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Supporting Information

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**Cobalt(II)-Catalyzed Regio- and Stereoselective Hydroarylation of
Alkynes with Organoboronic Acids**

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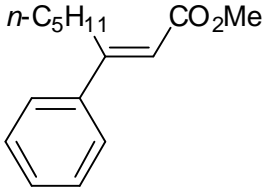
E-mail: chcheng@mx.nthu.edu.tw

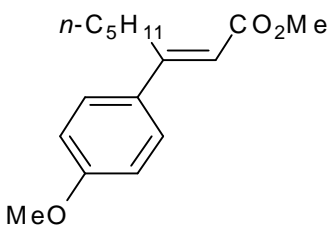
Supporting Information

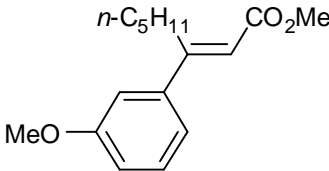
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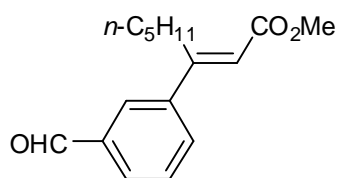
1	Spectral data for hydroarylation compounds 3 and 4	S2-S5
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General procedure for the addition reaction of arylboronic acid 1 with alkyne 2: A sealed tube containing $\text{Co}(\text{acac})_2$ (0.050 mmol, 5.0 mol%) and arylboronic acid 1 (2.00 mmol) was evacuated and purged with nitrogen gas three times. Freshly distilled solvents CH_3CN (1.6 mL) and THF (0.4 mL) and alkyne 2 (1.00 mmol) were added to the system. The dark-red reaction mixture was stirred at 80 °C for 12 h. The mixture was filtered through a short Celite column and a silica-gel pad and washed with dichloromethane. The filtrate was concentrated, and the residue was purified on a silica-gel column with hexanes/ethyl acetate as eluent to afford the desired addition product 3.

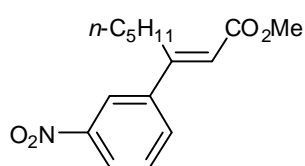

Methyl (*E*)-3-phenyl-2-octenoate (3aa): ^1H NMR (400 MHz; CDCl_3): δ = 0.83 (t, J = 7.2 Hz; 3 H; CH_3), 1.23-1.40 (m, 6 H; CH_2), 3.07 (t, J = 7.6 Hz; 2 H; CH_2), 3.73 (s, 3 H; OCH_3), 6.00 (s, 1 H; $\text{HC}=\text{C}$), 7.34-7.36 (m, 3 H; aromatic C-H), 7.40-7.42 (m, 2 H; aromatic C-H); ^{13}C NMR (100 MHz; CDCl_3): δ = 166.91 (C=O), 161.38 (C), 141.39 (C), 128.83 (CH), 128.49 (CH), 126.65 (CH), 116.70 (CH), 51.08 (CH_3), 31.88 (CH_2), 30.96 (CH_2), 28.69 (CH_2), 22.41 (CH_2), 13.98 ppm (CH_3); HRMS (EI): calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$: 232.1463 $[\text{M}]^+$; found: 232.1465. **Registry Number:** 189890-29-7.


Methyl (*E*)-3-(4-methoxyphenyl)-2-octenoate (3ba): ^1H NMR (400 MHz; CDCl_3): δ = 0.83 (t, J = 7.2 Hz; 3 H; CH_3), 1.25-1.43 (m, 6 H; CH_2), 3.05 (t, J = 7.6 Hz; 2 H; CH_2), 3.71 (s, 3 H; OCH_3), 3.81 (s, 3 H; OCH_3), 5.98 (s, 1 H; $\text{HC}=\text{C}$), 6.87 (d, J = 8.8 Hz; 2 H; aromatic C-H), 7.39 (d, J = 8.8 Hz; 2 H; aromatic C-H); ^{13}C NMR (100 MHz; CDCl_3): δ = 167.05 (C=O), 160.75 (C), 160.32 (C), 133.36 (C), 127.97 (CH), 114.89 (CH), 113.86 (CH), 55.29 (CH_3), 50.97 (CH_3), 31.93 (CH_2), 30.66 (CH_2), 28.91 (CH_2), 22.43 (CH_2), 13.99 ppm (CH_3); HRMS (EI): calcd for $\text{C}_{16}\text{H}_{22}\text{O}_3$: 262.1569 $[\text{M}]^+$; found: 262.1566. **Registry Number:** 176246-71-2.

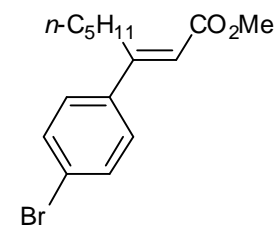

Methyl (*E*)-3-(3-methoxyphenyl)-2-octenoate (3ca): ^1H NMR (400 MHz; CDCl_3): δ = 0.83 (t, J = 7.2 Hz; 3 H; CH_3), 1.24-1.42 (m, 6 H; CH_2), 3.05 (t, J = 7.6 Hz; 2 H; CH_2), 3.72 (s, 3 H; OCH_3), 3.81 (s, 3 H; OCH_3), 6.00 (s, 1 H; $\text{HC}=\text{C}$), 6.88 (dd, J = 7.6 Hz, J = 2.4 Hz; 1 H; aromatic C-H), 6.92 (t, J = 2.0 Hz; 1 H; aromatic C-H), 6.99 (d, J = 7.6 Hz; 1 H; aromatic C-H), 7.27 (t, J = 7.6 Hz; 1 H; aromatic C-H); ^{13}C NMR (100 MHz; CDCl_3): δ = 166.83 (C=O), 161.19 (C), 159.62 (C), 142.95 (C), 129.45 (CH), 116.81 (CH), 114.07 (CH), 112.52 (CH), 55.23 (CH_3), 51.03 (CH_3), 31.87 (CH_2), 31.04 (CH_2), 28.66 (CH_2), 22.37 (CH_2), 13.94 ppm (CH_3); HRMS (EI): calcd for $\text{C}_{16}\text{H}_{22}\text{O}_3$: 262.1569 $[\text{M}]^+$; found: 262.1568.



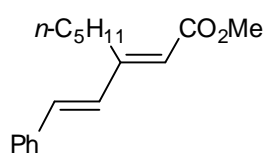
Methyl (*E*)-3-(3-formylphenyl)-2-octenoate (3da): ^1H NMR (400 MHz; CDCl_3): δ = 0.82 (t, J = 7.2 Hz; 3 H; CH_3), 1.22-1.40 (m, 6 H; CH_2), 3.09 (t, J = 7.6 Hz; 2 H; CH_2), 3.74 (s, 3 H; OCH_3), 6.04 (s, 1 H; HC=), 7.53 (t, J = 7.6 Hz; 1 H; aromatic C-H), 7.66 (dt, J = 7.6 Hz, J = 1.6 Hz; 1 H; aromatic C-H), 7.85 (d, J = 7.6 Hz; 1 H; aromatic C-H), 7.91 (s, 1 H; aromatic C-H), 10.02 (s, 1 H; aromatic CHO); ^{13}C NMR (100 MHz; CDCl_3): δ = 166.22 (C=O), 158.28 (C), 148.43 (C), 143.12 (C), 132.56 (CH), 129.59 (CH), 123.46 (CH), 121.60 (CH), 118.98 (CH), 51.32 (CH_3), 31.67 (CH_2), 30.78 (CH_2), 28.41 (CH_2), 22.29 (CH_2), 13.86 ppm (CH_3); HRMS (EI): calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$: 260.1412 [M] $^+$; found: 260.1412.



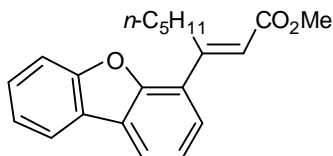
Methyl (*E*)-3-(3-nitrophenyl)-2-octenoate (3ea): ^1H NMR (400 MHz; CDCl_3): δ = 0.82 (t, J = 7.2 Hz; 3 H; CH_3), 1.23-1.40 (m, 6 H; CH_2), 3.10 (t, J = 7.6 Hz; 2 H; CH_2), 3.74 (s, 3 H; OCH_3), 6.04 (s, 1 H; HC=), 7.54 (t, J = 7.6 Hz; 1 H; aromatic C-H), 7.71 (dt, J = 7.6 Hz, J = 1.6 Hz; 1 H; aromatic C-H), 8.19 (dt, J = 7.6 Hz, J = 1.6 Hz; 1 H; aromatic C-H), 8.25 (t, J = 1.6 Hz; 1 H; aromatic C-H); ^{13}C NMR (100 MHz; CDCl_3): δ = 191.92 (C=O), 166.51 (C=O), 159.61 (C), 142.43 (C), 136.63 (C), 132.50 (CH), 130.03 (CH), 129.31 (CH), 127.71 (CH), 118.07 (CH), 51.21 (CH_3), 31.71 (CH_2), 30.83 (CH_2), 28.49 (CH_2), 22.32 (CH_2), 13.89 ppm (CH_3); HRMS (EI): calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_4$: 277.1314 [M] $^+$; found: 277.1319. **Registry Number:** 1033424-68-8.



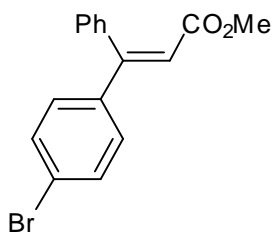
Methyl (*E*)-3-(4-bromophenyl)-2-octenoate (3fa): ^1H NMR (400 MHz; CDCl_3): δ = 0.83 (t, J = 7.2 Hz; 3 H; CH_3), 1.25-1.43 (m, 6 H; CH_2), 3.03 (t, J = 7.6 Hz; 2 H; CH_2), 3.72 (s, 3 H; OCH_3), 5.97 (s, 1 H; HC=), 7.27 (dd, J = 6.8 Hz, J = 2.0 Hz; 2 H; aromatic C-H), 7.47 (dd, J = 6.8 Hz, J = 2.0 Hz; 2 H; aromatic C-H); ^{13}C NMR (100 MHz; CDCl_3): δ = 166.61 (C=O), 159.85 (C), 140.31 (C), 131.69 (CH), 128.27 (CH), 123.04 (C), 117.20 (CH), 51.09 (CH_3), 31.77 (CH_2), 30.80 (CH_2), 28.57 (CH_2), 22.35 (CH_2), 13.91 ppm (CH_3); HRMS (EI): calcd for $\text{C}_{15}\text{H}_{19}\text{BrO}_2$: 310.0568 [M] $^+$ (^{79}Br); found: 310.0569. **Registry Number:** 1033424-53-1.



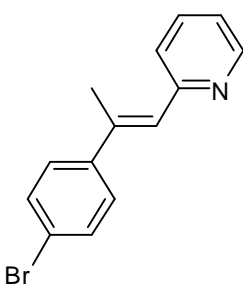
Methyl (2*E*,4*E*)-3-pentyl-5-phenyl-2,4-pentadienoate (3ga): ^1H NMR (400 MHz; CDCl_3): δ = 0.90 (t, J = 7.2 Hz; 3 H; CH_3), 1.33-1.55 (m, 6 H; CH_2), 2.89 (t, J = 7.6 Hz; 2 H; CH_2), 3.71 (s, 3 H; OCH_3), 5.85 (s, 1 H; HC=), 6.71 (d, J = 16.4 Hz; 1 H; HC=), 6.93 (d, J = 16.4 Hz; 1 H; HC=), 7.27-7.36 (m, 3 H; aromatic C-H), 7.46 (d, J = 7.2 Hz; 2 H; aromatic C-H); ^{13}C NMR (100 MHz; CDCl_3): δ = 167.00 (C=O), 157.57 (C), 136.38 (C), 133.78 (CH), 130.81 (CH), 128.75 (CH), 128.58 (CH), 127.02 (CH), 118.51 (CH), 51.00 (CH_3), 32.19 (CH_2), 29.51 (CH_2), 27.64 (CH_2), 22.51 (CH_2), 14.04 ppm (CH_3); HRMS (EI): calcd for $\text{C}_{17}\text{H}_{22}\text{O}_2$: 258.1620 [M] $^+$; found: 258.1617.



