Supporting Information

Direct Use of Allylic Alcohols and Allylic Amines in Palladium-Catalyzed Allylic Amination

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CONTENTS

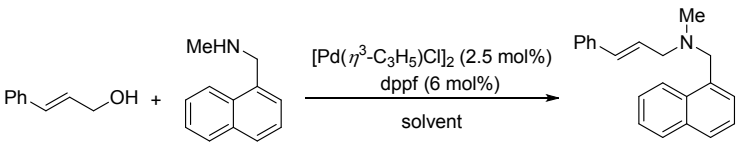
1. General Experimental Details

All reactions were performed in flame-dried glassware under an atmosphere of dry nitrogen, and the workup was carried out in air, unless otherwise noted. All solvents were purchased from commercial sources and used as such. The NMR spectra were recorded on a Varian MERCURY plus-400 (400 MHz, ^{1}H; 101 MHz, ^{13}C) spectrometer with chemical shifts reported in ppm relative to the residual deuterated solvent and the internal standard tetramethylsilane. ^{19}F NMR spectra were recorded on a Varian instrument (376 MHz, respectively) and referenced relative to $PhCF_3$. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Mass spectrometry analysis was carried out using an electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer. Melting points were measured with SGW X-4 micro melting point apparatus. IR was measured on a PerkinElmer Spectrum 100 FT-IR Spectrometer.

DPPF (1,1'-Bis(diphenylphosphino)ferrocene) was purchased from Energy Chemical Inc. The other chemicals were purchased from Energy Chemical Inc. or J&K Scientific Inc. and used without further purification unless otherwise stated. Substituted cinnamyl alcohols were prepared according to the literature procedure [1].

2. Optimization of the Reaction Conditions Using Allylic Alcohol

Table S1. Optimization of the Reaction Conditions Using Allylic Alcohol[a]



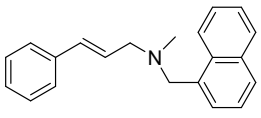
Entry	The amount of amine	Solvent	pK_a [b]	Temp. (°C)	*t* (h)	Yield (%)[c]
1	1.5 (equiv)	MeOH	15.5	rt	12	96
2	1.5 (equiv)	EtOH	15.9	rt	12	84
3	1.5 (equiv)	*n*-PrOH	16.1	rt	12	71
4	1.5 (equiv)	*i*-PrOH	17.1	rt	12	67
5[d]	1.5 (equiv)	*t*-BuOH	18.0	30	12	52
6	1.5 (equiv)	CF_3CH_2OH	12.4	rt	24	trace
7	1.5 (equiv)	Toluene	--	rt	24	NR
8	1.5 (equiv)	THF	--	rt	24	NR
9	1.5 (equiv)	MeOH	15.5	60	4	96
10	1.0 (equiv)	MeOH	15.5	rt	12	79
11	2.0 (equiv)	MeOH	15.5	rt	12	96

[a]Reaction of cinnamyl alcohol (0.50 mmol, 1.0 equiv) with 1-methyl-aminomethyl naphthalene (0.75 mmol, 1.5 equiv) was performed using dppf (5.0 mol%) and [Pd(η^3-allyl)Cl]$_2$ (2.5 mol%) as a catalytic system in solvent (2 mL) at rt. [b] See ref 2. [c] Yield of isolated product. [d] 30 °C instead of rt; The ligand was 1,1′-bis(diphenylphosphino)ferrocene (dppf), NR = no reaction.

3. General Procedure for Allylic Amination with Allylic Alcohols

A mixture of phosphine ligand (14.0 mg, 0.025 mmol) and [Pd(η^3-C_3H_5)Cl]$_2$ (4.6 mg, 0.0125 mmol) in dry MeOH (2 mL) was stirred at room temperature under a N_2 atmosphere for 60 min. Allylic alcohol (0.50 mmol, 1.0 equiv) was added and the mixture was stirred for another 10 min, followed by the addition of amine (0.75 mmol, 1.5 equiv). The reaction was monitored by GC-MS or TLC. The crude reaction mixture was concentrated by rotary evaporation and the residue was then purified by SiO_2 column chromatography (PE/EA/TEA = 10:1/0.4) to give the desired products.

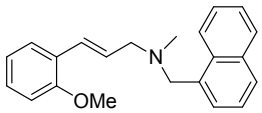
(*E*)-*N*-Methyl-*N*-(naphthalen-1-ylmethyl)-3-phenylprop-2-en-1-amine (3a) [3]



3a

Yellow oil, 137.5 mg, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.16 (m, 9H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.36 (dt, *J* = 12.0, 4.0 Hz, 1H), 3.92 (s, 2H), 3.25 (d, *J* = 8.0 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 134.9, 134.0, 132.8, 132.6, 128.6, 128.5, 128.0, 127.8, 127.6, 127.5, 126.4, 126.0, 125.7, 125.2, 124.7, 60.5, 60.2, 42.6.

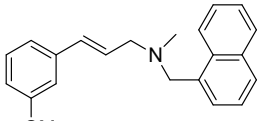
(*E*)-3-(2-Methoxyphenyl)-*N*-methyl-*N*-(naphthalen-1-ylmethyl)prop-2-en-1-amine (3b)



3b

Yellow oil, 152.1 mg, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.60 – 7.32 (m, 5H), 7.20 (t, *J* = 7.1 Hz, 1H), 6.99 – 6.87 (m, 2H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.40 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.93 (s, 2H), 3.82 (s, 3H), 3.30 (d, *J* = 6.3 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 135.2, 134.1, 132.8, 128.7, 128.4, 128.2, 127.8, 127.8, 127.1, 126.4, 126.2, 125.8, 125.4, 125.0, 120.9, 111.1, 61.3, 60.2, 55.7, 42.8; HRMS (Q–TOF Premier) calcd for $C_{22}H_{24}NO$ $(M+H)^+$: 318.1858; found: 318.1852.

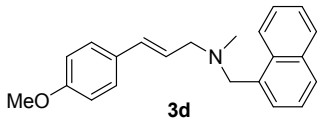
(*E*)-3-(3-Methoxyphenyl)-*N*-methyl-*N*-(naphthalen-1-ylmethyl)prop-2-en-1-amine (3c)



3c

Light yellow oil, 131.2 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.63 – 7.46 (m, 4H), 7.19 (dd, *J* = 16.7, 8.7 Hz, 1H), 7.03 – 6.86 (m, 2H), 6.76 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.35 (dt, *J* = 15.9, 6.6 Hz, 1H), 3.91 (s, 2H), 3.76 (s, 3H), 3.24 (d, *J* = 6.6 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 138.9, 135.1, 134.2, 132.9, 132.8, 129.8, 128.8, 128.3, 127.8, 126.2, 125.9, 125.4, 124.9, 119.3, 113.4, 111.8, 60.7, 60.5, 55.5, 42.8; HRMS (Q–TOF Premier) calcd for $C_{22}H_{24}NO$ $(M+H)^+$: 318.1858; found: 318.1852.

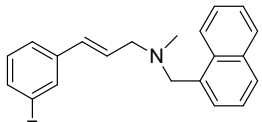
(*E*)-3-(4-Methoxyphenyl)-*N*-methyl-*N*-(naphthalen-1-ylmethyl)prop-2-en-1-amine (3d)[4]



3d

Yellow oil, 145.7 mg, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.20 (m, 4H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 13.9, 6.7 Hz, 1H), 3.92 (s, 2H), 3.79 (s, 3H), 3.25 (d, *J* = 6.8 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 135.1, 134.1, 132.7, 132.5, 130.1, 128.7, 128.2, 127.7, 126.2, 125.8, 125.5, 125.4, 124.9, 114.2 , 60.8, 60.3, 55.5, 42.7.

(*E*)-3-(3-Fluorophenyl)-*N*-methyl-*N*-(naphthalen-1-ylmethyl)prop-2-en-1-amine (3e)

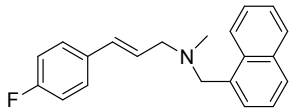


3e

Yellow oil, 138.6 mg, 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 7.4 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.35 (m, 4H), 7.28 – 7.18 (m, 1H), 7.12 – 7.05 (m, 2H), 6.92 – 6.87 (m, 1H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.35 (dt, *J* = 15.9, 6.6 Hz, 1H), 3.93 (s, 2H), 3.26 (d, *J* = 6.6

Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, J_{C-F} = 246.4 Hz), 139.5 (d, J_{C-F} = 8.08 Hz), 134.7, 133.9, 132.5, 131.6, 130.0 (d, J_{C-F} = 8.08 Hz), 129.2, 128.5, 128.1, 127.5, 126.0, 125.7, 125.2, 124.6, 122.2 (d, J_{C-F} = 3.03 Hz), 114.2 (d, J_{C-F} = 21.2 Hz), 112.8 (d, J_{C-F} = 21.2 Hz), 60.2, 60.1, 42.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.53; HRMS (Q–TOF Premier) calcd for $C_{21}H_{21}FN$ $(M+H)^+$: 306.1658; found: 306.1652.

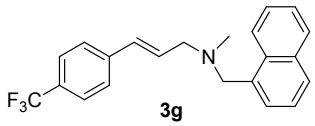
(*E*)-3-(4-Fluorophenyl)-*N*-methyl-*N*-(naphthalen-1-ylmethyl)prop-2-en-1-amine (3f)[4]



3f

Yellow oil, 133.8 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.37 (m, 4H), 7.36 – 7.30 (m, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.27 (dt, *J* = 15.9, 6.7 Hz, 1H), 3.94 (s, 2H), 3.25 (d, *J* = 6.7 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ162.4 (d, J_{C-F} = 246.4 Hz), 135.0, 134.1, 133.5, 132.7, 131.7, 128.7, 128.2, 128.0 (d, J_{C-F} = 7.1 Hz), 127.7, 127.5, 126.2, 125.8, 125.4, 124.8, 115.7 (d, J_{C-F} = 22.2 Hz), 60.6, 60.4, 42.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.79.

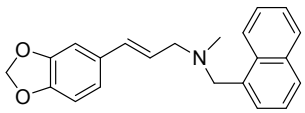
(*E*)-*N*-Methyl-*N*-(naphthalen-1-ylmethyl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-amin (3g)[4]



3g

Yellow oil, 118.6 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.57 – 7.41 (m, 8H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.44 (dt, *J* = 15.9, 6.5 Hz, 1H), 3.96 (s, 2H), 3.29 (d, *J* = 6.3 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 134.5, 134.1, 132.6, 131.6, 130.5, 129.3, 128.7, 128.4, 127.9, 126.7, 126.2, 125.9, 125.7 (q, J_{C-F} = 3.4 Hz), 125.4, 124.7, 60.4, 60.3, 42.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.44.

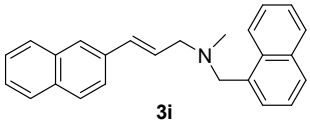
(*E*)-3-(Benzo[*d*][1,3]dioxol-5-yl)-*N*-methyl-*N*-(naphthalen-1-ylmethyl)prop-2-en-1-amine (3h)



3h

Yellow solid, 140.1 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.45 (m, 4H), 7.05 (d, *J* = 1.5 Hz, 1H), 6.89 – 6.82 (m, 2H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.29 (dt, *J* = 15.8, 6.7 Hz, 1H), 5.97 (s, 2H), 4.01 (s, 2H), 3.32 (d, *J* = 6.7 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 147.1, 135.0, 134.0, 132.6, 132.4, 131.7, 128.5, 128.0, 127.5, 126.0, 125.8, 125.7, 125.2, 124.7, 121.0, 108.3, 105.7, 101.1, 60.5, 60.1, 42.5; HRMS (Q–TOF Premier) calcd for $C_{12}H_{22}NO_2$ $(M+H)^+$: 332.1650; found: 332.1644; m.p. 68.5-69.5 ^{o}C.

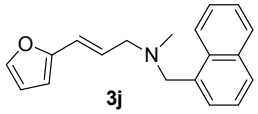
(*E*)-*N*-Methyl-*N*-(naphthalen-1-ylmethyl)-3-(naphthalen-2-yl)prop-2-en-1-amine (3i)



3i

Yellow solid, 154.5 mg, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.90 – 7.86 (m, 4H), 7.81 (s, 1H), 7.76 – 7.48 (m, 7H), 6.83 (d, *J* = 15.9 Hz, 1H), 6.60 (dt, *J* = 15.8, 6.6 Hz, 1H), 4.07 (s, 2H), 3.42 (d, *J* = 6.7 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 134.9, 134.3, 134.0, 133.3, 133.1, 132.9, 128.8, 128.5, 128.4, 128.35, 128.3, 128.0, 127.9, 126.6, 126.5, 126.3, 126.1, 126.0, 125.5, 125.0, 124.0, 60.8, 60.6, 42.9; HRMS (Q–TOF Premier) calcd for $C_{25}H_{24}N$ $(M+H)^+$: 338.1908; found: 338.1902; m.p. 82.0-83.0 °C.

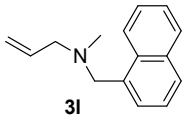
(*E*)-3-(Furan-2-yl)-*N*-methyl-*N*-(naphthalen-1-ylmethyl)prop-2-en-1-amine (3j)



3j

Yellow oil, 113.1 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.51 – 7.33 (m, 4H), 7.29 (d, *J* = 1.7 Hz, 1H), 6.40 – 6.32 (m, 1H), 6.33 – 6.29 (m, 1H), 6.24 (m, 1H), 6.16 (d, *J* = 3.3 Hz, 1H), 3.90 (s, 2H), 3.21 (d, *J* = 6.4 Hz, 2H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 128.7, 128.3, 127.8, 126.2, 125.9, 125.4, 124.8, 121.7, 111.4, 107.6, 60.0, 42.4; HRMS (Q–TOF Premier) calcd for $C_{19}H_{20}NO$ $(M+H)^+$: 278.1545; found: 278.1538.

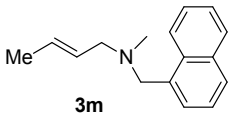
***N*-Methyl-*N*-(naphthalen-1-ylmethyl)prop-2-en-1-amin (3l)[4]**



3l

Colorless oil, 88.6 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 7.3 Hz, 1H), 7.56 – 7.35 (m, 4H), 5.99 (dt, *J* = 16.7, 6.6 Hz, 1H), 5.21 (dd , *J* = 23.9, 13.8 Hz, 2H), 3.88 (s, 2H), 3.12 (d, *J* = 6.3 Hz, 2H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 135.1, 134.1, 132.7, 128.7, 128.2, 127.7, 126.1, 125.8, 125.4, 124.9, 118.0, 61.5, 60.1, 42.6.

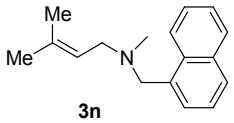
(*E*)-*N*-Methyl-*N*-(naphthalen-1-ylmethyl)but-2-en-1-amine (3m)



3m

Colorless oil, 87.9 mg, 78% yield (*E*:*Z* = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 9.5 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.34 (m, 4H), 5.74 – 5.58 (m, 2H), 3.87 (s, 2H), 3.06 (d, *J* = 5.3 Hz, 2H), 2.19 (s, 3H), 1.72 (d, *J* = 4.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0, 133.9, 132.5, 129.0, 128.44, 128.4, 127.9, 127.5, 125.9, 125.6, 125.1, 124.7, 60.4, 59.8, 42.3, 17.9; HRMS (Q–TOF Premier) calcd for $C_{16}H_{20}N$ $(M+H)^+$: 226.1595; found: 226.1590.

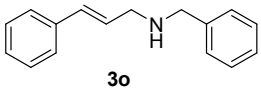
***N*,3-Dimethyl-*N*-(naphthalen-1-ylmethyl)but-2-en-1-amine (3n)**



3n

Light yellow oil, 60.5 mg, 51% yield, (l:b = 8:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.54 – 7.35 (m, 4H), 5.44 – 5.36 (m, 1H), 3.87 (s, 2H), 3.07 (d, *J* = 7.0 Hz, 2H), 2.20 (s, 3H), 1.77 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4, 135.1, 133.9, 132.5, 128.4, 127.8, 127.5, 125.9, 125.5, 125.1, 124.7, 121.7, 60.0, 55.6, 42.4, 26.0, 18.1; HRMS (Q–TOF Premier) calcd for $C_{17}H_{22}N$ $(M+H)^+$: 240.1752; found: 240.1747.

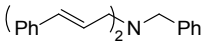
(*E*)-*N*-Benzyl-3-phenylprop-2-en-1-amine (3o)[5]



3o

Yellow oil, 69.8 mg, 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.19 (m, 10H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.34 (dt, *J* = 12.0, 4.0 Hz, 1H), 3.86 (s, 2H), 3.46 (s, 2H), 1.83 (br, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 137.1, 131.6, 128.6, 128.5, 128.45, 128.3, 127.4, 127.1, 126.3, 53.3, 51.2.

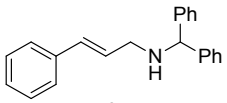
(*E*)-*N*-Benzyl-*N*-cinnamyl-3-phenylprop-2-en-1-amine[5]



3o'

Yellow oil, 8.1 mg, 6% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.30 – 7.41 (m, 15H), 6.56 (d, *J* = 16.0 Hz, 2H), 6.34 (dt, *J* = 16.0, 5.9 Hz, 2H), 3.70 (s, 2H), 3.32 (d, *J* = 6.6 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 131.0, 129.3, 128.8, 128.7, 128.5, 128.2, 127.7, 127.2, 126.5, 58.1, 56.2.

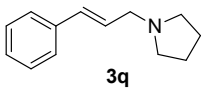
(*E*)-*N*-Benzhydryl-3-phenylprop-2-en-1-amine (3p)[6]



3p

Yellow oil, 116.2 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.17 (m, 15H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.31 (dt, *J* = 16.0, 8.0 Hz, 1H), 4.91 (s, 1H), 3.36 (dd, *J* = 6.2, 1.3 Hz, 2H), 1.74 (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 137.2, 131.4, 128.6, 128.5, 127.4, 127.1, 126.3, 66.6, 50.0.

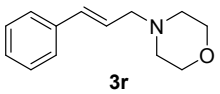
1-Cinnamylpyrrolidine (3q)[7]



3q

Yellow oil, 88.7 mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.16 (m, 5H), 6.54 (d, *J* =16.0 Hz, 1H), 6.30 – 6.38 (dt, *J* = 16.0, 8.0 Hz, 1H), 3.27 (d, *J* = 4.0 Hz, 2H), 2.58 (t, *J* = 4.0 Hz, 4H), 1.86 – 1.76 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 132.0, 128.5, 127.6, 127.4, 126.3, 58.4, 54.1, 23.5.

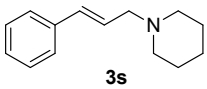
4-Cinnamylmorpholine (3r)[7]



3r

Light yellow oil, 97.3 mg, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.32-7.28 (m, 2H), 7.27 – 7.19 (m, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.25 (dt, *J* = 12.0, 8.0 Hz, 1H), 3.73 (t, *J* = 4.0 Hz, 4H), 3.15 (dd, *J* = 6.8, 0.8 Hz, 2H), 2.50 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 133.4, 128.6, 127.6, 126.3, 126.0, 67.0, 61.5, 53.7.

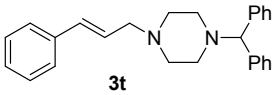
1-Cinnamylpiperidine (3s)[8]



3s

Light yellow oil, 83.2 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.31 (dt, *J* = 16.0, 8.0 Hz, 1H), 3.12 (d, *J* = 8.0 Hz, 2H), 2.43 (br s, 4H), 1.67 – 1.54 (m, 4H), 1.45 (br s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 132.6, 128.5, 127.4, 127.2, 126.3, 61.9, 54.6, 26.0, 24.4.

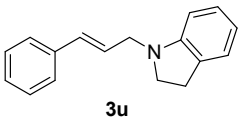
1-Benzhydryl-4-cinnamylpiperazine (3t)[7]



3t

White solid, 165.1 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 4H), 7.35 – 7.29 (m, 2H), 7.29 – 7.16 (m, 7H), 7.16 – 7.08 (m, 2H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.24 (dt, *J* = 15.8, 6.8 Hz, 1H), 4.20 (s, 1H), 3.13 (d, *J* = 6.8 Hz, 2H), 2.50 (br s, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 137.2, 133.4, 128.9, 128.8, 128.2, 127.8, 127.2, 126.8, 126.6, 76.5, 61.3, 53.7, 52.1; m.p. 120.0-121.0 ^{o}C.

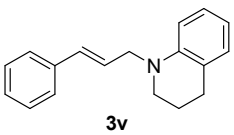
1-Cinnamylindoline (3u)[9]



3u

Colorless oil, 97.3 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.21 – 7.17 (m, 1H), 7.08 – 7.02 (m, 2H), 6.71 – 6.49 (m, 3H), 6.28 (dt, *J* = 12.0, 4.0 Hz, 1H), 3.83 (d, *J* = 8.0 Hz, 2H), 3.34 (t, *J* = 8.0 Hz, 2H), 2.94 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 137.2, 132.6, 130.6, 128.9, 127.8, 127.6, 126.7, 126.2, 124.8, 118.1, 107.8, 53.7, 51.9, 28.9.

(*E*)-1-(3-Phenyl-2-propenyl)-1,2,3,4-tetrahydroquinoline (3v)[9]

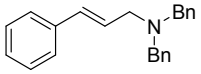


3v

Colorless oil, 92.1 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.24 – 7.21 (m, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.69 – 6.56 (m,

2H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.25 (dt, *J* = 16.0, 8.0 Hz, 1H), 4.03 (dd, *J* = 5.4, 1.6 Hz, 2H), 3.37 – 3.25 (m, 2H), 2.78 (t, *J* = 6.4 Hz, 2H), 2.03 – 1.92 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 137.0, 131.0, 129.1, 128.5, 127.4, 127.2, 126.3, 125.6, 122.6, 115.9, 111.1, 53.5, 49.2, 28.2, 22.4.

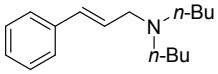
(*E*)-*N*,*N*-Dibenzyl-3-phenylprop-2-en-1-amine (3w)[7]



3w

Colorless oil, 102.3 mg, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 4H), 7.35 – 7.25 (m, 8H), 7.24 – 7.15 (m, 3H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.29 (dt, *J* = 16.0, 12.0 Hz, 1H), 3.61 (d, *J* = 4.0 Hz, 4H), 3.21 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 137.5, 132.8, 129.1, 128.8, 128.5, 128.0, 127.6, 127.1, 126.5, 58.2, 56.1.

***N*-Butyl-*N*-cinnamylbutan-1-amine (3x)[7]**



3x

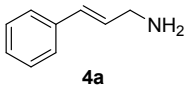
Light yellow oil, 64.1 mg, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.23 (dd, *J* = 12.0, 8.0 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.29 (dt, *J* = 12.0, 4.0 Hz, 1H), 3.25 (d, *J* =4.0 Hz, 2H), 2.53 – 2.41 (m, 4H), 1.50 – 1.43 (m, 4H), 1.35 – 1.26 (m, 4H), 0.91 (t, *J* = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 132.0, 128.5, 127.9, 127.2, 126.2, 56.7, 53.6, 29.1, 20.8, 14.1.

4. General Procedure for Allylic Amination with Allylic Amines

4.1 General procedure for the synthesis of allylic amine substrates [10]

To a solution of cinnamyl alcohol (4.20 mmol, 1.0 equiv) in anhydrous THF (8 mL) under N_2 atmosphere at 0 °C was added triphenylphosphine (5.46 mmol, 1.3 equiv) and phthalimide (6.29 mmol, 1.5 equiv). Then DEAD (5.46 mmole, 1.3 equiv) was added over 10 min at 0 °C. After one hour at 0 °C, the reaction mixture was warmed up to room temperature and stirred overnight. The resulting mixture was concentrated and the residue was purified by flash chromatography (SiO_2, 20% EA/ PE). The residue was dissolved in 20 mL EtOAc and 20 mL KOH (1 M). The aqueous phase was extracted with EtOAc (3 x 10 mL) and the combined organic layers were dried ($MgSO_4$). After removal the solvent, 2-cinnamylisoindoline-1,3-dione was obtained smoothly (57-65%). To a solution of 2-cinnamylisoindoline-1,3-dione (2.0 mmol, 1.0 equiv) in MeOH (40 mL) at room temperature was added hydrazine monohydrate (8.0 mmol, 4.0 equiv). The mixture was stirred overnight. The solution was concentrated under reduced pressure. The reaction mixture was diluted with 20 mL of DCM and 20 mL of KOH (1 M) and stirred for 30 min. The aqueous phase was extracted with DCM (3 x 20 mL) and the combined organic layers were dried ($MgSO_4$). After removal of the solvent, the corresponding amine was obtained (90-99%).

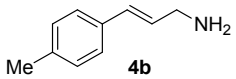
(*E*)-3-Phenylprop-2-en-1-amine[10]



4a

Yellow oil, 318.9 mg, 57% yield (two steps); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.21 (m, 5H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.32 (dt, *J* = 15.9, 5.9 Hz, 1H), 3.47 (d, *J* = 5.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 131.4, 129.7, 128.8, 127.5, 126.5, 44.5.

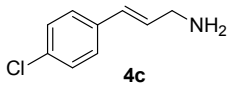
(*E*)-3-(*p*-Tolyl)prop-2-en-1-amine[11]



4b

Yellow oil, 358.1 mg, 58% yield (two steps); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.46 (d, *J* = 15.9 Hz, 1H), 6.26 (dt, *J* = 15.8, 5.9 Hz, 1H), 3.46 (d, *J* = 5.9 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 134.6, 130.4, 129.6, 129.5, 126.3, 44.6, 21.4.

(*E*)-3-(4-Chlorophenyl)prop-2-en-1-amine



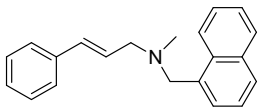
4c

Yellow oil, 441.9 mg, 63% yield (two steps); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 4H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.29 (dt, *J* = 15.9, 5.8 Hz, 1H), 3.47 (d, *J* = 5.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 132.1, 129.9, 128.9, 128.5, 127.6, 44.4.

4.2 General procedure for allylic amination with allylic amines

A mixture of phosphine ligand (14.0 mg, 0.025 mmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (4.6 mg, 0.0125 mmol) in dry MeOH (2 mL) was stirred at room temperature under a N_2 atmosphere for 30 min. Prop-2-en-1-amine (0.75 mmol, 1.5 equiv) was added and the mixture was stirred for another 10 min, followed by the addition of amine (0.50 mmol, 1.0 equiv). The reaction was monitored by TLC. The crude reaction mixture was concentrated by rotary evaporation and the residue was then purified by SiO_2 column chromatography (PE/EA/TEA = 10/1/0.4) to give the desired products.

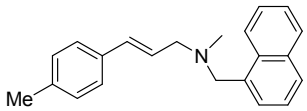
(*E*)-*N*-Methyl-*N*-(naphthalen-1-ylmethyl)-3-phenylprop-2-en-1-amine (3a)[3]



3a

Yellow oil, 138.7 mg, 97% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.16 (m, 9H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.36 (dt, *J* = 12.0, 4.0 Hz, 1H), 3.92 (s, 2H), 3.25 (d, *J* = 8.0 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 134.9, 134.0, 132.8, 132.6, 128.6, 128.5, 128.0, 127.8, 127.6, 127.5, 126.4, 126.0, 125.7, 125.2, 124.7, 60.5, 60.2, 42.6.

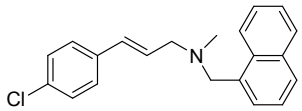
(*E*)-*N*-Methyl-*N*-(naphthalen-1-ylmethyl)-3-(p-tolyl)prop-2-en-1-amine (3y)[4]



3y

Yellow oil, 122.1 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.45 (m, 4H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.41 (dt, *J* = 15.8, 6.7 Hz, 1H), 4.02 (s, 2H), 3.35 (dd, *J* = 6.6, 0.5 Hz, 2H), 2.41 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 134.9, 134.4, 134.0, 132.7, 132.6, 129.3, 128.5, 128.0, 127.5, 126.5, 126.3, 126.0, 125.6, 125.2, 124.7, 60.6, 60.1, 42.5, 21.3.

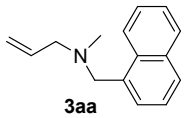
(*E*)-3-(4-Chlorophenyl)-*N*-methyl-*N*-(naphthalen-1-ylmethyl)prop-2-en-1-amine (3z)[4]



3z

Yellow oil, 143.2 mg, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.54 – 7.37 (m, 4H), 7.30 – 7.21 (m, 4H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.9, 6.6 Hz, 1H), 3.93 (s, 2H), 3.25 (dd, *J* = 6.6, 1.1 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.6, 134.8, 133.9, 133.0, 132.5, 131.4, 128.7, 128.51, 128.45, 128.0, 127.53, 127.50, 125.9, 125.6, 125.2, 124.6, 60.3, 42.6.

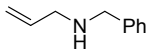
***N*-Methyl-*N*-(naphthalen-1-ylmethyl)prop-2-en-1-amine (3aa)[12]**



3aa

Yellow oil, 82.3 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.66 – 7.38 (m, 4H), 6.11 – 6.00 (m, 1H), 5.34 – 5.21 (m, 2H), 3.94 (s, 2H), 3.18 (d, *J* = 6.5 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2, 135.1, 134.1, 132.8, 128.7, 128.2, 127.7, 126.1, 125.8, 125.4, 124.9, 118.0, 61.5, 60.2, 42.6.

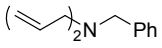
***N*-Benzylprop-2-en-1-amine (3ab)[13]**



3ab

Yellow oil, 34.3 mg, 47% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 5H), 5.94 (m, 1H), 5.17 (m, 2H), 3.80 (s, 2H), 3.28 (dt, *J* = 6.0, 1.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 128.7, 128.5, 127.3, 116.5, 53.4, 51.9, 29.9.

