Supporting Information for:

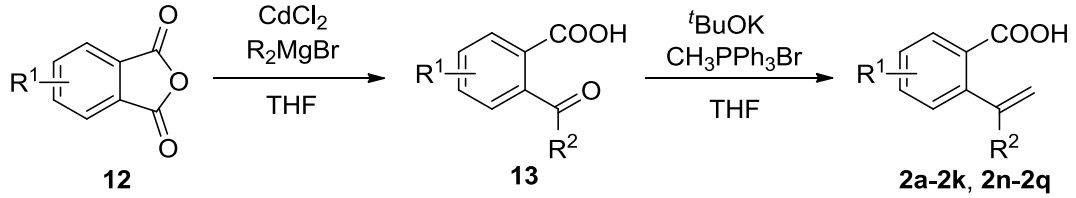
Carboxy-Directed Asymmetric Hydrogenation of α-Alkyl-α-aryl Terminal Olefins: A Highly Enantioselective and Regioselective Access to Chiral Benzylmethyl Center

CONTENTS:

General: All the air or moisture sensitive reactions and manipulations were performed under an nitrogen atmosphere by using standard Schlenk techniques and a Vacuum Atmospheres Drybox (VAC DRI-LAB HE 493). Melting points were measured on a RY-I apparatus and uncorrected. ^{1}H, ^{31}P NMR and ^{13}C NMR spectra were recorded on a Brucker AV 400 spectrometers or a Brucker AV 300 spectrometers or a Varian Mercury Plus 400 spectrometer. Chemical shifts were reported in *ppm* down field from internal Me_4Si. Mass spectra were recorded on IonSpec FT-ICR mass spectrometer with ESI or MAIDI resource. Optical rotations were determined by a Perkin Elmer 341 MC polarimeter. Enantiomeric excesses (ee) of the asymmetric hydrogenation products were determined by chiral SFC. SFC analyses were performed using a Mettler-Toledo Model Analytix SFC. Anhydrous Et_2O, THF and dioxane were distilled from sodium benzophenone ketyl. Anhydrous CH_2Cl_2, NEt_3 were freshly distilled from calcium hydride under nitrogen atmosphere. Anhydrous MeOH was distilled from magnesium under nitrogen atmosphere. $[Ir(COD)Cl]_2$ was purchased from Aldrich Co. and used as received. Hydrogen gas (99.999%) was purchased from Boc Gas Inc., Tianjin.

(A) Preparation and Analytical Data of Unsaturated Carboxylic Acids

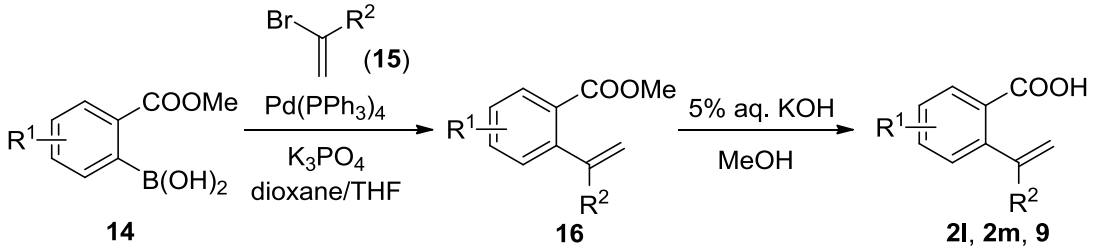
General procedure for the preparation of substrates 2a–2k, 2n–2q:



To a suspension of $CdCl_2$ (3.7 g, 20 mmol) in THF (10 mL) was added Grignard reagent (40 mmol) at 0 °C. The mixture was stirred at 45 °C for 1 h. Then the system was cooled to 0 °C again and a solution of anhydride **12** (15 mmol) was added to the mixture. The mixture was stirred at 45 °C for 12 h. After evaporation of THF, the mixture was treated with 1N HCl (100 mL). The aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined extracts were washed with brine (100 mL), dried over $MgSO_4$, and concentrated. The residue was used in the following step without further purification.

To a suspension of methyltriphenylphosphonium bromide (20.0 mmol) in THF (100 mL) was added potassium *tert*-butoxide (30.0 mmol) at 0 °C. The mixture was stirred for 30 min. Acid **13** (10.0 mmol) was added to the reaction mixture at 0 °C. The mixture was allowed to warm to room temperature, and stirred for 6 h. After evaporation of THF, the mixture was treated with 10% NaOH (100 mL). The aqueous layer was washed with CH_2Cl_2 (50 mL) and acidified (pH = 1) with 3 N HCl. The aqueous layer was extracted with ether (3 × 50 mL). The combined extracts were washed with brine (100 mL), dried over $MgSO_4$, and concentrated. The residue was purified by flash chromatography on silica gel (PE/EA = 4:1) to give the product **2**.

General procedure for the preparation of substrates 2l, 2m and 9:

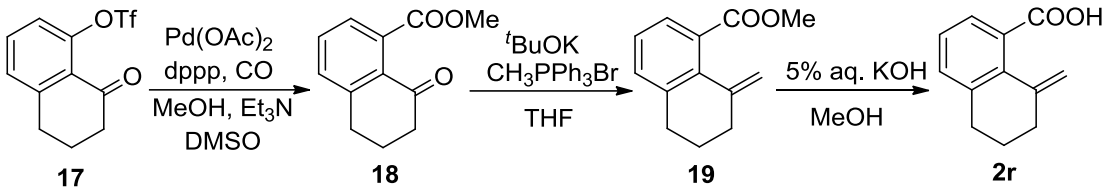


To a solution of vinyl bromide **15** (10.0 mmol) in 100 mL of dioxane/THF (1:1). was added boronic acid **14** (15.0 mmol), followed by $Pd(PPh_3)_4$ (0.5 mmol) and K_3PO_4 (40.0 mmol, 4.0 equiv). The reaction mixture was heated for 12 h under 85 °C. The solvent was removed by rotary evaporation and purified by chromatography on silica gel (PE/EA = 20:1) to give the product **16**.

To the solution of ester **16** (8.0 mmol) in MeOH (50 mL) was added 5% KOH (30 mL). The suspension was stirred at 45 °C for 3 h. After evaporation of MeOH, the mixture was treated with 1N HCl (50 mL). The aqueous layer was extracted with ethyl

acetate (3 × 50 mL). The combined extracts were washed with brine (100 mL), dried over $MgSO_4$, and concentrated. The residue was purified by flash chromatography on silica gel (PE/EA = 4:1) to give the product.

General procedure for the preparation of substrate 2r:



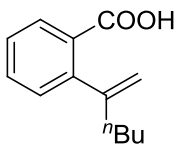
17 **18** **19** **2r**

17 was prepared according to the reported procedure.[1] A mixture of triflates **17** (13.0 mmol), $Pd(OAc)_2$ (1.3 mmol), dppp (1.3 mmol), MeOH (100 mL), DMSO (160 mL), and Et_3N (40 mL) was saturated with CO and stirred under a CO atmosphere at 70 °C. The reaction mixture was monitored by TLC for full conversion. After cooling to room temperature, the mixture was concentrated at reduced pressure. The residue was purified by flash chromatography on silica gel (PE/EA = 16:1) to give the product **18**.

To a suspension of methyltriphenylphosphonium bromide (20.0 mmol) in THF (100 mL) was added potassium *tert*-butoxide (20.0 mmol) at 0 °C. The mixture was stirred for 30 min. and was added **18** (10.0 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature, and stirred for 6 h. After evaporation of THF, the mixture was purified by flash chromatography on silica gel (PE/EA = 20:1) to give the product **19**.

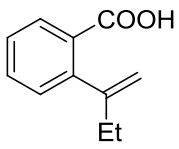
To the solution of ester **19** (8.0 mmol) in MeOH (50 mL) was added 5% KOH (30 mL). The suspension was stirred at 45 °C for 3 h. After evaporation of MeOH, the mixture was treated with 1N HCl (50 mL). The aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined extracts were washed with brine (100 mL), dried over $MgSO_4$, and concentrated. The residue was purified by flash chromatography on silica gel (PE/EA = 4:1) to give the product **2r**.

2-(Hex-1-en-2-yl)benzoic acid (2a)



Colorless oil, 65 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 6.8 Hz, 1H), 7.36 (t, J = 6.8 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 5.12 (s, 1H), 4.92 (s, 1H), 2.41 (t, J = 6.8 Hz, 2H), 1.43–1.28 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.2, 151.2, 145.9, 132.4, 130.8, 130.4, 128.1, 127.0, 112.6, 37.4, 30.3, 22.4, 14.0. HRMS (ESI) Calcd for $[C_{13}H_{15}O_2, M - H]^-$: 203.1078, Found: 203.1081.

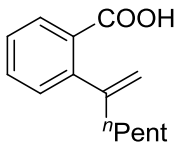
2-(But-1-en-2-yl)benzoic acid (2b)



White solid, 75% yield, m.p.: 45–46 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.2 Hz, 1H), 7.23 (d, J = 7.2 Hz, 1H), 5.13 (s, 1H), 4.92 (s, 1H), 2.43 (q, J = 6.8 Hz, 2H), 1.07 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.4, 152.5, 146.0, 132.4, 130.8, 130.3, 128.2, 127.0, 111.6, 30.5, 12.6. HRMS (ESI)

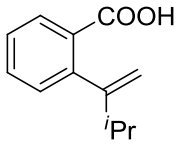
Calcd for [$C_{11}H_{11}O_2$, M − H]$^-$: 175.0765, Found: 175.0769.

2-(Hept-1-en-2-yl)benzoic acid (2c)



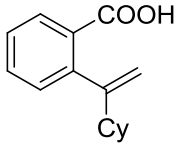
Colorless oil, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 5.13 (s, 1H), 4.93 (s, 1H), 2.41 (t, J = 7.6 Hz, 2H), 1.43 (t, J = 7.2 Hz, 2H), 1.31–1.27 (m, 4H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.4, 151.2, 145.9, 132.4, 130.8, 130.4, 128.1, 127.0, 112.6, 37.6, 31.6, 27.8, 22.6, 14.1. HRMS (ESI) Calcd for [$C_{14}H_{17}O_2$, M − H]$^-$: 217.1234, Found: 217.1229.

2-(3-Methylbut-1-en-2-yl)benzoic acid (2d)



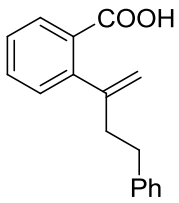
White solid, 45% yield, m.p.: 73–74 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.2 Hz, 1H), 7.37 (t, J = 7.2 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 5.13 (s, 1H), 4.91 (s, 1H), 2.62–2.55 (m, 1H), 1.09 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.1, 157.4, 146.4, 132.4, 131.0, 130.8, 128.0, 127.0, 110.0, 34.8, 21.8. HRMS (ESI) Calcd for [$C_{12}H_{13}O_2$, M − H]$^-$: 189.0921, Found: 189.0924.

2-(1-Cyclohexylvinyl)benzoic acid (2e)



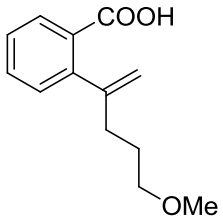
White solid, 42% yield, m.p.: 98–99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.0 Hz, 1H), 7.51–7.47 (m, 1H), 7.38–7.34 (m, 1H), 7.20 (d, J = 7.6 Hz, 1H), 5.10 (s, 1H), 4.90 (s, 1H), 2.20–2.15 (m, 1H), 1.86–1.65 (m, 5H), 1.25–1.15 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.2, 156.5, 146.3, 132.2, 130.9, 130.8, 128.0, 126.9, 110.4, 44.9, 32.4, 26.8, 26.4. HRMS (ESI) Calcd for [$C_{15}H_{17}O_2$, M − H]$^-$: 229.1234, Found: 229.1236.

2-(4-Phenylbut-1-en-2-yl)benzoic acid (2f)



White solid, 50% yield, m.p.: 95–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 7.6 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.2 Hz, 1H), 7.23–7.12 (m, 6H), 5.17 (s, 1H), 4.97 (s, 1H), 2.78–2.71 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.4, 150.5, 145.7, 142.0, 132.7, 131.1, 130.5, 128.4, 128.3, 128.1, 127.2, 125.9, 113.2, 39.4, 34.7. HRMS (ESI) Calcd for [$C_{17}H_{15}O_2$, M − H]$^-$: 251.1078, Found: 251.1076.

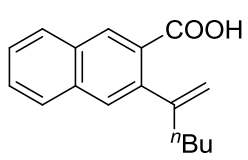
2-(5-Methoxypent-1-en-2-yl)benzoic acid (2g)



Colorless oil, 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 5.15 (s, 1H), 4.95 (s, 1H), 3.41 (t, J = 6.4 Hz, 2H), 3.29 (s, 3H), 2.50 (t, J = 7.6 Hz, 2H), 1.76–1.69 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.5, 150.2, 145.3, 132.3, 130.8, 130.2, 128.6, 127.1, 113.1, 72.3, 58.4, 34.0, 27.9. HRMS (ESI) Calcd for [$C_{13}H_{15}O_3$, M − H]$^-$: 219.1027, Found: 219.1026.

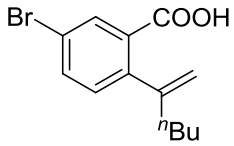
3-(Hex-1-en-2-yl)-2-naphthoic acid (2h)

White solid, 72% yield, m.p.: 89–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H),



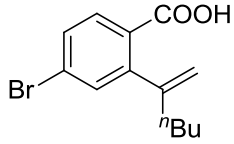
7.94 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.68 (s, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 5.20 (s, 1H), 5.06 (s, 1H), 2.48 (t, *J* = 7.2 Hz, 2H), 1.46–1.32 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 172.1, 150.4, 140.3, 134.0, 131.7, 130.4, 128.0, 127.9, 127.6, 126.6, 125.5, 125.4, 111.7, 36.5, 29.5, 21.4, 12.9. HRMS (ESI) Calcd for $[C_{17}H_{17}O_2, M - H]^-$: 253.1234, Found: 253.1236.

5-Bromo-2-(hex-1-en-2-yl)benzoic acid (2i)



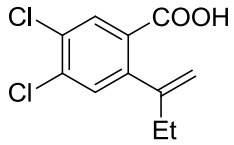
White solid, 9% yield, m.p.: 79–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.11 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 5.13 (s, 1H), 4.91 (s, 1H), 2.38 (t, *J* = 6.8 Hz, 2H), 1.43–1.26 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 172.1, 150.0, 144.8, 135.4, 133.6, 132.0, 129.8, 120.6, 113.2, 37.2, 30.3, 22.4, 14.0. HRMS (ESI) Calcd for $[C_{13}H_{14}BrO_2, M - H]^-$: 281.0183, Found: 281.0178.

4-Bromo-2-(hex-1-en-2-yl)benzoic acid (2j)



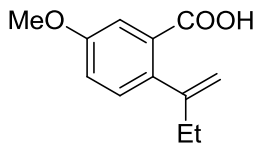
White solid, 23% yield, m.p.: 90–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.85 (d, *J* = 8.4 Hz, 1H), 7.50 (dd, *J* = 8.4 and 2.0 Hz, 1H), 7.40 (d, *J* = 2.0 Hz, 1H), 5.14 (s, 1H), 4.93 (s, 1H), 2.38 (t, *J* = 6.8 Hz, 2H), 1.45–1.29 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 172.7, 150.0, 147.9, 133.3, 132.4, 130.2, 127.4, 126.9, 113.3, 37.1, 30.2, 22.4, 14.0. HRMS (ESI) Calcd for $[C_{13}H_{14}BrO_2, M - H]^-$: 281.0183, Found: 281.0182.

2-(But-1-en-2-yl)-4,5-dichlorobenzoic acid (2k)



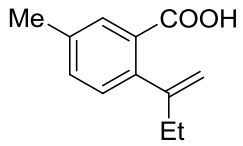
White solid, 68% yield, m.p.: 110–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.08 (s, 1H), 7.34 (s, 1H), 5.15 (s, 1H), 4.92 (s, 1H), 2.37 (q, *J* = 7.6 Hz, 2H), 1.07 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 171.2, 150.4, 145.8, 137.0, 132.7, 132.2, 131.3, 127.5, 112.8, 30.2, 12.5. HRMS (ESI) Calcd for $[C_{11}H_9Cl_2O_2, M - H]^-$: 242.9985, Found: 242.9986.

2-(But-1-en-2-yl)-5-methoxybenzoic acid (2l)



White solid, 65% yield, m.p.: 87–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.50 (d, *J* = 2.8 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.05 (dd, *J* = 8.4 and 2.8 Hz, 1H), 5.10 (s, 1H), 4.89 (s, 1H), 3.86 (s, 3H), 2.40 (q, *J* = 7.2 Hz, 2H), 1.06 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 173.1, 158.3, 152.2, 138.4, 131.5, 129.0, 118.8, 115.1, 111.6, 55.5, 30.7, 12.7. HRMS (ESI) Calcd for $[C_{12}H_{13}O_3, M - H]^-$: 205.0870, Found: 205.0873.

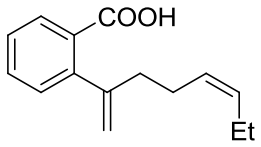
2-(But-1-en-2-yl)-5-methylbenzoic acid (2m)



White solid, 73% yield, m.p.: 84–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.81 (s, 1H), 7.32 (dd, *J* = 10.4 and 1.6 Hz, 1H), 7.13 (d, *J* = 10.4 Hz, 1H), 5.11 (s, 1H), 4.90 (s, 1H), 2.46–2.40 (m, 5H), 1.07 (t, *J* = 9.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): *δ*

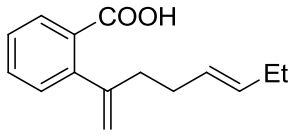
173.7, 152.5, 143.1, 136.8, 133.1, 131.2, 130.3, 128.0, 111.4, 30.6, 20.9, 12.6. HRMS (ESI) Calcd for [$C_{12}H_{13}O_2$, M − H]$^-$: 189.0921, Found: 189.0925.

(*Z*)-2-(Octa-1,5-dien-2-yl)benzoic acid (2n)



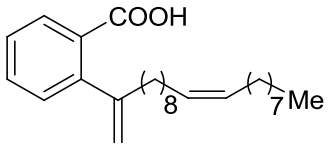
Colorless oil, 69% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 5.42–5.32 (m, 2H), 5.15 (s, 1H), 4.95 (s, 1H), 2.48 (t, J = 7.2 Hz, 2H), 2.20–2.15 (m, 2H), 2.04–1.97 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.4, 150.6, 145.7, 132.5, 132.1, 130.9, 130.5, 128.4, 128.1, 127.1, 112.9, 37.6, 25.8, 20.6, 14.3. HRMS (ESI) Calcd for [$C_{15}H_{17}O_2$, M − H]$^-$: 229.1234, Found: 229.1234.

(*E*)-2-(Octa-1,5-dien-2-yl)benzoic acid (2o)



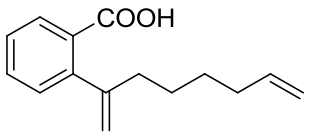
Colorless oil, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 5.49–5.36 (m, 2H), 5.14 (s, 1H), 4.94 (s, 1H), 2.48 (t, J = 7.2 Hz, 2H), 2.14–2.09 (m, 2H), 2.01–1.94 (m, 2H), 0.94 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.9, 150.6, 145.7, 132.5, 132.4, 130.9, 130.5, 128.4, 128.0, 127.0, 113.0, 37.6, 31.2, 25.6, 13.9. HRMS (ESI) Calcd for [$C_{15}H_{17}O_2$, M − H]$^-$: 229.1234, Found: 229.1233.

(*Z*)-2-(Icosa-1,11-dien-2-yl)benzoic acid (2p)



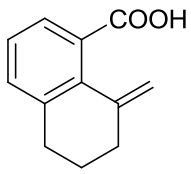
Colorless oil, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 5.39–5.34 (m, 2H), 5.13 (s, 1H), 4.93 (s, 1H), 2.42 (t, J = 7.2 Hz, 2H), 2.02–1.97 (m, 4H), 1.44–1.41 (m, 2H), 1.31–1.27 (m, 22H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.3, 151.3, 145.9, 132.4, 130.8, 130.4, 130.3, 129.9, 128.1, 127.0, 112.6, 37.7, 32.7, 32.0, 29.81, 29.75, 29.69, 29.57, 29.54, 29.37, 29.28, 29.23, 29.21, 28.2, 27.2, 22.7, 14.2. HRMS (ESI) Calcd for [$C_{27}H_{41}O_2$, M − H]$^-$: 397.3112, Found: 397.3114.

2-(Octa-1,7-dien-2-yl)benzoic acid (2q)



Colorless oil, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 5.84–5.73 (m, 1H), 5.12 (s, 1H), 5.00–4.90 (m, 3H), 2.42 (t, J = 6.0 Hz, 2H), 2.04 (q, J = 6.8 Hz, 2H), 1.44–1.42 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.6, 151.0, 145.9, 138.9, 132.5, 130.9, 130.4, 128.2, 127.1, 114.4, 112.7, 37.5, 33.7, 28.6, 27.6. HRMS (ESI) Calcd for [$C_{15}H_{17}O_2$, M − H]$^-$: 229.1234, Found: 229.1233.

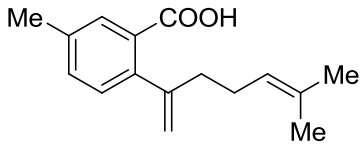
8-Methylene-5,6,7,8-tetrahydronaphthalene-1-carboxylic acid (2r)



White solid, 94% yield, m.p.: 120–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (t, J = 4.0 Hz, 1H), 7.26 (d, J = 4.0 Hz, 2H), 5.24 (s, 1H), 5.23 (s, 1H), 2.83 (t, J = 6.4 Hz, 2H), 2.68 (t, J = 6.4 Hz, 2H), 2.00–1.94 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 175.6, 141.4,

138.8, 135.9, 129.9, 128.7, 126.3, 125.5, 113.8, 31.0, 28.8, 22.7. HRMS (ESI) Calcd for [$C_{12}H_{11}O_2$, M − H]$^-$: 187.0765, Found: 187.0766.

5-Methyl-2-(6-methylhepta-1,5-dien-2-yl)benzoic acid (9)



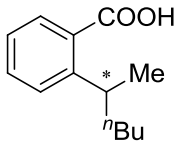
Colorless oil, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 5.19 (t, J = 6.4 Hz, 1H), 5.17 (s, 1H), 4.98 (s, 1H), 2.49 (t, J = 7.6 Hz, 2H), 2.44 (s, 3H), 2.19−2.14 (m, 2H), 1.73 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.8, 150.8, 143.0, 136.8, 133.2, 131.7, 131.3, 130.5, 128.0, 124.1, 112.6, 37.7, 26.8, 25.7, 20.9, 17.7. HRMS (ESI) Calcd for [$C_{16}H_{19}O_2$, M − H]$^-$: 243.1391, Found: 243.1396.

(B) Asymmetric Hydrogenation and Analytical Data of Products

General procedure for asymmetric hydrogenation

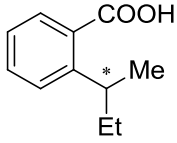
A hydrogenation tube was charged with a stirring bar, 2-(hex-1-en-2-yl)benzoic acid **2a** (102 mg, 0.5 mmol), catalyst (S_a)-**1b** (2.3 mg, 0.00125 mmol), NEt_3 (51 mg, 0.5 mmol) and 2 mL MeOH. The hydrogenation tube was then put into an autoclave. The autoclave was sealed and purged five times with hydrogen. The autoclave was then charged with hydrogen to 6 atm, and the reaction mixture was stirred at 45 °C for 3.5 h. After releasing hydrogen, 20 mg of NaOH was added to the reaction mixture, which was then concentrated on a rotary vapor. The mixture was added 25 mL water and washed with Et_2O. The aqueous layer was acidified with conc. HCl, and extracted with Et_2O. The organic layer was dried with Na_2SO_4. The conversion of substrate was determined by ^{1}H NMR analysis. The crude product was purified by a flash chromatography on silica gel column to give pure product **3a** as a colorless oil. The ee value of product was determined by SFC using a Chiralpak AD-H column. The analysis data for hydrogenation products were listed as below.

2-(Hexan-2-yl)benzoic acid (3a)



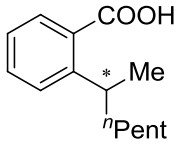
Colorless oil, 98% yield; 99.1% ee, $[\alpha]_D^{25}$ +41.3 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 90:10, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 5.42 min for minor isomer and t_R = 6.46 min for major isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 3.83–3.74 (m, 1H), 1.71–1.52 (m, 2H), 1.30–1.23 (m, 6H), 1.20–1.13 (m, 1H), 0.85 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.7, 149.8, 132.4, 130.6, 129.6, 126.9, 125.4, 38.1, 34.5, 29.9, 22.9, 22.4, 14.1. HRMS (ESI) Calcd for $[C_{13}H_{17}O_2, M - H]^-$: 205.1234, Found: 205.1230.

2-*sec*-Butylbenzoic acid (3b)[2]



Colorless oil, 99% yield; 98 % ee, $[\alpha]_D^{25}$ +22.4 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 90:10, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 5.19 min for minor isomer and t_R = 6.40 min for major isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 3.73–3.68 (m, 1H), 1.72–1.58 (m, 2H), 1.27 (d, *J* = 6.4 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H).

