

Supporting Information

Selective Hydrosilylation of *N*-Allylimines using a (3-Iminophosphine)Palladium Precatalyst

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General methods and instrumentation: All NMR-scale reactions were set up in a nitrogen-filled glovebox. CDCl_3 was purchased from Cambridge Isotope Laboratories, dried over calcium hydride, freeze-pump-thawed three times, vacuum transferred, and stored over molecular sieves in the glovebox. [(3IP)Pd(allyl)]OTf (**3a** and **3b**) precatalysts were synthesized via the reported procedures.^{1, 2} PhSiH₃ was purchased from Acros. All aldehydes and allylamine required to synthesize **1a-1x** were supplied by Alfa Aesar, AK Scientific, Sigma-Aldrich or Acros. ¹H and ¹³C NMR data were obtained on either a 400 MHz Varian VXRS NMR spectrometer at 399.95 MHz for ¹H NMR and 100.56 MHz for ¹³C NMR or on a 600 MHz Bruker Avance III at 599.9 MHz for ¹H NMR and 150.8 MHz for ¹³C NMR. ¹⁹F NMR was obtained on the 400 MHz Varian NMR at 376.29 MHz. High resolution mass spectrometry data were determined by either the University of Illinois Mass Spectrometry Laboratory, Urbana, IL, USA or the University of Toledo Mass Spectrometry Laboratory, Toledo, OH, USA.

Synthesis of allylimines: Aldehydes (1 equiv.) and allylamine (1.2 equiv.) were dissolved in either diethylether or dichloromethane and stirred over molecular sieves overnight. After reaction completion, the mixture was filtered, dried over MgSO_4 in a Schlenk flask, cannula filtered, and the volatiles were removed under vacuum (in an ice bath for compound **1w** and **1x**, due to their low boiling points). The resulting allylimine was further degassed under vacuum, transferred to the glovebox and kept over molecular sieves in the freezer. All known allylimines were confirmed by ¹H and ¹³C NMR spectroscopy with the *E* isomer as the major product. Reactions to form **1w** and **1x** were performed in dichloromethane over magnesium sulfate instead of molecular sieves.

Catalytic reactions and isolation of allylamines: All catalytic reactions were set up inside a nitrogen-filled glovebox in an NMR tube. Allylimine (0.5 mmol) was added to a mixture of PhSiH₃ (0.6 mmol) and palladium precatalyst (5 mol%, **3a** or **3b**) dissolved in CDCl_3 . Temperature was controlled with an oil bath on a hot plate connected to a thermoprobe. ¹H NMR was collected frequently to check the reaction completion detected by disappearance of the iminic proton or corresponding starting material. Then, the mixture was hydrolyzed in H_2O and extracted with diethylether (3x2 ml) and dried over either MgSO_4 or Na_2SO_4 . The dried solution was filtered with a small plug of celite and after removal of volatiles (in an ice bath for compound **2w** and **2x**, due to their low boiling points, was purified via silica column chromatography (hexanes : ethylacetate, 90 : 10). It was also noted that the hydrosilylated product can be hydrolyzed to the corresponding allylamine product over silica gel directly.

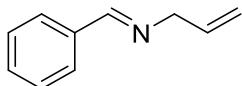
Table S1. Solvent Optimization.

<p>1a 1 equiv.</p> <p>2a</p>				
Solvent	CDCl ₃	C ₆ D ₆	CD ₃ CN	Pyridine-d ₅
Conversion (20 h)	79%	43%	51%	34%

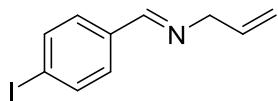
Table S2. Catalytic hydrosilylation of allylimine using other Pd-systems.^a

<p>1a 1 equiv.</p> <p>2a</p>	
Catalyst (5 mol% palladium)	Conversion in 48h, 40 °C
Pd ₂ dba ₃ +PPh ₃ (1:2)	No product formation
PdCl ₂ +PPh ₃ (1:2)	Reaction reached completion in 24 h
Pd(OAc) ₂ + PPh ₃ (1:2)	25% (longer time resulted in a complex mixture of compounds)
Pd(PPh ₃) ₄	18%
(AllylPdCl) ₂ + PPh ₃ (1:2)	28% (longer time resulted in a complex mixture of compounds)
3a	Reaction was complete in 8 h

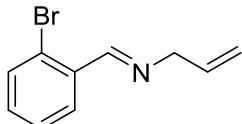
^a ¹H NMR spectra was observed frequently to monitor reaction completion.



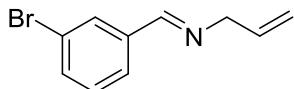
N-allyl-1-phenylmethanimine (**1a**):³ Colorless liquid, 92% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.29 (s, 1H), 7.79-7.74 (m, 2H), 7.44-7.40 (m, 3H), 6.09 (ddt, ³J=17.2 Hz, ³J=10.4 Hz, ³J=5.6 Hz, 1H), 5.25 (dq, ³J=17.2 Hz, ⁴J=2J=1.6 Hz, 1H), 5.17 (dq, ³J=10.4 Hz, ⁴J=2J=1.6 Hz, 1H), 4.27 (dt, ³J=5.6 Hz, ⁴J=1.6 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 162.0, 136.2, 135.9, 130.7, 128.6, 128.2, 116.1, 63.6.



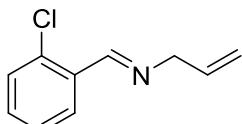
N-allyl-1-(4-iodophenyl)methanimine (**1b**): Colorless liquid, 77% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.21 (s, 1H), 7.75 (d, ³J=8.4 Hz, 2H), 7.47 (d, ³J=8.4 Hz, 2H), 6.05 (ddt, ³J=17.2 Hz, ³J=10.4 Hz, ³J=5.6 Hz, 1H), 5.22 (dq, ³J=17.2 Hz, ⁴J=2J=1.6 Hz, 1H), 5.16 (dq, ³J=10.4 Hz, ⁴J=2J=1.6 Hz, 1H), 4.24 (dm, ³J=5.6 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 161.0, 137.9, 135.7, 129.7, 116.4, 97.4, 63.6.



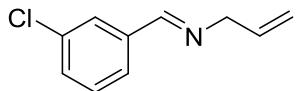
N-allyl-1-(2-bromophenyl)methanimine (**1c**):⁴ Pale yellow oily liquid, 90% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.67 (s, 1H), 8.05 (d, ³J=8.0 Hz, 1H), 7.55 (d, ³J=8.0 Hz, 1H), 7.32 (t, ³J=8.0 Hz, 1H), 7.24 (t, ³J=8.0 Hz, 1H), 6.08 (m, 1H), 5.25 (dm, ³J=17.2 Hz, 1H), 5.18 (dm, ³J=10.4 Hz, 1H), 4.30 (dm, ³J=6.0 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 400 MHz) 161.0, 135.6, 134.5, 133.0, 131.9, 128.8, 127.6, 125.1, 116.4, 63.6.



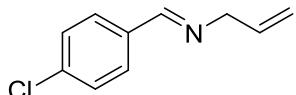
N-allyl-1-(3-bromophenyl)methanimine (**1d**):⁵ Pale yellow oily liquid, 86% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.18 (s, 1H), 7.92 (s, 1H), 7.60 (d, ³J=7.6 Hz, 1H), 7.51 (d, ³J=7.6 Hz, 1H), 7.24 (t, ³J=7.6 Hz, 1H), 6.04 (ddt, ³J=17.2 Hz, ³J=10.4 Hz, ³J=5.6 Hz, 1H), 5.22 (dq, ³J=17.2 Hz, ⁴J=2J=1.6 Hz, 1H), 5.16 (dq, ³J=10.4 Hz, ⁴J=2J=1.6 Hz, 1H), 4.24 (dm, ³J=5.6 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 160.2, 138.1, 135.5, 133.5, 130.6, 130.1, 126.9, 122.9, 116.3, 63.4.



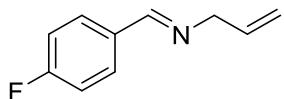
N-allyl-1-(2-chlorophenyl)methanimine (**1e**):⁴ Colorless oily liquid, 86% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.72 (s, 1H), 8.07 (dd, ³J=7.6 Hz, ⁴J=2.0 Hz, 1H), 7.35-7.25 (m, 3H), 6.12-6.02 (m, 1H), 5.24 (dd, ³J=17.2 Hz, ²J=1.6 Hz, 1H), 5.17 (dd, ³J=10.0 Hz, ²J=1.6 Hz, 1H), 4.29 (dm, ³J=5.6 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 158.6, 135.7, 135.1, 133.1, 131.5, 129.7, 128.3, 127.0, 116.3, 63.7.



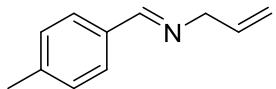
N-allyl-1-(3-chlorophenyl)methanimine (**1f**).⁶ Colorless oily liquid, 84% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.20 (s, 1H), 7.76 (d, ⁴J=1.6 Hz, 1H), 7.55 (dt, ³J=7.6 Hz, ⁴J=1.6 Hz, 1H), 7.36-7.27 (m, 2H), 6.09-5.99 (m, 1H), 5.22 (dm, ³J=17.2 Hz, 1H), 5.15 (dm, ³J=10.4 Hz, 1H), 4.23 (dm, ³J=6.0 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 160.3, 137.9, 135.5, 134.7, 130.6, 129.8, 127.7, 126.5, 116.3, 63.4.



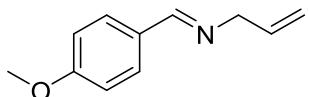
N-allyl-1-(4-chlorophenyl)methanimine (**1g**).⁷ Pale yellow oily liquid, 80% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.23 (s, 1H), 7.67 (d, ³J=8.4 Hz, 2H), 7.37 (d, ³J=8.4 Hz, 2H), 6.05 (ddt, ³J=17.2 Hz, ³J=10.0 Hz, ³J=5.6 Hz, 1H), 5.22 (dq, ³J=17.2 Hz, ⁴J= ²J=1.6 Hz, 1H), 5.16 (dq, ³J=10.0 Hz, ⁴J= ²J=1.6 Hz, 1H), 4.24 (dm, ³J=5.6 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 160.6, 136.7, 135.7, 134.7, 129.4, 128.9, 116.3, 63.6.



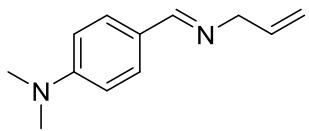
N-allyl-1-(4-fluorophenyl)methanimine (**1h**).⁸ Pale yellow oily liquid, 83% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.25 (s, 1H), 7.76-7.71 (m, 2H), 7.12-7.06 (m, 2H), 6.06 (ddt, ³J=17.2 Hz, ³J=10.4 Hz, ³J=6.0 Hz, 1H), 5.23 (dq, ³J=17.2 Hz, ⁴J= ²J=1.6 Hz, 1H), 5.15 (dq, ³J=10.4 Hz, ⁴J= ²J=1.6 Hz, 1H), 4.24 (dm, ³J=6.0 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 164.3 (d, ¹J_{CF}=250.6 Hz), 160.6, 135.9, 132.6 (d, ⁴J_{CF}=2.9 Hz), 130.1 (d, ³J_{CF}=8.7 Hz), 116.2, 115.8 (d, ²J_{CF}=21.9 Hz), 63.5; ¹⁹F{¹H} NMR (CDCl₃, 400 MHz): 109.9.



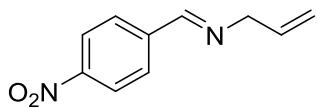
N-allyl-1-(p-tolyl)methanimine (**1i**).⁸ Colorless oily liquid, 92% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.25 (s, 1H), 7.66 (d, ³J=8.0 Hz, 2H), 7.22 (d, ³J=8.0 Hz, 2H), 6.08 (ddt, ³J=17.2 Hz, ³J=10.4 Hz, ³J=5.6 Hz, 1H), 5.27 (dq, ³J=17.2 Hz, ²J= ⁴J=1.6 Hz, 1H), 5.16 (dq, ³J=10.4 Hz, ²J= ⁴J=1.6 Hz, 1H), 4.25 (dm, ³J=5.6 Hz, 2H), 2.38 (s, 3H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 161.8, 140.9, 136.0, 133.6, 129.3, 128.1, 115.9, 63.5, 21.5.



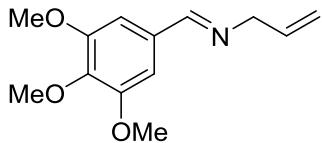
N-allyl-1-(4-methoxyphenyl)methanimine (**1j**).⁷ Colorless oily liquid, 94% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.19 (s, 1H), 7.68 (d, ³J=8.8 Hz, 2H), 6.90 (d, ³J=8.8 Hz, 2H), 6.05 (ddt, ³J=17.2 Hz, ³J=10.4 Hz, ³J=5.6 Hz, 1H), 5.22 (dq, ³J=17.2 Hz, ²J= ⁴J=1.6 Hz, 1H), 5.13 (dq, ³J=10.4 Hz, ²J= ⁴J=1.6 Hz, 1H), 4.20 (dm, ³J=5.6 Hz, 2H), 3.80 (s, 3H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 161.6, 161.3, 136.2, 129.7, 129.1, 115.9, 114.0, 63.5, 55.3.



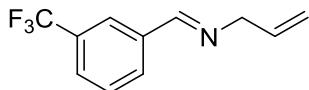
N-allyl-1-(4-N,N-dimethylaminophenyl)methanimine (**1k**):⁶ Colorless oily liquid, 81% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.14 (s, 1H), 7.63 (d, ³J=8.8 Hz, 2H), 6.68 (d, ³J=8.8 Hz, 2H), 6.07 (ddt, ³J=17.2 Hz, ³J=10.2 Hz, ³J=5.8 Hz, 1H), 5.23 (dq, ³J=17.2 Hz, ⁴J= ²J=1.8 Hz, 1H), 5.14 (dq, ³J=10.2 Hz, ⁴J= ²J=1.8 Hz, 1H), 4.20 (dm, ³J=5.8 Hz, 2H), 2.98 (s, 6H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 161.9, 152.0, 136.6, 129.5, 124.3, 115.5, 111.5, 63.5, 40.1.



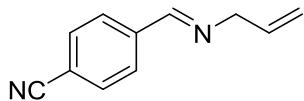
N-allyl-1-(4-nitrophenyl)methanimine (**1l**):⁹ Pale yellow solid, 86% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.38 (s, 1H), 8.26 (d, ³J=8.8 Hz, 2H), 7.91 (d, ³J=8.8 Hz, 2H), 6.07 (ddt, ³J=17.2 Hz, ³J=10.4 Hz, ³J=6.0 Hz, 1H), 5.24 (dq, ³J=17.2 Hz, ⁴J= ²J=1.6 Hz, 1H), 5.19 (dq, ³J=10.4 Hz, ⁴J= ²J=1.6 Hz, 1H), 4.32 (dm, ³J=6.0 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 159.7, 149.1, 141.7, 135.2, 128.9, 124.0, 116.8, 63.8.



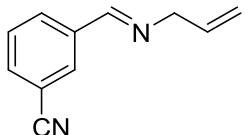
N-allyl-1-(3,4,5-trimethoxyphenyl)methanimine (**1m**):¹⁰ Colorless oily liquid, 86% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.15 (s, 1H), 6.96 (s, 2H), 6.05-5.97 (m, 1H), 5.19 (dm, ³J=17.2 Hz, 1H), 5.12 (dm, ³J=10.4 Hz, 1H), 4.21 (dm, ³J=5.6 Hz, 2H), 3.86 (s, 6H), 3.84 (s, 3H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 161.6, 153.4, 140.2, 135.8, 131.7, 116.2, 105.0, 63.4, 60.9, 56.2.



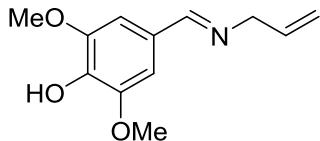
N-allyl-1-(3-(trifluoromethyl)phenyl)methanimine (**1n**):¹¹ Colorless oily liquid, 81% isolated yield, ¹H NMR (CDCl₃, 600 MHz): 8.33 (s, 1H), 8.04 (s, 1H), 7.92 (d, ³J=7.6 Hz, 1H), 7.67 (d, ³J=7.6 Hz, 1H), 7.53 (t, ³J=7.6 Hz, 1H), 6.06 (ddt, ³J=17.2 Hz, ³J=10.0 Hz, ³J=5.6 Hz, 1H), 5.25 (dq, ³J=17.2 Hz, ⁴J= ²J=1.6 Hz, 1H), 5.18 (dq, ³J=10.0 Hz, ⁴J= ²J=1.6 Hz, 1H), 4.29 (dm, ³J=5.6 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 600 MHz): 160.4, 137.0, 135.5, 131.4, 131.2 (q, ²J_{C,F}=32.7 Hz), 129.2, 127.2 (q, ³J_{C,F}=3.5 Hz), 124.9 (q, ³J_{C,F}=3.0 Hz), 124.0 (q, ¹J_{C,F}=272.2 Hz), 116.5, 63.6; ¹⁹F{¹H} NMR (CDCl₃, 400 MHz): -63.16.



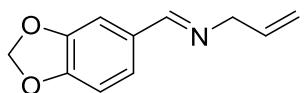
N-allyl-1-(4-cyanophenyl)methanimine (**1o**):¹² Colorless liquid, 86% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.31 (s, 1H), 7.84 (d, ³J=7.6 Hz, 2H), 7.68 (d, ³J=7.6 Hz, 2H), 6.04 (ddt, ³J=17.2 Hz, ³J=10.4 Hz, ³J=5.6 Hz, 1H), 5.22 (dq, ³J=17.2 Hz, ²J= ⁴J=1.6 Hz, 1H), 5.17 (dq, ³J=10.4 Hz, ²J= ⁴J=1.6 Hz, 1H), 4.28 (dm, ³J=5.6 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 160.0, 140.0, 135.2, 132.5, 128.6, 118.6, 116.7, 114.0, 63.6.



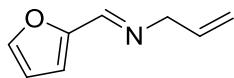
N-allyl-1-(3-cyanophenyl)methanimine (**1p**): Colorless liquid, 81% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.27 (s, 1H), 8.03 (s, 1H), 7.94 (d, ³J=7.6 Hz, 1H), 7.66 (d, ³J=7.6 Hz, 1H), 7.50 (t, ³J=7.6 Hz, 1H), 6.03 (ddt, ³J=17.2 Hz, ³J=10.4 Hz, ³J=6.0 Hz, 1H), 5.21 (dq, ³J=17.2 Hz, ⁴J= ²J=1.6 Hz, 1H), 5.15 (dq, ³J=10.4 Hz, ⁴J= ²J=1.6 Hz, 1H), 4.26 (dm, ³J=6.0 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 159.4, 137.2, 135.2, 133.7, 132.2, 131.5, 129.5, 118.3, 116.6, 112.9, 63.4.



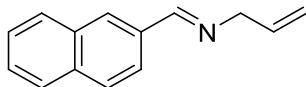
4-((allylimino)methyl)-2,6-dimethoxyphenol (**1q**): Pale orange solid, 91% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.15 (s, 1H), 7.00 (s, 2H), 6.09-6.00 (m, 1H), 5.22 (dm, ³J=17.2 Hz, 1H), 5.14 (dm, ³J=10.2 Hz, 1H), 4.22 (dm, ³J=5.2 Hz, 2H), 3.88 (s, 6H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 161.9, 147.4, 137.7, 136.1, 127.6, 116.2, 105.1, 63.4, 56.4.



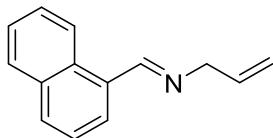
N-allyl-1-(benzo[1,3]dioxol-5-yl)methanimine (**1r**):¹³ Colorless liquid, 85% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.15 (s, 1H), 7.37 (d, ⁴J=1.6 Hz, 1H), 7.10 (dd, ³J=7.8 Hz, ⁴J=1.6 Hz, 1H), 6.81 (d, ³J=7.8 Hz, 1H), 6.04 (ddt, ³J=17.2 Hz, ³J=10.6 Hz, ³J=5.8 Hz, 1H), 5.98 (s, 2H), 5.21 (dq, ³J=17.2 Hz, ⁴J= ²J=1.8 Hz, 1H), 5.14 (dq, ³J=10.6 Hz, ⁴J= ²J=1.8 Hz, 1H), 5.20 (dm, ³J=5.8 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 161.2, 149.9, 148.3, 136.1, 131.1, 124.5, 116.0, 108.1, 106.6, 101.5, 63.3.



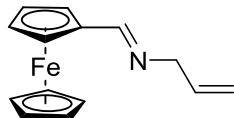
N-allyl-1-(furan-2-yl)methanimine (**1s**):¹⁴ Dark red liquid, 81% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.07 (s, 1H), 7.49 (d, ³J=1.6 Hz, 1H), 6.74 (d, ³J=3.6 Hz, 1H), 6.45 (dd, ³J=3.6 Hz, ³J=1.6 Hz, 1H), 6.08-5.98 (m, 1H), 5.19 (dd, ³J=17.2 Hz, ²J=1.6 Hz, 1H), 5.13 (dd, ³J=10.0 Hz, ²J=1.6 Hz, 1H), 4.20 (dd, ³J=5.6 Hz, ⁴J=1.2 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 151.6, 150.4, 144.8, 135.6, 116.5, 114.1, 111.7, 63.7.



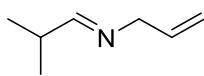
N-allyl-1-(naphthalen-2-yl)methanimine (**1t**):¹⁵ Colorless liquid, 91% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.39 (s, 1H), 8.08 (dd, ³J=8.8 Hz, ⁴J=1.1 Hz, 1H), 8.02 (s, 1H), 7.89-7.84 (m, 3H), 7.54-7.50 (m, 2H), 6.20-6.13 (m, 1H), 5.34 (dm, ³J=17.2 Hz, 1H), 5.25 (dm, ³J=10.3 Hz, 1H), 4.34 (dm, ³J=5.5 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 162.0, 135.9, 134.7, 133.8, 133.0, 130.0, 128.6, 128.4, 127.8, 127.1, 126.4, 123.8, 116.1, 63.6.



N-allyl-1-(naphthalen-1-yl)methanimine (**1u**):¹⁵ Colorless liquid, 90% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 9.00 (d, ³J=5.6 Hz, 1H), 8.96 (s, 1H), 7.95-7.90 (m, 3H), 7.63-7.52 (m, 3H), 6.25-6.15 (m, 1H), 5.34 (dm, ³J=17.2 Hz, 1H), 5.23 (dm, ³J=10.0 Hz, 1H), 4.41 (dm, ³J=4.4 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 161.7, 136.2, 133.9, 131.7, 131.4, 131.1, 128.8, 128.7, 127.2, 126.1, 125.3, 124.3, 116.1, 64.6.

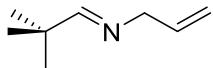


N-allyl-1-(ferrocenyl)methanimine (**1v**):¹⁶ Dark red oily liquid, 80% isolated yield, ¹H NMR (CDCl₃, 400 MHz): 8.13 (s, 1H), 6.03 (ddt, ³J=17.2 Hz, ³J=10.4 Hz, ³J=5.6 Hz, 1H), 5.21 (dm, ³J=17.2 Hz, 1H), 5.14 (dm, ³J=10.4 Hz, 1H), 4.66 (t, J=2.0 Hz, 2H), 4.37 (t, J=2.0 Hz, 2H), 4.18 (s, 5H), 4.09 (dm, ³J=5.6 Hz, 2H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 162.3, 136.5, 115.8, 80.5, 70.6, 69.2, 68.6, 63.8.

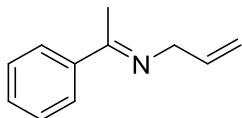


N-allyl-2-methylpropan-1-imine (**1w**):¹⁷ Colorless liquid, 87% isolated yield, ¹H NMR (CDCl₃, 600 MHz): 7.54 (dm, ³J=4.8 Hz, 1H), 5.96 (m, 1H), 5.13 (dm, ³J=15.6 Hz, 1H), 5.08 (dm, ³J=10.2 Hz, 1H), 3.98 (d, ³J=5.4 Hz, 2H),

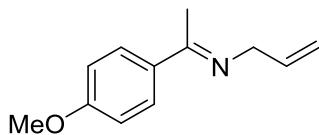
2.44 (sept, $^3J=7.2$ Hz, 1H), 1.08 (d, $^3J=7.2$ Hz, 6H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3 , 600 MHz): 171.1, 136.3, 115.7, 63.4, 34.3, 19.4.



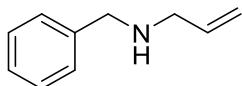
N-allyl-2,2-dimethylpropan-1-imine (**1x**):¹⁸ Colorless liquid, 90% isolated yield, ^1H NMR (CDCl_3 , 600 MHz): 7.52 (s, 1H), 5.96 (m, 1H), 5.13 (dm, $^3J=17.4$ Hz, 1H), 5.07 (dm, $^3J=10.2$ Hz, 1H), 3.99 (dm, $^3J=6.0$ Hz, 2H), 1.08 (s, 9H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3 , 600 MHz): 173.5, 136.4, 115.5, 63.2, 36.3, 27.0.



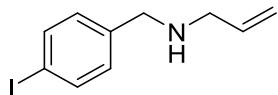
N-allyl-1-phenylethan-1-imine (**1y**):¹⁹ (E:Z 91:9 by ^1H NMR) Colorless oily liquid, 90% isolated yield, ^1H NMR (CDCl_3 , 400 MHz): 7.81-7.80 (m, 2H), 7.40-7.37 (m, 3H), 6.12 (ddt, $^3J=17.4$ Hz, $^3J=10.2$ Hz, $^3J=5.4$ Hz, 1H), 5.26 (dq, $^3J=17.4$ Hz, $^4J=^2J=1.8$ Hz, 1H), 5.15 (dq, $^3J=10.2$ Hz, $^4J=^2J=1.8$ Hz, 1H), 4.19 (d, $^3J=5.4$ Hz, 2H), 2.25 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3 , 600 MHz): 166.4, 141.3, 136.2, 129.7, 128.4, 126.8, 115.3, 54.7, 15.8.



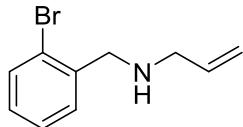
N-allyl-1-(4-methoxyphenyl)ethan-1-imine (**1z**):²⁰ (E:Z 96:4 by ^1H NMR) Colorless oily liquid, 86% isolated yield, ^1H NMR (CDCl_3 , 600 MHz): 7.78 (dm, $^3J=8.9$ Hz, 2H), 6.89 (dm, $^3J=8.9$ Hz, 2H), 6.11 (ddt, $^3J=17.2$ Hz, $^3J=10.4$ Hz, $^3J=5.4$ Hz, 1H), 5.24 (dq, $^3J=17.2$ Hz, $^4J=^2J=1.8$ Hz, 1H), 5.14 (dq, $^3J=10.4$ Hz, $^4J=^2J=1.8$ Hz, 1H), 4.16 (dm, $^3J=5.4$ Hz, 2H), 3.84 (s, 3H), 2.22 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3 , 600 MHz): 165.6, 160.9, 136.4, 133.9, 128.3, 115.1, 113.6, 55.5, 54.6, 15.4.



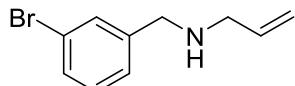
N-benzylprop-2-en-1-amine (**2a**):²¹ Colorless liquid (60 mg, 81% isolated yield), ^1H NMR (CDCl_3 , 600 MHz): 7.34-7.31 (m, 4H), 7.28-7.24 (m, 1H), 5.94 (ddt, $^3J=16.3$ Hz, $^3J=10.3$ Hz, $^3J=6.0$ Hz, 1H), 5.20 (dq, $^3J=16.3$ Hz, $^4J=^2J=1.7$ Hz, 1H), 5.13 (dq, $^3J=10.3$ Hz, $^4J=^2J=1.7$ Hz, 1H), 3.80 (s, 2H), 3.29 (dt, $^3J=6.0$ Hz, $^4J=1.7$ Hz, 2H), 1.60 (s, broad, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3 , 600 MHz): 140.3, 136.8, 128.5, 128.3, 127.1, 116.2, 53.4, 51.9; HRMS (ESI) (m/z): [M+H]⁺ calc for $\text{C}_{10}\text{H}_{14}\text{N}$, 148.1126; found, 148.1120.



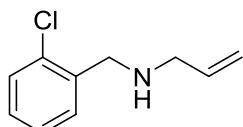
N-(4-iodobenzyl)prop-2-en-1-amine (**2b**): Colorless oily liquid (121 mg, 89% isolated yield), ¹H NMR (CDCl₃, 400 MHz): 7.64 (d, ³J=8.0 Hz, 2H), 7.08 (d, ³J=8.0 Hz, 2H), 5.91 (ddt, ³J=17.2 Hz, ³J=10.4 Hz, ³J=6.0 Hz, 1H), 5.18 (dq, ³J=17.2 Hz, ⁴J= ²J=1.6 Hz, 1H), 5.11 (dq, ³J=10.4 Hz, ⁴J= ²J=1.6 Hz, 1H), 3.73 (s, 2H), 3.25 (dt, ³J=6.0 Hz, ⁴J=1.6 Hz, 2H), 1.43 (broad s, 1H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 140.0, 137.5, 136.7, 130.3, 116.3, 92.3, 52.7, 51.8; HRMS (ESI) (m/z): [M+H]⁺ calc for C₁₀H₁₃IN, 274.0093; found, 274.0103.



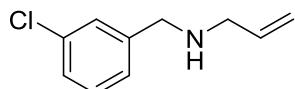
N-(2-bromobenzyl)prop-2-en-1-amine (**2c**):²² Colorless oily liquid (89 mg, 79% isolated yield), ¹H NMR (CDCl₃, 600 MHz): 7.54 (d, ³J=7.8 Hz, 1H), 7.39 (dd, ³J=7.2 Hz, ⁴J=1.2 Hz, 1H), 7.28 (t, ³J=7.8 Hz, 1H), 7.13 (td, ³J=7.2 Hz, ⁴J=1.2 Hz, 1H), 5.98-5.91 (m, 1H), 5.22 (dm, ³J=17.4 Hz, 1H), 5.13 (dm, ³J=10.2 Hz, 1H), 3.87 (s, 2H), 3.28 (dm, ³J=6.0 Hz, 2H), 1.83 (broad s, 1H); ¹³C{¹H} NMR (CDCl₃, 600 MHz): 139.0, 136.5, 133.0, 130.6, 128.8, 127.6, 124.2, 116.6, 53.1, 51.6; HRMS (ESI) (m/z): [M+H]⁺ calc for C₁₀H₁₃BrN, 226.0231; found, 226.0230.



N-(3-bromobenzyl)prop-2-en-1-amine (**2d**):²³ Colorless oily liquid (101 mg, 76% isolated yield), ¹H NMR (CDCl₃, 600 MHz): 7.50 (s, 1H), 7.38 (d, ³J=7.2 Hz, 1H), 7.25 (d, ³J=7.2 Hz, 1H), 7.19 (t, ³J=7.2 Hz, 1H), 5.92 (ddt, ³J=17.2 Hz, ³J=10.2 Hz, ³J=5.8 Hz, 1H), 5.20 (dq, ³J=17.2 Hz, ⁴J= ²J=1.8 Hz, 1H), 5.13 (dq, ³J=10.2 Hz, ⁴J= ²J=1.8 Hz, 1H), 3.76 (s, 2H), 3.26 (dt, ³J=5.8 Hz, ⁴J=1.8 Hz, 2H), 1.37 (broad s, 1H); ¹³C{¹H} NMR (CDCl₃, 600 MHz): 142.8, 136.7, 131.3, 130.2, 130.1, 126.9, 122.7, 116.4, 52.7, 51.8; HRMS (ESI) (m/z): [M+H]⁺ calc for C₁₀H₁₃BrN, 226.0231; found, 226.0227.

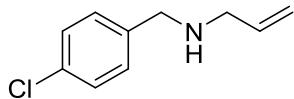


N-(2-chlorobenzyl)prop-2-en-1-amine (**2e**):²⁴ Colorless oily liquid (74 mg, 82% isolated yield), ¹H NMR (CDCl₃, 600 MHz): 7.39-7.35 (m, 2H), 7.25-7.19 (m, 2H), 5.94 (ddt, ³J=17.2 Hz, ³J=10.2 Hz, ³J=5.8 Hz, 1H), 5.21 (dq, ³J=17.2 Hz, ⁴J= ²J=1.8 Hz, 1H), 5.13 (dq, ³J=10.2 Hz, ⁴J= ²J=1.8 Hz, 1H), 3.89 (s, 2H), 3.28 (dt, ³J=5.8 Hz, ⁴J=1.8 Hz, 2H), 1.59 (broad s, 1H); ¹³C{¹H} NMR (CDCl₃, 600 MHz): 137.7, 136.8, 133.9, 130.4, 129.7, 128.5, 126.9, 116.3, 51.8, 50.8; HRMS (ESI) (m/z): [M+H]⁺ calc for C₁₀H₁₃ClN, 182.0737; found, 182.0736.

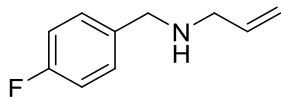


N-(3-chlorobenzyl)prop-2-en-1-amine (**2f**):²³ Colorless oily liquid (76 mg, 84% isolated yield), ¹H NMR (CDCl₃, 400 MHz): 7.34 (s, 1H), 7.26-7.19 (m, 3H), 5.97-5.87 (m, 1H), 5.20 (dm, ³J=17.4 Hz, 1H), 5.13 (dm, ³J=10.2 Hz,

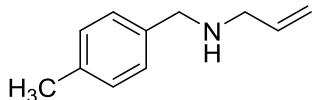
1H), 3.77 (s, 2H), 3.26 (dm, $^3J=6.0$ Hz, 2H), 1.43 (broad s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 600 MHz): 142.5, 136.7, 134.4, 129.7, 128.4, 127.2, 126.4, 116.3, 52.7, 51.8; HRMS (ESI) (m/z): $[M+H]^+$ calc for $C_{10}H_{13}ClN$, 182.0737; found, 182.0731.



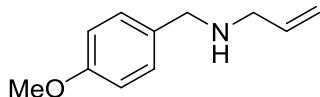
N-(4-chlorobenzyl)prop-2-en-1-amine (**2g**):⁷ Colorless oily liquid (84 mg, 92% isolated yield), 1H NMR ($CDCl_3$, 400 MHz): 7.30-7.24 (m, 4H), 5.91 (ddt, $^3J=17.2$ Hz, $^3J=10.4$ Hz, $^3J=6.0$ Hz, 1H), 5.19 (dm, $^3J=17.2$ Hz, 1H), 5.12 (dm, $^3J=10.4$ Hz, 1H), 3.76 (s, 2H), 3.25 (dm, $^3J=6.0$ Hz, 2H), 1.40 (broad s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): 138.9, 136.7, 132.7, 129.6, 128.6, 116.3, 52.6, 51.8; HRMS (ESI) (m/z): $[M+H]^+$ calc for $C_{10}H_{13}ClN$, 182.0737; found, 182.0739.



N-(4-fluorobenzyl)prop-2-en-1-amine (**2h**):²⁵ Colorless oily liquid (74 mg, 90% isolated yield), 1H NMR ($CDCl_3$, 400 MHz): 7.30-7.26 (m, 2H), 7.03-6.97 (m, 2H), 5.92 (ddt, $^3J=17.2$ Hz, $^3J=10.0$ Hz, $^3J=6.0$ Hz, 1H), 5.19 (dq, $^3J=17.2$ Hz, $^4J=^2J=1.6$ Hz, 1H), 5.11 (dq, $^3J=10.0$ Hz, $^4J=^2J=1.6$ Hz, 1H), 3.75 (s, 2H), 3.26 (dt, $^3J=6.0$ Hz, $^4J=1.6$ Hz, 2H), 1.39 (broad s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): 162.0 (d, $^1J_{C,F}=244.0$ Hz), 136.8, 136.1 (d, $^4J_{C,F}=2.9$ Hz), 129.8 (d, $^3J_{C,F}=7.8$ Hz), 116.2, 115.2 (d, $^2J_{C,F}=21.5$ Hz), 52.6, 51.8; $^{19}F\{^1H\}$ NMR ($CDCl_3$, 400 MHz): -116.49; HRMS (ESI) (m/z): $[M+H]^+$ calc for $C_{10}H_{13}FN$, 166.1032; found, 166.1040.

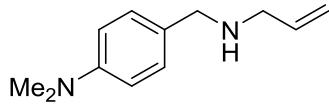


N-(4-methylbenzyl)prop-2-en-1-amine (**2i**): Colorless liquid (70 mg, 84% isolated yield), 1H NMR ($CDCl_3$, 600 MHz): 7.21 (d, $^3J=7.9$ Hz, 2H), 7.14 (d, $^3J=7.9$ Hz, 2H), 5.96-5.90 (m, 1H), 5.19 (dm, $^3J=17.2$ Hz, 1H), 5.11 (dm, $^3J=10.2$ Hz, 1H), 3.76 (s, 2H), 3.27 (dt, $^3J=5.9$ Hz, $^4J=1.4$ Hz, 2H), 2.33 (s, 3H), 1.52 (broad s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 600 MHz): 137.3, 136.9, 136.6, 129.2, 128.3, 116.1, 53.1, 51.8, 21.2; HRMS (ESI) (m/z): $[M+H]^+$ calc for $C_{11}H_{16}N$, 162.1283; found, 162.1288.

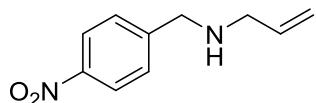


N-(4-methoxybenzyl)prop-2-en-1-amine (**2j**):²⁶ Colorless oily liquid (67 mg, 76% isolated yield), 1H NMR ($CDCl_3$, 400 MHz): 7.24 (d, $^3J=8.8$ Hz, 2H), 6.91 (d, $^3J=8.8$ Hz, 2H), 5.97 (ddt, $^3J=17.2$ Hz, $^3J=10.2$ Hz, $^3J=5.8$ Hz, 1H), 5.23 (dq, $^3J=17.2$ Hz, $^4J=^2J=1.8$ Hz, 1H), 5.16 (dq, $^3J=10.2$ Hz, $^4J=^2J=1.8$ Hz, 1H), 3.85 (s, 3H), 3.77 (s, 2H), 3.31 (dt,

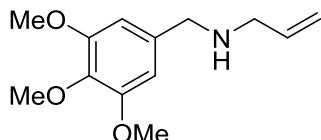
$^3J=5.8$ Hz, $^4J=1.8$ Hz, 2H), 1.52 (broad s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3 , 600 MHz): 158.7, 137.0, 132.6, 129.5, 116.1, 113.9, 55.4, 52.8, 51.9; HRMS (ESI) (m/z): $[\text{M}+\text{H}]^+$ calc for $\text{C}_{11}\text{H}_{16}\text{NO}$, 178.1232; found, 178.1238.



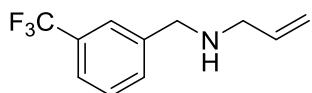
N-(4-N,N-dimethylaminobenzyl)prop-2-en-1-amine (**2k**): Colorless oily liquid (87 mg, 91% isolated yield), ^1H NMR (CDCl_3 , 400 MHz): 7.20 (dm, $^3J=8.8$ Hz, 2H), 6.72 (dm, $^3J=8.8$ Hz, 2H), 5.94 (ddt, $^3J=16.8$ Hz, $^3J=10.0$ Hz, $^3J=6.0$ Hz, 1H), 5.19 (dq, $^3J=16.8$ Hz, $^4J=^2J=1.6$ Hz, 1H), 5.11 (dq, $^3J=10.0$ Hz, $^4J=^2J=1.6$ Hz, 1H), 3.70 (s, 2H), 3.27 (dt, $^3J=6.0$ Hz, $^4J=1.6$ Hz, 2H), 2.94 (s, 6H), 1.42 (broad s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3 , 400 MHz): 149.9, 137.1, 129.2, 128.4, 115.9, 112.8, 52.9, 51.8, 40.9; HRMS (ESI) (m/z): $[\text{M}+\text{H}]^+$ calc for $\text{C}_{12}\text{H}_{19}\text{N}_2$, 191.1548; found, 191.1557.



N-(4-nitrobenzyl)prop-2-en-1-amine (**2l**):²⁴ Pale yellow oily liquid (75 mg, 78% isolated yield), ^1H NMR (CDCl_3 , 400 MHz): 8.18 (d, $^3J=8.4$ Hz, 2H), 7.51 (d, $^3J=8.4$ Hz, 2H), 5.91 (ddt, $^3J=17.6$ Hz, $^3J=10.4$ Hz, $^3J=6.0$ Hz, 1H), 5.20 (dq, $^3J=17.6$ Hz, $^4J=^2J=1.6$ Hz, 1H), 5.14 (dq, $^3J=10.4$ Hz, $^4J=^2J=1.6$ Hz, 1H), 3.90 (s, 2H), 3.28 (dt, $^3J=6.0$ Hz, $^4J=1.6$ Hz, 2H), 1.50 (broad s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3 , 400 MHz): 148.4, 136.5, 128.9, 123.9, 116.7, 52.6, 52.0; HRMS (ESI) (m/z): $[\text{M}+\text{H}]^+$ calc for $\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_2$, 193.0977; found, 193.0975.

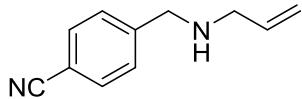


N-(3,4,5-trimethoxybenzyl)prop-2-en-1-amine (**2m**): Colorless oily liquid (106 mg, 89% isolated yield), ^1H NMR (CDCl_3 , 400 MHz): 6.56 (s, 2H), 5.94 (ddt, $^3J=17.2$ Hz, $^3J=10.4$ Hz, $^3J=6.0$ Hz, 1H), 5.21 (dm, $^3J=17.2$ Hz, 1H), 5.12 (dm, $^3J=10.4$ Hz, 1H), 3.86 (s, 6H), 3.83 (s, 3H), 3.73 (s, 2H), 3.29 (dm, $^3J=6.0$ Hz, 2H), 1.48 (broad s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3 , 400 MHz): 153.3, 136.8, 136.2, 116.3, 105.0, 61.0, 56.2, 53.7, 52.0; HRMS (ESI) (m/z): $[\text{M}+\text{H}]^+$ calc for $\text{C}_{13}\text{H}_{20}\text{NO}_3$, 238.1443; found, 238.1447.

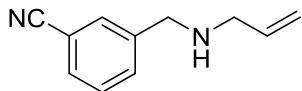


N-(3-(trifluoromethyl)benzyl)prop-2-en-1-amine (**2n**):²⁷ Colorless oily liquid (99 mg, 92% isolated yield), ^1H NMR (CDCl_3 , 600 MHz): 7.61 (s, 1H), 7.53-7.50 (m, 2H), 7.45-7.42 (m, 1H), 5.93 (ddt, $^3J=16.4$ Hz, $^3J=10.2$ Hz, $^3J=6.0$

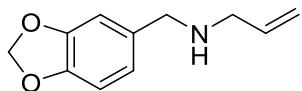
Hz, 1H), 5.21 (dq, $^3J=16.4$ Hz, $^4J=2J=1.6$ Hz, 1H), 5.13 (dq, $^3J=10.2$ Hz, $^4J=2J=1.6$ Hz, 1H), 3.85 (s, 2H), 3.28 (dt, $^3J=6.0$ Hz, $^4J=1.6$ Hz, 2H), 1.43 (broad s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl₃, 400 MHz): 141.4, 136.6, 131.6, 130.8 (q, $^2J_{\text{C}-\text{F}}=32.3$ Hz), 128.9, 125.0 (q, $^3J_{\text{C}-\text{F}}=3.5$ Hz), 124.3 (q, $^1J_{\text{C}-\text{F}}=271.8$ Hz), 123.9 (q, $^3J_{\text{C}-\text{F}}=3.8$ Hz), 116.4, 52.8, 51.9; $^{19}\text{F}\{\text{H}\}$ NMR (CDCl₃, 400 MHz): -62.96; HRMS (ESI) (m/z): [M+H]⁺ calc for C₁₁H₁₃F₃N, 216.1000; found, 216.0998.



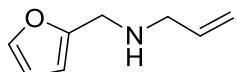
N-(4-cyanobenzyl)prop-2-en-1-amine (**2o**):²⁴ Colorless oily liquid (75 mg, 83% isolated yield), ^1H NMR (CDCl₃, 400 MHz): 7.61 (d, $^3J=8.4$ Hz, 2H), 7.45 (d, $^3J=8.4$ Hz, 2H), 5.90 (ddt, $^3J=17.2$ Hz, $^3J=10.4$ Hz, $^3J=6.0$ Hz, 1H), 5.19 (dq, $^3J=17.2$ Hz, $^4J=2J=1.6$ Hz, 1H), 5.13 (dq, $^3J=10.4$ Hz, $^4J=2J=1.6$ Hz, 1H), 3.85 (s, 2H), 3.26 (dt, $^3J=6.0$ Hz, $^4J=1.6$ Hz, 2H), 1.44 (broad s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl₃, 400 MHz): 146.1, 136.4, 132.3, 128.8, 119.1, 116.5, 110.8, 52.7, 51.9; HRMS (ESI) (m/z): [M+H]⁺ calc for C₁₁H₁₃N₂, 173.1079; found, 173.1087.