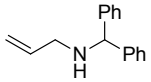
***N*-Allyl-*N*-benzylprop-2-en-1-amine[14]**



3ab'

Yellow oil, 7.0 mg, 7% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.20 (m, 5H), 5.88 (ddt, *J* = 16.6, 10.2, 6.4 Hz, 2H), 5.22 – 5.12 (m, 4H), 3.57 (s, 2H), 3.07 (dt, *J* = 6.4, 1.3 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 135.7, 129.0, 128.2, 126.9, 117.5, 57.5, 56.4

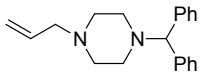
***N*-Benzhydrylprop-2-en-1-amine (3ac)** [15]



3ac

Yellow oil, 68.2 mg, 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.15 (m, 10H), 5.93 (m, 1H), 5.20 – 5.07 (m, 2H), 4.86 (s, 1H), 3.20 (dt, *J* = 5.9, 1.4 Hz, 2H), 1.85 (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 136.9, 128.8, 127.6, 127.3, 116.3, 66.7, 50.7.

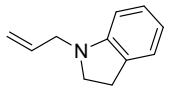
1-Allyl-4-benzhydrylpiperazine (3ad)



3ad

Yellow solid, 119.9 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.1, 0.9 Hz, 4H), 7.28 – 7.09 (m, 6H), 5.85 (m, 1H), 5.19 – 5.07 (m, 2H), 4.22 (s, 1H), 2.99 (d, *J* = 6.6 Hz, 2H), 2.46 (s, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 135.3, 128.7, 128.2, 127.1, 118.3, 76.5, 62.1, 53.6, 52.1.

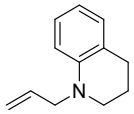
1-Allylindoline (3ae)[16]



3ae

Yellow oil, 63.8 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.04 (m, 2H), 6.70 (dt, *J* = 7.4, 0.9 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 5.95 (m, 1H), 5.38 – 5.18 (m, 2H), 3.74 (dt, *J* = 6.0, 1.5 Hz, 2H), 3.37 (dd, *J* = 8.9, 7.7 Hz, 2H), 2.99 (t, *J* = 8.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 134.4, 130.5, 127.5, 124.7, 118.0, 117.6, 107.7, 53.5, 52.5, 28.8.

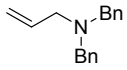
1-Allyl-1,2,3,4-tetrahydroquinoline (3af)[17]



3af

Yellow oil, 56.8 mg, 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (m, 2H), 6.56 (m, 2H), 5.89 – 5.78 (m, 1H), 5.22 – 5.10 (m, 2H), 3.85 (dt, *J* = 4.9, 1.7 Hz, 2H), 3.29 – 3.22 (m, 2H), 2.75 (t, *J* = 6.3 Hz, 2H), 1.99 – 1.91 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 133.8, 129.3, 127.3, 122.7, 116.2, 116.0, 111.3, 54.1, 49.4, 28.4, 22.6.

***N*,*N*-Dibenzylprop-2-en-1-amine (3ag)**[18]

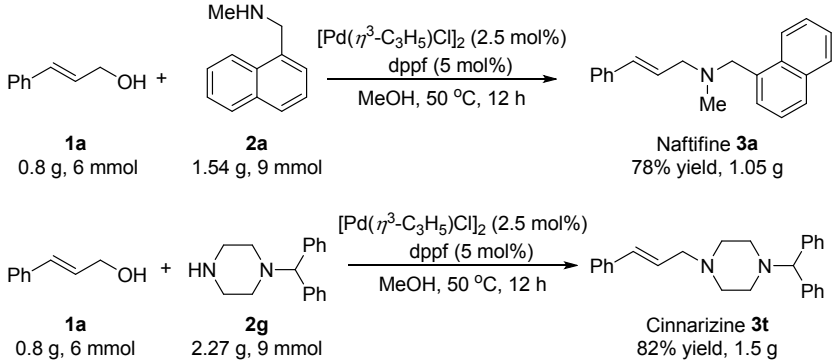


3ag

Colorless oil, 67.6 mg, 57% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.25 (m, 10H), 5.99 (m, 1H), 5.33 – 5.19 (m, 2H), 3.65 (s, 4H), 3.14 (dt, *J* = 6.3, 1.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 136.3, 129.1, 128.5, 127.1, 117.7, 58.0, 56.6.

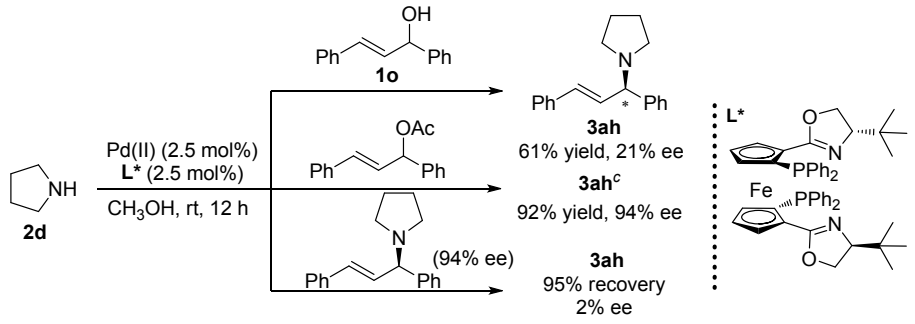
5. Direct One-step Synthesis of Cinnarizine and Naftifine

A mixture of phosphine ligand (166.3 mg, 0.30 mmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (54.6 mg, 0.15 mmol) in dry MeOH (24 mL) was stirred at room temperature under a N_2 atmosphere for 60 min. Cinnamyl alcohol (6.0 mmol, 1.0 equiv) was added and the mixture was stirred for another 10 min, followed by the addition of amine (9.0 mmol, 1.5 equiv). The reaction was monitored by TLC. The crude reaction mixture was concentrated by rotary evaporation and the residue was then purified by SiO_2 column chromatography (PE/EA/TEA = 10:1/0.4) to give the desired products.

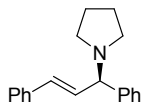


6. Asymmetric Catalysis and Control Experiments

A mixture of chiral ferrocene-based phosphinooxazoline ligand (30.0 μmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (25.0 μmol) in dry MeOH (2 mL) was stirred at room temperature under N_2 atmosphere for 1 h. Allylic substrates (0.50 mmol, 1.0 equiv) were added and the mixture was stirred for another 10 min, followed by the addition of amine (0.75 mmol, 1.5 equiv). The reaction was monitored by TLC. The crude reaction mixture was concentrated by rotary evaporation and the residue was then purified by SiO_2 column chromatography (PE/EA/TEA = 10:1/0.4) to give the desired products.



(*E*)-1-(1,3-Diphenylallyl)pyrrolidine (3ah)



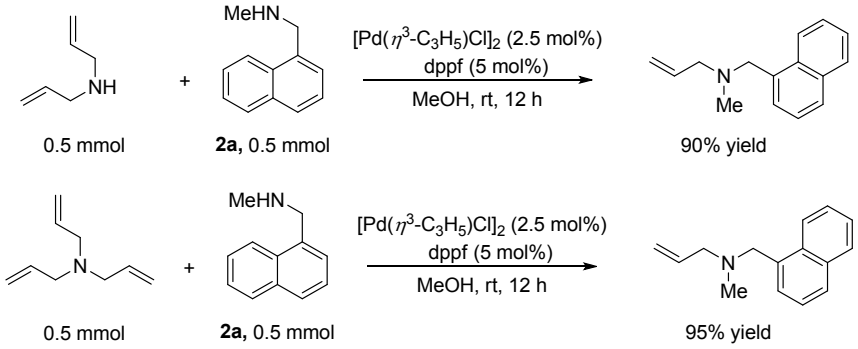
3ah

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.17 (m, 10H), 6.59 (d, *J* = 15.8 Hz, 1H), 6.45 (dd, *J* = 15.8, 8.6 Hz, 1H), 3.79 (d, *J* = 8.6 Hz, 1H), 2.59 (m, 2H), 2.47 (m, 2H), 1.87 – 1.74 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 137.3, 133.3, 130.1, 128.8, 128.7, 127.9, 127.6, 127.4, 126.7, 74.7, 53.4, 23.6.

Using chiral OD-H (95/5 *n*-hexane/i-PrOH, 0.5 mL min^{-1}, 254 nm, t (minor) = 7.8 min, t (major) = 8.3 min, 94% ee.

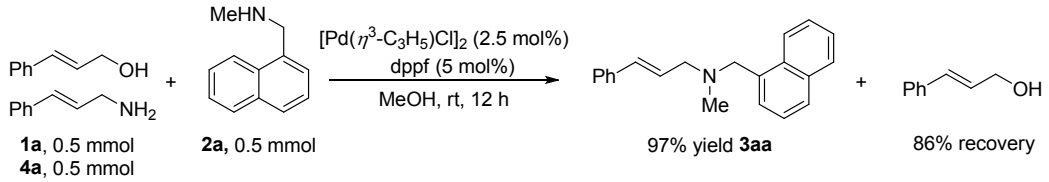
7. The Allylic Aminations with Diallylamine and Triallylamine

A mixture of phosphine ligand (14.0 mg, 0.025 mmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (4.6 mg, 0.0125 mmol) in dry MeOH (2 mL) was stirred at room temperature under a N_2 atmosphere for 30 min. diallylamine (0.50 mmol, 1.0 equiv) was added and the mixture was stirred for another 10 min, followed by the addition of 1-methyl-aminomethyl naphthalene (0.50 mmol, 1.0 equiv). Using the same method, triallylamine was reacted at the same time. The reaction was monitored by TLC. After 3 h, the crude reaction mixture was concentrated by rotary evaporation and the residue was then purified by SiO_2 column chromatography (PE/EA/TEA = 10/1/0.4) to give the desired products (90% yield for diallylamine; 95% yield for triallylamine).



8. The Competition Reaction with a 1:1 Mixture of Cinnamyl Alcohol and Cinnamyl Amine

A mixture of phosphine ligand (14.0 mg, 0.025 mmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (4.6 mg, 0.0125 mmol) in dry MeOH (2 mL) was stirred at room temperature under a N_2 atmosphere for 30 min. Then the mixture was added to a 1:1 mixture of cinnamyl alcohol (0.5 mmol, 1.0 equiv) and cinnamyl amine (0.5 mmol, 1.0 equiv), which was stirred for another 10 min, followed by the addition of 1-methyl-aminomethyl naphthalene (0.50 mmol, 1.0 equiv). The reaction was monitored by TLC. After 12 h, 1-methyl-aminomethyl naphthalene was completely transformed into the desired product (97% yield) with 86% cinnamyl alcohol recovery.



9. References

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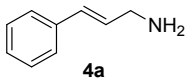
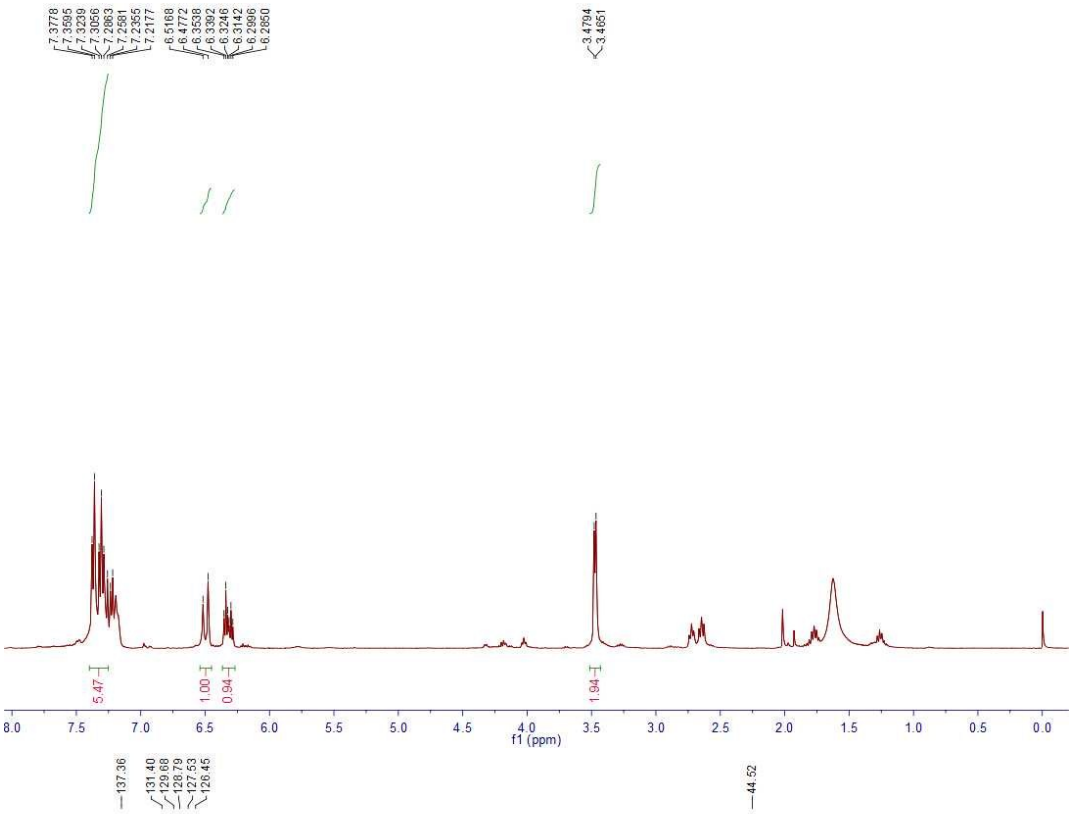
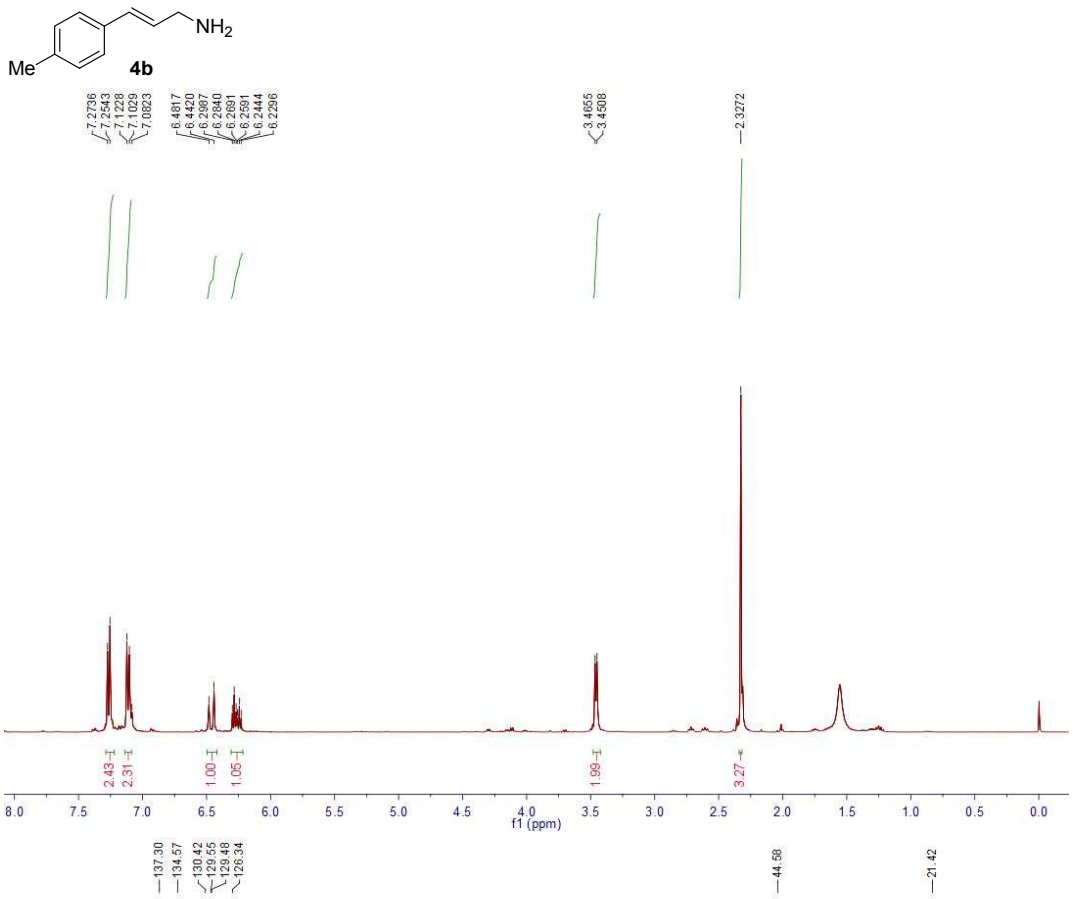
10. NMR Spectra



4a




NH2
Me
4b
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7.2543
7.1228
7.1029
7.0823
6.4817
6.4420
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6.2840
6.2691
6.2591
6.2444
6.2296
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3.4508
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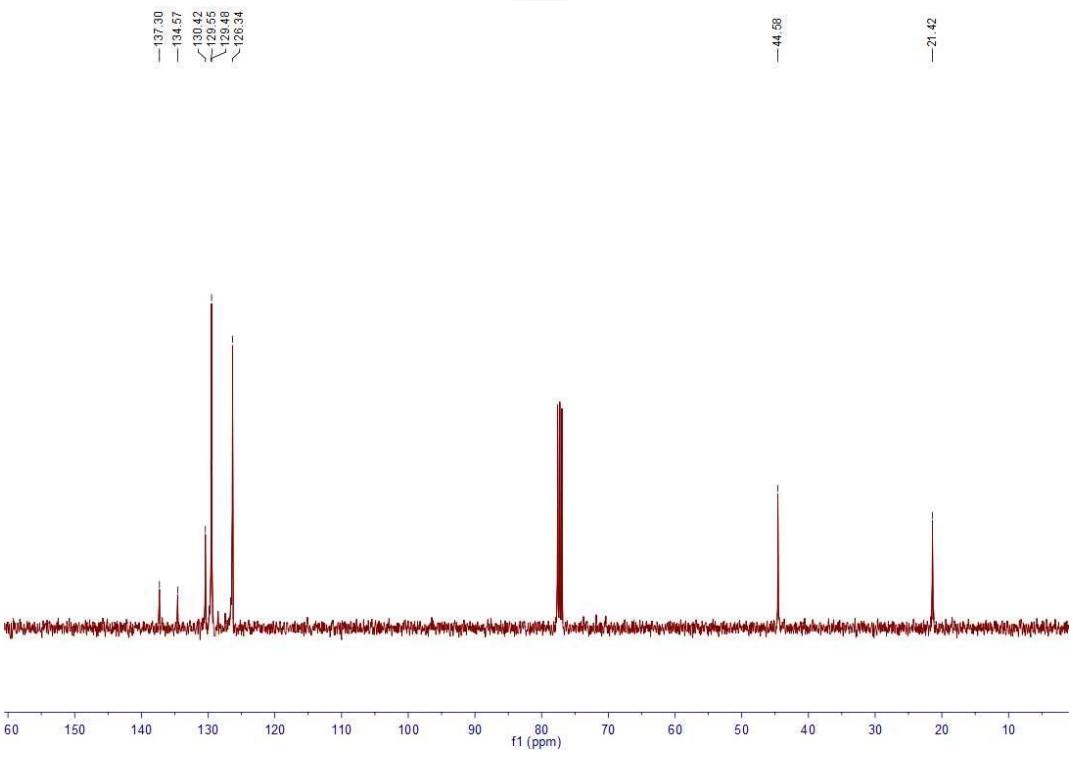
2.43
2.31
1.00
1.05
1.99
3.27
f1 (ppm)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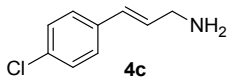
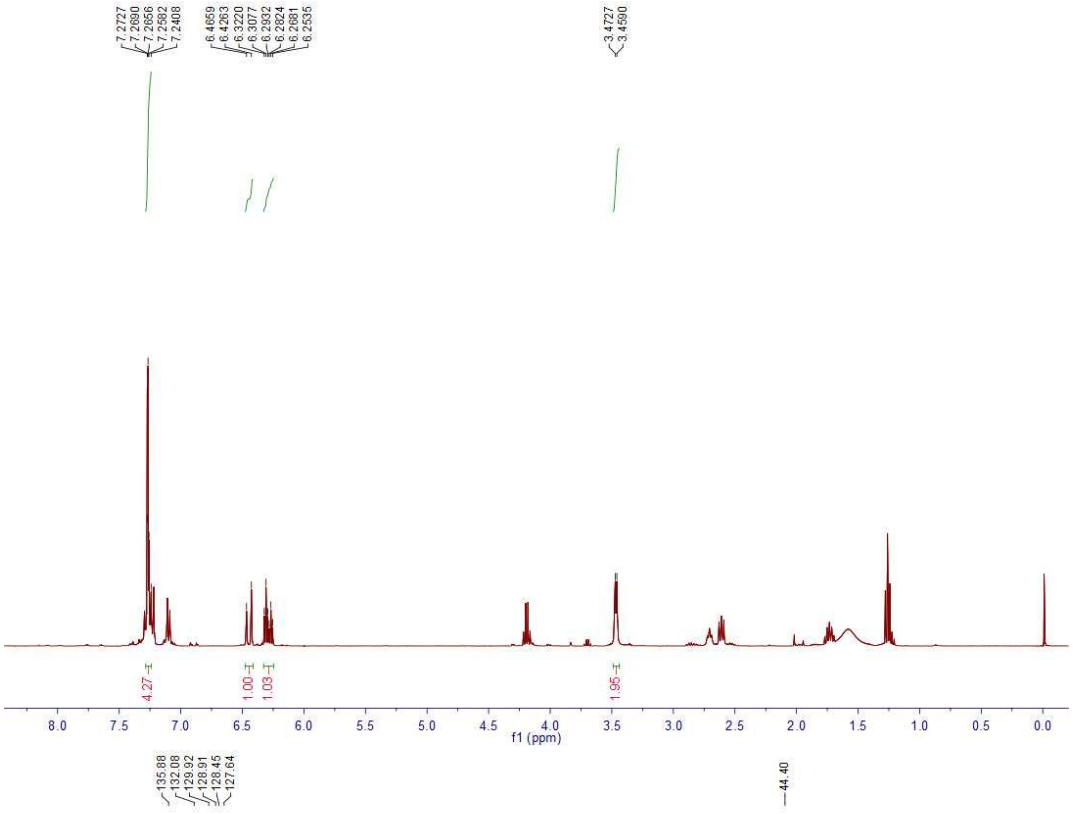
f1 (ppm)


NH2
Cl

4c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7.2656
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7.2408
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6.4263
6.3220
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6.2824
6.2681
6.2535
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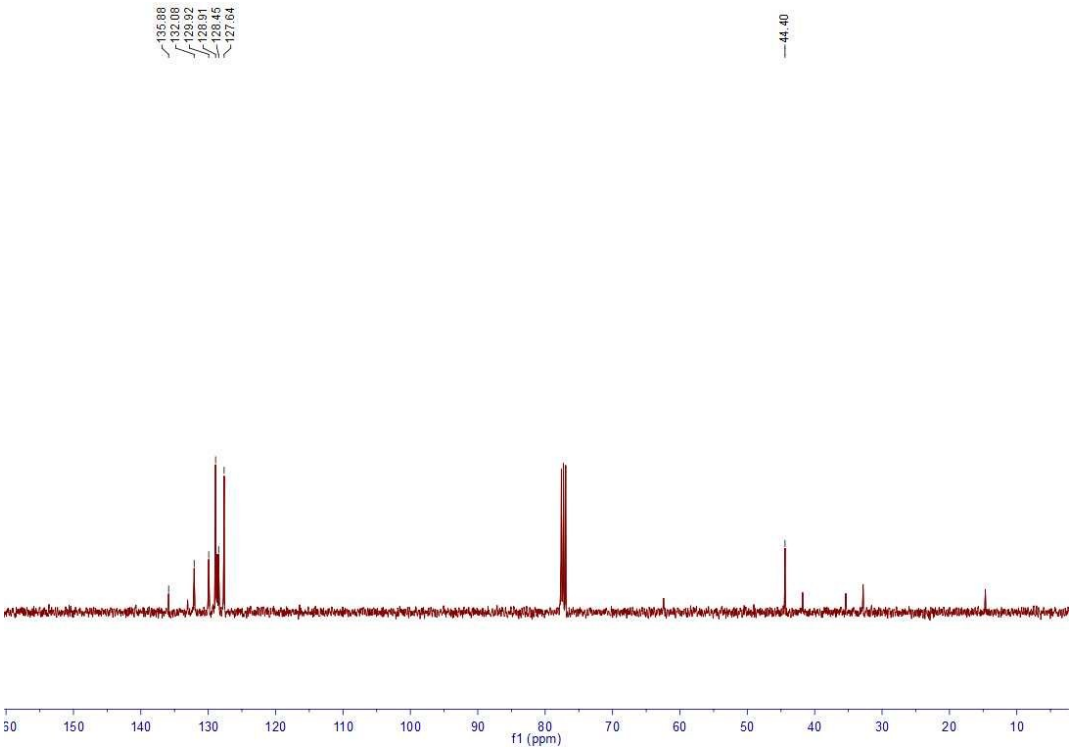
3.4590
4.27
1.00
1.03
1.95
f1 (ppm)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128.45
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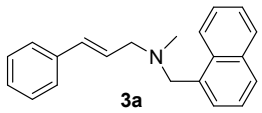
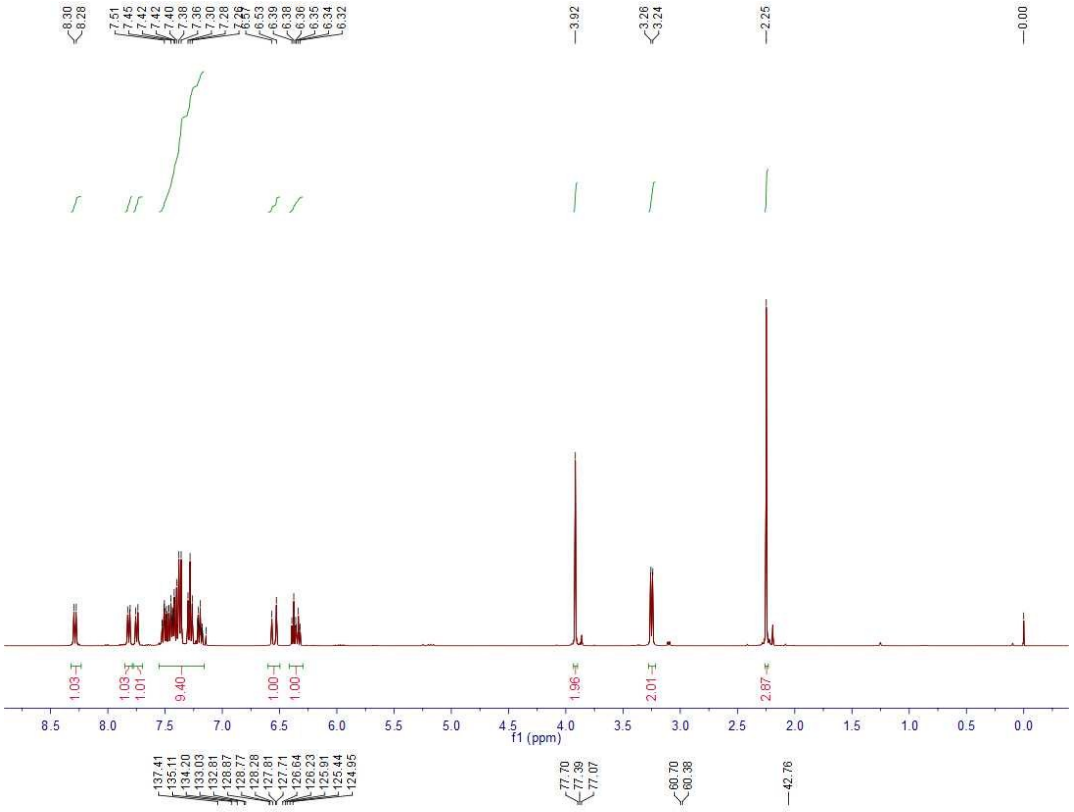
44.40
f1 (ppm)



