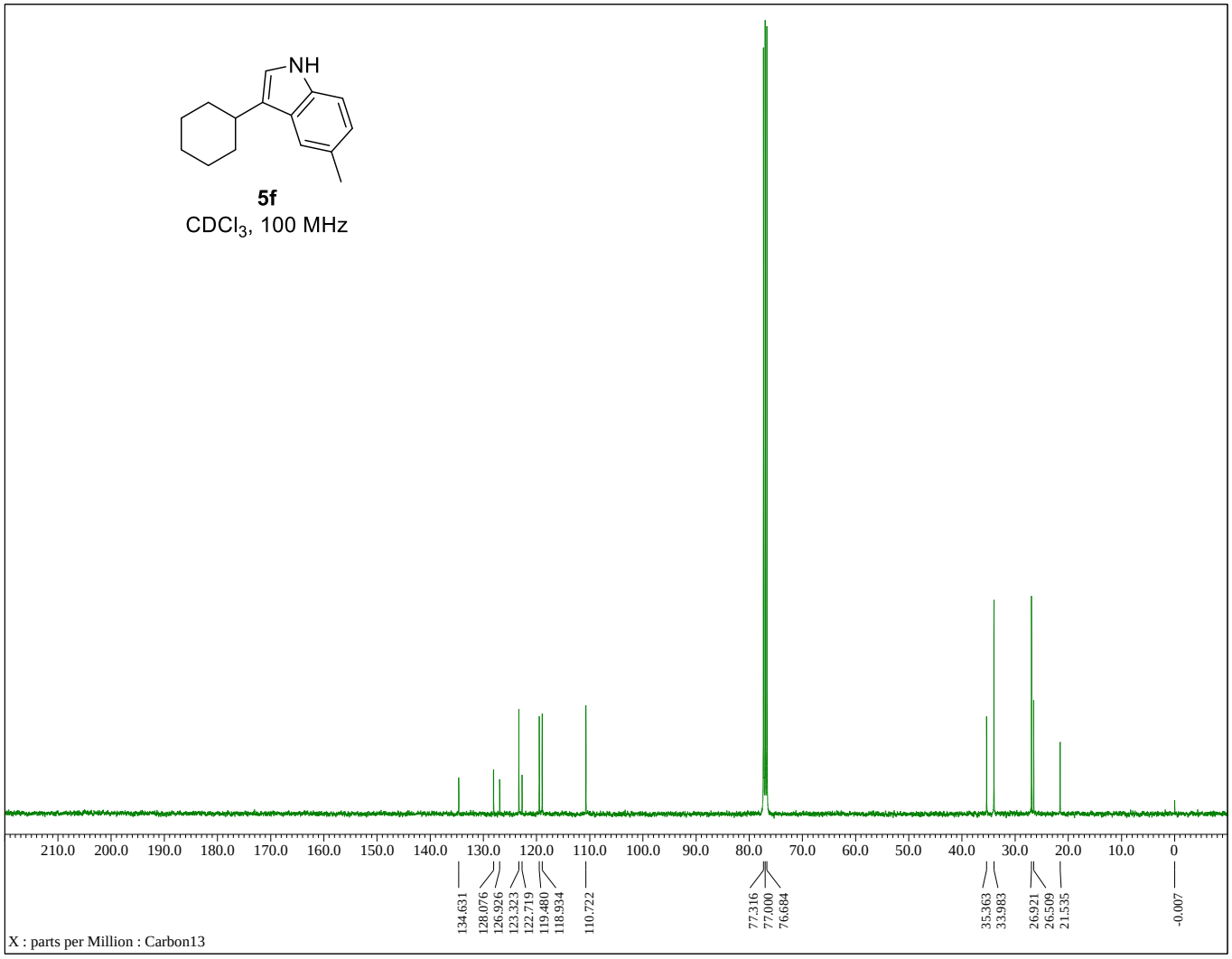
^{1}H NMR of 5-methyl-3-phenyl-1*H*-indole (4f)



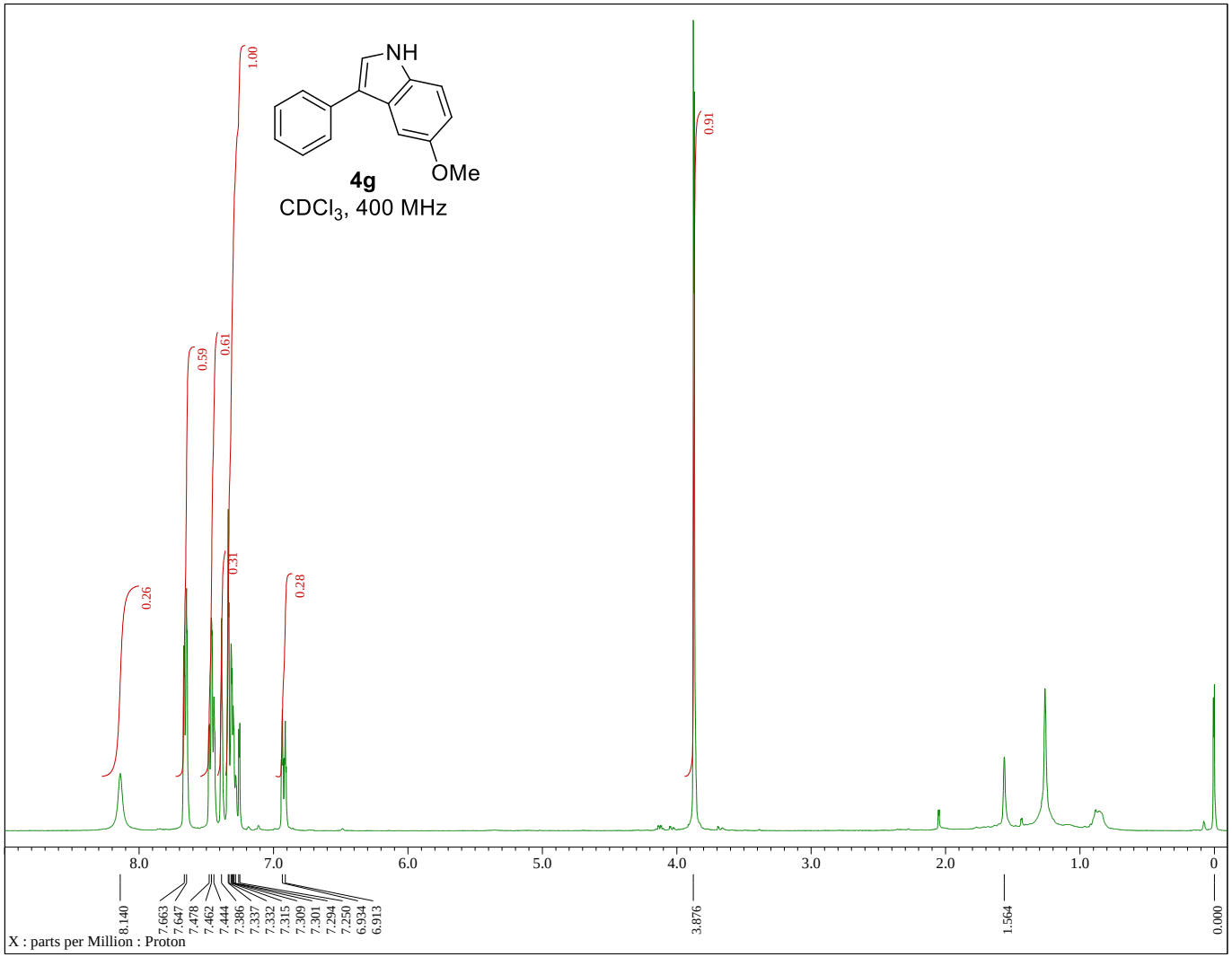
^{1}H NMR of 5-methyl-3-cyclohexyl-1*H*-indole (5f)



