Supplementary Information

Nickel-Catalyzed Reductive Allylation of Aryl Halides with Allylic Acetates

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1. Instrumentation and Chemicals

All reagents were reagent grade quality and used as received from Aladdin Co. (China), unless otherwise indicated. All reactions were carried out under an atmosphere of nitrogen unless otherwise indicated. Anhydrous THF and Toluene were distilled from sodium/benzophenone ketyl prior to use. Anhydrous DCM and MeOH were distilled over CaH_2. All other solvents were technical grade unless noted. Anhydrous DMF (Acros), DMA (anhydrous and 99.5% ultrapure, Acros), NiCl2 (Alfa Aesar), NiBr2 (Alfa Aesar), NiI2 (anhydrous, Alfa Aesar), Ni(COD)2 (Aldrich), zinc power (Aldrich), anhydrous MgCl2 (Alfa Aesar), **1a**, **1b**, **1c, 4a, 4b, 4c** (Aldrich) were purchased, **6**[1], **8**[2] were synthesized according to the literature procedures. All HPLC solvents were obtained from Aldrich.

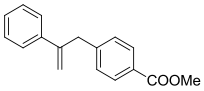
Column chromatography was performed using silica gel 300-400 mesh (purchased from QingdaoHaiyang Co. China) as the solid support. All NMR spectra were recorded on Bruker Avance 500 MHz spectrometer at STP unless otherwise indicated. 1H NMR and 13C NMR chemical shifts are reported in δ units, parts per million (ppm) relative to the chemical shift of residual solvent. Deuterated solvents were used as received from Cambridge Isotope Laboratories, Inc. NMR chemical shifts are reported in units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in ^{1}H NMR and 13C NMR spectra were set at 7.26 ppm and 77.36 ppm, respectively. High-resolution mass spectra (HRMS) were obtained using a Bruker APEXIII 7.0 and IonSpec 4.7 TESLA FTMS. IR data were obtained using an AVATAR370. HPLC spectra were obtained using a SHIMADZU, LC-2010AHT and chromatographic column (CHIRALPAK. AD-H, Lot No. ADHOCE-OB110; DAICEL CHEMICAL INDUSTRIES, LTD.).

2. Reductive Coupling of Aryl Halides with Allylic Acetates

General Procedure for Reductive Coupling of Aryl Halides with Allylic Acetates: To a flame-dried Schlenk tube equipped with a magnetic stir bar was loaded alkyl bromide (0.15 mmol, 100 mol%), followed by addition of 4-chloro-2-(4,5-dihydro-1H-imidazol-2-yl)pyridine (**3a**) (2.7 mg, 0.015 mmol, 10 mol%), zinc powder (19.6 mg, 0.3 mmol, 200 mol%) and Bu_4NBr (48.4 mg, 0.15 mmol, 100 mol%). The tube was moved into a dry glove box, at which point NiI_2 (4.7 mg, 0.015 mmol, 10 mol%) and $MgCl_2$ (14.3 mg, 0.15 mmol, 100 mol%) were added. The tube was

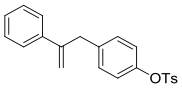
capped with a rubber septum, and it was moved out of the glove box. Allylic Acetates (0.3 mmol, 200 mol%), pyridine (11.9 mg, 0.15 mmol, 100 mol%) and DMA (1.0 mL) were then added via syringe. After the reaction mixture was allowed to stir for 12 h under N_2 atmosphere at 60 ℃, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography (SiO_2: ethyl acetate in petroleum ether) provided the coupling product.

3. *Spectral Data of New Compounds*



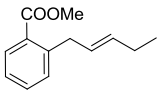
methyl 4-(2-phenylallyl)benzoate(24).

Colorless oil. Yield: 94% (36 mg); purification by column chromatography (SiO2: 5% ethyl acetate in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.40 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.34 – 7.20 (m, 5H), 5.52 (d, *J* = 0.7 Hz, 1H), 5.05 (d, *J* = 1.2 Hz, 1H), 3.89 (s, 5H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.44, 146.53, 145.40, 140.70, 130.05, 129.27, 128.67, 128.49, 127.97, 126.45, 115.43, 52.33, 42.04; IR (KBr) ν 3419.32, 2920.47, 2850.45, 1721.06, 1610.93, 1434.87, 1280.96, 1109.55, 1020.50, 900.37, 779.05, 702.78； HRMS (ESI) calcd. For $C_{17}H_{16}O_2$ [MH+]: 252.1150; Found: 252.1145.



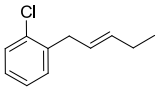
4-(2-phenylallyl)phenyl 4-methylbenzenesulfonate(30).

Colorless oil. Yield: 82% (45 mg); purification by column chromatography (SiO2: 5% ethyl acetate in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.38 (s, 2H), 7.28 (ddd, *J* = 21.7, 19.4, 17.2 Hz, 6H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.48 (s, 1H), 4.99 (s, 1H), 3.79 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 148.31, 146.81, 145.54, 140.73, 138.89, 132.73, 130.31, 129.99, 128.86, 128.62, 127.93, 126.44, 122.57, 115.20, 41.33, 22.05; IR (KBr) ν 3438.25, 3094.26, 3049.14, 2920.33, 2850.68, 1629.01, 1597.13, 1499.65, 1368.69, 1197.10, 1197.10, 1176..06, 1152.41, 1093.29, 910.82, 857.59, 814.59, 777.38, 706.89, 660.95, 576.13, 552.51; HRMS (ESI) calcd. For $C_{22}H_{20}O_3S$ [MH+]: 364.1133; Found: 364.1130.



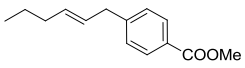
(E)-methyl 2-(pent-2-en-1-yl)benzoate(27).

Colorless oil. Yield: 89% (27 mg); purification by column chromatography (SiO2: 5% ethyl acetate in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.43 (td, *J* = 7.6, 1.3 Hz, 1H), 7.31 – 7.20 (m, 2H), 5.63 – 5.45 (m, 2H), 3.89 (s, 3H), 3.68 (d, *J* = 6.2 Hz, 2H), 2.07 – 1.96 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.60, 142.84, 133.86, 132.25, 131.05, 130.74, 130.09, 127.94, 126.27, 52.24, 37.56, 25.92, 14.14; IR (KBr) ν 3026.73, 2961.92, 2930.78, 2873.30, 2850.16, 1724.50, 1448.52, 1264.22, 1079.62, 968.73, 750.45; HRMS (ESI) calcd. For $C_{13}H_{16}O_2$ [MH+]: 204.1150; Found: 204.1148.



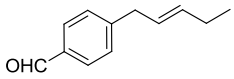
(E)-1-chloro-2-(pent-2-en-1-yl)benzene(28).

Colorless oil. Yield: 91% (35 mg); purification by column chromatography (SiO2: 2% ethyl acetate in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.18 (dqd, *J* = 27.4, 7.5, 1.8 Hz, 3H), 5.59 – 5.53 (m, 2H), 3.44 (d, *J* = 2.8 Hz, 2H), 2.10 – 1.94 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 139.08, 134.72, 134.30, 130.60, 129.70, 127.66, 127.09, 126.09, 36.80, 25.91, 14.08; IR (KBr) ν 3065.34, 3027.21, 2963.60, 2931.12, 2873.04, 2848.68, 1473.05, 1441.95, 1051.04, 1037.64, 967.98, 749.40, 680.10; HRMS (ESI) calcd. For $C_{11}H_{13}Cl$ [MH+]: 180.0706; Found: 180.0705.



