Electronic Supplementary Information

Stille couplings in water at room temperature

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1. Experimental

1.1 General

All reactions were carried out under an Ar atmosphere with flame-dried microwave vials. Column chromatography was preformed using Silicycle Silia-P 60 mesh flash silica gel. Thin-Layer-Chromatography analysis was conducted using commercially available EMD silica gel 60 F_{254} plates. alkenyl halides and alkenyl trifates were prepared following literature procedures.[1] Organotin reagents such as (*E*)-3-(tributylstannyl)prop-2-en-1-ol and (*E*)-3-(tributylstannyl)allyl acetate were synthesized according to known procedures.[2] Solvents and other reagents were all obtained from commercial vendors and used with no further purification. All known compounds were identified by appropriate technique such as ^{1}H NMR, and compared with previously reported data. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, and HRMS analyses. TPGS-750-M can be obtained from Sigma-Aldrich as a 2 wt % solution in water (catalog #733857).

Nuclear Magnetic Resonance spectra were obtained on a Varian Inova system, in $CDCl_3$, with ^{1}H, ^{13}C resonances at 500 and 125 MHz, respectively, and are referenced to the residual solvent signal at d 7.26 ppm for ^{1}H and d 77.00 ppm for ^{13}C. Data for ^{1}H are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant and integration. Data for ^{13}C NMR are reported in terms of chemical shift. GC/MS data was recorded on a 5975C Mass Selective Detector, coupled with a 7890A Gas Chromatograph (Agilent Technologies). As capillary column a HP-5MS cross-linked 5% phenylmethylpolysiloxanediphenyl column (30 m x 0.250 mm, 0.25 micron, Agilent Technologies) was employed. Helium was used as carrier gas at a constant flow of 1 mL/min. Retention times (t_R) refer to the following temperature program: 70 °C for 0 min; heating rate 16 °C/min; 300°C for 5.625 min; injection temperature 250 °C; detection temperature 280 °C. GC analyses were recorded on a Hewlett-Packard HP 6890 chromatograph equipped with a capillary column HP-1 (30 m × 0.25 mm × 0.25 μm). Retention times (t_R) refer to the following temperature program: 70 °C for 0 min; heating rate 20 °C/min; 280°C for 8.50 min; injection temperature 200 °C; detection temperature 290 °C. High resolution mass spectral data were acquired on either a VF Autospec or an analytical VG-70-250 HF spectrometer.

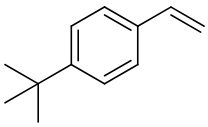
1.2 Experimental Procedures

General procedure for Stille couplings in aqueous TPGS-750-M micelles: Palladium catalyst (0.005 mmol), organohalides (0.250 mmol), DABCO (0.750 mmol), and NaCl (0.250 mmol) were weighed into a microwave vial at rt, and the organotin reagent (0.275 mmol) and 2 wt.% aqueous TPGS-750-M solution (1.0 mL) were then added by syringe (liquid organohaildes were also added by syringe). The resulting solution was allowed to stir at rt, monitored by GC or TLC (slight of heating was needed in some cases). When the reaction was complete, the mixture was diluted with NEt_3 (0.3 mL) and EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite. The volatiles were removed *in vacuo* to afford the crude product that was analyzed by GC to obtain the extent of conversion (and *Z*/*E* ratio

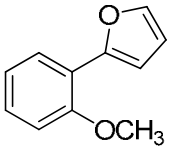
in the case of *Z*-alkenyl halides). Further column chromatography on silica gel was needed to afford the pure desired product.

Procedure for recycling the aqueous solution of TPGS-750-M. After completion of the reaction, the mixture was extracted with hexane (1 mL x 4). The organic layer was removed from the aqueous layer by syringe. The remaining hexane in the micellar solution was removed *in vacuo*. For the second run, fresh starting materials, along with $Pd(P(t\text{-}Bu)_3)_2$ (2 mol %) and DABCO were added to the aqueous solution, and the reaction was conducted as described for the first run.

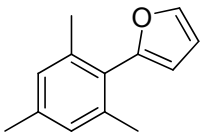
2. Characterization Data



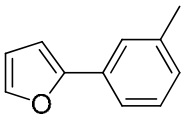
1-*tert*-Butyl-4-vinylbenzene[3] (**1**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (br, 9H), 5.20-5.22 (dd, J = 10.5, 1.0 Hz, 1H), 5.71-5.74 (dd, *J* = 17.5, 1.0 Hz, 1H), 6.69-6.75 (m, 1H), 7.37 (br, 4H).



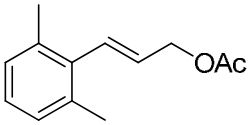
2-(2-Methoxyphenyl)furan[4] **(2)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.96 (s, 3H), 6.51-6.52 (q, *J* = 1.5 Hz, 1H), 6.97-7.06 (m, 3H), 7.24-7.28 (m, 1H), 7.87-7.89 (dd, *J* = 8.0, 2.0 Hz, 1H).



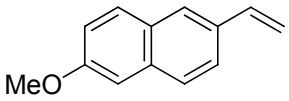
2-Mesitylfuran[5] (**3**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.18 (s, 6H), 2.32 (s, 3H), 6.25-6.26 (dd, *J* = 3.0, 0.5 Hz, 1H), 6.48-6.49 (q, *J* = 1.5 Hz, 1H), 6.93 (s, 2H), 7.50-7.51 (dd, *J* = 2.0, 1.0 Hz, 1H).



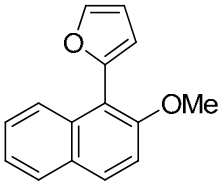
2-*m*-Tolylfuran[6] **(4)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.39 (s, 3H), 6.46-6.47 (q, *J* = 2.0 Hz, 1H), 6.63-6.64 (dd, *J* = 3.0, 0.5 Hz, 1H) 7.08 (d, *J* = 8.0 Hz, 1H), 7.26-7.29 (t, *J* = 7.5 Hz, 1H), 7.46-7.51 (m, 3H).



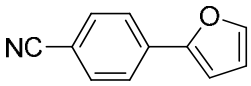
(*E*)-3-(2,6-Dimethylphenyl)allyl acetate (5). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.11 (s, 3H), 2.29 (s, 6H), 4.75-4.76 (dd, *J* = 6.5, 1.5 Hz, 2H), 5.77-5.87 (dt, *J* = 16.0, 6.3 Hz, 1H), 6.63-6.66 (d, *J* = 16.5 Hz, 1H), 7.02-7.08 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 21.0, 65.2, 126.9, 127.7, 128.6, 131.9, 135.9, 170.8. HRMS (EI) Calcd. for $C_{13}H_{16}O_2$ 204.1150, found 204.1142.



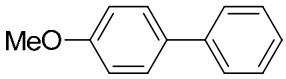
2-Methoxy-6-vinylnaphthalene[7] **(6).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.02 (s, 3H), 5.27-5.29 (dd, *J* = 11.0, 0.5 Hz, 1H), 5.80-5.84 (dd, *J* = 17.5, 0.5 Hz, 1H), 6.82-6.88 (dd, *J* = 18.0, 11.0 Hz, 1H), 7.11-7.15 (m, 2H), 7.60-7.72 (m, 4H).



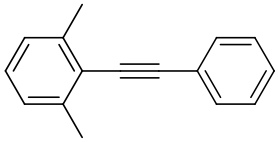
2-(2-Methoxynaphthalen-1-yl)furan (7). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.93 (s, 3H), 6.30 (d, *J* = 1.5 Hz, 2H), 7.34-7.46 (m, 3H), 7.66-7.67 (t, *J* = 1.5 Hz, 1H), 7.81-7.91 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.8, 110.8, 111.3, 113.5, 114.5, 123.8, 125.1, 126.9, 128.0, 129.0, 130.7, 133.7, 142.2, 148.8, 155.6. HRMS (EI) Calcd. for $C_{15}H_{12}O_2$ 224.0837, found 224.0839.



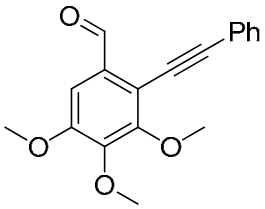
4-(Furan-2-yl)benzonitrile[8] **(8**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.52-6.53 (dd, *J* = 3.5, 2.0 Hz, 1H), 6.81-6.82 (dd, *J* = 3.5, 0.5 Hz, 1H), 7.53-7.54 (m, 1H), 7.64-7.66 (m, 2H), 7.73-7.75 (m, 2H).