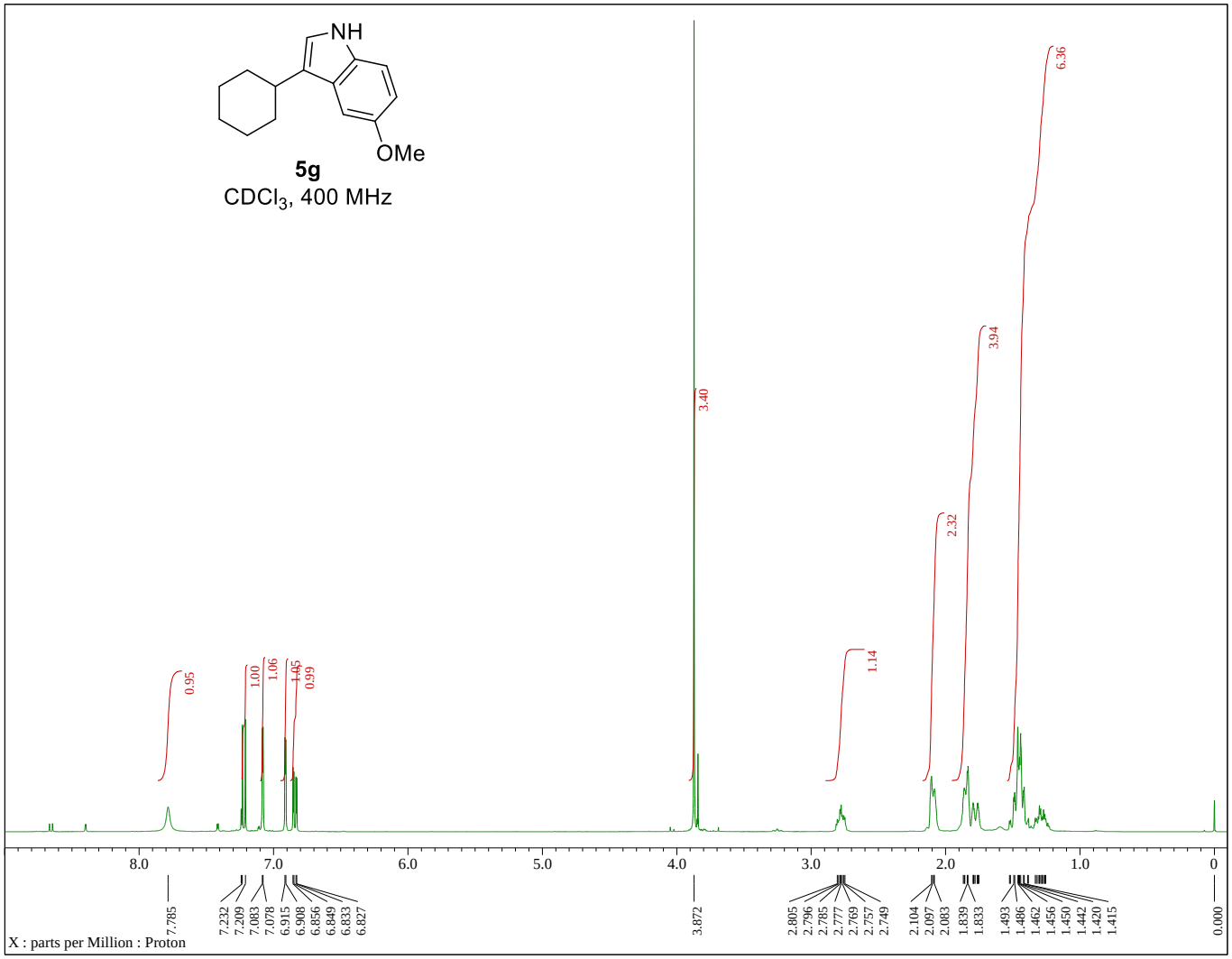
^{13}C NMR of 5-methyl-3-cyclohexyl-1*H*-indole (5f)



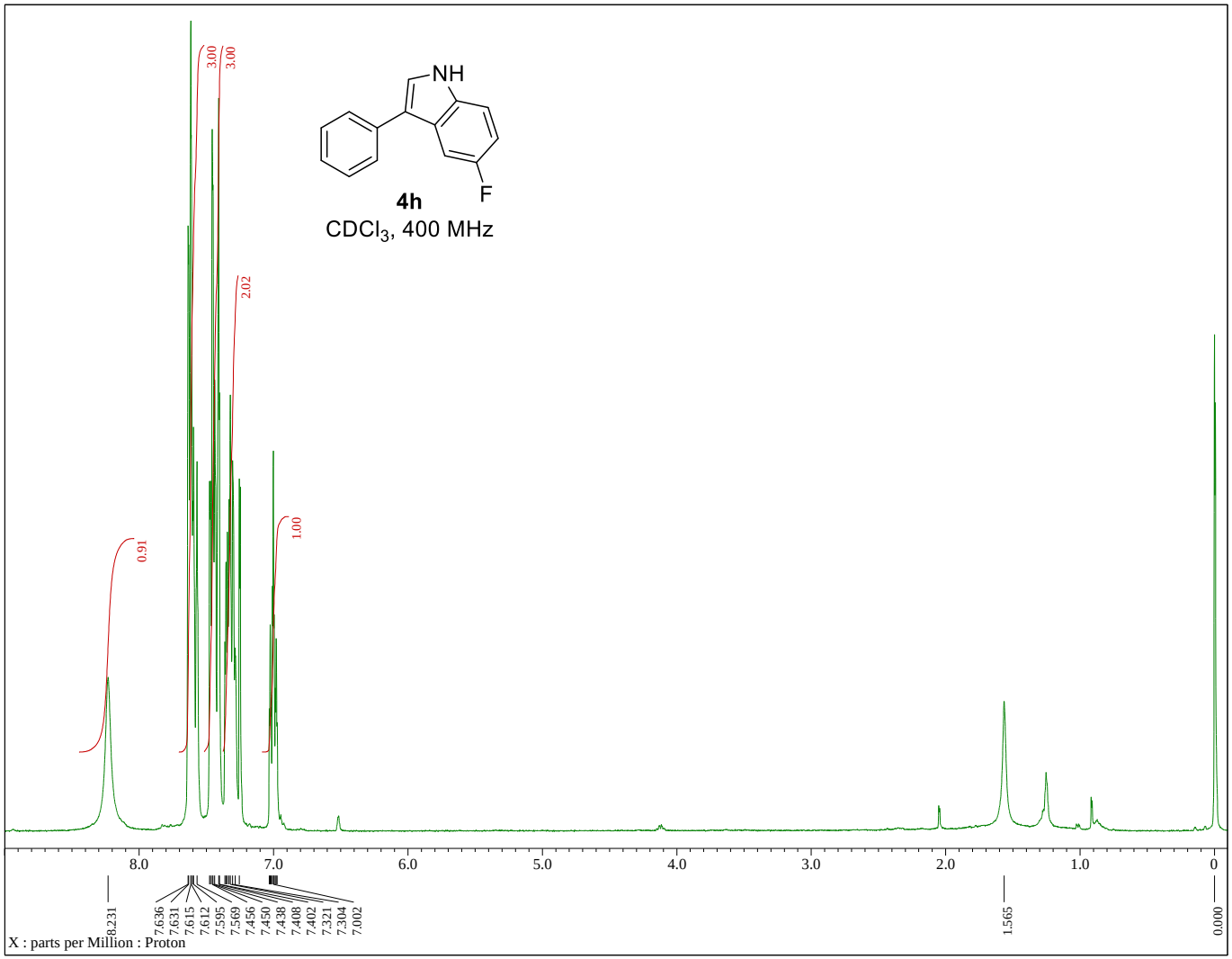
^{1}H NMR of 5-methoxy-3-phenyl-1*H*-indole (4g)



