Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Ligand influence in the selective gold-mediated synthesis of allenes

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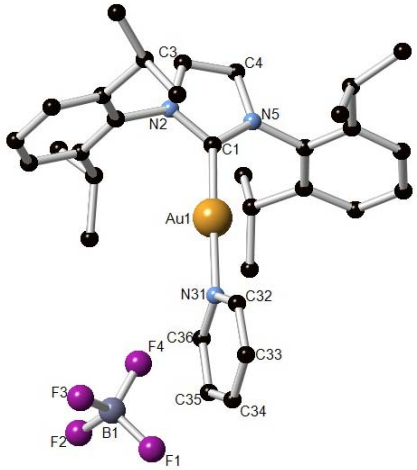
General considerations

All reageants and solvents were used as purchased. NMR spectra were recorded on a 400 MHz Varian Gemini spectrometer. High Resolution Mass Spectrometry analyses were performed by St Andrews analytical services.

Preparation of complexes 4 and 6:

[(IPr)Au(pyr)]BF_4 (4): Complex **4** was prepared according to litterature procedure.[1]
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (t, *J* = 7.8 Hz, 1H, CH^{pyr}), 7.88-7.84 (m, 2H, CH^{pyr}), 7.65-7.60 (m, 2H, CH^{pyr}), 7.56 (t, *J* = 7.8 Hz, 2H, CH^{Ar}), 7.48 (s, 2H, $CH^{Imidazole}$), 7.33 (d, *J* = 7.8 Hz, 2H, CH^{Ar}), 2.53 (septuplet, *J* = 6.9 Hz, 4H, CH^{IPr}), 1.31 (d, *J* = 6.9 Hz, 12H, CH_3^{IPr}), 1.26 (d, *J* = 6.9 Hz, 12H, CH_3^{IPr}).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 167.3 (C, $C^{carbene}$), 150.6 (CH, C^{pyr}), 145.7 (C, C^{Ar}), 142.3 (CH, C^{Pyr}), 133.4 (C, C^{Ar}), 131.4 (CH, C^{Ar}), 127.6 (CH, C^{Pyr}), 125.1 (CH, C^{Ar}), 124.6 (CH, $C^{Imidazole}$), 29.0 (CH, C^{IPr}), 24.9 (CH_3, C^{IPr}), 24.1 (CH_3, C^{IPr}).Anal calcd for $C_{32}H_{41}AuBF_4N_3$: C, 51.15; H, 5.50; N, 5.59. Found : C, 51.46; H, 5.78; N, 5.38.

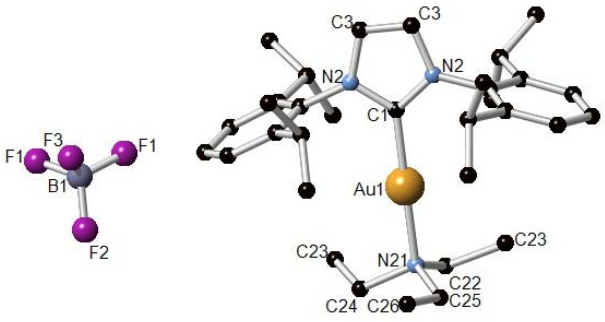
X-Ray analysis : Ball and stick representation of **4**:



Selected bond distances (Å) and angles (deg), for **4**: Au1-C1, 1.988(5); Au1-N31, 2.065(4); C1-Au1-N31, 177.2(18);

[(IPr)Au(Et_3N)]BF_4 (6): In a scintillation vial, [(IPr)AuOH][2] **5** (100 mg, 1 equiv, 0.166 mmol) was dissolved in benzene (2 mL) and Et_3N•HBF_4 was added (31.4 mg, 1 equiv, 0.166 mmol). The mixture was stirred overnight at room temperature, then concentrated under vacuo. Pentane was added and the mixture filtered to isolate **6** as a white powder (115.6 mg, 90%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.55-7.49 (m, 2H, CH^{Ar}), 7.48 (s, 2H, $CH^{Imidazole}$), 7.30 (d, *J* = 7.8 Hz, 4H, CH^{Ar}), 2.66 (q, *J* = 7.2 Hz, 6H, CH_2) 2.47 (septuplet, *J* = 6.9 Hz, 4H, CH^{IPr}), 1.25 (d, *J* = 3.4 Hz, 12H, CH_3^{IPr}), 1.23 (d, *J* = 3.4 Hz, 12H, CH_3^{IPr}), 0.79 (t, *J* = 7.2 Hz, 9H, CH_3). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.4 (C, $C^{carbene}$), 145.7 (C, C^{Ar}), 133.6 (C, C^{Ar}), 131.2 (CH, C^{Ar}), 124.8 (CH, C^{Ar}), 124.4 (CH, $C^{Imidazole}$), 52.0 (CH_2), 28.9 (CH, C^{IPr}), 24.5 (CH_3, C^{IPr}), 24.2 (CH_3, C^{IPr}), 11.0 (CH_3, Et_3N). Anal calcd for $C_{33}H_{51}AuBF_4N_3$: C, 51.24; H, 6.65; N, 5.43. Found : C, 51.07; H, 6.42; N, 5.40.

X-Ray analysis : Ball and stick representation of **6** :



Selected bond distances (Å) and angles (deg), for **6** : Au1-C1, 1.987(7); Au1-N21, 2.104(6); C1-Au1-N21, 176.2(3).

Crystallographic data for 4 and 6 :

	4	**6**
Formula	$C_{32}H_{41}AuN_3BF_4 \bullet CH_2Cl_2$	$C_{33}H_{52}AuN_3BF_4$
M /g.mol^{-1}	836.38	774.55
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	Pnma
a/ Å	9.473(2)	19.742(4)
b/ Å	17.138(4)	16.997(3)
c/ Å	11.355(3)	10.3318(19)
β/ °	90.00	90.00
V/ Å^3	1767.3(7)	3466.9(11)
Z	2	4
ρ_{calcd}/ g.cm^{-3}	1.572	1.484
μ (Mo Kα)/ mm^{-1}	4.361	4.290
T/ K	93(2)	93(2)
Number of reflections	11013	20777
Number of unique reflections	5892	3290
R_{int}	0.0332	0.0643
$R1$, w$R2$ (I > 2σ(I))	0.0271, 0.0572	0.0427, 0.1092
$R1$, w$R2$ (all data)	0.0283, 0.0581	0.0474, 0.1111
GOF	1.036	1.258

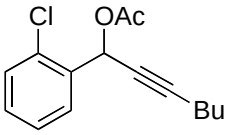
Preparation of propargylic acetates 1:

Propargylic acetates **1a**,[3] **1b**,[3] **1c**,[3] **1d**,[3] **1f**,[3] **1h**,[4] **1j**,[5] **1k**,[5] were prepared according to literature procedures.

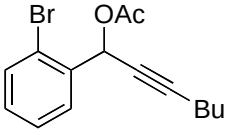
Compounds **1e, 1g, 1i:**
Alkynylation: In an oven-dried round-bottom flask, the alkyne (13 mmol,1.3 equiv) and 1.6M *n*BuLi (12 mmol, 1.2 equiv) were added to THF (20 mL) and stirred for 20 min under nitrogen at -78°C. The aldehyde (10 mmol, 1 equiv) was added and the reaction mixture stirred for 20 min. The mixture was then allowed to warm up to room temperature, quenched with a saturated aqueous NH_4Cl solution, and extracted with diethyl ether. The combined

organic layers were washed with brine, dried with magnesium sulfate, filtered, and evaporated to give the crude propargylic alcohol which was engaged in the next step without further purification.

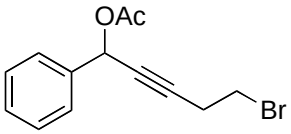
Acylation: The propargylic alcohol (10 mmol, 1 equiv), 1,2-dichloroethane (DCE) (30 mL), 4-dimethylaminopyridine (DMAP) (0.360 g, 3.0 mmol, 0.3 equiv), Et_3N (5.6 mL, 40 mmol, 4 equiv), and Ac_2O (1.8 mL, 20 mmol, 2 equiv) were added in turn to a round-bottom flask. The reaction mixture was stirred at romm temperature for 3h, quenched with a saturated aqueous NH_4Cl solution, and extracted with diethyl ether. The combined organic layers were washed with brine, dried with magnesium sulfate, filtered, and evaporated to give a crude product that was purified by flash chromatography on silica gel.



1-(2-chlorophenyl)hept-2-ynyl acetate (1e): The above general procedure gave the title product (1.1 g, 85%), after flash column chromatography on silica gel (Pentane/Et_2O 95/5).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.75 (m, 1H), 7.40-7.36 (m, 1H), 7.34-7.28 (m, 2H), 6.73 (t, *J* = 2.1 Hz, 1H), 2.27 (dt, *J* = 2.1 Hz, *J* = 7.0 Hz, 2H), 2.11 (s, 3H), 1.57-1.48 (m, 2H), 1.45-1.35 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.2, 135.0, 133.2, 129.9, 129.5, 129.3, 126.9, 88.5, 75.7, 63.1, 30.3, 21.8, 20.6, 18.4, 13.4. **HRMS** calculated for $C_{15}H_{18}O_2Cl$: 265.0995. Found : 265.1003.