N-(3-cyanobenzyl)prop-2-en-1-amine (**2p**):²³ Colorless oily liquid (76 mg, 88% isolated yield), ^1H NMR (CDCl₃, 400 MHz): 7.66 (s, 1H), 7.59-7.53 (m, 2H), 7.42 (t, $^3J=7.6$ Hz, 1H), 5.91 (ddt, $^3J=17.2$ Hz, $^3J=10.2$ Hz, $^3J=5.8$ Hz, 1H), 5.20 (dq, $^3J=17.2$ Hz, $^4J=2J=1.6$ Hz, 1H), 5.14 (dq, $^3J=10.2$ Hz, $^4J=2J=1.6$ Hz, 1H), 3.83 (s, 2H), 3.27 (dt, $^3J=5.8$ Hz, $^4J=1.6$ Hz, 2H), 1.46 (broad s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl₃, 400 MHz): 142.0, 136.5, 132.7, 131.8, 130.8, 129.3, 119.1, 116.6, 112.5, 52.4, 51.9; HRMS (ESI) (m/z): [M+H]⁺ calc for C₁₁H₁₃N₂, 173.1079; found, 173.1084.

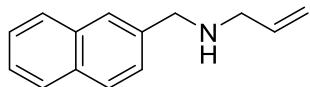


N-2-propen-1-yl-1,3-benzodioxole-5-methanamine (**2r**):²⁸ Colorless liquid (80 mg, 79% isolated yield), ^1H NMR (CDCl₃, 600 MHz): 6.83 (s, 1H), 6.75 (s, 2H), 5.94-5.88 (m, 1H), 5.93 (s, 2H), 5.18 (dq, $^3J=17.2$ Hz, $^4J=2J=1.7$ Hz, 1H), 5.10 (dq, $^3J=10.3$ Hz, $^4J=2J=1.7$ Hz, 1H), 3.69 (s, 2H), 3.25 (dt, $^3J=6.0$ Hz, $^4J=1.7$ Hz, 2H), 1.43 (broad s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl₃, 600 MHz): 147.8, 146.6, 136.9, 134.4, 121.4, 116.1, 108.9, 108.2, 101.0, 53.2, 51.7; HRMS (ESI) (m/z): [M+H]⁺ calc for C₁₁H₁₄NO₂, 192.1025; found, 192.1032.

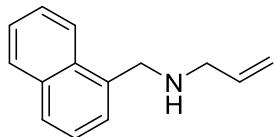


N-(furan-2-ylmethyl)prop-2-en-1-amine (**2s**):²⁹ Colorless liquid (55 mg, 81% isolated yield), ^1H NMR (CDCl₃, 600 MHz): 7.36-7.35 (m, 1H), 6.31-6.30 (m, 1H), 6.17 (d, $^3J=3.2$ Hz, 1H), 5.90 (ddt, $^3J=16.8$ Hz, $^3J=10.2$ Hz, $^3J=6.6$ Hz, 1H), 5.19 (dm, $^3J=16.8$ Hz, 1H), 5.11 (dm, $^3J=10.2$ Hz, 1H), 3.78 (s, 2H), 3.25 (dm, $^3J=6.6$ Hz, 2H), 1.57 (broad s,

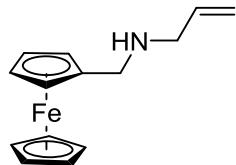
1H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3 , 600 MHz): 153.9, 141.9, 136.6, 116.4, 110.2, 107.1, 51.6, 45.5; HRMS (ESI) (m/z): $[\text{M}+\text{H}]^+$ calc for $\text{C}_8\text{H}_{12}\text{NO}$, 138.0919; found, 138.0907.



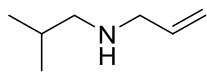
N-(naphthalen-2-ylmethyl)prop-2-en-1-amine (**2t**):³⁰ White solid (88 mg, 89% isolated yield), ^1H NMR (CDCl_3 , 400 MHz): 7.85-7.81 (m, 3H), 7.78 (s, 1H), 7.50-7.45 (m, 3H), 5.97 (ddt, $^3\text{J}=17.2$ Hz, $^3\text{J}=10.4$ Hz, $^3\text{J}=6.0$ Hz, 1H), 5.23 (dm, $^3\text{J}=17.2$ Hz, 1H), 5.15 (dm, $^3\text{J}=10.4$ Hz, 1H), 3.97 (s, 2H), 3.33 (dm, $^3\text{J}=6.0$ Hz, 2H), 1.52 (broad s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3 , 400 MHz): 137.9, 136.9, 133.5, 132.7, 128.2, 127.81, 127.76, 126.7, 126.6, 126.1, 125.7, 116.2, 53.5, 51.9; HRMS (ESI) (m/z): $[\text{M}+\text{H}]^+$ calc for $\text{C}_{14}\text{H}_{16}\text{N}$, 198.1283; found, 198.1285.



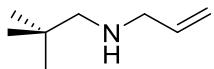
N-(naphthalen-1-ylmethyl)prop-2-en-1-amine (**2u**):³¹ Colorless oily liquid (86 mg, 87% isolated yield), ^1H NMR (CDCl_3 , 400 MHz): 8.13 (d, $^3\text{J}=8.0$ Hz, 1H), 7.87 (d, $^3\text{J}=8.0$ Hz, 1H), 7.78 (d, $^3\text{J}=8.0$ Hz, 1H), 7.56-7.41 (m, 4H), 6.00 (ddt, $^3\text{J}=17.2$ Hz, $^3\text{J}=10.2$ Hz, $^3\text{J}=6.2$ Hz, 1H), 5.25 (dq, $^3\text{J}=17.2$ Hz, $^4\text{J}=^2\text{J}=1.8$ Hz, 1H), 5.16 (dq, $^3\text{J}=10.2$ Hz, $^4\text{J}=^2\text{J}=1.8$ Hz, 1H), 4.24 (s, 2H), 3.40 (dt, $^3\text{J}=6.2$ Hz, $^4\text{J}=1.8$ Hz, 2H), 1.50 (broad s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3 , 400 MHz): 137.0, 136.0, 134.0, 131.9, 128.8, 127.9, 126.24, 126.20, 125.7, 125.5, 123.8, 116.4, 52.5, 51.0; HRMS (ESI) (m/z): $[\text{M}+\text{H}]^+$ calc for $\text{C}_{14}\text{H}_{16}\text{N}$, 198.1283; found, 198.1288.



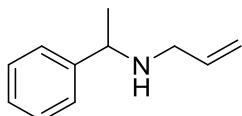
N-allyl-1-(ferrocenyl)methanamine (**2v**):³² Red oily liquid (107 mg, 84% isolated yield), ^1H NMR (CDCl_3 , 400 MHz): 5.97-5.87 (m, 1H), 5.19 (dm, $^3\text{J}=16.8$ Hz, 1H), 5.11 (dm, $^3\text{J}=10.4$ Hz, 1H), 4.19 (t, $J=2.0$ Hz, 2H), 4.12 (s, 5H), 4.11 (t, $J=2.0$ Hz, 2H), 3.51 (s, 2H), 3.28 (dm, $^3\text{J}=6.0$ Hz, 2H), 1.44 (broad s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3 , 400 MHz): 137.0, 116.1, 86.9, 68.54, 68.51, 67.9, 52.1, 48.4; HRMS (ESI) (m/z): $[\text{M}+\text{H}]^+$ calc for $\text{C}_{14}\text{H}_{18}\text{FeN}$, 256.0789; found, 256.0793.



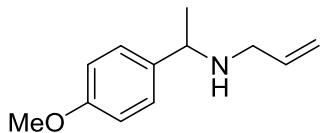
N-isobutylprop-2-en-1-amine (**2w**):³³ Colorless liquid (49 mg, 88% isolated yield), ^1H NMR (CDCl_3 , 400 MHz): 5.88 (ddt, $^3\text{J}=17.2$ Hz, $^3\text{J}=10.4$ Hz, $^3\text{J}=6.0$ Hz, 1H), 5.14 (dm, $^3\text{J}=17.2$ Hz, 1H), 5.05 (dm, $^3\text{J}=10.4$ Hz, 1H), 3.21 (dm, $^3\text{J}=6.0$ Hz, 2H), 2.39 (d, $^3\text{J}=6.8$ Hz, 2H), 1.72 (m, 1H), 1.65 (broad s, 1H), 0.88 (d, $^3\text{J}=6.8$ Hz, 6H); $^{13}\text{C}\{\text{H}\}$ NMR (CDCl_3 , 400 MHz): 137.1, 115.8, 57.5, 52.7, 28.4, 20.8; HRMS (ESI) (m/z): $[\text{M}+\text{H}]^+$ calc for $\text{C}_7\text{H}_{16}\text{N}$, 114.1283; found, 114.1282.



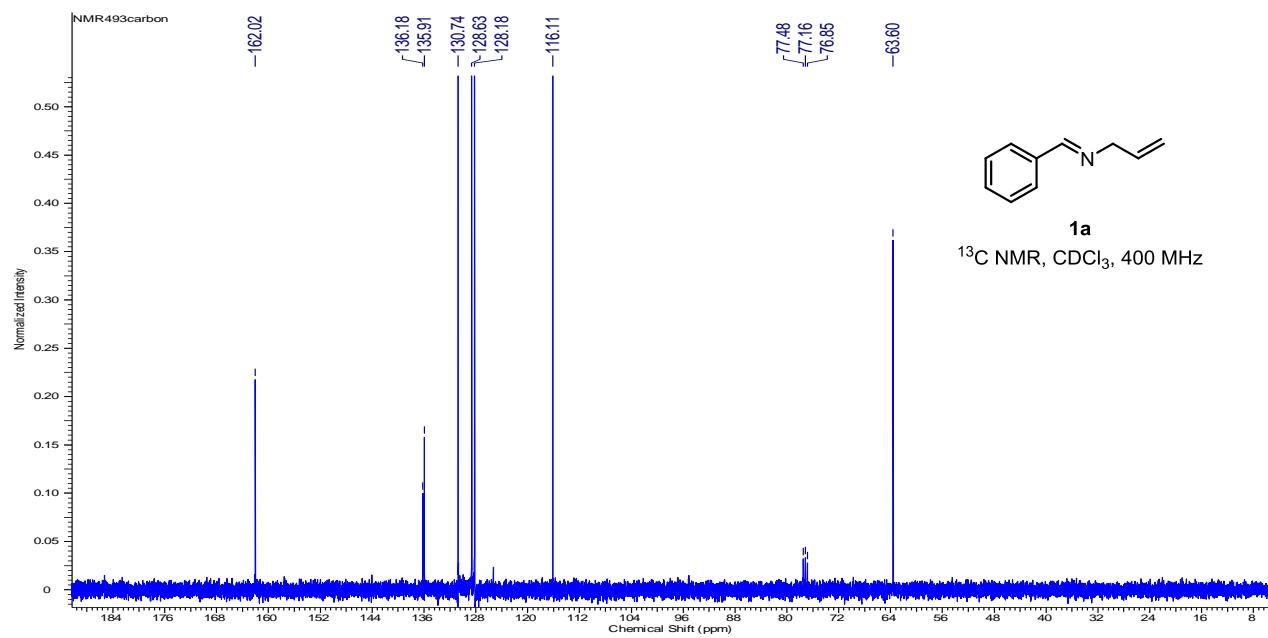
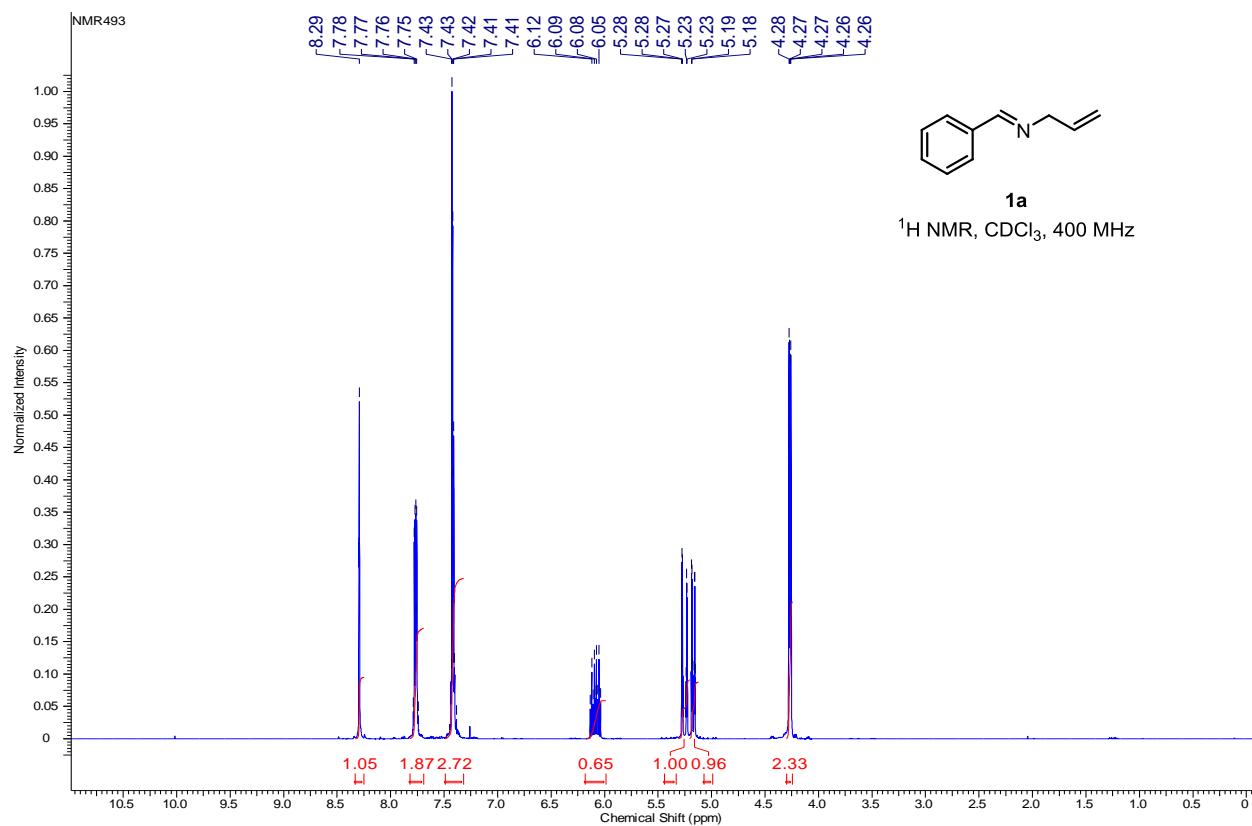
N-neopentylprop-2-en-1-amine (**2x**):³⁴ Colorless liquid (51 mg, 81% isolated yield), ¹H NMR (CDCl₃, 400 MHz): 5.89 (ddt, ³J=17.2 Hz, ³J=10.4 Hz, ³J=6.0 Hz, 1H), 5.16 (dm, ³J=17.2 Hz, 1H), 5.07 (dm, ³J=10.4 Hz, 1H), 3.24 (dm, ³J=6.0 Hz, 2H), 2.33 (s, 2H), 1.13 (broad s, 1H), 0.91 (s, 9H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 137.5, 115.7, 62.0, 53.5, 31.5, 28.0; HRMS (ESI) (m/z): [M+H]⁺ calc for C₈H₁₈N, 128.1439; found, 128.1432.

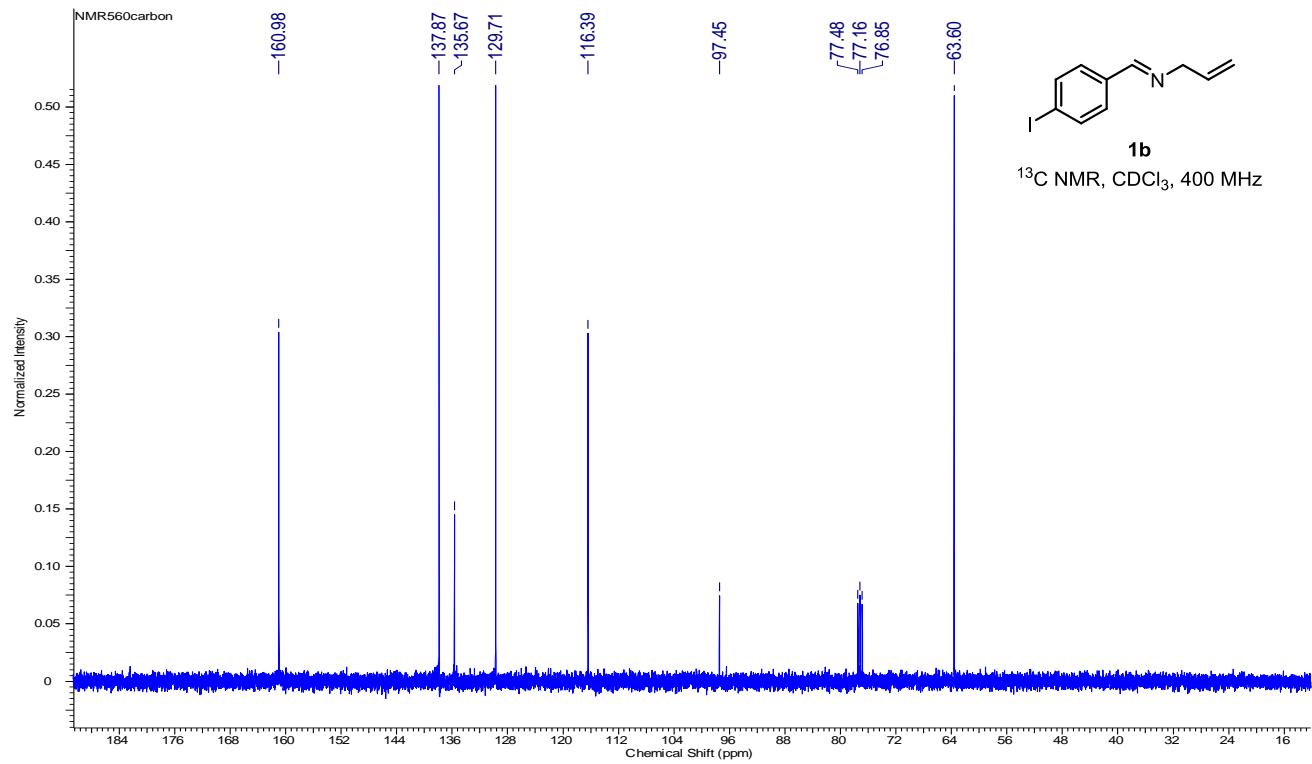
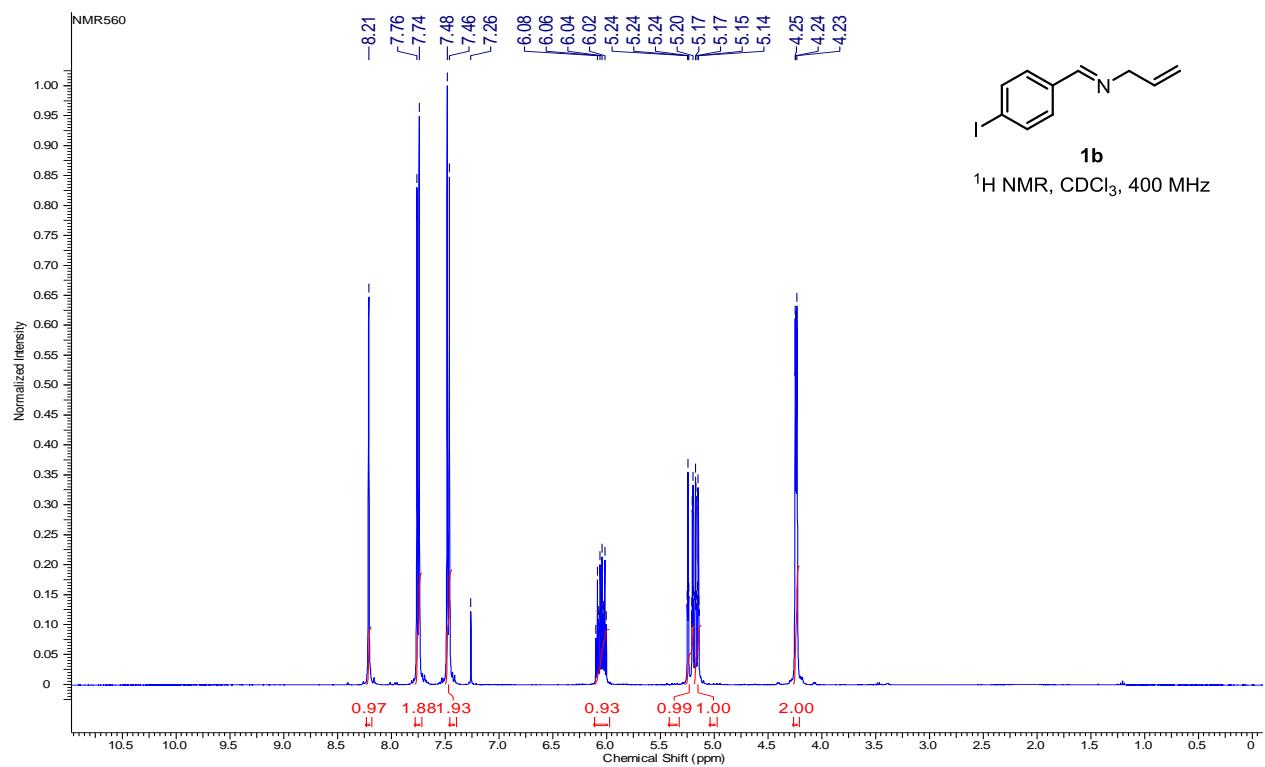


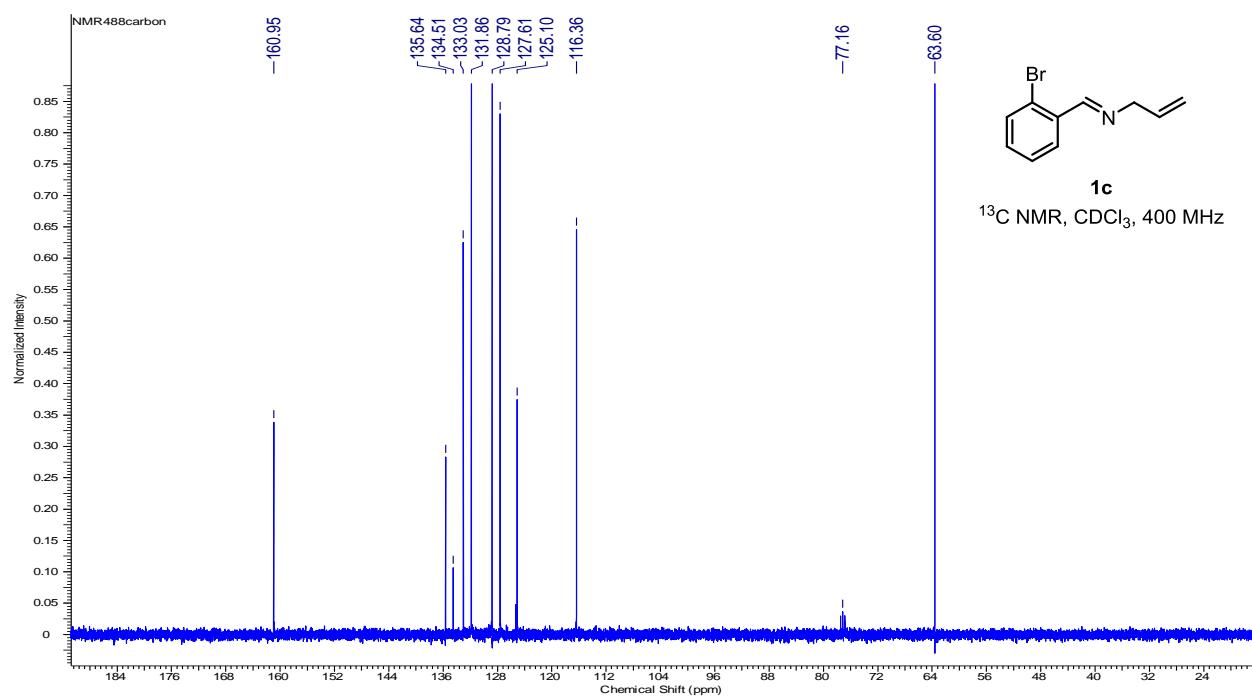
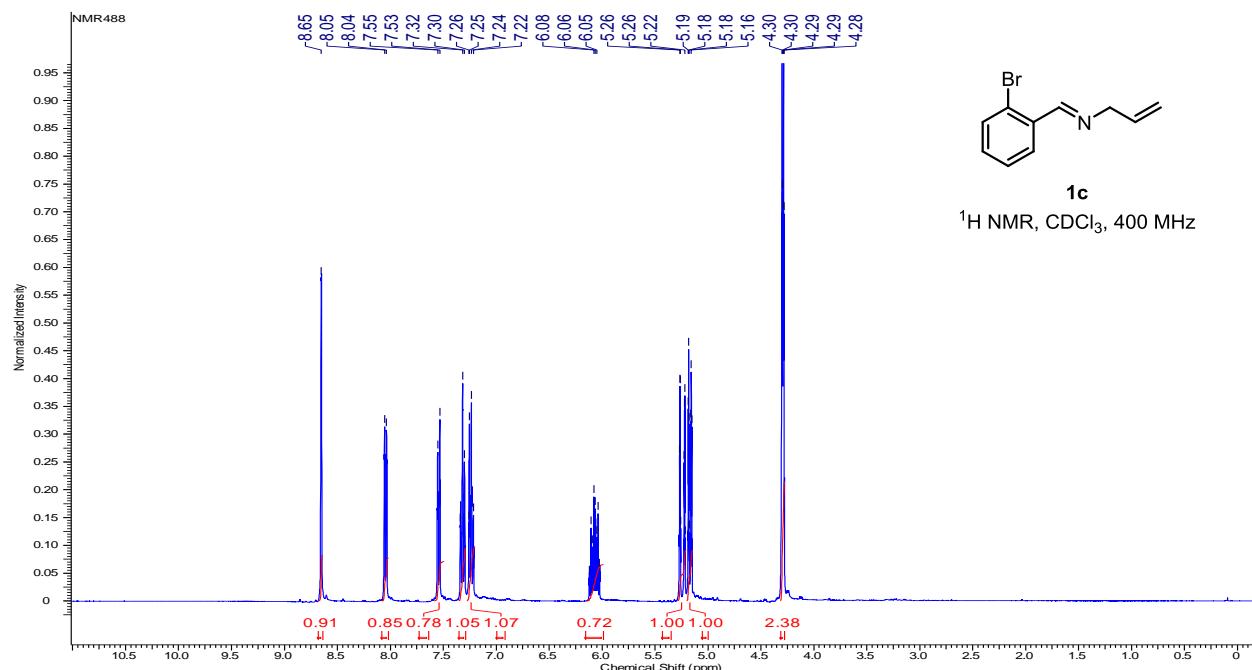
N-(1-phenylethyl)prop-2-en-1-amine (**2y**):³⁵ Pale yellow oily liquid (55 mg, 68% isolated yield), ¹H NMR (CDCl₃, 600 MHz): 7.34-7.31 (m, 4H), 7.26-7.23 (m, 1H), 5.89 (ddt, ³J=16.8 Hz, ³J=10.2 Hz, ³J=6.0 Hz, 1H), 5.13 (dq, ³J=16.8 Hz, ⁴J= ²J=1.8 Hz, 1H), 5.07 (dq, ³J=10.2 Hz, ⁴J= ²J=1.8 Hz, 1H), 3.80 (q, ³J=6.6 Hz, 1H), 3.10 (dm, ³J=6.0 Hz, 2H), 1.37 (d, ³J=6.6 Hz, 3H), 1.35 (broad s, 1H); ¹³C{¹H} NMR (CDCl₃, 600 MHz): 145.6, 137.1, 128.6, 127.0, 126.7, 115.8, 57.7, 50.4, 24.4; HRMS (ESI) (m/z): [M+H]⁺ calc for C₁₁H₁₆N, 162.1283; found, 162.1284.

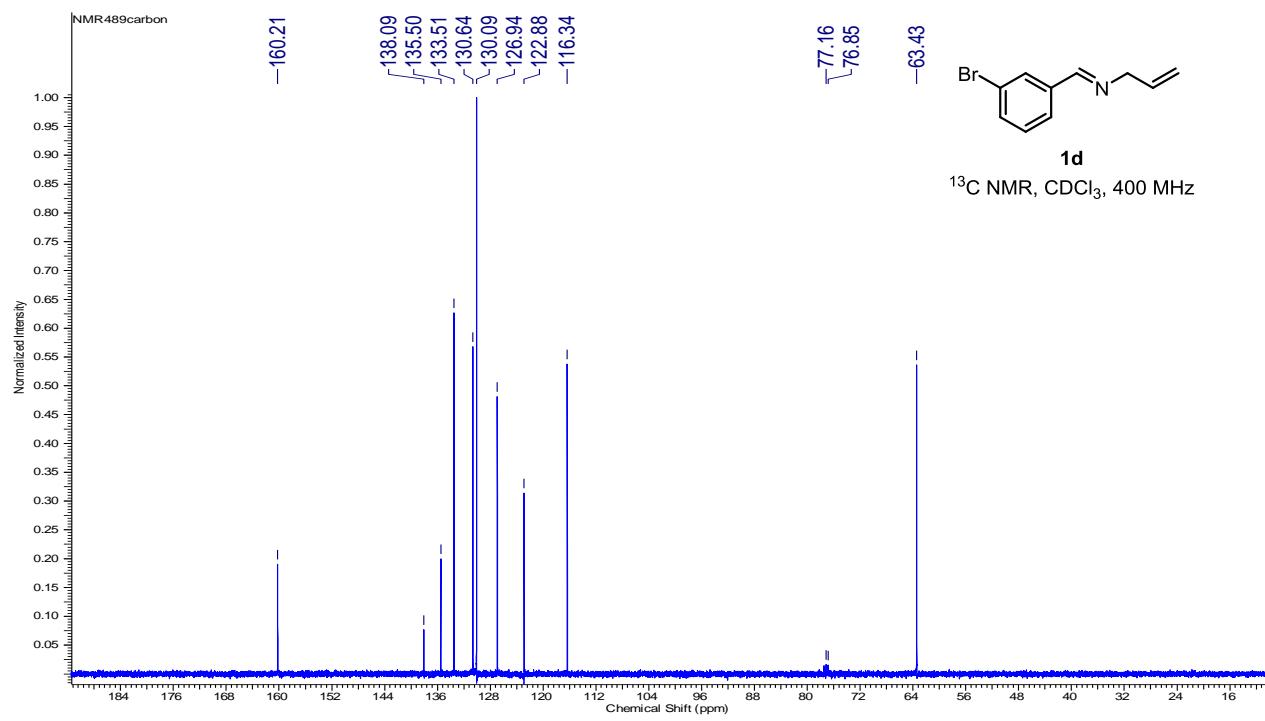
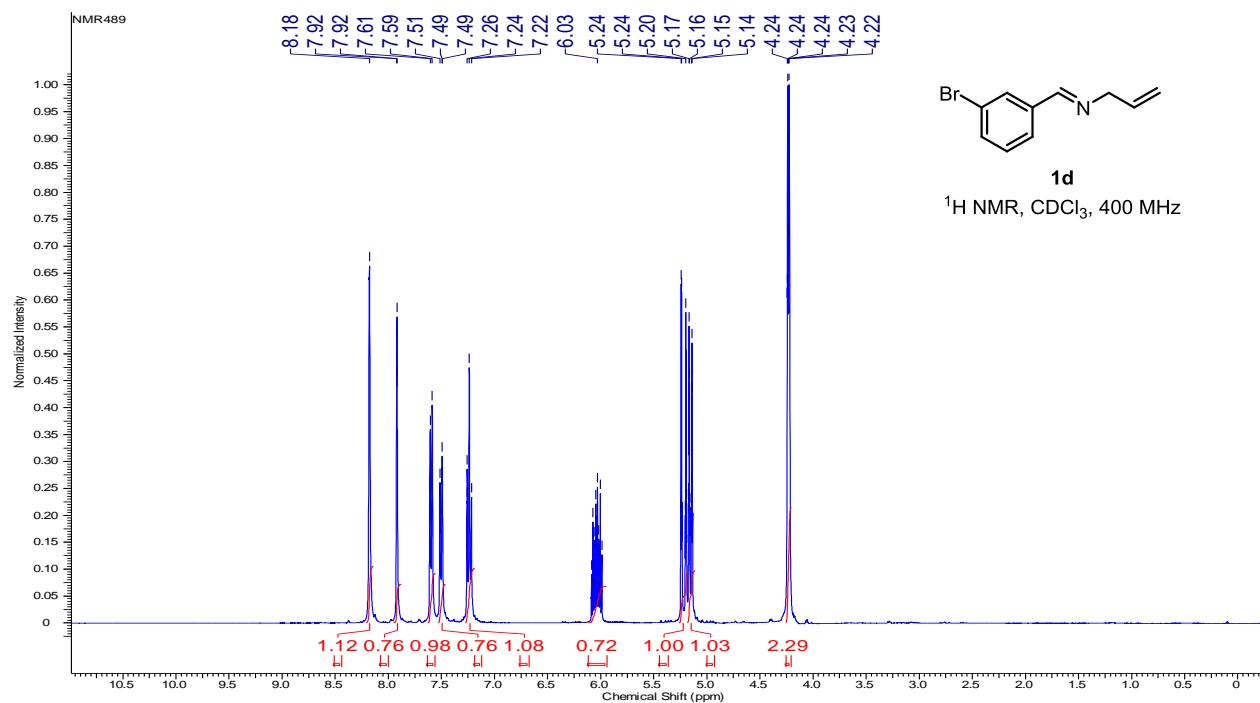


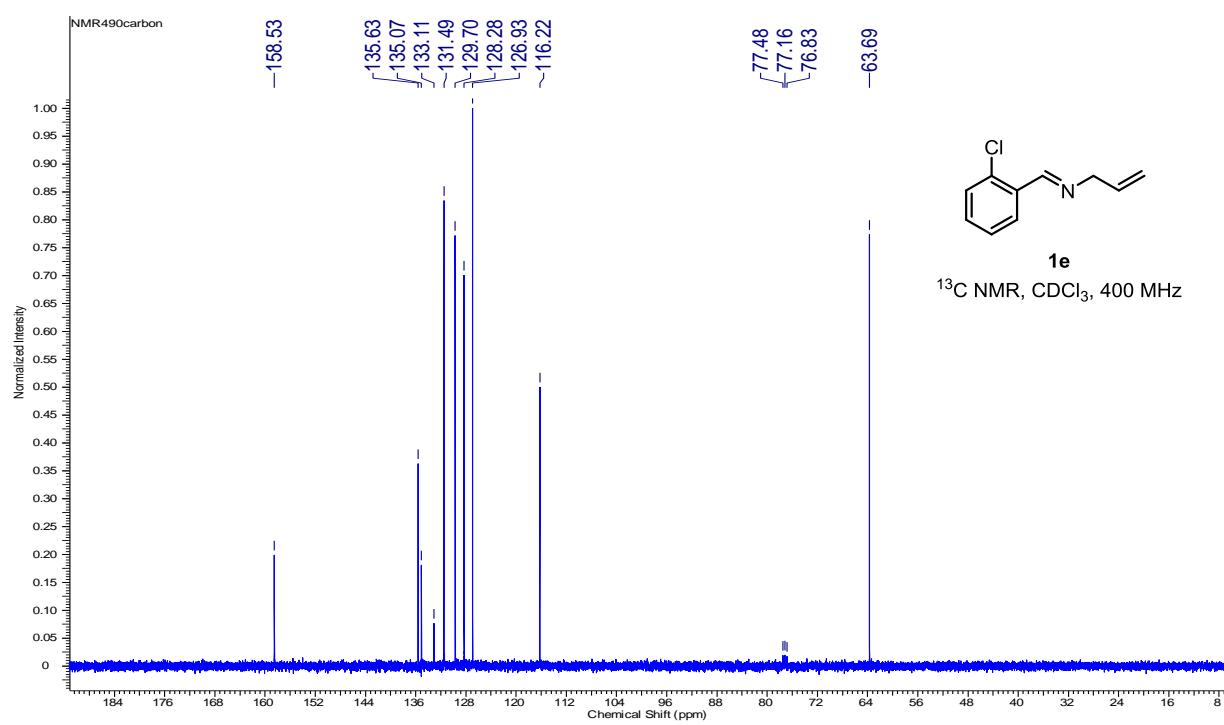
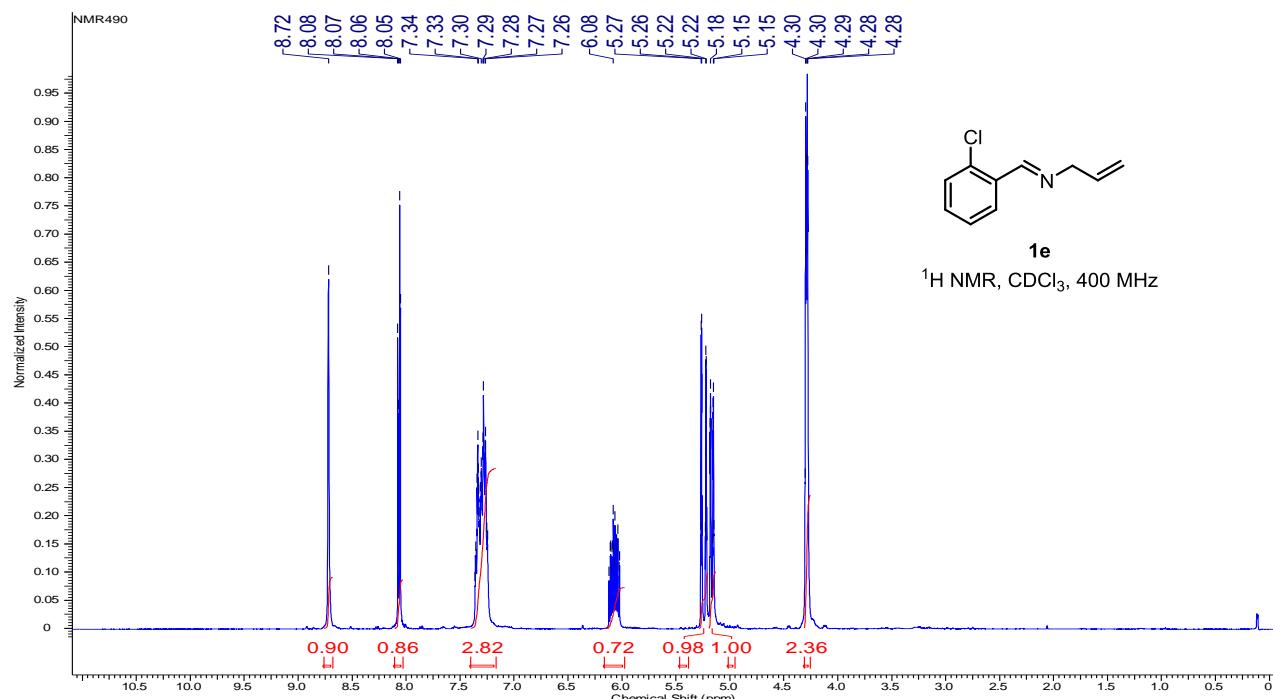
N-(1-(4-methoxyphenyl)ethyl)prop-2-en-1-amine (**2z**):³⁵ Colorless oily liquid (51 mg, 53% isolated yield), ¹H NMR (CDCl₃, 400 MHz): 7.23 (dm, ³J=13.2 Hz, 2H), 6.87 (dm, ³J=13.2 Hz, 2H), 5.88 (ddt, ³J=17.2 Hz, ³J=10.4 Hz, ³J=6.0 Hz, 1H), 5.12 (dm, ³J=17.2 Hz, 1H), 5.06 (dm, ³J=10.4 Hz, 1H), 3.80 (s, 3H), 3.76 (q, ³J=6.4 Hz, 1H), 3.09 (dm, ³J=6.0 Hz, 2H), 1.36 (broad s, 1H), 1.34 (d, ³J=6.4 Hz, 3H); ¹³C{¹H} NMR (CDCl₃, 400 MHz): 158.6, 137.6, 137.1, 127.7, 115.8, 113.9, 57.0, 55.4, 50.3, 24.4; HRMS (ESI) (m/z): [M+H]⁺ calc for C₁₂H₁₈NO, 192.1388; found, 192.1385.

