Supporting information for

Palladium-Catalyzed Cross-Coupling Reaction of Secondary Benzylic Bromides with Grignard Reagents

Ana López-Pérez, Javier Adrio*and Juan C. Carretero*

Departamento de Química Orgánica. Facultad de Ciencias. Universidad Autónoma de Madrid. Cantoblanco.28049 Madrid. Spain.

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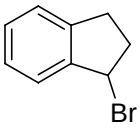
General methods

All anaerobic and moisture-sensitive manipulations were carried out in anhydrous solvents and under nitrogen. Dichloromethane, THF and CH_3CN were dried and stored over microwave-activated 4Å molecular sieves. Melting points were taken in open-end capillary tubes. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm silica gel plates (230-400 mesh). Flash column chromatographies were performed using silica gel (230-400 mesh). NMR spectra were recorded on AC-300 MHz instrument and calibrated using residual undeuterated solvent ($CDCl_3$) as internal reference. MS spectra were recorded on a VG *AutoSpec* mass spectrometer. (1-Bromoethyl)benzene and bromodiphenylmethane are commercially available. Grignard reagents were purchased from Aldrich excepting biphenylmagnesium bromide and *m*-methoxyphenylmagnesium bromide which were prepared from the corresponding bromides and magnesium under usual reaction conditions. The HPLC chromatograms of the racemic and enantiomerically enriched products are also included.

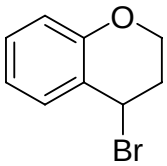
Typical procedure for the synthesis of benzylic bromides.

1-Bromo-2,3-dihydro-1*H*-indene[1]



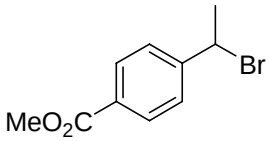
A dry round-bottomed flask was charged with 1-indanol (1.00 g, 7.5 mmol) and then placed under a nitrogen atmosphere. Dry CH_2Cl_2 (12 mL) and pyridine (25µl) were added, and the reaction mixture was cooled to -10ºC. PBr_3 (1.01 g, 3.7 mmol) was dissolved separately in dry CH_2Cl_2 (1,5 mL) and the resulting solution was added dropwise for a period of 10 min to the reaction mixture. The solution was stirred at -10 ºC for 12 h and 5% aqueous Na_2CO_3 was added to the mixture. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (10 mL). The combined organic layers were dried over Na_2SO_4, and concentrated under vacuum to give a yellow residue that was taken up in Et_2O (10 mL), passed through an nylon syringe filter, and evaporated under reduced pressure to afford 1-bromo-2,3-dihydro-1*H*-indene (905 mg, 90%, yellow oil) which was used in the next step without further purification. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.18-7.16 (m, 1H), 7.01-6.98 (m, 3H), 5.33 (dd, J = 5.9, 2.5 Hz, 1H), 2.99-2.88 (m, 1H), 2.67-2.58 (m, 1H), 2.39-2.22 (m, 2H).

4-Bromo-3,4-dihydro-2*H*-chromene[1]



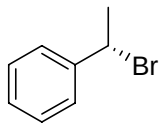
Following the above procedure, the reaction of 1-chromanol (200 mg, 1.3 mmol) with pyridine (5µl) and PBr_3 (180 mg, 0.6 mmol) in CH_2Cl_2 (2.5 mL) at room temperature afforded, 4-bromo-3,4-dihydro-1*H*-chromene (235 mg, 85%, yellow oil) which was used in the next step without further purification. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.34-7.1626 (m, 2H), 7.02-6.90 (m, 2H), 5.57 (m, 1H), 4.73-4.65 (m, 1H), 4.50-4.45 (m, 1H), 2.67-2.56 (m, 1H), 2.51-2.44 (m, 1H).

Methyl 4-(1-bromoethyl)benzoate[2]

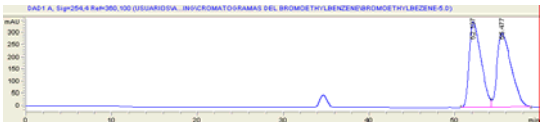


To a solution of methyl 4-ethylbenzoate (200 mg, 1.2 mmol) in benzene, N-bromosuccinimide (320 mg, 1.8 mmol) and AIBN (9.8 mg, 0.06 mmol) were added. The reaction mixture was refluxed for 14 h and then concentrated under vacuum. The residue was purified by silica gel flash chromatography (hexane-CH_2Cl_2 10:1) to afford methyl 4-(1-bromoethyl)benzoate (158 mg, 54%, colourless oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 5.19 (q, *J* = 6.9 Hz, 1H), 3.91 (s, 3H), 2.03 (d, *J* = 6.9 Hz, 3H).

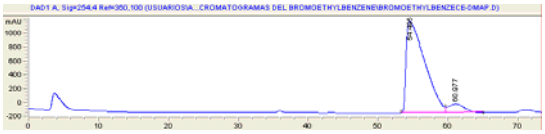
(*S*)-(1-Bromoethyl)benzene[3]



To a solution of (*R*)-1-phenyl-1-ethanol (200 mg, 1.6 mmol) in dry hexane (8 mL), DMAP (400 mg, 3.2 mmol) was added and the reaction mixture was cooled to 0 ºC. $POBr_3$ (300 mg, 1.1 mmol) was dissolved separately in dry hexane (2.0 mL) and the resulting solution was added dropwise. The mixture was stirred at room temperature for 2 h, then filtered and the solid washed with hexane. The combined filtrate was washed with water and saturated aqueous solution Na_2CO_3. The organic layer was dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel flash chromatography (hexane) to afford methyl (*S*)-(1-bromoethyl)benzene (250 mg, 82%, colourless oil). **$[\alpha]_D^{20}$:** -40.6 (*c* 1 $CHCl_3$), 86% *ee*.**$[\alpha]_D^{20}$** Lit[3]**:** -67 (neat). **HPLC:** 85-86% *ee* (reaction running twice) Daicel Chiralpak OJ, *i*-PrOH-hexane 0/100, flow rate 0.2 mL/min, t_R: 52.1 min (*S*)-isomer and 55.5 min (*R*)-isomer, 256 nm. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.46-7.43 (m, 2H), 7.38-7.26 (m, 3H), 5.22 (q, *J* = 6.9 Hz, 1H), 2.05 (d, *J* = 6.9 Hz, 3H).



#	Time	Area	Height	Width	Area%	Symmetry
1	52.137	34349.6	351.7	1.4455	49.519	0.52
2	55.477	35016.7	302.8	1.6273	50.481	0.495

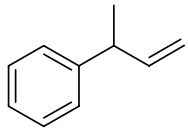


#	Time	Area	Height	Width	Area%	Symmetry
1	54.495	242608.4	1311.6	2.454	92.904	0.221
2	60.977	18529.1	119.1	2.2068	7.096	0.701

Typical procedure for the cross-coupling reaction:

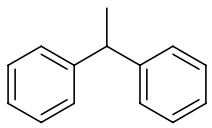
To a solution of Xantphos ligand (4.6 mg, 0.008 mmol) and $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) in THF (1.0 mL) or CH_3CN (1.0 mL), under nitrogen atmosphere, (1-bromoethyl)benzene (35 µl, 0.26 mmol) was added. The resulting solution was cooled to 0 ºC and vinylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol) was added dropwise. The mixture was stirred overnight (10-14h) at room temperature and filtered through a plug of Celite® with the aid of CH_2Cl_2 (5.0 mL). The solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (the eluent is indicated in each case).

1-(But-2-en-2-yl)benzene[4]



Following the typical procedure, the reaction of 1-(1-bromoethyl)benzene (35 µl, 0.26 mmol) with vinylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in THF (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane) 1-(but-2-en-2-yl)benzene (32.8 mg, 98%, colourless oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.32-7.18 (m, 5H), 6.00 (ddd, *J* =16.8, 10.3, 6.9 Hz, 1H), 5.07-5.00 (m, 2H), 3.46 (quin, *J* = 6.9 Hz, 1H), 1.36 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 145.6, 143.3, 128.3, 127.2, 126.0, 113.1, 43.2, 20.7. **MS** (EI^+) 132 (M^+, 19%), 117 (100), 115 (35), 91 (14). **HRMS** (EI^+): Calcd for $C_{10}H_{12}$ [M^+]: 132.0950, found: 132.0939.

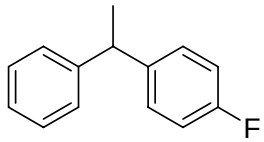
1,1-Diphenylethane[5]



Following the typical procedure, the reaction of (1-bromoethyl)benzene (35 µl, 0.26 mmol) with phenylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in THF (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane),

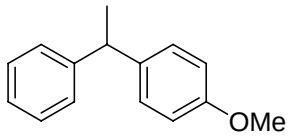
1,1-diphenylethane (44.7 mg, 96%, colourless oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.37-7.26 (m, 10H), 4.24 (quin, *J* = 7.3 Hz, 1H), 1.74 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 146.3, 128.3, 127.6, 126.0, 44.8, 21.8. **MS** (EI^+) 182 (M^+, 26%), 167 (100), 165 (24), 152 (16). **HRMS** (EI^+): Calcd for $C_{14}H_{14}$ [M^+]: 182.1100, found: 182.1096.

1-Fluoro-4-(1-phenylethyl)benzene



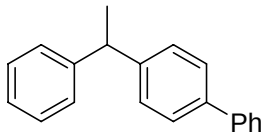
Following the typical procedure, the reaction of (1-bromoethyl)benzene (35 μl, 0.26 mmol) with *p*-fluorophenylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in THF (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane), 1-fluoro-4-(1-phenylethyl)benzene (48.6 mg, 95%, yellow oil). This reaction was scaled up to 500 mg, 2.6 mmol of (1-bromoethyl)benzene using 20mg of $Pd(CH_3CN)_2Cl_2$ and 40mg of Xantphos, providing the product in 93% yield (476 mg). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.33-7.31 (m, 2H), 7.26-7.19 (m, 5H), 7.03-6.90 (m, 2H), 4.18 (quin, *J* = 7.3 Hz, 1H), 1.67 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 162.9, 146.1, 142.0, 128.9, 128.4, 127.5, 126.1, 114.9, 44.0, 22.0. **MS** (EI^+) 200 (M^+, 24%), 185 (100), 183 (21), 165 (20). **HRMS** (EI^+): Calcd for $C_{14}H_{13}F$ [M^+]:200.1007, found: 200.1001.

4-(1-Phenylethyl)anisole[6]



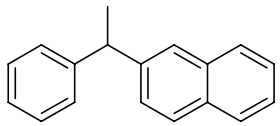
Following the typical procedure, the reaction of (1-bromoethyl)benzene (35 μl, 0.26 mmol) with *p*-methoxyphenylmagnesium bromide (0.5 M in THF, 0.66 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in THF (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane), 4-(1-phenylethyl)anisole (53.2 mg, 98%, colourless oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.26-7.13 (m, 5H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 4.08 (q, *J* = 7.2 Hz, 1H), 3.75 (s, 3H), 1.59 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 157.8, 146.7, 138.5, 128.5, 128.3, 127.5, 125.9, 113.7, 55.2, 43.9, 22.0. **MS** (EI^+) 212 (M^+, 23%), 197 (100), 165 (14), 153 (11). **HRMS** (EI^+): Calcd for $C_{15}H_{16}O$ [M^+]: 212.1203, found: 212.1201.

4-(1-Phenylethyl)biphenyl[7]



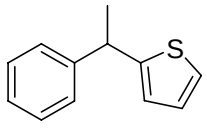
Following the typical procedure, the reaction of (1-bromoethyl)benzene (35 μl, 0.26 mmol), biphenylmagnesium bromide (0.7 M in THF, 0.47 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in THF (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane), 4-(1-phenylethyl)biphenyl (62.2 mg, 94%, white solid). **m.p.:** 61-62ºC. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.59-7.48 (m, 8H), 7.44-7.25 (m, 6H), 4.17 (q, *J* = 7.2 Hz, 1H), 1.66 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 146.2, 145.5, 141.2, 138.9, 128.7, 128.4, 127.6, 127.1, 127.0, 126.9, 126.1, 44.4, 21.8. **MS** (EI^+) 258 (M^+, 38%), 243 (100), 165 (20). **HRMS** (EI^+): Calcd for $C_{20}H_{18}$ [M^+]: 258.1410, found: 258.1409.

2-(1-Phenylethyl)naphthalene[8]



Following the typical procedure, the reaction of (1-bromoethyl)benzene (35 μl, 0.26 mmol), 2-naphthalenmagnesium bromide (0.5 M in THF, 0.66 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in THF (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane), 2-(1-phenylethyl)naphthalene (33.9 mg, 57%, colourless oil) and styrene (11 mg 40%, colourless oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.78-7.68 (m, 4H), 7.62-7.39 (m, 6H), 7.30-7.18 (m, 2H), 4.30 (q, *J* = 7.2 Hz, 1H), 1.72 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 146.2, 143.7, 133.5, 132.0, 128.4, 127.9, 127.7, 127.6, 127.5, 126.8, 126.1, 125.9, 125.4, 125.3, 44.8, 21.7.

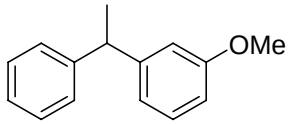
2-(1-Phenylethyl)thiophene[9]



Following the typical procedure, the reaction of (1-bromoethyl)benzene (35 μl, 0.26 mmol), 2-thiophenylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in THF (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane), 2-(1-phenylethyl)thiophene (45.8 mg, 95%, colourless oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.30-7.13 (m, 5H), 7.02-6.99 (m, 1H), 6.92-6.89 (m, 1H), 6.80-6.79 (m, 1H), 4.35 (q,

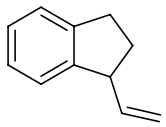
J = 7.2 Hz, 1H), 1.70 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 150.7, 146.0, 128.5, 127.3, 126.5, 124.3, 123.6, 123.5, 40.7, 23.3. **MS** (EI^+) 188 (M^+, 27%), 173 (100), 129 (12). **HRMS** (EI^+): Calcd for $C_{12}H_{12}S$ [M^+]: 188.0663, found: 188.0660.

1-Methoxy-3-(1-phenylethyl)benzene



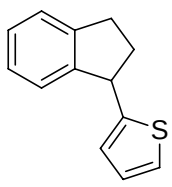
Following the typical procedure, the reaction of (1-bromoethyl)benzene (35 µl, 0.26 mmol) with *m*-methoxyphenylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in THF (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane), 1-methoxy-3-(1-phenylethyl)benzene (38.0 mg, 70%, colourless oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.26-7.19 (m, 6H), 6.86-6.82 (m, 2H), 6.76-6.72 (m, 1H), 4.14 (q, *J* = 7.3 Hz, 1H), 3.76 (s, 3H), 1.65 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 159.6, 147.9, 146.1, 129.2, 128.3, 127.5, 126.0, 120.1, 113.7, 110.9, 56.0, 44.7, 21.7.

1-Vinylindane[10]



Following the typical procedure, the reaction of 1-bromo-2,3-dihydro-1*H*-indene (50.6 mg, 0.26 mmol), vinylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in CH_3CN (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane), 1-vinylindane (34.7 mg, 94%, colourless oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.23-7.13 (m, 4H), 5.86 (ddd, , *J* = 17.3, 9.9, 8.3 Hz, 1H), 5.17-5,06 (m, 2H), 3.75 (q, *J* = 8.3 Hz, 1H), 2.93-2.84 (m, 2H), 2.46-2.27 (m, 1H), 2.17-2.03 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 141.1, 134.1, 126.3, 126.0, 125.8, 124.5, 121.0, 114.8, 49.8, 33.1, 32.0. **MS** (EI^+) 144 (M^+, 62%), 143 (20), 129 (100), 128 (48), 127 (11). **HRMS** (EI^+): Calcd for $C_{11}H_{12}$ [M^+]: 144.0938, found: 144.0939.

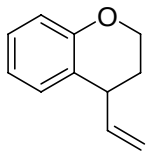
2-(2,3-Dihydro-1H-inden-1-yl)thiophene



Following the typical procedure, the reaction of 1-bromo-2,3-dihydro-1*H*-indene (50.6 mg, 0.26 mmol), 2-thiophenylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008

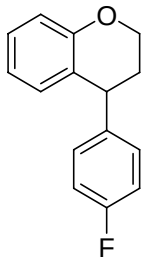
mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in CH_3CN (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane), 2-(2,3-dihydro-1H-inden-1-yl)thiophene (47.6 mg, 93%, yellow oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.39-7.19 (m, 4H), 7.09 (dd, , *J* = 5.0, 3.7 Hz, 1H), 6.69-6.63 (m, 2H), 4.42 (t, *J* = 7.6 Hz, 1H), 3.14-2.98 (m, 2H), 2.61-2.50 (m, 1H), 2.27-2.13 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 152.4, 145.2, 143.8, 127.7, 126.3, 124.5, 120.2, 47.3, 38.7, 31.7. **MS** (EI^+) 200 (M^+, 2%), 117 (100), 115 (30). **HRMS** (EI^+): Calcd for $C_{13}H_{12}S$ [M^+]: 200.0638, found: 200.0660.

