Electronic Supplementary Information

Ruthenium-Catalyzed C-H Allylation of Arenes with Allylic Amines

Rui Yan[†] and Zhong-Xia Wang[*,†,‡]

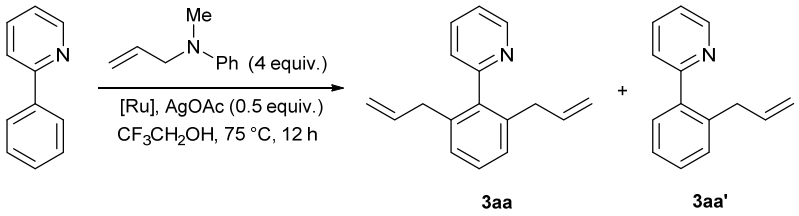
[†] *CAS Key Laboratory of Soft Matter Chemistry and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China*

[‡] *Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, People's Republic of China*

E-mail: zxwang@ustc.edu.cn; Tel: 86 551 63603043

Content

1. Table S1. The Ru catalyst screening[a]



Entry	Catalyst (mol%)	Yield (%) **3aa** (**3aa'**)
1	$RuH_2(CO)(PPh_3)_3$ (10)	–
2	$Cp^*Ru(PPh_3)_2Cl$ (10)	trace
3	$RuCl_2(PPh_3)_3$ (10)	0 (7)
4	$[Cp^*RuCl]_4$ (2.5)	–

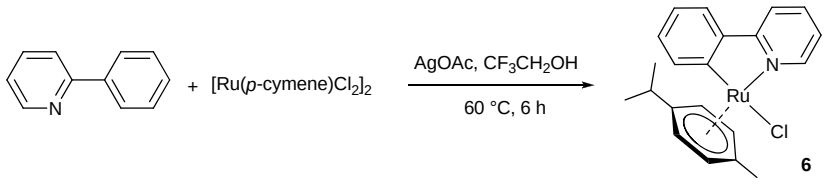
[a] The reactions were carried out on a 0.2 mmol scale according to the conditions indicated by above equation.

2. Ru-catalyzed reaction of 2-phenylpyridine with *N*-allyl-*N*-methylaniline on a 4 mmol scale

2-Phenylpyridine (0.62 g, 4 mmol), *N*-allyl-*N*-methylaniline (2.36 g, 16 mmol), AgOAc (0.334 g, 2 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (0.124 g, 0.2 mol), and CF_3CH_2OH (20 cm^3) were successively added into a Schlenk tube. The mixture was stirred at 75°C for 12 hours. Upon cooling to room temperature, the reaction mixture was diluted with EtOAc and filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel using EtOAc/petroleum ether 1/20 (v/v) as eluent to afford **3aa** as colorless oil (0.8273 g, 88%).

3. Mechanism study

3.1 Reaction of 2-phenylpyridine with [Ru(p-cymene)Cl$_2$]$_2$



2-Phenylpyridine (155.0 mg, 1.0 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (61.2 mg, 0.1 mmol), AgOAc (16.7 mg, 0.1 mmol) and CF_3CH_2OH (5 cm^3) were added to a Schlenk tube. The mixture was stirred at 60 °C for 6 hours and then cooled to room temperature. The resulting solution was concentrated under vacuum to remove solvent. The residue was purified by column

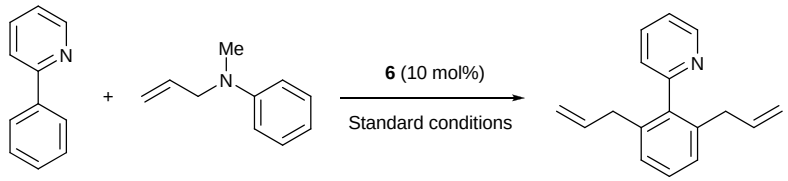
chromatography to give **6** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.23 (d, *J* = 5.6 Hz, 1H), 8.16 (d, *J* = 7.4 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.68–7.58 (m, 2H), 7.21-7.14 (m, 1H), 7.08–6.99 (m, 2H), 5.62–5.52 (m, 2H), 5.17 (d, *J* = 5.9 Hz, 1H), 4.98 (d, *J* = 5.8 Hz, 1H), 2.50–2.38 (m, 1H), 2.04 (s, 3H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 181.47, 165.41, 154.70, 143.43, 139.67, 136.73, 129.56, 123.97, 122.59, 121.51, 118.88, 100.72, 100.55, 90.84, 89.72, 84.23, 82.30, 30.88, 22.63, 21.81 18.86. The spectral data matched the values reported in literature.[1]

*3.2 Reaction of complex **6** with N-allyl-N-methylaniline*

Complex **6** (85 mg, 0.2 mmol), *N*-allyl-*N*-methylaniline (118 mg, 0.8 mmol), AgOAc (16.7 mg, 0.1 mmol), and CF_3CH_2OH (1.5 cm^3) were successively added into a Schlenk tube. The mixture was stirred at 75 °C for 12 hours and then cooled to room temperature. The mixture was diluted with EtOAc and filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: EtOAc/petroleum ether 1/20) to afford the desired product **3aa** (13.7 mg, 29%).

*3.3 Complex **6**-catalyzed allylation reactions*

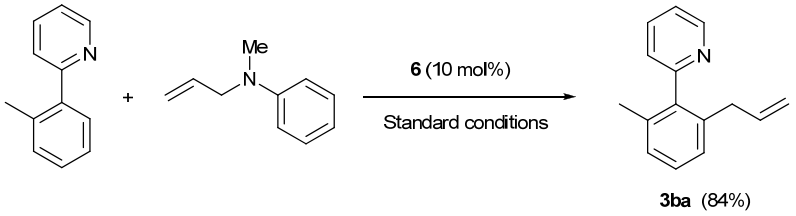
(1) Complex **6**-catalyzed reaction of 2-phenylpyridine with *N*-allyl-*N*-methylaniline



3aa (89%)

2-Phenylpyridine (31 mg, 0.2 mmol), *N*-allyl-*N*-methylaniline (118 mg, 0.8 mmol), AgOAc (16.7 mg, 0.1 mmol), complex **6** (8.5 mg, 0.02 mol), and CF_3CH_2OH (1.5 cm^3) were successively added into a Schlenk tube. The mixture was stirred at 75 °C for 12 hours and then cooled to room temperature. The resulting mixture was diluted with EtOAc and filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel using EtOAc/petroleum ether 1/20 (v/v) as eluent to afford pure product **3aa** (41.9 mg, 89%).

(2) Complex **6**-catalyzed reaction of 2-(*o*-tolyl)pyridine with *N*-allyl-*N*-methylaniline



3ba (84%)

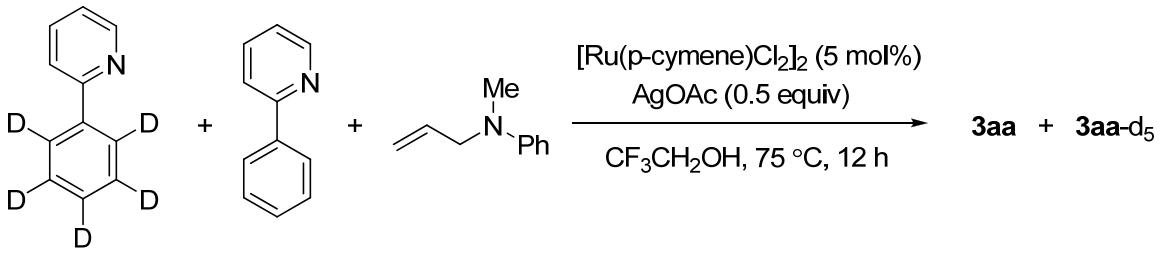
2-(*o*-Tolyl)pyridine (33.8 mg, 0.2 mmol), *N*-allyl-*N*-methylaniline **2a** (59 mg, 0.4 mmol), AgOAc (16.7 mg, 0.1 mmol), complex **6** (8.5 mg, 0.02 mol), and CF_3CH_2OH (1.5 cm^3) were successively added into a Schlenk tube. The mixture was stirred at 75 °C for 12 hours and then cooled to room temperature. The resulting mixture was diluted with EtOAc and filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel using EtOAc/petroleum ether 1/20 (v/v) as eluent to afford pure product **3ba** (35.2 mg, 84%).

3.4 Determination of intermolecular kinetic isotope effect (KIE)

(1) Synthesis of 2-(pentadeuteriophenyl)pyridine (**1a**-d_5)

Bromobenzene-d_5 (0.972 g, 6 mmol) was added slowly to a mixture of Mg turnings (0.144 g, 6 mmol), THF (20 cm^3) and a grain of iodine. The resulting mixture was stirred at room temperature for 3 hours. The resulting solution was slowly added to a solution of 2-bromopyridine (0.632 g, 4 mmol) and Pd(dppf)Cl_2 (146.4 mg, 0.2 mol, 5 mol%) in THF (20 cm^3) at −42 °C over a period of 60 minutes. After stirring for additional 2 hours at room temperature the reaction was stopped by adding a saturate NH_4Cl solution (10 cm^3). The aqueous layer was extracted with ethyl acetate (3 × 40 cm^3). The combined organic phases was dried over Na_2SO_4, concentrated by rotary evaporation and purified by column chromatography on silica gel using EtOAc/petroleum ether 1/20 (v/v) as eluent to afford 2-(pentadeuteriophenyl)pyridine (**1a**-d_5) (0.544 g, 85%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 4.8 Hz, 1H), 7.72–7.66 (m, 2H), 7.23–7.14 (m, 1H). The spectral data were consistent with those reported in literature.[2]

(2) Determination of intermolecular kinetic isotope effect



Following our general procedure: 2-(pentadeuteriophenyl)pyridine (16.2 mg, 0.1 mmol), 2-phenylpyridine (15.5 mg, 0.1 mmol), *N*-allyl-*N*-methylaniline (118 mg, 0.8 mmol), AgOAc (16.7 mg, 0.1 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (6.2 mg, 0.01 mol), and CF_3CH_2OH (1.5 cm^3) were successively added into a Schlenk tube. The mixture was stirred at 75°C for 12 hours and then cooled to room temperature. The reaction mixture was diluted with EtOAc and filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography to afford a mixture of **3aa** and **3aa**-d_5. The ratio of **3aa** to **3aa**-d_5 was obtained via the integral of their ^{1}H NMR spectra. The intermolecular KIE was 1.1.

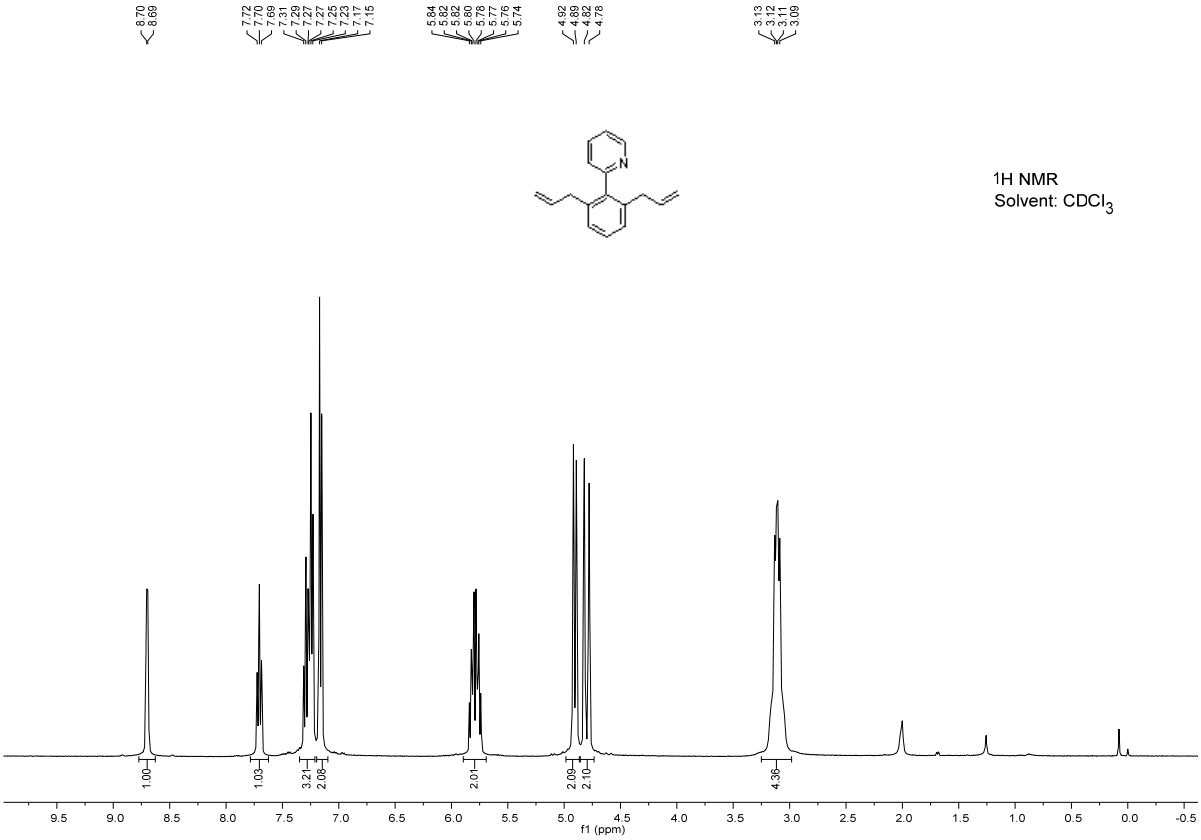
References

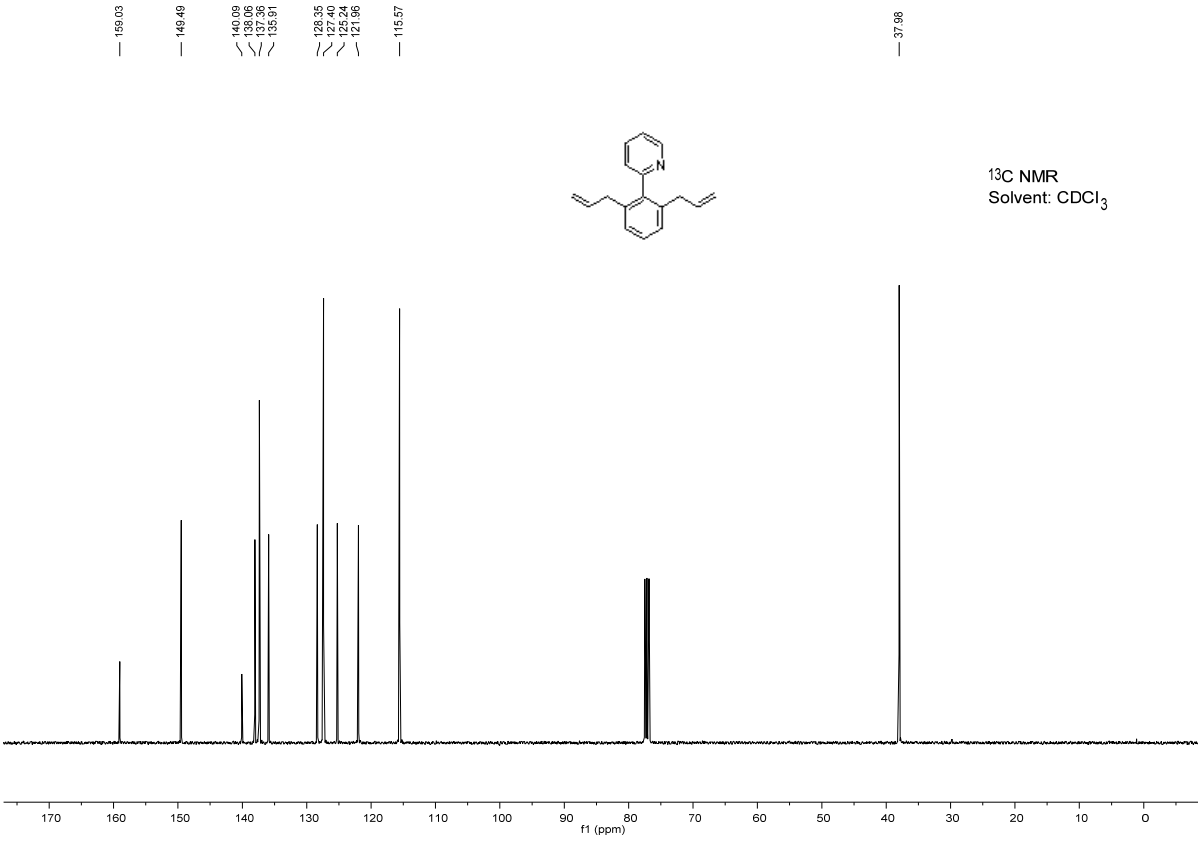
1 L. L. Zhang, L. H. Li, Wang, Y. Q. Y. F. Yang, X. Y. Liu, and Y. M. Liang, *Organometallics*, 2014, **33**, 1905.

2 J. Wippich, N. Truchan, and T. Bach, *Adv. Synth. Catal*., 2016, **358**, 2083.

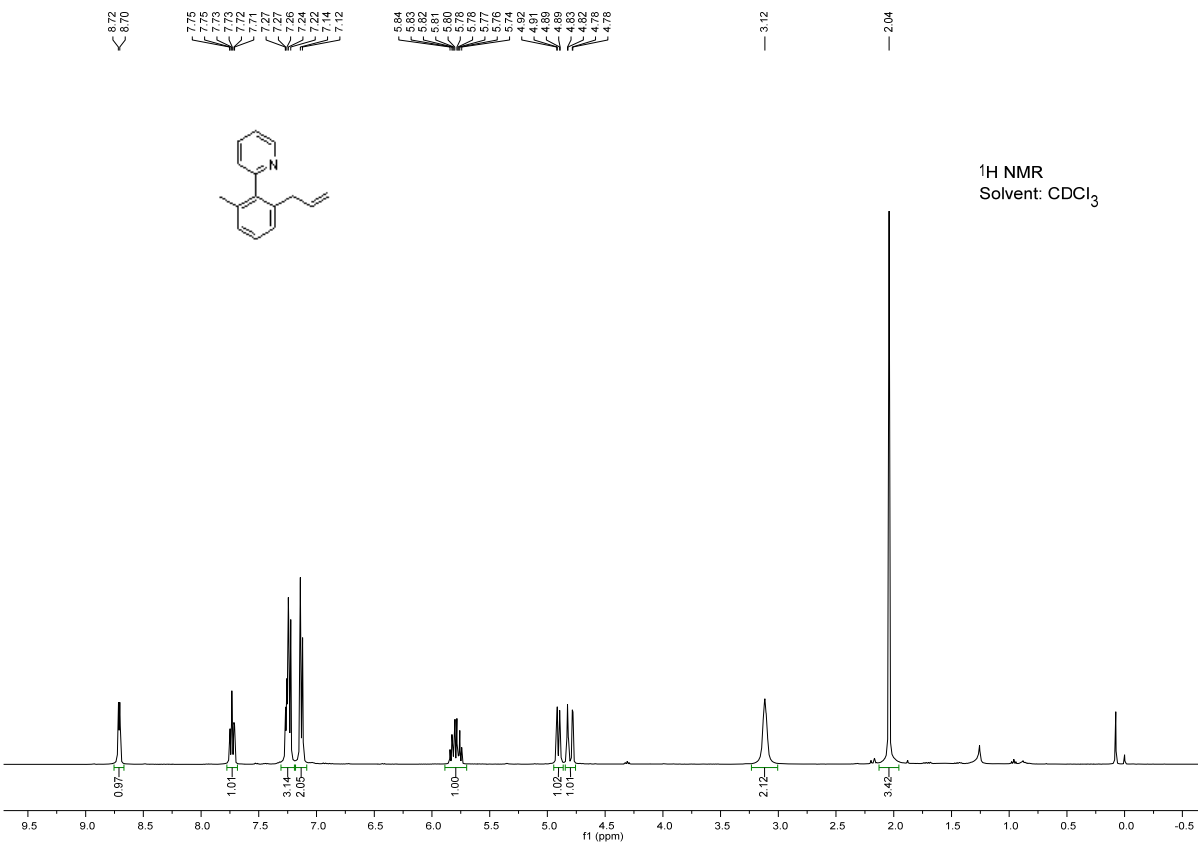
4. Copies of NMR spectra of the allylation products

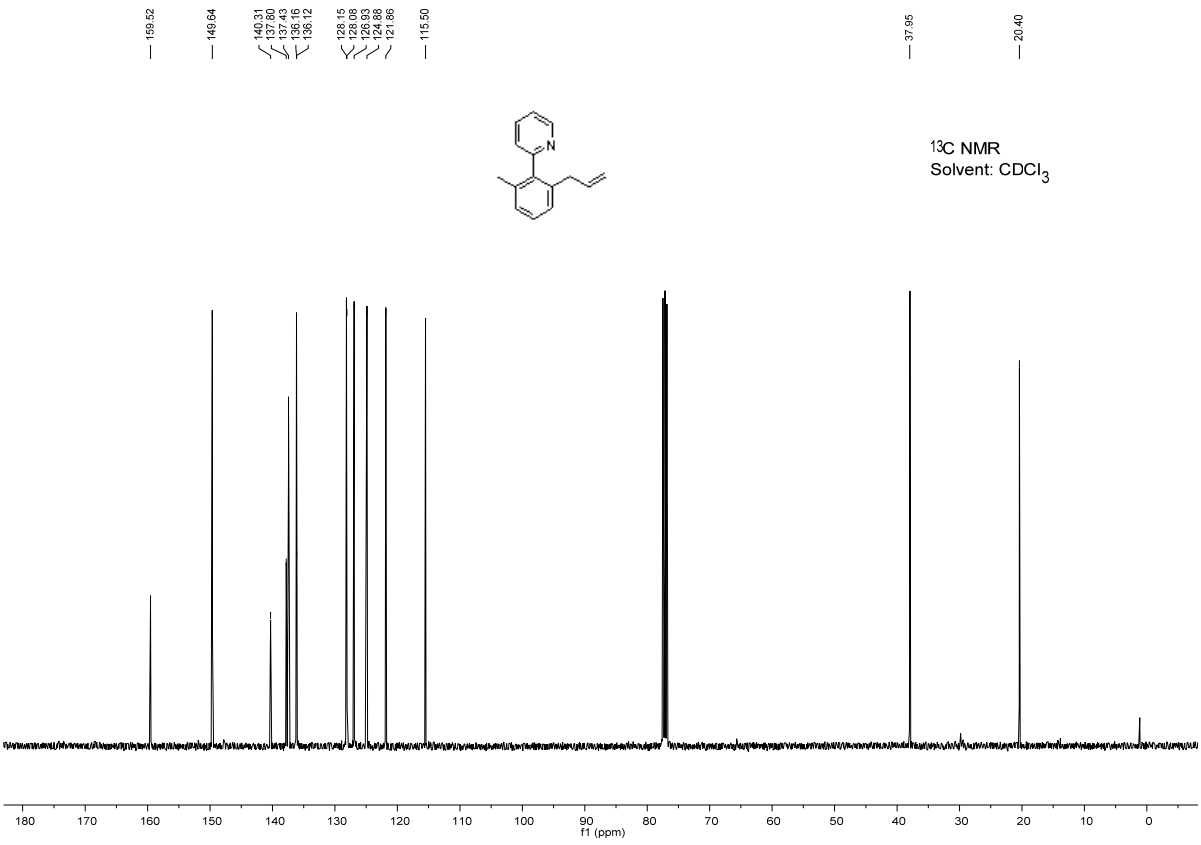
(1) 2-(2,6-diallylphenyl)pyridine (**3aa**)



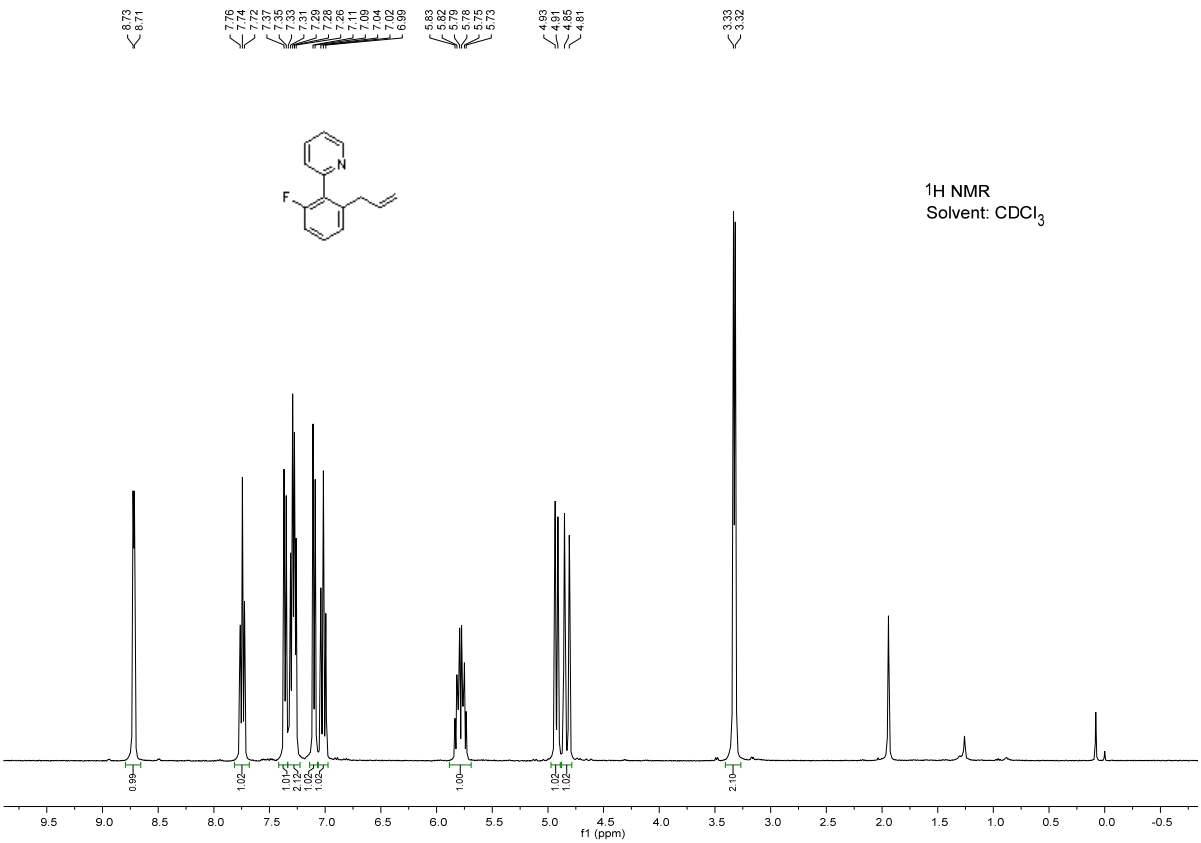


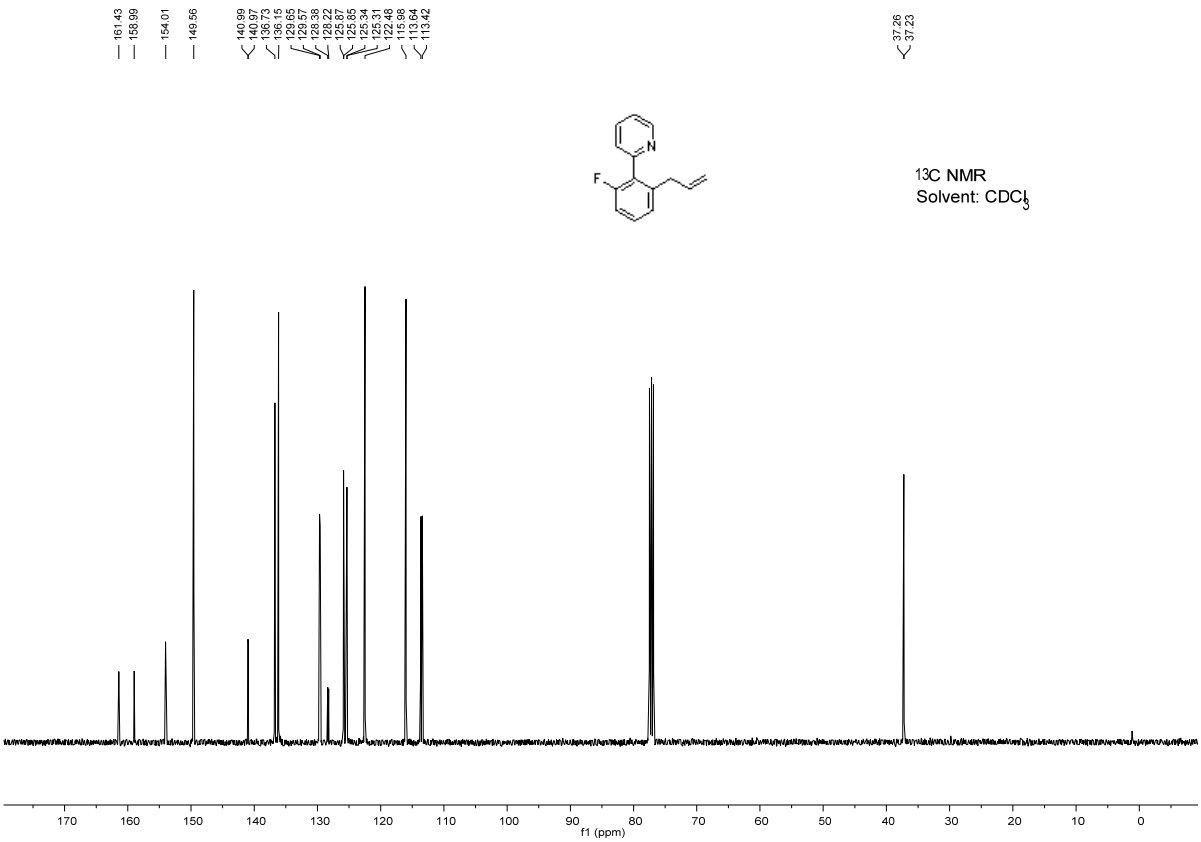
(2) 2-(2-allyl-6-methylphenyl)pyridine (**3ba**)