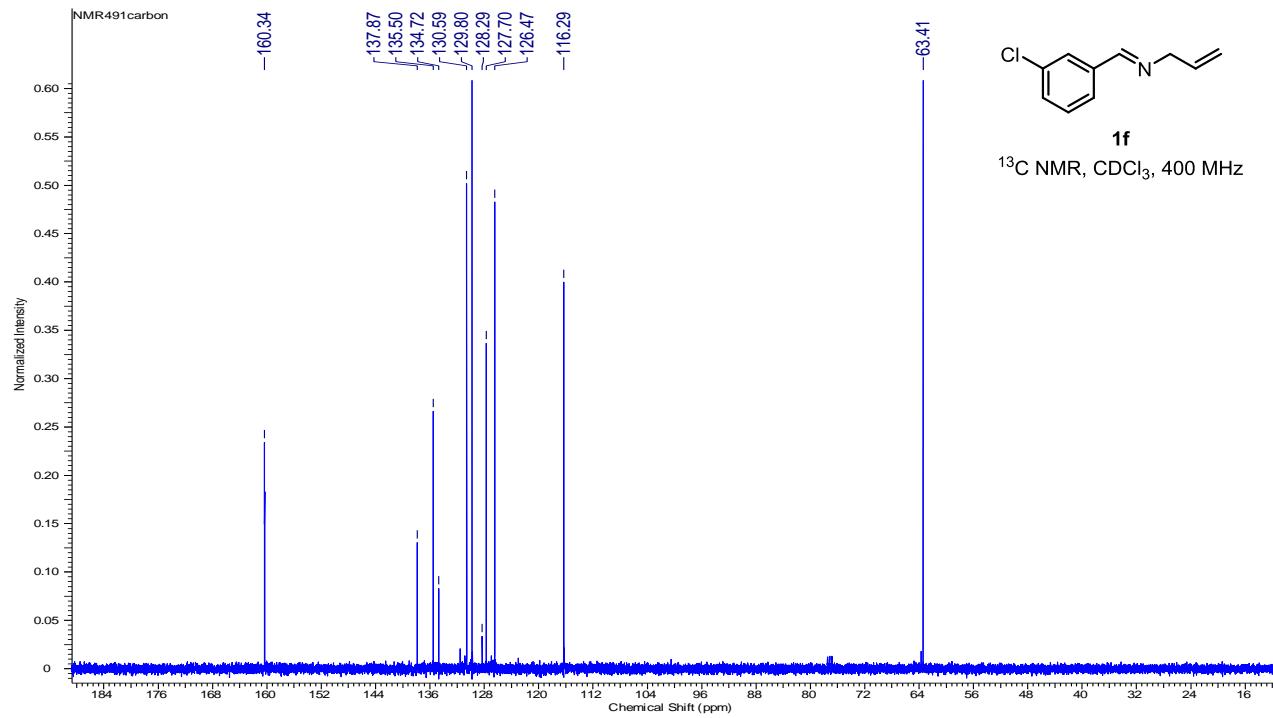
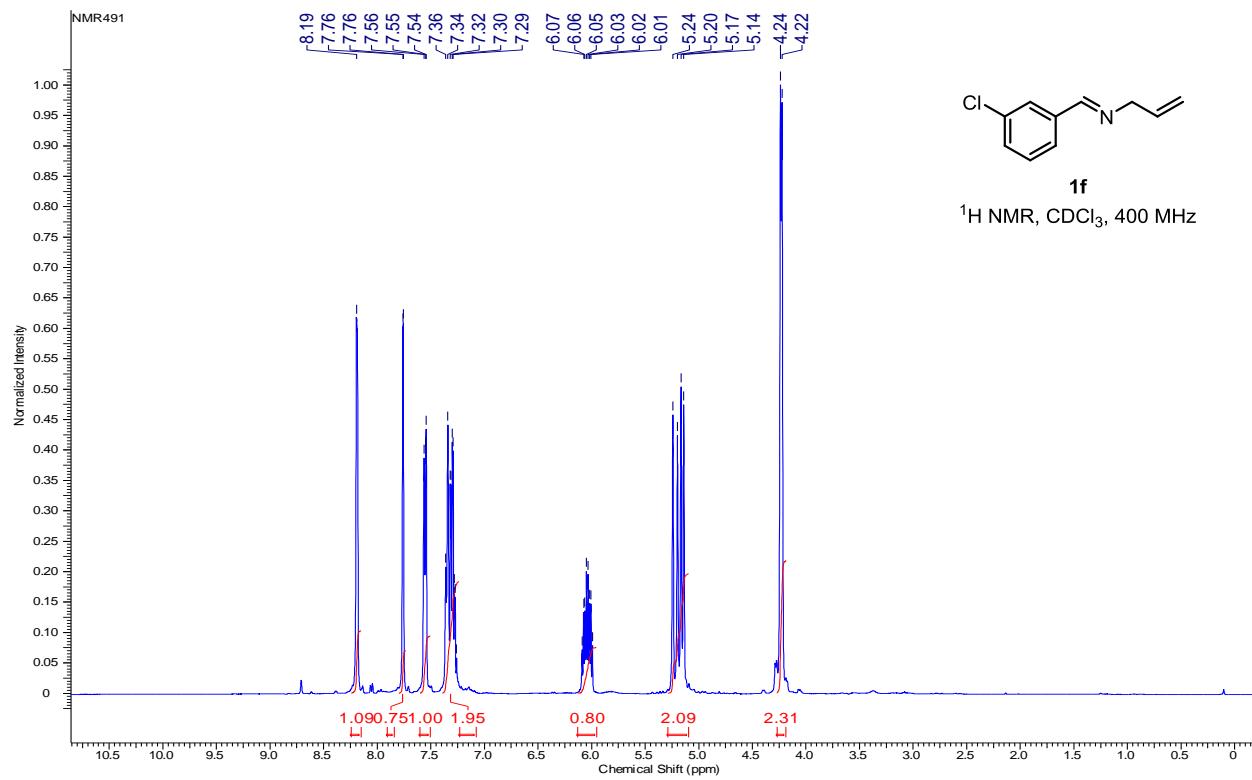


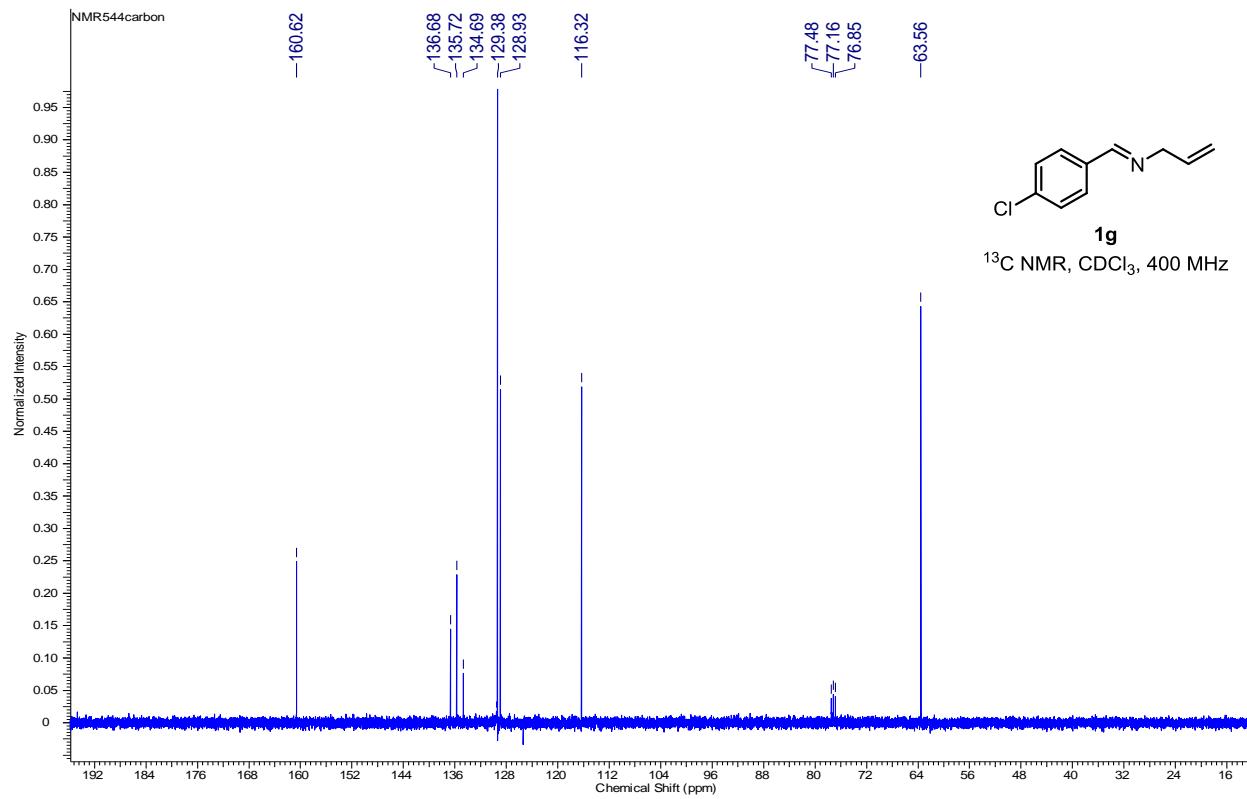
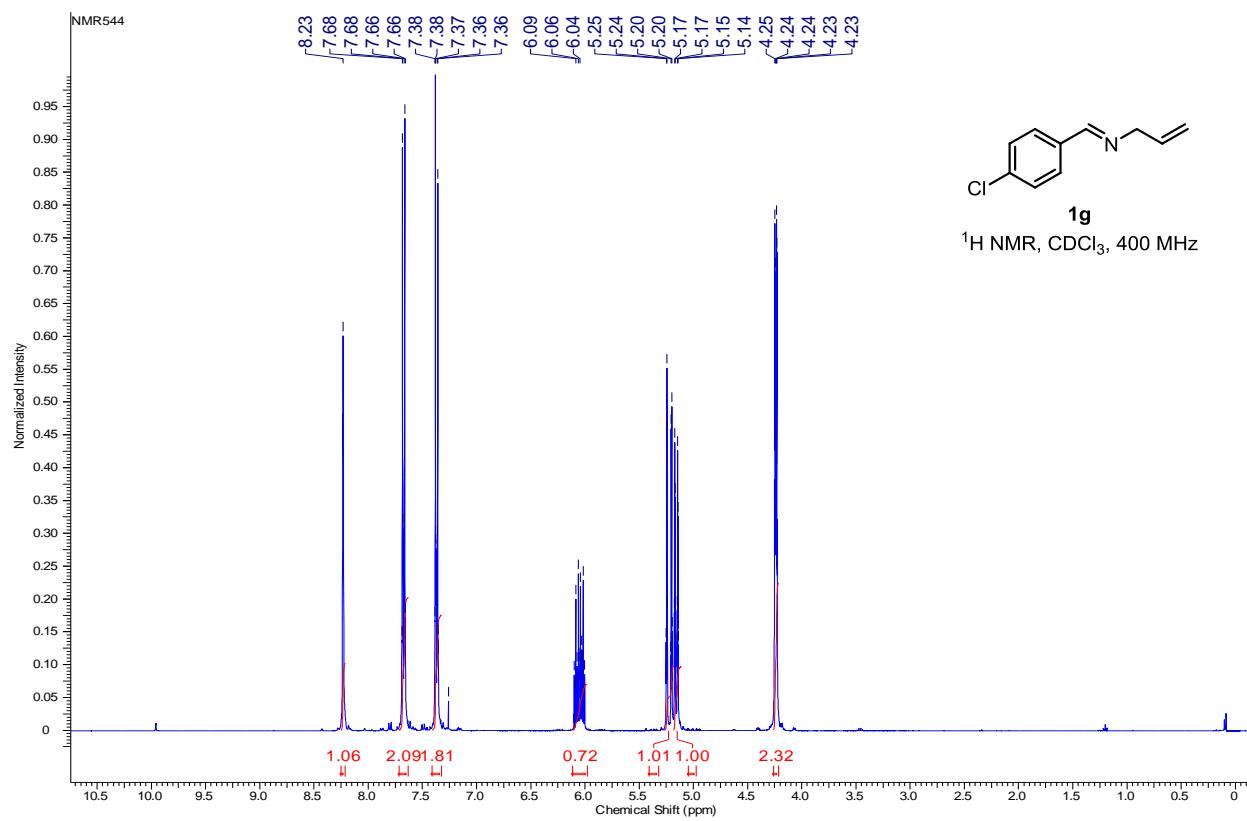


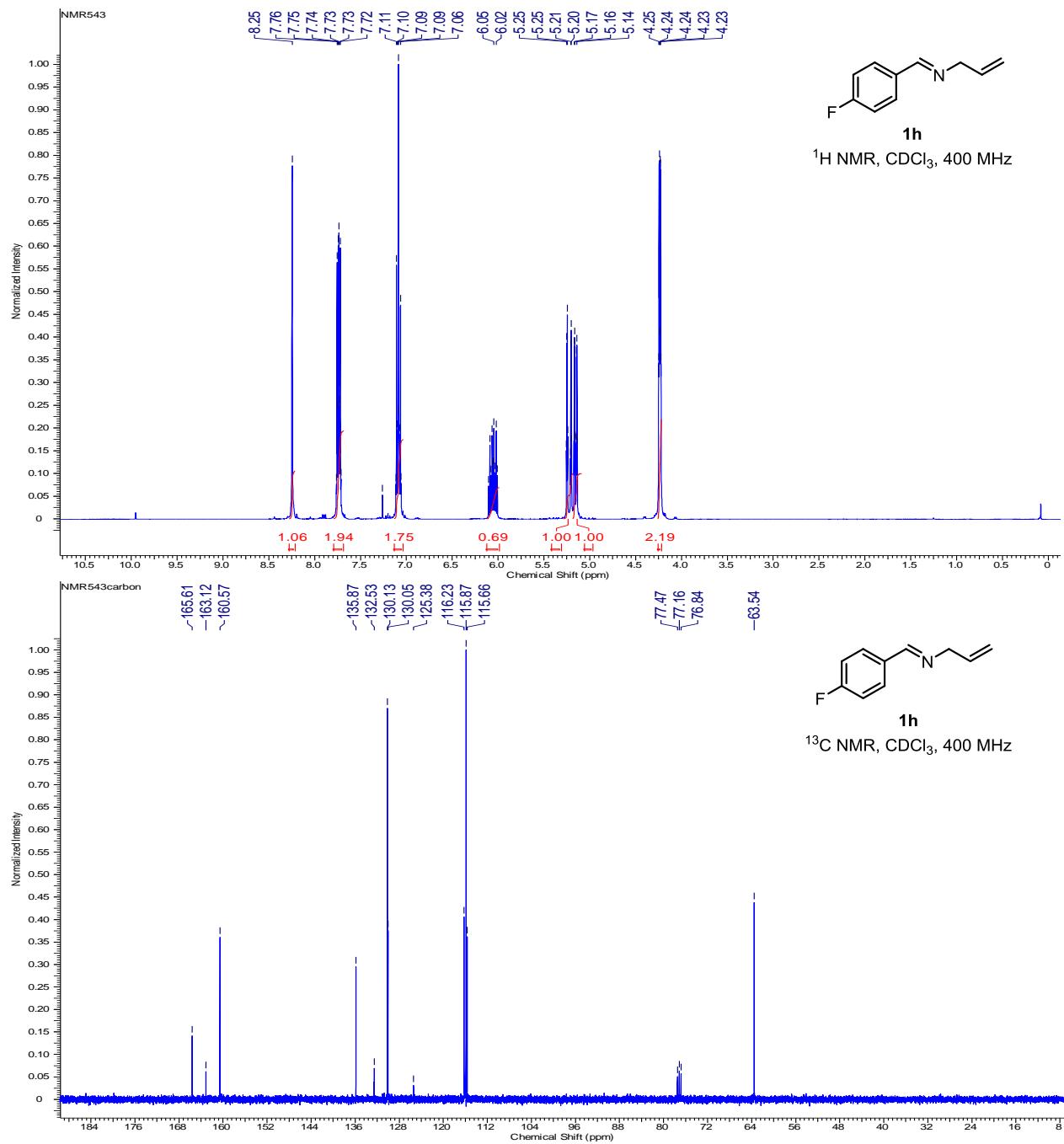


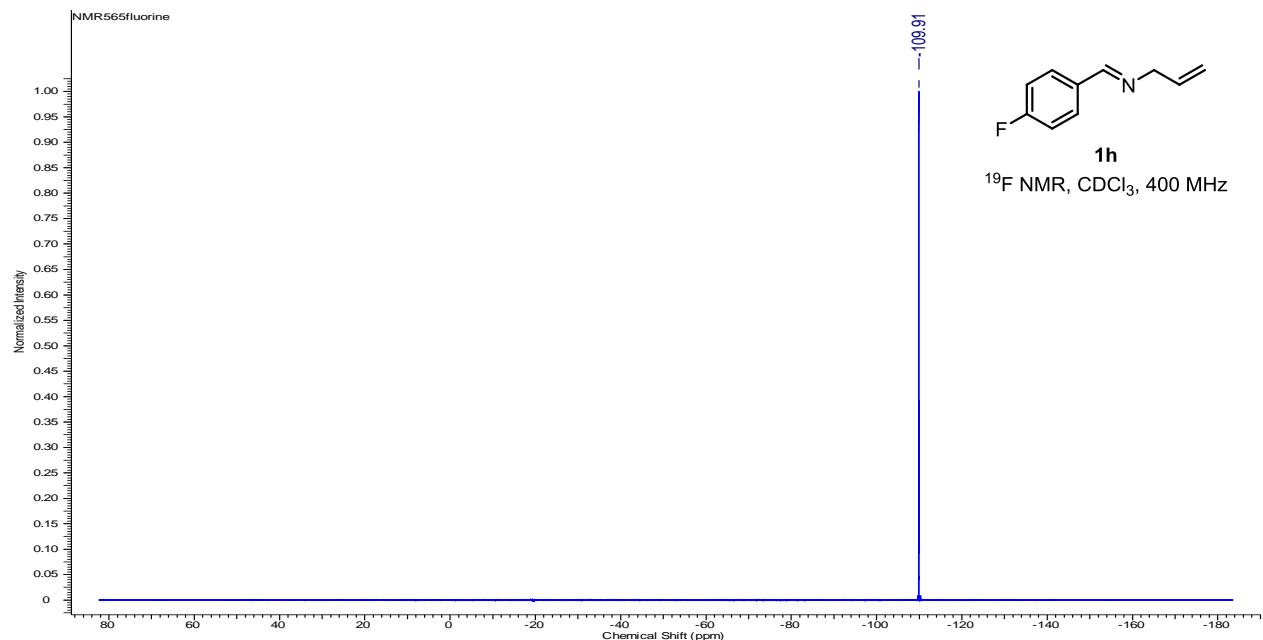


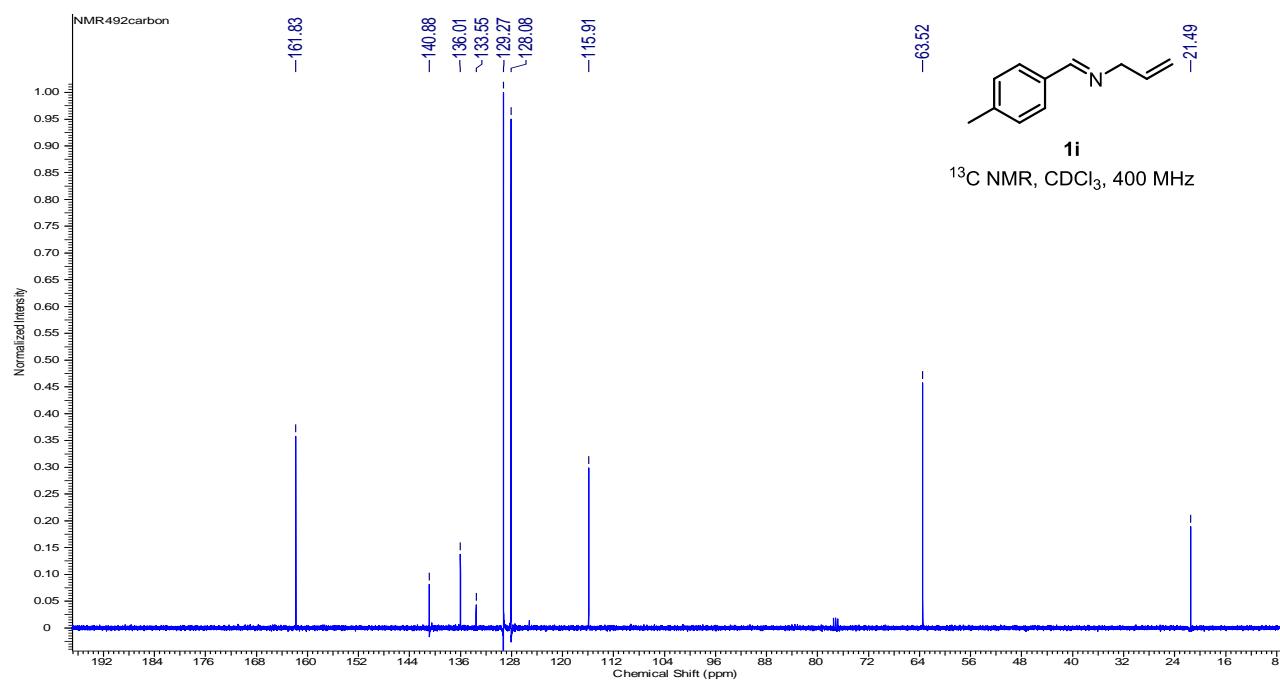
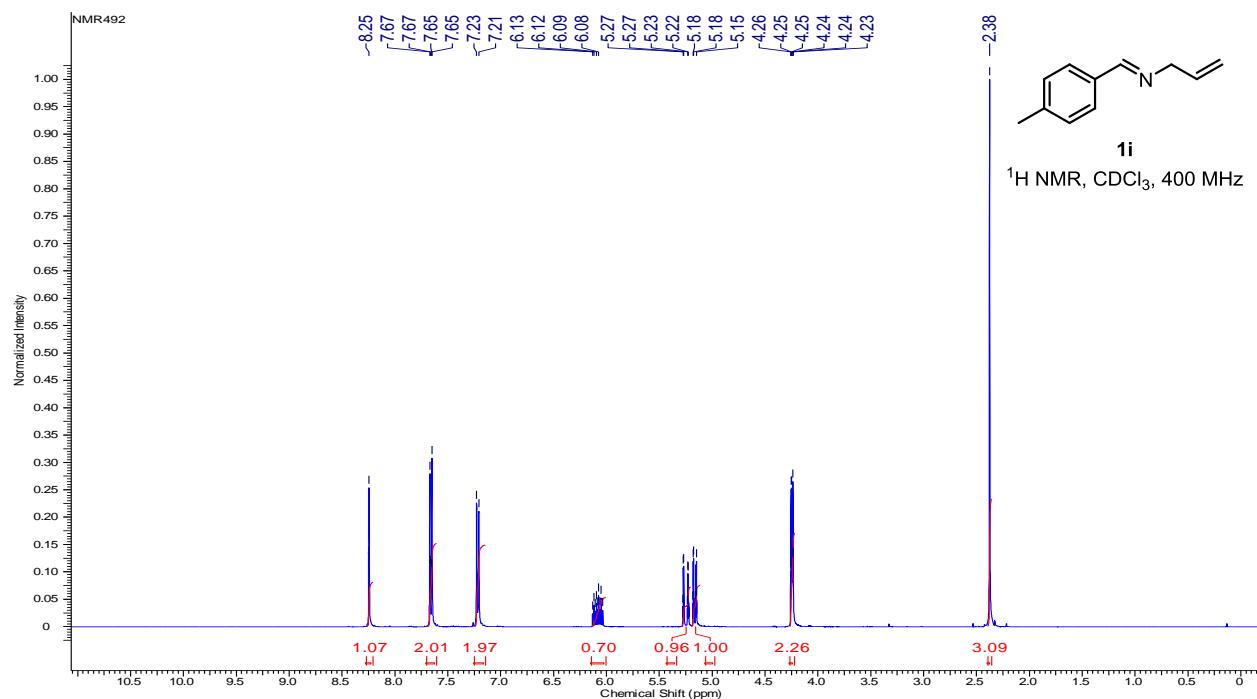


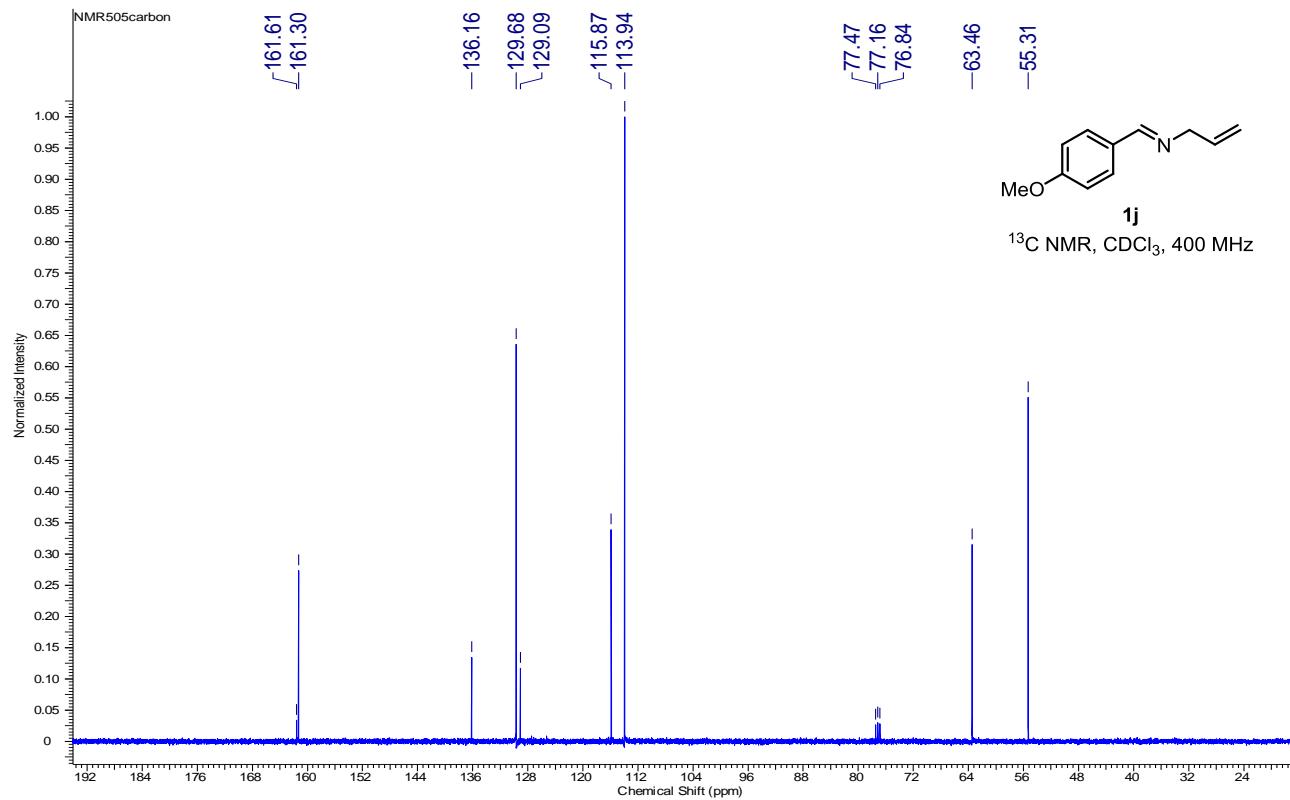
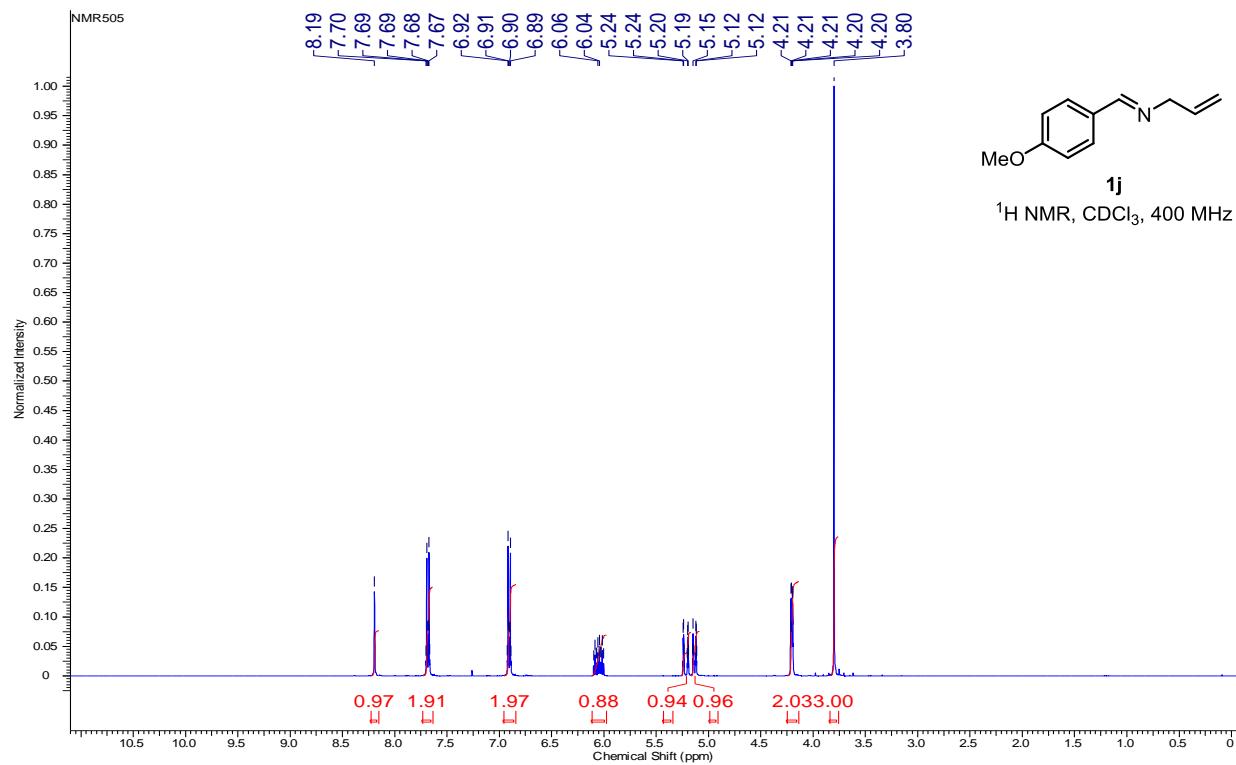


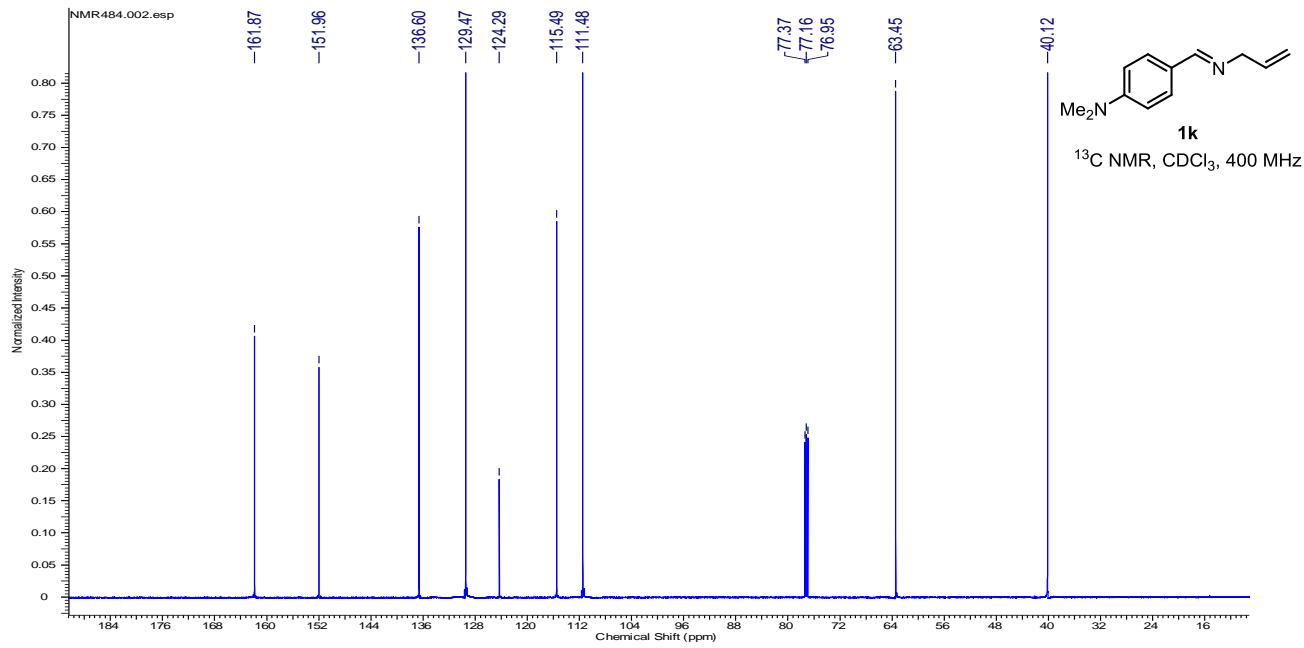
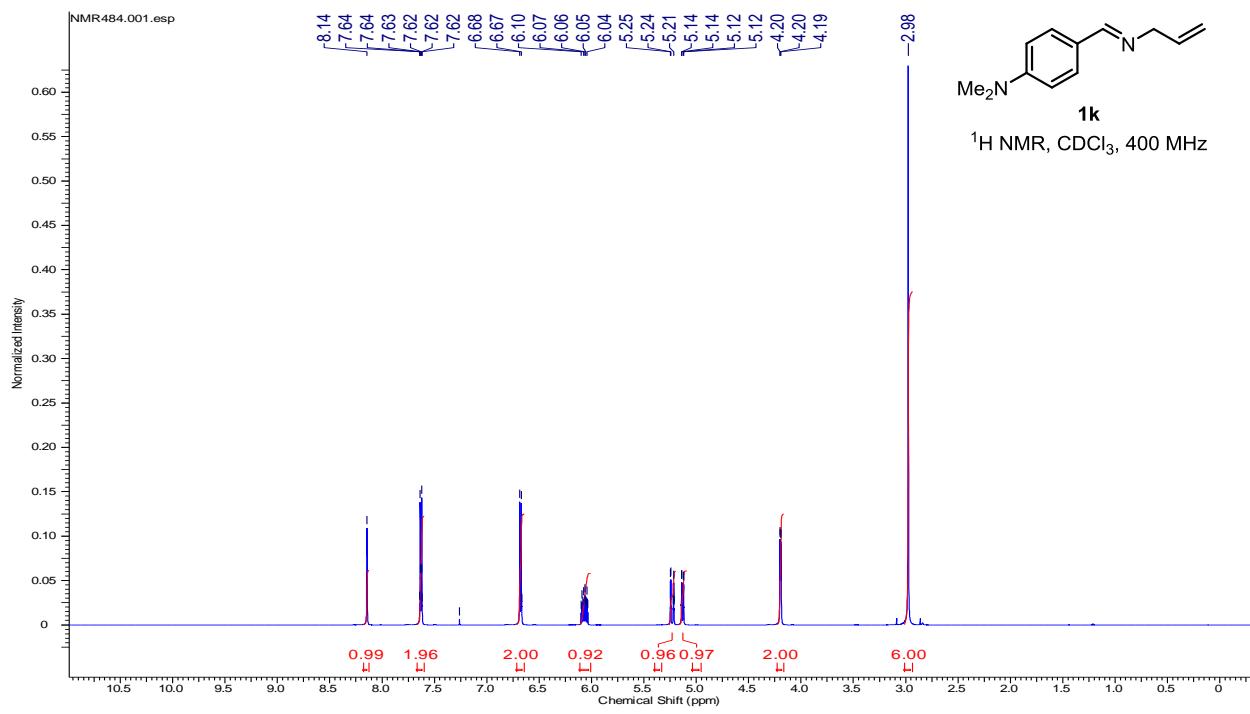


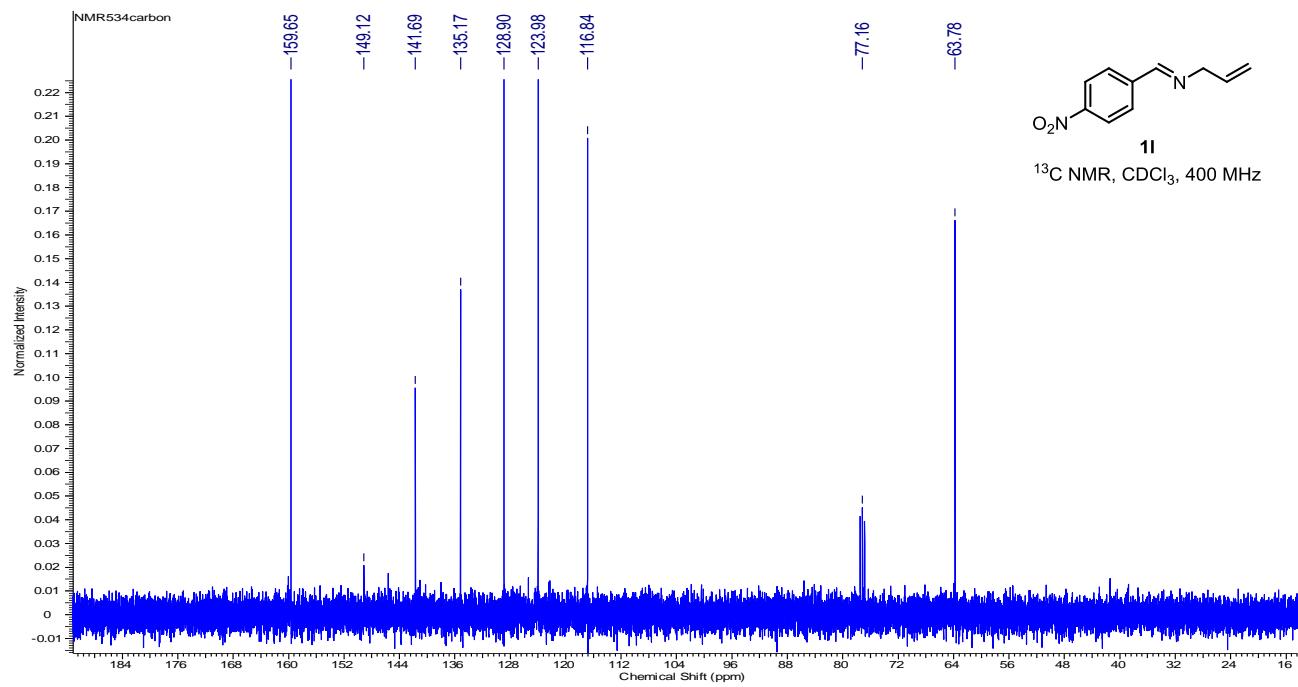
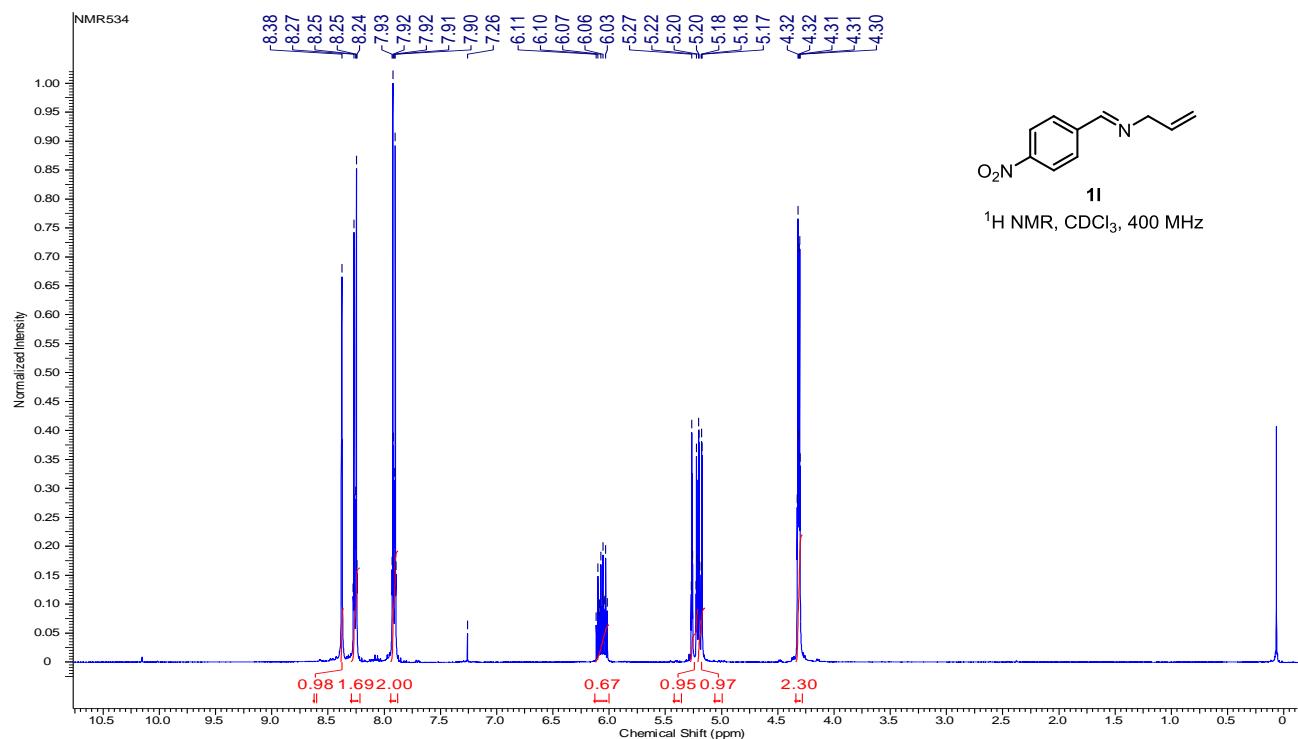


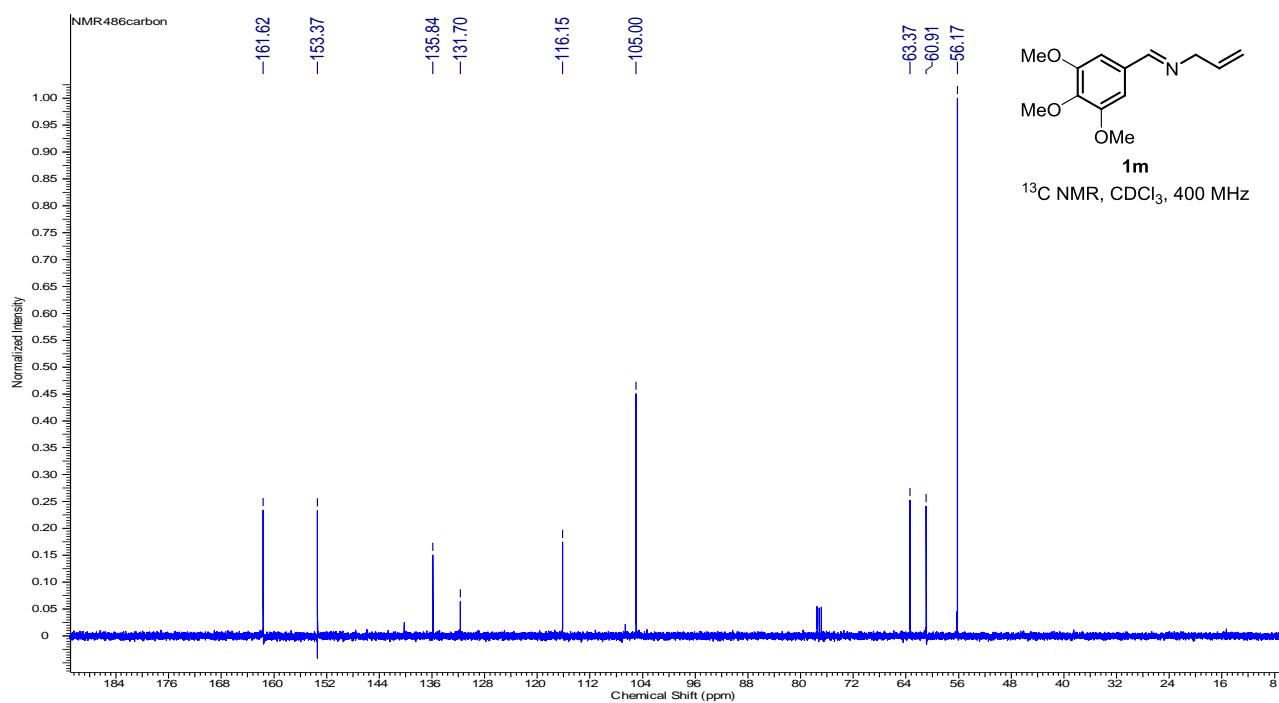
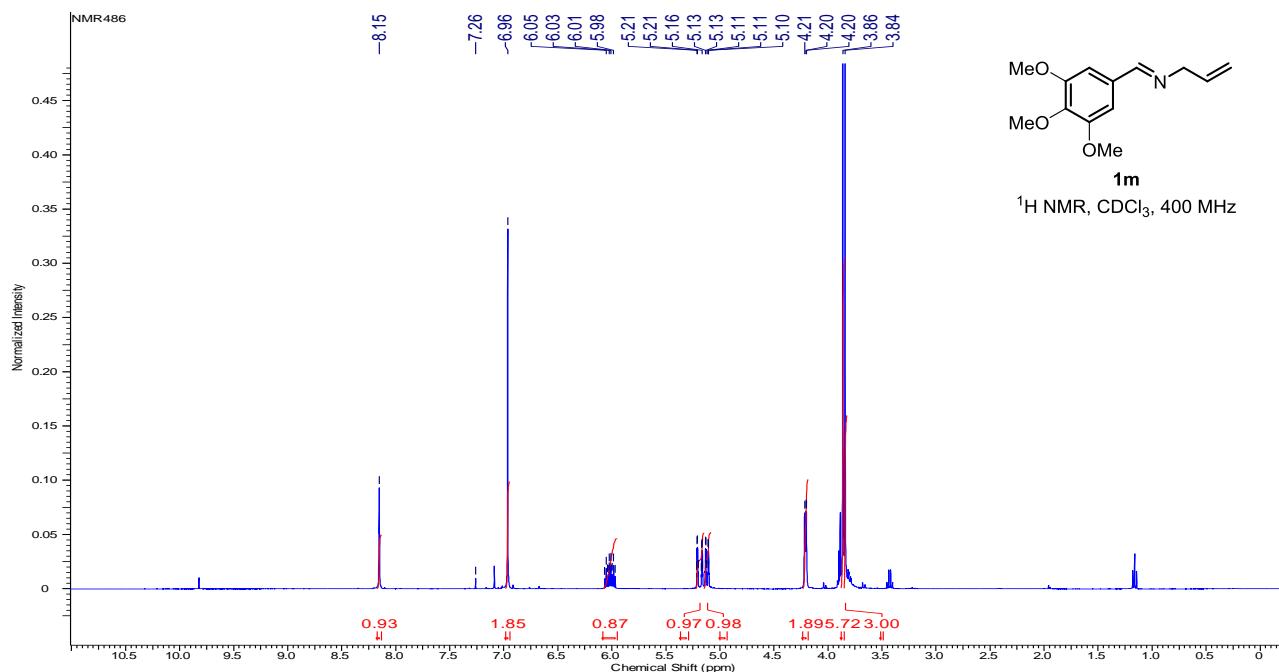


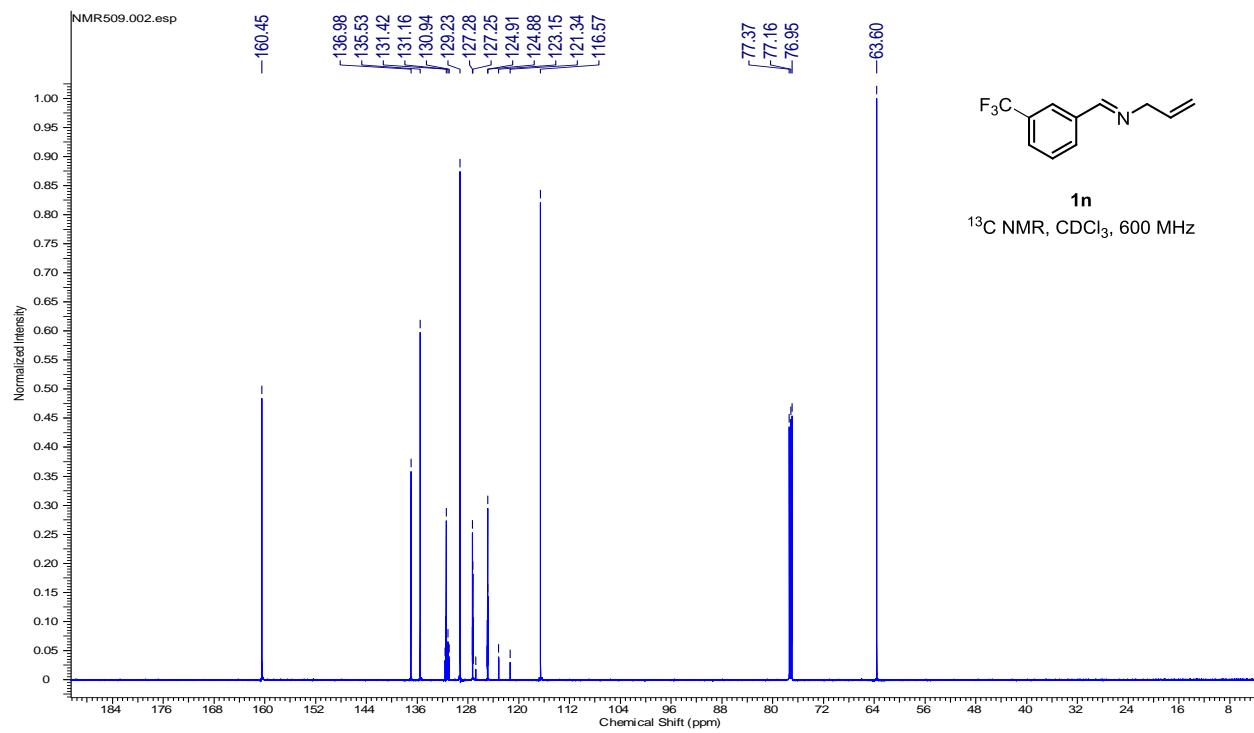
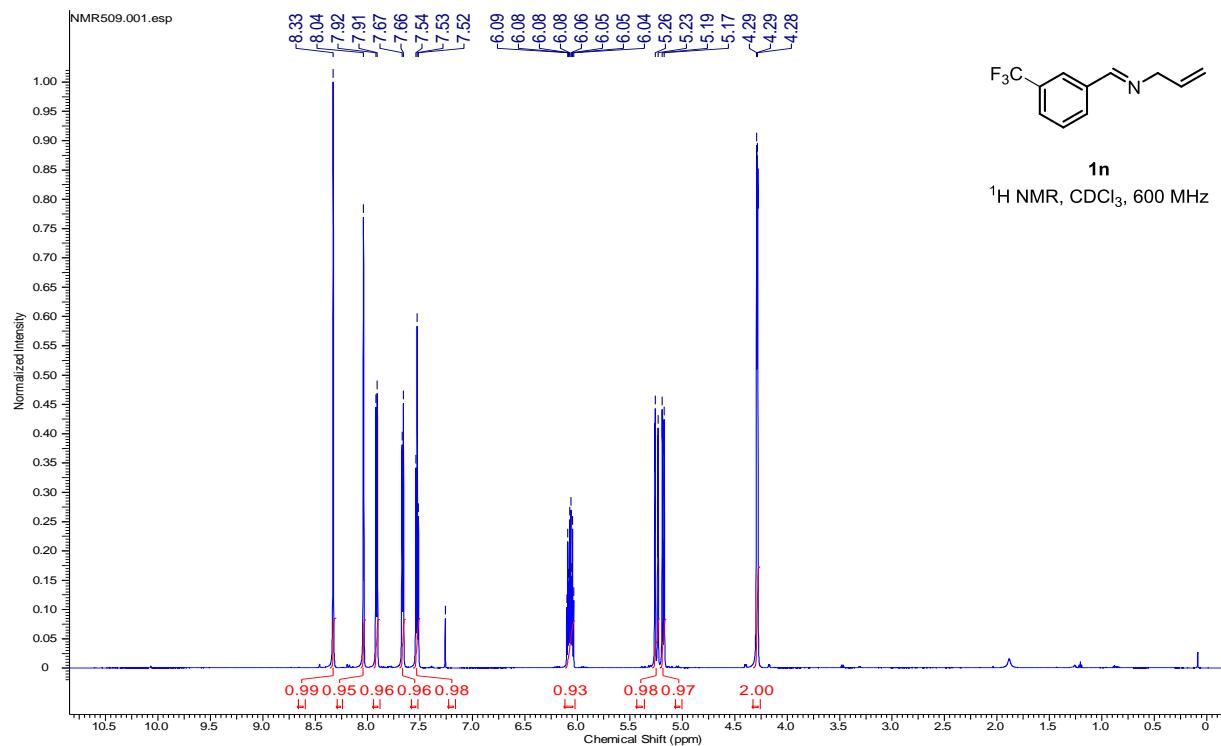


