Supporting Information

Synthesis of Allenyl-Bdan via a Cu(I)-catalyzed Borylation of Propargylic Alcohols with the Unsymmetric Diboron Reagent (Bpin-Bdan)

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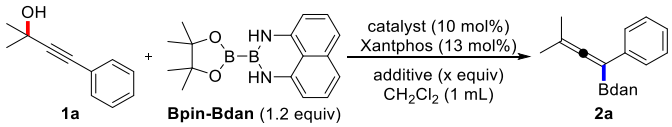
I. Optimization of Reaction Conditions

Table S1. General[a]

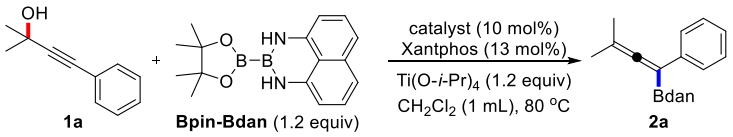


entry	catalyst	additive	temperature (ºC)	yield of 2a (%)[b]
1	$Cu(acac)_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	80	16
2	$Cu(acac)_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	80	15
3	$Cu(acac)_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	60	16
4	$Cu(acac)_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	60	15
5	$Cu(acac)_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	40	10
6	$Cu(acac)_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	100	24
7	$Cu(acac)_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	room temperature	10
8	$Cu(acac)_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	40	12
9	$Cu(acac)_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	100	16
10	$Cu(acac)_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	room temperature	12
11	$Cu(acac)_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	100	8
12	$Cu(acac)_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	100	17
13	$Cu(acac)_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	80	10
14	$Cu(OAc)_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	100	11
15	$Cu(OAc)_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	100	21
16	$Cu(OTf)_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	100	N.D.[c]
17	$CuCl_2$	Ti(O-*i*-Pr)$_4$ (1 equiv)	100	N.D.[c]
18	CuCl	Ti(O-*i*-Pr)$_4$ (1 equiv)	100	N.D.[c]
19	CuI	Ti(O-*i*-Pr)$_4$ (1 equiv)	100	N.D.[c]
20	CuOAc	Ti(O-*i*-Pr)$_4$ (1 equiv)	100	9
21	CuOAc	Ti(O-*i*-Pr)$_4$ (1 equiv)	100	14
22	-	Ti(O-*i*-Pr)$_4$ (1 equiv)	100	N.D.[c]

23	$Cu(acac)_2$	$Ti(OMe)_4$ (1 equiv)	80	9
24	$Cu(acac)_2$	$Ti(OEt)_4$ (1 equiv)	80	11
25	$Cu(acac)_2$	$Ti(O\text{-}n\text{-}Pr)_4$ (1 equiv)	80	trace
26	$Cu(acac)_2$	$Ti(O\text{-}i\text{-}Pr)_4$ (0.5 equiv)	80	<5
27	$Cu(acac)_2$	-	80	trace
28	$Cu(acac)_2$	$Ti(O\text{-}i\text{-}Pr)_4$ (1.5 equiv)	80	35
29	$Cu(OAc)_2$	$Ti(O\text{-}i\text{-}Pr)_4$ (1.5 equiv)	80	33
30	CuOAc	$Ti(O\text{-}i\text{-}Pr)_4$ (1.5 equiv)	80	40
31	$Cu(acac)_2$	$Ti(O\text{-}i\text{-}Pr)_4$ (2.2 equiv)	80	37
32	$Cu(OAc)_2$	$Ti(O\text{-}i\text{-}Pr)_4$ (2.2 equiv)	80	40
33	CuOAc	$Ti(O\text{-}i\text{-}Pr)_4$ (2.2 equiv)	80	42

[a] All reactions were carried out on a 0.2 mmol scale under argon atmosphere. Catalyst (10 mol%), Xantphos (13 mol%), Bpin-Bdan (1.2 equiv), additive (x equiv), CH_2Cl_2 (1 mL), 18 h. [b] Isolated yields. [c] N.D. = not detected.

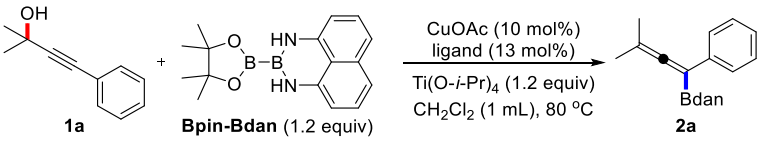
Table S2. Catalyst[a]



entry	catalyst	Yield of 2a (%)[b]
1	$Cu(OAc)_2$	43
2	$Cu(OTf)_2$	N.D.[c]
3	$CuCl_2$	N.D.[c]
4	CuCl	N.D.[c]
5	CuI	N.D.[c]
6	CuOAc	63
7	$Fe(acac)_3$	N.D.[c]
8	$FeCl_3$	N.D.[c]
9	$Fe(OTf)_3$	N.D.[c]
10	$FeCl_2$	N.D.[c]
11	$Fe(OTf)_2$	N.D.[c]

[a] All reactions were carried out on a 0.2 mmol scale under argon atmosphere. Catalyst (10 mol%), Xantphos (13 mol%), Bpin-Bdan (1.2 equiv), Ti(O-*i*-Pr)$_4$ (1.2 equiv), CH_2Cl_2 (1 mL), 80 °C, 18 h. [b] Isolated yields. [c] N.D. = not detected.

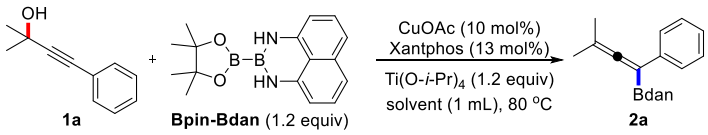
Table S3. Ligand[a]



entry	ligand	yield of 2a (%)[b]
1	P(*p*-tol)$_3$	N.D.[c]
2	dppp	N.D.[c]
3	dppe	N.D.[c]
4	dppbe	N.D.[c]
5	PPh$_3$	N.D.[c]

[a] All reactions were carried out on a 0.2 mmol scale under argon atmosphere. CuOAc (10 mol%), ligand (13 mol%), Bpin-Bdan (1.2 equiv), Ti(O-*i*-Pr)$_4$ (1.2 equiv), CH_2Cl_2 (1 mL), 80 °C, 18 h. [b] Isolated yields. [c] N.D. = not detected.

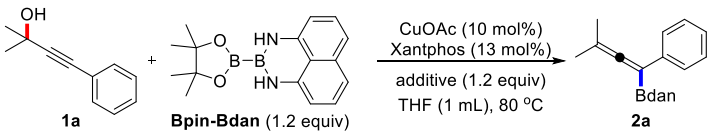
Table S4. Solvent[a]



entry	solvent	yield of 2a (%)[b]
1	toluene	62
2	MTBE	43
3	Et_2O	32
4	THF	87

[a] All reactions were carried out on a 0.2 mmol scale under argon atmosphere. CuOAc (10 mol%), Xantphos (13 mol%), Bpin-Bdan (1.2 equiv), Ti(O-*i*-Pr)$_4$ (1.2 equiv), solvent (1 mL), 80 °C, 18 h. [b] Isolated yields.

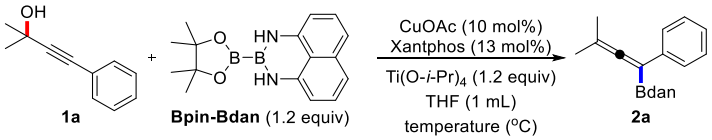
Table S5. Additive[a]



entry	additive	yield of 2a (%)[b]
1	B(O-*i*-Pr)$_3$	N.D.[c]
2	B(OMe)$_3$	N.D.[c]
3	BEt$_3$	N.D.[c]
4	Na(O-*t*-Bu)	N.D.[c]
5	K(O-*t*-Bu)	N.D.[c]
6	Ti(OMe)$_4$	9
7	Ti(O-*n*-Pr)$_4$	23
8	Ti(OEt)$_4$	11

[a] All reactions were carried out on a 0.2 mmol scale under argon atmosphere. CuOAc (10 mol%), Xantphos (13 mol%), Bpin-Bdan (1.2 equiv), additive (1.2 equiv), THF (1 mL), 80 °C, 18 h. [b] Isolated yields. [c] N.D. = not detected.

Table S6. Temperature[a]



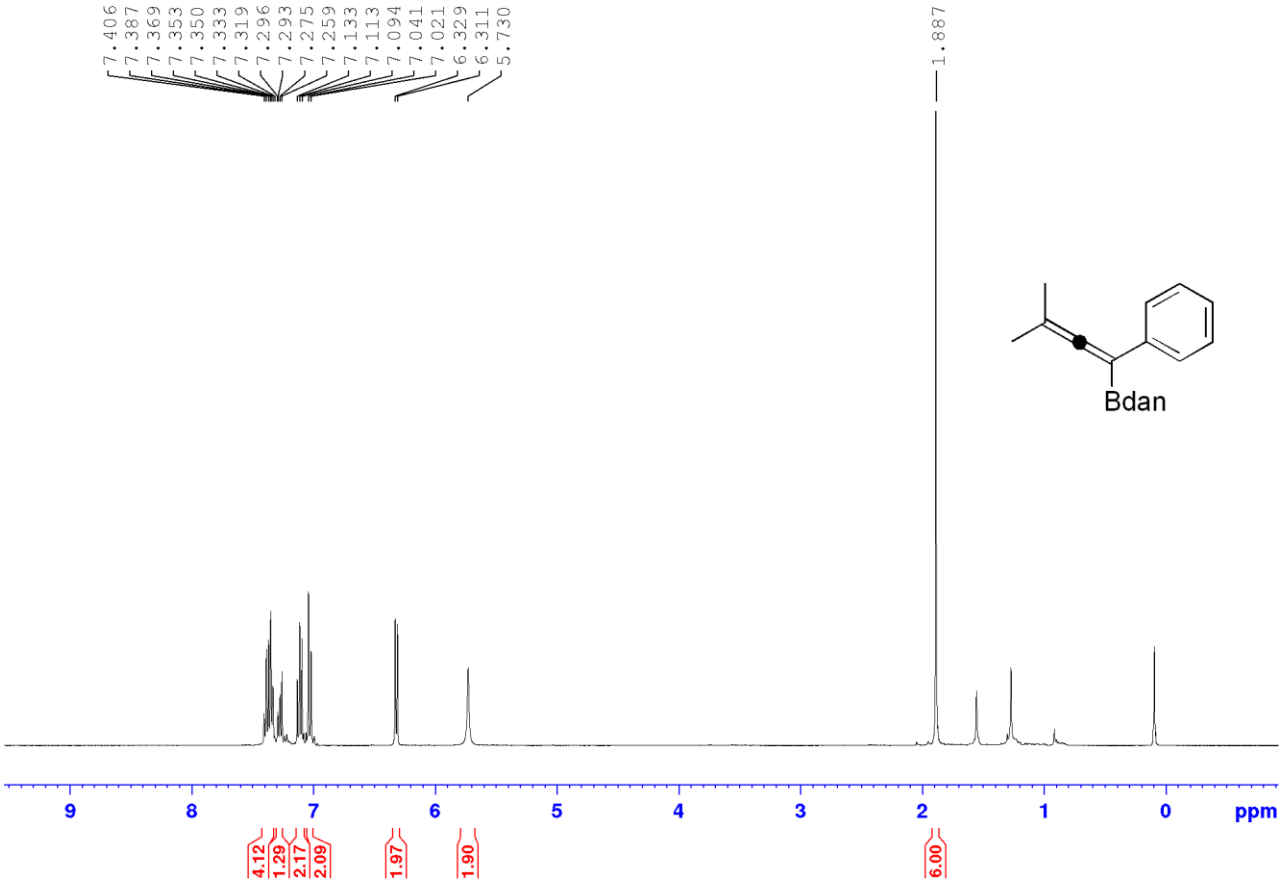
entry	temperature (°C)	yield of 2a (%)[b]
1	60	72
2	40	31
3	room temperature	N.D.[c]

[a] All reactions were carried out on a 0.2 mmol scale under argon atmosphere. CuOAc (10 mol%), Xantphos (13 mol%), Bpin-Bdan (1.2 equiv), additive (1.2 equiv), THF (1 mL), temperature (°C), 18 h. [b] Isolated yields. [c] N.D. = not detected.

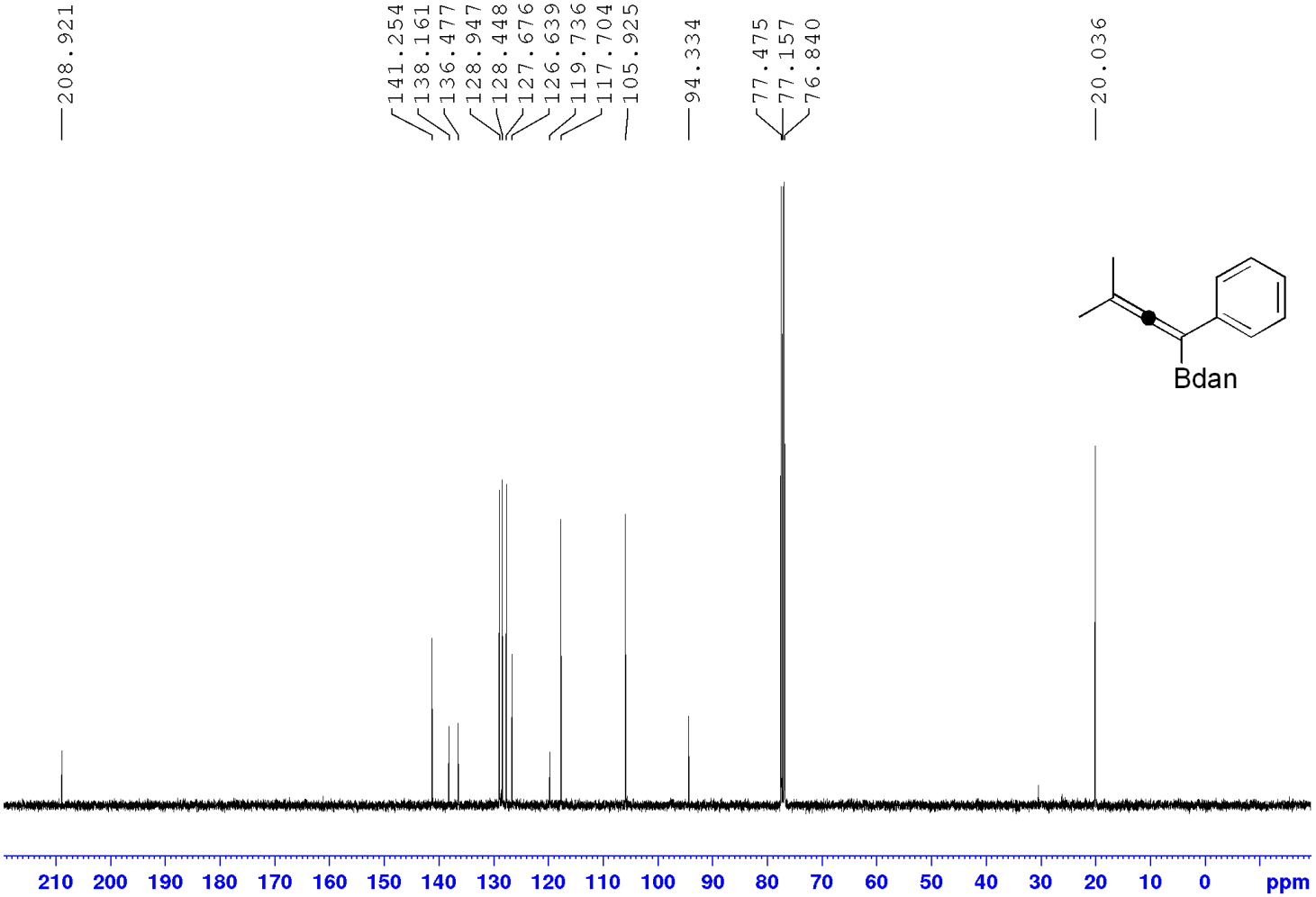
II. ^{1}H, ^{13}C, and ^{11}B NMR Spectra

Compound 2a

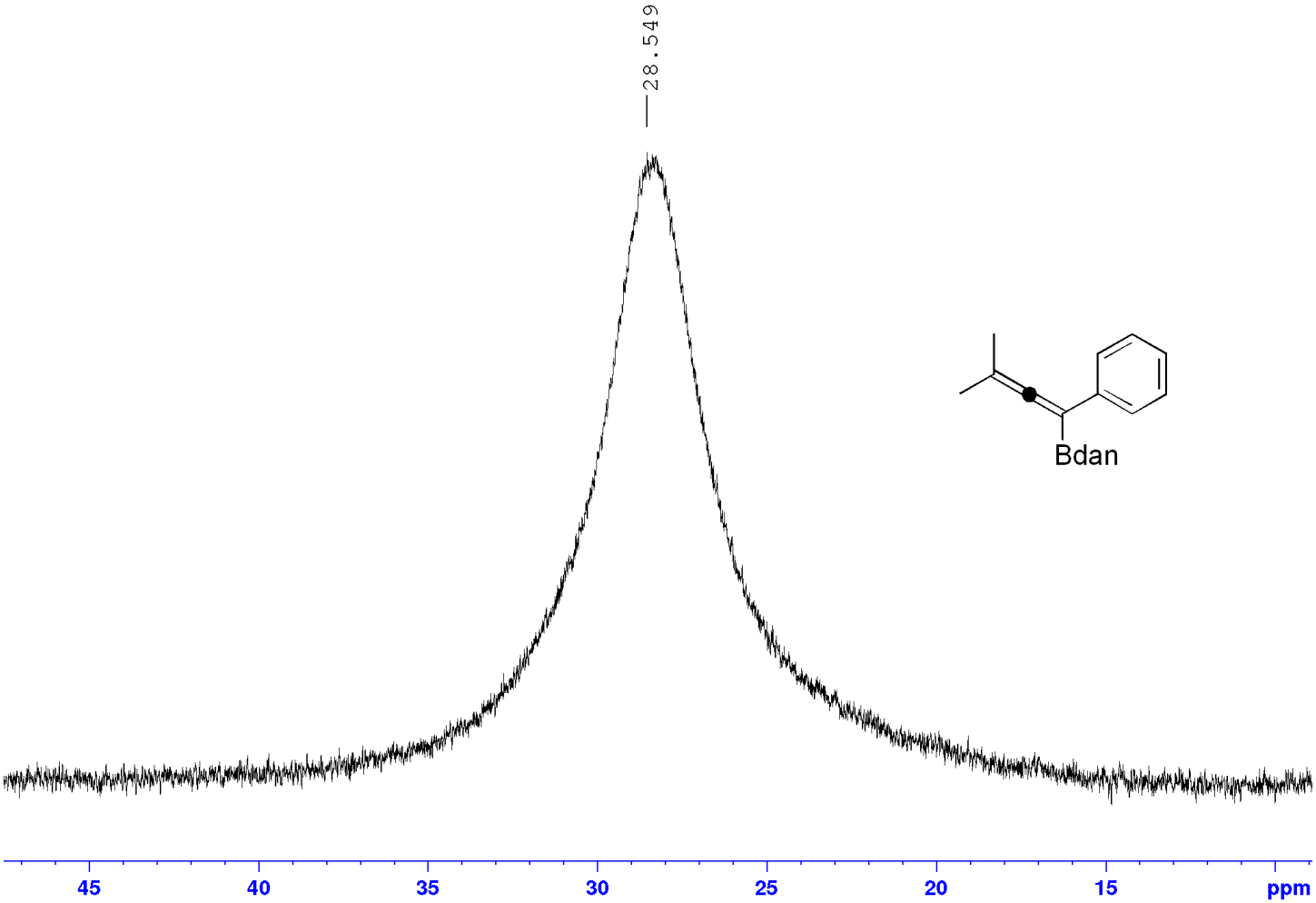
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

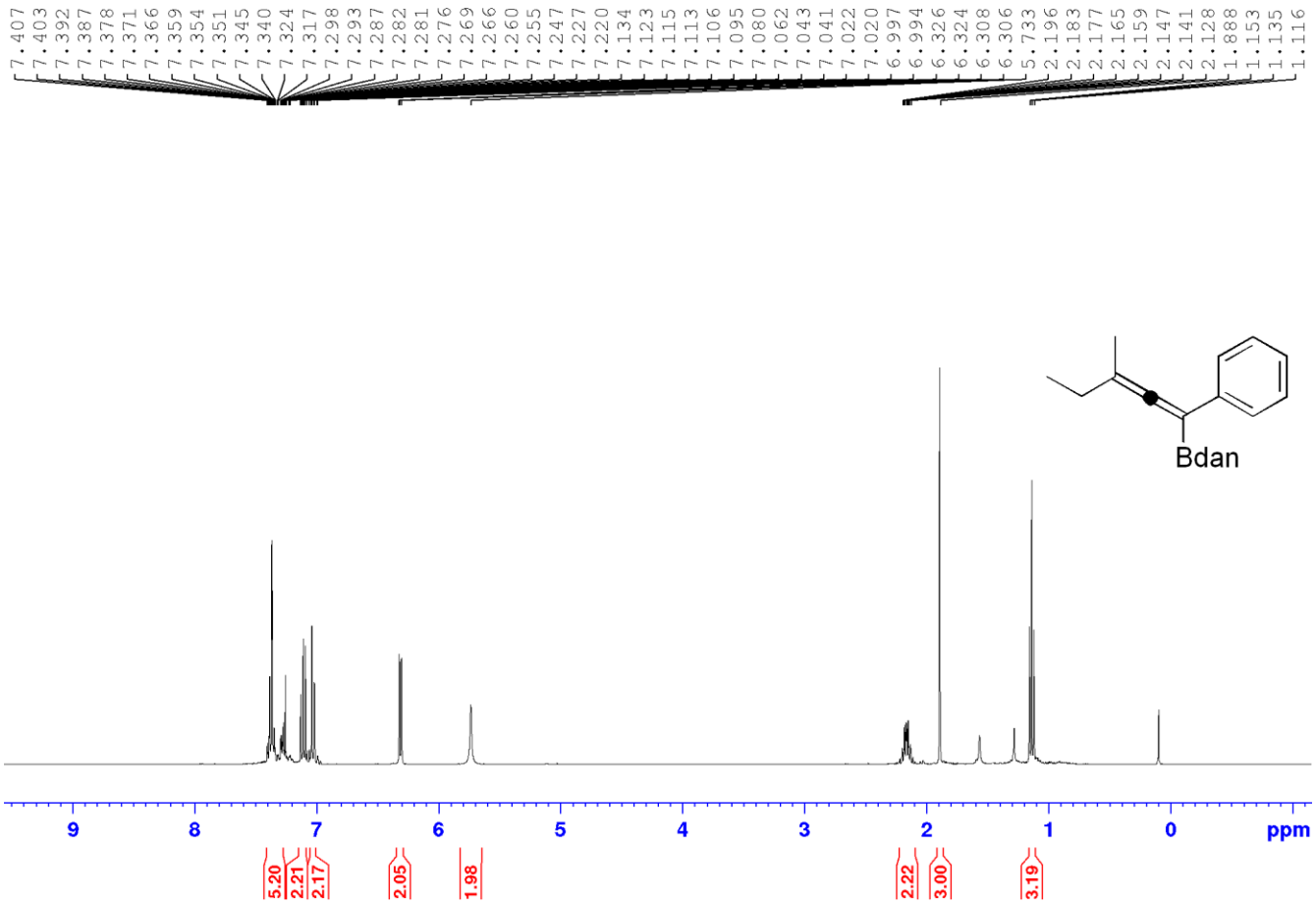


^{11}B NMR (128 MHz, $CDCl_3$)

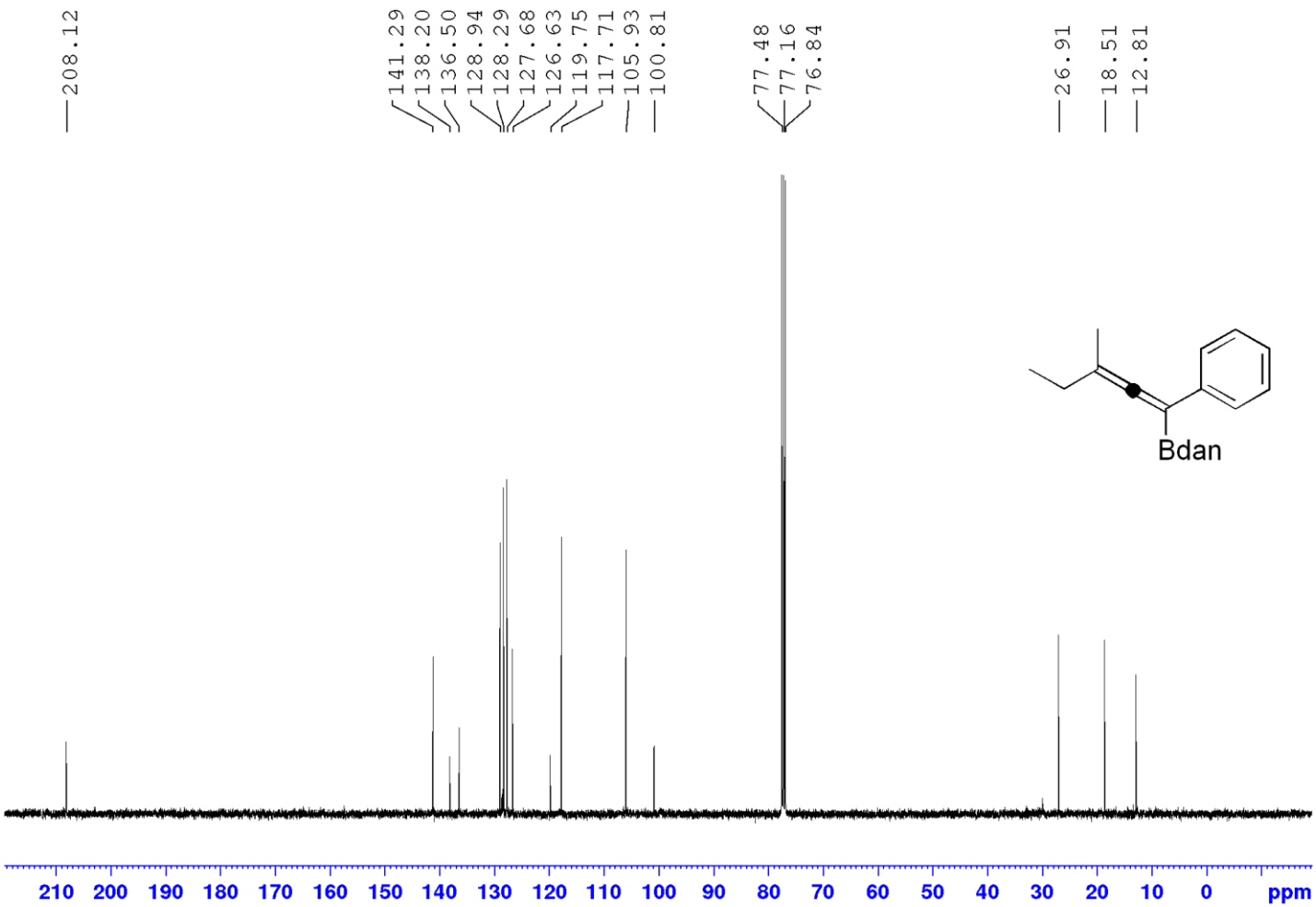


Compound 2b

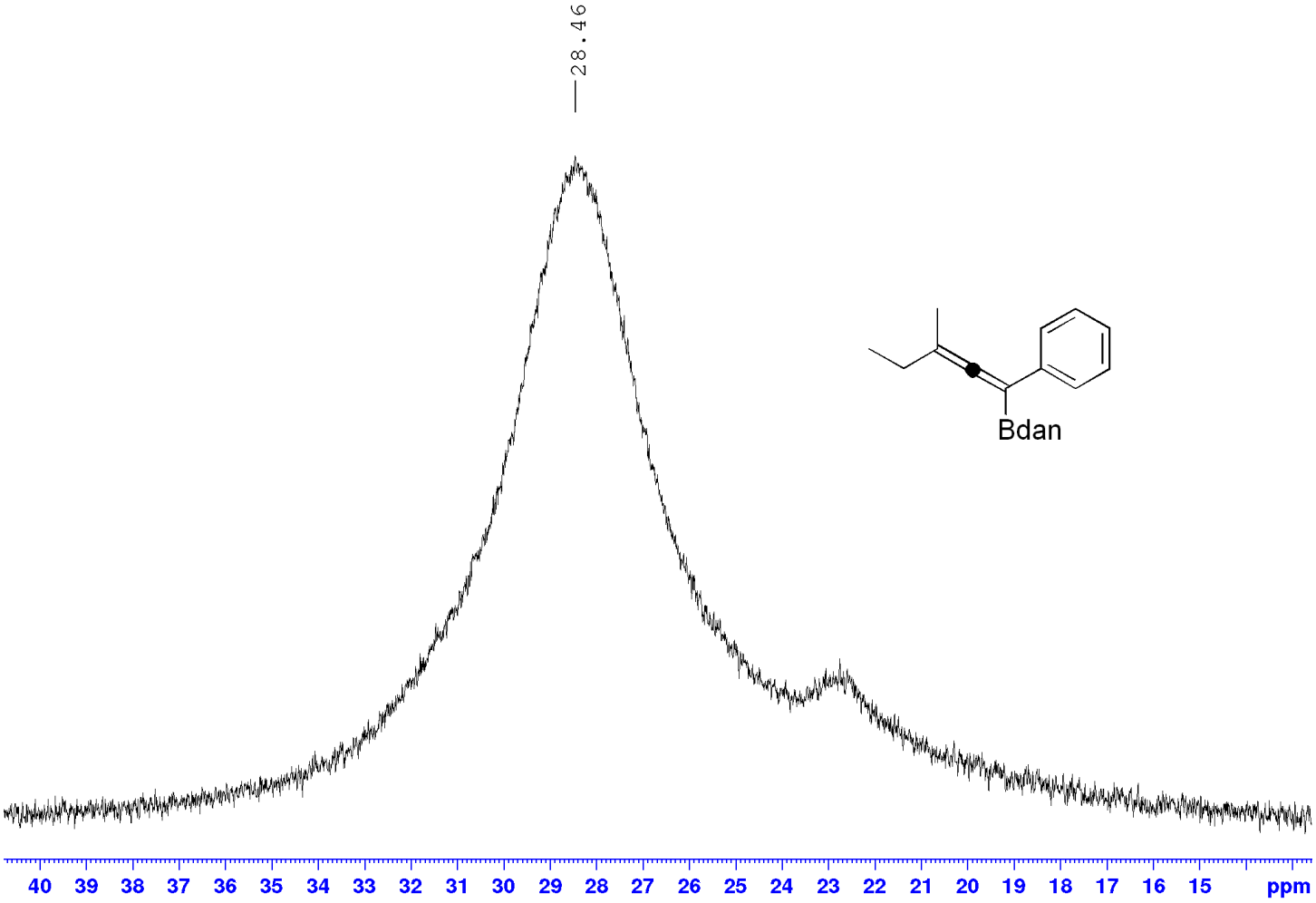
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

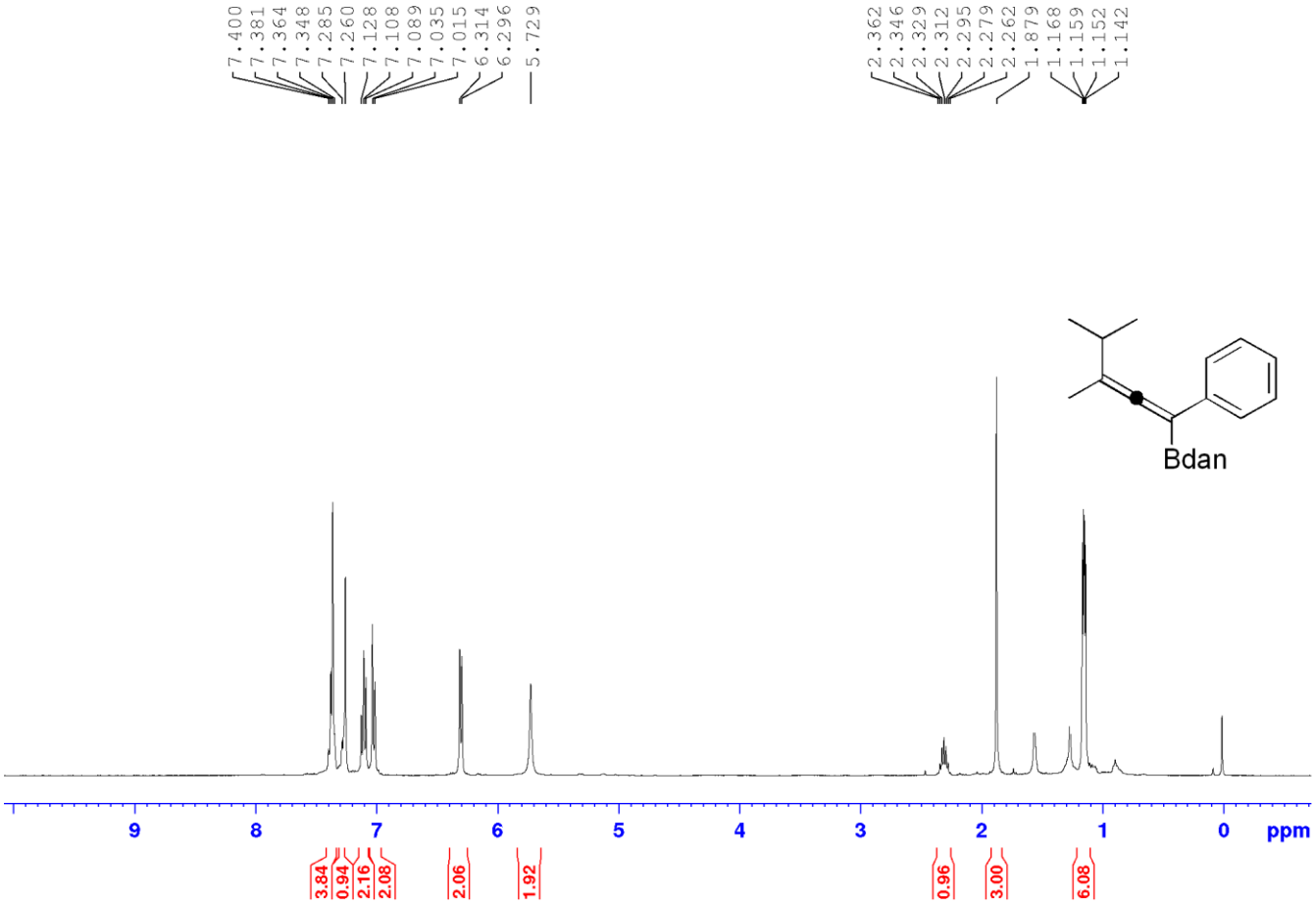


^{11}B NMR (128 MHz, $CDCl_3$)

