Supporting Information for: Operationally Simple and Highly *(E)*-Styrenyl-Selective Heck Reactions of Electronically Non-Biased Olefins

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General Considerations:

Dry dimethylacetamide (DMA) was purchased from Aldrich and stored over activated 3 Å molecular sieves (3 Å MS). Terminal olefins were purchased from Aldrich, TCI or Acros, or synthesized according to the procedures referenced. Aniline precursors to aryldiazonium tetrafluoroborates were purchases from Aldrich. Palladium(II) chloride was purchased from Pressure Chemicals. (*S*)-1-octene-3-ol was purchased from Fluka. Pd_2dba_3 was synthesized according to the literature procedure.[1] I^{i}Pr carbene was synthesized according to the literature procedure.[2] ^{1}H-NMR spectra were obtained at 300 MHz or 400 MHz, chemical shifts are reported in ppm, and referenced to the $CHCl_3$ singlet at 7.26 ppm. ^{13}C-NMR spectra were obtained at 75 MHz or 100 MHz and referenced to the center peak of the $CDCl_3$ triplet at 77.23 ppm. The abbreviations s, d, t, quint, dd, dt, m stand for the resonance multiplicities singlet, doublet, triplet, quintet, doublet of doublets, doublet of triplets and multiplet, respectively. Thin-layer chromatography was performed with EMD silica gel 60 F254 plates eluting with solvents

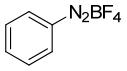
indicated, visualized by a 254 nm UV lamp and stained with phosphomolybdic acid. Flash chromatography was performed using EM reagent silica 60 (230-400 mesh). IR spectra were recorded using a Thermo Nicolet FT-IR. HRMS data were obtained on a Waters LCP Premier XE instrument by ESI/TOF. Achiral GC (gas chromatography) was performed using a Hewlett Packard HP 6890 series GC system fitted with an Agilent HP-5 column. Chiral GC analysis was performed using a Hewlett Packard HP 6890 Series CG system fitted with a HP-Chiral permethylated β-cyclodextrin column. SFC (supercritical fluid chromatography) analysis was performed at 40 ºC, using a Thar instrument fitted with an AD-H column. ***It should be noted that while no incident occurred during this study, aryldiazonium salts can be explosive.*** It is also important to note that these reactions should be monitored carefully, as the products decompose under the reaction conditions.

Synthesis of alkene substrates

tert-Butyldimethyl((1-phenylbut-3-en-1-yl)oxy)silane (**1c**),[3] 1-phenylbut-3-en-1-ol (**1d**),[3] oct-1-en-3-yl acetate (**1e**),[4] and 4-vinylphenol (**1n**)[5] were prepared following literature procedures and purity confirmed via ^{1}H NMR. (N-Cbz-N-Boc) allylamine (**1f**) was prepared following the literature procedure,[6] and its purity confirmed via ^{1}H NMR.[7] (*S*)-1-Octene-3-ol was converted to **1e** using the same procedure as that used to synthesize racemic **1a**. The enantiomeric excess of **1e** was determined by GC equipped with a chiral column (see below).

Synthesis of aryldiazonium tetrafluoroborate salts

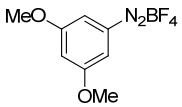
Benzenediazonium tetrafluoroborate (4a)



4a

Benzenediazonium salt **4a** was synthesized according to a previously reported procedure[8] and the ^{1}H NMR spectrum was compared to the previously reported spectrum.[9]

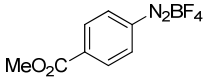
3,5-Dimethoxybenzenediazonium tetrafluoroborate (4b)



4b

Aryldiazonium salt **4b** was synthesized according to a previously reported procedure[8] and the ^{1}H NMR spectrum was compared to the previously reported spectrum.[10]

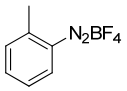
4-Methoxycarbonylbenzenediazonium tetrafluoroborate (4c)



4c

Aryldiazonium salt **4c** was synthesized according to a previously reported procedure[8] and the ^{1}H NMR spectrum was compared to the previously reported spectrum.[11]

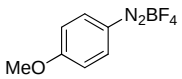
2-Methylbenzenediazonium tetrafluoroborate (4d)



4d

Aryldiazonium salt **4d** was synthesized according to a previously reported procedure[8] and the ^{1}H NMR spectrum was compared to the previously reported spectrum.[12]

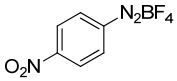
4-Methoxybenzenediazonium tetrafluoroborate (4e)



4e

Aryldiazonium salt **4e** was synthesized according to a previously reported procedure[8] and the ^{1}H NMR spectrum was compared to the previously reported spectrum.[11]

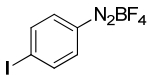
4-Nitrobenzenediazonium tetrafluoroborate (4f)



4f

Aryldiazonium salt **4f** was synthesized according to a previously reported procedure[8] and the ^{1}H NMR spectrum was compared to the previously reported spectrum.[9]

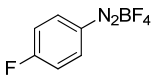
4-Iodobenzenediazonium tetrafluoroborate (4g)



4g

Aryldiazonium salt **4g** was synthesized according to a previously reported procedure[8] and the ^{1}H NMR spectrum was compared to the previously reported spectrum.[13]

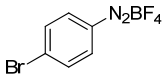
4-Fluorobenzenediazonium tetrafluoroborate (4h)



4h

Aryldiazonium salt **4h** was synthesized according to a previously reported procedure[8] and the ^{1}H NMR spectrum was compared to the previously reported spectrum.[11]

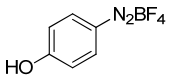
4-Bromobenzenediazonium tetrafluoroborate (4i)



4i

Aryldiazonium salt **4i** was synthesized according to a previously reported procedure[8] and the ^{1}H NMR spectrum was compared to the previously reported spectrum.[13]

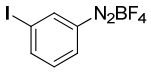
4-Hydroxybenzenediazonium tetrafluoroborate (4i)



4j

Aryldiazonium salt **4j** was synthesized according to a previously reported procedure[14] and the ^{1}H NMR spectrum was compared to the previously reported spectrum.[14]

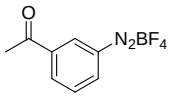
3-Iodobenzenediazonium tetrafluoroborate (4k)



4k

Aryldiazonium salt **4k** was synthesized according to a previously reported procedure[8] and the ^{1}H NMR spectrum was compared to the previously reported spectrum.[15]

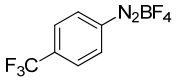
3-Acetylbenzenediazonium tetrafluoroborate (4l)



4l

Aryldiazonium salt **4l** was synthesized according to a previously reported procedure[8] and the ^{1}H NMR spectrum was compared to the previously reported spectrum.[16]

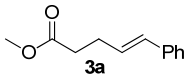
4-Trifluoromethylbenzenediazonium tetrafluoroborate (4m)



4m

Aryldiazonium salt **4m** was synthesized according to a previously reported procedure[8] and the ^{1}H NMR spectrum was compared to the previously reported spectrum.[17]

Procedure for the synthesis of (*E*)-methyl 6-phenylhex-5-enoate (3a) under initial conditions (Table 1 entry 1).



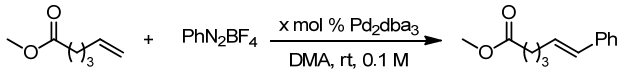
3a

In the dry box, an oven dried 25 mL round bottomed flask equipped with a stir bar was charged with 58 mg benzenediazonium tetrafluoroborate (**4a**) (0.3 mmol, 1.5 equiv). To a separate vial equipped with a stir bar was added 9 mg Pd_2dba_3 (0.01 mmol, 0.05 equiv), 10 mg I^iPr carbene (0.03 mmol, 0.125 equiv) and 1 mL DMA, and the mixture was stirred for 10 minutes. To a separate vial was added 26 mg methyl hex-5-enoate (**1a**) (0.2 mmol) and 1 mL DMA. To the flask containing **4a** was added the solution containing **1a**, followed quickly by the solution containing Pd_2dba_3 and I^iPr carbene. The flask was fitted with a septum, removed from the dry box, and stirred for 16 hours. The mixture was diluted with 10 mL Et_2O and transferred to a separatory funnel. To this, 15 mL of distilled water was added, and the aqueous layer was extracted twice with 10 mL Et_2O. The combined organic extracts were washed three times with 15 mL distilled water then 15 mL brine followed by drying over Na_2SO_4. The mixture was filtered and the solvent was removed in vacuo. This material was purified by silica gel flash chromatography eluting with 1% acetone in hexanes and a mixture containing **3a** and decomposition products was obtained.

Optimization of the Heck reaction.

The procedure for the preparation of **3a** described above was used with the following modifications. The reaction was performed using ~10 wt% (to **1a**) tetradecane as an internal standard. After either 16 h or 15 minutes (see Table 2) aliquots (~50 mL) were taken, passed through a small silica pipet with ether, and analyzed for conversion, product formation, and selectivity by gas chromatography. The modifications described below were applied in order to optimize the reaction.

Modifications:



1a **4a** (y equiv) **3a**

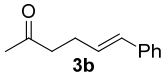
entry	x	y	time	% conversion[a]	% yield[a]	selectivity[a,b]
1[c]	5	1.5	16 h	>99	68.4	3.8
2	5	1.5	16 h	>99	43.3	6.8
3	5	1.5	15 min	>99	62.6	7.1
4	3	1.5	15 min	>99	86.2	7.5
5	3	1.1	15 min	>99	>99	10.7
6	0	1.1	15 min	3.6	0	-
7[d]	3	1.1	15 min	>99	20	0.2:1
8[e]	3	1.1	15 min	98.1	15	0.3:1

[a]Conversion and yield calculated by comparing starting material and product peak integration to integration of internal standard using corrected GC analysis. Yields refers to the sum of all product isomers. [b]Selectivity refers to the ratio of (*E*)-styrene to all other isomers. [c]12.5 mol % I^iPr carbene added. [d]MeOH used as solvent. [e]MeCN used as solvent.

General procedure for the preparation of 3a under optimized conditions (Table 2, entry 1).

In the dry box, an oven dried 25 mL round bottomed flask equipped with a stir bar was charged with 106 mg **4a** (0.55 mmol, 1.1 equiv). To a separate vial was added 14 mg Pd_2dba_3 (0.02 mmol, 0.03 equiv) and 3 mL DMA. To a separate vial was added 64 mg **1a** (0.5 mmol) and 2 mL DMA. To the flask containing **4a** was added the solution containing **1a**, followed quickly by the solution containing Pd_2dba_3. The flask was fitted with a septum, removed from the dry box, and stirred for 20 minutes. The mixture was diluted with 20 mL Et_2O and transferred to a separatory funnel. To this, 20 mL of distilled water was added, and the aqueous layer was extracted twice with 20 mL Et_2O. The combined organic extracts were washed three times with 15 mL distilled water then 15 mL brine followed by drying over Na_2SO_4. The mixture was filtered and the solvent was removed *in vacuo*. The product was purified by silica gel flash chromatography eluting with 1% acetone in hexanes and was isolated as a clear oil in 97% yield (97 mg and 101 mg)**.** The ^{1}H NMR spectrum, see below, was compared with the previously reported spectrum.[18]

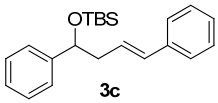
Table 2 entry 2 ((*E*)-6-phenylhex-5-en-2-one) (3b).



3b

The general procedure for the preparation of **3a** was used with the modifications that 49 mg hex-5-en-2-one **1b** (0.50 mmol) and 106 mg **4a** (0.55 mmol, 1.1 equiv) was used, and the mixture was stirred for 20 minutes before workup. The product was purified by silica gel flash chromatography by eluting with 2% acetone in hexanes to give **3b** as a clear oil in 89% yield (77 and 78 mg). The ^{1}H NMR spectrum, see below, was compared with the previously reported spectrum.[18]

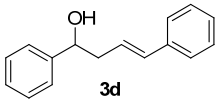
Table 2, entry 3 ((*E*)-*tert*-butyl((1,4-diphenylbut-3-en-1-yl)oxy)dimethylsilane) (3c).



3c

The general procedure for the preparation of **3a** was used with the modifications that 131 mg *tert*-butyldimethyl((1-phenylbut-3-en-1-yl)oxy)silane (**1c**) (0.50 mmol) and 106 mg **4a** (0.55 mmol, 1.1 equiv) was used, and the mixture was stirred for 16 h before workup. The product was purified by silica gel flash chromatography by eluting with 1% acetone in hexanes to give **3c** as a clear oil in 87% yield (145 and 144 mg). The ^{1}H NMR spectrum, see below, was compared with the previously reported spectrum.[18]

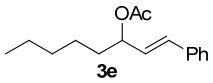
Table 2, entry 4 ((*E*)-1,4-diphenylbut-3-en-1-ol (3d).



