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Supporting information

Copper Catalysed Protoboration of Allenyl-Bdans: Efficient Synthesis of β-Boryl Allyl-Bdans

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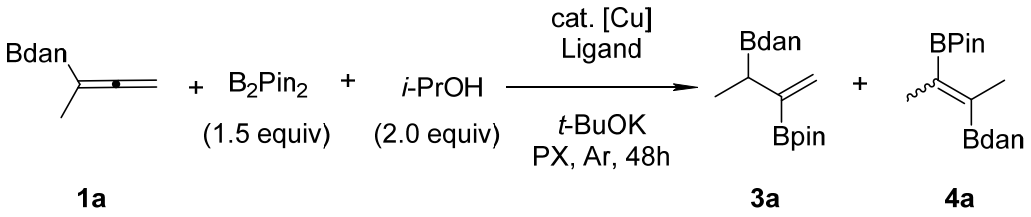
General Information. ^{1}H NMR and ^{13}C NMR spectra were recorded on BRUKER AVANCE III (500 MHz) spectrometers. ^{1}H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm, integration, multiplicities (s = singlet, d =doublet, t = triplet, m = multiplet, appt = apparently triplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on BRUKER AVANCE III (126 MHz) spectrometers with complete proton decoupling, and chemical shift reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77.0 ppm. High resolution mass spectra (HRMS) were obtained on a BRUKER autoflex maX MALDI-TOF(TOF) instrument. Column chromatography and filtration via silica plug were carried out employing silica gel (Qingdao Haiyang Chem, neutral, 300-400 Mesh). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck).

Materials. Unless otherwise noted, commercially available chemicals were used as received. The structures of new products were determined by ^{1}H, ^{13}CNMR, and high-resolution mass.

Table S1. Detailed optimization of reaction conditions[a]



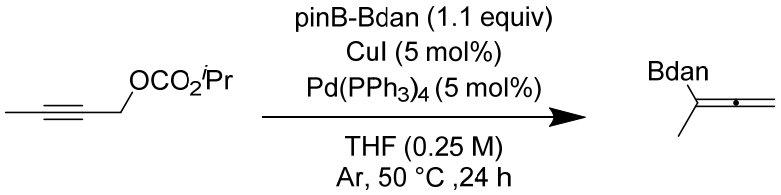
1a **3a** **4a**

Enrty	[Cu]/ 10 mol%	Ligang/ 12 mol%	Conversion of **1a** / %[b]	Yield of **3a** / %[b]	Yield of **4a** / %[b]
1	CuI	Xantphos	100	90(73)	0
2	CuCl	Xantphos	100	57	0
3	CuOAc	Xantphos	100	87	0
4	$CuCl_2$•$2H_2O$	Xantphos	100	86	0
5	CuI	DPEphos	57	32	0
6	CuI	*rac*-BINAP	82	40	0
7	CuI	DPPE	100	70	10
8	CuI	DPPBZ	100	60	9
9	CuI	-	76	54	20
10[c]	CuI	P(*p*-$OMeC_6H_4)_3$	100	23	29
11[c]	CuI	PCy_3	100	32	35
12[c]	CuI	P(2-furyl)$_3$	100	61	20
13[c]	CuI	PPh_3	100	46	20
14[d]	CuI	Xantphos	48	38	0
15[e]	CuI	Xantphos	64	48	0
16[f]	CuI	Xantphos	85	84	0
17[g]	CuI	Xantphos	100	86	0
18	-	Xantphos	0	-	-
19[h]	CuI	Xantphos	0	-	-

[a] General reaction condition: a mixture of **1a** (0.1 mmol), B_2Pin_2 (0.15 mmol, 1.5 equiv), Cu catalyst (10 mol%), Ligand (12 mol%), *t*-BuOK (30 mol%) and *i*-PrOH (0.2 mmol, 2.0 equiv) in PX (0.1 M, 1 mL) was reacted at 30°C for 48 h under Ar. [b] The conversions of **1a** and yields of **3a**/**4a** were determined by crude ^{1}H NMR spectrum with naphthalene as an internal standard, the yield of isolated **3a** is given in parentheses. [c] 20 mol% ligand was used in the reaction. [d] DCM was used in the reaction. [e] 1,4-Dioxane was used in the reaction. [f] Toluene was used in the reaction. [g] THF was used in the reaction. [h] *t*-BuOK was omitted in the reaction. DPPBZ = 1,2-bis(diphenylphosphino)benzene. DPPE = 1,2-bis(diphenylphosphino)ethane. DPEphos = bis(2-diphenylphosphinophenyl)ether. *rac*-BINAP = (±)-2,2′-bis(diphenylphosphino)-1,1′-binaphthalene, P(2-furyl)$_3$ = tri(2-furyl)phosphine.

Experimental Procedures and Spectral Data

1. Synthesis of Allenyl-Bdan 1



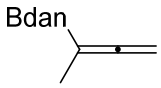
S1 **1a**

The allenyl-Bdan **1** were synthesized according to reported procedure by Szabó and co-works.[1]

Representative procedure: An oven-dried Schlenk flask was equipped with a Teflon coated stirrer bar and charged with copper iodide (9.5 mg, 0.05 mmol), $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), pinB-Bdan (323.4 mg, 1.1 mmol) and THF (4 mL, 0.25 M). The resulted solution was stirred for 10 min at r.t., then propargylic carbonate **S1** (156.2 mg, 1.0 mmol) was added to the mixture via syringe. The final reaction mixture was heated at 50 °C for 24 hours, then the reaction mixture was diluted by petroleum ether (about 5 mL). The precipitate was filtered off by a short silica pad (Qingdao Haiyang Chem, neutral, 300-400 Mesh, about 2-3 cm in pipette) using EtOAc/petroleum ether (1:20 v/v) as an eluent. The solvent was removed and the residue was purified by a rapid silica gel chromatography (within 10 min) using a mixture of petroleum ether/EtOAc (1:100-1:20) as eluent affording pure product **1a**.

Analytical Data:

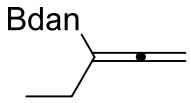
2-(Buta-2,3-dien-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1a)



1a

White solid (132.0 mg, 60%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.34 (d, *J* = 7.2 Hz, 2H), 5.71 (brs, 2H), 4.69 (q, *J* = 3.0 Hz, 2H), 1.81 (t, *J* = 2.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.4, 140.9, 136.2, 127.5, 119.4, 117.5, 105.6, 71.4, 14.2; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{14}H_{14}BN_2]^+$ 221.12407, found 221.12446.

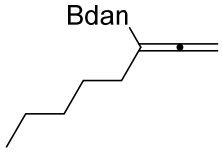
2-(Penta-1,2-dien-3-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*] [1,3,2]diazaborinine (1b)



1b

White solid (152.2 mg, 65%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.34 (d, *J* = 7.2 Hz, 2H), 5.71 (brs, 2H), 4.78 (t, *J* = 3.3 Hz, 2H), 2.14–2.04 (m, 2H), 1.13 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.7, 140.9, 136.2, 127.4, 119.4, 117.4, 105.6, 73.3, 20.7, 13.2; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{15}H_{16}BN_2]^+$ 235.13956, found 235.14011.

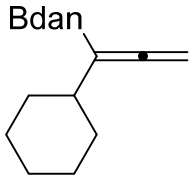
2-(Octa-1,2-dien-3-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1c)



1c

White solid (165.7 mg, 60%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.34 (d, *J* = 7.3 Hz, 2H), 5.71 (brs, 2H), 4.74 (t, *J* = 2.9 Hz, 2H), 2.10–2.02 (m, 2H), 1.55–1.47 (m, 2H), 1.38–1.32 (m, 4H), 0.92 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.9, 140.9, 136.2, 127.4, 119.4, 117.4, 105.6, 72.6, 31.5, 28.5, 27.7, 22.5, 14.0; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{18}H_{22}BN_2]^+$ 277.18655, found 277.18706.

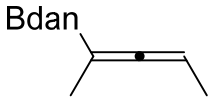
2-(1-Cyclohexylpropa-1,2-dien-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1d)



1d

White solid (149.9 mg, 52%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 7.9, 7.9 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.34 (d, *J* = 7.2 Hz , 2H), 5.71 (brs, 2H), 4.76 (s, 2H), 1.94–1.86 (m, 1H), 1.86–1.75 (m, 4H), 1.75–1.66 (m, 1H), 1.41–1.29 (m, 2H), 1.28–1.14 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 141.0, 136.2, 127.5, 119.5, 117.4, 105.6, 73.6, 36.4, 33.6, 26.6, 26.0; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{19}H_{22}BN_2]^+$ 289.18643, found 289.18706.

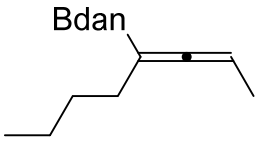
2-(Penta-2,3-dien-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1e)



1e

White solid (149.8 mg, 64%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.33 (d, *J* = 7.3 Hz, 2H), 5.68 (brs, 2H), 5.13–5.05 (m, 1H), 1.78 (d, *J* = 1.5 Hz, 3H), 1.72 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.7, 141.0, 136.2, 127.5, 119.4, 117.4, 105.6, 83.2, 14.9, 13.6; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{15}H_{16}BN_2]^+$ 235.13966, found 235.14011.

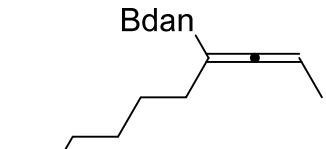
2-(Octa-2,3-dien-4-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1f)



1f

White solid (182.3 mg, 66%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.33 (d, *J* = 7.3 Hz, 2H), 5.68 (brs, 2H), 5.20–5.10 (m, 1H), 2.11–2.01 (m, 2H), 1.73 (d, *J* = 7.0 Hz, 3H), 1.52–1.44 (m, 2H), 1.44–1.34 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.3, 141.1, 136.3, 127.5, 119.4, 117.3, 105.5, 83.4, 31.2, 28.1, 22.3, 13.9, 13.6; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{18}H_{22}BN_2]^+$ 277.18652, found 277.18706.

2-(Deca-2,3-dien-4-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1g)

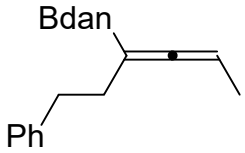


1g

White solid (152.1 mg, 50%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 7.9, 7.9 Hz, 2H), 7.00 (d, *J* =

8.2 Hz, 2H), 6.33 (d, *J* = 7.3 Hz, 2H), 5.68 (brs, 2H), 5.18–5.10 (m, 1H), 2.05 (t, *J* = 6.1 Hz, 2H), 1.73 (d, *J* = 7.0 Hz, 3H), 1.52–1.45 (m, 2H), 1.41–1.20 (m, 6H), 0.90 (t, *J* = 6.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.3, 141.1, 136.3, 127.5, 119.4, 117.3, 105.5, 83.4, 31.7, 28.9(6), 28.9(5), 28.4, 22.6, 14.1, 13.6; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{20}H_{26}BN_2]^+$ 305.21774, found 305.21836.

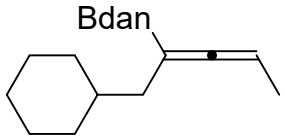
2-(1-Phenylhexa-3,4-dien-3-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1h)



1h

Colorless oil (194.5 mg, 60%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 7.5 Hz, 2H), 7.26–7.18 (m, 3H), 7.09 (dd, *J* = 7.9, 7.9 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.28 (d, *J* = 7.3 Hz, 2H), 5.60 (brs, 2H), 5.22–5.14 (m, 1H), 2.86–2.75 (m, 2H), 2.42–2.33 (m, 2H), 1.69 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.4, 142.0, 141.0, 136.2, 128.5, 128.3, 127.4, 125.9, 119.4, 117.4, 105.6, 84.2, 35.3, 30.5, 13.5; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{22}H_{21}BN_2]^+$ 325.18597, found 325.18706.

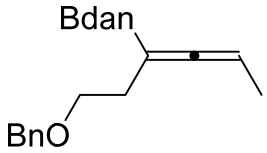
2-(1-Cyclohexylpenta-2,3-dien-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1i)



1i

White solid (189.7 mg, 60%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.33 (d, *J* = 7.3 Hz, 2H), 5.67 (brs, 2H), 5.10 (q, *J* = 6.8 Hz, 1H), 1.94 (d, *J* = 6.3 Hz, 2H), 1.84–1.76 (m, 2H), 1.73 (d, *J* = 6.9 Hz, 3H), 1.71–1.62 (m, 3H), 1.48–1.36 (m, 1H), 1.30–1.10 (m, 3H), 0.99–0.88 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.8, 141.1, 136.3, 127.5, 119.4, 117.3, 105.6, 82.6, 37.8, 36.7, 33.3, 26.5, 26.2, 13.5; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{21}H_{26}BN_2]^+$ 317.21771, found 317.21836.

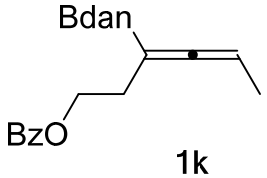
2-(1-(Benzyloxy)hexa-3,4-dien-3-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1j)



1j

Colorless oil (233.8 mg, 66%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.28 (m, 5H), 7.04 (dd, *J* = 7.8, 7.8 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.12 (d, *J* = 7.2 Hz, 2H), 6.05 (brs, 2H), 5.13 (q, *J* = 6.6 Hz, 1H), 4.55 (s, 2H), 3.72–3.62 (m, 2H), 2.40 (t, *J* = 6.8 Hz, 2H), 1.72 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.9, 141.2, 137.9, 136.2, 128.4, 127.9, 127.6, 127.4, 119.5, 117.1, 105.5, 82.8, 73.3, 71.3, 30.5, 13.5; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{23}H_{23}BN_2O]^+$ 355.19632, found 355.19762.

3-(1*H*-Naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)hexa-3,4-dien-1-yl benzoate (1k)

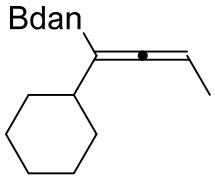


1k

White solid (206.2 mg, 56%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.55 (dd, *J* = 7.1,

7.1 Hz, 1H), 7.41 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.10 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.36 (d, *J* = 7.2 Hz, 2H), 5.98 (brs, 2H), 5.21 (q, *J* = 7.1 Hz, 1H), 4.46 (t, *J* = 7.0 Hz, 2H), 2.54 (t, *J* = 7.0 Hz, 2H), 1.72 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.9, 166.8, 141.0, 136.2, 132.9, 130.0, 129.5, 128.2, 127.4, 119.5, 117.4, 105.7, 83.9, 64.6, 28.4, 13.4; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{23}H_{22}BN_2O_2]^+$ 369.17581, found 369.17688.

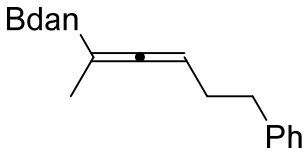
2-(1-Cyclohexylbuta-1,2-dien-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1l)



1l

White solid (211.6 mg, 70%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 7.9, 7.9 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.34 (d, *J* = 7.2 Hz, 2H), 5.68 (brs, 2H), 5.18 (q, *J* = 6.6 Hz, 1H), 1.95–1.86 (m, 1H), 1.86–1.76 (m, 4H), 1.74 (d, *J* = 6.9 Hz, 3H), 1.71–1.65 (m, 1H), 1.43–1.29 (m, 2H), 1.26–1.10 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.7, 141.1, 136.3, 127.4, 119.4, 117.3, 105.5, 84.4, 37.1, 33.8, 33.7, 26.6(9), 26.6(8), 26.1, 13.8; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{20}H_{24}BN_2]^+$ 303.20233, found 303.20271.

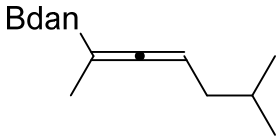
2-(6-Phenylhexa-2,3-dien-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1m)



1m

Colorless oil (227.0 mg, 70%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.19 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.09 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.28 (d, *J* = 7.3 Hz, 2H), 5.56 (brs, 2H), 5.18–5.11 (m, 1H), 2.78 (t, *J* = 7.4 Hz, 2H), 2.43 (dt, *J* = 14.1, 7.0 Hz, 2H), 1.73 (d, *J* = 2.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.1, 141.4, 141.0, 136.2, 128.4, 128.3, 127.4, 125.9, 119.4, 117.4, 105.7, 87.0, 35.5, 29.4, 14.9; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{22}H_{22}BN_2]^+$ 325.18622, found 325.18706.

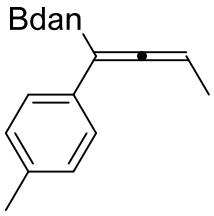
2-(6-Methylhepta-2,3-dien-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1n)



1n

Colorless oil (157.4 mg, 57%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.31 (d, *J* = 7.3 Hz, 2H), 5.69 (brs, 2H), 5.11–5.04 (m, 1H), 2.02–1.91 (m, 2H), 1.79 (d, *J* = 2.7 Hz, 3H), 1.70 (septet, *J* = 6.6 Hz, 1H), 0.98 (t, J = 6.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.5, 141.1, 136.3, 127.5, 119.4, 117.4, 105.5, 86.2, 37.6, 28.6, 22.2(4), 22.2(1), 14.8; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{18}H_{22}BN_2]^+$ 277.18643, found 277.18706.

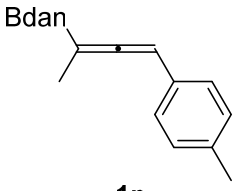
2-(1-(*p*-Tolyl)buta-1,2-dien-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1o)



1o

Colorless oil (124.1 mg, 40%). NMR data: ^{1}H NMR (500 MHz, CDCl3) δ 7.25 (d, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.11 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.31 (d, J = 7.2 Hz, 2H), 5.76 (brs, 2H), 5.42 (q, *J* = 7.1 Hz, 1H), 2.38 (s, 3H), 1.83 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl3) δ 210.5, 141.0, 136.4, 136.3, 133.9, 129.5, 128.0, 127.5, 119.6, 117.5, 105.7, 84.3, 21.0, 13.5; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{21}H_{20}BN_2]^+$ 311.17141, found 311.17053.

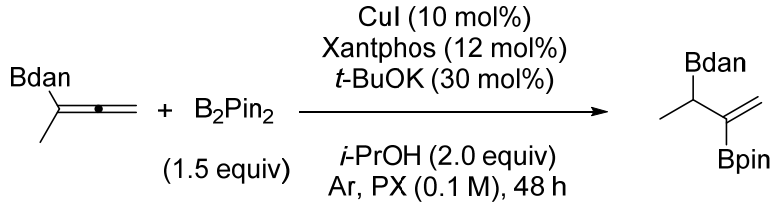
2-(4-(*p*-Tolyl)buta-2,3-dien-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1p)



1p

Purple oil (114.8 mg, 37%). NMR data: ^{1}H NMR (500 MHz, CDCl3) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.12 (dd, *J* = 7.9, 7.9 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.34 (d, *J* = 7.2 Hz, 2H), 6.21 (q, *J* = 2.8 Hz, 1H), 5.77 (brs, 2H), 2.38 (s, 3H), 1.96 (d, *J* = 2.8 Hz, 3H); HRMS (ESI): m/z calcd. for $[C_{21}H_{20}BN_2]^+$ 311.17141, found 311.17059. Due to the severe decomposition of **1p**, we could not get pure ^{13}C NMR spectrum.

2. Synthesis of β-Boryl Allyl-Bdan 3

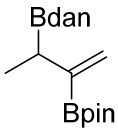


1a **3a**

Representative procedure: An oven-dried Schlenk flask was equipped with a Teflon coated stirrer bar and charged with copper iodide (3.8 mg, 0.02 mmol), Xantphos (13.9 mg, 0.024 mmol), *t*-BuOK (6.8 mg, 0.06 mmol), B_2Pin_2 (76.2 mg, 0.3 mmol), allenyl-Bdan **1a** (44.0 mg, 0.20 mmol) and Xylene (2 mL, 0.1 M). The resulted solution was stirred at r.t. for 15 min, then the *i*-PrOH (31.0 uL, 0.40 mmol) was added to the mixture via syringe. The final reaction mixture was stirred at 30 °C for 48 h. Then the reaction mixture was diluted by petroleum ether (about 5 mL). The precipitate was filtered off by a short silica pad (Qingdao Haiyang Chem, neutral, 300-400 Mesh, about 2-3 cm in pipette) using EtOAc/petroleum ether (1:20 v/v) as an eluent. The solvent was removed and the residue was purified by a rapid silica gel chromatography (within 10 min) using a mixture of petroleum ether/EtOAc (1:100-1:20) as eluent affording pure product **3a**.

Analytical data:

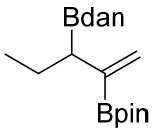
2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3a)



3a

White solid (51 mg, 73%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 8.0, 8.0 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.27 (d, *J* = 7.2 Hz, 2H), 5.94 (brs, 2H), 5.82 (d, *J* =2.5 Hz, 1H), 5.61(brs, 1H), 2.15 (q, *J* = 7.0 Hz, 1H), 1.29 (s, 12H), 1.20 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 136.3, 127.5, 126.4, 119.5, 117.1, 105.3, 83.6, 24.9, 24.7, 14.6; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{20}H_{27}B_2N_2O_2]^+$ 349.22348, found 349.22532.

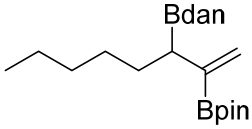
2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-3-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3b)



3b

White solid (57 mg, 79%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 7.8, 7.8 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.26 (d, *J* = 7.2 Hz , 2H), 6.04 (brs, 2H), 5.80 (d, *J* =2.9 Hz, 1H), 5.60 (d, *J* = 2.3 Hz, 1H), 1.87 (t, *J* = 7.8 Hz, 1H), 1.74–1.60 (m, 2H), 1.30 (s, 6H), 1.29 (s, 6H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 136.3, 127.8, 127.5, 119.6, 117.0, 105.3, 83.6, 24.9, 24.6, 23.0, 14.0; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{21}H_{29}B_2N_2O_2]^+$ 363.24069, found 363.24097.

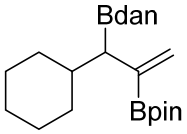
2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-en-3-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3c)



3c

White solid (44 mg, 54%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 7.9, 7.9 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.26 (d, *J* = 7.3 Hz, 2H), 6.03 (brs, 2H), 5.79 (d, *J* = 2.3 Hz, 1H), 5.59 (d, *J* = 1.8 Hz, 1H), 1.95 (t, *J* = 7.8 Hz, 1H), 1.70–1.45 (m, 4H), 1.35–1.21 (m, 16H), 0.87 (t, *J* = 6.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 136.3, 127.7, 127.5, 119.6, 117.0,105.3, 83.6, 32.0, 30.0, 29.0, 25.0, 24.6, 22.5, 14.1; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{24}H_{34}B_2N_2O_2Na]^+$ 427.26886, found 427.26986.

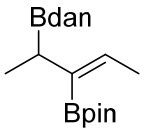
2-(1-Cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3d)



3d

White solid (35 mg, 42%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 7.8, 7.8 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.29 (brs, 2H), 6.26 (d, *J* = 8.2 Hz, 2H), 5.71 (d, *J* = 2.6 Hz, 1H), 5.55 (d, *J* = 2.2 Hz, 1H), 1.89–1.76 (m, 2H), 1.75–1.59 (m, 5H), 1.56 (d, *J* = 6.5 Hz, 1H), 1.36 (s, 6H), 1.30 (s, 6H), 1.20–1.08 (m, 2H), 0.94–0.81 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 136.3, 129.0, 127.5, 119.6, 116.9, 105.2, 83.6, 37.9, 33.9, 33.5, 26.5(7), 26.5(6), 26.4, 25.1, 24.4; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{25}H_{35}B_2N_2O_2]^+$ 417.28656, found 417.28792.

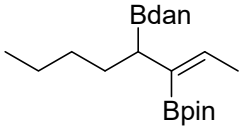
(*E*)-2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3e)



3e

White solid (46 mg, 63%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 7.8, 7.8 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.27 (d, *J* = 7.3 Hz, 2H), 6.10 (q, *J* = 6.9 Hz, 1H), 5.94 (brs, 2H), 2.00 (q, *J* = 7.2 Hz, 1H), 1.92 (d, *J* = 6.9 Hz, 3H), 1.29 (s, 6H), 1.28 (s, 6H), 1.16 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 138.3, 136.3, 127.4, 119.5, 116.9, 105.3, 83.1, 24.9, 24.8, 17.4, 15.7; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{21}H_{28}B_2N_2O_2Na]^+$ 385.22177, found 385.22291.

(*E*)-2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oct-2-en-4-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3f)

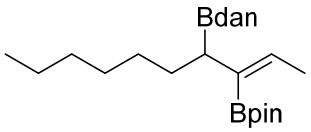


3f

White solid (62 mg, 76%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (dd, *J* = 7.7, 7.7 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.26 (d, *J* = 7.3 Hz, 2H), 6.09 (brs, 2H), 6.07 (q, *J* = 7.0 Hz, 1H), 1.89 (d, *J* = 6.9 Hz, 3H), 1.80 (t, *J* = 7.8 Hz, 1H), 1.65–1.51 (m, 6H), 1.36 (s, 12H), 0.92–0.81 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 139.2, 136.3, 127.4, 119.6, 116.8, 105.2, 83.1, 31.7, 30.4, 25.0, 24.7, 22.8, 17.4, 14.0; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for

$[C_{24}H_{35}B_2N_2O_2]^+$ 405.28671, found 405.28792.

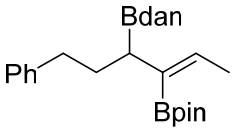
(*E*)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dec-2-en-4-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3g)



3g

White solid (52 mg, 60%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 7.9, 7.9 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.26 (d, *J* = 7.2 Hz, 2H), 6.09 (brs, 2H), 6.07 (q, *J* = 6.7 Hz, 1H), 1.89 (d, *J* = 6.8 Hz, 3H), 1.81 (t, *J* = 7.8 Hz, 1H), 1.31 (s, 12H), 1.29–1.18 (m, 10H), 0.87 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 139.2, 136.3, 127.5, 119.6, 116.8, 105.2, 83.1, 31.8, 30.7, 29.4(6), 29.4(2), 25.1, 24.7, 22.6, 17.4, 14.0; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{26}H_{39}B_2N_2O_2]^+$ 433.31766, found 433.31922.

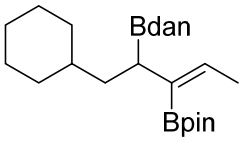
(*E*)-2-(1-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-en-3-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3h)



3h

Colorless oil (70 mg, 78%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.26 (m, 2H), 7.21–7.14 (m, 3H), 7.07 (dd, *J* = 7.9, 7.9 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.25 (d, *J* = 7.2 Hz, 2H), 6.12 (q, *J* = 6.9 Hz, 1H), 6.05 (brs, 2H), 2.72–2.64 (m, 1H), 2.59–2.49 (m, 1H), 2.01–1.93 (m, 1H), 1.93 (d, *J* = 6.8 Hz, 3H), 1.90–1.82 (m, 2H), 1.31 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 141.6, 140.1, 136.3, 128.4, 128.2, 127.4, 125.5, 119.6, 116.9, 105.3, 83.1, 35.4, 32.4, 25.0, 24.7, 17.4; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{28}H_{34}B_2N_2O_2]^+$ 453.28629, found 453.28792.

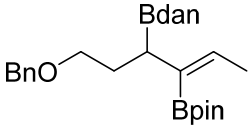
(*E*)-2-(1-Cyclohexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3i)



3i

White solid (48 mg, 54%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 7.8, 7.8 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.26 (d, *J* = 7.2 Hz, 2H), 6.09 (brs, 2H), 6.07 (q, *J* = 7.6 Hz, 1H), 1.98 (t, *J* = 7.8 Hz, 1H), 1.89 (d, *J* = 6.8 Hz, 3H), 1.79–1.71 (m, 1H), 1.71–1.58 (m, 5H), 1.58–1.47 (m, 2H), 1.31 (s, 12H), 1.30–1.08 (m, 3H), 0.95–0.84 (m, 1H), 0.83–0.73 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 139.3, 136.3, 127.4, 119.5, 116.8, 105.2, 83.1, 38.3, 36.0, 34.2, 32.5, 26.7, 26.3, 26.1, 25.0, 24.7, 17.4; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{27}H_{39}B_2N_2O_2]^+$ 445.31873, found 445.31922.

(*E*)-2-(1-(Benzyloxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-en-3-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3j)

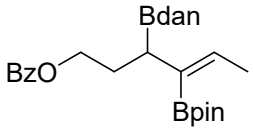


3j

Colorless oil (71 mg, 74%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.27 (m, 5H), 7.06 (dd, *J* = 7.8, 7.8 Hz,

2H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.20 (d, *J* = 7.3 Hz, 2H), 6.15–6.07 (m, 3H), 4.49 (s, 2H), 3.55–3.51 (m, 1H), 3.50–3.43 (m, 1H), 2.02–1.90 (m, 3H), 1.90 (d, *J* = 6.9 Hz, 3H), 1.28 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 140.2, 138.5, 136.3, 128.3, 127.6, 127.4, 119.6, 116.8, 105.3, 83.1, 72.9, 70.1, 30.8, 25.0, 24.7, 17.4; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{29}H_{36}B_2N_2O_3Na]^+$ 505.27792, found 505.28043.

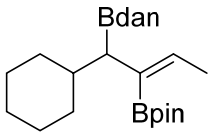
(*E*)-3-(1*H*-Naphtho[1,8-*de*][1,3,2]diazaborinin-2(3H)-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-en-1-yl benzoate (3k)



3k

White solid (69 mg, 70%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 2H), 7.48 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.30 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.06 (dd, *J* = 7.8, 7.8 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.26 (d, *J* = 7.8 Hz, 2H), 6.18 (q, *J* = 6.8 Hz, 1H), 6.11 (brs, 2H), 4.44–4.35 (m, 1H), 4.34–4.25 (m, 1H), 2.19–2.09 (m, 1H), 2.06–2.01 (m, 2H), 1.92 (d, *J* = 6.9 Hz, 3H), 1.29 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 141.4, 141.1, 136.2, 132.7, 130.2, 129.5, 128.1, 127.4, 119.6, 117.0, 105.4, 83.2, 64.9, 29.6, 25.0, 24.8, 17.4; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{29}H_{34}B_2N_2O_4]^+$ 497.27563, found 497.27775.

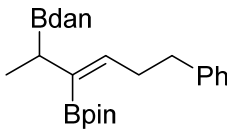
(*E*)-2-(1-Cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3l)



3l

White solid (69 mg, 80%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 7.9, 7.9 Hz, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.36 (brs, 2H), 6.25 (d, *J* = 7.3 Hz, 2H), 6.04 (q, *J* = 6.9 Hz, 1H), 1.85 (d, *J* = 6.9 Hz, 3H), 1.81–1.67 (m, 4H), 1.43 (d, *J* = 11.0 Hz, 1H), 1.37 (s, 6H), 1.34 (s, 6H), 1.30–1.20 (m, 3H), 1.18–1.08 (m, 2H), 0.92–0.80 (m, 1H), 0.76–0.65 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.9, 139.9, 136.4, 127.4, 119.6, 116.7, 105.2, 83.2, 38.3, 34.1, 33.6, 26.6, 26.5, 26.4, 25.2, 24.5, 17.3; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{26}H_{37}B_2N_2O_2]^+$ 431.30209, found 431.30357.

(*E*)-2-(6-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-3-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3m)

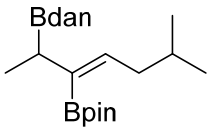


3m

White solid (73 mg, 81%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.19 (d, *J* = 7.3 Hz, 2H), 7.15 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.08 (dd, *J* = 7.7, 7.7 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.25 (d, *J* = 7.2 Hz, 2H), 6.05 (t, *J* = 6.5 Hz, 1H), 5.86 (brs, 2H), 2.73–2.63 (m, 4H), 2.00 (q, *J* = 7.4 Hz, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 1.15(d, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 142.1, 141.6, 136.3, 128.6, 128.1, 127.4, 125.6, 119.5, 116.9, 105.3, 83.1, 36.6, 33.0, 24.9 , 24.7, 15.6; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{28}H_{35}B_2N_2O_2]^+$ 453.28757, found 453.28792.

(*E*)-2-(6-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-3-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-

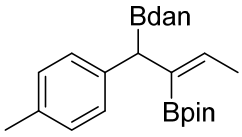
***de*][1,3,2]diazaborinine (3n)**



3n

White solid (66 mg, 82%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (dd, *J* = 7.7, 7.7 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.26 (d, *J* = 7.1 Hz, 2H), 6.02 (t, *J* = 7.3 Hz, 1H), 5.92 (brs, 2H), 2.30–2.17 (m, 2H), 2.03 (q, *J* = 7.1 Hz, 1H), 1.71–1.55 (m, 1H), 1.27 (s, 12H), 1.18 (d, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 5.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 141.6, 136.3, 127.5, 119.5, 116.9, 105.2, 83.1, 40.2, 29.1, 24.9, 24.7, 22.4, 22.3, 15.8; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{24}H_{35}B_2N_2O_2]^+$ 405.28735, found 405.28792.

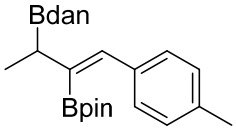
(*E*)-2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(p-tolyl)but-2-en-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3o)



3o

White solid (49.3 mg, 57%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15-7.10 (m, 2H), 7.10-7.05 (m, 4H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.25 (d, *J* = 7.2 Hz, 2H), 6.04 (q, *J* = 6.8 Hz, 1H), 5.92 (brs, 2H), 3.36 (s, 1H), 2.32 (s, 3H), 1.93 (d, *J* = 6.8 Hz, 3H), 1.19 (s, 6H), 1.17 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 140.4, 139.7, 136.3, 134.8, 129.4, 129.0, 127.4, 119.5, 117.1, 105.5, 83.2, 24.7, 24.6, 20.9, 17.5; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{27}H_{33}B_2N_2O_2]^+$ 439.27227, found 439.27075.

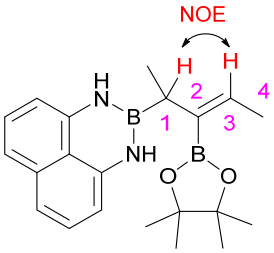
(*E*)-2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(p-tolyl)but-3-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3p)



3p

White solid (46.0 mg, 52%). NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.7 Hz, 2H), 7.11-7.05 (m, 4H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.87 (s, 1H), 6.29 (d, *J* = 7.2 Hz, 2H), 6.03 (brs, 2H), 2.33 (s, 3H), 2.19 (q, *J* = 7.4 Hz, 1H), 1.30 (d, *J* = 7.4 Hz, 3H), 1.26 (brs, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 138.2, 136.6, 136.3, 136.1, 128.5, 127.9, 127.5, 119.6, 117.1, 105.5, 83.7, 24.8, 21.1, 16.0; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{27}H_{33}B_2N_2O_2]^+$ 439.27227, found 439.27127.

3. **Determination of the stereochemistry of 3e using a NOESY spectrum**



3e

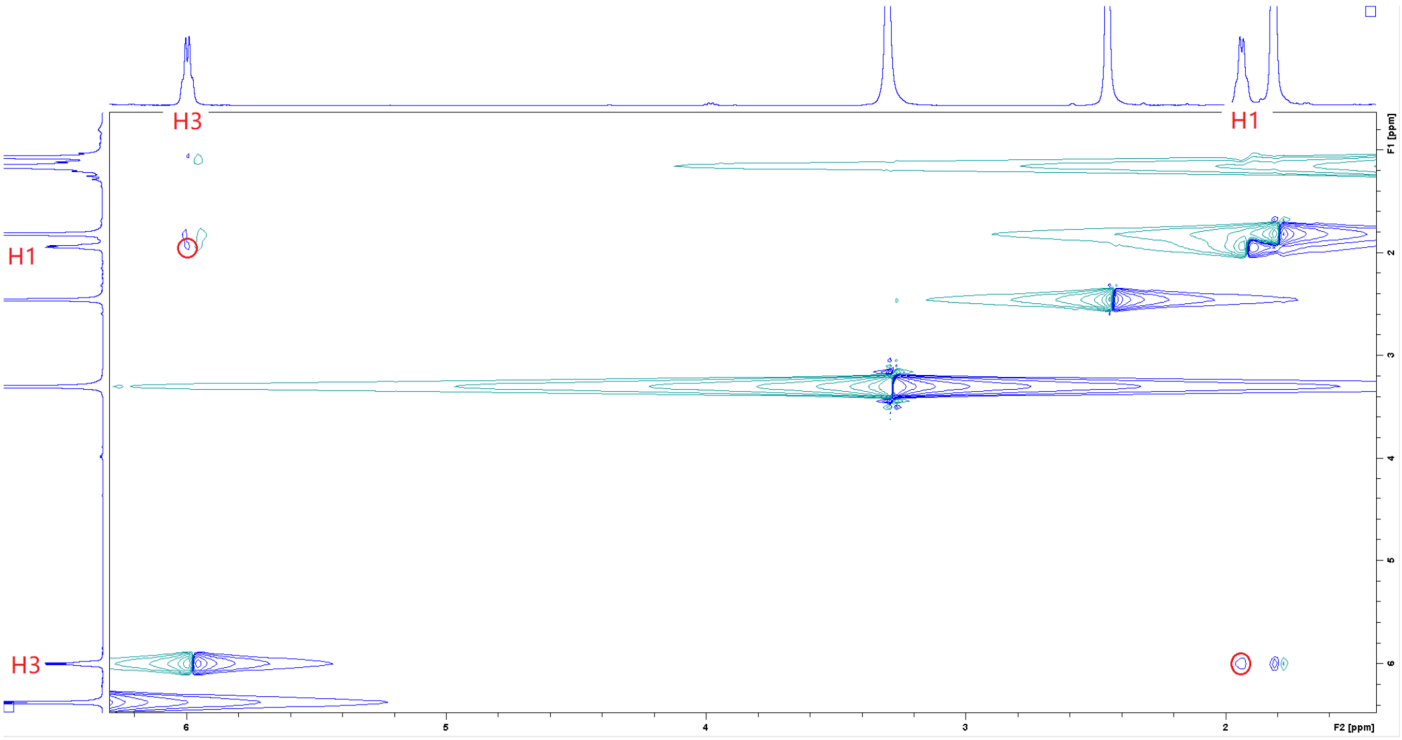
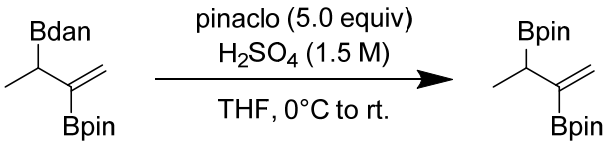


Figure S1. Observed NOESY effect between the C1 proton and C3 proton

The NOESY experiment (Figure S1) indicated a through space NOE effect between C(1)-H and C(3)-H. This indicates that C(1)-H and C(3)-H are close in space, and the C2-C3 double bond has an *E* geometry.

