Supporting Information

for

Triazole–Au(I) complex as chemoselective catalyst in promoting propargyl ester rearrangements

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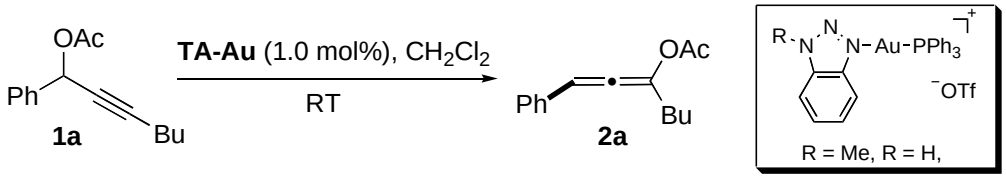
General methods, characterization data and NMR spectra of synthesized compounds.

1. General methods and materials:

All of the reactions dealing with air and/or moisture-sensitive react were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from a commercial provider and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR. Flash column chromatography was performed on 230–430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS were recorded on LTQ-FTUHRA spectrometer.

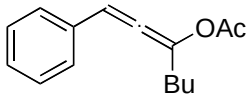
Substrates **1** and **5** were synthesized according to the literature [1-3].

Representative procedure for the preparation of allene 2a



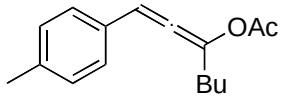
To a solution of **1a** (58 mg, 0.25 mmol) in dry CH_2Cl_2 (2.5 mL, 0.1 M), was added Au(I) catalyst (1.9 mg, 0.0025 mol, 1.0 mol %) at RT. The reaction mixture was stirred at RT and monitored by TLC. After the reaction was completed (2–10 h), the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane = 1 : 20, v/v) to give **2a** (91% yield) as colorless oil.

2. Compounds characterization



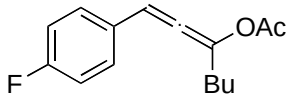
2a

1-Phenylhepta-1,2-dien-3-yl acetate (2a): (Known compound, see [4].) 91% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43-7.44 (m, 2H), 7.32-7.35 (m, 2H), 7.25-7.27 (m, 1H), 6.59 (t, *J* = 3.0 Hz, 1H), 2.33-2.37 (m, 2H), 2.15 (s, 3H), 1.46-1.51 (m, 2H), 1.38-1.43 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.7, 168.6, 133.9, 129.2, 128.6, 127.9, 127.0, 104.5, 31.5, 28.3, 22.1, 21.0, 13.8.



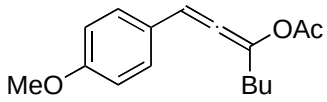
2b

1-*p*-Tolylhepta-1,2-dien-3-yl acetate (**2b**): (Known compound, see [4].) 90% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.56 (t, *J* = 3.0 Hz, 1H), 2.31-2.35 (m, 2H), 2.33 (s, 3H), 2.13 (s, 3H), 1.45-1.48 (m, 2H), 1.34-1.40 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.1, 168.6, 137.9, 131.0, 129.3, 127.7, 126.7, 104.4, 31.5, 28.3, 22.1, 21.2, 21.0, 13.8.



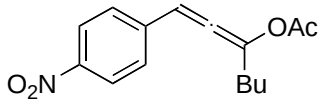
2c

1-(4-Fluorophenyl)hepta-1,2-dien-3-yl acetate (**2c**): (Known compound, see [4].) 87% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39-7.41 (m, 2H), 7.00-7.03 (m, 2H), 6.55 (t, *J* = 3.0 Hz, 1H), 2.31-2.35 (m, 2H), 2.15 (s, 3H), 1.44-1.49 (m, 2H), 1.36-1.41 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.4, 168.6, 161.8 (d, *J* = 246.5 Hz), 130.0 (d, *J* = 3.2 Hz), 129.4 (d, *J* = 8.3 Hz), 126.9, 115.5 (d, *J* = 21.9 Hz), 103.4 (d, *J* = 2.7 Hz), 31.5, 28.3, 22.1, 21.0, 13.8.



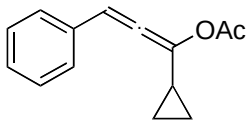
2d

1-(4-Methoxyphenyl)hepta-1,2-dien-3-yl acetate (**2d**): (Known compound, see [4].) 89% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.54 (t, *J* = 3.0 Hz, 1H), 3.81 (s, 3H), 2.28-2.34 (m, 2H), 2.14 (s, 3H), 1.44-1.47 (m, 2H), 1.35-1.39 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 195.3, 168.8, 159.6, 129.0, 126.6, 126.4, 114.2, 104.0, 55.3, 31.6, 28.4, 22.1, 21.1, 13.8.



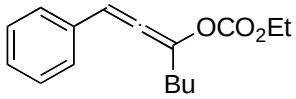
2e

1-(4-Nitrophenyl)hepta-1,2-dien-3-yl acetate (**2e**): 89% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.18-8.20 (m, 2H), 7.56-7.58 (m, 2H), 6.63 (t, *J* = 3.0 Hz, 1H), 2.34-2.37 (m, 2H), 2.17 (s, 3H), 1.45-1.55 (m, 2H), 1.37-1.41 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.2, 168.2, 147.2, 140.9, 128.3, 127.5, 124.0, 102.6, 31.4, 28.2, 22.1, 22.0, 13.8. HRMS Calculated for $[C_{15}H_{17}NO_4+Na]^+$: 298.1050, Found: 298.1050.



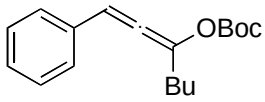
2f

1-Cyclopropyl-3-phenylpropa-1,2-dienyl acetate (**2f**): 85% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39-7.40 (m, 2H), 7.31-7.33 (m, 2H), 7.23-7.24 (m, 1H), 6.59 (d, *J* = 2.4 Hz, 1H), 2.16 (s, 3H), 1.55-1.59 (m, 1H), 0.77-0.80 (m, 2H), 0.59-0.65(m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.4, 168.6, 133.7, 128.7, 128.1, 127.8, 105.1, 93.0, 20.9, 11.9, 6.4, 5.9. HRMS Calculated for $[C_{14}H_{14}O_2+H]^+$: 215.1066, Found: 215.1059.



