Highly regioselective iridium-catalyzed and samarium-promoted coupling of allylic carbonates with ketones: New approach toward homoallylic alcohols

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Experimental section

General: ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded as solutions in $CDCl_3$ with a Bruker NMR (400 MHz) spectrometer. The chemical shifts are reported in δ units downfield from the Me_4Si internal reference. High-resolution mass spectra were obtained with a Finnigan VG Platform or a Finnigan MAT 95S.

Reaction procedure for preparation of **3**: $[Ir(COD)Cl]_2$ (2.6 mg, 0.004 mmol) was dissolved in THF (5 mL) with SmI_2 [1] (0.1 M) in a Schlenk tube under argon. Allylic carbonate **1** (0.2 mmol) and ketone **2a** (0.3 mmol) or **2b** (0.4 mmol) were dissolved in THF (2.5 mL), then the solution was slowly added to the Schlenk tube *via* a syringe pump during 1 h. The mixture was stirred for an additional period of 5 h. The crude reaction mixture was filtered through celite and the solvent was removed by rotary evaporation. The crude residue was purified by flash column chromatography (ethyl acetate/petroleum ether, 1:10) to give the desired products.

Procedure for preparation of **3ea**,**3ja**: compound **3a** or **3j** (0.10 mmol) was dissolved in EtOH (2 mL) with 10% Pd/C (3 mg) in a Schlenk tube under H_2. The solution was stirred at 60 °C in 12 h. The solvent was removed by rotary evaporation. Then the crude residue was purified by flash column chromatography (ethyl acetate/petroleum ether, 1:10) to give the desired product **3ea**, **3ja**.

Procedure for preparation of **3eb**,**3jb**: **3ea** or **3ja** (0.10 mmol) was dissolved in dry DCM (2 mL) in a Schlenk tube under argon. Diethylaminosulfur trifluoride (DAST) (0.15 mmol) was added by a syringe at room temperature. The solution was stirred for 5 min, and then $NaHCO_3$ solution (2 mL, 1.5 M) was added. After stirred for an additional 5 min, the mixture was extracted with DCM. The organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. Then the crude residue was purified by flash column chromatography (petroleum ether) to give the desired product **3eb**,**3jb**.

1-Cinnamylcyclohexanol (**3a**).[2] Colorless oil. Yield: 35.9 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 (d, J = 7.3 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 6.49 (d, J = 15.9 Hz, 1H), 6.34 (dt, J = 15.8, 7.5 Hz, 2H), 2.40 (d, J = 7.5 Hz, 2H), 1.71-1.46 (m, 10H).

(*E*)-1-(3-(3-Methoxyphenyl)allyl)cyclohexanol (**3b**). Colorless oil. Yield: 37.4 mg (76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 (dd, J = 16.1, 8.2 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 6.91 (s, 1H), 6.77 (d, J = 8.2 Hz, 1H), 6.42 (d, J = 15.9 Hz, 1H), 6.31 (dt, J = 15.4, 7.7 Hz, 1H), 3.81 (s, 3H), 2.36 (d, J = 7.4 Hz, 2H), 1.65-1.45 (m, 10H). ^{13}C NMR (100 Hz, $CDCl_3$) δ = 159.8, 138.9, 133.5, 129.5, 125.8, 118.8, 112.9, 111.5, 71.6, 55.2, 45.9, 37.6, 25.8, 22.2. HRMS (ESI) calcd for $C_{16}H_{22}O_2Na$, $[M+Na]^+$: 269.1517, Found: 269.1474. IR(KBr): ν_{max} (cm^{-1}) = 3780, 3610, 3453, 3125, 2450, 1555, 1450, 1230, 1157, 1142, 1121, 1055, 998, 755, 600, 490.

(*E*)-1-(3-(*p*-Tolyl)allyl)cyclohexanol (**3c**).Colorless oil. Yield: 33.0 mg (72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 6.45 (d, J = 15.8 Hz, 1H), 6.29 (dt, J = 15.6, 7.8 Hz, 1H), 2.38 (d, J = 7.7 Hz, 2H), 2.36 (s, 3H), 1.70-1.47 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 135.9, 132.7, 132.3, 128.7, 127.3, 126.3, 71.6, 45.9, 37.6, 29.7, 25.7, 22.3. HRMS (ESI) calcd for $C_{16}H_{22}ONa$, $[M+Na]^+$: 253.1568, Found: 253.1558. IR(KBr): ν_{max} (cm^{-1}) = 3770, 3650, 3443, 3225, 2450, 1505, 1220, 1150, 1117, 1040, 740, 600.

(*E*)-1-(3-(2-Chlorophenyl)allyl)cyclohexanol (**3d**). Colorless oil. Yield: 25.0 mg (50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 (dd, J = 7.6, 1.3 Hz, 1H), 7.37-7.31 (m, 1H), 7.17 (m, 2H), 6.82 (d, J = 15.8 Hz, 1H), 6.30

(dt, *J* = 15.5, 7.6 Hz, 1H), 2.42 (d, *J* = 7.6 Hz, 2H), 1.68-1.44 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 135.6, 132.6, 129.7, 129.6, 128.7, 128.2, 126.8, 126.8, 71.6, 46.0, 37.6, 25.7, 22.2. HRMS (ESI) calcd for $C_{15}H_{19}ClONa$. $[M+Na]^+$: 273.1022, Found: 273.1026. IR(KBr): ν_{max} (cm^{-1}) = 3730, 3655, 3435, 3158, 2422, 1578, 1456, 1225, 1158, 1147, 1154, 1152, 980, 765, 652.

(*E*)-1-(3-([1,1'-Biphenyl]-4-yl)allyl)cyclohexanol (**3e**). White solid. Melting point: 85−86˚C. Yield: 28.6 mg (49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 7.2 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.47 (t, *J* = 8.3 Hz, 4H), 7.37 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.39 (dt, *J* = 15.8, 7.2 Hz, 1H), 2.42 (d, *J* = 7.4 Hz, 2H), 1.71-1.48 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.8, 140.0, 136.5, 133.2, 128.8, 127.3, 126.9, 126.6, 125.6, 71.7, 46.0, 37.6, 25.8, 22.2. HRMS (ESI) calcd for $C_{21}H_{24}ONa$. $[M+Na]^+$: 315.1725, Found: 315.1718. IR(KBr): ν_{max} (cm^{-1}) = 3885, 3652, 3553, 3120, 2435, 1570, 1447, 1215, 1168, 1157, 1065, 998, 765, 580.

1-(3-([1,1'-Biphenyl]-4-yl)propyl)cyclohexanol (**3ea**). Colorless oil. Yield: 28.6 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 7.2 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 1.82-1.71 (m, 2H), 1.65-1.42 (m, 10H), 1.39-1.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.7, 141.2, 138.7, 128.8, 128.7, 127.1, 127.0, 71.4, 42.1, 37.5, 36.0, 25.9, 24.8, 22.3. HRMS (ESI) calcd for $C_{21}H_{26}ONa$. $[M+Na]^+$: 317.1881, Found: 317.1890. IR(KBr): ν_{max} (cm^{-1}) = 3875, 3620, 3553, 3135, 2440, 1655, 1550, 1330, 1165, 1150, 1120, 1080, 787, 650, 500.

4-(3-(1-Fluorocyclohexyl)propyl)-1,1'-biphenyl (**3eb**). Colorless oil. Yield: 22.1 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 7.3 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 1.91-1.75 (m, 4H), 1.73-1.60 (m, 5H), 1.58-1.44 (m, 3H), 1.41-1.23 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ = -155.6. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.5, 139.9, 132.3, 132.2, 129.7, 126.1, 124.6, 122.9, 121.7, 64.8, 30.7, 29.7, 21.3, 19.2, 19.1, 13.7. HRMS (ESI) calcd for $C_{21}H_{25}FNa$. $[M+Na]^+$: 319.1838, Found: 319.1830. IR(KBr): ν_{max} (cm^{-1}) = 3880, 3650, 3120, 2455, 1678, 1562, 1352, 1171, 1100, 1070, 800, 653, 585.

(*E*)-2-Methyl-5-phenylpent-4-en-2-ol (**3f**).[2] Colorless oil. Yield: 31.3 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.23 (dd, *J* = 6.7, 6.7 Hz, 1H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.30 (dt, *J* = 15.5, 7.8 Hz, 1H), 2.39 (d, *J* = 7.5 Hz, 2H), 1.28 (s, 6H).

(*E*)-2-Methyl-5-(*p*-tolyl)pent-4-en-2-ol (**3g**). Colorless oil. Yield: 29.6 mg (78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.24 (dt, *J* = 15.5, 7.8 Hz, 1H), 2.37 (d, *J* = 7.5 Hz, 2H), 2.33 (s, 3H), 1.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.1, 134.6, 133.6, 129.3, 126.1, 124.7, 70.9, 47.4, 29.3, 21.2. HRMS (ESI) calcd for $C_{13}H_{18}ONa$. $[M+Na]^+$: 213.1255, Found: 213.1250. IR(KBr): ν_{max} (cm^{-1}) = 3790, 3600, 3458, 3112, 2583, 1595, 1480, 1208, 1186, 1132, 1086, 795, 665, 508.

(*E*)-5-(4-Methoxyphenyl)-2-methylpent-4-en-2-ol (**3h**). Colorless oil. Yield: 30.9 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.14 (dt, *J* = 15.5, 7.6 Hz, 1H), 3.81 (s, 3H), 2.36 (d, *J* = 7.6 Hz, 2H), 1.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.0, 133.2, 130.2, 127.3, 123.4, 114.0, 70.9, 55.3, 47.3, 29.2. HRMS (ESI) calcd for $C_{13}H_{18}O_2Na$. $[M+Na]^+$: 229.1204, Found: 229.1211. IR(KBr): ν_{max} (cm^{-1}) = 3785, 3605, 3450, 3120, 2443, 1555, 1440, 1233, 1168, 1145, 1132, 1065, 777, 615, 500.

(*E*)-2-Methyl-5-(naphthalen-1-yl)pent-4-en-2-ol (**3i**). Colorless oil. Yield: 24.4 mg (54%). ^{1}H NMR (400

MHz, $CDCl_3$) δ = 8.12 (d, J = 7.8 Hz, 1H), 7.87-7.83 (m, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.59 (d, J = 7.1 Hz, 1H), 7.54-7.41 (m, 3H), 7.21 (d, J = 15.5 Hz, 1H), 6.31 (dt, J = 15.4, 7.6 Hz, 1H), 2.51 (d, J = 7.6 Hz, 2H), 1.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 135.2, 133.6, 131.1, 131.0, 129.2, 128.5, 127.7, 126.0, 125.8, 125.7, 123.8, 123.8, 71.0, 47.8, 29.3. HRMS (ESI) calcd for $C_{16}H_{18}ONa$. $[M+Na]^+$: 249.1255, Found: 249.1257. IR(KBr): ν_{max} (cm^{-1}) = 3800, 3750, 3554, 3085, 2395, 1600, 1480, 1250, 1158, 1100, 1085, 968, 727, 650, 490.