4. Synthesis of reported compound 5

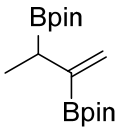


3a **5**

Compound **5** was synthesized according to the reported procedures by Santos and co-works.[2] The product β-boryl allyl-Bdan **3a** (69.7 mg, 0.20 mmol) and pinacol (118.2 mg, 1.0 mmol) was dissolved in THF (2 mL), then cooled at 0°C for 10 min, sulfuric acid (aq.) (1.5 M, 0.80 mL, 1.20 mmol) was added sequentially. The contents were stirred at r.t. for 24 h. Water was added and the mixture was extracted with EtOAc. The organic layer was dried over magnesium sulfate, filtered, concentrated in vacuo and purified by flash chromatography (petroleum ether/EtOAc = 30:1) to yield the title compound (46.8 mg, 76%) as a colorless oil.

Analytical data:

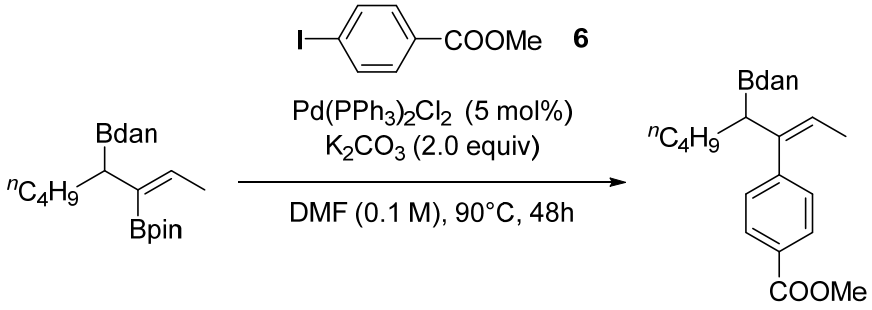
2,2'-(But-1-ene-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5)



5

NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.75 (d, *J* = 2.3 Hz, 1H), 5.55 (brs, 1H), 2.03 (q, *J* = 7.1 Hz, 1H), 1.25 (s, 12H), 1.22 (s, 12H), 1.12 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 125.6, 83.2, 83.0, 24.8, 24.6(7), 24.6(5), 24.6(4), 14.1; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{16}H_{30}B_2O_4Na]^+$ 331.22202, found 331.22224.

5. Procedure for Suzuki-Miyaura cross-coupling of Methyl 4-iodobenzoate 6 with 3f

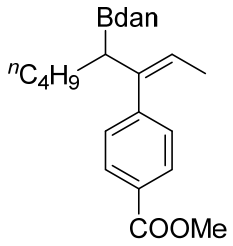


3f **7**

Methyl 4-iodobenzoate **6** (26.2 mg, 0.10 mmol), **3f** (60.6 mg, 0.15 mmol), $Pd(PPh_3)_2Cl_2$ (3.5 mg, 0.005 mmol) and K_2CO_3 (27.6 mg, 0.20 mmol) were added to a 10 mL schlenk flask fitted with a reflux condenser and purged 3 times with vacuum and Ar. DMF (1 ml) was added, then the reaction was heated to 90 °C and stirred for 48 hours. The crude mixture was diluted with EtOAc and DMF was removed by washing with water. The organic layer was dried over magnesium sulfate, filtered, concentrated in vacuo and purified by flash chromatography (petroleum ether/EtOAc = 30:1) to yield the compound **7** (30.1 mg, 73%) as a white solid.

Analytical data:

Methyl (*Z*)-4-(4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)oct-2-en-3-yl)benzoate (7)



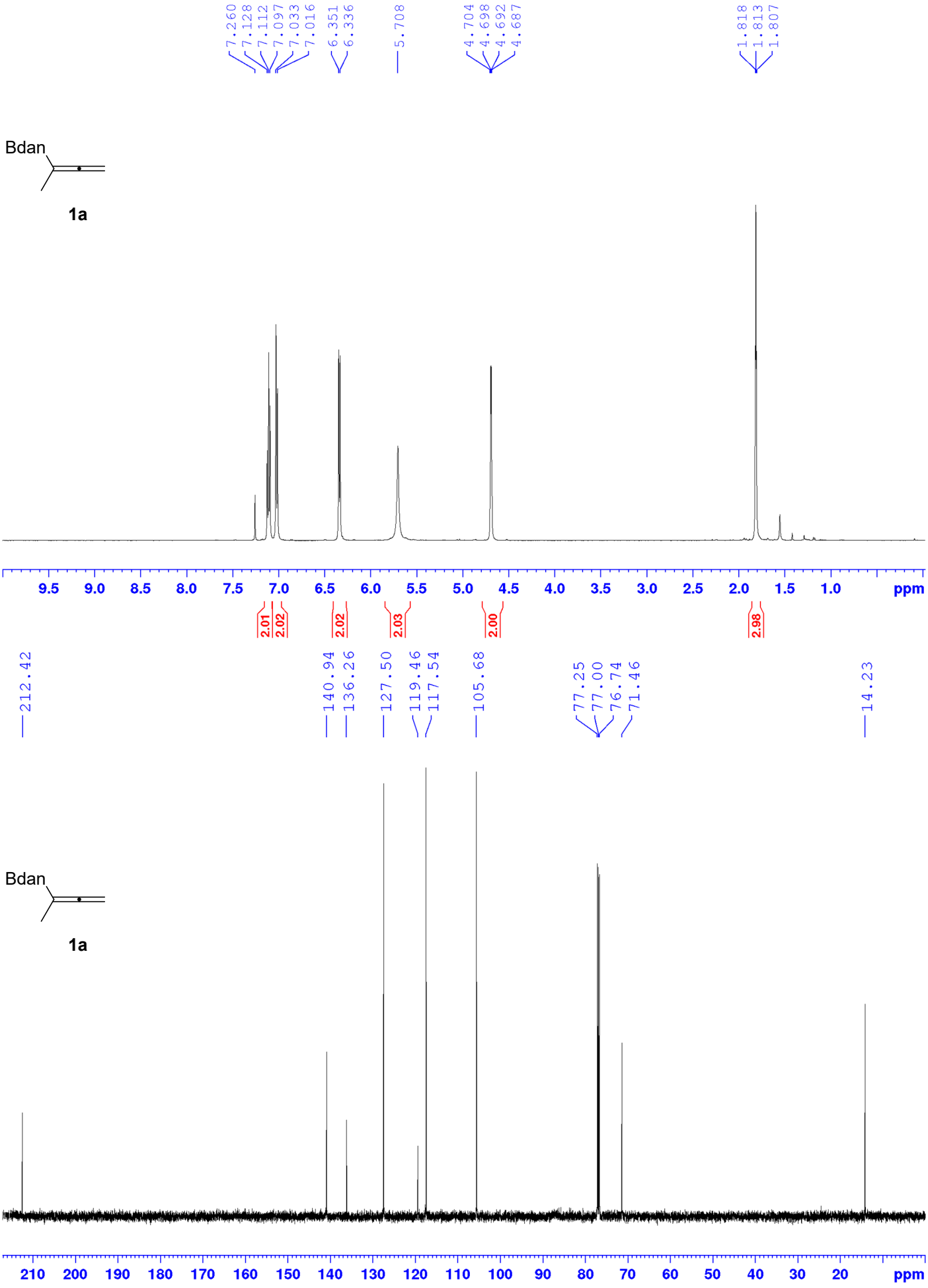
7

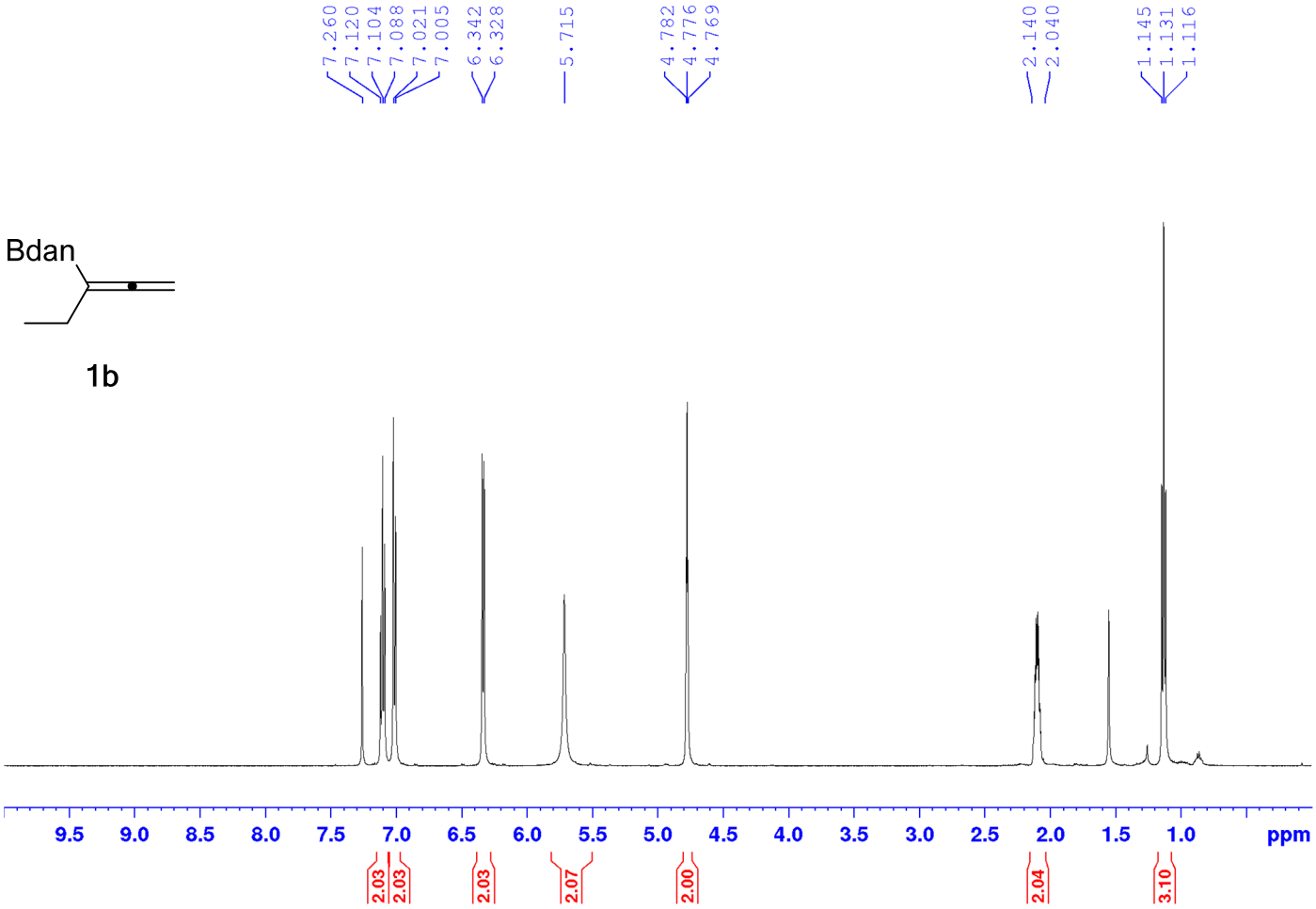
NMR data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.10 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.28 (d, *J* = 7.2 Hz, 2H), 5.62 (q, *J* = 6.8 Hz, 1H), 5.58 (brs, 2H), 3.90 (s, 3H), 2.02 (t, *J* = 7.7 Hz, 1H), 1.59 (d, *J* = 6.8 Hz, 3H), 1.53-1.46 (m, 2H), 1.36-1.22 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 146.6, 143.1, 140.9, 136.2, 129.4, 128.6, 127.5, 121.0, 119.5, 127.5, 105.7, 52.0, 31.3, 29.2, 22.7, 14.8, 14.0; Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation. HRMS (ESI): m/z calcd. for $[C_{26}H_{30}BN_2O_2]^+$ 413.23949, found 413.23849.

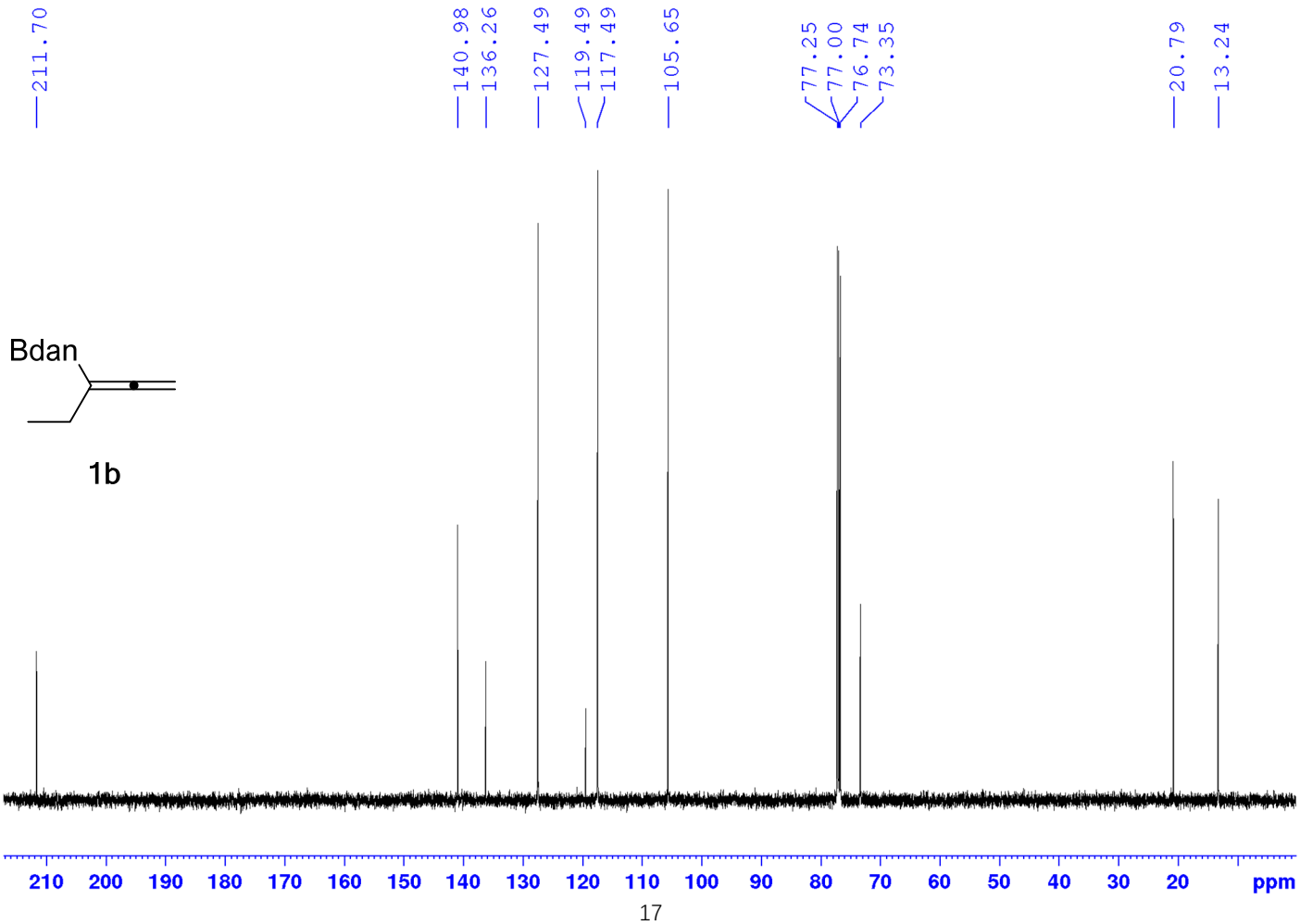
6. References:

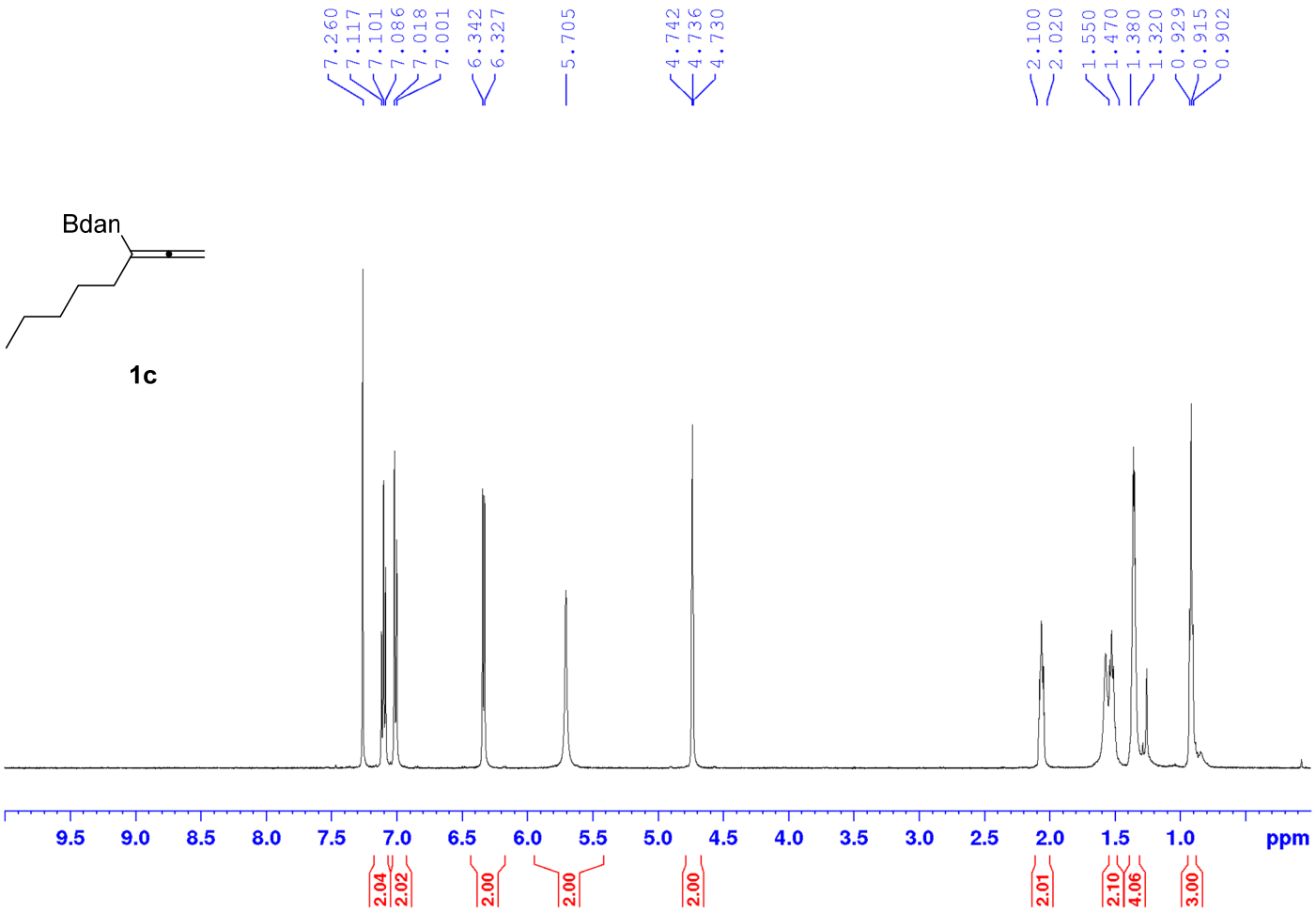
1. T. S. N. Zhao, Y. Yang, T. Lessing and K. J. Szabó, *J. Am. Chem. Soc.*, **2014**, *136*, 7563.
2. X. Guo, A. K. Nelson, C. Slebodnick and W. L. Santos, *ACS Catal.*, **2015**, *5*, 2172.

7. NMR Spectra of 1, 3, 5 and 7




7.260
7.120
7.104
7.088
7.021
7.005
6.342
6.328
5.715
4.782
4.776
4.769
2.140
2.040
1.145
1.131
1.116
Bdan
1b
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 ppm
2.03
2.03
2.03
2.07
2.00
2.04
3.10