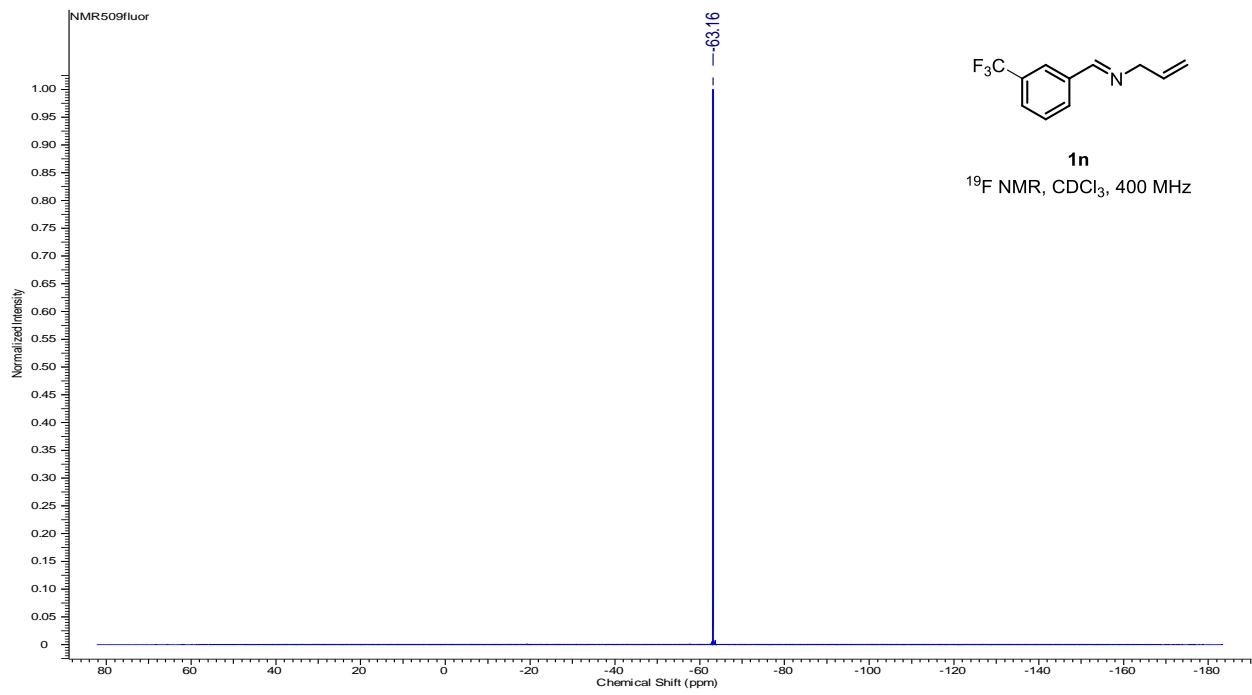


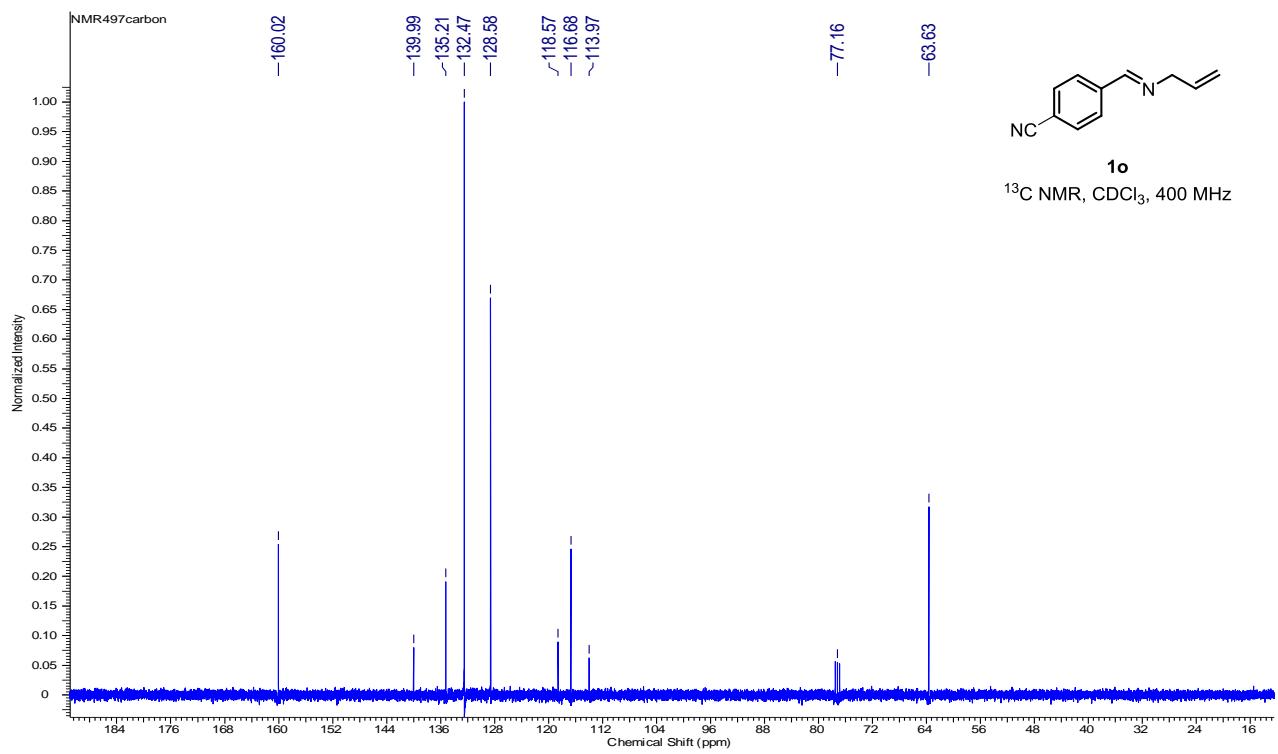
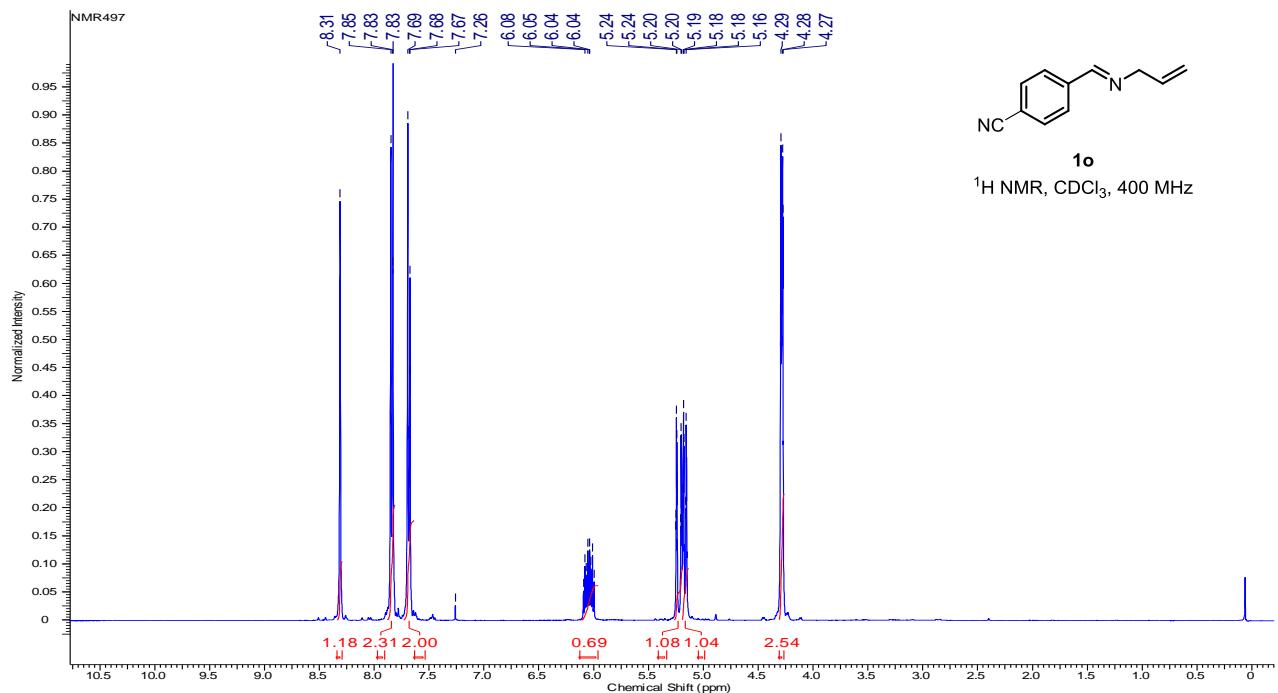


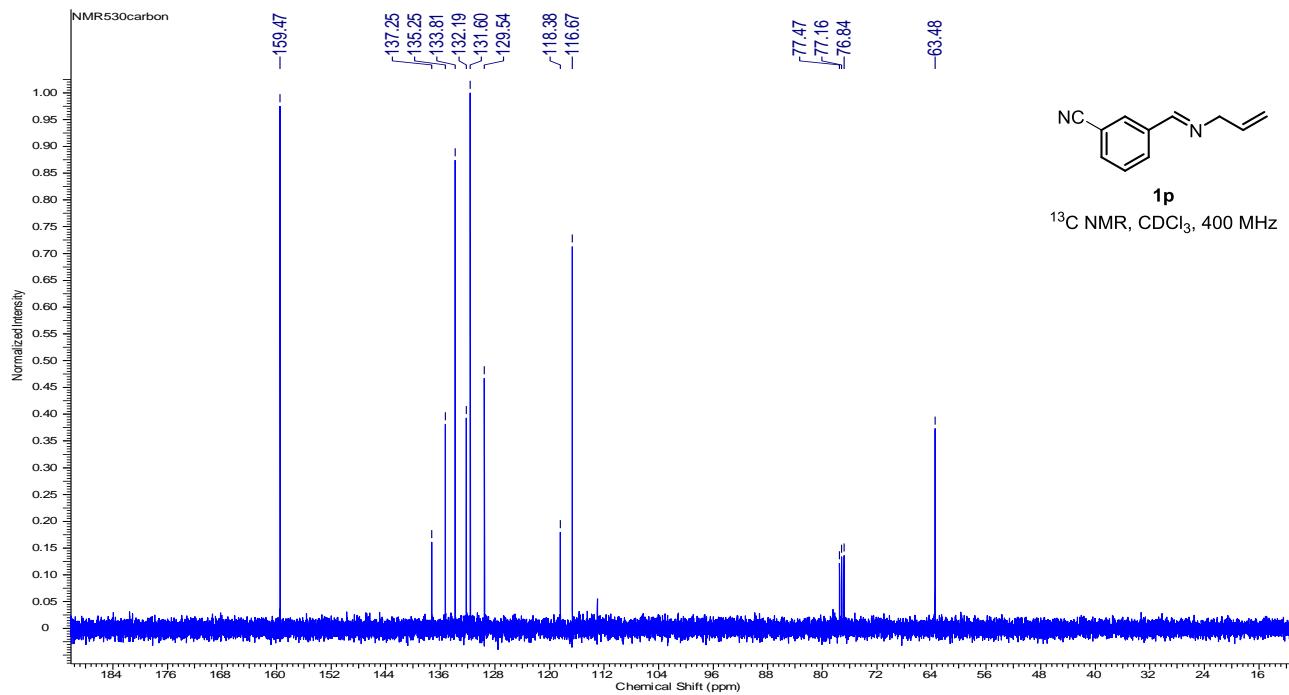
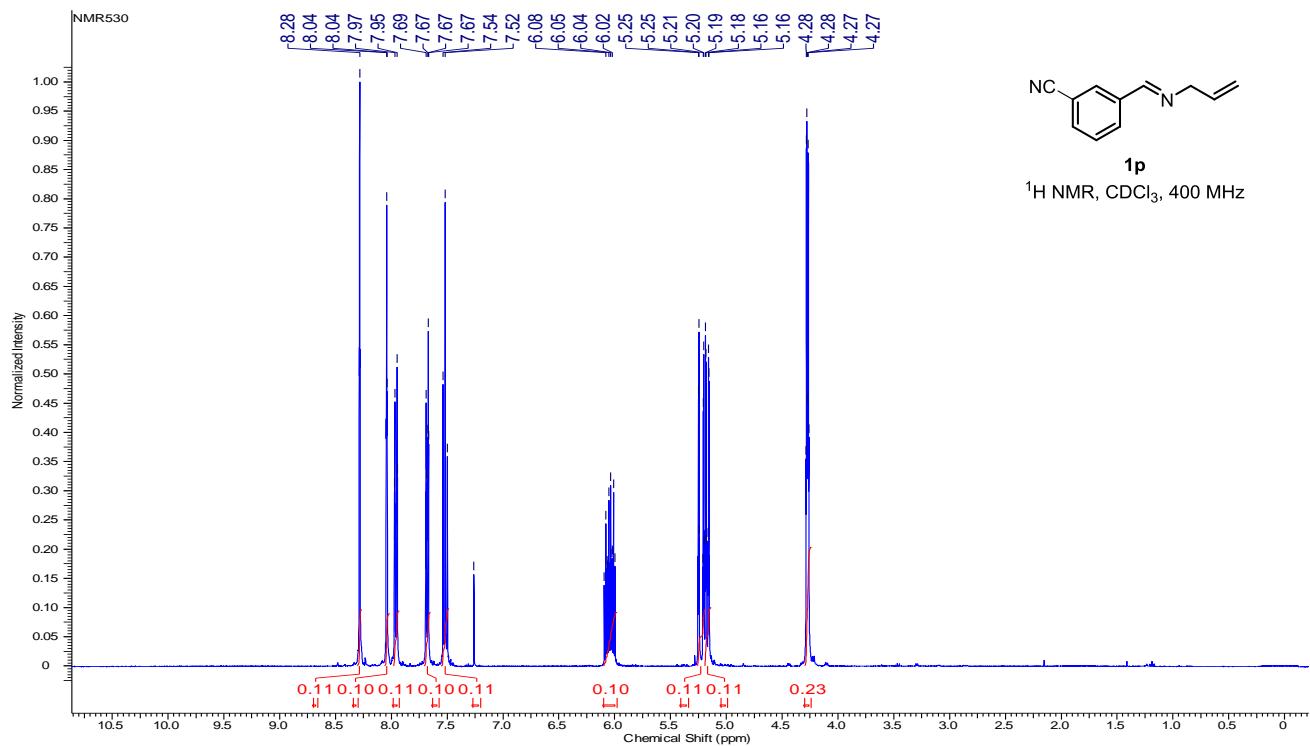


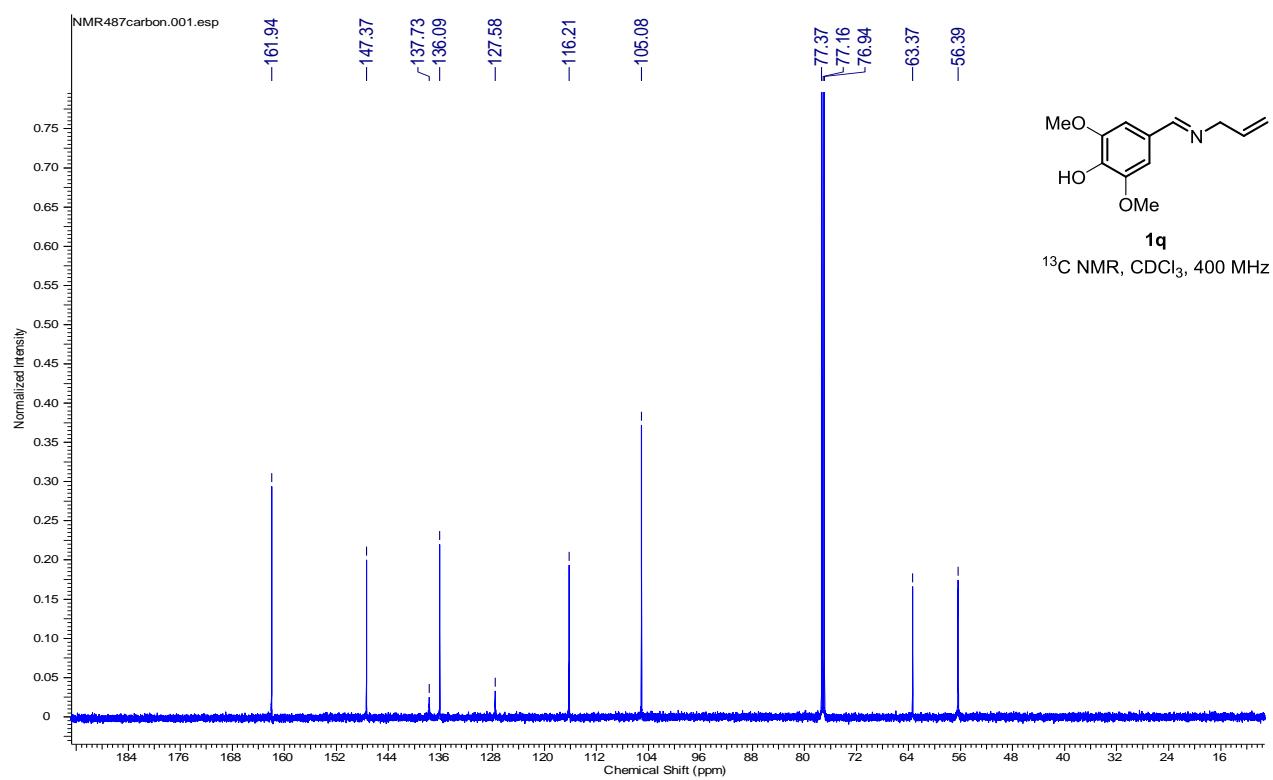
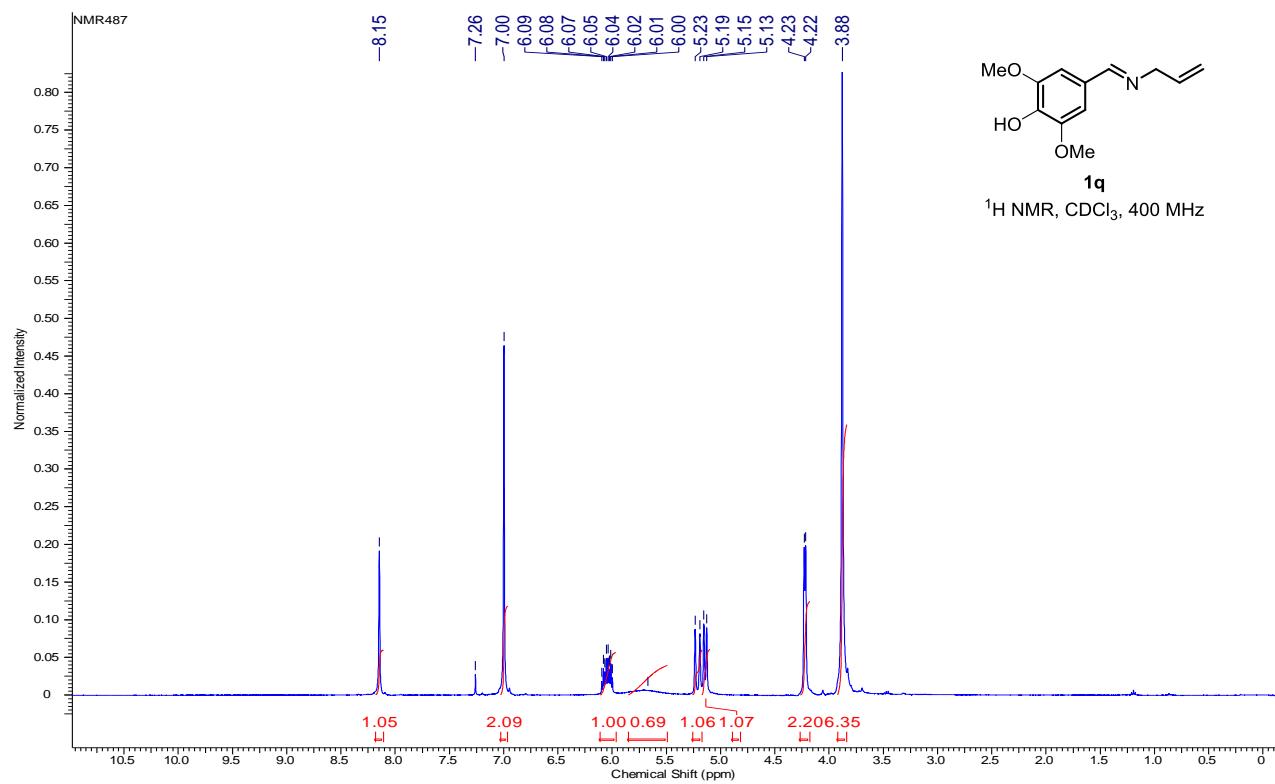


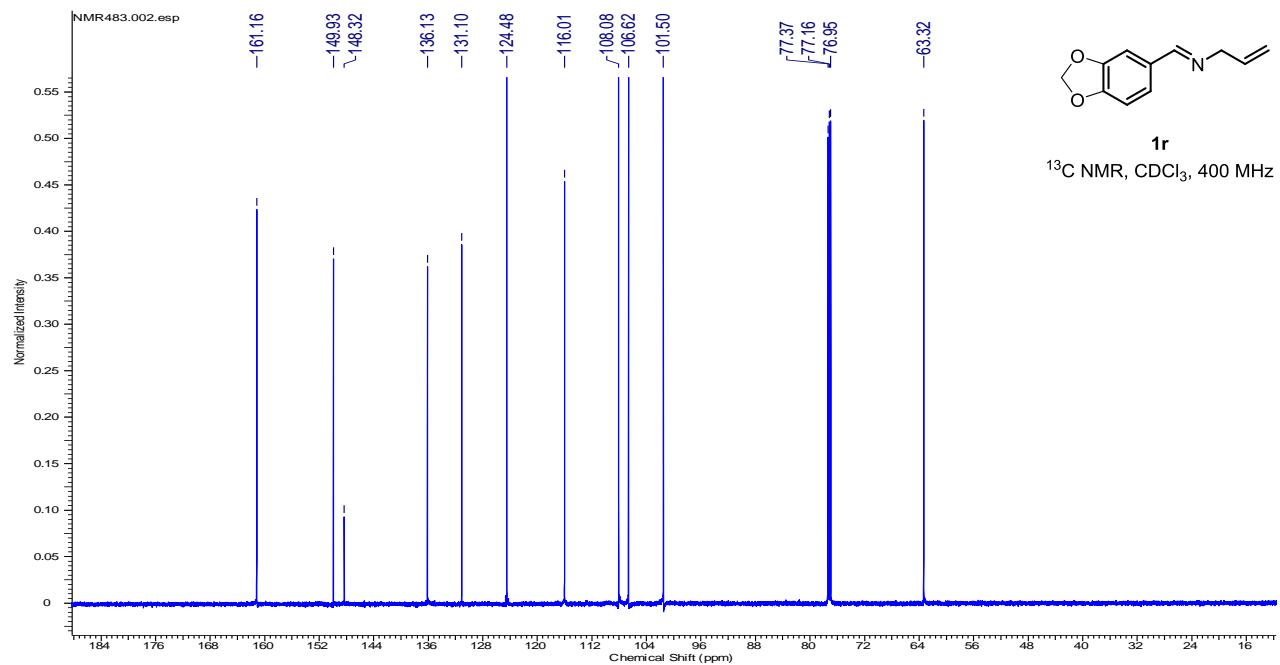
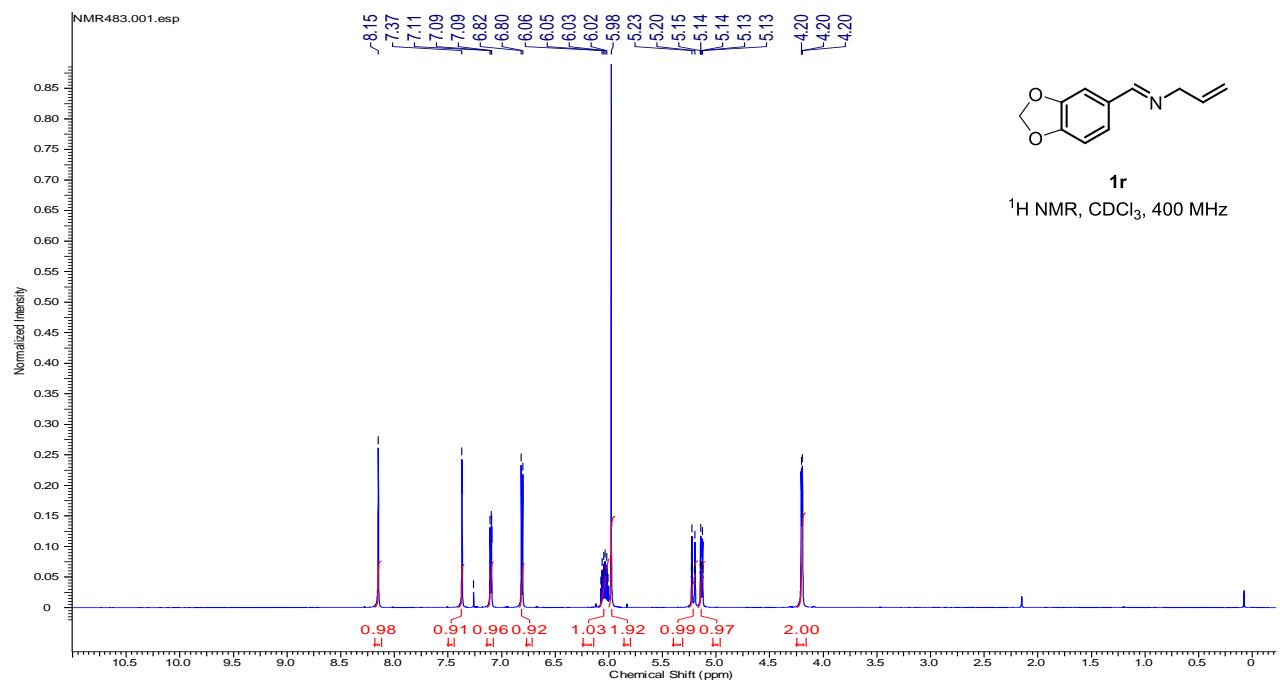


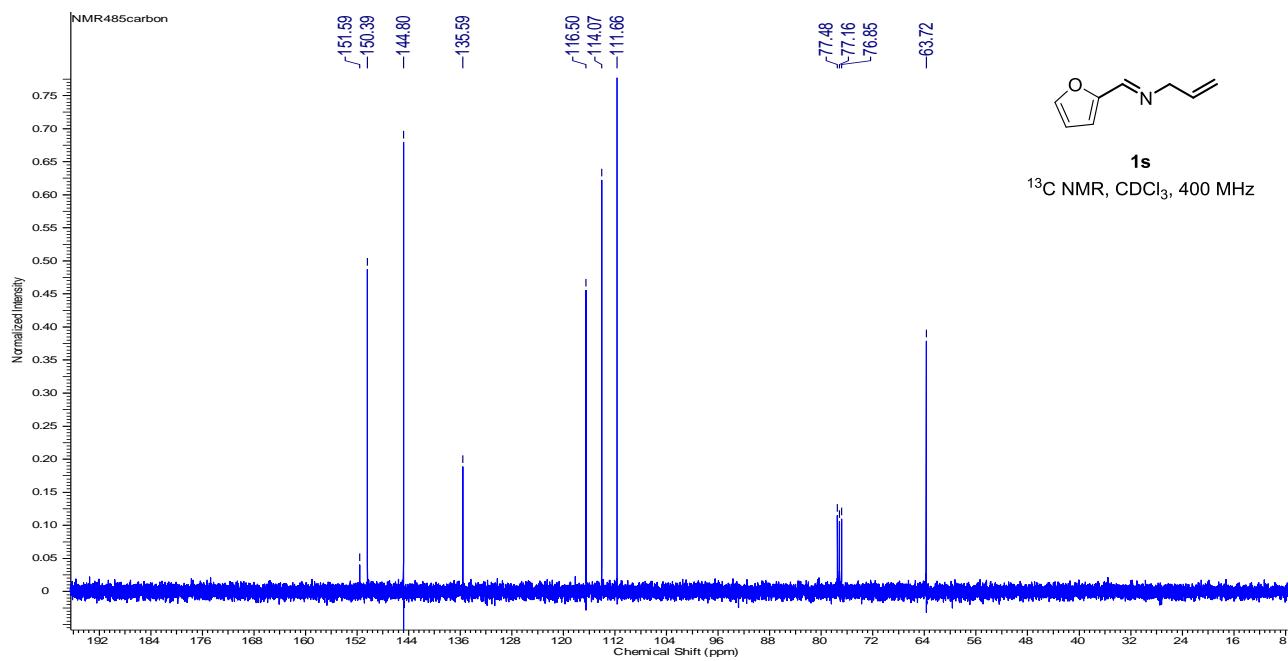
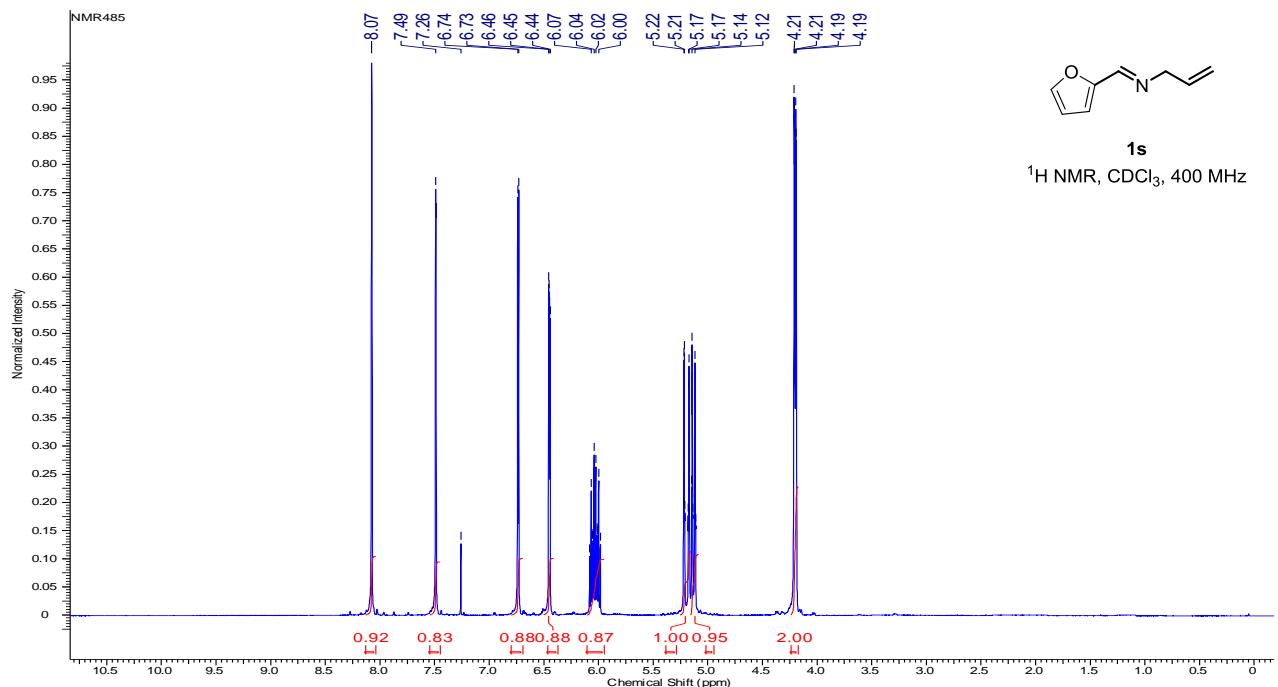


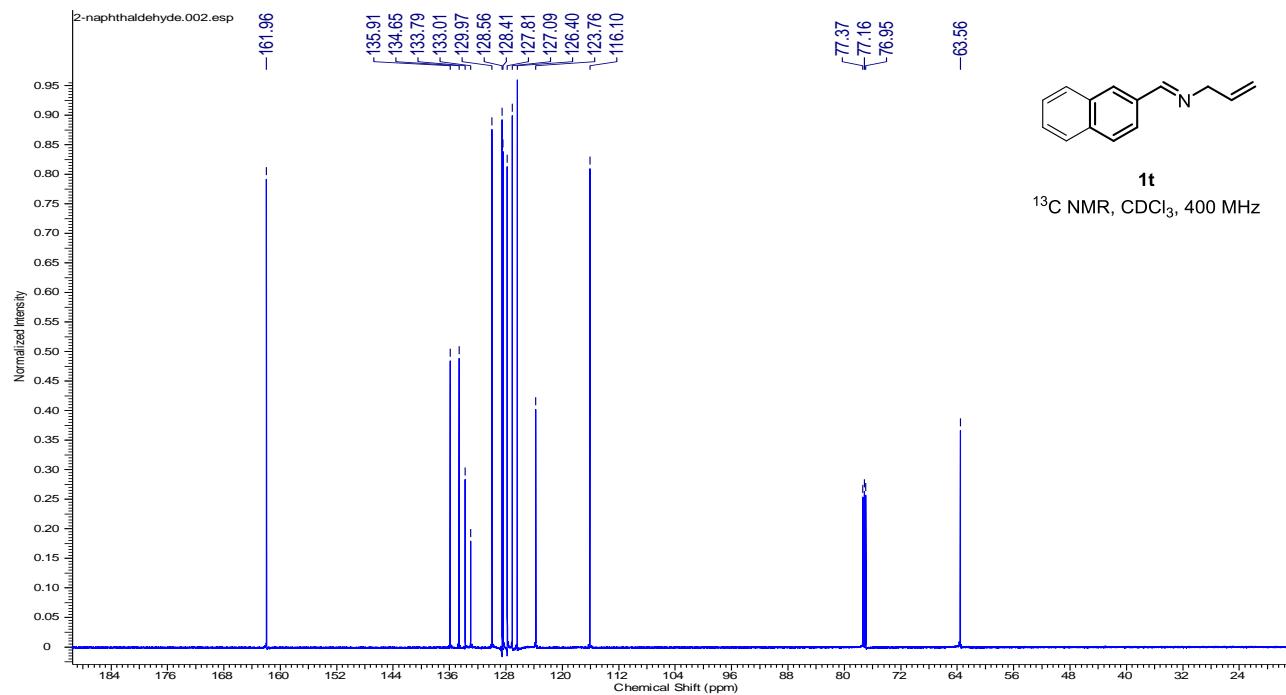
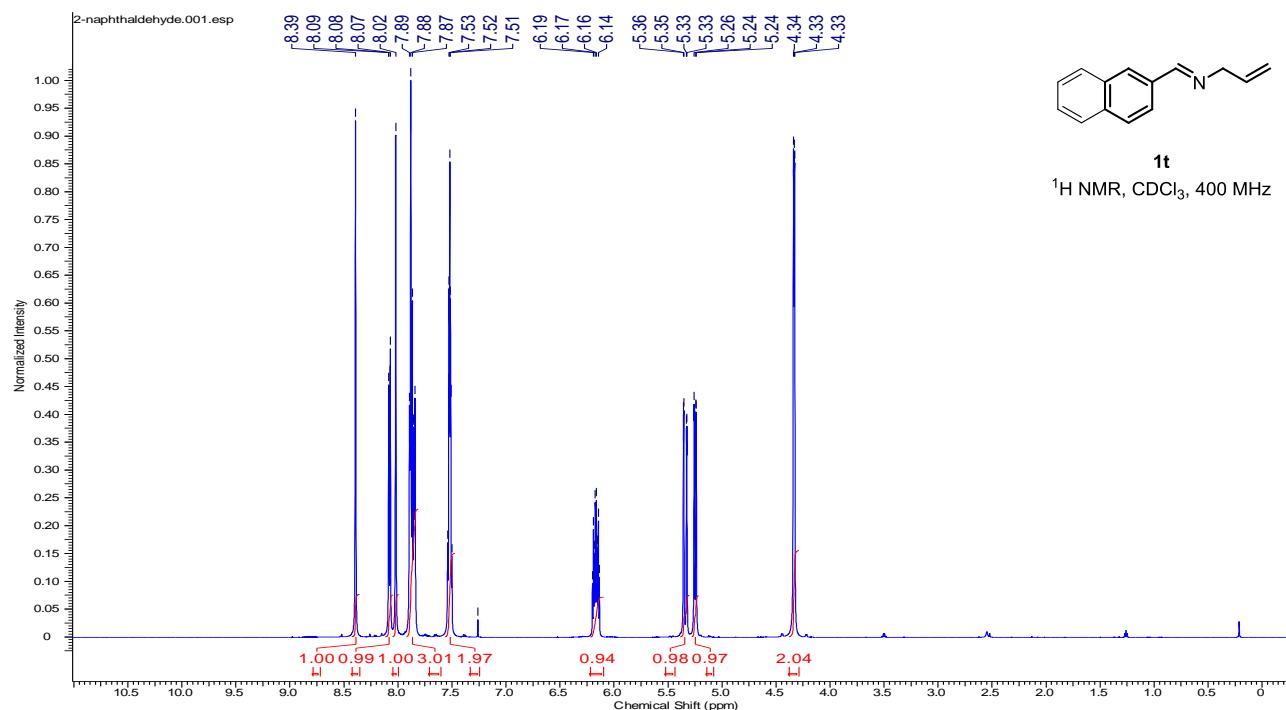


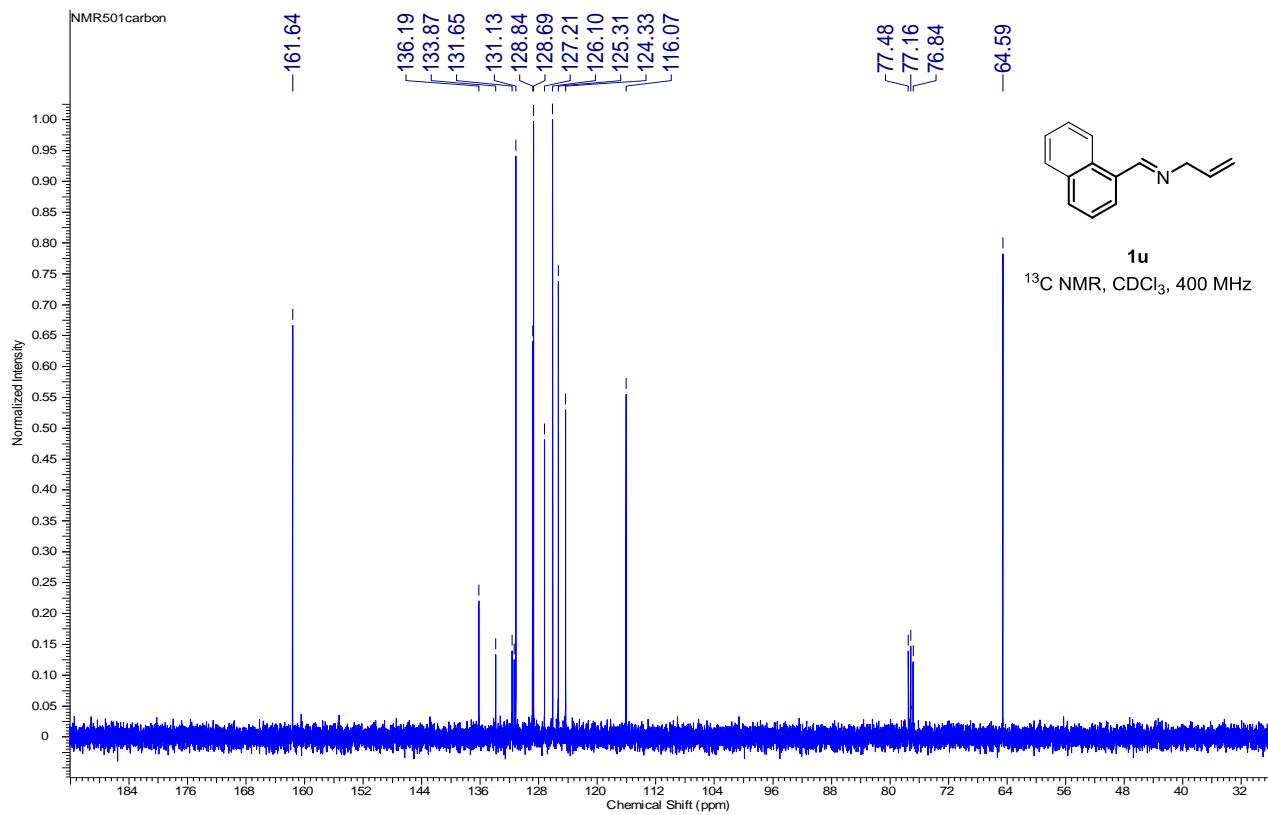
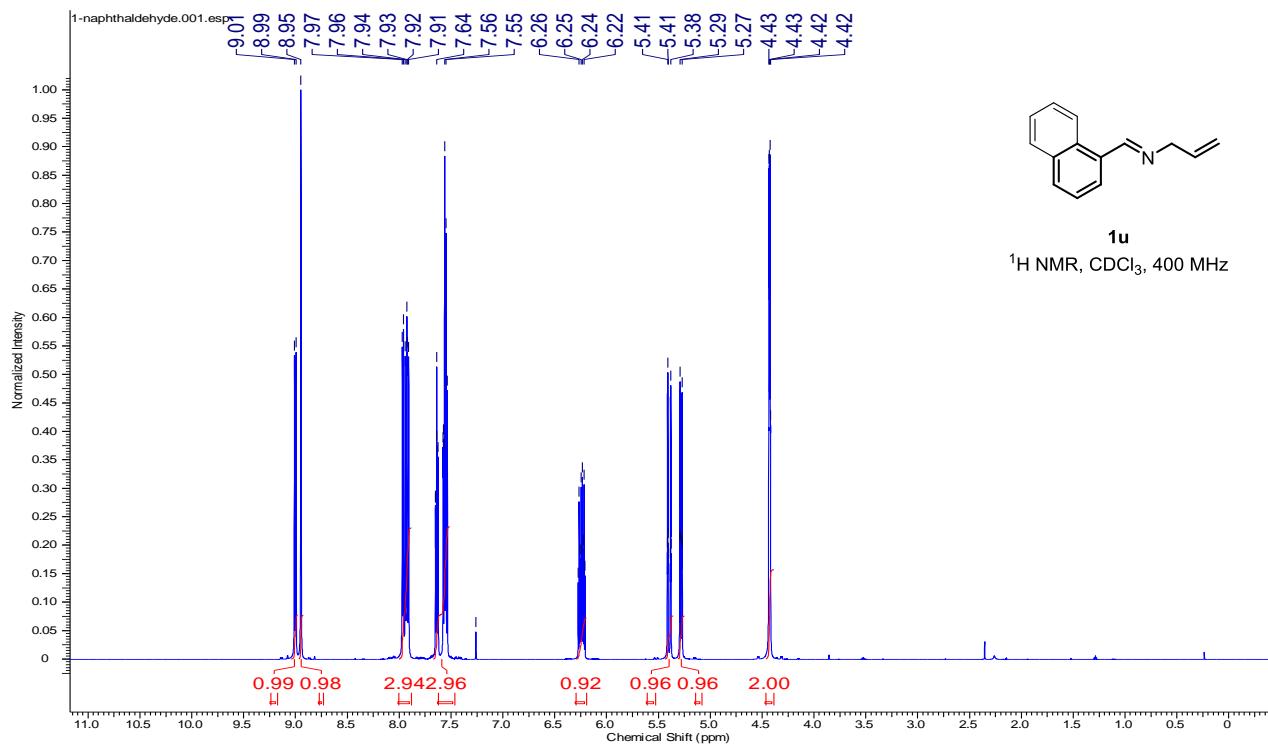