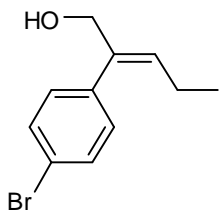
Methyl (*E*)-3-dibenzo[*b,d*]furan-4-yl-2-octenoate (3ha): ^1H NMR (400 MHz; CDCl_3): δ = 0.80 (t, J = 7.2 Hz; 3 H; CH_3), 1.24-1.45 (m, 6 H; CH_2), 3.30 (t, J = 7.6 Hz; 2 H; CH_2), 3.78 (s, 3 H; OCH_3), 6.35 (s, 1 H; $\text{HC}=\text{C}$), 7.31-7.36 (m, 2 H; aromatic C-H), 7.41 (d, J = 6.8 Hz; 1 H; aromatic C-H), 7.46 (t, J = 7.6 Hz; 1 H; aromatic C-H), 7.93 (t, J = 8.8 Hz; 2 H; aromatic C-H), 7.59 (d, J = 7.6 Hz; 1 H; aromatic C-H); ^{13}C NMR (100 MHz; CDCl_3): δ = 166.93 (C=O), 157.24 (C), 155.98 (C), 153.14 (C), 127.39 (CH), 126.34 (CH), 126.31 (C), 124.84 (C), 123.81 (C), 122.91 (CH), 122.84 (CH), 120.84 (CH), 120.61 (CH), 119.62 (CH), 51.17 (CH_3), 31.80 (CH_2), 31.19 (CH_2), 28.55 (CH_2), 22.39 (CH_2), 13.95 ppm (CH_3); HRMS (EI): calcd for $\text{C}_{21}\text{H}_{22}\text{O}_3$: 322.1569 $[\text{M}]^+$; found: 322.1571.



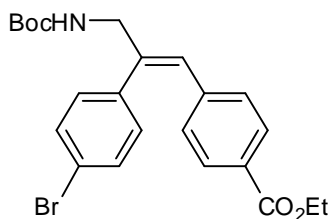
Methyl (*E*)-3-(4-bromophenyl)-3-phenyl-2-propenoate (3fb): ^1H NMR (400 MHz; CDCl_3): δ = 3.59 (s, 3 H; OCH_3), 6.33 (s, 1 H; $\text{HC}=\text{C}$), 7.14 (dt, J = 8.0 Hz, J = 2.0 Hz; 2 H; aromatic C-H), 7.16-7.18 (m, 2 H; aromatic C-H), 7.37-7.39 (m, 3 H; aromatic C-H), 7.43 (dt, J = 6.8 Hz, J = 2.0 Hz; 2 H; aromatic C-H); ^{13}C NMR (100 MHz; CDCl_3): δ = 166.17 (C=O), 155.76 (C), 139.73 (C), 138.23 (C), 131.59 (CH), 129.82 (CH), 129.05 (CH), 128.44 (CH), 128.01 (CH), 123.92 (C), 117.17 (CH), 51.32 ppm (CH_3); HRMS (EI): calcd for $\text{C}_{16}\text{H}_{13}\text{BrO}_2$: 316.0099 $[\text{M}]^+$ (^{79}Br); found: 316.0102.



2-[(*Z*)-1-(4-bromophenyl)-1-propenyl]pyridine (3fc): ^1H NMR (400 MHz; CDCl_3): δ = 2.47 (s, 3 H; CH_3), 6.80 (s, 1 H; $\text{HC}=\text{C}$), 7.10-7.13 (m, 1 H; aromatic C-H), 7.29 (d, J = 8.0 Hz; 1 H; aromatic C-H), 7.41 (d, J = 8.4 Hz; 2 H; aromatic C-H), 7.48 (d, J = 8.4 Hz; 2 H; aromatic C-H), 7.66 (td, J = 8.0 Hz, J = 1.6 Hz; 1 H; aromatic C-H), 7.63 (d, J = 4.0 Hz; 1 H; aromatic C-H); ^{13}C NMR (100 MHz; CDCl_3): δ = 156.85 (C), 149.24 (CH), 142.84 (C), 140.59 (C), 136.04 (CH), 131.41 (CH), 127.78 (CH), 127.27 (CH), 124.64 (CH), 121.54 (C), 121.18 (CH), 17.55 ppm (CH_3); HRMS (EI): calcd for $\text{C}_{14}\text{H}_{12}\text{BrN}$: 273.0153 $[\text{M}]^+$ (^{79}Br); found: 273.0150. **Registry Number:** 58754-30-6.

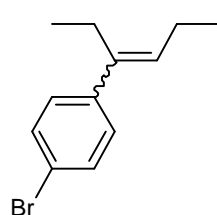


(*E*)-2-(4-bromophenyl)-2-penten-1-ol (4fd): ^1H NMR (400 MHz; CDCl_3): δ = 0.94 (t, J = 7.6 Hz; 3 H; CH_3), 1.98 (quintet, 2 H; J = 7.6 Hz; CH_2), 4.28 (d, 2 H; J = 0.8 Hz; CH_2), 5.72 (t, J = 7.6 Hz; 1 H; $\text{HC}=\text{C}$), 7.08 (d, J = 8.4 Hz; 2 H; aromatic C-H), 7.46 (d, J = 8.4 Hz; 2 H; aromatic C-H); ^{13}C NMR (100 MHz; CDCl_3): δ = 138.41 (C), 137.42 (C), 131.66 (CH), 131.42 (CH), 130.32 (CH), 121.05 (C), 67.87 (CH_2), 21.91 (CH_2), 14.23 ppm (CH_3); HRMS (EI): calcd for $\text{C}_{11}\text{H}_{13}\text{BrO}$: 240.0150 $[\text{M}]^+$ (^{79}Br); found: 240.0149.

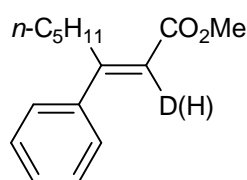


Ethyl-4-((E)-2-(4-bromophenyl)-3-[(tert-butoxycarbonyl)-

amino]-1-propenyl}benzoate (4fe): ^1H NMR (400 MHz; CDCl_3): δ = 1.31 (t, J = 7.2 Hz; 3 H; CH_3), 1.39 (s, 9 H; CH_3), 4.09 (d, 2 H; J = 6.0 Hz; CH_2), 4.28 (q, 2 H; J = 7.2 Hz; CH_2), 4.81 (s, 1 H; NH), 6.57 (s, 1 H; HC=), 6.97 (d, J = 8.0 Hz; 2 H; aromatic C-H), 7.01 (d, J = 8.0 Hz; 2 H; aromatic C-H), 7.40 (d, J = 8.0 Hz; 2 H; aromatic C-H), 7.77 (d, J = 8.0 Hz; 2 H; aromatic C-H); ^{13}C NMR (100 MHz; CDCl_3): δ = 166.26 (C=O), 155.64 (C=O), 140.80 (C), 140.53 (C), 137.13 (C), 131.93 (CH), 130.35 (CH), 129.22 (CH), 128.98 (CH), 128.59 (C), 79.64 (C), 60.82 (CH_2), 47.75 (CH_2), 28.25 (CH_3), 14.22 ppm (CH_3); HRMS (EI): calcd for $\text{C}_{23}\text{H}_{26}\text{BrNO}_4$: 459.1045 $[\text{M}]^+$ (^{79}Br); found: 459.1049.

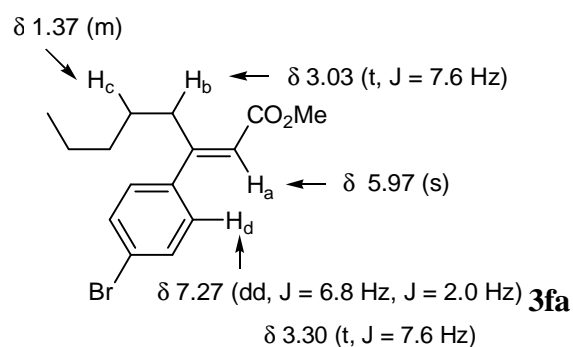


3-(4-bromophenyl)-3-hexene (3ff/4ff): ^1H NMR (400 MHz; CDCl_3): δ = 0.87-0.96 (m, 9 H; CH_3), 1.03 (t, J = 7.6 Hz; 3 H; CH_3), 1.88 (quintet, J = 7.6 Hz; 2 H; CH_2), 2.17 (quintet, J = 7.6 Hz; 2 H; CH_2), 2.27 (q, J = 7.6 Hz; 2 H; CH_2), 2.45 (q, J = 7.6 Hz; 2 H; CH_2), 5.41 (t, J = 7.2 Hz; 1 H; HC=), 5.60 (t, J = 7.2 Hz; 1 H; HC=), 6.99 (d, J = 8.4 Hz; 2 H; aromatic C-H), 7.19 (d, J = 8.4 Hz; 2 H; aromatic C-H), 7.39 (d, J = 8.4 Hz; 2 H; aromatic C-H), 7.42 (d, J = 8.4 Hz; 2 H; aromatic C-H); ^{13}C NMR (100 MHz; CDCl_3): δ = 141.95 (C), 140.79 (C), 140.43 (C), 139.96 (C), 131.16 (CH), 131.08 (CH), 130.60 (CH), 130.14 (CH), 128.36 (CH), 127.93 (CH), 120.14 (C), 109.75 (C), 31.79 (CH_2), 22.67 (CH_2), 22.15 (CH_2), 21.71 (CH_2), 14.61 (CH_3), 14.36 (CH_3), 13.57 (CH_3), 13.02 ppm (CH_3); HRMS (EI): calcd for $\text{C}_{12}\text{H}_{15}\text{Br}$: 238.0357 $[\text{M}]^+$ (^{79}Br); found: 238.0358.

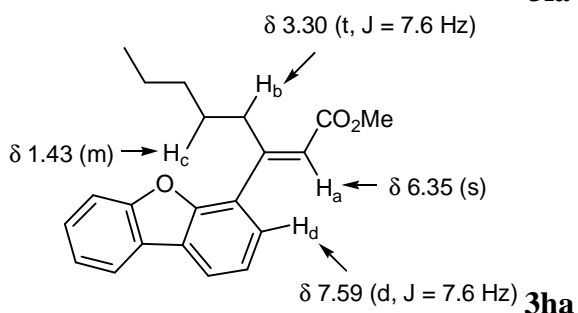


Methyl (E)-3-phenyl-2-octenoate (3aa-D): ^1H NMR (400 MHz; CDCl_3): δ = 0.83 (t, 3 H; J = 7.2 Hz; CH_3), 1.23-1.40 (m, 6 H; CH_2), 3.07 (t, J = 7.6 Hz; 2 H; CH_2), 3.73 (s, 3 H; OCH_3), 7.34-7.36 (m, 3 H; aromatic C-H), 7.40-7.42 (m, 2 H; aromatic C-H); ^{13}C NMR (125 MHz; CDCl_3): δ = 166.89 (C=O), 161.37 (C), 161.31 (C), 141.38 (C), 141.34 (C), 128.82 (CH), 128.48 (CH), 126.64 (CH), 116.69 (CH), 116.38 (C, $J_{\text{C-D}}$ = 20.375 Hz), 51.06 (CH_3), 31.87 (CH_2), 30.95 (CH_2), 28.68 (CH_2), 22.40 (CH_2), 13.97 ppm (CH_3); HRMS (EI): calcd for $\text{C}_{15}\text{H}_{19}\text{DO}_2$: 233.1526 $[\text{M}]^+$; found: 233.1524. **Registry Number:** 1033424-99-5.