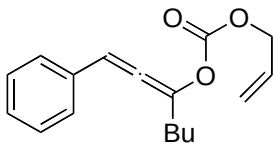
5a

Ethyl 1-phenylhepta-1,2-dien-3-yl carbonate (5a): 92% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42-7.43 (m, 2H), 7.32-7.35 (m, 2H), 7.24-7.27 (m, 1H), 6.65 (t, *J* = 3.0 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.37-2.41 (m, 2H), 1.47-1.51 (m, 2H), 1.37-1.41 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.4, 153.1, 133.7, 128.7, 128.3, 128.1, 127.9, 105.7, 64.5, 31.3, 28.2, 22.1, 14.2, 13.8. HRMS Calculated for $[C_{16}H_{20}O_3+Na]^+$: 283.1305, Found: 283.1305.



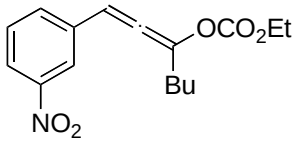
5b

***t*-Butyl 1-phenylhepta-1,2-dien-3-yl carbonate** (**5b**): 91% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41-7.42 (m, 2H), 7.31-7.34 (m, 2H), 7.23-7.26 (m, 1H), 6.63 (t, *J* = 3.0 Hz, 1H), 2.35-2.39 (m, 2H), 1.50 (s, 9H), 1.46-1.48 (m, 2H), 1.37-1.41 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.7, 151.2, 134.0, 128.6, 128.1, 128.0, 127.8, 105.2, 82.9, 31.4, 28.3, 27.9, 22.1, 13.8. HRMS Calculated for $[C_{18}H_{24}O_3+Na]^+$: 311.1618, Found: 311.1604.



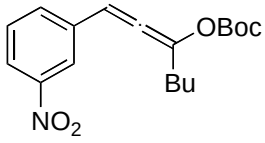
5c

Allyl 1-phenylhepta-1,2-dien-3-yl carbonate (5c): 88% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.24-7.27 (m, 1H), 6.65 (s, 1H), 5.91-5.97 (m, 1H), 5.35 (d, *J* = 17.4 Hz, 1H), 5.26 (d, *J* = 10.2 Hz, 1H), 4.65 (d, *J* = 6.0 Hz, 2H), 2.30-2.34 (m, 2H), 1.47-1.53 (m, 2H), 1.36-1.43 (m, 2H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.3, 152.9, 133.7, 131.3, 128.7, 128.4, 128.1, 127.9, 119.2, 105.8, 68.9, 31.3, 28.2, 22.1, 13.8. HRMS Calculated for $[C_{17}H_{20}O_3+Na]^+$: 295.1305, Found: 295.1306.



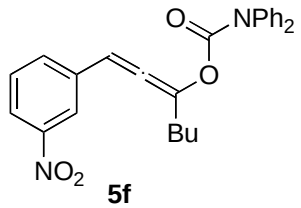
5d

Ethyl 1-(3-nitrophenyl)hepta-1,2-dien-3-yl carbonate (**5d**): 92% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.25-8.26 (m, 1H), 8.09-8.12 (m, 1H), 7.77-7.78 (m, 1H), 7.51 (t, *J* = 8.1 Hz, 1H), 6.70 (t, *J* = 3.0 Hz, 1H), 4.24 (q, *J* = 7.4 Hz, 1H), 2.39-2.43 (m, 2H), 1.48-1.56 (m, 2H), 1.39-1.44 (m, 2H), 1.33 (t, *J* = 8.1 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.3, 152.7, 148.7, 135.9, 133.4, 129.5, 129.2, 122.7, 122.5, 103.6, 64.8, 31.3, 28.1, 22.1, 14.2, 13.7. HRMS Calculated for $[C_{16}H_{19}NO_5+Na]^+$: 328.1155, Found: 328.1142.



5e

***t*-Butyl 1-(3-nitrophenyl)hepta-1,2-dien-3-yl carbonate** (**5e**): 89% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.23-8.24 (m, 1H), 8.09-8.11 (m, 1H), 7.77 (dt, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.50 (t, *J* = 8.1 Hz, 1H), 6.68 (t, *J* = 3.0 Hz, 1H), 2.37-2.41 (m, 2H), 1.51 (s, 9H), 1.47-1.50 (m, 2H), 1.38-1.42 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.6, 150.8, 148.7, 136.2, 133.4, 129.5, 128.9, 122.5, 122.4, 103.2, 83.4, 31.4, 28.2, 27.7, 22.1, 13.8. HRMS Calculated for $[C_{18}H_{23}NO_5+Na]^+$: 356.1468, Found: 356.1454.