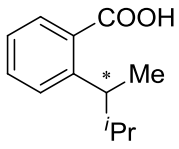
2-(Heptan-2-yl)benzoic acid (3c)



Colorless oil, 98% yield; 99.1% ee, $[\alpha]_D^{25}$ +51.7 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 90:10, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 6.29 min for minor isomer and t_R = 7.81 min for major isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 3.89–3.82 (m, 1H), 1.76–1.58 (m, 2H), 1.34–1.32 (m, 9H), 0.91 (t, *J* = 5.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.7,

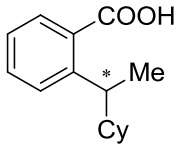
150.3, 132.7, 130.8, 129.0, 126.9, 125.5, 38.4, 34.5, 32.0, 27.4, 22.6, 22.3, 14.1. HRMS (ESI) Calcd for $[C_{14}H_{19}O_2, M - H]^-$: 219.1391, Found: 219.1393.

2-(3-Methylbutan-2-yl)benzoic acid (3d)



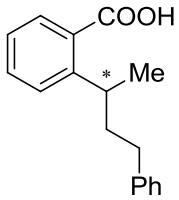
Colorless oil, 98% yield; 99.5% ee, $[\alpha]_D^{25}$ +39.6 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 90:10, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 4.82 min for minor isomer and t_R = 6.49 min for major isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (br, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 3.46–3.39 (m, 1H), 1.84–1.76 (m, 1H), 1.21 (d, *J* = 6.4 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.71 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.5, 149.7, 132.4, 130.7, 129.4, 127.5, 125.4, 41.0, 34.5, 21.6, 19.9, 19.0. HRMS (ESI) Calcd for $[C_{12}H_{15}O_2, M - H]^-$: 191.1078, Found: 191.1080.

2-(1-Cyclohexylethyl)benzoic acid (3e)



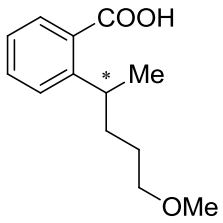
Colorless oil, 98% yield; 99.6% ee, $[\alpha]_D^{25}$ +80.4 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 90:10, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 7.93 min for minor isomer and t_R = 10.23 min for major isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.23 (br, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 3.50−3.46 (m, 1H), 1.92 (d, *J* = 12.0 Hz, 1H), 1.73 (d, *J* = 11.6 Hz, 3H), 1.45–0.83 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.6, 148.9, 131.9, 130.6, 130.2, 127.4, 125.3, 44.3, 40.1, 31.6, 30.4, 26.6, 26.5, 19.2. HRMS (ESI) Calcd for $[C_{15}H_{19}O_2, M - H]^-$: 231.1391, Found: 231.1389.

2-(4-Phenylbutan-2-yl)benzoic acid (3f)



White solid, 98% yield, m.p.: 66–67 ºC; 99.1% ee, $[\alpha]_D^{25}$ +94.4 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 80:20, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 5.46 min for major isomer and t_R = 7.39 min for minor isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 6.4 Hz, 1H), 7.52–7.46 (m, 2H), 7.27–7.12 (m, 6H), 3.88−3.86 (m, 1H), 2.60 (s, 1H), 2.51 (s, 1H), 2.00–1.92 (m, 2H), 1.33 (d, *J* = 5.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.5, 149.6, 142.5, 132.9, 131.0, 129.2, 128.4, 128.3, 127.0, 125.8, 125.7, 40.2, 34.3, 34.1, 22.5. HRMS (ESI) Calcd for $[C_{17}H_{17}O_2, M - H]^-$: 253.1234, Found: 253.1237.

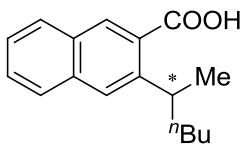
2-(5-Methoxypentan-2-yl)benzoic acid (3g)



Colorless oil, 98% yield; 99.2% ee, $[\alpha]_D^{25}$ +33.3 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 90:10, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 7.13 min for minor isomer and t_R = 8.61 min for major isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 1H), 3.87–3.78 (m, 1H), 3.41–3.34 (m, 2H), 3.31 (s, 3H), 1.77–1.41 (m,

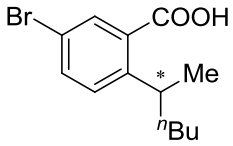
4H), 1.28 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.7, 149.5, 132.6, 130.8, 129.2, 126.9, 125.6, 72.9, 58.4, 34.7, 34.2, 27.6, 22.4. HRMS (ESI) Calcd for [$C_{13}H_{17}O_3$, M − H]$^-$: 221.1183, Found: 221.1185.

3-(Hexan-2-yl)-2-naphthoic acid (3h)



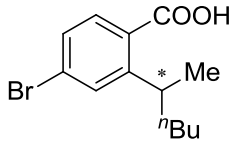
White solid, 98% yield, m.p.: 72–73 °C; 99.4% ee, $[\alpha]_D^{25}$ +13.2 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 70:30, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 4.60 min for minor isomer and t_R = 14.41 min for major isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 7.93–7.85 (m, 3H), 7.59–7.51 (m, 2H), 3.94 (d, J = 5.6 Hz, 1H), 1.84–1.69 (m, 2H), 1.42–1.29 (m, 7H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.4, 145.7, 135.5, 132.5, 130.7, 128.8, 128.3, 127.8, 127.4, 126.0, 125.7, 38.5, 34.4, 30.0, 22.9, 22.5, 14.1. HRMS (ESI) Calcd for [$C_{17}H_{19}O_2$, M − H]$^-$: 255.1391, Found: 255.1391.

5-Bromo-2-(hexan-2-yl)benzoic acid (3i)



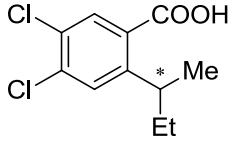
White solid, 98% yield, m.p.: 65–66 °C; 98% ee, $[\alpha]_D^{25}$ +25.6 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 90:10, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 8.97 min for minor isomer and t_R = 12.02 min for major isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 3.75–3.70 (m, 1H), 1.59–1.57 (m, 2H), 1.25–1.14 (m, 7H), 0.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.7, 149.2, 135.7, 133.4, 130.6, 128.9, 118.9, 37.9, 34.2, 29.8, 22.8, 22.2, 14.0. HRMS (ESI) Calcd for [$C_{13}H_{16}BrO_2$, M − H]$^-$: 283.0339, Found: 283.0336.

4-Bromo-2-(hexan-2-yl)benzoic acid (3j)



White solid, 98% yield, m.p.: 75–76 °C; 99% ee, $[\alpha]_D^{25}$ +9.17 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 90:10, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 6.70 min for minor isomer and t_R = 14.66 min for major isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.4 Hz, 1H), 7.59 (s, 1H), 7.44 (d, J = 8.4 Hz, 1H), 3.86–3.81 (m, 1H), 1.66–1.58 (m, 2H), 1.34–1.22 (m, 7H), 0.91 (t, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.6, 152.7, 132.5, 130.4, 128.9, 128.1, 127.5, 38.0, 34.5, 29.9, 22.8, 22.1, 14.0. HRMS (ESI) Calcd for [$C_{13}H_{16}BrO_2$, M − H]$^-$: 283.0339, Found: 283.0338.

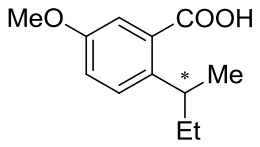
2-*sec*-Butyl-4,5-dichlorobenzoic acid (3k)



White solid, 98% yield, m.p.: 108–109 °C; 99.8% ee, $[\alpha]_D^{25}$ +5.14 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 90:10, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 8.09 min for minor isomer and t_R = 12.22 min for major isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.46 (s, 1H), 3.73–3.65 (m, 1H), 1.67–1.55 (m, 2H), 1.24 (d, J = 6.8 Hz, 3H), 0.86 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.4, 150.4, 137.6, 132.8, 129.8, 129.3, 128.3, 35.8, 31.0, 21.6, 12.1. HRMS (ESI) Calcd for [$C_{11}H_{11}Cl_2O_2$, M − H]$^-$:

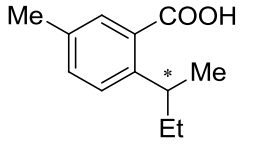
245.0142, Found: 245.0144.

2-*sec*-Butyl-5-methoxybenzoic acid (3l)



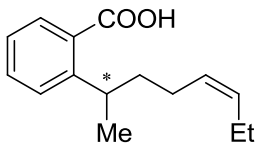
Colorless oil, 98% yield; 99.3% ee, $[\alpha]_D^{25}$ +16.7 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 90:10, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 7.10 min for minor isomer and t_R = 10.10 min for major isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (s, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 6.8 Hz, 1H), 3.85 (s, 3H), 3.69–3.64 (m, 1H), 1.70–1.57 (m, 2H), 1.26 (d, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.2, 157.0, 142.1, 129.8, 128.1, 119.5, 114.8, 55.4, 35.5, 31.2, 22.0, 12.2. HRMS (ESI) Calcd for $[C_{12}H_{15}O_3, M - H]^-$: 207.1027, Found: 207.1030.

2-*sec*-Butyl-5-methylbenzoic acid (3m)



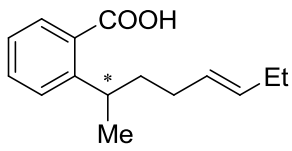
Colorless oil, 99% yield; 99.1% ee, $[\alpha]_D^{25}$ +18.5 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 90:10, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 6.02 min for minor isomer and t_R = 7.86 min for major isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (s, 1H), 7.32–7.23 (m, 2H), 3.69–3.63 (m, 1H), 2.35 (s, 3H), 1.70–1.56 (m, 2H), 1.25 (d, *J* = 6.4 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.7, 146.9, 135.0, 133.5, 131.2, 128.9, 126.8, 35.8, 31.2, 22.0, 20.8, 12.3. HRMS (ESI) Calcd for $[C_{12}H_{15}O_2, M - H]^-$: 191.1078, Found: 191.1076.

(*Z*)-2-(Oct-5-en-2-yl)benzoic acid (3n)



Colorless oil, 99% yield; 98% ee, $[\alpha]_D^{25}$ +51.1 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 90:10, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 7.30 min for minor isomer and t_R = 10.98 min for major isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 5.21–5.09 (m, 2H), 3.68–3.56 (m, 1H), 1.93–1.72 (m, 4H), 1.59–1.39 (m, 2H), 1.10 (d, *J* = 6.8 Hz, 3H), 0.72 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.3, 149.9, 132.7, 131.9, 130.9, 129.0, 128.8, 126.9, 125.6, 38.3, 34.2, 25.4, 22.2, 20.5, 14.4. HRMS (ESI) Calcd for $[C_{15}H_{19}O_2, M - H]^-$: 231.1391, Found: 231.1391.

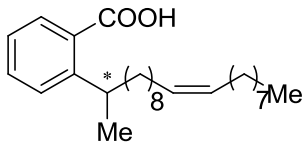
(*E*)-2-(Oct-5-en-2-yl)benzoic acid (3o)



Colorless oil, 99% yield; 97% ee, $[\alpha]_D^{25}$ +43.2 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 85:15, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 4.37 min for minor isomer and t_R = 5.36 min for major isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 8.4 Hz, 1H), 5.25–5.14 (m, 2H), 3.67–3.59 (m, 1H), 1.82–1.68 (m, 4H), 1.60–1.41 (m, 2H), 1.09 (d, *J* = 6.8 Hz, 3H), 0.75 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.2, 149.8, 132.7, 132.2, 130.8, 129.0, 128.8, 127.0, 125.5, 38.1, 33.9, 30.6, 25.6, 22.3, 13.9.

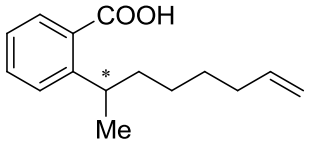
HRMS (ESI) Calcd for [$C_{15}H_{19}O_2$, M − H]$^-$: 231.1391, Found: 231.1390.

(*Z*)-2-(Icos-11-en-2-yl)benzoic acid (3p)



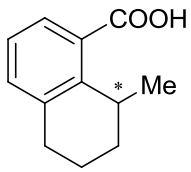
Colorless oil, 99% yield; 99.7% ee, $[\alpha]_D^{25}$ +56.5 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 85:15, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 8.02 min for minor isomer and t_R = 9.98 min for major isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 6.8 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 6.8 Hz, 1H), 5.37–5.32 (m, 2H), 3.84–3.74 (m, 1H), 2.00–1.94 (m, 4H), 1.68–1.51 (m, 2H), 1.31–1.23 (m, 27H), 0.87 (m, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.0, 150.2, 132.6, 130.7, 130.3, 129.9, 128.9, 126.9, 125.4, 38.3, 34.4, 32.6, 31.9, 29.78, 29.71, 29.67, 29.65, 29.54, 29.51, 29.3, 29.19, 29.17, 27.7, 27.2, 22.7, 22.3, 14.1. HRMS (ESI) Calcd for [$C_{27}H_{43}O_2$, M − H]$^-$: 399.3269, Found: 399.3266.

2-(Oct-7-en-2-yl)benzoic acid (3q)



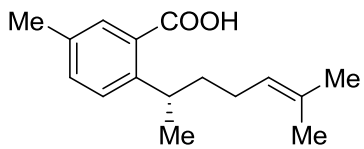
Colorless oil, 83% yield (with 17% over hydrogenation product); 99.6% ee, SFC condition for the corresponding over hydrogenation product: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 90:10, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 5.23 min for minor isomer and t_R = 6.65 min for major isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 9.2 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 1H), 5.82–5.72 (m, 1H), 4.99–4.88 (m, 2H), 3.83–3.78 (m, 1H), 2.03–1.98 (m, 2H), 1.70–1.55 (m, 2H), 1.41–1.34 (m, 2H), 1.28–1.20 (m, 2H), 1.27 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.4, 150.1, 139.1, 132.7, 130.8, 129.0, 126.9, 125.5, 114.2, 38.2, 34.4, 33.7, 29.0, 27.2, 22.3. HRMS (ESI) Calcd for [$C_{15}H_{19}O_2$, M − H]$^-$: 231.1391, Found: 231.1389.

8-Methyl-5,6,7,8-tetrahydronaphthalene-1-carboxylic acid (3r)



White solid, 99% yield, m.p.: 115–116 °C; 91% ee, $[\alpha]_D^{25}$ -90.5 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 80:20, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 7.27 min for major isomer and t_R = 8.44 min for minor isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.6 Hz ,1H), 4.05–4.00 (m, 1H), 2.90–2.77 (s, 2H), 1.94–1.73 (m, 4H), 1.24 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.2, 144.7, 137.7, 134.2, 129.3, 128.7, 125.1, 30.1, 29.9, 28.8, 23.4, 17.6. HRMS (ESI) Calcd for [$C_{12}H_{13}O_2$, M − H]$^-$: 189.0921, Found: 189.0923.

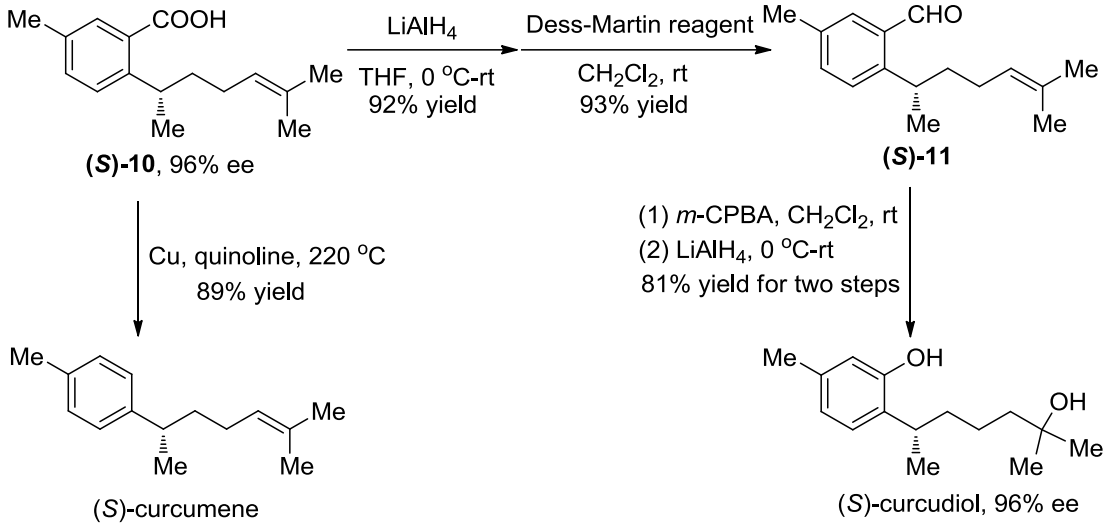
(*S*)-5-Methyl-2-(6-methylhept-5-en-2-yl)benzoic acid (10)



Colorless oil, 98% yield; 96% ee, $[\alpha]_D^{25}$ -37.4 (*c* 1.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 85:15, flow rate = 2.0 mL/min, 254 nm UV detector, t_R = 5.37 min for *S* isomer and t_R = 6.69 min for *R* isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (s,

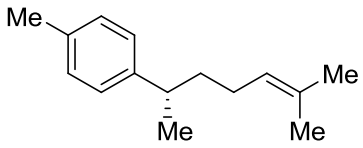
1H), 7.37 (s, 2H), 5.16 (t, J = 6.8 Hz, 1H), 3.87–3.79 (m, 1H), 2.42 (s, 3H), 2.03–1.91 (m, 2H), 1.80–1.60 (m, 2H), 1.72 (s, 3H), 1.56 (s, 3H), 1.32 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.6, 145.8, 133.9, 132.5, 130.4, 130.1, 127.8, 125.8, 123.4, 37.2, 32.7, 25.1, 24.6, 21.3, 19.7, 16.5. HRMS (ESI) Calcd for [$C_{16}H_{21}O_2$, M − H]$^-$: 245.1547, Found: 245.1546.

(C) Synthesis of (*S*)-Curcumene and (*S*)-Curcudiol



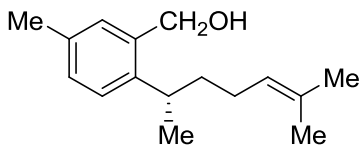
(*S*)-Curcumene[3]

Copper powder (96 mg, 1.5 mmol) was added to a solution of **10** (122 mg, 0.50 mmol) in quinoline (3 mL) under nitrogen atmosphere. The mixture was heated at 220 °C for 3 h. After cooling, the reaction mixture was diluted with 3 N HCl (15 mL) and extracted with Et_2O (3 × 15 mL). The organic phase was washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was chromatographied on silica gel (PE) to give (*S*)-curcumene (90 mg, 89 % yield) as a colorless oil. $[\alpha]_D^{25}$ +44.6 (*c* 1.0, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10–7.05 (m, 4H), 5.09 (t, *J* = 7.2 Hz, 1H), 2.69–2.61 (m, 1H), 2.31 (s, 3H), 1.93–1.82 (m, 2H), 1.67 (s, 3H), 1.65–1.54 (m, 2H), 1.52 (s, 3H), 1.21 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.7, 135.2, 131.4, 129.0, 127.0, 124.6, 39.1, 38.5, 26.2, 25.8, 22.6, 21.1, 17.7.



(*S*)-(5-Methyl-2-(6-methylhept-5-en-2-yl)phenyl)methanol

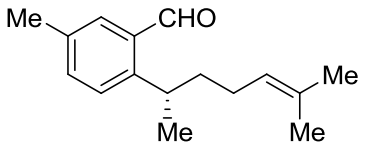
To a suspension of $LiAlH_4$ (87 mg, 2.3 mmol) in 2 mL of anhydrous THF was added a solution of of **10** (114 mg, 0.46 mmol) in 2 mL THF at 0 °C over a period of 15 min. The resulting mixture was stirred at 0 °C for 2 h, and quenched with saturated $NaHCO_3$ and 10% NaOH at 0 °C. The mixture was filtered through Celite and washed thoroughly with ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was chromatographied on silica gel (PE/EA = 8:1) to give desired product (102 mg, 96 % yield) as a colorless oil. $[\alpha]_D^{25}$ +23.4 (*c* 1.0, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19–7.11 (m, 3H), 5.10 (t, *J* = 7.2 Hz, 1H), 4.71−4.64 (m, 2H), 3.08–2.99 (m, 1H), 2.33 (s, 3H), 2.00–1.82 (m, 2H), 1.67 (s, 3H), 1.66–1.53 (m, 2H), 1.49 (s, 3H), 1.22 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz,



$CDCl_3$): δ 142.9, 137.7, 135.3, 131.8, 129.2, 129.0, 125.9, 124.5, 63.4, 38.1, 33.1, 26.2, 25.7, 22.8, 21.0, 17.7. HRMS (ESI) Calcd for $[C_{16}H_{24}ONa, M + Na]^+$: 255.1719, Found: 255.1718.

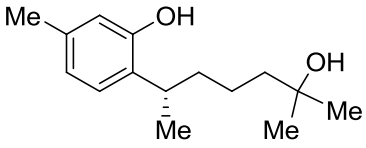
(*S*)-5-Methyl-2-(6-methylhept-5-en-2-yl)benzaldehyde (11)

Dess–Martin periodinane (254 mg, 0.6 mmol) was added to a solution of the alcohol (90 mg, 0.4 mmol) in CH_2Cl_2 (4 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 0.5 h. The reaction was quenched by adding saturated $NaHCO_3$ (4 mL) and saturated $NaHSO_3$ (4 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic extracts were dried over $MgSO_4$, and concentrated. The residue was chromatographied on silica gel (PE/EA = 20:1) to afford the product **11** (81 mg, 93% yield) as a colorless oil. $[\alpha]_D^{25}$ -14.5 (*c* 1.0, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.34 (s, 1H), 7.63 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 5.07 (t, *J* = 6.0 Hz, 1H), 3.80–3.71 (m, 1H), 2.37 (s, 3H), 1.93–1.87 (m, 2H), 1.74–1.61 (m, 2H), 1.65 (s, 3H), 1.46 (s, 3H), 1.27 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.2, 147.6, 135.7, 134.9, 133.4, 131.9, 130.7, 126.7, 124.1, 38.1, 31.7, 26.0, 25.7, 22.4, 20.7, 17.6.