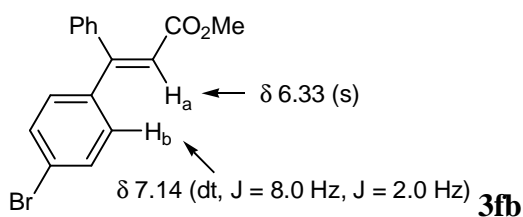
The data of NOE experiments for hydroarylation adducts **3fa**, **3ha**, **3fb**, and **4fd** were recorded on the VARIAN UNITYINOVA 500 NMR spectrometer, and products **3fc** and **4fe** were recorded on the BRUKER DMX-600 NMR spectrometer.



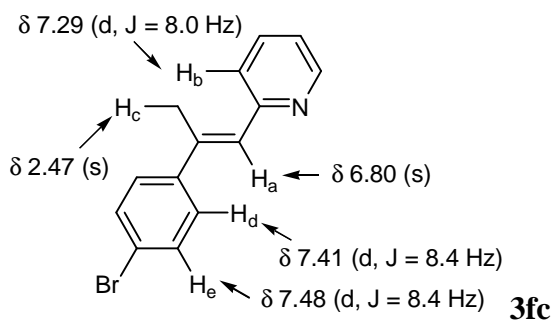
Irradiate	Observed Enhancement (%)
H _a	H _d (2.01)
H _b	H _d (2.07), H _c (1.47)



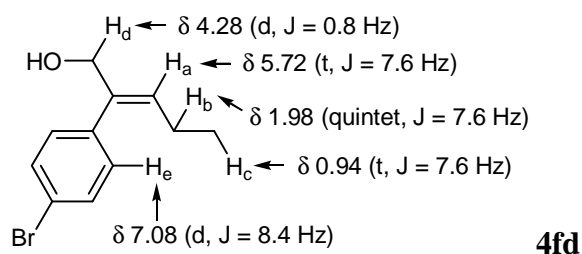
Irradiate	Observed Enhancement (%)
H _a	H _d (1.30)
H _b	H _c (1.57), H _d (0.64)



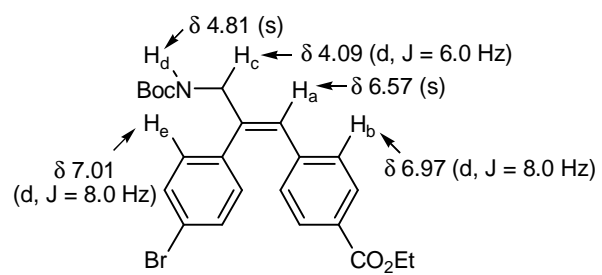
Irradiate	Observed Enhancement (%)
H _a	H _b (4.54)



Irradiate	Observed Enhancement (%)
H _a	H _d (6.20), H _b (2.39)
H _c	H _d (2.25), H _b (0.33)
H _d	H _e (4.85), H _a (3.67), H _c (2.81)



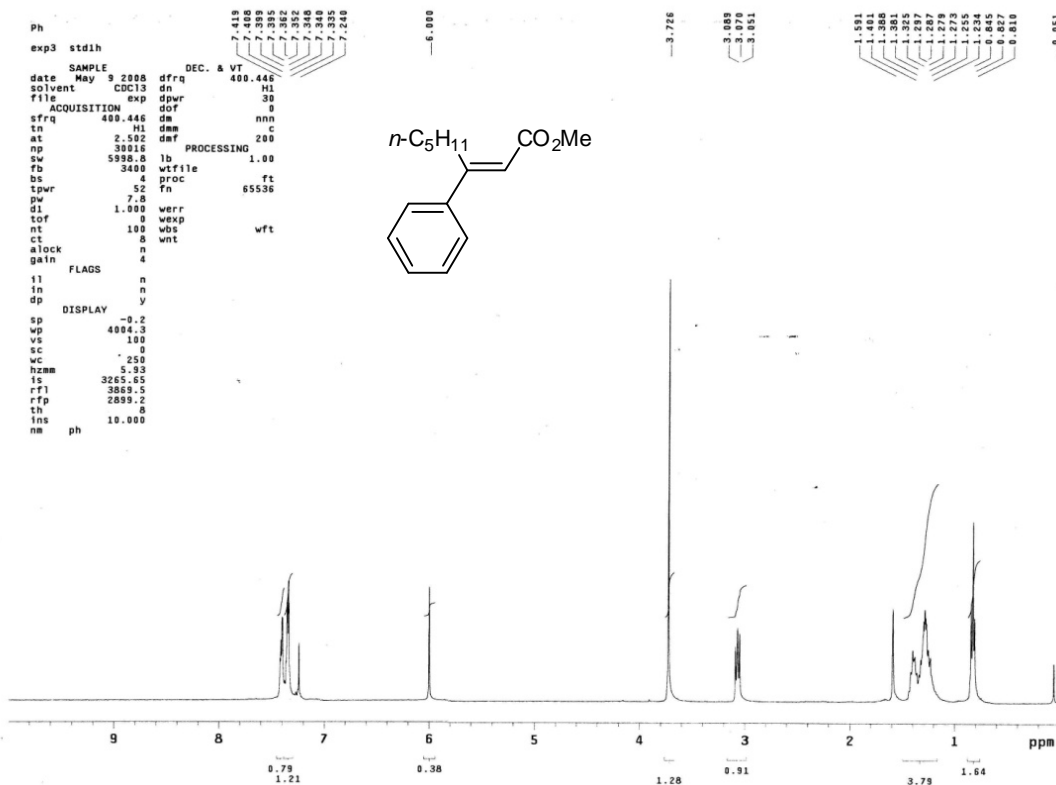
Irradiate	Observed Enhancement (%)
H _a	H _b (1.13), H _d (0.90), H _c (0.62)
H _b	H _c (0.89), H _a (0.56), H _e (0.40)



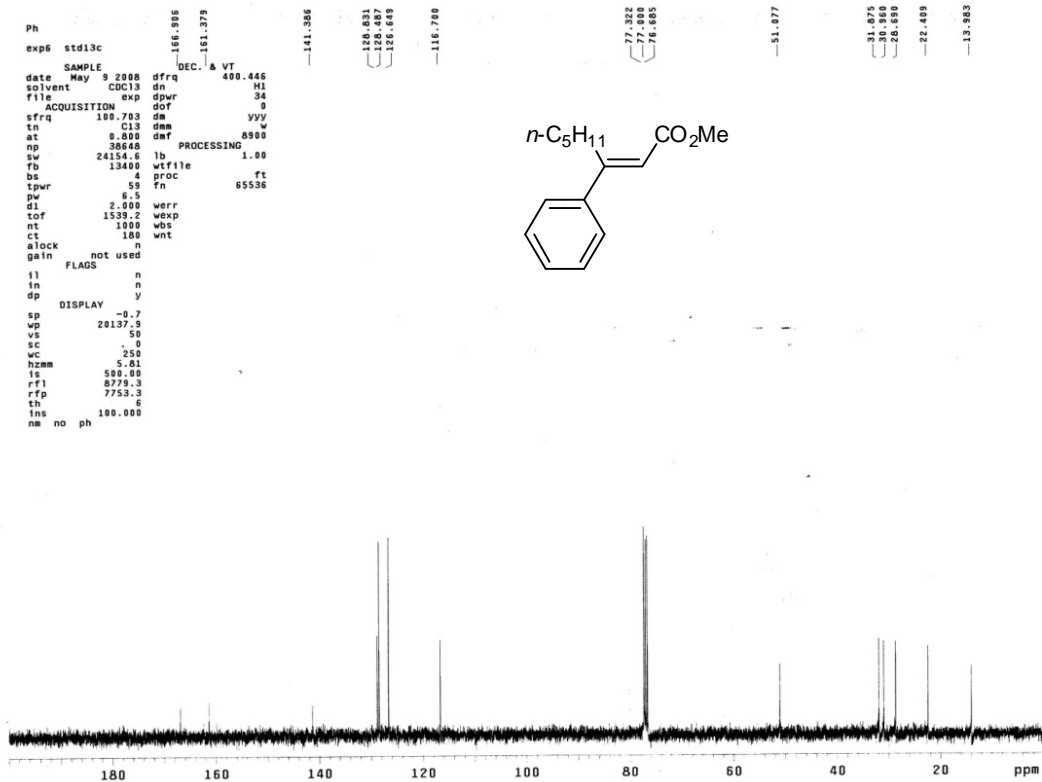
4fe

Irradiate	Observed Enhancement (%)
H _a	H _b (9.6), H _c (4.8), H _d (2.6)
H _c	H _a (5.72), H _e (5.06), H _d (4.31)