3a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7.40
7.38
7.36
7.30
7.28
6.53
6.39
6.38
6.36
6.35
6.34
6.32
3.92
3.26
3.24
2.25
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1.03
1.03
1.01
9.40
1.00
1.00
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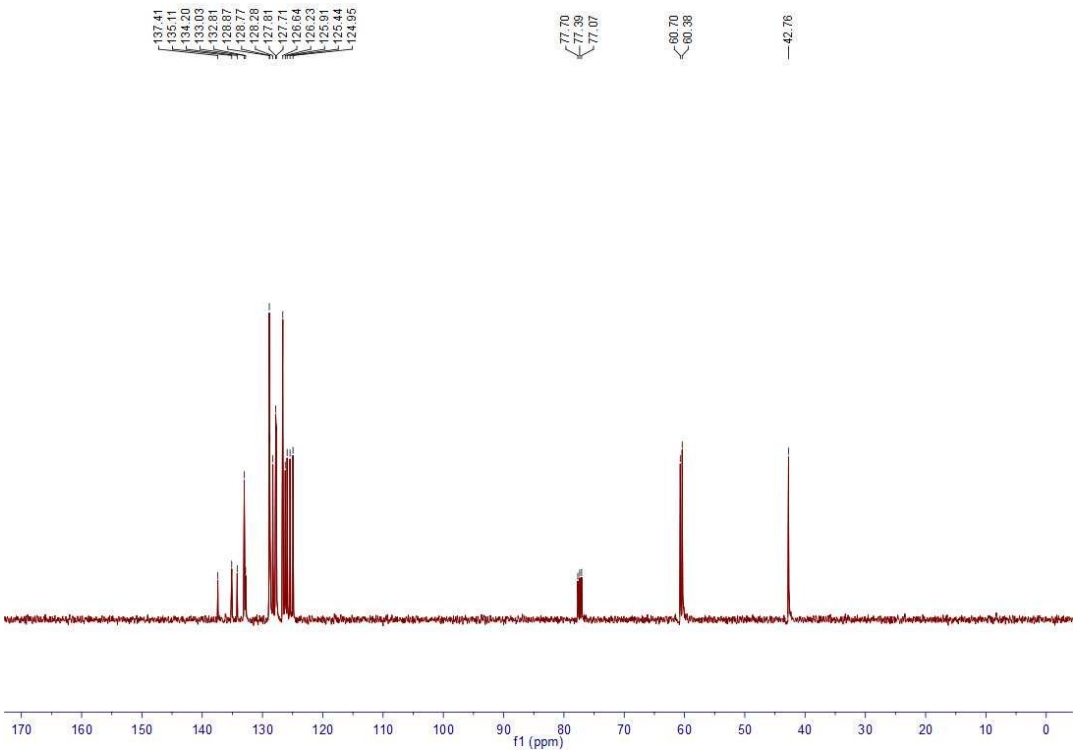
2.87
f1 (ppm)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127.71
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125.44
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60.70
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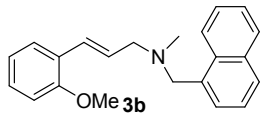
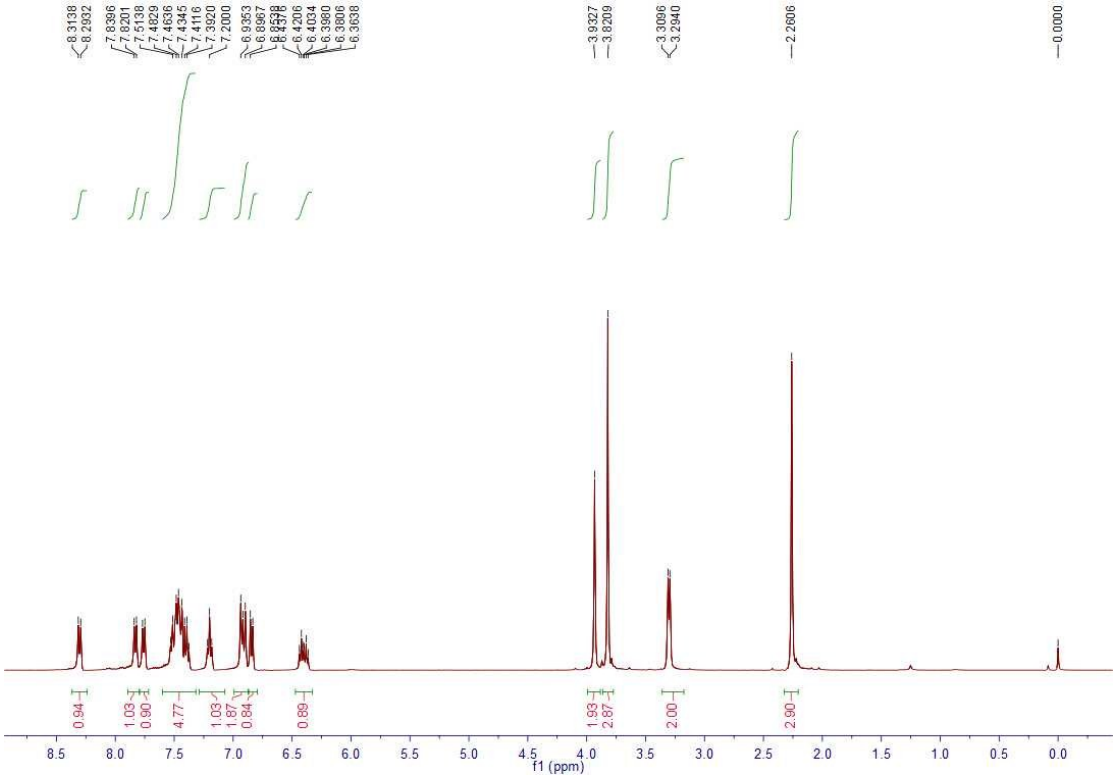
42.76
f1 (ppm)


N
OMe

3b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6.9353
6.8967
6.4206
6.4034
6.3960
6.3806
6.3638
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3.8209
3.3096
3.2940
2.2606
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0.94
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0.90
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1.03
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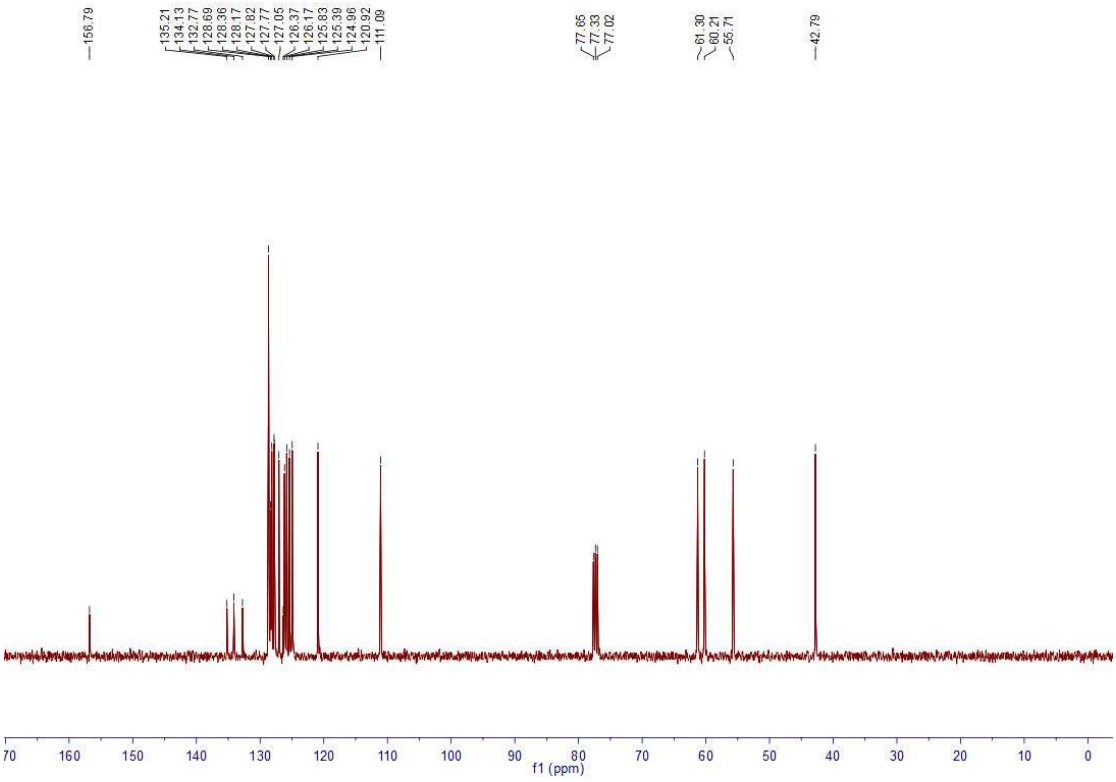
0.84
0.89
1.93
2.87
2.00
2.90
f1 (ppm)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125.83
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77.02
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60.21
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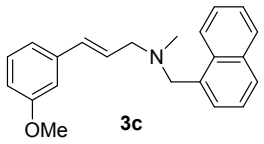
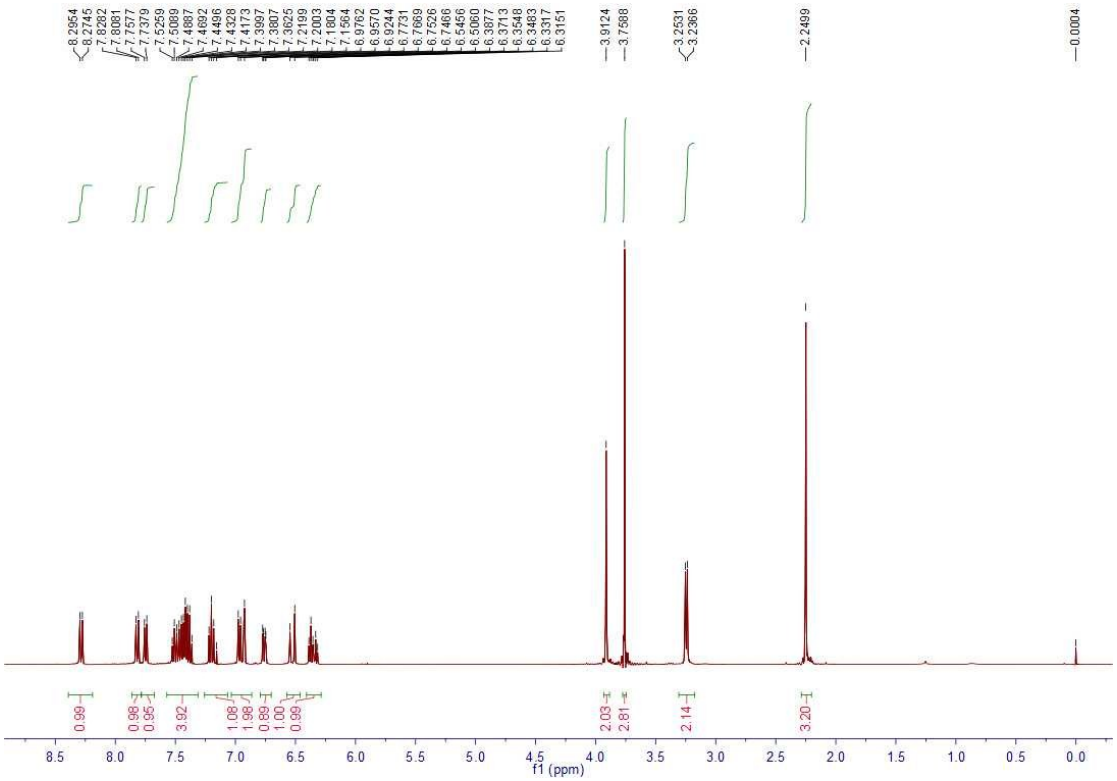
42.79
f1 (ppm)


N
OMe

3c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7.2003
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0.99
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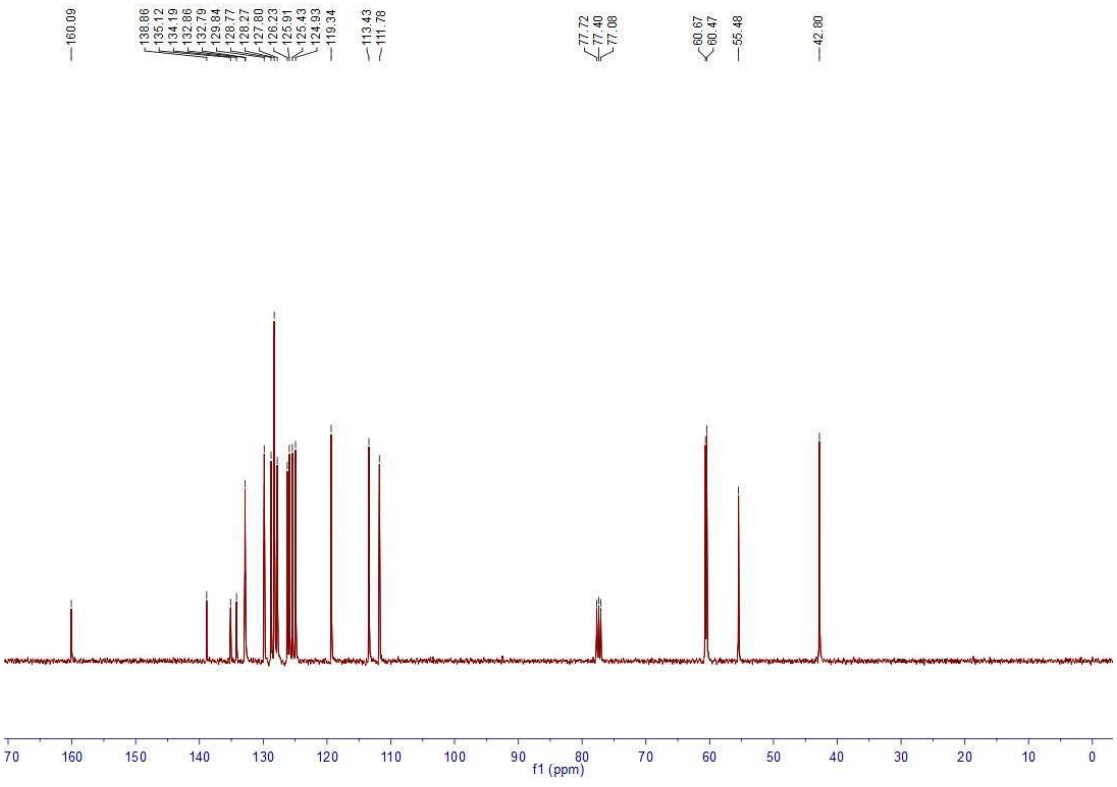
3.20
f1 (ppm)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124.93
119.34
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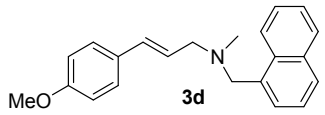
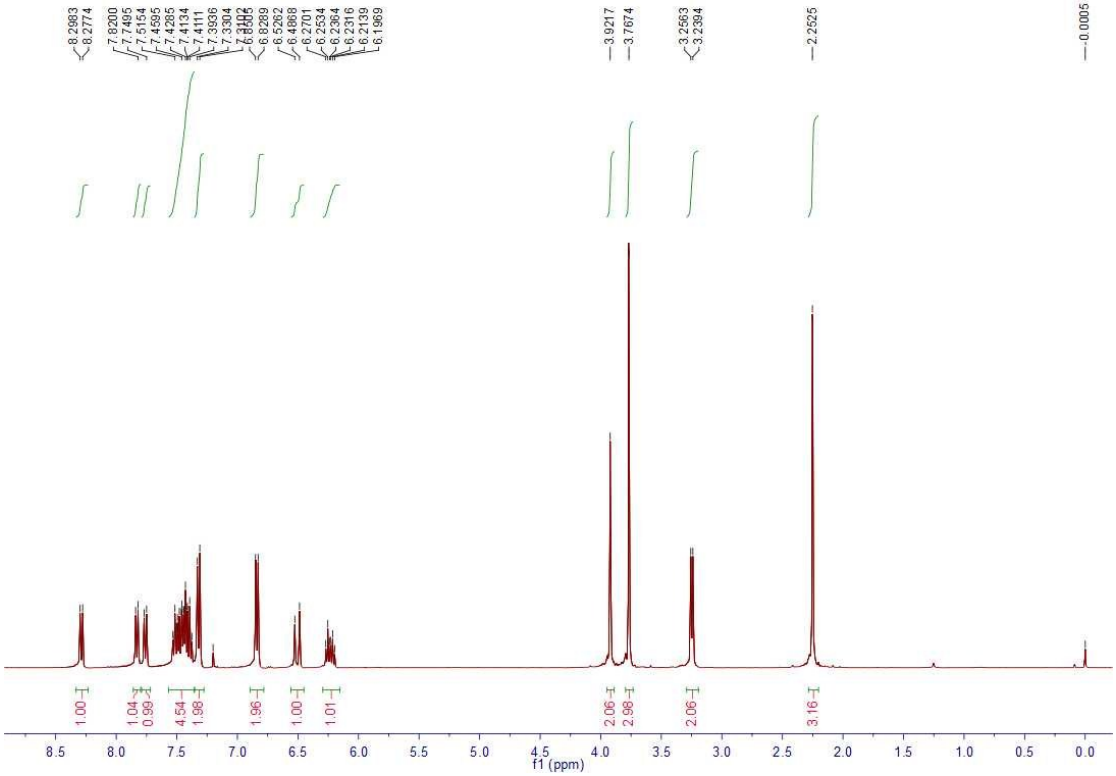
77.72
77.40
77.08
60.67
60.47
55.48
42.80
f1 (ppm)


MeO
N

3d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7.3304
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6.5262
6.4866
6.2701
6.2534
6.2364
6.2316
6.2139
6.1969
3.9217
3.7674
3.2563
3.2394
2.2525
0.0005
1.00
1.04
0.99
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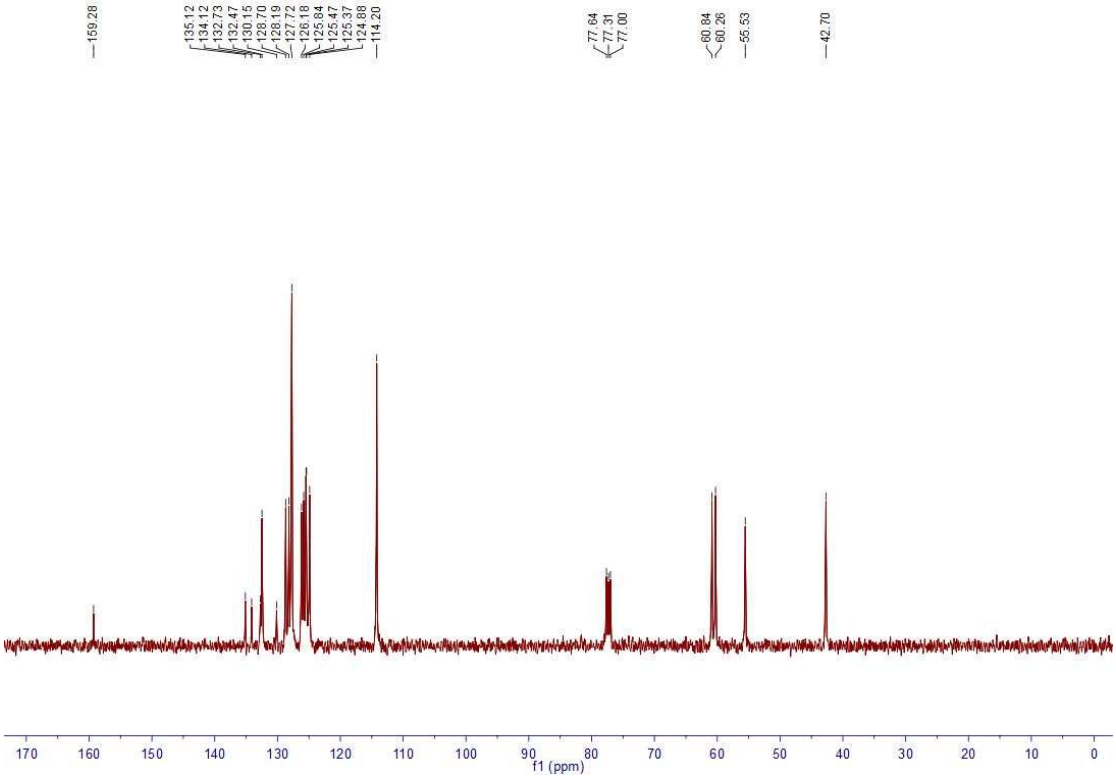
1.96
1.00
1.01
2.06
2.98
2.06
3.16
f1 (ppm)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128.19
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126.18
125.84
125.47
125.37
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114.20
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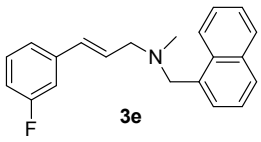
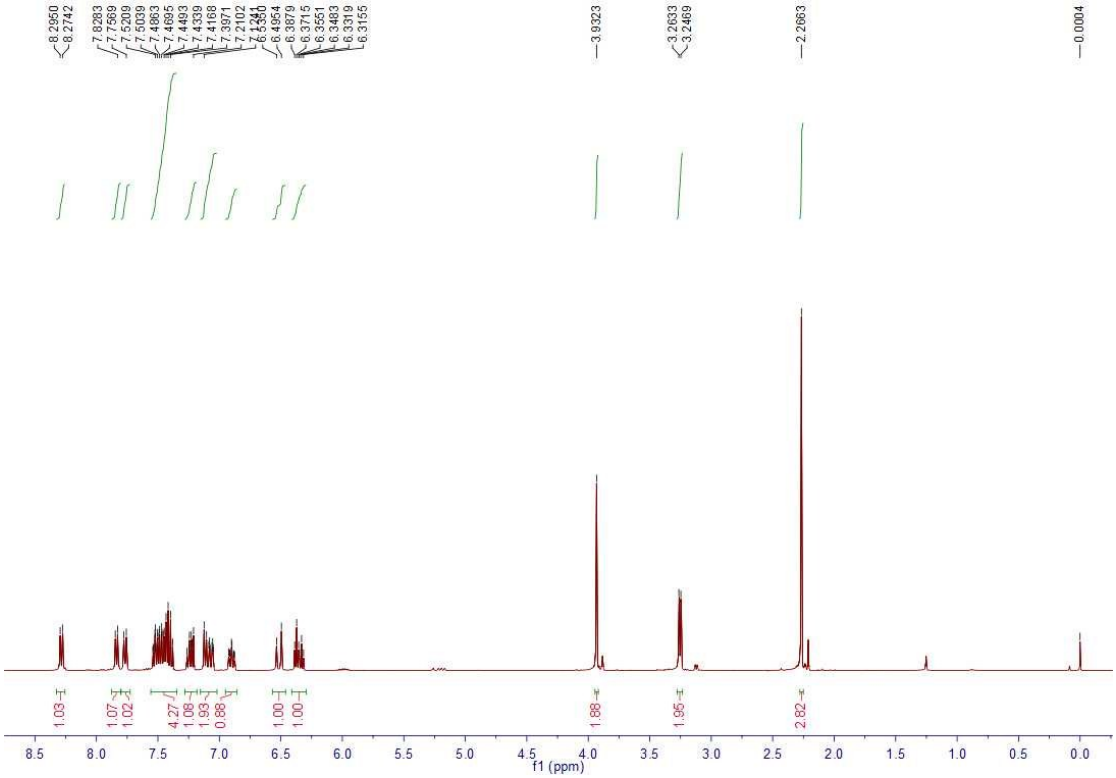
77.31
77.00
60.84
60.26
55.53
42.70
f1 (ppm)


N
F

3e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7.2102
7.1941
6.4954
6.3879
6.3715
6.3551
6.3483
6.3319
6.3155
3.9323
3.2633
3.2469
2.2663
0.0004
1.03
1.07
1.02
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1.08
1.93
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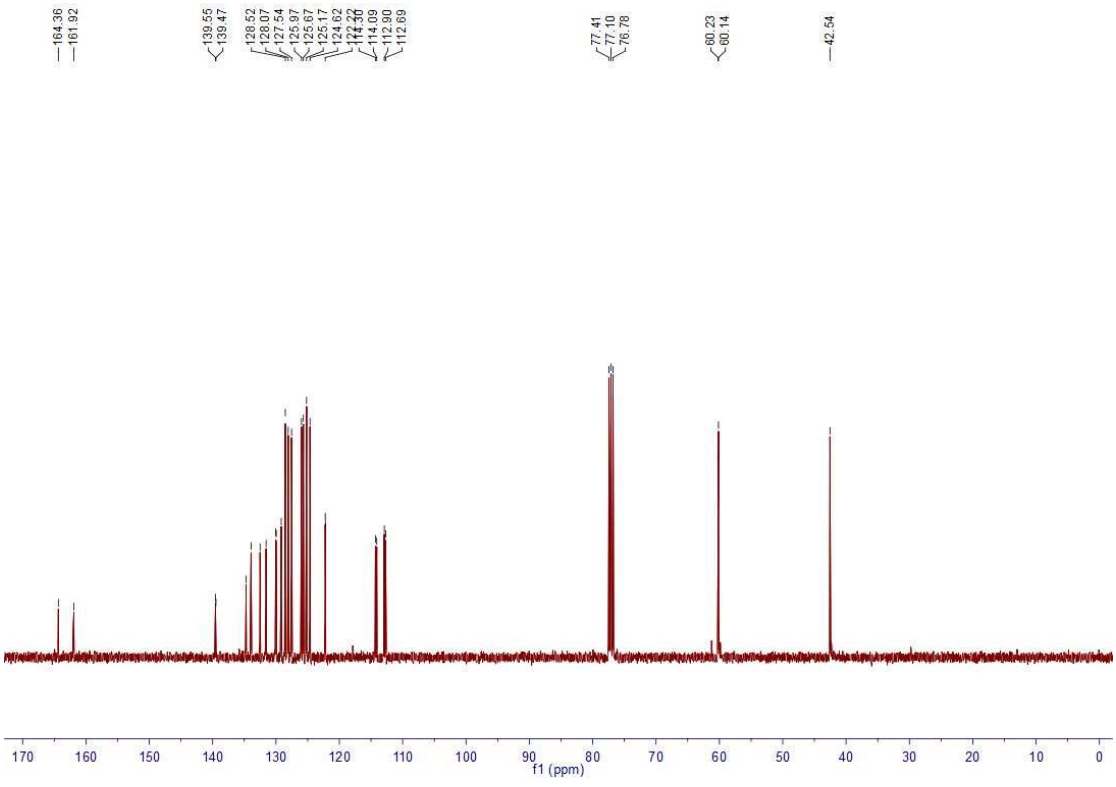
1.00
1.00
1.88
1.95
2.82
f1 (ppm)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127.54
125.97
125.67
125.17
124.62
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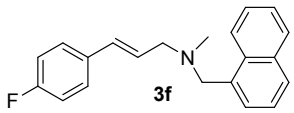
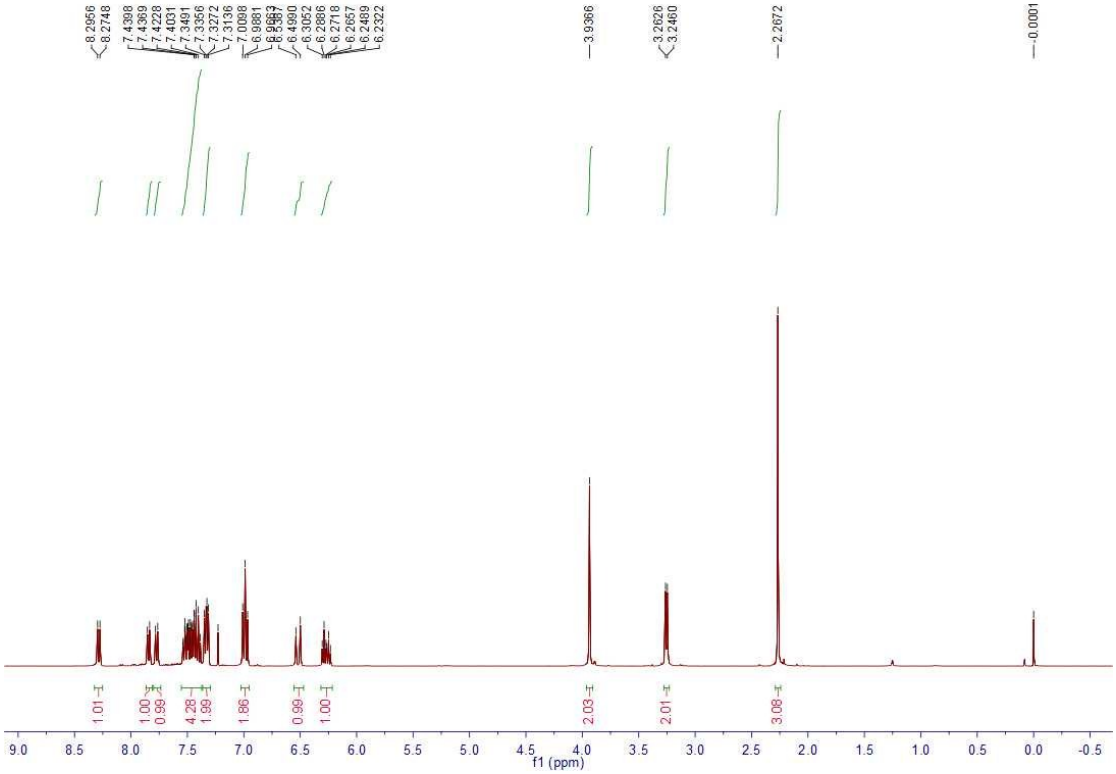
112.90
112.69
77.41
77.10
76.78
60.23
60.14
42.54
f1 (ppm)


F
N
3f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6.4990
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6.2718
6.2657
6.2489
6.2322
3.9366
3.2626
3.2460
2.2672
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1.00
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0.99
1.00
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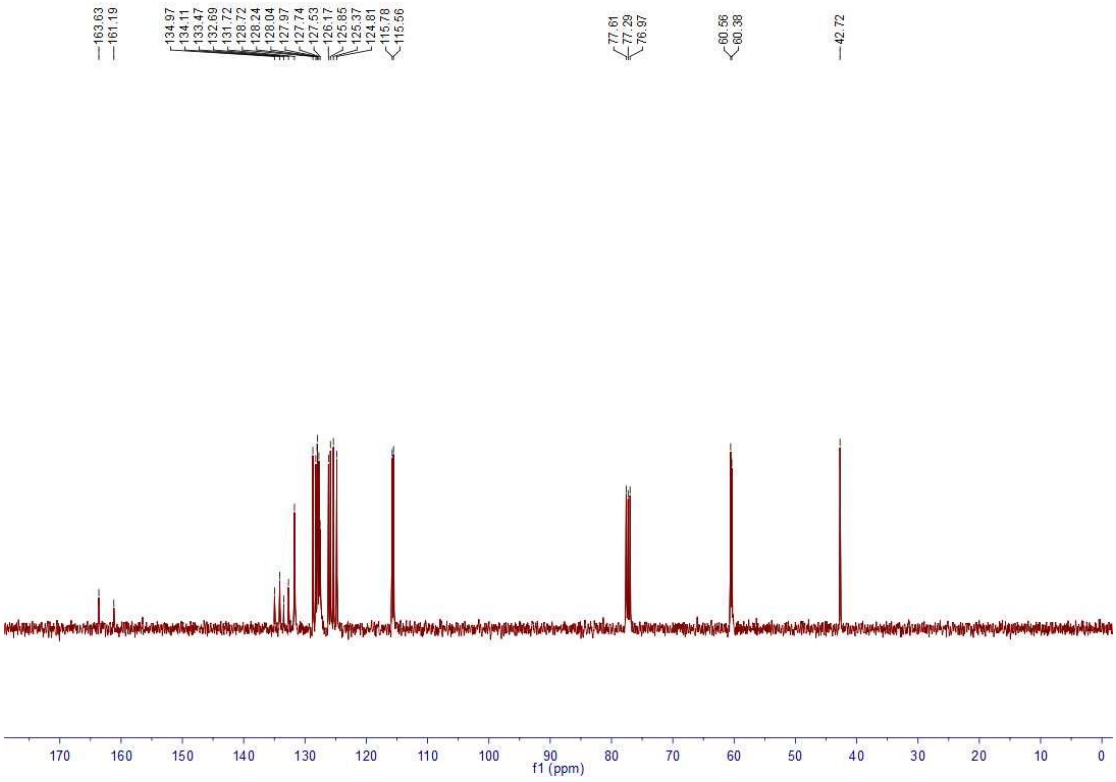
2.01
3.08
f1 (ppm)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131.73
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127.97
127.74
127.53
126.17
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115.56
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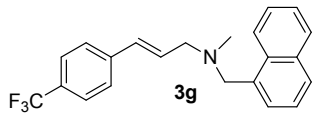
76.97
60.56
60.38
42.72
f1 (ppm)