3,4-Dihydro-4-vinyl-2*H*-chromene



Following the typical procedure, the reaction of 4-bromo-3,4-dihydro-1*H*-chromene (40.0 mg, 0.26 mmol), vinylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in CH_3CN (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane), 3,4-dihydro-4-vinyl-2*H*-chromene (17.2 mg, 42%, colourless oil) and the β-elimination product[11] (13.7 mg, 40%, colourless oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.38-7.07 (m, 2H), 7.97-6.76 (m, 2H), 5.87 (ddd, , *J* = 17.4, 10.2, 7.8 Hz, 1H), 5.19-5.05 (m, 2H), 4.26-4.16 (m, 2H), 3.56-3-49 (m, 1H), 2.14-2.01 (m, 1H), 1.94-1.86 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 155.9, 141.4, 128.9, 127.9, 127.4, 120.5, 117.3, 117.2, 65.4, 37.6, 36.5. **MS** (EI^+) 160 (M^+, 35%), 133 (100), 105 (26). **HRMS** (EI^+): Calcd for $C_{11}H_{12}O$ [M^+]: 160.0888, found: 160.0878.

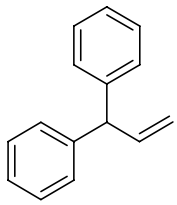
4-(4-Fluorophenyl)-3,4-dihydro-2*H*-chromene



Following the typical procedure, the reaction of 4-bromo-3,4-dihydro-1*H*-chromene (40.0 mg, 0.26 mmol), *p*-fluorophenylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in CH_3CN (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane), 4-(4-fluorophenyl)-3,4-dihydro-2*H*-chromene (30.9 mg, 53%, yellow oil) and the β-elimination product[11] (11.3 mg, 33%, colourless oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.28-7.23 (m, 2H), 7.11-7.08 (m, 2H), 7.03-6.90 (m, 4H), 4.47-4.26 (m, 3H), 2.24-2.13 (m, 1H), 1.95-1.83 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 155.9, 155.2, 128.9, 127.9, 127.6, 124.5, 123.8, 120.5, 117.2, 117.1, 65.4,

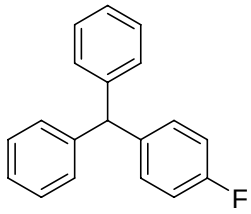
37.8, 36.6. **MS** (EI^+) 228 (M^+, 15%), 133 (100), 105 (26). **HRMS** (EI^+): Calcd for $C_{15}H_{13}FO$ [M^+]: 228.0950, found: 228.0953.

3,3-Diphenylprop-1-ene



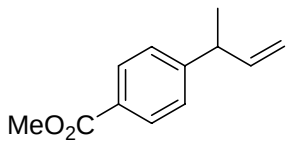
Following the typical procedure, the reaction of bromodiphenylmethane (50.0 mg, 0.26 mmol), vinylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in CH_3CN (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane), 3,3-diphenylprop-1-ene (24.8 mg, 50%, colourless oil) and the reduction product[12] (14.0 mg, 32%, colourless oil).. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.32-7.26 (m, 10H), 6.36 (ddd, *J* = 17.2, 10.1, 7.2 Hz, 1H), 5.29-5.26 (m, 1H), 5.07-5.02 (m, 1H), 4.78 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 142.2, 141.0, 128.5, 128.1, 125.8, 116.3, 56.3. **MS** (EI^+) 194 (M^+, 100%), 193 (71), 180 (12), 179 (53), 178 (46). **HRMS** (EI^+): Calcd for $C_{15}H_{14}$ [M^+]: 194.1104, found: 194.1096.

Diphenyl 4-fluorophenyl methane[13]



Following the typical procedure, the reaction of diphenylbromomethane (50.0 mg, 0.26 mmol), *p*-fluorophenylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in CH_3CN (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane), diphenyl 4-fluorophenyl methane (65.8 mg, 98%, yellow solid). **m.p.:** 59-60ºC. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.40-7.39 (m, 2H), 7.11-6.98 (m, 10H), 6.93-6.90 (m, 2H), 4.74 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 160.7, 143.4, 136.3, 128.6, 128.5, 128.1, 125.8, 115.8, 56.3. **MS** (EI^+) 262 (M^+, 100%), 261 (31), 185 (54), 183 (57), 165 (44).. **HRMS** (EI^+): Calcd for $C_{19}H_{15}F$ [M^+]: 262.1154, found: 262.1158.

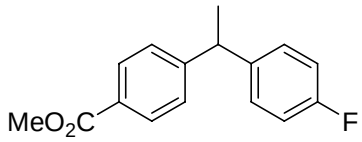
Methyl 4-(but-3-en-2-yl)benzoate



Following the typical procedure, the reaction of methyl 4-(1-bromoethyl)benzoate (52.0 mg, 0.26 mmol) vinylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol),

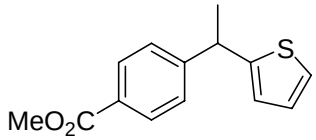
$Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in CH_3CN (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane:AcOEt 30:1), methyl 4-(but-3-en-2-yl)benzoate (29.0 mg, 61%, colourless oil) and the β-elimination product[14] (18.5 mg, 43%, colourless oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 5.84 (ddd, *J* = 16.3, 9.8, 6.9 Hz, 1H), 4.94-4.89 (m, 2H), 3.75 (s, 3H), 3.38 (quin, *J* = 6.9 Hz, 1H), 1.22 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.1, 150.9, 142.3, 129.8, 127.3, 126.1, 113.6, 51.9, 43.2, 20.5. **MS** (EI^+) 190 (M^+, 24%), 131 (100), 116 (23), 115 (33), 91 (25). **HRMS** (EI^+): Calcd for $C_{12}H_{14}O_2$ [M^+]: 190.0987, found: 190.0994.

Methyl 4-(1-(4-fluorophenyl)ethyl)benzoate



Following the typical procedure, the reaction of methyl 4-(1-bromoethyl)benzoate (52.0 mg, 0.26 mmol), *p*-fluorophenylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in CH_3CN (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane:AcOEt 30:1), methyl 4-(1-(4-fluorophenyl)ethyl)benzoate (63.4 mg, 94%, colourless oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.18-7.13 (m, 2H), 7.00-6.94 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 1H), 3.90 (s, 3H), 1.63 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.0, 163.0, 151.4, 141.1, 129.8, 129.0, 128.9, 127.5, 115.3, 52.0, 44.1, 21.7. **MS** (EI^+) 258 (M^+, 22%), 243 (100), 199 (11), 184 (22), 183 (35). **HRMS** (EI^+): Calcd for $C_{16}H_{15}FO_2$ [M^+]: 258.1068, found: 258.1056.

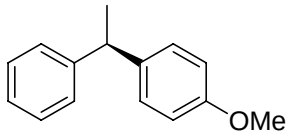
Methyl 4-(1-(thiophen-2-yl)ethyl)benzoate



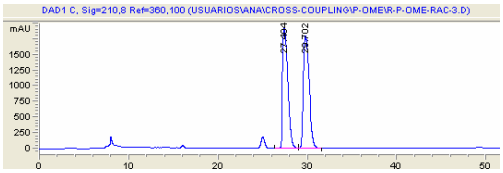
Following the typical procedure, the reaction of methyl 4-(1-bromoethyl)benzoate (52.0 mg, 0.26 mmol), 2-thiophenylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in CH_3CN (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane:AcOEt 30:1), methyl 4-(1-(thiophen-2-yl)ethyl)benzoate (45.4 mg, 72%, yellow oil) and the β-elimination product[14] (7.2 mg, 17%, colourless oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ

7.98 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.18-7.15 (m, 1H), 6.95-6.92 (m, 1H), 6.81-6.80 (m, 1H), 4.39 (q, *J* = 7.1 Hz, 1H), 3.90 (s, 3H), 1.71 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 166.9, 151.2, 149.5, 129.9, 127.3, 126.6, 126.1, 123.8, 52.0, 40.7, 23.0. **MS** (EI^+) 246 (M^+, 32%), 231 (100), 172 (16), 171 (22). **HRMS** (EI^+): Calcd for $C_{16}H_{15}FO_2$ [M^+]: 246.0718, found: 247.0715.

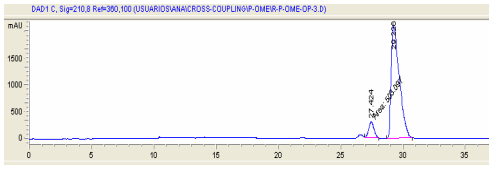
(*R*)-4-(1-Phenylethyl)anisole[6] (1)



Following the typical procedure, the reaction of (*S*)-(1-bromoethyl)benzene (85%ee) (35 µl, 0.26 mmol) with *p*-methoxyphenylmagnesium bromide (0.5 M in THF, 0.66 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in THF (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane), **(*R*)-1** (52.6 mg, 97%, colourless oil). **$[\alpha]_D^{20}$:** -10.6 (*c* 0.60 $CHCl_3$), 84% *ee*. **$[\alpha]_D^{20}$** Lit[6]**:** -12.7 (*c* 0.65 $CHCl_3$), 94% ee. **HPLC:** Daicel Chiralpak OJ, *i*-PrOH-hexane 15/85, flow rate 0.5 mL/min, t_R: 27.4 min (*S*)-isomer and 29.7 min (*R*)-isomer, 210 nm.

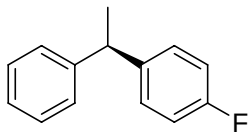


#	Time	Area	Height	Width	Area%	Symmetry
1	27.404	80498.3	1905.7	0.6728	49.168	0.512
2	29.702	83222.9	1797.8	0.7321	50.832	0.487

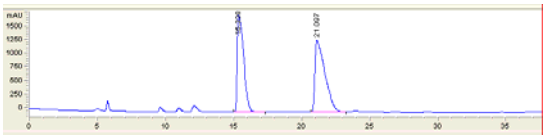


#	Time	Area	Height	Width	Area%	Symmetry
1	27.424	503.1	17.9	0.4694	8.135	0.895
2	29.226	5681.4	124.8	0.661	91.865	0.391

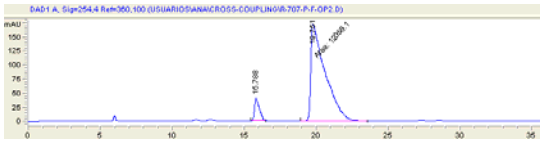
***(R)*-1-Fluoro-4-(1-phenylethyl)benzene (2)**



Following the typical procedure, the reaction of (*S*)-(1-bromoethyl)benzene (86% *ee*) (35 µl, 0.26 mmol) with *p*-fluorophenylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in THF (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane), **(*R*)-2** (48.1 mg, 94%, yellow oil). **$[\alpha]_D^{20}$:** -3.3 (*c* 0.60 $CHCl_3$), 85% *ee*. **HPLC:** Daicel Chiralpak OJ, *i*-PrOH-hexane 0/100, flow rate 0.8 mL/min, t_R: 15.3 min (*S*)-isomer and 21.1 min (*R*)-isomer, 210 nm.



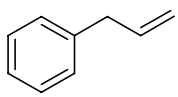
#	Time	Area	Height	Width	Area%	Symmetry
1	15.338	59688.8	1765	0.5446	47.019	0.306
2	21.097	67258.1	1319.3	0.7808	52.981	0.244



#	Time	Area	Height	Width	Area%	Symmetry
1	15.788	992.8	41.6	0.3562	7.609	0.414
2	19.751	12056.1	171.3	1.1731	92.391	0.184

Cross-coupling reaction example using a primary benzylic bromide

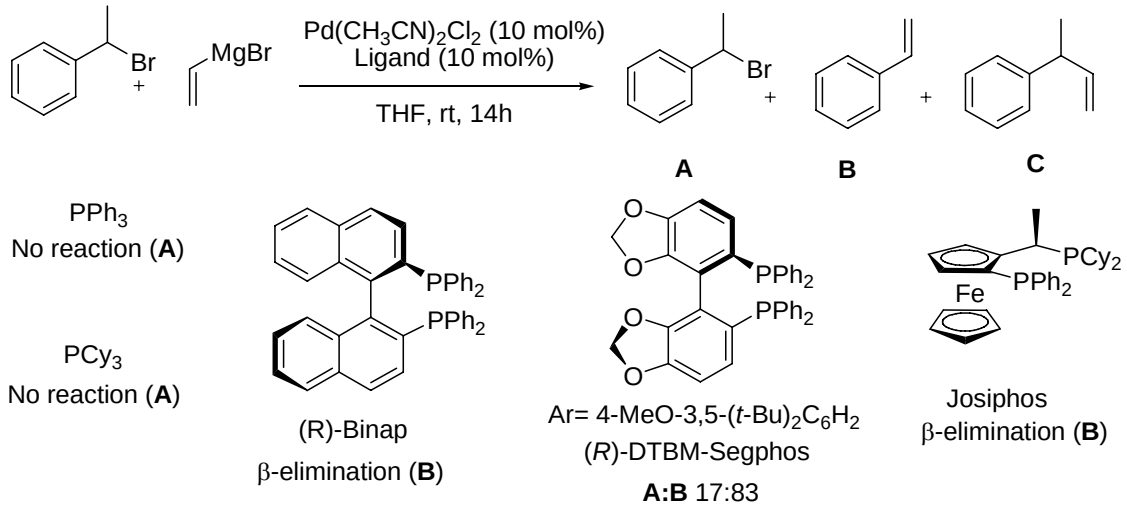
1-Allylbenzene[12]



Following the typical procedure, the reaction of 1-bromomethylbenzene (43.0 mg, 0.26 mmol) vinylmagnesium bromide (1.0 M in THF, 0.33 mL, 0.33 mmol), $Pd(CH_3CN)_2Cl_2$ (2.0 mg, 0.008 mmol) and Xantphos ligand (4.6 mg, 0.008 mmol) in THF (2.0 mL) at room temperature afforded, after purification by silica gel flash chromatography (hexane), 1-allylbenzene (28.7 mg, 95%, colourles oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.36-7.14 (m, 5H), 6.03-5.89 (m, 1H), 5.10-5.03 (m, 2H), 3.39-3.37 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 142.3, 136.1, 129.8, 127.3, 126.1, 113.8, 43.2. **MS** (EI^+) 118 (M^+, 68%), 117 (100), 115 (40), 91 (19). **HRMS** (EI^+): Calcd for C_9H_{10} [M^+]: 118.0788, found: 118.0783.

Screening of other ligands for cross-coupling reaction of 1-bromoethylbenzene with vinyl magnesium bromide.

Several ligands were tested in the model reaction using 10 mol% of $Pd(CH_3CN)_2Cl_2$ as catalyst and THF as solvent at room temperature. No reaction was observed in the absence of ligand or when PPh_3 or PCy_2 were used. In the presence of the bidentate phosphines Binap, DTBM-Segphos, or Josiphos the reaction afforded styrene as major product, likely as result of a β-hydride elimination process. The coupling product C was not detected with these ligands.



