Immobilized NNN Pd-complex on magnetic nanoparticles: Efficient and reusable catalyst for Heck and Sonogashira coupling reactions

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Outline

1. Synthesis and characterization of the NNN Schiff base ligand

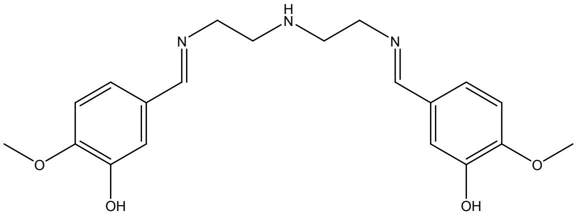
2. Spectral data for the synthesized compounds

3. ^{1}HNMR and ^{13}CNMR spectra for all synthesized compounds

4. FT-IR spectra of the recovered catalyst.

5. References

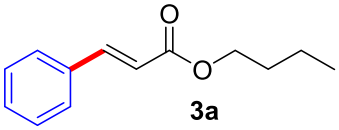
1. Synthesis and characterization of the NNN Schiff base ligand



To a vigorously stirred solution of isovanillin (3.7 mmol, 0.56 g) in 10 mL ethanol, a stoichiometric amount of diethylenetriamine (1.85 mmol, 0.2 mL) was added dropwise. A red solution, which was obtained due to the imine formation, was refluxed for 6 h. The resulting pure precipitate was extracted from oily liquid by n-hexane and ether and then dried in a vacuum. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 8.10 (d, *J* = 8.9 Hz, 2H), 7.18-6.76 (m, 8H), 3.74 (d, *J* = 11.0 Hz, 6H), 3.58-3.48 (m, 4H), 3.09-2.71 (m, 4H), 2.31 (s, 1H). Anal. Calcd. for $C_{20}H_{25}N_3O_4$: C, 64.67; H, 6.78; N, 11.31. Found: C, 64.07; H, 6.67; N, 11.65. IR (KBr, cm^{-1}): 3420 (ν_{O-H}), 3282 (ν_{N-H}), 2943-2839 (ν_{C-H}), 1643 ($\nu_{C=N}$), 1585 ($\nu_{C=C}$).

2. Spectral data for the synthesized compounds

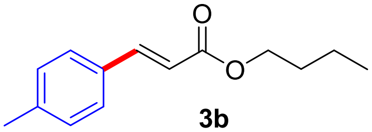
2.1. butyl cinnamate (3a)



3a

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 8.15 (d, *J*= 9.3 Hz, 2H), 7.97-7.54 (m, 4H), 6.49 (d, *J* = 16.1 Hz, 1H), 4.15 (t, *J* = 7.0 Hz, 2H), 1.62 (t, 2H), 1.34 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ (ppm) = 166.1, 141.5, 140.6, 128.60, 124.8, 124.1, 122.6, 64.9, 30.64, 19.1, 13.7.

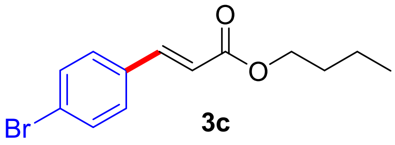
2.2. (E)-butyl 3-p-tolylacrylate (3b)



3b

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.60-7.52 (m, 1H), 7.41-7.30 (m, 2H), 7.17-7.07 (m, 2H), 6.34-6.25 (m, 1H), 4.26-4.07 (m, 2H), 2.27 (s, 3H), 1.59 (m, 2H), 1.35 (m, 2H), 0.88 (m, 3H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ (ppm) = 167.3, 144.5, 140.6, 131.7, 129.6, 128.0, 117.2, 64.3, 30.8, 21.4, 19.2, 13.7.

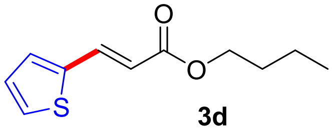
2.3. (E)-butyl 3-(4-bromophenyl) acrylate (3c)



3c

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.53-7.25 (m, 5H), 6.32 (d, *J* = 16.3 Hz, 1H), 4.11 (t, *J* = 6.4 Hz, 2H), 1.63-1.53 (m, 2H), 1.39-1.29 (m, 2H), 0.89-0.76 (m, 3H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ (ppm) = 165.6, 142.0, 132.3, 131.0, 128.3, 123.4, 117.9, 63.4, 29.7, 18.1, 12.7.

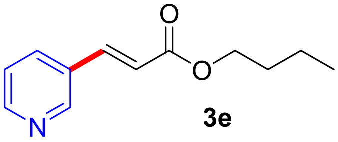
2.4. (E)-butyl 3-(thiophen-2-yl) acrylate (3d)



3d

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 8.49 (d, *J* = 15.7 Hz, 1H), 8.13-7.87 (m, 2H), 7.80-7.69 (m, 1H), 6.96 (d, *J* = 15.7 Hz, 1H), 4.90 (t, *J* = 6.7 Hz, 2H), 2.45-2.35 (m, 2H), 2.19-2.04 (m, 2H), 1.66 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ (ppm) = 166.9, 139.6, 136.9, 130.8, 128.3, 128.0, 117.0, 64.4, 30.8, 19.2, 13.7.

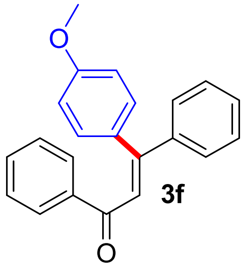
2.5. (E)-butyl 3-(pyridin-3-yl) acrylate (3e)



3e

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 8.67 (s, 1H), 8.52 (d, 1H, *J* = 4.2 Hz), 7.76 (d, 1H, *J* = 7.5 Hz), 7.59 (d, 1H, *J* = 16.0 Hz), 7.28-7.23 (m, 1H), 6.44 (d, 1H, *J* = 16.0 Hz), 4.15 (m, 2H, *J* = 6.5 Hz), 1.67-1.56 (m, 2H), 1.40-1.25 (m, 2H), 0.89 (m, 3H, *J* = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ (ppm) =13.7, 19.1, 27.8, 30.6, 64.7, 114.3, 115.8, 129.7, 144.2, 161.3.

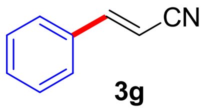
2.6. (Z)-3-(4-methoxyphenyl)-1,3-diphenylprop-2-en-1-one (3f)



3f

^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.70-7.64 (m, 2H), 7.20-6.89 (m, 11H), 6.65-6.51 (m, 2H), 3.50 (s, 3H). ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ (ppm) = 192.1, 160.8, 154.9, 139.4, 138.6, 133.1, 132.5, 131.5, 130.1, 129.8, 129.4, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 122.2, 113.9, 55.4.

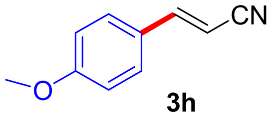
2.7. (Z)-3-phenylacrylonitrile (3g)



3g

^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.43-7.34 (m, 5H), 7.27 (d, *J* = 16.11 Hz, 1H), 5.79 (d, *J* = 16.11 Hz, 1H). ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ (ppm) = 150.5, 133.56, 131.09, 129.01, 127.44, 118.32, 96.31.

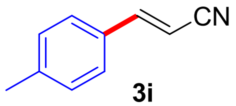
2.8. (Z)-3-(4-methoxyphenyl) acrylonitrile (3h)



3h

^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.32 (d, *J* = 10.1 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.90-6.83 (m, 2H), 5.47 (d, *J* = 10.1 Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ (ppm) = 161.0, 145.1, 130.7, 129.1, 118.8, 114.5, 101.6, 55.4

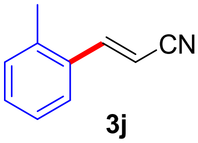
2.9. (Z)-3-p-tolylacrylonitrile (3i)



3i

^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.35-7.20 (m, 5H), 5.77 (d, *J* = 15.4 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ (ppm) = 148.6, 141.8, 130.8, 129.8, 129.6, 129.1, 127.4, 118.5, 95.0, 21.5.

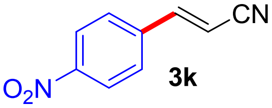
2.10. (Z)-3-o-tolylacrylonitrile (3j)



3j

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.55 (d, *J* = 16.3 Hz, 1H), 7.34-7.11 (m, 4H), 5.65 (d, *J* = 16.3 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ (ppm) = 147.5, 137.2, 132.5, 131.0, 127.6, 126.6, 125.5, 118.4, 97.2, 19.6.

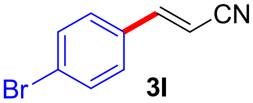
2.11. (Z)-3-(4-nitrophenyl) acrylonitrile (3k)



3k

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 8.30-8.25 (m, 2H), 7.66-7.59 (m, 2H), 7.47 (d, *J* = 16.7 Hz, 1H), 6.06 (d, *J* = 16.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ (ppm) = 147.7, 146.1, 139.3, 129.9, 128.1, 124.3, 117.0, 101.1.

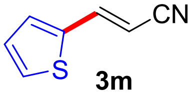
2.12. (Z)-3-(4-bromophenyl) acrylonitrile (3l)



3l

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.47 (d, *J* = 9.9 Hz, 2H), 7.30-7.23 (m, 3H), 5.85 (d, *J* = 17.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ (ppm) = 147.55, 132.19, 130.40, 128.80, 125.63, 117.94, 97.1.

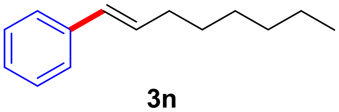
2.13. (Z)-3-(thiophen-2-yl) acrylonitrile (3m)



3m

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.52-7.01 (m, 4H), 5.58 (d, *J* = 15.03 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ (ppm) = 142.7, 140.9, 131.3, 129.4, 128.4, 94.3, 91.7.

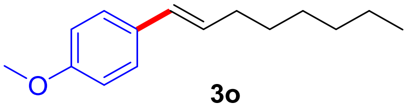
2.14. (E)-1-(oct-1-enyl) benzene (3n)



3n

^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.32-7.17 (m, 5H), 6.44-6.13 (m, 2H), 2.23-2.15 (m, 2H), 1.46-1.31 (m, 8H), 0.91-0.86 (m, 3H). ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ (ppm) = 137.8, 129.7, 128.8, 128.4, 127.2, 125.7, 31.8, 31.4, 29.4, 29.0, 22.7, 14.1.

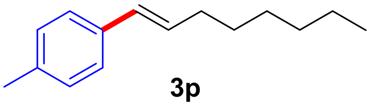
2.15. (E)-1-methoxy-4-(oct-1-enyl) benzene (3o)



3o

^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.18 (d, *J* = 7.2 Hz, 2H), 6.74 (d, *J* = 7.5 Hz, 2H), 6.24 (d, *J* = 15.3 Hz, 1H), 6.06-5.94 (m, 1H), 3.70 (s, 3H), 2.12-2.06 (m, 2H), 1.38-1.12 (m, 8H), 0.86-0.74 (m, 3H). ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ (ppm) = 158.6, 130.8, 128.7, 126.6, 113.7, 55.2, 31.6, 29.6, 29.1, 22.6, 14.2.

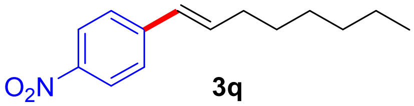
2.16. (E)-1-methyl-4-(oct-1-enyl) benzene (3p)



3p

^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.31-7.08 (m, 4H), 6.39 (d, *J* = 17.2 Hz, 1H), 6.27-6.15 (m, 1H), 2.35 (s, 3H), 2.26-2.17 (m, 2H), 1.52-1.23 (m, 8H), 0.95 – 0.86 (m, 3H). ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ (ppm) = 137.1, 135.1, 129.4, 128.9, 128.3, 125.7, 31.8, 29.4, 29.0, 22.7, 21.1, 14.1.

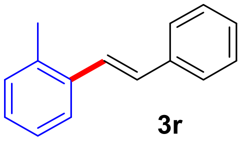
2.17. (E)-1-nitro-4-(oct-1-enyl) benzene (3q)



3q

^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) = 8.14-8.04 (m, 2H), 7.46-7.21 (m, 2H), 6.37 (d, *J* = 2.1 Hz, 1H), 5.95-5.63 (m, 2H), 2.26-2.14 (m, 2H), 1.47-1.16 (m, 8H), 0.90-0.75 (m, 3H). ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ (ppm) = 144.6, 136.7, 128.0, 126.2, 126.0, 123.9, 123.5, 33.2, 31.6, 28.9, 22.6, 14.0.

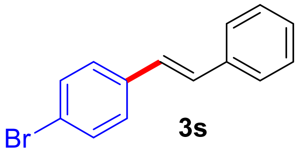
2.18. (E)-1-methyl-2-styryl benzene (3r)



3r

^{1}H NMR (CDCl$_3$, 250 MHz): δ (ppm) = 7.48-7.39 (m, 3 H), 7.27-7.07 (m, 7 H), 6.89 (d, 1 H, *J*= 16.63 Hz), 2.33 (s, 3 H). ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ (ppm) = 137.8, 136.5, 135.9, 130.1, 128.8, 127.7, 126.7, 126.6, 126.3, 125.5, 20.0.

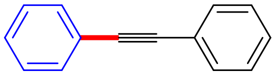
2.19. (E)-1-bromo-4-styryl benzene (3s)



3s

^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.55-7.29 (m, 9H), 7.07 (m, 2H). ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ (ppm) = 136.9, 136.3, 131.8, 129.4, 128.8, 127.9, 127.4, 126.6, 121.3.

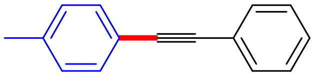
2.20. 1,2-diphenylethyne (5a)



5a

^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.49-7.41 (m, 4H), 7.30-7.23 (m, 6H). ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ (ppm) = 131.6, 128.3, 128.2, 123.4, 89.5.

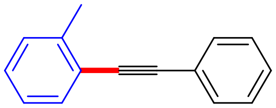
2.21. 1-(2-p-tolylethynyl) benzene (5b)



5b

^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) = 7.46-7.42 (m, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.27-7.22 (m, 3H), 7.06 (d, *J* = 7.8 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ (ppm) = 138.4, 132.6, 131.6, 129.1, 128.3, 128.1, 123.6, 120.3, 89.6, 21.5.

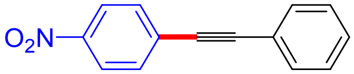
2.22. 1-(2-o-tolylethynyl) benzene (5c)



5c

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.50-7.40 (m, 3H), 7.30-7.20 (m, 3H), 7.17-7.06 (m, 3H), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ (ppm) = 140.2, 131.8, 131.5, 129.6, 128.4, 128.3, 128.2, 125.5, 123.5, 122.8, 88.3, 82.0, 20.7.

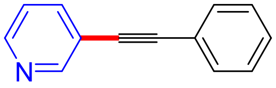
2.23. 1-(2-(4-nitrophenyl)ethynyl) benzene (5d)



5d

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 8.23-8.19 (m, 2H), 7.70-7.63 (m, 2H), 7.59-7.53 (m, 2H), 7.41-7.36 (m, 3H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ (ppm) = 146.1, 132.3, 131.5, 130.3, 129.2, 128.5, 123.6, 122.1, 94.6, 87.6.

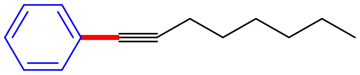
2.24. 3-(2-phenylethynyl) pyridine (5e)



5e

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 8.69 (s, 1H), 8.48-8.44 (m, 1H), 7.75-7.68 (m, 1H), 7.50-7.42 (m, 2H), 7.29-7.15 (m, 4H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ (ppm) = 152.1, 148.3, 138.3, 131.8, 128.8, 128.5, 123.1, 122.6, 120.4, 92.7, 85.8.