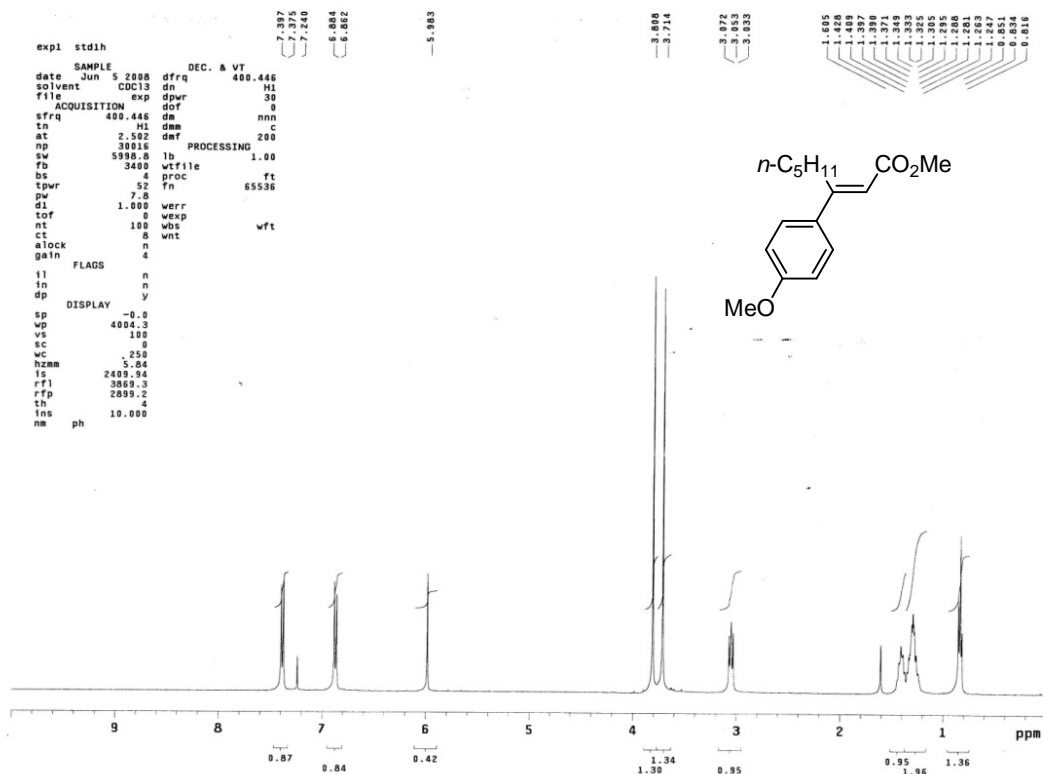
¹H NMR for 3aa



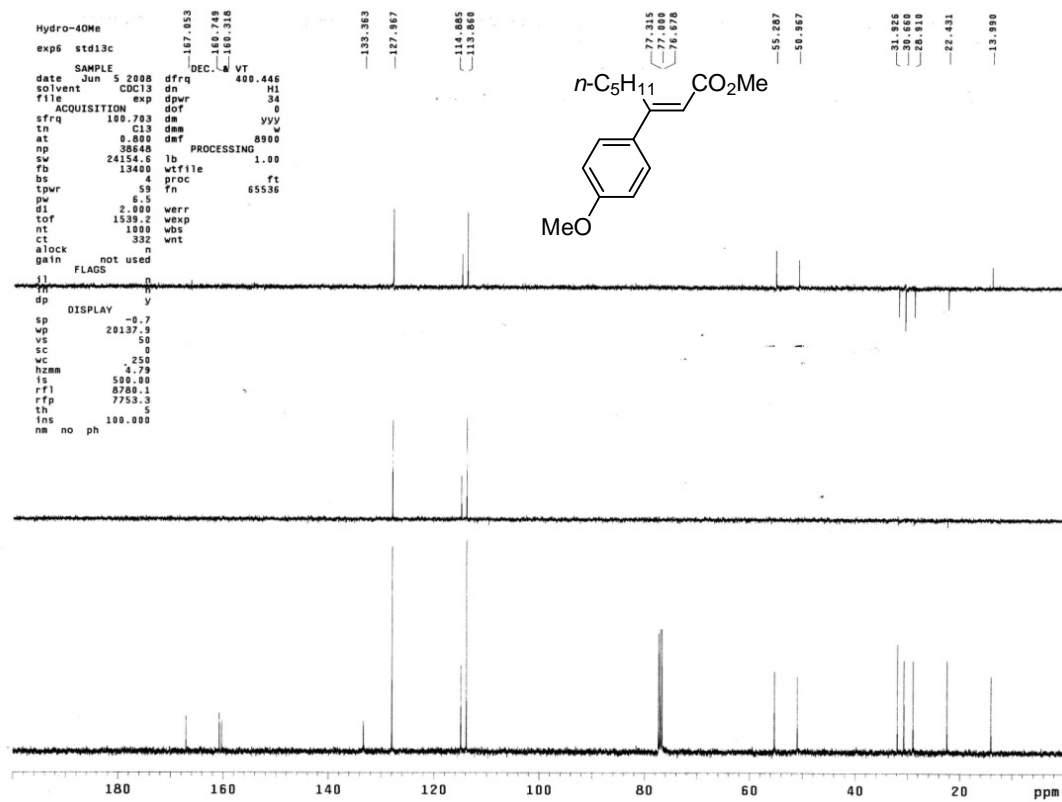
¹³C NMR for 3aa



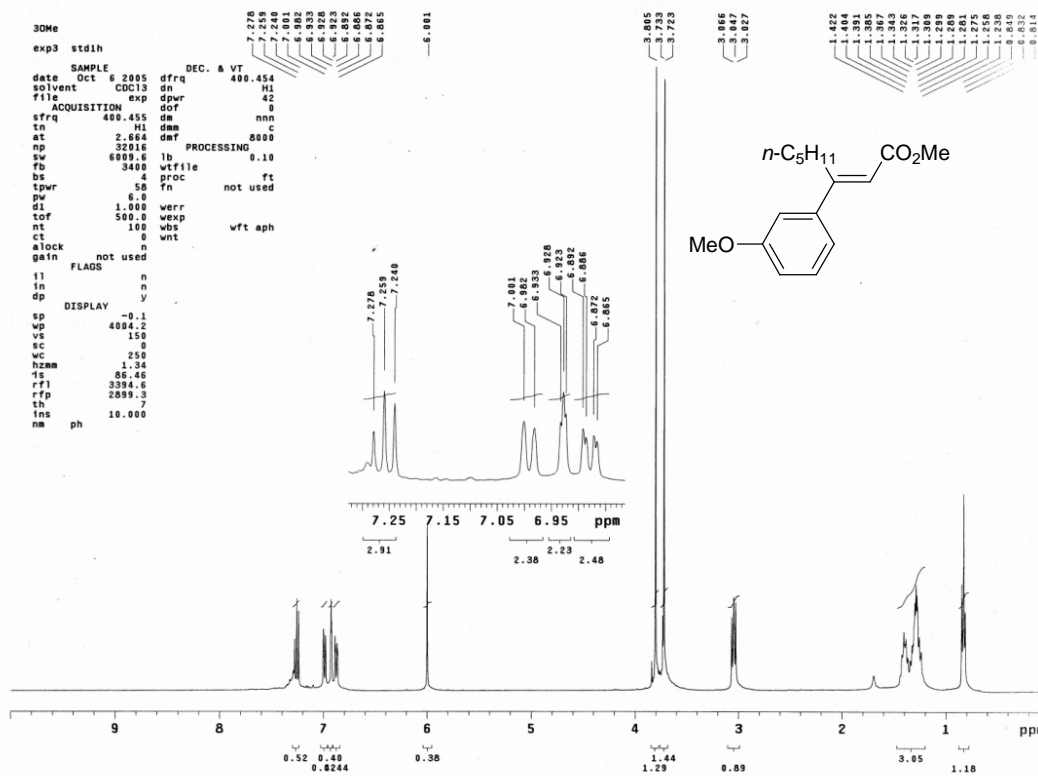
¹H NMR for 3ba



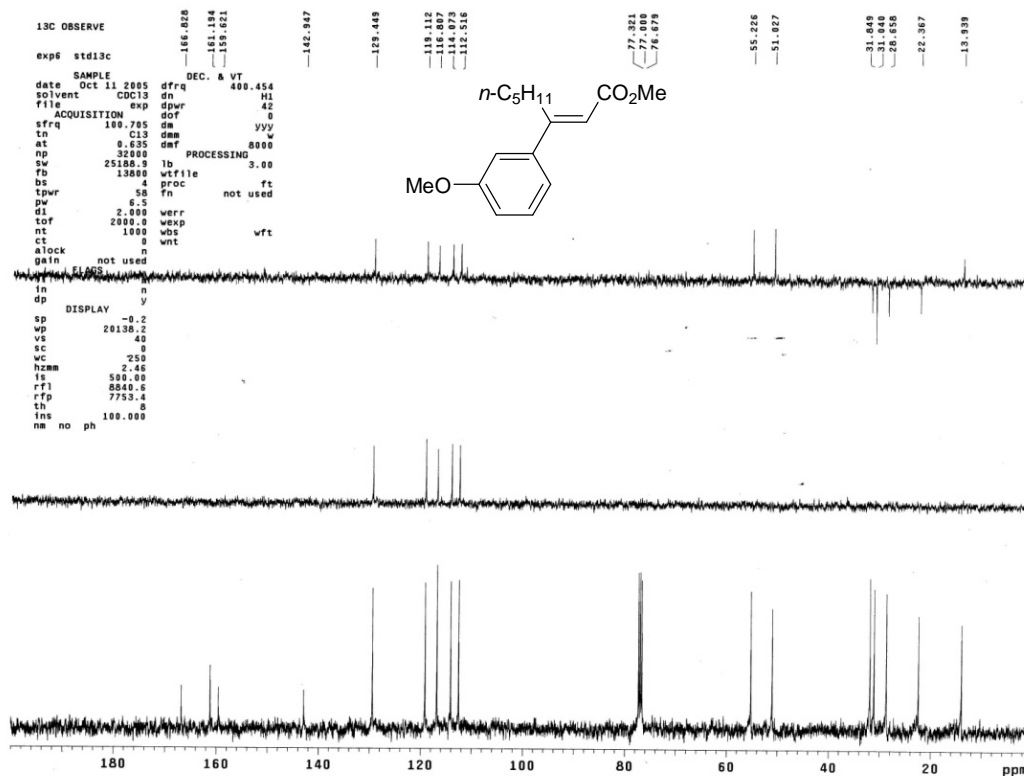
¹³C NMR for 3ba



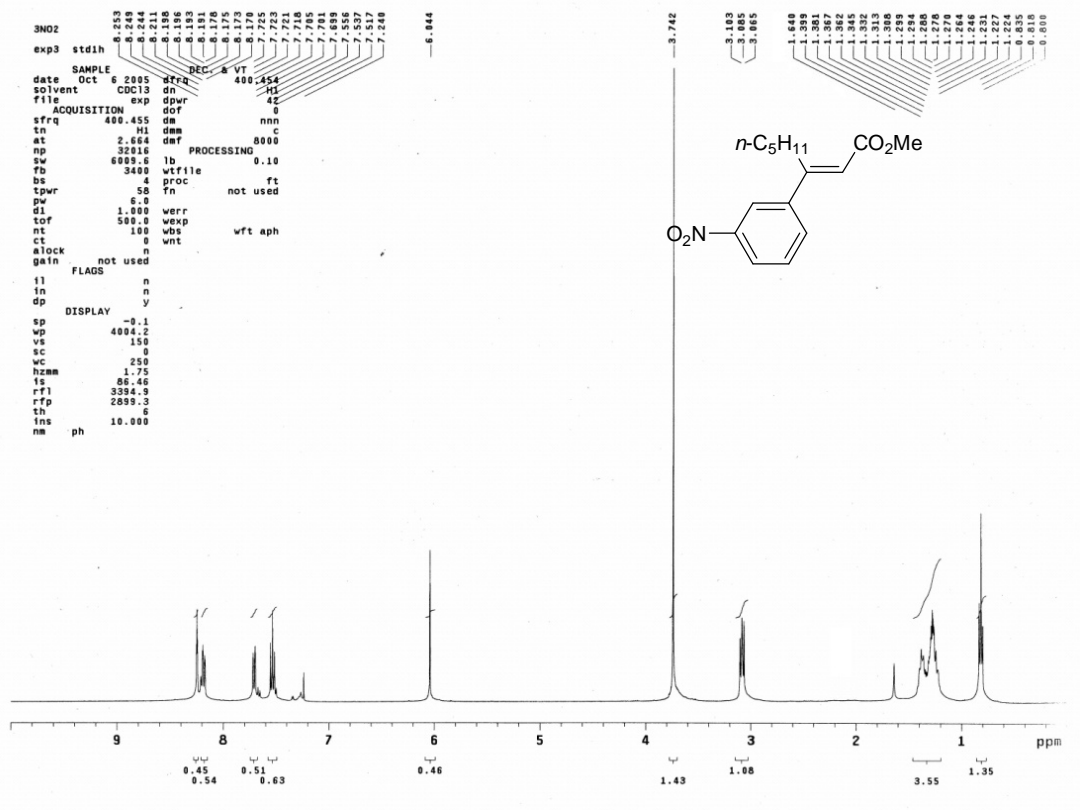
¹H NMR for 3ca