3d

The general procedure for the preparation of **3a** was used with the modifications that 74 mg 1-phenylbut-3-en-1-ol **1d** (0.50 mmol) and 106 mg **4a** (0.55 mmol, 1.1 equiv) was used, and the mixture was stirred for 1.5 h before workup. The product was purified by silica gel flash chromatography by eluting with 10% acetone in hexanes to give **3d** as a white solid in 72% yield (75 and 84 mg). The ^{1}H NMR spectrum, see below, was compared with the previously reported spectrum.[18]

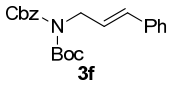
Table 2 entry 5 (*E*)-1-phenyloct-1-en-3-yl acetate (3e)



3e

The general procedure for the preparation of **3a** was used with the modifications that 23 mg Pd_2dba_3 (0.03 mmol, 0.05 equiv), 85 mg oct-1-en-3-yl acetate **1e** (0.50 mmol) and 144 mg **4a** (0.75 mmol, 1.5 equiv) was used, and the mixture was stirred for 16 h before workup. The product was purified by silica gel flash chromatography by eluting with 2% acetone in hexanes to give **3e** as a clear oil in 87% yield (108 and 105 mg). The ^{1}H NMR spectrum, see below, was compared with the previously reported spectrum.[18]

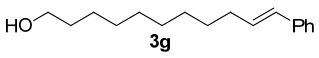
Table 2, entry 6 ((*E*)-N-Cbz-N-Boc-3-phenylprop-2-en-1-amine) (3f).



3f

The general procedure for the preparation of **3a** was used with the modifications that 87 mg N-Cbz-N-Boc-prop-2-en-1-amine (**1f**) (0.30 mmol) and 86 mg **4a** (0.45 mmol, 1.5 equiv) was used in 3.0 mL DMA, and the mixture was stirred for 16 h before workup. The product was purified by silica gel flash chromatography by eluting with 2% acetone in hexanes to give **3f** as a white solid in 96% yield (105 and 106 mg). The ^{1}H NMR spectrum, see below, was compared with the previously reported spectrum.[18]

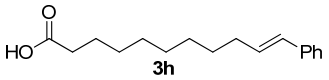
Table 2, entry 7 ((*E*)-11-phenylundec-10-en-1-ol) (3g).



3g

The general procedure for the preparation of **3a** was used with the modifications that 85 mg undec-10-en-1-ol **1g** (0.50 mmol) and 106 mg **4a** (0.55 mmol, 1.1 equiv) was used, and the mixture was stirred for 40 minutes before workup. The product was purified by silica gel flash chromatography by eluting with 5% acetone in hexanes to give **3g** as a white solid in 77% yield (97 and 93 mg). The ^{1}H NMR spectrum, see below, was compared with the previously reported spectrum.[18]

Table 2, entry 8 ((*E*)-11-phenylundec-10-enoic acid (3h).



3h

The general procedure for the preparation of **3a** was used with the modifications that 92 mg undec-10-enoic acid **1g** (0.50 mmol) and 106 mg **4a** (0.55 mmol, 1.1 equiv) was used, and the mixture was stirred for 2 h before workup. The product was purified by silica gel flash chromatography by eluting with 5% acetone in hexanes to give **3h** as a clear oil in 95% yield (125 and 122 mg).

R_f (15% acetone in hexanes) = 0.26 (UV).

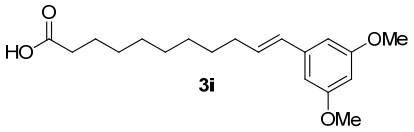
IR(neat): 3024, 2924, 2853, 1704, 1494, 1411, 1284, 1239, 963, 743, 693 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): 1.49-1.26 (m, 10H), 1.66-1.59 (m, 2H), 2.19 (dt, *J* = 7.0, 6.7 Hz, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 6.22 (dt, *J* = 15.9, 6.7 Hz, 1H) 6.38 (d, *J* = 15.9 Hz, 1H) 7.36-7.16 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): 24.8, 29.2, 29.3, 29.4, 29.5, 29.5, 33.2, 34.3, 126.1, 126.9, 128.6, 129.9, 131.3, 138.1, 180.8.

HRMS $(M+Na)^+$ calcd.; 283.1674 obsd.; 283.1675.

Table 2, entry 9 ((*E*)-(3,5-dimethoxyphenyl)undec-10-enoic acid (3i).



3i

The general procedure for the preparation of **3a** was used with the modifications that 92 mg **1g** (0.50 mmol) and 139 mg 3,5-dimethoxyphenyldiazonium tetrafluoroborate **4b** (0.55 mmol, 1.1 equiv) was used, and the mixture was stirred for 2 h before workup. The product was purified by silica gel flash chromatography by eluting with 10% acetone in hexanes to give **3i** as a white solid (MP = 45-47 ^oC) in 69% yield (108 and 113 mg).

R_f (15% acetone in hexanes) = 0.18 (UV).

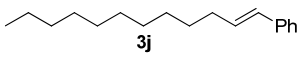
IR(neat): 2967, 2853, 1707, 1592, 1458, 1425, 1293, 1204, 1152, 1065, 965, 927, 827, 683, 668 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): 1.49-1.25 (m, 10H), 1.69-1.57 (m, 2H), 2.19 (dt, *J* = 7.5, 6.9 Hz, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 3.79 (s, 6H), 6.34-6.15 (m, 3H), 6.51 (d, *J* = 2.2 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 24.8, 29.2, 29.3, 29.4, 29.5, 29.5, 33.1, 34.3, 55.9, 99.3, 104.2, 129.9, 132.0, 140.2, 161.0, 180.4.

HRMS $(M+Na)^+$ calcd.; 343.1885 obsd.; 343.1880.

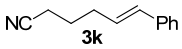
Table 2, entry 10 ((*E*)-docec-1-en-1-ylbenzene) (3j).



3j

The general procedure for the preparation of **3a** was used with the modifications that 84 mg undecene **1h** (0.50 mmol) and 106 mg **4a** (0.55 mmol, 1.1 equiv) was used, and the mixture was stirred for 20 minutes before workup. The product was purified by silica gel flash chromatography by eluting with 5% acetone in hexanes to give **3j** as a clear oil in 77% yield (94 and 93 mg). The ^{1}H NMR spectrum, see below, was compared with the previously reported spectrum.[19]

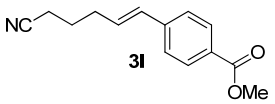
Table 2, entry 11 ((*E*)-6-phenylhex-5-enenitrile) (3k).



3k

The general procedure for the preparation of **3a** was used with the modifications that 48 mg hex-5-enenitrile **1i** (0.50 mmol) and 106 mg **4a** (0.55 mmol, 1.1 equiv) was used, and the mixture was stirred for 3 h before workup. The product was purified by silica gel flash chromatography by eluting with 5% acetone in hexanes to give **3j** as a white solid in 96% yield (82 and 81 mg). The ^{1}H NMR spectrum, see below, was compared with the previously reported spectrum.[20]

Table 2, entry 12 ((*E*)-methyl 4-(5-cyanopent-1-en-1-yl)benzoate) (3l).



3l

The general procedure for the preparation of **3a** was used with the modifications that 48 mg **1i** (0.50 mmol) and 138 mg 4-methoxycarbonylbenzenediazonium tetrafluoroborate **4c** (0.55 mmol, 1.1 equiv) was used, and the mixture was stirred for 3 h before workup. The product was purified by silica gel flash chromatography by eluting with 10% acetone in hexanes to give **3l** as a white solid (MP = 49-50 ^{o}C)in 98% yield (113 and 110 mg).

R_f (5% acetone in hexanes) = 0.11 (UV).

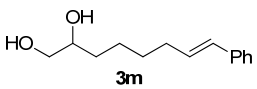
IR(neat): 1951, 2246, 1713, 1650, 1605, 1434, 1413, 1274, 1177, 1107, 1016, 961, 872, 761 697 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): 1.87 (quint, *J* = 7.2, 2H), 2.46-2.39 (m, 4H), 3.90 (s, 3H), 6.27 (dt, *J* = 15.8, 7.0 Hz, 1H) 6.50 (d, *J* = 15.9 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.97 (d, *J* = 8.3 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 16.7, 24.9, 31.9, 52.2, 119.6, 126.1, 128.9, 130.1, 130.7, 131.3, 141.7, 167.0.

HRMS $(M+Na)^{+}$ calcd.; 252.1000 obsd.; 252.0986.

Table 2, entry 13 ((*E*)-8-phenyloct-7-ene-1,2-diol) (3m).



3m

The general procedure for the preparation of **3a** was used with the modifications that 72 mg oct-7-ene-1,2-diol **1j** (0.50 mmol) and 106 mg **4a** (0.55 mmol, 1.1 equiv) was used, and the mixture was stirred for 2 h before workup. The product was purified by silica gel flash chromatography by eluting with 20% acetone in hexanes to give **3m** as a white solid (MP = 44-46 ^{o}C) in 83% yield (93 and 89 mg).

R_f (15% acetone in hexanes) = 0.05 (UV).

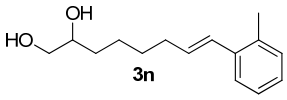
IR(neat): 3343, 3057, 3024, 2929, 2856, 1598, 1493, 1447, 1070, 963, 864, 744, 693, 668 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): 1.54-1.47 (m, 6H) 1.88 (br s, 1H), 2.03 (br s, 1H), 2.27- 2.20 (m, 2H) 3.47-3.41 (m, 1H) 3.74-3.66 (m, 2H), 6.21 (dt, *J* = 15.8, 6.8 Hz, 1H), 6.33 (d, *J* = 15.9 Hz, 1H), 7.44-7.17 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): 25.3, 29.5, 33.1, 33.2, 67.0, 72.4, 126.1, 127.0, 128.7, 130.2, 130.9, 137.9.

HRMS $(M+Na)^+$ calcd.; 243.1361 obsd.; 243.1355.

Table 2, entry 14 ((*E*)-8-(*o*-tolyl)oct-7-ene-1,2-diol (1n).



3n

The general procedure for the preparation of **3a** was used with the modifications that 23 mg Pd_2dba_3 (0.03 mmol, 0.05 equiv), 72 mg **1j** (0.50 mmol) and 155 mg 2-methylbenzenediazonium tetrafluoroborate **4d** (0.75 mmol, 1.5 equiv) was used, and the mixture was stirred for 2 h before workup. The product was purified by silica gel flash chromatography by eluting with 20% acetone in hexanes to give **3n** as a clear oil in 66% yield (76 and 77 mg).

R_f (15% acetone in hexanes) = 0.07 (UV).

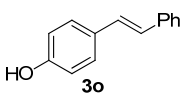
IR(neat): 3350, 3020, 2930, 2857, 1652, 1601, 1484, 1460, 1101, 1053, 964, 866, 746 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): 1.58-1.44 (m, 6H), 1.90-1.80 (m, 1H), 2.04-1.99 (m, 1H), 2.30-2.22 (m, 2H), 2.33 (s, 3H), 3.49-3.40 (m, 1H), 3.75-3.65 (m, 2H), 6.08 (dt, *J* = 15.7, 6.9 Hz, 1H), 6.57 (d, *J* = 15.5 Hz, 1H), 7.21-7.10 (m, 3H), 7.40 (d, *J* = 5.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): 20.0, 25.3, 29.6, 33.1, 33.4, 67.0, 72.4, 125.6, 126.2, 127.0, 128.0, 130.3, 132.2, 135.0, 137.1.

HRMS $(M+Na)^+$ calcd.; 257.1517 obsd.; 257.1505.

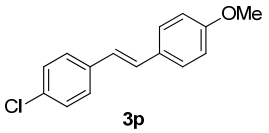
Table 2, entry 15 ((*E*)-4-styrylphenol (3o).



3o

The general procedure for the preparation of **3a** was used with the modifications that 60 mg 4-vinylphenol **1k** (0.50 mmol) and 106 mg **4a** (0.55 mmol, 1.1 equiv) was used, and the mixture was stirred for 1.5 h before workup. The product was purified by silica gel flash chromatography by eluting with 10% acetone in hexanes to give **3j** as a white solid in 98% yield (95 and 97 mg). The ^{1}H NMR spectrum, see below, was compared with the previously reported spectrum.[21]

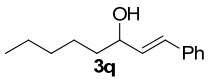
Table 2, entry 16 ((*E*)-1-chloro-4-(4-methoxystyryl)benzene (1p).