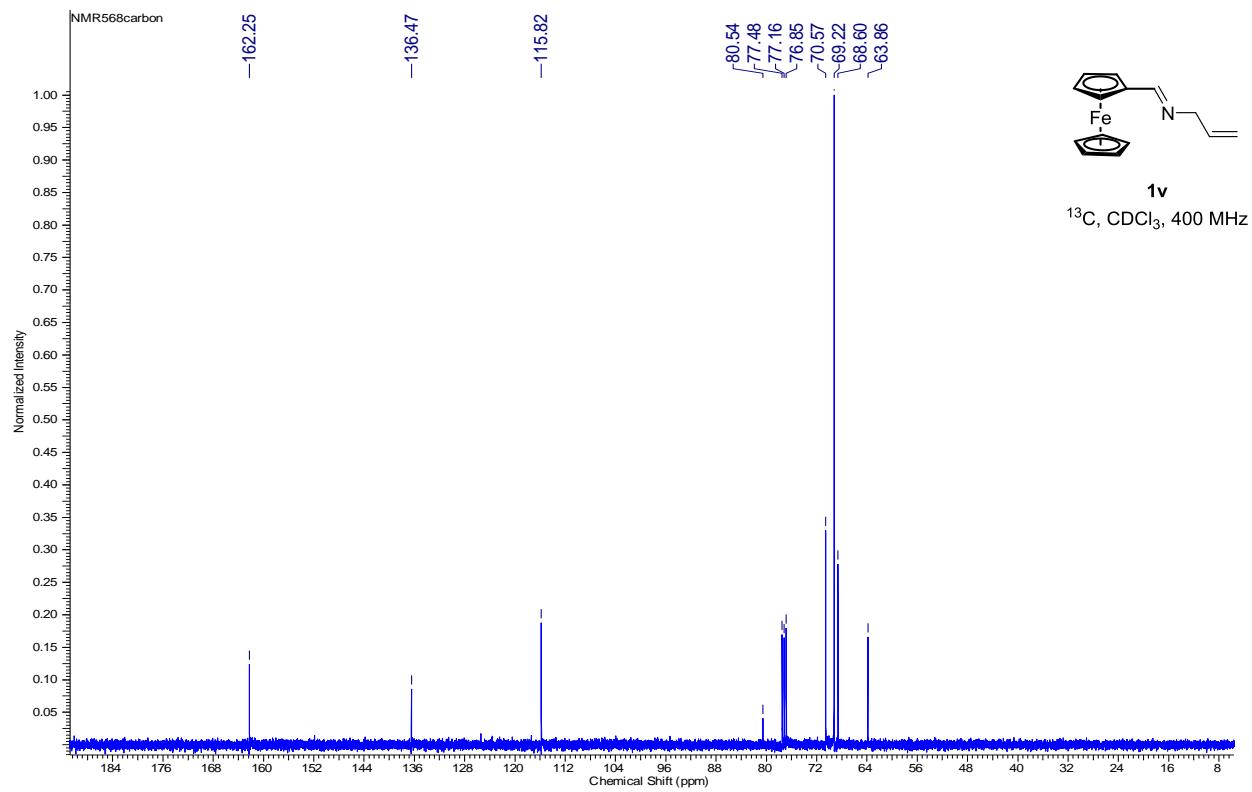
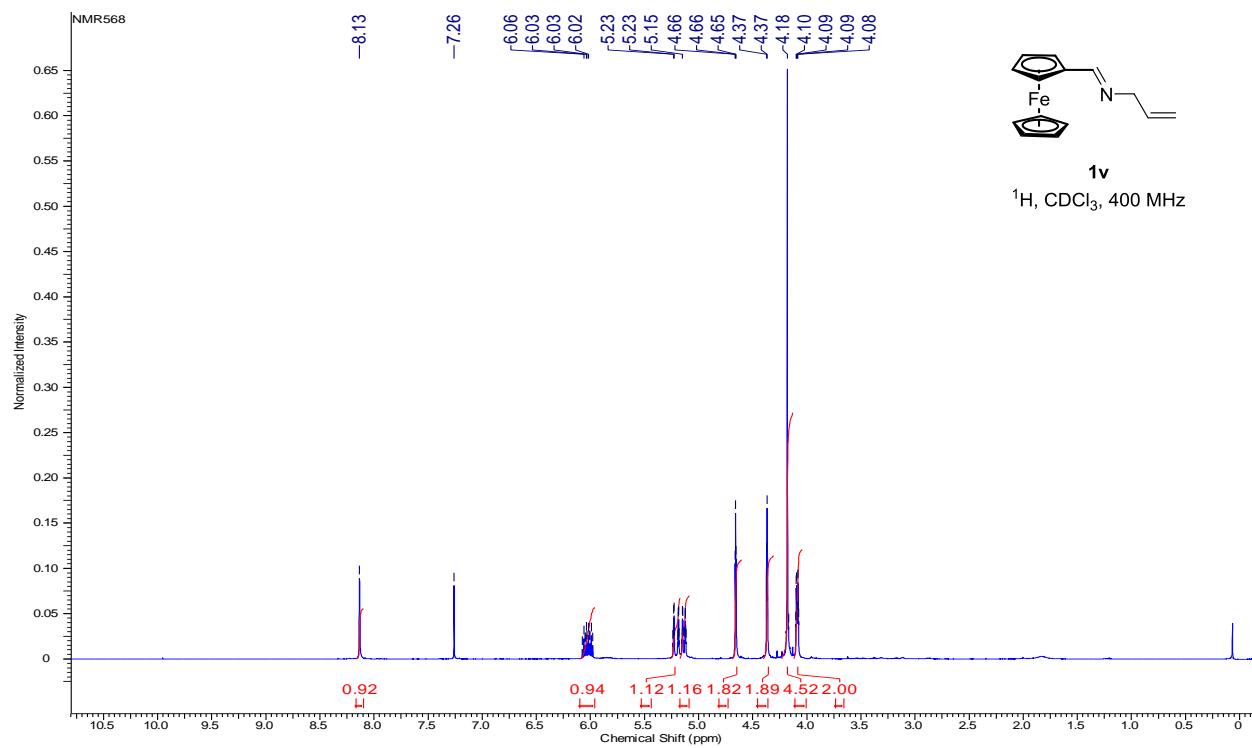


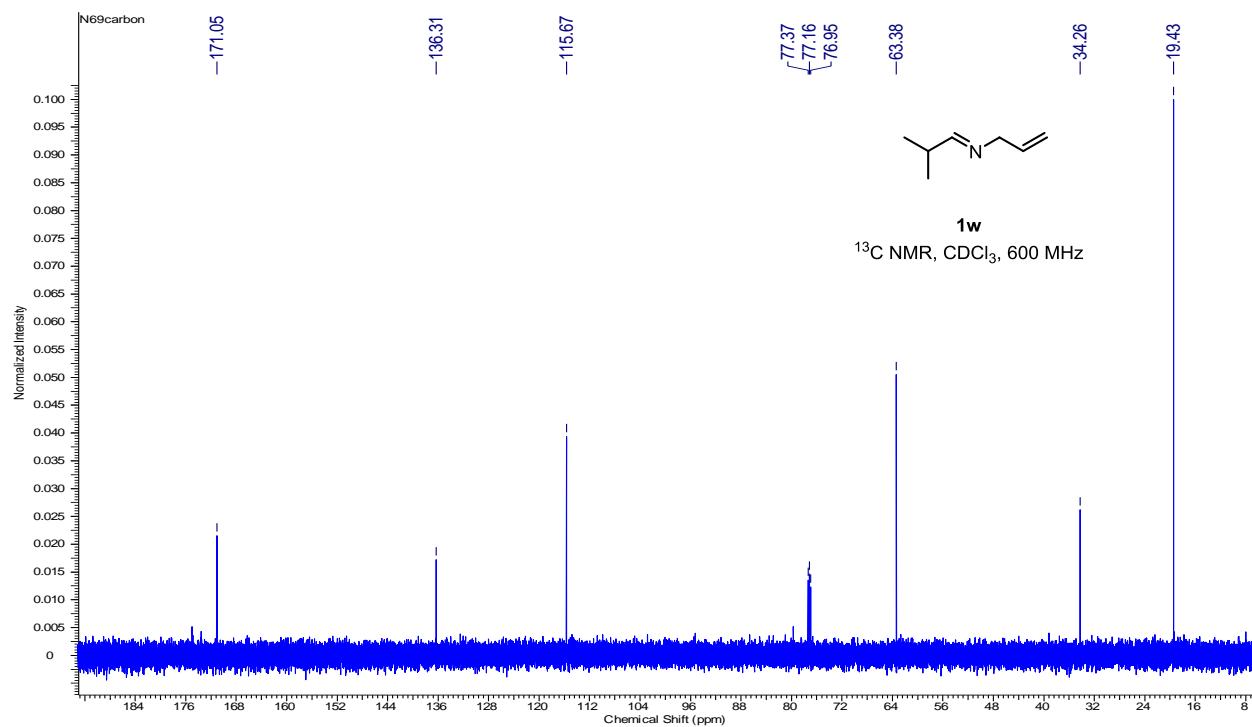
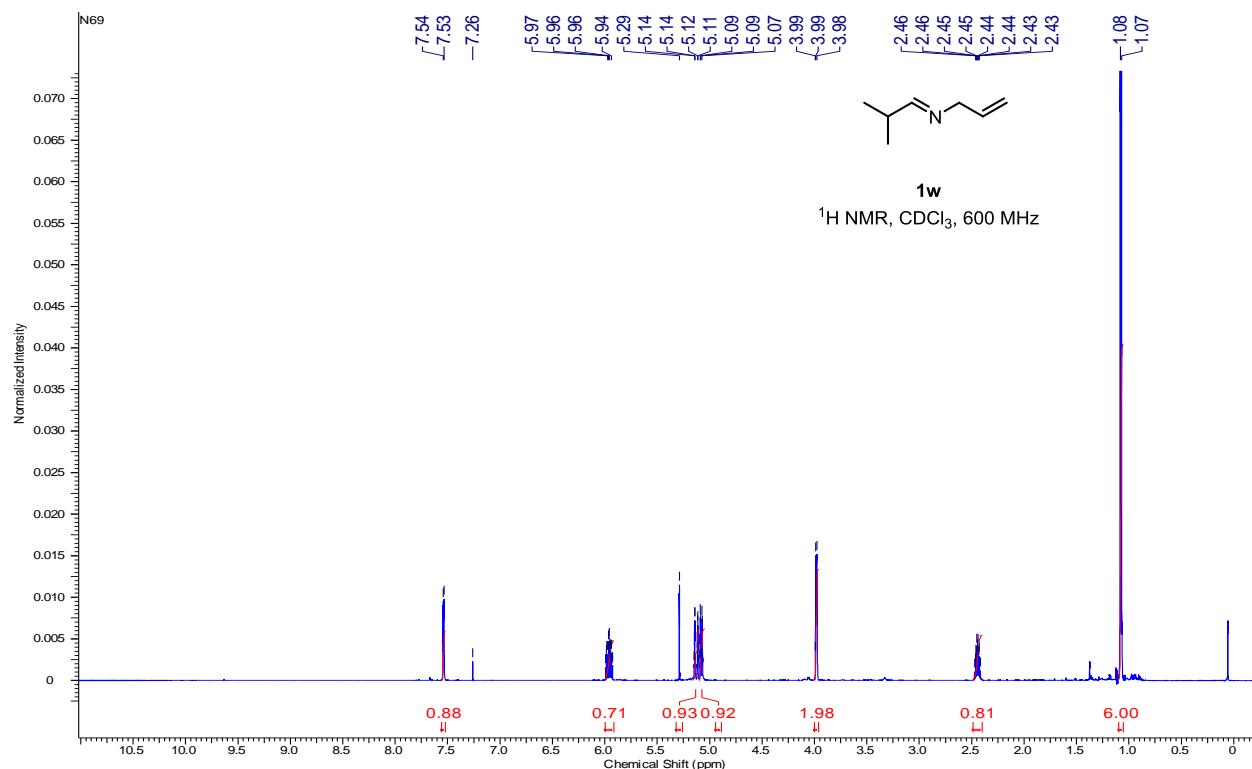


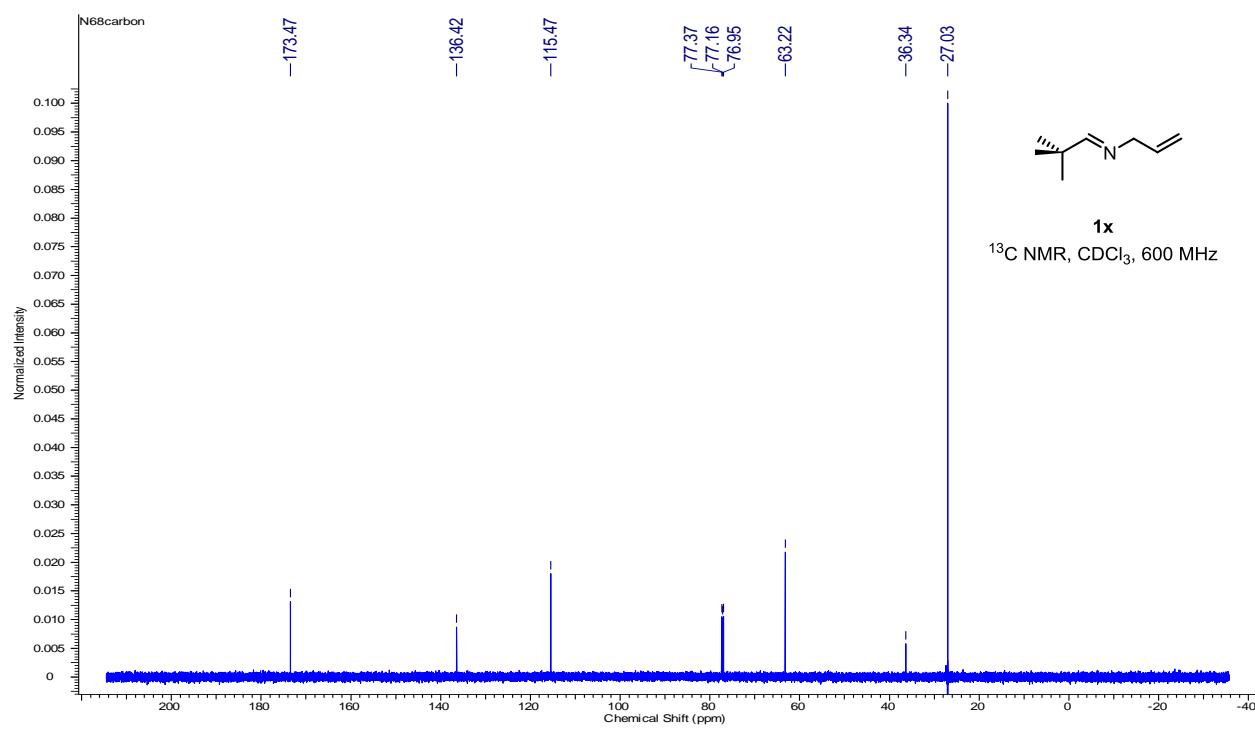
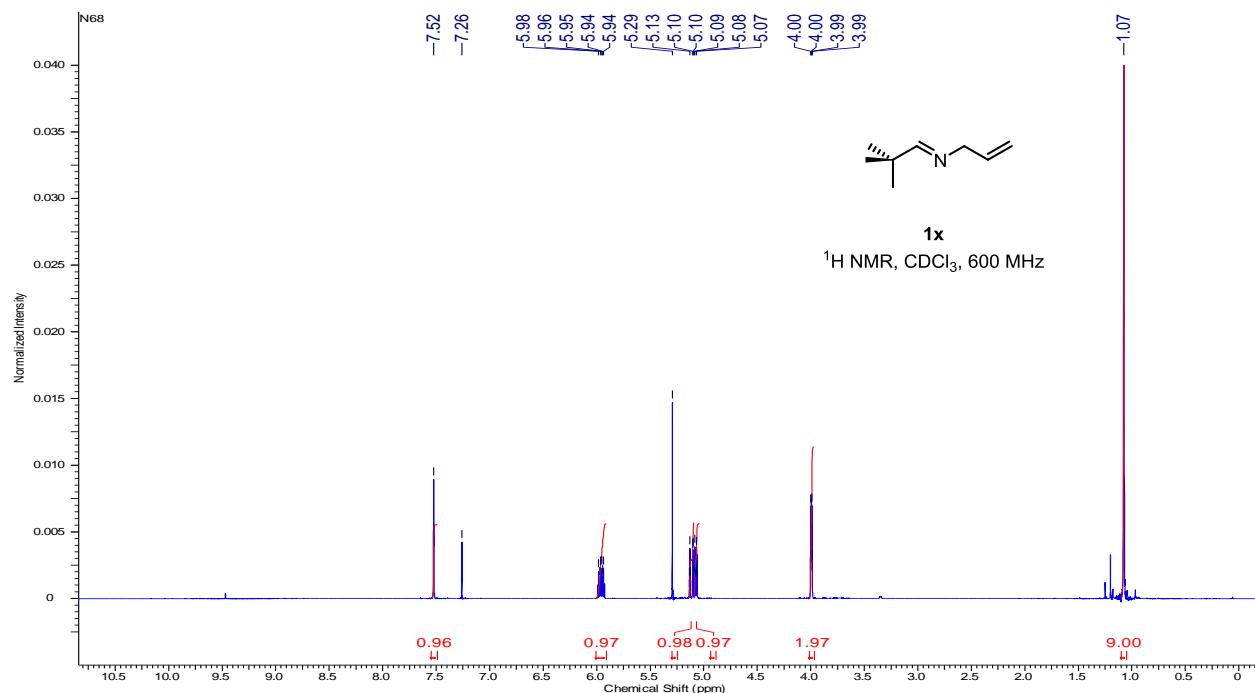


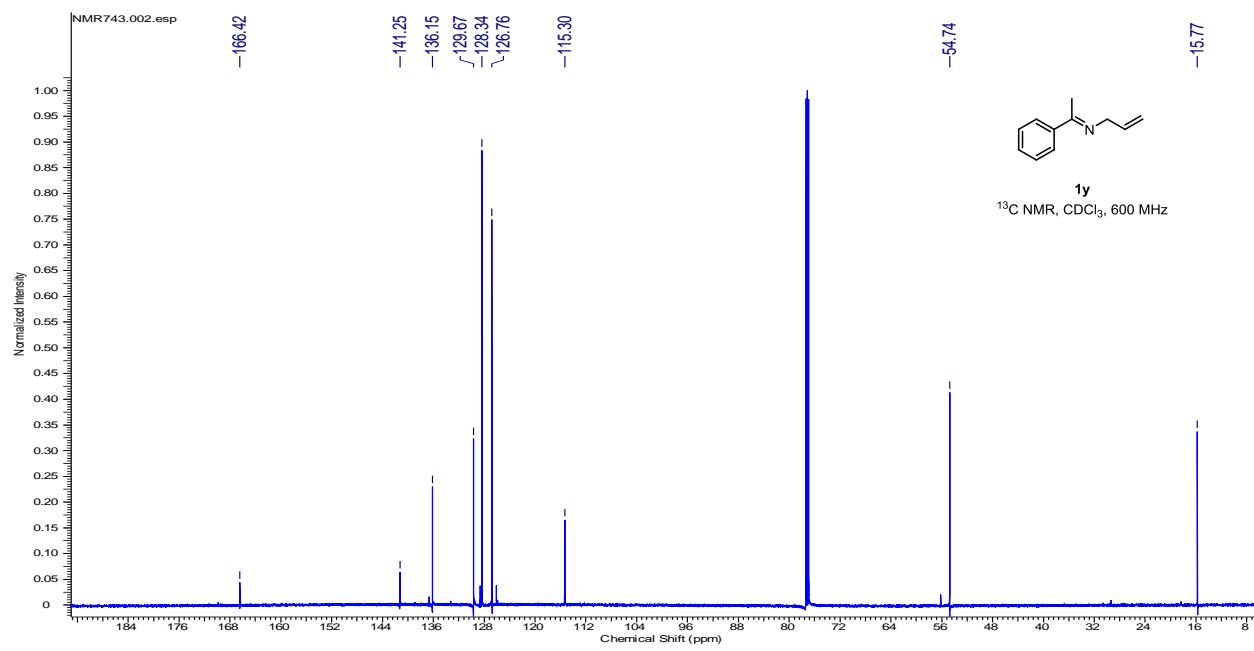
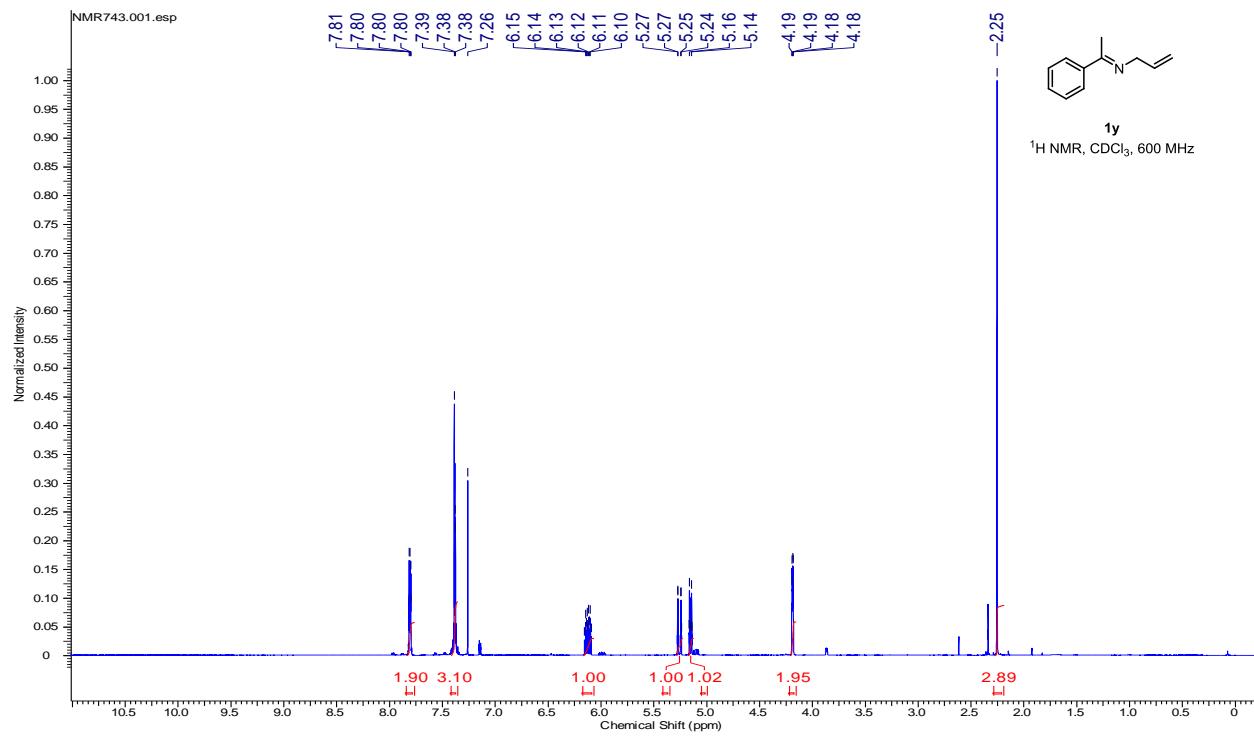


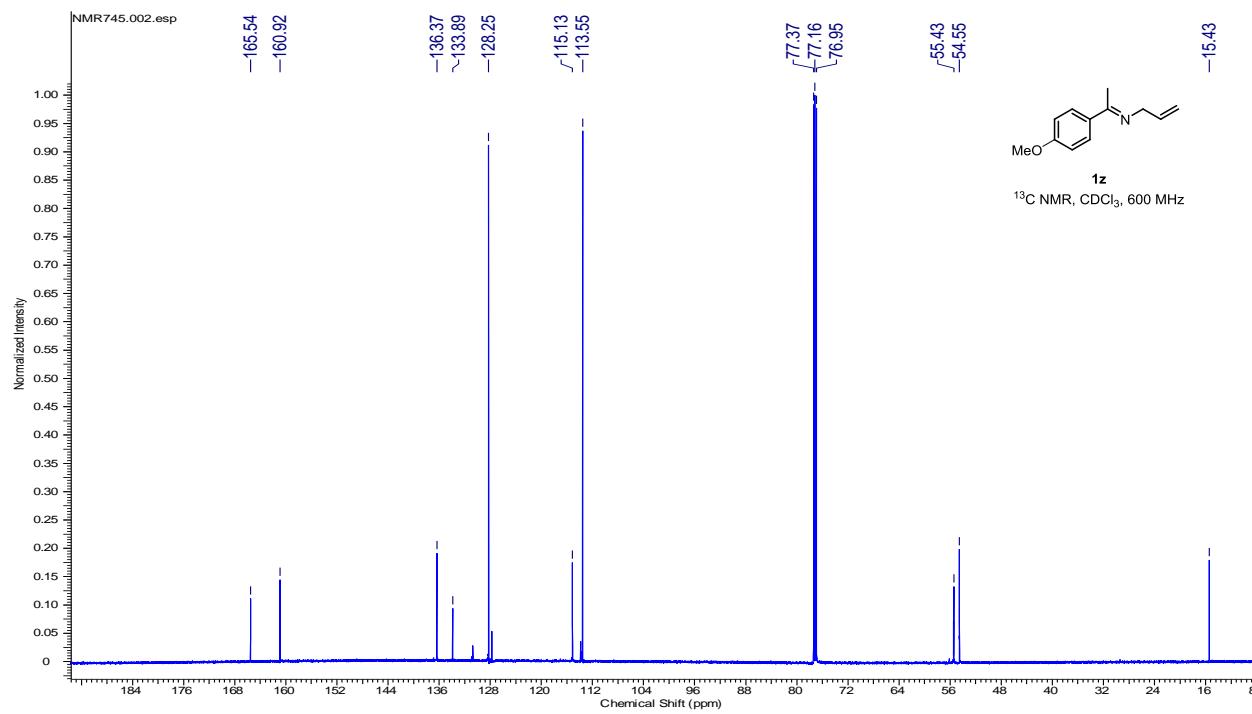
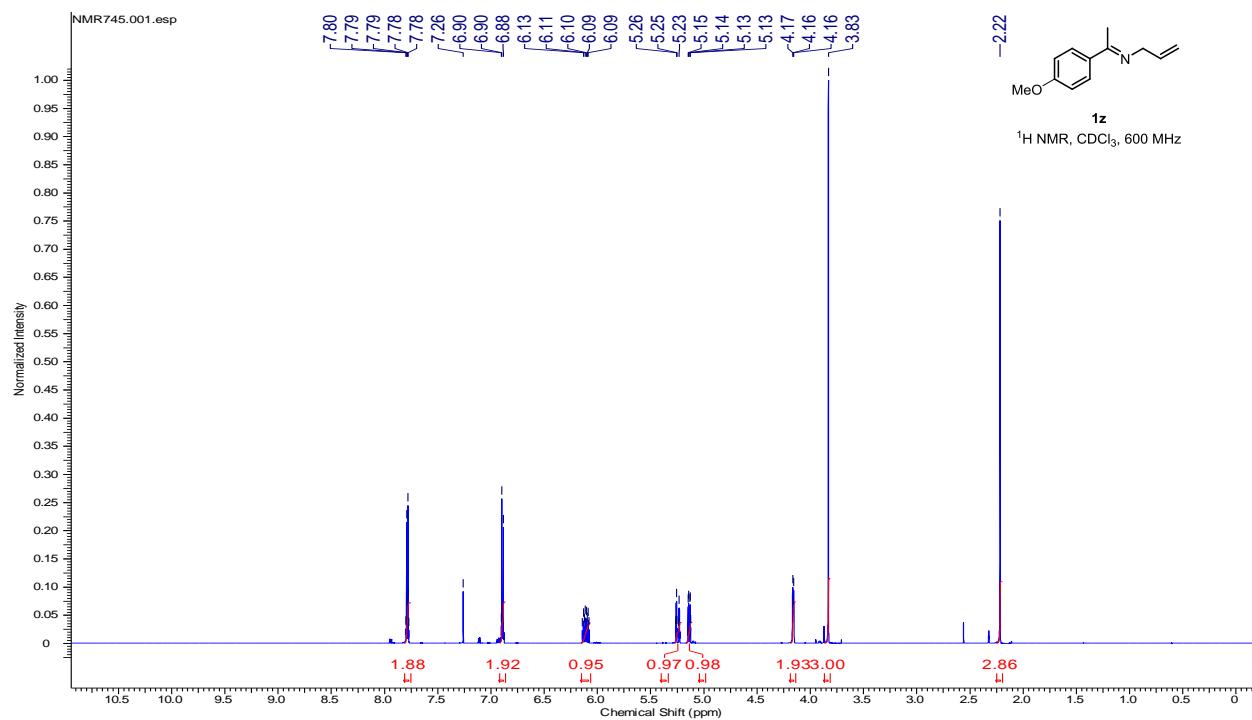


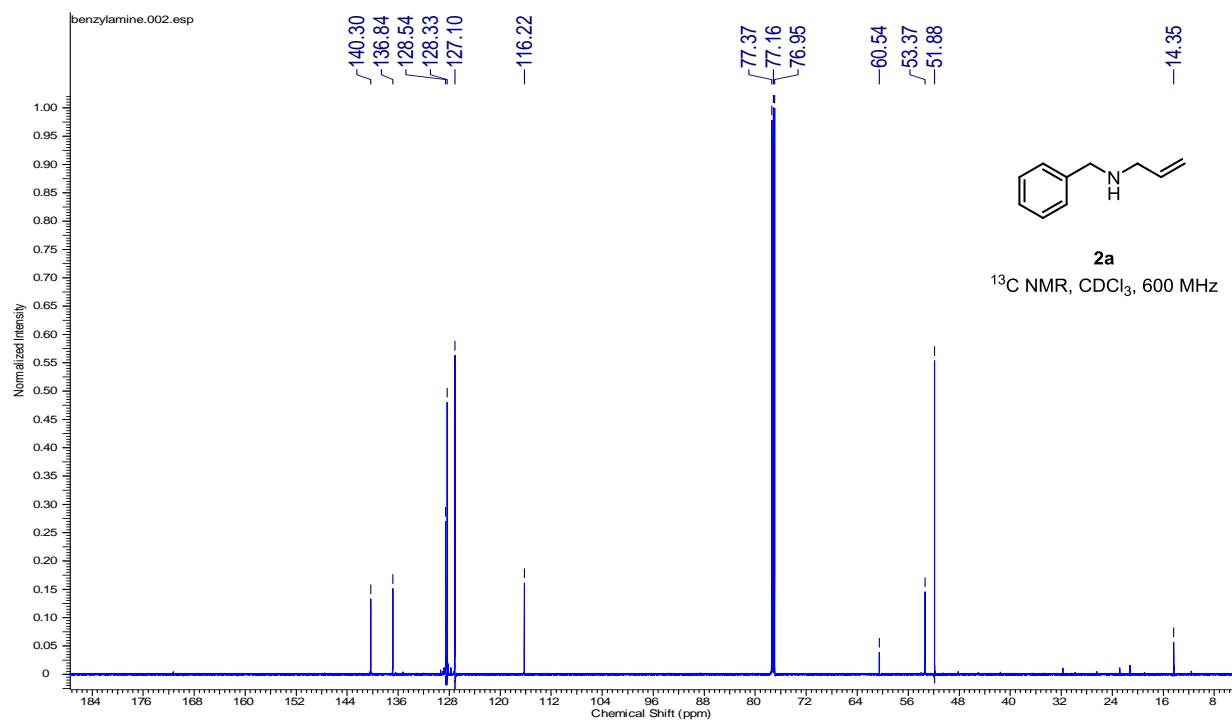
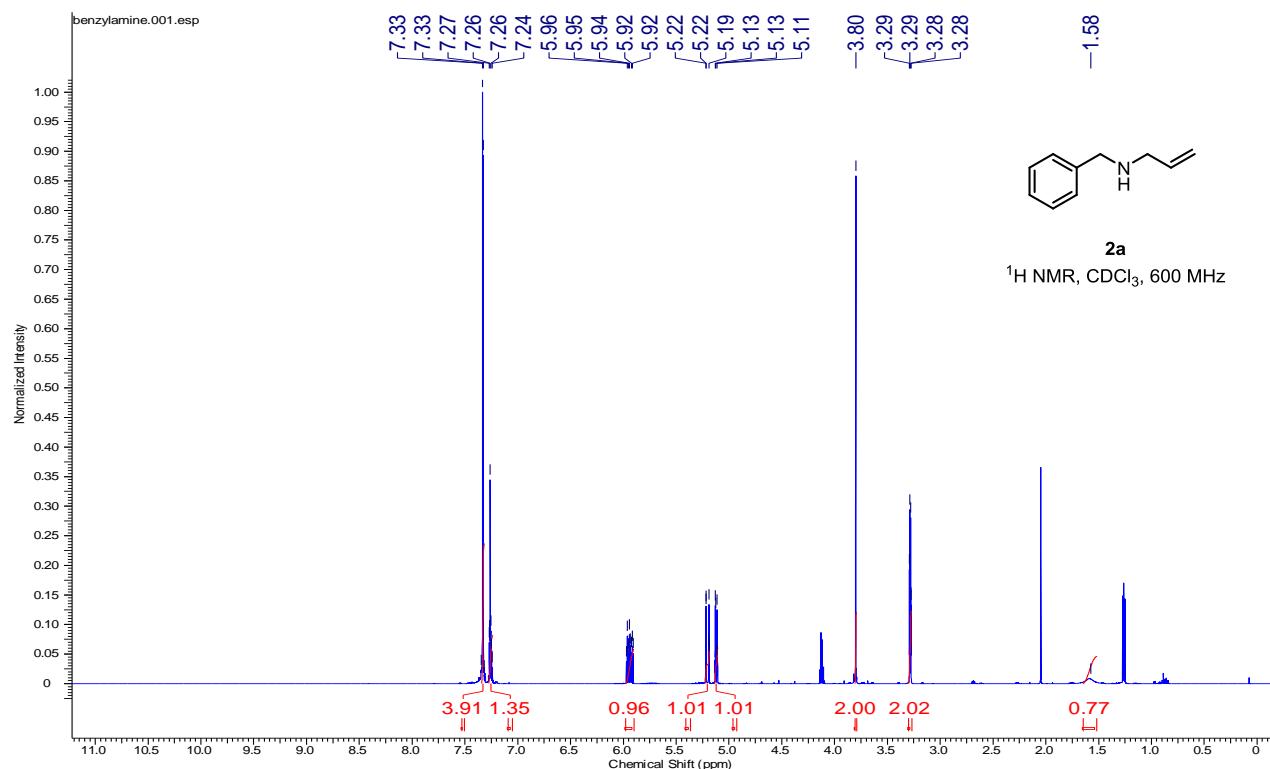


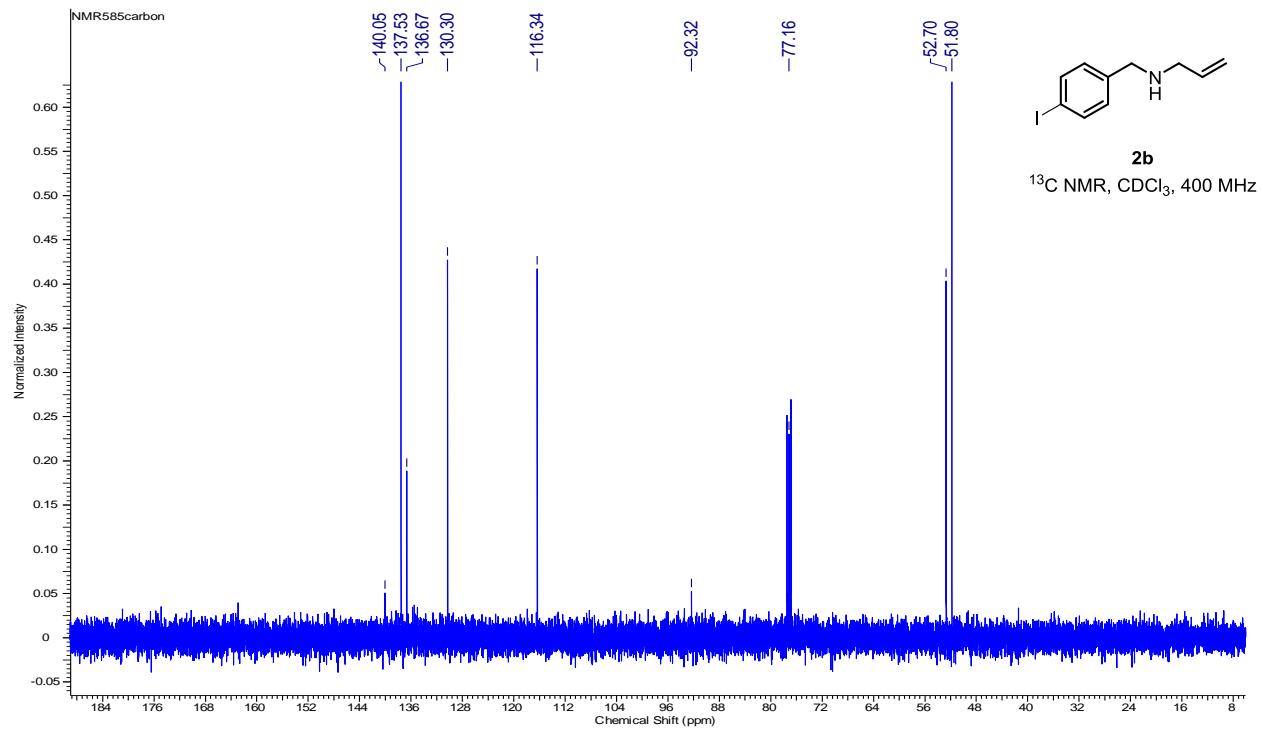
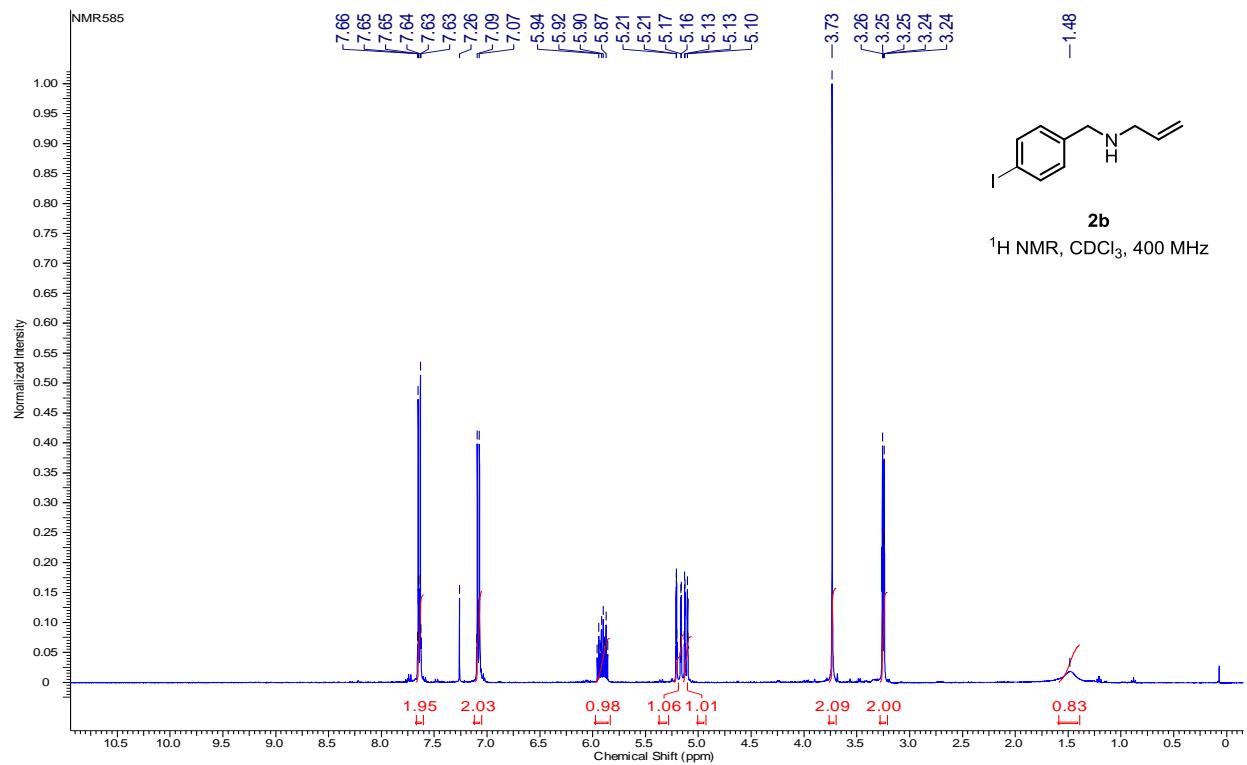


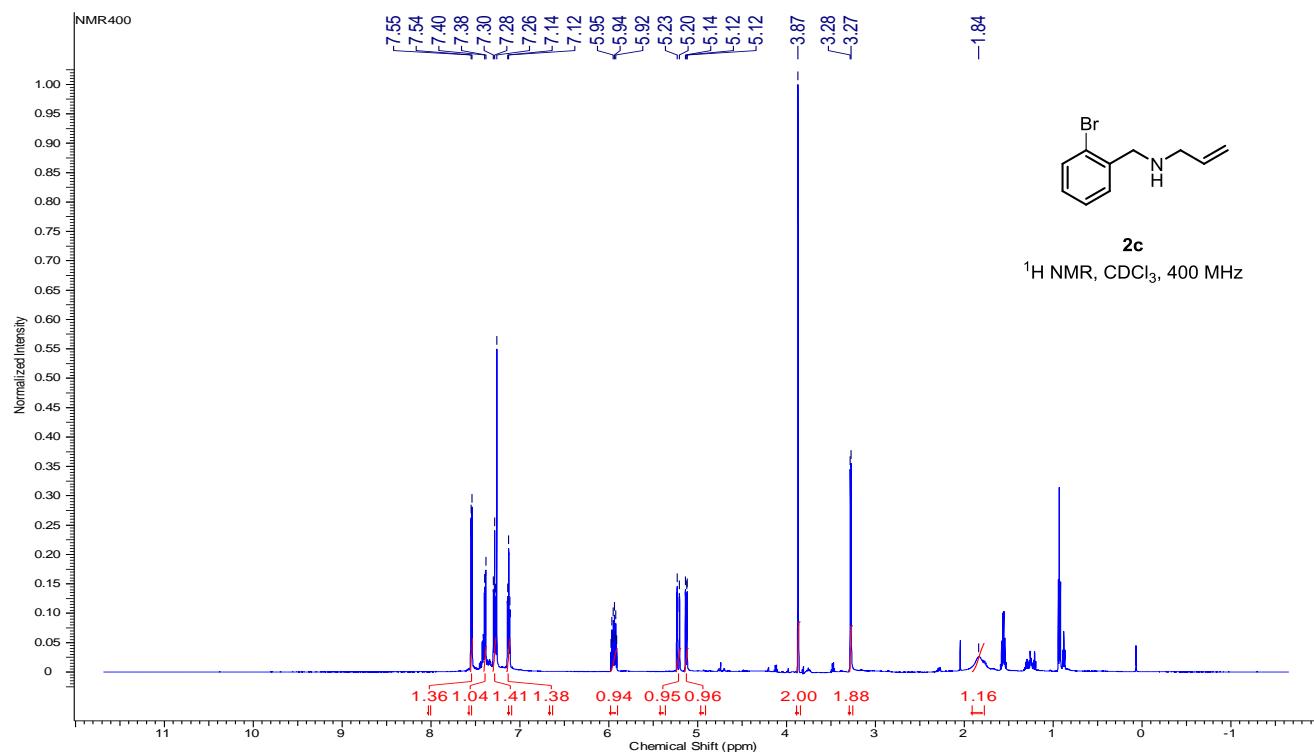


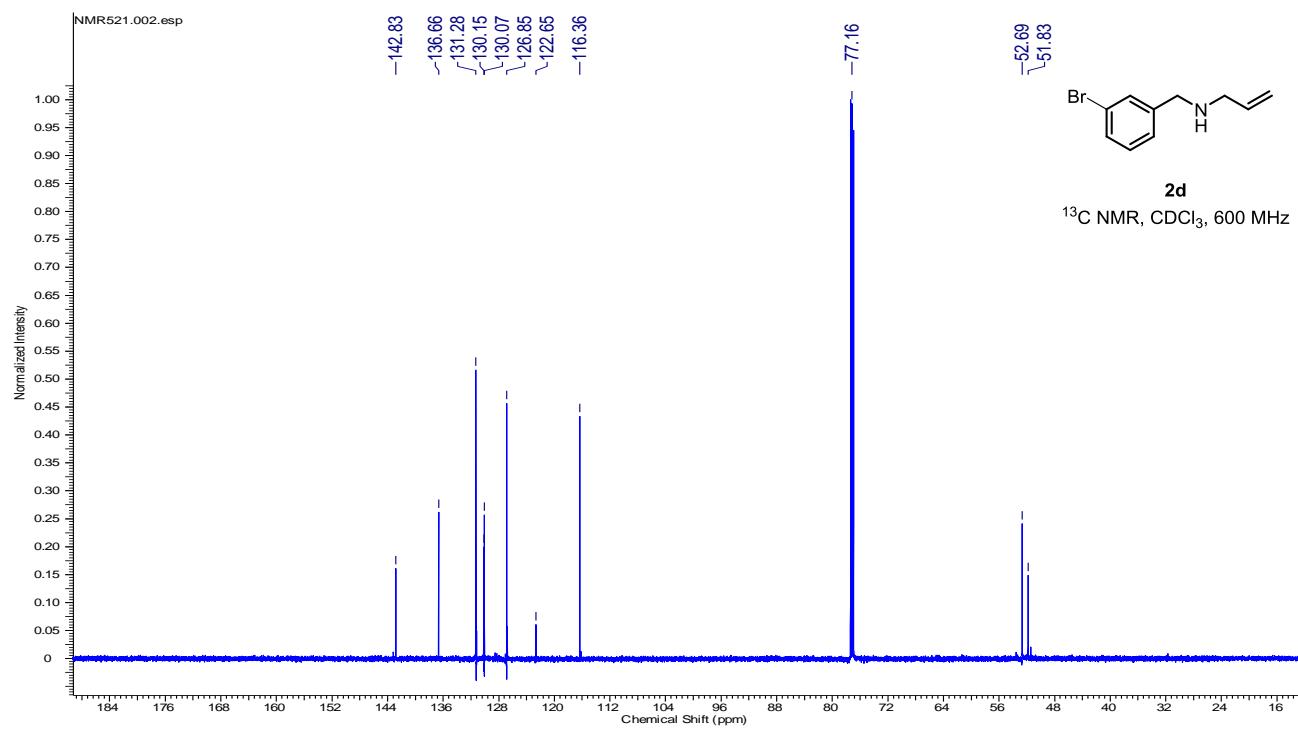
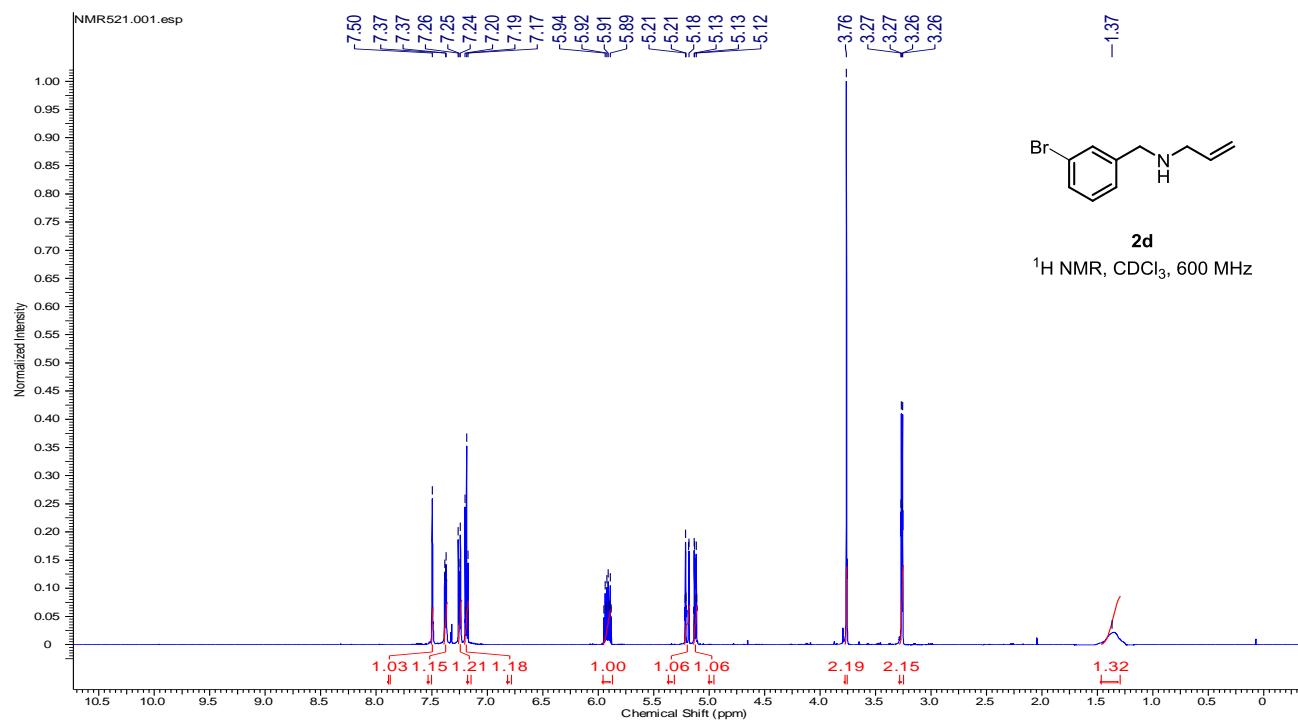