1-(2-bromophenyl)hept-2-ynyl acetate (1g): The above general procedure gave the title product (1.36 g, 88%), after flash column chromatography on silica gel (Pentane/Et_2O 95/5).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, *J* = 1.7 Hz, *J* = 7.7 Hz, 1H), 7.57 (dd, *J* = 1.2 Hz, *J* = 8.0 Hz, 1H), 7.36 (dt, *J* = 7.7 Hz, *J* = 1.3 Hz, 1H), 7.24- 7.19 (m, 1H), 6.66 (t, *J* = 2.1 Hz, 1H), 2.27 (dt, *J* = 2.1 Hz, *J* = 7.0 Hz, 2H), 2.11 (s, 3H), 1.57-1.48 (m, 2H), 1.46-1.35 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.4, 136.7, 133.0, 130.3, 129.6, 127.6, 123.4, 88.9, 75.8, 65.6, 30.4, 21.9, 20.9, 18.5, 13.6. **HRMS** calculated for $C_{15}H_{17}O_2Na^{79}Br$: 331.0310 Found : 331.0313.



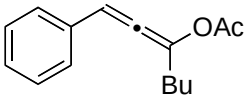
5-bromo-1-phenylpent-2-ynyl acetate (1i): The above general procedure gave the title product (1.07g, 76%), after flash column chromatography on silica gel (Pentane/Et_2O 95/5).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.50 (m, 2H), 7.42-7.34 (m, 2H), 6.45 (t, *J* = 2.0 Hz, 1H), 3.46 (t, *J* = 7.3 Hz, 2H), 2.85 (dt, *J* = 2.0 Hz, *J* = 7.3 Hz, 2H), 2.10 (s, 3H), 1.57-1.48 (m, 2H), 1.46-1.35 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 169.9, 137.0, 128.9, 128.6, 127.7, 84.7, 78.9, 65.8, 29.1, 23.3, 21.1.**HRMS** calculated for $C_{13}H_{13}O_2Na^{81}Br$: 304.9976. Found: 304.9973.

Synthesis of allenes 3 :

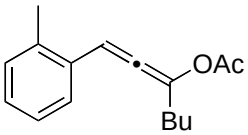
Conditions A: In a vial, a solution of propargylic acetate (0.2 mmol) in dichloromethane (1 mL) was added to a solution of [(IPr)AuOH] (4.10^{-3} mmol, 2.4 mg) and Et_3N•HBF_4 (6.10^{-3} mmol, 1.2 mg) in dichloromethane (1 mL). The reaction mixture was stirred at 40°C during 30 min, then concentrated under vacuum. Et_2O was added and the solution filtered over a plug of silica (~1 cm). Filtrate was concentrated to afford the desired allene.

Conditions B: In a vial, a solution of propargylic acetate (0.2 mmol) in 1,2-dichloroethane (1 mL) was added to a solution of [(IPr)AuOH] (4.10^{-3} mmol, 2.4 mg) and Et_3N•HBF_4 (6.10^{-3} mmol, 1.2 mg) in 1,2-dichloroethane (1 mL). The reaction mixture was stirred at 80°C during 60 min, then concentrated under vacuum. The crude product was then purified by flash chromatography on silica gel using pentane/Et_2O as eluant.

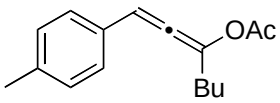
Conditions C: In a vial, a solution of propargylic acetate (0.2 mmol) in dichloromethane (1 mL) was added to a solution of [(IPr)AuOH] (4.10^{-3} mmol, 2.4 mg) and Pyr•HBF_4 (6.10^{-3} mmol, 1.2 mg) in dichloromethane (1 mL). The reaction mixture was stirred at 40°C during 30 min, then concentrated under vacuum. The crude product was then purified by flash chromatography on silica gel using pentane/Et_2O as eluant.



1-phenylhepta-1,2-dien-3-yl acetate[3] (3a): General procedure using conditions A yielded 42.8 mg (93%) of the title compound. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45-7.40 (m, 2H), 7.36-7.30 (m, 2H), 7.26- 7.20 (m, 1H), 6.59 (t, *J* = 3.1 Hz, 1H), 2.37-2.31 (m, 2H), 2.15 (s, 3H), 1.51-1.34 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.8, 168.8, 134.0, 128.8, 128.1, 127.9, 127.0, 104.6, 31.6, 28.4, 22.3, 21.2, 14.0.

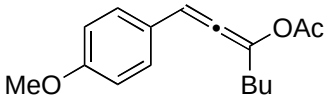


1-*o*-tolylhepta-1,2-dien-3-yl acetate (3b): General procedure using conditions A yielded 43.5 mg (89%) of the title compound.**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52 (d, *J* = 6.2 Hz, 2H), 7.24-7.13 (m, 3H), 6.82 (t, *J* = 3.1 Hz, 1H), 2.4 (s, 3H), 2.37-2.30 (m, 2H), 2.15 (s, 3H), 1.53-1.35 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.6, 168.8, 136.0, 132.1, 130.7, 128.3, 128.0, 126.8, 126.4, 102.1, 31.6, 28.5, 22.4, 21.2, 19.9, 14.0.
HRMS calculated for $C_{16}H_{20}O_2Na$: 267.1361. Found : 267.1360.

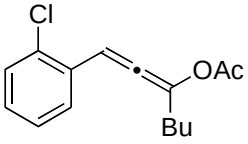


1-*p*-tolylhepta-1,2-dien-3-yl acetate[3] (3c):General procedure using conditions A yielded 42 mg (86%) of the title compound. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.31 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.56 (t, *J* = 3.1 Hz, 1H), 2.35-2.30 (m, 2H), 2.34 (s, 3H), 2.14 (s,

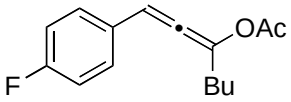
3H), 1.51-1.35 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.1, 168.7, 138.0, 131.0, 129.4, 127.8, 126.9, 104.4, 31.6, 28.4, 22.2, 21.3, 21.1, 13.9.



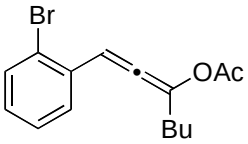
1-(4-methoxyphenyl)hepta-1,2-dien-3-yl acetate[3] (3d): General procedure using conditions A yielded 51 mg (98%) of the title compound.**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.36 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.55 (t, *J* = 3.1 Hz, 1H), 3.81 (s, 3H), 2.36-2.29 (m, 2H), 2.14 (s, 3H), 1.49-1.32 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.5, 169.0, 159.8, 129.3, 126.8, 126.5, 114.3, 104.3, 55.5, 31.8, 28.5, 22.4, 21.3, 14.1.



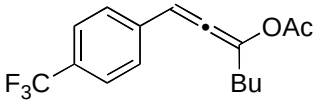
1-(2-chlorophenyl)hepta-1,2-dien-3-yl acetate (3e): General procedure using conditions A yielded 50.8 mg (96%) of the title compound.**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.34 (dd, *J* = 1.5 Hz, *J* = 7.6 Hz, 1H), 7.27-7.13 (m, 2H), 7.05 (t, *J* = 3.0 Hz, 1H), 2.38-2.30 (m, 2H), 2.16 (s, 3H), 1.53-1.32 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.4, 168.7, 133.2, 131.7, 129.8, 129.4, 129.1, 127.4, 127.1, 100.7, 31.6, 28.4, 22.3, 21.2, 14.0. **HRMS** calculated for $C_{15}H_{18}O_2Cl$: 265.0995. Found : 265.1005.



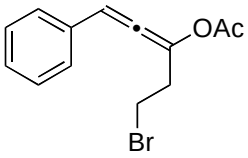
1-(4-fluorophenyl)hepta-1,2-dien-3-yl acetate (3f): General procedure using conditions A yielded 47.1 mg (95%) of the title compound.**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.43-7.37 (m, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.55 (t, *J* = 3.1 Hz, 1H), 2.37-2.28 (m, 2H), 2.15 (s, 3H), 1.50-1.34 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.5, 168.7, 161.1 (d, *J* = 247.5 Hz), 130.1 (d, *J* = 3.3Hz), 129.5 (d, *J* = 8.2 Hz), 127.0, 115.7 (d, *J* = 21.9 Hz), 103.5, 31.6, 28.4, 22.3, 21.2, 14.0. **HRMS** calculated for $C_{15}H_{18}O_2F$: 249.1291. Found: 249.1296.