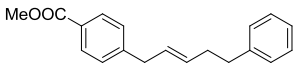
(E)-methyl 4-(hex-2-en-1-yl)benzoate(21).

Colorless oil. Yield: 85% (28 mg); purification by column chromatography (SiO2: 5% ethyl acetate in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 5.60 – 5.47 (m, 2H), 3.90 (s, 3H), 3.38 (d, *J* = 5.0 Hz, 2H), 2.01 (dd, *J* = 13.5, 6.4 Hz, 2H), 1.40 (dd, *J* = 14.7, 7.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.19, 146.67, 132.77, 129.71, 128.51, 127.89, 51.98, 39.05, 34.59, 22.54, 13.67; IR (KBr) ν 2956.20, 2926.22, 2852.64, 1724.40, 1611.03, 1435.30, 1280.02, 1192.28, 1110.64, 1020.51, 968.73, 750.45; HRMS (ESI) calcd. For $C_{14}H_{18}O_2$ [MH+]: 218.1307; Found: 218.1305.



(E)-4-(pent-2-en-1-yl)benzaldehyde(26).

Colorless oil. Yield: 80% (21 mg); purification by column chromatography (SiO2: 5% ethyl acetate in petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.64 – 5.42 (m, 2H), 3.40 (d, *J* = 6.1 Hz, 2H), 2.11 – 1.99 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 192.38, 148.94, 135.12, 134.92, 130.30, 129.50, 126.73, 39.51, 25.87, 14.05; IR (KBr) ν 3449.48, 2960.11, 2921.40, 2850.47, 2730.68, 1704.41, 1606.06, 1461.29, 1305.27, 1211.84, 1167.77, 968.52, 849.59, 829.88; HRMS (ESI) calcd. For $C_{12}H_{14}O$ [MH+]: 174.1045; Found: 174.1047.



(E)-methyl 4-(5-phenylpent-2-en-1-yl)benzoate(18).

Colorless oil. Yield: 87% (37 mg); purification by column chromatography (SiO2: 5% ethyl acetate in petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.19 (dd, *J* = 14.5, 7.7 Hz, 5H), 5.56 (t, *J* = 3.7 Hz, 2H), 3.91 (s, 3H), 3.37 (d, *J* = 3.5 Hz, 2H), 2.76 – 2.67 (m, 2H), 2.38 (dd, *J* = 11.0, 7.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.49, 146.70, 142.13, 132.20, 130.02, 128.86, 128.62, 128.23, 126.13, 52.32, 39.27, 36.12, 34.59; IR (KBr) ν 3415.75, 3027.09, 2924.28, 2852.25, 1721.67, 1609.90, 1435.14, 1280.74, 1109.89, 968.80, 758.55, 699.94; HRMS (ESI) calcd. For $C_{19}H_{20}O_2$ [MH+]: 280.1463; Found: 280.1464.

4. Synthesis the Key Ligand 3a.

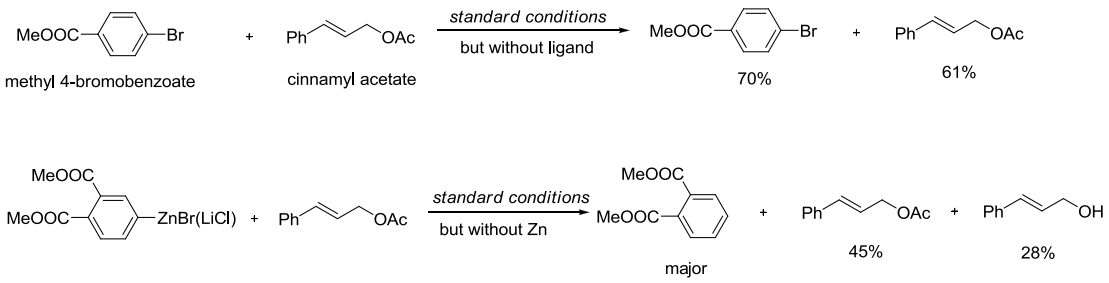
4-Chloro-2-(4,5-dihydro-1H-imidazol-2-yl)pyridine(3a). Following the literature procedures,[3] sodium methoxide (7.8 mg, 0.144 mmol, 10 mol %) was added to a solution of 4-chloropicolinonitrile (200 mg, 1.44 mmol, 100 mol %) in methanol (1.5 mL). After the reaction mixture was allowed to stir for 15 h under N_2 atmosphere at 25 ℃, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography (SiO_2: 30% ethyl acetate in hexanes) provided methyl 4-chloropicolinimidate as a colorless oil (209 mg, 1.22 mmol, 85% yield).

Ethylene diamine (0.15 mL, 2.32 mmol, 493 mol %) was added to a mixture of methyl 4-chloropicolinimidate (80mg, 0.47 mmol, 100 mol %) in MeOH (1.5 mL). The reaction mixture

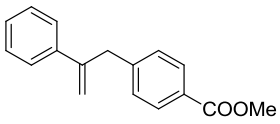
was allowed to stir for 20 h under N_2 atmosphere at 50 ℃. The solution was cooled to room temperature and quenched with H_2O (5 mL) and diluted with CH_2Cl_2 (5 mL). The layers were separated and the aqueous layer was extracted with DCM (2 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure to provided **3a** as a light yellow solid (68 mg, 0.376 mmol, 80% yield).

White solid, M.p. = 77-78 ℃; ^{1}H NMR (500 MHz, DMSO): δ 8.60 (dd, *J* = 5.5, 0.5 Hz, 1H), 8.03 (d, *J* = 2.2 Hz, 1H), 7.65 (dd, *J* = 5.5, 2.2 Hz, 1H), 7.05 (s, 1H), 3.64 (s, 4H). 13C NMR (125 MHz, DMSO): δ 162.7, 150.4, 150.4, 143.3, 125.2, 121.9. IR (KBr) ν 3404.41, 3366.61, 3129.82, 3102.11, 3042.73, 2994.41, 2953.90, 2867.58, 2477.48, 1940.50, 1817.74, 1775.85, 1696.72, 1614.94, 1579.14, 1553.27, 1495.55, 1472.91, 1456.77, 1384.40, 1321.03, 1287.14, 1275.96, 1236.91, 1183.14, 1136.25, 1083.26, 1025.92, 979.23, 890.57, 848.65, 766.33, 689.71, 610.56, 532.32; MS (EI) m/z (M+) calcd for $C_8H_8ClN_3$: 181, found: 181.

