Experimental Section

GENERAL REMARKS

Reactions, Solvents and Chromatography

All reactions discussed as results of this work were carried out using oven dried glassware under an atmosphere of argon (99.999%).

1,2-Dichloroethane was distilled from CaH_2. Commercial reagents were purchased with the best quality affordable and used without further purification unless otherwise stated.

Final reactions at 80 ºC were performed in a Carousel Reaction Station from Radleys Discovery Technologies, equipped with gastight threaded caps with a valve, cooling reflux head system, and digital temperature controller.

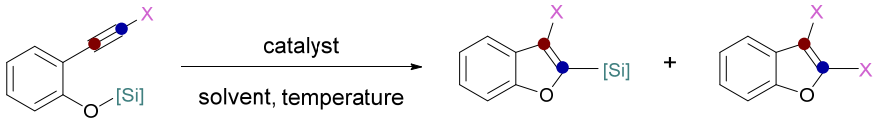
TLC was performed on aluminum-backed plates coated with silica gel 60, with F245 indicator, and developed with *p*-anisaldehyde, phosphomolybdic acid or potassium permanganate stains. Column chromatography was carried out on silica gel (230 - 400 mesh) or Florisil. Solvents used in column chromatography were obtained from commercial suppliers and used without further purification.

Data Collection

^{1}H-NMR (300, 400 MHz) and ^{13}C-NMR (75, 100MHz) spectra were measured in $CDCl_3$, at room temperature, on a Bruker DPX-300 MHz, Bruker AV-300 MHz, and Bruker AV-400 MHz apparatus. Data are reported as follows: chemical shift (δ) in parts per million (ppm), multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, sep: septet, non: nonet, dd: double doublet, dt: double triplet, m: multiplet), coupling constants (*J*) in Hertz (Hz) and integration. ^{13}C multiplicities were assigned by DEPT experiments.

High resolution mass spectra (HRMS) were determined by the University of Oviedo with a high-resolution mass spectrometer (IMPACT II, BRUKER) with a *quadrupole* and a *Time-Of-Flight* (TOF) tube as analyzers, and a conventional *Electrospray Ion Source* (ESI). The equipment uses N_2 at the nebulization (2.4 Bar), and as drying gas (250 ºC, 6.0 L/min). Mass spectra were acquired in full scan mode (4 eV) and positive ion polarity. Br-79 isotope was used for HRMS calculations.

Table S1. Optimization complete



X = Br, **1a**
X = I, **1a'**

X = Br, **2a**
X = I, **2a'**

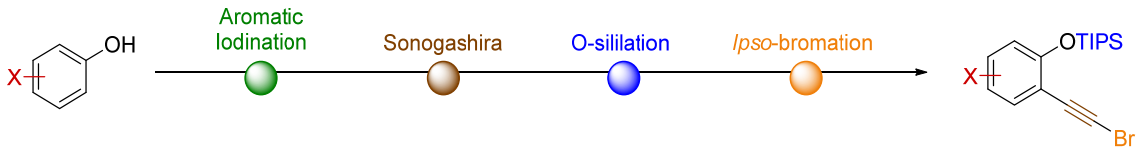
X = Br, **3a**
X = I, **3a'**

Entry	X	[Si]	Catalyst (2.5 mol%)	solvent	T (ºC)	**1** (%)	**2** (%)	**3**[a] (%)
1	I	TBS	$IPrAuNTf_2$	DCE	80	20	0	60
2	Br	TBS	$IPrAuNTf_2$	DCE	80	30	10	-
3	I	TIPS	$IPrAuNTf_2$	DCE	80	30	-	40
4	Br	TIPS	$IPrAuNTf_2$	DCE	80	10	60	-
5	Br	TIPS	$IPrAuNTf_2$	dioxane	80	15	-	-
6	Br	TIPS	$IPrAuNTf_2$	toulene	80	-	-	-
7	Br	TIPS	$[IPrAu(NCMe)]SbF_6$	DCE	80	5	71	-
8	Br	TIPS	$[IPrAu(NCMe)]SbF_6$	THF	80	76	-	14
9	Br	TIPS	$[IPrAu(NCMe)]SbF_6$	MeCN	80	57	-	22
10	Br	TIPS	$[IPrAu(NCMe)]SbF_6$	$CHCl_3$	80	55	-	-
11	Br	TIPS	$[IPrAu(NCMe)]SbF_6$	HFIP	80	74	5	-
12	Br	TIPS	$[IPrAu(NCMe)]SbF_6$	DCM	80	36	47	-
13	Br	TIPS	$[IPrAu(NCMe)]SbF_6$	DCE	rt	40	10	-
14	Br	TIPS	[IPrAu(NCMe)]BARF	DCE	80	-	78	-
15	Br	TIPS	$(ArO)_3PAuNTf_2$	DCE	80	89	-	-
16	Br	TIPS	AuCl[b]	DCE	rt	67	23	-
17	Br	TIPS	$PicAuCl_2$	DCE	80	84	-	-

[a] Other by-products observed include terminal alkyne, arising from protodehalogenation, and halomethylketon, arising from alkyne hydration with adventitious water. [b]5 mol% of catalyst was used, and the reaction mixture was stirred for 96h.

SYNTHESIS OF STARTING MATERIAL (1)

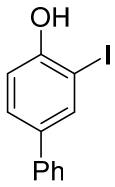
General procedure for the synthesis of derivatives (2-(bromoethynyl)phenoxy)triisopropylsilanes (1)



Most of the substrates were synthesized by means of a 3-step reaction sequence consisting of a Sonogashira coupling with trimethylsilylacetylene, followed by O-silylation and final ipso-bromination of the silylalkyne. The whole sequence can be carried out using the crude reaction

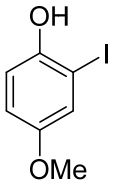
mixtures, requiring a single purification step. In a few examples, the corresponding 2-iodophenol derivative was not available and they were synthesized as follows:

3-Iodo-[1,1'-biphenyl]-4-ol



$NaClO_{aq}$ (5% w/w, 17.86 g, 12 mmol) was added to an ice cooled solution of [1,1'-biphenyl]-4-ol (1.70 g, 10 mmol), NaI (1.5 g, 10 mmol) and NaOH (0.48g, 12 mmol).[1] Upon completion, as judged by TLC analysis, the reaction was quenched with 5% aqueous $Na_2S_2O_3$ (14 mL), neutralized with 2M HCl, extracted with Et_2O (3 x 50 mL), washed with brine, dried over anhydrous Na_2SO_4 and concentrated in the rotavap. Purification by flash column chromatography afforded the title compound as a white solid (2.44 g, 82%). The spectroscopic data matched those reported in the literature.[1]

2-Iodo-4-methoxyphenol



NaH (99%, 360 mg, 15 mmol) was added portionwise to a solution of 4-methoxyphenol (1.24 g, 10 mmol) in anhydrous DMF (10 mL). Once the addition was complete, MOMCl (1.1 mL, 15 mmol) was added dropwise. Once the addition was complete, the reaction mixture was stirred an additional 1 hour. The reaction mixture was then poured into H_2O (30 mL) and extracted with pentane (3 x 10 mL). The combined organic extracts were washed sequentially with H_2O (10 mL) and brine (10 mL), dried with Na_2SO_4 and concentrated. The crude residue was used without further purification. To a solution of the crude methoxymethyl ether (1.47 g, 8.74 mmol) and TMEDA (1.6 mL, 10.49 mmol) in anhydrous Et_2O (10 mL) at -78 °C was added *n*-BuLi (2.5 M in hexanes, 4.2 mL, 10.49 mmol) dropwise. The reaction mixture was stirred at this temperature for 5 minutes and then allowed to warm to -20 °C and stir for an additional 30 minutes. The reaction mixture was then cooled to -78 °C and a solution of I_2 (2.88 g, 11.36 mmol) in Et_2O (20 mL) was added via cannula. During this addition, the reaction mixture became a thick slurry, and manual swirling was necessary to ensure full mixing. When the addition was complete, the reaction mixture was swirled an additional 5 minutes at -78 °C and then allowed to warm to ambient temperature with occasional swirling. Once the reaction mixture had reached ambient temperature, it was poured into a mixture of 1 M aq. $NaHCO_3$ (10 mL) and sat. aq. $Na_2S_2O_3$ (10 mL). The organic layer was separated and washed sequentially with 1 M aq. HCl (10 mL), 1 M aq. NaOH (10 mL) and brine (10 mL). The organic extract was dried with Na_2SO4 and concentrated to give the aryl iodide (R*f* = 0.89 in 9:1 hexanes/EtOAc) as a yellow oil that was used immediately without further purification. To a solution of the crude aryl iodide (assume 100% yield) in MeOH (10 mL) was added 10% aq. HCl (3 mL, 10 mmol). The reaction mixture was heated to reflux for 20 minutes, then it was allowed to cool to ambient temperature and concentrated to remove MeOH. The resulting residue was partitioned between EtOAc (10 mL) and brine (10 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (5 mL). The combined organic extracts were washed with brine (10 mL), dried with Na_2SO4, and concentrated. The crude residue was purified by flash column chromatography (10:1 to 5:1 hexanes/EtOAc eluent) to give phenol as a colorless solid (1.84 g, 84% yield over 2 steps, R*f* = 0.27 in 3:1 hexanes/EtOAc).[2] The spectroscopic data for phenol matched those presented in the literature.[3]

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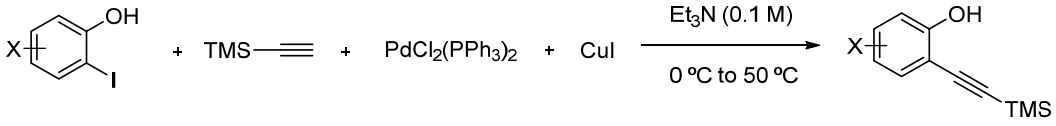
[1] Ji, F.; Lv, M.-F.; Yi, W.-B.; Cai, C. *Adv. Synth. Catal.* **2013**, *355*, 3401-3406.

[2] Huynh, K. Q.; Seizert, C. A.; Ozumerzifon, T. J.; Allegretti, P. A.; Ferreira, E. M. *Org. Lett.* **2017**, *19*, 294-297.

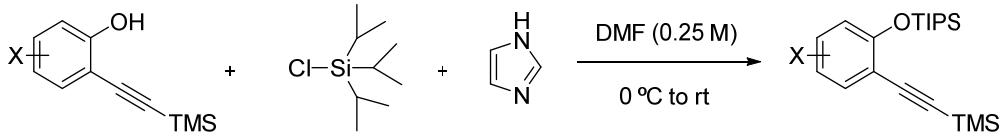
[3] Inoue, M.; Carson, M. W.; Frontier, A. J.; Danishefsky, S. J. *J. Am. Chem. Soc*. **2001**, *123*, 1878-1889.

Sonogashira:



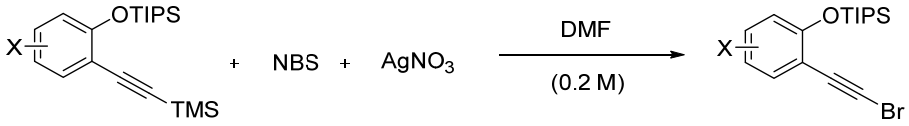
$(Ph_3P)PdCl_2$ (2 mol%) and CuI (2 mol%) were suspended in anhydrous trimethylamine (0.1 M) and stirred at room temperature for 5 minutes. Then, the corresponding 2-iodophenol derivative was added and stirring was maintained for 5 more minutes. Finally, the suspension was cooled to 0 ºC and trimethylsilylacetylene was added dropwise and the reaction mixture was stirred at 50 ºC for 5h. Upon completion, n-hexane was added and resulting suspension was filtered through celite and concentrated. The crude material was used in the next step without further purification.

O-sililation:



To a solution of the crude material obtained in step 1 and imidazole (2.5 equiv) in anhydrous DMF (0.25 M) TIPSCl (1.4 equiv) was added dropwise at 0 ºC. After stirring at room temperature for 1 hour the reaction mixture was quenched with NH_4Cl and stirred for 20 minutes. Brine and Et_2O were added and the organic layer were separated and washed 5 times with brine, dried over Na_2SO_4 and concentrated. The crude material was used in the next step without further purification.

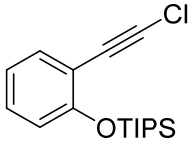
Ipso-bromination:



NBS (1.5 equiv) and $AgNO_3$ (1.1 equiv) were added to a solution of substrate in anhydrous DMF (0.2 M) and the resulting mixture was stirred at room temperature. Upon completion (typically 1-2 hours), the reaction was quenched by addition of aqueous NH_4Cl, filtered through celite, extracted with Et_2O and the organic layer washed with brine (5 times). The obtained residue was purified by means of flash chromatography using hexane : ethyl acetate (100:1), unless otherwise stated.

Yields correspond to the three steps after a single purification.

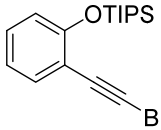
(2-(Chloroethynyl)phenoxy)triisopropylsilane (S1)



TIPSCl (0.29 mL, 1.4 equiv), was added dropwise to a solution of 2-(2-trimethylsylilethynyl)phenol (190 mg, 1mmol) and imidazole (170mg, 2.5 equiv) in anhydrous DMF (4 mL). The reaction mixture was stirred for 1h, quenched with $NH4Cl_{sat}$, diluted with brine and extracted with Et_2O (3x5 mL). The crude product obtained after removal of the volatiles was used in the next step without further purification. This crude material was dissolved in anhydrous acetonitrile (10 mL) and NCS (267mg, 2 mmol), $AgNO_3$ (51mg, 0.3 mmol) and TBAF (1M in THF, 0.6 mL, 0.6 mmol) were successively added.[4] The reaction mixture was stirred at room temperature for 1.5 hour. The solvent was evaporated under vacuum and the crude reaction mixture was purified by flash column chromatography on silica gel plug using a hexane: ethyl acetate mixture (200:1) as eluent affording product **S1** as a colorless oil (238 mg, 77%). Chloro derivative **S1** did not provide the desired cyclization under any of the studied reaction conditions.

CHARACTERIZATION DATA FOR STARTING MATERIAL (1)

[2-(bromoethynyl)phenoxy]triisopropylsilane (1a)



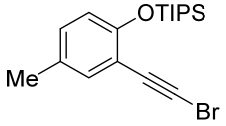
Molecular formula: $C_{17}H_{25}BrOSi$
Appearance: Colourless oil
Yield: 74 %

HRMS calc for $C_{17}H_{25}BrNaOSi$ (M+Na): 375.0750; **found (ESI):** 375.0749

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.41 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.22 (td, *J* = 8.0, 1.7 Hz, 1H), 6.95-6.82 (m, 2H), 1.35 (septet, *J* = 7.1 Hz, 3H), 1.17 (d, *J* = 7.1 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 157.8 (C), 133.6 (CH), 129.8 (CH), 120.8 (CH), 119.2 (CH), 114.9 (C), 77.5 (C), 52.7 (C-Br), 18.0 (6xCH_3), 12.9 (3xCH).

[2-(bromoethynyl)-4-methylphenoxy]triisopropylsilane (1b)



Molecular formula: $C_{18}H_{27}BrOSi$
Appearance: Colourless oil
Yield: 76 %

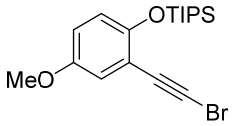
HRMS calc. for $C_{18}H_{27}BrKOSi$ (M+K): 405.0646; **found (ESI):** 405.0641

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.18 (d, *J* = 2.3 Hz, 1H), 6.98 (ddd, *J* = 8.3, 2.3, 0.6 Hz, 1H), 6.72 (d, *J* = 8.3 Hz, 1H), 2.24 (s, 3H), 1.29 (m, 3H), 1. 13 (d, *J* = 7.0 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 155.7 (C), 133.9 (CH), 130.6 (CH), 130.1 (C), 119.1 (CH), 114.6 (C), 77.8 (C), 52.3 (C-Br), 20.5 (CH_3), 18.1 (6xCH_3), 13.0 (3xCH).

[4] Gulia, N.; Pigulski, B.; Charewicz, M.; Szafert, S. *Chem. Eur. J.* **2014**, *20*, 2746-2749.

[2-(bromoethynyl)-4-methoxyphenoxy]triisopropylsilane (1c)



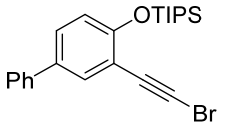
Molecular formula: $C_{18}H_{27}BrO_2Si$
Appearance: Colourless oil
Yield: 25 %

HRMS calc. for $C_{18}H_{27}BrO_2Si$ (M+H): 383,1036; **found (APCI):** 383,1031

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 6.88 (dd, *J* = 2.1, 1.4 Hz, 1H), 6.76 – 6.75 (m, 2H), 3.74 (s, 3H), 1.33 – 1.21 (m, 3H), 1.11 (d, *J* = 7.0 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 153.1 (C), 151.9 (C), 119.9 (CH), 117.2 (CH), 116.5 (CH), 114.9 (C), 77.5 (C), 55.7 (CH_3), 52.8 (C-Br), 17.9 (6xCH_3), 12.8 (3xCH).

{3-(bromoethynyl)-[1,1'-biphenyl-4-yl]oxy}triisopropylsilane (1d)



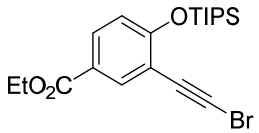
Molecular formula: $C_{23}H_{29}BrOSi$
Appearance: Colourless oil
Yield: 53 %

HRMS calc. for $C_{23}H_{29}BrKOSi$ (M+K): 467.0803; **found (ESI):** 467.0803

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.63 (d, *J* = 2.4 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.45 – 7.39 (m, 3H), 7.34 – 7.28 (m, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 1.39 – 1.37 (m, 3H), 1.16 (d, *J* = 7.0 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): 157.4 (C), 140.0 (C), 133.9 (C), 132.2 (CH), 128.9 (2 CH), 128.6 (CH), 127.1 (CH), 126.8 (2 CH), 119.6 (CH), 115.3 (C), 77.6 (C), 52.9 (C-Br), 18.1 (6xCH_3), 13.0 (3xCH).

Ethyl 3-(bromoethynyl)-4-[(triisopropylsilyl)oxy]benzoate (1e)



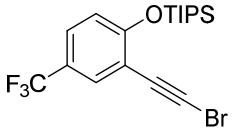
Molecular formula: $C_{20}H_{29}BrO_3Si$
Appearance: Colourless oil
Yield: 68 %

HRMS calc. for $C_{20}H_{29}BrNaO_3Si$ (M+Na): 447.0962; **found (ESI):** 447.0954

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 8.10 (d, *J* = 2.2 Hz, 1H), 7.91 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 4.35 (c, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.35 – 1.26 (m, 3H), 1.14 (d, *J* = 7.2 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 165.6 (C), 161.5 (C), 135.4 (CH), 131.5 (CH), 123.2 (C), 118.8 (CH), 115.0 (C), 76.5 (C), 60.9 (CH_2), 53.6 (C-Br), 17.9 (6xCH_3), 14.3 (CH_3), 12.8 (3xCH).

(2-(bromoethynyl)-4-(trifluoromethyl)phenoxy]triisopropylsilane (1f)



Molecular formula: $C_{18}H_{24}BrF_3OSi$
Appearance: Colourless oil
Yield: 75 %

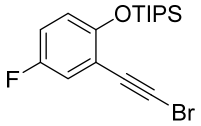
HRMS calc. for $C_{18}H_{24}BrF_3NaOSi$ (M+Na): 443.0624; **found (ESI):** 443.0626

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.65 (d, *J* = 2.4 Hz, 1H), 7.43 (ddd, *J* = 8.6, 2.4, 0.6 Hz, 1H), 6.89 (d, *J* = 8.6 Hz, 1H), 1.37 – 1.25 (m, 3H), 1.13 (d, *J* = 7.0 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 160.5 (C), 131.1 (c, *J* = 3.5 Hz, CH), 126.9 (c, *J* = 3.4 Hz, CH), 123.1 (c, *J* = 33.1 Hz, C), 122.5 (c, *J* = 271 Hz, CF_3), 119.3 (2 CH), 115.6 (CH), 76.3 (C), 54.7 (C-Br), 18.0 (6xCH_3), 13.0 (3xCH).

^{19}F NMR (282 MHz, $CDCl_3$): δ(ppm) -61.9 (s).

[2-(bromoethynyl)-4-fluorophenoxy]triisopropylsilane (1g)



Molecular formula: $C_{17}H_{24}BrFOSi$
Appearance: Colourless oil
Yield: 72 %

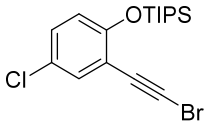
HRMS calc. for $C_{17}H_{24}BrFOSi$ (M): 371.0837; **found (ESI):** 371.0839

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.05 (dd, *J* = 8.6, 3.2 Hz, 1H), 6.93 – 6.86 (ddd, *J* = 9.0, 7.9, 3.2 Hz, 1H), 6.78 – 6.73 (dd, *J* = 9.0, 4.7 Hz, 1H), 1.27 (septet, *J* = 7.0 Hz, 3H), 1.11 (d, *J* = 7.0 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 156.3 (d, *J* = 239.8 Hz, C-F), 154.1 (d, *J* = 2.2 Hz, C), 119.9 (d, *J* = 8.5 Hz, CH), 119.5 (d, *J* = 24.2 Hz, CH), 116.7 (d, *J* = 23.1 Hz, CH), 115.6 (d, *J* = 9.8 Hz, C), 76.5 (C), 54.1 (C-Br), 17.9 (6 CH_3), 12.8 (3 CH).

^{19}F NMR (282 MHz, $CDCl_3$): δ(ppm) -123.1 (td, *J* = 8.2, 4.7 Hz, F).

[2-(bromoethynyl)-4-chlorophenoxy]triisopropylsilane (1h)



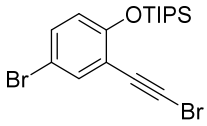
Molecular formula: $C_{17}H_{24}BrClOSi$
Appearance: Colourless oil
Yield: 46 %

HRMS calc. for $C_{17}H_{25}BrClOSi$ (M+H): 387.0541; **found (APCI):** 387.0544

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.34 (d, *J* = 2.7 Hz, 1H), 7.15 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 1.30 (septet, *J* = 7.1 Hz, 3H), 1.14 (d, *J* = 7.1 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 156.6 (C), 133.1 (CH), 129.9 (CH), 125.4 (C), 120.3 (CH), 116.5 (C), 76.4 (C), 54.5 (C-Br), 18.0 (6 CH_3), 12.9 (3 CH).

[2-(bromoethynyl)-4-bromophenoxy]triisopropylsilane (1i)



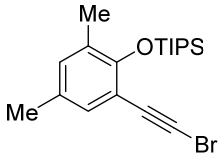
Molecular formula: $C_{17}H_{24}Br_2OSi$
Appearance: Colourless oil
Yield: 63 %

HRMS calc. for $C_{17}H_{25}Br_2OSi$ (M+H): 431.0036; **found (APCI):** 431.0032.

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.50 (d, J = 2.6 Hz, 1H), 7.29 (dd, J = 8.8, 2.5 Hz, 1H), 6.72 (d, J = 8.7 Hz, 1H), 1.41 – 1.21 (m, 3H), 1.13 (d, J = 7.2 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 157.0 (C), 135.9 (CH), 132.7 (CH), 120.7 (CH), 116.9 (C), 112.4 (C), 76.1 (C), 54.5 (C-Br), 17.9 (6xCH_3), 12.8 (3xCH).

[2-(bromoethynyl)-4,6-dimethylphfenoxy]triisopropylsilane (1j)



Molecular formula: $C_{19}H_{29}BrOSi$

Appearance: Colourless oil

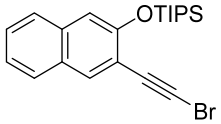
Yield: 71 %

HRMS calc. for $C_{19}H_{29}BrKOSi$ (M+K): 419.0803; **found (ESI):** 419.0796

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.03 (d, *J* = 1.6 Hz, 1H), 6.91 (d, *J* = 1.6 Hz, 1H), 2.21 (s, 6H), 1.37 (septet, *J* = 7.0 Hz, 3H), 1.13 (d, *J* = 7.4 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 154.3 (C), 132.9 (CH), 132.0 (CH), 130.1 (C), 128.9 (C), 114.1 (C), 78.9 (C), 52.2 (C-Br), 20.4 (CH_3), 18.2 (6 CH_3), 17.7 (CH_3), 14.5 (3 CH).

[(3-(bromoethynyl)naphthalen-2-yl)oxy]triisopropylsilane (1k)



Molecular formula: $C_{21}H_{27}BrOSi$

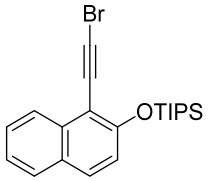
Appearance: Colourless oil

Yield: 15 %

HRMS calc. for $C_{17}H_{25}BrFOSi$ (M+H): 403.1087; **found (APCI):** 403.1093

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.96 (s, 1H), 7.73 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.66 (dd, *J* = 8.2, 0.5 Hz, 1H), 7.45 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.35 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.18 (s, 1H), 1.49 – 1.31 (m, 3H), 1.20 (d, *J* = 7.2 Hz, 18H).

[(1-(bromoethynyl)naphthalen-2-yl)oxy]triisopropylsilane (1l)



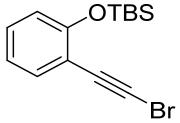
Molecular formula: $C_{21}H_{27}BrOSi$

Appearance: Colourless oil

Yield: 22 %

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.86 – 7.64 (m, 1H), 7.44 (ddt, J = 8.1, 6.8, 1.1 Hz, 0H), 7.35 (ddt, J = 9.0, 6.9, 0.9 Hz, 0H), 7.28 – 7.22 (m, 0H), 7.15 (ddd, J = 8.7, 2.5, 1.0 Hz, 0H), 1.47 – 1.28 (m, 1H), 1.16 (d, J = 7.5 Hz, 4H).

(2-(bromoethynyl)phenoxy)(tert-butyl)dimethylsilane (1m)



Molecular formula: $C_{14}H_{19}BrOSi$

Appearance: Colourless oil

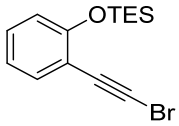
Yield: 53 %

HRMS calc. for $C_{14}H_{20}BrOSi$ (M+H): 311.0461**; found (APCI):** 311.0469

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.43 (dd, J = 7.7, 1.8 Hz, 1H), 7.26 (ddd, J = 8.2, 7.4, 1.8 Hz, 1H), 6.95 (td, J = 7.6, 1.2 Hz, 1H), 6.87 (dd, J = 8.2, 1.2 Hz, 1H), 1.12 (s, 9H), 0.29 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 157.4 (C), 133.6 (CH), 129.9 (CH), 121.2 (CH), 119.9 (CH), 115.4 (C), 77.6 (C), 52.7 (C-Br), 25.7 (3xCH_3), 18.3 (C), -4.3 (2xCH_3).

(2-(bromoethynyl)phenoxy)triethylsilane (1n)



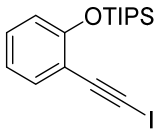
Molecular formula: $C_{14}H_{19}BrOSi$
Appearance: Colourless oil
Yield: 38 %

HRMS calc. for $C_{14}H_{20}BrOSi$ (M+H): 311.0461; **found (APCI):** 311.0472.

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.40 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.23 (ddd, *J* = 8.2, 7.4, 1.8 Hz, 1H), 6.92 (td, *J* = 7.5, 1.2 Hz, 1H), 6.84 (dd, *J* = 8.3, 1.1 Hz, 1H), 1.05 (t, *J* = 7.8 Hz, 9H), 0.80 (q, *J* = 7.8 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 157.4 (C), 133.5 (CH), 129.9 (CH), 121.2 (CH), 119.8 (CH), 115.2 (C), 77.3 (C), 52.5 (C-Br), 6.6 (3xCH_3), 5.2 (3xCH_2).

[2-(iodoethynyl)phenoxy]triisopropylsilane (1o)



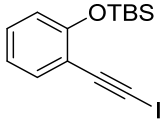
Molecular formula: $C_{17}H_{25}IOSi$
Appearance: Colourless oil
Yield: 74 %

HRMS calc for $C_{17}H_{25}BrNaOSi$ (M+Na): 423.0612; **found (ESI):** 423.0611

^{1}H NMR (300 MHz, acetone-d_6): δ(ppm) 7.38 (dd, J = 7.9, 1.8 Hz, 1H), 7.32 – 7.22 (m, 1H), 7.03 – 6.86 (m, 2H), 1.46 – 1.29 (m, 3H), 1.16 (d, J = 7.2 Hz, 18H).

^{13}C NMR (75 MHz, acetone-d_6): δ(ppm) 157.9 (C), 133.7 (CH), 130.1 (CH), 120.9 (CH), 119.2 (CH), 115.7 (C), 90.5 (C), 17.5 (6xCH_3), 13.4 (C-I), 12.8 (3xCH).

(2-(iodoethynyl)phenoxy)(tert-butyl)dimethylsilane (1p)



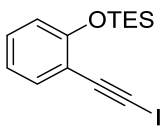
Molecular formula: $C_{14}H_{19}IOSi$
Appearance: Colourless oil
Yield: 47 %

HRMS calc. for $C_{14}H_{20}IOSi$ (M+H): 359.0323**; found (APCI):** 359.0330.

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.49 – 7.41 (m, 1H), 7.27 (t, J = 7.8 Hz, 1H), 7.03 – 6.82 (m, 2H), 1.20 – 1.01 (m, 9H), 0.37 – 0.22 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 157.8 (C), 134.0 (CH), 130.1 (CH), 121.3 (CH), 119.9 (CH), 116.1 (C), 91.5 (C), 25.9 (3xCH_3), 18.4 (C), 9.7 (C-I), -4.1 (2xCH_3).

(2-(iodoethynyl)phenoxy)triethylsilane (1p)



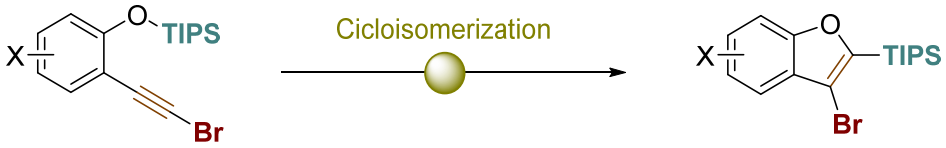
Molecular formula: $C_{14}H_{19}IOSi$
Appearance: Colourless oil
Yield: 43%

HRMS calc. for $C_{14}H_{20}IOSi$ (M+H): 359.0323; **found (APCI):** 359.0330

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.41 (dd, J = 7.7, 1.8 Hz, 1H), 7.23 (ddd, J = 8.2, 7.4, 1.8 Hz, 1H), 6.99 – 6.82 (m, 2H), 1.18 – 0.99 (m, 9H), 0.83 (qd, J = 7.8, 1.2 Hz, 6H).

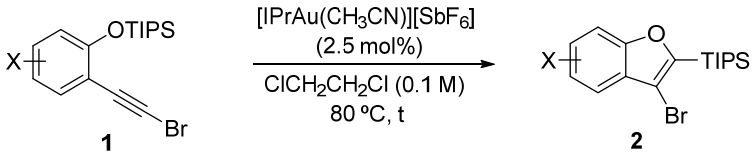
^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 157.8 (C), 133.9 (CH), 130.1 (CH), 121.2 (CH), 119.8 (CH), 116.0 (C), 91.2 (C), 9.2 (C-I), 6.8 (3xCH_3), 5.3 (3xCH_2).

SYNTHESIS OF PRODUCTS (2)



General procedure for the gold-catalyzed cyclization of

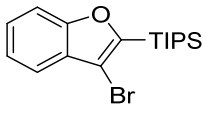
(2-(bromoethynyl)phenoxy)triisopropylsilanes (2):



[IPrAuNCMe][SbF_6] (2.5 mol%) was introduced in a flame dried Schlenck flask under an atmosphere of Argon. A solution of the corresponding substrate (0.2 mmol) in anhydrous DCE (0.1 M) was added and the reaction mixture was stirred at 80 ºC until TLC analysis confirmed consumption of the starting material (typically 1-2 hours). Solvent was removed in vacuum and the residue purified by flash chromatography using n-hexane as eluent, unless otherwise stated.

CHARACTERIZATION DATA FOR PRODUCTS (2)

(3-bromobenzofuran-2-yl)triisopropylsilane (2a)



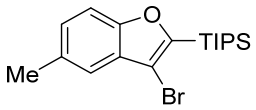
Molecular formula: $C_{17}H_{25}BrOSi$
Appearance: White solid; **m.p.**: 64-67ºC
Yield: 71 %

HRMS calc. for $C_{17}H_{26}BrOSi$ (M+H): 353.0931; **found (APCI):** 353.0941

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.58 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.39 – 7.29 (m, 2H), 1.67 (septet, *J* = 7.5 Hz, 3H), 1.19 (d, *J* = 7.5 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 157.3 (C), 157.1 (C), 128.3 (C), 125.2 (CH), 122.8 (CH), 119.7 (CH), 111.4 (CH), 109.7 (CBr), 18.6 (6 CH_3), 11.5 (3 CH).

(3-bromo-5-methylbenzofuran-2-yl)triisopropylsilane (2b)



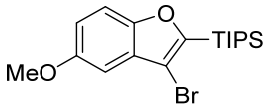
Molecular formula: $C_{18}H_{27}BrOSi$
Appearance: Colourless oil
Yield: 65 %

HRMS calc. for $C_{36}H_{54}Br_2NaO_2Si_2$ (2M+H): 755.1921; **found (ESI):** 757.1916

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.36 (d, *J* = 8.4 Hz, 1H), 7.33 (bs, 1H), 7.15 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.48 (s, 3H), 1.63 (septet, *J* = 7.5 Hz, 3H), 1.16 (d, *J* = 7.0 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 157.5 (C), 155.7 (C), 132.6 (C), 128.4 (C), 126.7 (CH), 119.4 (CH), 111.1 (CH), 109.5 (CBr), 21.4 (CH_3), 18.7 (6 CH_3), 11.6 (3 CH).

(3-bromo-5-methoxybenzofuran-2-yl)triisopropylsilane (2c)



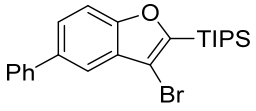
Molecular formula: $C_{18}H_{27}BrO_2Si$
Appearance: Colourless oil
Yield: 37 %

HRMS calculated for $C_{17}H_{25}BrFOSi$ (M+H): 383,1042; **found (APCI):** 383,1042

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.39 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.97 – 6.94 (m, 2H), 3.90 (s, 3H), 1.64 (septet, *J* = 7.5 Hz, 3H), 1.17 (d, *J* = 7.5 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 158.3 (C), 156.3 (C), 152.1 (C), 128.7 (C), 114.8 (CH), 112.0 (CH), 109.4 (CBr), 101.1 (CH), 56.0 (CH_3), 18.6 (6 CH_3), 11.5 (CH).

(3-bromo-5-phenylbenzofuran-2-yl)triisopropylsilane (2d)



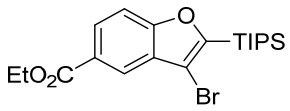
Molecular formula: $C_{23}H_{29}BrOSi$
Appearance: Colourless oil
Yield: 69 %

HRMS calculated for $C_{17}H_{25}BrFOSi$ (M+H): 429.1244; **found (APCI):** 429.1241

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.75 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.61 – 7.54 (m, 2H), 7.51 – 7.46 (m, 2H), 7.41 – 7.35 (m, 1H), 1.68 (septet, *J* = 7.5 Hz, 3H), 1.20 (d, *J* = 7.5 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 158.4 (C), 156.9 (C), 141.5 (C), 136.9 (C), 129.0 (C), 128.9 (2 CH), 127.7 (2 CH), 127.2 (CH), 125.2 (CH), 118.2 (CH), 111.8 (CH), 110.0 (CBr), 18.8 (6 CH_3), 11.6 (3 CH).

Ethyl 3-bromo-2-(triisopropylsilyl)benzofuran-5-carboxilate (2e)



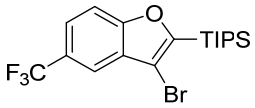
Molecular formula: $C_{20}H_{29}BrO_3Si$
Appearance: Colourless oil
Yield: 57 %

HRMS calc. for $C_{17}H_{25}BrFOSi$ (M+H): 425.1142; **found (APCI):** 425.1146

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 8.29 (d, *J* = 0.9 Hz, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 4.44 (c, *J* = 7.1 Hz, 2H), 1.71 – 1.55 (m, 3H), 1.45 (t, *J* = 7.1 Hz, 3H), 1.18 (d, *J* = 7.5 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 166.5 (C), 159.6 (C), 159.4 (C), 128.4 (C), 126.9 (CH), 125.7 (C), 122.2 (CH), 111.3 (CH), 110.1 (CBr), 61.1 (CH_2), 18.6 (6 CH_3), 14.4 (CH_2), 11.4 (3 CH).