F3C
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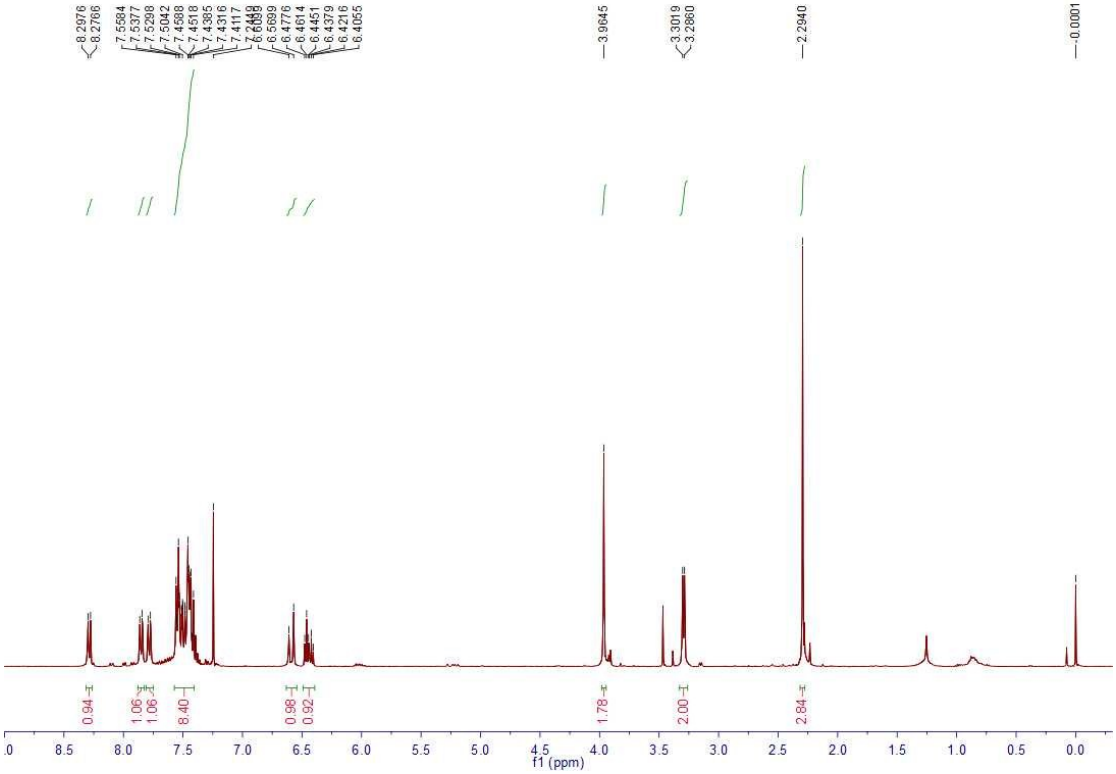
3g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7.4385
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7.4117
6.5899
6.4776
6.4614
6.4451
6.4379
6.4216
6.4055
3.9645
3.3019
3.2860
2.2940
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1.06
1.06
8.40
0.98
0.92
1.78
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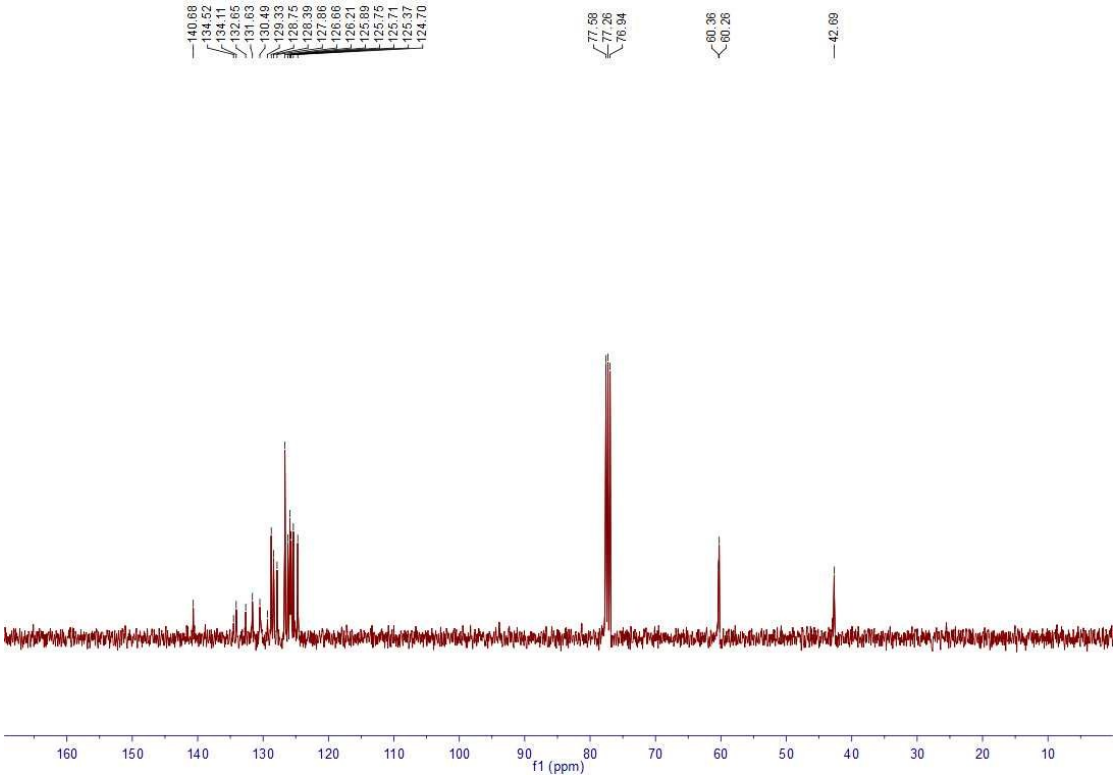
2.84
f1 (ppm)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128.75
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127.86
126.66
126.21
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125.75
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125.37
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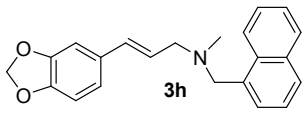
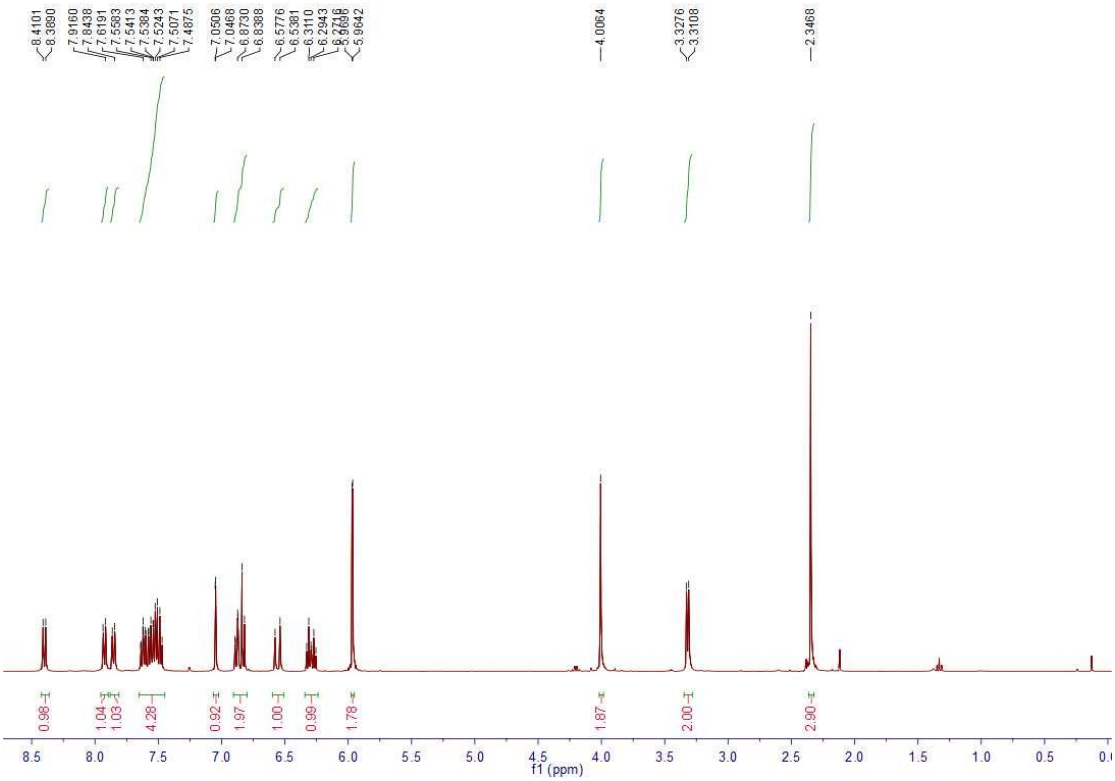
77.58
77.26
76.94
60.36
60.26
42.69
f1 (ppm)


O
O
N
3h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7.4875
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6.8388
6.5776
6.5381
6.3110
6.2943
5.9668
5.9642
4.0064
3.3276
3.3108
2.3468
0.98
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1.00
0.99
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1.87
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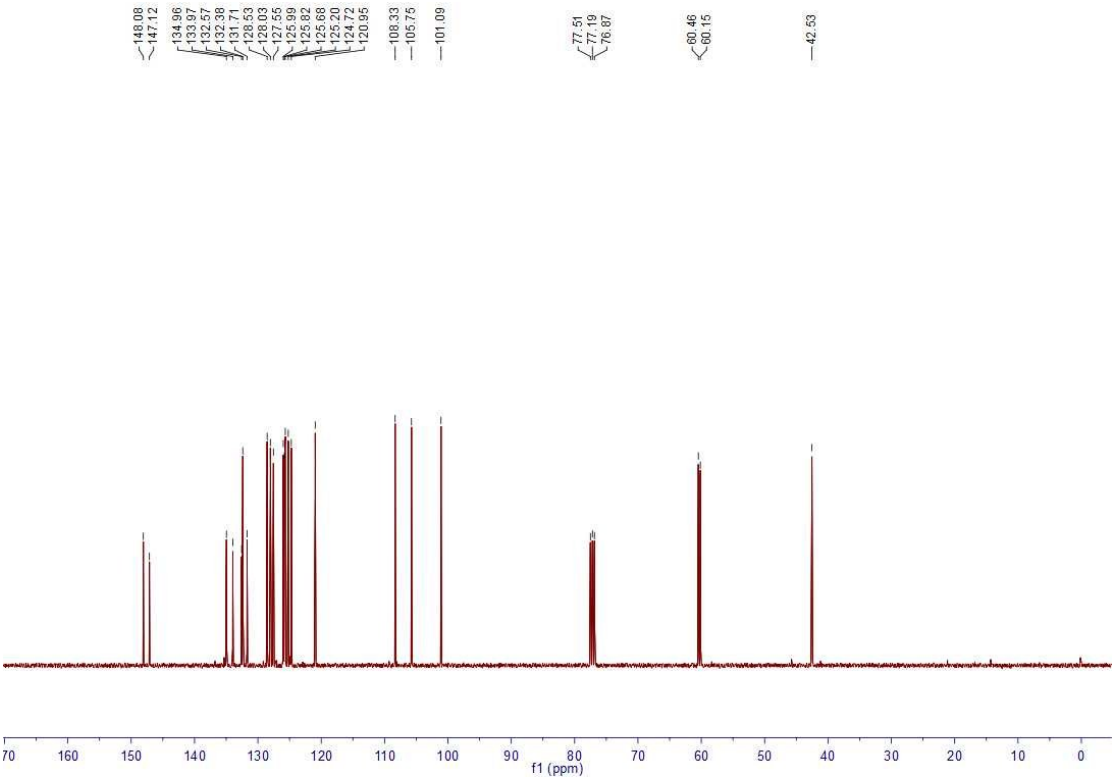
2.90
f1 (ppm)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132.38
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127.55
125.99
125.82
125.68
125.20
124.72
120.95
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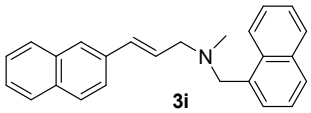
77.51
77.19
76.87
60.46
60.15
42.53
f1 (ppm)



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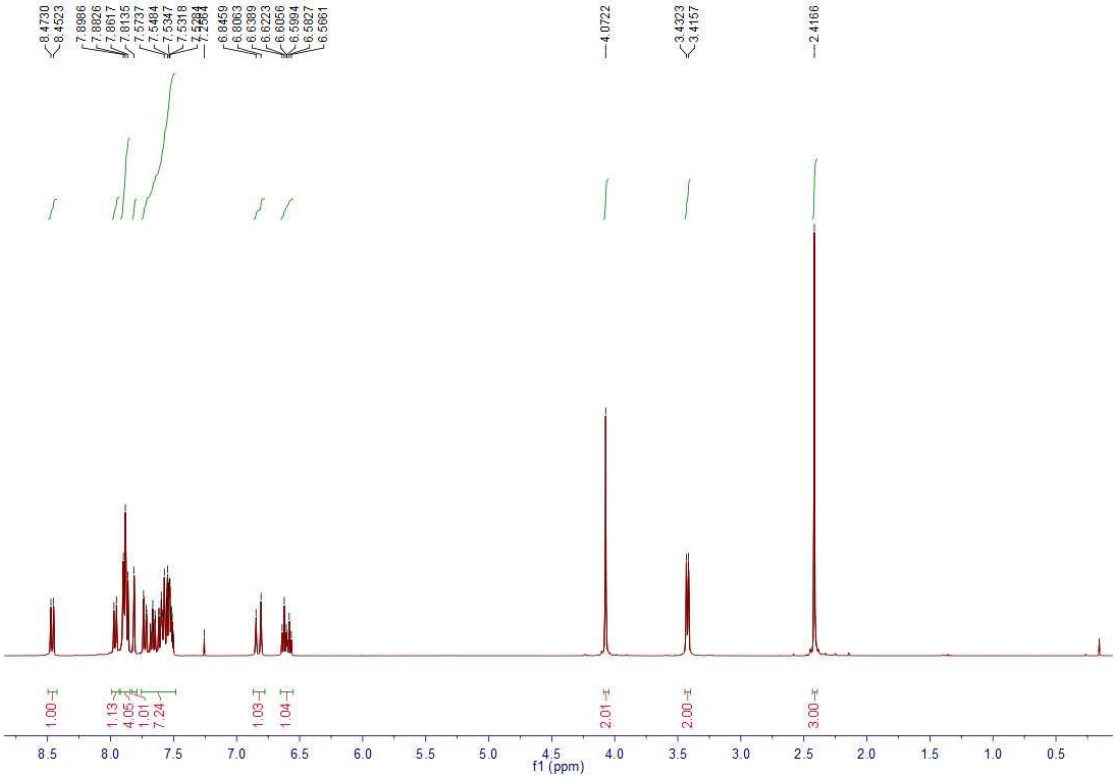
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7.5347
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6.6389
6.6223
6.6056
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6.5827
6.5661
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3.4157
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4.05
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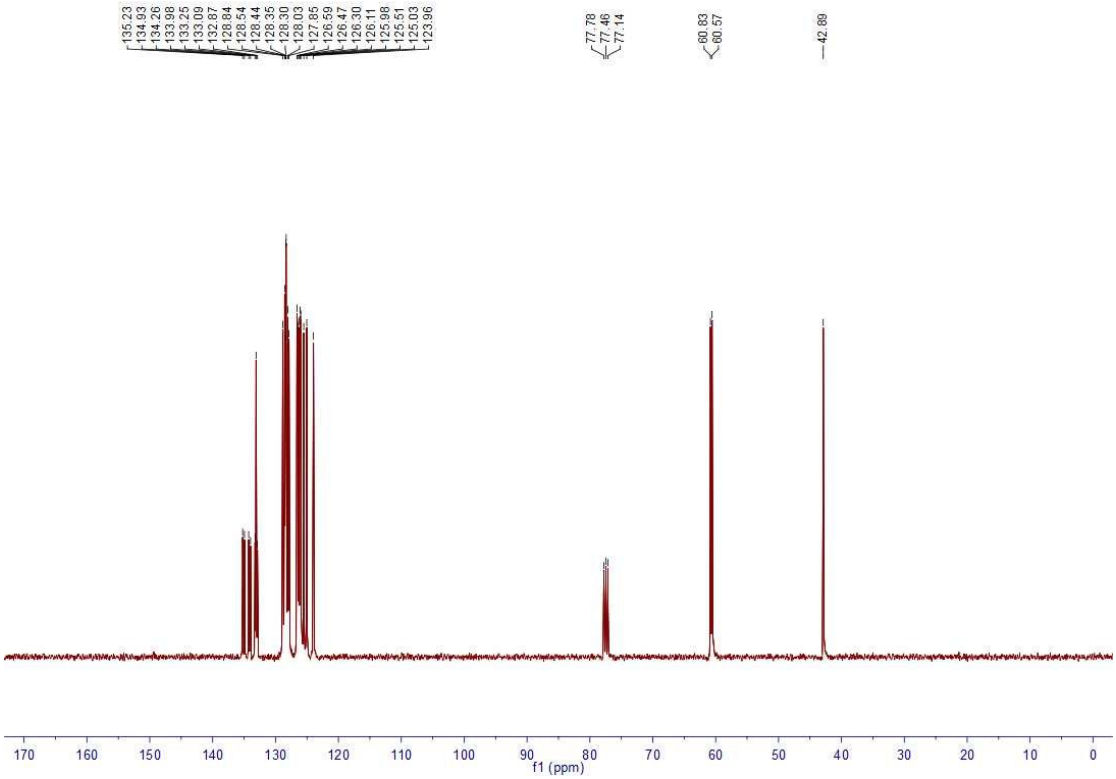
7.24
1.03
1.04
2.01
2.00
3.00
f1 (ppm)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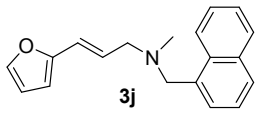
128.30
128.03
127.85
126.59
126.47
126.30
126.11
125.98
125.51
125.03
123.96
77.78
77.46
77.14
60.83
60.57
42.89
f1 (ppm)


O
N

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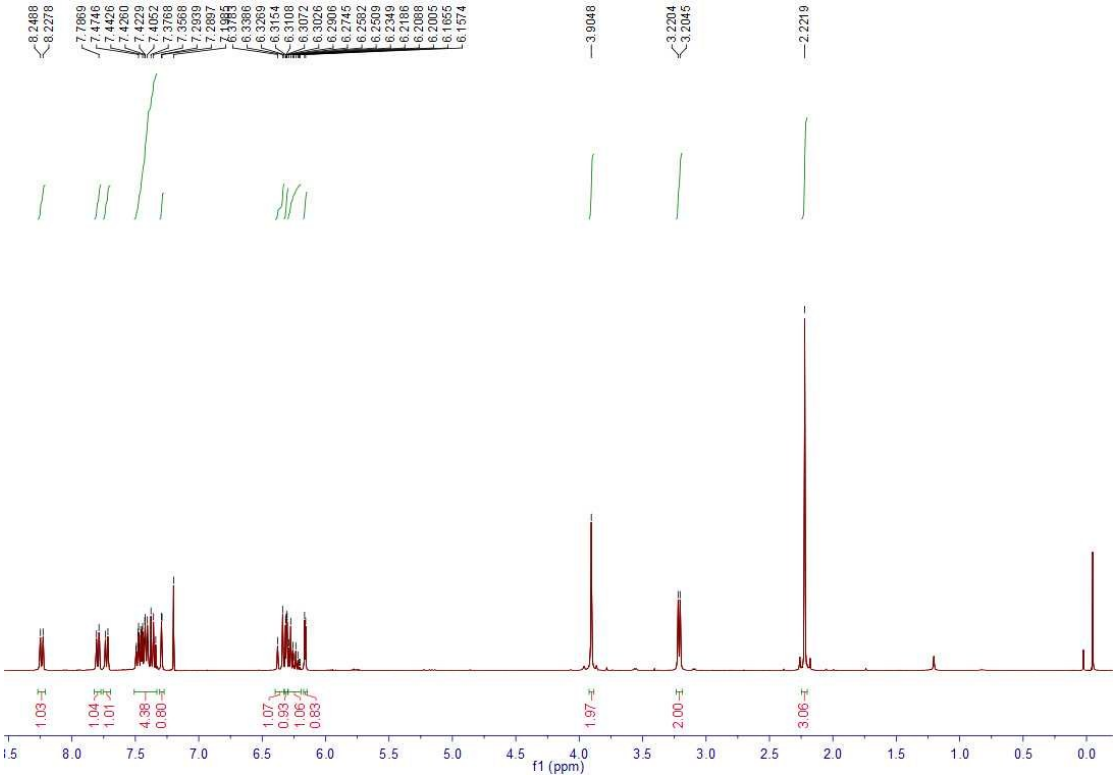
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6.2906
6.2745
6.2582
6.2509
6.2349
6.2186
6.2088
6.2005
6.1655
6.1574
3.9048
3.2204
3.2045
2.2219
1.03
1.04
1.01
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1.06
0.83
1.97
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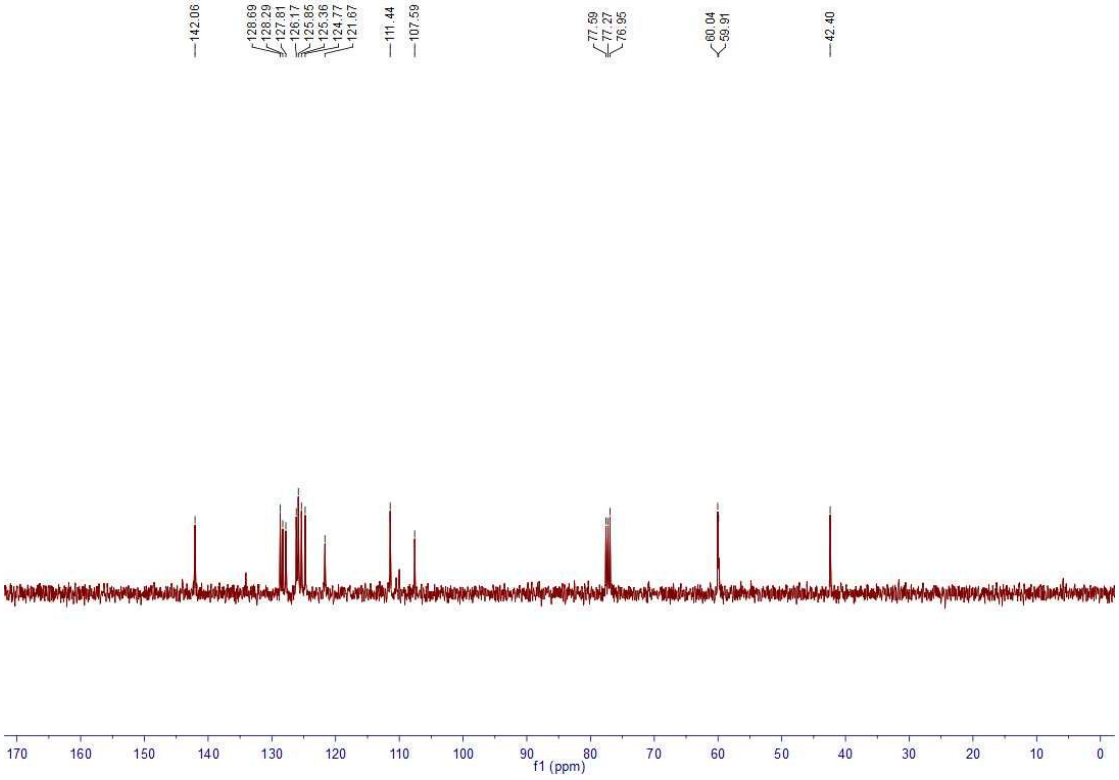
3.06
f1 (ppm)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111.44
107.59
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77.27
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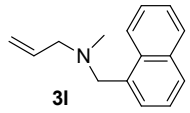
60.04
59.91
42.40
f1 (ppm)