2.25. 1-(oct-1-ynyl)benzene (5f)

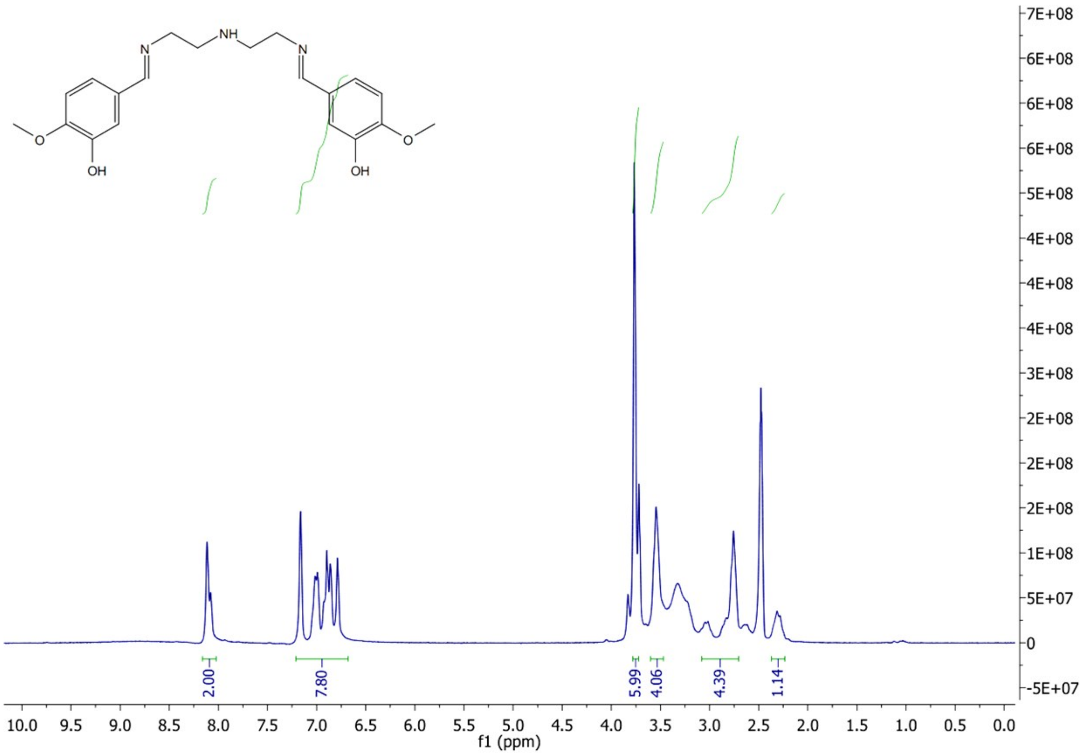


5f

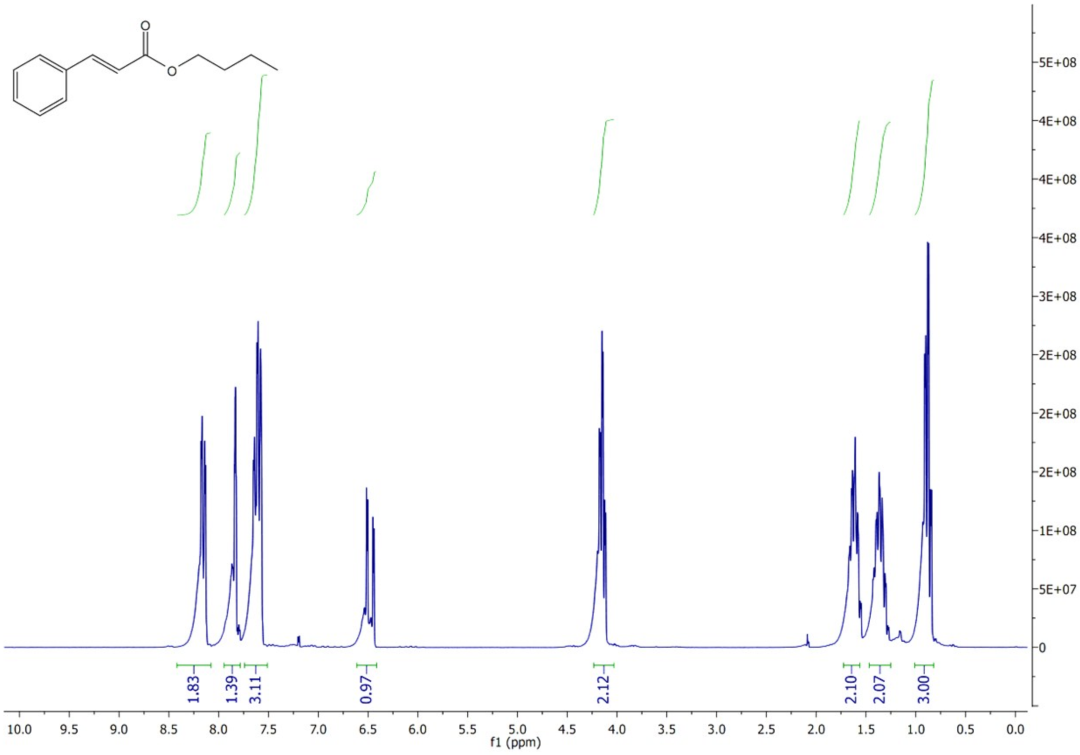
The general procedure afforded 76% for the reaction of 1-octyne with iodobenzene. The product was oily and the spectral data were previously reported in literature.[1]

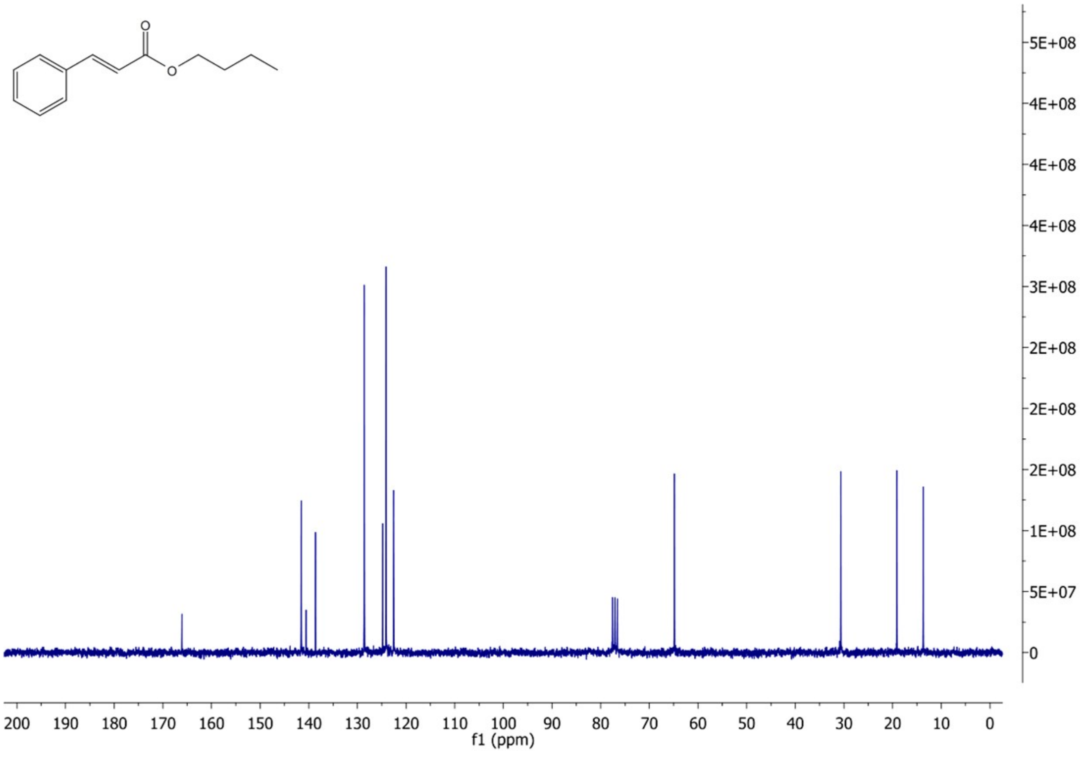
3. ^{1}HNMR and ^{13}CNMR spectra for all synthesized compounds

3.1. NNN Schiff base ligand

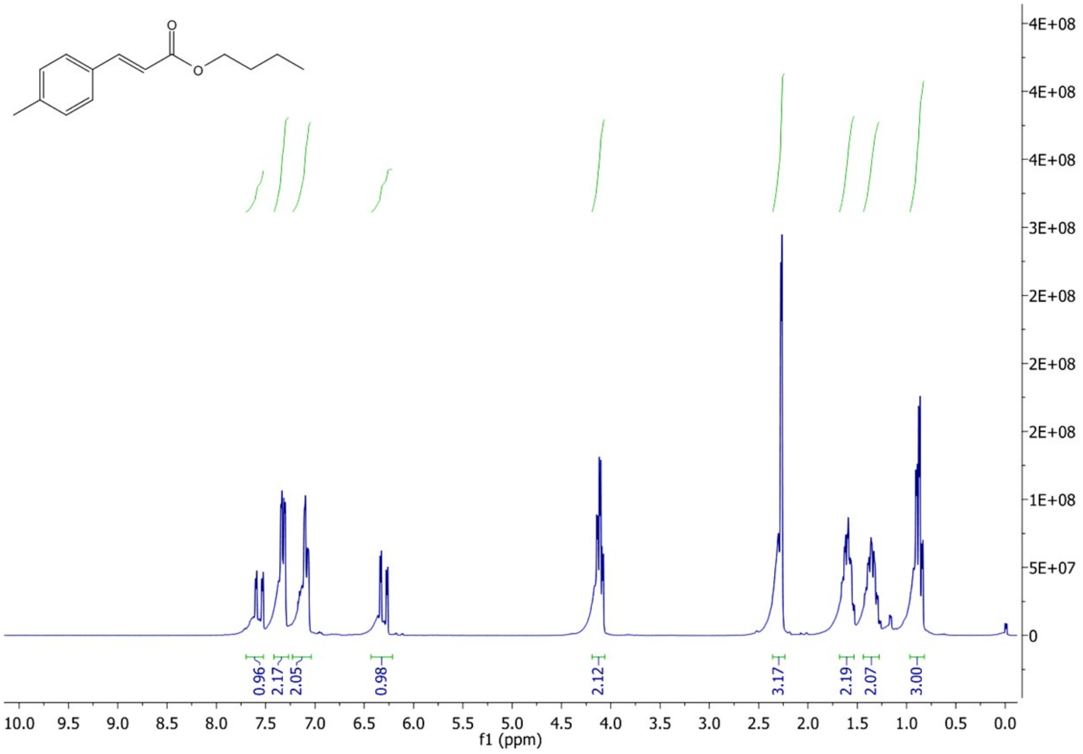


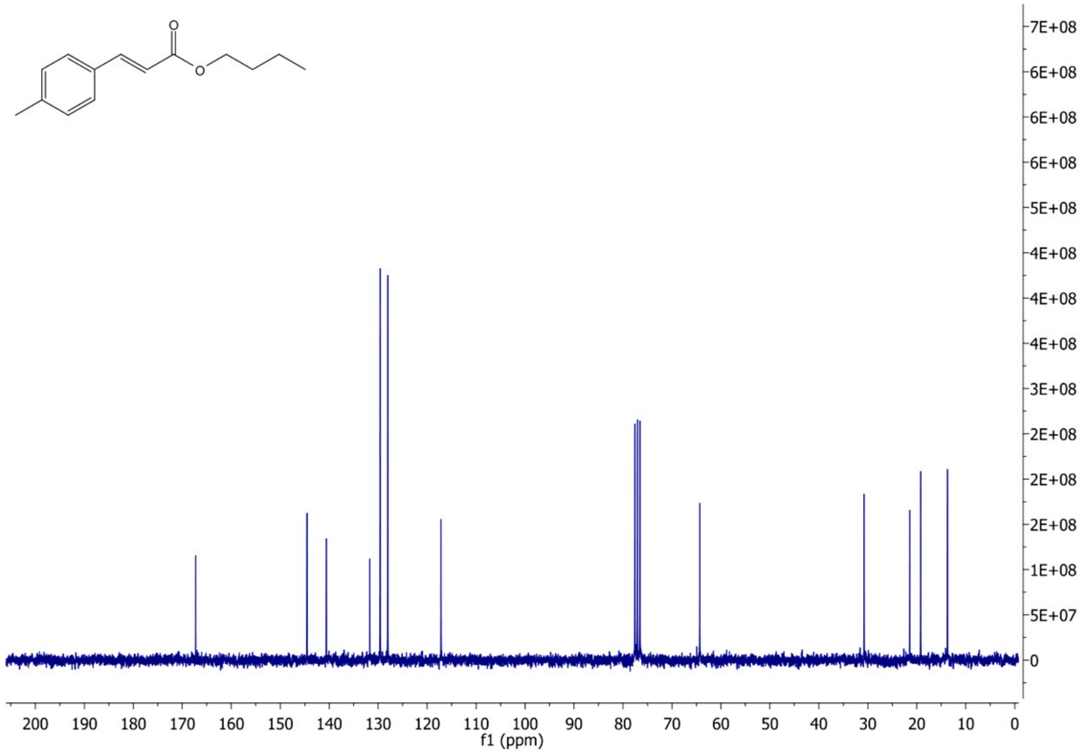
3.2. butyl cinnamate (3a)



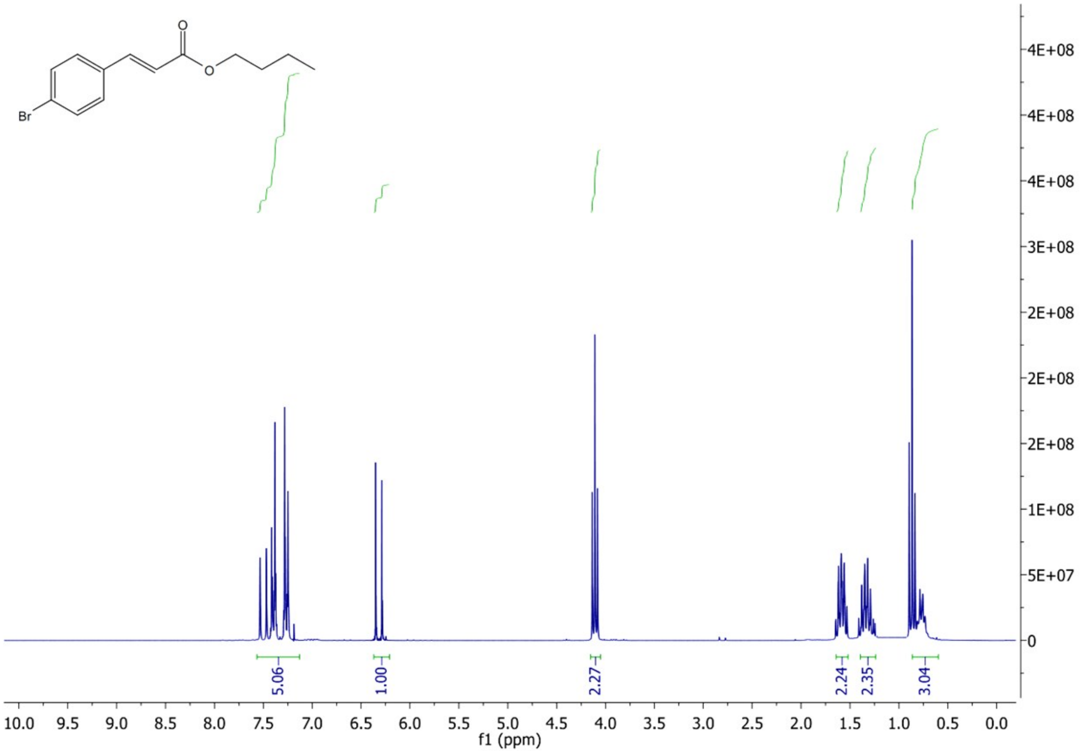


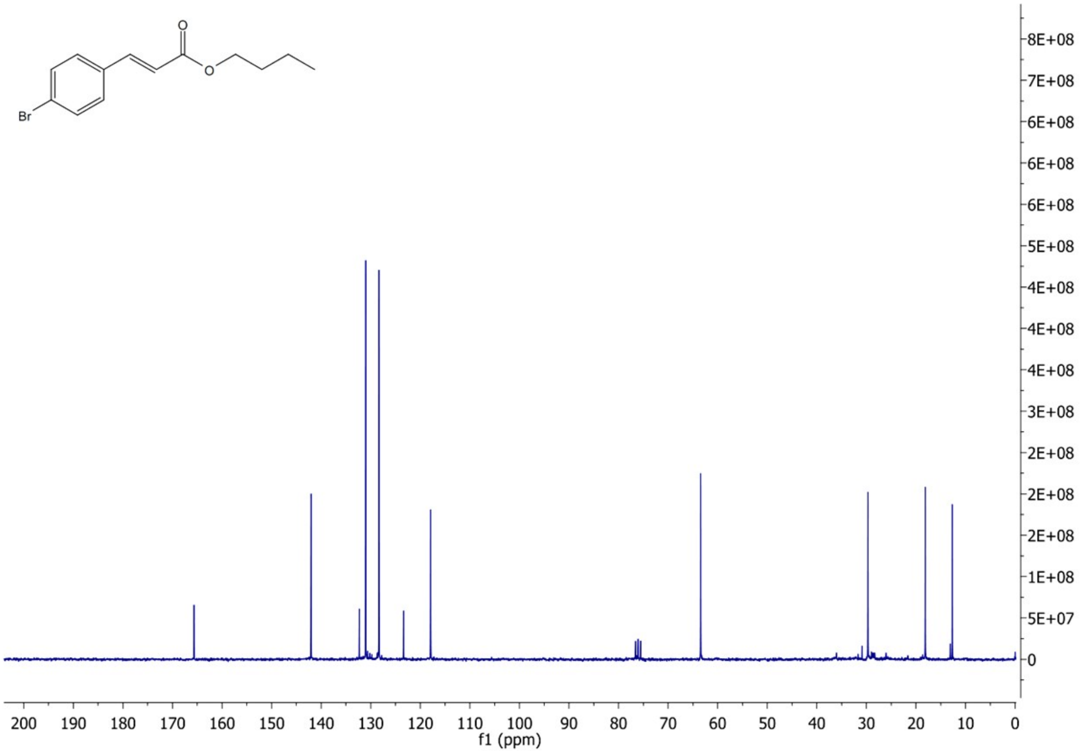
3.3. (E)-butyl 3-p-tolylacrylate (3b)



