Electronic Supplementary Material (ESI) for ChemComm.


# Supporting Information

## Sterically Controlled C–H Alkenylation of Pyrroles and Thiophenes

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## II. General Information

Flash column chromatography was performed on silica gel (40-63 μm) using the indicated solvent system. NMR spectra were recorded in $CDCl_3$ at 300 K on Agilent 300 MHz and Bruker 400 MHz NMR spectrometers. Proton chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to residual protium in the NMR solvent ($CDCl_3$, δ 7.26, and AcOD-$d_4$, δ 2.04). Carbon chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to the carbon resonance of the NMR solvent ($CDCl_3$, δ 77.16). Crude yields were determined by $^1H$ NMR using either of the following internal NMR standards, trichloroethylene (1H, 6.45 ppm) and 1,3,5-trimethoxybenzene (3H, 6.08 ppm), which was added to reaction mixtures after cooling to 25 °C. Infrared (IR) spectra are reported as absorption wavenumbers ($cm^{-1}$). High-resolution mass spectra (HRMS) were acquired on high-resolution mass spectrometers: Q-TOF (ionization mode: ESI) and magnetic sector-electric sector (ionization mode: EI). Melting points (MP) were measured using an Electrothermal IA9100X1 digital melting point instrument.

## III. Optimization Studies

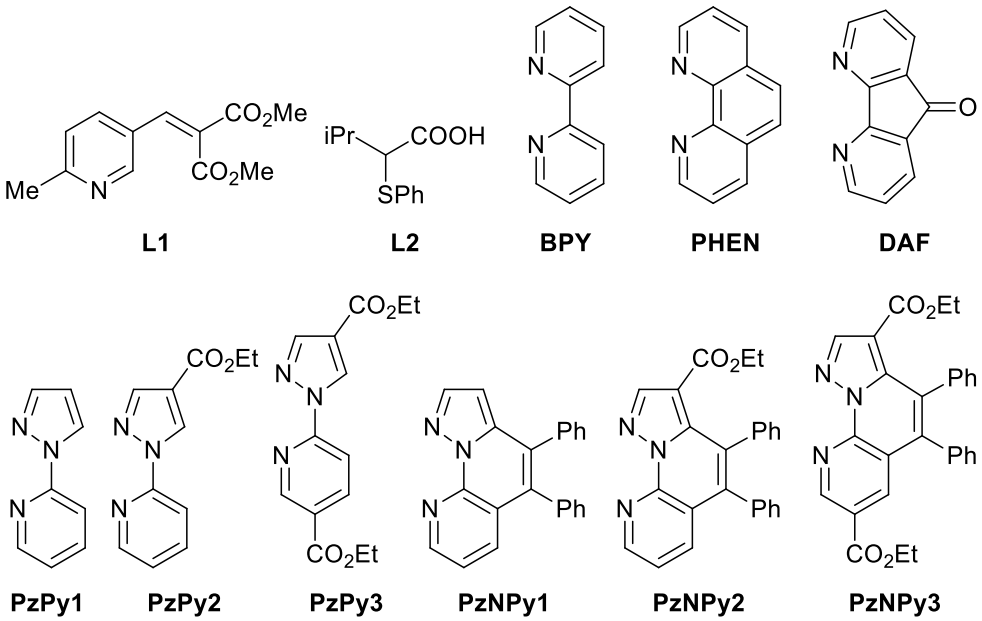
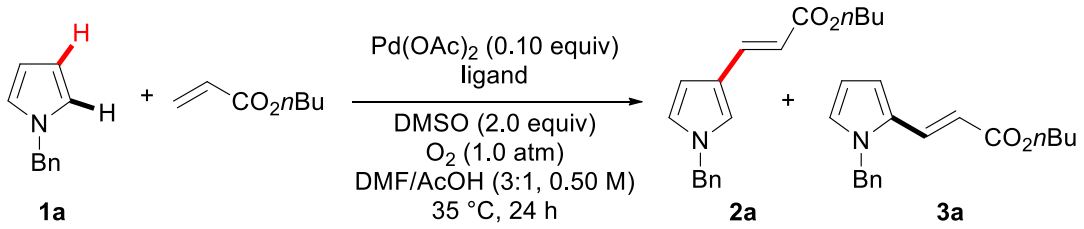



**Figure S1.** List of ligands used in optimization studies.

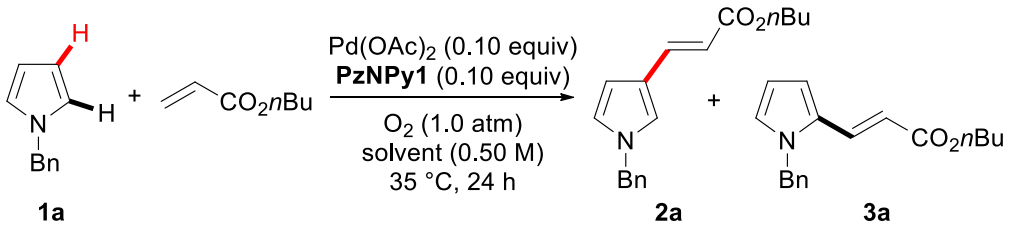
**Table S1.** Ligand effect on the C–H alkenylation of *N*-benzyl pyrrole (**1a**)[a]




| entry | ligand (mol%) | isolated yield (%) | |
|---|---|---|---|
| | | **2a** | **3a** |
| 1 | – | 7 | 47 |
| 2 | **L1** (10) | 14 | 25 |
| 3 | **L2** (10) | 31 | 31 |
| 4 | **L2** (20) | 31 | 21 |
| 5 | BPY (10) | 0 | 0 |
| 6 | PHEN (10) | 6 | 2 |
| 7 | DAF (10) | 21 | 20 |
| 8[b] | DAF (10) | 29 | 24 |
| 9 | **PzPy1** (10) | 46 | 6 |
| 10 | **PzPy2** (10) | 62 | 8 |
| 11[c] | **PzPy2** (10) | 23 | 2 |
| 12 | **PzPy3** (10) | 54 | 10 |
| 13 | **PzNPy1** (10) | 62 | 4 |
| 14[c] | **PzNPy1** (10) | 46 | 2 |
| 15[d] | **PzNPy1** (5) | 49 | 4 |
| 16[d,e] | **PzNPy1** (5) | 66 | 6 |
| 17 | **PzNPy2** (10) | 54 | 5 |
| 18 | **PzNPy3** (10) | 58 | 10 |
| 19[f] | **PzNPy3** (10) | 5 | 68 |
| 20 | $Pd(OAc)_2$-**PzNPy1** complex (10) | 64 | 3 |

[a] Reaction conditions: **1a** (118 mg, 0.75 mmol), *n*-butyl acrylate (71.0 μL, 0.50 mmol), $Pd(OAc)_2$ (11.2 mg, 0.050 mmol), ligand (0.050 mmol), DMF (0.75 mL), AcOH (0.25 mL), DMSO (83.0 μL), and $O_2$ balloon at 35 °C for 24 h. [b] 1,4-Dioxane (0.75 mL) was used instead of DMF. [c] Under air for 5 h. [d] $Pd(OAc)_2$ (5.6 mg, 0.025 mmol). [e] 48 h. [f] DMSO (1.0 mL, 0.50 M) was used instead of DMF/AcOH.

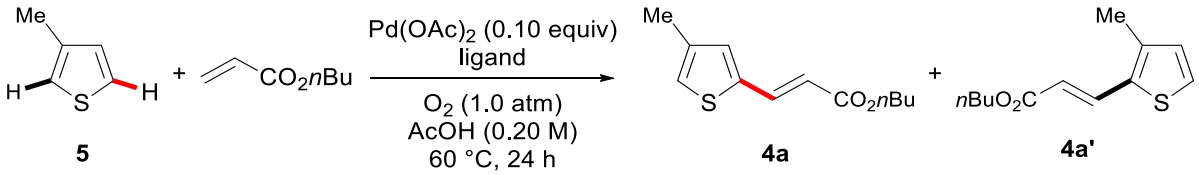
**Table S2.** Solvent effect of the C–H alkenylation of *N*-benzyl pyrrole (**1a**)[a]




| entry | **1a** (equiv) | additive | solvent | isolated yield (%) | |
|---|---|---|---|---|---|
| | | | | **2a** | **3a** |
| 1 | 1.5 | – | DMF | 7 | 30 |
| 2 | 1.5 | – | AcOH | 11 | 24 |
| 3 | 1.5 | – | DMSO | 8 | 60 |
| 4[b] | 1.5 | – | DMSO | 1 | 72 |
| 5 | 1.5 | – | 1,4-dioxane | 0 | 18 |
| 6 | 1.5 | – | DMF/AcOH (3:1) | 31 | 19 |
| 7 | 1.5 | – | DMSO/AcOH (3:1) | 61 | 6 |
| 8 | 1.5 | DMSO (2 equiv) | DMF | 14 | 37 |
| 9 | 1.5 | DMSO (2 equiv) | AcOH | 14 | 4 |
| 10 | 1.5 | DMSO (2 equiv) | 1,4-dioxane/AcOH (3:1) | 54 | 10 |
| 11 | 1.5 | DMSO (2 equiv) | DMF/AcOH (3:1) | 62 | 4 |
| 12 | 1.0 | DMSO (2 equiv) | DMF/AcOH (3:1) | 42 | 4 |
| 13[c] | 1.0 | DMSO (2 equiv) | DMF/AcOH (3:1) | 57 | 6 |

[a] Reaction conditions: **1a** (as indicated), *n*-butyl acrylate (71.0 μL, 0.50 mmol), $Pd(OAc)_2$ (11.2 mg, 0.050 mmol), **PzNPy1** (16.1 mg, 0.050 mmol), solvent (1.0 mL, 0.50 M), and $O_2$ balloon at 35 °C for 24 h. [b] Without **PzNPy1**. [c] *n*-Butyl acrylate (107 μL, 0.75 mmol).

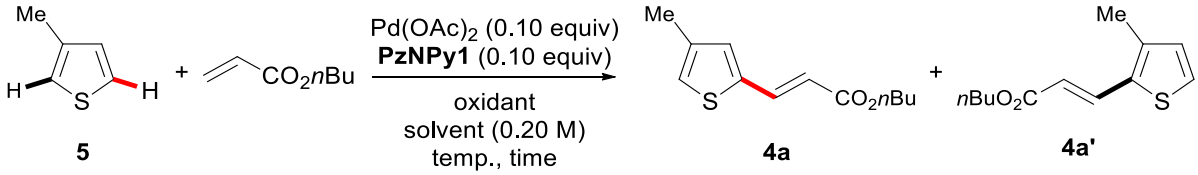
**Table S3.** Ligand effect on the C–H alkenylation of 3-methyl thiophene (**5**)[a]




| entry | ligand (mol%) | $^1$H NMR yield (%)[b] | |
|---|---|---|---|
| | | **4a** | **4a'** |
| 1 | – | 8 | 8 |
| 2 | BPY (10) | – | – |
| 3 | PHEN (10) | 10 | – |
| 4 | DAF (10) | 16 | 14 |
| 5 | **L1** (10) | 9 | 31 |
| 6 | **L2** (20) | 16 | – |
| 7 | **PzPy1** (10) | 57 | 4 |
| 8 | **PzPy2** (10) | 67 | 8 |
| 9 | **PzPy3** (10) | 66 | 6 |
| 10 | **PzNPy1** (10) | 74 | 7 |
| 11[c] | **PzNPy1** (5) | 45 | 5 |
| 12[c,d] | **PzNPy1** (5) | 54 | 6 |
| 13 | **PzNPy1** (15) | 62 | 1 |
| 14 | **PzNPy1** (20) | 44 | 2 |
| 15 | **PzNPy2** (10) | 64 | 8 |
| 16 | **PzNPy3** (10) | 64 | 14 |
| 17[e] | **PzNPy3** (10) | 7 | 42 |
| 18[f] | **PzNPy3** (10) | 11 | 77 |
| 19 | $Pd(OAc)_2$-**PzNPy1** complex (10) | 66 | 5 |

[a] Reaction conditions: **5** (77.0 µL, 0.80 mmol), *n*-butyl acrylate (51.3 mg, 0.40 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol), ligand (as indicated), AcOH (2.0 mL, 0.20 M), and $O_2$ balloon at 60 °C for 24 h. [b] Trichloroethylene (36.0 µL, 0.40 mmol) was utilized as an internal standard. [c] $Pd(OAc)_2$ (4.5 mg, 0.02 mmol). [d] 48 h. [e] DMF (2.0 mL, 0.20 M) was used instead of AcOH. [f] DMA (2.0 mL, 0.20 M) was used instead of AcOH.

**Table S4.** Solvent effect on the C–H alkenylation of 3-methyl thiophene (**5**)[a]




| entry | solvent | oxidant (equiv) | time (h) | temp. (°C) | $^1$H NMR yield (%)[b] | |
|---|---|---|---|---|---|---|
| | | | | | **4a** | **4a'** |
| 1 | AcOH | $O_2$ (balloon) | 24 | 60 | 74 | 7 |
| 2 | 1,4-dioxane | $O_2$ (balloon) | 24 | 60 | 7 | 19 |
| 3 | DMF | $O_2$ (balloon) | 24 | 60 | 16 | 58 |
| 4 | DMA | $O_2$ (balloon) | 24 | 60 | 12 | 56 |
| 5[c] | DMA | $O_2$ (balloon) | 24 | 60 | 1 | 8 |
| 6 | DMSO | $O_2$ (balloon) | 24 | 60 | 11 | 55 |
| 7 | AcOH:DMSO (3:1) | $O_2$ (balloon) | 24 | 60 | 74 | 11 |
| 8[d] | 1,4-dioxane:AcOH (3:1) | $O_2$ (balloon) | 24 | 60 | 45 | 38 |
| 9[d] | AcOH:DCE (3:1) | $O_2$ (balloon) | 24 | 60 | 38 | 1 |
| 10 | AcOH | $Cu(OAc)_2$ (2.0) | 24 | 60 | 14 | – |
| 11 | AcOH | AgOAc (2.0) | 24 | 60 | 70 | 3 |
| 12 | AcOH | $O_2$ (balloon) | 24 | 40 | 47 | 8 |
| 13 | AcOH | $O_2$ (balloon) | 24 | 80 | 56 | 8 |
| 14 | AcOH | $O_2$ (balloon) | 12 | 60 | 68 | 4 |
| 15 | AcOH | $O_2$ (balloon) | 48 | 60 | 67 | 5 |
| 16[e] | AcOH | $O_2$ (balloon) | 24 | 60 | 50 | 5 |
| 17[f] | AcOH | $O_2$ (balloon) | 24 | 60 | 45 | 5 |

[a] Reaction conditions: **5** (77.0 µL, 0.80 mmol), *n*-butyl acrylate (51.3 mg, 0.40 mmol), $Pd(OAc)_2$ (9.0 mg, 0.040 mmol), **PzNPy1** (12.9 mg, 0.040 mmol), solvent (as indicated, 2.0 mL, 0.20 M), and oxidant (as indicated). [b] Trichloroethylene (36.0 µL, 0.40 mmol) was utilized as an internal standard. [c] Without **PzNPy1**. [d] DMSO (166 µL) was added. [e] **5** (58.0 µL, 0.60 mmol). [f] **5** (39.0 µL, 0.40 mmol).

# IV. Experimental Procedures

## IV.A. C3-alkenylation of *N*-substituted pyrroles

An alkene (0.50 mmol), $Pd(OAc)_2$ (11.2 mg, 0.050 mmol), and **PzNPy1** (16.1 mg, 0.050 mmol) were added to a solution of a pyrrole substrate (0.75 mmol), DMF (0.75 mL), AcOH (0.25 mL), and DMSO (83.0 μL) in an 8 mL-glass vial. Then, the vial was evacuated and filled with oxygen for three times. After stirring in a preheated reaction block at 35 °C for 24 h under 1 atm of oxygen (balloon), the reaction mixture was cooled to 25 °C and concentrated. The residue was purified by flash column chromatography to afford the desired product.

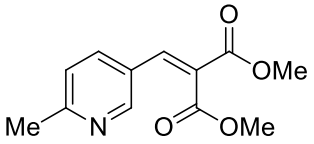
## IV.B. C5-alkenylation of 3-substituted thiophenes

A thiophene substrate (0.80 mmol), $Pd(OAc)_2$ (9.0 mg, 0.040 mmol), and **PzNPy1** (12.9 mg, 0.040 mmol) were added to a solution of an alkene (0.40 mmol) and AcOH (2.0 mL, 0.20 M) in an 8 mL-glass vial. Then, the vial was evacuated and filled with oxygen for three times. After stirring in a preheated reaction block at 60 °C for 24 h under 1 atm of oxygen (balloon), the reaction mixture was cooled to 25 °C and concentrated. The residue was purified by flash column chromatography to afford the desired product.

# V. Compound Characterization Data

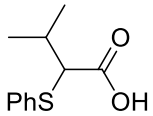
## V.A. Starting materials

### dimethyl 2-((6-methylpyridin-3-yl)methylene)malonate (L1)[1]



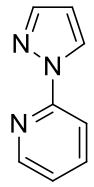

**L1** was obtained as a colorless solid by a reported procedure (89 mg, 63% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.72 (s, 1H), 7.63 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 3.86 (d, *J* = 1.7 Hz, 6H), 2.59 (s, 3H).

### 3-methyl-2-(phenylthio)butanoic acid (L2)[2]



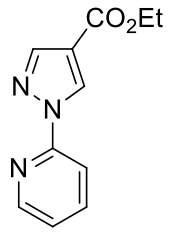

**L2** was obtained as a colorless oil by a reported procedure (720 mg, 68% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.49-7.44 (m, 2H), 7.33-7.26 (m, 3H), 3.44 (d, *J* = 8.5 Hz, 1H), 2.21-2.13 (m, 1H), 1.18 (d, *J* = 6.7 Hz, 3H), 1.10 (d, *J* = 6.7 Hz, 3H).

### 2-(1*H*-pyrazol-1-yl)pyridine (PzPy1)[3]



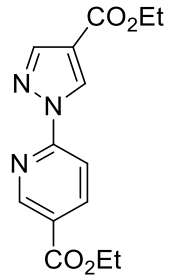

**PzPy1** was prepared by the procedures reported in our previous study (4.43 g, 83% yield).[4] $^1$H NMR (300 MHz, $CDCl_3$) δ 8.57 (d, *J* = 2.5 Hz, 1H), 8.41 (d, *J* = 4.0 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.85-7.78 (m, 1H), 7.74 (s, 1H), 7.22-7.15 (m, 1H), 6.47 (s, 1H).

### ethyl 1-(pyridin-2-yl)-1*H*-pyrazole-4-carboxylate (PzPy2)[5]



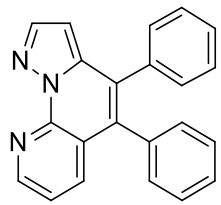
**PzPy2** was prepared by the procedures reported in our previous study (2.17 g, 83% yield).[4] $^1$H NMR (300 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.45 (dd, *J* = 4.0, 0.9 Hz, 1H), 8.11 (s, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.89-7.83 (m, 1H), 7.29-7.26 (m, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).

**ethyl 6-(4-(ethoxycarbonyl)-1*H*-pyrazol-1-yl)nicotinate (PzPy3)[4]**



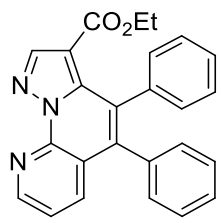

**PzPy3** was prepared by the procedures reported in our previous study (921 mg, 74% yield).[4] $^1$H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 9.06 (d, *J* = 1.8 Hz, 1H), 8.45 (dd, *J* = 8.6, 2.2 Hz, 1H), 8.14 (s, 1H), 8.07 (d, *J* = 8.6 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.39 (t, *J* = 7.1 Hz, 3H).

**4,5-diphenylpyrazolo[1,5-*a*][1,8]naphthyridine (PzNPy1)[4]**



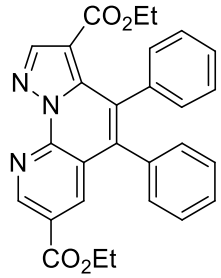

**PzNPy1** was prepared by the procedures reported in our previous study (128 mg, 80% yield).[4] $^1$H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 3.1 Hz, 1H), 8.12 (d, *J* = 2.0 Hz, 1H), 7.88 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.36 (dd, *J* = 8.1, 4.6 Hz, 1H), 7.34-7.29 (m, 3H), 7.26-7.22 (m, 5H), 7.20-7.15 (m, 2H), 6.46 (d, *J* = 1.9 Hz, 1H).

**ethyl 4,5-diphenylpyrazolo[1,5-*a*][1,8]naphthyridine-3-carboxylate (PzNPy2)[4]**



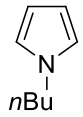
**PzNPy2** was prepared by the procedures reported in our previous study (147 mg, 75% yield).[4] $^1$H NMR (400 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.5, 1.6 Hz, 1H), 8.51 (s, 1H), 7.84 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.42 (dd, *J* = 8.1, 4.5 Hz, 1H), 7.33-7.28 (m, 3H), 7.23-7.17 (m, 3H), 7.16-7.07 (m, 4H), 3.74 (q, *J* = 7.1 Hz, 2H), 1.01 (t, *J* = 7.1 Hz, 3H).

**diethyl 4,5-diphenylpyrazolo[1,5-*a*][1,8]naphthyridine-3,7-dicarboxylate (PzNPy3)[4]**



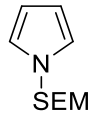

**PzNPy3** was prepared by the procedures reported in our previous study (344 mg, 74% yield).[4] $^1$H NMR (300 MHz, $CDCl_3$) δ 9.43 (d, *J* = 1.6 Hz, 1H), 8.54 (s, 1H), 8.46 (d, *J* = 2.0 Hz, 1H), 7.34-7.29 (m, 3H), 7.24-7.19 (m, 3H), 7.15-7.06 (m, 4H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.74 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H).

**1-butyl pyrrole[6]**



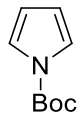

1*H*-pyrrole (3.47 mL, 50 mmol), KOH (8.42 g, 150 mmol), and DMSO (100 mL, 0.50 M) were added to a 250 mL-RBF, and the resulting mixture was stirred at 25 °C for 30 min. Then, 1-iodobutane (5.69 mL, 50 mmol) was added dropwise to the reaction mixture at 0 °C with an ice bath, and the reaction mixture was stirred for further 45 min. The resulting solution was transferred to a 125 mL-separatory funnel and treated with water (20 mL) and EtOAc (20 mL). The aqueous layer was extracted with EtOAc (30 mL × 3). The combined organic layers were washed with brine (50 mL), dried over $Na_2SO_4$, and filtered. The filtrate was concentrated and then purified by flash column chromatography (hexanes/EtOAc = 20:1) to provide 1-butyl pyrrole as a yellow liquid (3.50 g, 57% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 6.66 (s, 2H), 6.14 (s, 2H), 3.88 (t, *J* = 7.1 Hz, 2H), 1.79-1.72 (m, 2H), 1.36-1.29 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

**1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-pyrrole[7]**



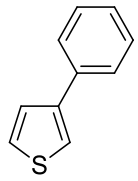

1*H*-pyrrole (347 μL, 5.0 mmol) and anhydrous DMF (10.0 mL, 0.50 M) were added to a flame-dried 100 mL-RBF. Then, NaH (60% in mineral oil, 220 mg, 5.5 mmol) was added to the solution under an atmosphere of argon at 0 °C with an ice bath. After the reaction mixture was stirred for 30 min at 25 °C, 2-(trimethylsilyl)ethoxymethyl chloride (885 μL, 5.0 mmol) was added dropwise, and the reaction mixture was stirred for further 30 min. The reaction mixture was quenched with ice cold water (40 mL), transferred to a 125 mL-separatory funnel, and extracted with EtOAc (30 mL × 3). The combined organic layers were washed with brine (50 mL), dried over $Na_2SO_4$, and filtered. The filtrate was concentrated and then purified by flash column chromatography (hexanes/EtOAc = 20:1) to provide 1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-pyrrole as a yellow liquid (110 mg, 11% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 6.84-6.70 (m, 2H), 6.26-6.15 (m, 2H), 5.20 (s, 2H), 3.48-3.40 (m, 2H), 0.92-0.86 (m, 2H), -0.02 (s, 9H).

***tert*-butyl 1*H*-pyrrole-1-carboxylate[8]**




Di-*tert*-butyl dicarbonate (2.76 mL, 12 mmol), 4-dimethylaminopyridine (183 mg, 1.5 mmol), and anhydrous acetonitrile (10 mL, 1.0 M) were added to a flame-dried 100 mL-RBF. Then, 1*H*-pyrrole (694 μL, 10 mmol) was added dropwise to the solution under argon atmosphere. The reaction mixture was stirred in a preheated oil bath at 30 °C. After stirring for 2.5 h, the reaction mixture was cooled to 25 °C and concentrated. Purification by flash column chromatography (hexanes/EtOAc = 10:1) provided *tert*-butyl 1*H*-pyrrole-1-carboxylate as a yellow liquid (1.55 g, 93% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.25-7.21 (m, 2H), 6.23-6.20 (m, 2H), 1.60 (s, 9H).

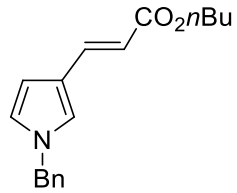
**3-phenyl thiophene**[9]



A solution of 3-bromothiophene (652 mg, 4.0 mmol), phenylboronic acid (585 mg, 4.8 mmol), $Cs_2CO_3$ (2.61 g, 8.0 mmol), and 1,4-dioxane (15 mL, 0.27 M) in an 8 mL-glass vial was degassed under argon and treated with $Pd(OAc)_2$ (44.9 mg, 0.20 mmol) and $PCy_3H{\cdot}BF_4$ (147 mg, 0.40 mmol). After stirring for 16 h in a preheated reaction block at 105 °C, the reaction mixture was cooled to 25 °C and treated with water (30 mL) and EtOAc (30 mL). The organic layer was collected, and the aqueous layer was extracted with EtOAc (30 mL × 2). The combined organic layers were washed with brine (20 mL), dried over $Na_2SO_4$, and filtered. The filtrate was concentrated and then purified by flash column chromatography (hexanes/dichloromethane = 80:1) to provide 3-phenyl thiophene as a white solid (474 mg, 74% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.62-7.59 (m, 2H), 7.46-7.45 (m, 1H), 7.43-7.37 (m, 4H), 7.32-7.27 (m, 1H).

## V.B. Alkenylated Products

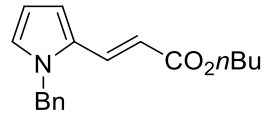
**(*E*)-butyl 3-(1-benzyl-1*H*-pyrrol-3-yl)acrylate (2a)**



Following the general procedure A, the reaction was set up with 1-benzylpyrrole (118 mg, 0.75 mmol) and *n*-butyl acrylate (71.0 μL, 0.50 mmol). Purification by flash column chromatography (hexanes/EtOAc = 20:1) provided alkenylated pyrrole **2a** as a yellow oil (88 mg, 62% yield) and **3a** as a yellow oil (5 mg, 4% yield). IR (film) 2956, 2870, 1696, 1624, 1453, 1387 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 15.8 Hz, 1H), 7.38-7.28 (m, 3H), 7.17-7.10 (m, 2H), 6.91 (t, *J* = 1.9 Hz, 1H), 6.66 (t, *J* = 2.4 Hz, 1H), 6.41 (dd, *J* = 2.5, 1.8 Hz, 1H), 6.08 (d, *J* = 15.7 Hz, 1H), 5.03 (s, 2H), 4.16 (t, *J* = 6.7 Hz, 2H), 1.69-1.63 (m, 2H), 1.46-1.39 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.2, 138.8, 137.1, 129.0, 128.1, 127.3, 124.5, 123.4, 121.1, 113.2, 107.3, 64.0, 53.7, 31.0, 19.3, 13.9; HRMS (ESI)

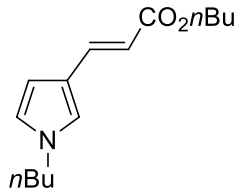
calcd for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1645, found 284.1646.

**(*E*)-butyl 3-(1-benzyl-1*H*-pyrrol-2-yl)acrylate (3a)**



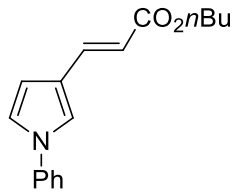

$^1$H NMR data was matched with the reported data.[10] $^1$H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 15.6 Hz, 1H), 7.35-7.26 (m, 3H), 7.08-6.98 (m, 2H), 6.84 (s, 1H), 6.75-6.69 (m, 1H), 6.31-6.22 (m, 1H), 6.13 (d, *J* = 15.6 Hz, 1H), 5.21 (s, 2H), 4.12 (t, *J* = 6.6 Hz, 2H), 1.66-1.59 (m, 2H), 1.42-1.34 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

**(*E*)-butyl 3-(1-butyl-1*H*-pyrrol-3-yl)acrylate (2b)**



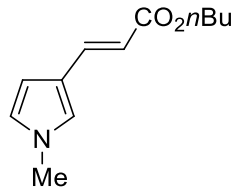

Following the general procedure A, the reaction was set up with 1-butyl pyrrole (92.4 mg, 0.75 mmol) and *n*-butyl acrylate (71.0 μL, 0.50 mmol). Purification by flash column chromatography (hexanes/EtOAc = 20:1) provided alkenylated pyrrole **2b** as a yellow oil (84 mg, 67% yield). IR (film) 2956, 2871, 1696, 1625, 1387, 1274 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 15.7 Hz, 1H), 6.86 (t, *J* = 1.8 Hz, 1H), 6.61 (t, *J* = 2.4 Hz, 1H), 6.36 (dd, *J* = 2.5, 1.9 Hz, 1H), 6.07 (d, *J* = 15.7 Hz, 1H), 4.16 (t, *J* = 6.7 Hz, 2H), 3.84 (t, *J* = 7.1 Hz, 2H), 1.75-1.64 (m, 4H), 1.45-1.39 (m, 2H), 1.34-1.28 (m, 2H), 0.97-0.91 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.3, 139.0, 124.0, 122.8, 120.5, 112.6, 106.6, 63.9, 49.7, 33.3, 31.0, 19.8, 19.3, 13.8, 13.6; HRMS (ESI) calcd for $C_{15}H_{24}NO_2$ $[M+H]^+$ 250.1802, found 250.1802. The corresponding C2-alkenylated product, **3b**, was also obtained (4 mg, 3% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 15.6 Hz, 1H), 6.83-6.73 (m, 1H), 6.70-6.64 (m, 1H), 6.23-6.10 (m, 2H), 4.18 (t, *J* = 6.6 Hz, 2H), 3.98 (t, *J* = 7.2 Hz, 2H), 1.73-1.64 (m, 4H), 1.45-1.29 (m, 4H), 0.98-0.90 (m, 6H).

**(*E*)-butyl 3-(1-phenyl-1*H*-pyrrol-3-yl)acrylate (2c)**



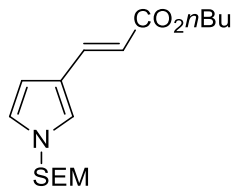

Following the general procedure A, the reaction was set up with 1-phenyl pyrrole (107 mg, 0.75 mmol) and *n*-butyl acrylate (71.0 μL, 0.50 mmol). Purification by flash column chromatography (hexanes/EtOAc = 20:1) provided alkenylated pyrrole **2c** as a brown solid (77 mg, 57% yield). mp 76-78 °C; IR (film) 2962, 2871, 1699, 1628, 1511, 1373 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 15.7 Hz, 1H), 7.47-7.42 (m, 2H), 7.40-7.36 (m, 2H), 7.32-7.27 (m, 2H), 7.07 (t, *J* = 2.6 Hz, 1H), 6.57 (dd, *J* = 3.0, 1.7 Hz, 1H), 6.17 (d, *J* = 15.7 Hz, 1H), 4.19 (t, *J* = 6.7 Hz, 2H), 1.71-1.65 (m, 2H), 1.48-1.40 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 168.1, 140.1, 138.3, 129.9, 126.6, 122.8, 122.2, 121.7, 120.7, 114.4, 108.8, 64.2, 31.0, 19.4, 13.9; HRMS (ESI) calcd for $C_{17}H_{20}NO_2$ $[M+H]^+$ 270.1489, found 270.1489.

**(*E*)-butyl 3-(1-methyl-1*H*-pyrrol-3-yl)acrylate (2d)[11]**



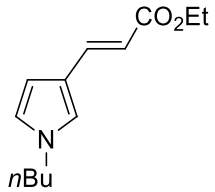

Following the general procedure A, the reaction was set up with 1-methyl pyrrole (81.1 mg, 1.00 mmol) and *n*-butyl acrylate (71.0 μL, 0.50 mmol). Purification by flash column chromatography (hexanes/EtOAc = 20:1) provided alkenylated pyrrole **2d** as a yellow oil (40 mg, 39% yield). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 15.7 Hz, 1H), 6.83 (t, *J* = 1.8 Hz, 1H), 6.57 (t, *J* = 2.4 Hz, 1H), 6.36 (dd, *J* = 2.5, 1.9 Hz, 1H), 6.07 (d, *J* = 15.7 Hz, 1H), 4.16 (t, *J* = 6.7 Hz, 2H), 3.64 (s, 3H), 1.69-1.64 (m, 2H), 1.45-1.39 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). Corresponding C2-alkenylated product, **3d** was also obtained (16 mg, 15% yield). $^1H$ NMR data was matched with the reported one.[10] $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 15.7 Hz, 1H), 6.76-6.72 (m, 1H), 6.65 (dd, *J* = 3.9 Hz, *J* = 1.5 Hz, 1H), 6.19-6.12 (m, 2H), 4.18 (t, *J* = 6.7 Hz, 2H), 3.71 (s, 3H), 1.70-1.64 (m, 2H), 1.46-1.39 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

**(*E*)-butyl 3-(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-pyrrol-3-yl)acrylate (2e)**



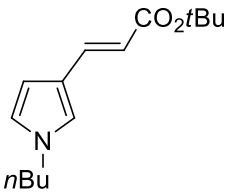

Following the general procedure A, the reaction was set up with 1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-pyrrole (148 mg, 0.75 mmol) and *n*-butyl acrylate (71.0 μL, 0.50 mmol). Purification by flash column chromatography (hexanes/EtOAc = 20:1) provided alkenylated pyrrole **2e** as a yellow oil (92 mg, 57% yield). IR (film) 2954, 1700, 1629, 1507, 1387, 1349 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 15.8 Hz, 1H), 6.98 (t, *J* = 1.8 Hz, 1H), 6.75 (t, *J* = 2.4 Hz, 1H), 6.42 (dd, *J* = 2.8, 1.7 Hz, 1H), 6.11 (d, *J* = 15.7 Hz, 1H), 5.16 (s, 2H), 4.17 (t, *J* = 6.7 Hz, 2H), 3.48-3.43 (m, 2H), 1.70-1.64 (m, 2H), 1.45-1.39 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.91-0.87 (m, 2H), -0.02 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 168.1, 138.6, 124.1, 123.0, 121.6, 113.9, 107.6, 78.7, 66.2, 64.0, 31.0, 19.3, 17.8, 13.9, -1.3; HRMS (ESI) calcd for $C_{17}H_{30}NO_3Si$ $[M+H]^+$ 324.1989, found 324.1987.

**(*E*)-ethyl 3-(1-butyl-1*H*-pyrrol-3-yl)acrylate (2f)**



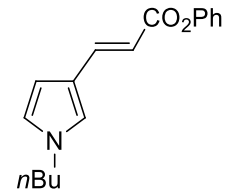

Following the general procedure A, the reaction was set up with 1-butyl pyrrole (92.4 mg, 0.75 mmol) and ethyl acrylate (53.0 μL, 0.50 mmol). Purification by flash column chromatography (hexanes/EtOAc = 20:1) provided alkenylated pyrrole **2f** as a yellow oil (71 mg, 64% yield). IR (film) 2931, 2872, 1695, 1623, 1460, 1367 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 15.7 Hz, 1H), 6.86 (t, *J* = 1.9 Hz, 1H), 6.61 (d, *J* = 2.5 Hz, 1H), 6.36 (dd, *J* = 2.6, 1.9 Hz, 1H), 6.07 (d, *J* = 15.7 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.84 (t, *J* = 7.1 Hz, 2H), 1.77-1.69 (m, 2H), 1.34-1.28 (m, 5H), 0.93 (t, *J* = 7.4 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 168.2, 139.1, 124.0, 122.8, 120.5, 112.6, 106.7, 59.9, 49.7, 33.4, 19.9, 14.5, 13.7; HRMS (ESI) calcd for $C_{13}H_{20}NO_2$ $[M+H]^+$ 222.1489, found 222.1486.

**(*E*)-*tert*-butyl 3-(1-butyl-1*H*-pyrrol-3-yl)acrylate (2g)**



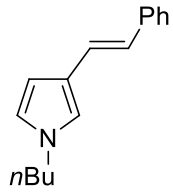

Following the general procedure A, the reaction was set up with 1-butyl pyrrole (92.4 mg, 0.75 mmol) and *tert*-butyl acrylate (73.0 μL, 0.50 mmol). Purification by flash column chromatography (hexanes/EtOAc = 20:1) provided alkenylated pyrrole **2g** as a yellow oil (96 mg, 77% yield). IR (film) 2930, 2872, 1694, 1624, 1455, 1364 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 15.7 Hz, 1H), 6.84 (t, *J* = 1.9 Hz, 1H), 6.60 (t, *J* = 2.4 Hz, 1H), 6.34 (dd, *J* = 2.5, 1.9 Hz, 1H), 6.00 (d, *J* = 15.7 Hz, 1H), 3.83 (t, *J* = 7.1 Hz, 2H), 1.77-1.70 (m, 2H), 1.51 (s, 9H), 1.33-1.26 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 167.6, 138.1, 123.7, 122.7, 120.6, 114.6, 106.6, 79.6, 49.7, 33.4, 28.4, 19.9, 13.7; HRMS (ESI) calcd for $C_{15}H_{24}NO_2$ $[M+H]^+$ 250.1802, found 250.1804.