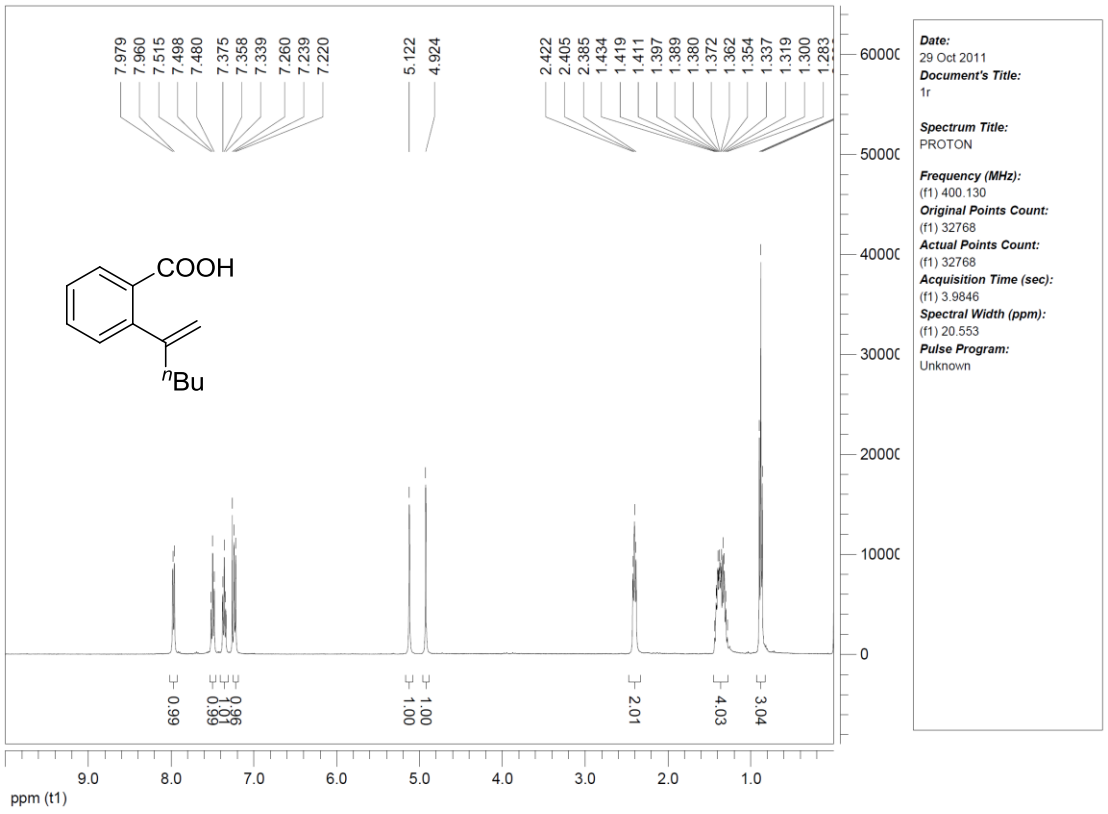
(*S*)-Curcudiol[4]

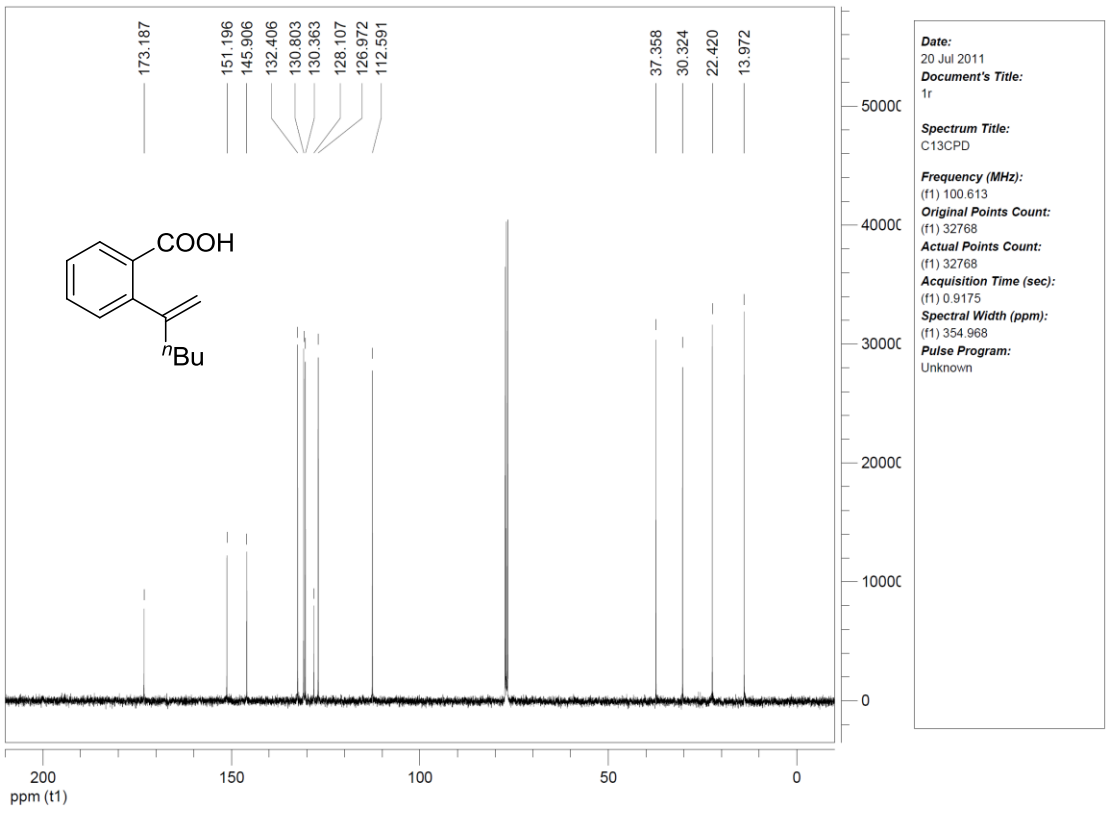
m-CPBA (241 mg, 1.4 mmol) was added to a solution of aldehyde **11** (81 mg, 0.35 mmol) and $KHCO_3$ (14 mg, 0.14 mmol) in CH_2Cl_2 (3 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperate overnight. The reaction was quenched by adding saturated $NaHCO_3$ (10 mL) and CH_2Cl_2 (10 mL). The layers were separated and the aqueous layer was further extracted with CH_2Cl_2 (2 × 10 mL). The combined organic extracts were dried over $MgSO_4$, and concentrated to get epoxide which was used immediately in the following step without further purification. To a suspension of $LiAlH_4$ (133 mg, 3.5 mmol) in 2 mL of anhydrous THF was added a solution of epoxide in 2 mL THF at 0 ^{o}C over a period of 15 min. The resulting mixture was stirred at the same temperature for 2 h, and quenched with H_2O at 0 ^{o}C. The mixture was filtered through Celite and washed thoroughly with ether. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was chromatographied on silica gel (PE/EA = 4:1) to give (*S*)-curcudiol (67 mg, 81 % yield) as a colorless oil. 96% ee, $[\alpha]_D^{25}$ +10.7 (*c* 5.0, chloroform), SFC condition: Chiralpak AD-H column (25 cm × 0.46 cm ID), sc CO_2/2-propanol = 80:20, flow rate = 2.0 mL/min, 220 nm UV detector, t_R = 9.17 min for *R* isomer and t_R = 10.55 min for *S* isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (d, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.58 (s, 1H), 5.34 (s, 1H), 3.12–3.04 (m, 1H), 2.26 (s, 3H), 1.68–1.29 (m, 8H), 1.22 (d, *J* = 7.2 Hz, 3H), 1.20 (s, 3H), 1.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.9, 135.4, 129.5, 125.8, 120.6, 115.3, 70.4, 42.3, 36.7, 30.3, 28.6, 27.8, 21.1, 19.9, 19.8. HRMS (ESI) Calcd for $[C_{15}H_{23}O_2, M - H]^-$: 235.1704, Found: 235.1710.



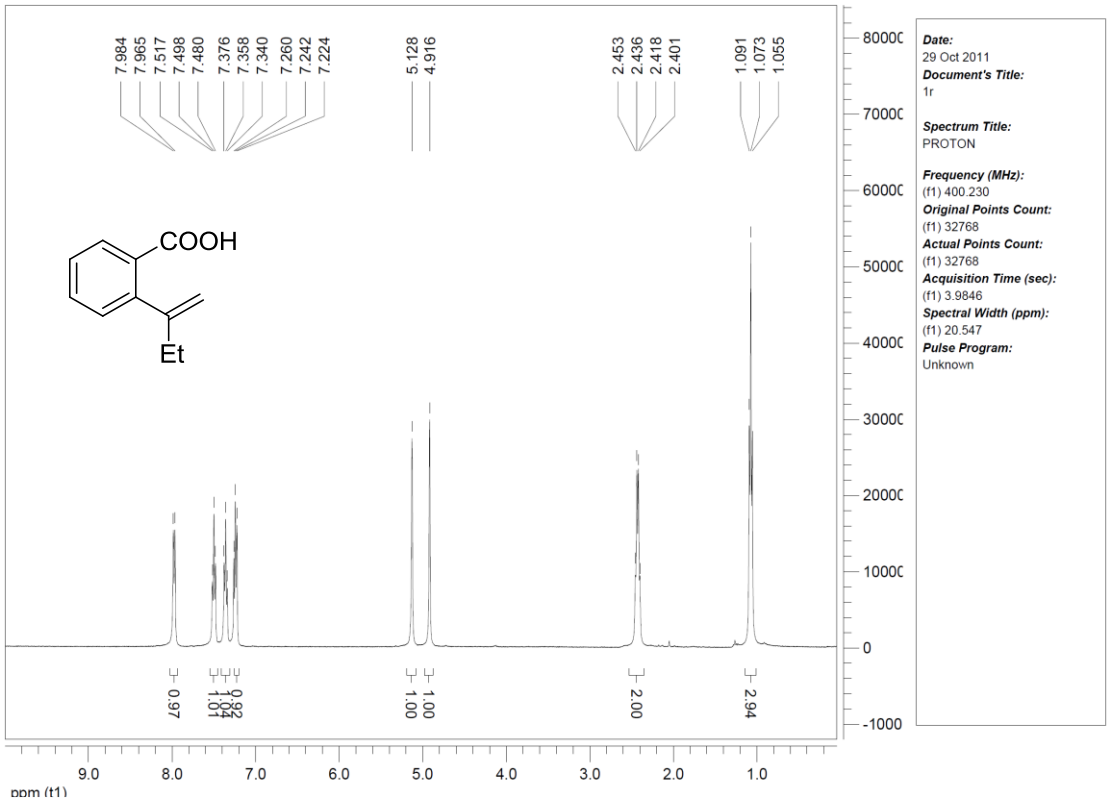
(D) NMR Spectra of New Compounds

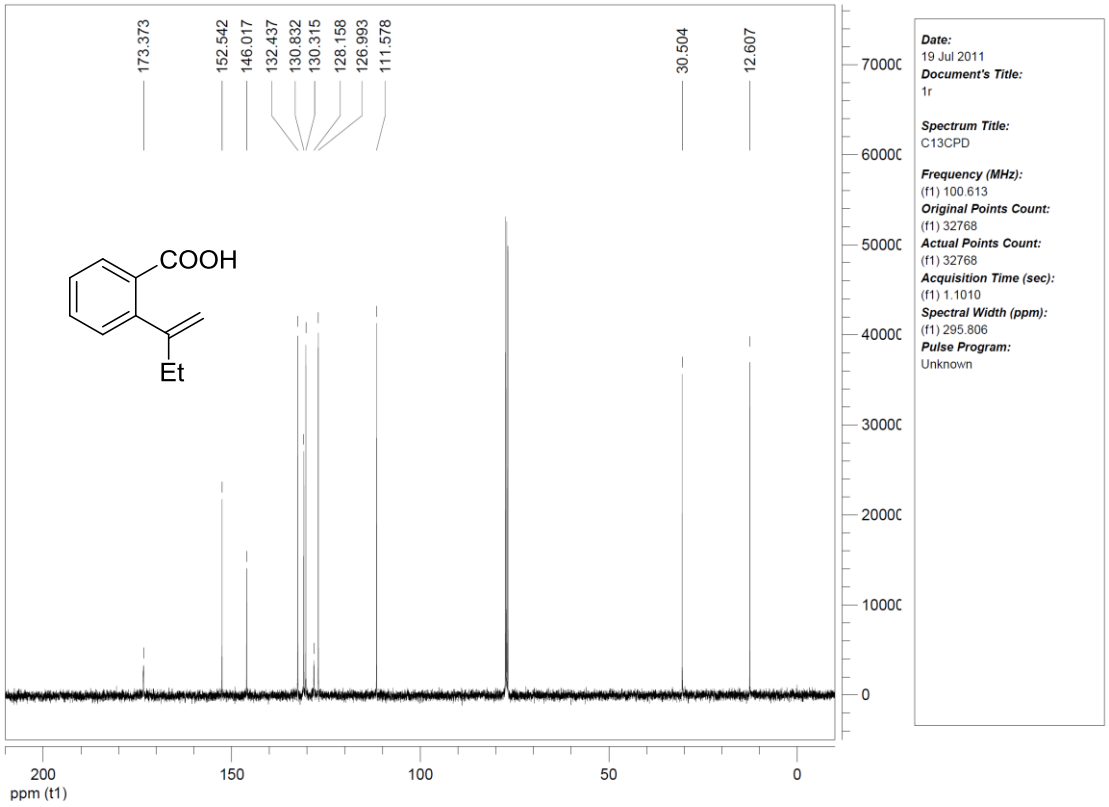
2-(Hex-1-en-2-yl)benzoic acid (2a)



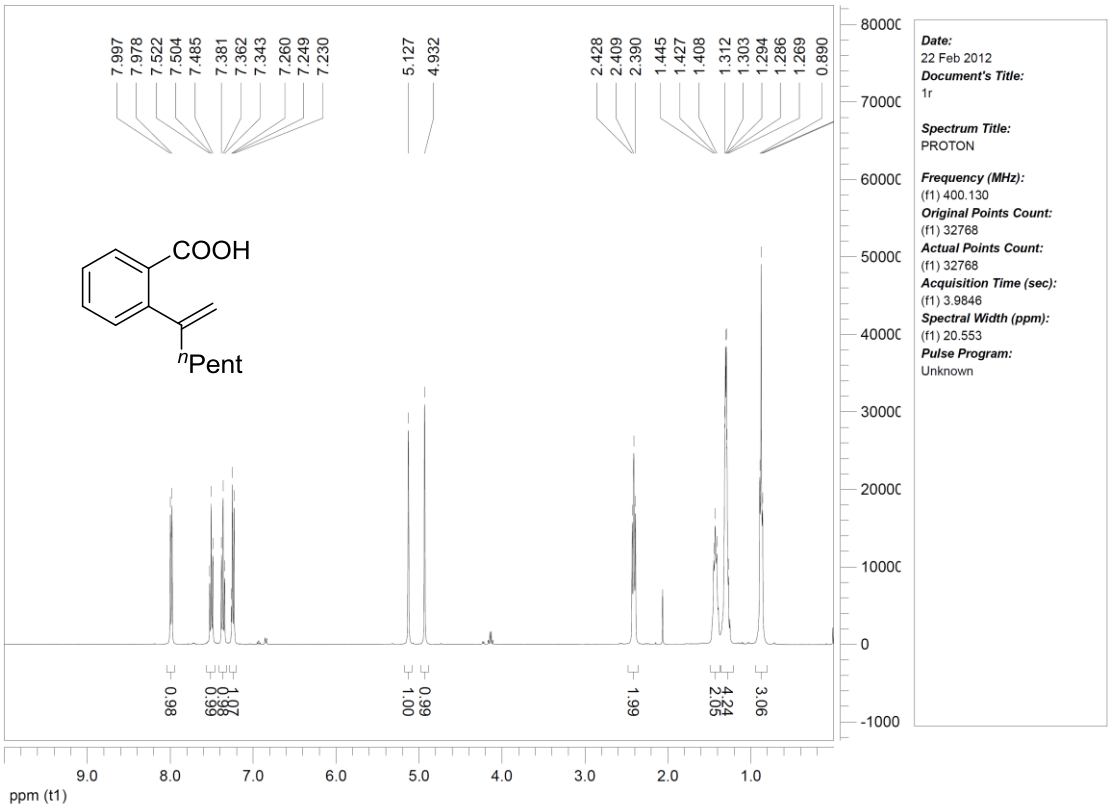


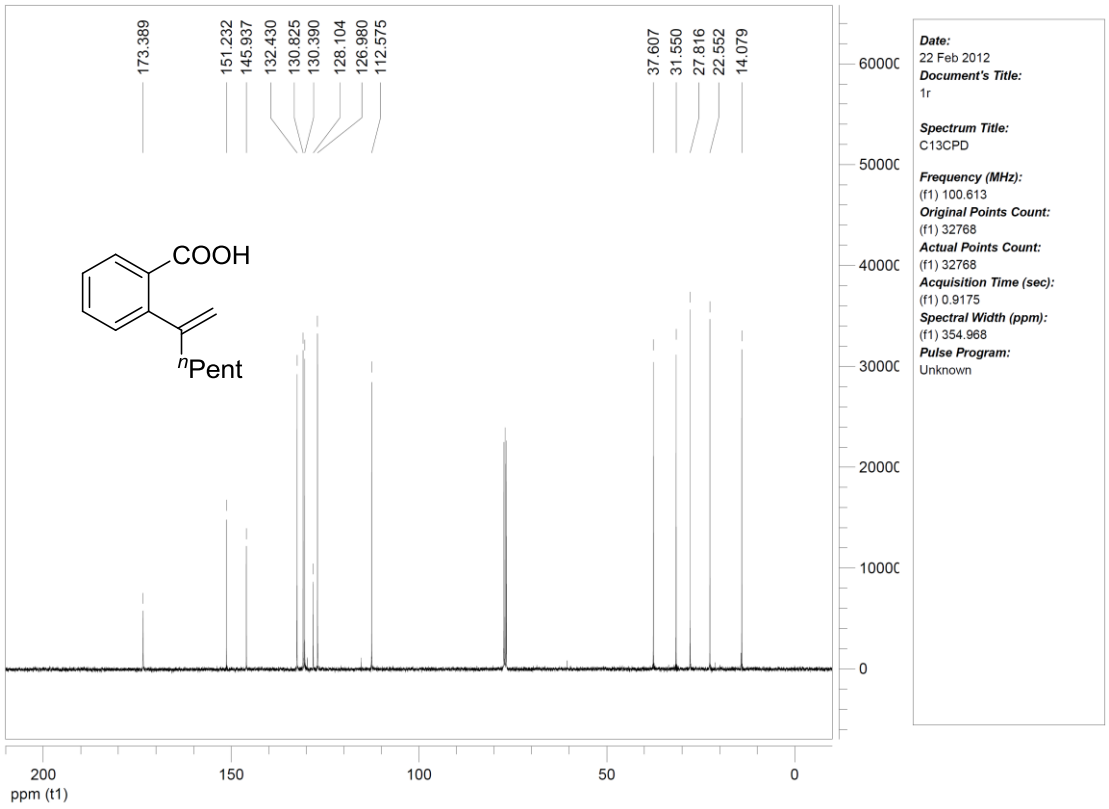
2-(But-1-en-2-yl)benzoic acid (2b)



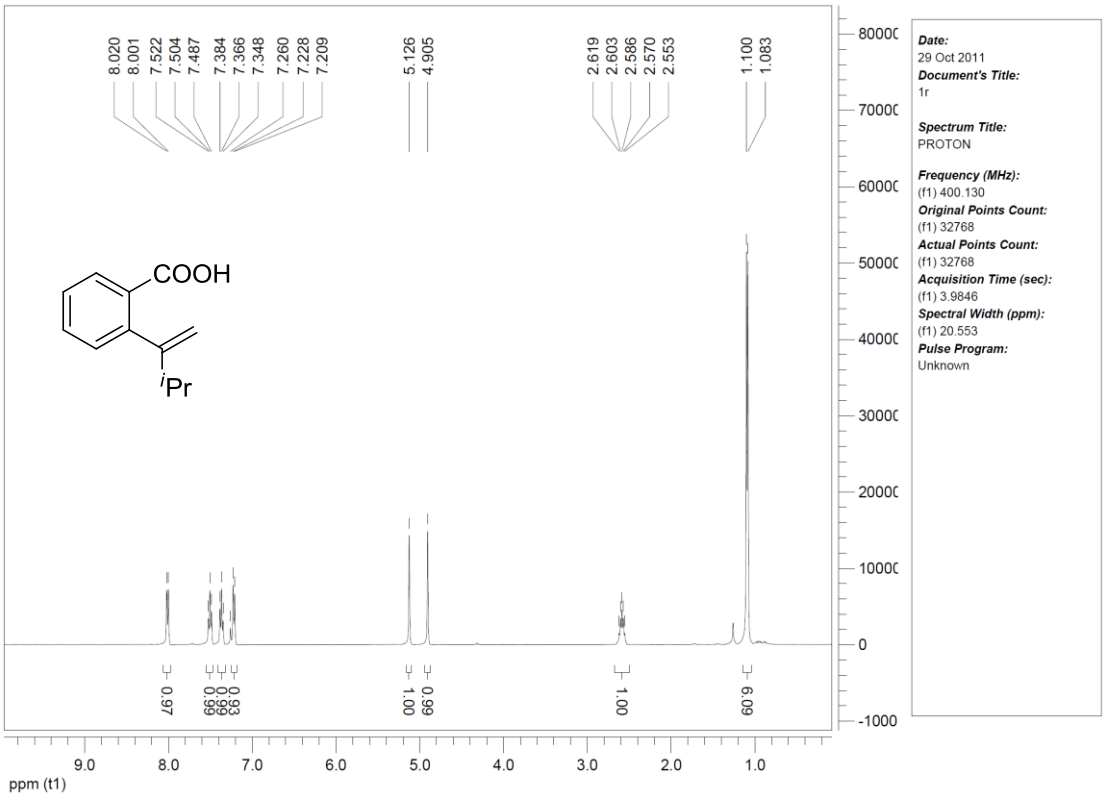


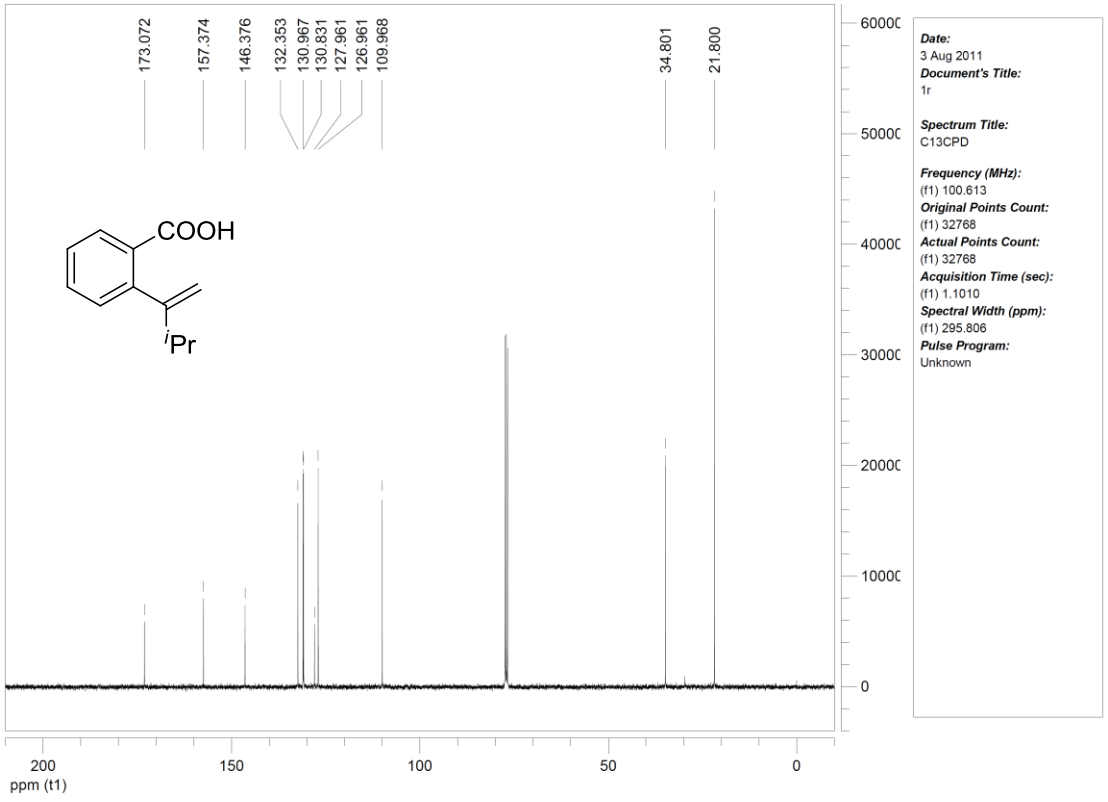
2-(Hept-1-en-2-yl)benzoic acid (2c)



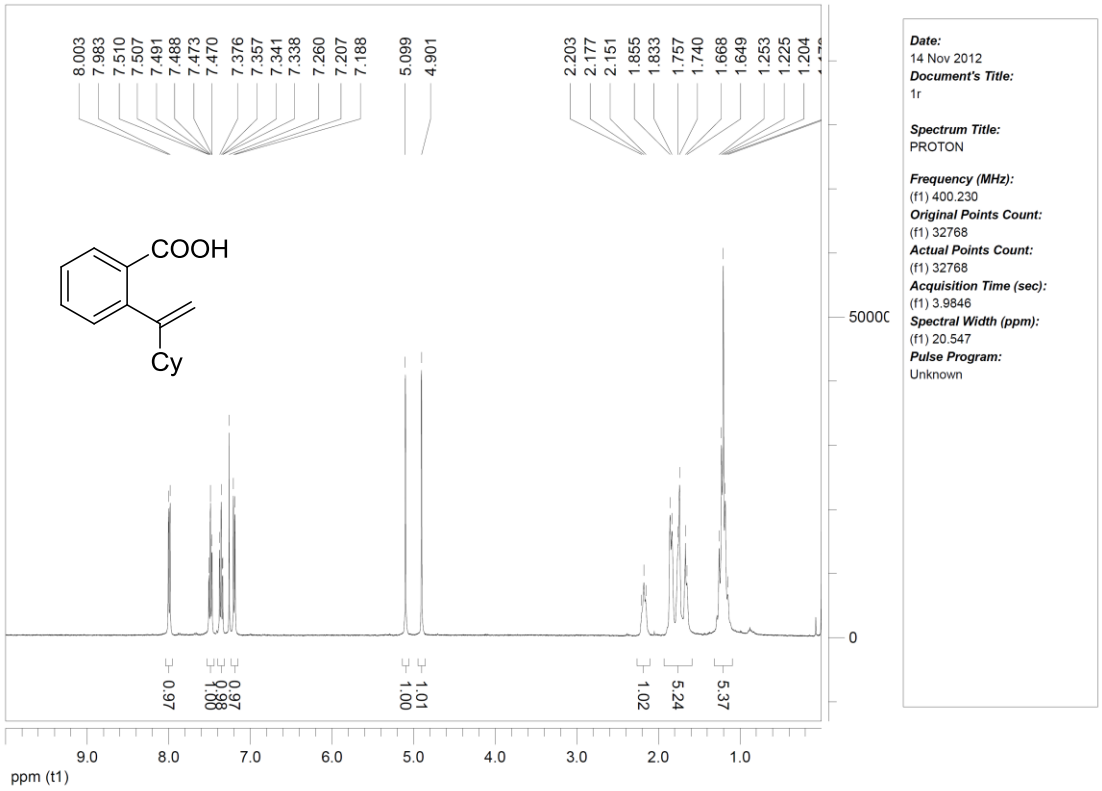


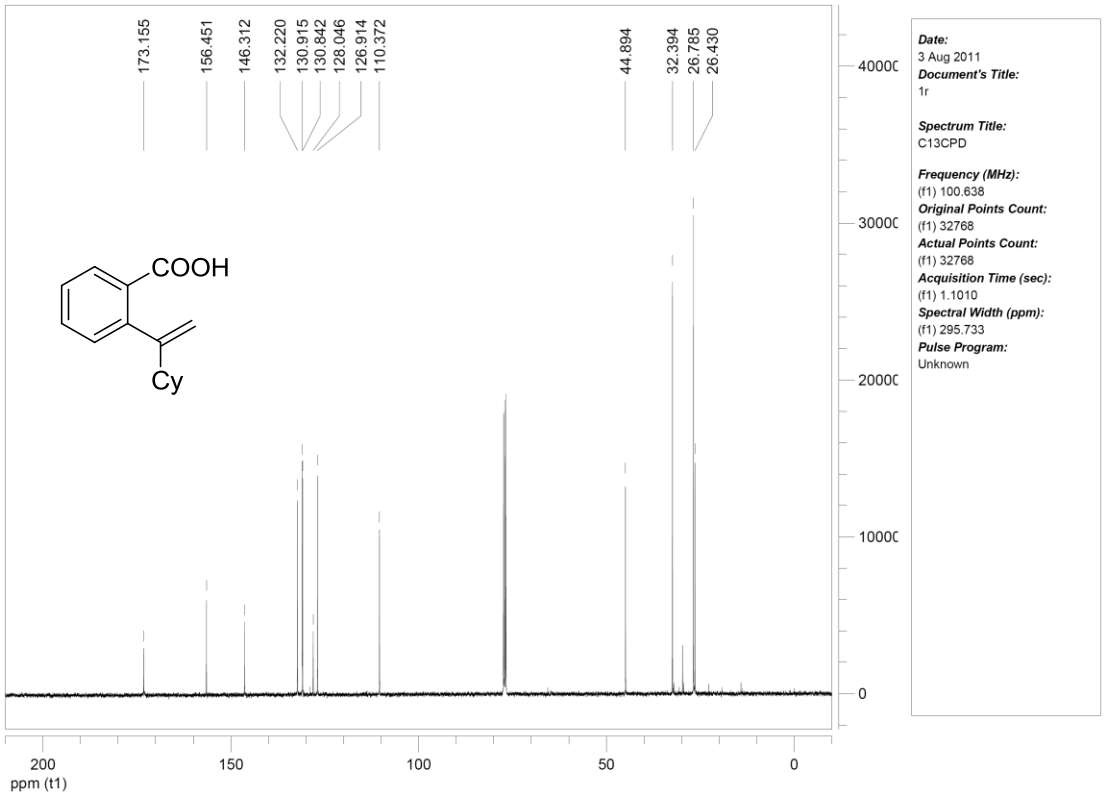
2-(3-Methylbut-1-en-2-yl)benzoic acid (2d)