211.70
140.98
136.26
127.49
119.49
117.49
105.65
77.25
77.00
76.74
73.35
20.79
13.24
Bdan
1b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.117
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7.018
7.001
6.342
6.327
5.705
4.742
4.736
4.730
2.100
2.020
1.550
1.470
1.380
1.320
0.929
0.915
0.902
Bdan
1c
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 ppm
2.04
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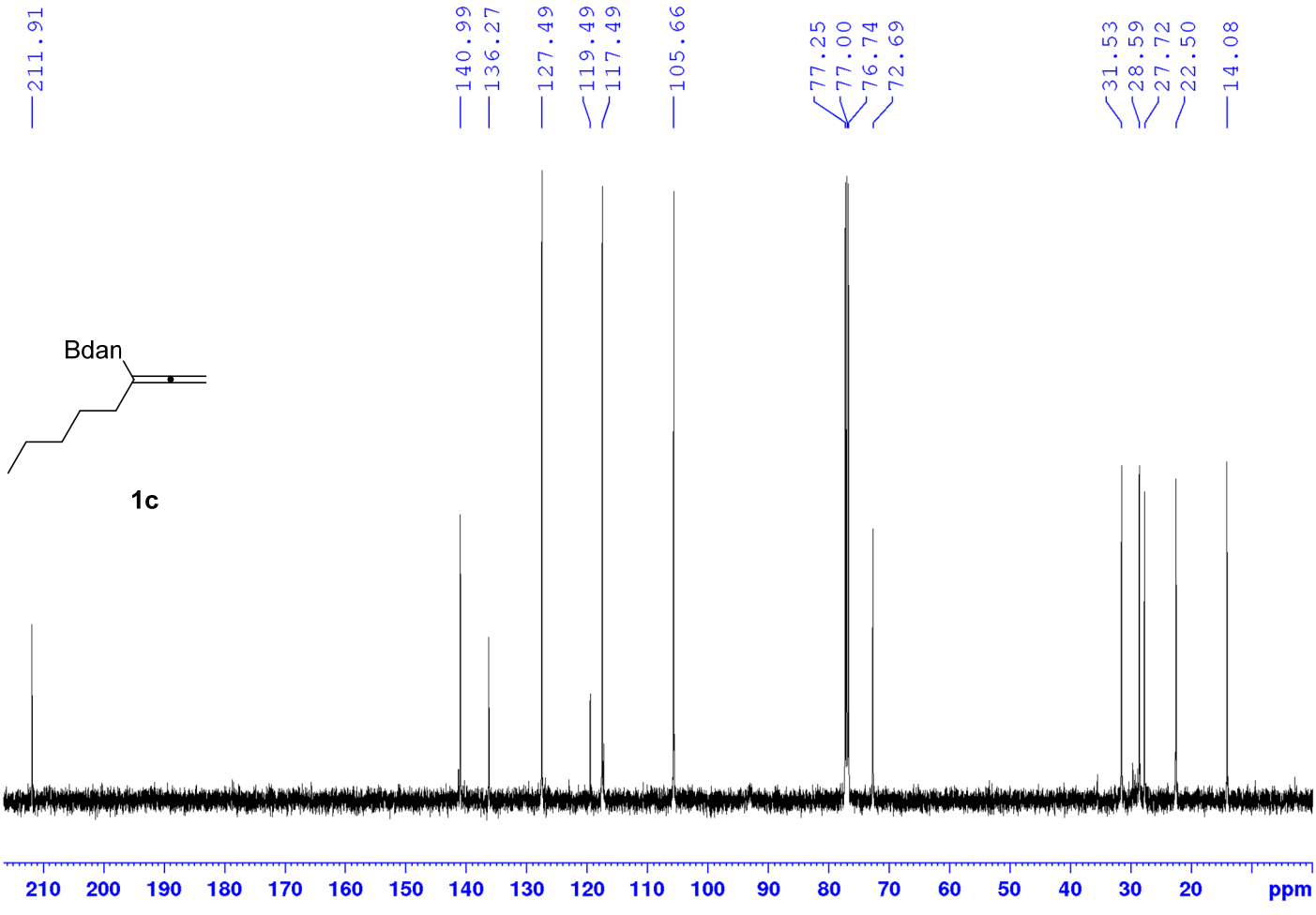
2.00
2.00
2.01
2.10
4.06
3.00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140.99
136.27
127.49
119.49
117.49
105.66
77.25
77.00
76.74
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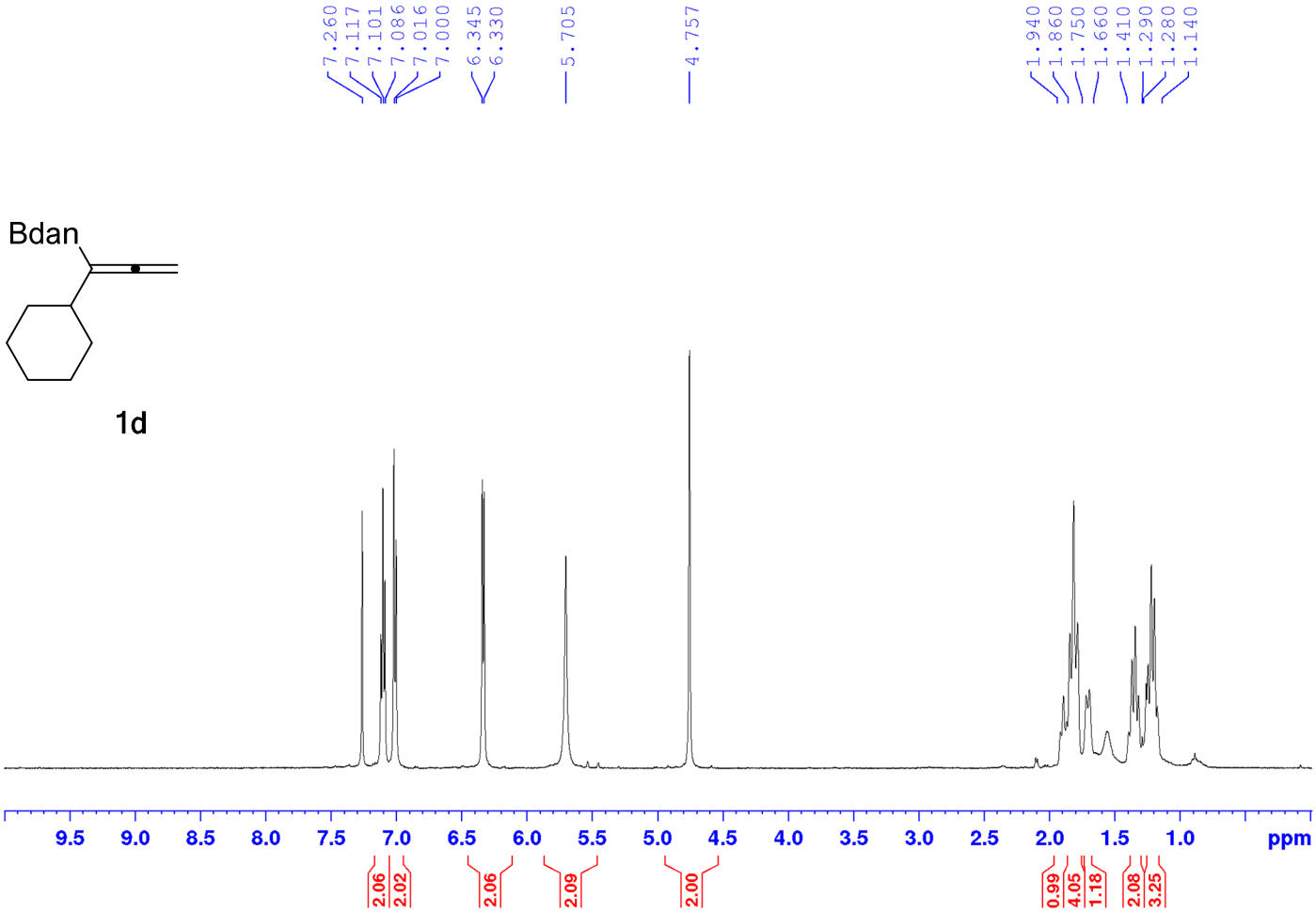
31.53
28.59
27.72
22.50
14.08
Bdan
1c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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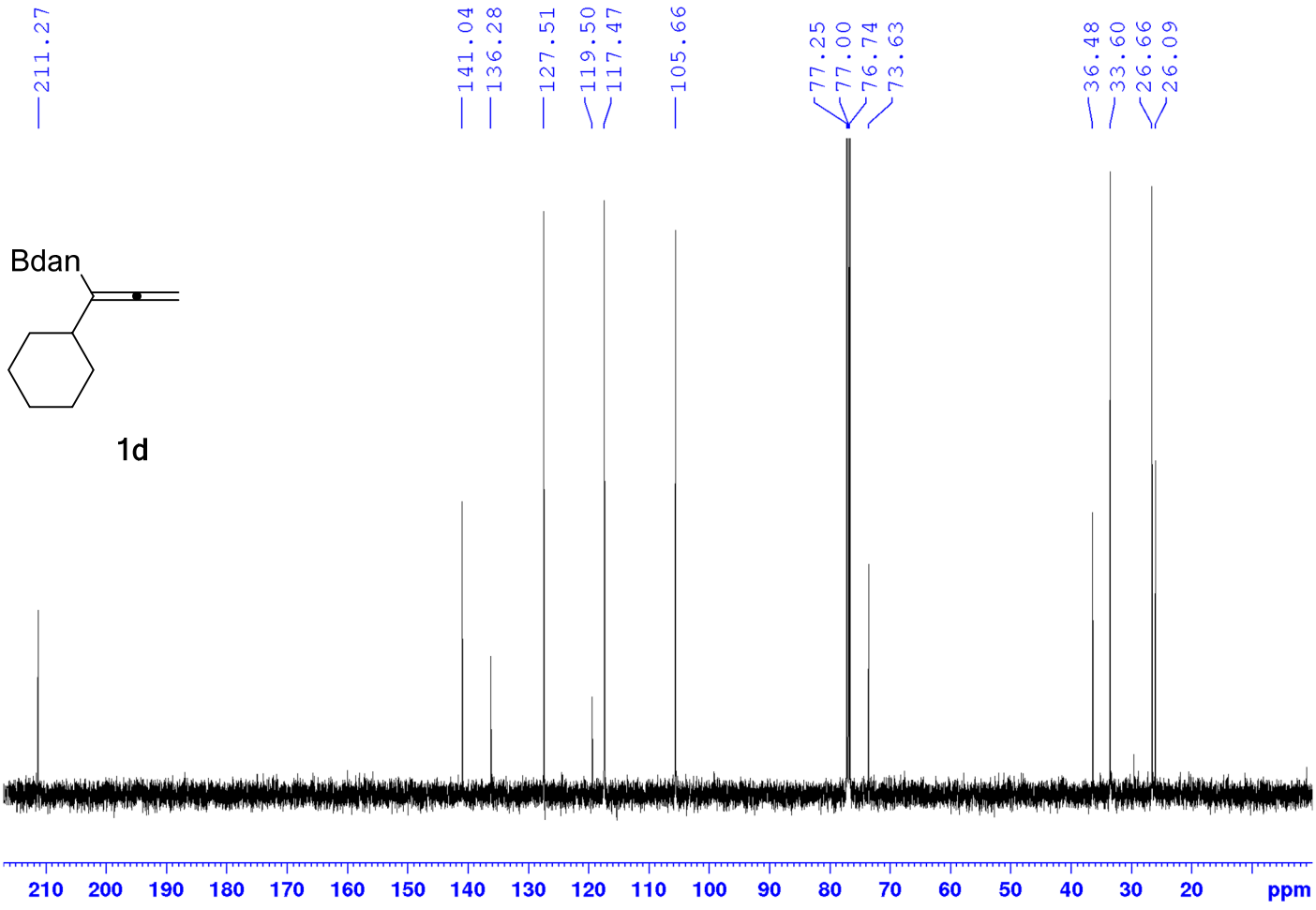
7.117
7.101
7.086
7.016
7.000
6.345
6.330
5.705
4.757
1.940
1.860
1.750
1.660
1.410
1.290
1.280
1.140
Bdan
1d
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.06
2.02
2.06
2.09
2.00
0.99
4.05
1.18
2.08
3.25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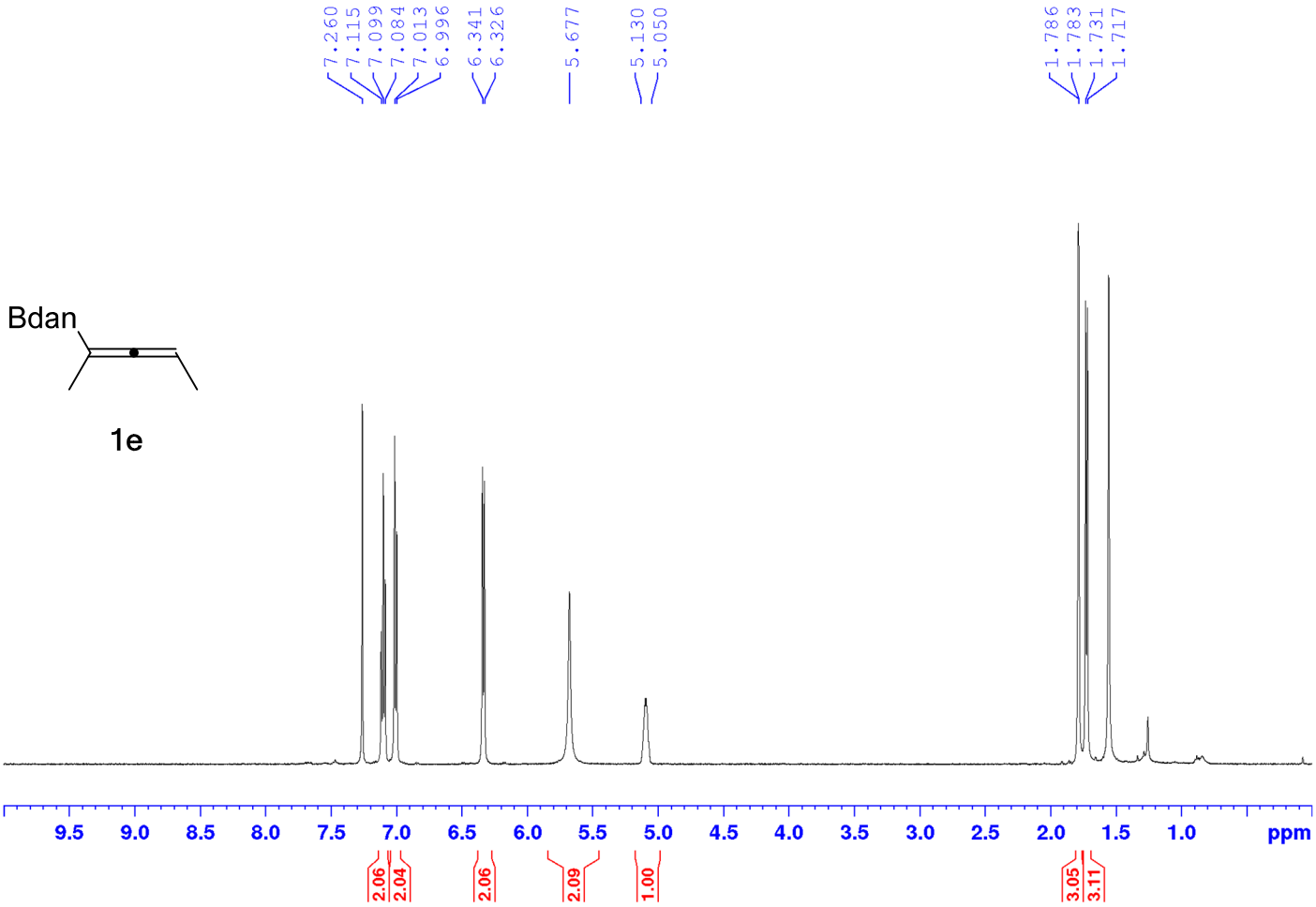
127.51
119.50
117.47
105.66
77.25
77.00
76.74
73.63
36.48
33.60
26.66
26.09
Bdan
1d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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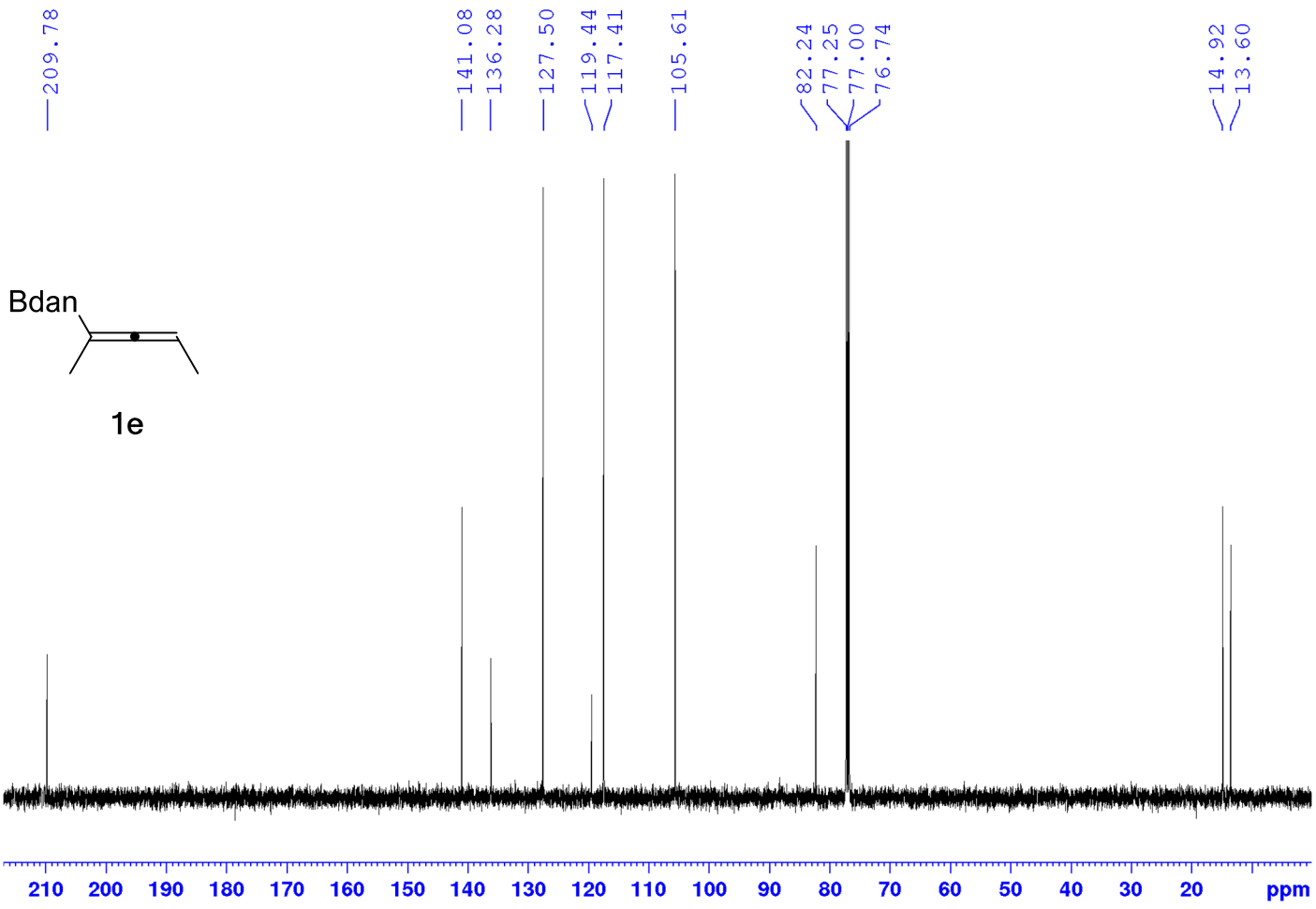
7.099
7.084
7.013
6.996
6.341
6.326
5.677
5.130
5.050
1.786
1.783
1.731
1.717
Bdan
1e
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.06
2.04
2.06
2.09
1.00
3.05
3.11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141.08
136.28
127.50
119.44
117.41
105.61
82.24
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77.00
76.74
14.92
13.60
Bdan
1e
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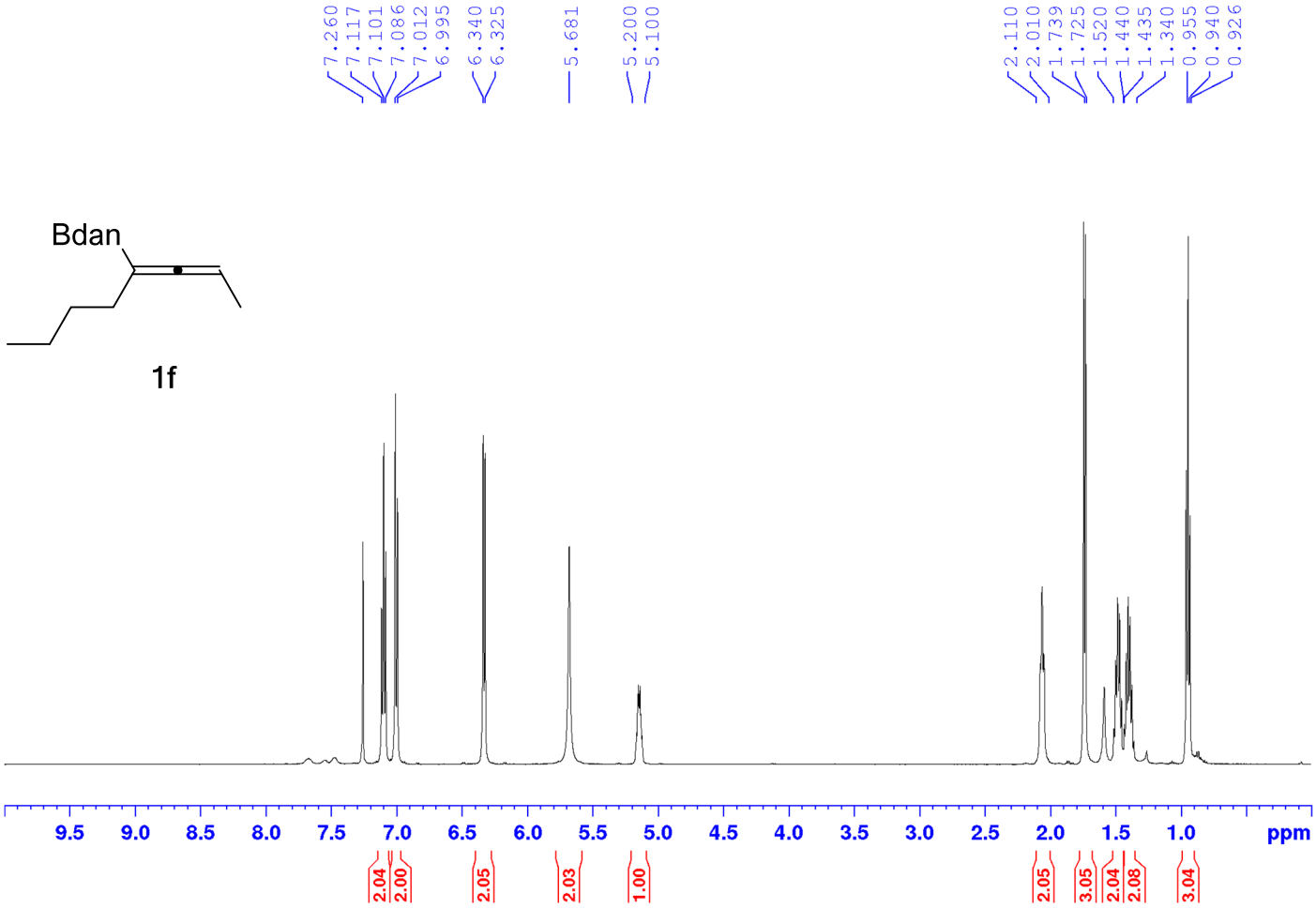
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7.012
6.995
6.340
6.325
5.681
5.200
5.100
2.110
2.010
1.739
1.725
1.520
1.440
1.435
1.340
0.955
0.940
0.926
Bdan
1f
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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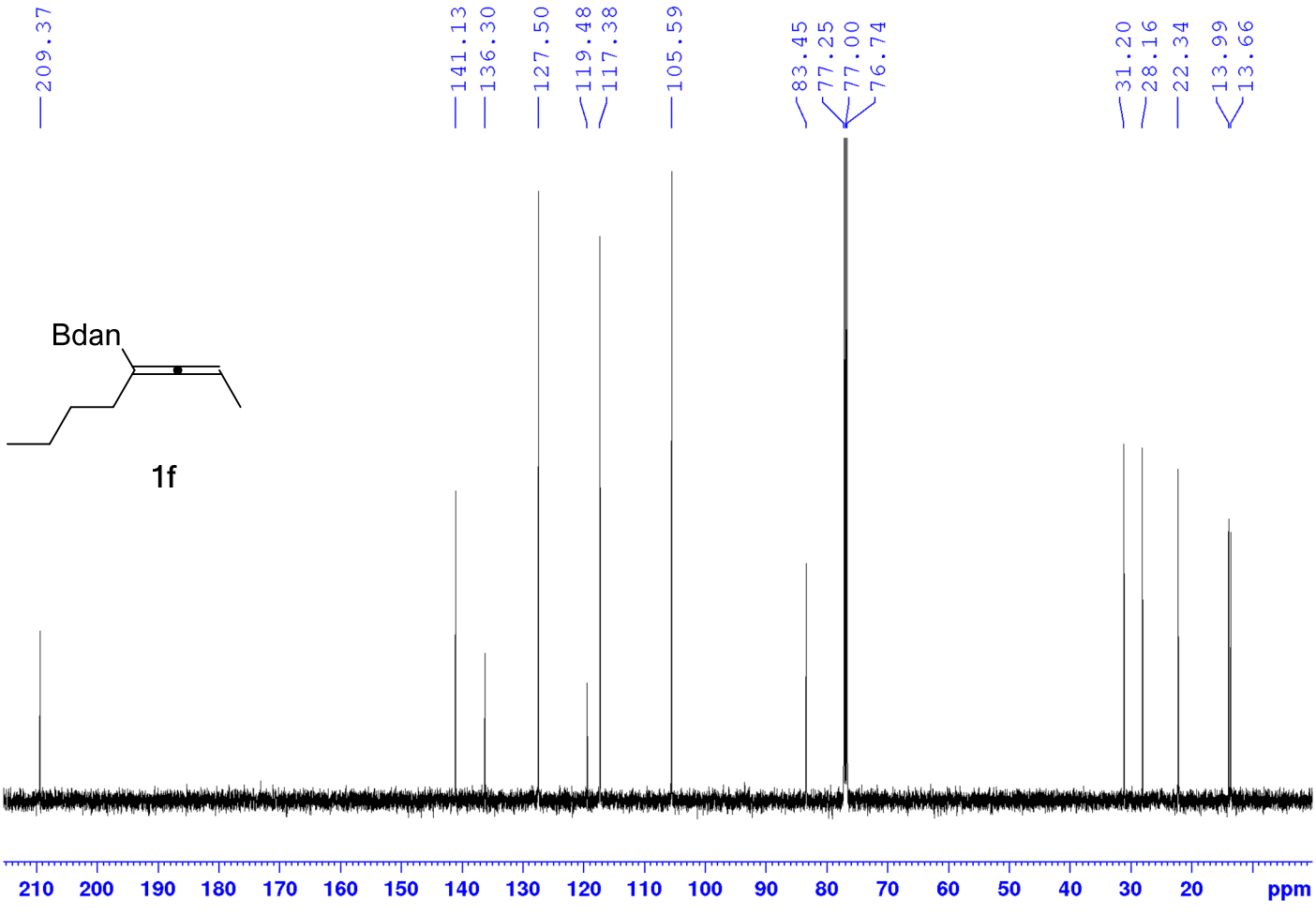
2.00
2.05
2.03
1.00
2.05
3.05
2.04
2.08
3.04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83.45
77.25
77.00
76.74
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22.34
13.99
13.66
Bdan
1f
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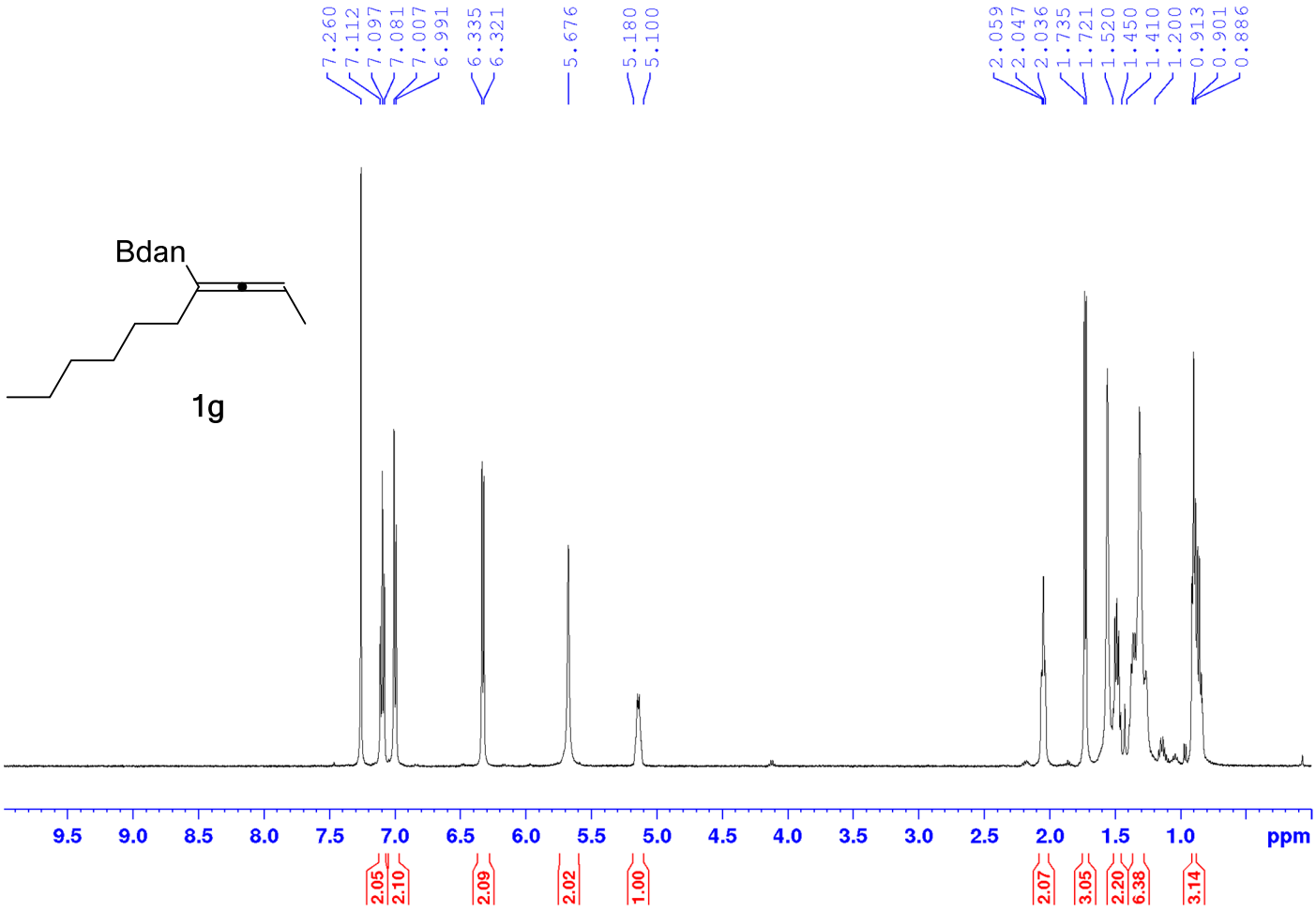
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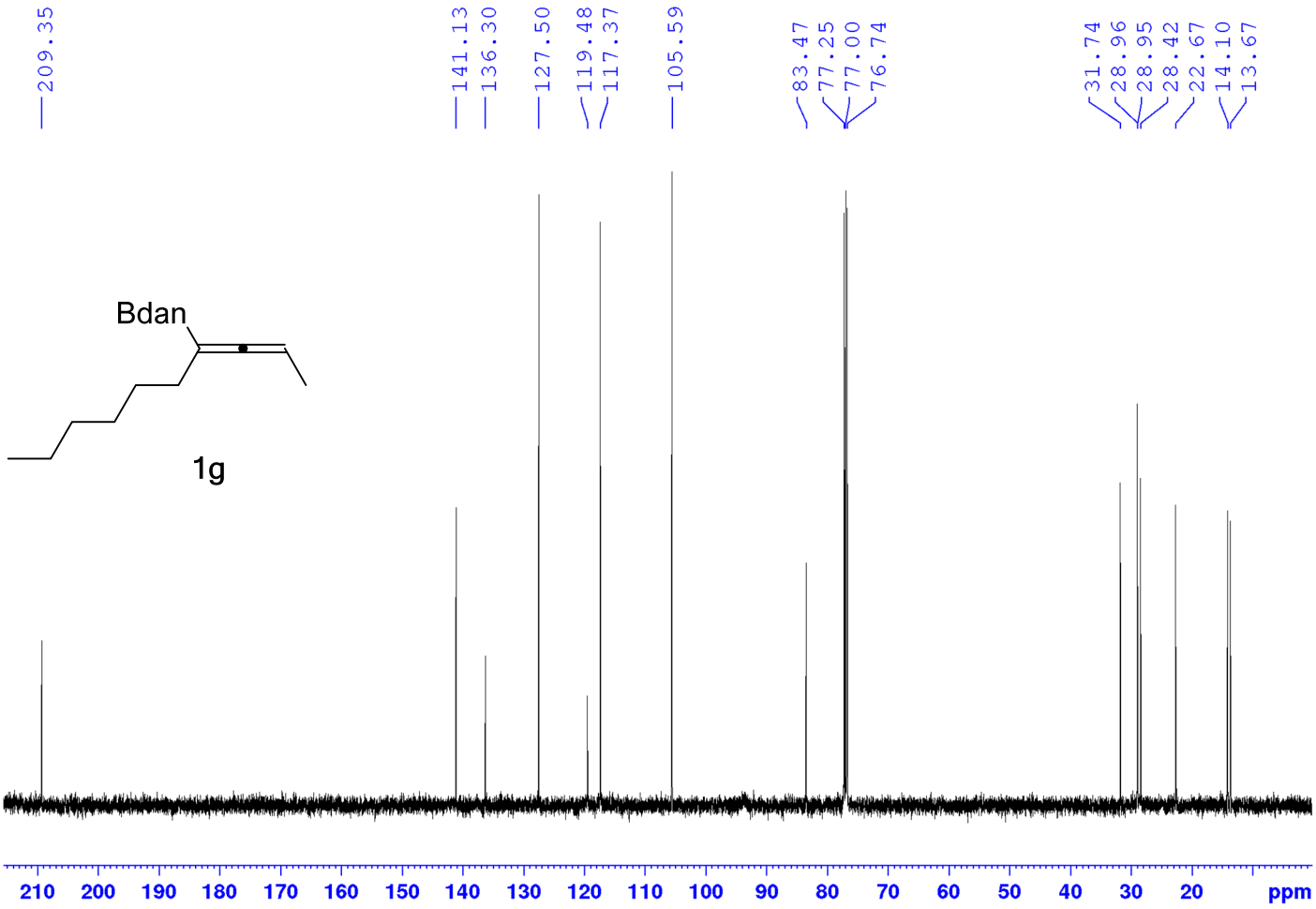
6.335
6.321
5.676
5.180
5.100
2.059
2.047
2.036
1.735
1.721
1.520
1.450
1.410
1.200
0.913
0.901
0.886
Bdan
1g
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.05
2.10
2.09
2.02
1.00
2.07
3.05
2.20
6.38
3.14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117.37
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83.47
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77.00
76.74
31.74
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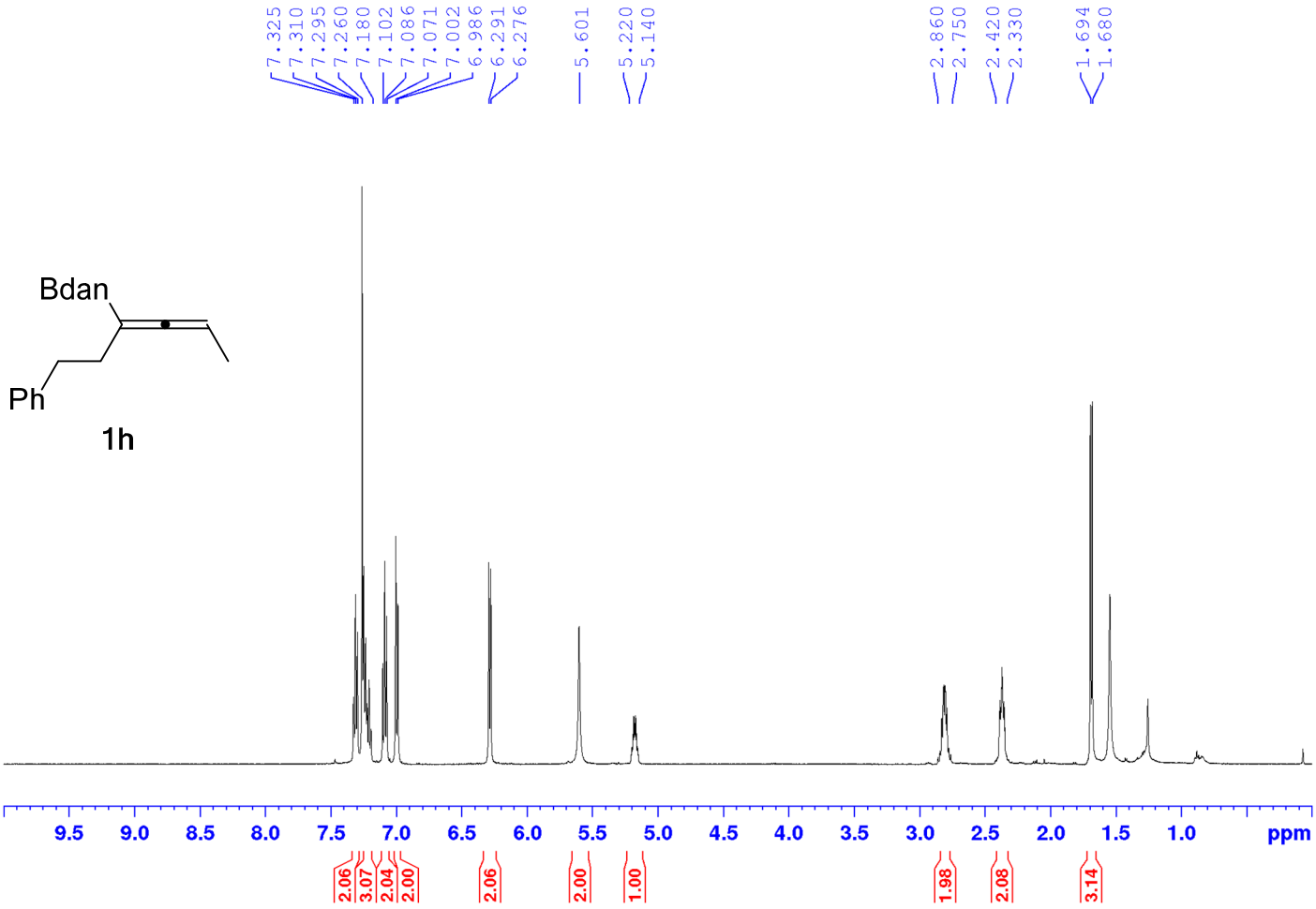
28.95
28.42
22.67
14.10
13.67
Bdan
1g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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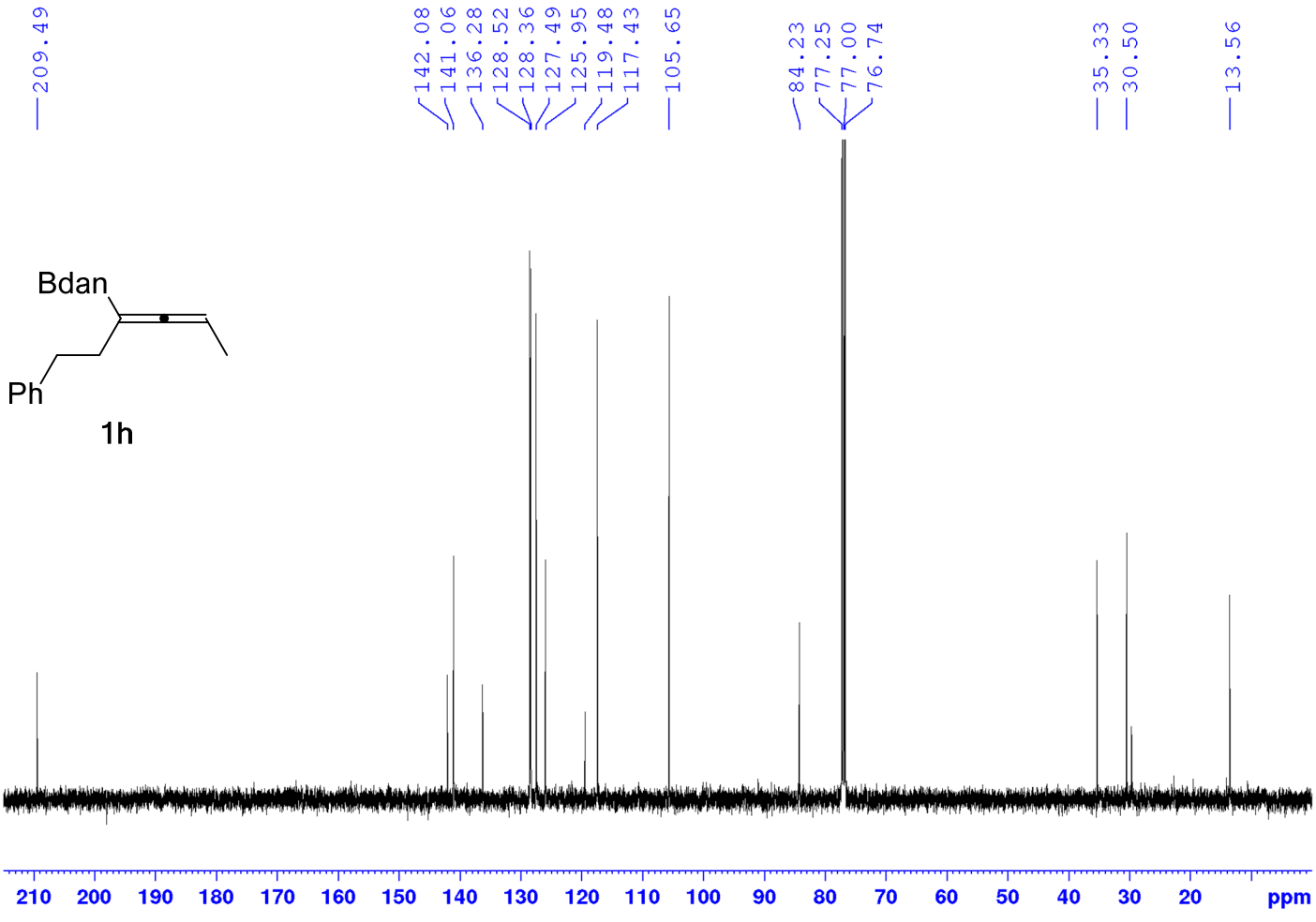
7.310
7.295
7.260
7.180
7.102
7.086
7.071
7.002
6.986
6.291
6.276
5.601
5.220
5.140
2.860
2.750
2.420
2.330
1.694
1.680
Bdan
Ph
1h
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.06
3.07
2.04
2.00
2.06
2.00
1.00
1.98
2.08
3.14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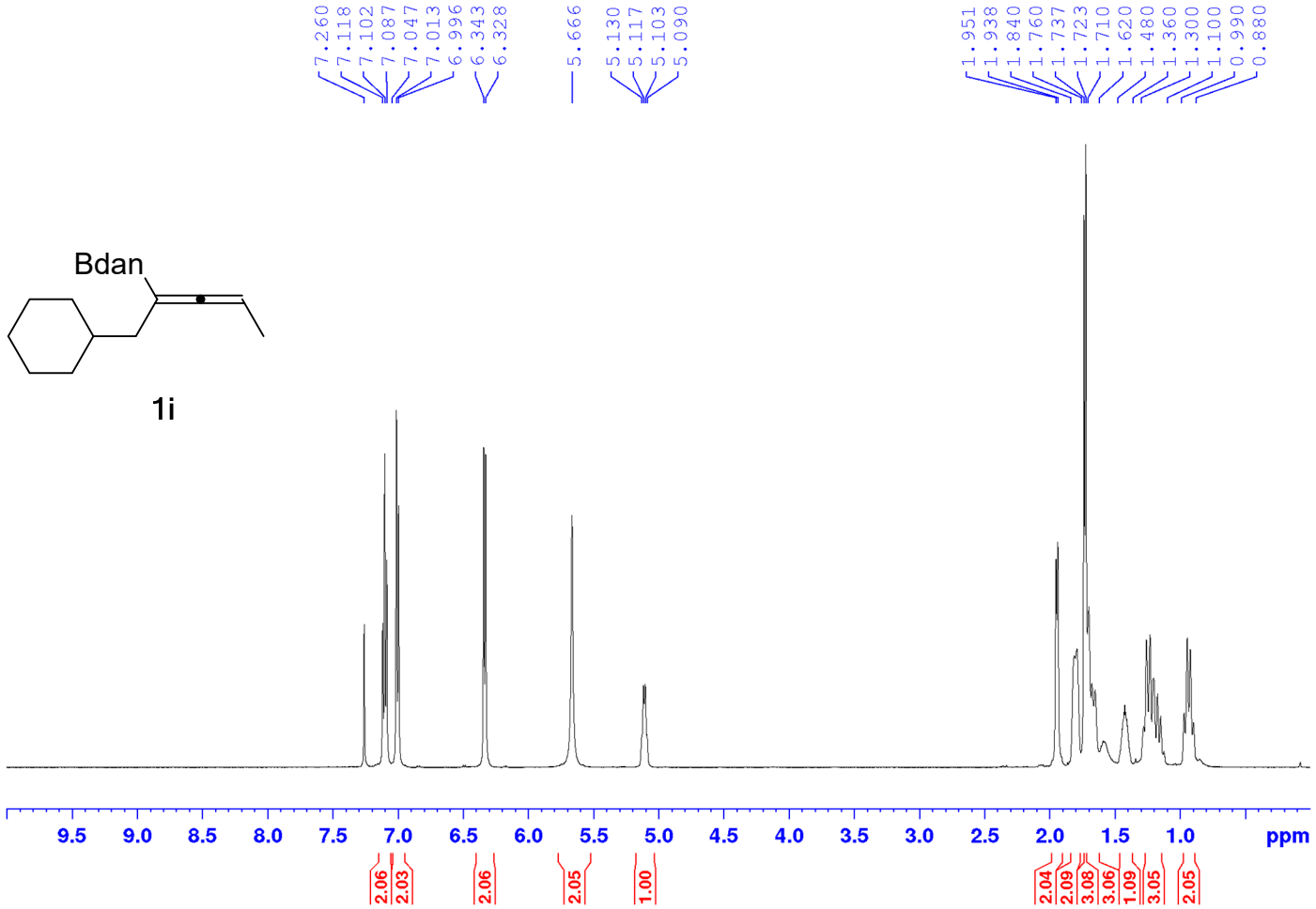
128.36
127.49
125.95
119.48
117.43
105.65
84.23
77.25
77.00
76.74
35.33
30.50
13.56
Bdan
Ph
1h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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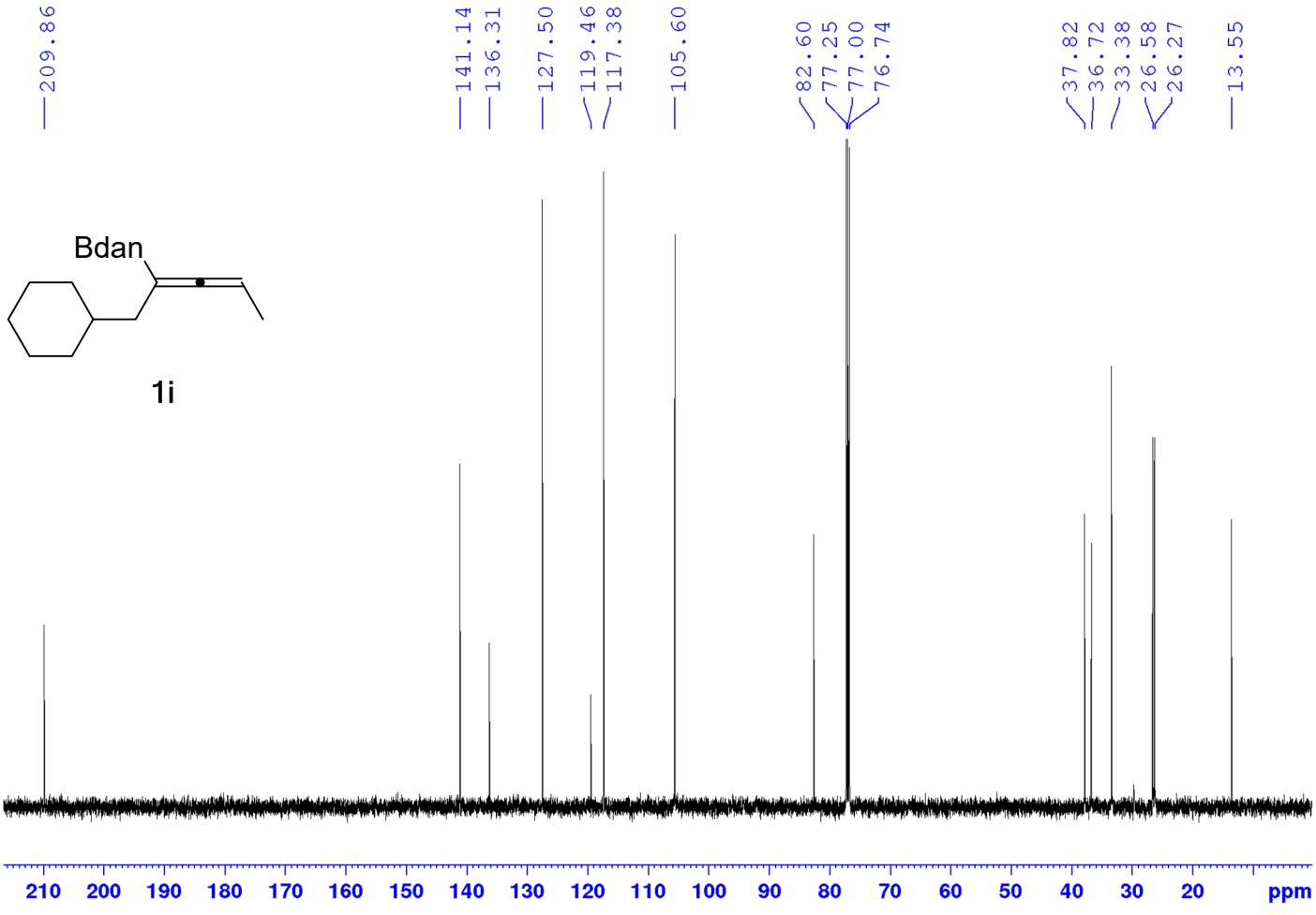
7.087
7.047
7.013
6.996
6.343
6.328
5.666
5.130
5.117
5.103
5.090
1.951
1.938
1.840
1.760
1.737
1.723
1.710
1.620
1.480
1.360
1.300
1.100
0.990
0.880
Bdan
1i
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.06 2.03 2.06 2.05 1.00 2.04 2.09 3.08 3.06 1.09 3.05 2.05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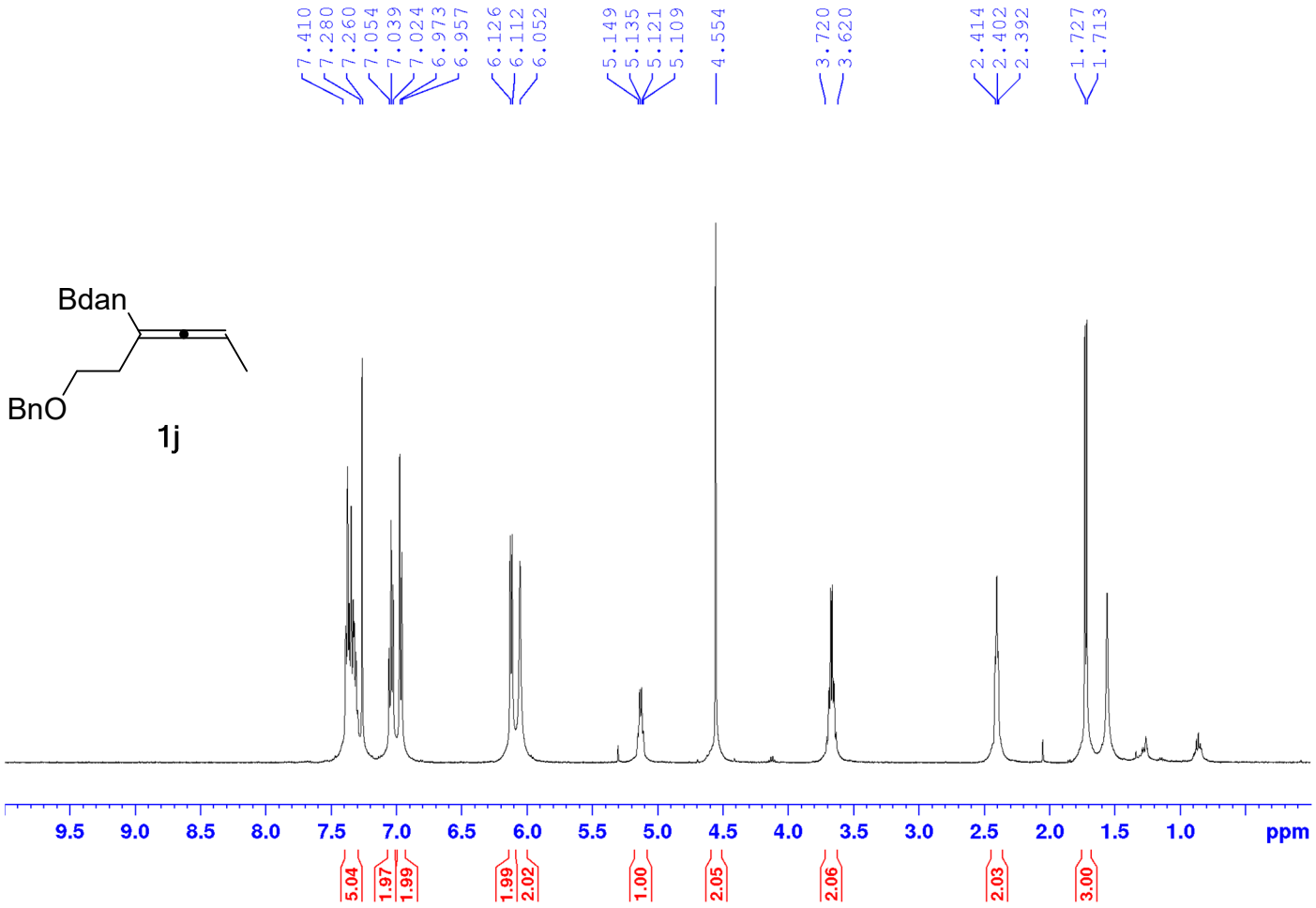
141.14
136.31
127.50
119.46
117.38
105.60
82.60
77.25
77.00
76.74
37.82