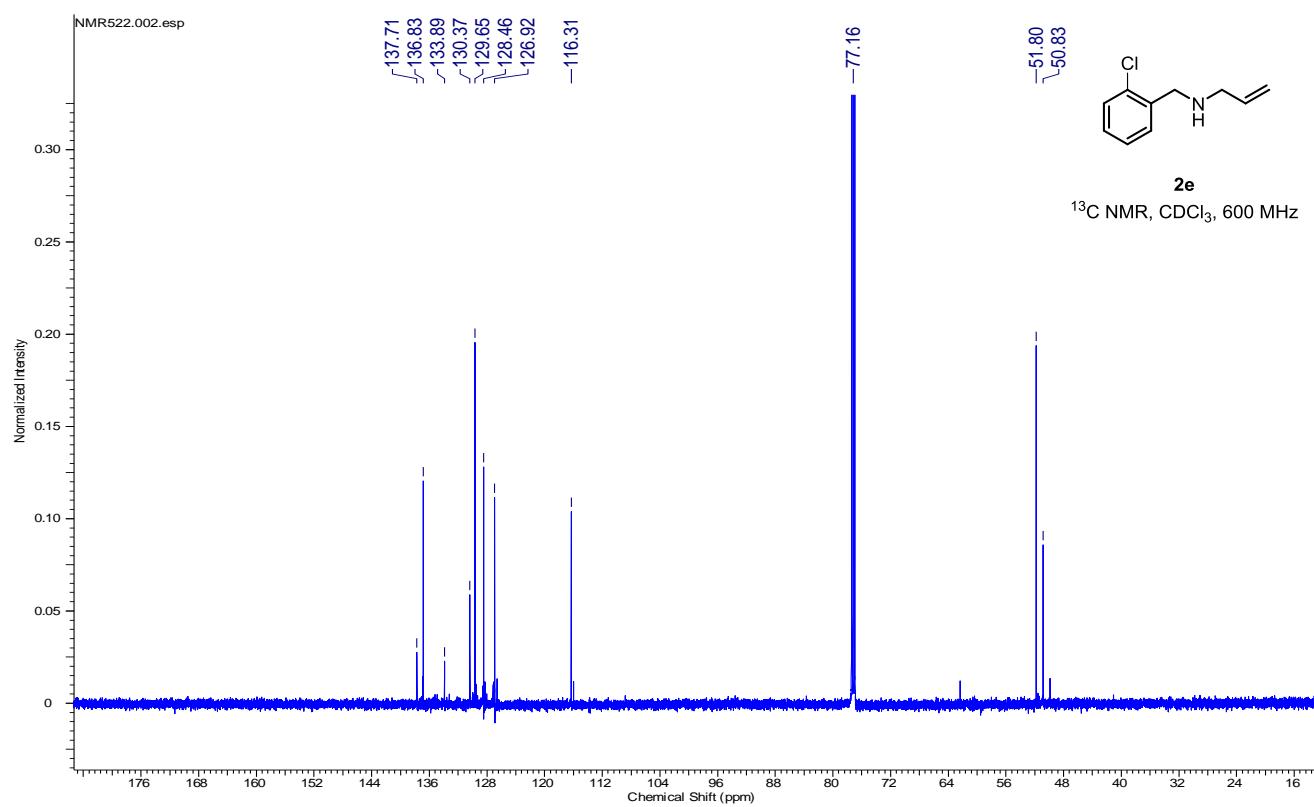
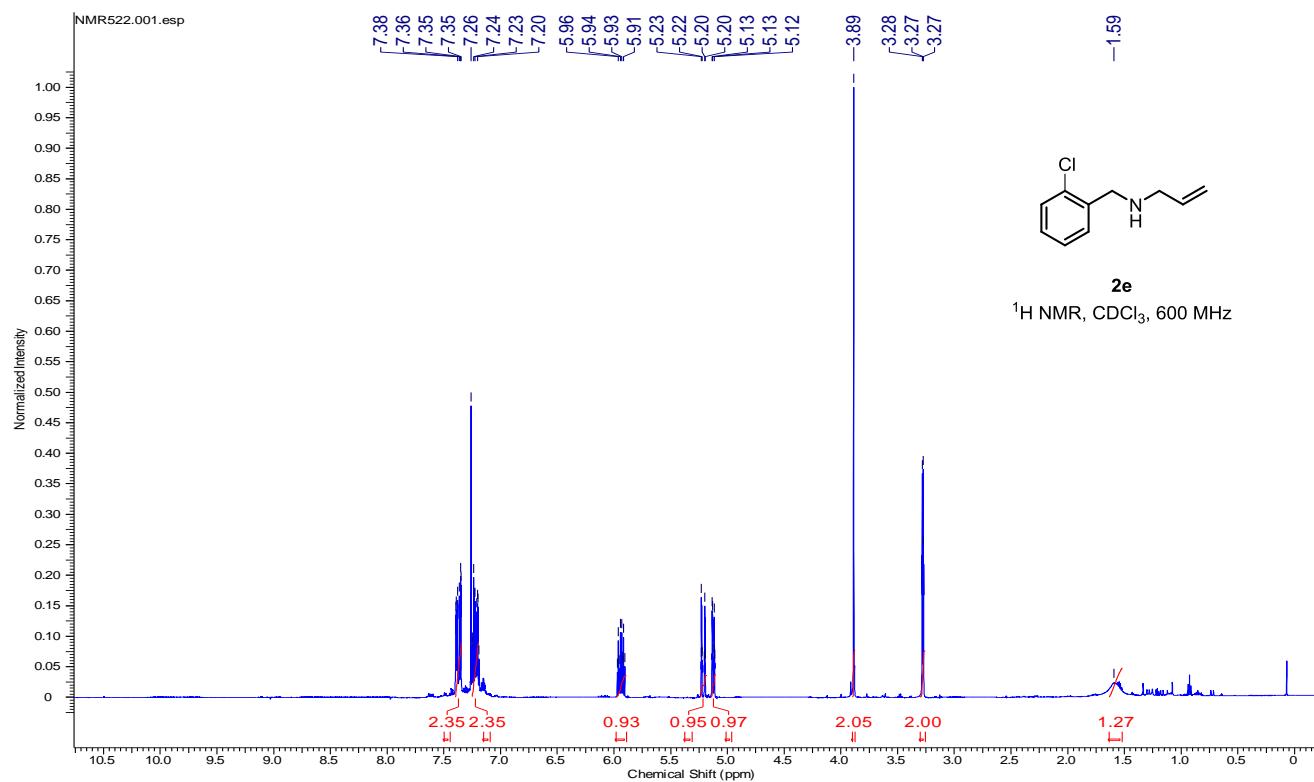


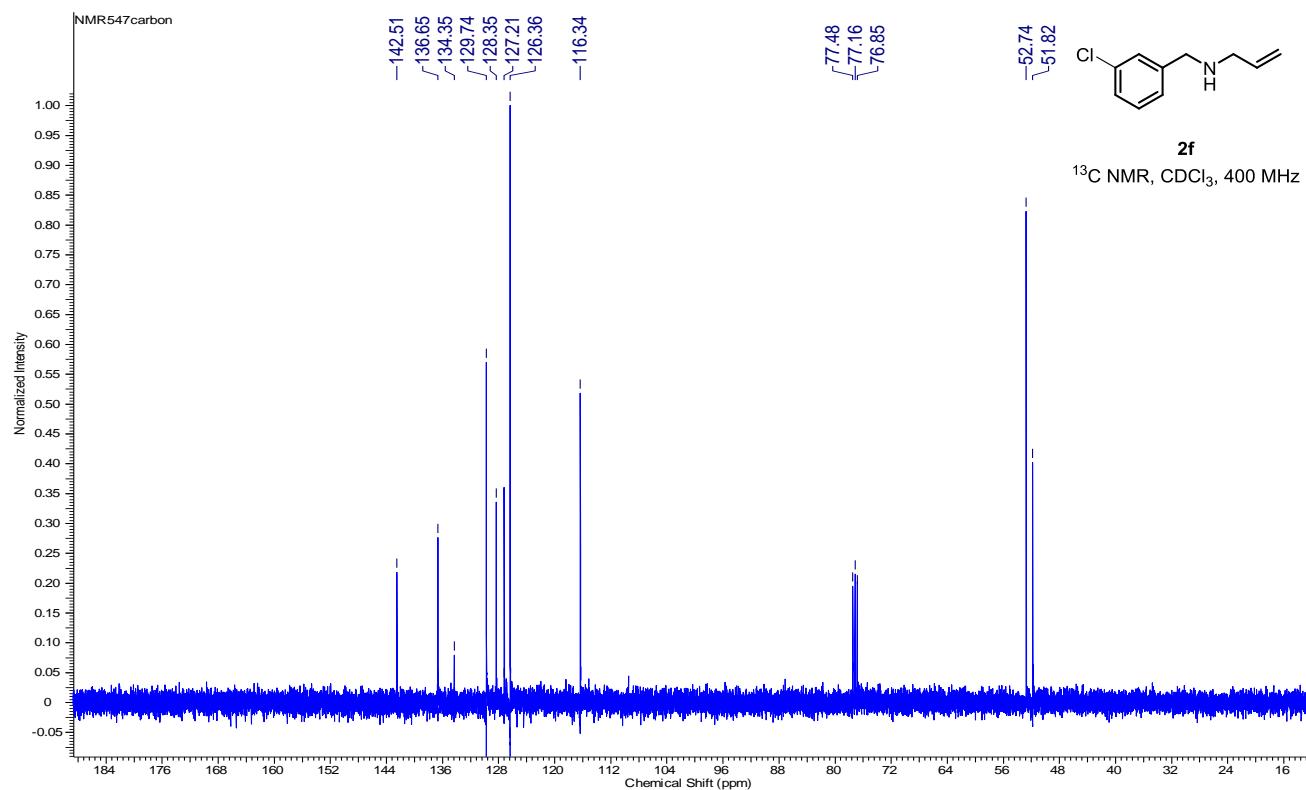
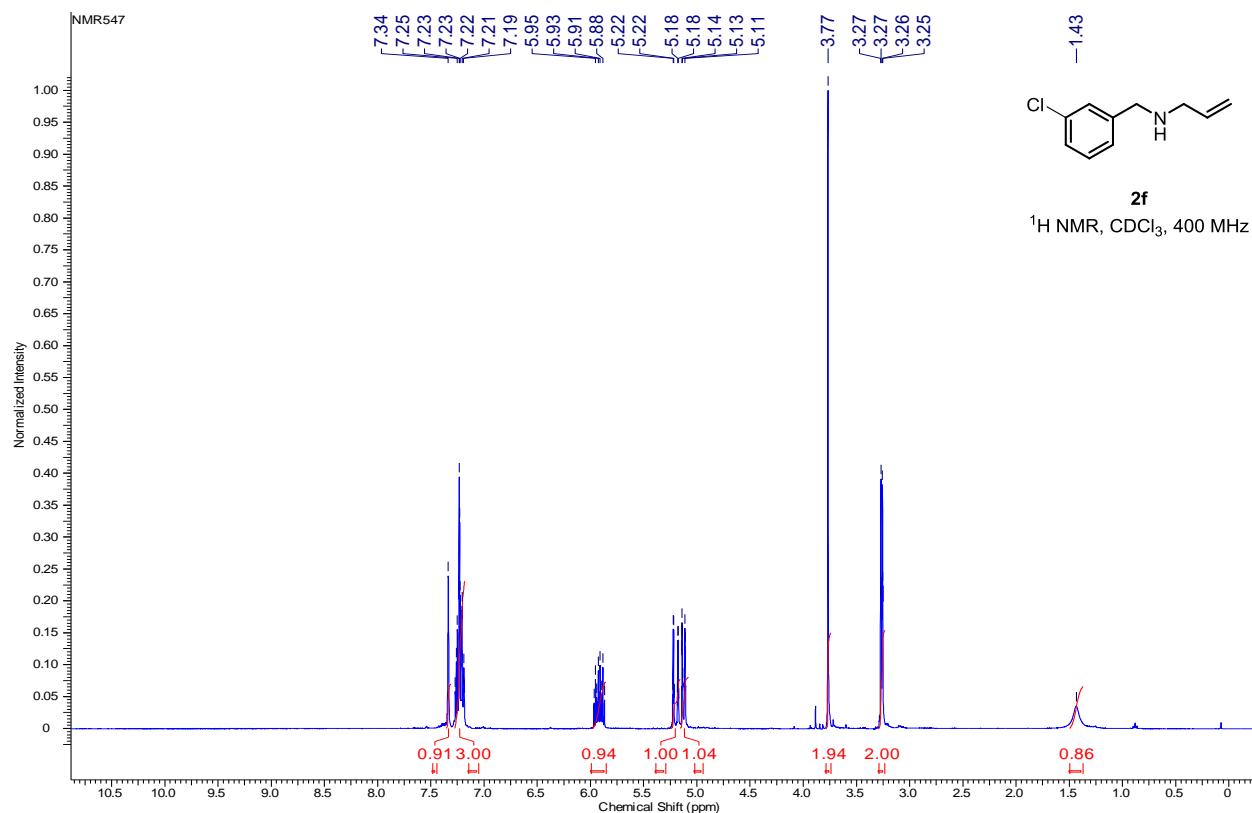


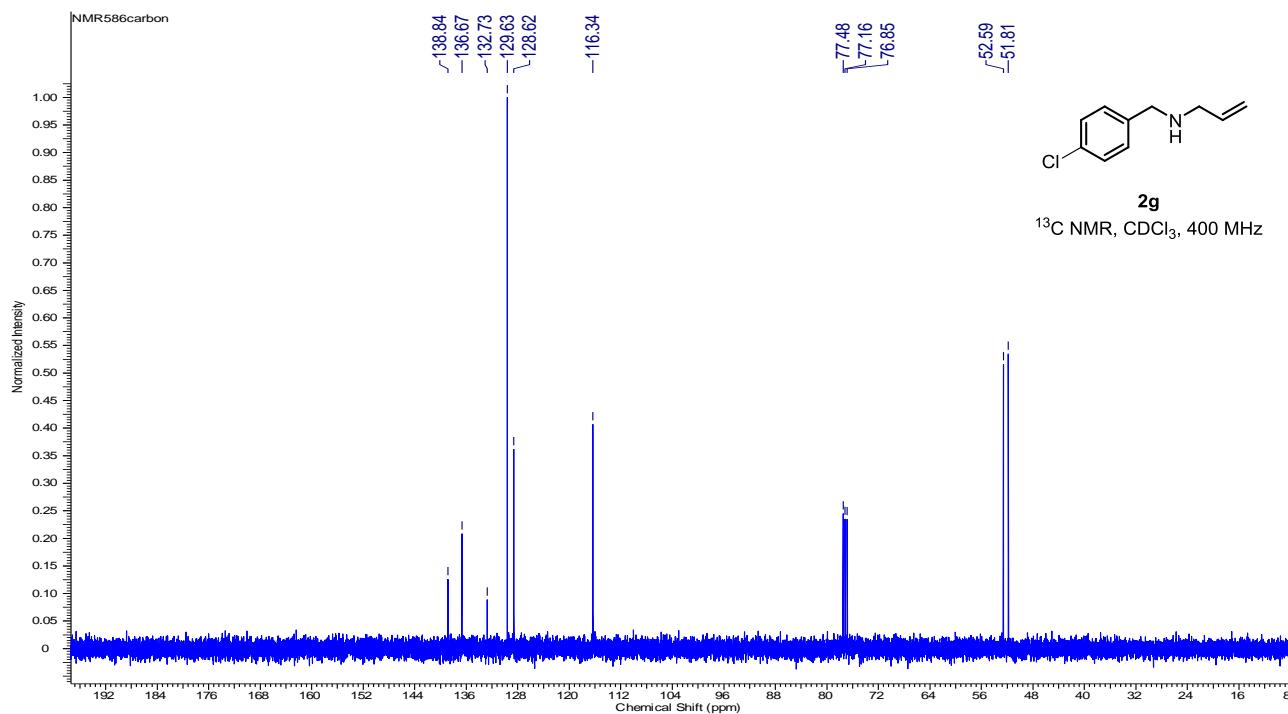
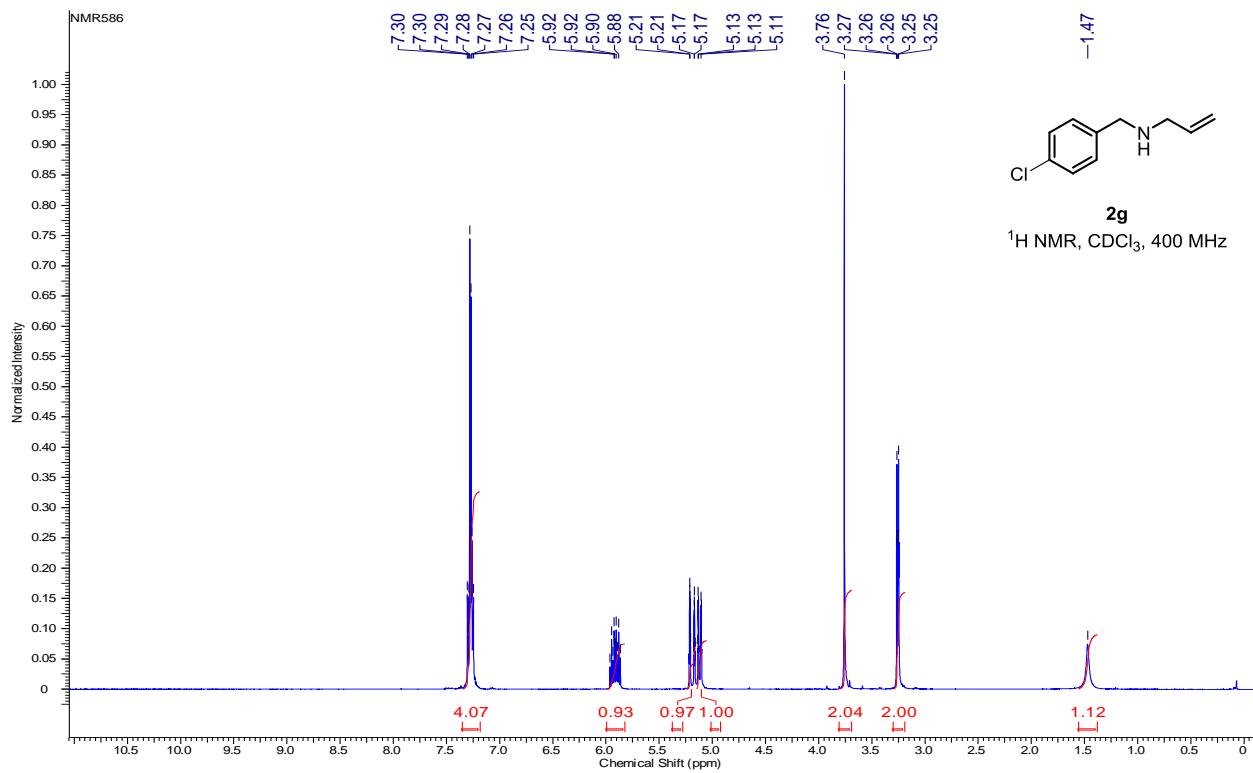


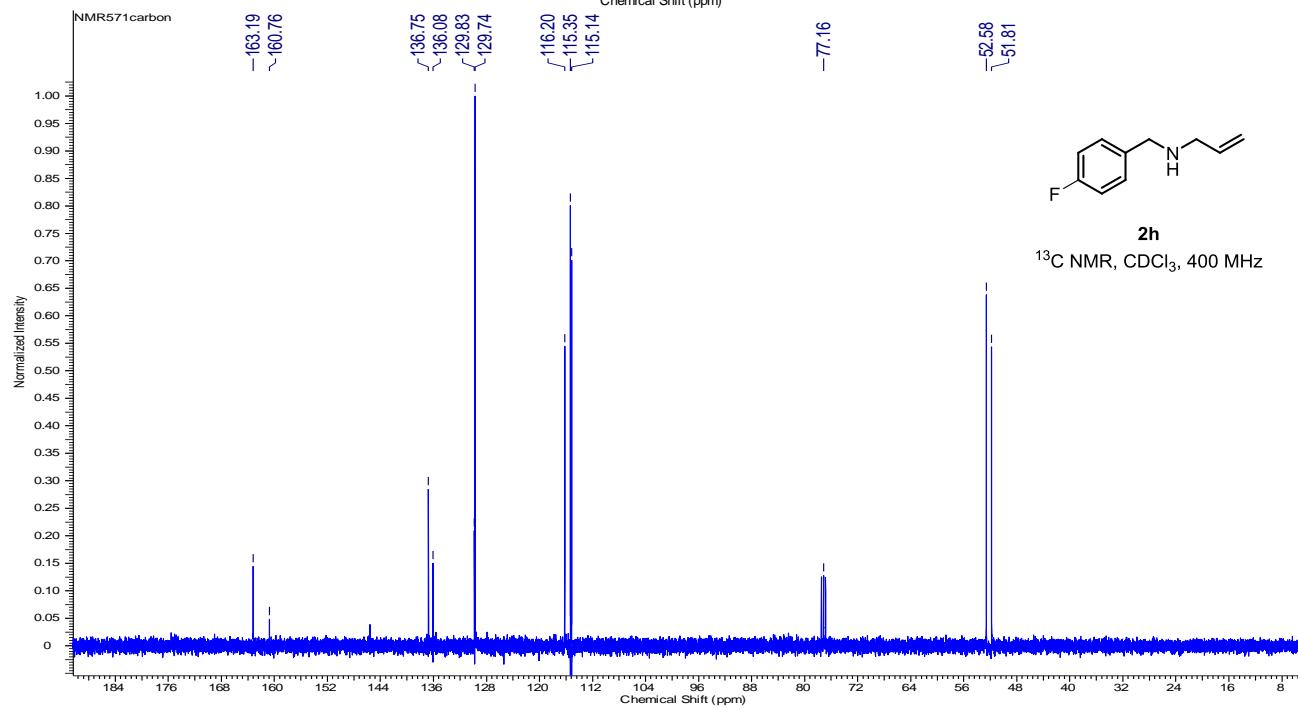
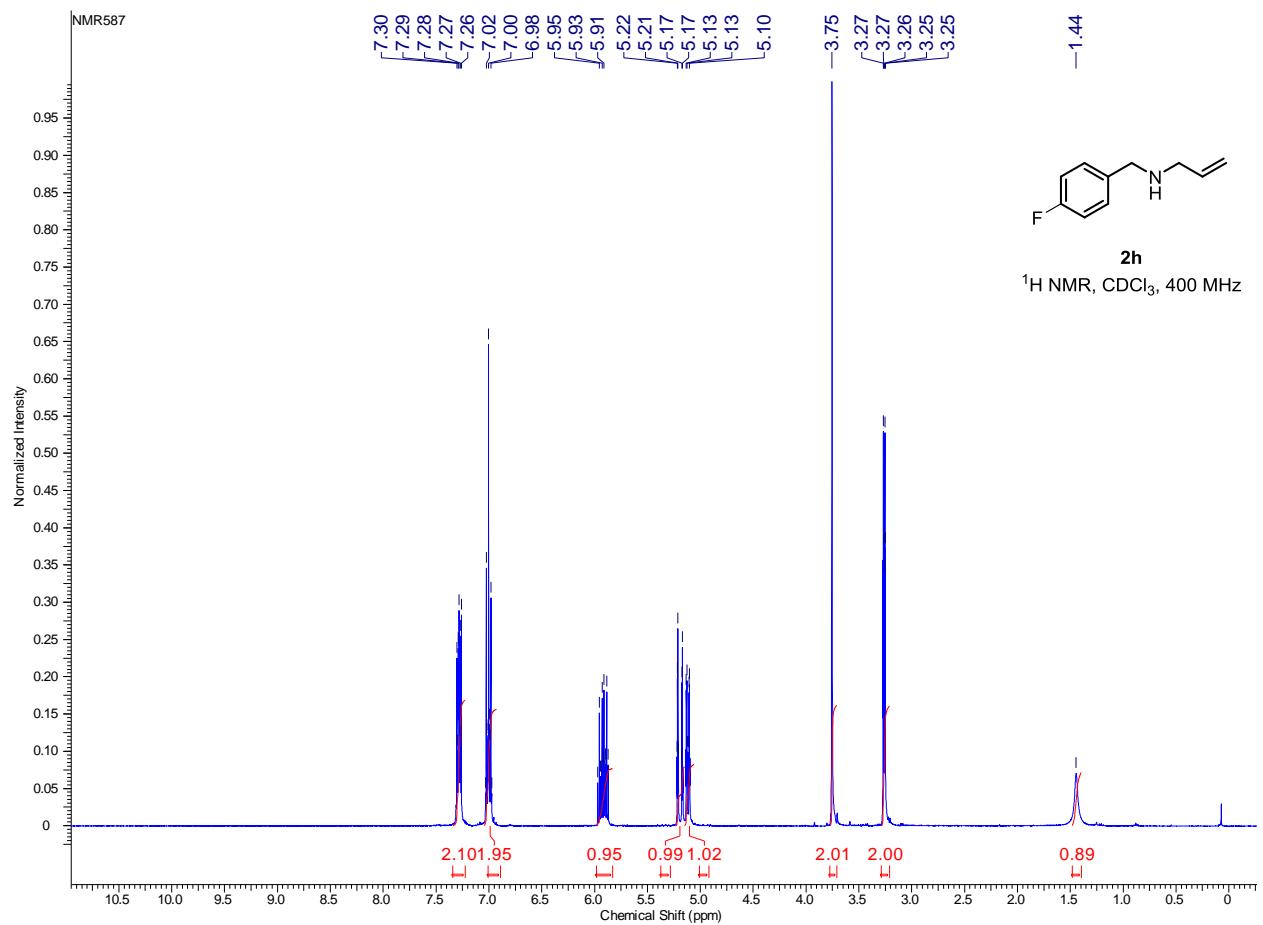


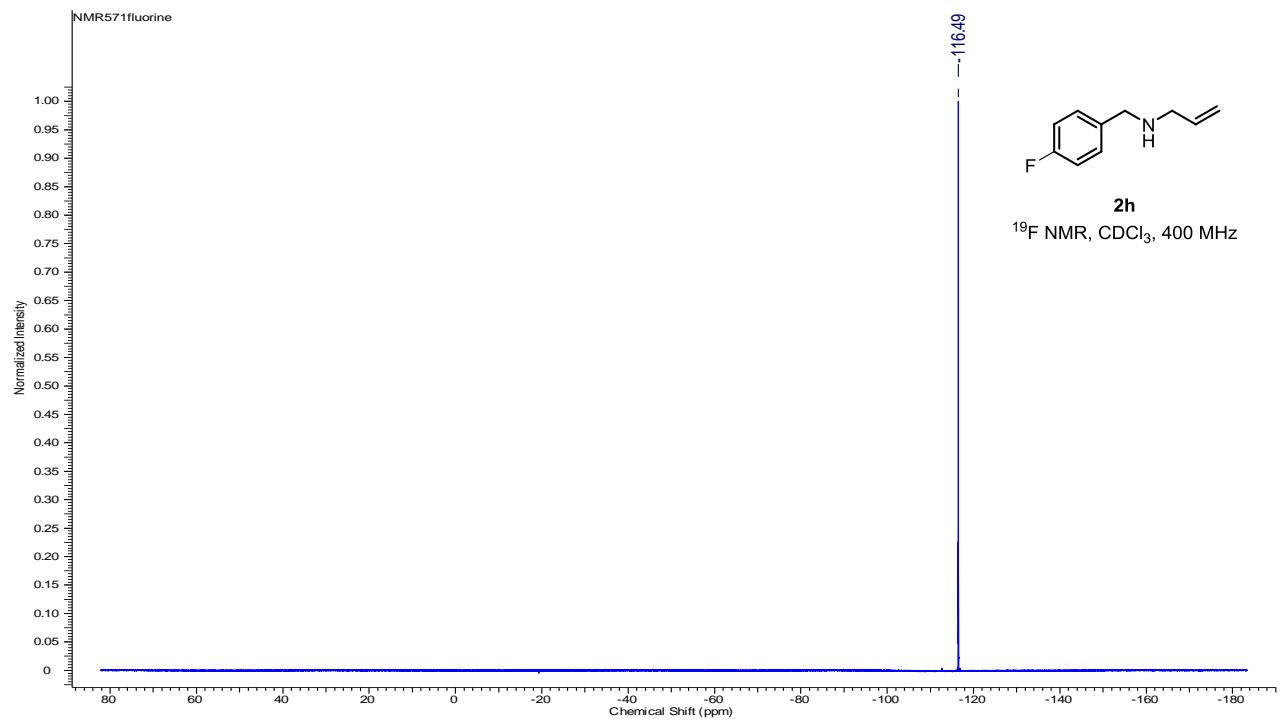


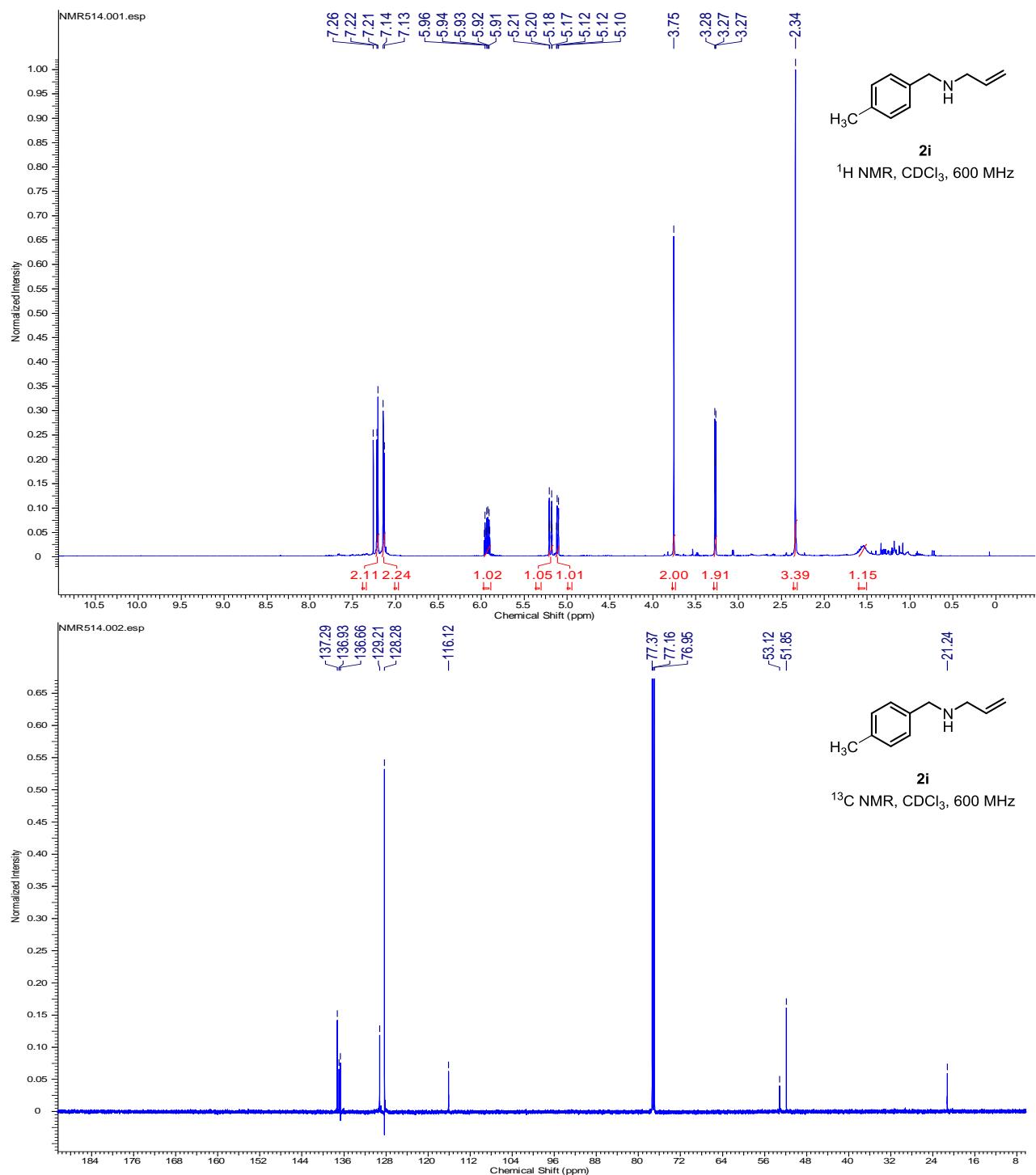


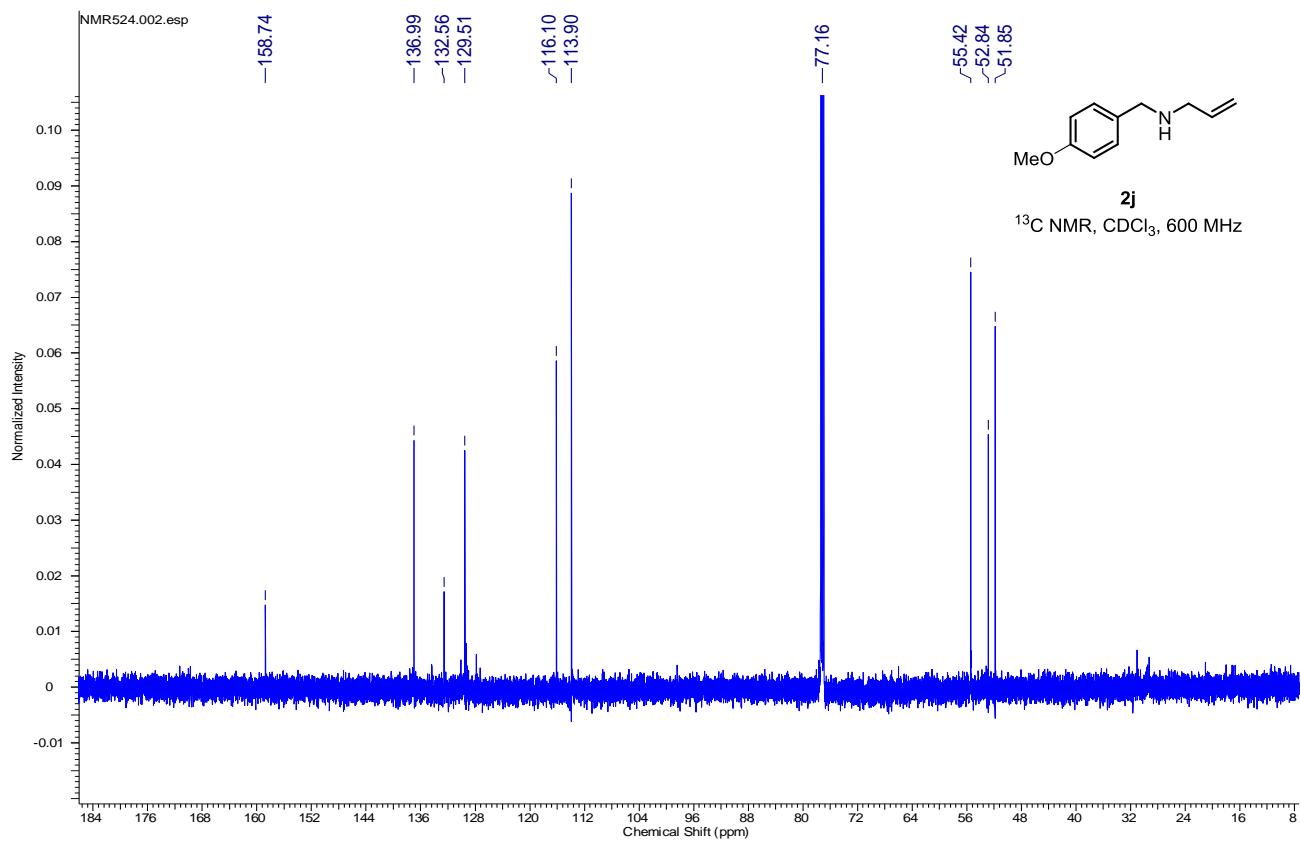
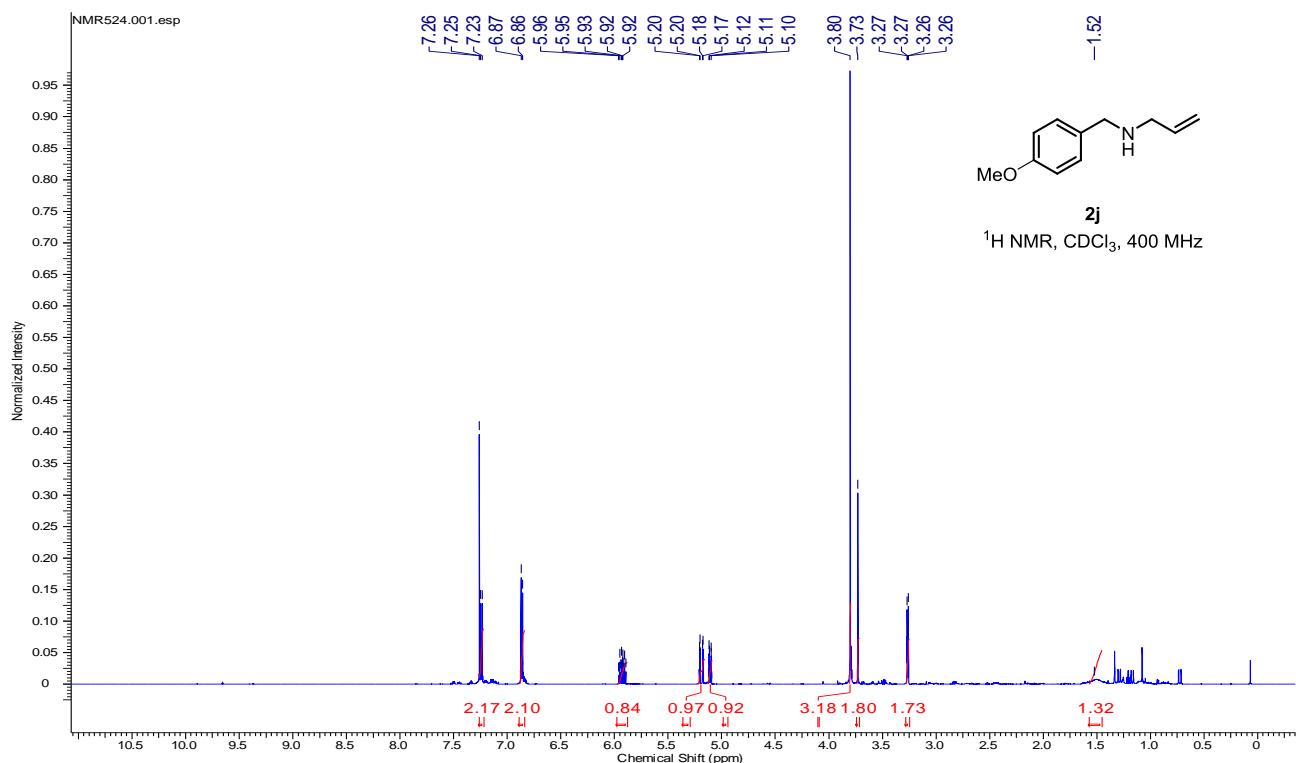