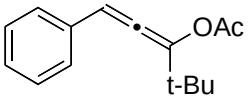
1-(2-bromophenyl)hepta-1,2-dien-3-yl acetate (3g): General procedure using conditions B yielded, after flash chromatography on silica gel (Pentane/Et_2O 97/3), 50.7 mg (82%) of the title compound.**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.66 (dd, *J* = 1.7 Hz, *J* = 7.8 Hz, 1H), 7.53 (dd, *J* = 1.2 Hz, *J* = 8.0 Hz, 1H), 7.31-7.26 (m, 1H), 7.12-7.06 (m, 1H), 7.04 (t, *J* = 3.0 Hz, 1H), 2.36-2.30 (m, 2H), 2.16 (s, 3H), 1.51-1.35 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.5, 168.6, 133.4, 133.1, 129.6, 129.3, 127.7, 127.4, 123.6, 103.3, 31.6, 28.4, 22.3, 21.2, 14.0. **HRMS** calculated for $C_{15}H_{17}O_2Na^{79}Br$: 331.0310 Found: 331.0303.



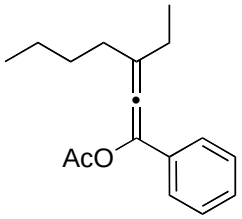
1-(4-(trifluoromethyl)phenyl)hepta-1,2-dien-3-yl acetate (3h): General procedure using conditions B yielded, after flash chromatography on silica gel (Pentane/Et_2O 97/3), 50.1 mg (84%) of the title compound.**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 6.60 (t, *J* = 3.0 Hz, 1H), 2.37-2.31 (m, 2H), 2.16 (s, 3H), 1.50-1.35 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.6, 168.5, 137.9, 129.4, 128.1, 127.9, 127.5, 125.7, 103.3, 31.6, 28.4, 22.3, 21.1, 13.9. **HRMS** calculated for $C_{16}H_{17}O_2F$: 298.1181. Found: 298.1180.



5-bromo-1-phenylpenta-1,2-dien-3-yl acetate (3i): General procedure using conditions B yielded, after flash chromatography on silica gel (Pentane/Et_2O 95/5), 41.6 mg (74%) of the title compound.**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47-7.43 (m, 2H), 7.36-7.31 (m, 2H), 7.29-7.23 (m, 1H), 6.70 (t, *J* = 2.8 Hz, 1H), 3.47 (t, *J* = 7.1 Hz, 2H), 2.95-2.85 (m, 2H), 2.17 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.7, 168.6, 133.2, 128.8, 128.5, 128.2, 123.7, 105.8, 35.6, 28.2, 21.1. **HRMS** calculated for $C_{13}H_{13}O_2Na^{81}Br$: 304.9976. Found: 304.9975.



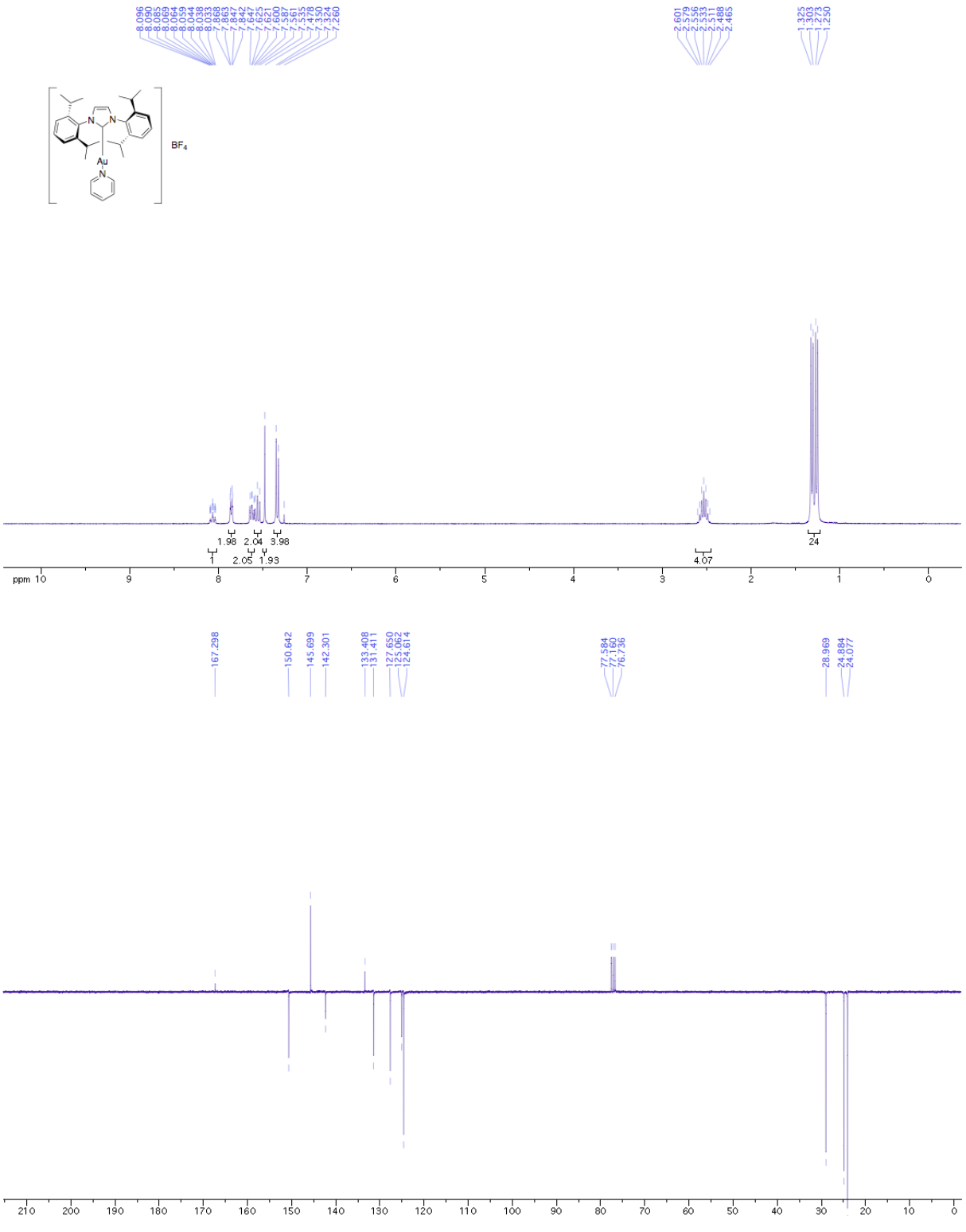
4,4-dimethyl-1-phenylpenta-1,2-dien-3-yl acetate (3j): General procedure using conditions B yielded, after flash chromatography on silica gel (Pentane/Et_2O 95/5), 37.7 mg (82%) of the title compound.**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47-7.40 (m, 2H), 7.36-7.30 (m, 2H), 7.26- 7.20 (m, 1H), 6.61 (s, 1H), 2.17 (s, 3H), 1.15 (s, 9H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.4, 168.4, 134.2, 128.7, 128.0, 127.9, 126.7, 105.1, 35.2, 28.0, 21.0. **HRMS** calculated for $C_{15}H_{18}O_2Na$: 253.1204. Found: 249.1199.



3-ethyl-1-phenylhepta-1,2-dienyl acetate (3k): General procedure using conditions C yielded, after flash chromatography on silica gel (Pentane/Et_2O 97/3), 36.7 mg (71%) of the title compound.**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.33-7.30 (m, 4H), 7.25-7.18 (m, 1H), 6.60 (t, *J* = 3.0 Hz, 1H), 2.27 (s, 3H), 2.25-2.17 (m, 4H), 1.56-1.47 (m, 4H), 1.40-1.29 (m, 4H), 1.11 (t, *J* = 7.3 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 3H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 192.2, 168.9, 133.9, 128.5, 127.3, 124.3, 124.3, 122.6, 33.9, 29.7, 27.4, 22.6, 21.2, 14.0, 12.2. **HRMS** calculated for $C_{17}H_{22}O_2Na$: 281.1517. Found: 281.1512.