3p

The general procedure for the preparation of **3a** was used with the modifications that 69 mg 1-chloro-4-vinylbenzene **1l** (0.50 mmol) and 122 mg 4-methoxybenzendiazonium tetrafluoroborate **4e** (0.55 mmol, 1.1 equiv) was used, and the mixture was stirred for 1.5 h before workup. The product was purified by silica gel flash chromatography by eluting with 3% acetone in hexanes to give **3j** as a white solid in 98% yield (117 and 121 mg). The ^{1}H NMR spectrum, see below, was compared with the previously reported spectrum.[22]

Table 2, entry 17 ((*E*)-1-phenyloct-1-en-3-ol) (3q).



3q

The general procedure for the preparation of **3a** was used with the modifications that 23 mg Pd_2dba_3 (0.03 mmol, 0.05 equiv), 64 mg oct-1-en-3-ol **1m** (0.50 mmol) and 144 mg **4a** (0.75 mmol, 1.5 equiv) was used, and the mixture was stirred for 16 h before workup. The product was purified by silica gel flash chromatography by eluting with 5% acetone in hexanes to give **3q** as a clear oil in 55% yield (53 and 58 mg).

R_f (5% acetone in hexanes) = 0.18 (UV).

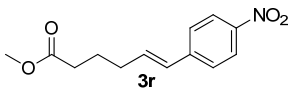
IR(neat): 3338, 3060, 3026, 2955, 2928, 2857, 1599, 1494, 1449, 1132, 1027, 965, 748, 692 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): 0.89 (t, *J* = 6.8 Hz, 3H), 1.43-1.26 (m, 6H), 1.68-1.57 (m, 3H), 4.32-4.24 (m, 1H), 6.22 (dd, *J* = 15.9, 6.8 Hz, 1H), 6.55 (d, *J* = 15.9 Hz, 1H), 7.40-7.22 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): 14.3, 22.8, 25.4, 32.0, 73.4, 126.7, 127.8, 128.8, 130.4, 132.8, 136.9.

HRMS $(M)^+$ calcd.; 205.1592 obsd.; 205.1582.

Table 2, entry 18 ((*E*)-methyl-6-(4-nitrophenyl)hex-5-enoate (3r).



3r

The general procedure for the preparation of **3a** was used with the modifications that 64 mg **1a** (0.50 mmol) and 130 mg 4-nitrobenzenediazonium tetrafluoroborate **4f** (0.55 mmol, 1.1 equiv) was used, and the mixture was stirred for 20 minutes before workup. The product was purified by silica gel flash chromatography by eluting with 10% acetone in hexanes to give **3r** as a clear oil in 97% yield (122 and 119 mg). Note: when submitting slower reacting substrates (or allowing this reaction to proceed longer than 20 minutes) to the Heck reaction with **4f** we observed decomposition of the desired product likely due to the highly reactive nitrostyrene product.

R_f (5% acetone in hexanes) = 0.21 (UV).

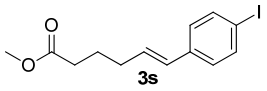
IR(neat): 2947, 1731, 1483, 1435, 1397, 1243, 1196, 1151, 1061, 1003, 966, 842, 797 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): 1.81 (quint, *J* = 7.6 Hz, 2H), 2.24 (dt, *J* = 7.6, 7.4 Hz, 2H), 2.39 (t, *J* = 7.5 Hz, 2H), 3.66 (s, 3H), 6.18 (dt, *J* = 15.8, 6.6 Hz, 1H), 6.31 (d, *J* = 15.9 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 24.2, 32.6, 33.5, 51.8, 124.1, 126.6, 129.2, 135.1, 144.2, 146.7, 173.9.

HRMS $(M+Na)^+$ calcd.; 272.0899 obsd.; 272.0893.

Table 2, entry 19 ((*E*)-methyl-6-(4-iodophenyl)hex-5-enoate (3s).



3s

The general procedure for the preparation of **3a** was used with the modifications that 64 mg **1a** (0.50 mmol) and 159 mg 4-iodobenzenediazonium tetrafluoroborate **4g** (0.55 mmol, 1.1 equiv) was used, and the mixture was stirred for 20 minutes before workup. The product was purified by silica gel flash chromatography by eluting with 2% acetone in hexanes to give **3s** as a clear oil in 66% yield (99, 122, 107 mg).

R_f (5% acetone in hexanes) = 0.40 (UV).

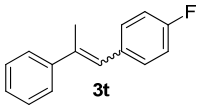
IR(neat): 2950, 1734, 1596 1515, 1436, 1342, 1180, 1109, 971, 858, 744, 691 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): 1.85 (quint, *J* = 7.2 Hz, 2H), 2.41-2.28 (m, 4H), 3.67 (s, 3H), 6.50-6.34 (m, 2H), 7.45 (d, *J* = 8.9 Hz, 2H), 8.16 (d, *J* = 9.0 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): 24.5, 32.5, 33.5, 51.7, 92.2, 128.0, 130.0, 130.7, 137.2, 137.7, 174.1.

HRMS $(M+Na)^+$ calcd.; 353.0015 obsd.; 353.0012.

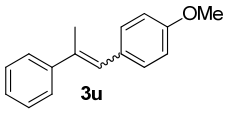
Table 2, entry 20 (1-fluoro-4-(2-phenylprop-1-en-1-yl)benzene) (3t).



3t

The general procedure for the preparation of **3a** was used with the modifications that 23 mg Pd_2dba_3 (0.03 mmol, 0.05 equiv), 59 mg α-methylstyrene **1n** (0.50 mmol) and 157 mg 4-fluorobenzenediazonium tetrafluoroborate **4h** (0.75 mmol, 151 equiv) was used, and the mixture was stirred for 2 h before workup. The product was purified by silica gel flash chromatography by eluting with 1% acetone in hexanes to give **3t** as a white solid in 99% yield (105 and 105 mg). The ^{1}H NMR spectrum, see below, was compared with the previously reported spectrum.[23] The (*E*)- and (*Z*)-olefin isomers have very similar spectra as reported in the literature; the methyl peak appearing at 2.3 ppm is overlapping singlets leading us to believe that the product is approximately an equimolar amount of the isomers.

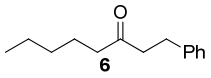
Table 2, entry 21 (1-methoxy-4-(2-phenylprop-1-en-1-yl)benzene) (3u).



3u

The general procedure for the preparation of **3a** was used with the modifications that 23 mg Pd_2dba_3 (0.03 mmol, 0.05 equiv), 59 mg **1n** (0.50 mmol) and 167 mg **4e** (0.75 mmol, 151 equiv) was used, and the mixture was stirred for 2 h before workup. The product was purified by silica gel flash chromatography by eluting with 3% acetone in hexanes to give **3u** as a white solid in 99% yield (111 and 110 mg). The ^{1}H NMR spectrum, see below, was compared with the previously reported spectrum.[24] The (*E*)- and (*Z*)-olefin isomers have very similar spectra as reported in the literature; the methyl peak appearing at 2.3 ppm is overlapping singlets leading us to believe that the product is approximately an equimolar amount of the isomers.

1-Phenyloctane-3-one (6).



6

1-Phenyloctane-3-one (**6**) was isolated as a clear oil in 44% yield as a byproduct of the reaction used to prepare **3q** (42 and 47 mg).

R_f (5% acetone in hexanes) = 0.41 (UV).

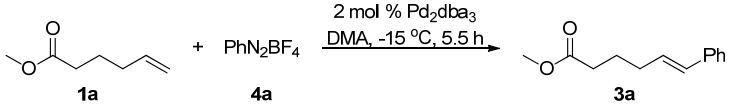
IR(neat): 3027, 2955, 2929, 2859, 1713, 1604, 1496, 1454, 1409, 1371, 1126, 1080, 748, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 0.88 (t, *J* = 7.1 Hz, 3H) 1.35-1.19 (m, 4H), 1.56 (quint, *J* = 7.3 Hz, 2H), 2.38 (t, *J* = 7.3 Hz, 2H), 2.73, (t, *J* = 7.5 Hz, 2H), 2.90 (t, *J* = 7.3 Hz, 2H) 7.20-7.17 (m, 3H), 7.30-7.26 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 14.1, 22.6, 23.7, 30.0, 31.6, 43.2, 44.5, 126.7, 128.5, 128.7, 141.4, 210.6.

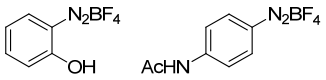
HRMS $(M+Na)^+$ calcd.; 227.1412 obsd.; 227.1408.

Procedure for the preparation of 3a on 5 mmol scale



In the dry box, an oven dried 250 mL round bottomed flask equipped with a stir bar was charged with 1.06 g (5.5 mmol, 1.1 equiv). To an oven dried 100 mL round bottomed flask with a stir bar was added 92 mg Pd_2dba_3 (0.1 mmol, 0.02 equiv), 641 mg **1a** (5 mmol) and 50 mL DMA. The flasks were fitted with septa, removed from the dry box, and placed in an ice/acetone bath. After cooling for 20 minutes, the solution containing **1a** and the catalyst was cannulated into the flask containing phenyldiazonium tetrafluoroborate. The mixture was stirred in the cold bath and starting material consumption was monitored by TLC. After 5.5 h the mixture was diluted with 50 mL Et_2O and transferred to a separatory funnel. To this, 50 mL of distilled water was added, and the aqueous layer was extracted twice with 50 mL Et_2O. The combined organic extracts were washed four times with 50 mL distilled water then 50 mL brine followed by drying over Na_2SO_4. The mixture was filtered and the solvent was removed *in vacuo*. The product was purified by silica gel flash chromatography eluting with 1% acetone in hexanes and was isolated as a clear oil in 92% yield (943 mg)**.**

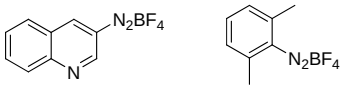
Unsuccessful reactions – Unsuccessful preparation of aryldiazonium tetrafluoroborates



Our attempts to prepare aryldiazonium tetrafluoroborate salts **4i** and **4j** were unsuccessful.

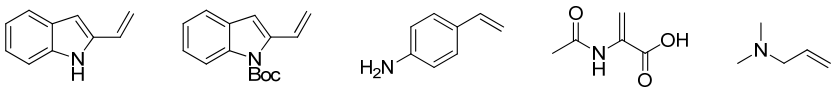
Unsuccessful reactions – Unsuccessful use of aryldiazonium tetrafluoroborates

The following reactions resulted in no conversion of starting alkene.



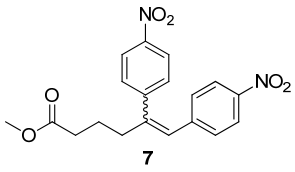
Unsuccessful reactions – Unsuccessful Heck reactions

The following reactions resulted in no conversion of starting alkene.



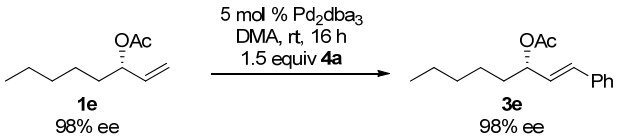
Byproduct of Heck reactions

Product **7** was obtained as a byproduct of the reaction used to prepare **3r**. See below for ^{1}H NMR spectrum. This type of product is not believed to be the major decomposition product of these reactions, however. The decomposition products are hypothesized to result from acid mediated oligomerization of the desired styrenyl products since the reaction produces a full equivalent of the strong acid HBF_4 which is not quenched by basic additives.