[3-bromo-5-(trifluoromethyl)benzofuran-2-yl]triisopropylsilane (2f)



Molecular formula: $C_{18}H_{24}BrF_3OSi$
Appearance: Colourless oil
Yield: 33 % (41% brsm)

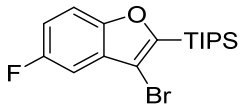
HRMS calculated for $C_{18}H_{24}BrF_3OSi$ (M+H): 421,0810; **found (APCI):** 421,0814

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.85 – 7.84 (m, 1H), 7.59 – 7.59 (m, 2H), 1.64 (septet, *J* = 7.5 Hz, 3H), 1.16 (d, *J* = 7.5 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 160.3 (C), 158.6 (C), 128.7 (C), 125.9 (c, *J* = 32.5 Hz, C), 124.6 (c, *J* = 271.9 Hz, CF_3), 122.5 (c, *J* = 3.4 Hz, CH), 117.8 (c, *J* = 3.9 Hz, CH), 112.1 (CH), 109.8 (CBr), 18.7 (6 CH_3), 11.6 (3 CH).

^{19}F NMR (282 MHz, $CDCl_3$): δ(ppm) -60.86 (s).

(3-bromo-5-fluorobenzofuran-2-yl)triisopropylsilane (2g)



Molecular formula: $C_{17}H_{24}BrFOSi$
Appearance: Colourless oil
Yield: 70 %

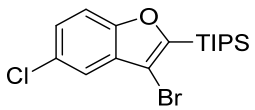
HRMS calc. for $C_{17}H_{25}BrFOSi$ (M+H): 371.0837; **found (APCI):** 371.0849

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.41 (dd, *J* = 8.9, 3.9 Hz, 1H), 7.20 (dd, *J* = 8.1, 2.6 Hz, 1H), 7.05 (td, *J* = 9.0, 2.6 Hz, 1H), 1.63 (septet, *J* = 7.5 Hz, 3H), 1.16 (d, *J* = 7.5 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 159.9 (C), 159.4 (d, *J* = 239.5 Hz, C), 153.3 (C), 129.2 (d, *J* = 10.8 Hz, C), 113.1 (d, *J* = 26.6 Hz, CH), 112.1 (d, *J* = 9.5 Hz, CH), 109.2 (d, *J* = 4.1 Hz, CBr), 105.2 (d, *J* = 25.7 Hz, CH), 18.6 (6 CH_3), 11.4 (3 CH).

^{19}F NMR (282 MHz, $CDCl_3$): δ(ppm) -120.5 (td, *J* = 8.6, 3.9 Hz).

(3-bromo-5-chlorobenzofuran-2-yl)triisopropylsilane (2h)



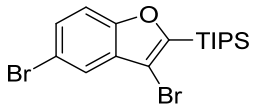
Molecular formula: $C_{17}H_{24}BrClOSi$
Appearance: Colourless oil
Yield: 54 %

HRMS calculated for $C_{17}H_{25}BrClOSi$ (M+H): 387,0547; **found (APCI):** 387,0549

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.52 (d, *J* = 2.1 Hz, 1H), 7.40 (d, *J* = 8.7 Hz, 1H), 7.28 (dd, *J* = 8.7, 2.1 Hz, 1H), 1.62 (septet, *J* = 7.5 Hz, 3H), 1.15 (d, *J* = 7.5 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 159.7 (C), 155.7 (C), 129.9 (C), 128.8 (C), 125.6 (CH), 119.5 (CH), 112.6 (CH), 108.9 (CBr), 18.7 (6xCH_3), 11.6 (3xCH).

(3,5-dibromobenzofuran-2-yl)triisopropylsilane (2i)



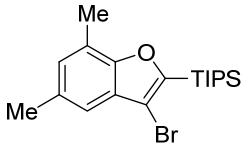
Molecular formula: $C_{17}H_{24}BrClOSi$
Appearance: Colourless oil
Yield: 72 %

HRMS calc. for $C_{17}H_{25}Br_2OSi$ (M+H): 431.0036; **found (APCI):** 431.0047.

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.70 (dd, J = 2.0, 0.6 Hz, 1H), 7.44 (dd, J = 8.7, 1.9 Hz, 1H), 7.38 (dd, J = 8.7, 0.6 Hz, 1H), 1.75 – 1.54 (m, 3H), 1.17 (d, J = 7.5 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 159.3 (C), 155.9 (C), 130.3 (C), 128.2 (CH), 122.4 (CH), 116.1 (C), 112.9 (CH), 108.6 (C), 18.6 (6xCH_3), 11.4 (3xCH).

(3-bromo-5,7-dimethylbenzofuran-2-yl)triisopropylsilane (2j)



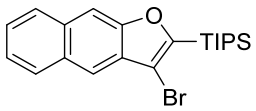
Molecular formula: $C_{19}H_{29}BrOSi$
Appearance: Colourless oil
Yield: 53 %

HRMS calculated for $C_{38}H_{58}Br_2NaO_2Si_2$ **(2M+Na):** 783.2234; **found (ESI):** 785.2223

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.16 (s, 1H), 6.97 (s, 1H), 2.48 (s, 3H), 2.44 (s, 3H), 1.67 –1.57 (m, 3H), 1.16 (d, *J* = 7.5 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 157.1 (C), 154.7 (C), 132.7 (C), 127.9 (C), 127.5 (CH), 121.3 (C), 116.8 (CH), 109.5 (CBr), 21.4 (CH_3), 18.8 (6 CH_3), 14.7 (CH_3), 11.6 (3 CH).

(3-Bromonaphto[2,3-b]furan-2-yl)triisopropylsilane (2k)



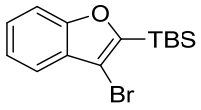
Molecular formula: $C_{21}H_{27}BrOSi$
Appearance: Colourless oil
Yield: 25 %

HRMS calculated for $C_{21}H_{28}BrOSi$ (M+H): 403.1087; **found (APCI):** 403.1080

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 8.04-8.01 (m, 2H), 7.97 – 7.92 (m, 2H), 7.50 – 7.46 (m, 2H), 1.71 (septet, *J* = 7.5 Hz, 3H), 1.22 (d, *J* = 7.5 Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 160.3 (C), 155.2 (C), 131.9 (C), 130.3 (C), 129.2 (C), 128.3 (CH), 127.8 (CH), 125.4 (CH), 124.2 (CH), 117.7 (CH), 109.4 (CBr), 106. 9 (CH), 18.7 (6 CH_3), 11.5 (3 CH).

(3-bromobenzofuran-2-yl)(tert-butyl)dimethylsilane (2m)



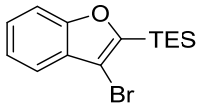
Molecular formula: $C_{14}H_{19}BrOSi$
Appearance: Colourless oil
Yield: 68 %

HRMS calc. for $C_{14}H_{20}BrOSi$ (M+H): 311.0461; **found (APCI):** 311.0467

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.63 – 7.43 (m, 1H), 7.42 – 7.25 (m, 1H), 1.02 (s, 4H), 0.47 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 158.0 (C), 157.0 (C), 128.2 (C), 125.4 (CH), 122.9 (CH), 119.7 (CH), 111.5 (CH), 109.2 (C), 26.5 (3xCH_3), 18.0 (C), -5.8 (2xCH_3).

(3-bromobenzofuran-2-yl)triethylsilane (2n)



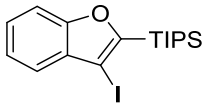
Molecular formula: $C_{14}H_{19}BrOSi$
Appearance: Colourless oil
Yield: 35 %

HRMS calc. for $C_{14}H_{20}BrOSi$ (M+H): 311.0461; **found (APCI):** 311.0457

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.60 – 7.45 (m, 2H), 7.42 – 7.30 (m, 2H), 1.15 – 0.94 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 157.9 (C), 157.1 (C), 128.1 (C), 125.3 (CH), 122.9 (CH), 119.6 (CH), 111.5 (CH), 108.9 (C), 7.3 (3xCH_3), 3.1 (3xCH_2).

(3-iodobenzofuran-2-yl)triisopropylsilane (2o)

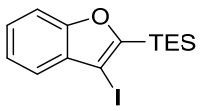


Molecular formula: $C_{17}H_{25}IOSi$
Appearance: Colourless oil
Yield: 25 %

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.55 – 7.42 (m, 2H), 7.43 – 7.10 (m, 2H), 1.73 (p, J = 7.5 Hz, 3H), 1.25 – 1.10 (m, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 160.9 (C), 157.0 (C), 131.3 (C), 125.4 (CH), 122.9 (CH), 121.5 (CH), 111.2 (CH), 78.0 (C-I), 18.8 (6xCH_3), 11.7 (3xCH).

(3-iodobenzofuran-2-yl)triethylsilane (2p)



Molecular formula: $C_{14}H_{19}IOSi$
Appearance: Colourless oil
Yield: 8%

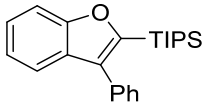
HRMS calc. for $C_{14}H_{20}IOSi$ (M+H): 359.0323; **found (APCI):** 359.0328.

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.53 – 7.42 (m, 2H), 7.40 – 7.29 (m, 2H), 1.11 – 0.92 (m, 15H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 161.5 (C), 157.1(C), 131.0 (C), 125.4 (CH), 122.9 (CH), 121.3 (CH), 111.3 (CH), 7.4 (3xCH_3), 3.3 (3xCH_2). C-I does not show.

EXPERIMENTAL PROCEDURES AND CHARACTERIZATION DATA FOR DERIVATIZATION PRODUCTS (5,6):

triisopropyl(3-phenylbenzofuran-2-yl)silane (5)



5

In a MW vial, **2a** (x mg, n mmol), phenylboronic acid (x mg, n equiv), $Pd(PPh_3)_4$ (x mg, n mol%) and Cs_2CO_3 (x mg, n equiv) were weighed. The vial was sealed, evacuated, and back filled with Ar (x3). THF (n mL) and water (n mL) were

then added, and the mixture was deoxygenated by vigorously bubbling Ar for 10 minutes. The reaction mixture was then stirred at 100 ºC overnight. Water and AcOEt were added, the two layers separated, and the aqueous layer was extracted with further AcOEt (x2). The combined organic layers were washed with brine (x2), dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by means of flash column chromatography on silica gel using hexane:AcOEt (100:1) as eluent, affording the title compound as a colorless oil (x mg, 76%).

Molecular formula: $C_{23}H_{30}OSi$
Appearance: white solid; **m.p.**: 72-75ºC

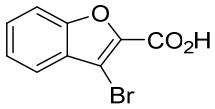
Yield: 76%

HRMS calc. for $C_{23}H_{31}OSi$ (M+H): 351,2144; **found:** 351,2149.

^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 7.64 (dt, J = 8.2, 0.9 Hz, 1H), 7.61 – 7.46 (m, 3H), 7.41 (ddd, J = 8.3, 7.2, 1.4 Hz, 1H), 7.29 (ddd, J = 8.0, 7.2, 1.0 Hz, 1H), 1.41 (dq, J = 14.1, 7.4 Hz, 1H), 1.15 (d, J = 7.5 Hz, 12H).

^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 157.7 (C), 156.2 (C), 133.8 (C), 133.5 (C), 130.2 (2xCH), 129.7 (C), 128.2 (2xCH), 127.7 (CH), 124.5 (CH), 122.3 (CH), 120.1 (CH), 111.2 (CH), 18.8 (6xCH_3), 11.8 (3xCH).

3-bromobenzofuran-2-carboxylic acid (6)



6

In a MW vial, CsF (36 mg, 2 equiv) was weighed and dried under vacuum at 100 ºC. The vial was taken to room temperature, and **2a** (42 mg, 0.12 mmol) was added. The vial was sealed, evacuated, and back filled with CO_2 (x3). DMF (0,7 mL) was then added, and CO_2 was vigorously bubbled through the reaction mixture for 10 minutes. The reaction mixture was then stirred at 100 ºC for 1h. Water and Et_2O were added, the two layers separated, and the aqueous layer was extracted with further Et_2O (x2). The aqueous layer was acidified with concentrated HCl, until a white precipitate appeared (the pH was checked with pH paper) and extracted with Et_2O (x3). The combined organic layers were washed with water (x3), and brine (x3), dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel using DCM:AcOEt 1:1 dopped with 2% AcOH as eluent, and the recrystallized by diffusion of pentane in diethyl ether (21 mg, 72%).

Molecular formula: $C_9H_5BrO_3$
Appearance: white solid; **m.p.**: 208-211ºC

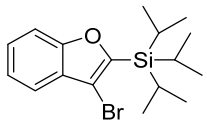
Yield: 72%

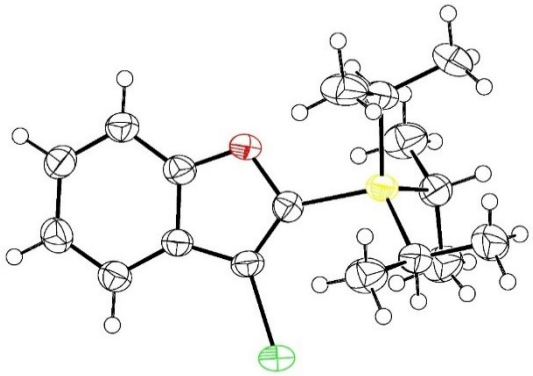
HRMS calc. for $C9H6BrO_3$ (M+H): 240.9495; **found:** 240.9494.

^{1}H NMR (300 MHz, acetone-d6): δ(ppm) 7.80 – 7.61 (m, 3H), 7.49 (ddd, J = 8.2, 6.9, 1.4 Hz, 1H).

^{13}C NMR (75 MHz, acetone-d6): δ(ppm) 158.7, 153.9, 142.1, 129.1, 128.0, 124.6, 121.4, 112.4, 104.9.

X-ray stucture of (3-bromobenzofuran-2-yl)triisopropylsilane (2a)





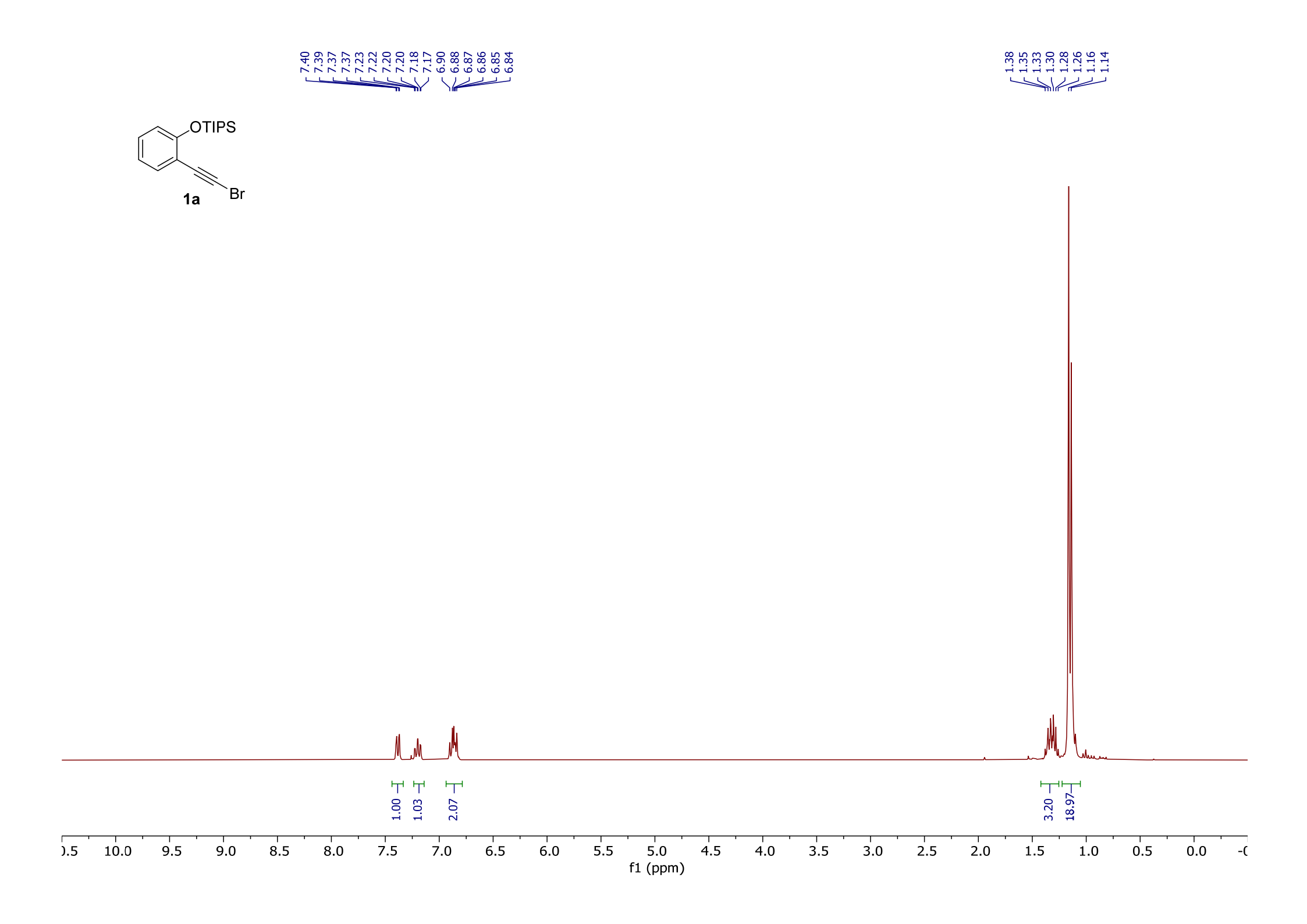
ORTEP diagram (50% probability level)

2a: $C_{17}H_{25}BrOSi$ M_r = 353.37; T = 149.9(2) K; λ = 1.54184 Å; **Crystal system:** Triclinic; **Space group:** P -1.

Unit cell dimensions: a = 7.7171(8), b = 8.9100(7), c =12.9401(8) Å, α = 82.729(6)º, β = 84.143(7)º, γ = 80.754(8)º. **Volume** = 868.09(13) Å^3; Z = 2**, Calculated density** = 1.352 Mgm^{-3}

Absorption coefficient: 3.829 mm^{-1}; **F(000) =** 368; **Crystal size:** 0.33 x 0.17 x 0.12 mm.

θ **range data collection** = 5.8027-69.5842º; **Index ranges:** -9≤h≤8, -10≤k≤10, -15≤l≤12; **Reflections collected/unique** = 6507 / 3166 [R_{int} = 0.0493]; **Completeness to** θ **=** 67.4579 (99.14%); **Absortion correction:** Semiempirical from equivalents; **Max. and min. transmission** = 1.0000 and 0.49738; **Refinement method:** full matrix least-squares on F^2; **Data /restraints / parameters** = 3166/0/187; **Goodness-of-fit on** F^2 = 1.137; **Final** R **indices [**I**>2**σ**(**I**)]:** R_1 = 0.0543, wR_2 = 0.1557; R **indices (all data):** R_1 = 0.0595, wR_2 = 0.1700; **Largest difference peak and hole** = 0.711 and -1.322 eÅ^{-3}. **Deposit number:** CCDC2174330.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7.37
7.37
7.23
7.22
7.20
7.20
7.18
7.17
6.90
6.88
6.87
6.86
6.85
6.84
1.38
1.35
1.33
1.30
1.28
1.26
1.16
1.14
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Br
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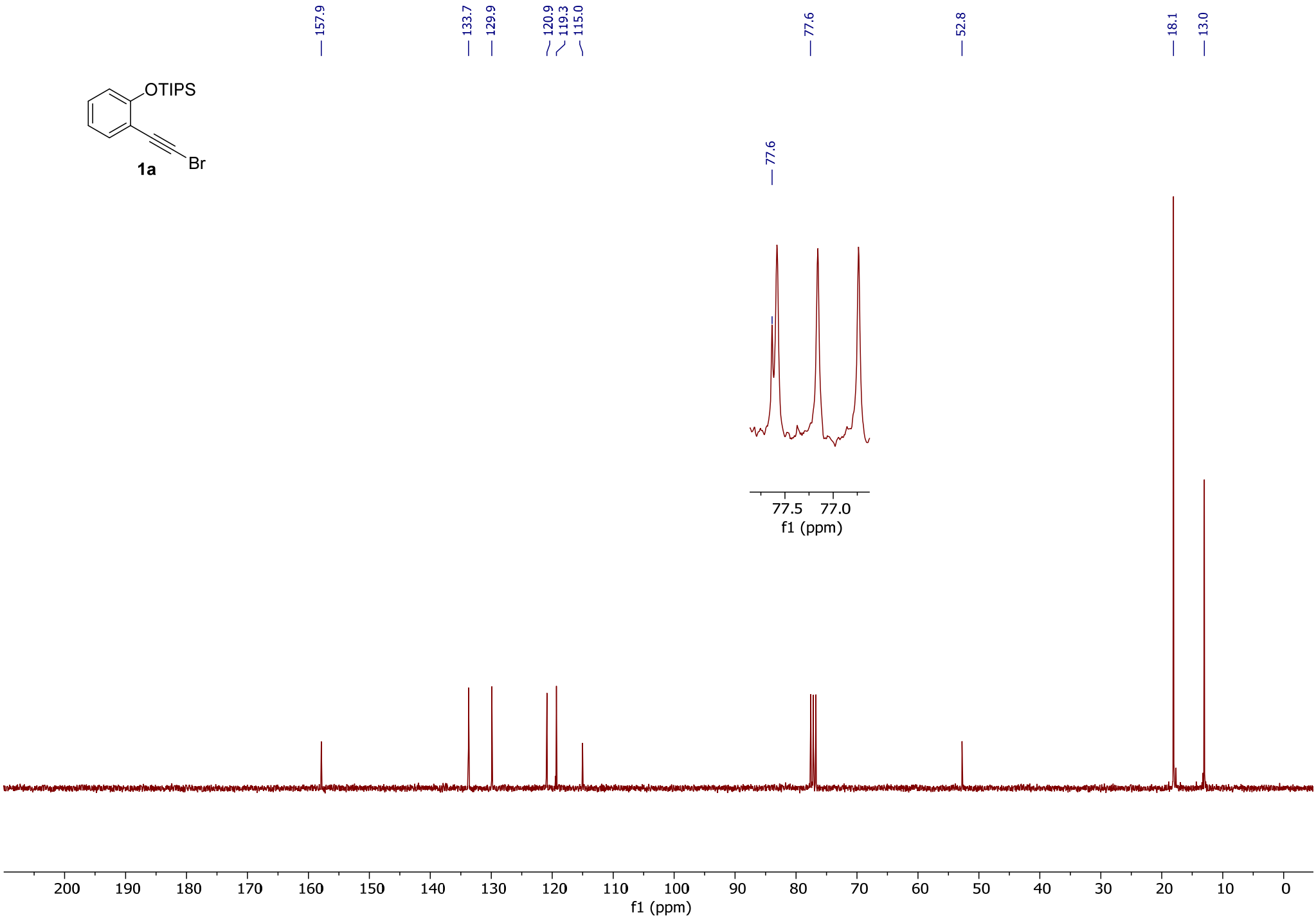
1.03
2.07
3.20
18.97
f1 (ppm)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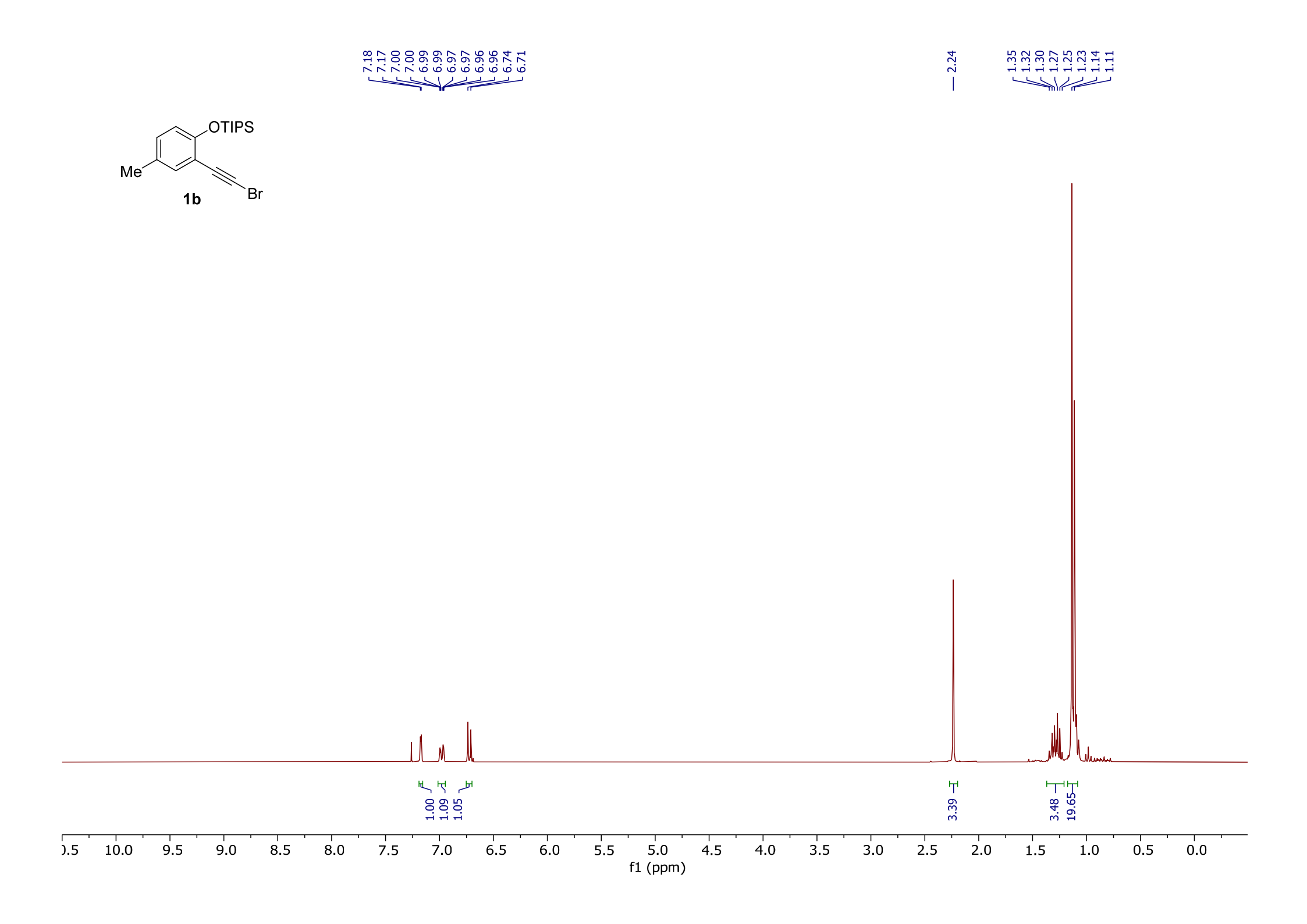
129.9
120.9
119.3
115.0
77.6
52.8
18.1
13.0
OTIPS
Br
1a
77.6
77.5
77.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.17
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7.00
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6.97
6.97
6.96
6.96
6.74
6.71
2.24
1.35
1.32
1.30
1.27
1.25
1.23
1.14
1.11
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Br
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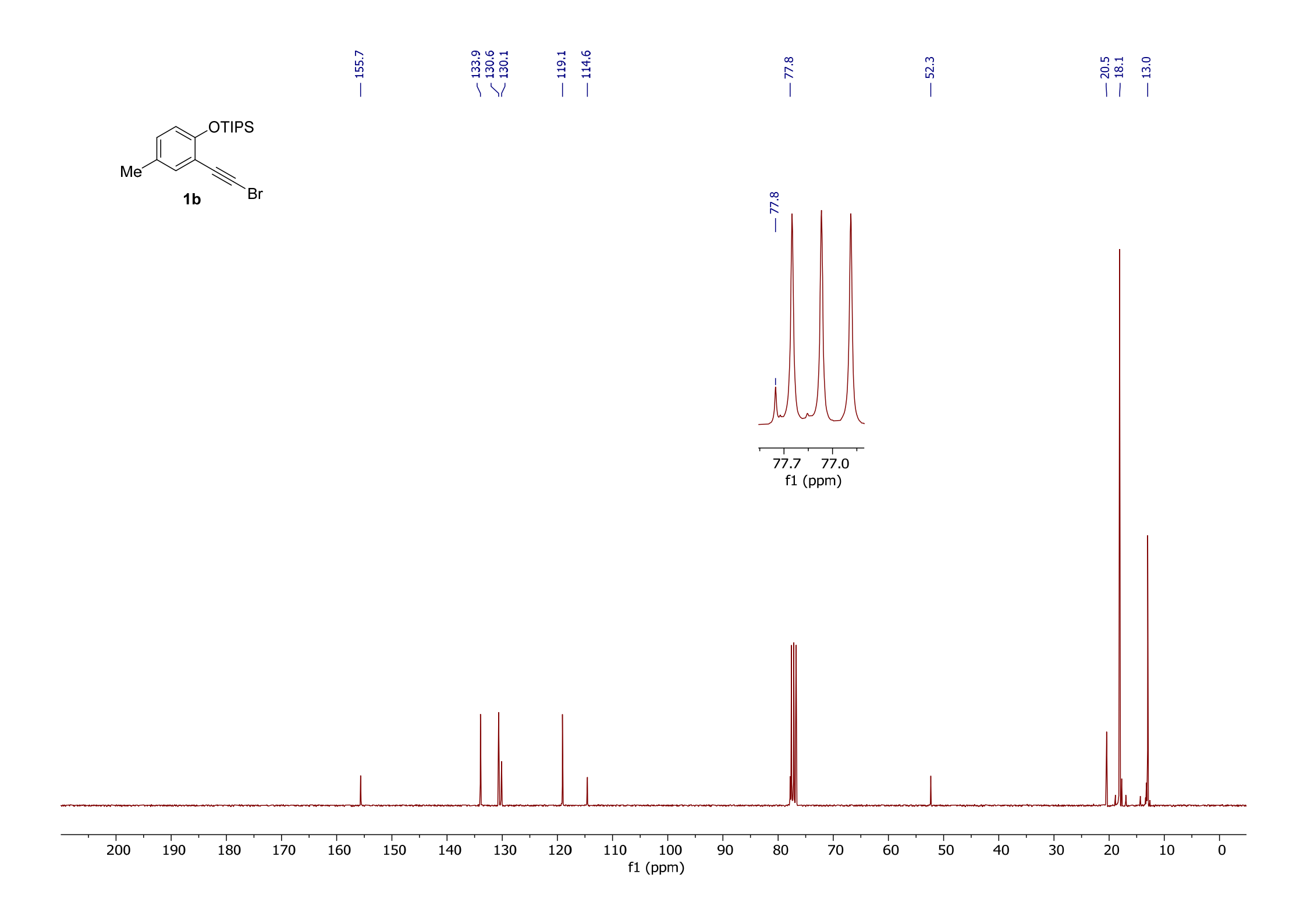
1.09
1.05
3.39
3.48
19.65
f1 (ppm)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130.6
130.1
119.1
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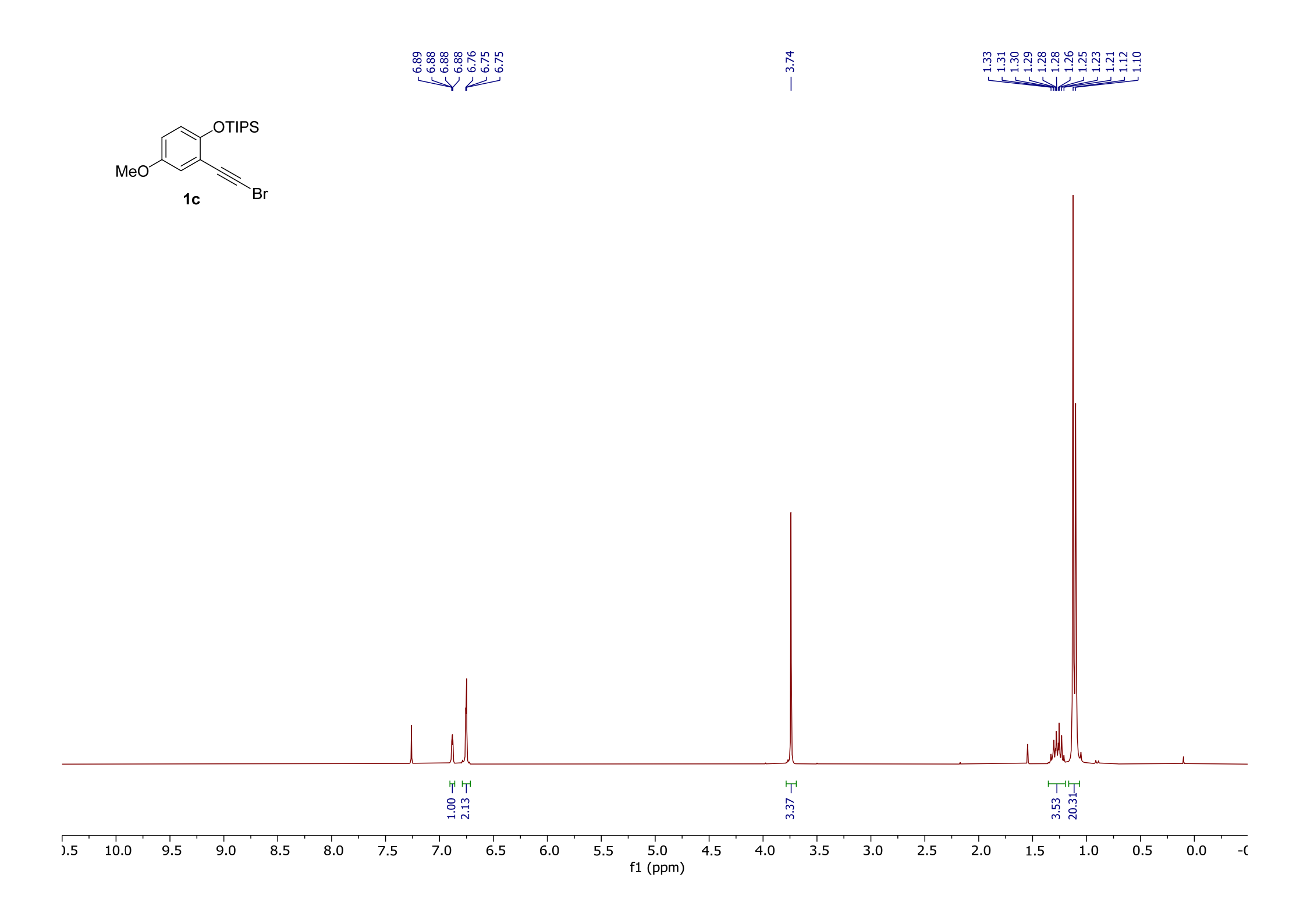
52.3
20.5
18.1
13.0
OTIPS
Me
Br
1b
77.8
77.7
77.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