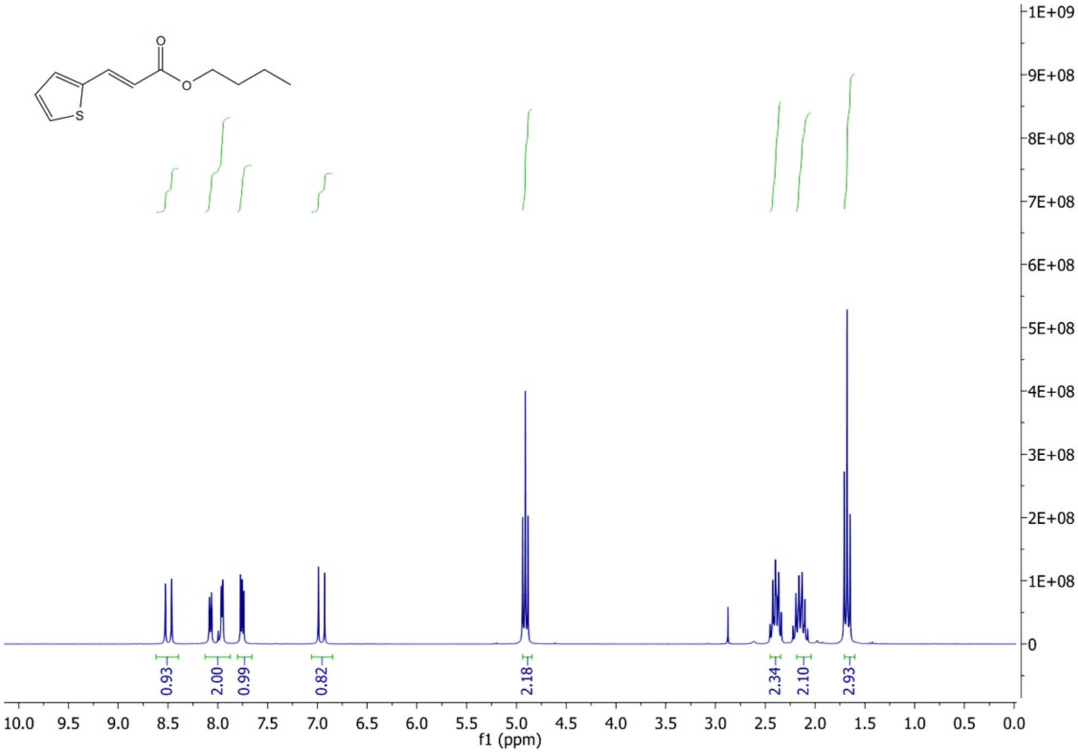


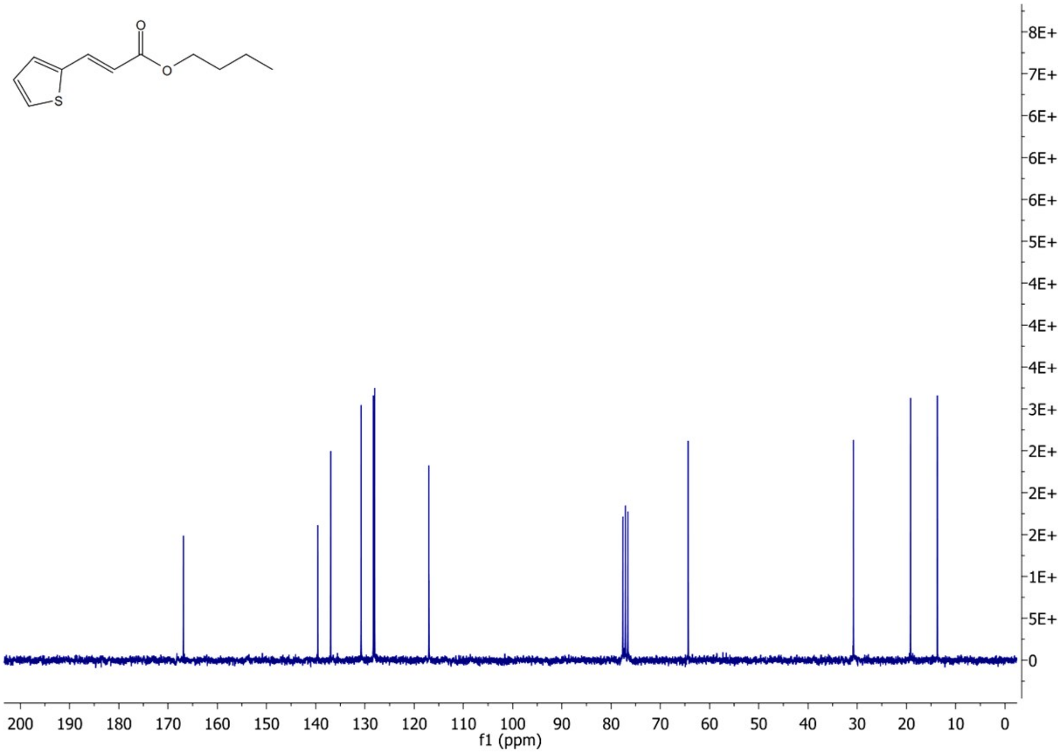
3.4. (E)-butyl 3-(4-bromophenyl)acrylate (3c)



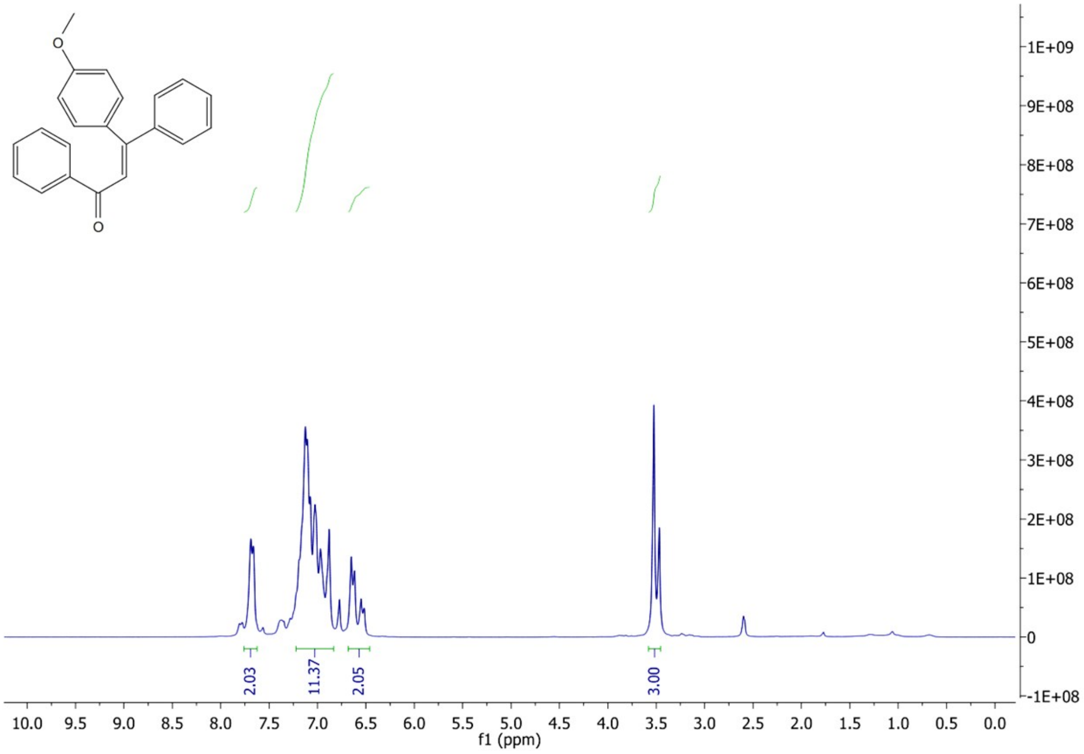


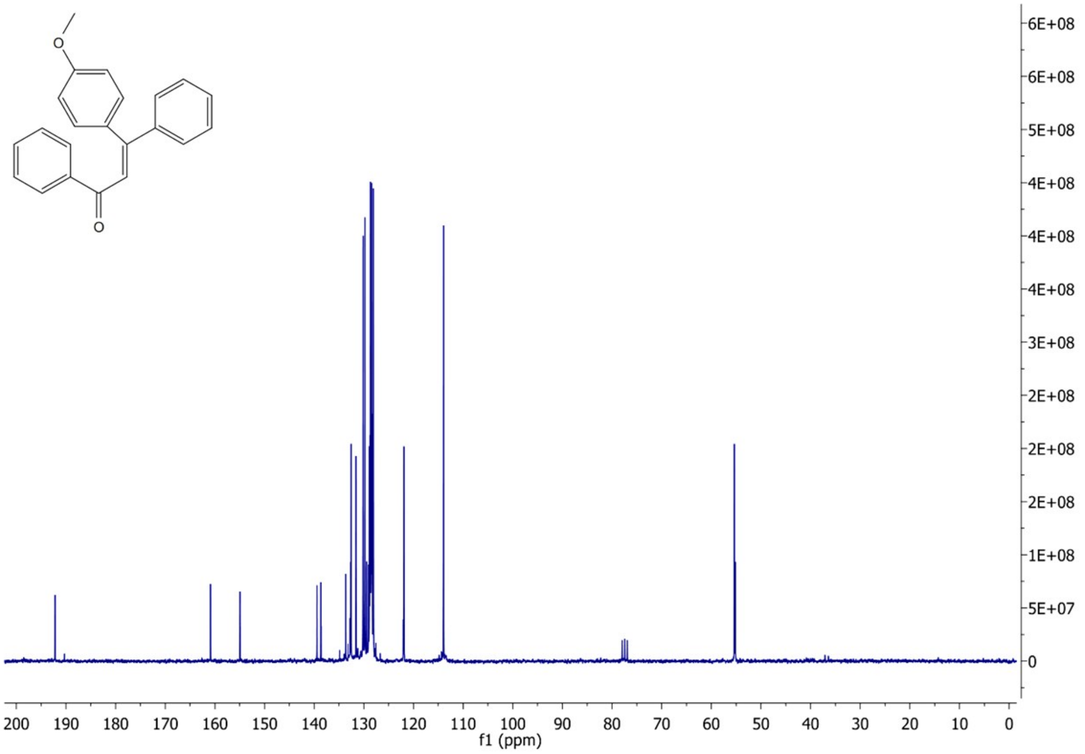
3.5. (E)-butyl 3-(thiophen-2-yl)acrylate (3d)



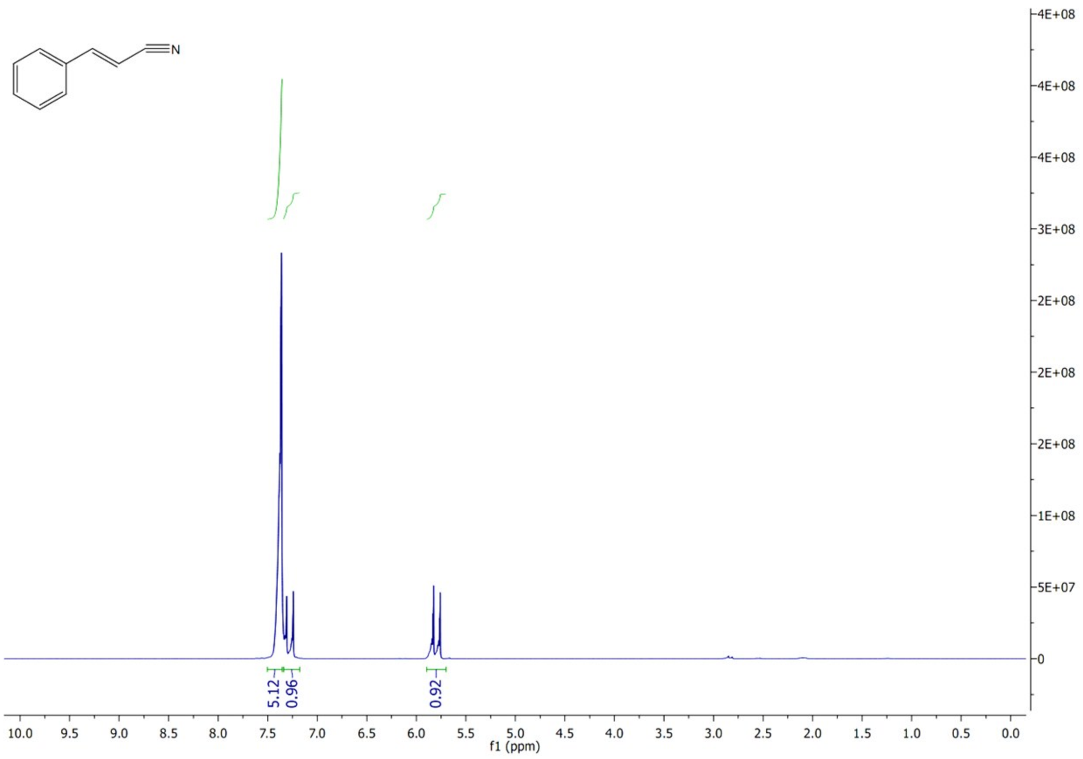


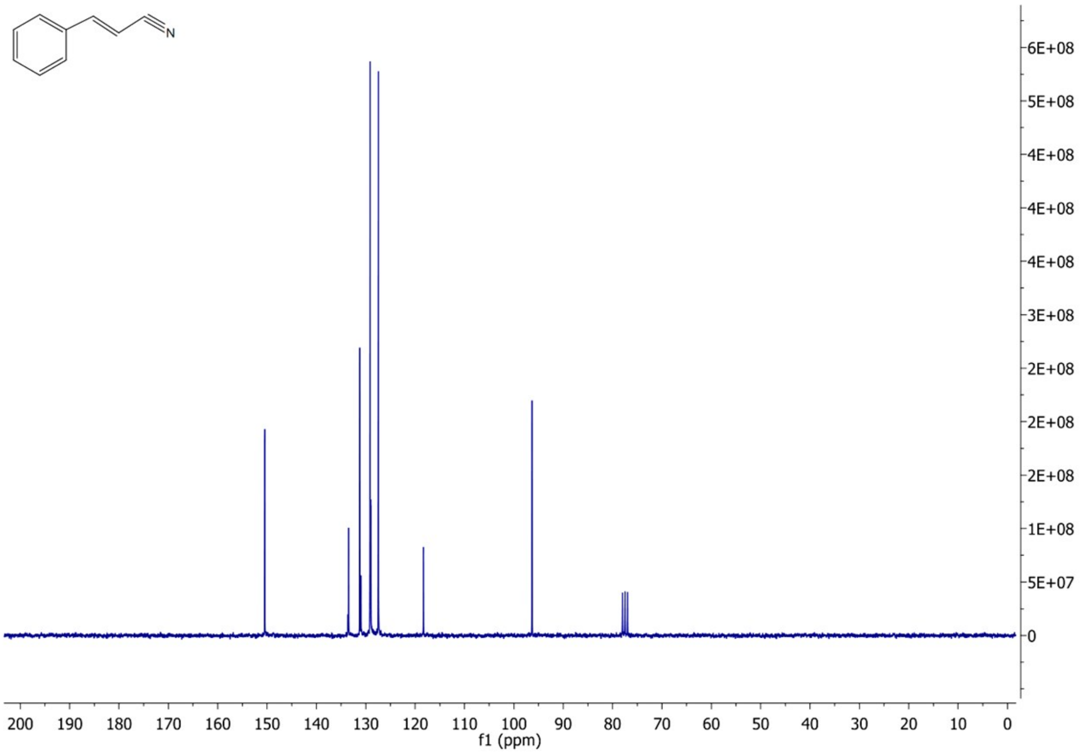
3.6. (Z)-3-(4-methoxyphenyl)-1,3-diphenylprop-2-en-1-one (3f)



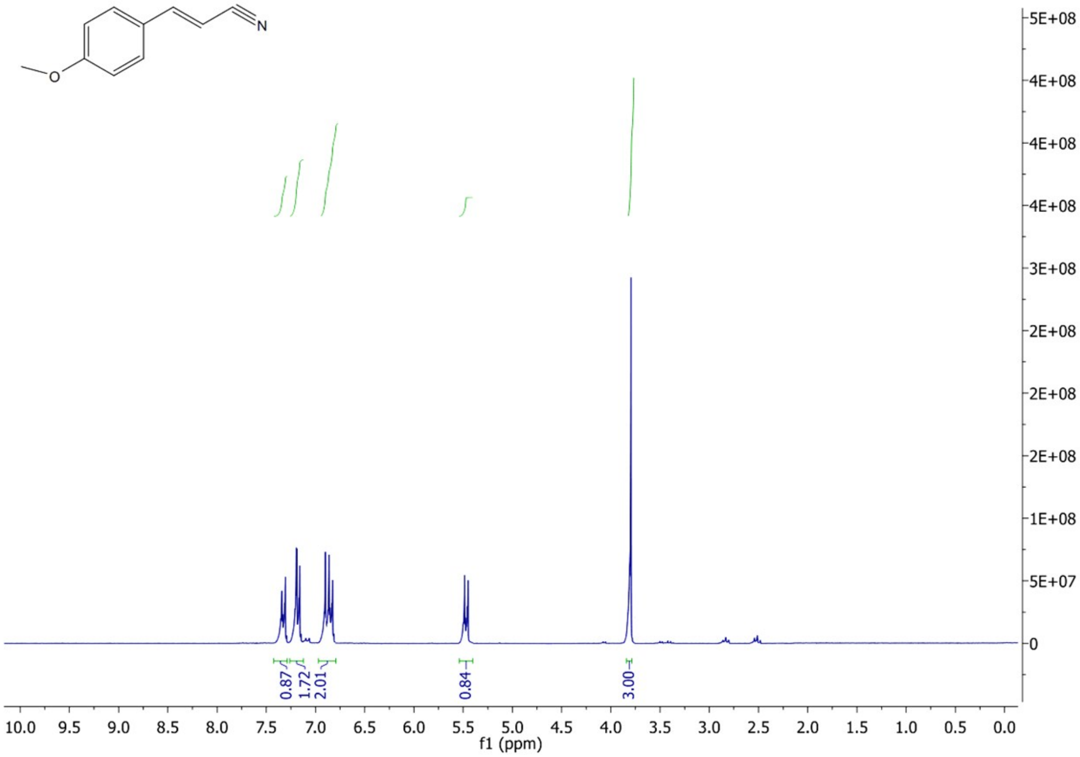


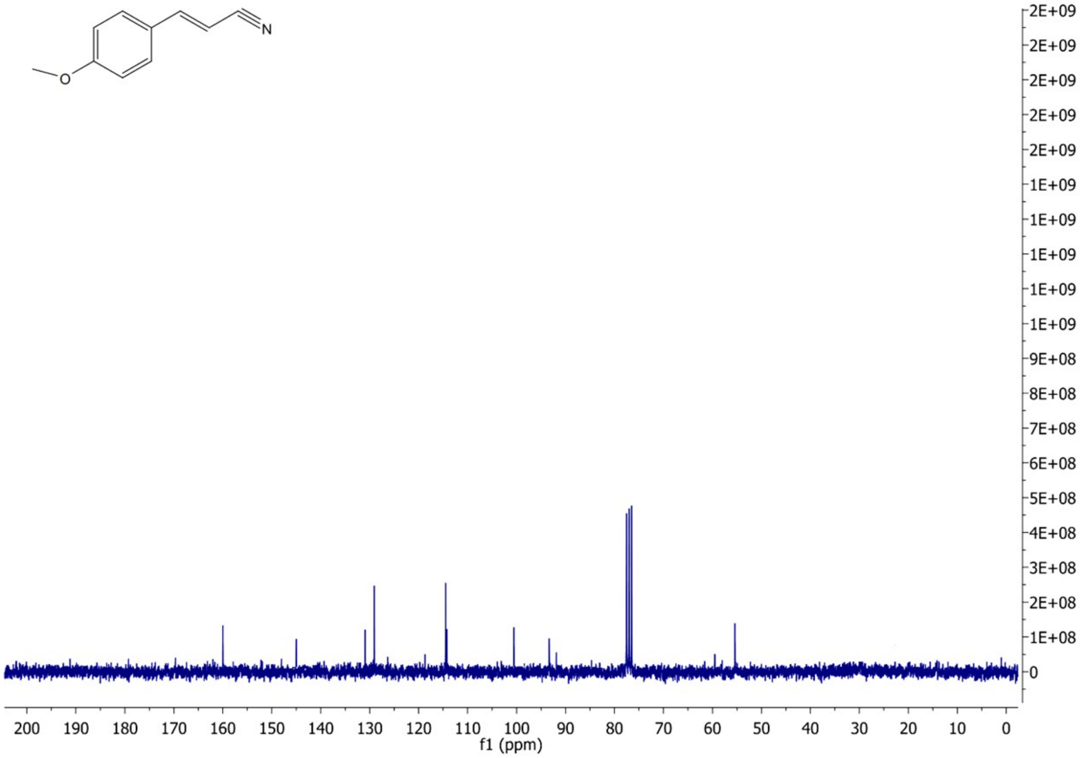
3.7. (Z)-3-phenylacrylonitrile (3g)



