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SUPPORTING INFORMATION

cis-Semihydrogenation of alkynes with amine borane complexes catalyzed by gold nanoparticles under mild conditions

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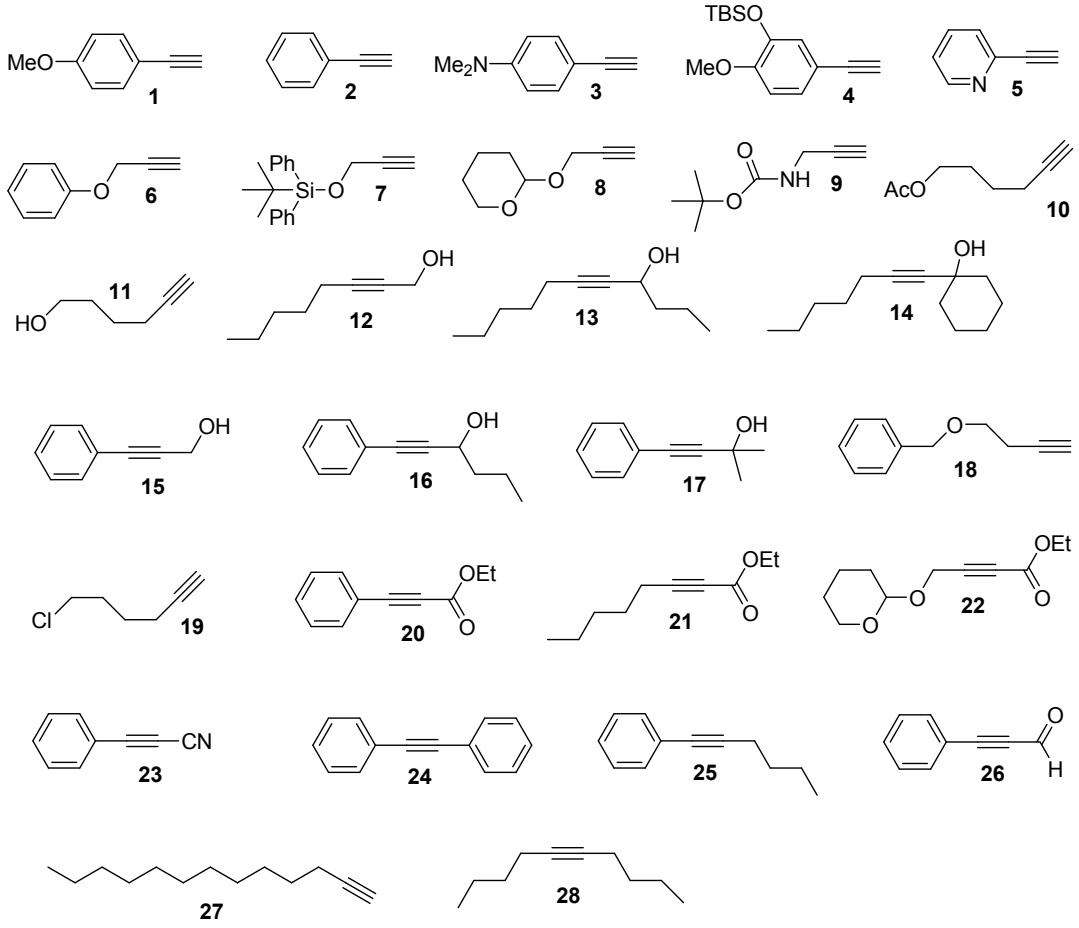
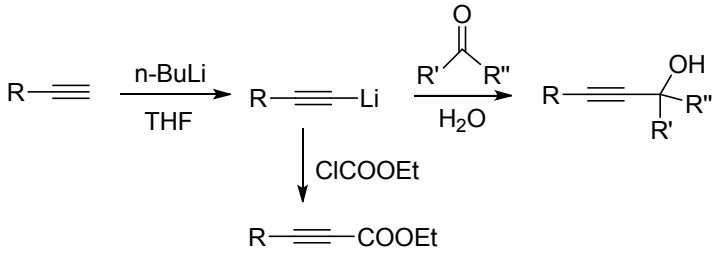
Experimental Section

List of alkynes used in our experiments



Substrates **1**, **2**, **3**, **5**, **9**, **11**, **12**, **15**, **19**, **20**, **23**, **24**, **25**, **26**, **27** and **28** are commercially available. Alkynes **6**, **7**, **8** and **10** were available from previous studies in our lab.[1] Substrate **4**[2] was prepared by protection of **30** with TBDPSCl under standard silyl protection conditions, and **18** via benzylation of 3-butyn-1-ol. Internal alkynes **13**,[3] **14**,[4] **16**,[5] **17**,[6] **21**[7] and **22**[8] were prepared by treatment of the corresponding precursor terminal alkyne with *n*-BuLi (THF, 1.1 equiv, -78 ^{o}C, 1h) followed by quench with a suitable electrophile (butyraldehyde for **13** and **16**, cyclohexanone for **14**, acetone for **17** and ClCOOEt for **21**-**22**). See the general synthetic Scheme below:

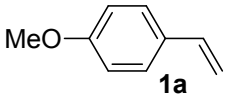


Typical procedure of the Au/TiO_2-catalyzed semireduction of alkynes

To a vial containing *p*-methoxyphenylacetylene, **1** (0.053 g, 0.4 mmol) and 1 mL ethanol were added at room temperature Me_2NHBH_3 (12 mg, 0.2 mmol) and immediately after Au/TiO_2 (79 mg, 1.0 mol%). The Au content in catalyst is ~1 wt%. The reaction was monitored by TLC and GC, and after 30 min (100% conversion) the slurry was filtered under reduced pressure through a short pad of silica gel with the aid of ethanol (2-3 mL) to withhold the supported catalyst and inorganic salts. The filtrate was evaporated under vacuum to afford *p*-methoxystyrene, **1a** (50 mg, 94% yield).

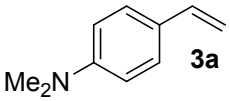
Spectroscopic data of products

1-Methoxy-4-vinylbenzene (1a)[9]



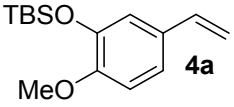
^{1}H NMR (500 MHz, $CDCl_3$): 7.36 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 6.66 (dd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, 1H), 5.61 (dd, J_1 = 17.0 Hz, J_2 = 1.2 Hz, 1H), 5.13 (dd, J_1 = 10.5 Hz, J_2 = 1.2 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 159.3, 136.2, 130.4, 127.4, 113.9, 111.5, 55.3.

***N*,*N*-Dimethyl-4-vinylaniline (3a)**[10]



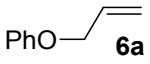
^{1}H NMR (300 MHz, $CDCl_3$): 7.33 (m, 2H), 6.72 (m, 2H), 6.66 (dd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, 1H), 5.57 (dd, J_1 = 17.0 Hz, J_2 = 1.2 Hz, 1H), 5.05 (dd, J_1 = 10.5 Hz, J_2 = 1.2 Hz, 1H), 2.98 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 150.2, 136.6, 127.1, 126.3, 112.3, 109.3, 40.5.

***tert*-Butyl(2-methoxy-5-vinylphenoxy)dimethylsilane (4a)**[11]



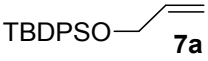
^{1}H NMR (500 MHz, $CDCl_3$): 6.96-6.94 (m, 2H), 6.79 (d, J = 8.5 Hz, 1H), 6.60 (dd, J_1 = 16.5 Hz, J_2 = 10.5 Hz, 1H), 5.57 (dd, J_1 = 16.5 Hz, J_2 = 1.0 Hz, 1H), 5.11 (dd, J_1 = 10.5 Hz, J_2 = 1.0 Hz, 1H), 3.81 (s, 3H), 1.01 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): 150.9, 145.0, 136.3, 130.8, 120.1, 118.3, 111.8, 111.6, 55.5, 25.7, 18.4, -4.6.

(Allyloxy)benzene (6a)[9]



^{1}H NMR (500 MHz, $CDCl_3$): 7.30-7.25 (m, 2H), 6.97-6.91 (m, 3H), 6.10-6.04 (m, 1H), 5.42 (dd, J_1 = 16.5 Hz, J_2 = 1.0 Hz, 1H), 5.29 (dd, J_1 = 10.5 Hz, J_2 = 1.0 Hz, 1H), 4.55 (d, J = 5.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 158.6, 133.3, 129.4, 120.8, 117.6, 114.7, 68.7.

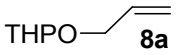
(Allyloxy)(*tert*-butyl)diphenylsilane (7a)[12]



^{1}H NMR (500 MHz, $CDCl_3$): 7.72-7.69 (m, 4H), 7.45-7.37 (m, 6H), 5.98-5.91 (m, 1H), 5.39 (dd, J_1 = 16.5 Hz, J_2 = 1.0 Hz, 1H), 5.12 (dd, J_1 = 10.5 Hz, J_2 = 1.0 Hz, 1H), 4.22 (m,

2H), 1.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): 137.0, 135.5, 133.7, 129.6, 127.6, 113.9, 64.6, 26.8, 19.3.

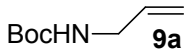
2-(Allyloxy)tetrahydro-2*H*-pyran (8a)[9]



8a

^{1}H NMR (300 MHz, $CDCl_3$): 5.98-5.90 (m, 1H), 5.30 (qd, J_1 = 16.5 Hz, J_2 = 1.5 Hz, 1H), 5.17 (qd, J_1 = 10.5 Hz, J_2 = 1.5 Hz, 1H), 4.65 (dd, J_1 = 4.0 Hz, J_2 = 3.5 Hz, 1H), 4.24 (tdd, J_1 = 13.0 Hz, J_2 = 5.5 Hz, J_3 = 1.5 Hz, 1H), 3.99 (tdd, J_1 = 13.0 Hz, J_2 = 5.5 Hz, J_3 = 1.5 Hz, 1H), 3.97-3.85 (m, 1H), 3.53-3.49 (m, 1H), 1.89-1.82 (m, 1H), 1.76-1.70 (m, 1H), 1.64-1.50 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): 134.7, 116.7, 97.9, 68.0, 62.2, 30.6, 25.4, 19.4.

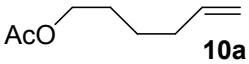
***tert*-Butyl allylcarbamate (9a)**[9]



9a

^{1}H NMR (300 MHz, $CDCl_3$): 5.89-5.76 (m, 1H), 5.16 (dd, J_1 = 16.5 Hz, J_2 = 1.5 Hz, 1H), 5.09 (dd, J_1 = 11.0 Hz, J_2 = 1.5 Hz, 1H), 4.62 (br s, 1H, NH), 3.74 (br m, 2H), 1.44 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): 155.8, 134.9, 115.7, 79.3, 43.0, 28.4.

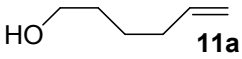
Hex-5-en-1-yl acetate (10a)[9]



10a

^{1}H NMR (500 MHz, $CDCl_3$): 5.73 (ddt, J_1 = 15.0 Hz, J_2 = 10.0 Hz, J_3 = 6.5 Hz, 1H), 5.01 (dd, J_1 = 15.0 Hz, J_2 = 1.0 Hz, 1H), 4.96 (dd, J_1 = 10.0 Hz, J_2 = 1.0 Hz, 1H), 4.06 (t, J = 6.5 Hz, 2H), 2.10-2.05 (m, 2H), 2.04 (s, 3H), 1.67-1.60 (m, 2H), 1.48-1.44 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 171.2, 138.3, 114.8, 64.4, 33.3, 28.0, 25.2, 21.0.

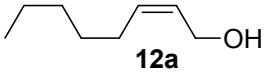
Hex-5-en-1-ol (11a)[9]



11a

^{1}H NMR (300 MHz, $CDCl_3$): 5.72 (ddt, J_1 = 15.5 Hz, J_2 = 10.0 Hz, J_3 = 6.5 Hz, 1H), 5.02 (dd, J_1 = 15.5 Hz, J_2 = 1.0 Hz, 1H), 4.96 (dd, J_1 = 10.0 Hz, J_2 = 1.0 Hz, 1H), 3.65 (t, J = 6.5 Hz, 2H), 2.13-2.05 (m, 2H), 1.64-1.42 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): 138.6, 114.6, 62.7, 33.4, 32.1, 25.0.

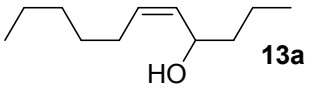
(*Z*)-Oct-2-en-1-ol (12a)[13]



12a

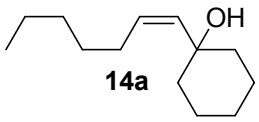
^{1}H NMR (500 MHz, $CDCl_3$): 5.63-5.52 (m, 2H), 4.19 (d, J = 6.5 Hz, 2H), 2.09-2.04 (m, 2H), 1.39-1.24 (m, 6H), 0.89 (t, J = 8.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): 133.3, 128.3, 58.6, 31.4, 29.3, 27.4, 22.5, 14.0.

(*Z*)-Undec-5-en-4-ol (13a)[3]



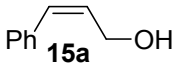
^{1}H NMR (300 MHz, $CDCl_3$): 5.52-5.32 (m, 2H), 4.45-4.40 (m, 1H), 2.13-1.98 (m, 2H), 1.62-1.24 (m, 10H), 0.92 (t, J = 7.5 Hz, 3H), 0.89 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 132.6, 132.3, 67.5, 39.7, 31.5, 29.4, 27.6, 22.5, 18.6, 14.0, 14.0.

(*Z*)-1-(Hept-1-en-1-yl)cyclohexanol (14a)[14]



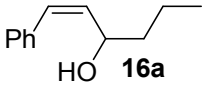
^{1}H NMR (300 MHz, $CDCl_3$): 5.45 (d, J = 10.5 Hz, 1H), 5.37 (td, J_1 = 10.5 Hz, J_2 = 6.5 Hz, 1H), 2.38-2.31 (m, 2H), 1.68-1.26 (m, 16H), 0.91 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 135.9, 132.6, 72.4, 39.3, 31.6, 29.8, 28.5, 25.5, 22.6, 22.4, 14.0.

(*Z*)-3-Phenylprop-2-en-1-ol (15a)[15]



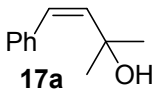
^{1}H NMR (300 MHz, $CDCl_3$): 7.38-7.20 (m, 5H), 6.58 (dd, J_1 = 11.0 Hz, J_2 = 1.5 Hz, 1H), 5.88 (td, J_1 = 11.0 Hz, J_2 = 6.5 Hz, 1H), 4.44 (dd, J_1 = 6.5 Hz, J_2 = 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 136.5, 131.1, 131.1, 128.8, 128.2, 127.2, 59.7.

(*Z*)-1-Phenylhex-1-en-3-ol (16a)[16]



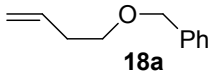
^{1}H NMR (300 MHz, $CDCl_3$): 7.37-7.22 (m, 5H), 6.56 (d, J = 11.5 Hz, 1H), 5.67 (dd, J_1 = 11.5 Hz, J_2 = 8.5 Hz, 1H), 4.63-4.55 (m, 1H), 1.67-1.36 (m, 4H), 0.92 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 136.7, 134.7, 131.0, 128.7, 128.3, 127.2, 67.6, 39.8, 18.6, 14.0.

(*Z*)-2-Methyl-4-phenylbut-3-en-2-ol (17a)[16]



^{1}H NMR (300 MHz, $CDCl_3$): 7.37-7.21 (m, 5H), 6.46 (d, J = 13.0 Hz, 1H), 5.76 (d, J = 13.0 Hz, 1H), 1.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 139.3, 137.5, 129.0, 128.1, 127.8, 126.9, 72.1, 31.2.

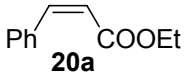
((But-3-en-1-yloxy)methyl)benzene (18a)[17]



18a

^{1}H NMR (500 MHz, $CDCl_3$): 7.36-7.27 (m, 5H), 5.89-5.81 (m, 1H), 5.11 (d, J = 17.0 Hz, 1H), 5.05 (d, J = 11.0 Hz, 1H), 4.53 (s, 2H), 3.54 (t, J = 7.0 Hz, 2H), 2.41-2.37 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 138.4, 135.3, 128.3, 127.6, 127.5, 116.3, 72.9, 69.6, 34.2.

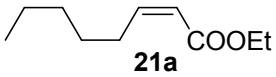
(*Z*)-Ethyl 3-phenylacrylate (20a)[18]



20a

^{1}H NMR (300 MHz, $CDCl_3$): 7.60-7.56 (m, 2H), 7.39-7.32 (m, 3H), 6.95 (d, J = 13.0 Hz, 1H), 5.95 (d, J = 13.0 Hz, 1H), 4.18 (q, J = 7.0 Hz, 2H), 1.25 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 166.2, 142.9, 134.9, 129.6, 128.9, 128.0, 119.9, 60.3, 14.1.