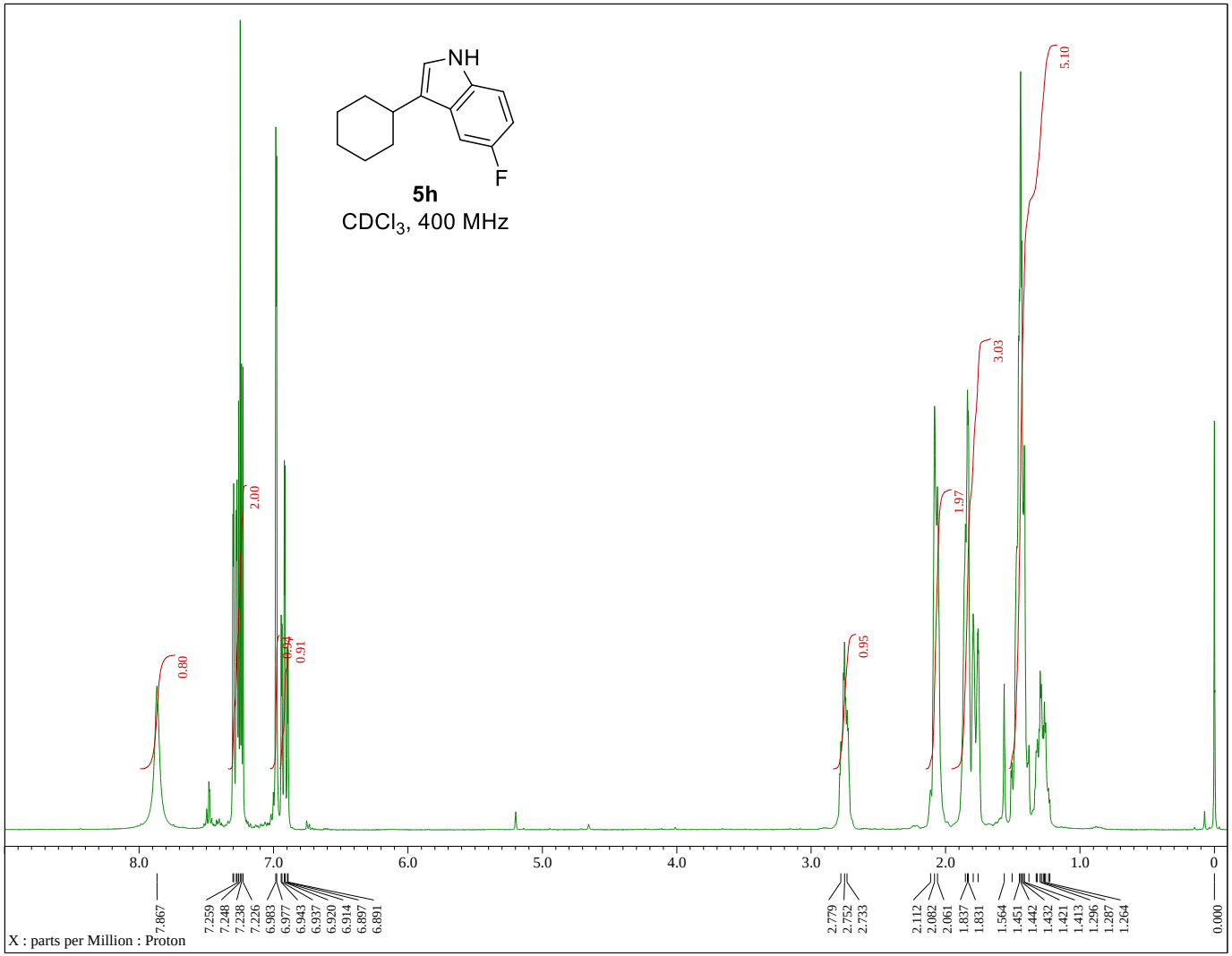
^{1}H NMR of 5-methoxy-3-cyclohexyl-1*H*-indole (5g)