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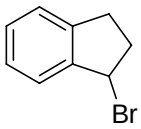
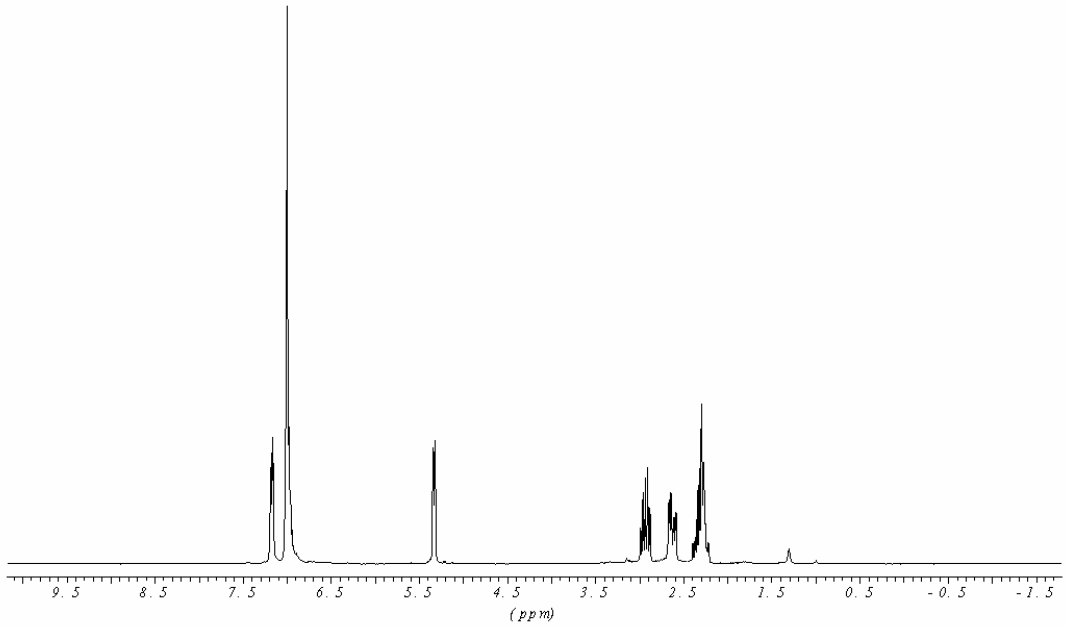
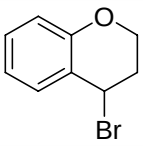
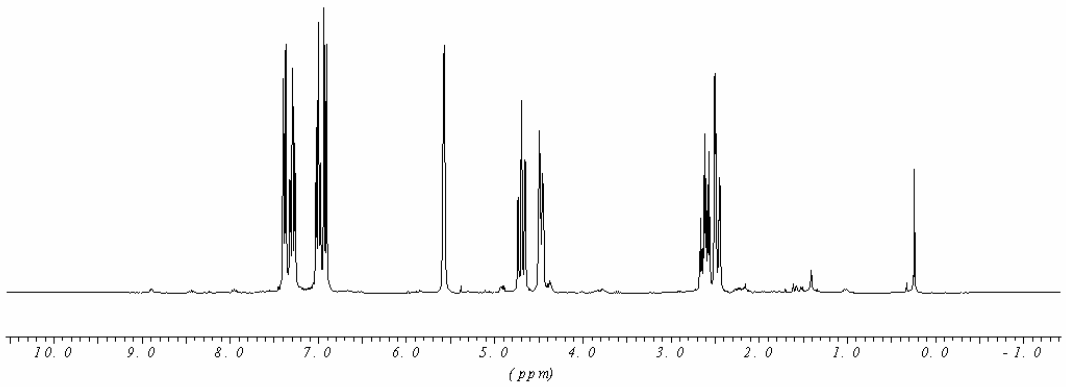

Br


9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
(ppm)


O
Br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7.0
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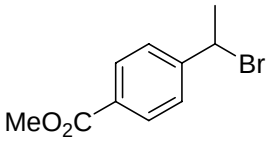
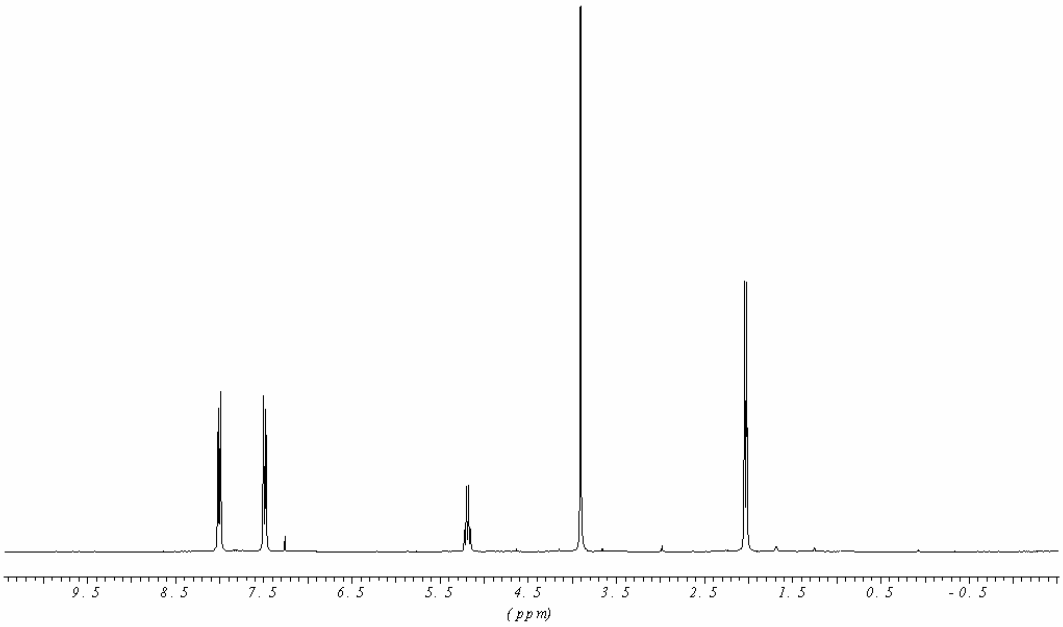
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)


Br
MeO2C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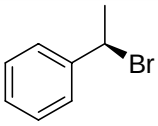
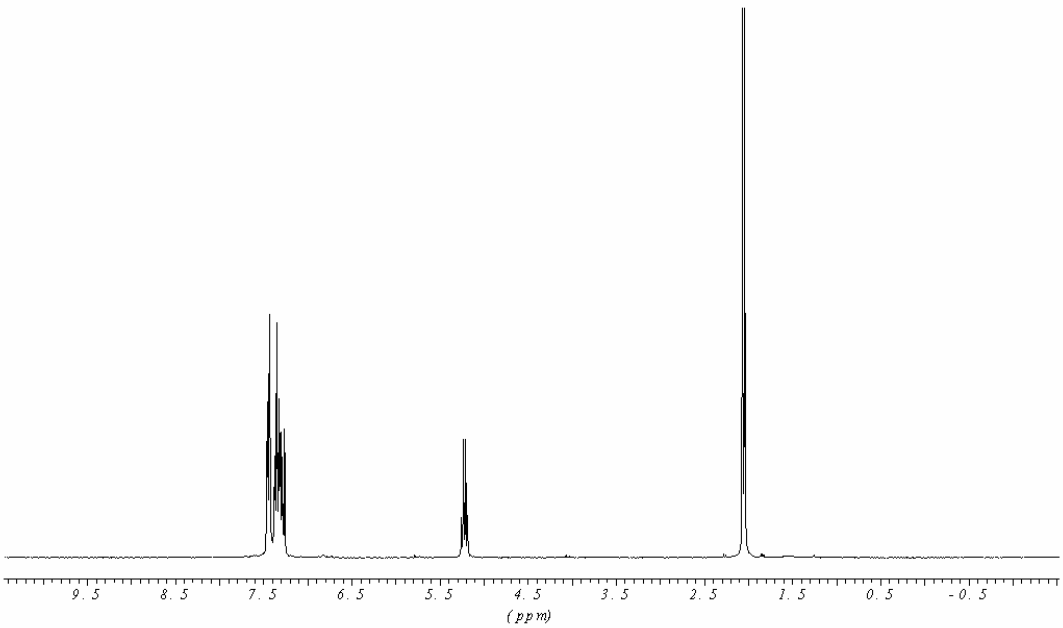
(ppm)


Br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8.5
7.5
6.5
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4.5
3.5
2.5
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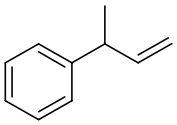
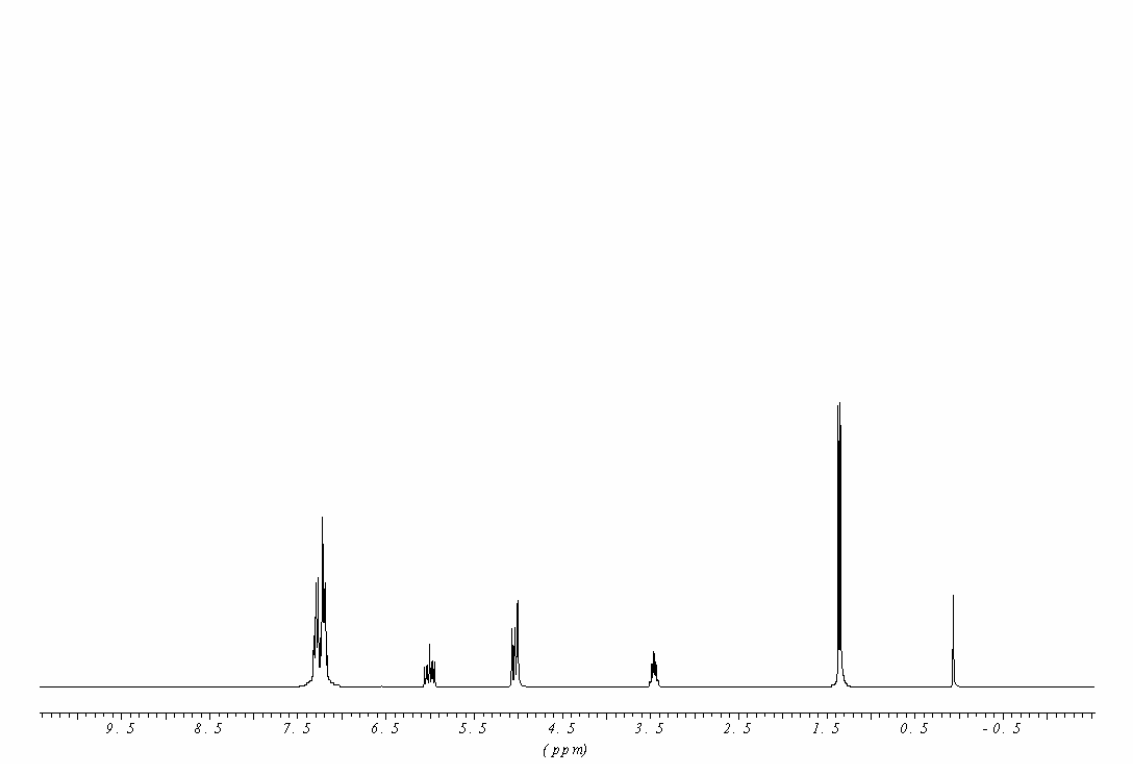
-0.5
(ppm)

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8.5
7.5
6.5
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4.5
3.5
2.5
1.5
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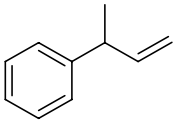
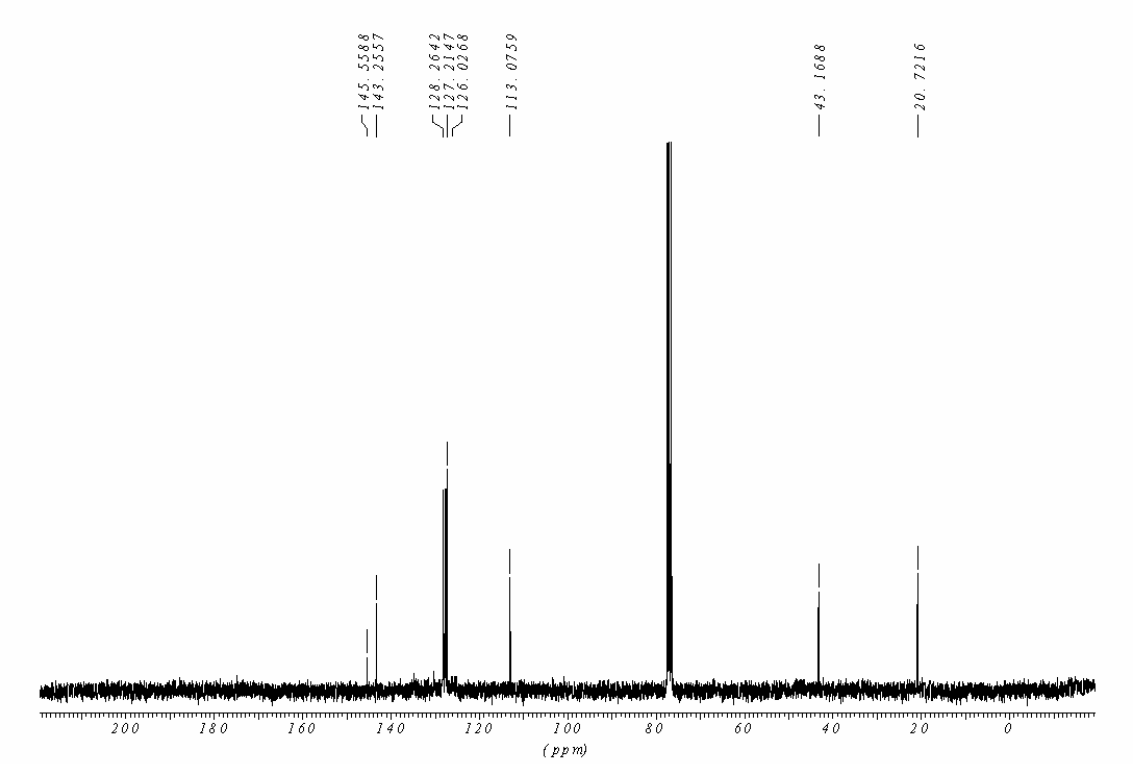
-0.5
(ppm)

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128.2642
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113.0759
43.1688
20.7216
200
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120
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80
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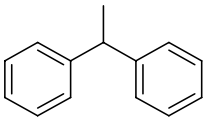
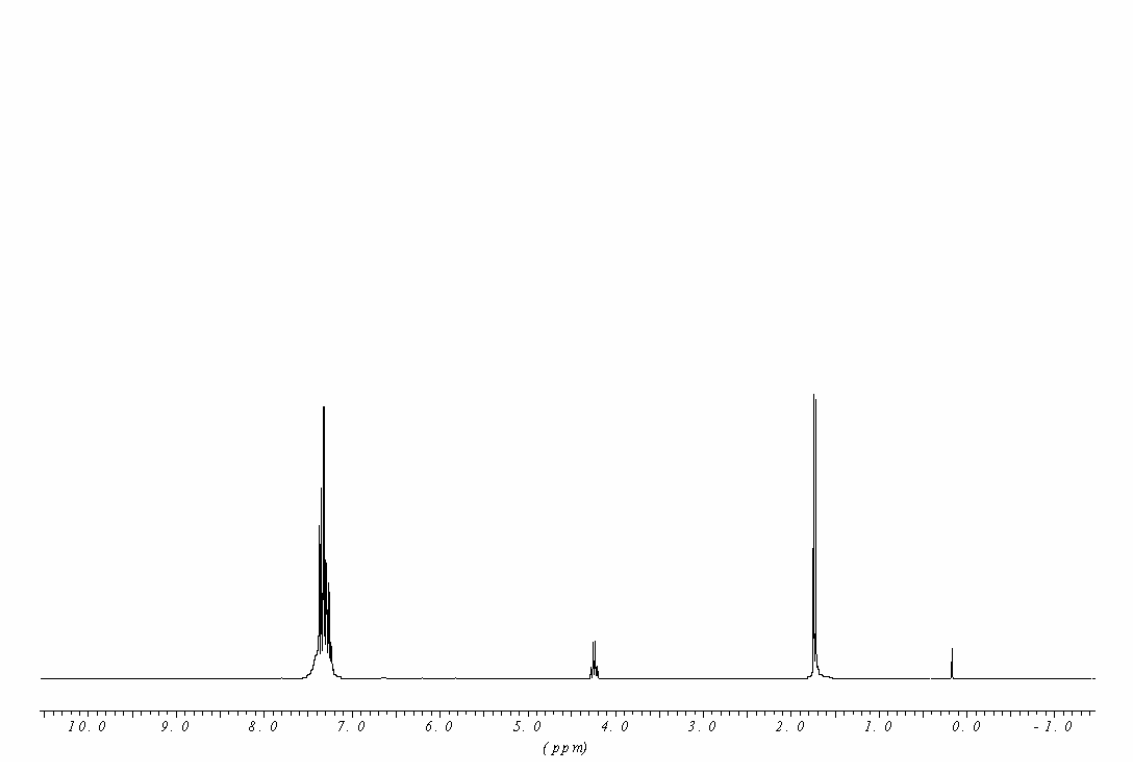
20
0
(ppm)