36.72
33.38
26.58
26.27
13.55
Bdan
1i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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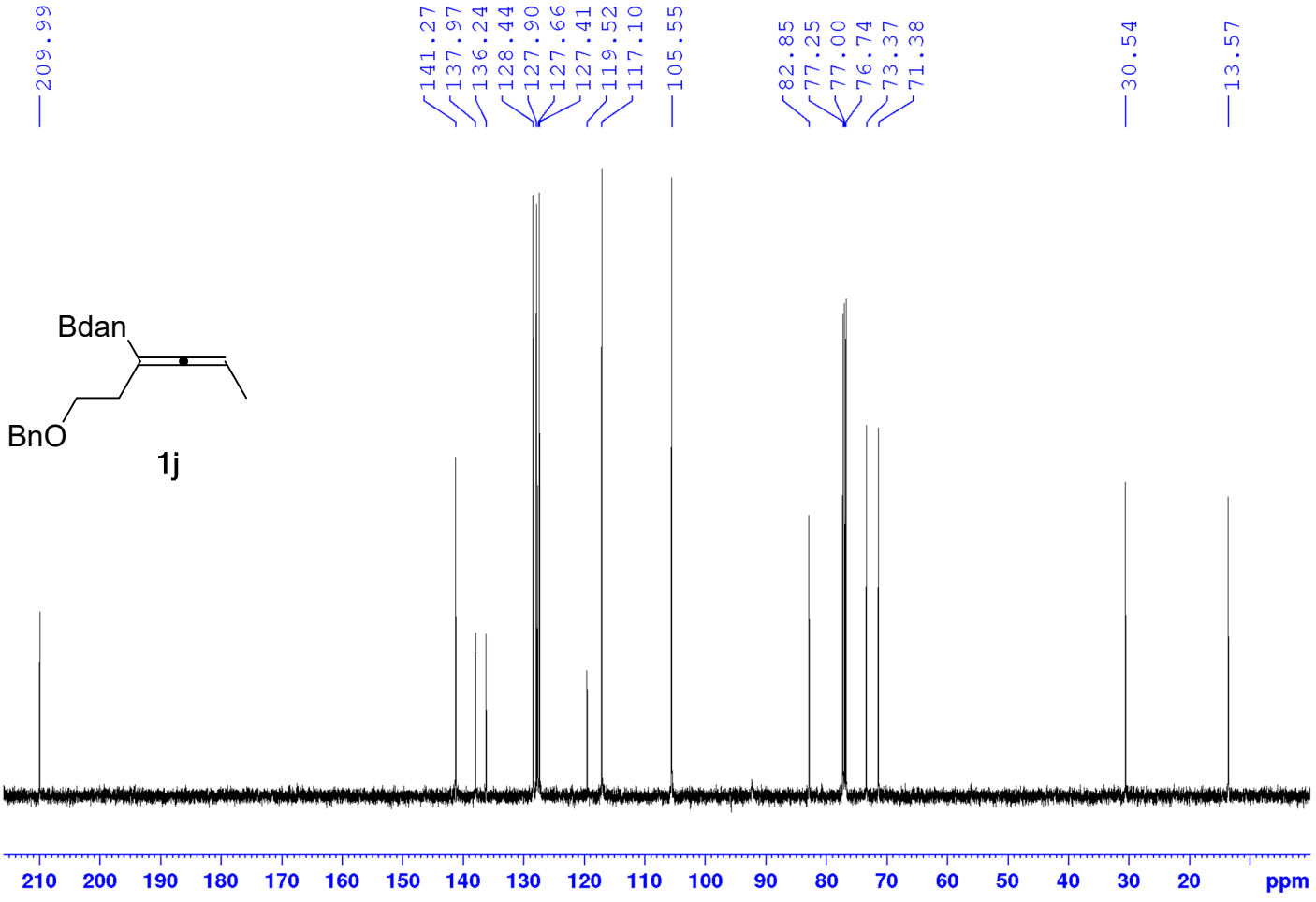
7.260
7.054
7.039
7.024
6.973
6.957
6.126
6.112
6.052
5.149
5.135
5.121
5.109
4.554
3.720
3.620
2.414
2.402
2.392
1.727
1.713
Bdan
BnO
1j
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
5.04
1.97
1.99
1.99
2.02
1.00
2.05
2.06
2.03
3.00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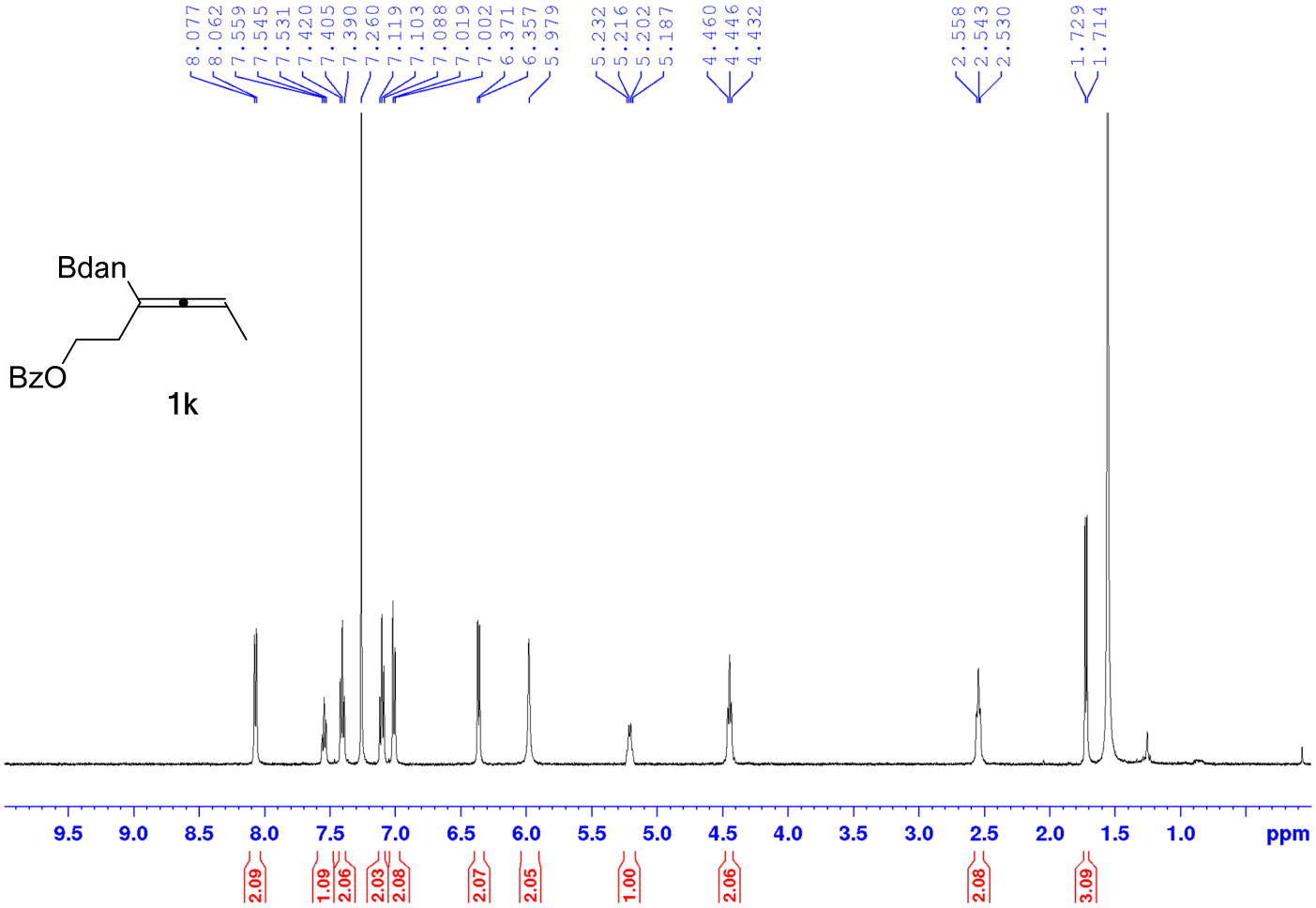
127.90
127.66
127.41
119.52
117.10
105.55
82.85
77.25
77.00
76.74
73.37
71.38
30.54
13.57
Bdan
BnO
1j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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8.062
7.559
7.545
7.531
7.420
7.405
7.390
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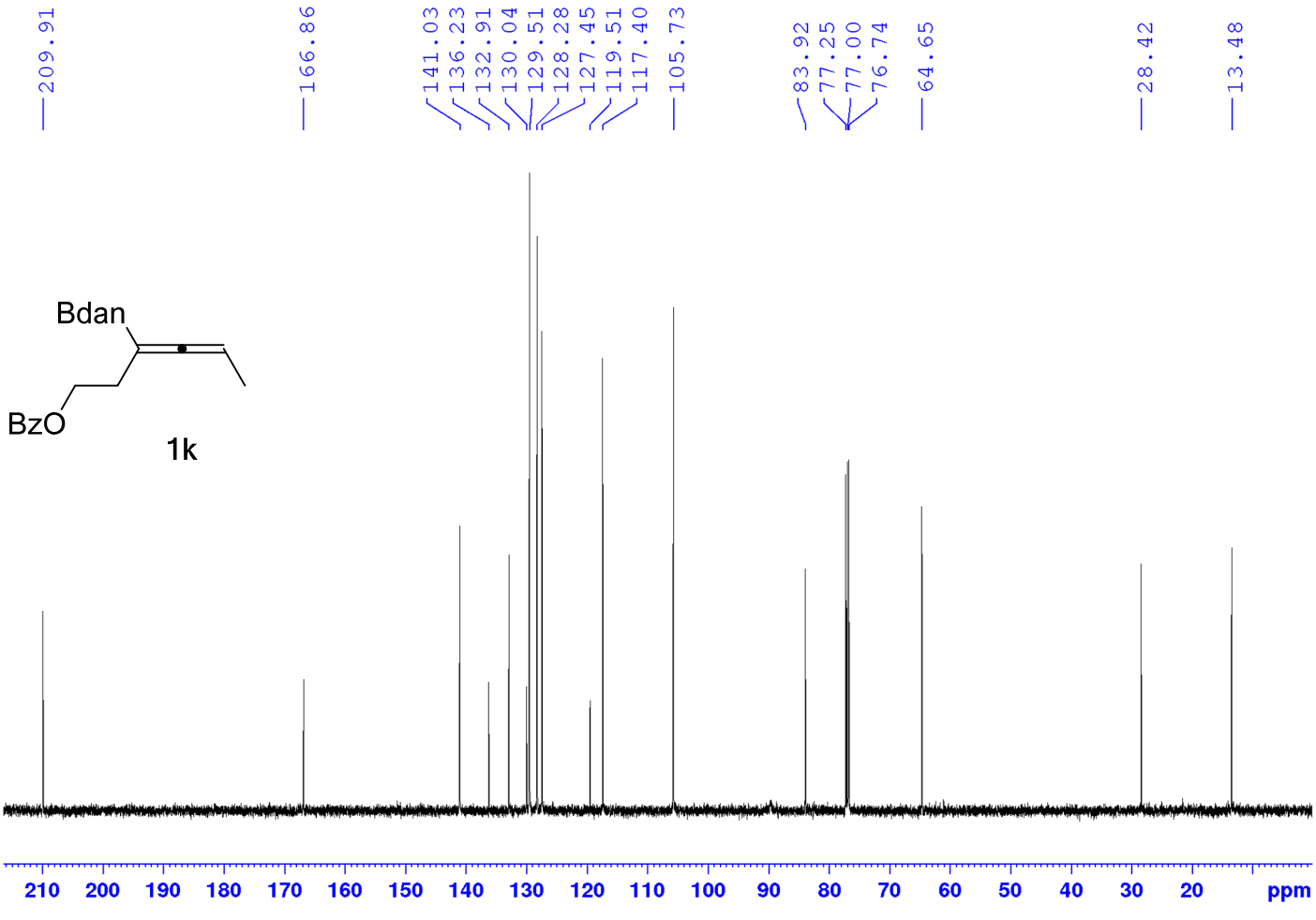
7.119
7.103
7.088
7.019
7.002
6.371
6.357
5.979
5.232
5.216
5.202
5.187
4.460
4.446
4.432
2.558
2.543
2.530
1.729
1.714
Bdan
BzO
1k
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.09
1.09
2.06
2.03
2.08
2.07
2.05
1.00
2.06
2.08
3.09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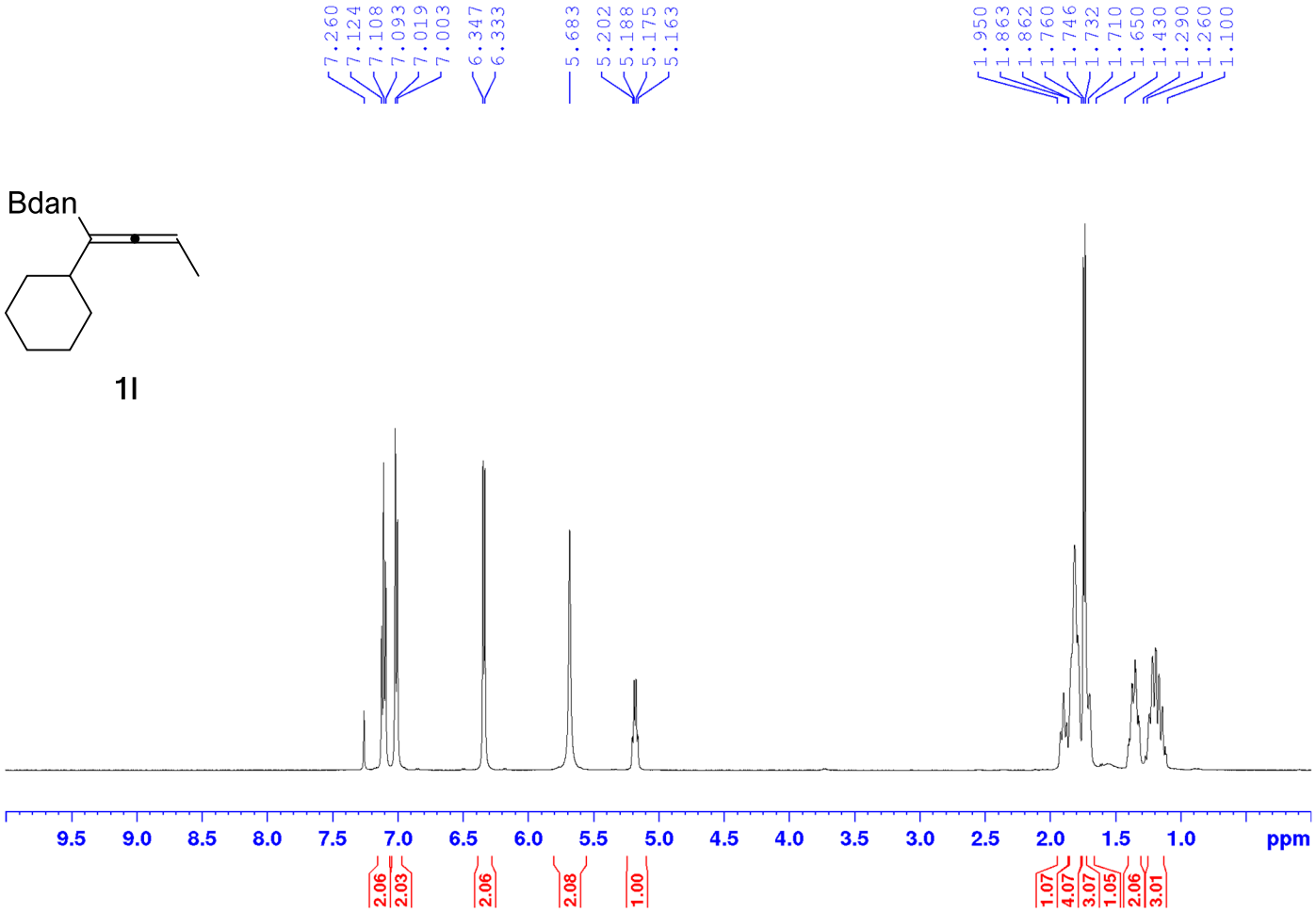
136.23
132.91
130.04
129.51
128.28
127.45
119.51
117.40
105.73
83.92
77.25
77.00
76.74
64.65
28.42
13.48
Bdan
BzO
1k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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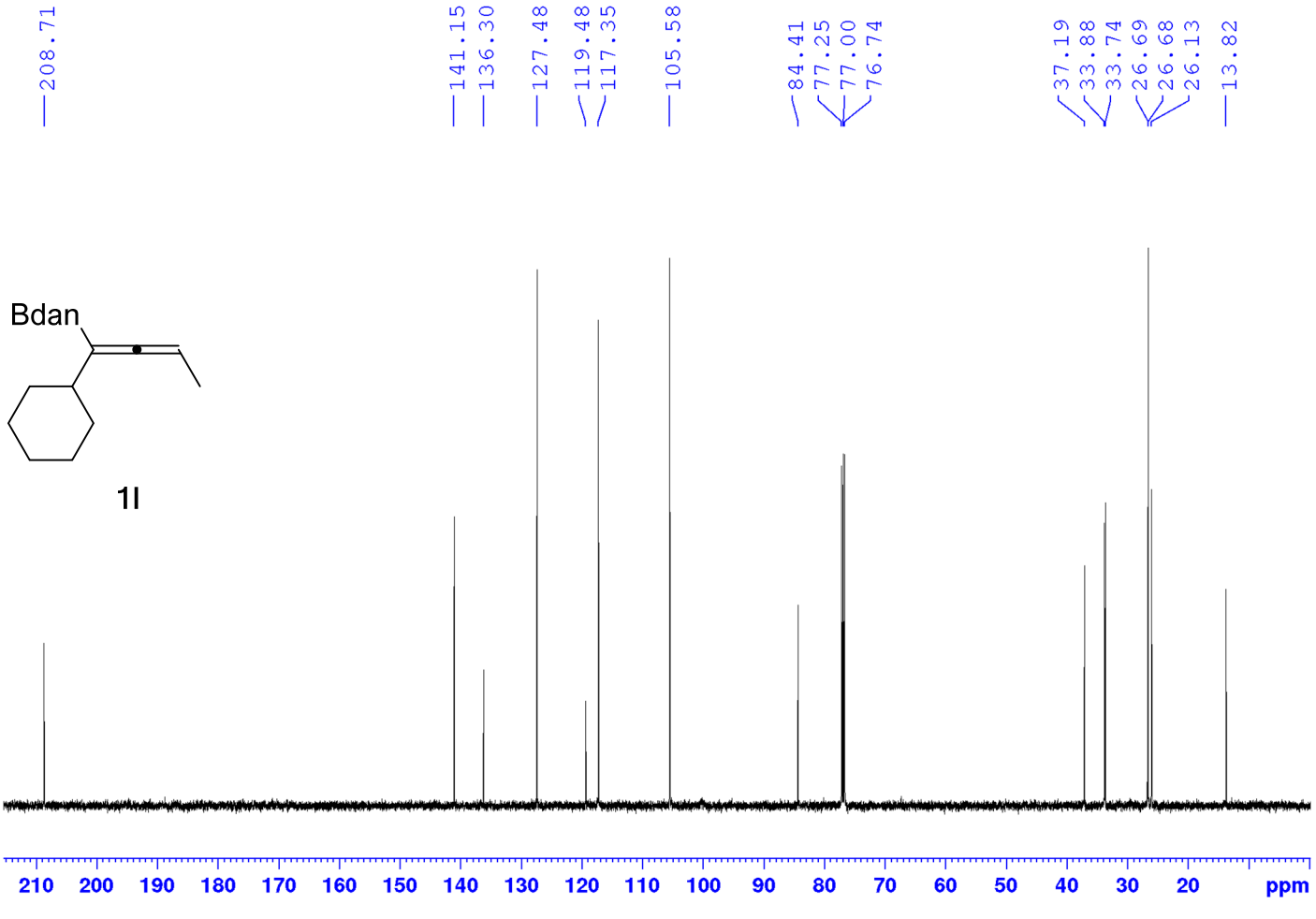
7.124
7.108
7.093
7.019
7.003
6.347
6.333
5.683
5.202
5.188
5.175
5.163
1.950
1.863
1.862
1.760
1.746
1.732
1.710
1.650
1.430
1.290
1.260
1.100
Bdan
1l
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.06 2.03 2.06 2.08 1.00 1.07 4.07 3.07 1.05 2.06 3.01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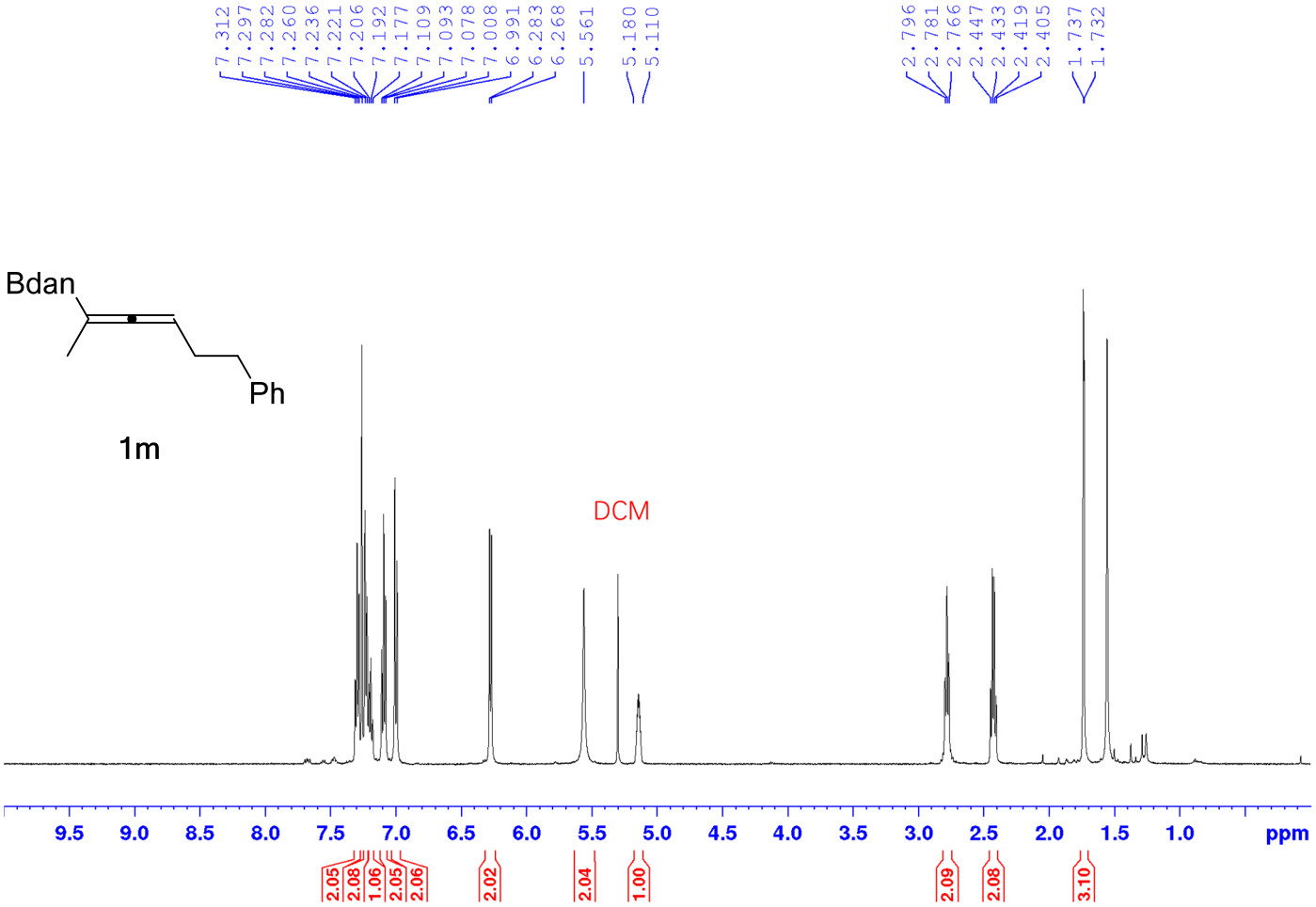
119.48
117.35
105.58
84.41
77.25
77.00
76.74
37.19
33.88
33.74
26.69
26.68
26.13
13.82
Bdan
1l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.260
7.236
7.221
7.206
7.192
7.177
7.109
7.093
7.078
7.008
6.991
6.283
6.268
5.561
5.180
5.110
2.796
2.781
2.766
2.447
2.433
2.419
2.405
1.737
1.732
Bdan
Ph
1m
DCM
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
ppm
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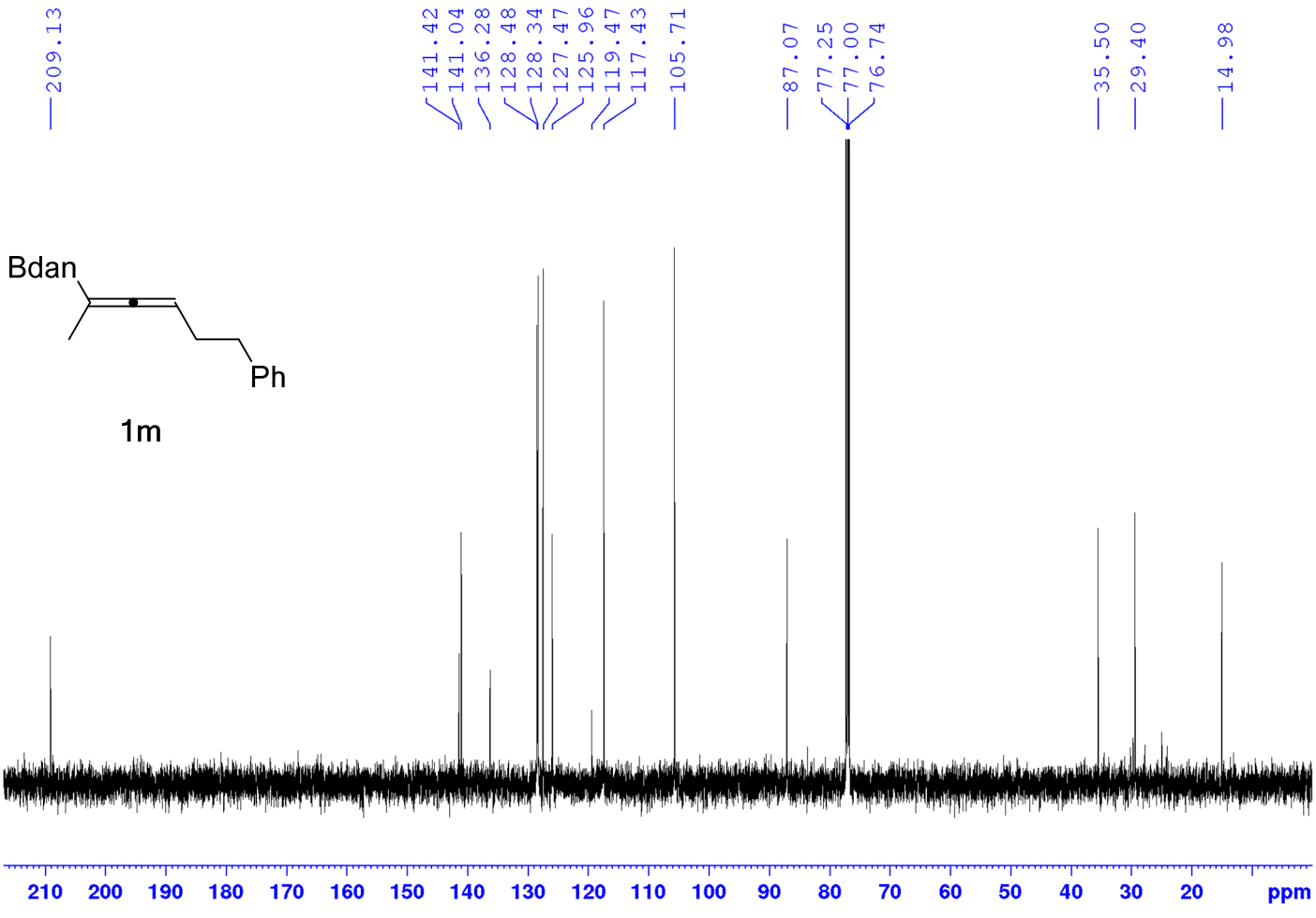
2.08
1.06
2.05
2.06
2.02
2.04
1.00
2.09
2.08
3.10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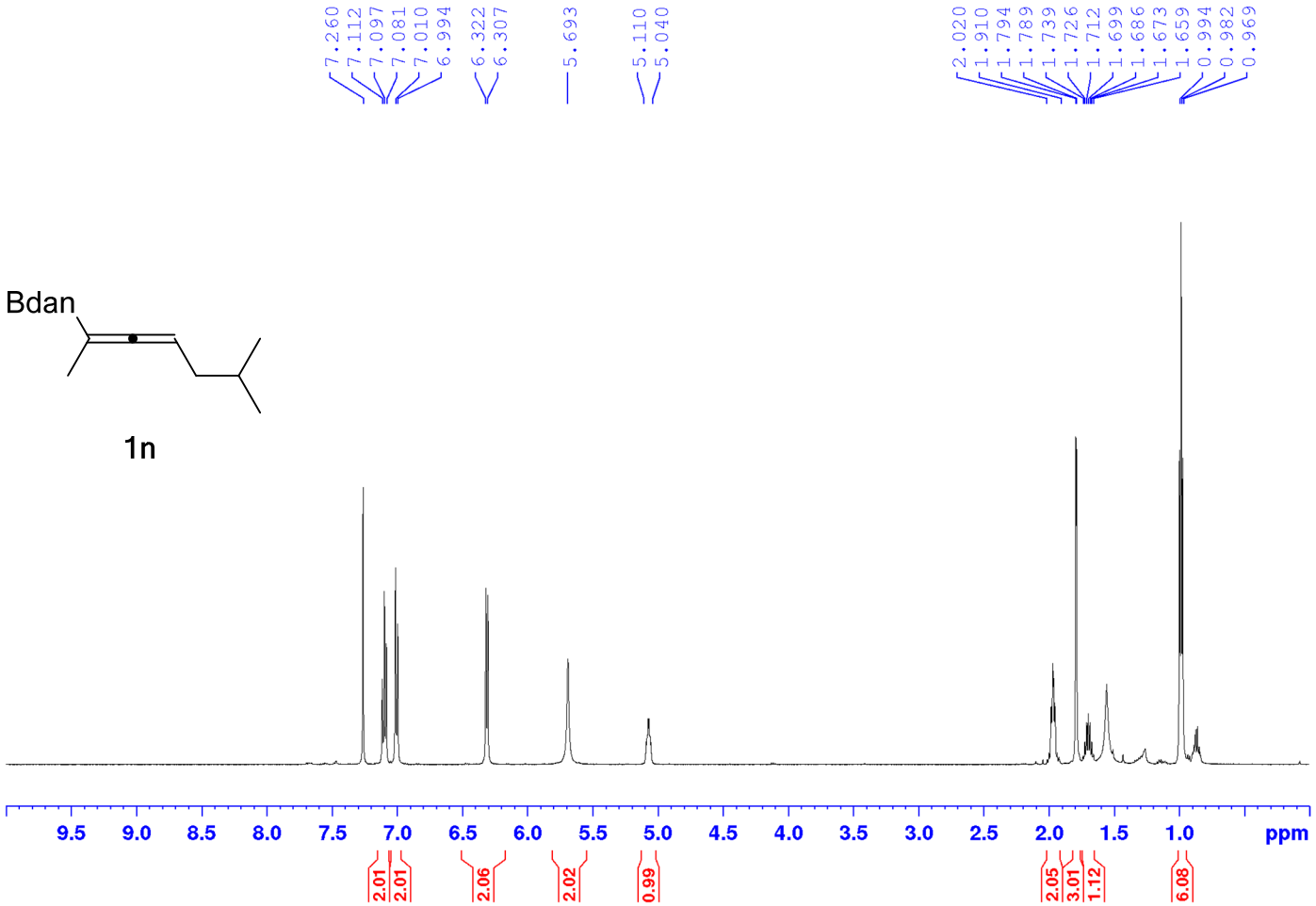
128.34
127.47
125.96
119.47
117.43
105.71
87.07
77.25
77.00
76.74
35.50
29.40
14.98
Bdan
Ph
1m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.010
6.994
6.322
6.307
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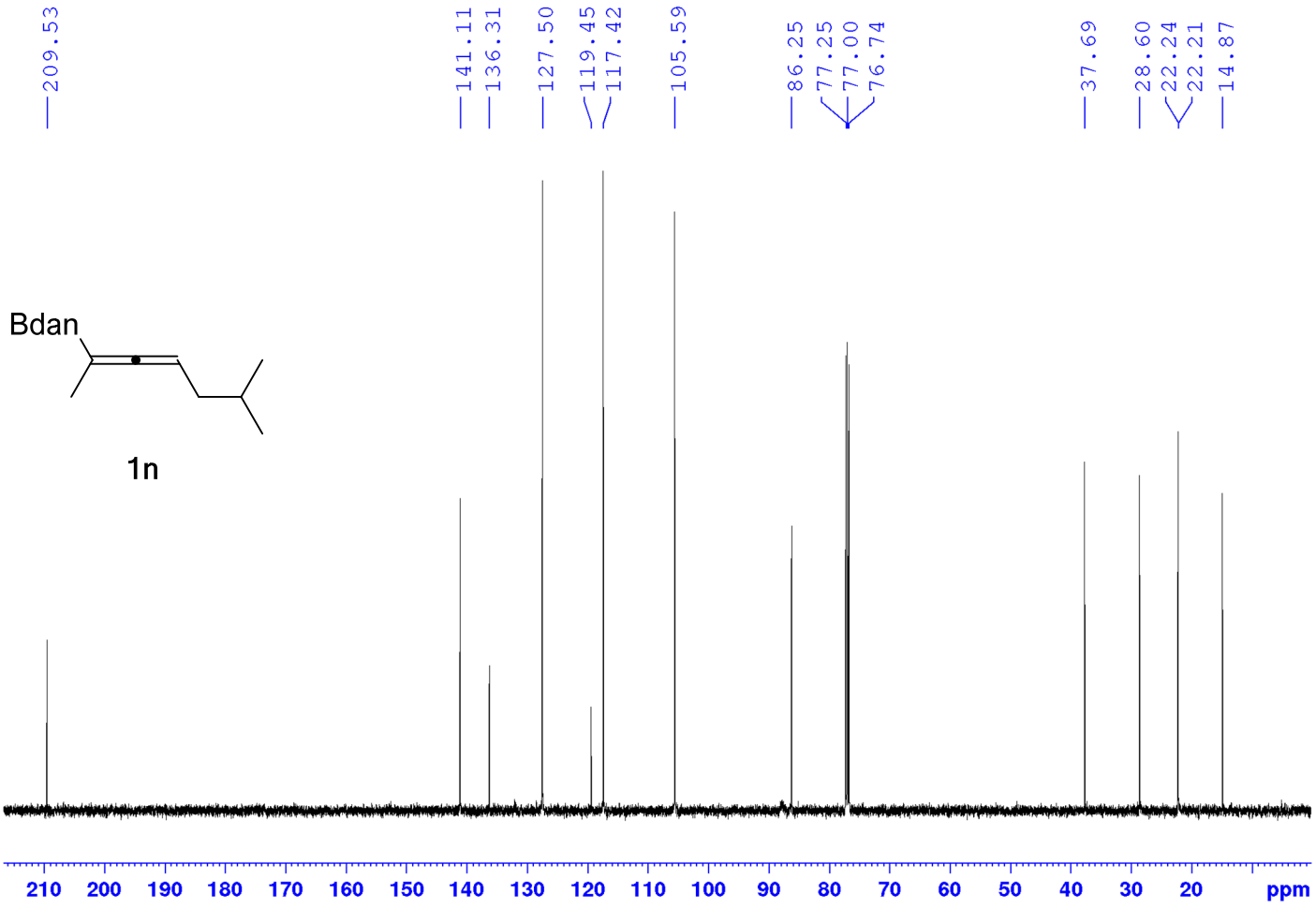
5.110
5.040
2.020
1.910
1.794
1.789
1.739
1.726
1.712
1.699
1.686
1.673
1.659
0.994
0.982
0.969
Bdan
1n
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.01
2.01
2.06
2.02
0.99
2.05
3.01
1.12
6.08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117.42
105.59
86.25
77.25
77.00
76.74
37.69
28.60
22.24
22.21
14.87
Bdan
1n
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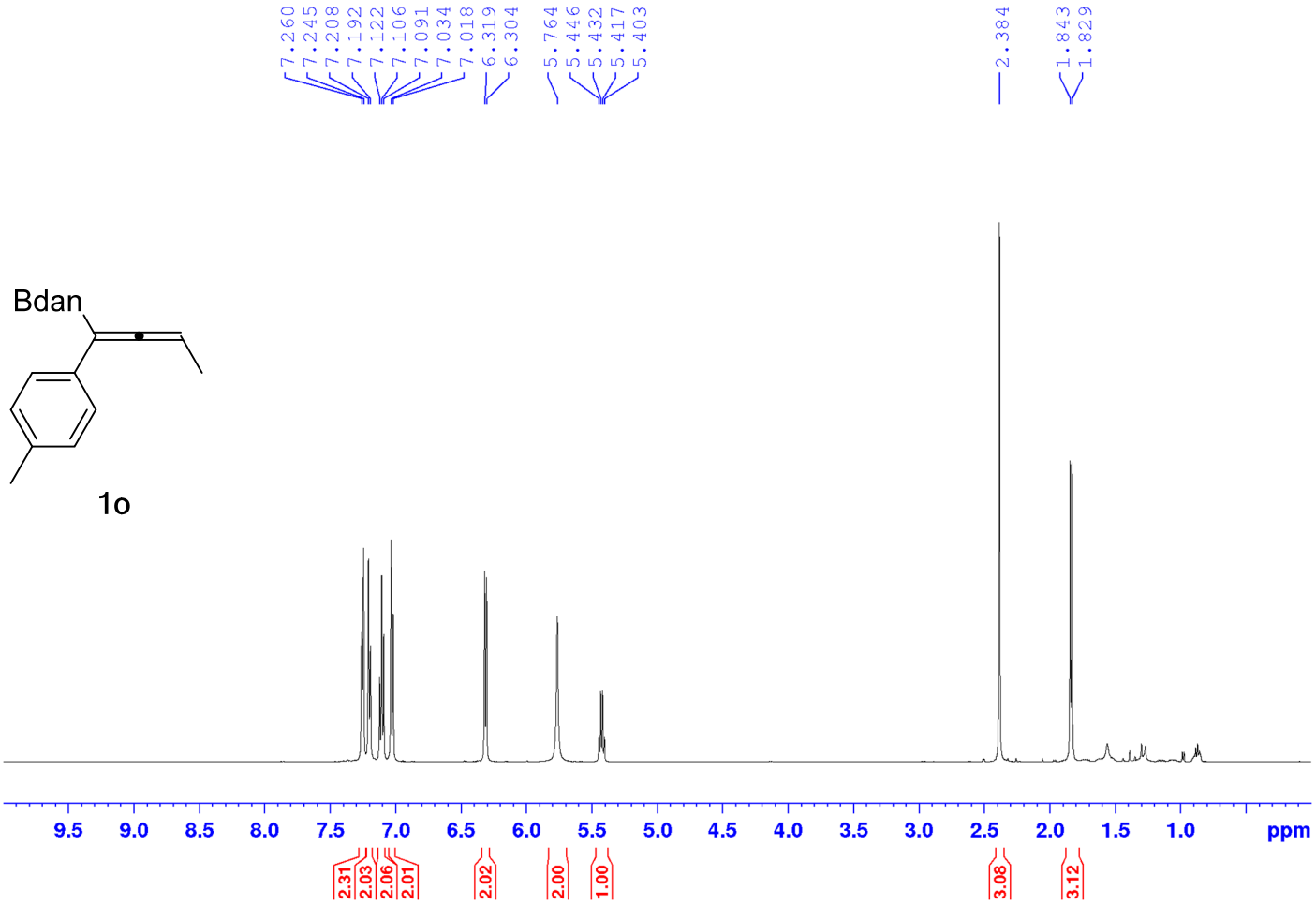
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.122
7.106
7.091
7.034
7.018
6.319
6.304
5.764
5.446
5.432
5.417
5.403
2.384
1.843
1.829
Bdan
1o
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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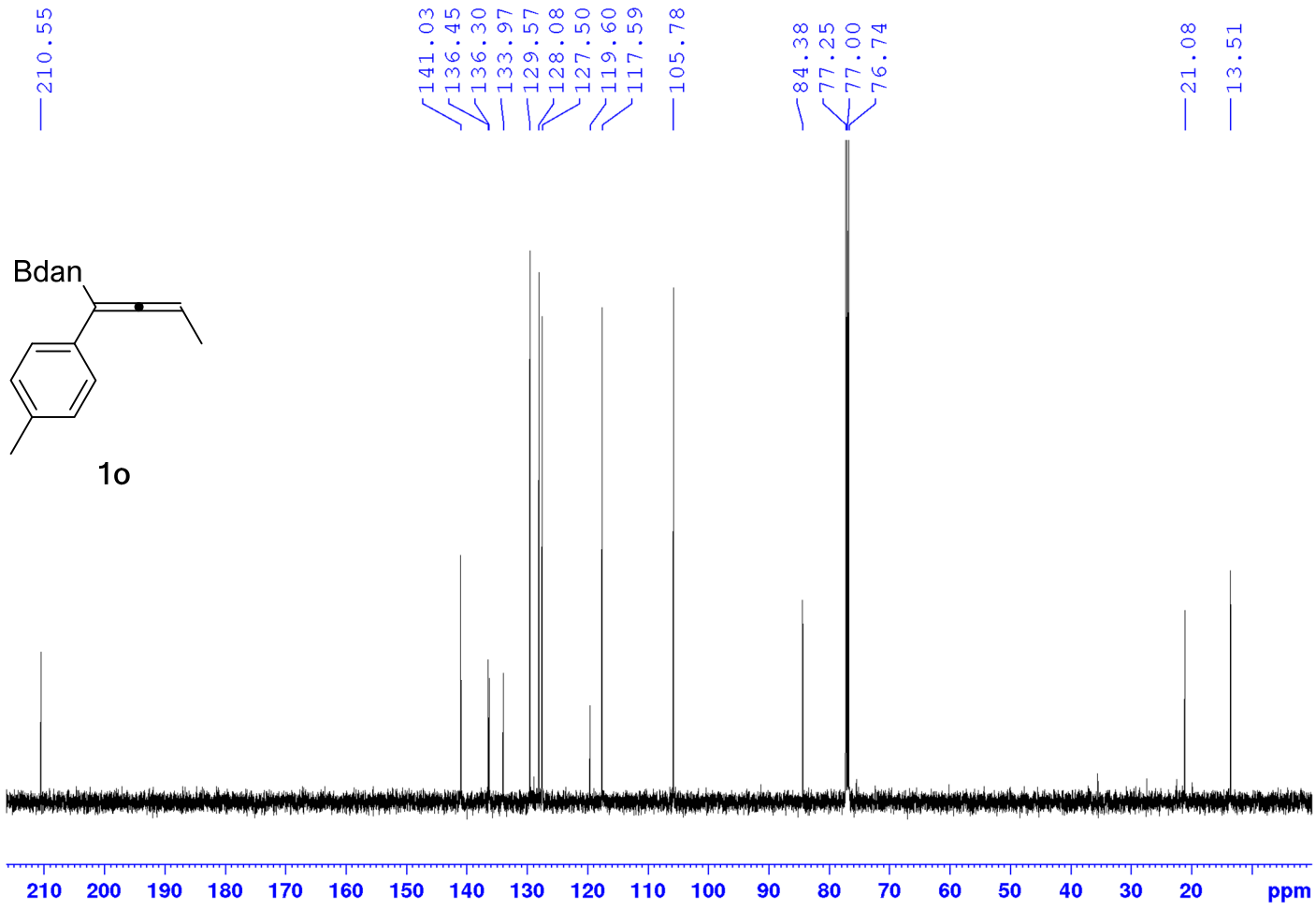
2.03
2.06
2.01
2.02
2.00
1.00
3.08
3.12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129.57
128.08
127.50
119.60
117.59
105.78
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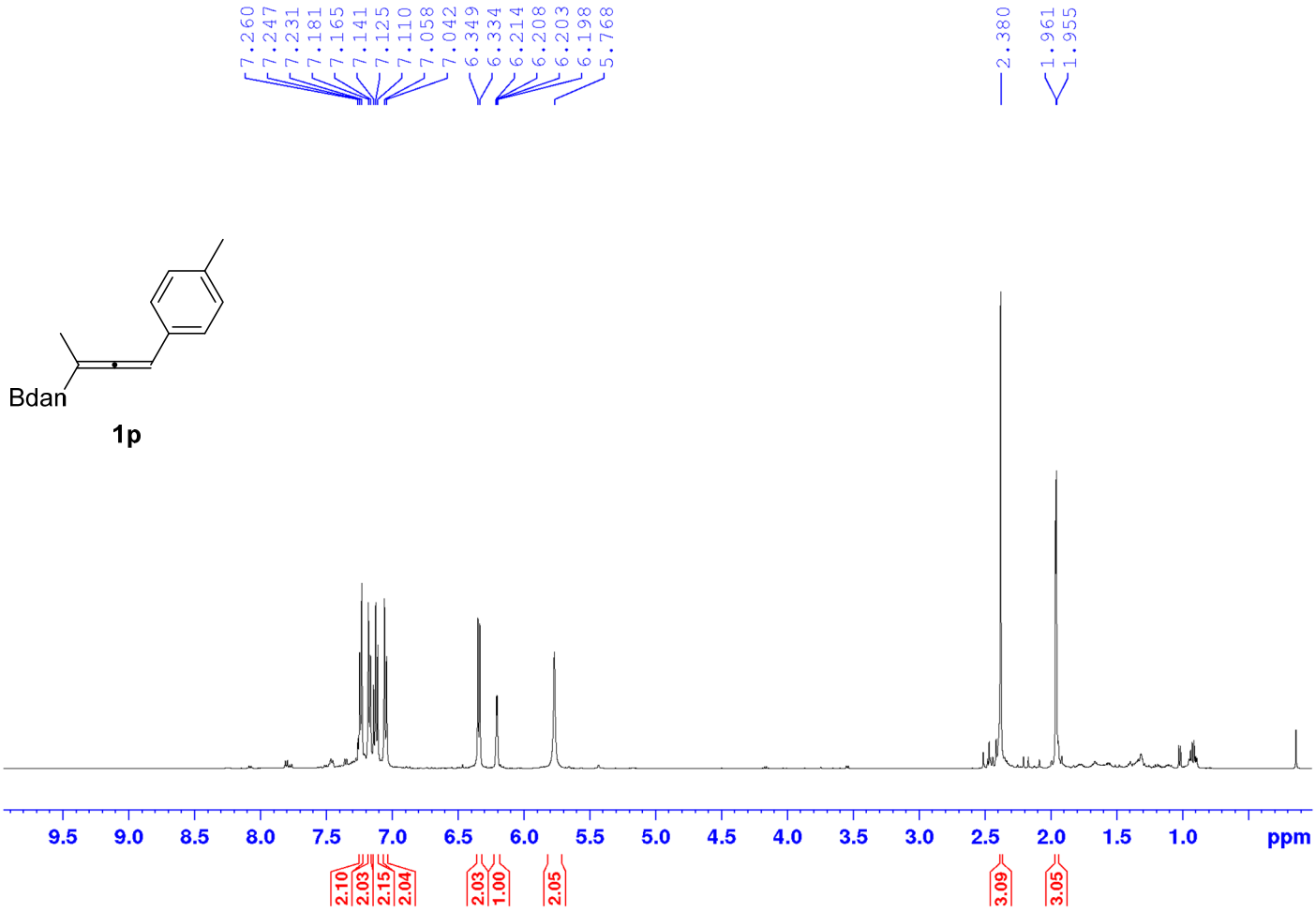
77.25
77.00
76.74
21.08
13.51
Bdan
1o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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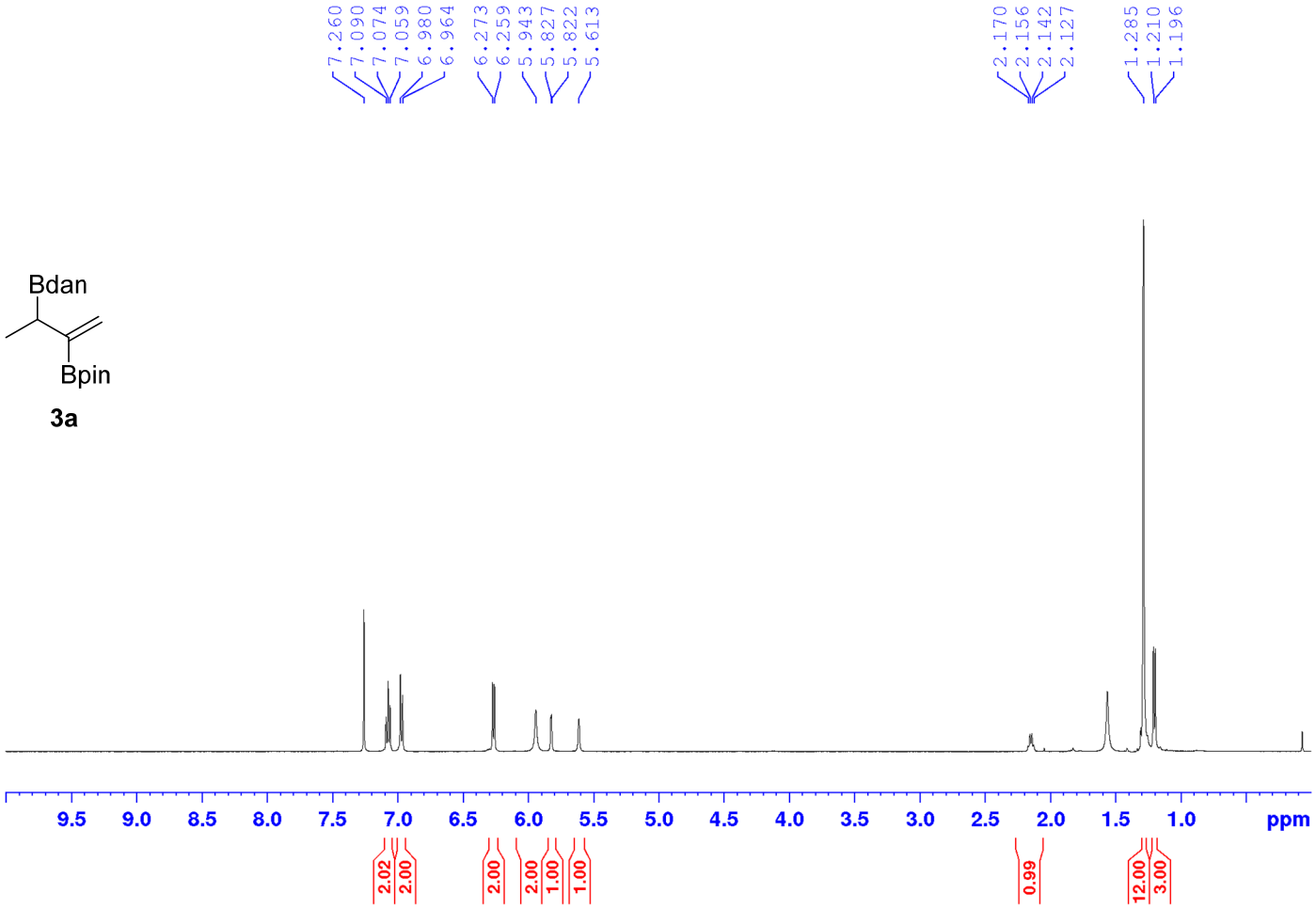
7.141
7.125
7.110
7.058
7.042
6.349
6.334
6.214
6.208
6.203
6.198
5.768
2.380
1.961
1.955
Bdan
1p
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.10
2.03
2.15
2.04
2.03
1.00
2.05
3.09
3.05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7.059
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6.273
6.259
5.943
5.827
5.822
5.613
2.170
2.156
2.142
2.127
1.285
1.210
1.196
Bdan
Bpin
3a
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 ppm
