Supplementary Information

Polymeric Iridium Catalysts for C–H Borylation under Batch and Continuous Flow Conditions

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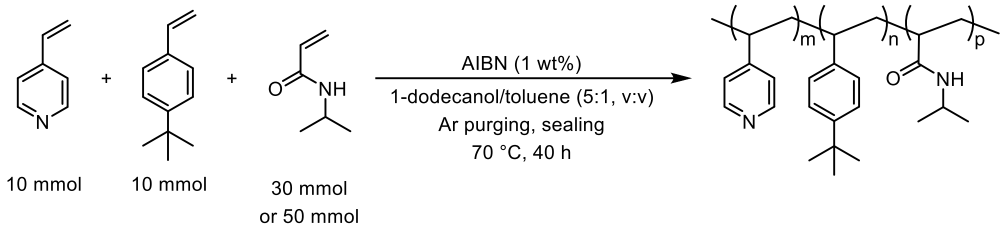
1. General Information

All reagents and solvents were obtained from commercial sources and used as received. Sodium hexachloroiridate(III) hydrate [$Na_3IrCl_6 \cdot xH_2O$] was purchased from Merck Chemicals Ltd., and Iridium(III) chloride hydrate was purchased from Tokyo Chemical Industry Co., Ltd.. Water was deionized with a Millipore system as a Milli-Q grade. All manipulations were performed under atmospheric conditions otherwise noted. Analytical thin-layer chromatography (TLC) was performed on glass plates pre-coated silica gel (Merck: Art 5715, Kieselgel 60 F254, 0.25 mm). Column chromatography was performed with silica gel (Wakogel C-300). Visualization was accomplished by UV light (254 nm).

GC analysis was measured by an Agilent 6850 equipped with a capillary column (Agilent HP-1, 30 m, 0.32 mm i.d.), GC-MS was measured by Agilent 7890B/5977B MSD equipped with a capillary column (Agilent HP-1-MS, 30 m, 0.25 mm i.d.). ESI-MS was measured by Bruker micrOTOF QIII. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a JEOL JNM-ECZL500G spectrometer. Chemical shifts for ^{1}H NMR were reported in parts per million of tetramethylsilane (TMS, 0.00 ppm) as internal standards. Chemical shifts for ^{13}C NMR were reported relative to $CDCl_3$ (77.0 ppm). Inductively coupled plasma mass spectrometry (ICP-MS) measurement was performed using Perkin Elmer Nexion 300D. The sample was pretreated by microwave digestion technique with high-purity nitric acid (69%, obtained from Kanto Chemical, Ultrapure-100 grade) as solvent (7 mL) using Perkin Elmer Titan MPS microwave sample preparation system. XAFS measurements were performed at the BL14B2 beamline of the synchrotron SPring-8 in Japan under standard beamline conditions. The Ir L_3-edge (11.21 keV) XAFS data were collected by transmission mode using Ar/Kr mixed gas-filled ionization chambers with the optimized gas ratio and pressure with Si (111) double-crystal monochromator. For the energy calibration of XANES spectra of Ir L_3-edge, iridium powder was used as a reference sample to set the inflection point determined by the maximum first-derivative of XANES spectra to 11214.9529 eV. Sample pellets of references and polymeric Ir catalysts were prepared with a BN dilution. XAFS data processing was carried out by using Athena and Artemis software.[S1], [S2]

2. Preparation of Copolymers



The stabilizer (hydroquinone, HQ) in 4-vinylpyridine (4VP) was removed by column chromatography with activated Al_2O_3 (~300 mesh, purchased from FUJIFILM Wako Pure Chemical Corporation). The stabilizer (4-*tert*-butylcatechol, TBC) in 4-*tert*-butylstyrene (4tBS) was washed out with aq. NaOH (0.9 M) in a separating funnel three times, and the resulting organic layer was washed with brine and dried over anhydrous $MgSO_4$ prior to use. *N*-Isopropylacrylamide (NIPAAm) was used as received.

The polymerization was carried out in a 50 mL two-necked round-bottomed flask equipped with a stopcock. The flask was charged with 10 mL of 1-dodecanol and 2 mL of toluene. The atmosphere was exchanged with argon gas three times, followed by the addition of 1.051 g (10 mmol) of 4VP, 1.603 g (10 mmol) of 4tBS, 3.395 g (30 mmol) or 5.658 g (50 mmol) of NIPAAm, and 1 wt% of AIBN relative to the total amount of monomers. The flask was sealed after exchanging the atmosphere with argon gas five more times, and the mixture was stirred at 70 °C. After 40 h, the formed precipitate was transferred into a 200 mL beaker, washed with hexane and H_2O, and dried under reduced pressure overnight to obtain the corresponding copolymers, which were then ground in a mortar. For copolymer F (using 30 mmol NIPAAm), 4.895 g (81% yield) of white powder was obtained. For copolymer G (using 50 mmol NIPAAm), 5.755 g (69% yield) of white powder was obtained.

The monomer composition of the prepared copolymers was investigated by ^1H NMR spectroscopy (solvent: $CDCl_3$), as shown below. For copolymer F, the ratio of 4VP, 4tBS, and NIPAAm was determined to be 1:1:2.4. For copolymer G, the ratio of 4VP, 4tBS, and NIPAAm was found to be 1:1:4.

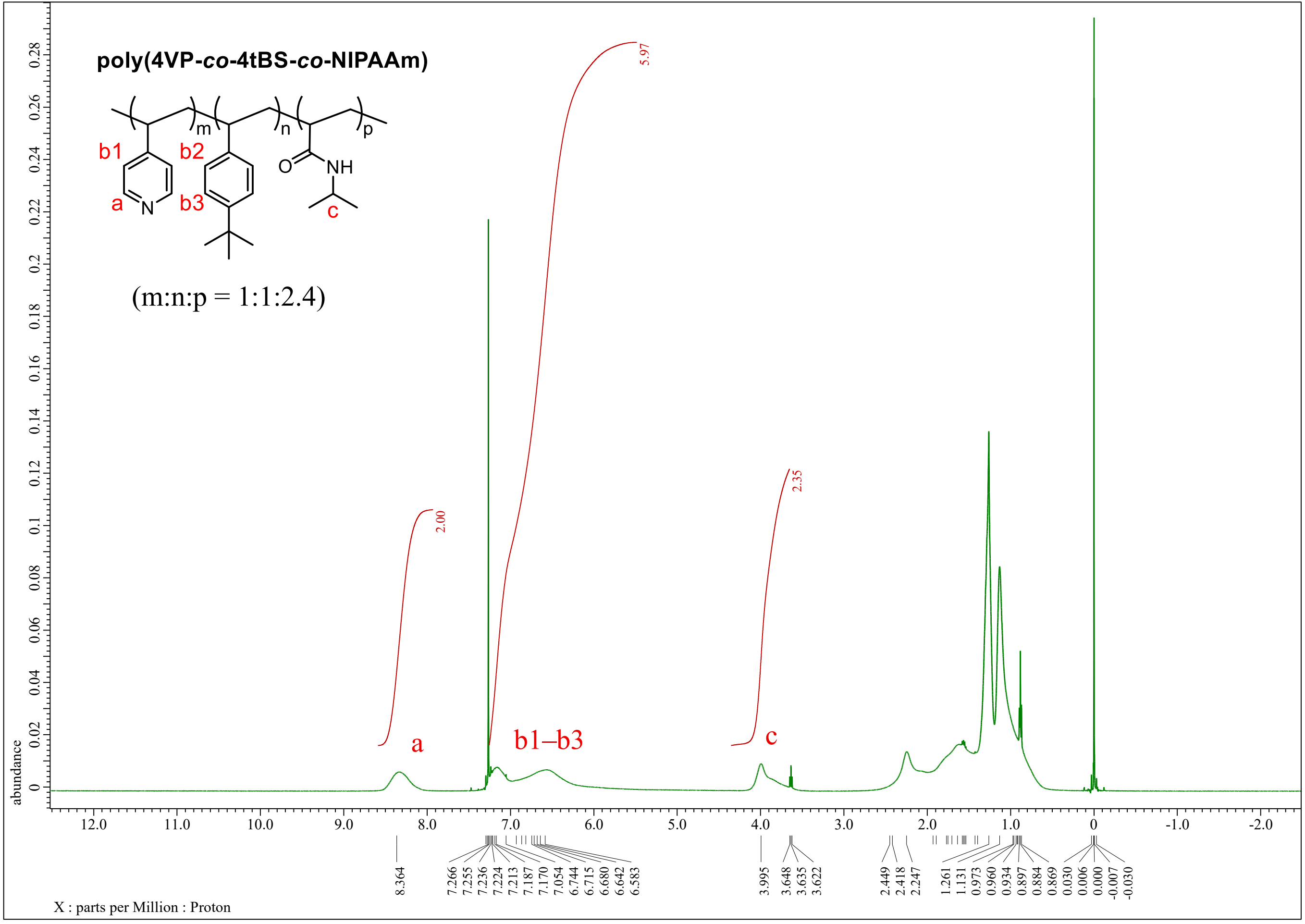


Fig. 1 ^1H NMR spectrum of poly(4VP-*co*-4tBS-*co*-NIPPAm) (4VP:4tBS:NIPAAm = 1:1:2.4).

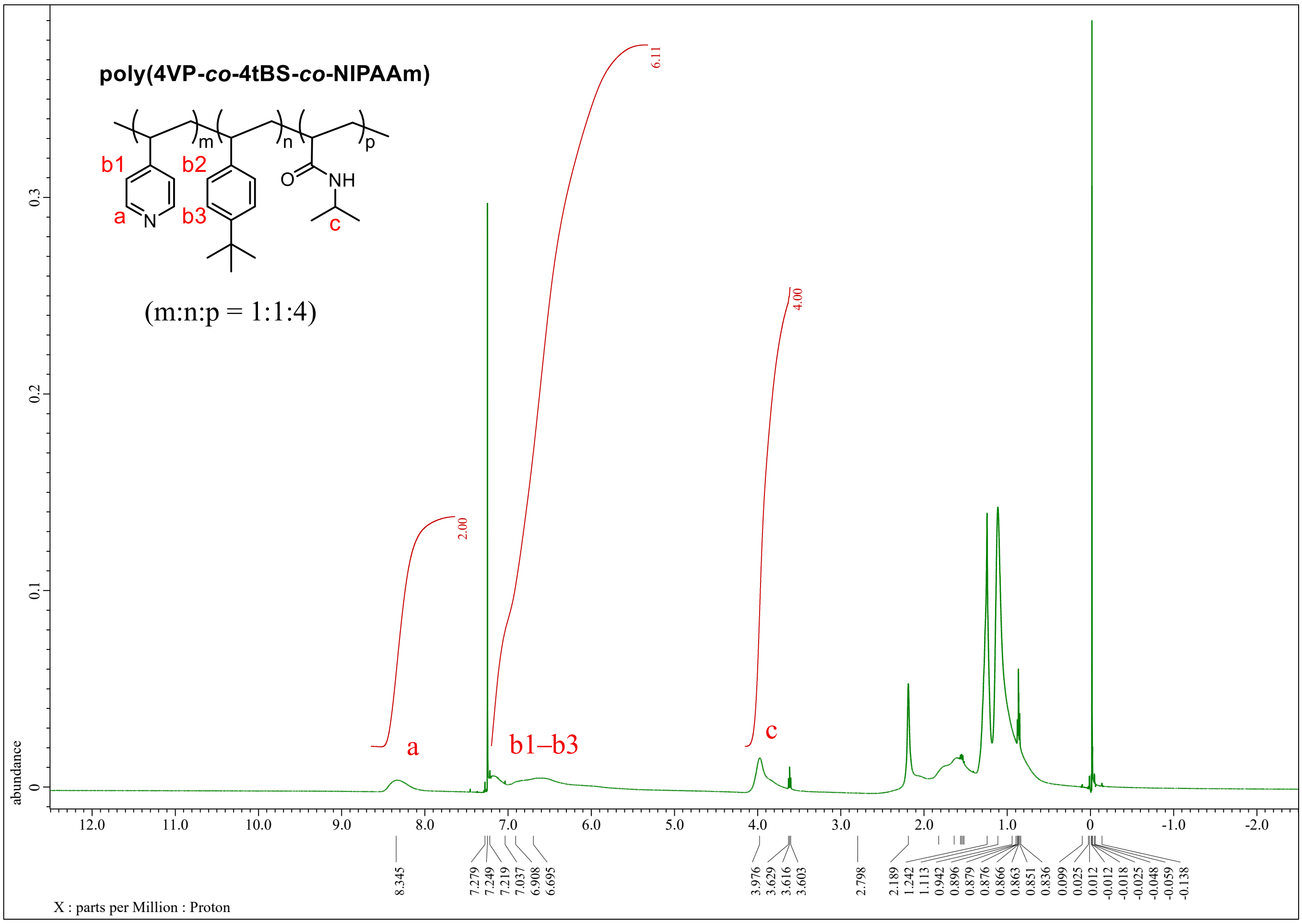
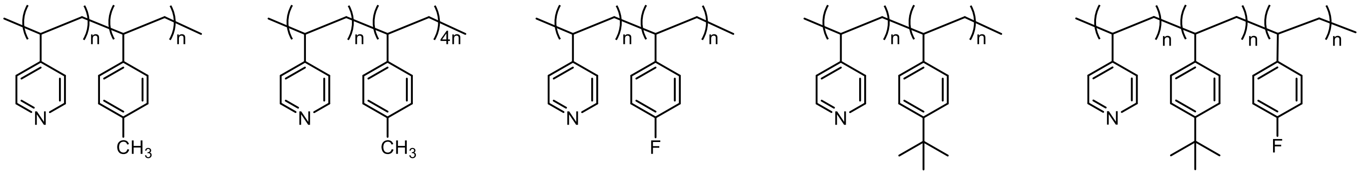


Fig. 2 ^{1}H NMR spectrum of poly(4VP-*co*-4tBS-*co*-NIPAAm) (4VP:4tBS:NIPAAm = 1:1:4).

Other copolymers mentioned in this work were prepared with similar procedures. The structure of the copolymers is shown below.



poly(4VP-*co*-4MeS) (4VP:4MeS = 1:1)

poly(4VP-*co*-4MeS) (4VP:4MeS = 1:4)

poly(4VP-*co*-4FS) (4VP:4FS = 1:1)

poly(4VP-*co*-4tBS) (4VP:4tBS = 1:1)

poly(4VP-*co*-4tBS-*co*-4FS) (4VP:4tBS:4FS = 1:1:1)

Fig. 3 Prepared copolymers.

3. Preparation of Polymeric Ir Catalysts

3.1 Preparation of P4VP-Ir catalyst: To a 50 mL flask, 126.0 mg (1.2 mmol) of poly(4-vinylpyridine) (P4VP, average Mw ~160000, purchased from Merck Chemicals Ltd.) was dissolved in 7.2 mL of EtOH and stirred at 23 °C. Iridium chloride hydrate ($IrCl_3 \cdot xH_2O$, 119.4 mg, 0.4 mmol, anhydrous basis) was dissolved in 2.4 mL of H_2O and added dropwise to the P4VP solution. The atmosphere was exchanged with argon three times, and the flask was sealed. The mixture was then stirred at 60 °C for 24 h, resulting in the formation of a yellow precipitate. The insoluble material was collected by filtration, washed with H_2O and MeOH, and dried under reduced pressure overnight to obtain 231.3 mg of the P4VP-Ir catalyst (yield: 94%). The filtrate was observed to be a clear, colorless solution. The iridium loading was calculated as 31.3 wt%.

Fig. 4 Preparation of P4VP-Ir catalyst.

3.2 Representative procedures for preparing the polymeric Ir catalyst: To a 20 mL flask, 997.4 mg of poly(4VP-*co*-4tBS-*co*-NIPAAm) (4VP:4tBS:NIPAAm = 1:1:4) was dispersed in 6 mL of EtOH and stirred at 23 °C. $Na_3IrCl_6 \cdot xH_2O$ (189.6 mg, 0.4 mmol, anhydrous basis) was dissolved in 2 mL of H_2O and added dropwise to the copolymer solution. The mixture was stirred at 23 °C under air for 1 h, resulting in the formation of a gray precipitate. Subsequently, 8 mL of a mixed solvent (EtOH/H_2O = 3:1) was added to the flask. The atmosphere was exchanged with argon three times, and the flask was sealed. The mixture was then stirred at 60 °C for 24 h, yielding a yellow precipitate. The insoluble material was collected by filtration, washed with H_2O and MeOH, and dried under reduced pressure overnight to obtain 1043.2 mg of the poly(4VP-*co*-4tBS-*co*-NIPAAm)-Ir (4VP:4tBS:NIPAAm = 1:1:4) catalyst (yield: 93%). The filtrate was observed to be a clear, colorless solution. The iridium loading was measured by ICP-MS, confirming an Ir content of 5.6 wt% in the catalyst.

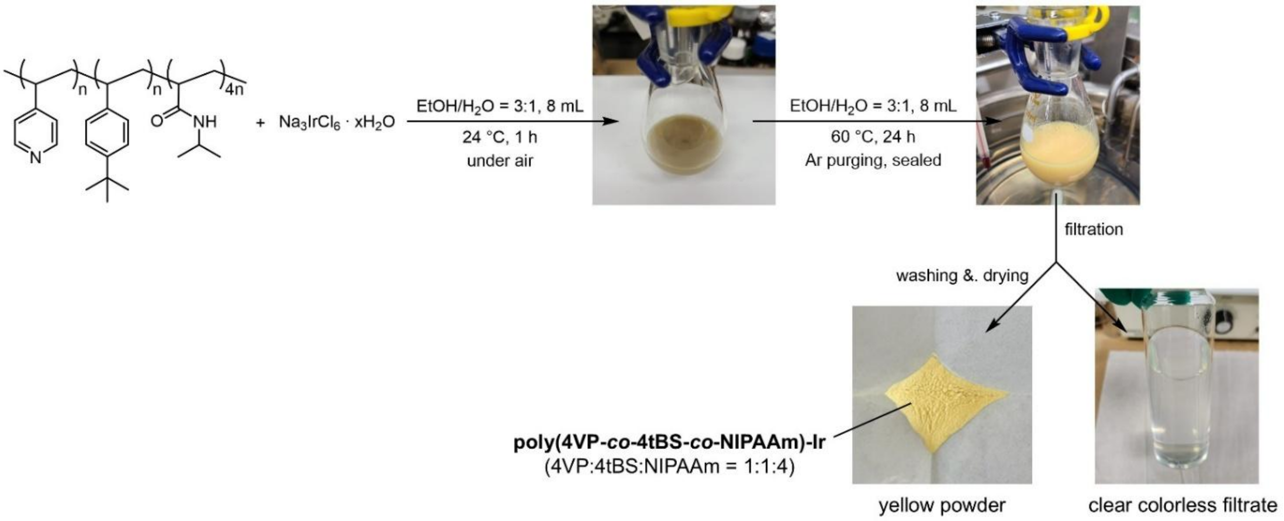


Fig. 5 Preparation of poly(4VP-*co*-4tBS-*co*-NIPAAm)-Ir (4VP:4tBS:NIPAAm = 1:1:4).