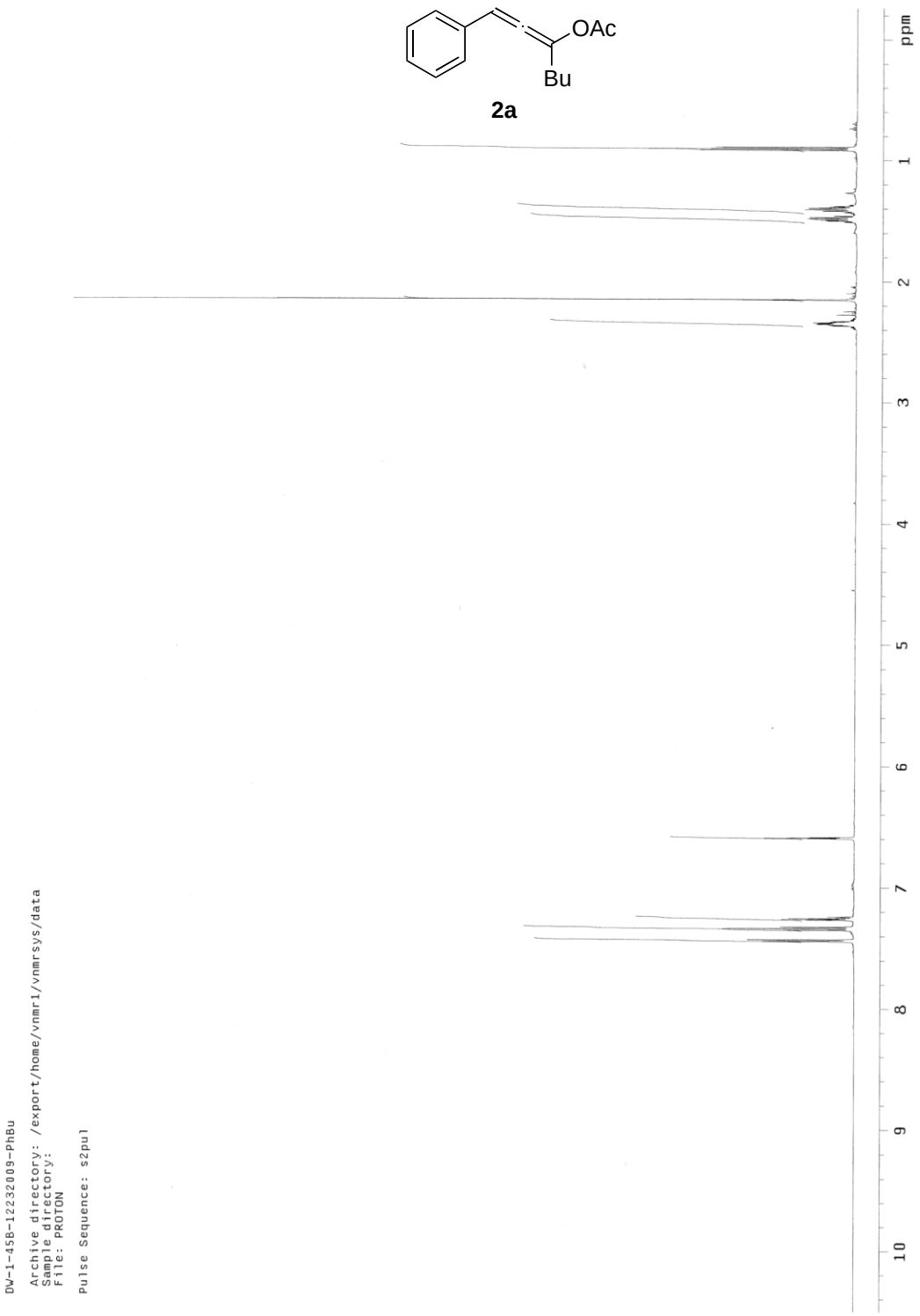
5f

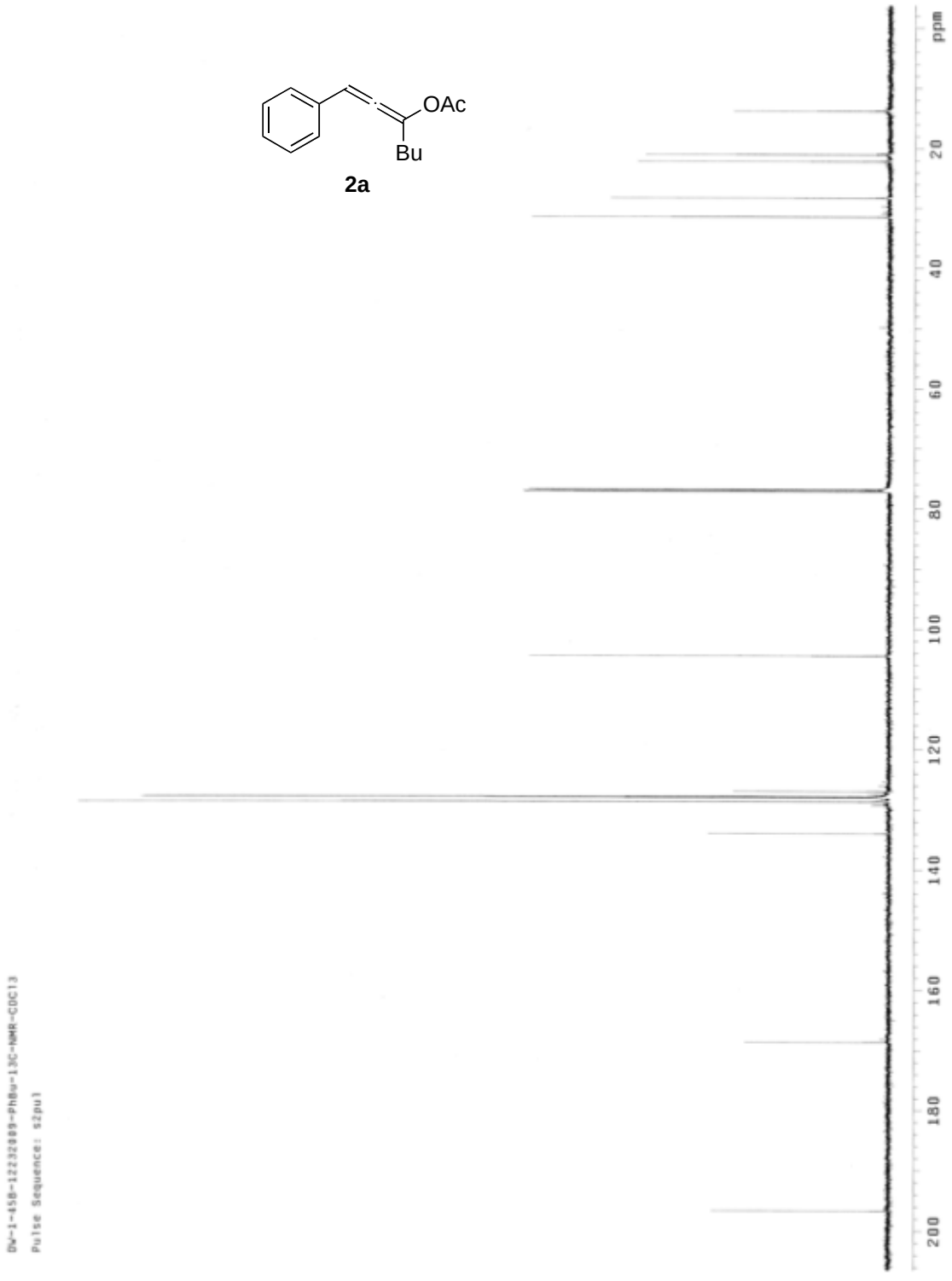
1-(3-Nitrophenyl)hepta-1,2-dien-3-yl diphenylcarbamate (**5f**): 85% yield, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.22 (t, *J* = 2.1 Hz, 1H), 8.07 (dq, *J* = 8.4 Hz, 1.0 Hz, 1H), 7.77 (dt, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 4H), 7.21-7.28 (m, 6H), 6.65 (t, *J* = 3.0 Hz, 1H), 2.30-2.34 (m, 2H), 1.31-1.41 (m, 4H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.7, 152.0, 148.6, 142.2, 136.4, 133.5, 129.5, 128.9, 128.3, 126.8, 126.4, 122.4, 122.3, 102.8, 31.6, 28.1, 21.9, 13.7. HRMS Calculated for $[C_{26}H_{24}N_2O_4+Na]^+$: 451.1628, Found: 451.1610.