6.89
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6.88
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6.75
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3.74
1.33
1.31
1.30
1.29
1.28
1.28
1.26
1.25
1.23
1.21
1.12
1.10
OTIPS
MeO
Br
1c
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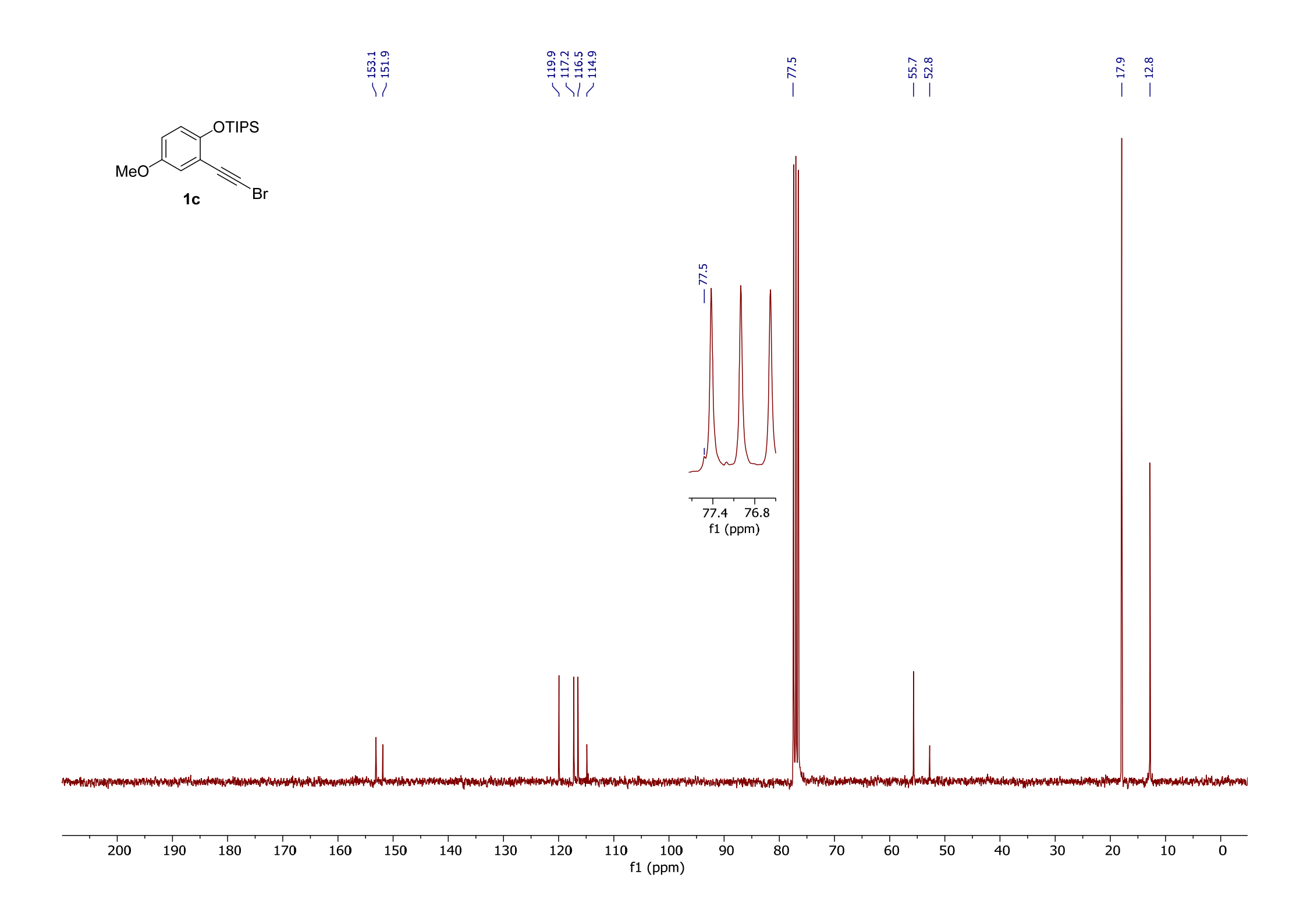
2.13
3.37
3.53
20.31
f1 (ppm)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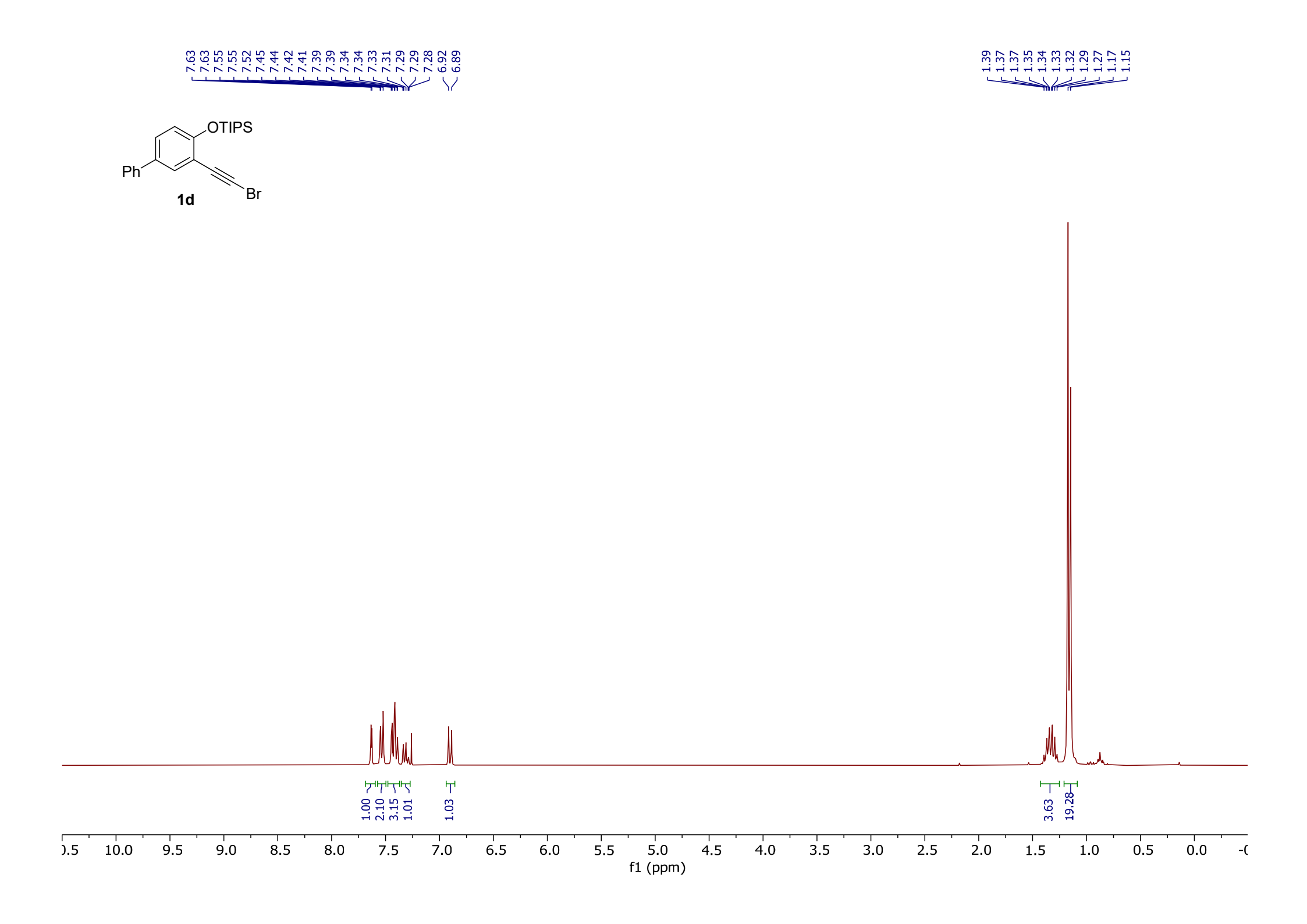
151.9
119.9
117.2
116.5
114.9
77.5
55.7
52.8
17.9
12.8
OTIPS
MeO
Br
1c
77.5
77.4
76.8
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.63
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7.39
7.39
7.34
7.34
7.33
7.31
7.29
7.29
7.28
6.92
6.89
1.39
1.37
1.37
1.35
1.34
1.33
1.32
1.29
1.27
1.17
1.15
OTIPS
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Br
1d
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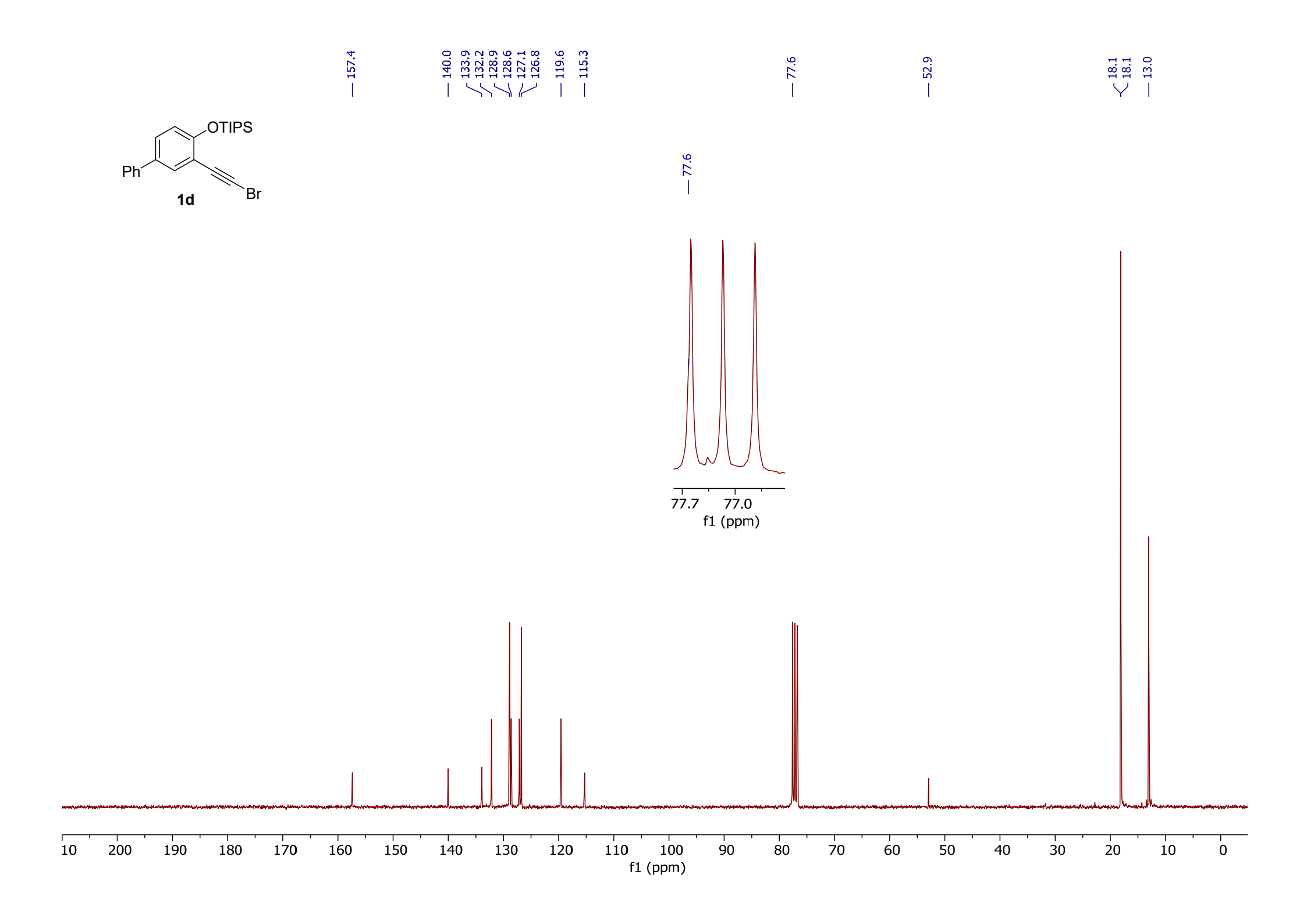
2.10
3.15
1.01
1.03
3.63
19.28
f1 (ppm)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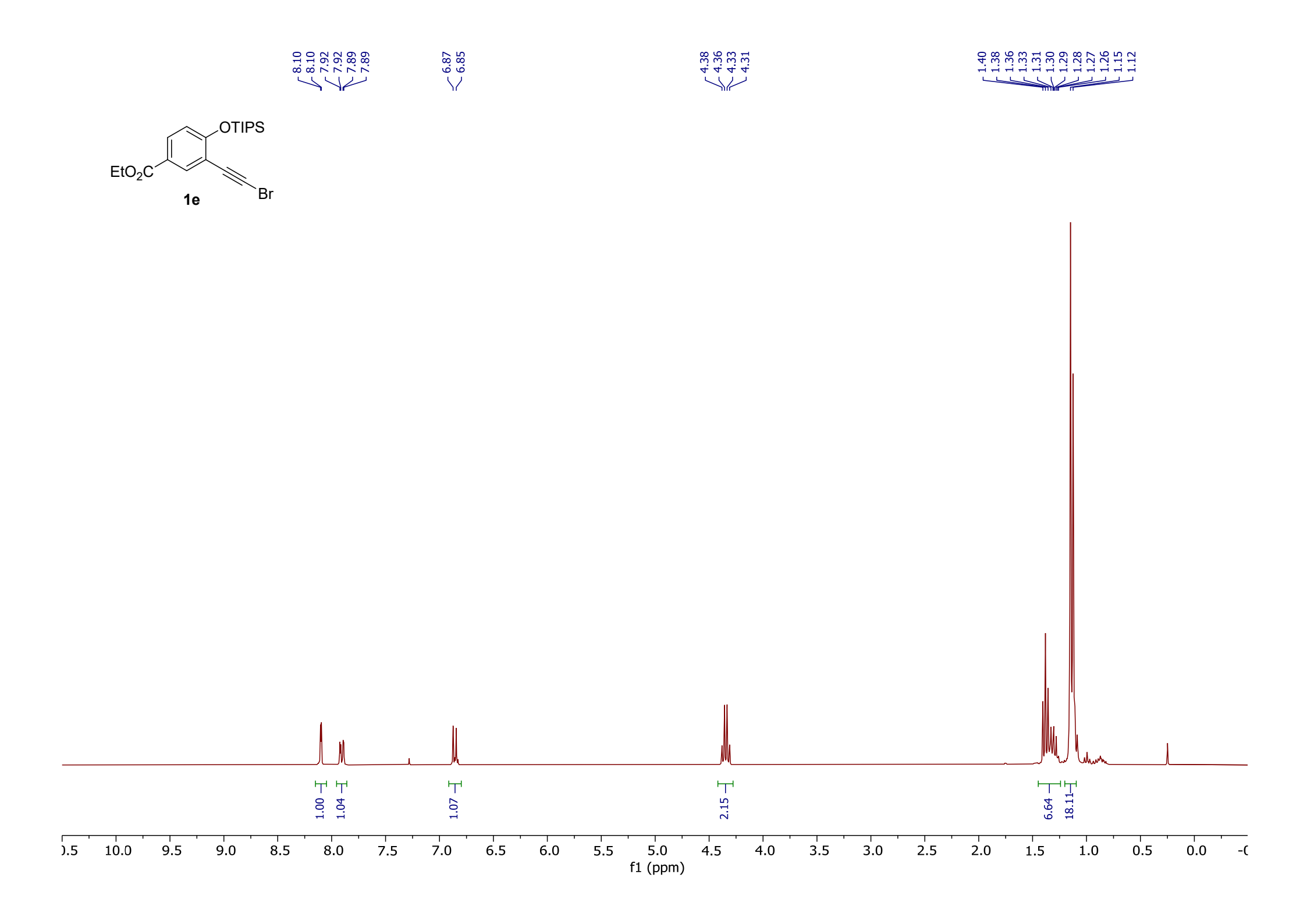
133.9
132.2
128.9
128.6
127.1
126.8
119.6
115.3
77.6
52.9
18.1
18.1
13.0
OTIPS
Ph
Br
1d
77.6
77.7
77.0
f1 (ppm)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.10
8.10
7.92
7.92
7.89
7.89
6.87
6.85
4.38
4.36
4.33
4.31
1.40
1.38
1.36
1.33
1.31
1.30
1.29
1.28
1.27
1.26
1.15
1.12
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EtO2C
Br
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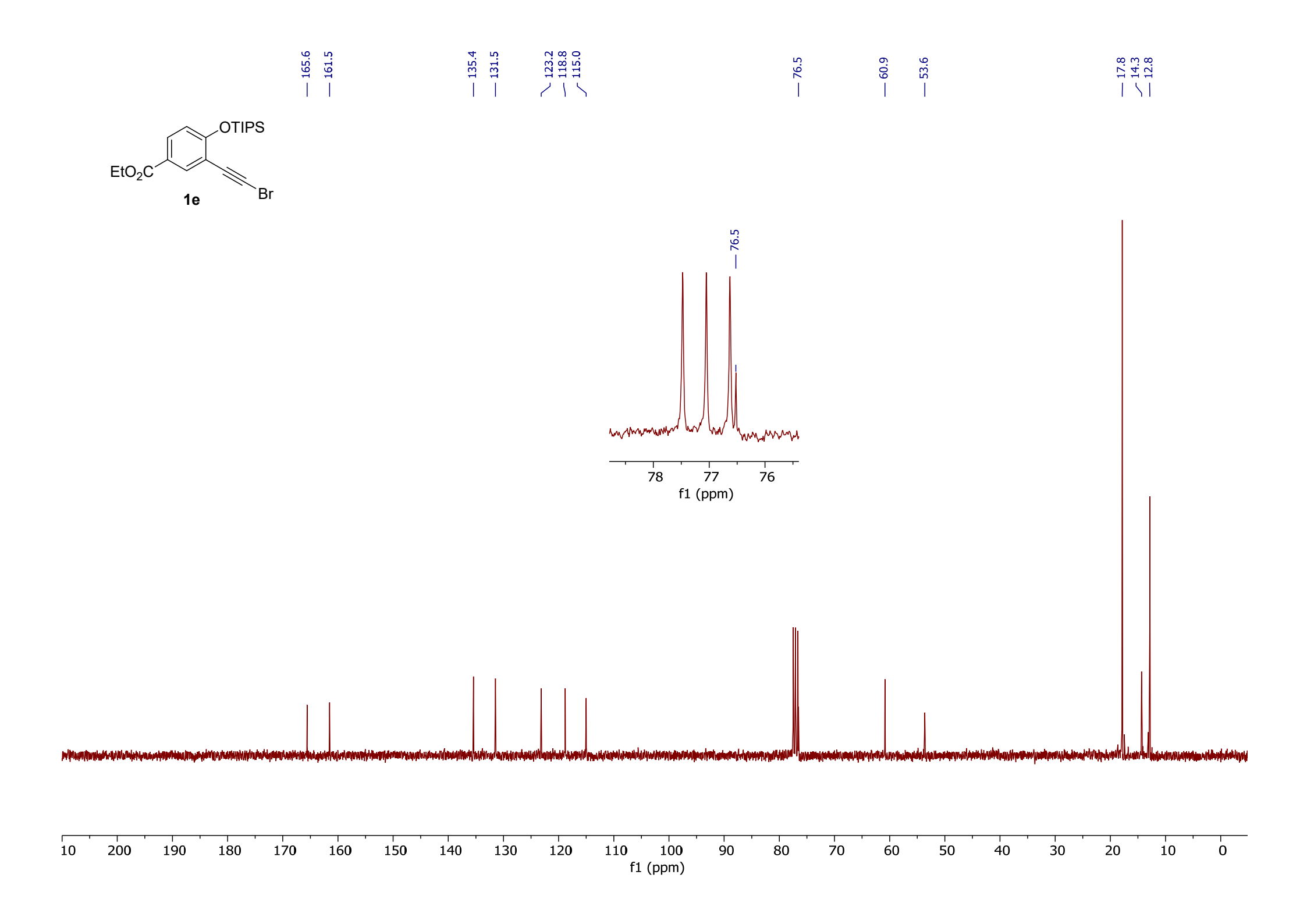
1.07
2.15
6.64
18.11
f1 (ppm)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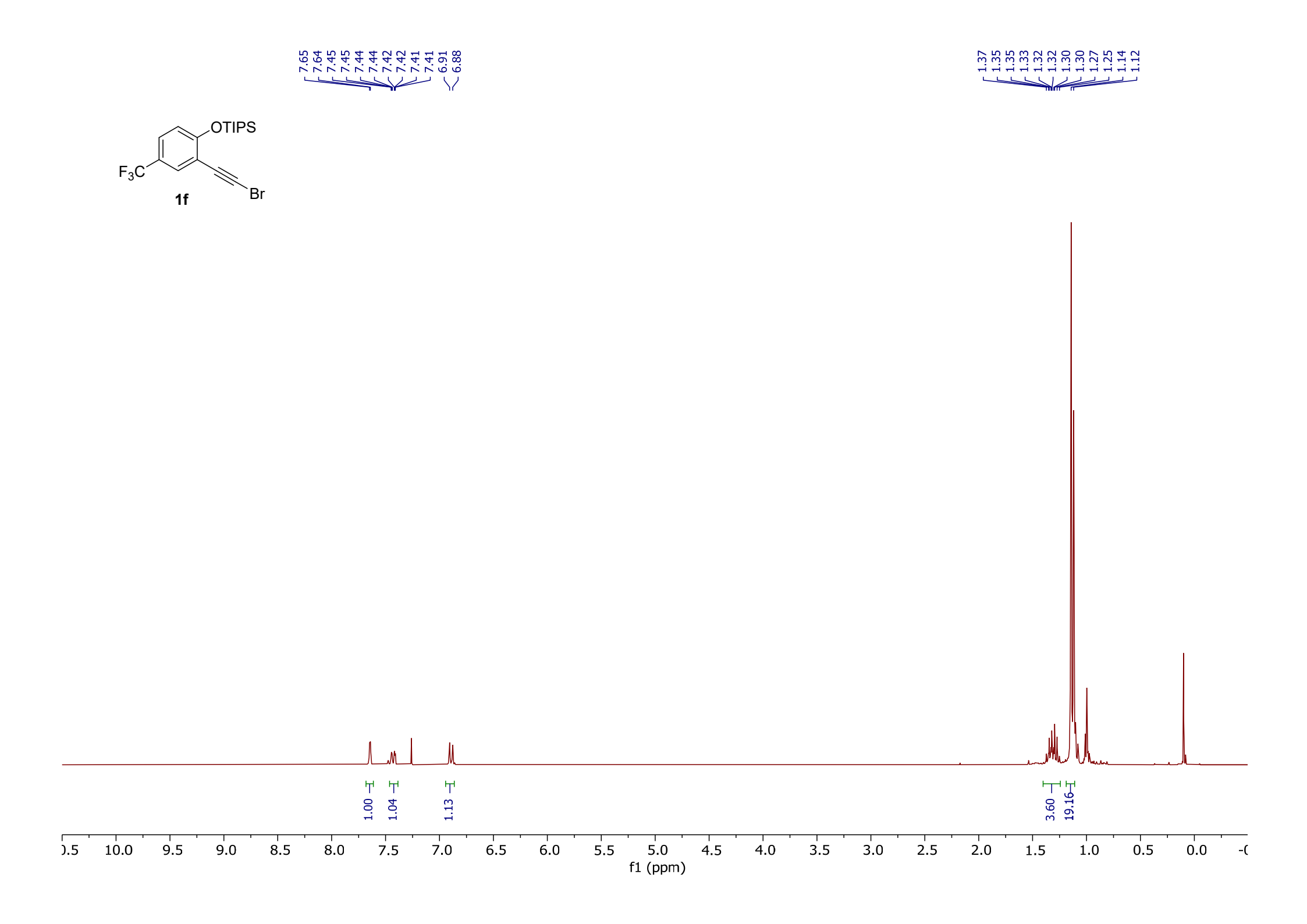
161.5
135.4
131.5
123.2
118.8
115.0
76.5
60.9
53.6
17.8
14.3
12.8
OTIPS
EtO2C
Br
1e
76.5
78
77
76
f1 (ppm)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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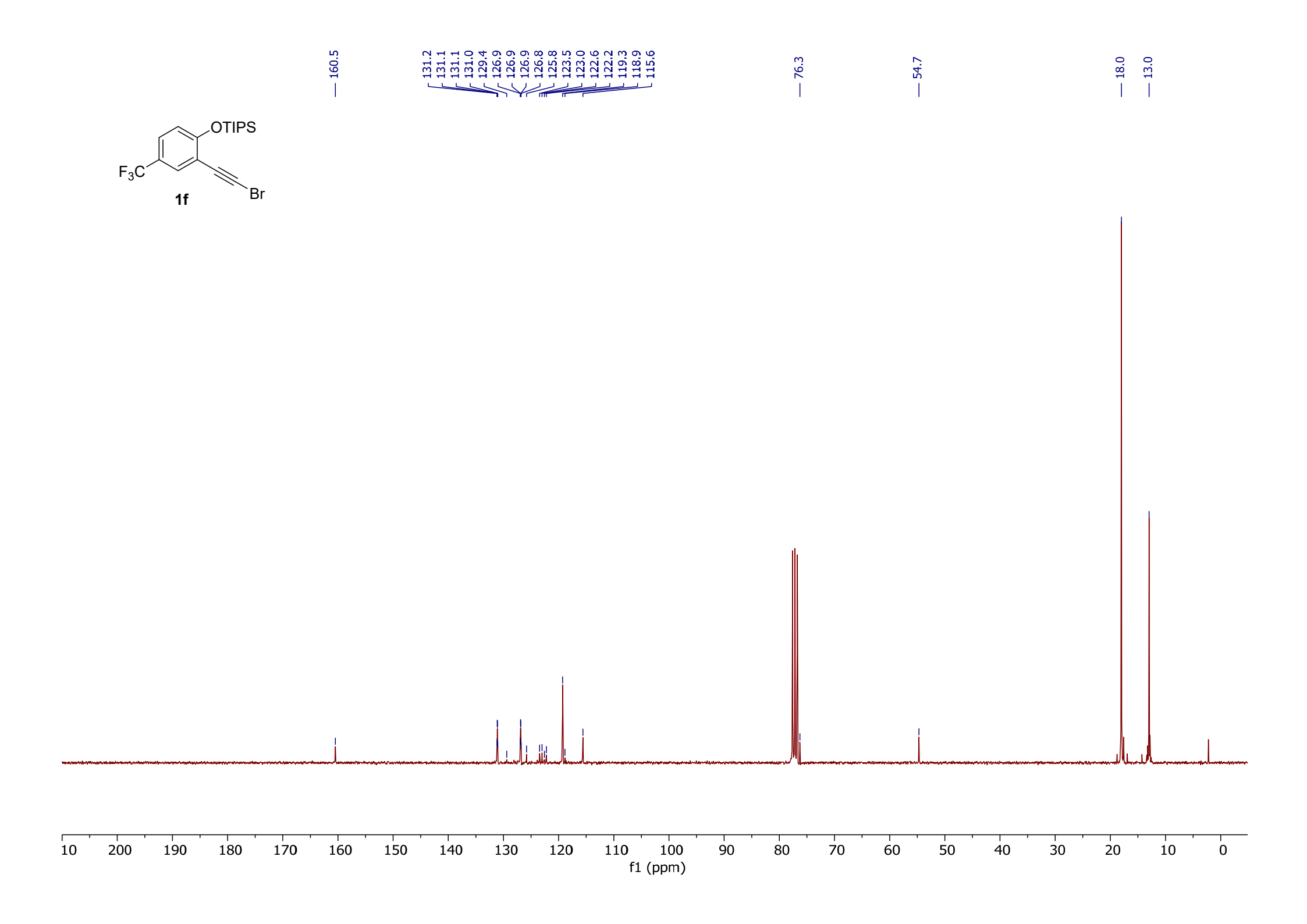
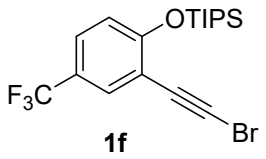
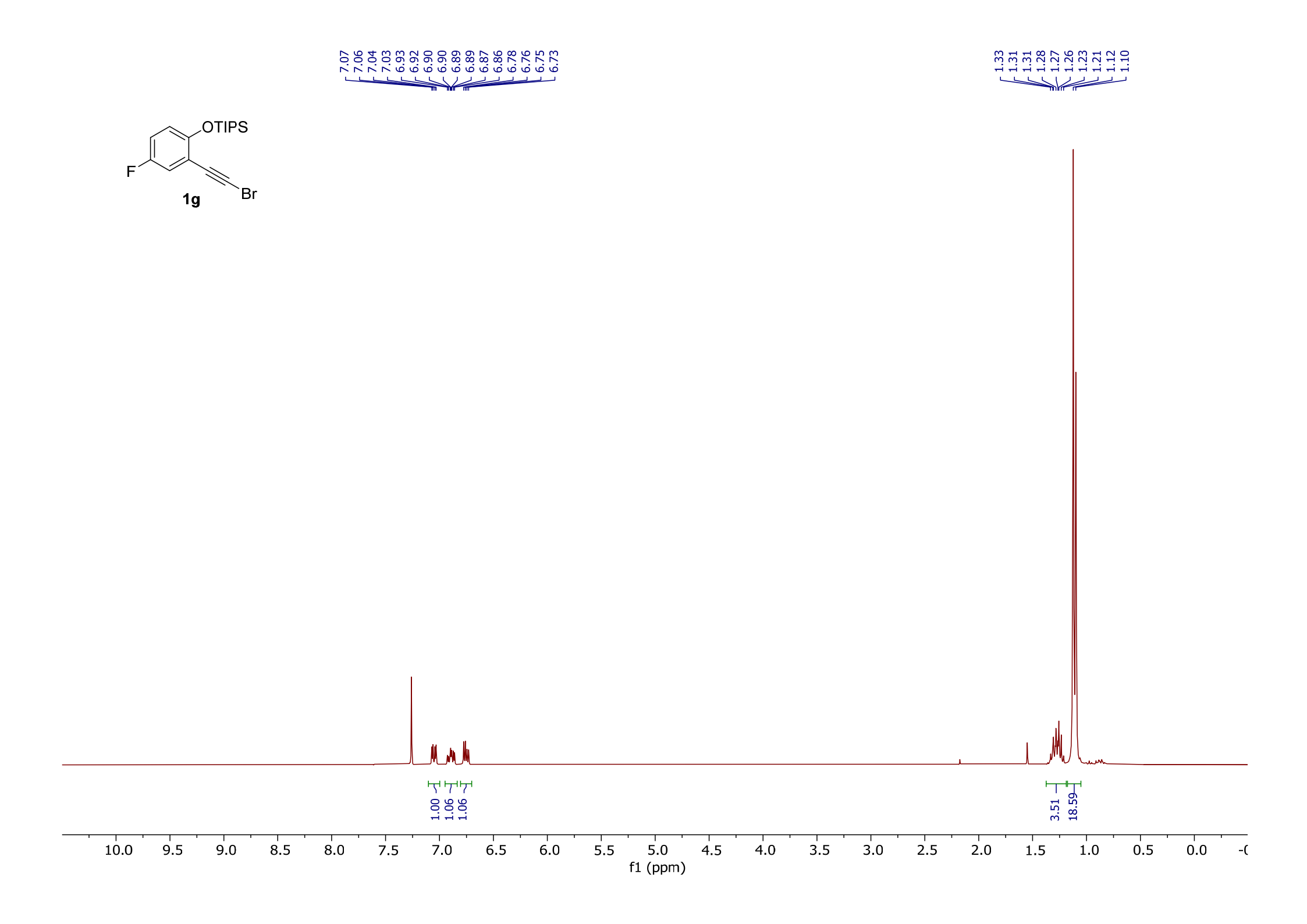
7.64
7.45
7.45
7.44
7.44
7.42
7.42
7.41
7.41
6.91
6.88
1.37
1.35
1.35
1.33
1.32
1.32
1.30
1.30
1.27
1.25
1.14
1.12
OTIPS
F3C
Br
1f
1.00
1.04
1.13
3.60
19.16
f1 (ppm)

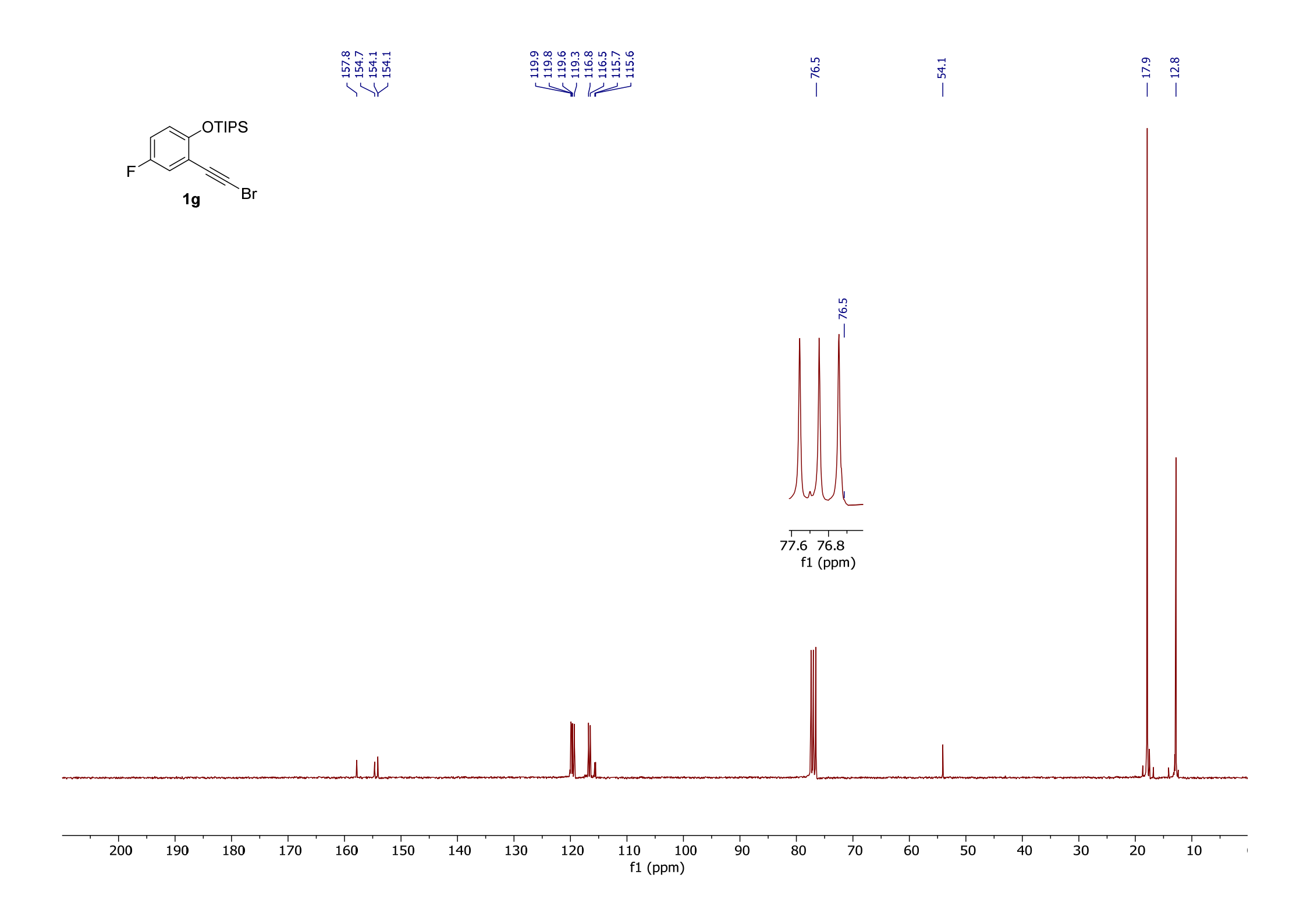

160.5
131.2
131.1
131.1
131.0
129.4
126.9
126.9
126.9
126.8
125.8
123.5
123.0
122.6
122.2
119.3
118.9
115.6
76.3
54.7
18.0
13.0
OTIPS
F3C
Br
1f
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OTIPS
F3C
Br

1f

-61.9
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)


7.07
7.06
7.04
7.03
6.93
6.92
6.90
6.90
6.89
6.89
6.87
6.86
6.78
6.76
6.75
6.73
1.33
1.31
1.31
1.28
1.27
1.26
1.23
1.21
1.12
1.10
OTIPS
F
Br
1g
1.00
1.06
1.06
3.51
18.59
10.0
9.5
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)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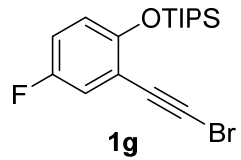
154.7
154.1
154.1
119.9
119.8
119.6
119.3
116.8
116.5
115.7
115.6
76.5
54.1
17.9
12.8
OTIPS
F
Br
1g
76.5
77.6
76.8
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

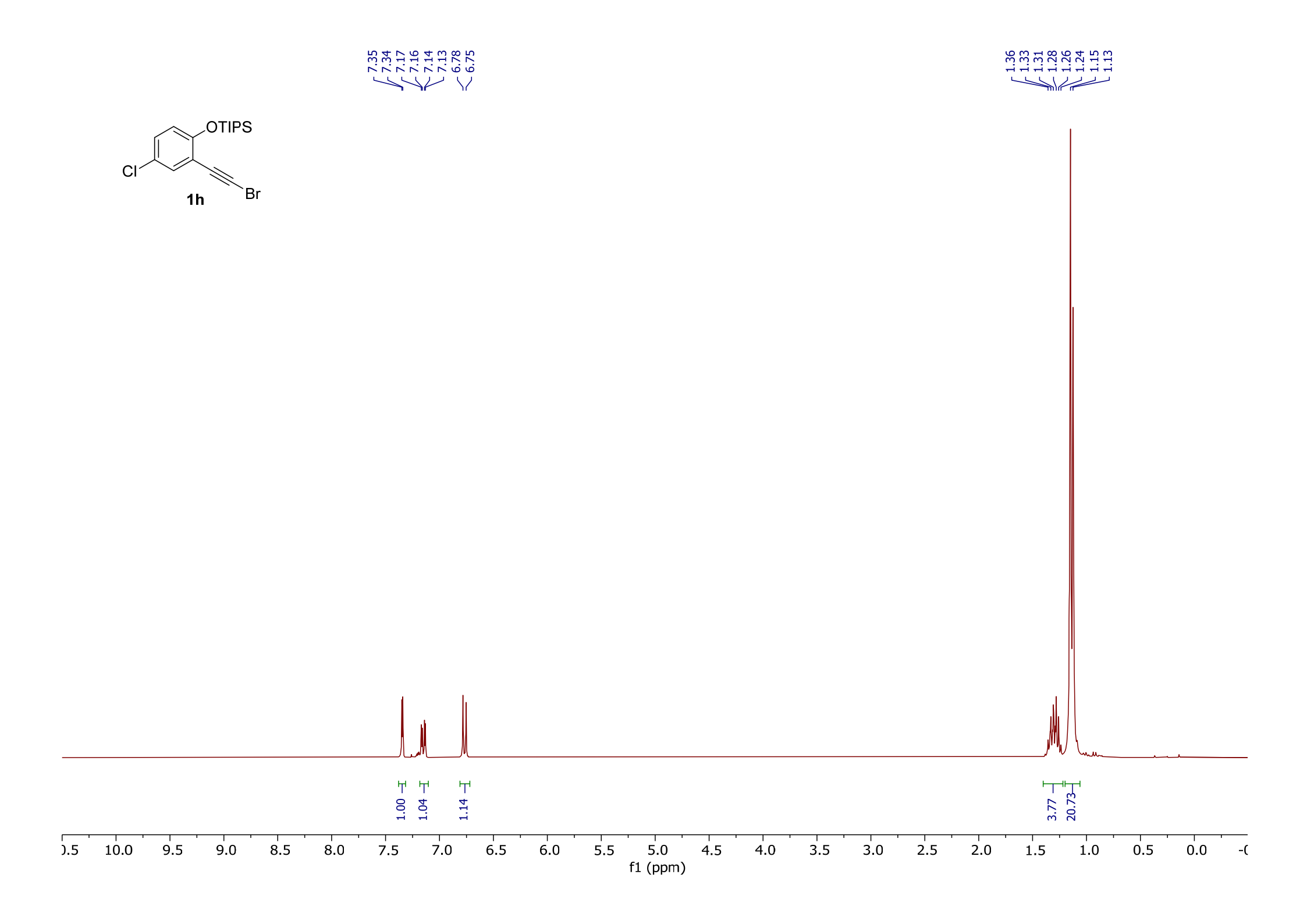


1g

-123.1
-123.1
-123.1
-123.1
-123.1
-123.1

-123.0
-123.2
f1 (ppm)