5. Examination of in situ organozinc formation.



6. ^{1}H and ^{13}C NMR Spectra of Reductive Coupling Products & Ligand 3a



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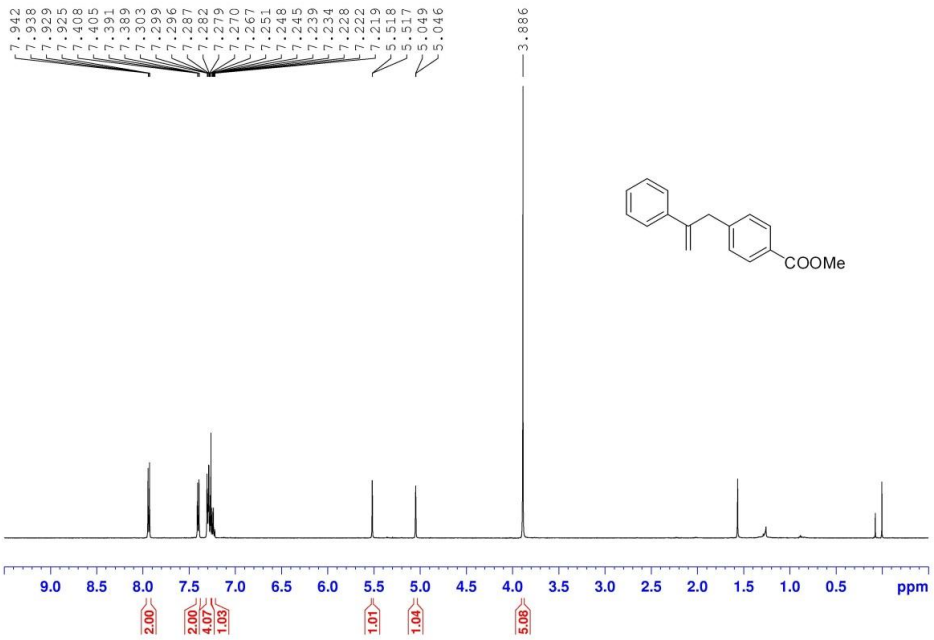

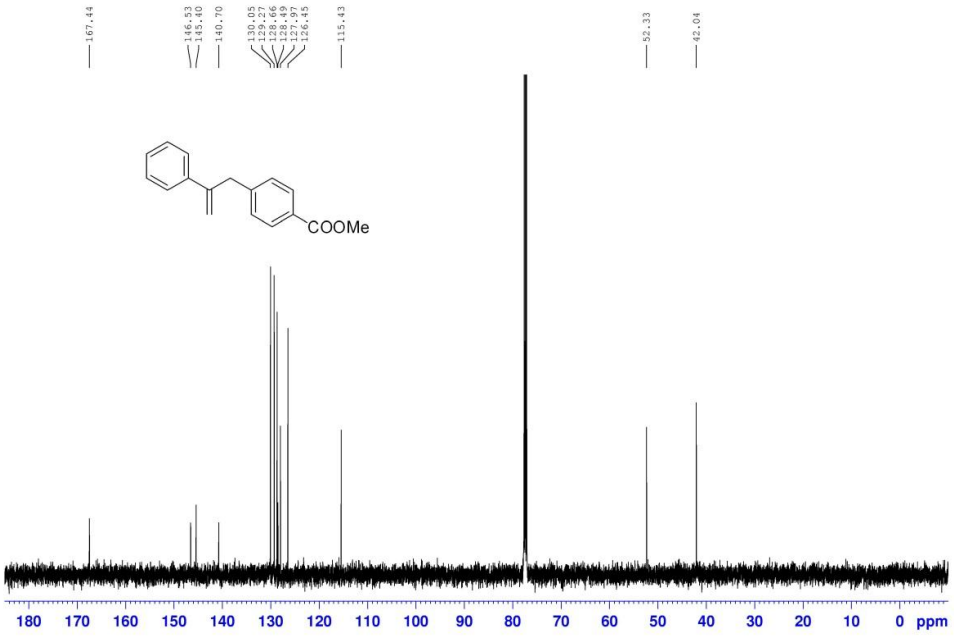

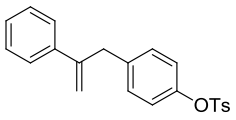
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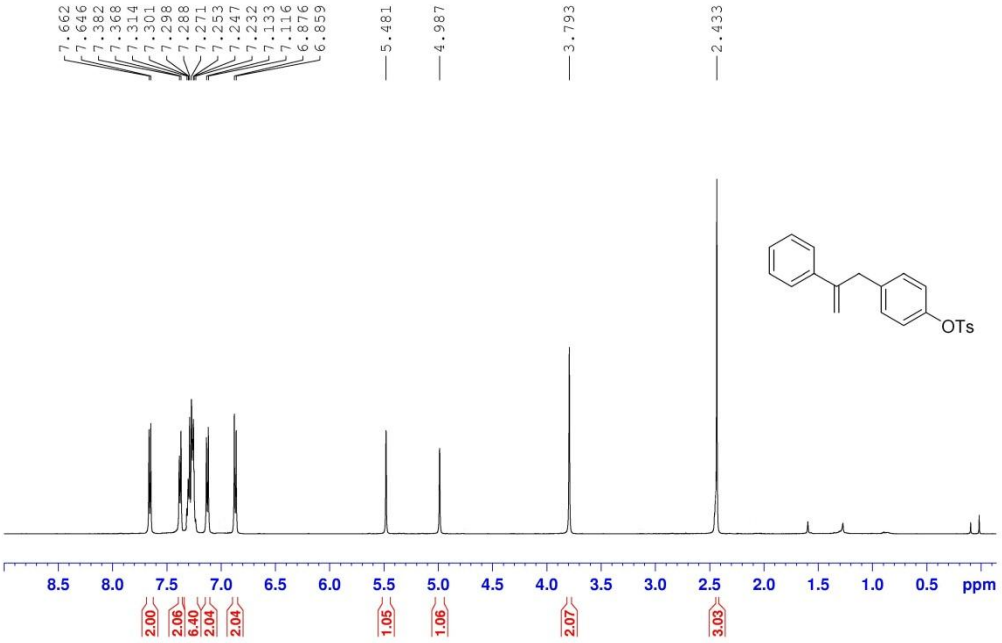
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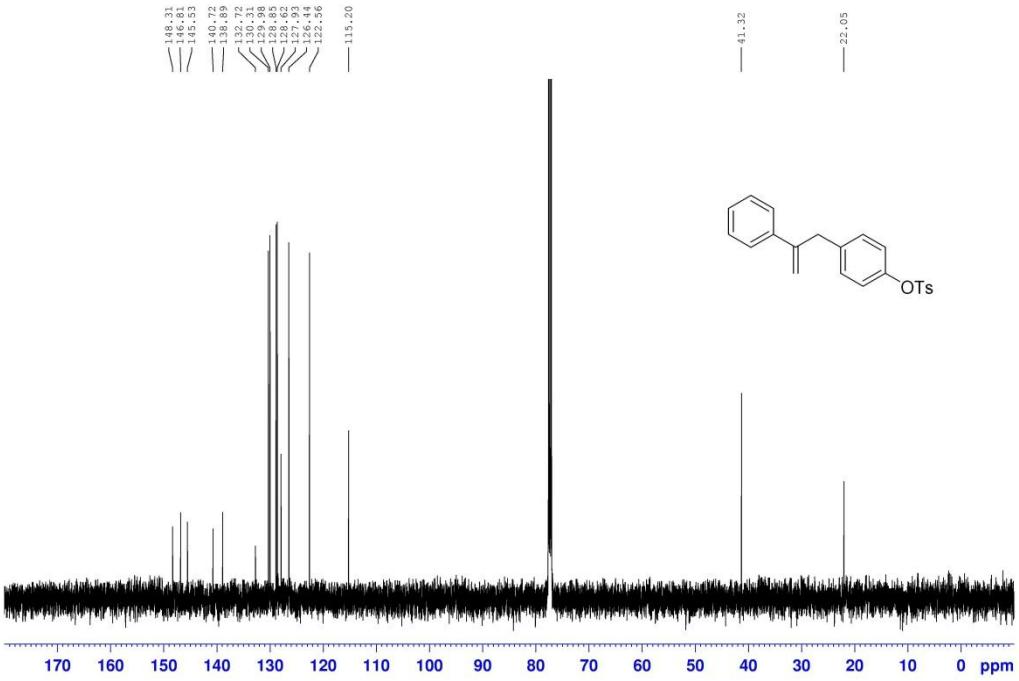
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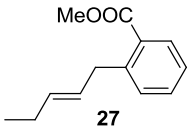