References

(1) de Frémont, P.; Marion, N.; Nolan, S. P. *J. Organomet. Chem.* 2009, *694*, 551-560.
(2) Gaillard, S.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Commun.* 2010, *46*, 2742-2744.
(3) Marion, N.; Diez-Gonzalez, S.; de Frémont, P.; Noble, A. R.; Nolan, S. P. *Angew. Chem. Int. Ed.* 2006, *45*, 3647-3650.
(4) Yu, M.; Zhang, G.; Zhang, L. *Org. Lett.* 2007, *9*, 2147-2150.
(5) Marion, N.; Carlqvist, P.; Gealageas, R.; de Frémont, P.; Maseras, F.; Nolan, S. P. *Chem. Eur. J.* 2007, *13*, 6437-6451.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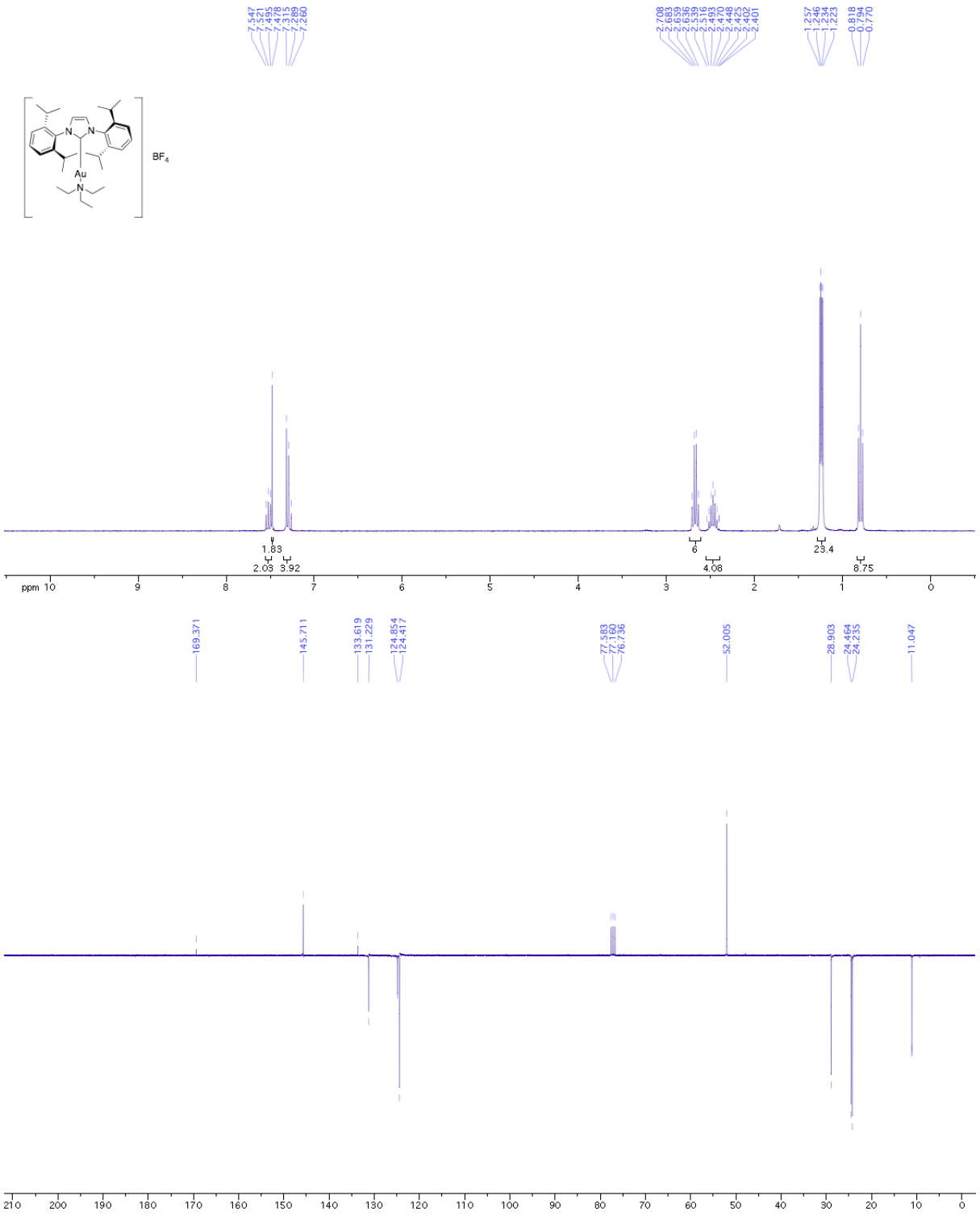
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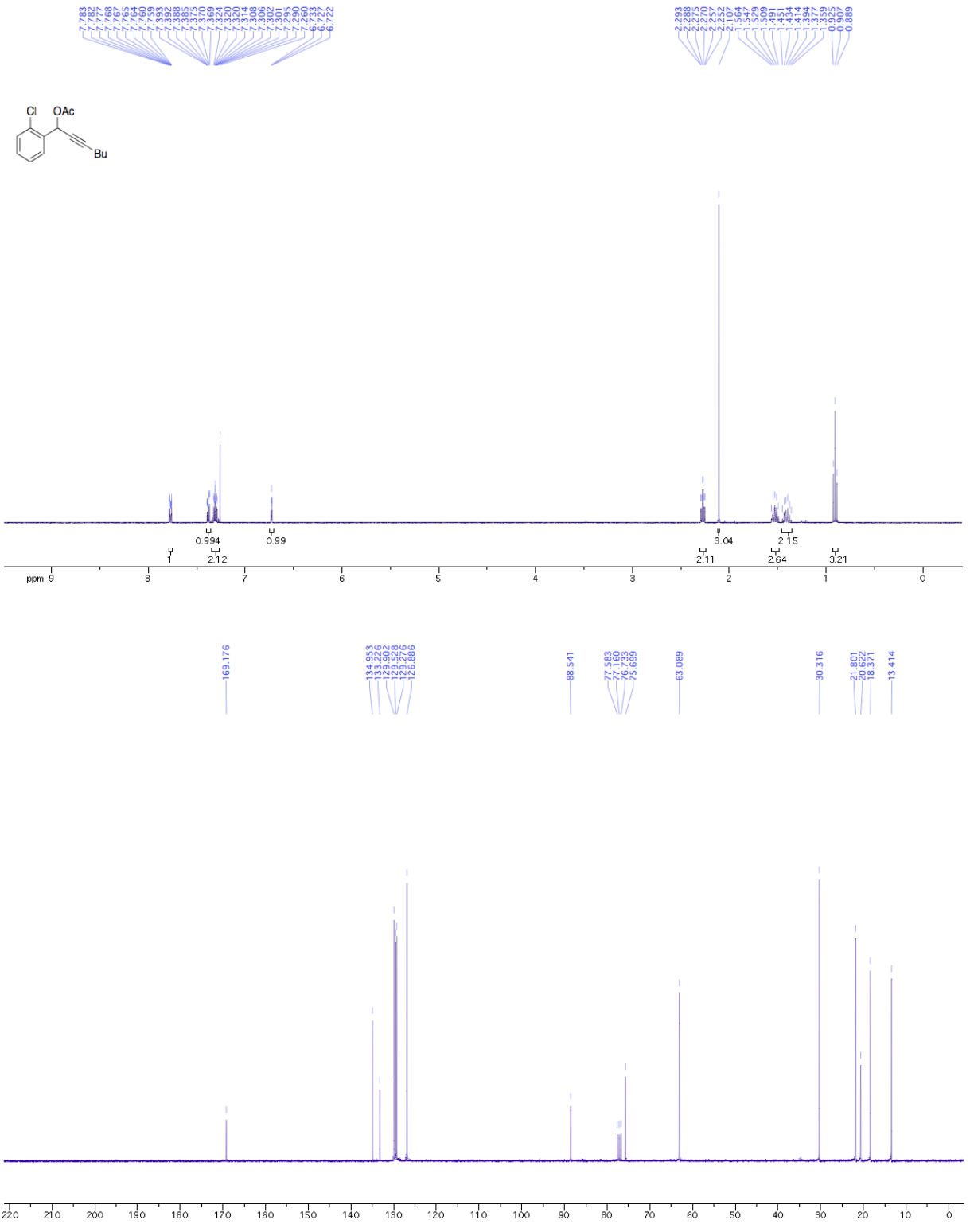