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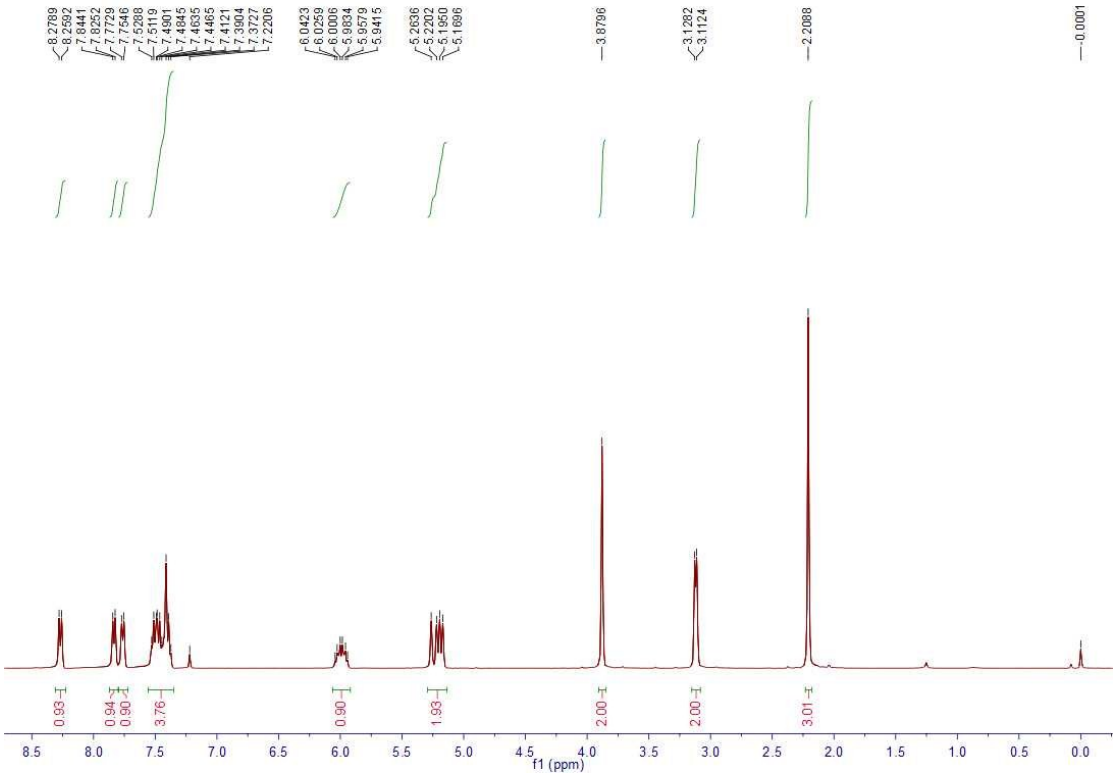
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7.4635
7.4465
7.4121
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7.3727
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5.9579
5.9415
5.2636
5.2202
5.1950
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3.8796
3.1282
3.1124
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0.90
1.93
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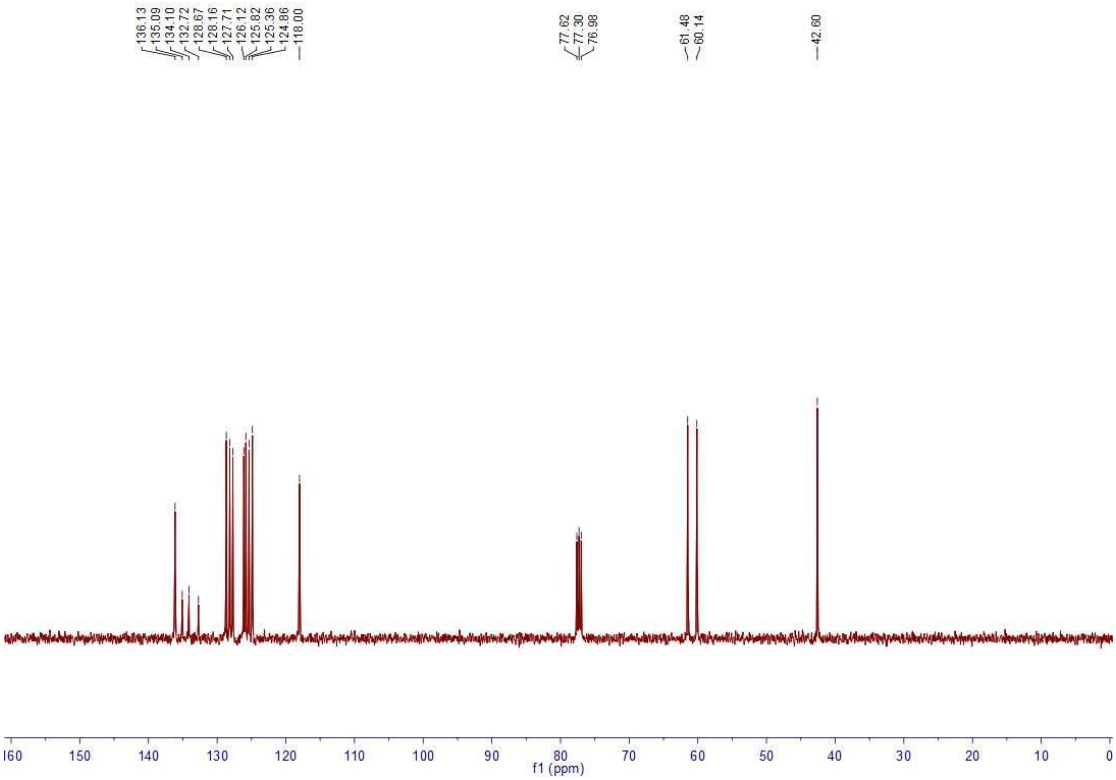
3.01
f1 (ppm)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61.48
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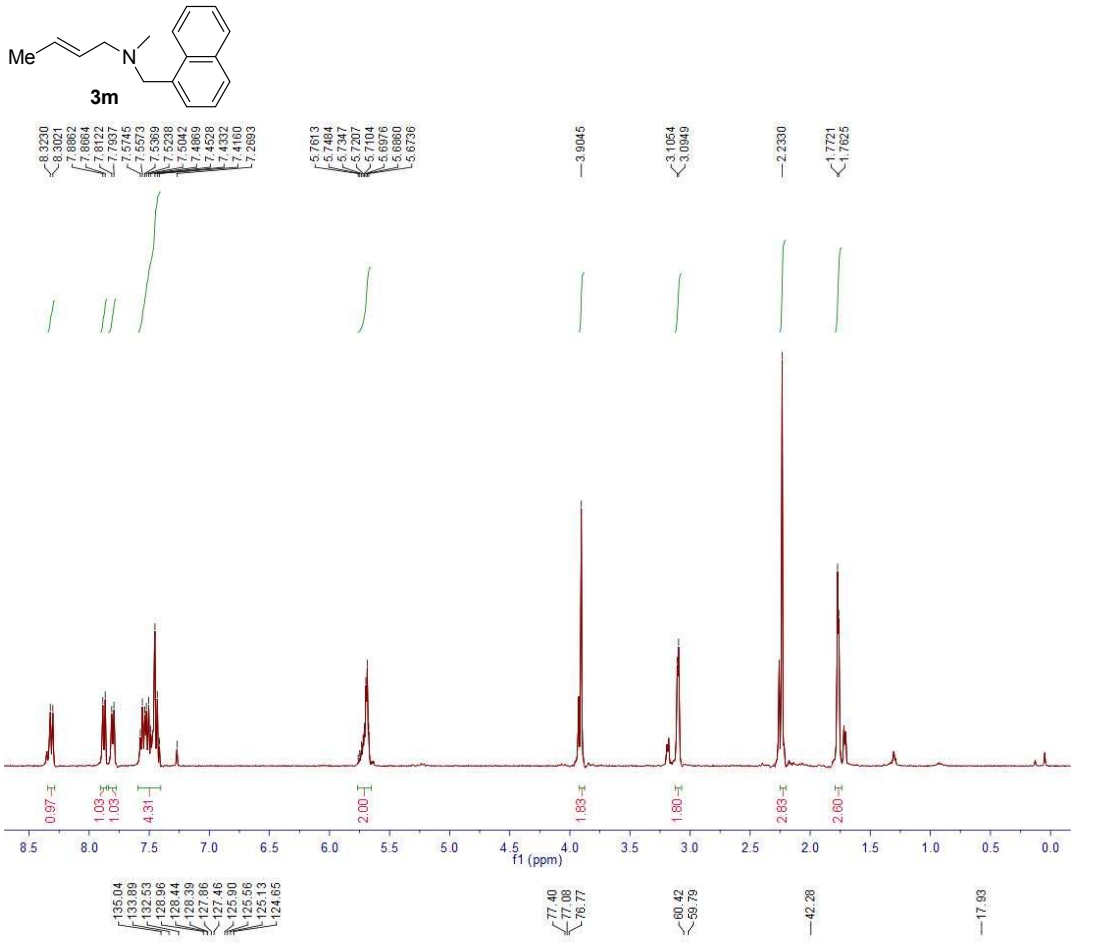
42.60
f1 (ppm)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3.0949
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1.80
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2.60
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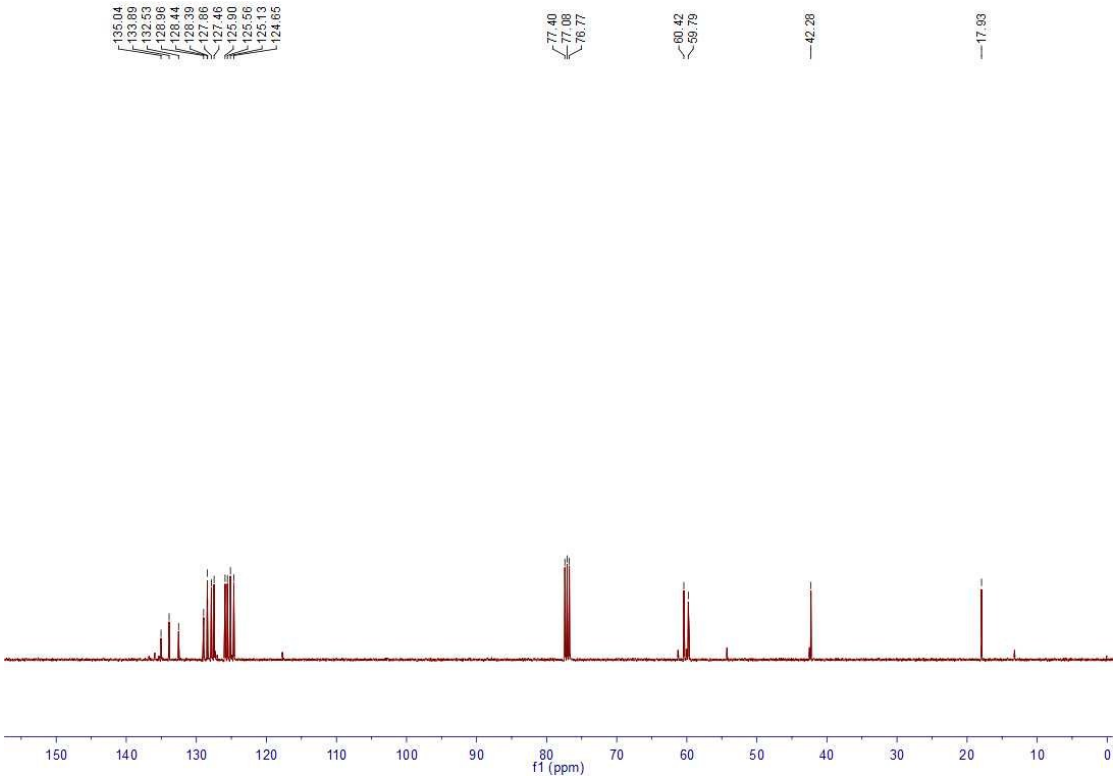
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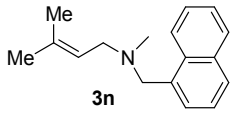
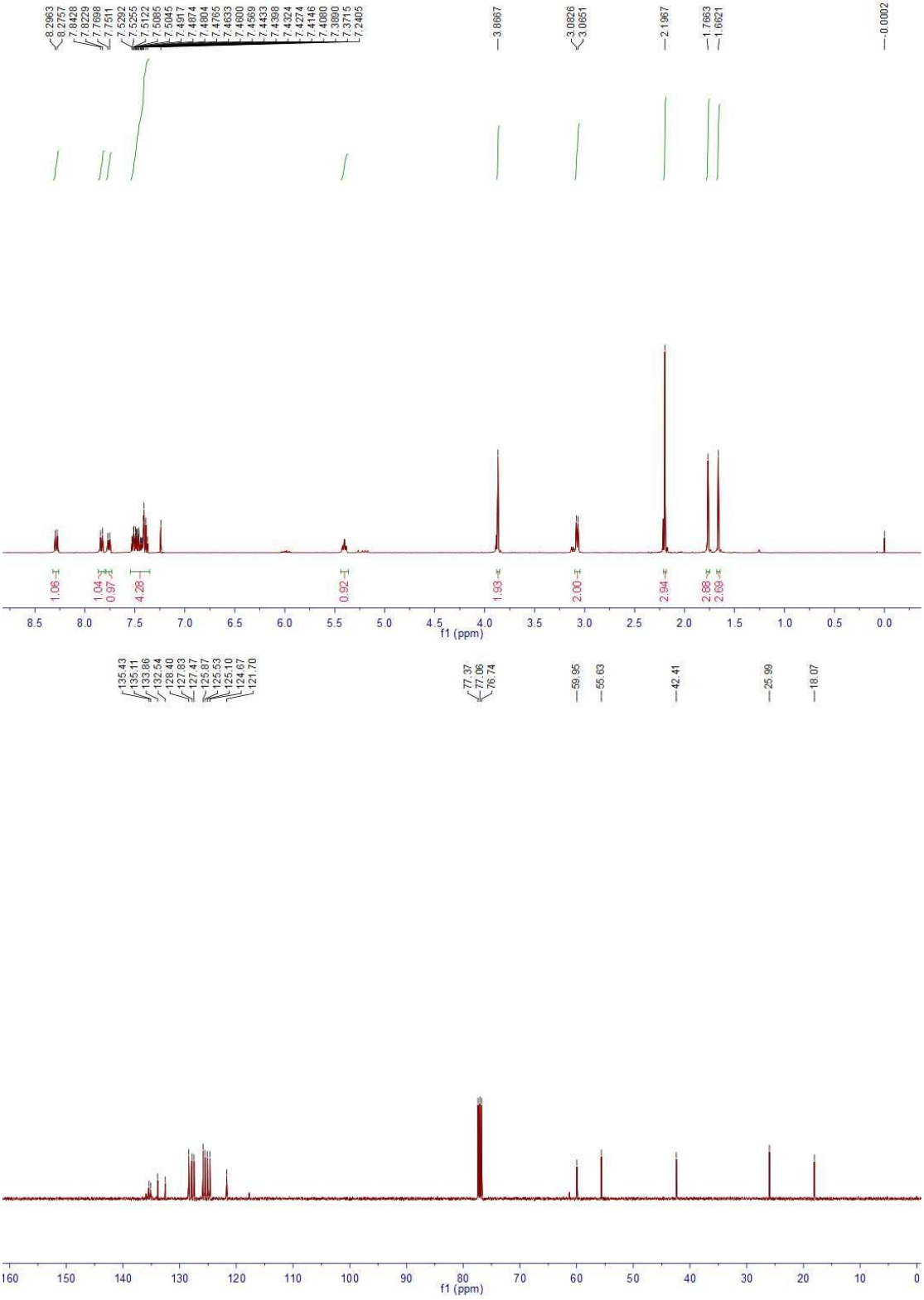
17.93
f1 (ppm)


Me
Me
N

3n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2.00
2.94
2.88
2.69
f1 (ppm)
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42.41
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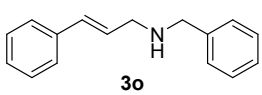
18.07
f1 (ppm)



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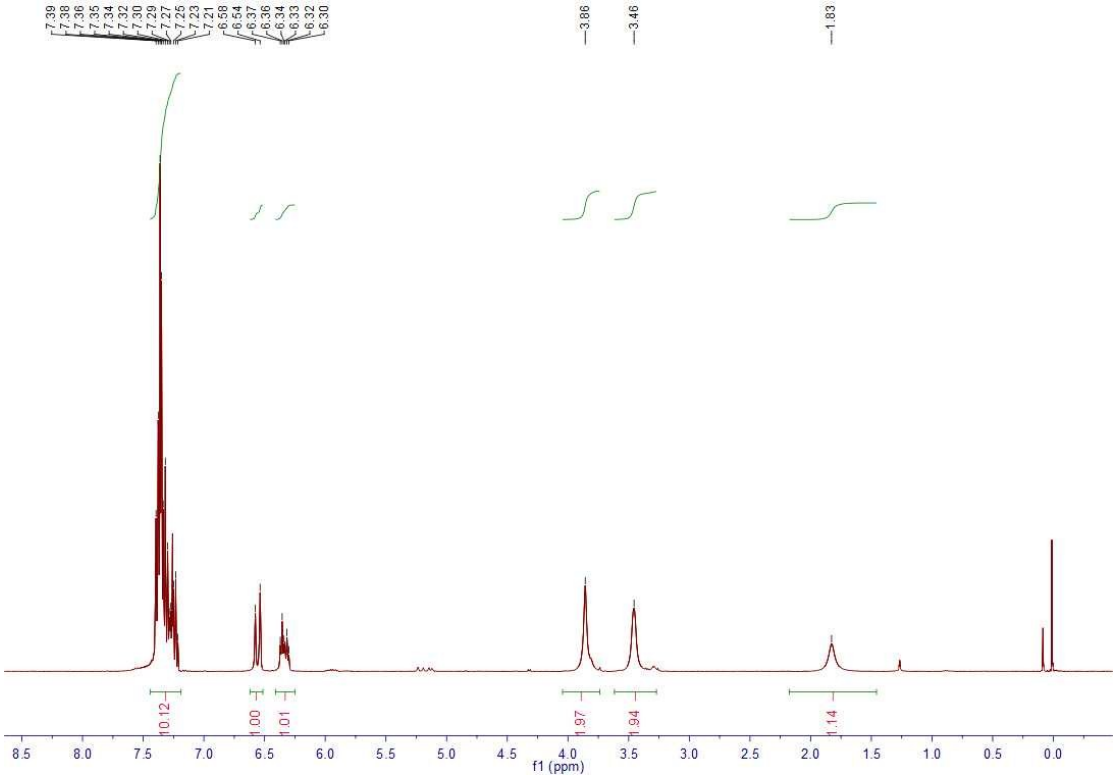
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6.54
6.37
6.36
6.34
6.33
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6.30
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10.12
1.00
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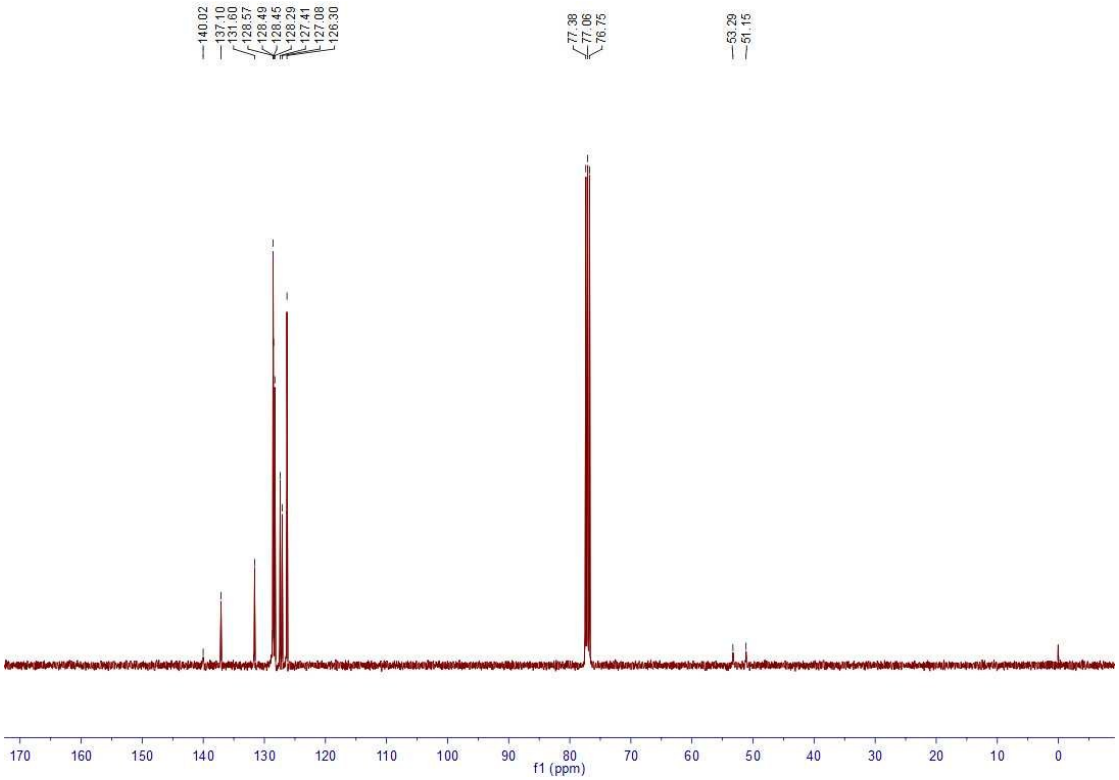
1.97
1.94
1.14
f1 (ppm)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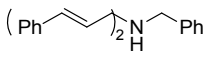
f1 (ppm)


Ph
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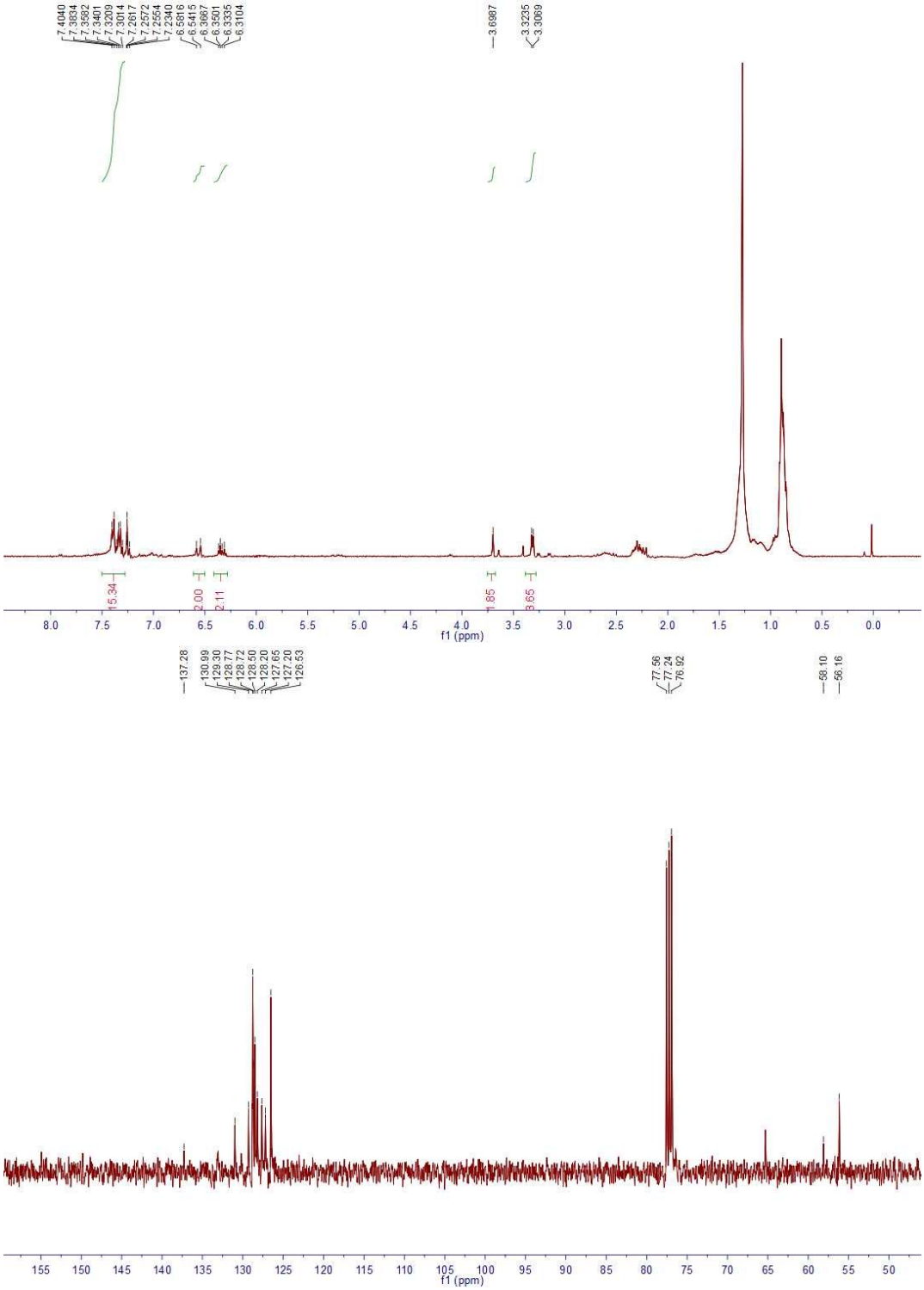
N
H
Ph

3o'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6.5816
6.5415
6.3667
6.3501
6.3335
6.3104
3.6987
3.3235
3.3069
15.34
2.00
2.11
1.85
3.65
f1 (ppm)
137.28
130.99
129.30
128.77
128.72
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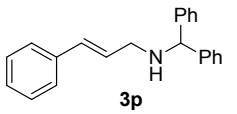
127.65
127.20
126.53
77.56
77.24
76.92
58.10
56.16
f1 (ppm)


Ph
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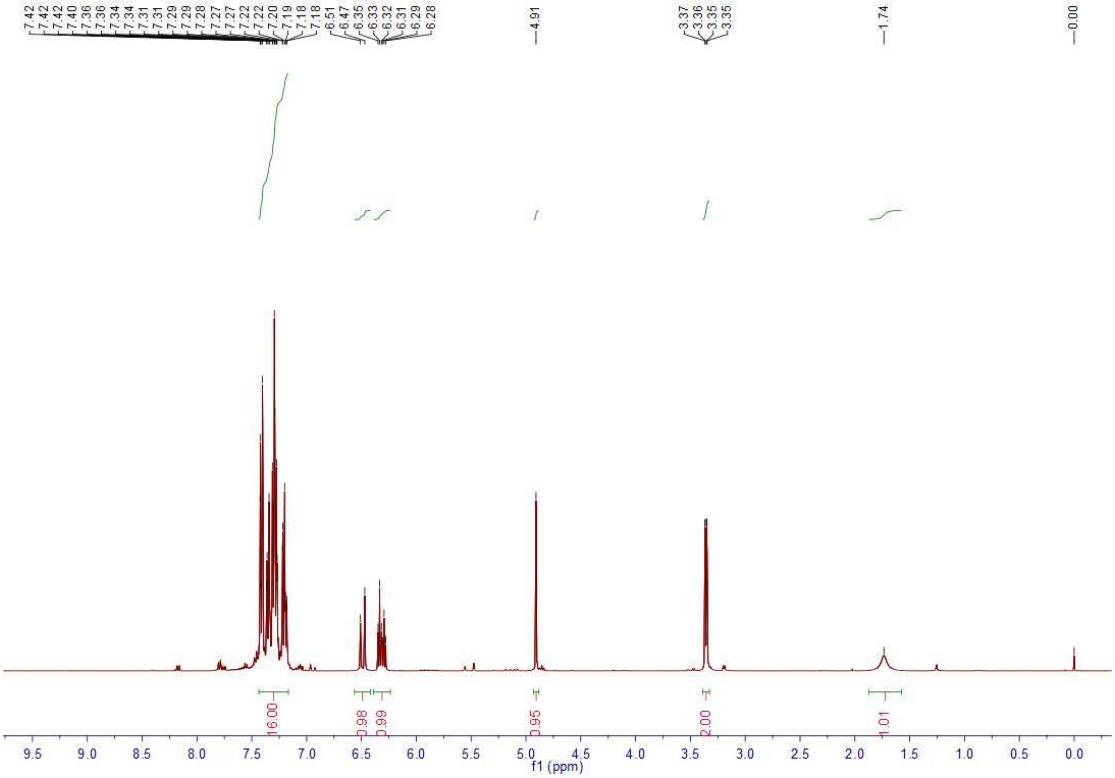
H
Ph

3p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7.27
7.22
7.22
7.20
7.19
7.18
6.51
6.47
6.35
6.33
6.32
6.31
6.29
6.28
4.91
3.37
3.36
3.35
3.35
1.74
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16.00
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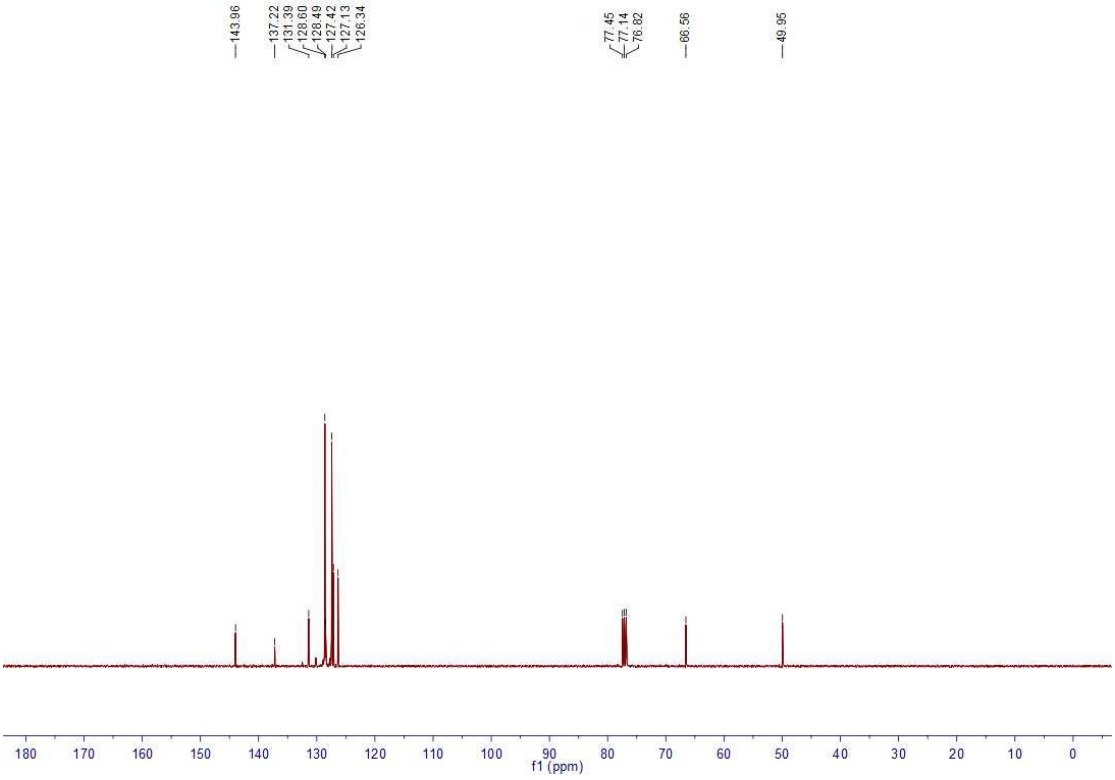
0.99
0.95
2.00
1.01
f1 (ppm)


143.96
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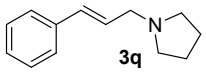
127.13
126.34
77.45
77.14
76.82
66.56
49.95
f1 (ppm)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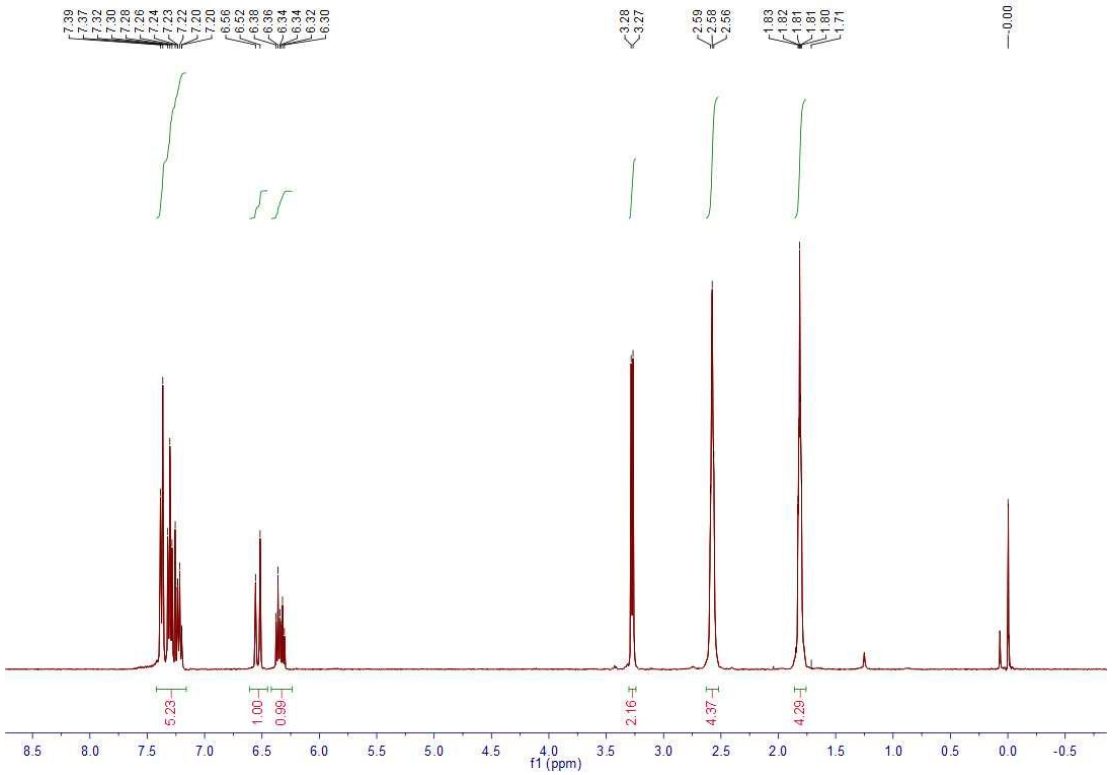
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7.37
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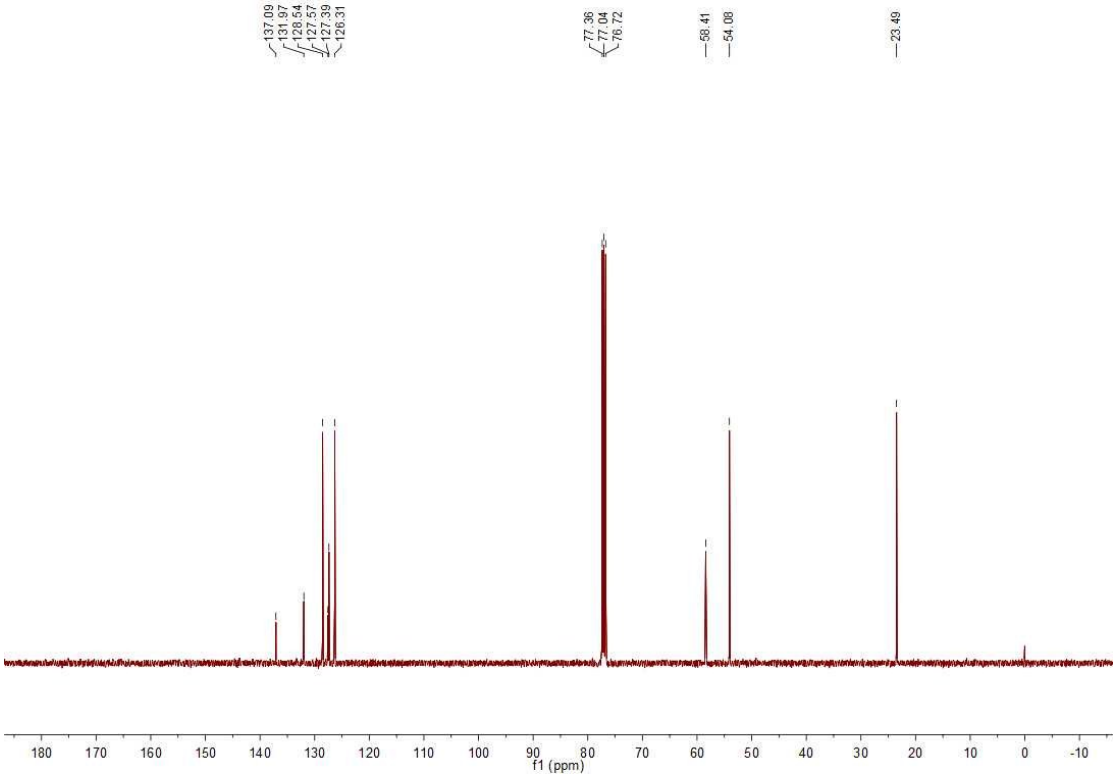
7.24
7.23
7.22
7.20
7.20
6.56
6.52
6.38
6.36
6.34
6.34
6.32
6.30
3.28
3.27
2.59
2.58
2.56
1.83
1.82
1.81
1.81
1.80
1.71
0.00
5.23
1.00
0.99
2.16
4.37
4.29
f1 (ppm)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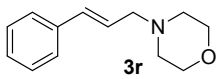
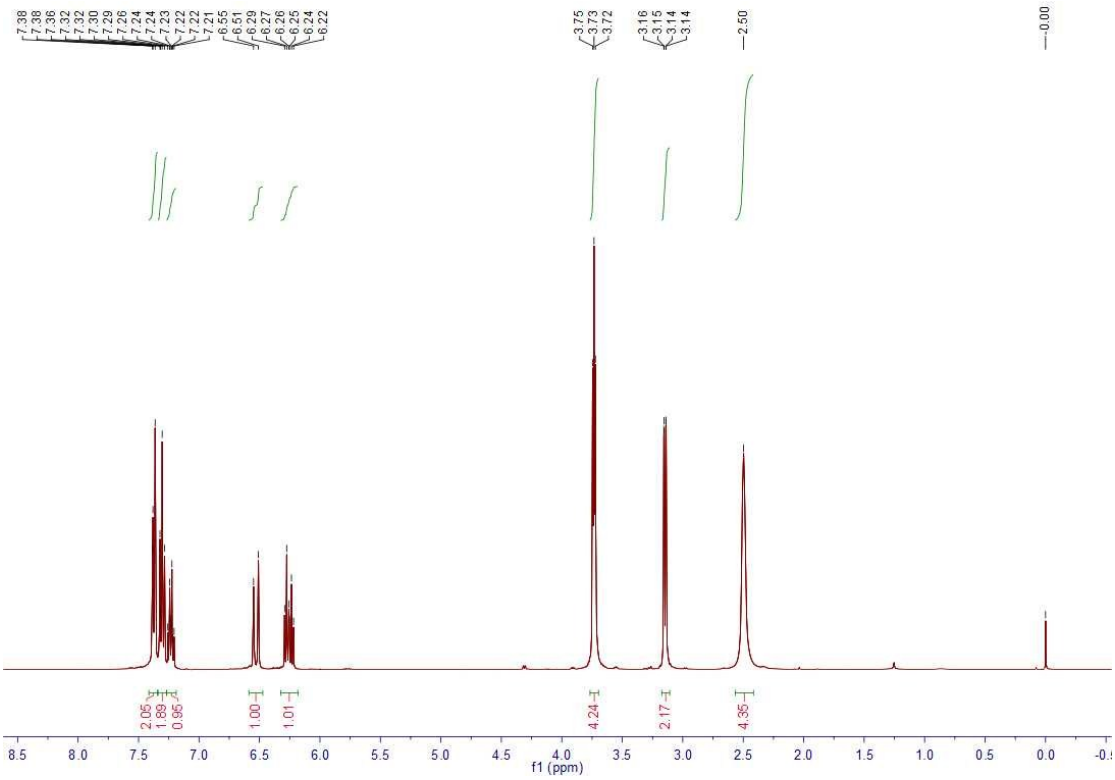
126.31
77.36
77.04
76.72
58.41
54.08
23.49
f1 (ppm)