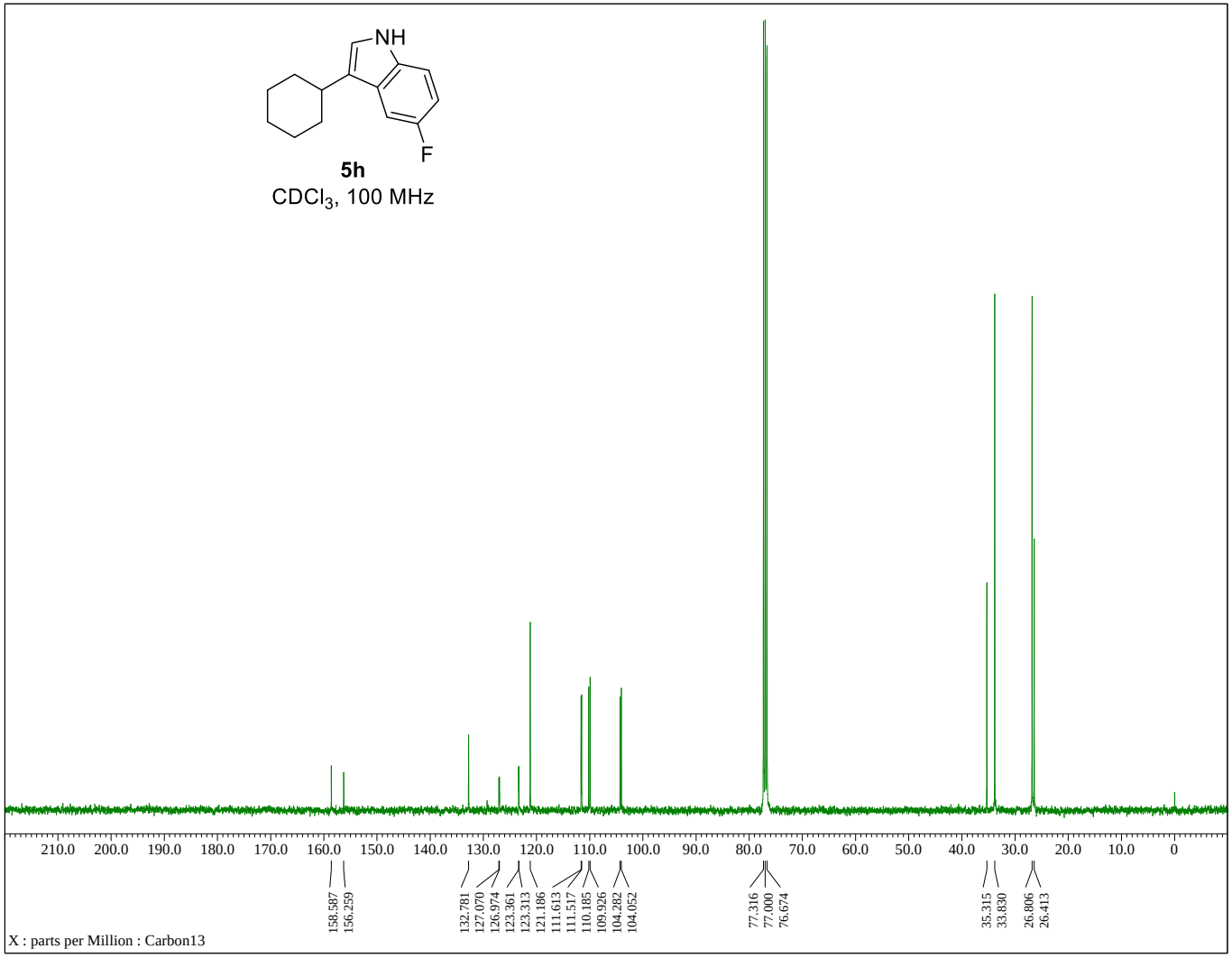
^{1}H NMR of 5-fluoro-3-phenyl-1*H*-indole (4h)



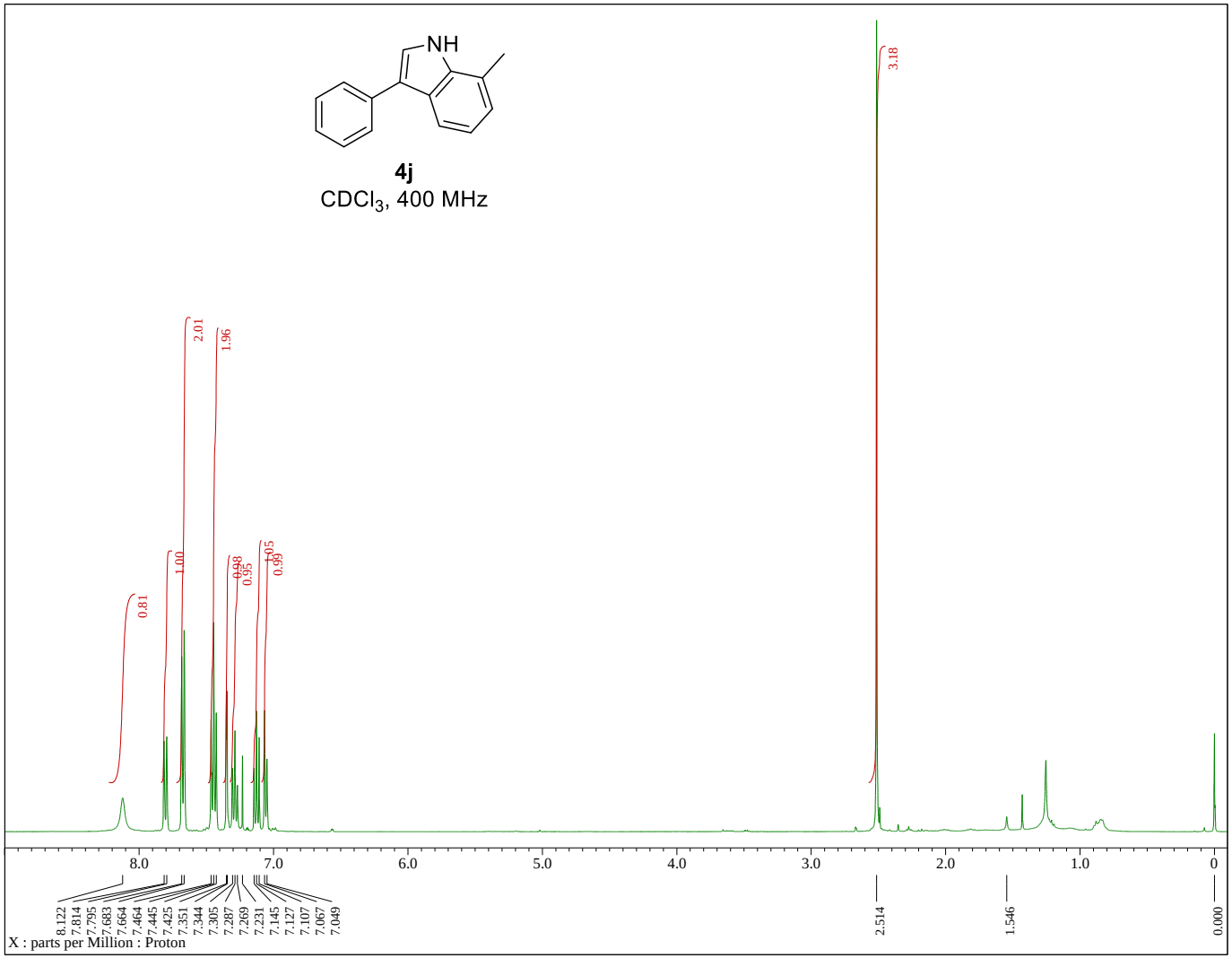
^{1}H NMR of 5-fluoro-3-cyclohexyl-1*H*-indole (5h)