**(*E*)-phenyl 3-(1-butyl-1*H*-pyrrol-3-yl)acrylate (2h)**



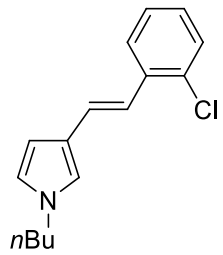

Following the general procedure A, the reaction was set up with 1-butyl pyrrole (92.4 mg, 0.75 mmol) and phenyl acrylate (69.0 μL, 0.50 mmol). Purification by flash column chromatography (hexanes/EtOAc = 20:1) provided alkenylated pyrrole **2h** as a yellow oil (105 mg, 78% yield). IR (film) 2929, 2870, 1717, 1619, 1490, 1366 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 15.7 Hz, 1H), 7.42-7.37 (m, 2H), 7.24-7.20 (m, 1H), 7.17-7.14 (m, 2H), 6.94 (t, *J* = 1.8 Hz, 1H), 6.66 (t, *J* = 2.4 Hz, 1H), 6.46-6.43 (m, 1H), 6.26 (d, *J* = 15.6 Hz, 1H), 3.87 (t, *J* = 7.1 Hz, 2H), 1.80-1.73 (m, 2H), 1.36-1.29 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 166.7, 151.3, 141.2, 129.4, 125.5, 124.8, 123.2, 122.0, 120.5, 111.4, 107.0, 49.8, 33.4, 19.9, 13.7; HRMS (ESI) calcd for $C_{17}H_{20}NO_2$ $[M+H]^+$ 270.1489, found 270.1490.

**(*E*)-1-butyl-3-styryl-1*H*-pyrrole (2i)**



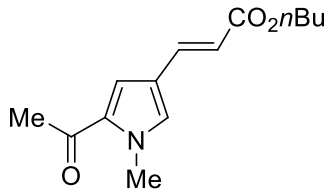

Following the general procedure A, the reaction was set up with 1-butyl pyrrole (92.4 mg, 0.75 mmol) and styrene (57.0 μL, 0.50 mmol). Purification by flash column chromatography (hexanes/EtOAc = 20:1) provided alkenylated pyrrole **2i** as a yellow oil (87 mg, 77% yield). IR (film) 2928, 2869, 1698, 1449, 1401, 1359 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.46-7.39 (m, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.19-7.13 (m, 1H), 7.01 (d, *J* = 16.2 Hz, 1H), 6.82-6.69 (m, 2H), 6.62 (t, *J* = 2.4 Hz, 1H), 6.43-6.34 (m, 1H), 3.84 (t, *J* = 7.1 Hz, 2H), 1.82-1.69 (m, 2H), 1.37-1.30 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 138.7, 128.6, 126.3, 125.8, 124.0, 122.8, 122.7, 122.0, 120.3, 105.4, 49.5, 33.5, 20.0, 13.7; HRMS (ESI) calcd for $C_{16}H_{20}N$ $[M+H]^+$ 226.1590, found 226.1592.

**(*E*)-1-butyl-3-(2-chlorostyryl)-1*H*-pyrrole (2j)**




Following the general procedure A, the reaction was set up with 1-butyl pyrrole (92.4 mg, 0.75 mmol) and 2-chlorostyrene (64.0 μL, 0.50 mmol). Purification by flash column chromatography (hexanes/EtOAc = 20:1) provided alkenylated pyrrole **2j** as a yellow oil (65 mg, 50% yield). IR (film) 2927, 2869, 1699, 1629, 1438, 1399 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.34 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.23-7.19 (m, 1H), 7.17-7.06 (m, 2H), 6.99 (d, *J* = 16.1 Hz, 1H), 6.81 (t, *J* = 1.9 Hz, 1H), 6.63 (t, *J* = 2.5 Hz, 1H), 6.43 (dd, *J* = 2.5, 1.9 Hz, 1H), 3.85 (t, *J* = 7.1 Hz, 2H), 1.81-1.71 (m, 2H), 1.37-1.31 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 136.7, 132.7, 129.8, 127.3, 126.8, 125.9, 125.3, 122.8, 122.2, 120.8, 120.0, 105.9, 49.7, 33.6, 20.0, 13.8; HRMS (ESI) calcd for $C_{16}H_{19}ClN$ $[M+H]^+$ 260.1201, found 260.1208.

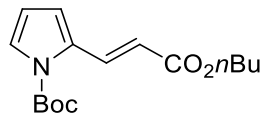
**(*E*)-butyl 3-(5-acetyl-1-methyl-1*H*-pyrrol-3-yl)acrylate (2l)**




Following the general procedure A, the reaction was set up with 2-acetyl-1-methylpyrrole (93.8 mg, 0.75 mmol) and *n*-butyl acrylate (71.0 μL, 0.50 mmol). Purification by flash column chromatography (hexanes/EtOAc = 20:1) provided alkenylated pyrrole **2l** as a yellow solid (78 mg, 63% yield). mp 43-45 °C; IR (film) 2957, 2872, 1700, 1627, 1429, 1400 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 15.9 Hz, 1H), 7.10 (d, *J* = 1.4 Hz, 1H), 7.00 (s, 1H), 6.15 (d, *J* = 15.9 Hz, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 3.92 (s, 3H), 2.44 (s, 3H), 1.69-1.64 (m, 2H), 1.45-1.39 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 189.0, 167.6, 137.2, 132.1, 131.9, 119.3, 117.3, 115.1, 64.2, 38.0, 30.9, 27.2, 19.3, 13.8; HRMS (ESI) calcd for $C_{14}H_{20}NO_3$ $[M+H]^+$ 250.1438, found 250.1436.

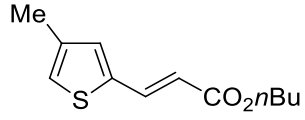
The corresponding C2 isomer has been reported,[10] but it was not observed in this experiment.

**(*E*)-*tert*-butyl 2-(3-butoxy-3-oxoprop-1-en-1-yl)-1*H*-pyrrole-1-carboxylate (2m)[12]**



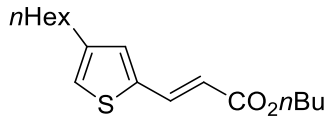

Following the general procedure A, the reaction was set up with *tert*-butyl 1*H*-pyrrole-1-carboxylate (125 mg, 0.75 mmol) and *n*-butyl acrylate (71.0 μL, 0.50 mmol). Purification by flash column chromatography (hexanes/EtOAc = 10:1) provided C2 alkenylated pyrrole **2m** as a yellow oil (75 mg, 51% yield). $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 15.9 Hz, 1H), 7.39 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.71-6.68 (m, 1H), 6.23-6.18 (m, 2H), 4.18 (t, *J* = 6.7 Hz, 2H), 1.71-1.65 (m, 2H), 1.63 (s, 9H), 1.50-1.39 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

**(*E*)-butyl 3-(4-methylthiophen-2-yl)acrylate (4a)[13]**



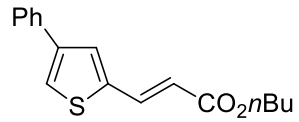
Following the general procedure B, the reaction was set up with 3-methyl thiophene (77.0 μL, 0.80 mmol) and *n*-butyl acrylate (51.3 mg, 0.40 mmol). Purification by flash column chromatography (hexanes/EtOAc = 60:1) provided alkenylated thiophene **4a** as a colorless oil (64 mg, 71% yield, C5:C2 = 12:1). IR (film) 2957, 2929, 2871, 1705, 1623, 1159 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 15.7 Hz, 1H), 7.05 (s, 1H), 6.94 (s, 1H), 6.19 (d, *J* = 15.7 Hz, 1H), 4.18 (t, *J* = 6.6 Hz, 2H), 2.24 (s, 3H), 1.70-1.63 (m, 2H), 1.46-1.38 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 167.1, 139.4, 138.8, 137.2, 133.0, 124.0, 116.7, 64.4, 30.9, 19.3, 15.6, 13.8; HRMS (ESI) calcd for $C_{12}H_{17}O_2S$ $[M+H]^+$ 225.0944, found 225.0945.

**(*E*)-butyl 3-(4-hexylthiophen-2-yl)acrylate (4b)**




Following the general procedure B, the reaction was set up with 3-hexyl thiophene (144 μL, 0.80 mmol) and *n*-butyl acrylate (51.3 mg, 0.40 mmol). Purification by flash column chromatography (hexanes/EtOAc = 60:1) provided alkenylated thiophene **4b** as a yellow oil (97 mg, 82% yield, C5:C2 > 20:1). IR (film) 2925, 2855, 1710, 1621, 1268, 1158 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 15.7 Hz, 1H), 7.07 (s, 1H), 6.95 (s, 1H), 6.19 (d, *J* = 15.7 Hz, 1H), 4.18 (t, *J* = 6.6 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.69-1.63 (m, 2H), 1.59-1.57 (m, 2H), 1.45-1.38 (m, 2H), 1.32-1.27 (m, 6H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.90-0.85 (m, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 167.1, 144.4, 139.4, 137.4, 132.1, 123.4, 116.6, 64.4, 31.7, 30.9, 30.41, 30.36, 29.0, 22.7, 19.3, 14.2, 13.8; HRMS (ESI) calcd for $C_{17}H_{27}O_2S$ $[M+H]^+$ 295.1726, found 295.1729.

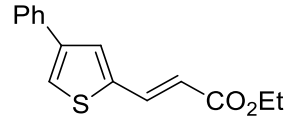
**(*E*)-butyl 3-(4-phenylthiophen-2-yl)acrylate (4c)[14]**




Following the general procedure B, the reaction was set up with 3-phenyl thiophene (128 mg, 0.80 mmol) and *n*-butyl acrylate (51.3 mg, 0.40 mmol). Purification by flash column chromatography (hexanes/EtOAc = 60:1) provided alkenylated thiophene **4c** as a white solid (92 mg, 80% yield, C5:C2 > 25:1). $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 15.7 Hz, 1H),

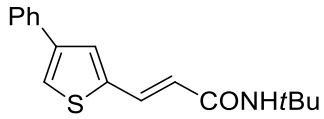
7.58-7.54 (m, 2H), 7.52 (s, 1H), 7.47 (s, 1H), 7.41 (t, $J$ = 7.4 Hz, 2H), 7.32 (t, $J$ = 7.3 Hz, 1H), 6.28 (d, $J$ = 15.7 Hz, 1H), 4.21 (t, $J$ = 6.6 Hz, 2H), 1.72-1.65 (m, 2H), 1.47-1.39 (m, 2H), 0.97 (t, $J$ = 7.3 Hz, 3H).

**(*E*)-ethyl 3-(4-phenylthiophen-2-yl)acrylate (4d)[14]**



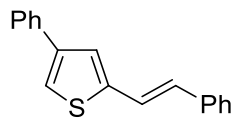

Following the general procedure B, the reaction was set up with 3-phenyl thiophene (128 mg, 0.80 mmol) and ethyl acrylate (40.0 mg, 0.40 mmol). Purification by flash column chromatography (hexanes/EtOAc = 60:1) provided alkenylated thiophene **4d** as a white solid (81 mg, 78% yield, C5 only). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, $J$ = 15.7 Hz, 1H), 7.59-7.55 (m, 2H), 7.52 (s, 1H), 7.47 (s, 1H), 7.41 (t, $J$ = 7.4 Hz, 2H), 7.32 (t, $J$ = 7.3 Hz, 1H), 6.27 (d, $J$ = 15.7 Hz, 1H), 4.26 (q, $J$ = 7.1 Hz, 2H), 1.34 (t, $J$ = 7.1 Hz, 3H).

**(*E*)-*N*-(*tert*-butyl)-3-(4-phenylthiophen-2-yl)acrylamide (4e)**




Following the general procedure B, the reaction was set up with 3-phenyl thiophene (128 mg, 0.80 mmol) and *N*-*tert*-butylacrylamide (50.9 mg, 0.40 mmol). Purification by flash column chromatography (hexanes/EtOAc = 6:1) provided alkenylated thiophene **4e** as a yellow solid (79 mg, 69% yield, C5 only). mp 123-125 °C; IR (film) 3291, 3061, 2965, 2925, 1613, 1546 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, $J$ = 15.2 Hz, 1H), 7.56 (d, $J$ = 7.3 Hz, 2H), 7.45-7.37 (m, 4H), 7.34-7.29 (m, 1H), 6.17 (d, $J$ = 15.2 Hz, 1H), 5.39 (br, 1H), 1.43 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.0, 143.2, 140.9, 135.3, 133.0, 129.0, 128.9, 127.6, 126.4, 121.7, 121.5, 51.7, 29.0; HRMS (ESI) calcd for $C_{17}H_{20}NOS$ $[M+H]^+$ 286.1260, found 286.1262.

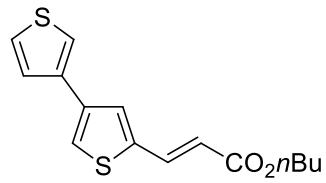
**(*E*)-4-phenyl-2-styrylthiophene (4f)[15]**




Following the general procedure B, the reaction was set up with 3-phenyl thiophene (128 mg, 0.80 mmol) and styrene (41.7 mg, 0.40 mmol). Purification by flash column chromatography

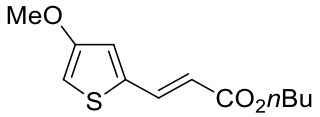
(hexanes/EtOAc = 100:1) provided alkenylated thiophene **4f** as a white solid (54 mg, 51% yield, C5 only). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.61-7.58 (m, 2H), 7.51-7.47 (m, 2H), 7.43-7.27 (m, 8H), 7.26-7.22 (m, 1H), 6.97 (d, *J* = 16.1 Hz, 1H).

**(*E*)-butyl 3-([3,3'-bithiophen]-5-yl)acrylate (4g)**



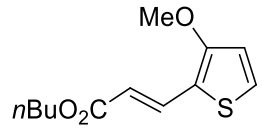

Following the general procedure B, the reaction was set up with 3,3'-bithiophene (133 mg, 0.80 mmol) and *n*-butyl acrylate (51.3 mg, 0.40 mmol) for 48 h. Purification by flash column chromatography (hexanes/EtOAc = 20:1) provided alkenylated thiophene **4g** as a yellow solid (55 mg, 47% yield, C5 only). mp 85-87 °C; IR (film) 3096, 2955, 2865, 1705, 1629, 1173 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 15.7 Hz, 1H), 7.45 (s, 1H), 7.41-7.33 (m, 3H), 7.30 (dd, *J* = 4.7, 1.3 Hz, 1H), 6.27 (d, *J* = 15.7 Hz, 1H), 4.20 (t, *J* = 6.6 Hz, 2H), 1.72-1.65 (m, 2H), 1.48-1.40 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 167.0, 140.1, 138.2, 137.0, 136.4, 129.7, 126.6, 126.1, 122.6, 120.4, 117.6, 64.6, 30.9, 19.3, 13.9; HRMS (ESI) calcd for $C_{15}H_{17}O_2S_2$ $[M+H]^+$ 293.0664, found 293.0658.

**(*E*)-butyl 3-(4-methoxythiophen-2-yl)acrylate (4h)**



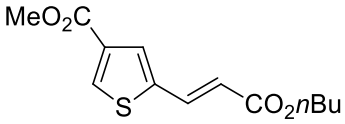

Following the general procedure B, the reaction was set up with 3-methoxy thiophene (80.0 μL, 0.80 mmol) and *n*-butyl acrylate (51.3 mg, 0.40 mmol). Purification by flash column chromatography (hexanes/EtOAc = 60:1 (**4h**) and 50:1 (**4h′**)) provided **4h** as a colorless oil (39 mg, 41% yield) and **4h′** as a colorless oil (7 mg, 7%). IR (film) 3116, 2957, 2872, 1705, 1550, 1162 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 15.7 Hz, 1H), 6.90 (d, *J* = 1.4 Hz, 1H), 6.31 (d, *J* = 1.4 Hz, 1H), 6.21 (d, *J* = 15.7 Hz, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 3.80 (s, 3H), 1.70-1.65 (m, 2H), 1.46-1.40 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.8, 158.6, 137.8, 137.0, 121.8, 117.1, 100.1, 64.5, 57.4, 30.8, 19.3, 13.8; HRMS (ESI) calcd for $C_{12}H_{17}O_3S$ $[M+H]^+$ 241.0893, found 241.0894.

**(*E*)-butyl 3-(3-methoxythiophen-2-yl)acrylate (4h′)[13]**



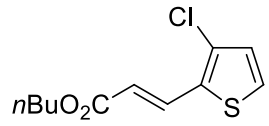

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 15.7 Hz, 1H), 7.28-7.26 (m, 1H), 6.83 (d, *J* = 5.5 Hz, 1H), 6.15 (d, *J* = 15.8 Hz, 1H), 4.17 (t, *J* = 6.7 Hz, 2H), 3.92 (s, 3H), 1.69-1.65 (m, 2H), 1.45-1.40 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

**(*E*)-methyl 5-(3-butoxy-3-oxoprop-1-en-1-yl)thiophene-3-carboxylate (4i)[13]**



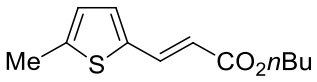

Following the general procedure B, the reaction was set up with methyl thiophene-3-carboxylate (97.0 μL, 0.80 mmol) and *n*-butyl acrylate (51.3 mg, 0.40 mmol). Purification by flash column chromatography (hexanes/EtOAc = 60:1) provided alkenylated thiophene **4i** as a white solid (71 mg, 66% yield, C5:C2 = 3:1). IR (film) 3107, 2956, 2872, 1714, 1245, 1165 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.72 (d, *J* = 15.7 Hz, 1H), 7.63 (s, 1H), 6.26 (d, *J* = 15.8 Hz, 1H), 4.20 (t, *J* = 6.6 Hz, 2H), 3.87 (s, 3H), 1.70-1.65 (m, 2H), 1.46-1.41 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

**(*E*)-butyl 3-(3-chlorothiophen-2-yl)acrylate (4j)[13]**



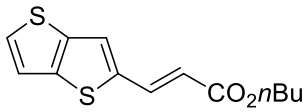

Following the general procedure B, the reaction was set up with 3-chlorothiophene (74.0 μL, 0.80 mmol) and *n*-butyl acrylate (51.3 mg, 0.40 mmol). Purification by flash column chromatography (hexanes/EtOAc = 60:1) provided alkenylated thiophene **4j** as a colorless oil (81 mg, 83% yield, C5:C2 = 1:3). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 15.8, 0.7 Hz, 1H), 7.32 (d, *J* = 5.3 Hz, 1H), 6.96 (d, *J* = 5.4 Hz, 1H), 6.27 (d, *J* = 15.8 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.71-1.66 (m, 2H), 1.47-1.40 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

**(*E*)-butyl 3-(5-methylthiophen-2-yl)acrylate (4k)[16]**




Following the general procedure B, the reaction was set up with 2-methyl thiophene (78.5 mg, 0.80 mmol) and *n*-butyl acrylate (58.0 μL, 0.40 mmol). Purification by flash column chromatography (hexanes/EtOAc = 20:1) provided alkenylated thiophene **4k** as a red liquid (82 mg, 91% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 15.6 Hz, 1H), 7.04 (d, *J* = 3.6 Hz, 1H), 6.70 (d, *J* = 3.6 Hz, 1H), 6.10 (d, *J* = 15.6 Hz, 1H), 4.18 (t, *J* = 6.6 Hz, 2H), 2.49 (s, 3H), 1.75-1.56 (m, 2H), 1.43 (q, *J* = 7.5 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

**(*E*)-butyl 3-(thieno[3,2-*b*]thiophen-2-yl)acrylate (4l)[17]**




Following the general procedure B, the reaction was set up with thieno[3,2-*b*]thiophene (112 mg, 0.80 mmol) and *n*-butyl acrylate (58.0 μL, 0.40 mmol). Purification by flash column chromatography (hexanes/EtOAc = 20:1) provided alkenylated product **4l** as a yellow liquid (79 mg, 74% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 15.6 Hz, 1H), 7.48 (d, *J* = 5.2 Hz, 1H), 7.40 (s, 1H), 7.23 (d, *J* = 5.2 Hz, 1H), 6.23 (d, *J* = 15.6 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.74-1.65 (m, 2H), 1.44 (q, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

# VI. Mechanistic Studies

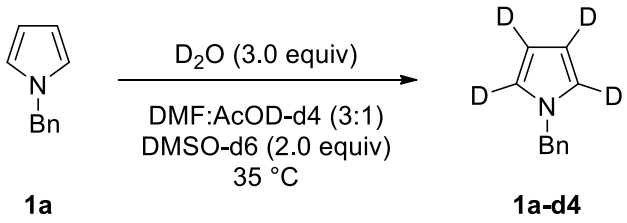
## VI.A. Deuterium Labeling Studies

### a) Deuterium exchange experiments of *N*-benzyl pyrrole

**Table S5.** Deuteration of *N*-benzyl pyrrole (**1a**)

| entry | conditions | time | deuterated ratio (%) | |
|---|---|---|---|---|
| | | | C2 | C3 |
| 1 | DMSO-d6, DMF, AcOH-d4, $D_2O$ | 20 min | 14 | 0 |
| | | 40 min | 27 | 0 |
| | | 1 h | 42 | 0 |
| | | 2 h | 59 | 15 |
| | | 3 h | 61 | 17 |
| 2 | $Pd(OAc)_2$, DMSO-d6, DMF, AcOD-d4, $D_2O$, $O_2$ balloon | 20 min | 62 | 29 |
| | | 40 min | 63 | 32 |
| | | 1 h | 67 | 33 |
| | | 2 h | 76 | 43 |
| | | 3 h | 82 | 52 |
| 3 | $Pd(OAc)_2$, **PzNPy1**, DMSO-d6, DMF, AcOD-d4, $D_2O$, $O_2$ balloon | 20 min | 91 | 51 |
| | | 40 min | 91 | 60 |
| | | 1 h | 95 | 75 |
| | | 2 h | 96 | 91 |
| | | 3 h | 98 | 91 |
| 4 | $Pd(OAc)_2$, DMSO-d6, $D_2O$, $O_2$ balloon | 20 min | 100 | 84 |
| | | 40 min | 100 | 85 |
| | | 1 h | 100 | 87 |
| | | 2 h | 100 | 89 |
| | | 3 h | 100 | 89 |

Table S5, entry 1)




**1a** **1a-d4**

**1a** (58.9 mg, 0.375 mmol) was added to a solution of DMSO-d6 (35.4 μL, 0.50 mmol), DMF (0.375 mL), AcOD-d4 (0.125 mL), and $D_2O$ (13.5 μL) in each of five 8 mL-glass vials. Reaction mixtures were stirred in a preheated reaction block at 35 °C. At each desired time point, a reaction mixture was cooled to 25 °C, and crude yields were obtained as $^1H$ NMR yields using mesitylene (52.2 μL, 0.375 mmol) as an internal standard.

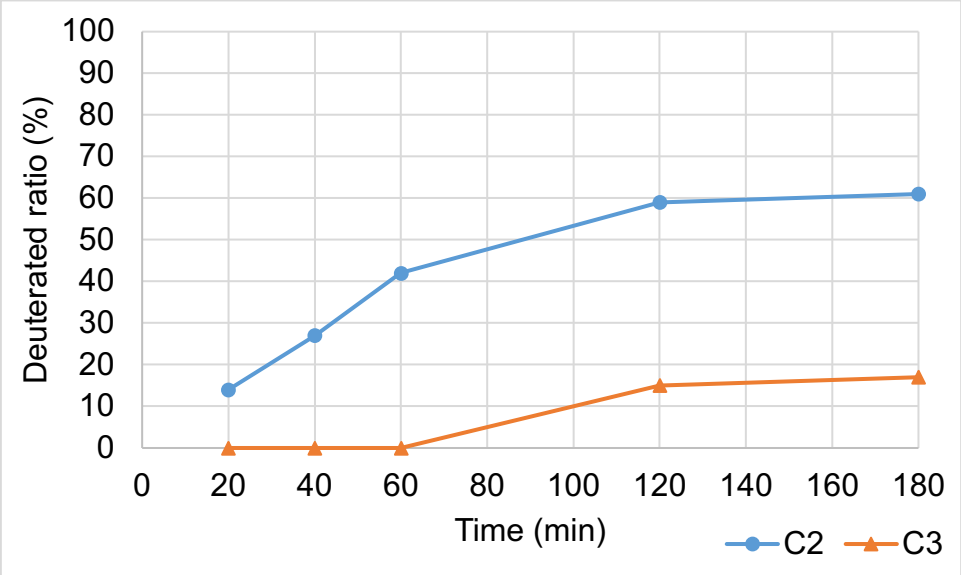
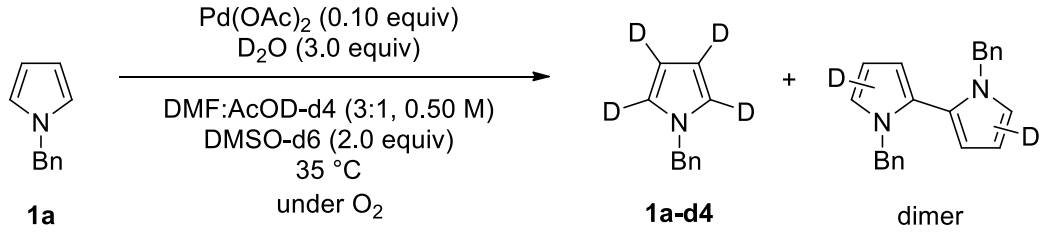



**Figure S2.** Deuteration of **1a** without the catalyst and ligand.

Table S5, entry 2)




$Pd(OAc)_2$ (5.6 mg, 0.025 mmol) was added to a solution of **1a** (58.9 mg, 0.375 mmol), DMSO-d6 (35.4 μL, 0.50 mmol), DMF (0.375 mL), AcOD-d4 (0.125 mL), and $D_2O$ (13.5 μL) in each of five 8 mL-glass vials. Then, vials were evacuated and filled with oxygen for five times. Reaction mixtures were stirred in a preheated reaction block at 35 °C under 1 atm of oxygen (balloon). At each desired time point, a reaction mixture was cooled to 25 °C, and crude yields were obtained as $^1$H NMR yields using mesitylene (52.2 μL, 0.375 mmol) as an internal standard. In the absence of the ligand, dimerization of **1a** occurred along with deuteration of both the monomer and the dimer. The ratio between the monomer and dimer was calculated based on undeuterated benzyl peak (2H) in $^1$H NMR spectra.

**Table S6.** The formation of the pyrrole dimer

| | 20 min | 40 min | 1 h | 2 h | 3 h |
|---|---|---|---|---|---|
| **1a** : dimer | 78% : 22% | 71% : 29% | 60% : 40% | 60% : 40% | 54% : 46% |

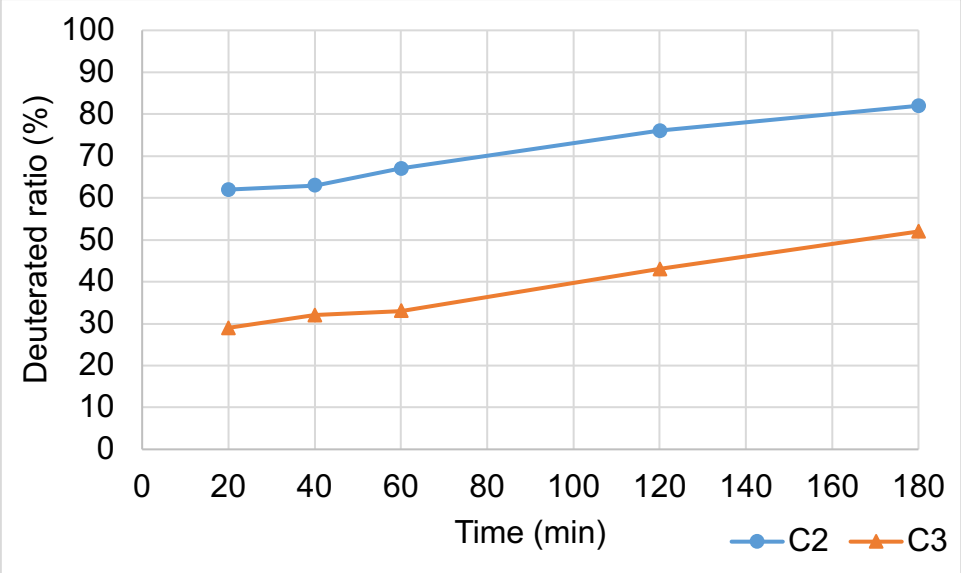
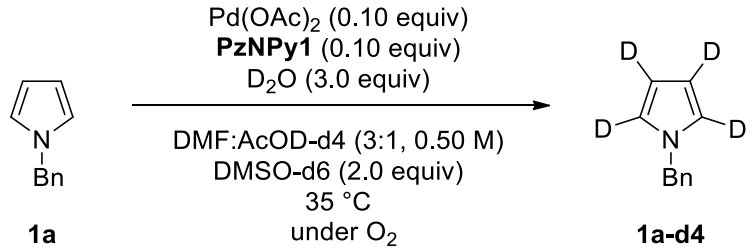



**Figure S3.** Deuteration of **1a** without the ligand.

Table S5, entry 3)




**1a** **1a-d4**

$Pd(OAc)_2$ (5.6 mg, 0.025 mmol) and **PzNPy1** (8.0 mg, 0.025 mmol) were added to a solution of **1a** (58.9 mg, 0.375 mmol), DMSO-d6 (35.4 μL, 0.50 mmol), DMF (0.375 mL), AcOD-d4 (0.125 mL), and $D_2O$ (13.5 μL) in each of five 8 mL-glass vials. Then, vials were evacuated and filled with oxygen for five times. Reaction mixtures were stirred in a preheated reaction block at 35 °C under 1 atm of oxygen (balloon). At each desired time point, a reaction mixture was cooled to 25 °C, and crude yields were obtained as $^1$H NMR yields using mesitylene (52.2 μL, 0.375 mmol) as an internal standard.

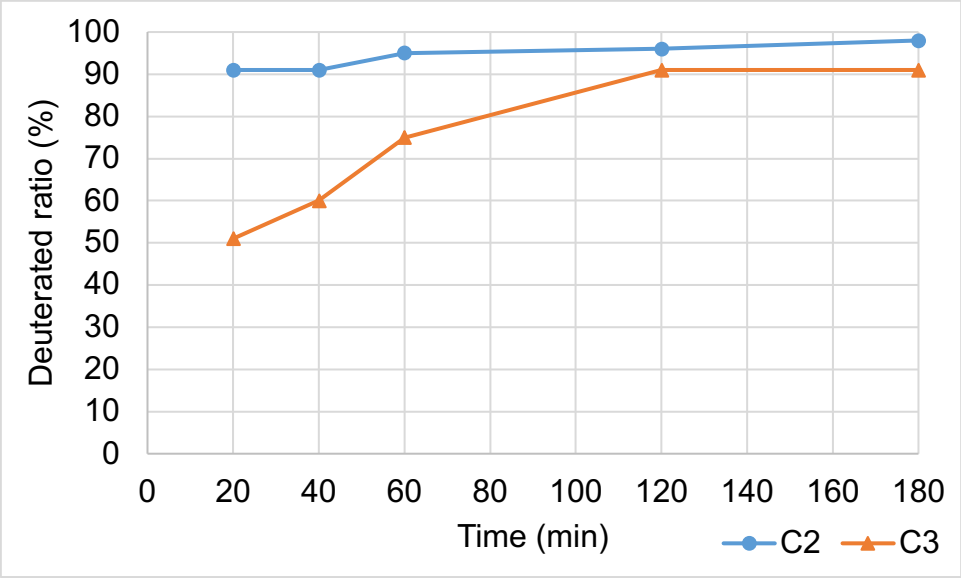
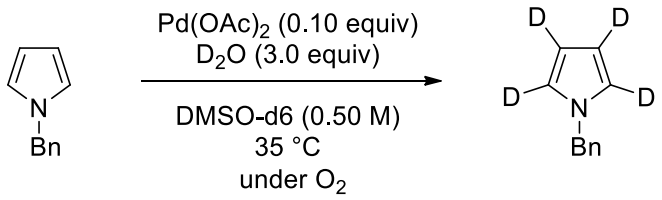



**Figure S4.** Deuteration of **1a** under the standard conditions.

Table S5, entry 4)




**1a** **1a-d4**

$Pd(OAc)_2$ (5.6 mg, 0.025 mmol) was added to a solution of **1a** (58.9 mg, 0.375 mmol), DMSO-d6 (0.50 mL, 0.50 M), and $D_2O$ (13.5 μL) in each of five 8 mL-glass vials. Then, vials were evacuated and filled with oxygen for five times. Reaction mixtures were stirred in a preheated reaction block at 35 °C under 1 atm of oxygen (balloon). At each desired time point, a reaction mixture was cooled to 25 °C, and crude yields were obtained as $^1$H NMR yields using mesitylene (52.2 μL, 0.375 mmol) as an internal standard.

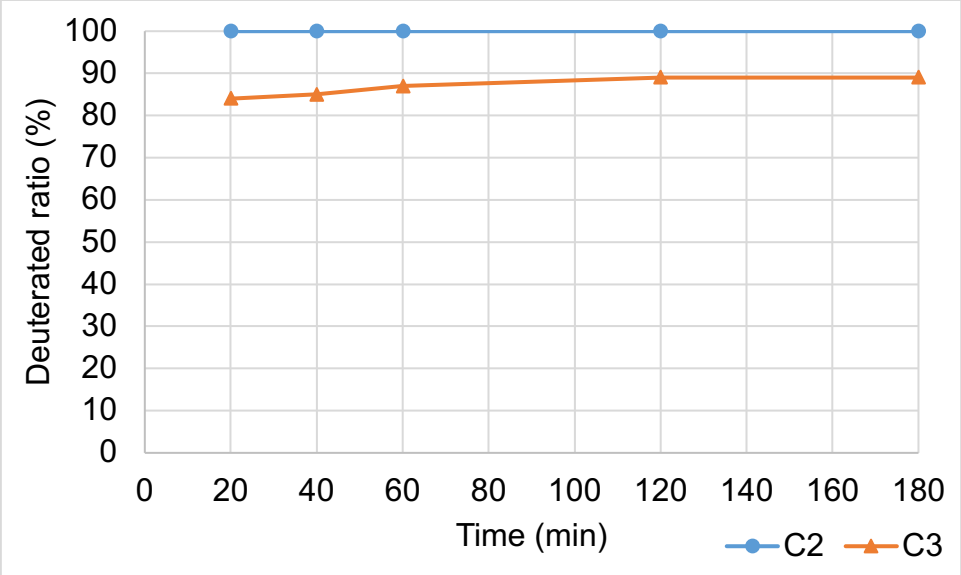


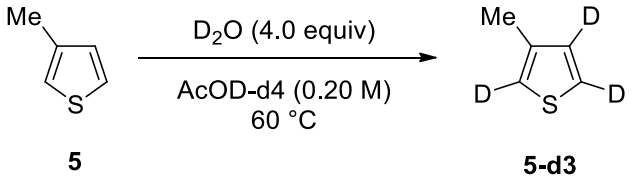

**Figure S5.** Deuteration of **1a** under the DMSO-only system without the ligand.

## b) Deuterium exchange experiments of 3-methyl thiophene

**Table S7.** Deuteration of 3-methyl thiophene (**5**)

| entry | conditions | time | deuterated ratio (%) | | |
|---|---|---|---|---|---|
| | | | C2 | C4 | C5 |
| 1 | AcOD-d4, $D_2O$ | 20 min | 0 | 0 | 0 |
| | | 40 min | 0 | 0 | 0 |
| | | 1 h | 0 | 0 | 0 |
| | | 2 h | 0 | 0 | 0 |
| | | 3 h | 0 | 0 | 0 |
| 2 | $Pd(OAc)_2$, AcOD-d4, $D_2O$, $O_2$ balloon | 20 min | 53 | 24 | 40 |
| | | 40 min | 60 | 24 | 40 |
| | | 1 h | 69 | 27 | 44 |
| | | 2 h | 81 | 26 | 48 |
| | | 3 h | 86 | 25 | 51 |
| 3 | $Pd(OAc)_2$, **PzNPy1**, AcOD-d4, $D_2O$, $O_2$ balloon | 20 min | 88 | 20 | 48 |
| | | 40 min | 93 | 21 | 64 |
| | | 1 h | 94 | 21 | 68 |
| | | 2 h | 94 | 23 | 81 |
| | | 3 h | 94 | 27 | 87 |

Table S7, entry 1)




**5** **5-d3**

**5** (39.3 mg, 0.40 mmol) was added to a solution of AcOD-d4 (1.0 mL, 0.20 M) and $D_2O$ (14.4 µL, 0.80 mmol) in each of five 8 mL-glass vials. Reaction mixtures were stirred in a preheated reaction block at 60 °C. At each desired time point, a reaction mixture was cooled to 25 °C, and crude yields were obtained as $^1H$ NMR yields using dibromomethane (28.1 µL, 0.40 mmol) as an internal standard. Deuteration of 3-methyl thiophene did not occur in the absence of the catalyst and ligand.

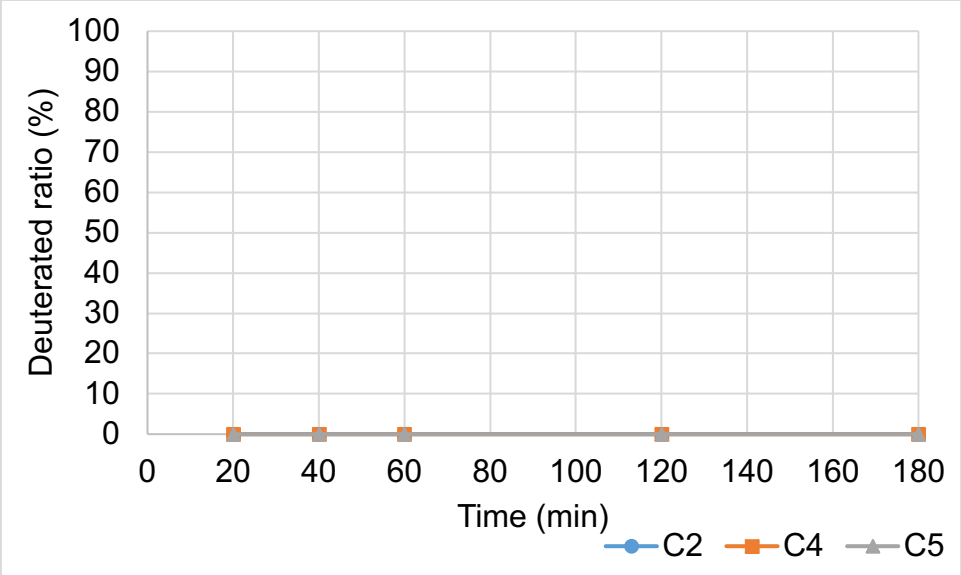
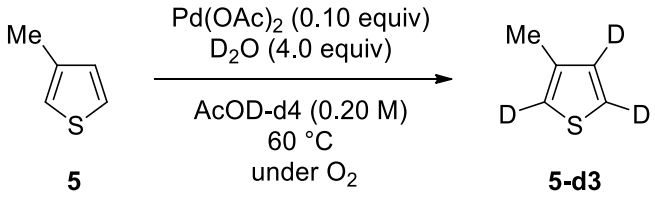



**Figure S6.** Deuteration of **5** without the catalyst and ligand.

Table S7, entry 2)




$Pd(OAc)_2$ (4.5 mg, 0.020 mmol) was added to a solution of **5** (39.3 mg, 0.40 mmol), AcOD-d4 (1.00 mL, 0.20 M), and $D_2O$ (14.4 μL, 0.80 mmol) in each of five 8 mL-glass vials. Then, vials were evacuated and filled with oxygen for five times. Reaction mixtures were stirred in a preheated reaction block at 60 °C under 1 atm of oxygen (balloon). At each desired time point, a reaction mixture was cooled to 25 °C, and crude yields were obtained as $^1H$ NMR yields using dibromomethane (28.1 μL, 0.40 mmol) as an internal standard.