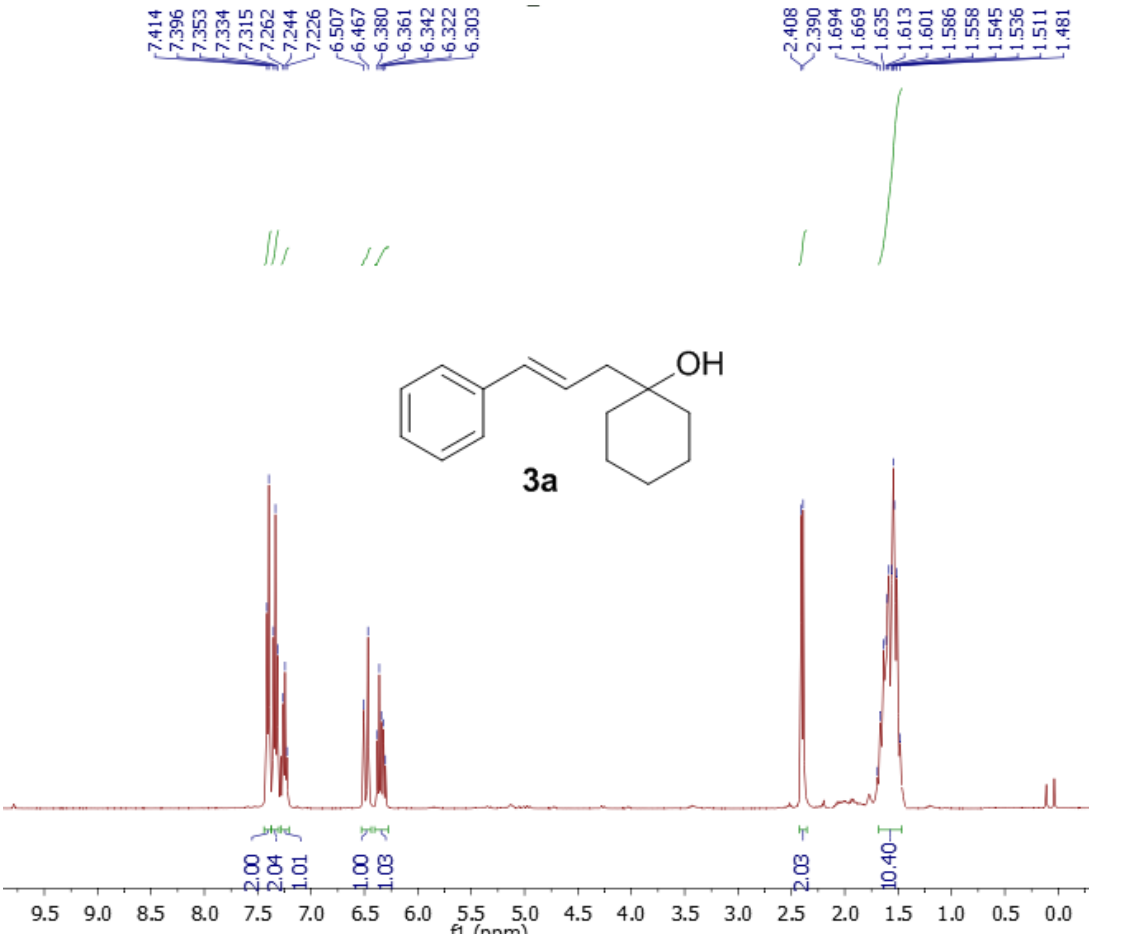
(*E*)-5-([1,1'-Biphenyl]-4-yl)-2-methylpent-4-en-2-ol (**3j**). White solid. Melting point 94–95°C. Yield: 21.7 mg (43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (d, J = 7.4 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.47 (dd, J = 10.2, 8.2 Hz, 4H), 7.37 (t, J = 7.3 Hz, 1H), 6.54 (d, J = 15.8 Hz, 1H), 6.39 (dt, J = 15.5, 7.8 Hz, 1H), 2.44 (d, J = 7.5 Hz, 2H), 1.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.8, 140.1, 136.4, 133.2, 128.8, 127.3, 126.9, 126.6, 126.0, 71.0, 47.4, 29.3. HRMS (ESI) calcd for $C_{18}H_{20}ONa$. $[M+Na]^+$: 275.1412, Found: 275.1420. IR(KBr): ν_{max} (cm^{-1}) = 3810, 3790, 3533, 3145, 2650, 1575, 1478, 1211, 1137, 1100, 1055, 915, 705, 618, 500.

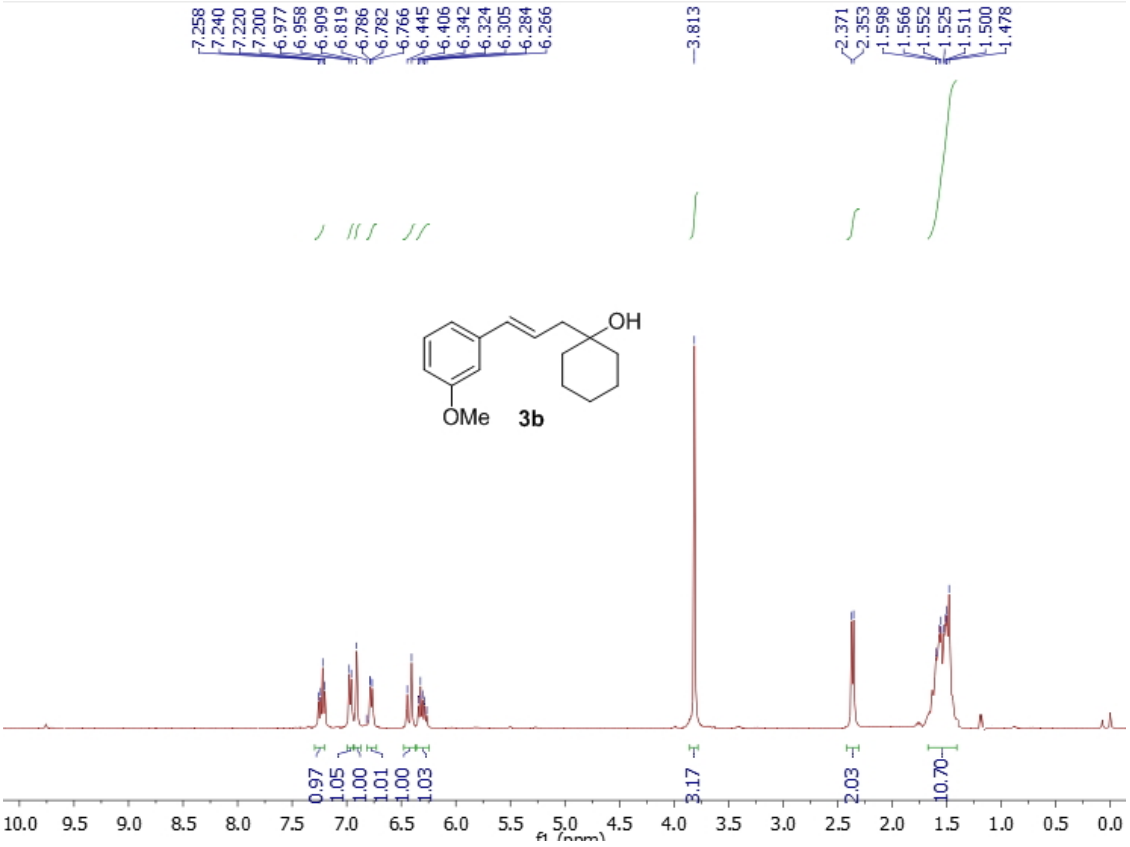
5-([1,1'-Biphenyl]-4-yl)-2-methylpentan-2-ol (**3ja**). White solid. Melting point 80–81°C. Yield: 21.7 mg (99%).^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (d, J = 7.7 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.26 (d, J = 8.5 Hz, 2H), 2.66 (t, J = 7.6 Hz, 2H), 1.77-1.69 (m, 2H), 1.54 (dd, J = 11.2, 5.5 Hz, 2H), 1.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.6, 141.1, 138.7, 128.8, 128.7, 127.1, 127.0, 71.0, 43.5, 36.0, 29.3, 26.3. HRMS (ESI) calcd for $C_{18}H_{22}ONa$. $[M+Na]^+$: 277.1568, Found: 277.1573. IR(KBr): ν_{max} (cm^{-1}) = 3910, 3720, 3358, 3205, 2650, 1745, 1500, 1600, 1157, 1121, 1050, 775, 615.

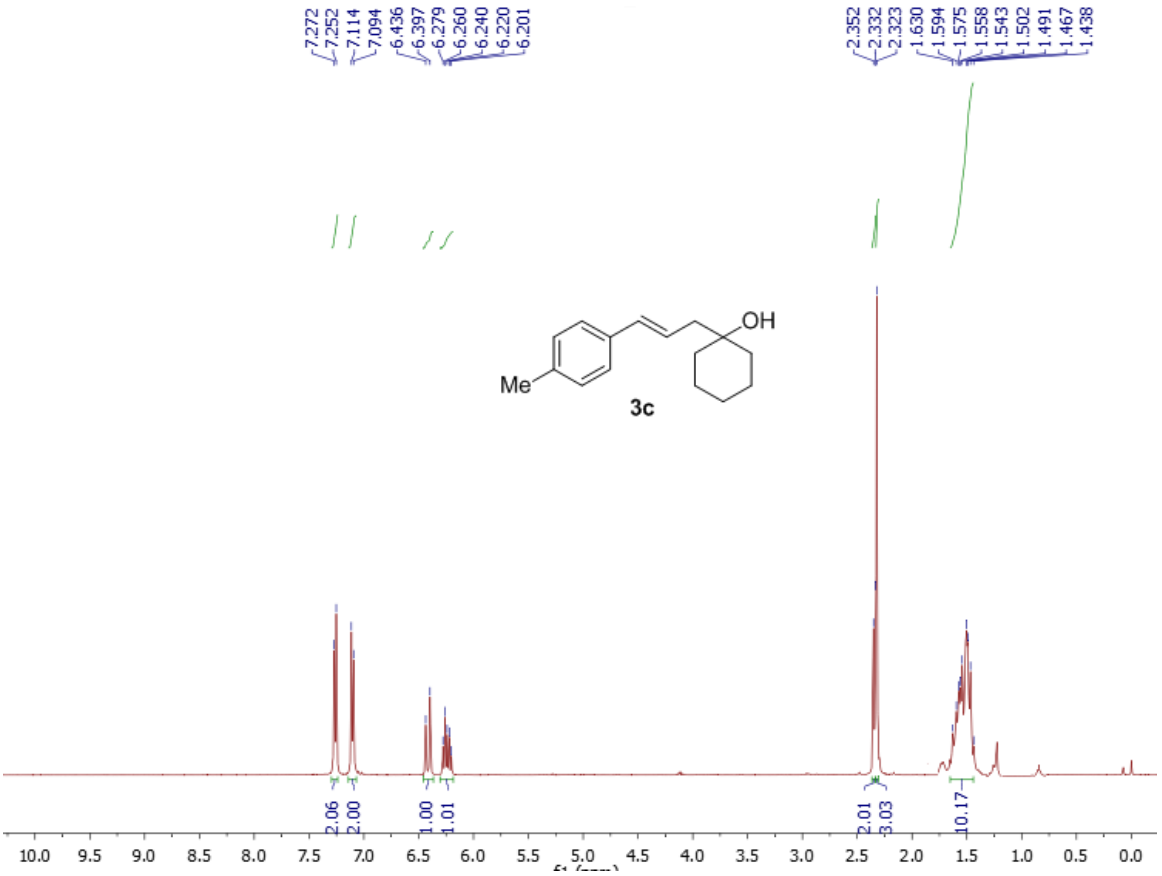
4-(4-Fluoro-4-methylpentyl)-1,1'-biphenyl (**3jb**). White solid. Melting point 49–50°C. Yield: 18.2 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 8.1 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.29 (d, J = 7.6 Hz, 2H), 2.70 (t, J = 7.4 Hz, 2H), 1.84-1.65 (m, 4H), 1.40 (s, 3H), 1.35 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ = -137.5. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.4, 141.1, 138.8, 128.8, 128.7, 127.1, 127.0, 41.1, 40.9, 35.7, 26.8, 26.6, 25.8, 25.8. HRMS (ESI) calcd for $C_{18}H_{21}FNa$. $[M+Na]^+$: 279.1525, Found: 279.1519. IR(KBr): ν_{max} (cm^{-1}) = 3905, 3715, 3370, 3115, 2785, 1768, 1620, 1605, 1142, 1115, 1035, 760, 610.

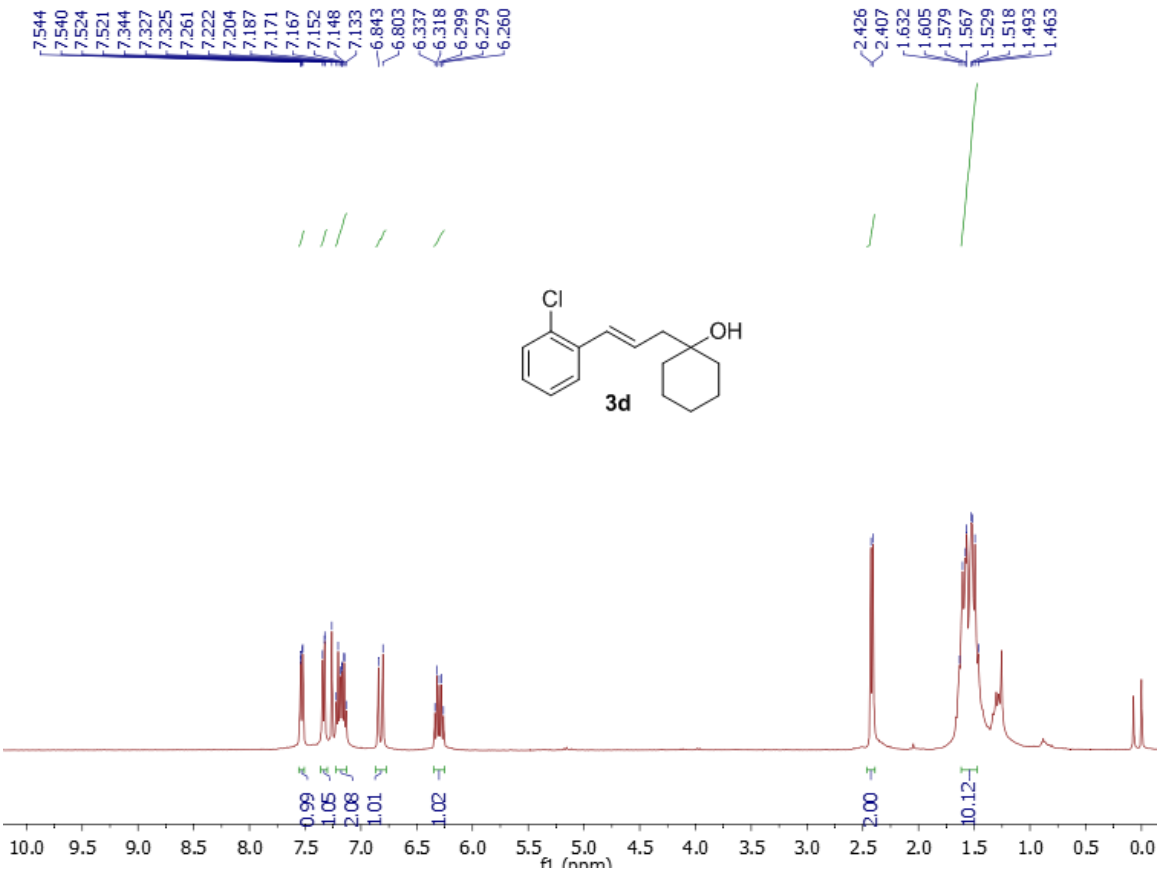
Procedure for the preparation of **3a** from Grignard reagent such as (*E*)-cinnamylmagnesium chloride: (*E*)-Cinnamylmagnesium chloride (0.20 mmol, 2 mL) made according to a known procedure[3] was added by a syringe into a Schlenk tube under argon. Then a solution of cyclohexanone (0.30 mmol, 1.5 eq) and THF (1 mL) was slowly added into the reaction mixture by a syringe. The mixture was stirred for 12 h. The crude reaction mixture was filtered through celite and the solvent was removed by rotary evaporation. The crude residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:10) to give the desired product **3a** in 46 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 (d, J = 7.3 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 6.49 (d, J = 15.9 Hz, 1H), 6.34 (dt, J = 15.8, 7.5 Hz, 2H), 2.40 (d, J = 7.5 Hz, 2H), 1.71-1.46 (m, 10H).