Other polymeric Ir catalysts including **Poly(4VP-*co*-4tBS-*co*-NIPAAm)-Ir** (4VP:4tBS:NIPAAm = 1:1:4) (yield: 91%), **poly(4VP-*co*-4MeS)-Ir** (4VP:4MeS = 1:1) (yield: 74%), **poly(4VP-*co*-4MeS)-Ir** (4VP: 4MeS = 1:4) (yield: 95%), **poly(4VP-*co*-4FS)-Ir** (4VP:4FS = 1:1) (yield: 96%), **poly(4VP-*co*-4tBS)-Ir** (4VP: 4tBS = 1:1) (yield: 89%), **poly(4VP-*co*-4tBS-*co*-4FS)-Ir** (4VP:4tBS:4FS = 1:1:1) (yield: 94%) were prepared using a similar method with Ir(III) precursors ($Na_3IrCl_6 \cdot xH_2O$ or $IrCl_3 \cdot xH_2O$), as described in **Fig. 5**. The structures of the corresponding copolymers are shown in **Fig. 3**.

4. XAFS measurements of Polymeric Ir Catalysts

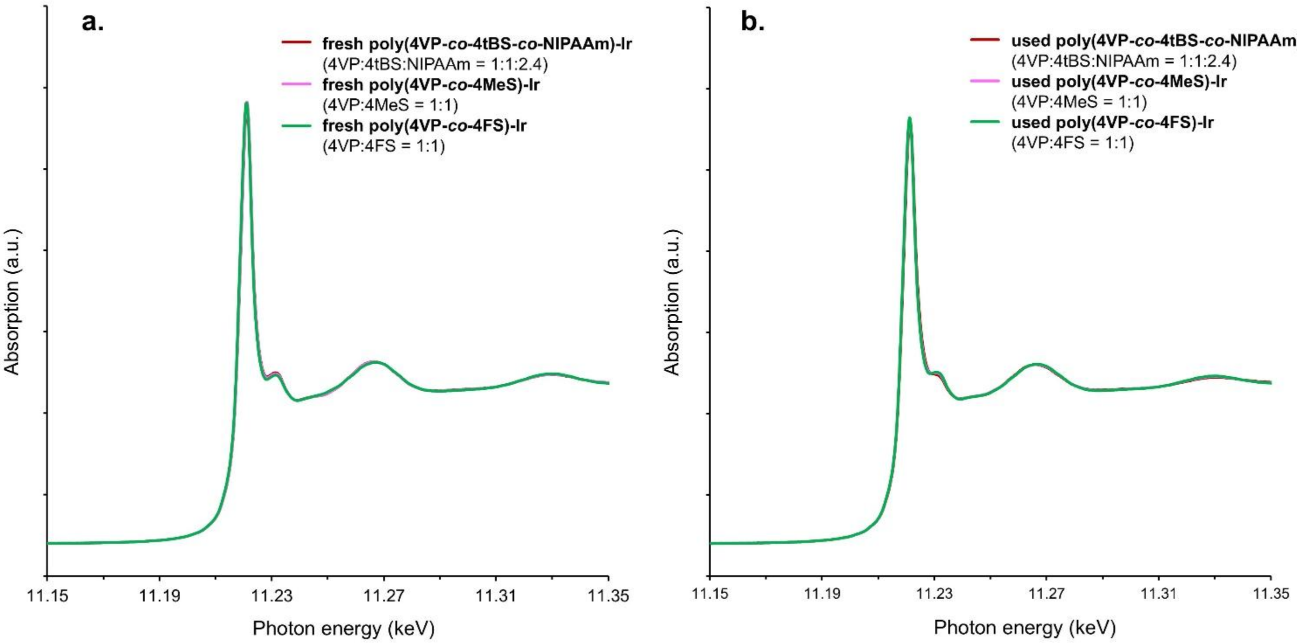
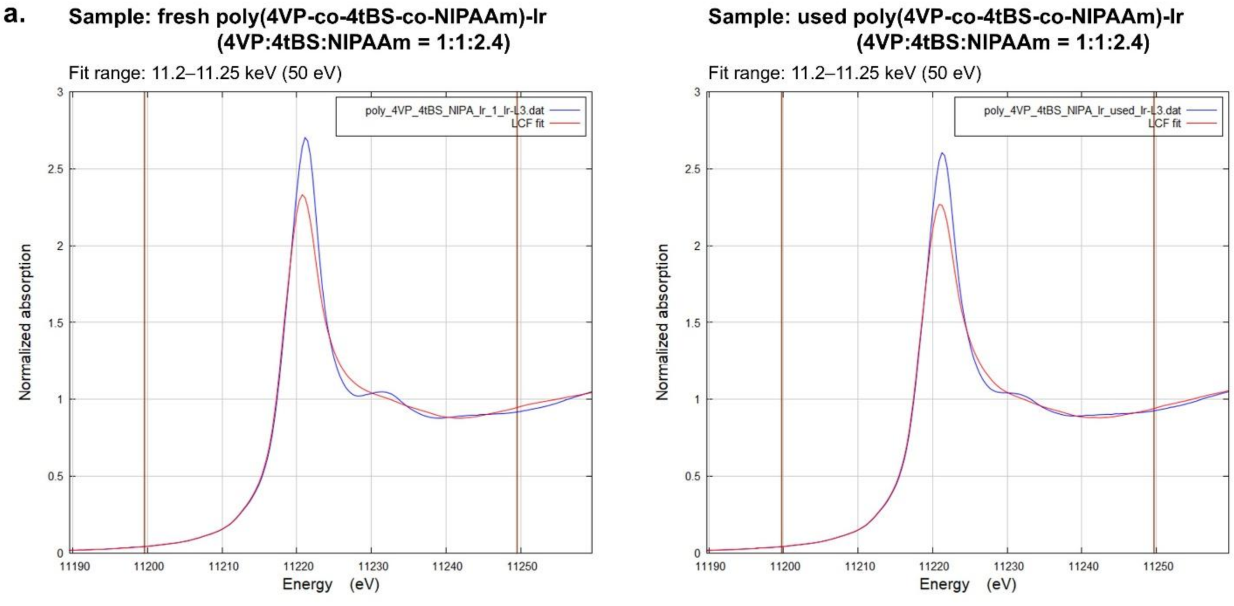


Fig. 6 L_3-edge XANES spectra of (**a**) fresh and (**b**) used poly(4VP-*co*-4tBS-co-NIPAAm)-Ir (4VP:4tBS:NIPAAm = 1:1:2.4) (red), poly(4VP-*co*-4MeS)-Ir (4VP:4MeS = 1:1) (pink), and poly(4VP-*co*-4FS)-Ir (4VP:4FS = 1:1) (green).

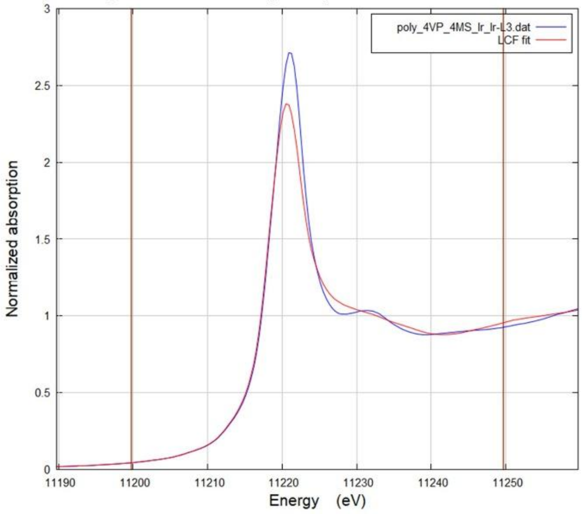


Standard	Weight
$[Ir(OMe)(cod)]_2$	0.52
$Na_3IrCl_6 \cdot xH_2O$	0.48

Standard	Weight
$[Ir(OMe)(cod)]_2$	0.661
$Na_3IrCl_6 \cdot xH_2O$	0.339

b. **Sample: fresh poly(4VP-*co*-4MeS)-Ir (4VP:4MeS = 1:1)**

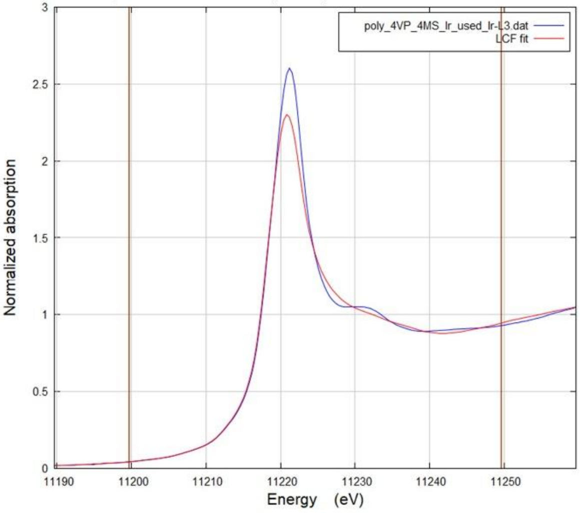
Fit range: 11.2–11.25 keV (50 eV)



Standard	Weight
$[Ir(OMe)(cod)]_2$	0.416
$Na_3IrCl_6 \cdot xH_2O$	0.584

Sample: used poly(4VP-*co*-4MeS)-Ir (4VP:4MeS = 1:1)

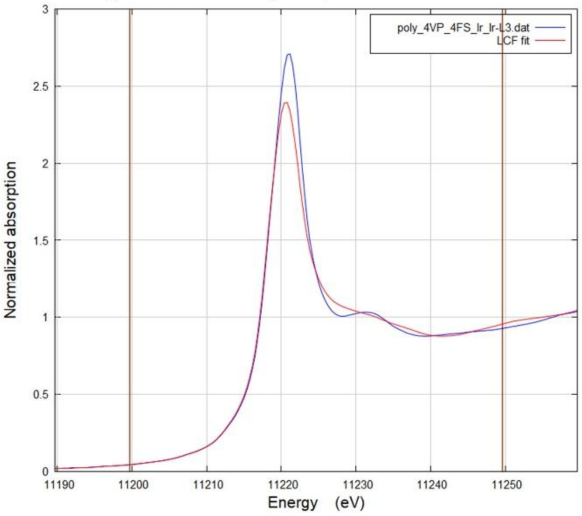
Fit range: 11.2–11.25 keV (50 eV)



Standard	Weight
$[Ir(OMe)(cod)]_2$	0.583
$Na_3IrCl_6 \cdot xH_2O$	0.417

c. **Sample: fresh poly(4VP-*co*-4FS)-Ir (4VP:4FS = 1:1)**

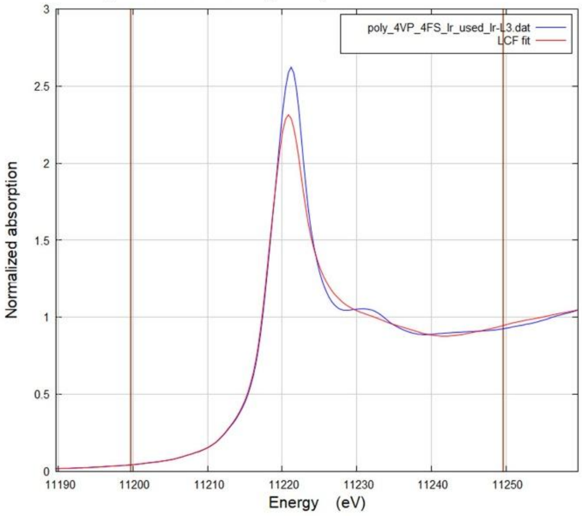
Fit range: 11.2–11.25 keV (50 eV)



Standard	Weight
$[Ir(OMe)(cod)]_2$	0.39
$Na_3IrCl_6 \cdot xH_2O$	0.61

Sample: used poly(4VP-*co*-4FS)-Ir (4VP:4FS = 1:1)

Fit range: 11.2–11.25 keV (50 eV)



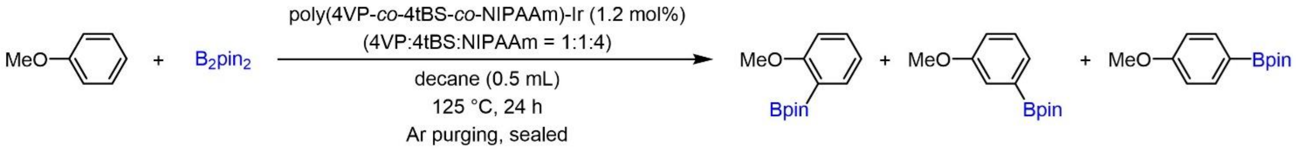
Standard	Weight
$[Ir(OMe)(cod)]_2$	0.555
$Na_3IrCl_6 \cdot xH_2O$	0.445

Fig. 7 Linear combination fitting of XANES spectra for fresh and used polymeric Ir catalysts. **a.** poly(4VP-*co*-4tBS-*co*-NIPAAm)-Ir (4VP:4tBS:NIPAAm = 1:1:2.4), **b.** poly(4VP-*co*-4MeS)-Ir (4VP:4MeS = 1:1), **c.** poly(4VP-*co*-4FS)-Ir (4VP:4FS = 1:1).

5. General Experimental Procedures of Polymeric Ir-Catalyzed C–H borylation under Batch

1a (2 mL) **2a** (1 mmol) *o*-**3a** *m*-**3a** *p*-**3a**

Experimental procedures for P4VP-Ir promoted batch reaction: To a 10 mL round-bottom screw-top vial, equipped with a stir bar, were added 31.3 wt% P4VP-Ir (30.71 mg, 5 mol% Ir), anisole (2 mL, 18.5 mmol), and bis(pinacolato)diboron (253.94 mg, 1.0 mmol). The vial was purged with argon gas, sealed, and stirred at 118 °C in a ChemiStation device (EYELA PPS-1511). After 24 h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate (8 mL), and 50 µL of tridecane was added as an internal standard. The mixture was then filtered through Celite, yielding a clear, colorless solution for GC analysis. The yield was determined using a GC calibration curve with tridecane as the internal standard.

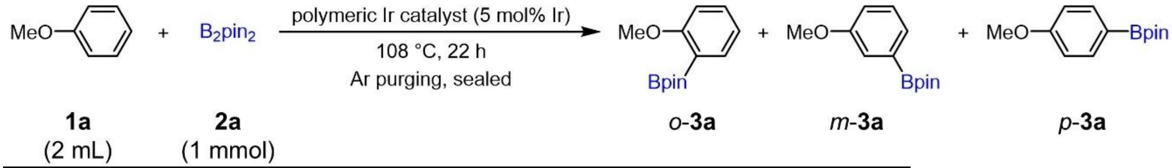


1a (1 mmol) **2a** (1.5 mol equiv) *o*-**3a** *m*-**3a** *p*-**3a**

Experimental procedures for the optimized batch reaction: To a 10 mL round-bottom screw-top vial, equipped with a stir bar, were added 5.6 wt% poly(4VP-*co*-4tBS-*co*-NIPAAm)-Ir (4VP:4tBS:NIPAAm = 1:1:4; 41.75 mg, 1.2 mol% Ir), anisole (108.1 mg, 1 mmol), bis(pinacolato)diboron (380.91 mg, 1.5 mmol), and decane (0.5 mL). The vial was purged with argon gas, sealed, and stirred at 125 °C in a ChemiStation device. After 24 h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate (8 mL), and 50 µL of tridecane was added as an internal standard. The mixture was then filtered through Celite, yielding a clear, colorless solution for GC analysis. The yield was determined using a GC calibration curve with tridecane as the internal standard.

6. Optimization of Batch Reaction Conditions

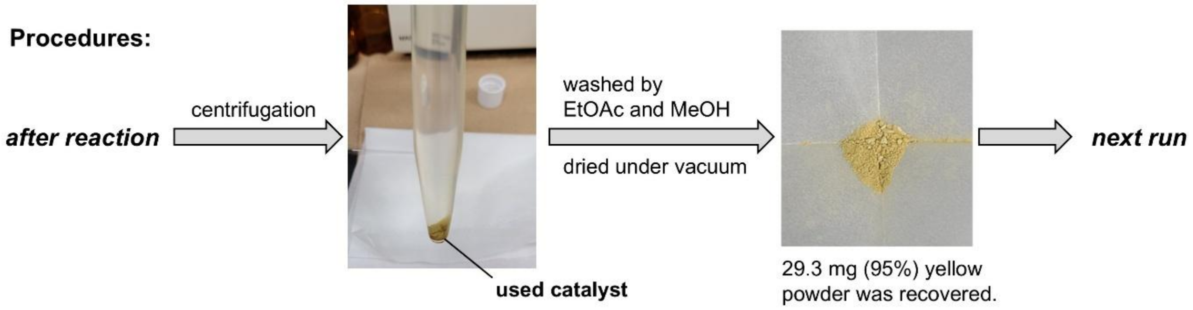
Table 1 Polymeric Ir catalyzed C–H borylation using excess amount of anisole under batch conditions.[a]



entry	polymeric Ir catalyst	yield (%) (*o*-, *m*-, *p*-isomers)	selectivity (%)
			o-**3a**/*m*-**3a**/*p*-**3a**
1	P4VP-Ir	70	7/67/26
2[b]	P4VP-Ir	74	6/71/23
3	P3VP-Ir	65	6/71/23
4	poly(4VP-*co*-4MeS)-Ir (4VP:4MeS = 1:1)	95	7/62/31

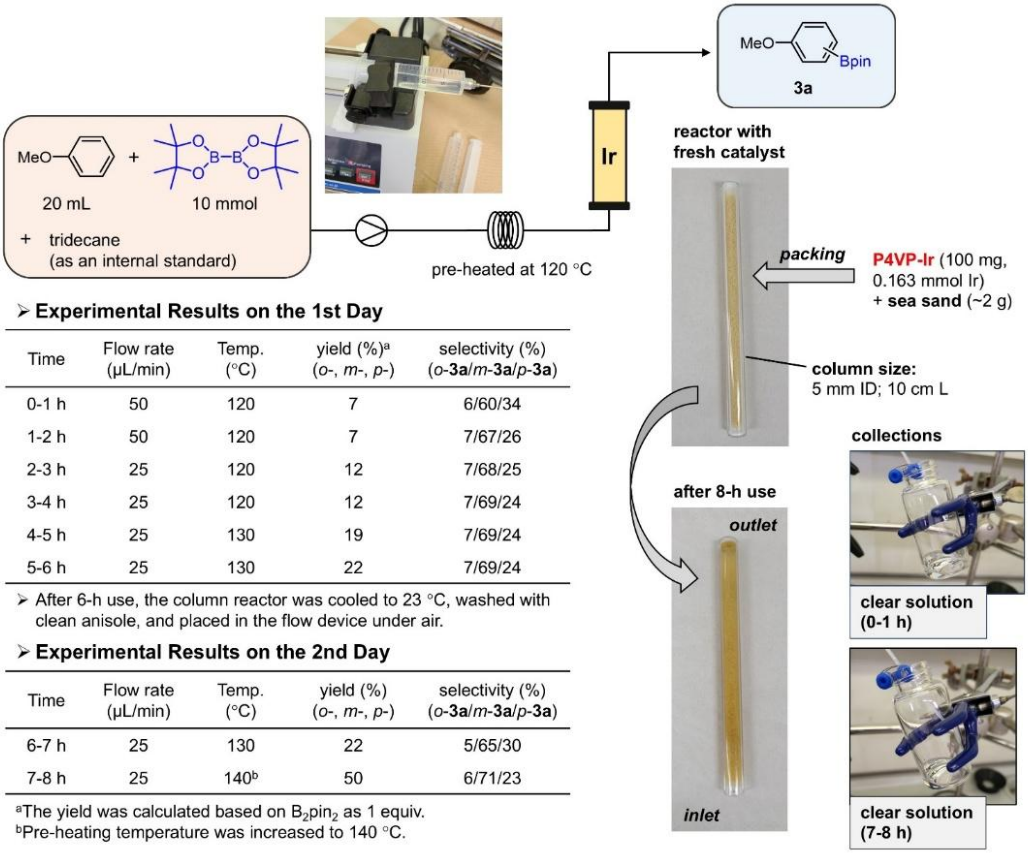
[a] GC yields, calculated by using a calibration curve based on B_2pin_2 as 1mol equiv.