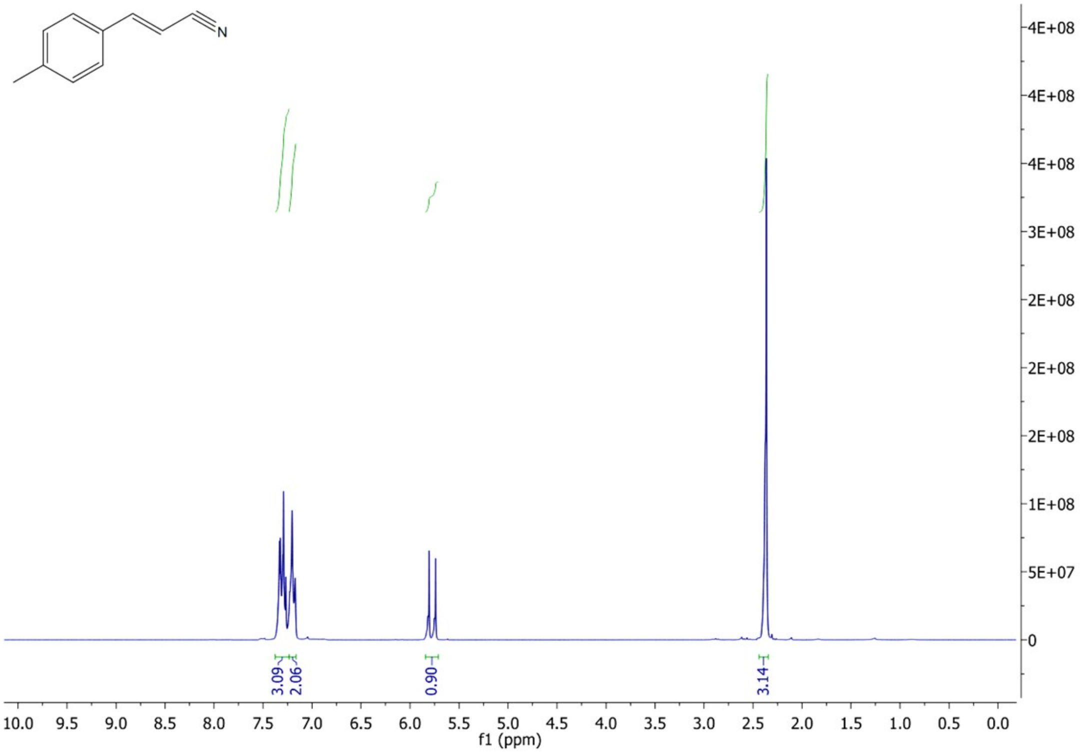


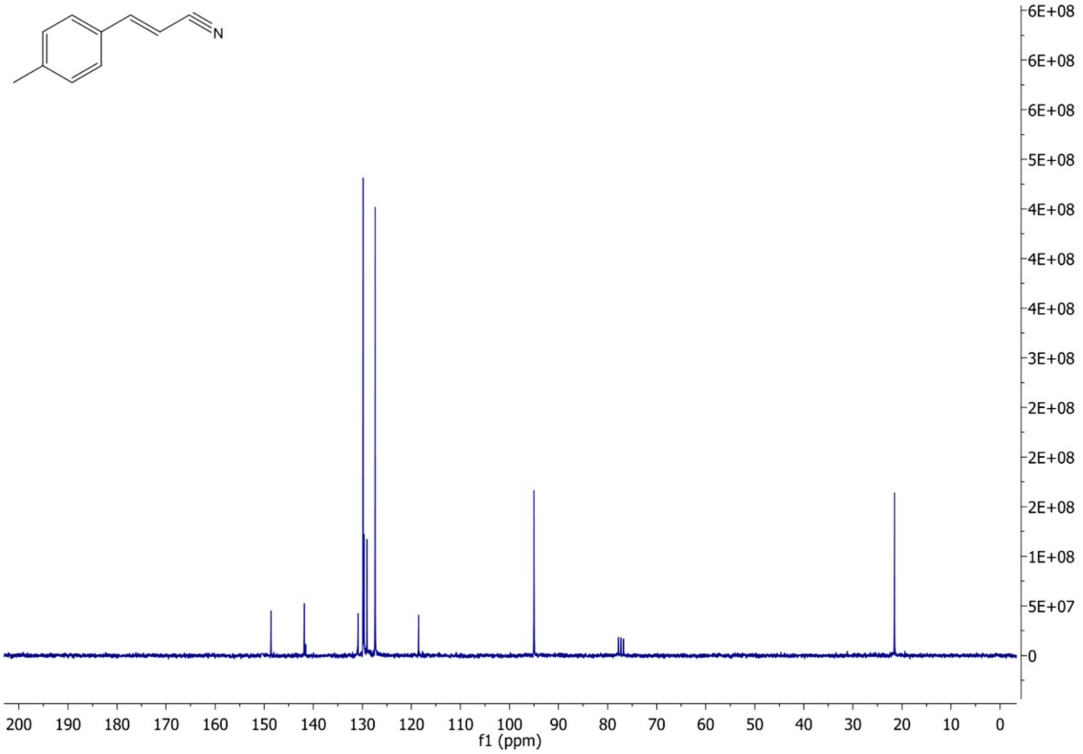
3.8. (Z)-3-(4-methoxyphenyl) acrylonitrile (3h)



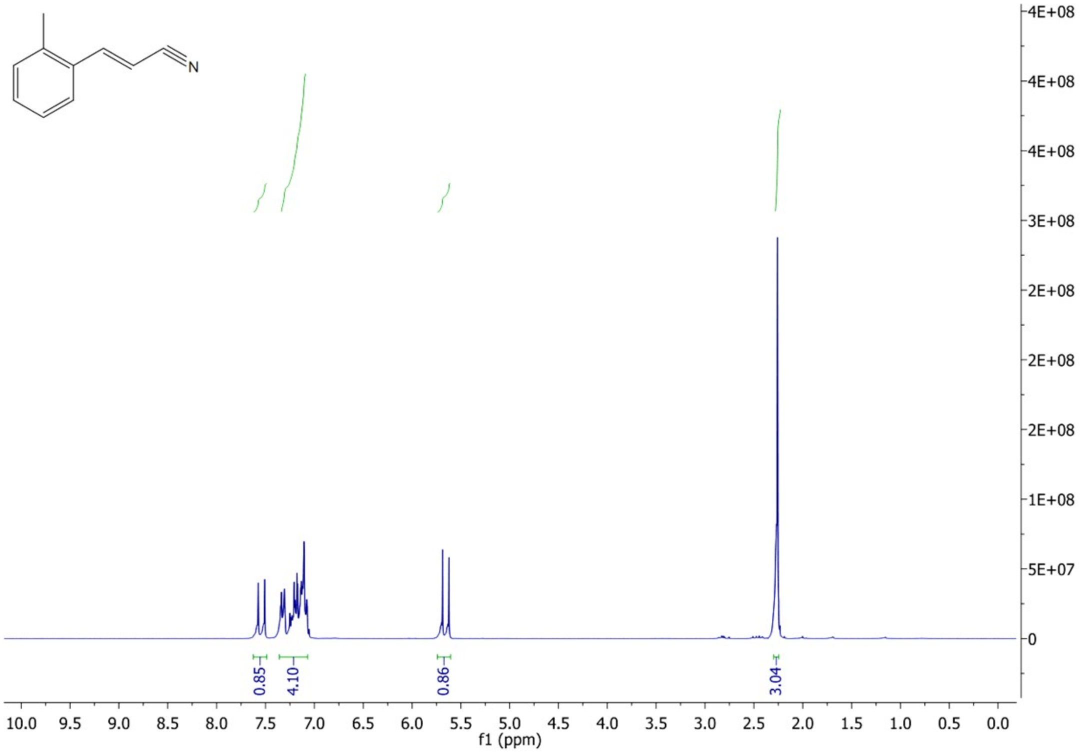


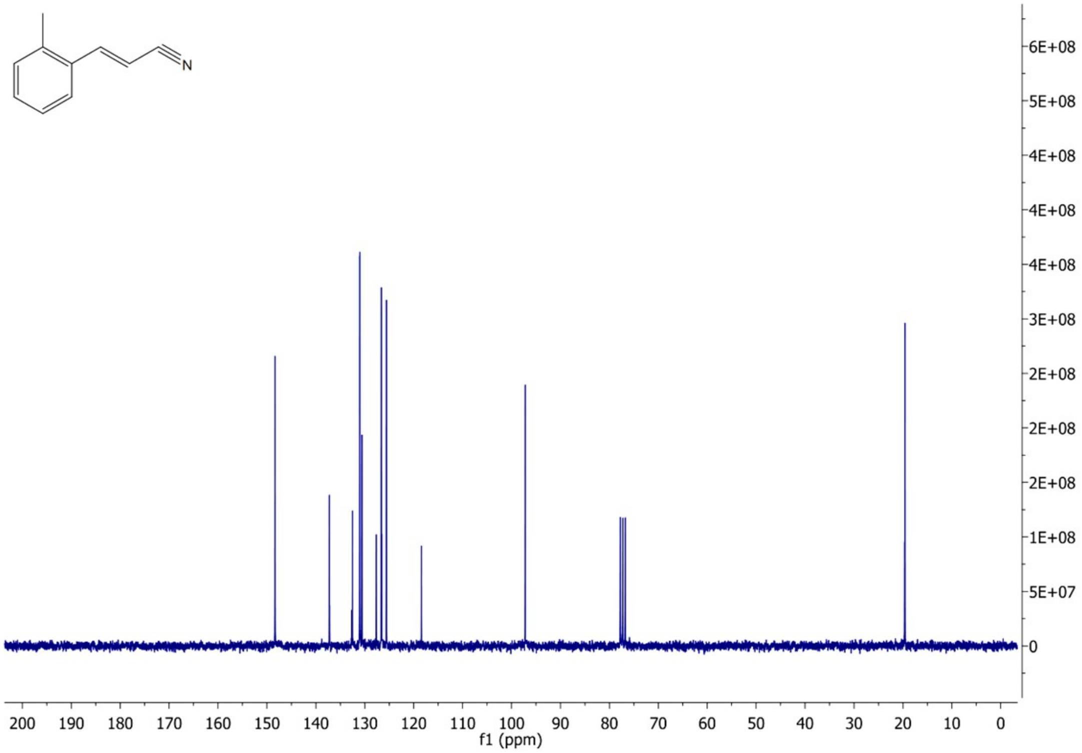
3.9. (Z)-3-p-tolylacrylonitrile (3i)



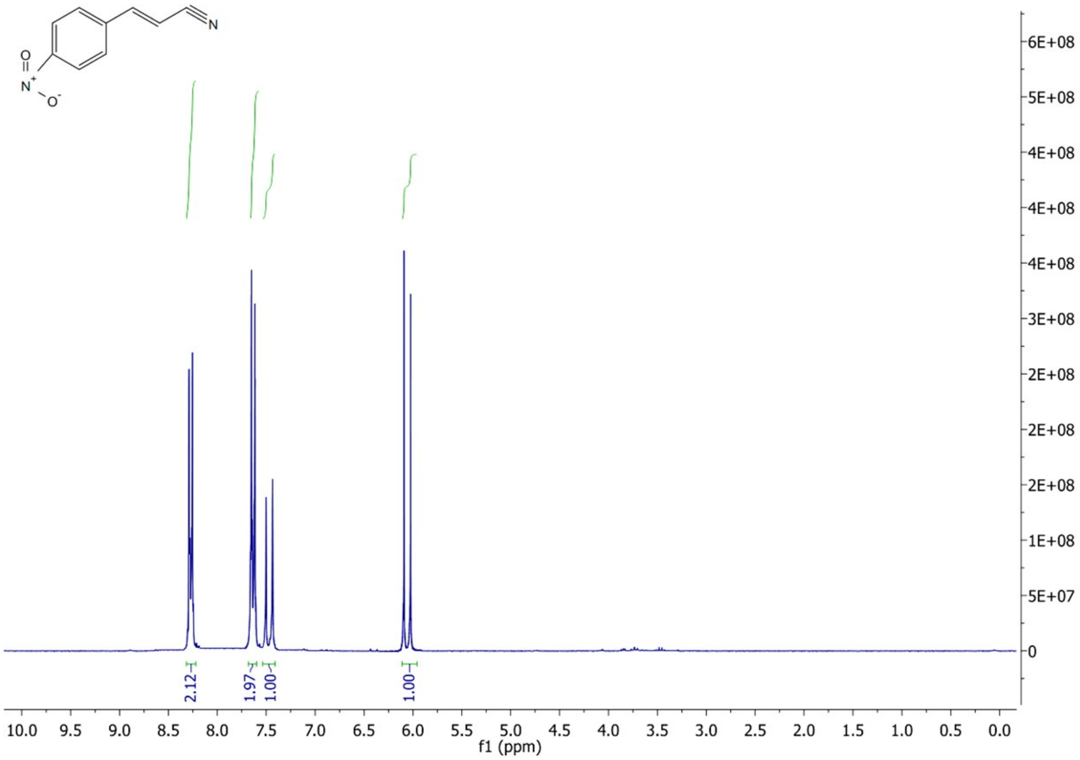


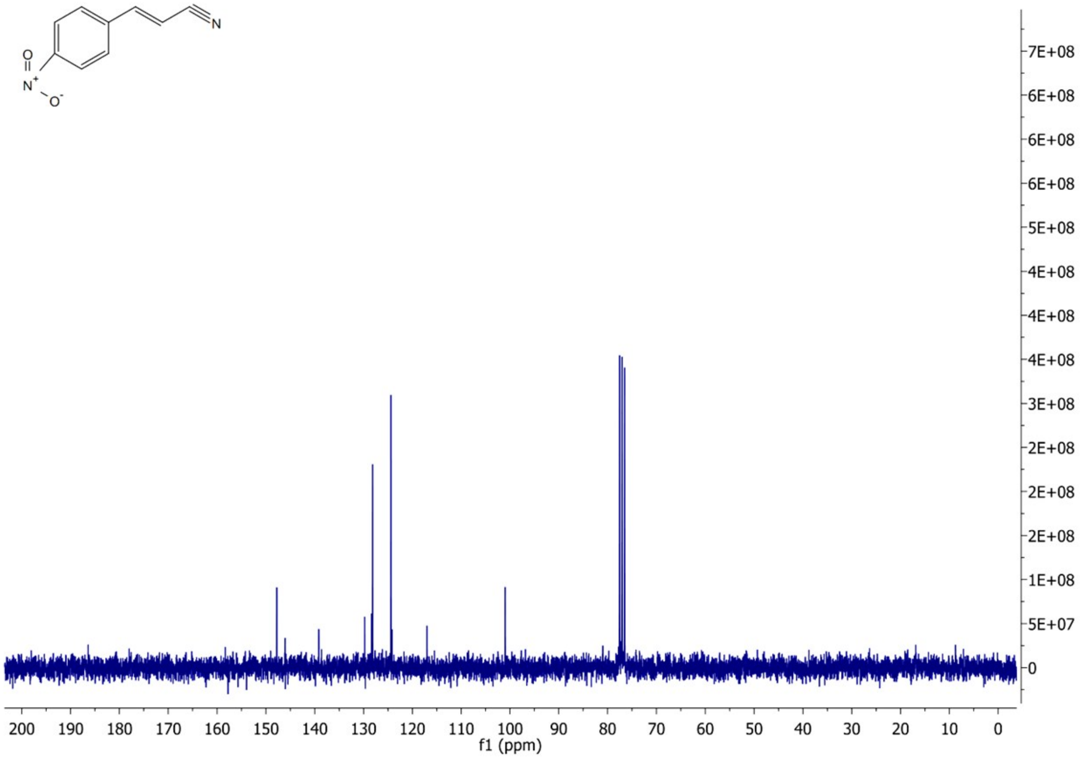
3.10. (Z)-3-o-tolylacrylonitrile (3j)