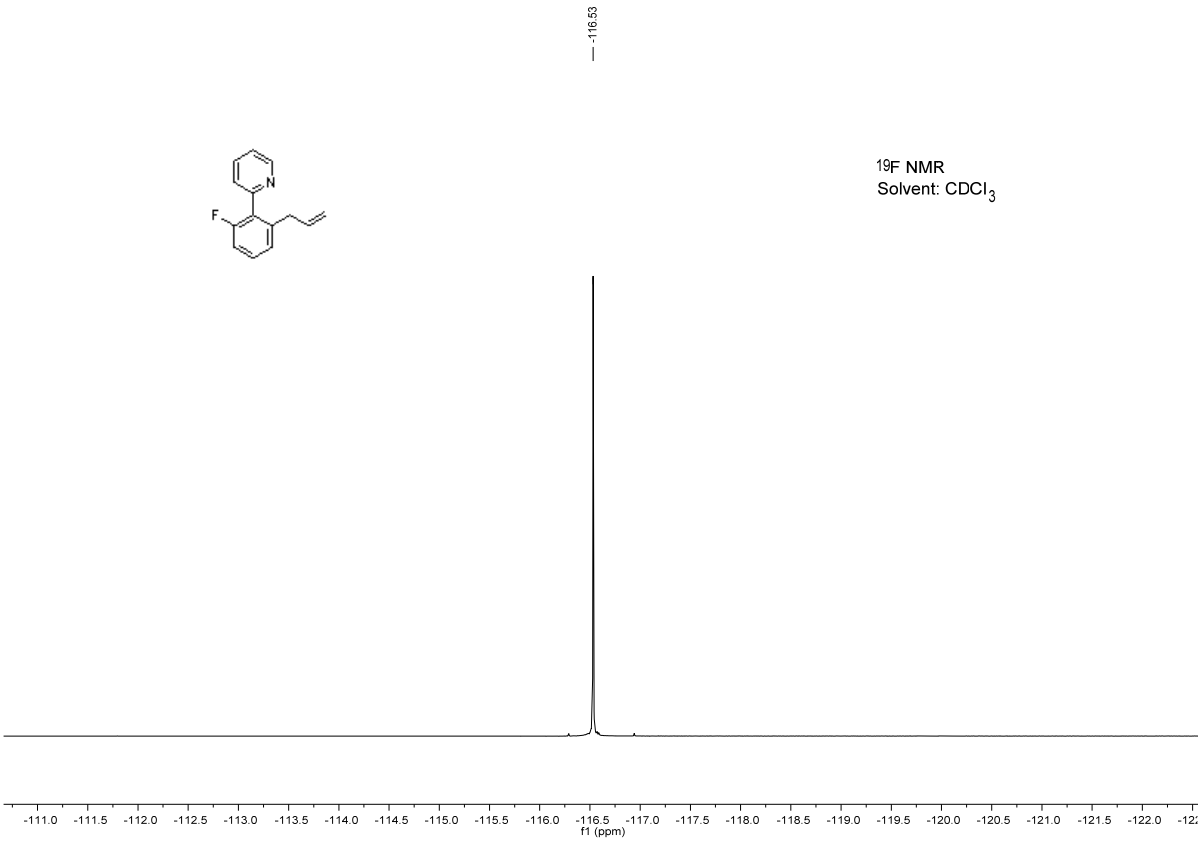




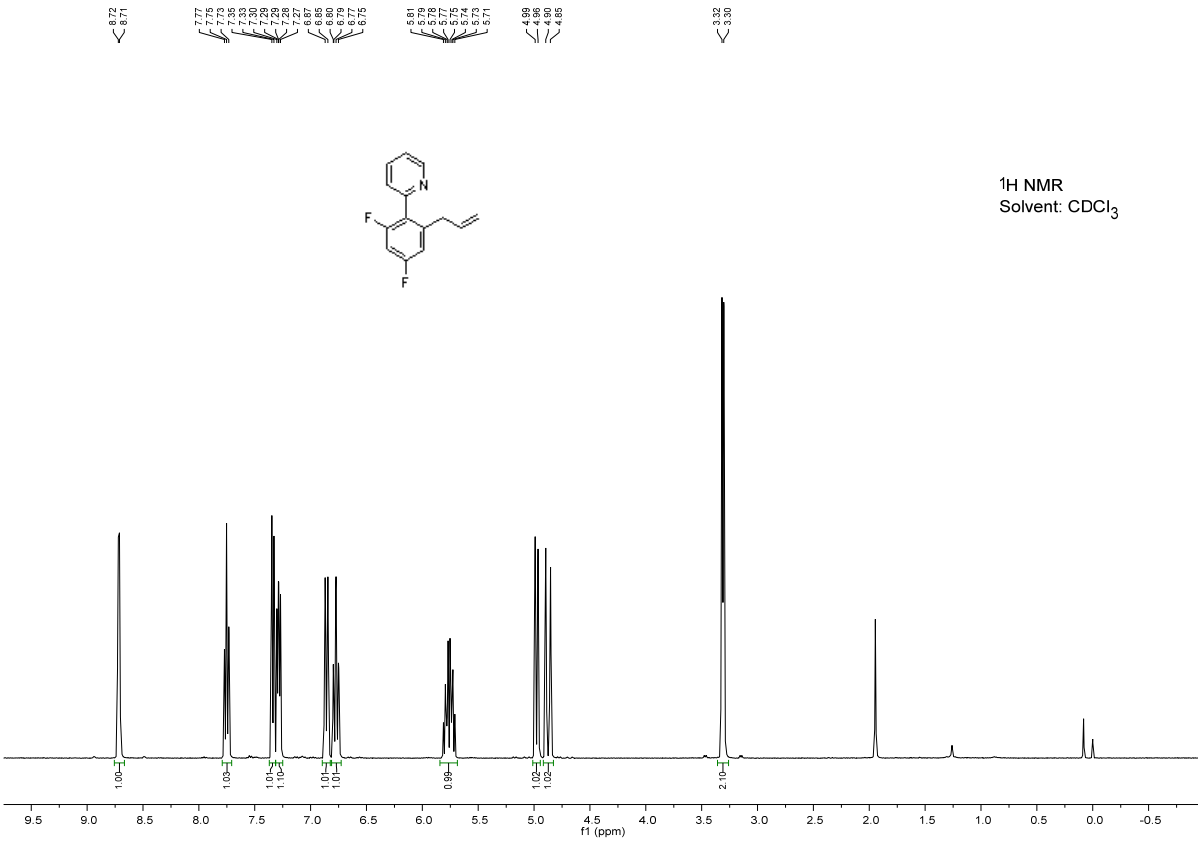
(3) 2-(2-allyl-6-fluorophenyl)pyridine (**3ca**)

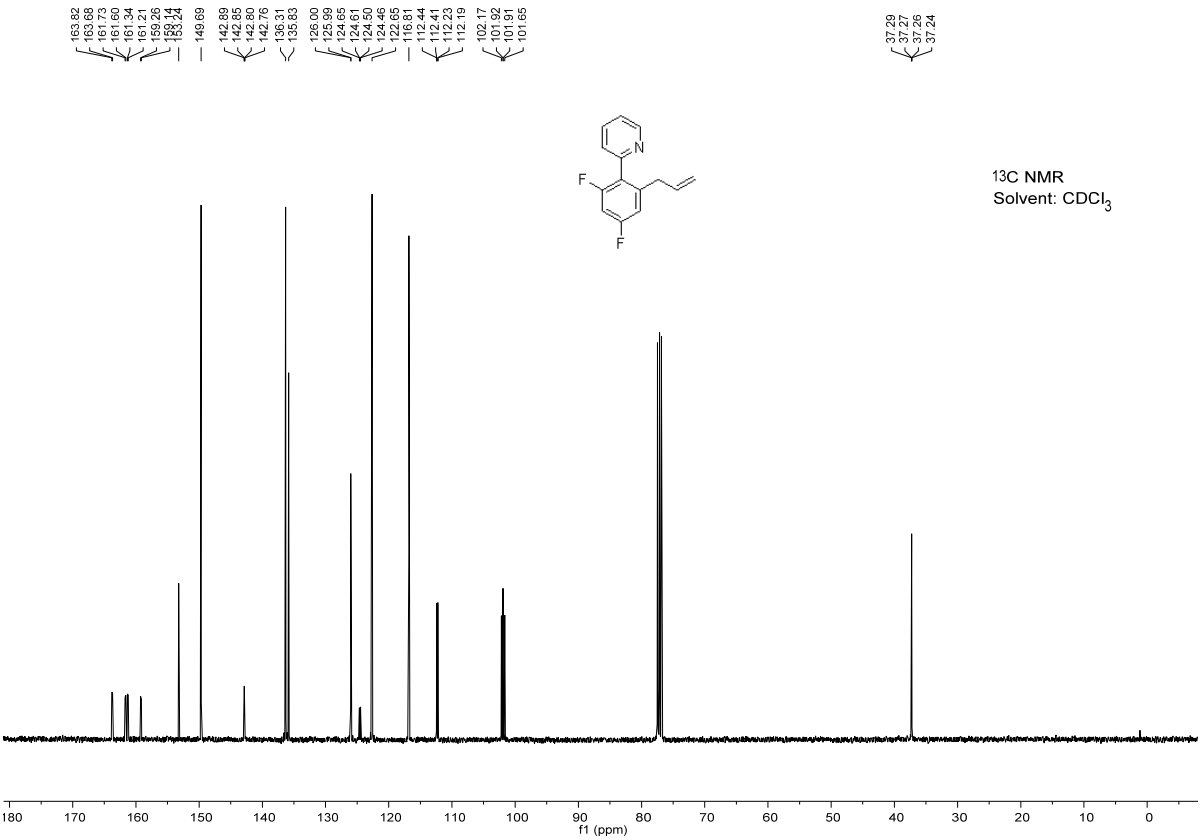


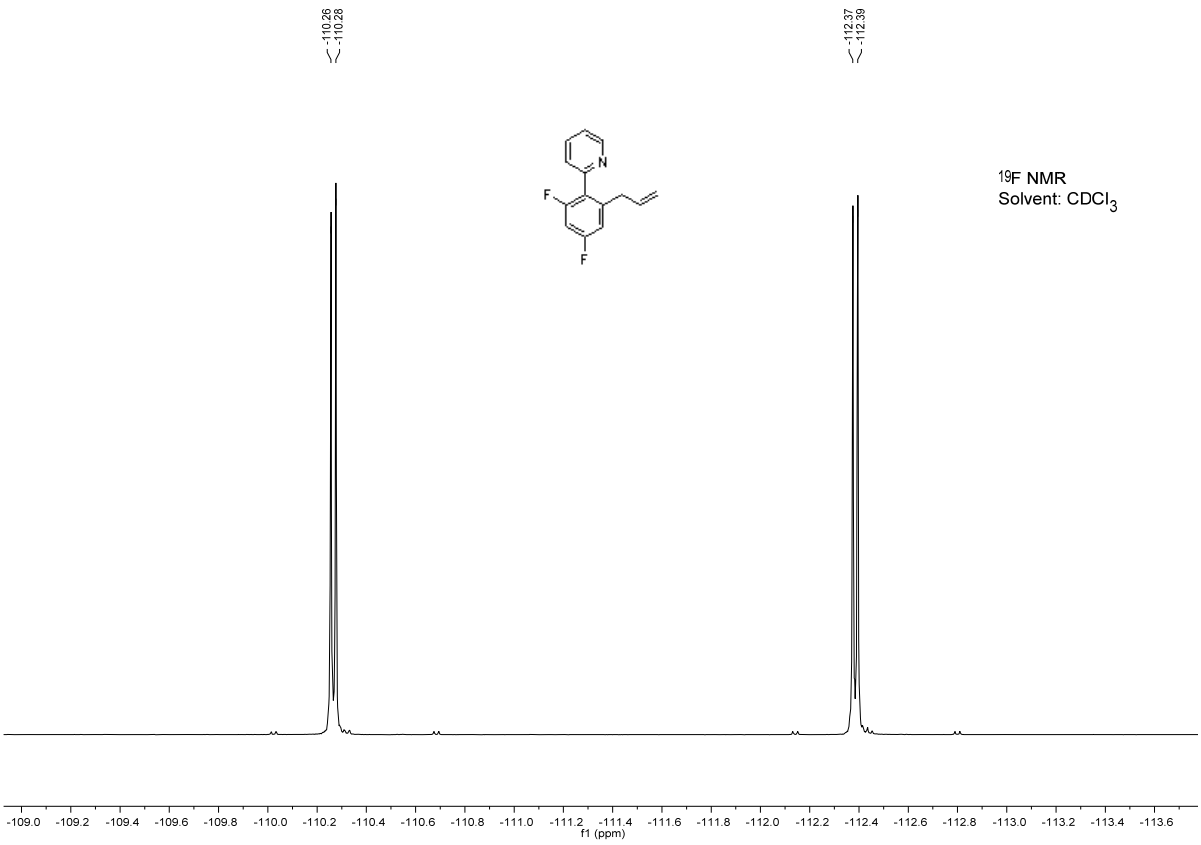



-116.53
N
F
19F NMR
Solvent: CDCl3
-111.0 -111.5 -112.0 -112.5 -113.0 -113.5 -114.0 -114.5 -115.0 -115.5 -116.0 -116.5 -117.0 -117.5 -118.0 -118.5 -119.0 -119.5 -120.0 -120.5 -121.0 -121.5 -122.0
f1 (ppm)

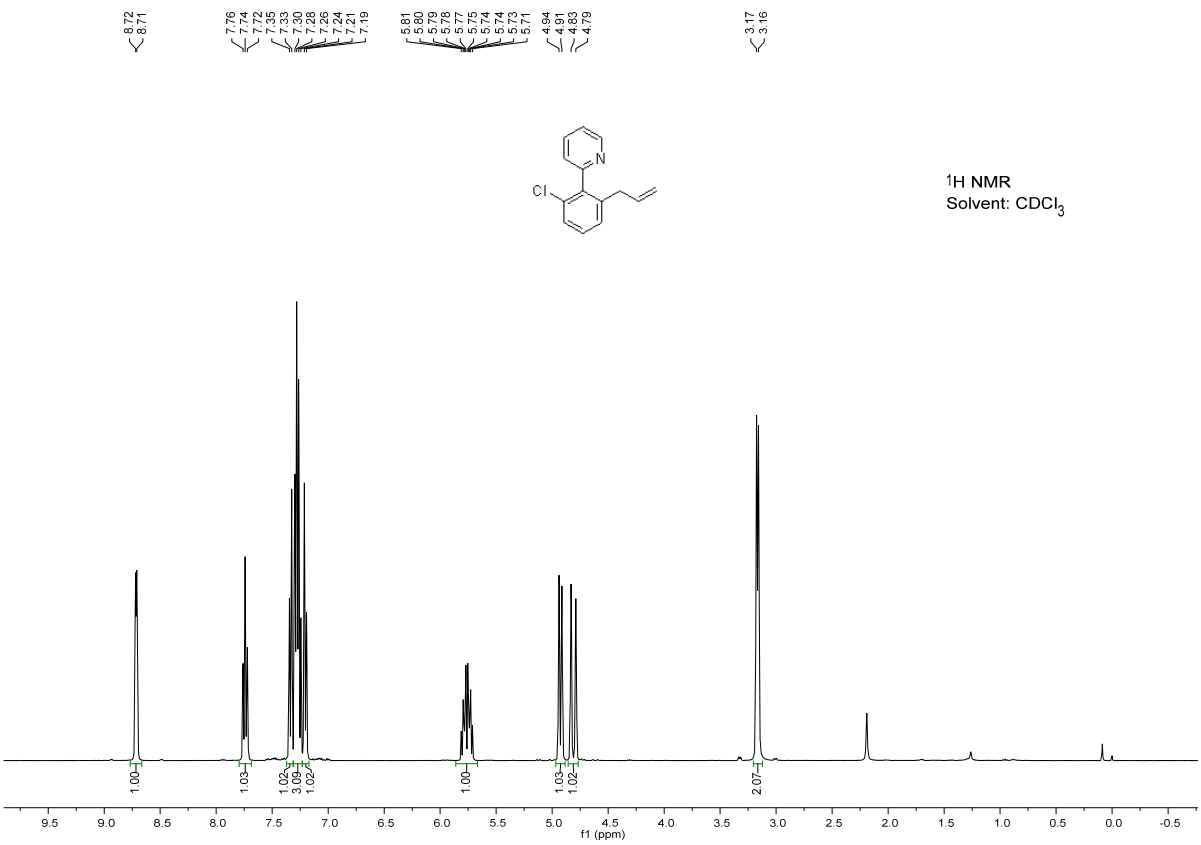
(4) 2-(2-allyl-4,6-difluorophenyl)pyridine (**3da**)

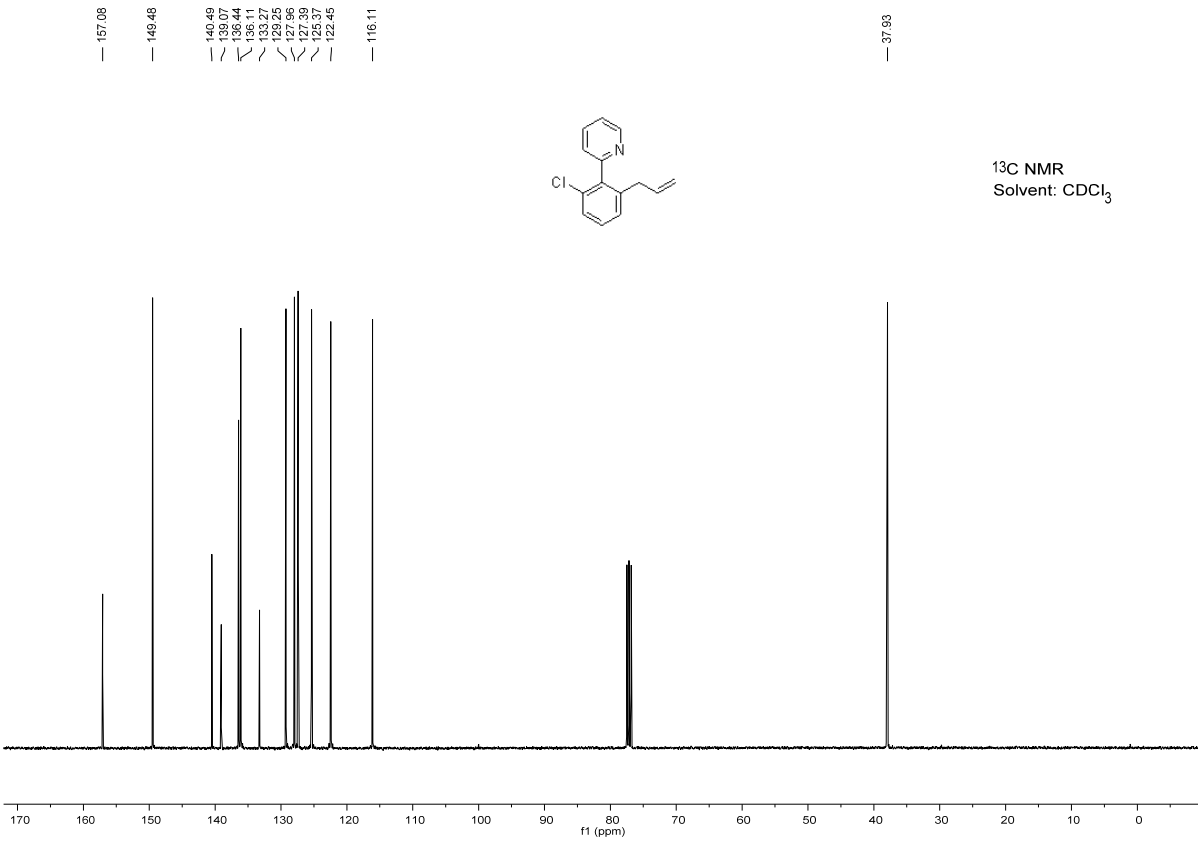




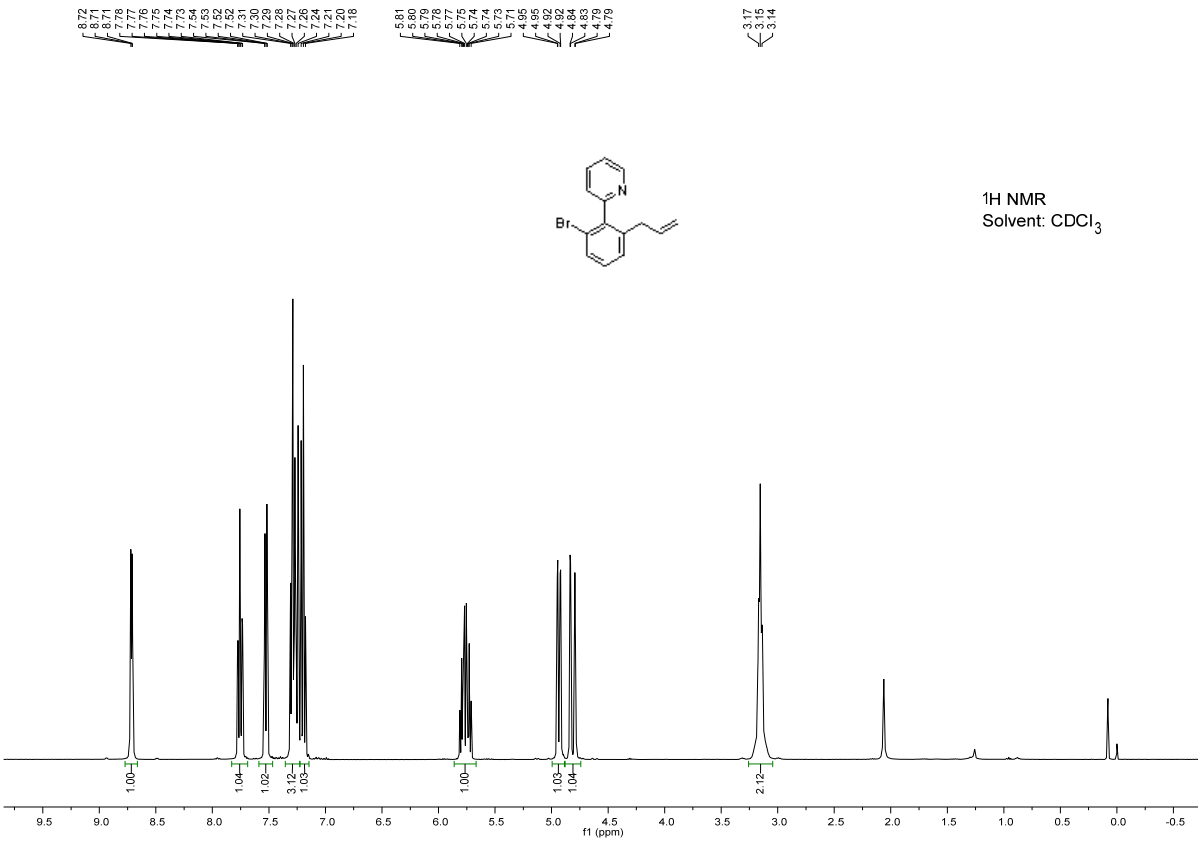

-110.26
-110.28
-112.37
-112.39
N
F
F
19F NMR
Solvent: CDCl3
-109.0 -109.2 -109.4 -109.6 -109.8 -110.0 -110.2 -110.4 -110.6 -110.8 -111.0 -111.2 -111.4 -111.6 -111.8 -112.0 -112.2 -112.4 -112.6 -112.8 -113.0 -113.2 -113.4 -113.6
f1 (ppm)