[b] The catalyst was recovered from entry 1 by centrifugation followed by washing and drying. The procedure was shown below.



7. General Experimental Procedures of Polymeric Ir-Catalyzed C–H borylation under Continuous Flow

P4VP-Ir-catalyzed continuous flow C–H borylation: P4VP-Ir (100 mg, 0.163 mmol Ir), and sea sand (~2.0 g) were mixed in a vial using vortex mixer (purchased from KENIS Ltd., Vortex-Genie 2) for 5 min at 1000 rpm, and then packed into a glass column (10 cm L × Φ5 mm) with two PTFE filters installed at the top and bottom. The packed glass column was placed in the heater of the flow device. A solution of B_2pin_2 (10 mmol) dissolved in 20 mL anisole, along with 500 µL of tridecane as an internal standard, was preheated and injected into the reactor using a syringe pump with a specific flow rate. The mixed solution was heated at 120 °C by a hot plate prior to the reaction. The crude reaction mixture was collected hourly from the outlet and diluted with EtOAc before analyzed by GC. The yield was calculated by GC analysis using tridecane as an internal standard.



➢ **Experimental Results on the 1st Day**

Time	Flow rate (µL/min)	Temp. (°C)	yield (%)[a] (*o*-, *m*-, *p*-)	selectivity (%) (*o*-**3a**/*m*-**3a**/*p*-**3a**)
0-1 h	50	120	7	6/60/34
1-2 h	50	120	7	7/67/26
2-3 h	25	120	12	7/68/25
3-4 h	25	120	12	7/69/24
4-5 h	25	130	19	7/69/24
5-6 h	25	130	22	7/69/24

➢ After 6-h use, the column reactor was cooled to 23 °C, washed with clean anisole, and placed in the flow device under air.

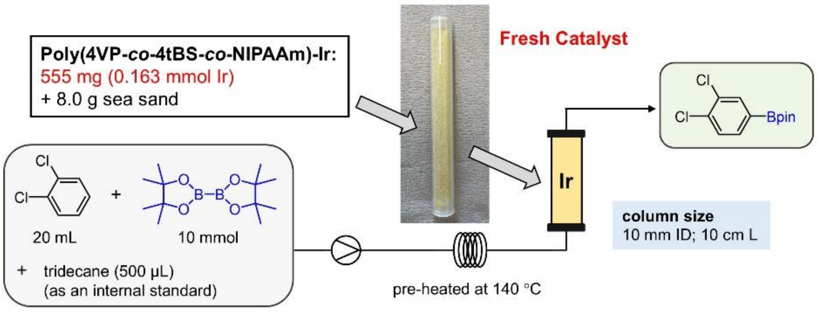
➢ **Experimental Results on the 2nd Day**

Time	Flow rate (µL/min)	Temp. (°C)	yield (%) (*o*-, *m*-, *p*-)	selectivity (%) (*o*-**3a**/*m*-**3a**/*p*-**3a**)
6-7 h	25	130	22	5/65/30
7-8 h	25	140[b]	50	6/71/23

[a] The yield was calculated based on B_2pin_2 as 1 equiv.
[b] Pre-heating temperature was increased to 140 °C.

Fig. 8 Continuous flow C–H borylation of anisole using P4VP-Ir as a catalyst.

Poly(4VP-*co*-4tBS-*co*-NIPAAm)-Ir-catalyzed continuous flow C–H borylation of multiple arenes: poly(4VP-*co*-4tBS-*co*-NIPAAm)-Ir (4VP:4tBS:NIPAAm = 1:1:4, 555 mg, 0.163 mmol Ir), and sea sand (~8.0 g) were mixed in a vial using vortex mixer (purchased from KENIS Ltd., Vortex-Genie 2) for 5 min at 1000 rpm, and then packed into a glass column (10 cm L × Φ10 mm) with two PTFE filters installed at the top and bottom. The packed glass column was placed in the heater of the flow device at 140 °C. A solution of B_2pin_2 (10 mmol) dissolved in 20 mL arene compound, along with 500 µL of tridecane as an internal standard, was preheated and injected into the reactor using a syringe pump at a flow rate of 25 µL/min. The mixed solution was heated at 140 °C by a hot plate prior to the reaction. The crude reaction mixture was collected hourly from the outlet and diluted with EtOAc before analyzed by GC. The yield was calculated by GC analysis using tridecane as an internal standard. After the reaction, the flow device was cooled to room temperature, and the reactor was stored under air. On the following day, the arene compound was changed and repeated the flow reaction using the same procedure.

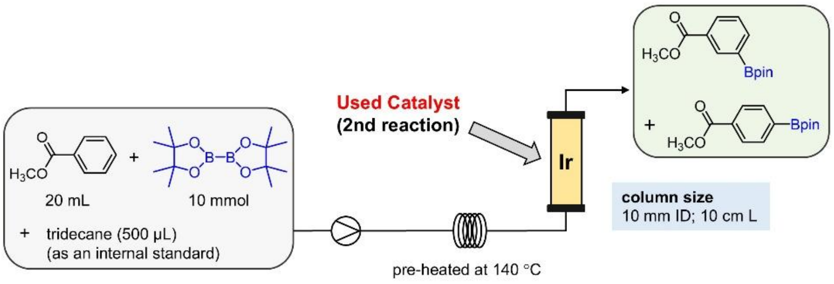


Results on the 1st Day

(After the reaction, the column reactor was stored under an air atmosphere)

Time (h)	Flow rate (µL/min)	Temp. (°C)	Yield (%)
1	25	140	61
2	25	140	126
3	25	140	156
4	25	140	168
5	25	140	171

[a] The yield was detected by GC using tridecane as an internal standard, the value was calculated based on B_2pin_2 as 1 equiv.

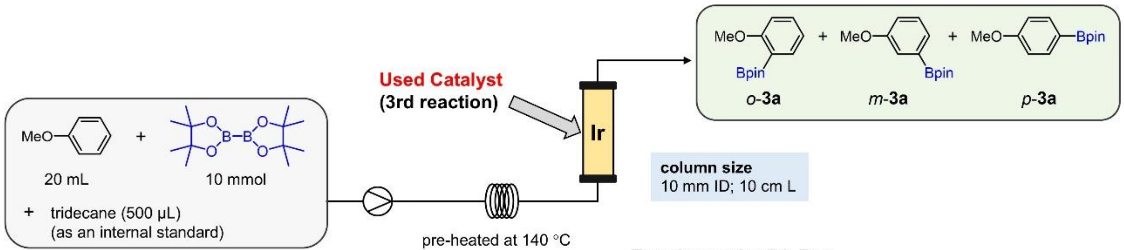


Results on the 2nd Day

(After the reaction, the column reactor was stored under an air atmosphere)

Time (h)	Flow rate (µL/min)	Temp. (°C)	Yield (%) (*m*- and *p*-)
1	25	140	88
2	25	140	95
3	25	140	92
4	25	140	86

[a] The yield was detected by GC using tridecane as an internal standard, the value was calculated based on B_2pin_2 as 1 equiv.



Results on the 3rd Day

(After the reaction, the column reactor was stored under an air atmosphere)

Time (h)	Flow rate (µL/min)	Temp. (°C)	Yield (%) (*o* + *m* + *p*)	Selectivity (%) *o*-3a	*m*-3a	*p*-3a
1	25	140	19	9	70	21
2	25	140	41	10	69	21
3	25	140	53	11	68	21
4	25	140	66	10	68	22

Results on the 4th Day

(After the reaction, the column reactor was stored under an air atmosphere)

Time (h)	Flow rate (µL/min)	Temp. (°C)	Yield (%) (*o* + *m* + *p*)	Selectivity (%) *o*-3a	*m*-3a	*p*-3a
5	25	140	57	11	67	22
6	25	140	66	11	68	21
7	25	140	64	11	68	21
8	25	140	65	11	67	22
9	25	140	66	11	67	22
10	25	140	67	11	67	22
11	25	140	67	11	67	22
12	25	140	68	11	67	22
13	25	140	69	11	67	22
14	25	140	70	11	67	22
15	25	140	69	11	67	22

Results on the 5th Day

(After the reaction, the column reactor was stored under an air atmosphere)

Time (h)	Flow rate (µL/min)	Temp. (°C)	Yield (%) (*o* + *m* + *p*)	Selectivity (%) *o*-3a	*m*-3a	*p*-3a
16	25	140	56	11	67	22
17	25	140	54	11	67	22
18	25	140	56	12	66	22
19	25	140	56	12	66	22
20	25	140	57	12	66	22
21	25	140	56	12	66	22
22	25	140	55	13	65	22
23	25	140	55	13	65	22
24	25	140	56	13	65	22

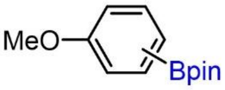
Results on the 6th Day

Time (h)	Flow rate (µL/min)	Temp. (°C)	Yield (%) (*o* + *m* + *p*)	Selectivity (%) *o*-3a	*m*-3a	*p*-3a
25	25	140	52	12	66	22
26	25	140	52	12	66	22
27	25	140	55	13	65	22
28	25	140	55	13	65	22
29	25	140	56	13	65	22
30	25	140	56	14	64	22
31	25	140	57	14	64	22
32	25	140	56	14	64	22
33	25	140	56	14	64	22

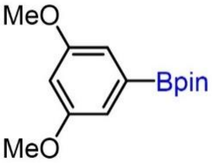
[a] The yield was detected by GC using tridecane as an internal standard, the value was calculated based on B_2pin_2 as 1 equiv.

Fig. 9 Continuous flow C–H borylation of multiple arenes using poly(4VP-*co*-4tBS-*co*-NIPAAm)-Ir catalyst.

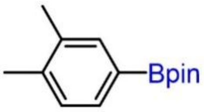
8. Spectral Data of the Isolated Products



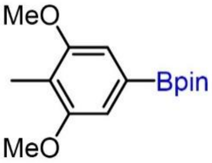
2-(3-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3a**)[S3]: the products (*m*-isomer and *p*-isomer) were isolated by silica gel column chromatography (hexane/EtOAc = 30:1) (clear colorless liquid, 121.8 mg, 52% yield, *m*-isomer:*p*-isomer = 67:33). ^{1}H NMR (500 MHz, $CDCl_3$) δ (*m*-isomer) 7.40 (d, *J* = 7.0 Hz, 1H), 7.33 (d, *J* = 2.5 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 1H), 3.82 (s, 3H), 1.34 (s, 12H), (*p*-isomer) 7.75 (d, *J* = 9.0 Hz, 2H), 7.00 (dd, *J* = 8.0 Hz, 2.5 Hz, 2H), 3.81 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (*m*-isomer) 159.14, 129.03, 127.28, 118.82, 117.98, 83.91, 55.31, 24.95, (*p*-isomer) 162.25, 136.61, 113.40, 83.63, 55.15, 24.95. GC/MS (EI) *m/z*: 234.2 [M^+].



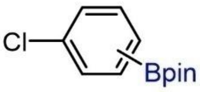
2-(3,5-Dimethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3b**)[S4]: the product was isolated by silica gel column chromatography (hexane/EtOAc = 30:1) (white solid, 150.3 mg, 57% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (d, *J* = 2.5 Hz, 2H), 6.57 (t, *J* = 2.5 Hz, 1H), 3.81 (s, 6H), 1.34 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.48, 111.70, 104.60, 83.96, 55.49, 24.92. GC/MS (EI) *m/z*: 264.1 [M^+].



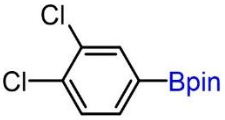
2-(3,4-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3c**)[S3]: the product was isolated by silica gel column chromatography (hexane/EtOAc = 20:1) (clear colorless liquid, 115.3 mg, 50% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.0 Hz, 1H), 2.27 (d, *J* = 5.0 Hz, 6H), 1.34 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.23, 136.02, 135.97, 132.50, 129.25, 83.67, 24.93, 20.10, 19.56. GC/MS (EI) *m/z*: 232.2 [M^+].



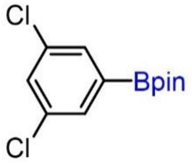
2-(3,5-Dimethoxy-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**)[S5]: the product was isolated by silica gel column chromatography (hexane/EtOAc = 30:1) (white solid, 169.3 mg, 61% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (s, 2H), 3.87 (s, 6H), 2.12 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 118.40, 109.43, 83.83, 55.92, 24.93, 8.58. GC/MS (EI) *m/z*: 278.1 [M^+].



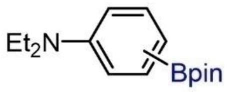
2-(3-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**)[S6]: the products (*m*-isomer and *p*-isomer) were isolated by silica gel column chromatography (hexane/EtOAc = 50:1) (clear colorless liquid, 147.6 mg, 62% yield, *m*-isomer:*p*-isomer = 69:31). ^{1}H NMR (500 MHz, $CDCl_3$) δ (*m*-isomer) 7.78 (d, *J* = 1.5 Hz, 1H), 7.66 (dt, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.42 (dq, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 1.34 (s, 12H), (*p*-isomer) 7.23 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (*m*-isomer) 134.64, 134.12, 132.74, 131.35, 129.27, 84.22, 24.94, (*p*-isomer) 137.61, 136.21, 128.09, 84.09, 24.94. GC/MS (EI) *m/z*: 238.1 [M^+].



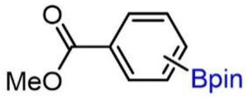
2-(3,4-Dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**)[S3]: the product was isolated by silica gel column chromatography (hexane/EtOAc = 50:1) (clear colorless liquid, 172.8 mg, 64% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 1.5 Hz, 1H), 7.60 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 1.34 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.64, 135.57, 133.85, 132.33, 130.09, 84.42, 24.92. GC/MS (EI) *m/z*: 272.1 [M^+].



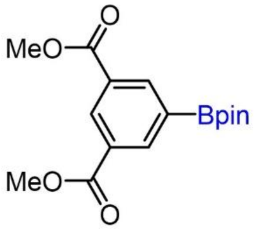
2-(3,5-Dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3g**)[S3]: the product was isolated by silica gel column chromatography (hexane/EtOAc = 50:1) (clear colorless liquid, 177.8 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J*=2.0 Hz, 2H), 7.42 (t, *J* = 2.0 Hz, 1H), 1.34 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.79, 132.78, 131.15, 84.58, 24.91. GC/MS (EI) *m/z*: 272.0 [M^+].



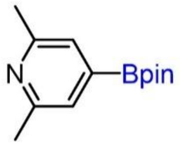
N,*N*-Diethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**3h**): the products (*m*-isomer and *p*-isomer) were isolated by silica gel column chromatography (hexane/EtOAc = 30:1) (*m*-isomer: clear colorless liquid and *p*-isomer: white solid, 150.4 mg, 55% yield, *m*-isomer:*p*-isomer = 79:21). ^{1}H NMR (500 MHz, $CDCl_3$) δ (*m*-isomer) 7.22 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 2.5 Hz, 1H), 7.10 (d, *J* = 2.5 Hz, 1H), 6.80–6.78 (m, 1H), 3.36 (q, *J* = 7.0 Hz, 4H), 1.32 (s, 12H), 1.15 (t, *J* = 7.5 Hz, 6H), (*p*-isomer) 7.66 (d, *J* = 9.0 Hz, 2H), 6.64 (d, *J* = 8.5 Hz, 2H), 3.37 (q, *J* = 7.0 Hz, 4H), 1.31 (s, 12H), 1.16 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (*m*-isomer) 147.46, 128.77, 122.20, 118.22, 115.25, 83.62, 44.27, 24.96, 12.71, (*p*-isomer) 149.97, 136.48, 110.62, 83.15, 44.29, 24.91, 12.65. HRMS (ESI) *m/z* calcd for $C_{12}H_{15}BCl_2O_2$: 276.21 $(M+H)^+$, found: 276.2129.



Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**3i**)[S3]: the products (*m*-isomer and *p*-isomer) were isolated by silica gel column chromatography (hexane/EtOAc = 20:1) (white solid, 186.8 mg, 71% yield, *m*-isomer:*p*-isomer = 52:48). ^{1}H NMR (500 MHz, $CDCl_3$) δ (*m*-isomer) 8.46 (s, 1H), 8.12–8.10 (m, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 3.90 (s, 3H), 1.33 (s, 12H), (*p*-isomer) 8.01 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 2H), 3.90 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (*m*-isomer) 167.17, 139.23, 135.91, 129.63, 127.88, 84.15, 52.08, 24.94, (*p*-isomer) 167.20, 134.73, 132.36, 128.66, 84.23, 52.19, 24.94. GC/MS (EI) *m/z*: 262.1 [M^+].

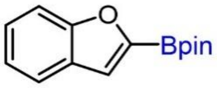


Dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene-1,3-dicarboxylate (**3j**)[S7]: the product was isolated by silica gel column chromatography (hexane/EtOAc = 20:1) (white solid, 210.9 mg, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (t, *J* = 1.5 Hz, 1H), 8.64 (d, *J* = 2.0 Hz, 2H), 3.95 (s, 6H), 1.37 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.41, 139.99, 133.39, 130.15, 84.51, 52.39, 24.96. GC/MS (EI) *m/z*: 320.1 [M^+].

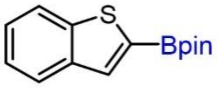


2,6-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**3k**)[S8]: the product was isolated by GPC (eluent: $CHCl_3$) (yellowish solid, 146.8 mg, 63% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (s, 2H), 2.54 (s, 6H), 1.35 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.02, 125.35, 84.42, 24.90, 24.23. GC/MS (EI) *m/z*: 233.2 [M^+].

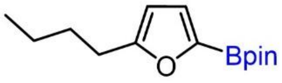
1-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indole (**3l**)[S9]: the product was isolated by silica gel column chromatography (hexane/EtOAc = 30:1) (white solid, 208.6 mg, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.27–7.24 (m, 1H), 7.13 (d, *J* = 1.0 Hz, 1H), 7.08 (t, *J* = 6.5 Hz, 1H), 3.96 (s, 3H), 1.36 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.25, 127.95, 123.28, 121.70, 119.39, 114.36, 109.79, 83.80, 32.33, 24.94. GC/MS (EI) *m/z*: 257.1 [M^{+}].



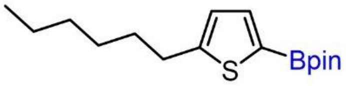
2-(1-Benzofuran-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3m**)[S10]: the product was isolated by silica gel column chromatography (hexane/EtOAc = 30:1) (white solid, 163.2 mg, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.40 (s, 1H), 7.36–7.32 (m, 1H), 7.24–7.21 (m, 1H), 1.39 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.61, 127.58, 126.03, 122.81, 121.98, 119.65, 112.05, 84.78, 24.89. GC/MS (EI) *m/z*: 244.1 [M^{+}].