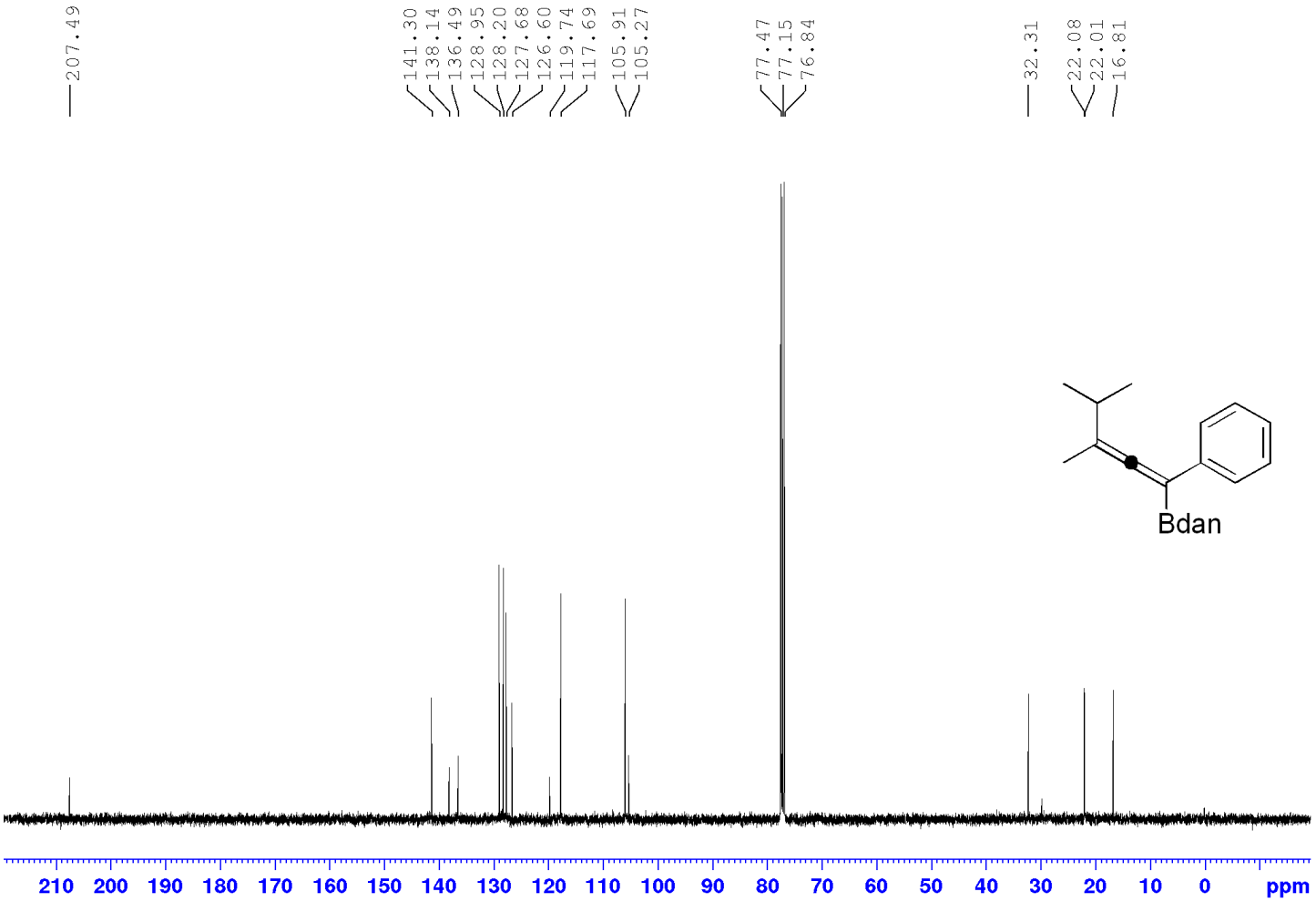


Compound 2c

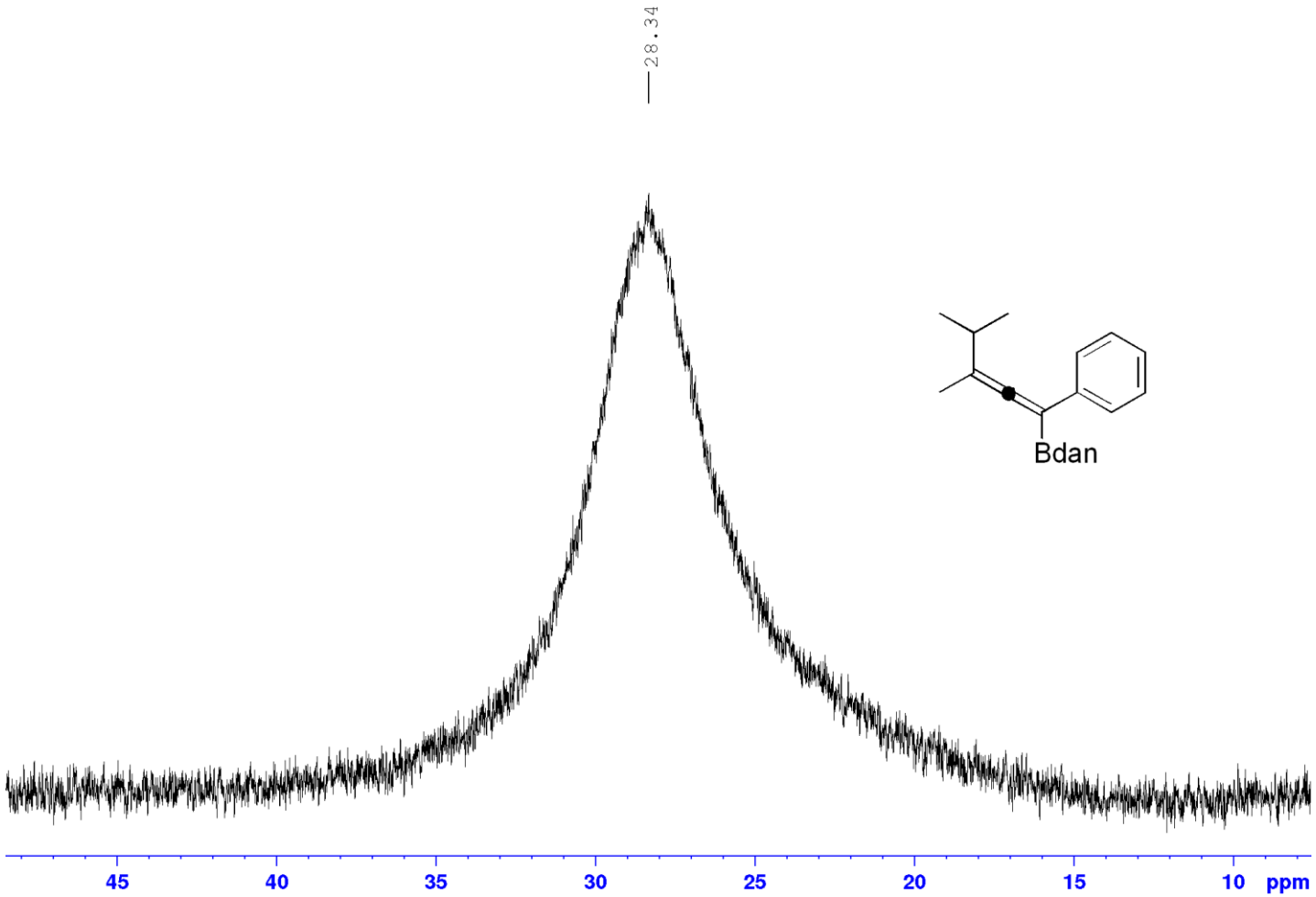
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

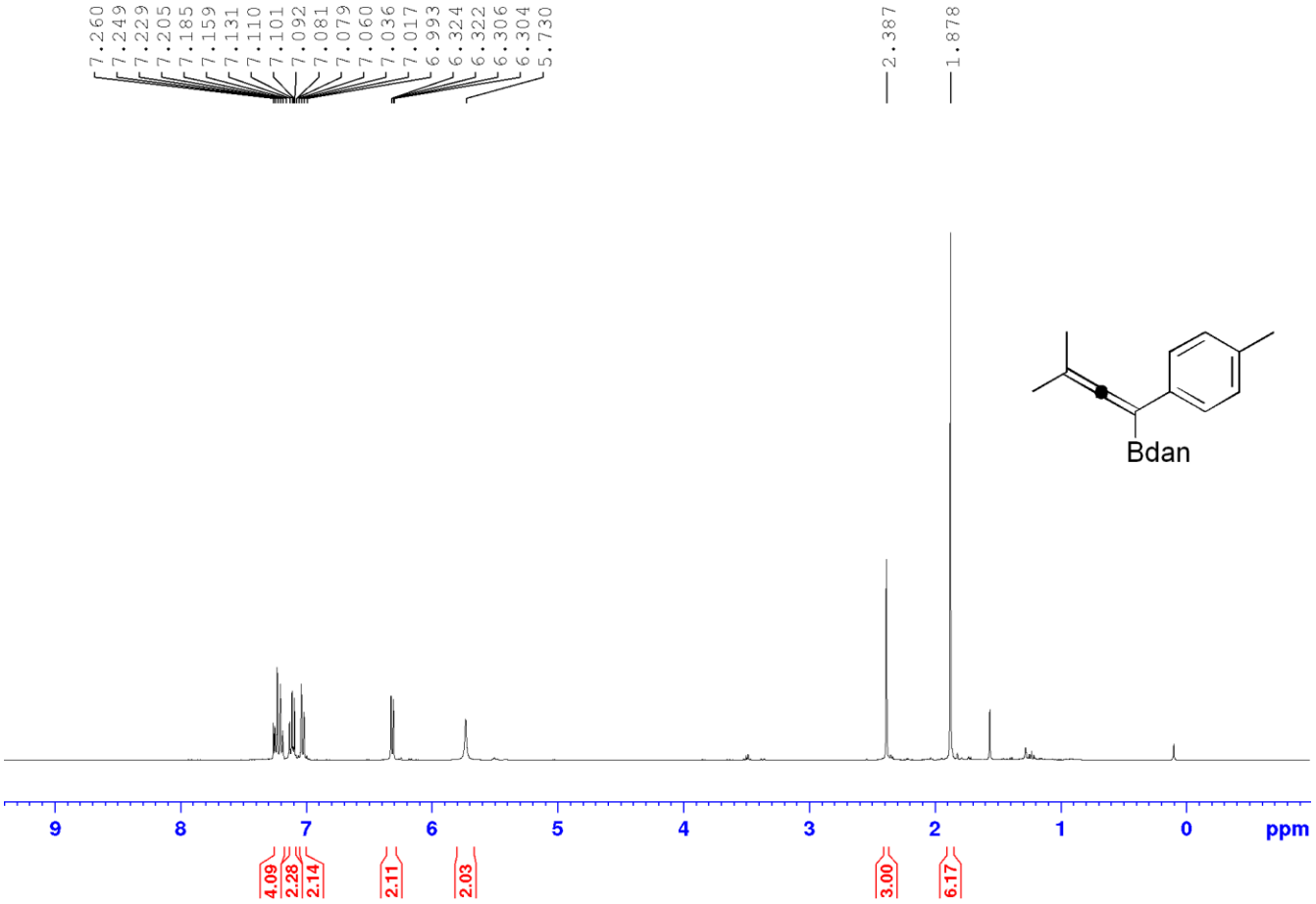


^{11}B NMR (128 MHz, $CDCl_3$)

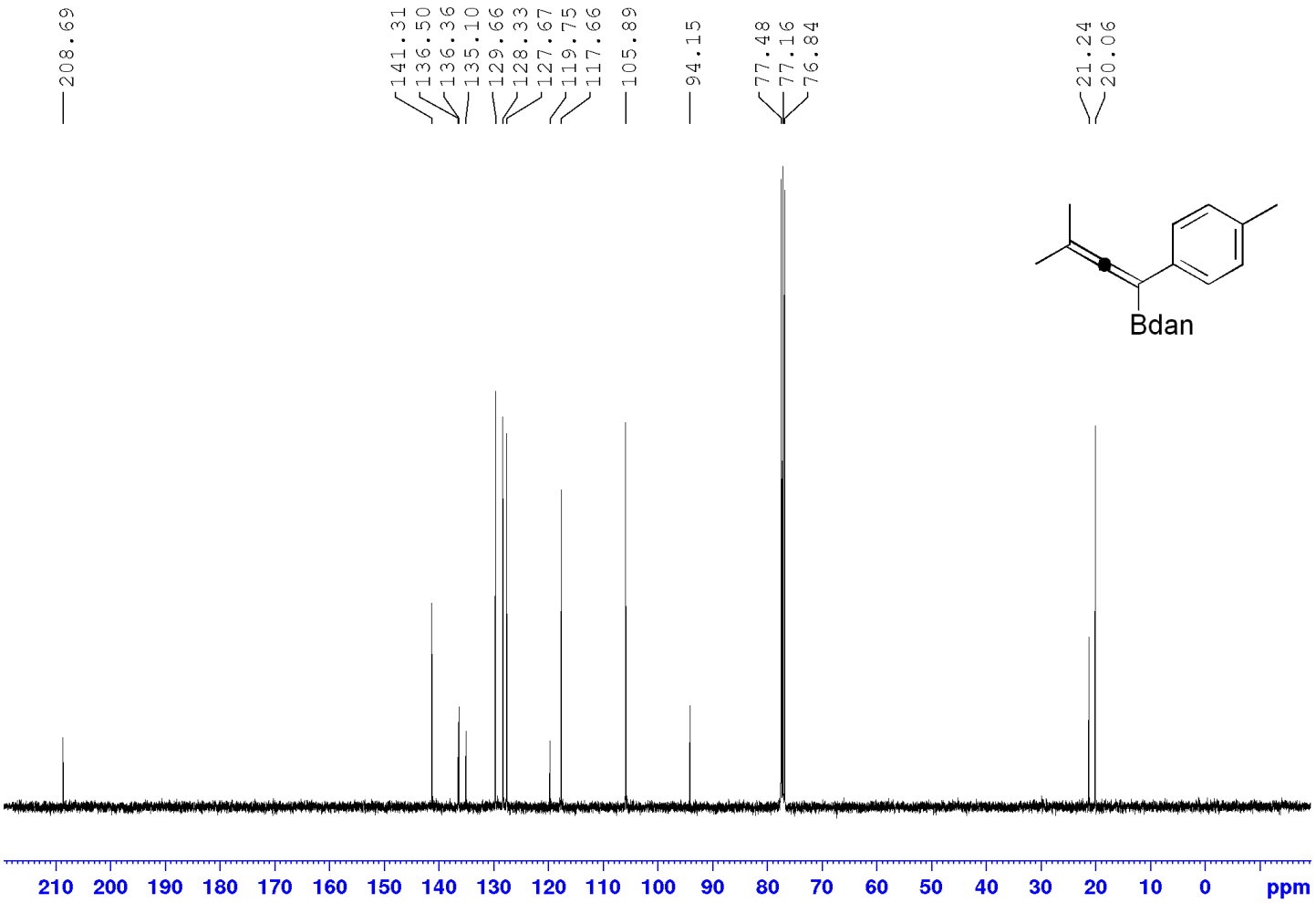


Compound 2d

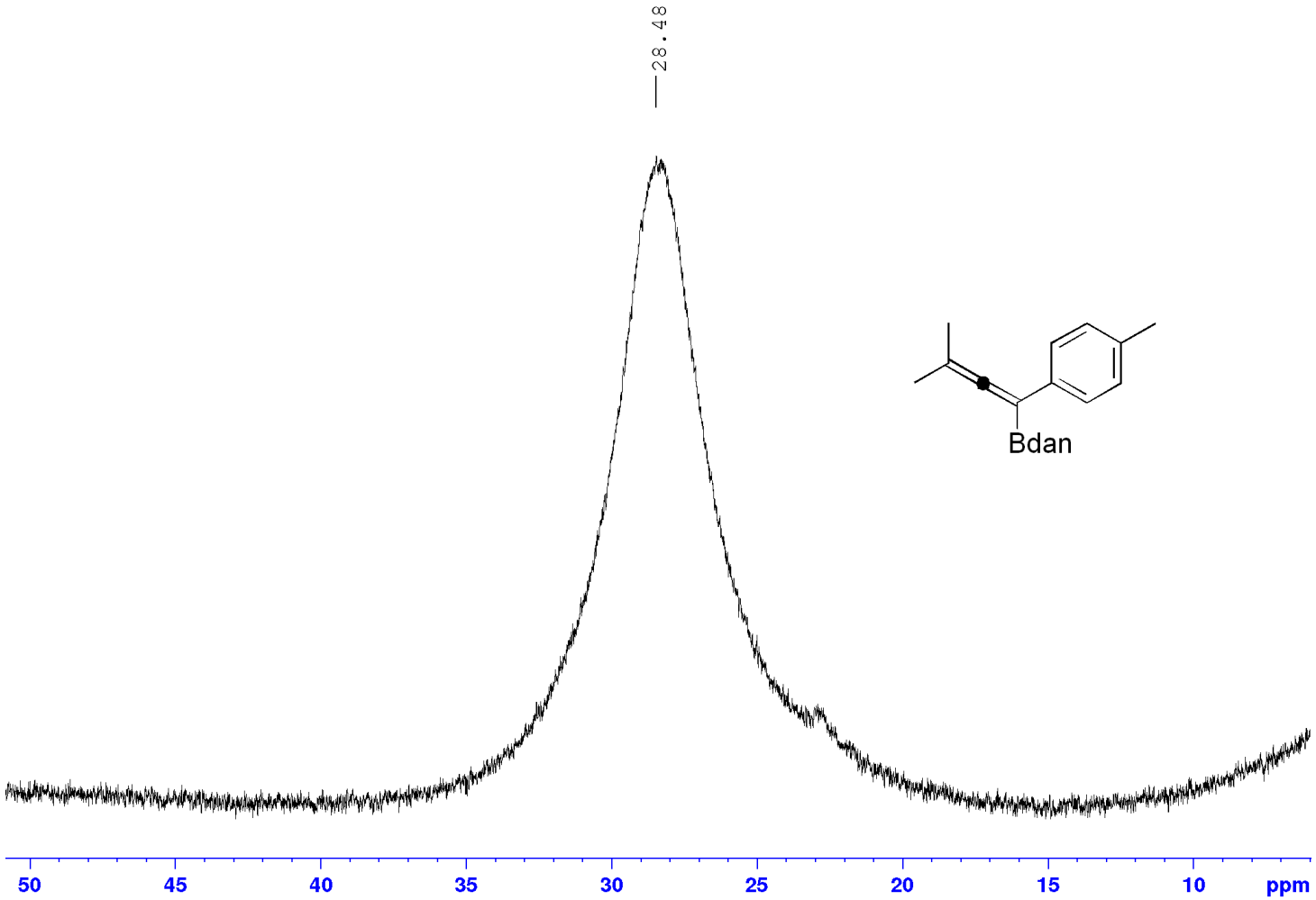
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

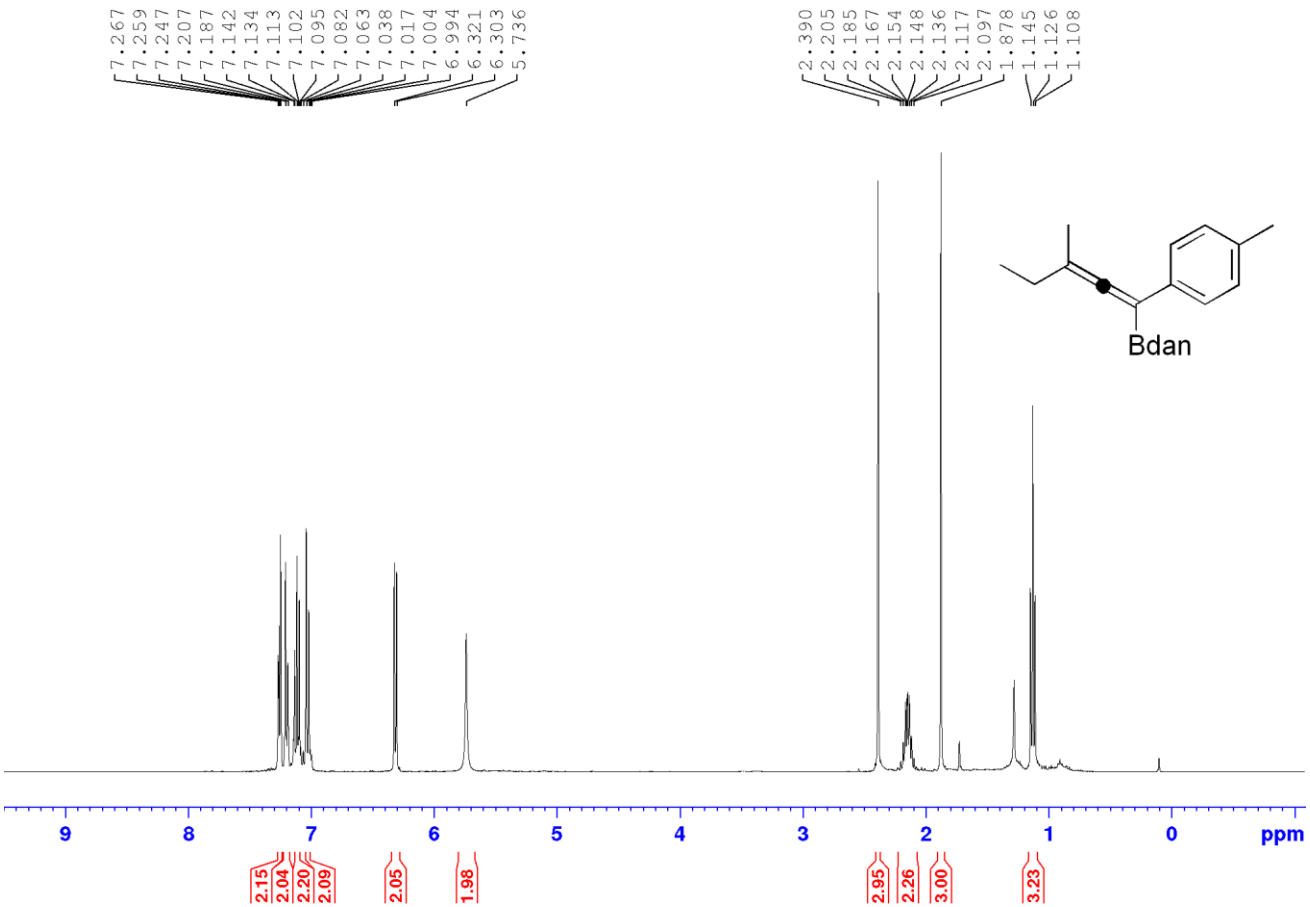


^{11}B NMR (128 MHz, $CDCl_3$)

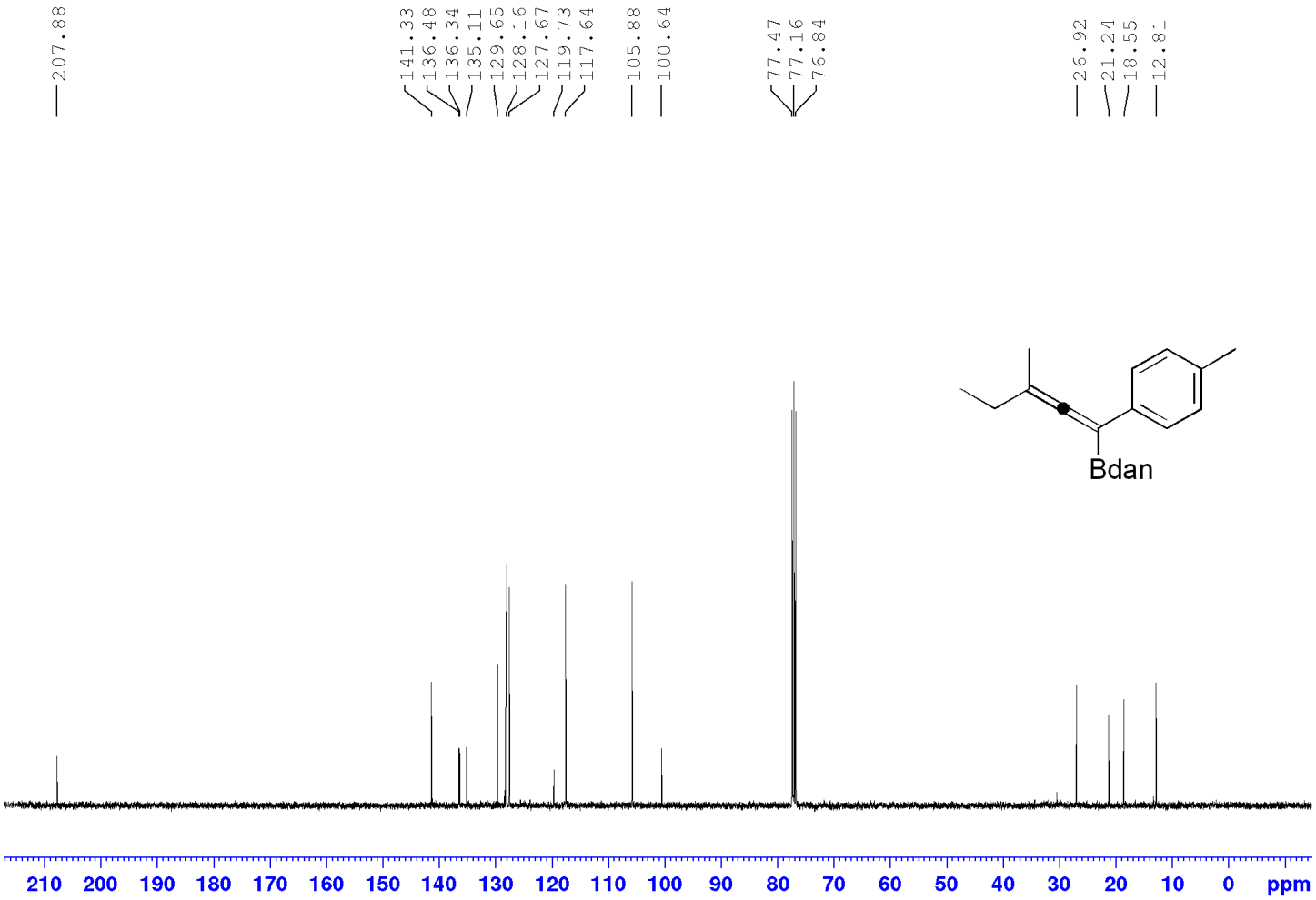


Compound 2e

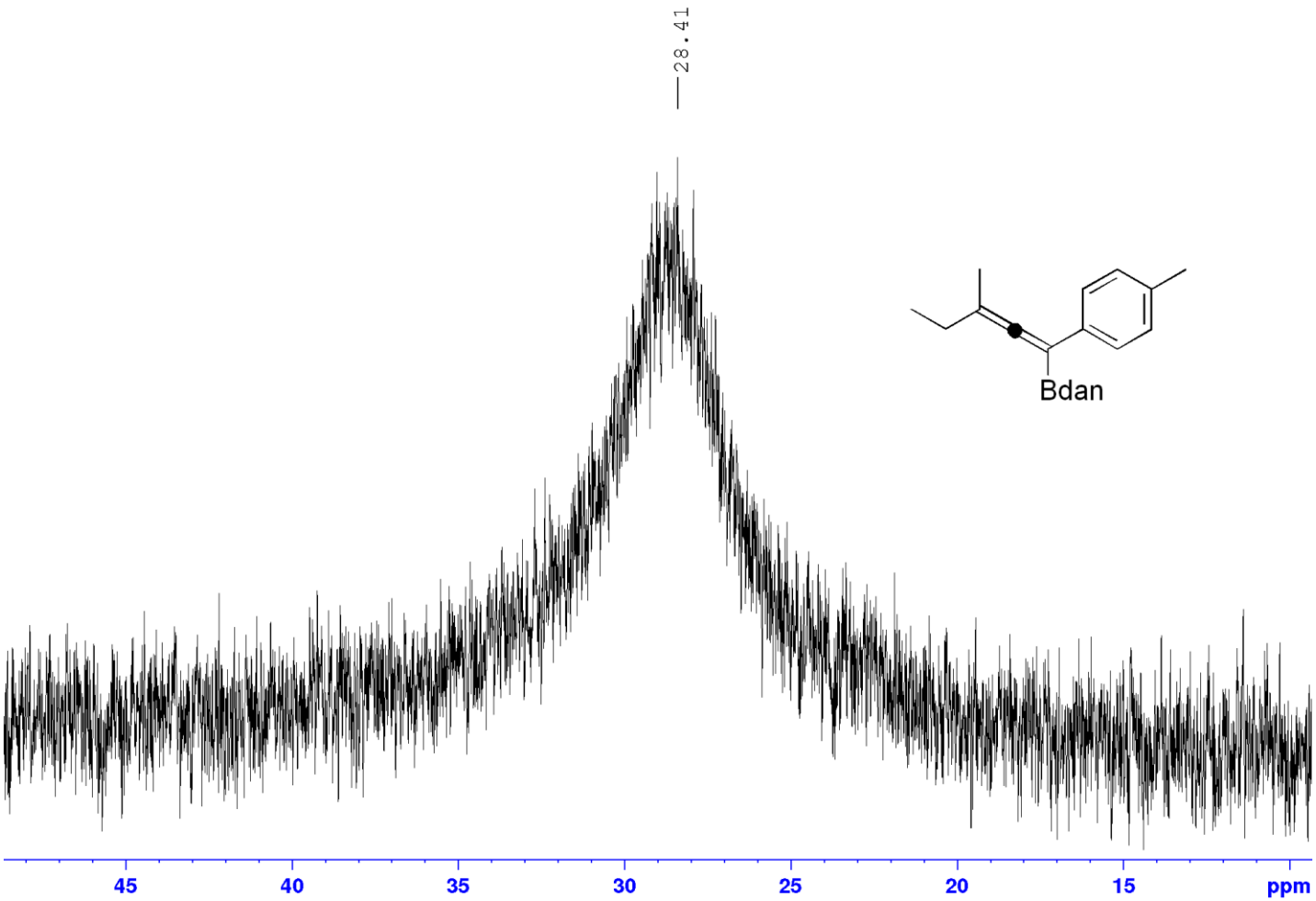
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

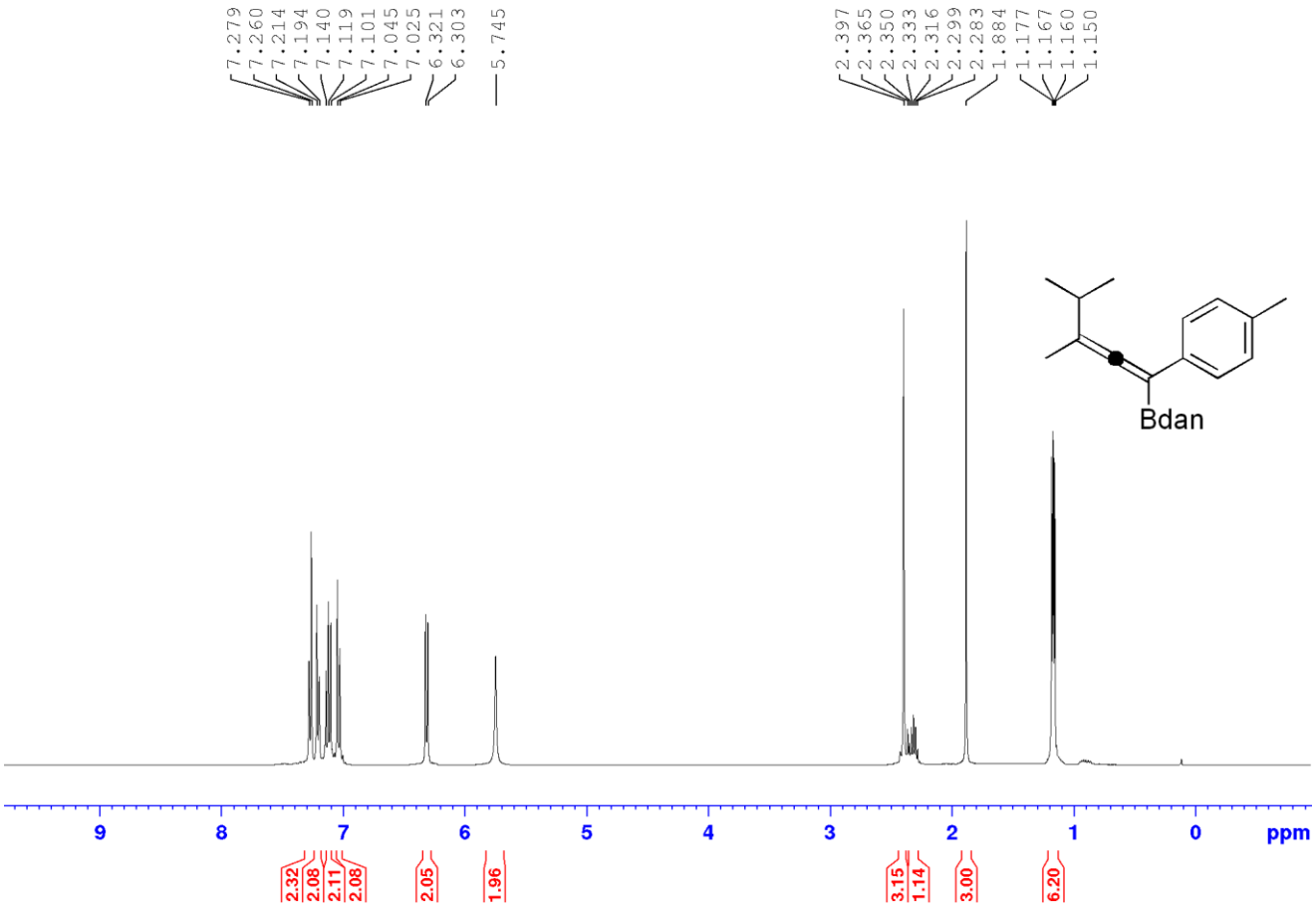


^{11}B NMR (128 MHz, $CDCl_3$)

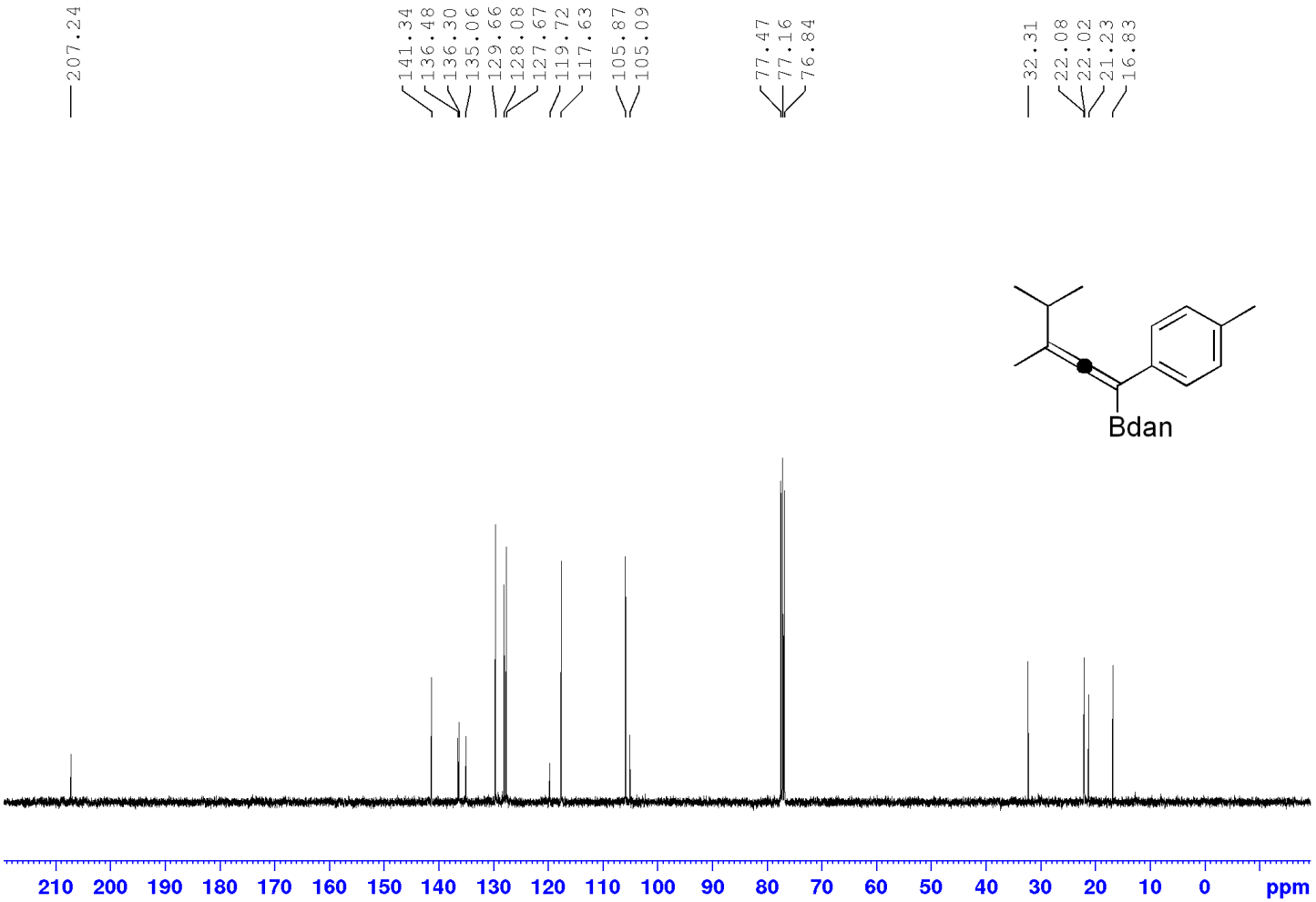


Compound 2f

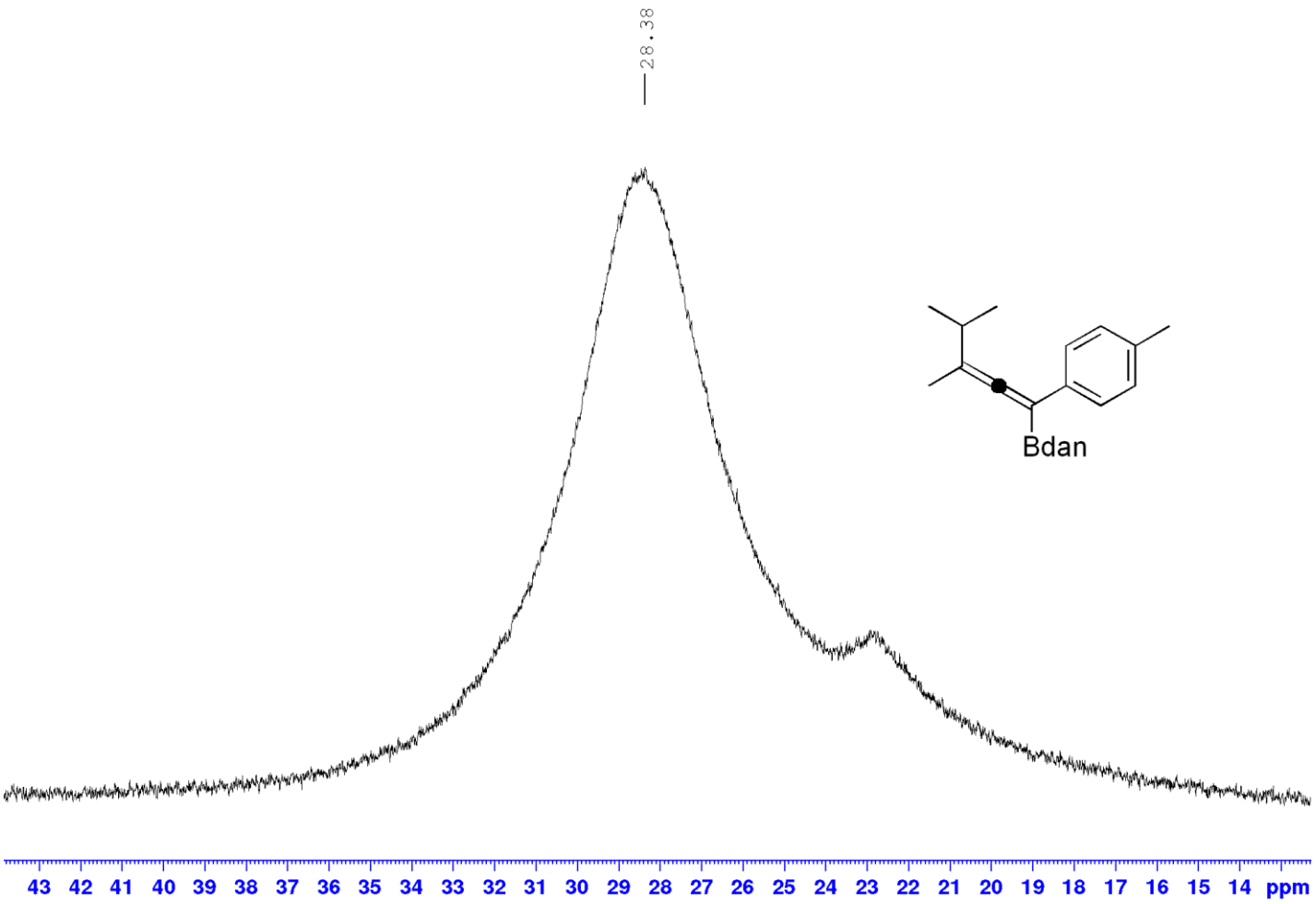
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