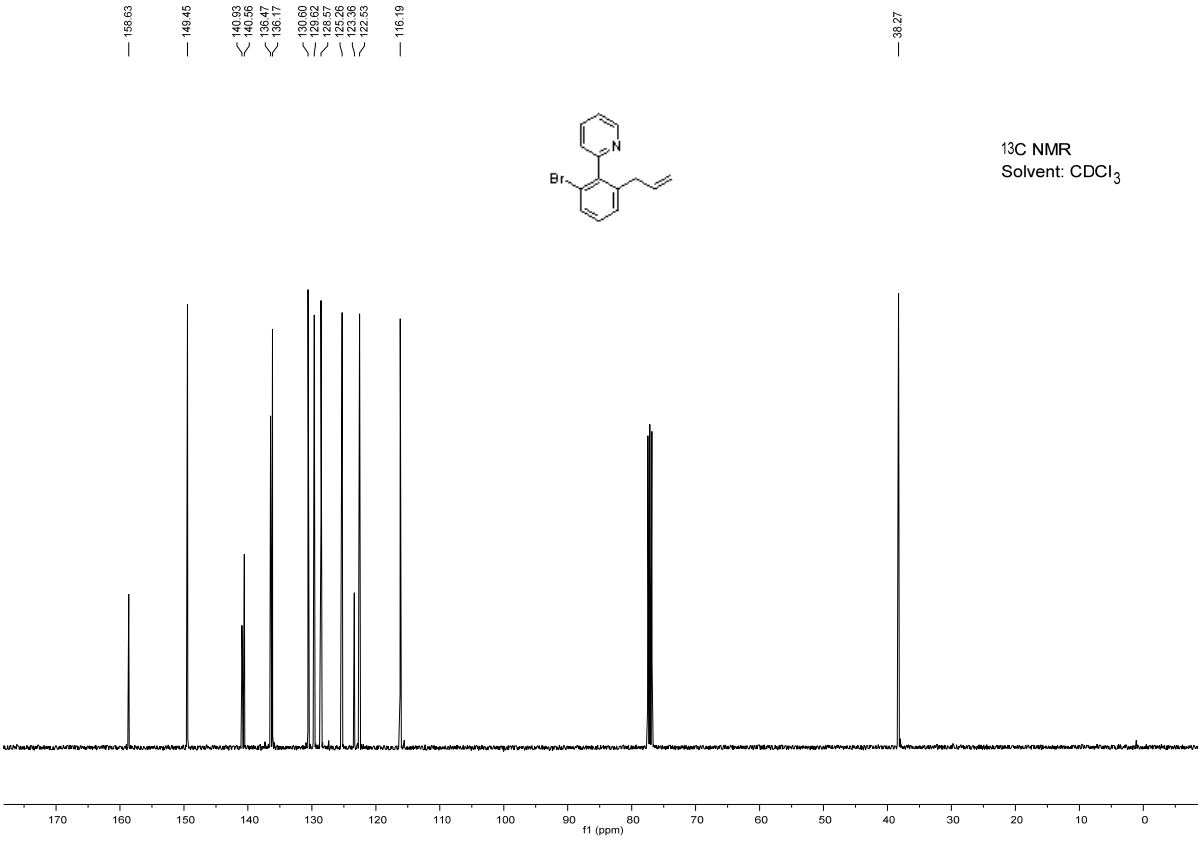
(5) 2-(2-allyl-6-chlorophenyl)pyridine (**3ea**)



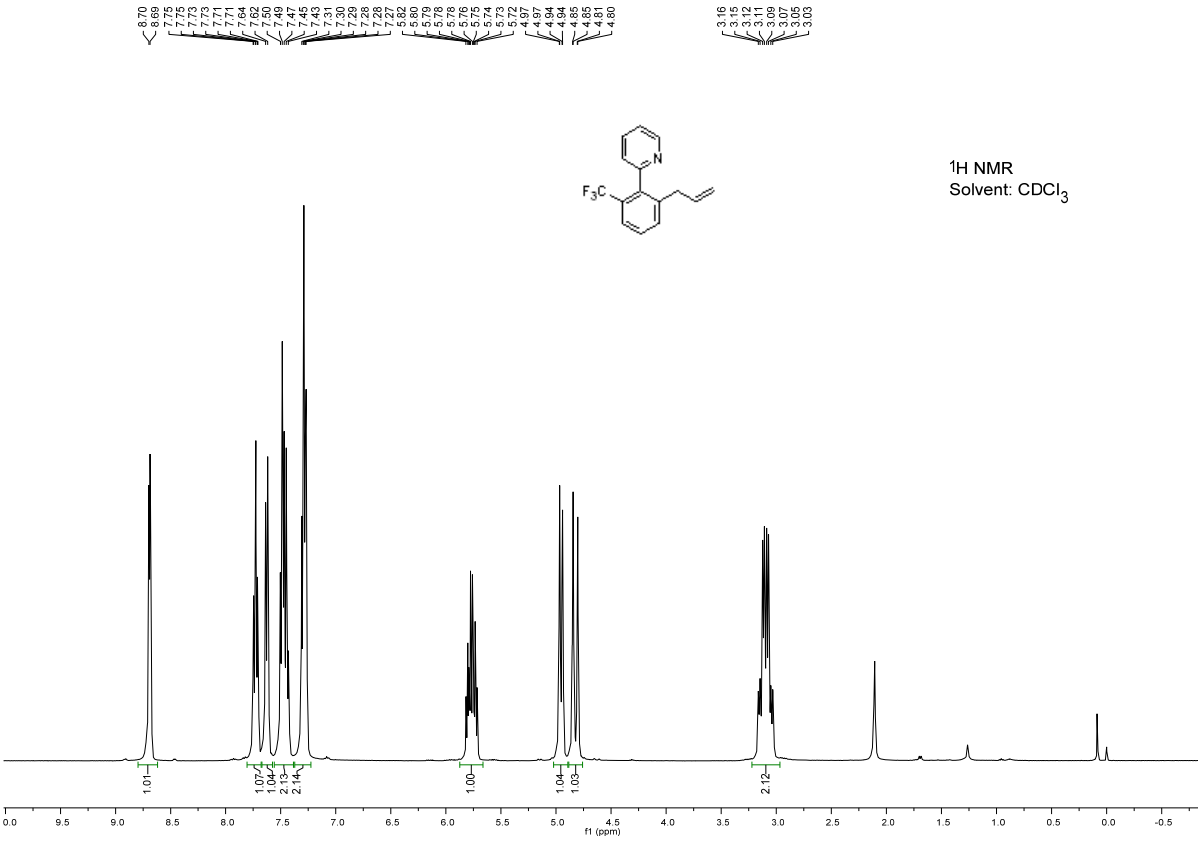


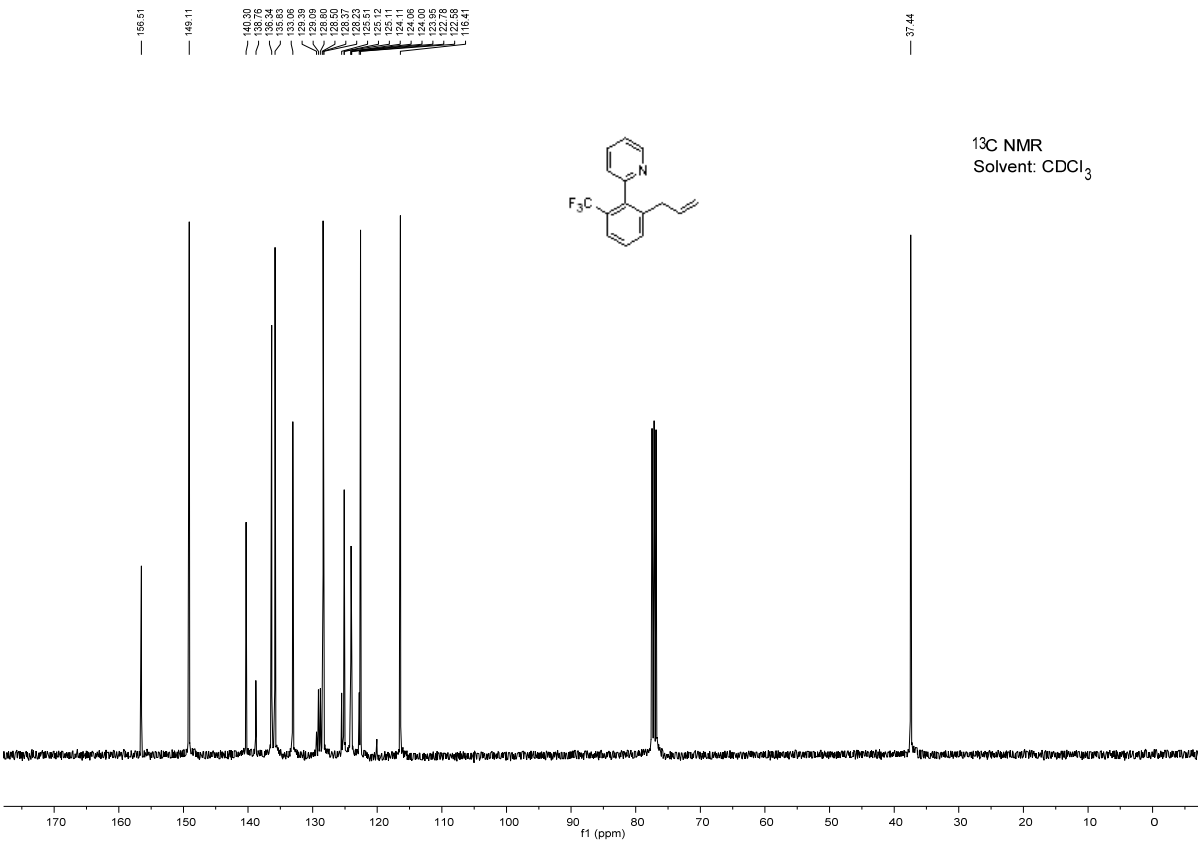
(6) 2-(2-allyl-6-bromophenyl)pyridine (**3fa**)

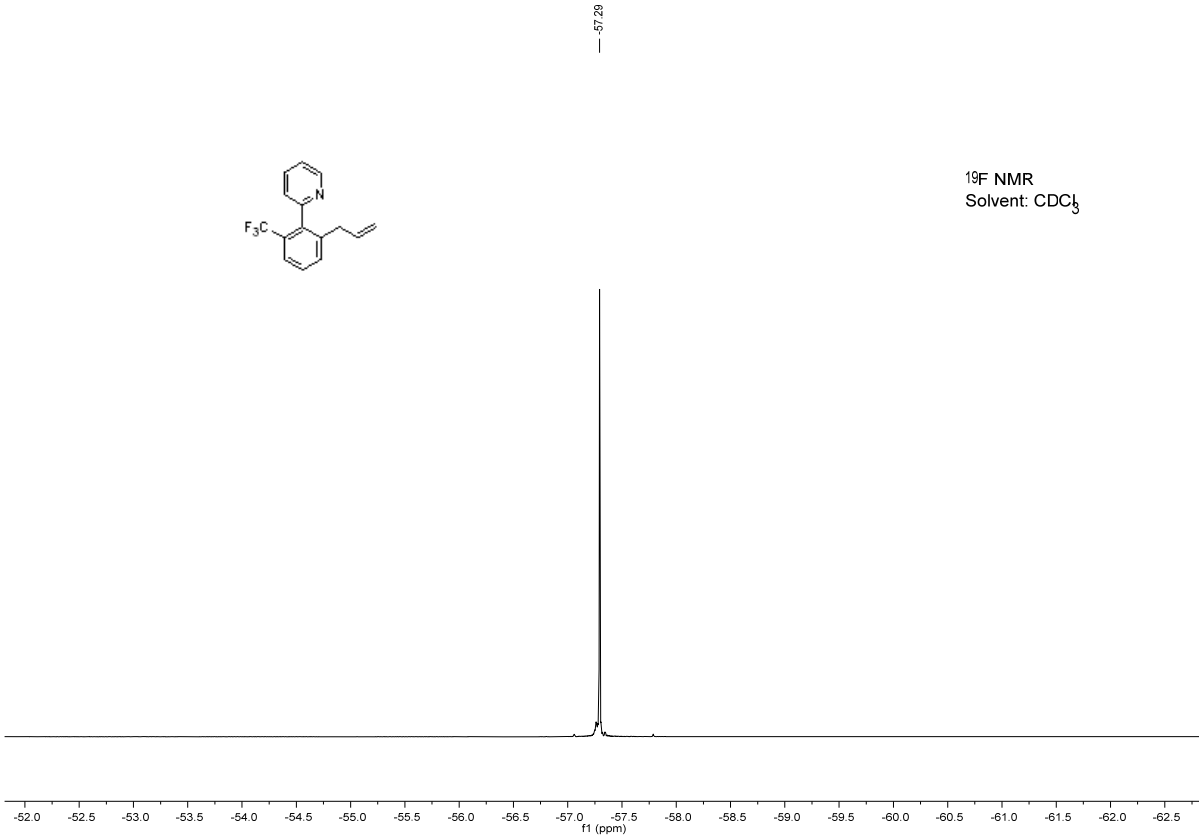




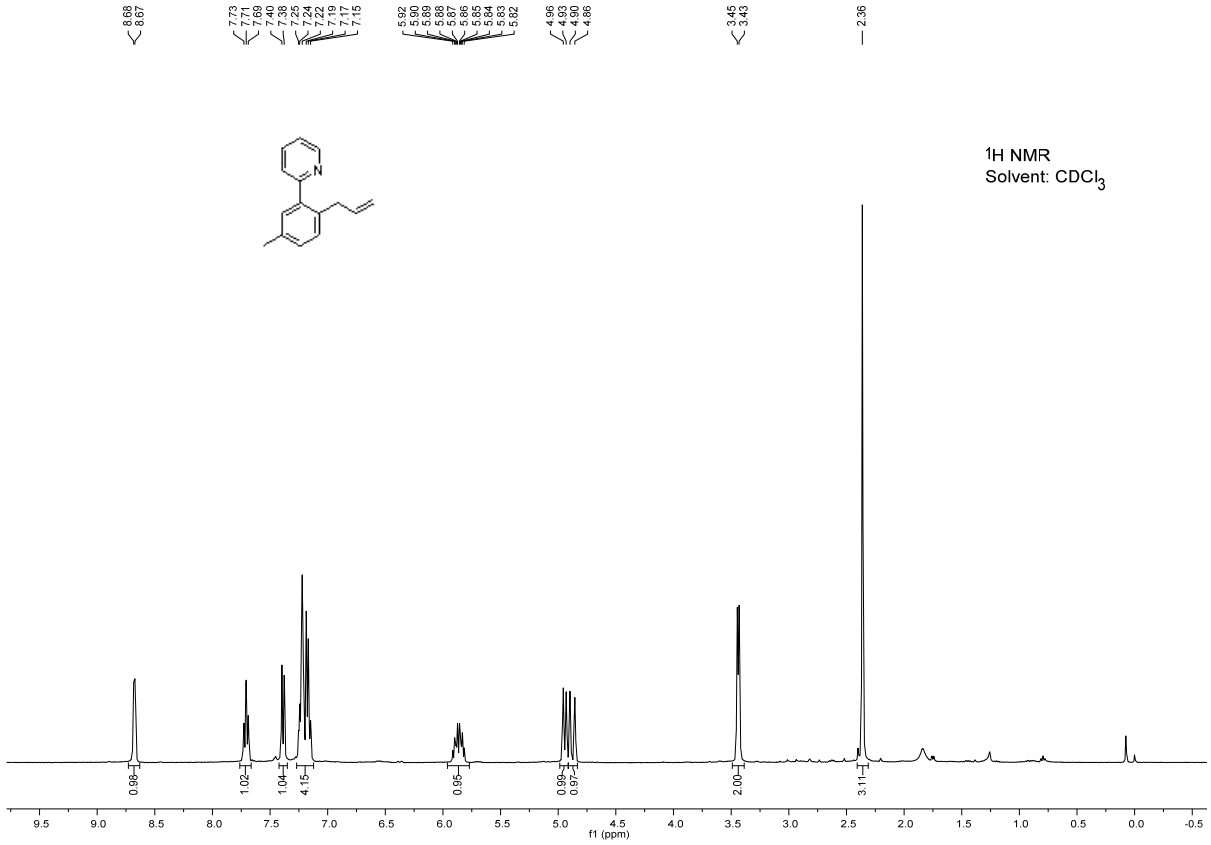
(7) 2-(2-allyl-6-(trifluoromethyl)phenyl)pyridine (**3ga**)

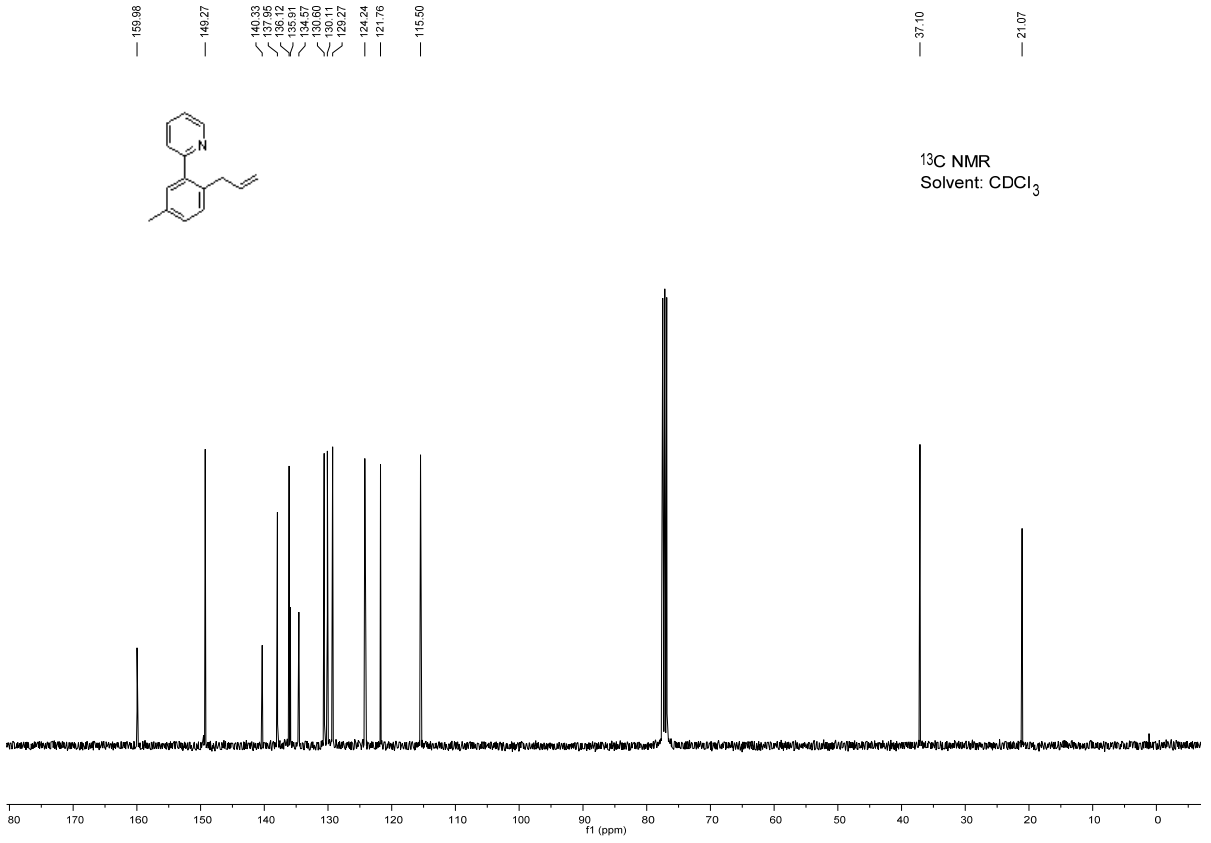




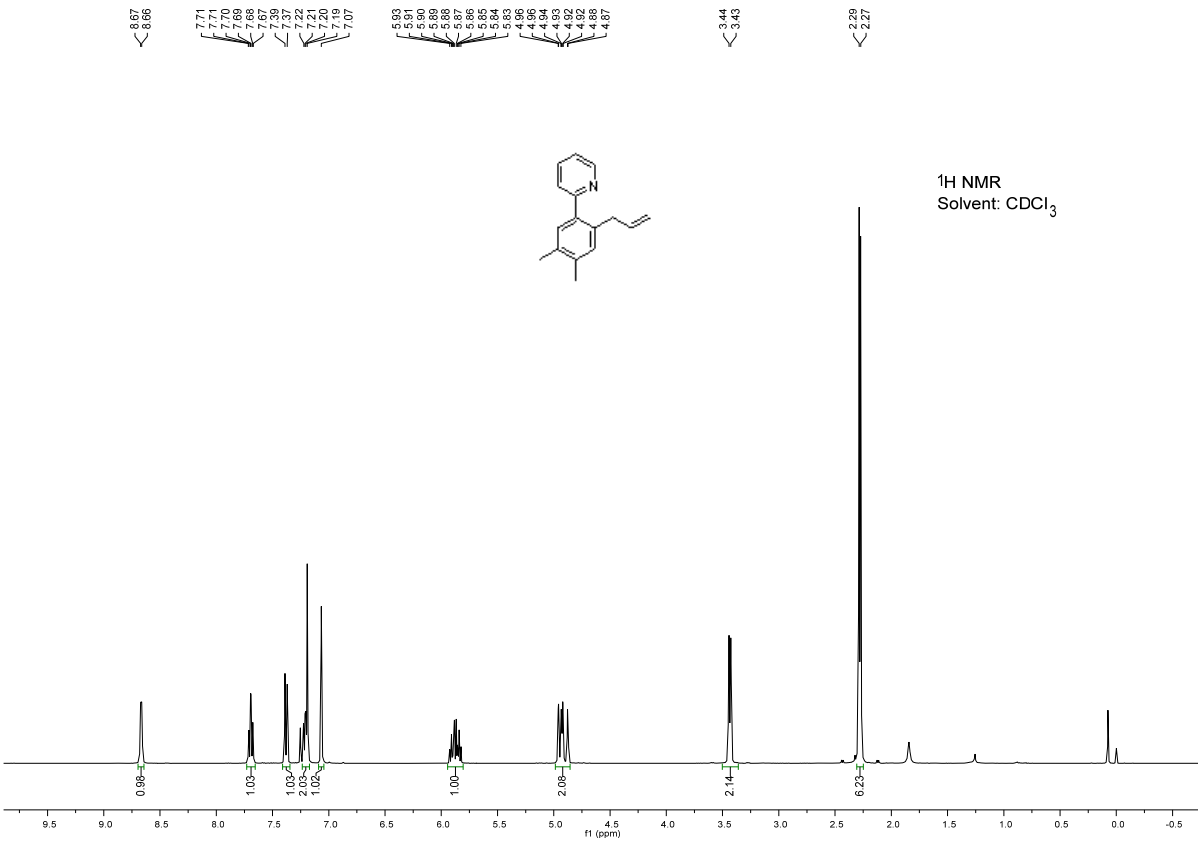

-57.29
N
F3C
19F NMR
Solvent: CDCl3
-52.0
-52.5
-53.0
-53.5
-54.0
-54.5
-55.0
-55.5
-56.0
-56.5
-57.0
-57.5
-58.0
-58.5
-59.0
-59.5
-60.0
-60.5
-61.0
-61.5
-62.0
-62.5
f1 (ppm)

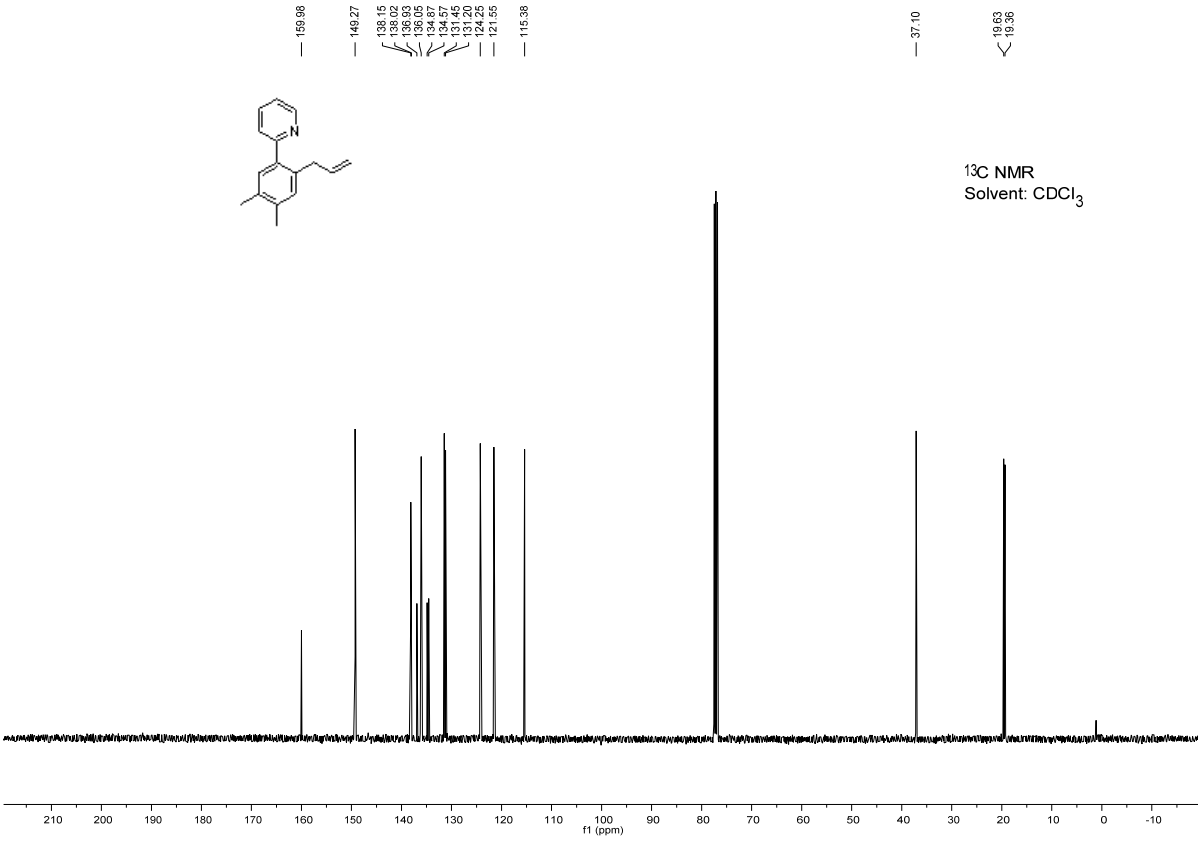
(8) 2-(2-allyl-5-methylphenyl)pyridine (**3ha**)