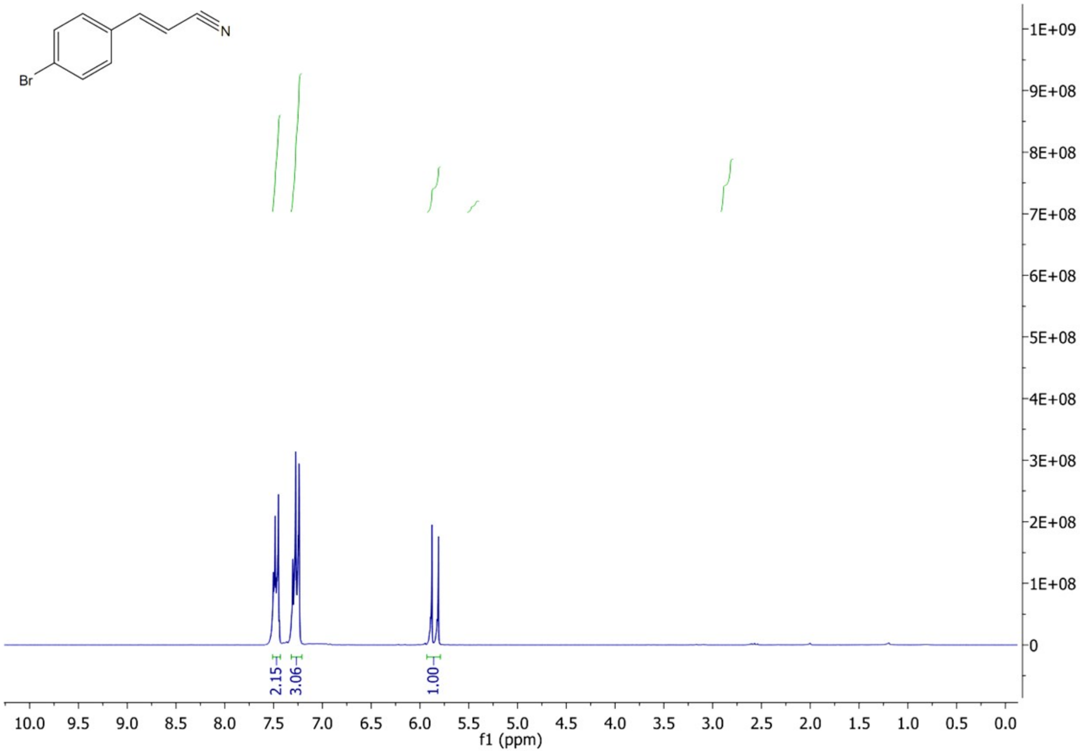


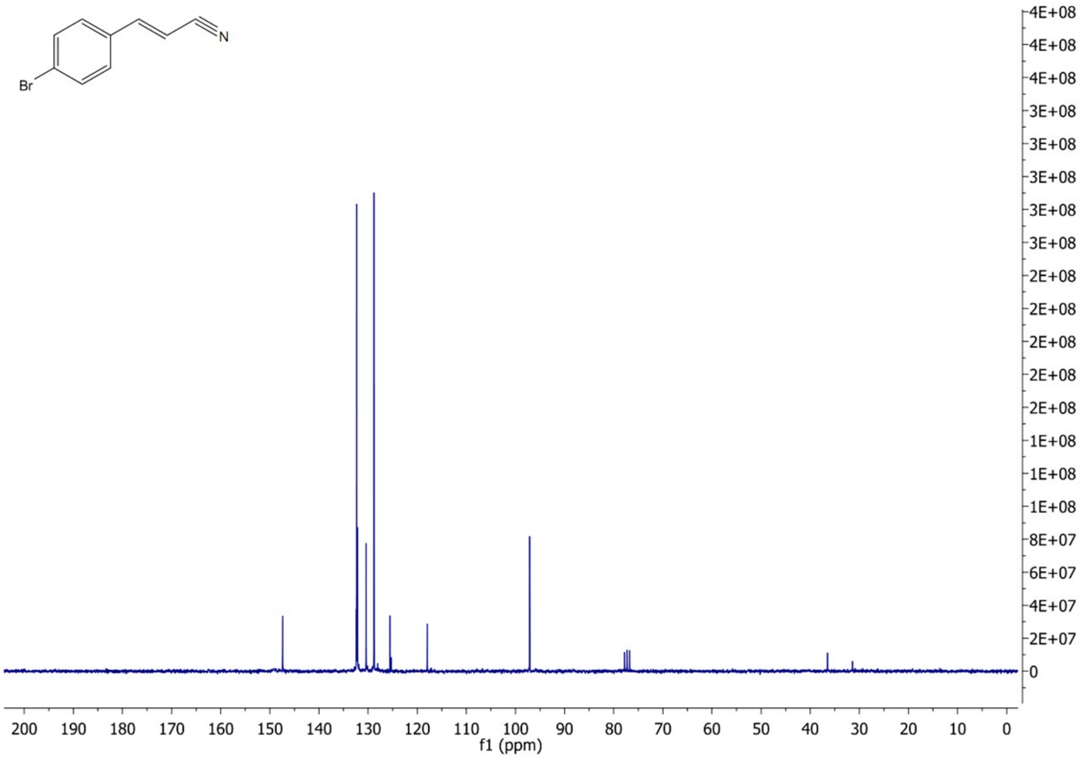
3.11. (Z)-3-(4-nitrophenyl) acrylonitrile (3k)



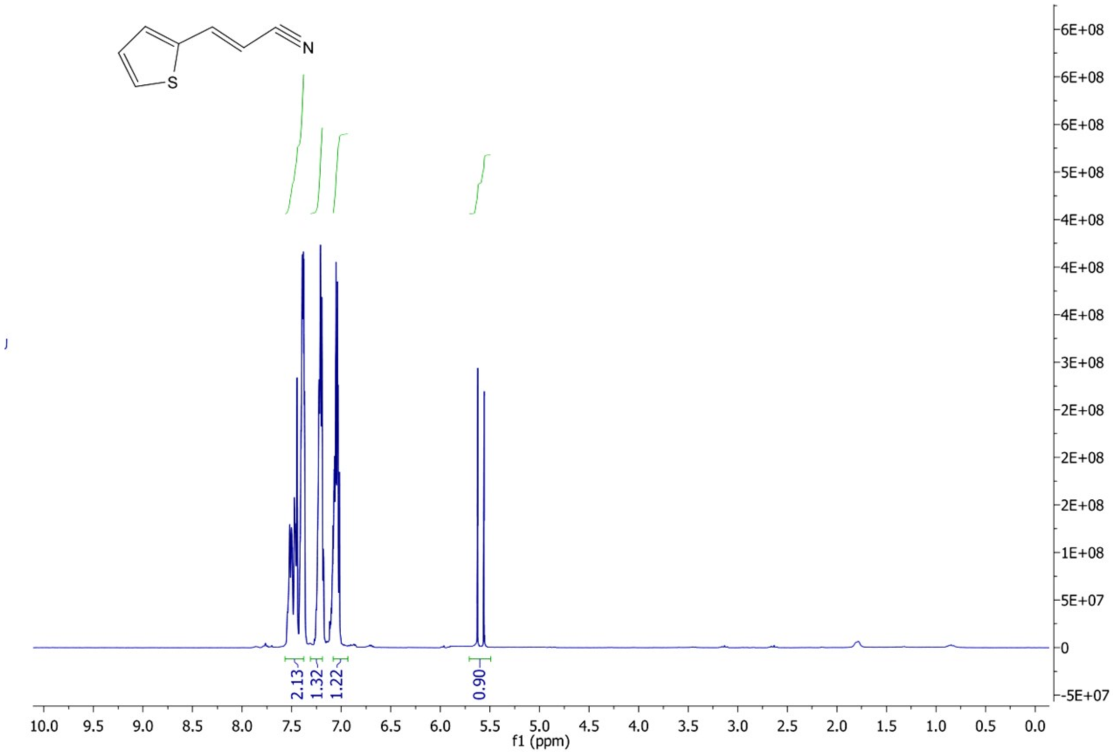


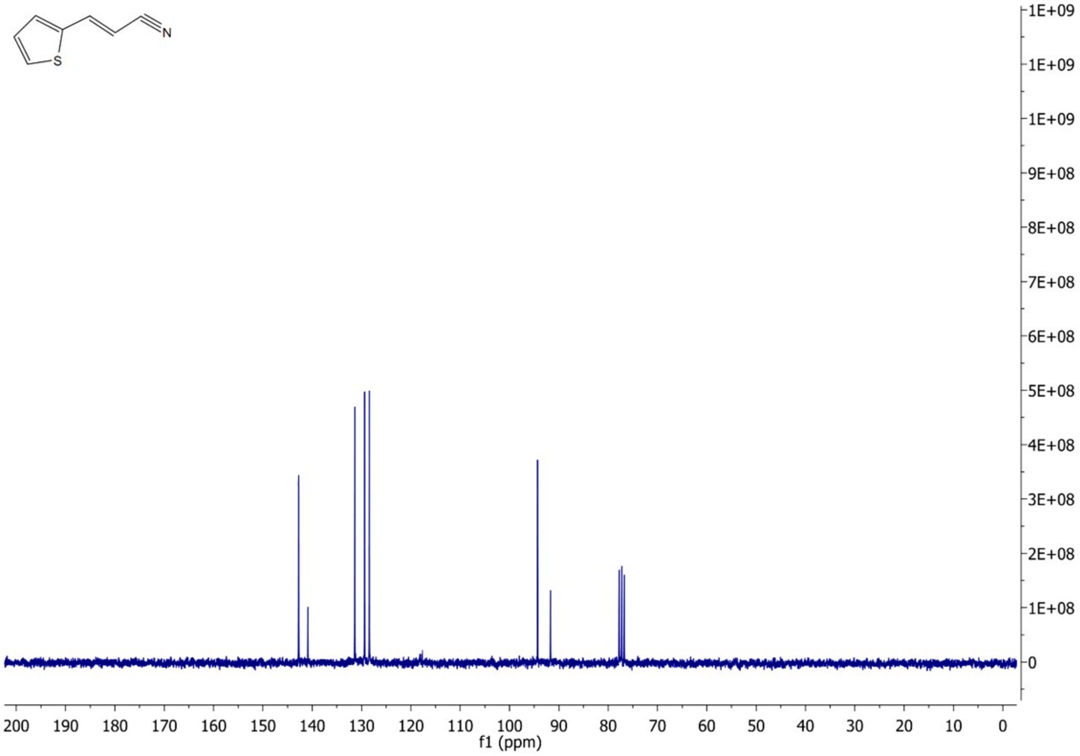
3.12. (Z)-3-(4-bromophenyl) acrylonitrile (3l)



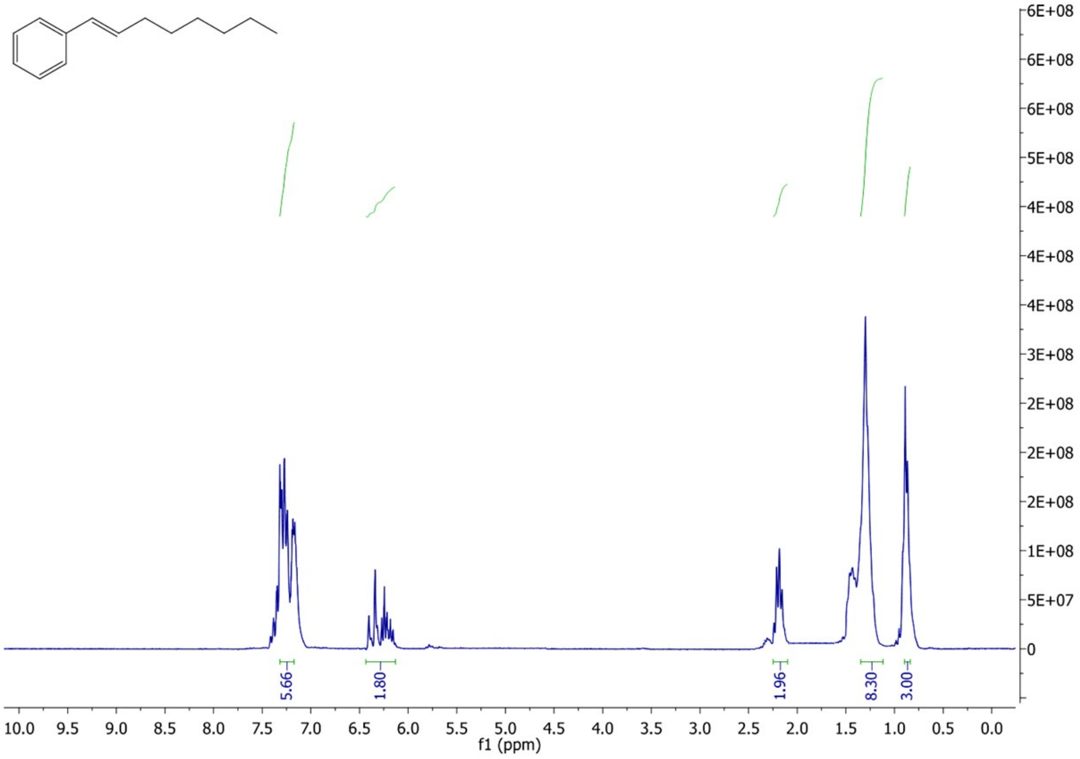


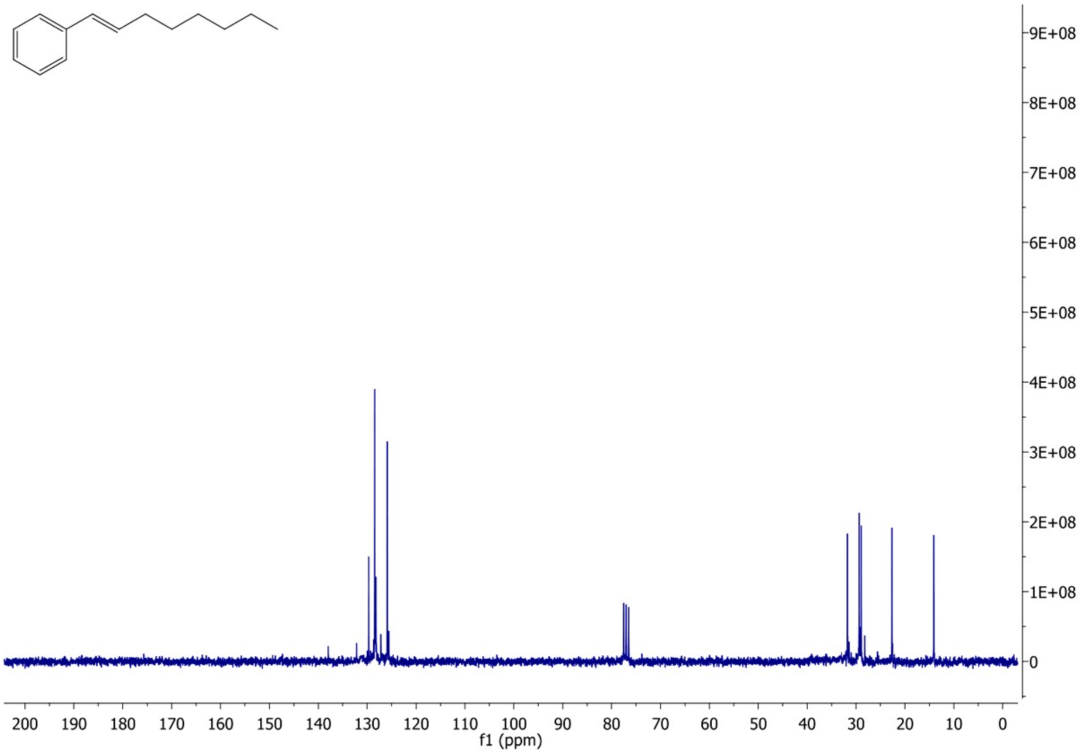
3.13. (Z)-3-(thiophen-2-yl) acrylonitrile (3m)