N
O

3r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7.29
7.26
7.24
7.24
7.23
7.22
7.22
7.21
6.55
6.51
6.29
6.27
6.26
6.25
6.24
6.22
3.75
3.73
3.72
3.16
3.15
3.14
3.14
2.50
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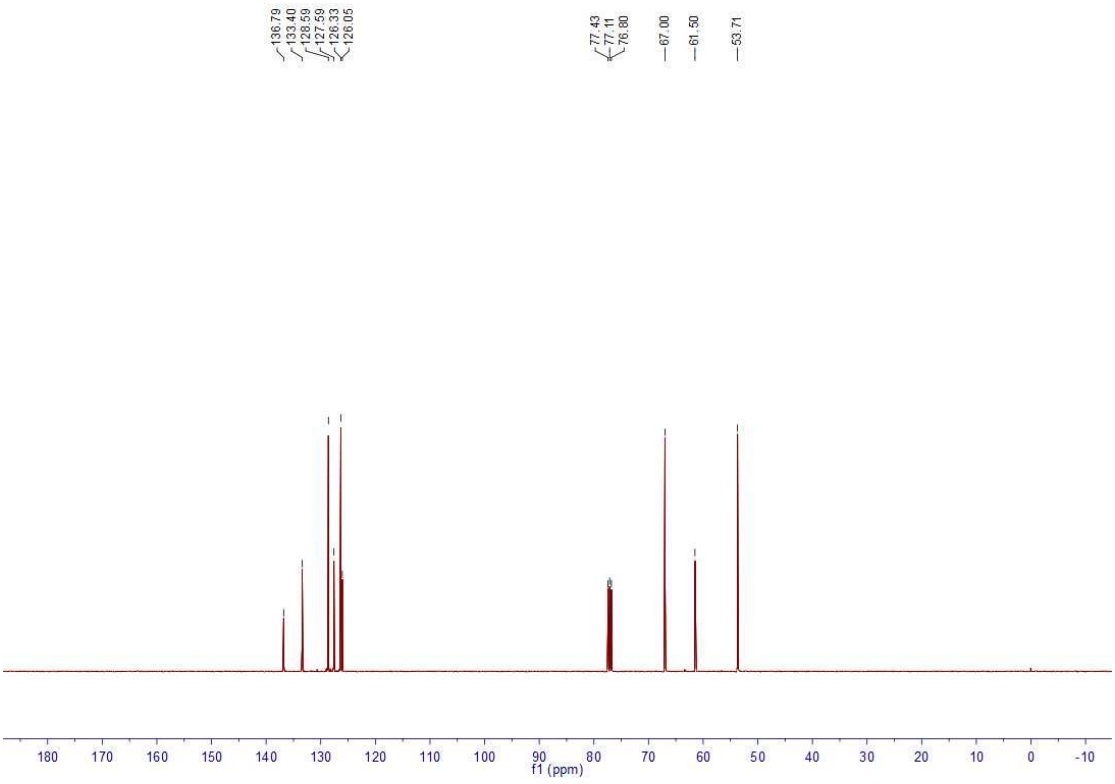
2.05
1.89
0.95
1.00
1.01
4.24
2.17
4.35
f1 (ppm)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133.40
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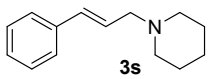
126.33
126.05
77.43
77.11
76.80
67.00
61.50
53.71
f1 (ppm)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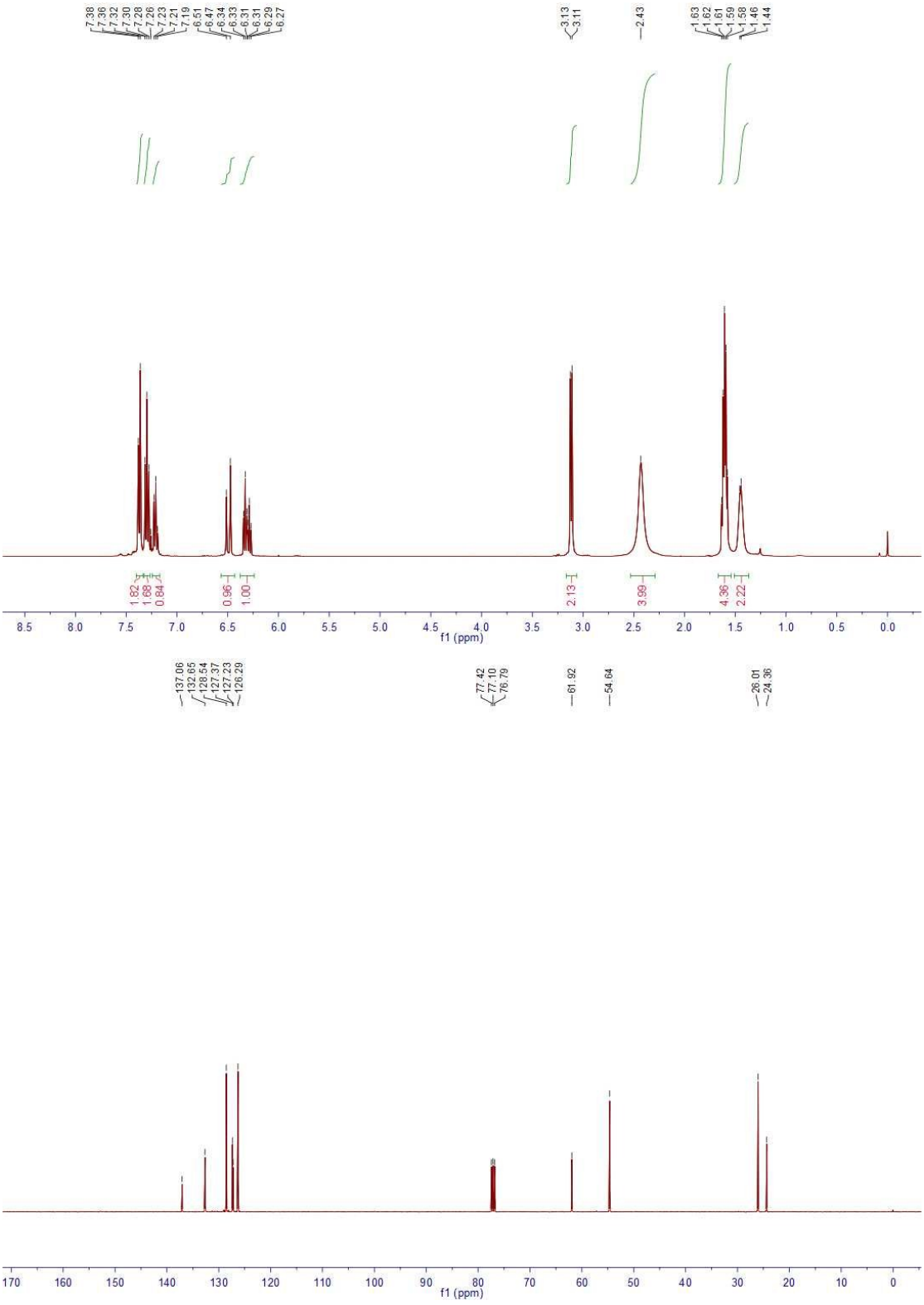
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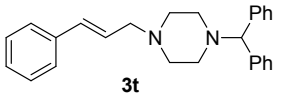
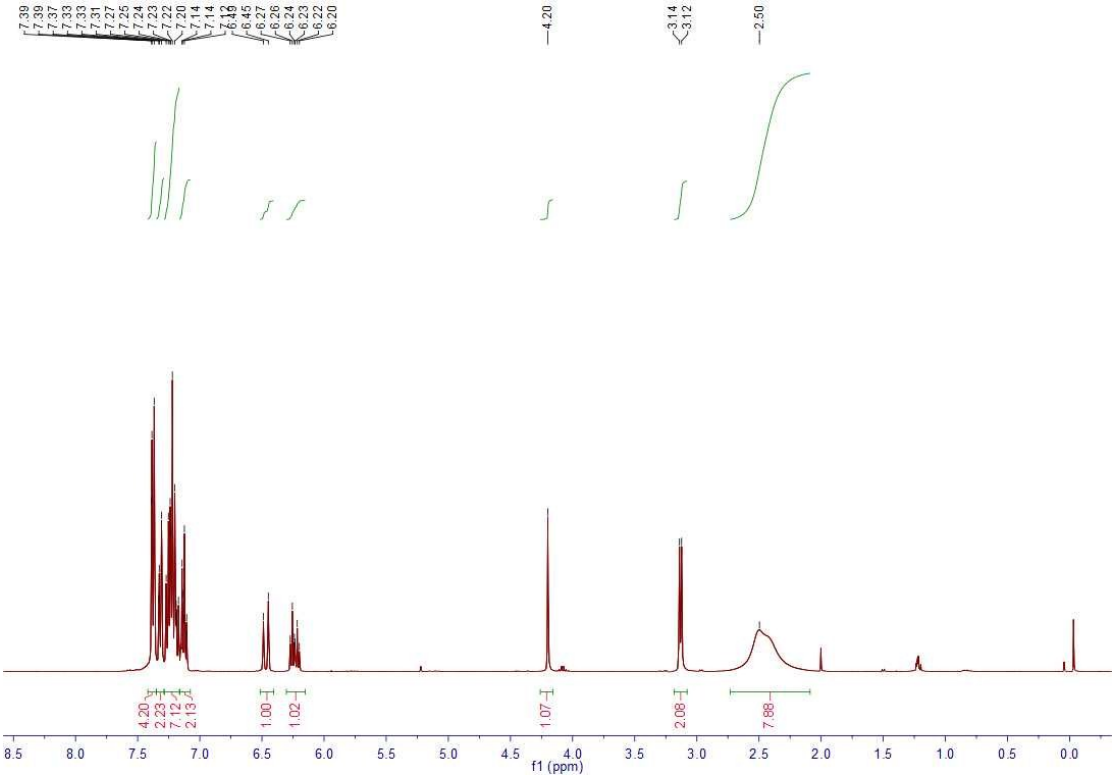
7.36
7.32
7.30
7.28
7.26
7.23
7.21
7.19
6.51
6.47
6.34
6.33
6.31
6.31
6.29
6.27
3.13
3.11
2.43
1.63
1.62
1.61
1.59
1.58
1.46
1.44
1.82
1.68
0.84
0.96
1.00
2.13
3.99
4.36
2.22
f1 (ppm)
137.06
132.65
128.54
127.37
127.23
126.29
77.42
77.10
76.79
61.92
54.64
26.01
24.36
f1 (ppm)


Ph
N
N
Ph

3t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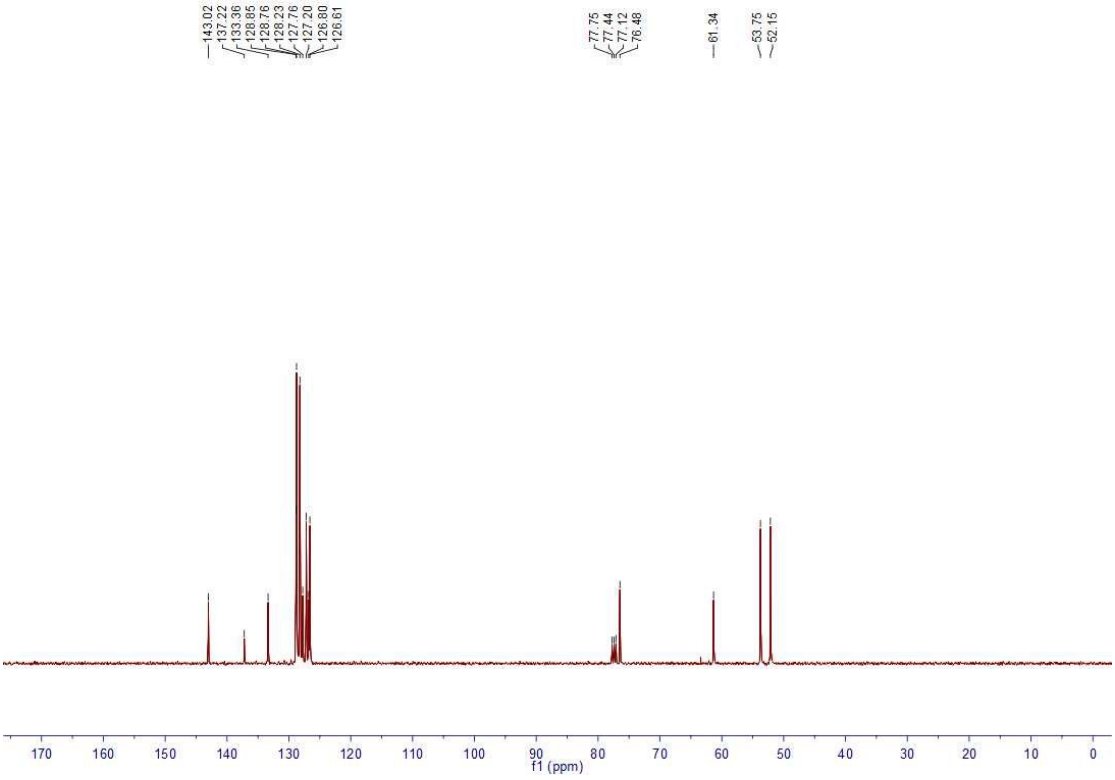
7.39
7.37
7.33
7.33
7.31
7.27
7.25
7.24
7.23
7.22
7.20
7.14
7.12
6.46
6.45
6.27
6.26
6.24
6.23
6.22
6.20
4.20
3.14
3.12
2.50
4.20
2.23
7.12
2.13
1.00
1.02
1.07
2.08
7.88
f1 (ppm)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128.76
128.23
127.76
127.20
126.80
126.61
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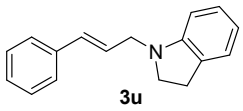
77.44
77.12
76.48
61.34
53.75
52.15
f1 (ppm)



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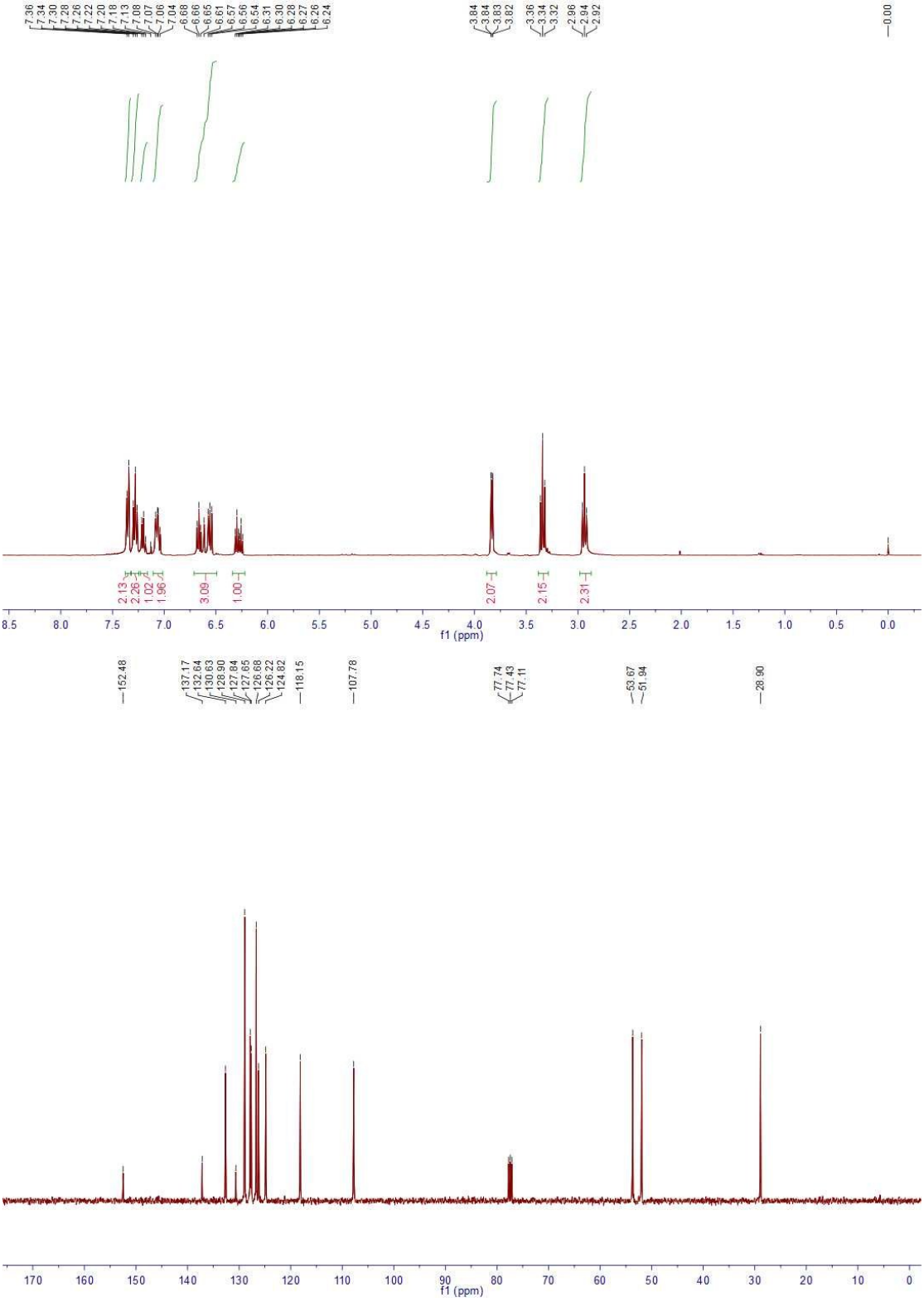
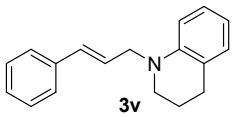

7.36
7.34
7.30
7.28
7.26
7.22
7.20
7.18
7.13
7.08
7.07
7.06
7.04
6.68
6.66
6.65
6.61
6.57
6.56
6.54
6.31
6.30
6.28
6.27
6.26
6.24
3.84
3.84
3.83
3.82
3.36
3.34
3.32
2.96
2.94
2.92
0.00
2.13
2.26
1.02
1.96
3.09
1.00
2.07
2.15
2.31
f1 (ppm)
152.48
137.17
132.64
130.63
128.90
127.84
127.65
126.68
126.22
124.82
118.15
107.78
77.74
77.43
77.11
53.67
51.94
28.90
f1 (ppm)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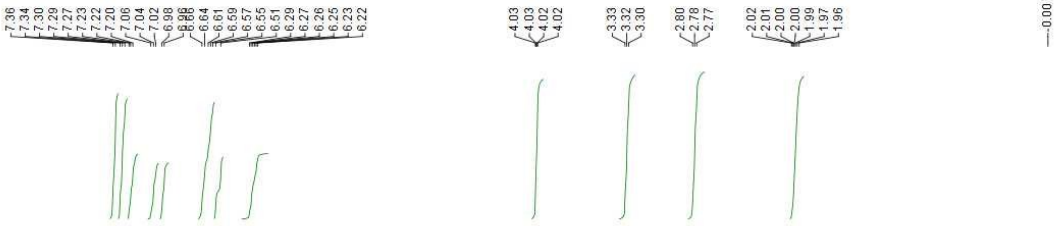
3v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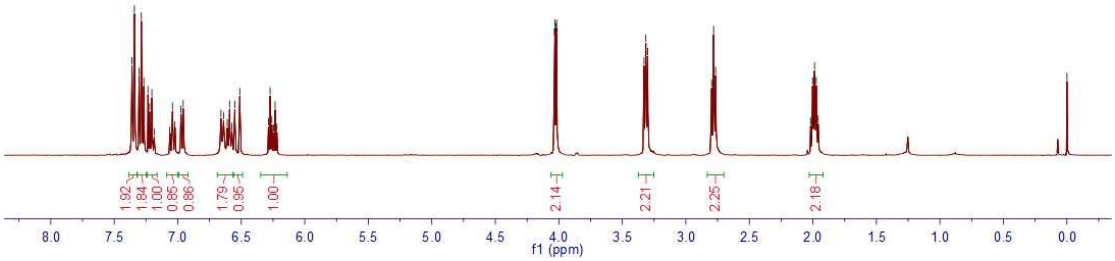
7.27
7.23
7.22
7.20
7.06
7.04
7.02
6.98
6.64
6.61
6.59
6.57
6.55
6.51
6.29
6.27
6.26
6.25
6.23
6.22
4.03
4.03
4.02
4.02
3.33
3.32
3.30
2.80
2.78
2.77
2.02
2.01
2.00
2.00
1.99
1.97
1.96
0.00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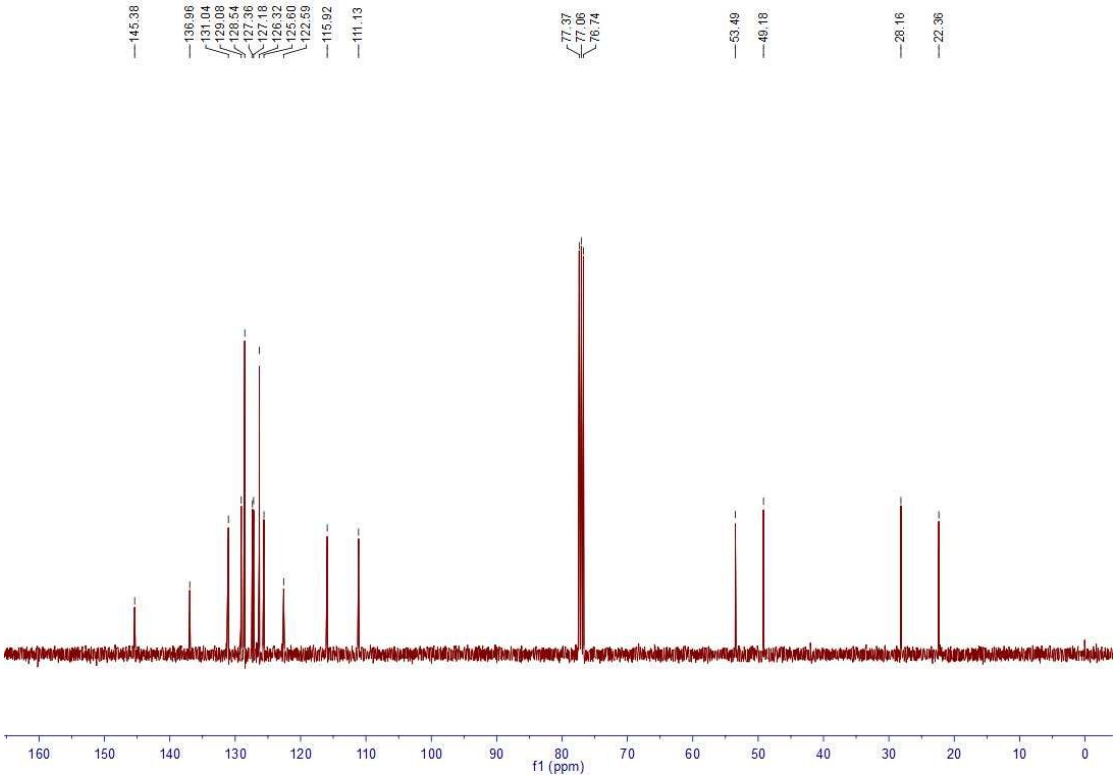
0.86
1.79
0.95
1.00
2.14
2.21
2.25
2.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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136.96
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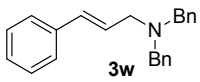
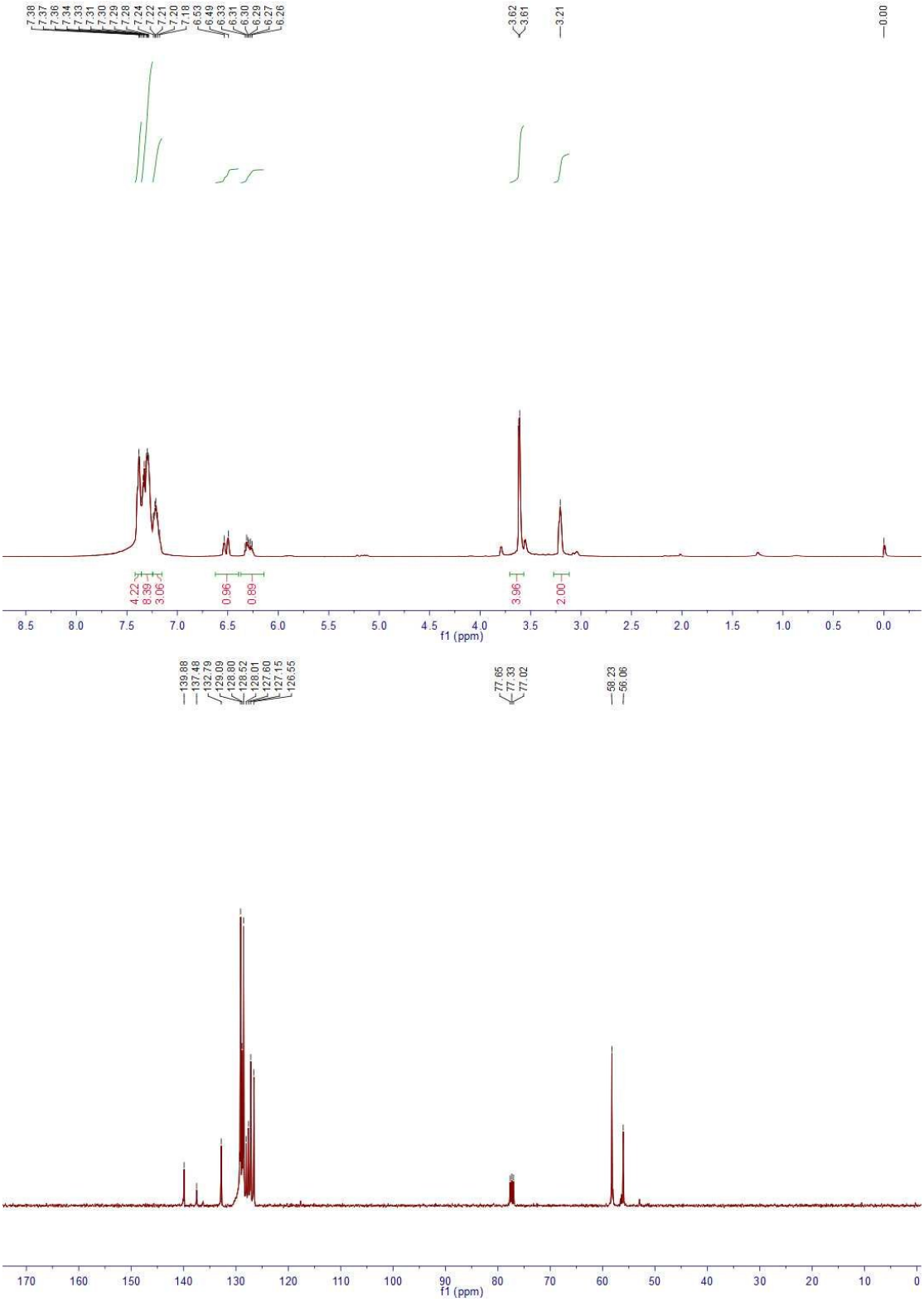
129.08
128.54
127.36
127.18
126.32
125.60
122.59
115.92
111.13
77.37
77.06
76.74
53.49
49.18
28.16
22.36
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Bn
N
Bn