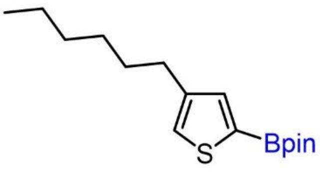
2-(1-Benzothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3n**)[S10]: the product was isolated by silica gel column chromatography (hexane/EtOAc = 50:1) (white solid, 175.3 mg, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91–7.89 (m, 2H), 7.86–7.84 (m, 1H), 7.38–7.33 (m, 2H), 1.38 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.81, 140.53, 134.58, 125.39, 124.46, 124.19, 122.62, 84.53, 24.90. GC/MS (EI) *m/z*: 260.1 [M^{+}].



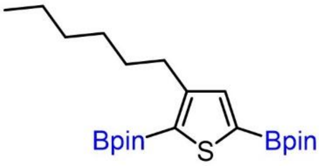
2-(5-Butylfuran-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3o**): the product was isolated by silica gel column chromatography (hexane/EtOAc = 50:1) (clear colorless liquid, 187.3 mg, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (d, *J* = 3.0 Hz, 1H), 6.04 (d, *J* = 3.5 Hz, 1H), 2.68 (t, *J* = 7.5 Hz, 2H), 1.64 (quin, *J* = 8.0 Hz, 2H), 1.40–1.30 (m, 14H), 0.92 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.35, 124.76, 105.95, 84.01, 30.18, 28.10, 24.79, 22.41, 13.86. HRMS (ESI) *m/z* calcd for $C_{14}H_{23}BO_3$: 251.17 (M+H)$^{+}$, found: 251.1813.



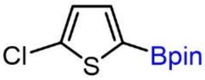
2-(5-Hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3p**)[S11]: the product was isolated by silica gel column chromatography (hexane/EtOAc = 50:1) (clear colorless liquid, 257.3 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 3.5 Hz, 1H), 6.85 (d, *J* = 3.0 Hz, 1H), 2.85 (t, *J* = 7.5 Hz, 2H), 1.71–1.65 (m, 2H), 1.37–1.27 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.86, 137.44, 125.90, 83.94, 31.74, 31.65, 30.24, 28.84, 24.83, 22.65, 14.16. GC/MS (EI) *m/z*: 294.1 [M^{+}].



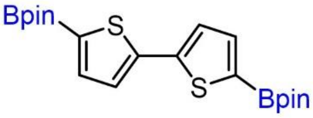
2-(4-Hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3q**)[S12]: the products were isolated by silica gel column chromatography (hexane/EtOAc = 50:1) (clear colorless liquid, 114.8 mg, 31% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 1.0 Hz, 1H), 7.20 (d, *J* = 0.5 Hz, 1H), 2.62 (t, *J* = 7.5 Hz, 2H), 1.71–1.65 (m, 2H), 1.37–1.27 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.86, 137.44, 125.90, 83.94, 31.74, 31.65, 30.24, 28.84, 24.83, 22.65, 14.16. GC/MS (EI) *m/z*: 294.1 [M^{+}].



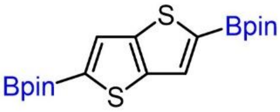
2-[3-Hexyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3qa**)[S13]: the product was obtained as a mixture with compound **3q** by silica gel column chromatography isolation (hexane/EtOAc = 50:1) (122.8 mg, 31% yield containing 5% compound **3q**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 2.86 (t, *J* = 8.0 Hz, 2H), 1.59–1.56 (m, 2H), 1.34–1.27 (m, 30H), 0.89–0.86 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.16, 139.70, 139.67, 84.09, 83.67, 31.82, 31.74, 29.98, 29.05, 24.84, 22.67, 14.20. GC/MS (EI) *m/z*: 420.3 [M$^+$].



2-(5-chlorothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3r**)[S14]: the product was isolated by silica gel column chromatography (hexane/EtOAc = 10:1) (colorless clear liquid, 139.1 mg, 57% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 3.5 Hz, 1H), 6.97 (d, *J* = 4.0 Hz, 1H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.85, 127.71, 84.38, 24.80. GC/MS (EI) *m/z*: 244.1 [M$^+$].



4,4,5,5-tetramethyl-2-[5-[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl]thiophen-2-yl]-1,3,2-dioxaborolane (**3s**)[S3]: the product was isolated by silica gel column chromatography (hexane/EtOAc = 10:1) (light-blue solid, 346.1 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J*=3.5 Hz, 2H), 7.29 (d, *J*=4.0 Hz, 2H), 1.35 (s, 24H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.96, 138.07, 125.71, 84.30, 24.84. GC/MS (EI) *m/z*: 418.2 [M$^+$].



4,4,5,5-tetramethyl-2-[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thieno[3,2-b]thiophen-2-yl]-1,3,2-dioxaborolane (**3t**)[S3]: the product was isolated by silica gel column chromatography (hexane/EtOAc = 10:1) (white solid, 282.2 mg, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 2H), 1.36 (s, 24H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.74, 128.98, 84.44, 24.86. GC/MS (EI) *m/z*: 392.2 [M$^+$].

9. References

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10. ^{1}H and ^{13}C NMR Spectra

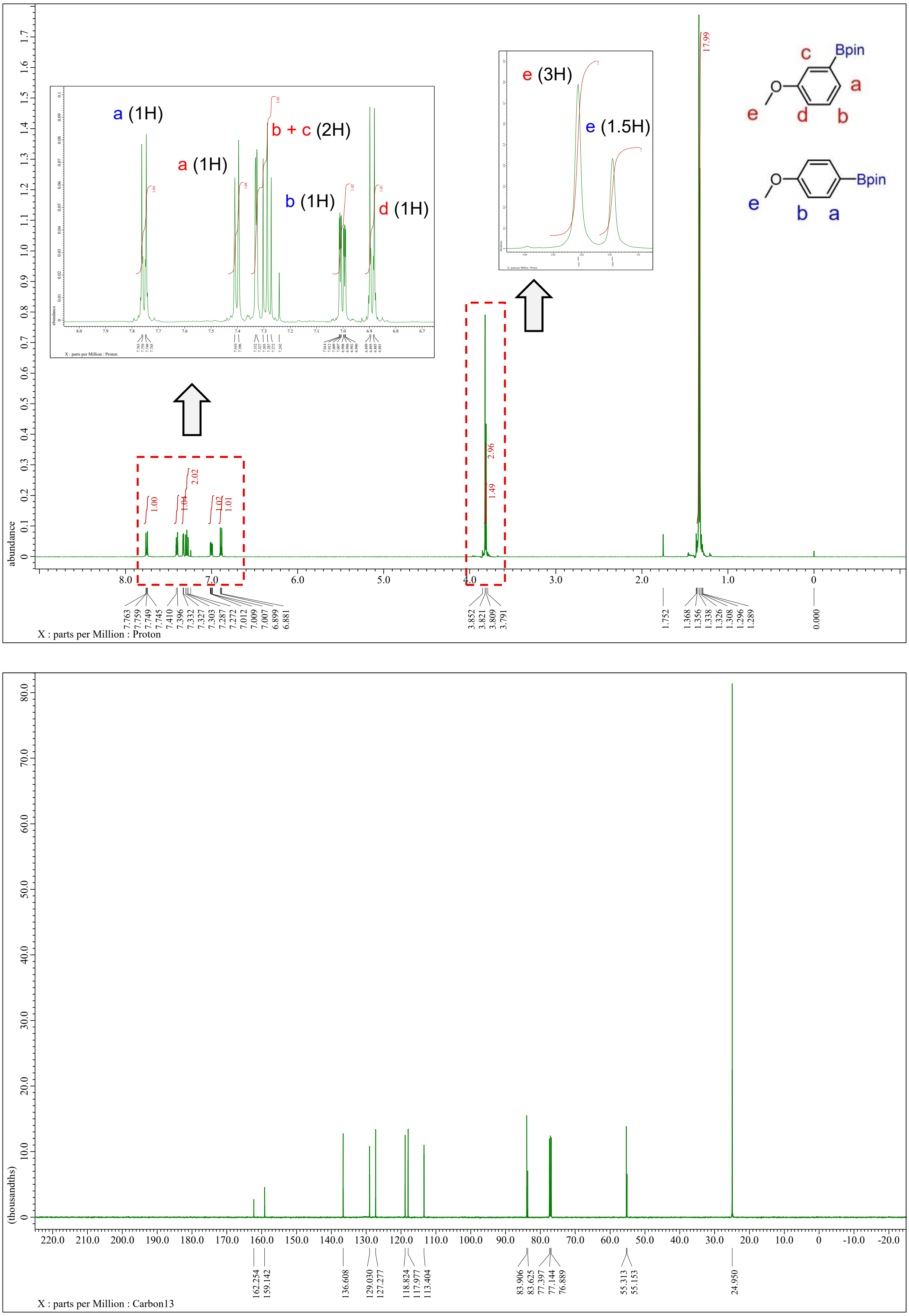


Fig. 10 ^{1}H and ^{13}C NMR spectra of product **3a**.

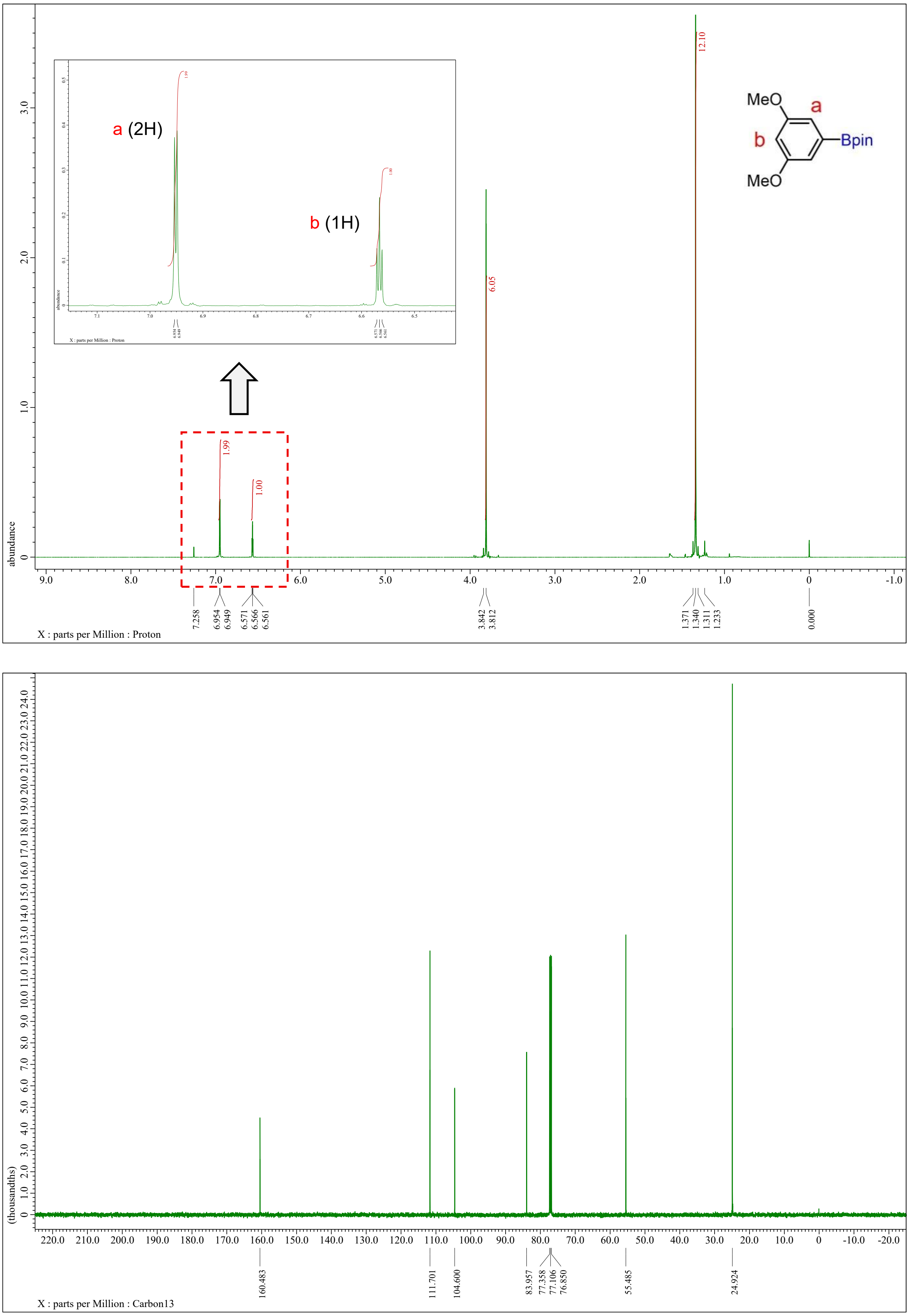


Fig. 11 ^{1}H and ^{13}C NMR spectra of product **3b**.

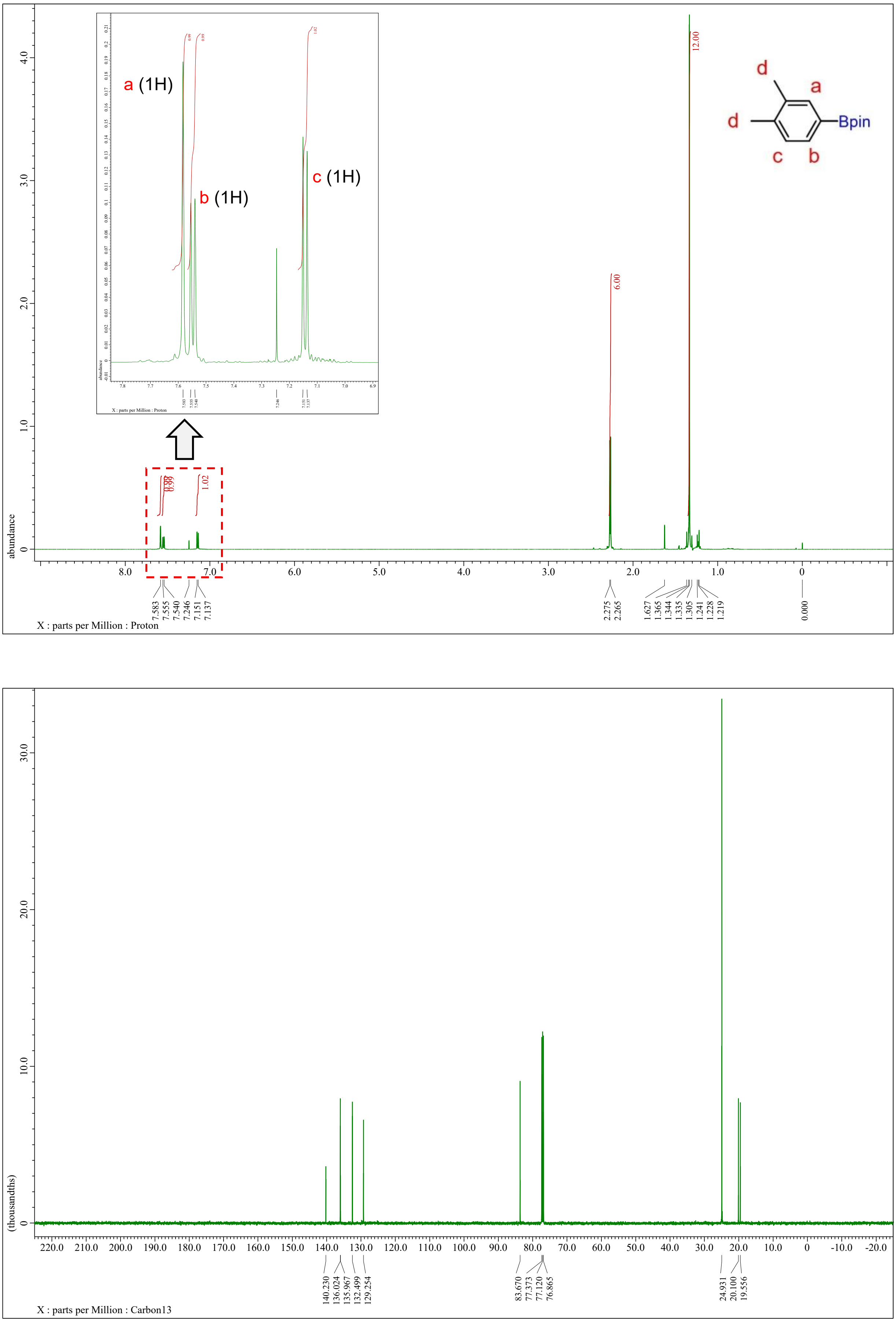


Fig. 12 ^{1}H and ^{13}C NMR spectra of product **3c**.

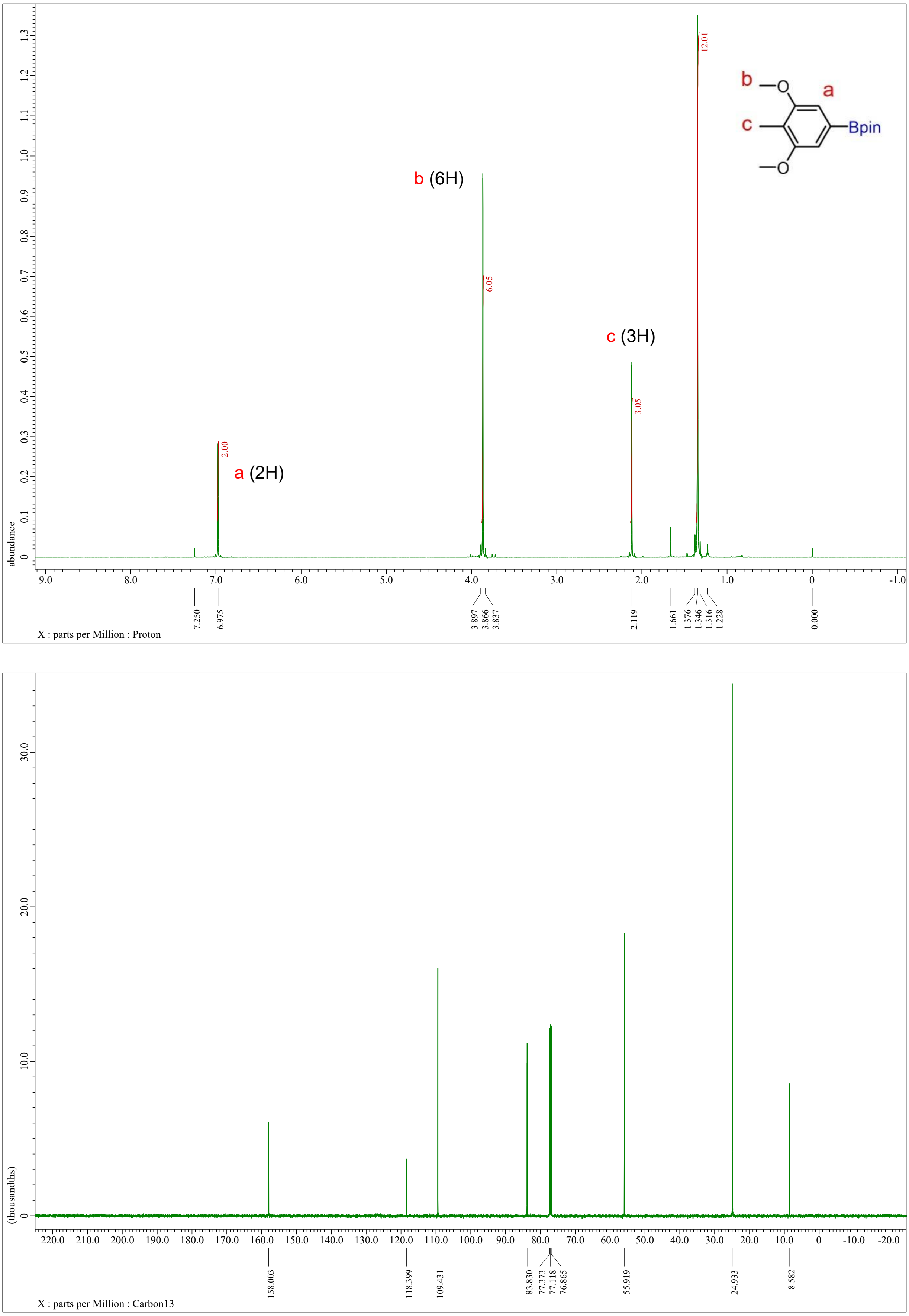


Fig. 13 ^{1}H and ^{13}C NMR spectra of product **3d**.