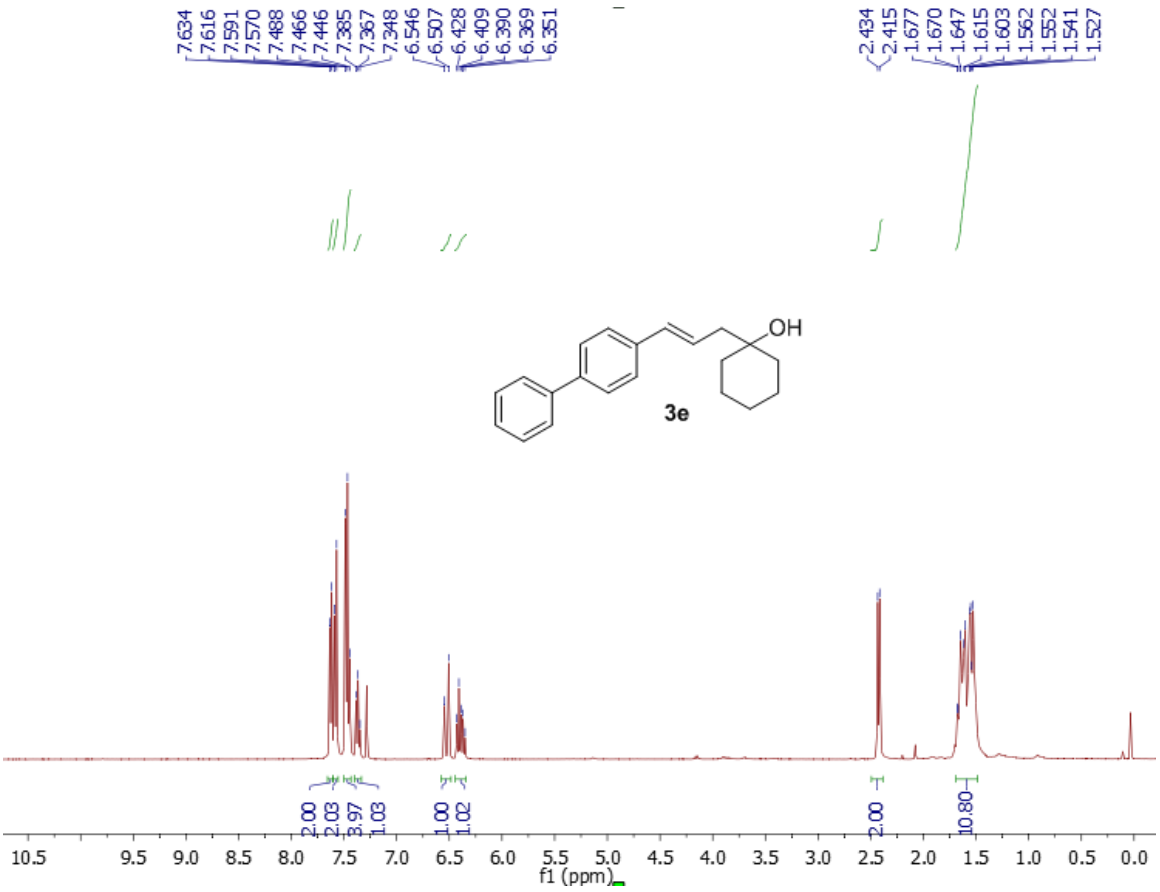
^{1}H NMR spectra







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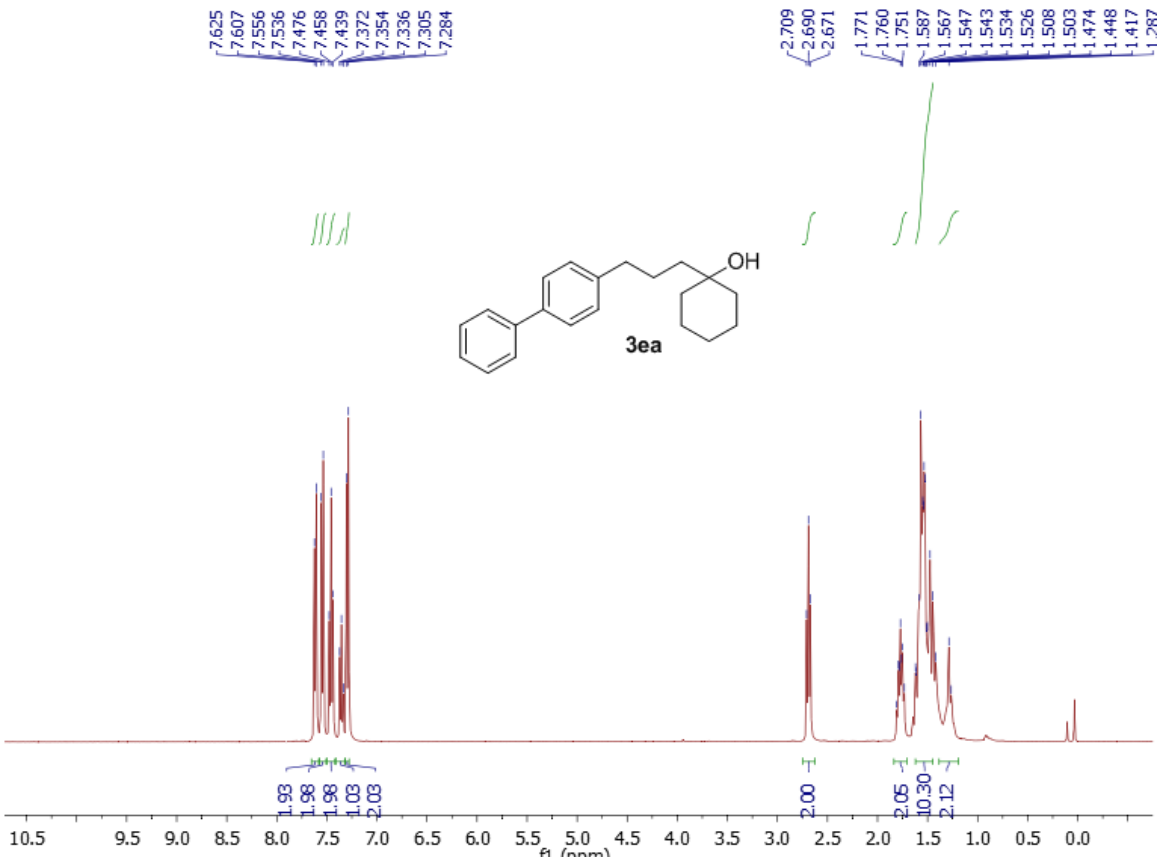
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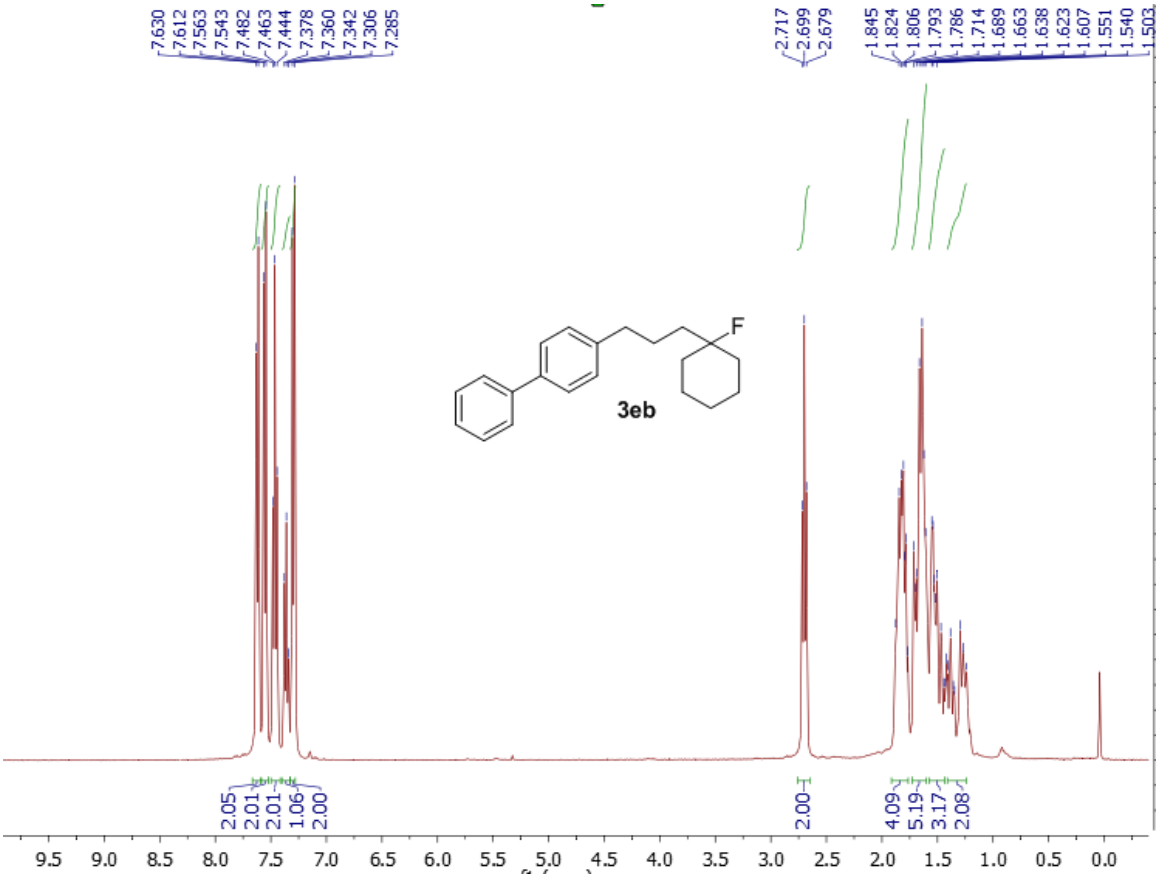