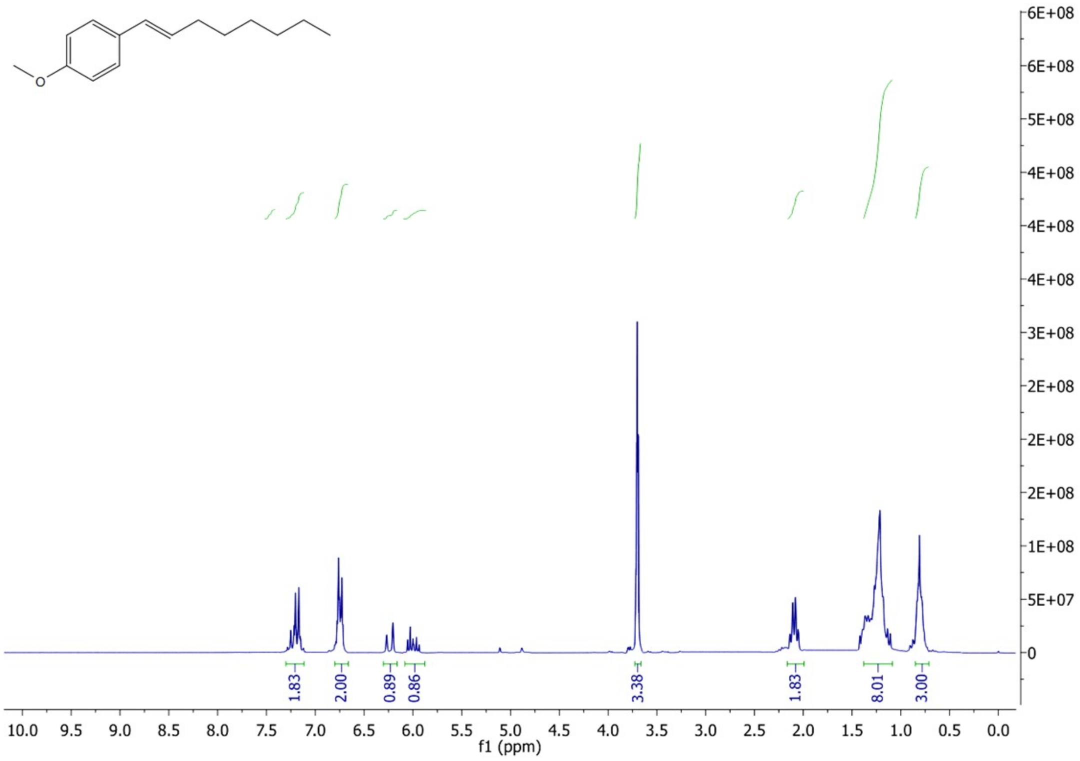


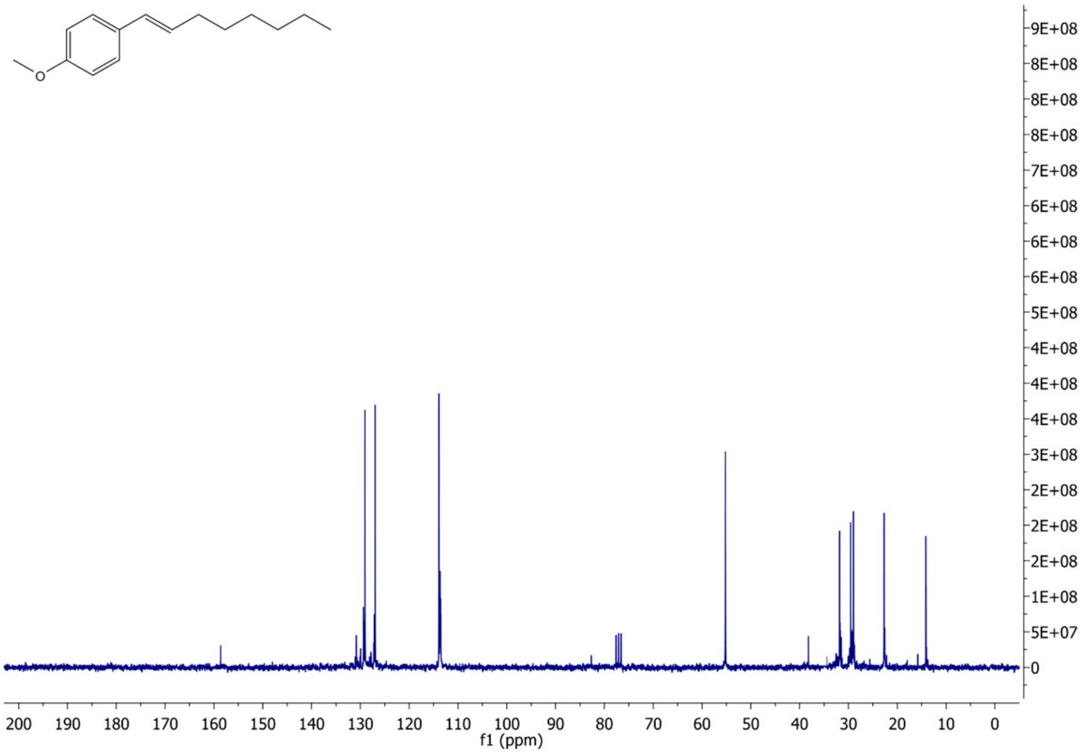
3.14. (E)-1-(oct-1-enyl) benzene (3n)



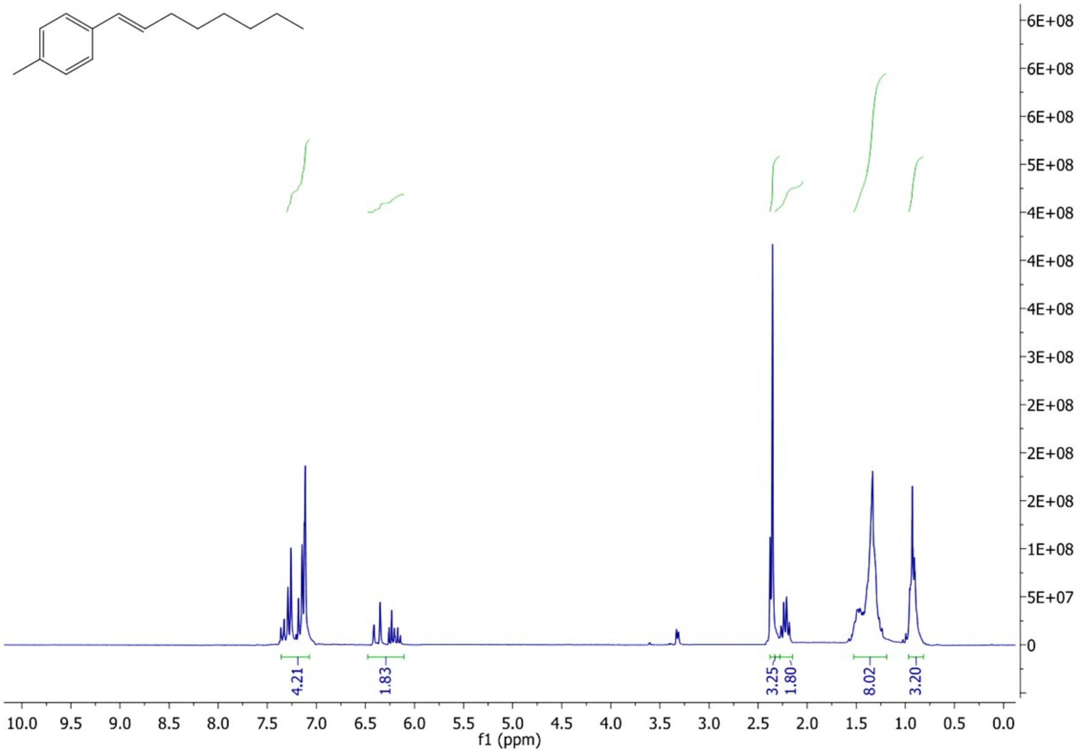


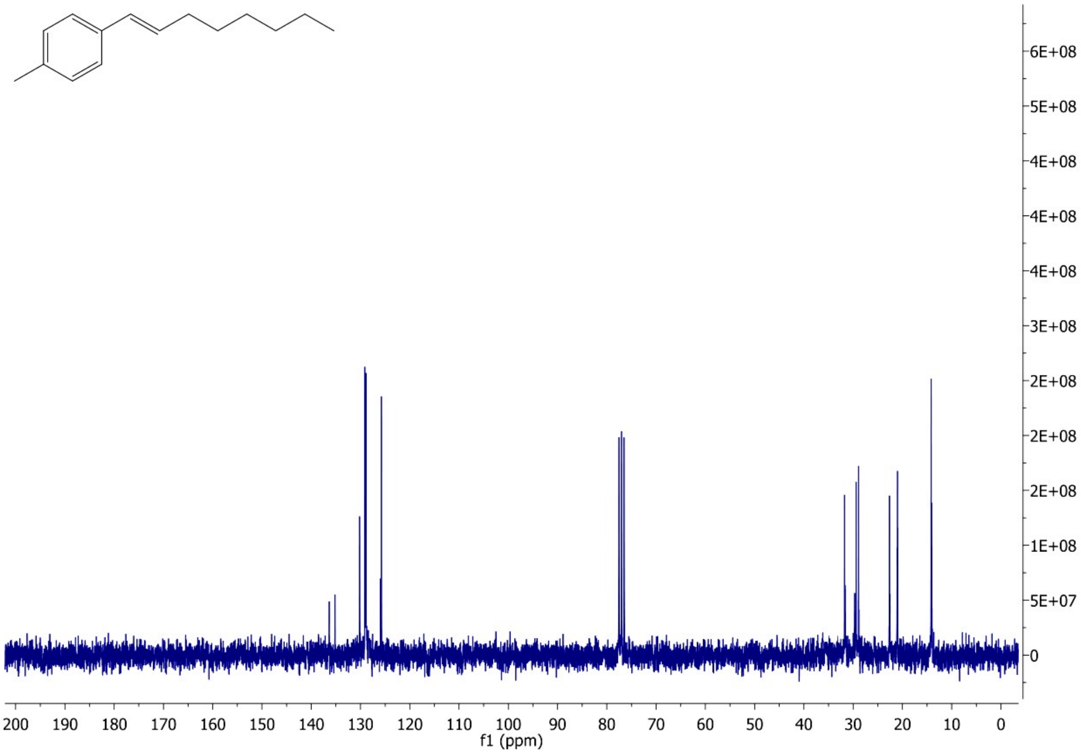
3.15. (E)-1-methoxy-4-(oct-1-enyl) benzene (3o)



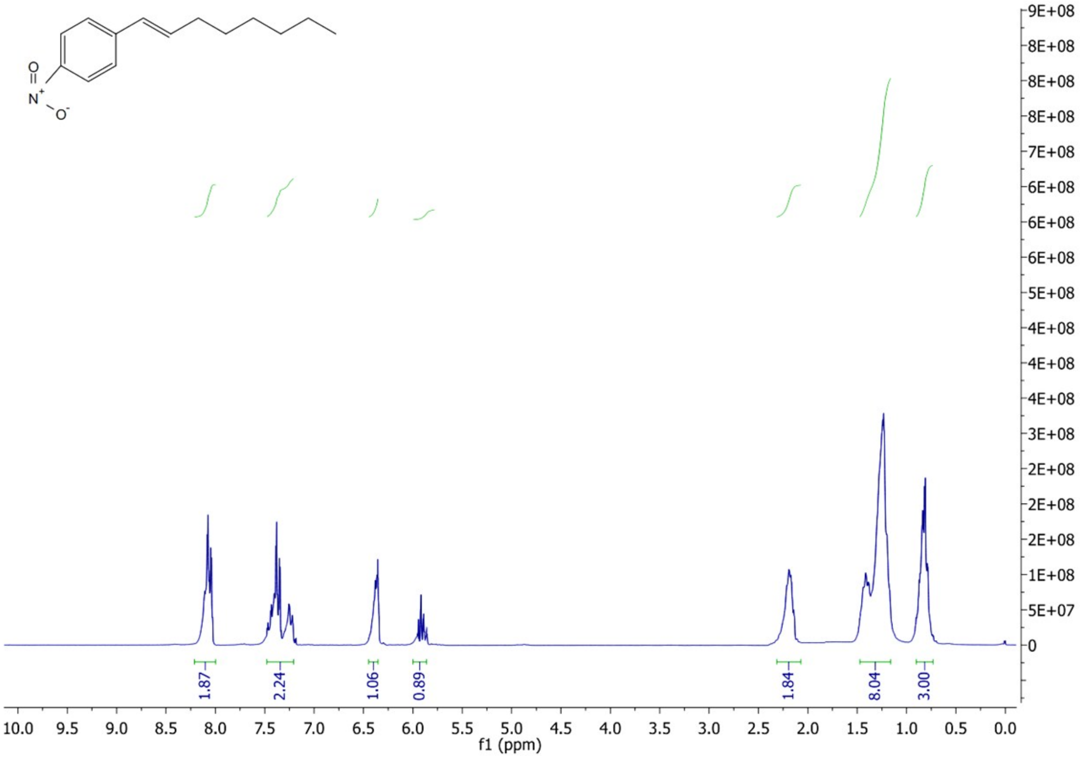


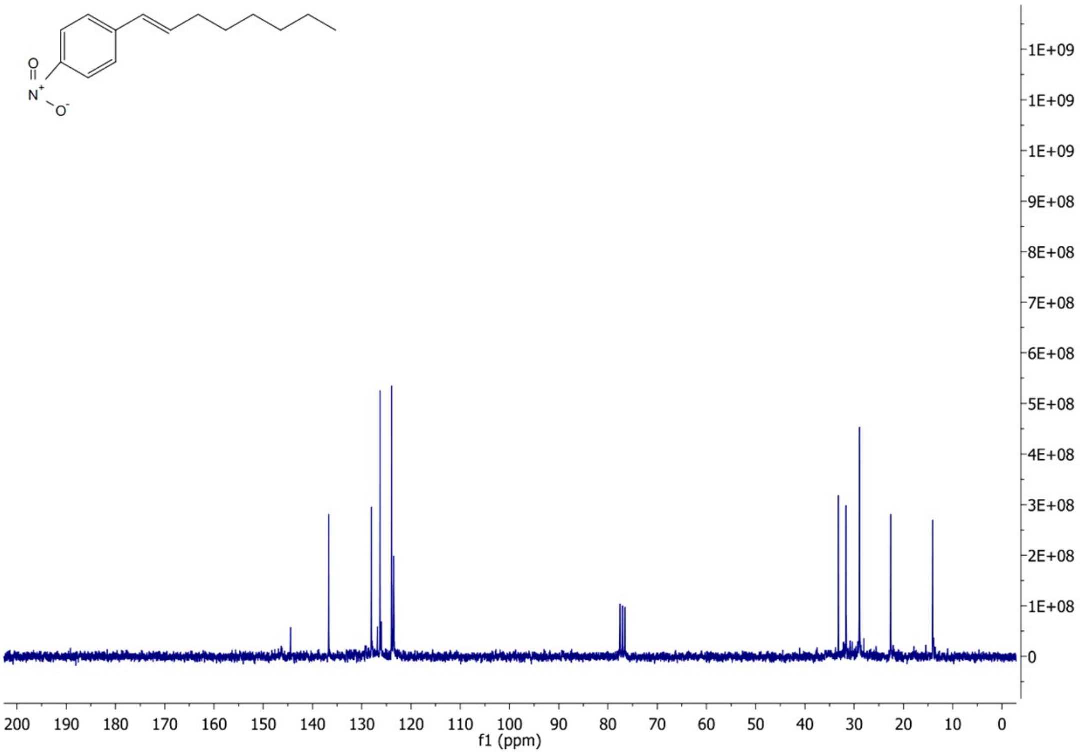
3.16. (E)-1-methyl-4-(oct-1-enyl) benzene (3p)



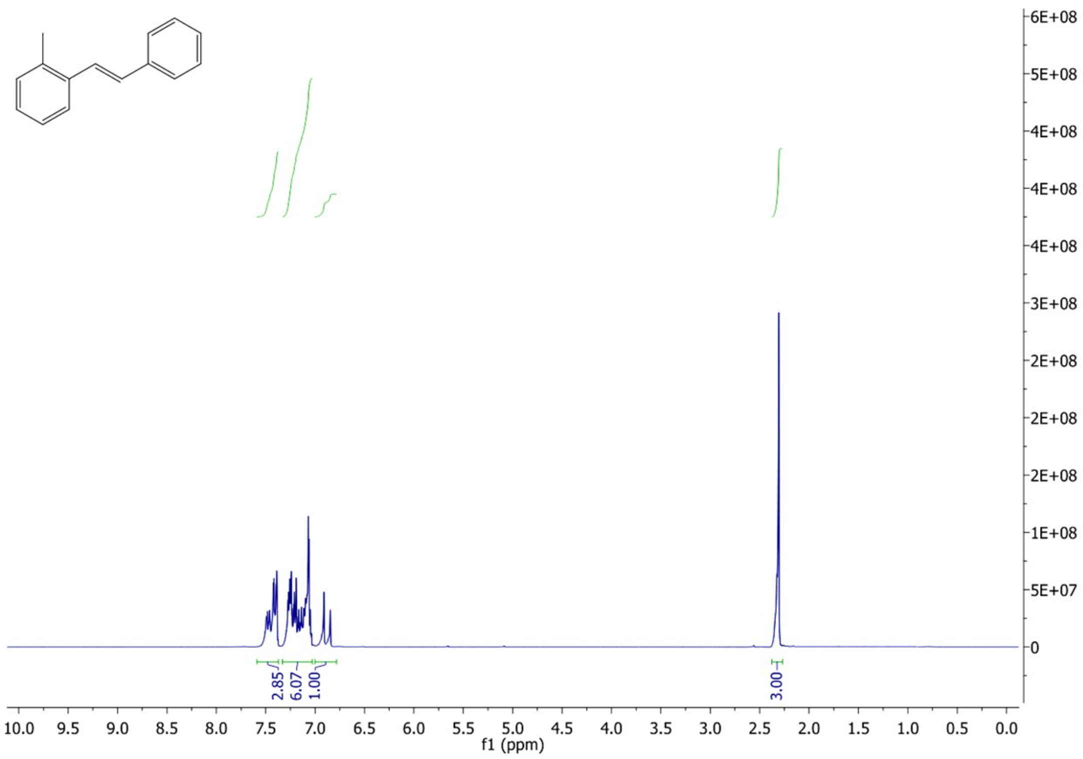


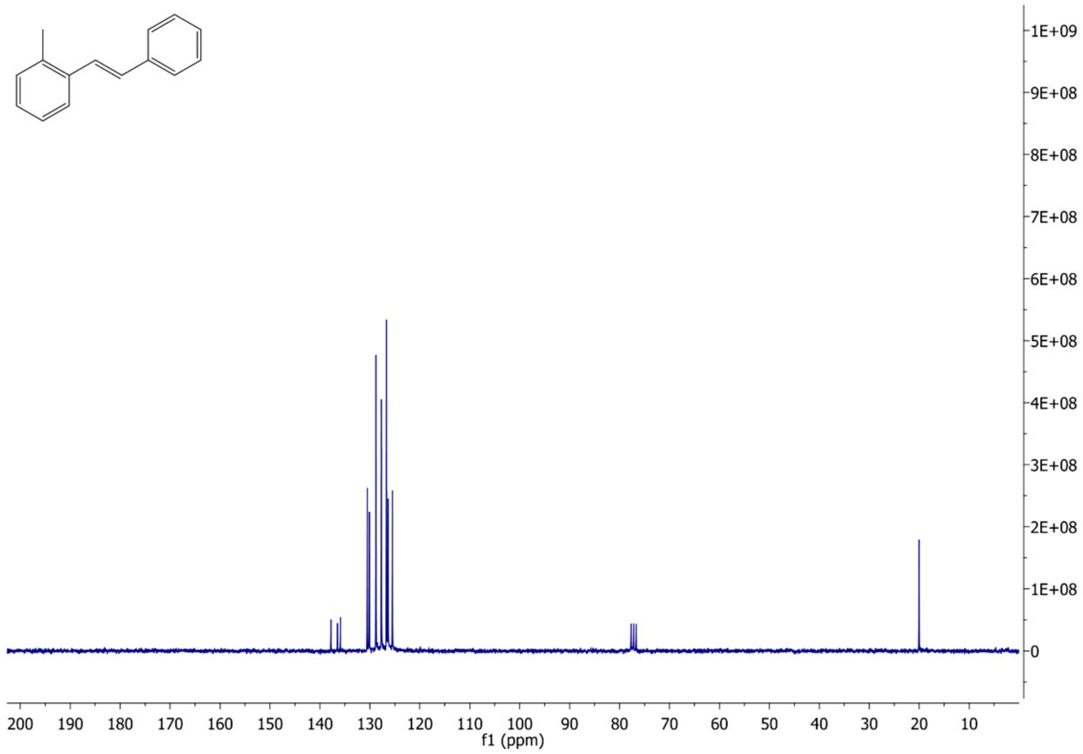
3.17. (E)-1-nitro-4-(oct-1-enyl) benzene (3q)