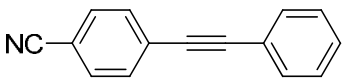
4-Methoxybiphenyl[9] **(9**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.98-7.00 (m, 2H), 7.30-7.33 (m, 1H), 7.41-7.44 (t, *J* = 7.5 Hz, 2H), 7.53-7.57 (m, 4H).



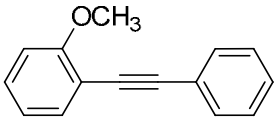
1,3-Dimethyl-2-(phenylethynyl)benzene[10] **(10**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.53 (s, 6H), 7.08 (d, *J* = 7.5 Hz, 2H), 7.13-7.16 (dd, *J* = 8.5, 6.5 Hz, 1H), 7.34-7.39 (m, 3H), 7.55-7.57 (m, 2H).



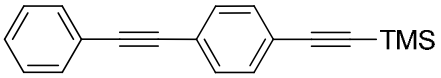
3,4,5-Trimethoxy-2-(phenylethynyl)benzaldehyde (11). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.94 (s, 3H), 3.99 (s, 3H), 4.04 (s, 3H), 7.28 (s, 1H), 7.37-7.38 (m, 3H), 7.55-7.57 (m, 2H), 10.53 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.2, 61.2, 61.5, 80.6, 99.2, 105.3, 115.9, 122.7, 128.5, 128.8, 131.5, 131.8, 147.6, 154.0, 154.6, 190.6. HRMS (ESI) Calcd. for $C_{18}H_{16}O_4$ 296.1049, found $(M+Na)^+$ 319.0933.



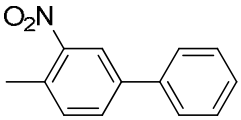
4-(Phenylethynyl)benzonitrile[11] **(12**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.39 (m, 3H), 7.53-7.56 (m, 2H), 7.60-7.65 (m, 4H).



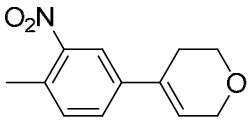
1-Methoxy-2-(phenylethynyl)benzene[12] (**13**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92 (s, 3H), 6.90-6.96 (m, 2H), 7.29-7.36 (m, 4H), 7.50-7.51 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.50-7.58 (m, 2H).



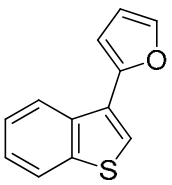
Trimethyl((4-(phenylethynyl)phenyl)ethynyl)silane[13] (**14**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.26 (s, 9H), 7.34-7.37 (m, 3H), 7.43-7.47 (m, 4H), 7.52-7.54 (m, 2H).



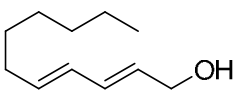
4-Methyl-3-nitrobiphenyl[14] **(15)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.64 (s, 3H), 7.39-7.49 (m, 4H), 7.59-7.61 (m, 2H), 7.72-7.74 (dd, *J* = 7.5, 1.5 Hz, 1H), 8.21 (d, *J* = 2.0 Hz, 1H).



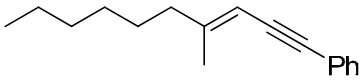
4-(4-Methyl-3-nitrophenyl)-3,6-dihydro-2H-pyran (16). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.50-2.53 (m, 2H), 2.59 (s, 3H), 3.94-3.96 (t, *J* = 5.5 Hz, 2H), 4.33-4.35 (q, *J* = 3.0 Hz, 2H), 6.22-6.24 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.51-7.53 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.98 (d, *J* = 1.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.1, 26.9, 64.2, 65.7, 120.7, 124.3, 128.9, 132.1, 132.2, 132.8, 139.3, 149.3 HRMS (ESI) Calcd. for $C_{12}H_{13}NO_3$ 219.0895, found ($M+Na^+$) 242.0781.



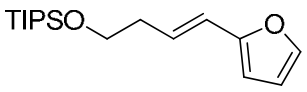
2-(Benzo[b]thiophen-3-yl)furan[15] (**17**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.55-6.56 (dd, *J* = 3.0, 1.5 Hz, 1H), 6.74 (d, *J* = 3.5 Hz, 1H), 7.39-7.49 (m, 3H), 7.69 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H).



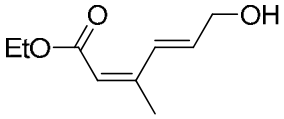
(2*E*, 4*E*)-Undeca-2,4-dien-1-ol (18). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87-0.90 (t, *J* = 7.0 Hz, 3H), 1.26-1.39 (m, 8H), 2.06-2.10 (q, *J* = 7.0 Hz, 2H), 4.15-4.17 (t, *J* = 5.8 Hz, 2H), 5.68-5.75 (m, 2H), 6.02-6.07 (dd, *J* = 15.0, 10.0 Hz, 1H), 6.19-6.24 (dd, *J* = 15.5, 10.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 28.9, 29.2, 31.7, 32.6, 63.6, 129.3, 132.2, 135.9. HRMS (EI) Calcd. for $C_{11}H_{20}O$ 168.1514, found 168.1513.



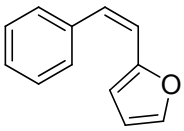
(*E*)-(4-Methyldec-3-en-1-ynyl)benzene (19). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88-0.91 (t, *J* =7.0 Hz, 3H) 1.26-1.33 (m, 6H), 1.43-1.54 (m, 2H), 1.97 (s, 3H), 2.21-2.15 (t, *J* = 7.5 Hz, 2H), 5.49 (s, 1H), 7.26-7.32 (m, 3H), 7.42-7.44 (dd, *J* = 7.5, 1.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 19.4, 22.6, 27.6, 28.9, 31.7, 38.8, 87.8, 91.7, 104.6, 124.1, 127.6, 128.2, 131.2, 153.0. HRMS (EI) Calcd. for $C_{17}H_{22}$ 226.1722, found 226.1728.



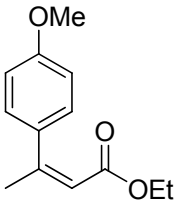
(*E*)-(4-(Furan-2-yl)but-3-enyloxy)triisopropylsilane (20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07 (s, 18H), 2.41-2.45 (m, 3H), 3.69-3.83 (m, 4H), 6.14-6.39 (m, 5H), 7.03 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.0, 18.0, 36.6, 63.1, 106.2, 111.0, 120.2, 126.2, 141.3, 153.2. HRMS (EI) Calcd. for $C_{17}H_{30}O_2Si$ 294.2015, found 294.1991.



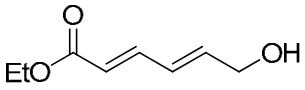
(2*Z*, 4*E*)-Ethyl 6-hydroxy-3-methylhexa-2,4-dienoate (21). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26-1.29 (t, *J* = 7.3 Hz, 3H), 2.01 (d, *J* = 1.0 Hz, 3H), 4.14-4.18 (q, *J* = 7.0 Hz, 2H), 4.32 (br, 2H), 5.70 (s, 1H), 6.20-6.25 (dt, *J*=16.0, 5.5 Hz, 1H), 7.72-7.76 (dd, *J* = 16.0, 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 21.0, 59.8, 63.6, 117.9, 127.8, 135.9, 150.0, 166.2. HRMS (EI) Calcd. for $C_9H_{14}O_3$ 170.0943, found 170.0950.



(*Z*)-2-Styrylfuran[16] (*Z*-**22**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.25 (d, *J* = 3.0 Hz, 1H,), 6.32-6.33 (dd, *J* = 3.5, 2.0 Hz, 1H), 6.38 (d, *J* = 12.5 Hz, 1H), 6.49 (d, *J* = 12.5 Hz 1H), 7.27-7.36 (m, 4H), 7.46 (d, *J* = 8.0 Hz, 2H).



(*Z*)-Ethyl 3-(4-methoxyphenyl)but-2-enoate[17] **(*Z*-24)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12-1.15 (t, *J* = 7.0 Hz, 3H), 2.16 (d, *J* =1.5 Hz, 3H), 3.82 (s, 3H), 4.01-4.06 (q, *J* = 7.5 Hz, 2H), 5.87-5.88 (q, *J* = 1.5 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 7.19 (d, *J* = 9.0 Hz, 2H).