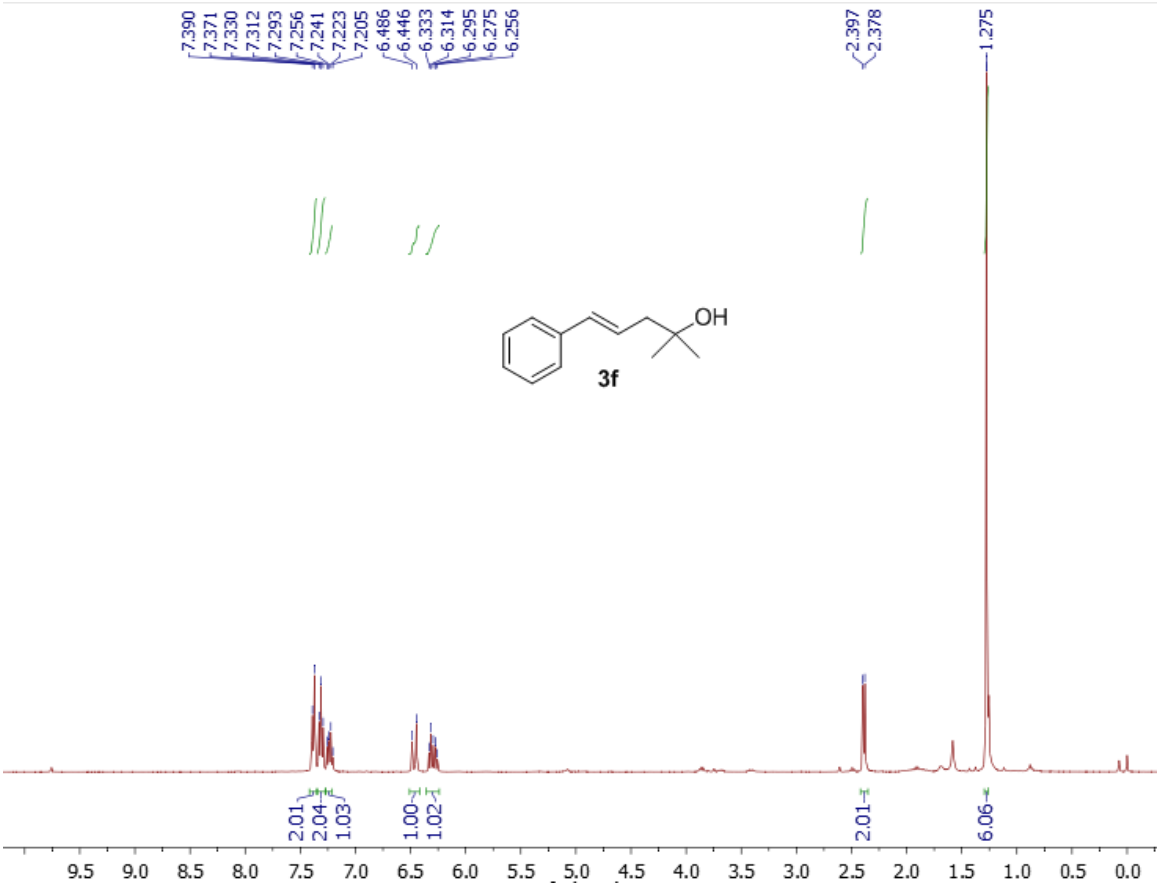

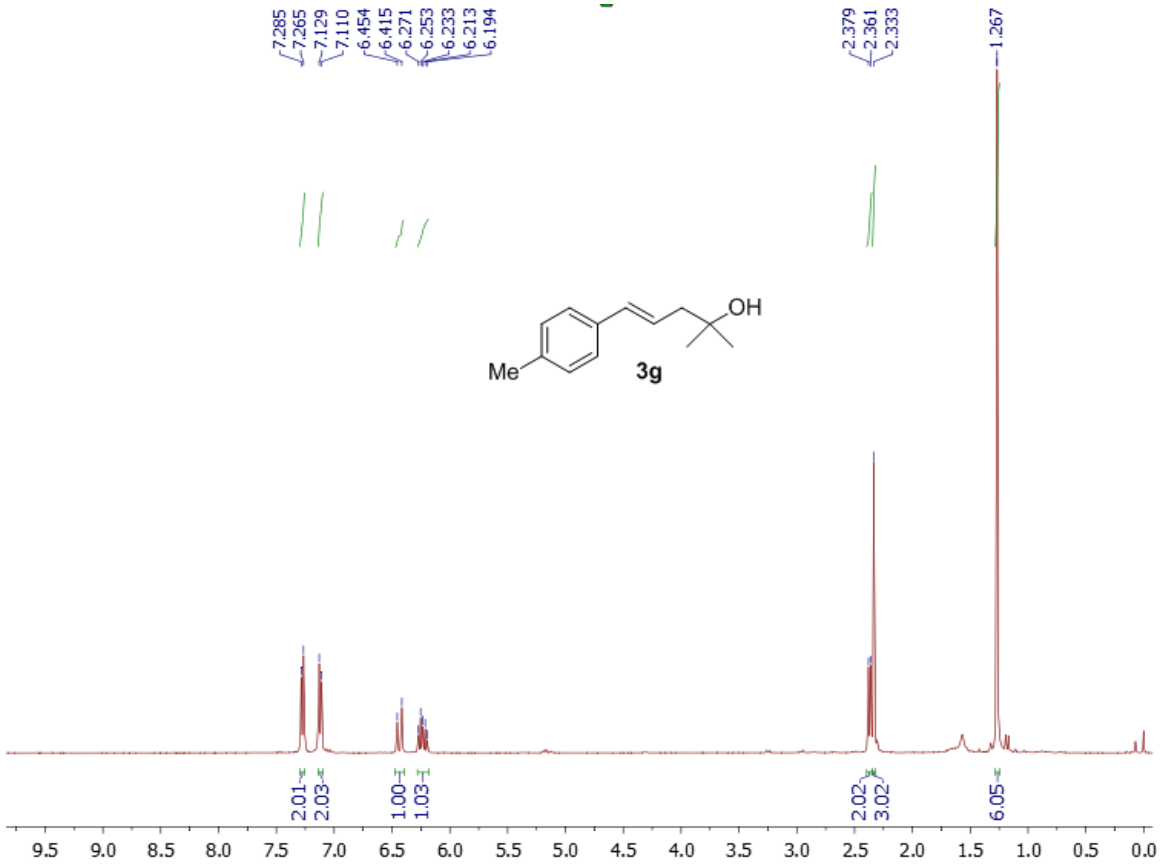

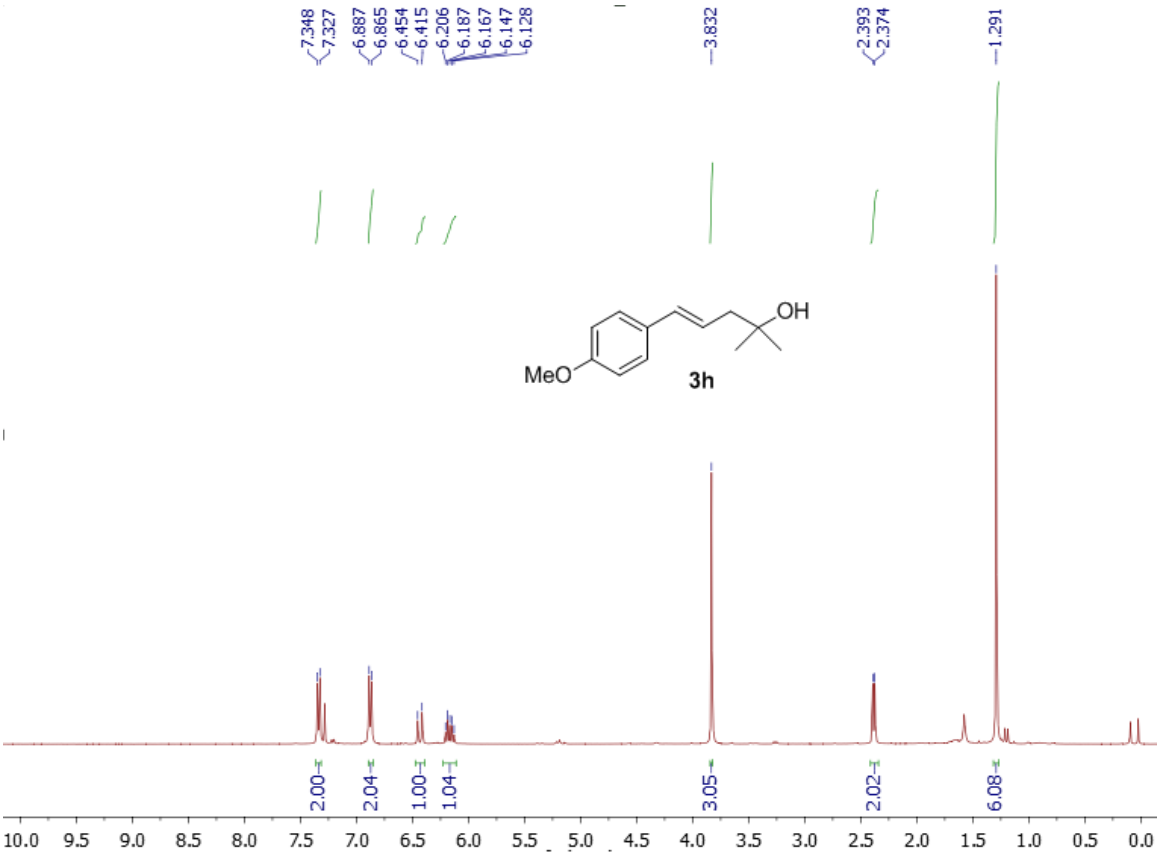

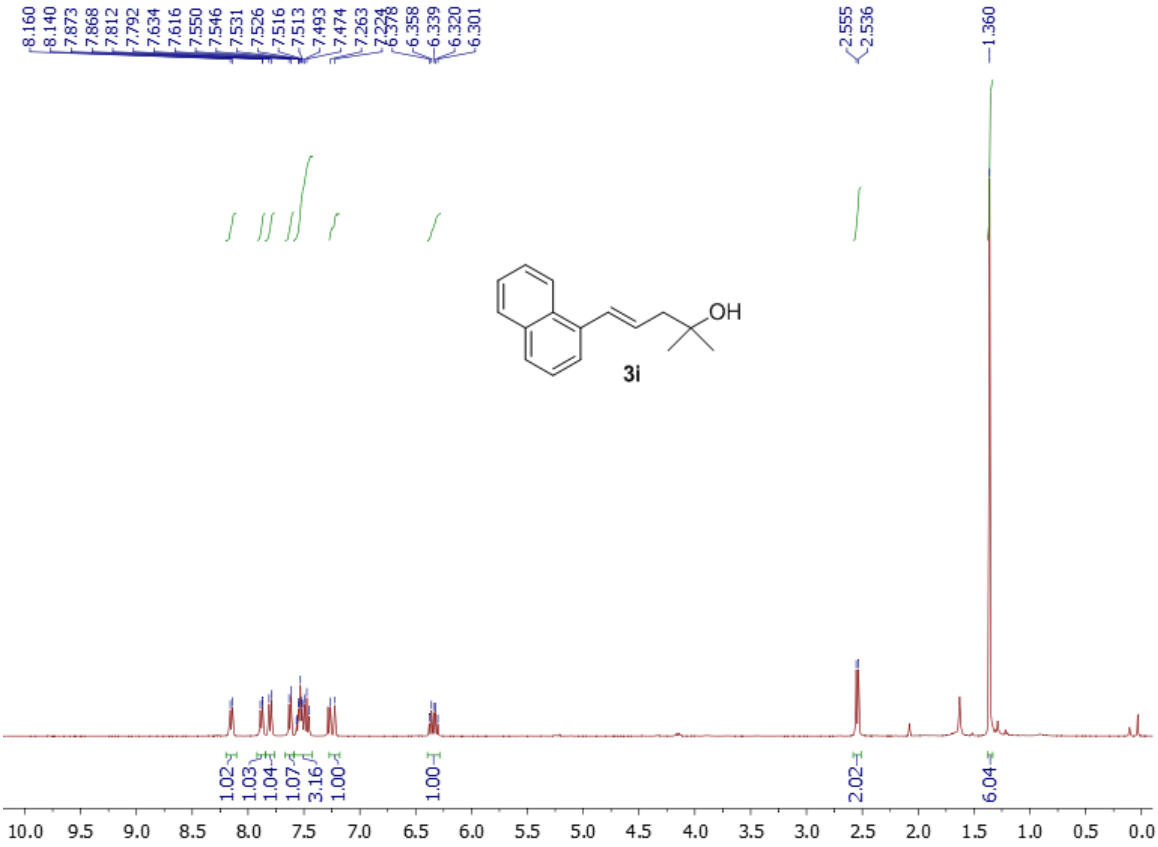

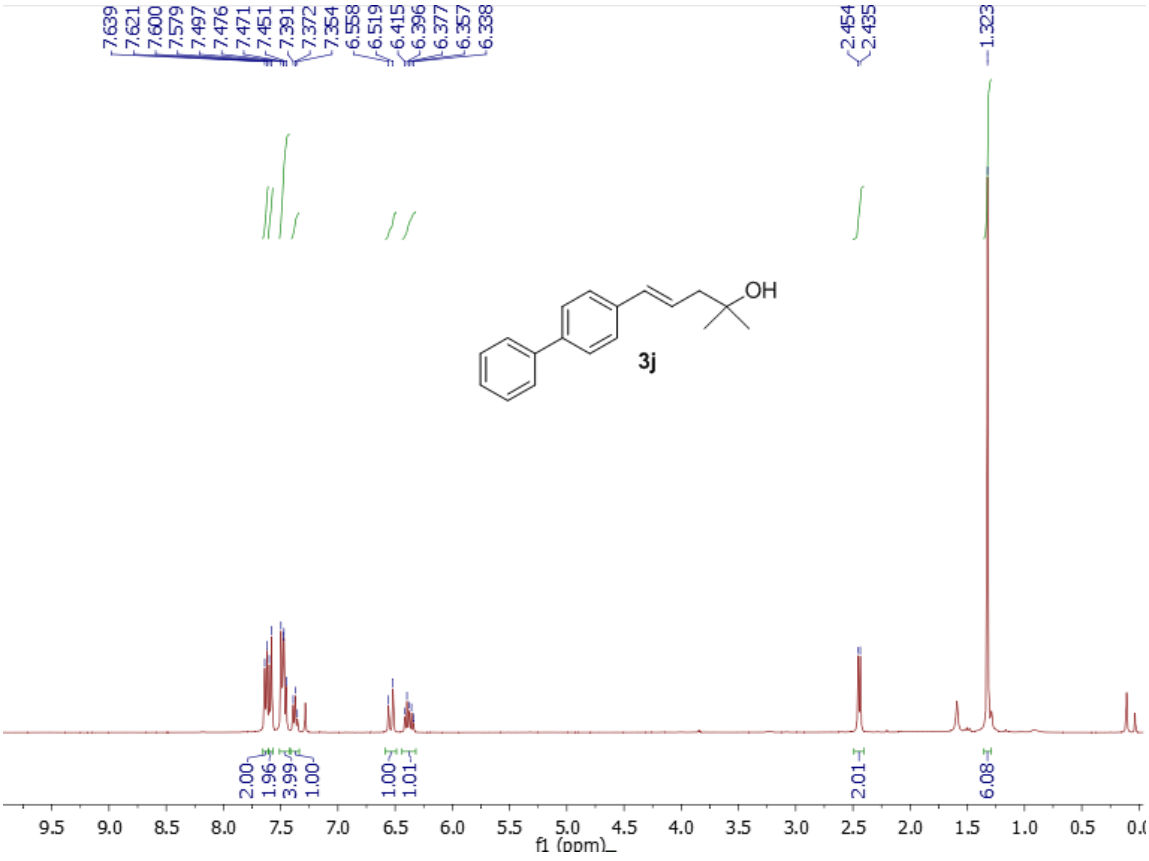

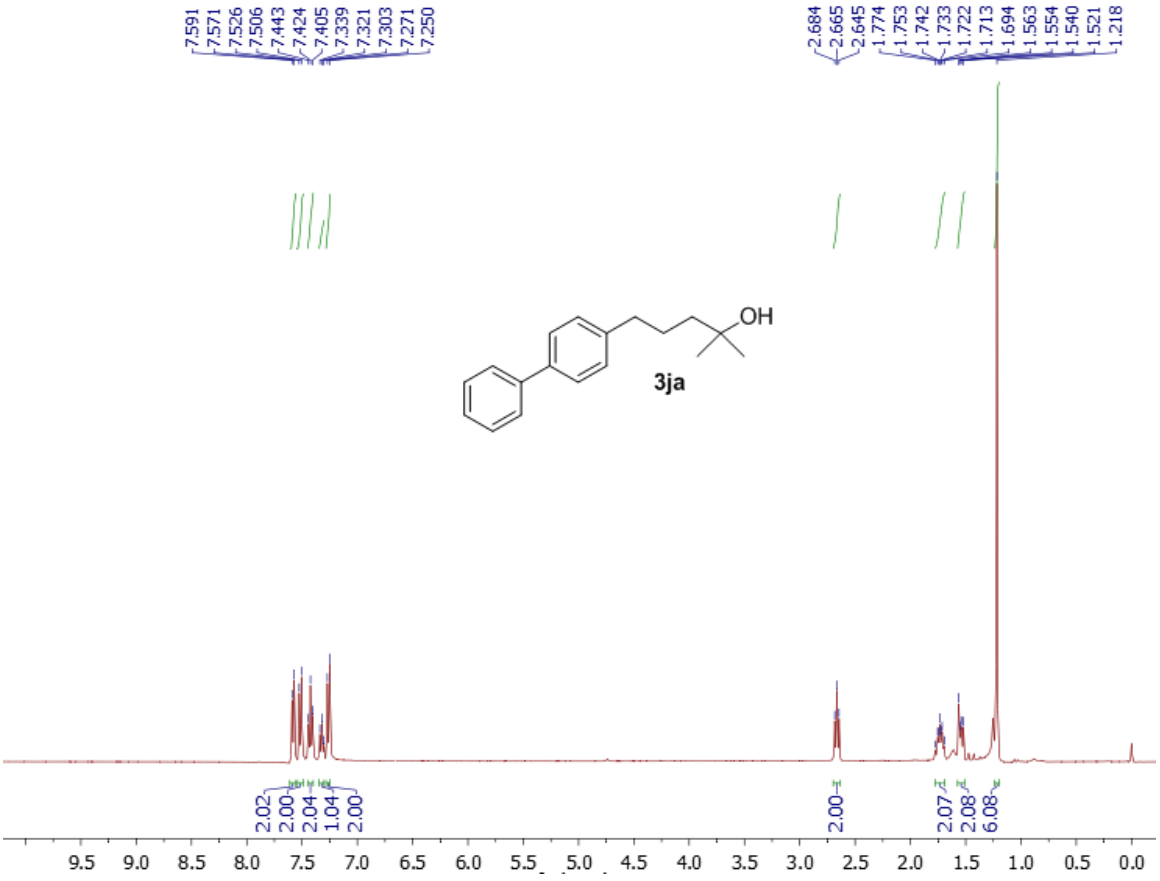
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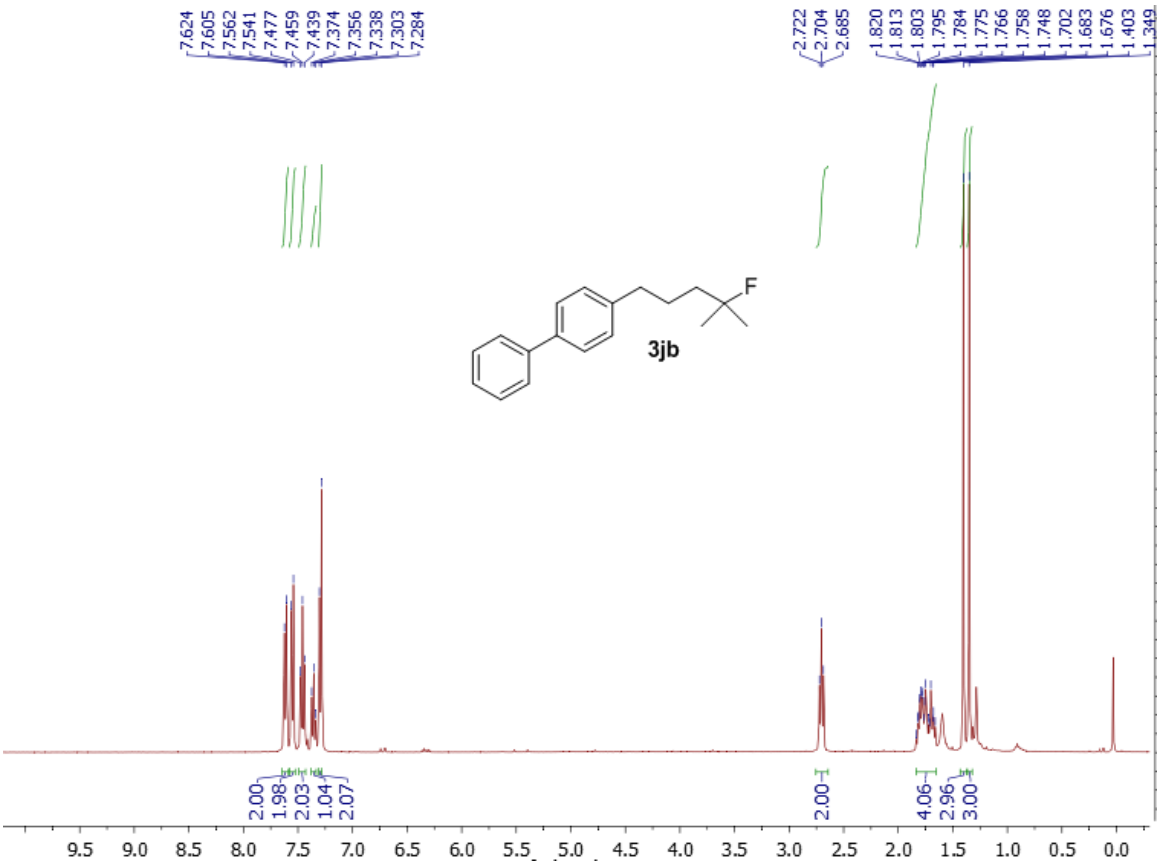
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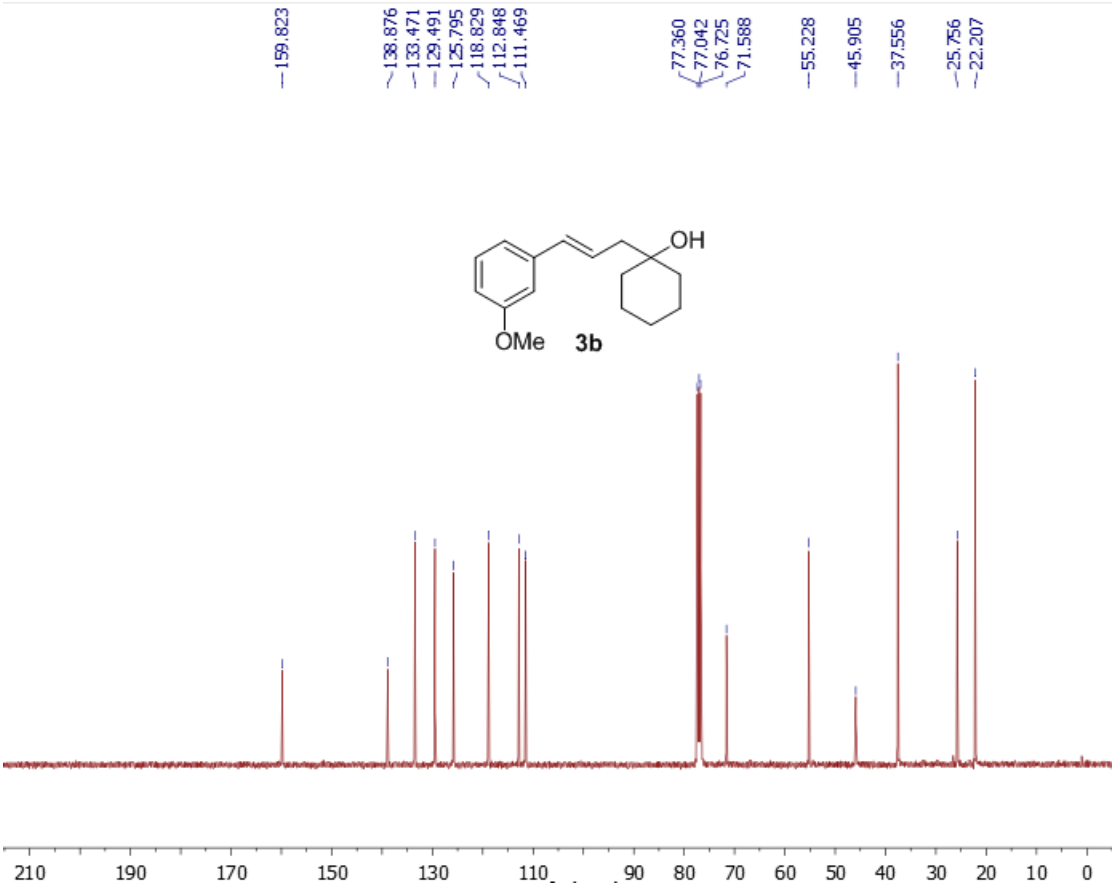