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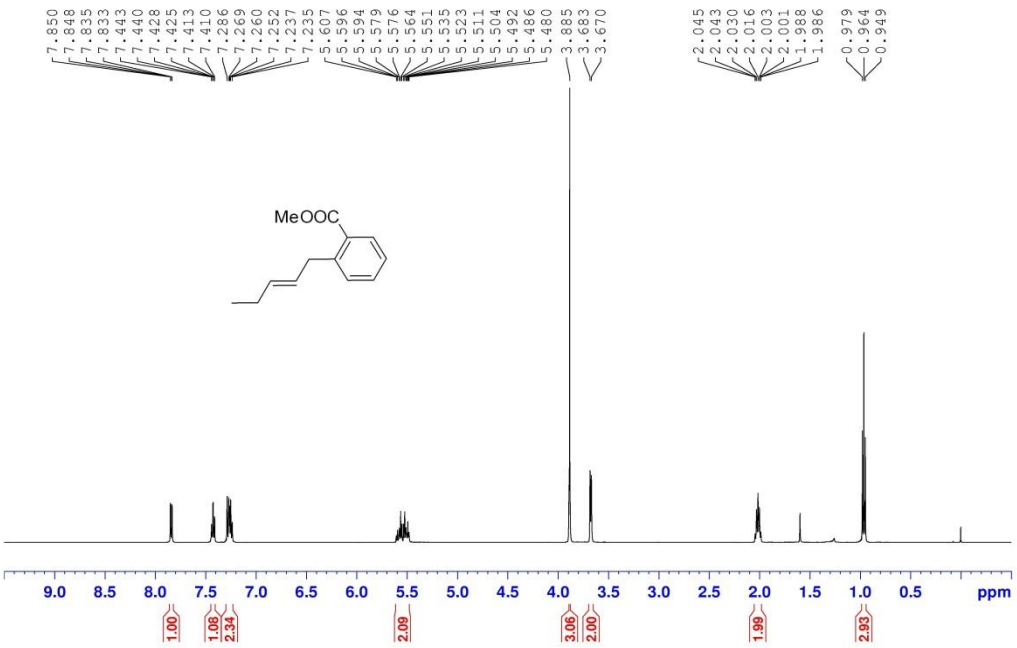

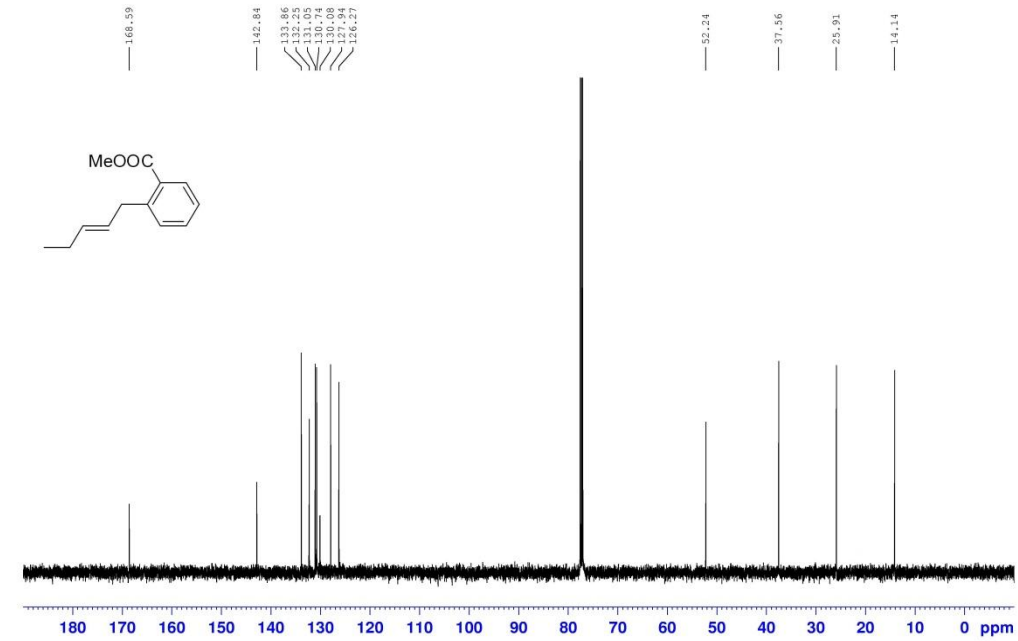

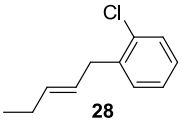
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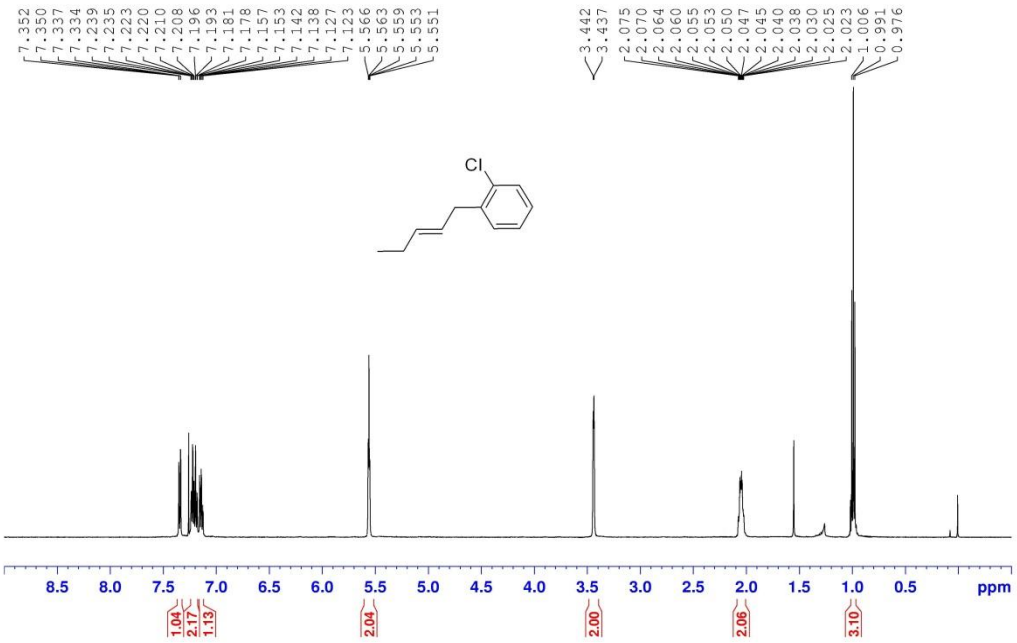
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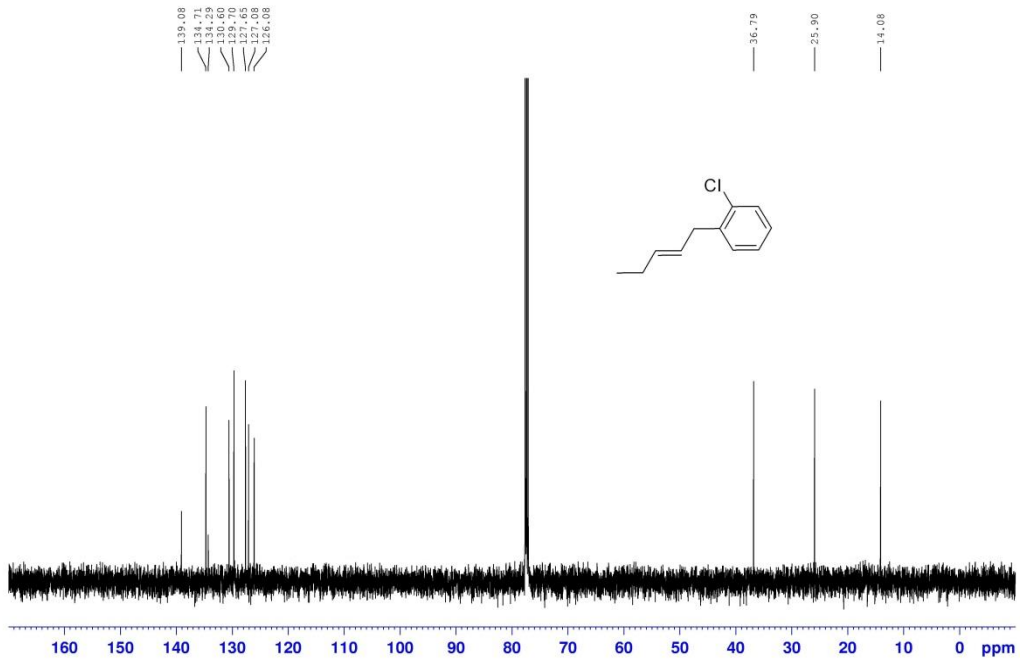
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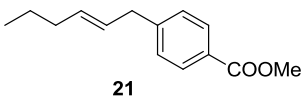