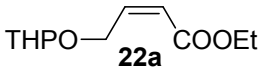
(*Z*)-Ethyl oct-2-enoate (21a)[19]



21a

^{1}H NMR (300 MHz, $CDCl_3$): 6.22 (td, J_1 = 11.5 Hz, J_2 = 7.5 Hz, 1H), 5.80 (td, J_1 = 11.5 Hz, J_2 = 1.5 Hz, 1H), 4.16 (q, J = 7.0 Hz, 2H), 2.68-2.60 (m, 2H), 1.50-1.39 (m, 2H), 1.28 (t, J = 7.0 Hz, 3H), 1.35-1.22 (m, 4H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 166.5, 150.7, 119.6, 59.7, 31.5, 28.9, 28.7, 22.5, 14.3, 14.0.

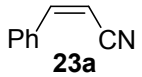
(*Z*)-Ethyl 4-((tetrahydro-2*H*-pyran-2-yl)oxy)but-2-enoate (22a)[20]



22a

^{1}H NMR (300 MHz, $CDCl_3$): 6.41 (td, J_1 = 11.5 Hz, J_2 = 7.5 Hz, 1H), 5.81 (td, J_1 = 11.5 Hz, J_2 = 2.5 Hz, 1H), 4.80 (ddd, J_1 = 17.0 Hz, J_2 = 5.0 Hz, J_3 = 2.5 Hz, 1H), 4.67 (ddd, J_1 = 17.0 Hz, J_2 = 5.0 Hz, J_3 = 2.5 Hz, 1H), 4.64-4.62 (m, 1H), 4.14 (q, J = 7.0 Hz, 2H), 3.90-3.83 (m, 1H), 3.54-3.47 (m, 1H), 1.86-1.48 (m, 6H), 1.28 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 166.0, 148.2, 119.3, 98.9, 62.7, 65.7, 62.5, 60.2, 30.6, 25.4, 19.6, 14.2.

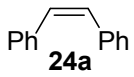
(*Z*)-3-Phenylacrylonitrile (23a)[21]



23a

^{1}H NMR (300 MHz, $CDCl_3$): 7.83-7.79 (m, 2H), 7.46-7.43 (m, 3H), 7.13 (d, J = 12.0 Hz, 1H), 5.45 (d, J = 12.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 148.7, 133.6, 131.0, 129.0, 128.9, 117.3, 95.1.

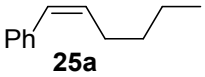
(*Z*)-1,2-Diphenylethene (24a)[9]



24a

^{1}H NMR (500 MHz, $CDCl_3$): 7.30-7.20 (m, 10H), 6.63 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 137.3, 130.3, 128.9, 128.2, 127.1.

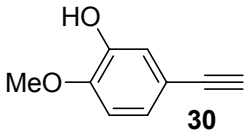
(*Z*)-Hex-1-en-1-ylbenzene (25a)[22]



25a

^{1}H NMR (300 MHz, $CDCl_3$): 7.38-7.20 (m, 5H), 6.43 (d, J = 11.5 Hz, 1H), 5.68 (td, J_1 = 11.5 Hz, J_2 = 6.5 Hz, 1H), 2.40-2.32 (m, 2H), 1.50-1.32 (m, 4H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 137.8, 133.2, 128.7, 128.6, 128.1, 126.4, 32.1, 28.3, 22.4, 14.0.

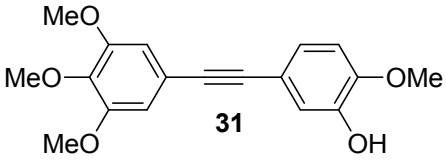
5-Ethynyl-2-methoxyphenol (30)[23]



30

^{1}H NMR (500 MHz, $CDCl_3$): 7.05 (d, J = 2.0 Hz, 1H), 7.03 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 6.78 (d, J = 8.5 Hz, 1H), 5.62 (br s, 1H, -OH), 3.89 (s, 3H), 2.97 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 147.3, 145.2, 124.8, 118.0, 114.8, 110.4, 83.5, 75.6, 55.9.

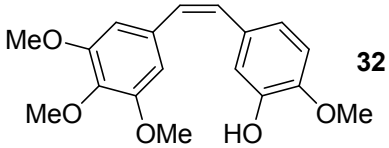
2-Methoxy-5-((3,4,5-trimethoxyphenyl)ethynyl)phenol (31)[24]



31

^{1}H NMR (500 MHz, $CDCl_3$): 7.09 (d, J = 2.0 Hz, 1H), 7.06 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 6.82 (d, J = 8.5 Hz, 1H), 6.75 (s, 2H), 5.60 (br s, 1H, -OH), 3.91 (s, 3H), 3.88 (s, 6H), 3.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): 153.0, 147.0, 145.3, 138.6, 124.2, 118.5, 117.5, 116.0, 110.5, 108.7, 88.4, 87.9, 61.0, 56.1, 55.9.

(*Z*)-2-Methoxy-5-(3,4,5-trimethoxystyryl)phenol (Compretastatin A-4, 32)[24]



32

^{1}H NMR (300 MHz, $CDCl_3$): 6.92 (d, J = 2.0 Hz, 1H), 6.80 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 6.73 (d, J = 8.5 Hz, 1H), 6.53 (s, 2H), 6.47 (d, J = 11.5 Hz, 1H), 6.41 (d, J = 11.5 Hz, 1H), 5.50 (br s, 1H, -OH), 3.87 (s, 3H), 3.84 (s, 3H), 3.70 (s, 6H); ^{13}C NMR (75 MHz,

$CDCl_3$): 152.9, 145.7, 145.2, 137.1, 132.7, 130.6, 129.5, 129.0, 121.1, 115.0, 110.3, 106.0, 60.9, 55.9, 55.9.

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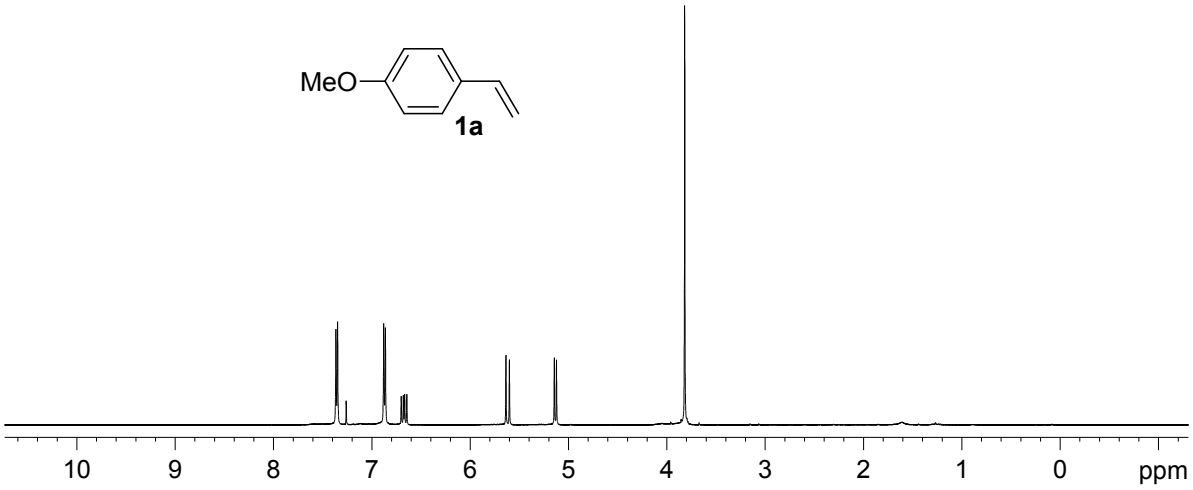
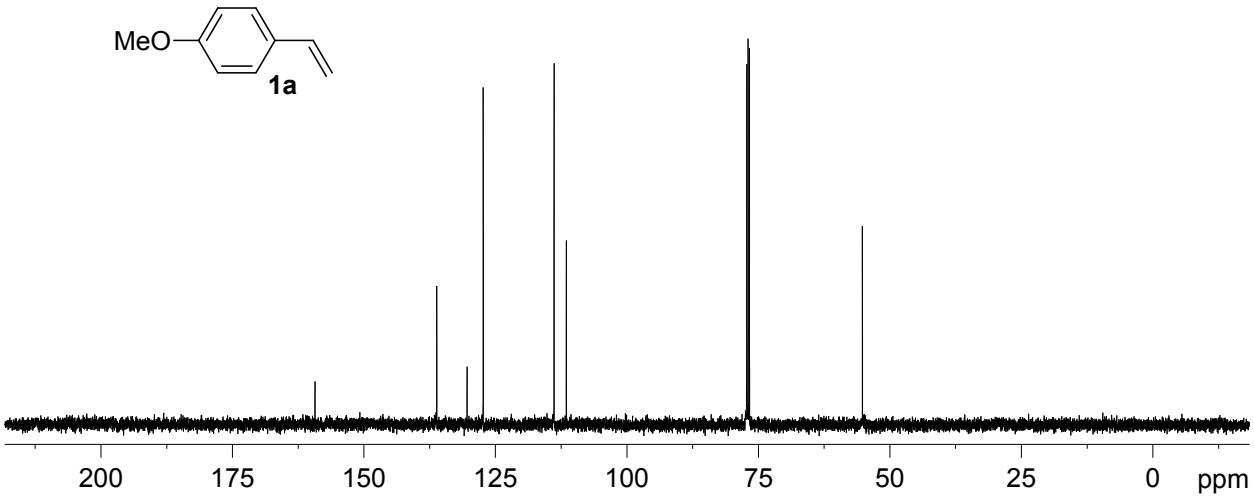
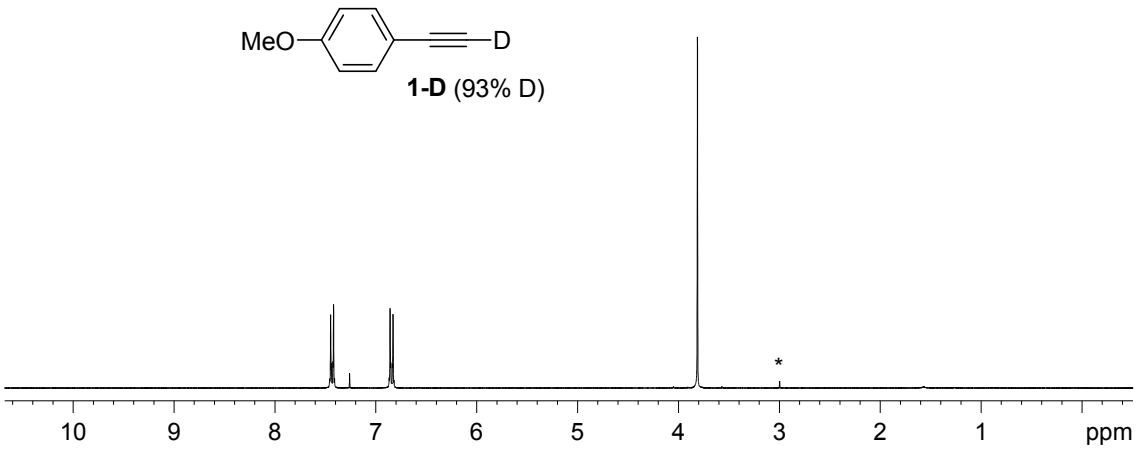
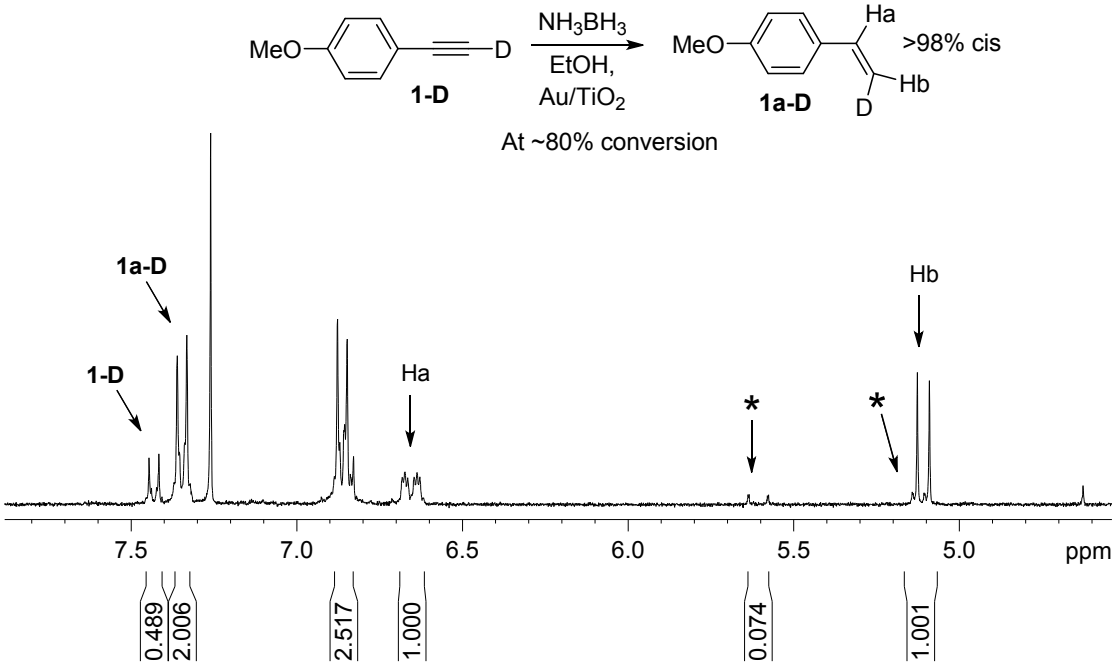
^{1}H and ^{13}C NMR spectra of products