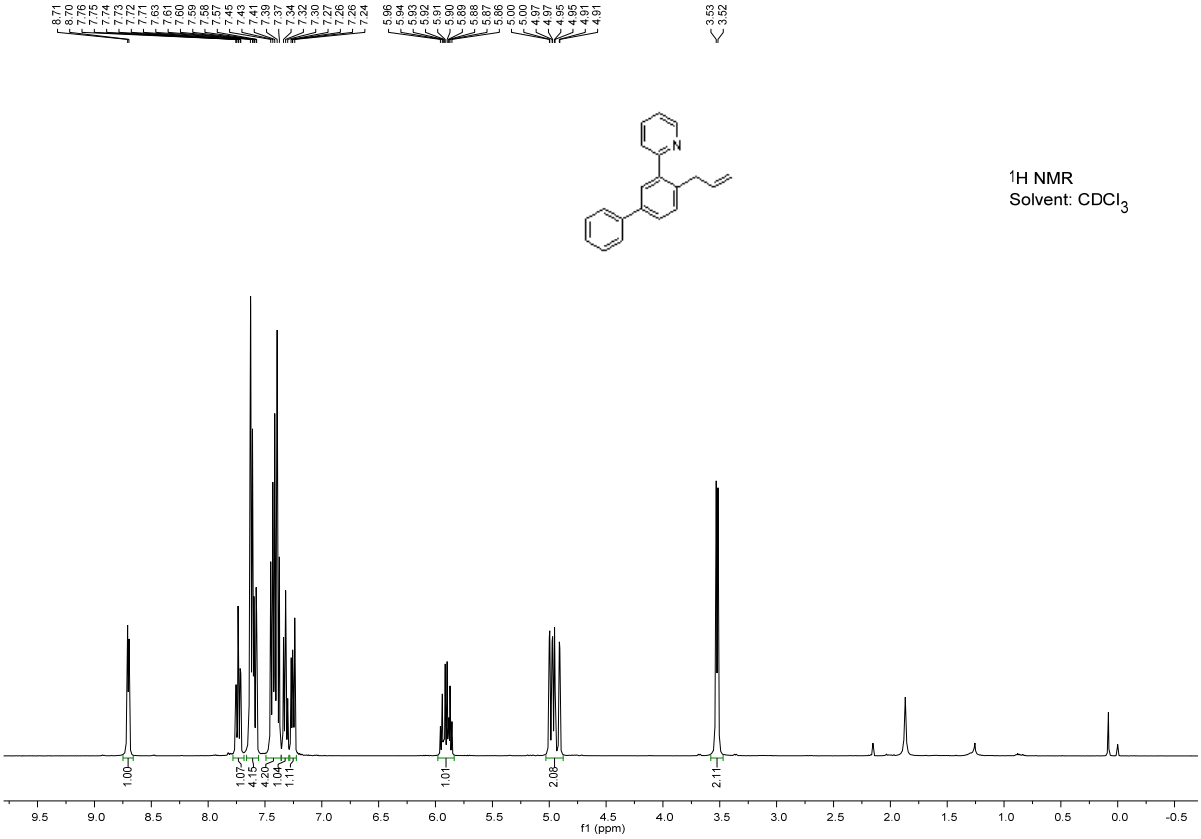


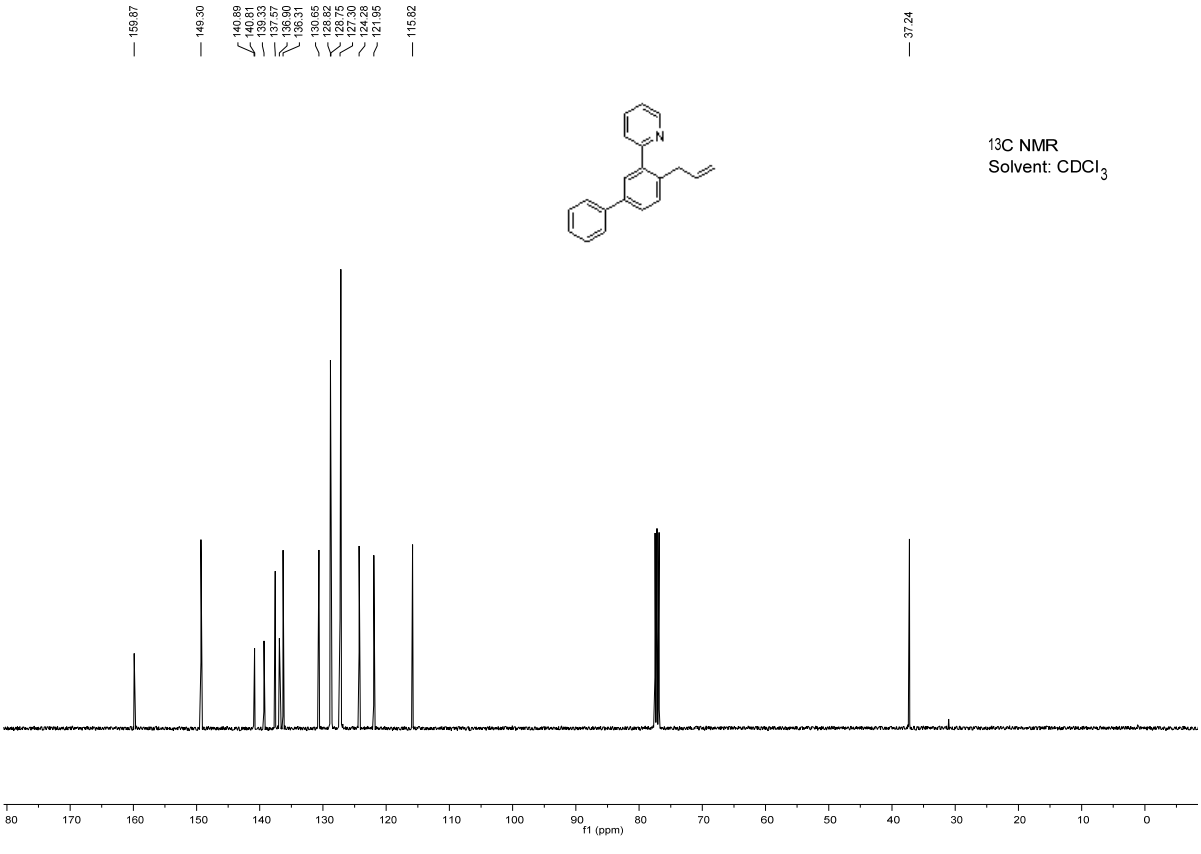
(9) 2-(2-allyl-4,5-dimethylphenyl)pyridine (**3ia**)



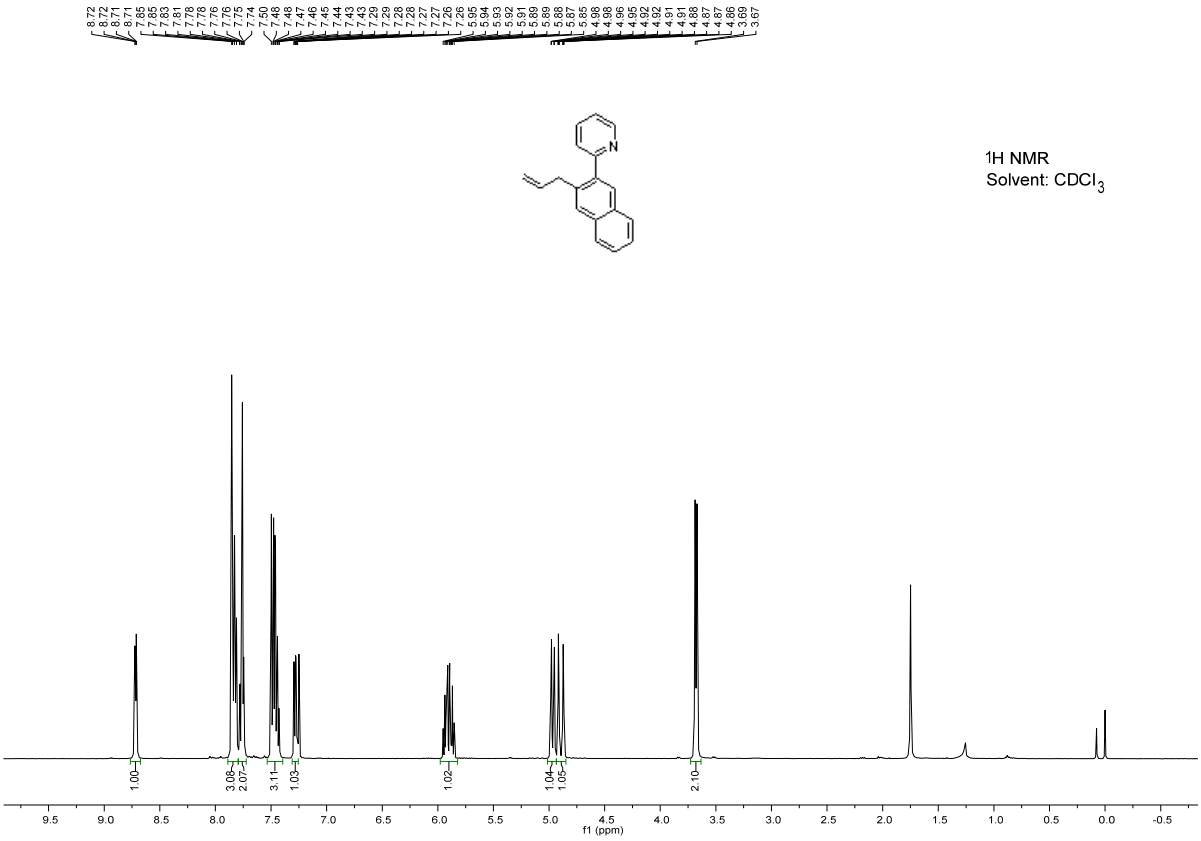


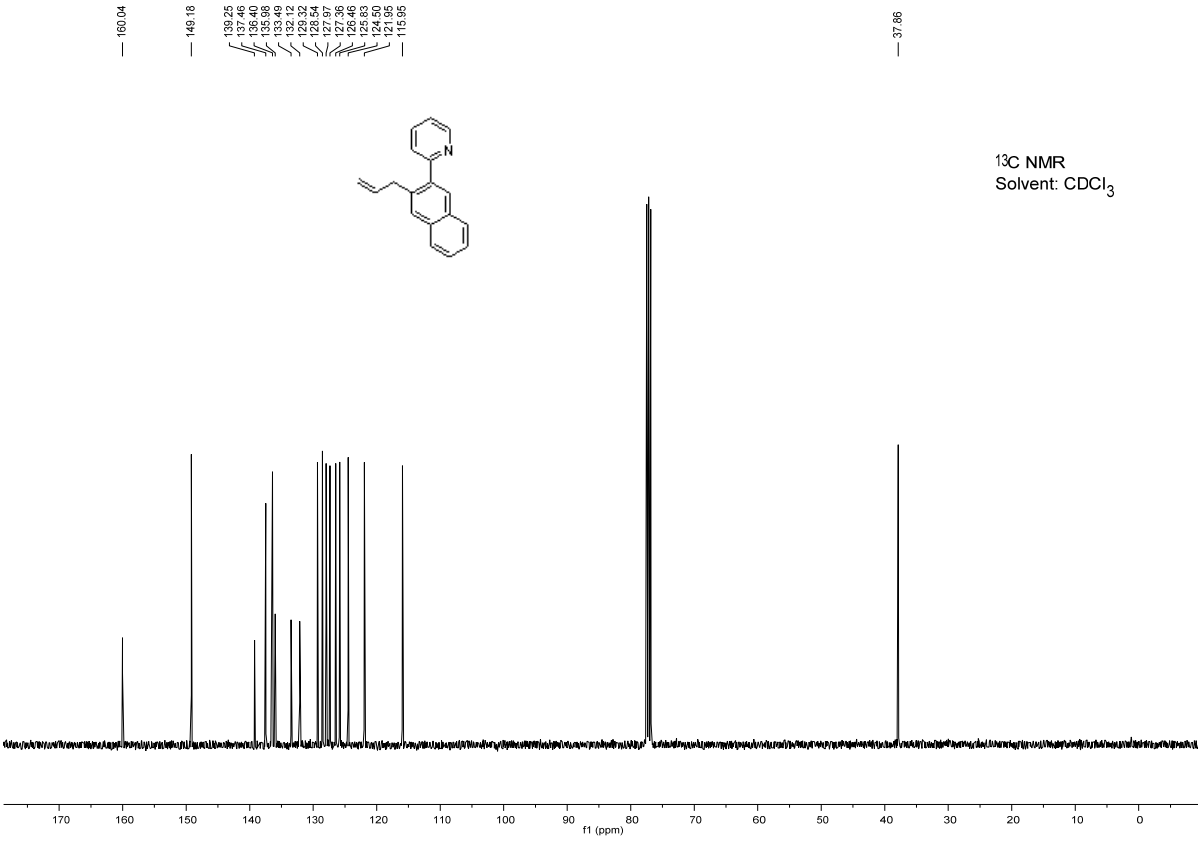
(10) 2-(4-allyl-[1,1'-biphenyl]-3-yl)pyridine (**3ja**)



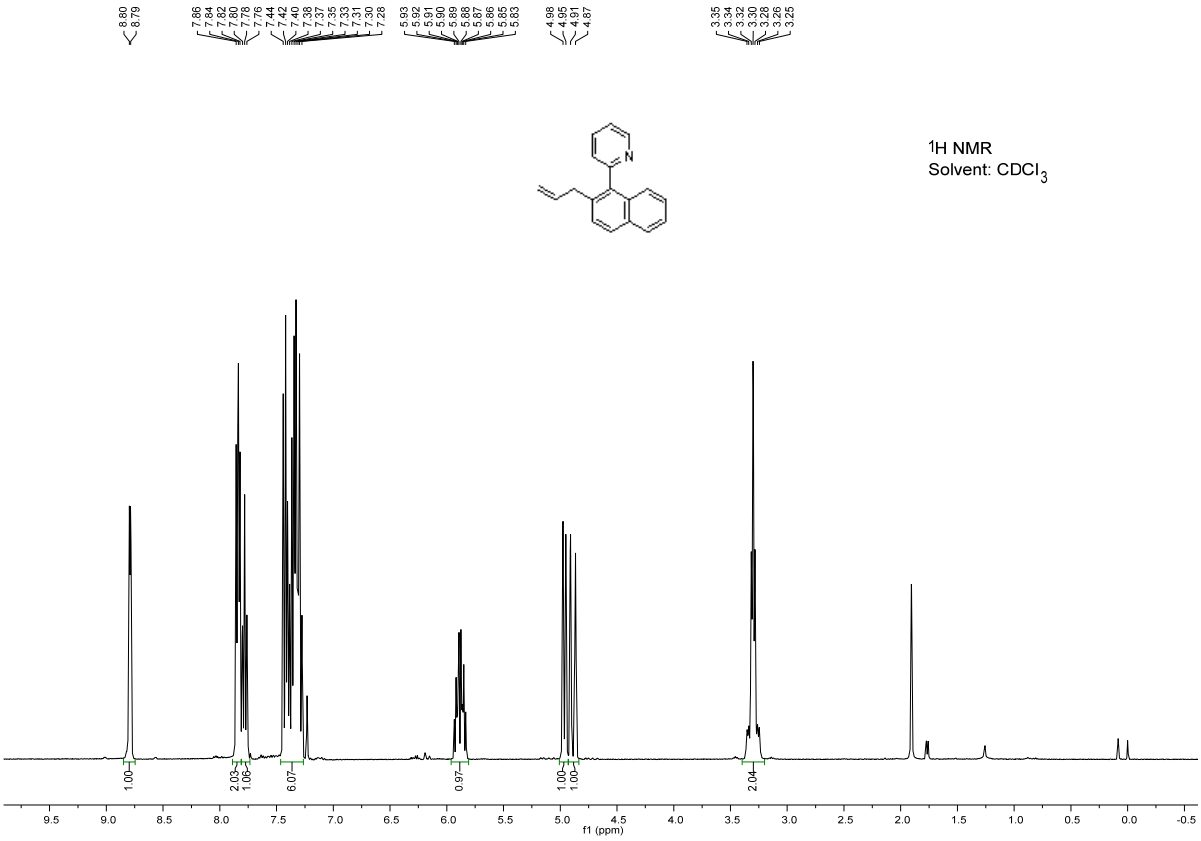


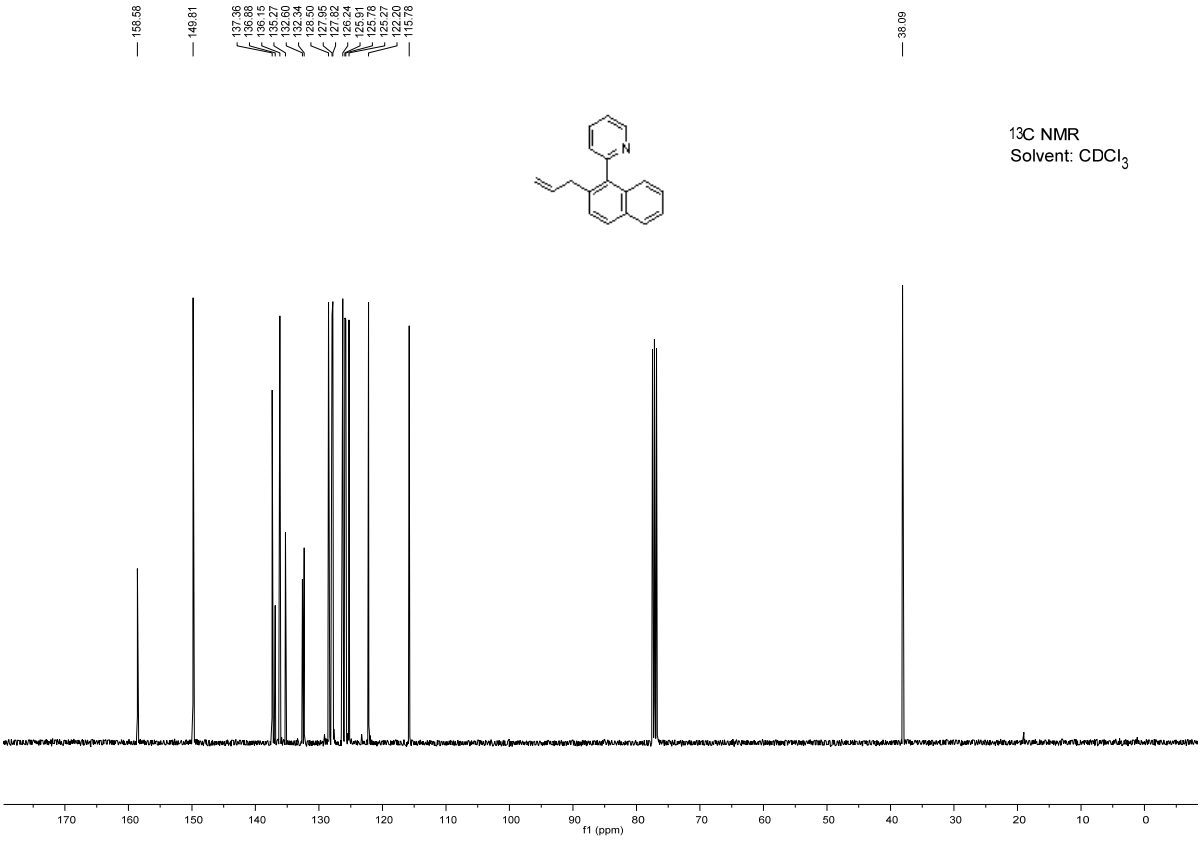
(11) 2-(3-allylnaphthalen-2-yl)pyridine (**3ka**)



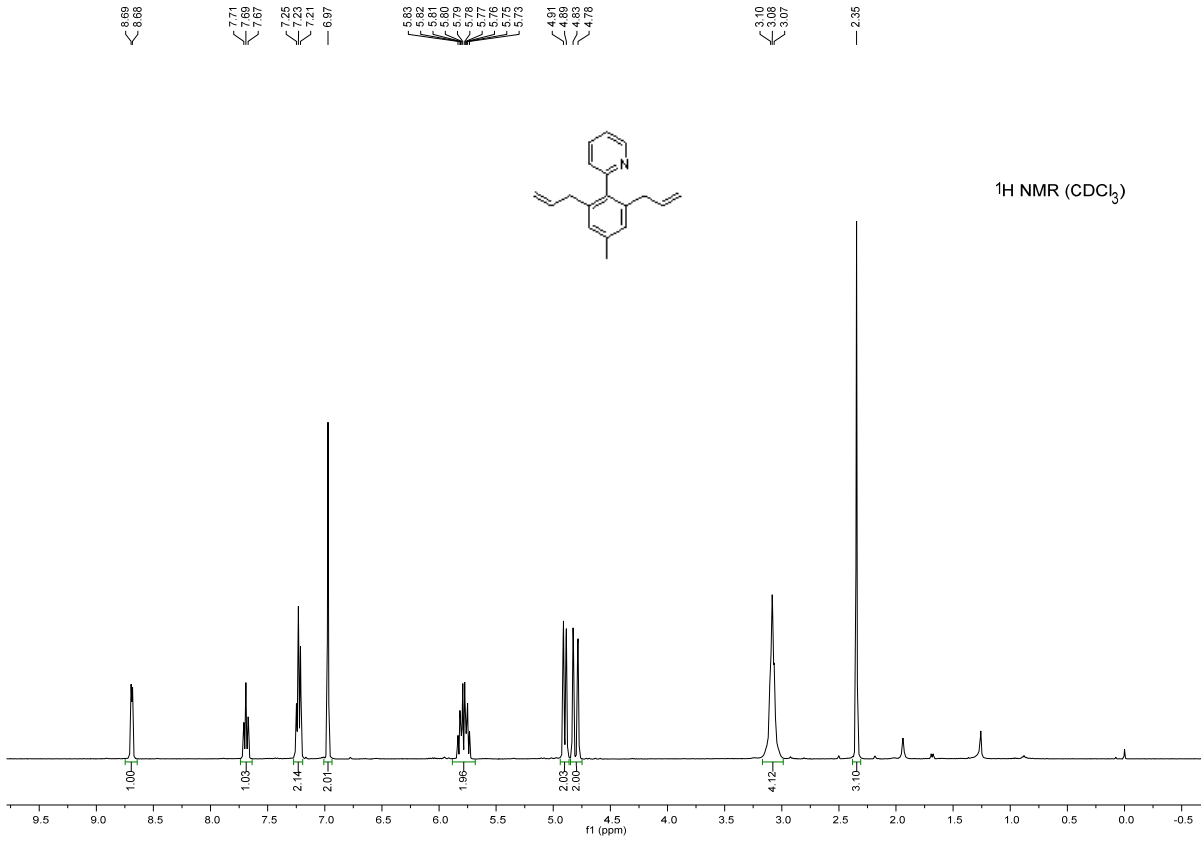


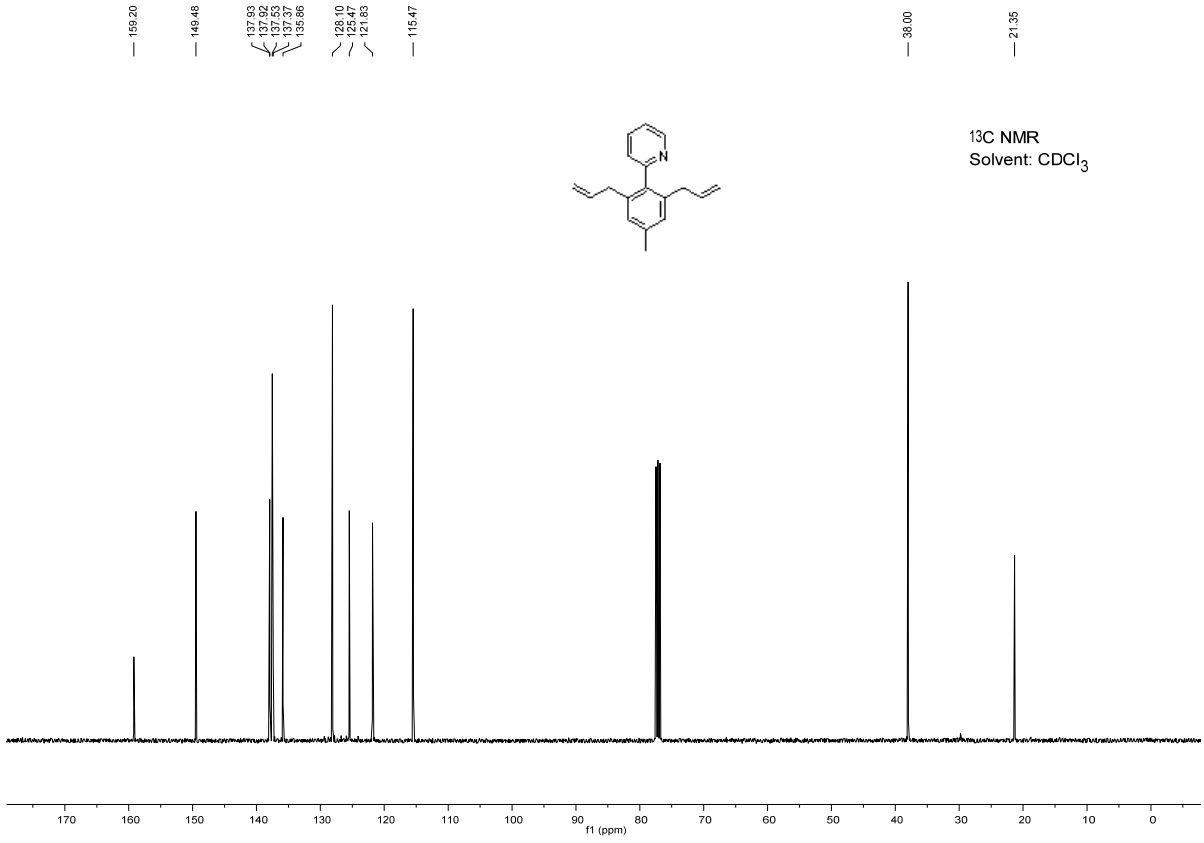
(12) 2-(2-allylnaphthalen-1-yl)pyridine (**3la**)