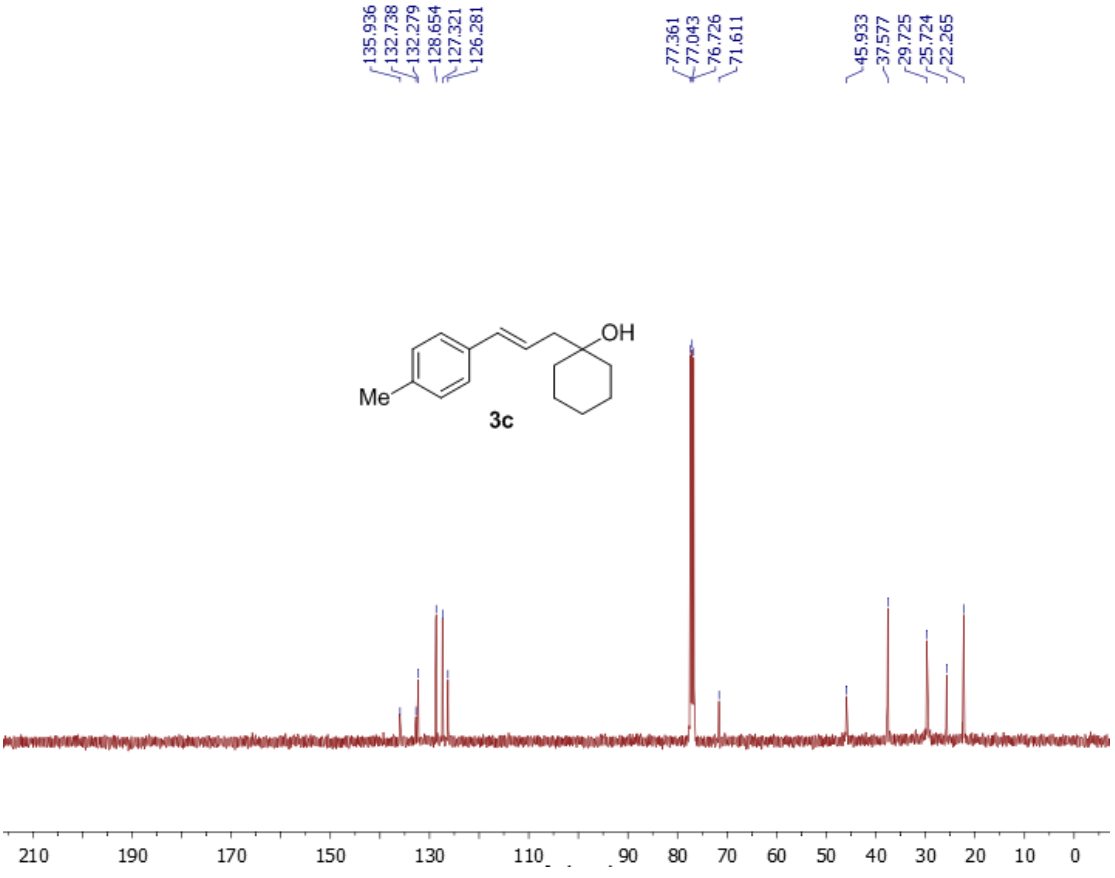
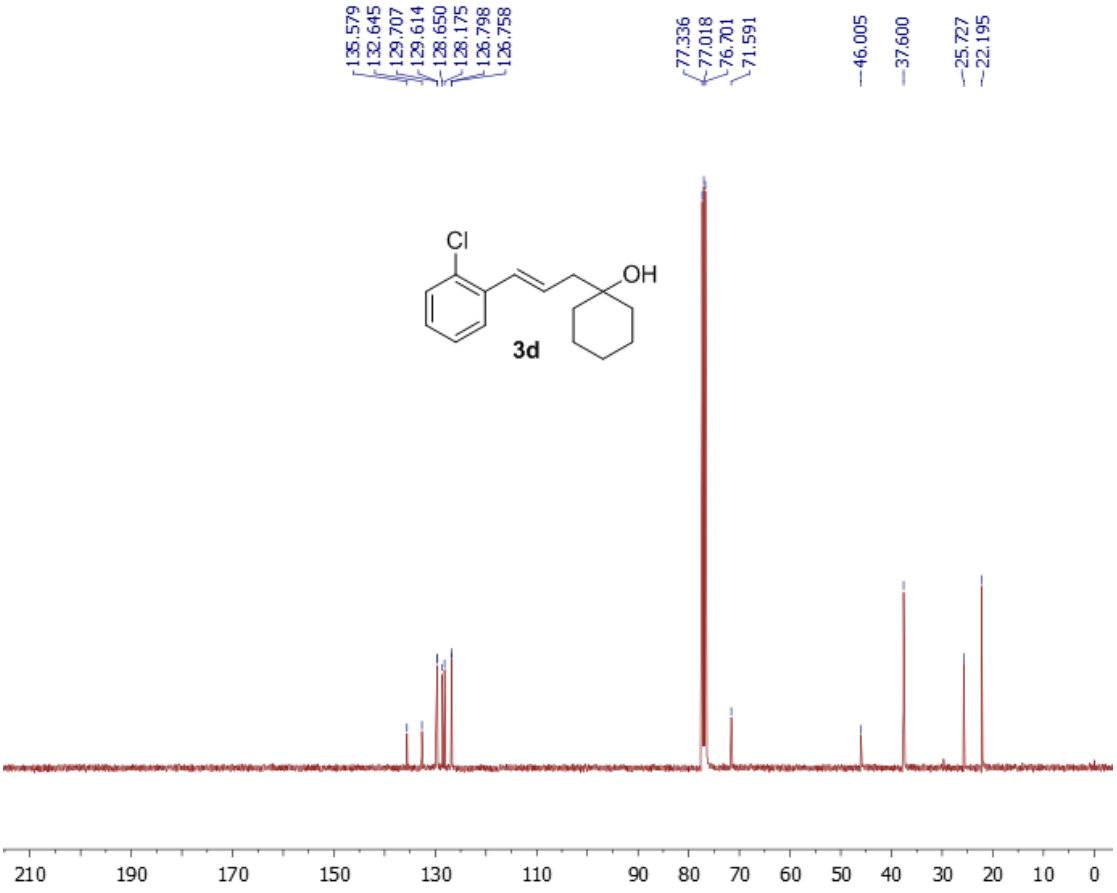
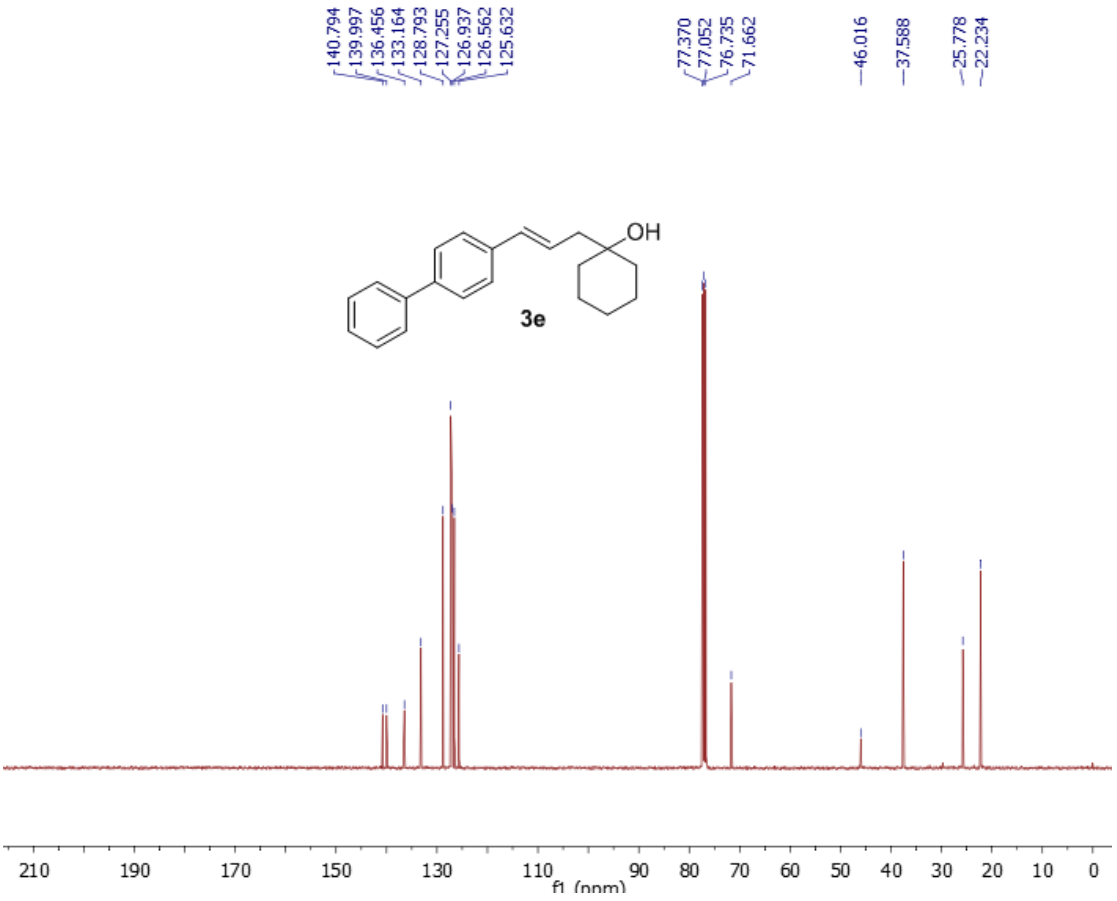
7.605
7.562
7.541
7.477
7.459
7.439
7.374
7.356
7.338
7.303
7.284
2.722
2.704
2.685
1.820
1.813
1.803
1.795
1.784
1.775
1.766
1.758
1.748
1.702
1.683
1.676
1.403
1.349
F
3jb
2.00
1.98
2.03
1.04
2.07
2.00
4.06
2.96
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