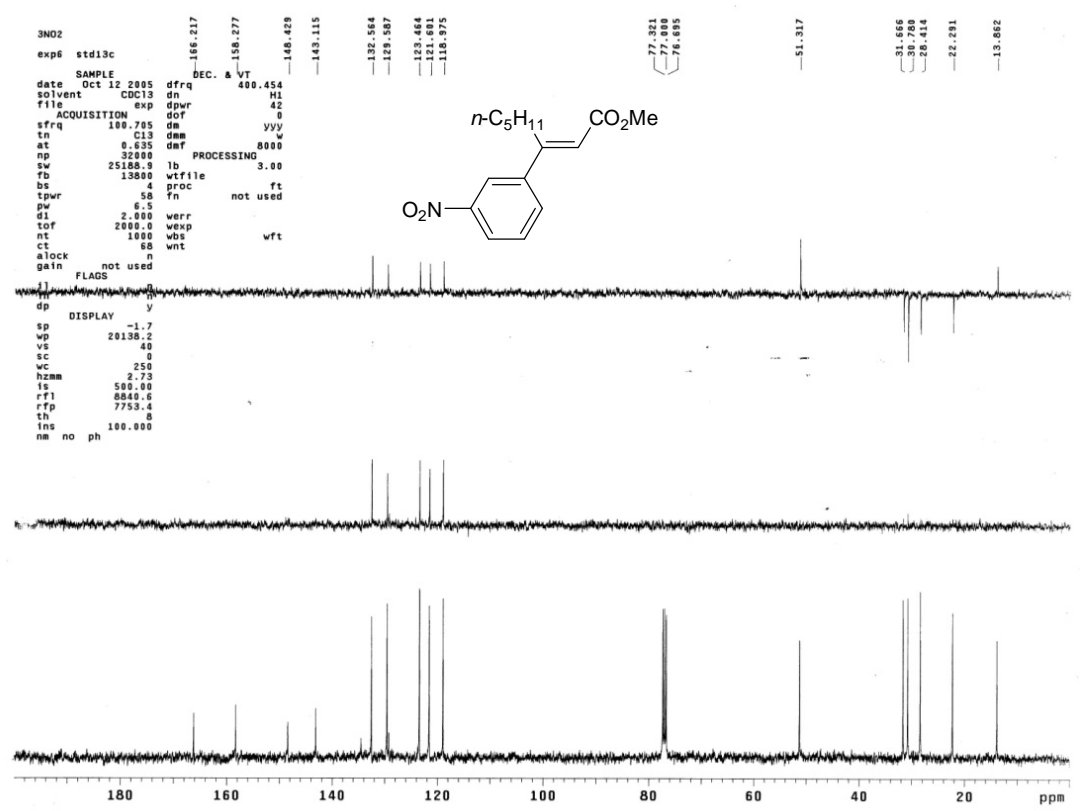
¹³C NMR for 3ca



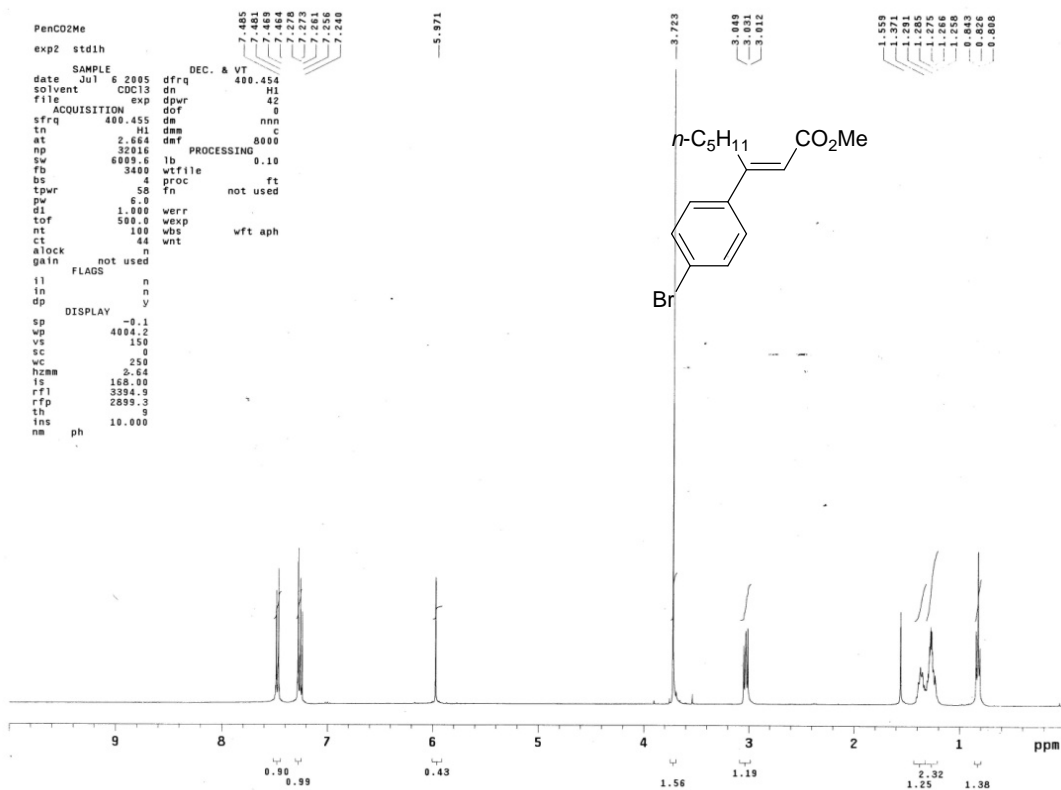
¹H NMR for 3ea



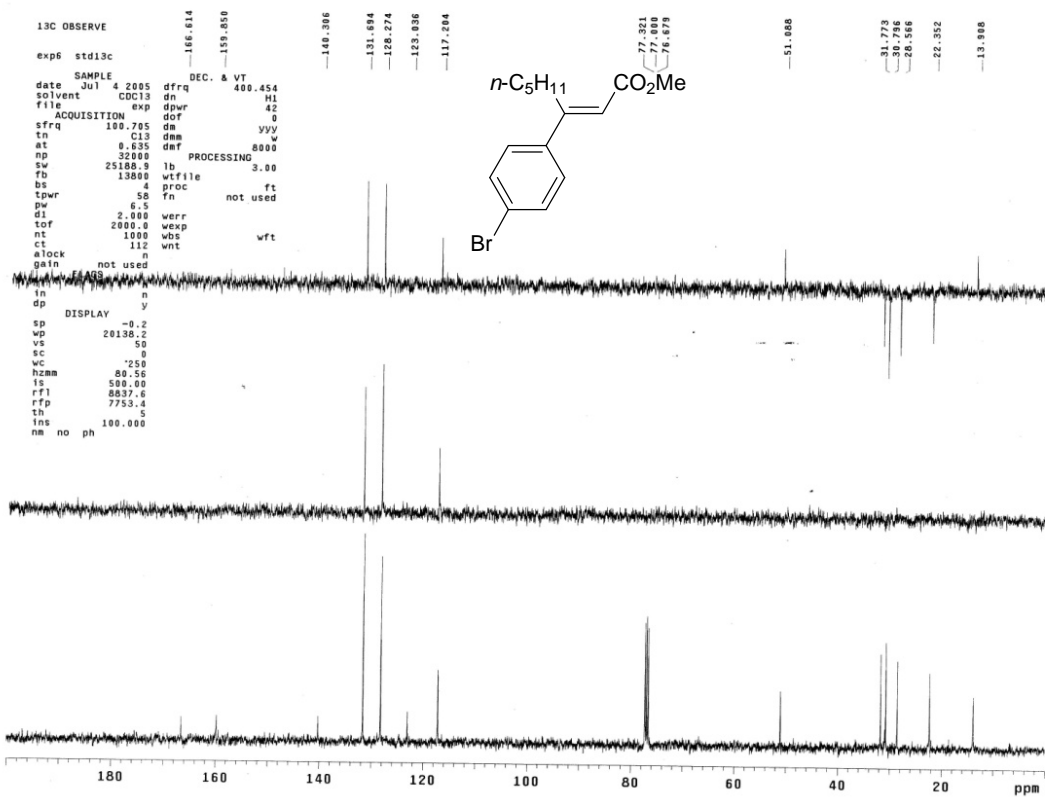
¹³C NMR for 3ea



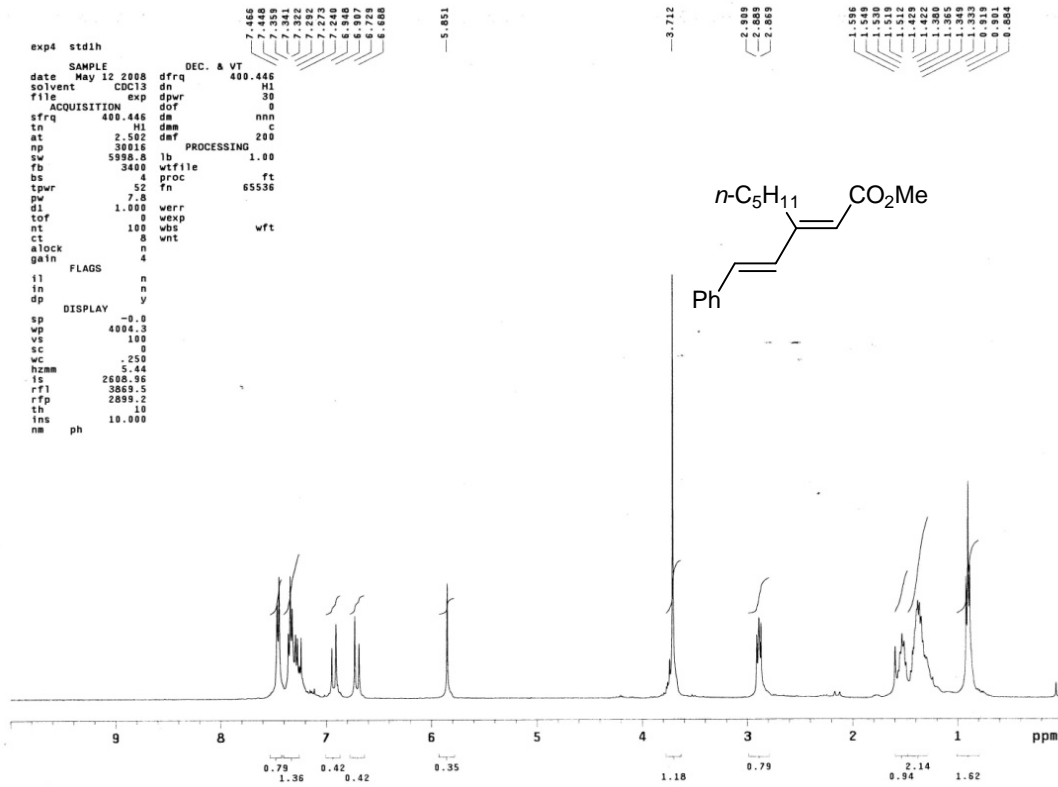
¹H NMR for 3fa



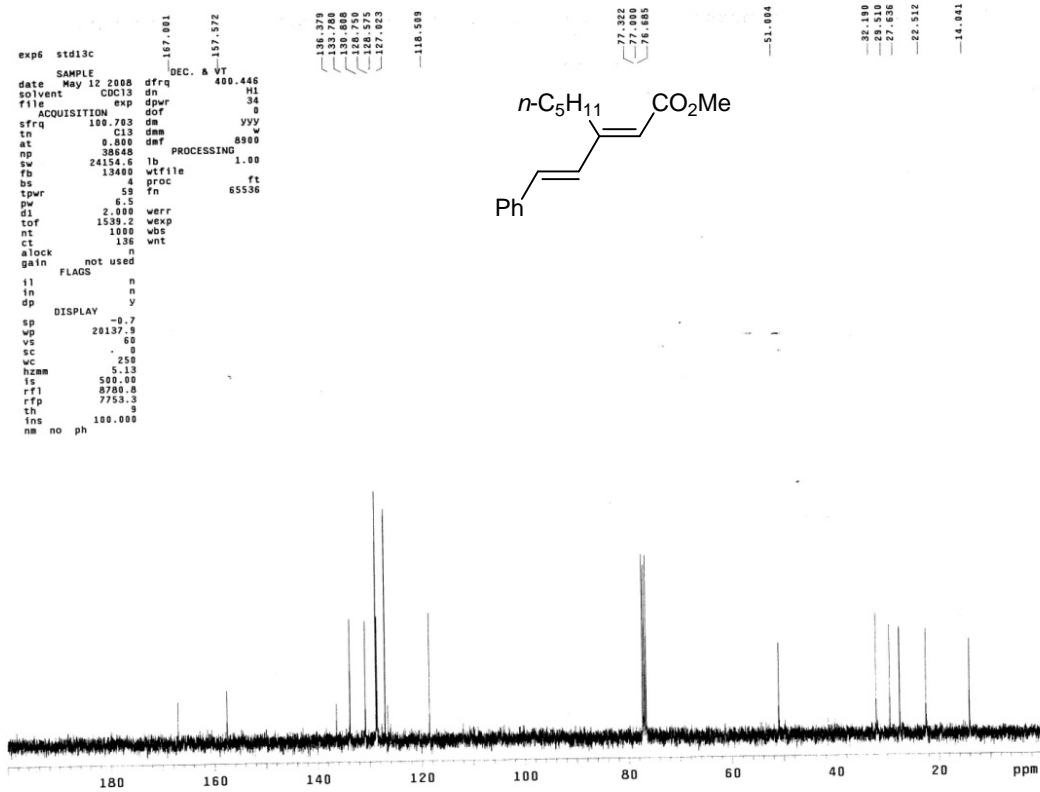