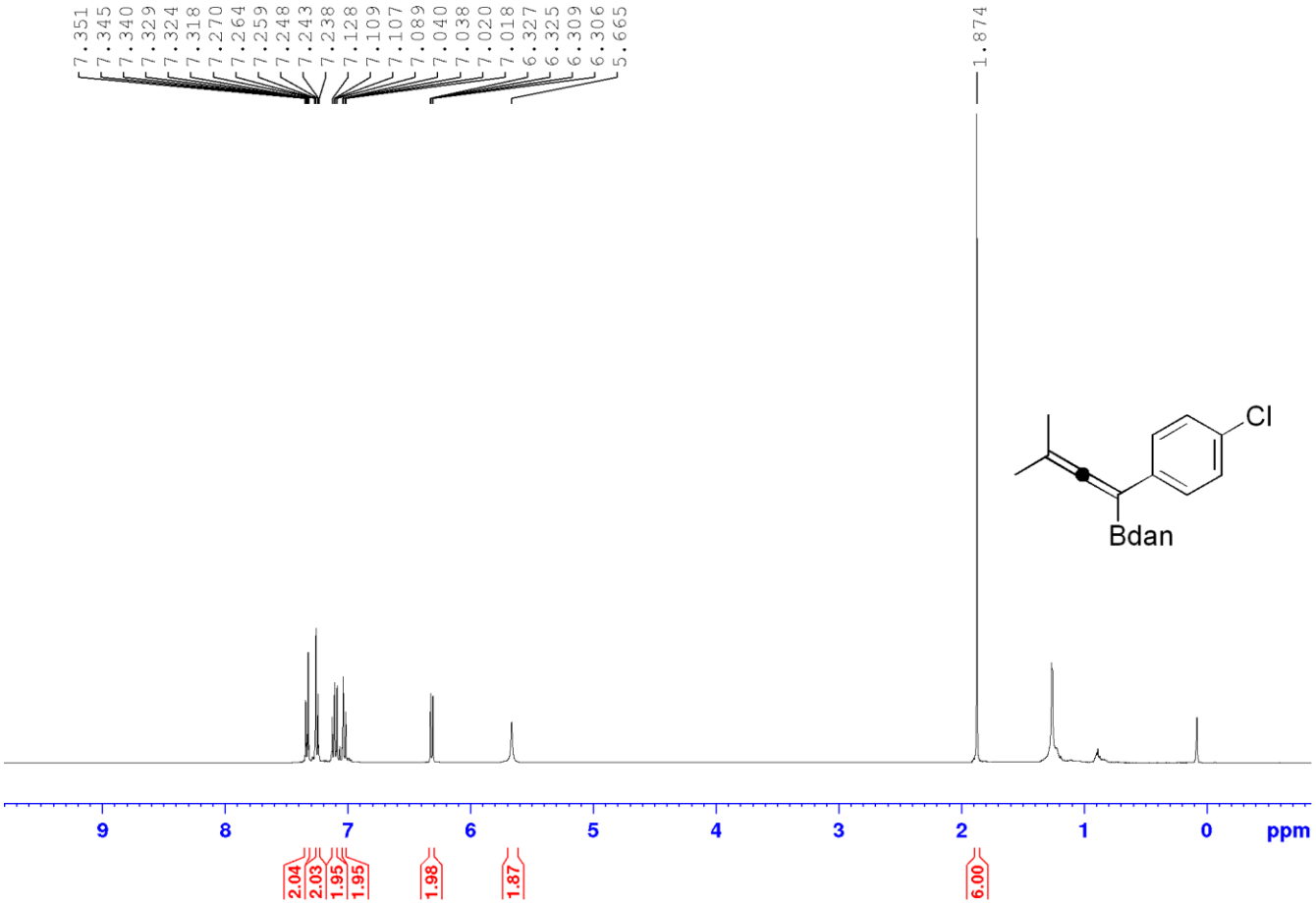


^{11}B NMR (128 MHz, $CDCl_3$)

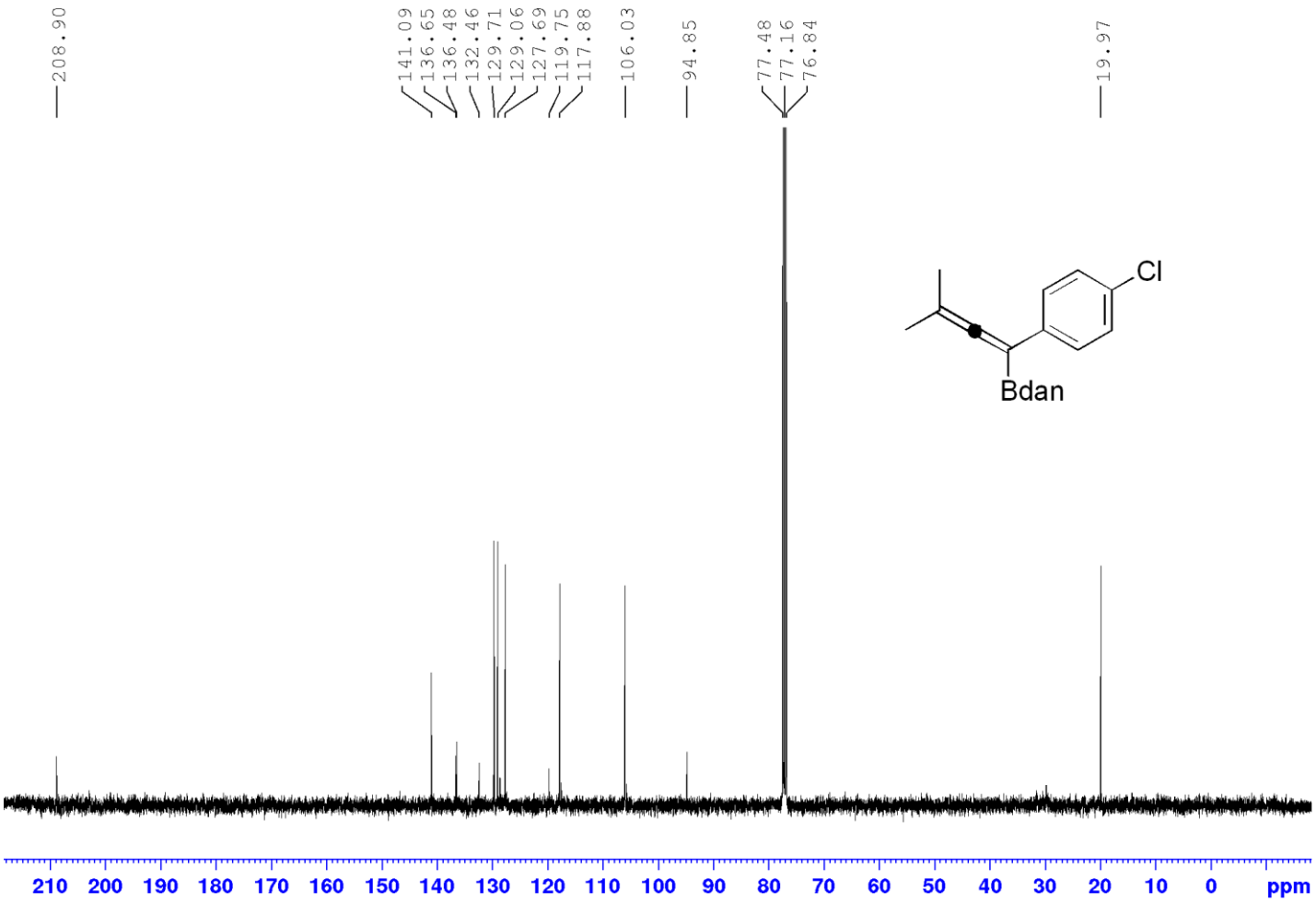


Compound 2g

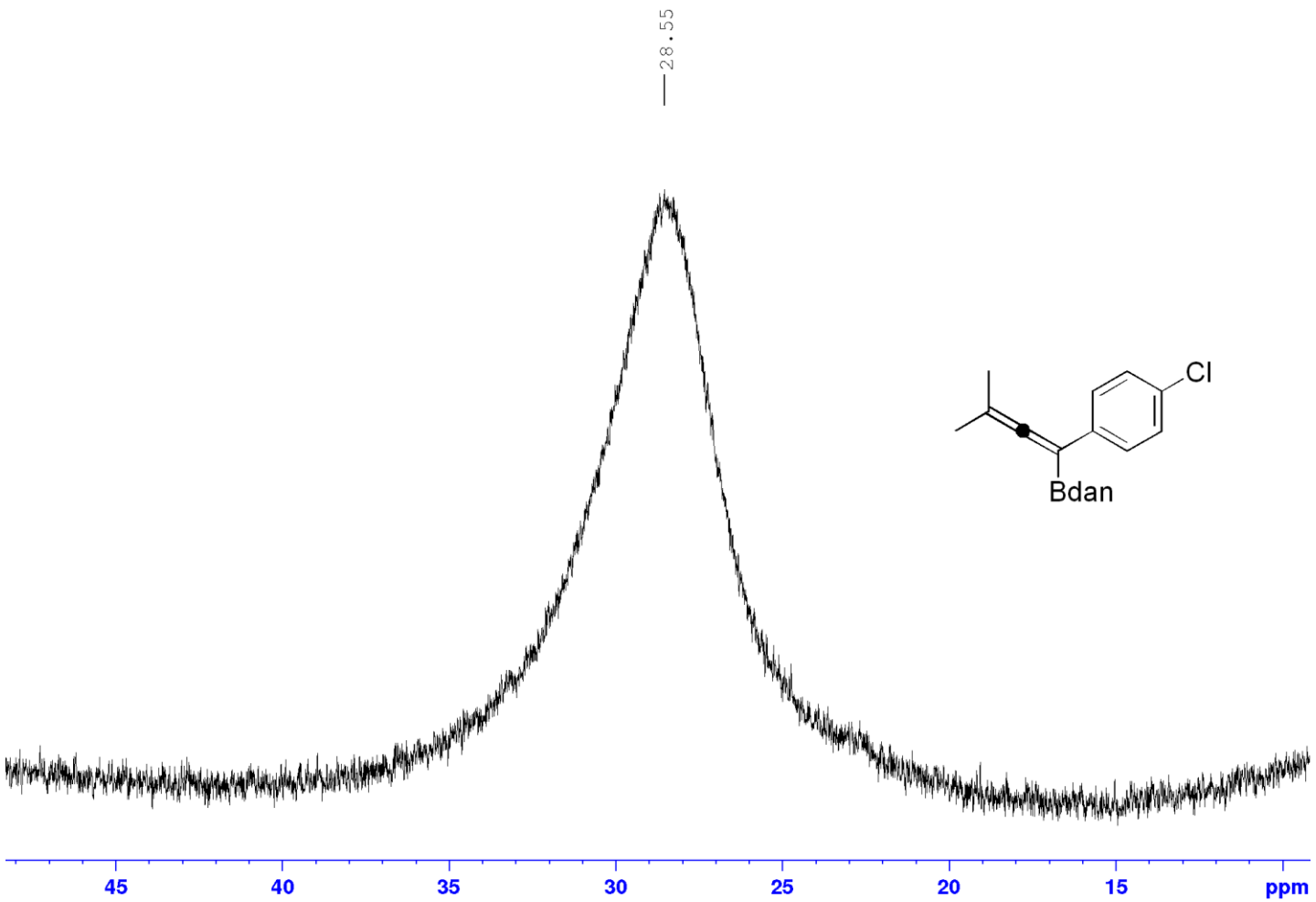
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

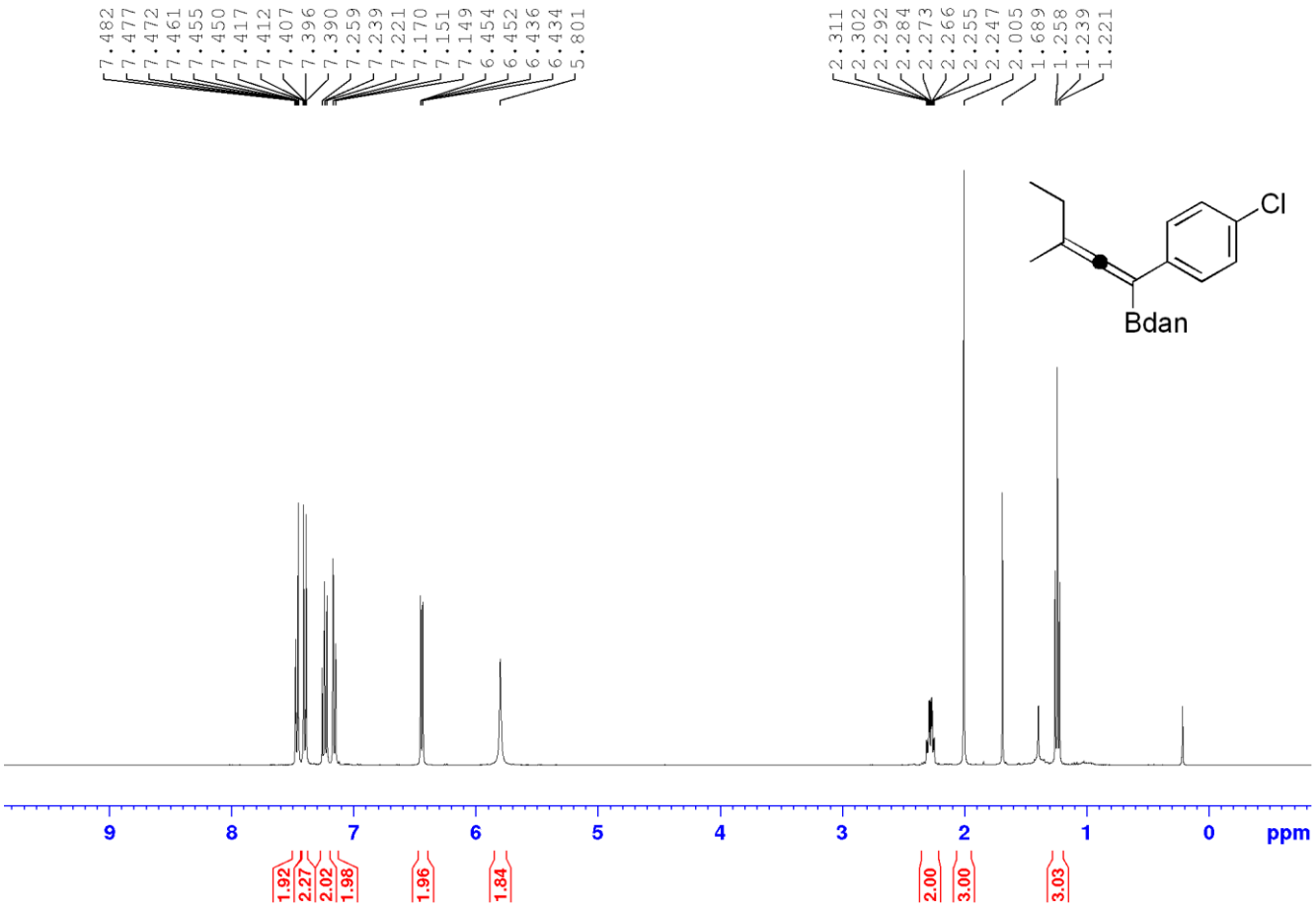


^{11}B NMR (128 MHz, $CDCl_3$)

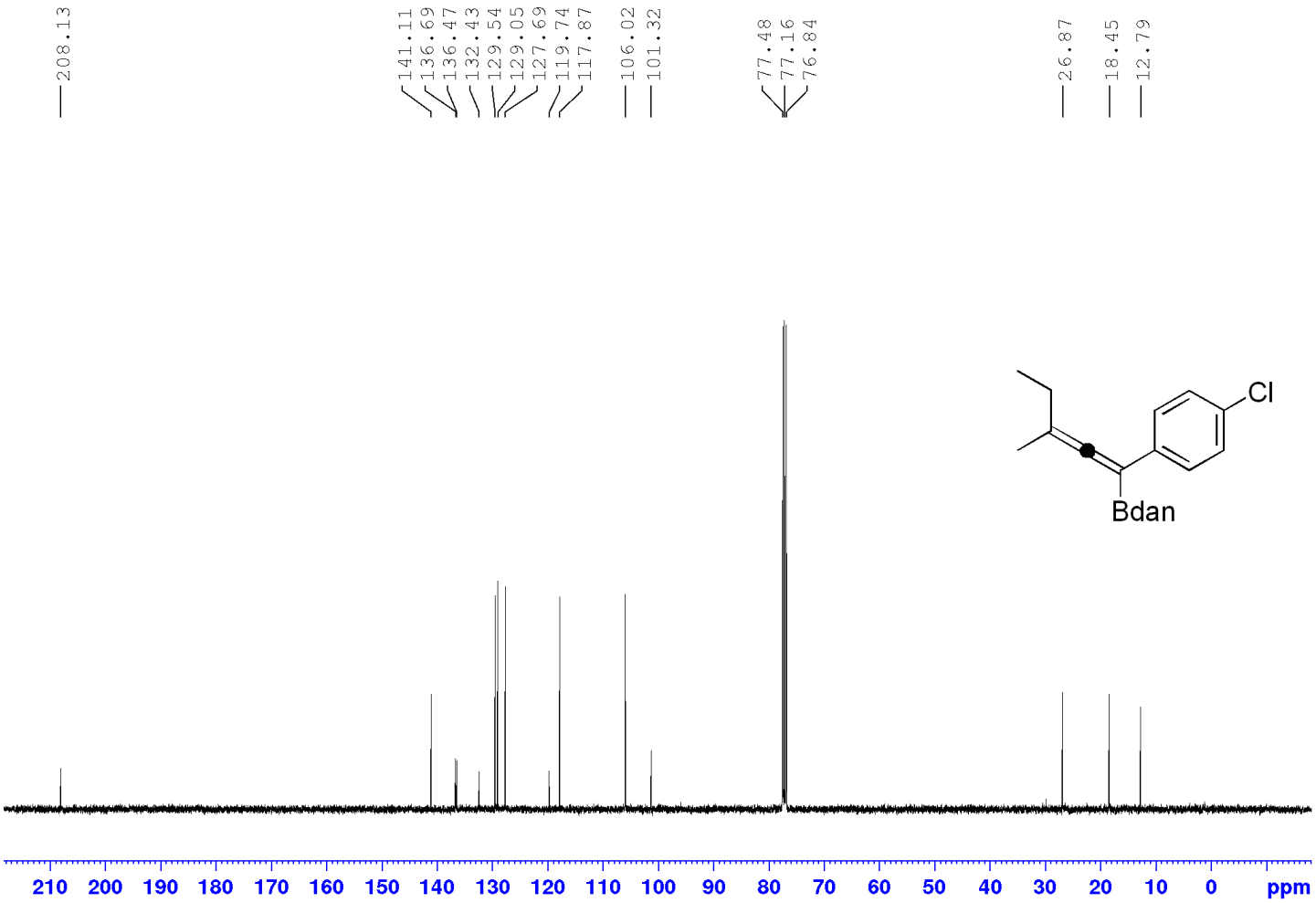


Compound 2h

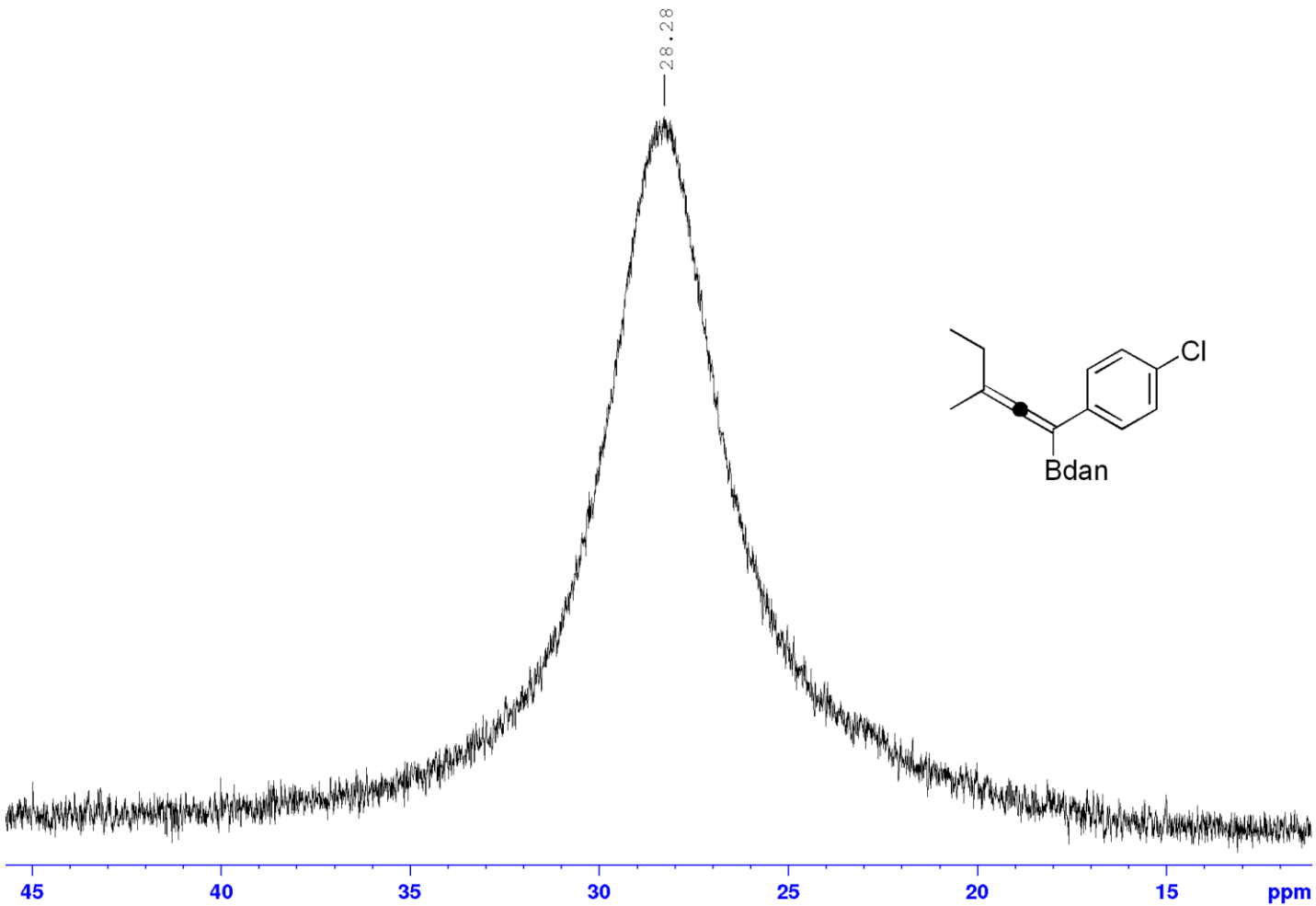
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

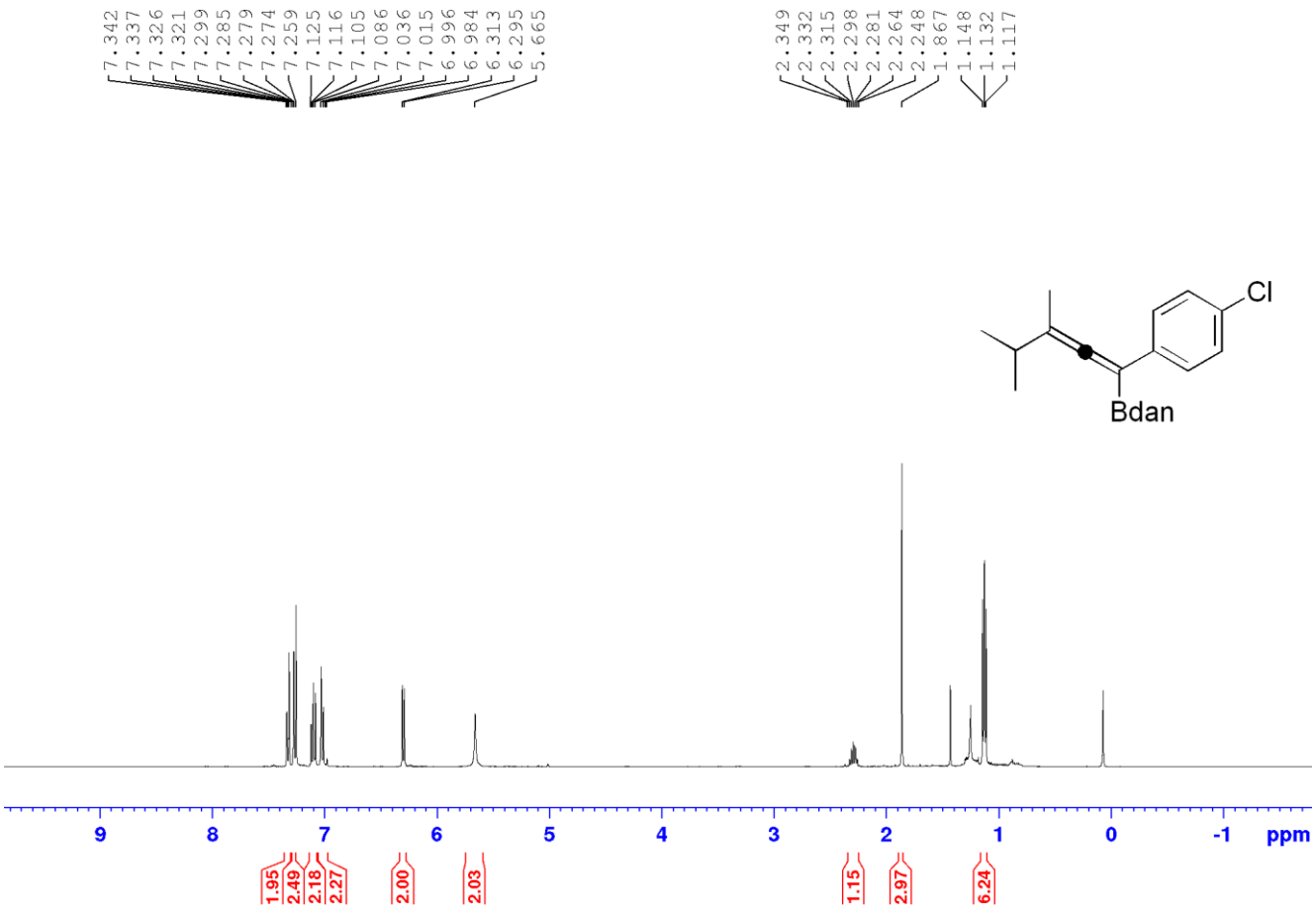


^{11}B NMR (128 MHz, $CDCl_3$)

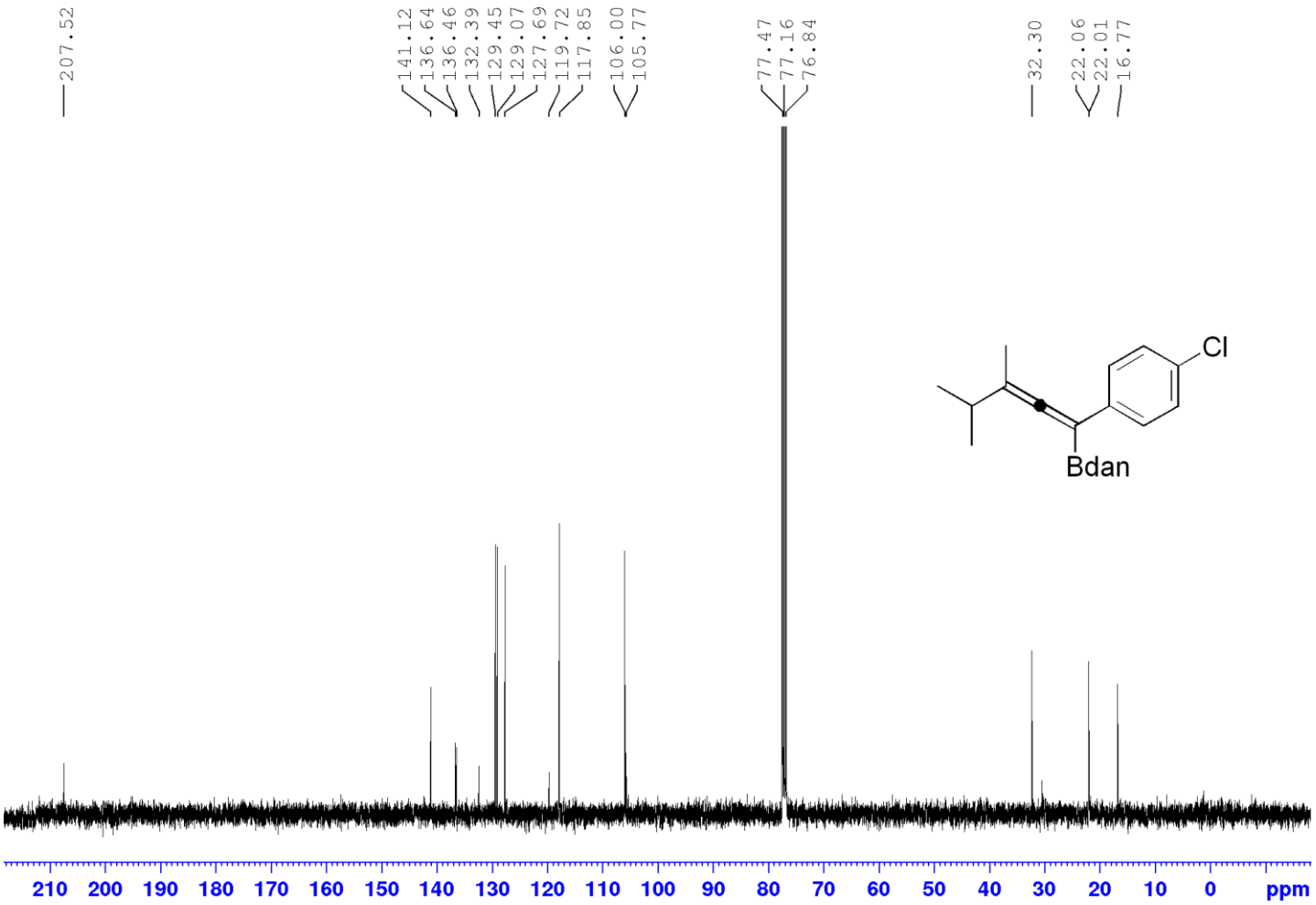


Compound 2i

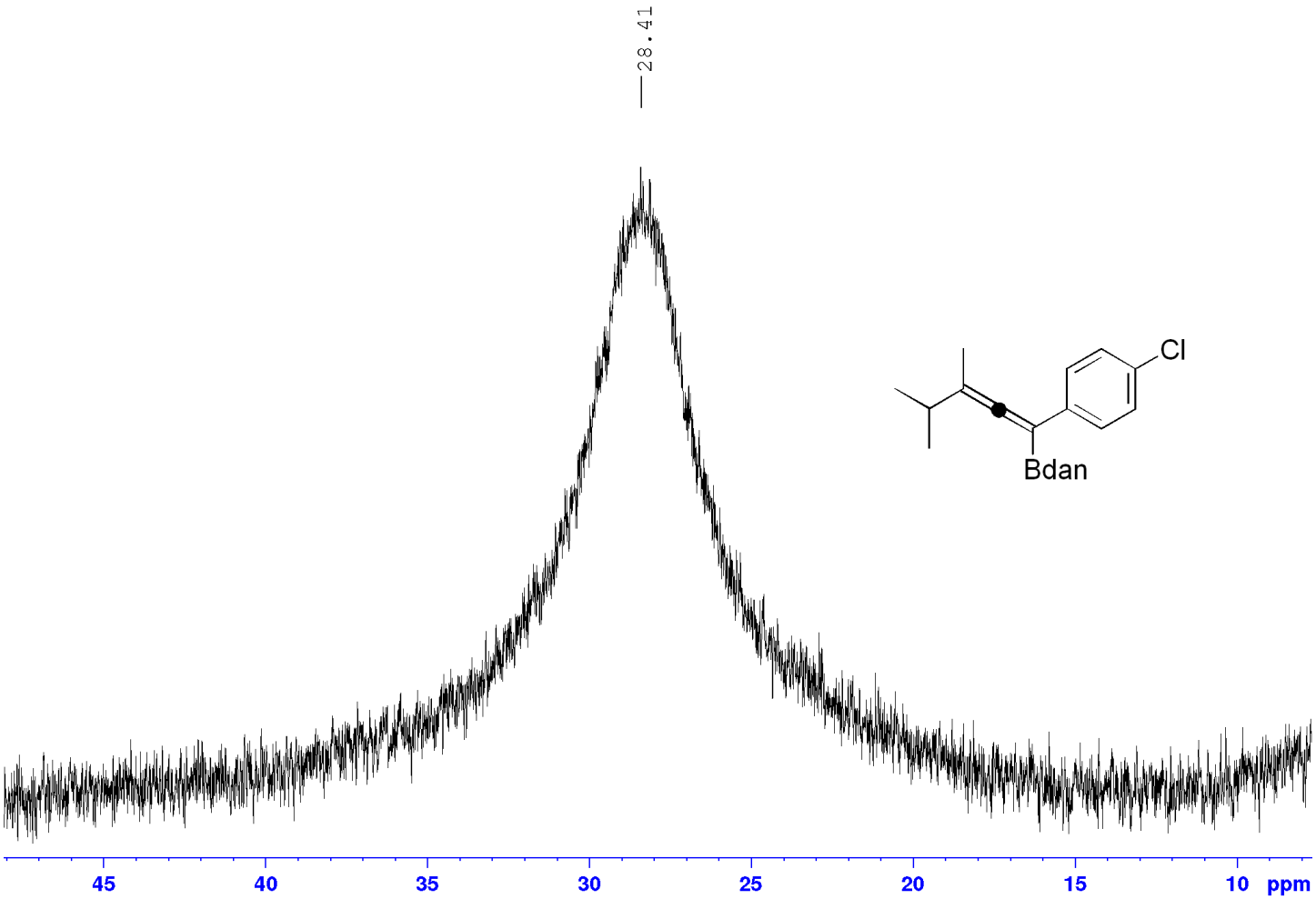
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