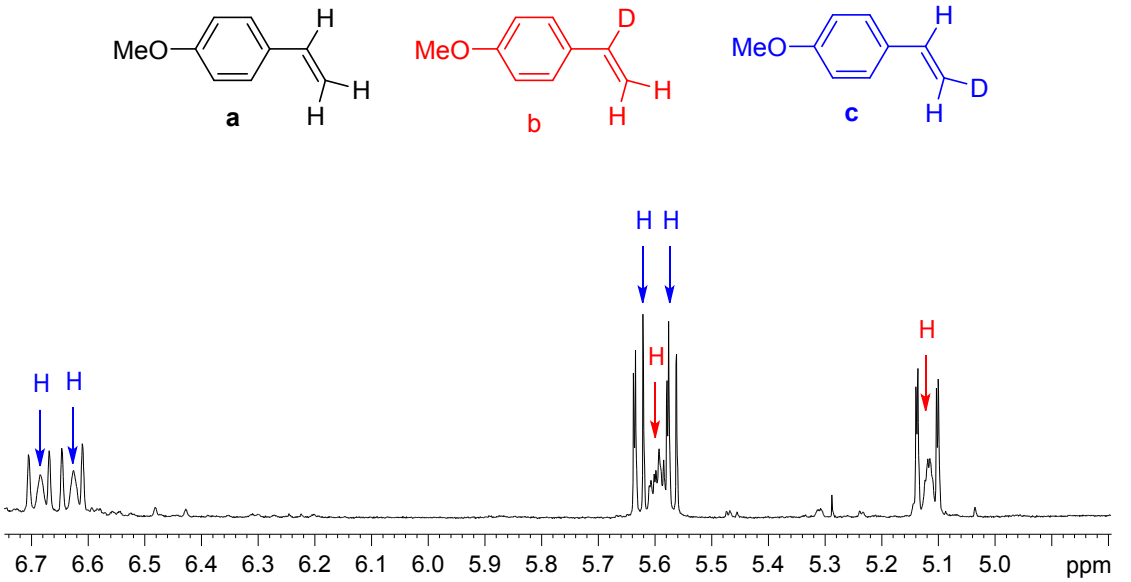




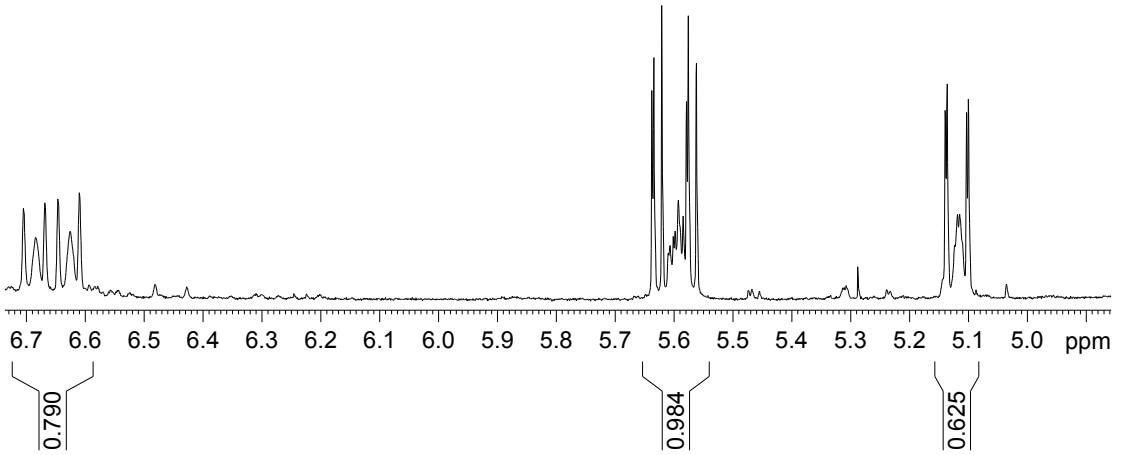
*: 7% of fully protonated **1**



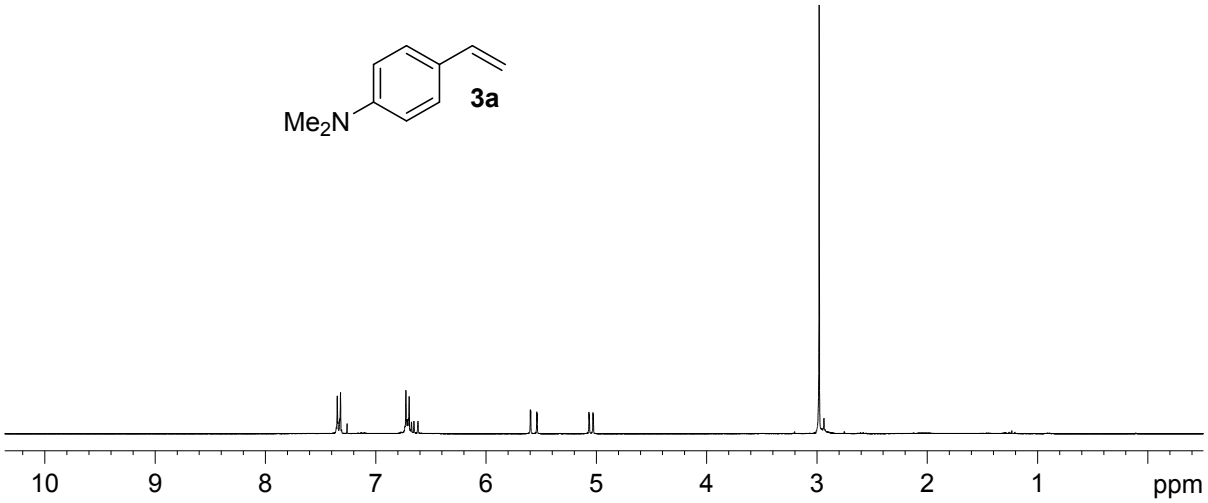
*: Absorptions from fully protonated **1a**, as starting material **1-D** had 93% deuterium content.



Region of the ^{1}H NMR spectrum from the crude reaction mixture in the Au/TiO_2-catalyzed reaction of alkyne **1** with ammonia borane in THF/D_2O, showing the presence of fully protonated product **a** and deuterated **b** (red)and **c** (blue). Non labelled by arrow absorptions correspond to fully protonated **a**.