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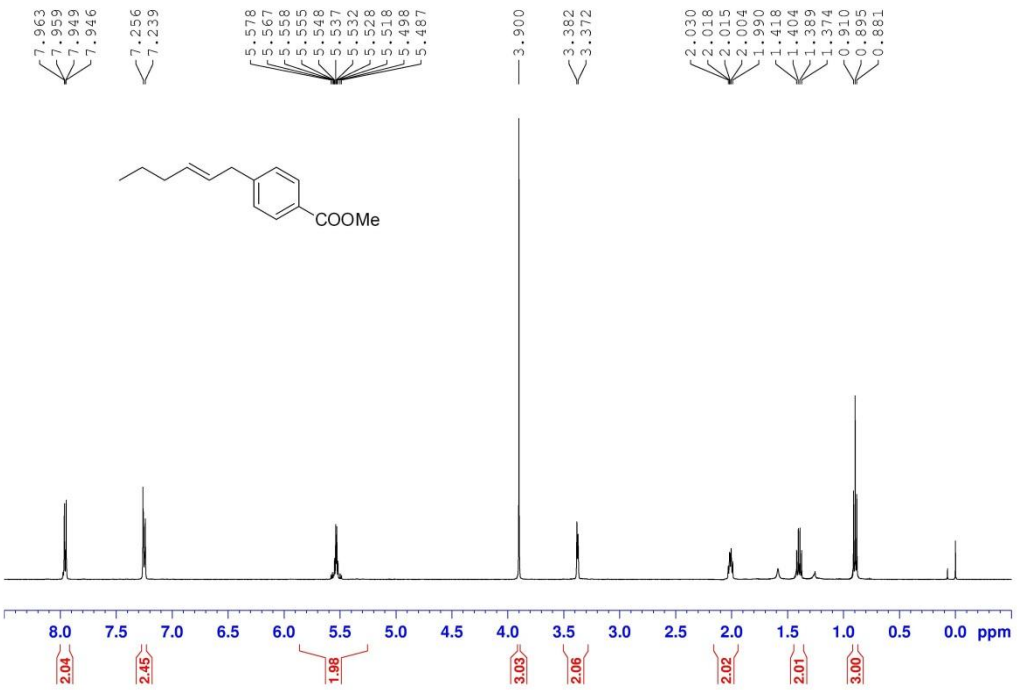