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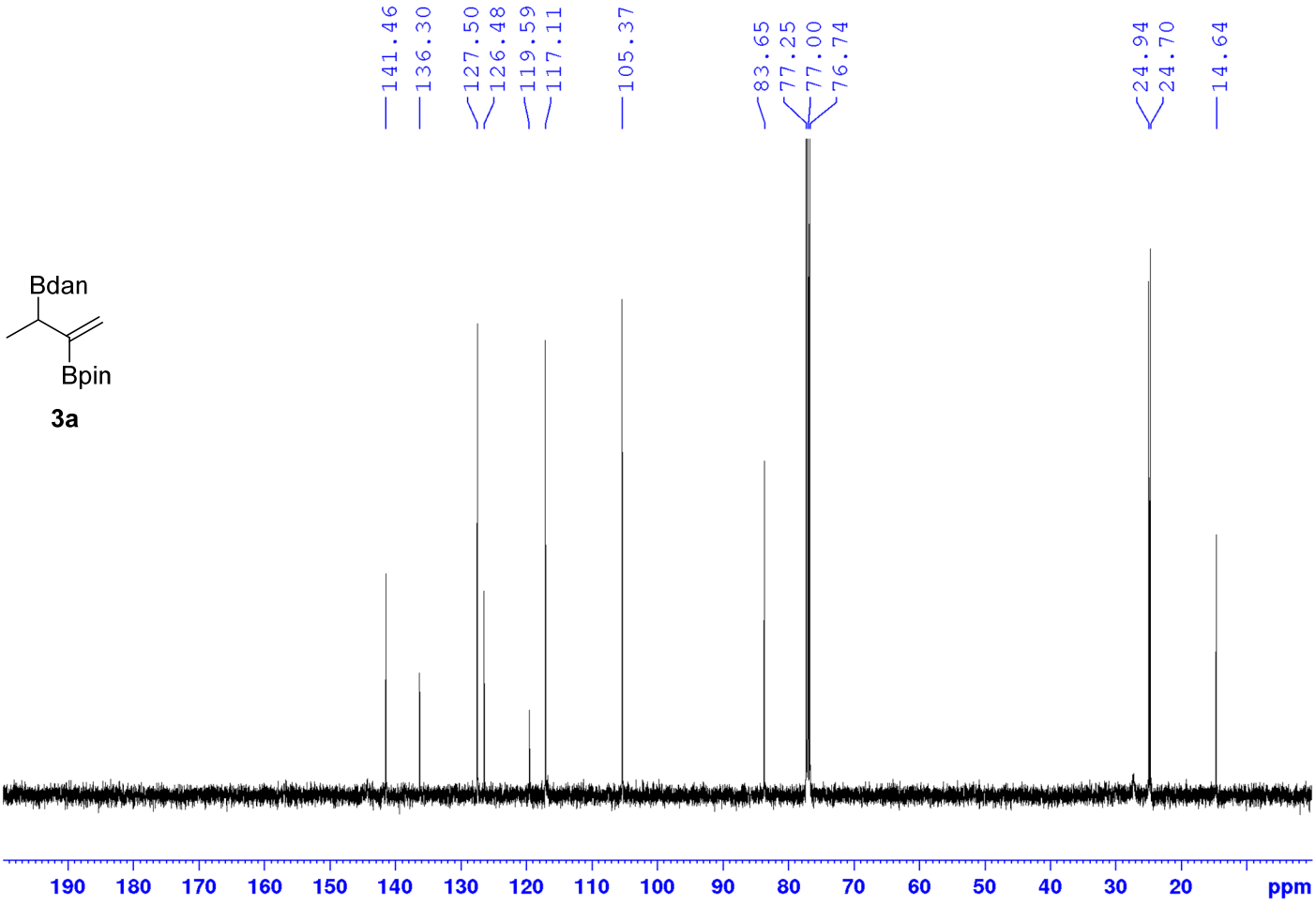
2.00
2.00
2.00
1.00
1.00
0.99
12.00
3.00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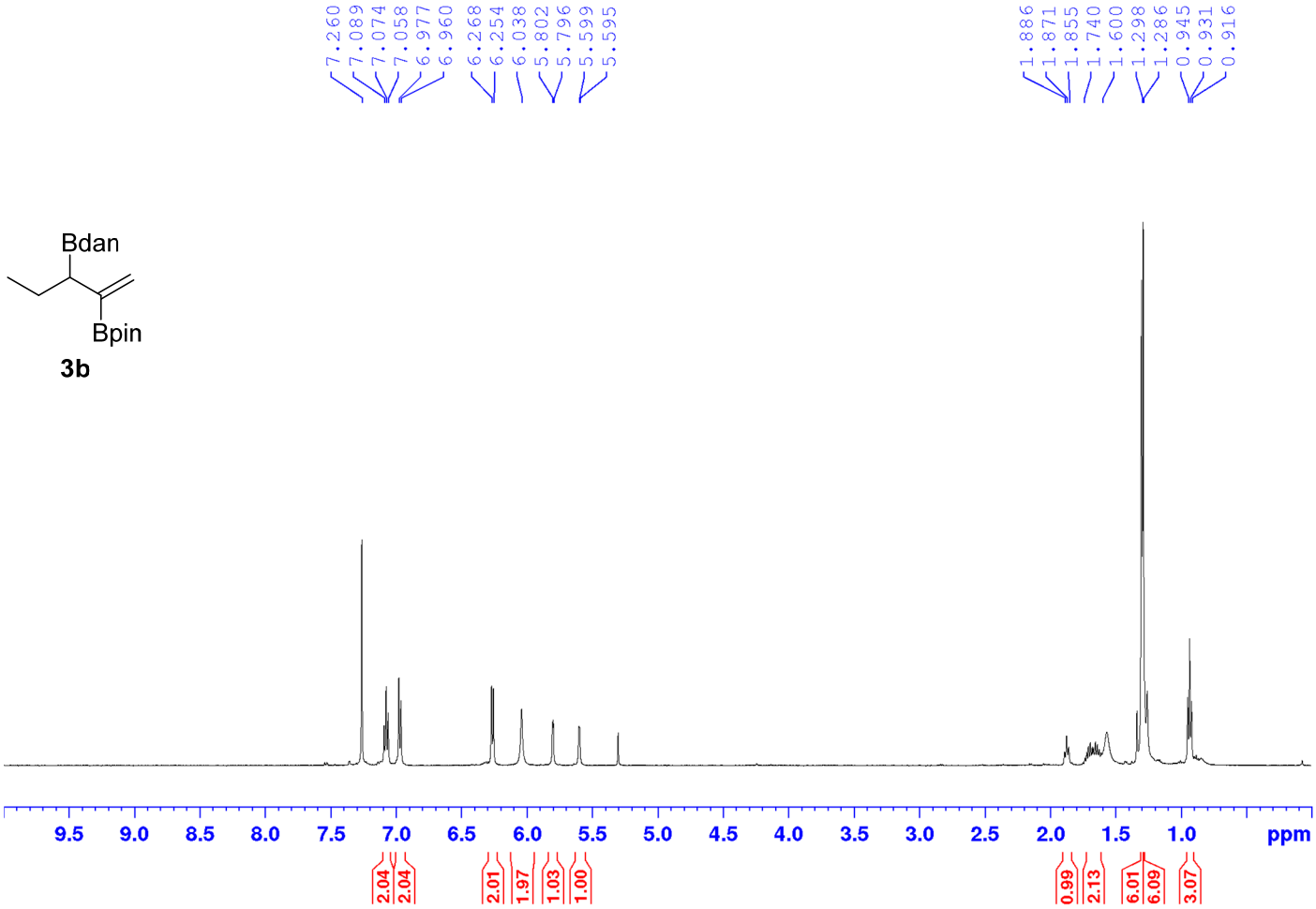
126.48
119.59
117.11
105.37
83.65
77.25
77.00
76.74
24.94
24.70
14.64
Bdan
Bpin
3a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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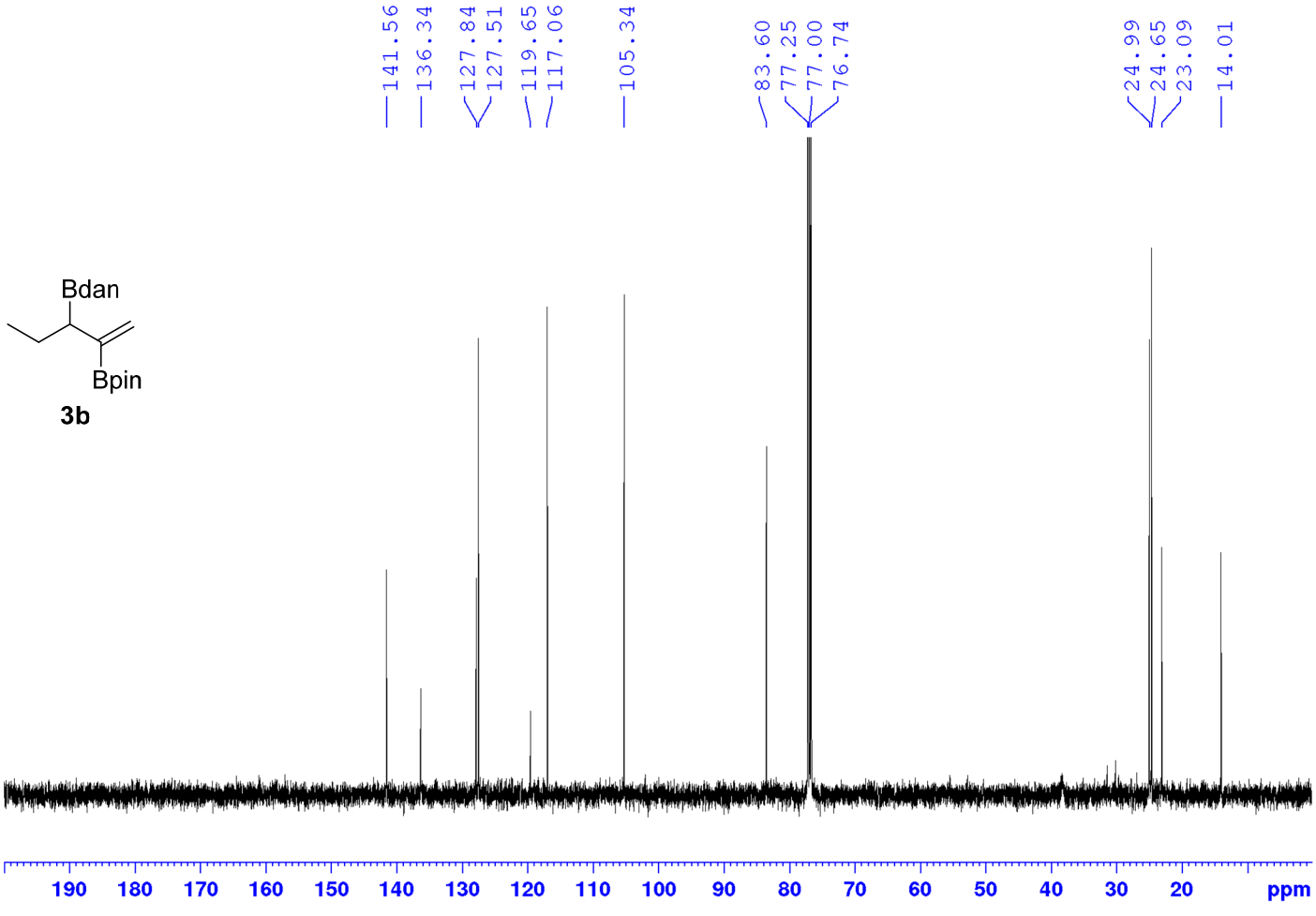
7.074
7.058
6.977
6.960
6.268
6.254
6.038
5.802
5.796
5.599
5.595
1.886
1.871
1.855
1.740
1.600
1.298
1.286
0.945
0.931
0.916
Bdan
Bpin
3b
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.04
2.04
2.01
1.97
1.03
1.00
0.99
2.13
6.01
6.09
3.07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127.51
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105.34
83.60
77.25
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24.65
23.09
14.01
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Bpin
3b
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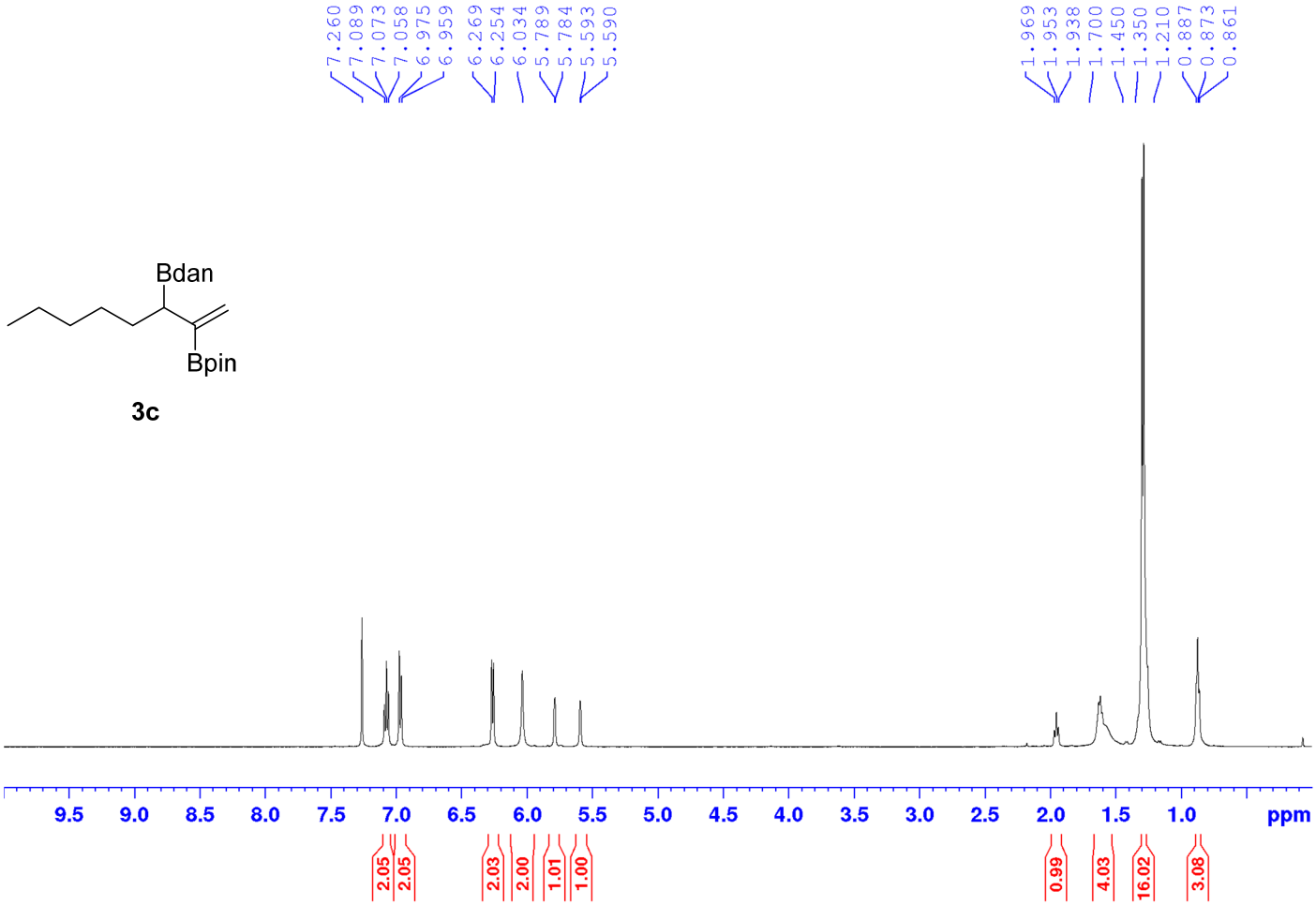
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7.073
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6.254
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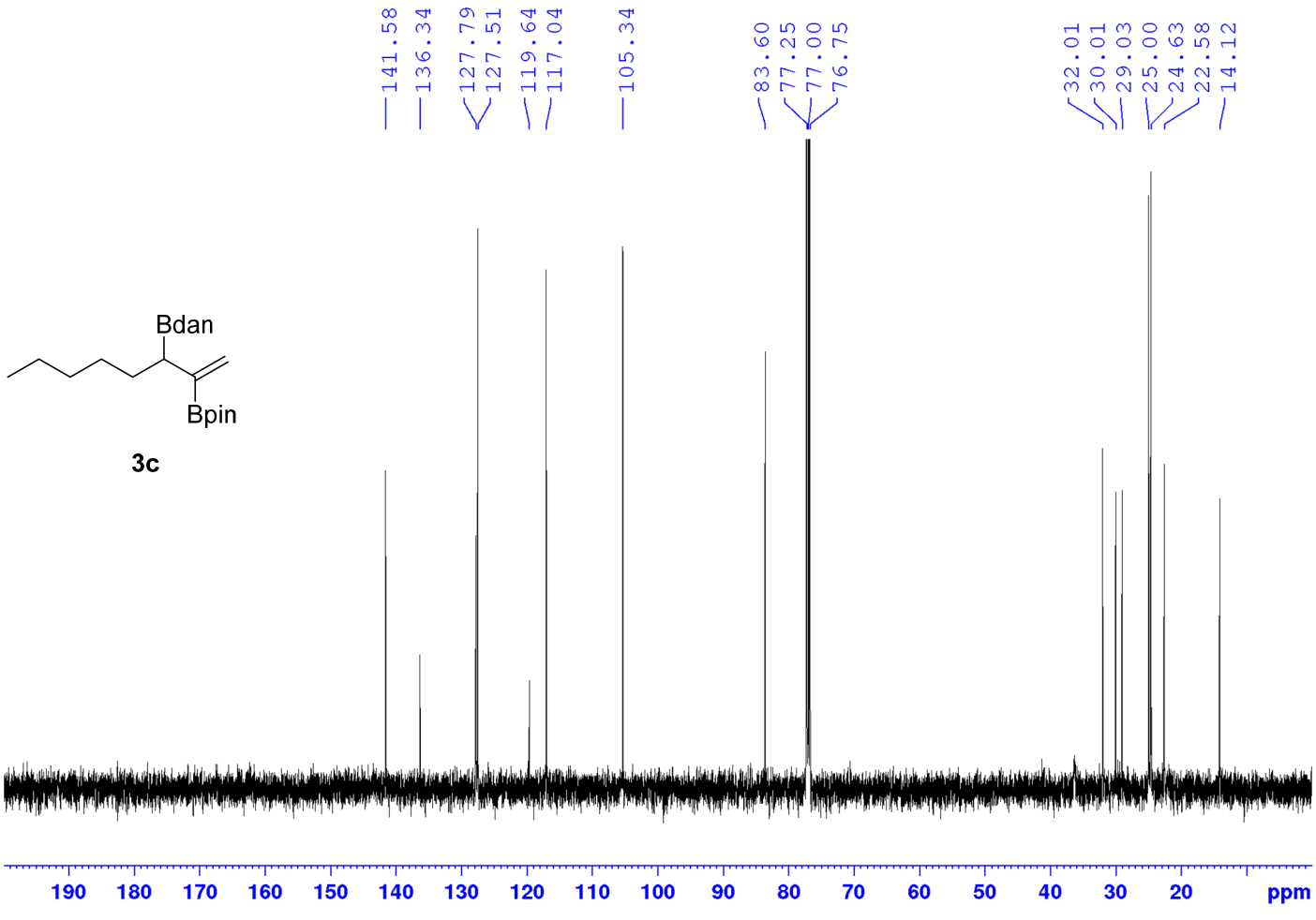
5.789
5.784
5.593
5.590
1.969
1.953
1.938
1.700
1.450
1.350
1.210
0.887
0.873
0.861
Bdan
Bpin
3c
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.05
2.05
2.03
2.00
1.01
1.00
0.99
4.03
16.02
3.08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117.04
105.34
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77.00
76.75
32.01
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24.63
22.58
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Bpin
3c
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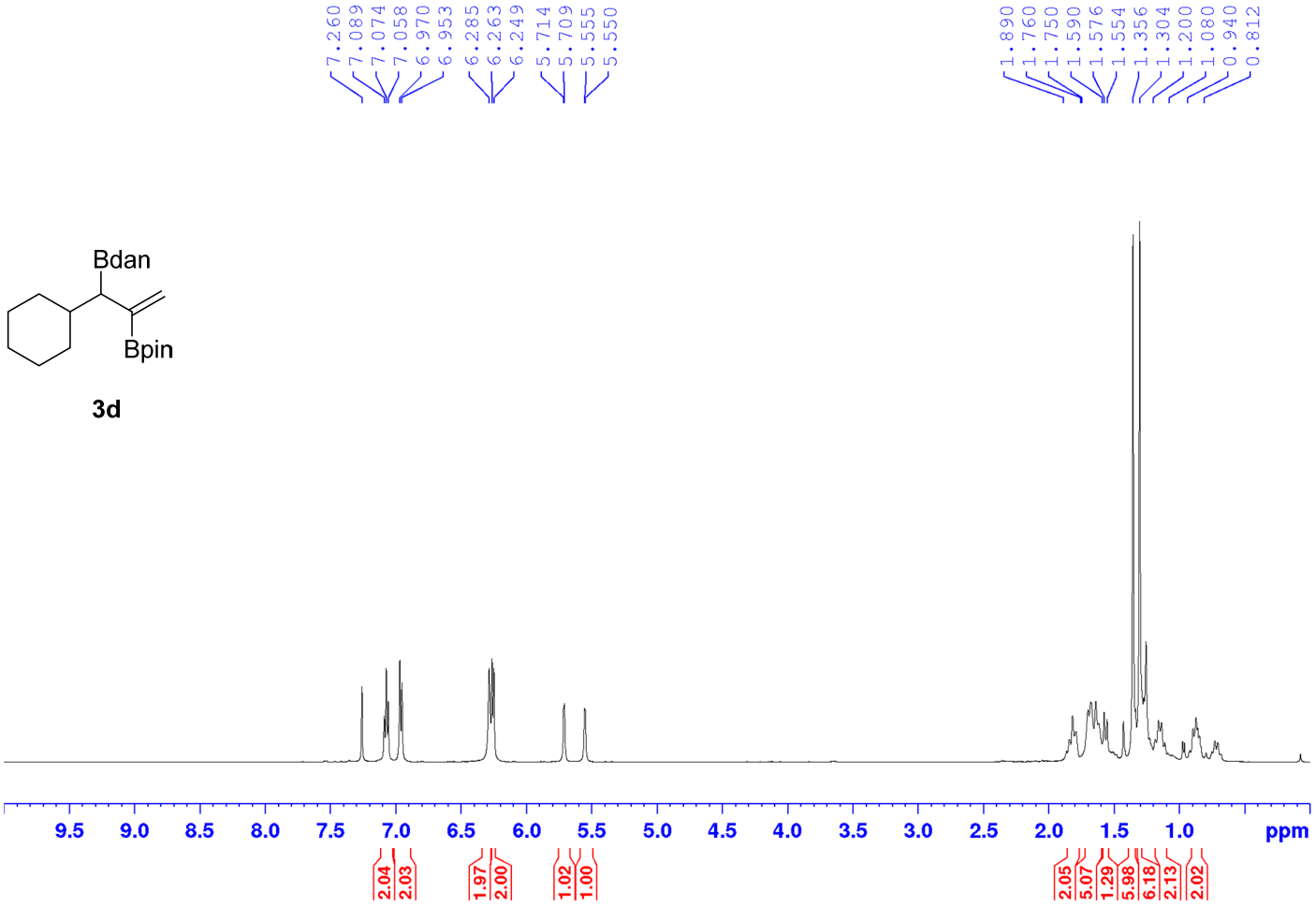
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5.714
5.709
5.555
5.550
1.890
1.760
1.750
1.590
1.576
1.554
1.356
1.304
1.200
1.080
0.940
0.812
Bdan
Bpin
3d
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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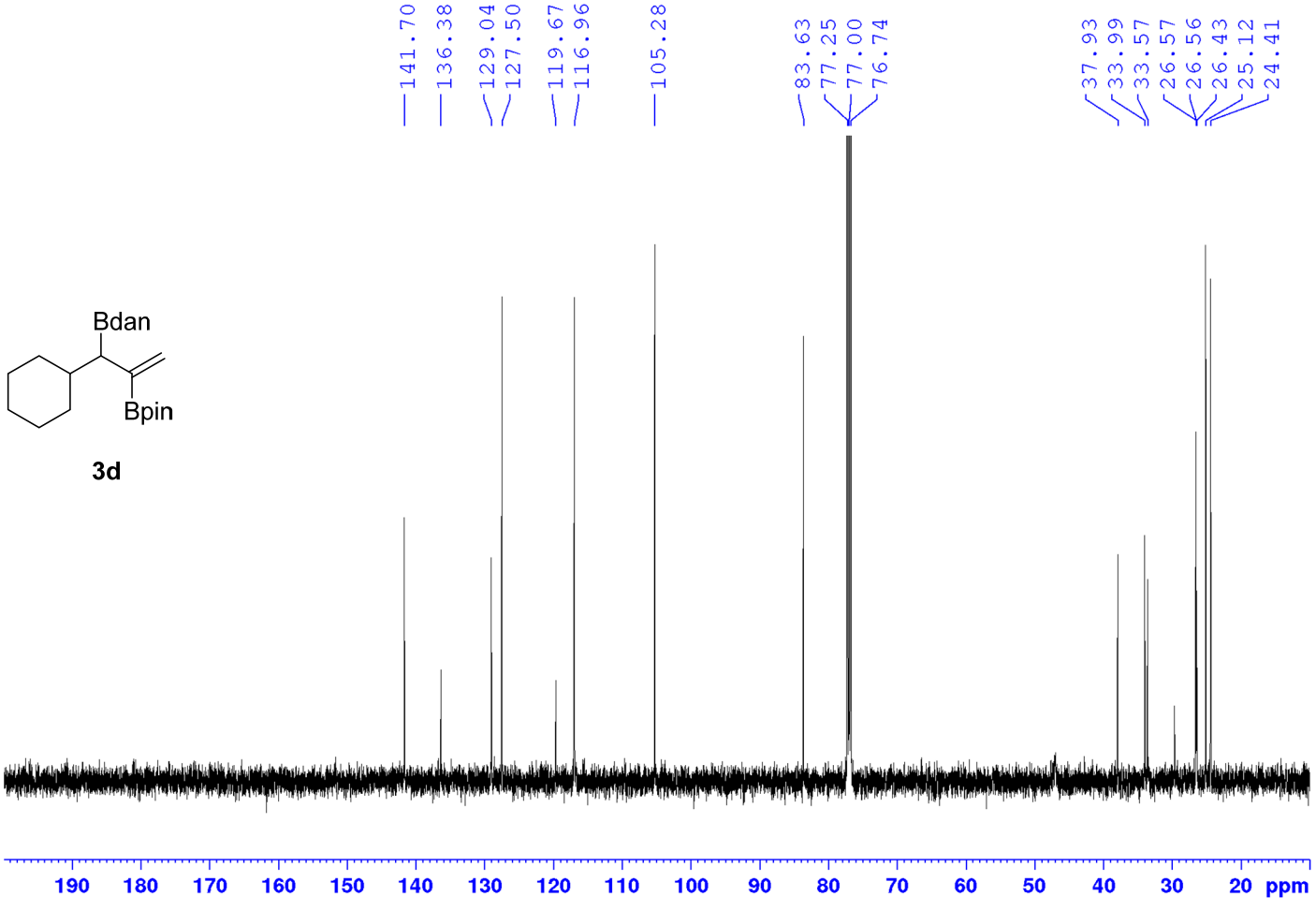
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129.04
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105.28
83.63
77.25
77.00
76.74
37.93
33.99
33.57
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26.43
25.12
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Bpin
3d
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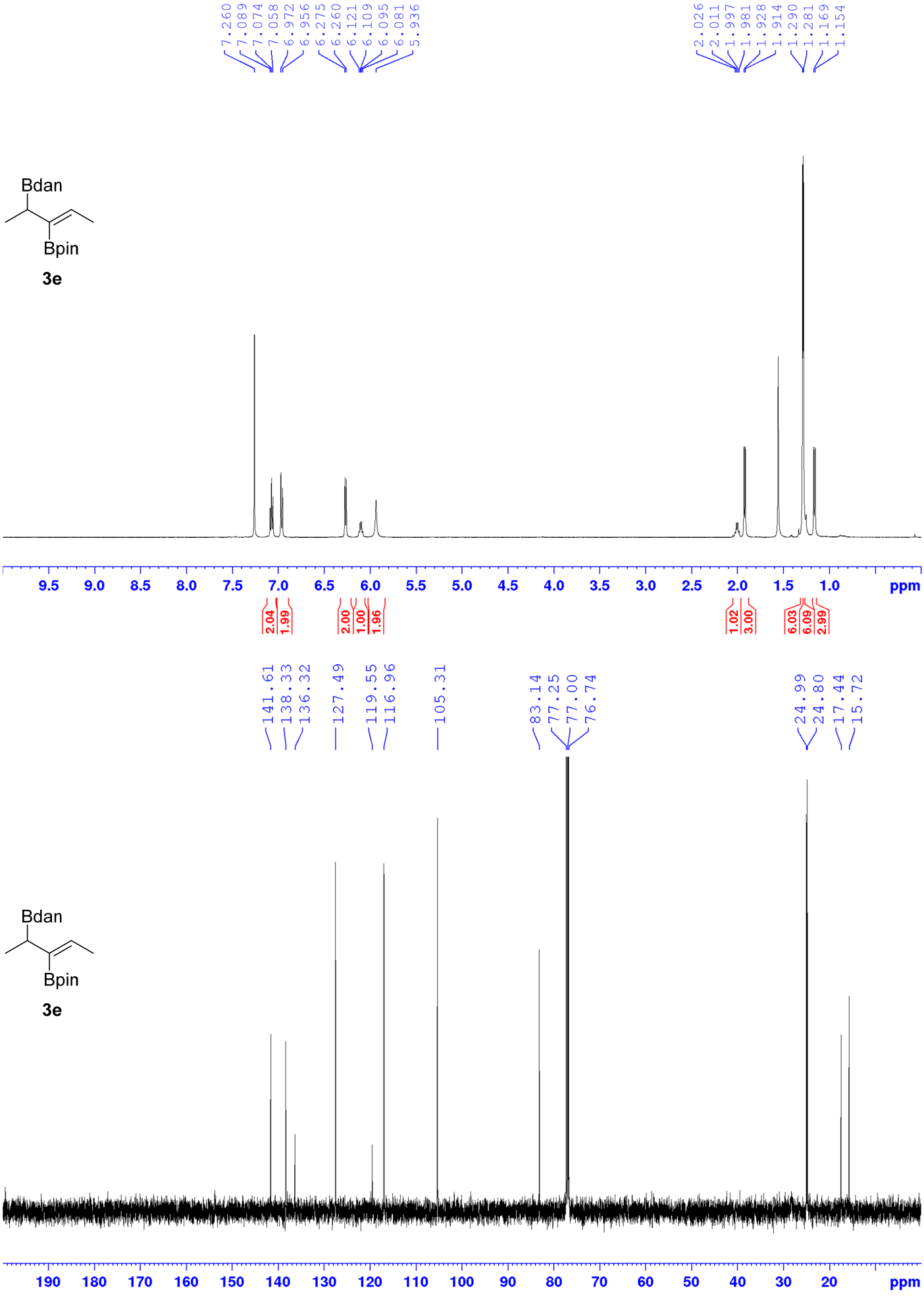
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6.956
6.275
6.260
6.121
6.109
6.095
6.081
5.936
2.026
2.011
1.997
1.981
1.928
1.914
1.290
1.281
1.169
1.154
Bdan
Bpin
3e
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.04 1.99 2.00 1.00 1.96 1.02 3.00 6.03 6.09 2.99
141.61
138.33
136.32
127.49
119.55
116.96
105.31
83.14
77.25
77.00
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17.44
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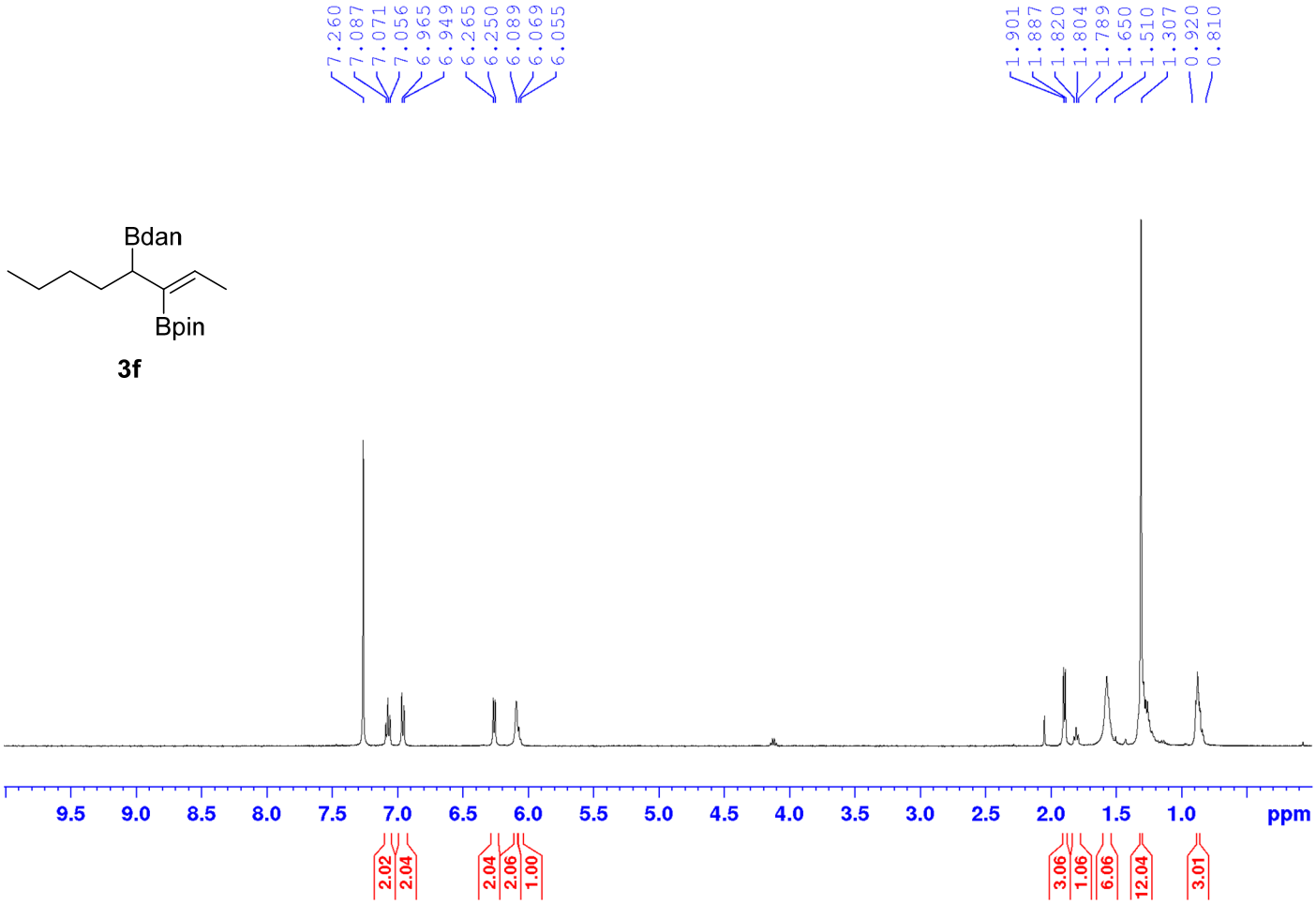
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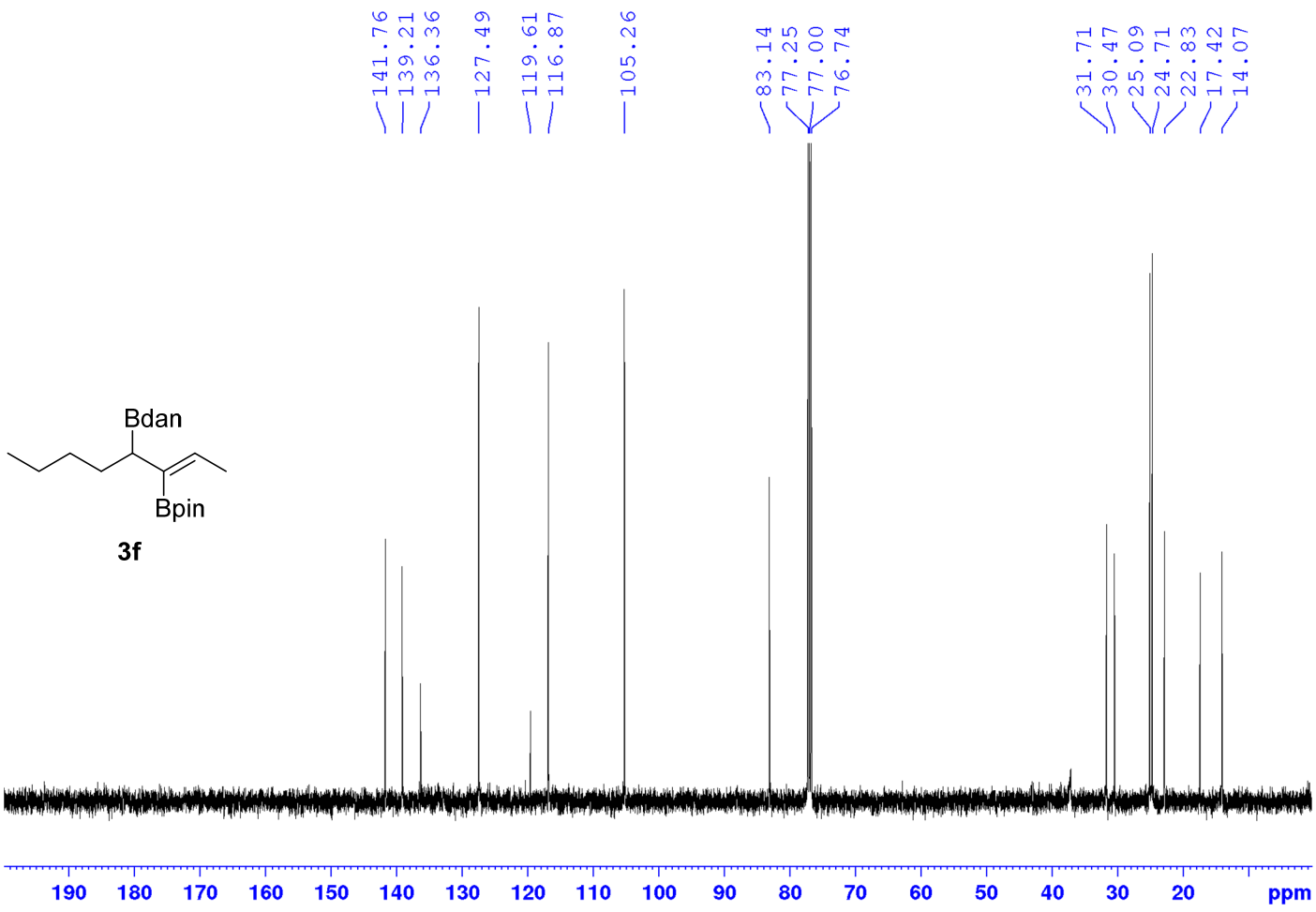
6.965
6.949
6.265
6.250
6.089
6.069
6.055
1.901
1.887
1.820
1.804
1.789
1.650
1.510
1.307
0.920
0.810
Bdan
Bpin
3f
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.02
2.04
2.04
2.06
1.00
3.06
1.06
6.06
12.04
3.01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136.36
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119.61
116.87
105.26
83.14
77.25
77.00
76.74
31.71
30.47
25.09
24.71
22.83
17.42
14.07
Bdan
Bpin
3f
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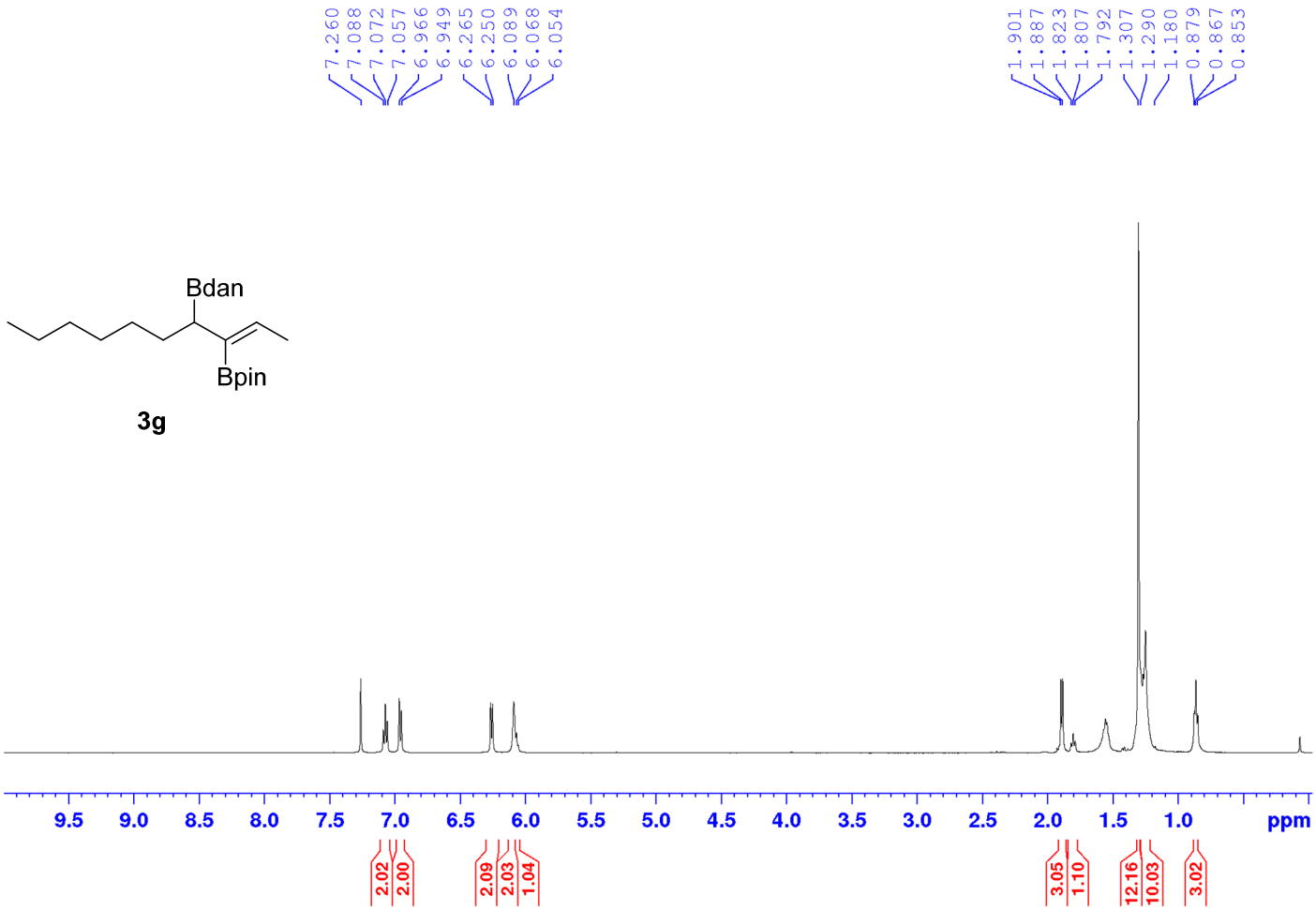
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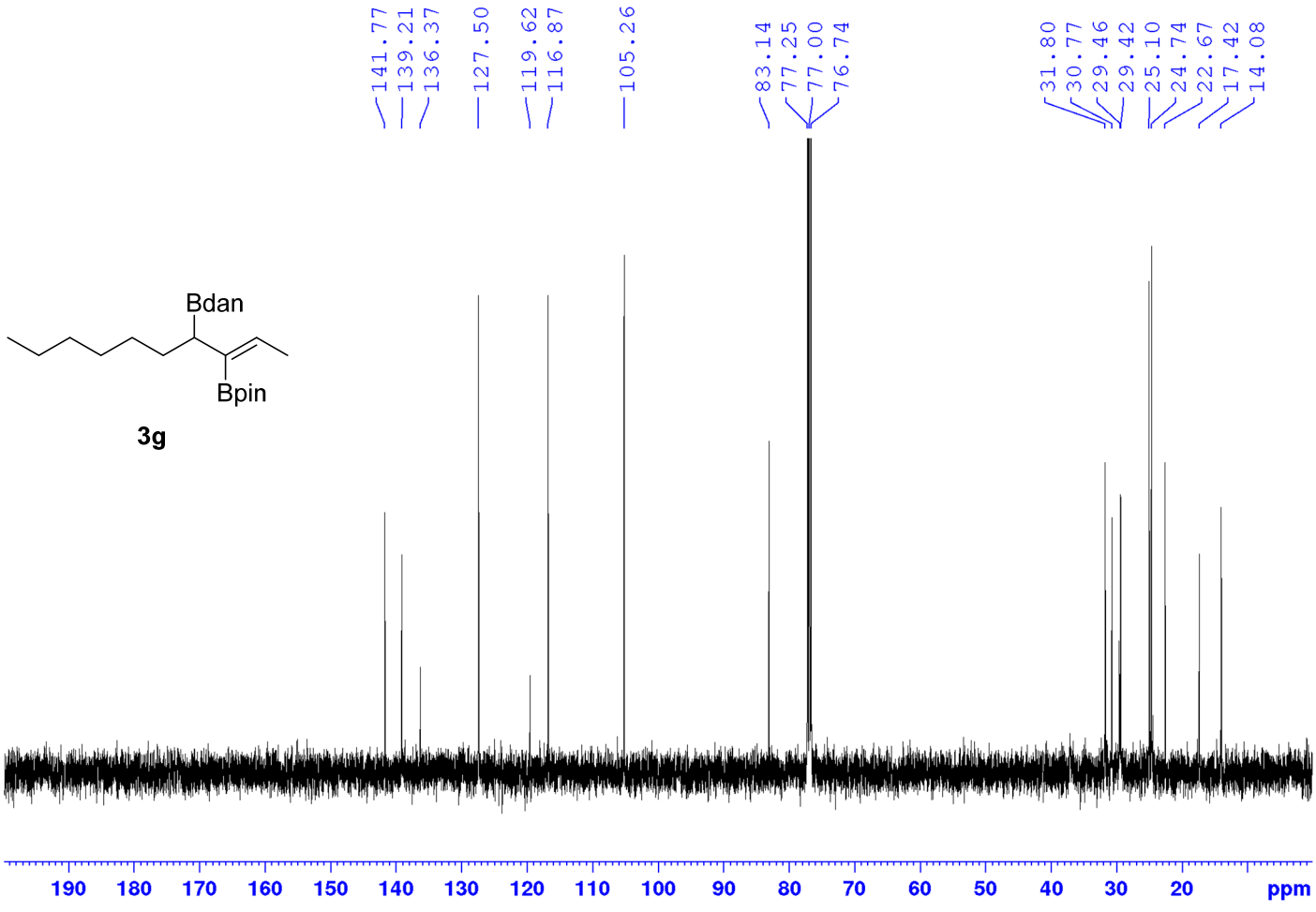
7.057
6.966
6.949
6.265
6.250
6.089
6.068
6.054
1.901
1.887
1.823
1.807
1.792
1.307
1.290
1.180
0.879
0.867
0.853
Bdan
Bpin
3g
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.02
2.00
2.09
2.03
1.04
3.05
1.10
12.16
10.03
3.02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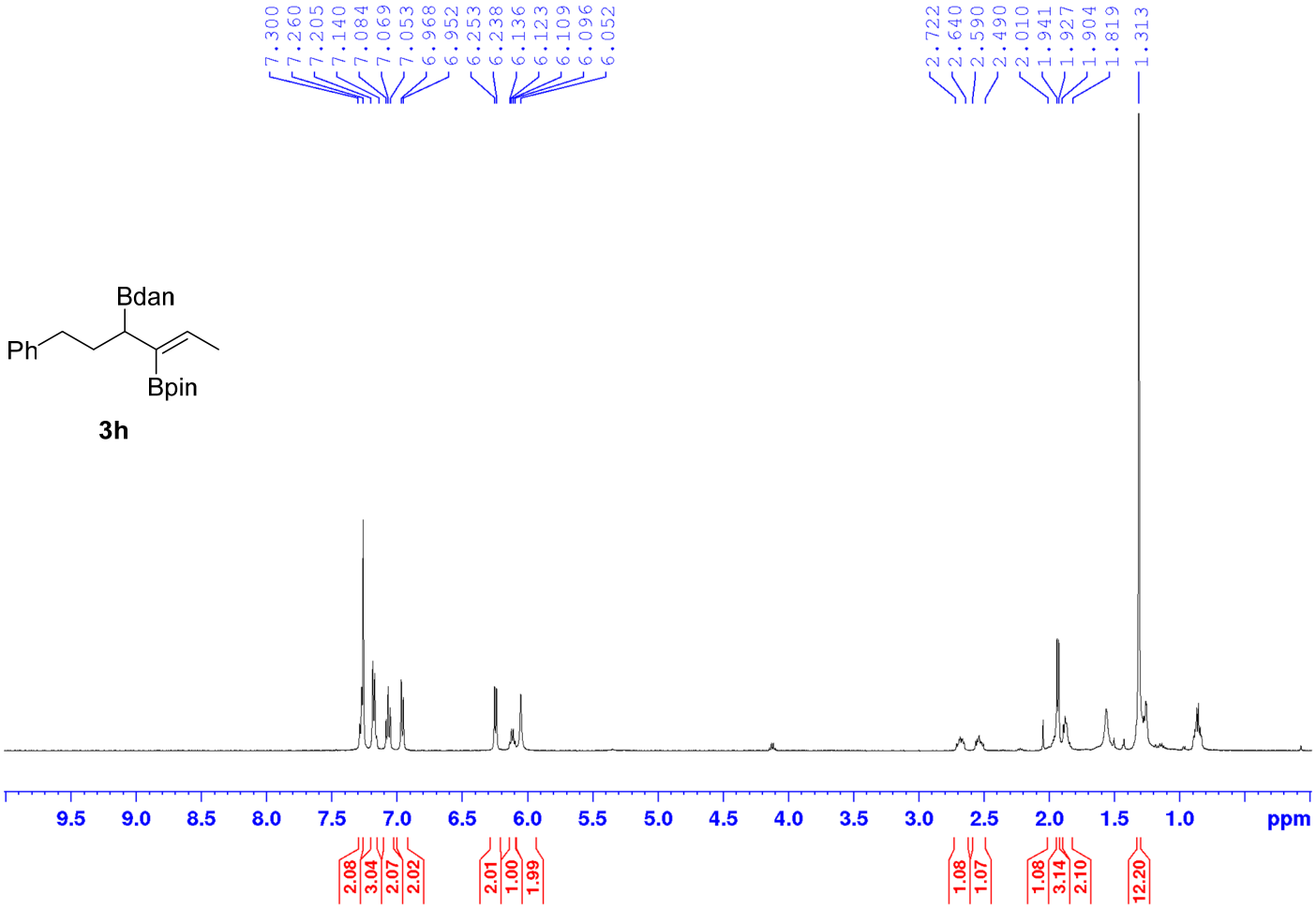
127.50
119.62
116.87
105.26
83.14
77.25
77.00
76.74
31.80
30.77
29.46
29.42
25.10
24.74
22.67
17.42
14.08
Bdan
Bpin
3g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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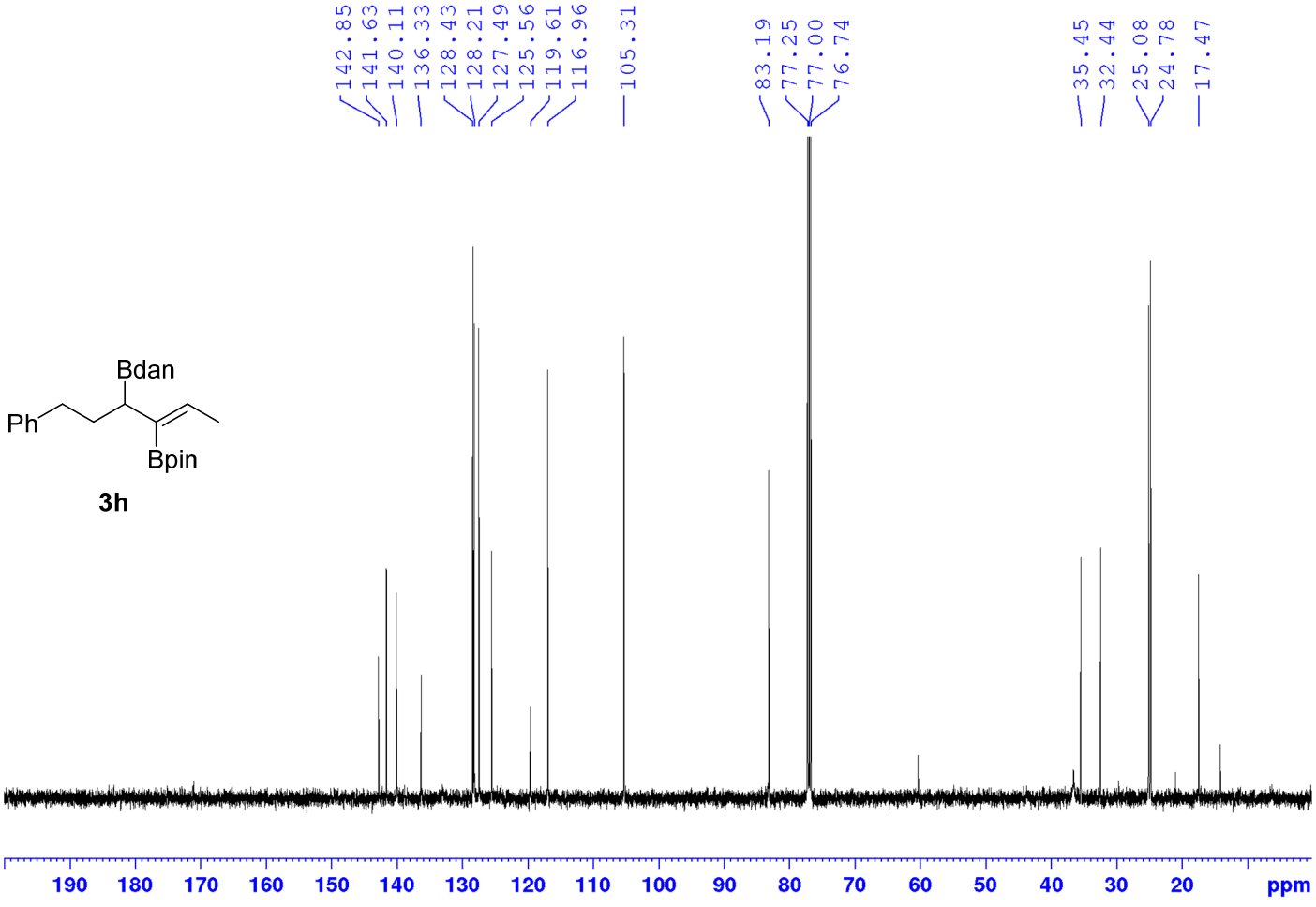