The current integrals appear based on the integration of the two aromatic protons set as 2.0. Based the above integrals, a relative ratio **1a**/**1b**/**1c** ~ 36/43/21 is calculated.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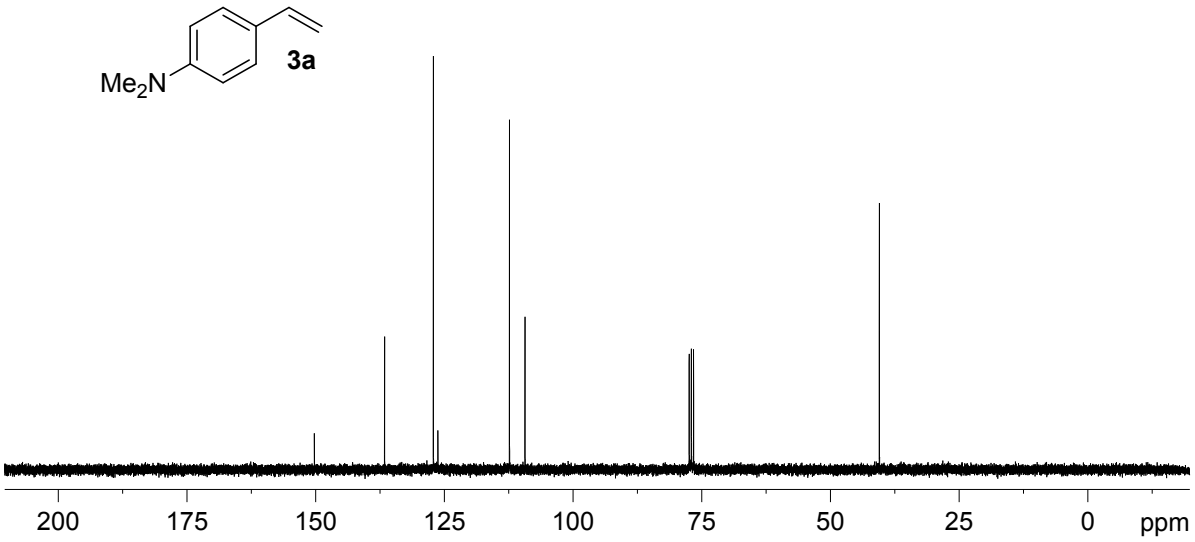
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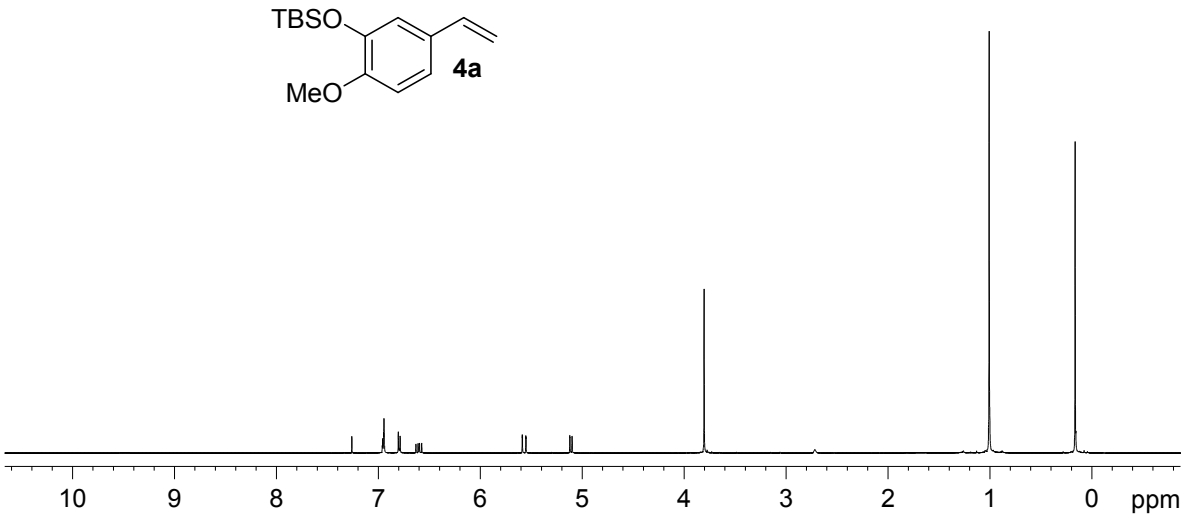
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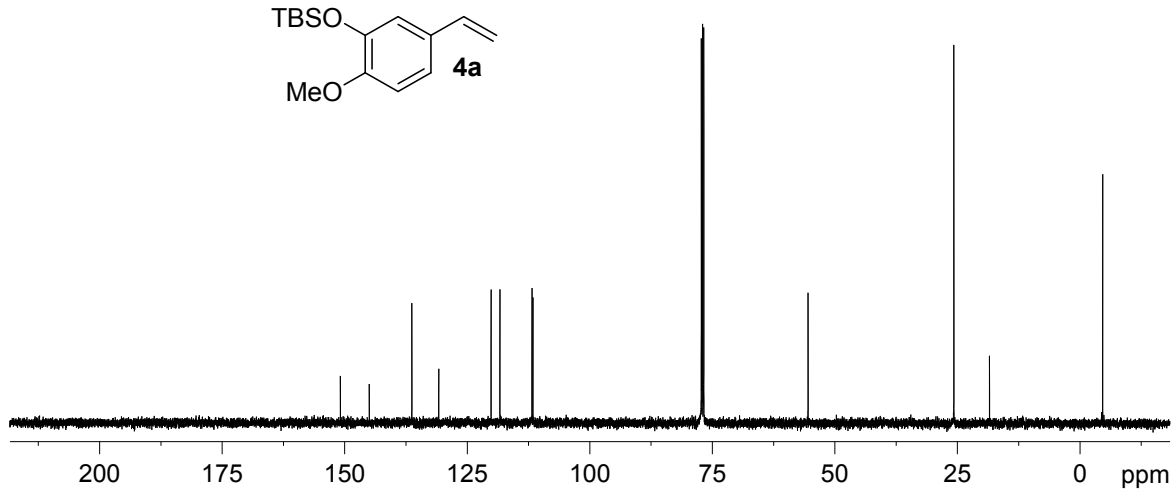
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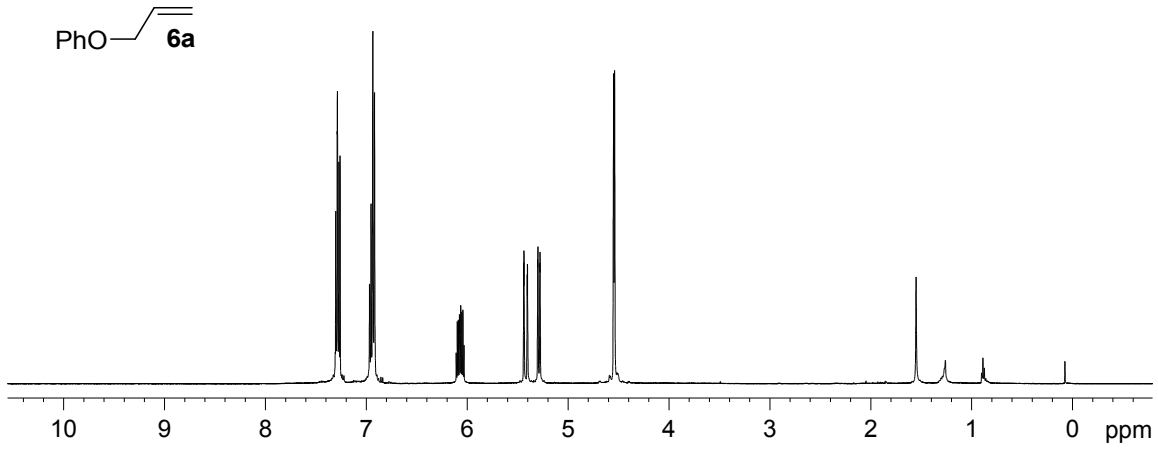
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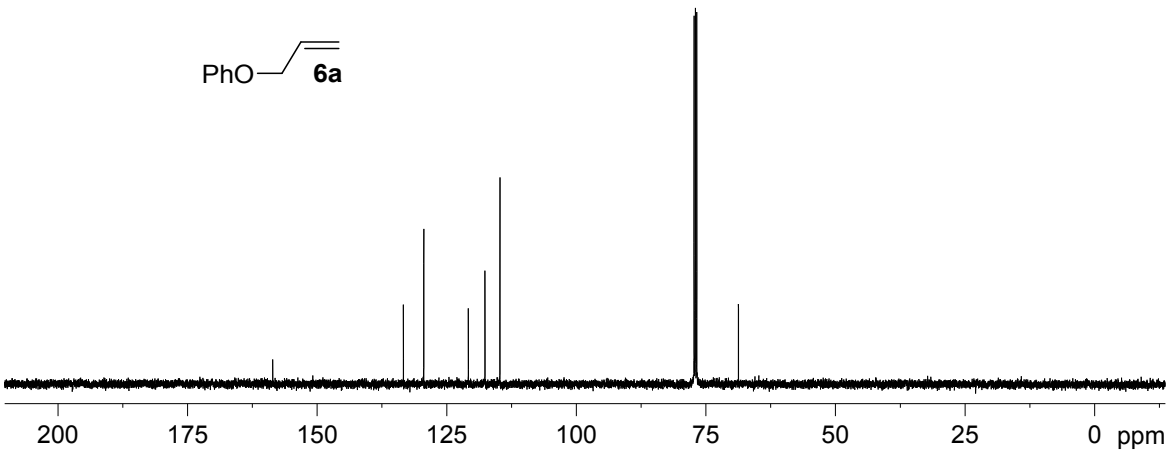
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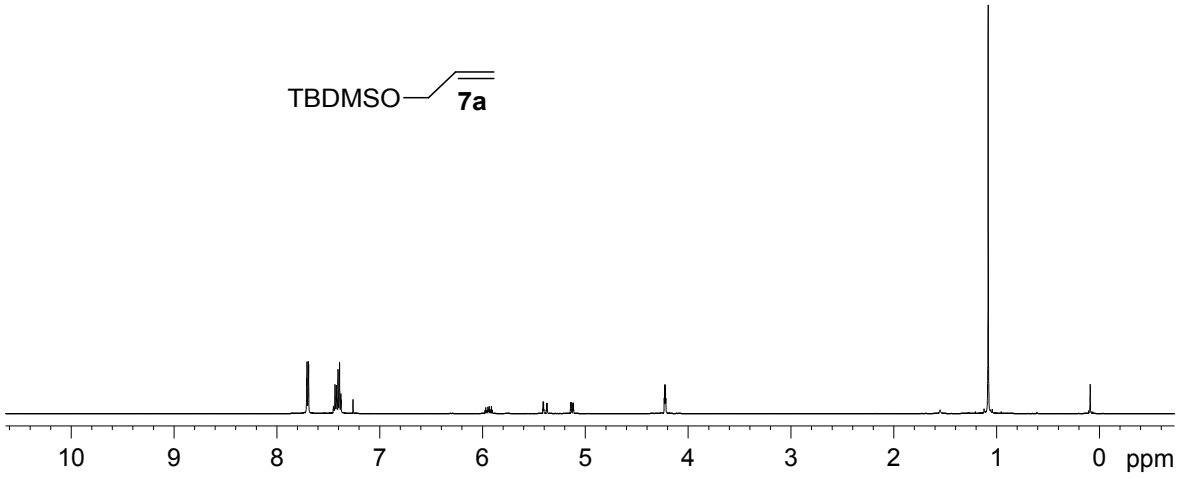
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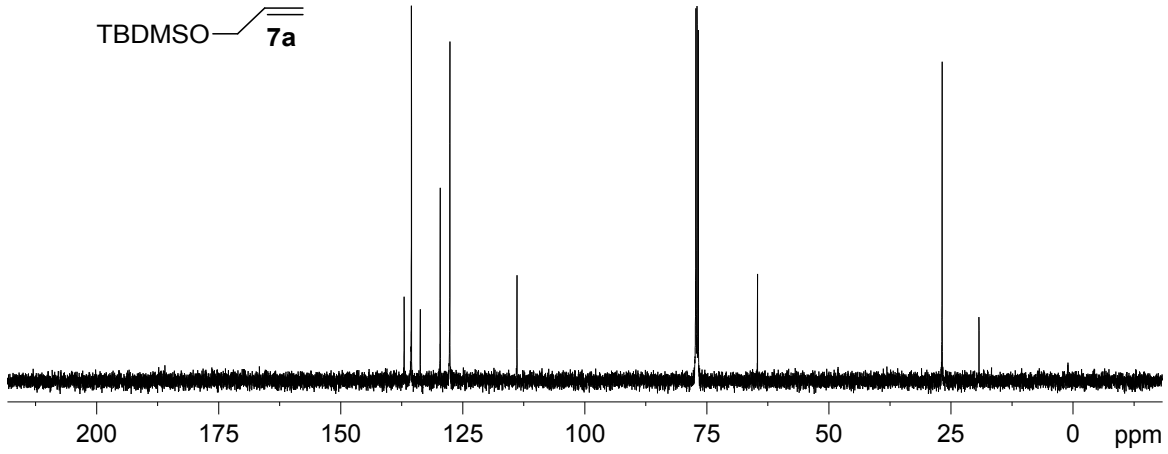
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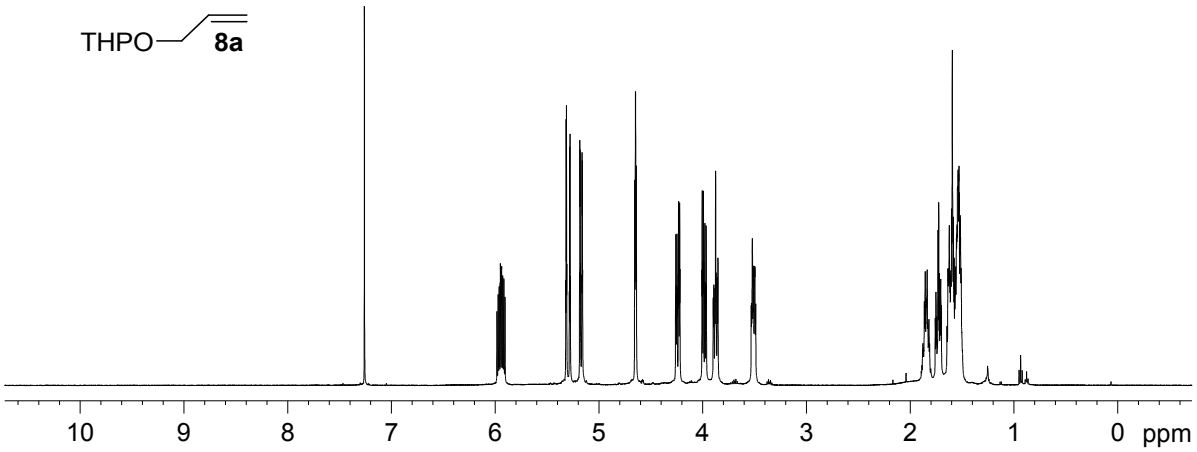