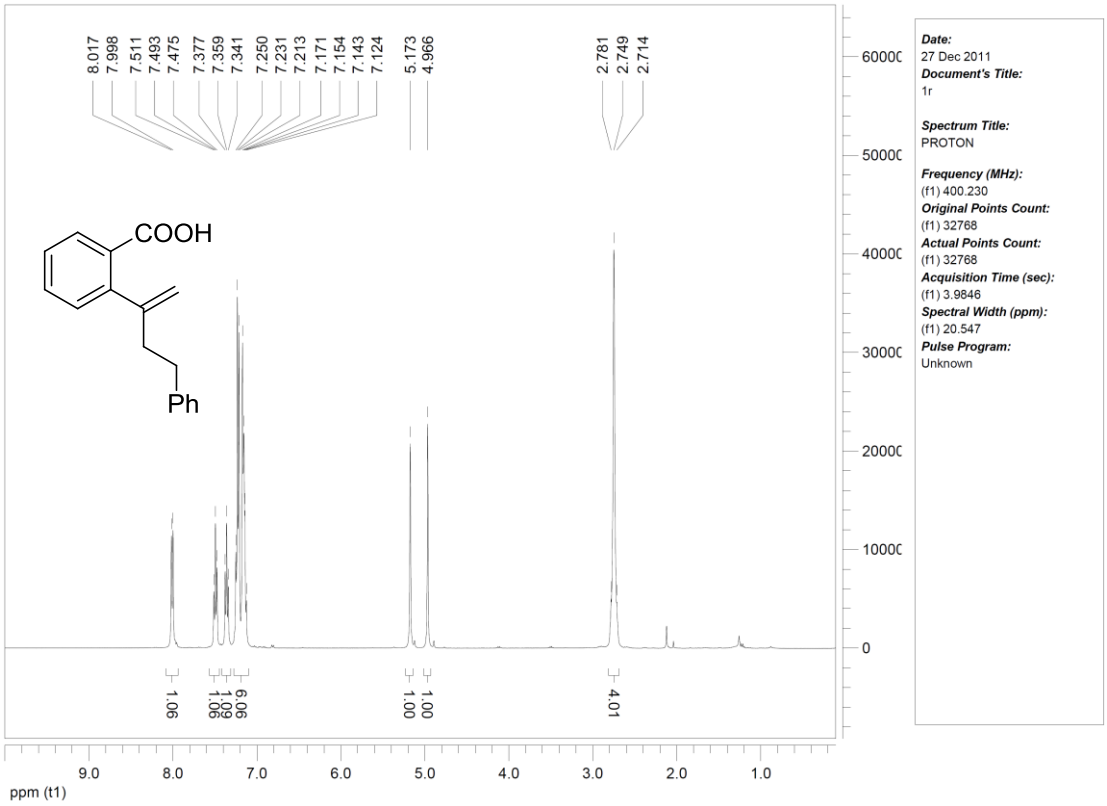


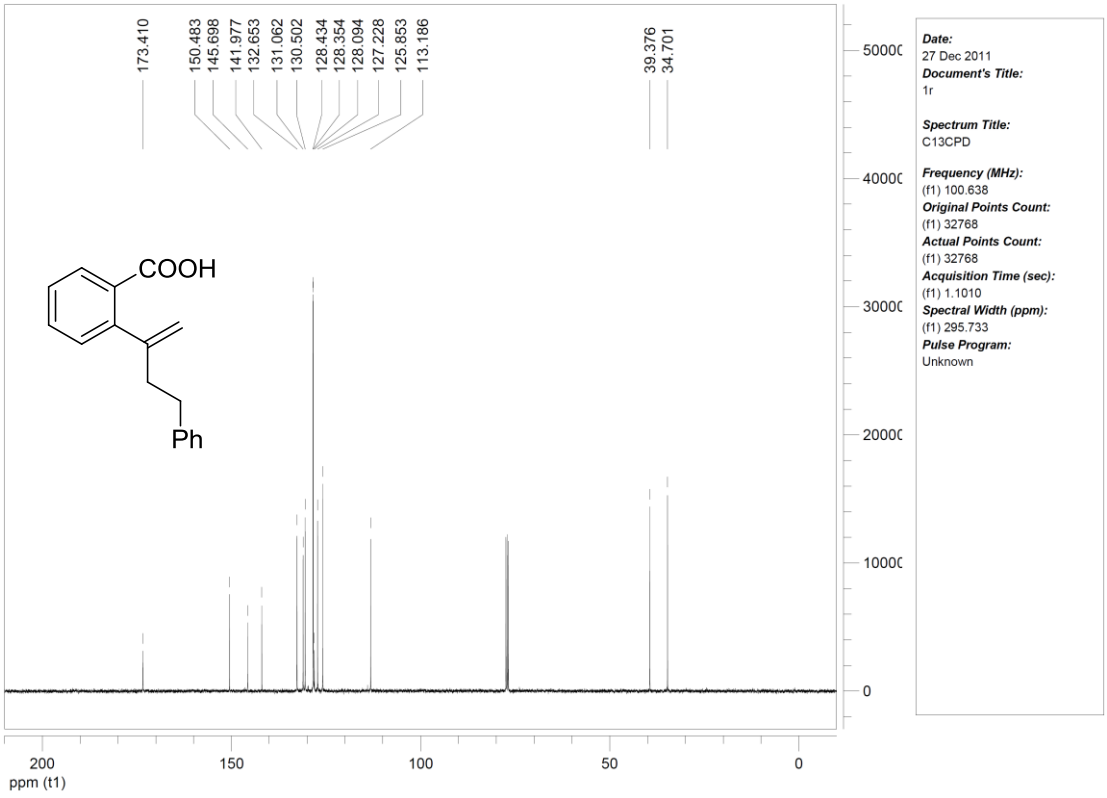
2-(1-Cyclohexylvinyl)benzoic acid (2e)



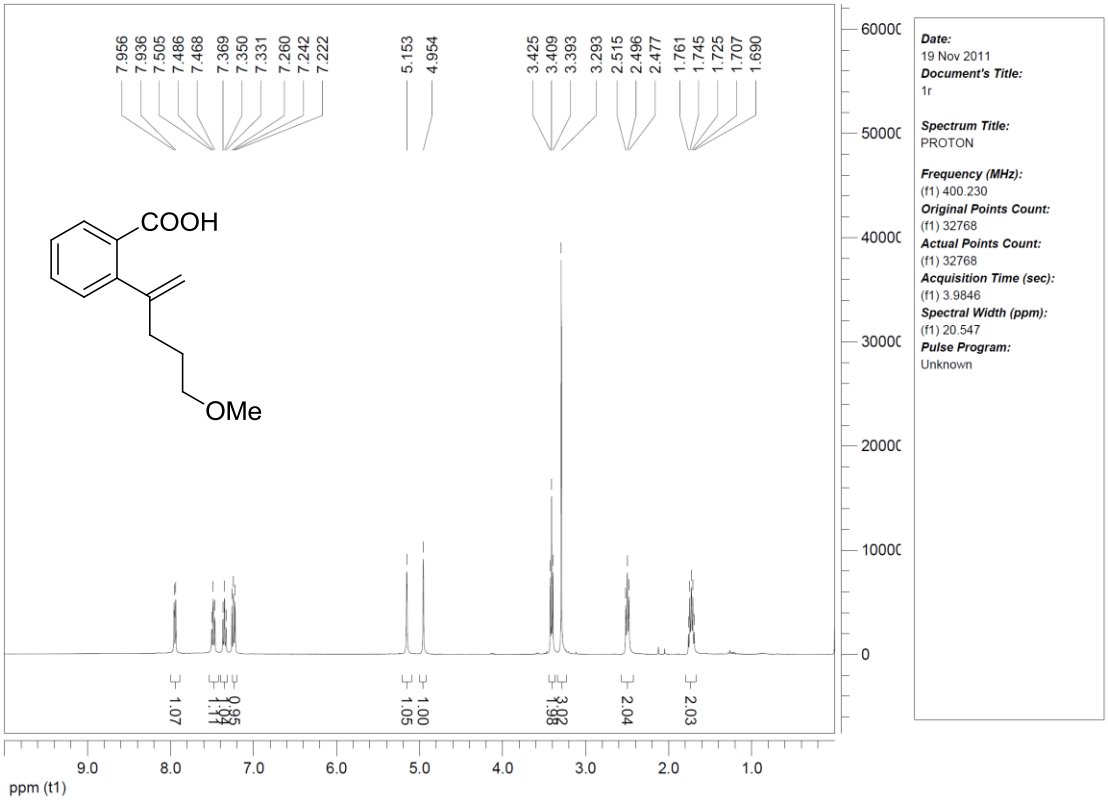


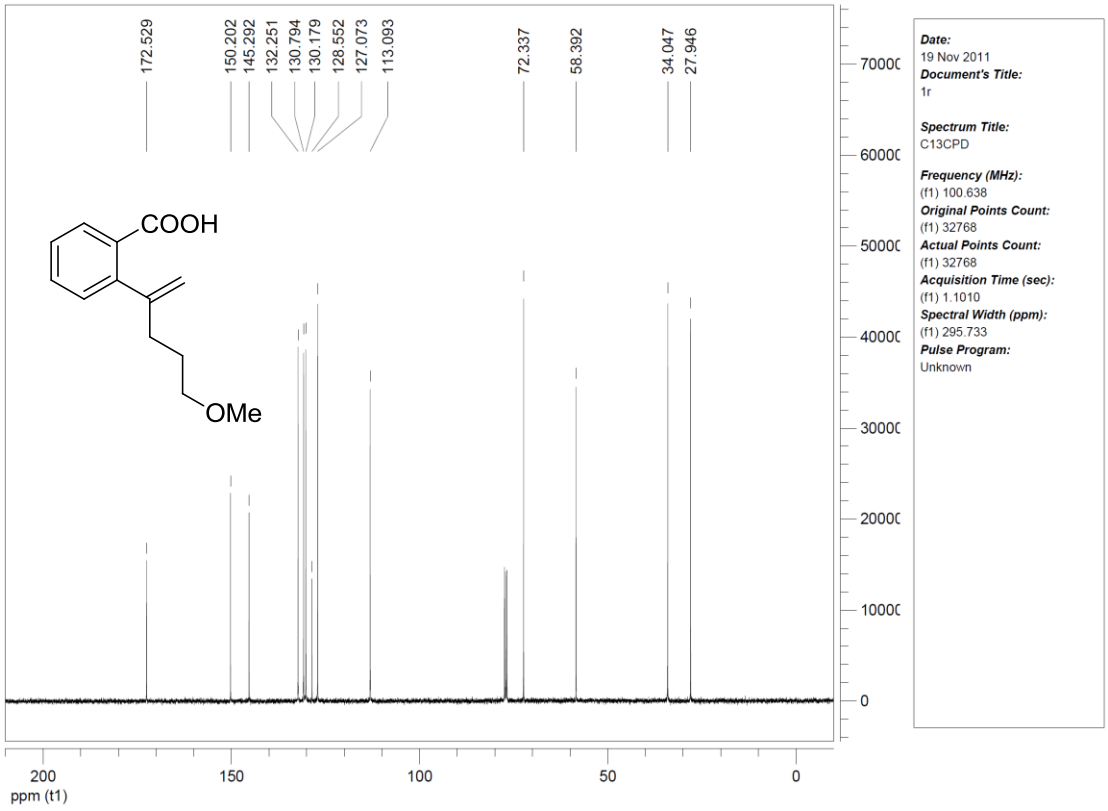
2-(4-Phenylbut-1-en-2-yl)benzoic acid (2f)



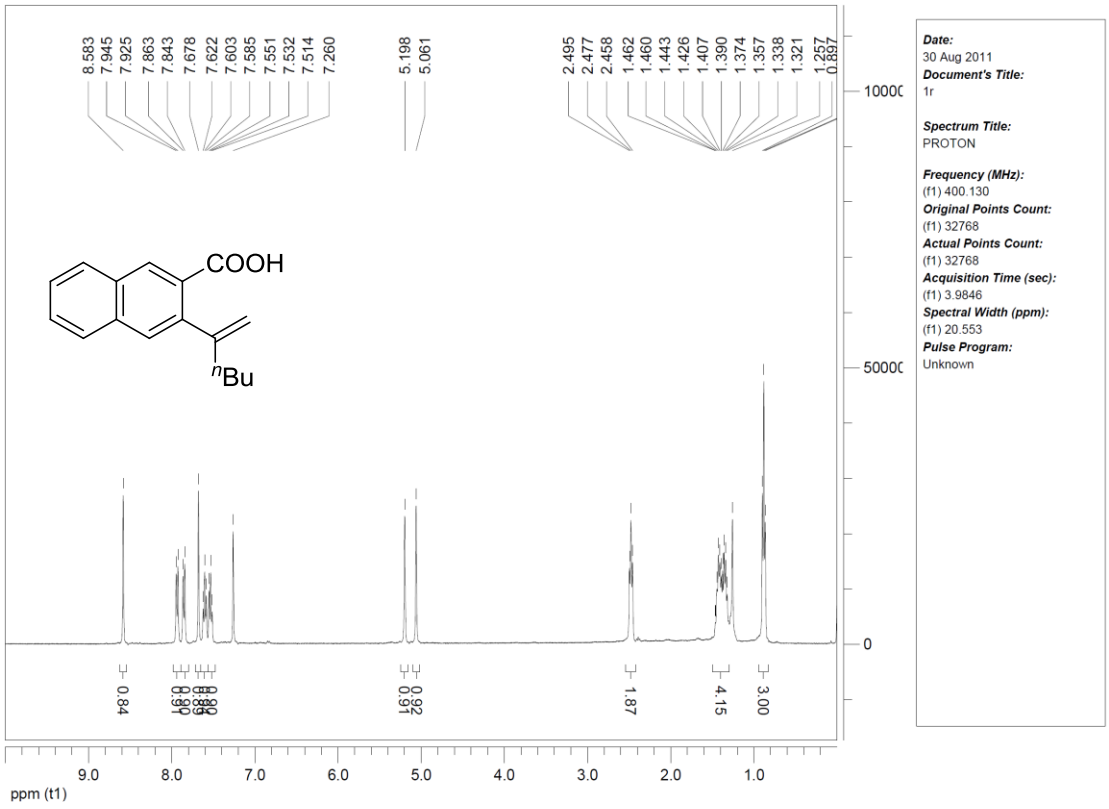


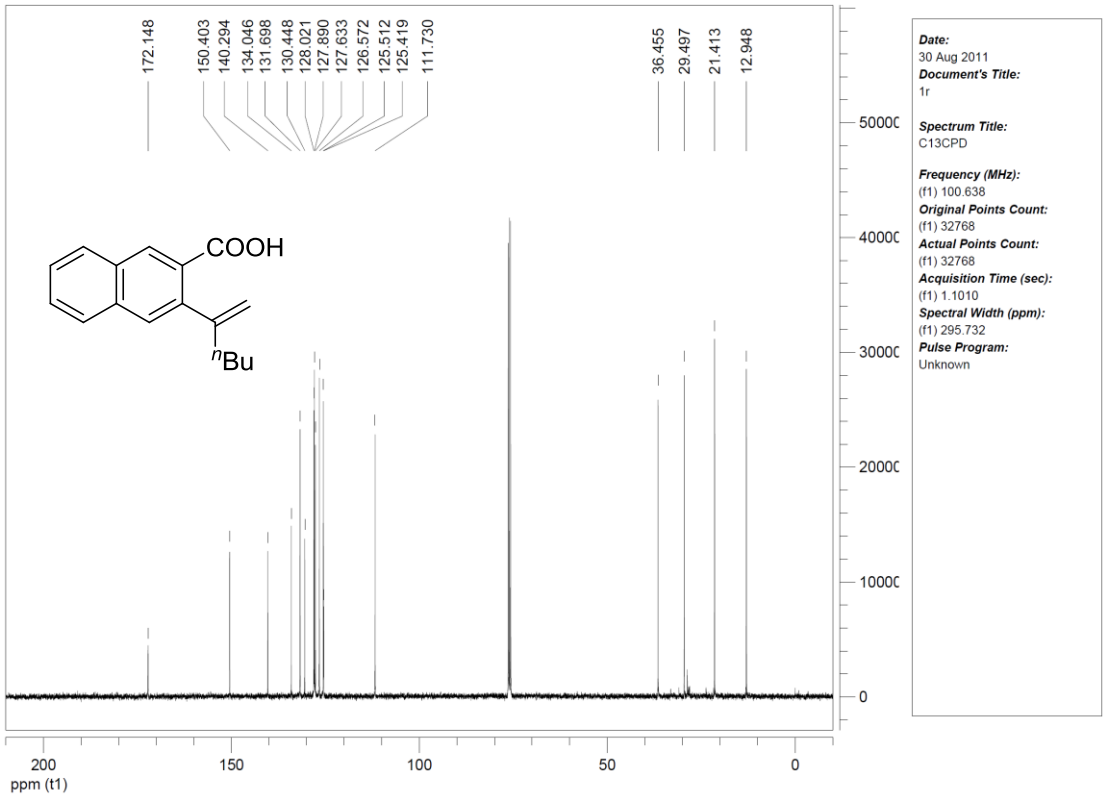
2-(5-Methoxypent-1-en-2-yl)benzoic acid (2g)



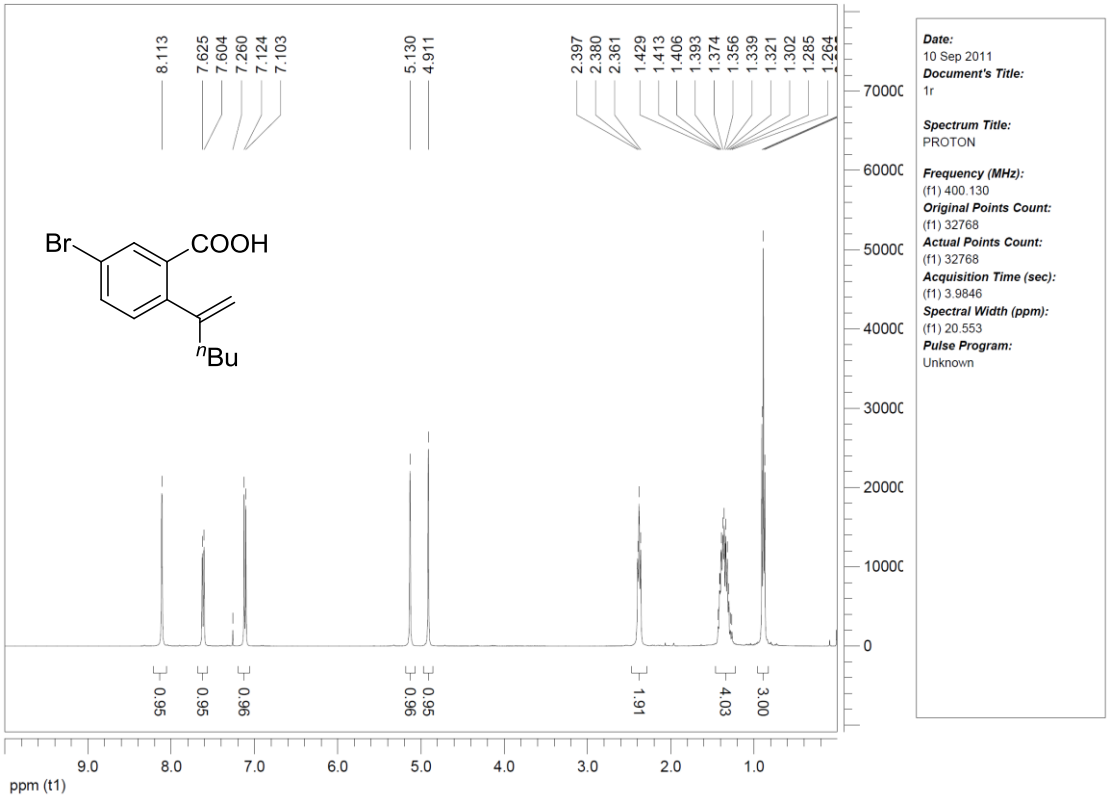


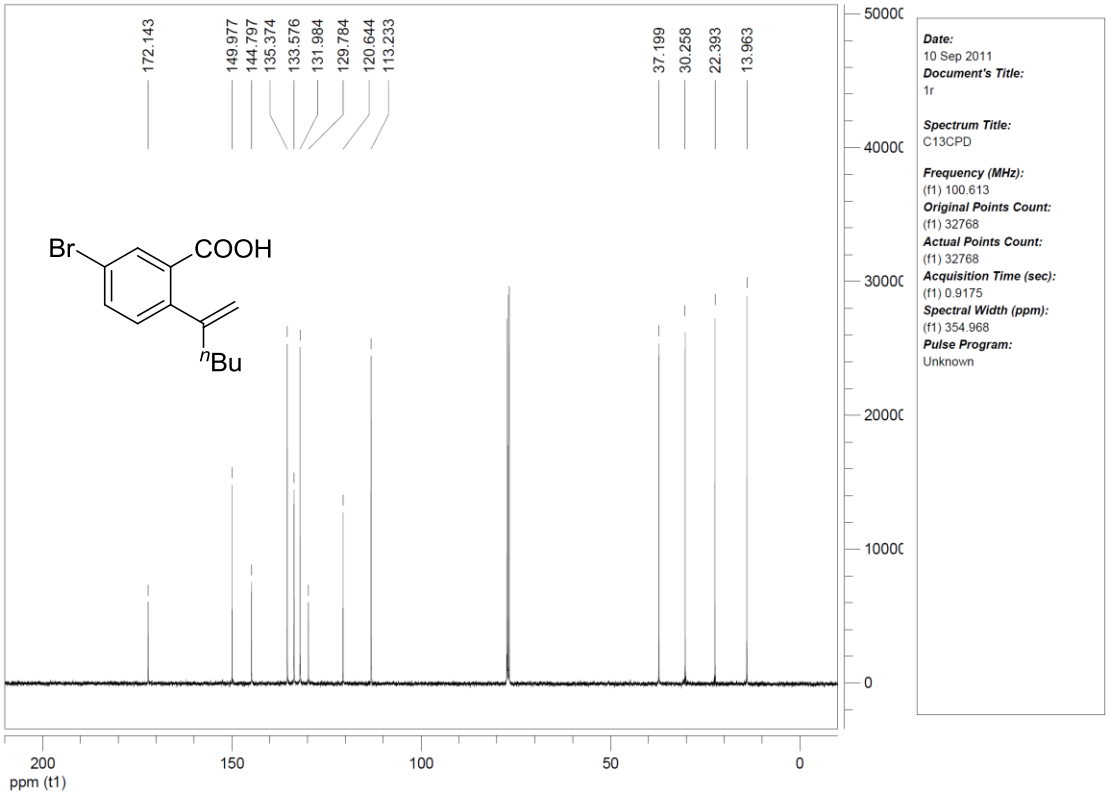
3-(Hex-1-en-2-yl)-2-naphthoic acid (2h)