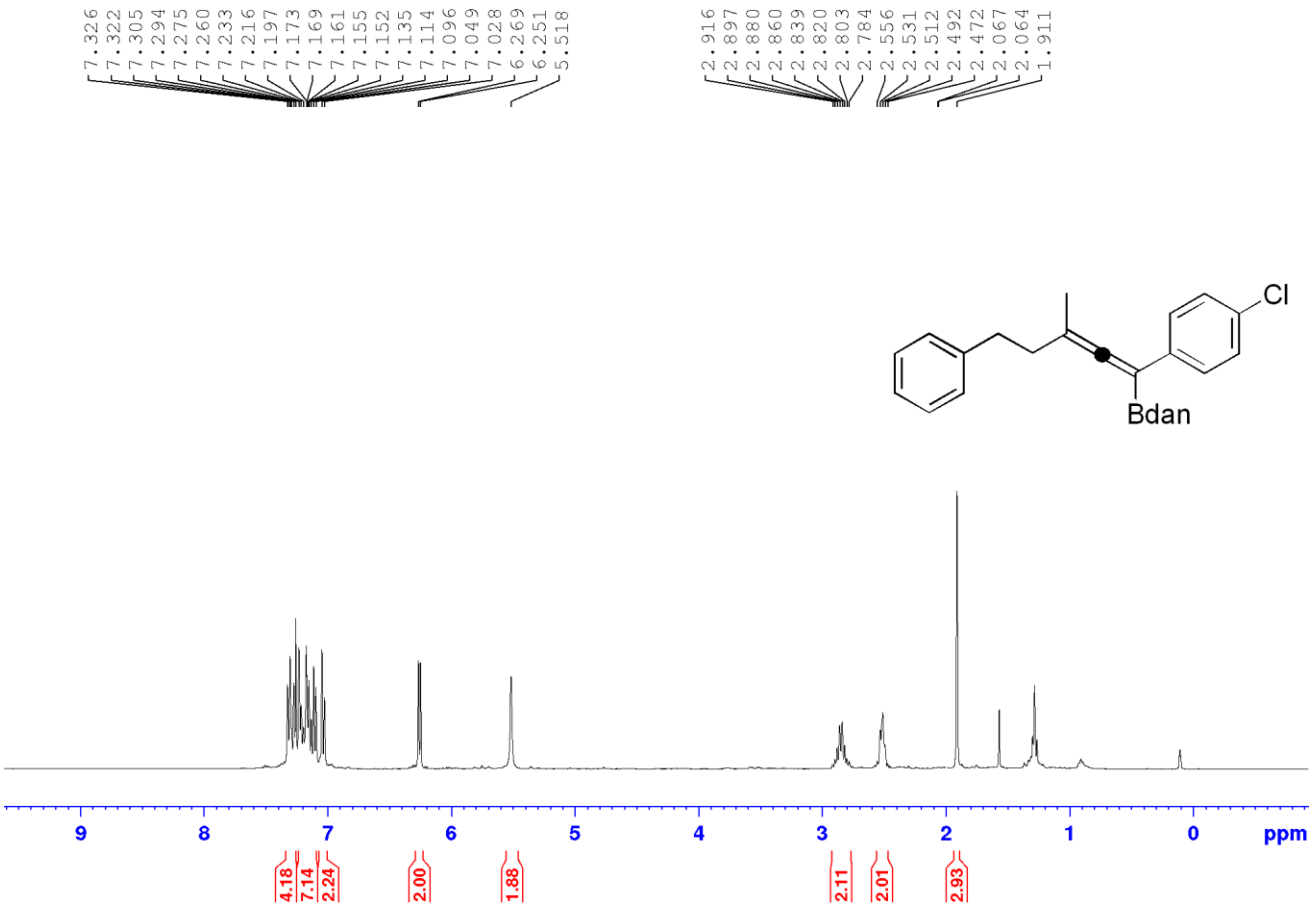


^{11}B NMR (128 MHz, $CDCl_3$)

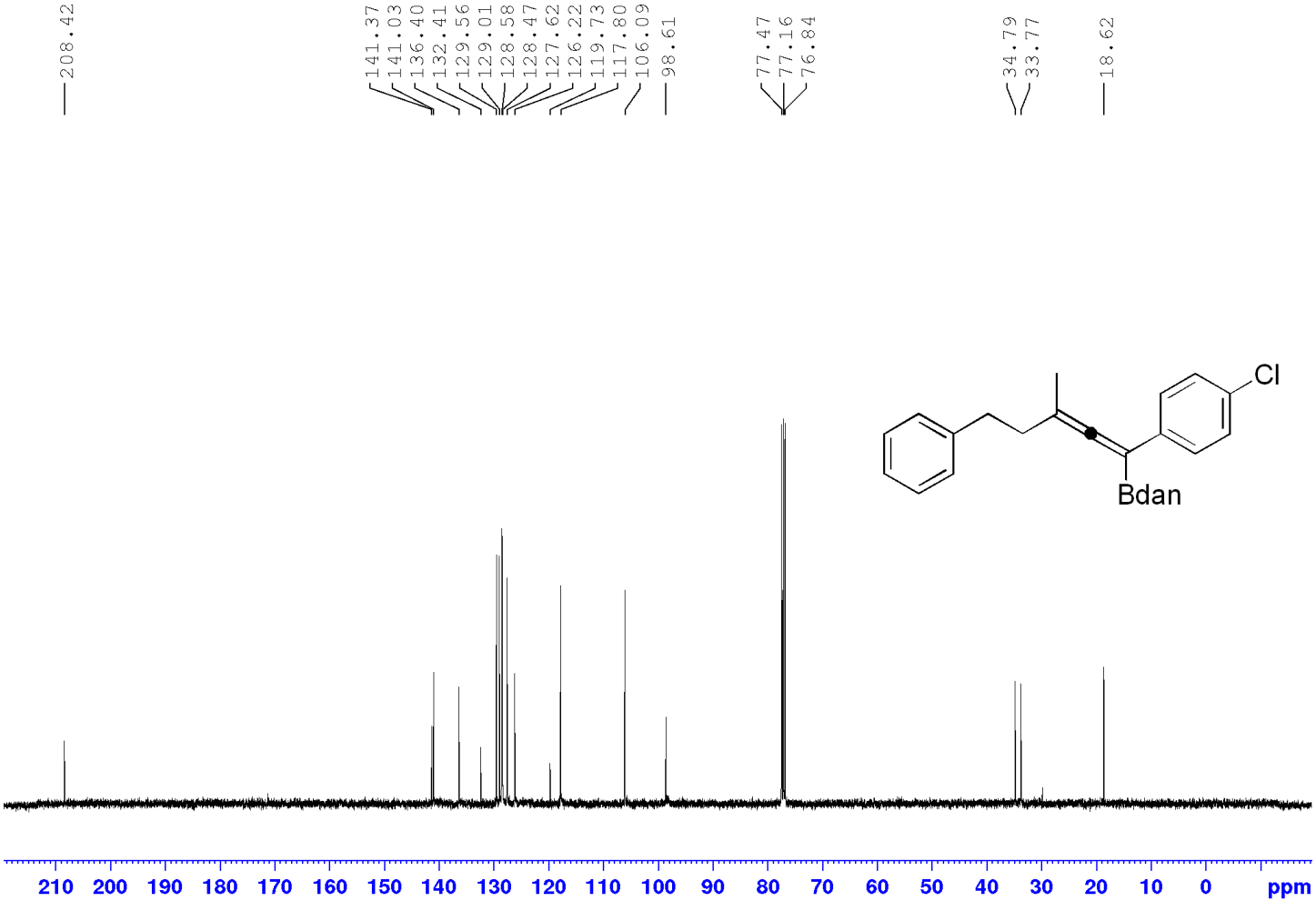


Compound 2j

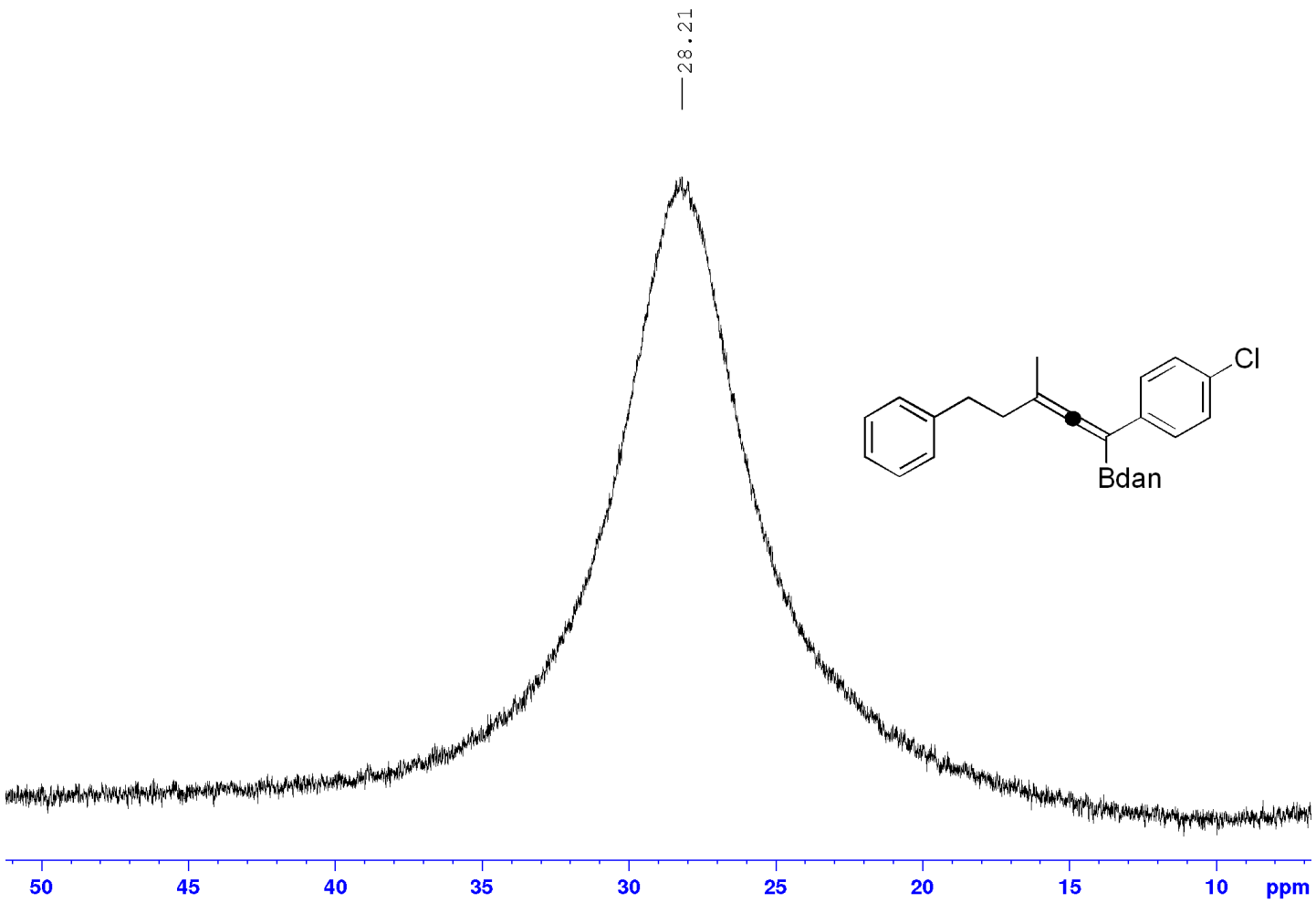
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

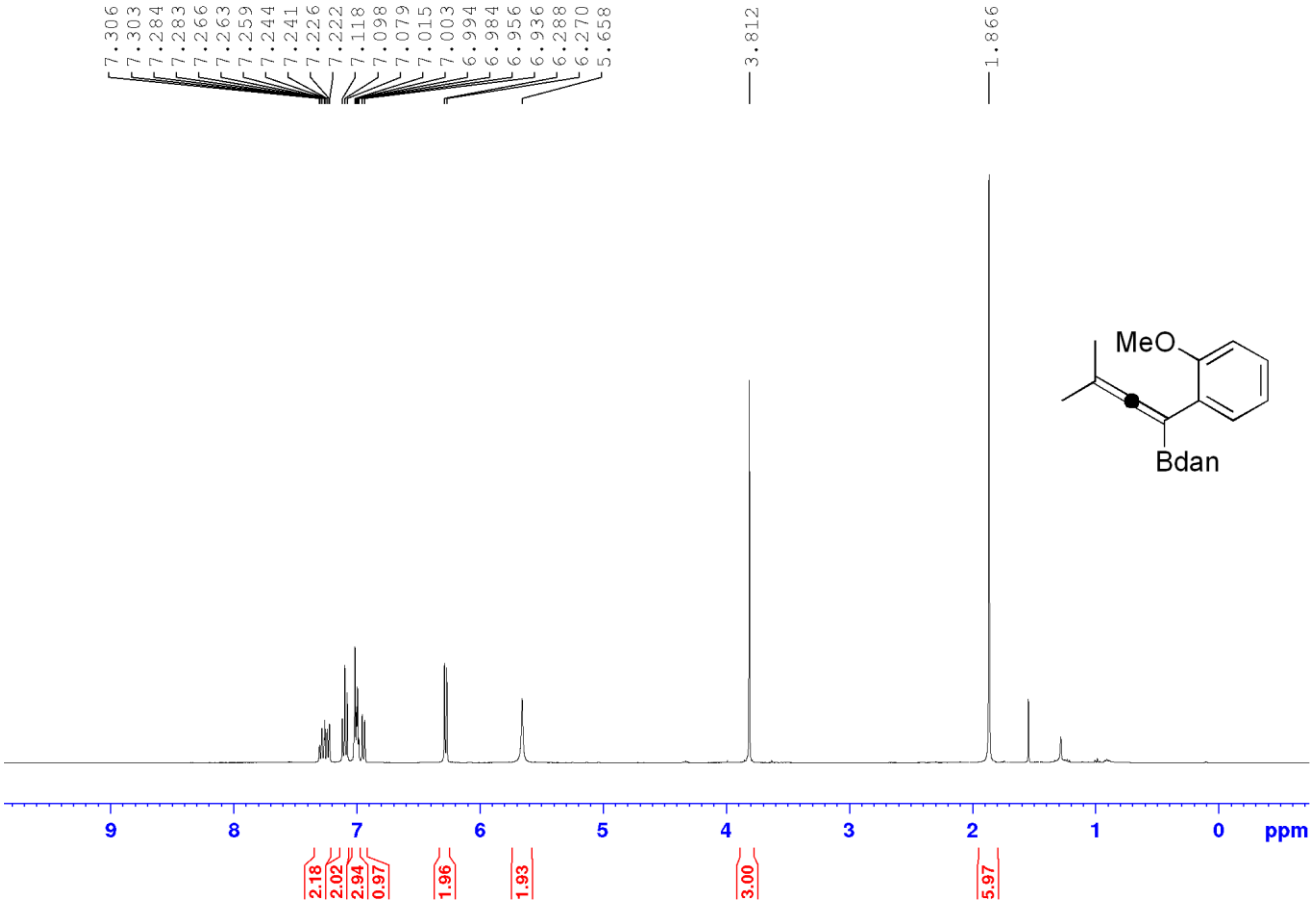


^{11}B NMR (128 MHz, $CDCl_3$)

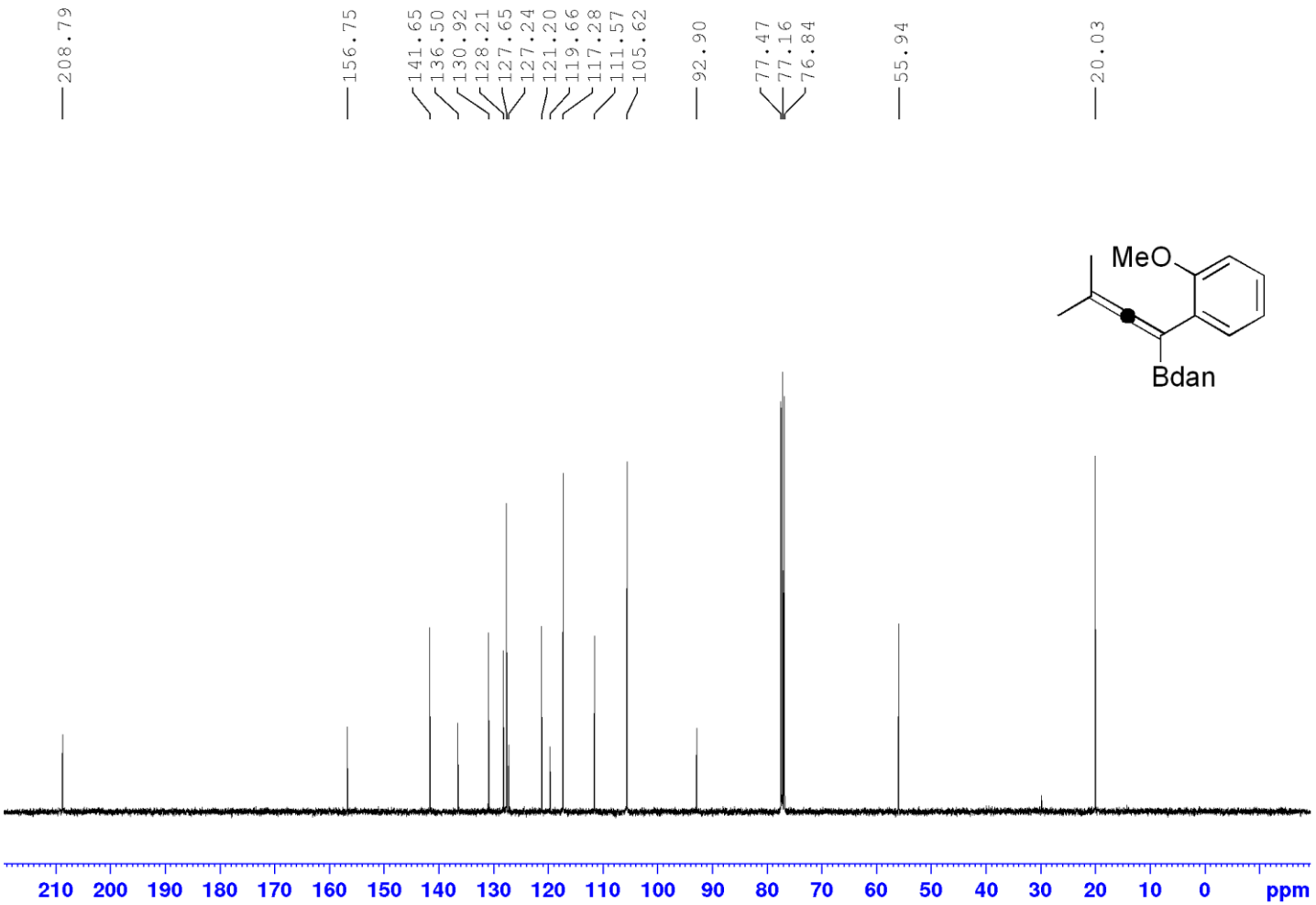


Compound 2k

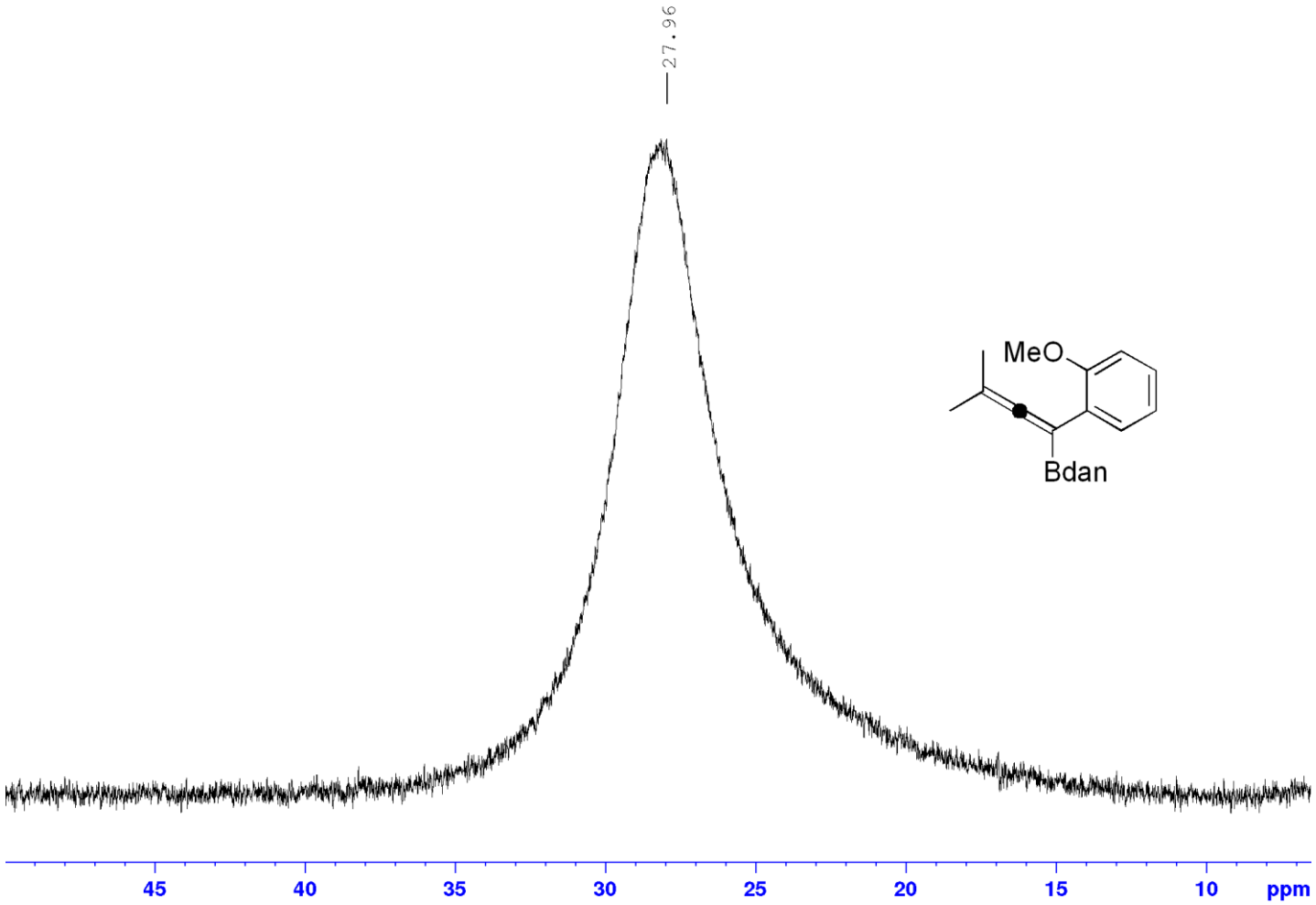
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

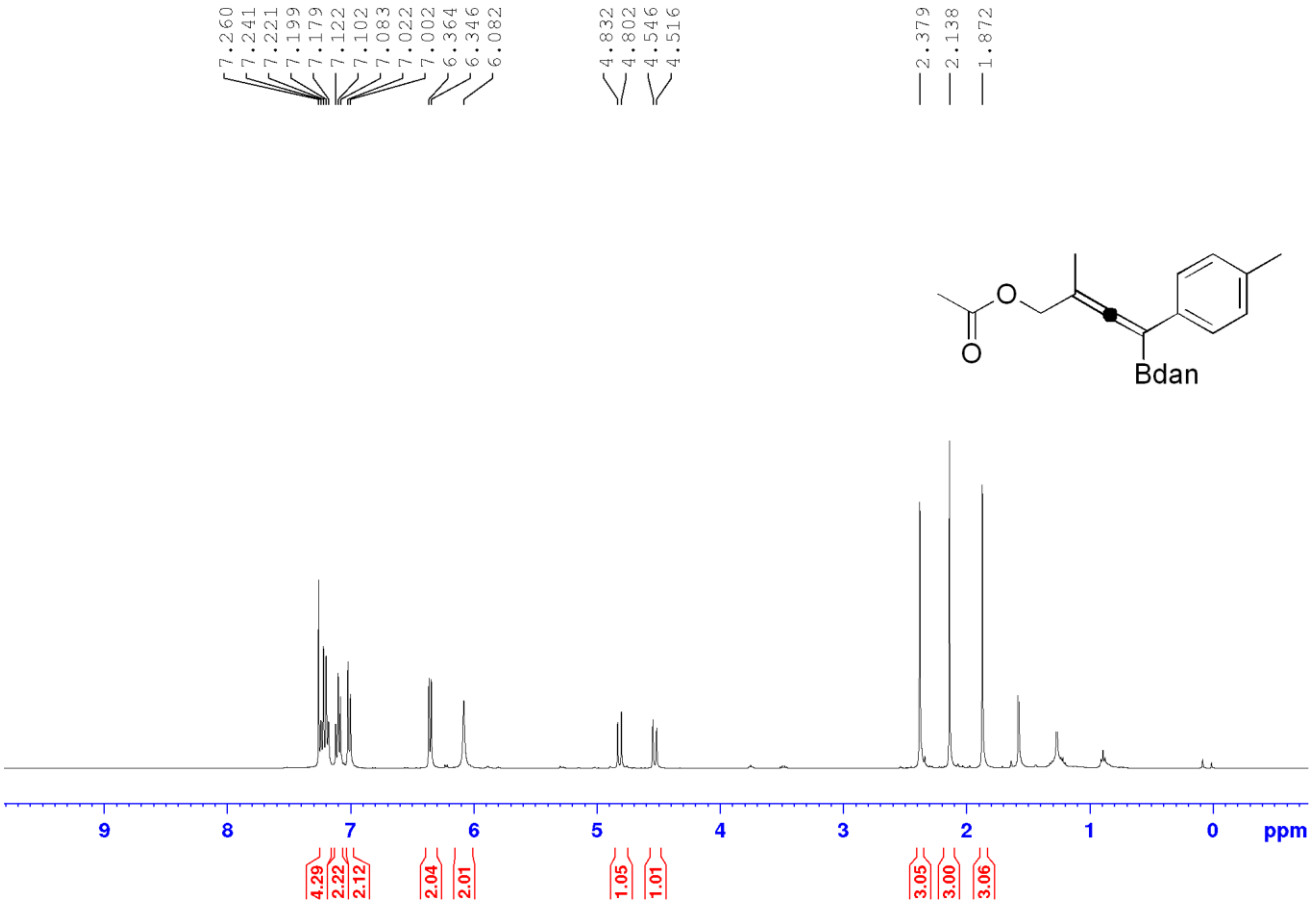


^{11}B NMR (128 MHz, $CDCl_3$)

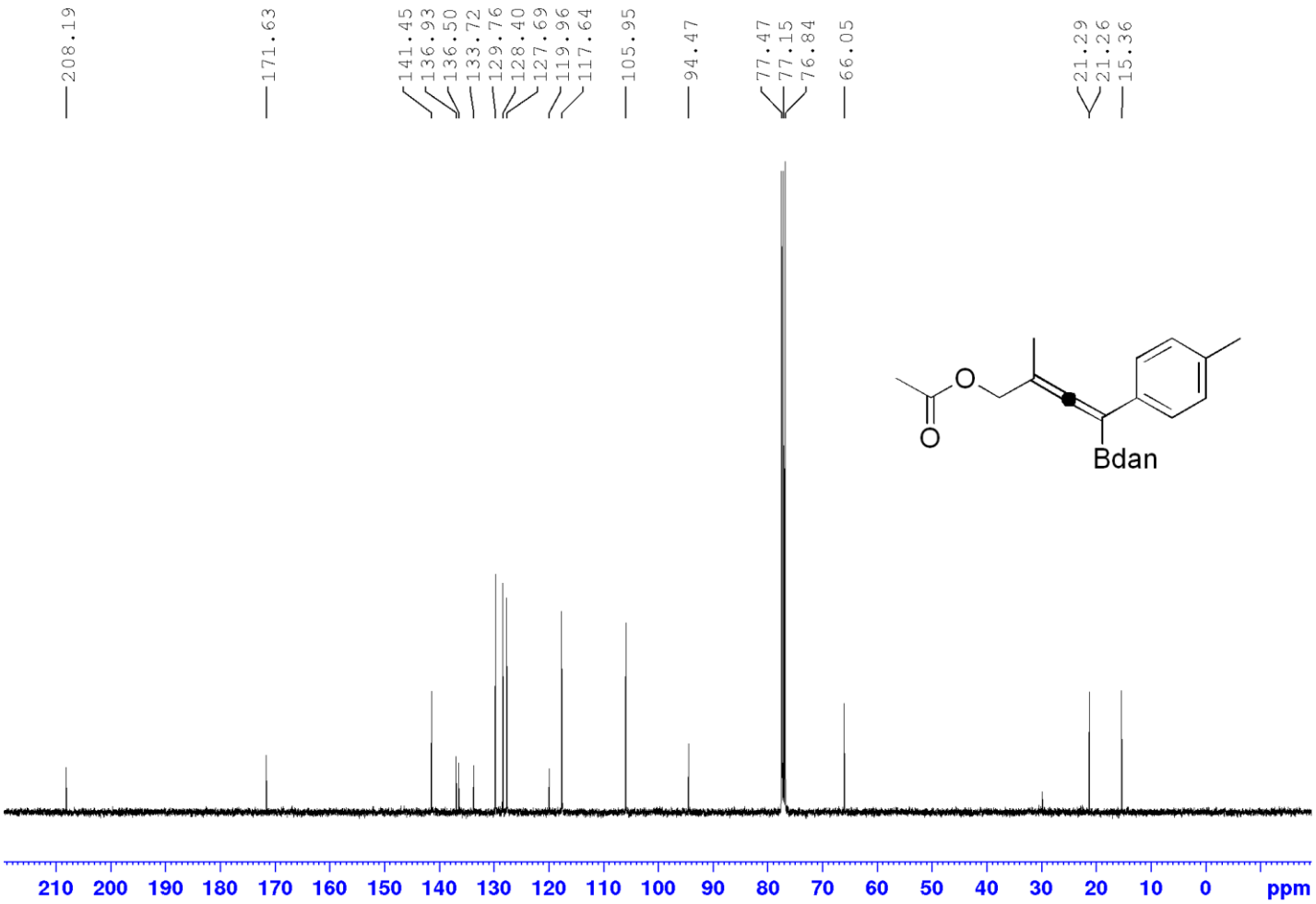


Compound 2l

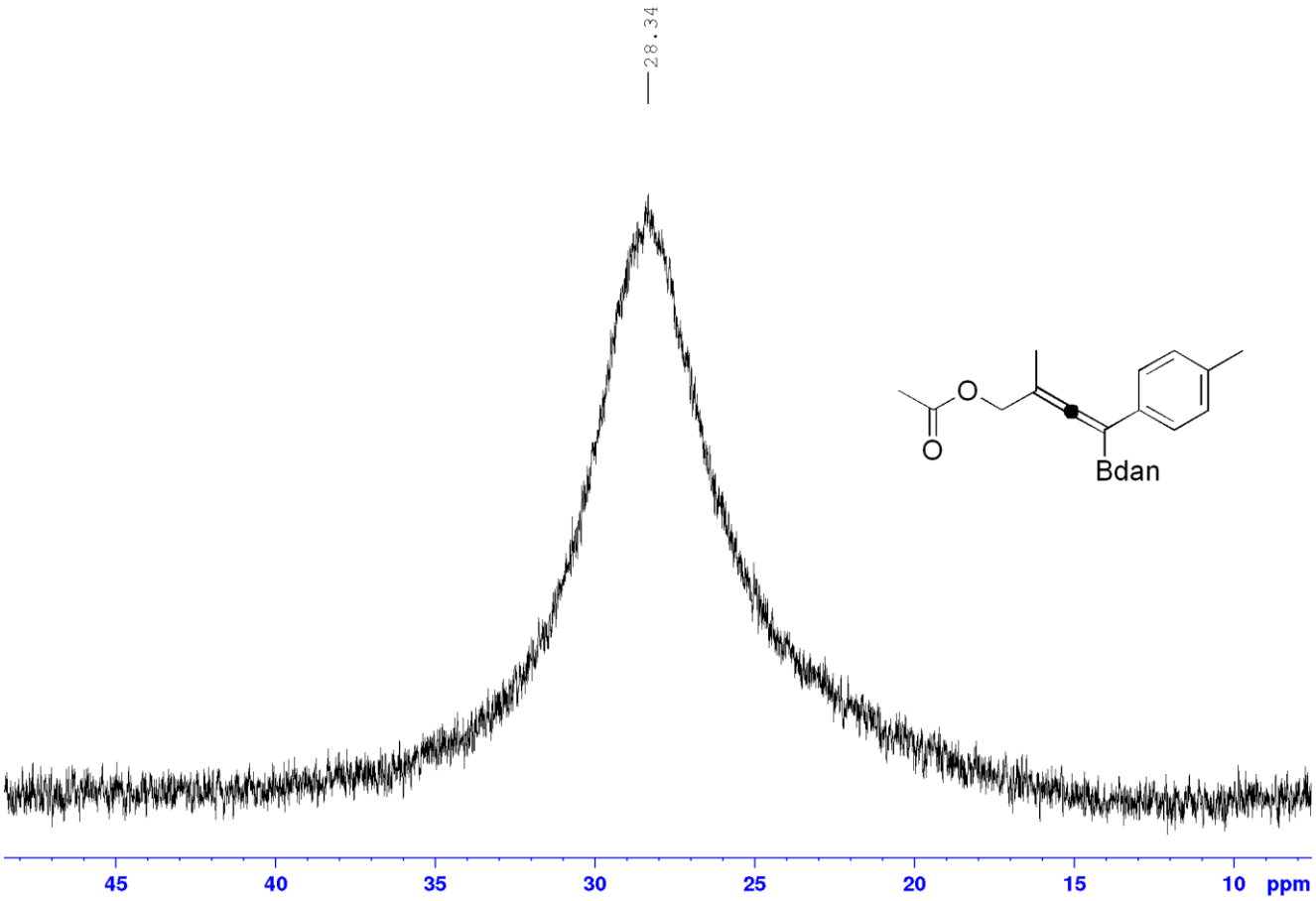
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

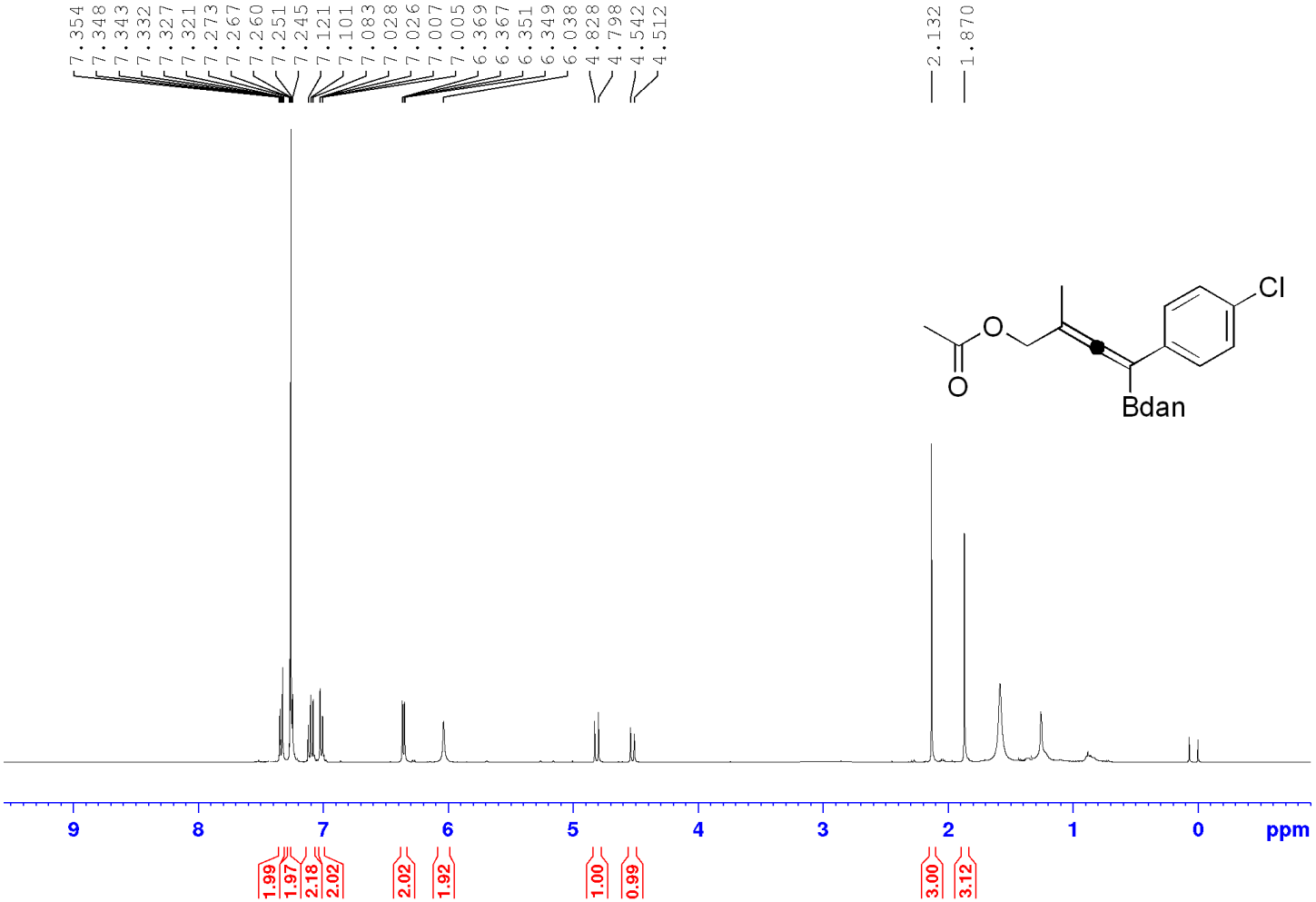


^{11}B NMR (128 MHz, $CDCl_3$)