7

Evaluation of retention of enantiomeric excess

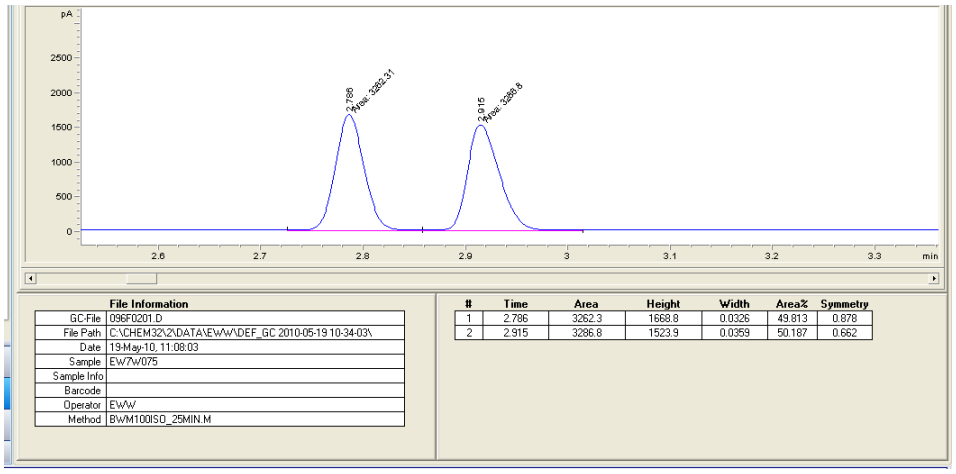


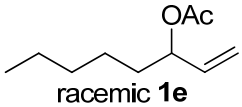
1e
98% ee

3e
98% ee

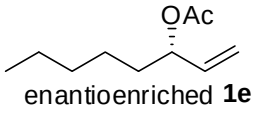
The same procedure used to synthesize racemic **3e** was used except 34 mg (*S*)-oct-1-en-3-yl acetate (**1e**) was added, and the product was purified after 16 h by silica gel chromatography by eluting with 1% acetone in hexanes. The purified product was evaluated for enantiomeric excess using chiral SFC (see below).

compound	method	retention times (min)
1e	GC. hold 100 °C 25 min	2.7 and 2.9
3e	SFC. 1% MeOH 2mL/min	4.3 and 5.5

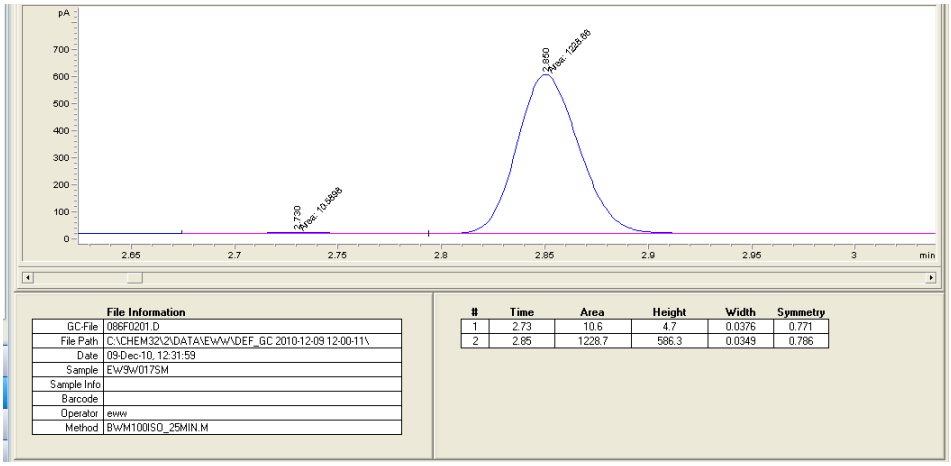


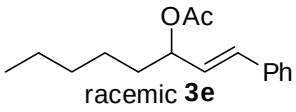


racemic **1e**

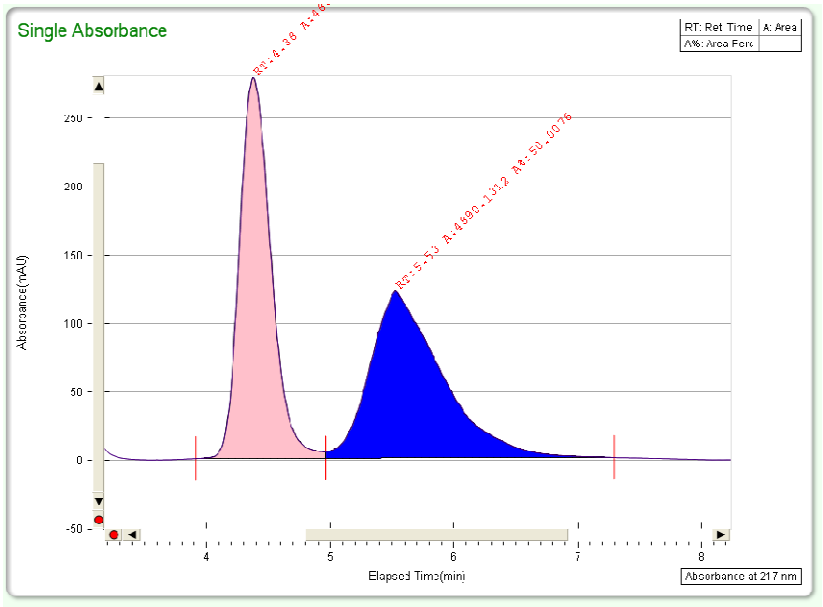


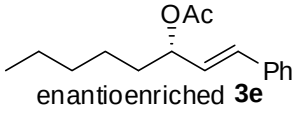
enantioenriched **1e**



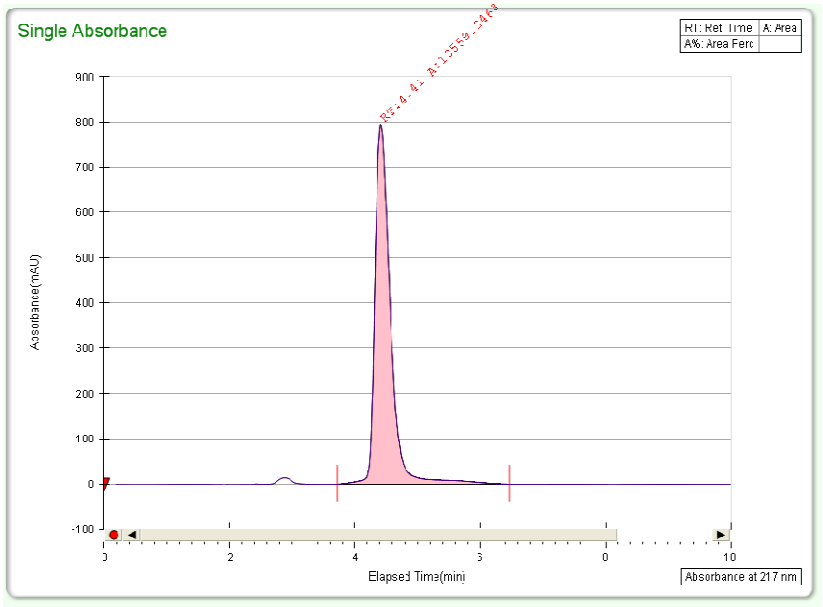


racemic **3e**



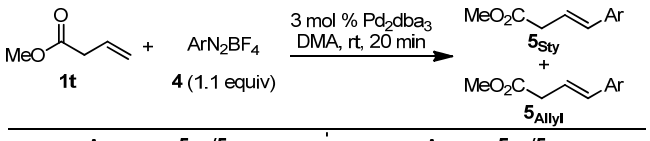


enantioenriched **3e**



Construction of Hammett plot

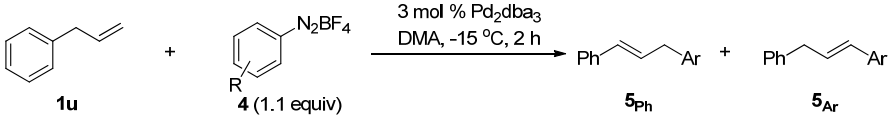
Results using α,β-unsaturated ester 1u (Figure 1)



Ar	$5_{Sty}/5_{Allyl}$	Ar	$5_{Sty}/5_{Allyl}$
4-H	6.03	4-CO_2Me	7.69
4-NO_2	6.11	4-Br	6.47
4-OMe	7.87	4-F	6.12

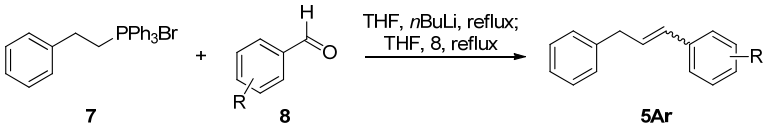
The general procedure for the preparation of **3a** was used with the modifications that 20 mg methyl but-3-enoate **1u** (0.20 mmol) and various aryldiazonium tetrafluoroborate salts **4** (0.22 mmol, 1.1 equiv) were used, and the mixtures were stirred for 20 minutes before workup. Following concentration *in vacuo*, the mixtures were analyzed by ^{1}H NMR to determine the ratio of $\mathbf{5_{Styr}}$:$\mathbf{5_{Allyl}}$ by comparing the integration of the vinyl or allylic protons of each product.

Results using allyl benzene 1u



The general procedure for the preparation of **3a** was used with the modifications that 5 mg Pd_2dba_3, 24 mg allyl benzene (**1u**) (0.2 mmol), and various aryldiazonium tetrafluoroborate salts **4** (0.22 mmol, 1.1 equiv) were use. The mixtures were stirred at -15 ^{o}C (using an ice/acetone bath) for 2 h before workup. The reactions were cooled because these Heck reactions are exothermic, and results were more consistent when using a heat sink. The crude mixtures were analyzed by a combination of ^{1}H NMR (comparing the integration of the allylic protons of each compound to determine which isomer was major) and GC (to accurately determine the ratio of $\mathbf{5_{Ph}}$:$\mathbf{5_{Ar}}$). In addition, authentic samples of $\mathbf{5_{Ar}}$ were prepared using the procedure described below to ensure the correct identification of each isomer.

General procedure for the synthesis of 5_{Ar}



Wittig reactions, performed based on a previously reported procedure,[25] were used to synthesize authentic samples of $\mathbf{5_{Ar}}$. To oven dried 50 mL round bottomed flasks equipped with stir bars was added 671 mg bromo(phenethyl)triphenylphosphorane (**7**) (1.5 mmol, 1.5 equiv). The flasks were fitted with reflux condensers, and placed under nitrogen. Tetrahydrofuran (THF) (5 mL)

was added, followed by n-butyllithium (660 µL of a 2.5 M solution in hexanes, 1.65 mmol, 1.65 equiv). The mixtures were heated to reflux, and stirred for 1 h, after which they were allowed to cool to room temperature. To the dark red mixtures was added various aldehydes **8** (1.0 mmol) in THF (2 mL). The mixtures were heated to reflux, and stirred for 12 h, followed by allowing them to cool to room temperature. To the cooled mixtures was added saturated NH_4Cl (5 mL), and the mixtures were stirred for 30 min, followed by transferring the biphasic mixtures to a separatory funnel with diethyl ether (10 mL). The layers were separated, and the aqueous layer was extracted with ether (15 mL). The combined organic layers were washed with saturated NH4Cl (10 mL), water (10 mL) and brine (10 mL). They were then dried over sodium sulfate, filtered, concentrated in vacuo, and the products purified by silica gel chromatography by eluting with 2% acetone in hexanes to give $\mathbf{5_{Ar}}$ along with the corresponding (*Z*)-$\mathbf{5_{Ar}}$ isomers. ^{1}H NMR analysis of the resulting mixtures allowed for the unambiguous determination of which benzylic protons correspond to the $\mathbf{5_{Ar}}$ products produced in the analysis of the Hammett plot described above.