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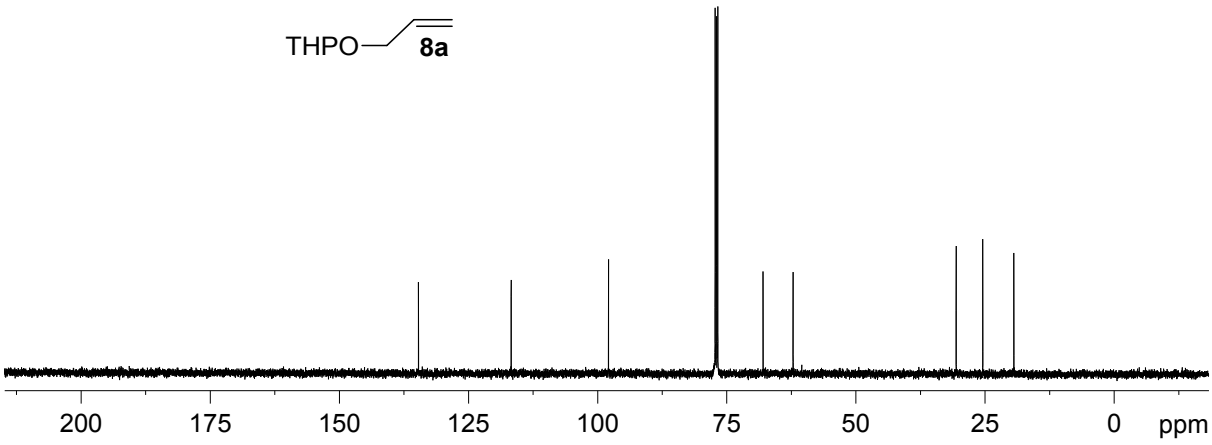
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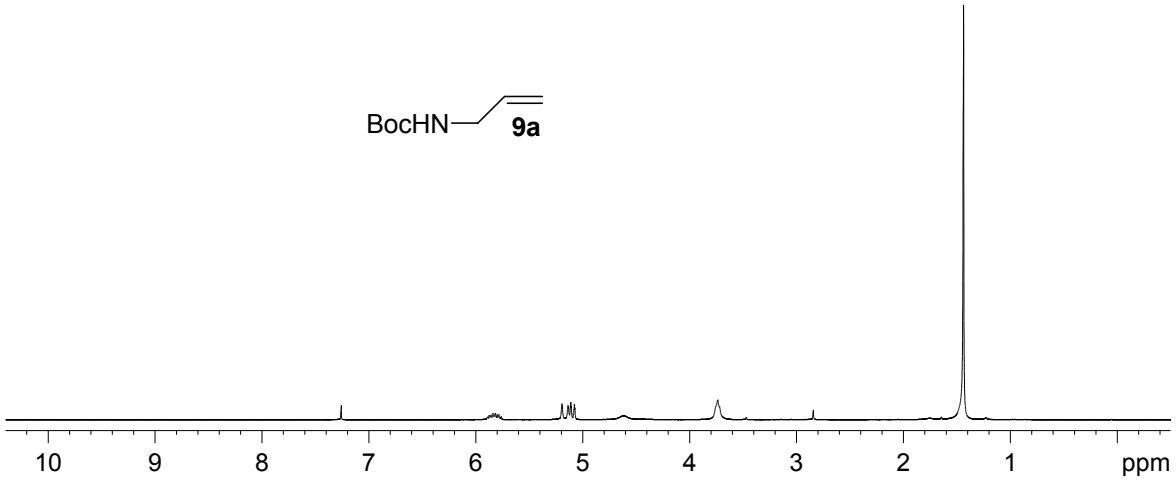
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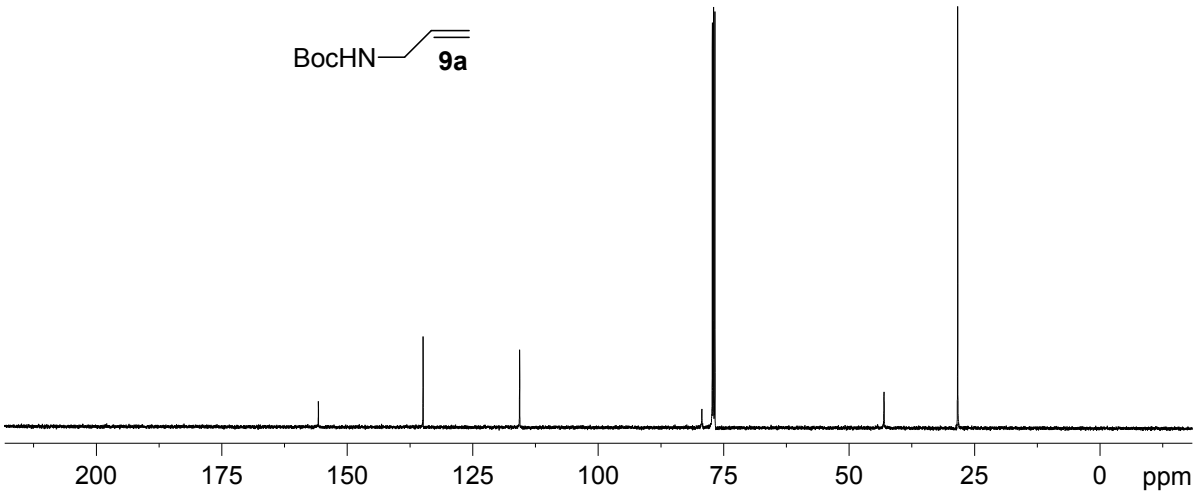
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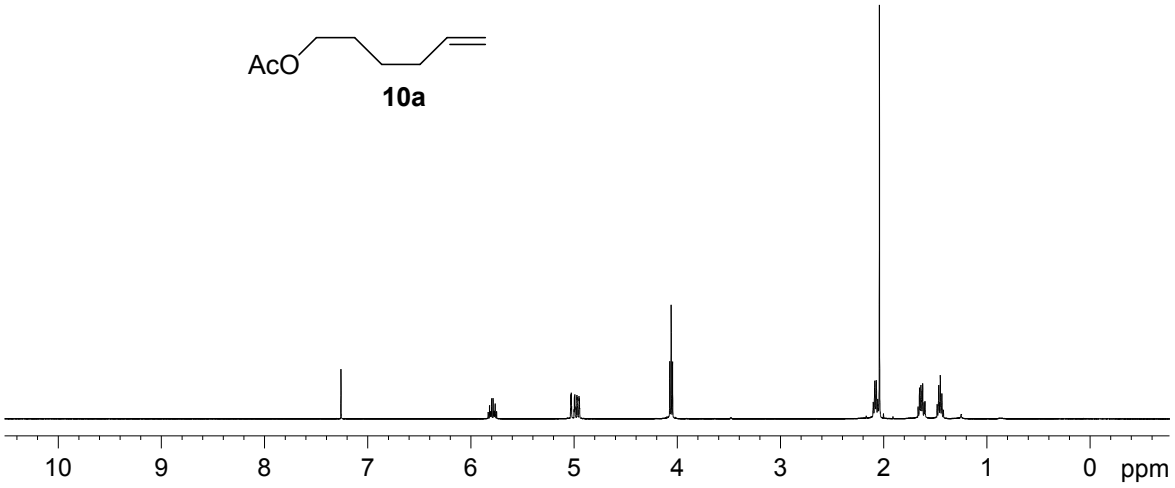
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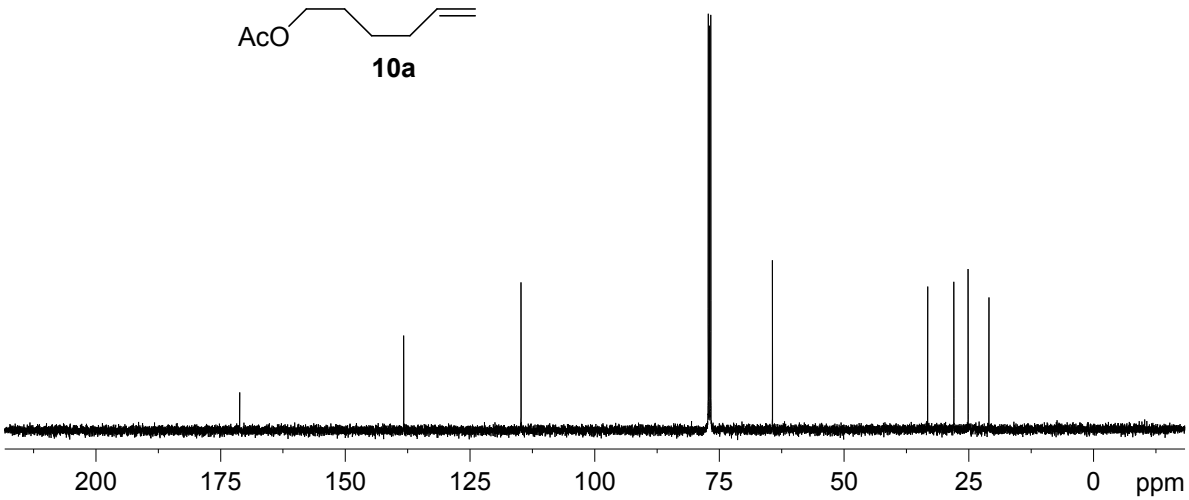
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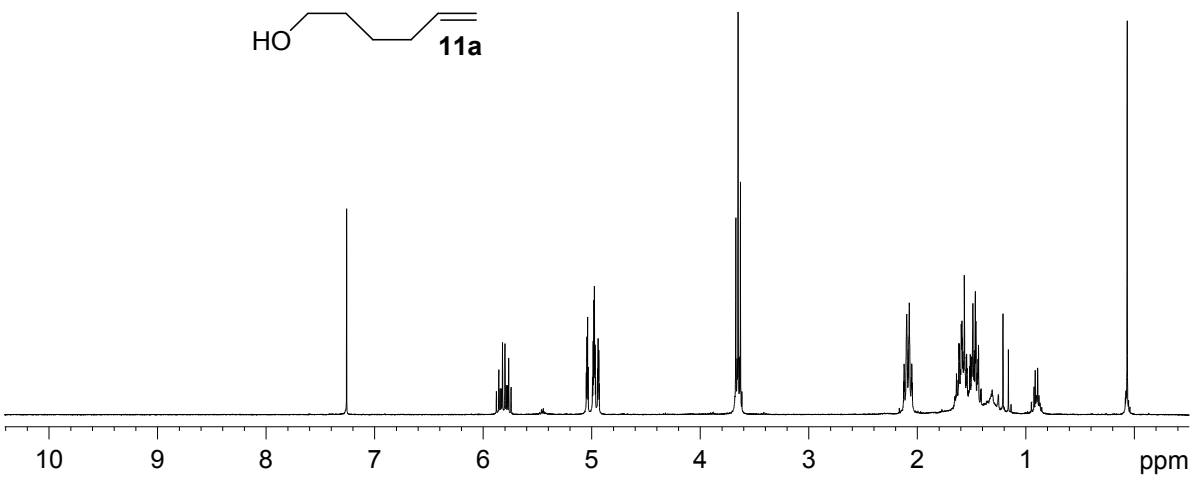
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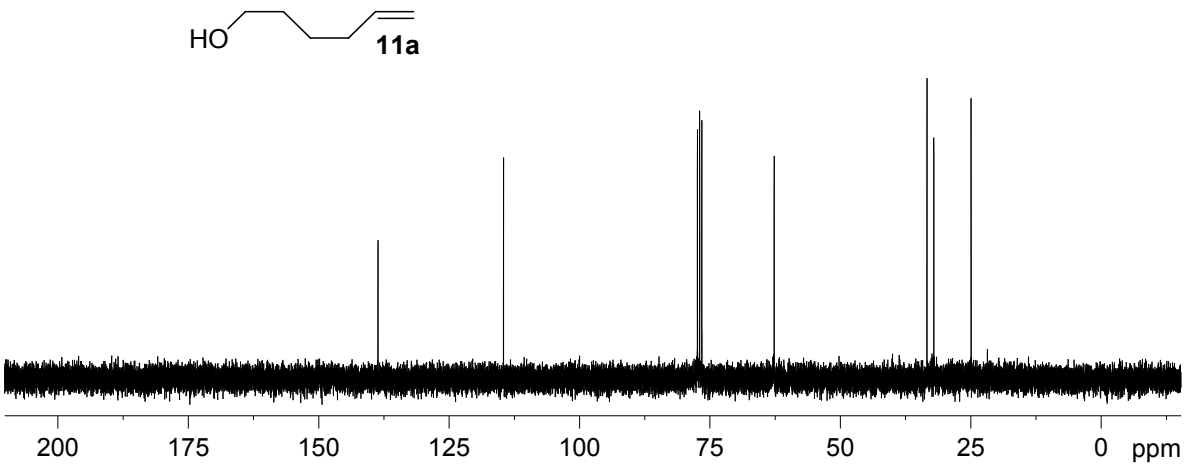
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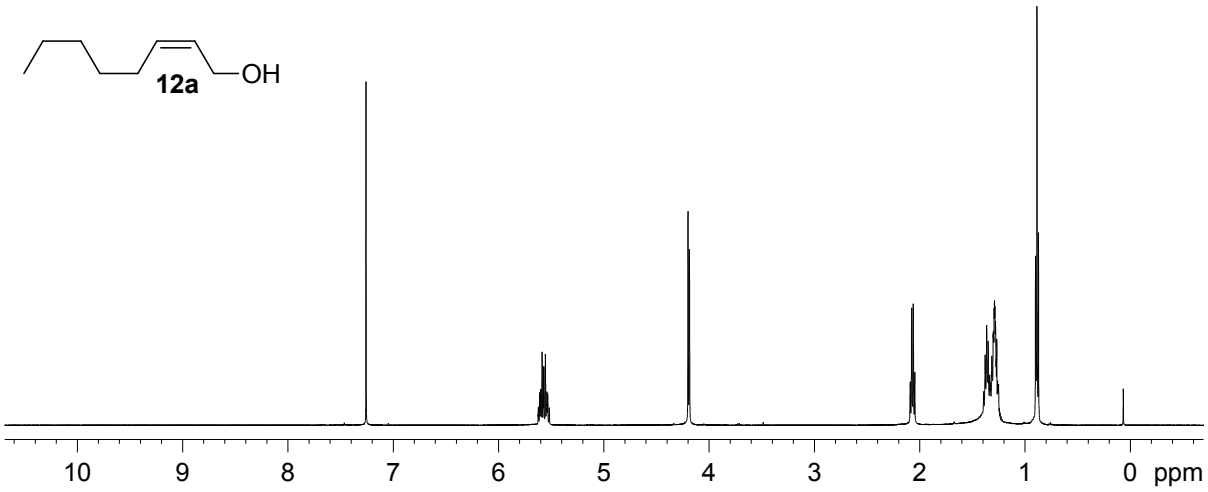
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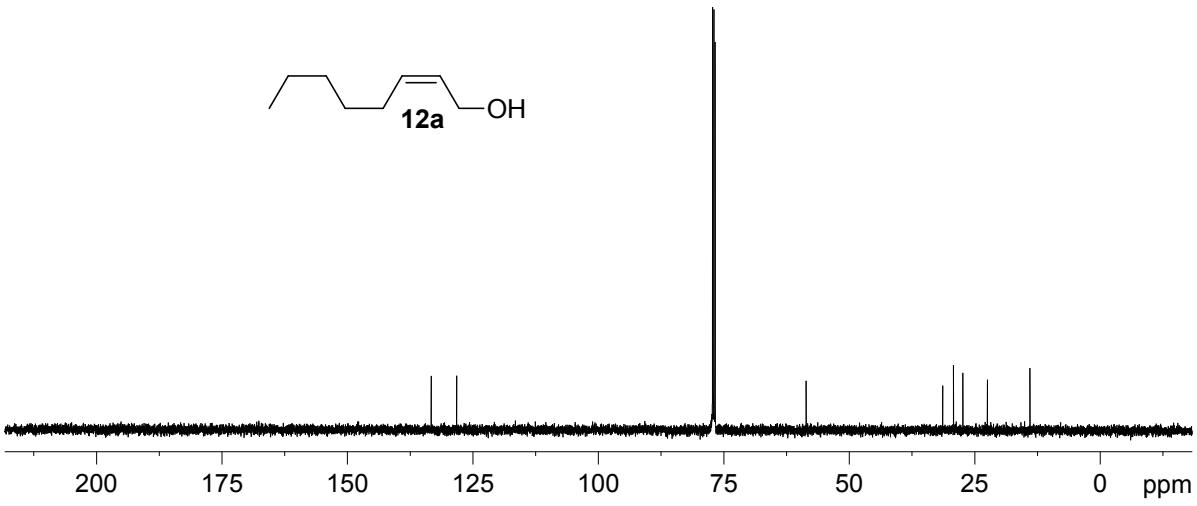
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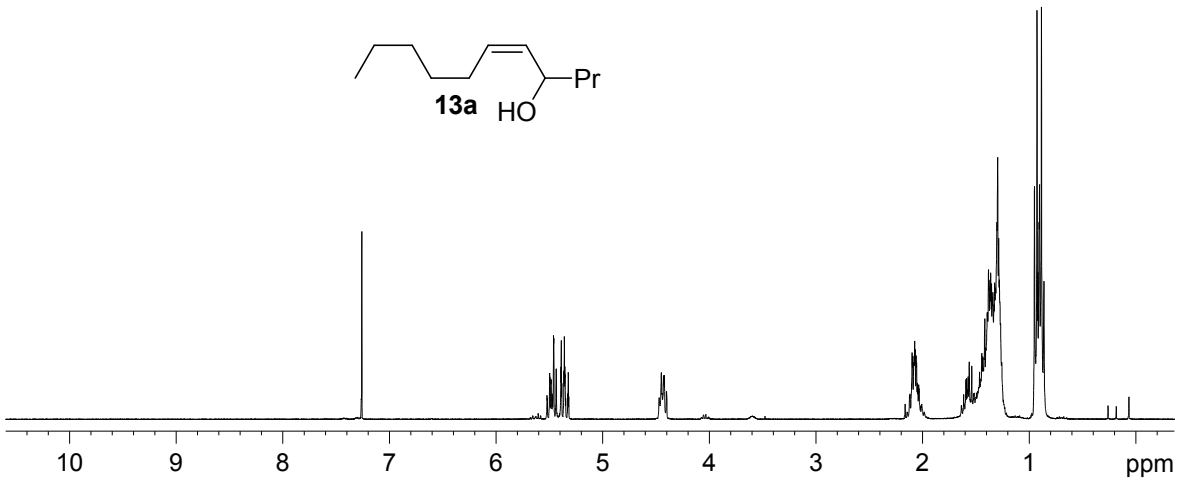
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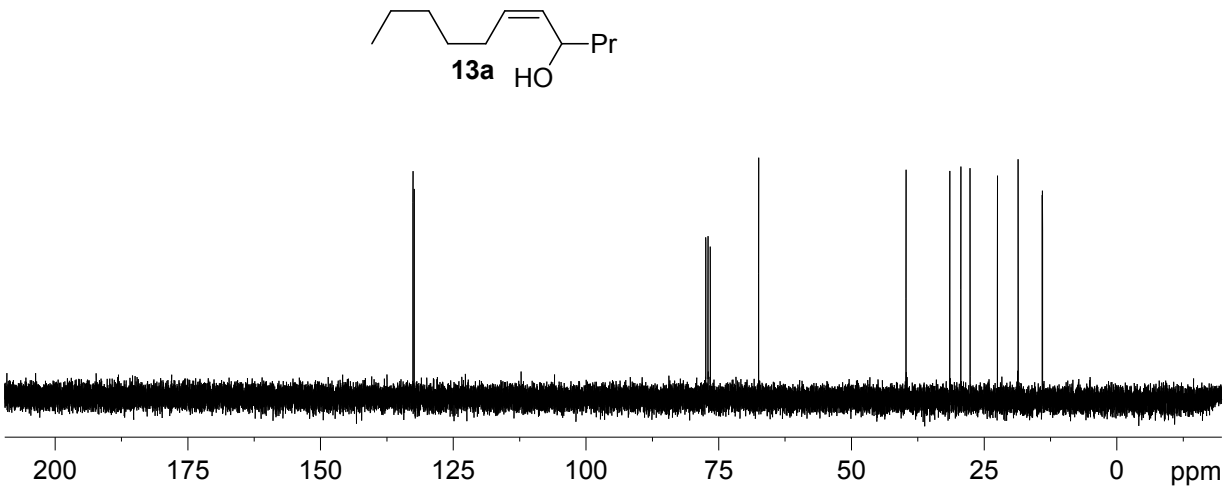