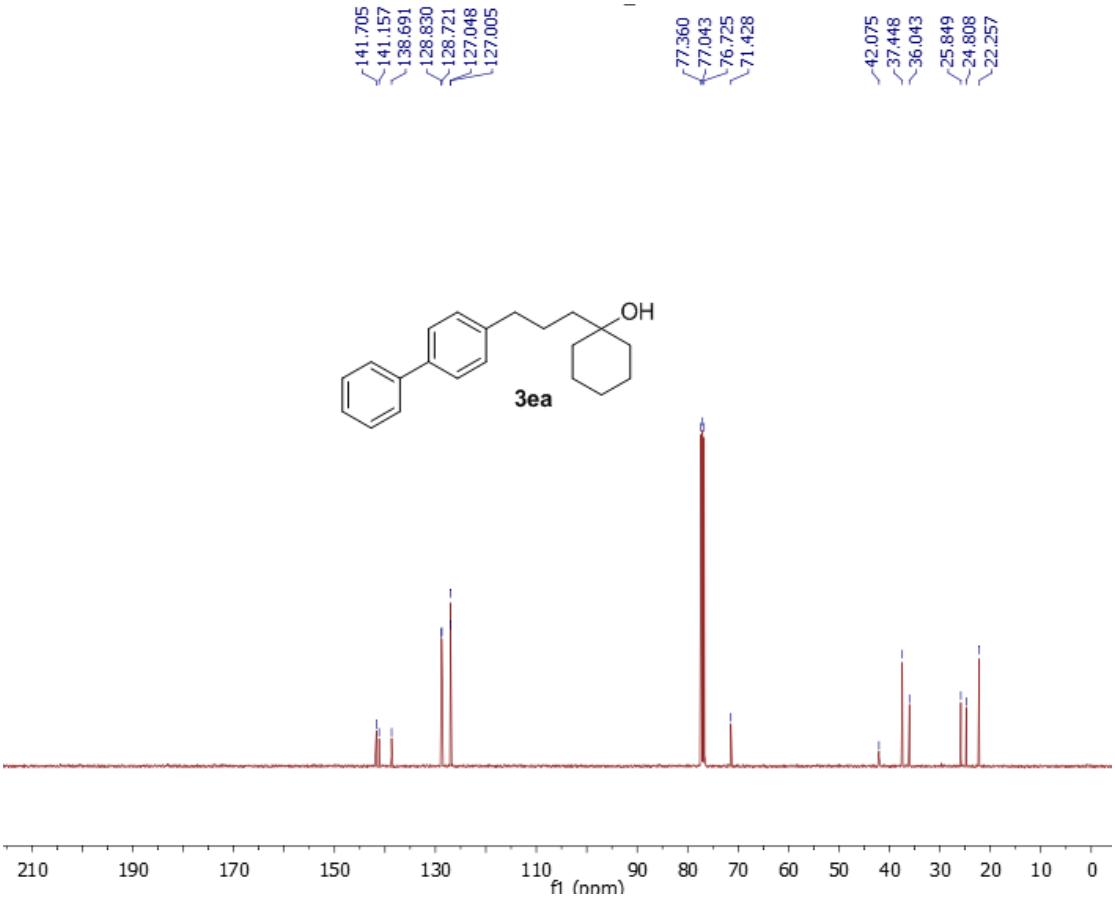
^{13}C NMR spectra

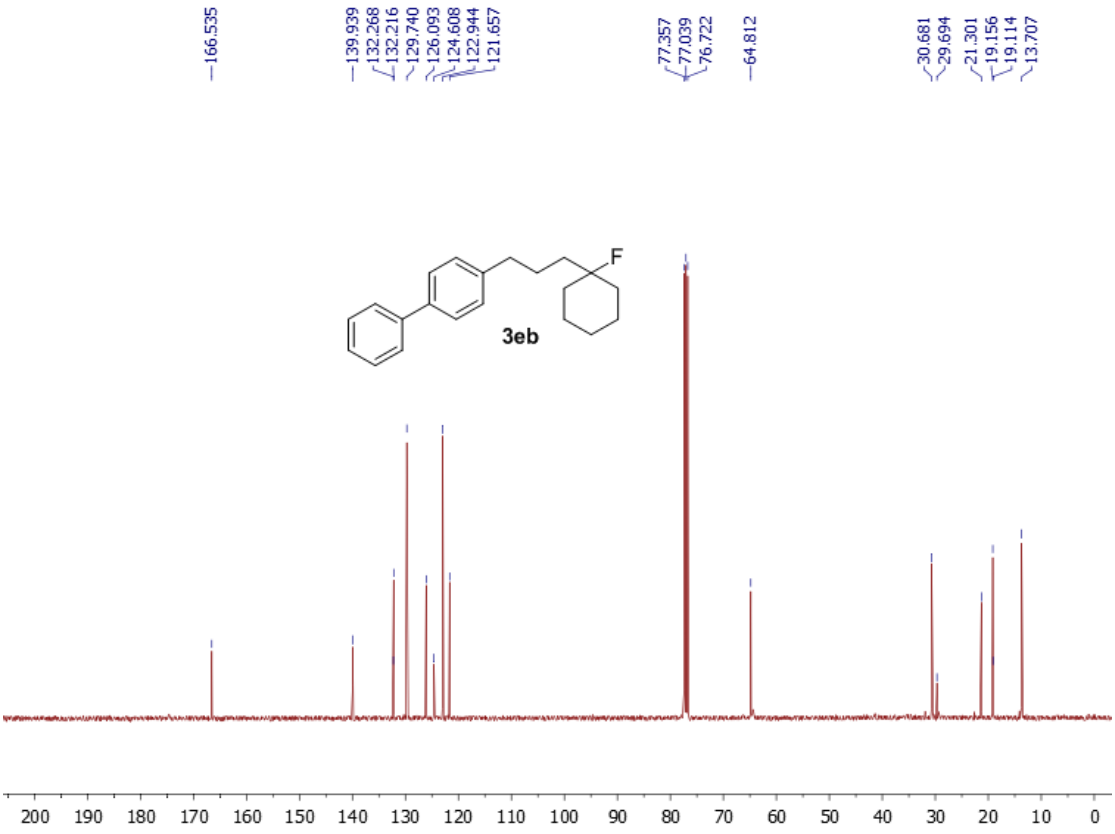


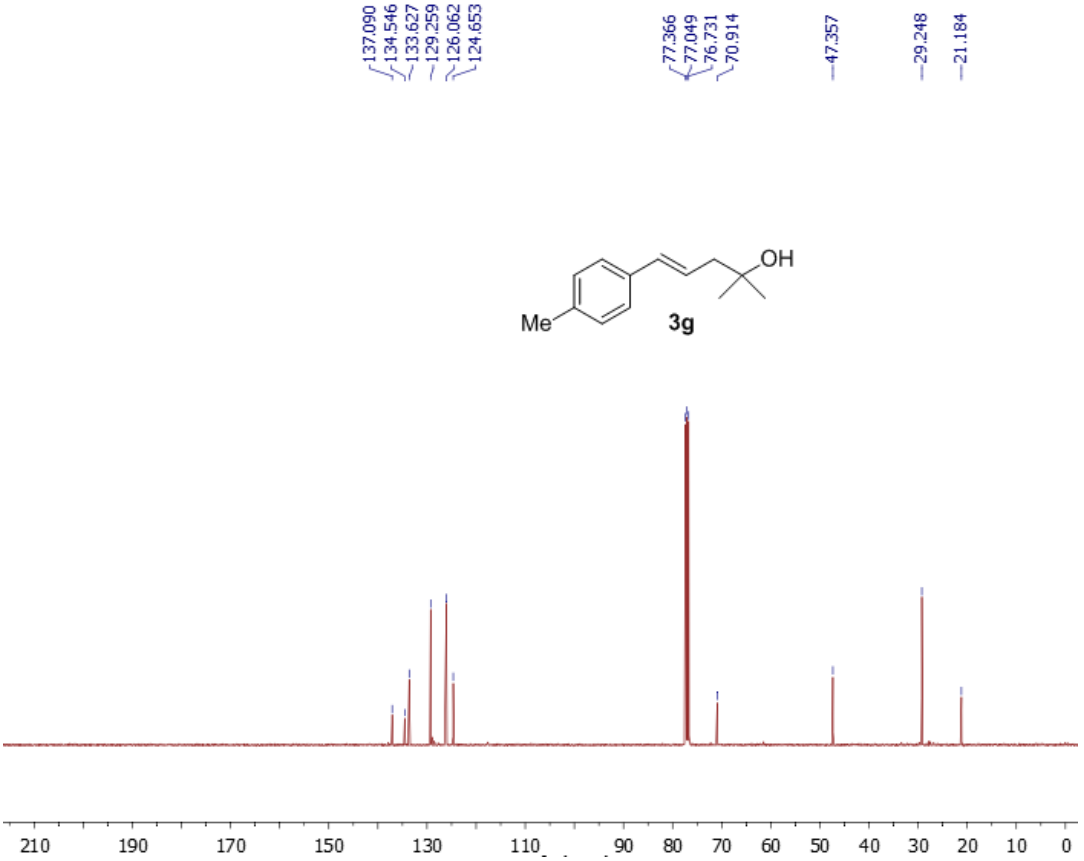








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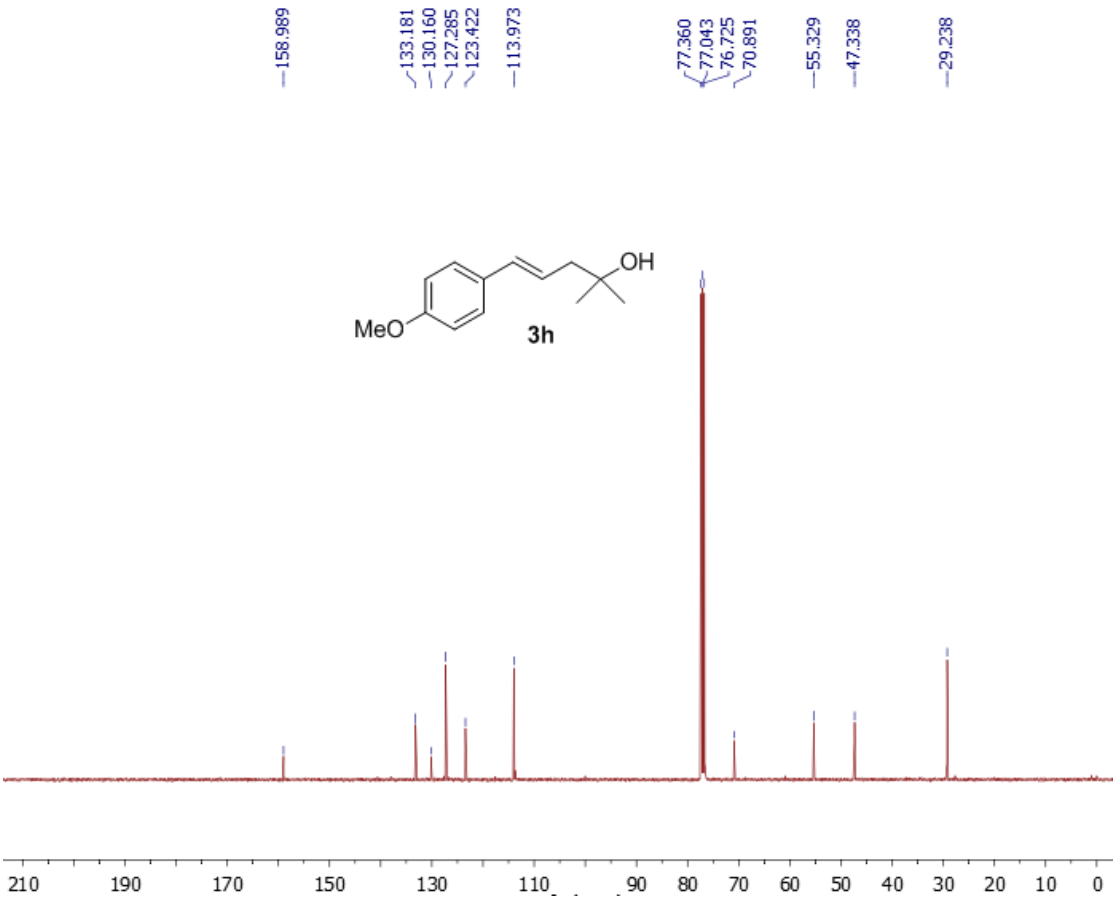
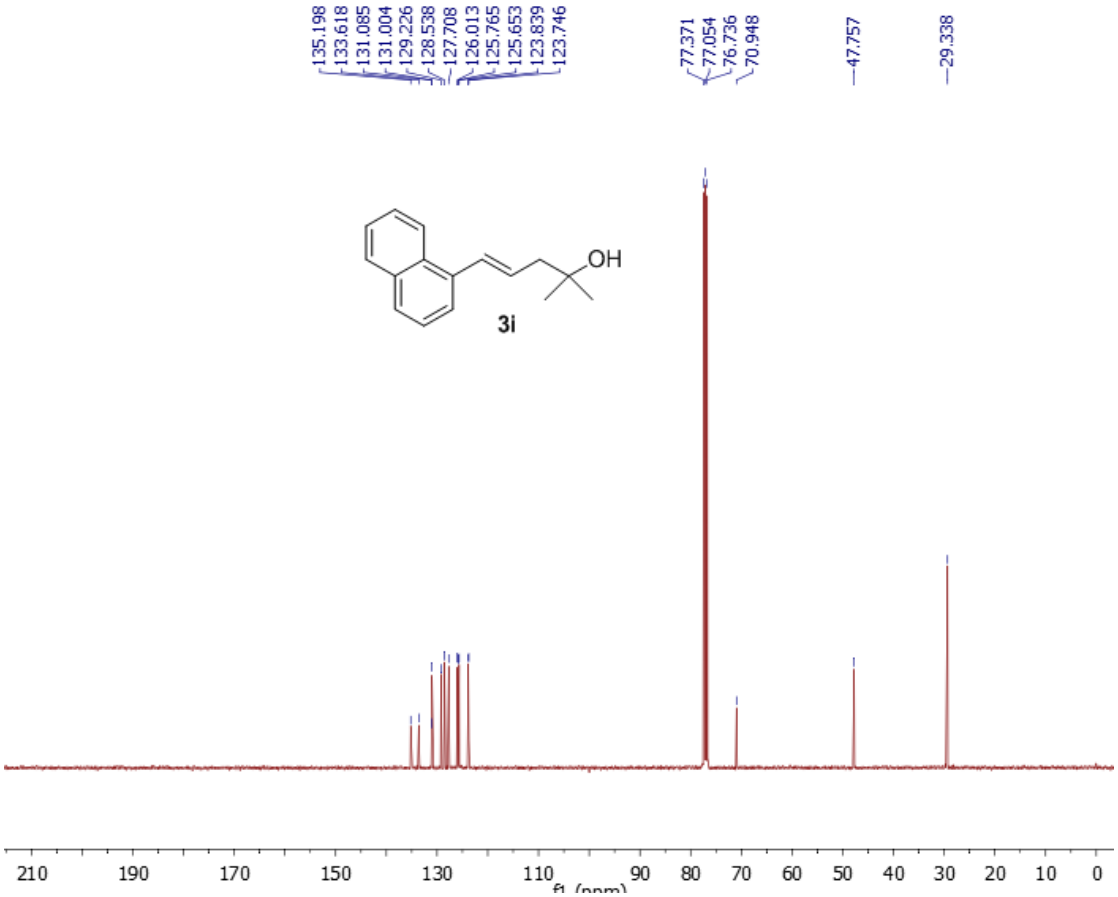