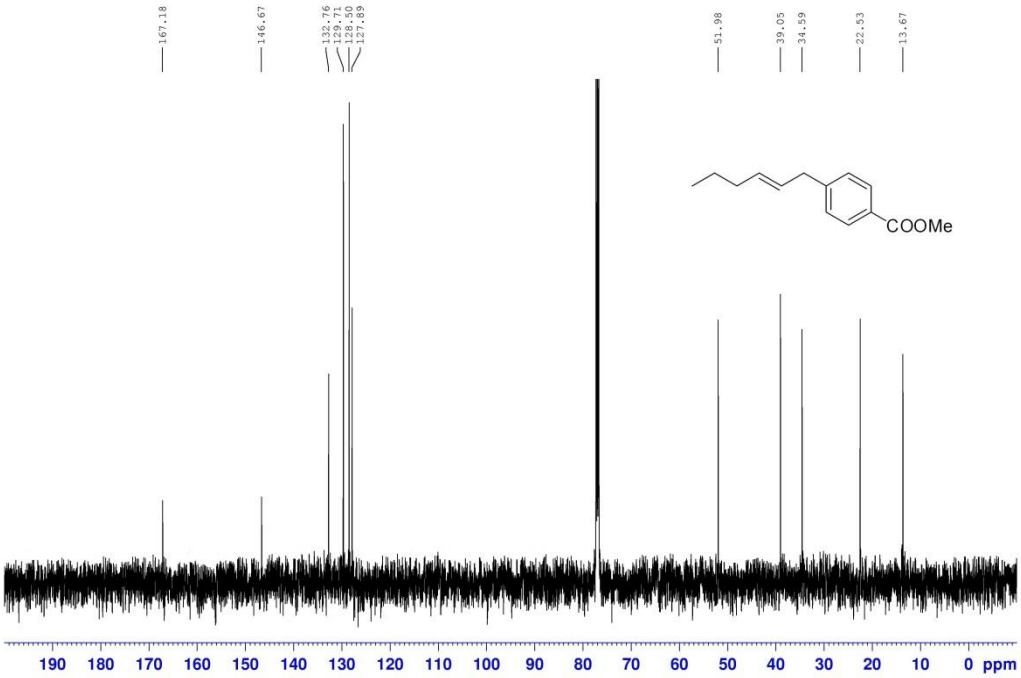

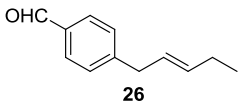

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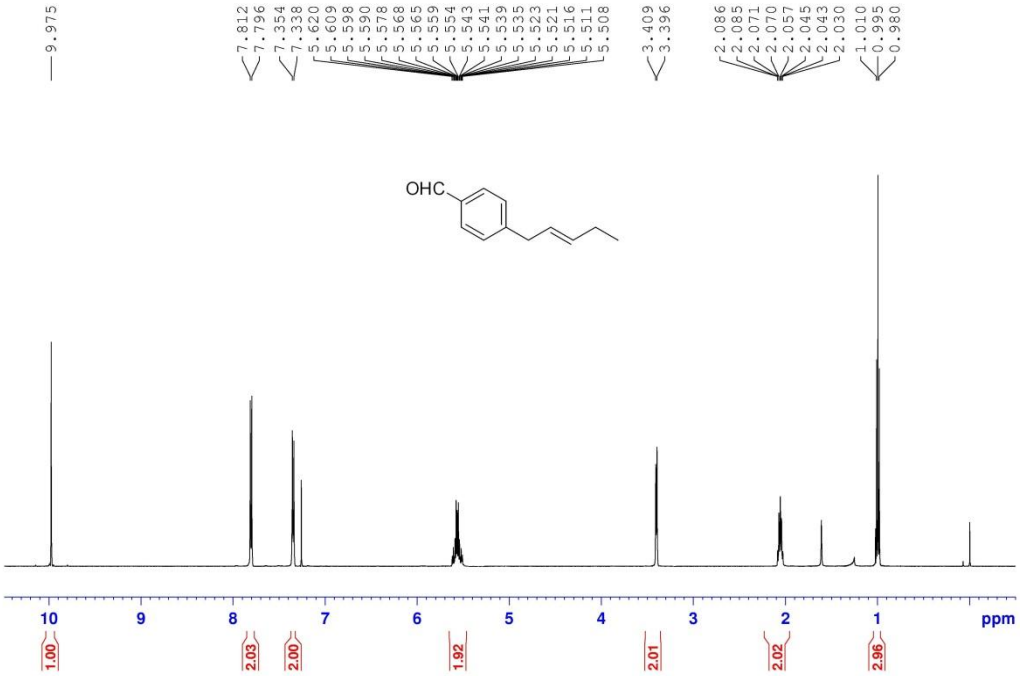

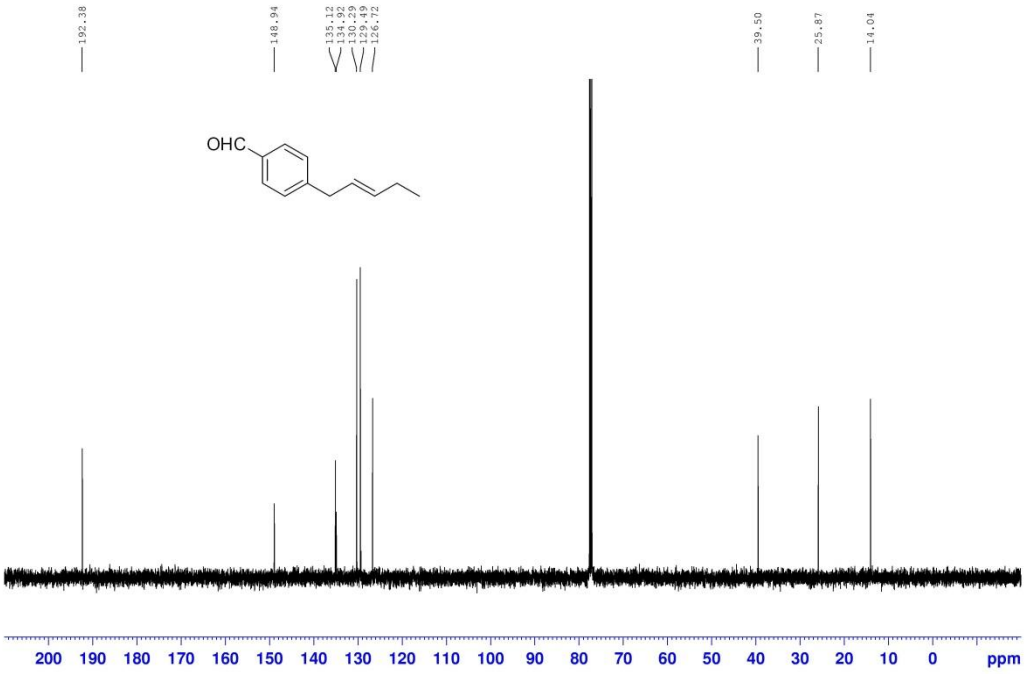

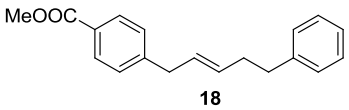

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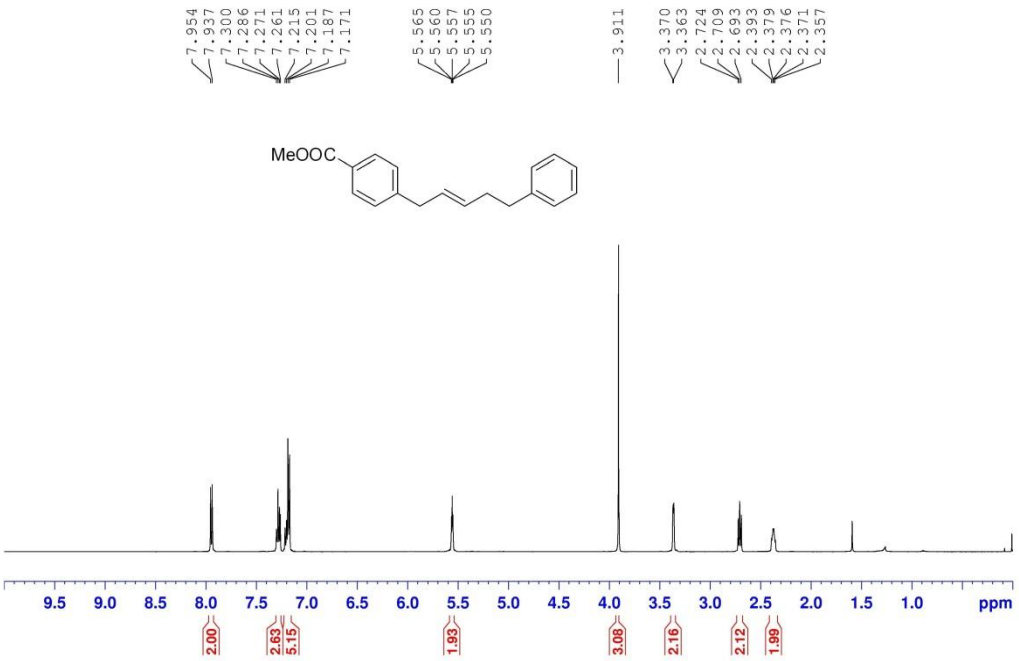