0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)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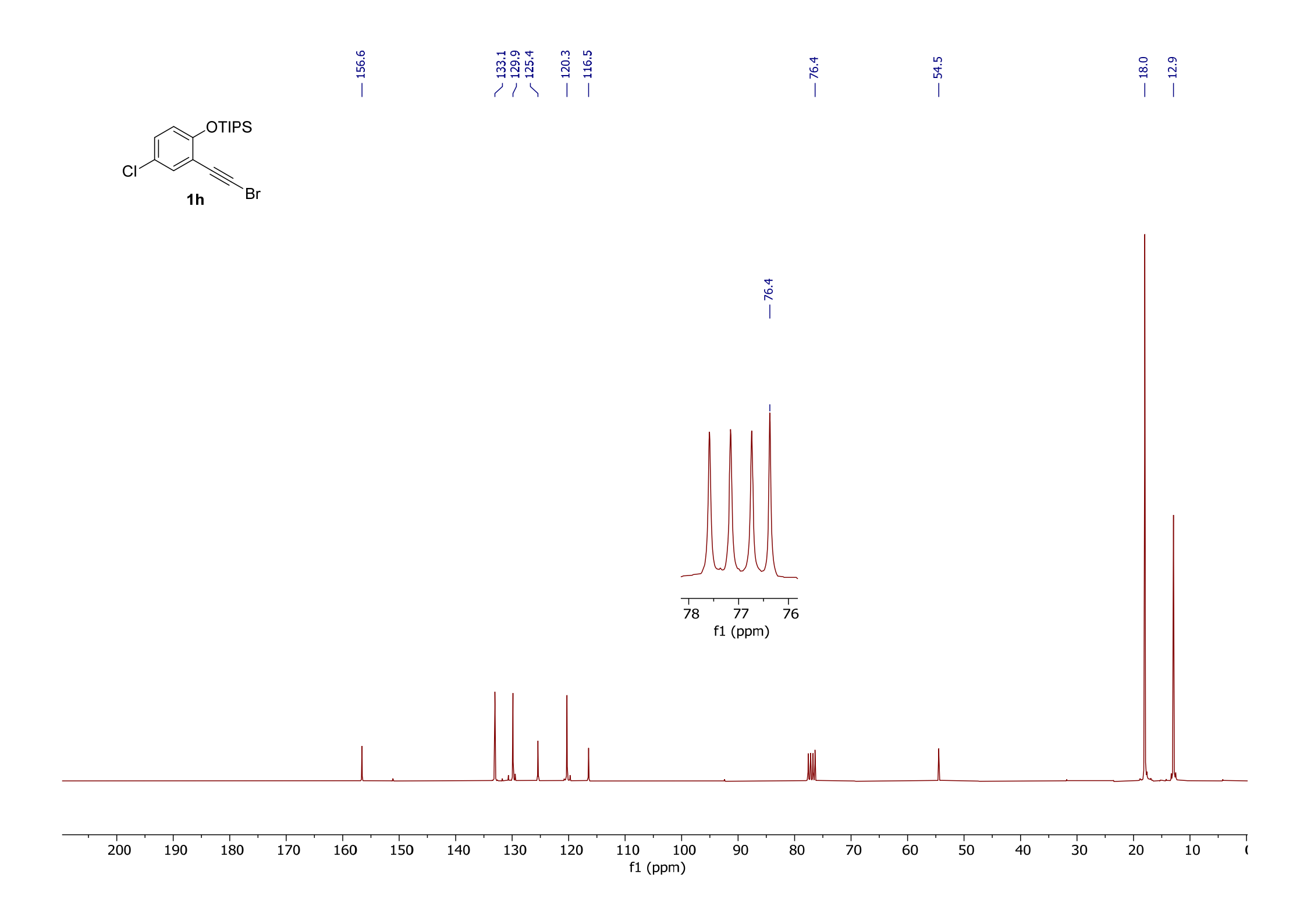
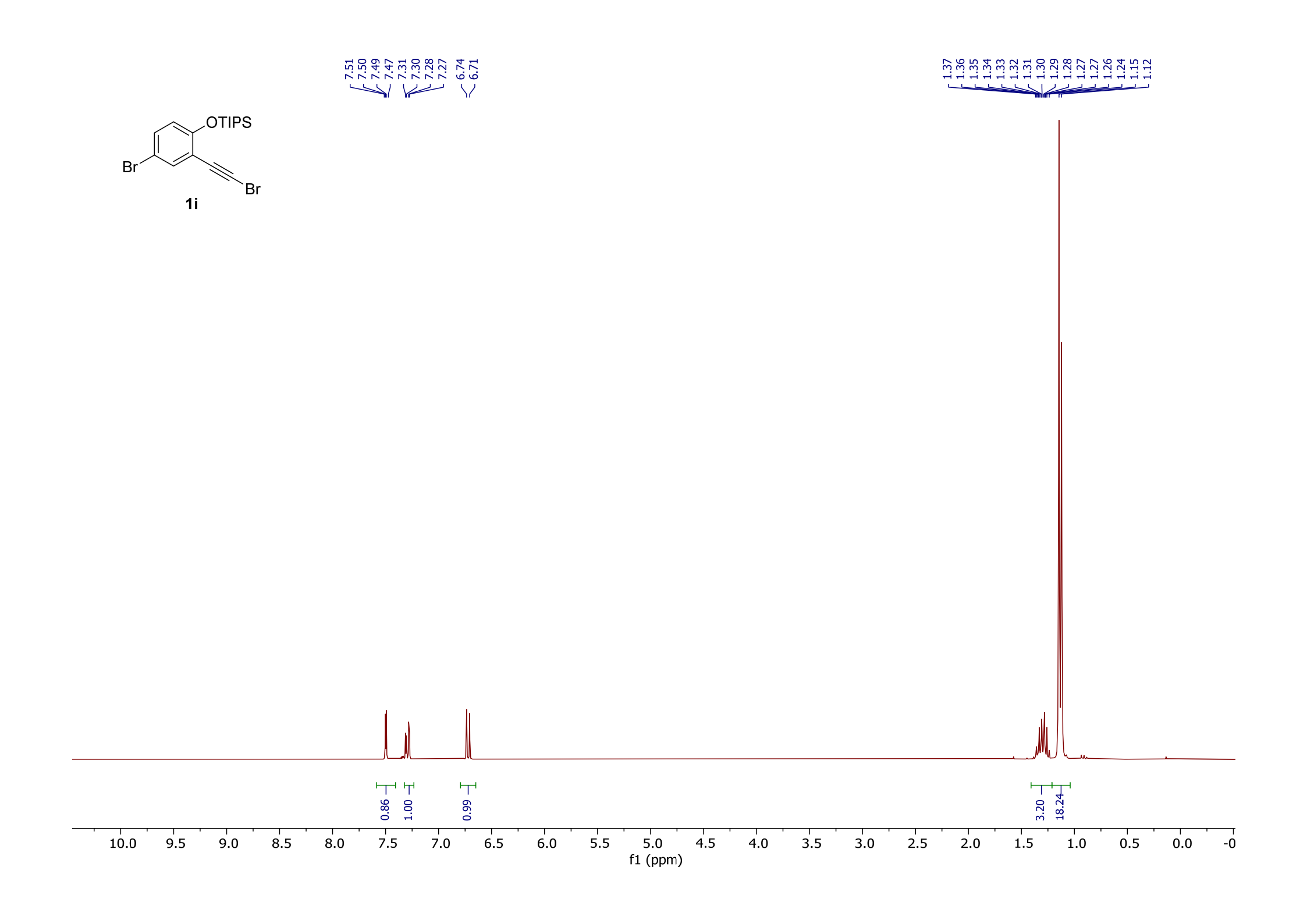
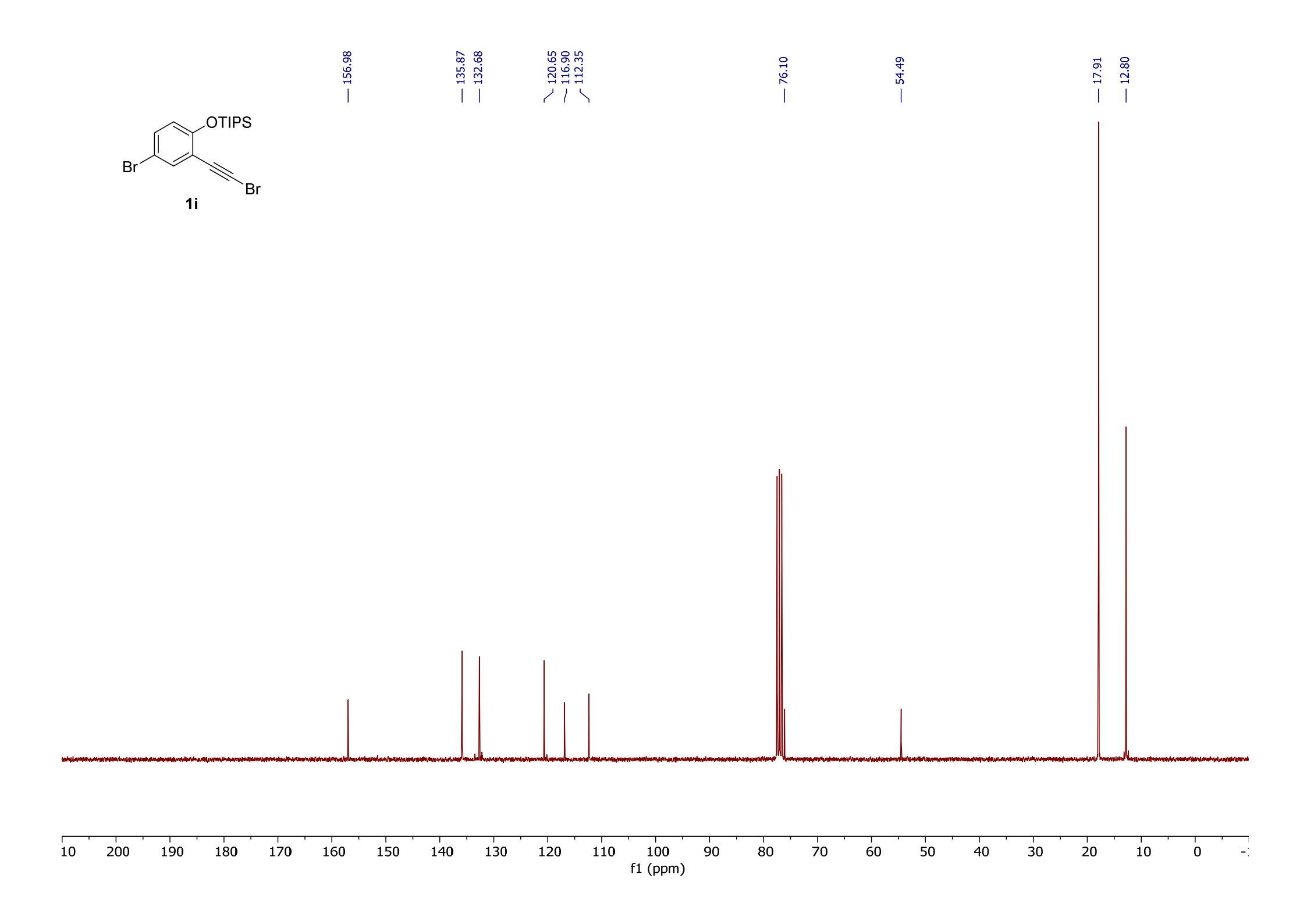
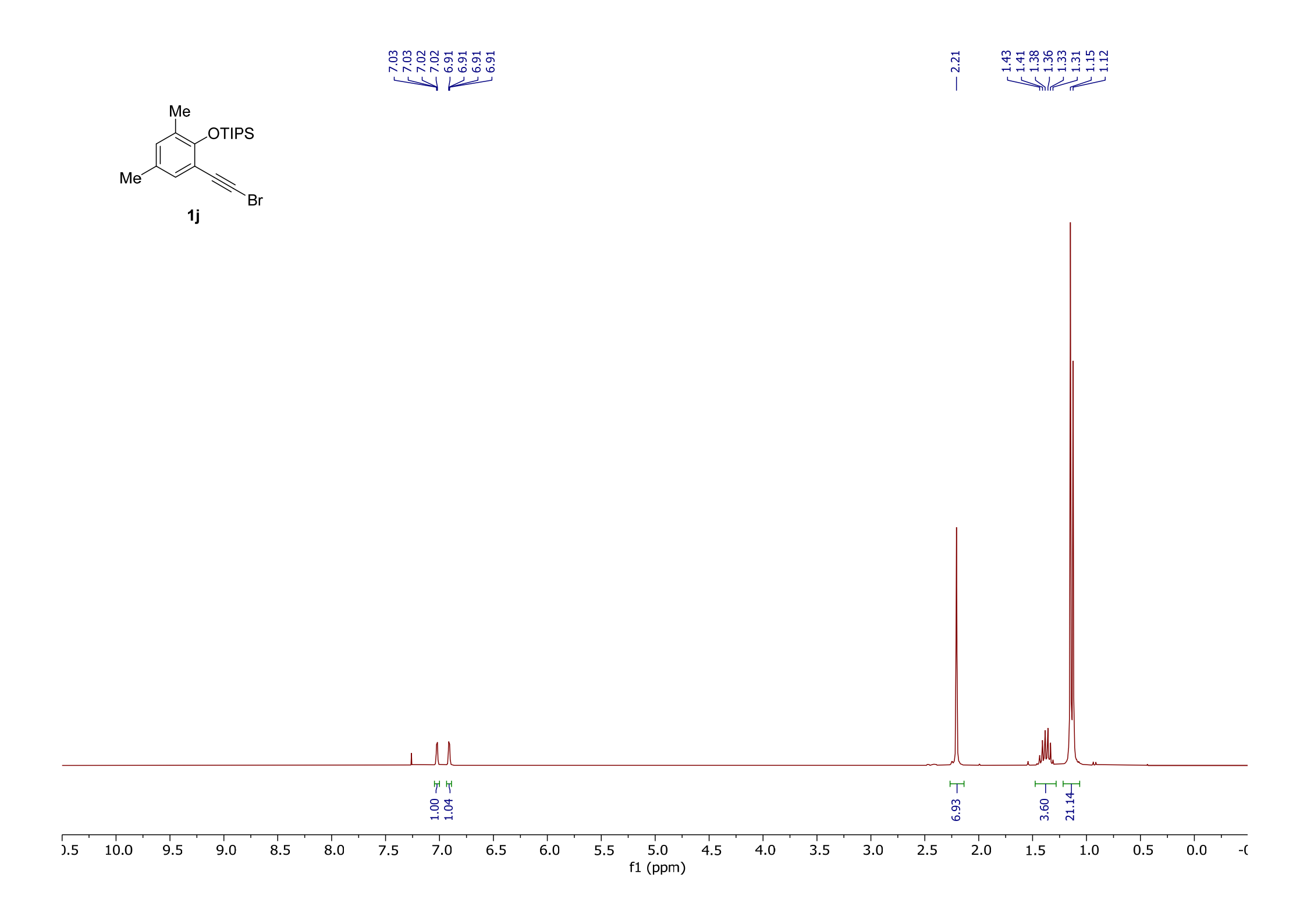
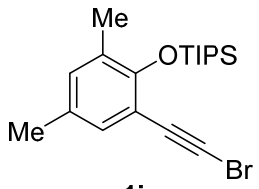
7.34
7.17
7.16
7.14
7.13
6.78
6.75
1.36
1.33
1.31
1.28
1.26
1.24
1.15
1.13
OTIPS
Cl
Br
1h
1.00
1.04
1.14
3.77
20.73
f1 (ppm)


156.6
133.1
129.9
125.4
120.3
116.5
76.4
54.5
18.0
12.9
OTIPS
Cl
Br
1h
76.4
78
77
76
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.51
7.50
7.49
7.47
7.31
7.30
7.28
7.27
6.74
6.71
1.37
1.36
1.35
1.34
1.33
1.32
1.31
1.30
1.29
1.28
1.27
1.27
1.26
1.24
1.15
1.12
OTIPS
Br
Br
1i
0.86
1.00
0.99
3.20
18.24
10.0
9.5
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
-0
f1 (ppm)

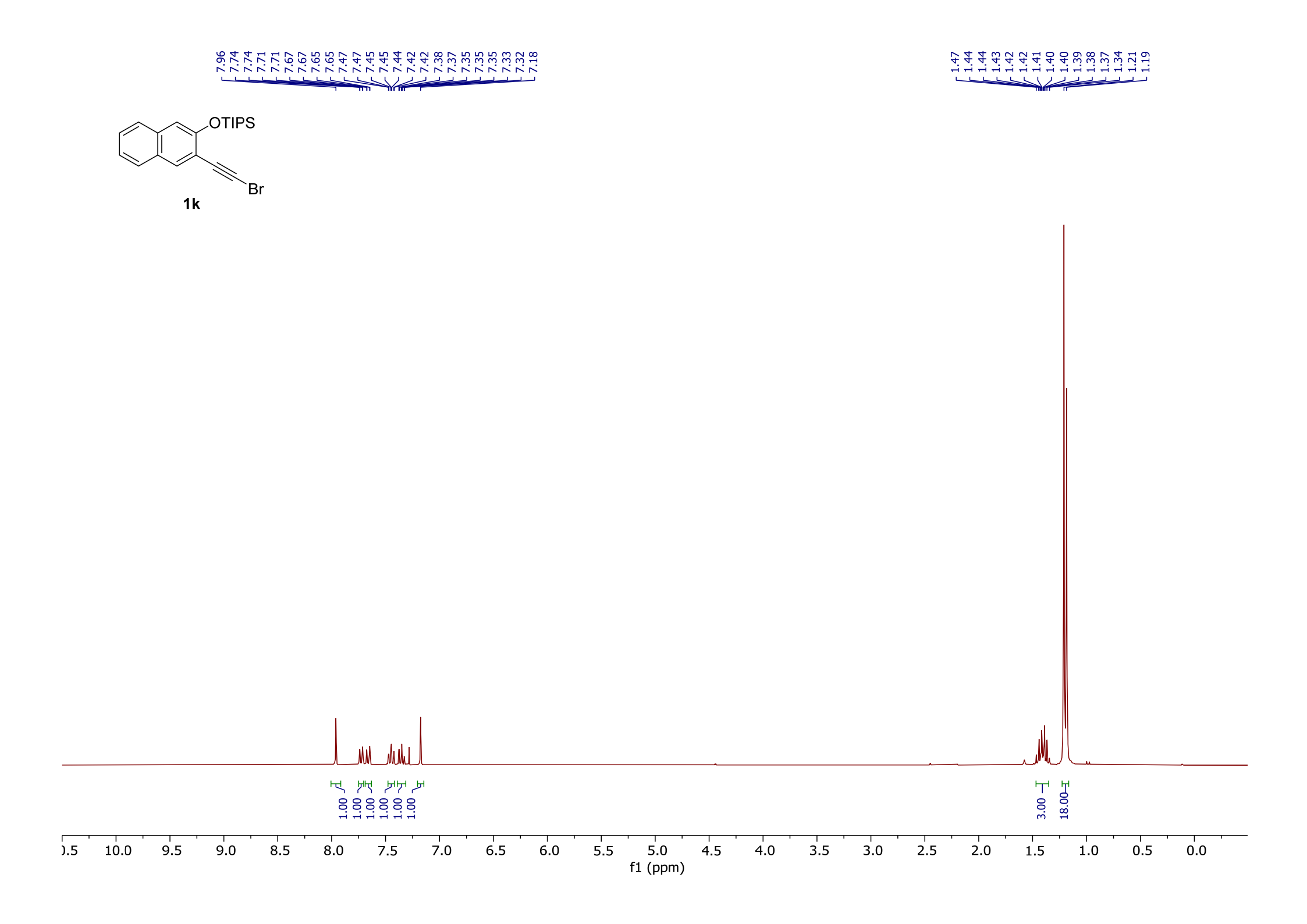

156.98
135.87
132.68
120.65
116.90
112.35
76.10
54.49
17.91
12.80
OTIPS
Br
Br
1i
f1 (ppm)

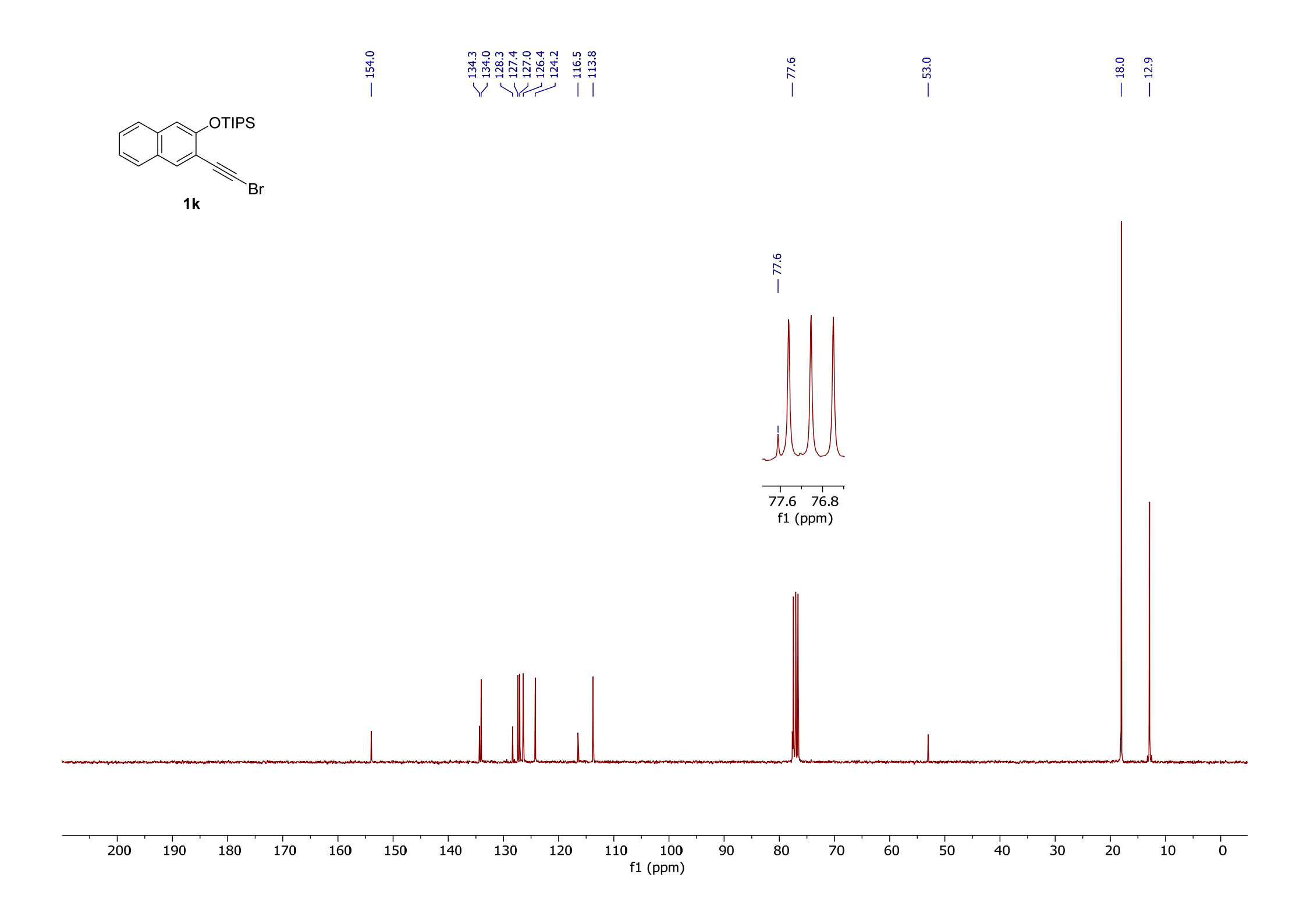

7.03
7.03
7.02
7.02
6.91
6.91
6.91
6.91
2.21
1.43
1.41
1.38
1.36
1.33
1.31
1.15
1.12
Me
OTIPS
Me
Br
1j
1.00
1.04
6.93
3.60
21.14
f1 (ppm)

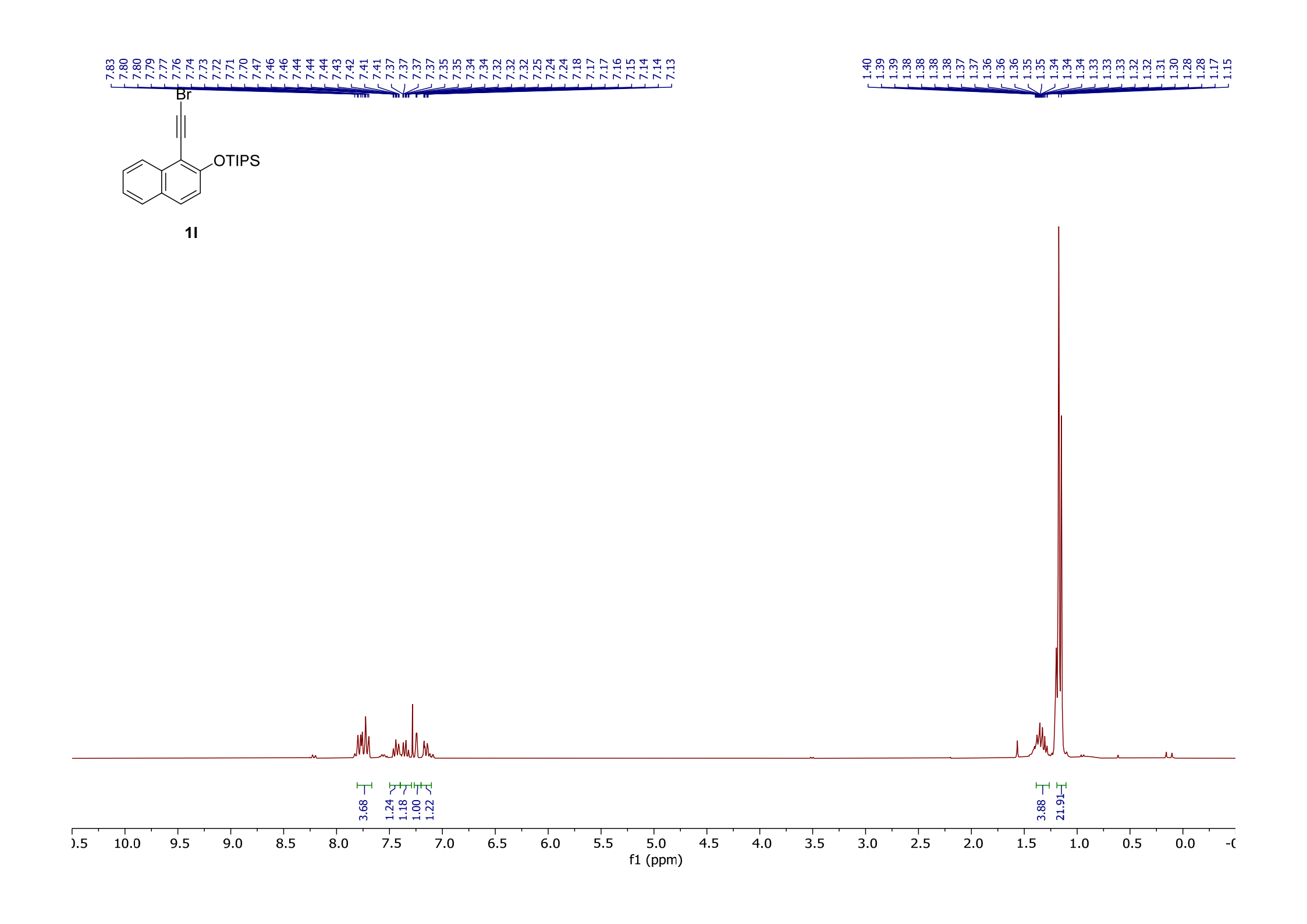

Me
OTIPS
Me
Br

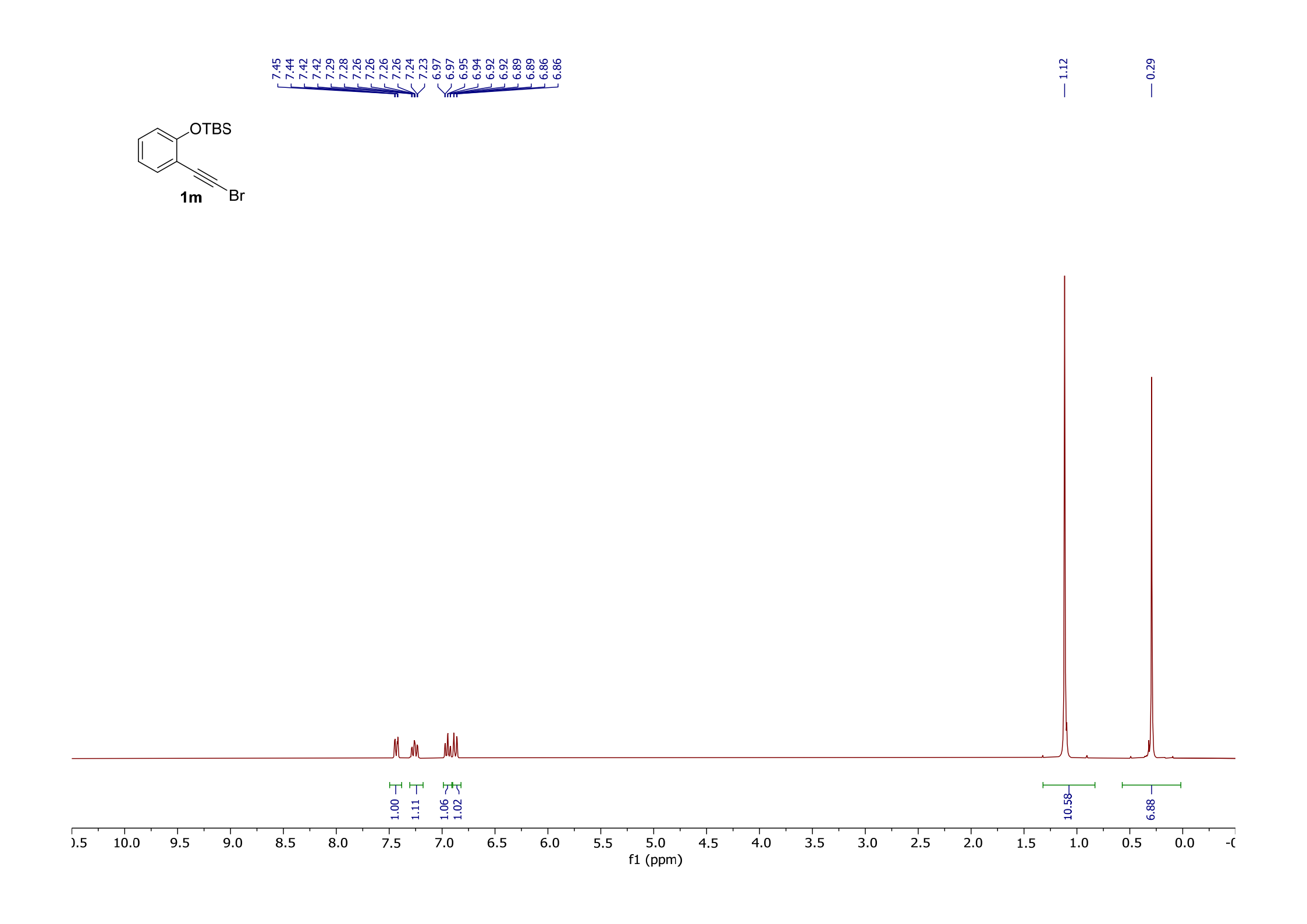
1j

154.3
132.9
132.0
130.1
128.9
114.1
78.9
52.2
20.4
18.2
17.7
14.5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.96
7.74
7.74
7.71
7.71
7.67
7.67
7.65
7.65
7.47
7.47
7.45
7.45
7.44
7.42
7.42
7.38
7.37
7.35
7.35
7.35
7.33
7.32
7.18
1.47
1.44
1.44
1.43
1.42
1.42
1.41
1.40
1.40
1.39
1.38
1.37
1.34
1.21
1.19
OTIPS
Br
1k
1.00
1.00
1.00
1.00
1.00
1.00
3.00
18.00
f1 (ppm)