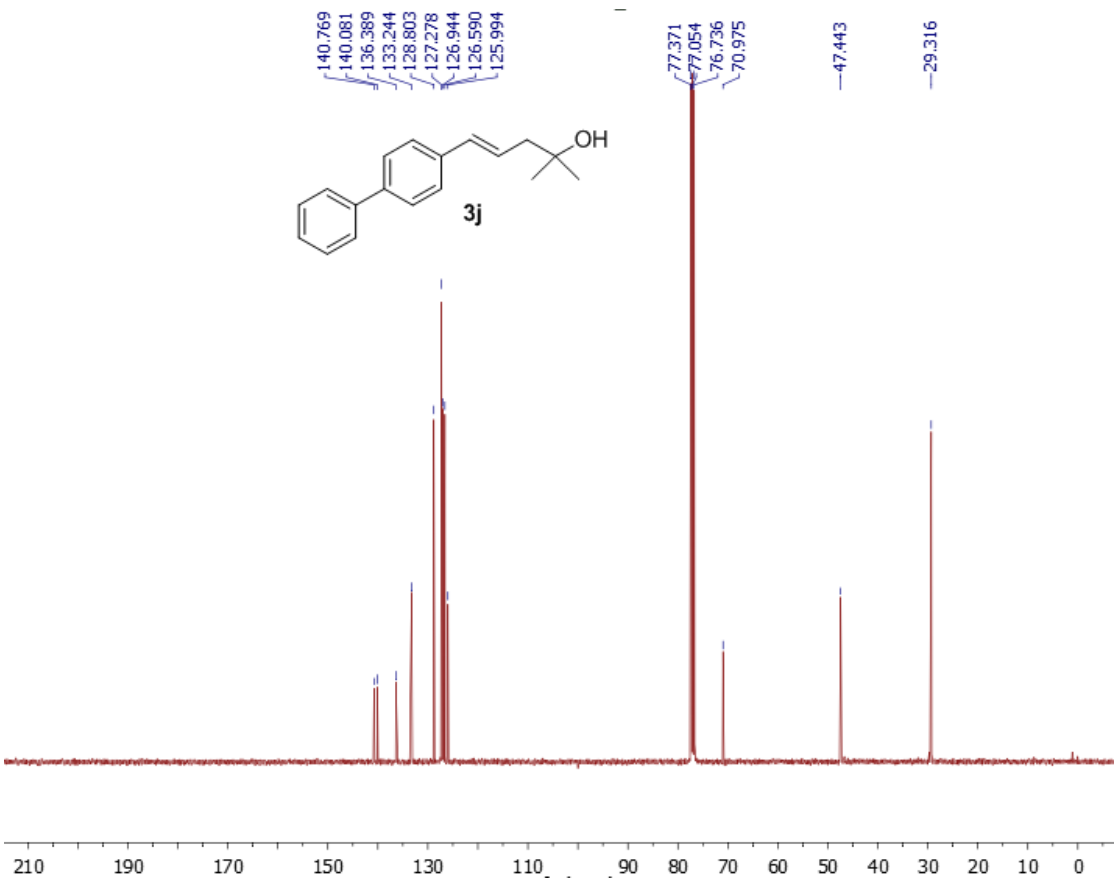
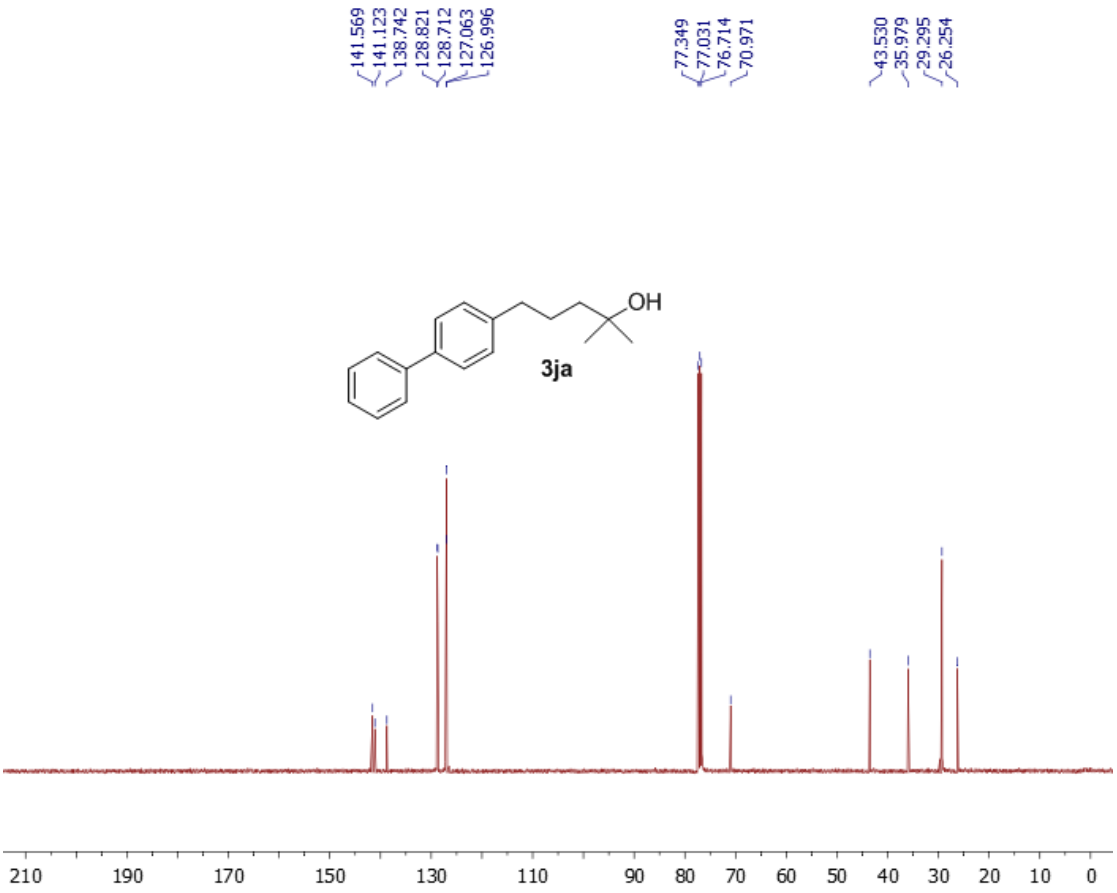
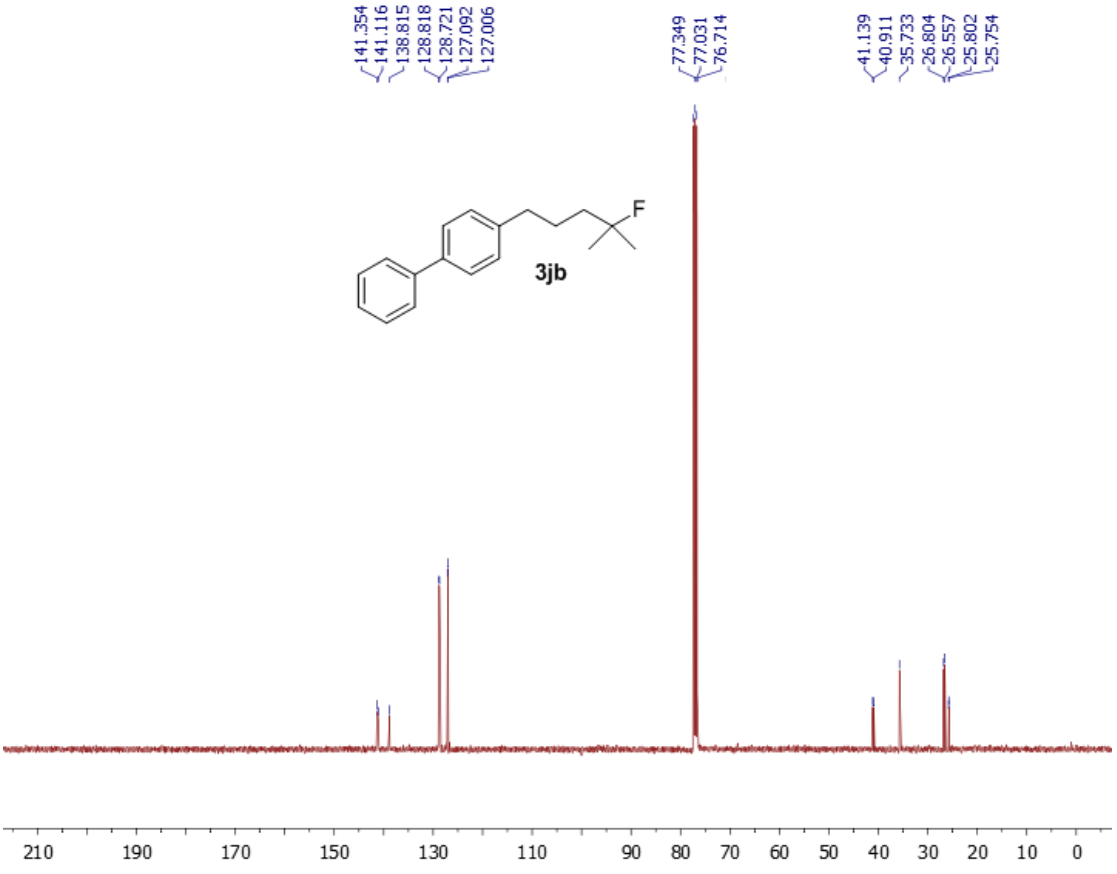
134.546
133.627
129.259
126.062
124.653
77.366
77.049
76.731
70.914
47.357
29.248
21.184
OH
Me
3g
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