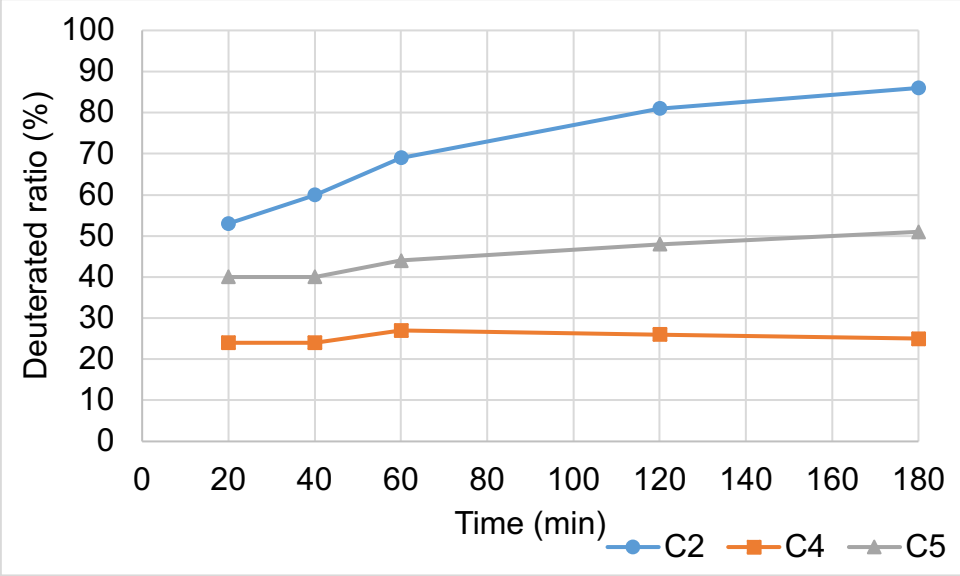
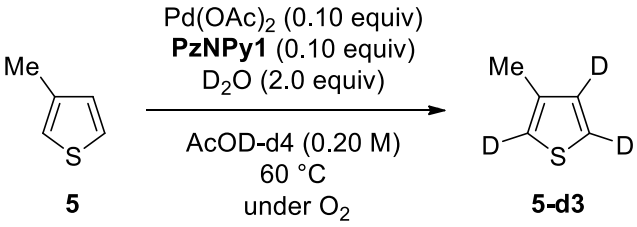



**Figure S7.** Deuteration of **5** without the ligand.

Table S7, entry 3)




$Pd(OAc)_2$ (9.0 mg, 0.04 mmol) and **PzNPy1** (12.9 mg, 0.04 mmol) were added to a solution of **5** (78.5 mg, 0.80 mmol), AcOD-d4 (2.0 mL, 0.20 M), and $D_2O$ (14.4 μL, 0.80 mmol) in each of five 8 mL-glass vials. Then, vials were evacuated and filled with oxygen for five times. Reaction mixtures were stirred in a preheated reaction block at 60 °C under 1 atm of oxygen (balloon). At each desired time point, a reaction mixture was cooled to 25 °C, and crude yields were obtained as $^1H$ NMR yields using trichloroethylene (72.0 μL, 0.80 mmol) as an internal standard.

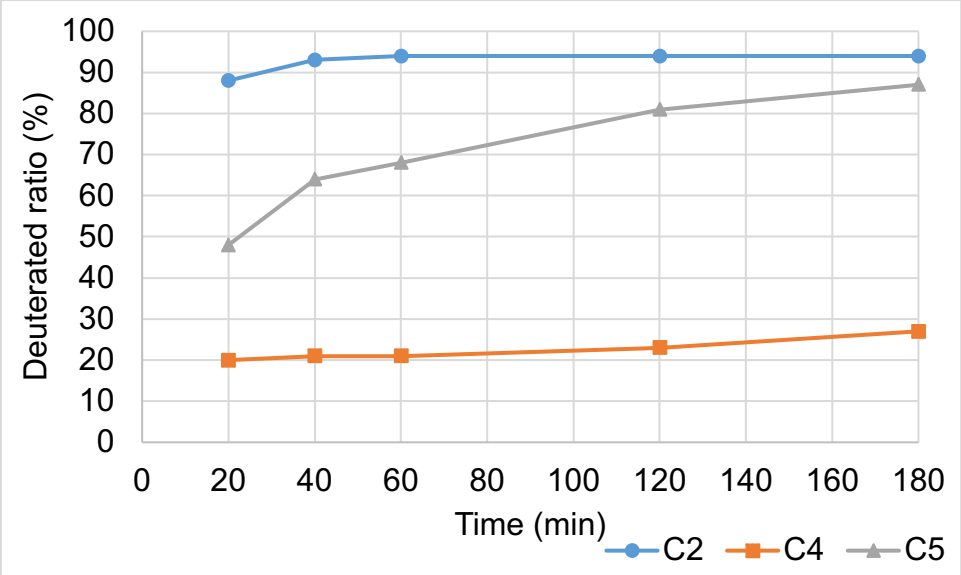



**Figure S8.** Deuterated of **5** under the standard conditions.

**VI.B. Ligand Competition Studies**

Increasing quantities of pyridine (0.5, 1.0, 2.0, 4.0 equiv to each vial) and $Pd(OAc)_2$ (44.9 mg, 0.20 mmol) were added to solutions of **PzPy1** and **PzNPy1** ligand (0.20 mmol) in $CDCl_3$ (4.0 mL, 0.50 M). The solution was stirred with a magnetic bar at 25 °C for 1 hour prior to data acquisition. The changes were monitored by $^1H$ NMR spectroscopy. Intermediate complexes were identified by comparing a given spectrum against free pyridine, $Pd(py)_2(OAc)_2$, and free **Pz(N)Py** ligand standards.

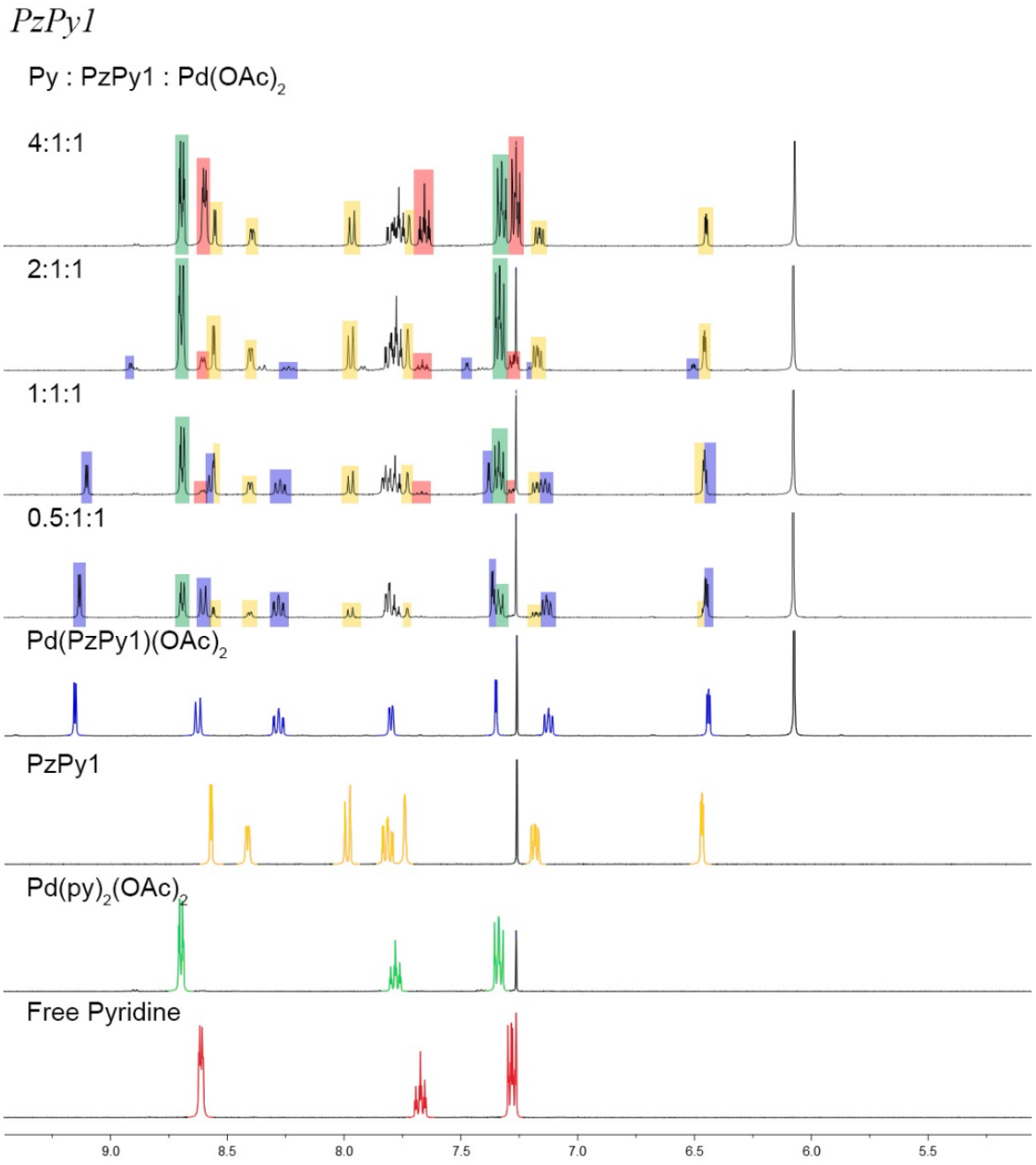



**Figure S9.** Titration of pyridine into a $CDCl_3$ solution containing $Pd(OAc)_2$, **PzPy1**, and 1,3,5-trimethoxybenzene (33.6 mg, 0.20 mmol) as an internal standard. Increasing concentration of pyridine resulted in the dissociation of **PzPy1** with dominant formation of $Pd(pyridine)_2(OAc)_2$. After four equivalents of pyridine were added, nearly all the **PzPy1** were dissociated and accounted for as $Pd(pyridine)_2(OAc)_2$.

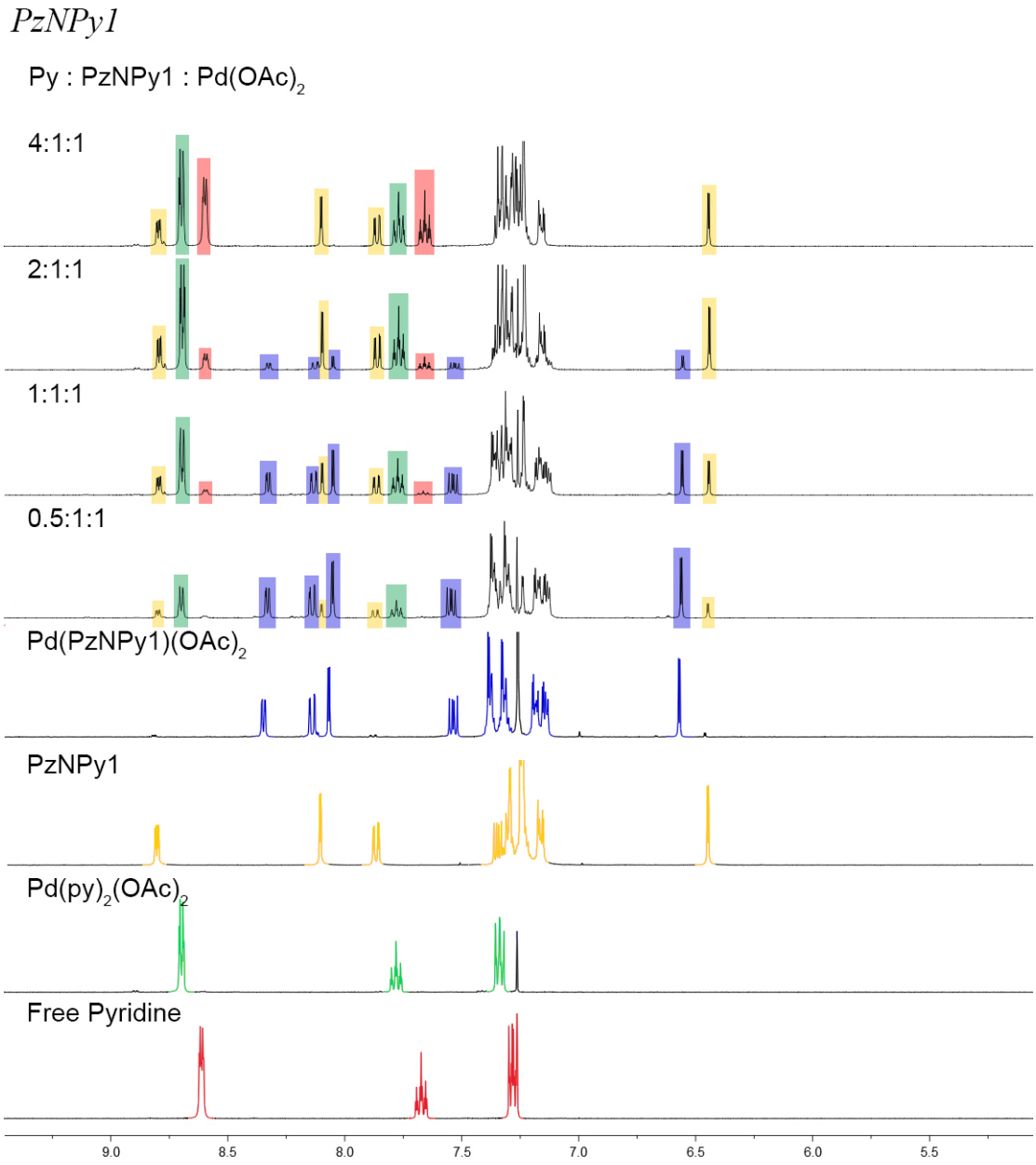



**Figure S10.** Titration of pyridine into a $CDCl_3$ solution containing $Pd(OAc)_2$ and **PzNPy1**. Increasing concentration of pyridine resulted in the dissociation of **PzNPy1** with dominant formation of $Pd(pyridine)_2(OAc)_2$. After four equivalents of pyridine were added, nearly all the **PzNPy1** were dissociated and accounted for as $Pd(pyridine)_2(OAc)_2$.

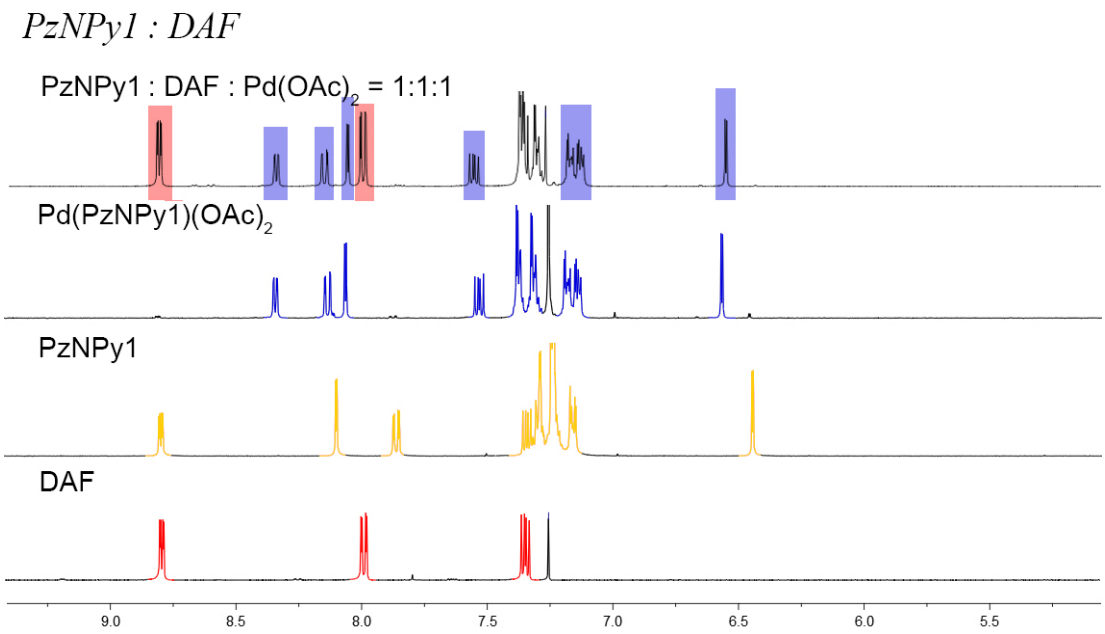



**Figure S11.** The competition test between **PzNPy1** and DAF. After $Pd(OAc)_2$ (44.9 mg, 0.20 mmol) was added to a solution of **PzNPy1** (64.3 mg, 0.20 mmol), DAF (36.4 mg, 0.20 mmol), and $CDCl_3$ (4.0 mL, 0.50 M), the solution was stirred for 1 h at 25 °C. The formation of complex **2** was strongly preferred to the formation of the DAF-ligated complex. Dissociated **PzNPy1** was observed as 2% and ligated DAF species were found in a trace amount.

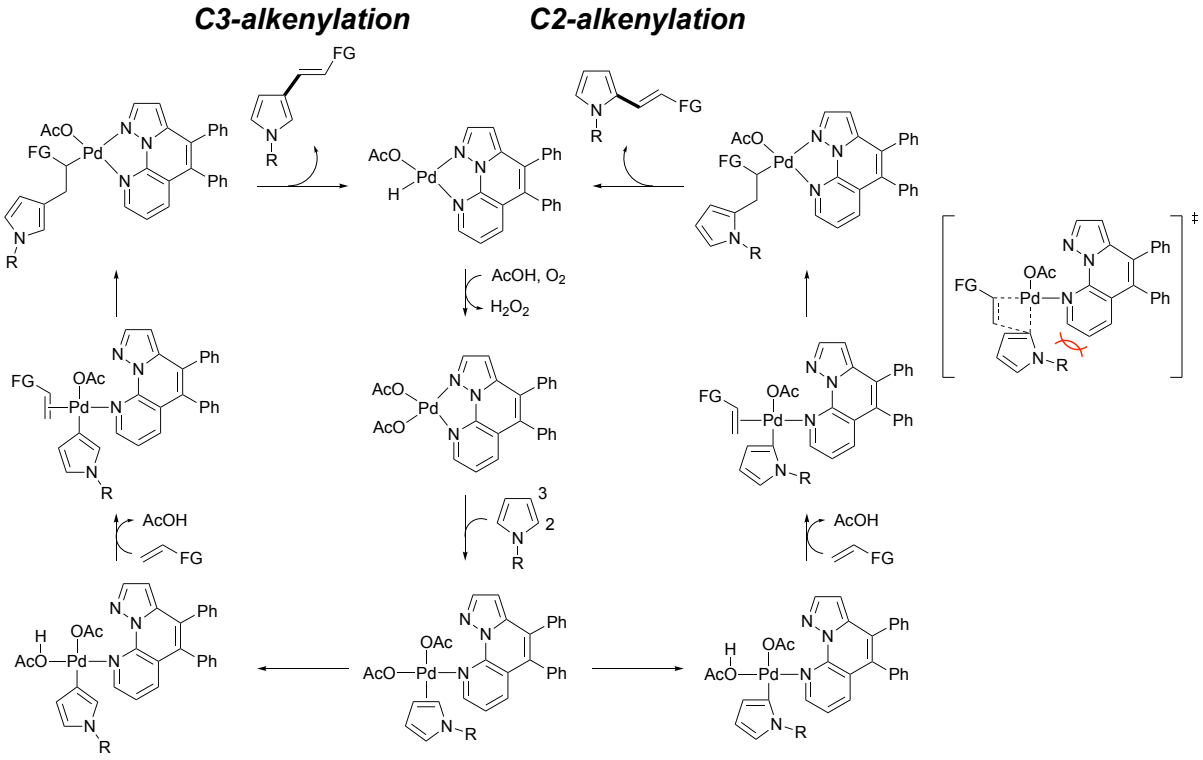



**Figure S12.** Proposed mechanism

## VII. References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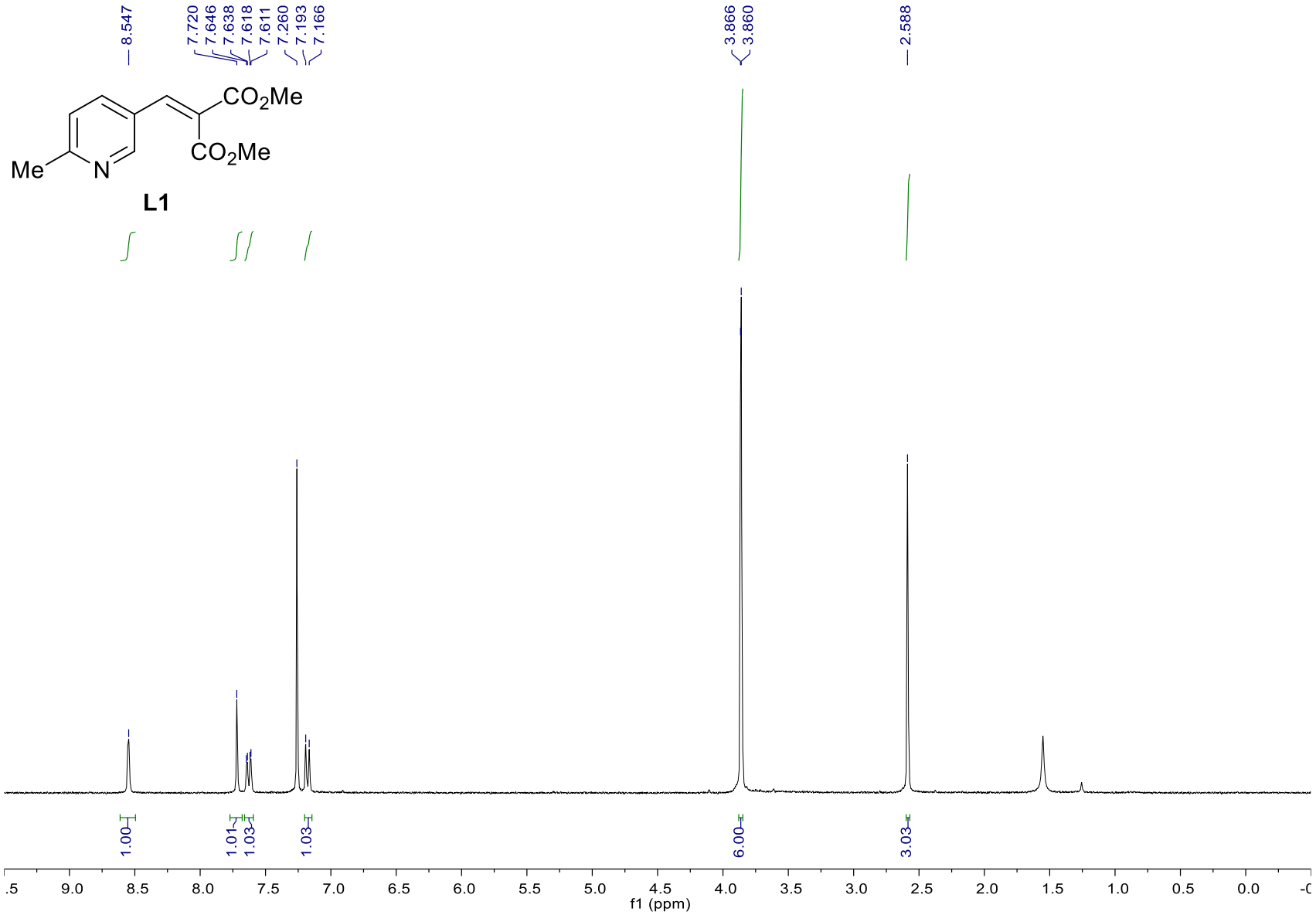
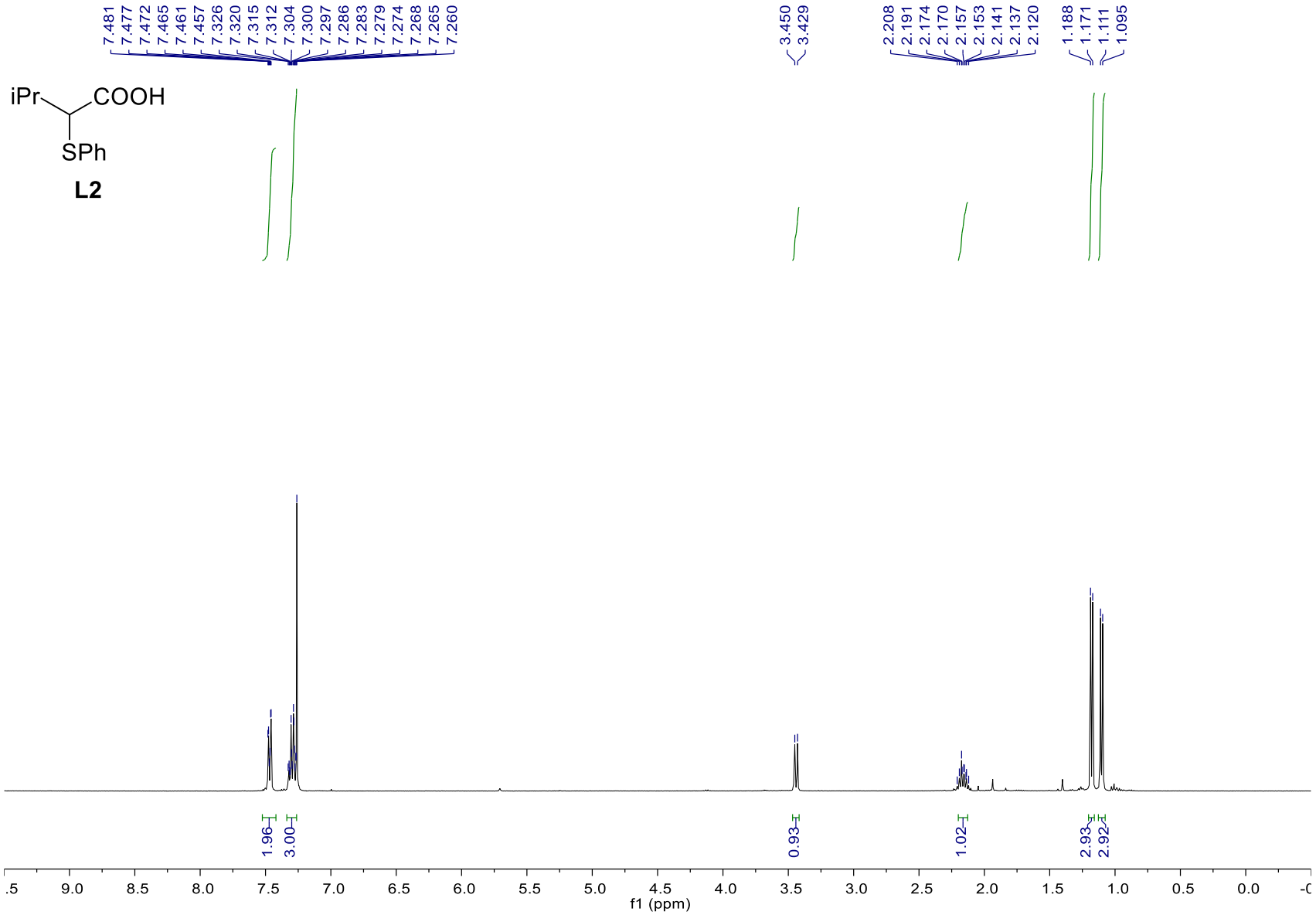
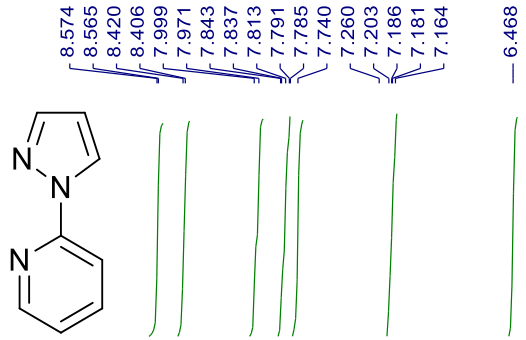
## VIII. $^{1}H$ and $^{13}C$ NMR Spectra