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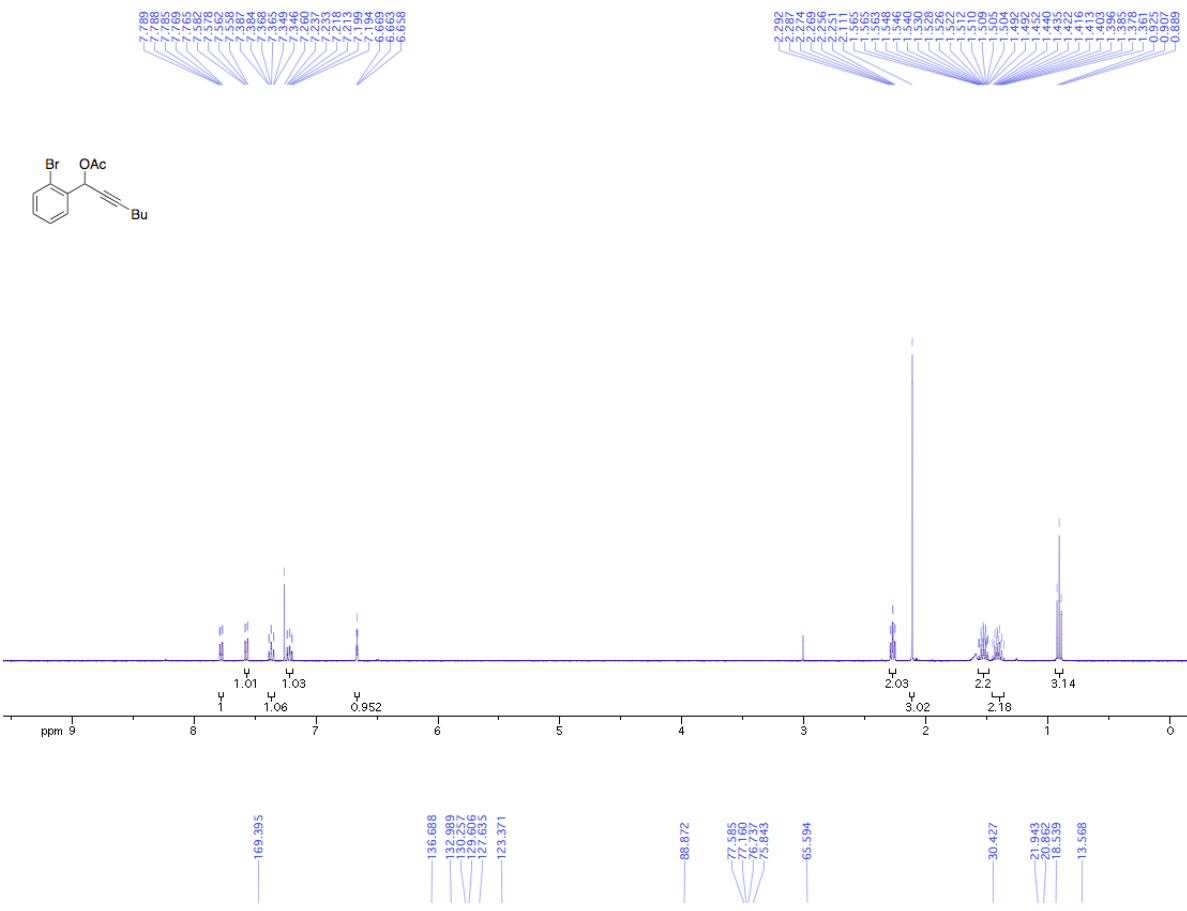
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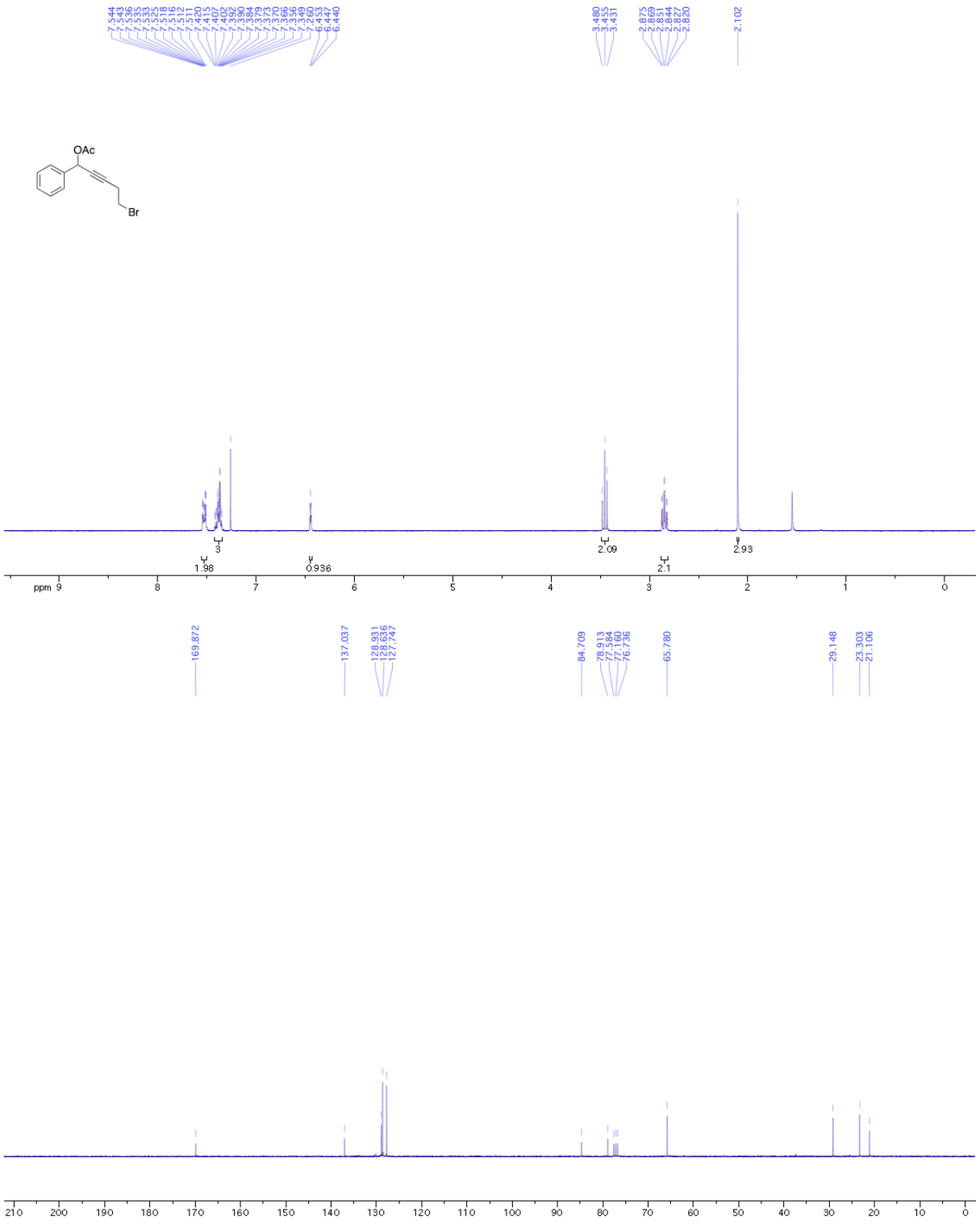
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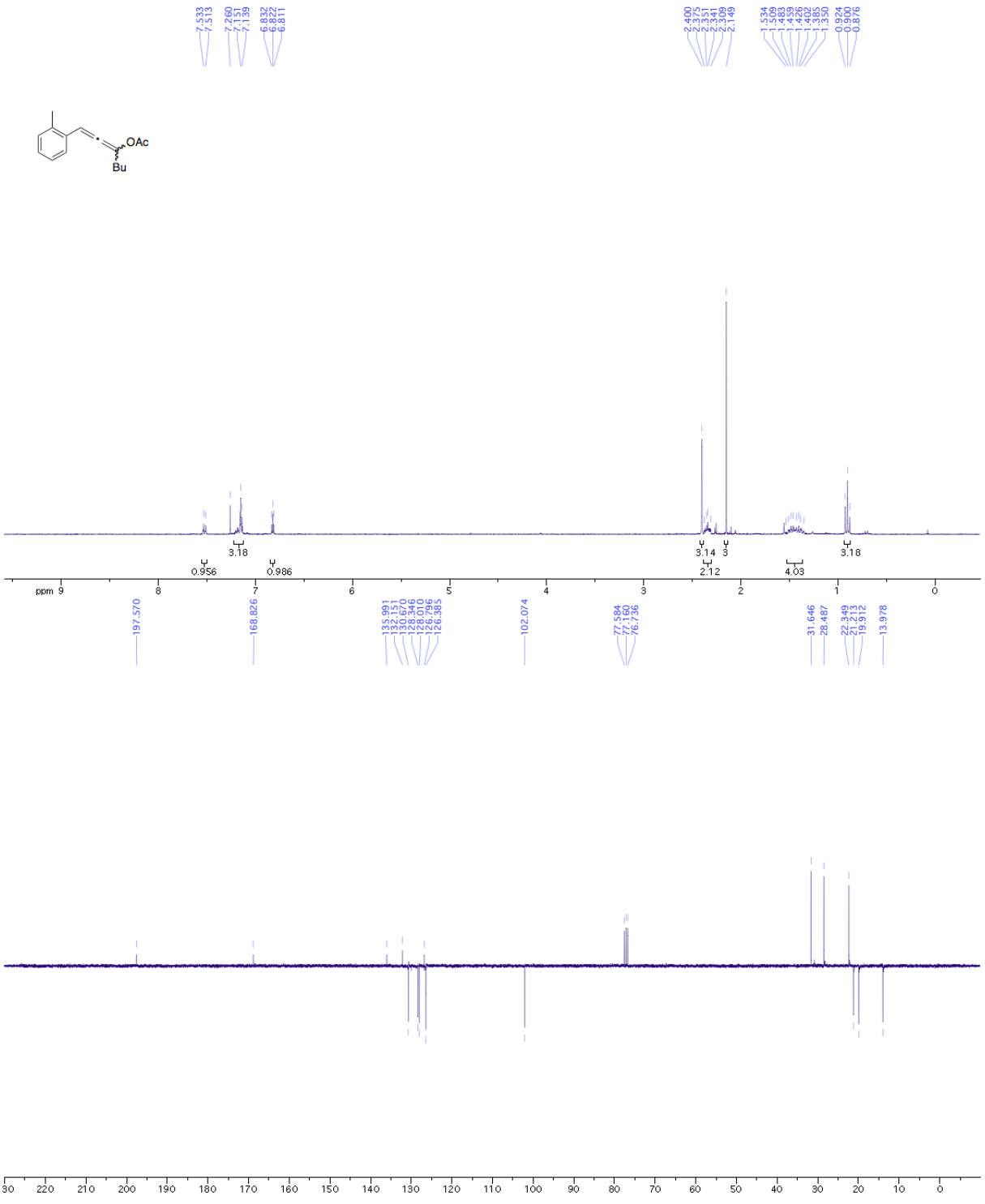
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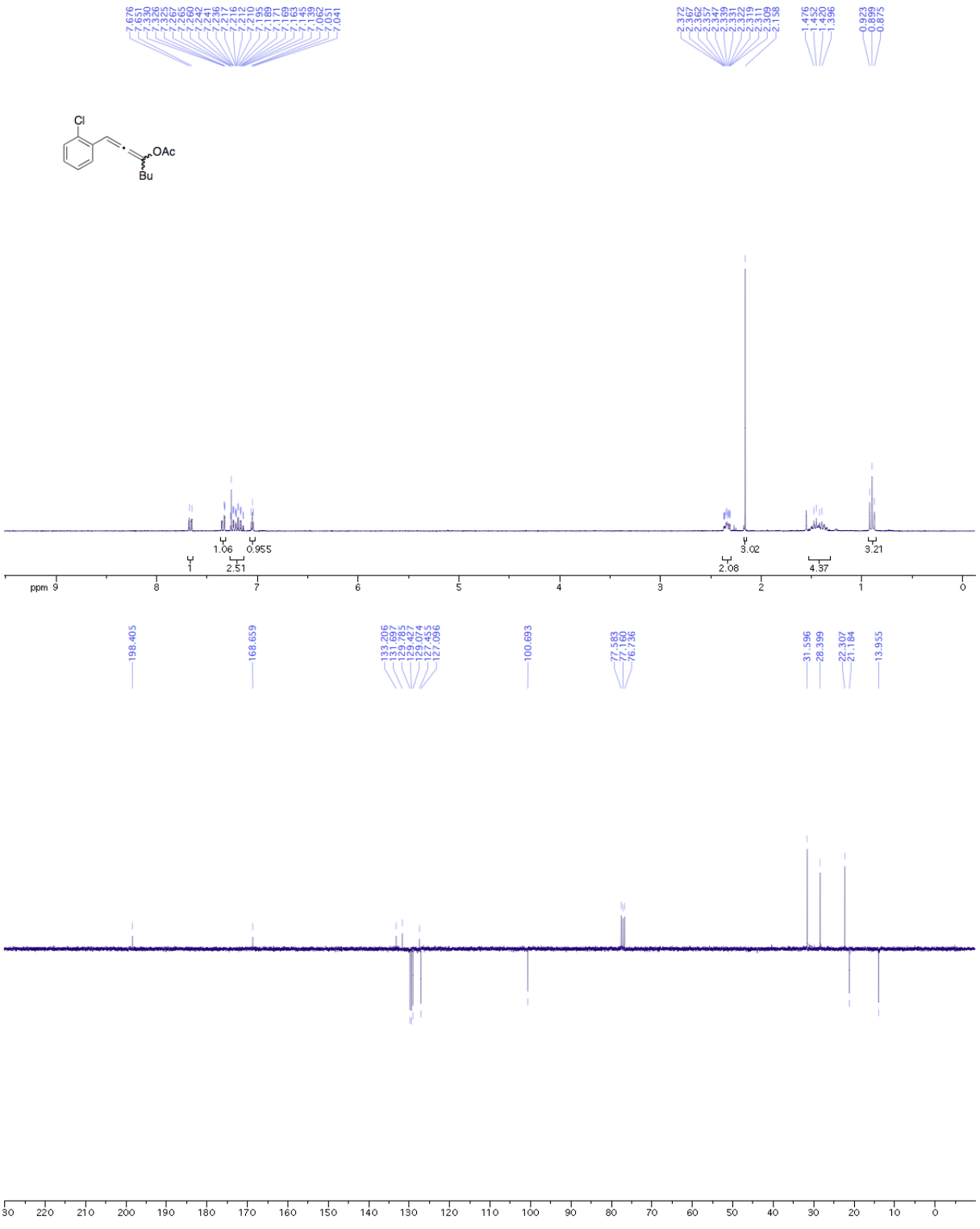