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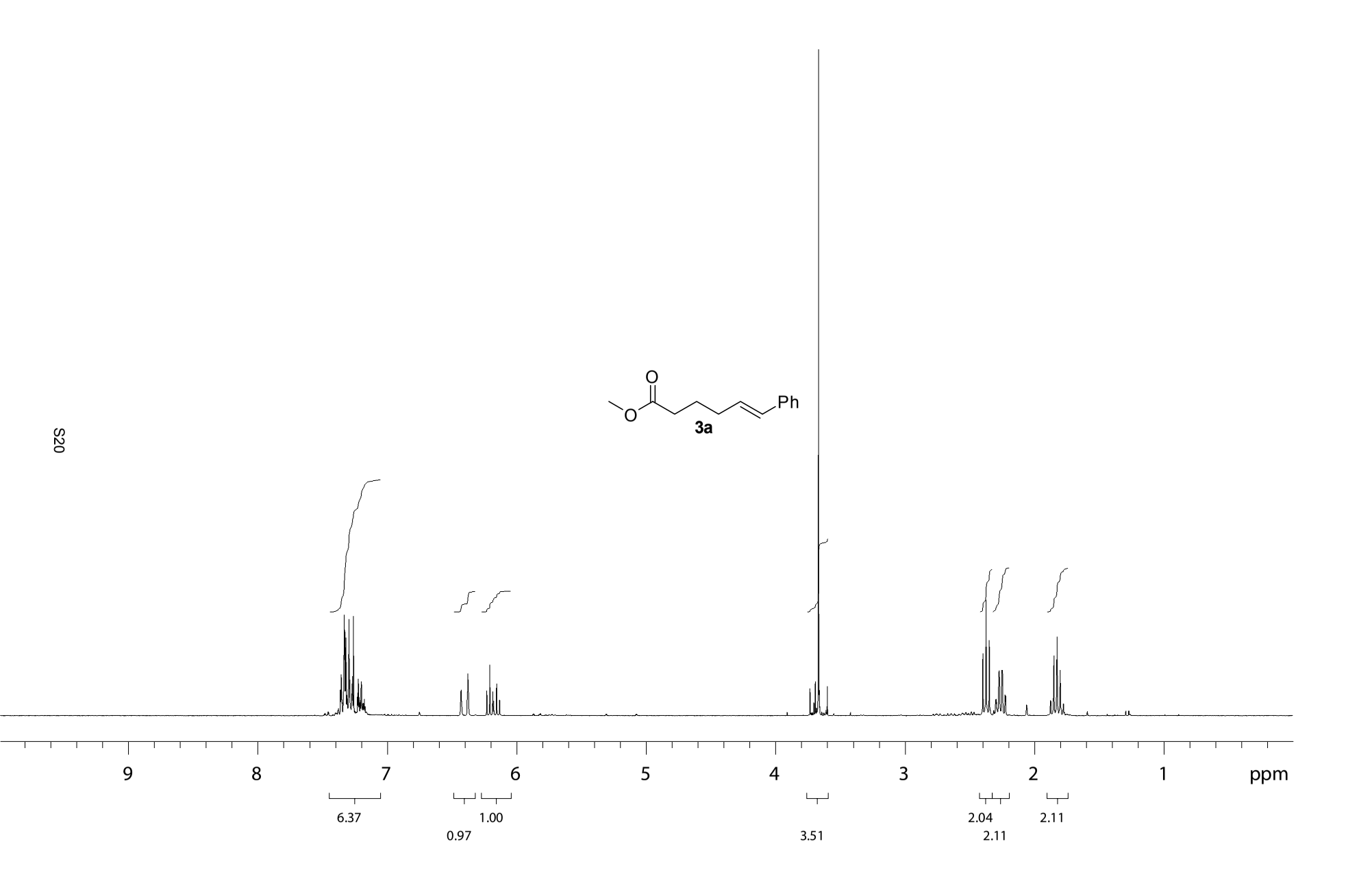
^{1}H and ^{13}C NMR spectra for new compounds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7
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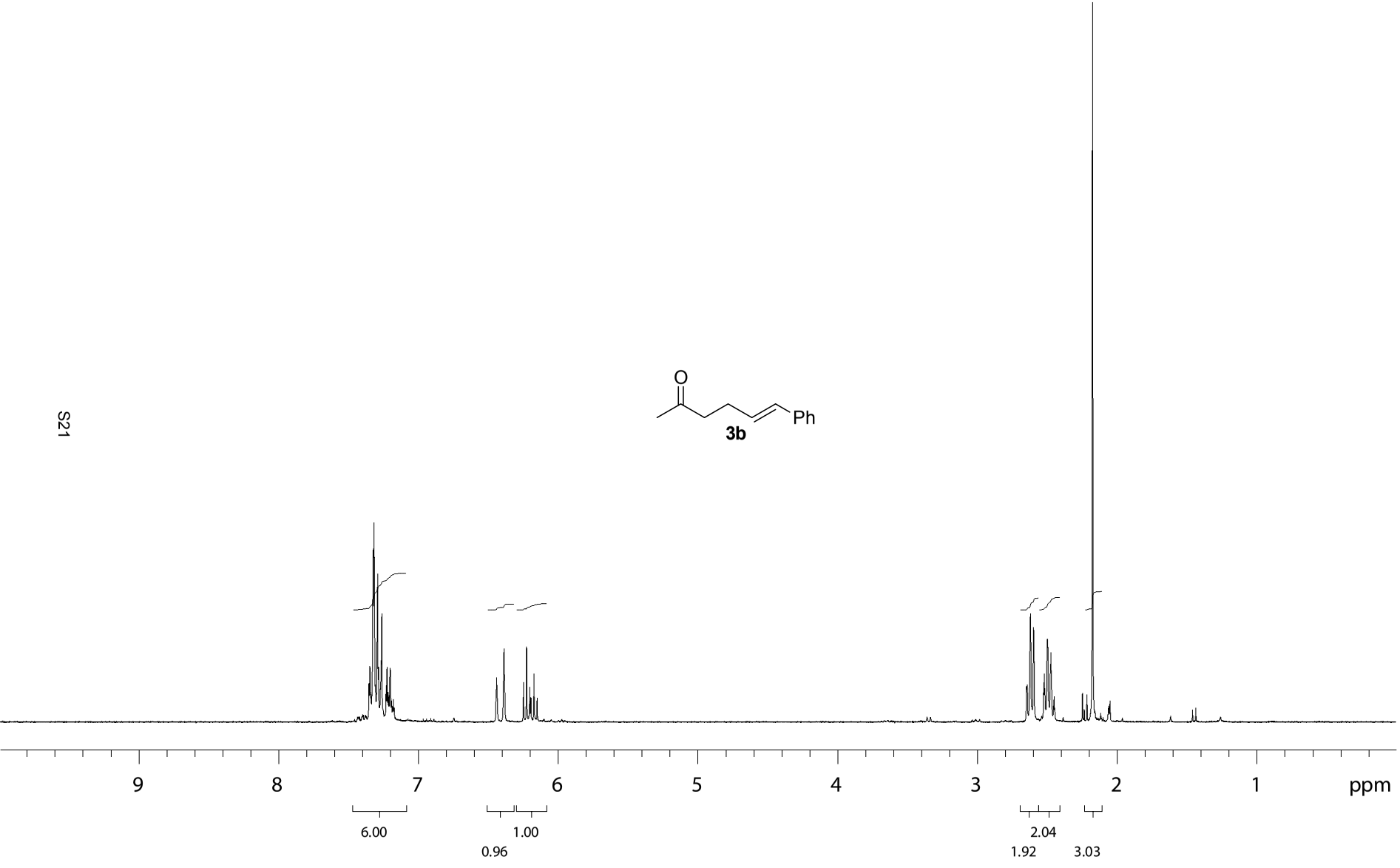
2.04
2.11
2.11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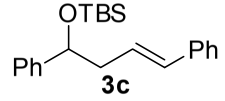

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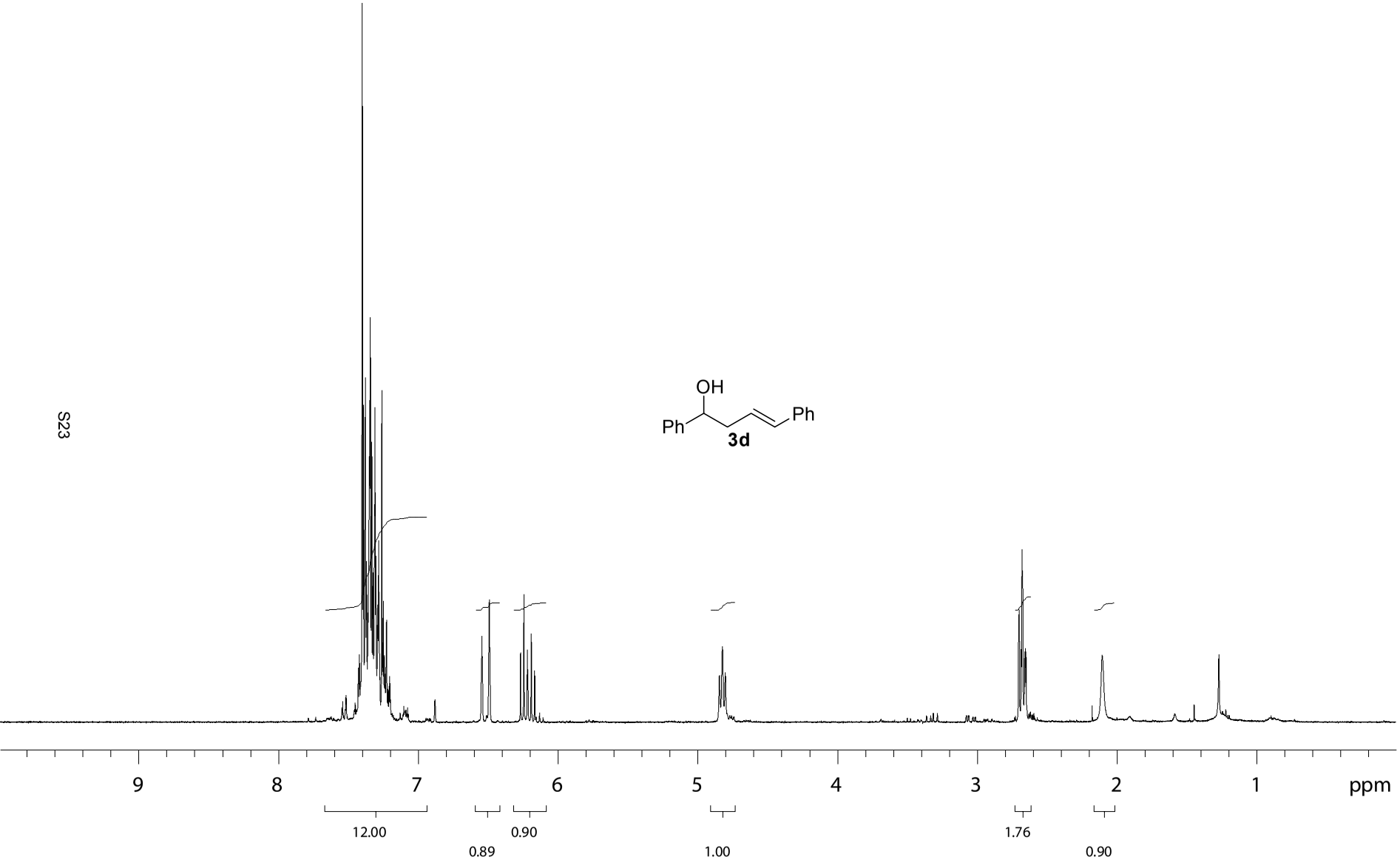
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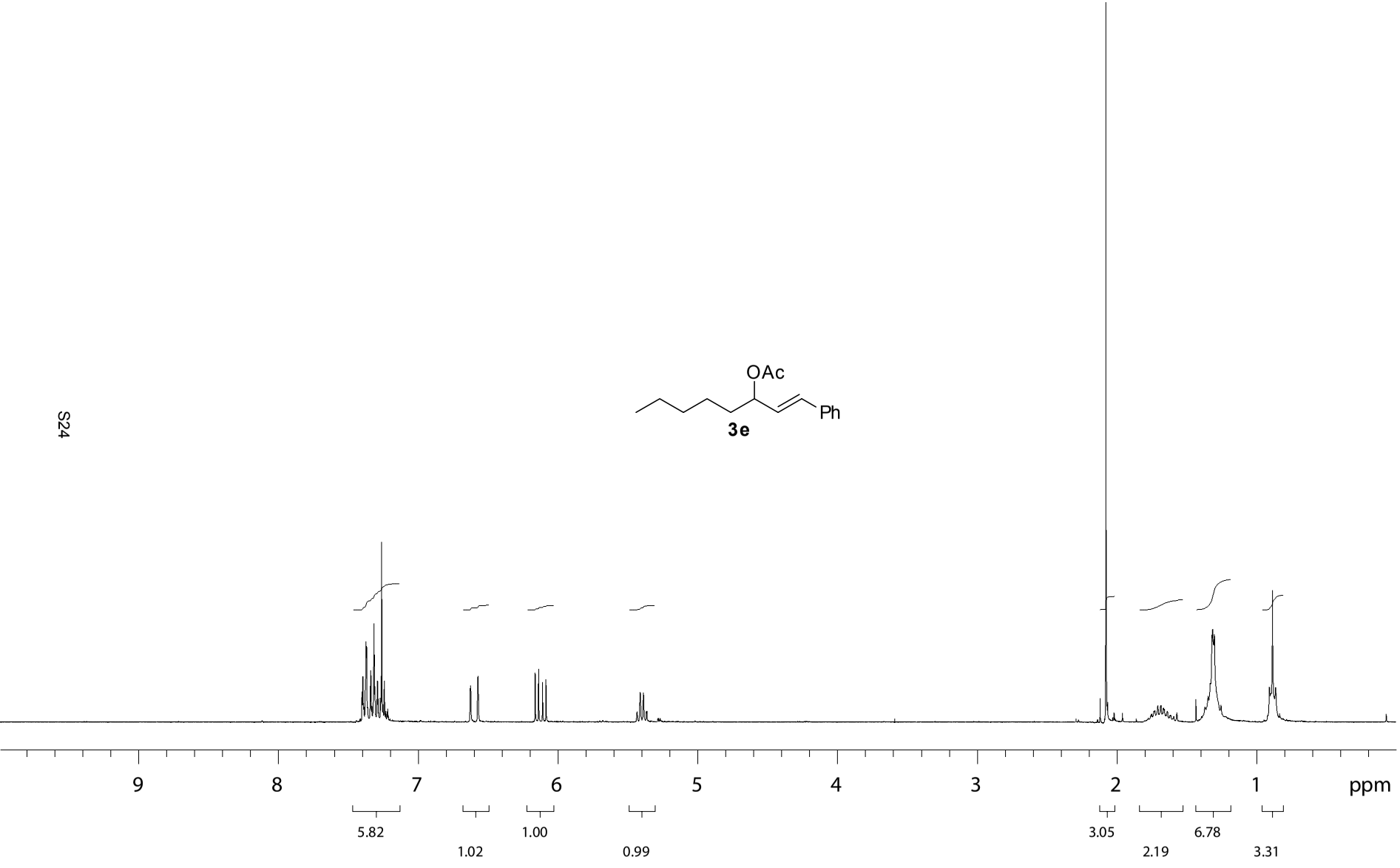
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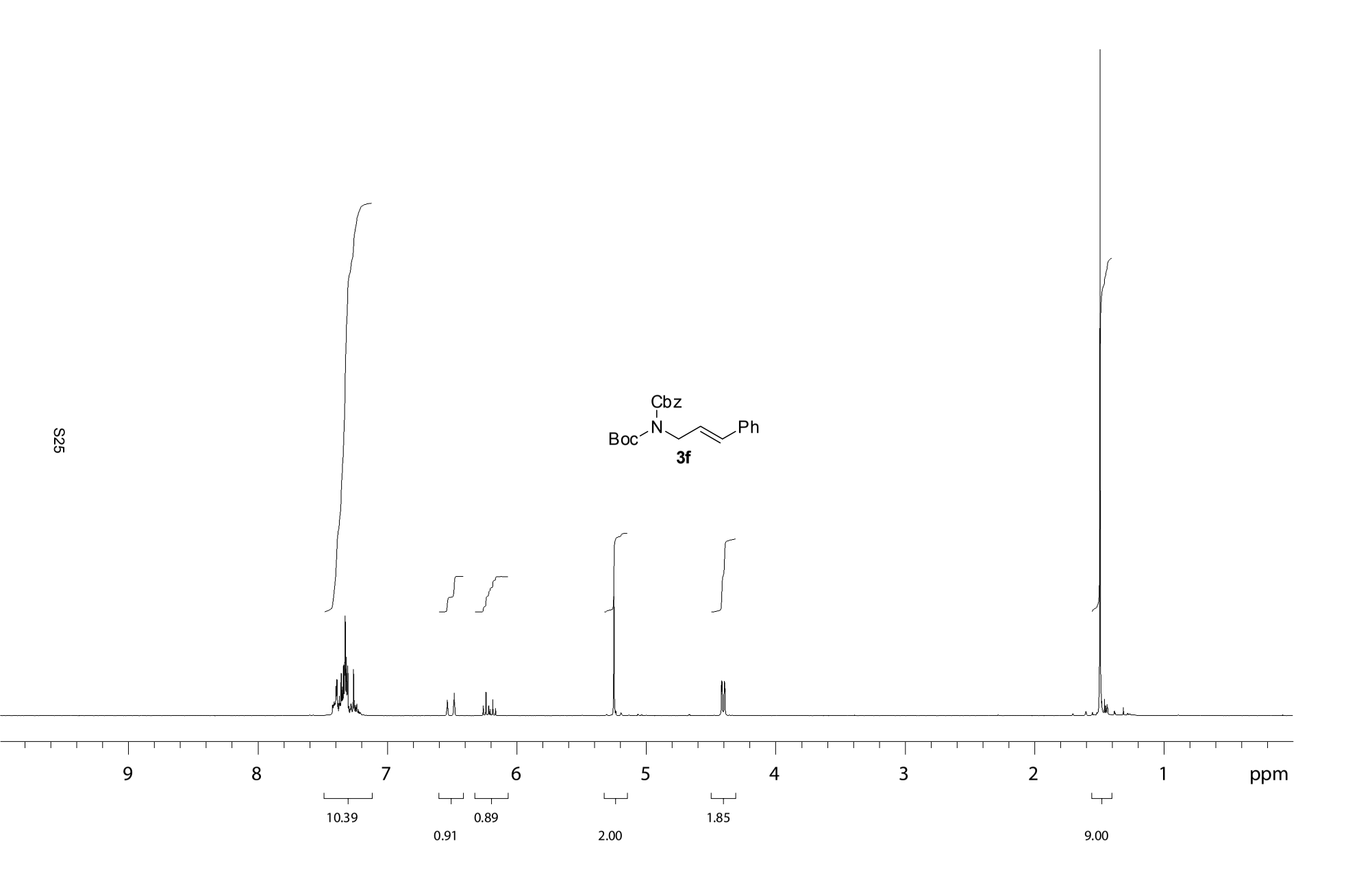
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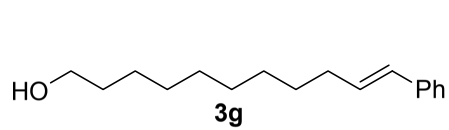