154.0
134.3
134.0
128.3
127.4
127.0
126.4
124.2
116.5
113.8
77.6
53.0
18.0
12.9
OTIPS
Br
1k
77.6
77.6
76.8
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.83 7.80 7.80 7.79 7.77 7.76 7.74 7.73 7.72 7.71 7.70 7.47 7.46 7.46 7.44 7.44 7.44 7.43 7.42 7.41 7.41 7.37 7.37 7.37 7.37 7.35 7.35 7.34 7.34 7.32 7.32 7.32 7.25 7.24 7.24 7.18 7.17 7.17 7.16 7.15 7.14 7.14 7.13
1.40 1.39 1.39 1.38 1.38 1.38 1.38 1.37 1.37 1.36 1.36 1.36 1.35 1.35 1.34 1.34 1.34 1.33 1.33 1.33 1.32 1.32 1.31 1.30 1.28 1.28 1.17 1.15
Br
OTIPS
1l
3.68
1.24
1.18
1.00
1.22
3.88
21.91
10.0 9.5 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)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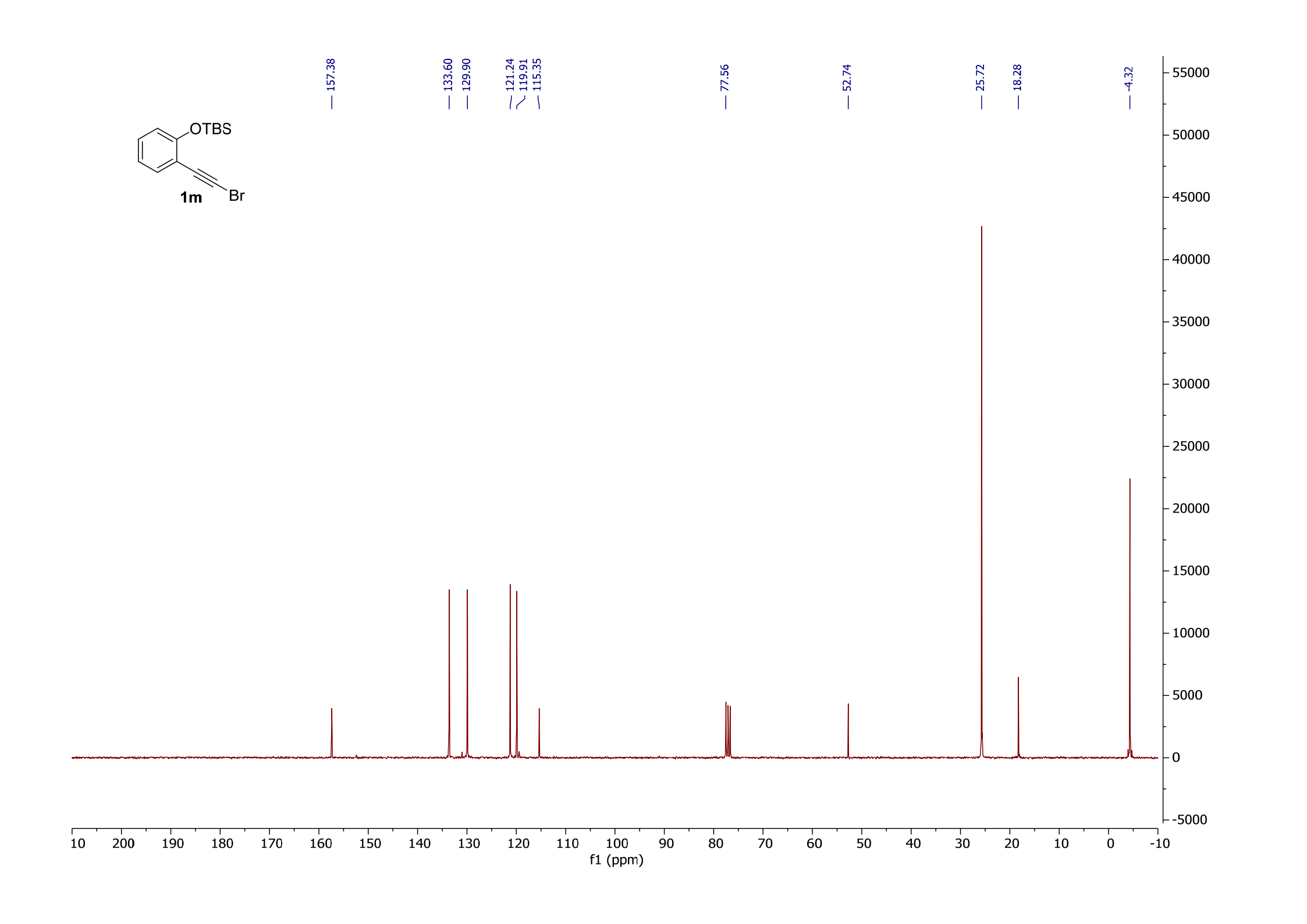
7.44
7.42
7.42
7.29
7.28
7.26
7.26
7.26
7.26
7.24
7.23
6.97
6.97
6.95
6.94
6.92
6.92
6.89
6.89
6.86
6.86
1.12
0.29
OTBS
Br
1m
1.00
1.11
1.06
1.02
10.58
6.88
f1 (ppm)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129.90
121.24
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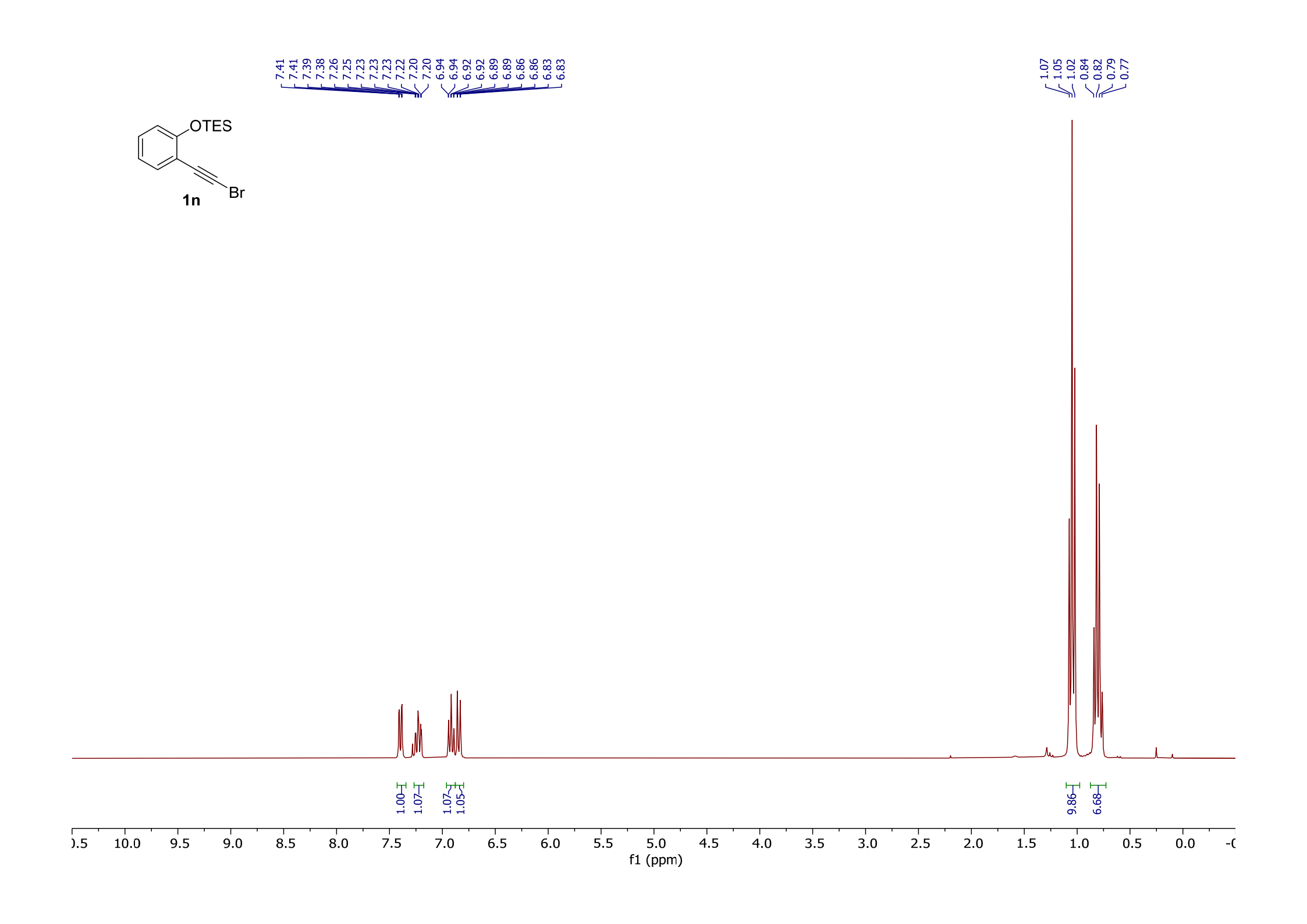
115.35
77.56
52.74
25.72
18.28
-4.32
OTBS
Br
1m
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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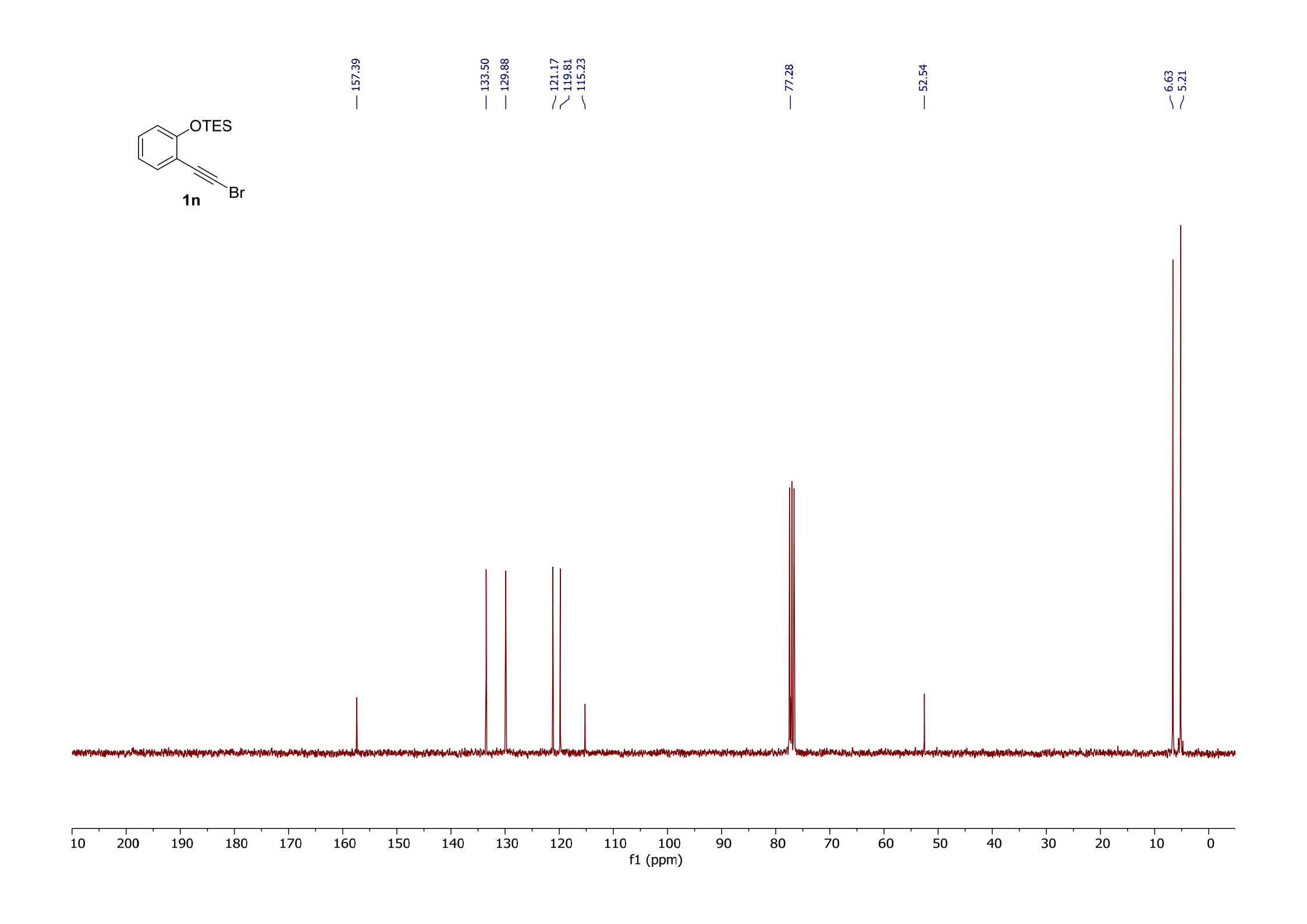
7.23
7.23
7.23
7.22
7.20
7.20
6.94
6.94
6.92
6.92
6.89
6.89
6.86
6.86
6.83
6.83
1.07
1.05
1.02
0.84
0.82
0.79
0.77
OTES
Br
1n
1.00
1.07
1.07
1.05
9.86
6.68
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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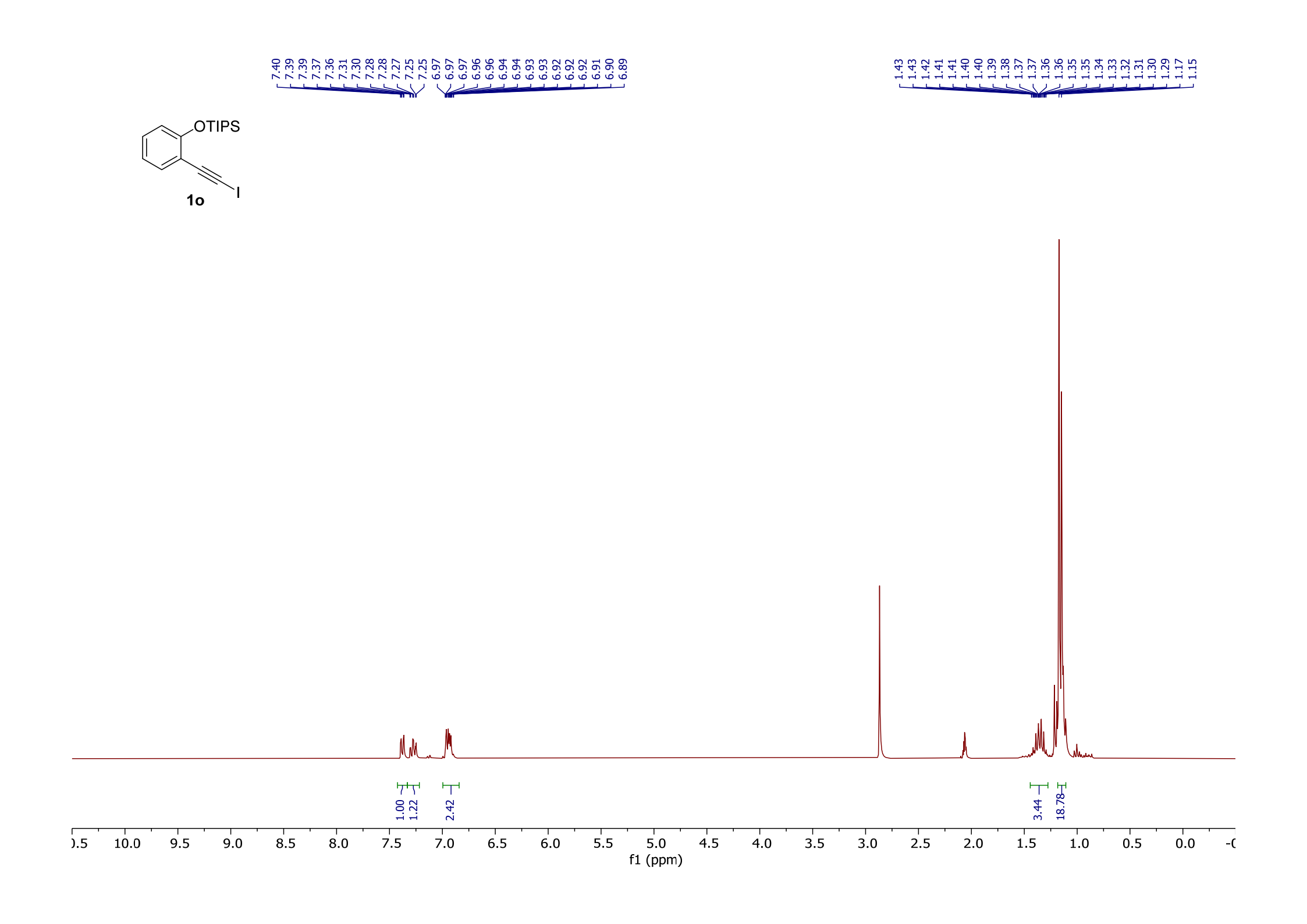
133.50
129.88
121.17
119.81
115.23
77.28
52.54
6.63
5.21
OTES
Br
1n
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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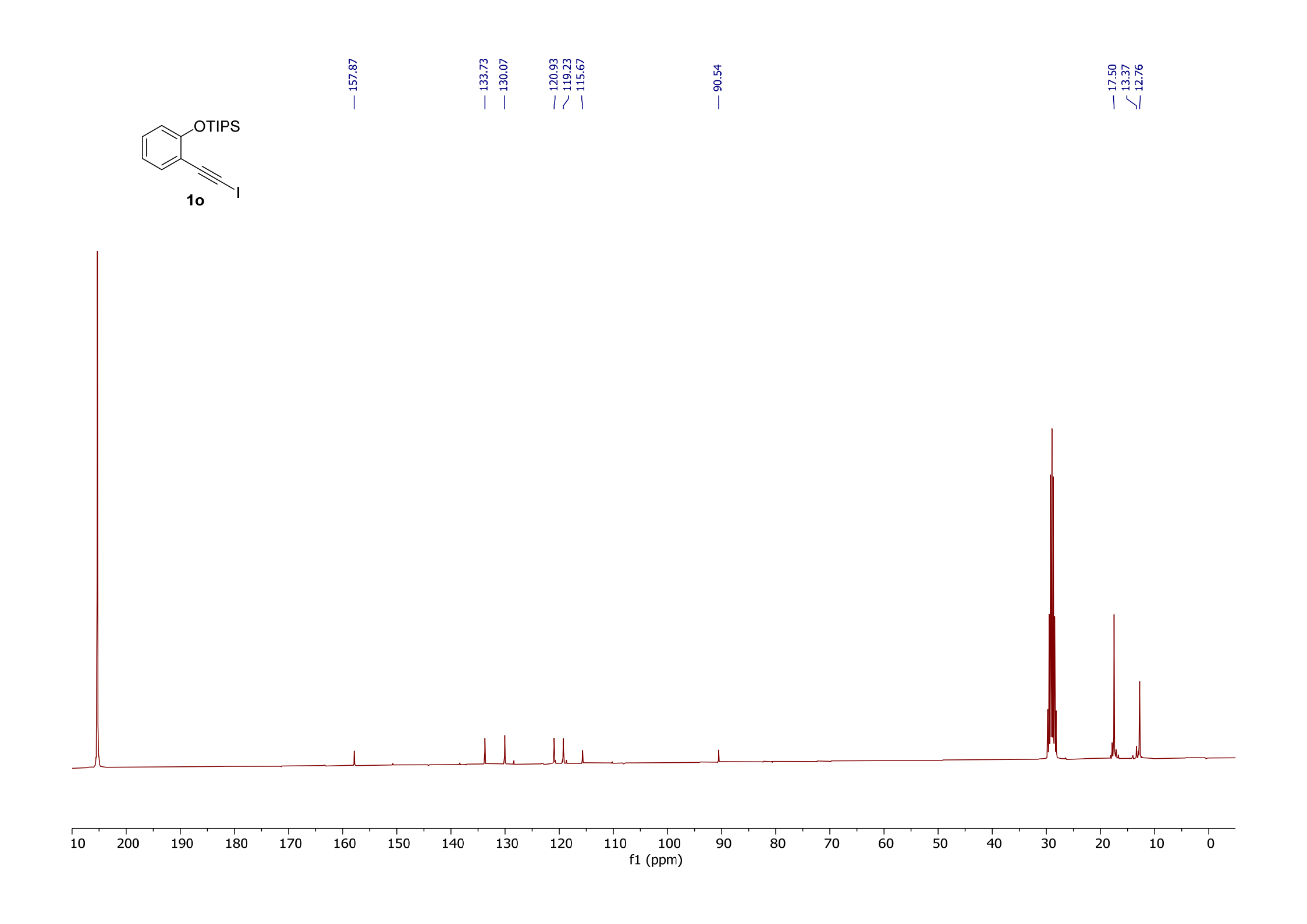
7.39
7.39
7.37
7.36
7.31
7.30
7.28
7.28
7.27
7.25
7.25
6.97
6.97
6.97
6.96
6.96
6.94
6.94
6.93
6.93
6.92
6.92
6.92
6.91
6.90
6.89
1.43
1.43
1.42
1.41
1.41
1.40
1.40
1.39
1.38
1.37
1.37
1.36
1.36
1.35
1.35
1.34
1.33
1.32
1.31
1.30
1.29
1.17
1.15
OTIPS
I
1o
1.00
1.22
2.42
3.44
18.78
f1 (ppm)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130.07
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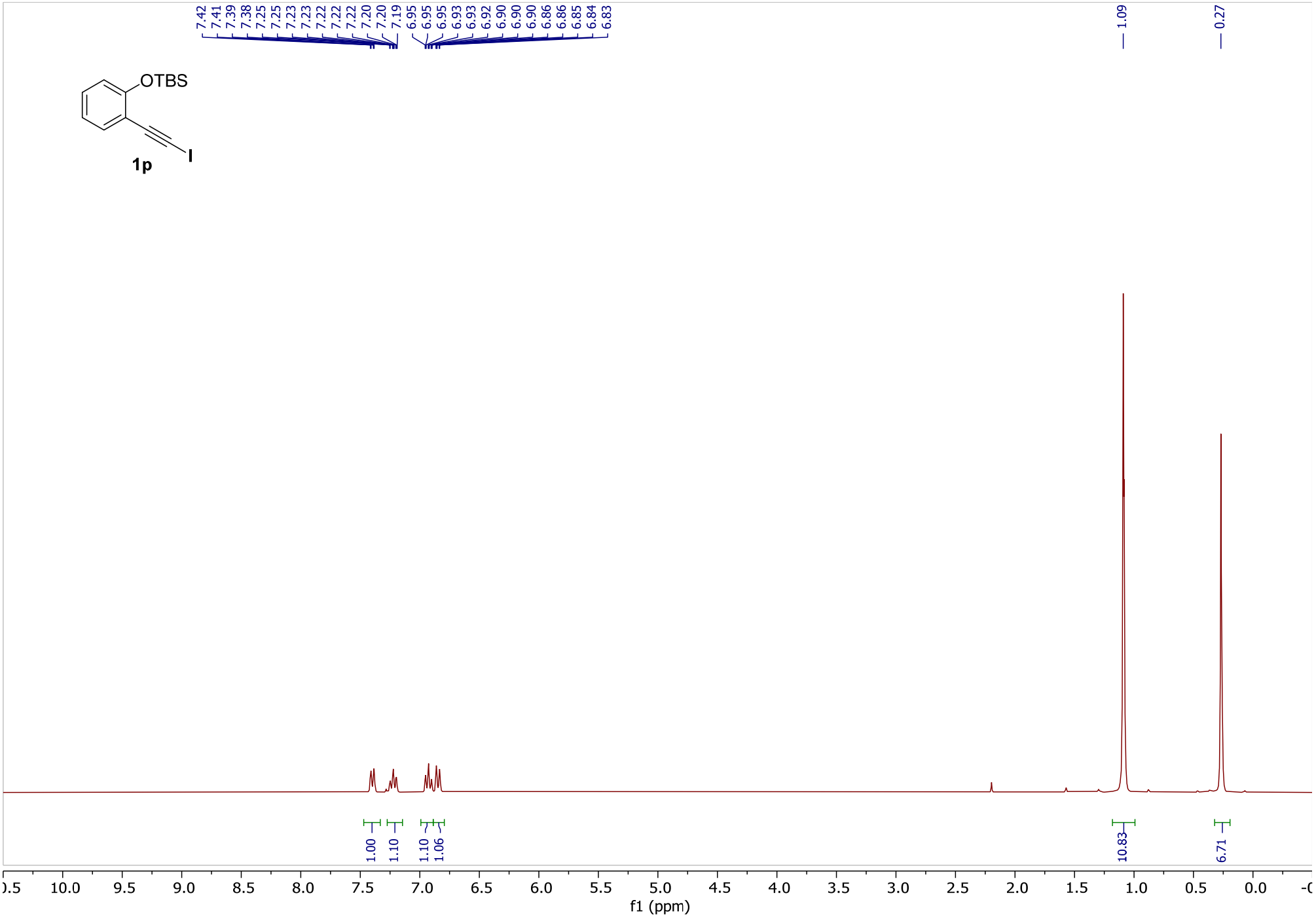
119.23
115.67
90.54
17.50
13.37
12.76
OTIPS
I
1o
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.41
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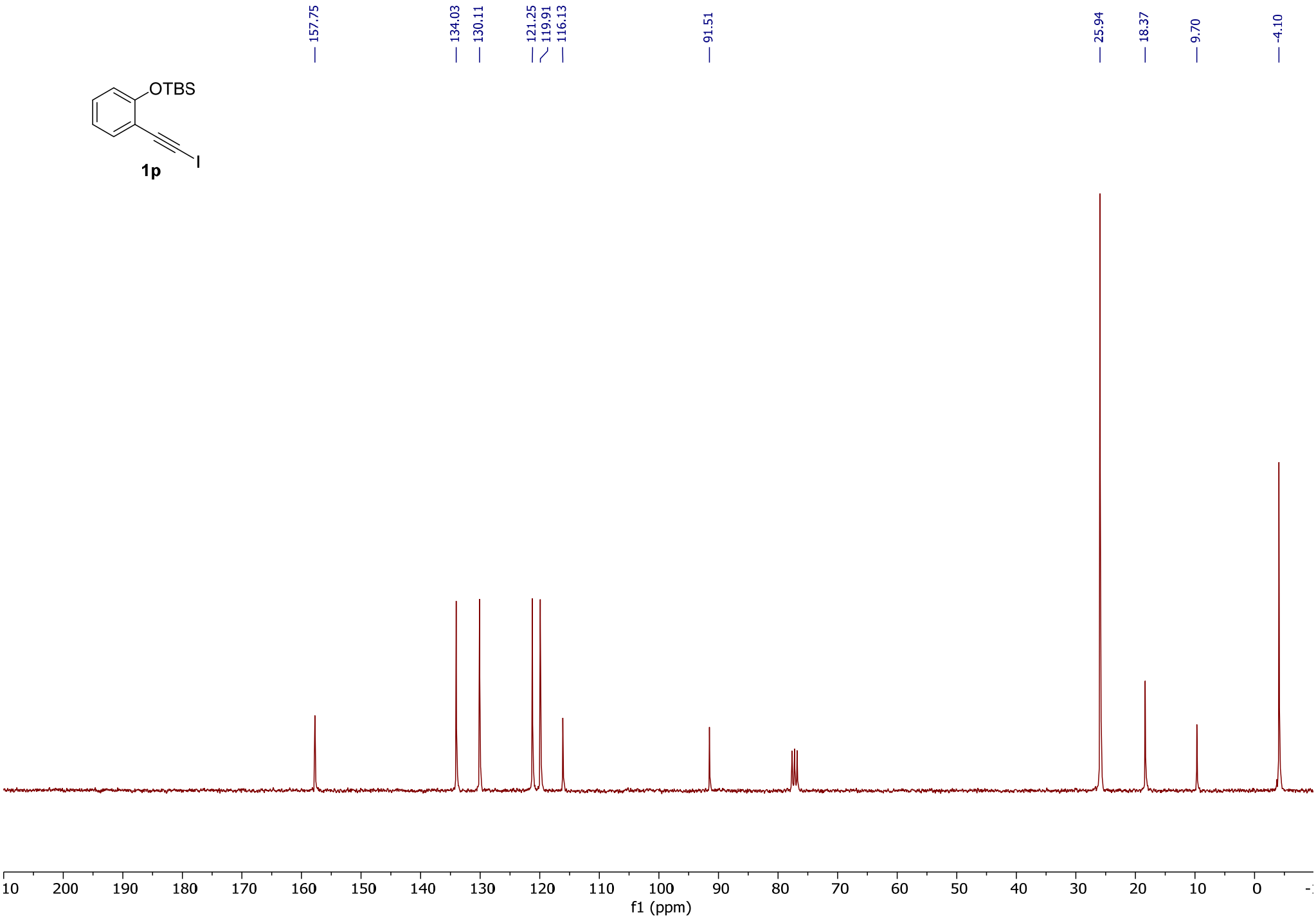
7.38
7.25
7.25
7.23
7.23
7.22
7.22
7.22
7.20
7.20
7.19
6.95
6.95
6.95
6.93
6.93
6.92
6.90
6.90
6.90
6.86
6.86
6.85
6.84
6.83
1.09
0.27
OTBS
I
1p
1.00
1.10
1.10
1.06
10.83
6.71
f1 (ppm)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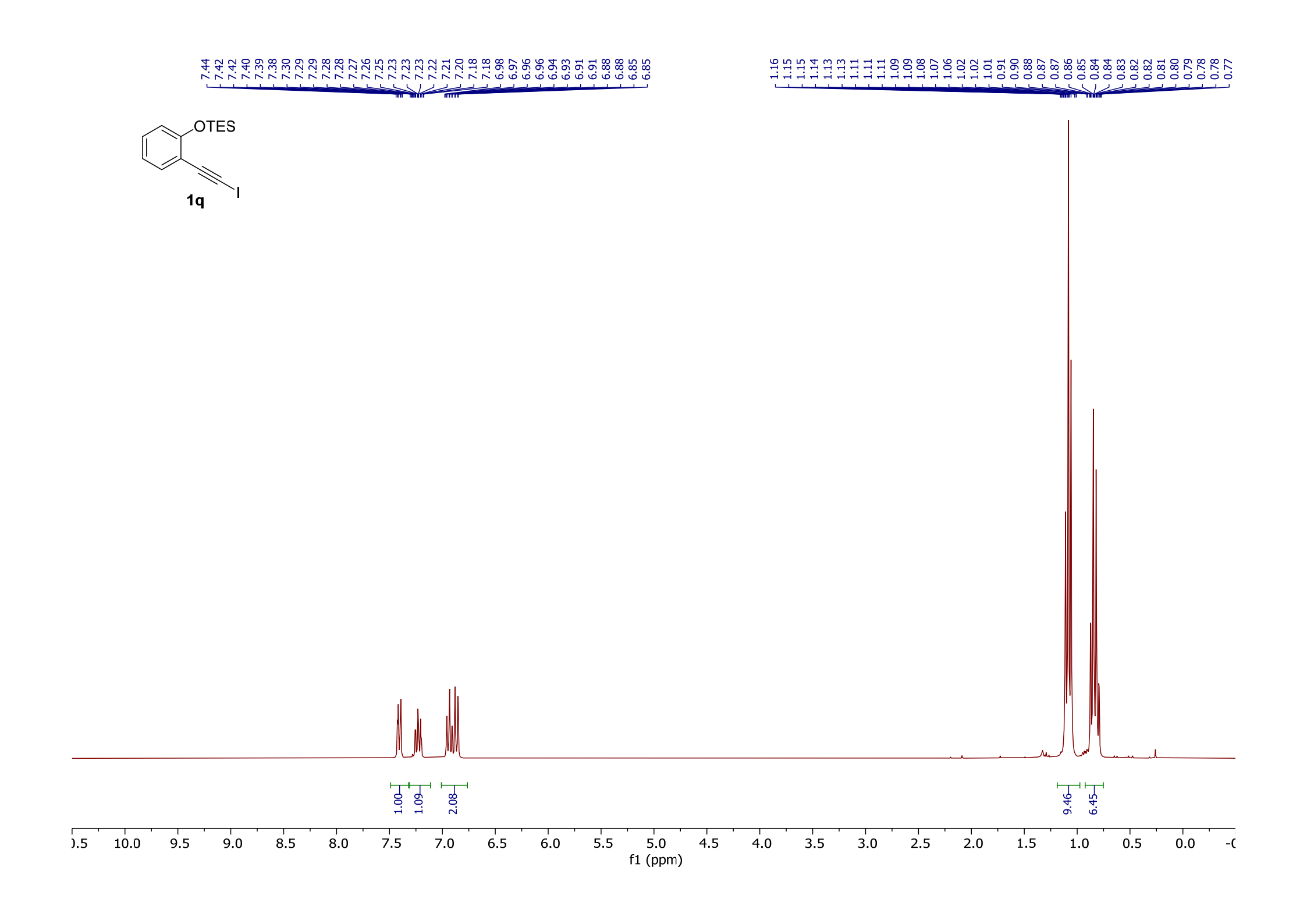
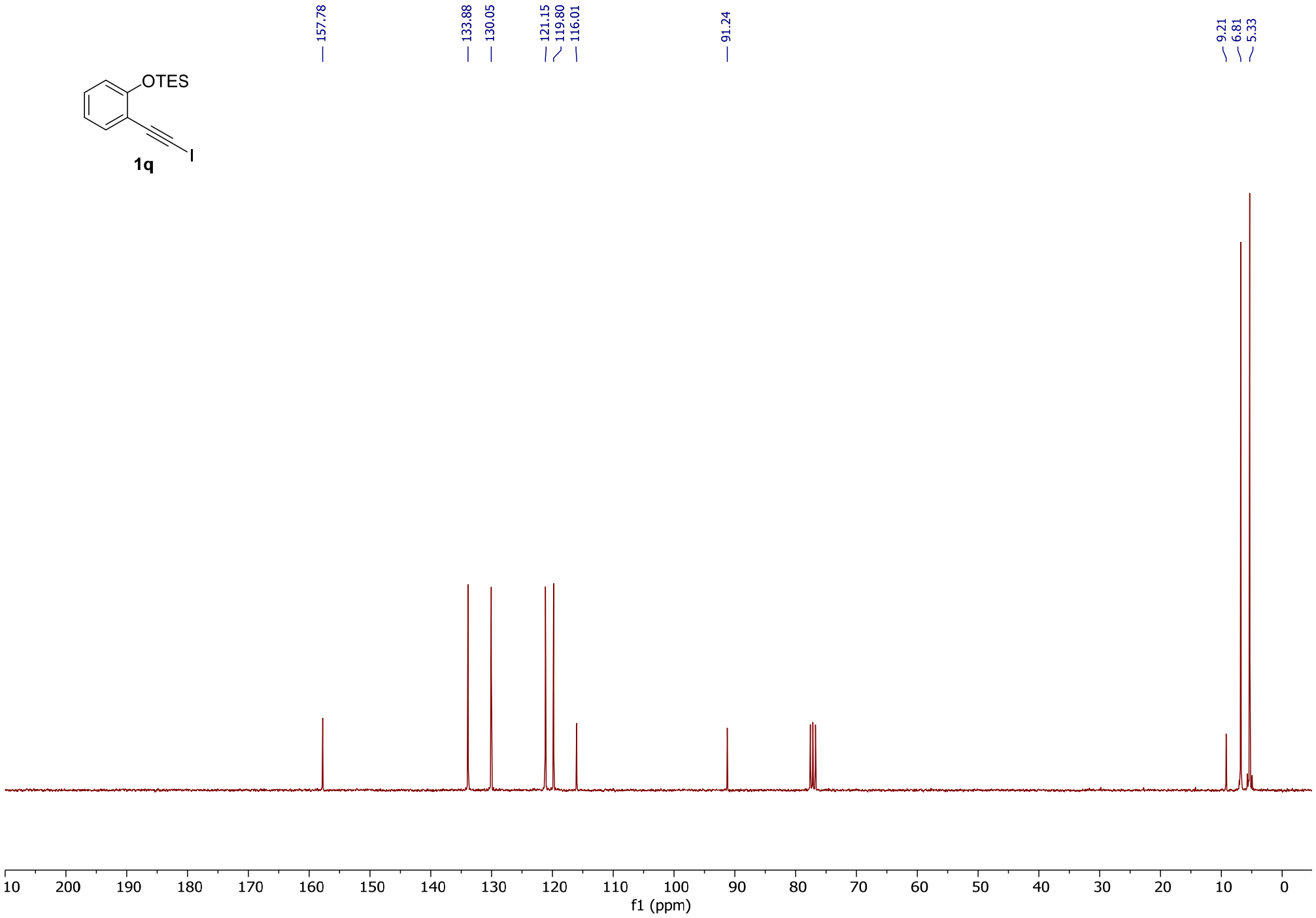
134.03
130.11
121.25
119.91
116.13
91.51
25.94
18.37
9.70
-4.10
OTBS
I
1p
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.44 7.42 7.42 7.40 7.39 7.38 7.30 7.29 7.29 7.28 7.28 7.27 7.26 7.25 7.23 7.23 7.23 7.22 7.21 7.20 7.18 7.18 6.98 6.97 6.96 6.96 6.94 6.93 6.91 6.91 6.88 6.85 6.85
1.16 1.15 1.15 1.14 1.13 1.13 1.11 1.11 1.11 1.09 1.09 1.08 1.07 1.06 1.02 1.02 1.01 0.91 0.90 0.88 0.87 0.87 0.86 0.85 0.84 0.84 0.83 0.82 0.82 0.81 0.80 0.79 0.78 0.78 0.77
OTES
I
1q
1.00
1.09
2.08
9.46
6.45
10.0 9.5 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)