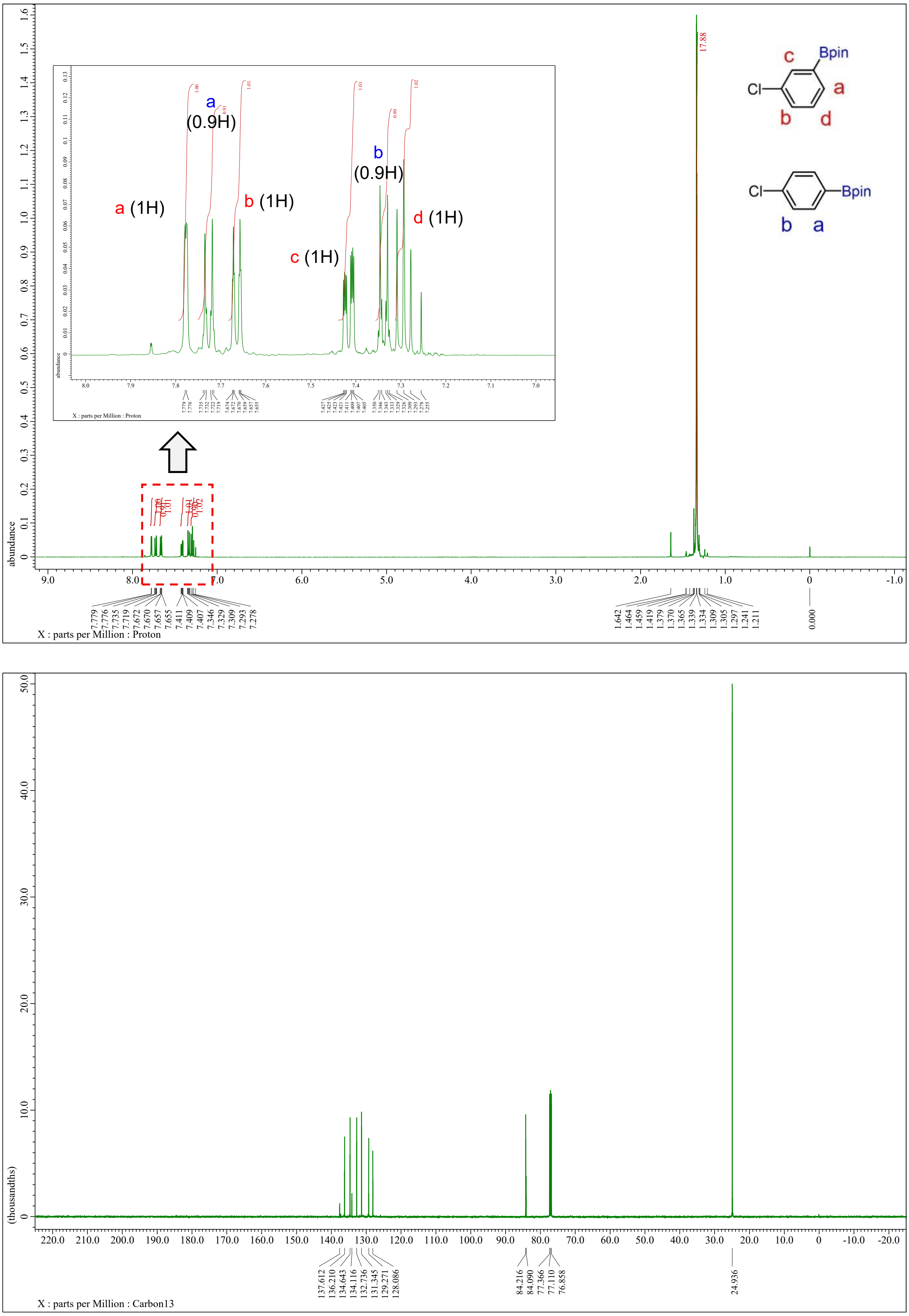


Fig. 14 ^{1}H and ^{13}C NMR spectra of product **3e**.

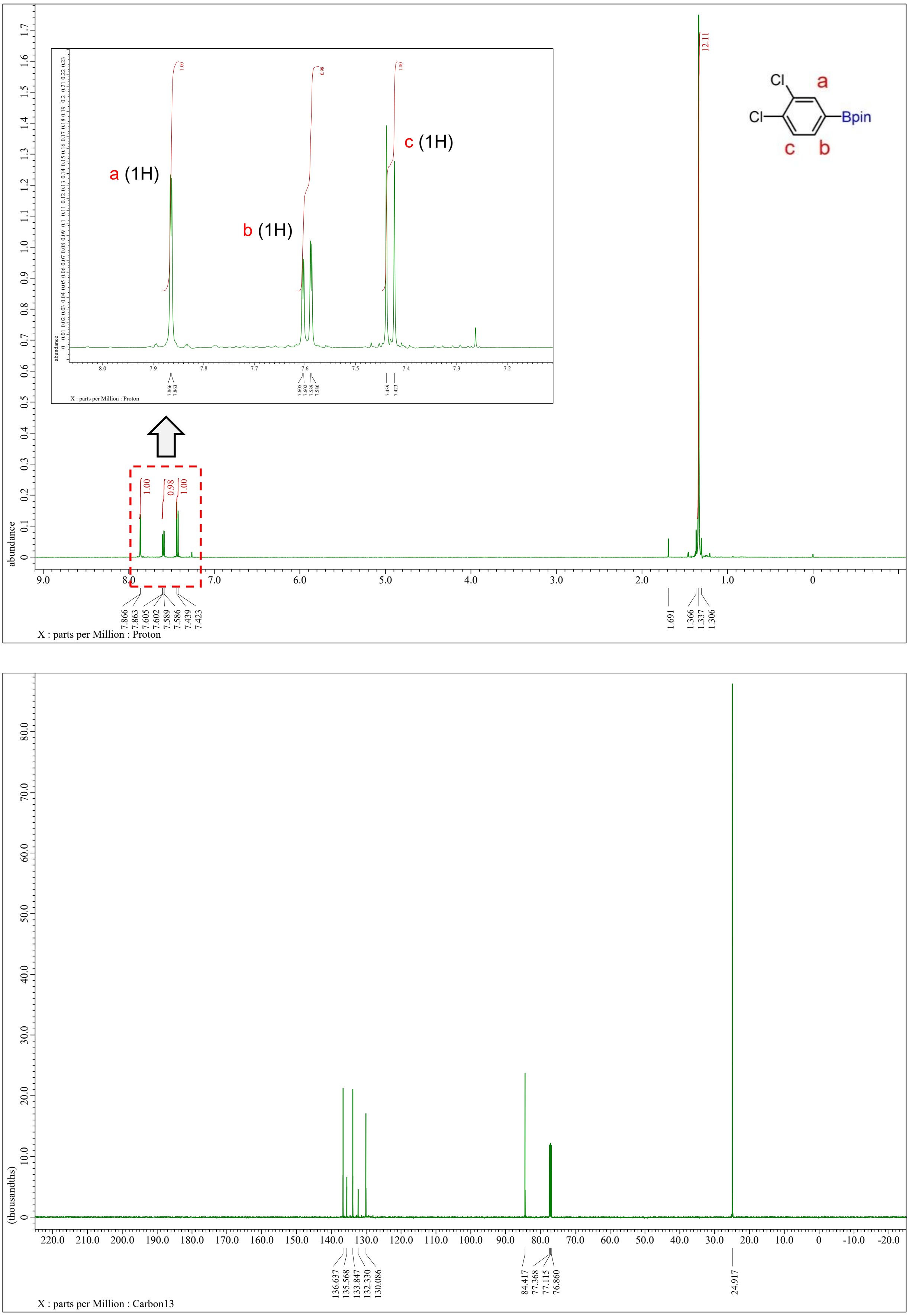


Fig. 15 ^{1}H and ^{13}C NMR spectra of product **3f**.

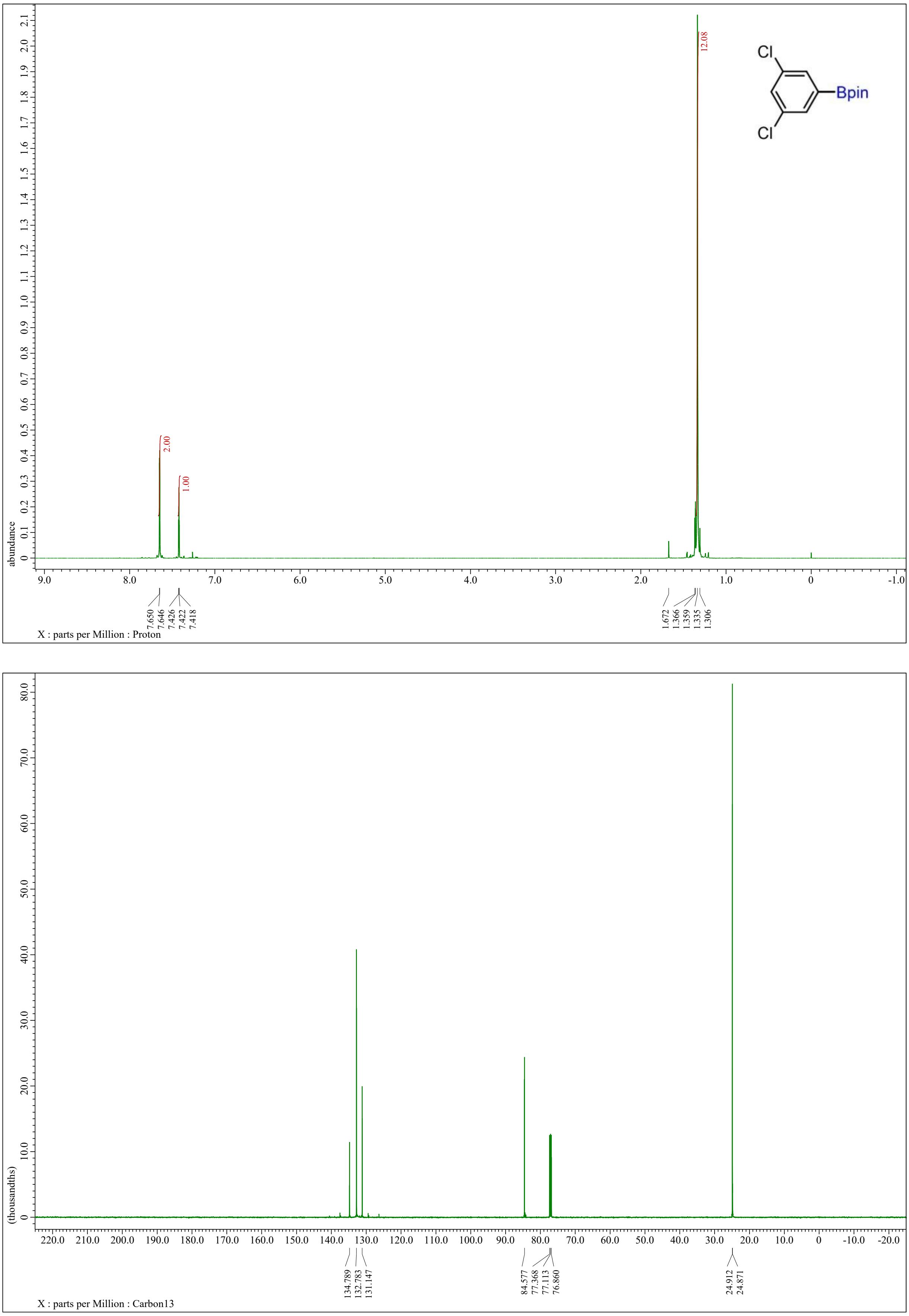


Fig. 16 ^{1}H and ^{13}C NMR spectra of product **3g**.

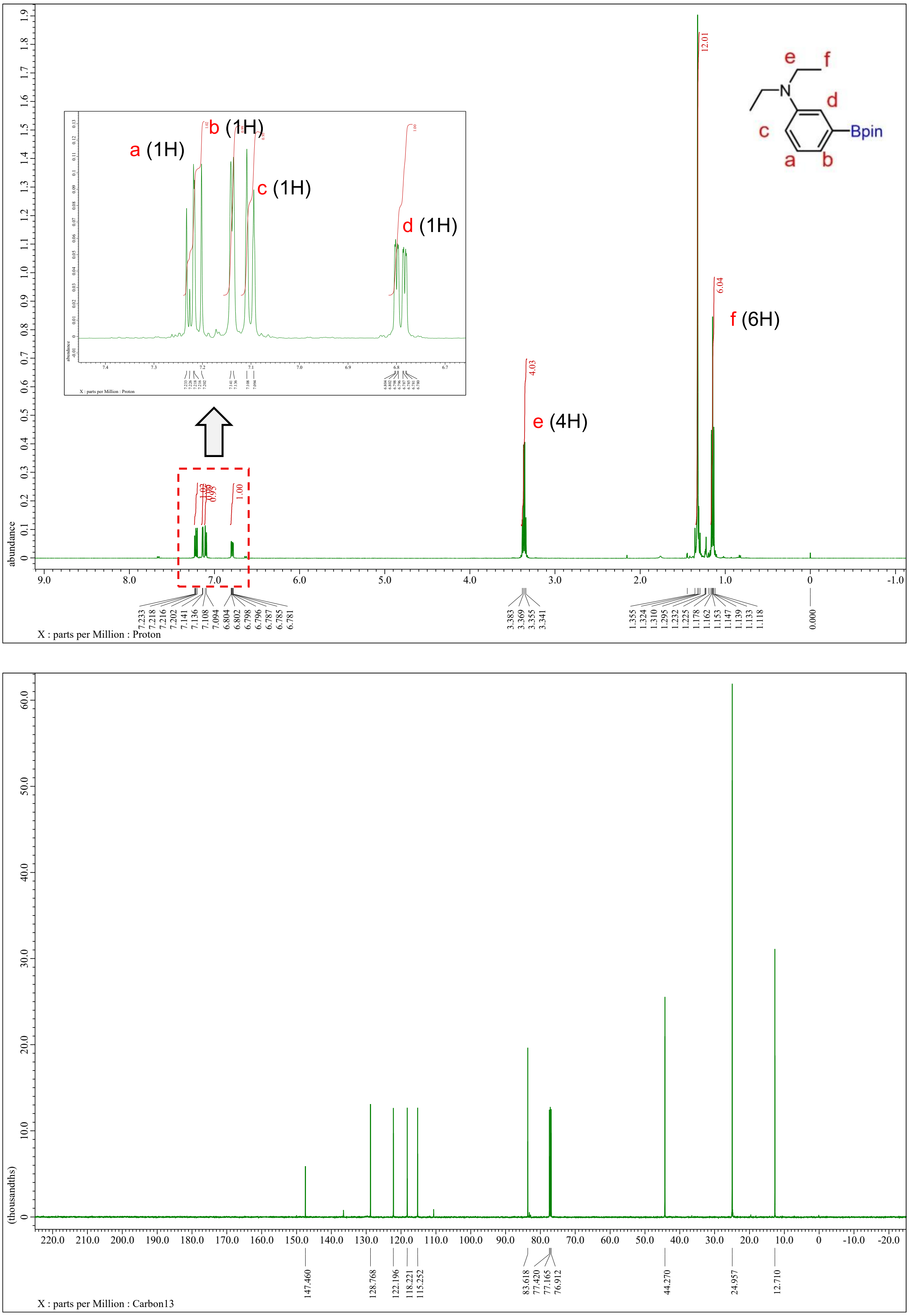


Fig. 17 ^{1}H and ^{13}C NMR spectra of product *m*-**3h**.

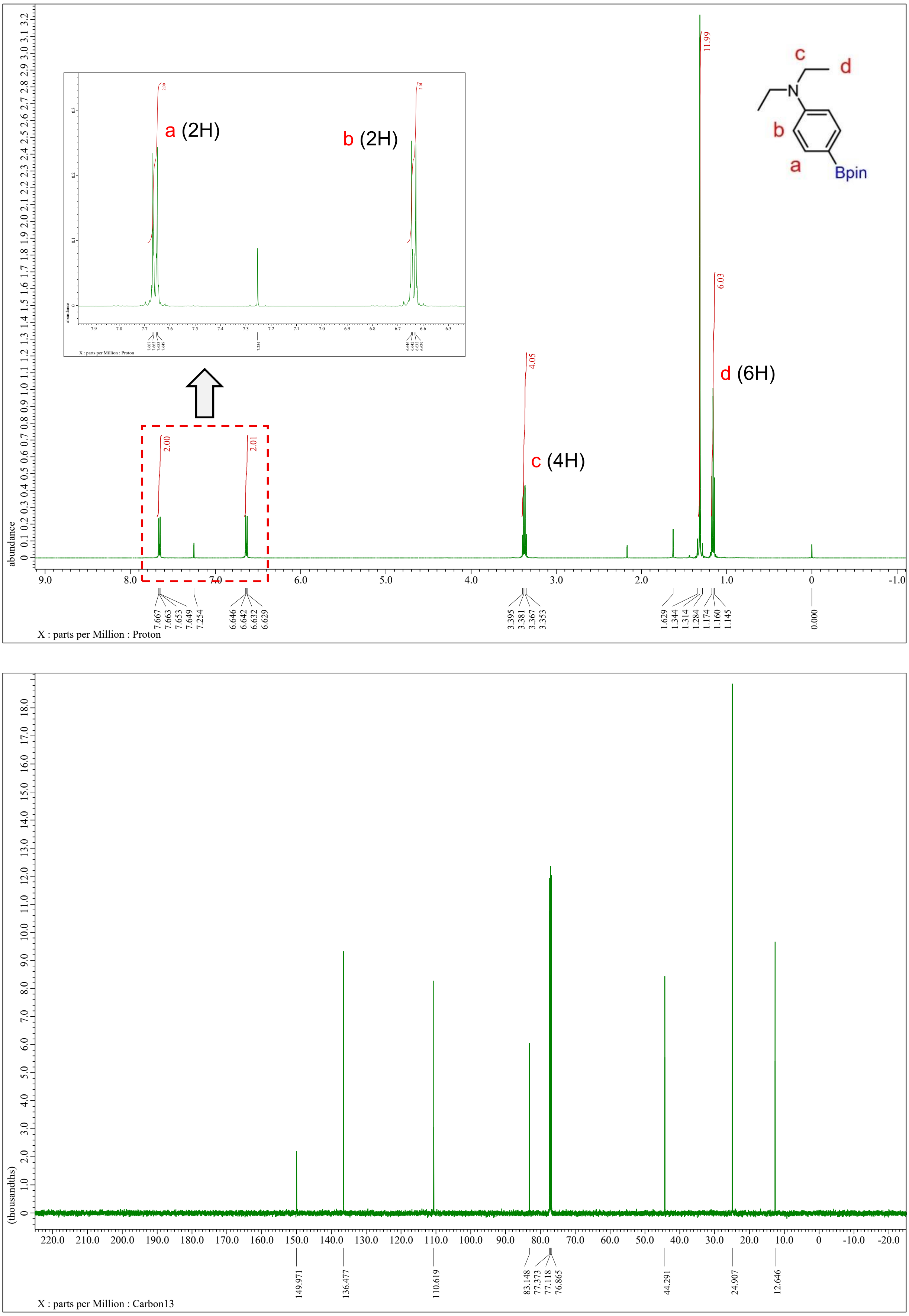


Fig. 18 ^{1}H and ^{13}C NMR spectra of product *p*-**3h**.