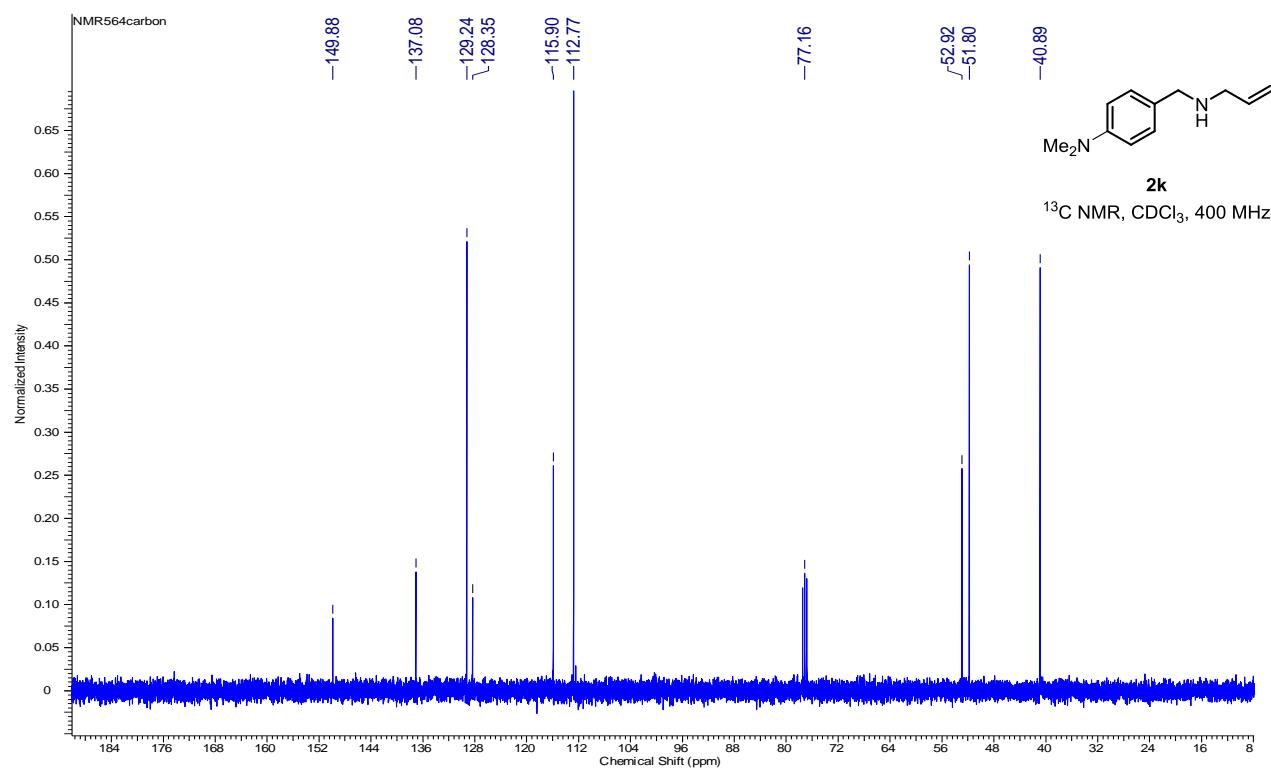
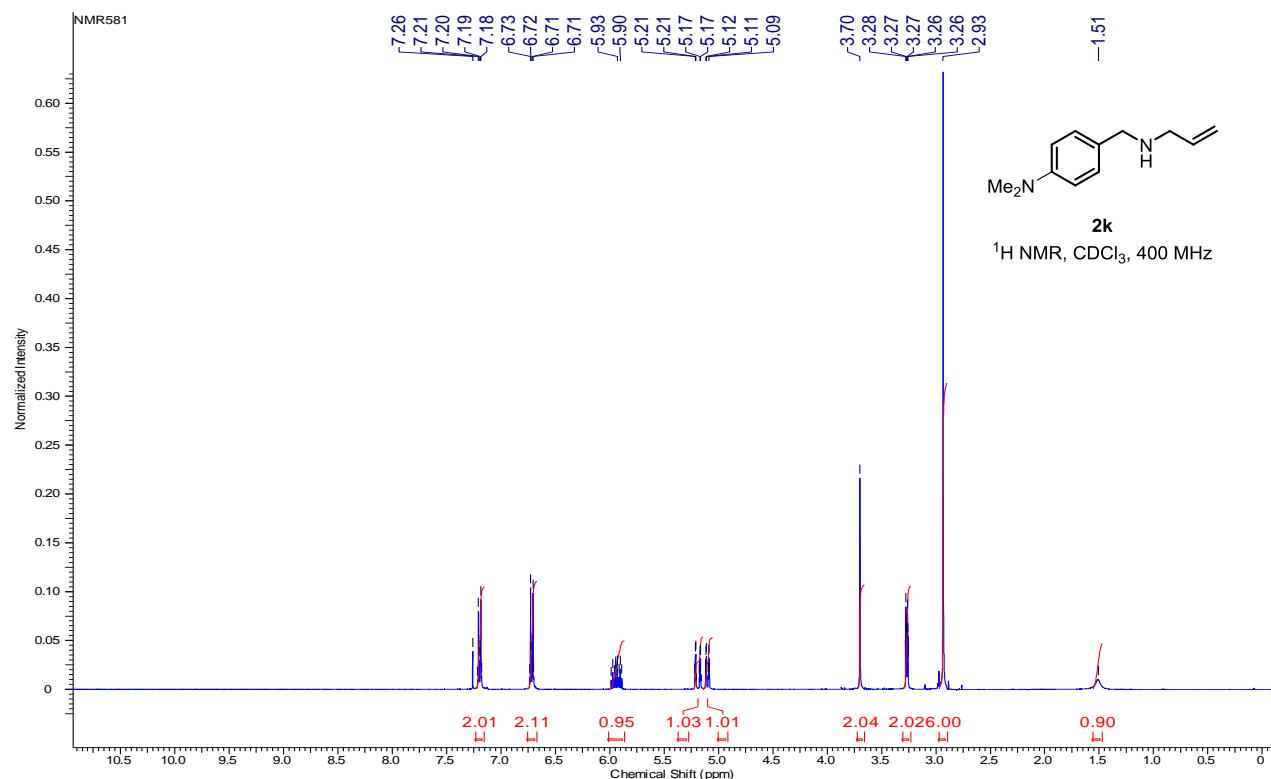


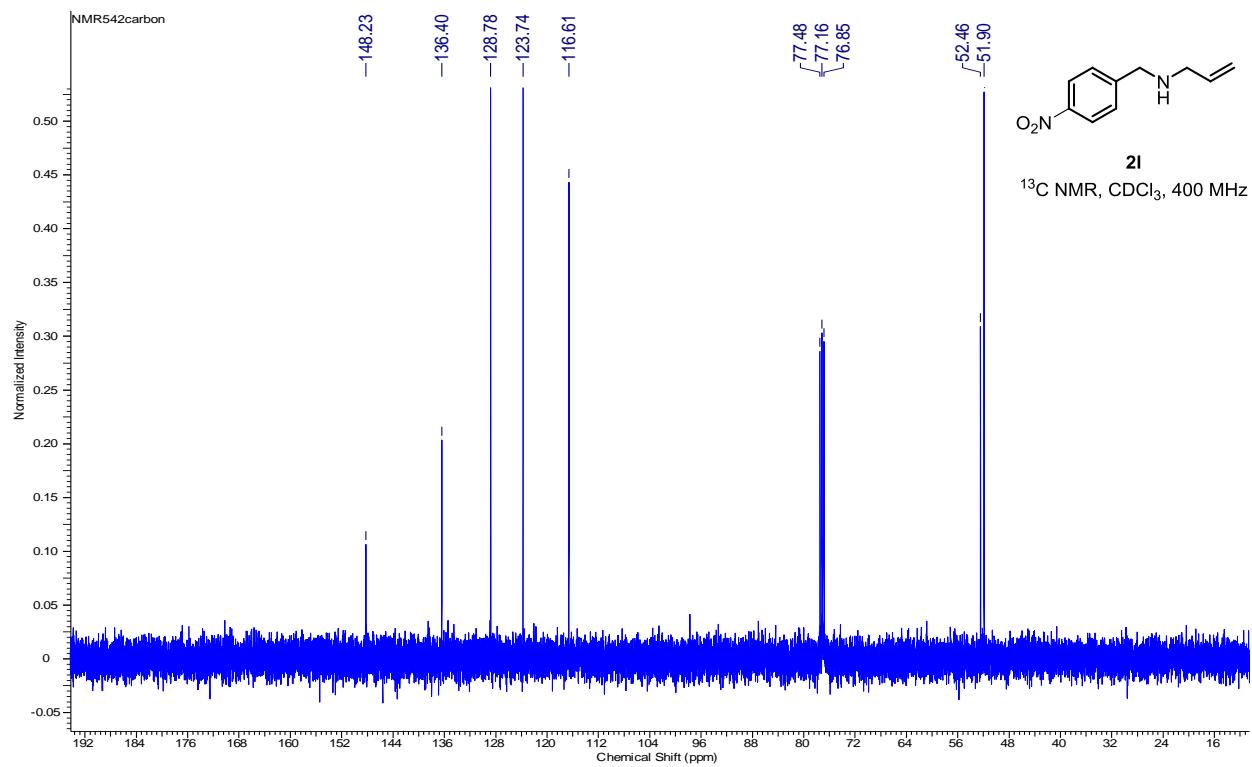
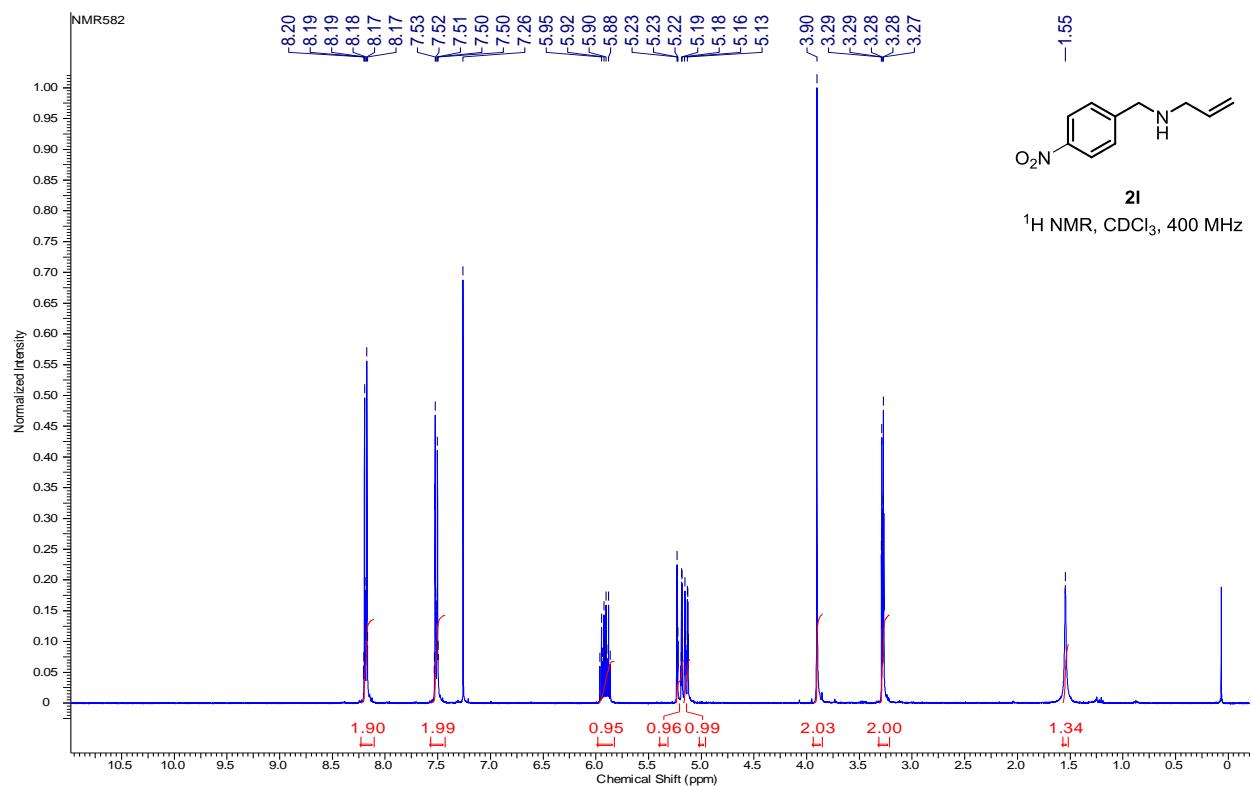


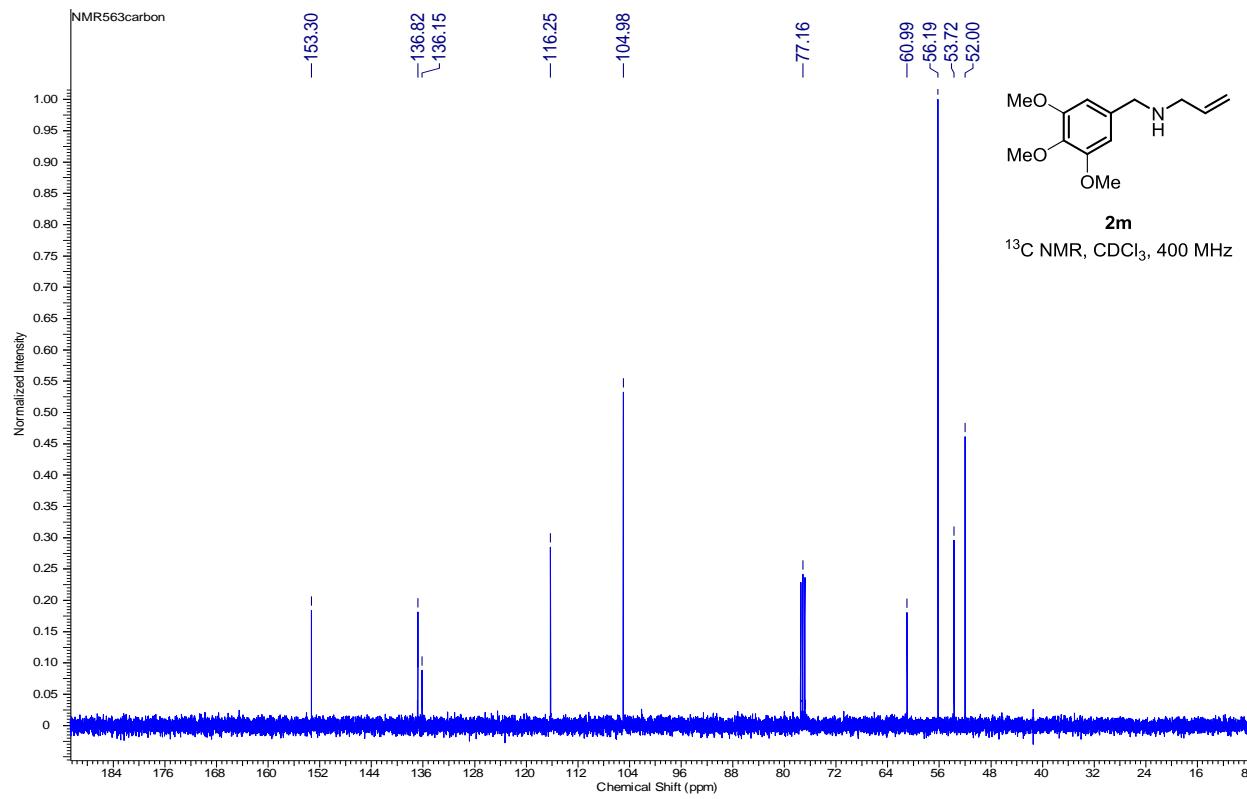
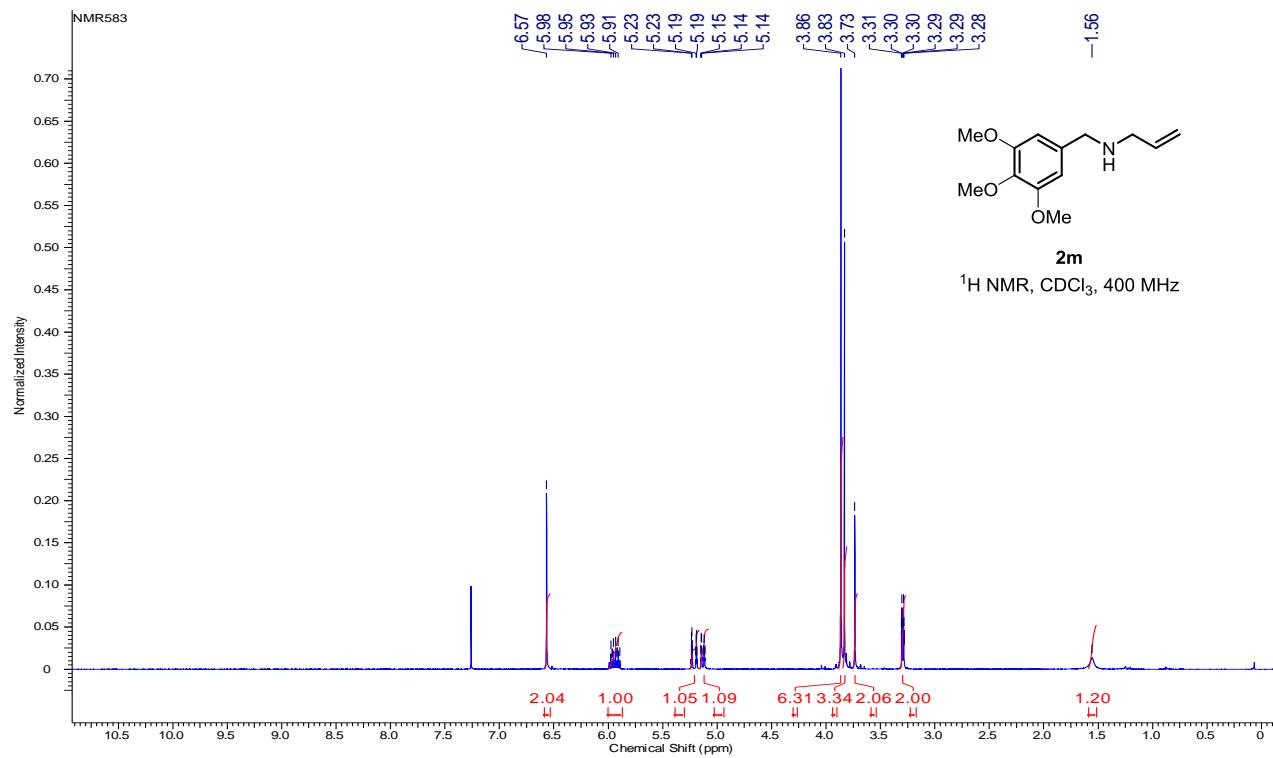


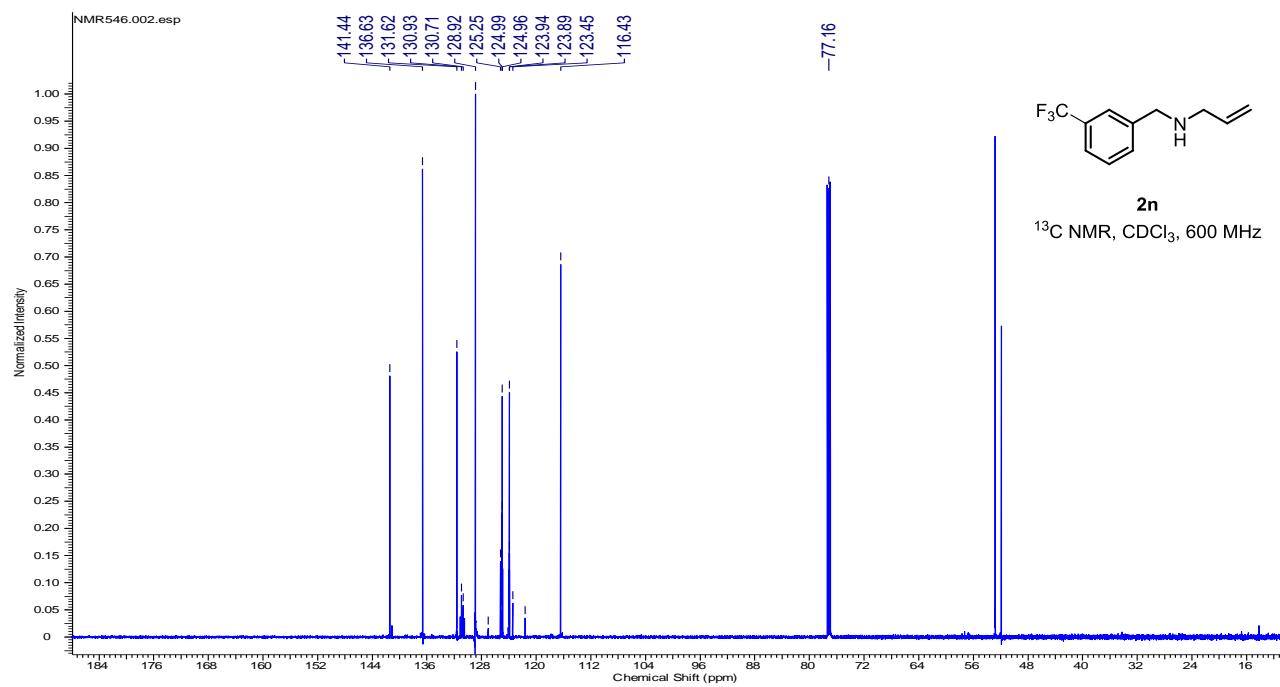
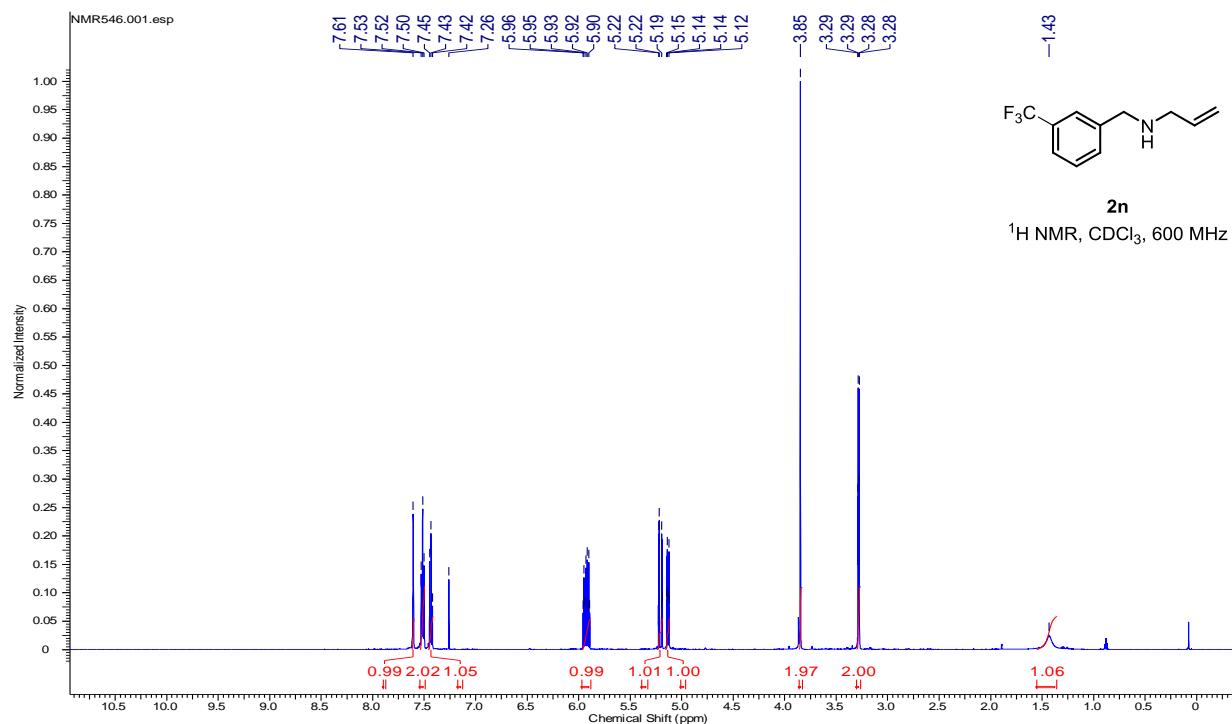


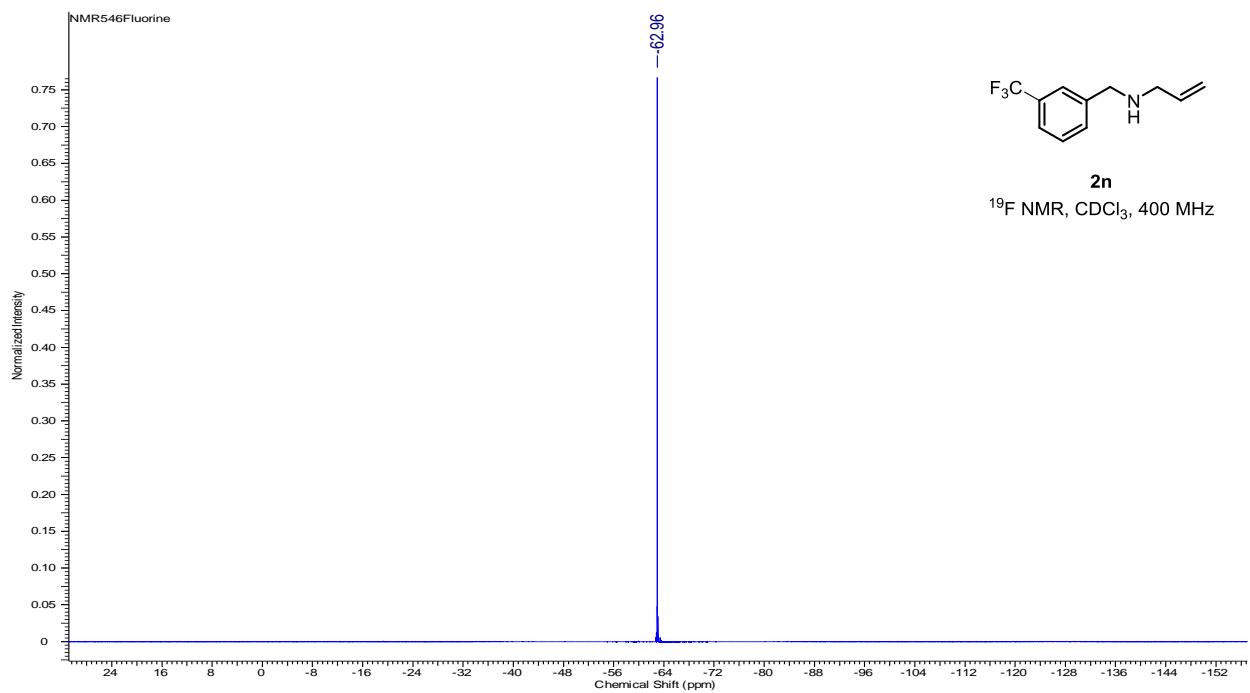


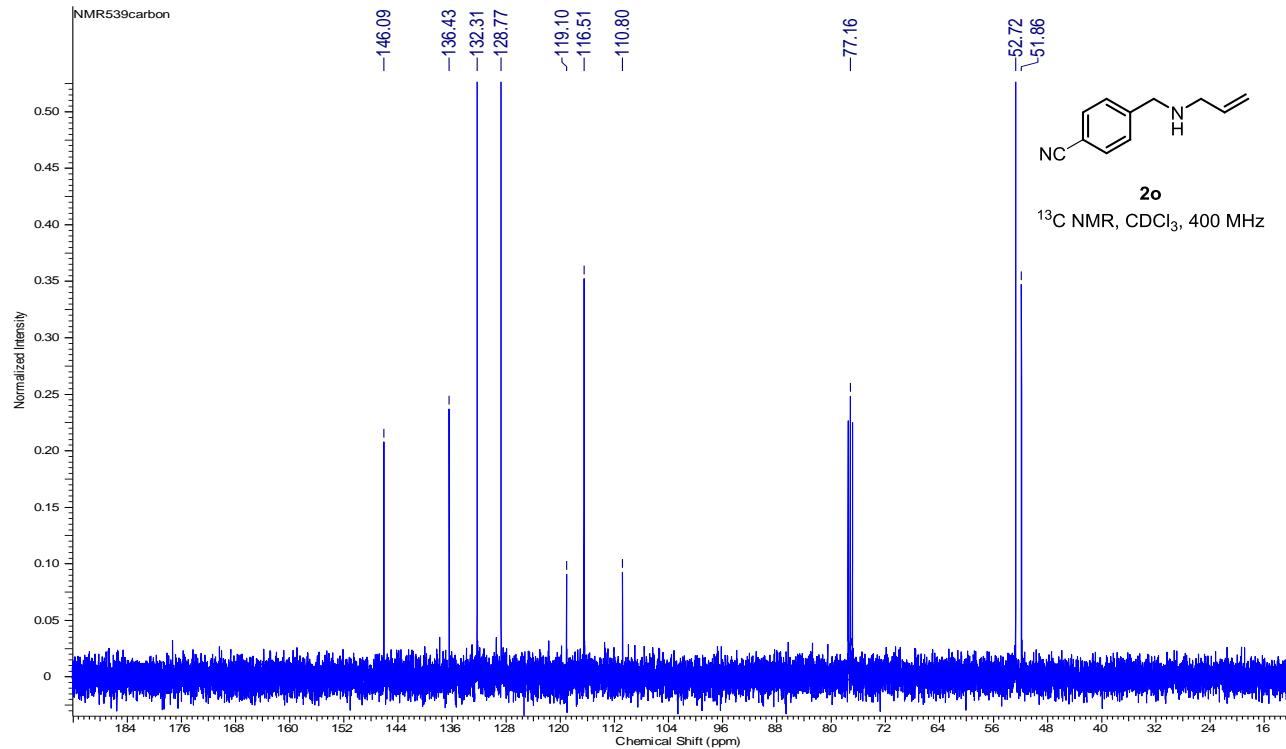
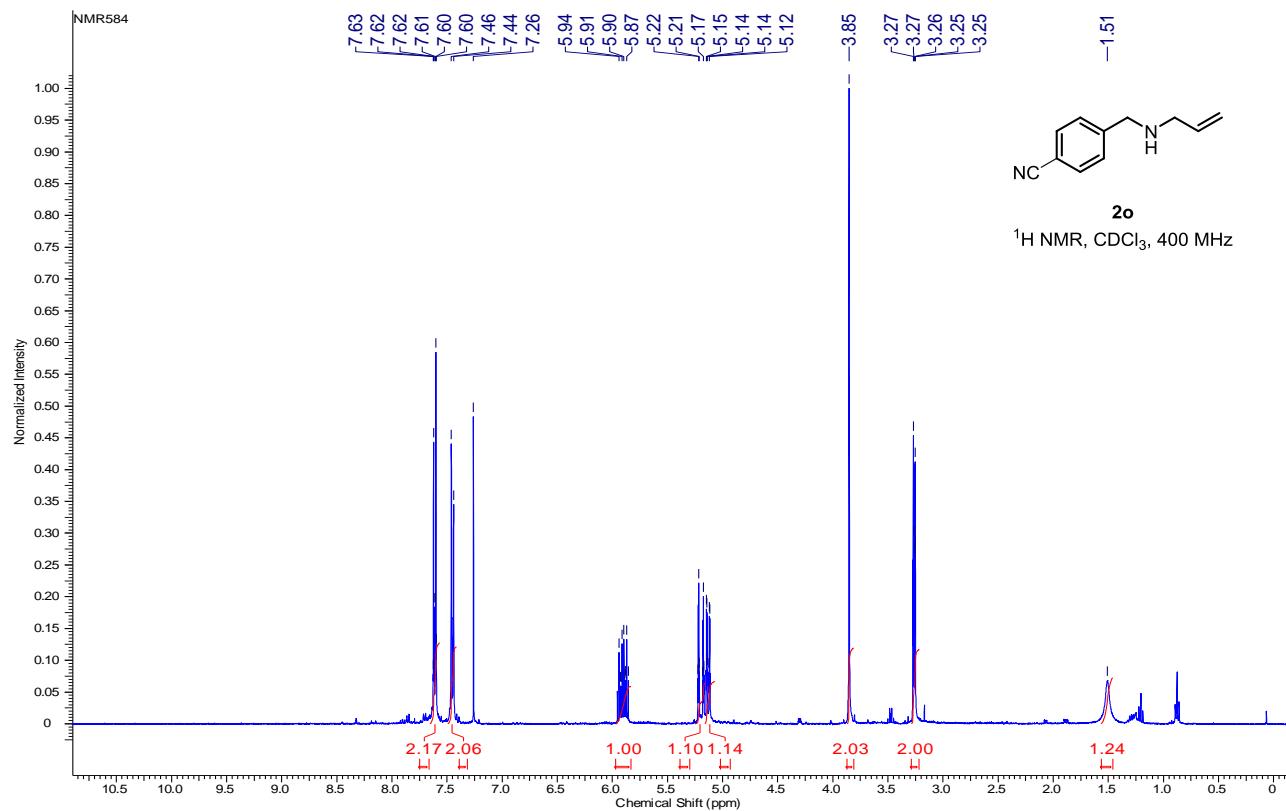


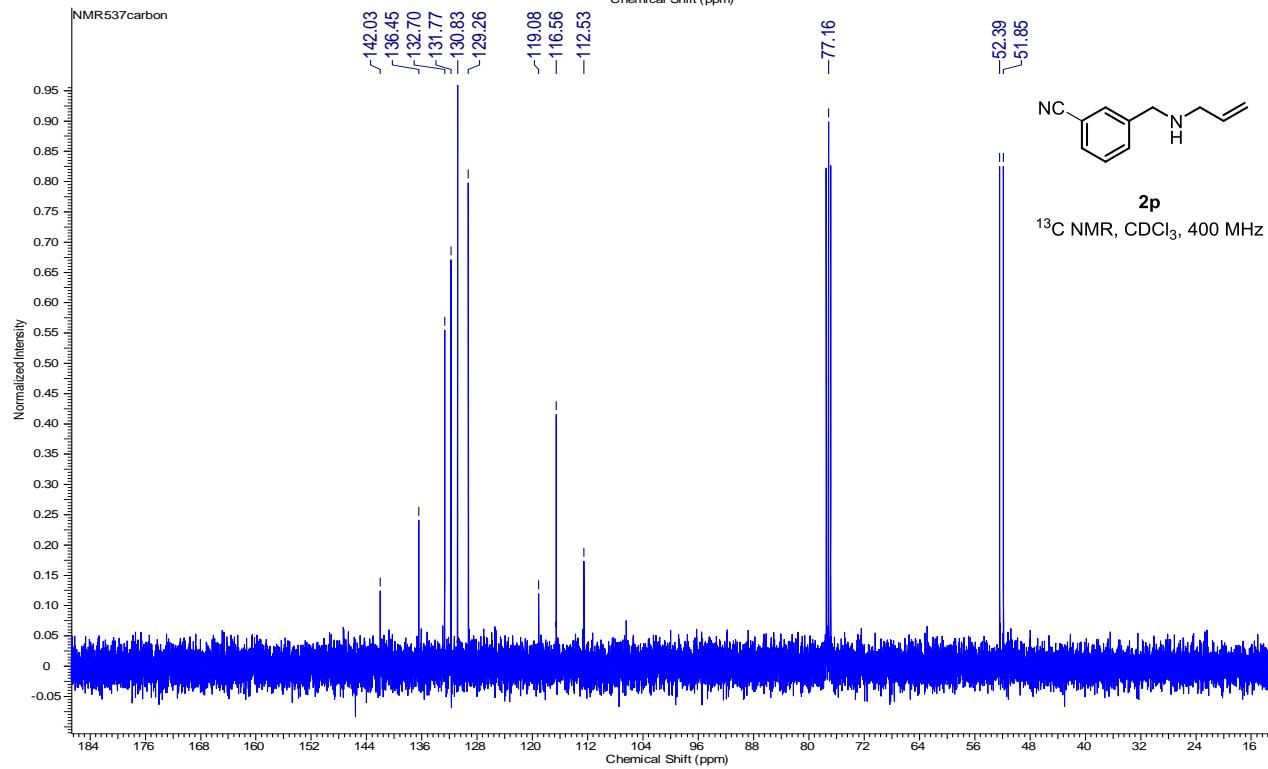
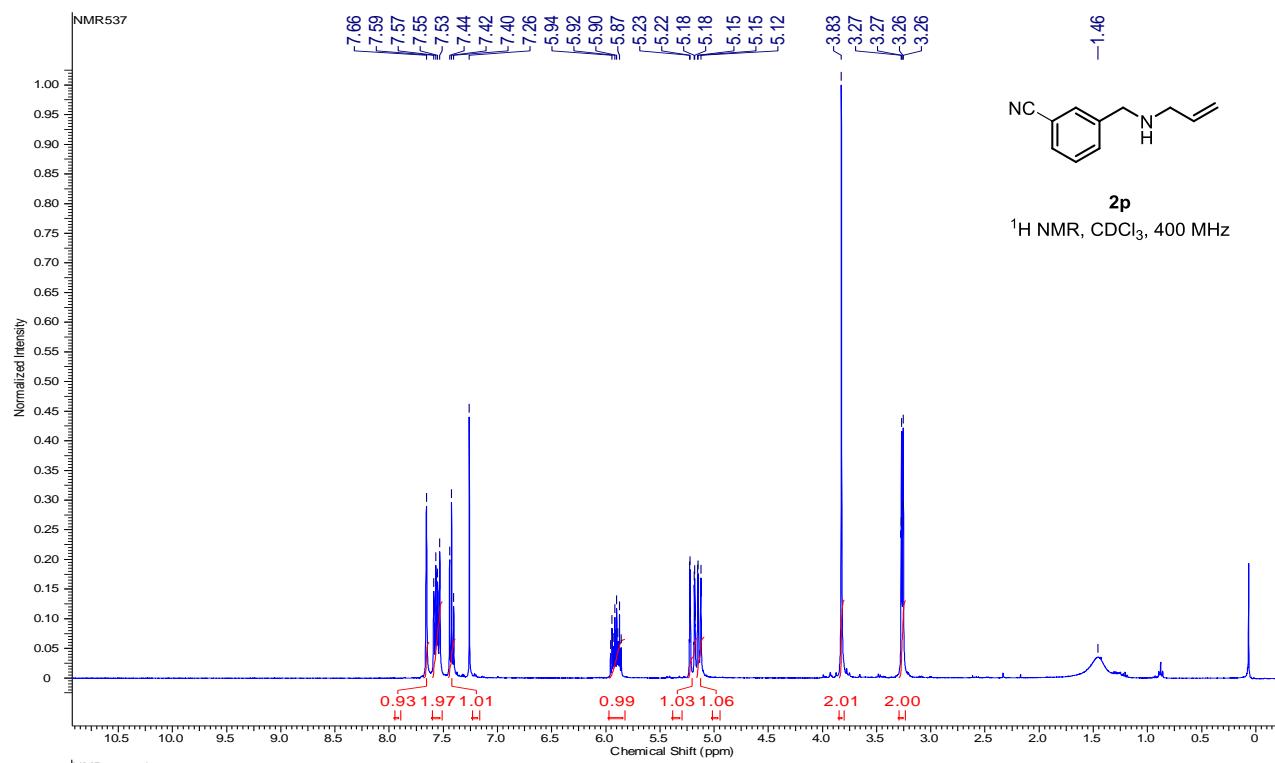


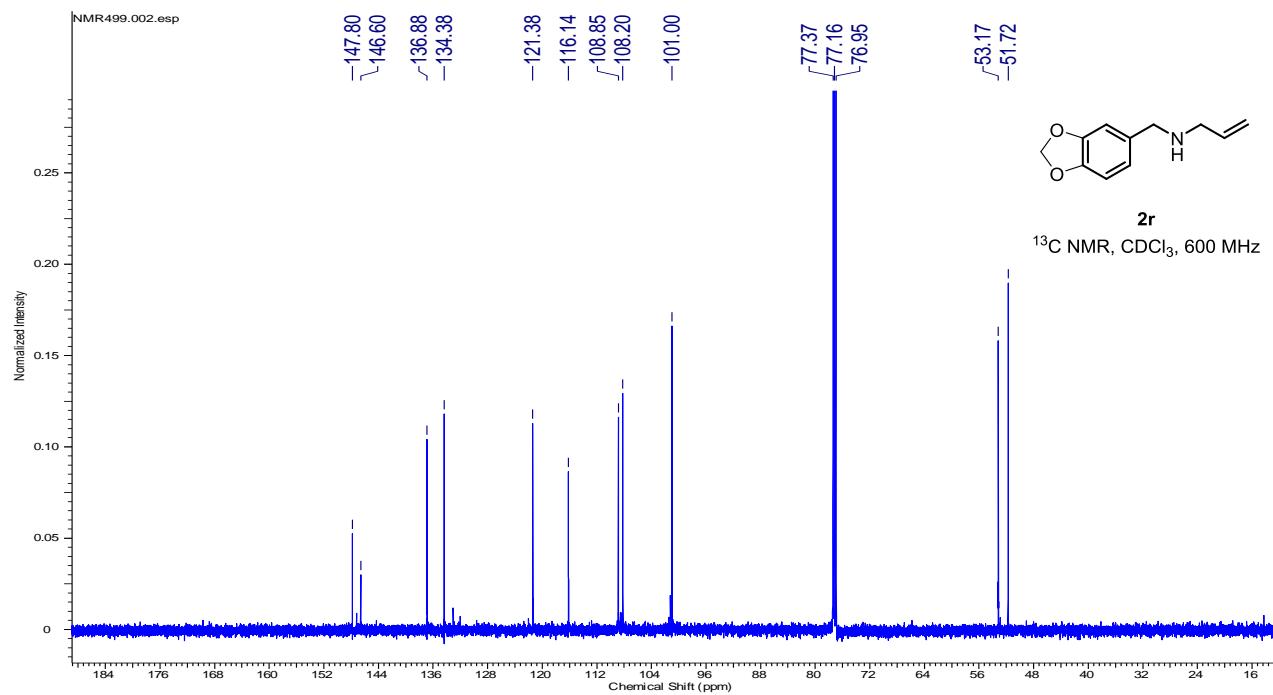
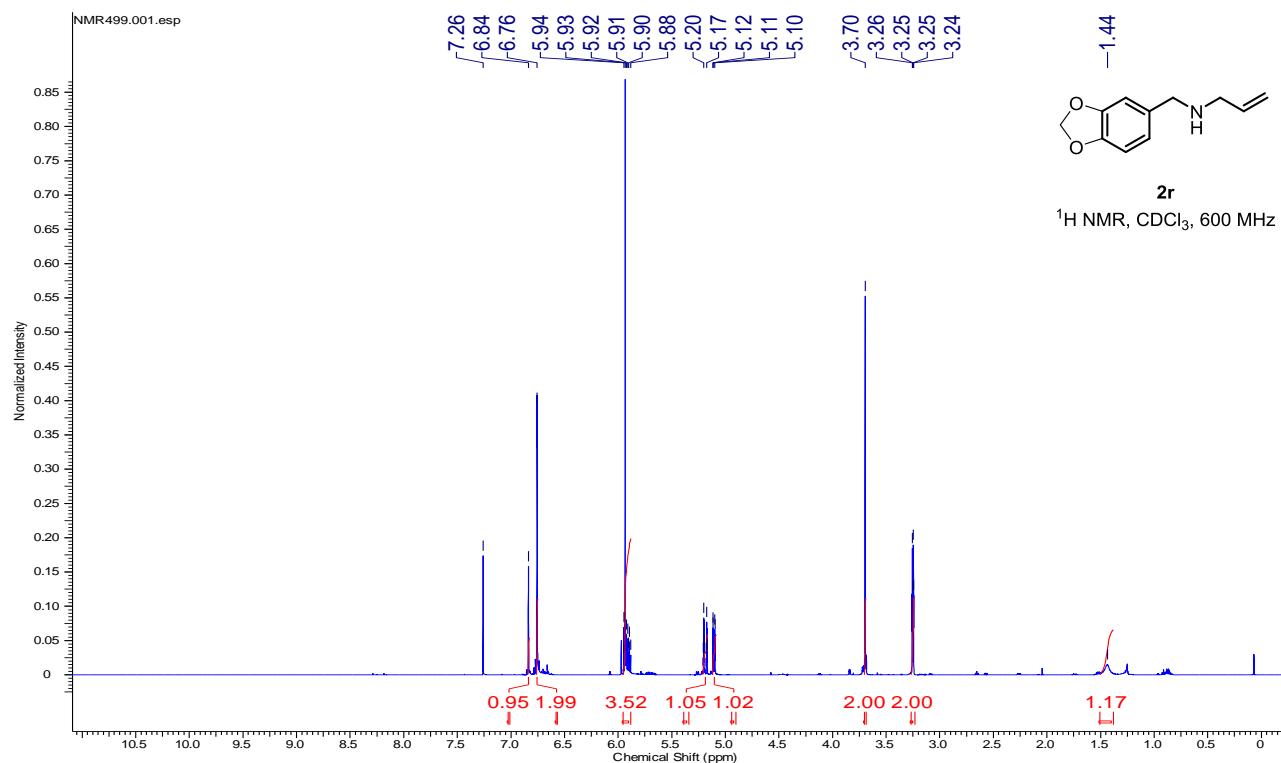


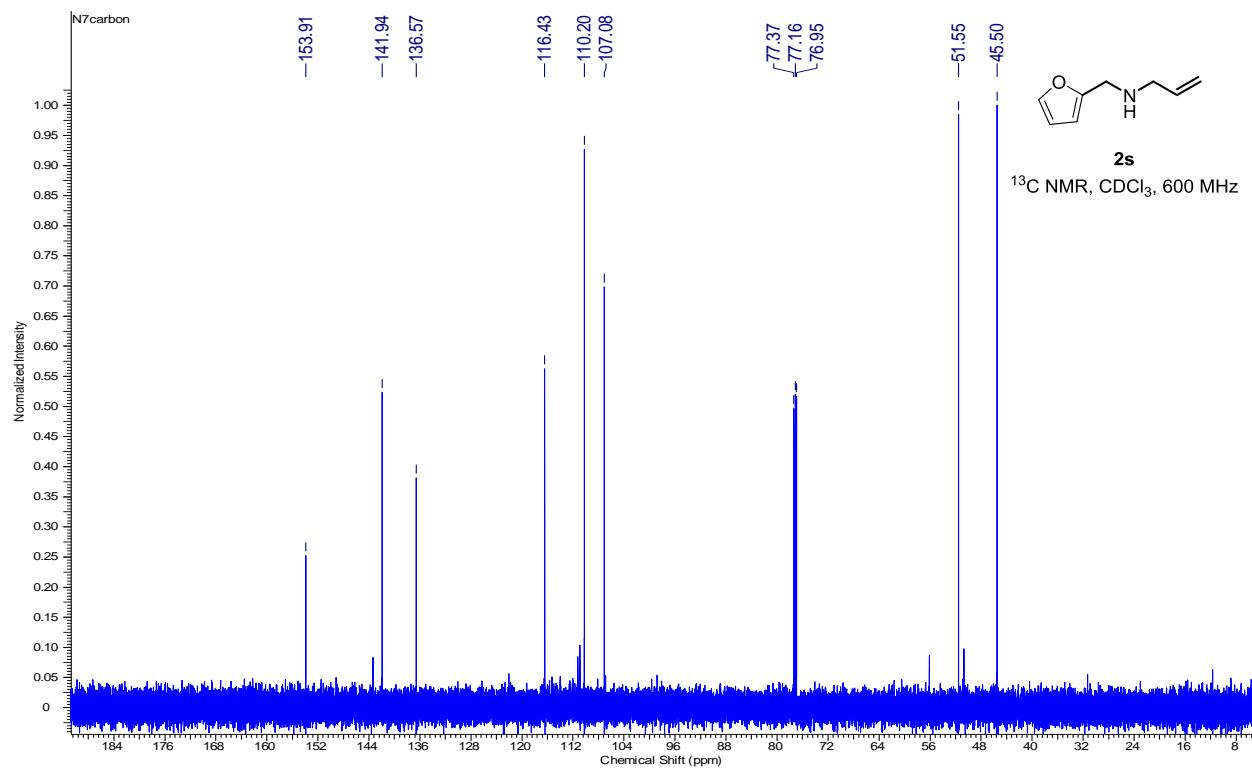
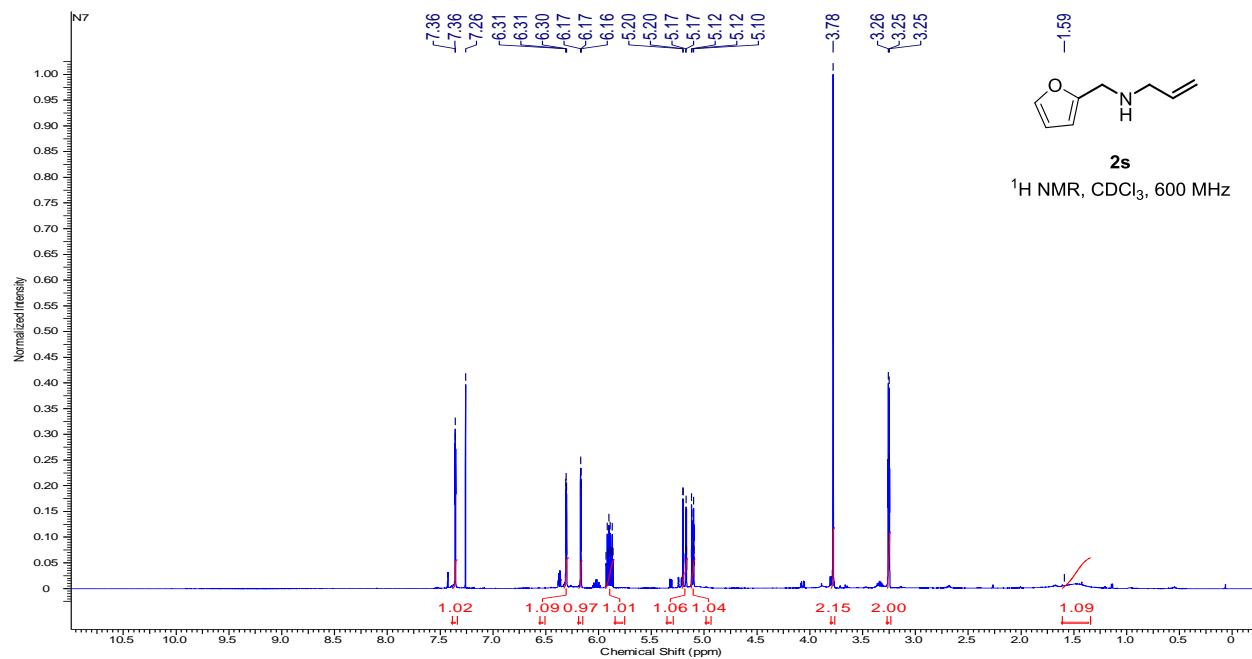