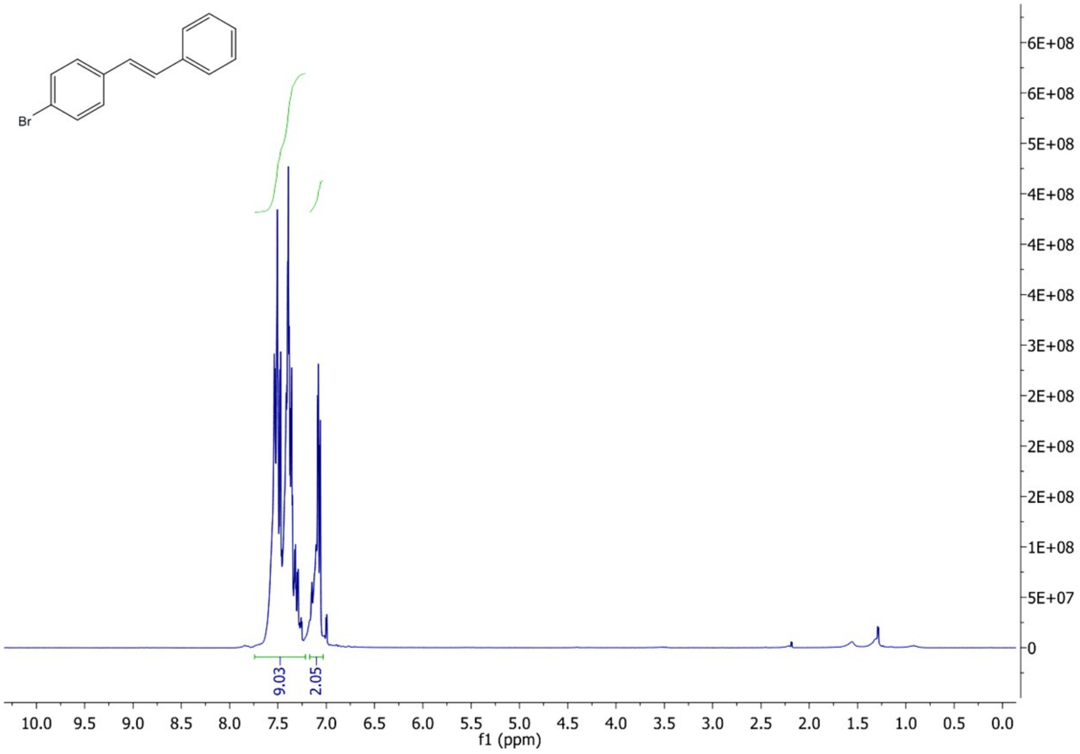


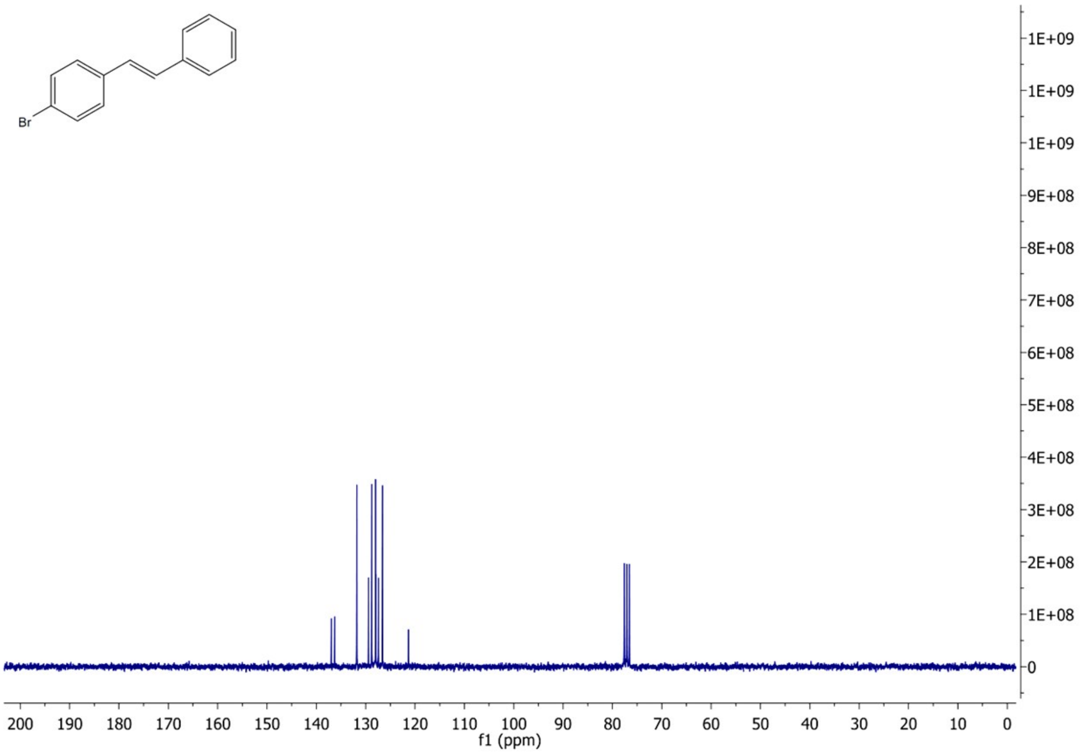
3.18. (E)-1-methyl-2-styrylbenzene (3r)



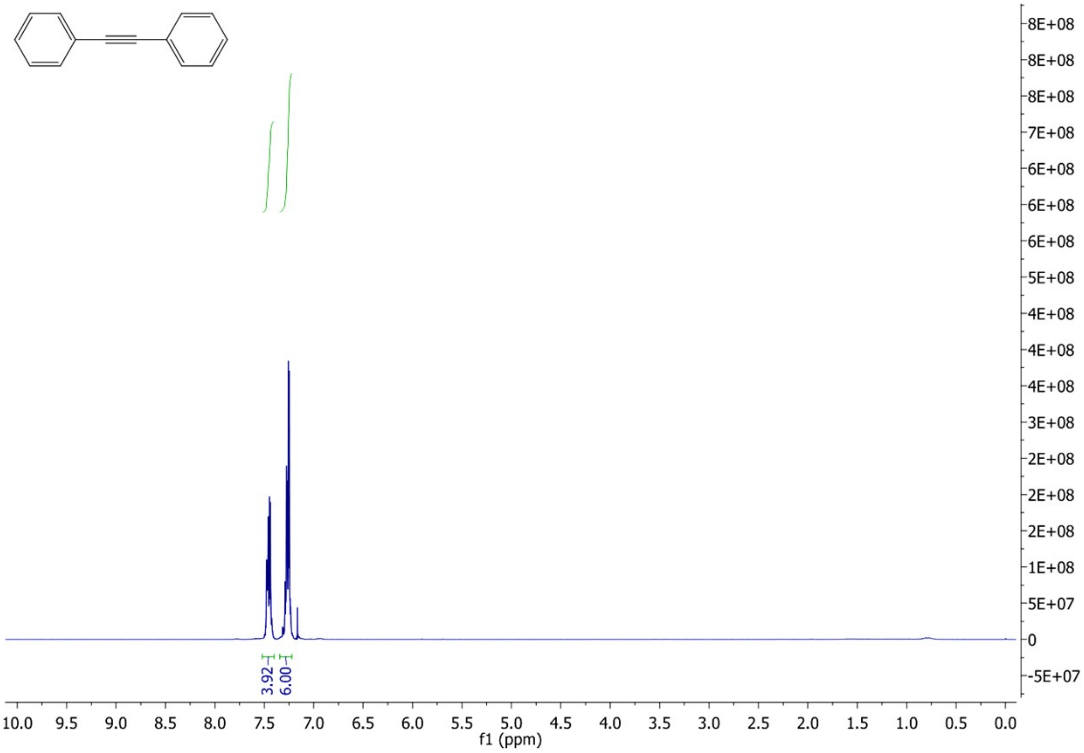


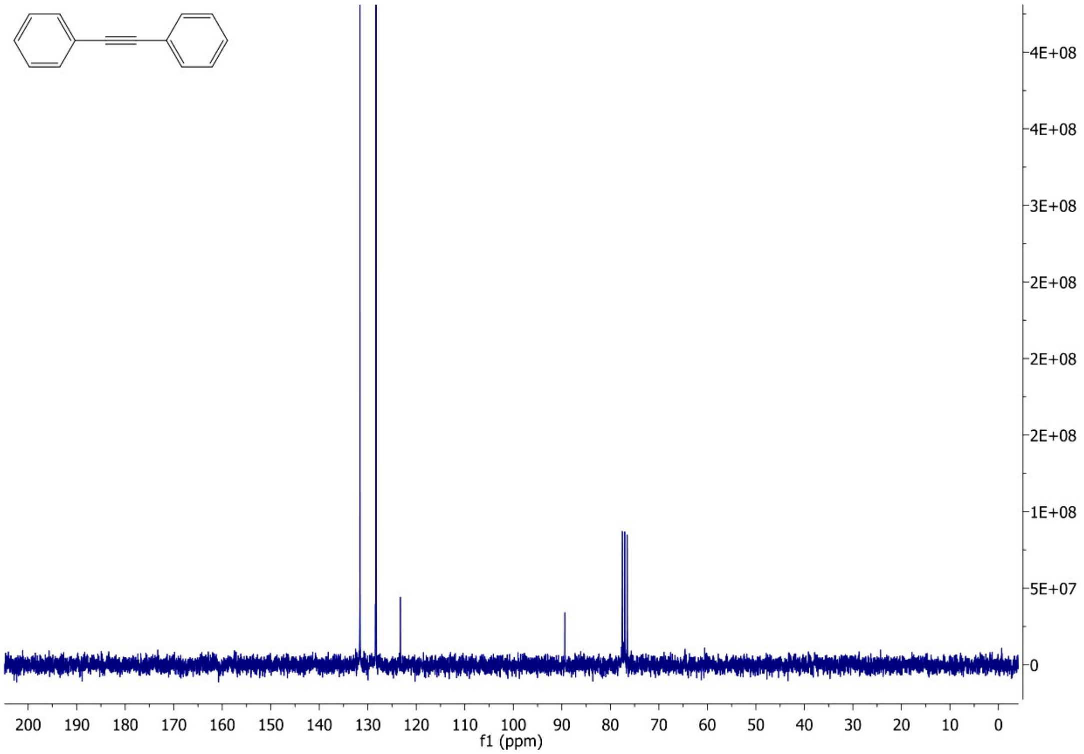
3.19. (E)-1-bromo-4-styrylbenzene (3s)



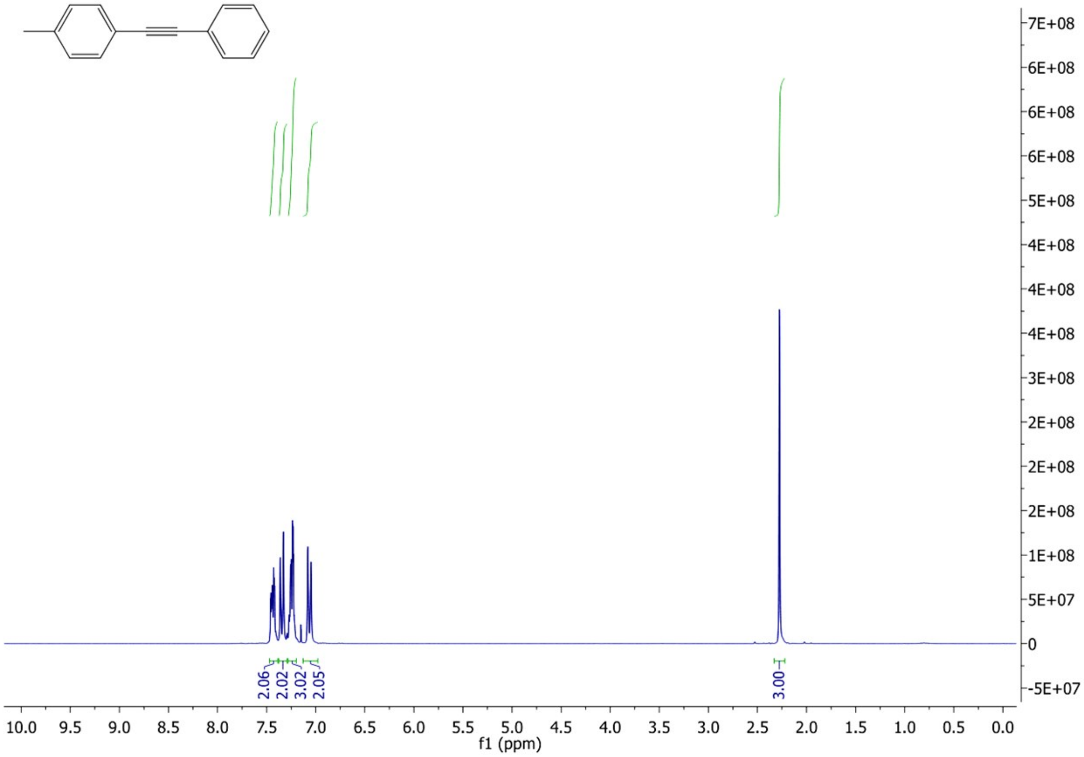


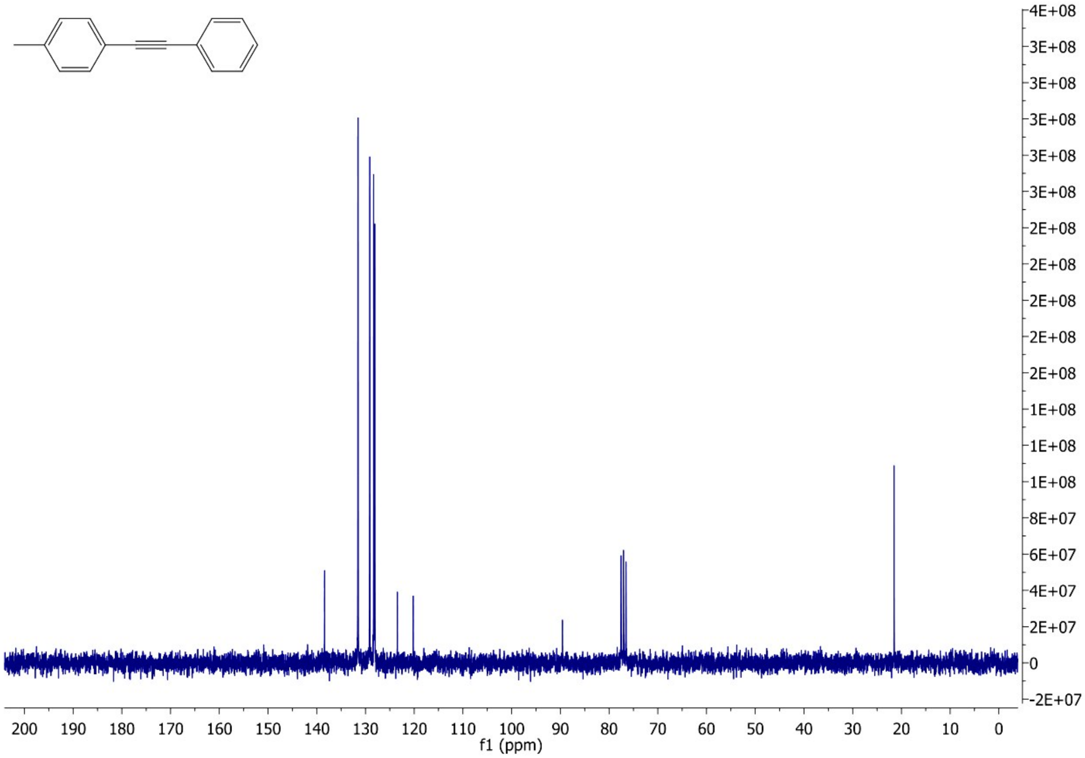
3.20. 1,2-diphenylethyne (5a)