158.989
133.181
130.160
127.285
123.422
113.973
77.360
77.043
76.725
70.891
55.329
47.338
29.238
OH
MeO
3h
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

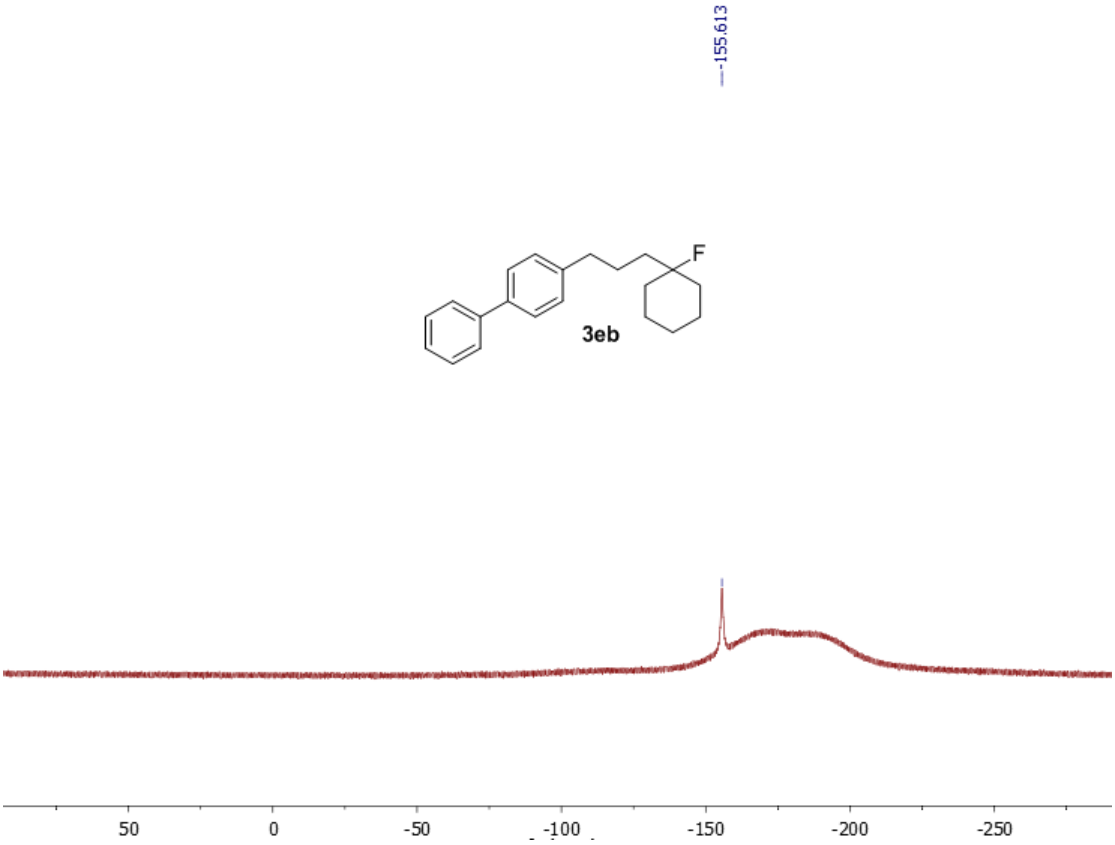


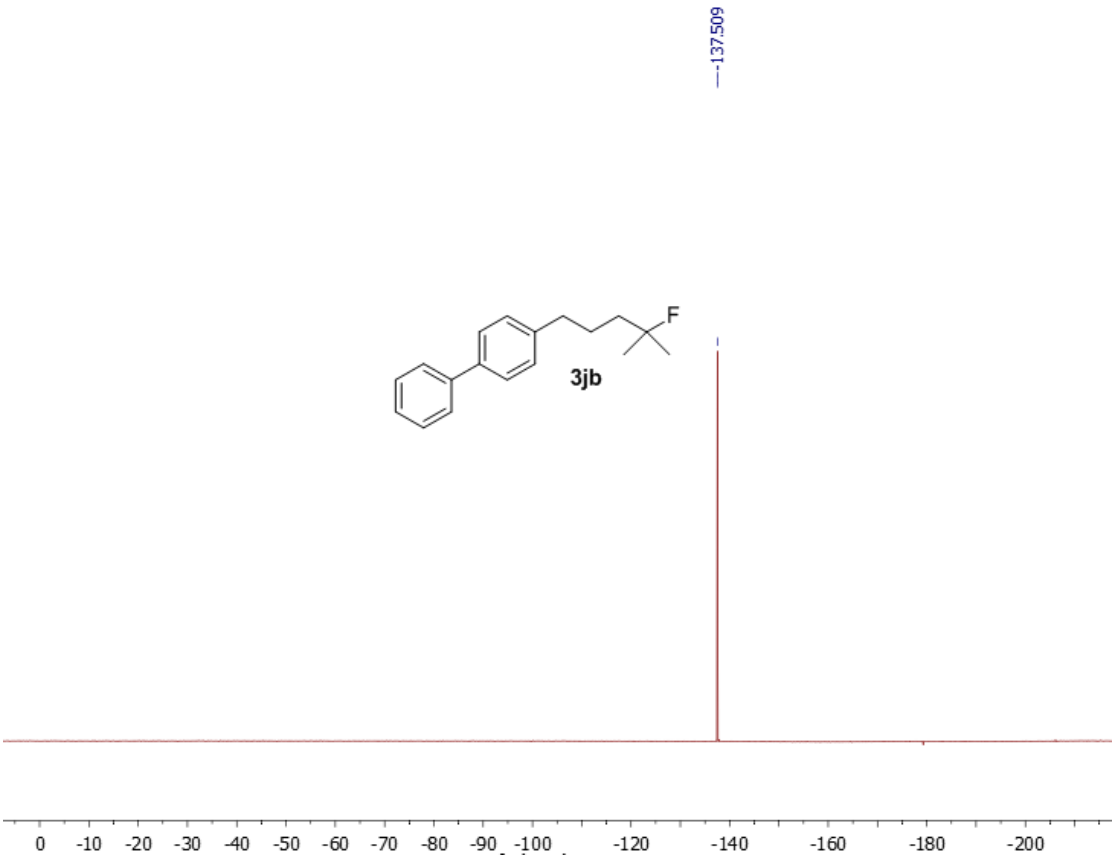






^{19}F NMR spectra





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