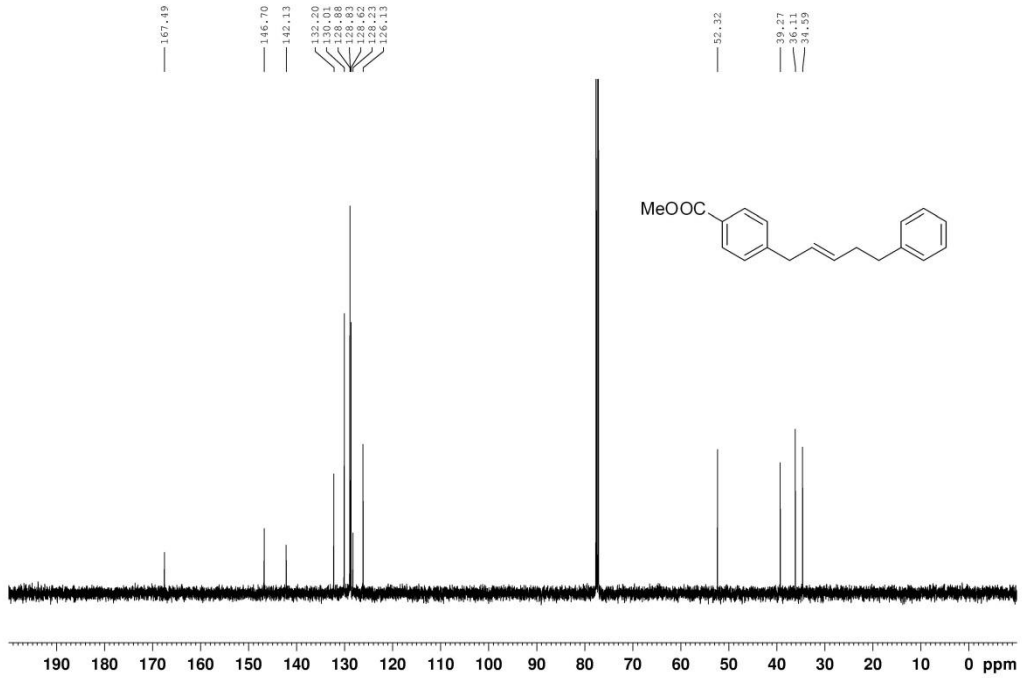

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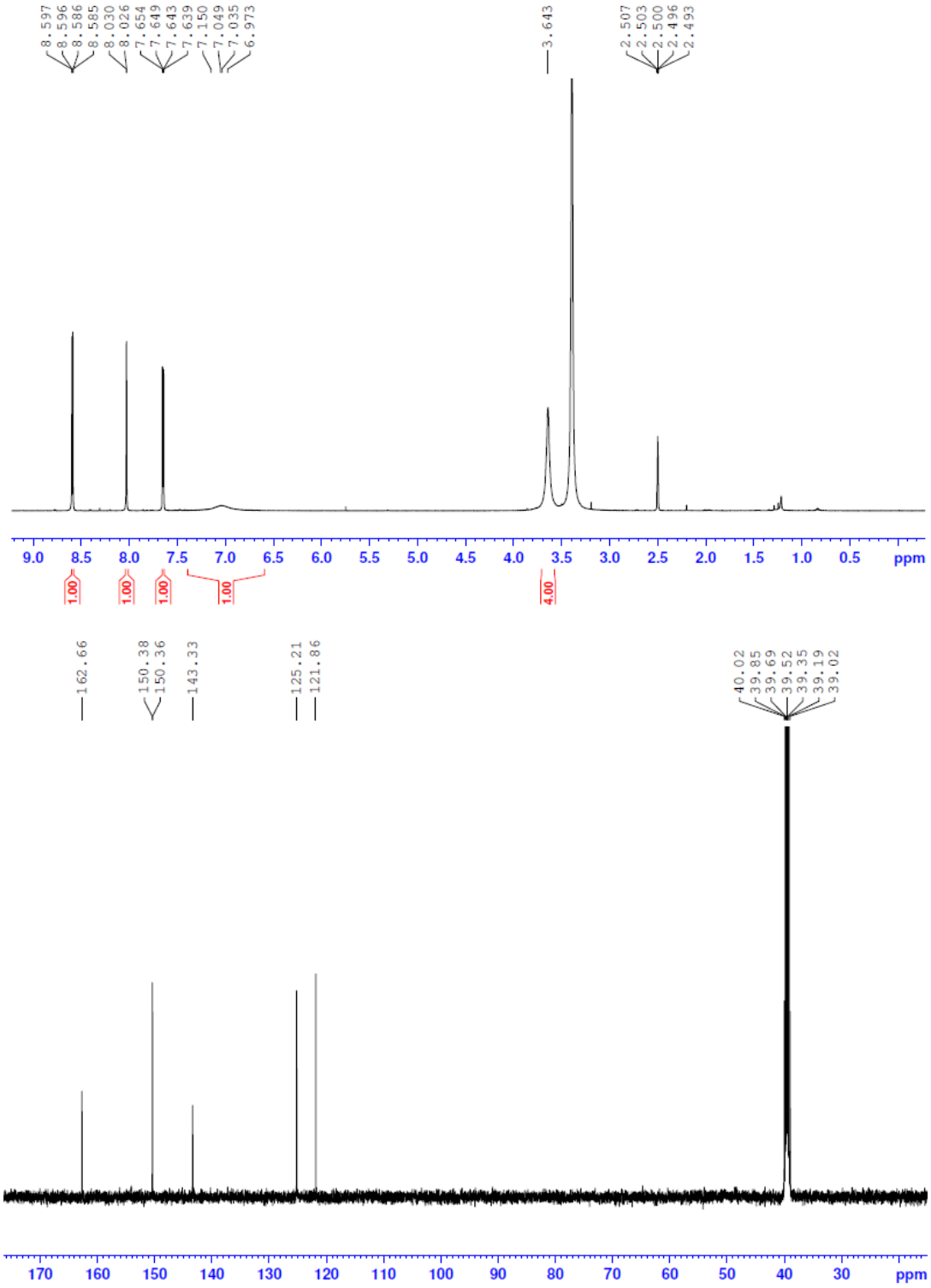

7. *The Data of HPLC for Asymmetric Coupling of 1,3-Disubsituted Allyl Acetate.*[4]

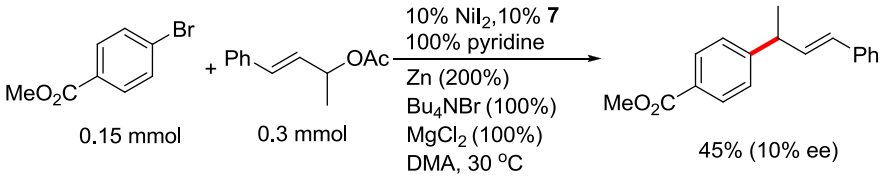

Figure 1. The HPLC Data for Enantiomeric Production.

2013-3-16 00:16:26 1 / 1

==== Shimadzu LCsolution 分析报告 ====

样品信息

采集人	: Admin
样品名称	: cxz-2
样品 ID	: cxz-2
样品架#	: 1
样品瓶#	: 16
进样体积	: 10 uL
数据文件名	: cxz-2.lcd
方法文件名	: 色谱条件.lcm
批处理文件名	:
报告文件名	: BG01.lcr
数据采集	: 2013-3-15 21:57:16
数据处理	: 2013-3-15 22:41:43

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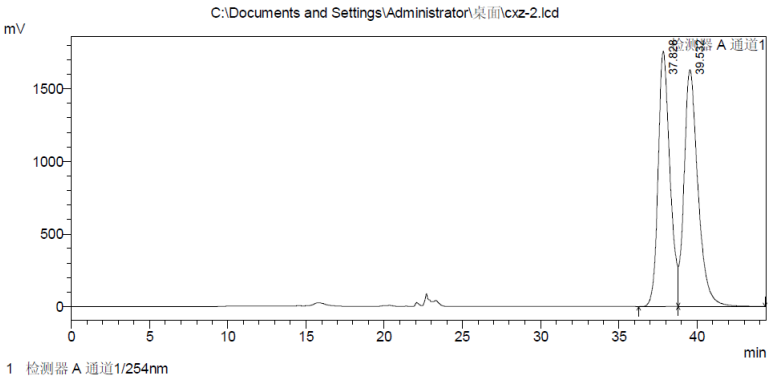

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	浓度	理论塔板#
1	37.828	91835274	1758964	47.686	0.000	12325.257
2	39.532	100748657	1632086	52.314	0.000	10182.476
总计		192583931	3391050	100.000		

C:\Documents and Settings\Administrator\桌面\cxz-2.lcd

Figure 2. The HPLC Data for Asymmetric Production.