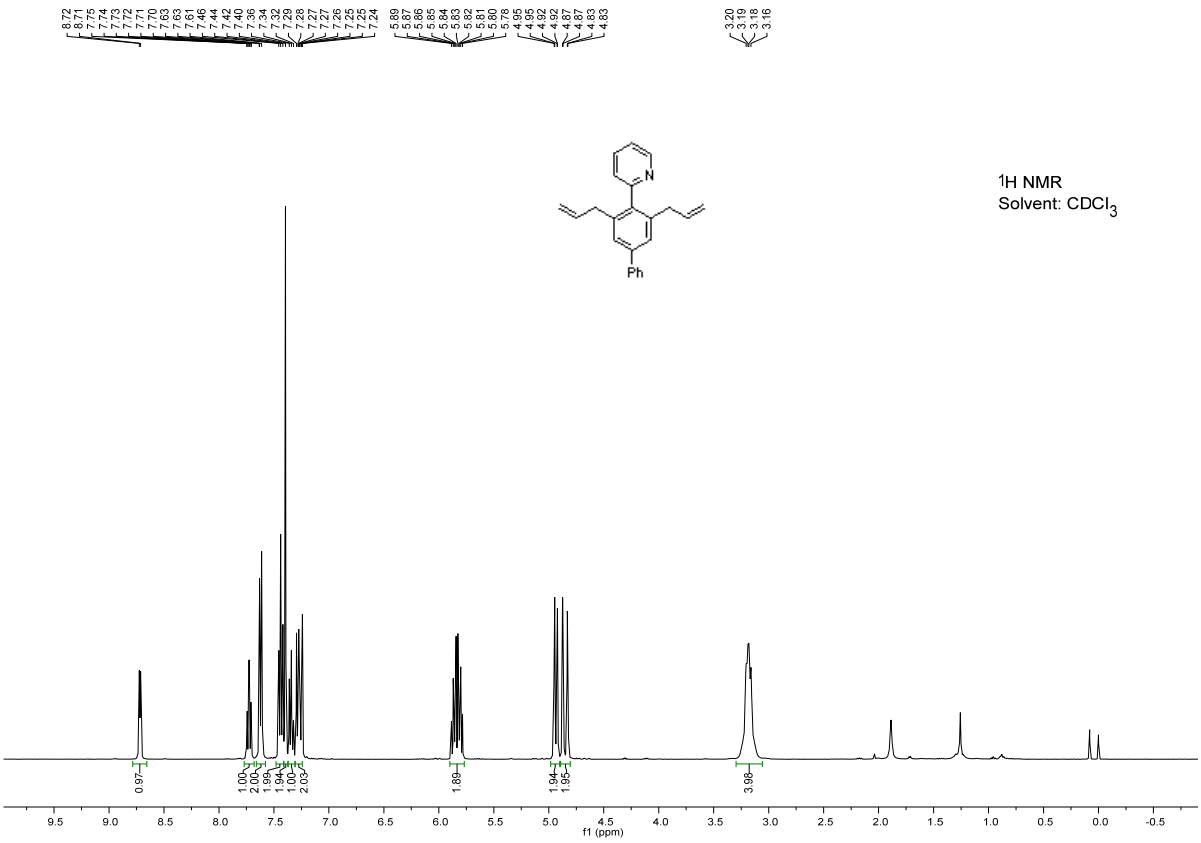


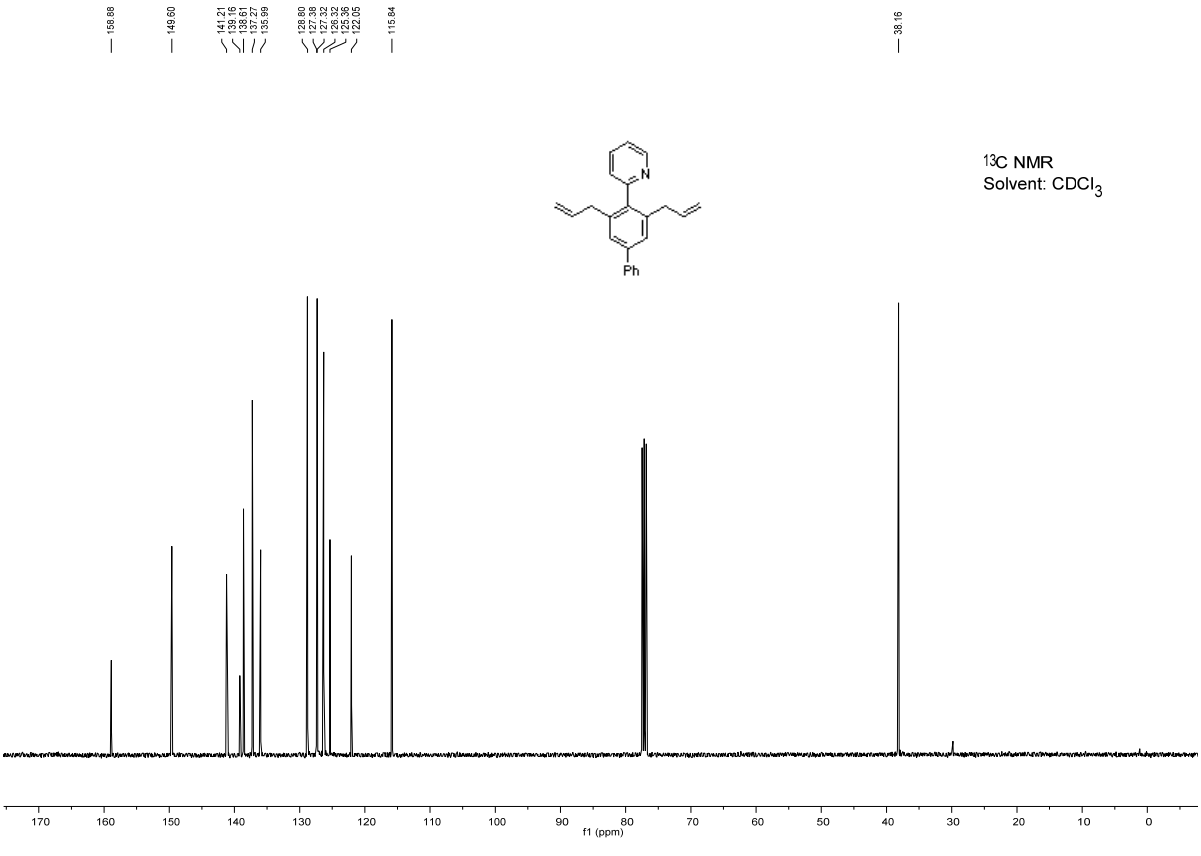
(13) 2-(2,6-diallyl-4-methylphenyl)pyridine (**3ma**)



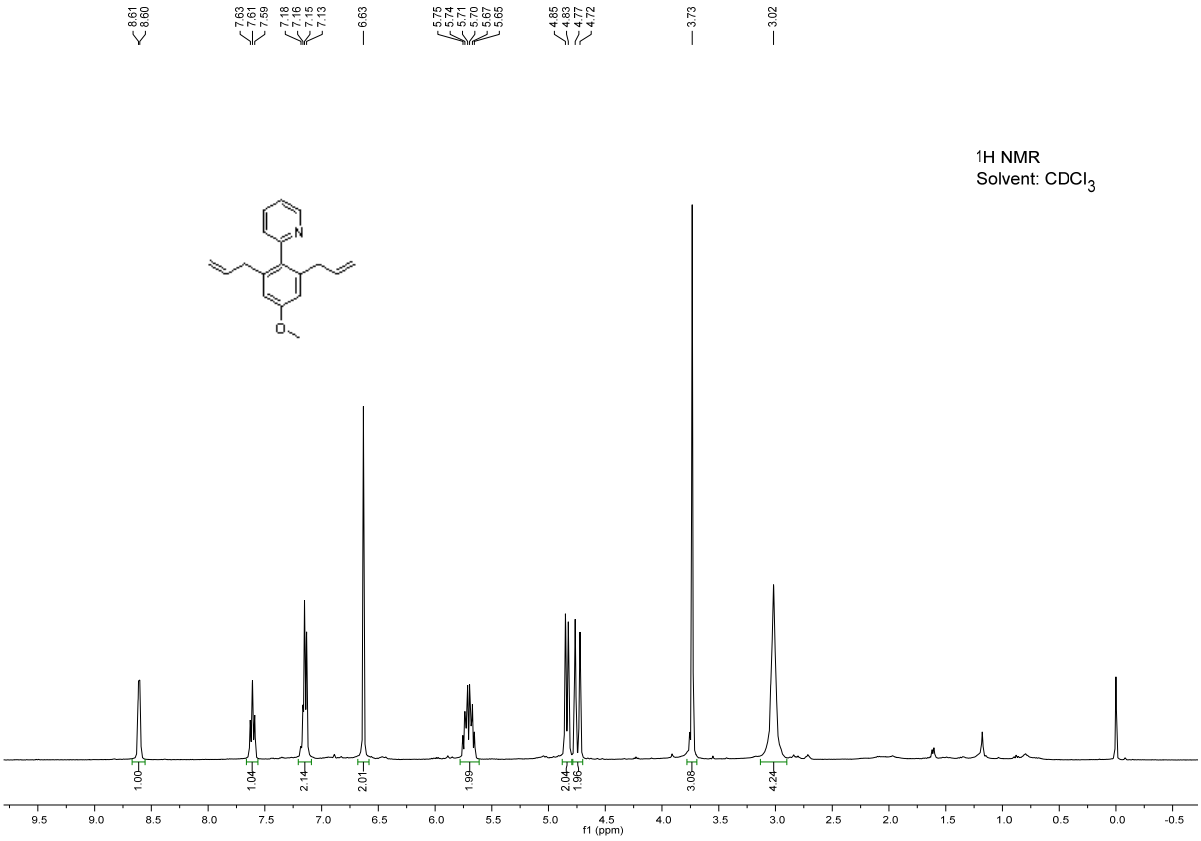


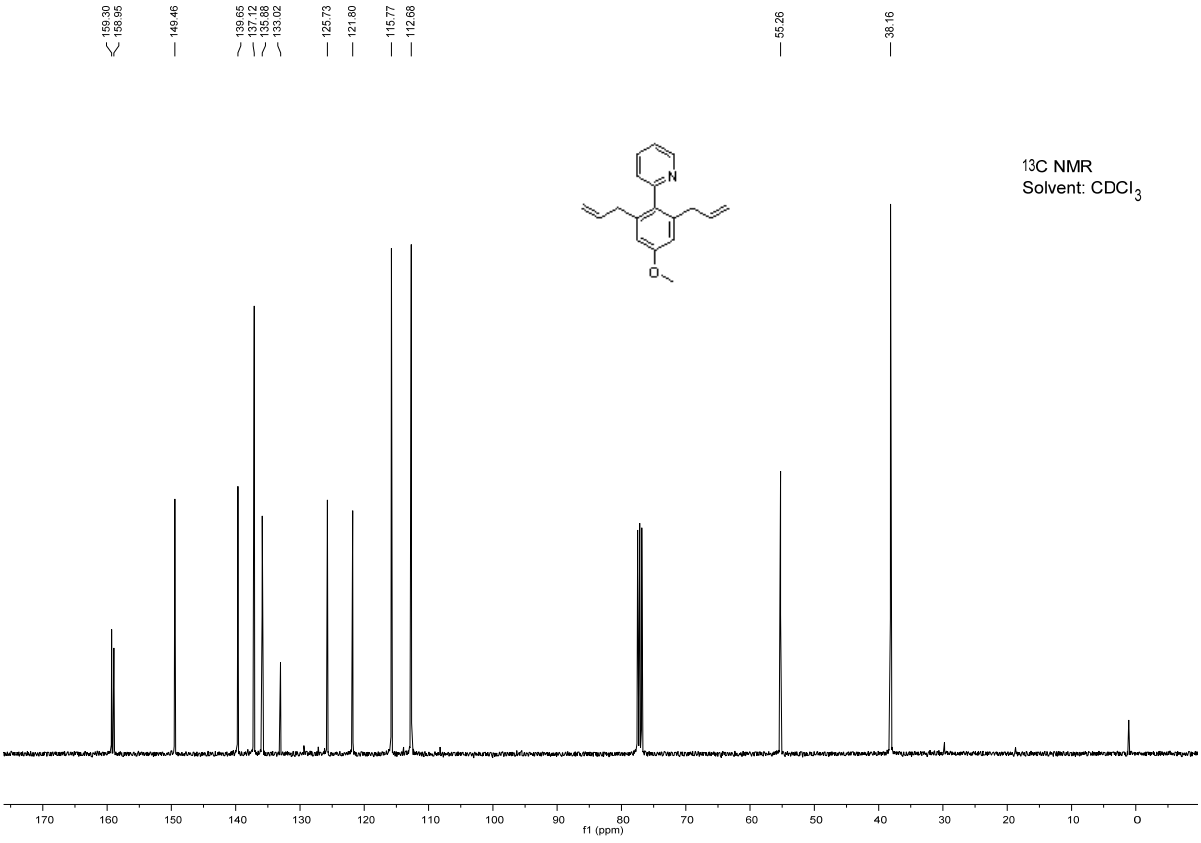
(14) 2-(3,5-diallyl-[1,1'-biphenyl]-4-yl)pyridine (**3na**)



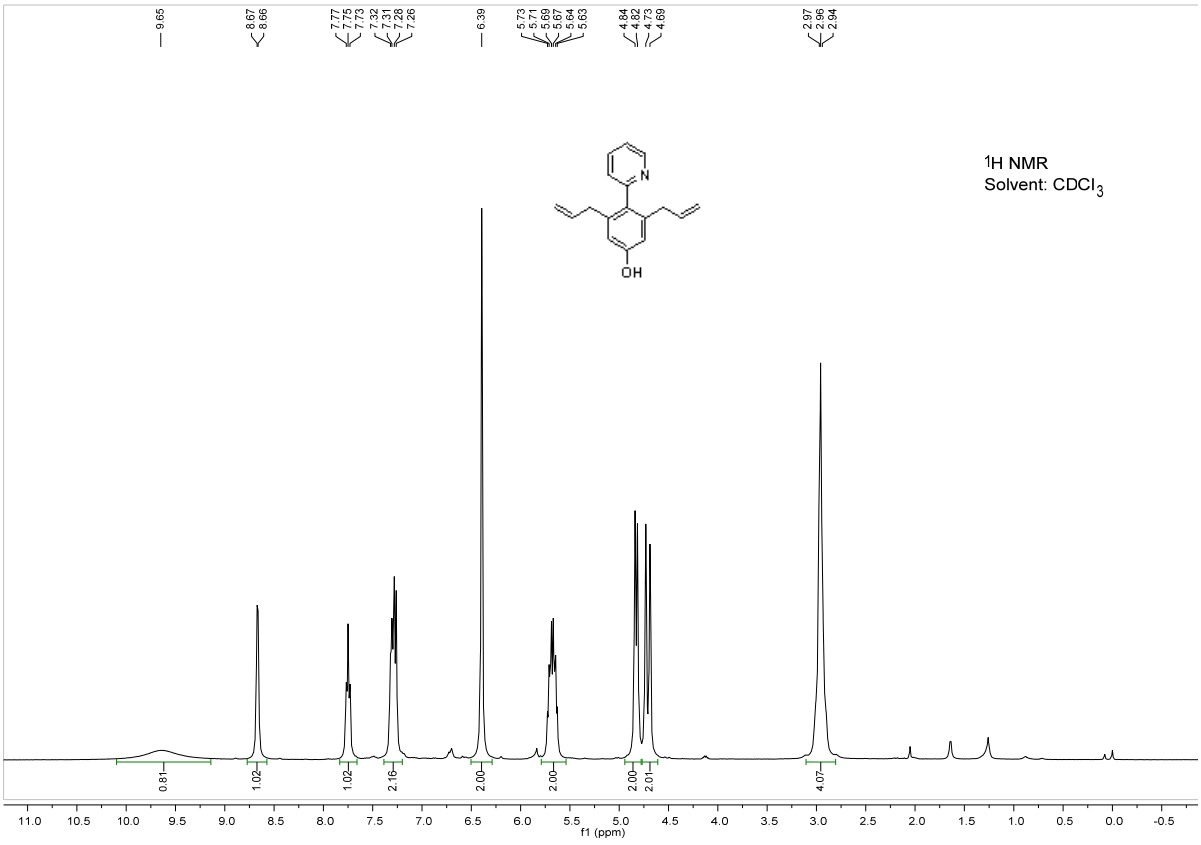


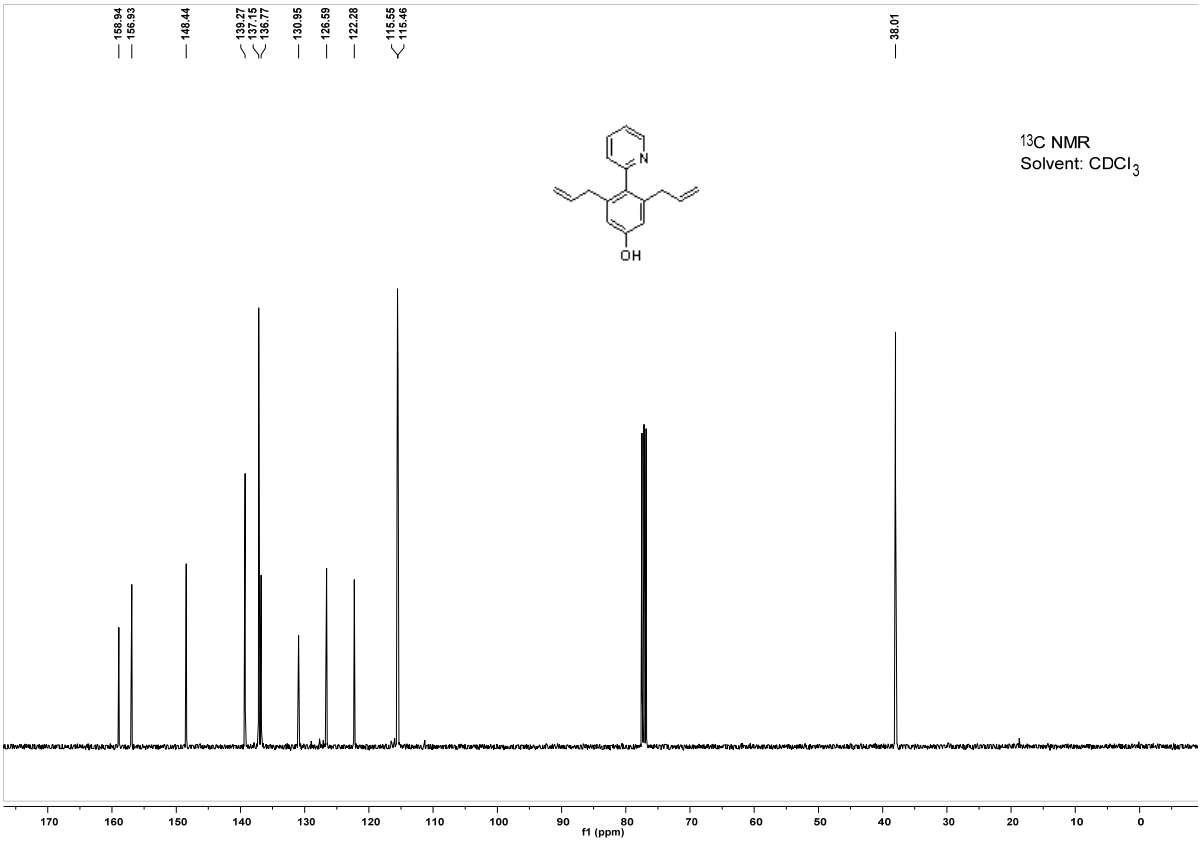
(15) 2-(2,6-diallyl-4-methoxyphenyl)pyridine (**3oa**)



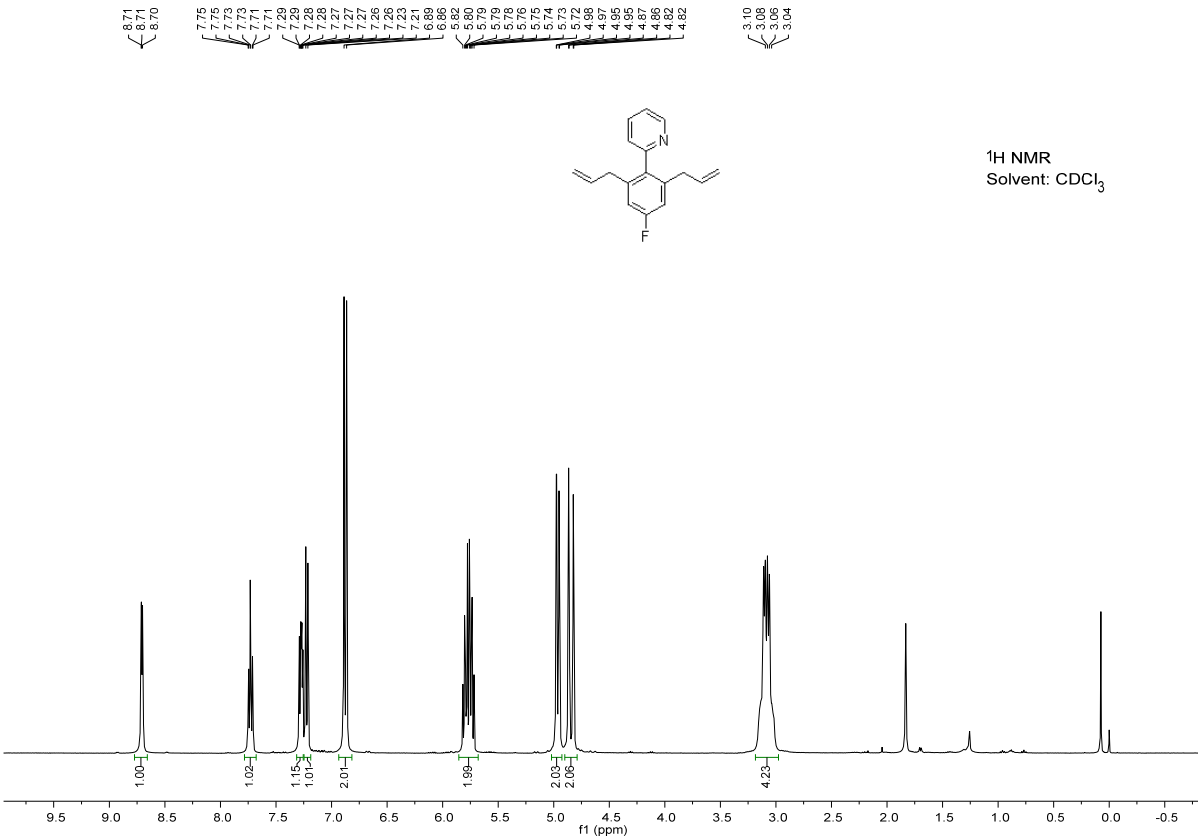


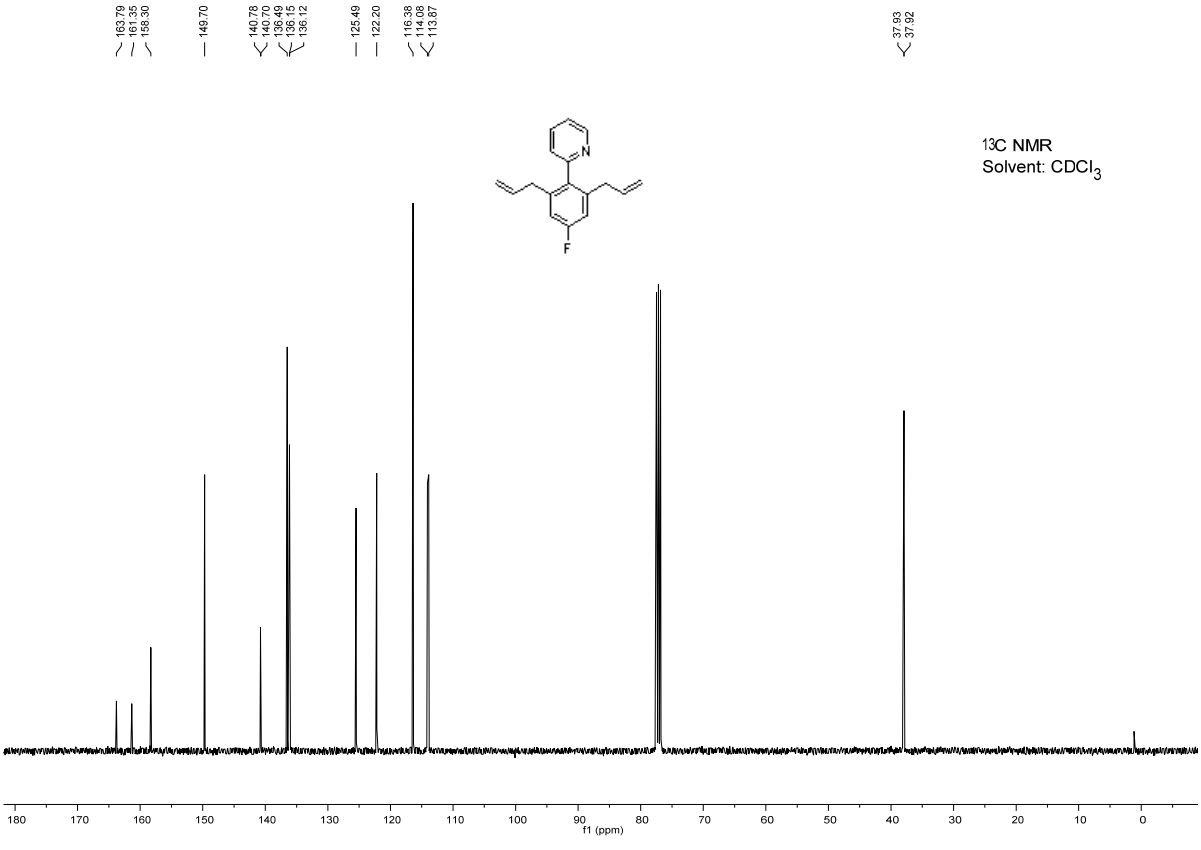
(16) 3,5-diallyl-4-(pyridin-2-yl)phenol (**3pa**)

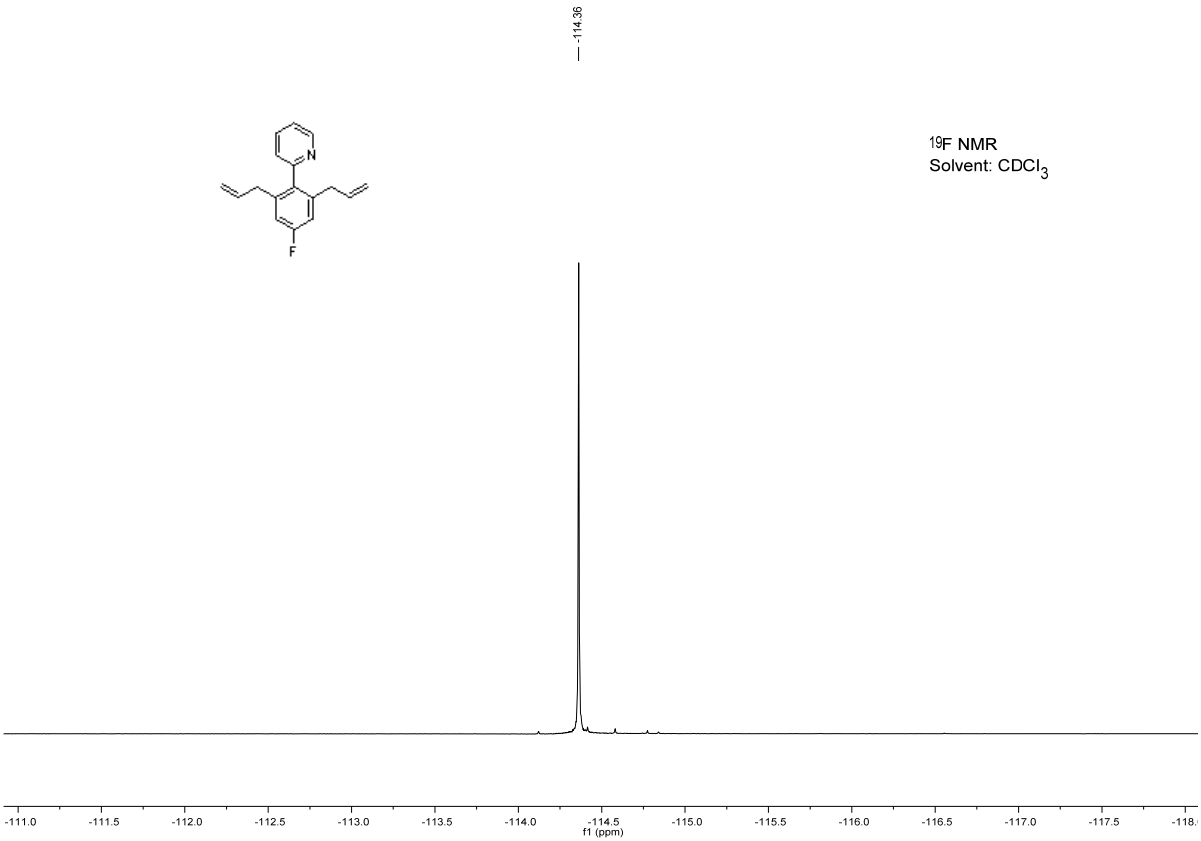




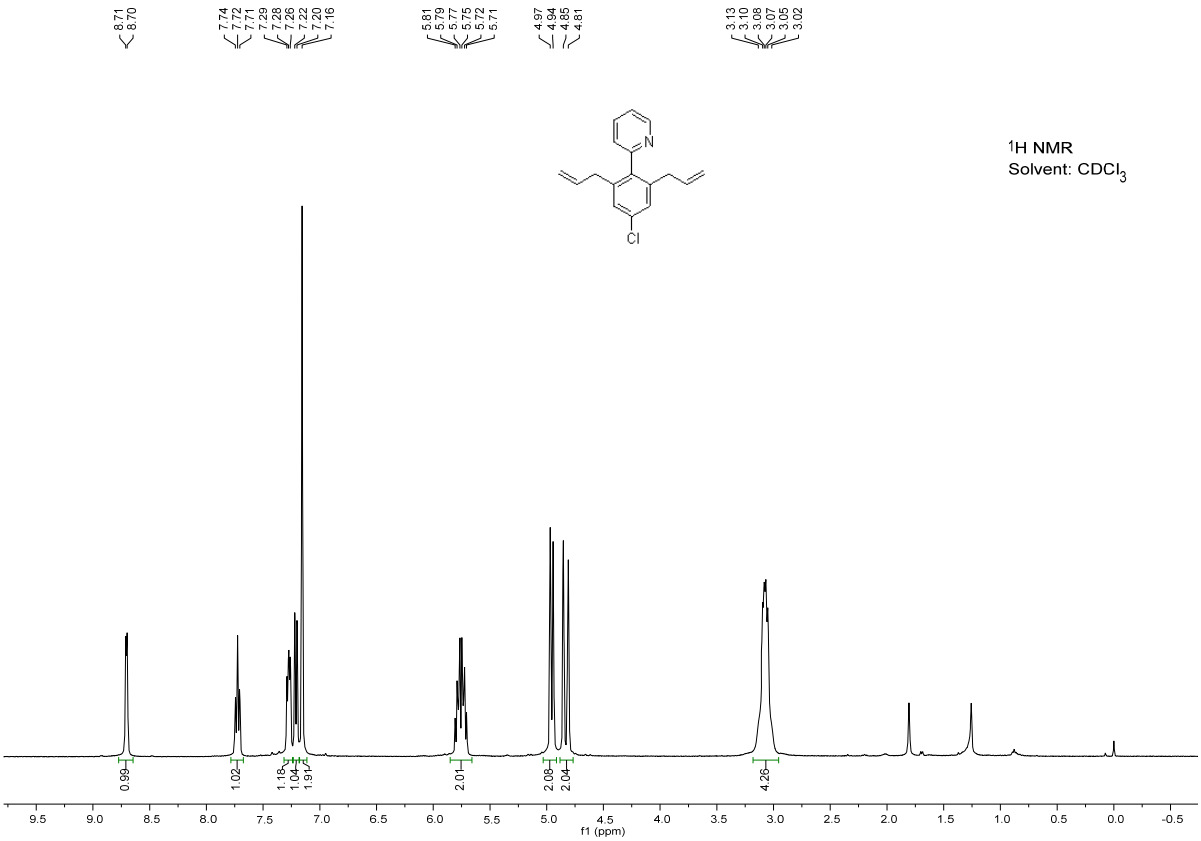
(17) 2-(2,6-diallyl-4-fluorophenyl)pyridine (**3qa**)