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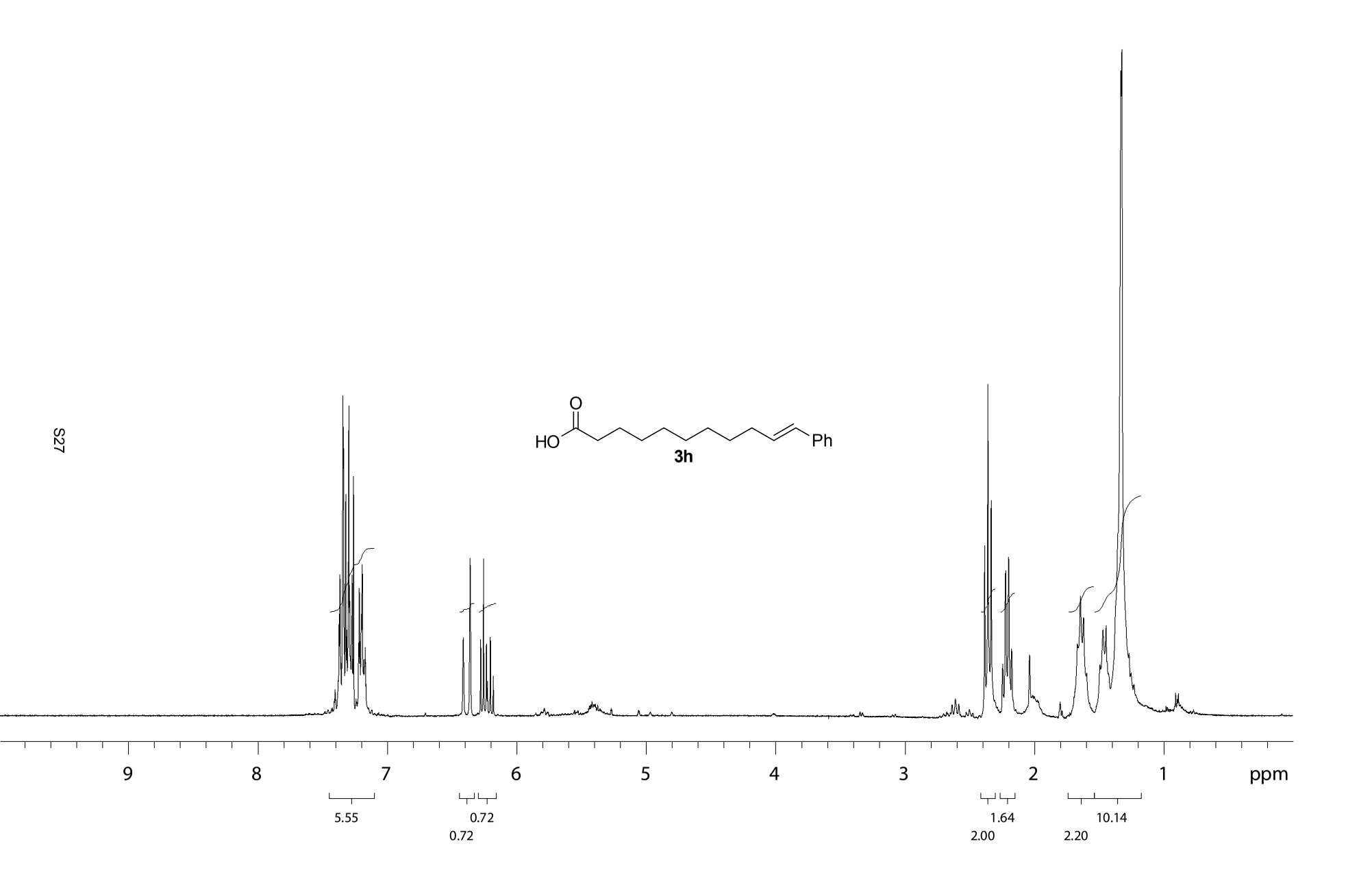
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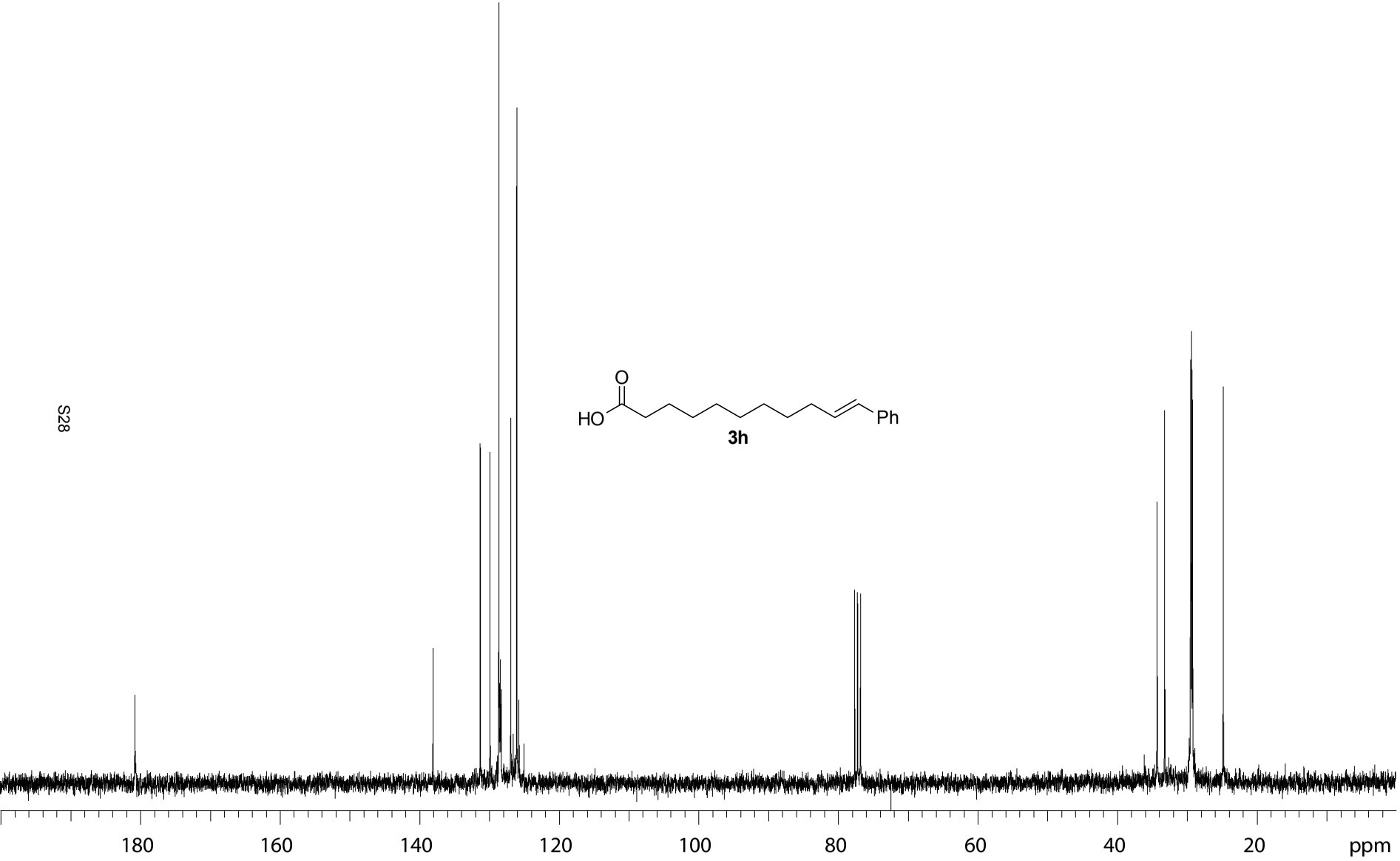
2.20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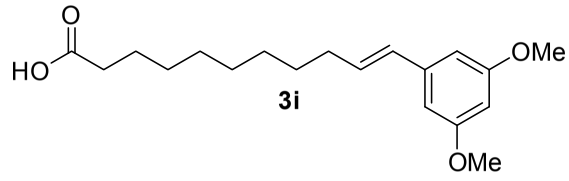