7.260
7.205
7.140
7.084
7.069
7.053
6.968
6.952
6.253
6.238
6.136
6.123
6.109
6.096
6.052
2.722
2.640
2.590
2.490
2.010
1.941
1.927
1.904
1.819
1.313
Bdan
Ph
Bpin
3h
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.08
3.04
2.07
2.02
2.01
1.00
1.99
1.08
1.07
1.08
3.14
2.10
12.20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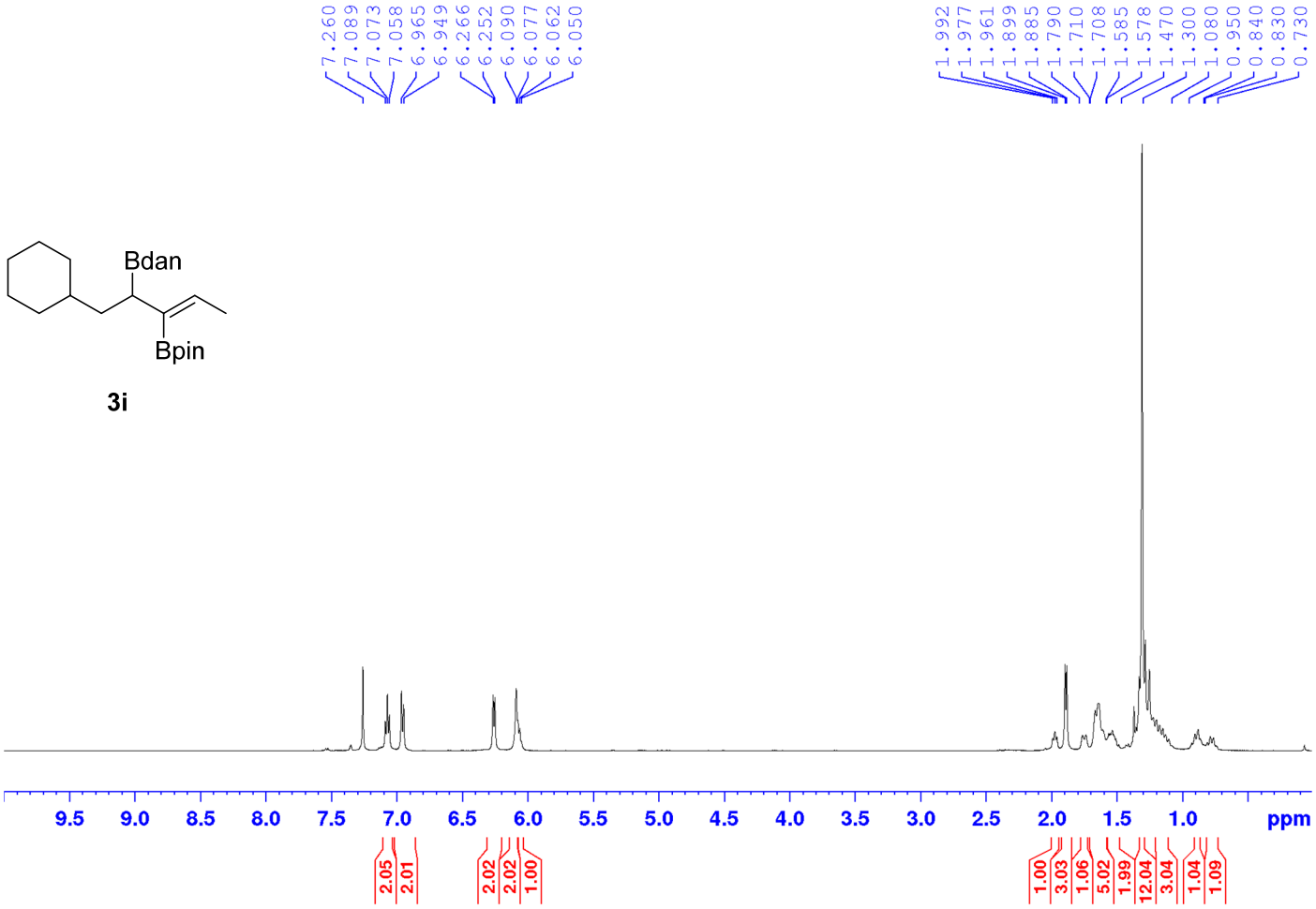
140.11
136.33
128.43
128.21
127.49
125.56
119.61
116.96
105.31
83.19
77.25
77.00
76.74
35.45
32.44
25.08
24.78
17.47
Bdan
Ph
Bpin
3h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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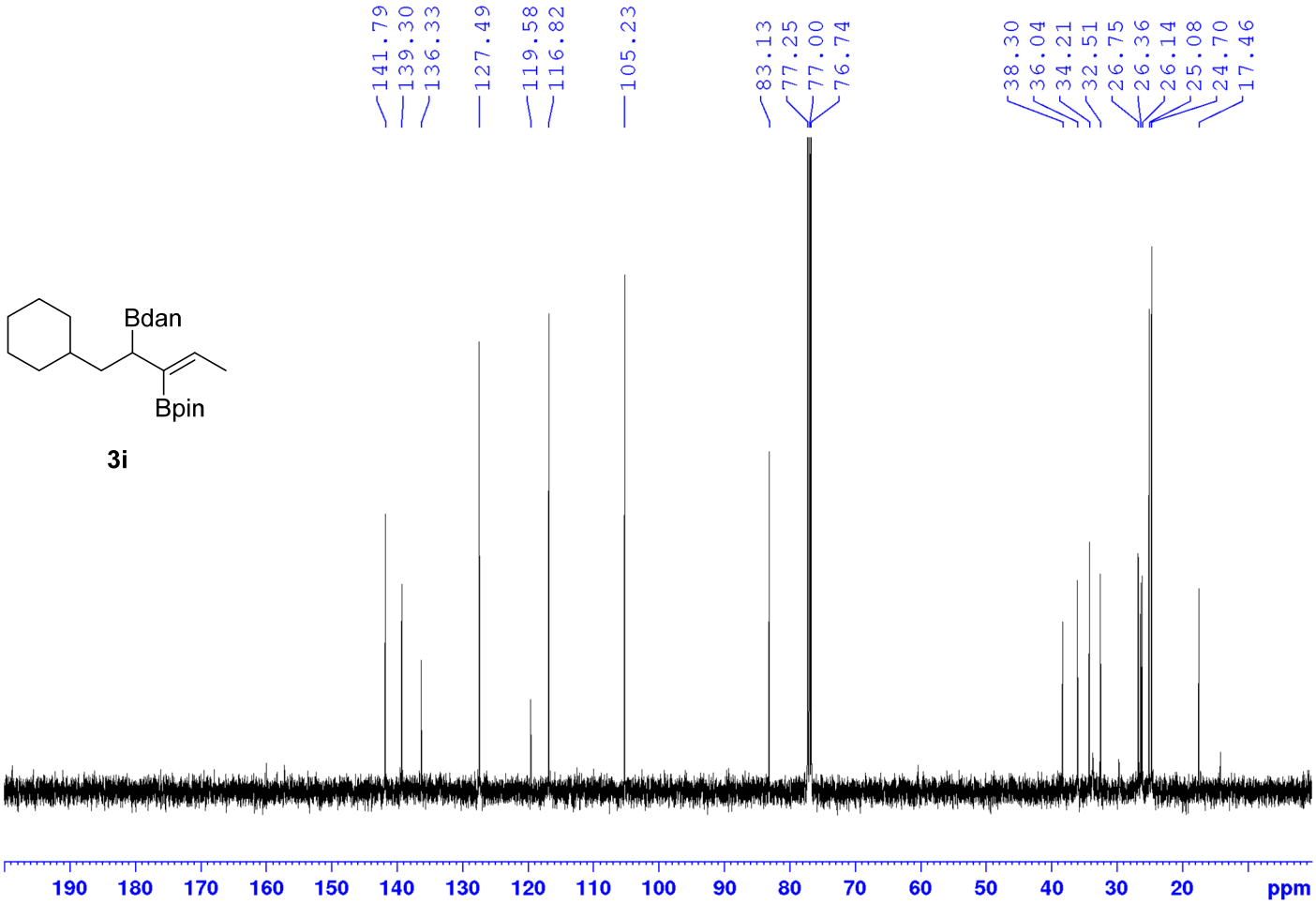
7.073
7.058
6.965
6.949
6.266
6.252
6.090
6.077
6.062
6.050
1.992
1.977
1.961
1.899
1.885
1.790
1.710
1.708
1.585
1.578
1.470
1.300
1.080
0.950
0.840
0.830
0.730
Bdan
Bpin
3i
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.05 2.01 2.02 2.02 1.00
1.00 3.03 1.06 5.02 1.99 12.04 3.04 1.04 1.09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139.30
136.33
127.49
119.58
116.82
105.23
83.13
77.25
77.00
76.74
38.30
36.04
34.21
32.51
26.75
26.36
26.14
25.08
24.70
17.46
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Bpin
3i
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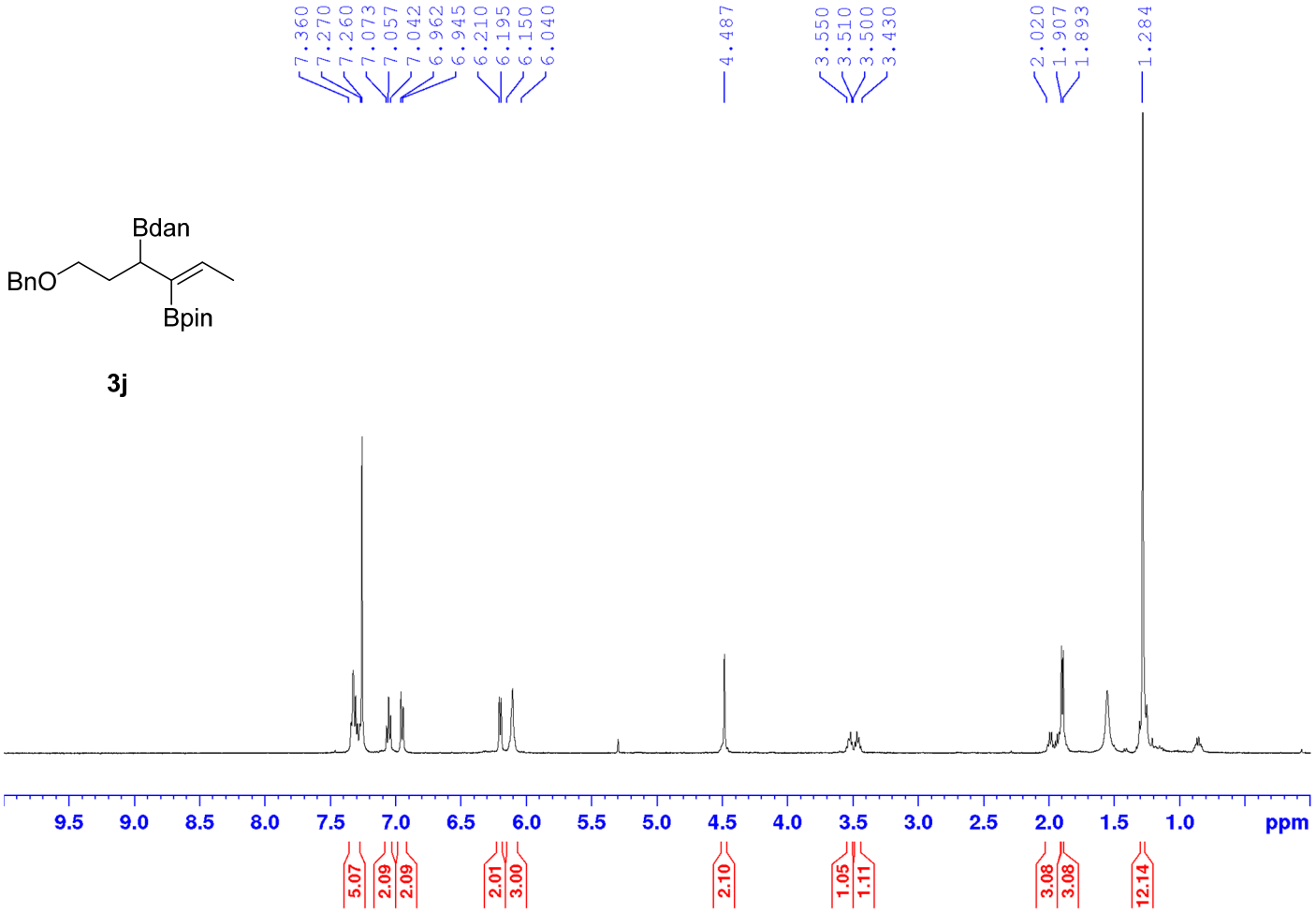
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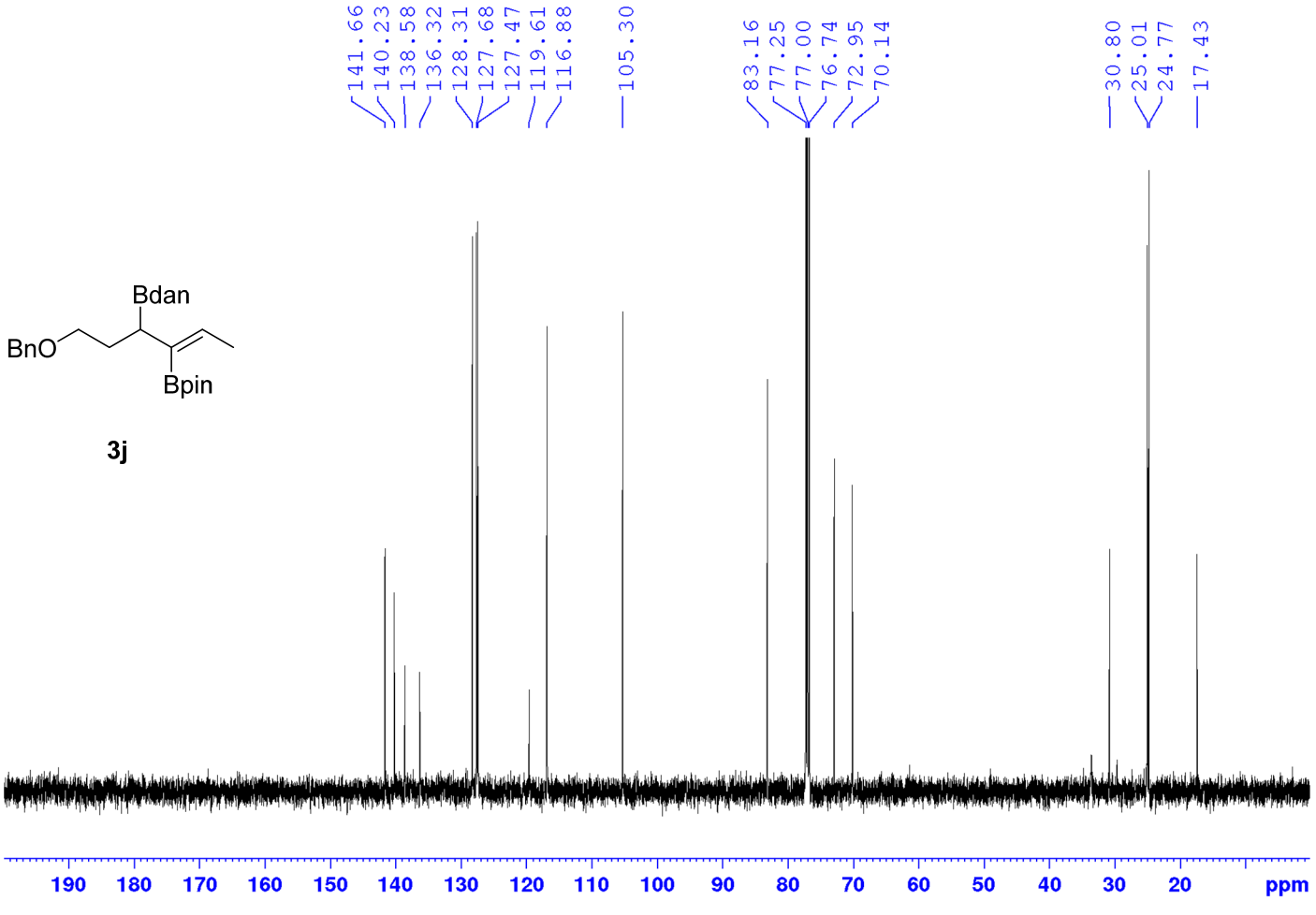
7.057
7.042
6.962
6.945
6.210
6.195
6.150
6.040
4.487
3.550
3.510
3.500
3.430
2.020
1.907
1.893
1.284
Bdan
BnO
Bpin
3j
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
5.07
2.09
2.09
2.01
3.00
2.10
1.05
1.11
3.08
3.08
12.14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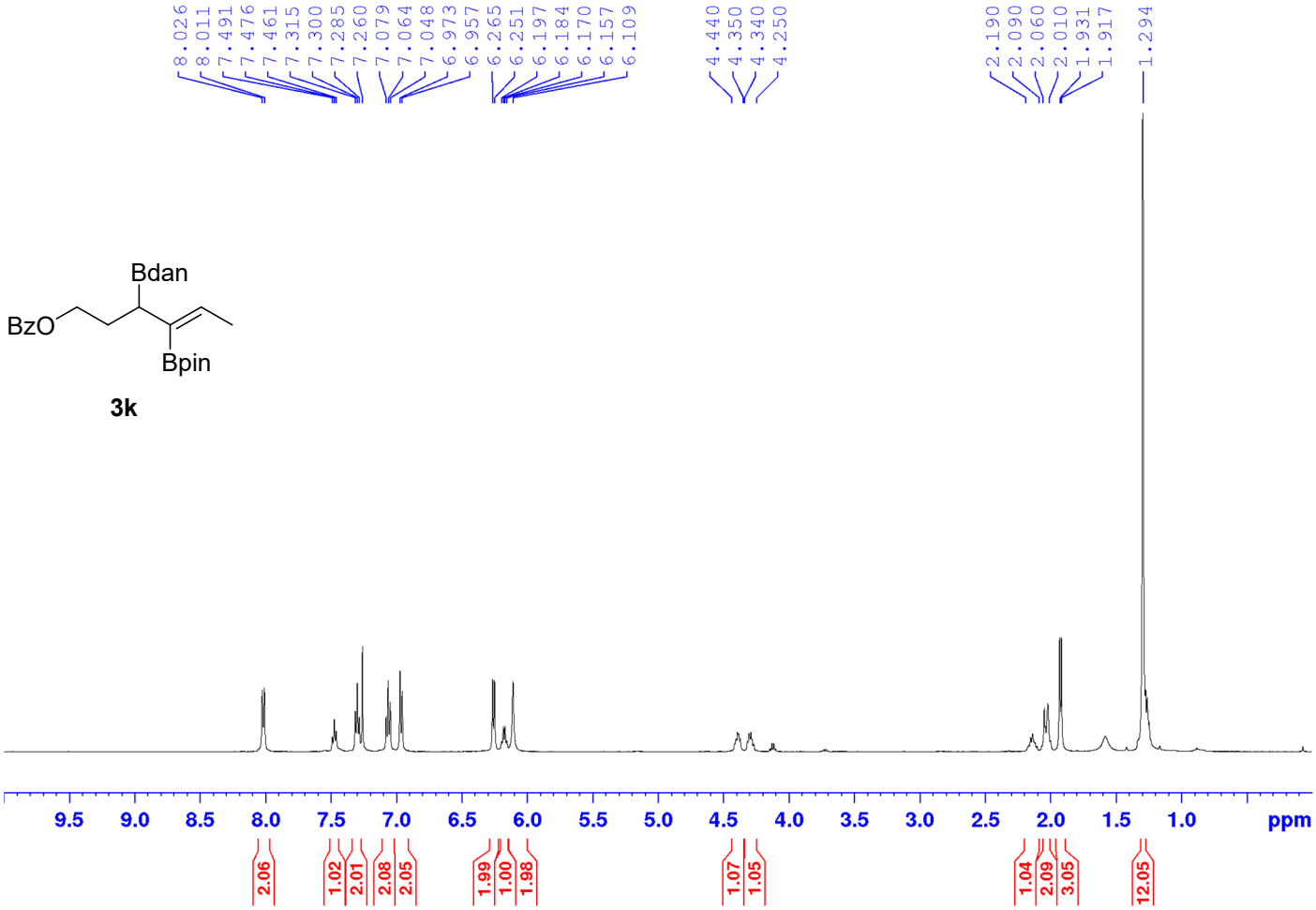
128.31
127.68
127.47
119.61
116.88
105.30
83.16
77.25
77.00
76.74
72.95
70.14
30.80
25.01
24.77
17.43
Bdan
BnO
Bpin
3j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.285
7.260
7.079
7.064
7.048
6.973
6.957
6.265
6.251
6.197
6.184
6.170
6.157
6.109
4.440
4.350
4.340
4.250
2.190
2.090
2.060
2.010
1.931
1.917
1.294
Bdan
BzO
Bpin
3k
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 ppm
2.06
1.02
2.01
2.08
2.05
1.99
1.00
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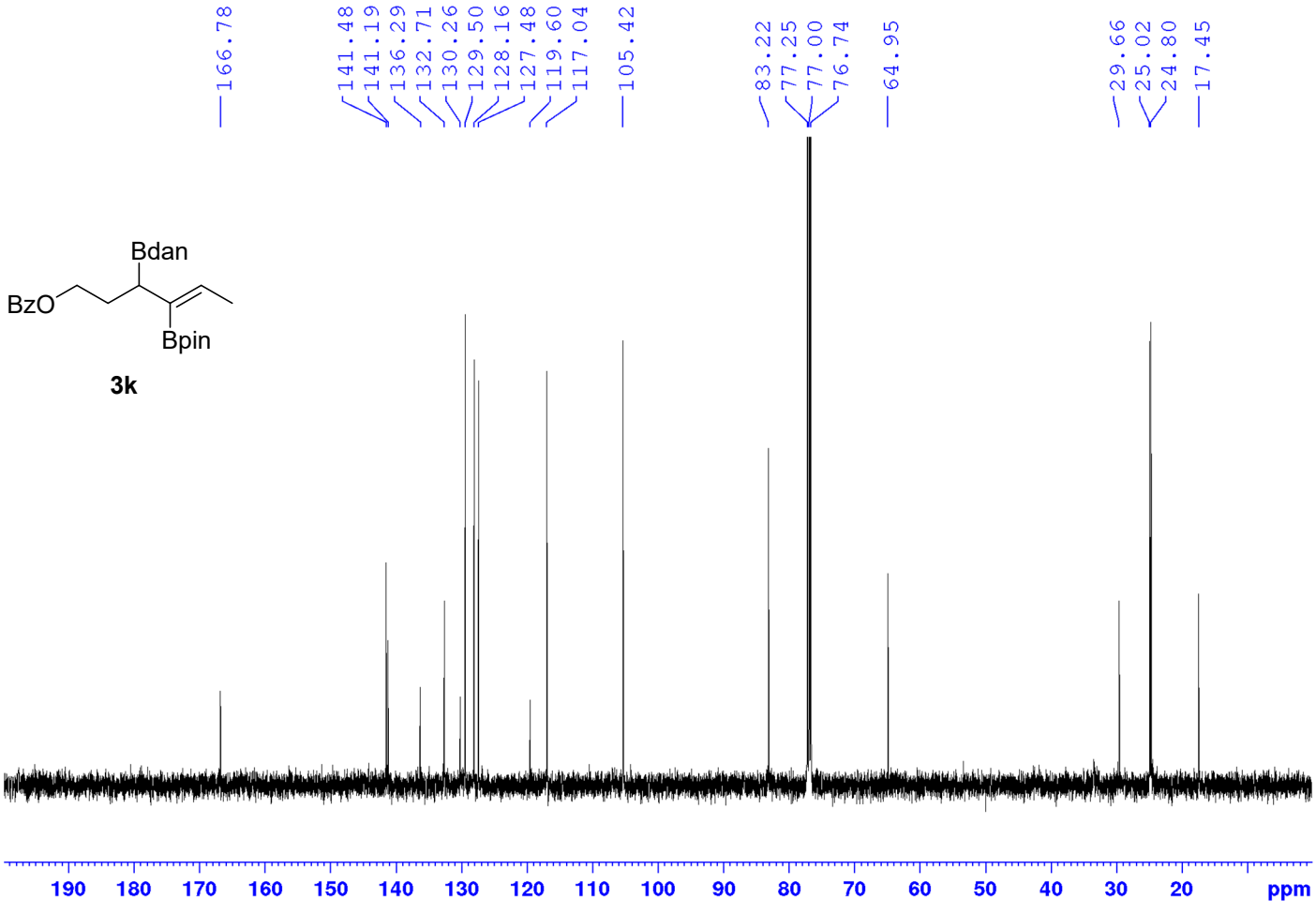
1.07
1.05
1.04
2.09
3.05
12.05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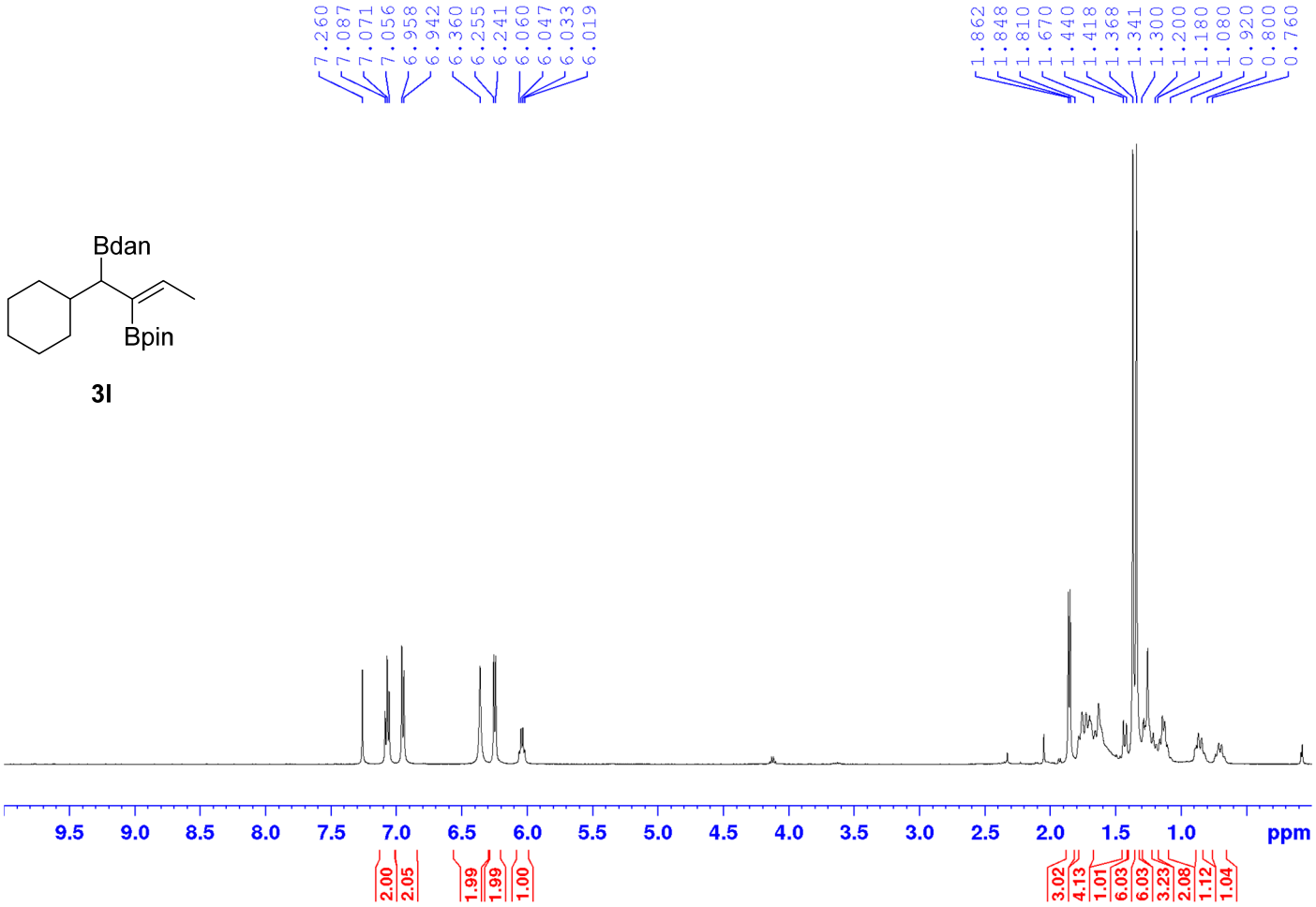
136.29
132.71
130.26
129.50
128.16
127.48
119.60
117.04
105.42
83.22
77.25
77.00
76.74
64.95
29.66
25.02
24.80
17.45
Bdan
BzO
Bpin
3k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.071
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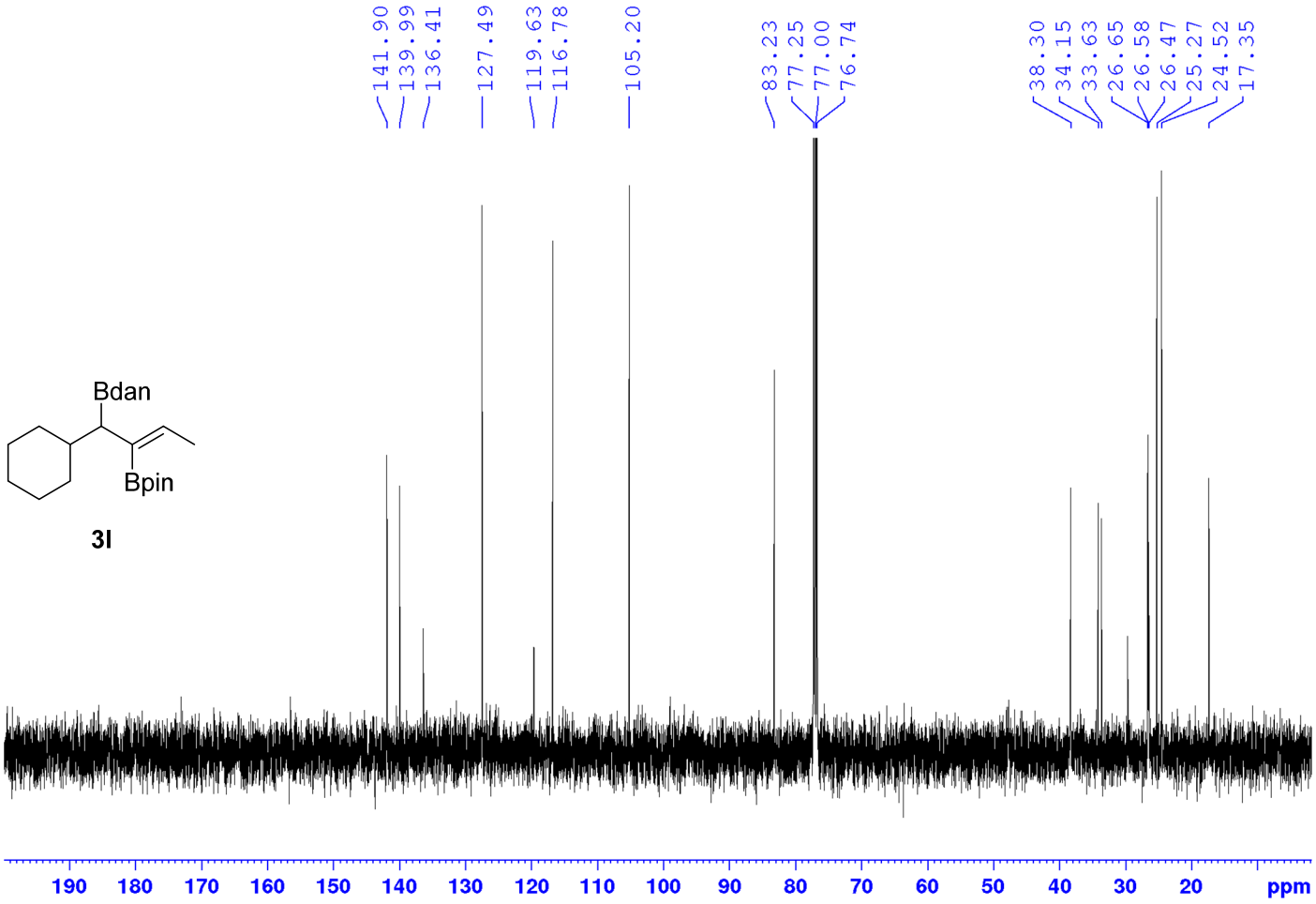
6.958
6.942
6.360
6.255
6.241
6.060
6.047
6.033
6.019
1.862
1.848
1.810
1.670
1.440
1.418
1.368
1.341
1.300
1.200
1.180
1.080
0.920
0.800
0.760
Bdan
Bpin
3l
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00 2.05 1.99 1.99 1.00
3.02 4.13 1.01 6.03 6.03 3.23 2.08 1.12 1.04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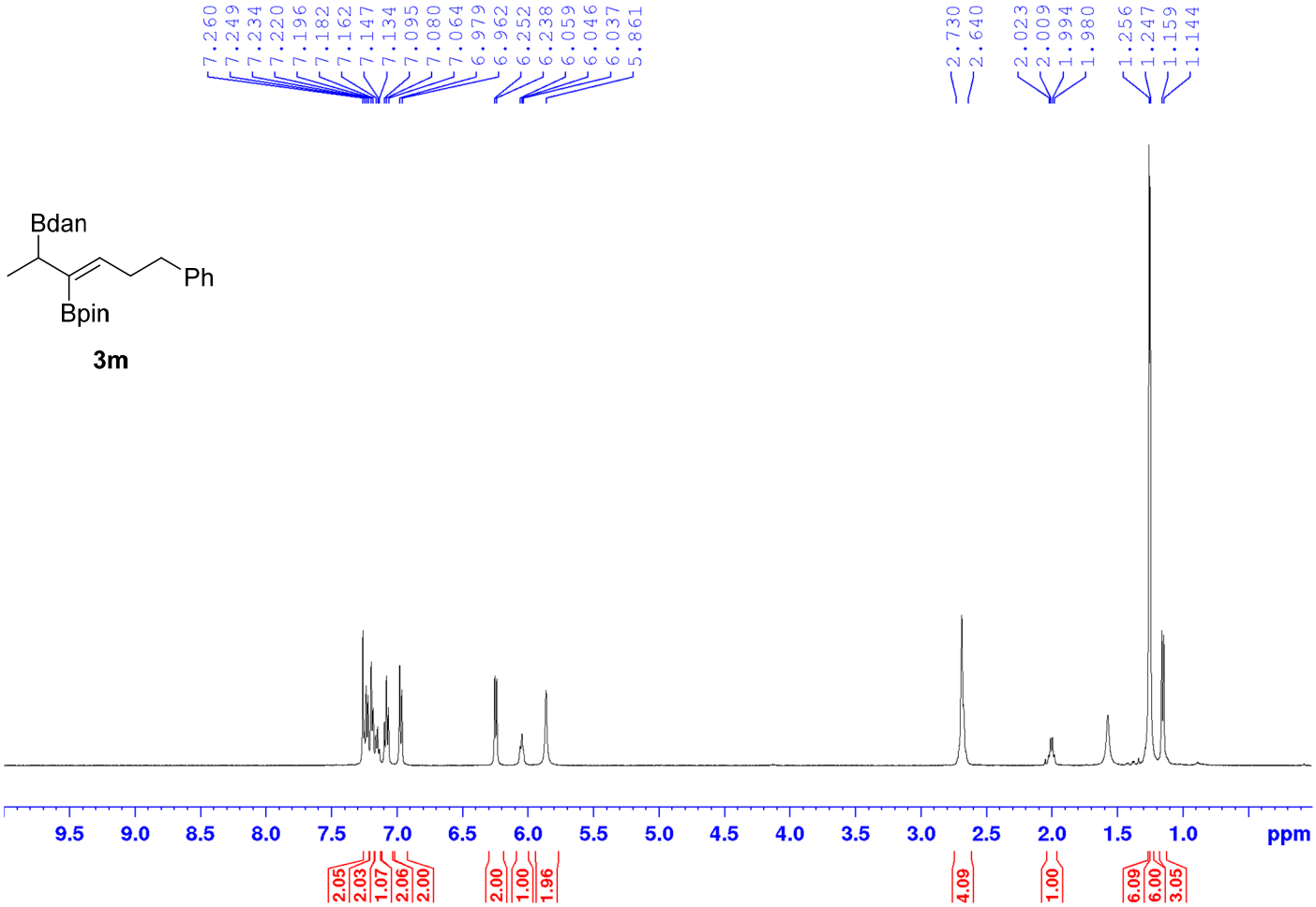
127.49
119.63
116.78
105.20
83.23
77.25
77.00
76.74
38.30
34.15
33.63
26.65
26.58
26.47
25.27
24.52
17.35
Bdan
Bpin
3l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.162
7.147
7.134
7.095
7.080
7.064
6.979
6.962
6.252
6.238
6.059
6.046
6.037
5.861
2.730
2.640
2.023
2.009
1.994
1.980
1.256
1.247
1.159
1.144
Bdan
Ph
Bpin
3m
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 ppm
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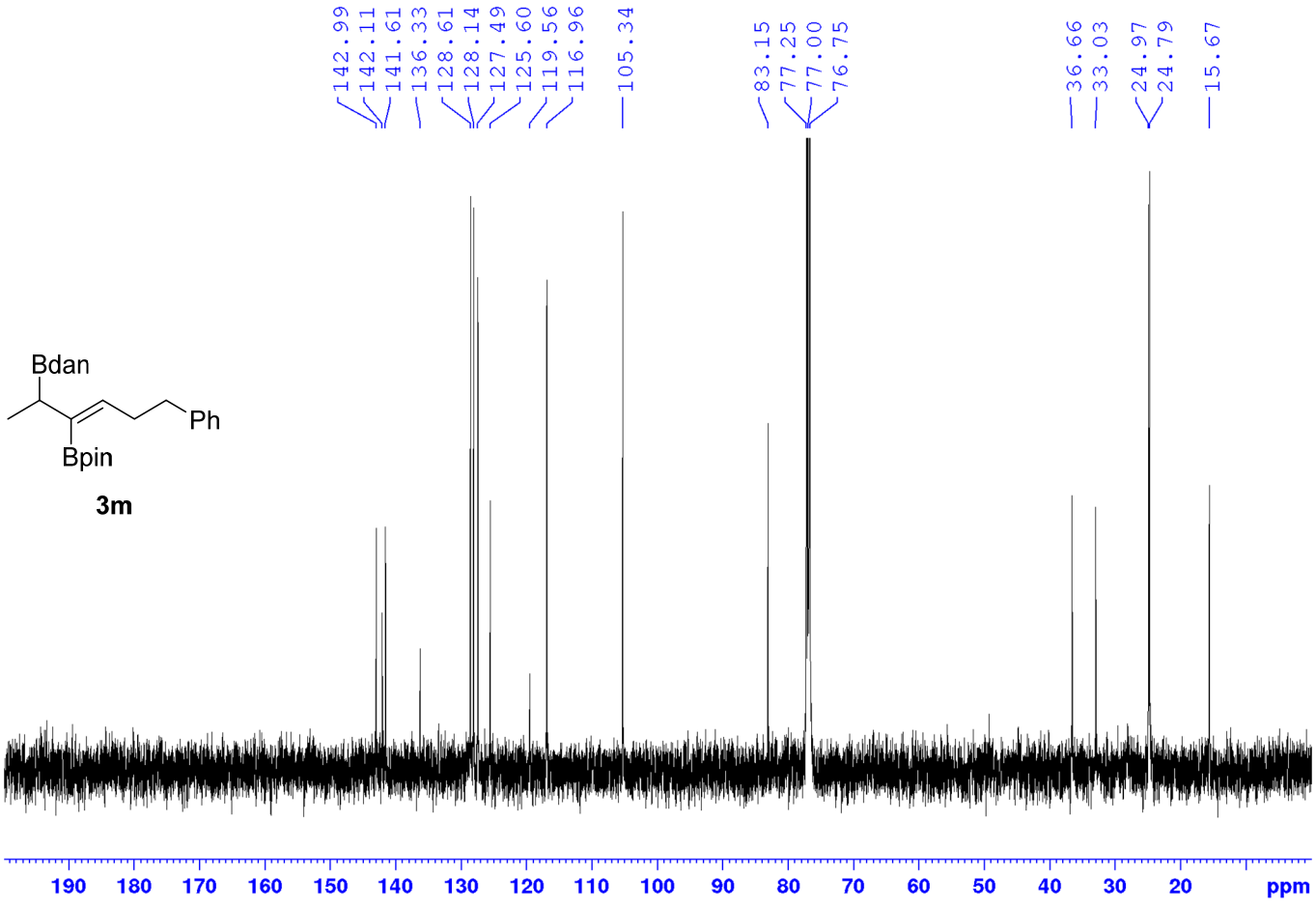
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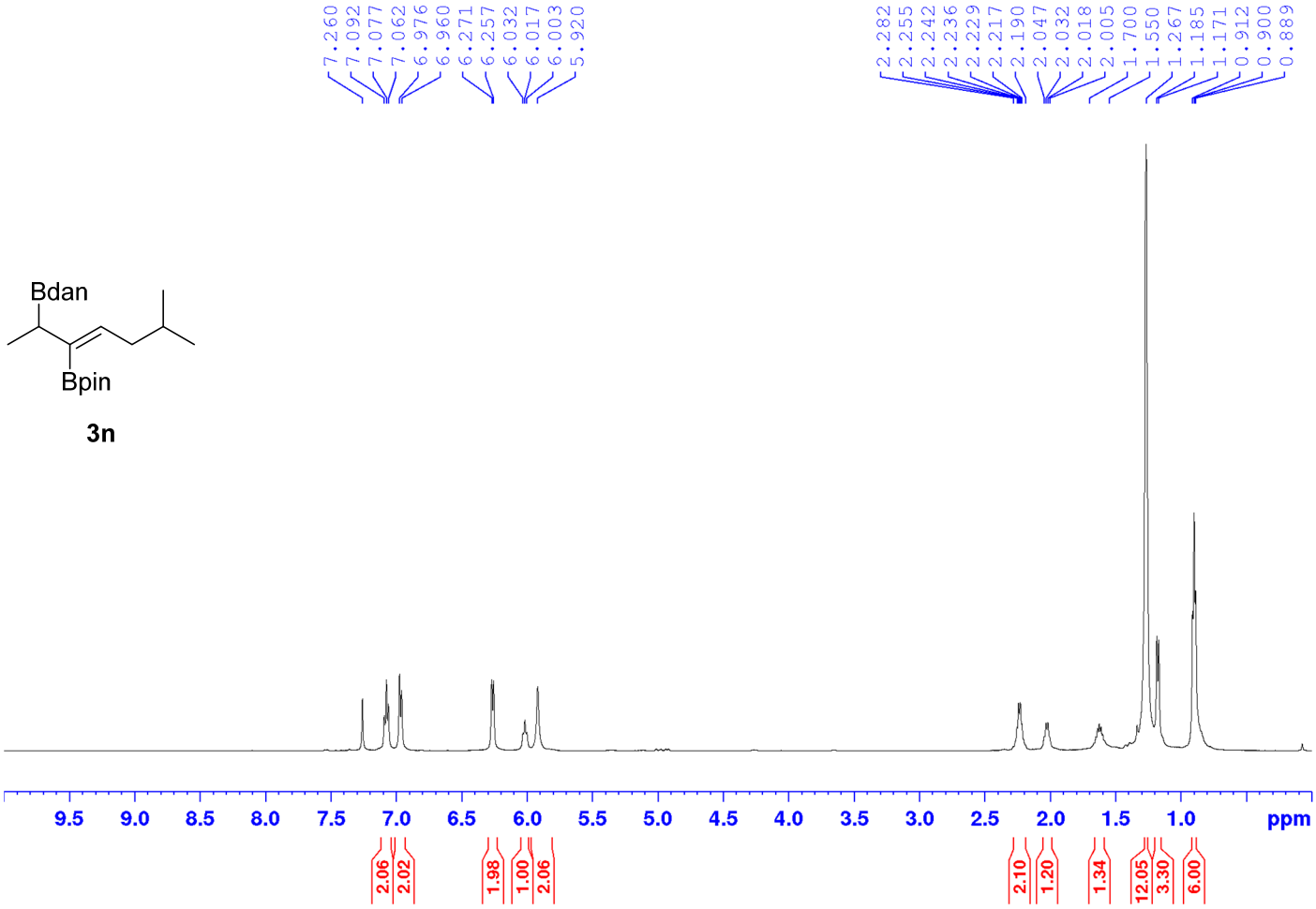
136.33
128.61
128.14
127.49
125.60
119.56
116.96
105.34
83.15
77.25
77.00
76.75
36.66
33.03
24.97
24.79
15.67
Bdan
Ph
Bpin
3m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.092
7.077
7.062
6.976
6.960
6.271
6.257
6.032
6.017
6.003
5.920
2.282
2.255
2.242
2.236
2.229
2.217
2.190
2.047
2.032
2.018
2.005
1.700
1.550
1.267
1.185
1.171
0.912
0.900
0.889
Bdan
Bpin
3n
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 ppm
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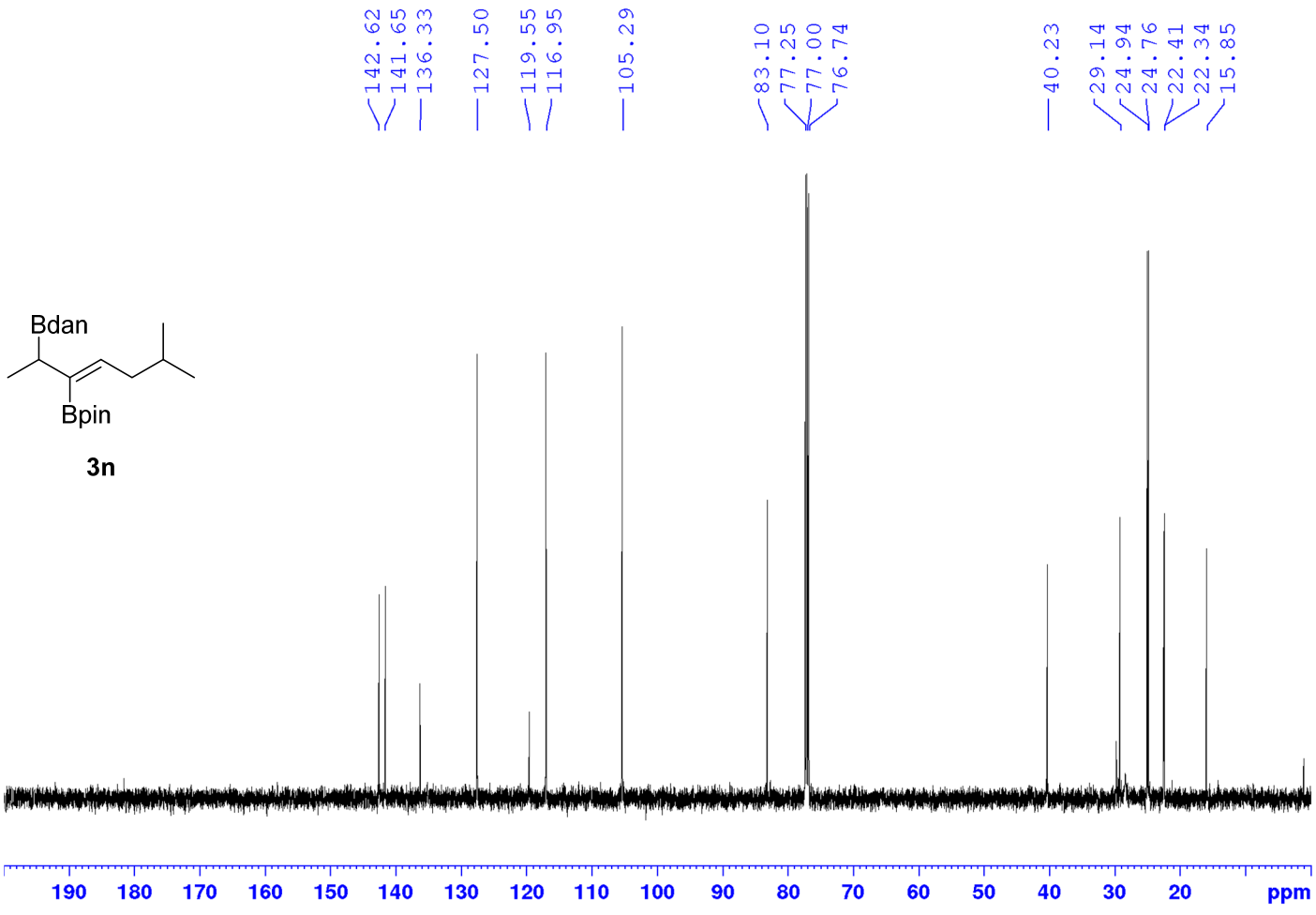
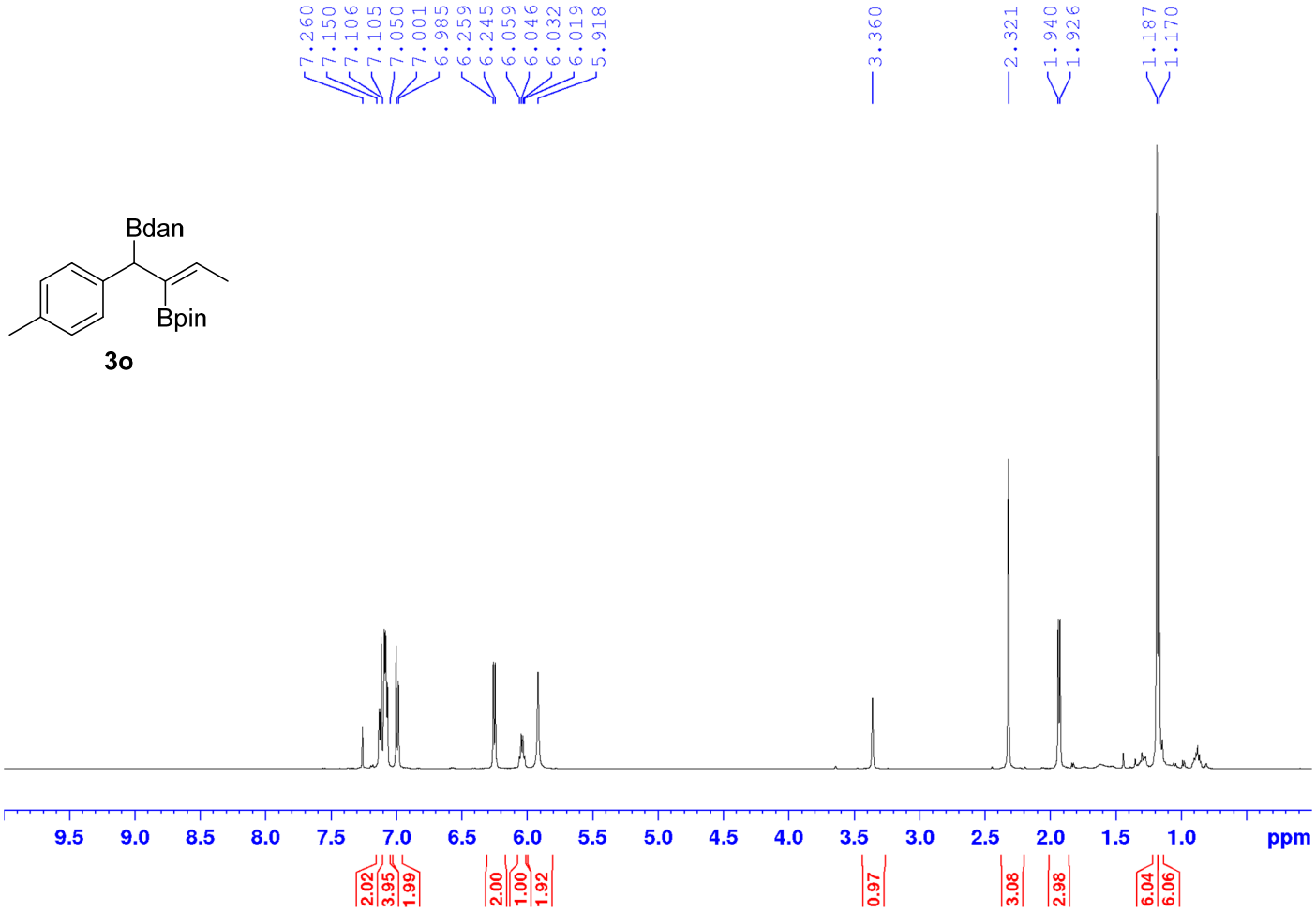
2.02
1.98
1.00
2.06
2.10
1.20
1.34
12.05
3.30
6.00