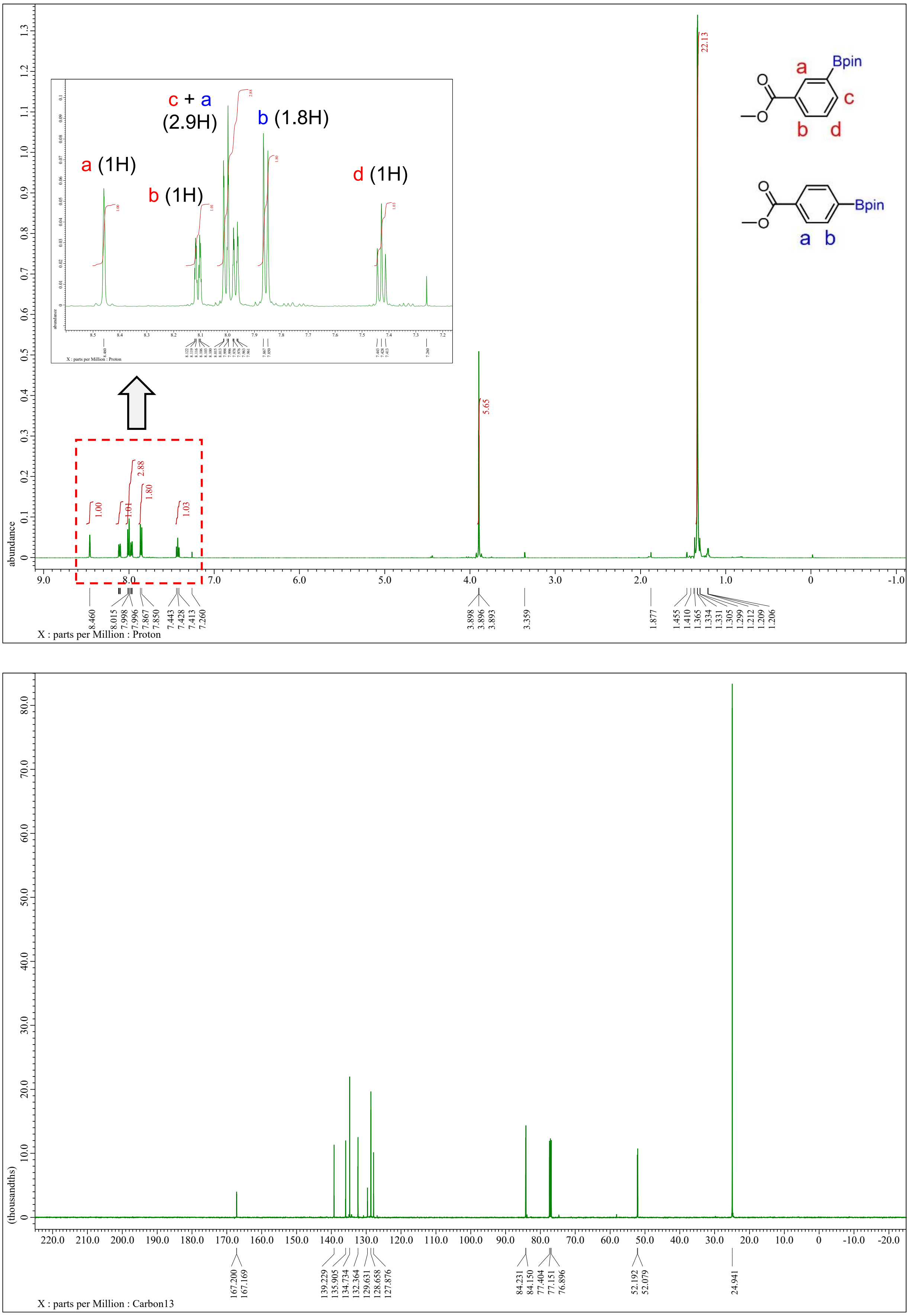


Fig. 19 ^{1}H and ^{13}C NMR spectra of product **3i**.

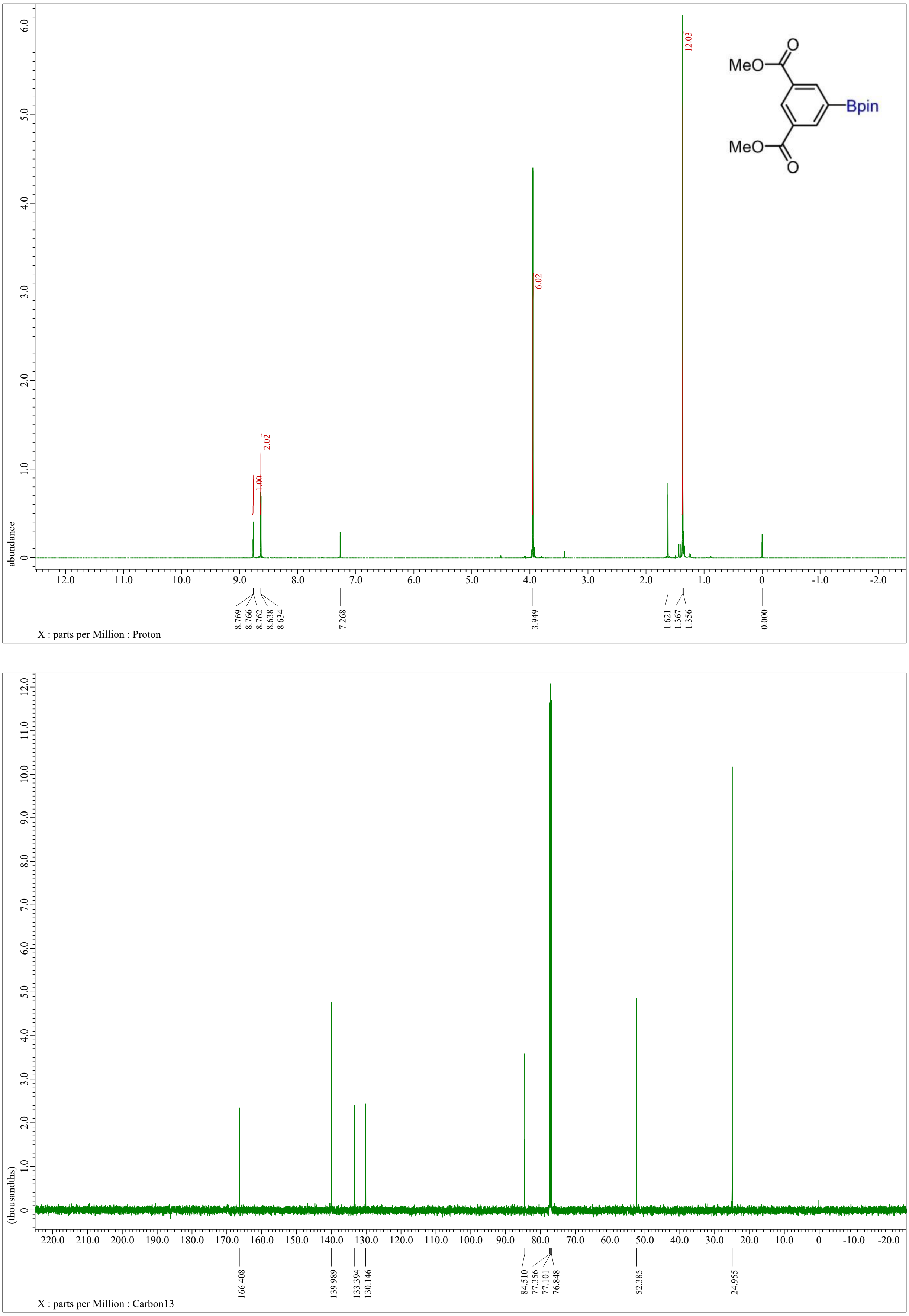


Fig. 20 ^{1}H and ^{13}C NMR spectra of product **3j**.

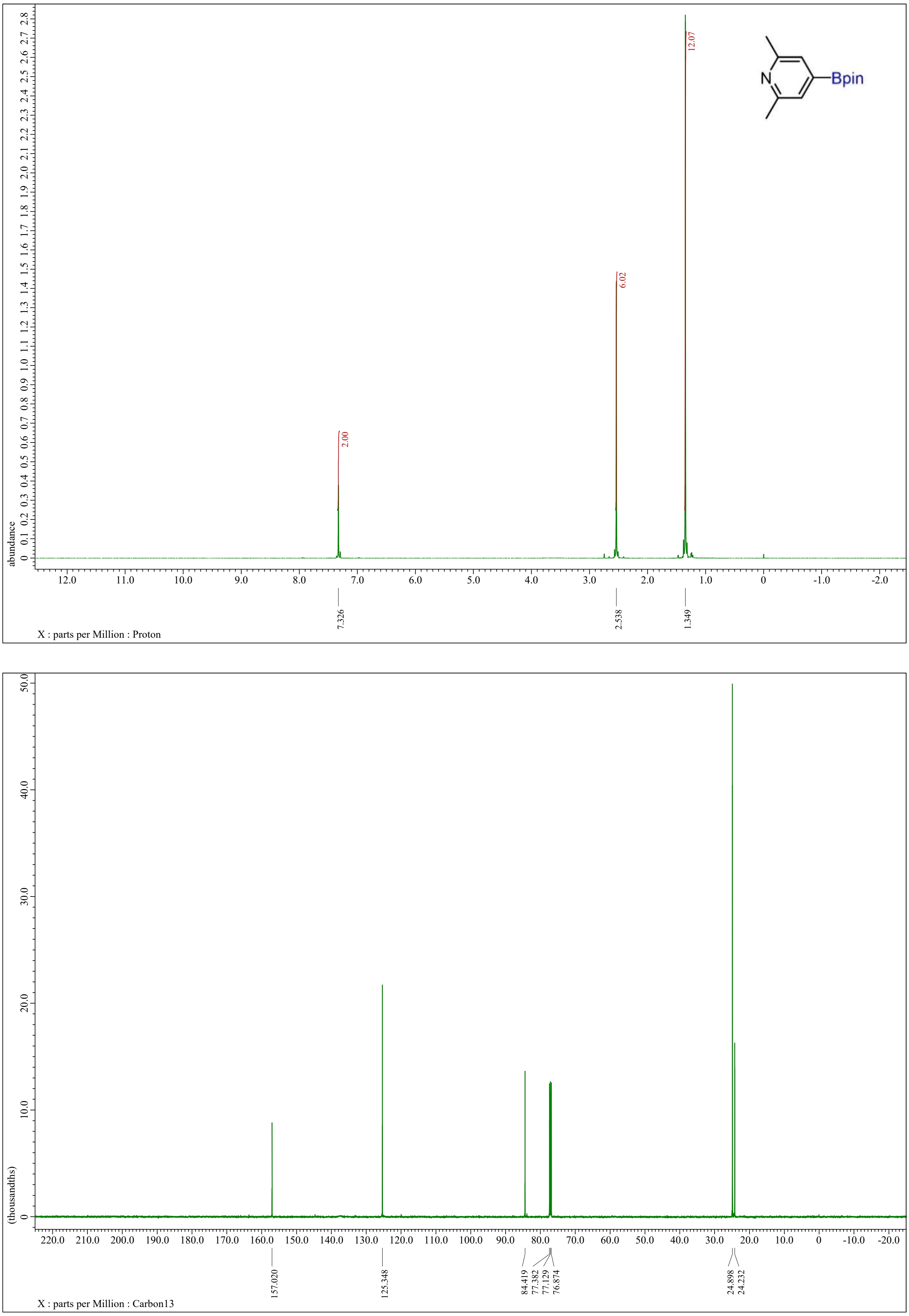


Fig. 21 ^{1}H and ^{13}C NMR spectra of product **3k**.

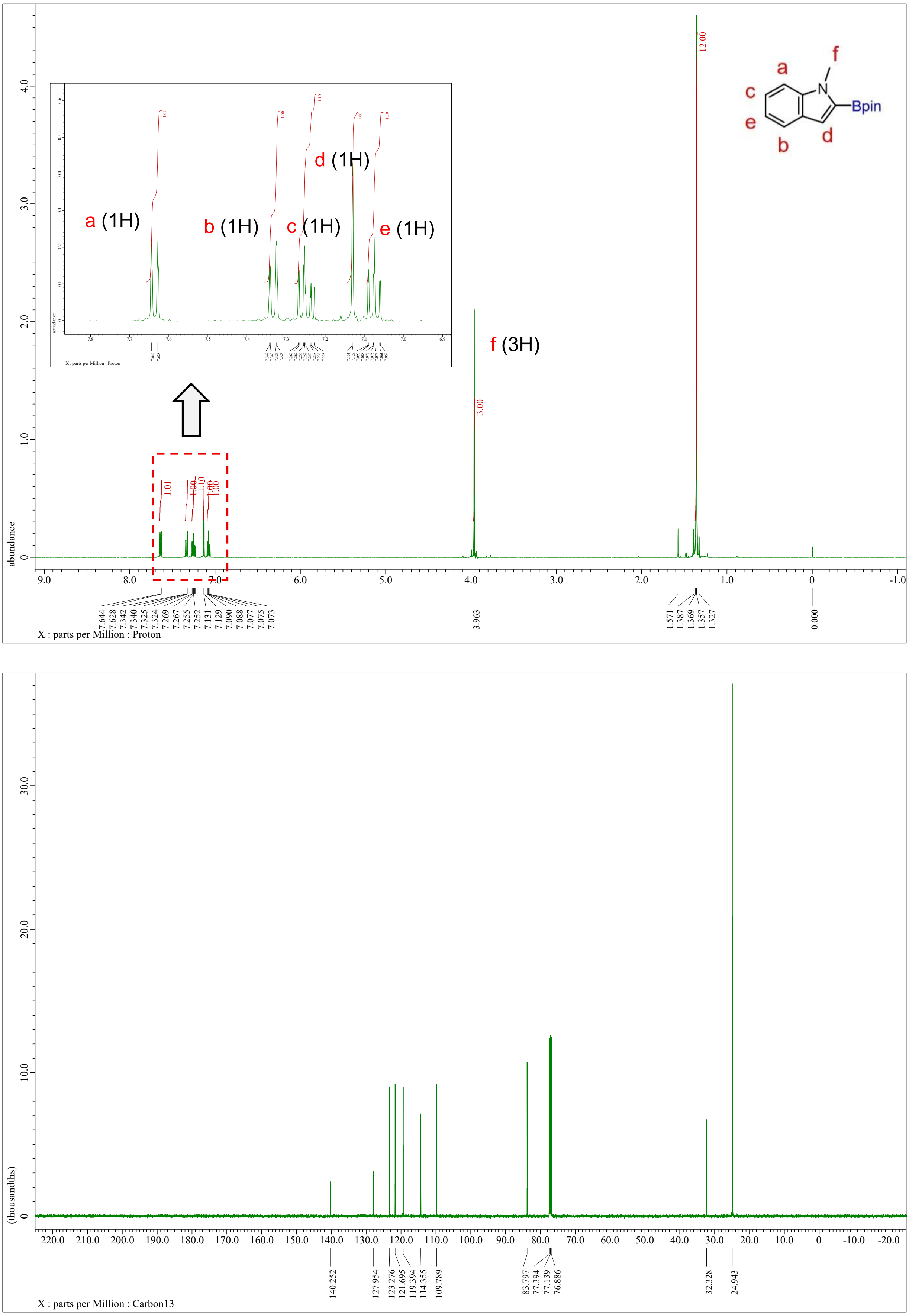


Fig. 22 ^{1}H and ^{13}C NMR spectra of product **3l**.

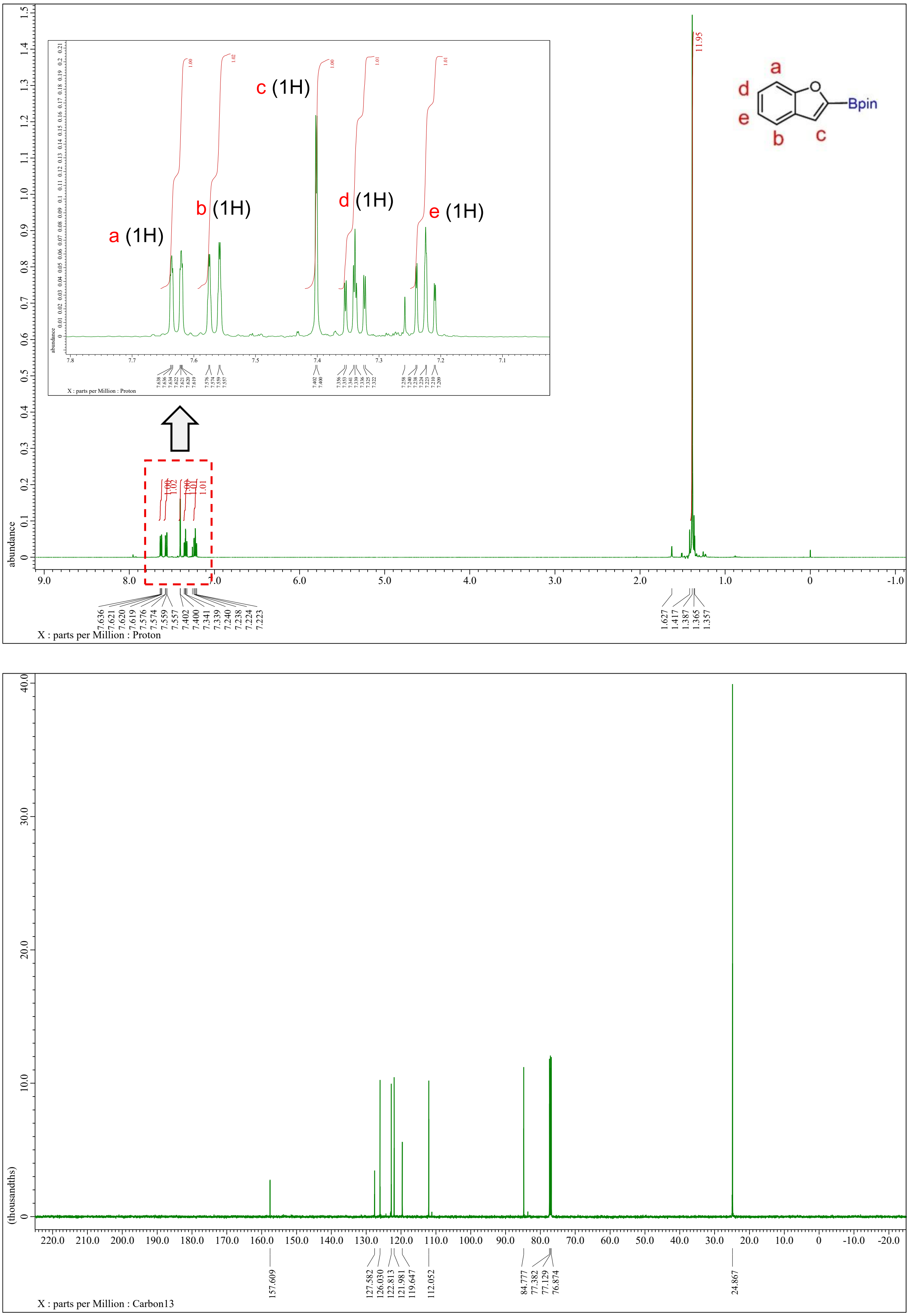


Fig. 23 ^{1}H and ^{13}C NMR spectra of product **3m**.