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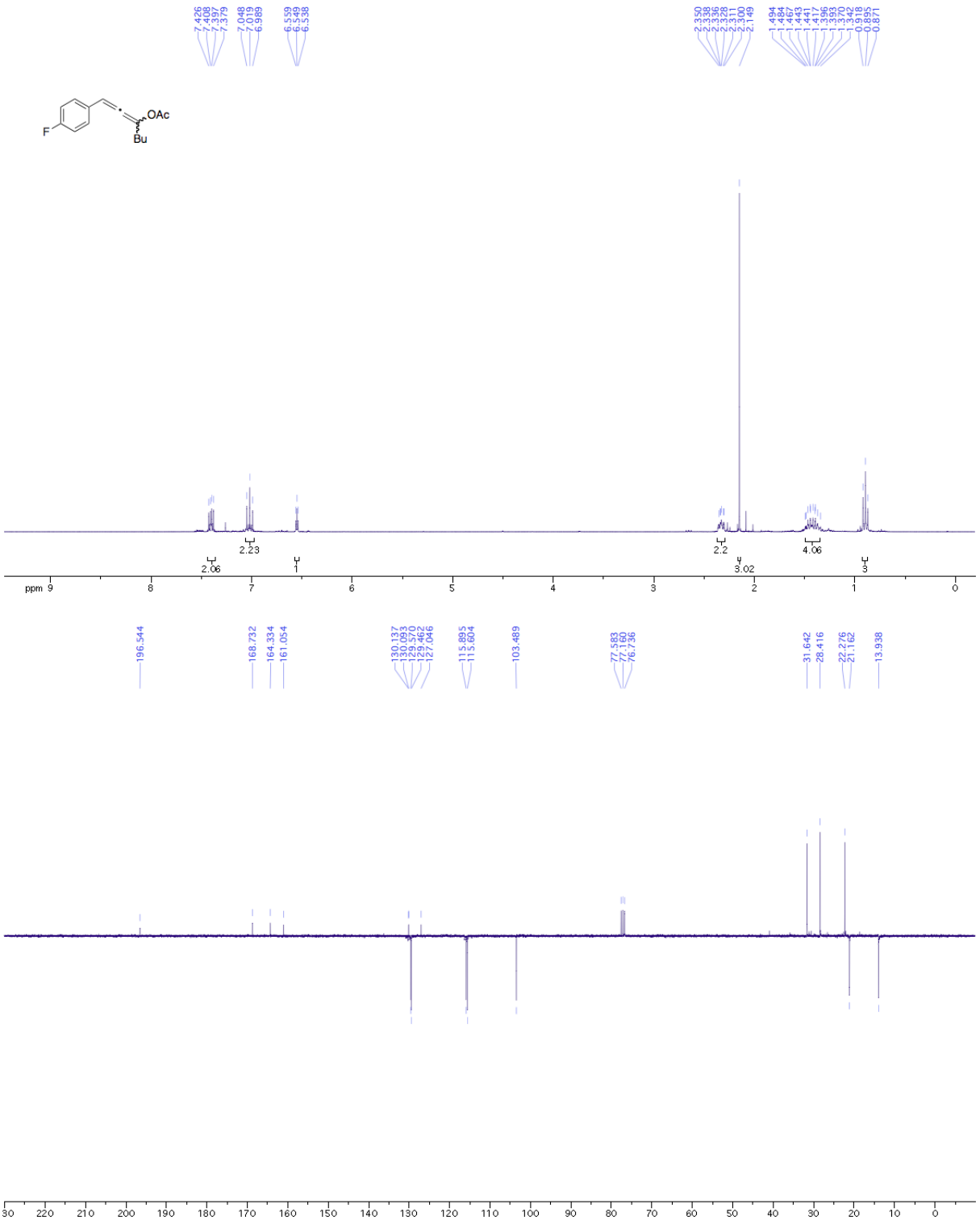
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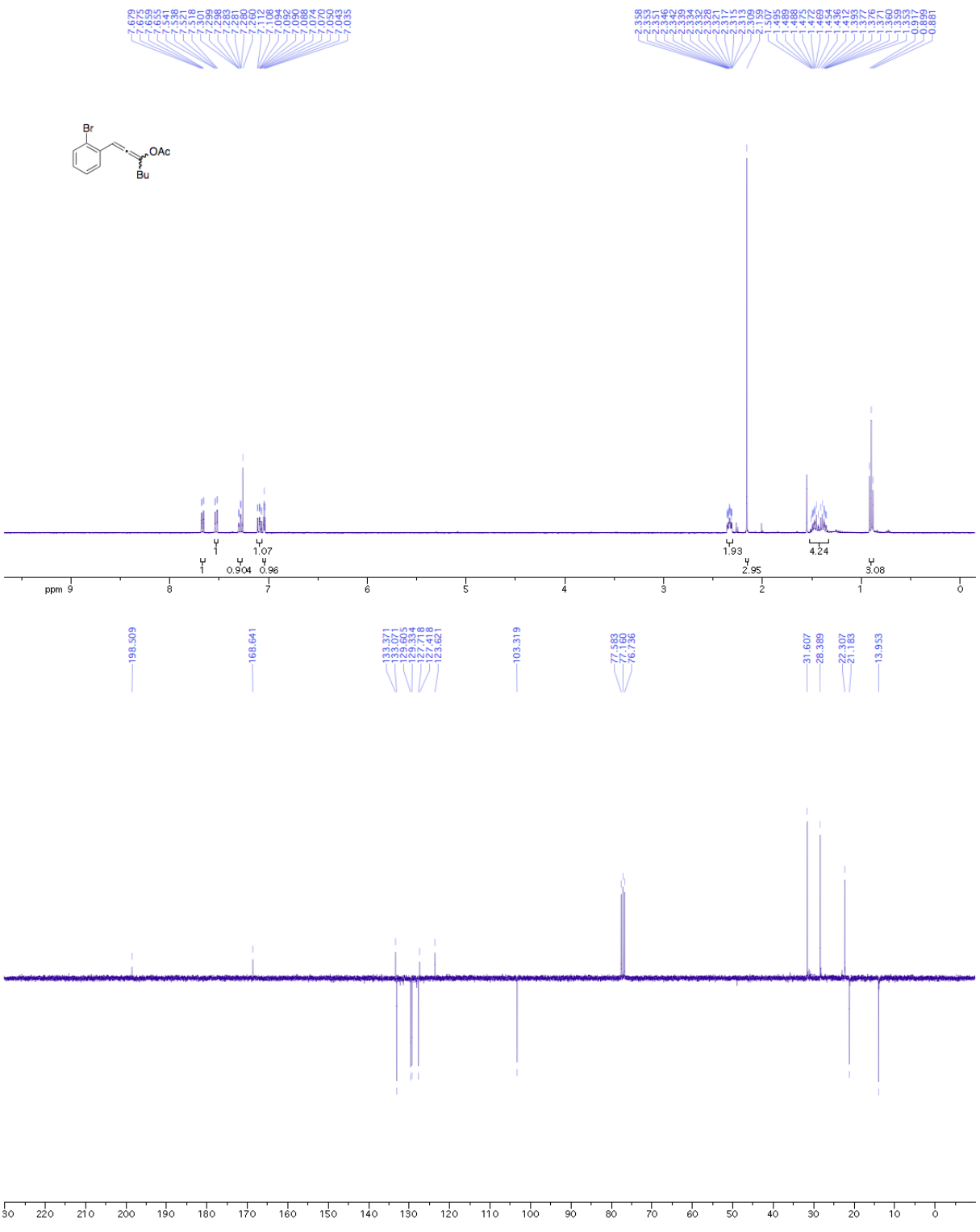
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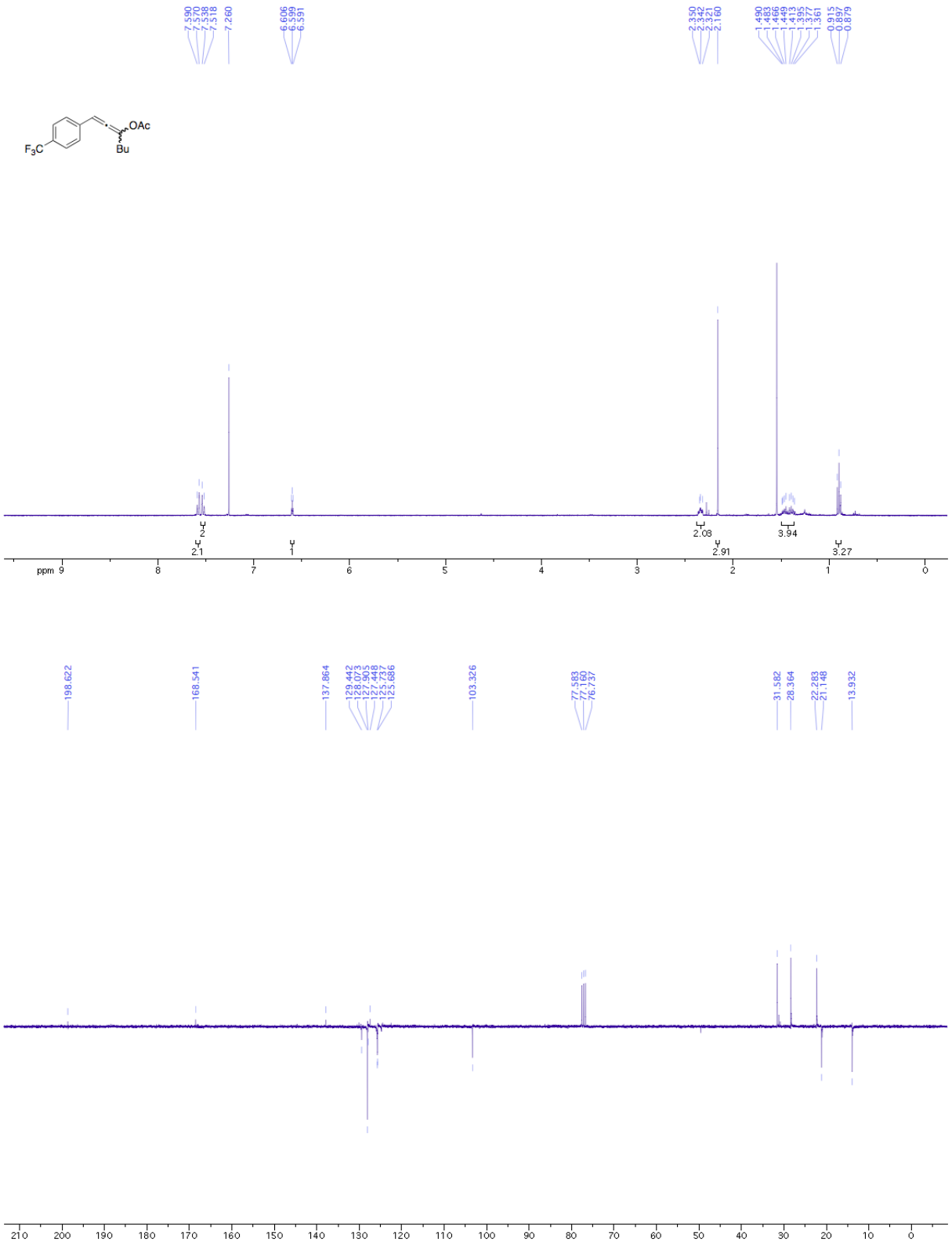
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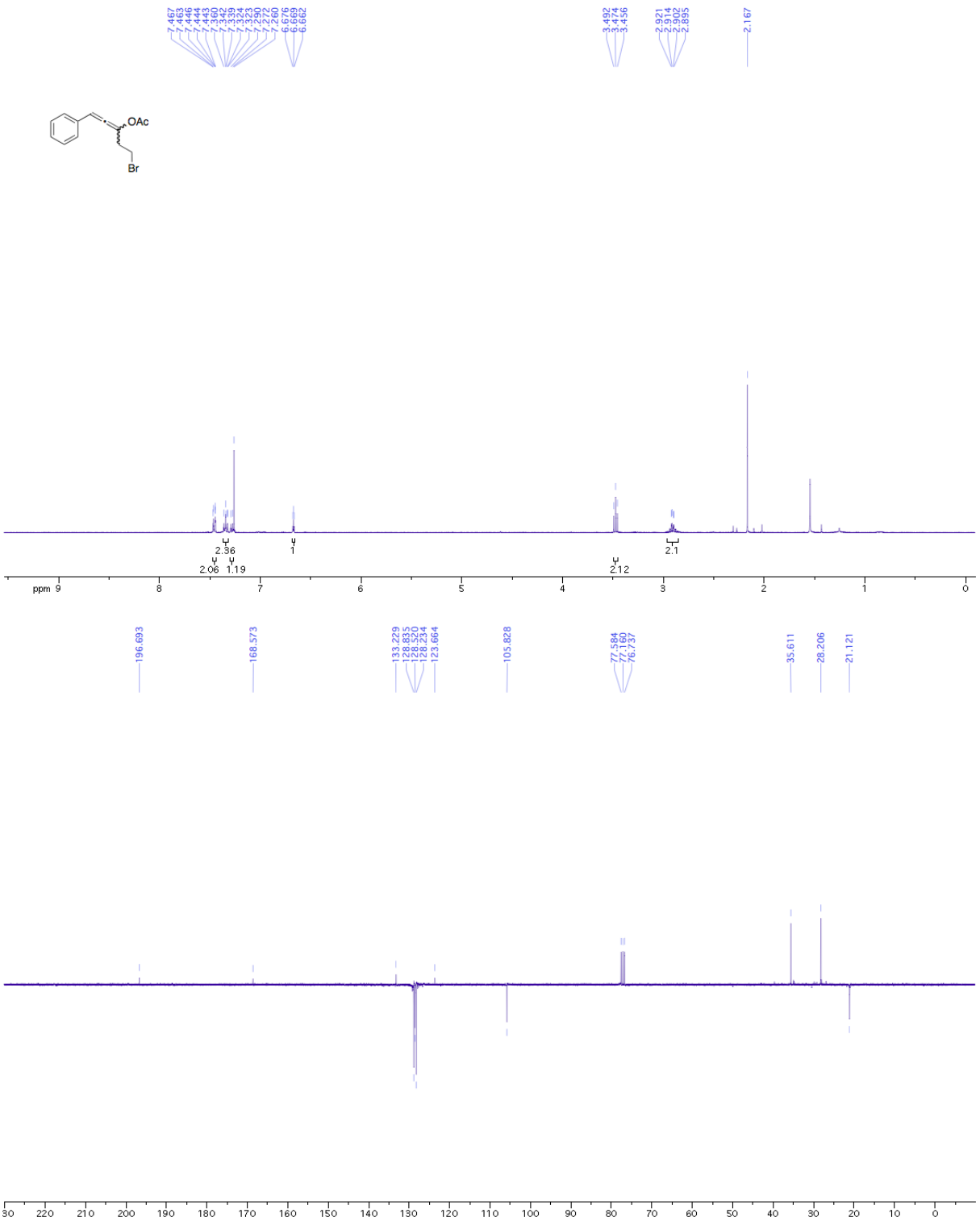