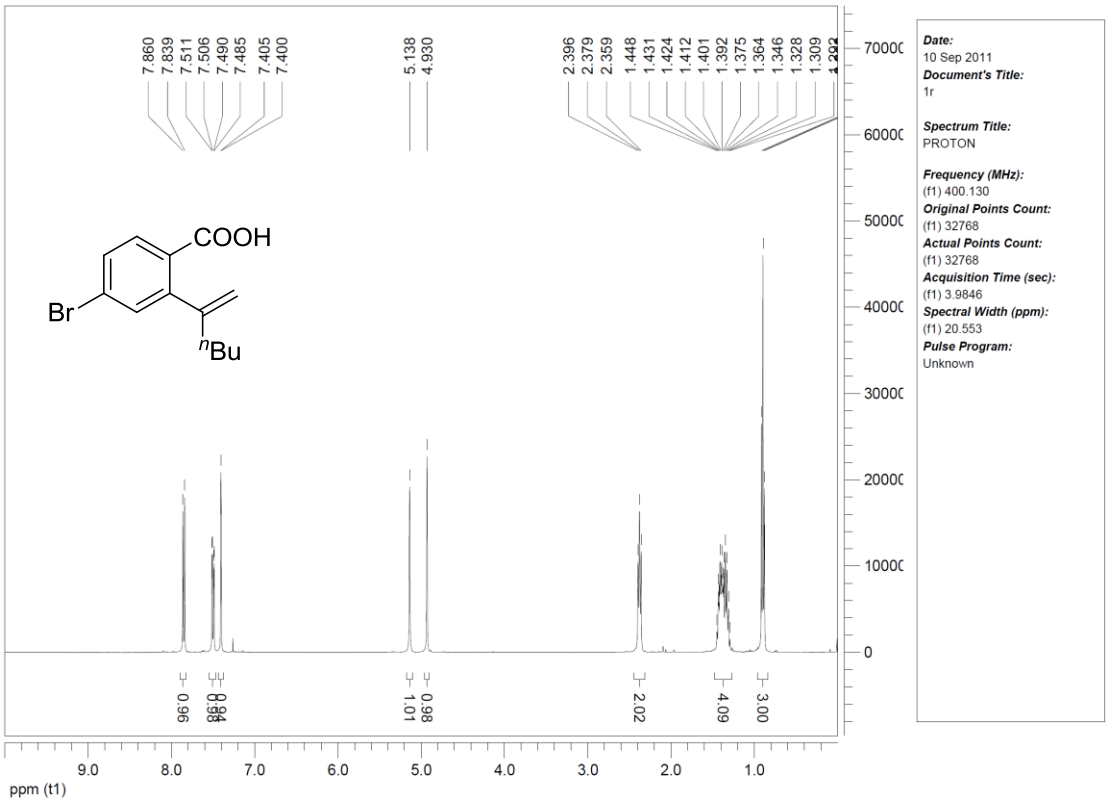


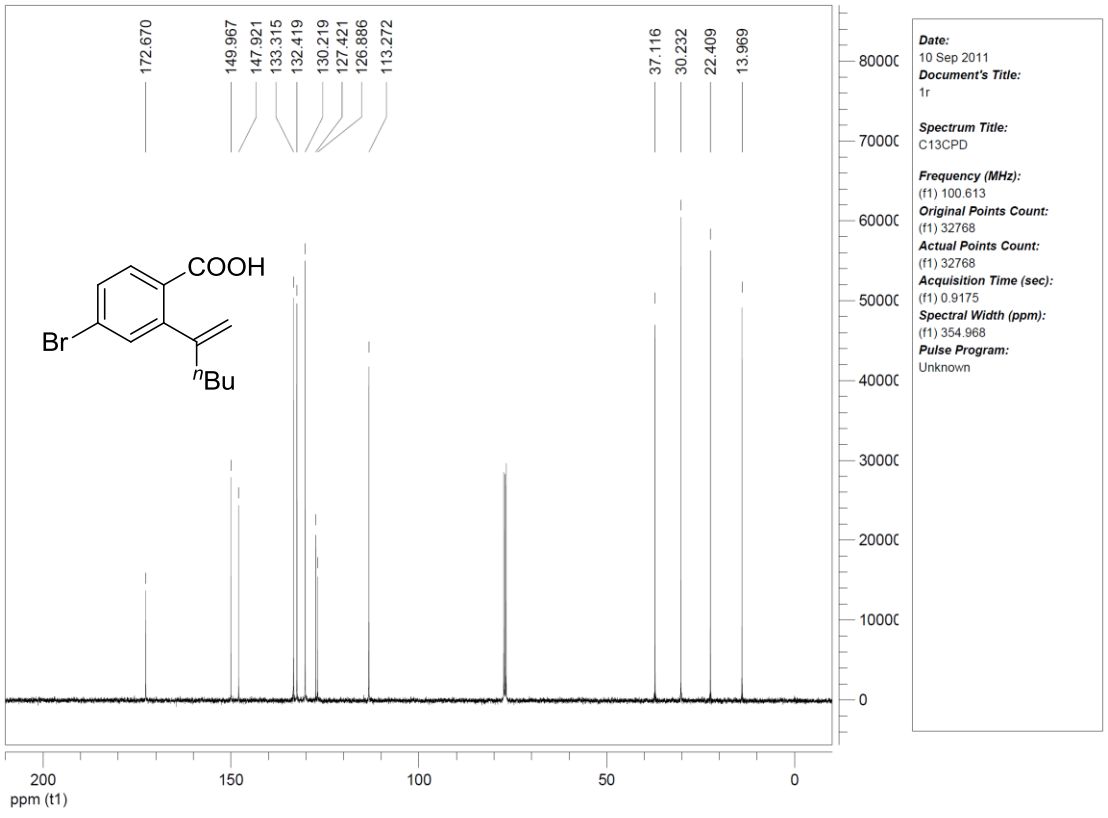
5-Bromo-2-(hex-1-en-2-yl)benzoic acid (2i)



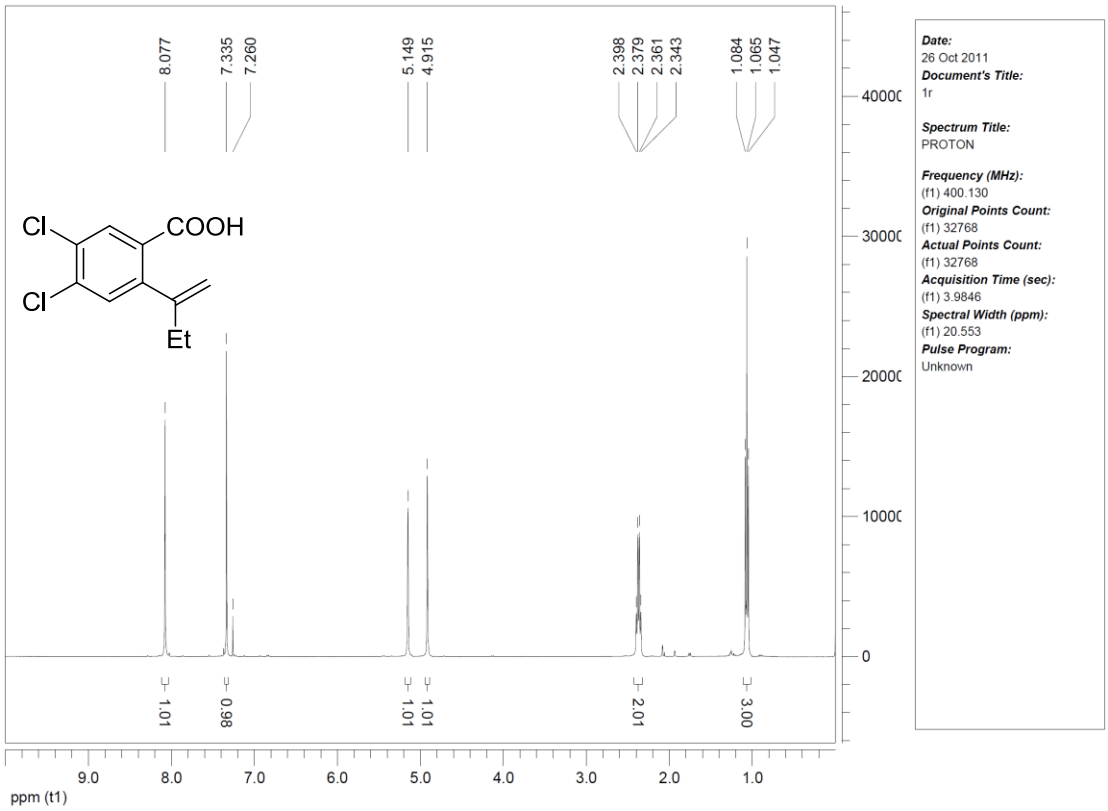


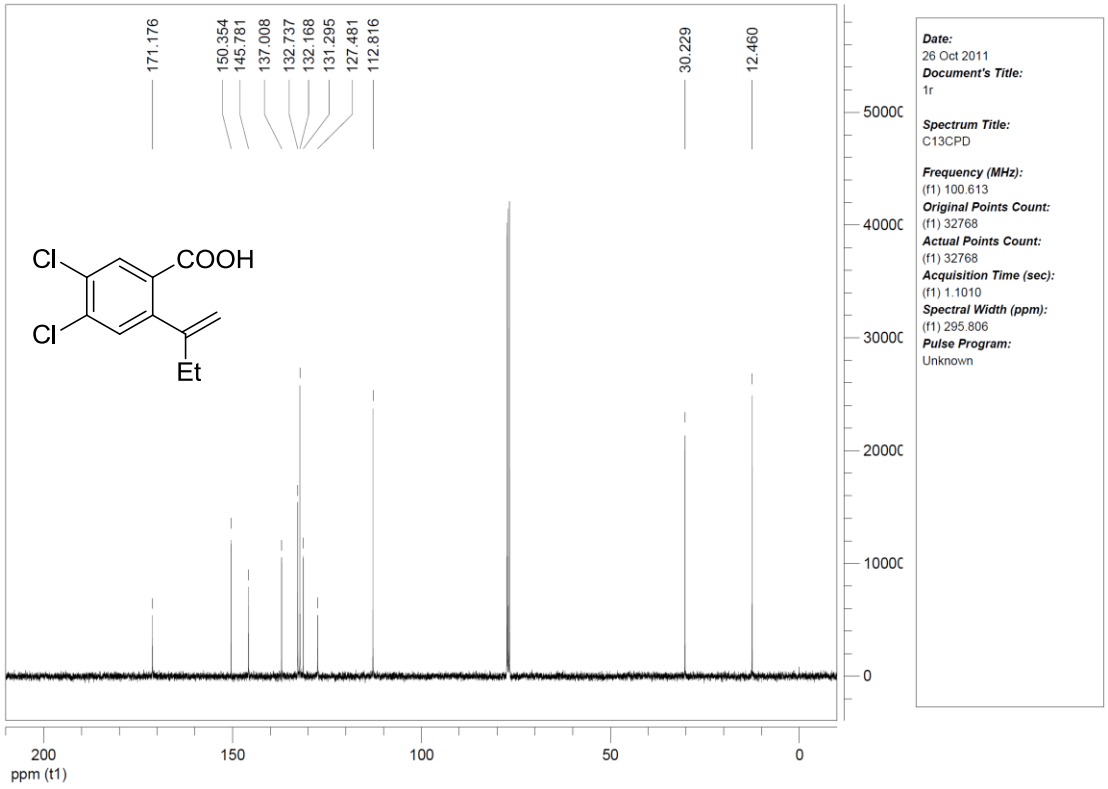
4-Bromo-2-(hex-1-en-2-yl)benzoic acid (2j)



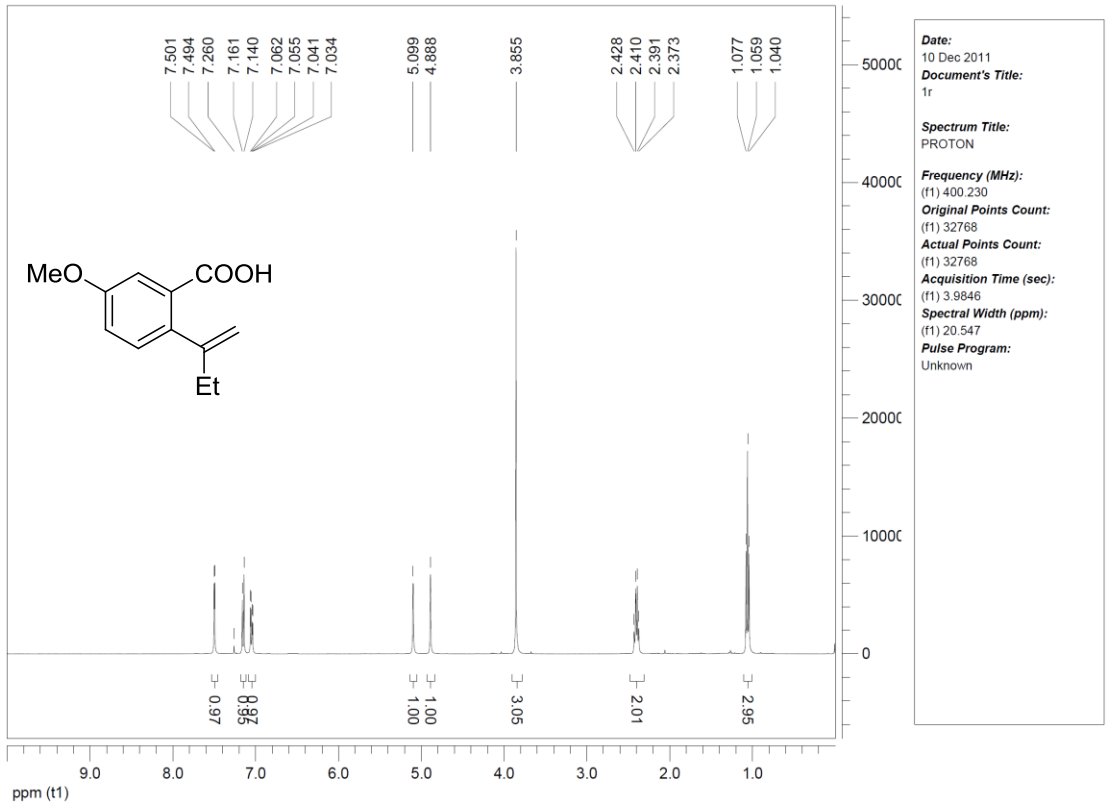


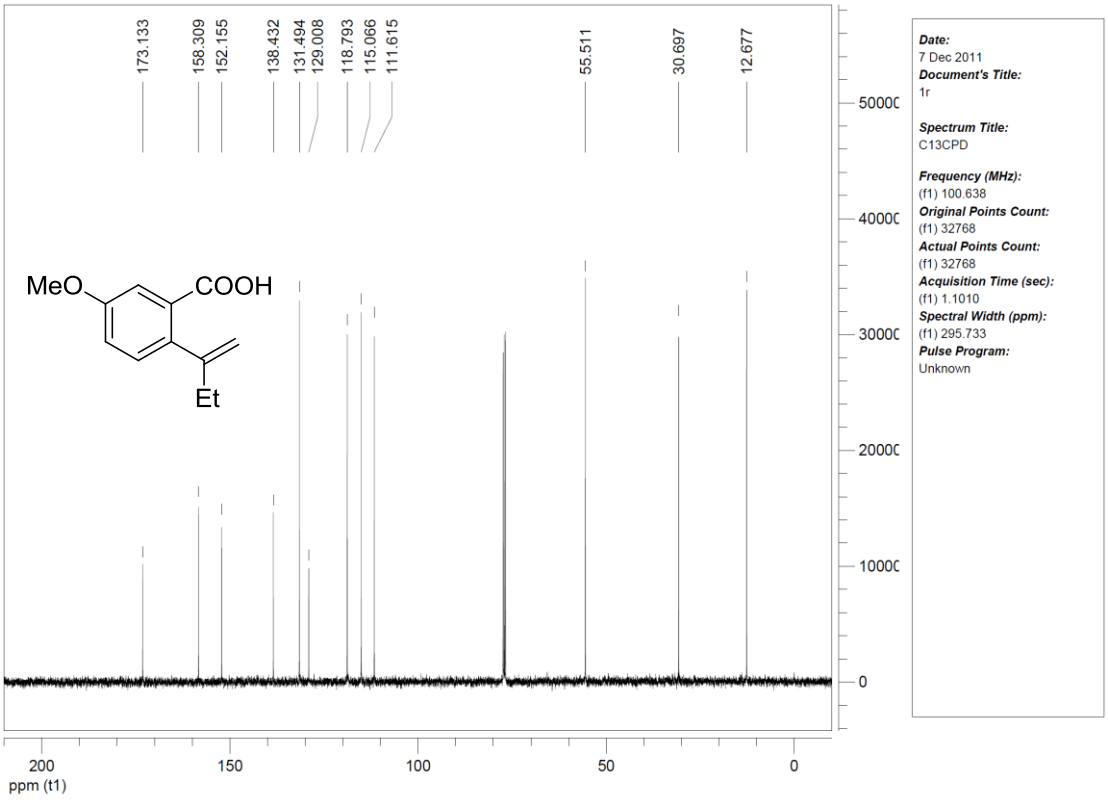
2-(But-1-en-2-yl)-4,5-dichlorobenzoic acid (2k)



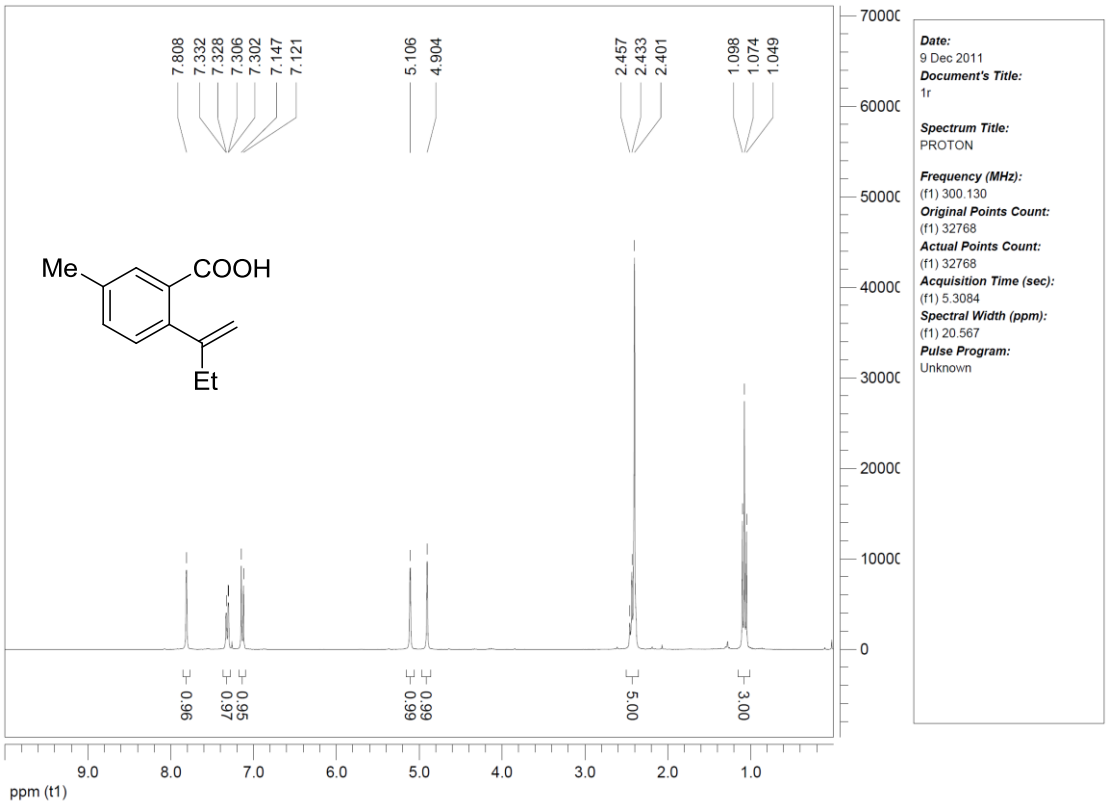


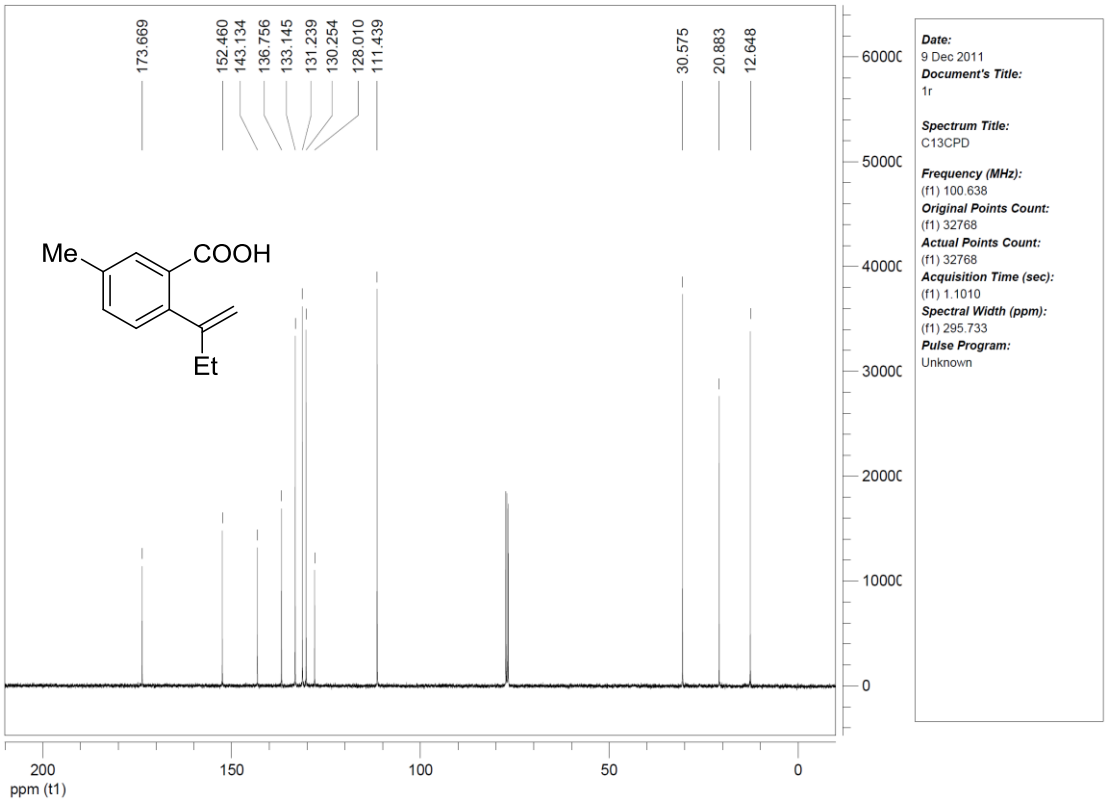
2-(But-1-en-2-yl)-5-methoxybenzoic acid (2l)



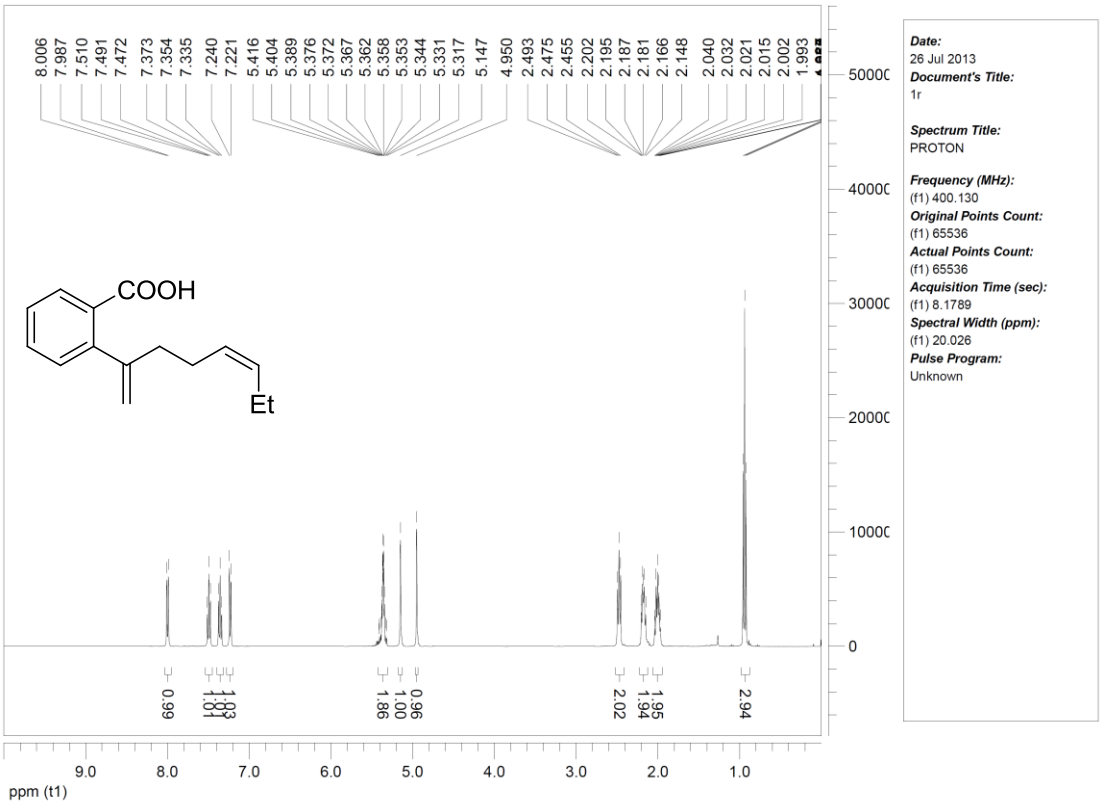


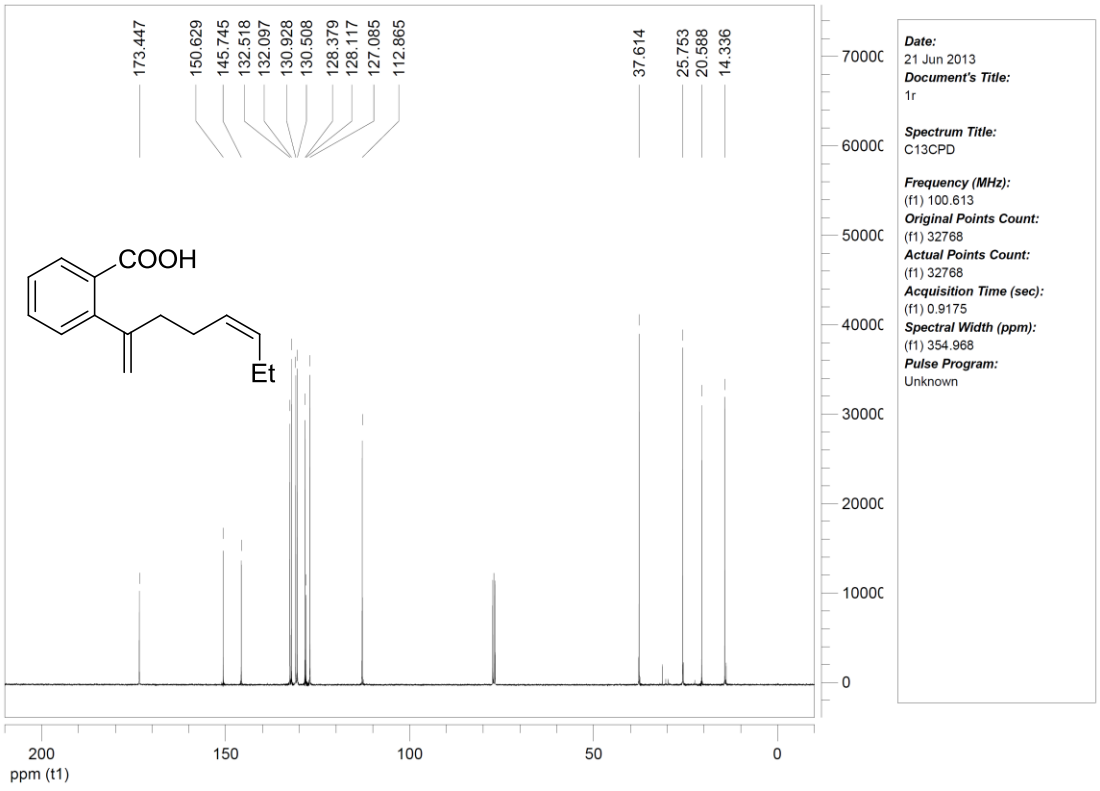
2-(But-1-en-2-yl)-5-methylbenzoic acid (2m)