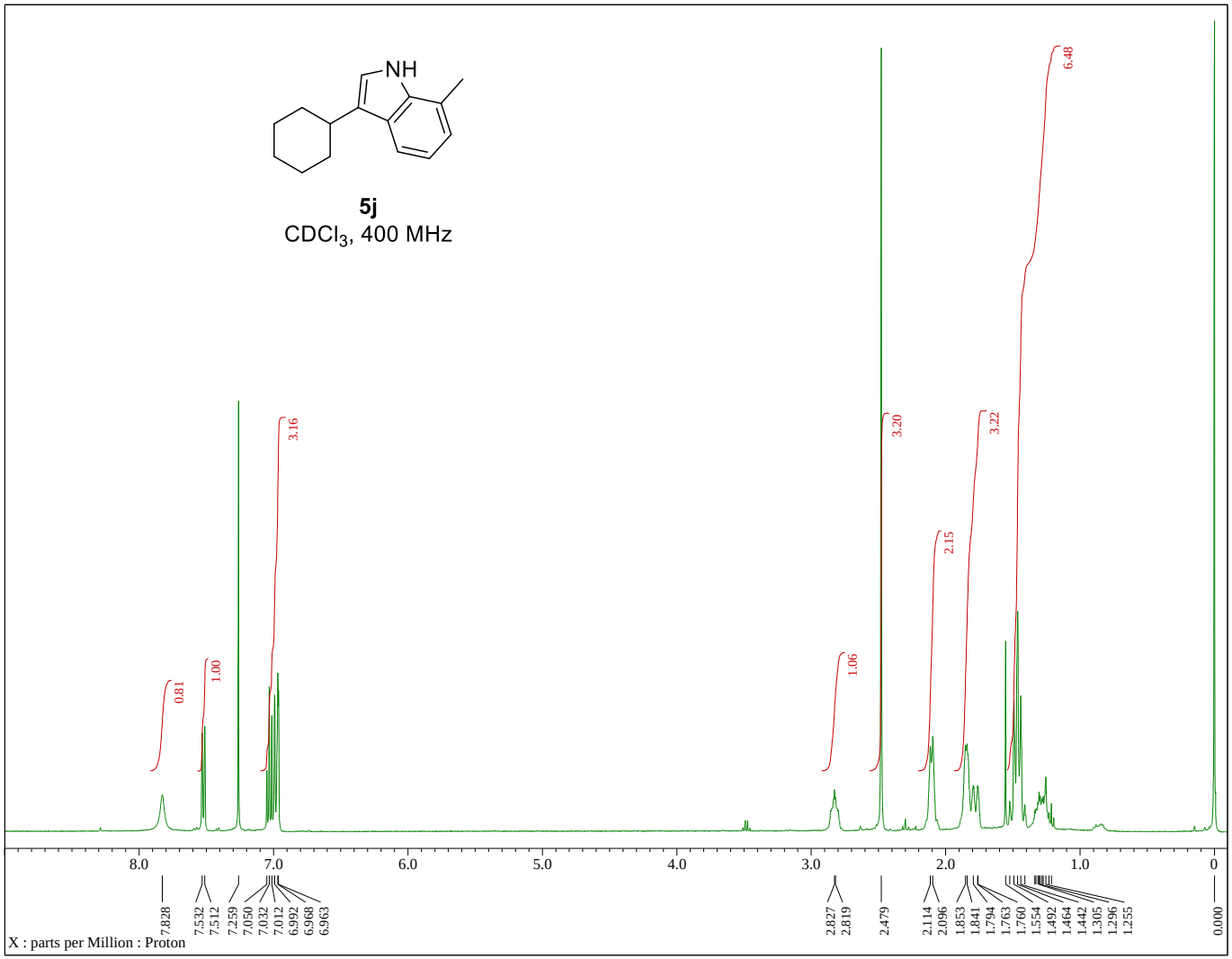
^{13}C NMR of 5-fluoro-3-cyclohexyl-1*H*-indole (5h)



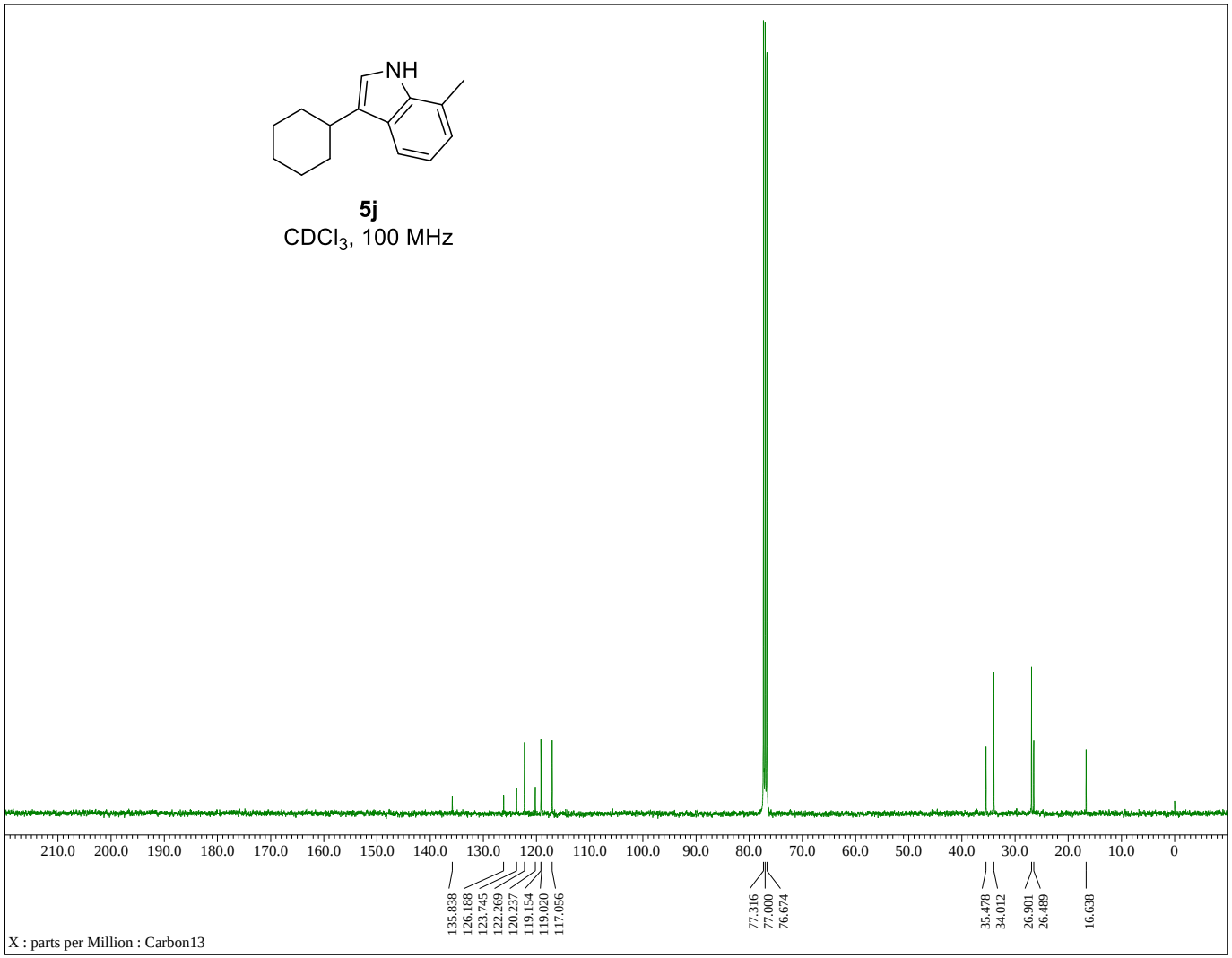
^{1}H NMR of 7-methyl-3-phenyl-1*H*-indole (5j)