2013-3-16 00:15:01 1 / 1

==== Shimadzu LCsolution 分析报告 ====

样品信息

采集人	: Admin
样品名称	: cxz-1
样品 ID	: cxz-1
样品架#	: 1
样品瓶#	: 31
进样体积	: 10 uL
数据文件名	: cxz-1.lcd
方法文件名	: 色谱条件.lcm
批处理文件名	:
报告文件名	: BG01.lcr
数据采集	: 2013-3-15 21:06:04
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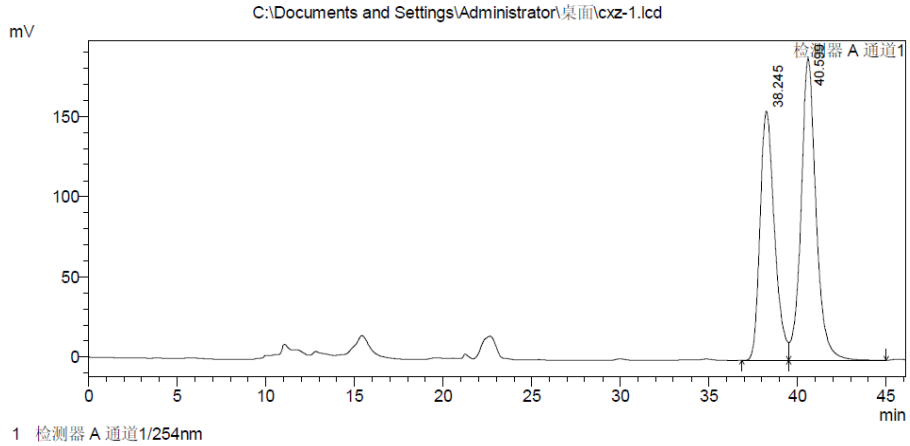


1 检测器 A 通道1/254nm

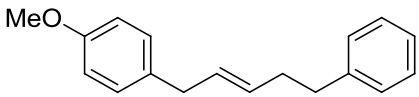
峰表

检测器 A Ch1 254nm

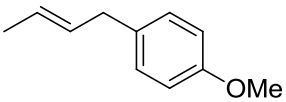
峰#	保留时间	面积	高度	面积 %	浓度	理论塔板#
1	38.245	8822389	155386	44.366	0.000	10717.999
2	40.599	11063201	188283	55.634	0.000	12391.365
总计		19885590	343669	100.000		

C:\Documents and Settings\Administrator\桌面\cxz-1.lcd

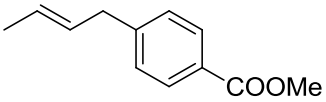
8. The references for known products



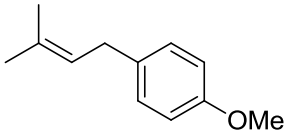
(E)-1-methoxy-4-(5-phenylpent-2-en-1-yl)benzene(10) [5]



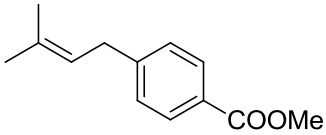
(E)-1-(but-2-en-1-yl)-4-methoxybenzene(11)[6]



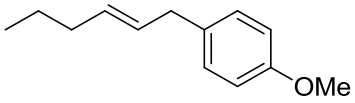
(E)-methyl 4-(but-2-en-1-yl)benzoate(19)[7]



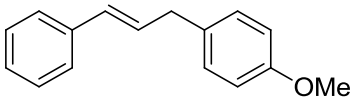
1-methoxy-4-(3-methylbut-2-en-1-yl)benzene(12)[8]



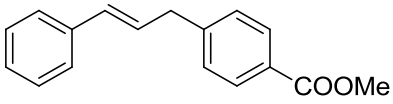
methyl 4-(3-methylbut-2-en-1-yl)benzoate(20)[9]



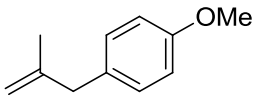
(E)-1-(hex-2-en-1-yl)-4-methoxybenzene(13)[10]



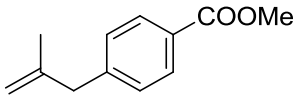
1-cinnamyl-4-methoxybenzene(14)[11]



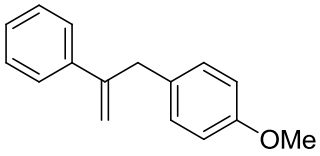
methyl 4-cinnamylbenzoate(22)[12]



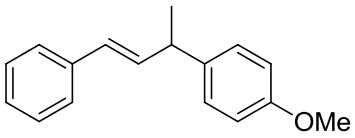
1-methoxy-4-(2-methylallyl)benzene(15)[13]



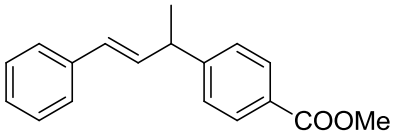
methyl 4-(2-methylallyl)benzoate(23)[14]



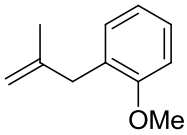
1-methoxy-4-(2-phenylallyl)benzene(16)[15]



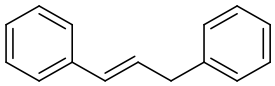
(E)-1-methoxy-4-(4-phenylbut-3-en-2-yl)benzene(17)[16]



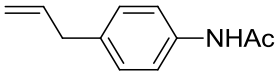
(E)-methyl 4-(4-phenylbut-3-en-2-yl)benzoate(25)[17]



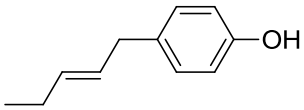
1-methoxy-2-(2-methylallyl)benzene(29)[18]



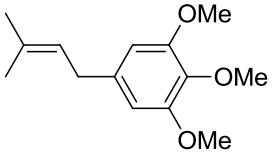
(E)-prop-1-ene-1,3-diyldibenzene(31)[19]



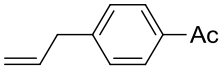
N-(4-allylphenyl)acetamide(32) [20]



(E)-4-(pent-2-en-1-yl)phenol(34)[21]



1,2,3-trimethoxy-5-(3-methylbut-2-en-1-yl)benzene(35)[22]



1-(4-allylphenyl)ethanone(33) [23]

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(4) Experimental conditions for HPLC: Isopropanol: Hexane = 5: 95; Pump pressure: 3.0 MPa. Column: CHIRALPAK. AD-H, Lot No. ADHOCE-OB110; DAICEL CHEMICAL INDUSTRIES, LTD; Column Size: 250 x 4.6 mm analytical; Detection wavelength: 254nm.

Time (min)	Mobile phase	Flow rate
0	95.0/5.0 Hexane: IPA	0.3 mL/min
45	95.0/5.0 Hexane: IPA	0.3 mL/min

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(17) Liao, Longyan; Sigman, Matthew S. *J. Am. Chem. Soc., 2010*, **132**, 10209 – 10211.

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