3w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7.33
7.31
7.30
7.29
7.28
7.24
7.22
7.21
7.20
7.18
6.53
6.49
6.33
6.31
6.30
6.29
6.27
6.26
3.62
3.61
3.21
0.00
4.22
8.39
3.06
0.96
0.89
3.96
2.00
f1 (ppm)
139.88
137.48
132.79
129.09
128.80
128.52
128.01
127.60
127.15
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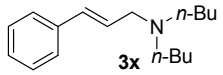
77.33
77.02
68.23
56.06
f1 (ppm)



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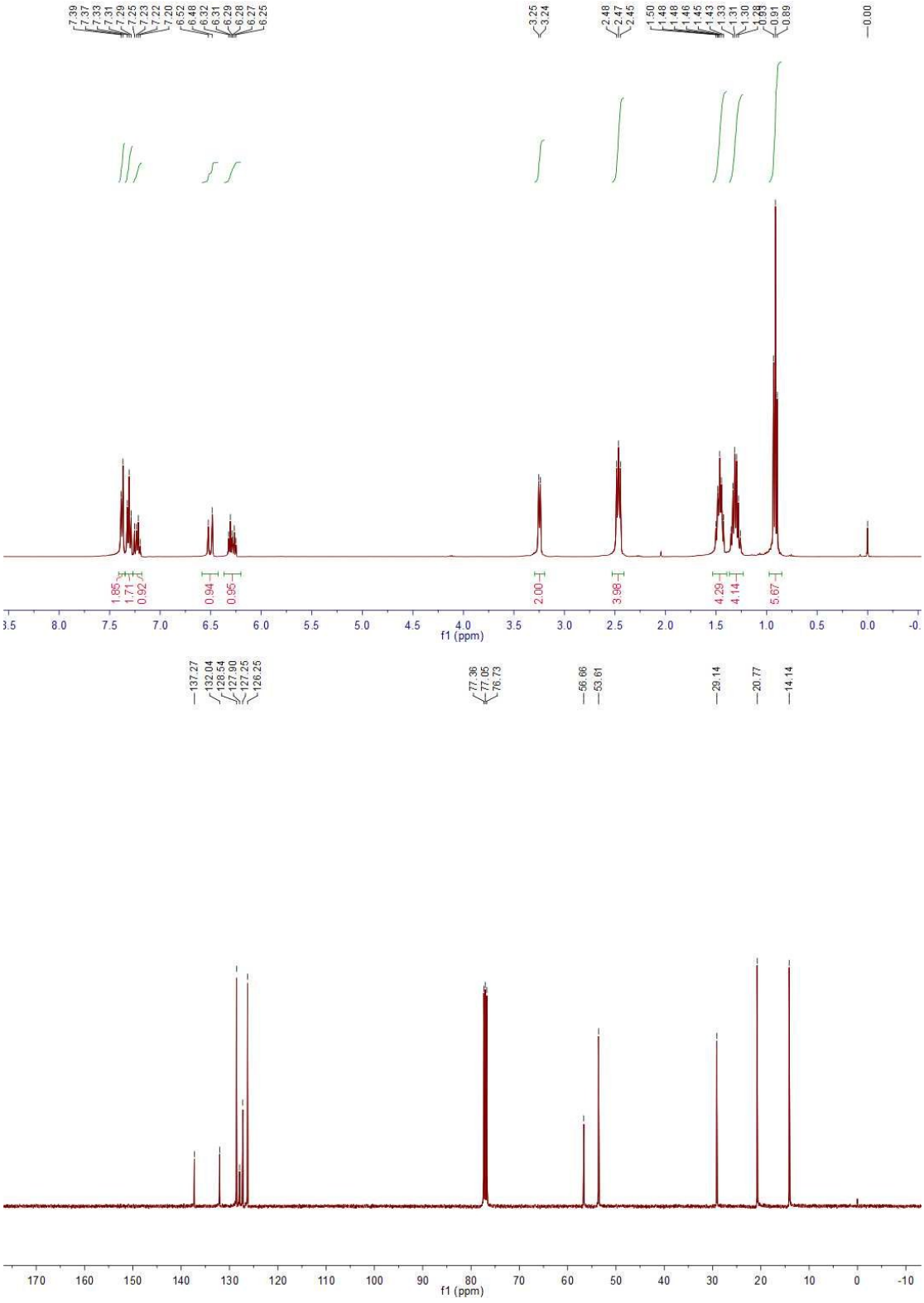

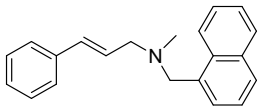

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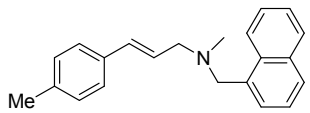
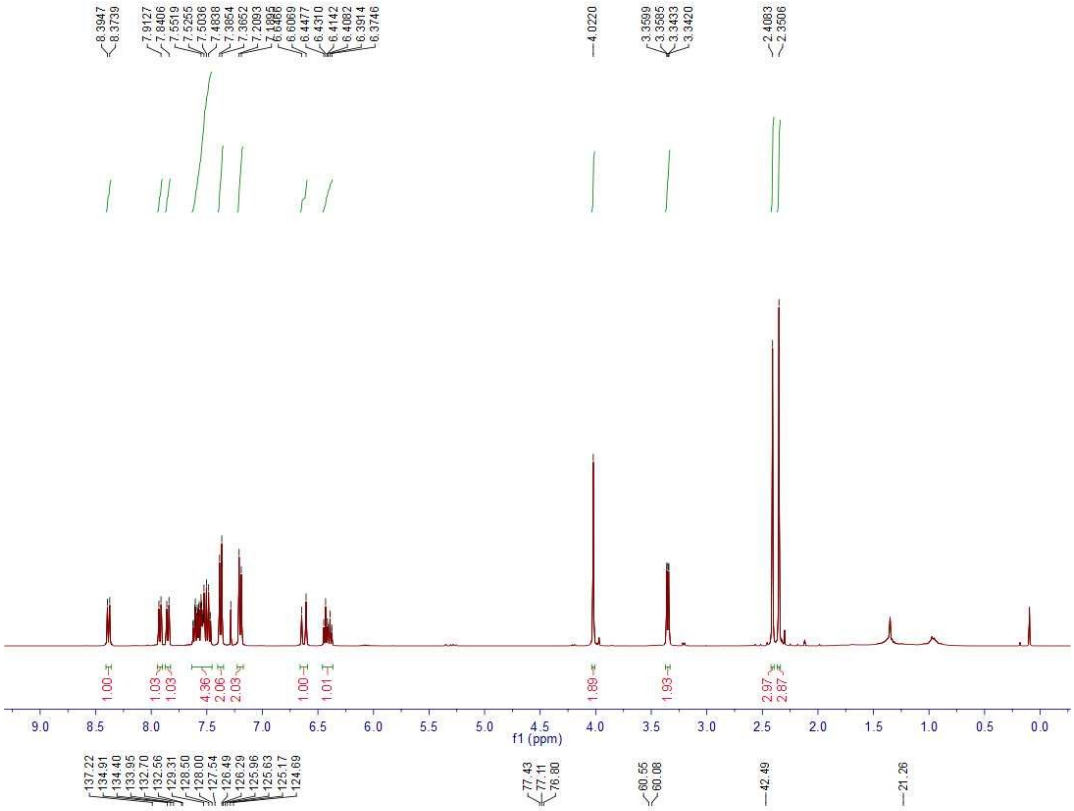

Me
N

3y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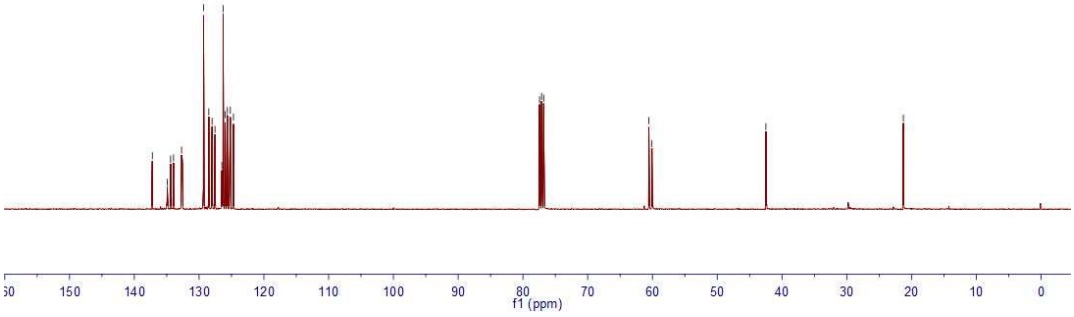
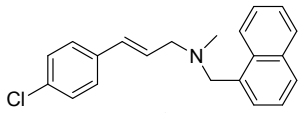
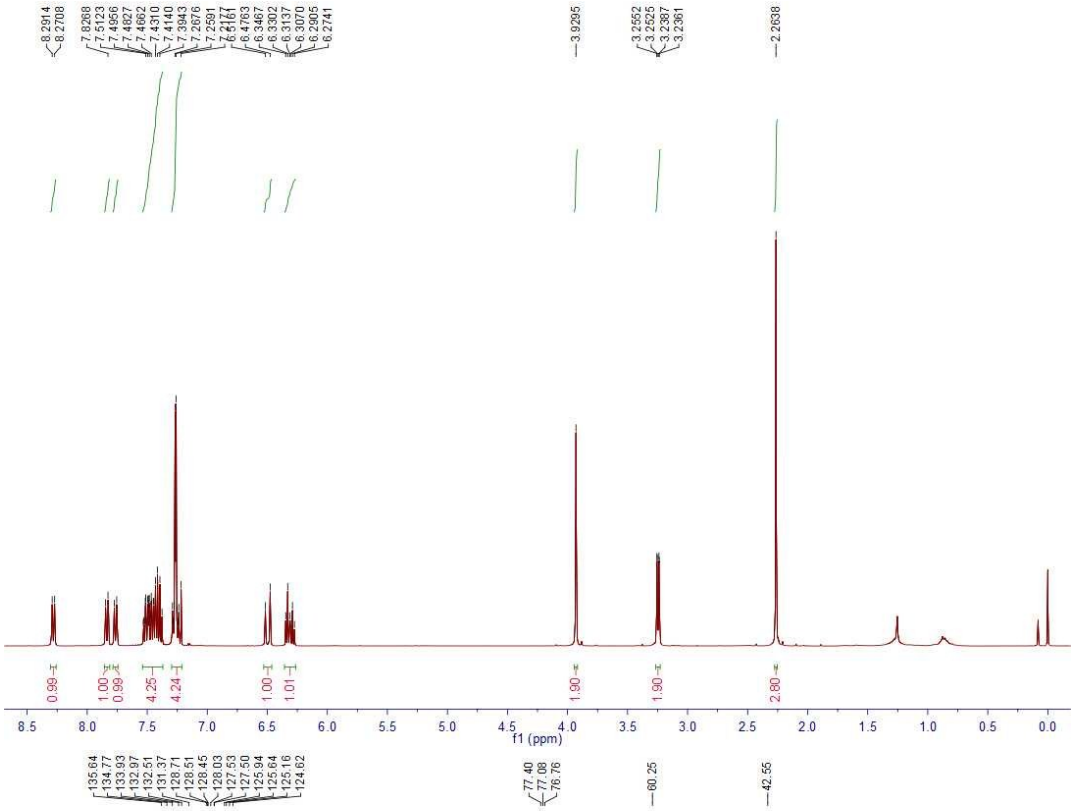
7.3652
7.2093
6.6069
6.4477
6.4310
6.4142
6.4082
6.3914
6.3746
4.0220
3.3599
3.3585
3.3433
3.3420
2.4083
2.3506
1.00
1.03
1.03
4.36
2.06
2.03
1.00
1.01
1.89
1.93
2.97
2.87
f1 (ppm)
137.22
134.91
134.40
133.95
132.70
132.56
129.31
128.50
128.00
127.54
126.49
126.29
125.86
125.63
123.17
124.69
77.43
77.11
76.80
60.55
60.08
42.49
21.26


f1 (ppm)


Cl
N

3z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7.4140
7.3943
7.2676
7.2591
7.2177
6.5161
6.4763
6.3467
6.3302
6.3137
6.3070
6.2905
6.2741
3.9295
3.2552
3.2525
3.2387
3.2361
2.2638
0.99
1.00
0.99
4.25
4.24
1.00
1.01
1.90
1.90
2.80
f1 (ppm)
135.64
134.77
133.93
132.97
132.51
131.37
128.71
128.51
128.45
128.03
127.53
127.50
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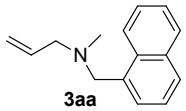
125.64
125.16
124.62
77.40
77.08
76.76
60.25
42.55
f1 (ppm)



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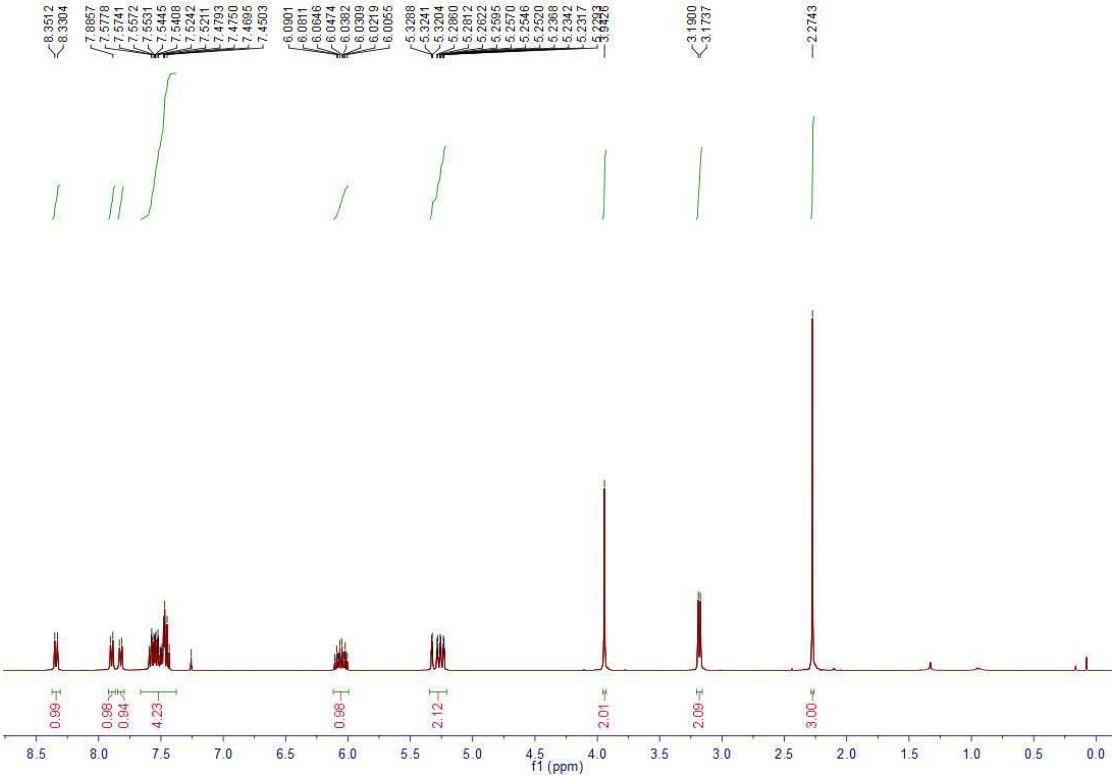
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7.5741
7.5572
7.5531
7.5445
7.5408
7.5242
7.5211
7.4793
7.4750
7.4695
7.4503
6.0901
6.0811
6.0646
6.0474
6.0382
6.0309
6.0219
6.0055
5.3288
5.3241
5.3204
5.2860
5.2812
5.2622
5.2595
5.2570
5.2546
5.2520
5.2368
5.2342
5.2317
3.9428
3.1900
3.1737
2.2743
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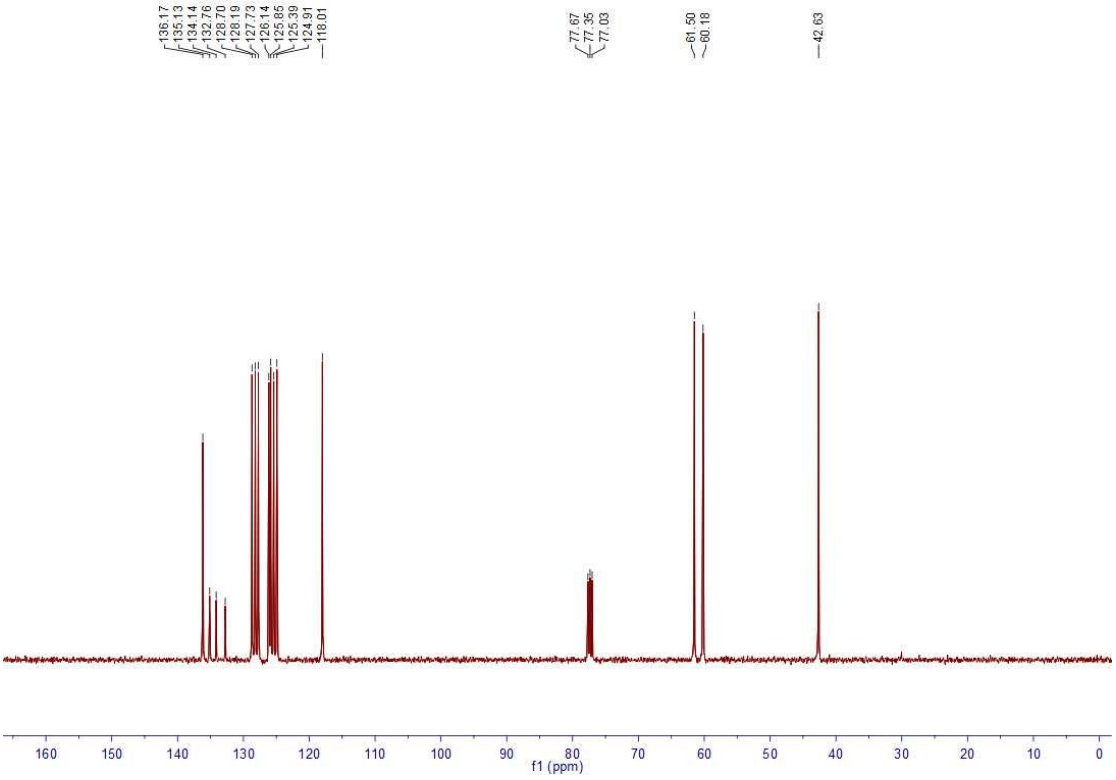
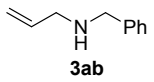
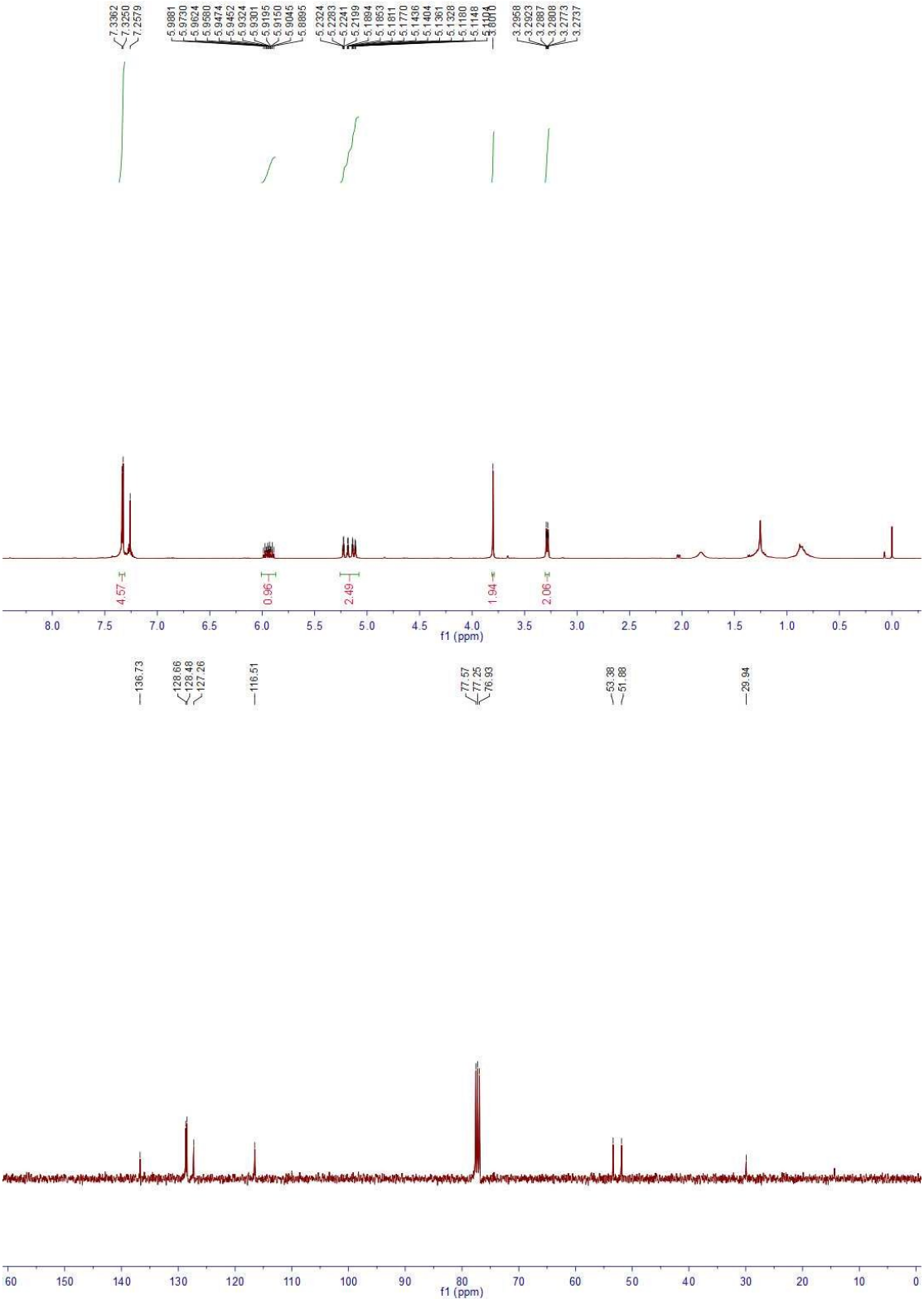
0.98
0.94
4.23
0.98
2.12
2.01
2.09
3.00
f1 (ppm)


136.17
135.13
134.14
132.76
128.70
128.19
127.73
126.14
125.85
125.39
124.91
118.01
77.67
77.35
77.03
61.50
60.18
42.63
f1 (ppm)


N
H
Ph

3ab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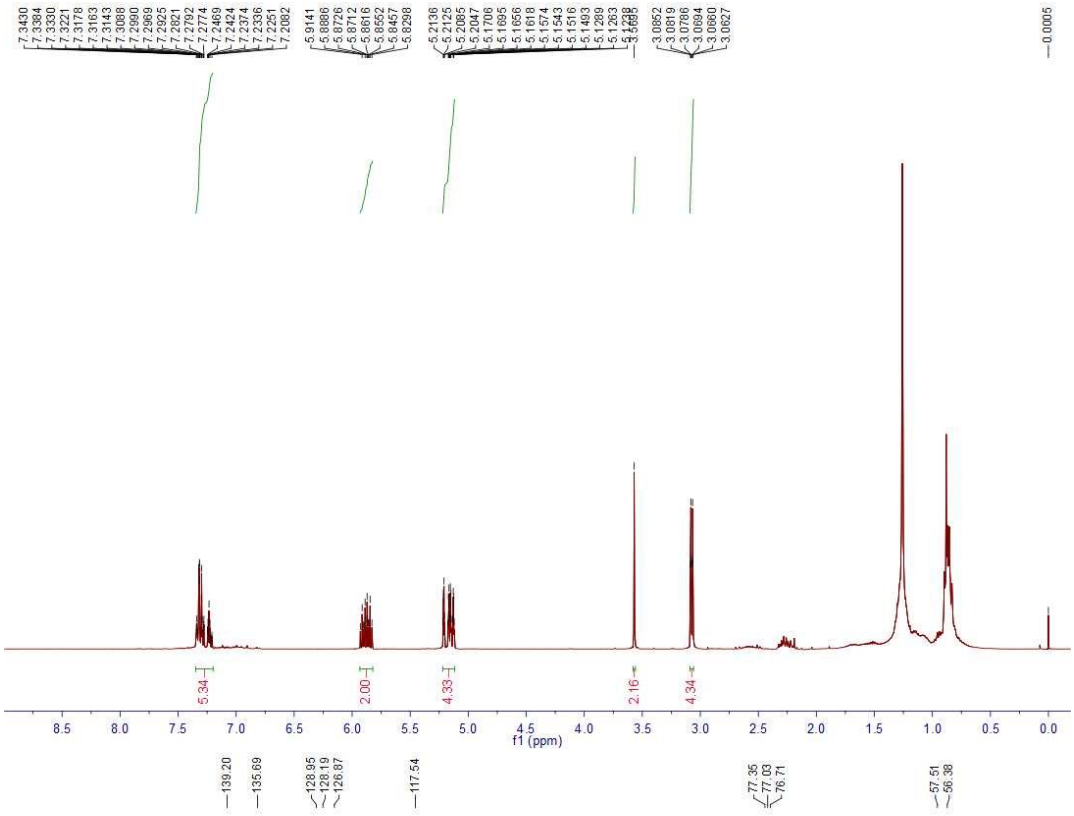
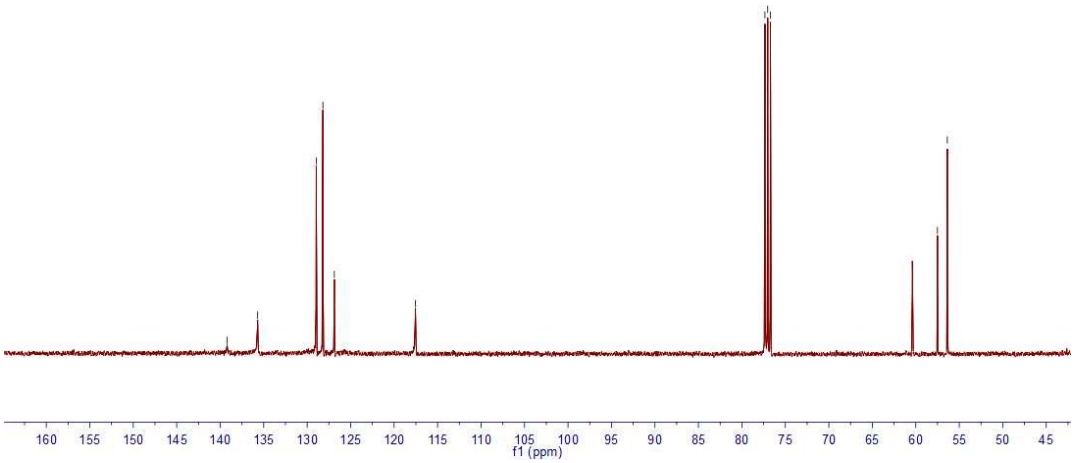
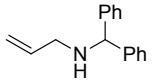
7.3250
7.2579
5.9881
5.9730
5.9624
5.9580
5.9474
5.9452
5.9324
5.9301
5.9195
5.9150
5.9045
5.8895
5.2324
5.2283
5.2241
5.2199
5.1894
5.1853
5.1811
5.1770
5.1436
5.1404
5.1361
5.1328
5.1180
5.1148
3.8010
3.2958
3.2923
3.2887
3.2808
3.2773
3.2737
4.57
0.96
2.49
1.94
2.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
136.73
128.66
128.48
127.26
116.51
77.57
77.25
76.93
53.38
51.88
29.94
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