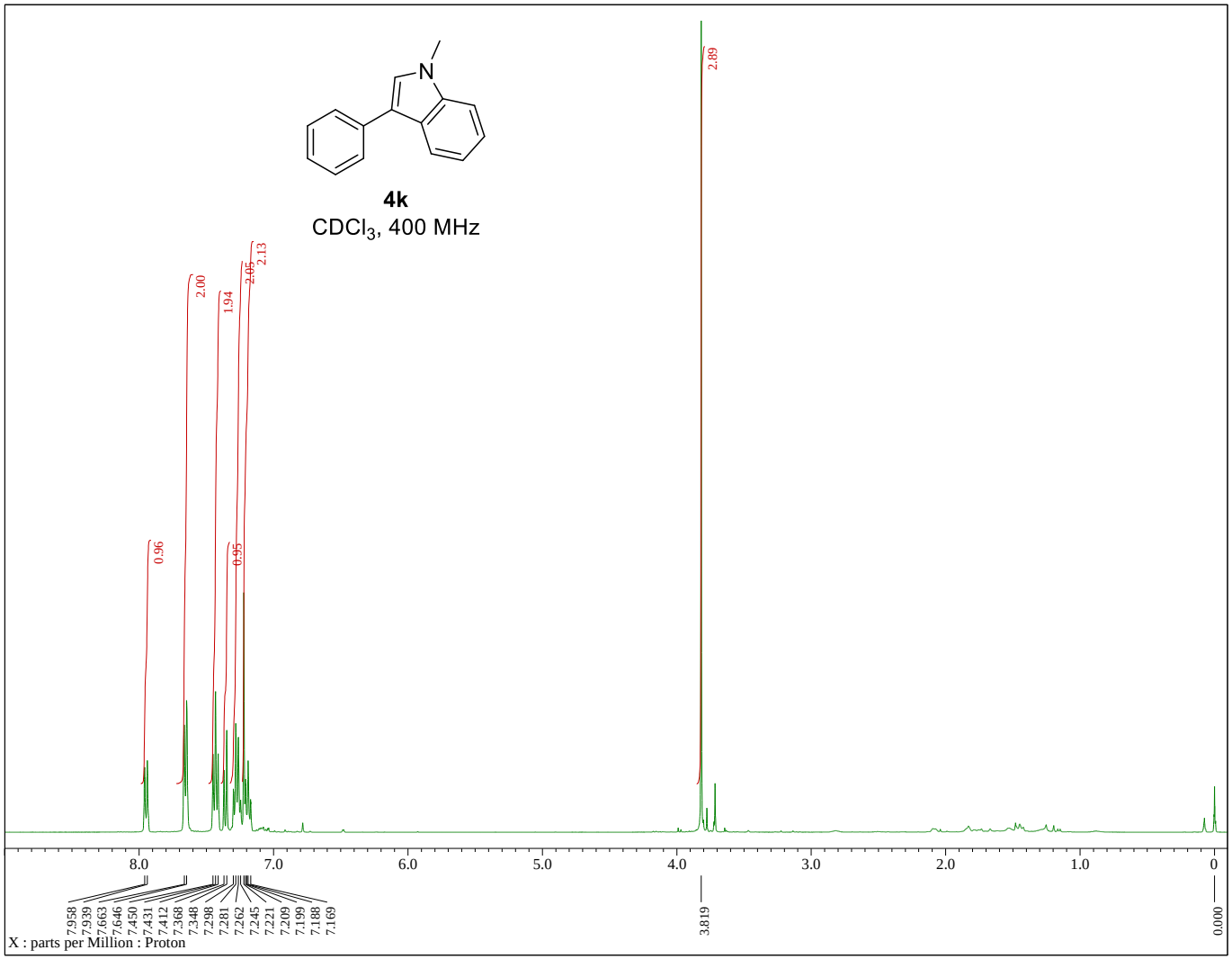
^{1}H NMR of 7-methyl-3-cyclohexyl-1*H*-indole (5j)



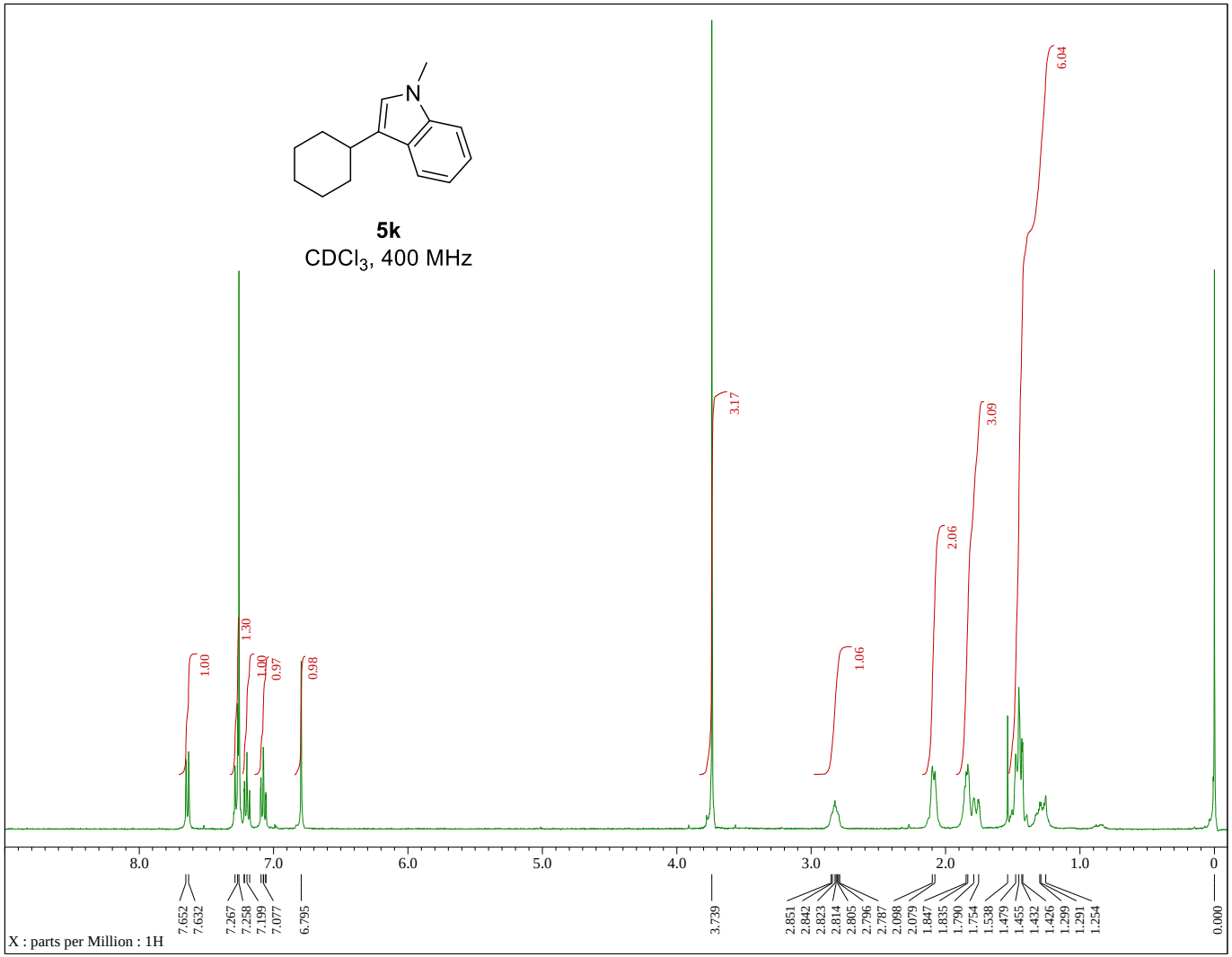
^{13}C NMR of 7-methyl-3-cyclohexyl-1*H*-indole (5j)