3. References

1. Yu, M.; Zhang, G.; Zhang, L. *Org. Lett*. **2007**, *9*, 2147–2150.
2. Marion, N.; Carlqvist, P.; Gealageas, R.; Fremont, P.; Maseras, F.; Nolan, S. P. *Chem. Eur. J*. **2007**, *13*, 6437–6451.
3. Nonoshita, K.; Banno, H.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1990**, *112*, 316–322.
4. Nun, P.; Gaillard S.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Commun.*, **2010**, *46*, 9113–9115

4. NMR spectra

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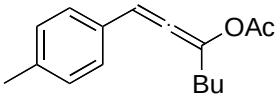
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2b, 90%

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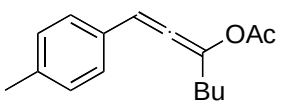
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2b, 90%

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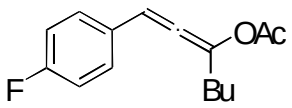
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2c

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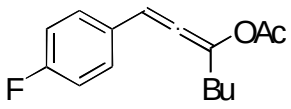
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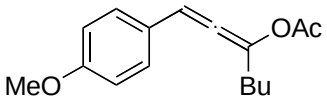
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2d, 89%

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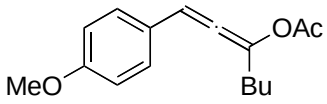
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2d, 89%

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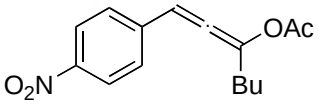
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2e, 89%

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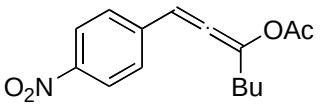
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2e, 89%

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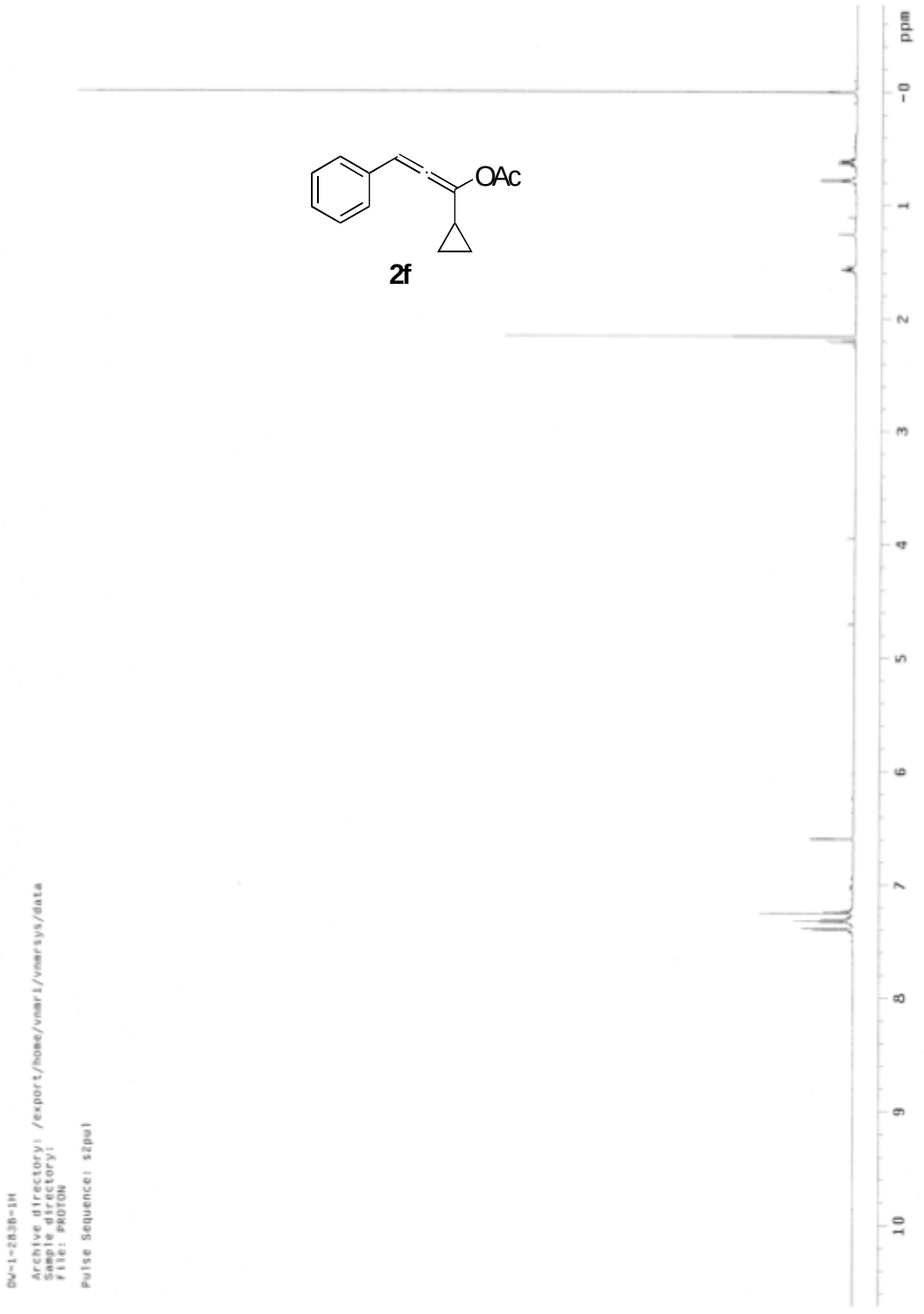
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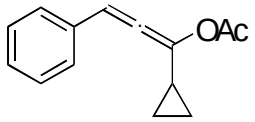
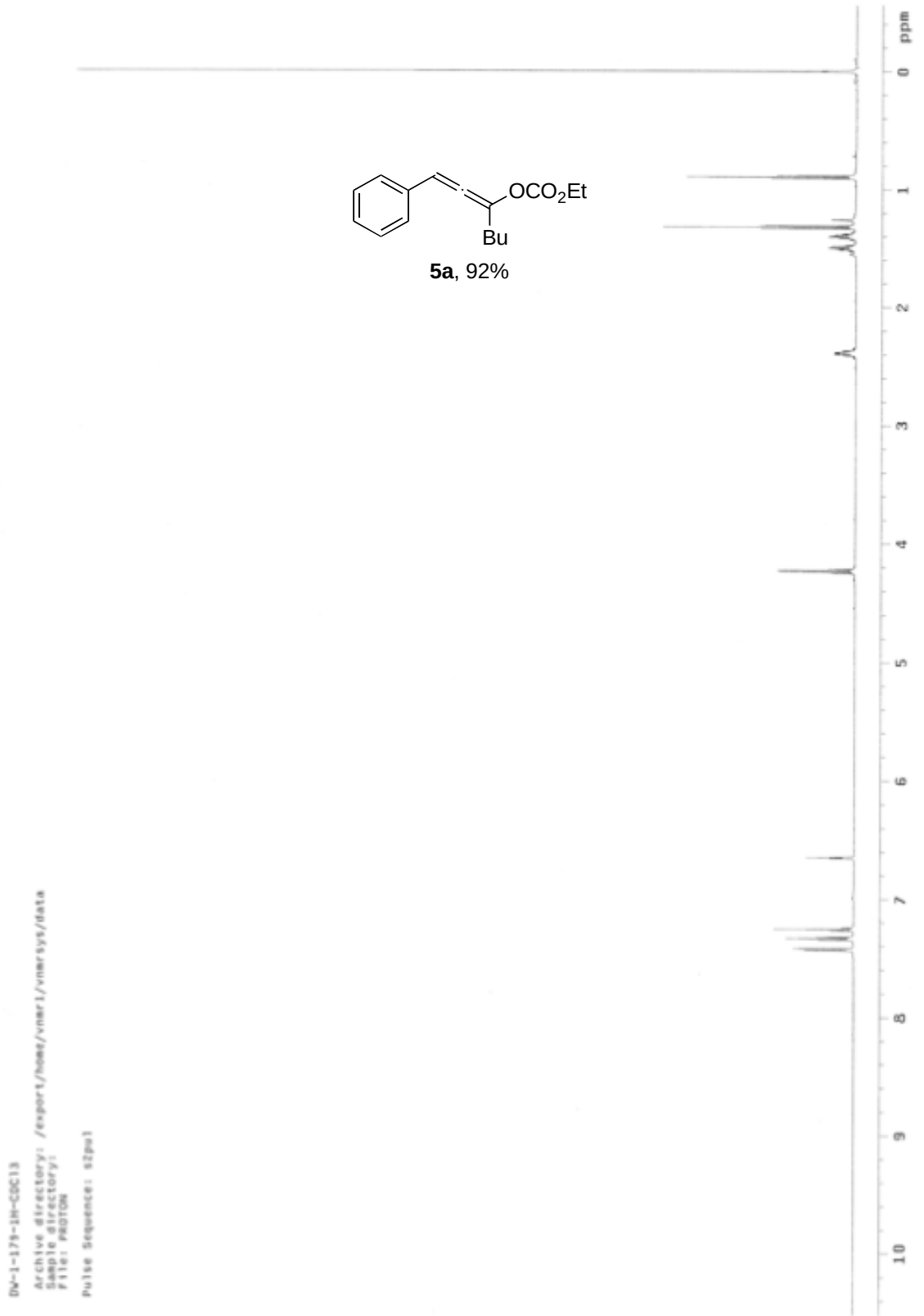
File: PROTON
Pulse Sequence: s2pul
ppm