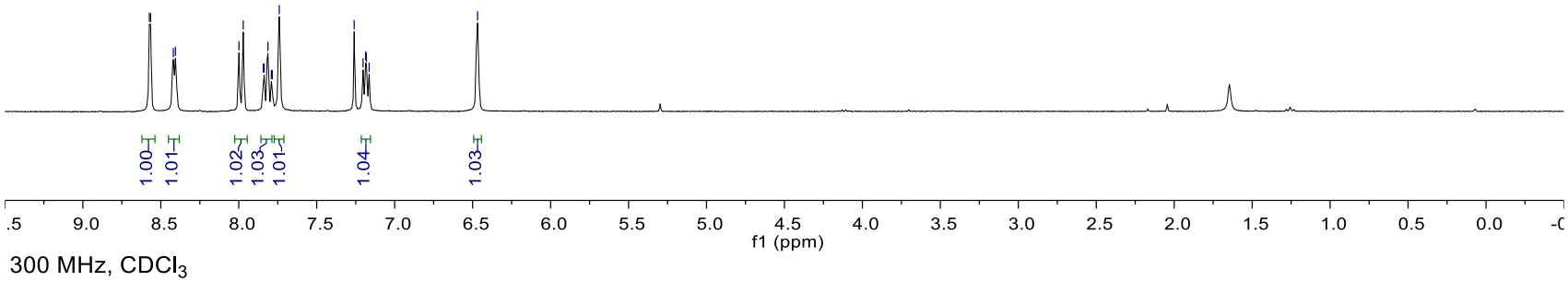

$CDCl_3$, 300 MHz



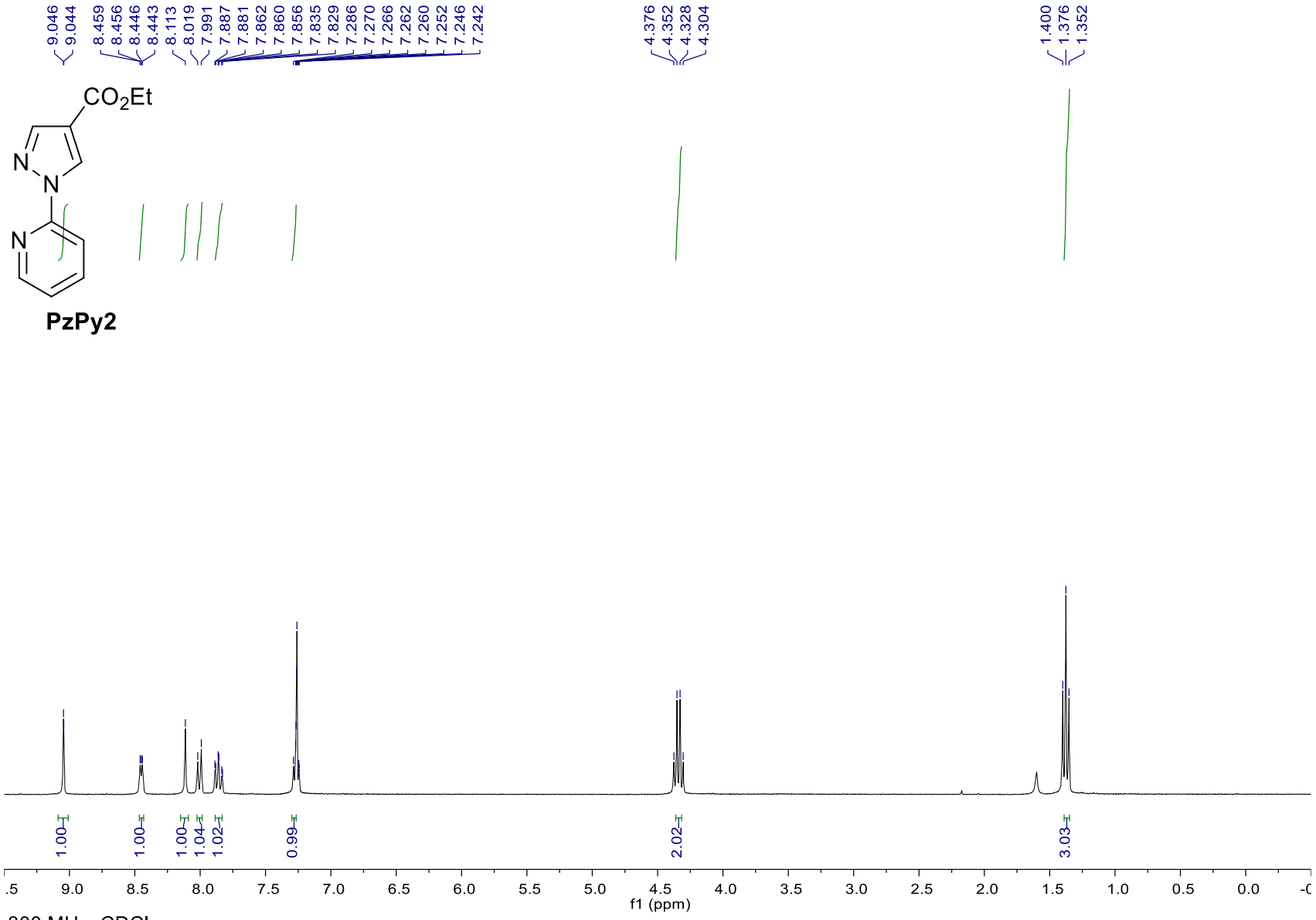

$CDCl_3$, 400 MHz




**PzPy1**




300 MHz, $CDCl_3$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7.887
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7.860
7.856
7.835
7.829
7.286
7.270
7.266
7.262
7.260
7.252
7.246
7.242
4.376
4.352
4.328
4.304
1.400
1.376
1.352
CO2Et
N
N
N
PzPy2
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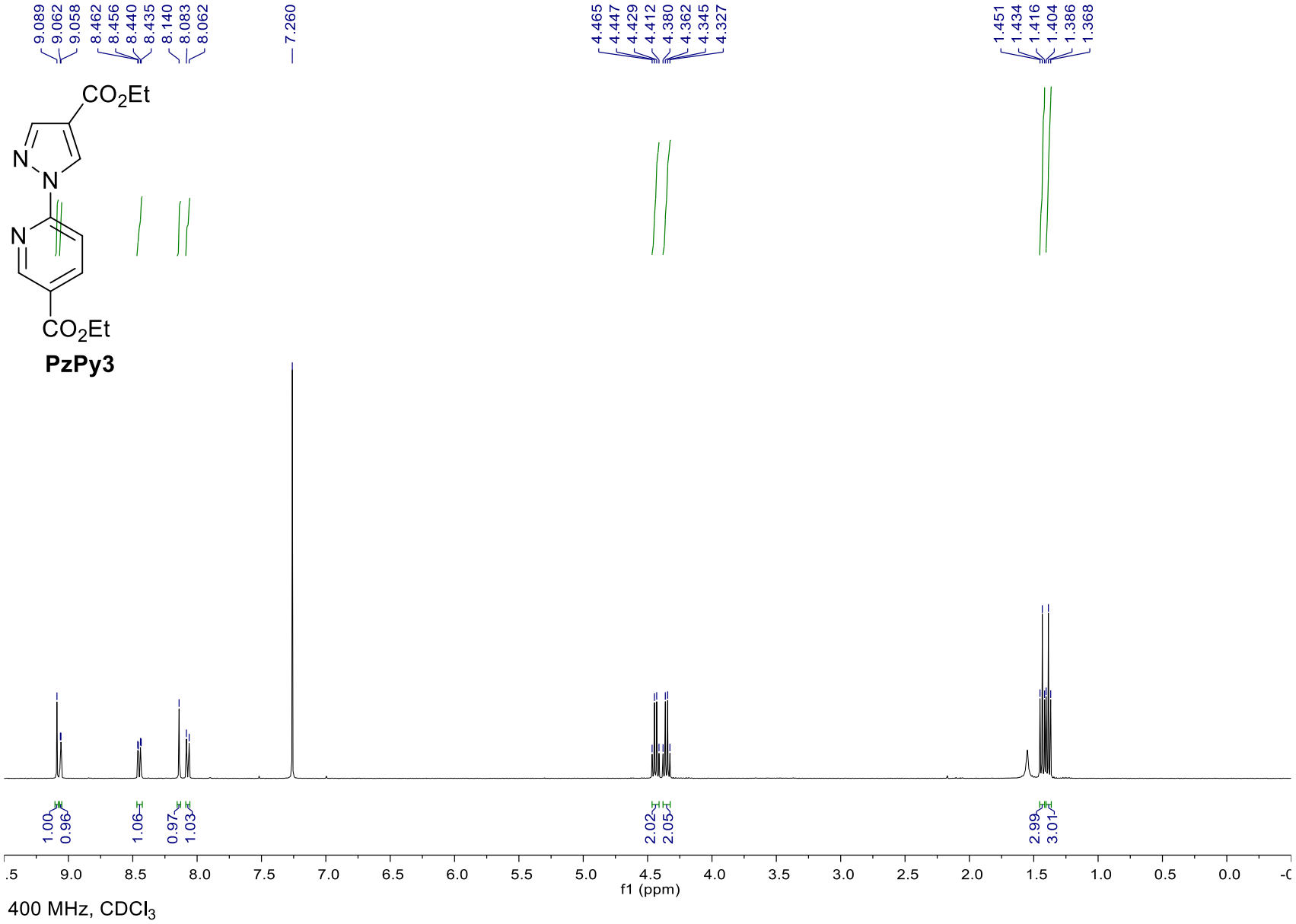
1.00
1.00
1.04
1.02
0.99
2.02
3.03
f1 (ppm)
300 MHz, CDCl3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CO2Et
PzPy3
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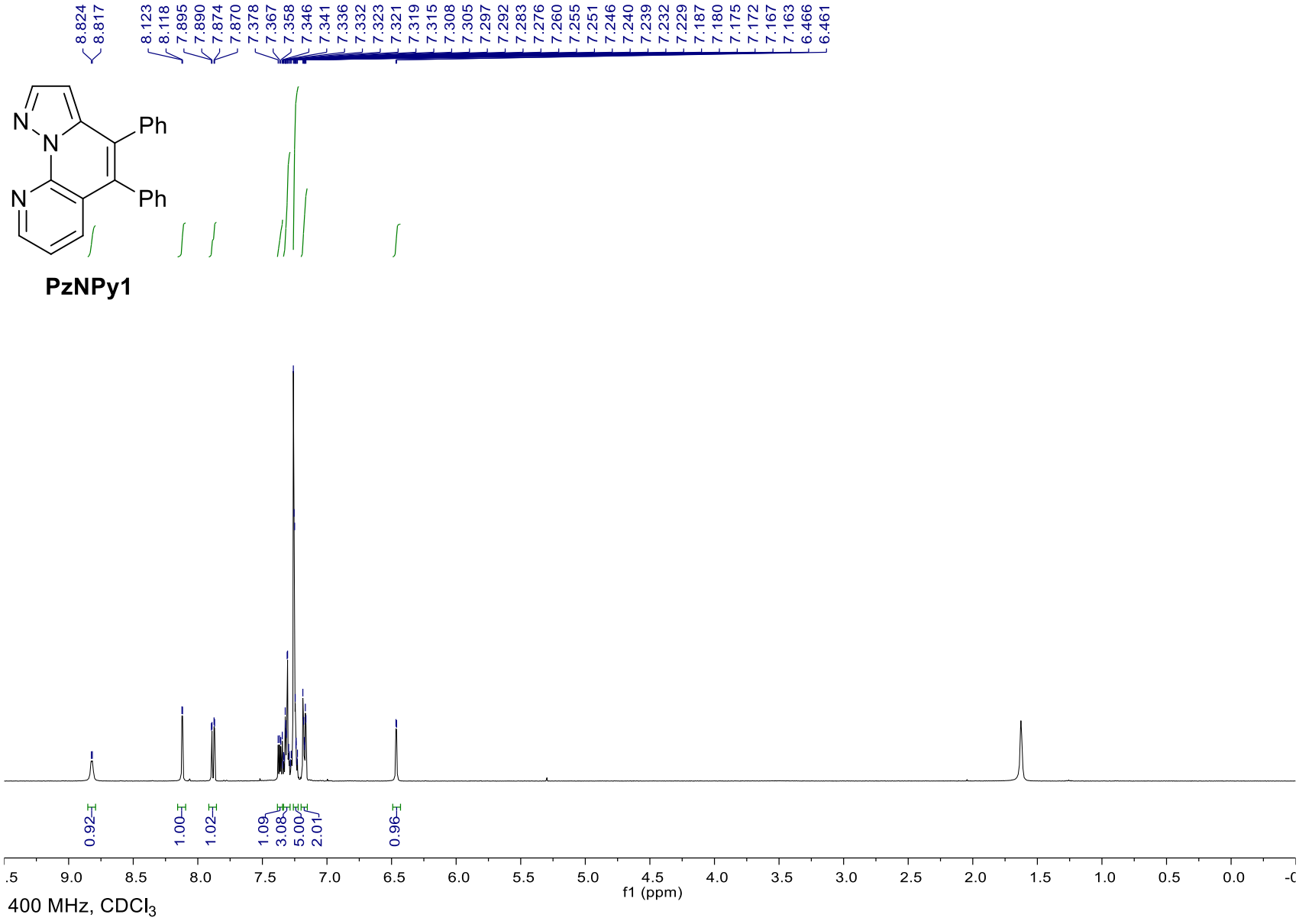
2.99
3.01
f1 (ppm)
400 MHz, CDCl3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PzNPy1
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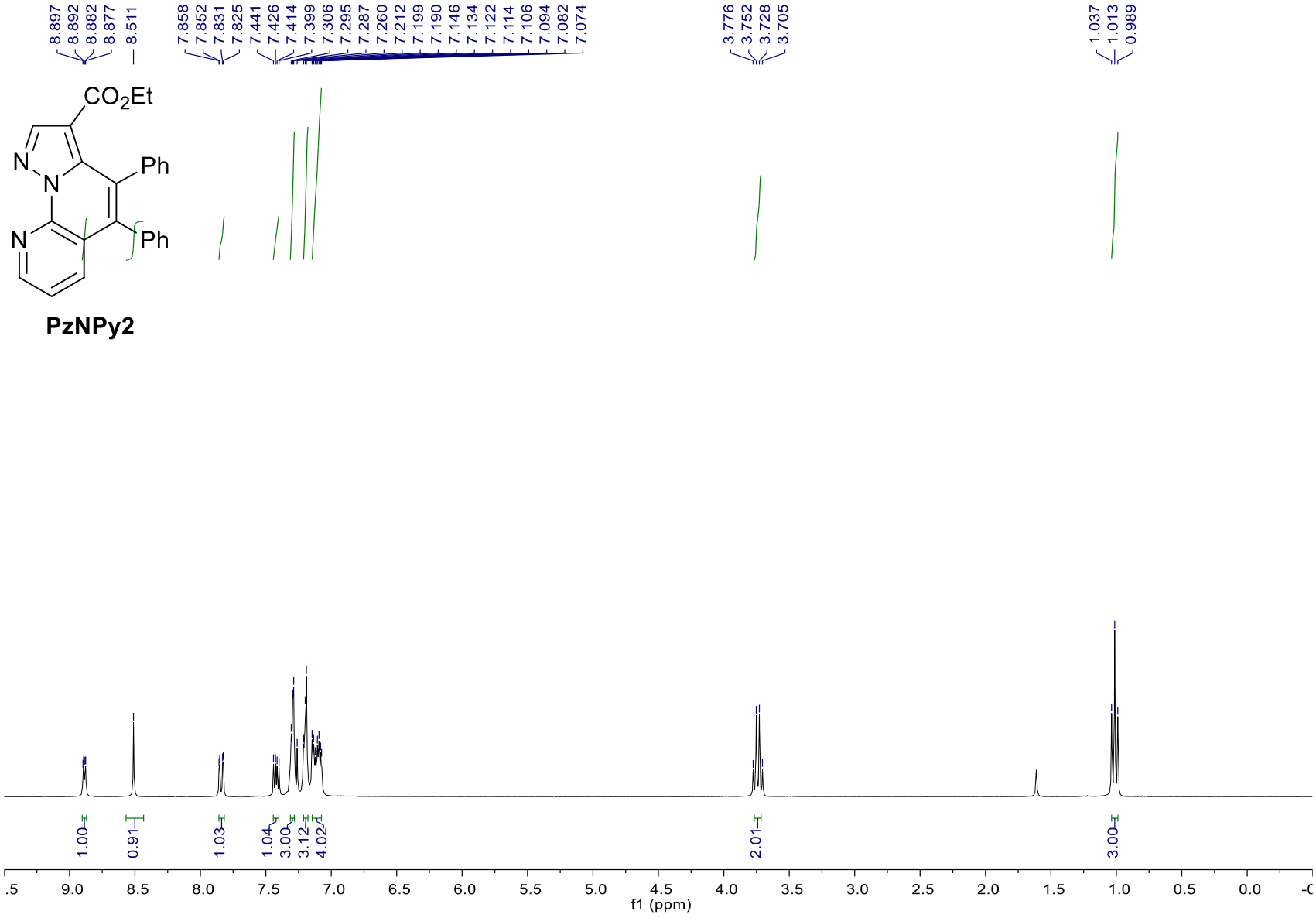
f1 (ppm)
400 MHz, CDCl3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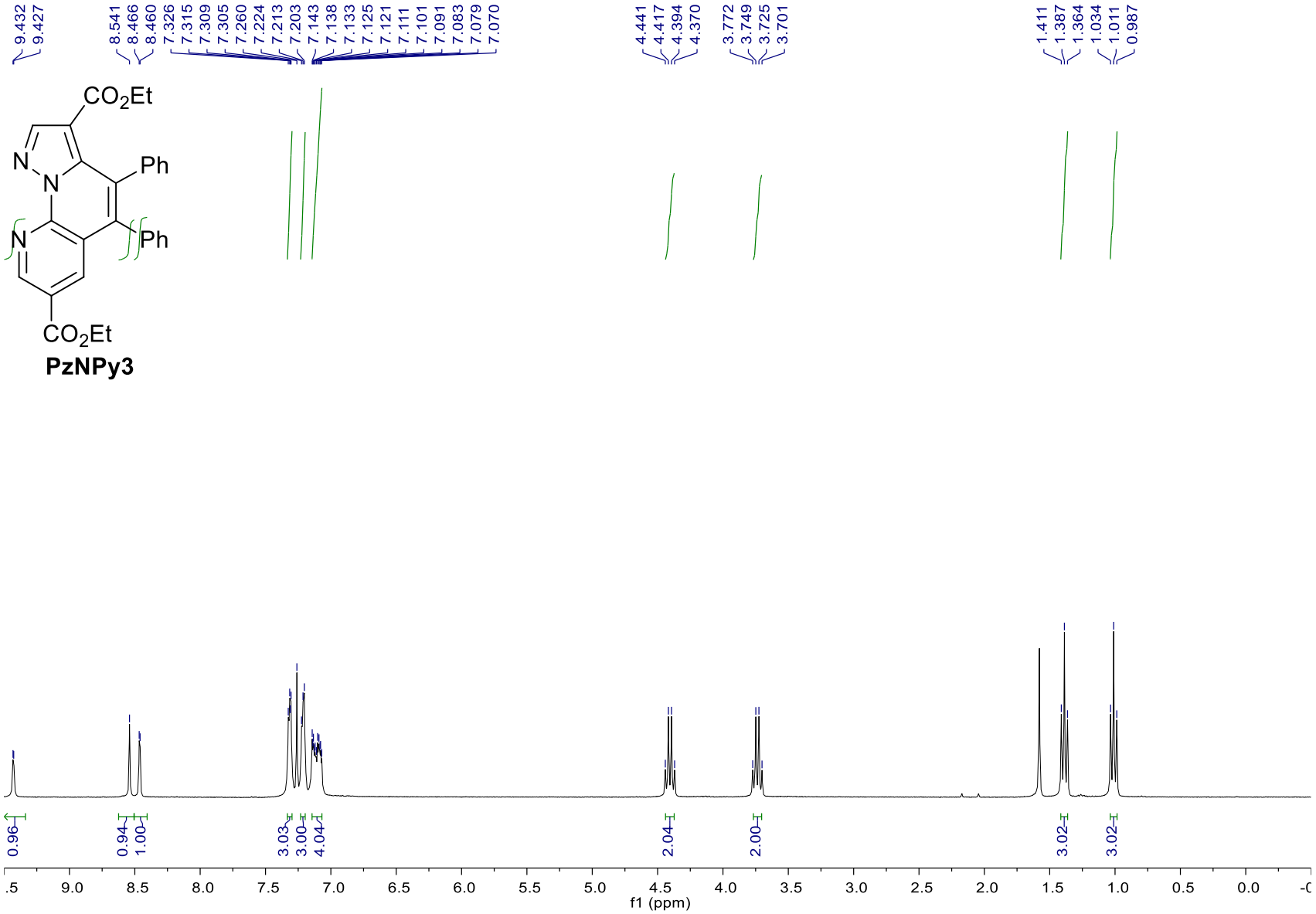
f1 (ppm)
400 MHz, CDCl3




**PzNPy3**

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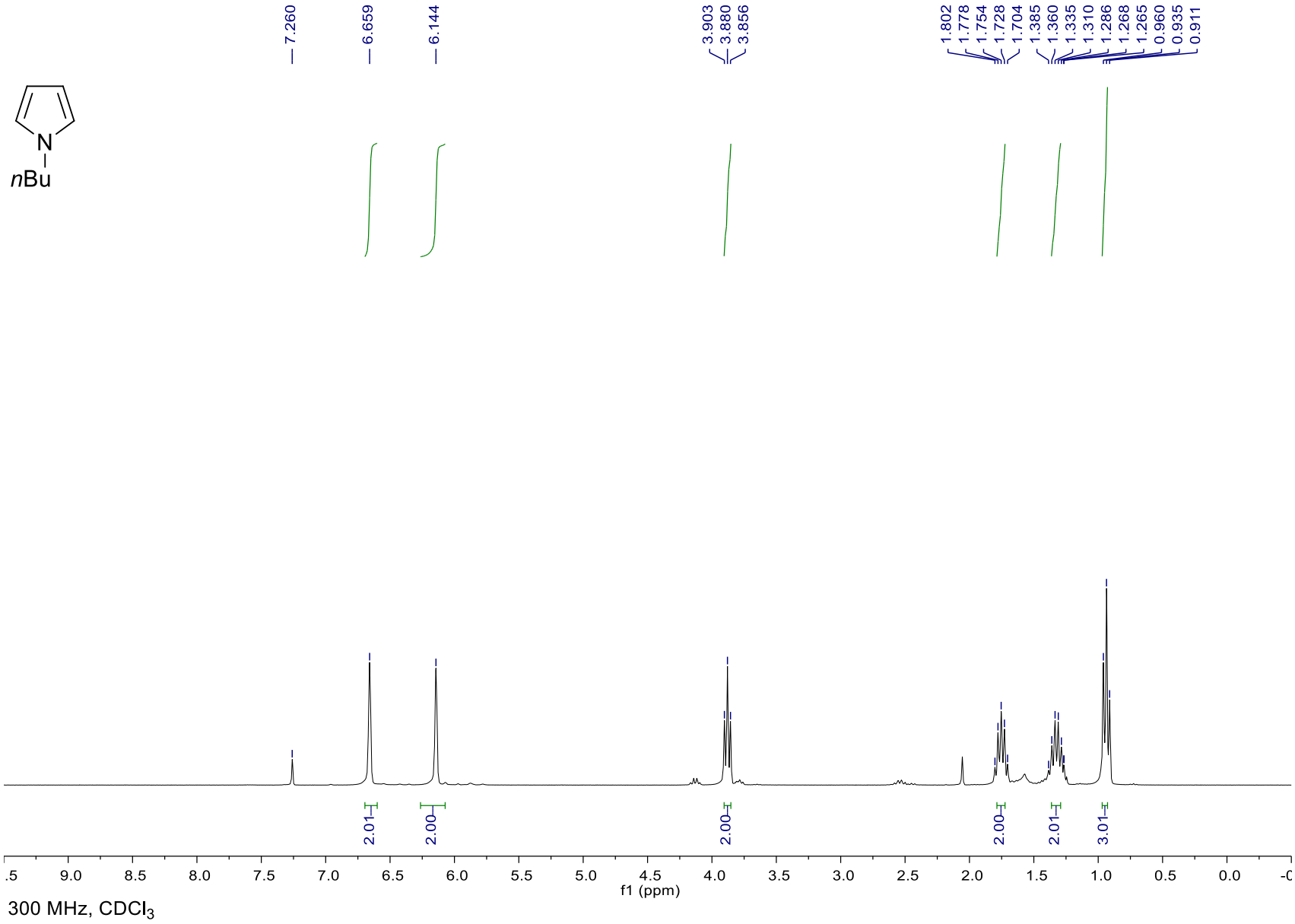
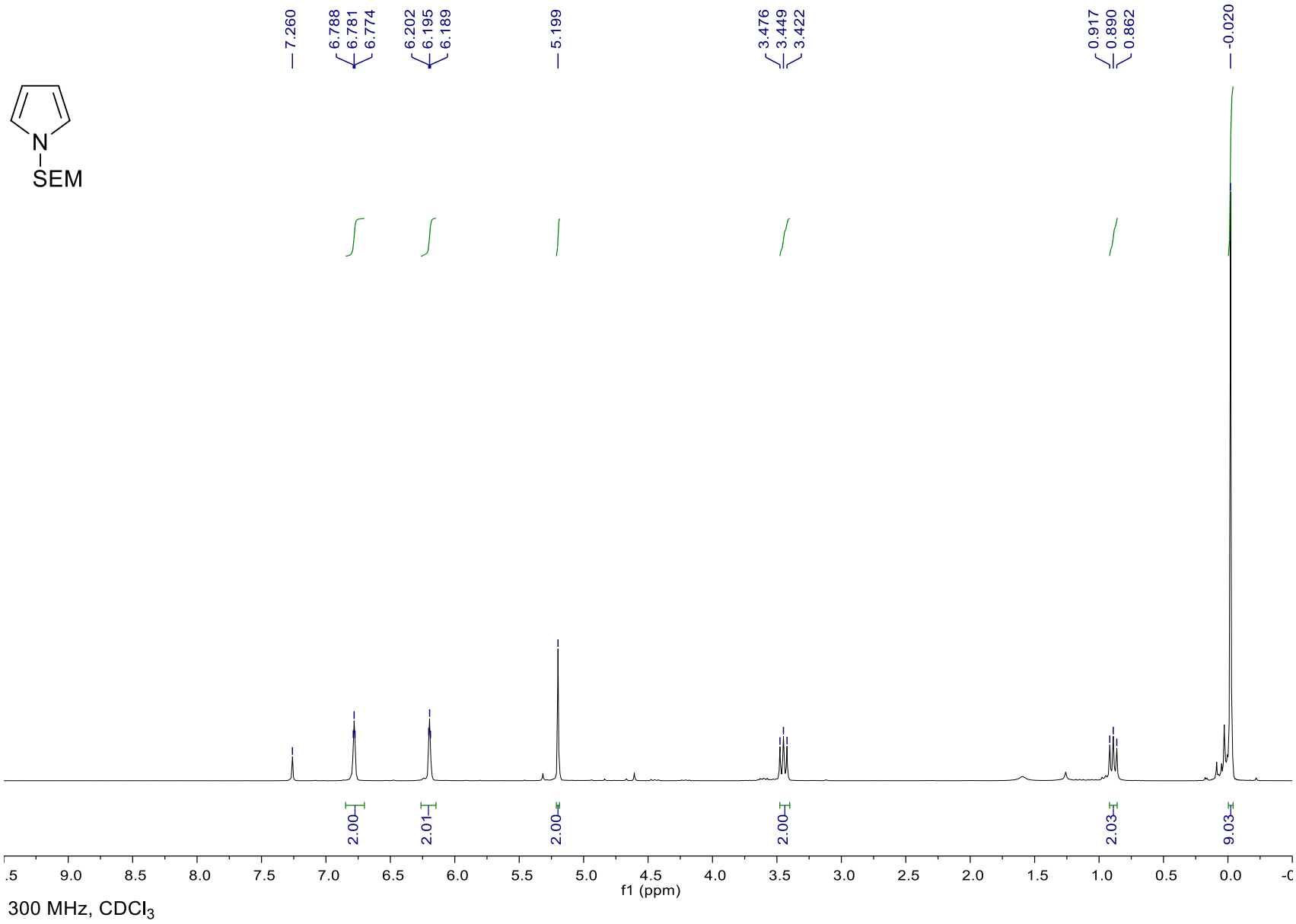
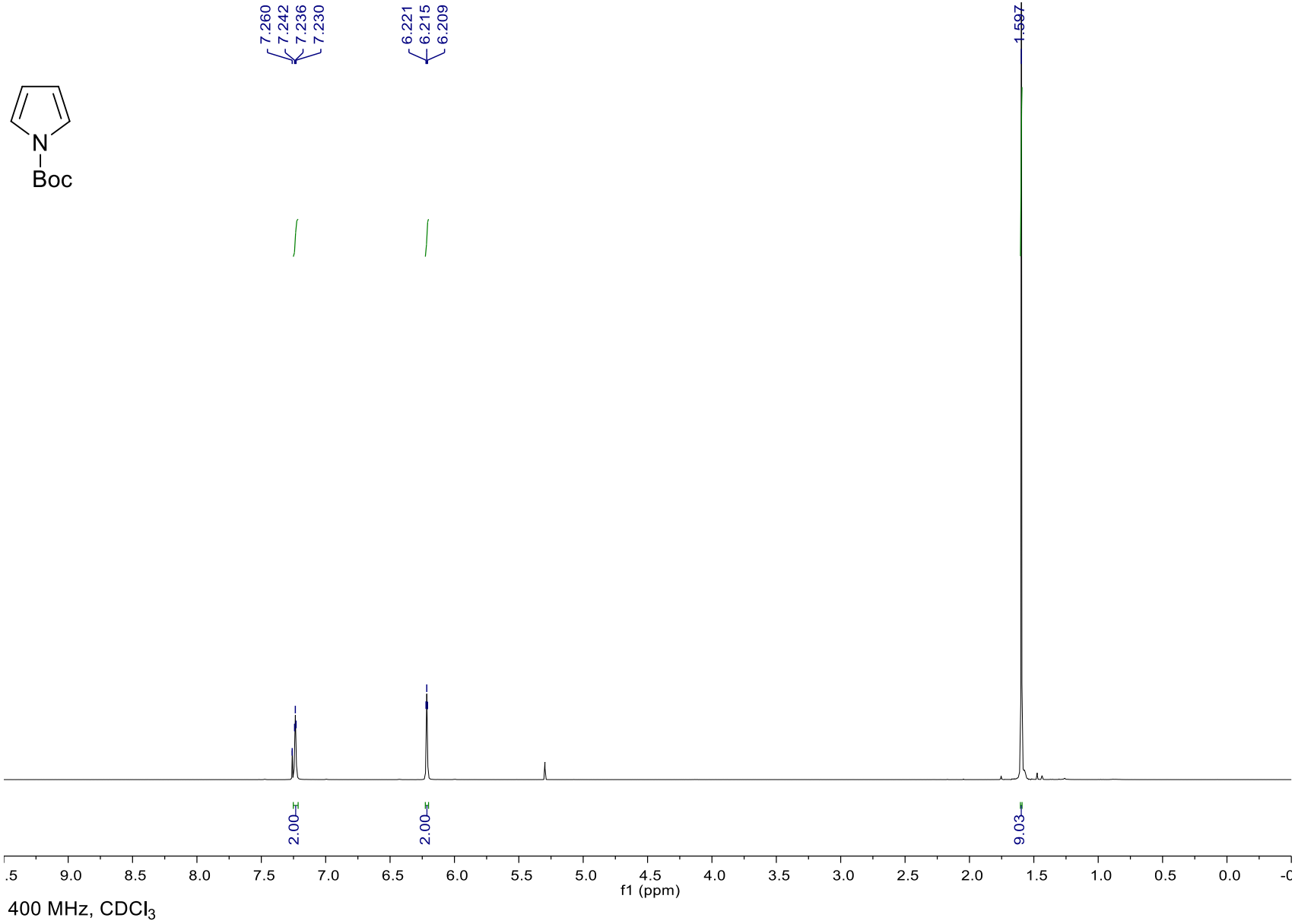



300 MHz, $CDCl_3$




300 MHz, $CDCl_3$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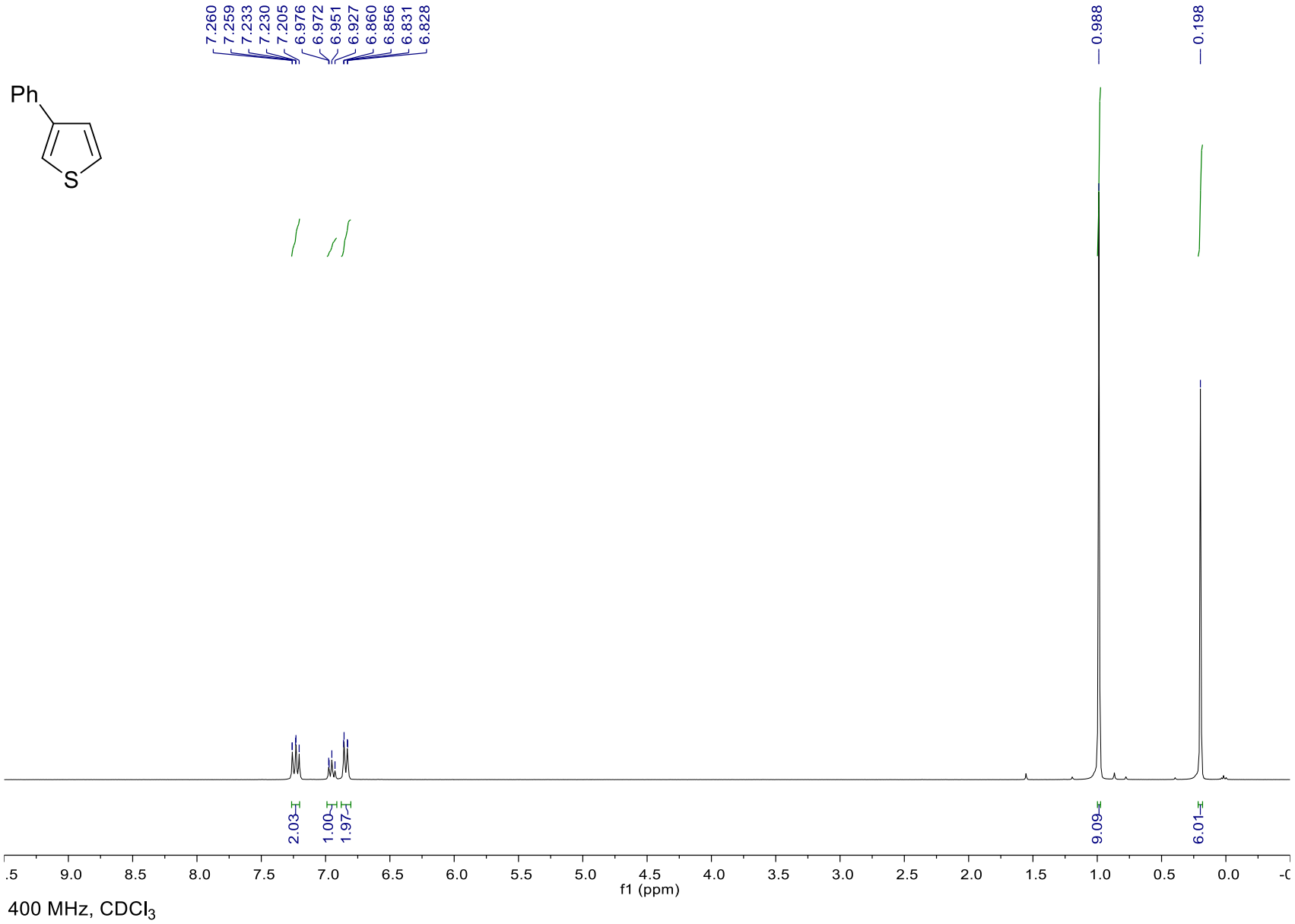
400 MHz, CDCl3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Ph
S
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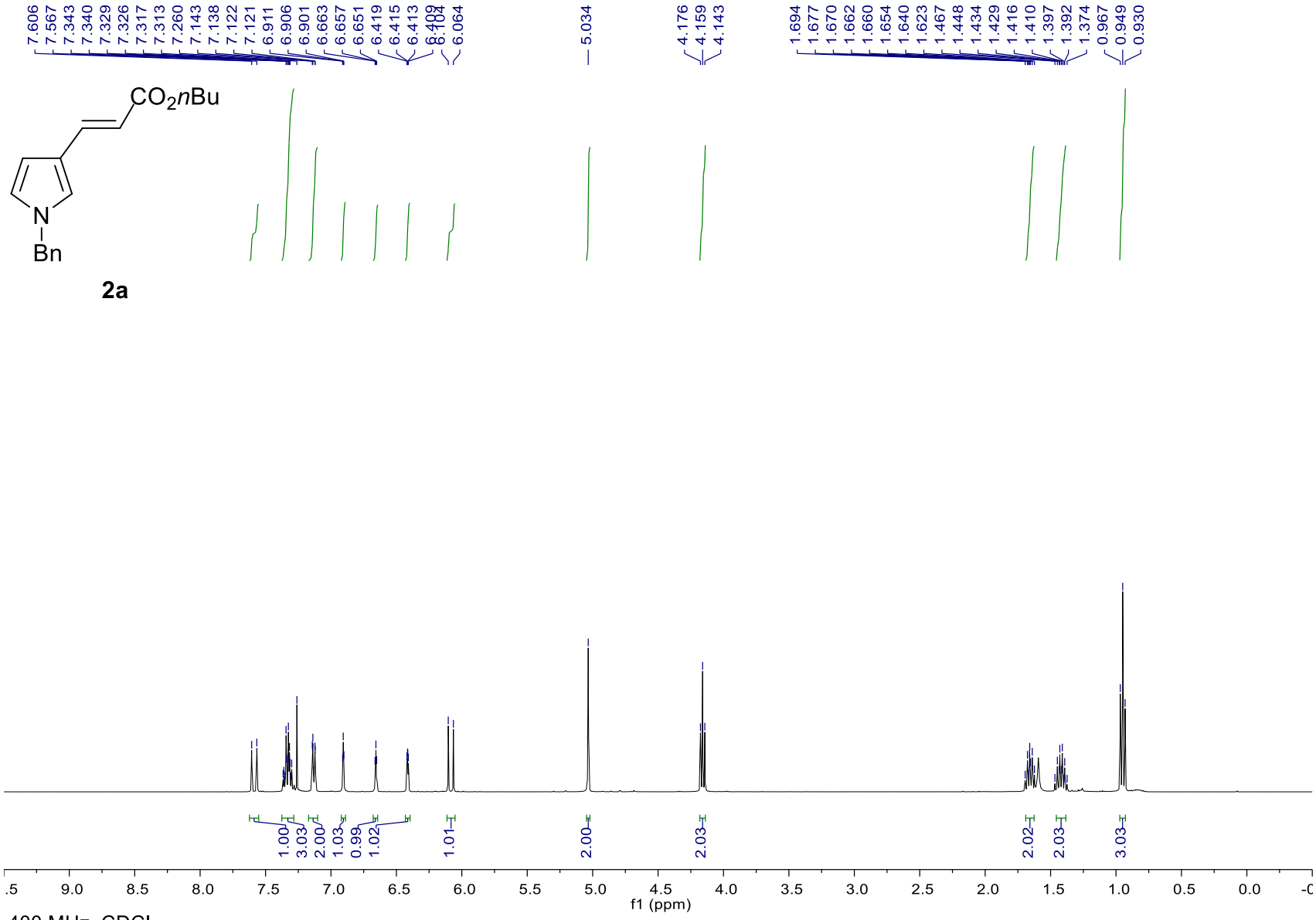
f1 (ppm)
400 MHz, CDCl3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N
Bn
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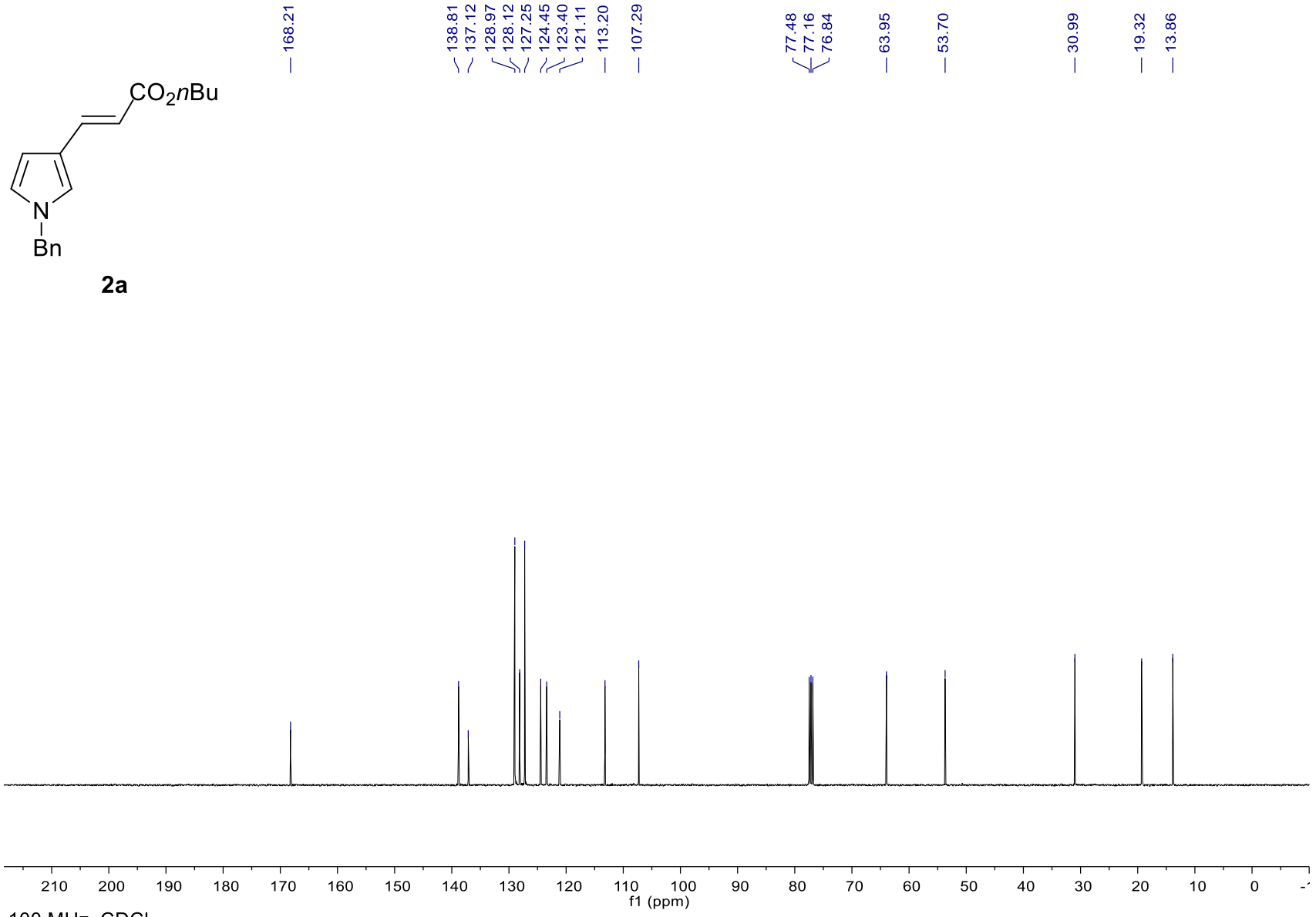
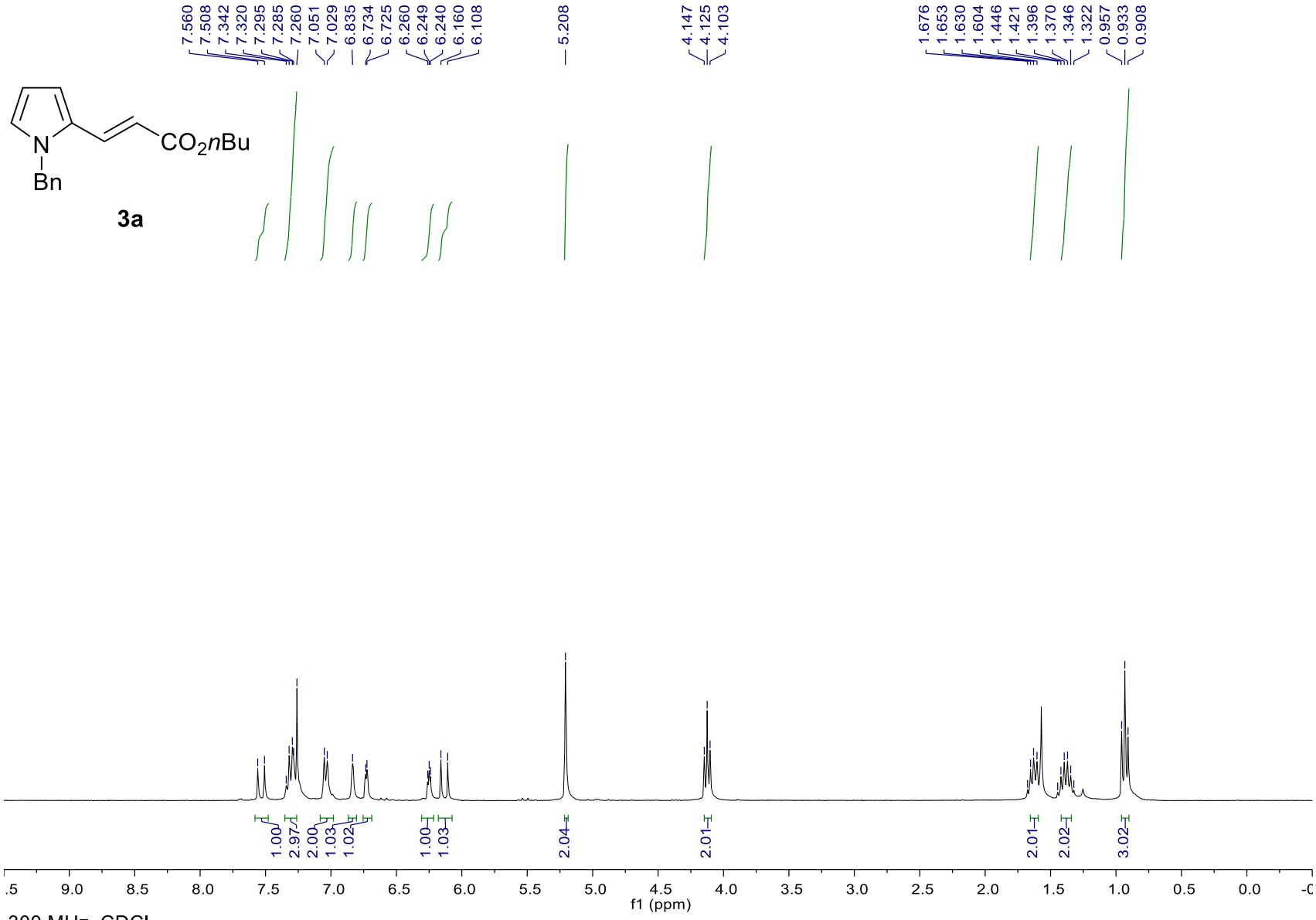
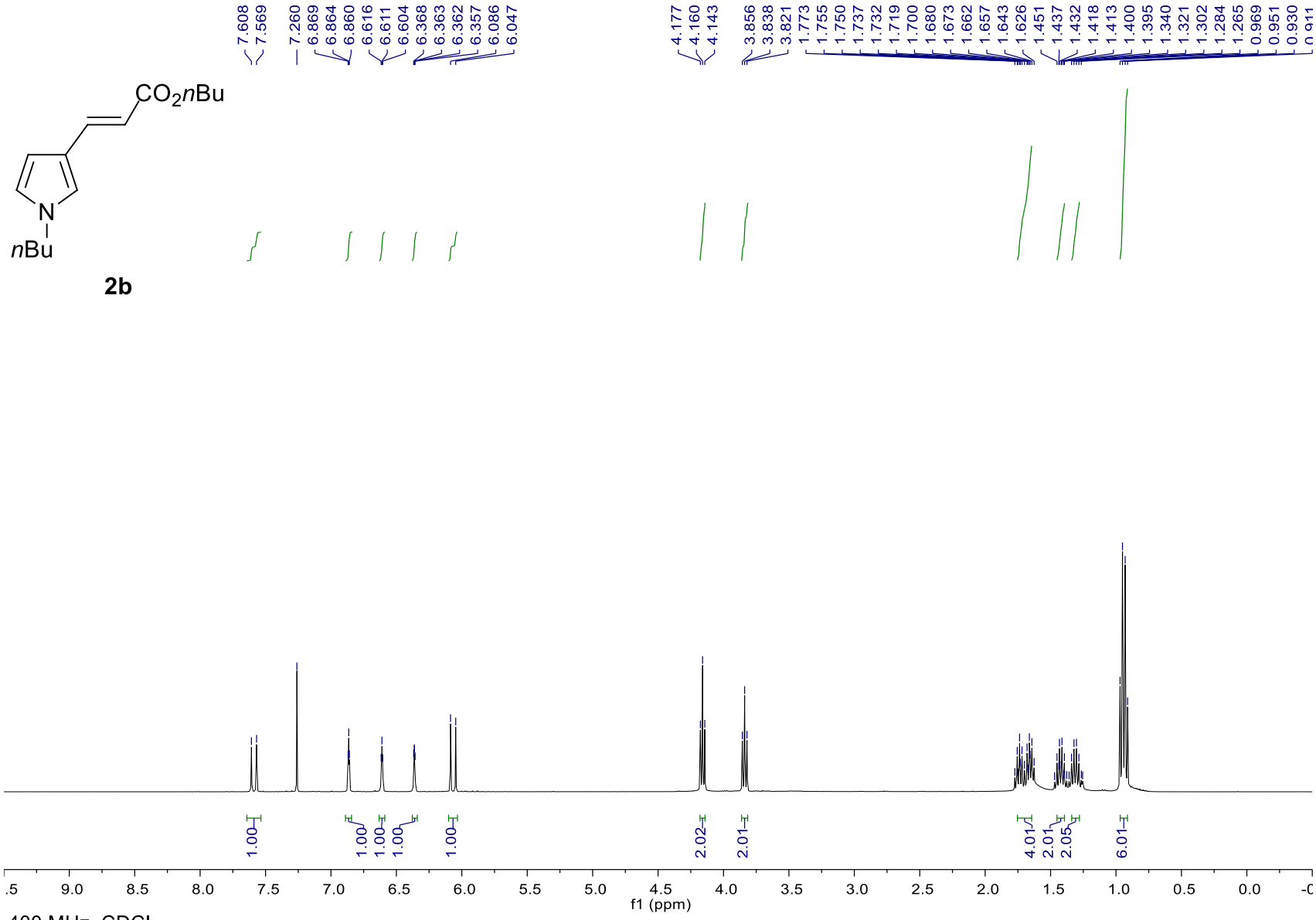
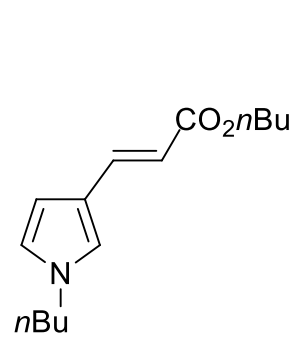
3.03
2.00
1.03
0.99
1.02
1.01
2.00
2.03
2.02
2.03
3.03
f1 (ppm)
400 MHz, CDCl3