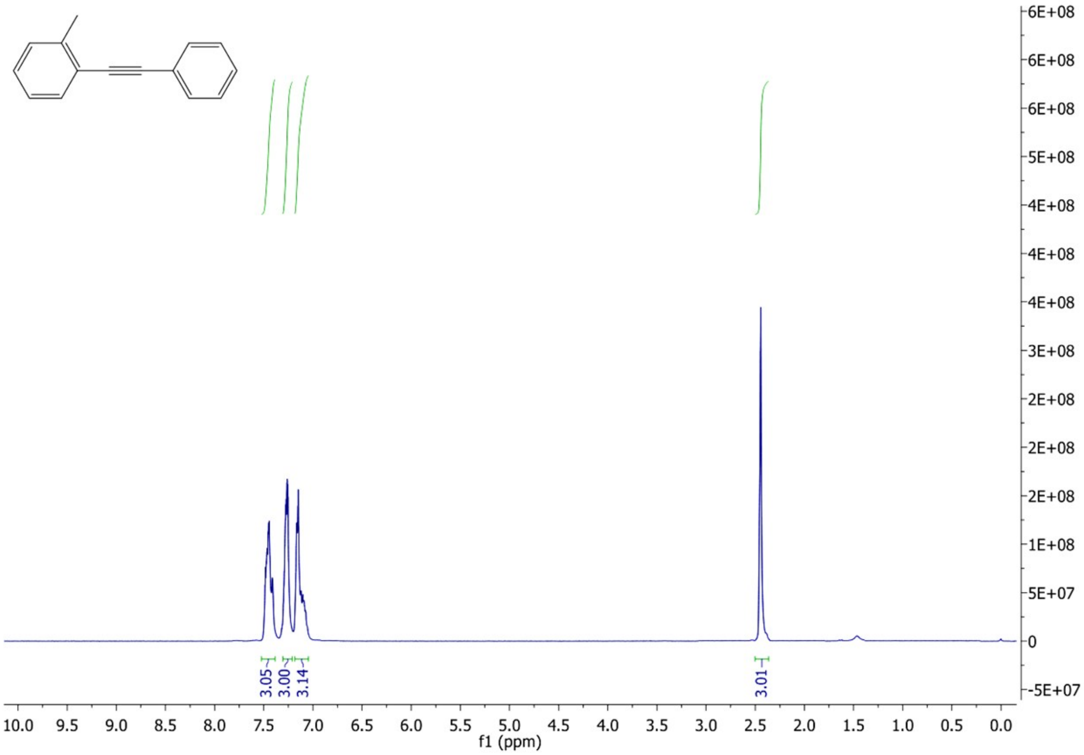


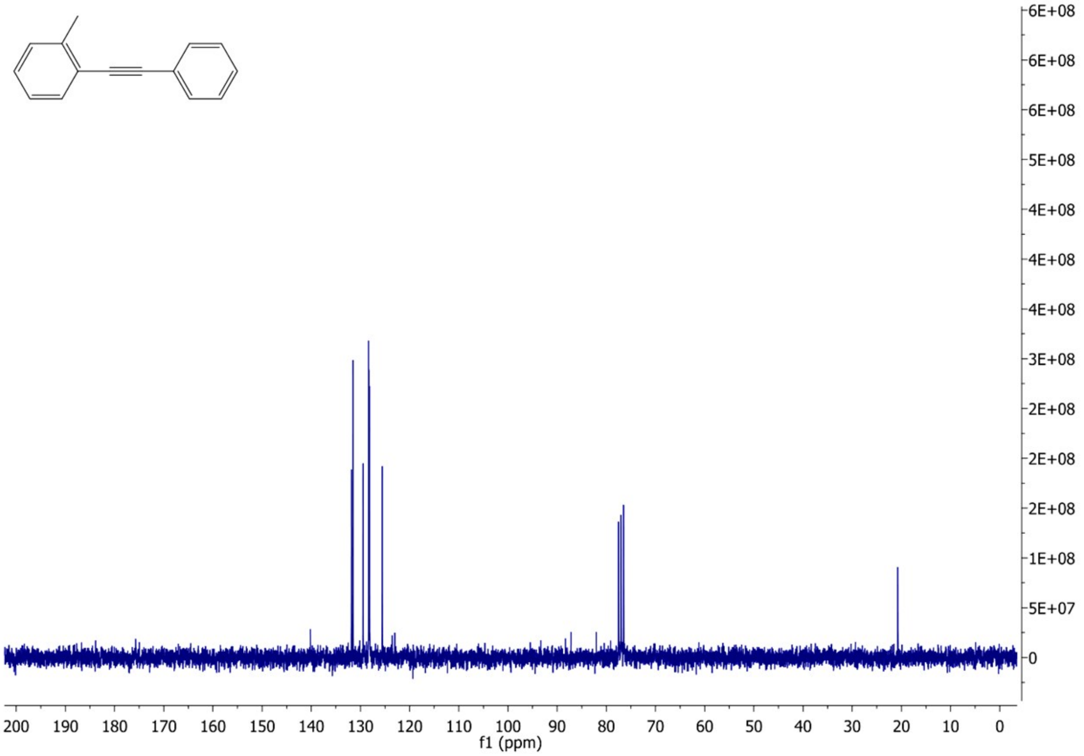
3.21. 1-(2-p-tolylethynyl) benzene (5b)



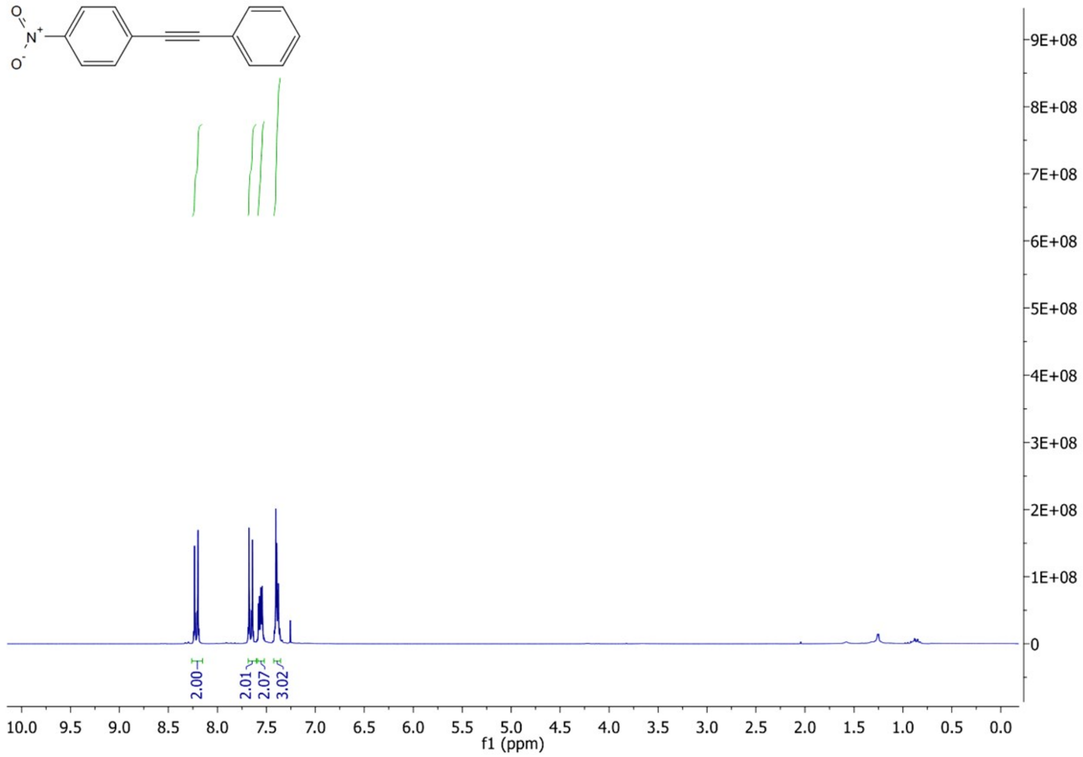


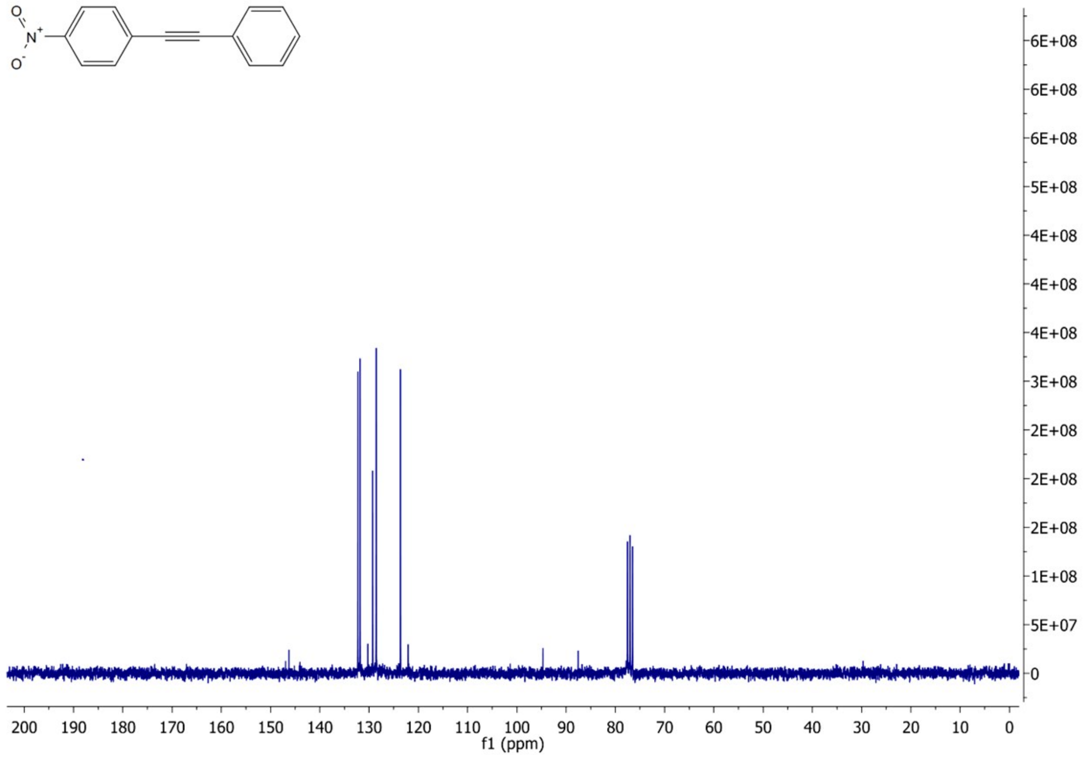
3.22. 1-(2-o-tolylethynyl) benzene (5c)



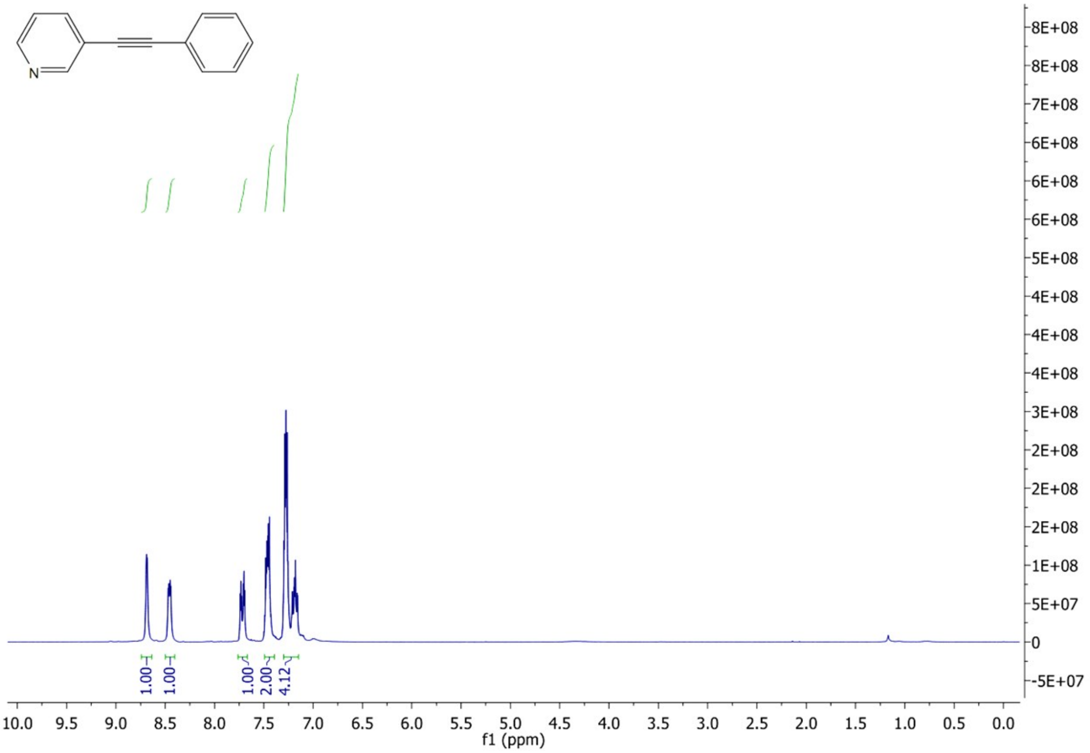


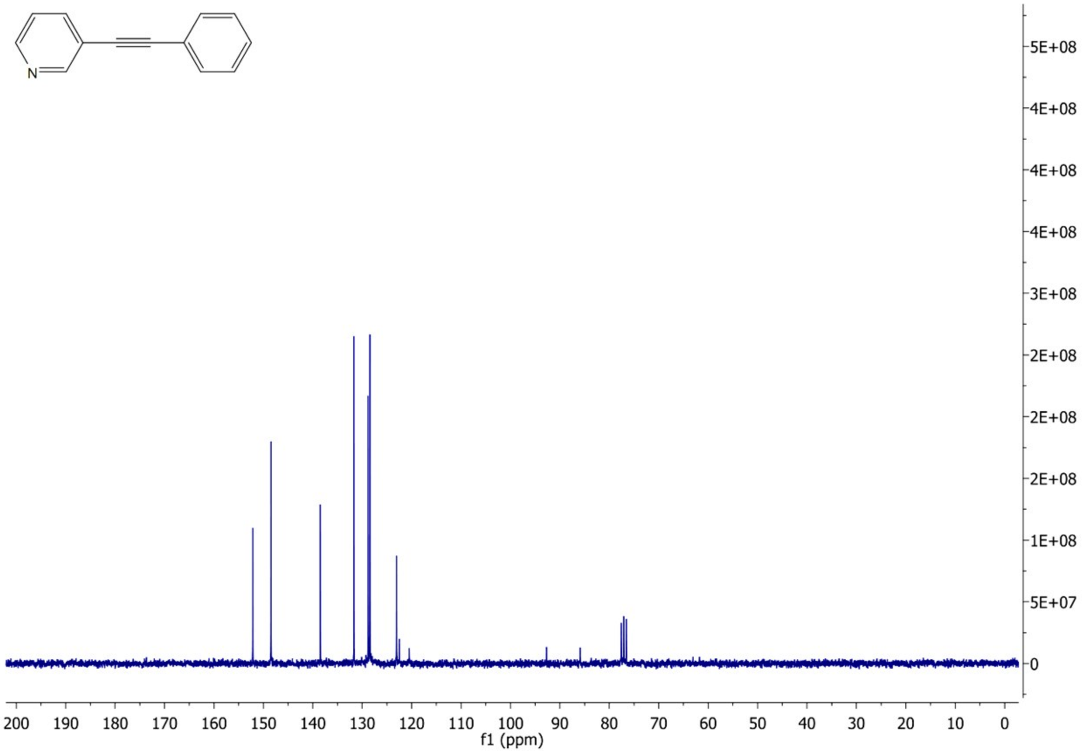
3.23. 1-(2-(4-nitrophenyl)ethynyl) benzene (5d)





3.24. 3-(2-phenylethynyl) pyridine (5e)





4. FT-IR spectra of the recovered catalyst.

FT-IR of the recovered catalyst also proved that this catalyst can be recycled without any change in its structure (Figure S1).

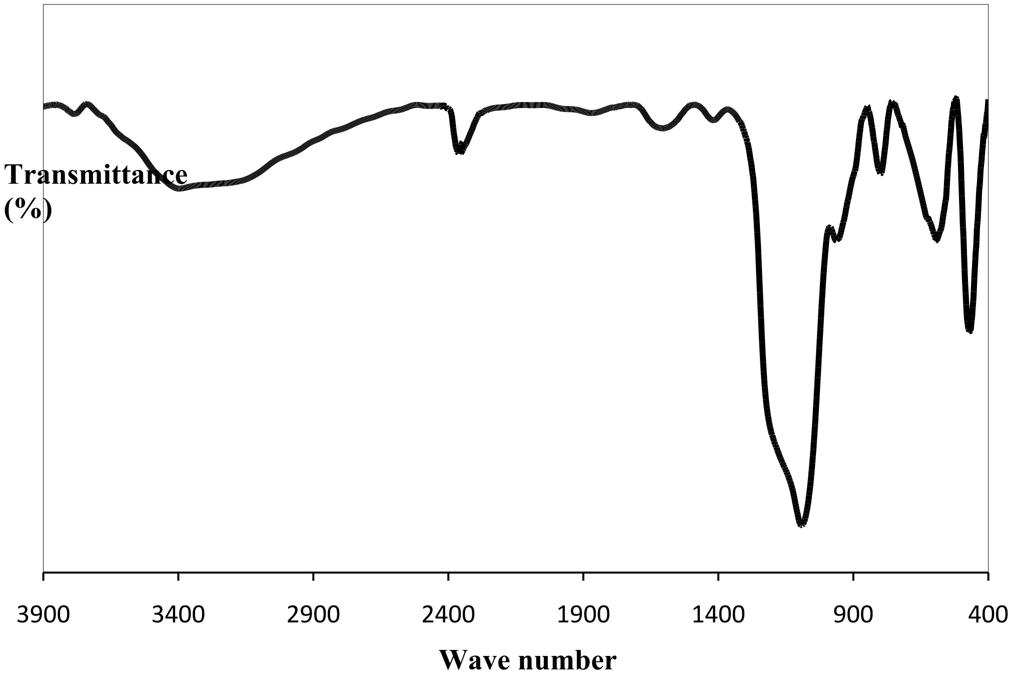


Figure S1. FT-IR spectra of the recovered catalyst.

5. References

1. L. Wang, P. Li, *Synth. Commun*., 2003, **33**, 3679.