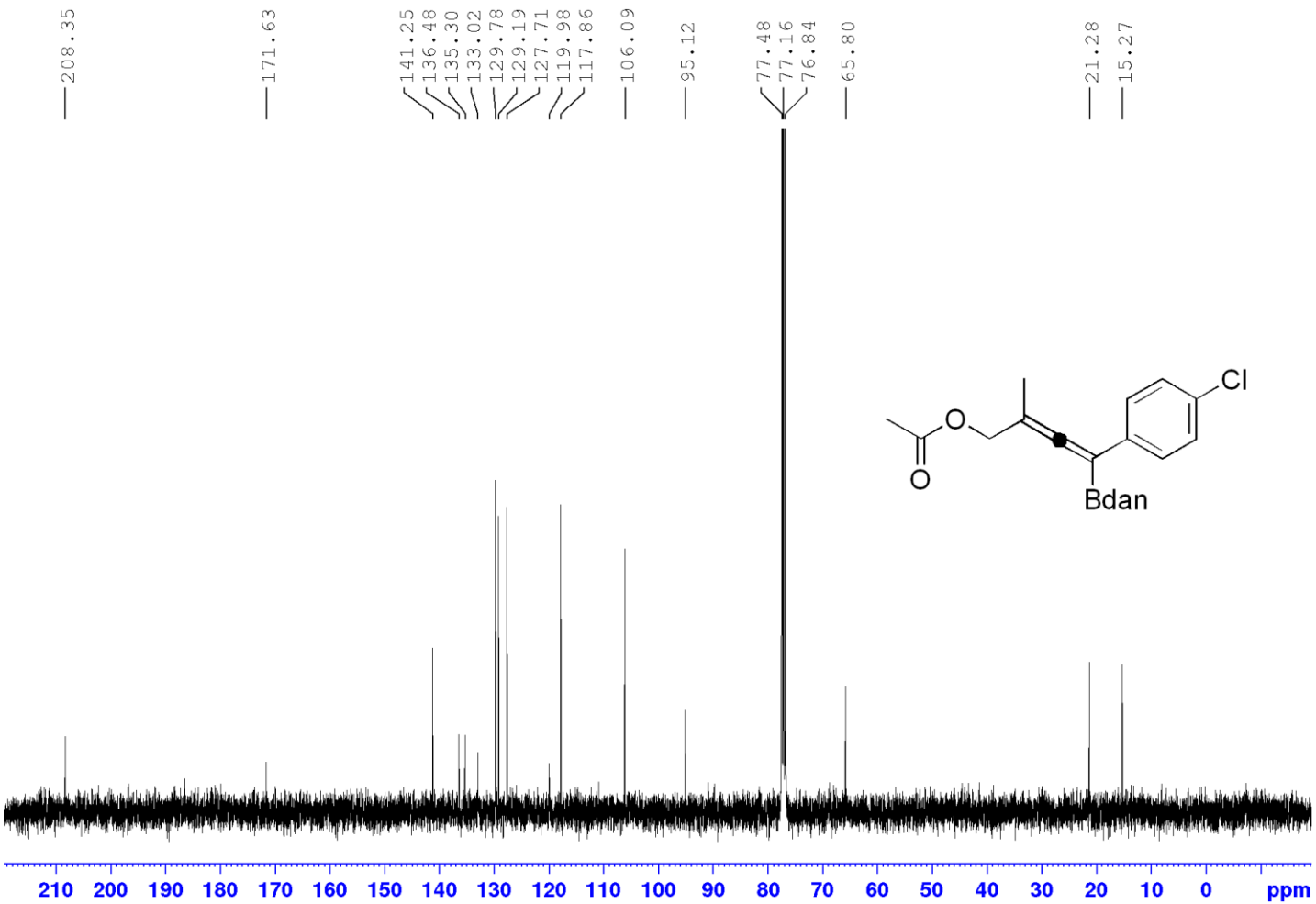


Compound 2m

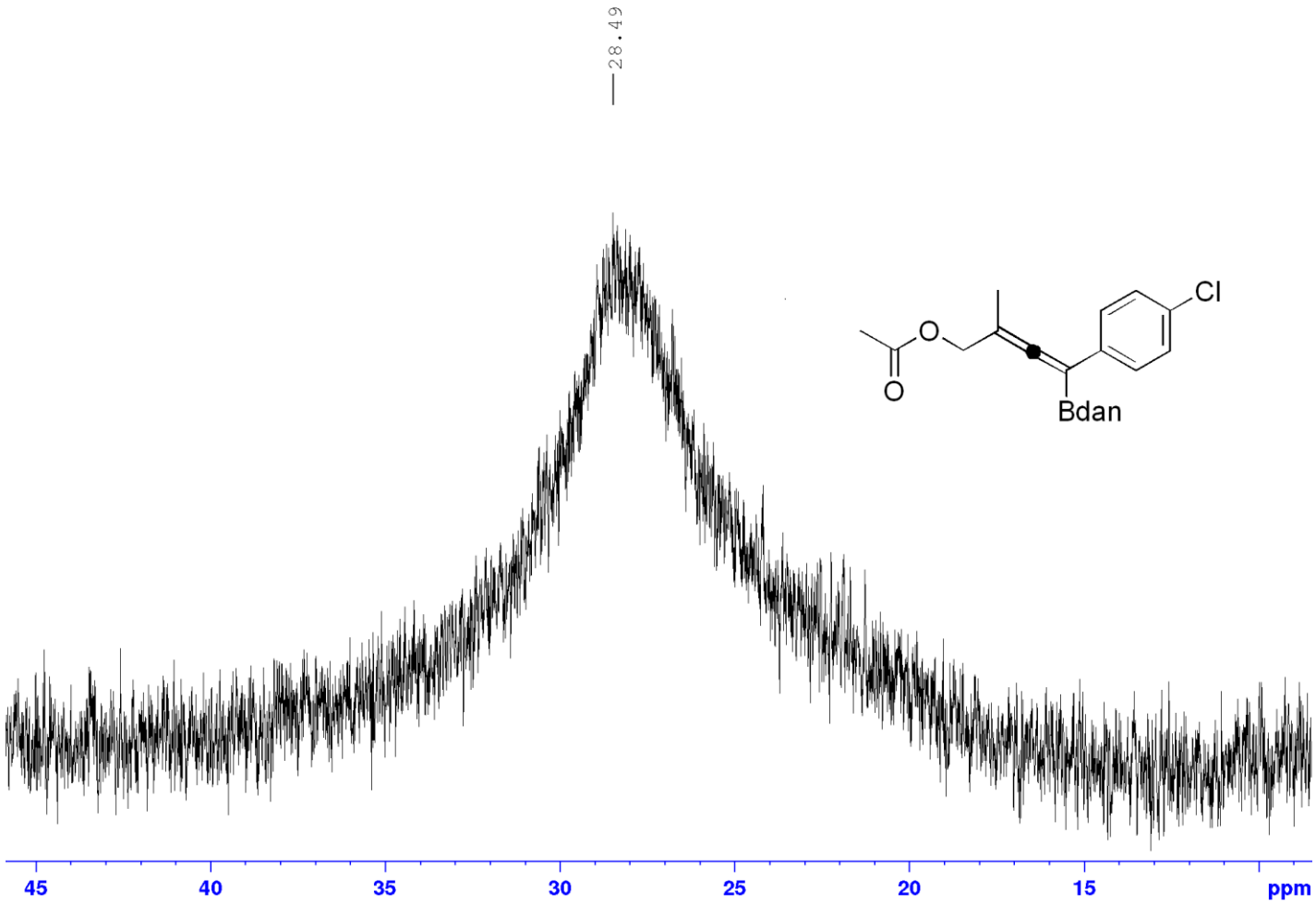
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

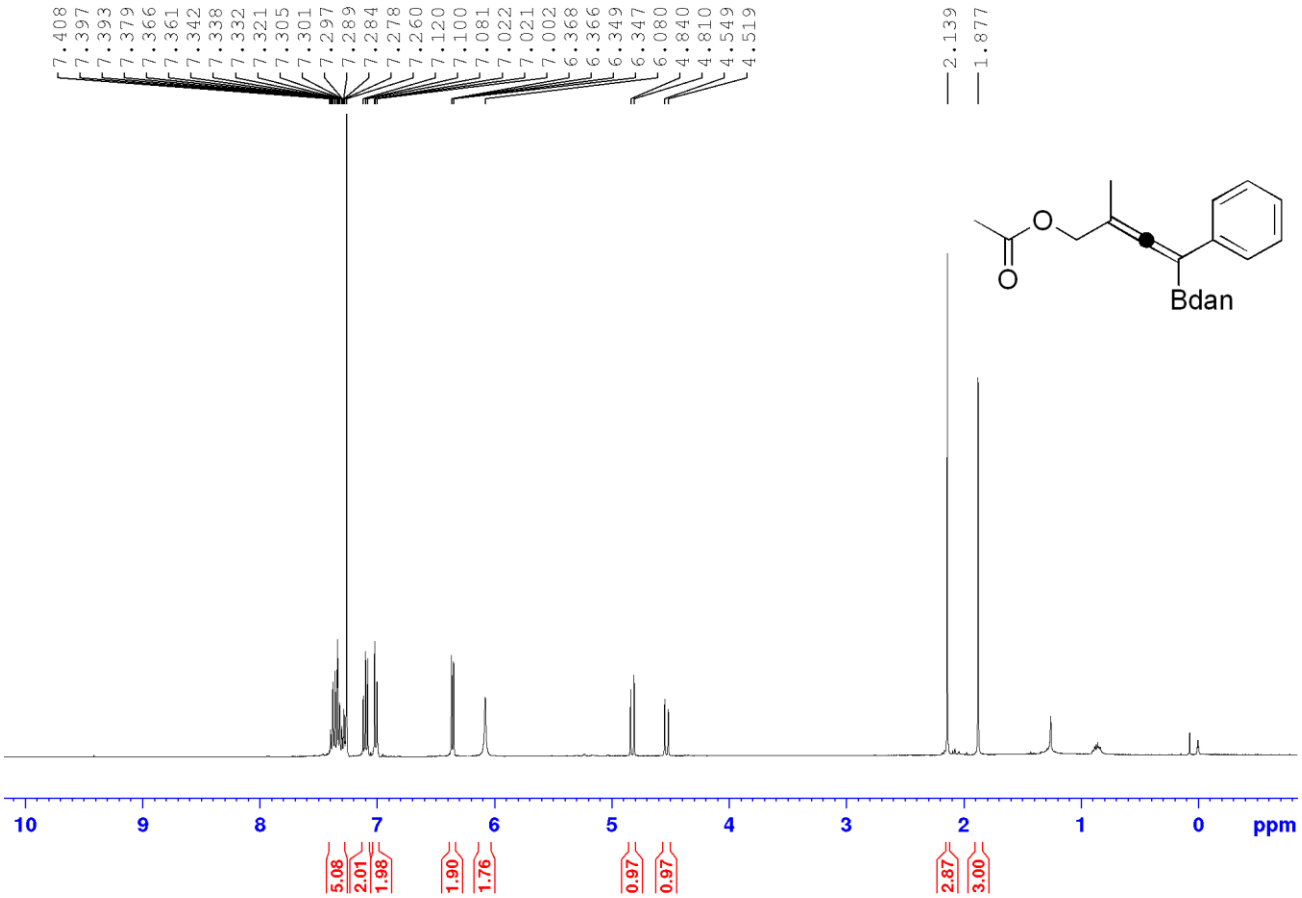


^{11}B NMR (128 MHz, $CDCl_3$)

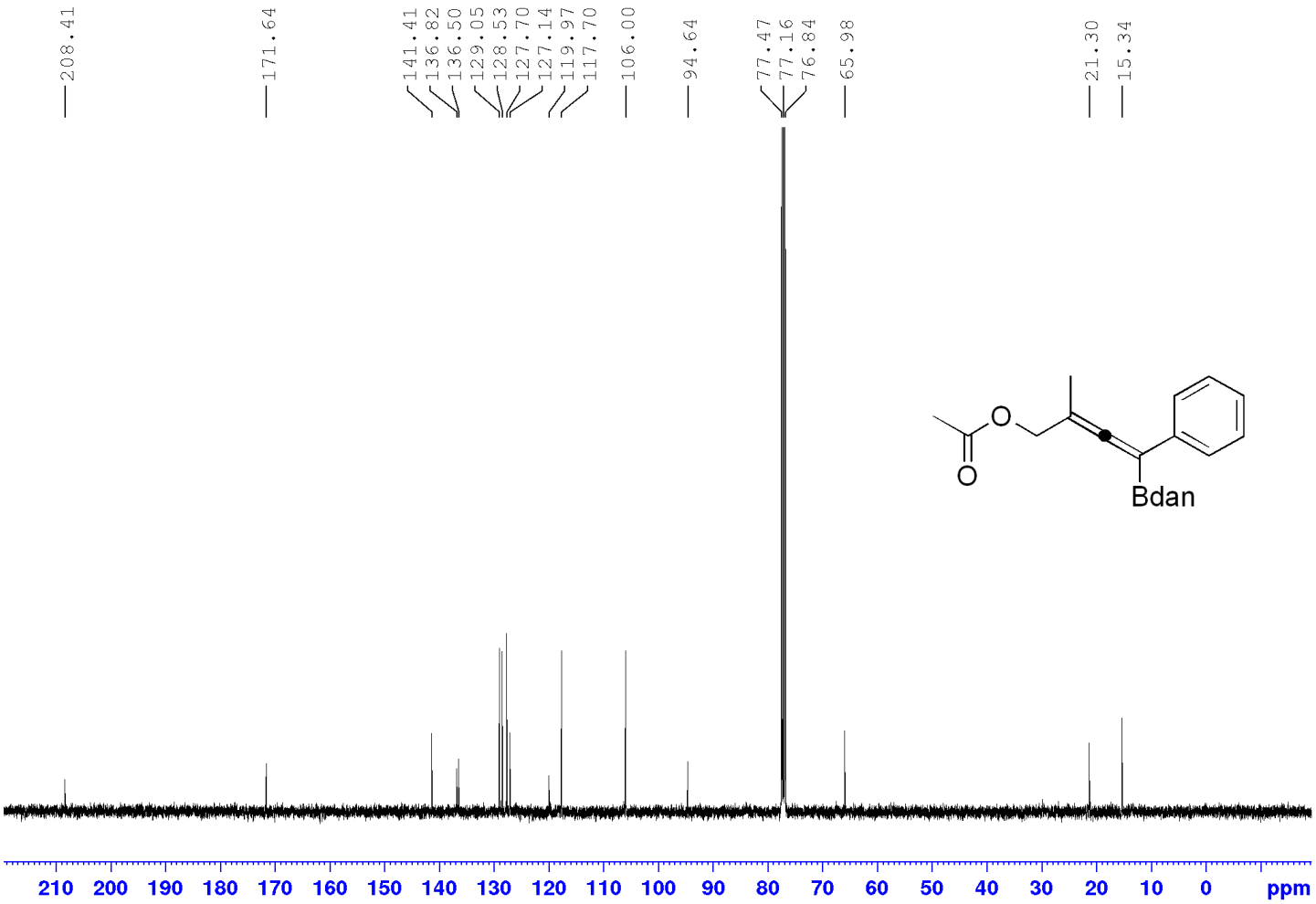


Compound 2n

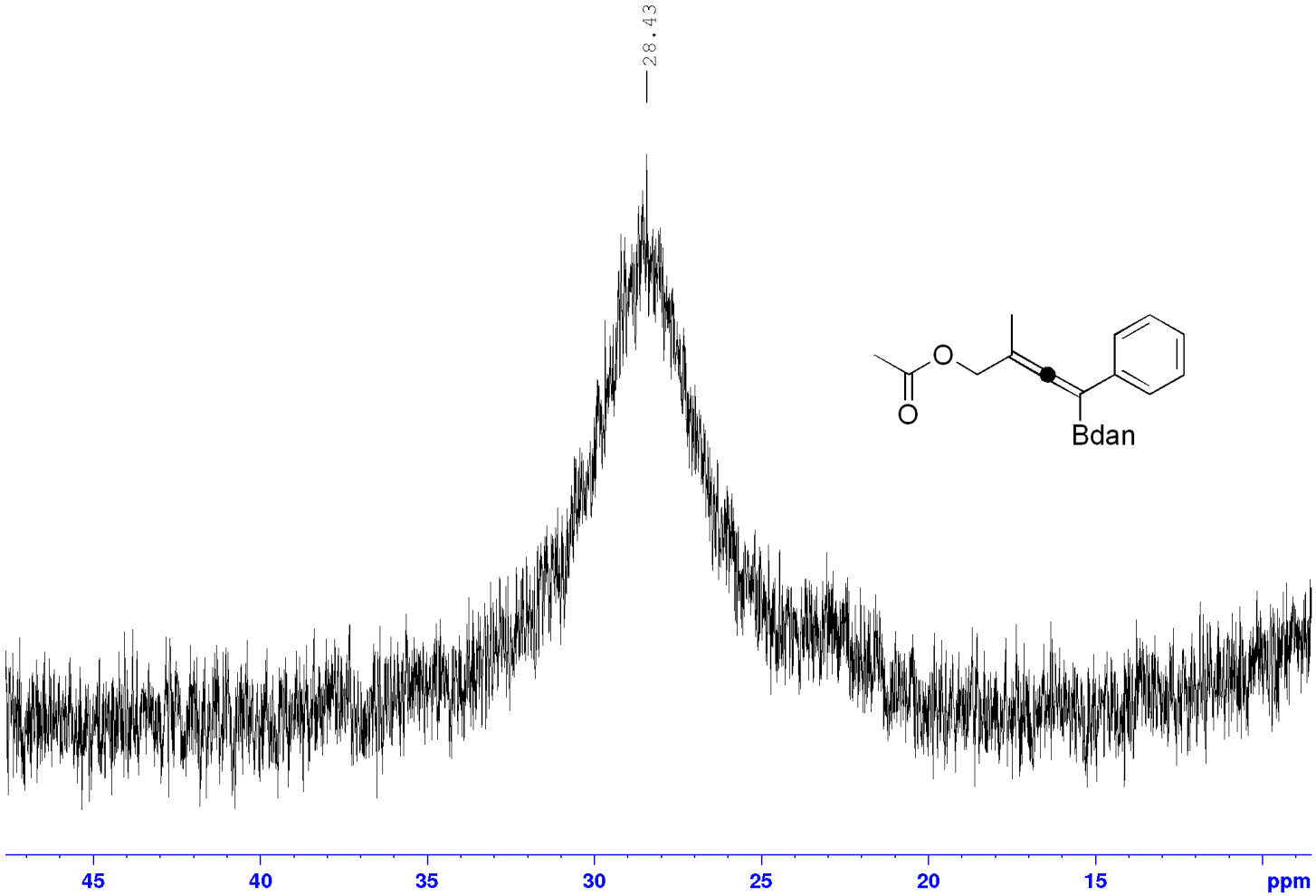
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

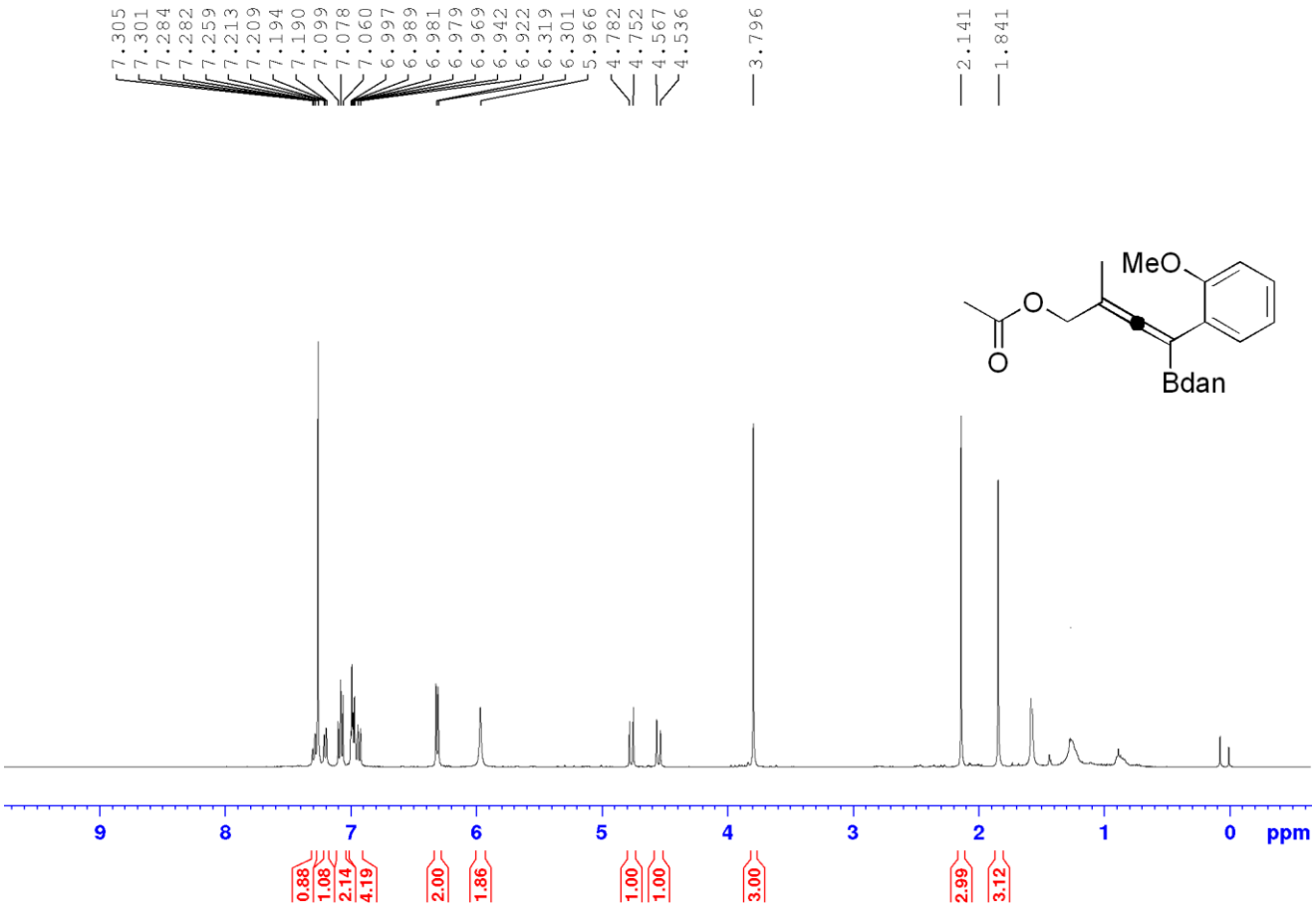


^{11}B NMR (128 MHz, $CDCl_3$)

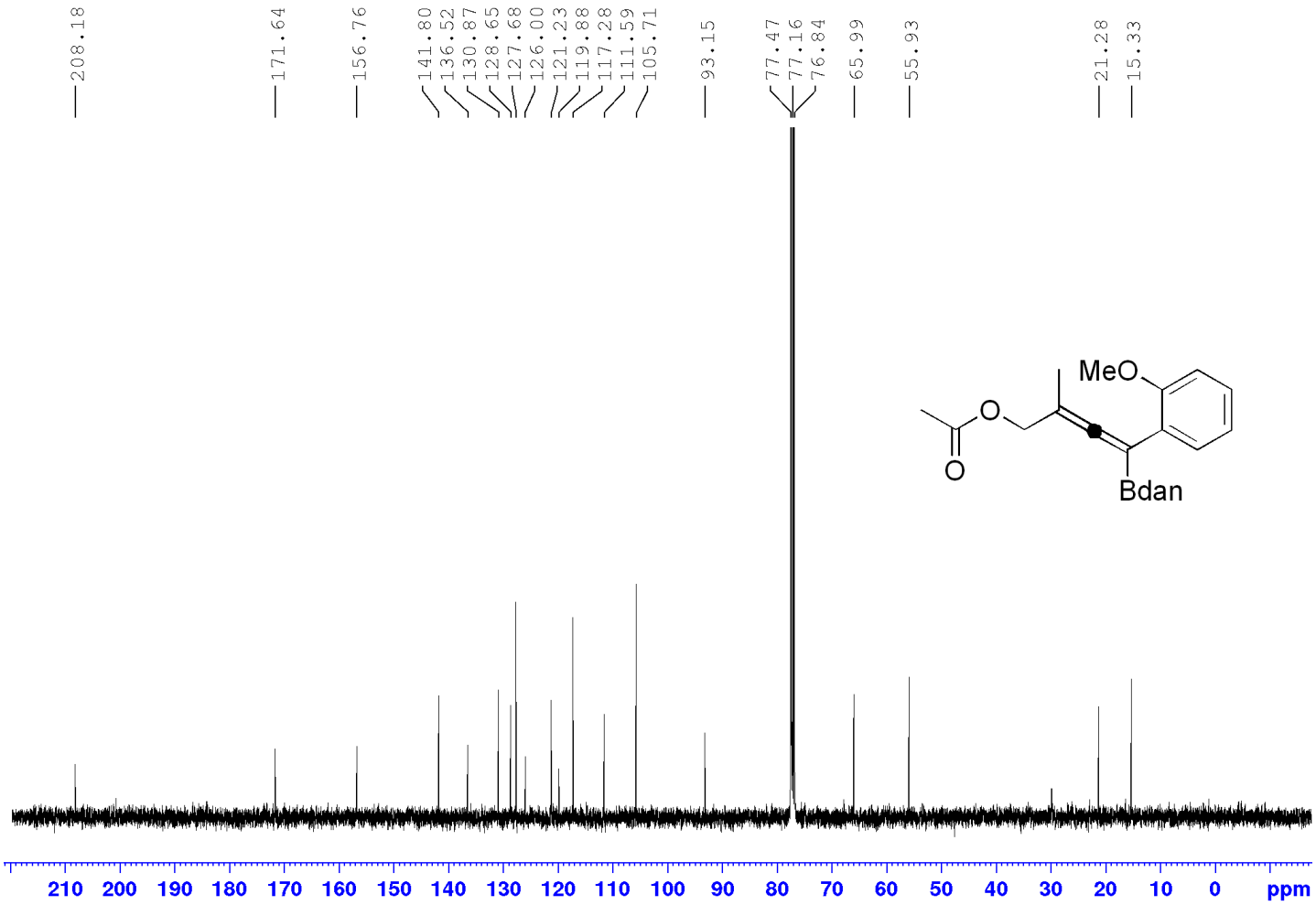


Compound 2o

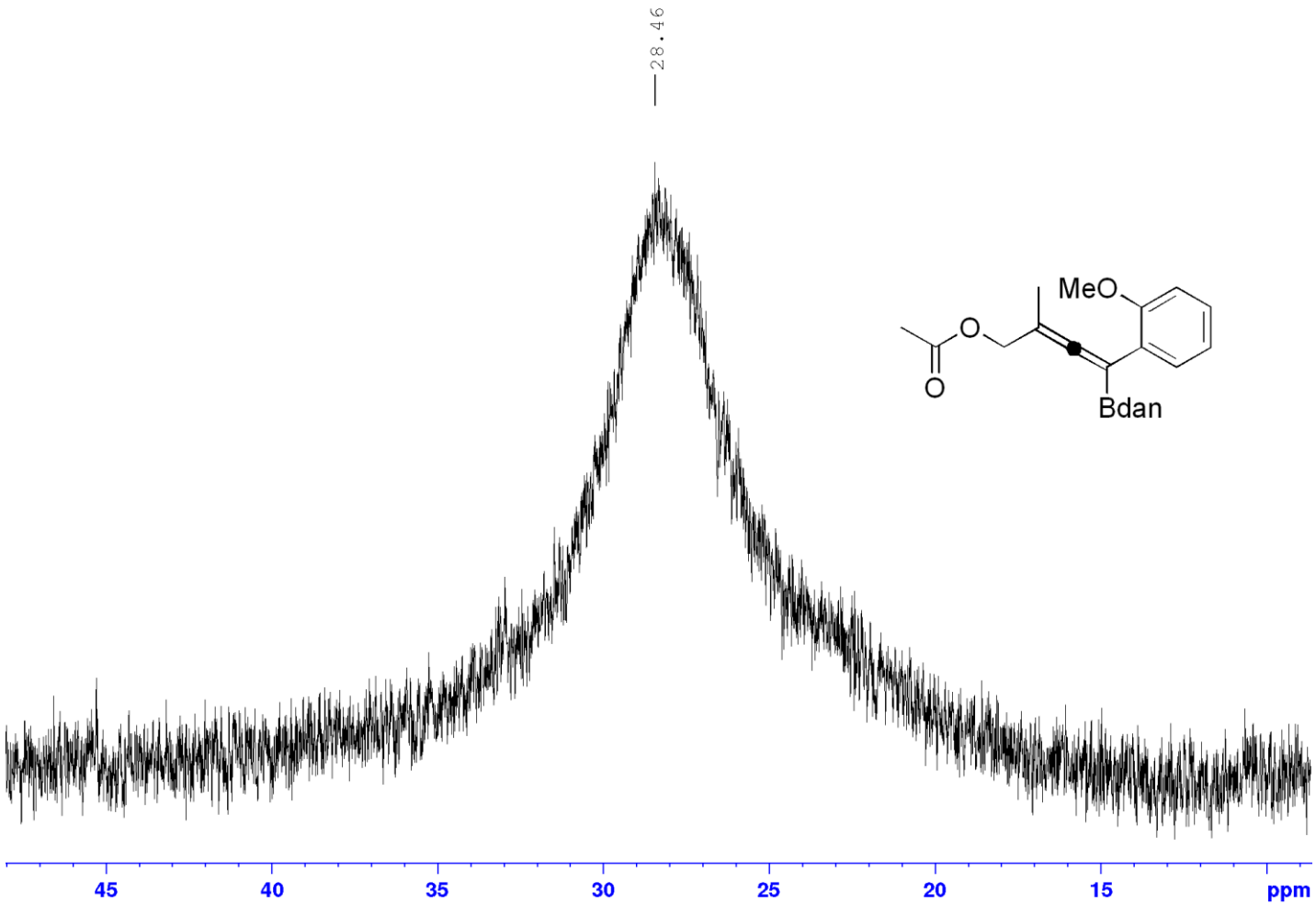
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

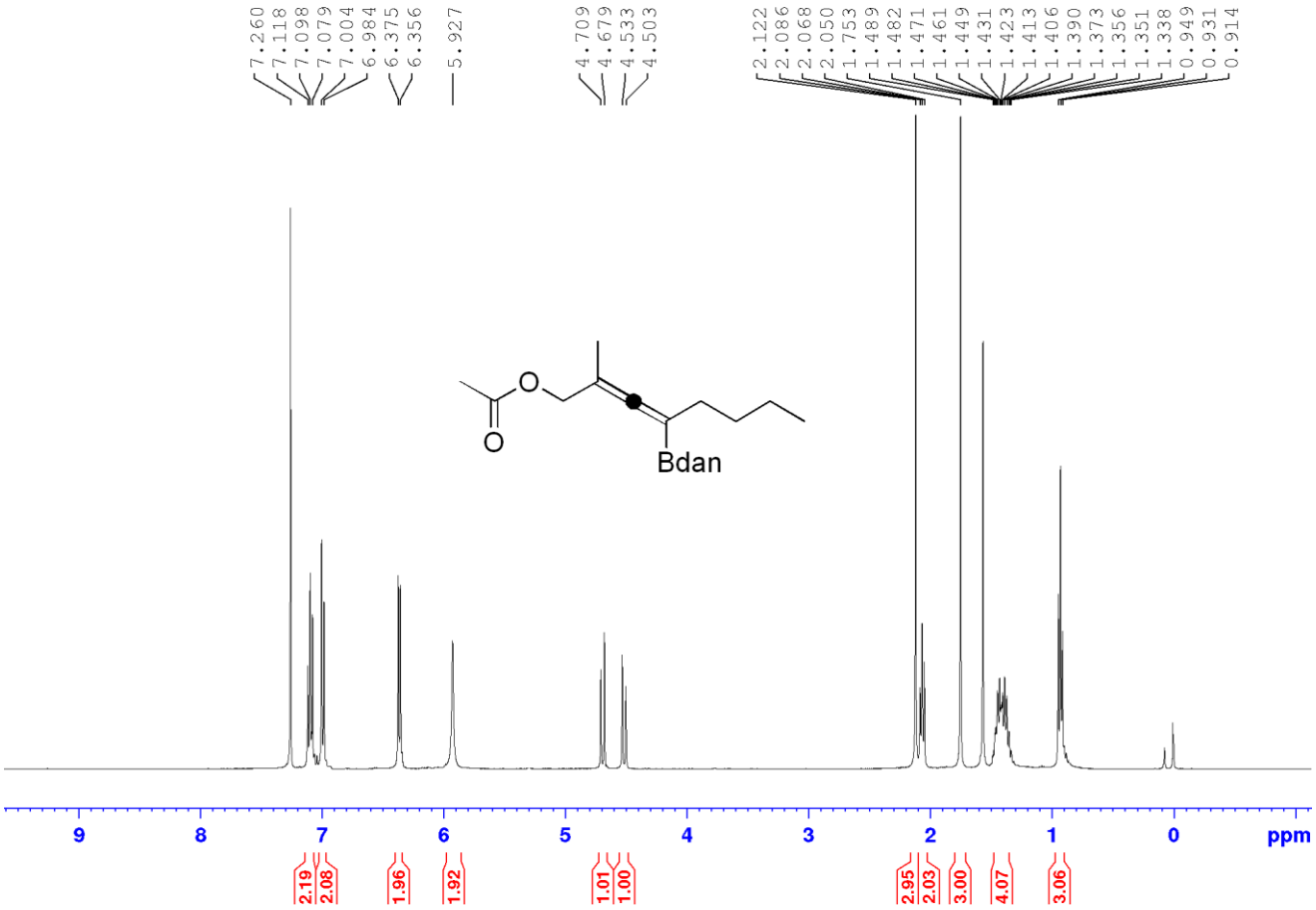


^{11}B NMR (128 MHz, $CDCl_3$)