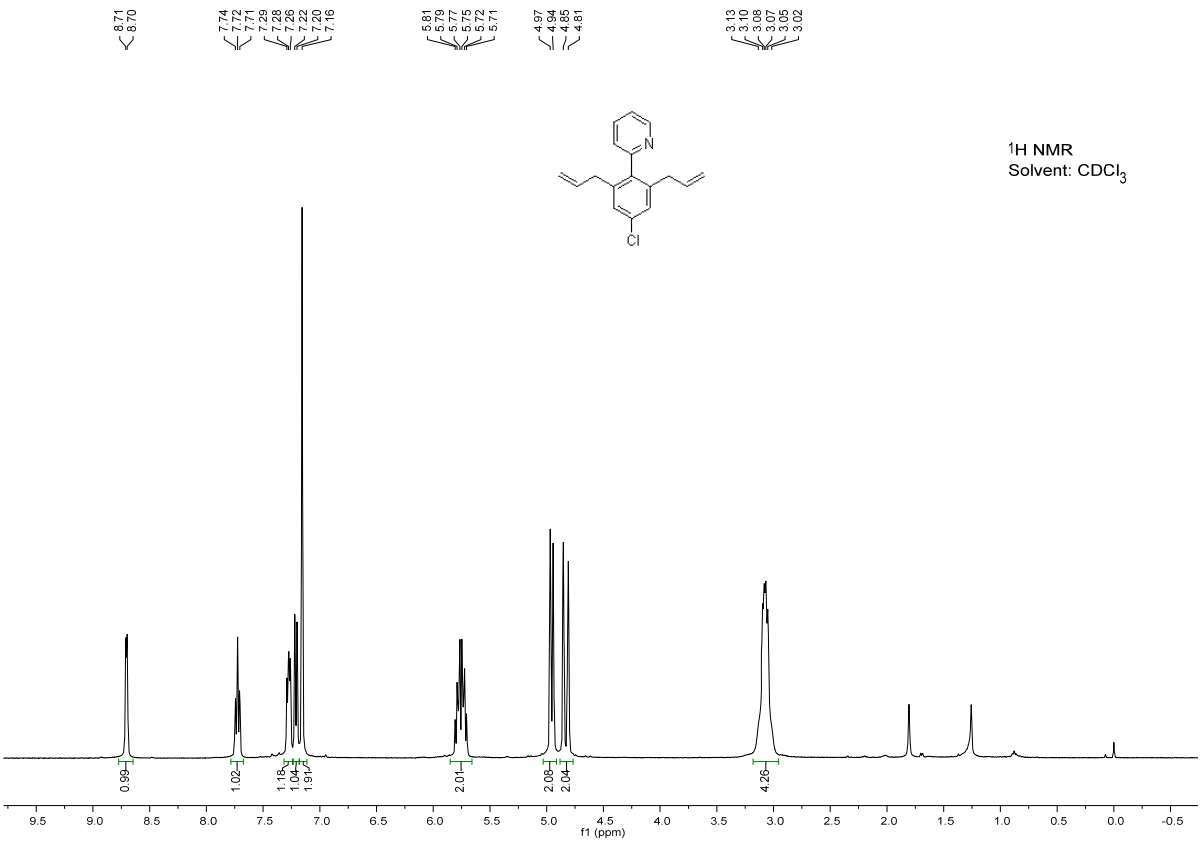




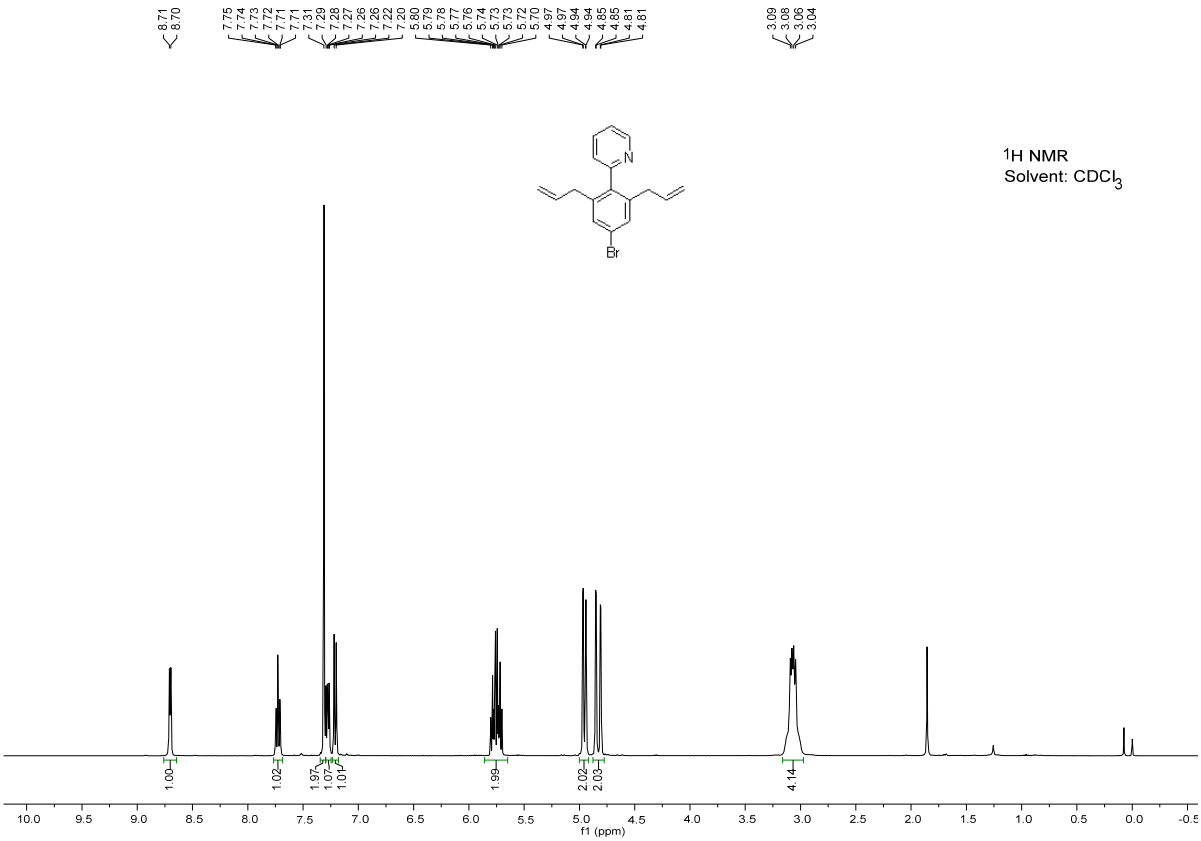

-114.36
N
F
19F NMR
Solvent: CDCl3
-111.0
-111.5
-112.0
-112.5
-113.0
-113.5
-114.0
-114.5
f1 (ppm)
-115.0
-115.5
-116.0
-116.5
-117.0
-117.5

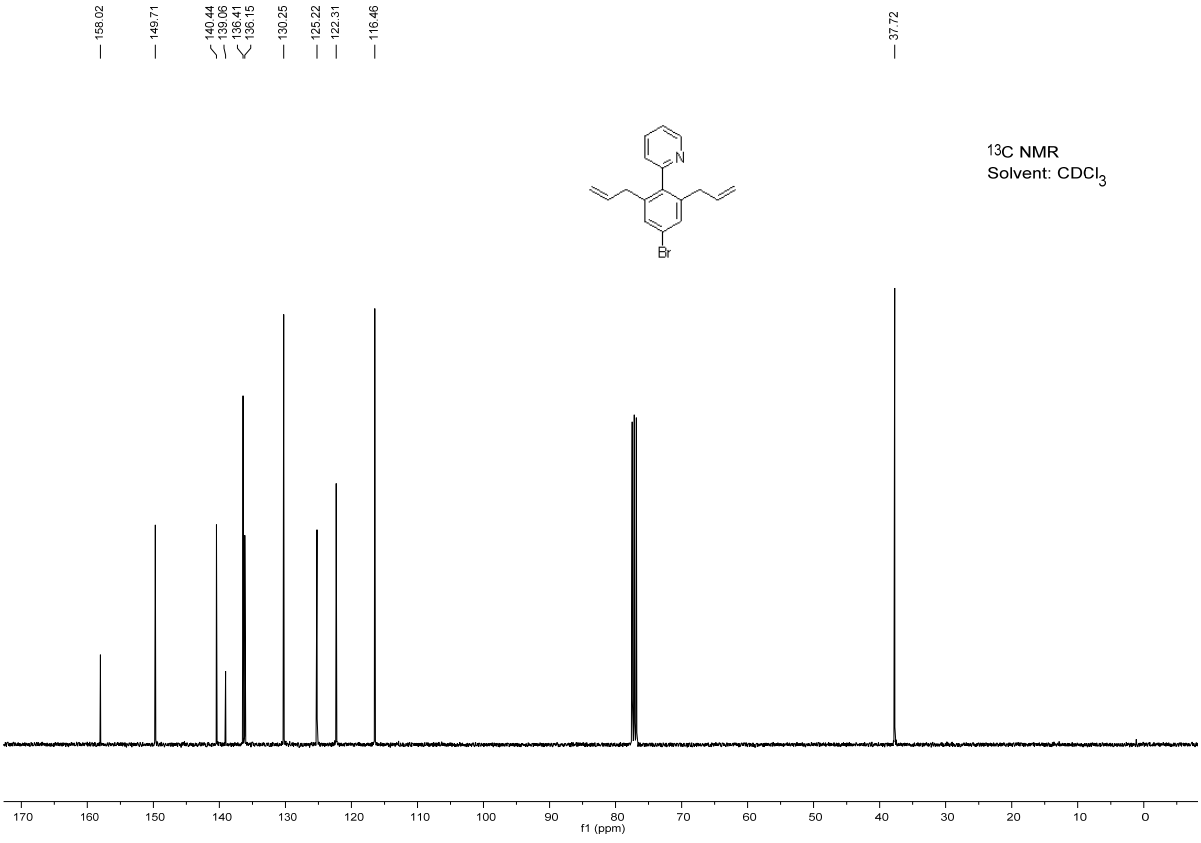
(18) 2-(2,6-diallyl-4-chlorophenyl)pyridine (**3ra**)



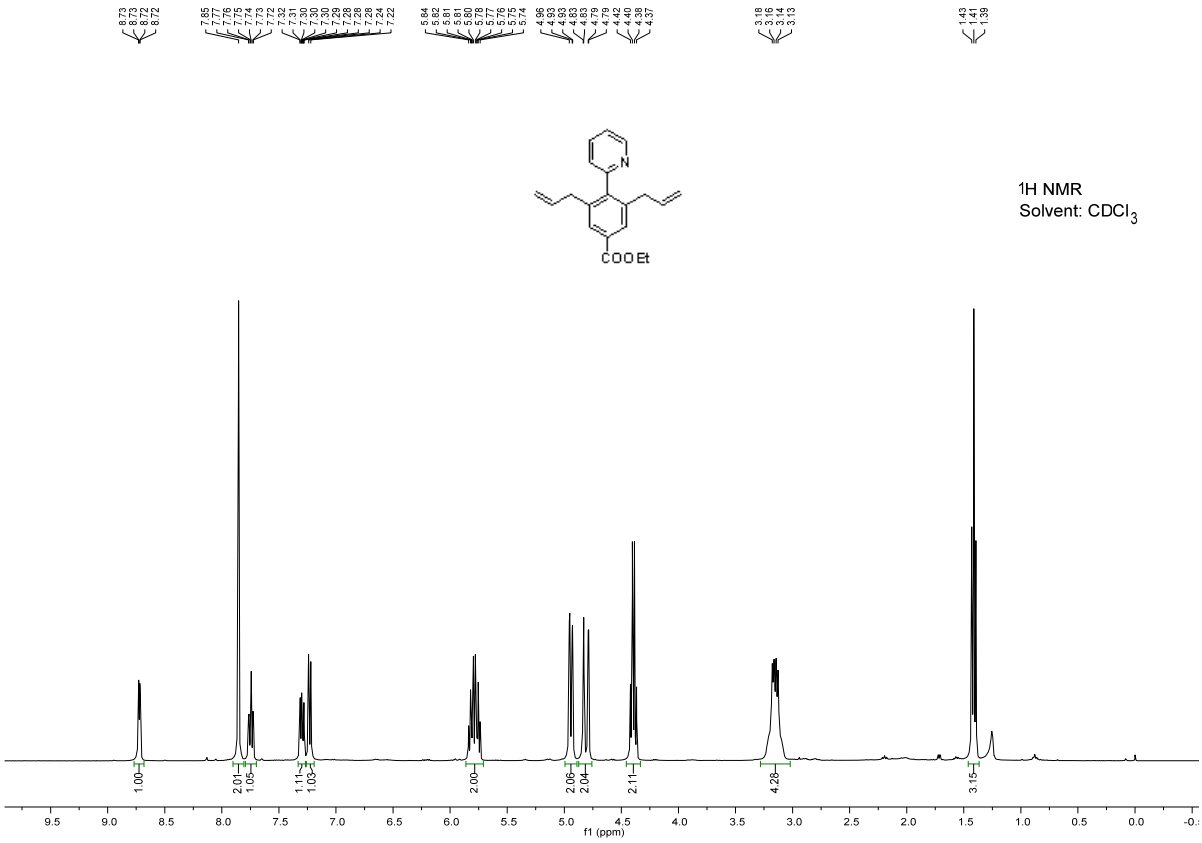


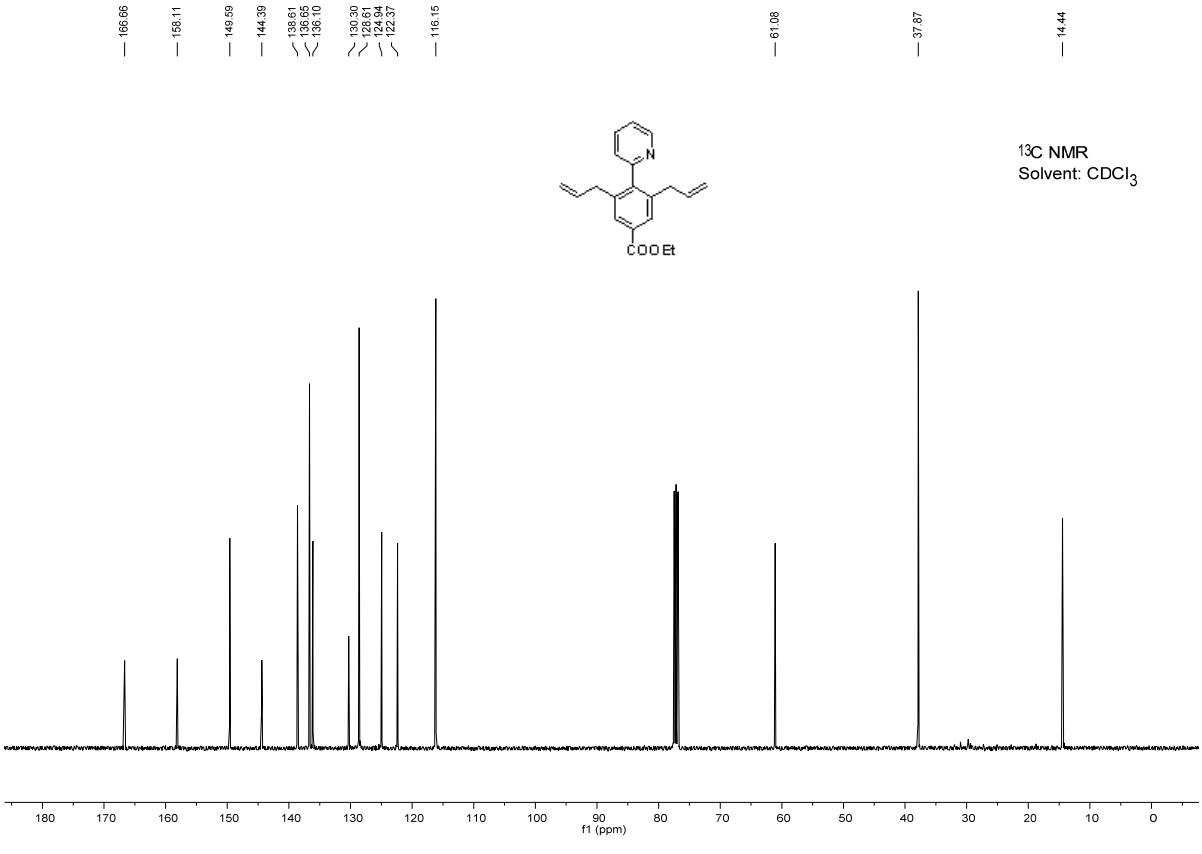
(19) 2-(2,6-diallyl-4-bromophenyl)pyridine (**3sa**)



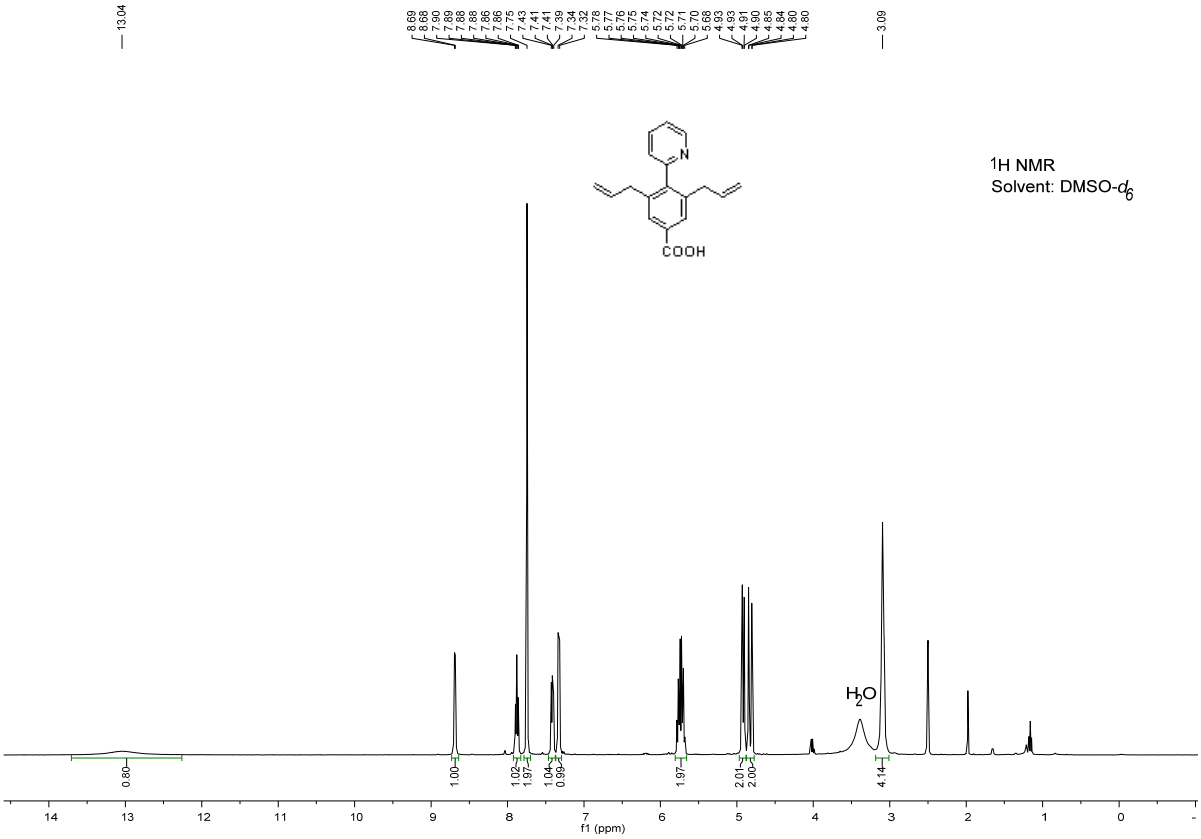


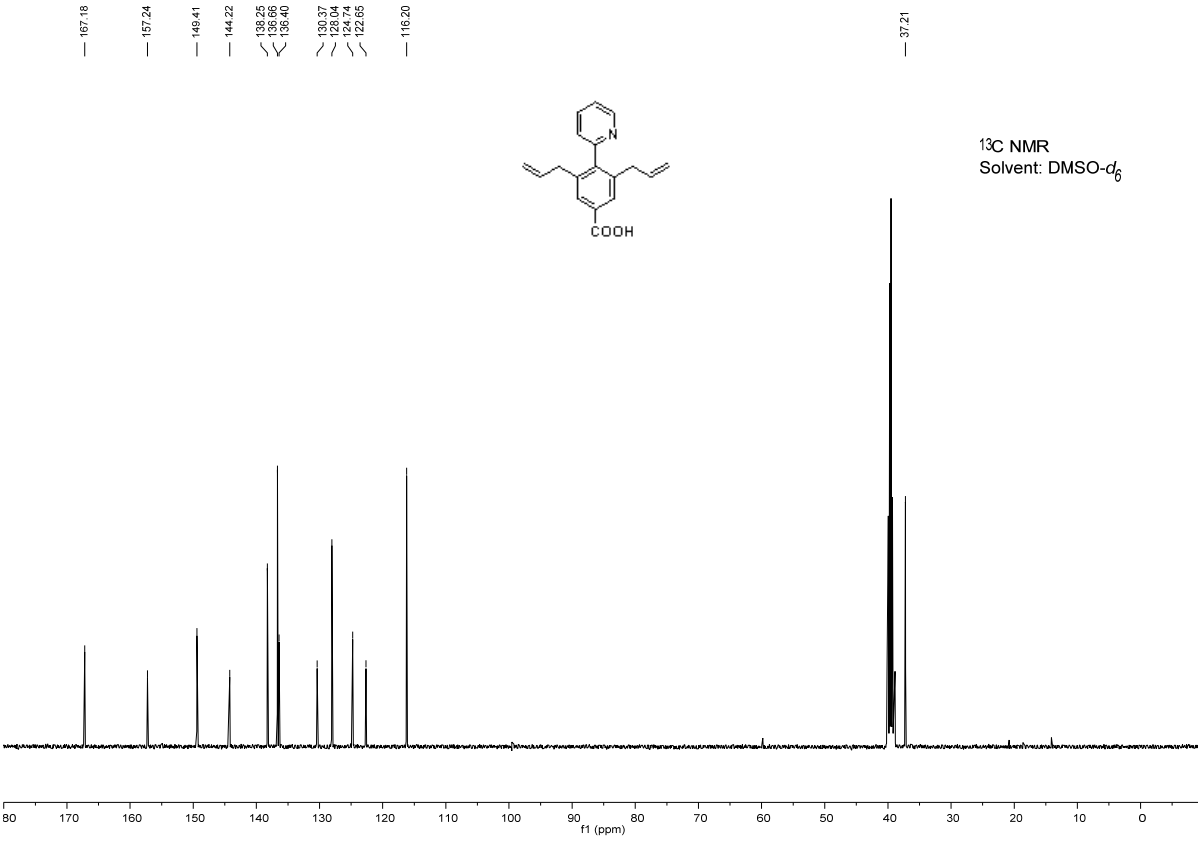
(20) ethyl 3,5-diallyl-4-(pyridin-2-yl)benzoate (**3ta**)