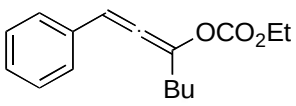

OAc

2f

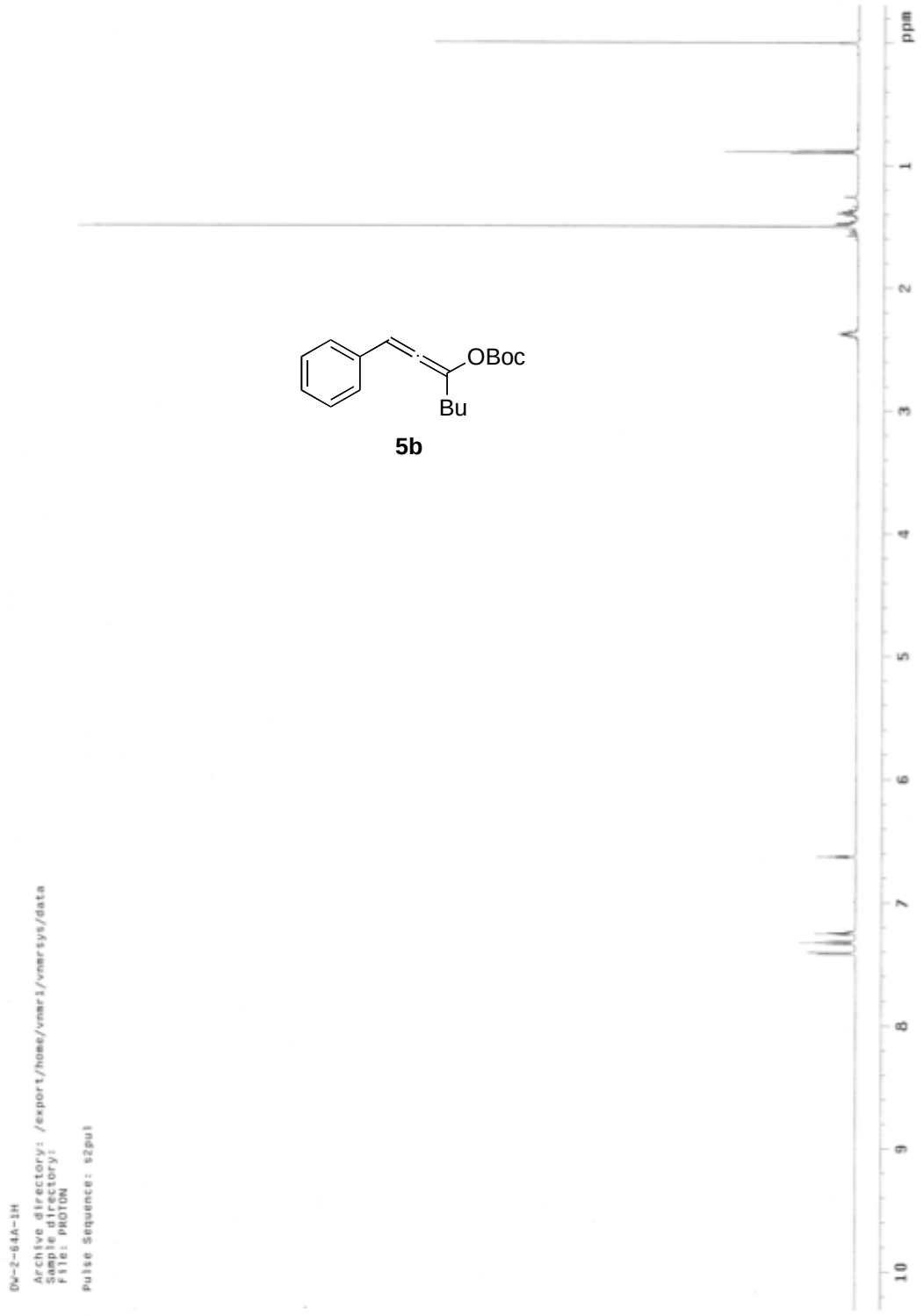
ppm
20
40
60
80
100
120
140
160
180
200
DW-1-283B-13C
Pulse Sequence: s2pul