(2*E*,4*E*)-Ethyl 6-hydroxyhexa-2,4-dienoate[18] **(25)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.29-1.31 (t, *J* = 7.0 Hz,

3H), 4.19-4.23 (q, *J* = 7.0 Hz, 2H), 4.30-4.31 (dd, *J* = 5.0, 1.0 Hz, 2H), 5.89 (d, *J* = 15.5 Hz, 1H), 6.20-6.25 (dt, *J* = 15.5, 5.0 Hz, 1H), 6.39-6.45 (m, 1H), 7.27-7.32 (dd, *J* = 15.5, 11.0 Hz, 1H).

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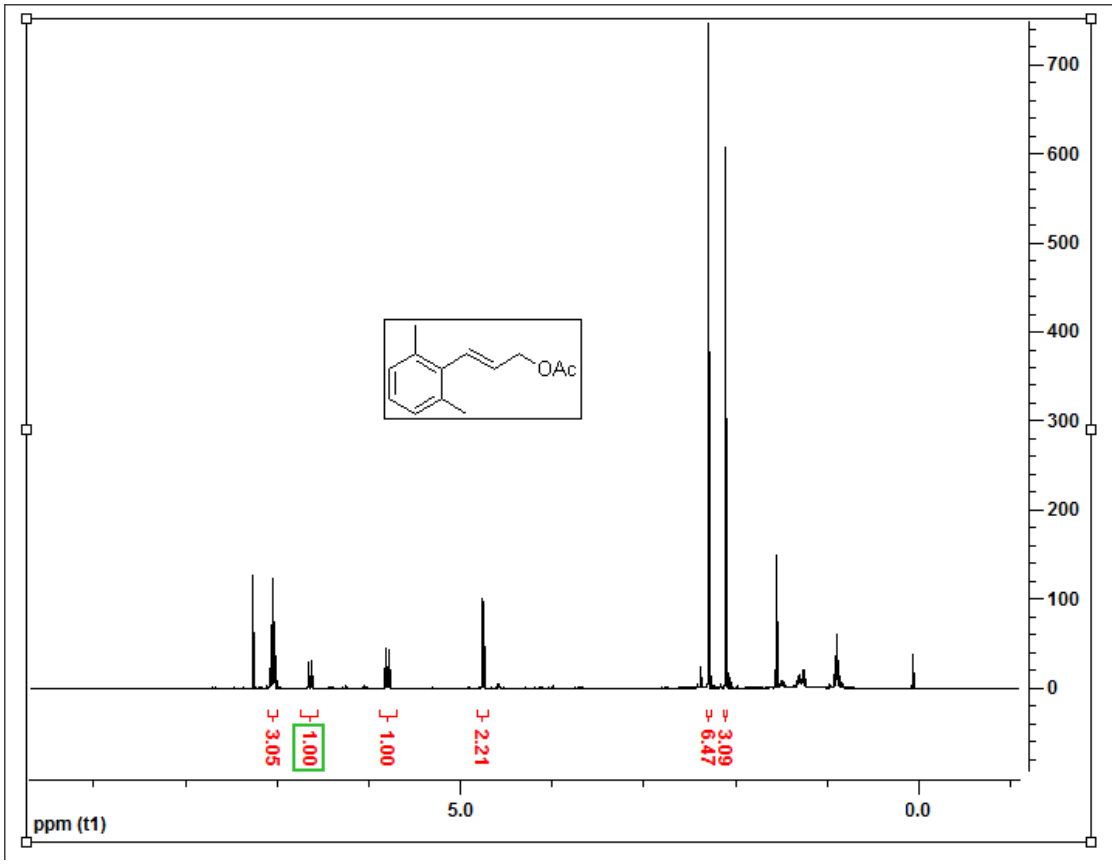
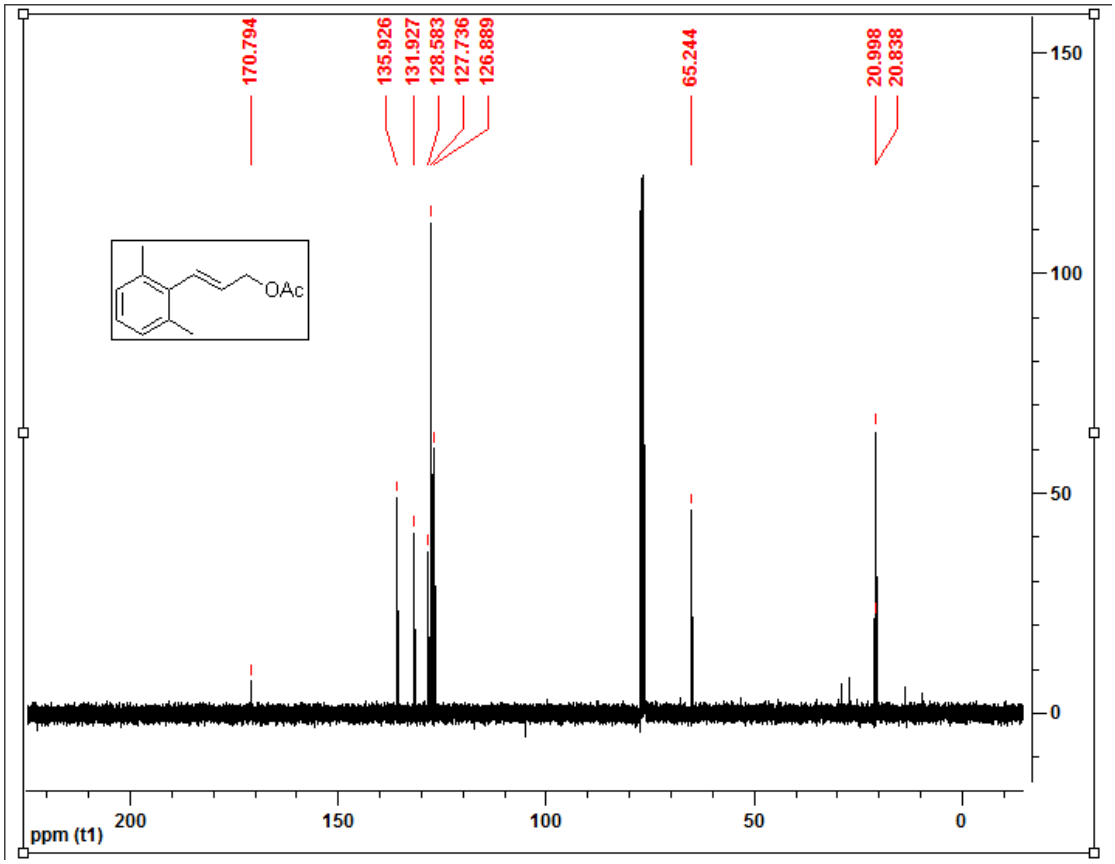
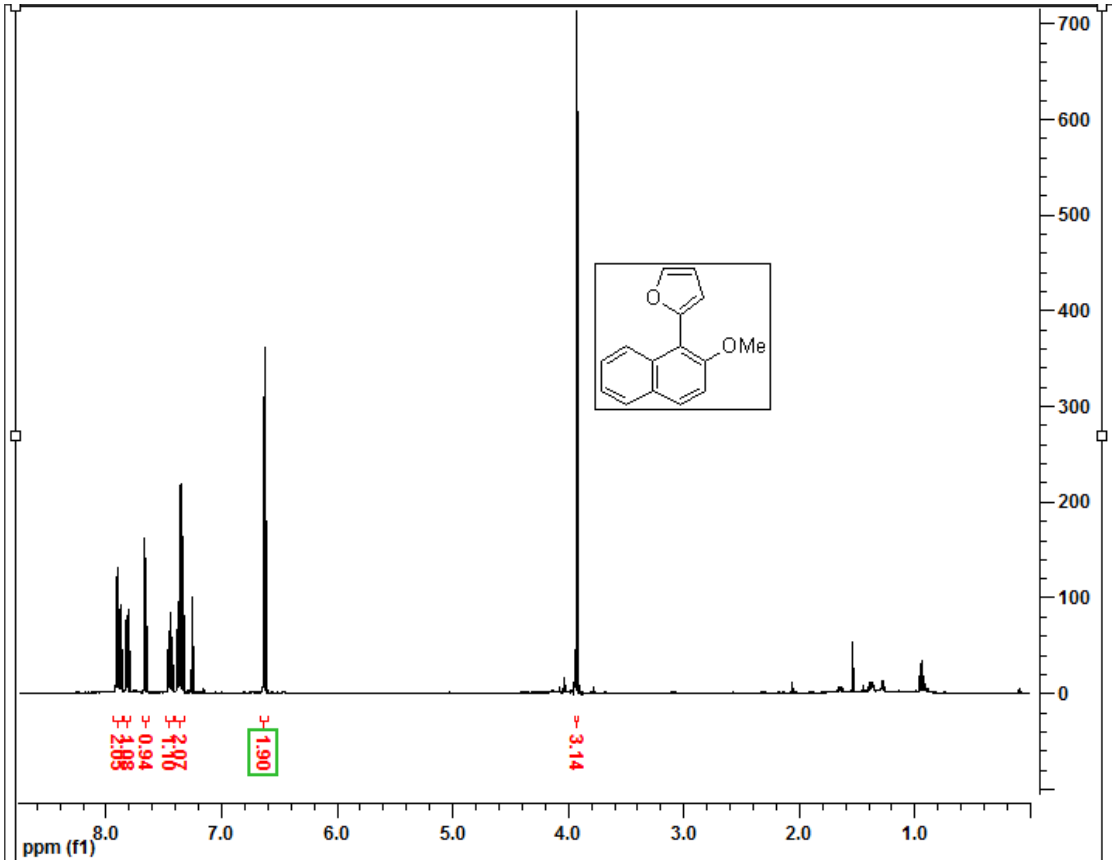
3. NMR Spectra of New Compounds



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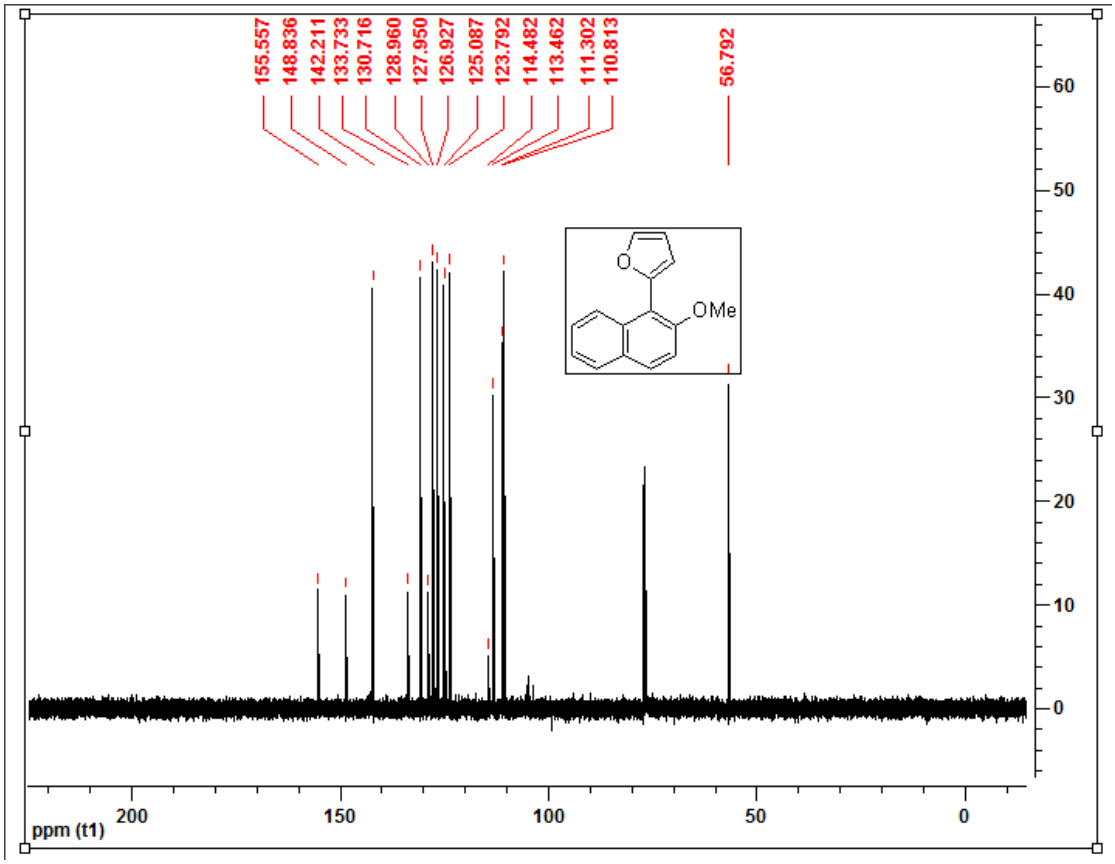
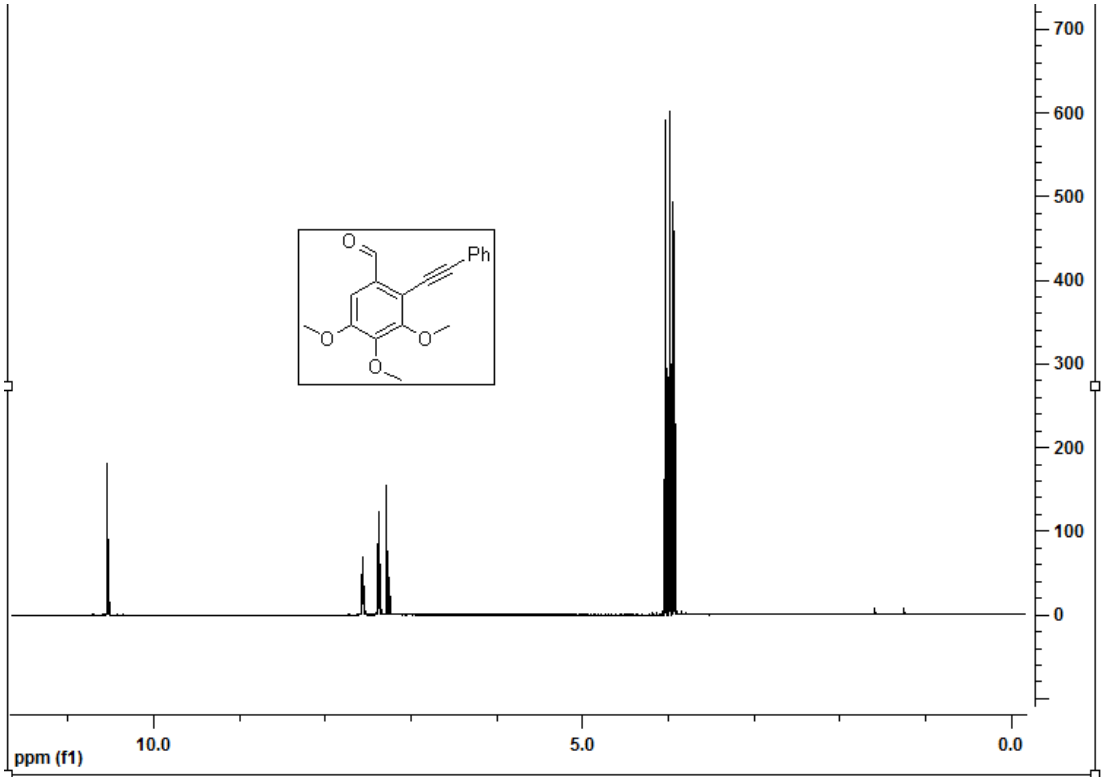
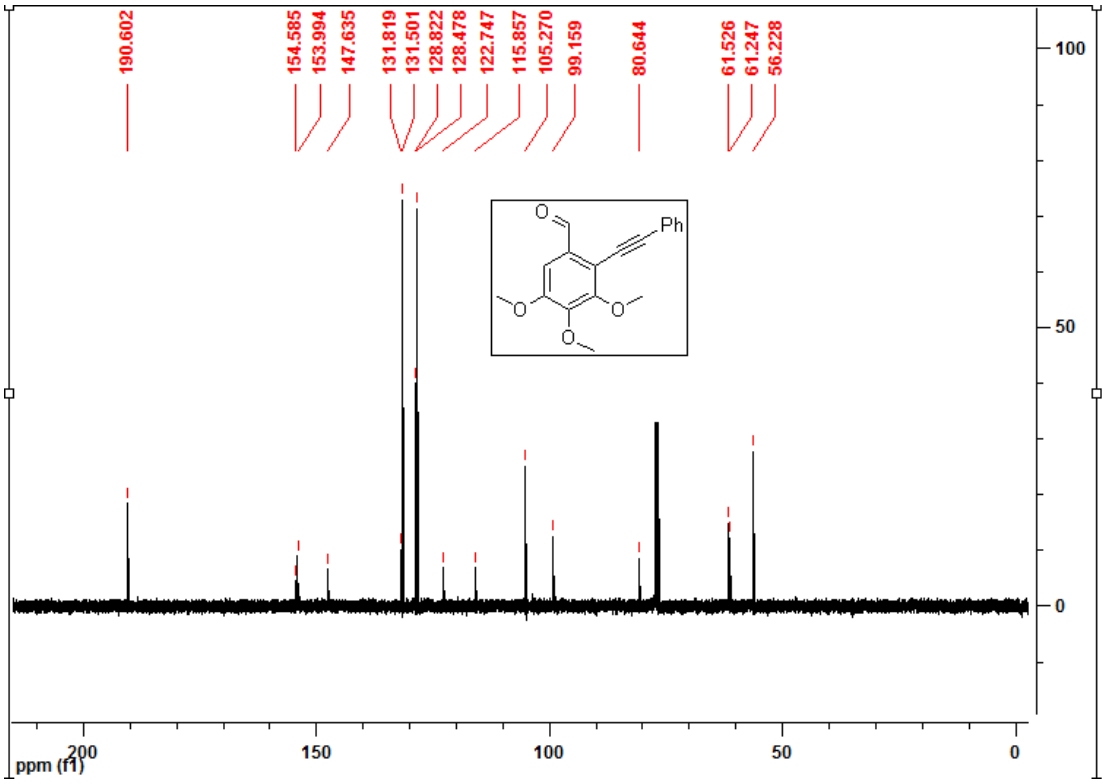
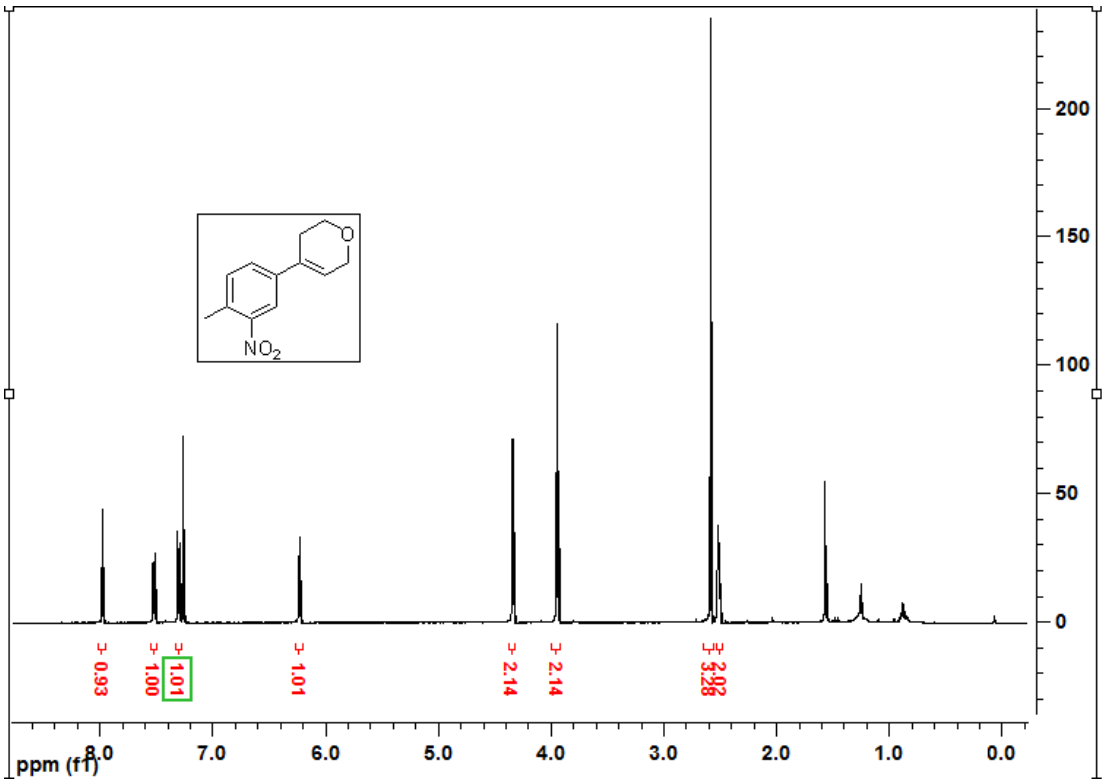
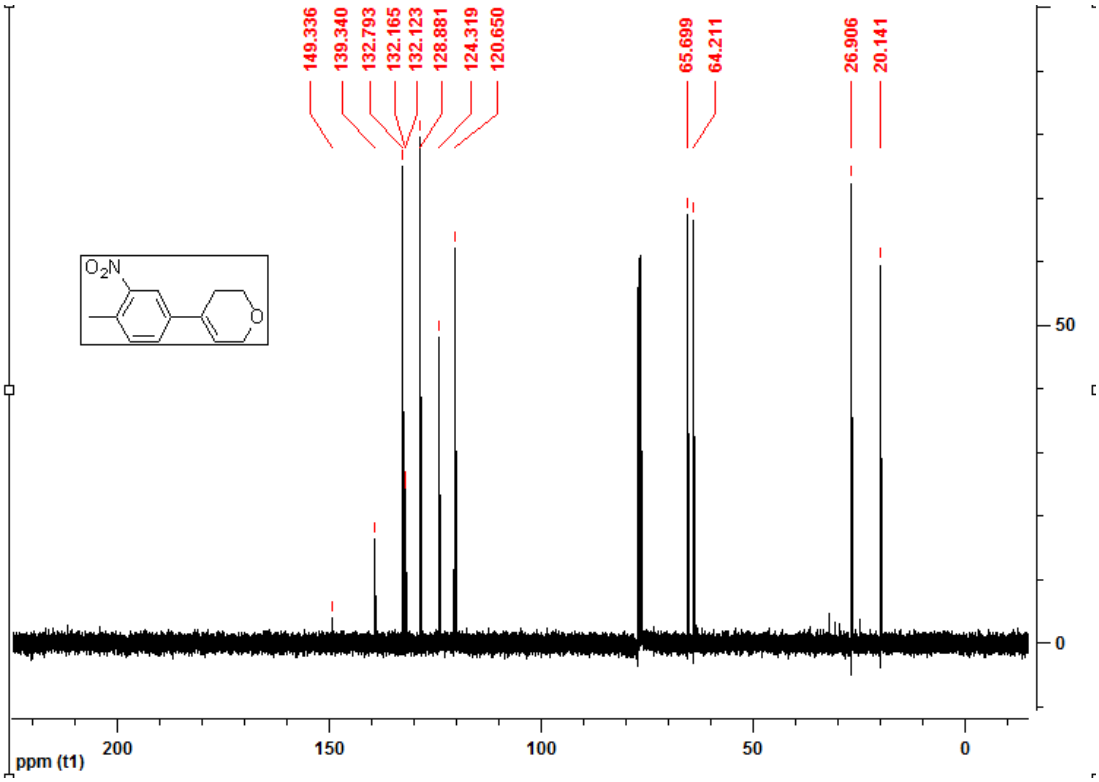
2.08
0.94
2.10
1.90
3.14
ppm (f1)

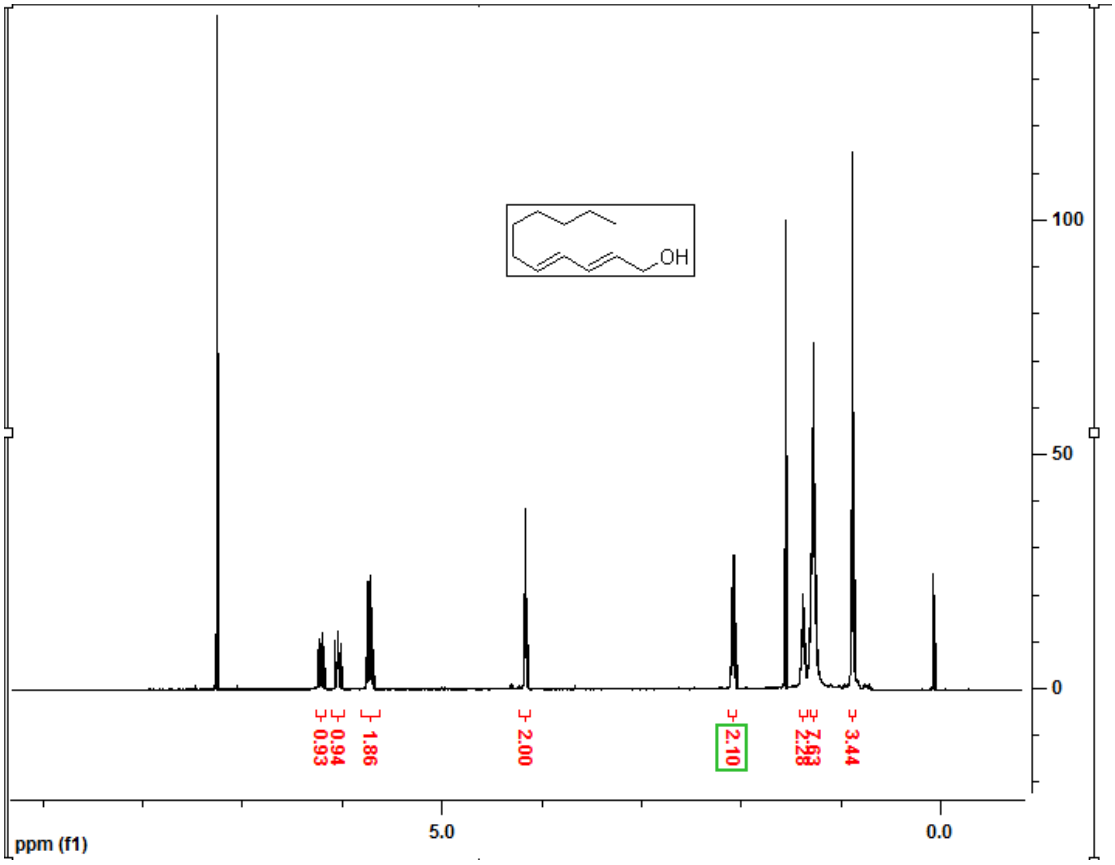

155.557
148.836
142.211
133.733
130.716
128.960
127.950
126.927
125.087
123.792
114.482
113.462
111.302
110.813
56.792
OMe
ppm (t1)

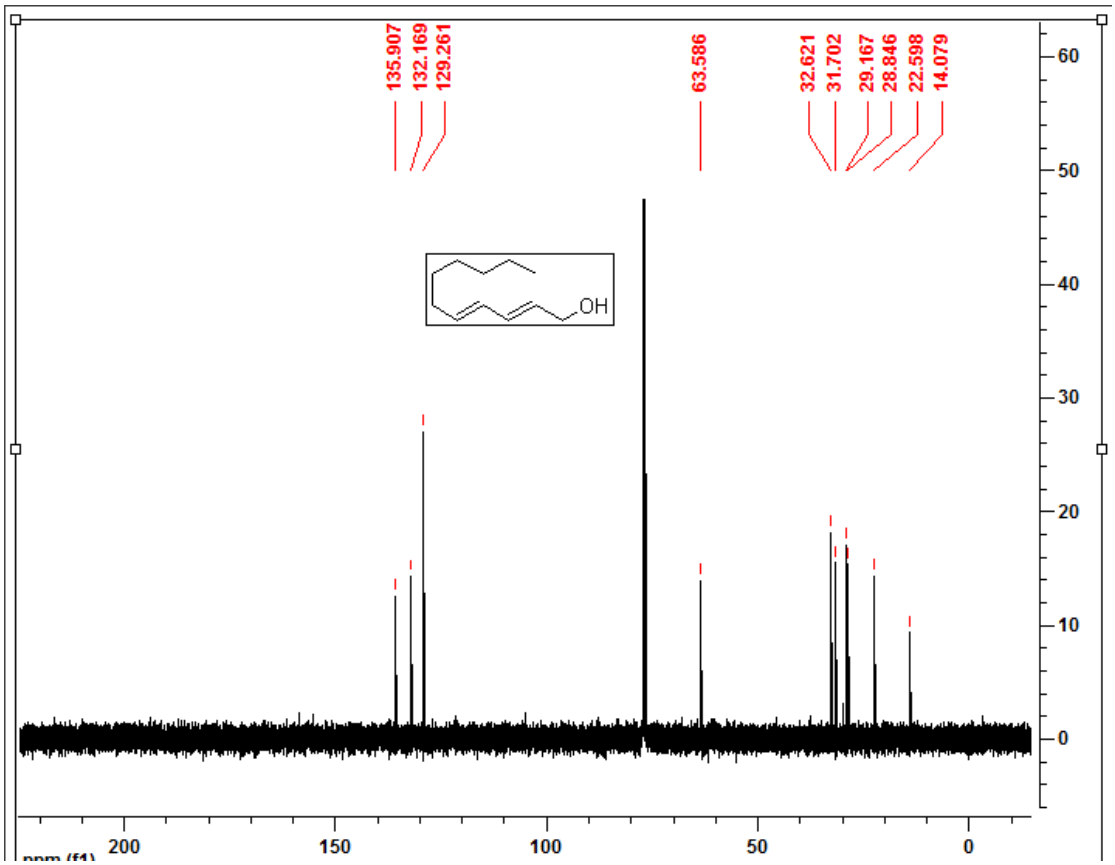

O
Ph
O
O
O
700
600
500
400
300
200
100
0
10.0
5.0
0.0
ppm (f1)

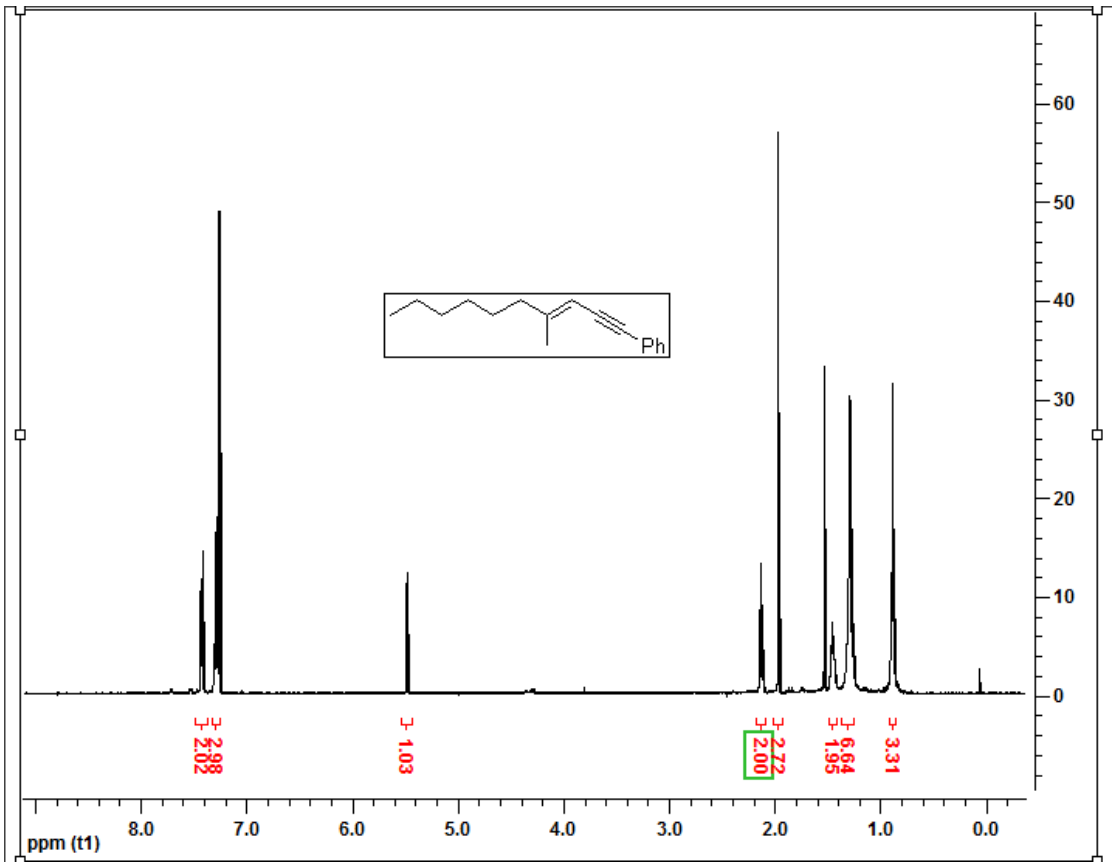

190.602
154.585
153.994
147.635
131.819
131.501
128.822
128.478
122.747
115.857
105.270
99.159
80.644
61.526
61.247
56.228
O
Ph
O
O
O
100
50
0
200
150
100
50
0
ppm (f1)

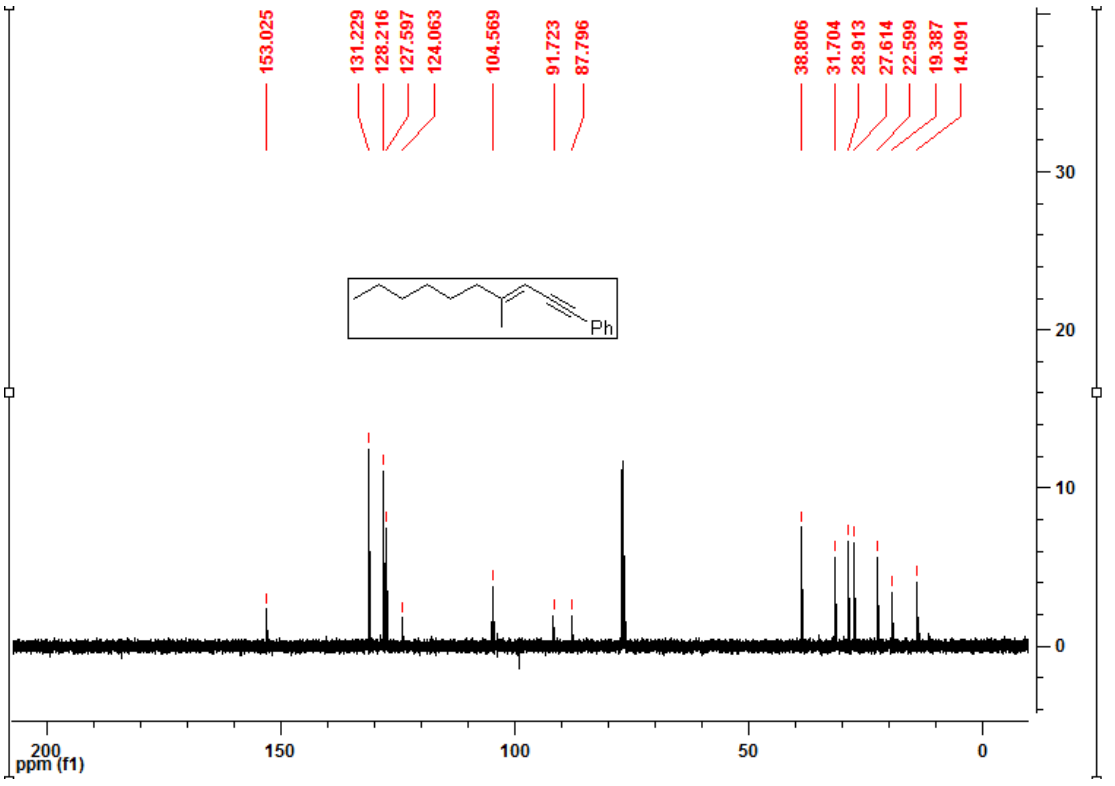

NO2
0.93
1.00
1.01
1.01
2.14
2.14
2.22
2.28
ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
200
150
100
50
0

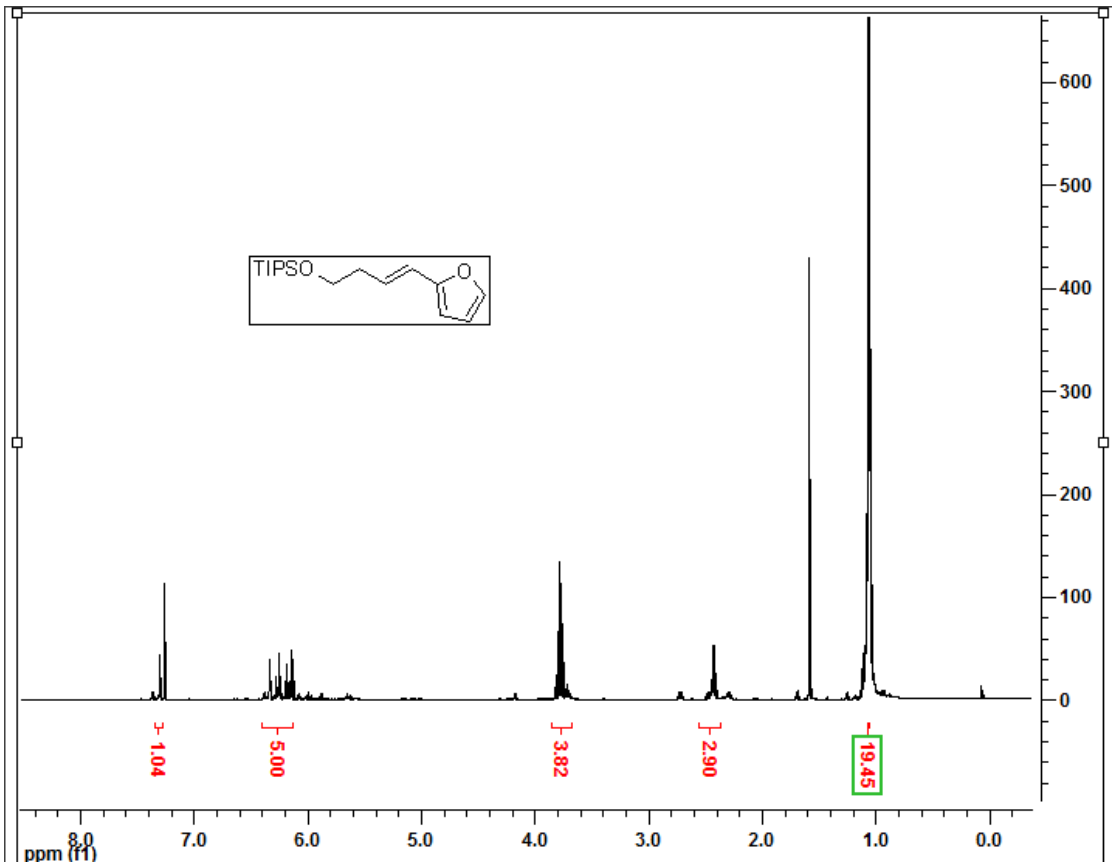

O2N
149.336
139.340
132.793
132.165
132.123
128.881
124.319
120.650
65.699
64.211
26.906
20.141
ppm (t1)
200
150
100
50
0
50
0

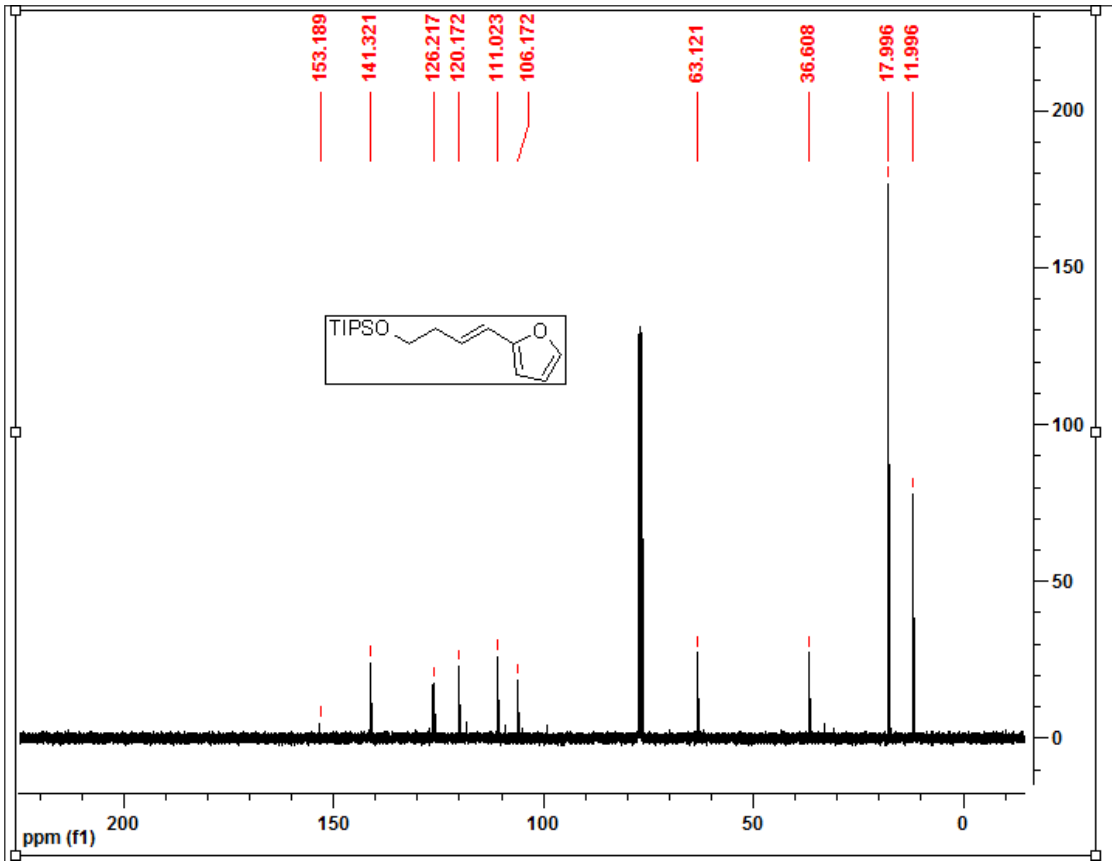

OH
100
50
0
0.93
0.94
1.86
2.00
2.10
2.58
2.93
3.44
5.0
0.0
ppm (f1)


135.907
132.169
129.261
63.586
32.621
31.702
29.167
28.846
22.598
14.079
OH
60
50
40
30
20
10
0
200
150
100
50
0


Ph
2.02
2.00
1.03
2.22
6.64
1.95
3.31
ppm (t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


153.025
131.229
128.216
127.597
124.063
104.569
91.723
87.796
38.806
31.704
28.913
27.614
22.599
19.387
14.091
Ph
ppm (f1)
200
150
100
50
0


TIPSO
O
1.04
5.00
3.82
2.90
19.45
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
600
500
400
300
200
100
0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141.321
126.217
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106.172
63.121
36.608
17.996
11.996
TIPSO
O
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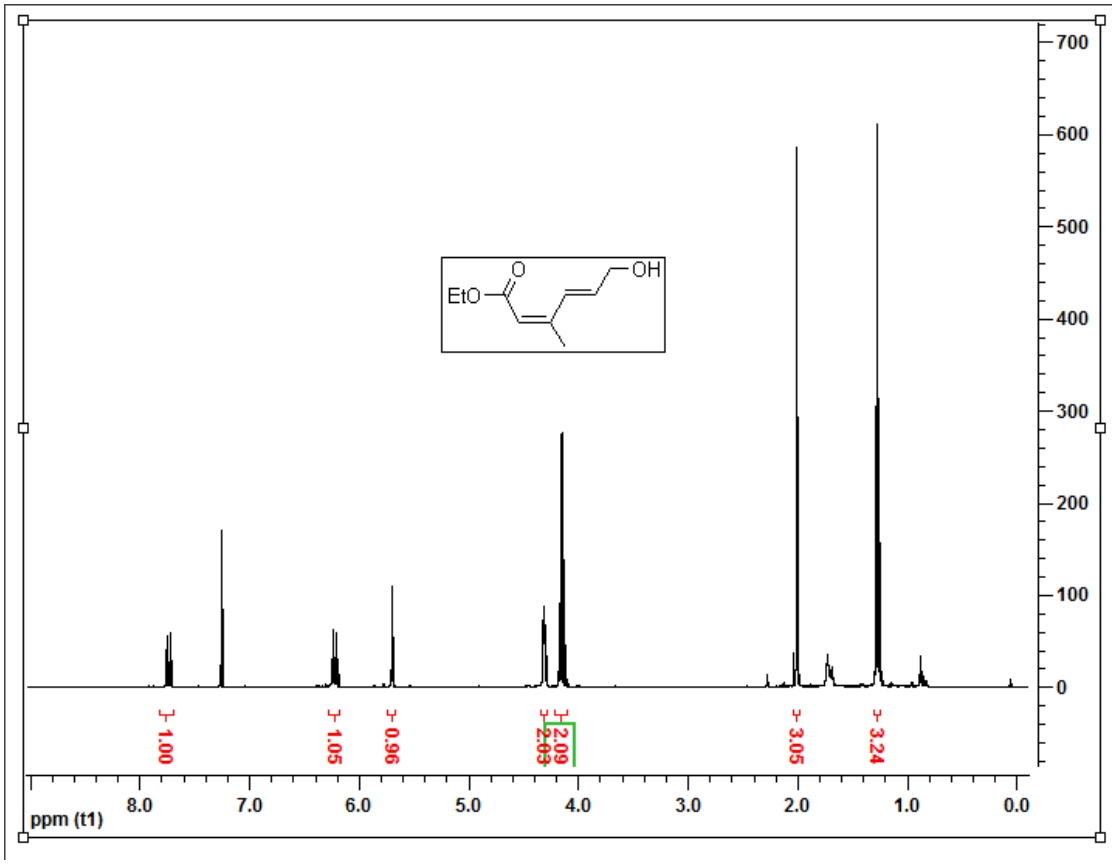
150
100
50
0
ppm (f1)


EtO
O
OH
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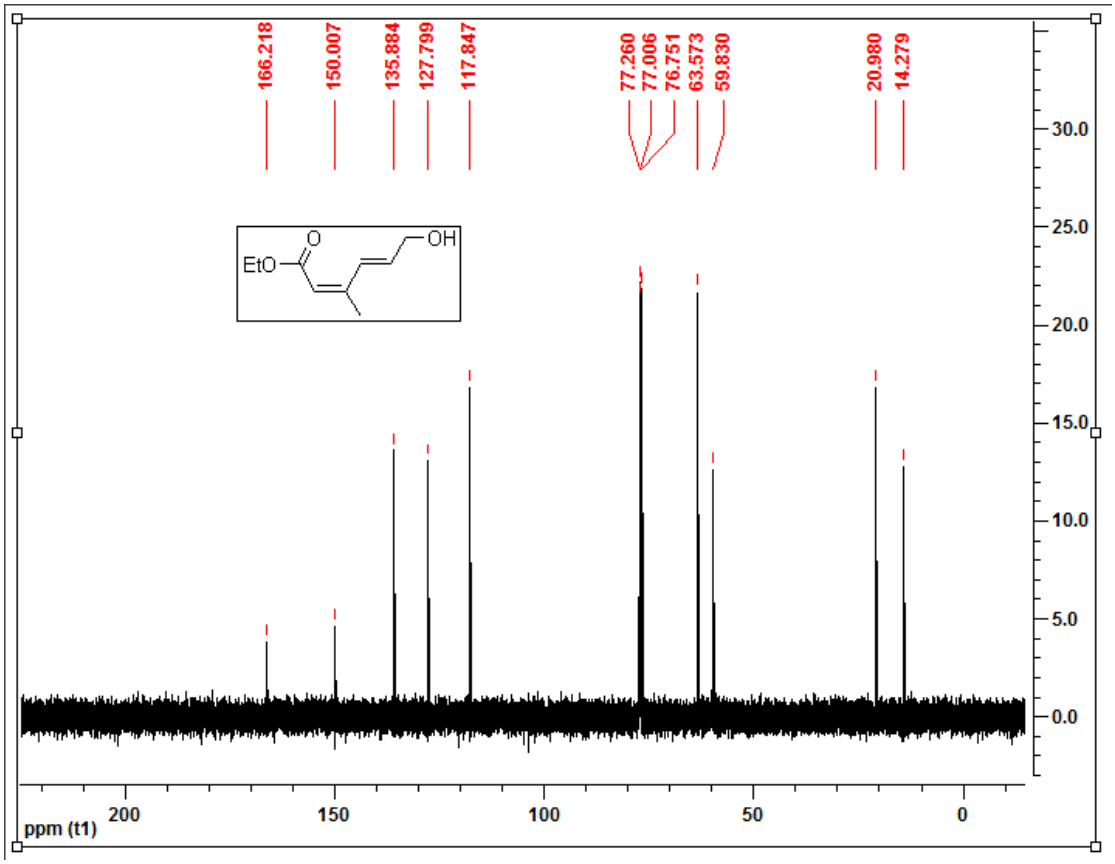
0.96
2.03
2.09
3.05
3.24
ppm (t1)


166.218
150.007
135.884
127.799
117.847
77.260
77.006
76.751
63.573
59.830
20.980
14.279
EtO
O
OH
ppm (t1)