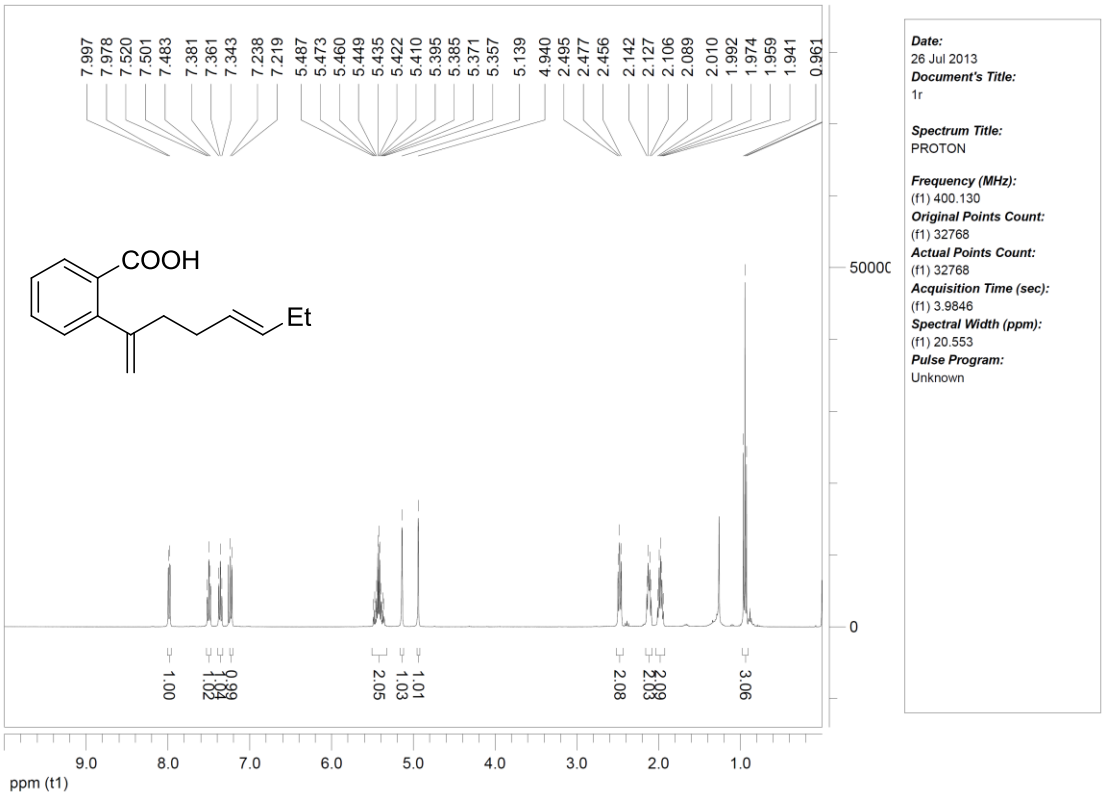


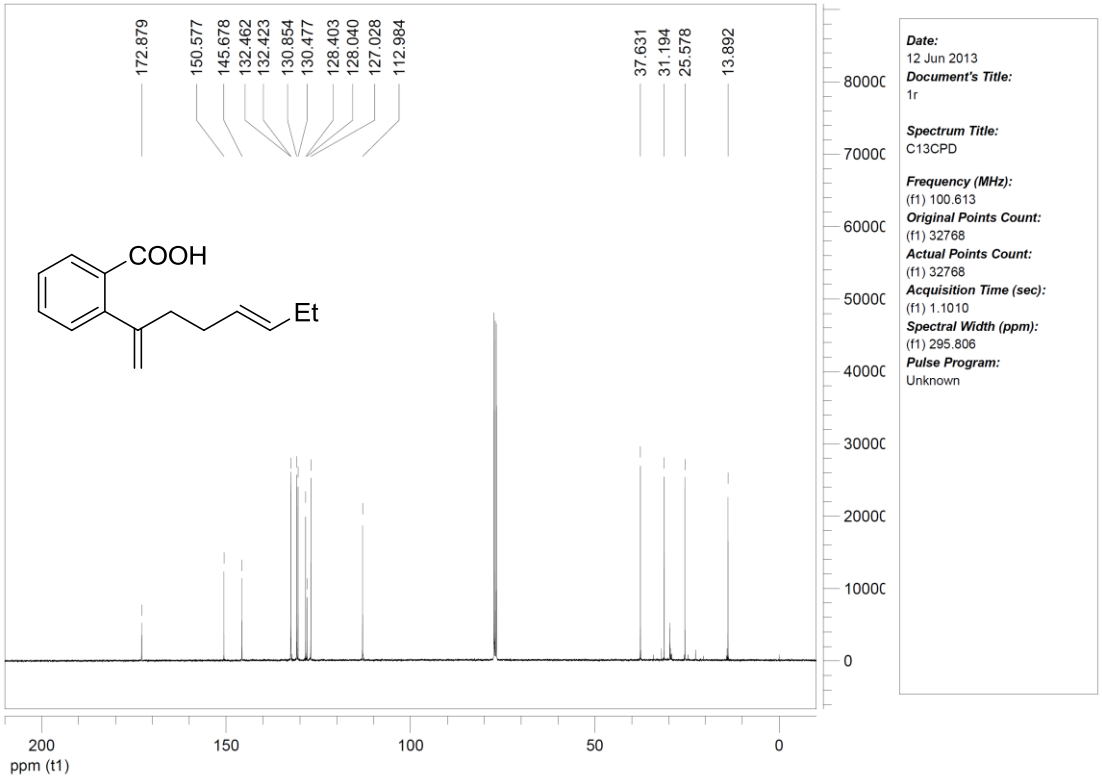
(*Z*)-2-(Octa-1,5-dien-2-yl)benzoic acid (2n)



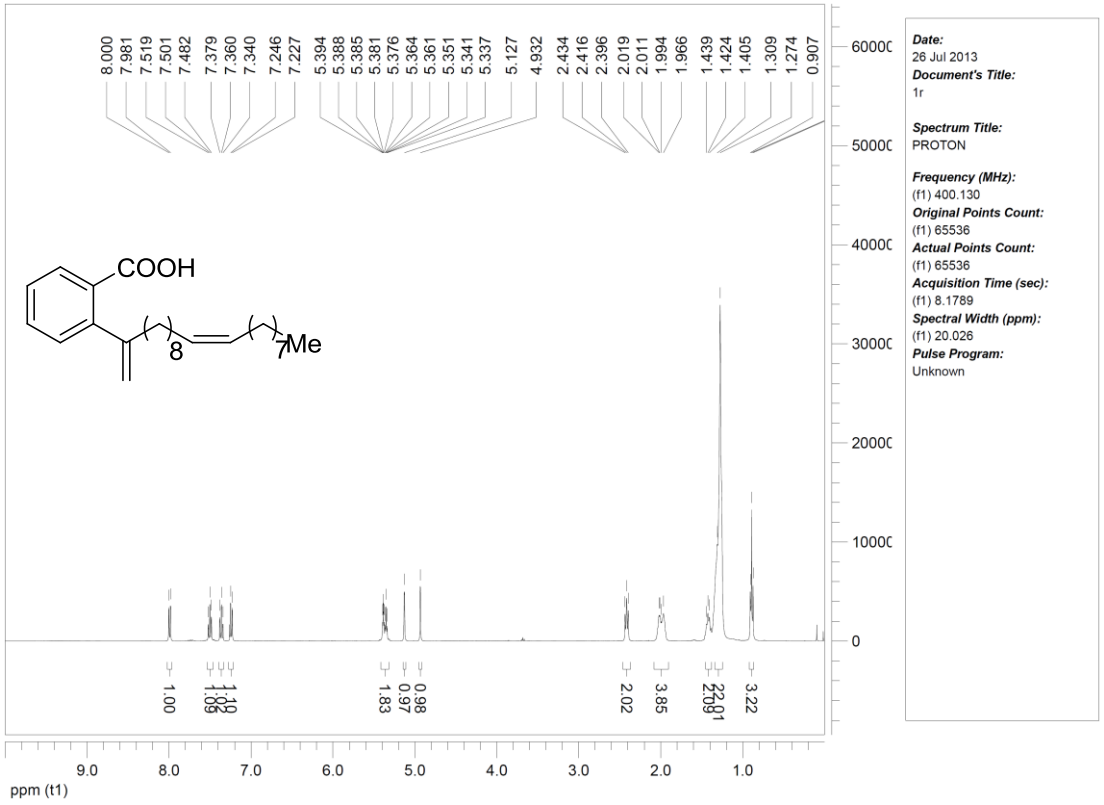


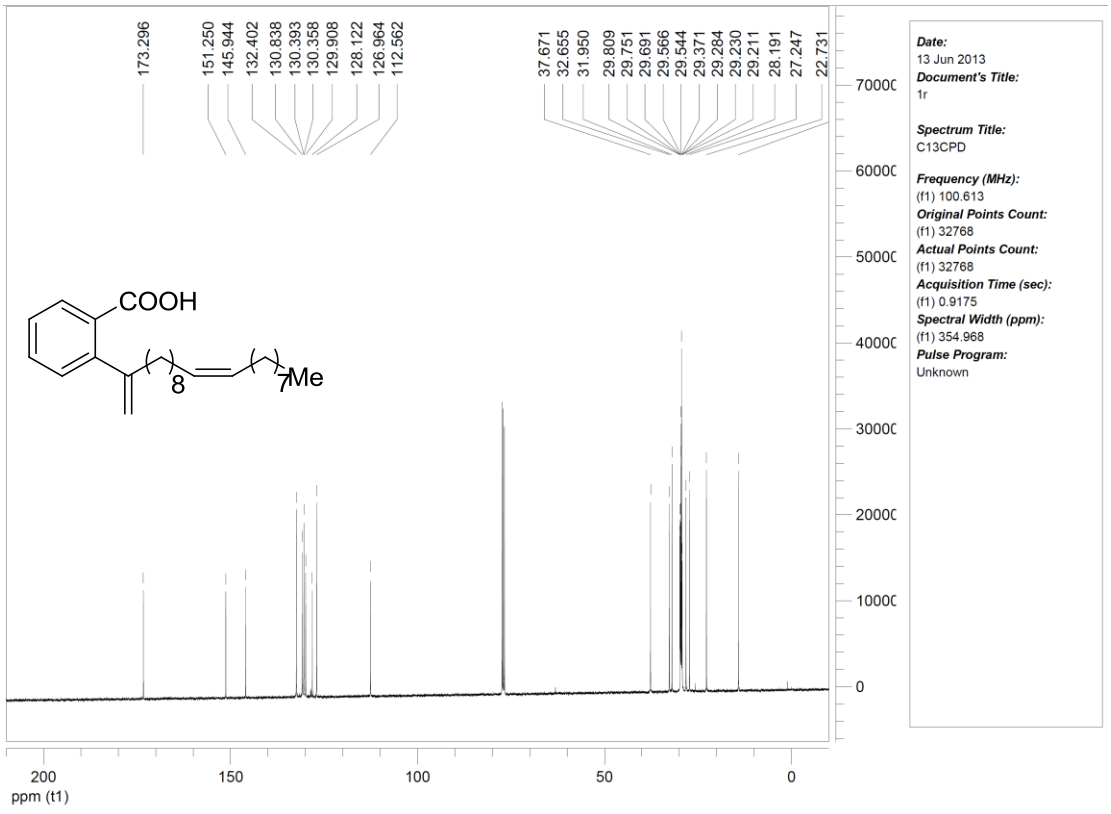
(*E*)-2-(Octa-1,5-dien-2-yl)benzoic acid (2o)



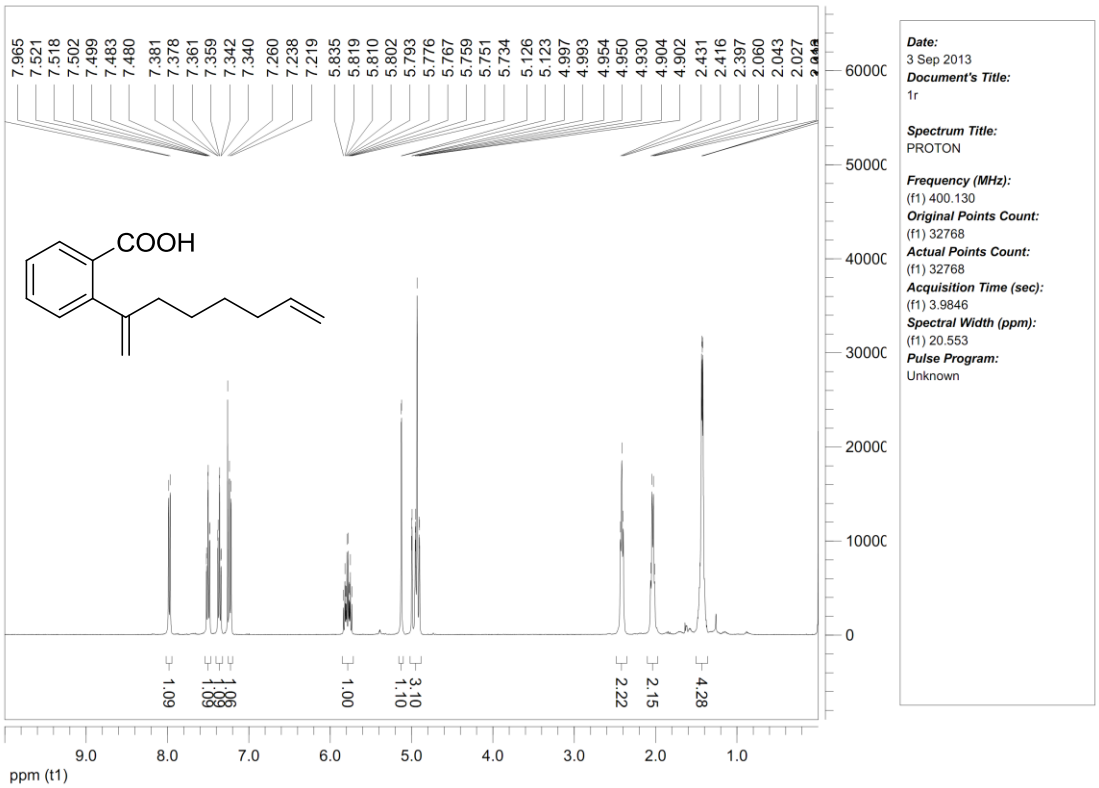


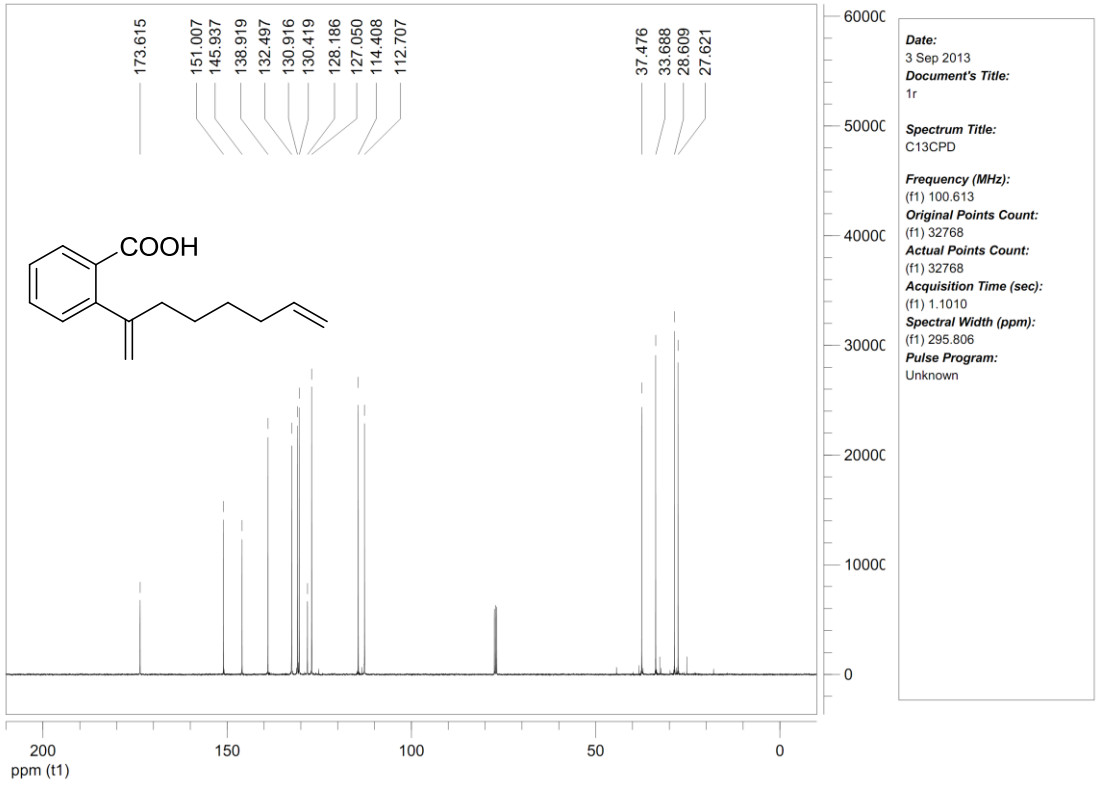
(*Z*)-2-(Icosa-1,11-dien-2-yl)benzoic acid (2p)



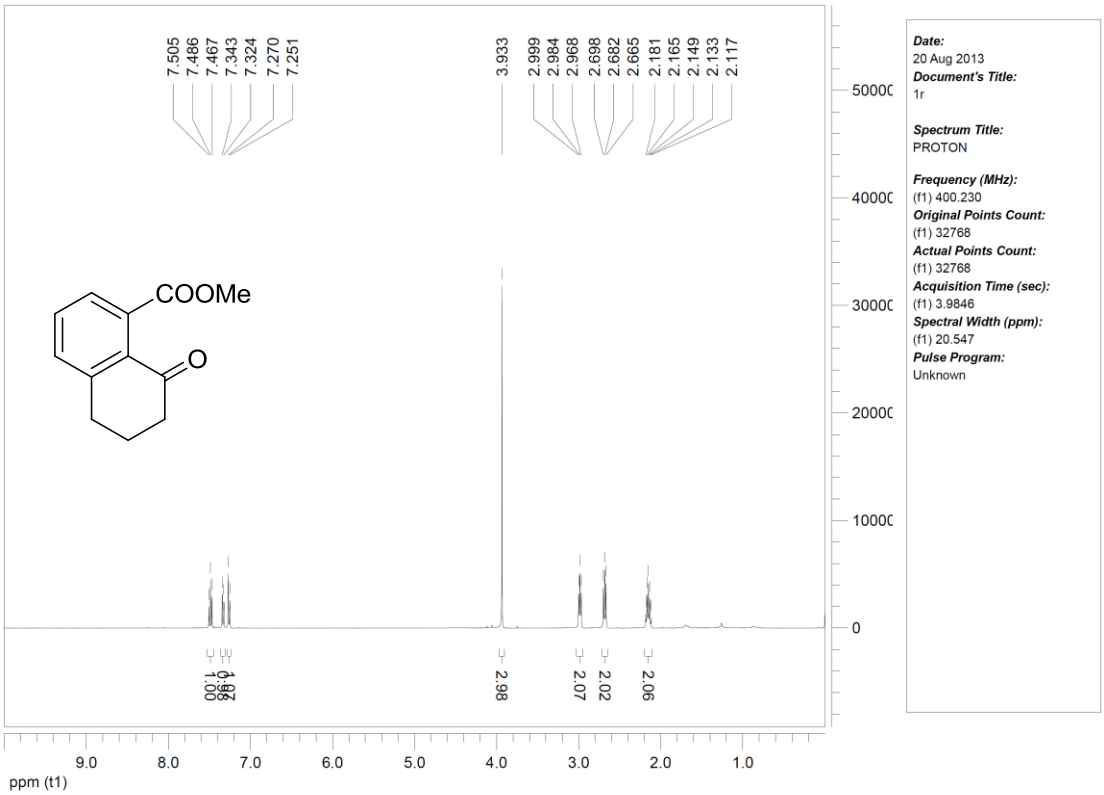


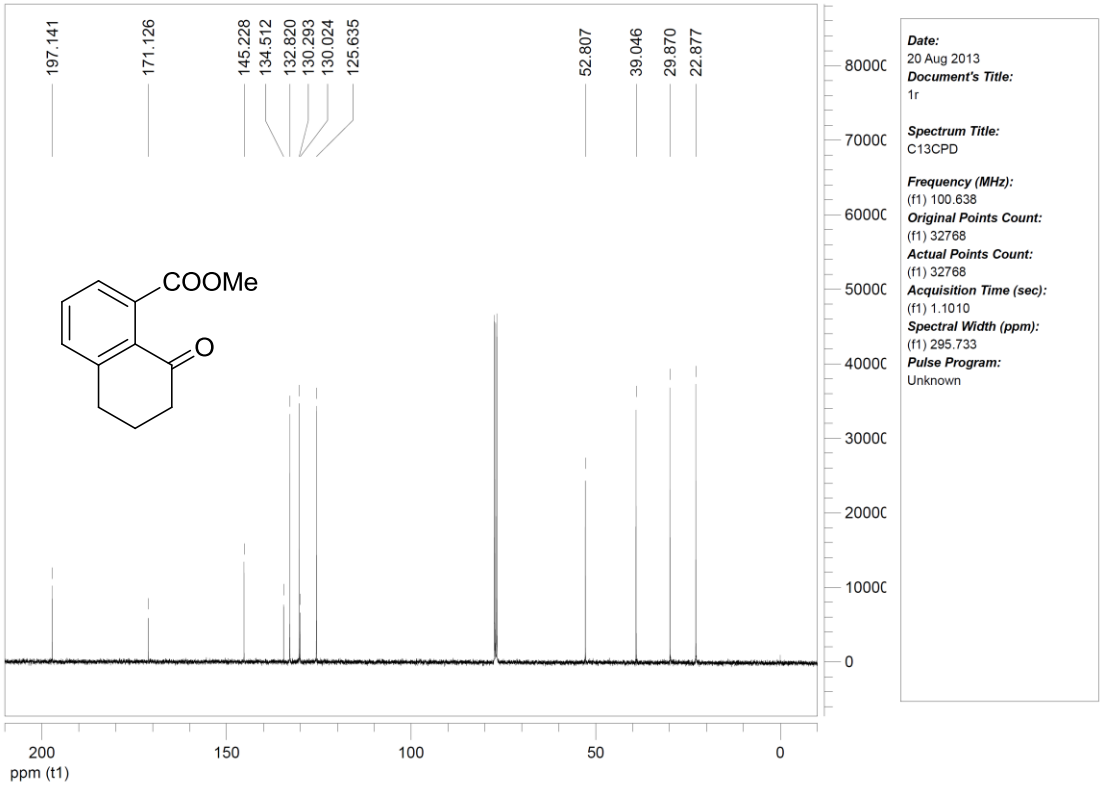
2-(Octa-1,7-dien-2-yl)benzoic acid (2q)