OCO2Et
Bu
ppm
0
1
2
3
4
5
6
7
8
9
10
DW-I-179-1H-CDCl3
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul

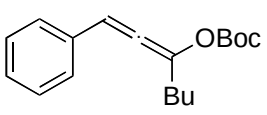
5a, 92%



5a, 92%

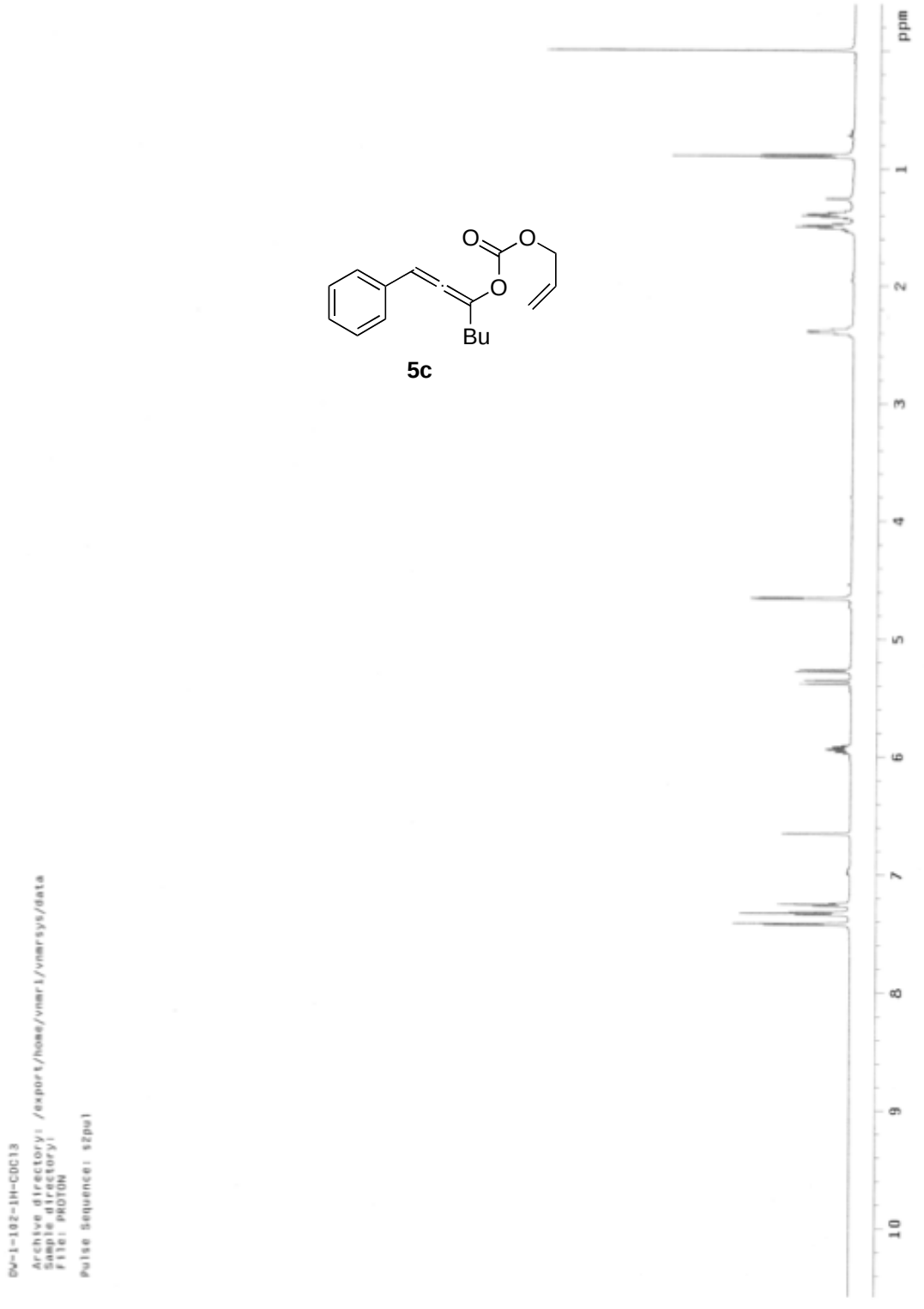

OBoc
Bu
ppm
1
2
3
4
5
6
7
8
9
10
Dw-2-64A-1H
Archive directory: /export/home/vnmrs1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul

5b

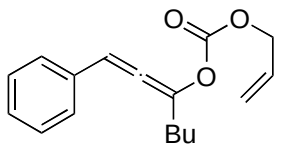

OBoc
Bu

5b

ppm
20
40
60
80
100
120
140
160
180
200
DV-2-64A1-13C
Pulse Sequence: s2pul

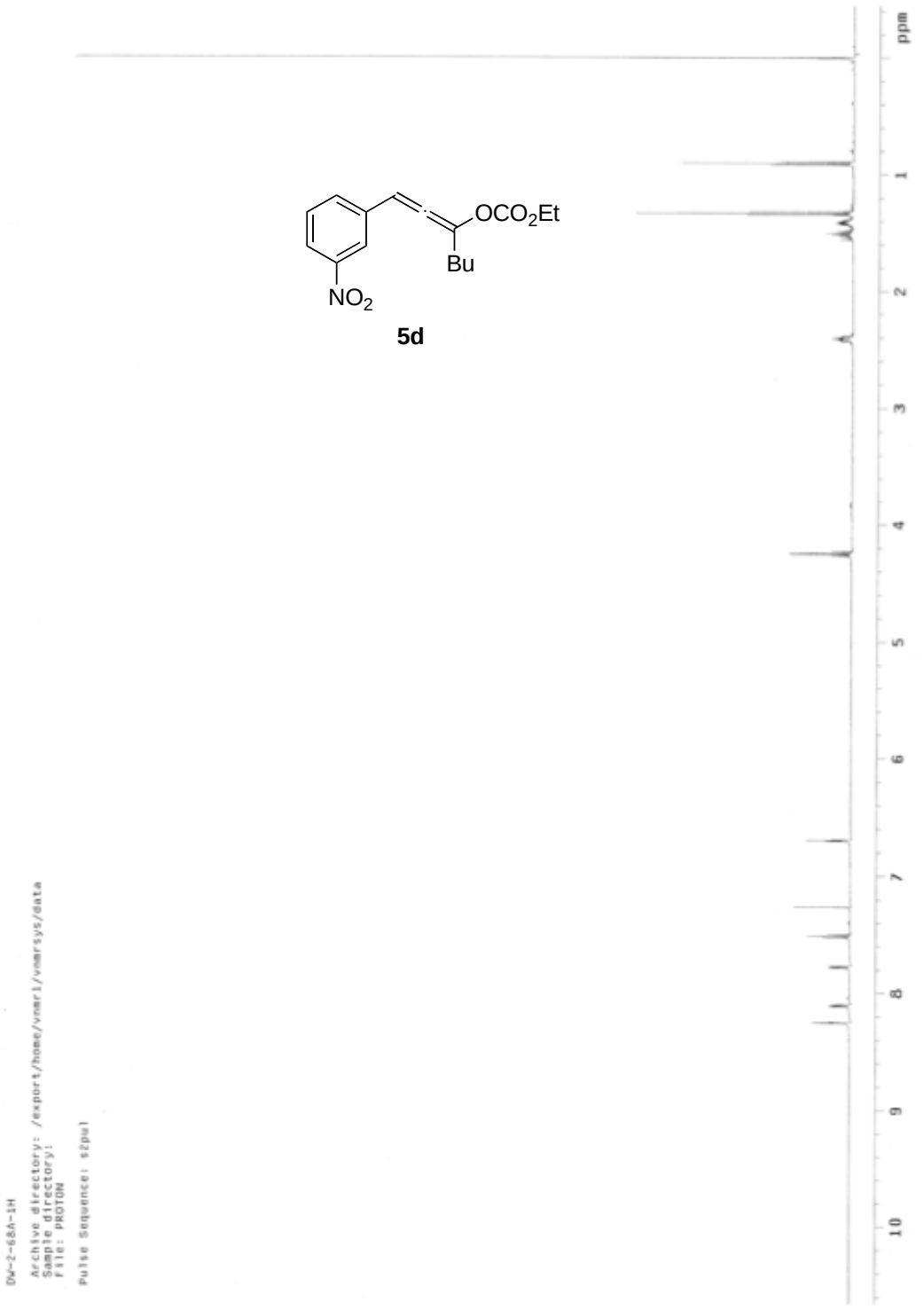


5c

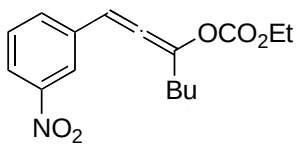

O
O
O
Bu

5c

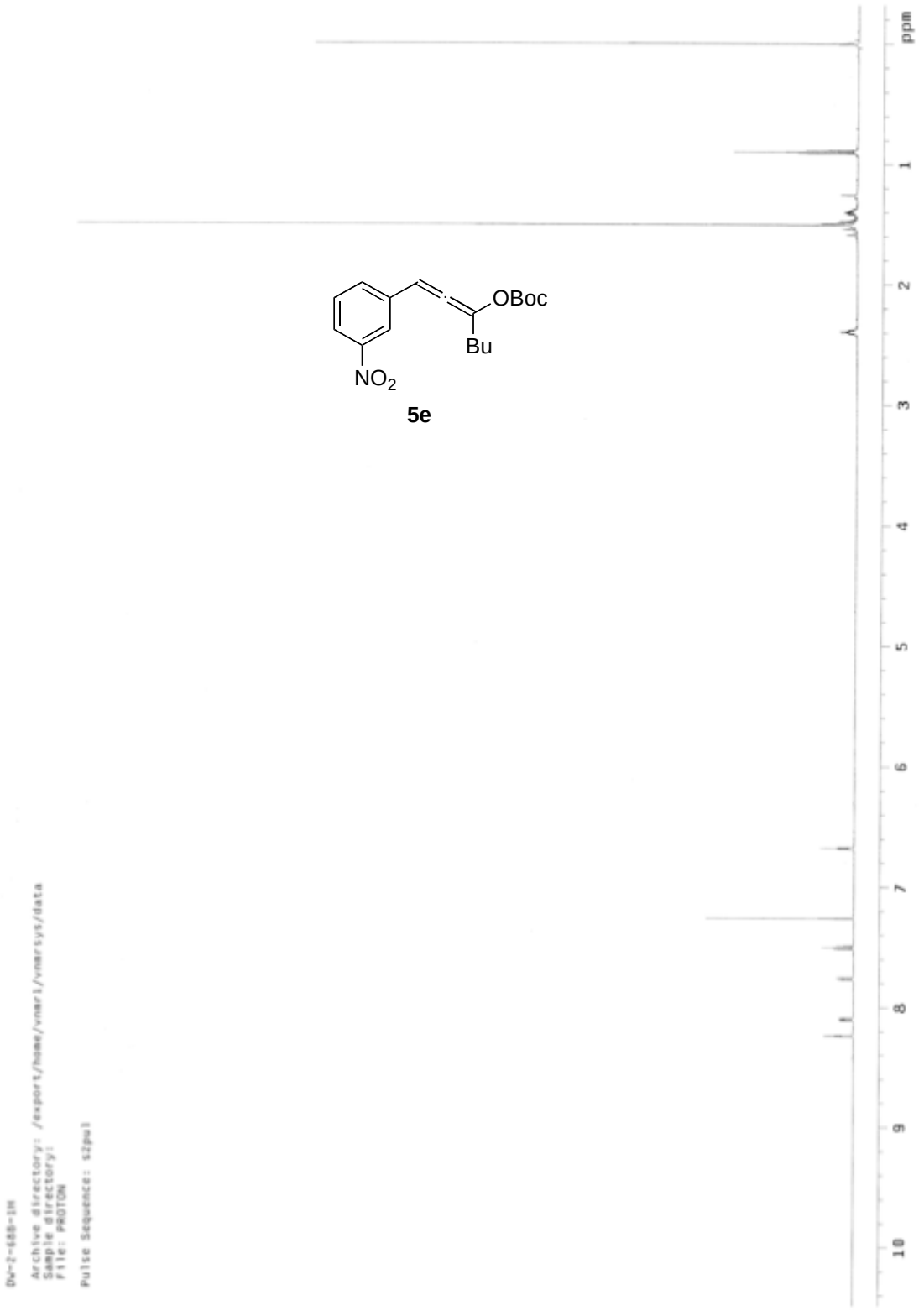
ppm
20
40
60
80
100
120
140
160
180
200
DW-1-192-13C
Pulse Sequence: s2pul