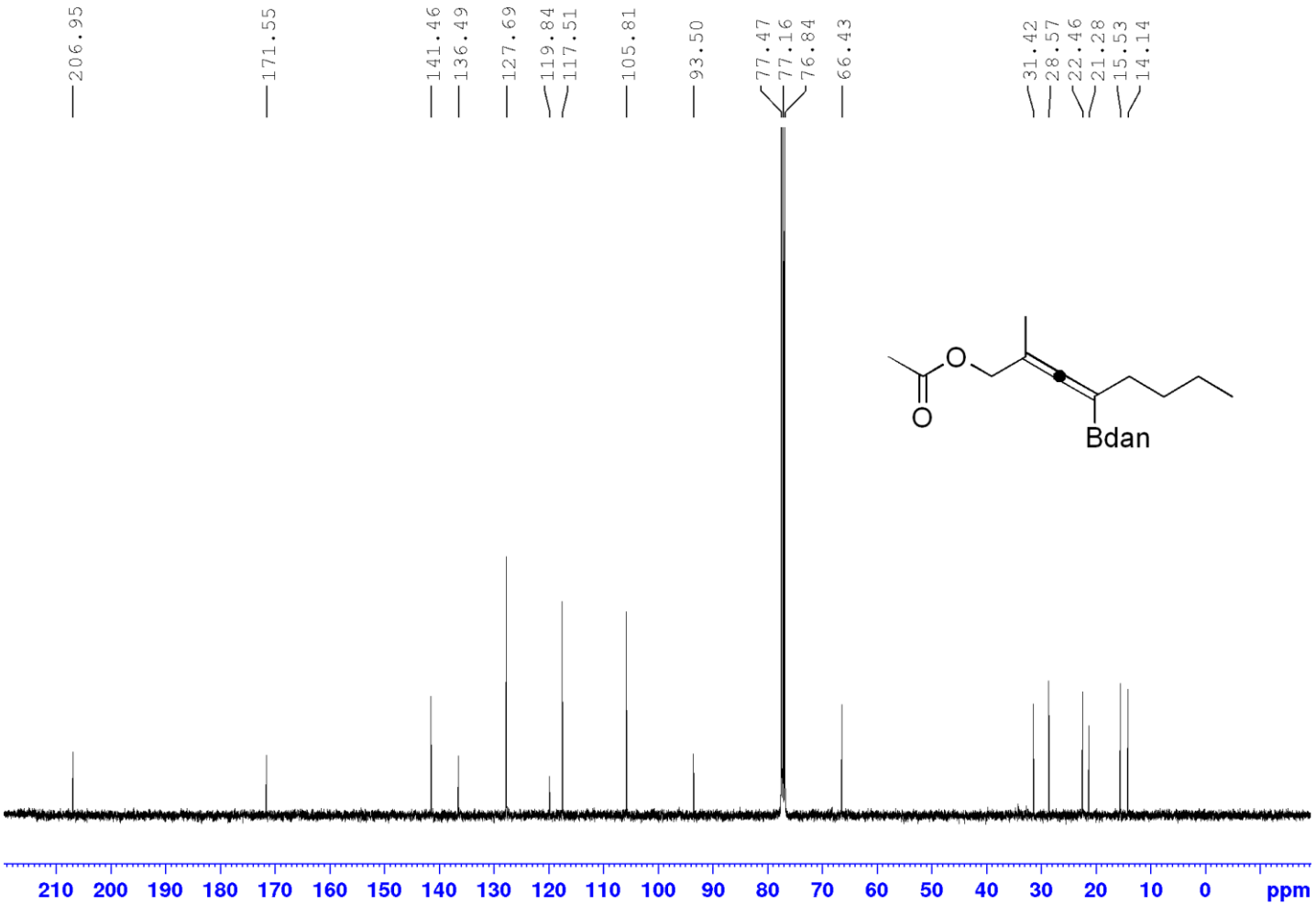


Compound 2p

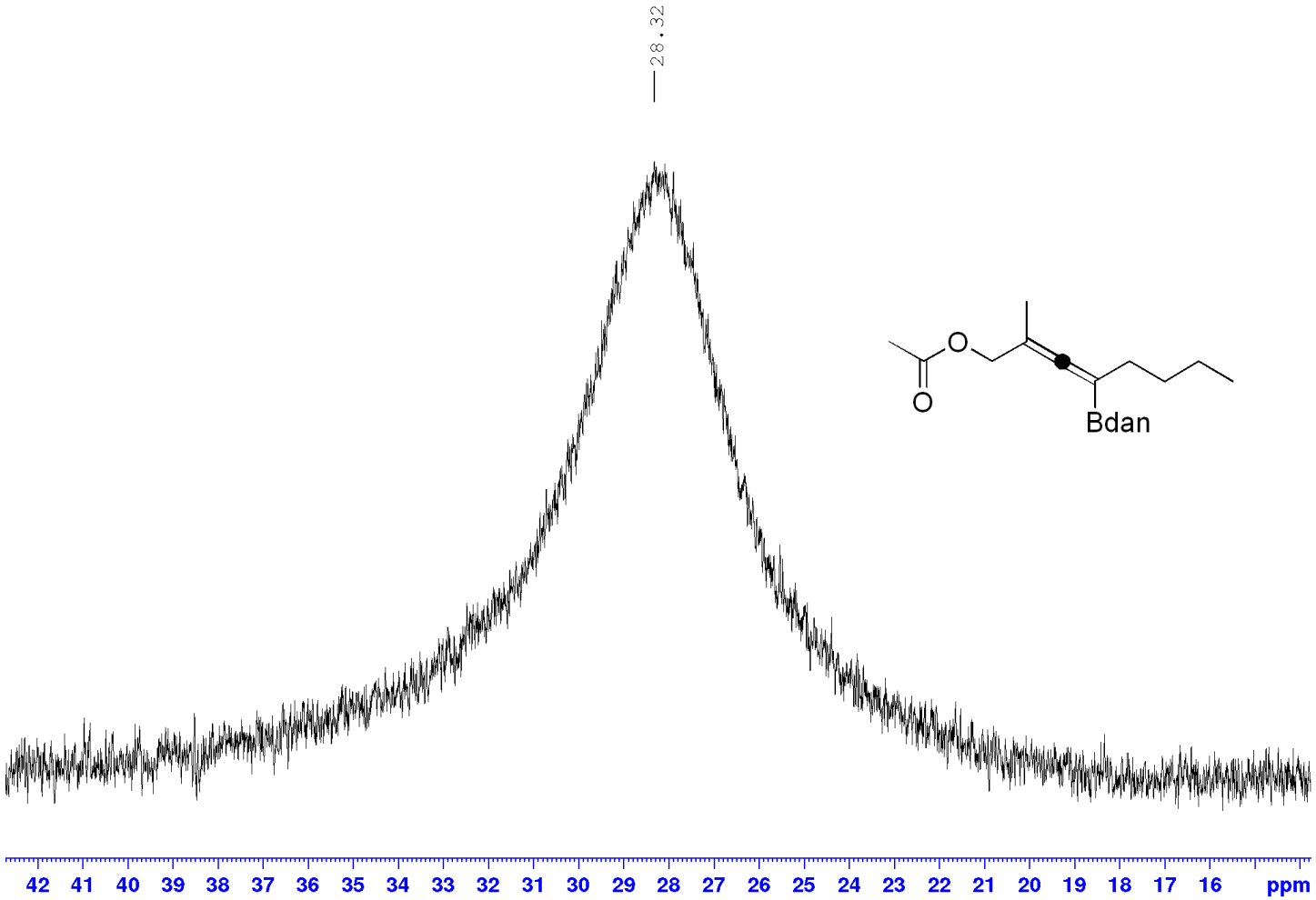
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

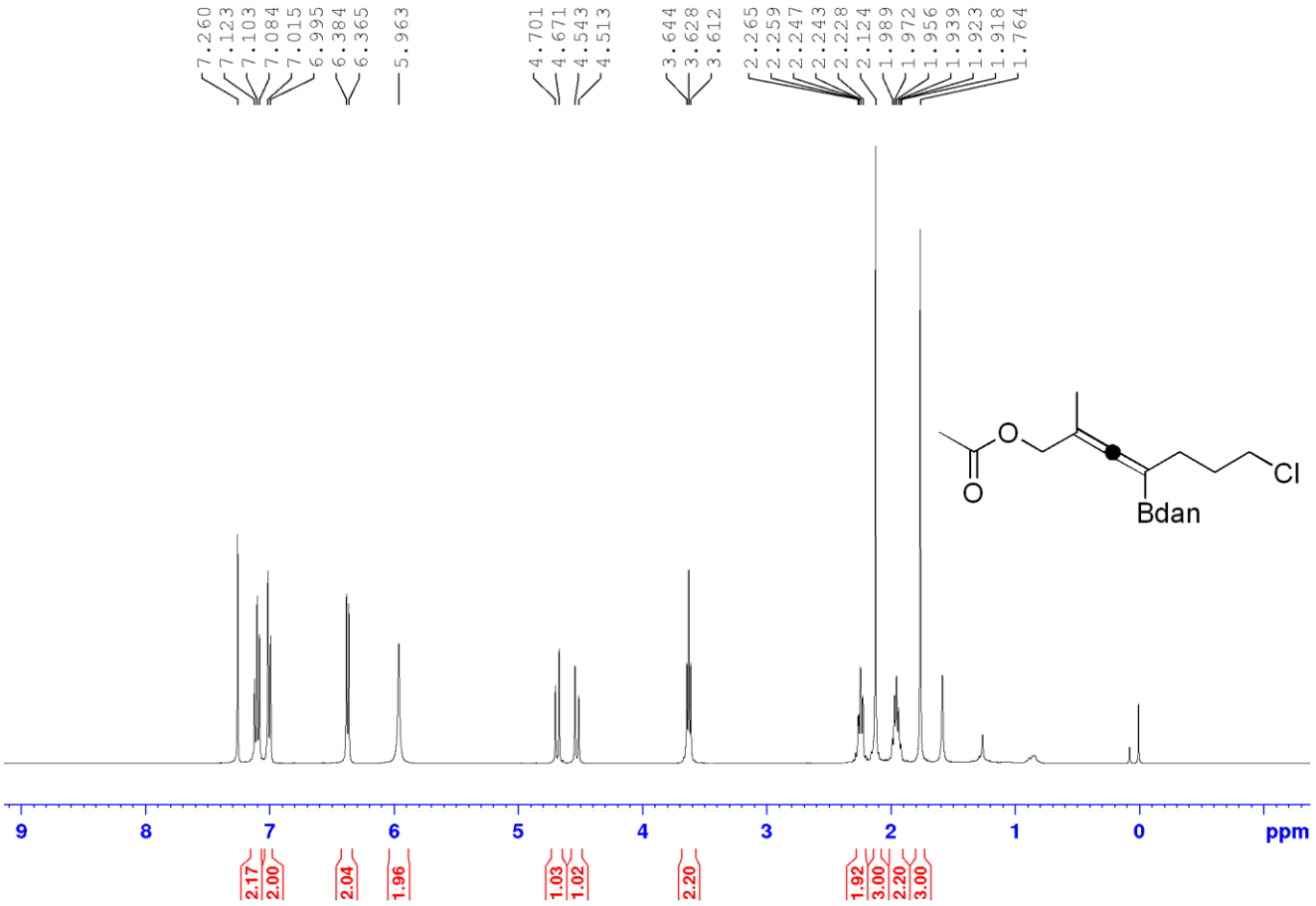


^{11}B NMR (128 MHz, $CDCl_3$)

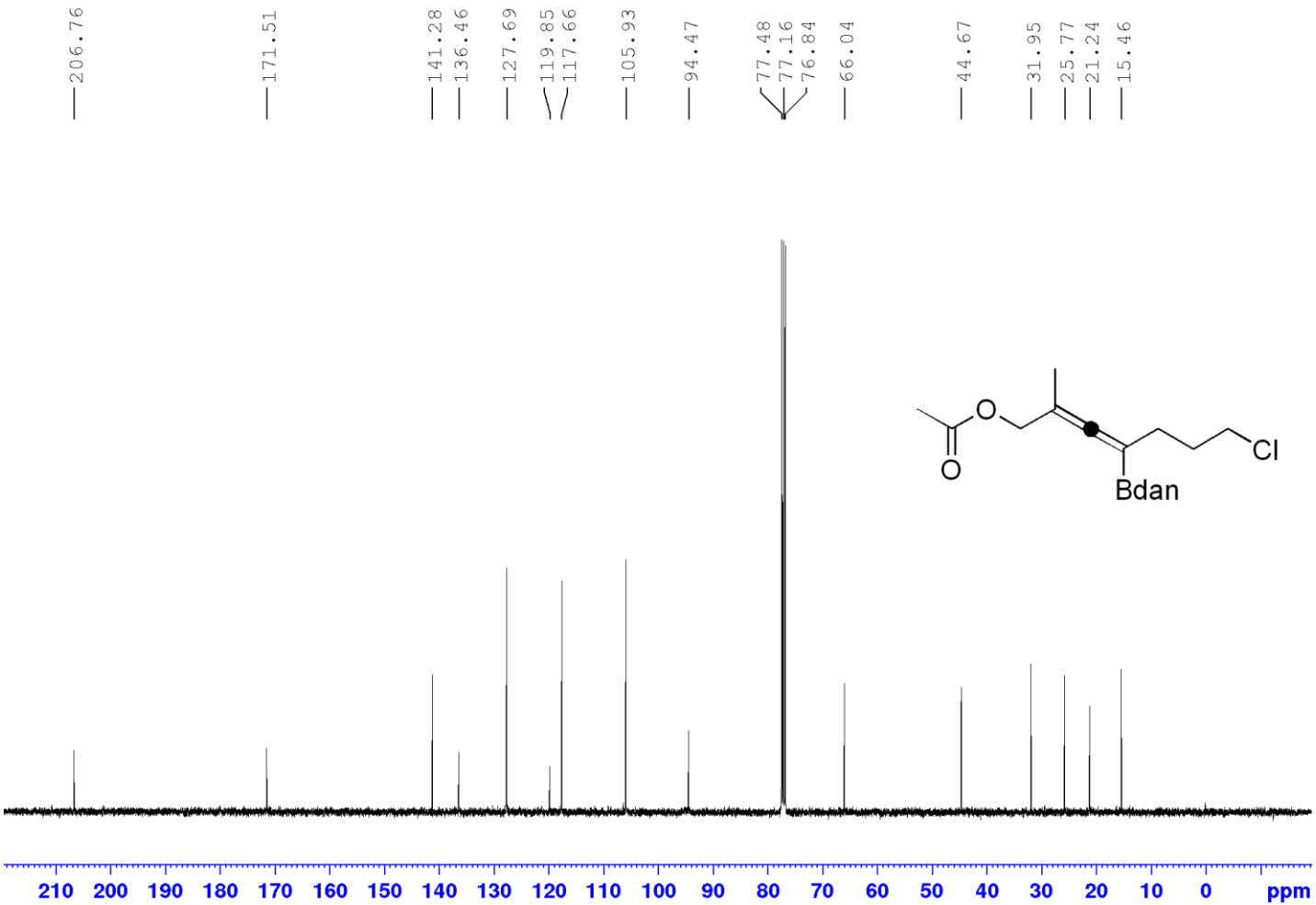


Compound 2q

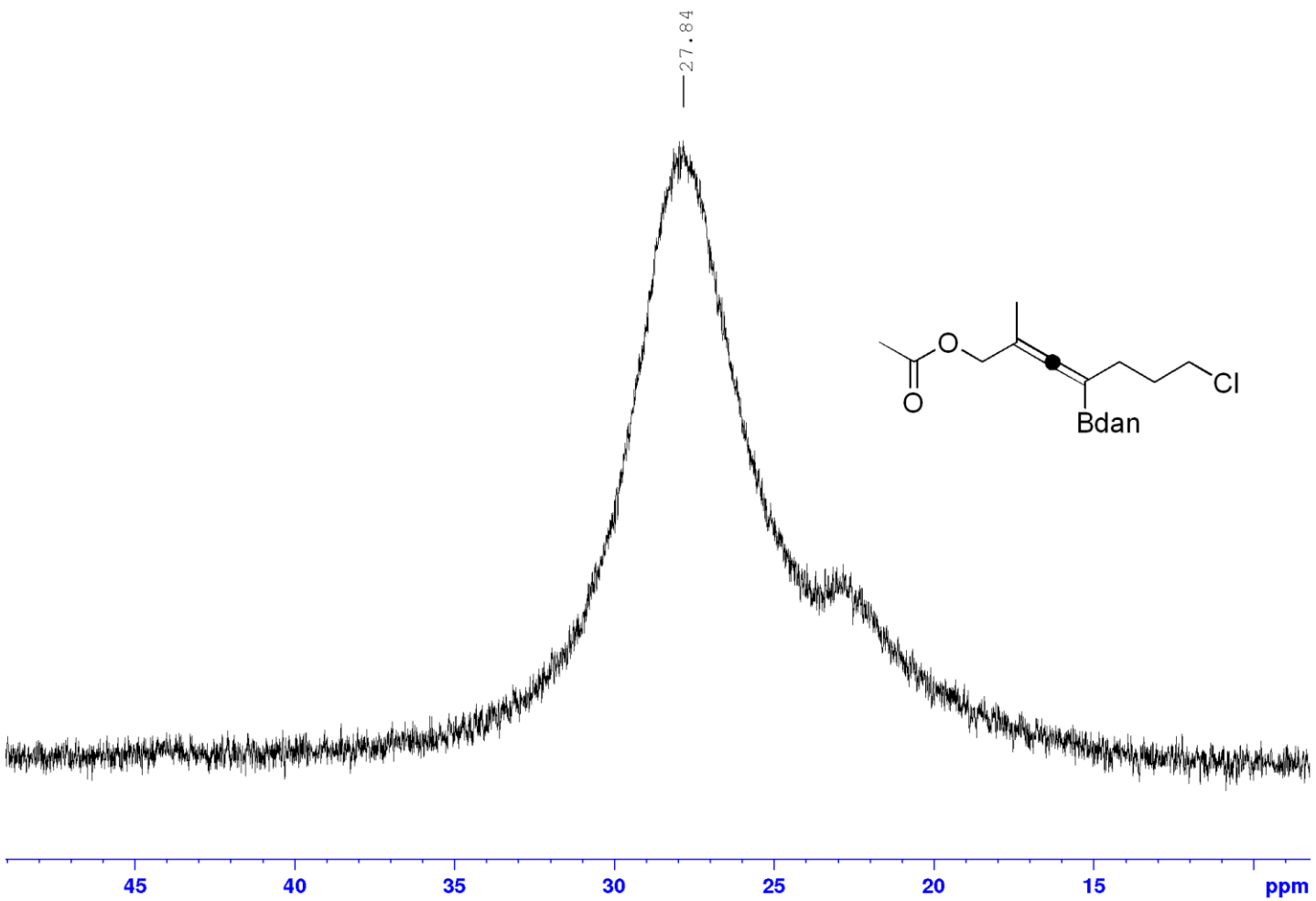
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

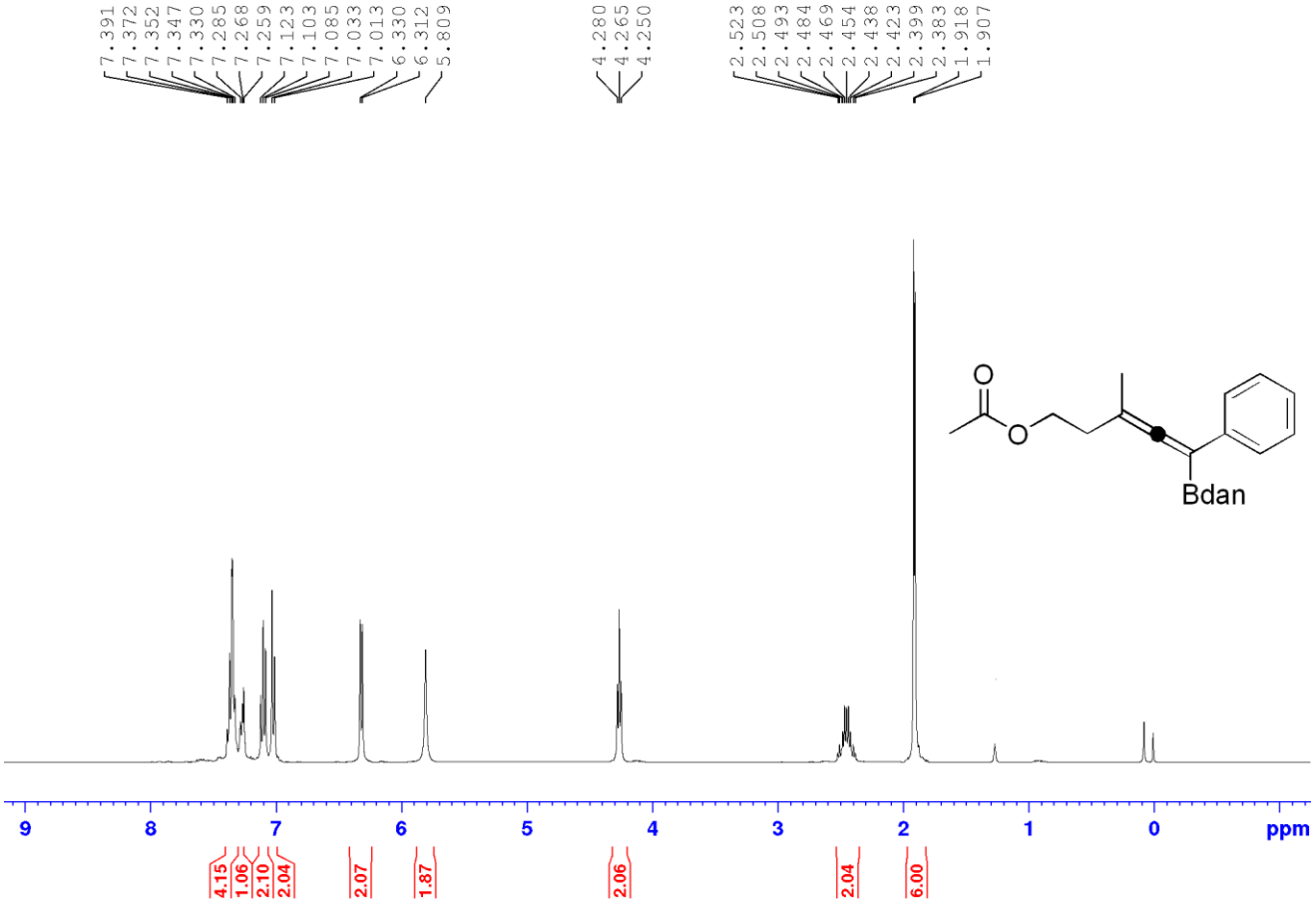


^{11}B NMR (128 MHz, $CDCl_3$)

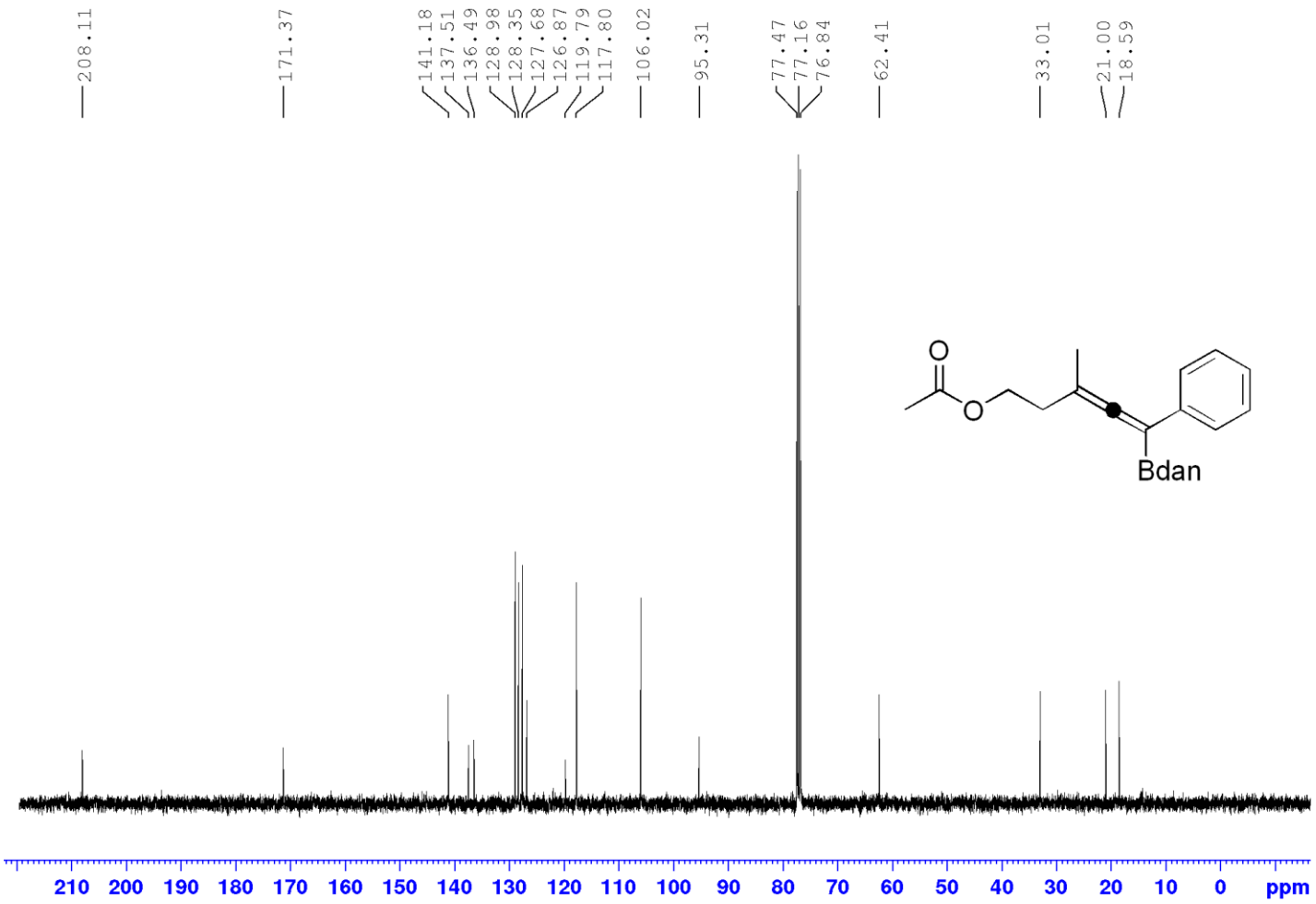


Compound 2r

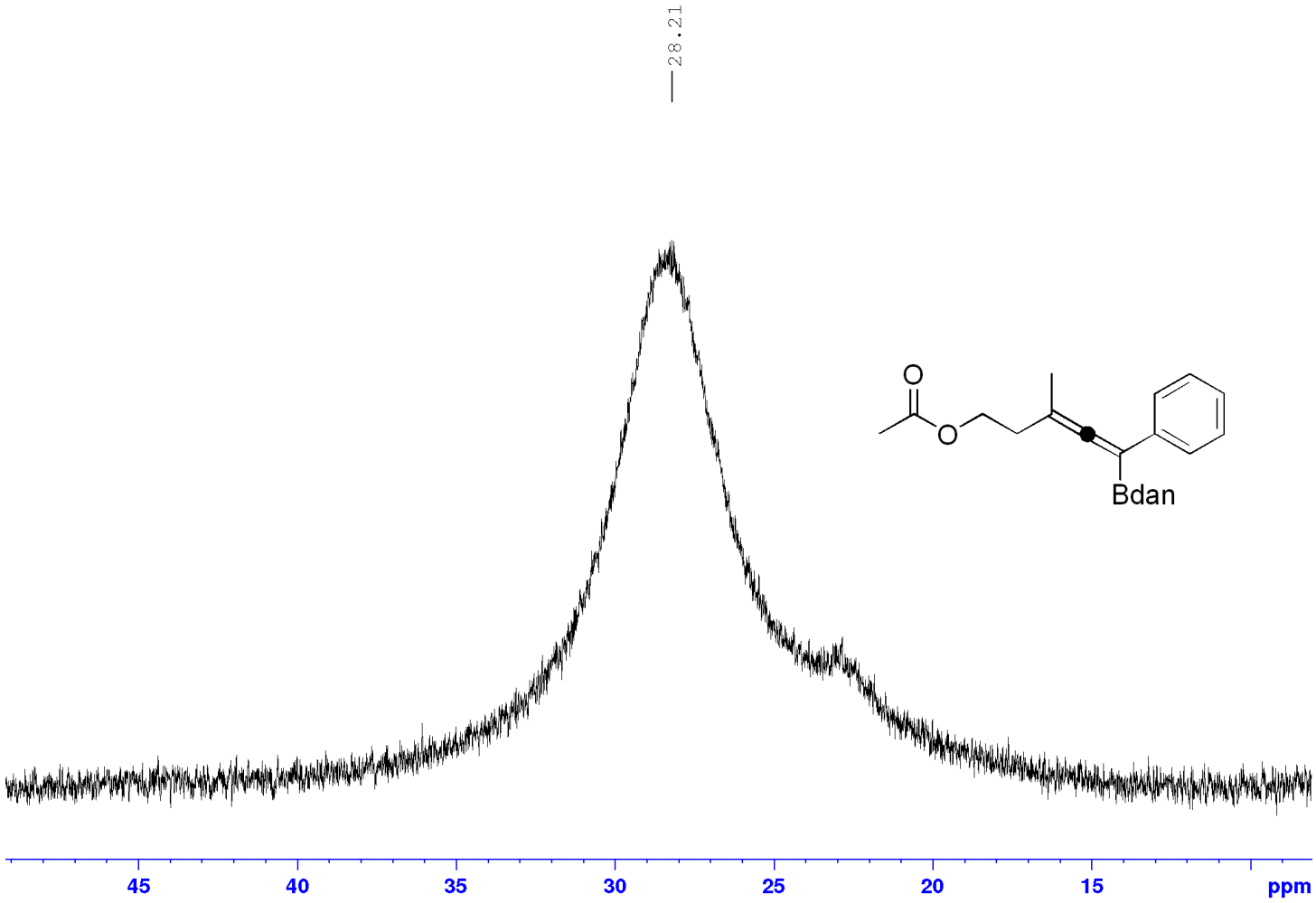
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

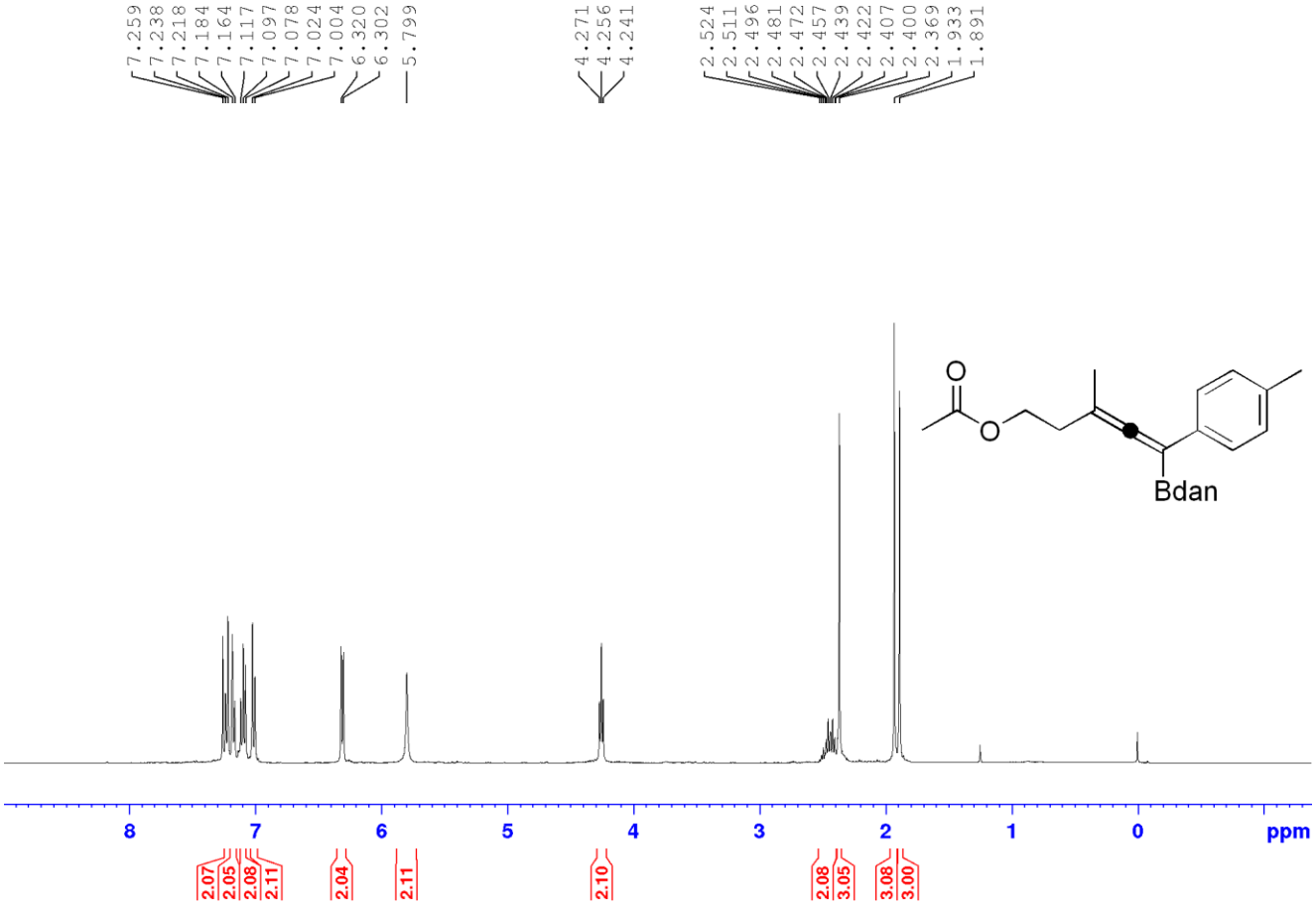


^{11}B NMR (128 MHz, $CDCl_3$)

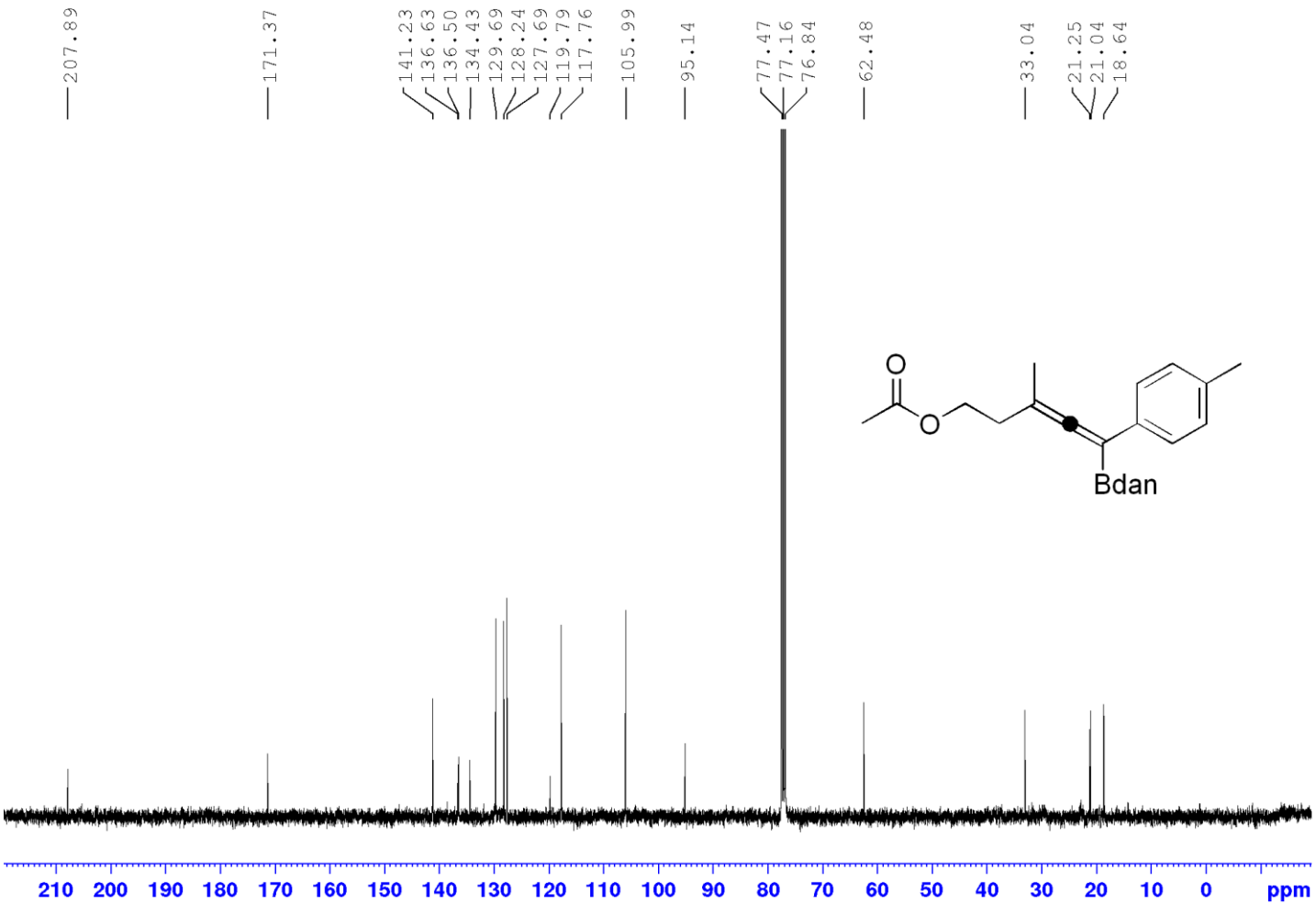


Compound 2s

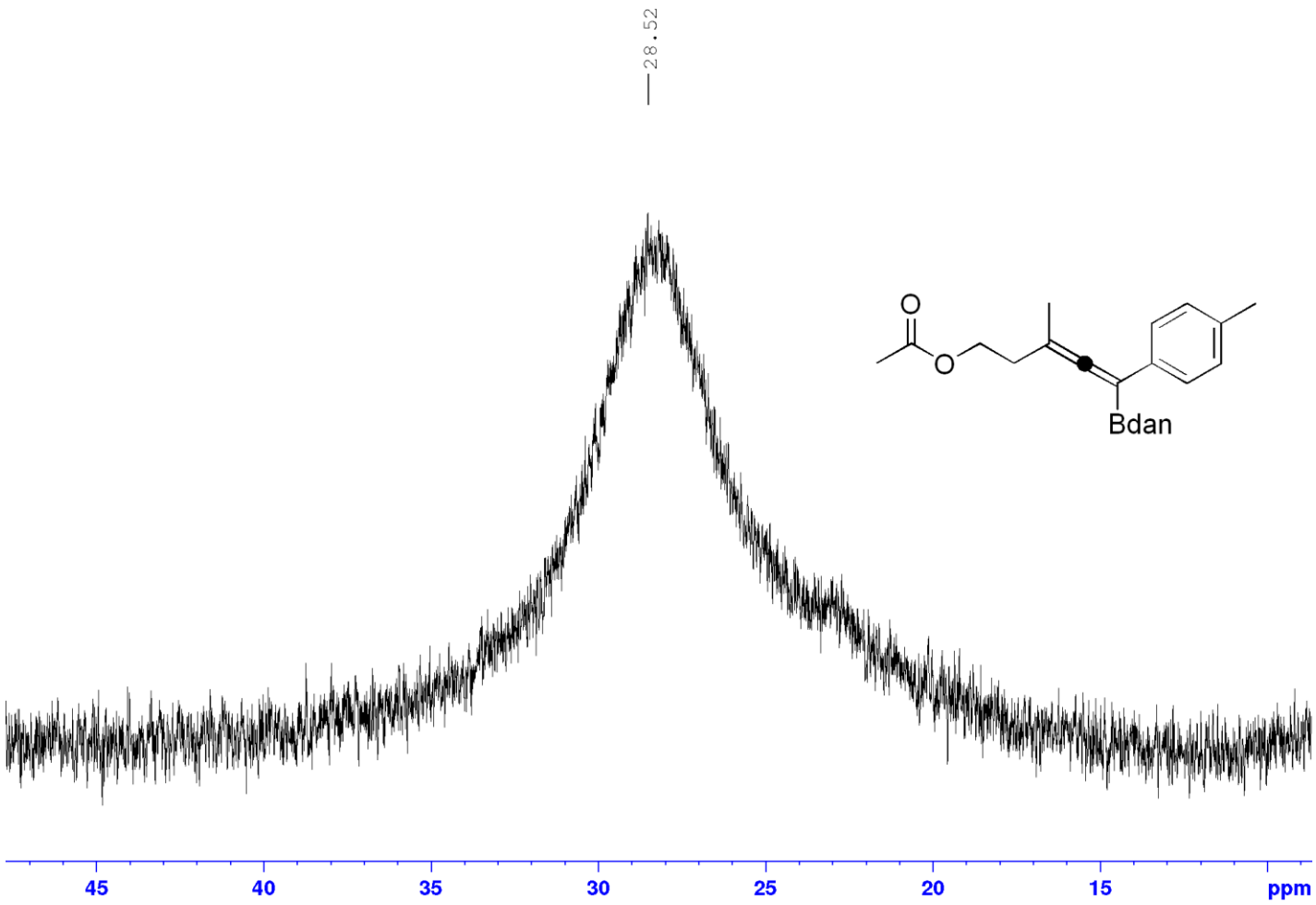
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