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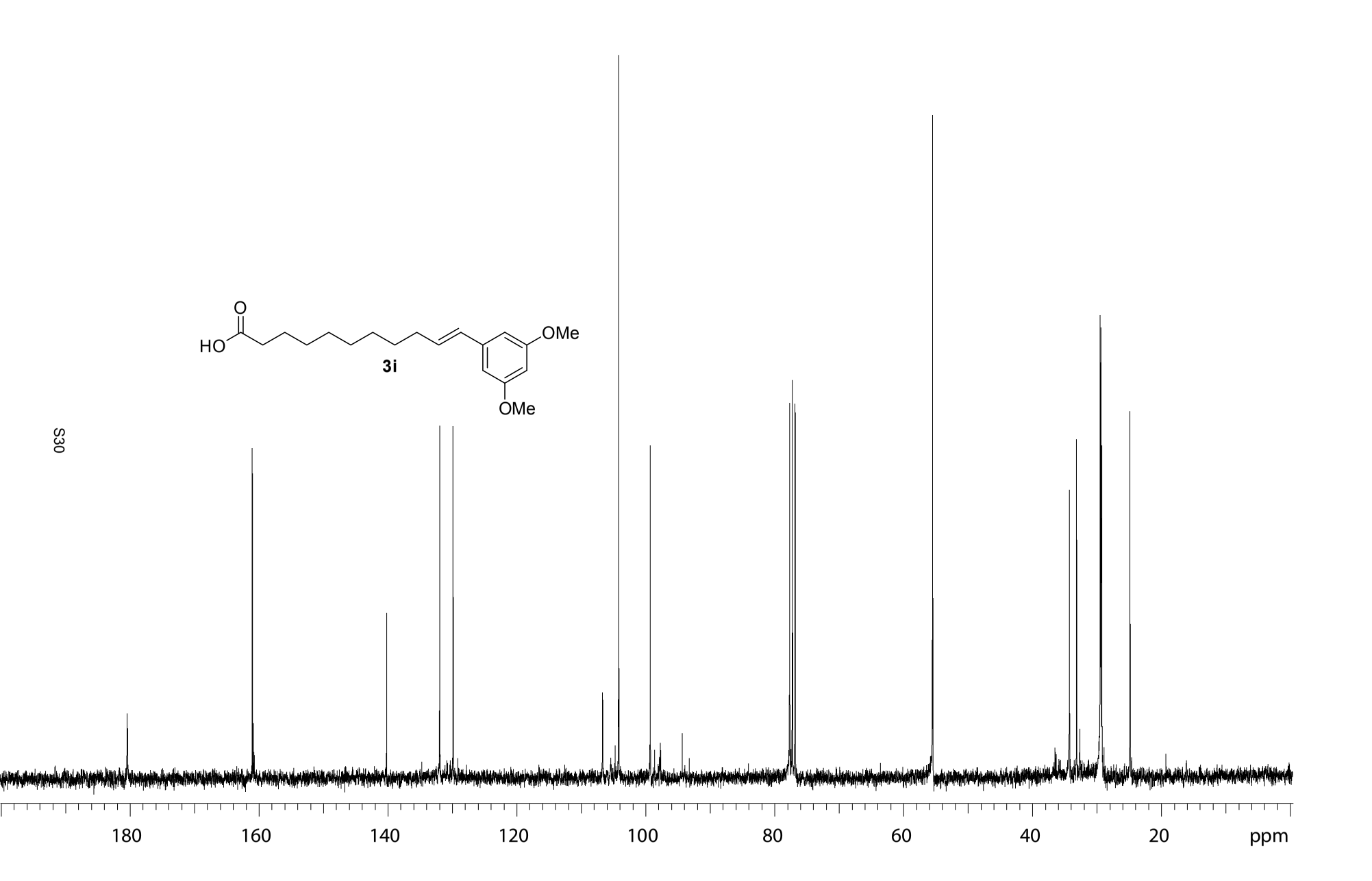
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OMe
3i
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140
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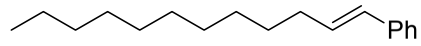
80
60
40
20
ppm



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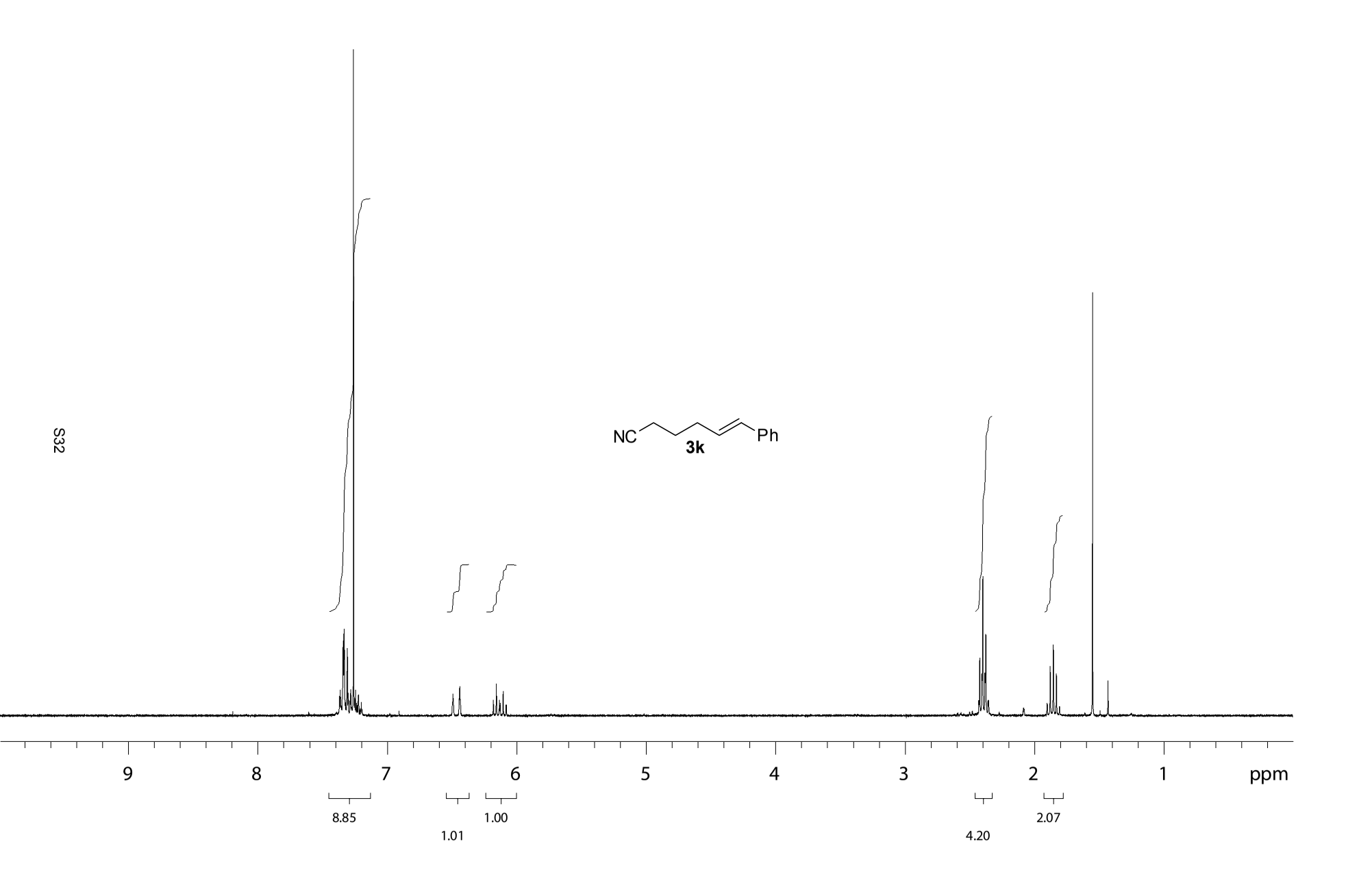
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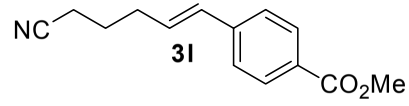

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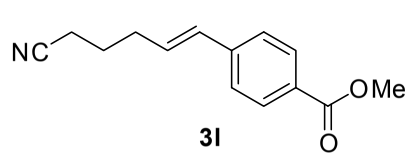

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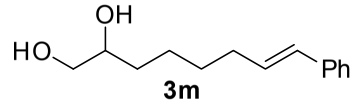

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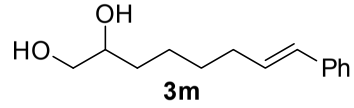

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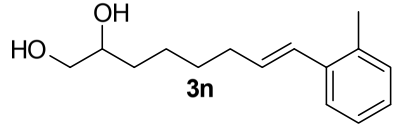

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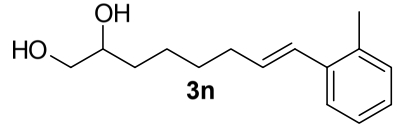

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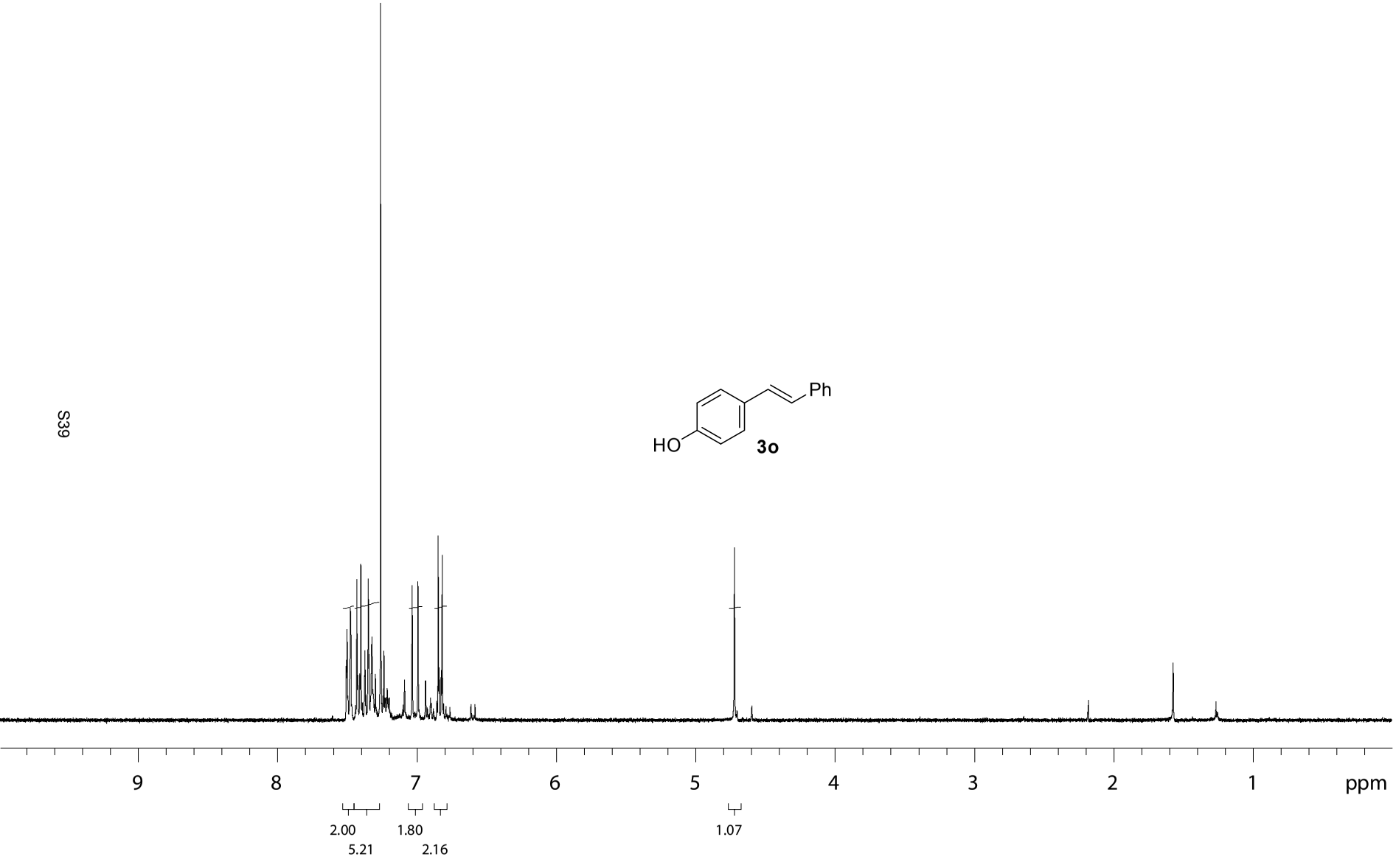
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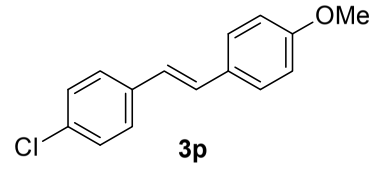

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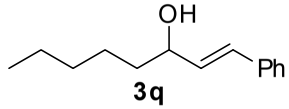