157.78
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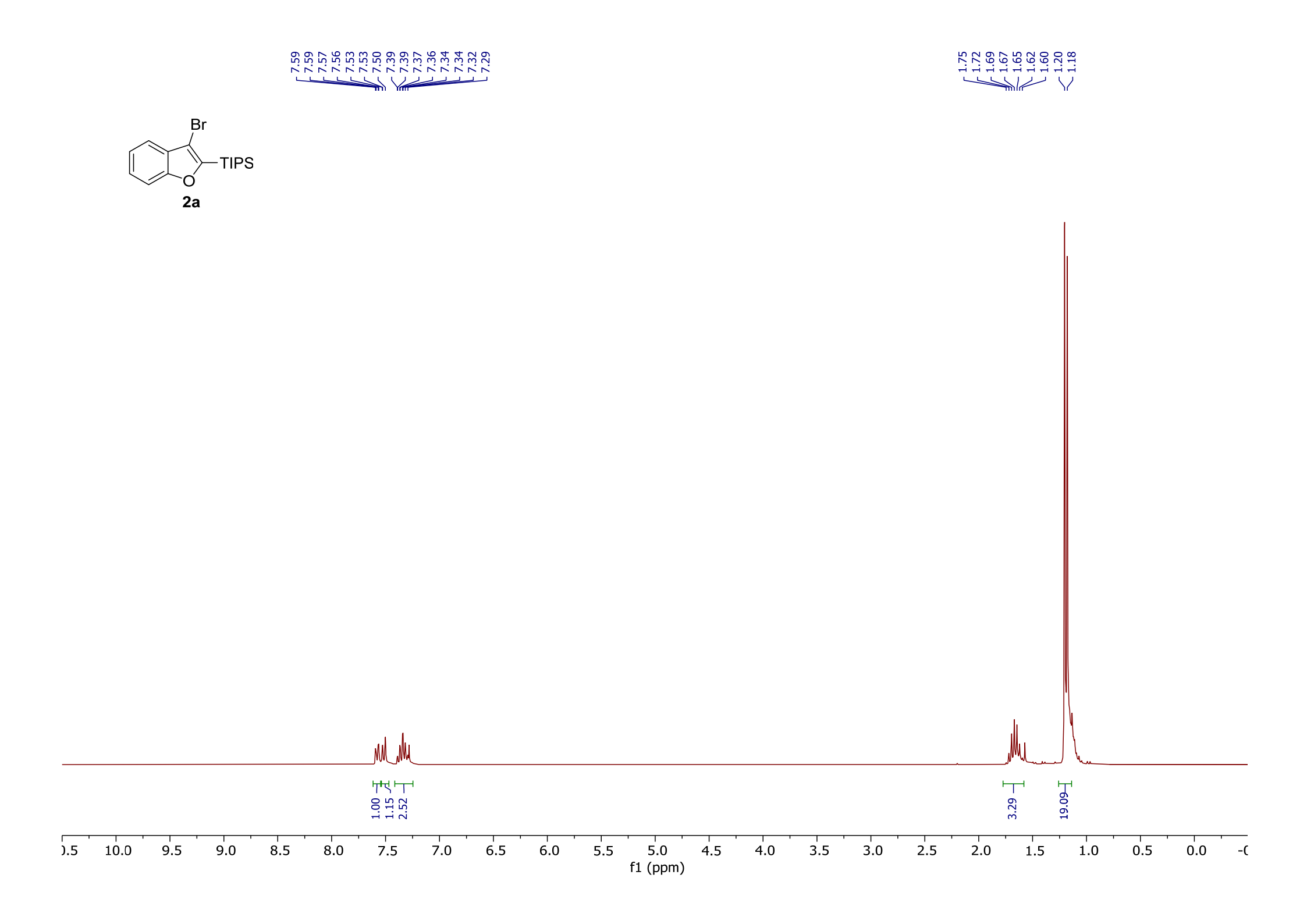
121.15
119.80
116.01
91.24
9.21
6.81
5.33
OTES
I
1q
f1 (ppm)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7.36
7.34
7.34
7.32
7.29
1.75
1.72
1.69
1.67
1.65
1.62
1.60
1.20
1.18
Br
TIPS
O
2a
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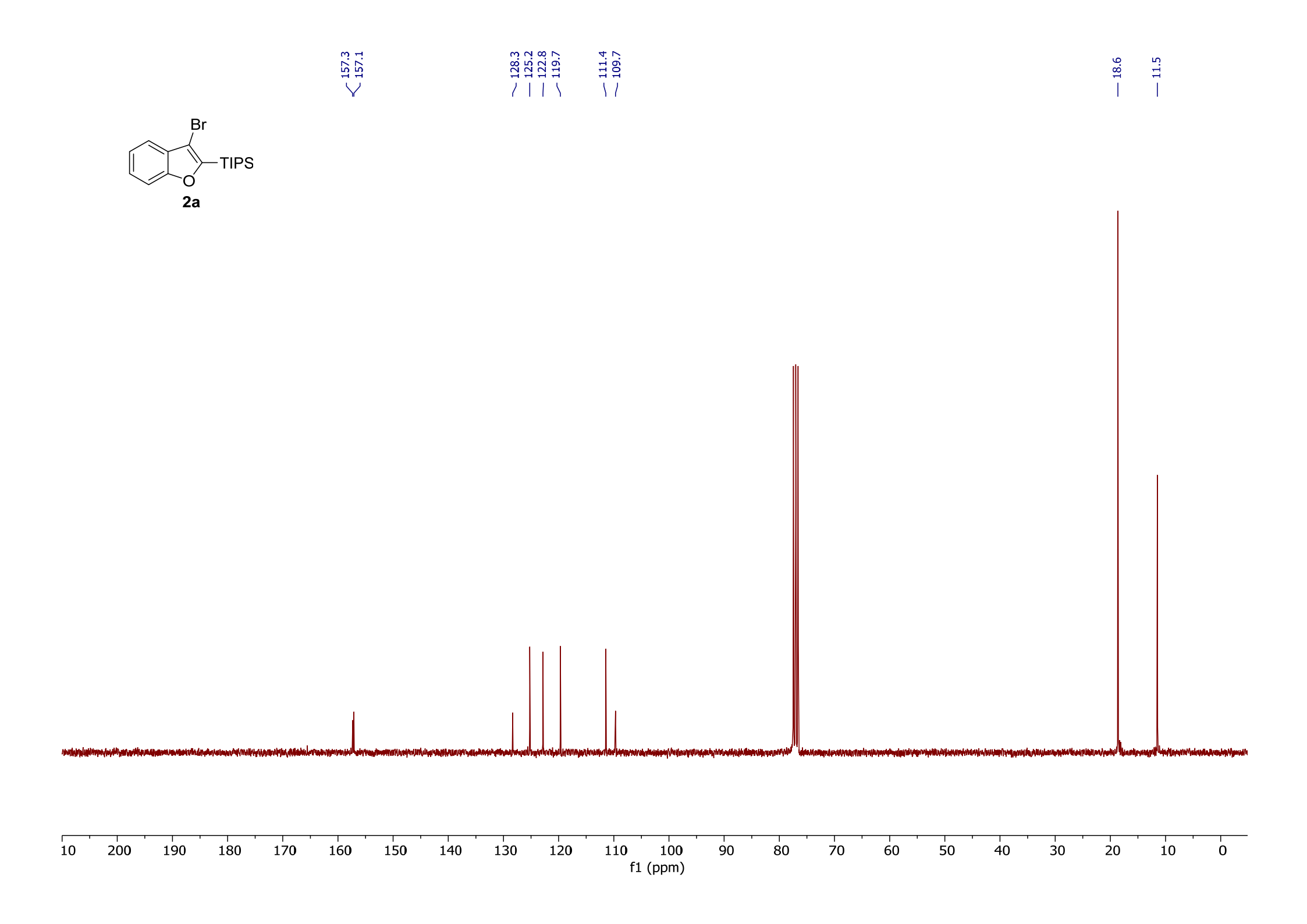
1.15
2.52
3.29
19.09
f1 (ppm)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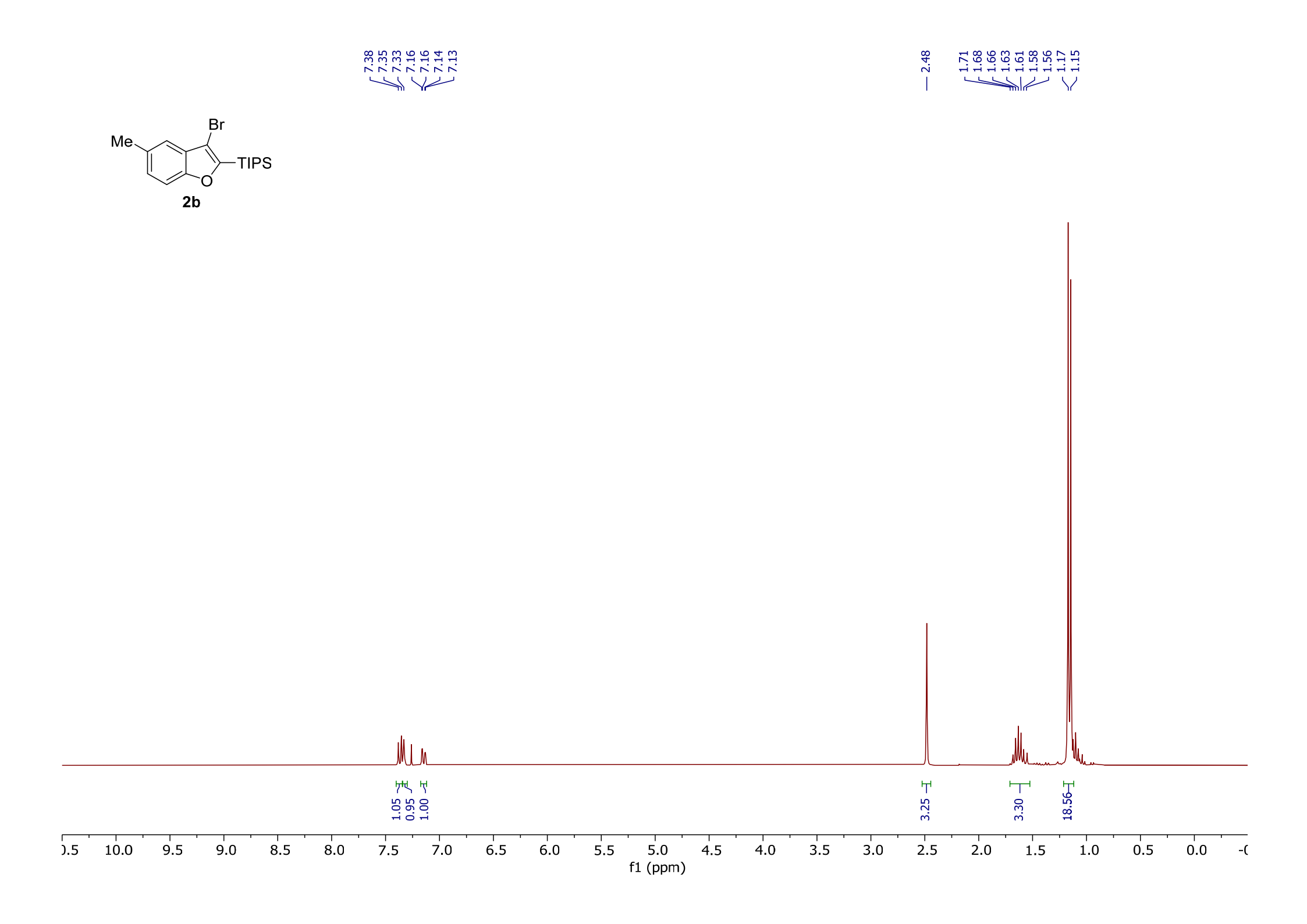
109.7
18.6
11.5
Br
TIPS
O
2a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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1.66
1.63
1.61
1.58
1.56
1.17
1.15
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Me
TIPS
O
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1.00
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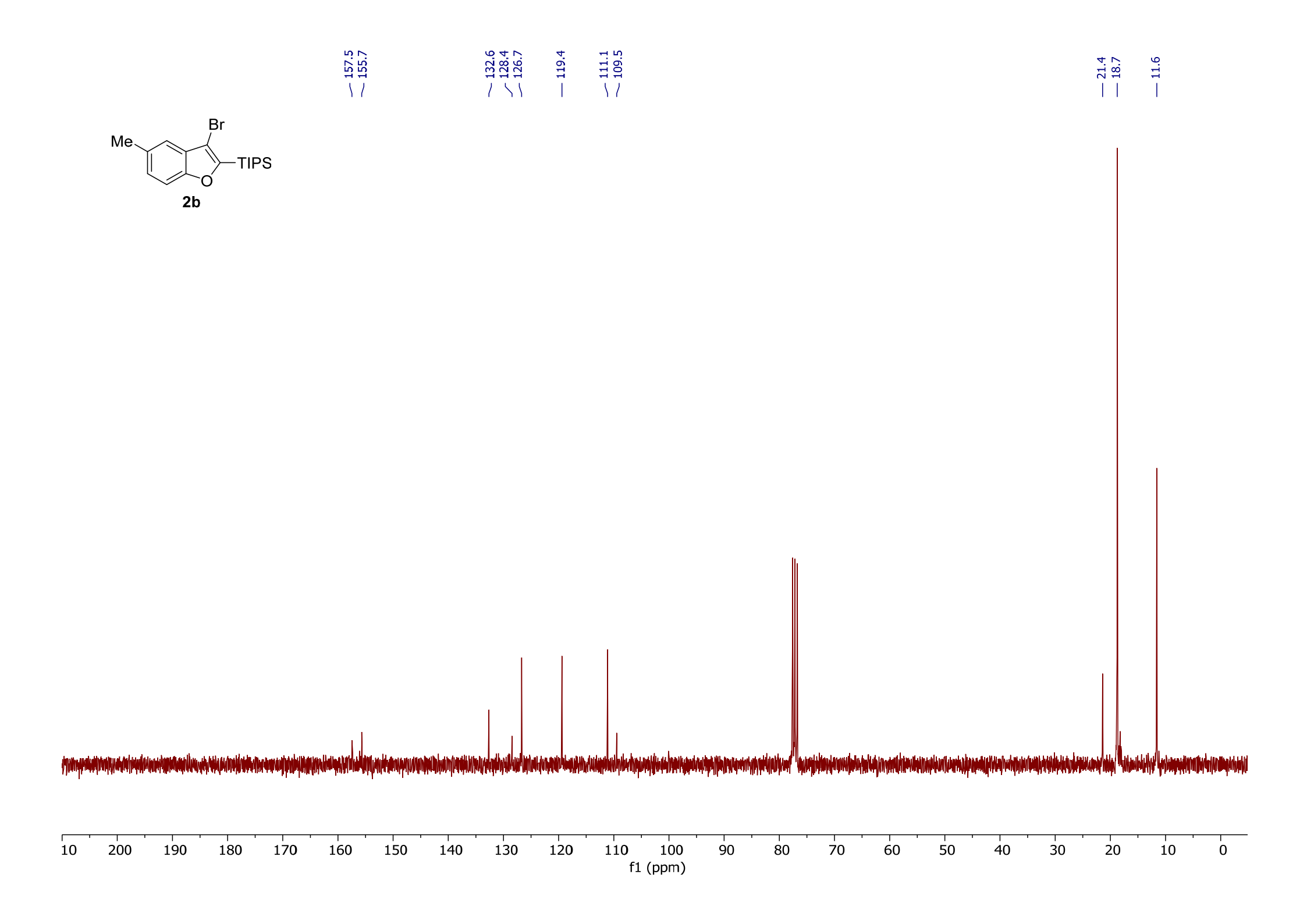
3.30
18.56
f1 (ppm)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109.5
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11.6
Br
Me
TIPS
O
2b
10
200
190
180
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130
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100
90
80
70
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50
40
30
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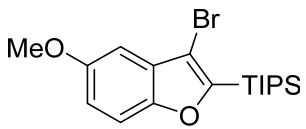
f1 (ppm)


Br
MeO
TIPS
O

2c

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7.40
7.38
7.37
6.97
6.95
6.94
3.90
1.69
1.67
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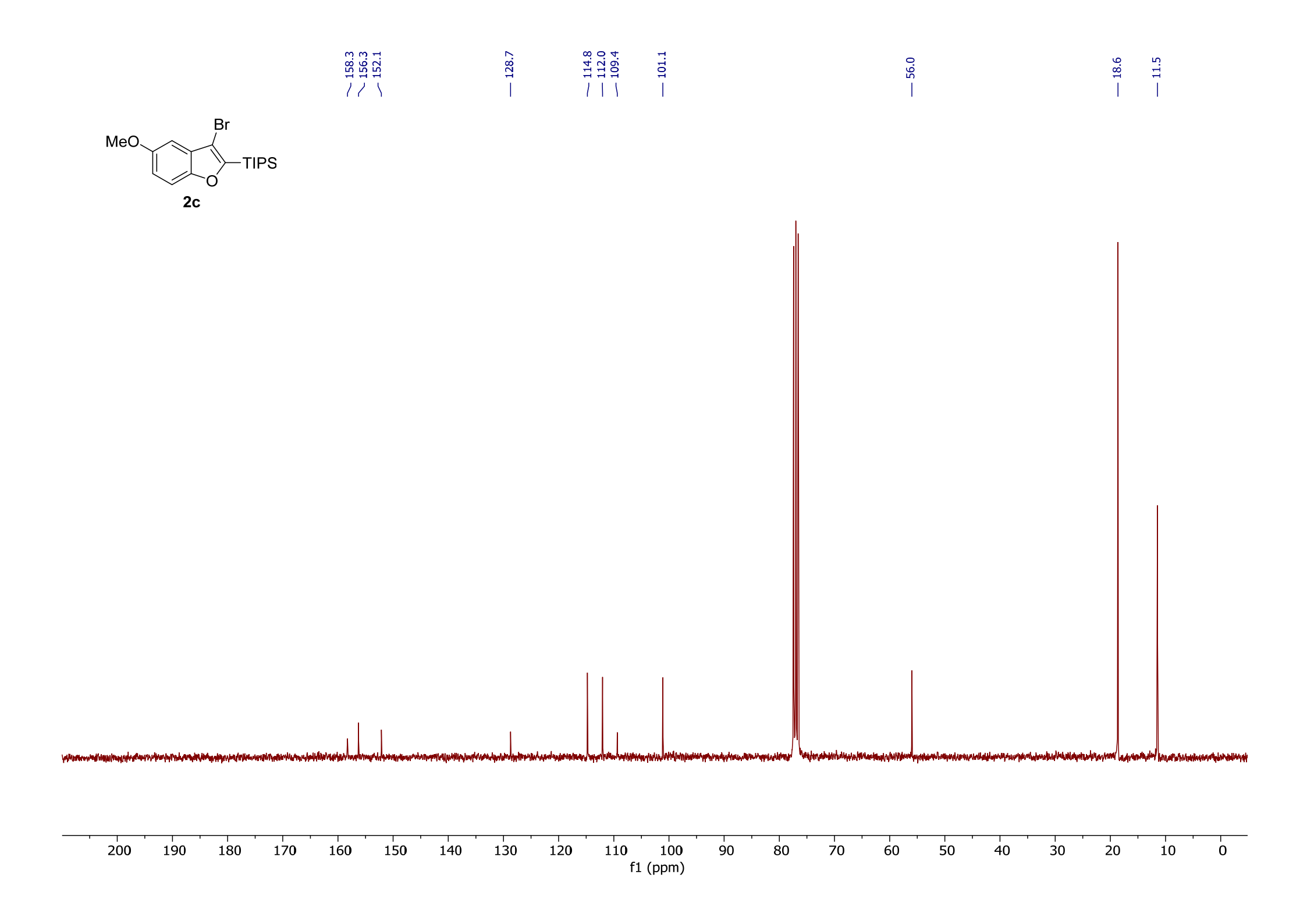
1.62
1.59
1.19
1.16
1.00
1.99
3.00
2.98
17.33
f1 (ppm)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11.5
Br
MeO
TIPS
O
2c
200
190
180
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130
120
110
100
90
80
70
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50
40
30
20
10
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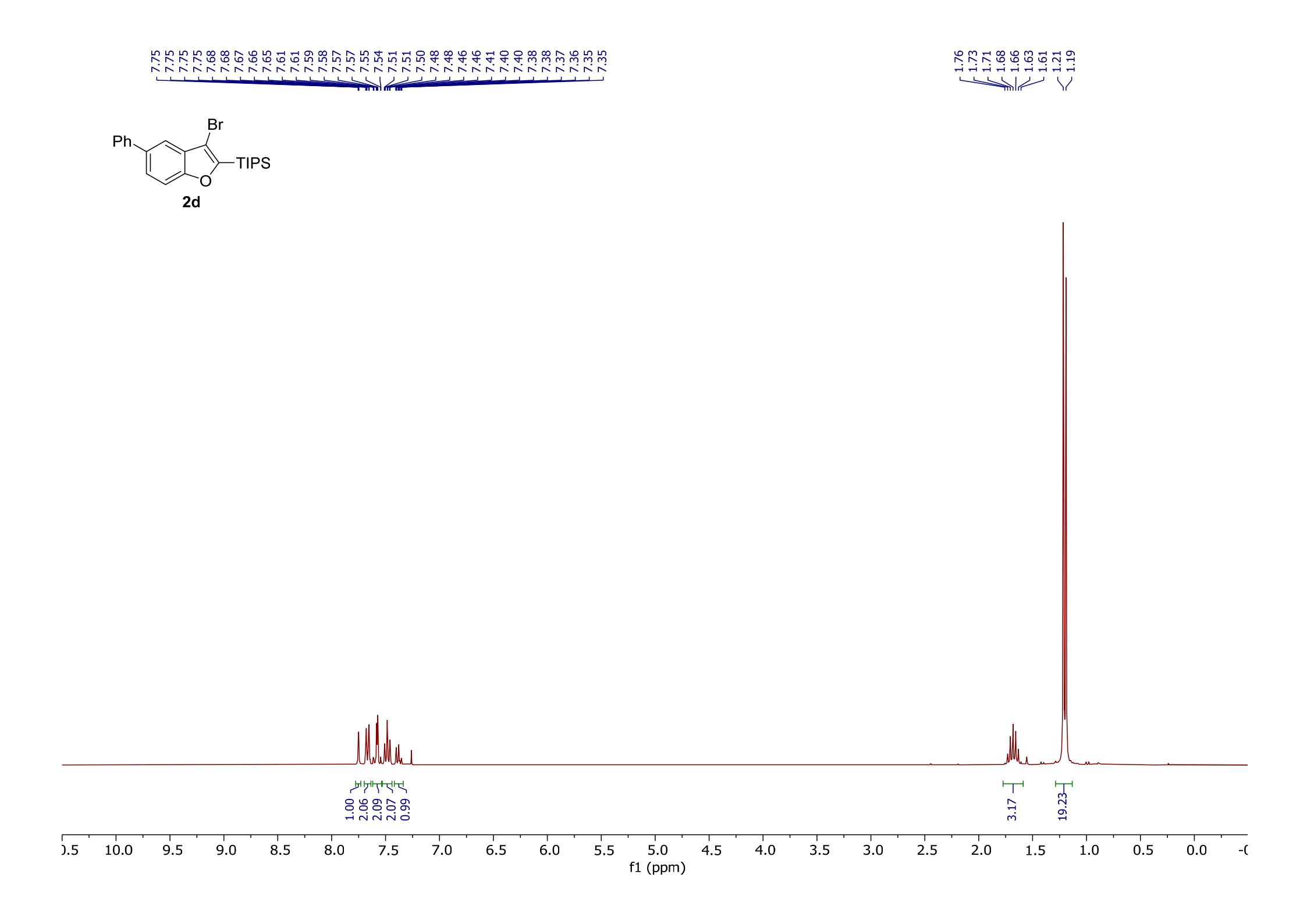
f1 (ppm)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7.51
7.51
7.50
7.48
7.48
7.46
7.46
7.41
7.40
7.40
7.38
7.38
7.37
7.36
7.35
7.35
1.76
1.73
1.71
1.68
1.66
1.63
1.61
1.21
1.19
Br
Ph
TIPS
O
2d
1.00
2.06
2.09
2.07
0.99
3.17
19.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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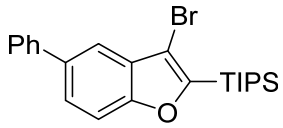
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



2d

158.4
156.9
141.5
136.9
129.0
128.9
127.7
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118.2
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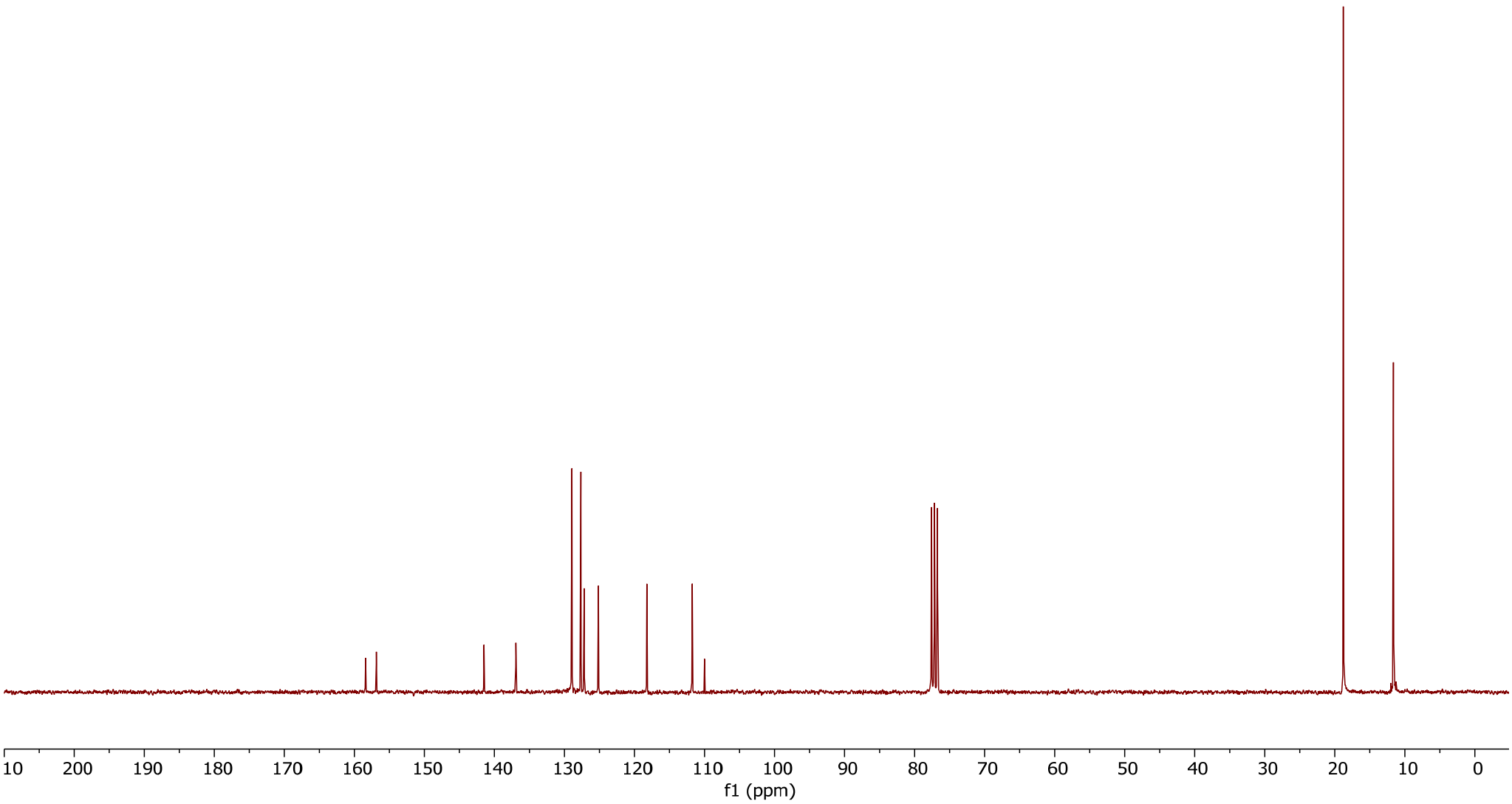
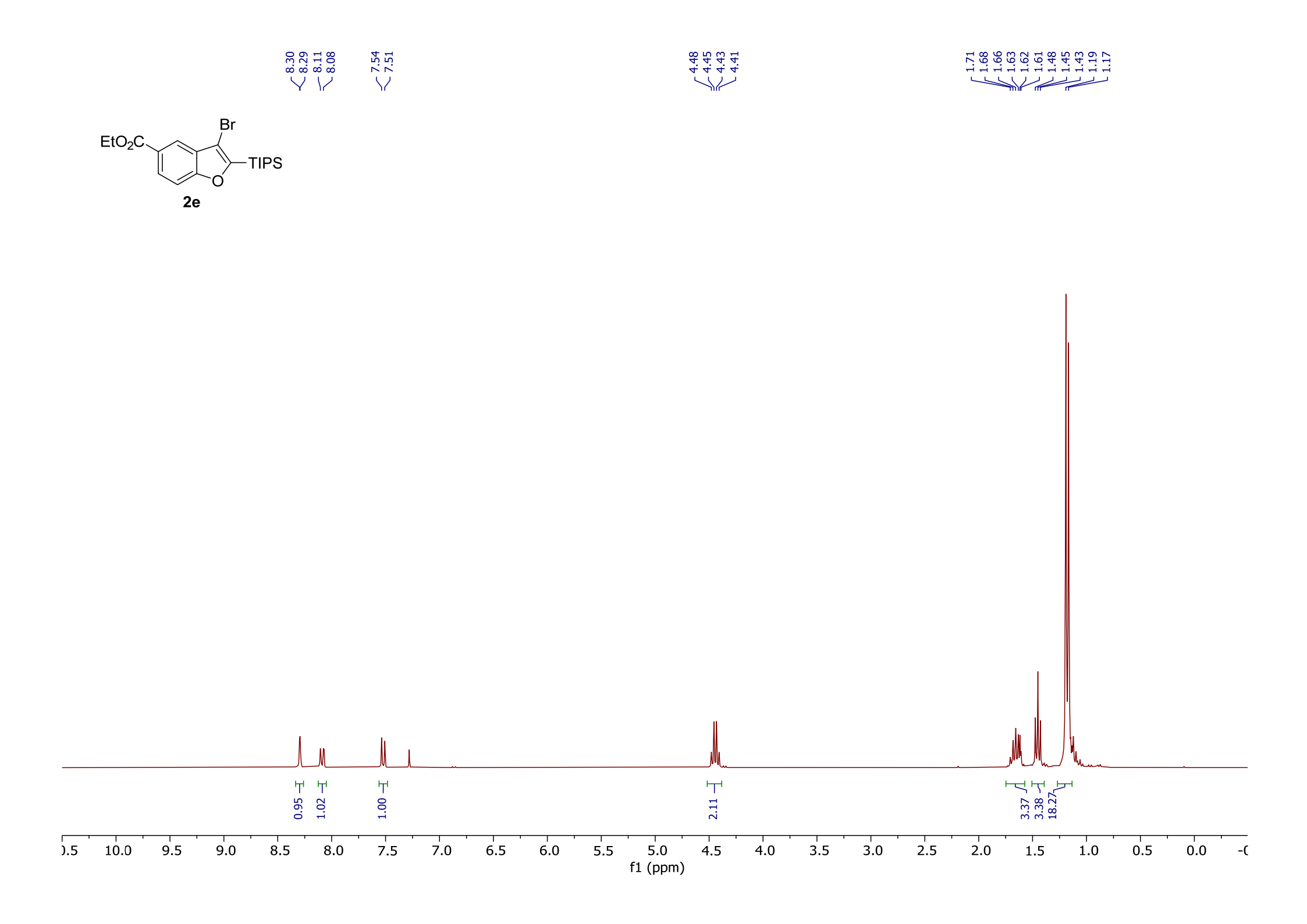
110.0
18.8
11.6

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4.41
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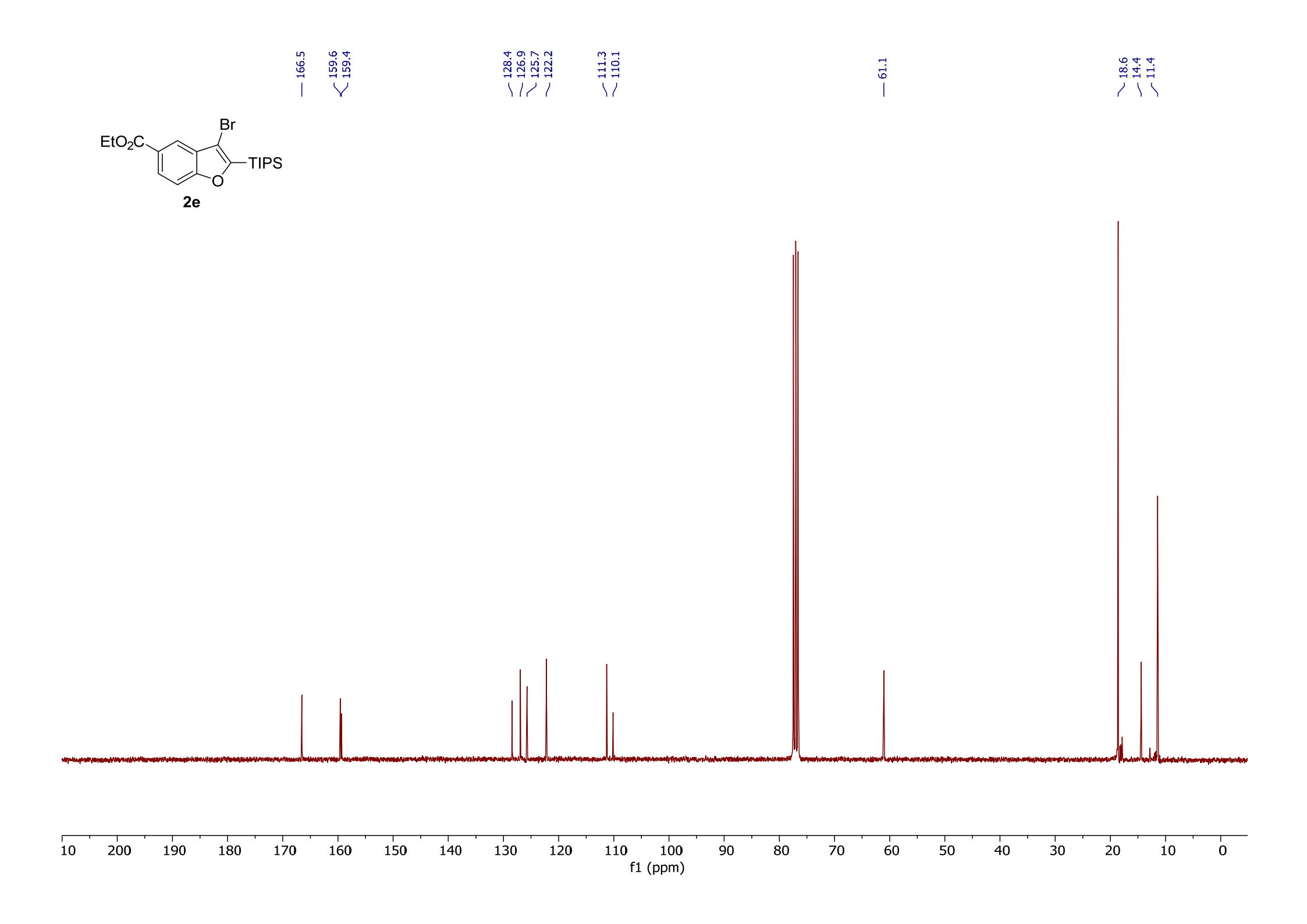
1.63
1.62
1.61
1.48
1.45
1.43
1.19
1.17
Br
EtO2C
TIPS
O
2e
0.95
1.02
1.00
2.11
3.37
3.38
18.27
f1 (ppm)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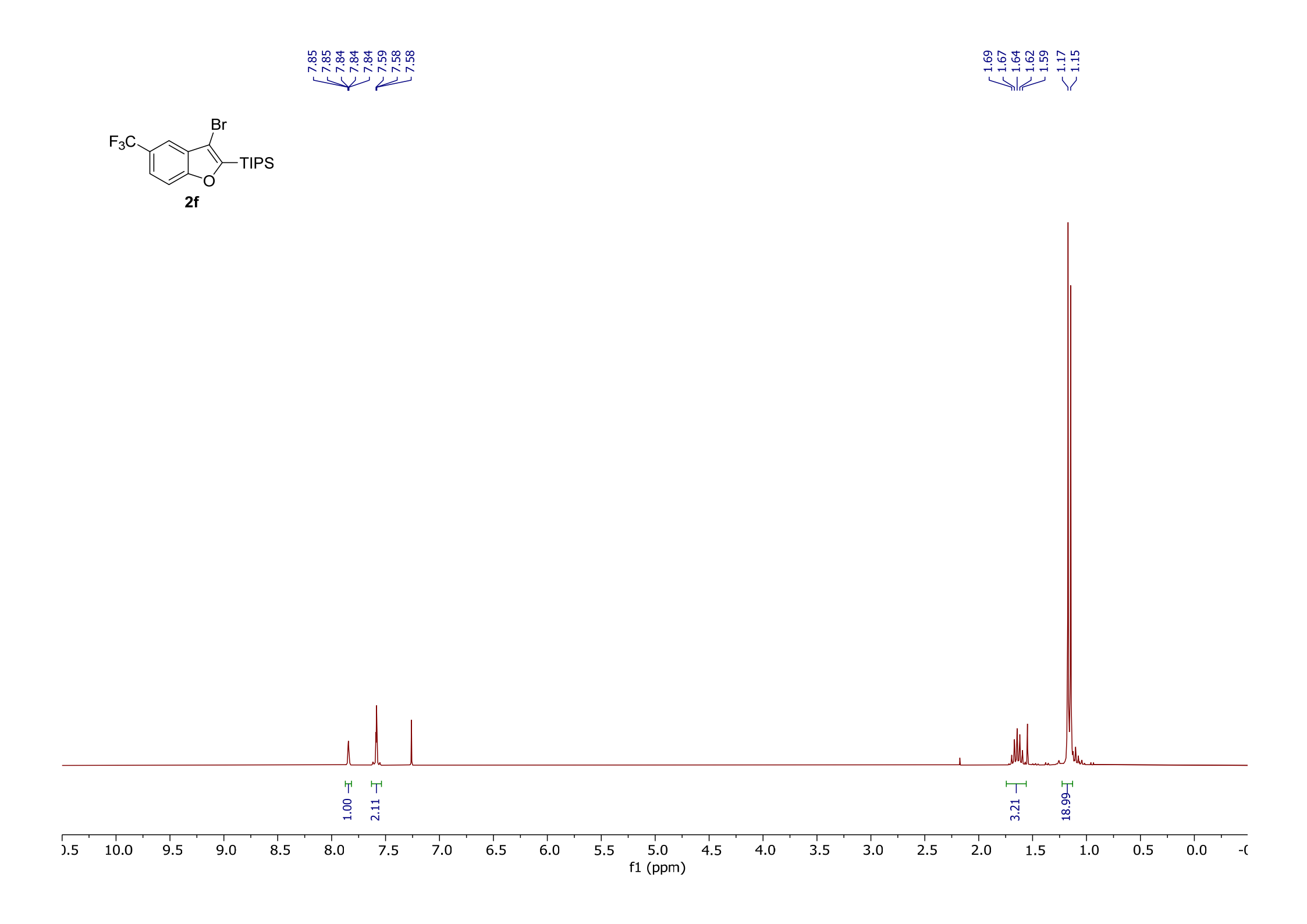
159.4
128.4
126.9
125.7
122.2
111.3
110.1
61.1
18.6
14.4
11.4
Br
EtO2C
TIPS
O
2e
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.84
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7.58
7.58
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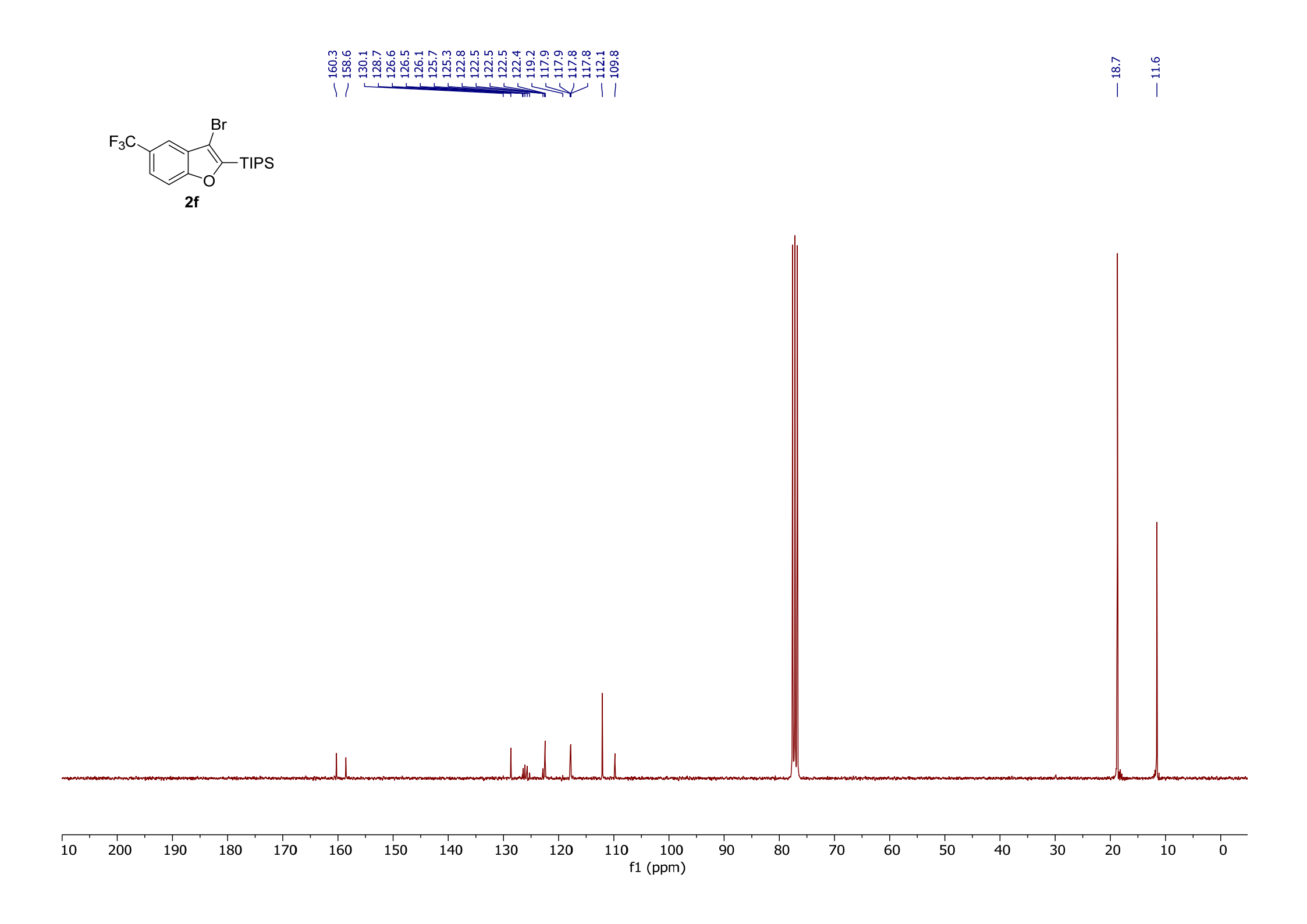
1.67
1.64
1.62
1.59
1.17
1.15
Br
F3C
TIPS
O
2f
1.00
2.11
3.21
18.99
f1 (ppm)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158.6
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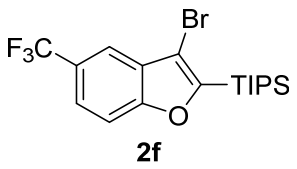
122.5
122.5
122.4
119.2
117.9
117.9
117.8
117.8
112.1
109.8
18.7
11.6
Br
F3C
TIPS
O
2f
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Br
F3C
TIPS
O