168.21
138.81
137.12
128.97
128.12
127.25
124.45
123.40
121.11
113.20
107.29
77.48
77.16
76.84
63.95
53.70
30.99
19.32
13.86
CO2nBu
N
Bn
2a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
100 MHz, CDCl3


7.560
7.508
7.342
7.320
7.295
7.285
7.260
7.051
7.029
6.835
6.734
6.725
6.260
6.249
6.240
6.160
6.108
5.208
4.147
4.125
4.103
1.676
1.653
1.630
1.604
1.446
1.421
1.396
1.370
1.346
1.322
0.957
0.933
0.908
N
Bn
CO2nBu
3a
1.00
2.97
2.00
1.03
1.02
1.00
1.03
2.04
2.01
2.01
2.02
3.02
f1 (ppm)
300 MHz, CDCl3

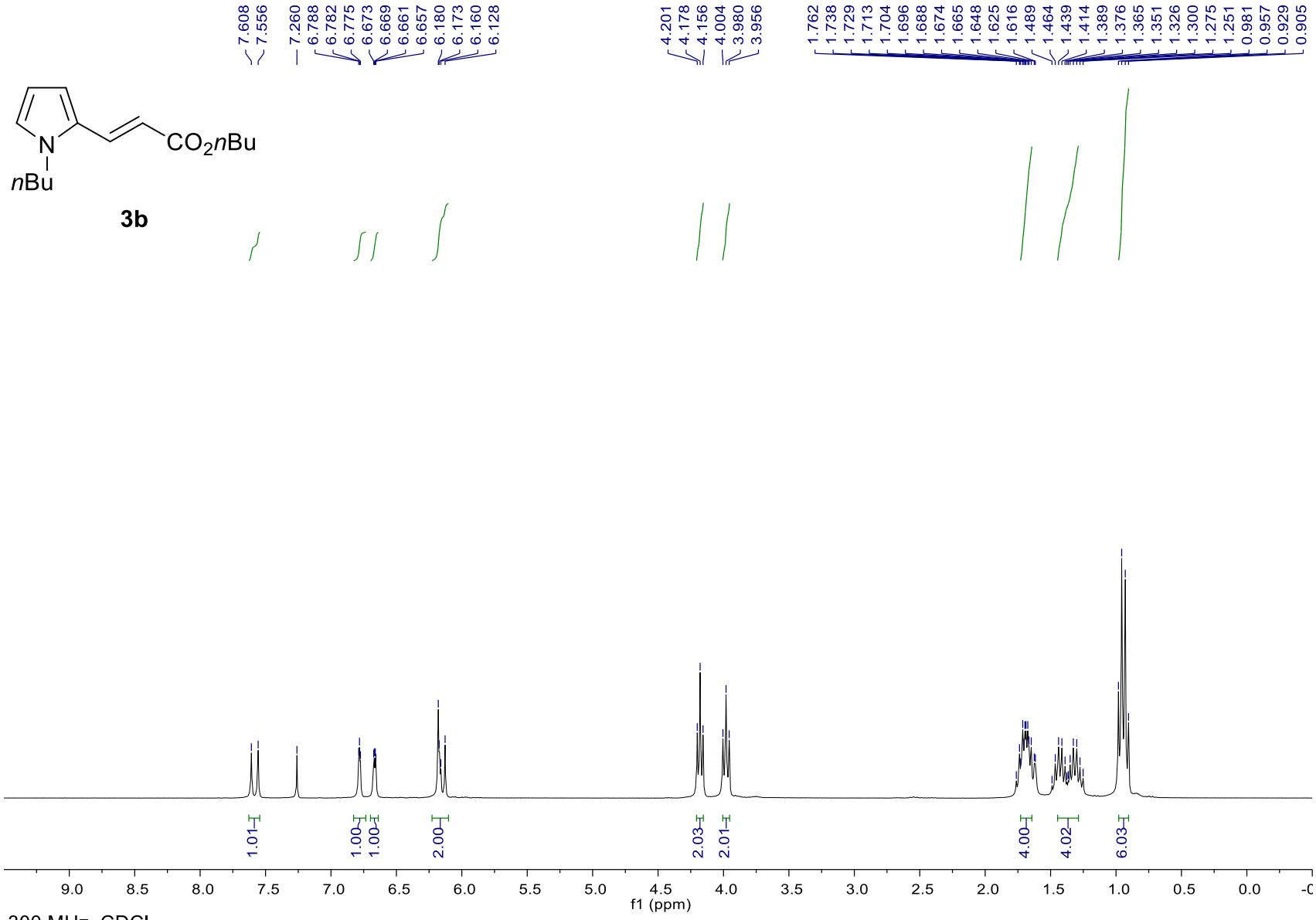

7.608
7.569
7.260
6.869
6.864
6.860
6.616
6.611
6.604
6.368
6.363
6.362
6.357
6.086
6.047
4.177
4.160
4.143
3.856
3.838
3.821
1.773
1.755
1.750
1.737
1.732
1.719
1.700
1.680
1.673
1.662
1.657
1.643
1.626
1.451
1.437
1.432
1.418
1.413
1.400
1.395
1.340
1.321
1.302
1.284
1.265
0.969
0.951
0.930
CO2nBu
N
nBu
2b
1.00
1.00
1.00
1.00
1.00
2.02
2.01
4.01
2.01
2.05
6.01
f1 (ppm)
400 MHz, CDCl3




**2b**

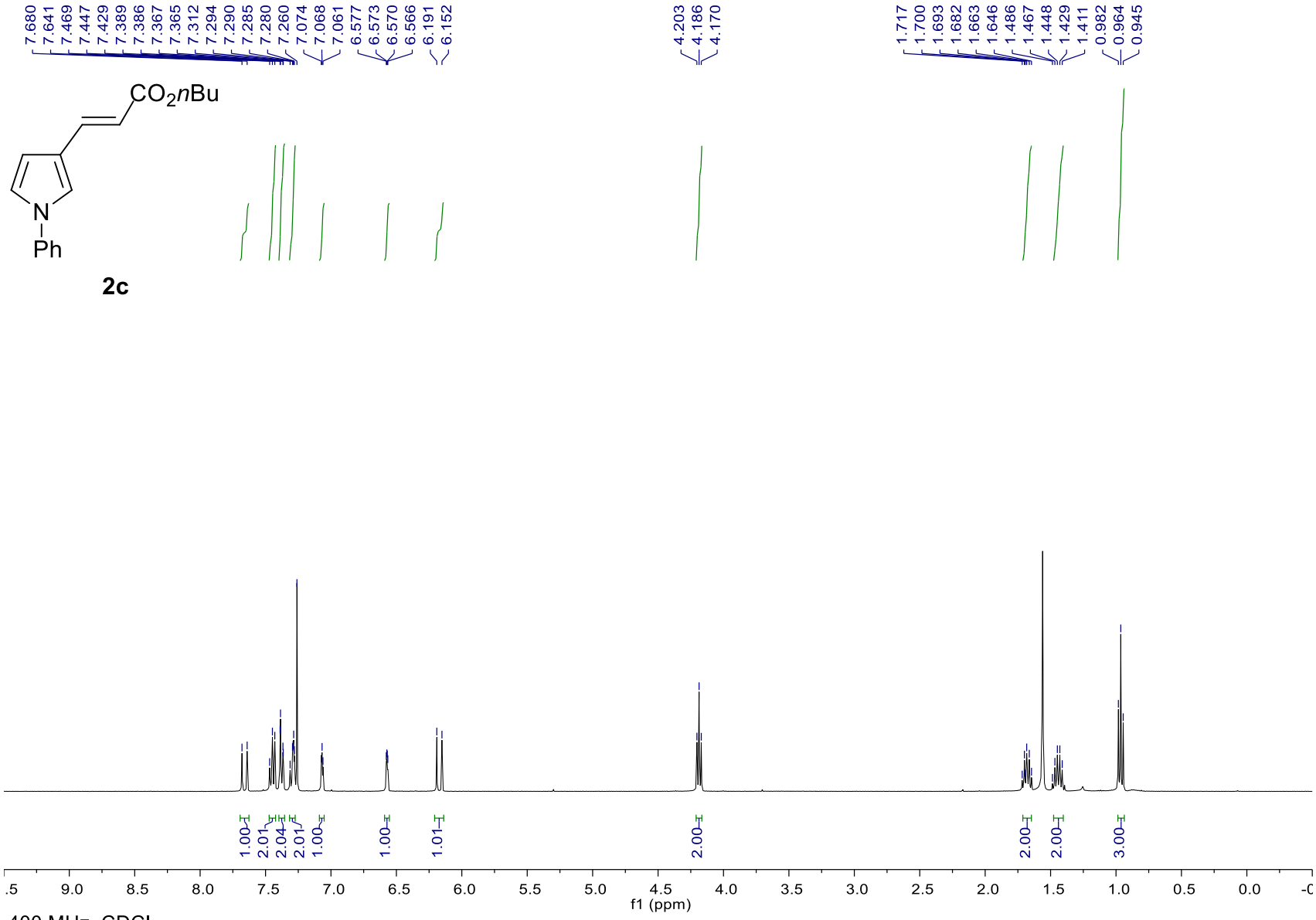


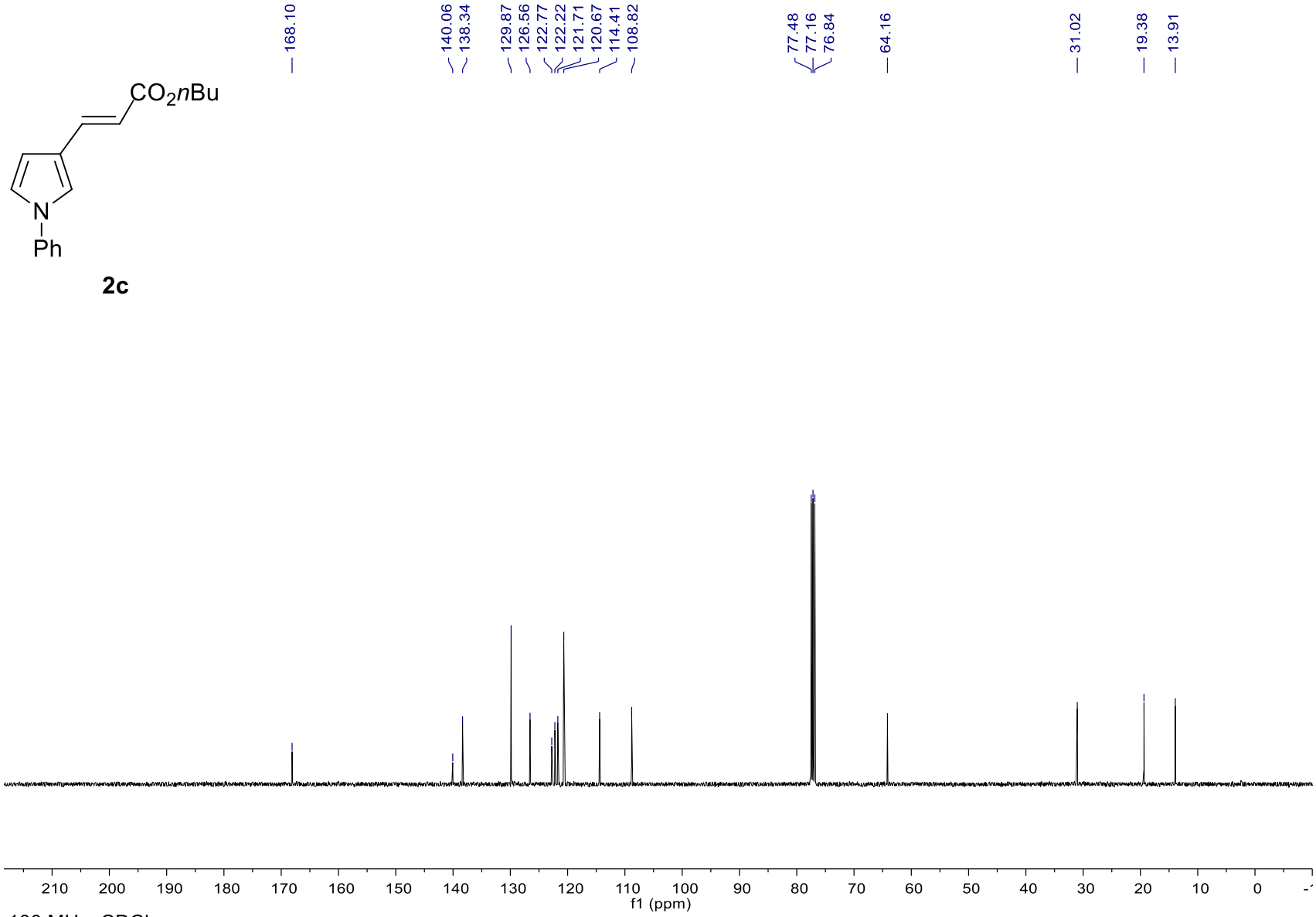

100 MHz, $CDCl_3$

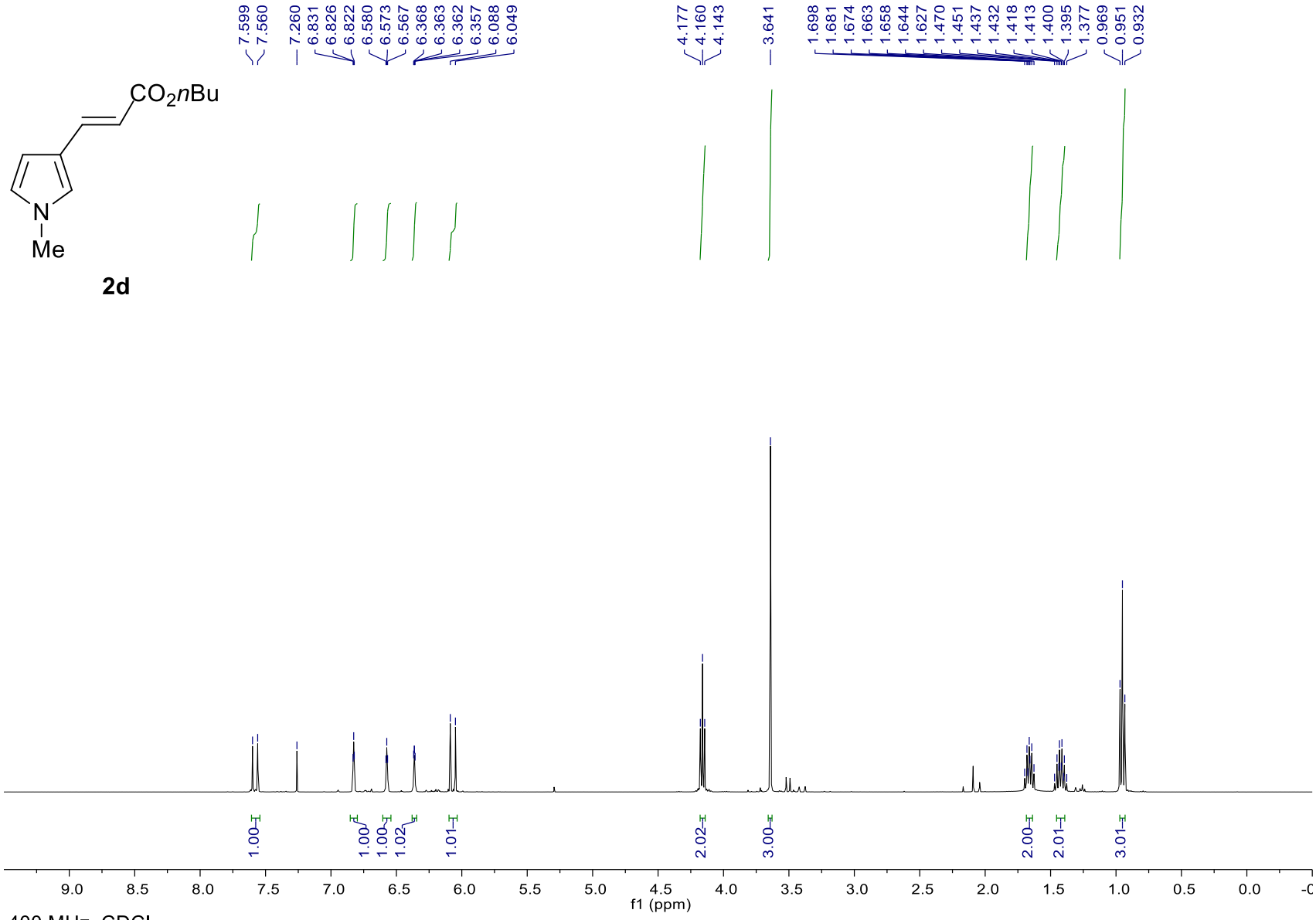


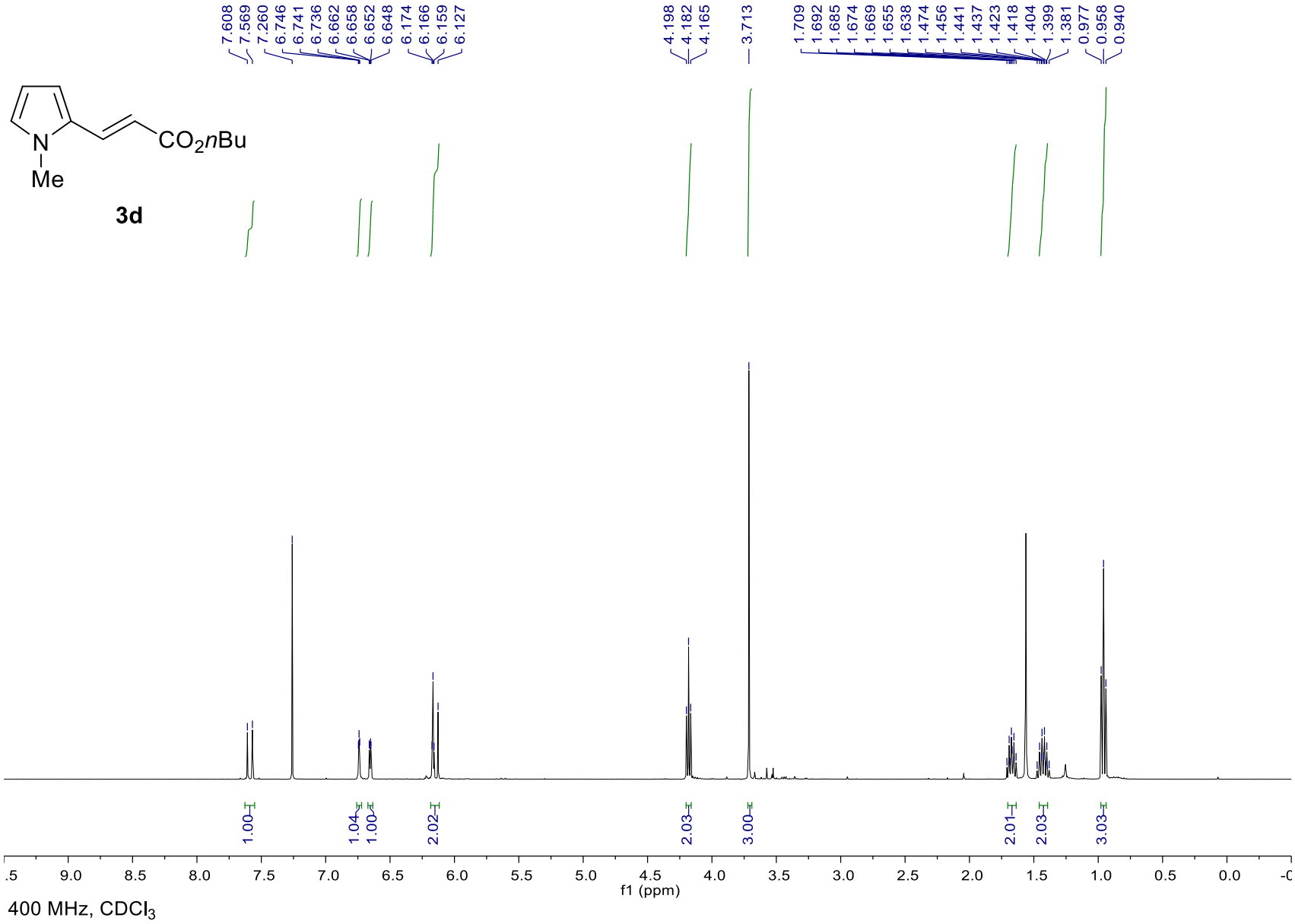

**3b**

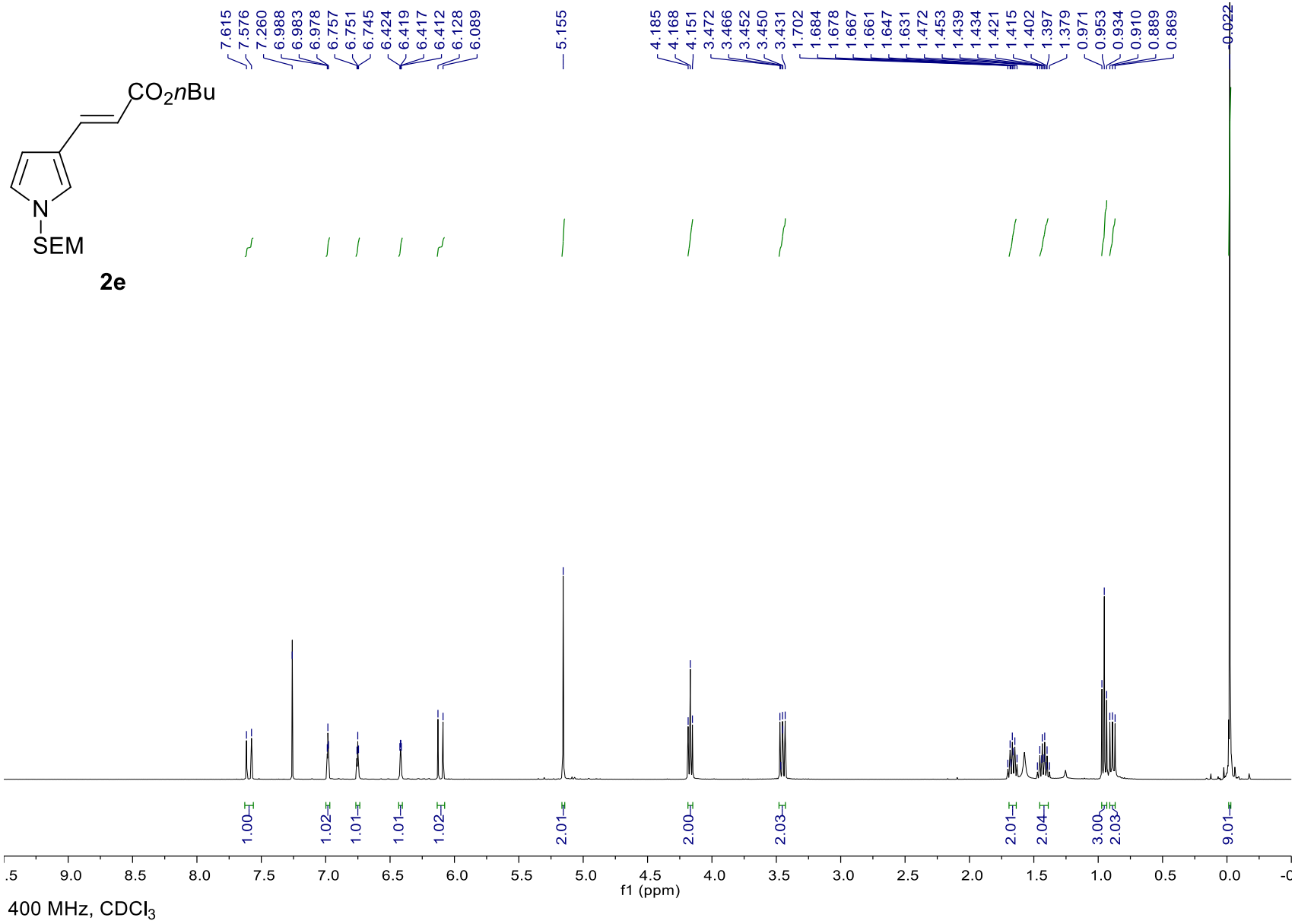
300 MHz, $CDCl_3$

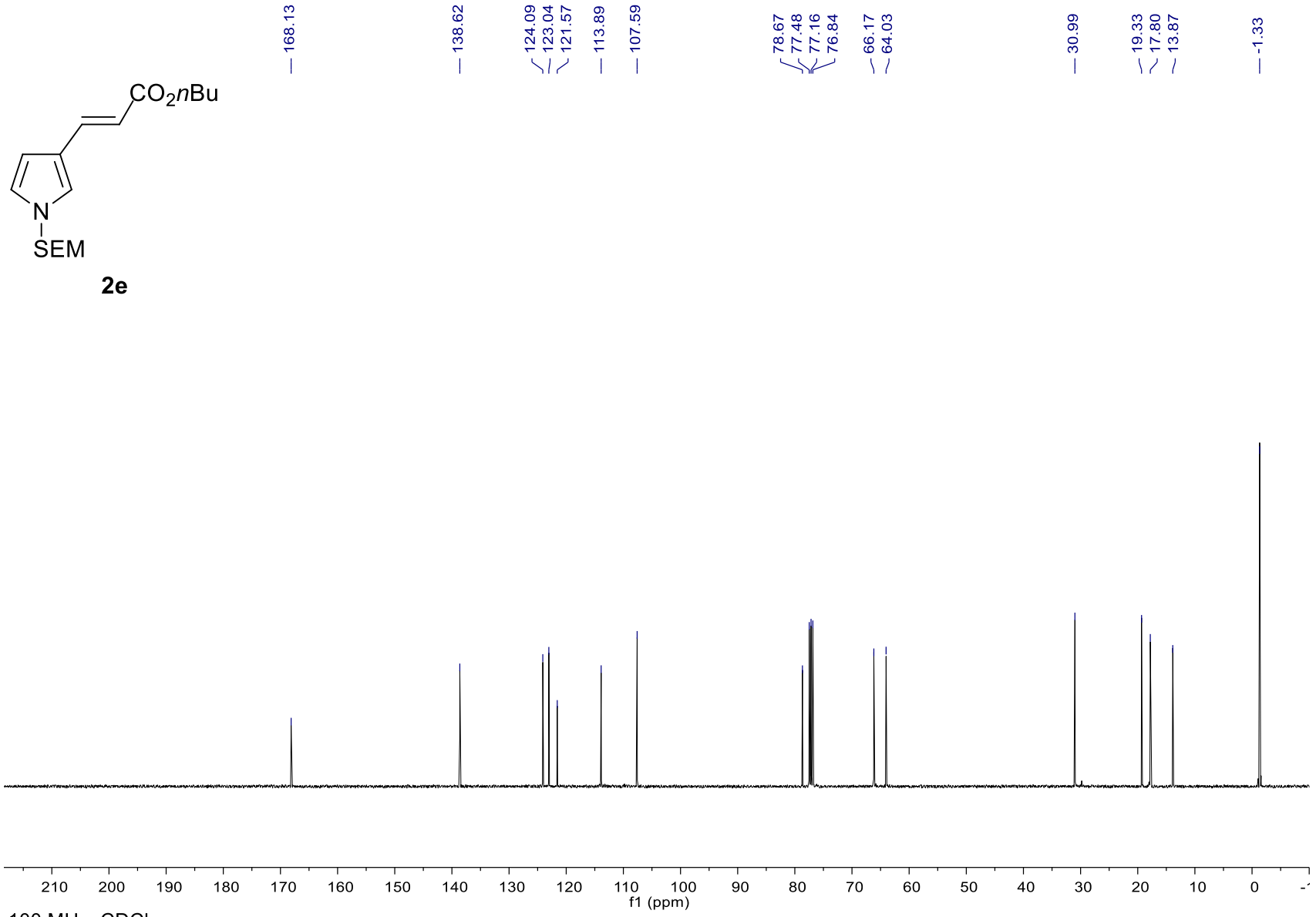

7.680
7.641
7.469
7.447
7.429
7.389
7.386
7.367
7.365
7.312
7.294
7.290
7.285
7.280
7.260
7.074
7.068
7.061
6.577
6.573
6.570
6.566
6.191
6.152
4.203
4.186
4.170
1.717
1.700
1.693
1.682
1.663
1.646
1.486
1.467
1.448
1.429
1.411
0.982
0.964
0.945
CO2nBu
N
Ph
2c
1.00
2.01
2.04
2.01
1.00
1.00
1.01
2.00
2.00
2.00
3.00
f1 (ppm)
400 MHz, CDCl3

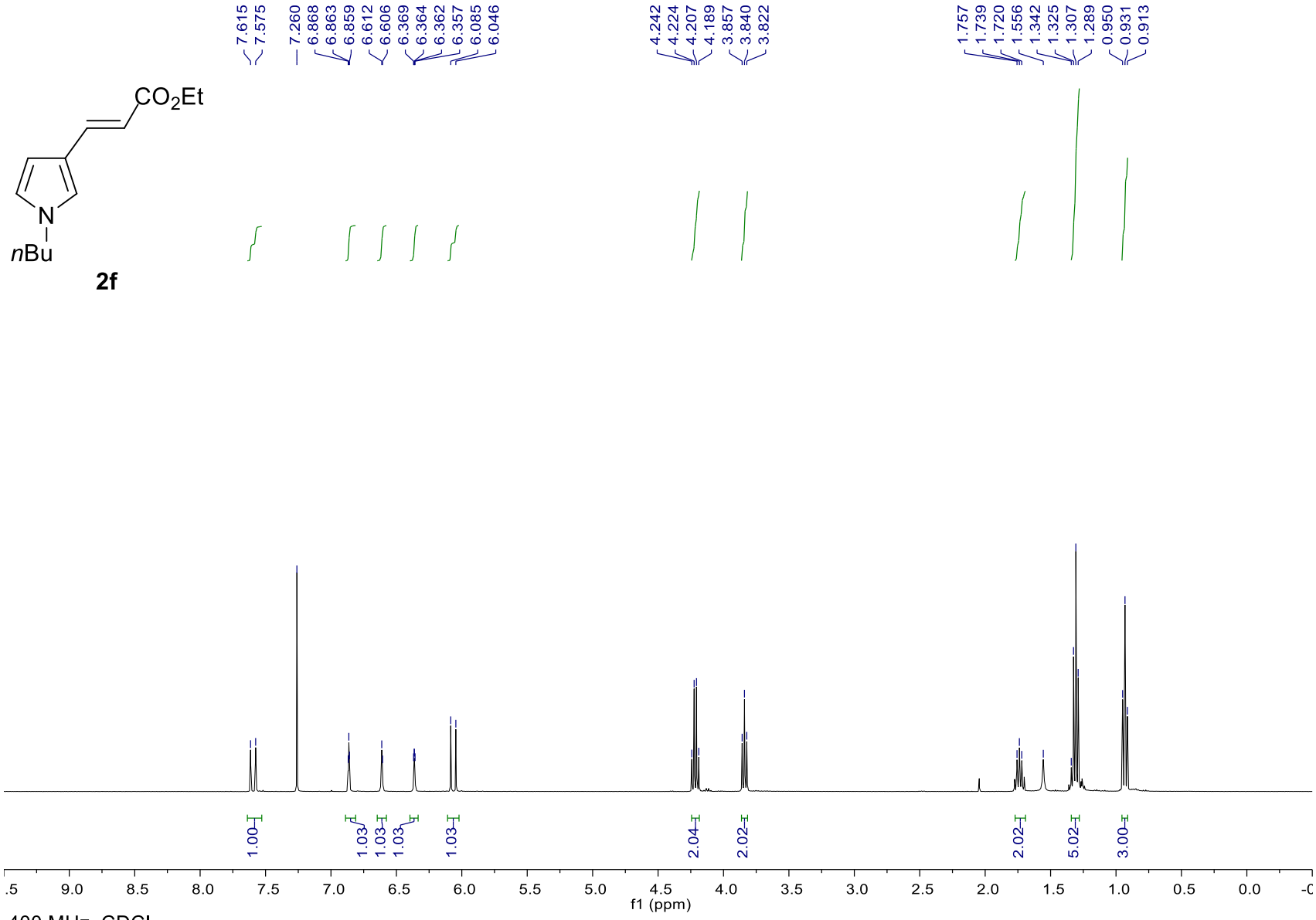

168.10
140.06
138.34
129.87
126.56
122.77
122.22
121.71
120.67
114.41
108.82
77.48
77.16
76.84
64.16
31.02
19.38
13.91
CO2nBu
N
Ph
2c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
100 MHz, CDCl3

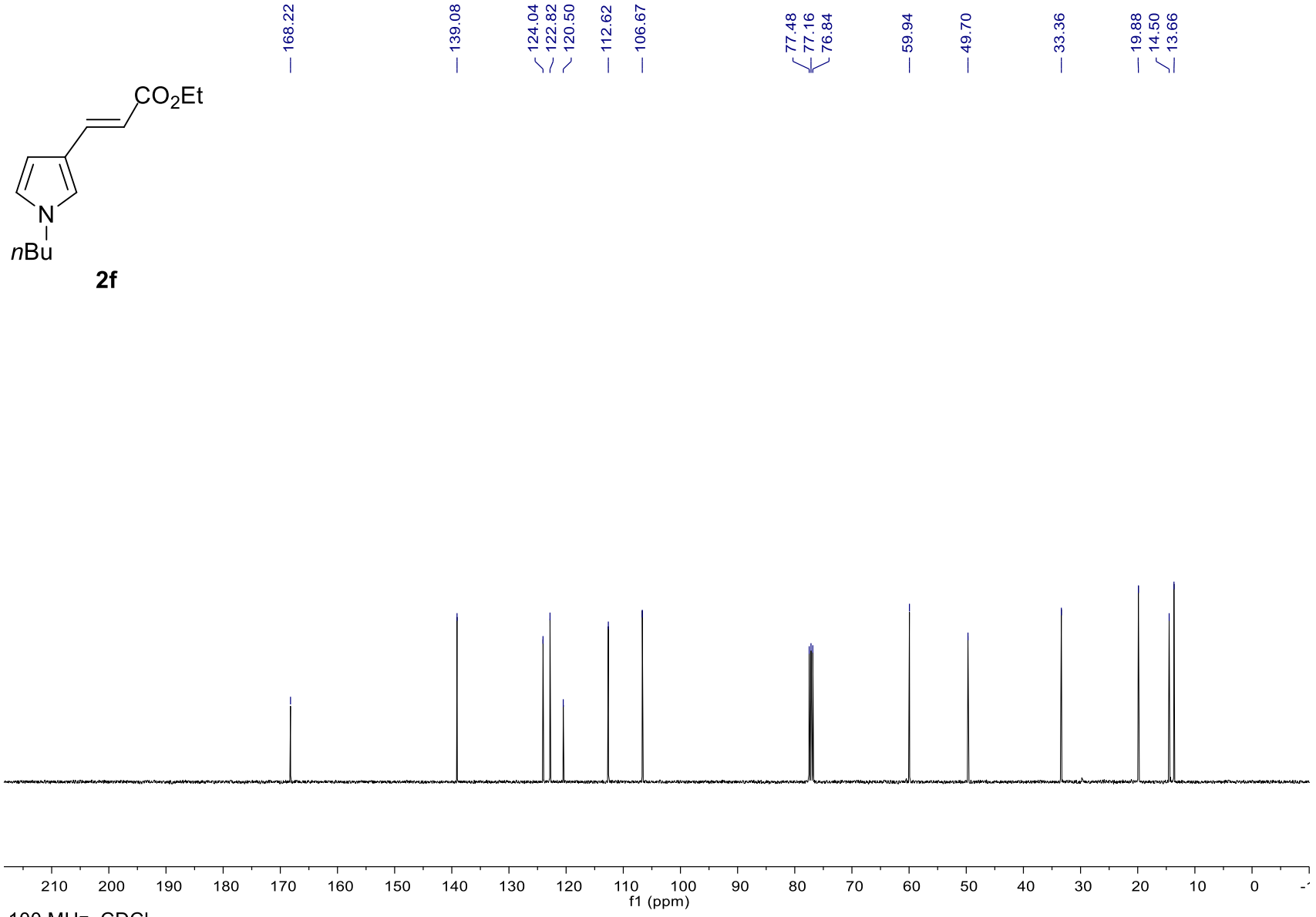

7.599
7.560
7.260
6.831
6.826
6.822
6.580
6.573
6.567
6.368
6.363
6.362
6.357
6.088
6.049
4.177
4.160
4.143
3.641
1.698
1.681
1.674
1.663
1.658
1.644
1.627
1.470
1.451
1.437
1.432
1.418
1.413
1.400
1.395
1.377
0.969
0.951
0.932
CO2nBu
N
Me
2d
1.00
1.00
1.00
1.02
1.01
2.02
3.00
2.00
2.01
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
400 MHz, CDCl3