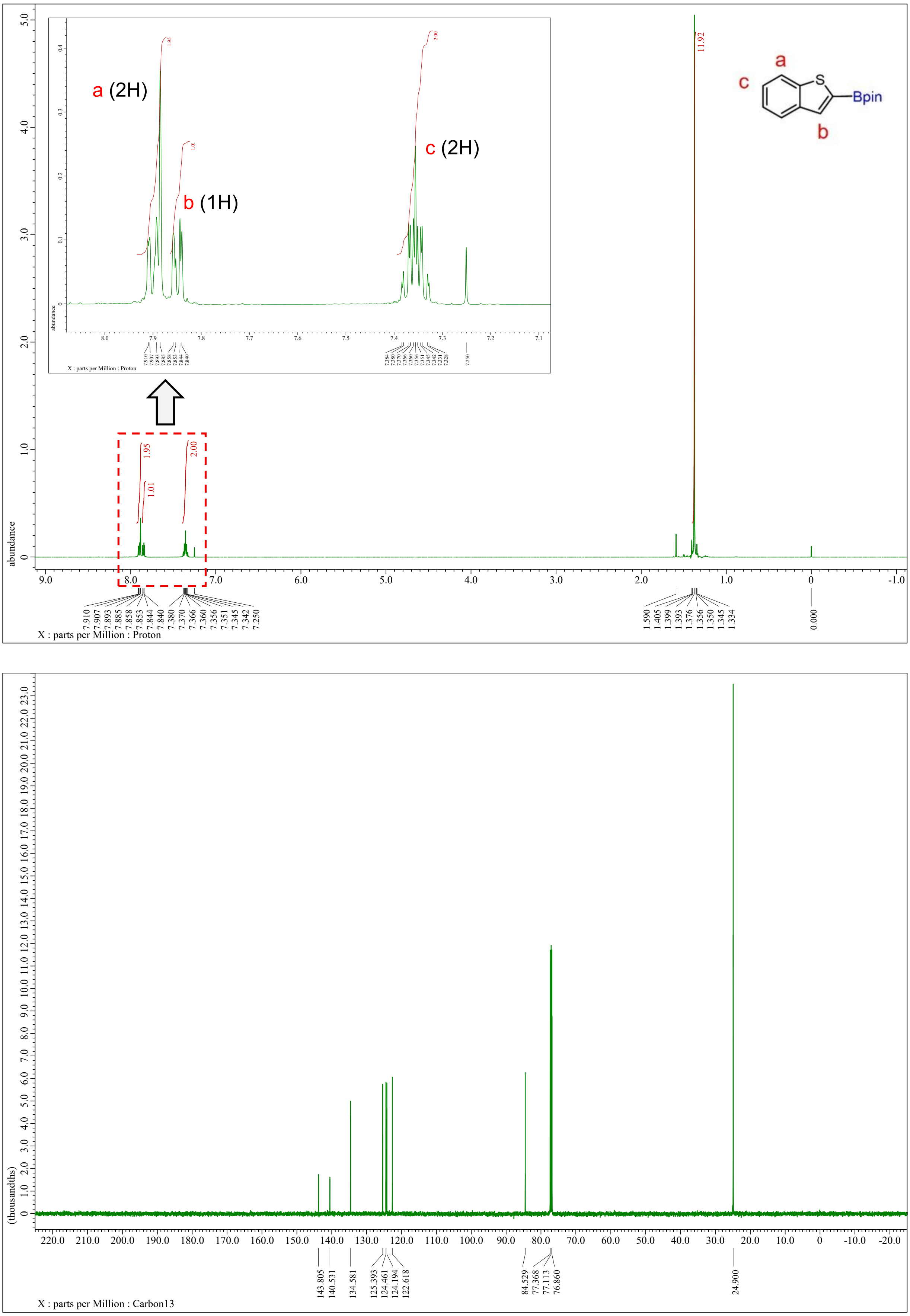


Fig. 24 ^{1}H and ^{13}C NMR spectra of product **3n**.

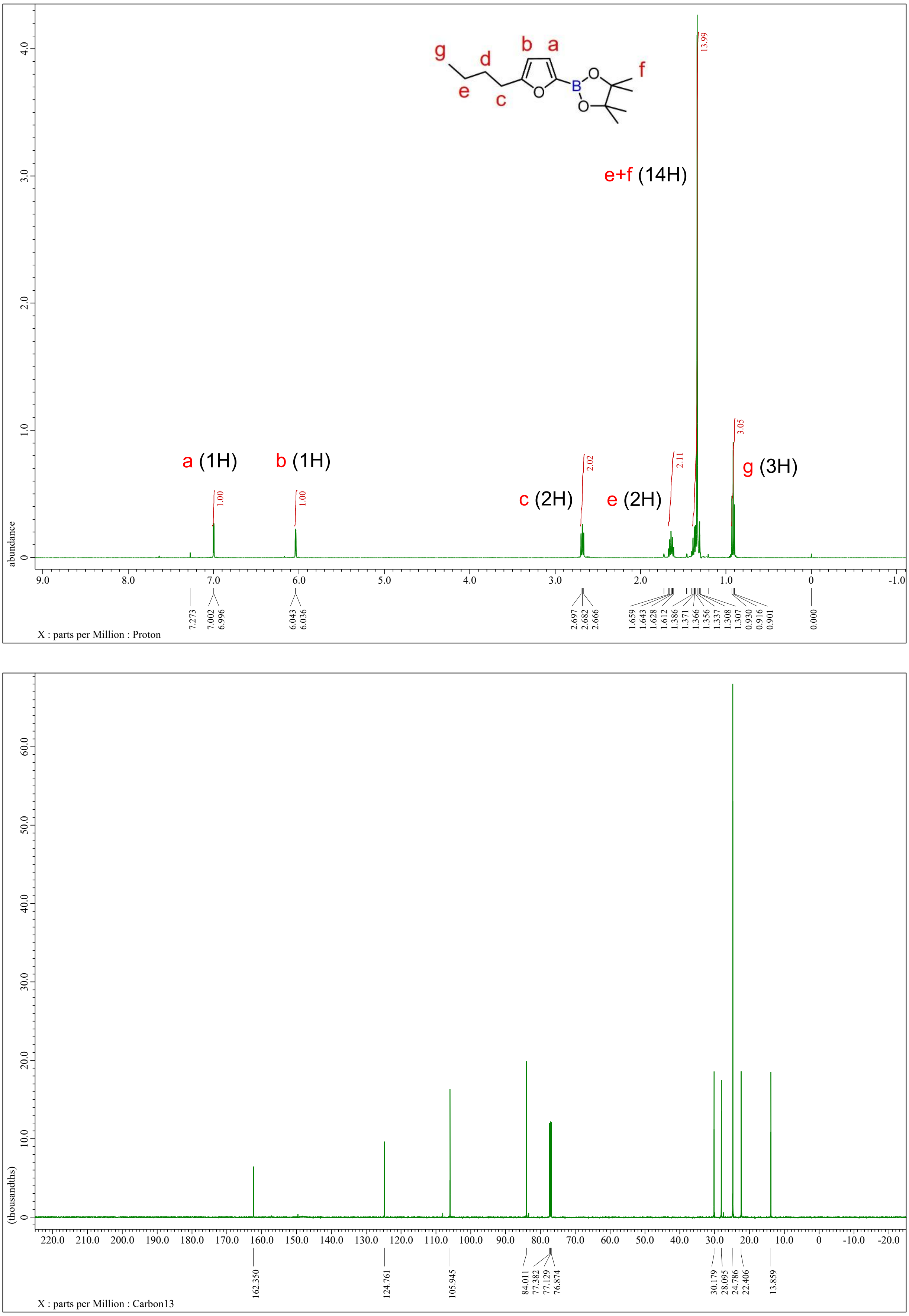


Fig. 25 ^{1}H and ^{13}C NMR spectra of product **3o**.

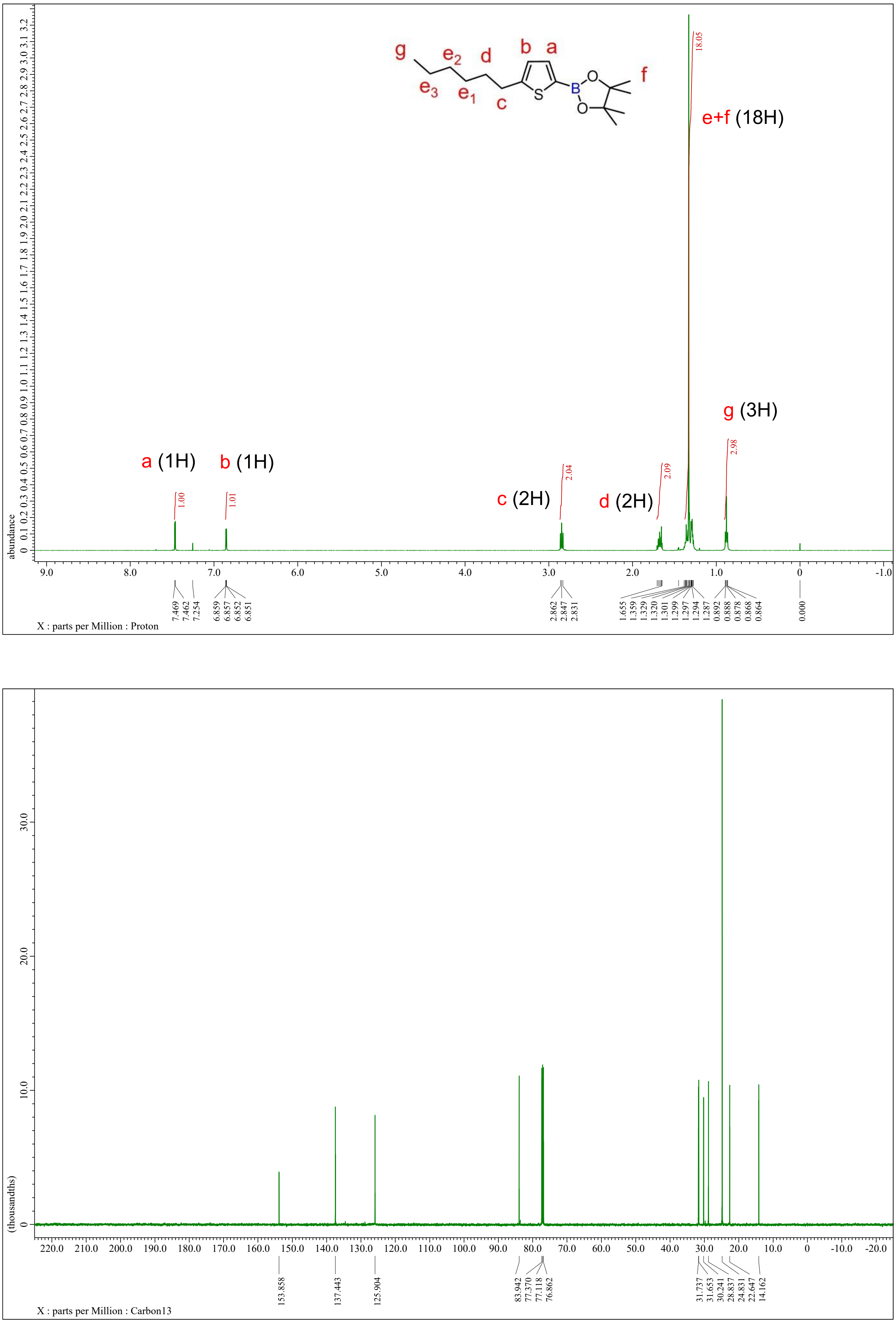


Fig. 26 ^{1}H and ^{13}C NMR spectra of product **3p**.

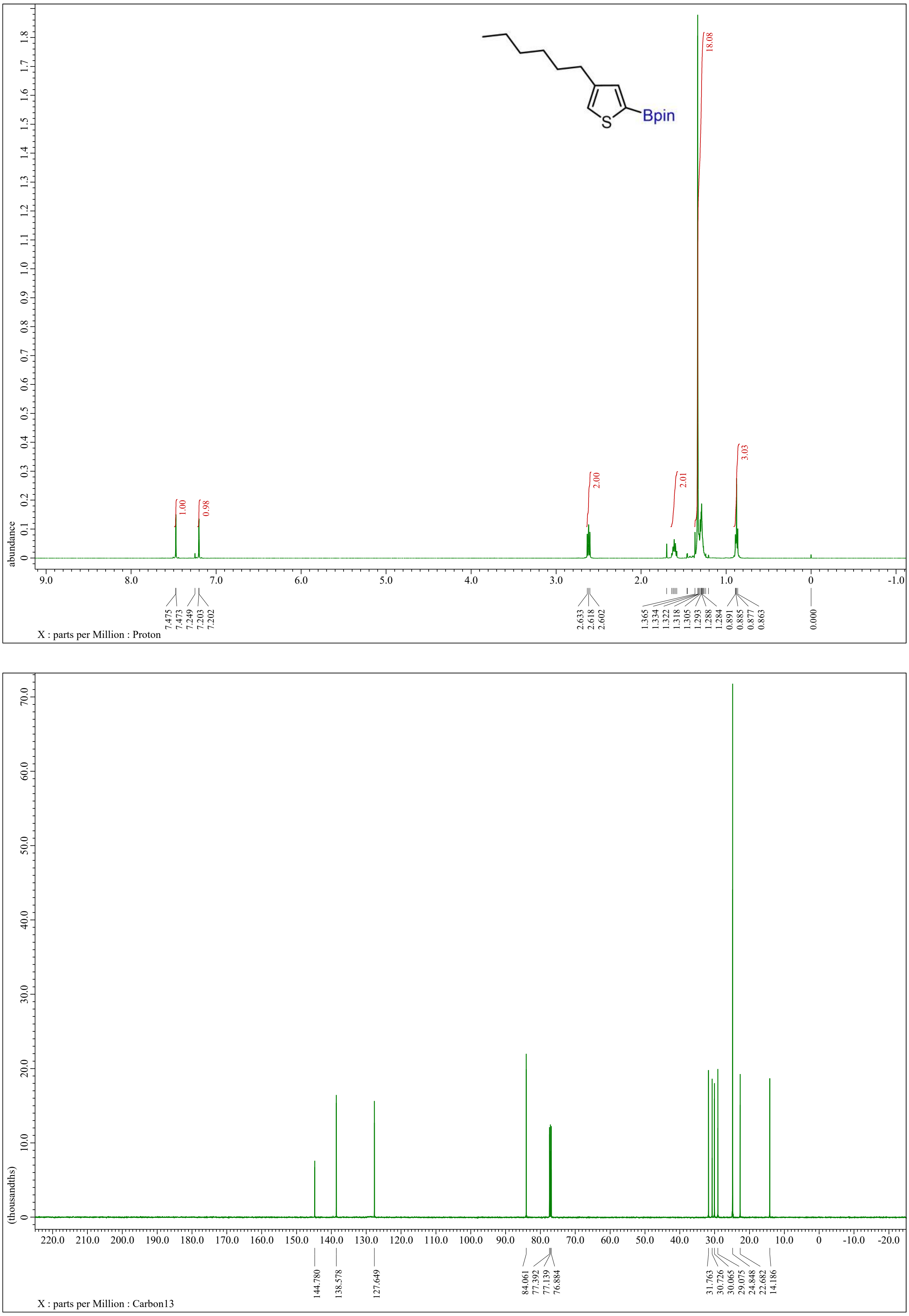


Fig. 27 ^{1}H and ^{13}C NMR spectra of product **3q**.

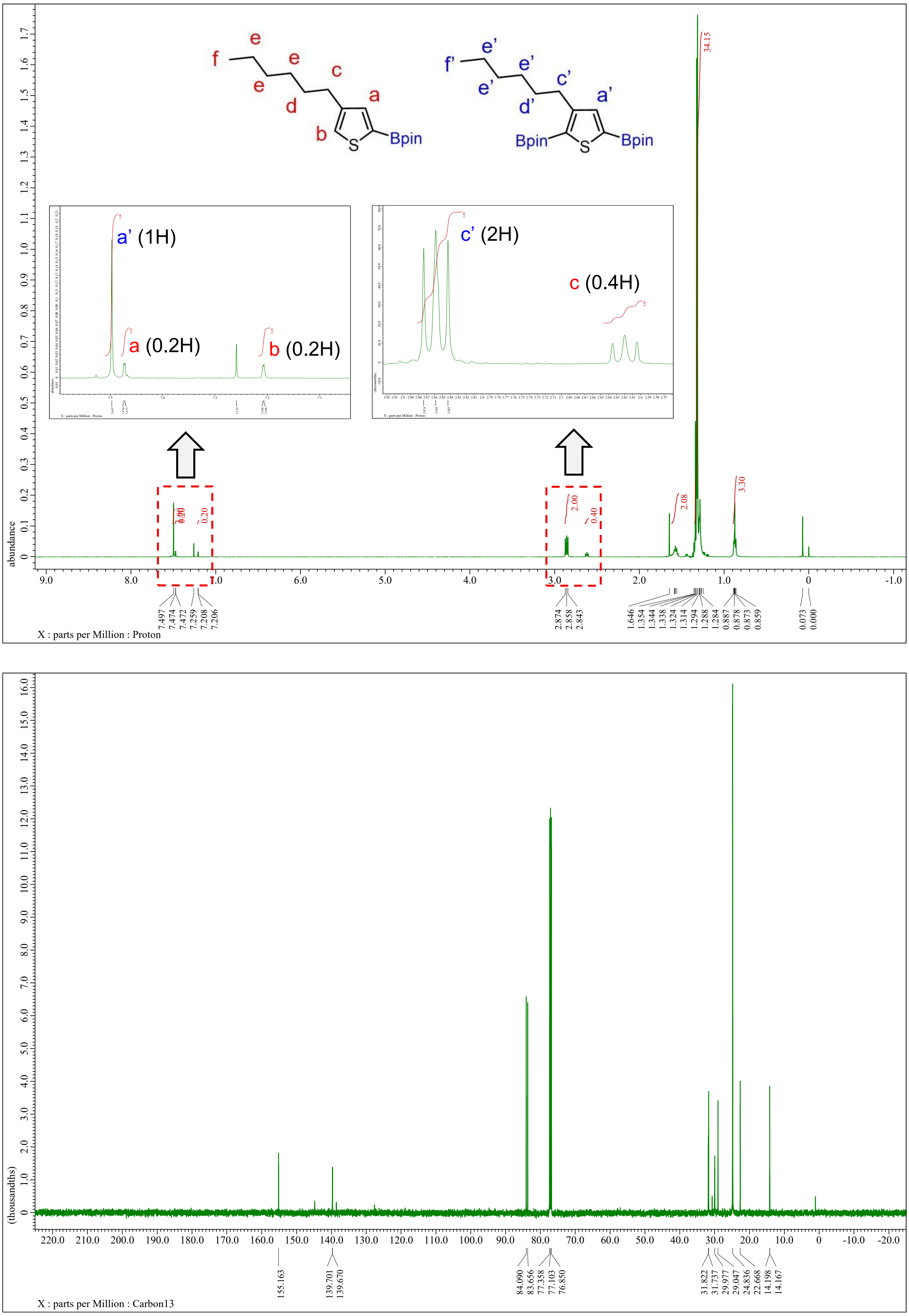


Fig. 28 ^{1}H and ^{13}C NMR spectra of product **3q** and **3qa**.