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3.0
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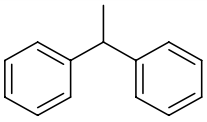
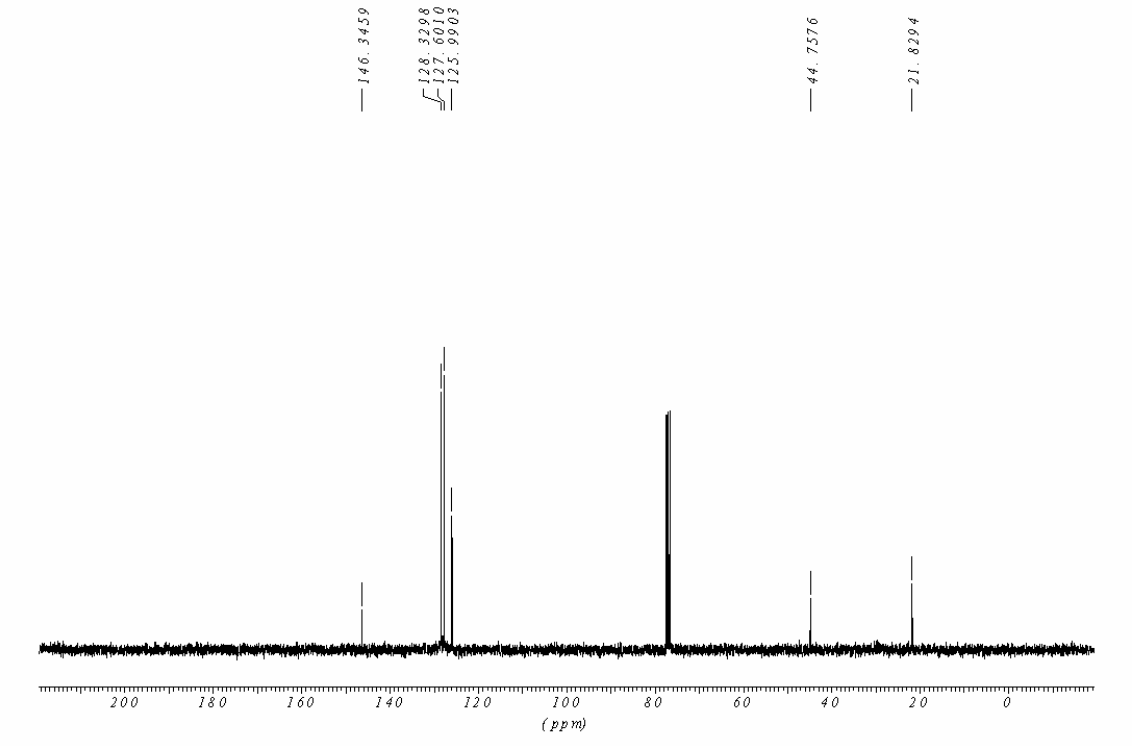
(ppm)

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44.7576
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120
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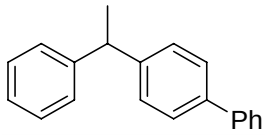
40
20
0
(ppm)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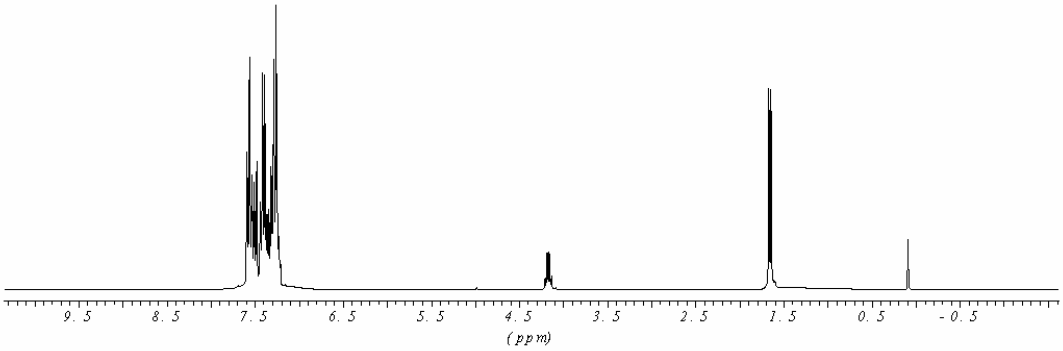
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3.5
2.5
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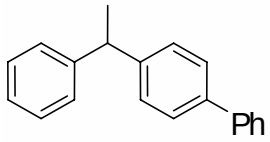
(ppm)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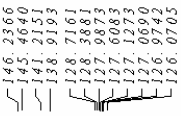
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141.2151
138.9193
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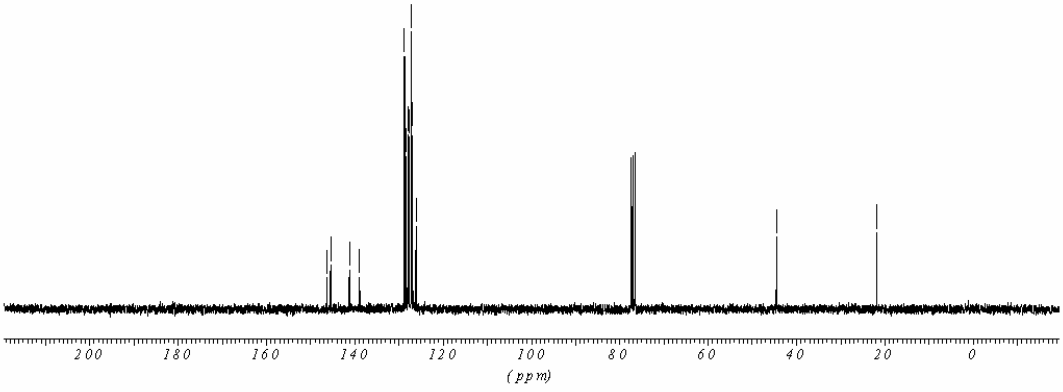
127.1273
127.0690
126.9742
126.0705


44.4588
21.8367


200
180
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120
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80
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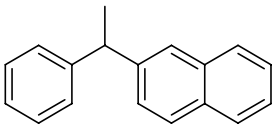
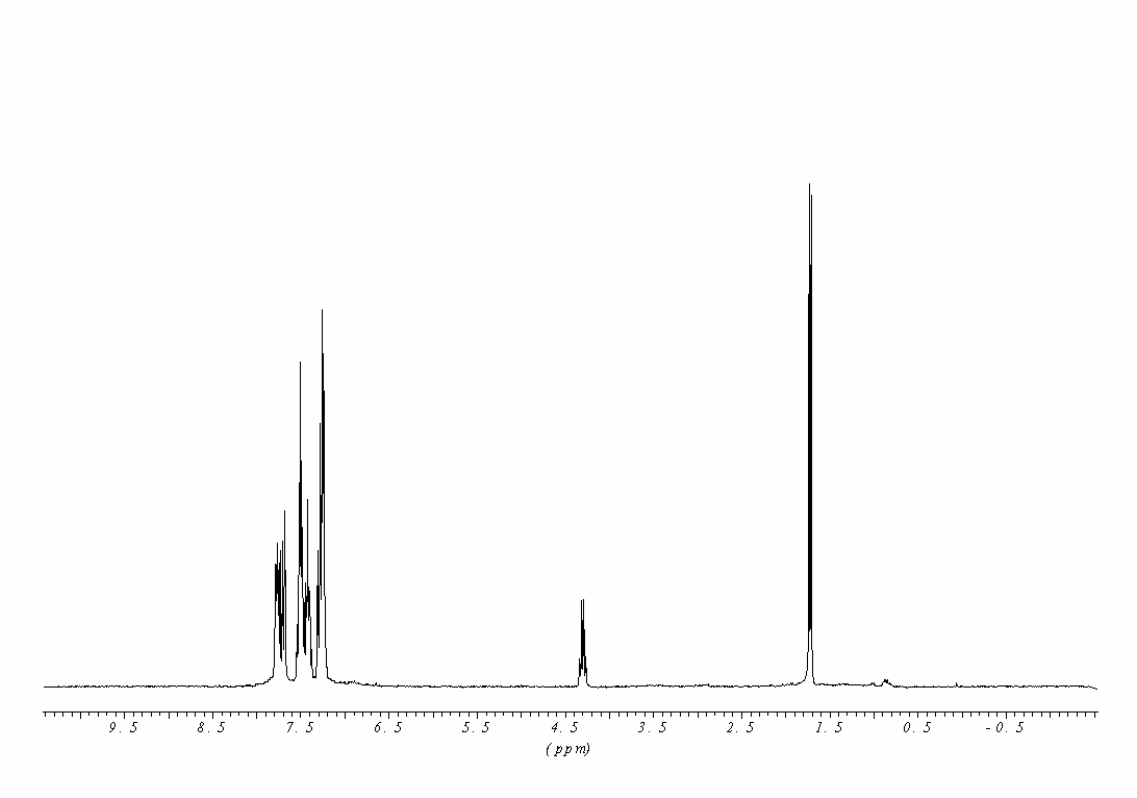
0
(ppm)

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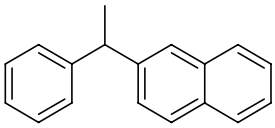
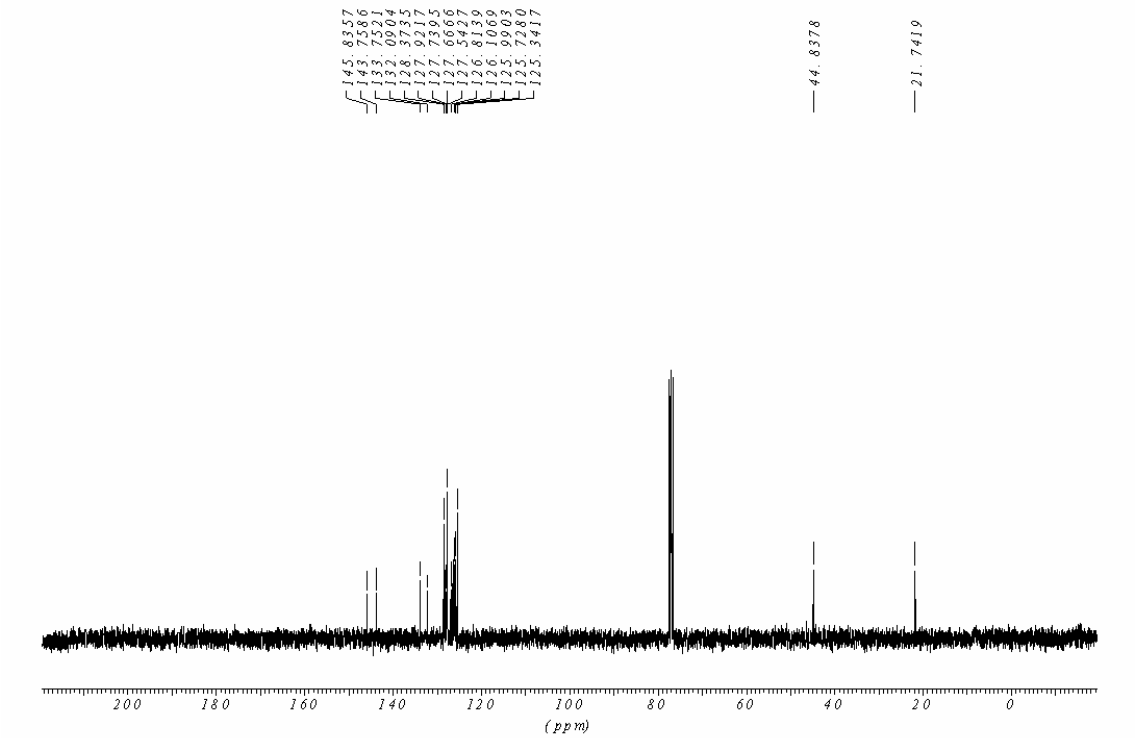
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
(ppm)

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127.9317
127.7395
127.6666
127.5427
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125.9903
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125.3417
44.8378
21.7419
200
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100
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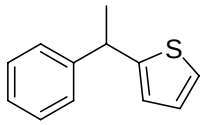
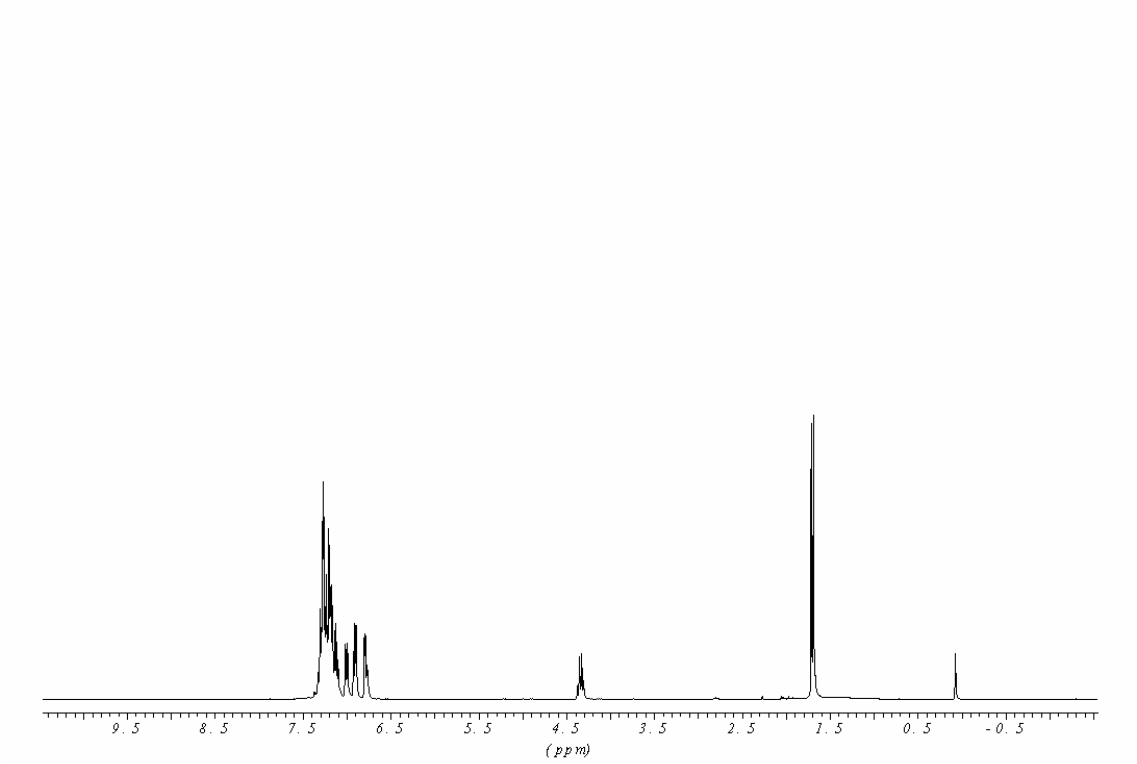
40
20
0
(ppm)


S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8.5
7.5
6.5
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4.5
3.5
2.5
1.5
0.5
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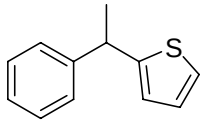
(ppm)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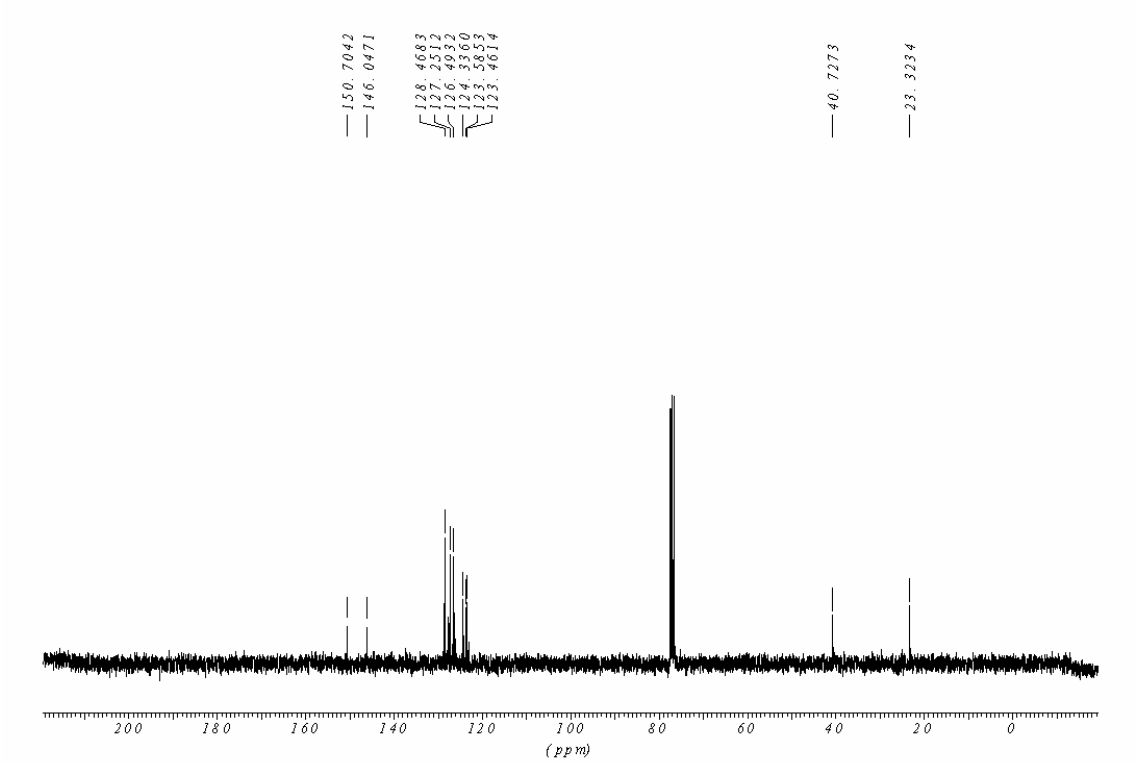
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23.3234
200
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160
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120
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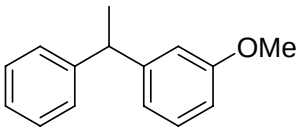
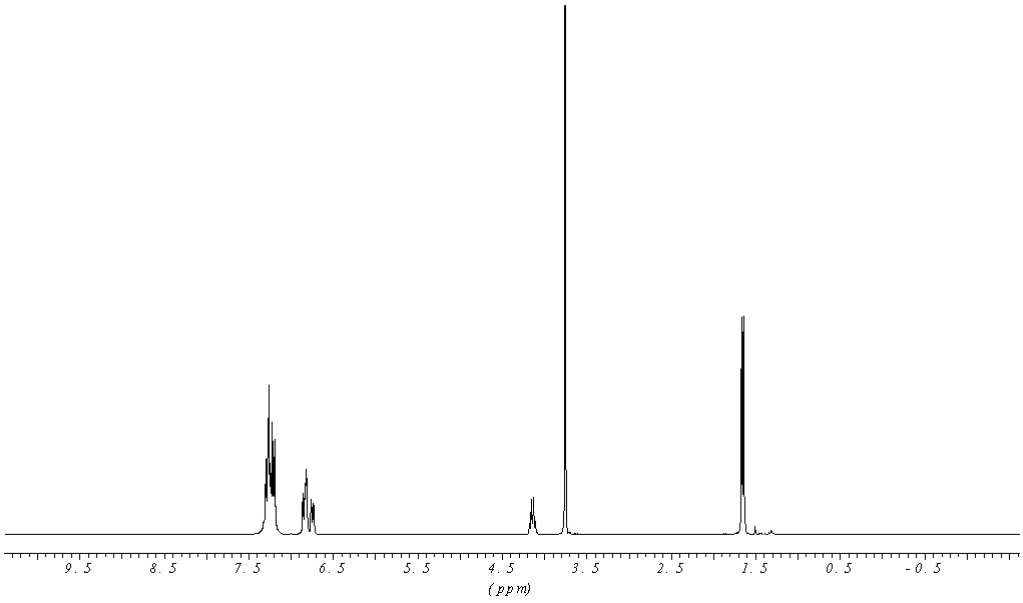
20
0
(ppm)