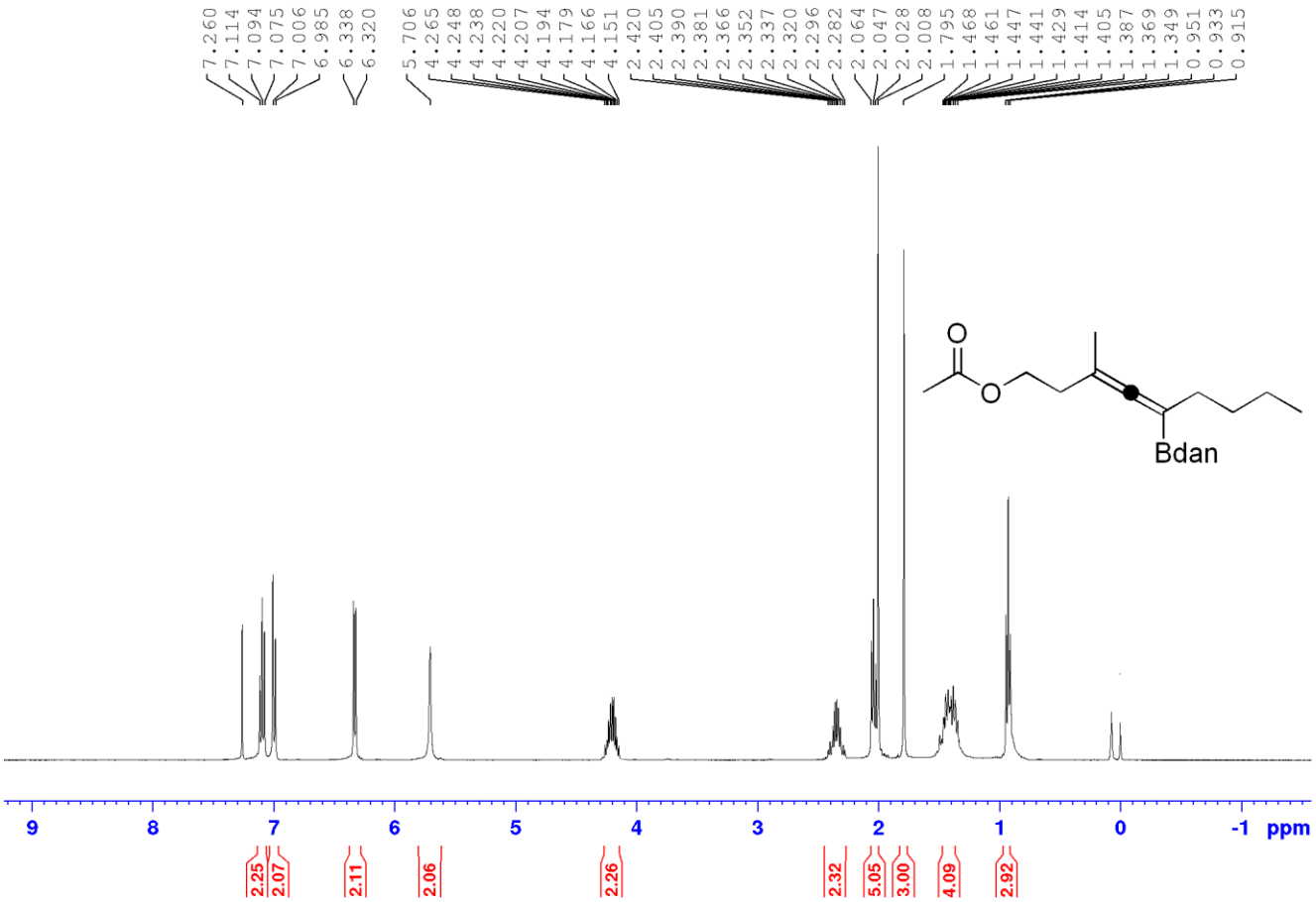


^{11}B NMR (128 MHz, $CDCl_3$)

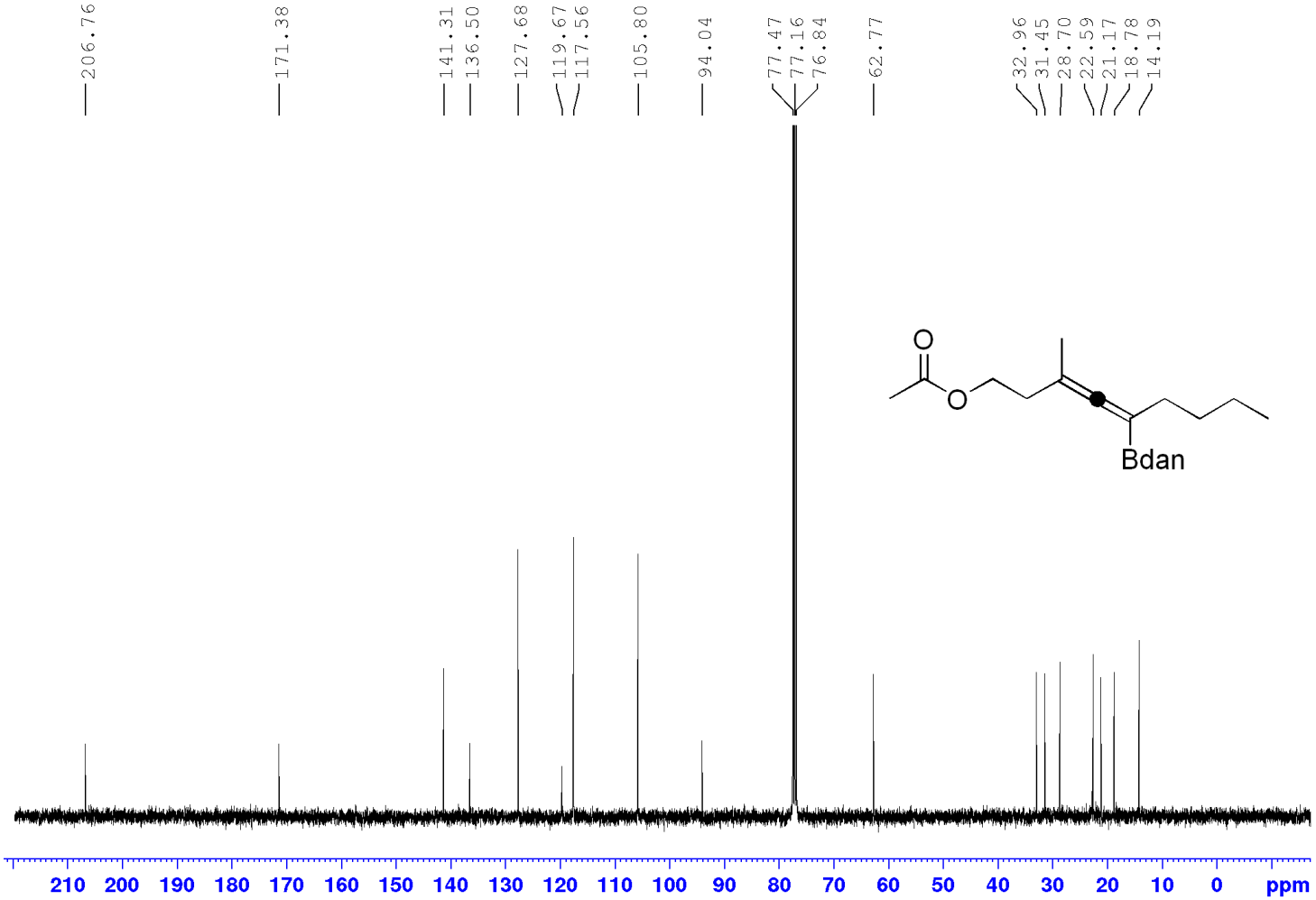


Compound 2t

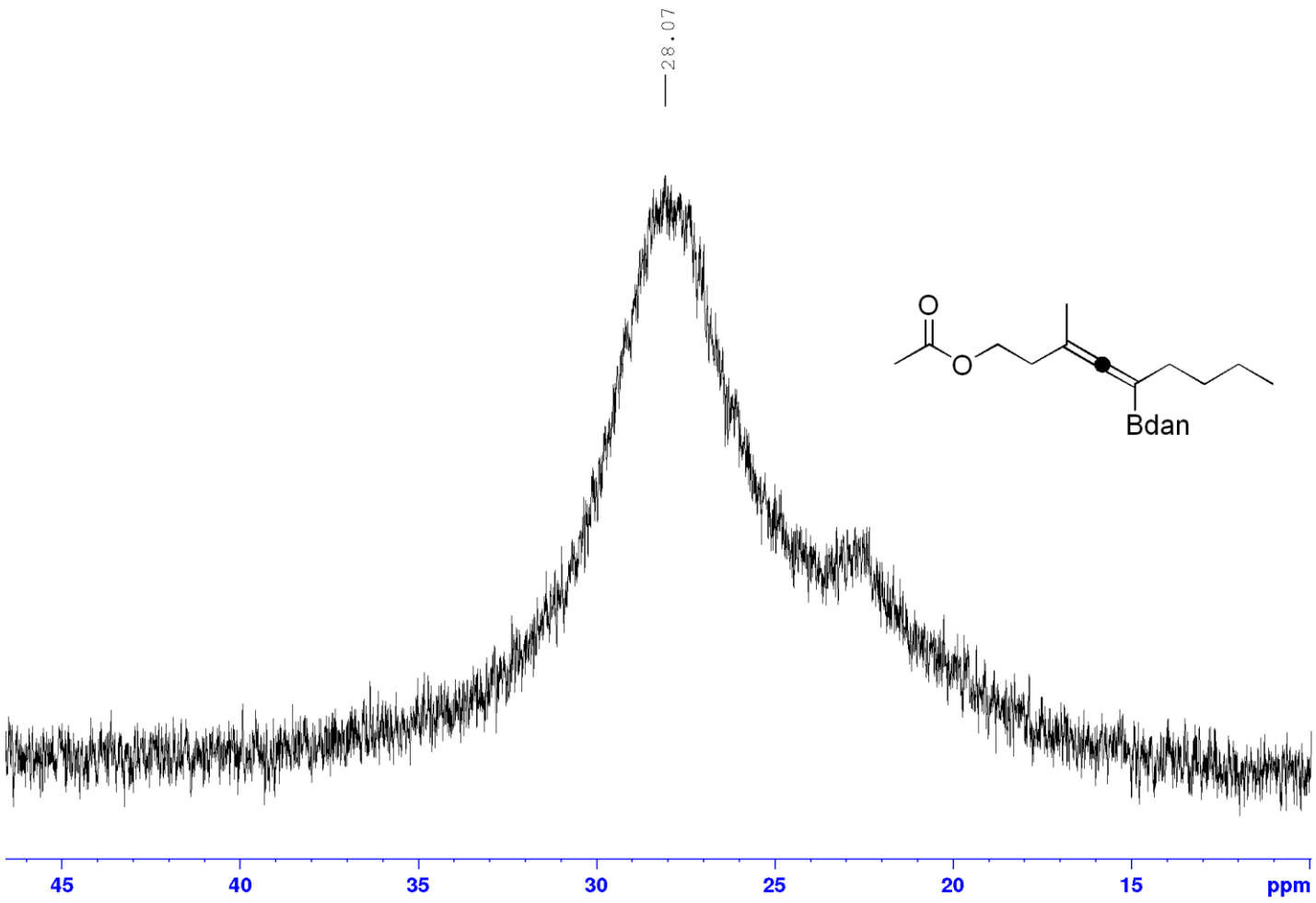
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

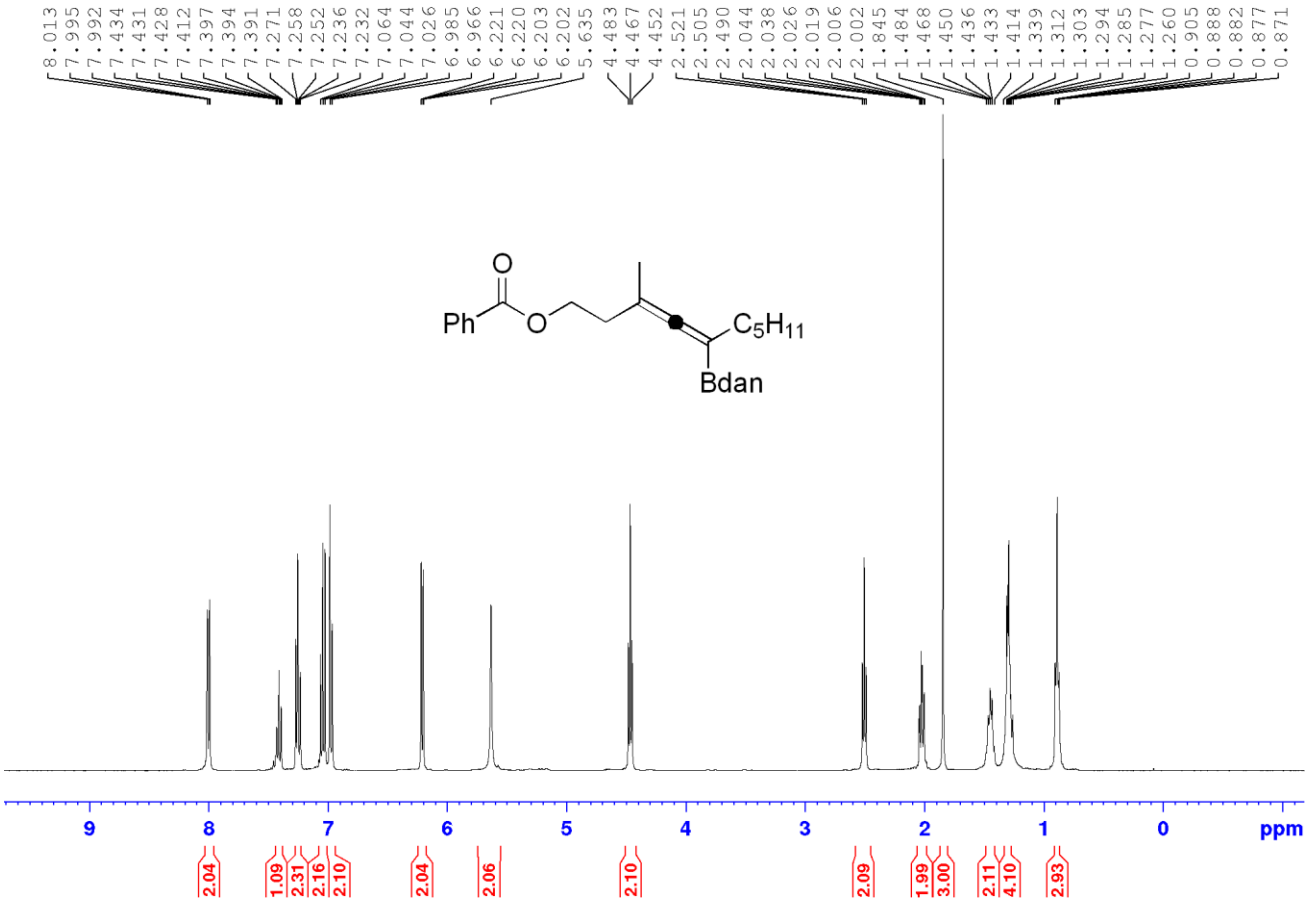


^{11}B NMR (128 MHz, $CDCl_3$)

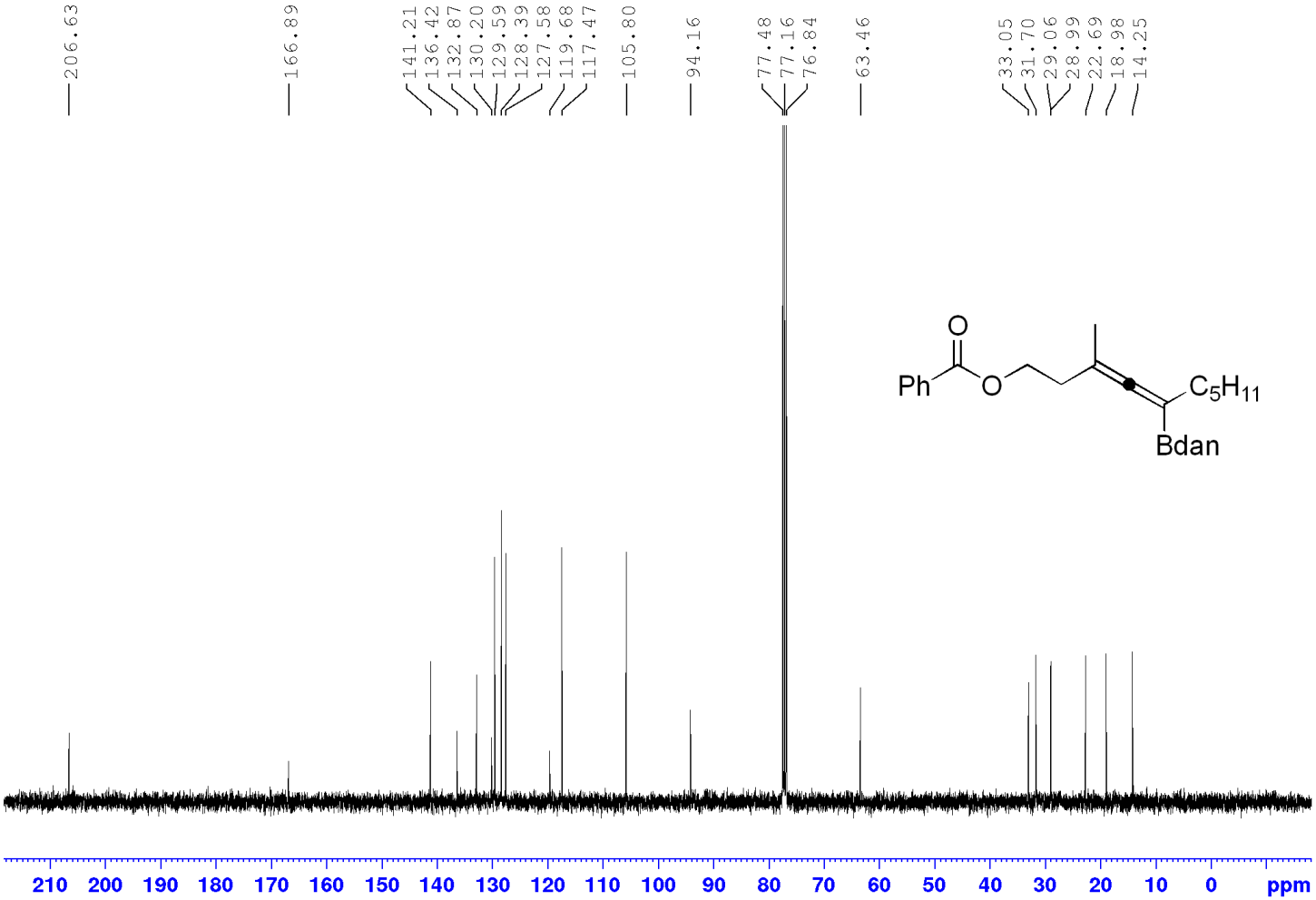


Compound 2u

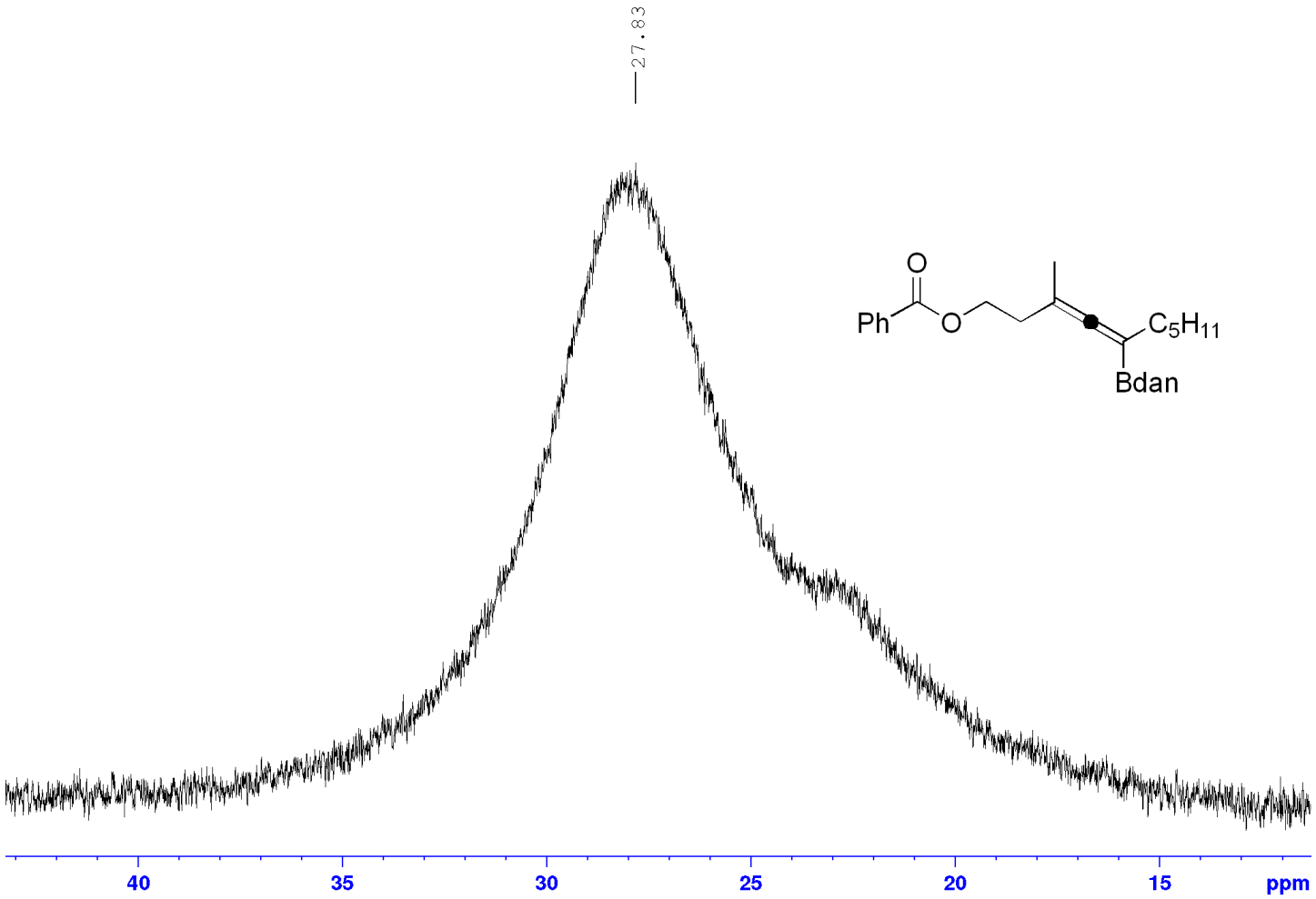
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

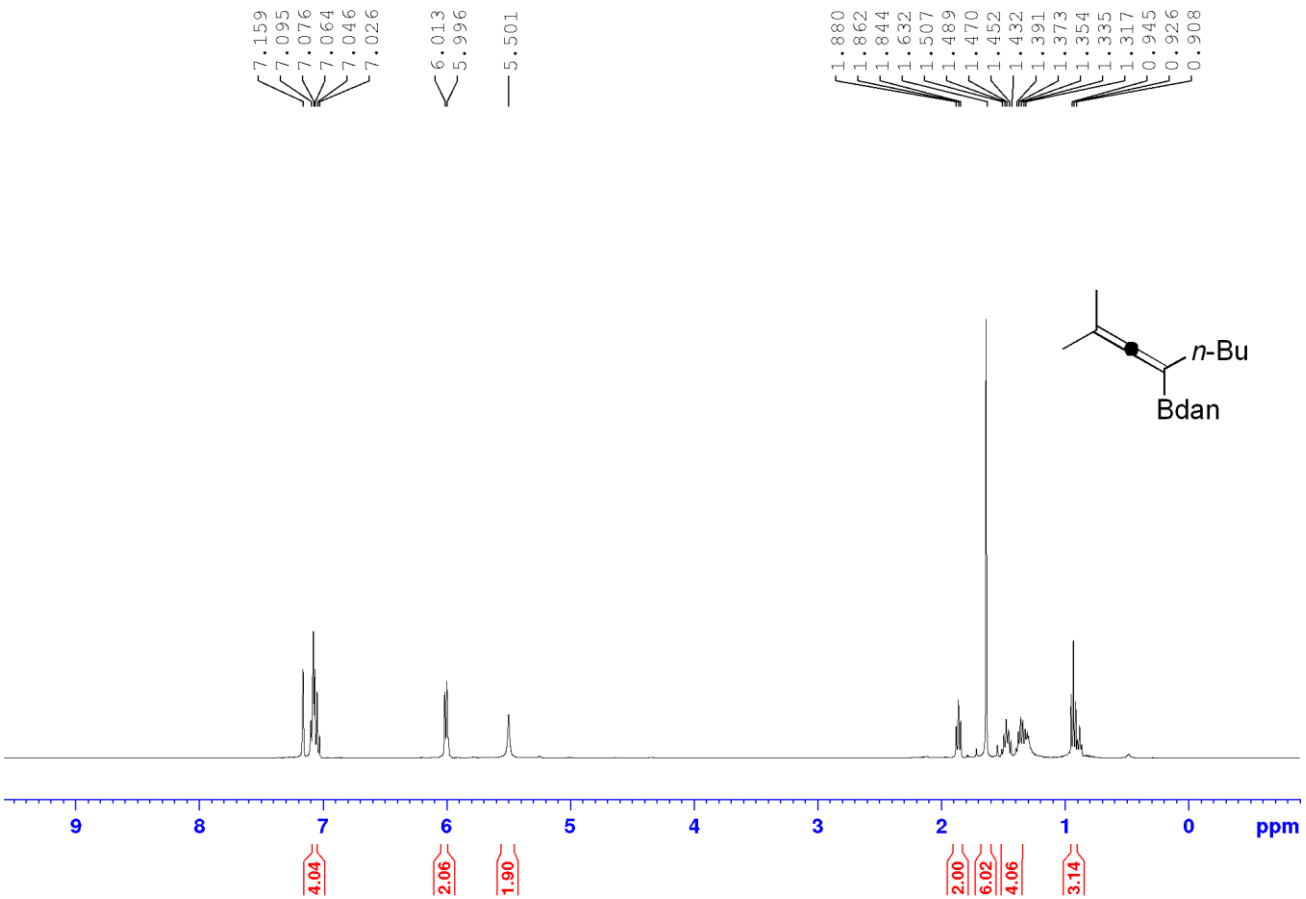


^{11}B NMR (128 MHz, $CDCl_3$)

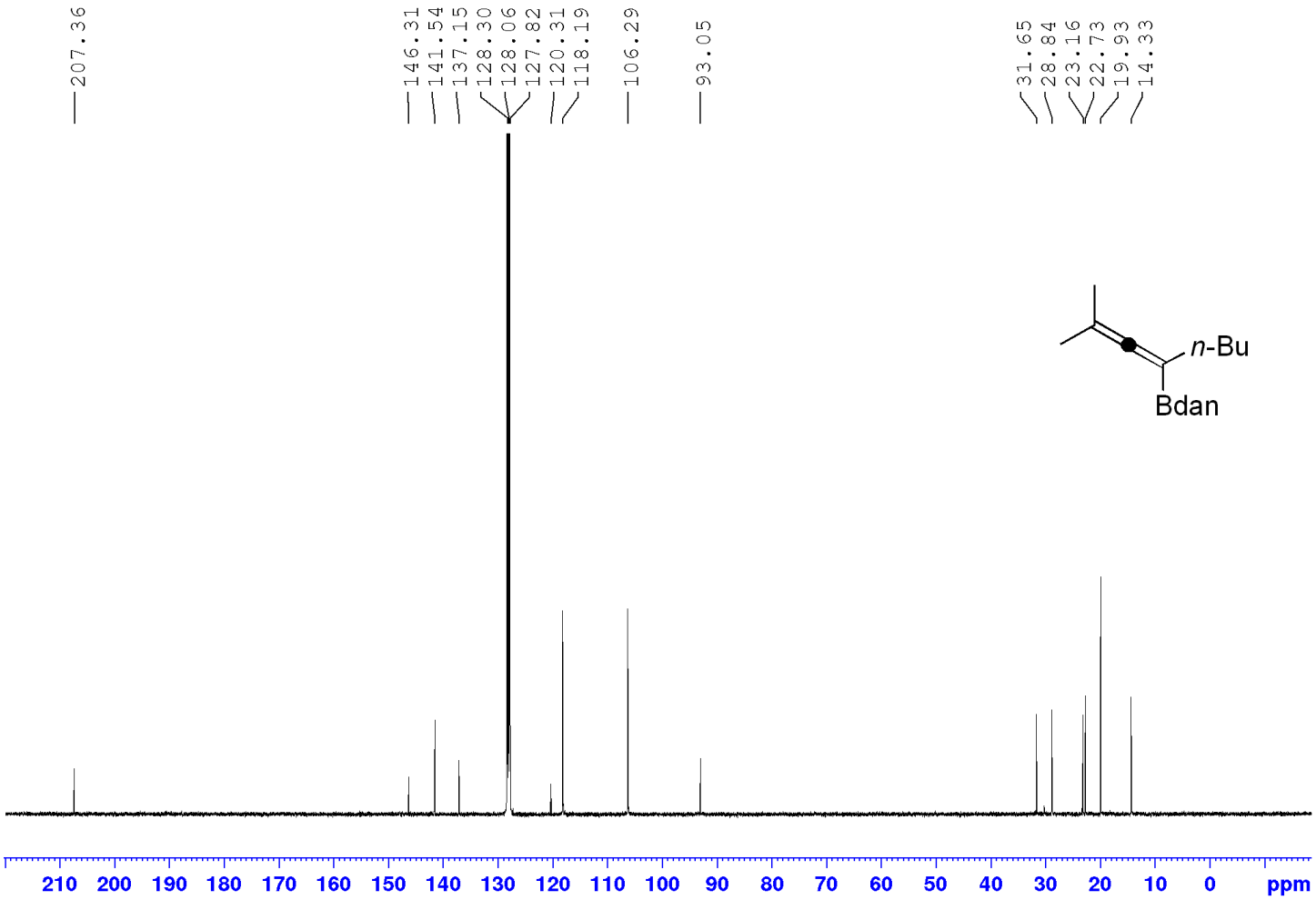


Compound 2v

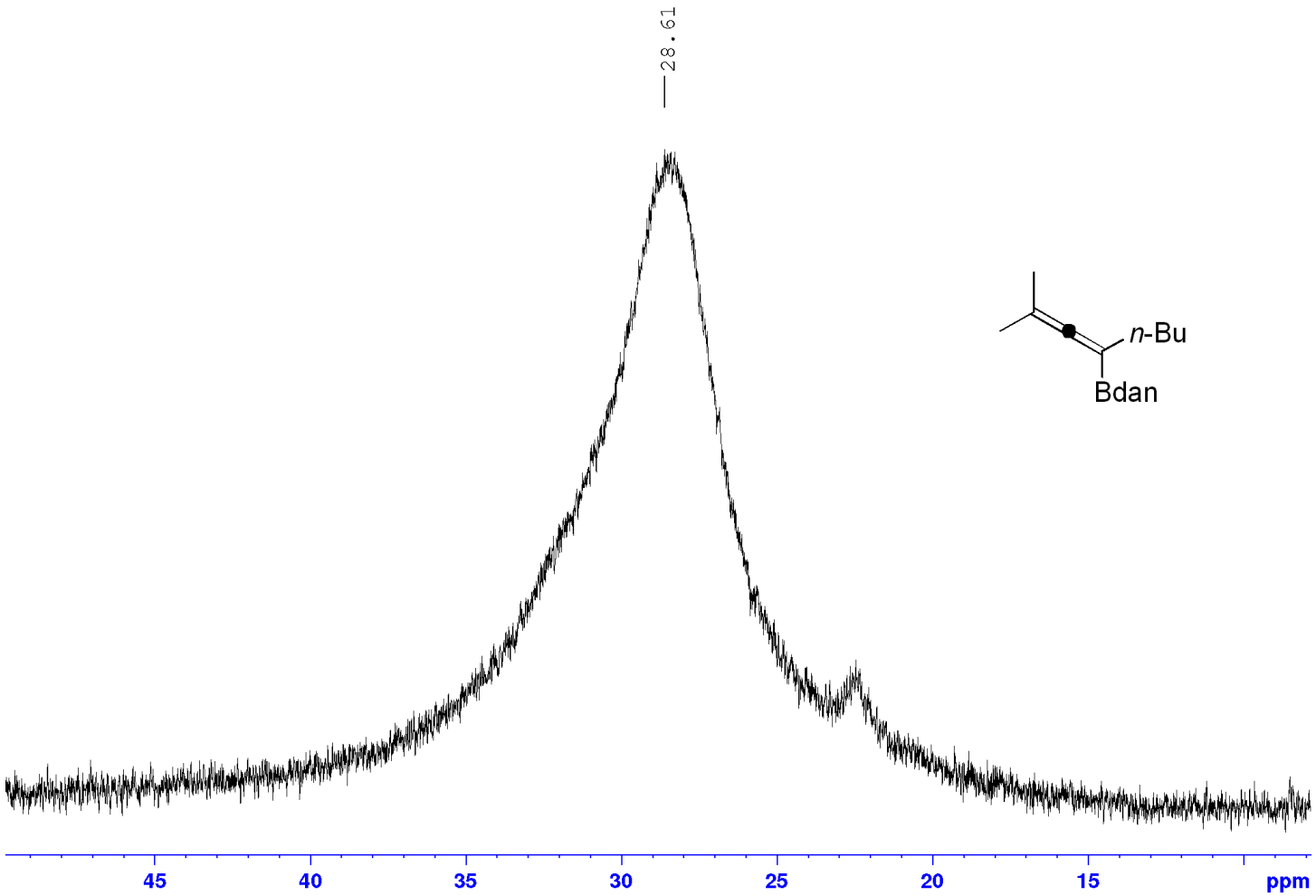
^{1}H NMR (400 MHz, C_6D_6)



$^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6)