OCO2Et
Bu
NO2
ppm
1
2
3
4
5
6
7
8
9
10
DW-2-68A-1H
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory!
File: PROTON
Pulse Sequence: s2pul

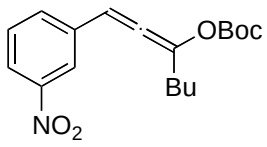
5d



5d

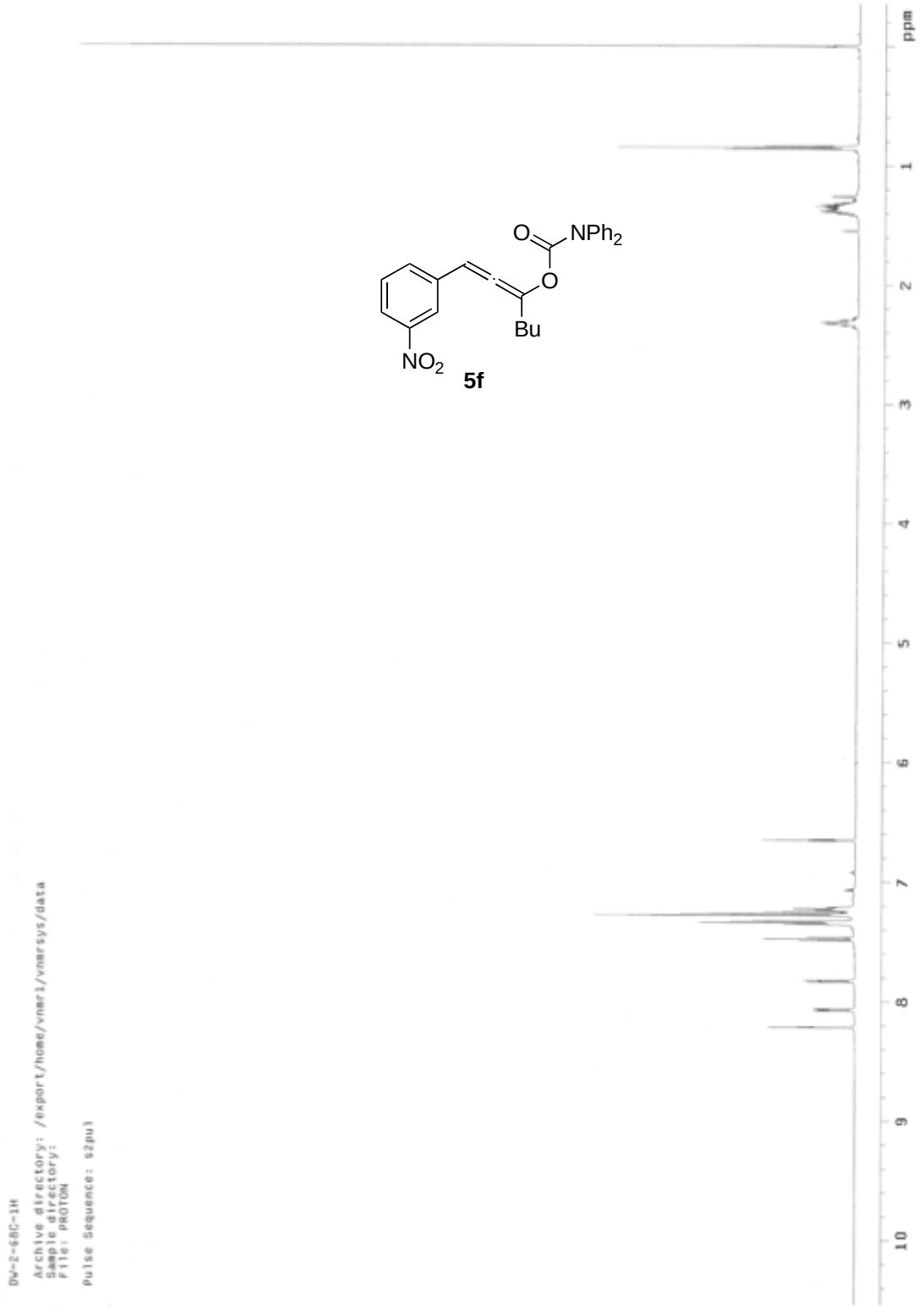

OBoc
Bu
NO2
ppm
1
2
3
4
5
6
7
8
9
10
Bv-2-488-1H
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul

5e

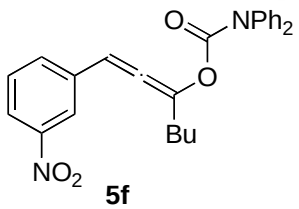

OBoc
Bu
NO2

5e

0 ppm
20
40
60
80
100
120
140
160
180
200
OW-2-688-13C
Pulse Sequence: s2pul


DW-2-68C-1H
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
O
NPh2
O
Bu
NO2
ppm
1
2
3
4
5
6
7
8
9
10

5f


O
NPh2
O
Bu
NO2

5f

ppm
20
40
60
80
100
120
140
160
180
200
DW-2-68C-13C
Pulse Sequence: s2pul