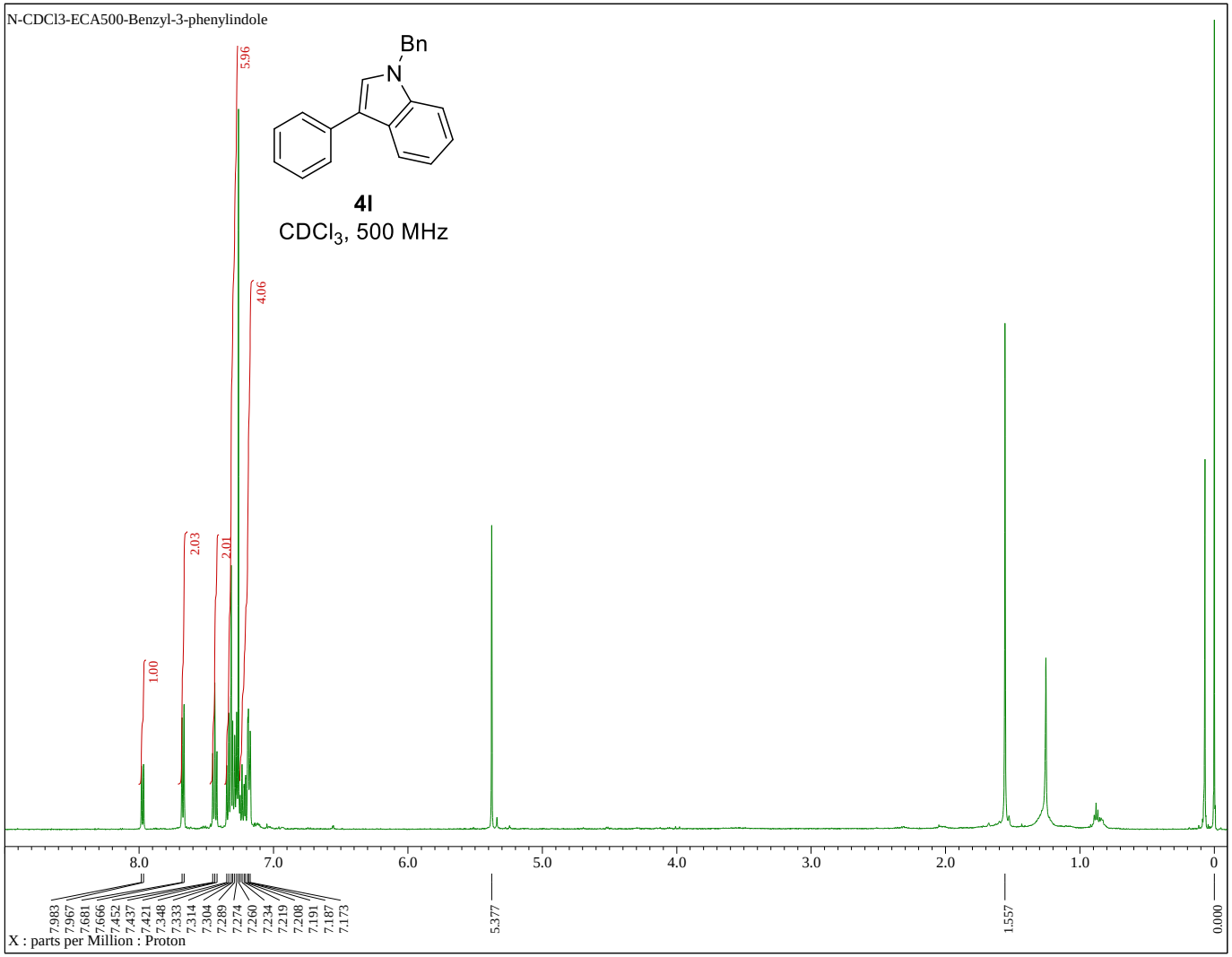
^{1}H NMR of *N*-methyl-3-phenyl-indole (4k)