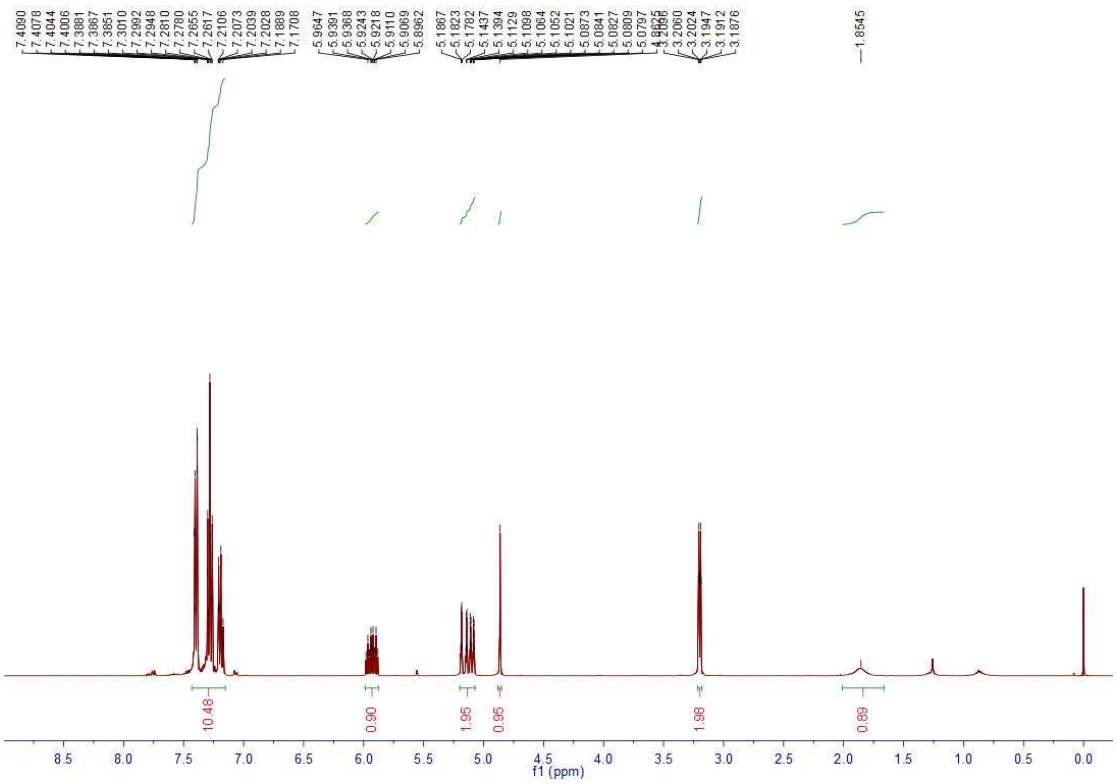
3ab'

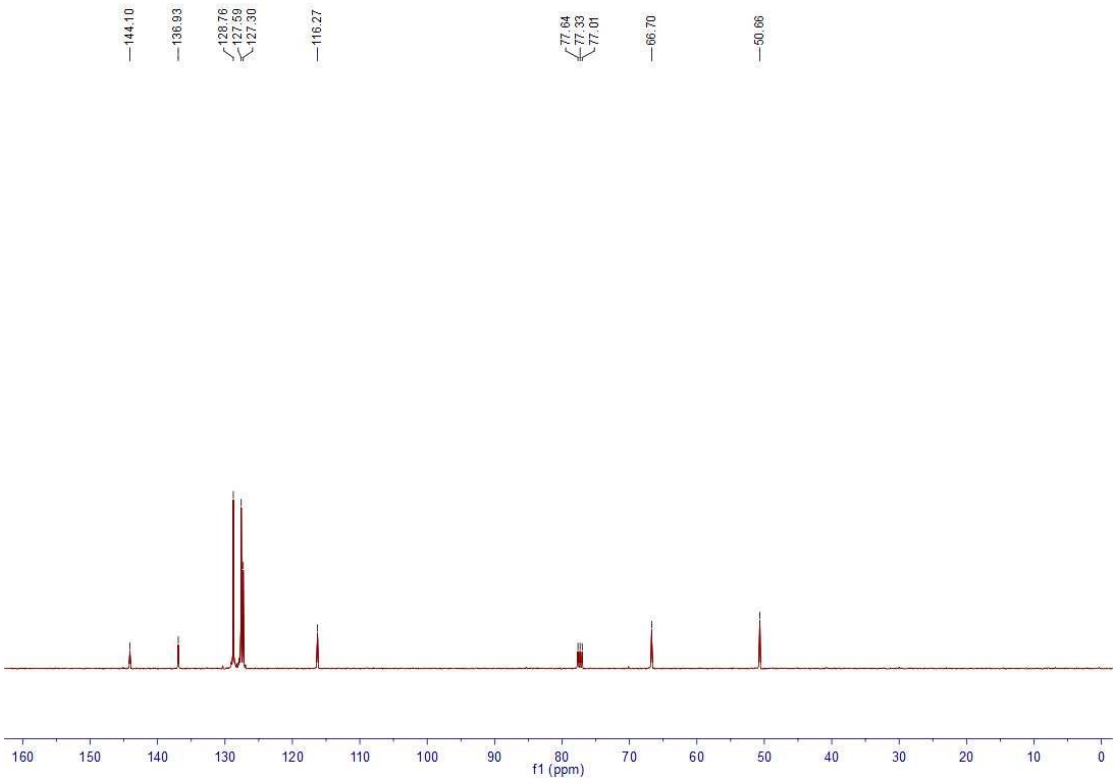


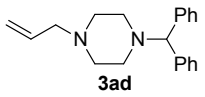



Ph
N
H
Ph

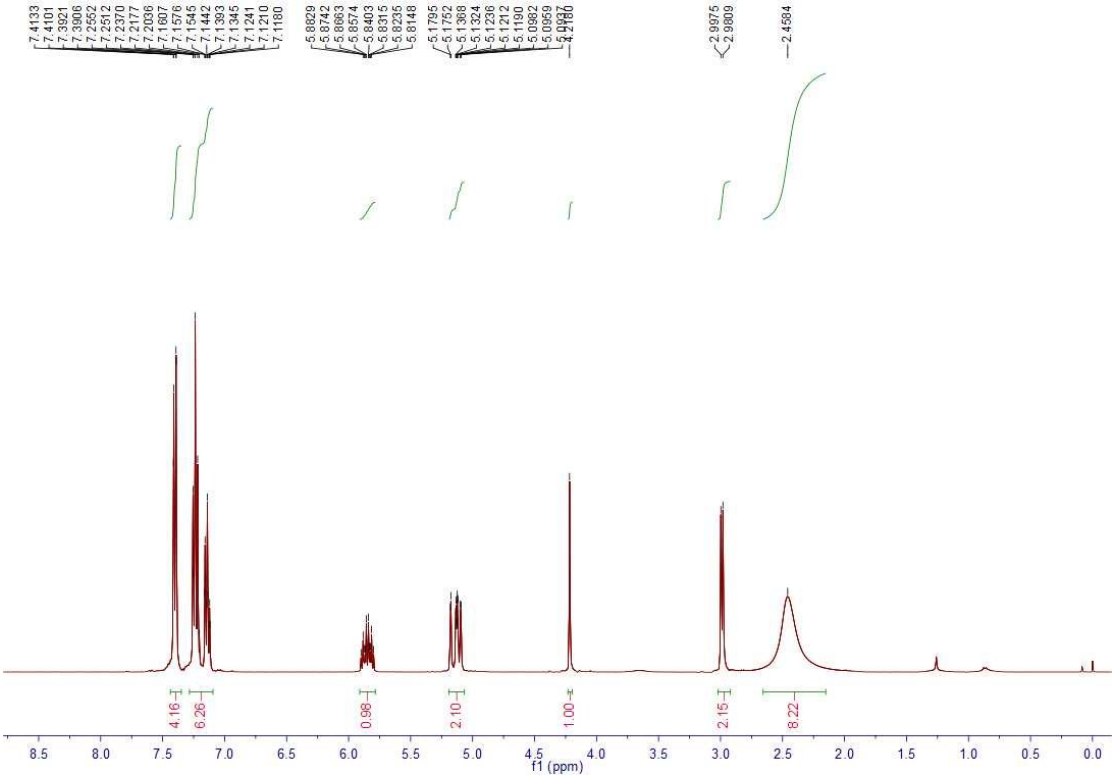
3ac


10.48
0.90
1.95
0.95
1.98
0.89
f1 (ppm)


144.10
136.93
128.76
127.59
127.30
116.27
77.64
77.33
77.01
66.70
50.66
f1 (ppm)


Ph
N
N
Ph

3ad


7.4133
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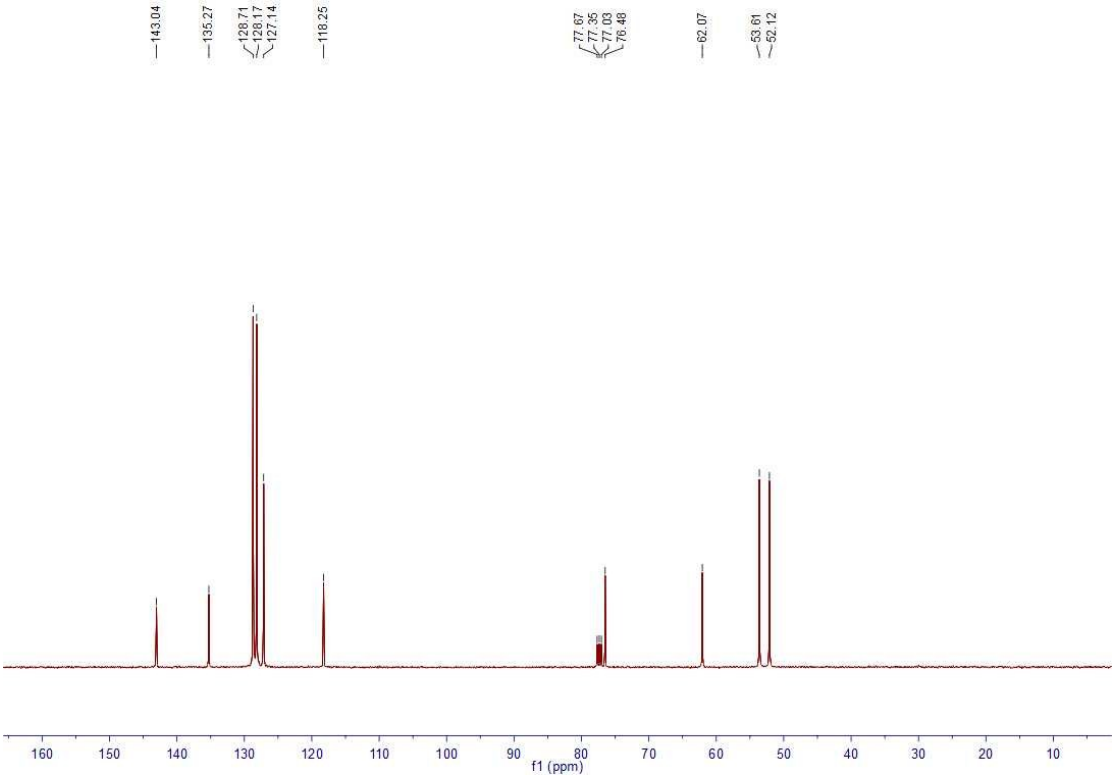
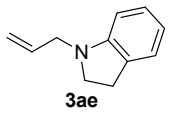
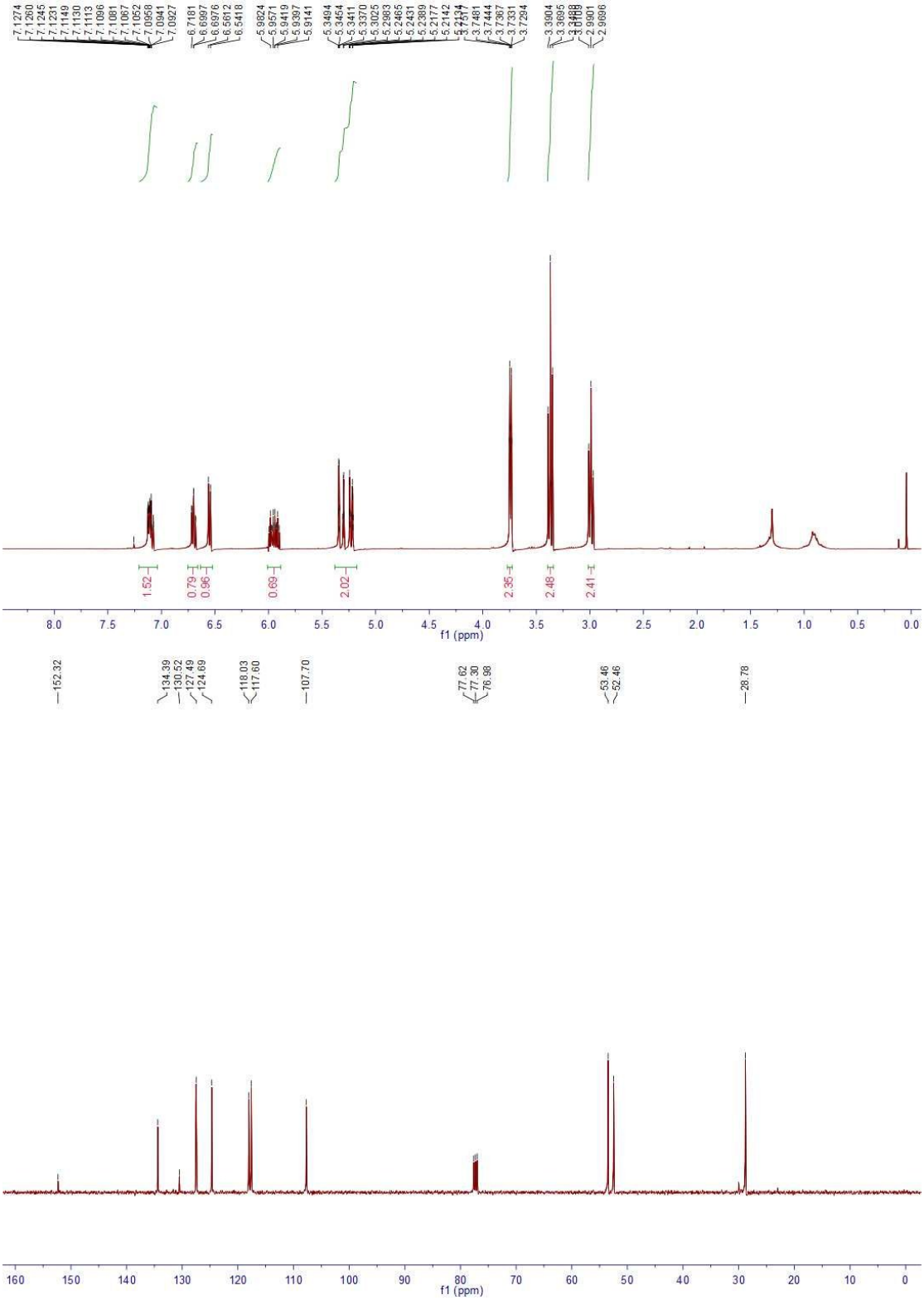
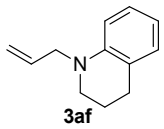
7.3921
7.3906
7.2552
7.2512
7.2370
7.2177
7.2036
7.1607
7.1576
7.1545
7.1442
7.1393
7.1345
7.1241
7.1210
7.1180
5.8829
5.8742
5.8663
5.8574
5.8403
5.8315
5.8235
5.8148
5.1795
5.1752
5.1368
5.1324
5.1236
5.1212
5.1190
5.0982
5.0959
2.9975
2.9809
2.4584
4.16
6.26
0.98
2.10
1.00
2.15
8.22
f1 (ppm)


143.04
135.27
128.71
128.17
127.14
118.25
77.67
77.35
77.03
76.48
62.07
53.61
52.12
f1 (ppm)

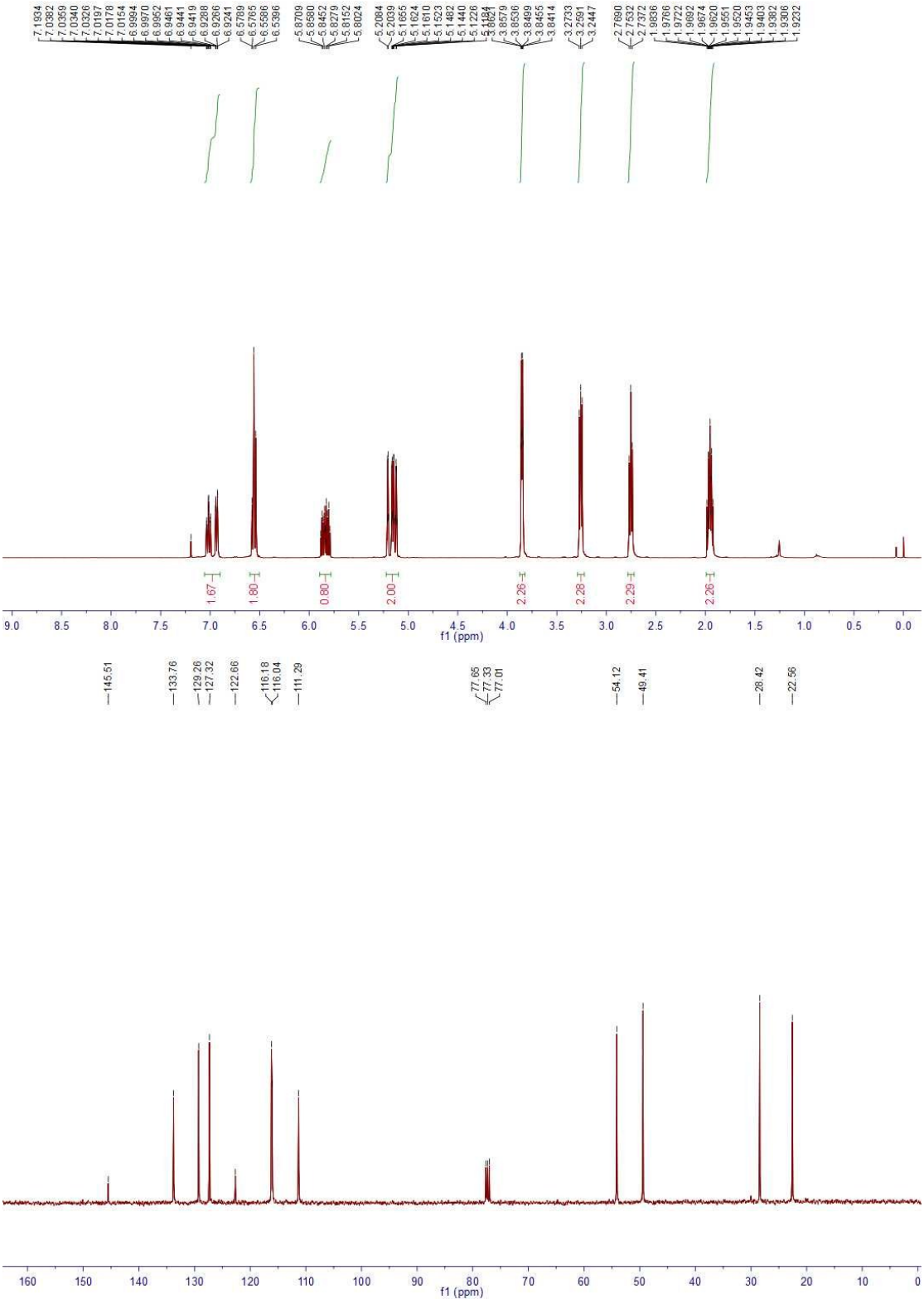


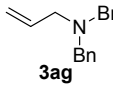
3ae


7.1274
7.1260
7.1245
7.1231
7.1149
7.1130
7.1113
7.1096
7.1081
7.1067
7.1052
7.0958
7.0941
7.0927
6.7181
6.6997
6.6976
6.5612
6.5418
5.9824
5.9571
5.9419
5.9397
5.9141
5.3494
5.3454
5.3411
5.3370
5.3025
5.2983
5.2465
5.2431
5.2389
5.2177
5.2142
3.7481
3.7444
3.7367
3.7331
3.7294
3.3904
3.3695
2.9901
2.9696
1.52
0.79
0.96
0.69
2.02
2.35
2.48
2.41
f1 (ppm)
152.32
134.39
130.52
127.49
124.69
118.03
117.60
107.70
77.62
77.30
76.98
53.46
52.46
28.78
f1 (ppm)

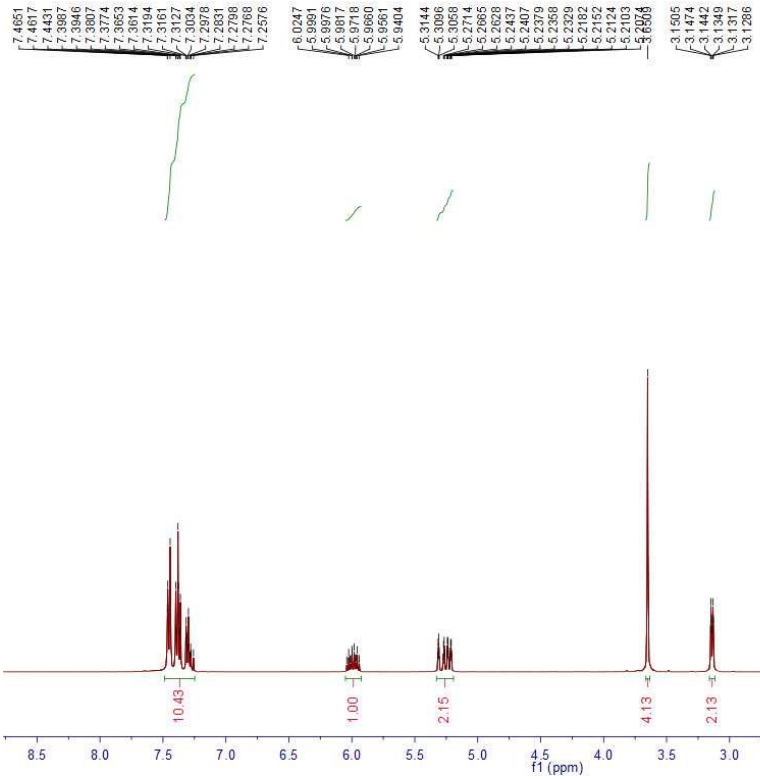


3af




Bn
N
Bn

3ag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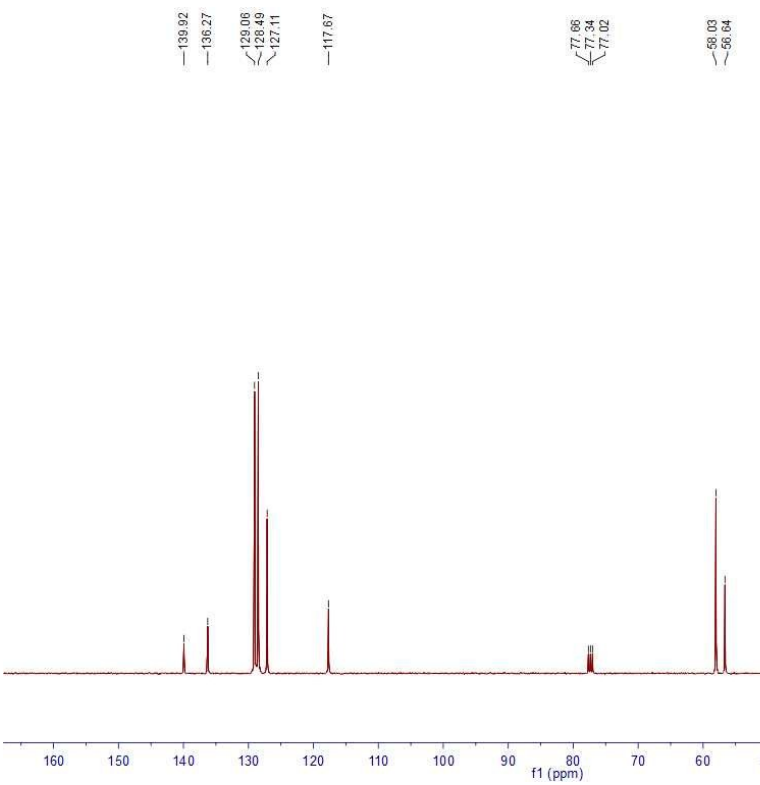
7.3987
7.3946
7.3807
7.3774
7.3653
7.3614
7.3194
7.3161
7.3127
7.3034
7.2978
7.2831
7.2798
7.2768
7.2576
6.0247
5.9991
5.9976
5.9817
5.9718
5.9660
5.9561
5.9404
5.3144
5.3096
5.3058
5.2714
5.2665
5.2628
5.2437
5.2407
5.2379
5.2358
5.2329
5.2182
5.2152
5.2124
5.2103
5.2074
3.6509
3.1505
3.1474
3.1442
3.1349
3.1317
3.1286
10.43
1.00
2.15
4.13
2.13
f1 (ppm)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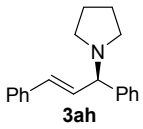
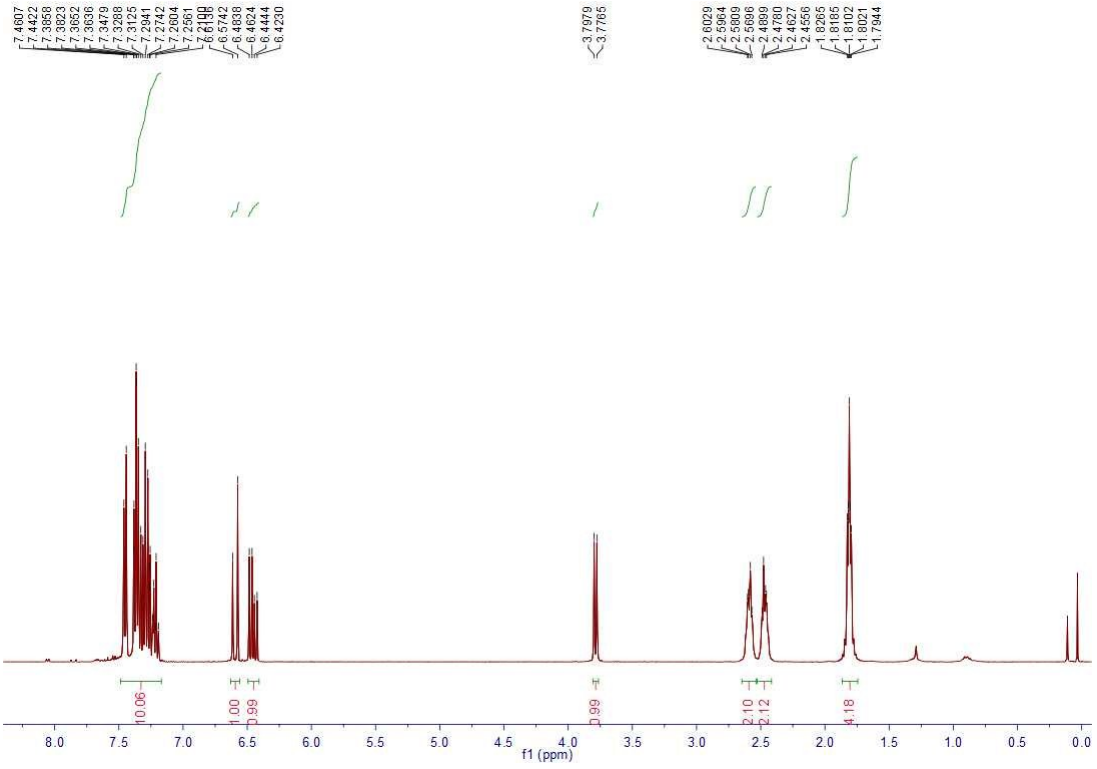
129.06
128.49
127.11
117.67
77.66
77.34
77.02
68.03
56.64
f1 (ppm)


N
Ph
Ph

3ah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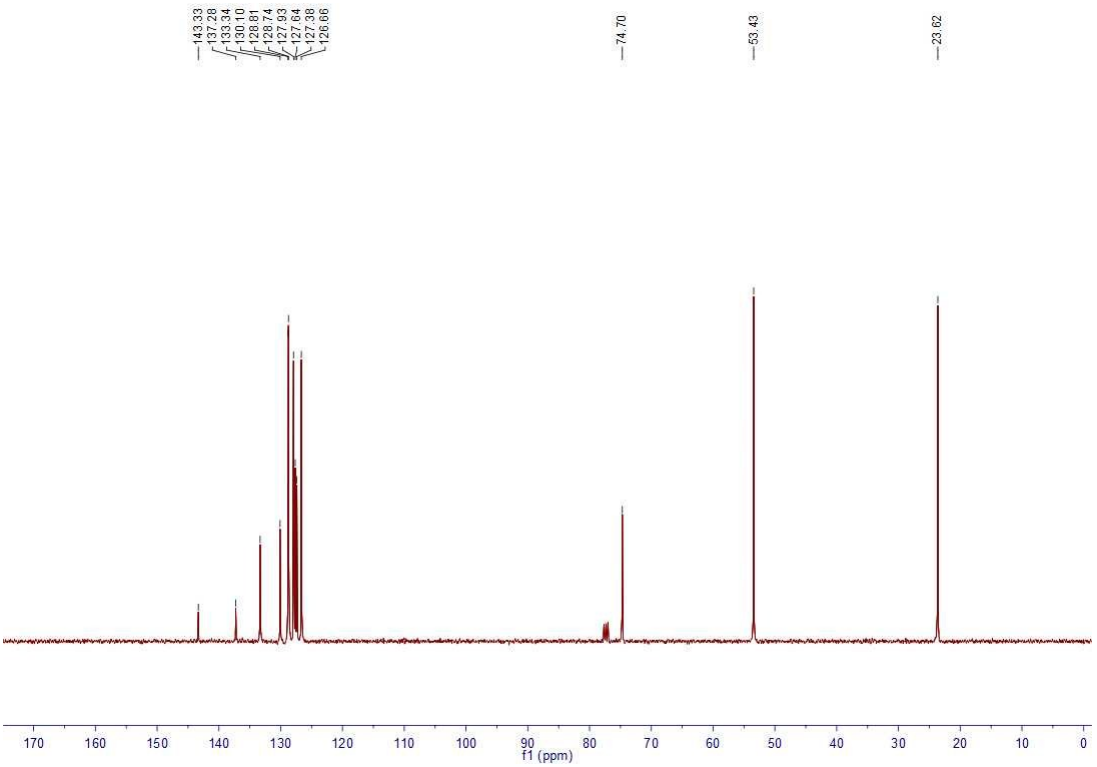
7.3858
7.3823
7.3652
7.3636
7.3479
7.3288
7.3125
7.2941
7.2742
7.2604
7.2561
6.5742
6.4838
6.4624
6.4444
6.4230
3.7979
3.7765
2.6029
2.5964
2.5809
2.5696
2.4899
2.4780
2.4627
2.4556
1.8265
1.8185
1.8102
1.8021
1.7944
10.06
1.00
0.99
0.99
2.10
2.12
4.18
f1 (ppm)


143.33
137.28
133.34
130.10
128.81
128.74
127.93
127.64
127.38
126.66
74.70
53.43
23.62
f1 (ppm)