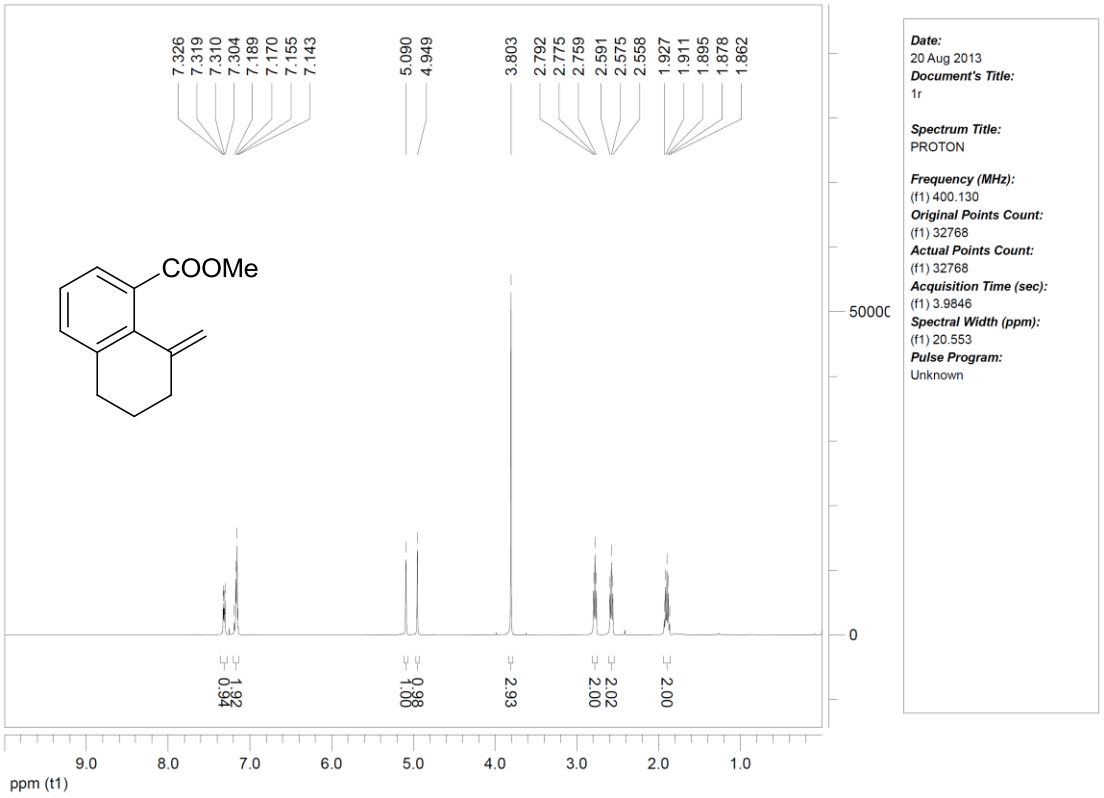


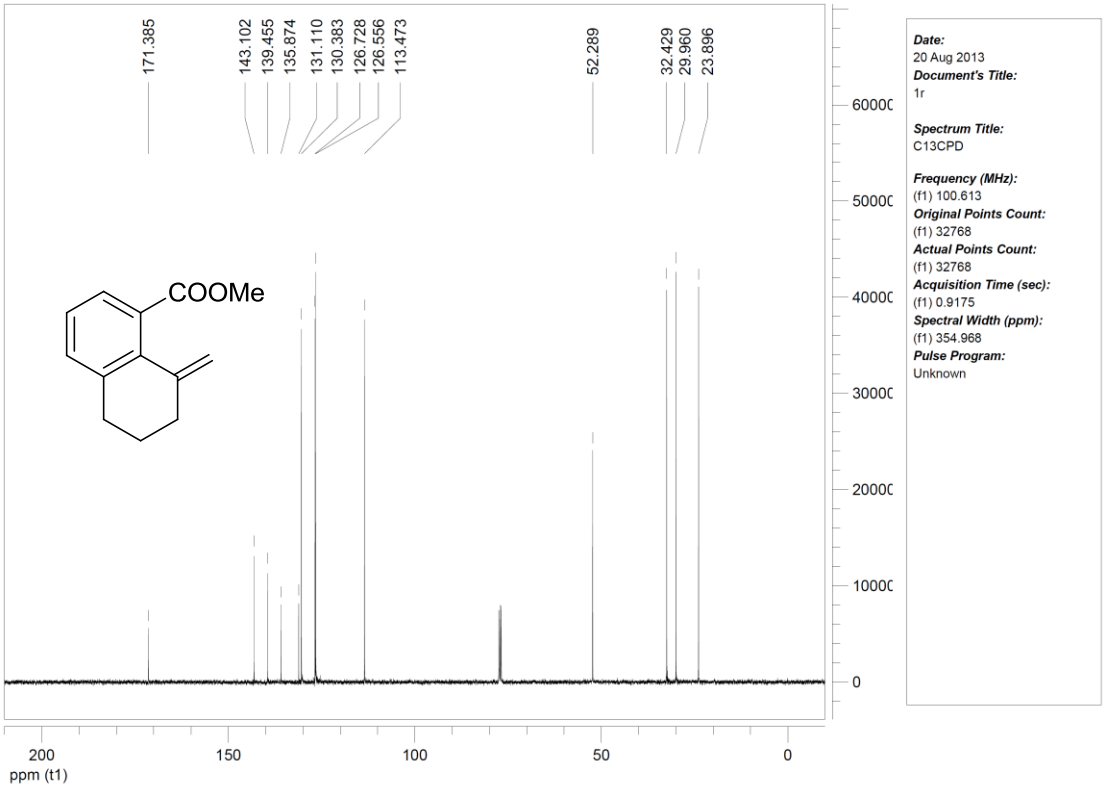
Methyl 8-oxo-5,6,7,8-tetrahydronaphthalene-1-carboxylate (18)



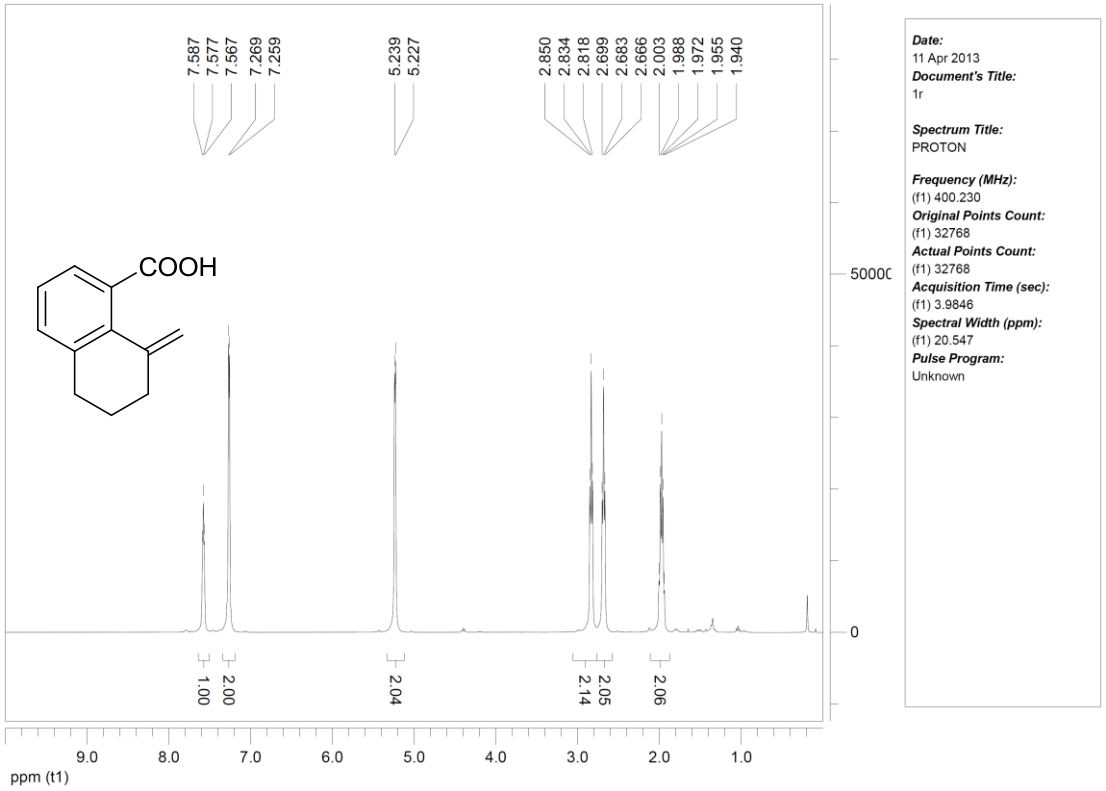


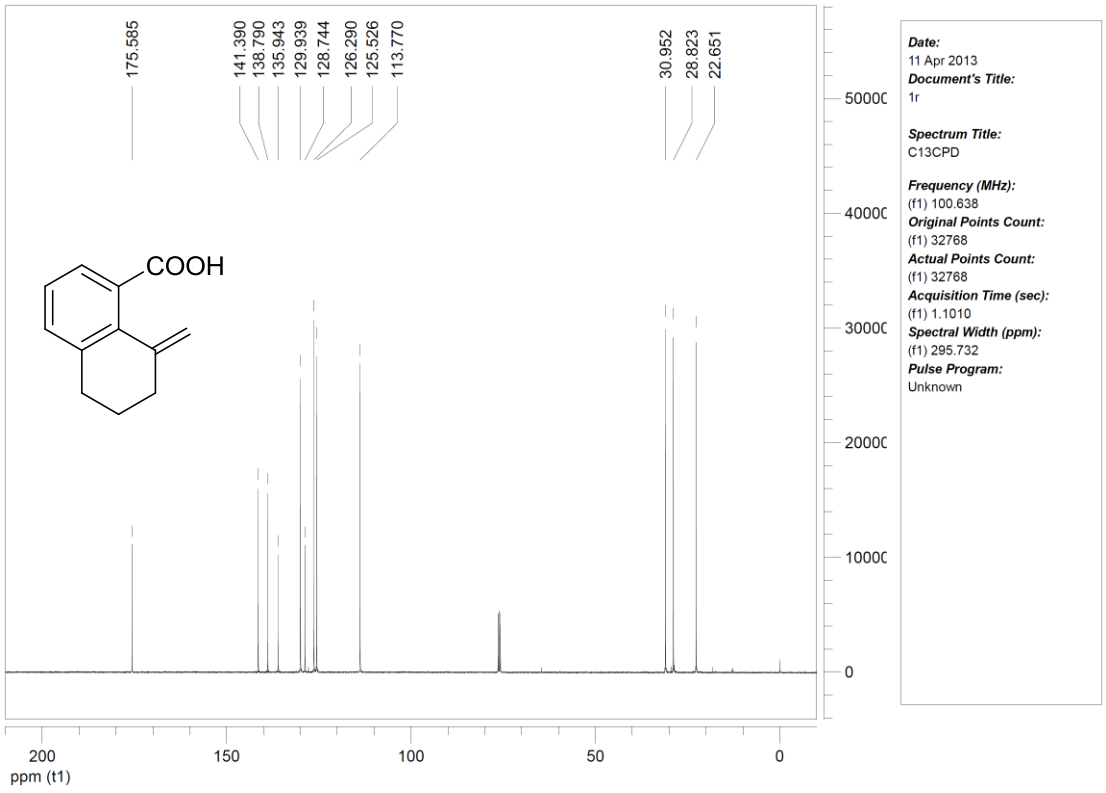
Methyl 8-methylene-5,6,7,8-tetrahydronaphthalene-1-carboxylate (19)



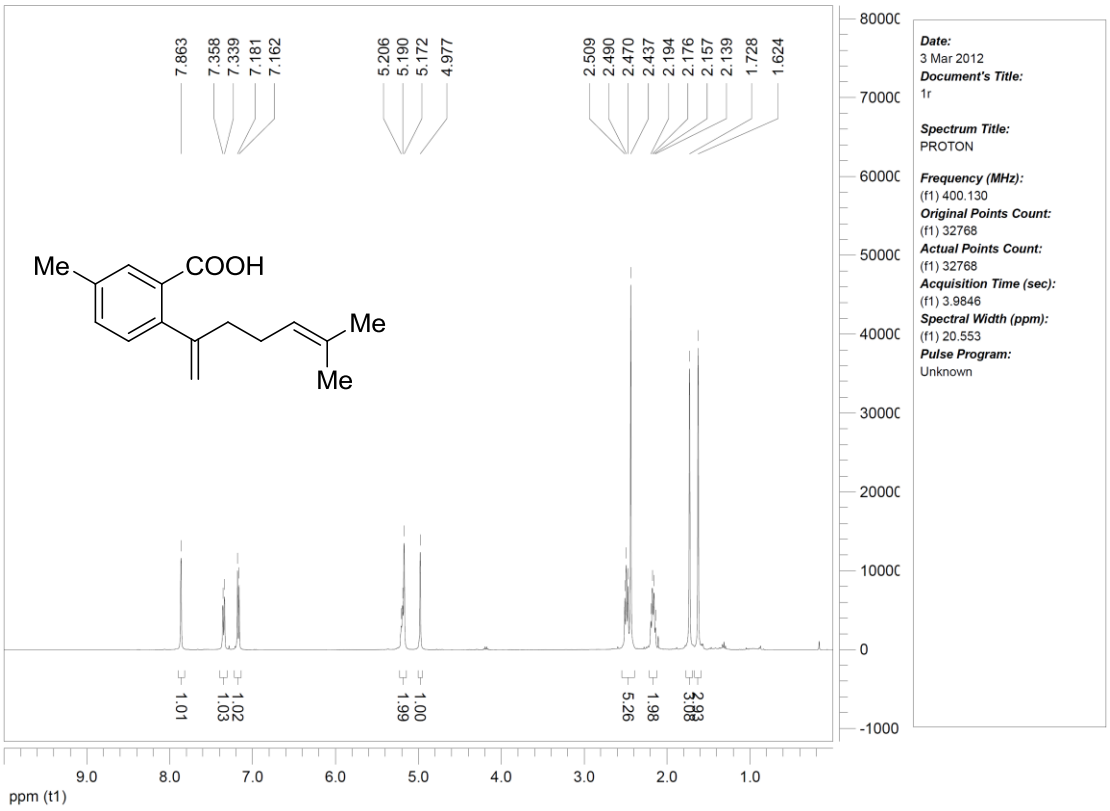


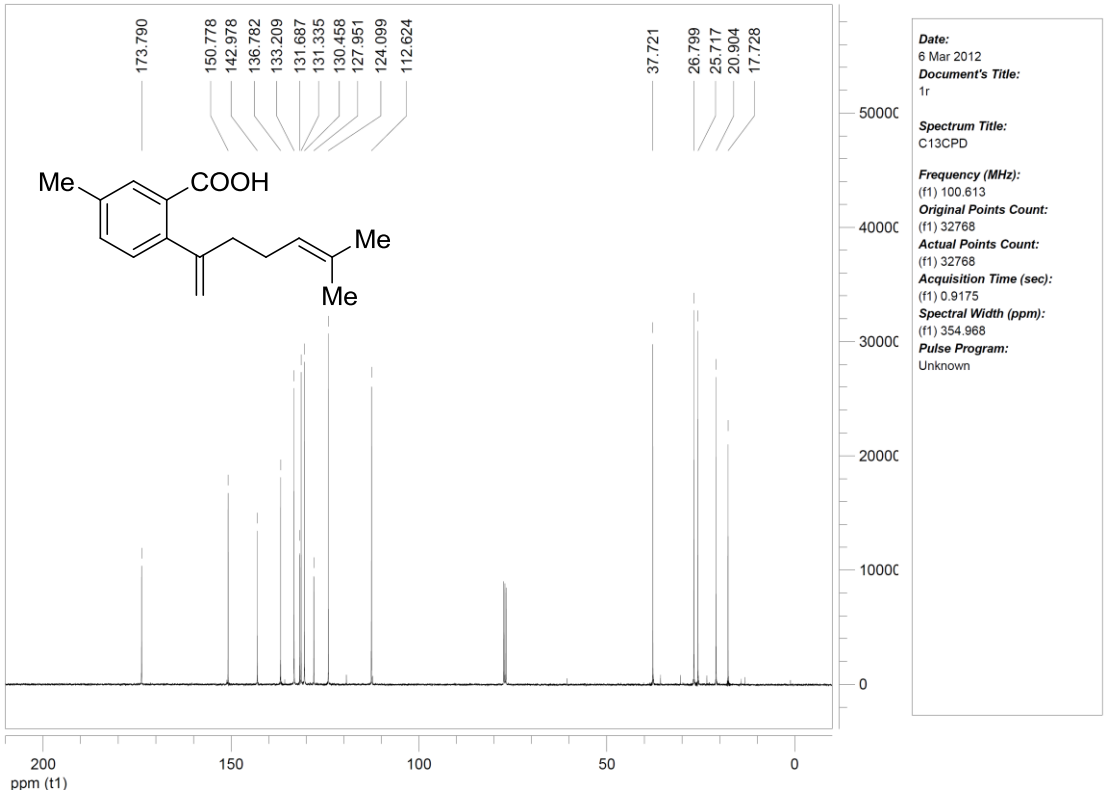
8-Methylene-5,6,7,8-tetrahydronaphthalene-1-carboxylic acid (2r)



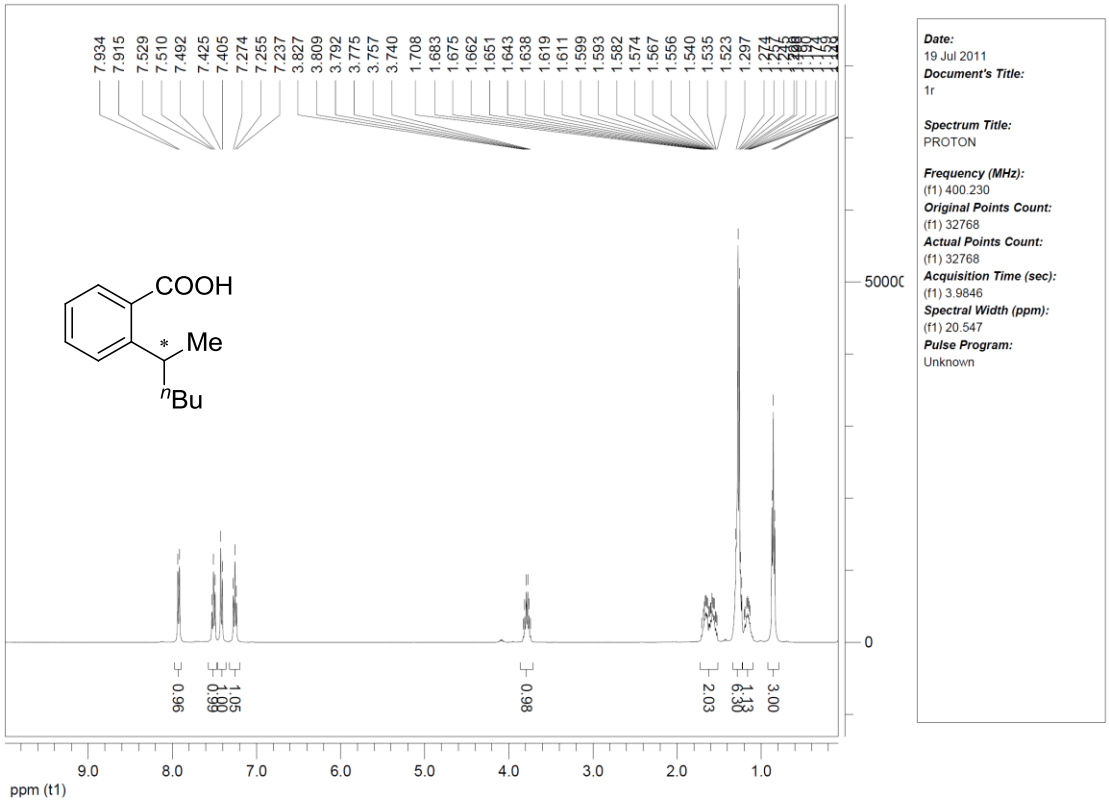


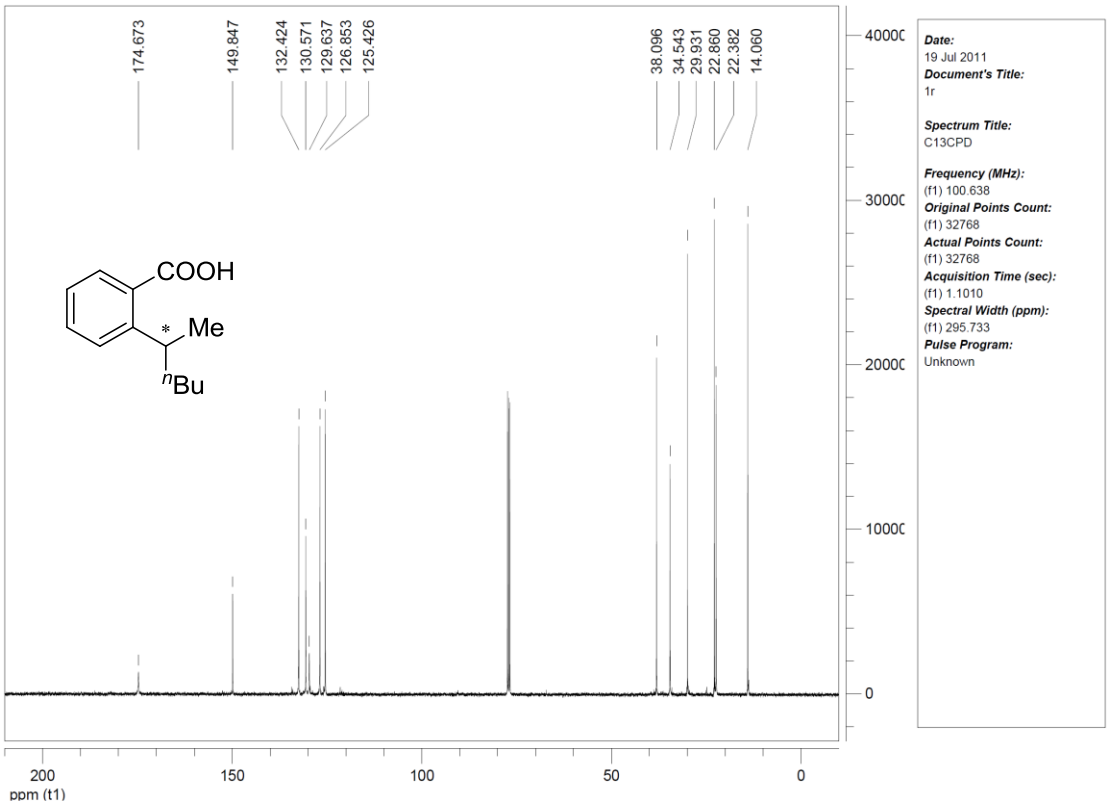
5-Methyl-2-(6-methylhepta-1,5-dien-2-yl)benzoic acid (9)



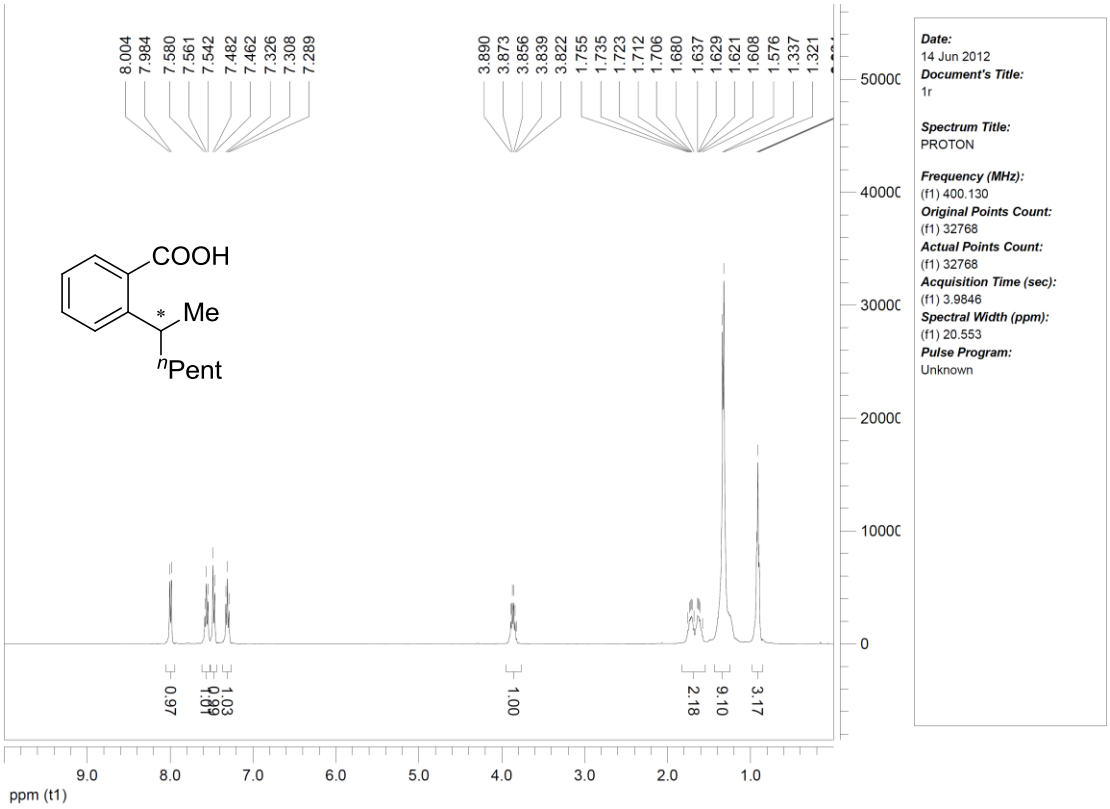


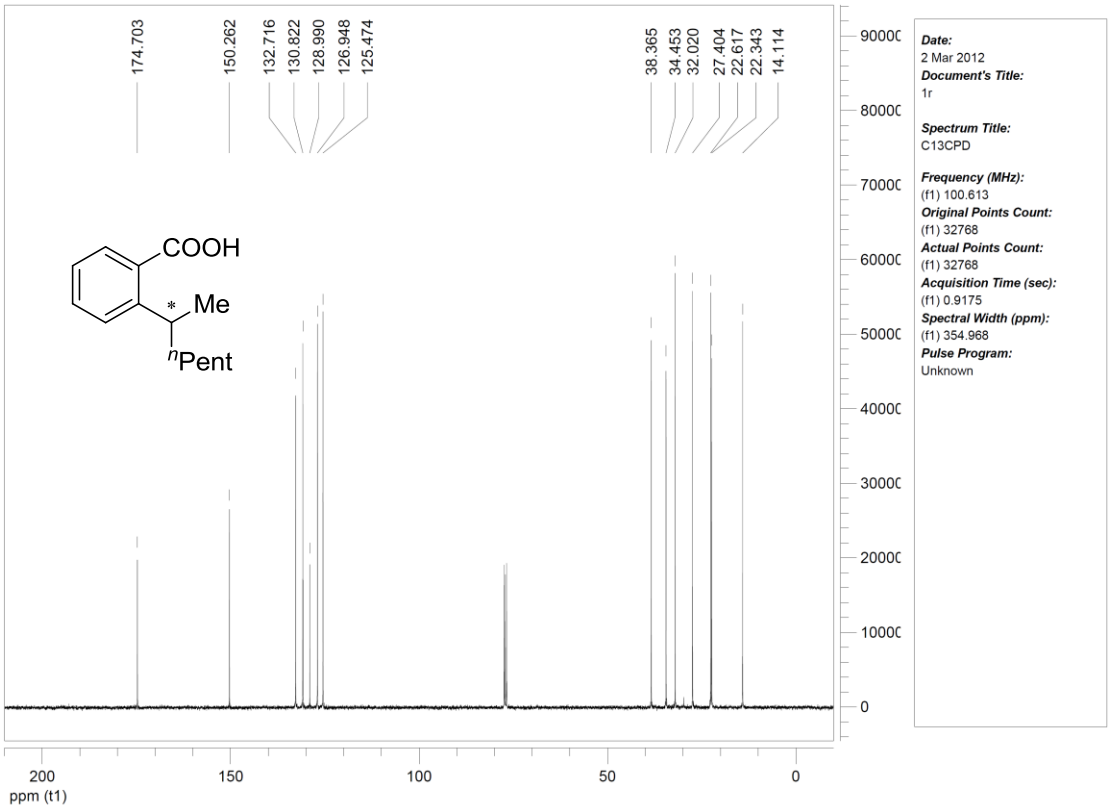
2-(Hexan-2-yl)benzoic acid (3a)