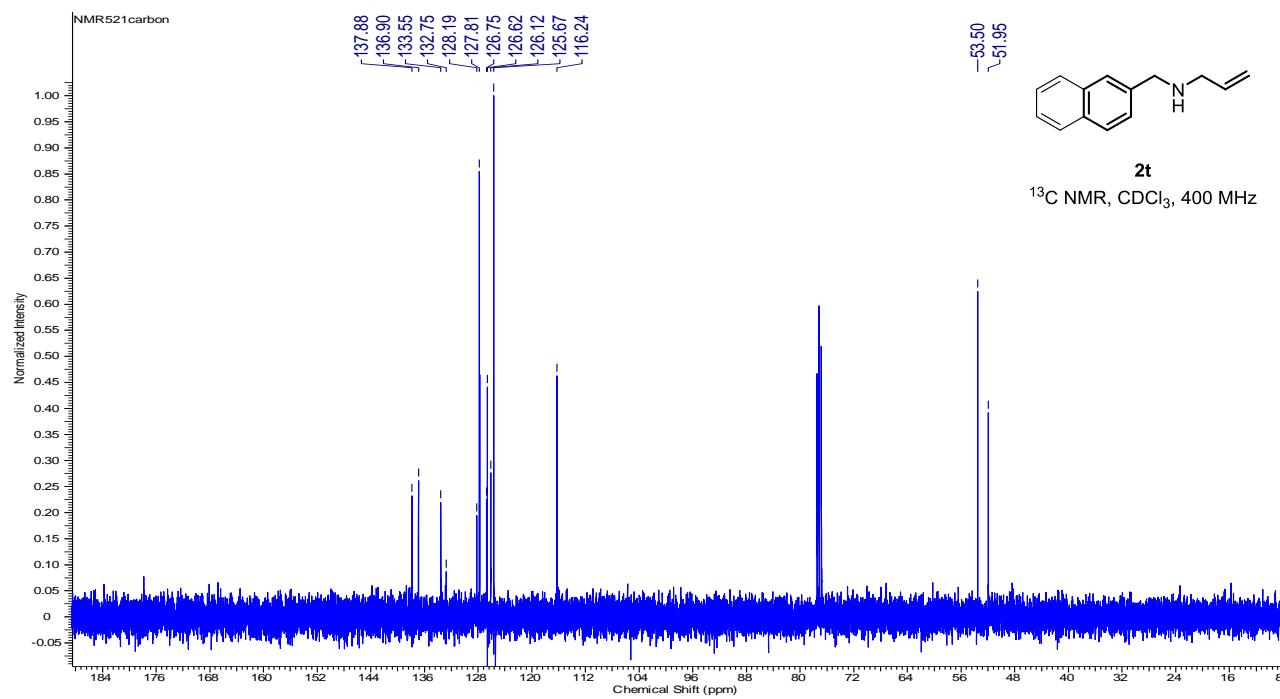
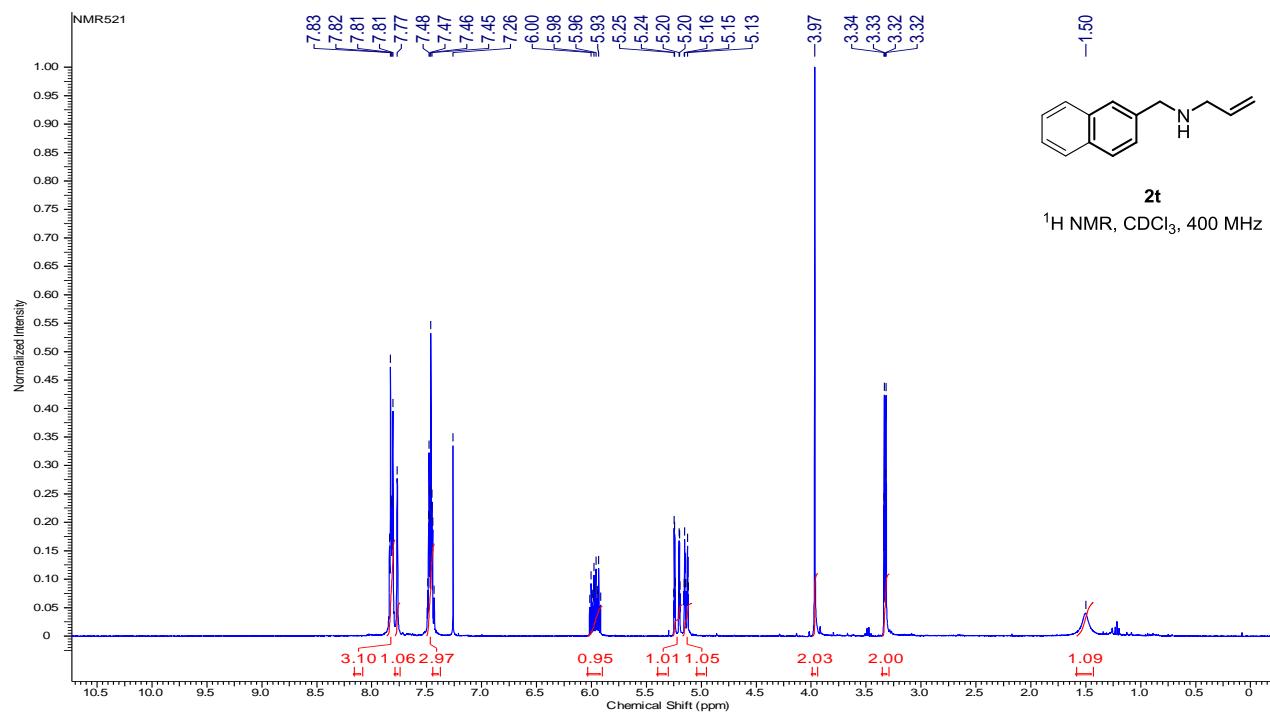


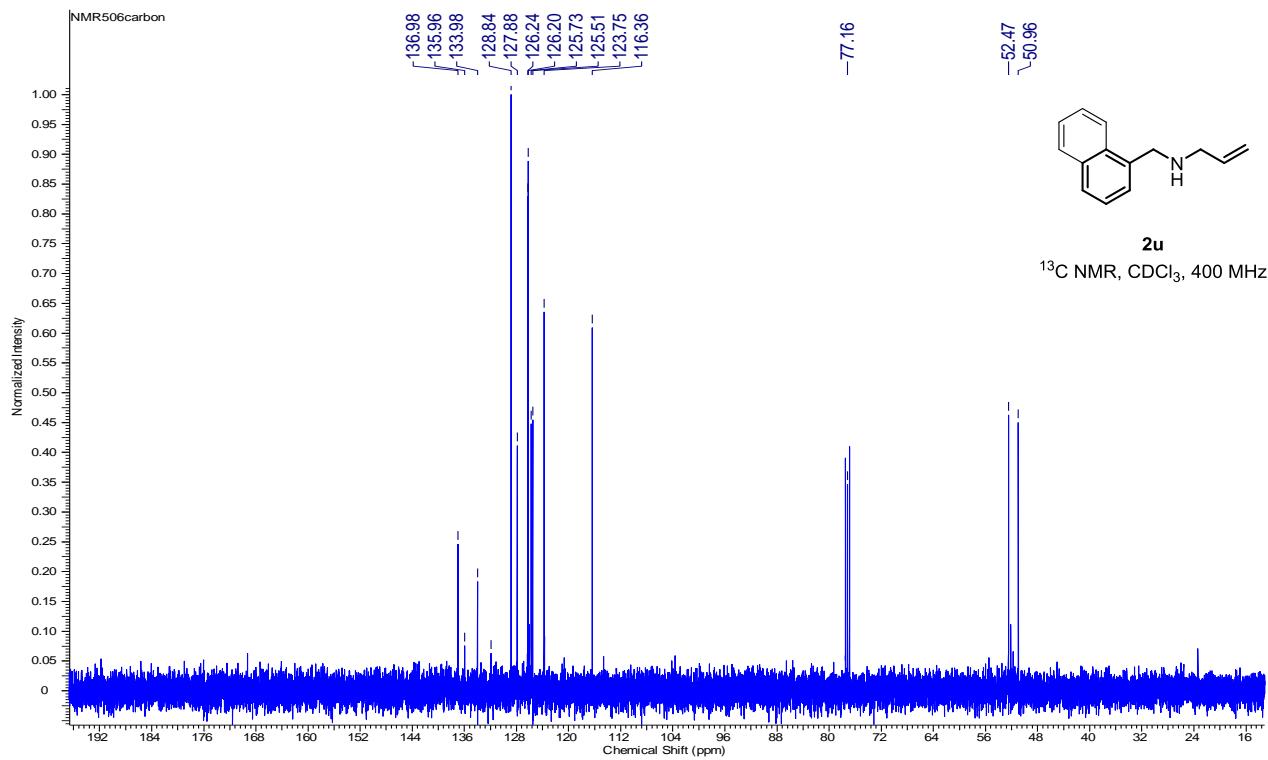
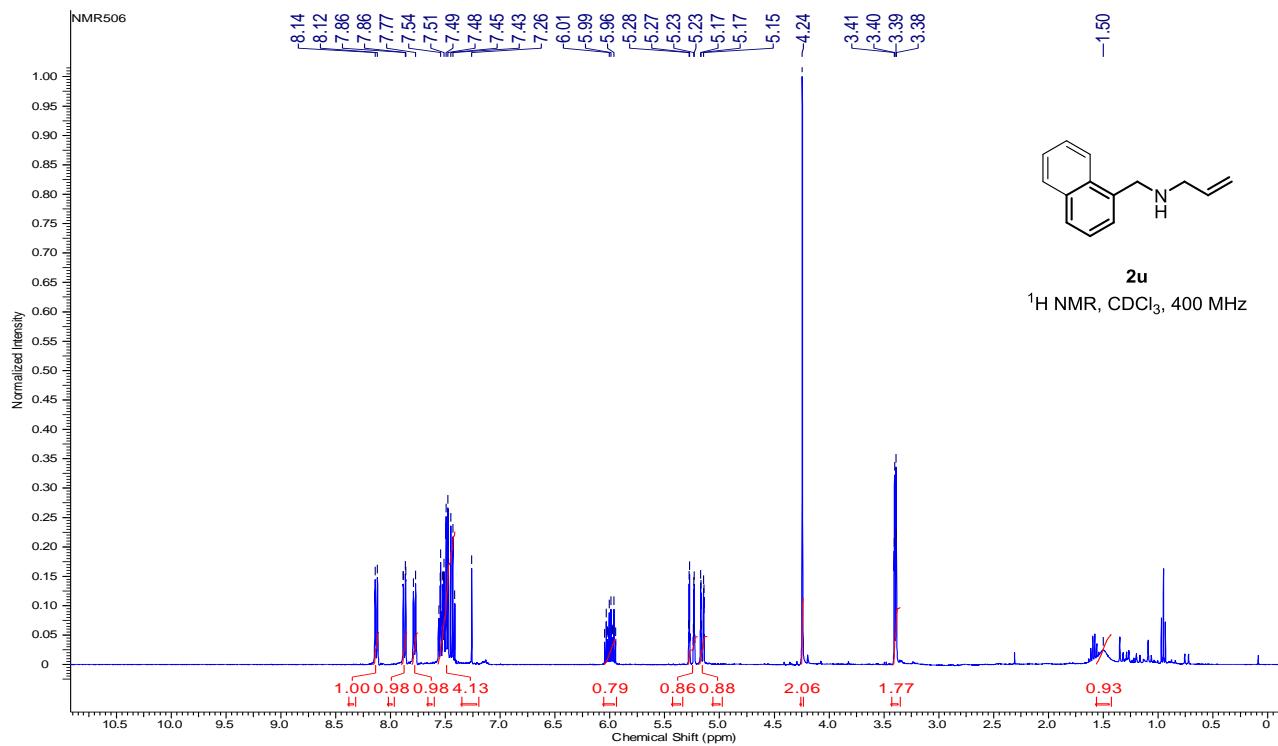


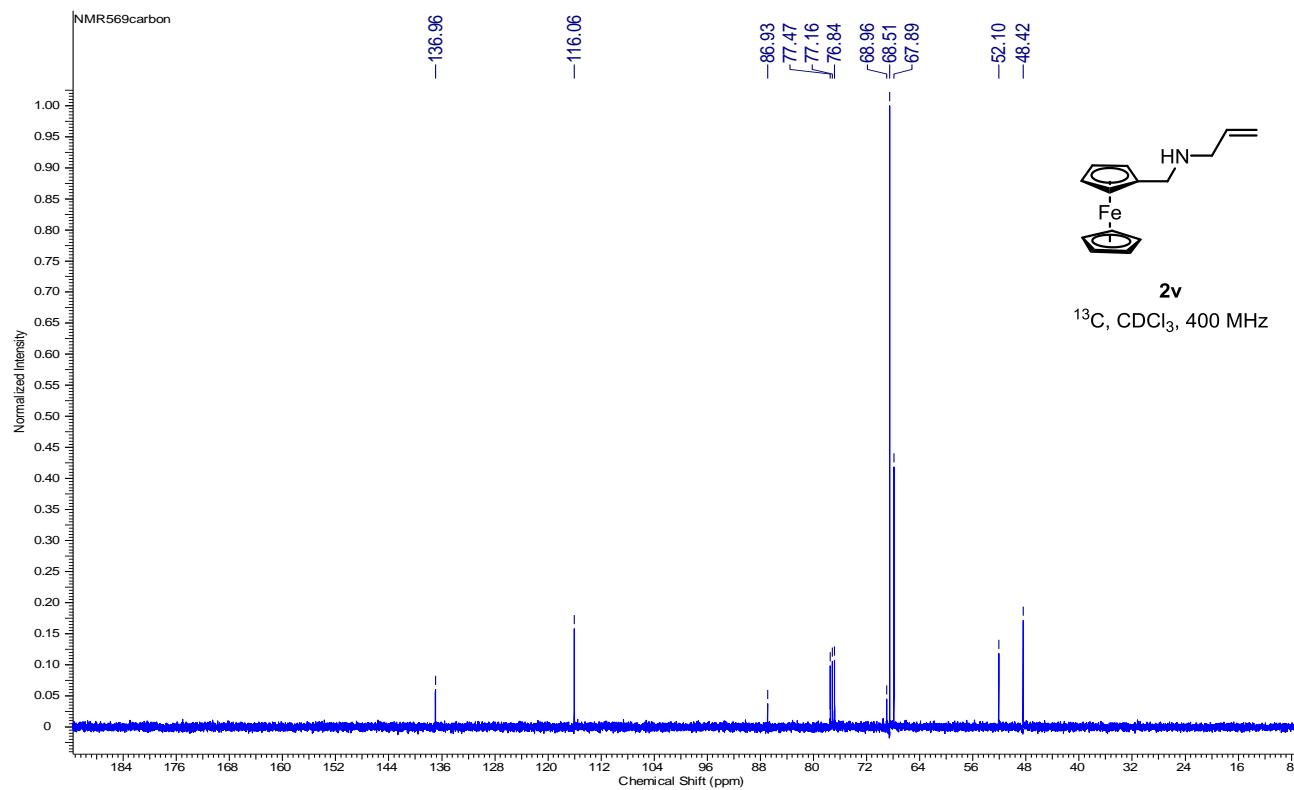
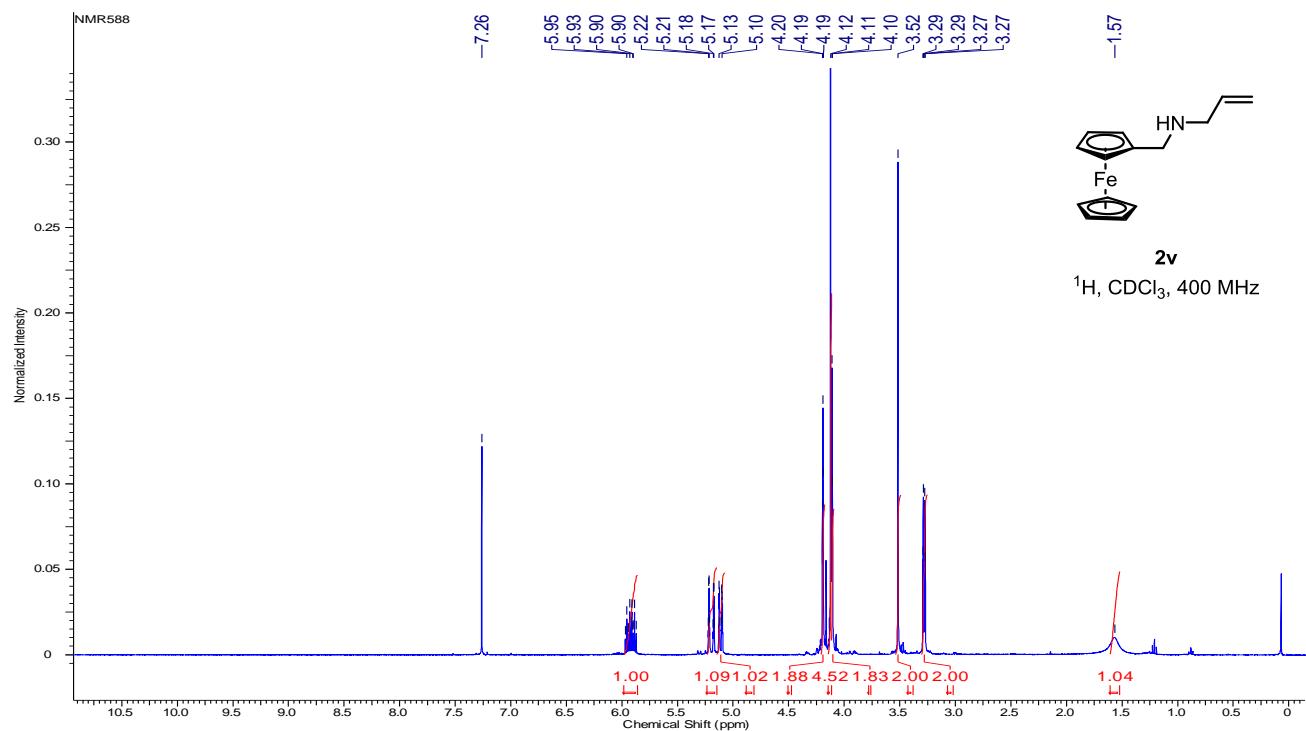


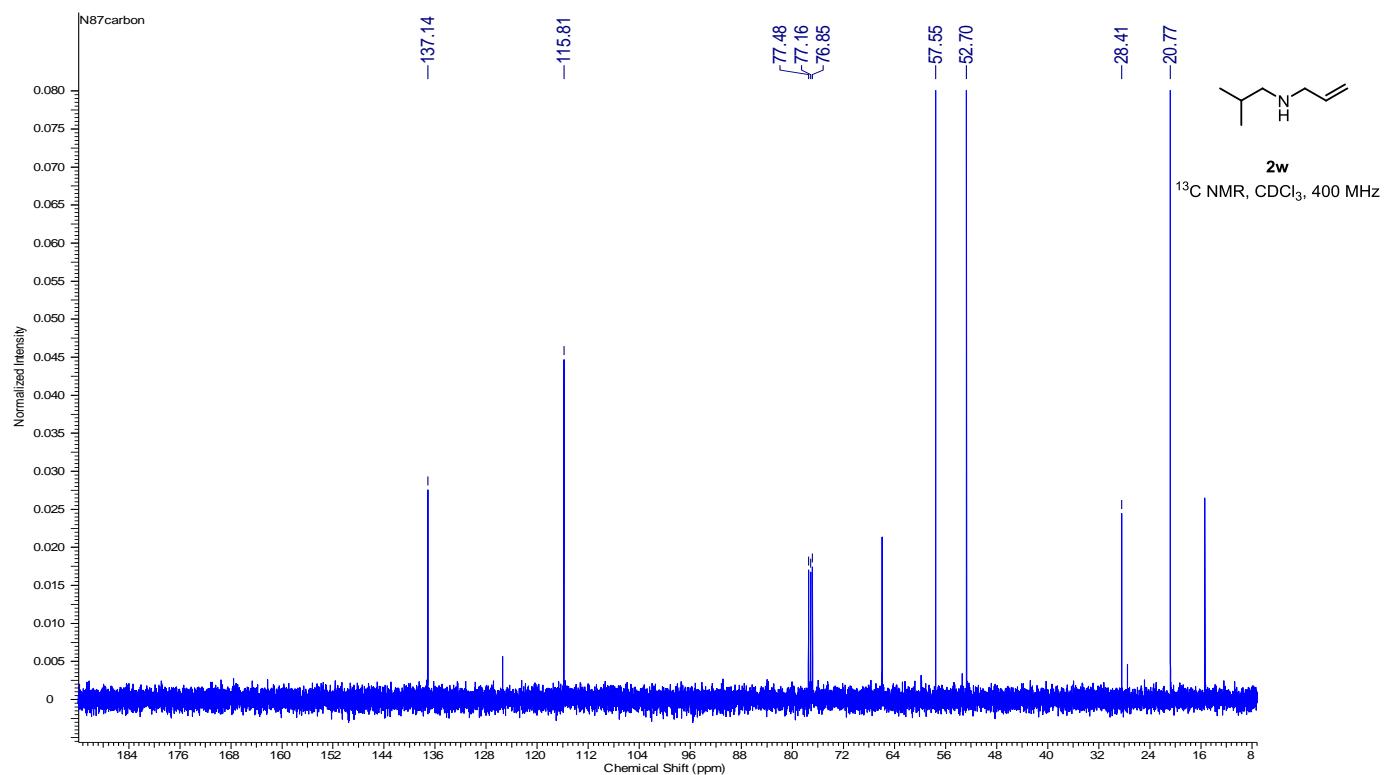
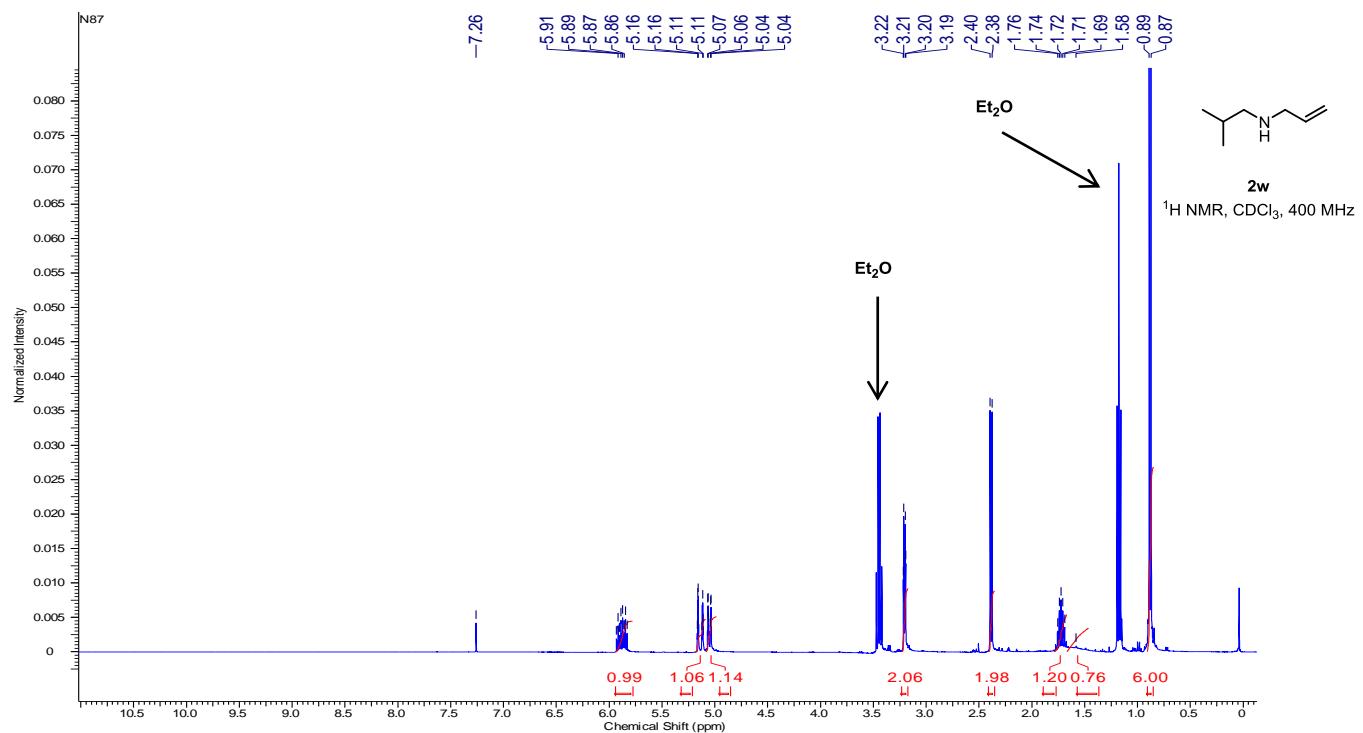


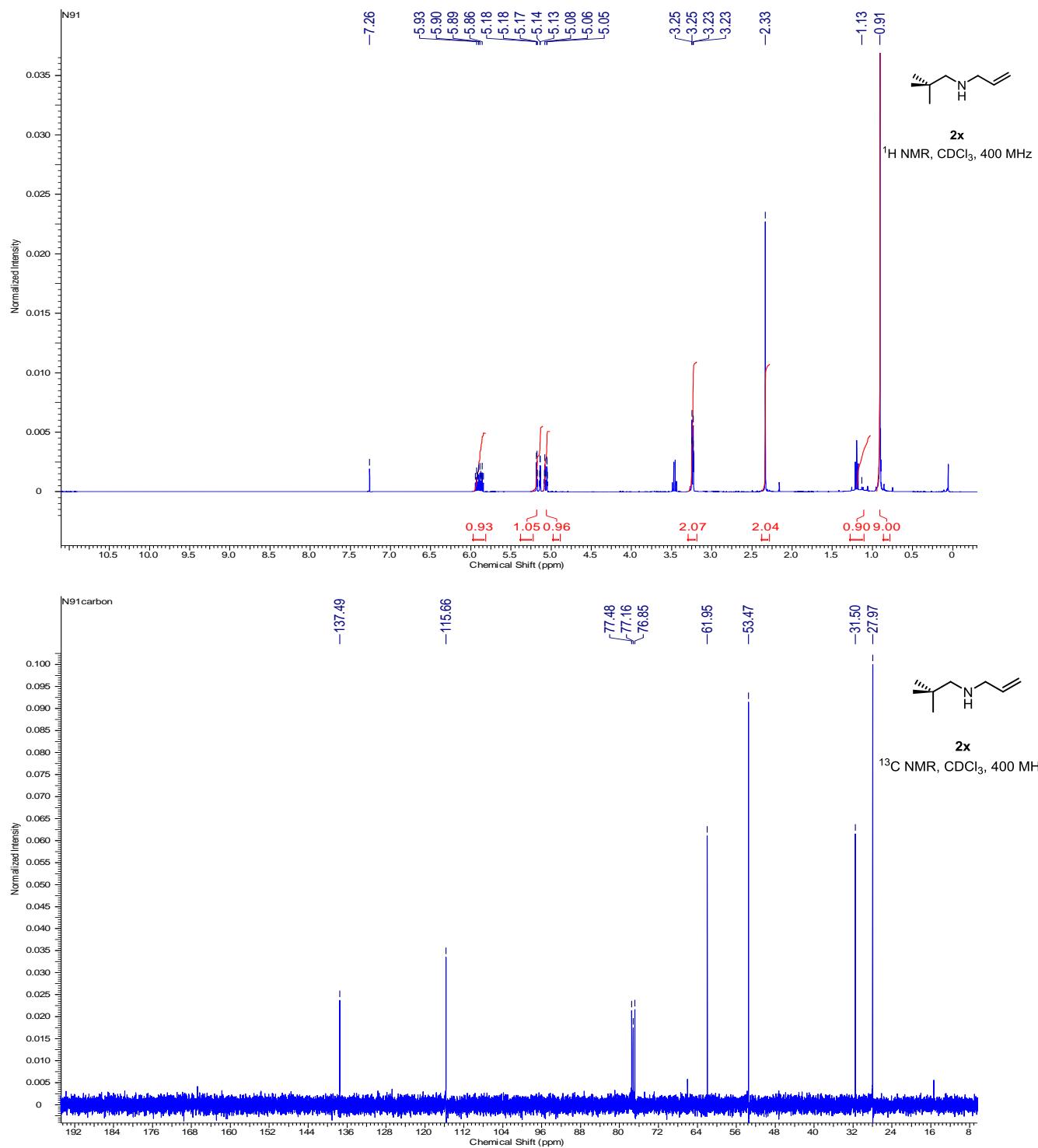


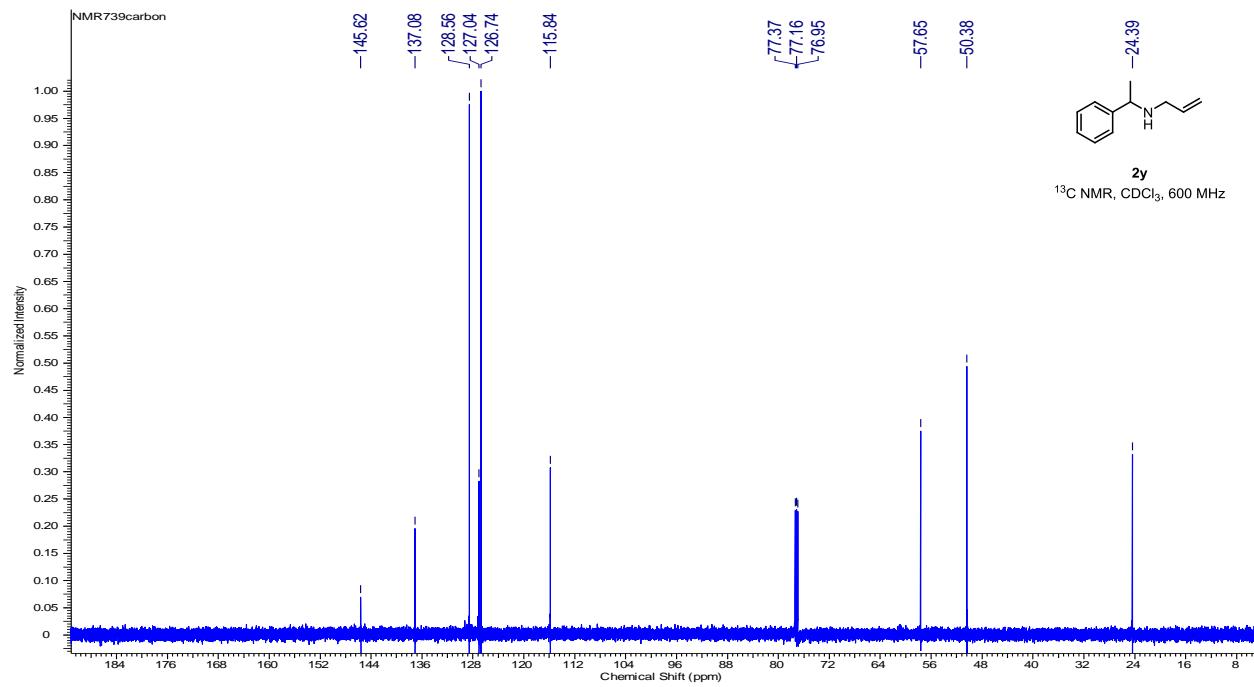
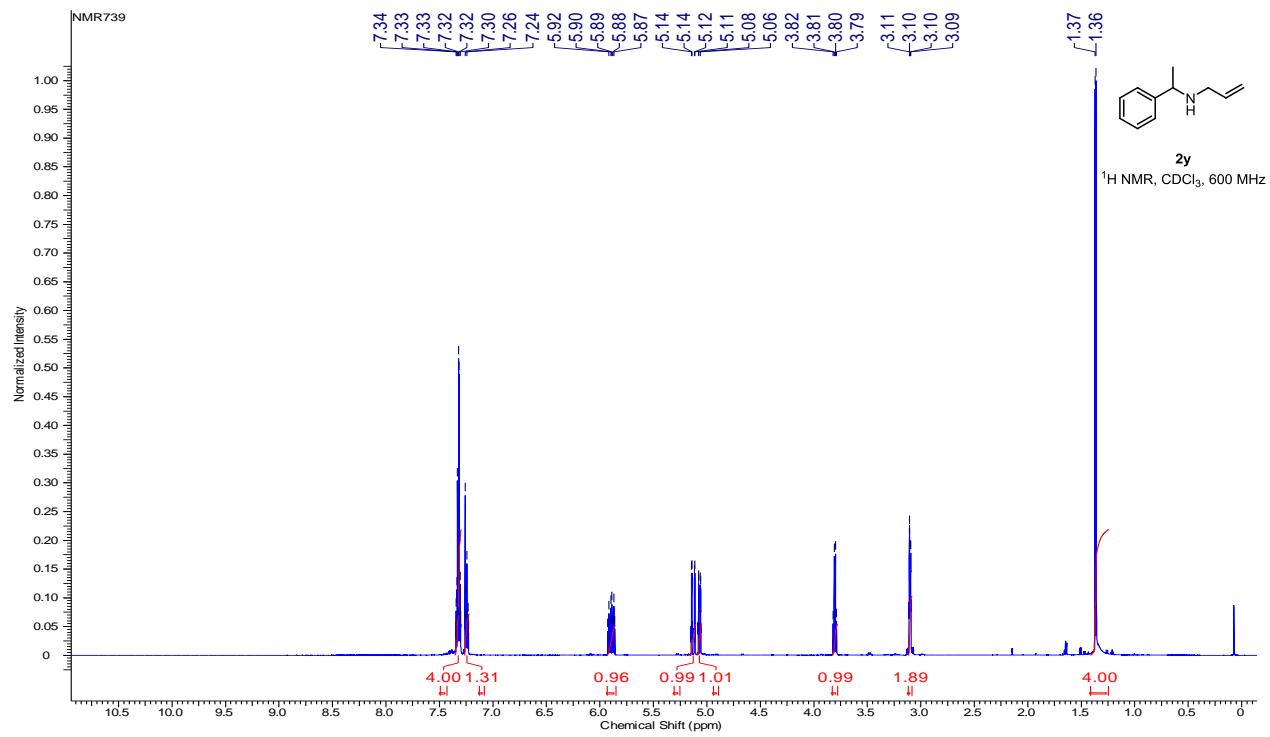


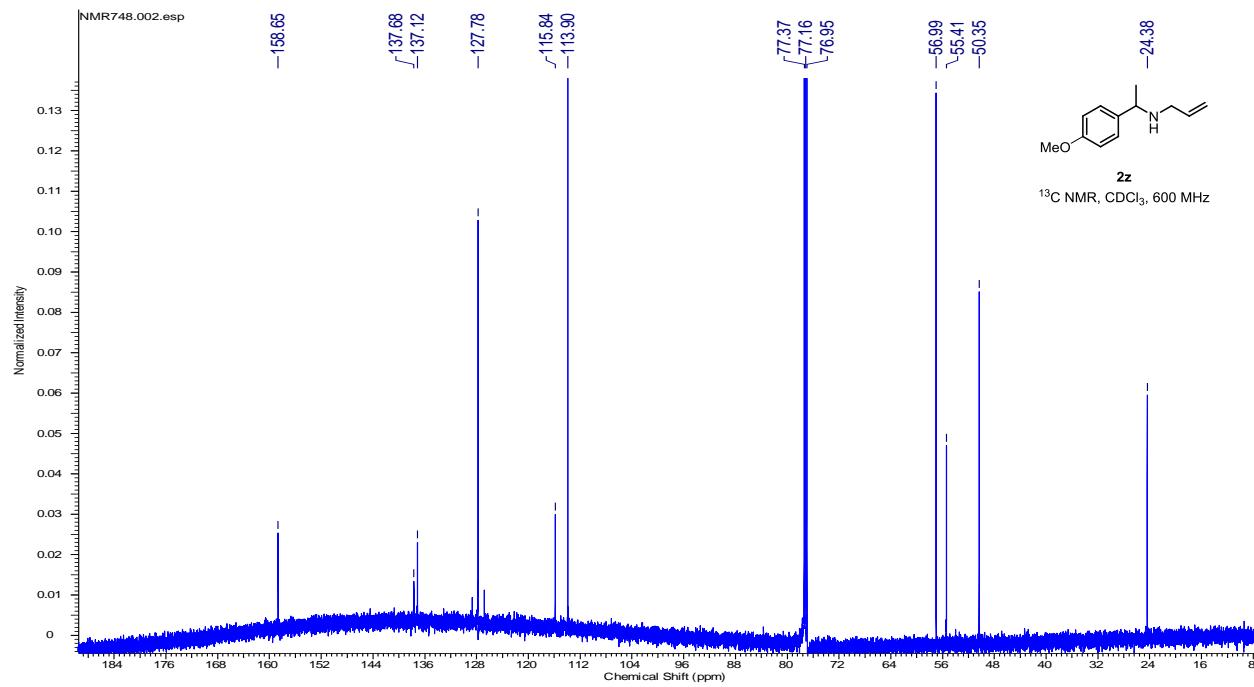
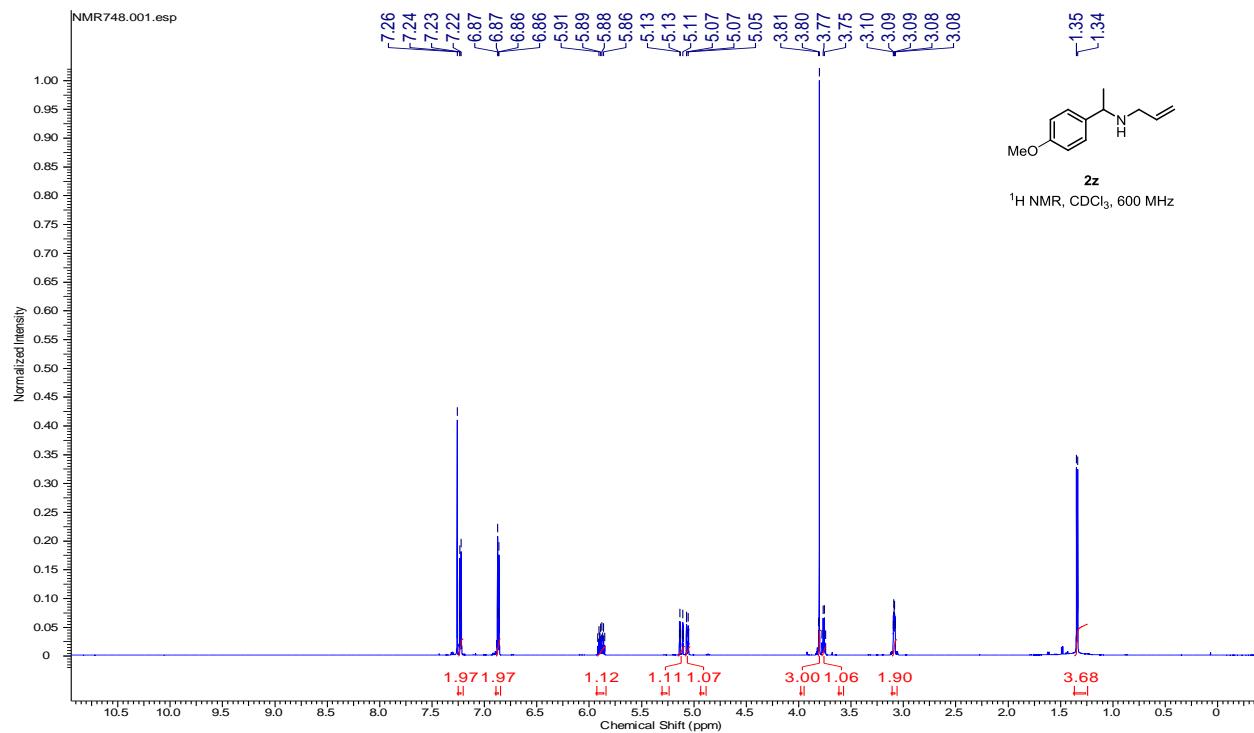


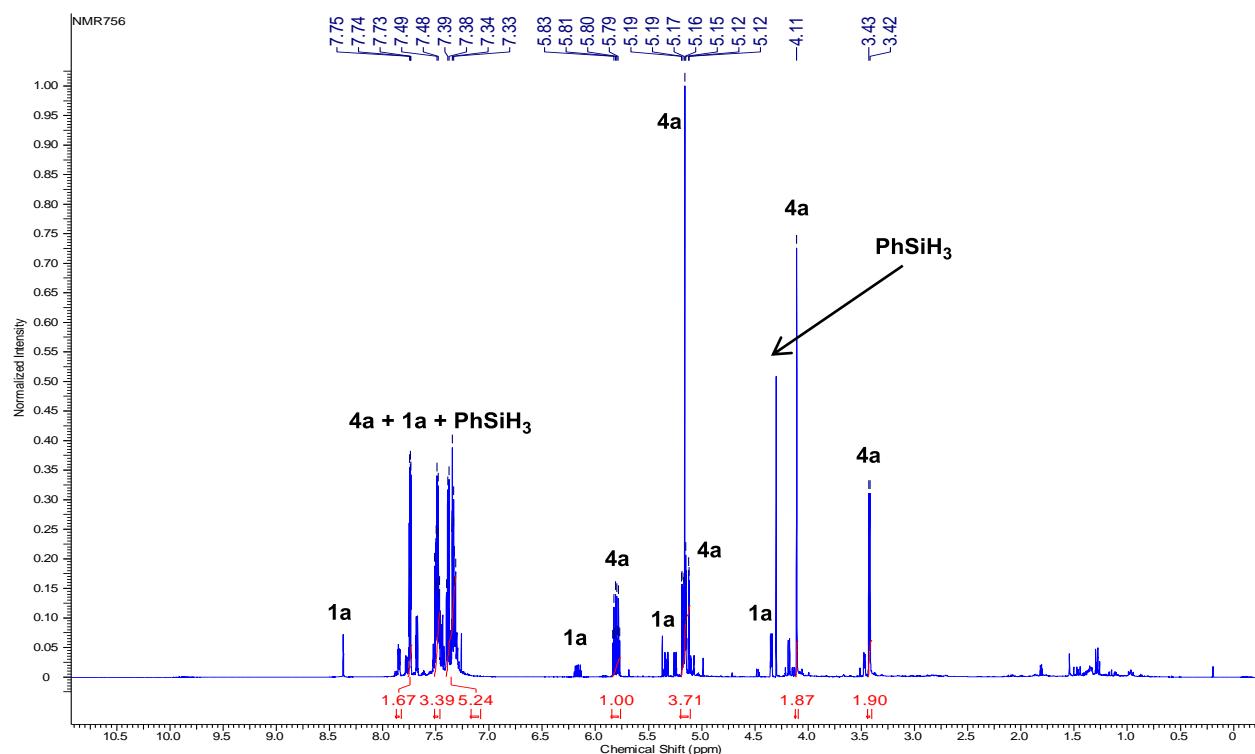
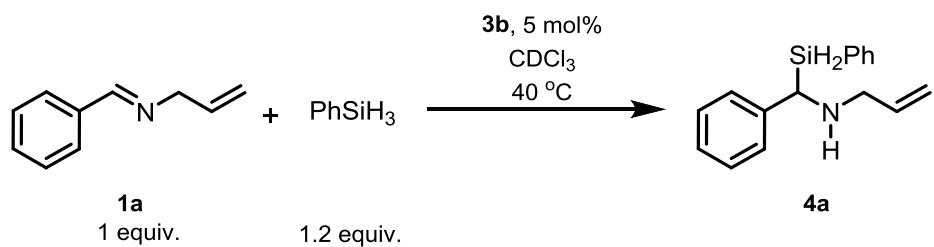












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