OMe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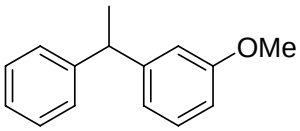
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
(ppm)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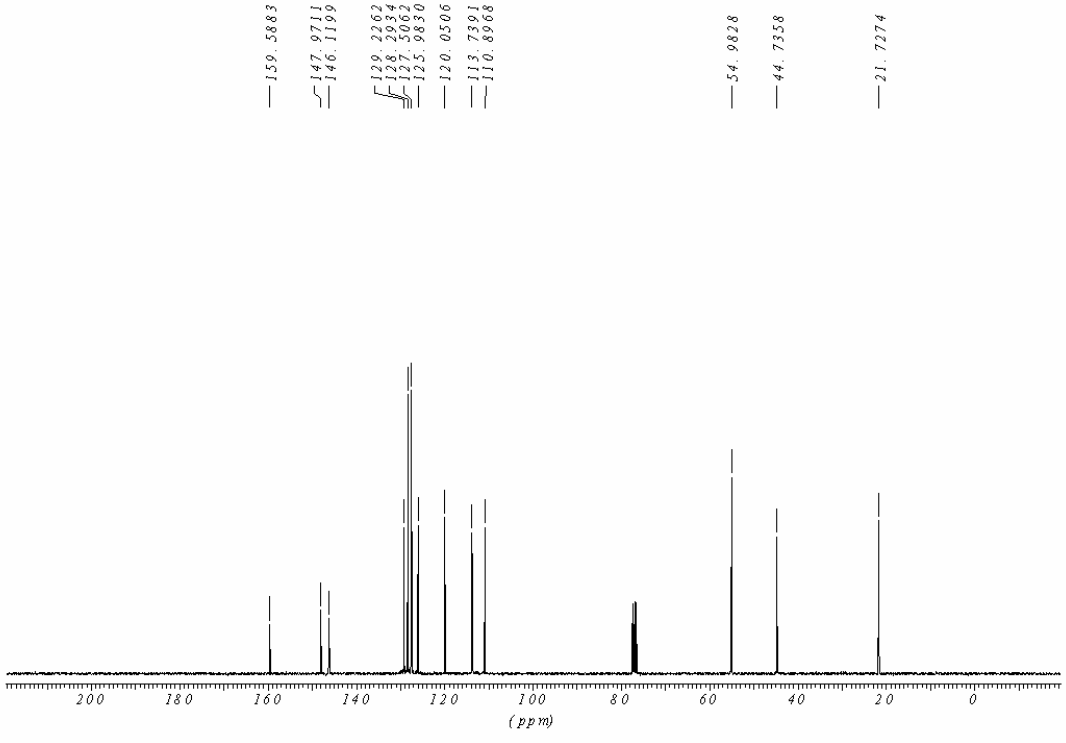
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128.2934
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125.9830
120.0506
113.7391
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54.9828
44.7358
21.7274
200
180
160
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120
100
80
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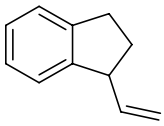
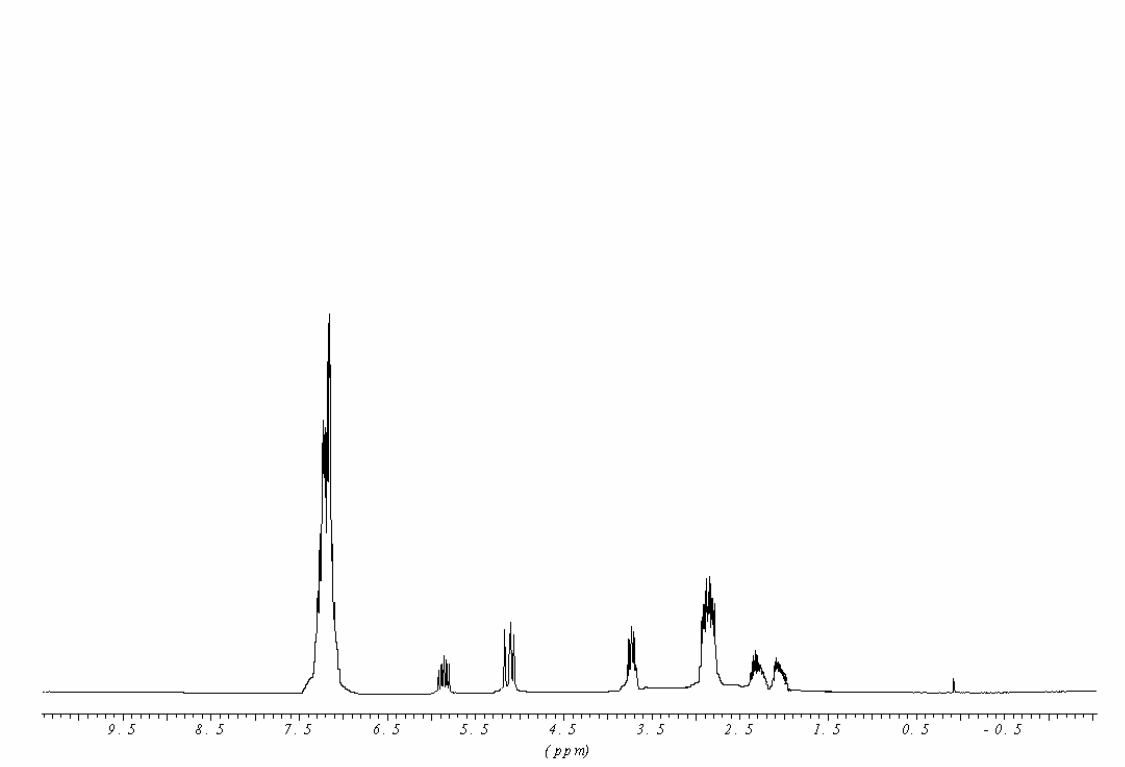
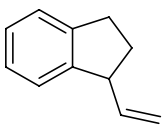
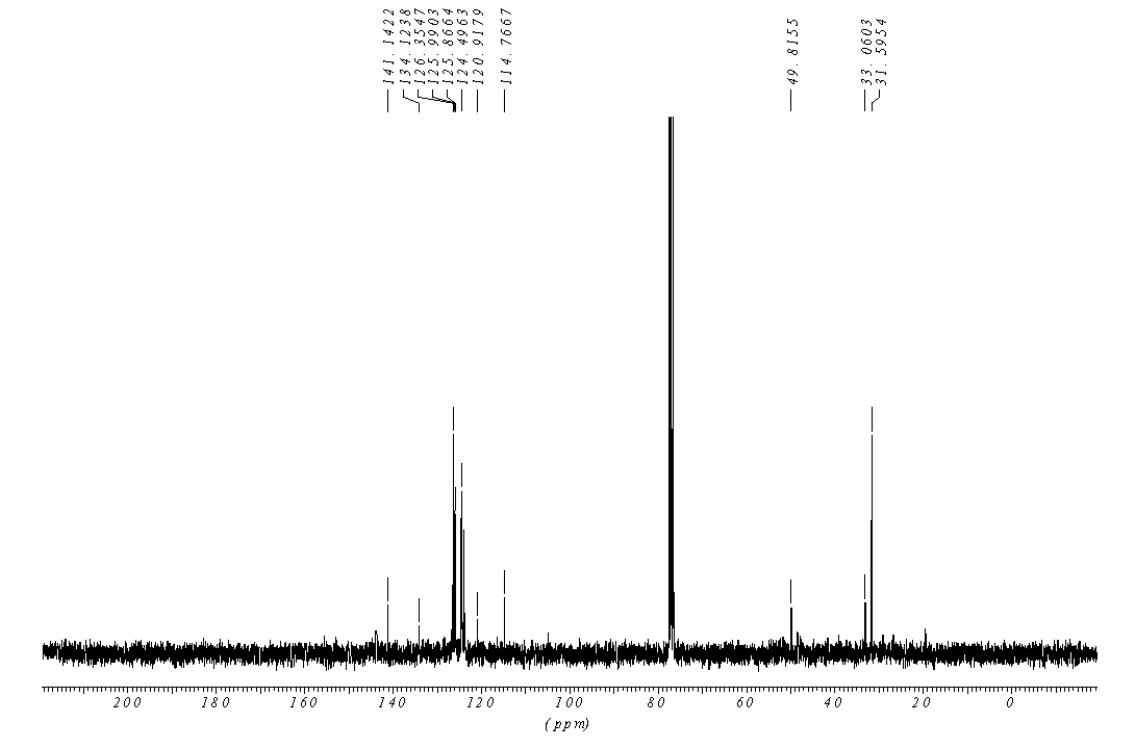
40
20
0
(ppm)




9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
(ppm)

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125.8664
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31.5954
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120
100
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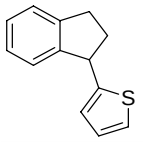
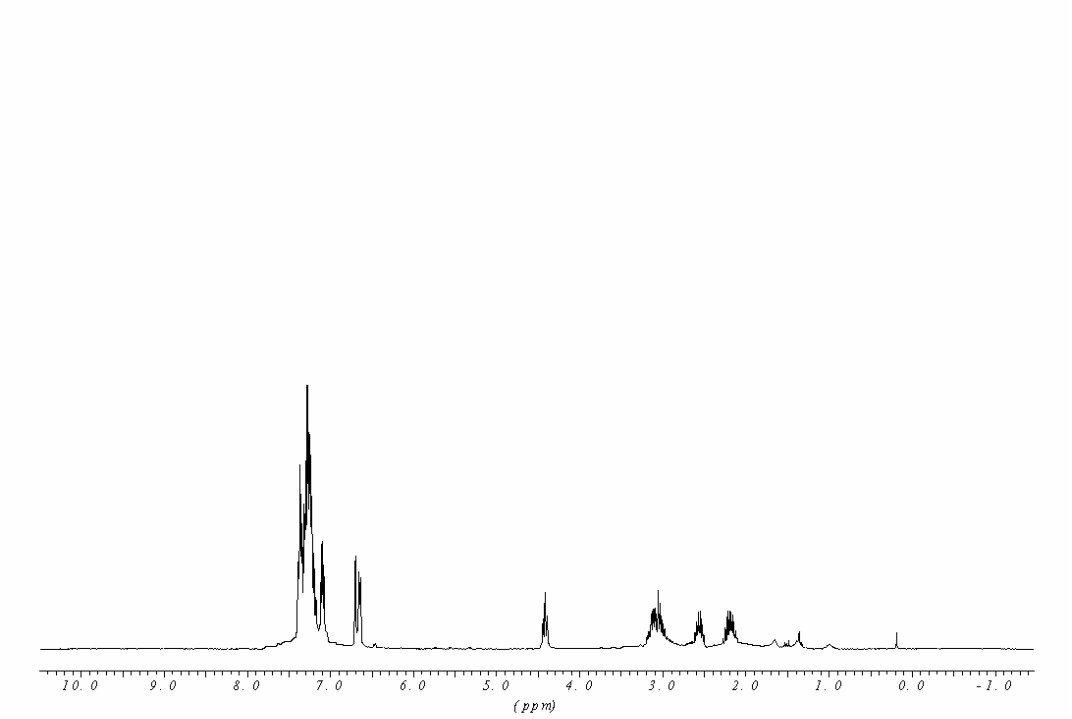
60
40
20
0
(ppm)


S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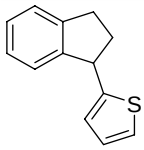
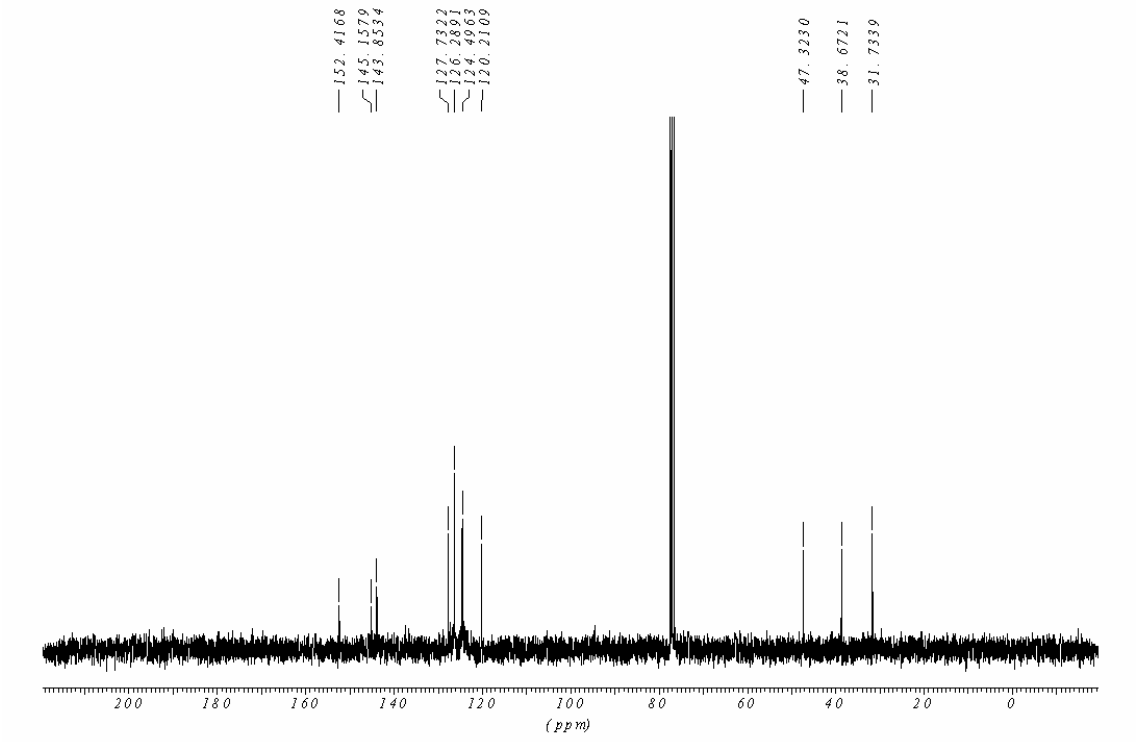
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)