¹³C NMR for 3fa



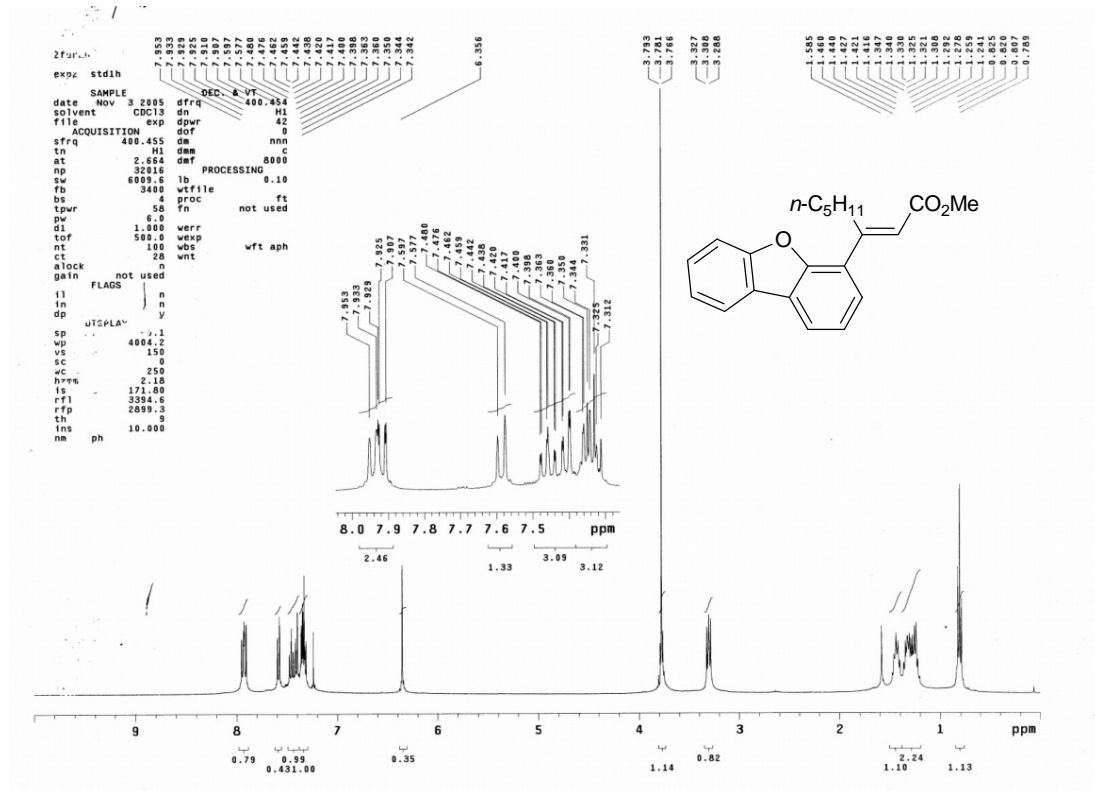
¹H NMR for 3ga



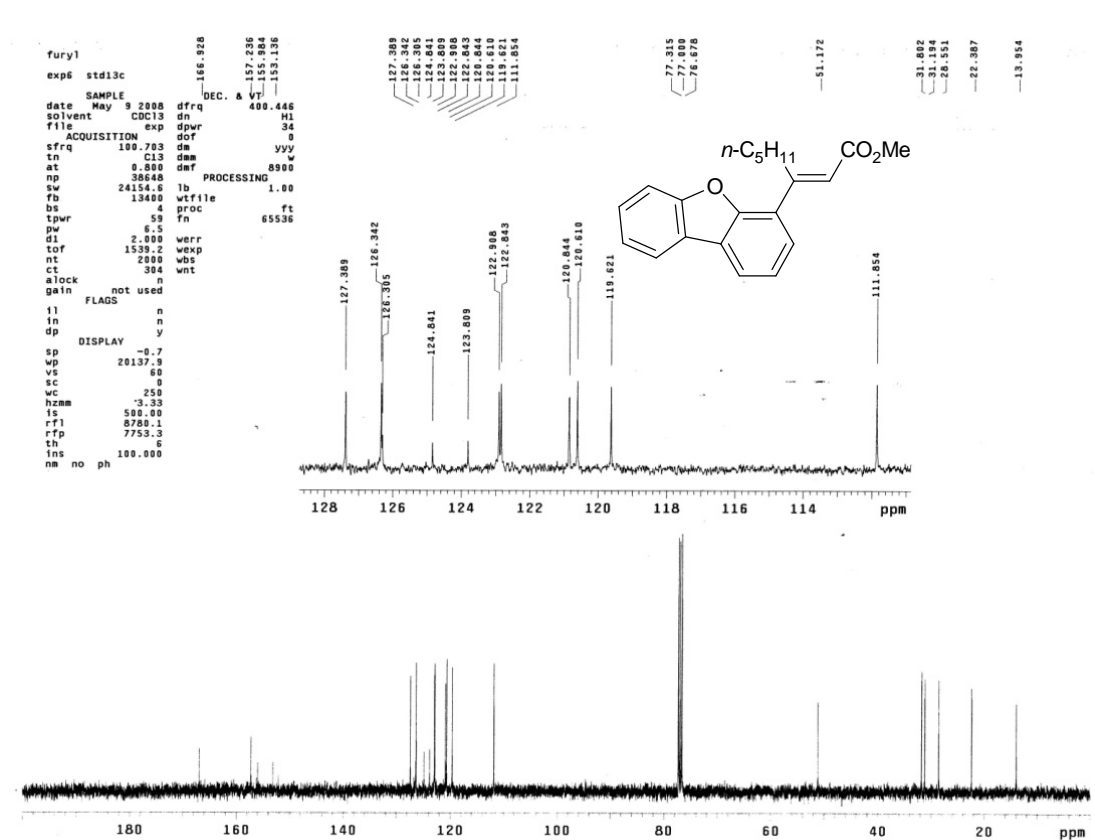
¹³C NMR for 3ga



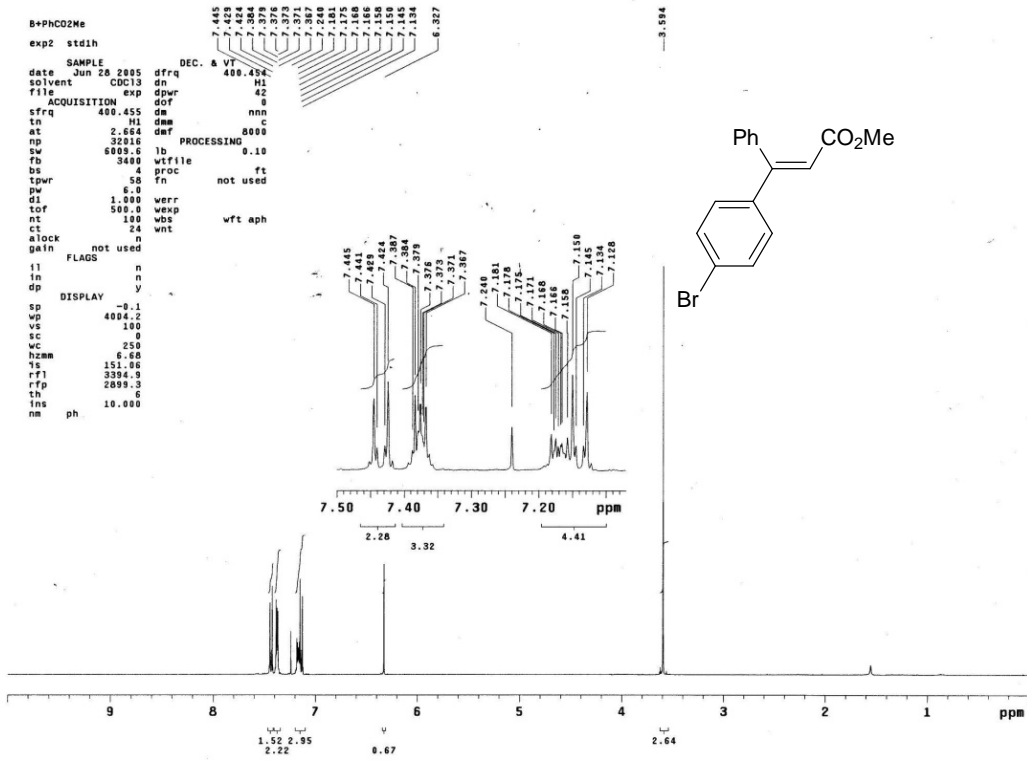
¹H NMR for 3ha



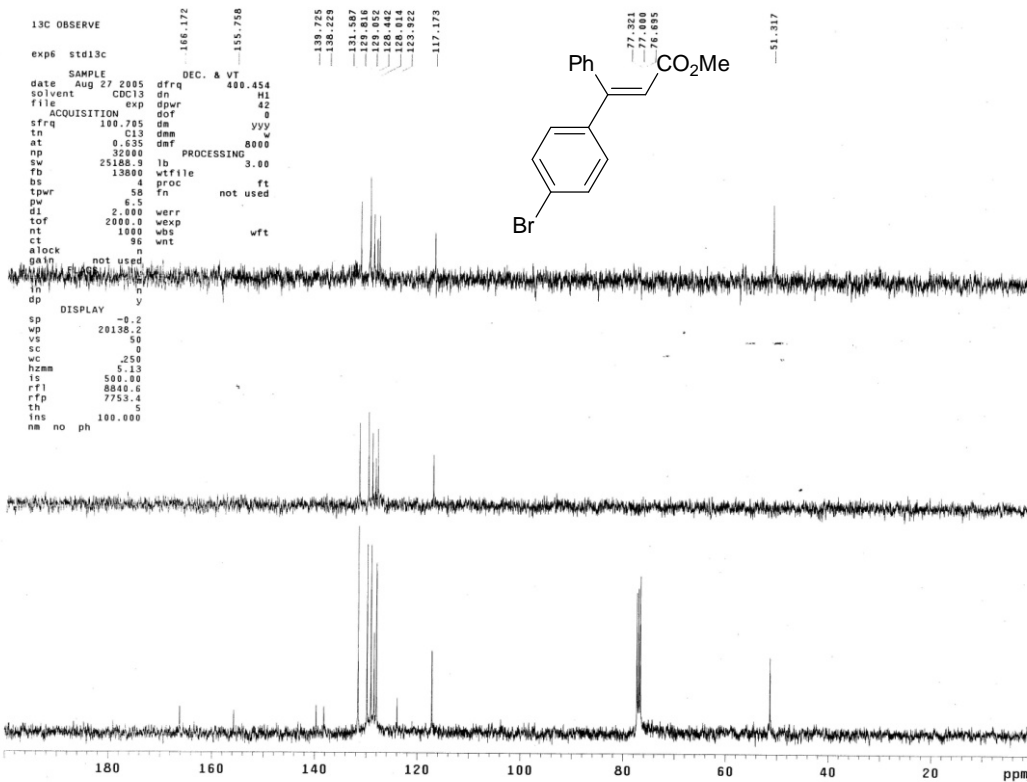
¹³C NMR for 3ha



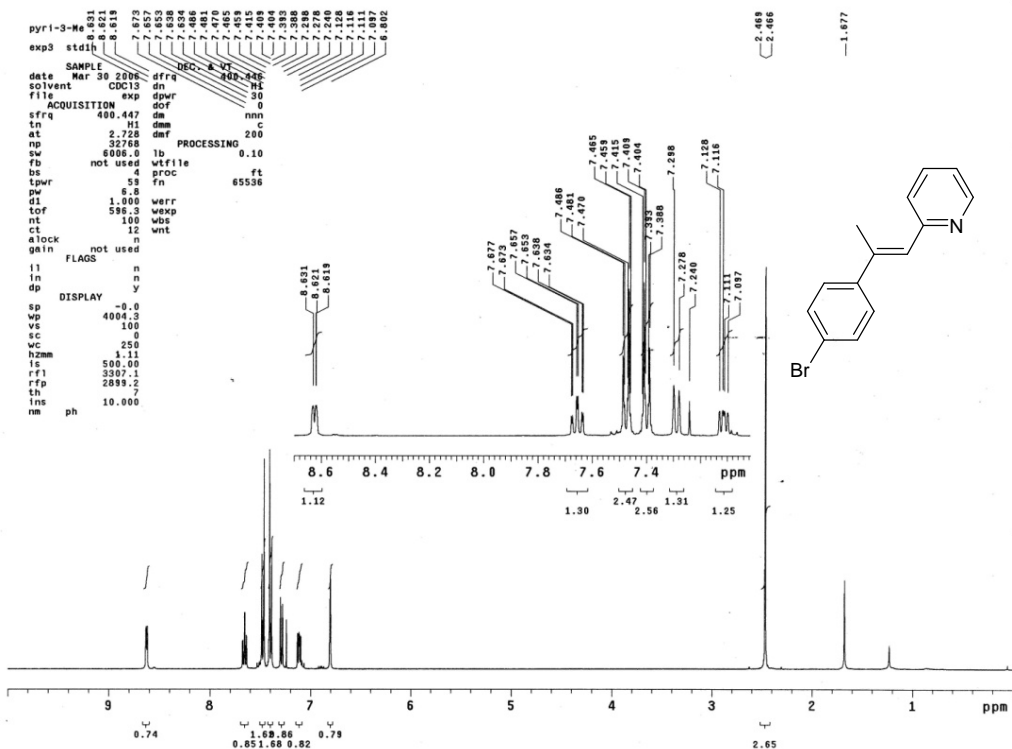