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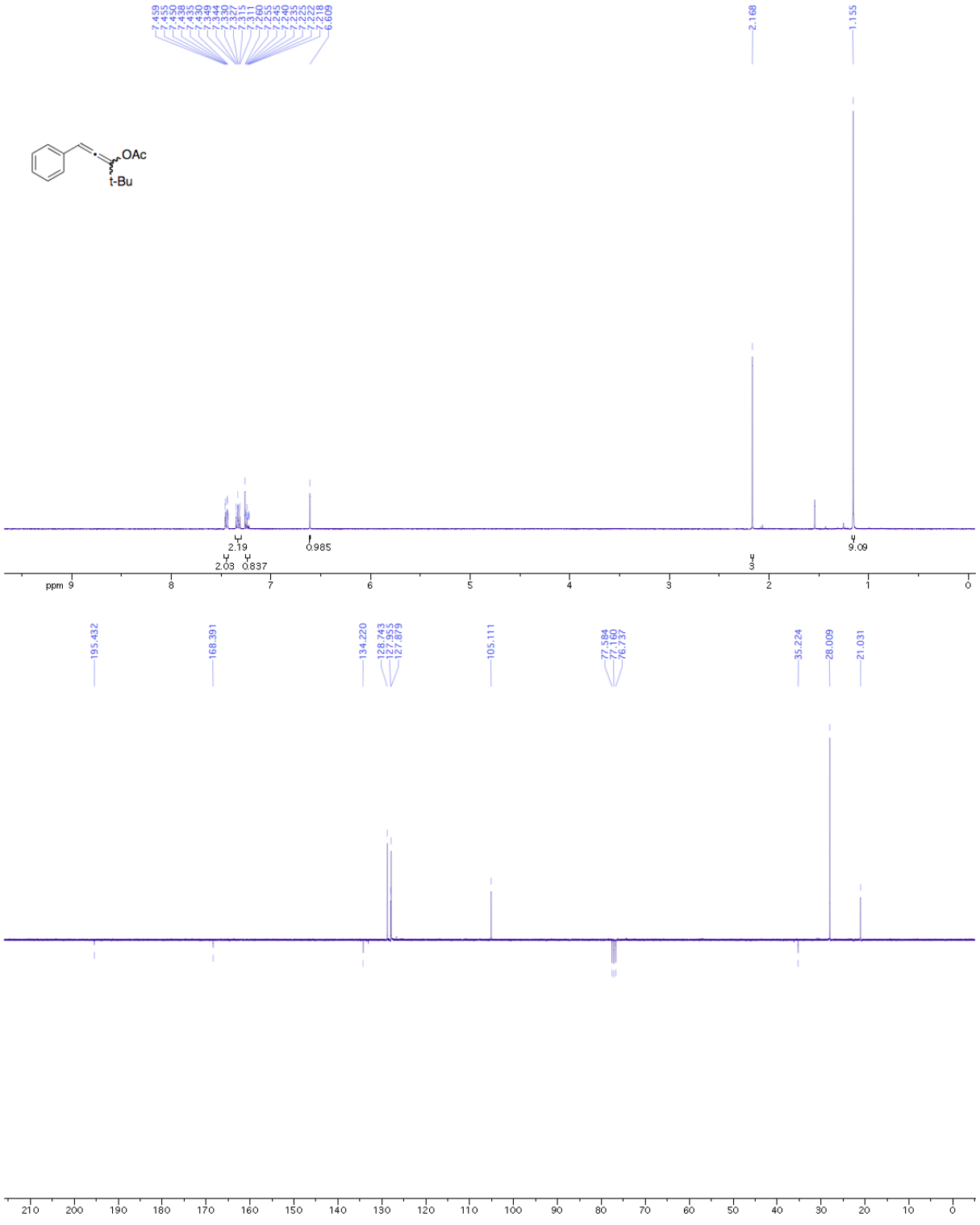
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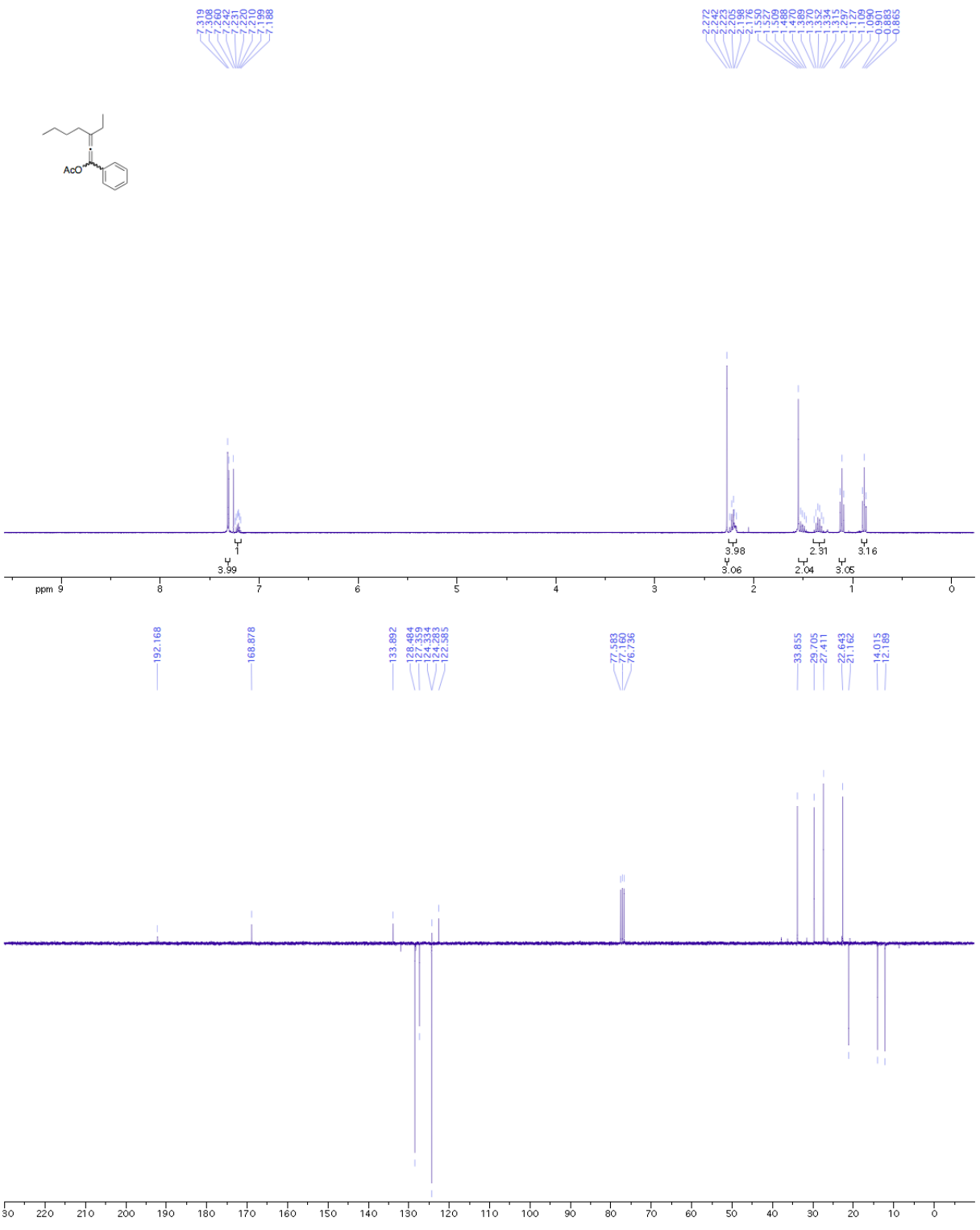
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76.736
33.855
29.705
27.411
22.643
21.162
14.015
12.189
230
220
210
200
190
180
170
160
150
140
130
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