S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124.4963
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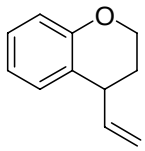
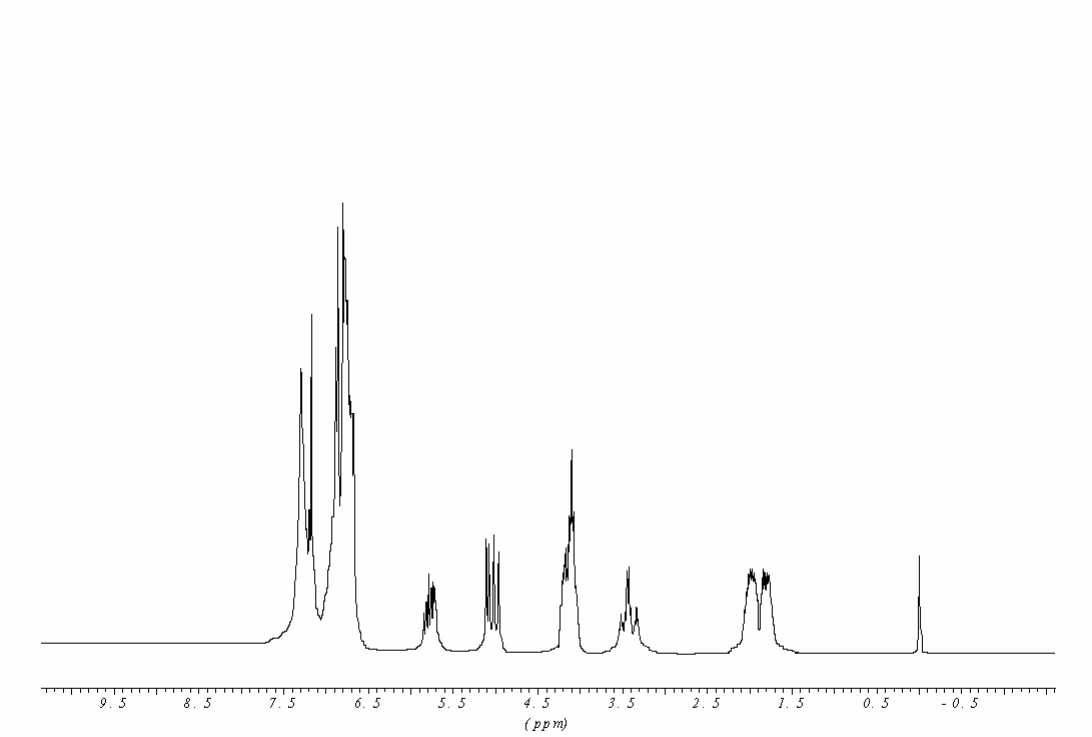
120
100
80
60
40
20
0
(ppm)

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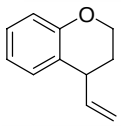
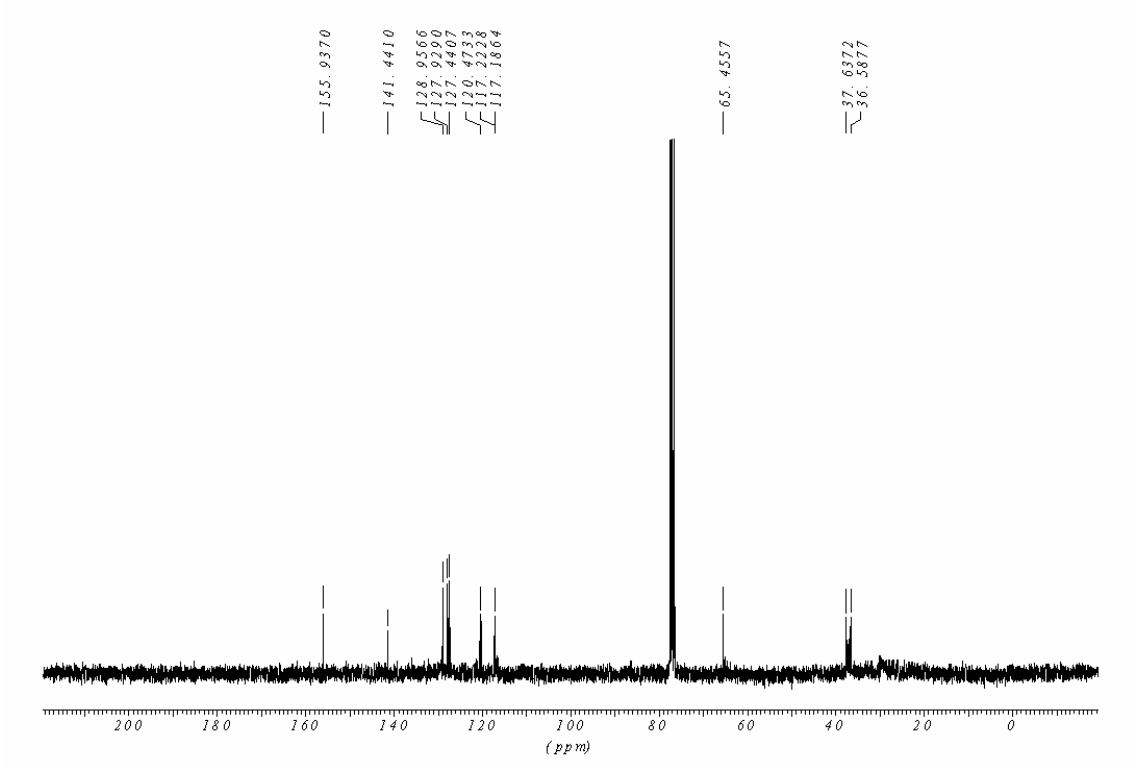
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
(ppm)

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127.9290
127.4407
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117.2228
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36.5877
200
180
160
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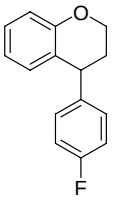
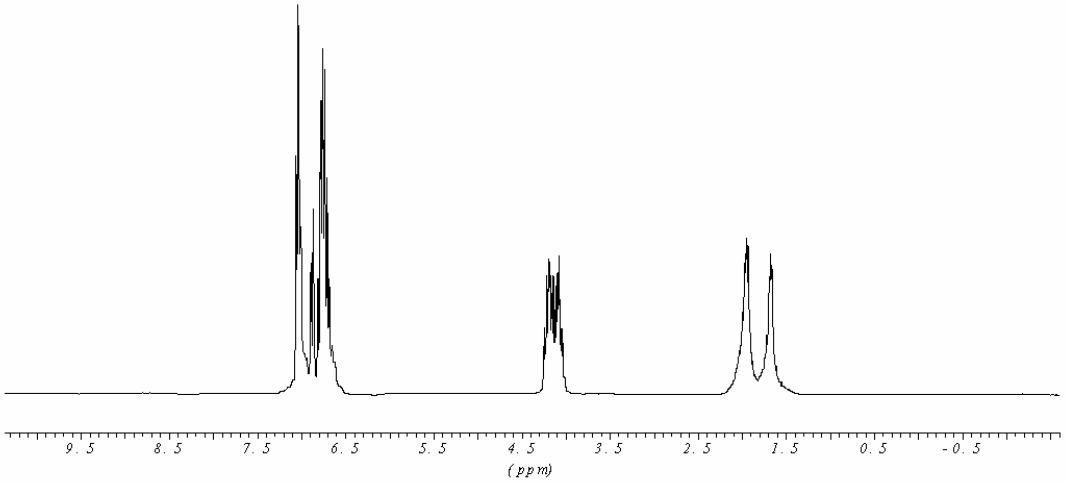
120
100
80
60
40
20
0
(ppm)


O
F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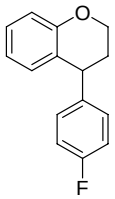
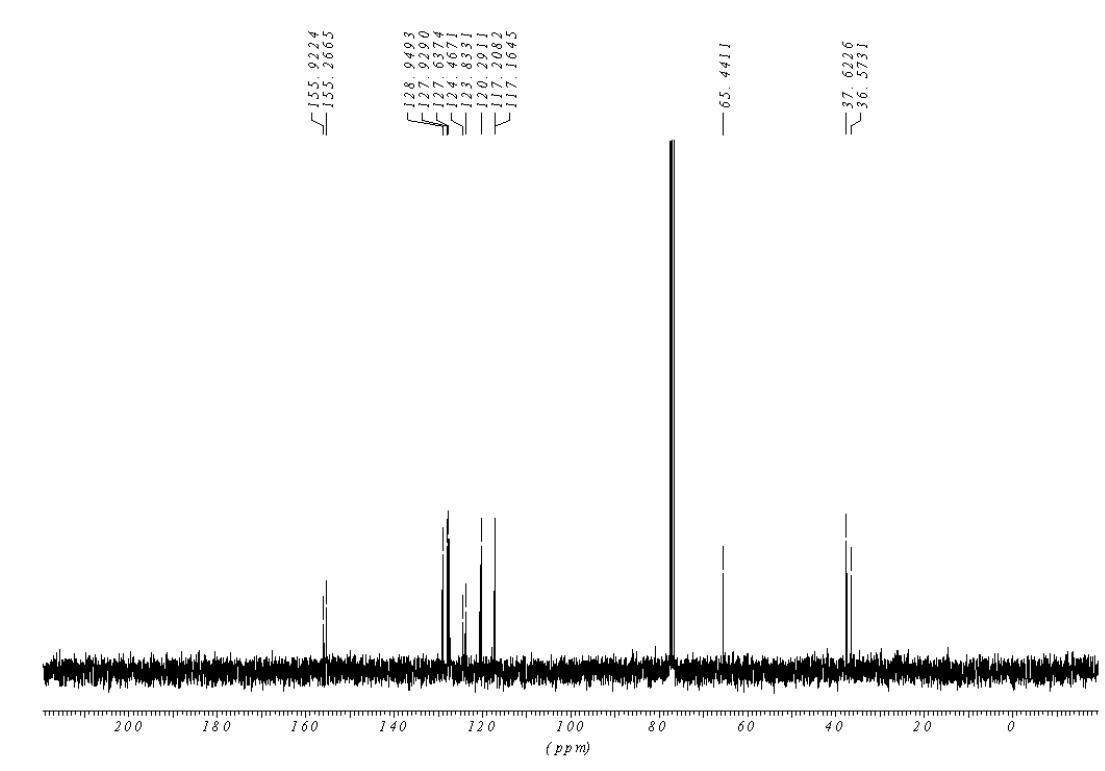
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
(ppm)


O
F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127.9290
127.6374
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123.8331
120.2911
117.2082
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37.6226
36.5731
200
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160
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120
100
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60
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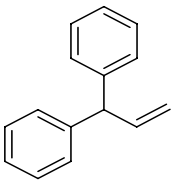
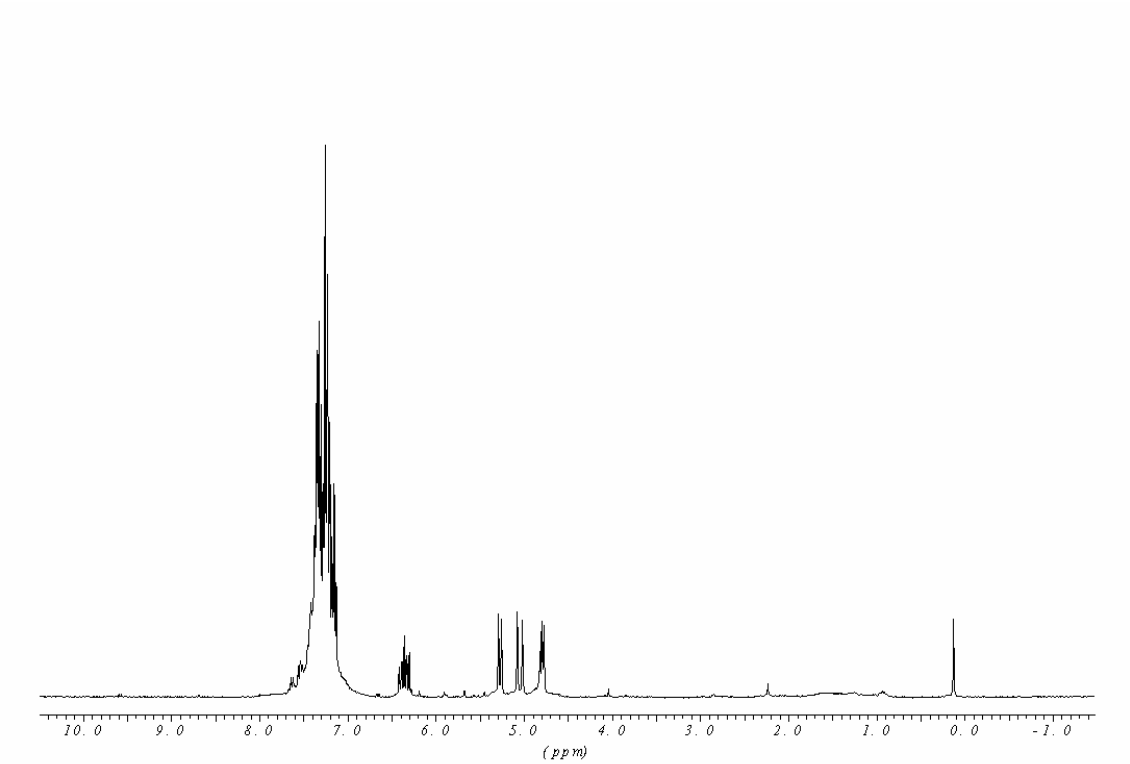
20
0
(ppm)