142.62
141.65
136.33
127.50
119.55
116.95
105.29
83.10
77.25
77.00
76.74
40.23
29.14
24.94
24.76
22.41
22.34
15.85
Bdan
Bpin
3n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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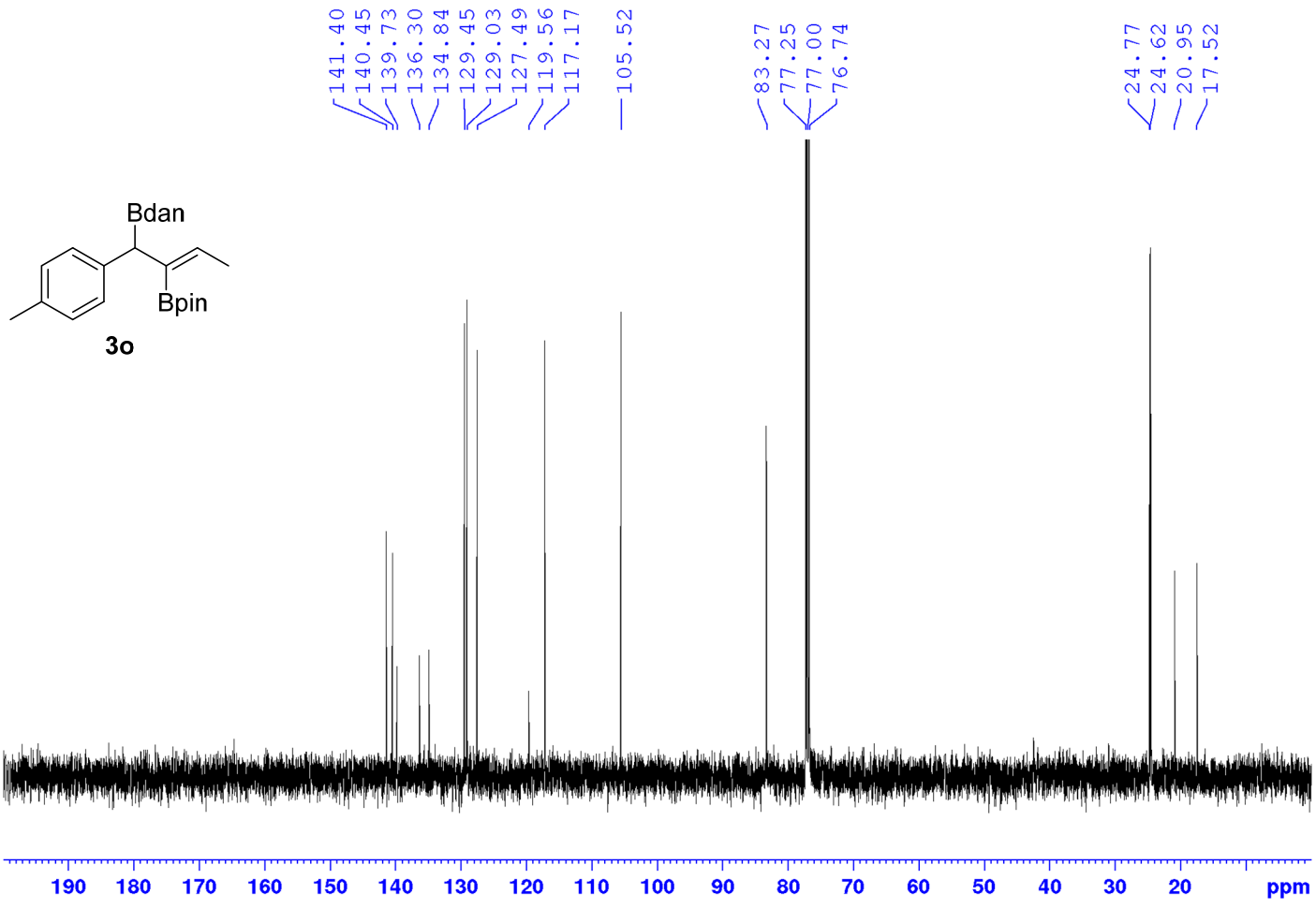
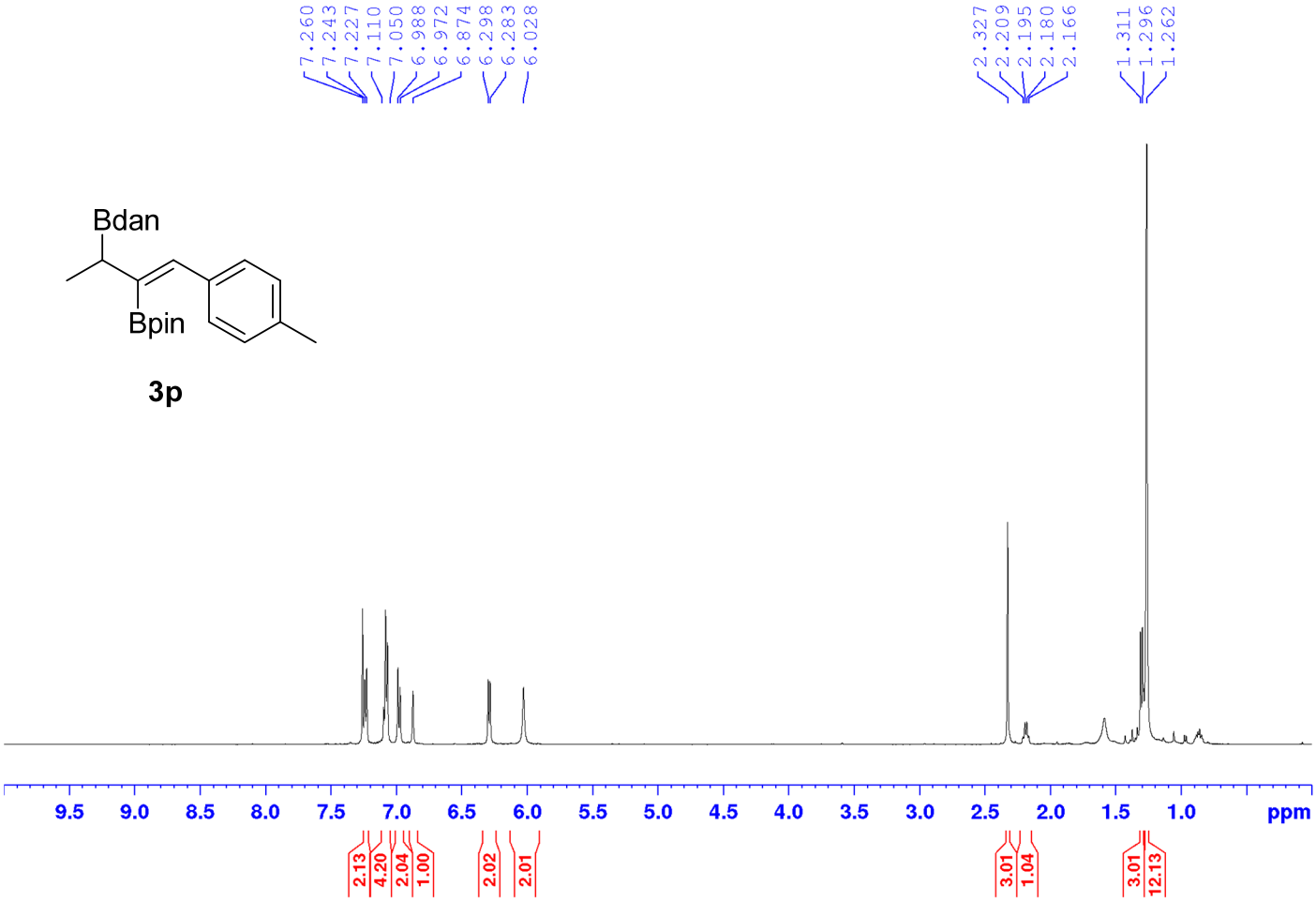
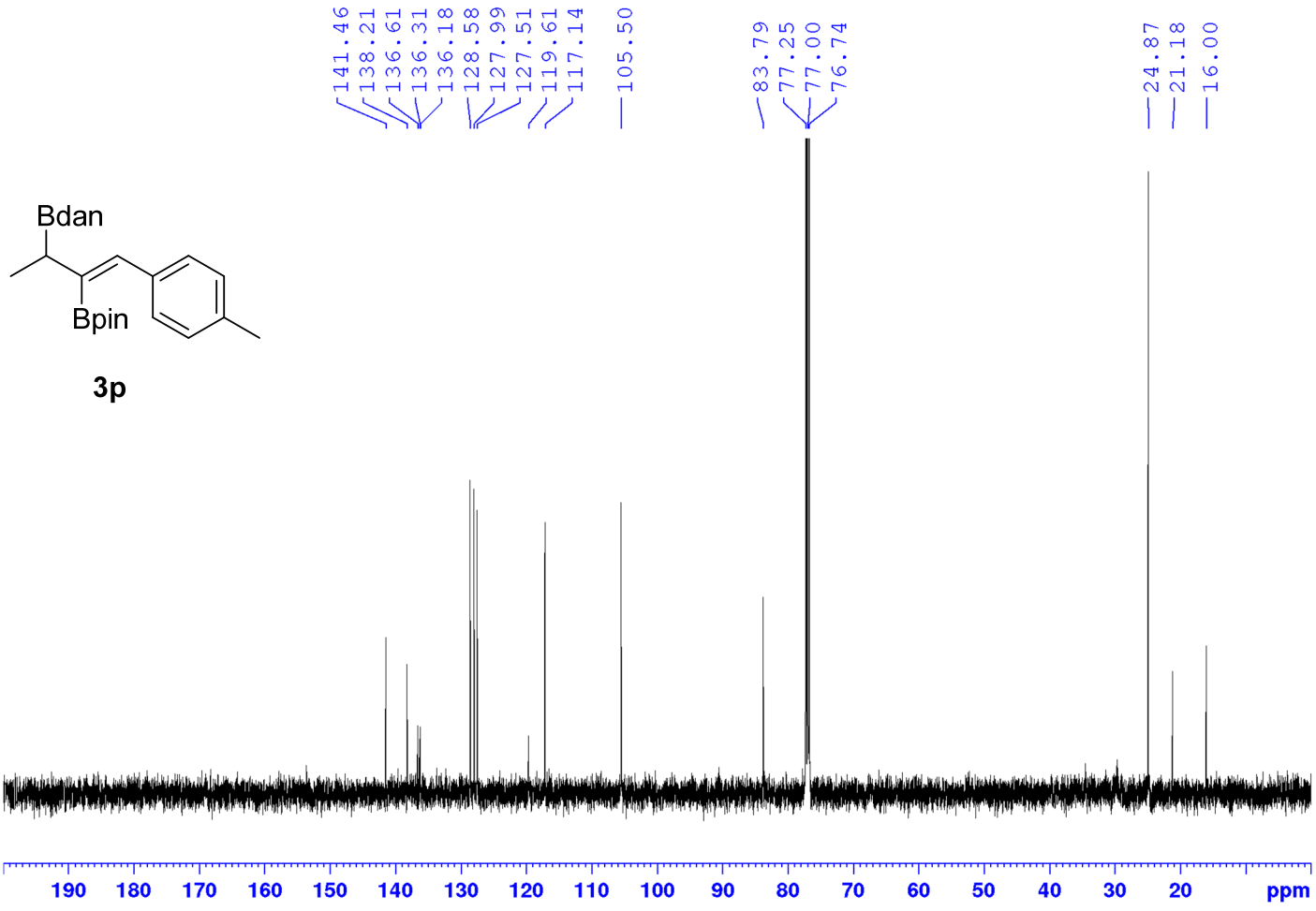
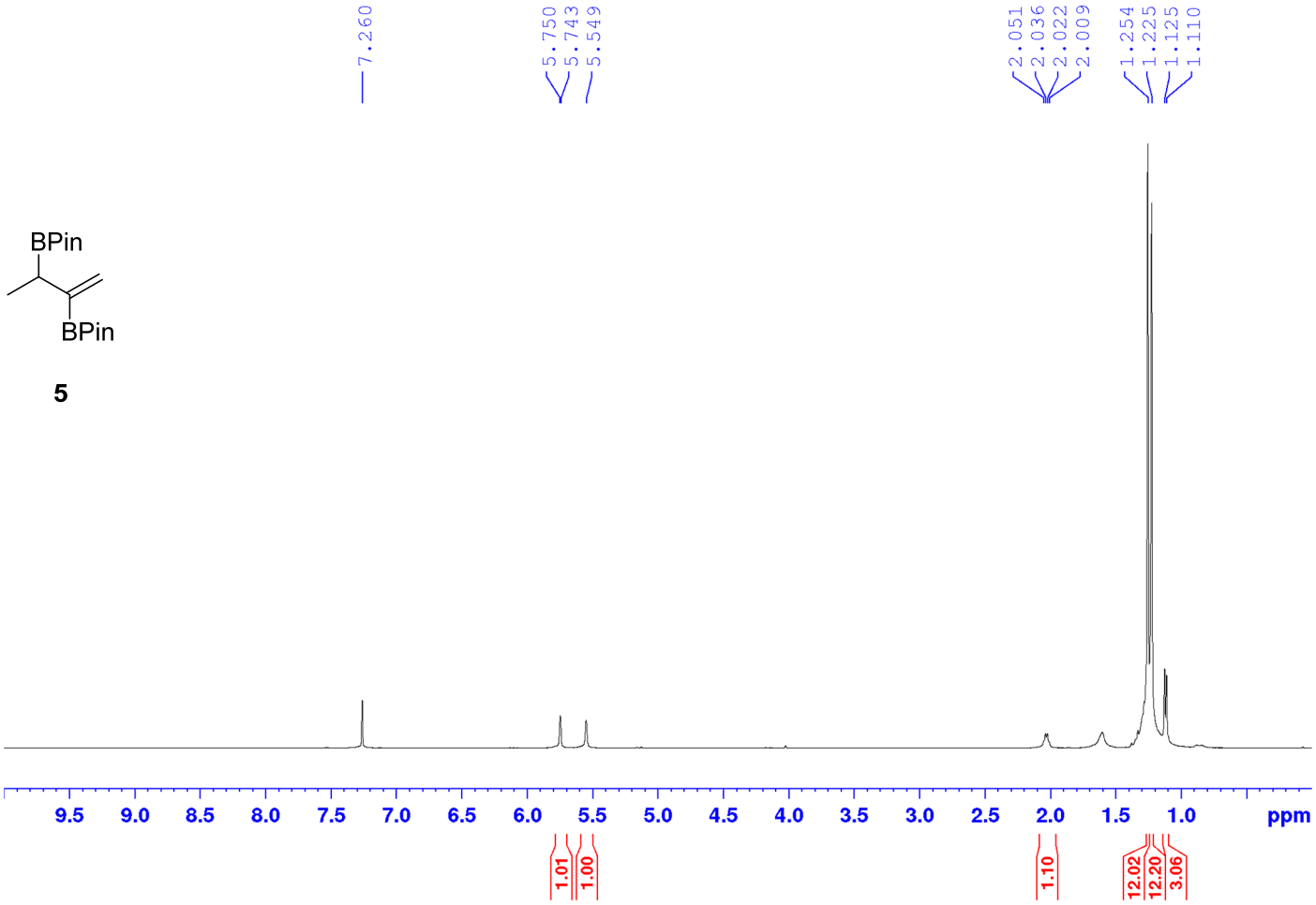
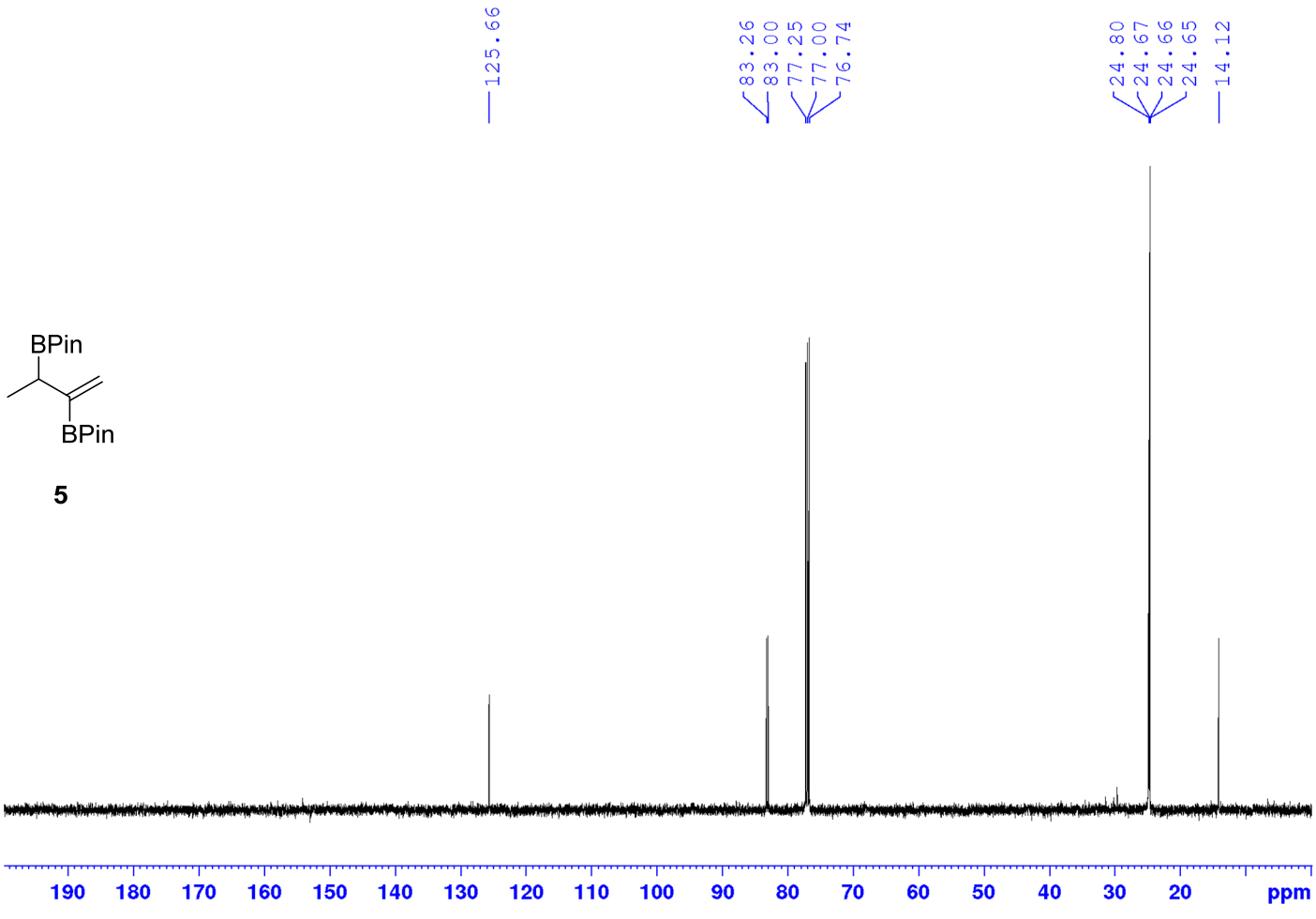
7.150
7.106
7.105
7.050
7.001
6.985
6.259
6.245
6.059
6.046
6.032
6.019
5.918
3.360
2.321
1.940
1.926
1.187
1.170
Bdan
Bpin
3o
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.02
3.95
1.99
2.00
1.00
1.92
0.97
3.08
2.98
6.04
6.06