2f

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-50
-60
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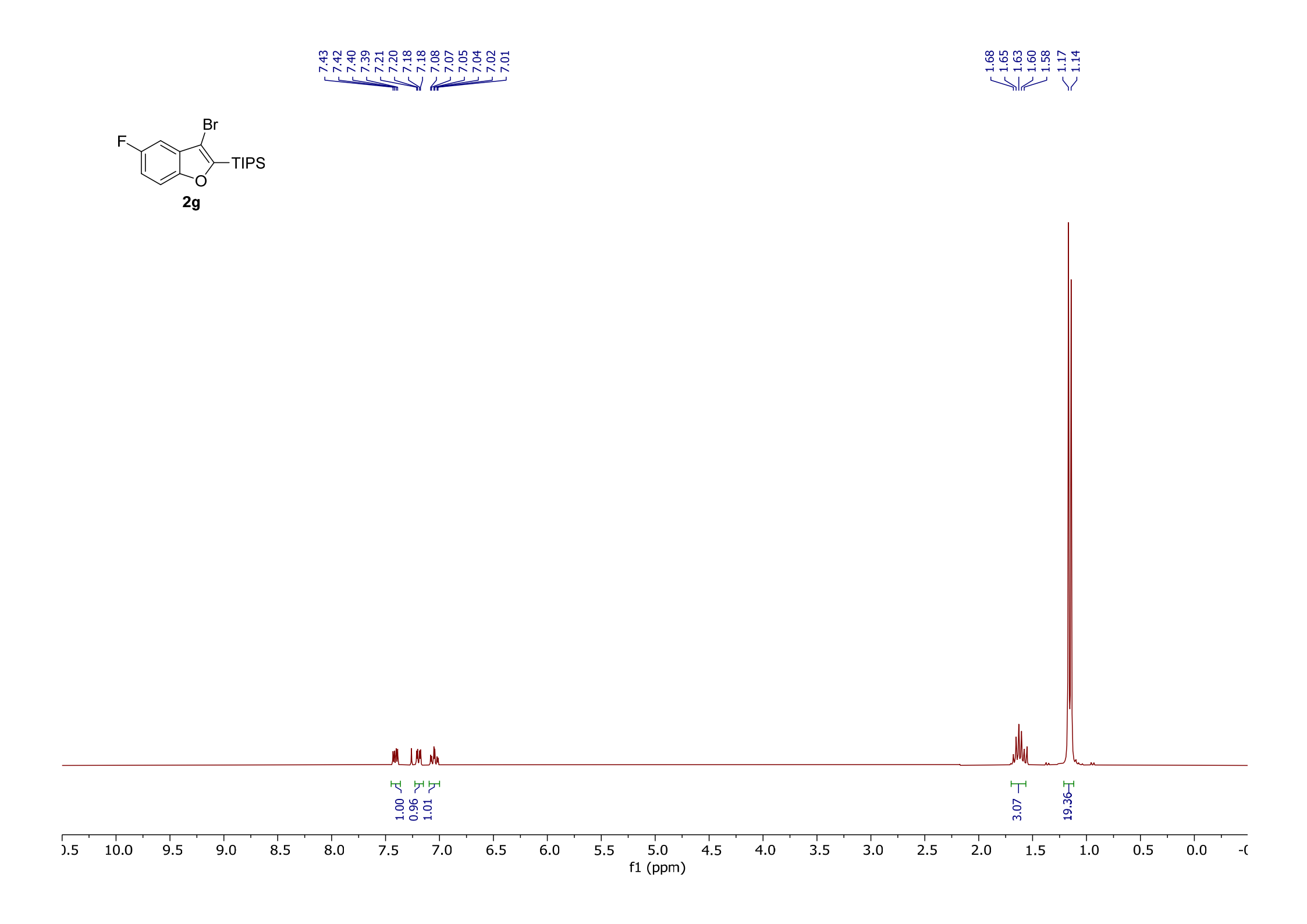
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)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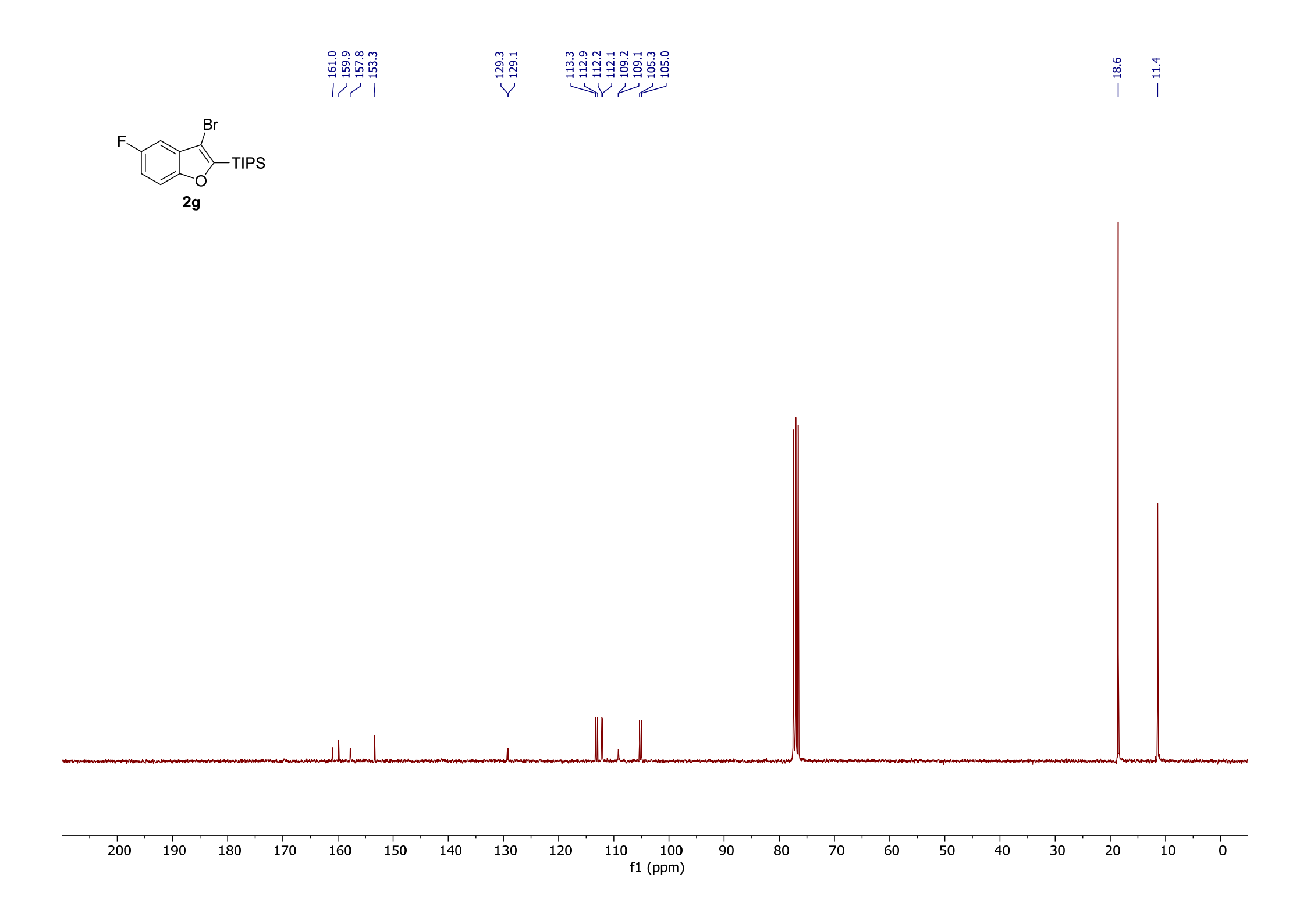
7.18
7.08
7.07
7.05
7.04
7.02
7.01
1.68
1.65
1.63
1.60
1.58
1.17
1.14
Br
F
TIPS
O
2g
1.00
0.96
1.01
3.07
19.36
f1 (ppm)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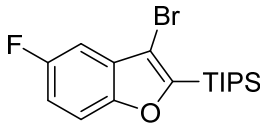
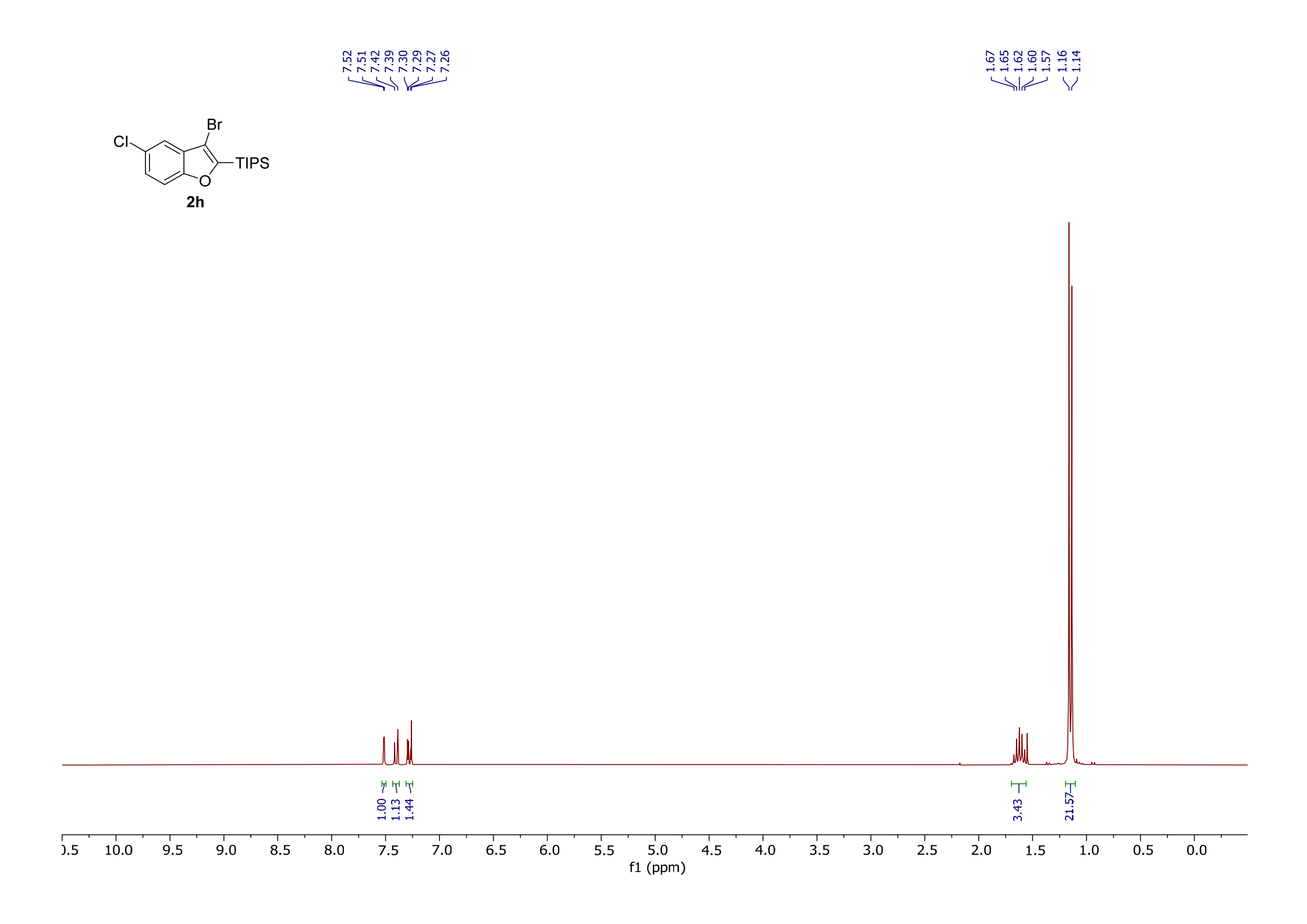
112.9
112.2
112.1
109.2
109.1
105.3
105.0
18.6
11.4
Br
F
TIPS
O
2g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Br
F
TIPS
O

2g

-120.5
-120.5
-120.5
-120.5
-120.6
-120.6
-120.50
-120.54
-120.58
f1 (ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)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Br
Cl
TIPS
O
2h
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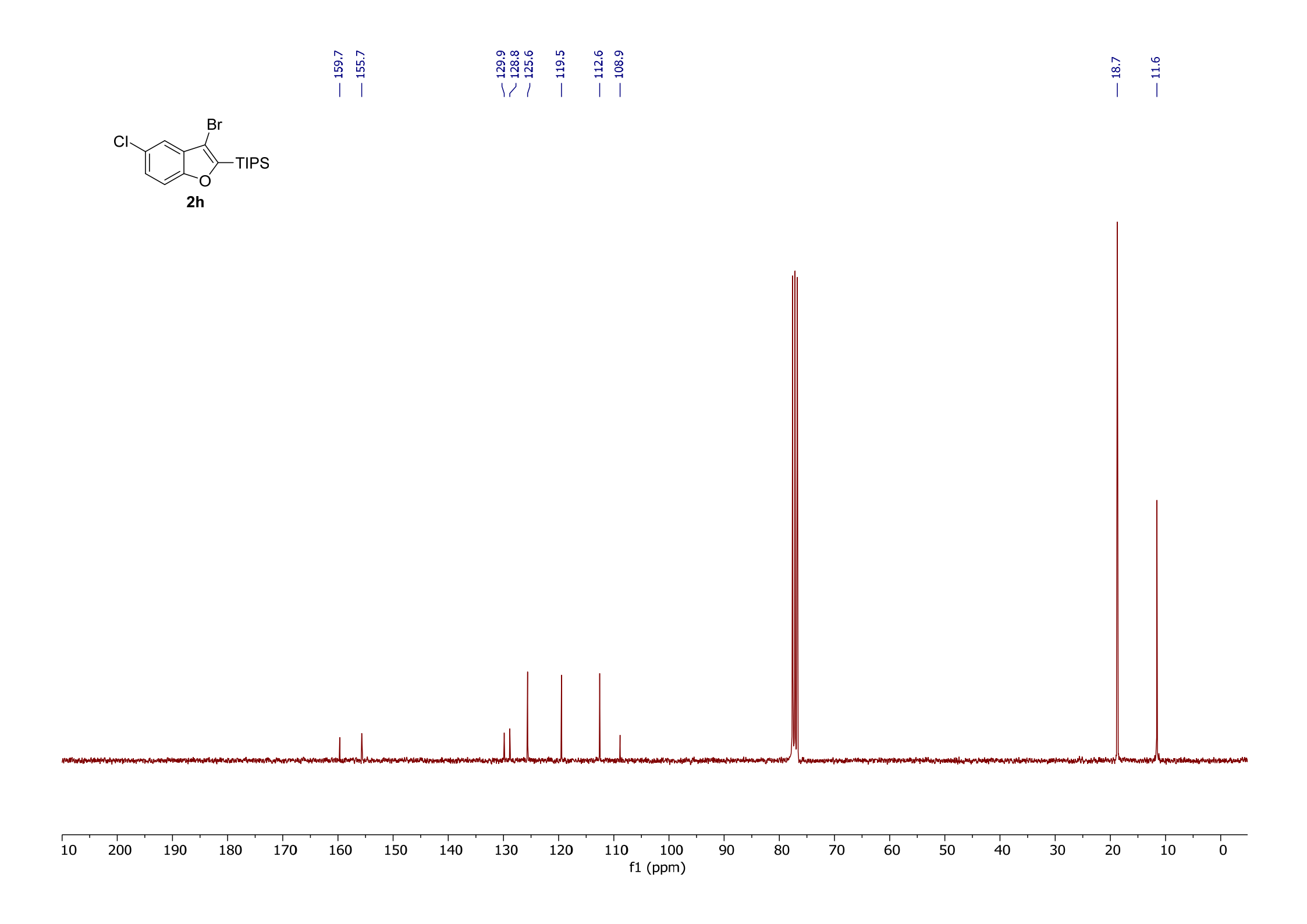
1.44
3.43
21.57
f1 (ppm)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129.9
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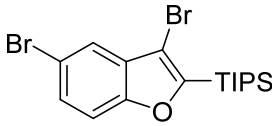
125.6
119.5
112.6
108.9
18.7
11.6
Br
Cl
TIPS
O
2h
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Br
Br
TIPS
O

2i

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7.39
7.37
7.36
1.70
1.67
1.65
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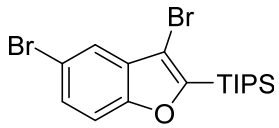
1.18
1.16
1.00
1.04
1.02
3.57
19.45
f1 (ppm)



2i

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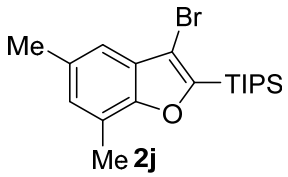
11.43

f1 (ppm)