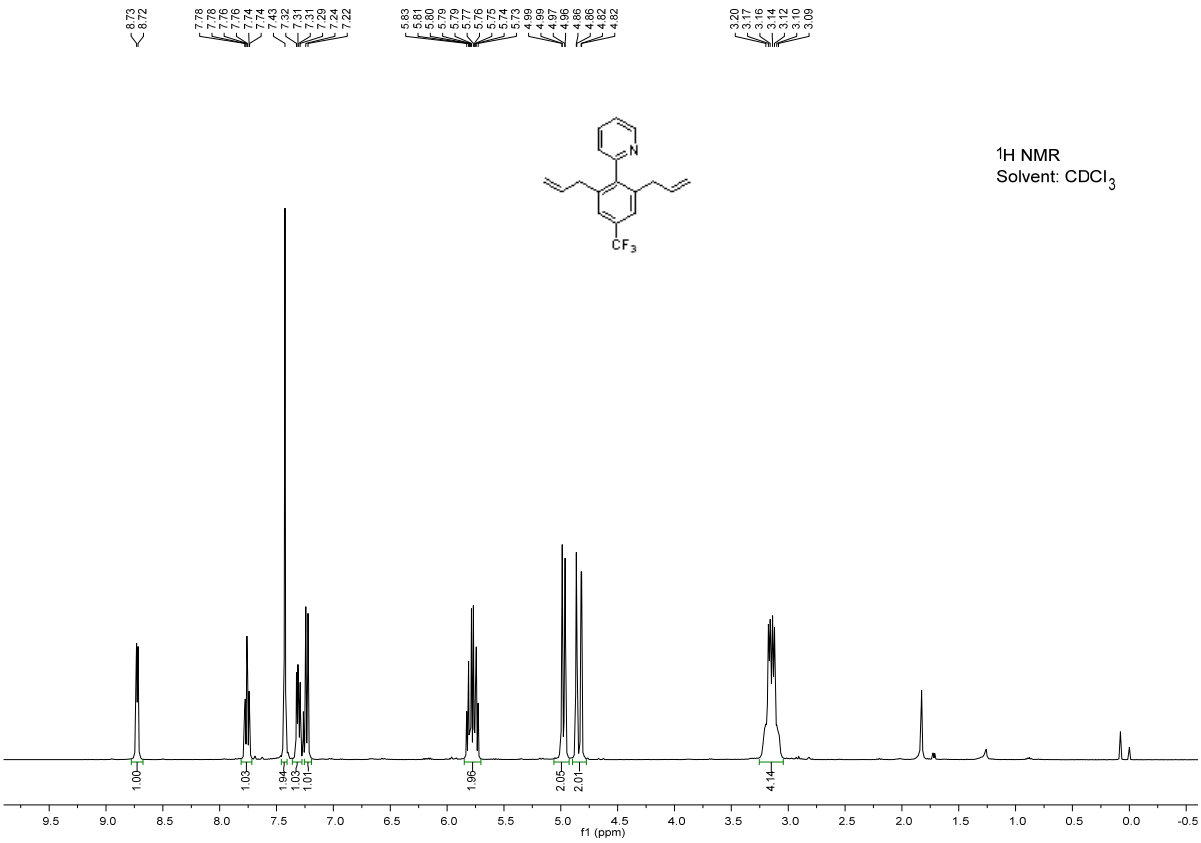


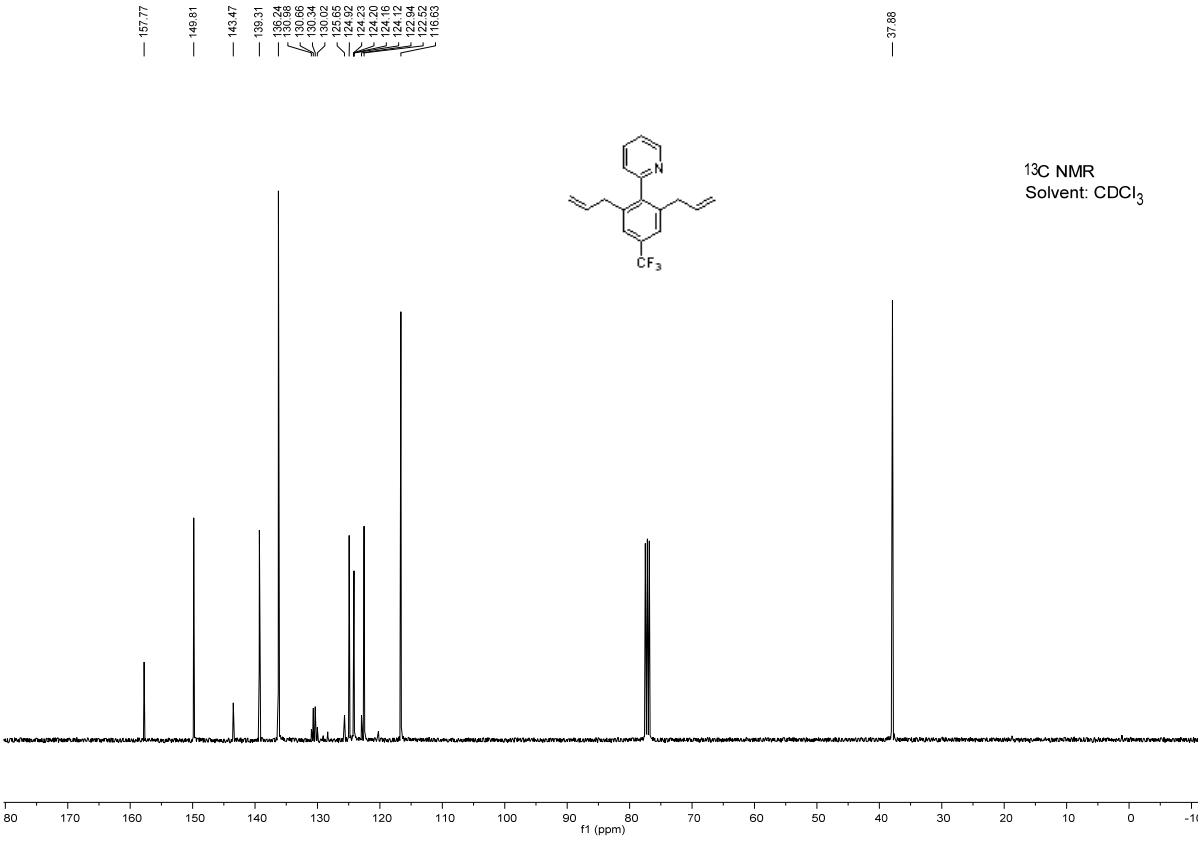
(21) 3,5-diallyl-4-(pyridin-2-yl)benzoic acid (**3ua**)

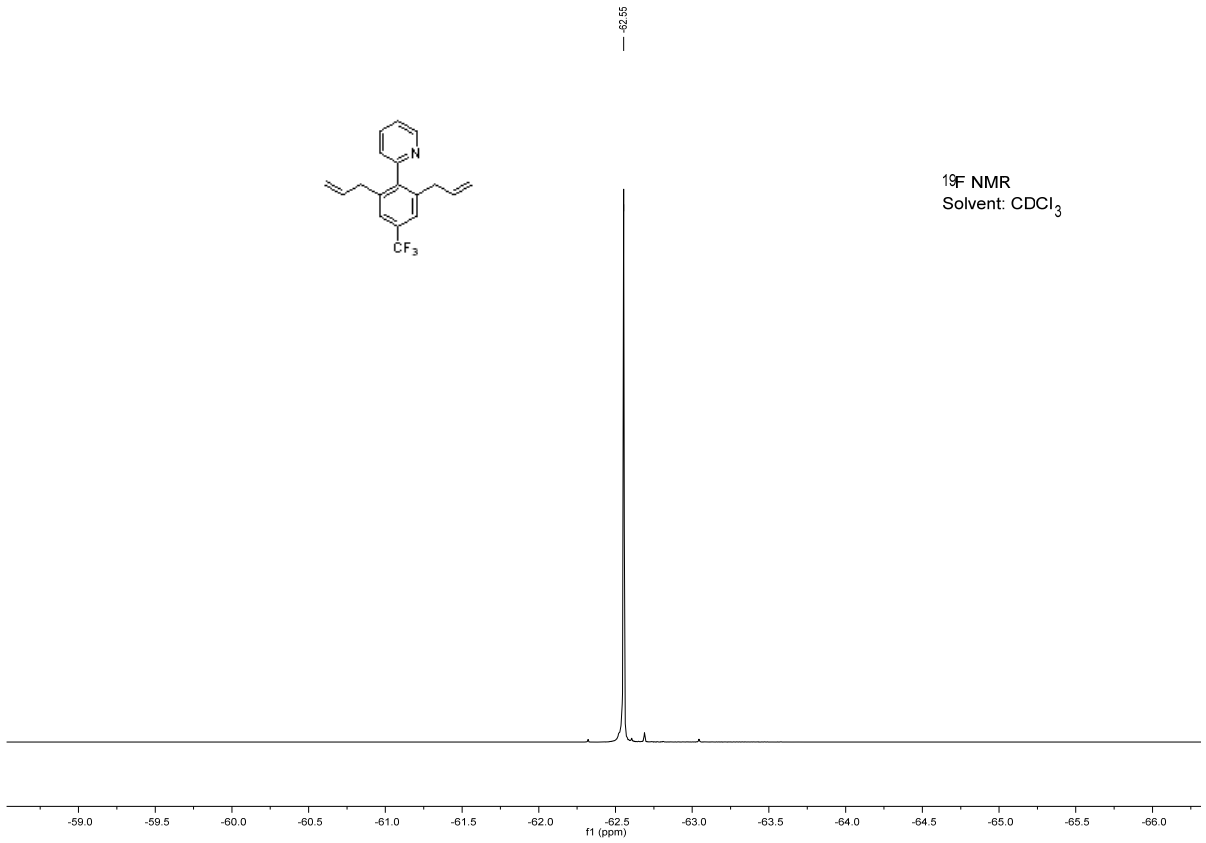




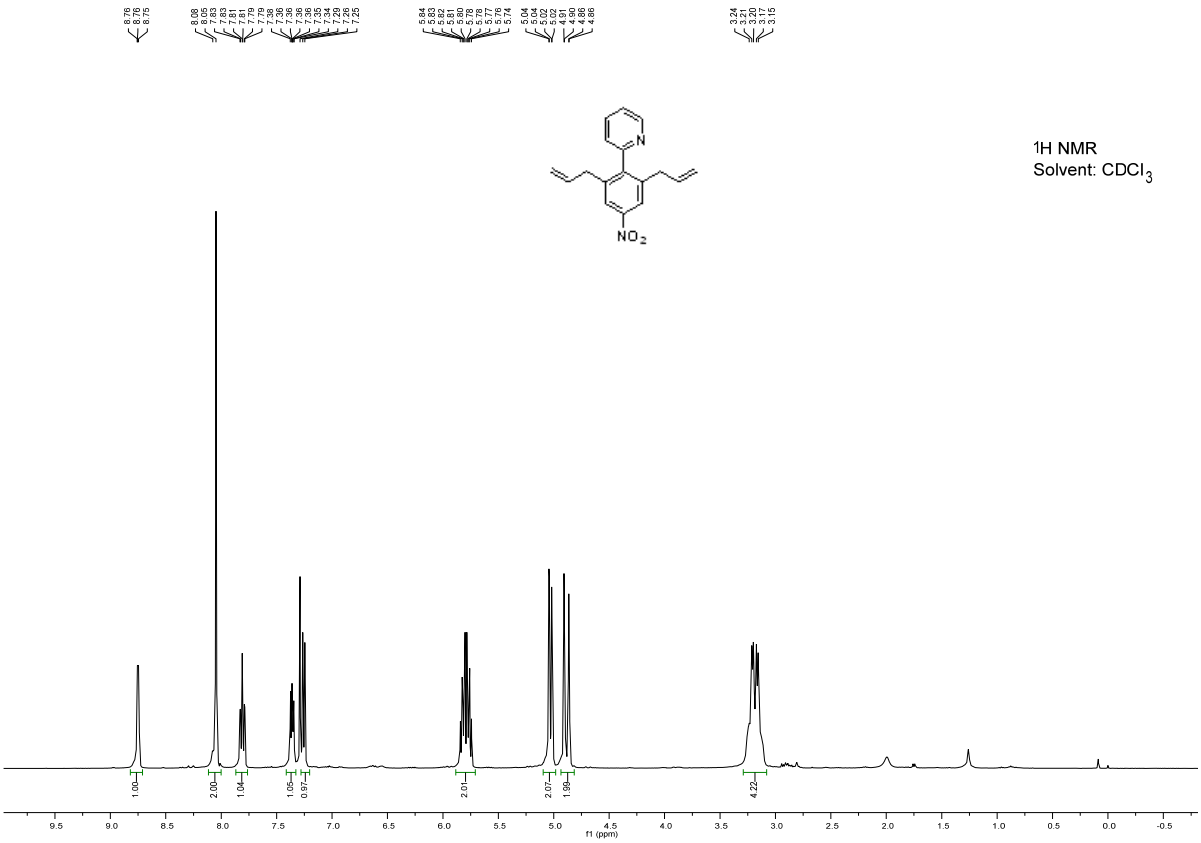
(22) 2-(2,6-diallyl-4-(trifluoromethyl)phenyl)pyridine (**3va**)

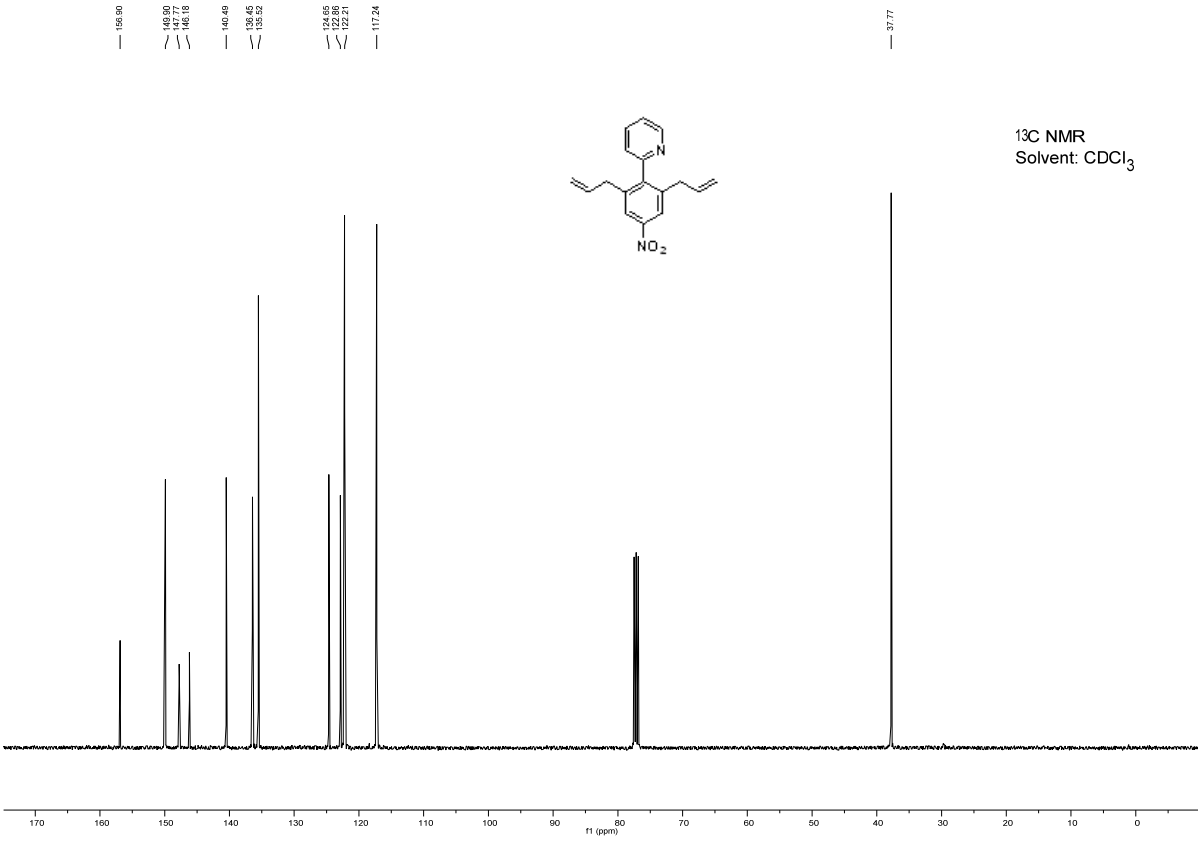




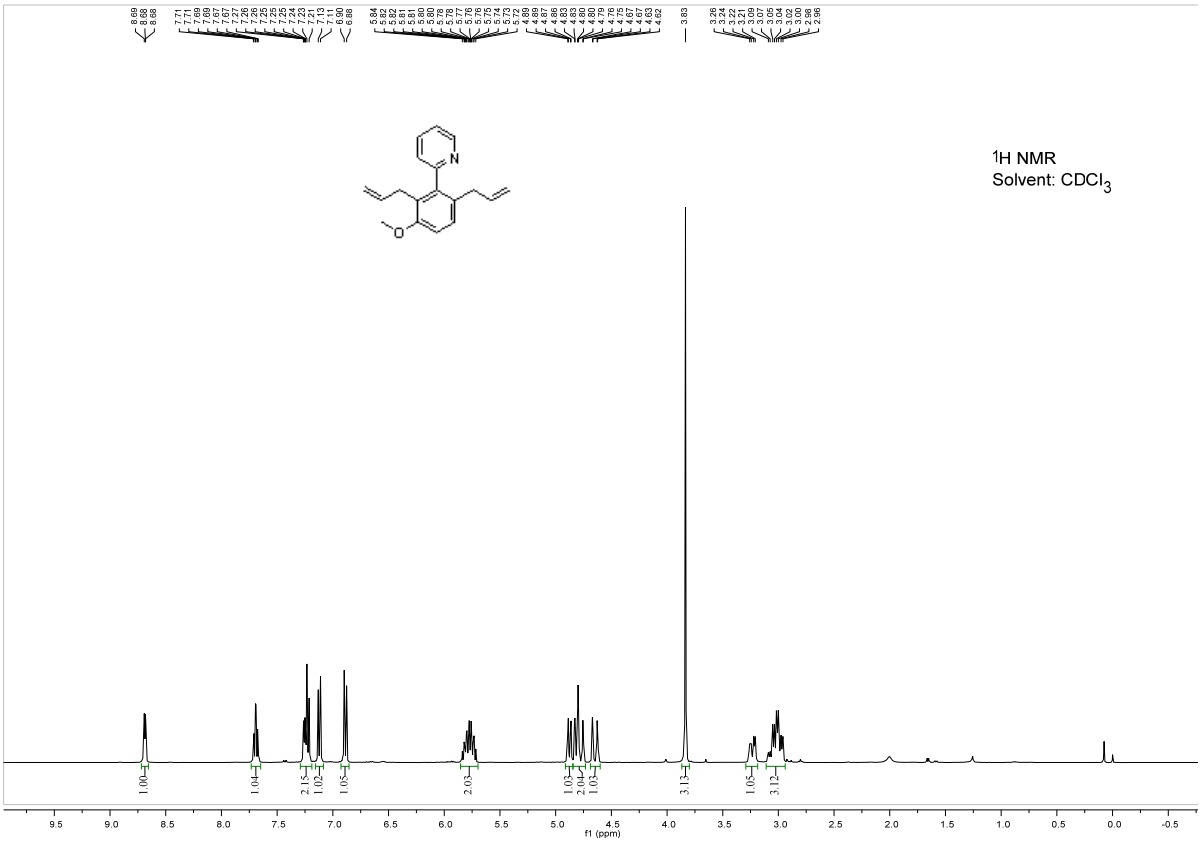

-62.55
N
CF3
19F NMR
Solvent: CDCl3
-59.0
-59.5
-60.0
-60.5
-61.0
-61.5
-62.0
-62.5
-63.0
-63.5
-64.0
-64.5
-65.0
-65.5
-66.0
f1 (ppm)

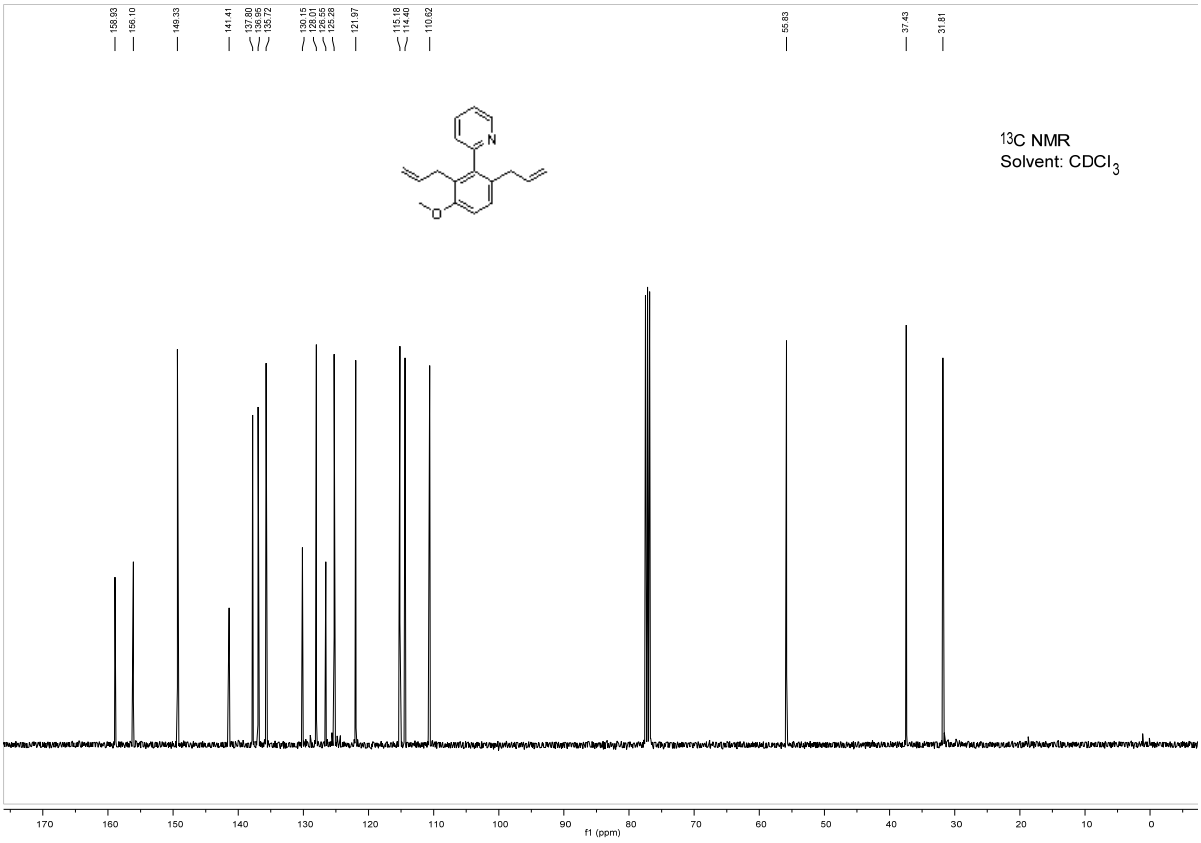
(23) 2-(2,6-diallyl-4-nitrophenyl)pyridine (**3wa**)



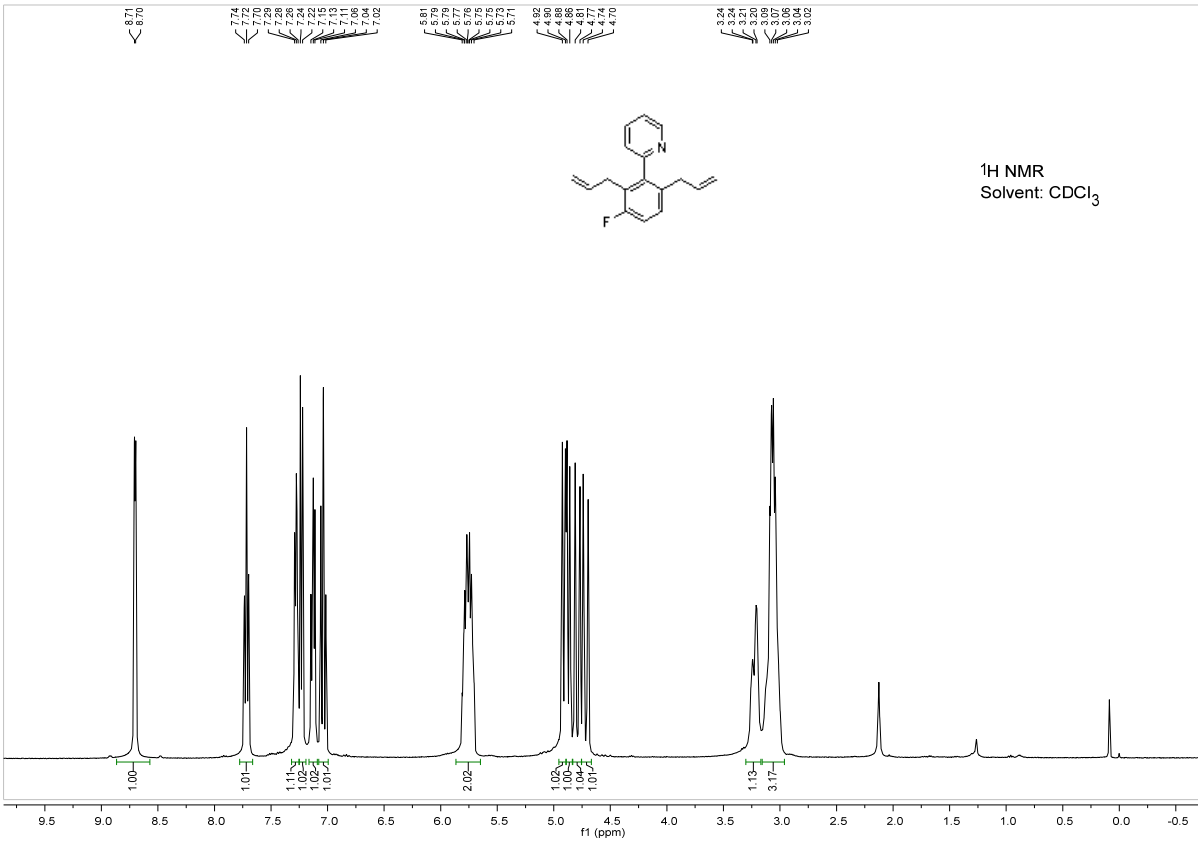


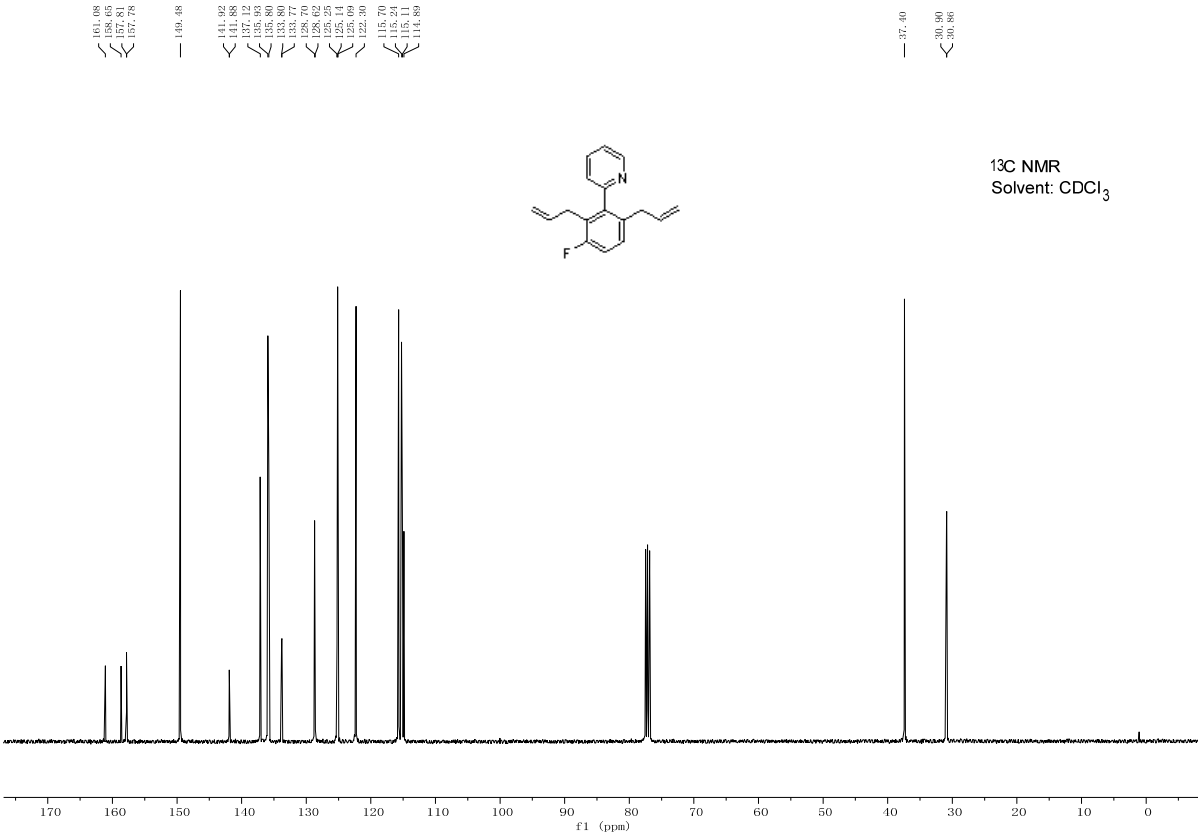
(24) 2-(2,6-diallyl-3-methoxyphenyl)pyridine (**3xa**)