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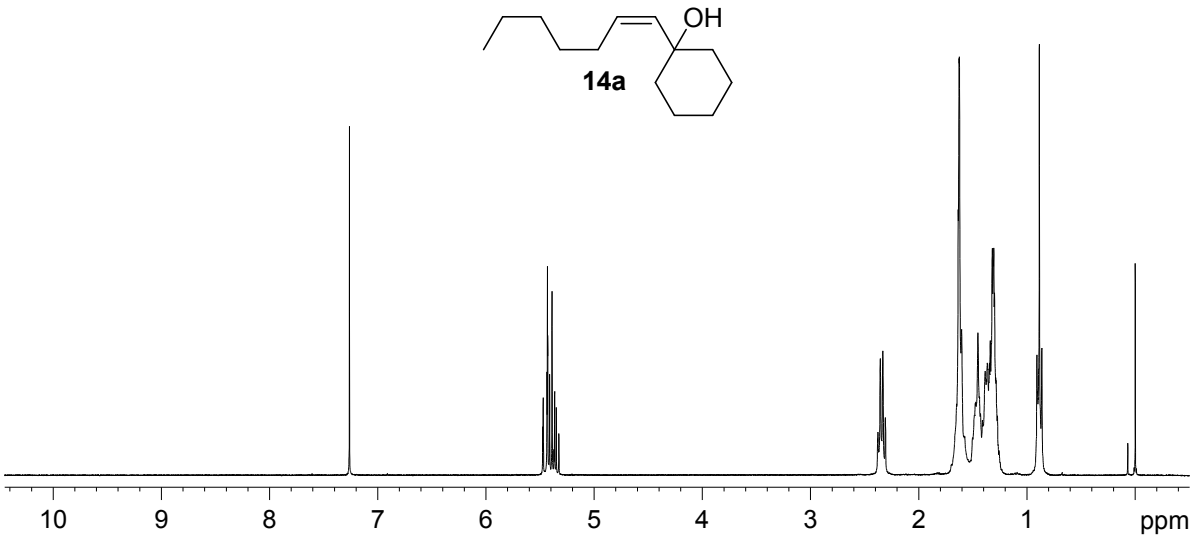
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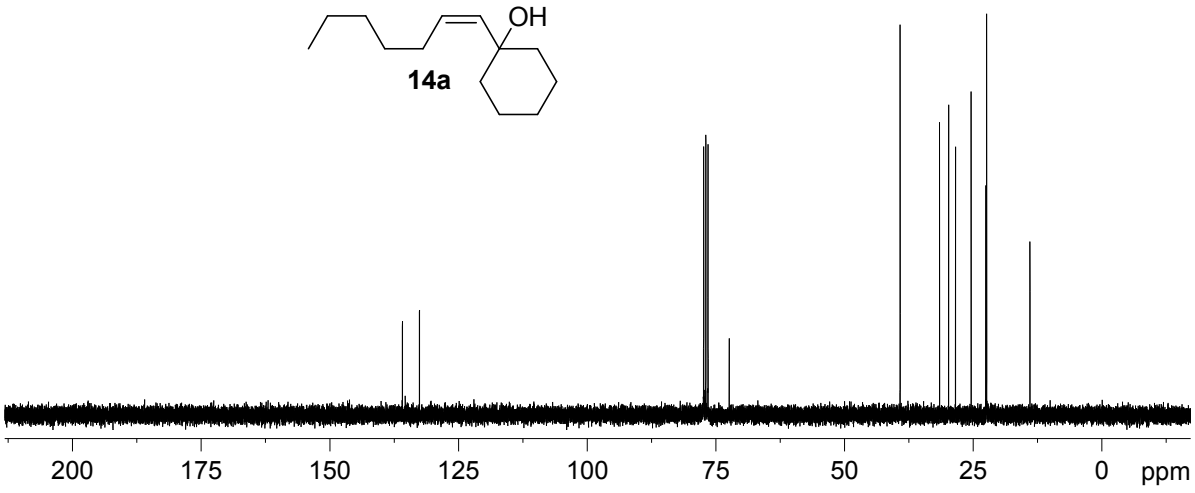
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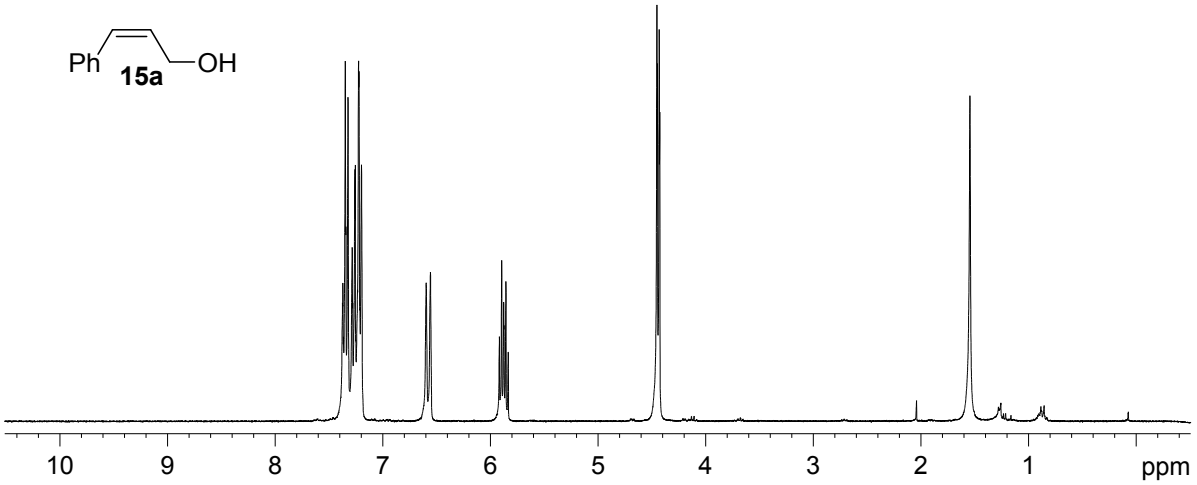
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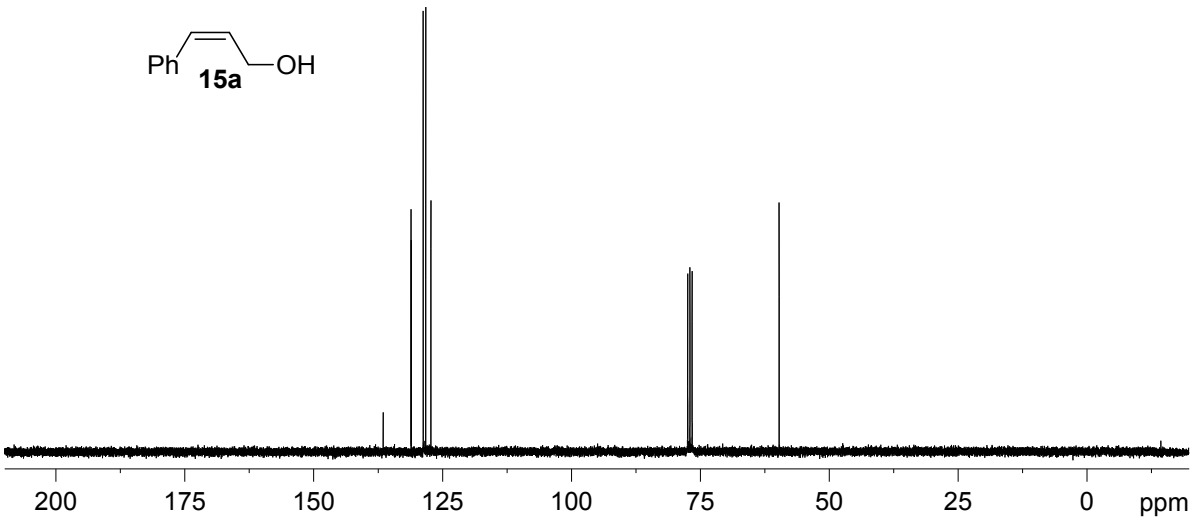
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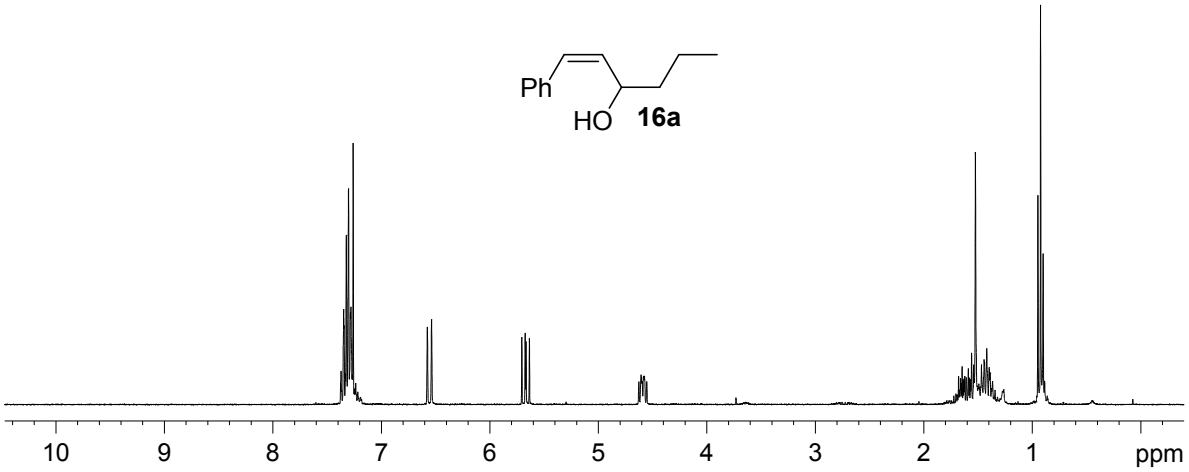
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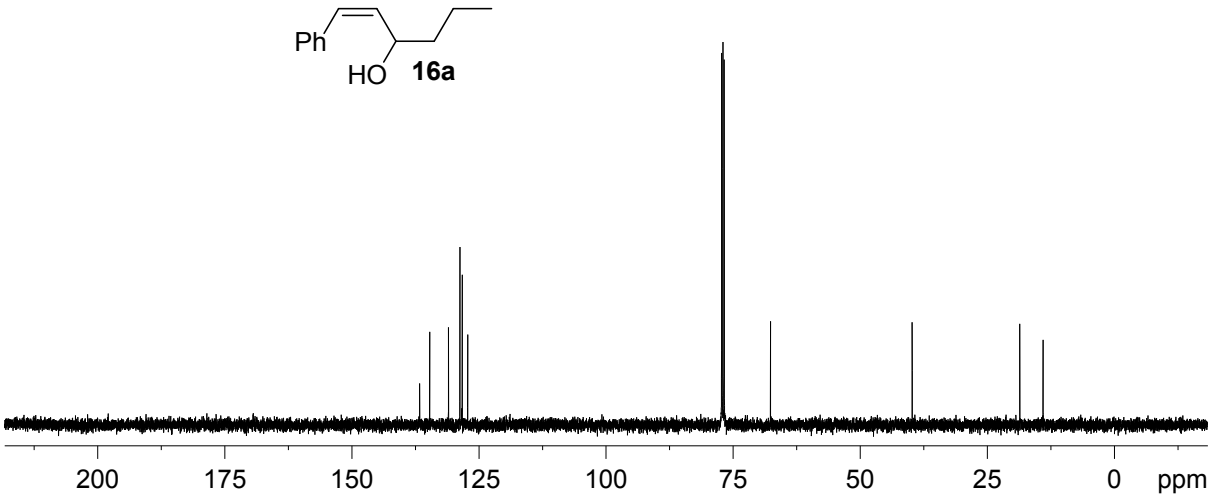
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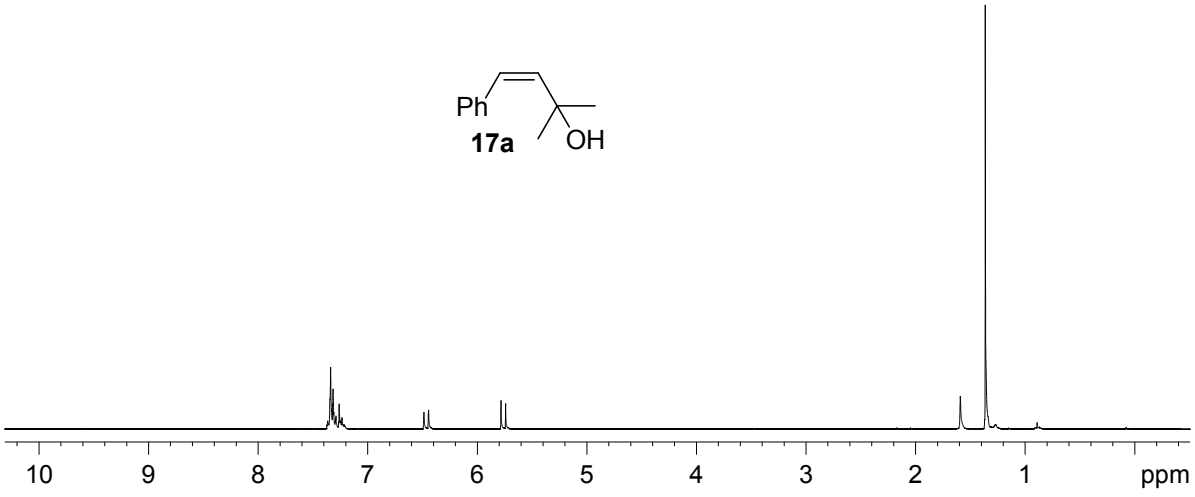
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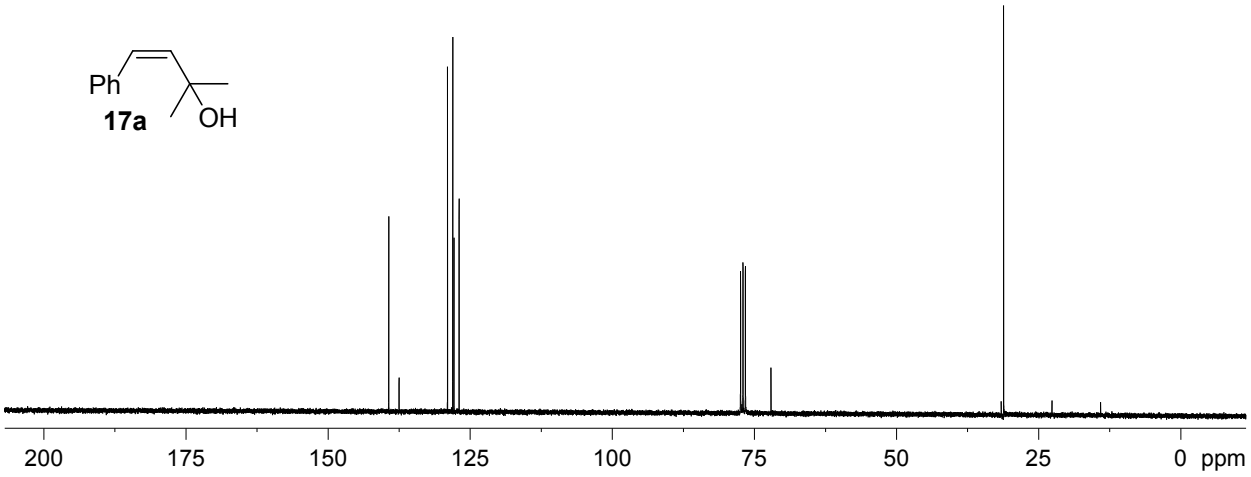
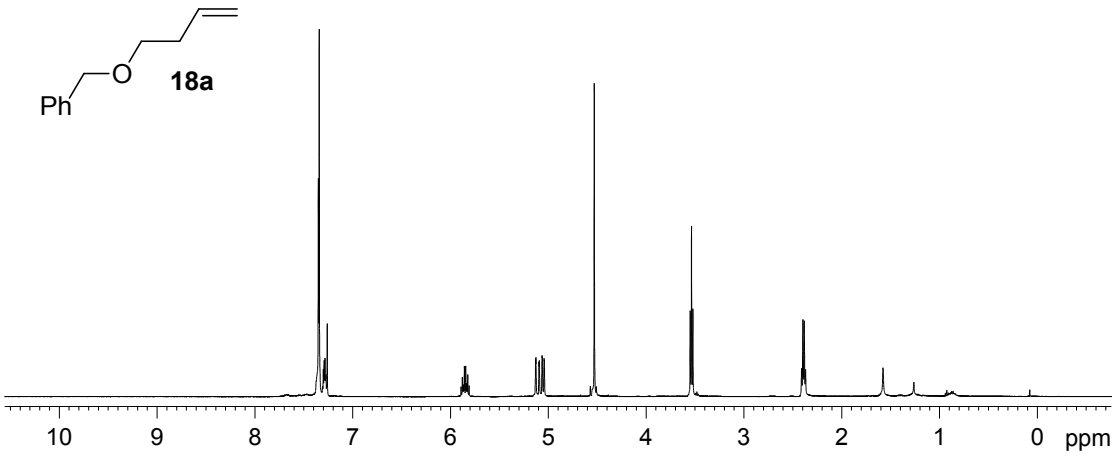
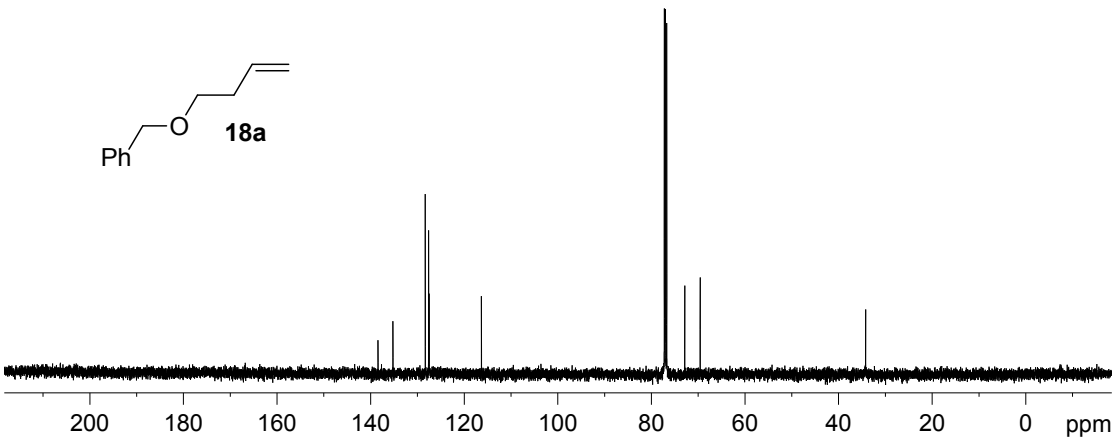
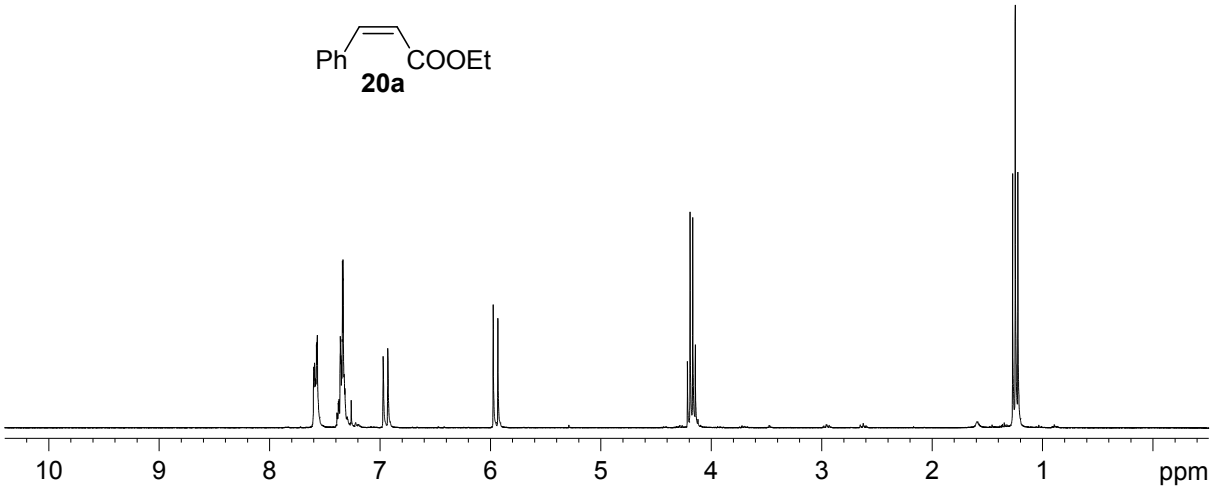
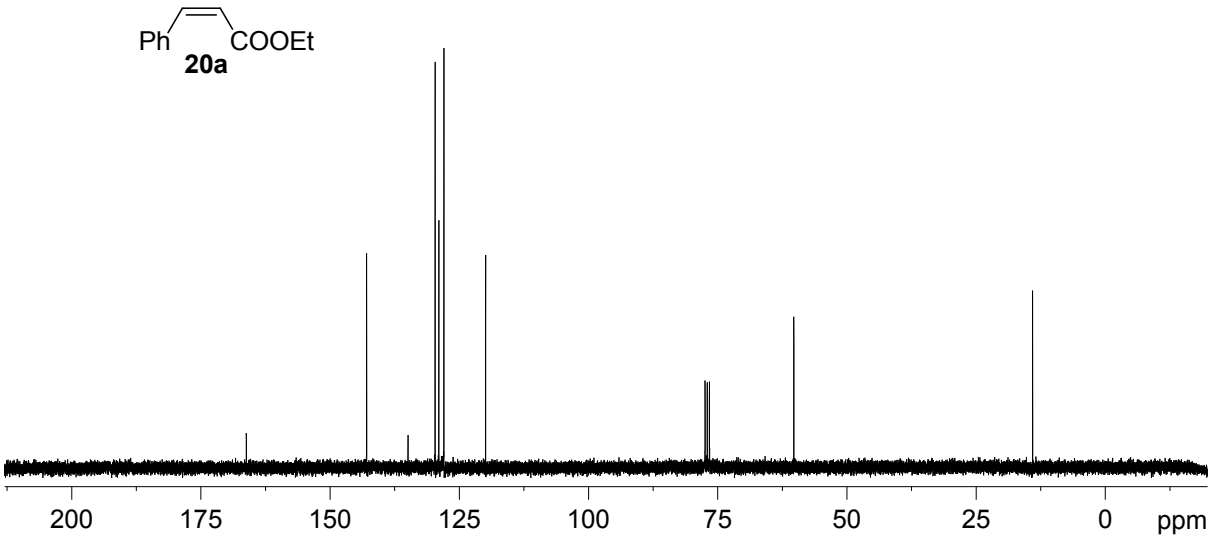
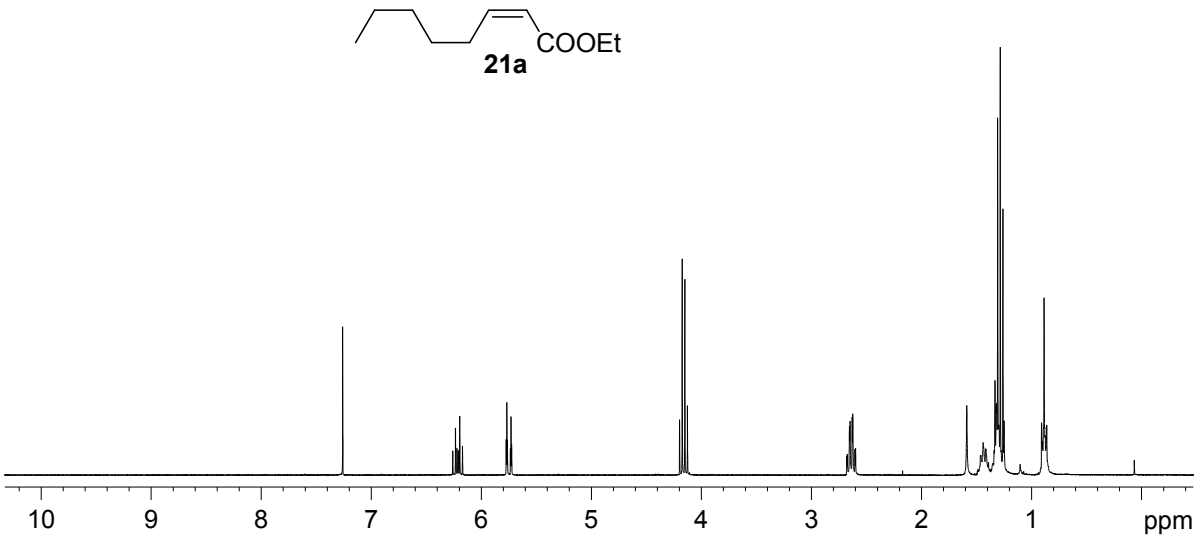