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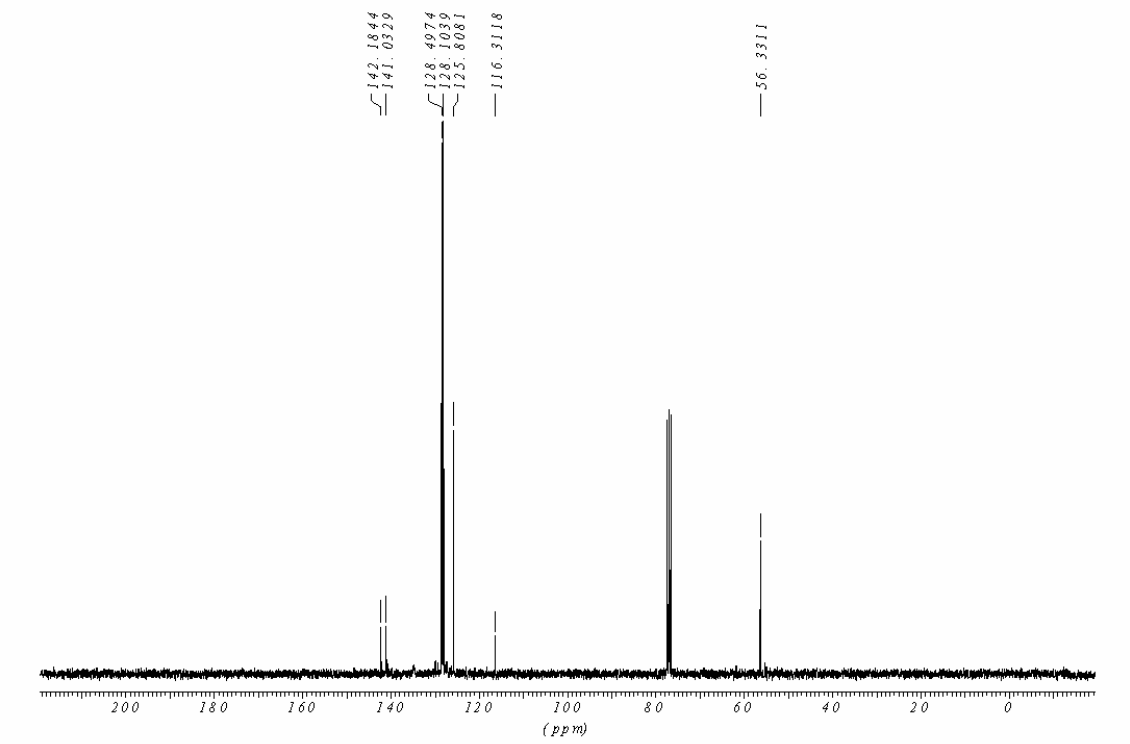
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)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160
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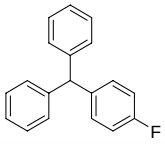
120
100
80
60
40
20
0
(ppm)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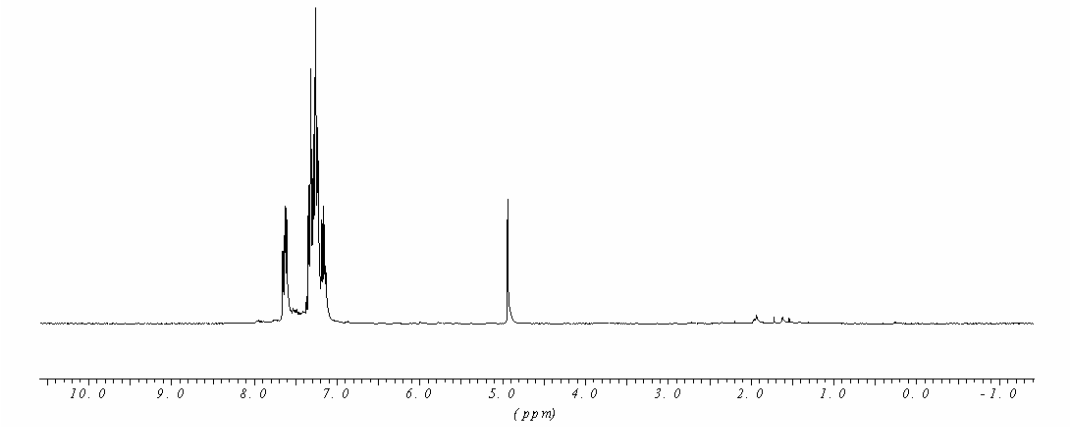
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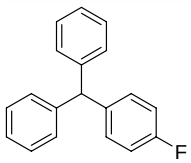
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)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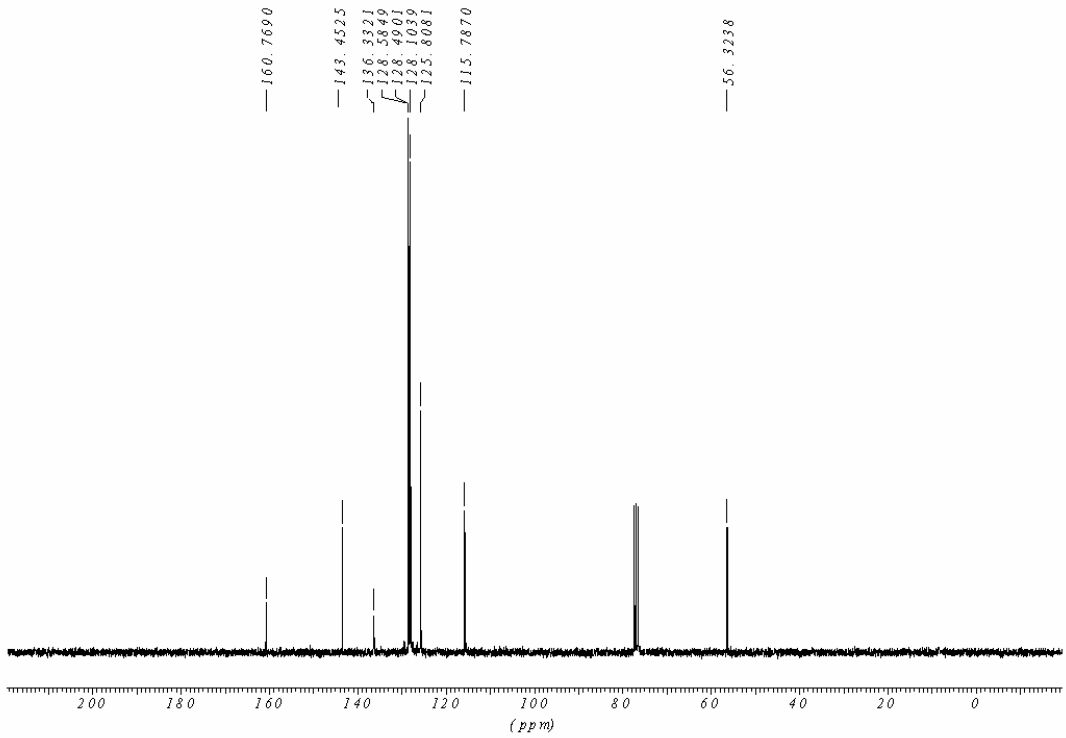
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143.4525
136.3321
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128.4401
128.1039
125.8081
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56.3238
200
180
160
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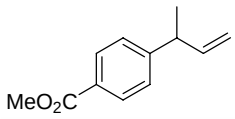
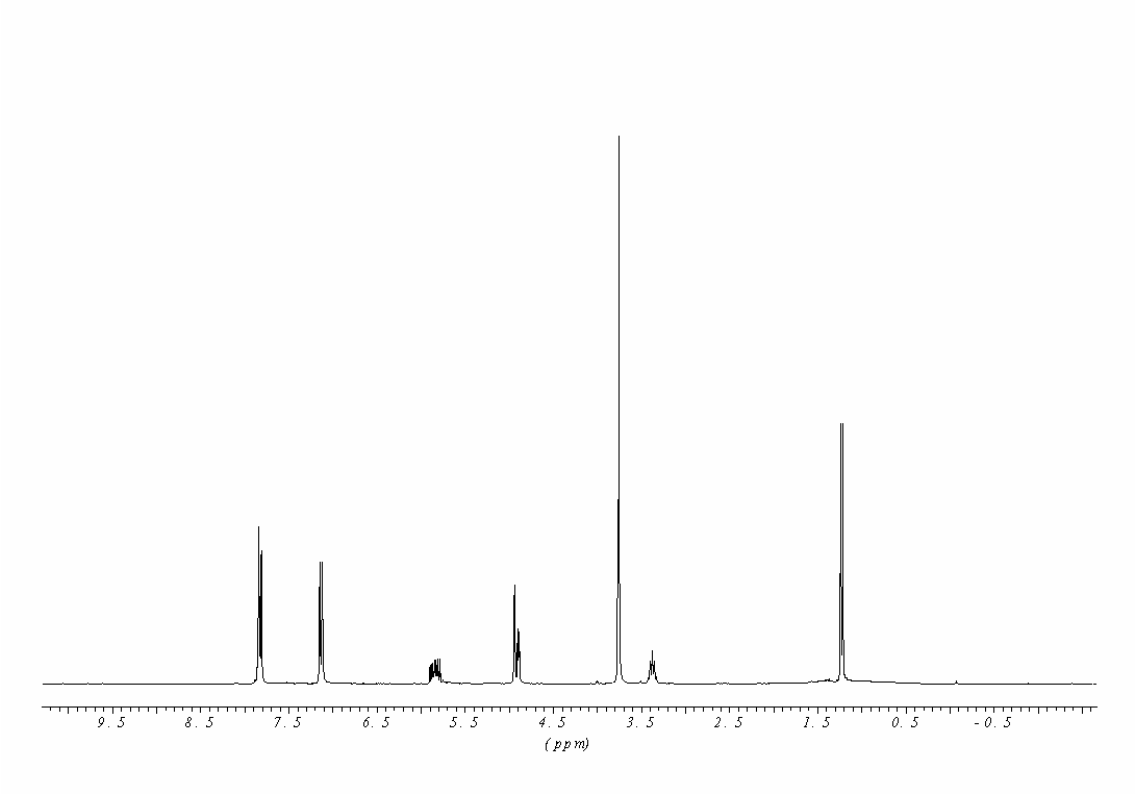
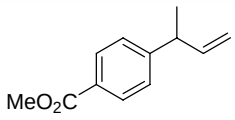
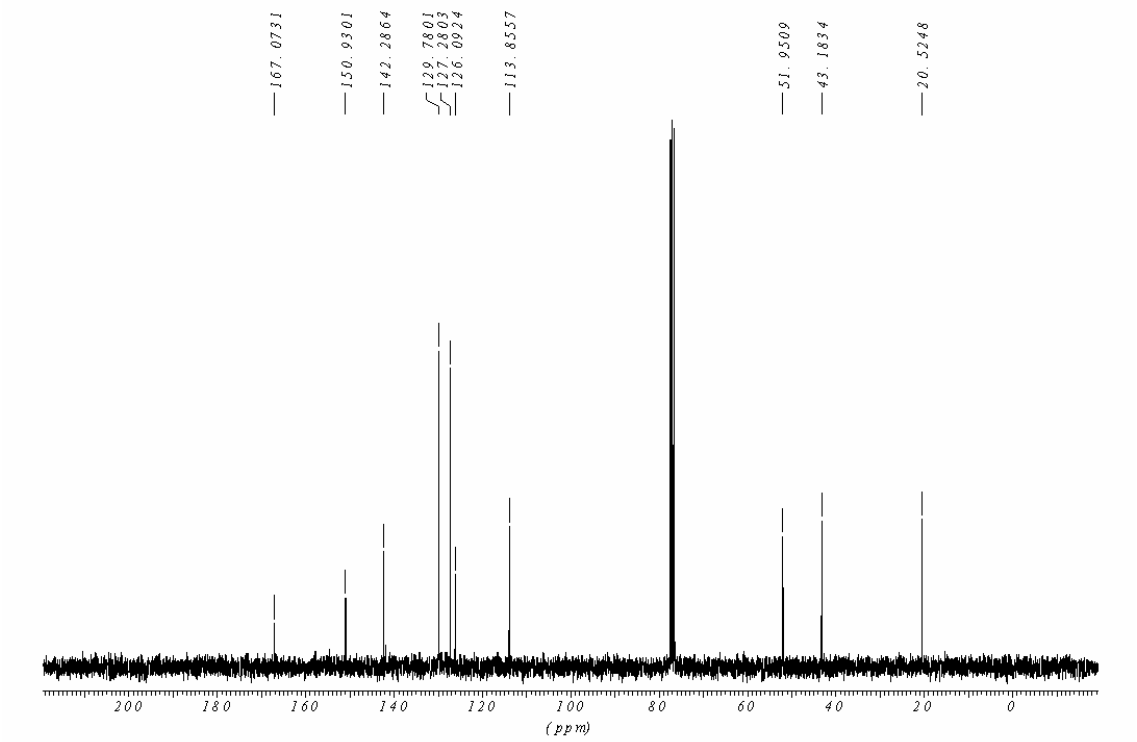
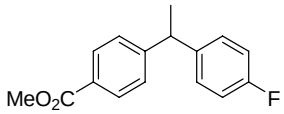
120
100
80
60
40
20
0
(ppm)

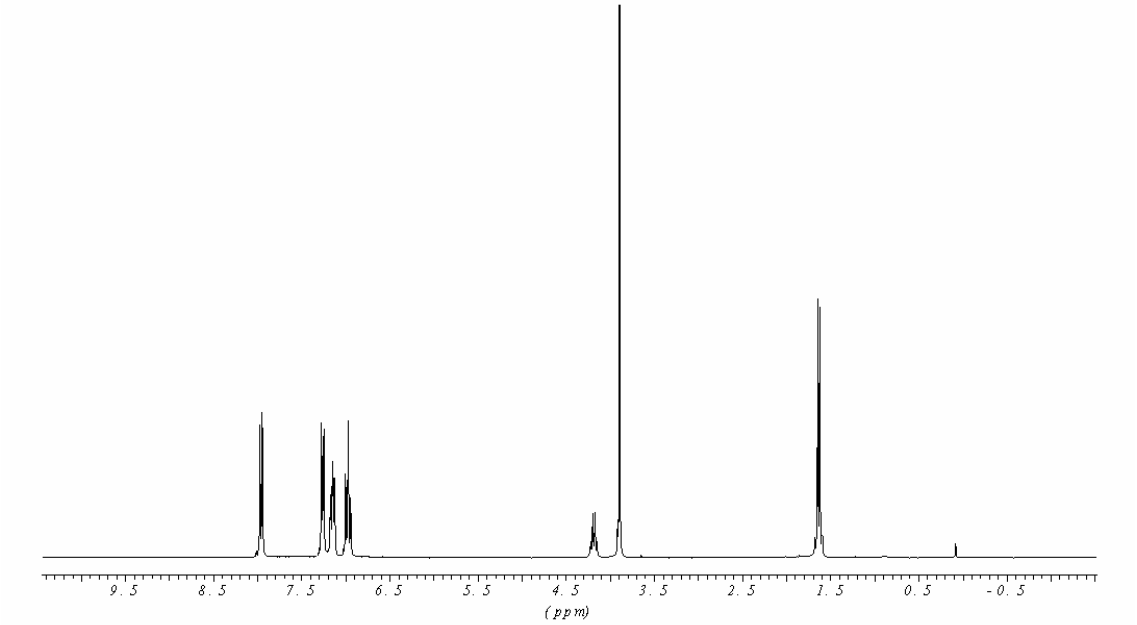

MeO2C

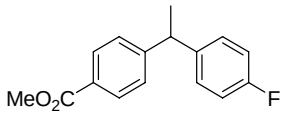

9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
(ppm)


MeO2C


167.0731
150.9301
142.2864
129.7801
127.2803
126.0924
113.8557
51.9509
43.1834
20.5248
200
180
160
140
120
100
80
60
40
20
0
(ppm)


MeO2C
F


9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
(ppm)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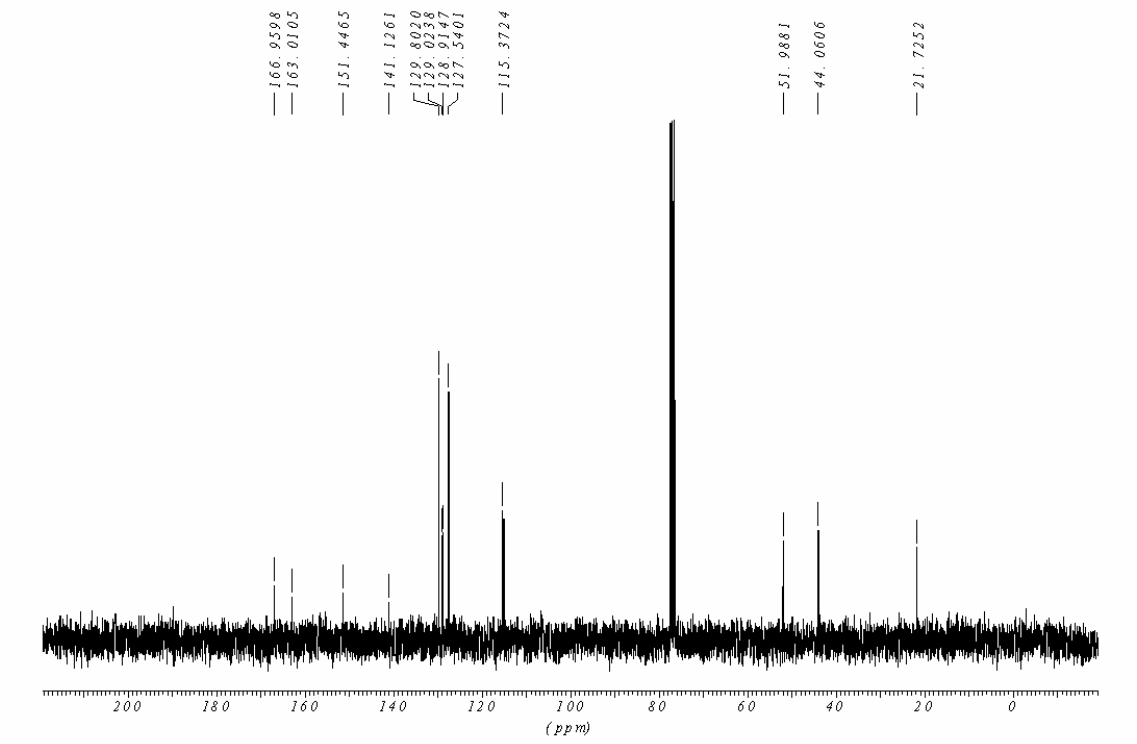
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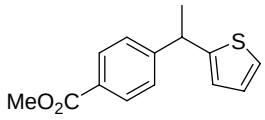
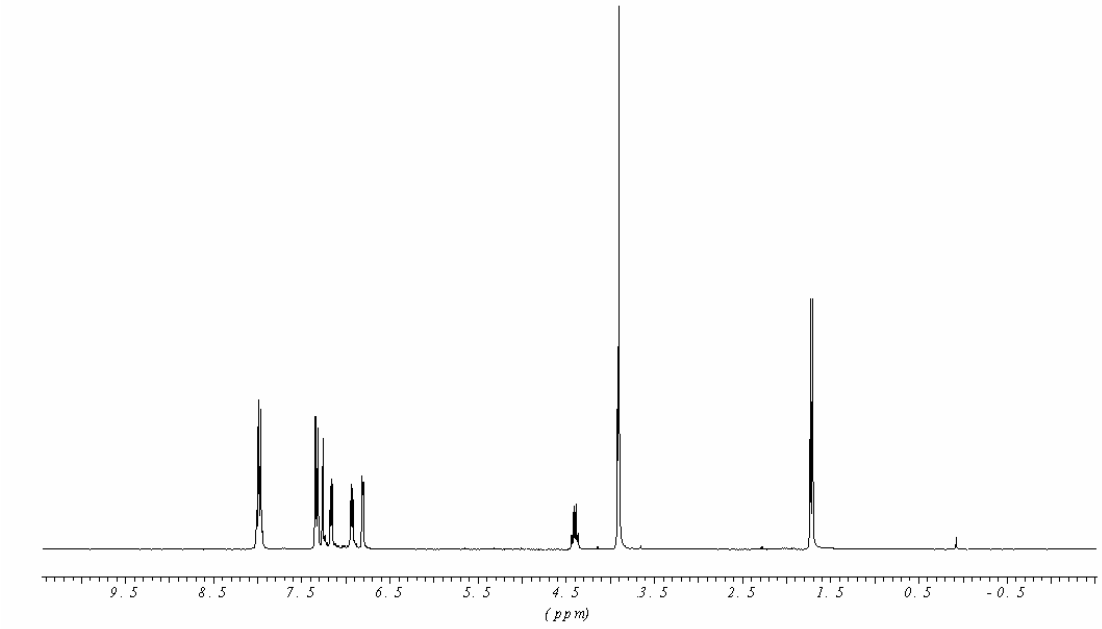
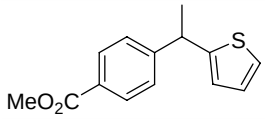
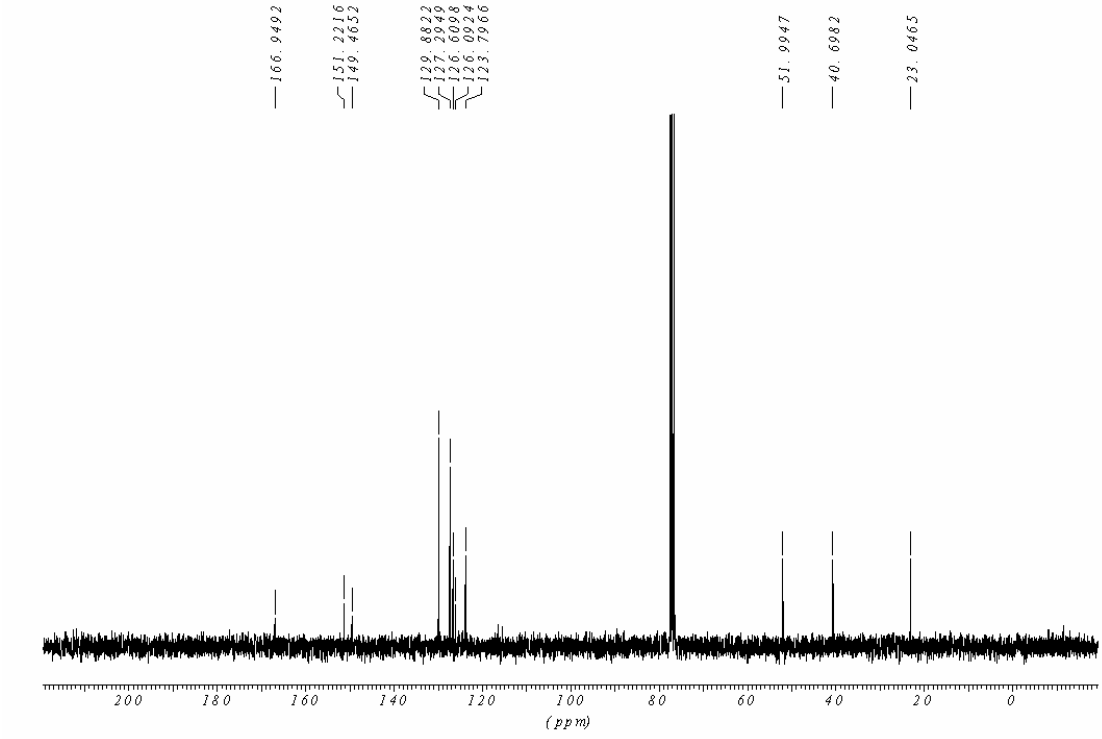
163.0105
151.4465
141.1261
129.8020
129.0238
128.9147
127.5401
115.3724
51.9881
44.0606
21.7252
200
180
160
140
120
100
80
60
40
20
0
(ppm)