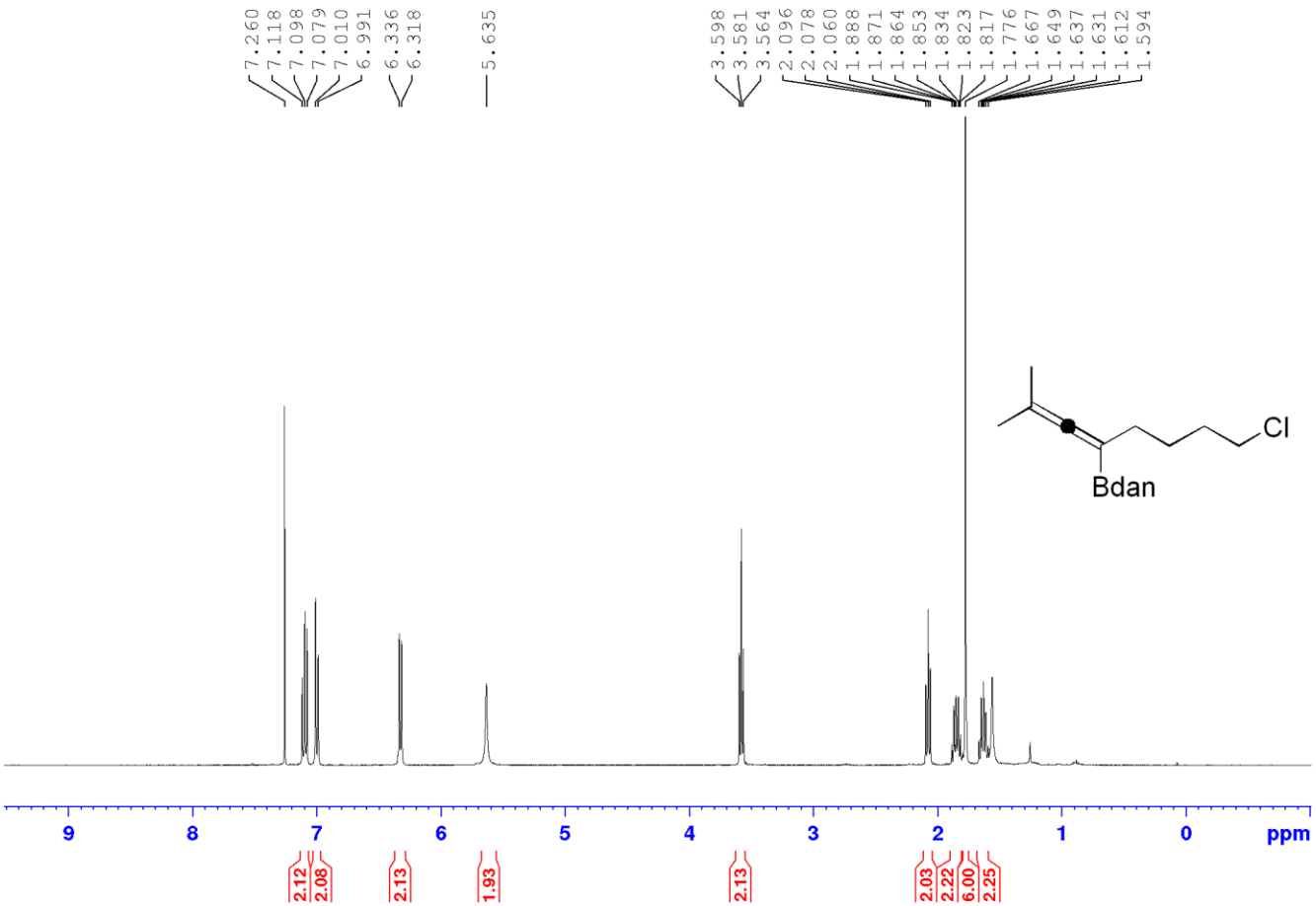


^{11}B NMR (128 MHz, C_6D_6)

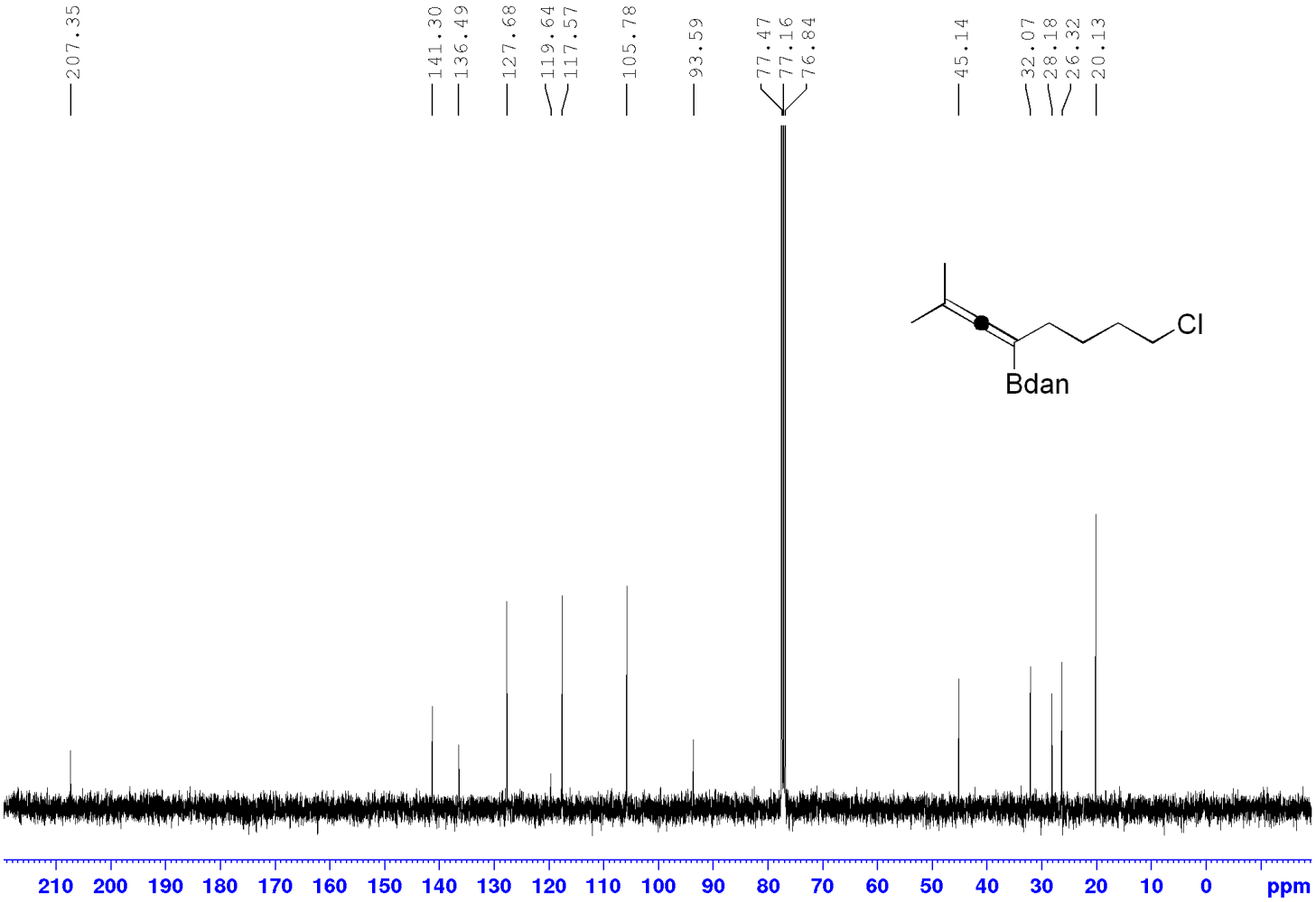


Compound 2w

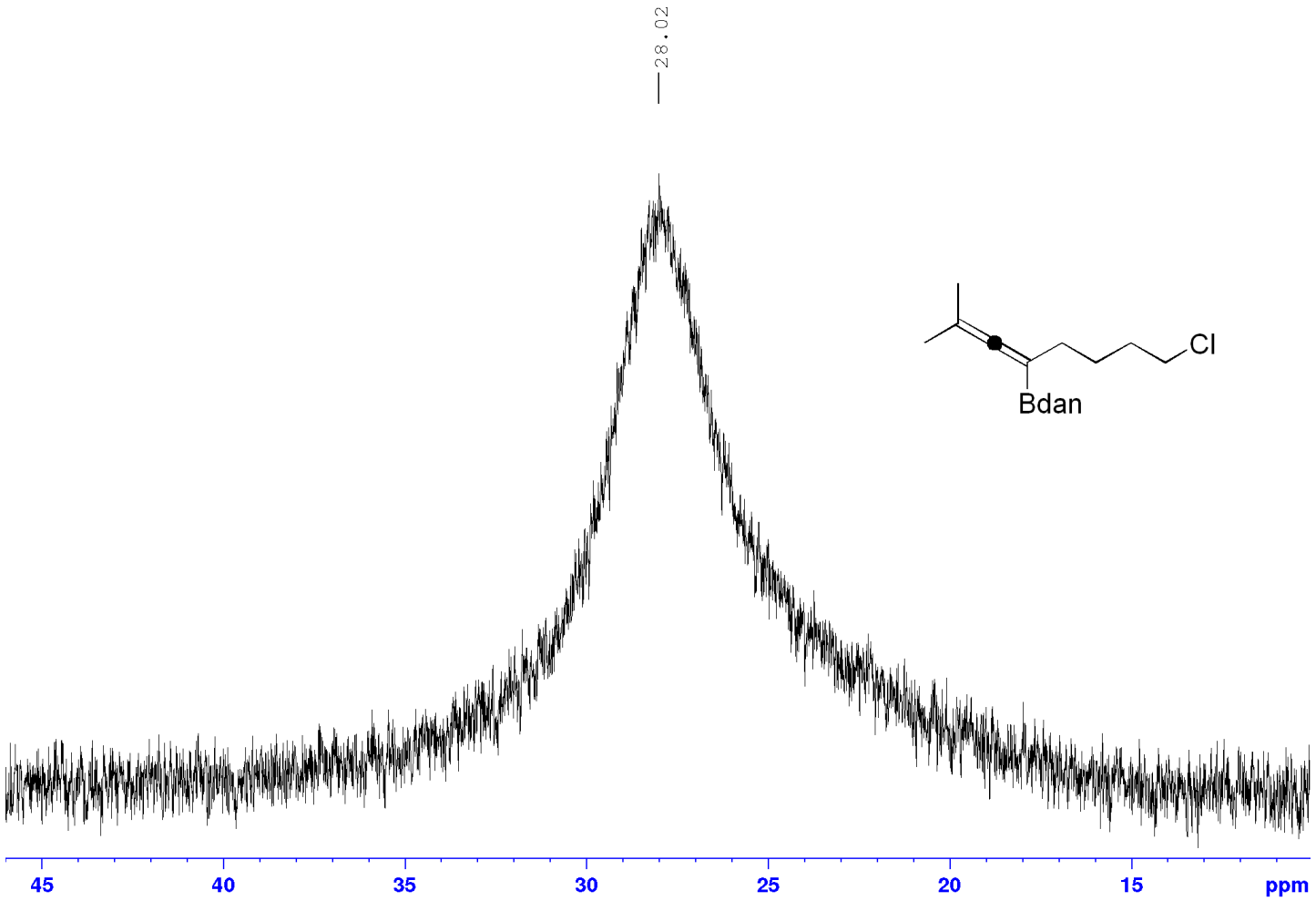
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

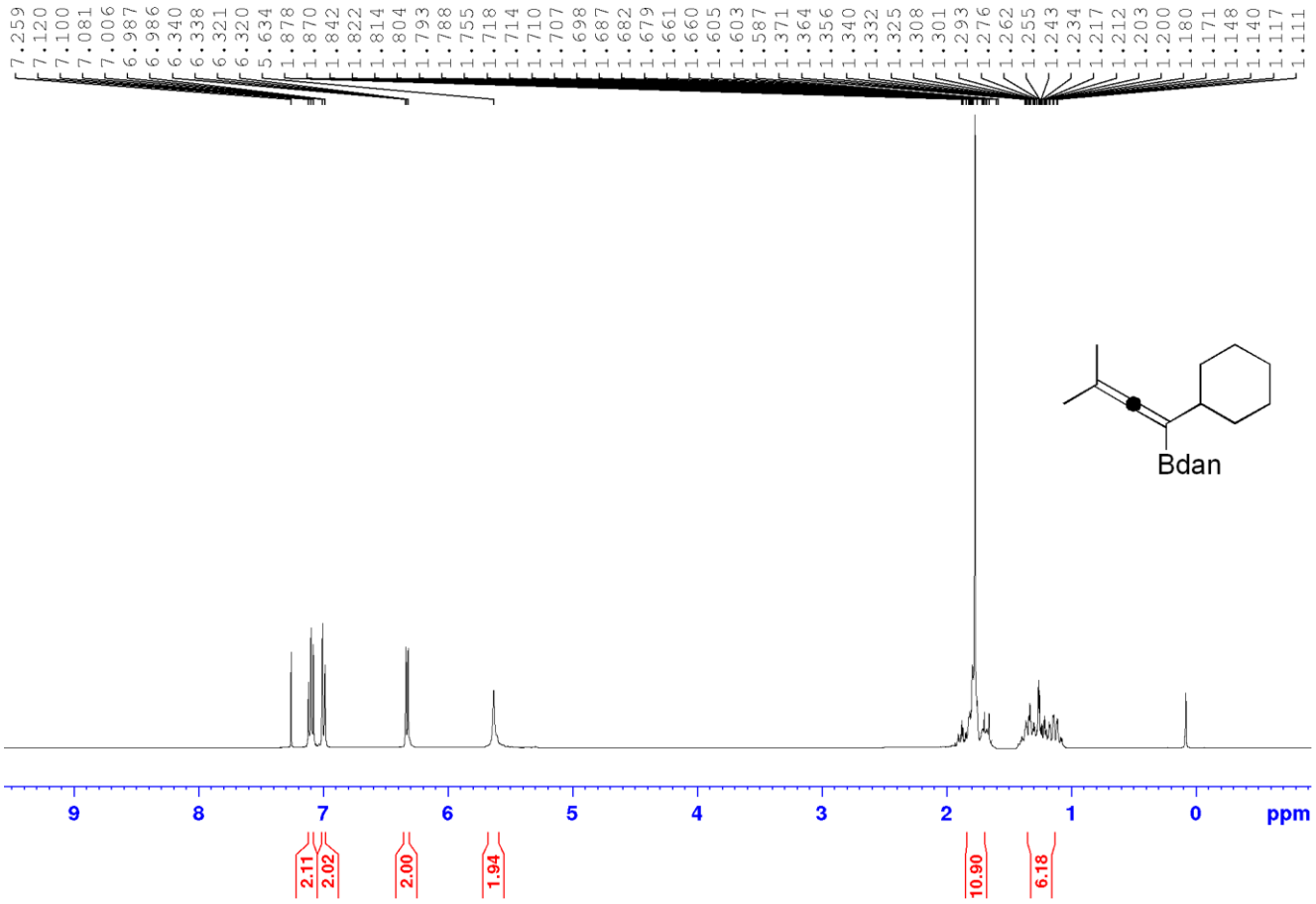


^{11}B NMR (128 MHz, $CDCl_3$)

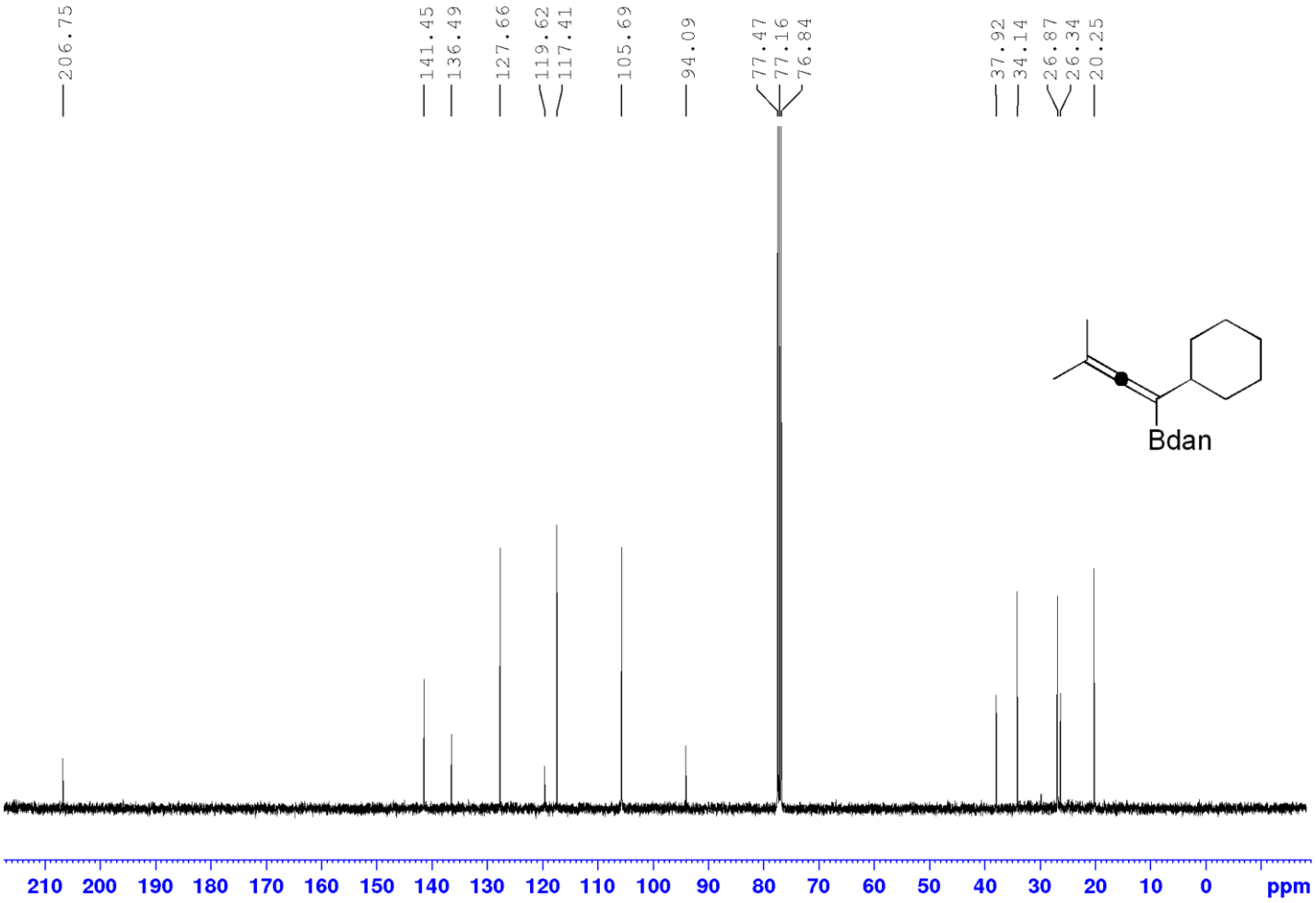


Compound 2x

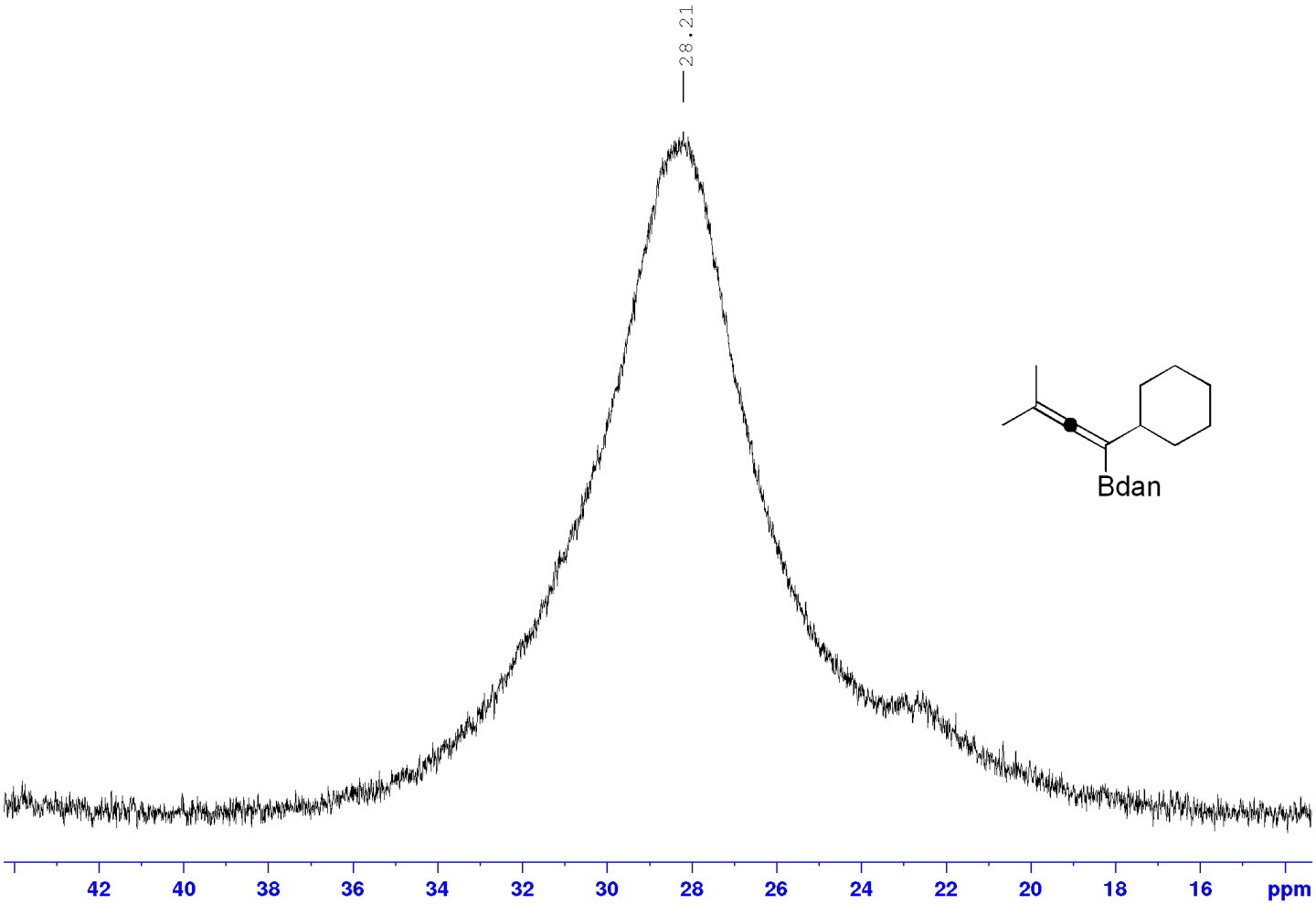
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

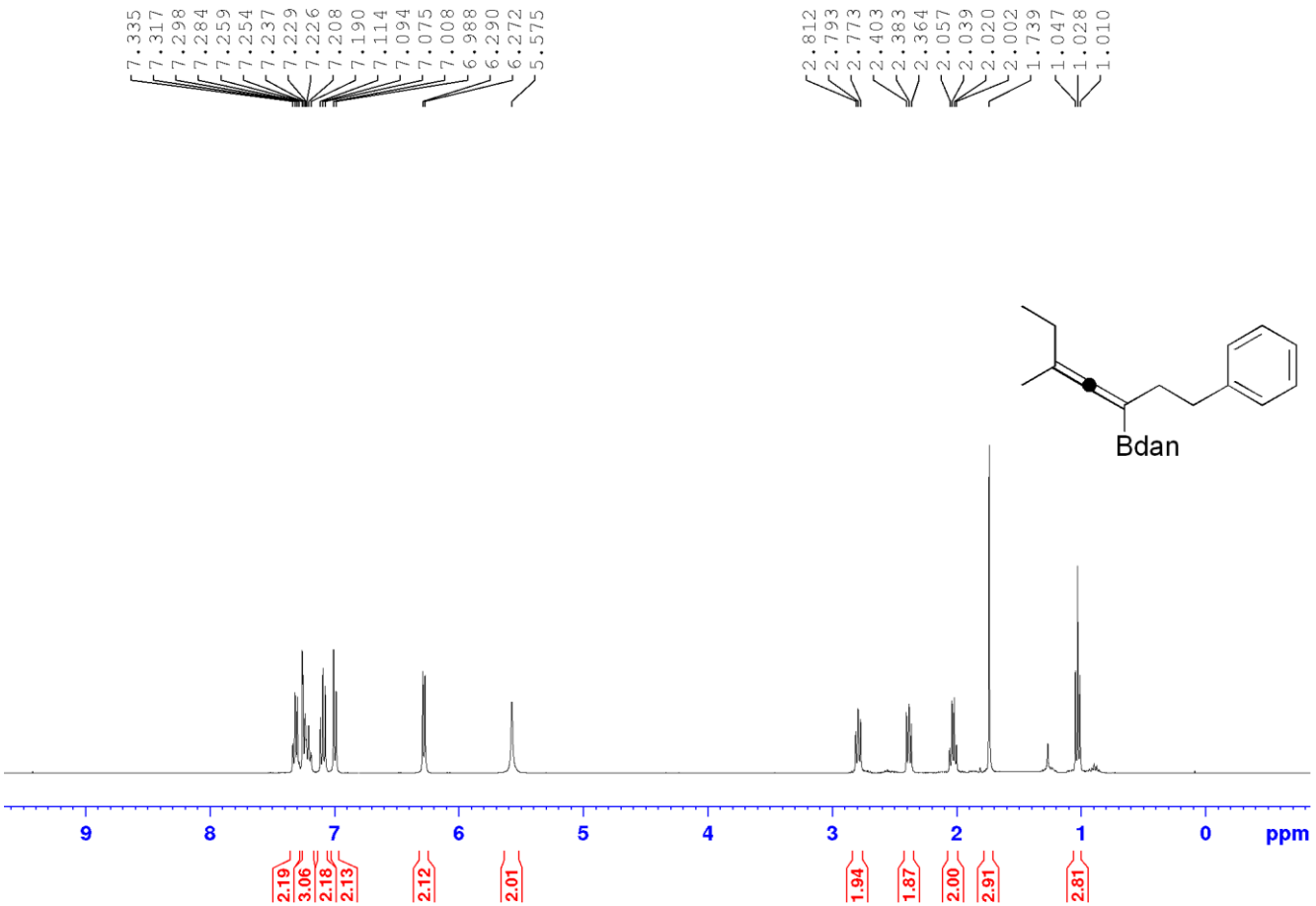


^{11}B NMR (128 MHz, $CDCl_3$)

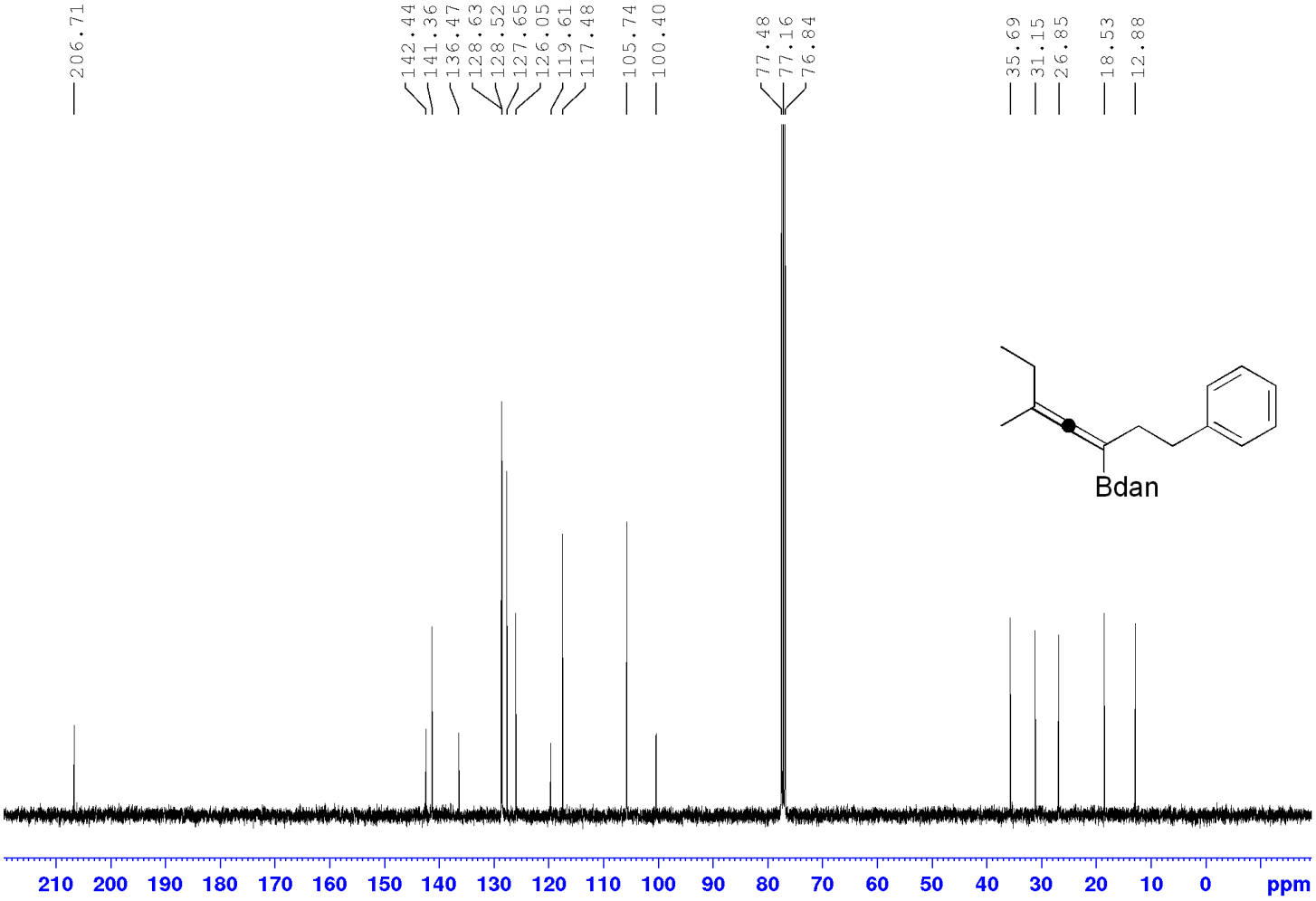


Compound 2y

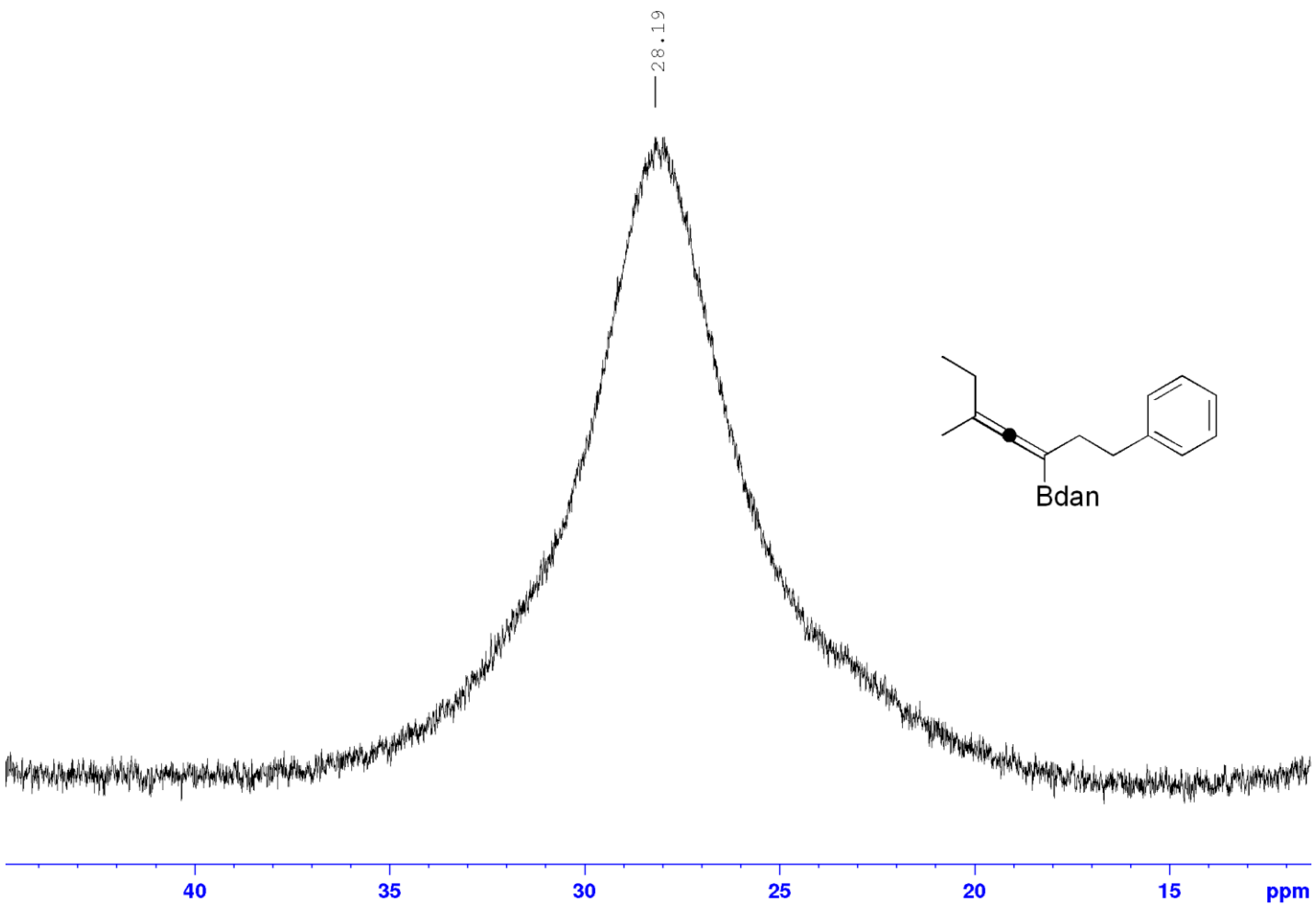
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



^{11}B NMR (128 MHz, $CDCl_3$)



III. Crystallographic Details

The single crystals of complex **2k** and **2w** suitable for X-ray analysis could be obtained by volatilization of pentane solution of **2k** and **2w** at room temperature for one week. The crystals were wrapped in mineral oil and then were frozen in low temperature. Data collections were performed on a Bruker D8 venture microsource diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 273 K. The structures were solved with the shelxs-97 or Olex2 and refined with the XL refinement package using Least Squares minimization. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for **2k** and **2w** were summarized.

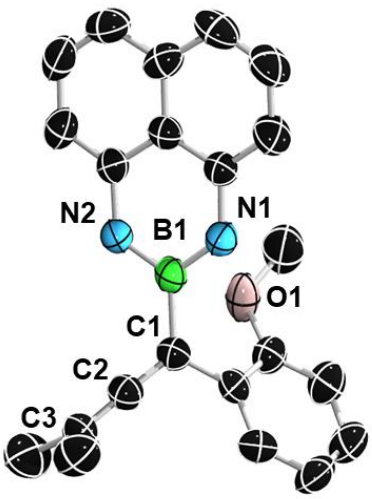


Figure S1. ORTEP drawing of **2k** with 50% thermal ellipsoids. H atoms are omitted for clarity.

Table S7. Crystal data and structure refinement for **2k**.

Identification code	**2k**
Empirical formula	$C_{22}H_{21}BN_2O$
Formula weight	340.22

Temperature/K	273.15
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	9.9494(7)
b/Å	9.2406(6)
c/Å	21.1428(13)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1943.8(2)
Z	4
ρ_{calc}mg/mm^3	1.163
μ/mm^{-1}	0.071
F(000)	720.0
Crystal size/mm^3	0.3 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2 Θ range for data collection	6.018 to 50.036°
Index ranges	$-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-25 \leq l \leq 25$
Reflections collected	49766
Independent reflections	3392 [R_{int} = 0.0984, R_{sigma} = 0.0379]
Data/restraints/parameters	3392/1/238
Goodness-of-fit on F^2	1.083

Final R indexes [I>=2σ (I)]	R_1 = 0.0374, wR_2 = 0.0894
Final R indexes [all data]	R_1 = 0.0478, wR_2 = 0.0966
Largest diff. peak/hole / e $Å^{-3}$	0.09/-0.11

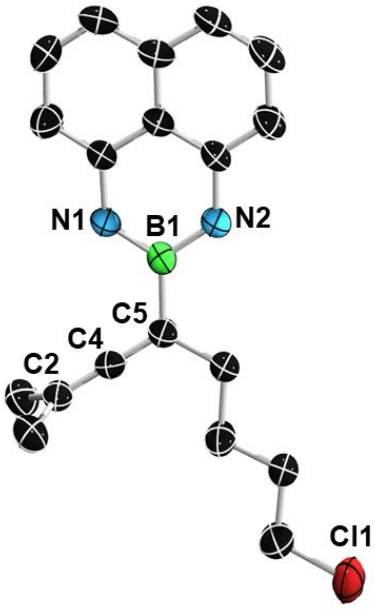


Figure S2. ORTEP drawing of **2w** with 50% thermal ellipsoids. H atoms are omitted for clarity.

Table S8. Crystal data and structure refinement for **2w**.

Identification code	**2w**
Empirical formula	$C_{19}H_{22}BClN_2$
Formula weight	324.64
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1/c$

a/Å	14.7636(14)
b/Å	5.5546(5)
c/Å	22.076(2)
α/°	90
β/°	101.332(3)
γ/°	90
Volume/$Å^3$	1775.0(3)
Z	4
ρ_{calc}mg/mm^3	1.215
μ/mm^{-1}	0.215
F(000)	688.0
Crystal size/mm^3	0.3 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2 Θ range for data collection	5.124 to 50.046 °
Index ranges	$-17 \leq h \leq 17$, $6 \leq k \leq 6$, $-26 \leq l \leq 26$
Reflections collected	46162
Independent reflections	3130 [R_{int} = 0.0591, R_{sigma} = 0.0233]
Data/restraints/parameters	3130/0/210
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0457, wR_2 = 0.1201
Final R indexes [all data]	R_1 = 0.0596, wR_2 = 0.1346
Largest diff. peak/hole / e $Å^{-3}$	0.43/-0.40