Ph
OH
17a
200
175
150
125
100
75
50
25
0 ppm

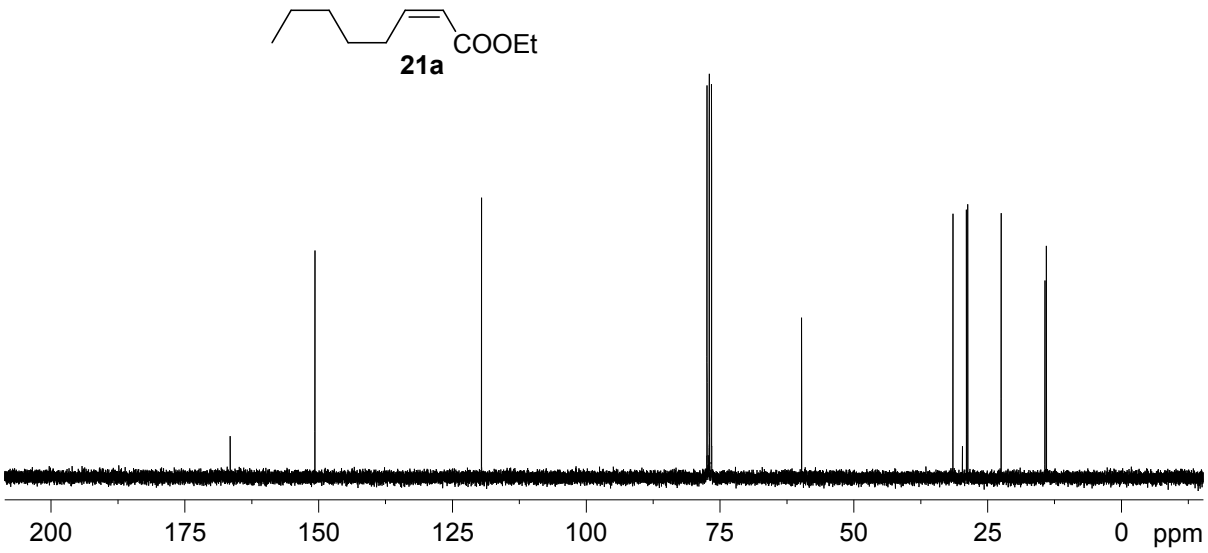

Ph
O
18a
10
9
8
7
6
5
4
3
2
1
0
ppm

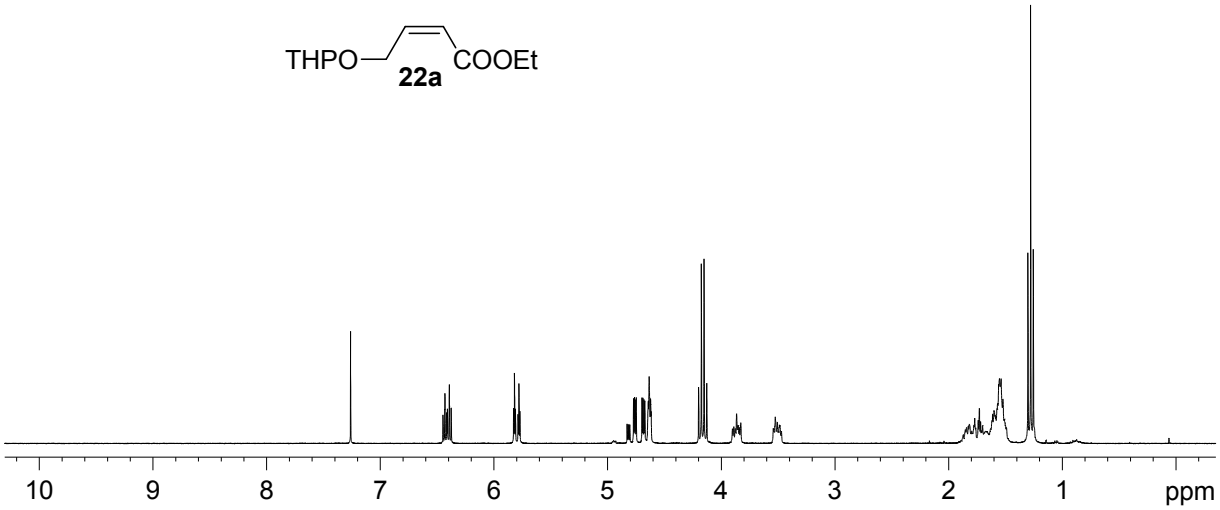

Ph
O
18a
200
180
160
140
120
100
80
60
40
20
0
ppm

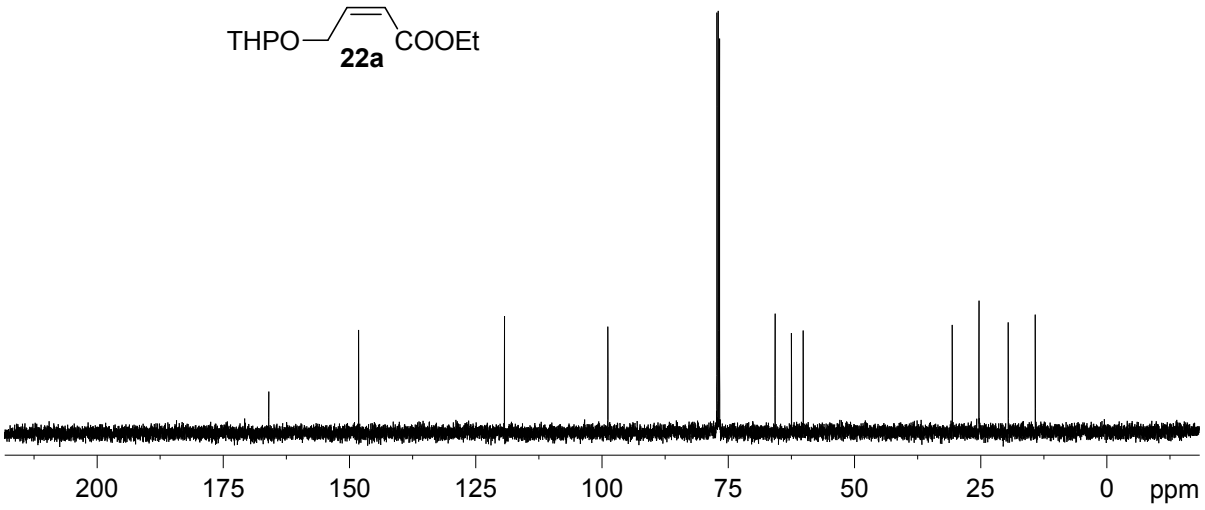

Ph
COOEt
20a
10
9
8
7
6
5
4
3
2
1
ppm

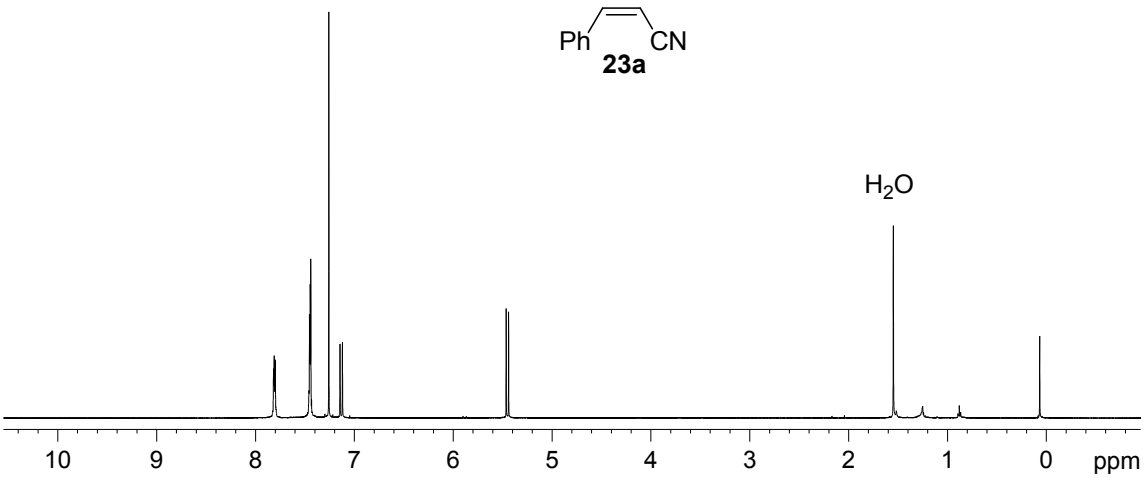

Ph
COOEt
20a
200
175
150
125
100
75
50
25
0
ppm

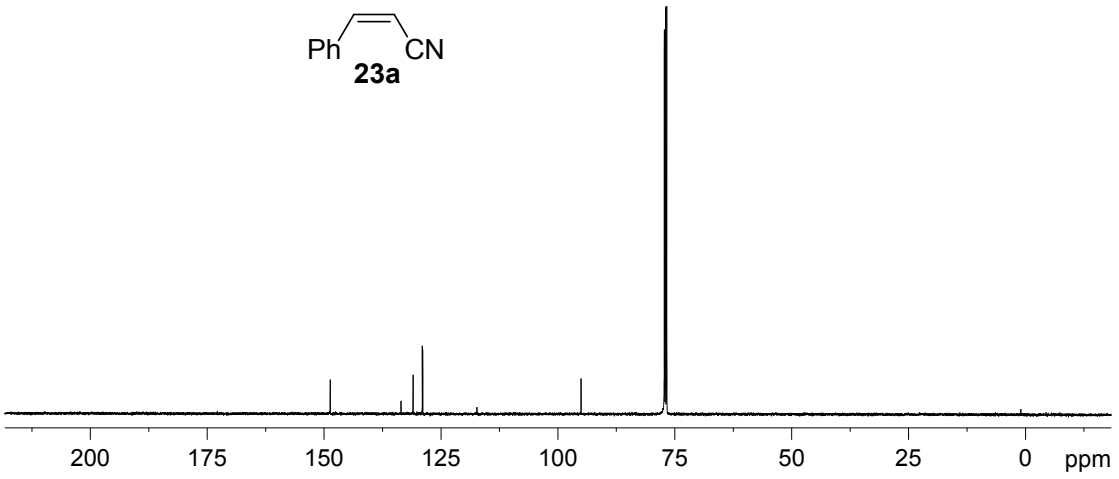

COOEt
21a
10
9
8
7
6
5
4
3
2
1
ppm

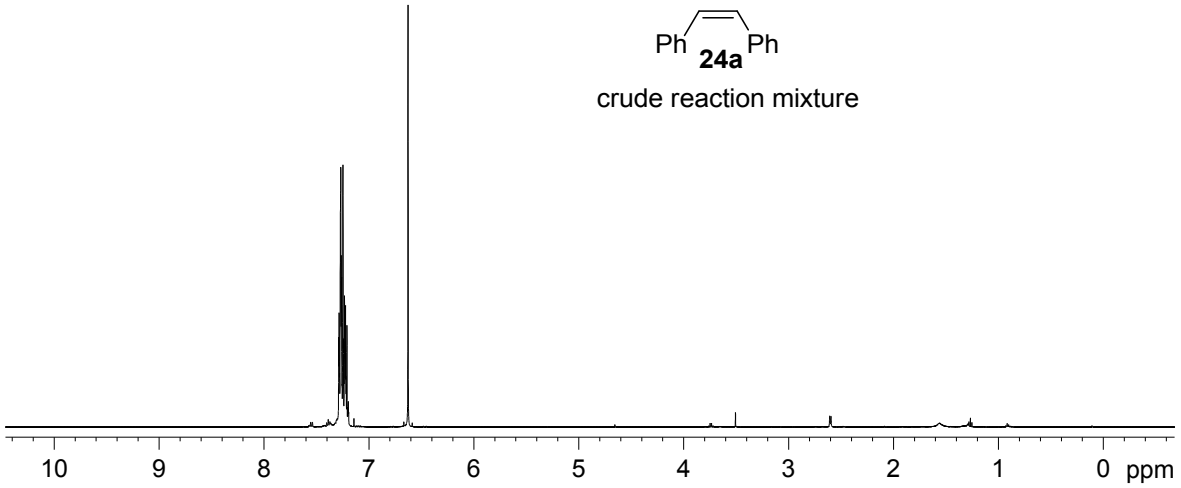

COOEt
21a
200
175
150
125
100
75
50
25
0
ppm

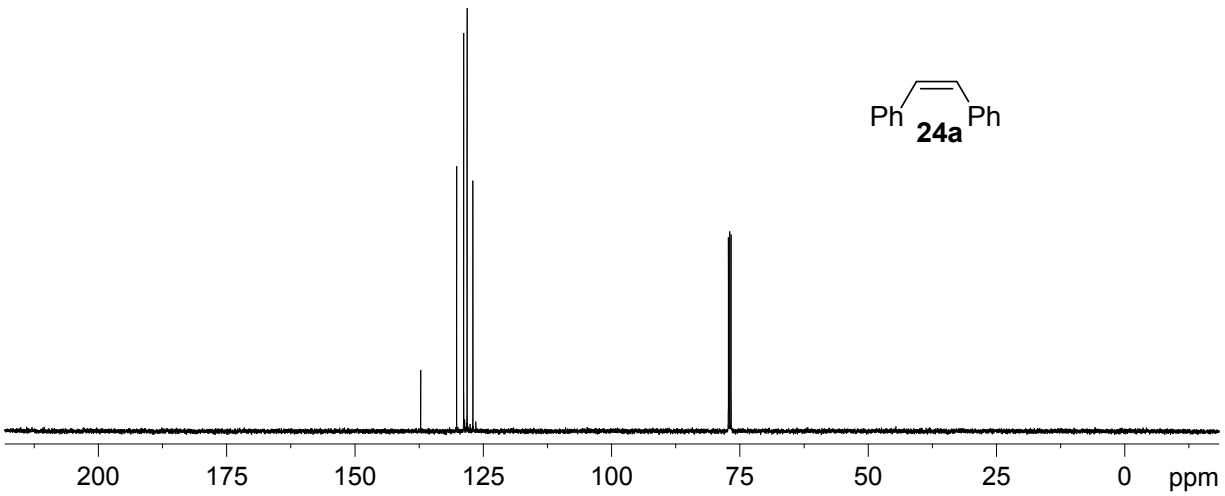

THPO
COOEt
22a
10
9
8
7
6
5
4
3
2
1
ppm

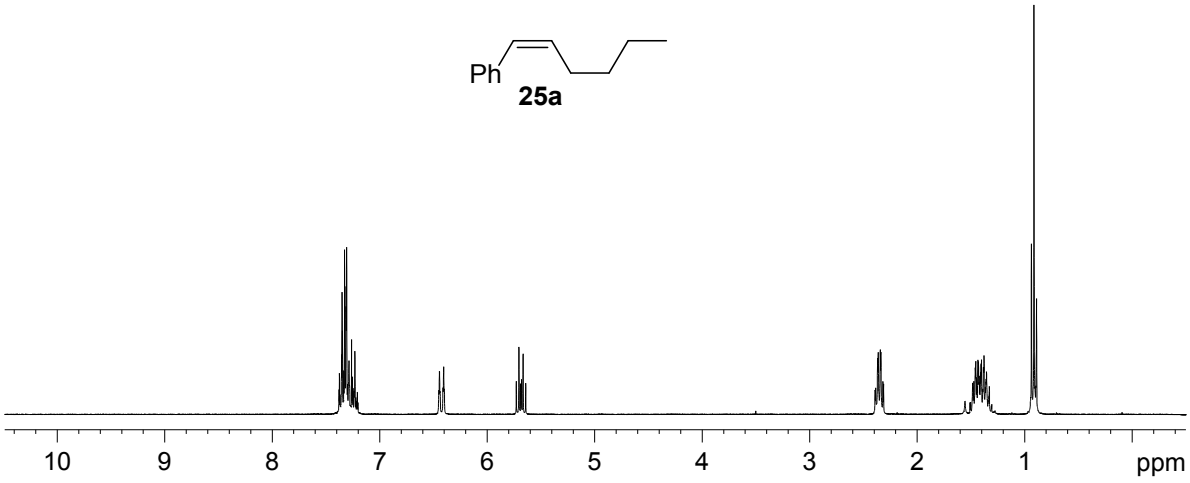

THPO
COOEt
22a
200
175
150
125
100
75
50
25
0
ppm

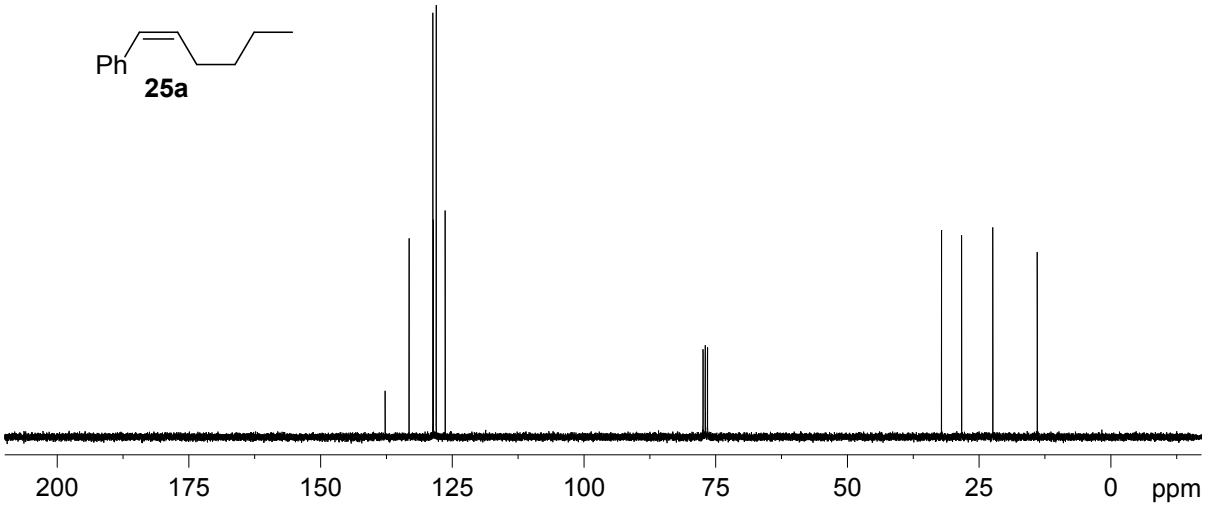

Ph
CN
23a
H2O
10
9
8
7
6
5
4
3
2
1
0
ppm

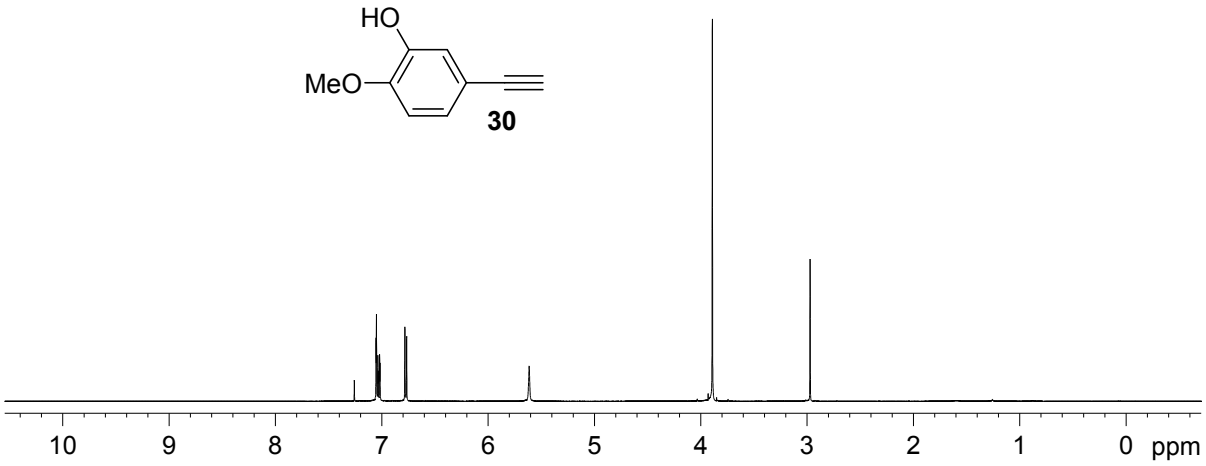

Ph
CN
23a
200
175
150
125
100
75
50
25
0
ppm

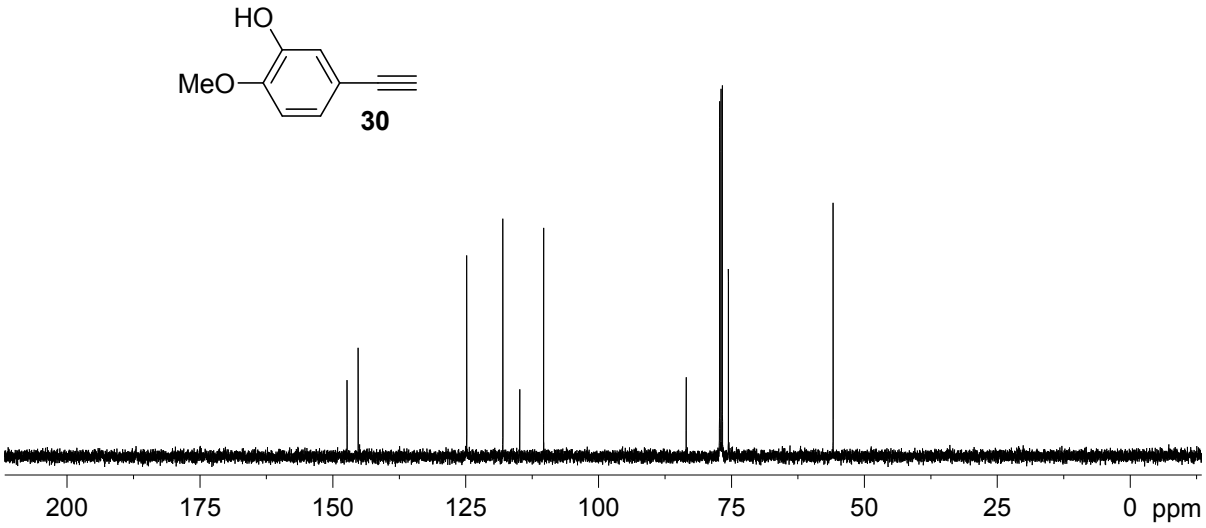

Ph
24a
Ph