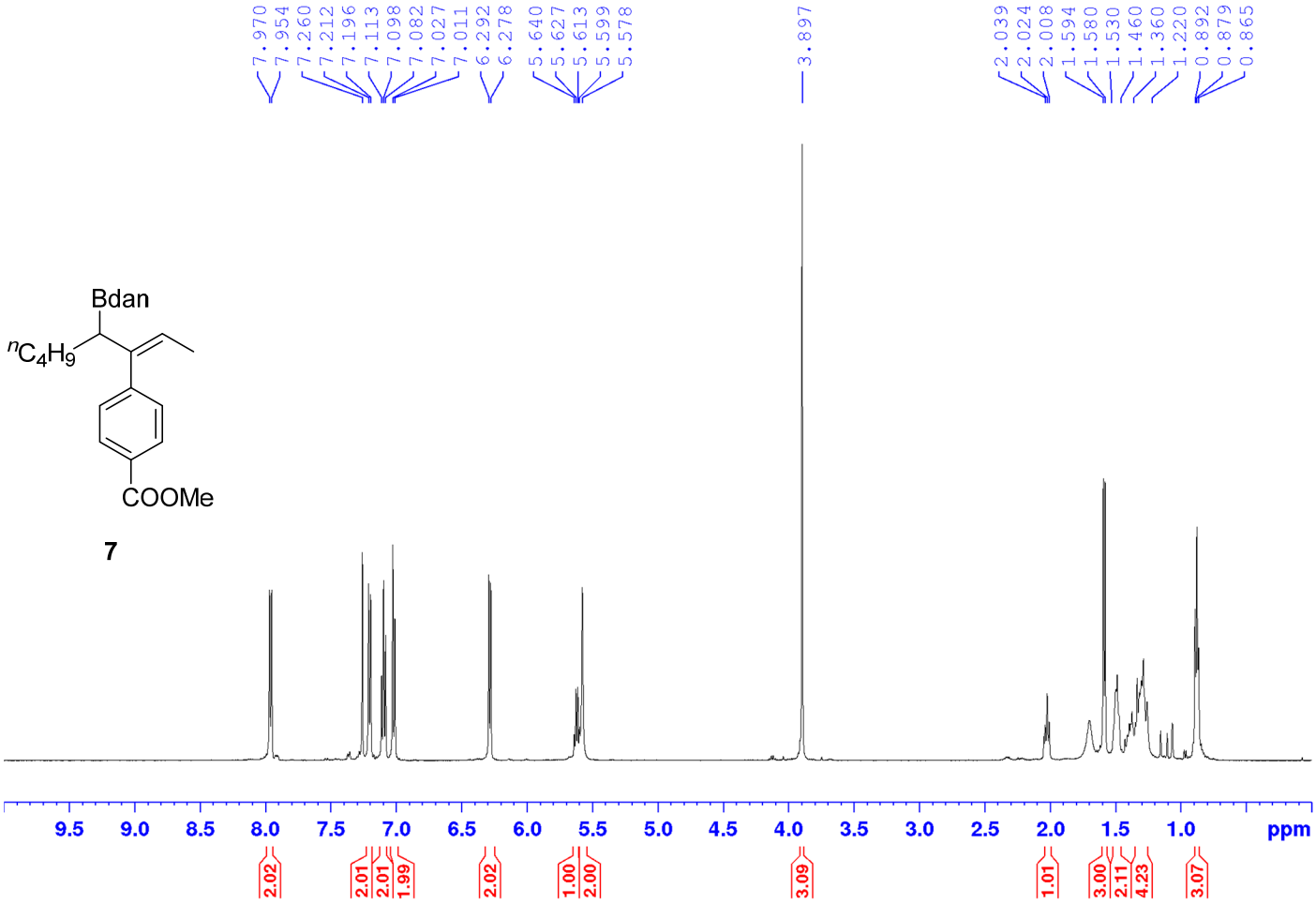

141.40
140.45
139.73
136.30
134.84
129.45
129.03
127.49
119.56
117.17
105.52
83.27
77.25
77.00
76.74
24.77
24.62
20.95
17.52
Bdan
Bpin
3o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

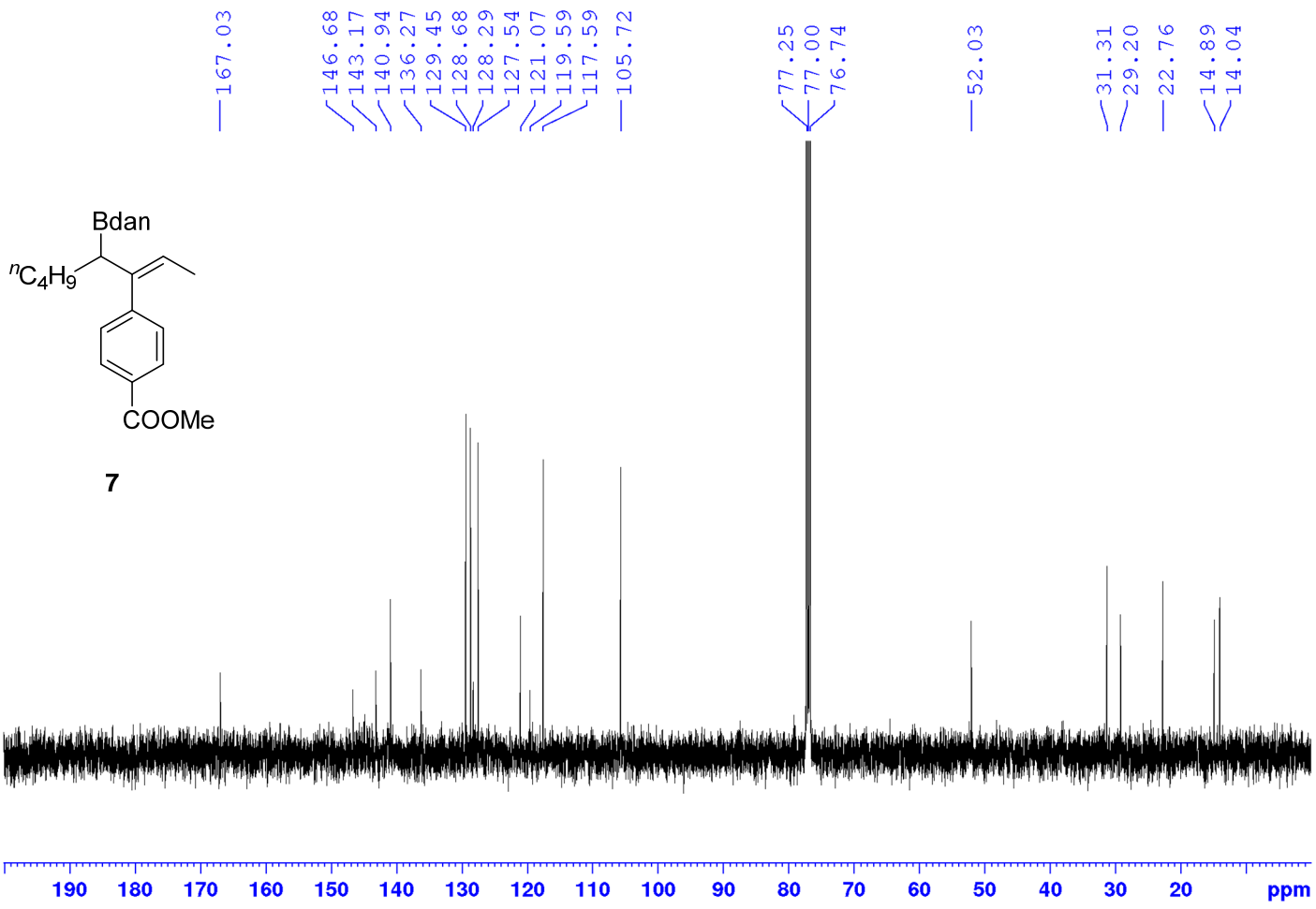

7.260
7.243
7.227
7.110
7.050
6.988
6.972
6.874
6.298
6.283
6.028
2.327
2.209
2.195
2.180
2.166
1.311
1.296
1.262
Bdan
Bpin
3p
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.13
4.20
2.04
1.00
2.02
2.01
3.01
1.04
3.01
12.13


141.46
138.21
136.61
136.31
136.18
128.58
127.99
127.51
119.61
117.14
105.50
83.79
77.25
77.00
76.74
24.87
21.18
16.00
Bdan
Bpin
3p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.260
5.750
5.743
5.549
2.051
2.036
2.022
2.009
1.254
1.225
1.125
1.110
BPin
BPin
5
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 ppm
1.01
1.00
1.10
12.02
12.20
3.06


125.66
83.26
83.00
77.25
77.00
76.74
24.80
24.67
24.66
24.65
14.12
BPin
BPin
5
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.970
7.954
7.260
7.212
7.196
7.113
7.098
7.082
7.027
7.011
6.292
6.278
5.640
5.627
5.613
5.599
5.578
3.897
2.039
2.024
2.008
1.594
1.580
1.530
1.460
1.360
1.220
0.892
0.879
0.865
Bdan
nC4H9
COOMe
7
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 ppm
2.02
2.01
2.01
1.99
2.02
1.00
2.00
3.09
1.01
3.00
2.11
4.23
3.07


167.03
146.68
143.17
140.94
136.27
129.45
128.68
128.29
127.54
121.07
119.59
117.59
105.72
77.25
77.00
76.74
52.03
31.31
29.20
22.76
14.89
14.04
Bdan
nC4H9
COOMe
7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm