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Supplementary material: *n*-selective Tsuji–Trost allylation promoted by a recyclable TSIL-palladium complex

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1. Optimimization of some reaction parameters

To find the optimum conditions of the reaction, it was decided to apply a Central Composite Design + star. This is a useful response surface methodology to build a second order model for the response variable. The temperature (A), the time (B) and the concentration of the TSIL (C) were chosen as the variables of study through 16 experiments. The results of the design show that the optimum conditions are the followings: temperature (120 °C), time (24 h), and TSIL concentration (18%). However, as we can see in the Pareto chart, the three variables are not critical, so it was decided to use commitment conditions to perform the reaction under milder conditions. These commitment conditions are the following: temperature (80 °C), time (17 h), and TSIL concentration (5%) (Figure 1). The presence of ligand **1** is crucial for the reaction completion.

* Corresponding author.

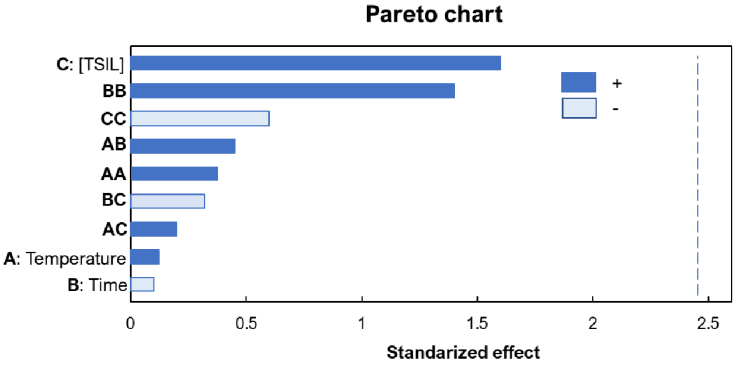
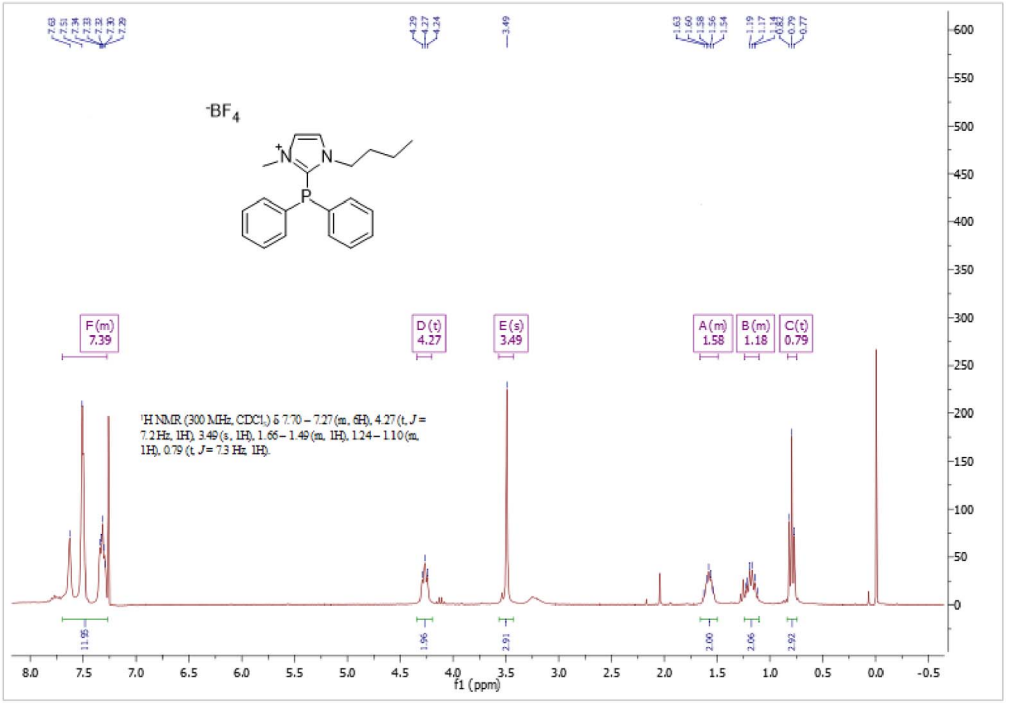
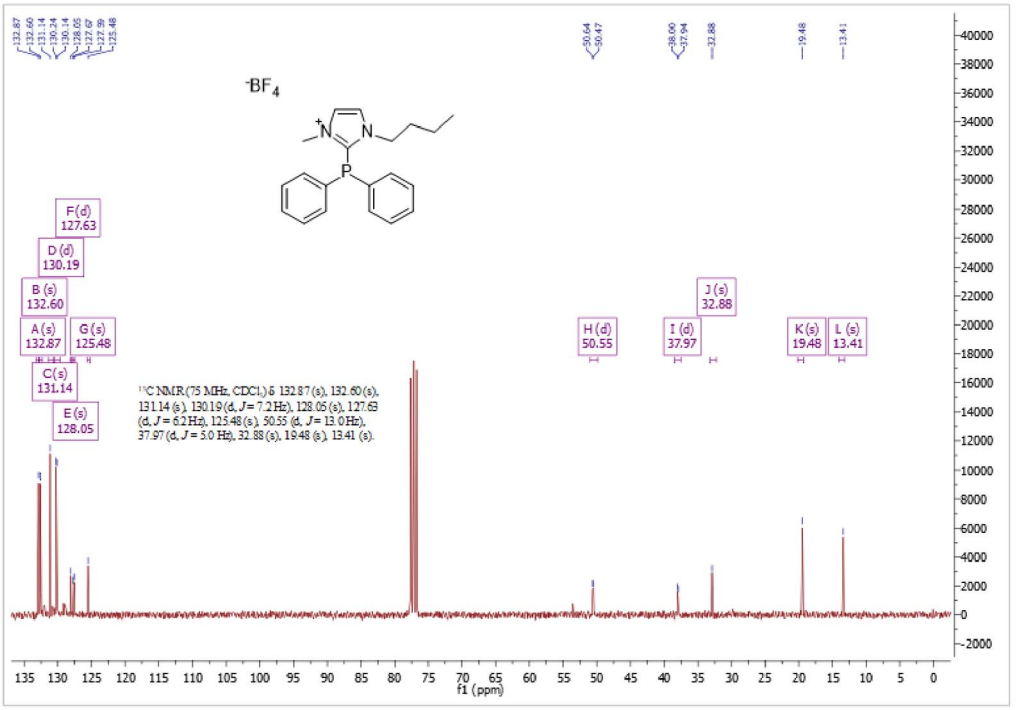


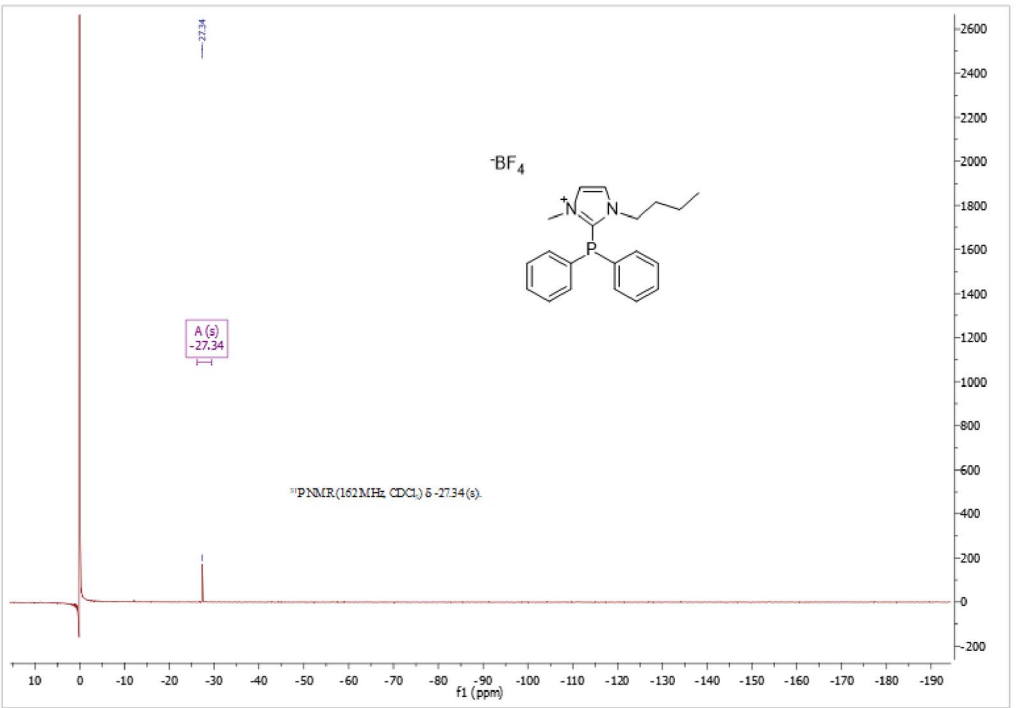
Figure 1. Pareto chart obtained from the application of Central Composite Design + star (CCD + star) to our Tsuji–Trost process.

2. ^{1}H and ^{13}NMR spectra

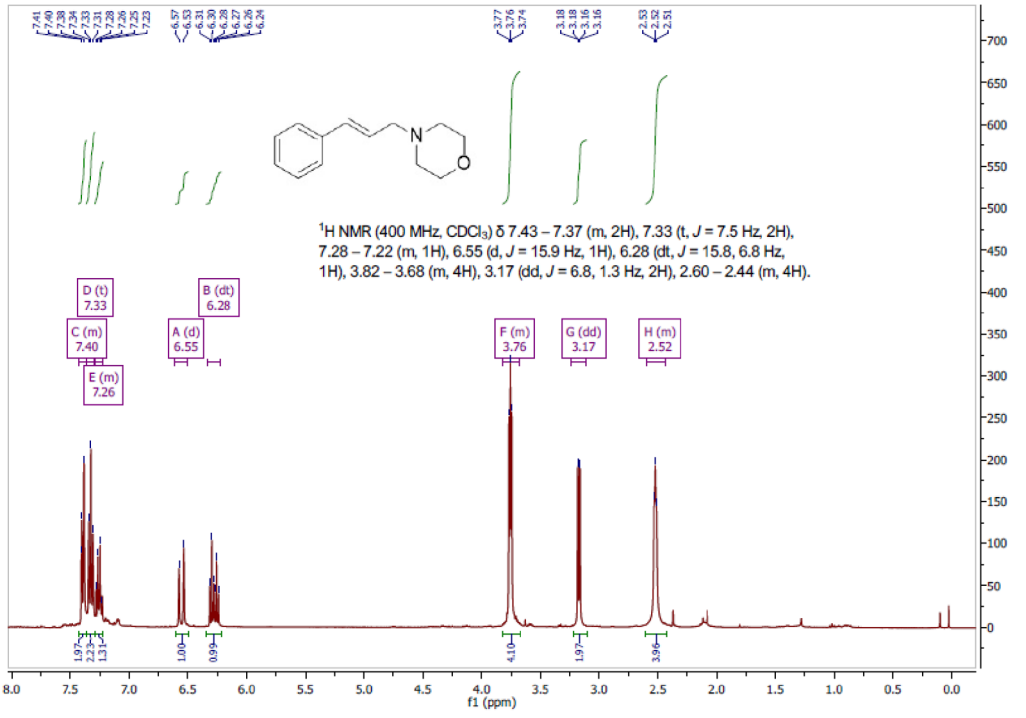
Compound ***1***

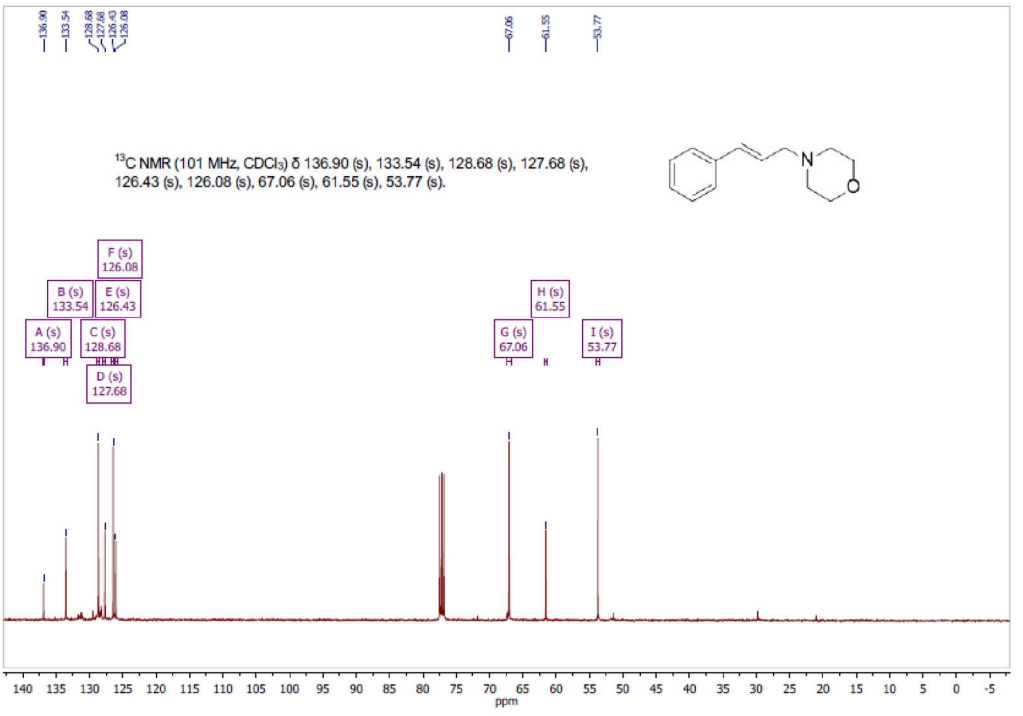



$^{-}BF_4$
F (d) 127.63
D (d) 130.19
B (s) 132.60
A (s) 132.87
G (s) 125.48
C (s) 131.14
E (s) 128.05
H (d) 50.55
I (d) 37.97
J (s) 32.88
K (s) 19.48
L (s) 13.41
^{13}C NMR (75 MHz, CDCl$_3$) δ 132.87 (s), 132.60 (s), 131.14 (s), 130.19 (d, J = 7.2 Hz), 128.05 (s), 127.63 (d, J = 6.2 Hz), 125.48 (s), 50.55 (d, J = 13.0 Hz), 37.97 (d, J = 5.0 Hz), 32.88 (s), 19.48 (s), 13.41 (s).
f1 (ppm)

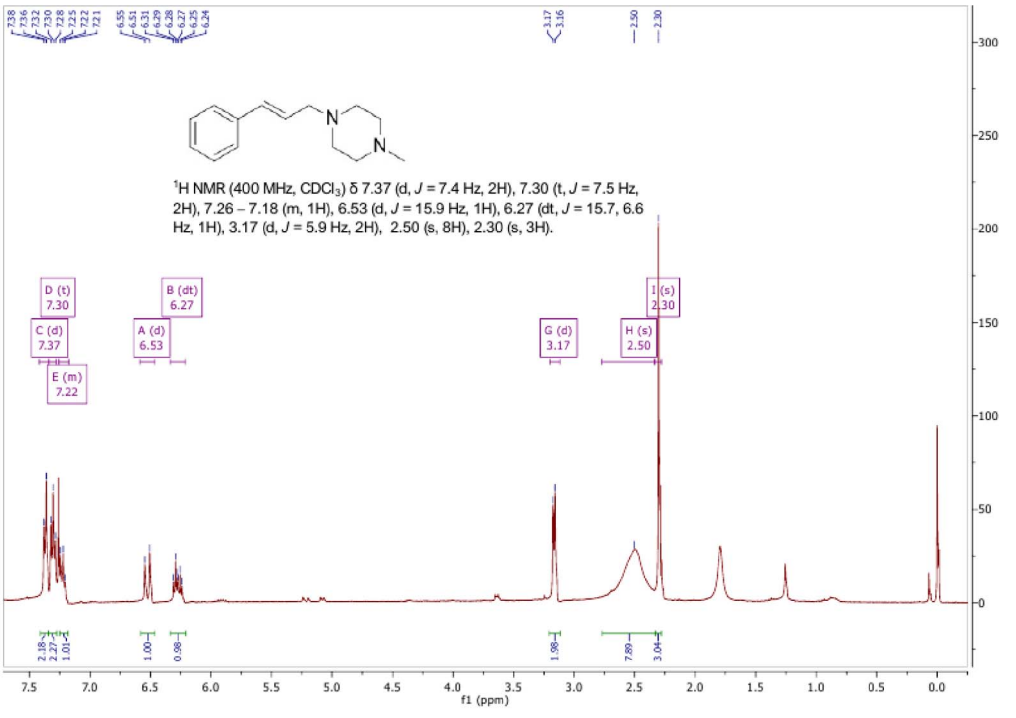

$^{-}BF_4$
A (s) -27.34
^{31}P NMR (162 MHz, CDCl$_3$) δ -27.34 (s).
f1 (ppm)

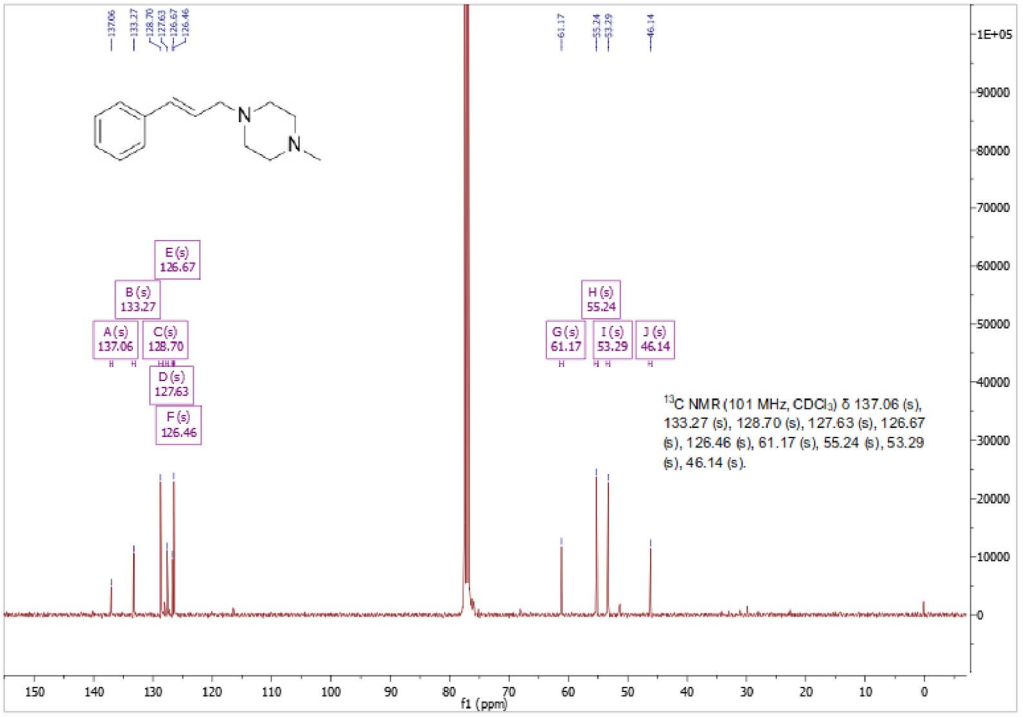
Compound ***4aa***



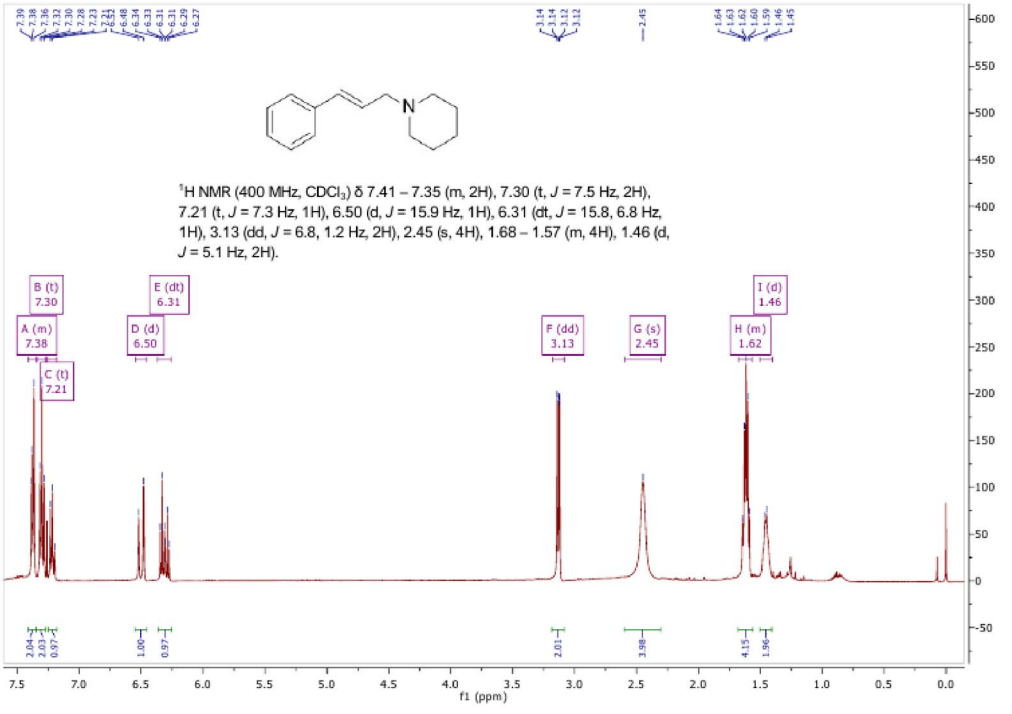


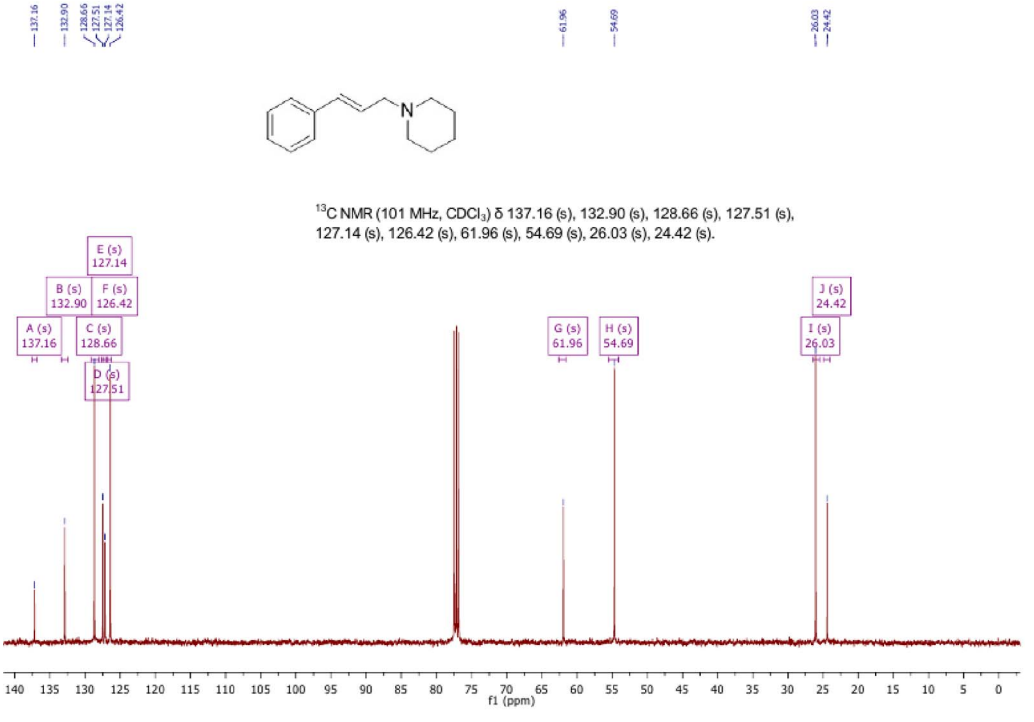
Compound ***4ab***



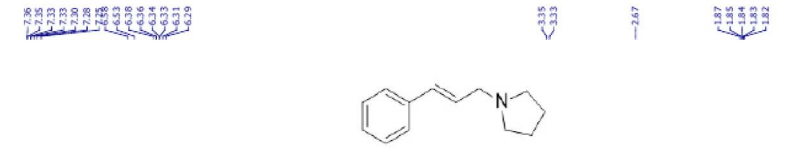


Compound ***4ac***

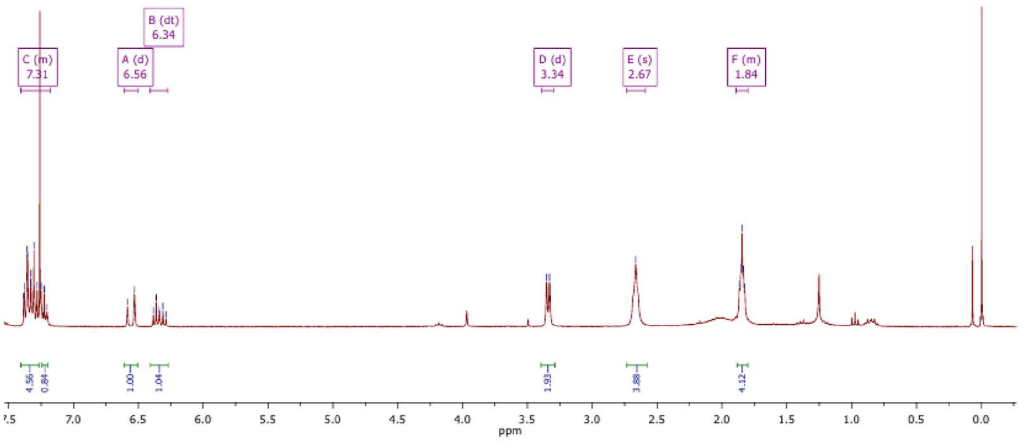


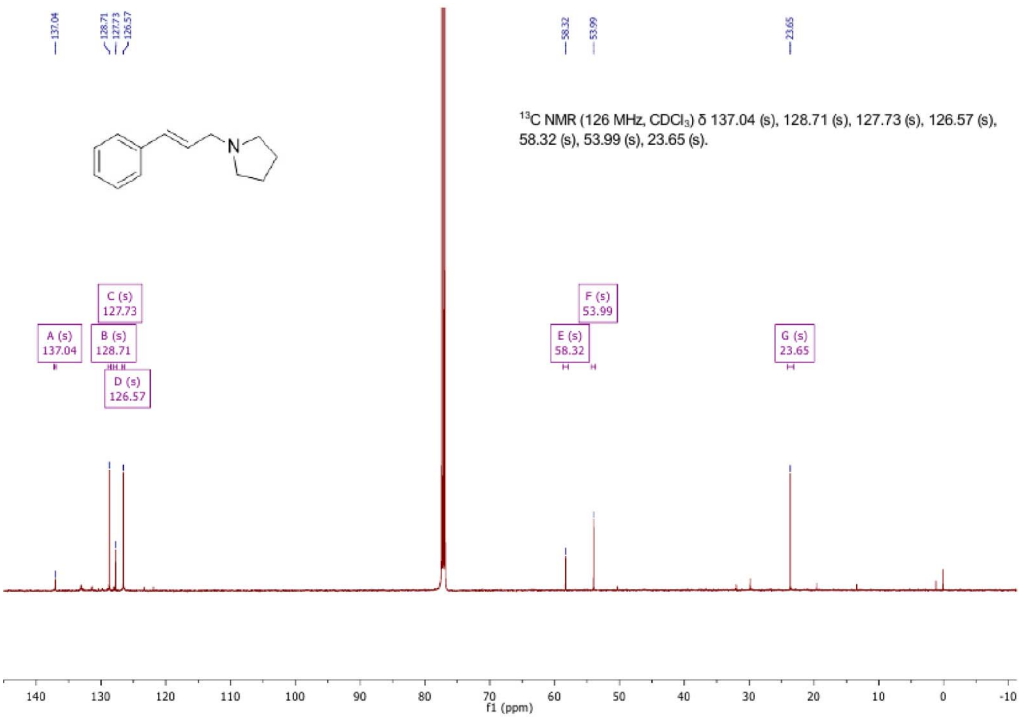


Compound ***4ad***



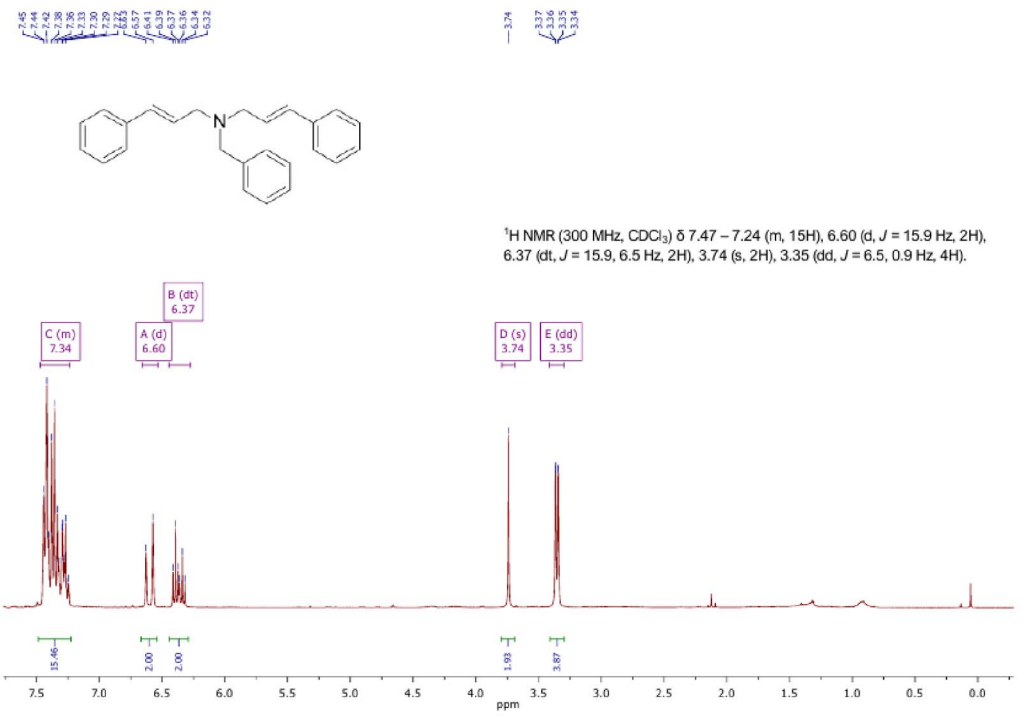
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.18 (m, 5H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.34 (dt, *J* = 15.8, 6.7 Hz, 1H), 3.34 (d, *J* = 6.4 Hz, 2H), 2.67 (s, 4H), 1.89 – 1.80 (m, 4H).



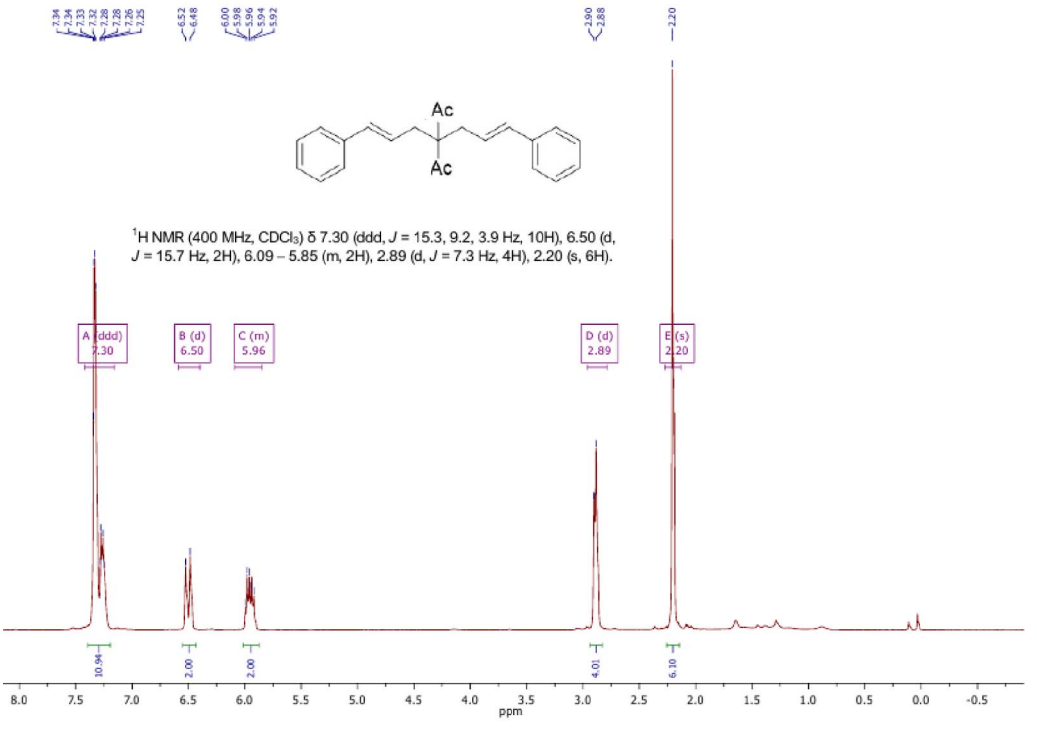


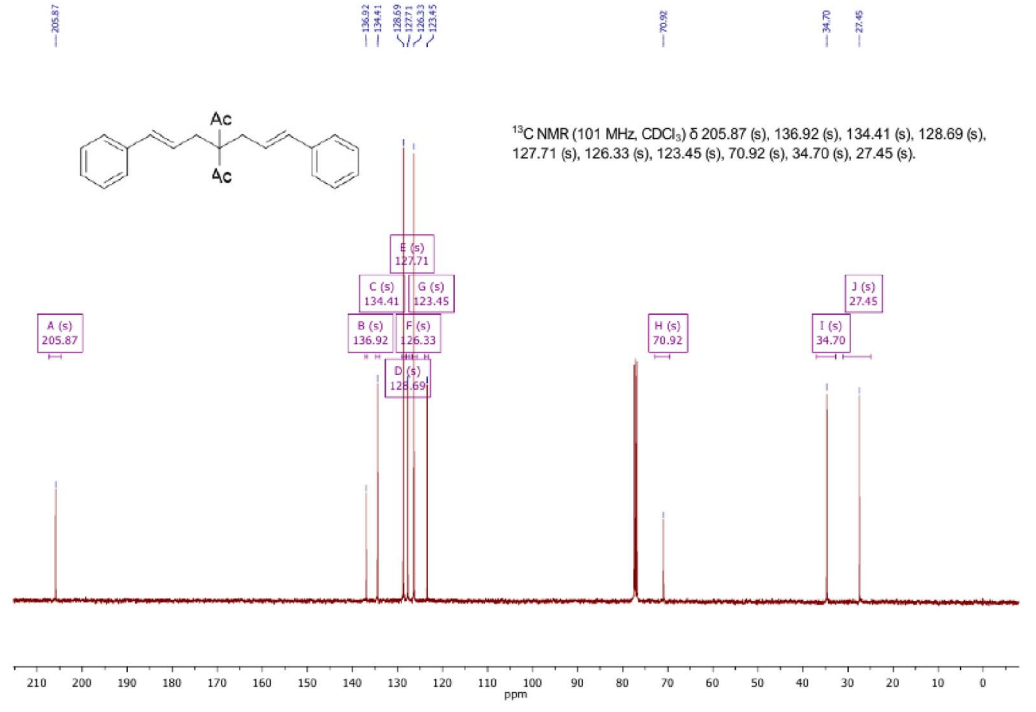
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.04 (s), 128.71 (s), 127.73 (s), 126.57 (s), 58.32 (s), 53.99 (s), 23.65 (s).

Compound ***4ae***

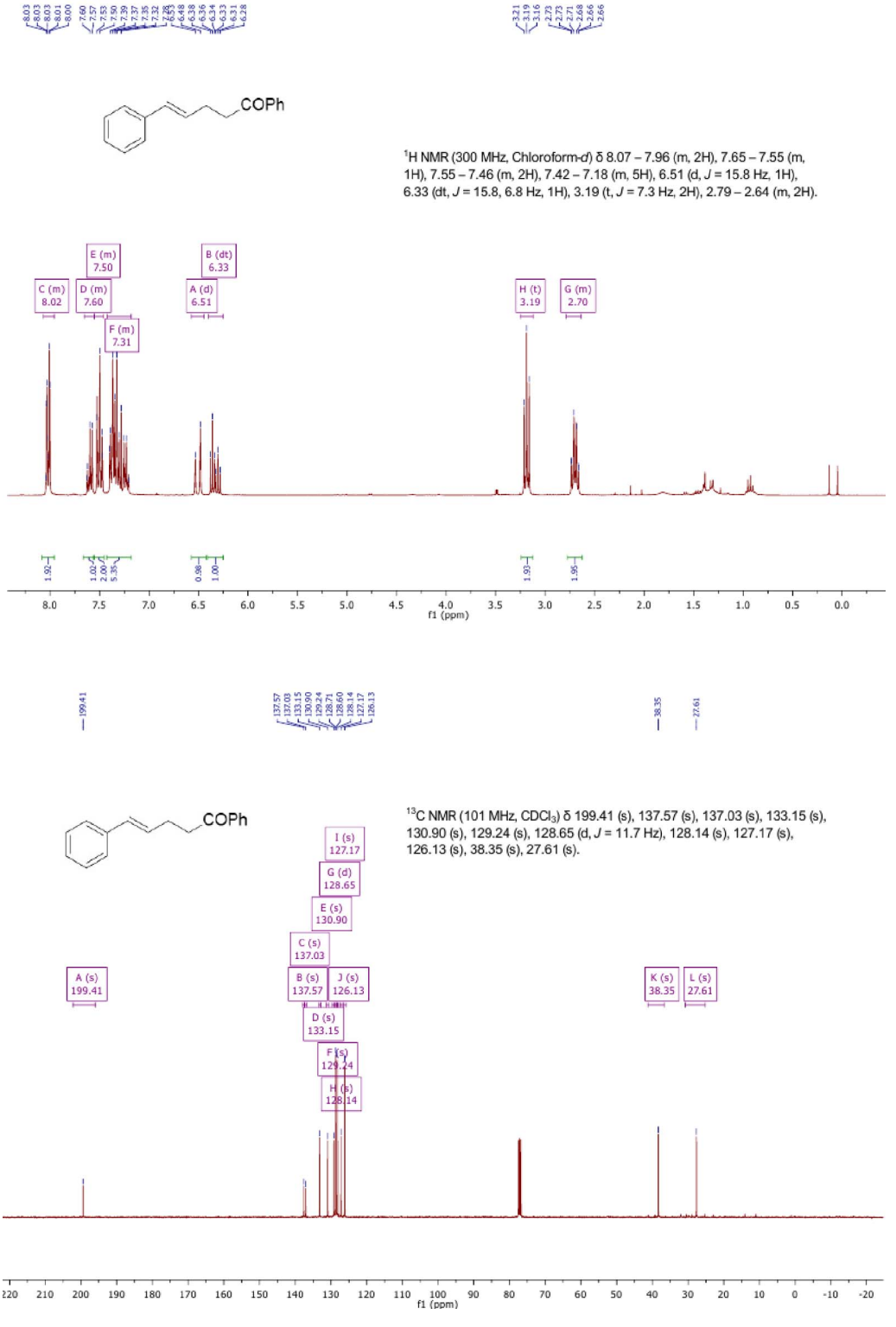


Compound ***4af***

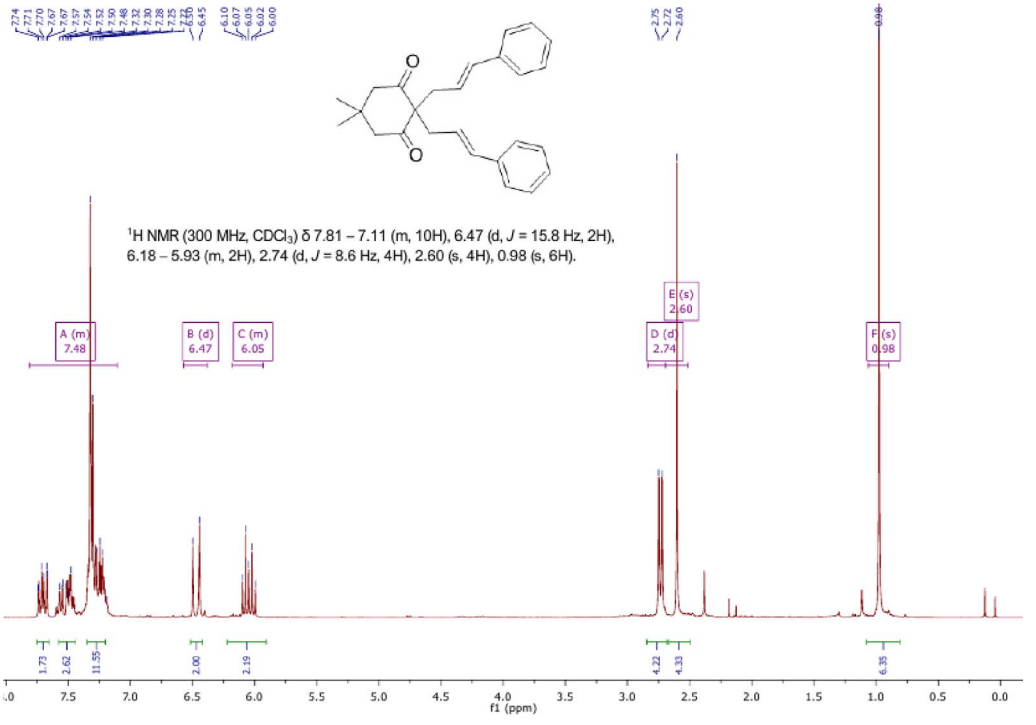


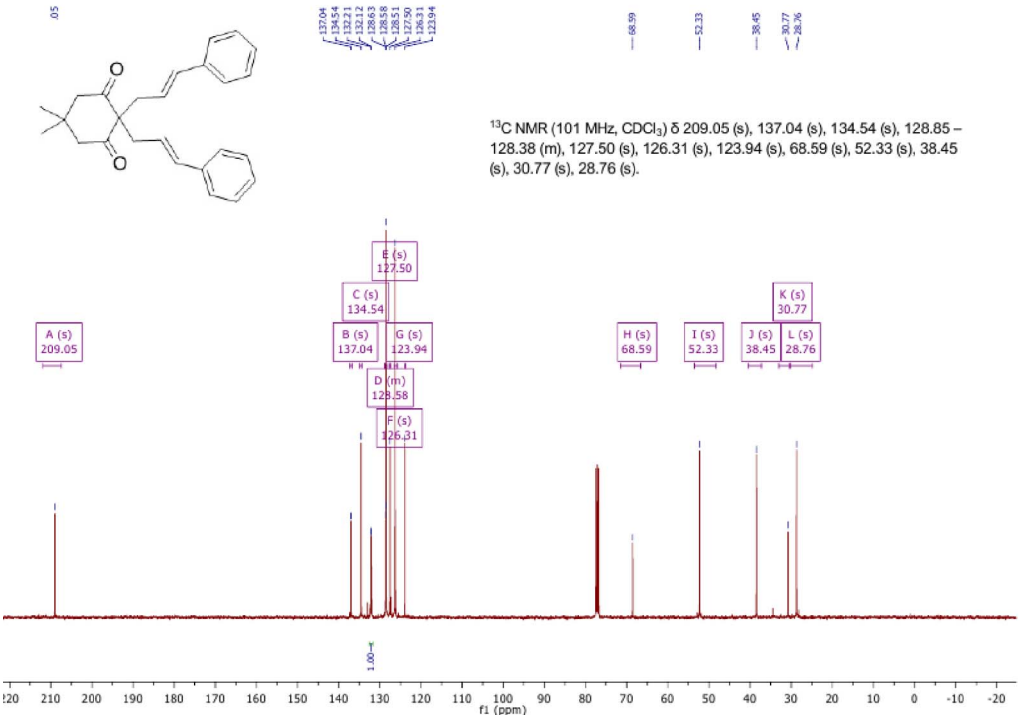


Compound ***4ag***

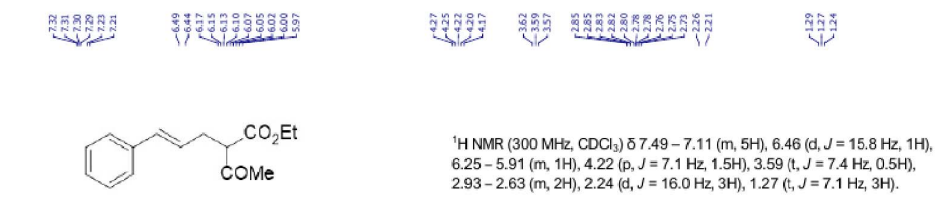


*Compound **4ah***

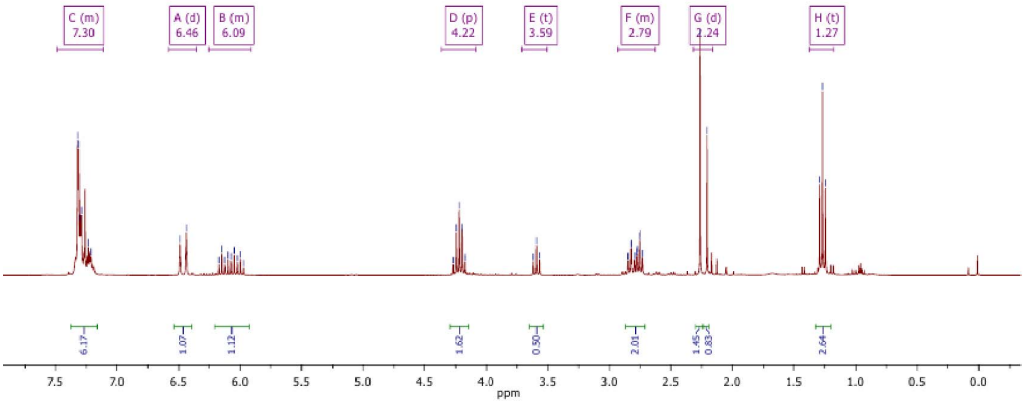


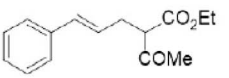


*Compound **4ai***

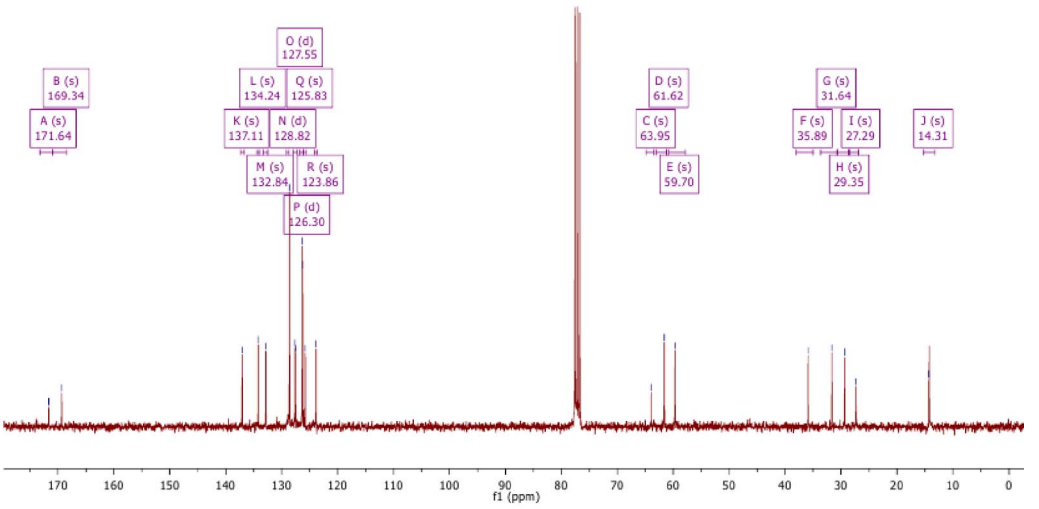


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.11 (m, 5H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.25 – 5.91 (m, 1H), 4.22 (p, *J* = 7.1 Hz, 1.5H), 3.59 (t, *J* = 7.4 Hz, 0.5H), 2.93 – 2.63 (m, 2H), 2.24 (d, *J* = 16.0 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).





^{13}C NMR (75 MHz, $CDCl_3$) δ 171.64 (s), 169.34 (s), 137.11 (s), 134.24 (s), 132.84 (s), 128.82 (d, *J* = 13.6 Hz), 127.55 (d, *J* = 7.0 Hz), 126.30 (d, *J* = 4.2 Hz), 125.83 (s), 123.86 (s), 63.95 (s), 61.62 (s), 59.70 (s), 35.89 (s), 31.64 (s), 29.35 (s), 27.29 (s), 14.31 (s).



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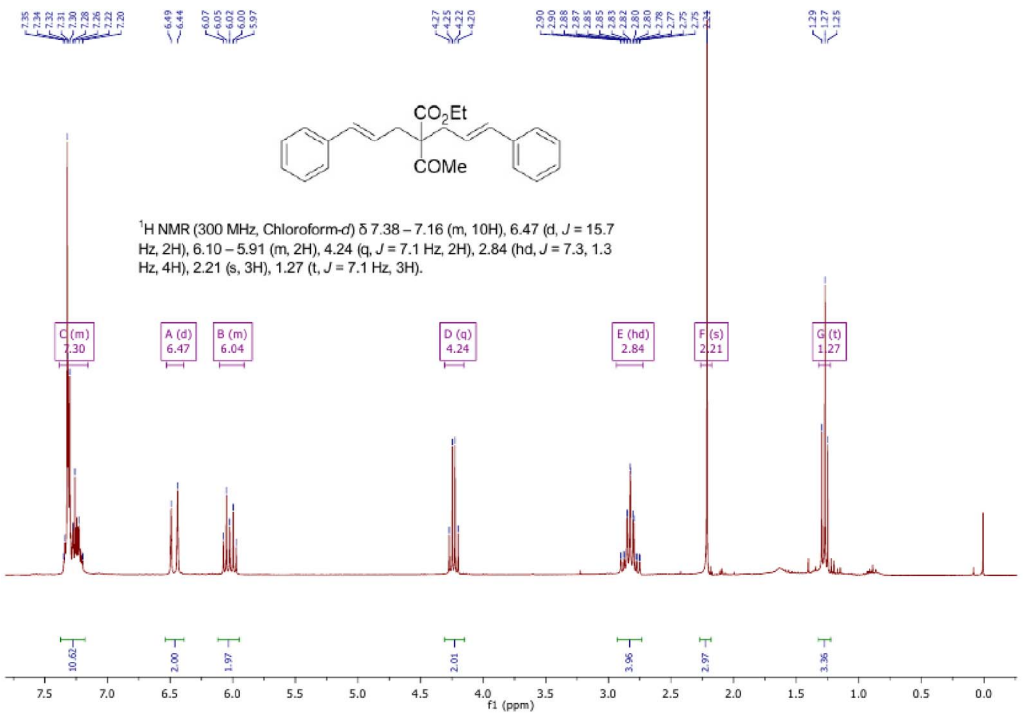
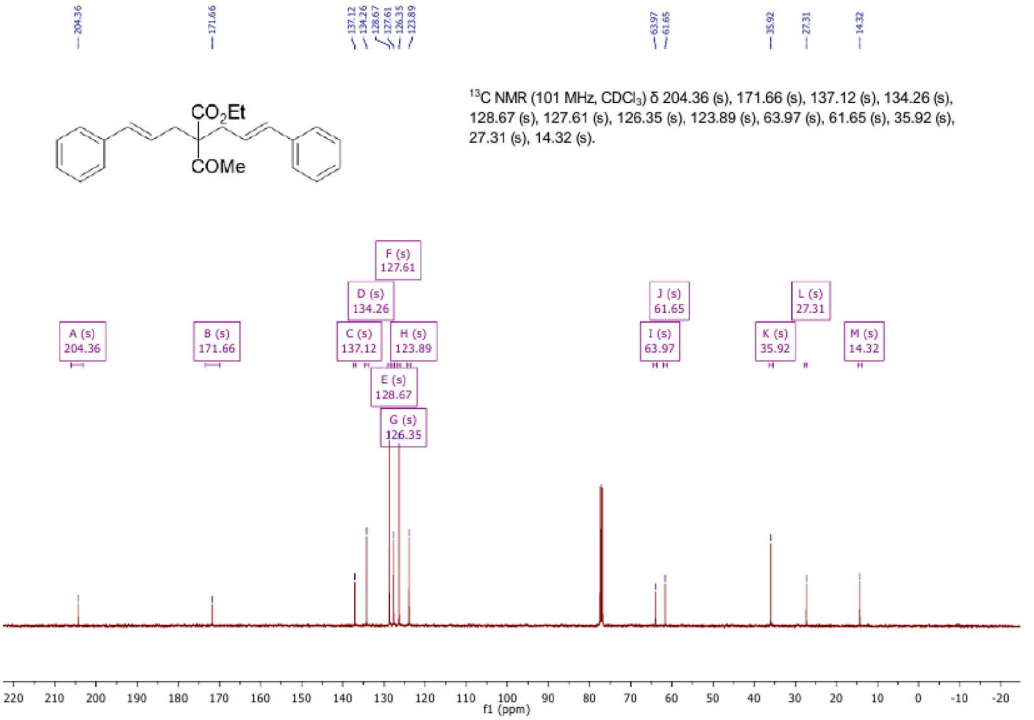
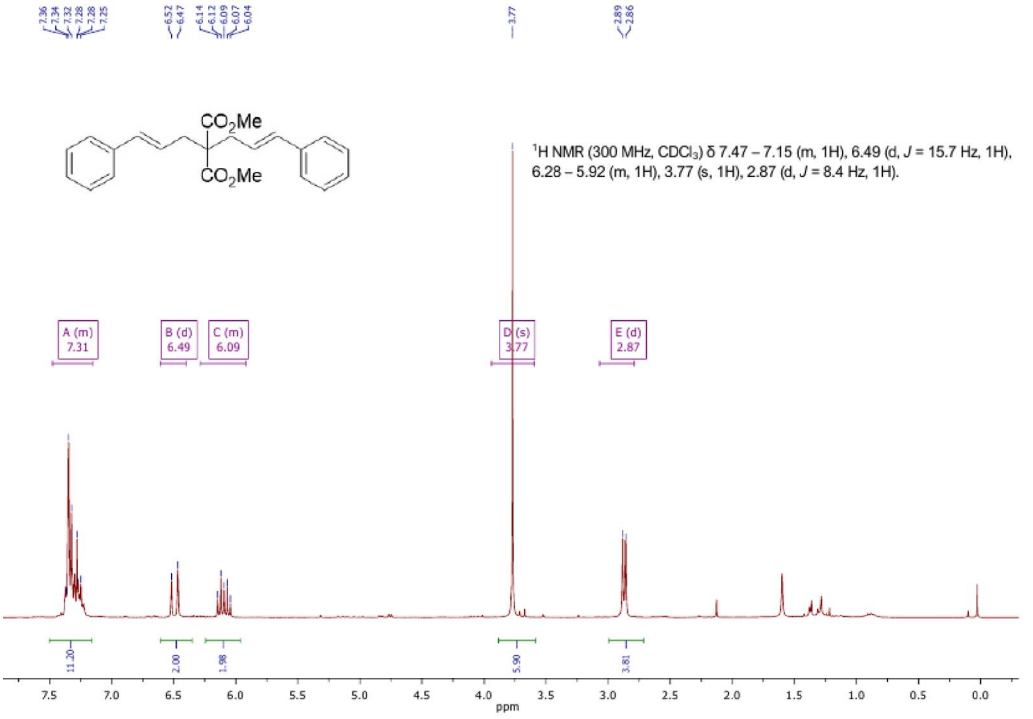
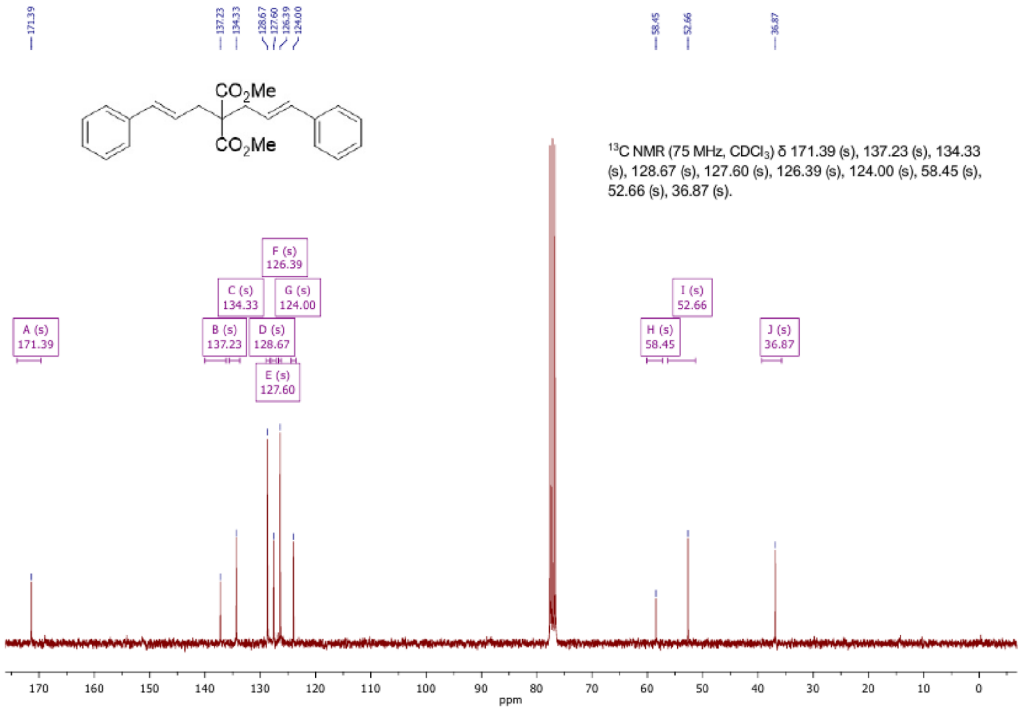




Compound ***4ak***





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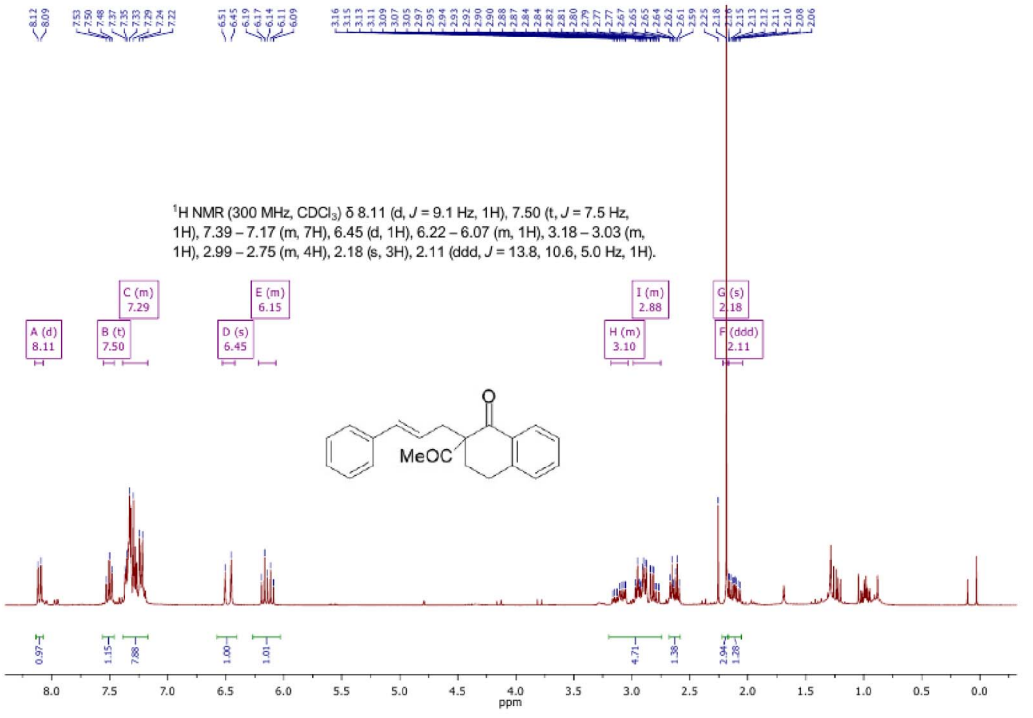
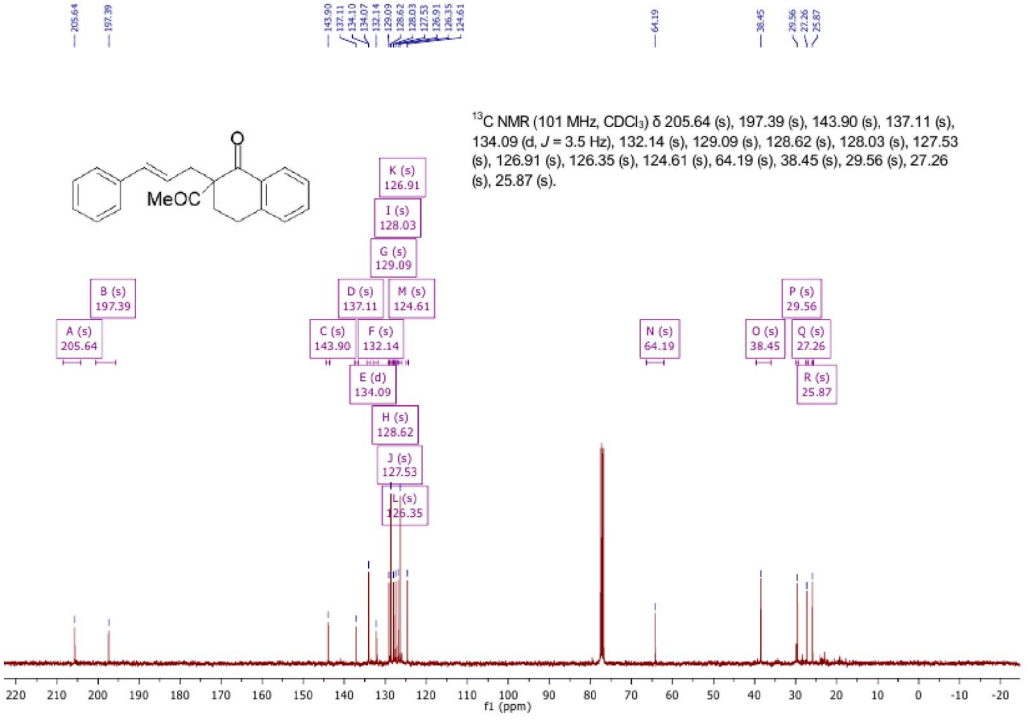
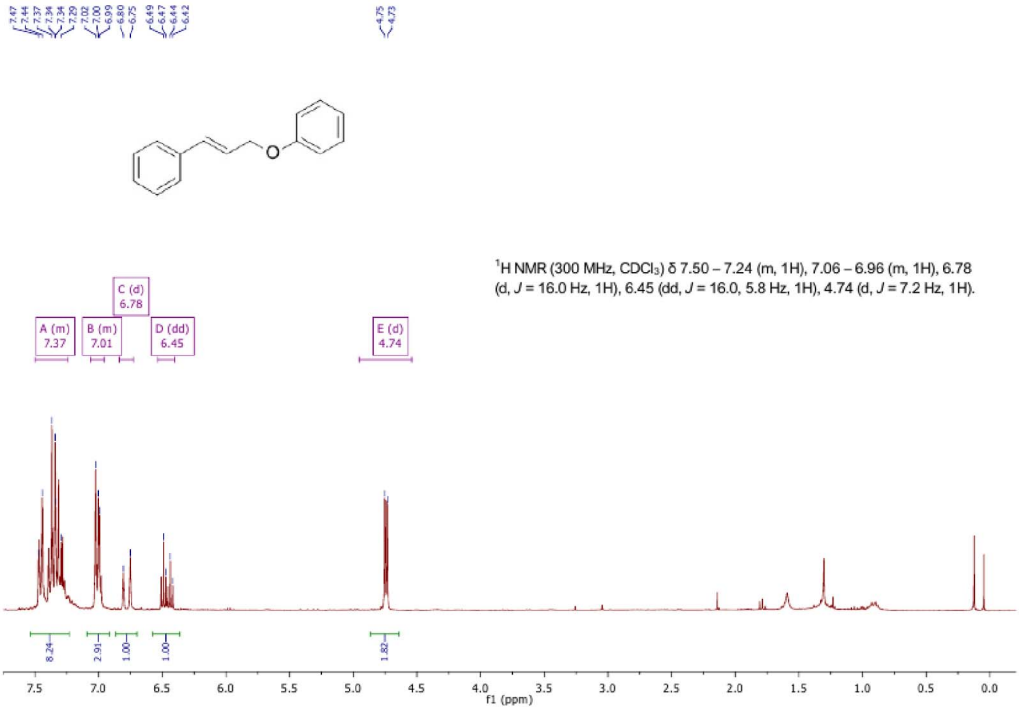
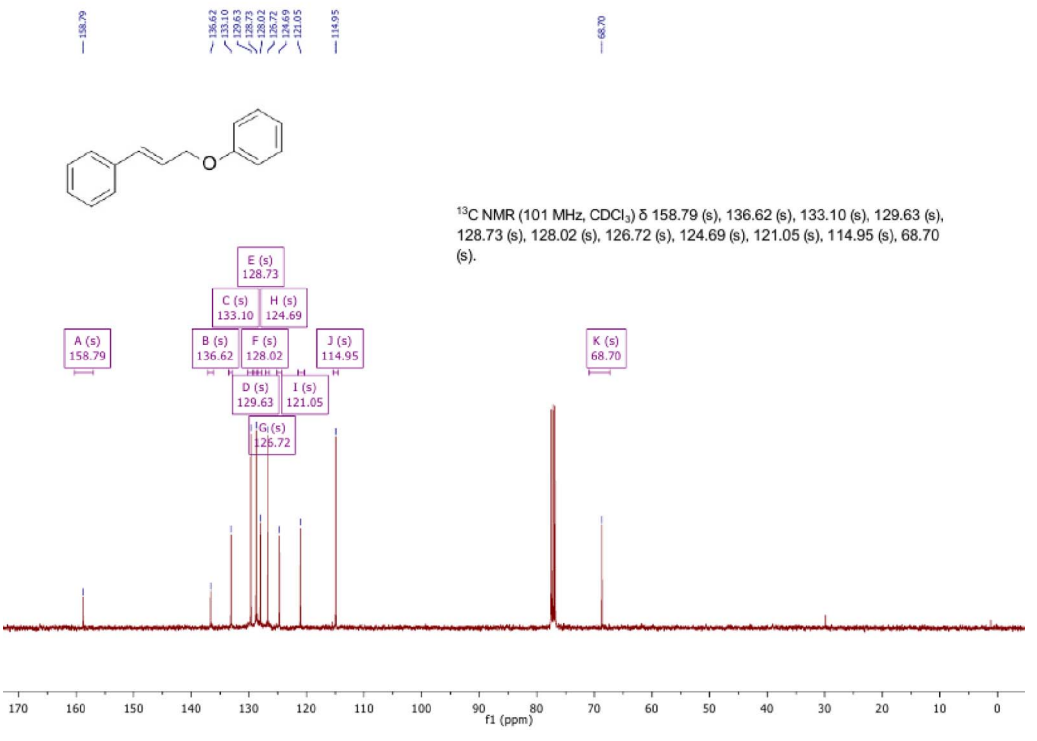




*Compound **4am***

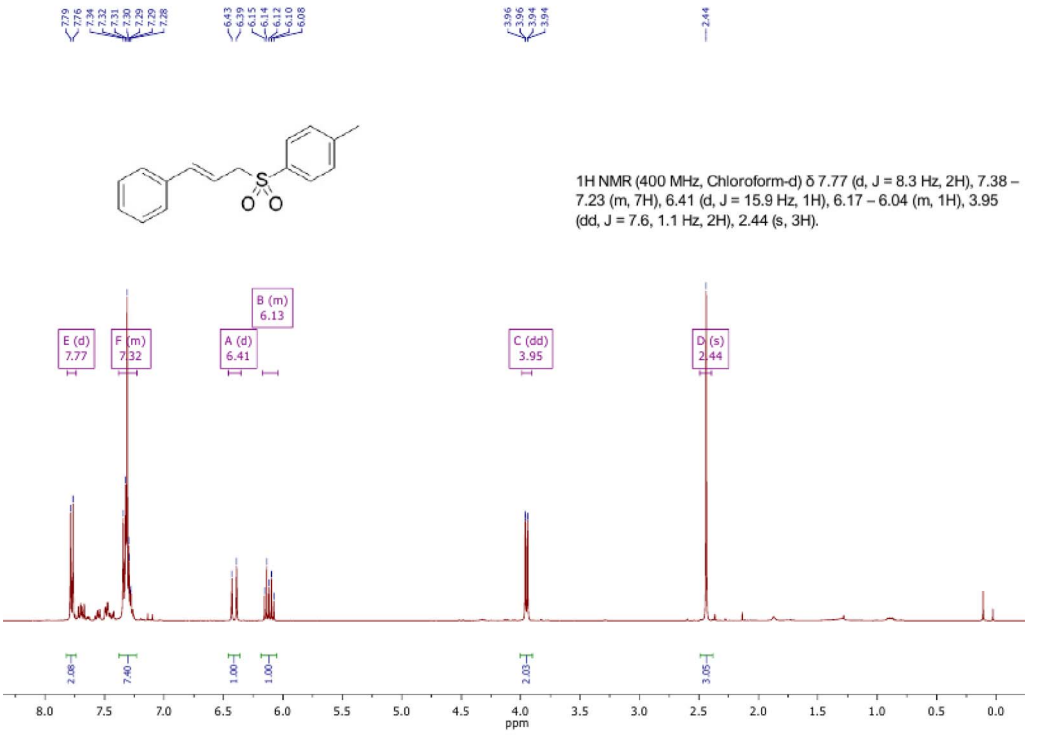


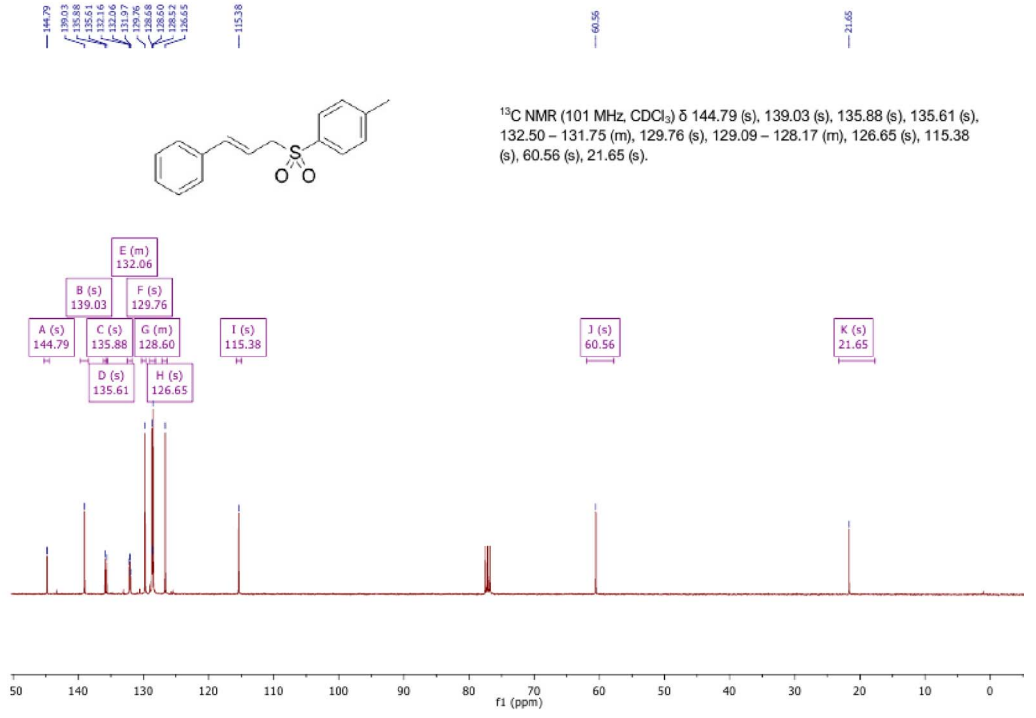
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.24 (m, 1H), 7.06 – 6.96 (m, 1H), 6.78 (d, *J* = 16.0 Hz, 1H), 6.45 (dd, *J* = 16.0, 5.8 Hz, 1H), 4.74 (d, *J* = 7.2 Hz, 1H).



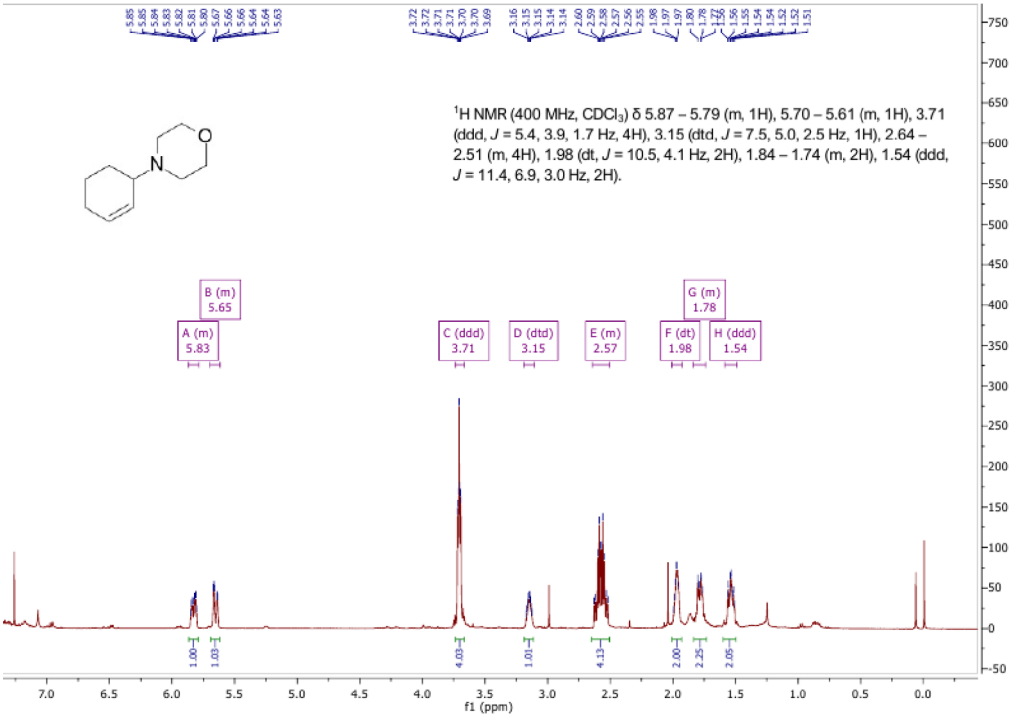
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.79 (s), 136.62 (s), 133.10 (s), 129.63 (s), 128.73 (s), 128.02 (s), 126.72 (s), 124.69 (s), 121.05 (s), 114.95 (s), 68.70 (s).

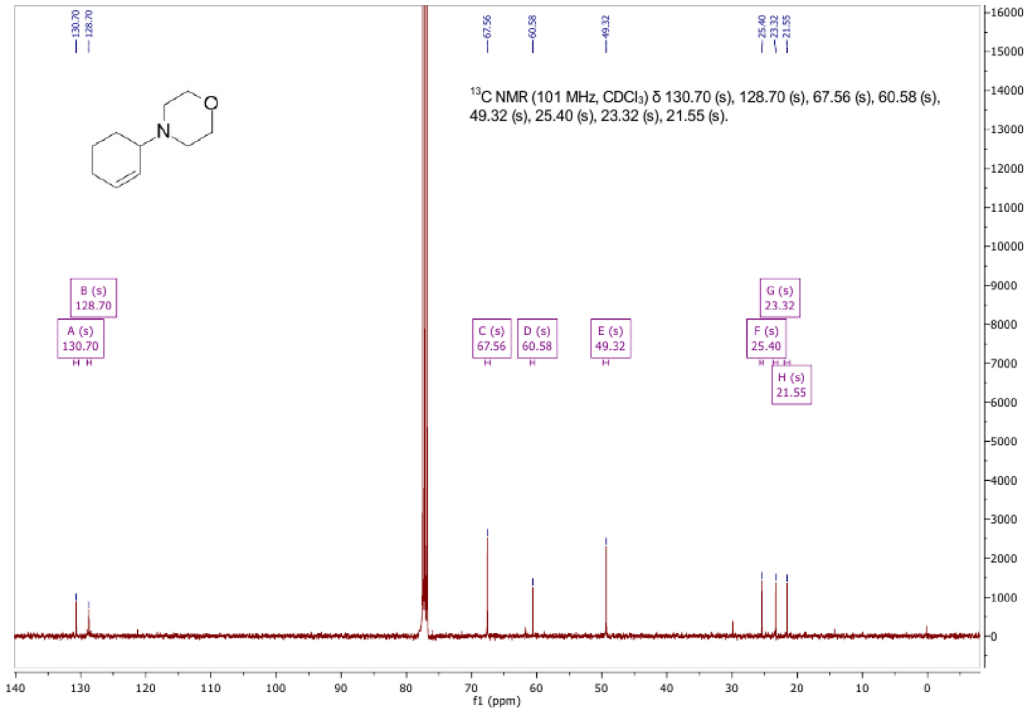
*Compound **4an***



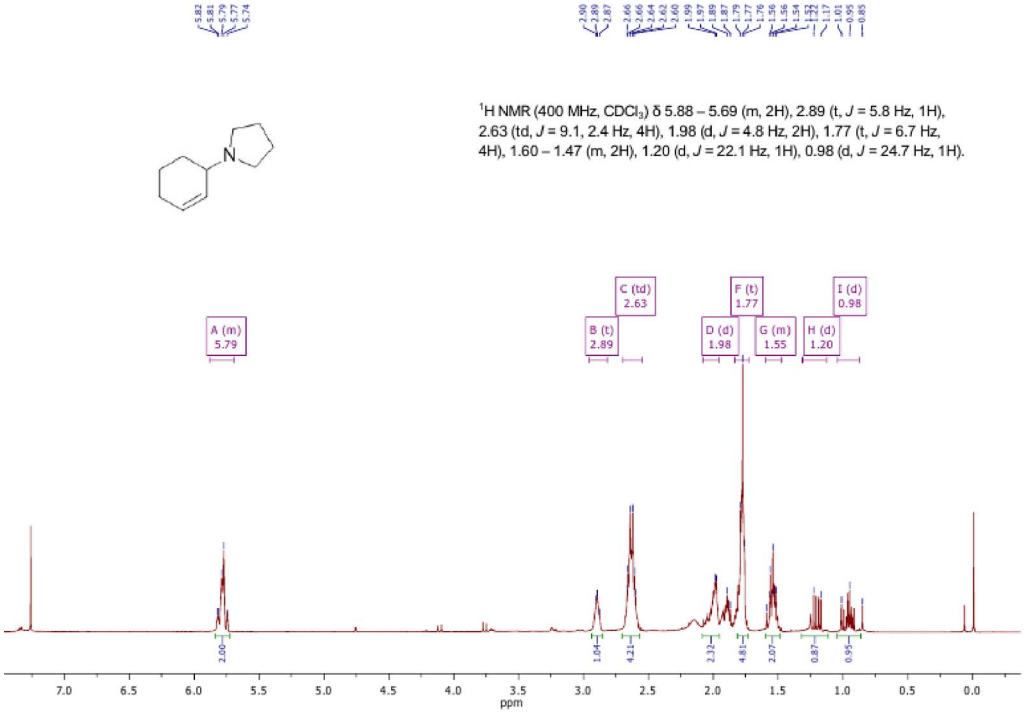


*Compound **4ba***

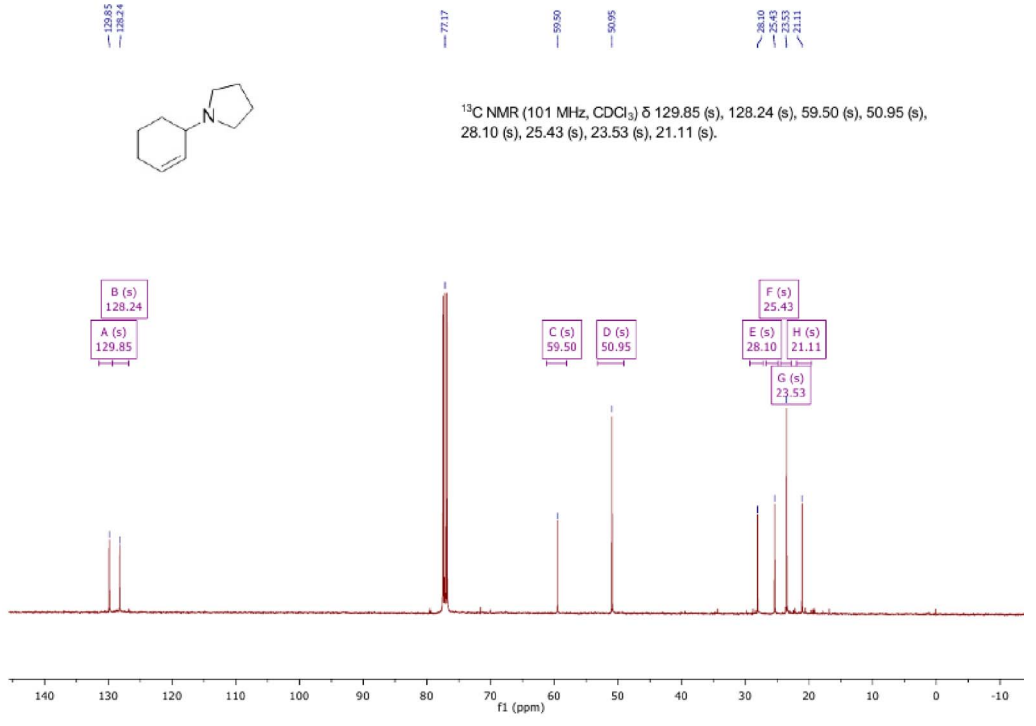




*Compound **4bd***

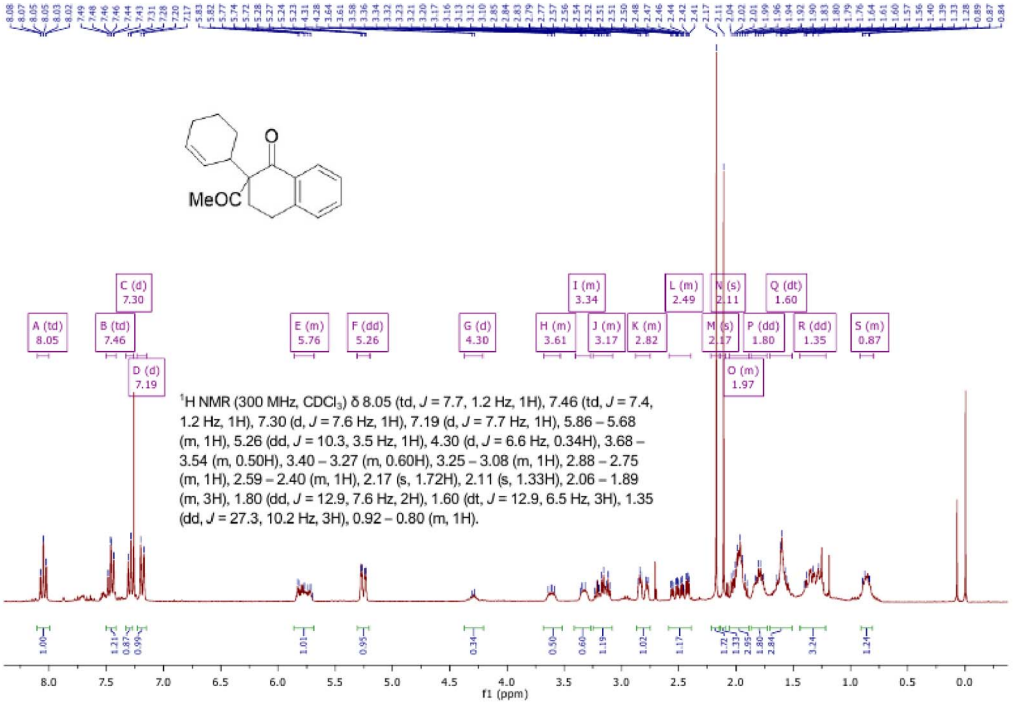


^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 – 5.69 (m, 2H), 2.89 (t, *J* = 5.8 Hz, 1H), 2.63 (td, *J* = 9.1, 2.4 Hz, 4H), 1.98 (d, *J* = 4.8 Hz, 2H), 1.77 (t, *J* = 6.7 Hz, 4H), 1.60 – 1.47 (m, 2H), 1.20 (d, *J* = 22.1 Hz, 1H), 0.98 (d, *J* = 24.7 Hz, 1H).

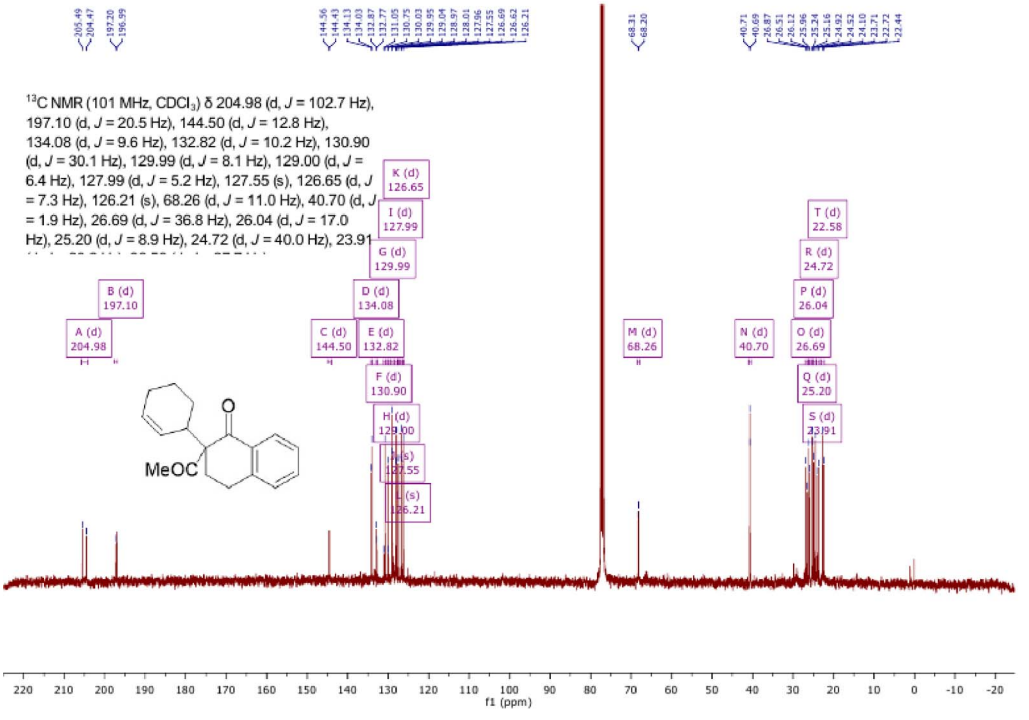


^{13}C NMR (101 MHz, $CDCl_3$) δ 129.85 (s), 128.24 (s), 59.50 (s), 50.95 (s), 28.10 (s), 25.43 (s), 23.53 (s), 21.11 (s).

*Compound **4bl***

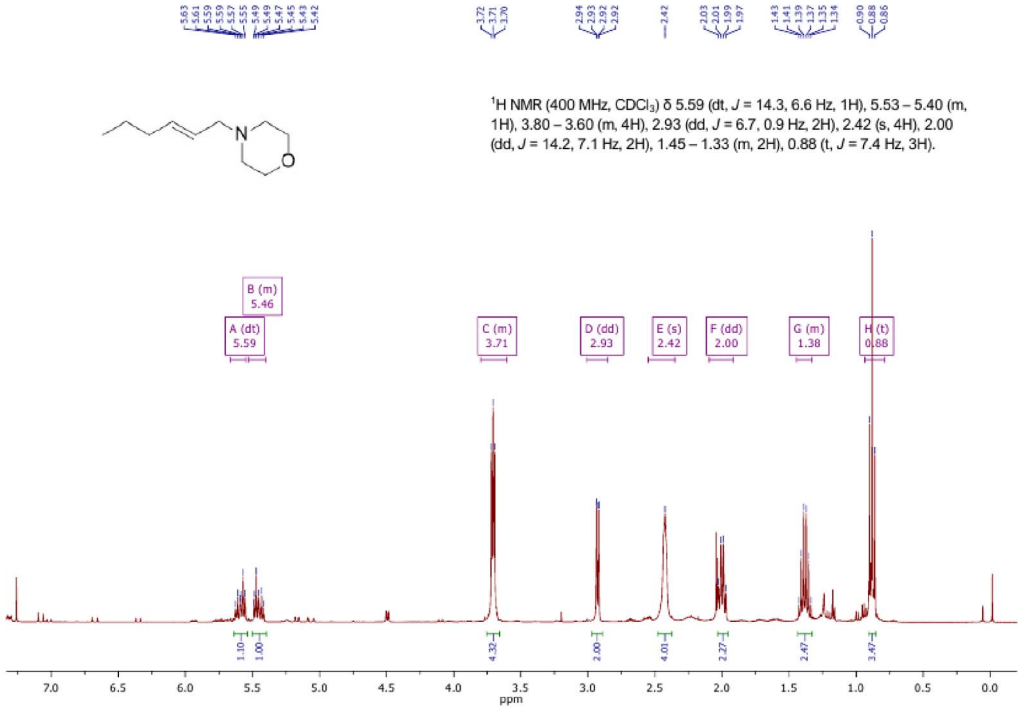


^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (td, *J* = 7.7, 1.2 Hz, 1H), 7.46 (td, *J* = 7.4, 1.2 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 5.86 – 5.68 (m, 1H), 5.26 (dd, *J* = 10.3, 3.5 Hz, 1H), 4.30 (d, *J* = 6.6 Hz, 0.34H), 3.68 – 3.54 (m, 0.50H), 3.40 – 3.27 (m, 0.60H), 3.25 – 3.08 (m, 1H), 2.88 – 2.75 (m, 1H), 2.59 – 2.40 (m, 1H), 2.17 (s, 1.72H), 2.11 (s, 1.33H), 2.06 – 1.89 (m, 3H), 1.80 (dd, *J* = 12.9, 7.6 Hz, 2H), 1.60 (dt, *J* = 12.9, 6.5 Hz, 3H), 1.35 (dd, *J* = 27.3, 10.2 Hz, 3H), 0.92 – 0.80 (m, 1H).



^{13}C NMR (101 MHz, $CDCl_3$) δ 204.98 (d, *J* = 102.7 Hz), 197.10 (d, *J* = 20.5 Hz), 144.50 (d, *J* = 12.8 Hz), 134.08 (d, *J* = 9.6 Hz), 132.82 (d, *J* = 10.2 Hz), 130.90 (d, *J* = 30.1 Hz), 129.99 (d, *J* = 8.1 Hz), 129.00 (d, *J* = 6.4 Hz), 127.99 (d, *J* = 5.2 Hz), 127.55 (s), 126.65 (d, *J* = 7.3 Hz), 126.21 (s), 68.26 (d, *J* = 11.0 Hz), 40.70 (d, *J* = 1.9 Hz), 26.69 (d, *J* = 36.8 Hz), 26.04 (d, *J* = 17.0 Hz), 25.20 (d, *J* = 8.9 Hz), 24.72 (d, *J* = 40.0 Hz), 23.91

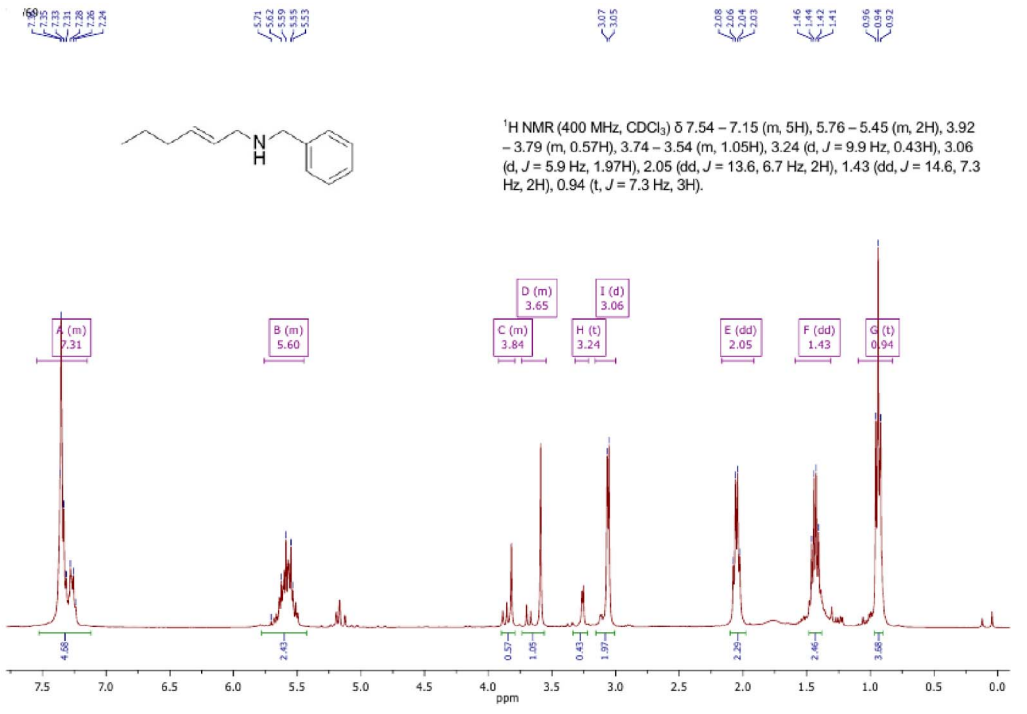
*Compound **4ca***



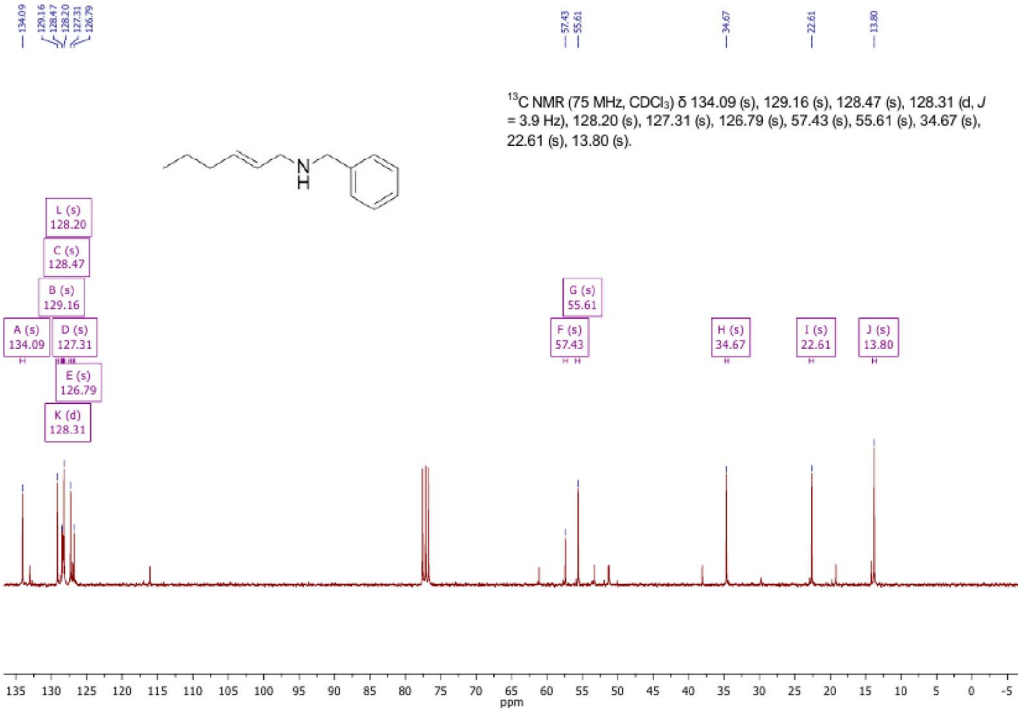
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (dt, *J* = 14.3, 6.6 Hz, 1H), 5.53 – 5.40 (m, 1H), 3.80 – 3.60 (m, 4H), 2.93 (dd, *J* = 6.7, 0.9 Hz, 2H), 2.42 (s, 4H), 2.00 (dd, *J* = 14.2, 7.1 Hz, 2H), 1.45 – 1.33 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.22 (s), 125.86 (s), 67.07 (s), 61.49 (s), 53.61 (s), 34.56 (s), 22.46 (s), 13.79 (s).

Compound ***4ce***

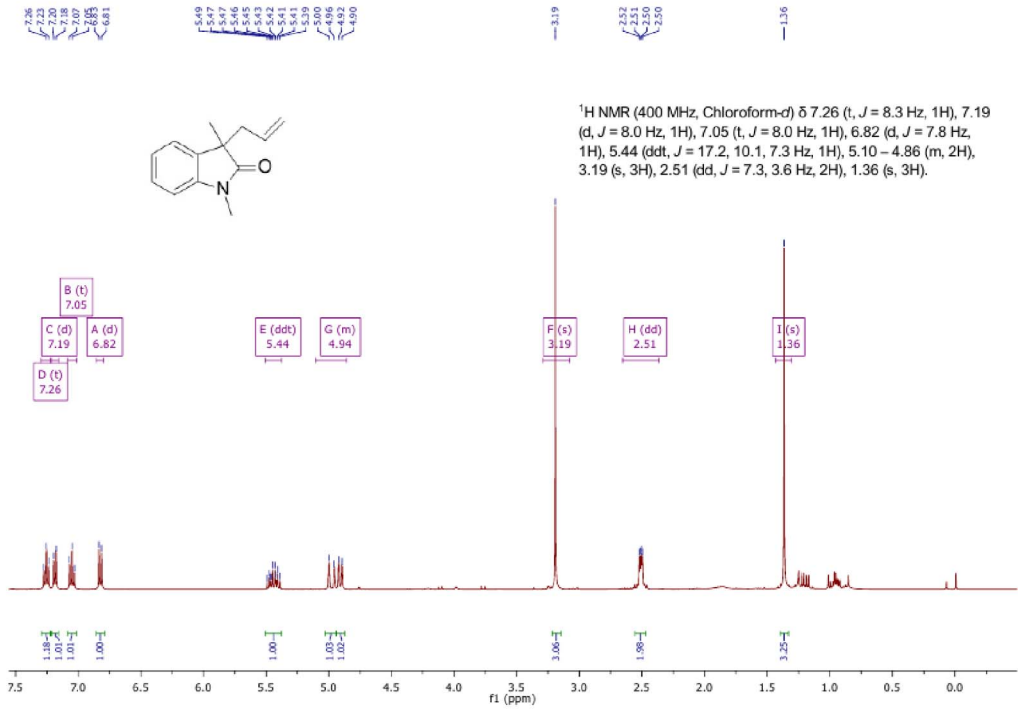


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.15 (m, 5H), 5.76 – 5.45 (m, 2H), 3.92 – 3.79 (m, 0.57H), 3.74 – 3.54 (m, 1.05H), 3.24 (d, *J* = 9.9 Hz, 0.43H), 3.06 (d, *J* = 5.9 Hz, 1.97H), 2.05 (dd, *J* = 13.6, 6.7 Hz, 2H), 1.43 (dd, *J* = 14.6, 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

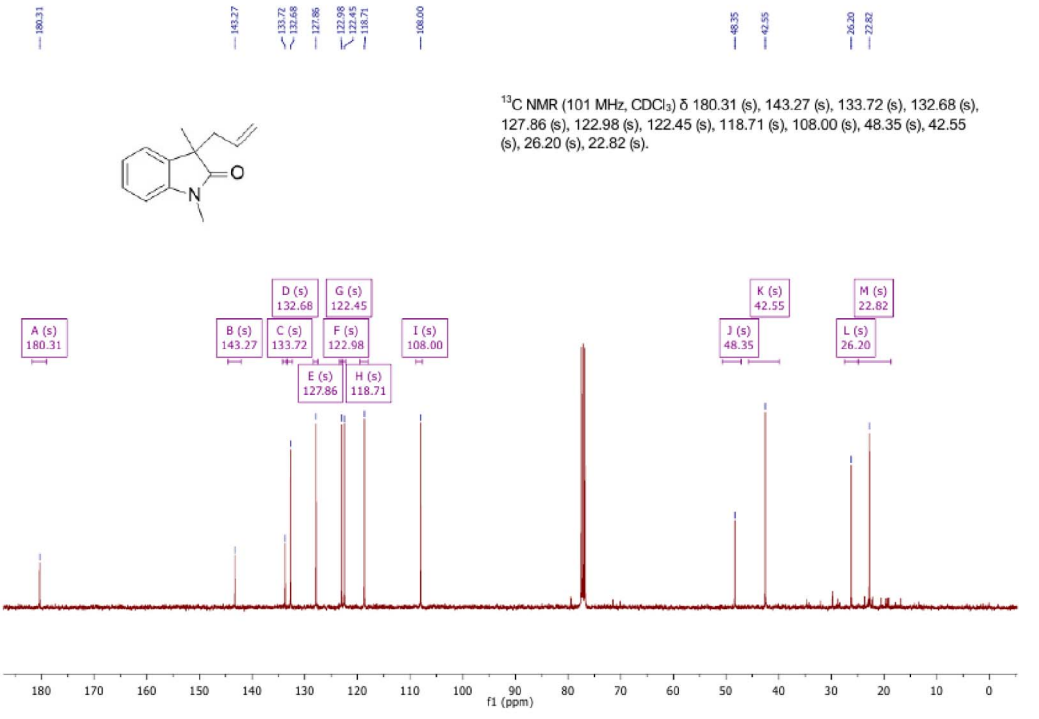


^{13}C NMR (75 MHz, $CDCl_3$) δ 134.09 (s), 129.16 (s), 128.47 (s), 128.31 (d, *J* = 3.9 Hz), 128.20 (s), 127.31 (s), 126.79 (s), 57.43 (s), 55.61 (s), 34.67 (s), 22.61 (s), 13.80 (s).

*Compound **4do***

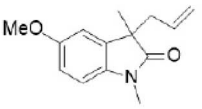


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (t, *J* = 8.3 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.44 (ddt, *J* = 17.2, 10.1, 7.3 Hz, 1H), 5.10 – 4.86 (m, 2H), 3.19 (s, 3H), 2.51 (dd, *J* = 7.3, 3.6 Hz, 2H), 1.36 (s, 3H).

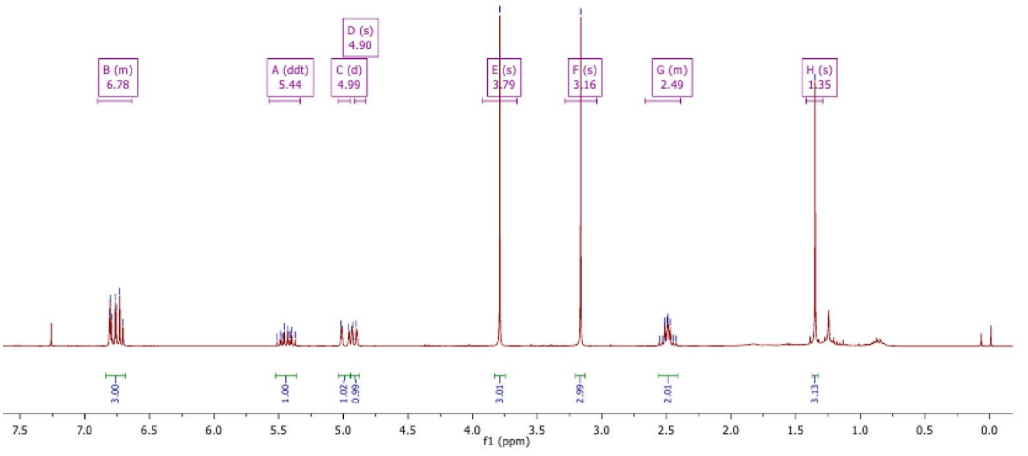


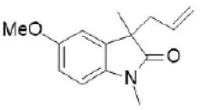
^{13}C NMR (101 MHz, $CDCl_3$) δ 180.31 (s), 143.27 (s), 133.72 (s), 132.68 (s), 127.86 (s), 122.98 (s), 122.45 (s), 118.71 (s), 108.00 (s), 48.35 (s), 42.55 (s), 26.20 (s), 22.82 (s).

Compound ***4dp***

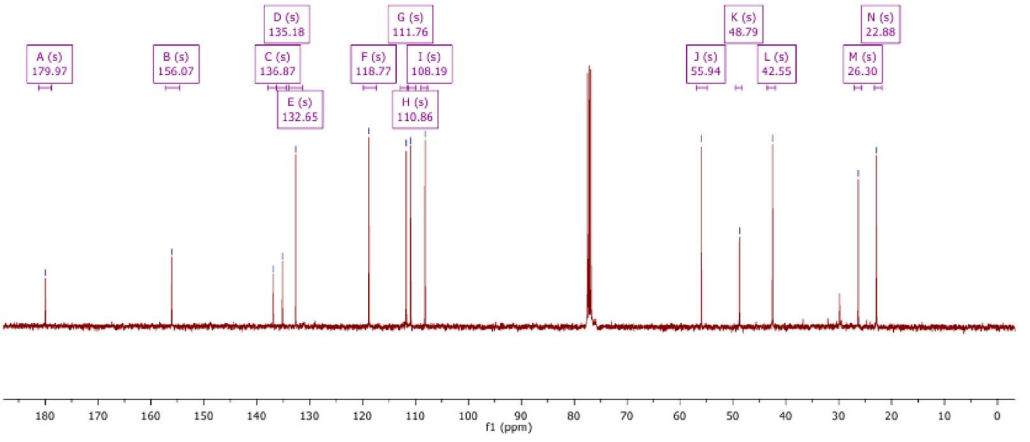


^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.90 – 6.63 (m, 3H), 5.44 (ddt, *J* = 17.6, 10.1, 7.3 Hz, 1H), 4.99 (d, *J* = 17.0 Hz, 1H), 4.90 (s,1H), 3.79 (s, 3H), 3.16 (s, 3H), 2.67 – 2.39 (m, 2H), 1.35 (s, 3H).

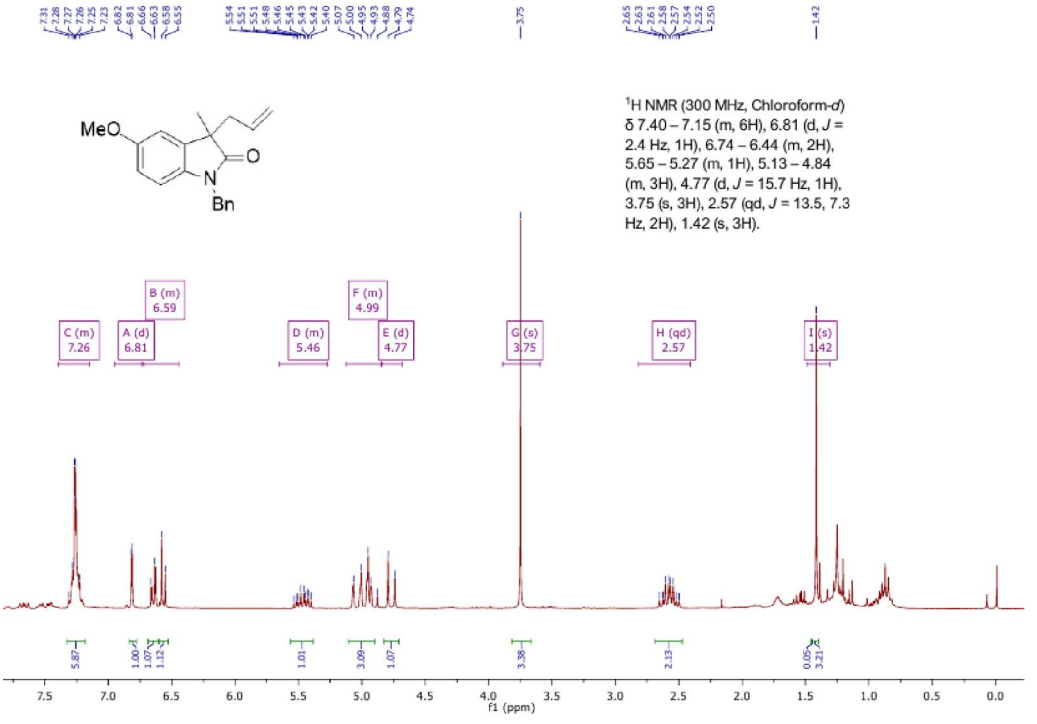


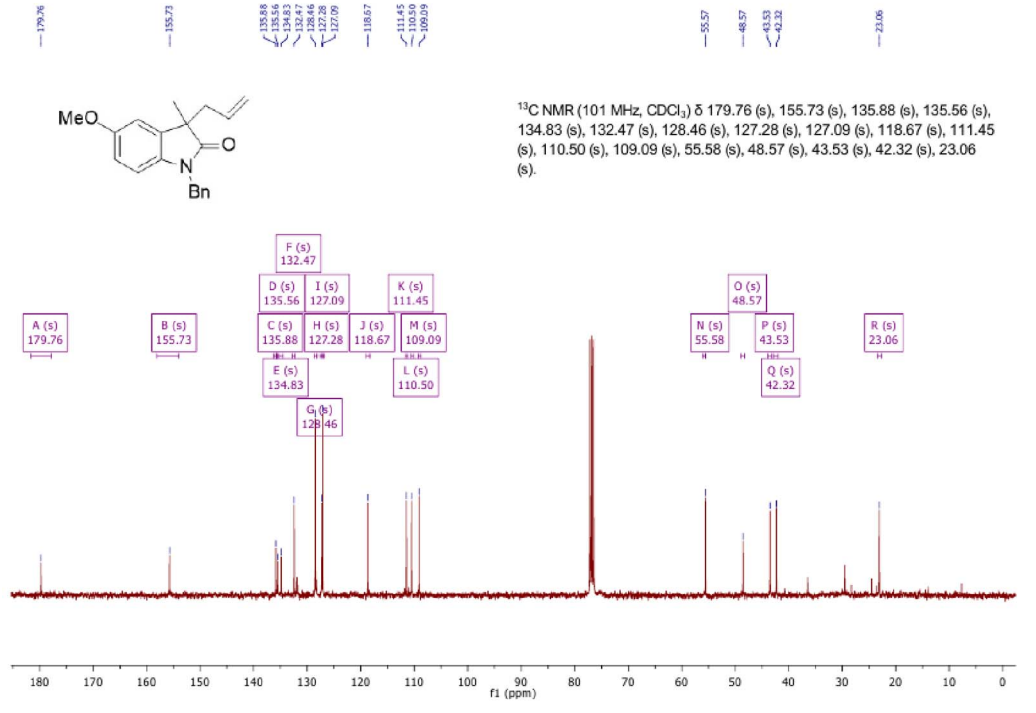


^{13}C NMR (101 MHz, $CDCl_3$) δ 179.97 (s), 156.07 (s), 136.87 (s), 135.18 (s), 132.65 (s), 118.77 (s), 111.76 (s), 110.86 (s), 108.19 (s), 55.94 (s), 48.79 (s), 42.55 (s), 26.30 (s), 22.88 (s).

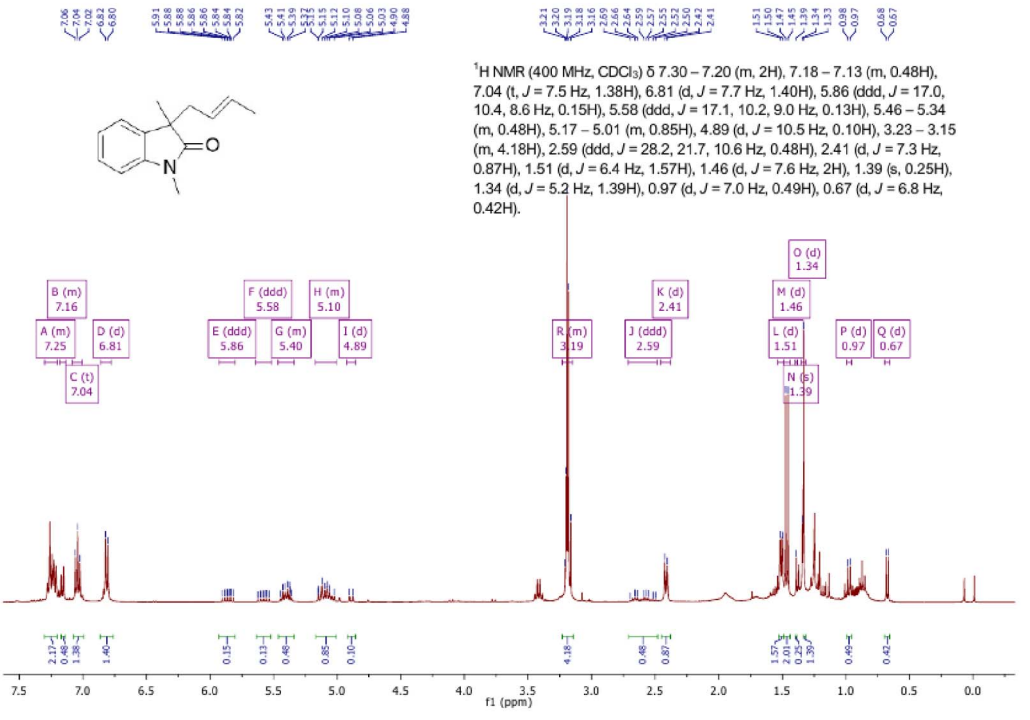


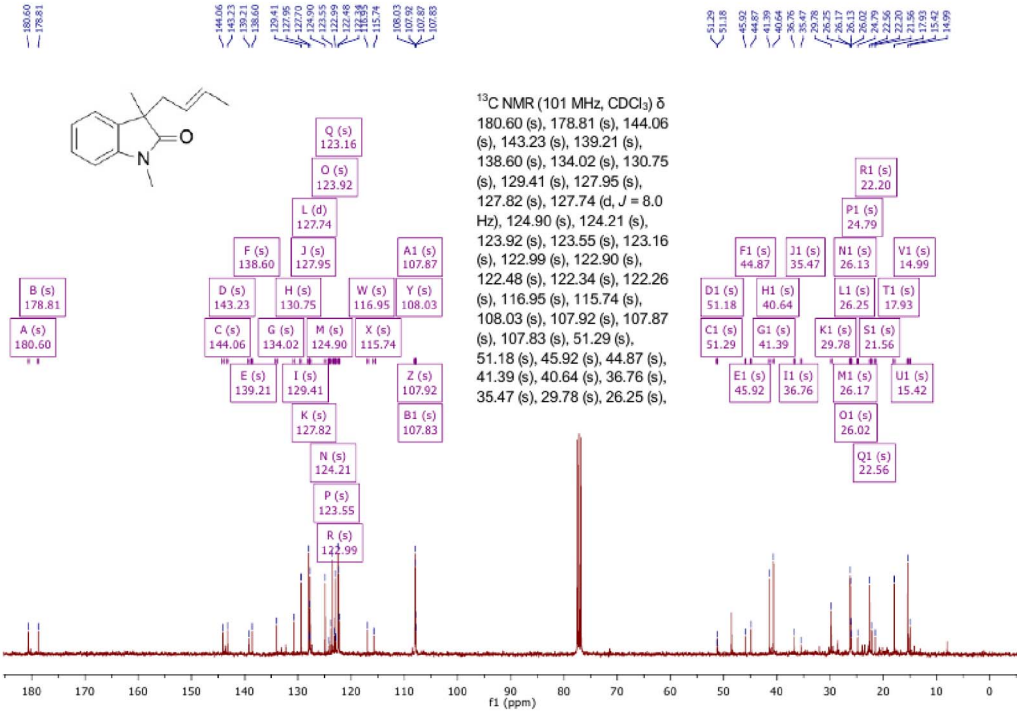
*Compound **4dq***



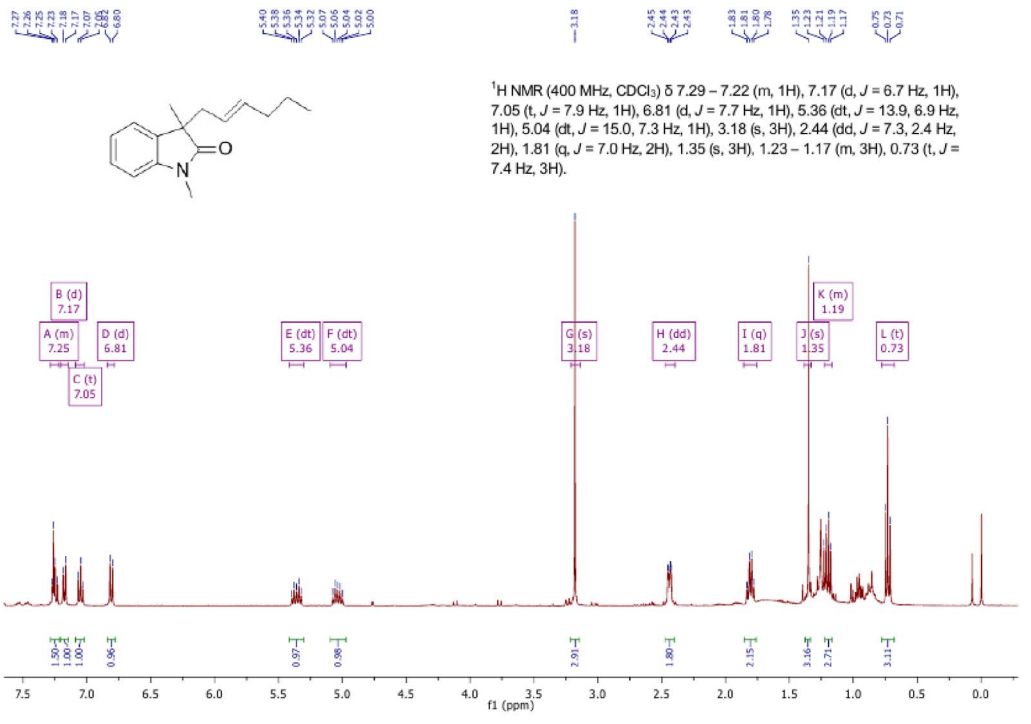


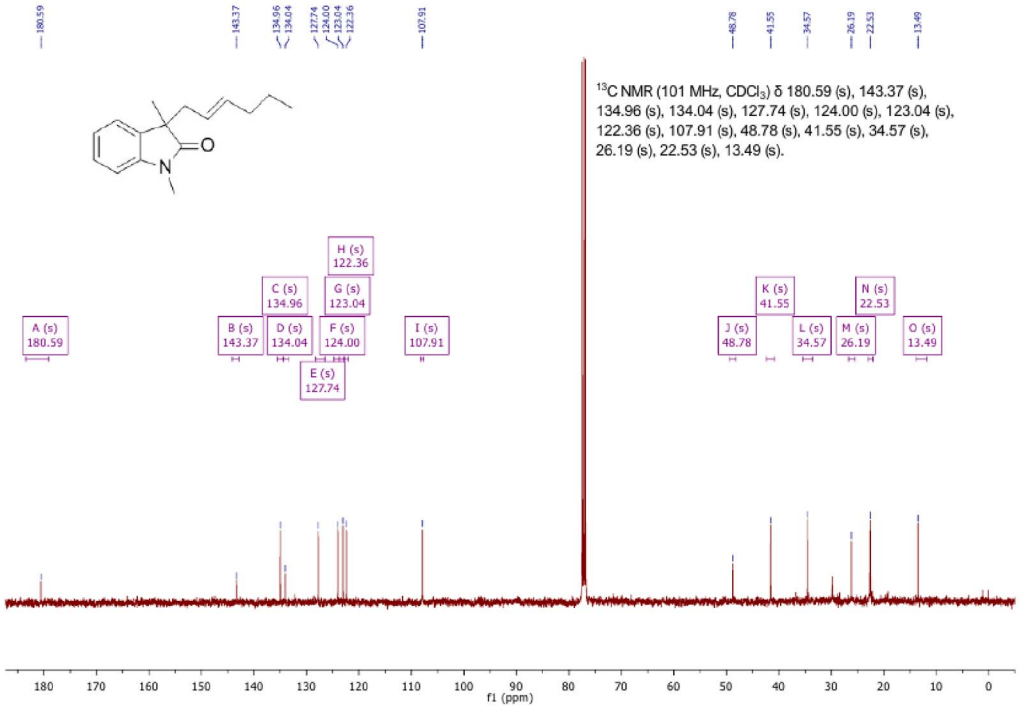
Compound ***4eo***



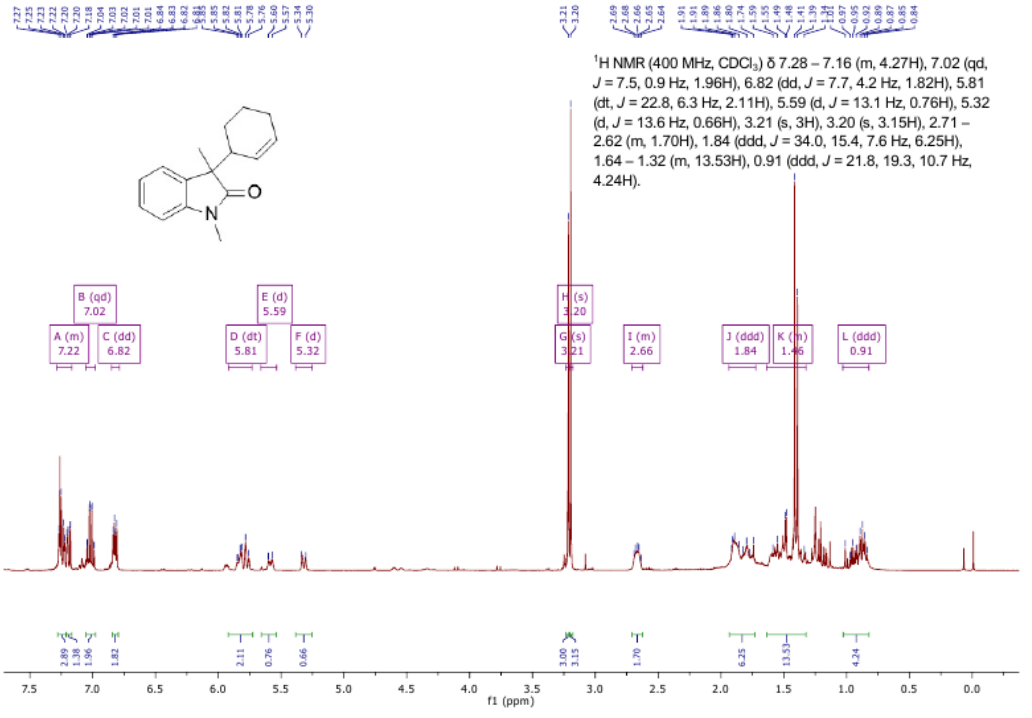


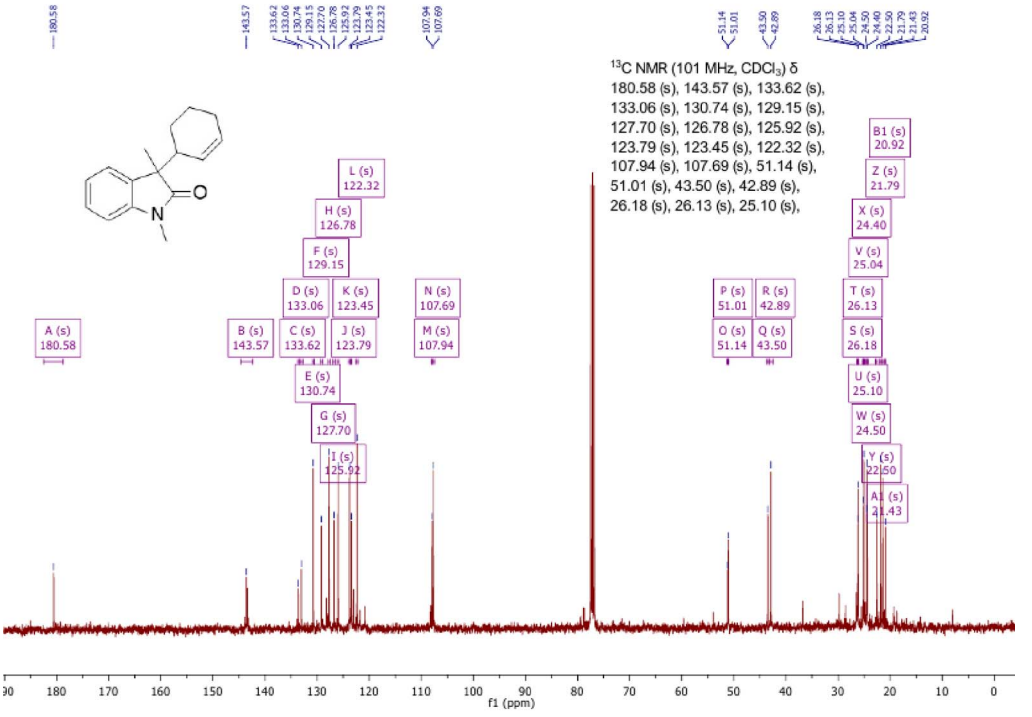
Compound ***4fo***





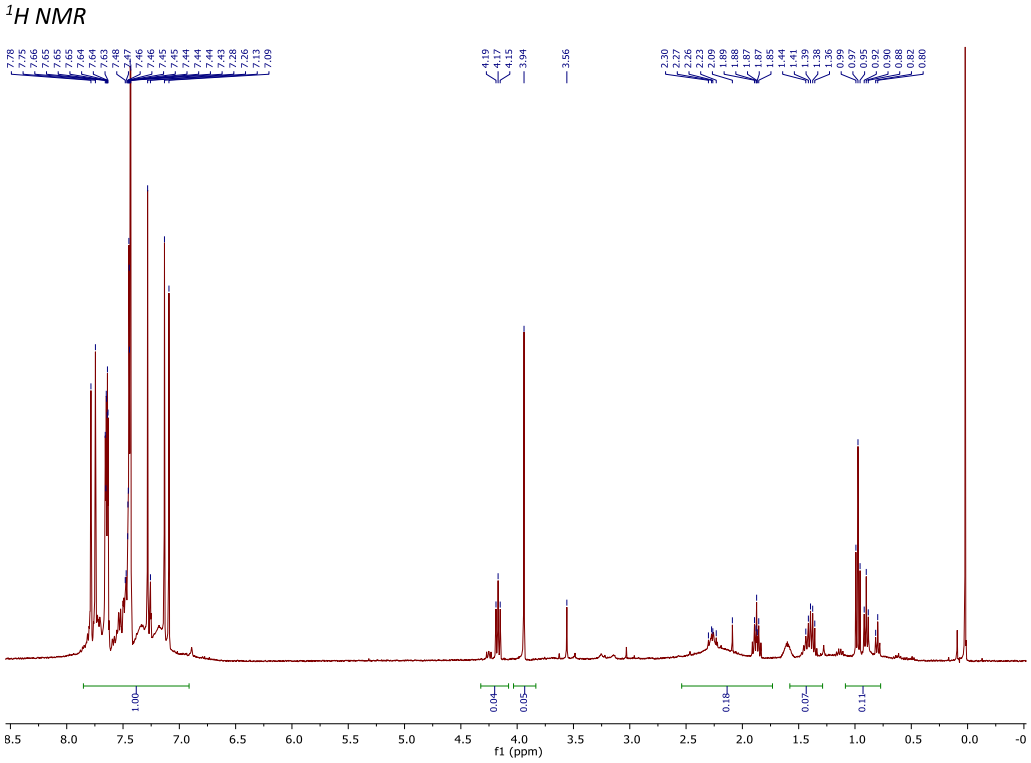
Compound ***4go***



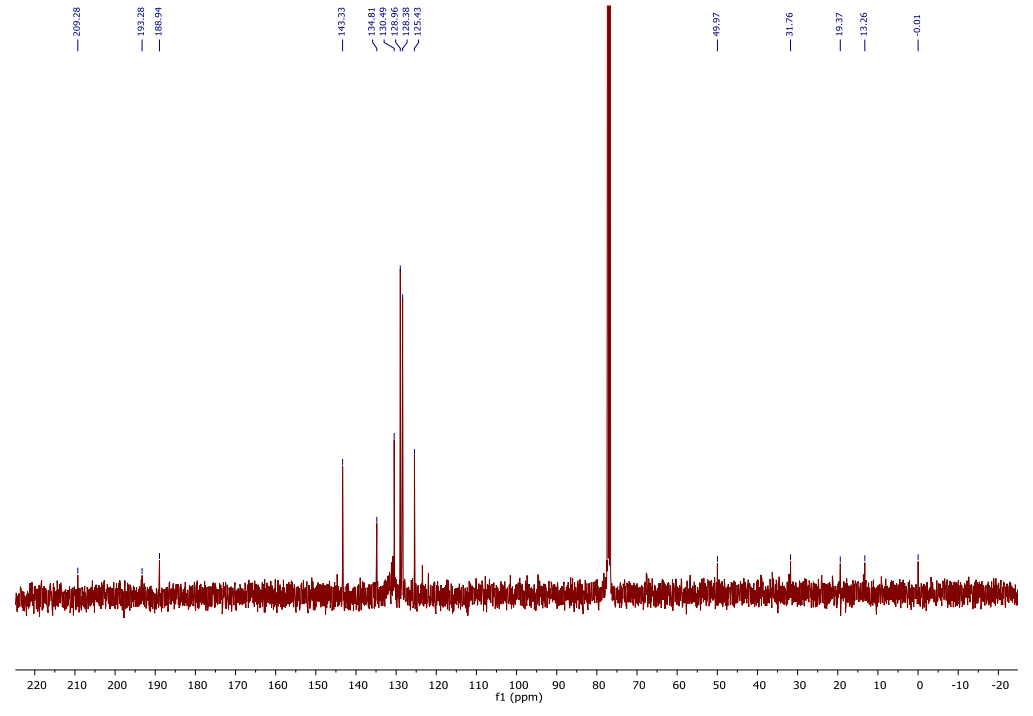


3. Characterization of the catalytic system 1·Pd(dba)$_2$

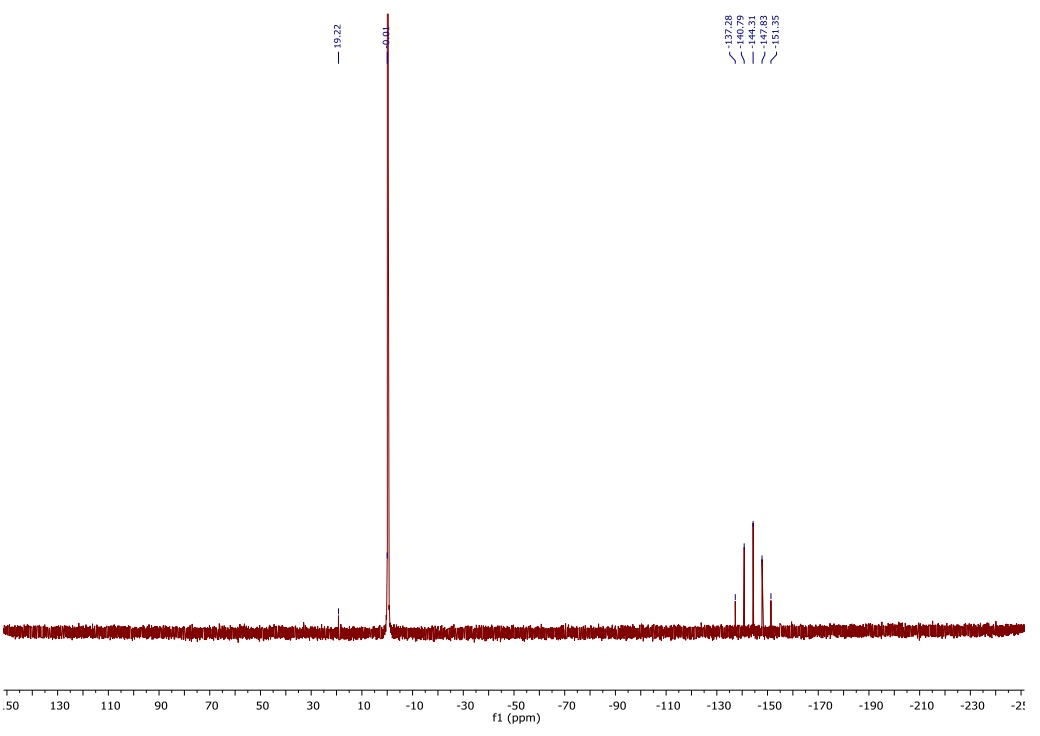
The data from the complex **1**-Pd(dba)$_2$ are the following: ^{1}H RMN (δ, ppm, 300 MHz, $CDCl_3$): 7.75–7.20 (m, 40H, HC=CHN, 2×CH=CH, Ar*H*), 4.20–4.12 (m, 2H, NCH_2CH$_2$CH$_2$CH$_3$), 3.93 (s, 3H, NCH$_3$), 2.04 (s, 3H, MeCO), 1.84 (m, 2H, NCH$_2$CH_2CH$_2$CH$_3$), 1.42–1.30 (m, 2H, NCH$_2$CH$_2$CH_2CH$_3$), 0.95 (t, 3H, J = 7.3 Hz, NCH$_2$CH$_2$CH$_2$CH_3). ^{13}C RMN (δ, ppm, 100 MHz, $CDCl_3$): 209.3, 193.3, 188.9, 136.5, 132.8, 132.1, 131.9, 131.4, 130.7, 130.6, 129.1, 128.9, 128.8, 128.6, 126.8, 123.5, 121.9, 49.7, 36.1, 31.8, 29.6, 20.7, 13.2. ^{31}P RMN (δ, ppm, 162 MHz): 19.22 (s, Pd-PPh$_2$), −144.31 (sept, PF_6^-). MS (ESI) m/z: 752 (**1**$_2$-Pd), 575 (**1**·Pd-dba), 429 (**1**·Pd), 323, 312, 144. IR (neat, ATR) υ_{max}: 2961, 2925, 2865, 1655, 1432, 1466, 1342, 1269, 1038, 998, 843, 670 cm^{-1}. XPS revealed the presence of palladium(0) species and TEM showed the existence of nanoparticles. Apparently, the recovered catalyst has the same morphology and spectroscopic data.



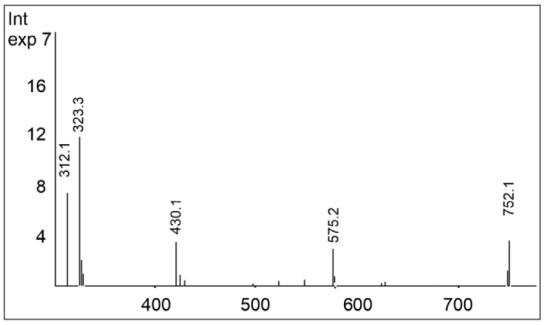
^{13}C NMR



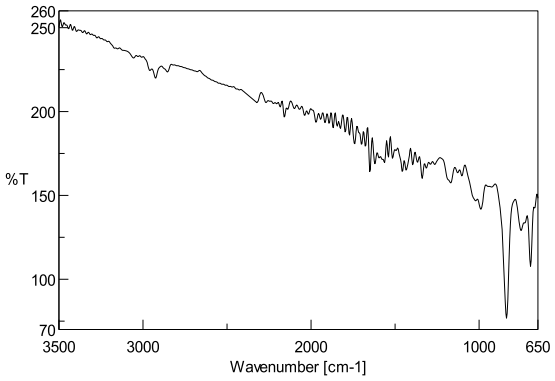
^{31}P NMR



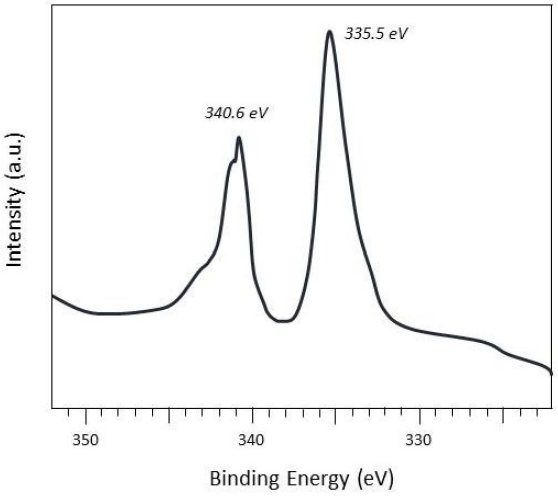
ESI


Int
exp 7
16
12
8
4
312.1
323.3
430.1
575.2
752.1
400
500
600
700

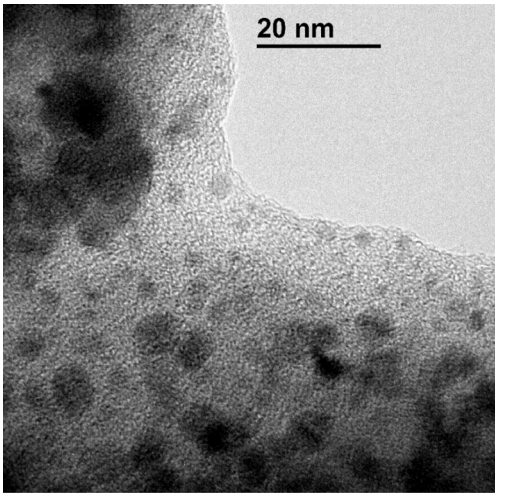
IR


260
250
200
%T
150
100
70
3500
3000
2000
1000
650
Wavenumber [cm-1]

XPS

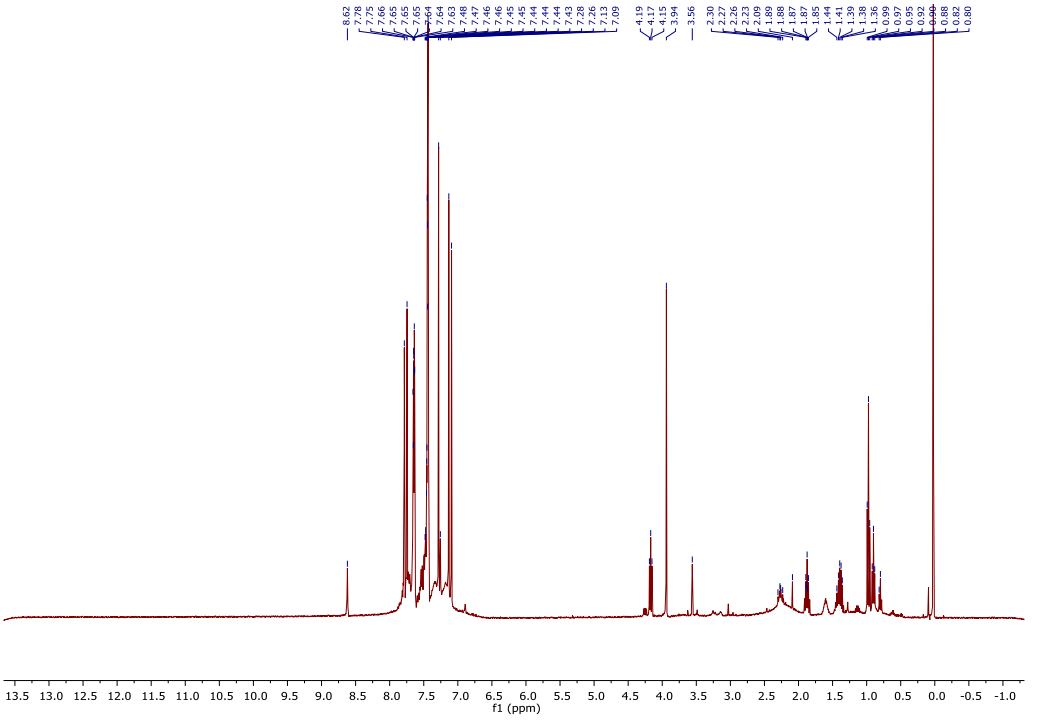

335.5 eV
340.6 eV
Intensity (a.u.)
350
340
330
Binding Energy (eV)

TEM

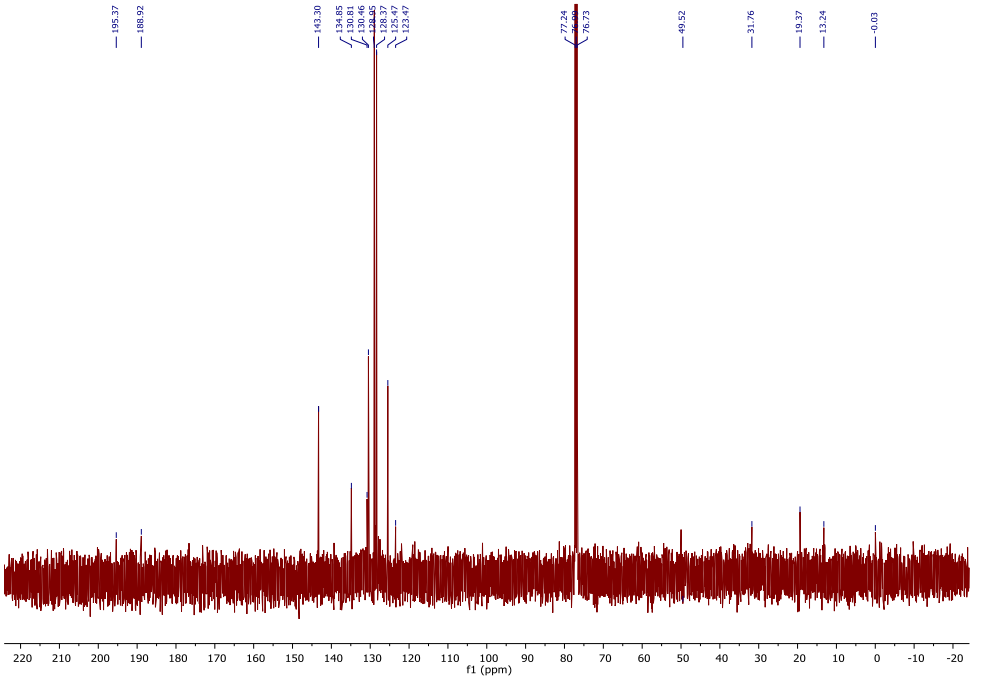


Analysis after the second cycle with the same catalyst

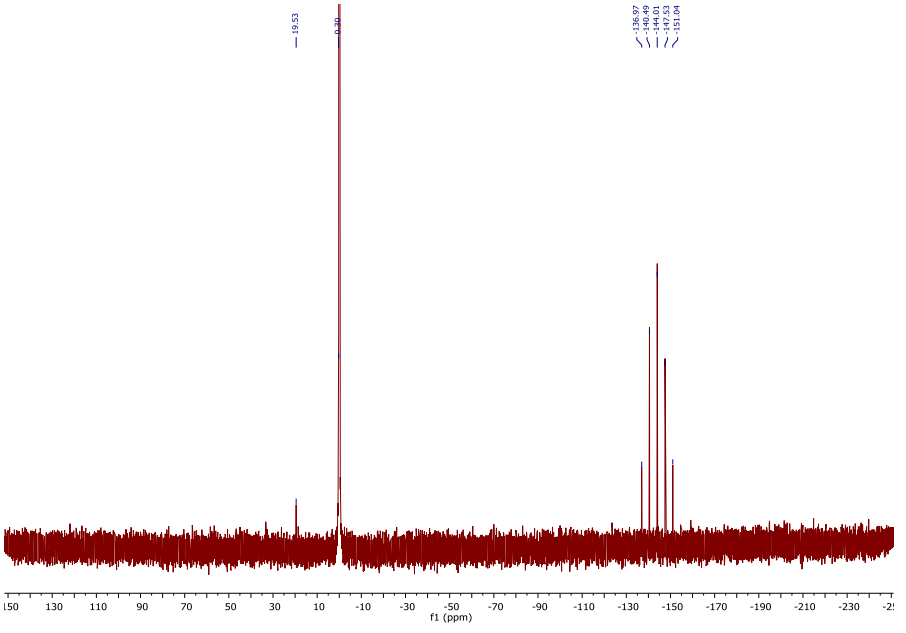
^{1}H NMR



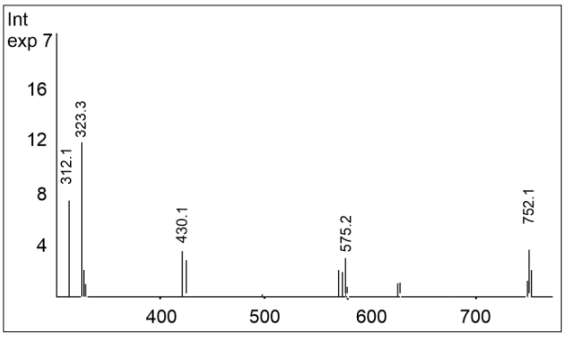
^{13}C NMR



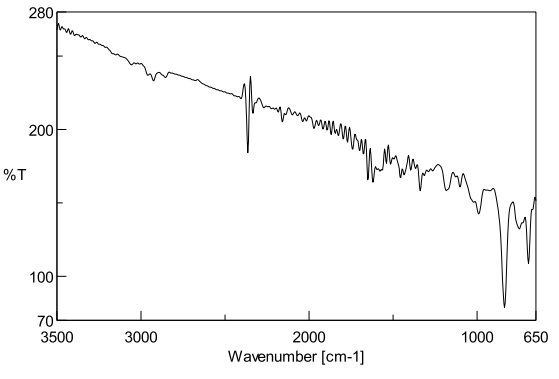
^{31}P NMR



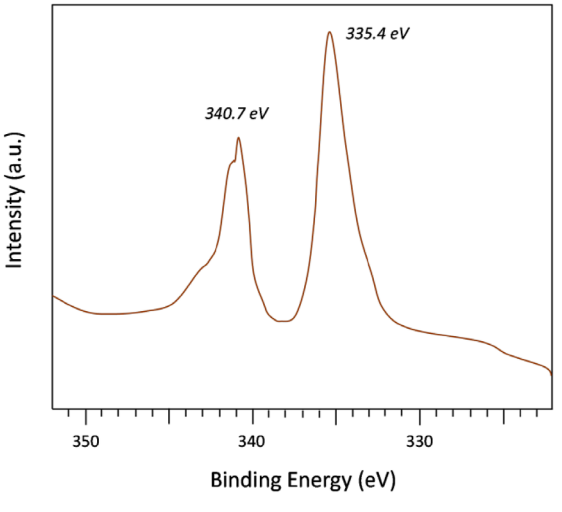
ESI


Int
exp 7
16
12
8
4
312.1
323.3
430.1
575.2
752.1
400
500
600
700

IR


280
200
%T
100
70
3500
3000
2000
1000
650
Wavenumber [cm-1]

XPS


335.4 eV
340.7 eV
Intensity (a.u.)
350
340
330
Binding Energy (eV)

TEM