¹H NMR for 3fb



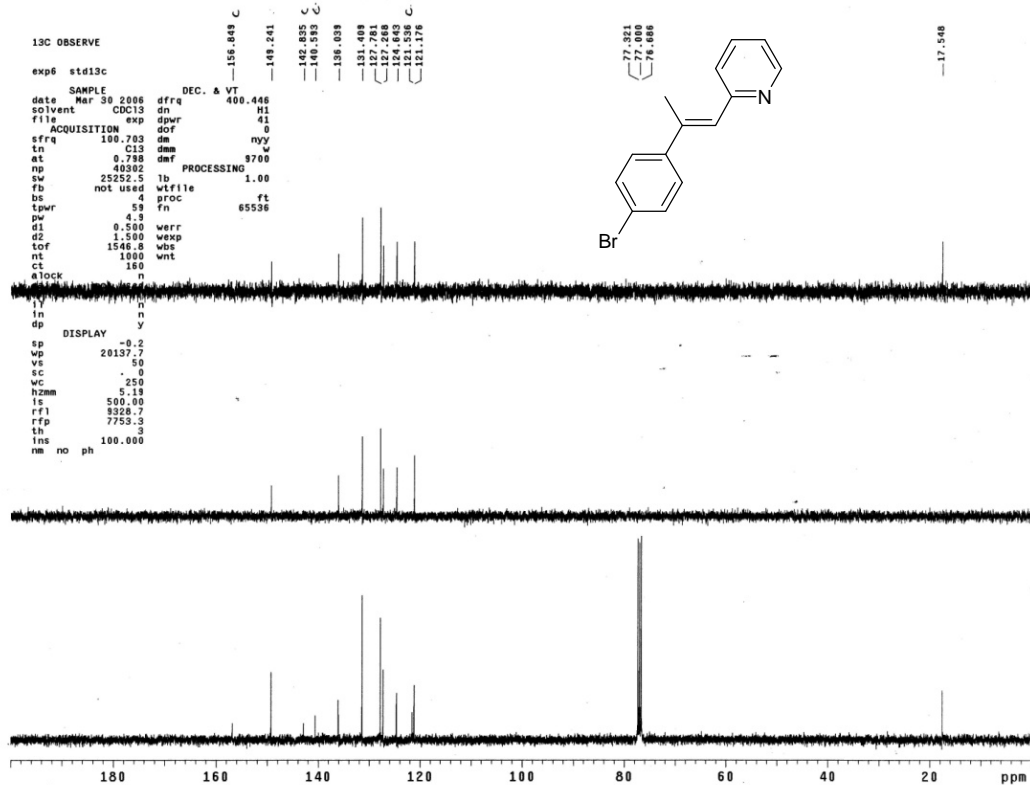
¹³C NMR for 3fb



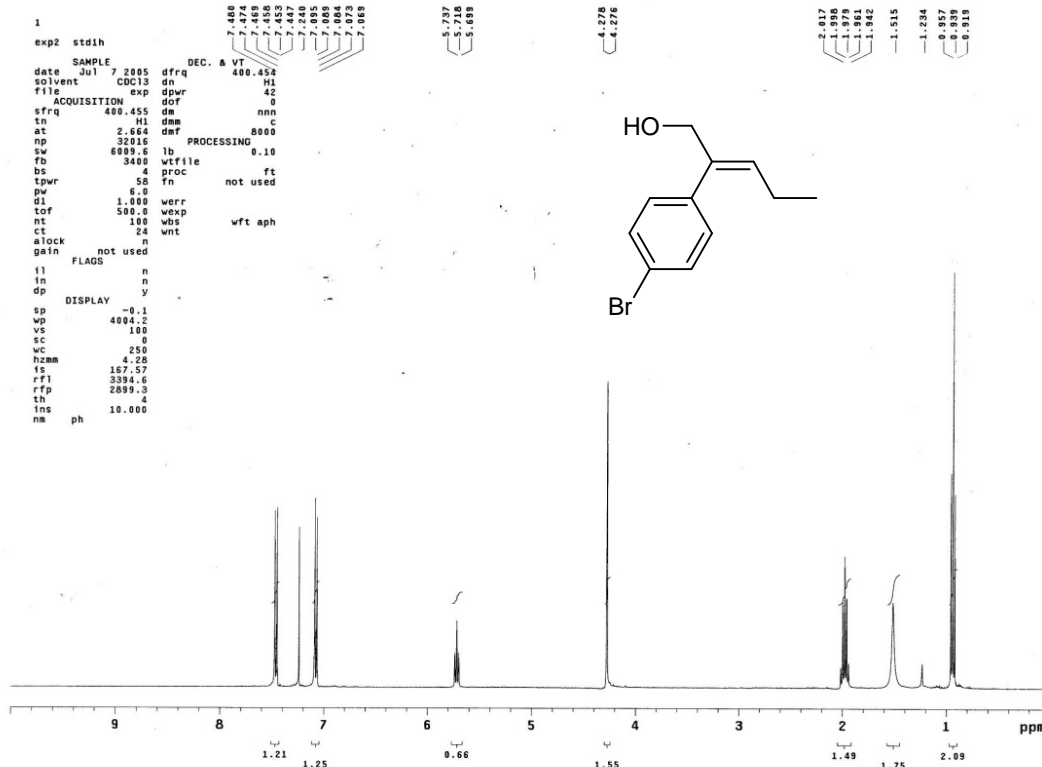
¹H NMR for 3fc



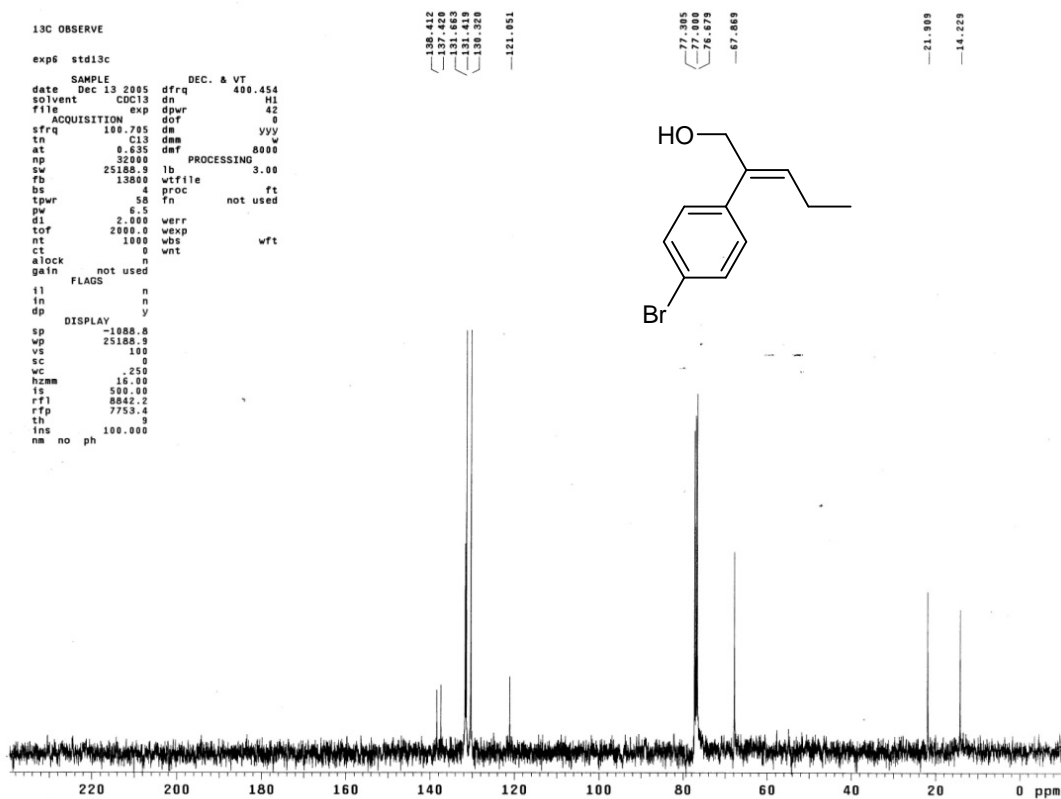
¹³C NMR for 3fc



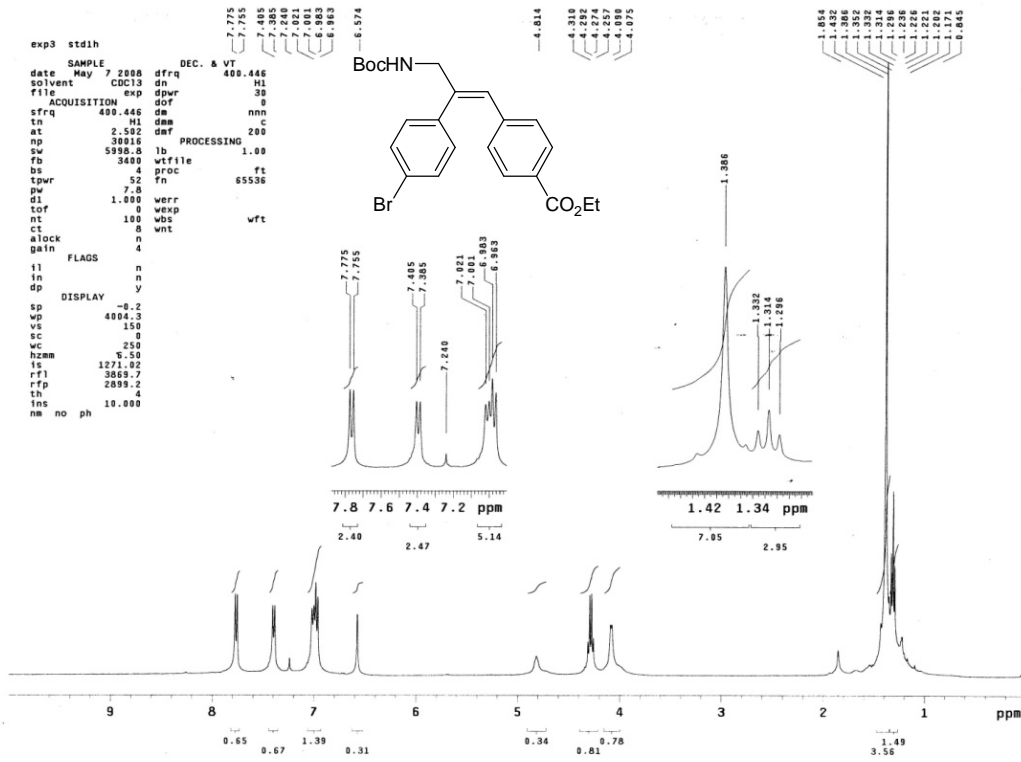
¹H NMR for 4fd



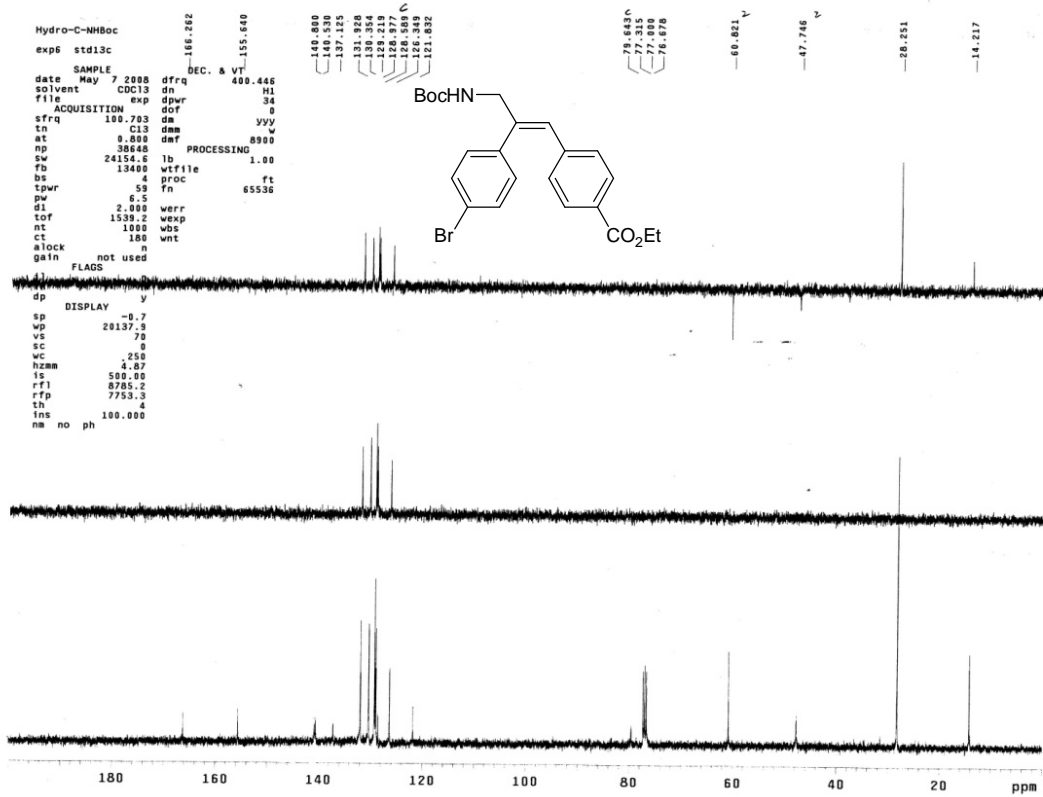