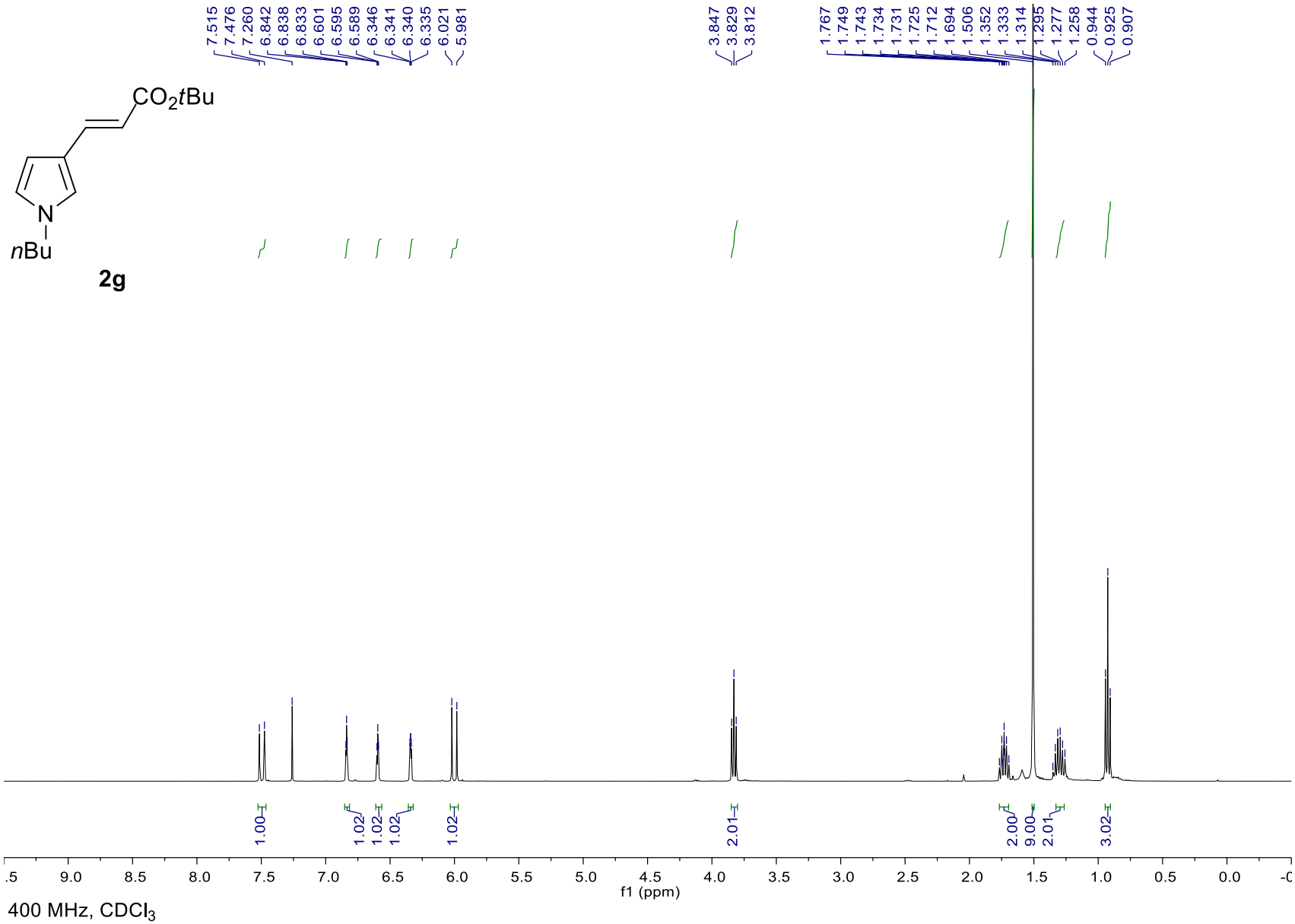

7.608
7.569
7.260
6.746
6.741
6.736
6.662
6.658
6.652
6.648
6.174
6.166
6.159
6.127
4.198
4.182
4.165
3.713
1.709
1.692
1.685
1.674
1.669
1.655
1.638
1.474
1.456
1.441
1.437
1.423
1.418
1.404
1.399
1.381
0.977
0.958
0.940
N
Me
CO2nBu
3d
1.00
1.04
1.00
2.02
2.03
3.00
2.01
2.03
3.03
f1 (ppm)
400 MHz, CDCl3

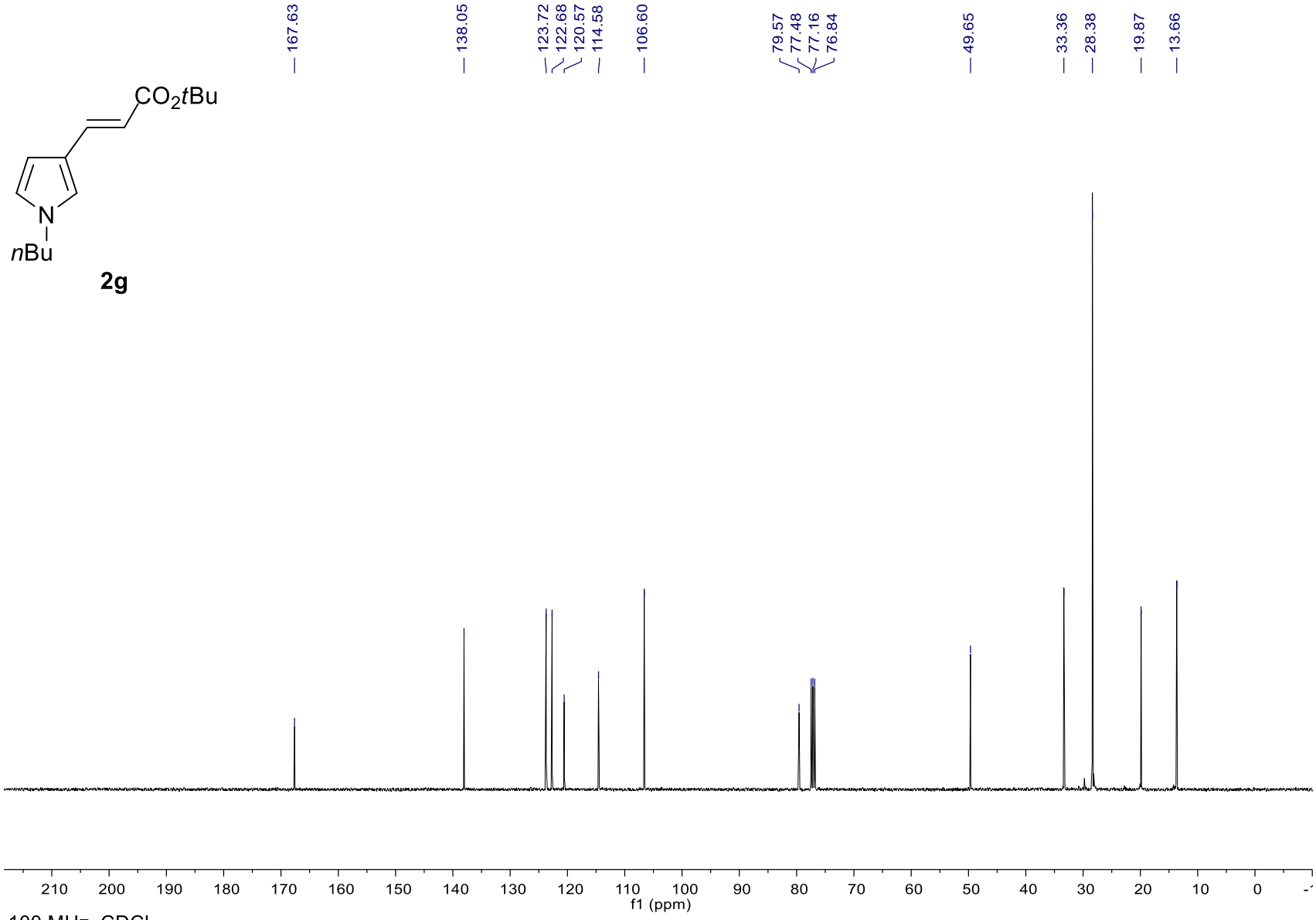

7.615
7.576
7.260
6.988
6.983
6.978
6.757
6.751
6.745
6.424
6.419
6.417
6.412
6.128
6.089
5.155
4.185
4.168
4.151
3.472
3.466
3.452
3.450
3.431
1.702
1.684
1.678
1.667
1.661
1.647
1.631
1.472
1.453
1.439
1.434
1.421
1.415
1.402
1.397
1.379
0.971
0.953
0.934
0.910
0.889
0.869
0.022
CO2nBu
N
SEM
2e
1.00
1.02
1.01
1.01
1.02
2.01
2.00
2.03
2.01
2.04
3.00
2.03
9.01
f1 (ppm)
400 MHz, CDCl3

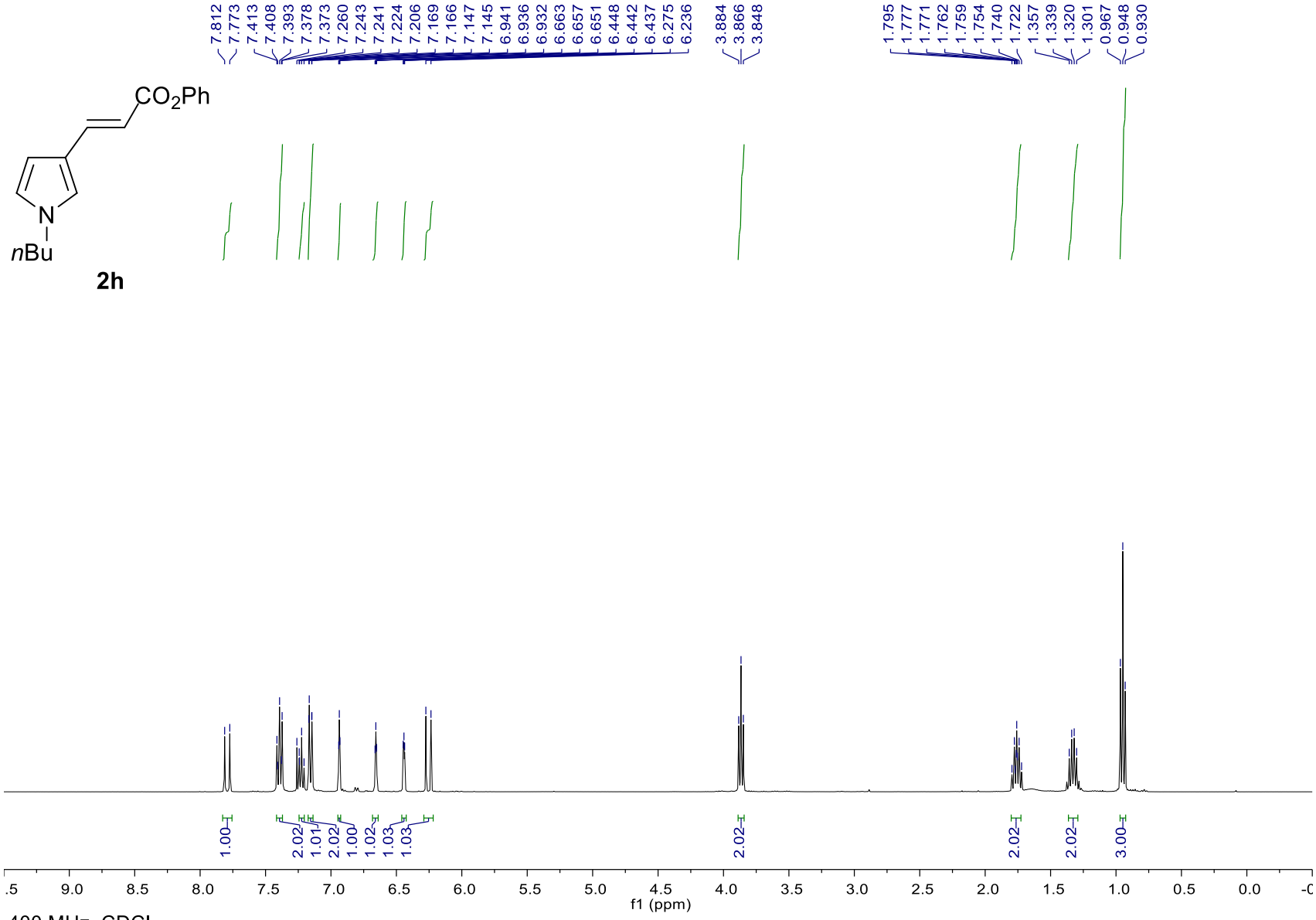

168.13
138.62
124.09
123.04
121.57
113.89
107.59
78.67
77.48
77.16
76.84
66.17
64.03
30.99
19.33
17.80
13.87
-1.33
CO2nBu
N
SEM
2e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
100 MHz, CDCl3

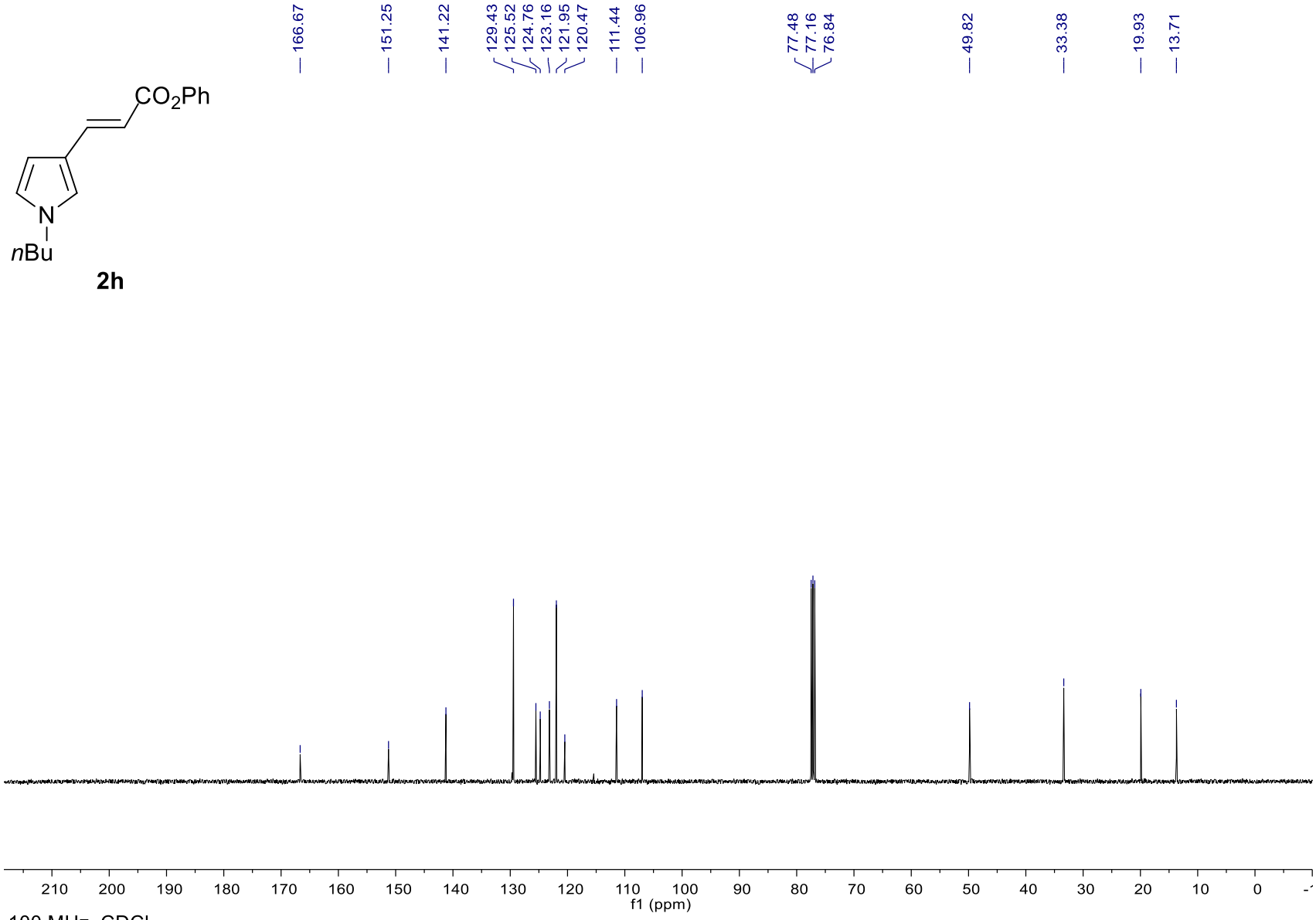

7.615
7.575
7.260
6.868
6.863
6.859
6.612
6.606
6.369
6.364
6.362
6.357
6.085
6.046
4.242
4.224
4.207
4.189
3.857
3.840
3.822
1.757
1.739
1.720
1.556
1.342
1.325
1.307
1.289
0.950
0.931
0.913
CO2Et
N
nBu
2f
1.00
1.03
1.03
1.03
1.03
2.04
2.02
2.02
5.02
3.00
f1 (ppm)
400 MHz, CDCl3

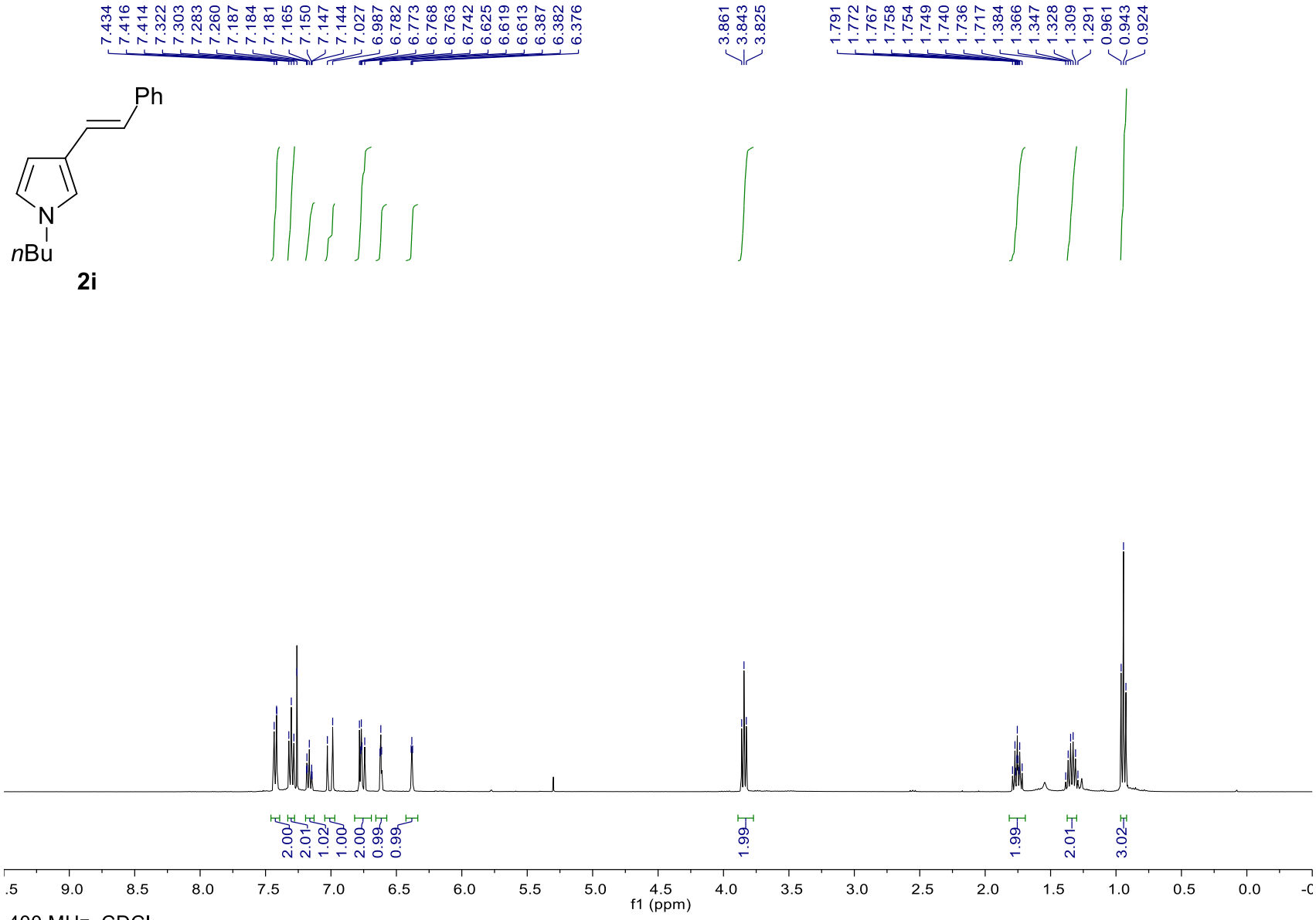

168.22
139.08
124.04
122.82
120.50
112.62
106.67
77.48
77.16
76.84
59.94
49.70
33.36
19.88
14.50
13.66
CO2Et
N
nBu
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
100 MHz, CDCl3

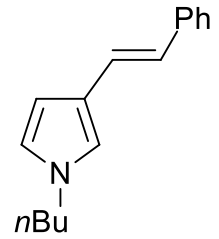

7.515
7.476
7.260
6.842
6.838
6.833
6.601
6.595
6.589
6.346
6.341
6.340
6.335
6.021
5.981
3.847
3.829
3.812
1.767
1.749
1.743
1.734
1.731
1.725
1.712
1.694
1.506
1.352
1.333
1.314
1.295
1.277
1.258
0.944
0.925
0.907
CO2tBu
N
nBu
2g
1.00
1.02
1.02
1.02
1.02
2.01
2.00
9.00
2.01
3.02
f1 (ppm)
400 MHz, CDCl3


167.63
138.05
123.72
122.68
120.57
114.58
106.60
79.57
77.48
77.16
76.84
49.65
33.36
28.38
19.87
13.66
CO2tBu
N
nBu
2g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
100 MHz, CDCl3


7.812
7.773
7.413
7.408
7.393
7.378
7.373
7.260
7.243
7.241
7.224
7.206
7.169
7.166
7.147
7.145
6.941
6.936
6.932
6.663
6.657
6.651
6.448
6.442
6.437
6.275
6.236
3.884
3.866
3.848
1.795
1.777
1.771
1.762
1.759
1.754
1.740
1.722
1.357
1.339
1.320
1.301
0.967
0.948
0.930
CO2Ph
N
nBu
2h
1.00
2.02
1.01
2.02
1.00
1.02
1.03
1.03
2.02
2.02
2.02
3.00
f1 (ppm)
400 MHz, CDCl3


166.67
151.25
141.22
129.43
125.52
124.76
123.16
121.95
120.47
111.44
106.96
77.48
77.16
76.84
49.82
33.38
19.93
13.71
CO2Ph
N
nBu
2h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
100 MHz, CDCl3

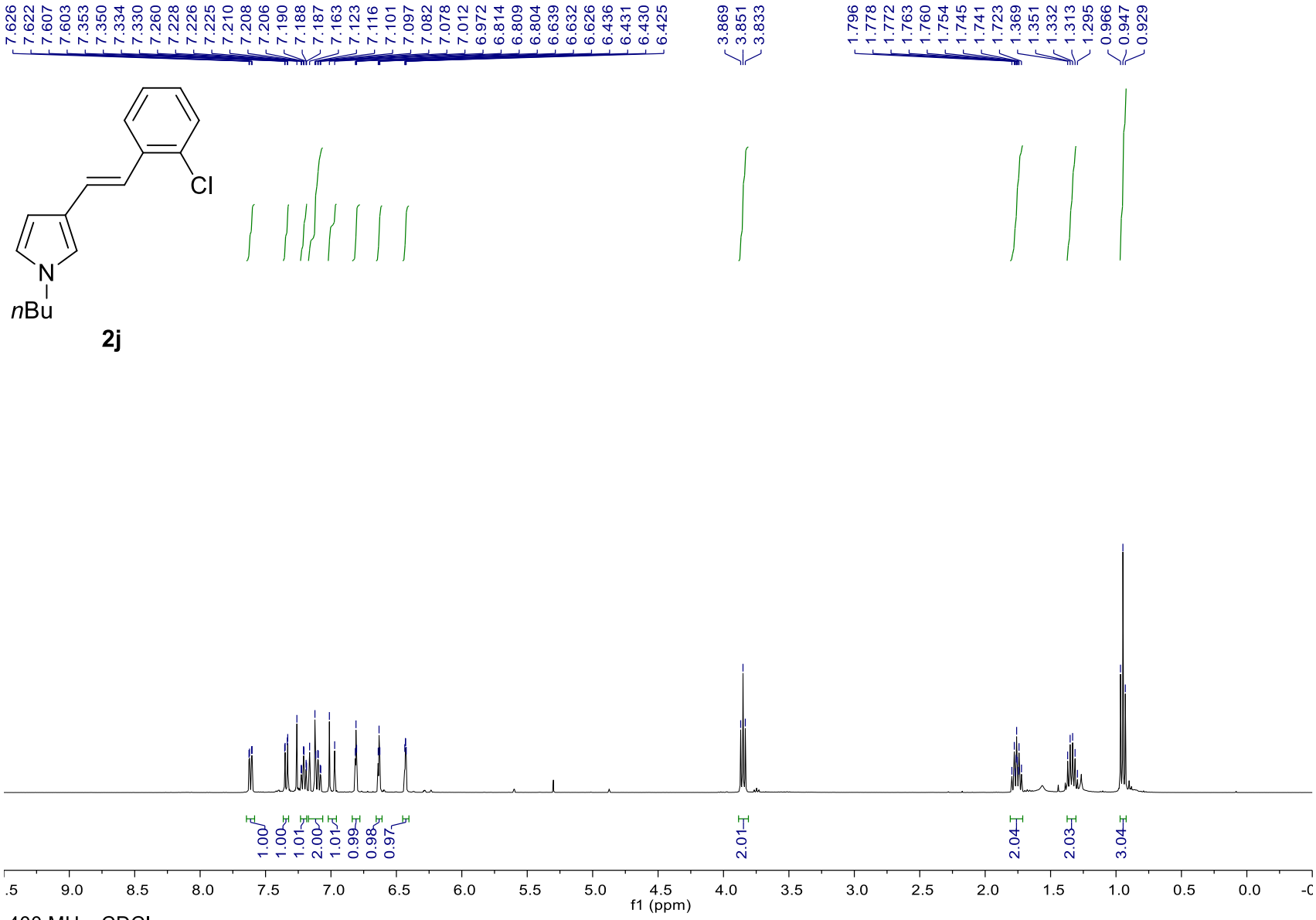

7.434
7.416
7.414
7.322
7.303
7.283
7.260
7.187
7.184
7.181
7.165
7.150
7.147
7.144
7.027
6.987
6.782
6.773
6.768
6.763
6.742
6.625
6.619
6.613
6.387
6.382
6.376
3.861
3.843
3.825
1.791
1.772
1.767
1.758
1.754
1.749
1.740
1.736
1.717
1.384
1.366
1.347
1.328
1.309
1.291
0.961
0.943
0.924
Ph
N
nBu
2i
2.00
2.01
1.02
1.00
2.00
0.99
0.99
1.99
1.99
2.01
3.02
f1 (ppm)
400 MHz, CDCl3




**2i**

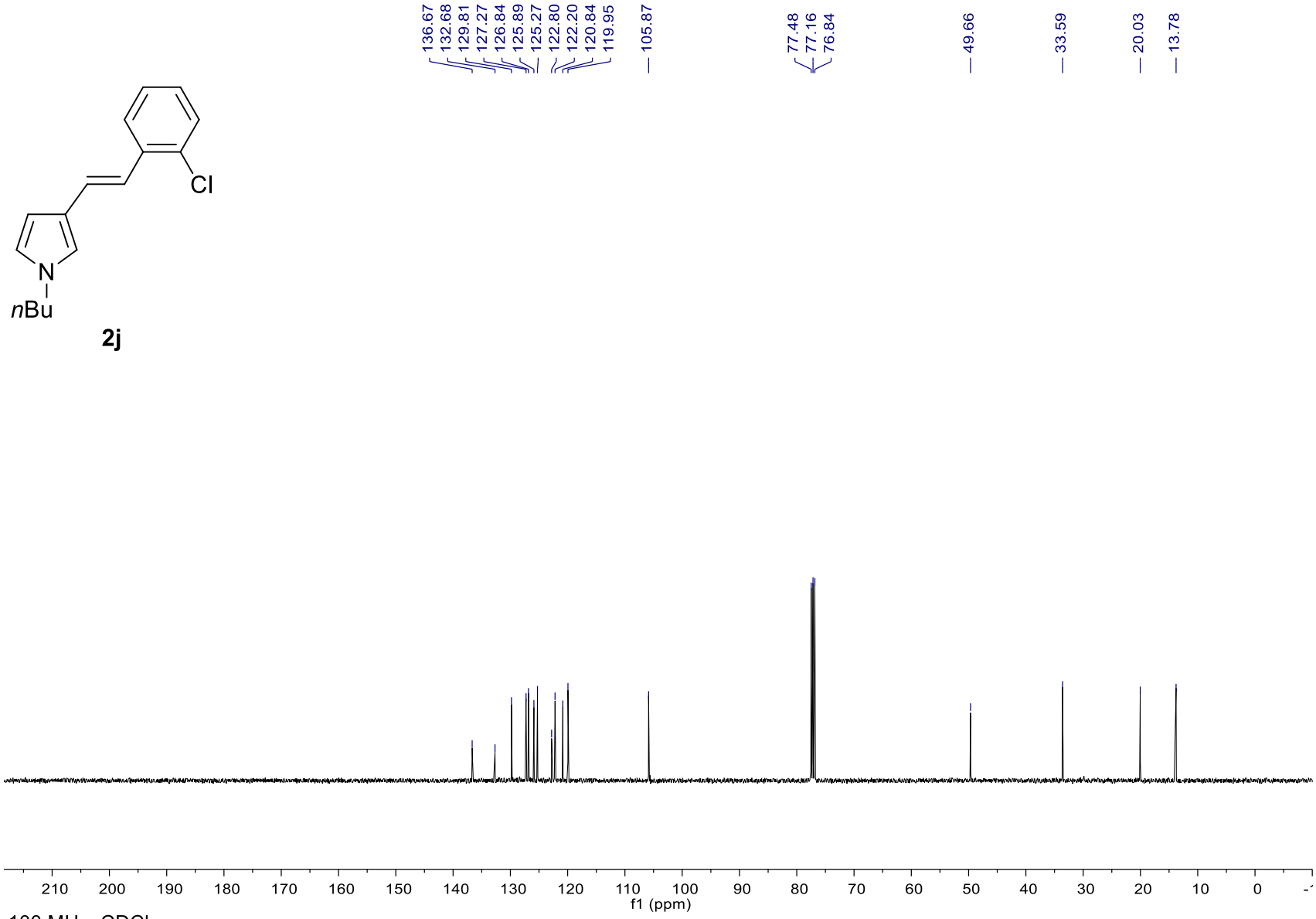


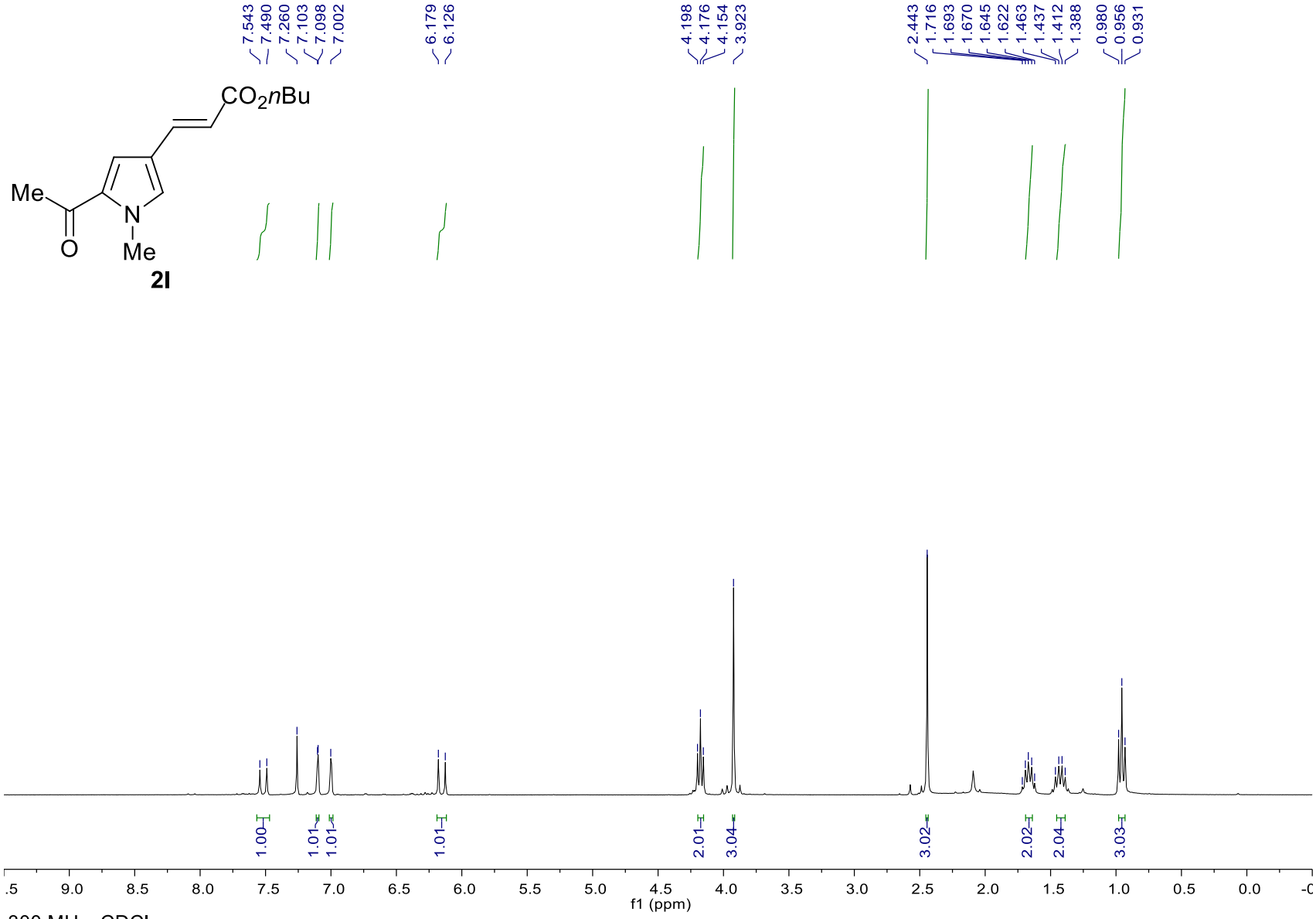

100 MHz, $CDCl_3$



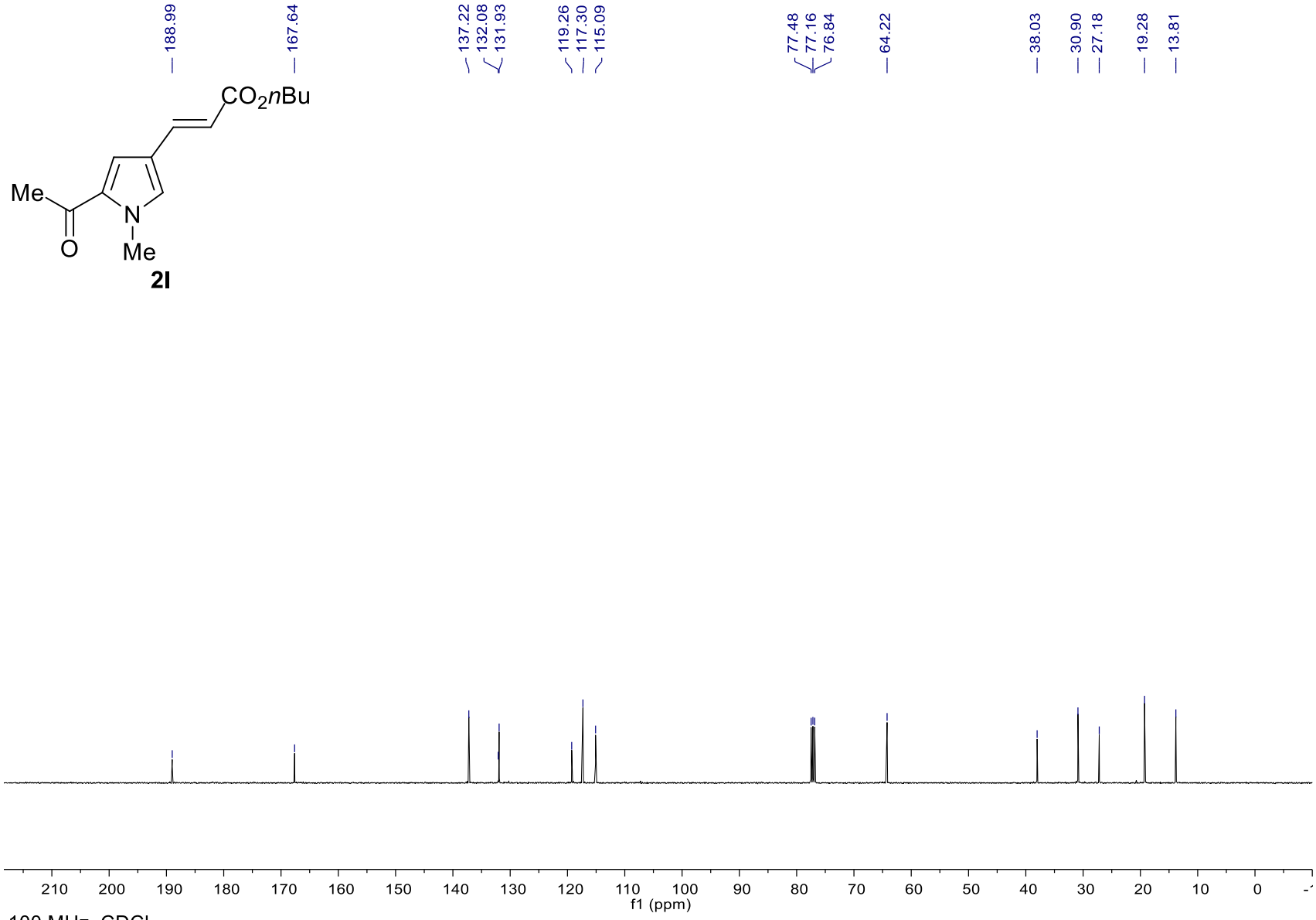

**2j**

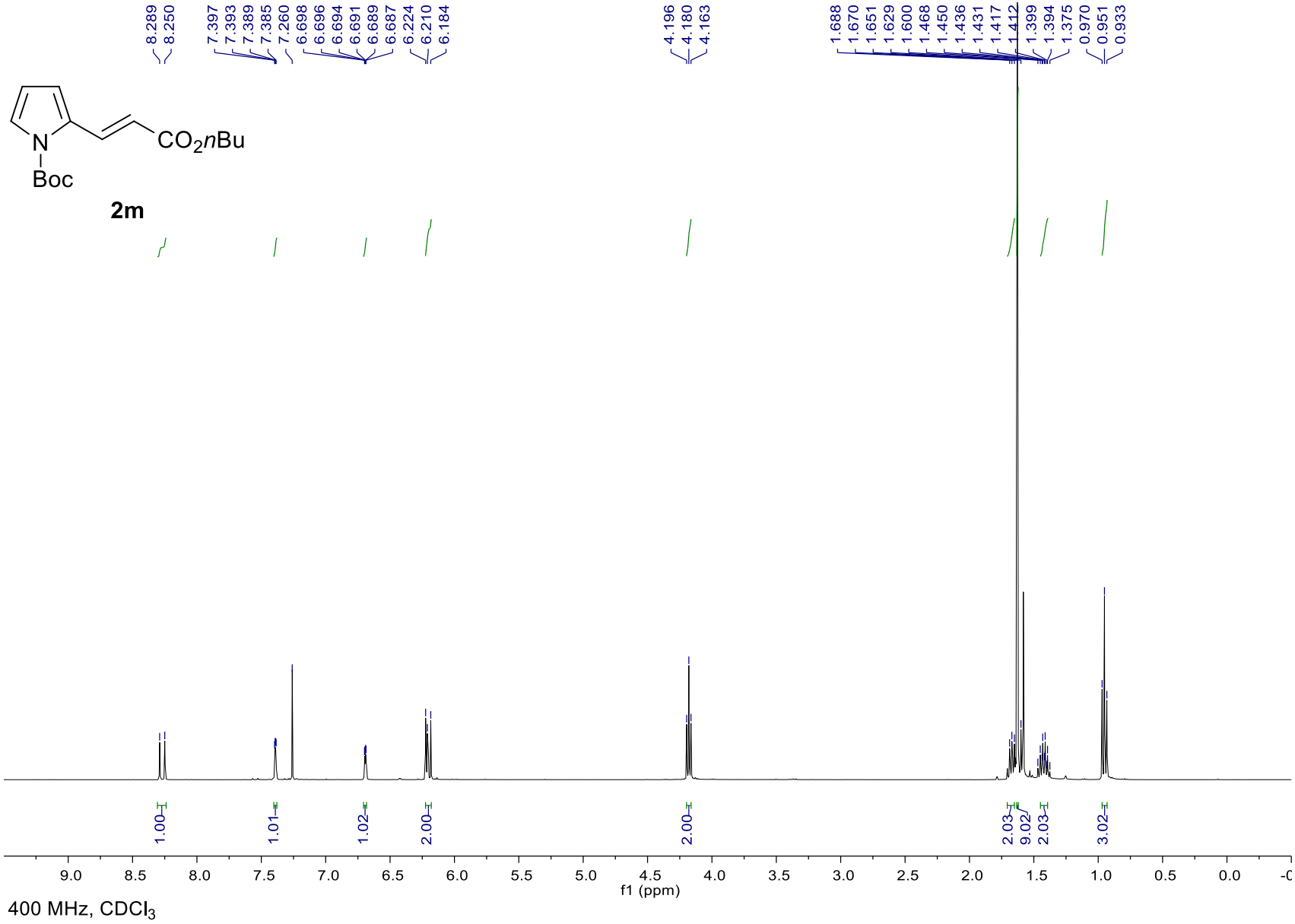
400 MHz, $CDCl_3$

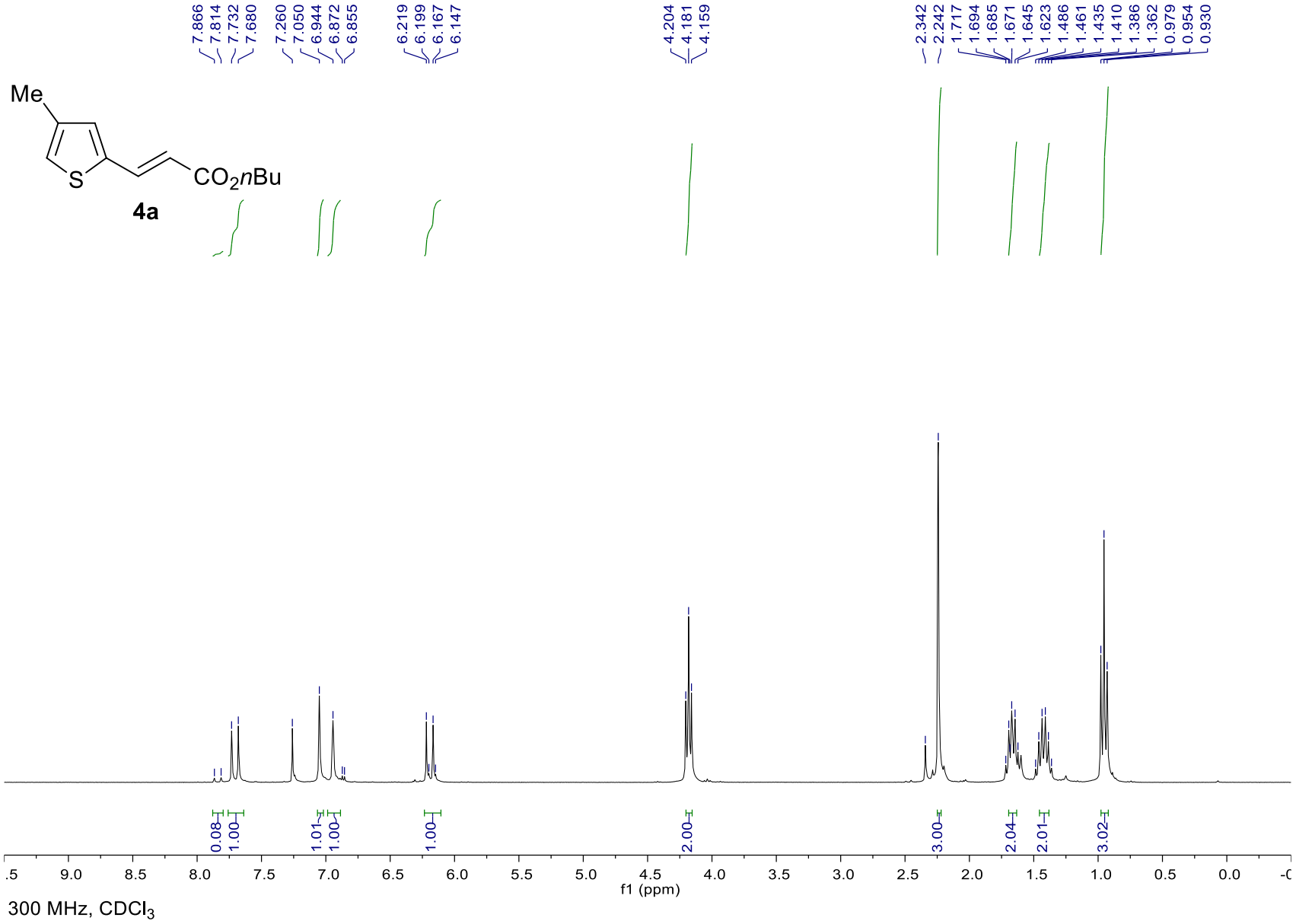

136.67
132.68
129.81
127.27
126.84
125.89
125.27
122.80
122.20
120.84
119.95
105.87
77.48
77.16
76.84
49.66
33.59
20.03
13.78
Cl
N
nBu
2j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
100 MHz, CDCl3

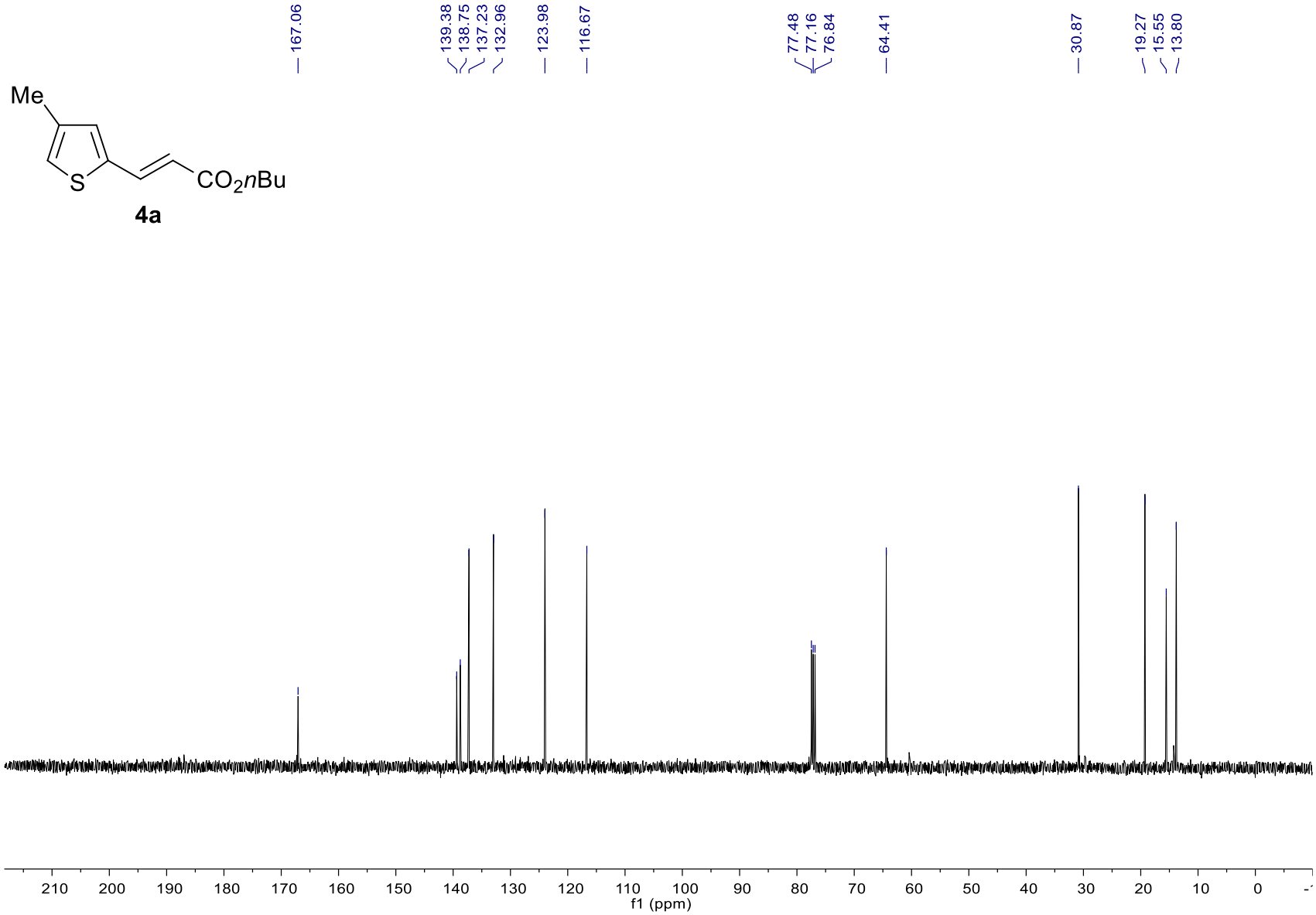


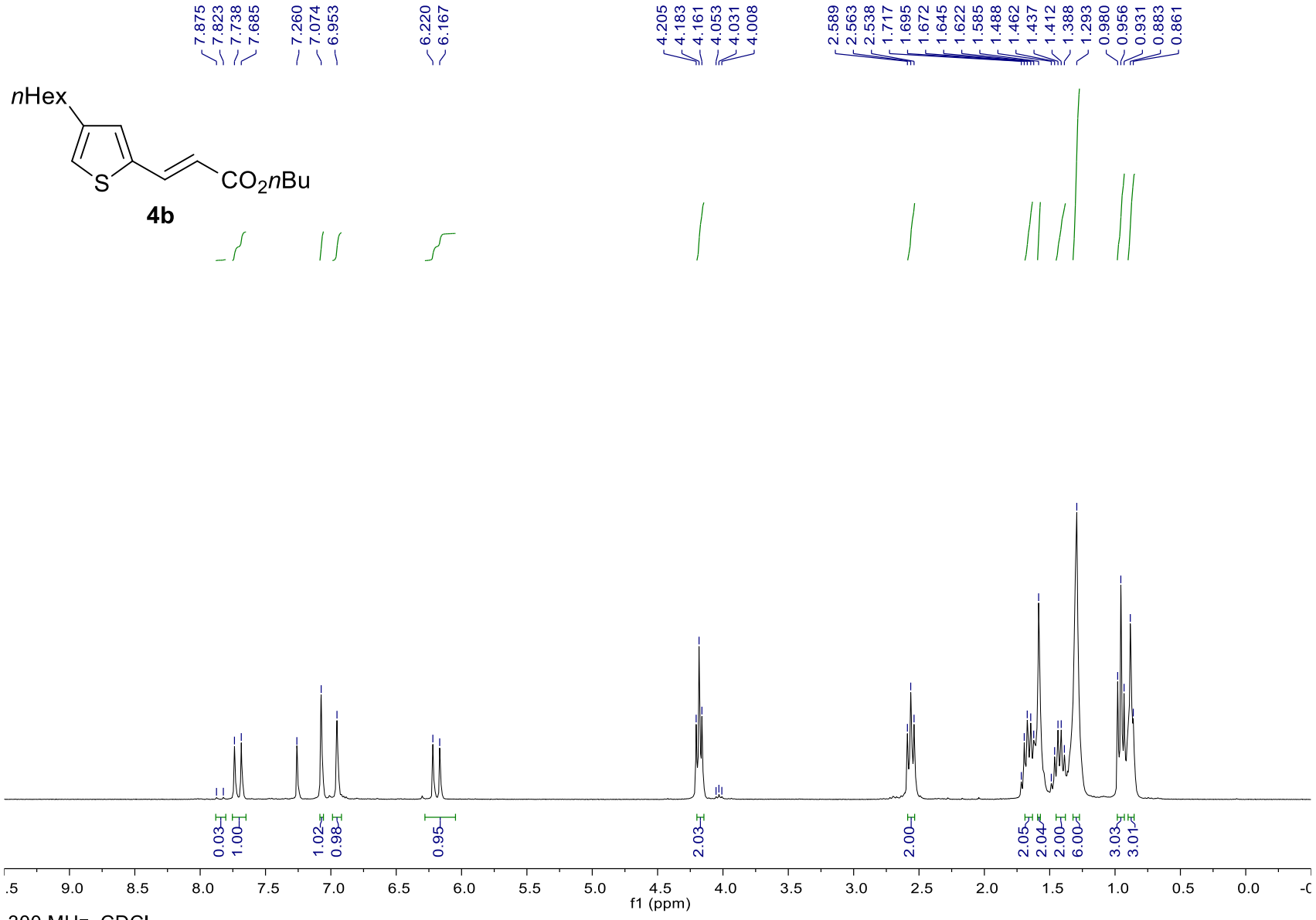

300 MHz, $CDCl_3$

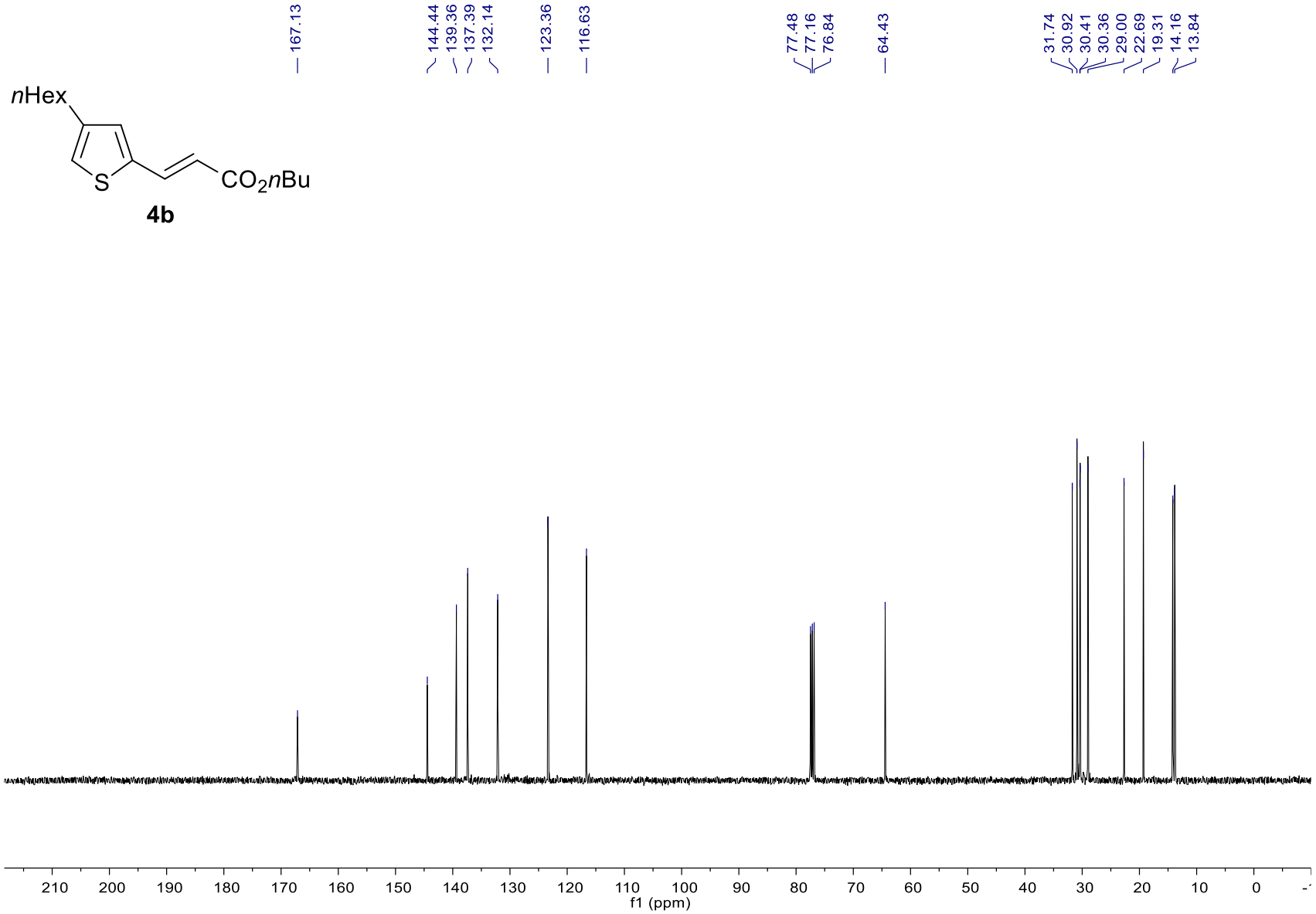

188.99
167.64
137.22
132.08
131.93
119.26
117.30
115.09
77.48
77.16
76.84
64.22
38.03
30.90
27.18
19.28
13.81
CO2nBu
Me
O
N
Me
2l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
100 MHz, CDCl3

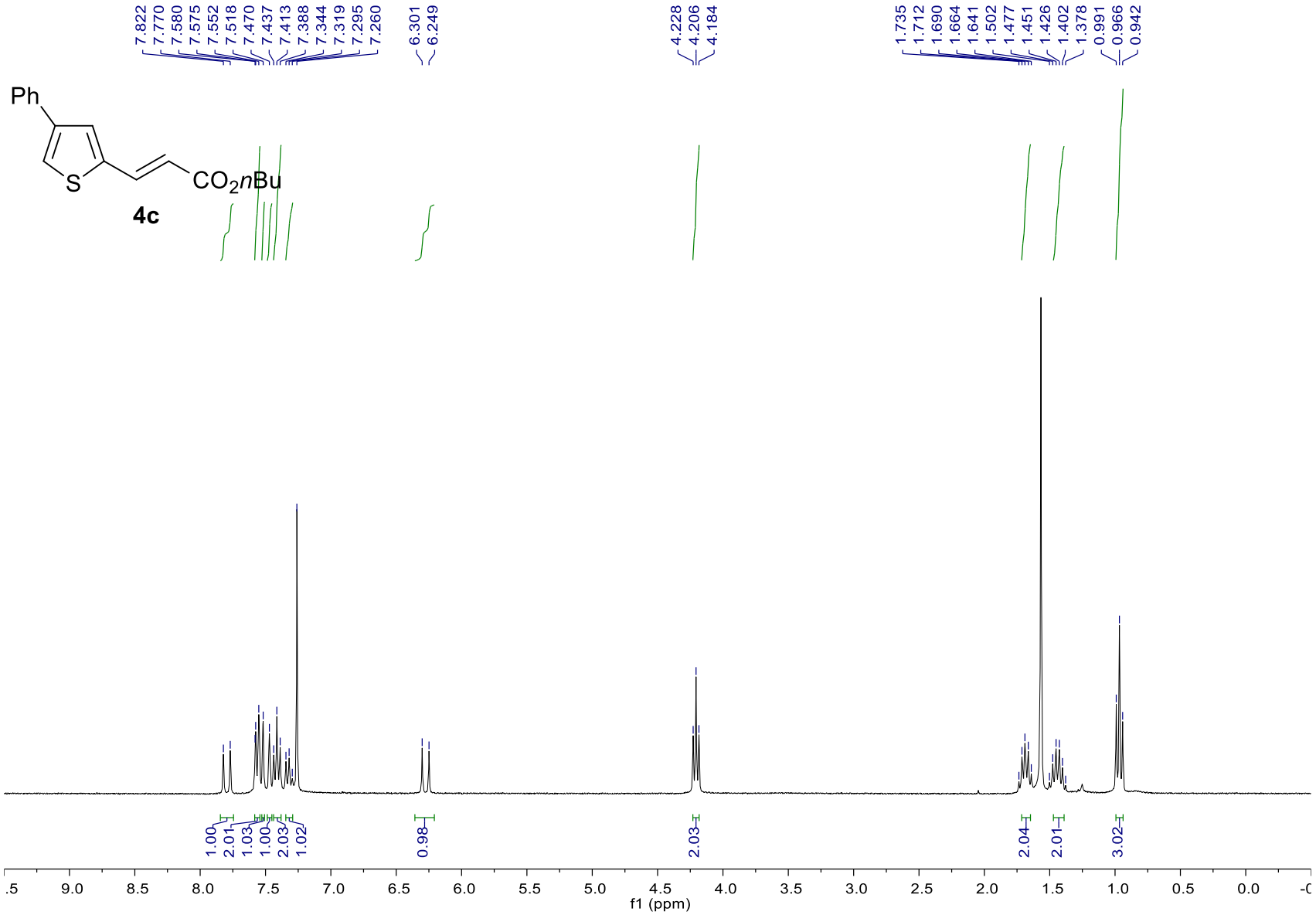

8.289
8.250
7.397
7.393
7.389
7.385
7.260
6.698
6.696
6.694
6.691
6.689
6.687
6.224
6.210
6.184
4.196
4.180
4.163
1.688
1.670
1.651
1.629
1.600
1.468
1.450
1.436
1.431
1.417
1.412
1.399
1.394
1.375
0.970
0.951
0.933
N
Boc
CO2nBu
2m
1.00
1.01
1.02
2.00
2.00
2.03
9.02
2.03
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
400 MHz, CDCl3

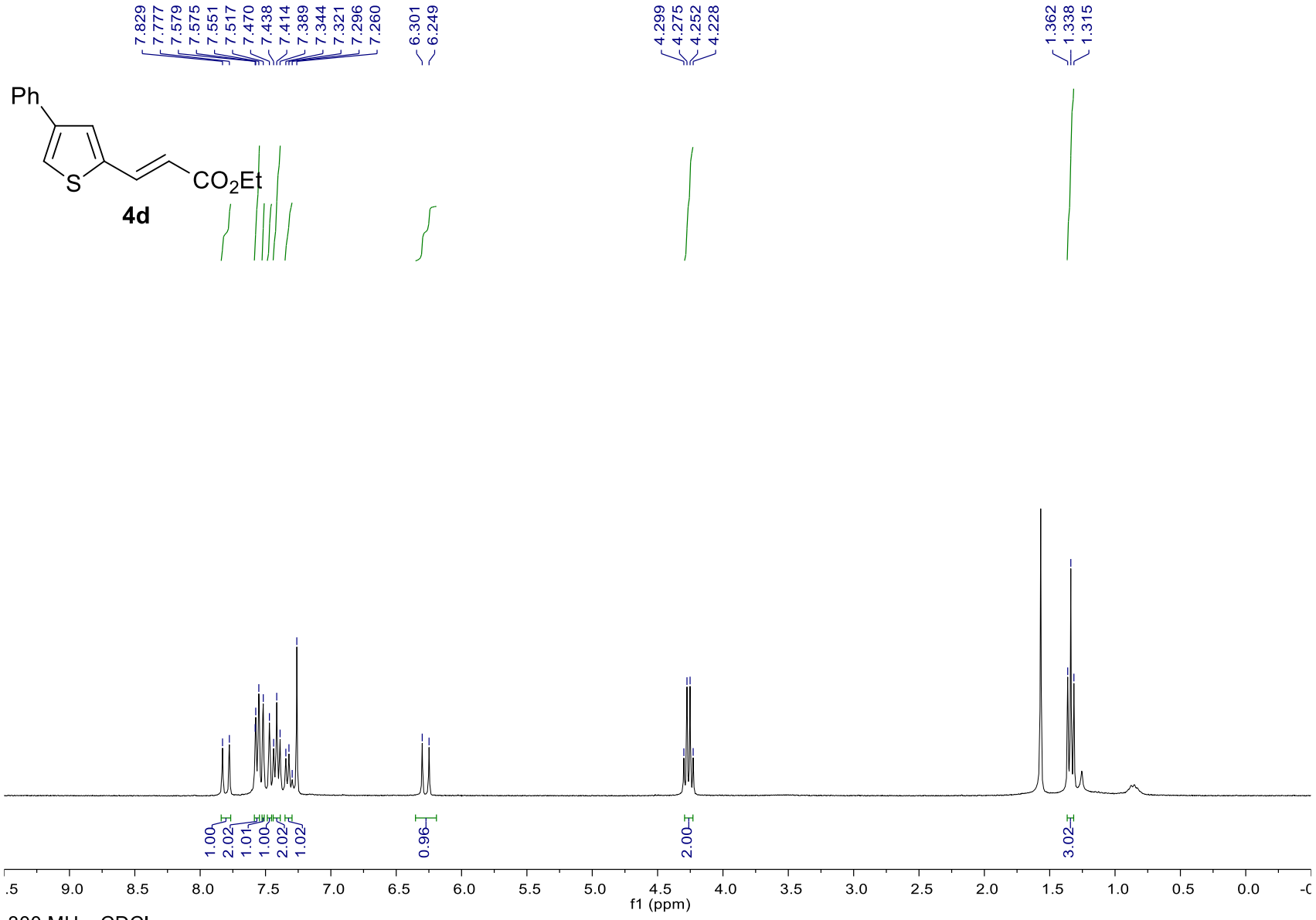

7.866
7.814
7.732
7.680
7.260
7.050
6.944
6.872
6.855
6.219
6.199
6.167
6.147
4.204
4.181
4.159
2.342
2.242
1.717
1.694
1.685
1.671
1.645
1.623
1.486
1.461
1.435
1.410
1.386
1.362
0.979
0.954
0.930
Me
S
CO2nBu
4a
0.08
1.00
1.01
1.00
1.00
2.00
3.00
2.04
2.01
3.02
f1 (ppm)
300 MHz, CDCl3


167.06
139.38
138.75
137.23
132.96
123.98
116.67
77.48
77.16
76.84
64.41
30.87
19.27
15.55
13.80
Me
S
CO2nBu
4a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
100 MHz, CDCl3

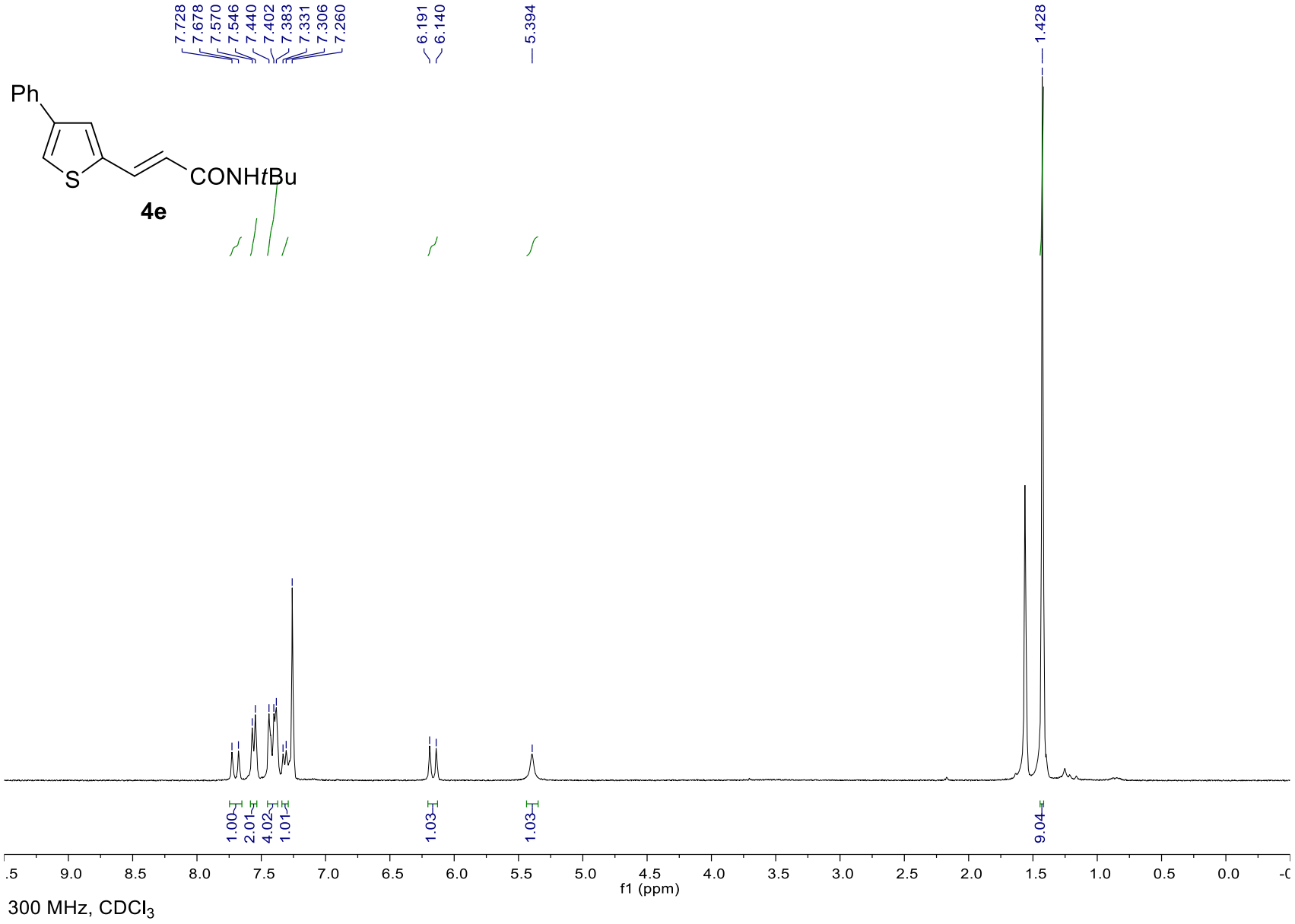

7.875
7.823
7.738
7.685
7.260
7.074
6.953
6.220
6.167
4.205
4.183
4.161
4.053
4.031
4.008
2.589
2.563
2.538
1.717
1.695
1.672
1.645
1.622
1.585
1.488
1.462
1.437
1.412
1.388
1.293
0.980
0.956
0.931
0.883
0.861
nHex
S
CO2nBu
4b
0.03
1.00
1.02
0.98
0.95
2.03
2.00
2.05
2.04
2.00
6.00
3.03
3.01
f1 (ppm)
300 MHz, CDCl3


167.13
144.44
139.36
137.39
132.14
123.36
116.63
77.48
77.16
76.84
64.43
31.74
30.92
30.41
30.36
29.00
22.69
19.31
14.16
13.84
nHex
S
CO2nBu
4b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
100 MHz, CDCl3

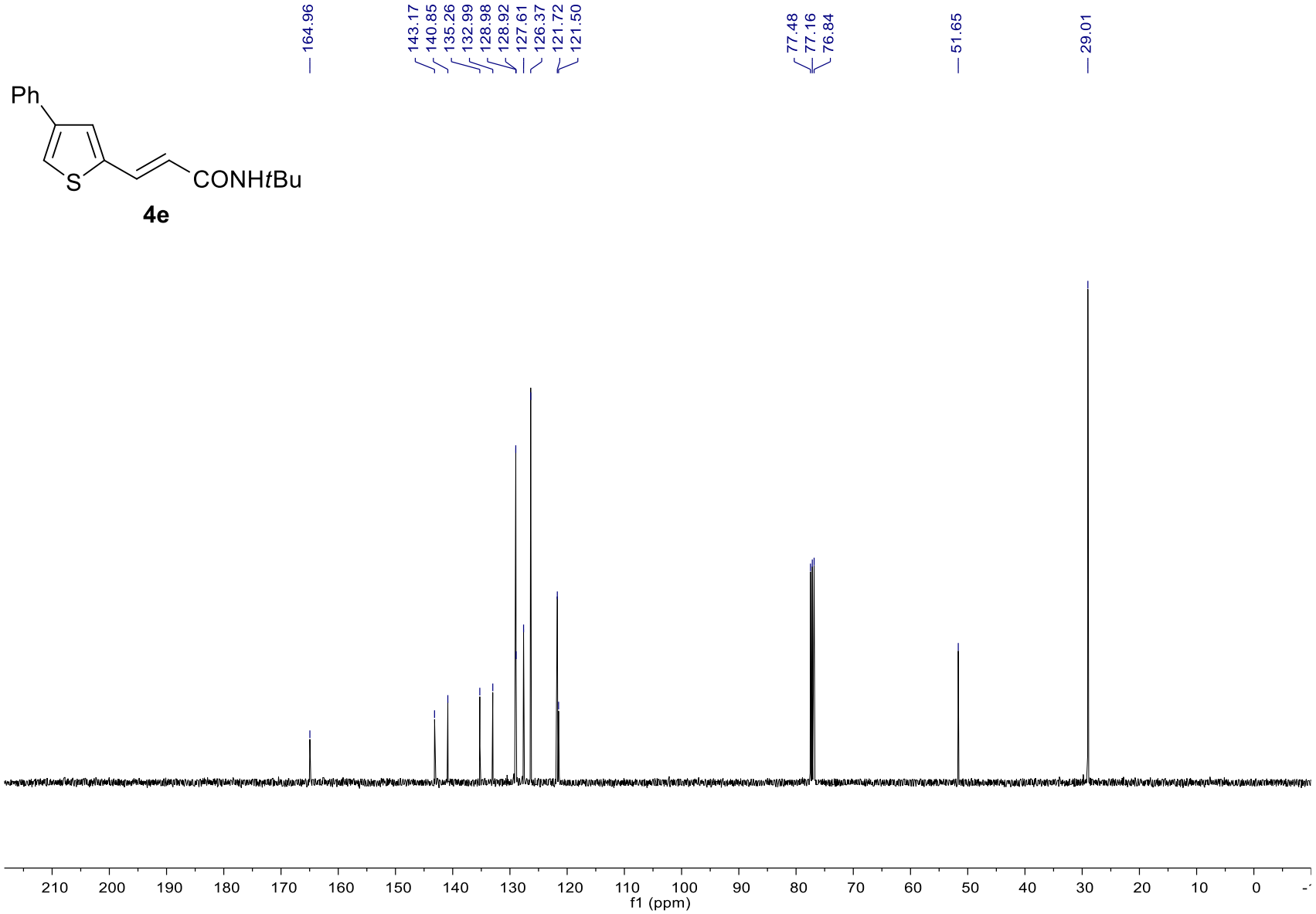

7.822
7.770
7.580
7.575
7.552
7.518
7.470
7.437
7.413
7.388
7.344
7.319
7.295
7.260
6.301
6.249
4.228
4.206
4.184
1.735
1.712
1.690
1.664
1.641
1.502
1.477
1.451
1.426
1.402
1.378
0.991
0.966
0.942
Ph
S
CO2nBu
4c
1.00
2.01
1.03
1.00
2.03
1.02
0.98
2.03
2.04
2.01
3.02
f1 (ppm)
300 MHz, CDCl3