crude reaction mixture
10
9
8
7
6
5
4
3
2
1
0
ppm

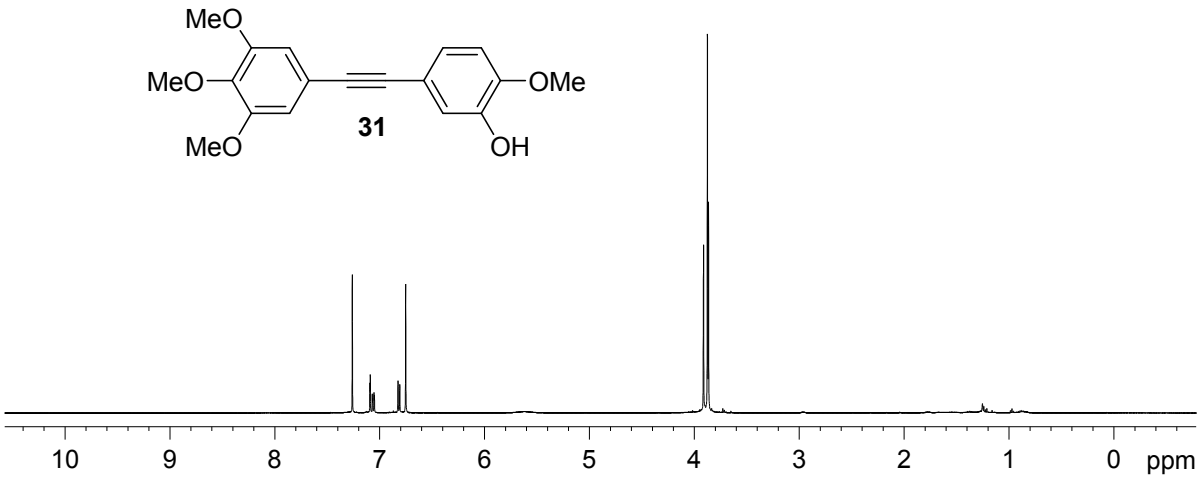

Ph
24a
Ph
200
175
150
125
100
75
50
25
0
ppm

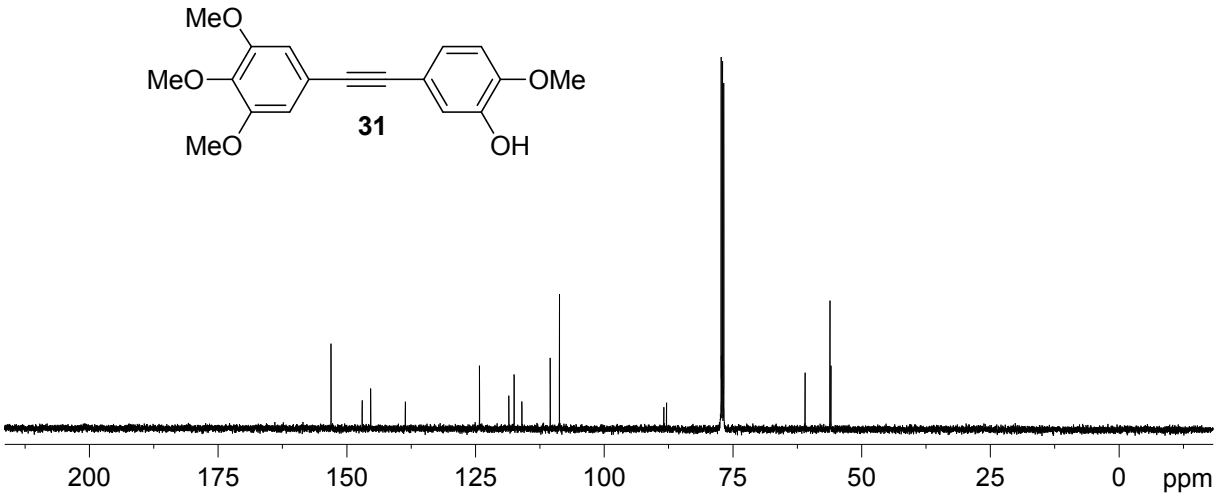

Ph
25a
10
9
8
7
6
5
4
3
2
1
ppm

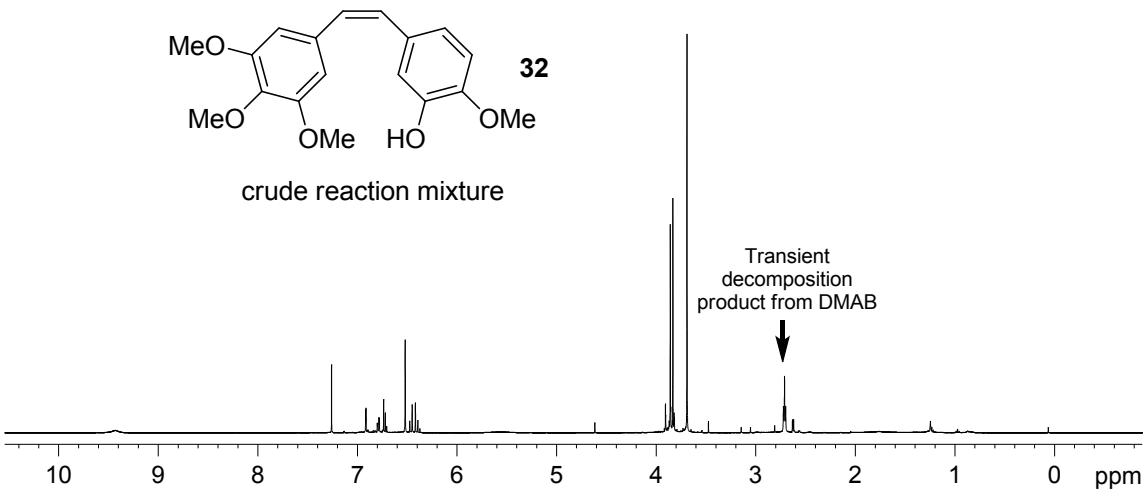

Ph
25a
200
175
150
125
100
75
50
25
0
ppm

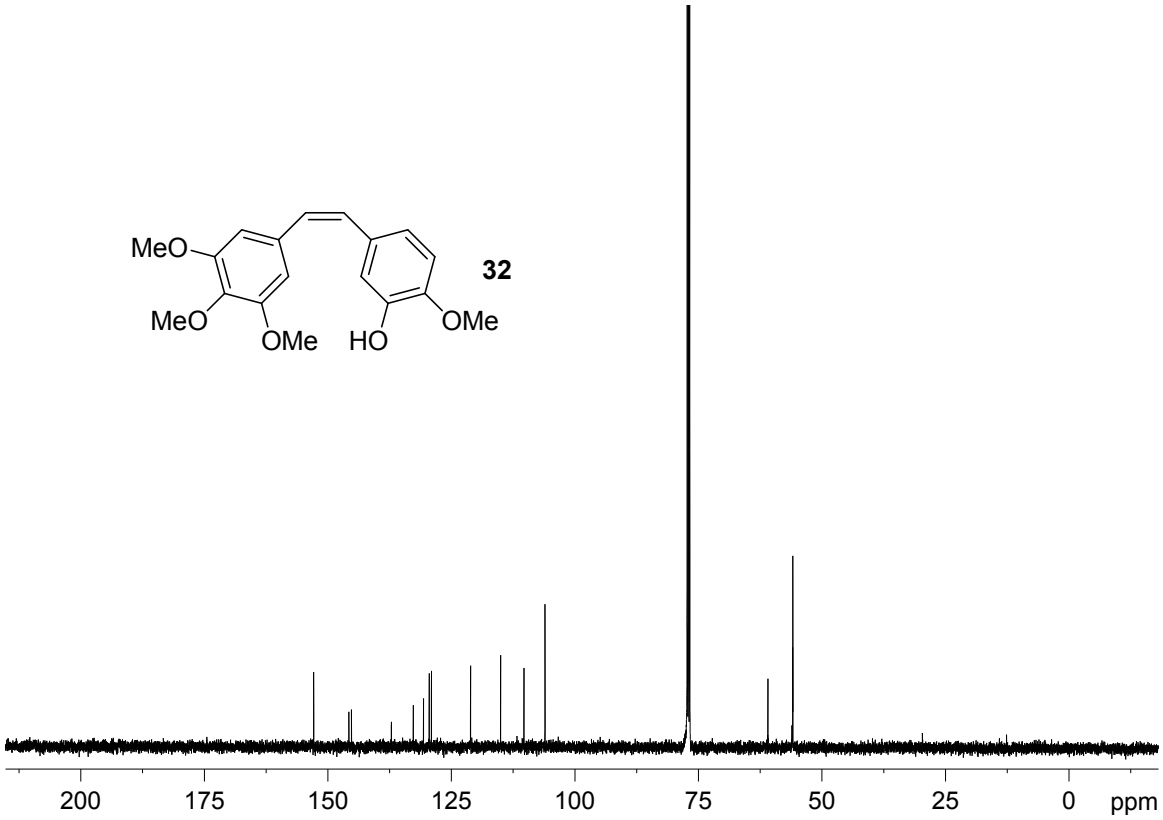

HO
MeO
30
10
9
8
7
6
5
4
3
2
1
0
ppm


HO
MeO
30
200
175
150
125
100
75
50
25
0
ppm

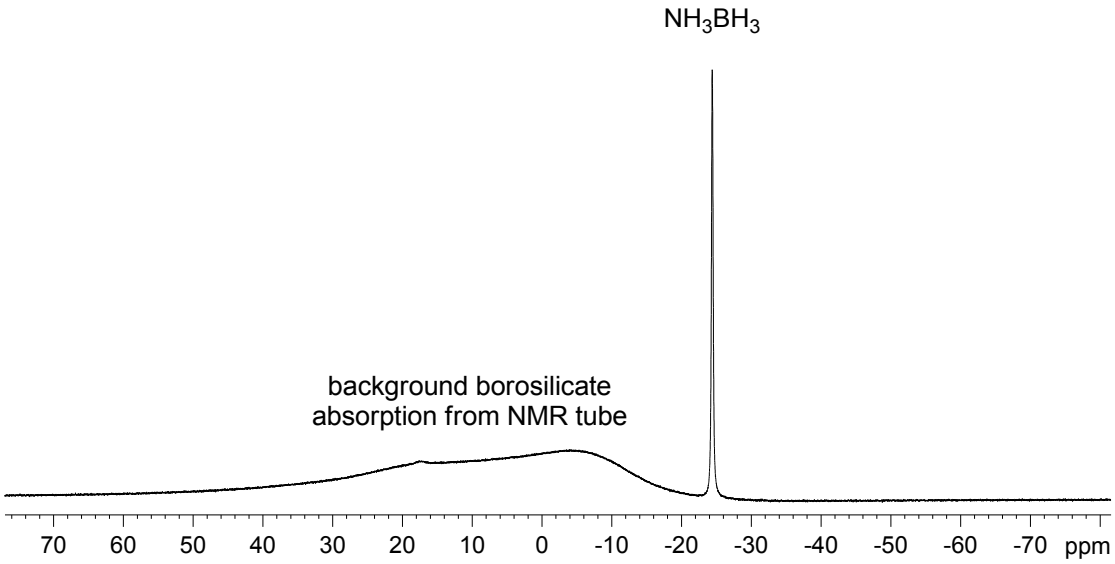

MeO
MeO
MeO
OMe
OH
31
10
9
8
7
6
5
4
3
2
1
0
ppm

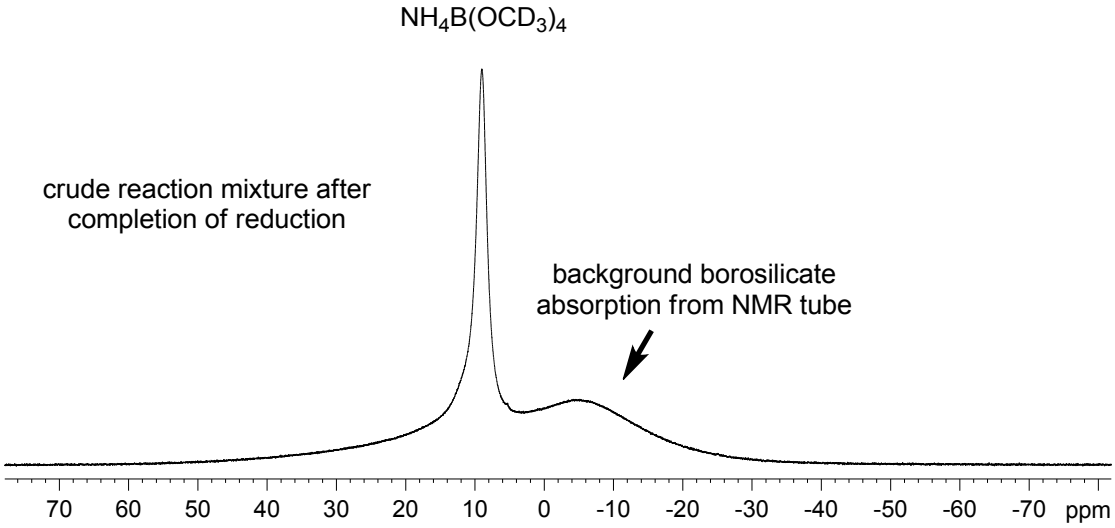

MeO
MeO
MeO
OMe
OH
31
200
175
150
125
100
75
50
25
0
ppm

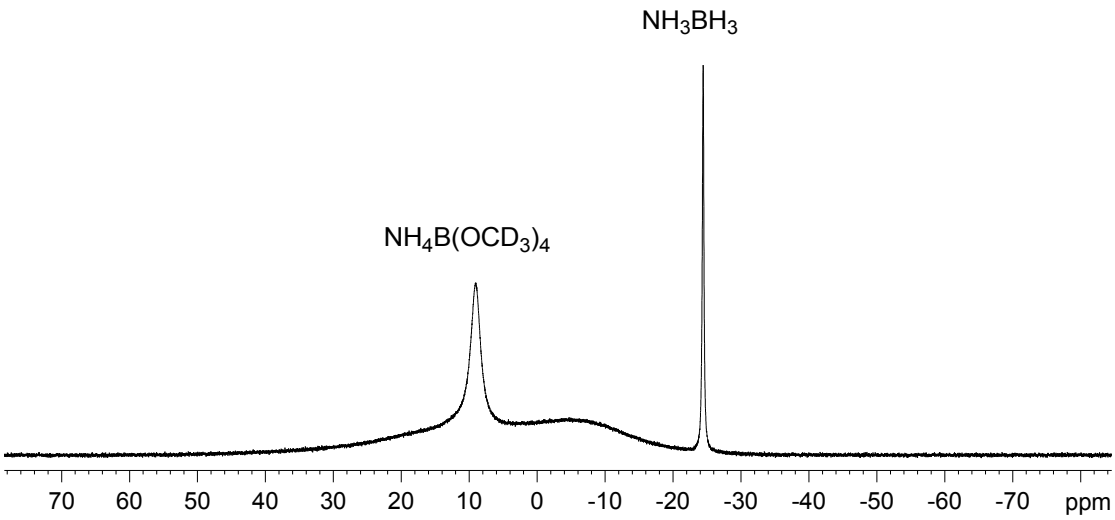

MeO
MeO
OMe
HO
OMe
32
crude reaction mixture
Transient
decomposition
product from DMAB
10
9
8
7
6
5
4
3
2
1
0
ppm


MeO
MeO
OMe
HO
OMe
32
200
175
150
125
100
75
50
25
0
ppm

^{11}B NMR spectra in CD_3OD







^{11}B NMR during the progress of reaction (~50% conversion) showing $NH_4B(OCD_3)_4$ and reacting NH_3BH_3.