Br
Me
TIPS
O
Me

2j

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1.18
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1.05
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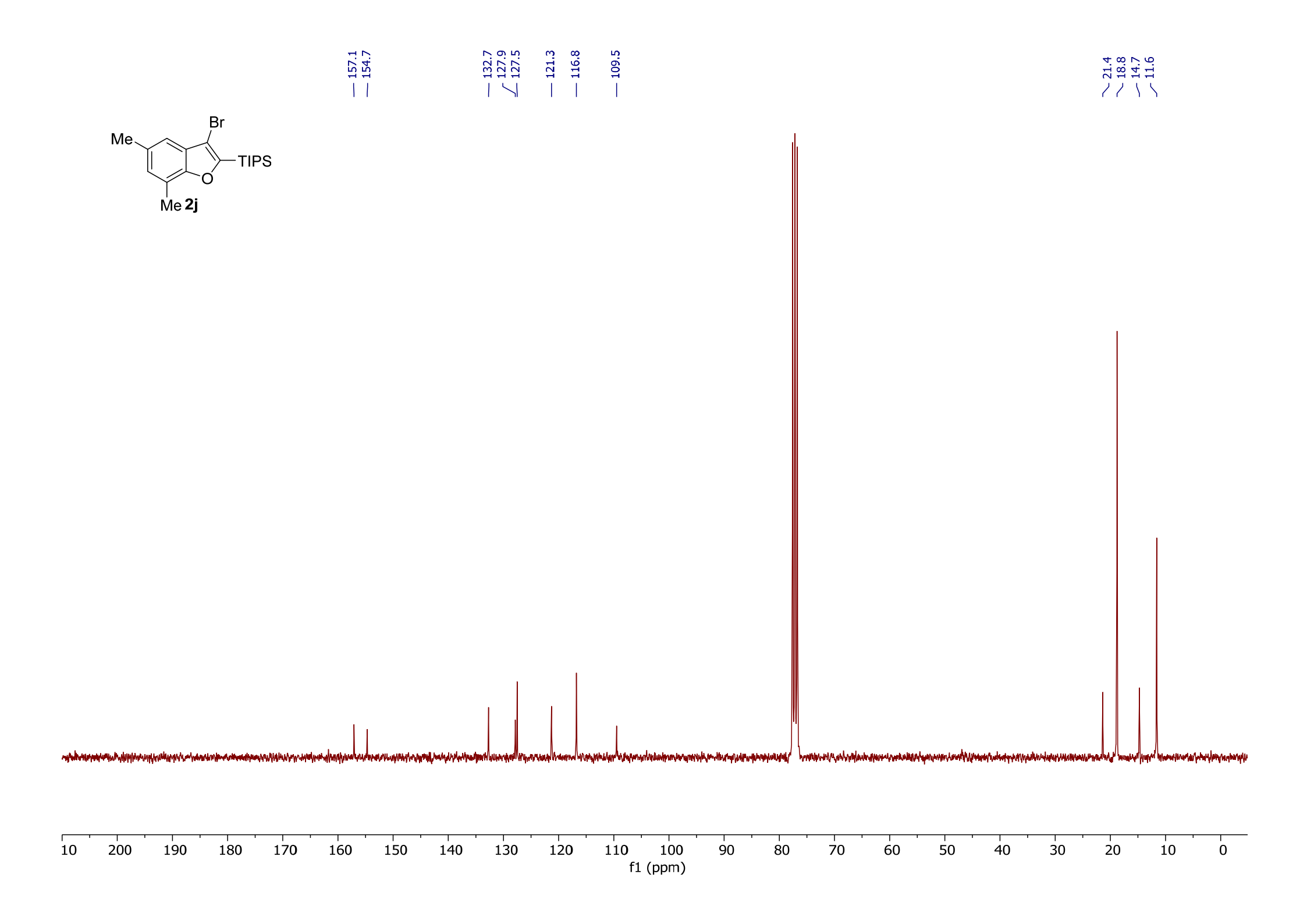
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18.8
14.7
11.6
Br
Me
TIPS
O
Me
2j
10
200
190
180
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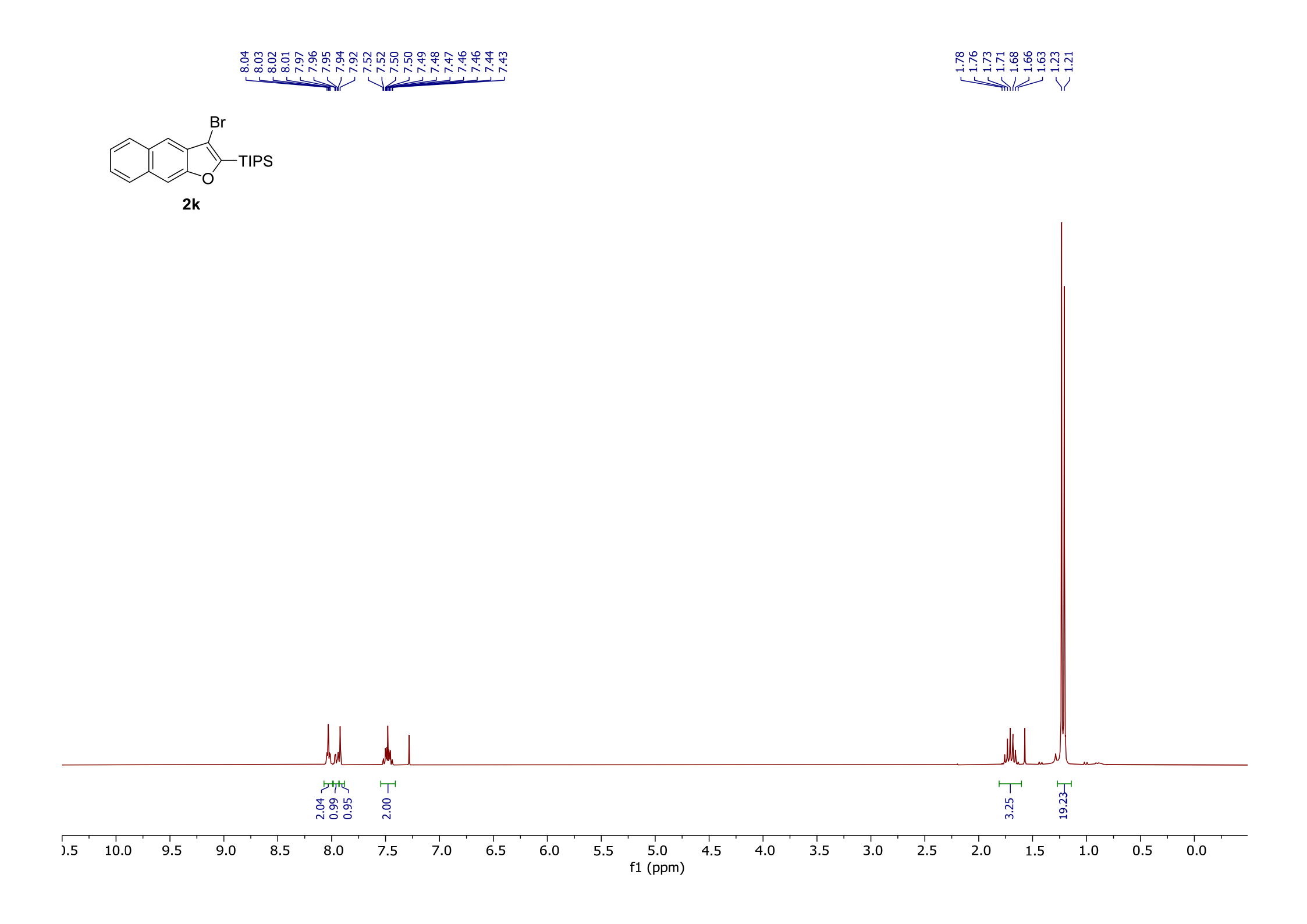
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.94
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7.44
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1.76
1.73
1.71
1.68
1.66
1.63
1.23
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TIPS
O
2k
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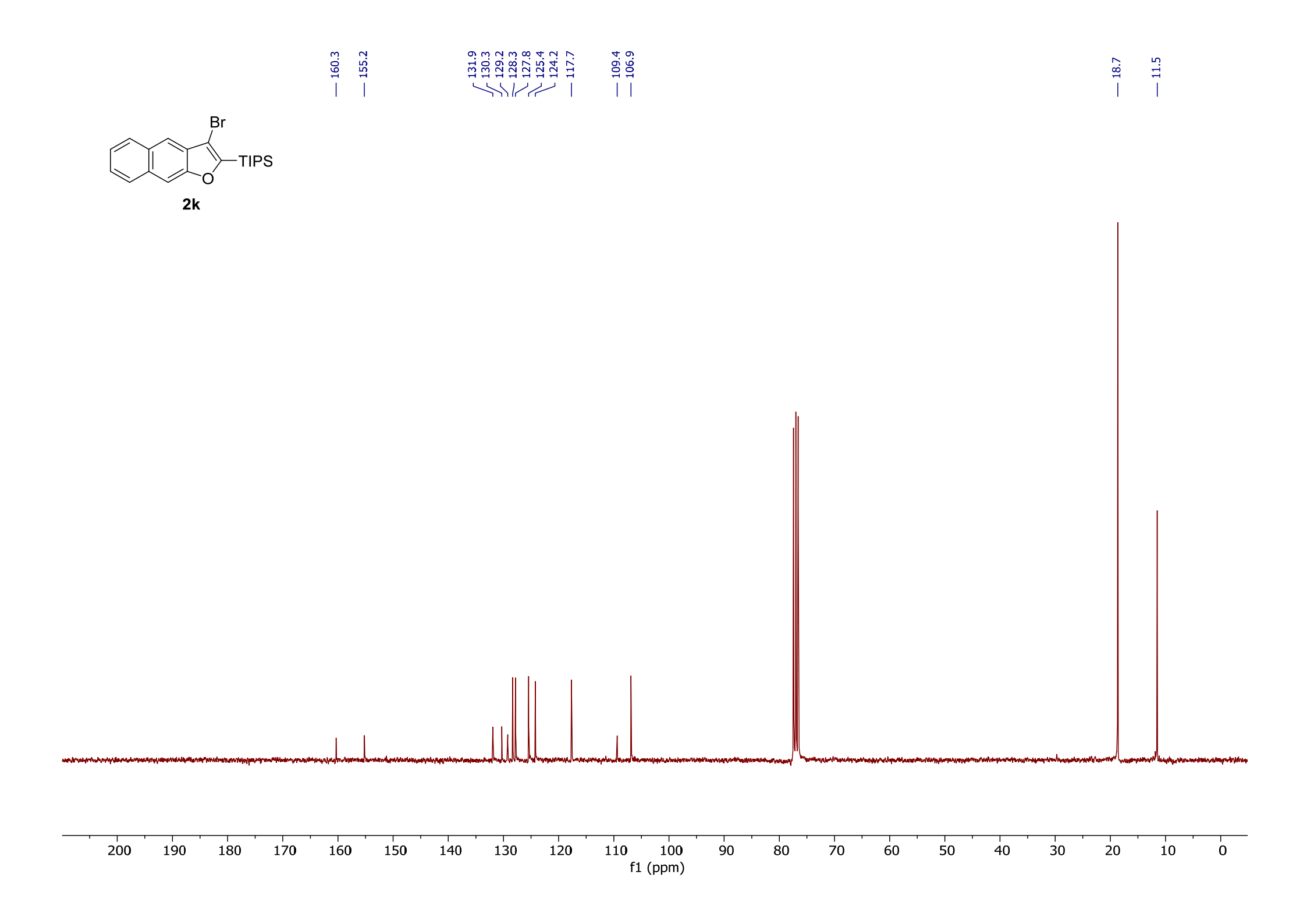
19.23
f1 (ppm)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125.4
124.2
117.7
109.4
106.9
18.7
11.5
Br
TIPS
O
2k
200
190
180
170
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150
140
130
120
110
100
90
80
70
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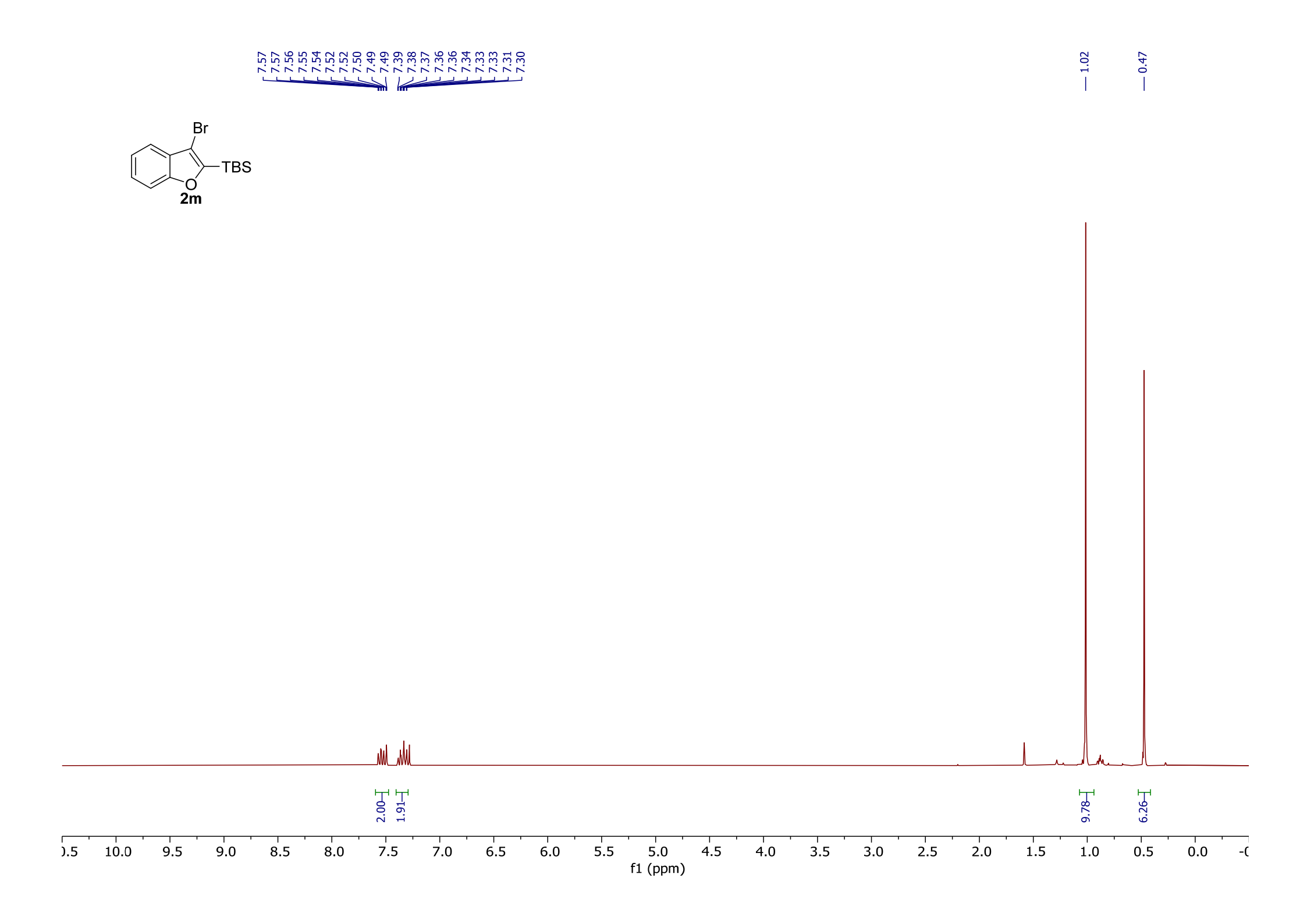
50
40
30
20
10
0
f1 (ppm)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7.36
7.36
7.34
7.33
7.33
7.31
7.30
1.02
0.47
Br
TBS
O
2m
2.00
1.91
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6.26
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
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2.0
1.5
1.0
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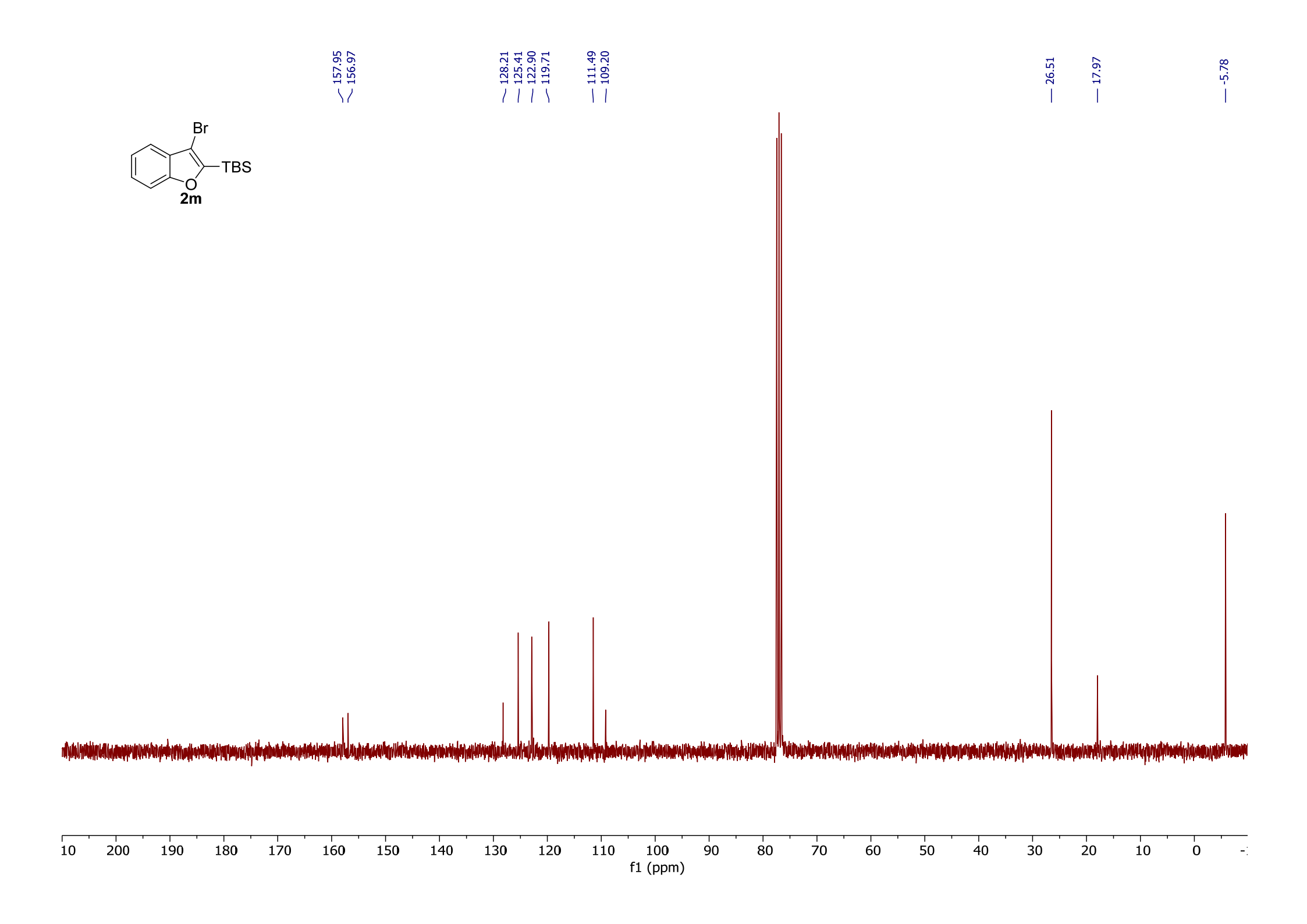
f1 (ppm)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111.49
109.20
26.51
17.97
-5.78
Br
TBS
O
2m
10
200
190
180
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120
110
100
90
80
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60
50
40
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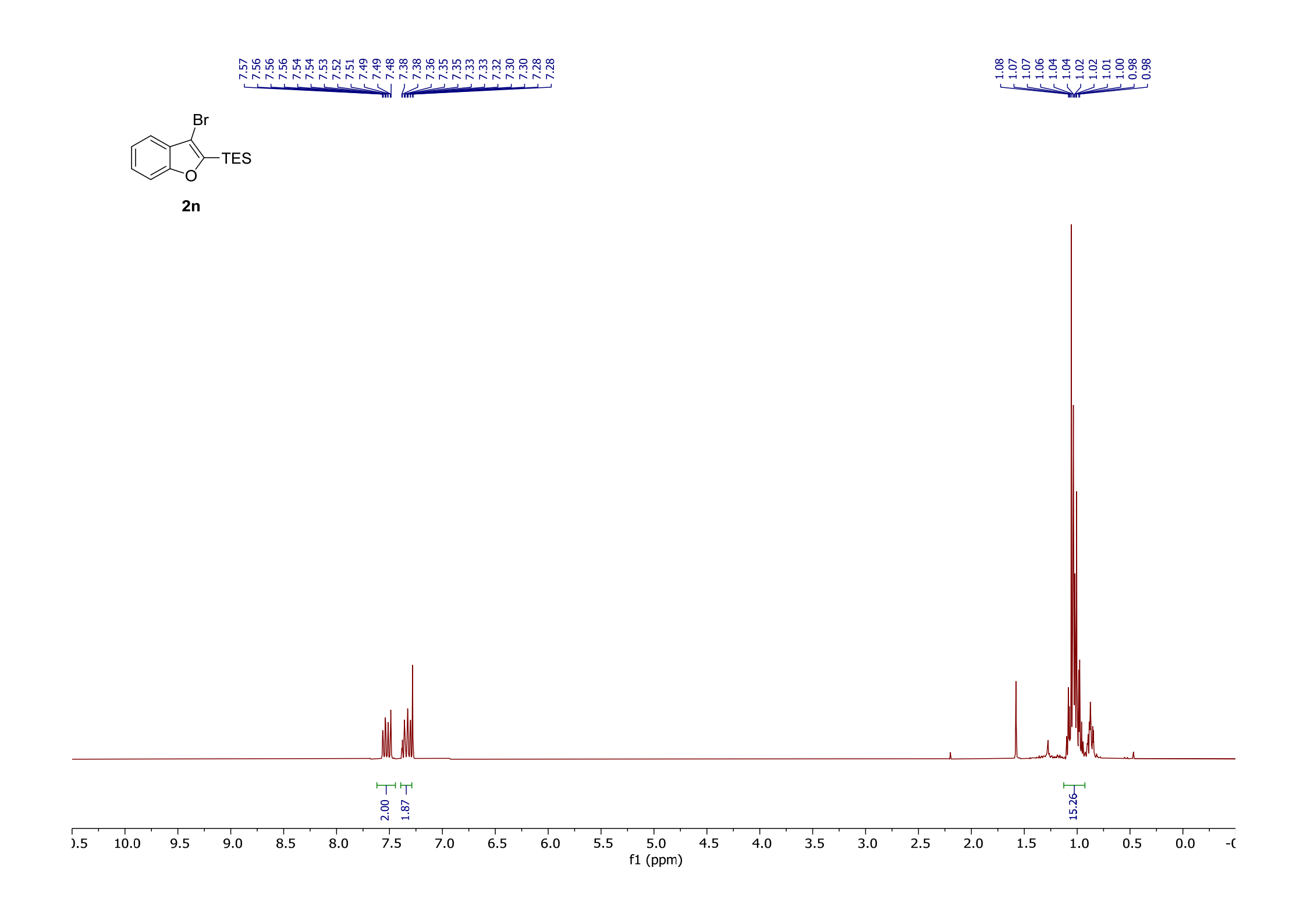
20
10
0
f1 (ppm)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7.38
7.36
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7.33
7.32
7.30
7.30
7.28
7.28
1.08
1.07
1.07
1.06
1.04
1.04
1.02
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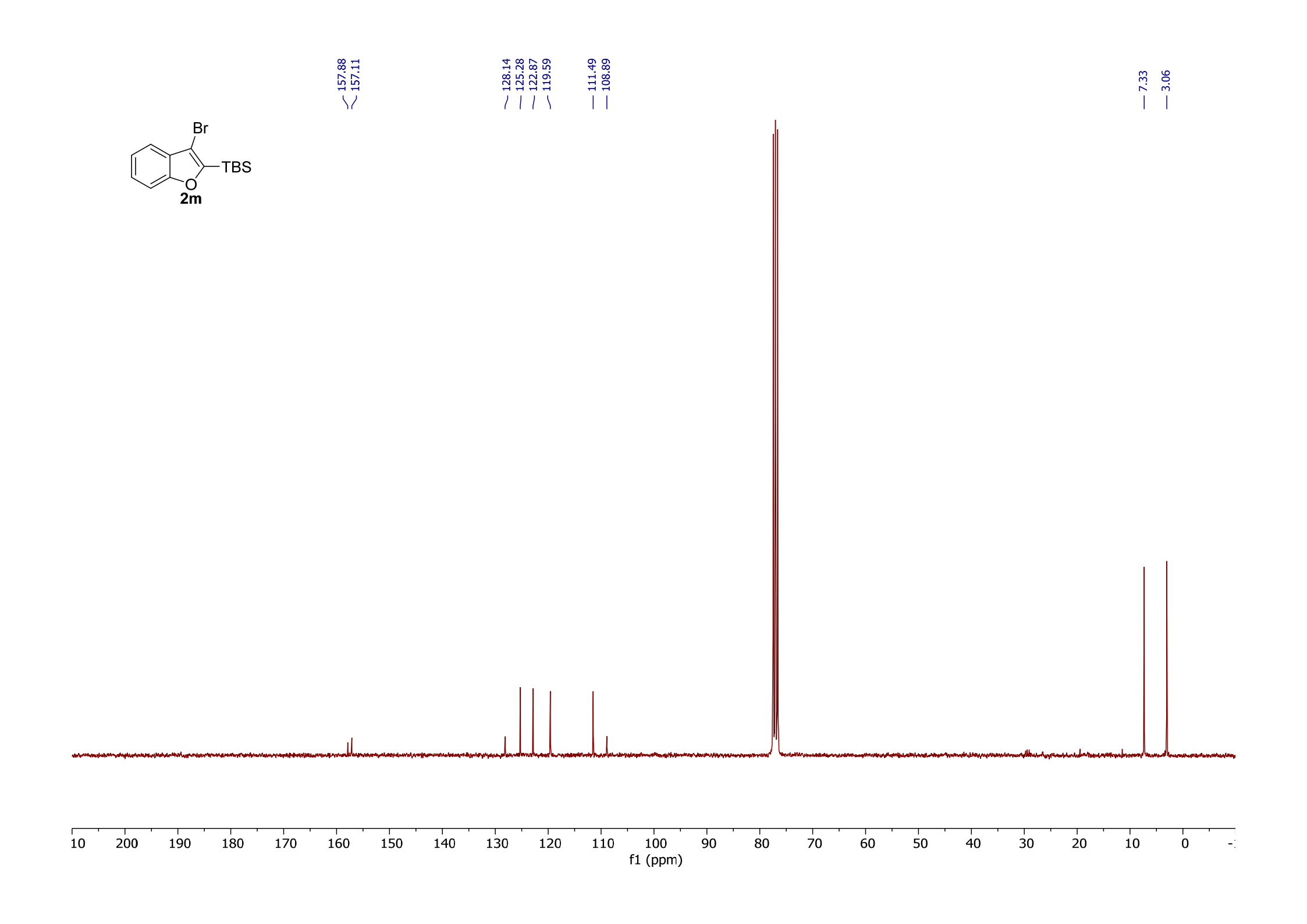
Br
TES
O
2n
2.00
1.87
15.26
f1 (ppm)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3.06
Br
TBS
O
2m
10
200
190
180
170
160
150
140
130
120
110
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90
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70
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50
40
30
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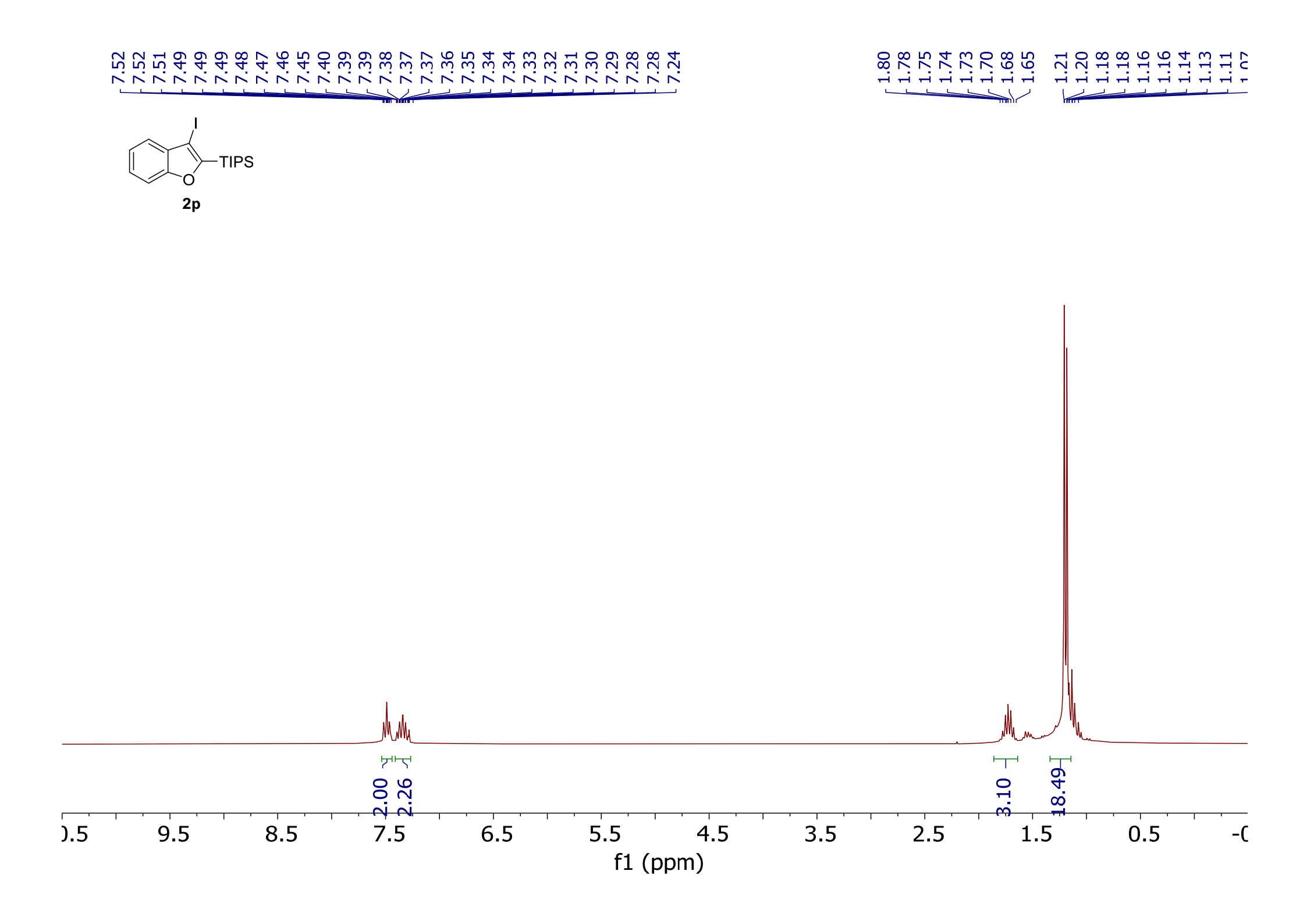
0
f1 (ppm)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7.47
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7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.28
7.24
1.80
1.78
1.75
1.74
1.73
1.70
1.68
1.65
1.21
1.20
1.18
1.18
1.16
1.16
1.14
1.13
1.11
I
TIPS
O
2p
2.00
2.26
3.10
18.49
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8.5
7.5
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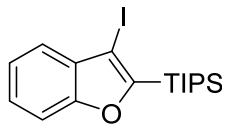
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

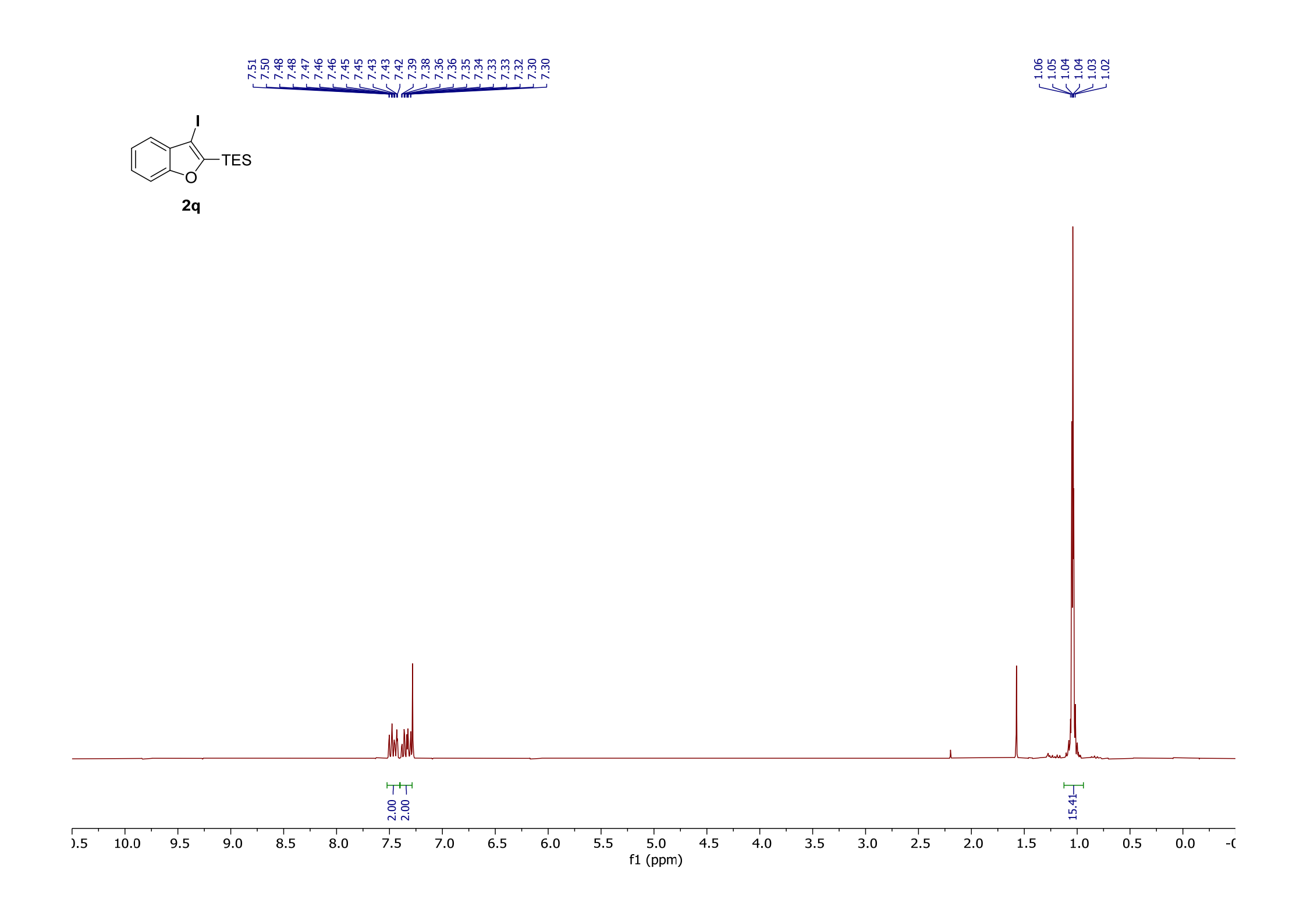


2p

160.9
157.0
131.3
125.3
122.9
121.5
111.2
78.0
18.7
11.7

10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)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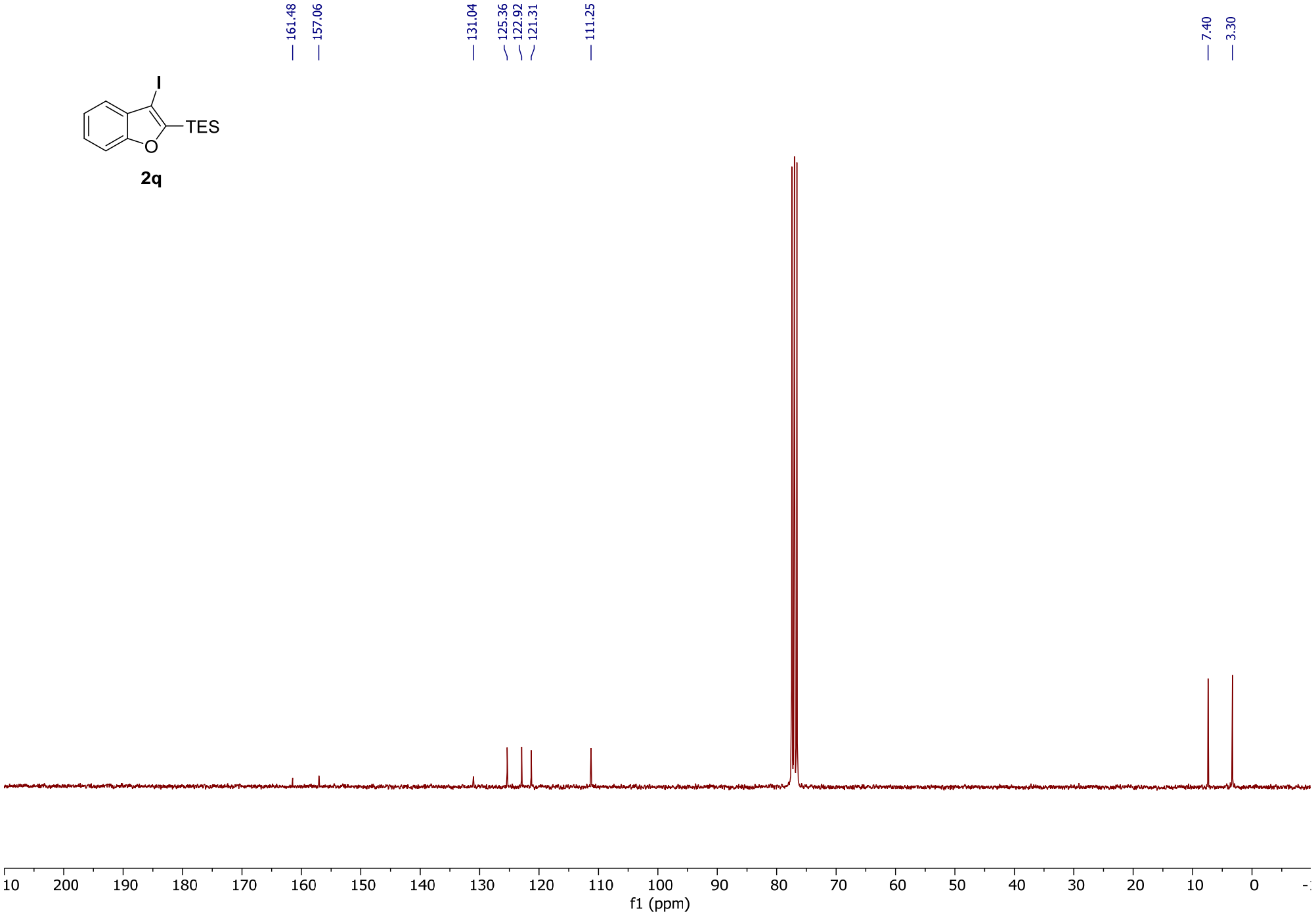
7.38
7.36
7.36
7.35
7.34
7.33
7.33
7.32
7.30
7.30
1.06
1.05
1.04
1.04
1.03
1.02
I
TES
O
2q
2.00
2.00
15.41
f1 (ppm)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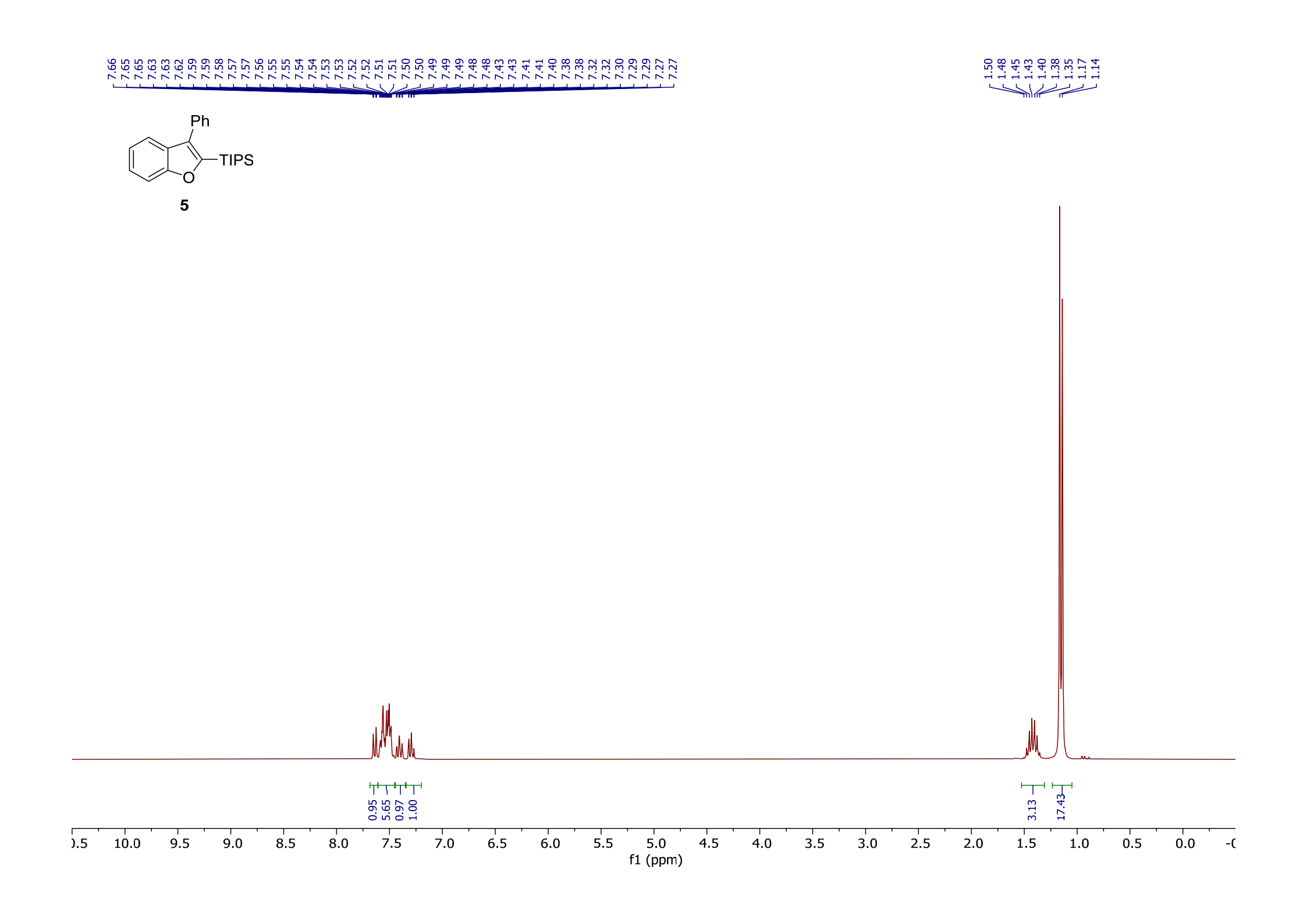
157.06
131.04
125.36
122.92
121.31
111.25
7.40
3.30
I
TES
O
2q
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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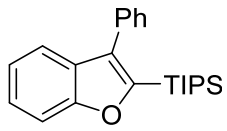
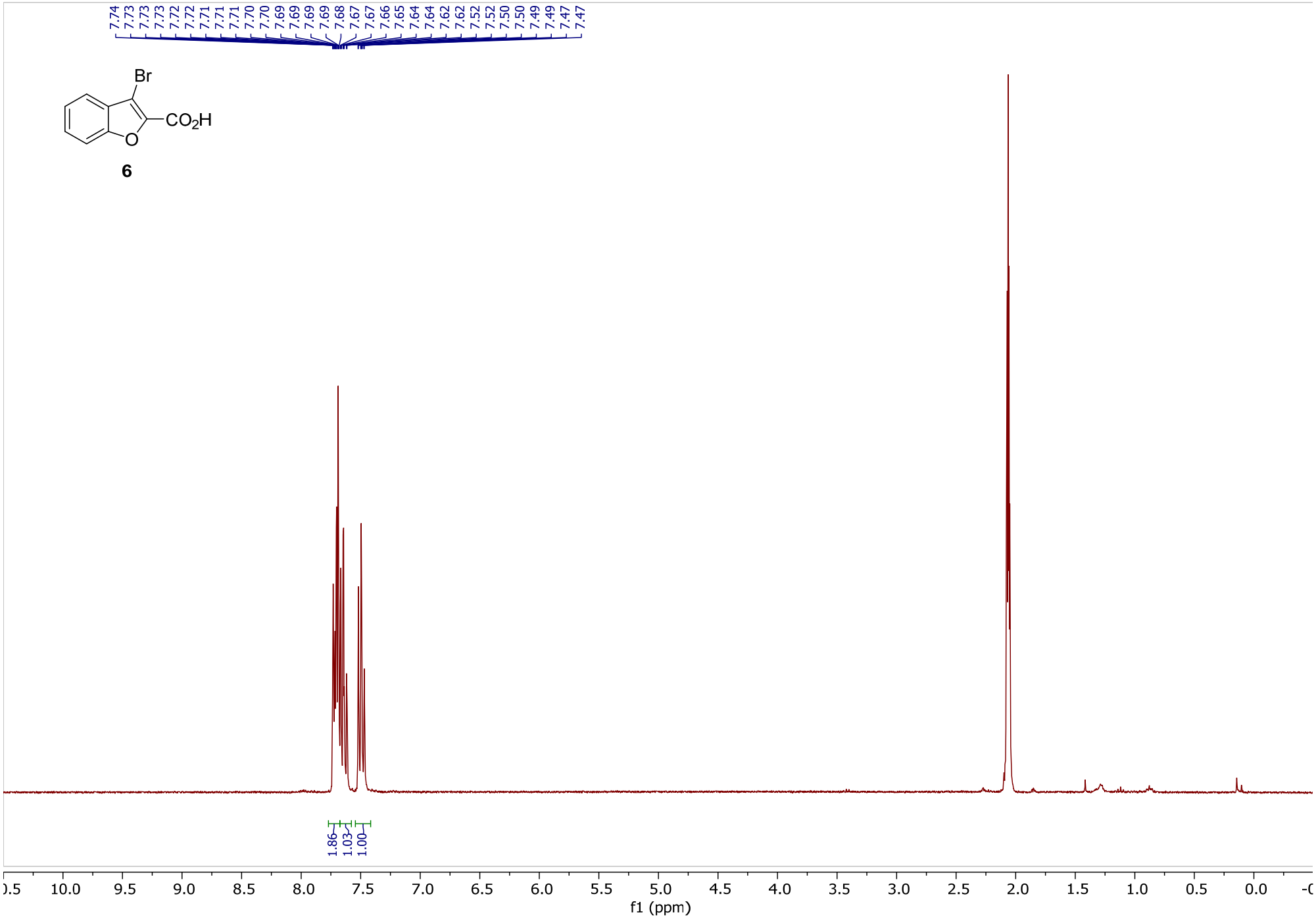
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.49
7.49
7.49
7.48
7.48
7.43
7.43
7.41
7.40
7.38
7.38
7.32
7.30
7.29
7.29
7.27
7.27
1.50
1.48
1.45
1.43
1.40
1.38
1.35
1.17
1.14
Ph
TIPS
O
5
0.95
5.65
0.97
1.00
3.13
17.43
f1 (ppm)


Ph
TIPS
O

5

157.65
156.23
133.82
133.52
130.16
129.67
128.22
127.73
124.50
122.28
120.14
111.21
18.80
11.82
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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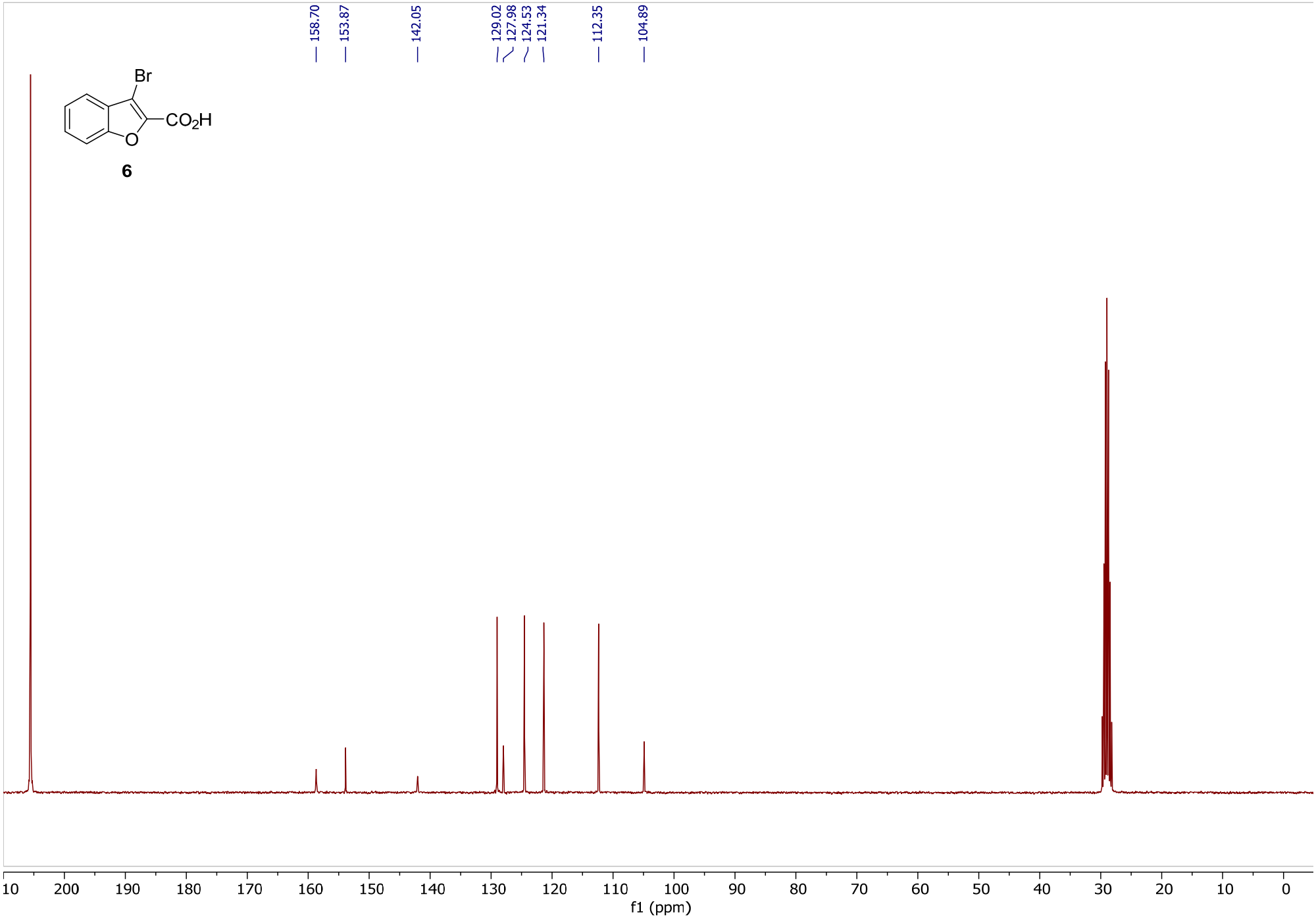
7.65
7.64
7.64
7.62
7.62
7.52
7.52
7.50
7.50
7.49
7.49
7.47
7.47
Br
CO2H
O
6
1.86
1.03
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


158.70
153.87
142.05
129.02
127.98
124.53
121.34
112.35
104.89
Br
CO2H
O
6
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)