S
MeO2C


9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
(ppm)


S
MeO2C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149.4652
129.8822
127.2949
126.6098
126.0924
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51.9947
40.6982
23.0465
200
180
160
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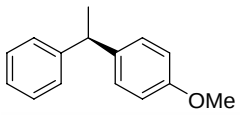
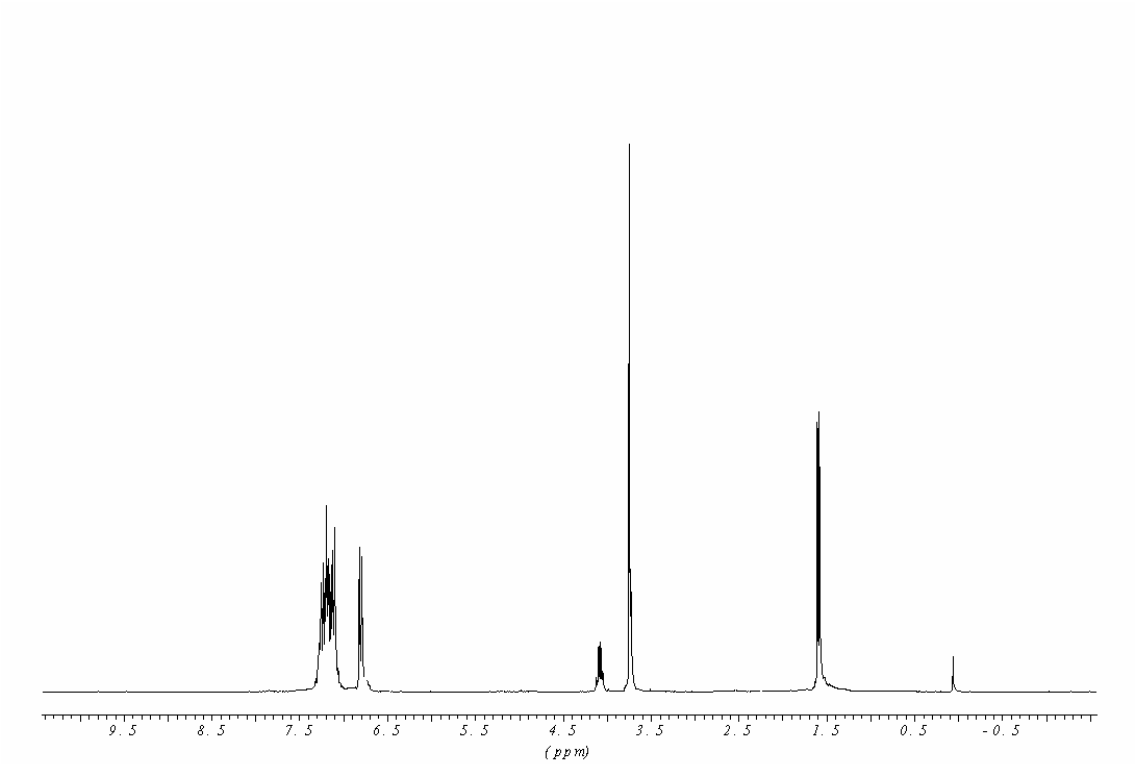
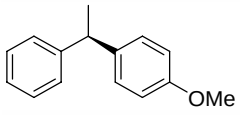
120
100
80
60
40
20
0
(ppm)







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127.5062
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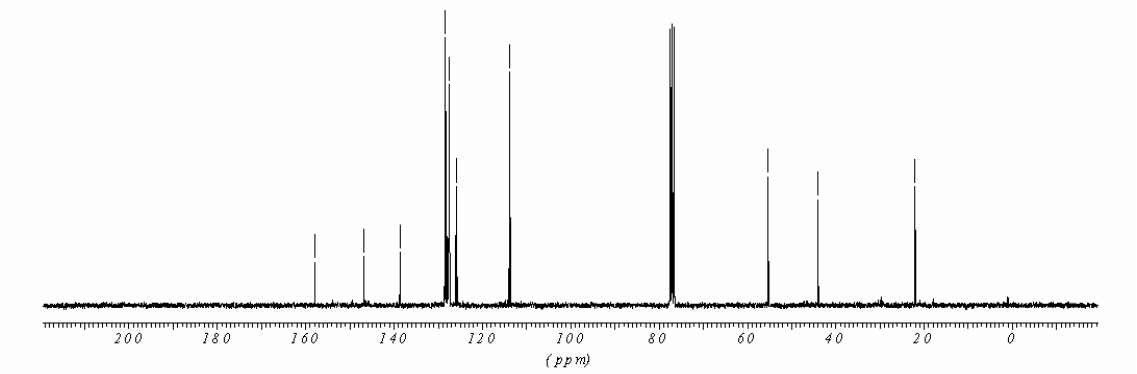
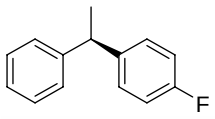
43.9195
22.0335

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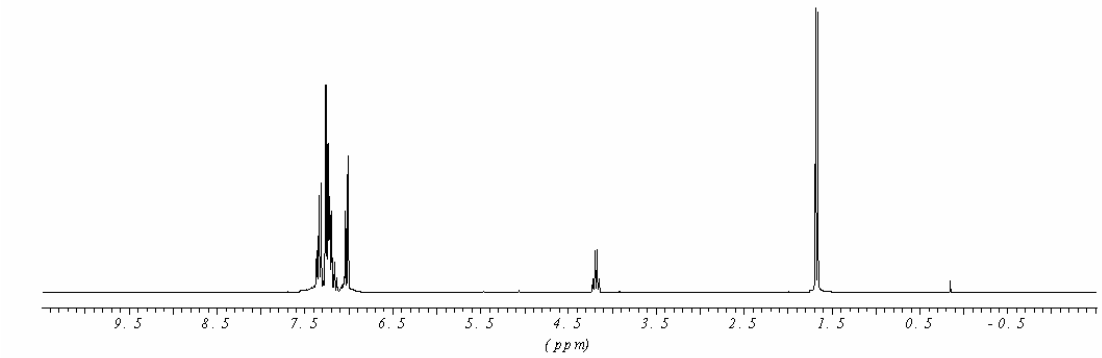
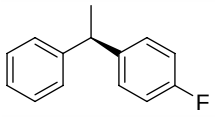
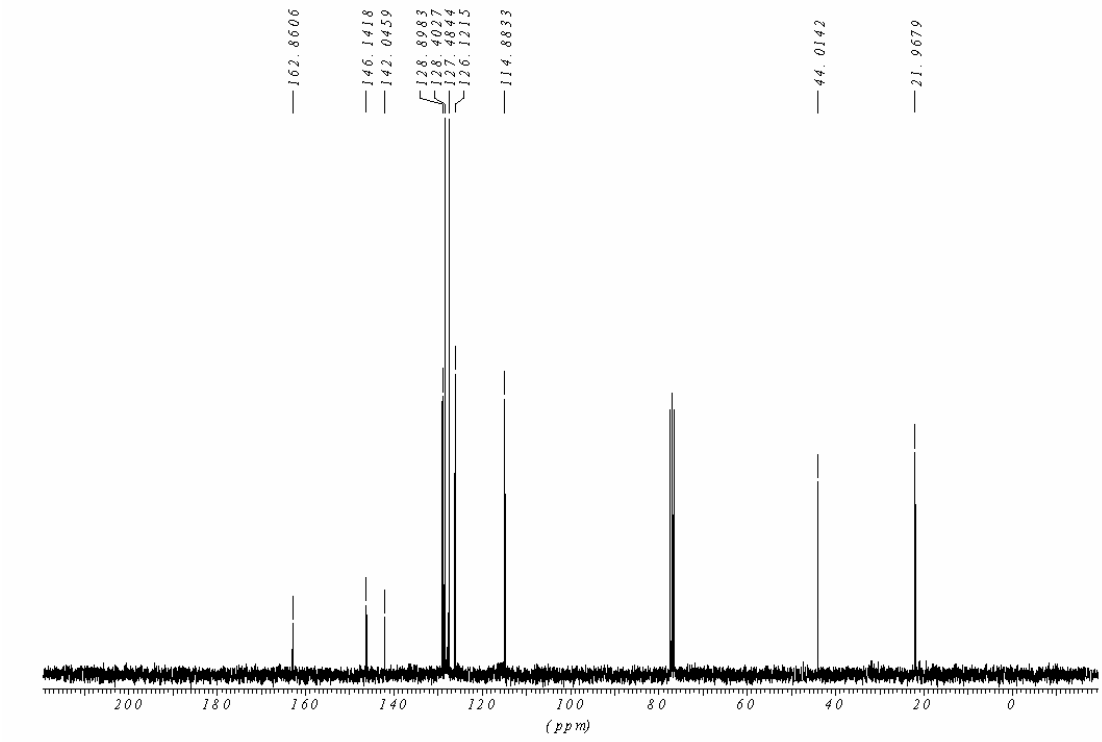

9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
(ppm)


F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21.9679
200
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120
100
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40
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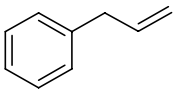
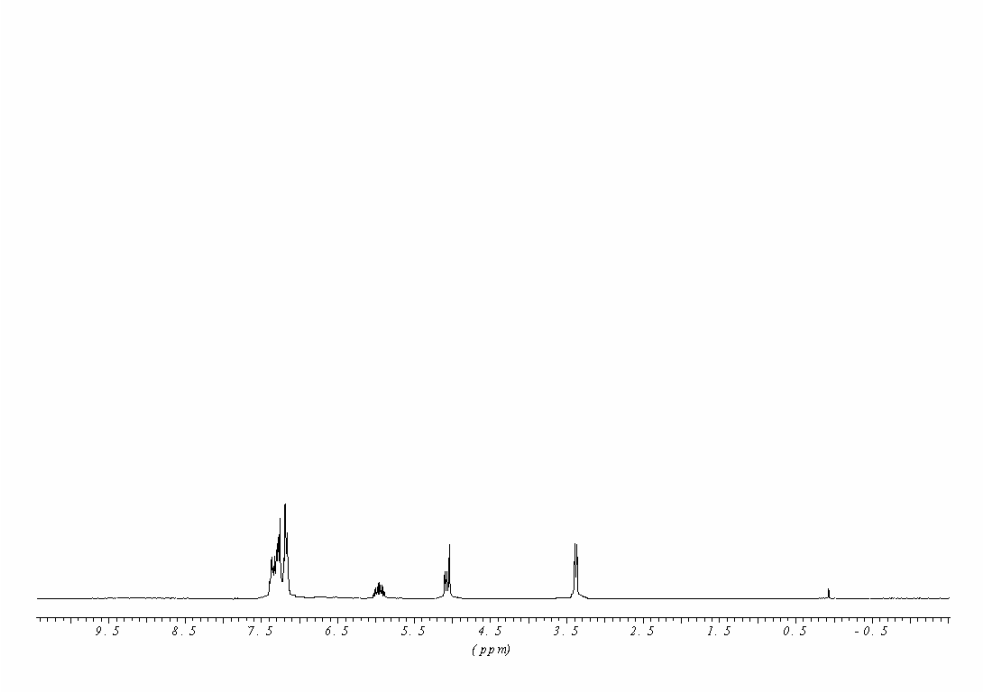
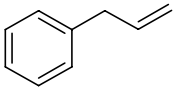
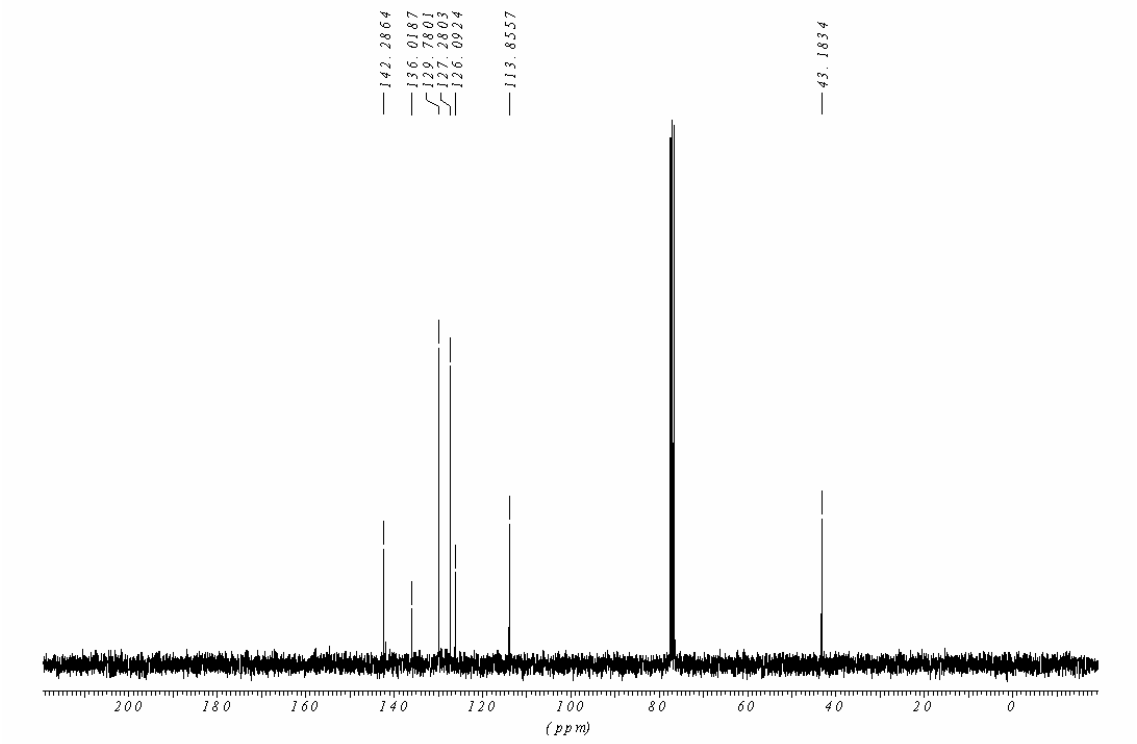
0
(ppm)




9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
(ppm)




142.2864
136.0187
129.7801
127.2803
126.0924
113.8557
43.1834
200
180
160
140
120
100
80
60
40
20
0
(ppm)