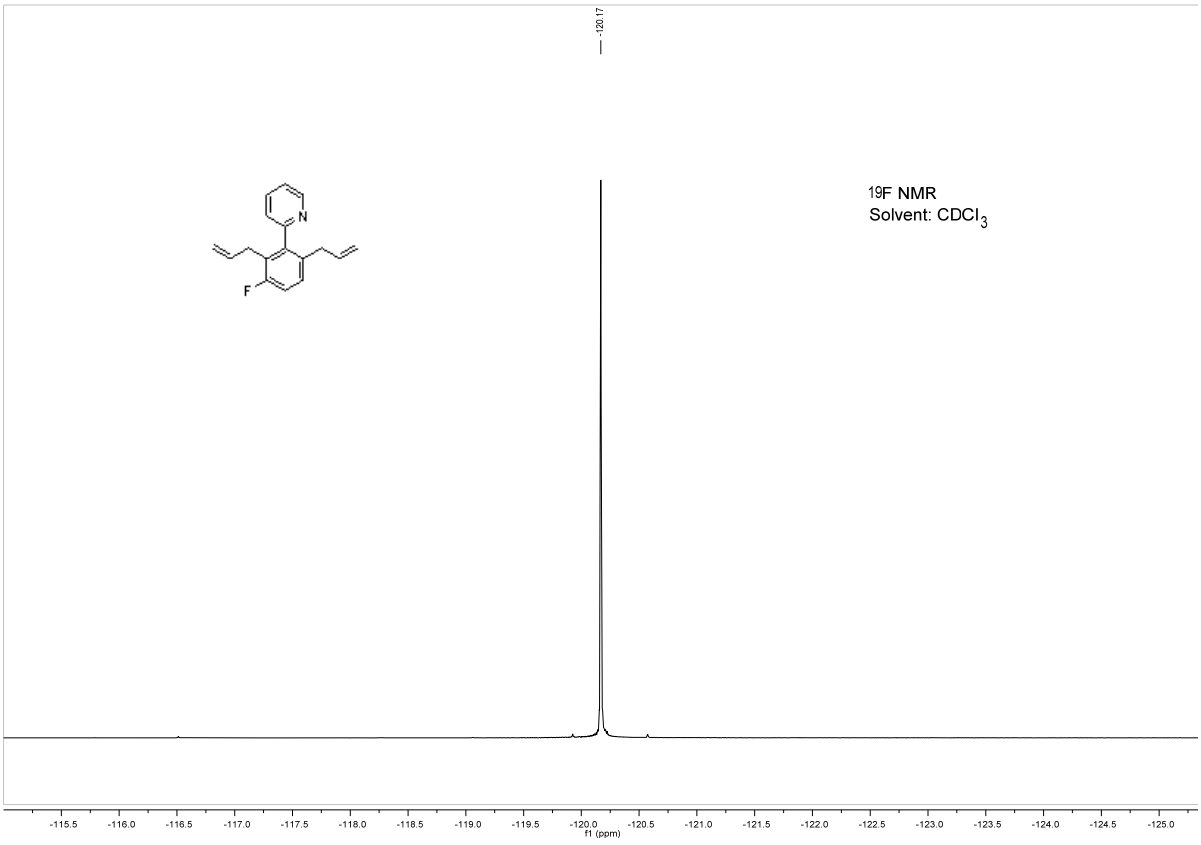




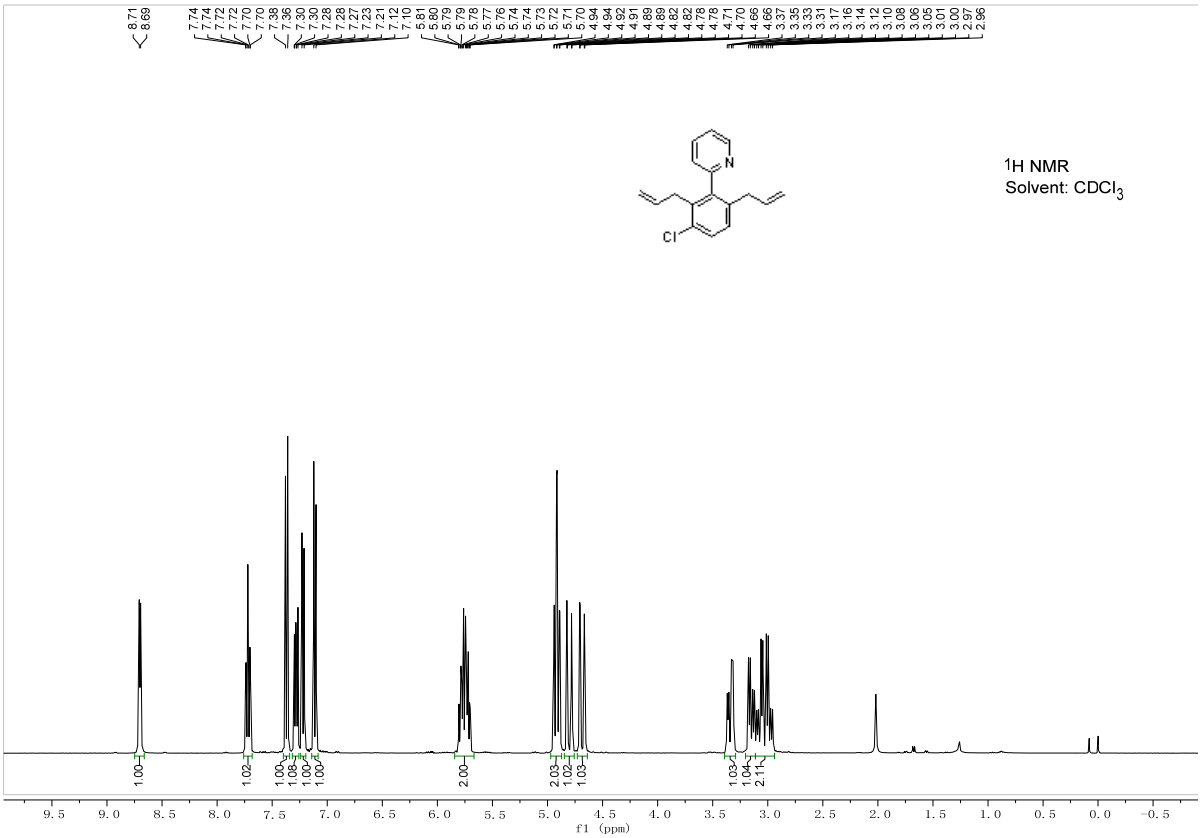
(25) 2-(2,6-diallyl-3-fluorophenyl)pyridine (**3ya**)

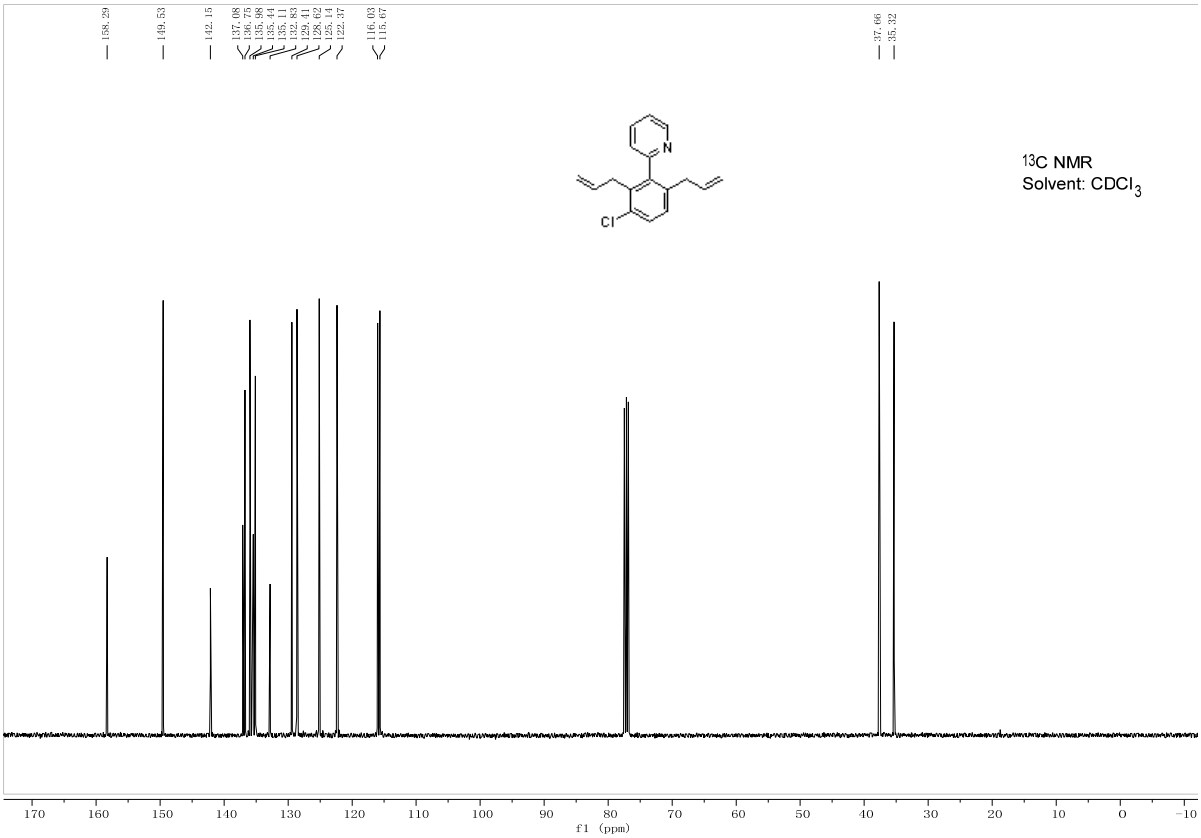




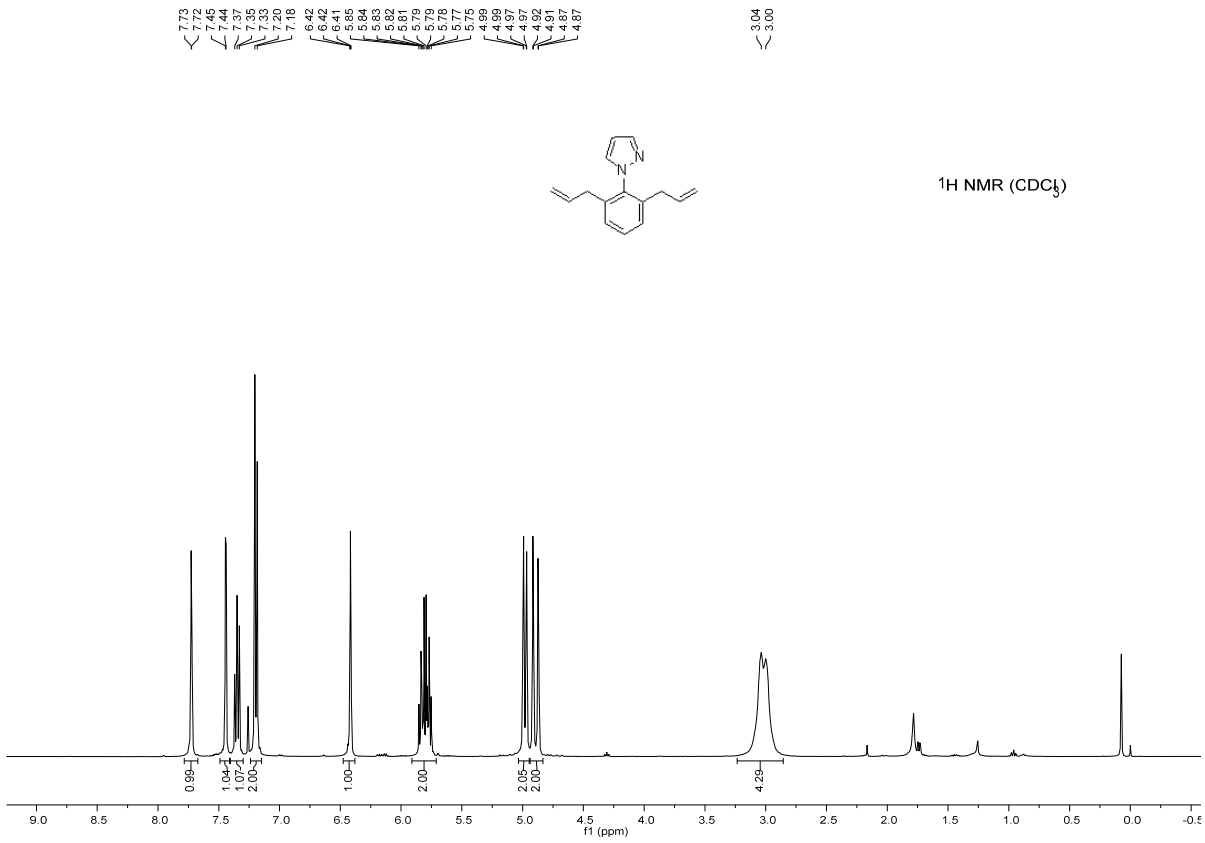

-120.17
N
F
19F NMR
Solvent: CDCl3
-115.5
-116.0
-116.5
-117.0
-117.5
-118.0
-118.5
-119.0
-119.5
-120.0
-120.5
-121.0
-121.5
-122.0
-122.5
-123.0
-123.5
-124.0
-124.5
-125.0
f1 (ppm)

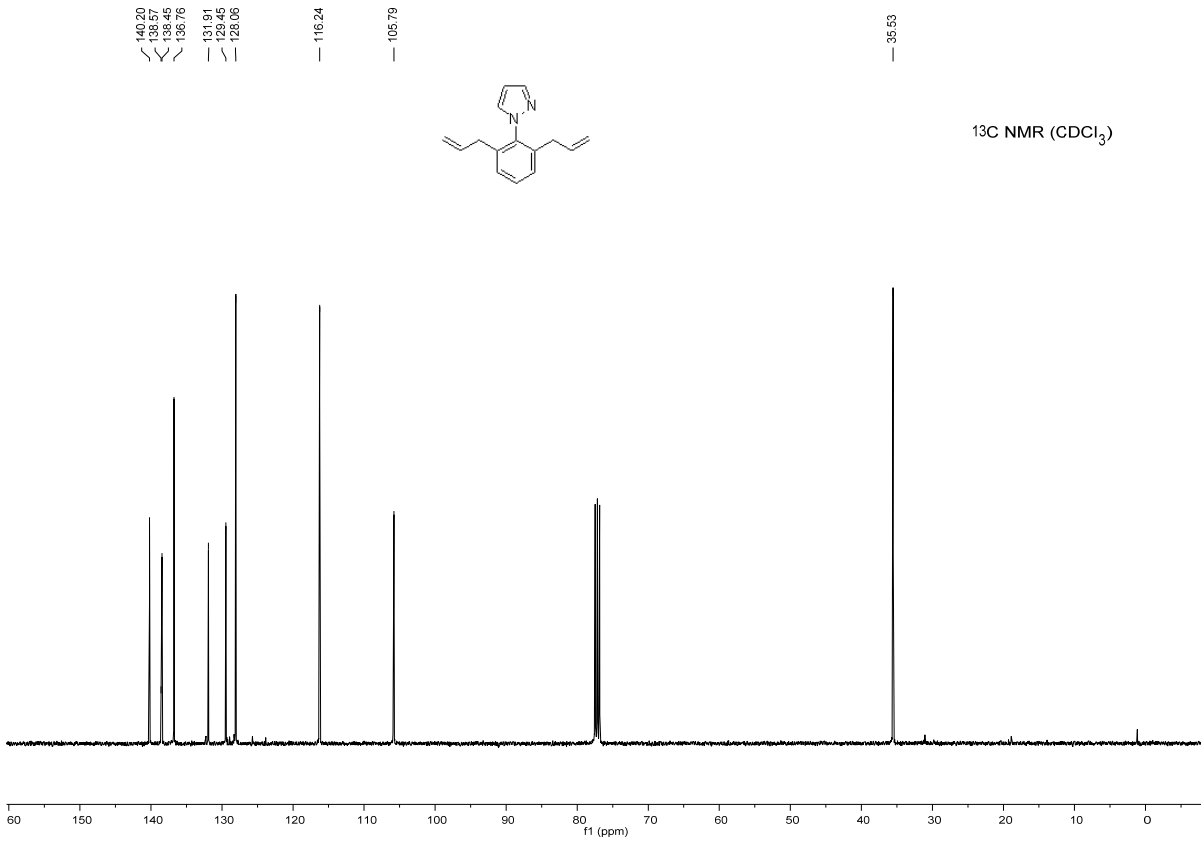
(26) 2-(2,6-diallyl-3-chlorophenyl)pyridine (**3za**)



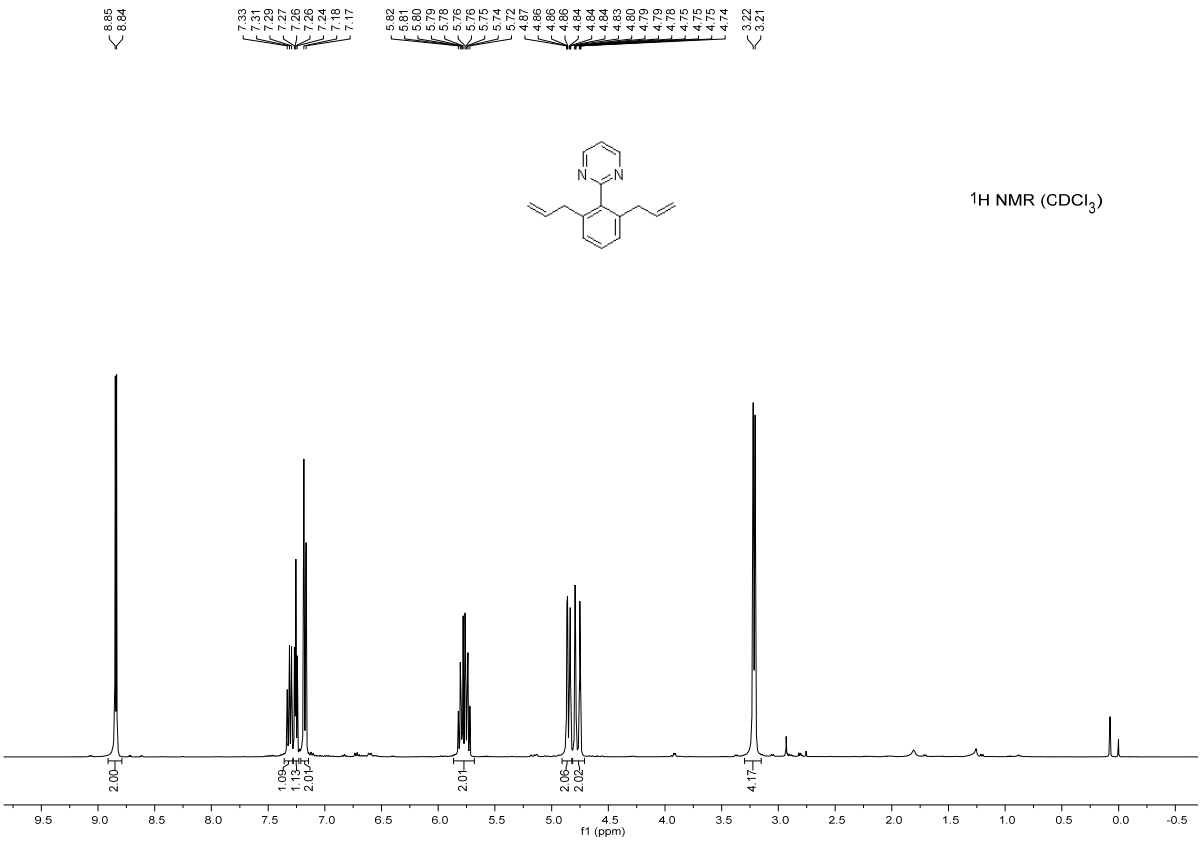


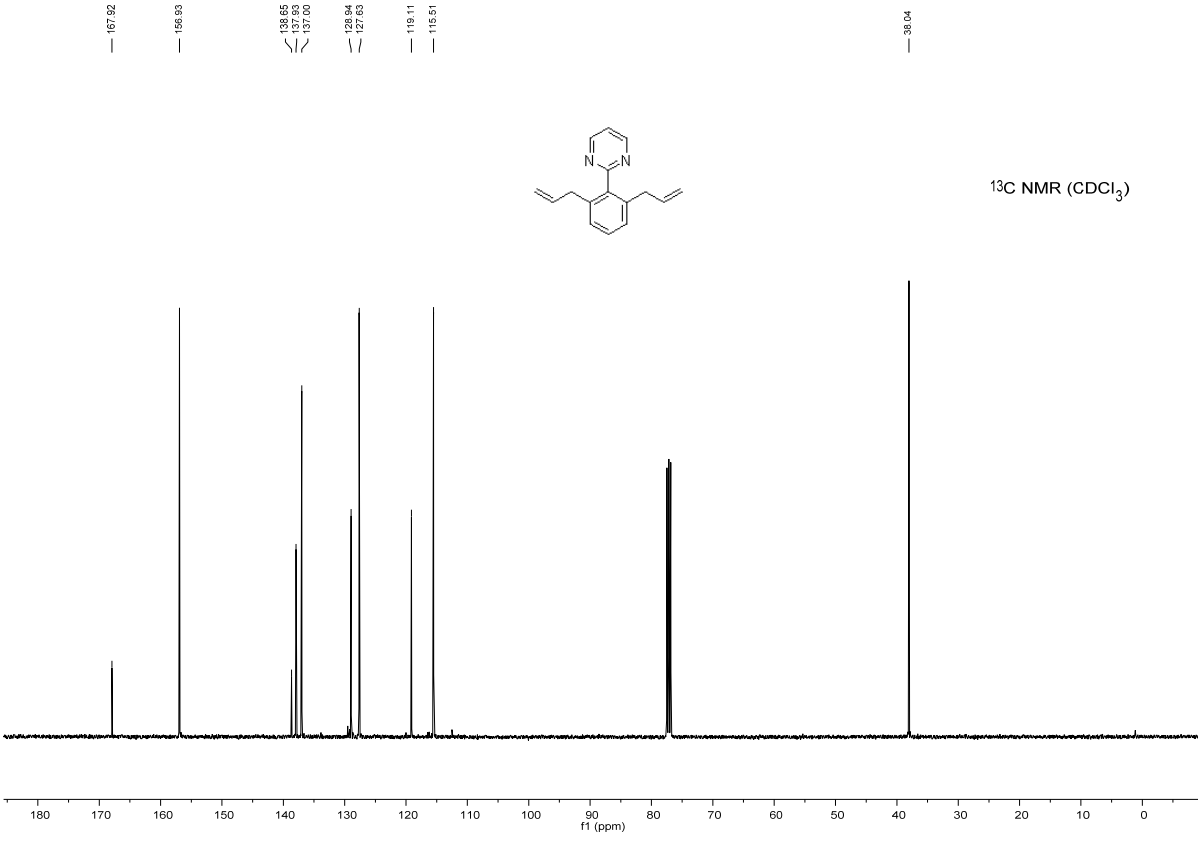
(27) 1-(2,6-diallylphenyl)-1H-pyrazole (**4**)



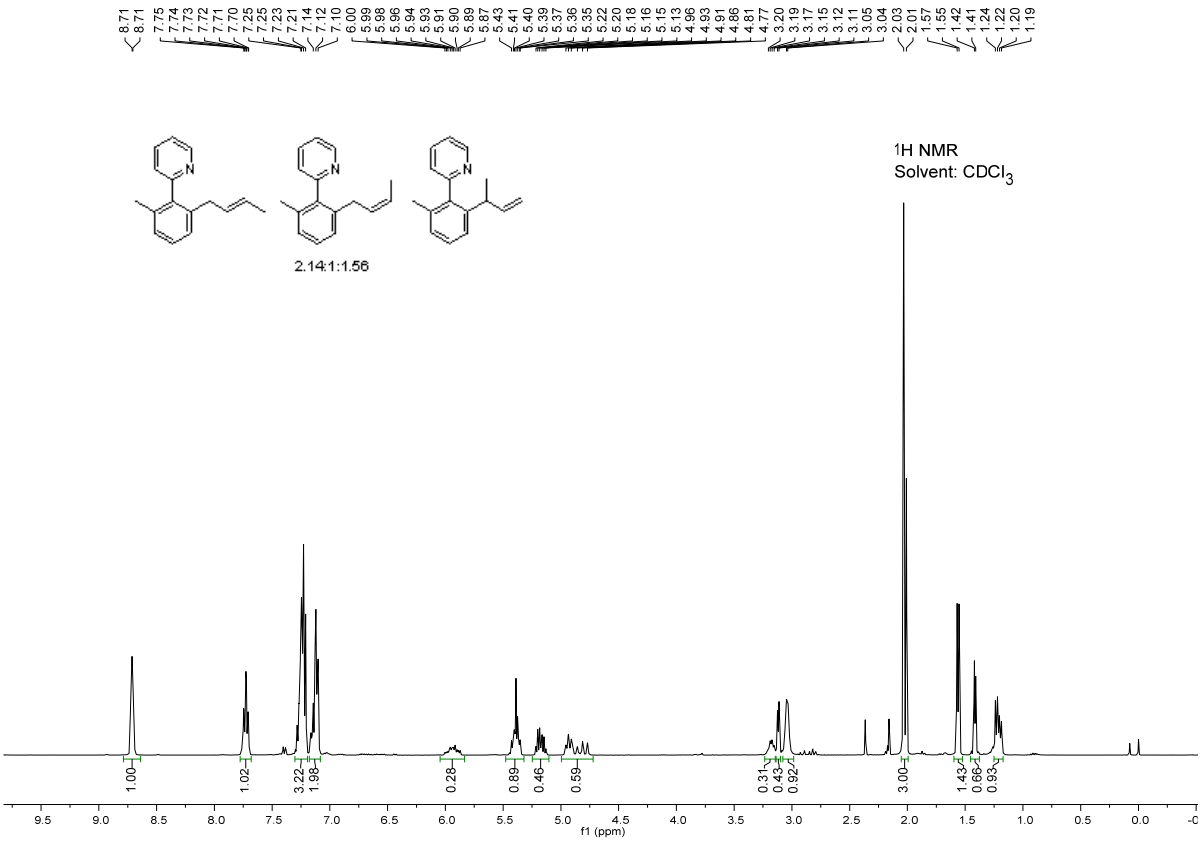


(28) 2-(2,6-diallylphenyl)pyrimidine (**5**)





(29) ^{1}H NMR spectrum of the products by reaction of 2-(*o*-tolyl)pyridine with *N*-(but-3-en-2-yl)-*N*-methylaniline



(30) ^{1}H NMR spectrum of the products by reaction of 2-(*o*-tolyl)pyridine with *N*-(but-2-en-1-yl)-*N*-methyl aniline