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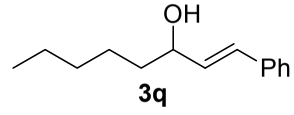

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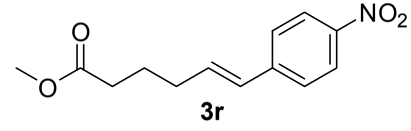

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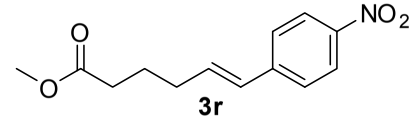

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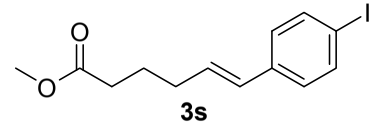

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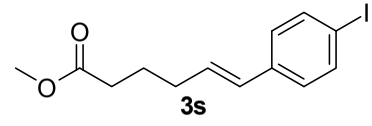

3s

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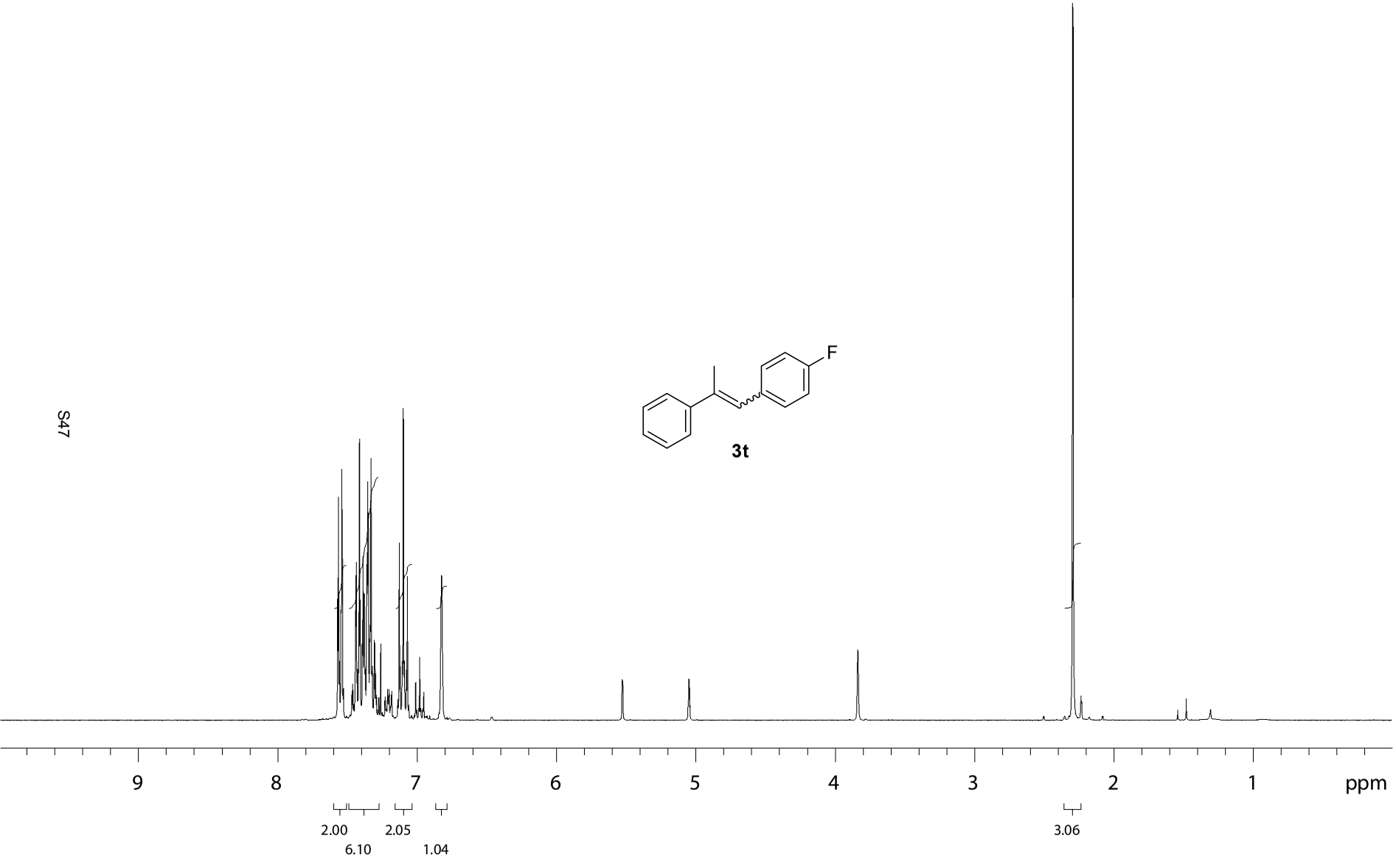
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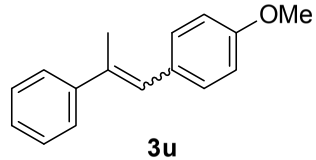

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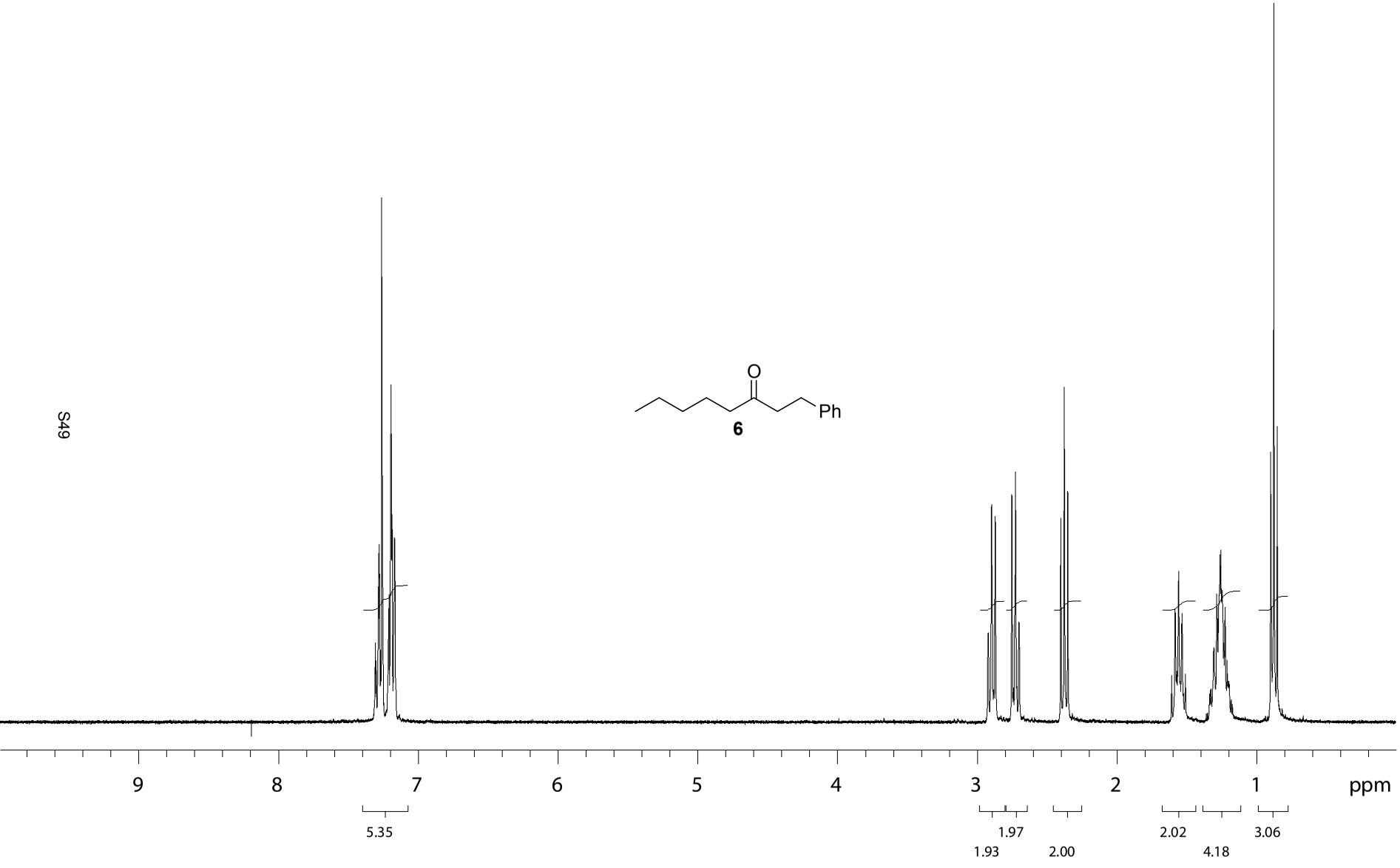
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Ph
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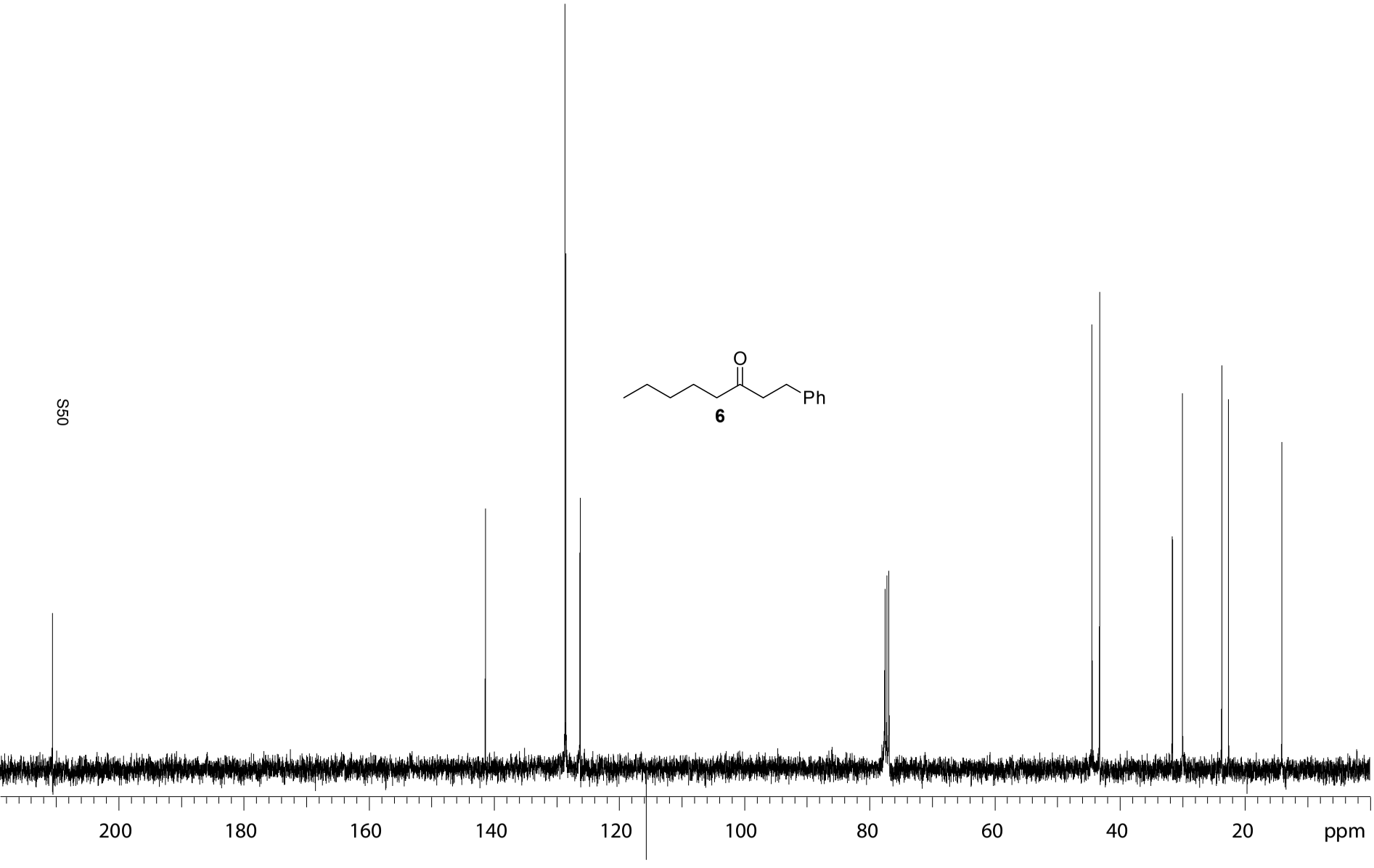
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Ph
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100
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60
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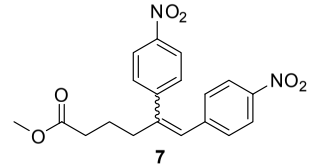
20
ppm



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