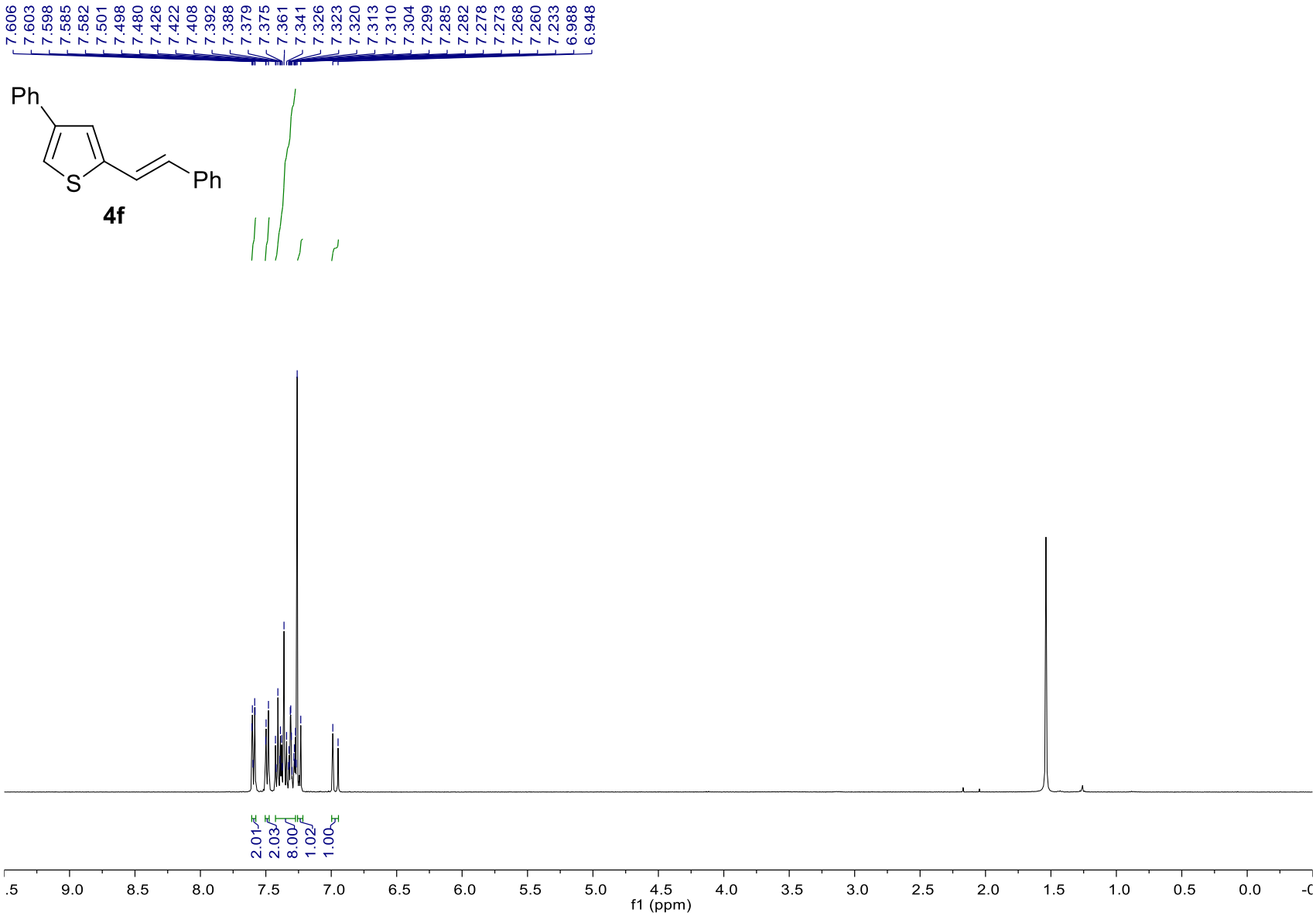


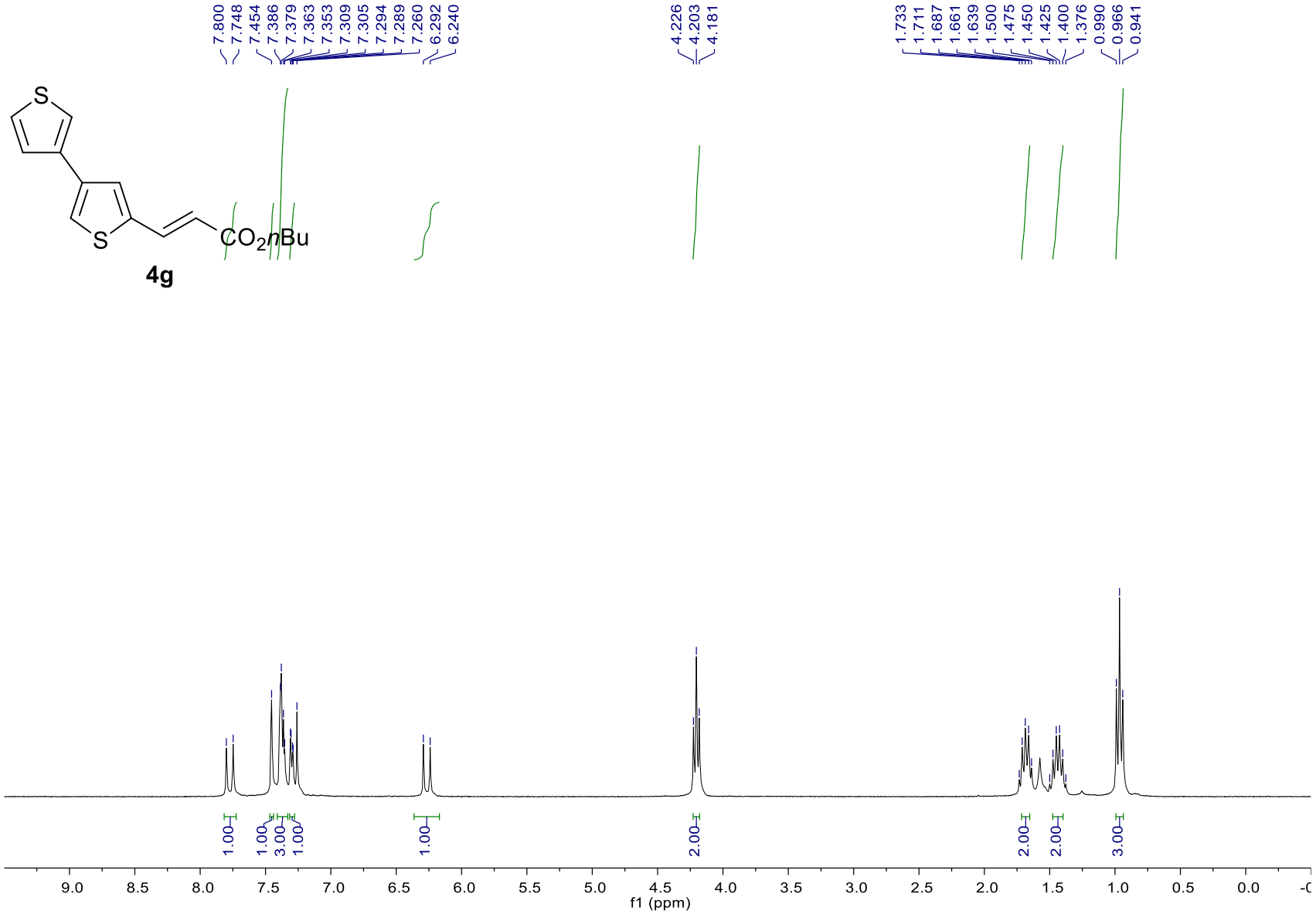

300 MHz, $CDCl_3$



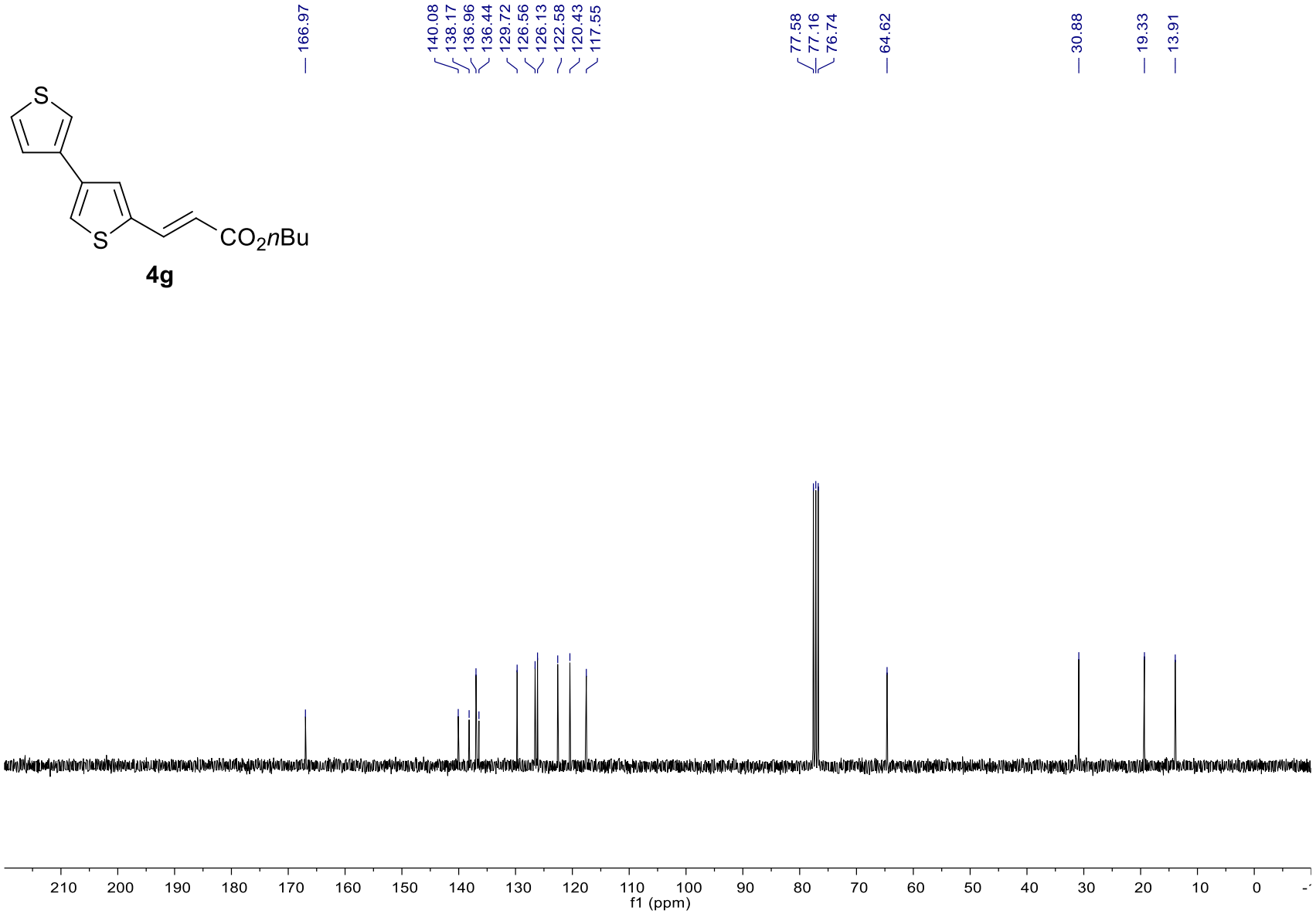

300 MHz, $CDCl_3$

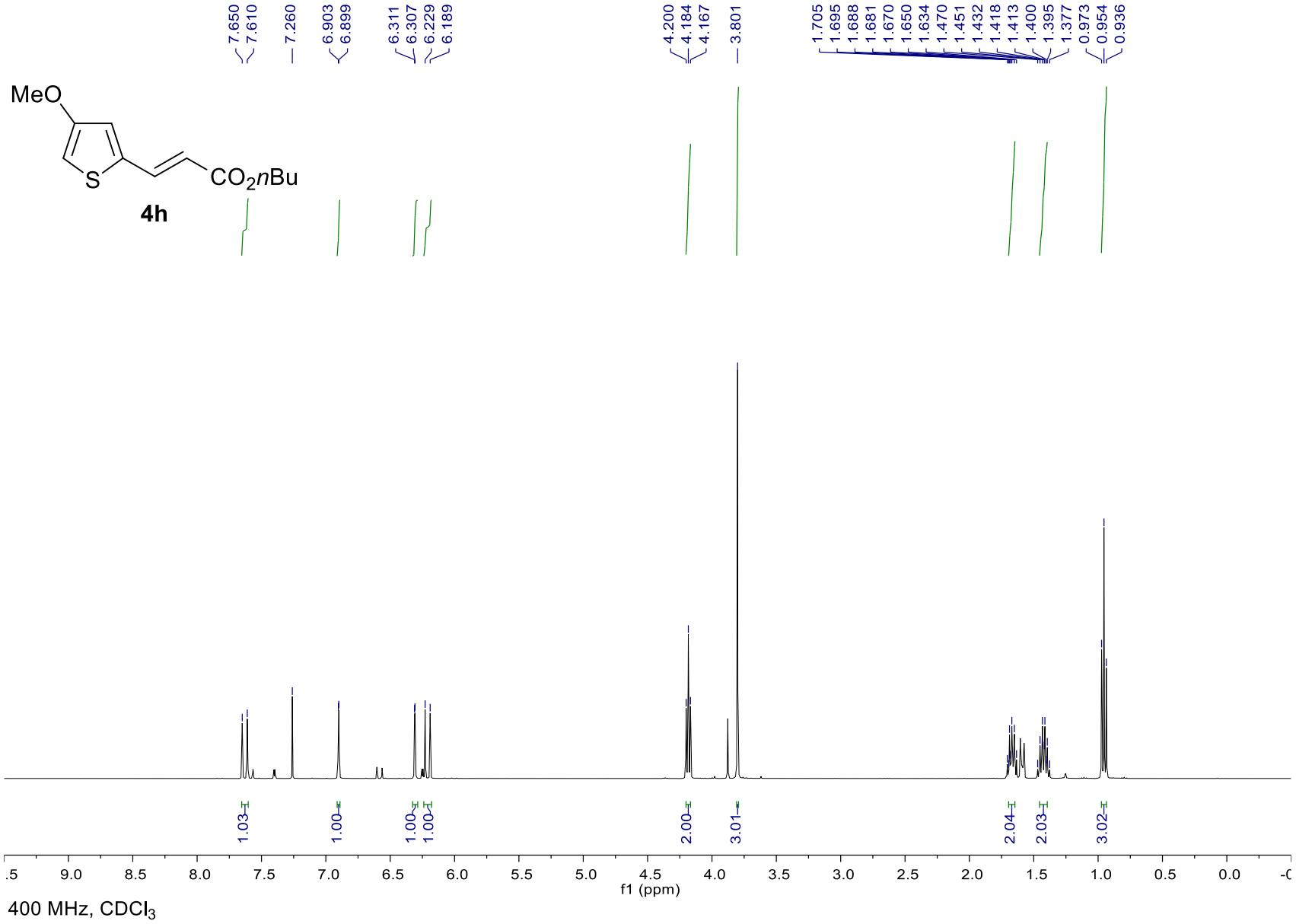

164.96
143.17
140.85
135.26
132.99
128.98
128.92
127.61
126.37
121.72
121.50
77.48
77.16
76.84
51.65
29.01
Ph
S
CONHtBu
4e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
100 MHz, CDCl3

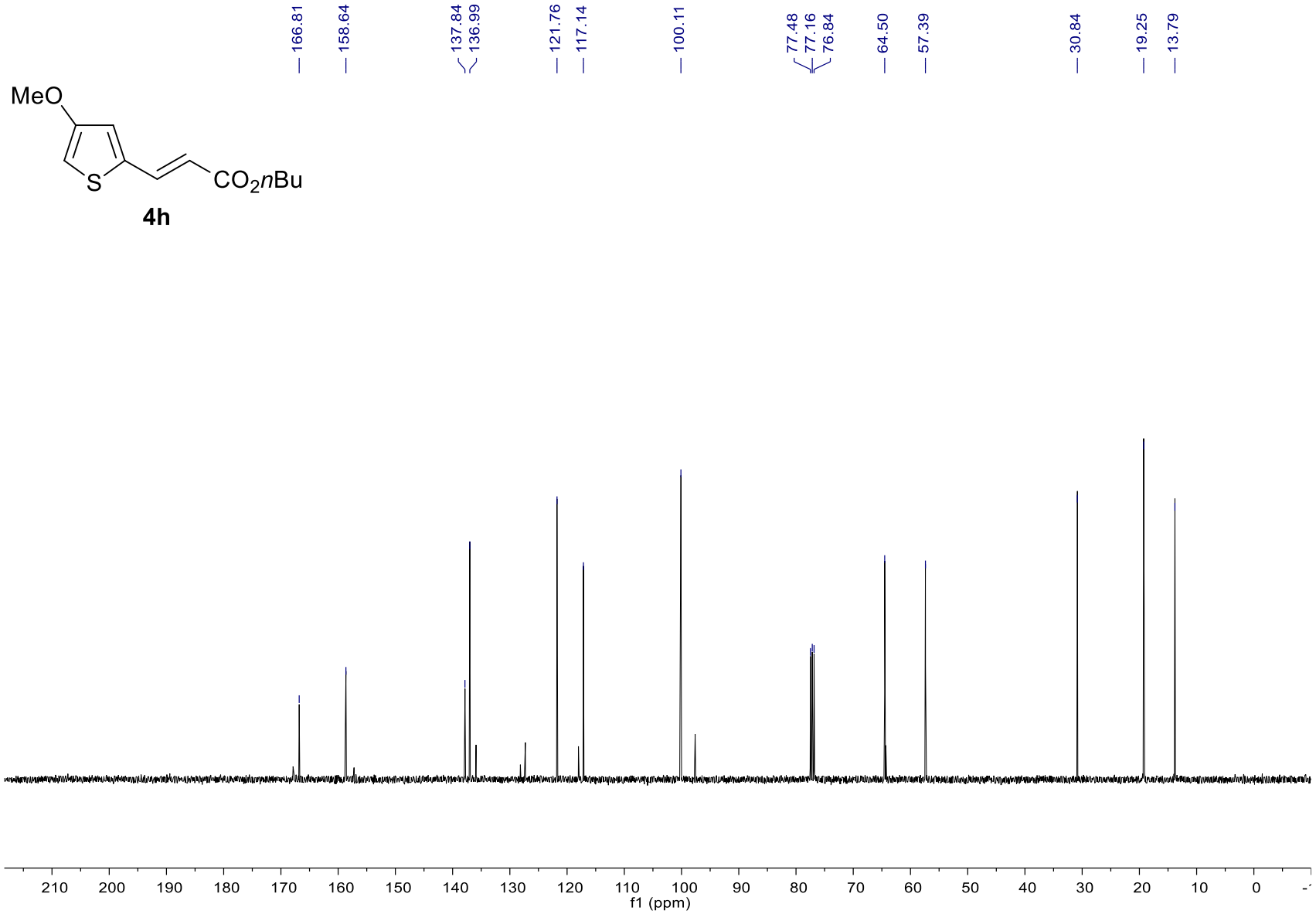

7.606
7.603
7.598
7.585
7.582
7.501
7.498
7.480
7.426
7.422
7.408
7.392
7.388
7.379
7.375
7.361
7.341
7.326
7.323
7.320
7.313
7.310
7.304
7.299
7.285
7.282
7.278
7.273
7.268
7.260
7.233
6.988
6.948
Ph
S
Ph
4f
2.01
2.03
8.00
1.02
1.00
f1 (ppm)
300 MHz, CDCl3

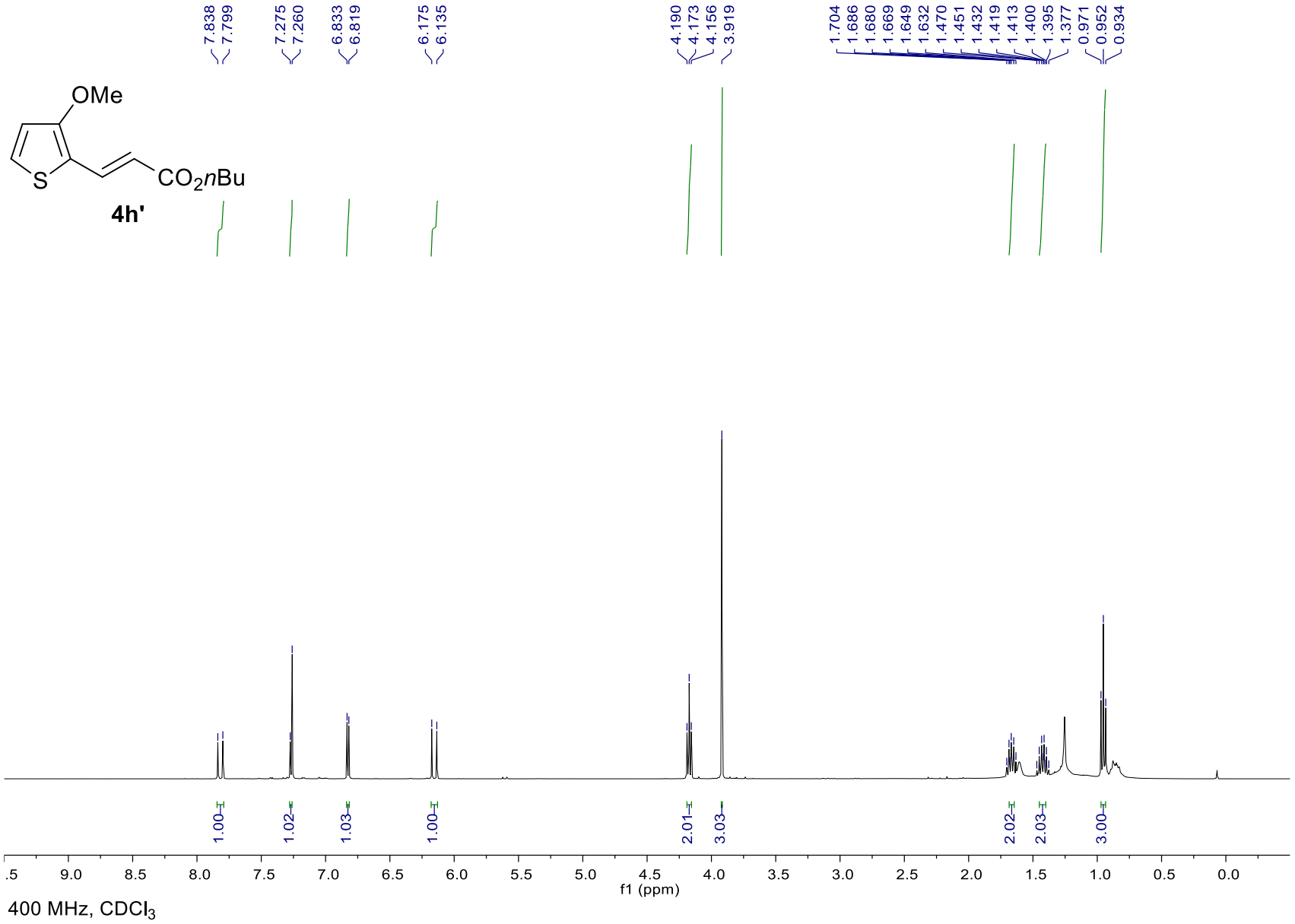


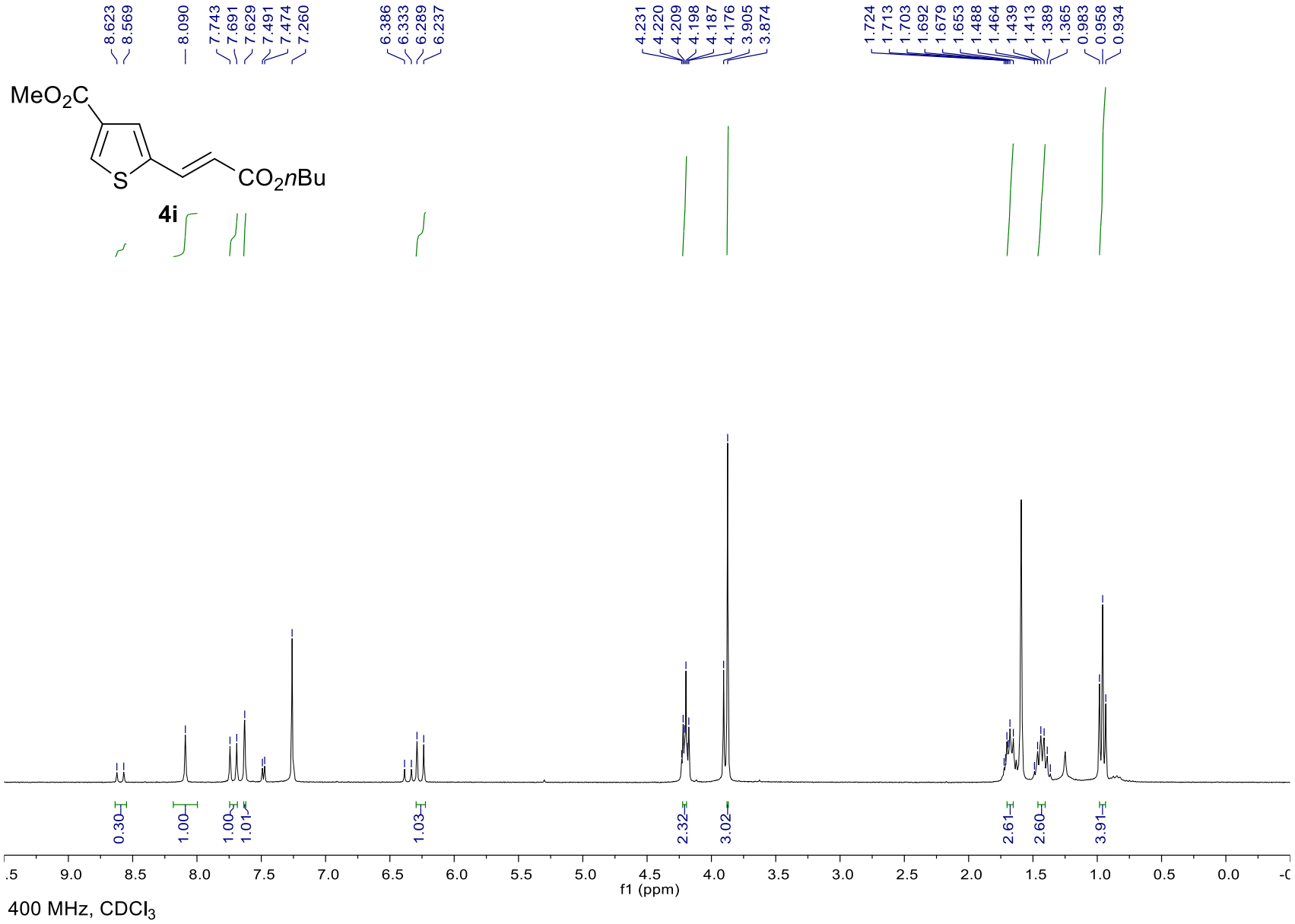

300 MHz, $CDCl_3$

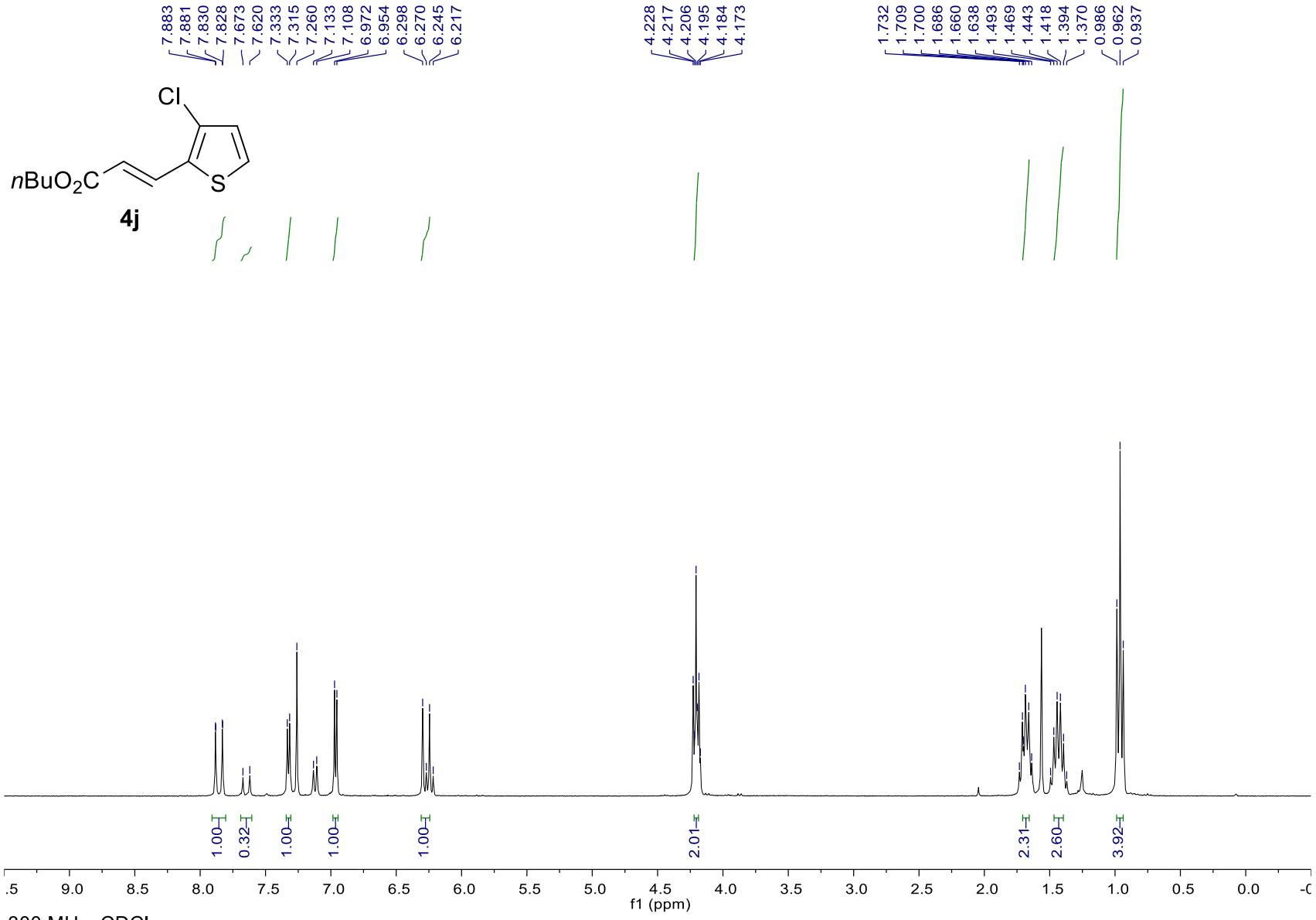

166.97
140.08
138.17
136.96
136.44
129.72
126.56
126.13
122.58
120.43
117.55
77.58
77.16
76.74
64.62
30.88
19.33
13.91
S
S
CO2nBu
4g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
75 MHz, CDCl3


7.650
7.610
7.260
6.903
6.899
6.311
6.307
6.229
6.189
4.200
4.184
4.167
3.801
1.705
1.695
1.688
1.681
1.670
1.650
1.634
1.470
1.451
1.432
1.418
1.413
1.400
1.395
1.377
0.973
0.954
0.936
MeO
S
CO2nBu
4h
1.03
1.00
1.00
1.00
2.00
3.01
2.04
2.03
3.02
f1 (ppm)
400 MHz, CDCl3

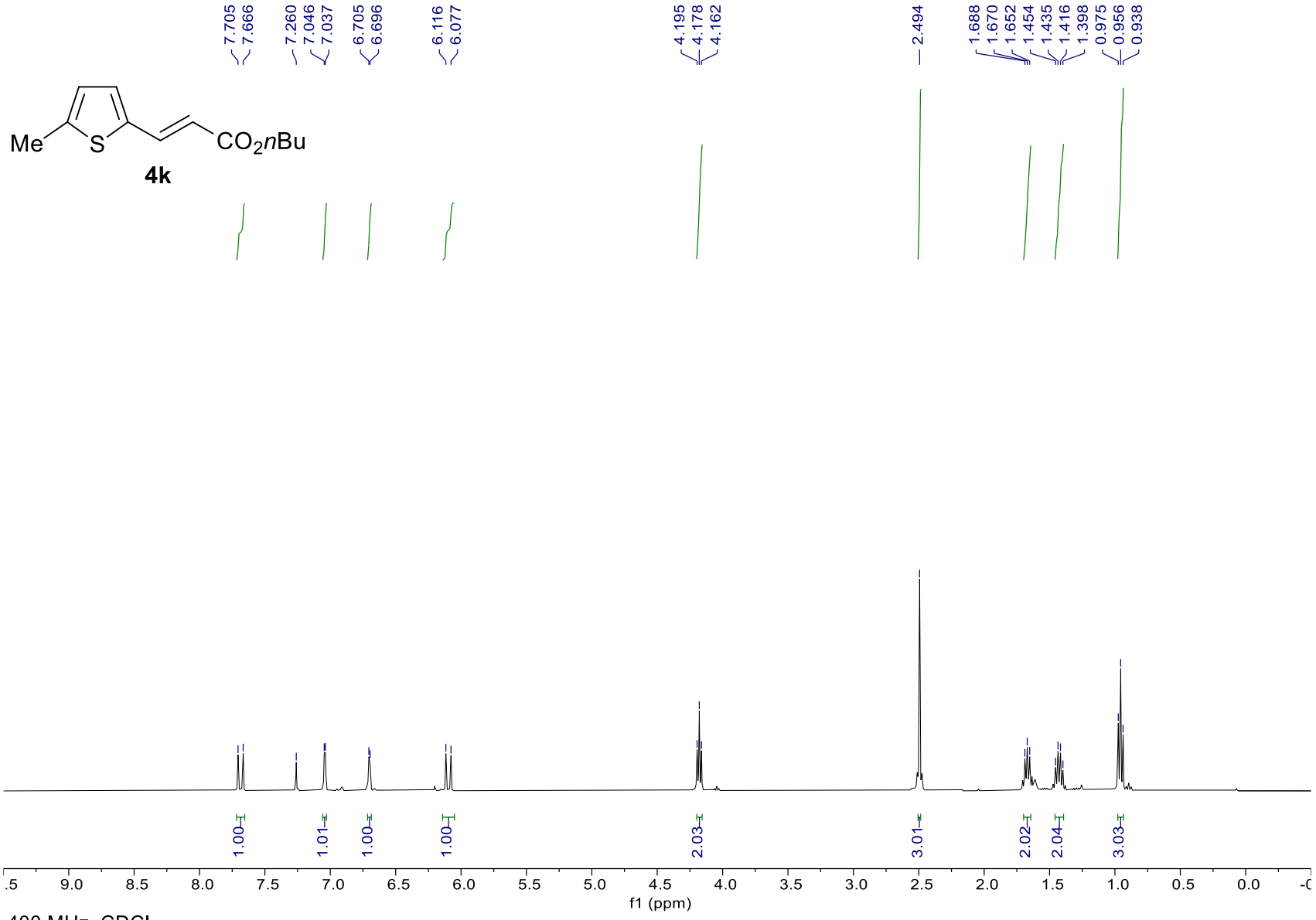

166.81
158.64
137.84
136.99
121.76
117.14
100.11
77.48
77.16
76.84
64.50
57.39
30.84
19.25
13.79
MeO
S
CO2nBu
4h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
100 MHz, CDCl3


7.838
7.799
7.275
7.260
6.833
6.819
6.175
6.135
4.190
4.173
4.156
3.919
1.704
1.686
1.680
1.669
1.649
1.632
1.470
1.451
1.432
1.419
1.413
1.400
1.395
1.377
0.971
0.952
0.934
OMe
S
CO2nBu
4h'
1.00
1.02
1.03
1.00
2.01
3.03
2.02
2.03
3.00
f1 (ppm)
400 MHz, CDCl3

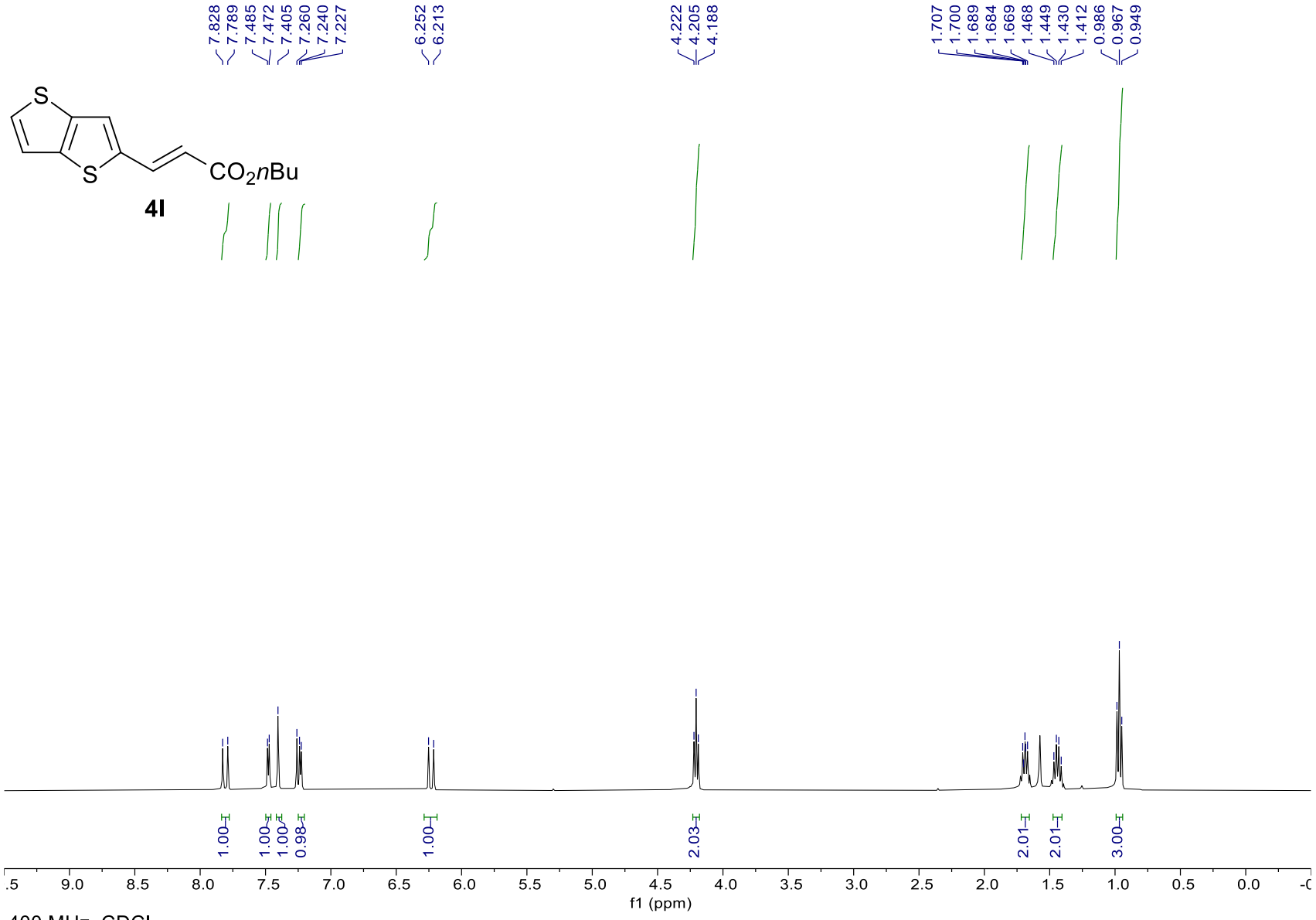

8.623
8.569
8.090
7.743
7.691
7.629
7.491
7.474
7.260
6.386
6.333
6.289
6.237
4.231
4.220
4.209
4.198
4.187
4.176
3.905
3.874
1.724
1.713
1.703
1.692
1.679
1.653
1.488
1.464
1.439
1.413
1.389
1.365
0.983
0.958
0.934
MeO2C
S
CO2nBu
4i
0.30
1.00
1.00
1.01
1.03
2.32
3.02
2.61
2.60
3.91
f1 (ppm)
400 MHz, CDCl3




300 MHz, $CDCl_3$




400 MHz, $CDCl_3$


7.828
7.789
7.485
7.472
7.405
7.260
7.240
7.227
6.252
6.213
4.222
4.205
4.188
1.707
1.700
1.689
1.684
1.669
1.468
1.449
1.430
1.412
0.986
0.967
0.949
S
S
CO2nBu
4I
1.00
1.00
1.00
0.98
1.00
2.03
2.01
2.01
3.00
f1 (ppm)
400 MHz, CDCl3