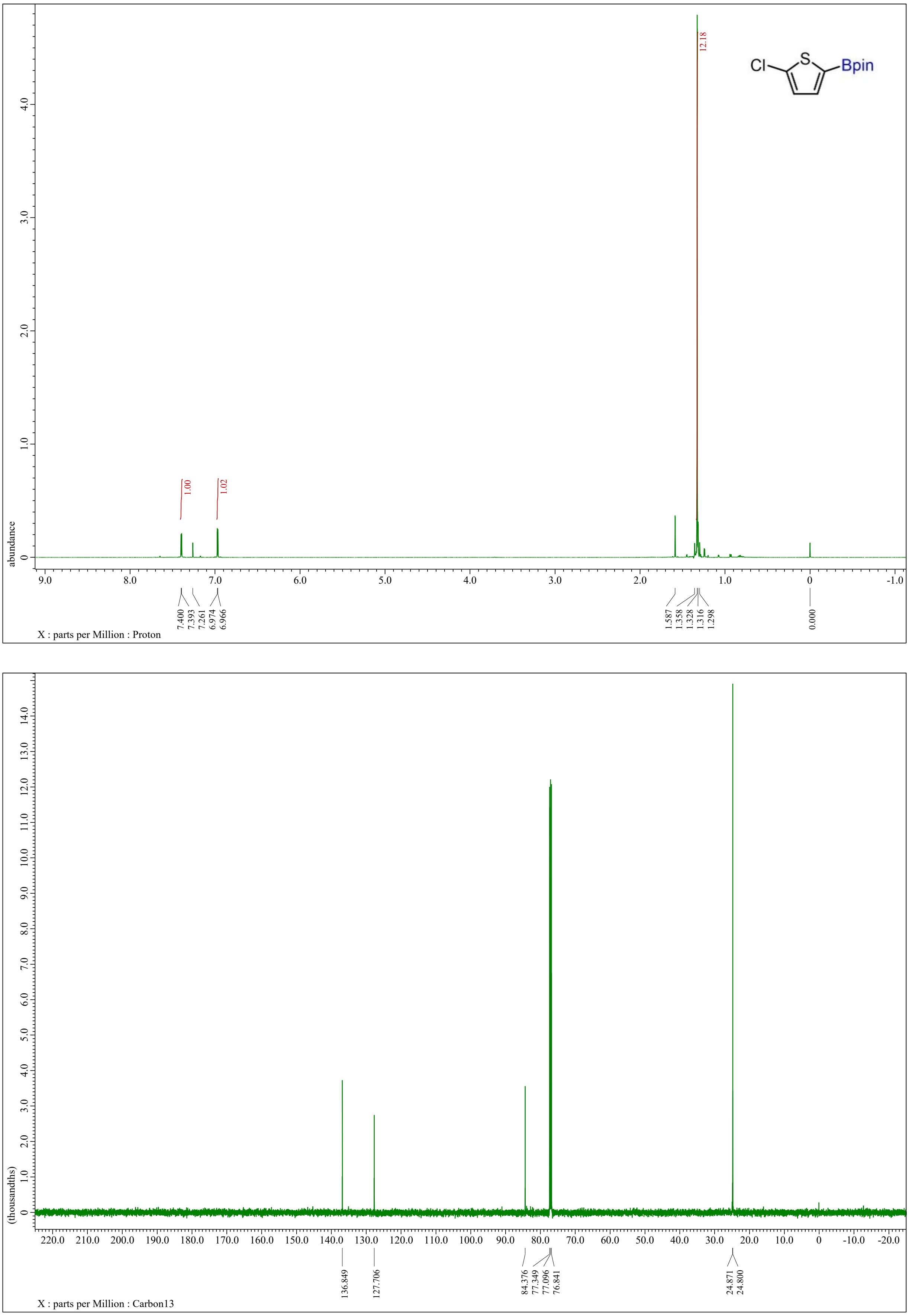
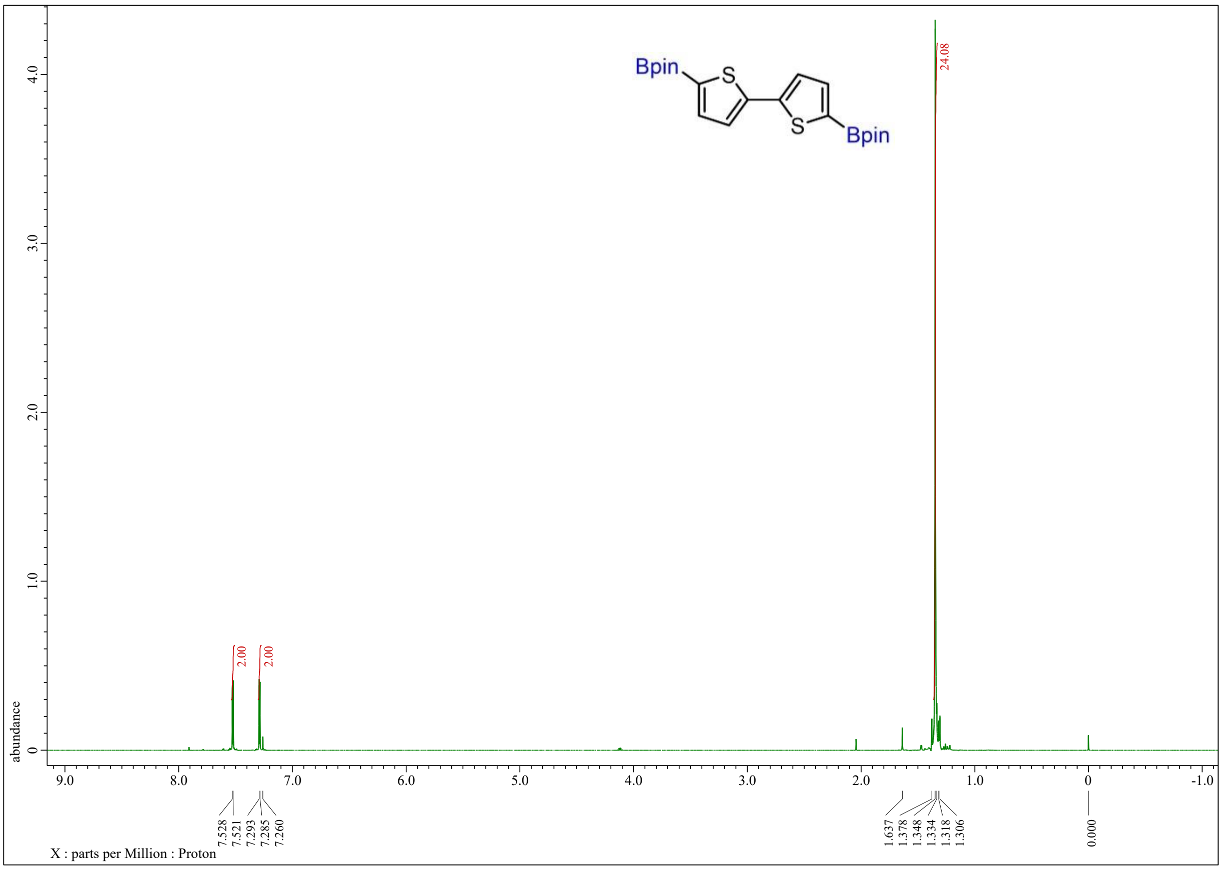


Fig. 29 ^{1}H and ^{13}C NMR spectra of product **3r**.



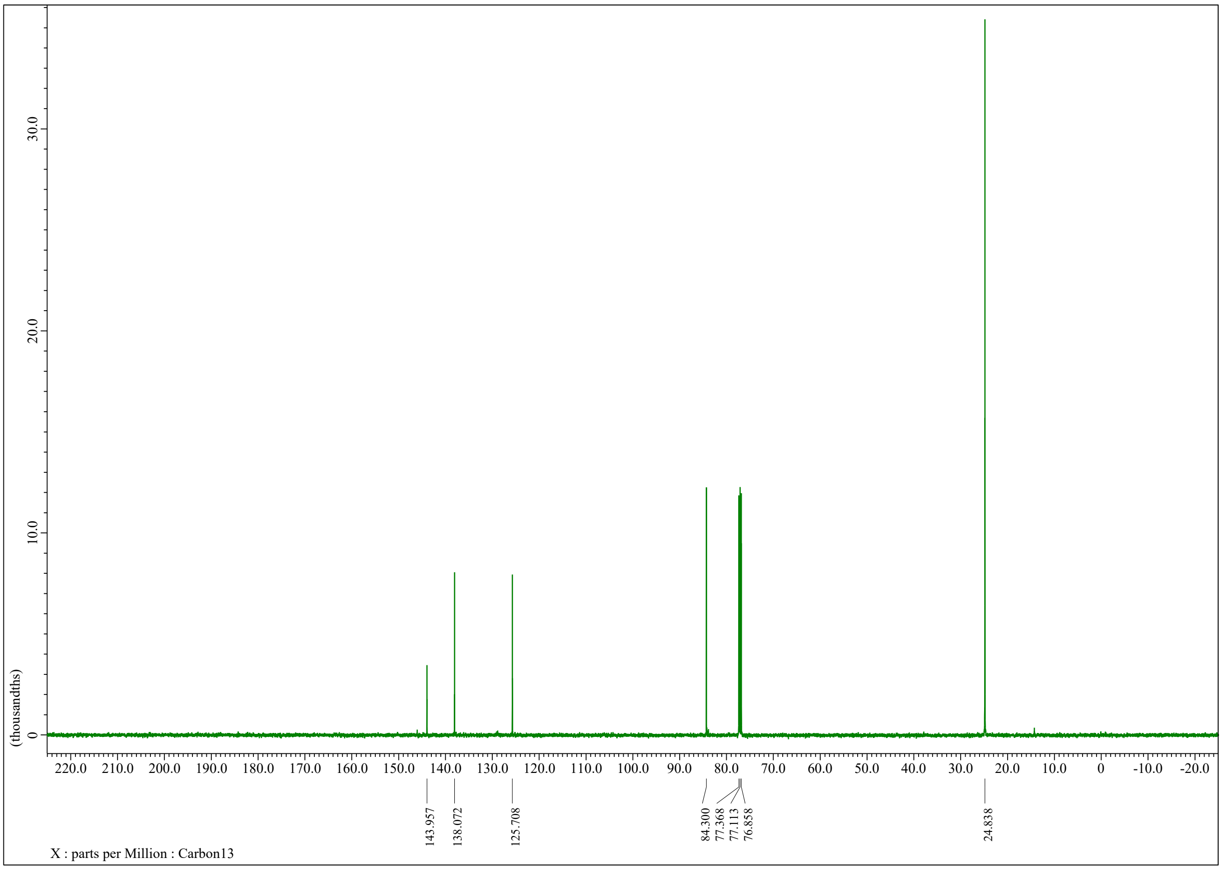
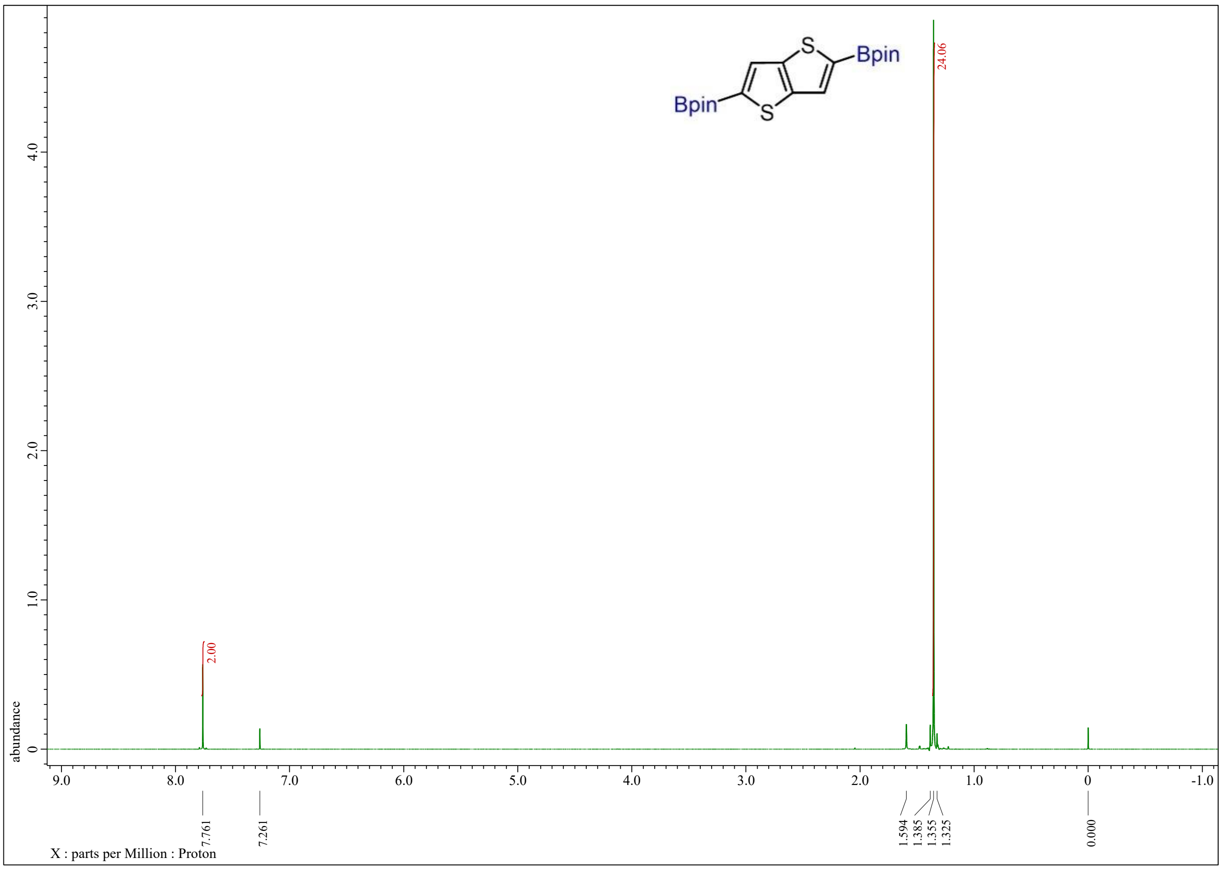


Fig. 30 ^{1}H and ^{13}C NMR spectra of product **3s**.



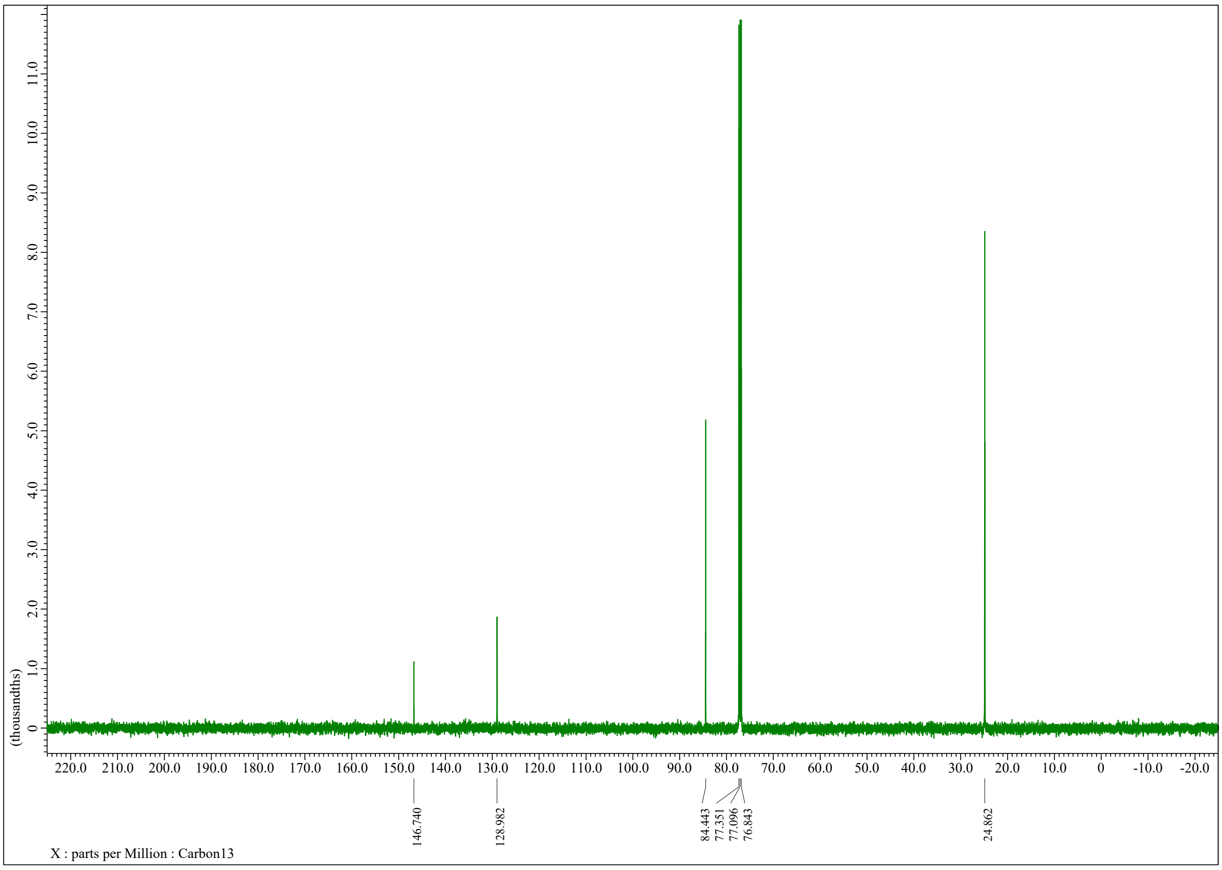


Fig. 31 ^{1}H and ^{13}C NMR spectra of product **3t**.