¹³C NMR for 4fd



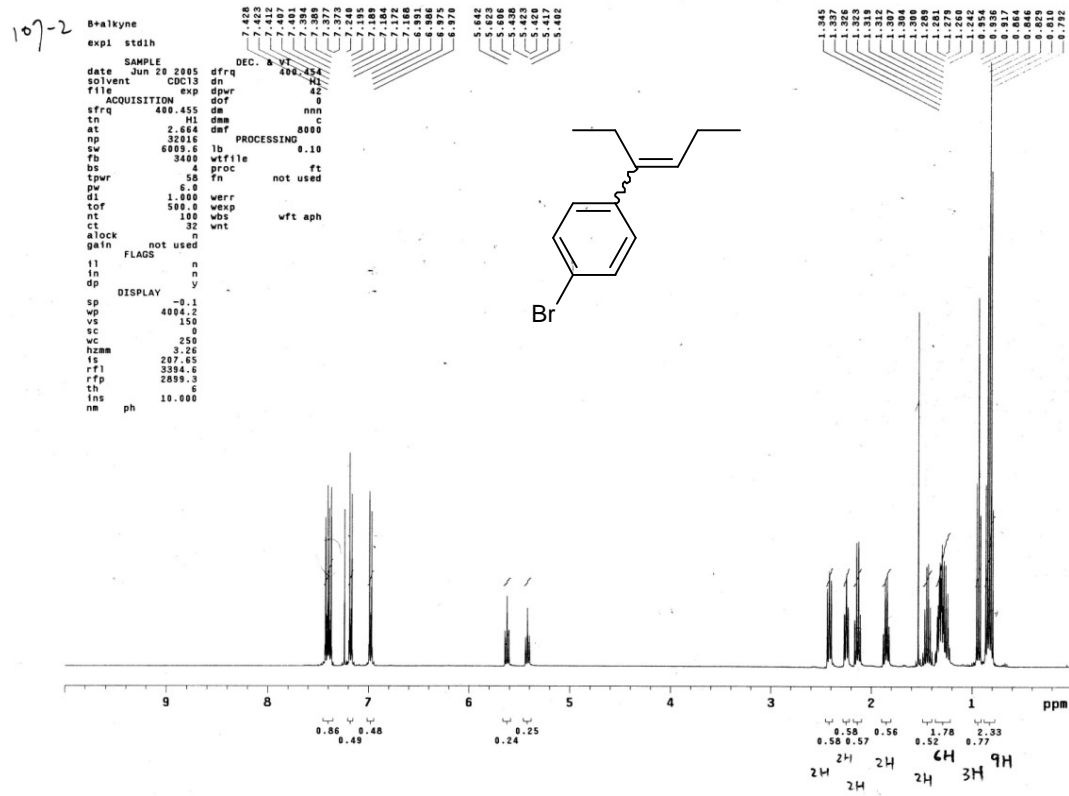
¹H NMR for 4fe



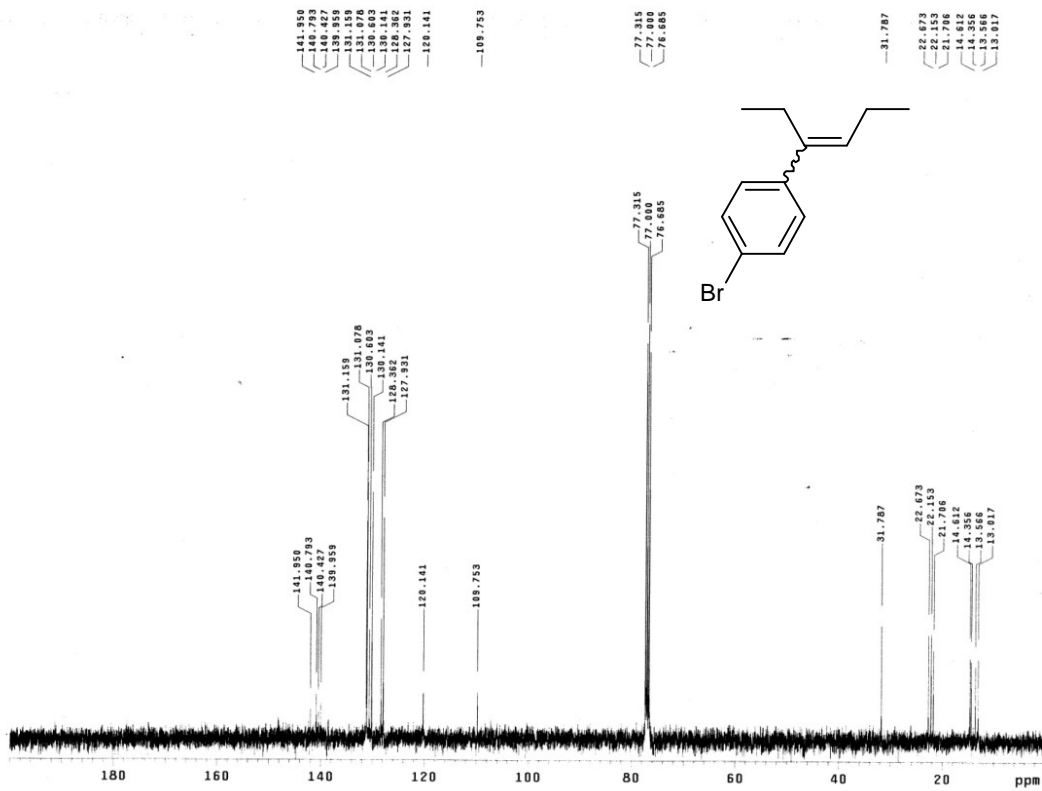
¹³C NMR for 4fe



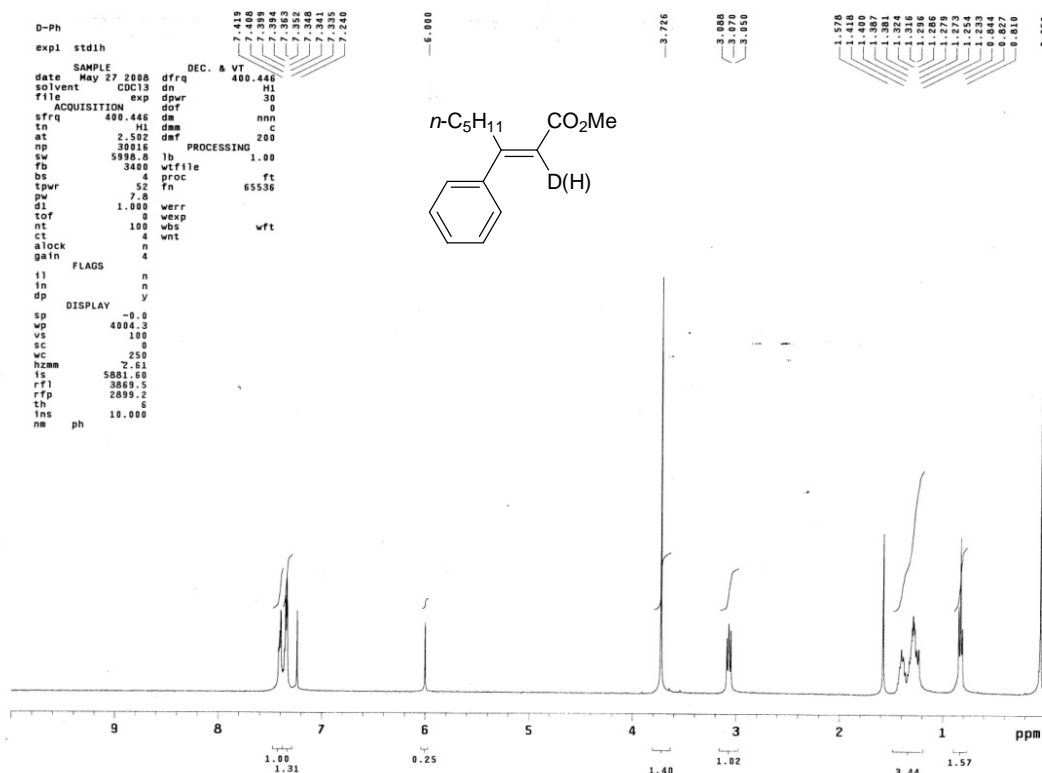
¹H NMR for 3ff and 4ff



¹³C NMR for 3ff and 4ff



¹H NMR for D-3aa



¹³C NMR for D-3aa