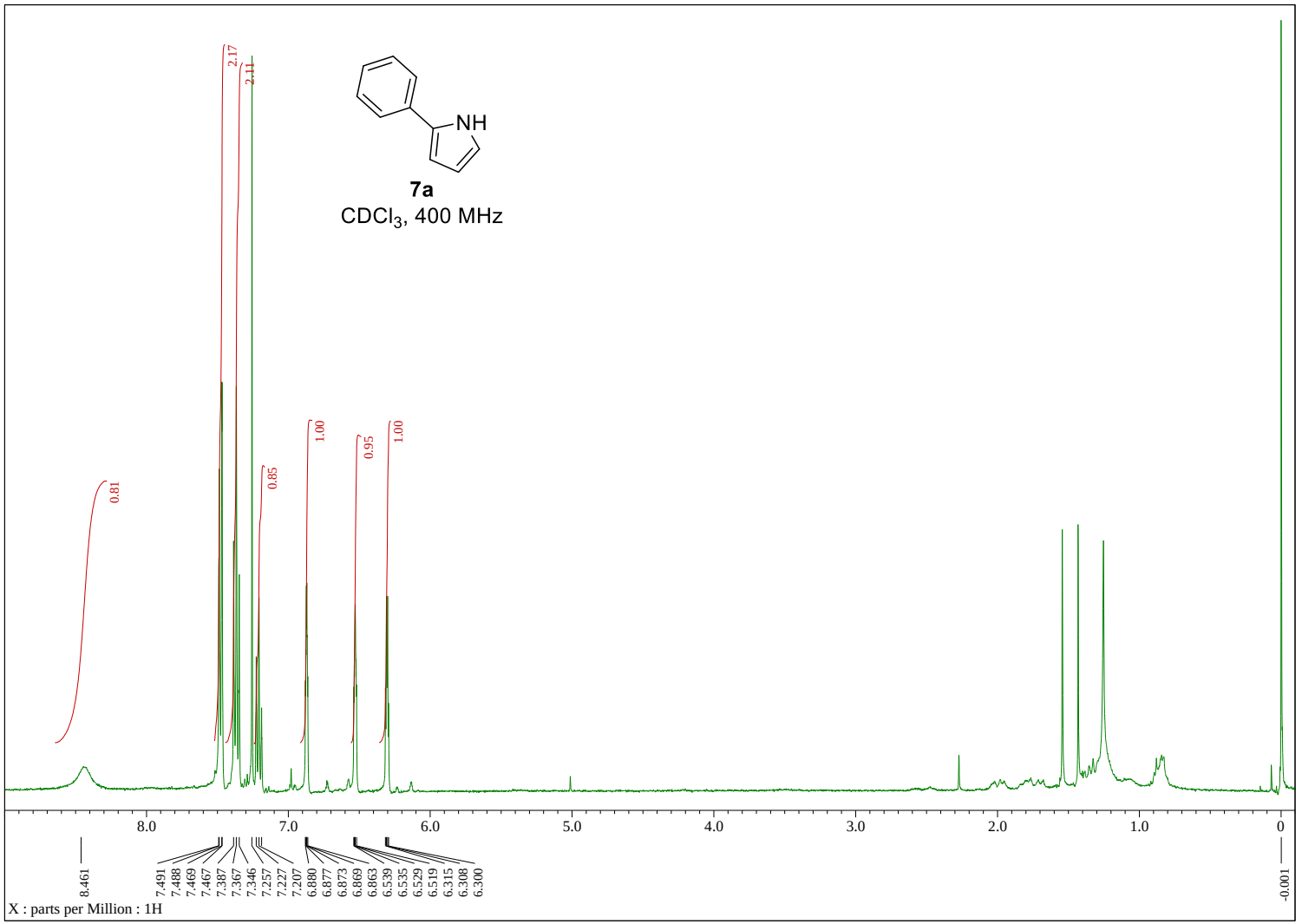
^{1}H NMR of *N*-methyl-3-cyclohexyl-indole (5k)



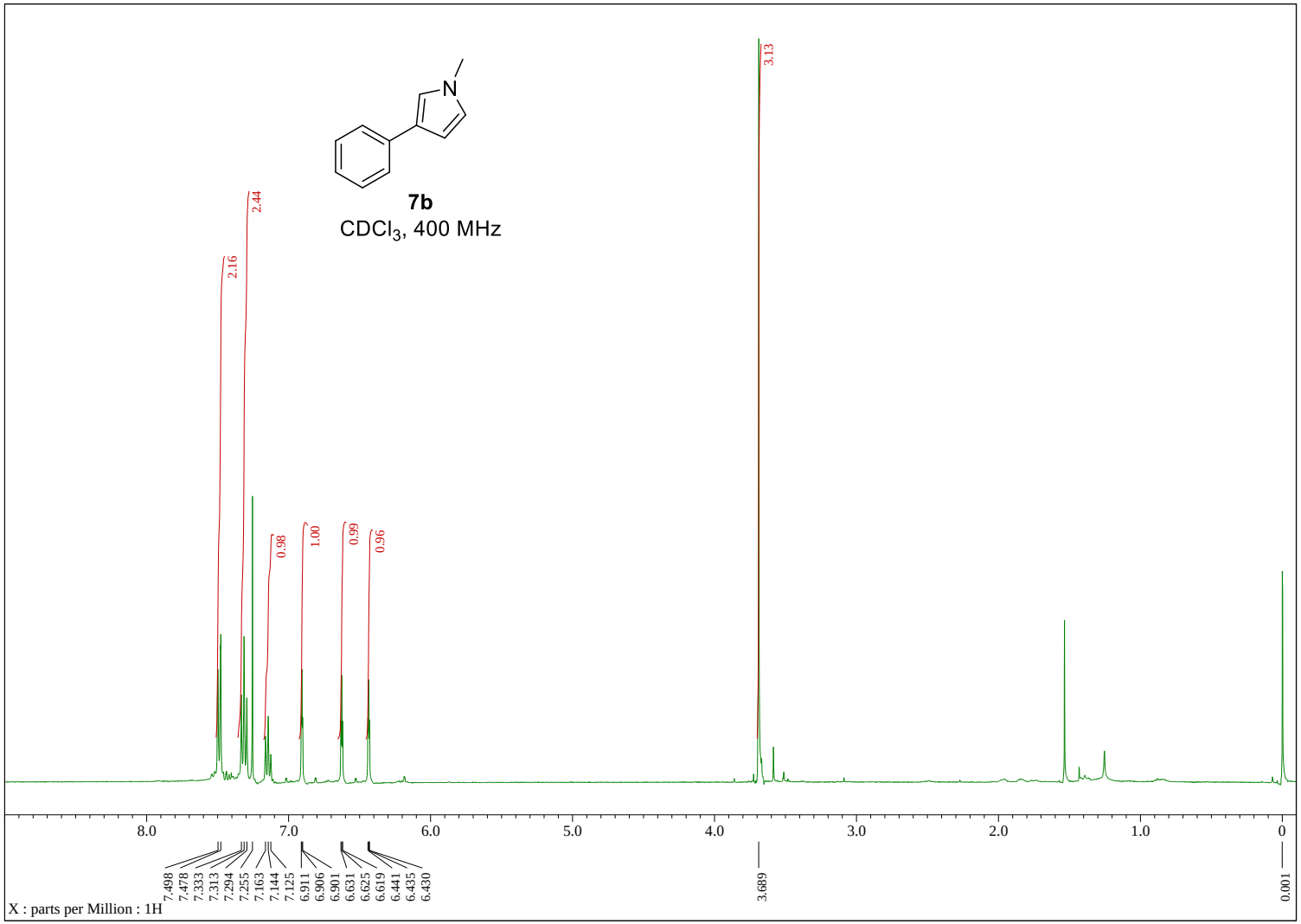
^{1}H NMR of *N*-benzyl-3-phenyl-indole (4l)



^{1}H NMR of 2-phenyl-1-*H*-pyrrole (7a)



^{1}H NMR of *N*-methyl-3-phenyl-pyrrole (7b)



^{1}H NMR of *N*-benzyl-3-phenyl-pyrrole (7c)