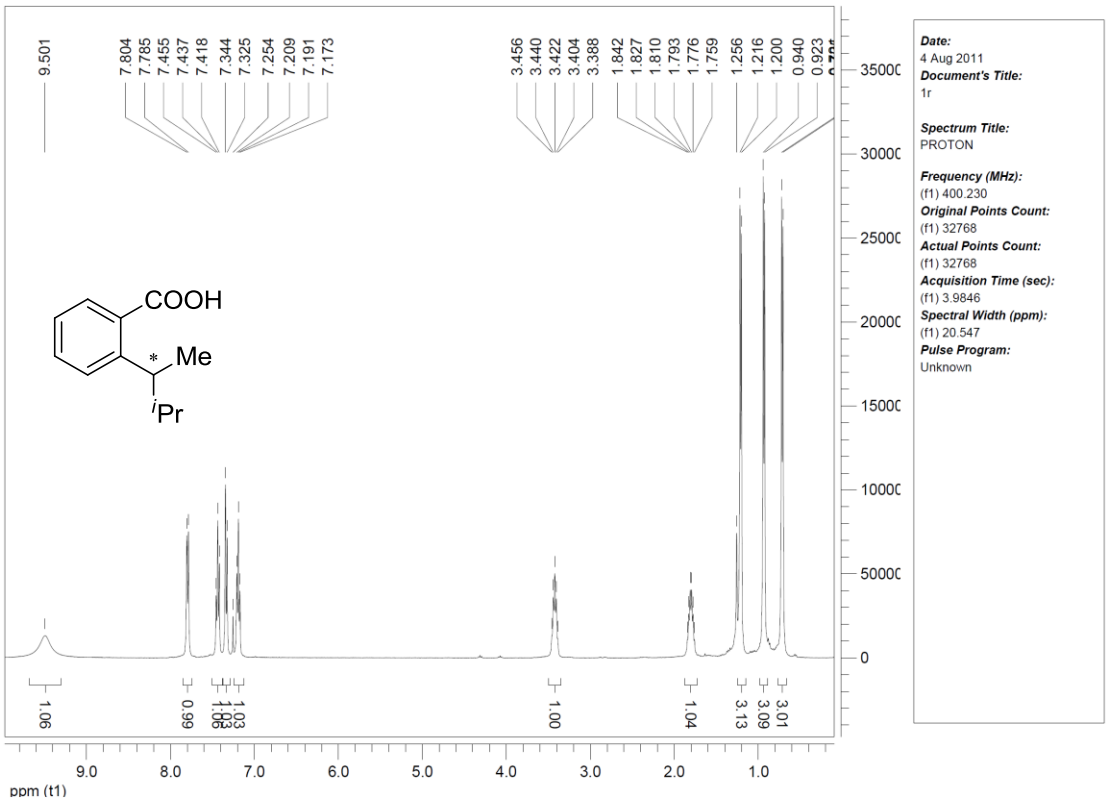


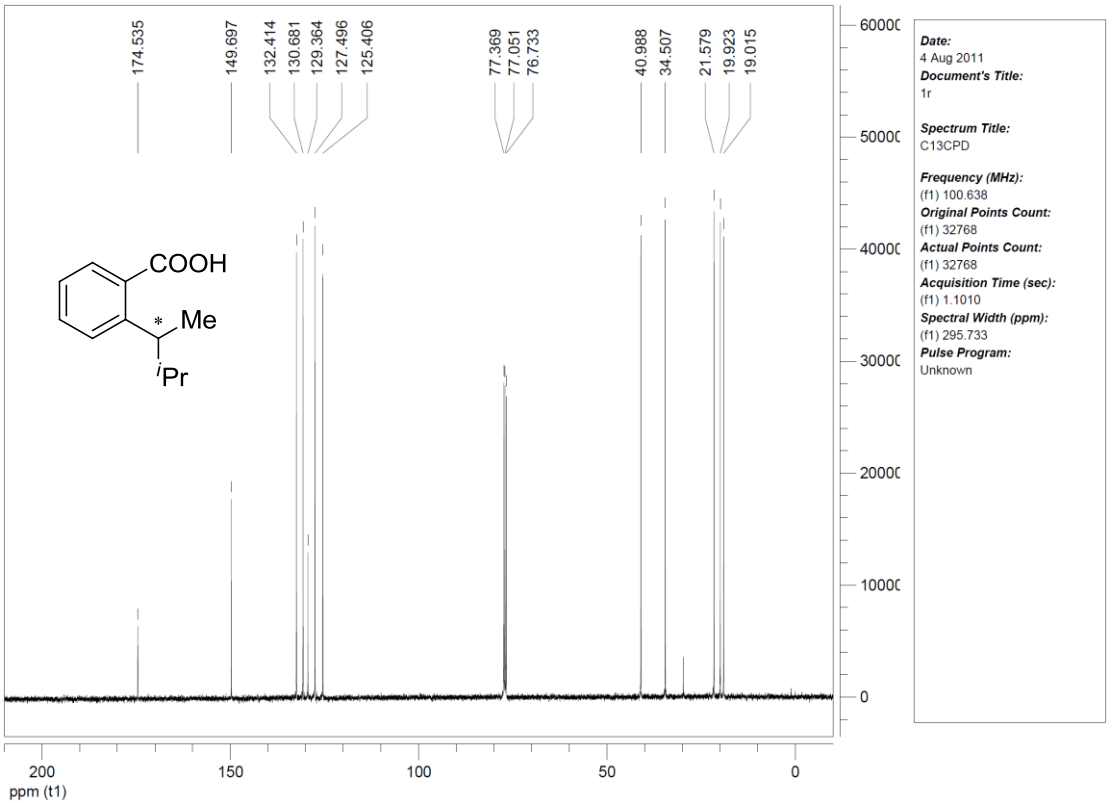
2-(Heptan-2-yl)benzoic acid (3c)



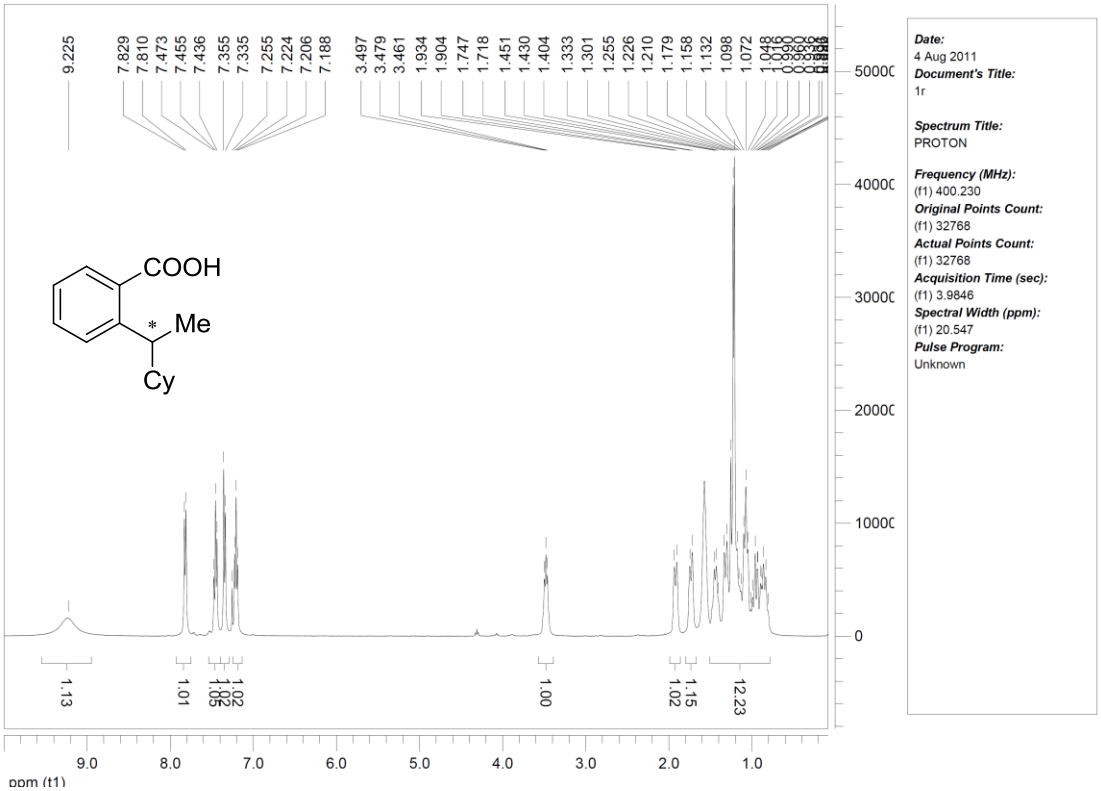


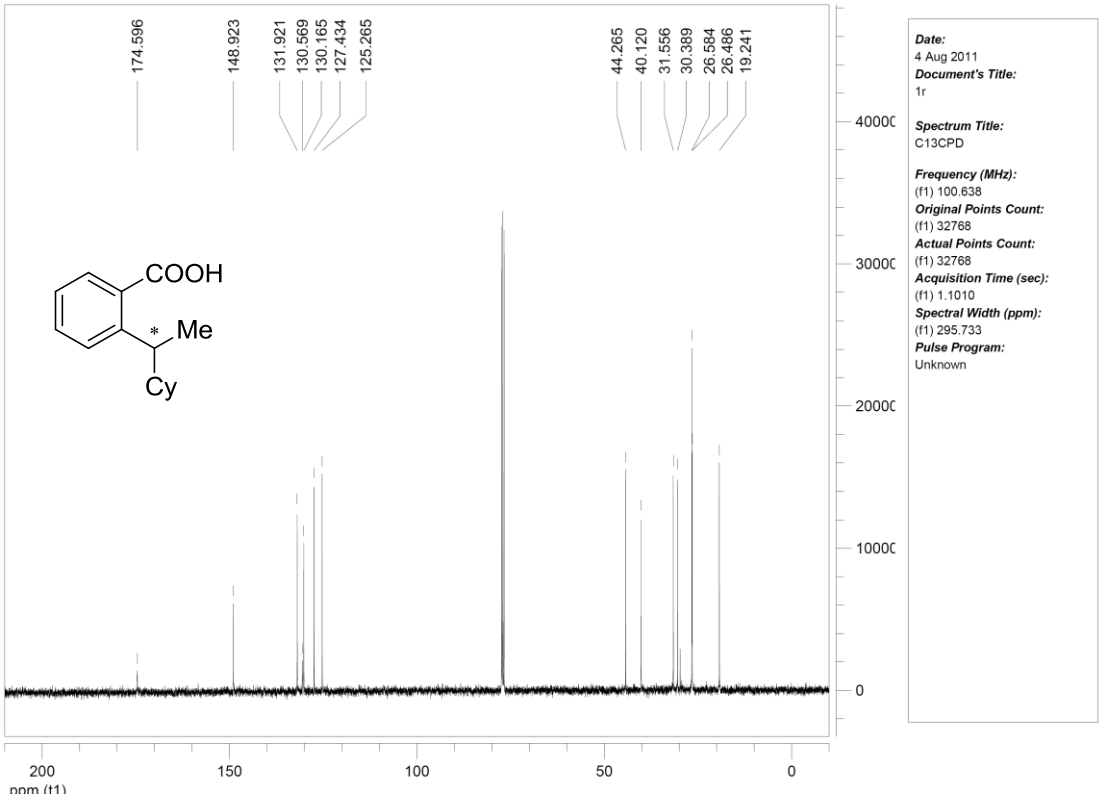
2-(3-Methylbutan-2-yl)benzoic acid (3d)



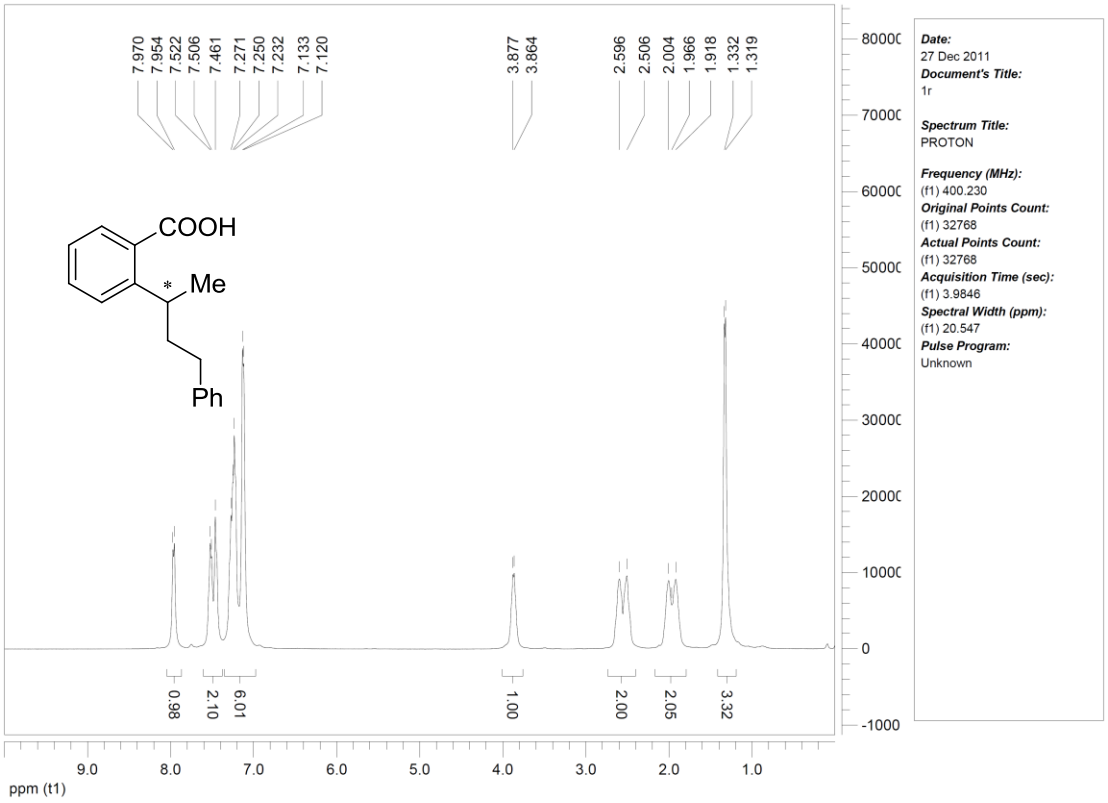


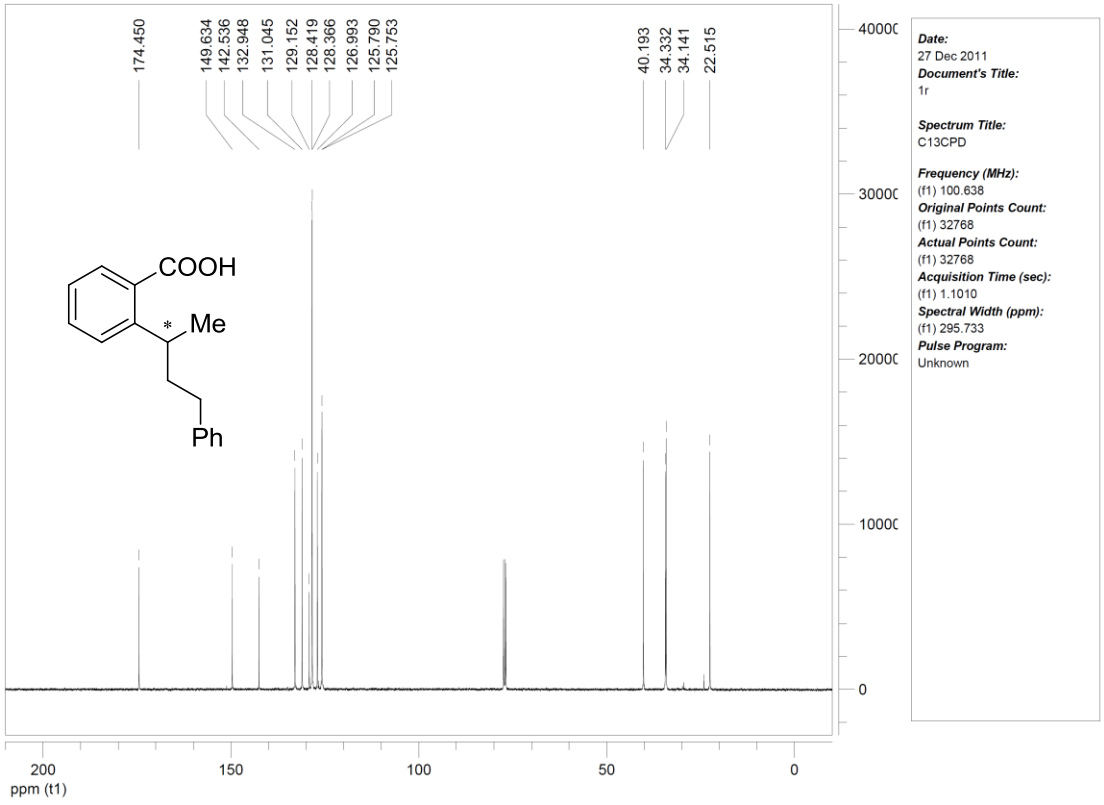
2-(1-Cyclohexylethyl)benzoic acid (3e)



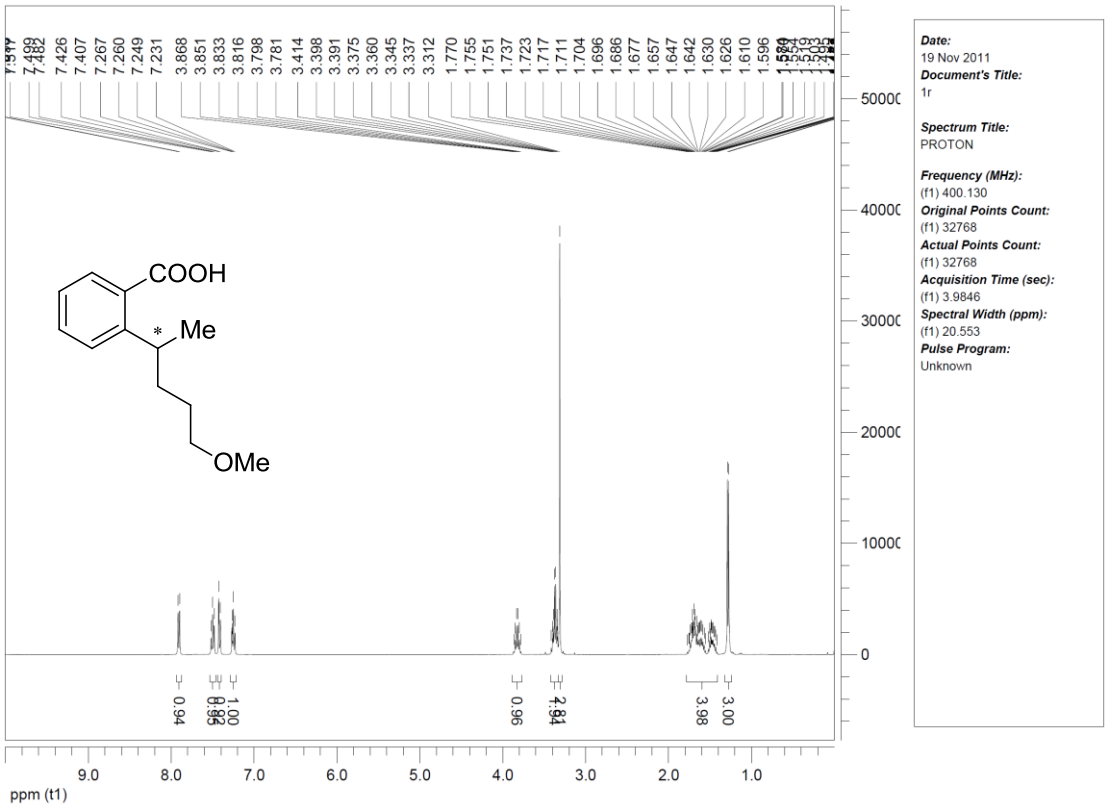


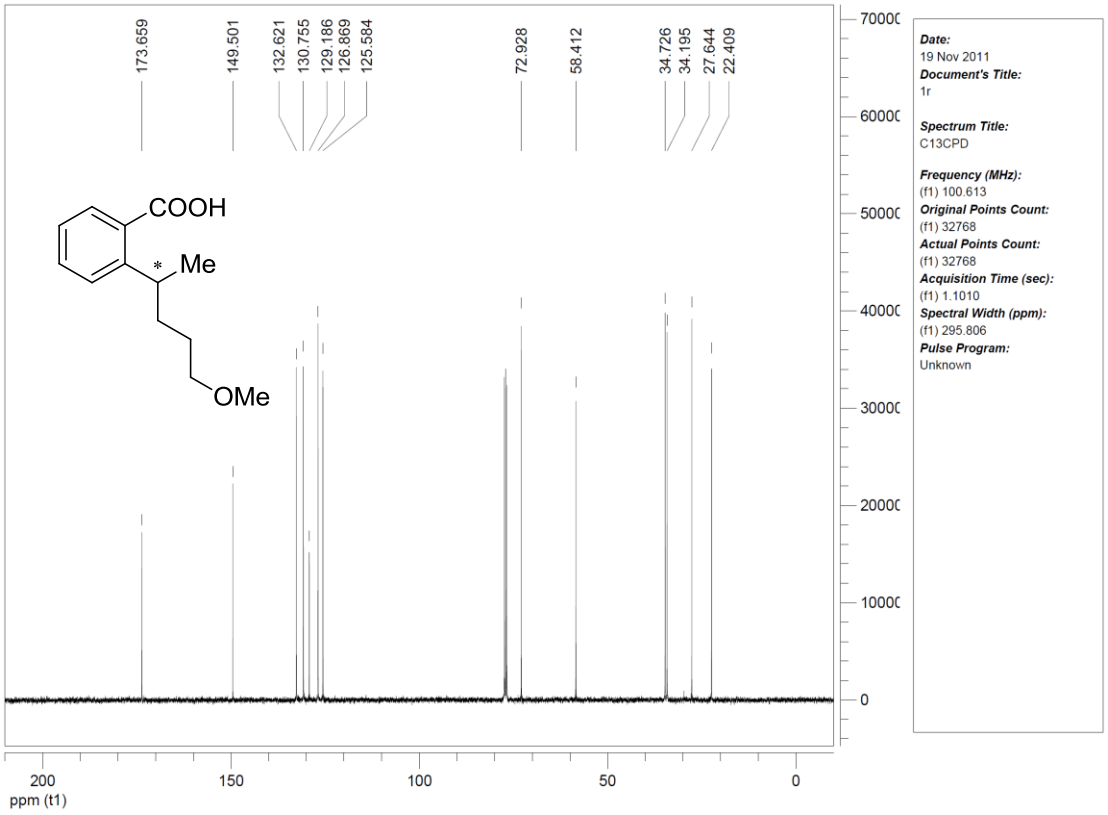
2-(4-Phenylbutan-2-yl)benzoic acid (3f)



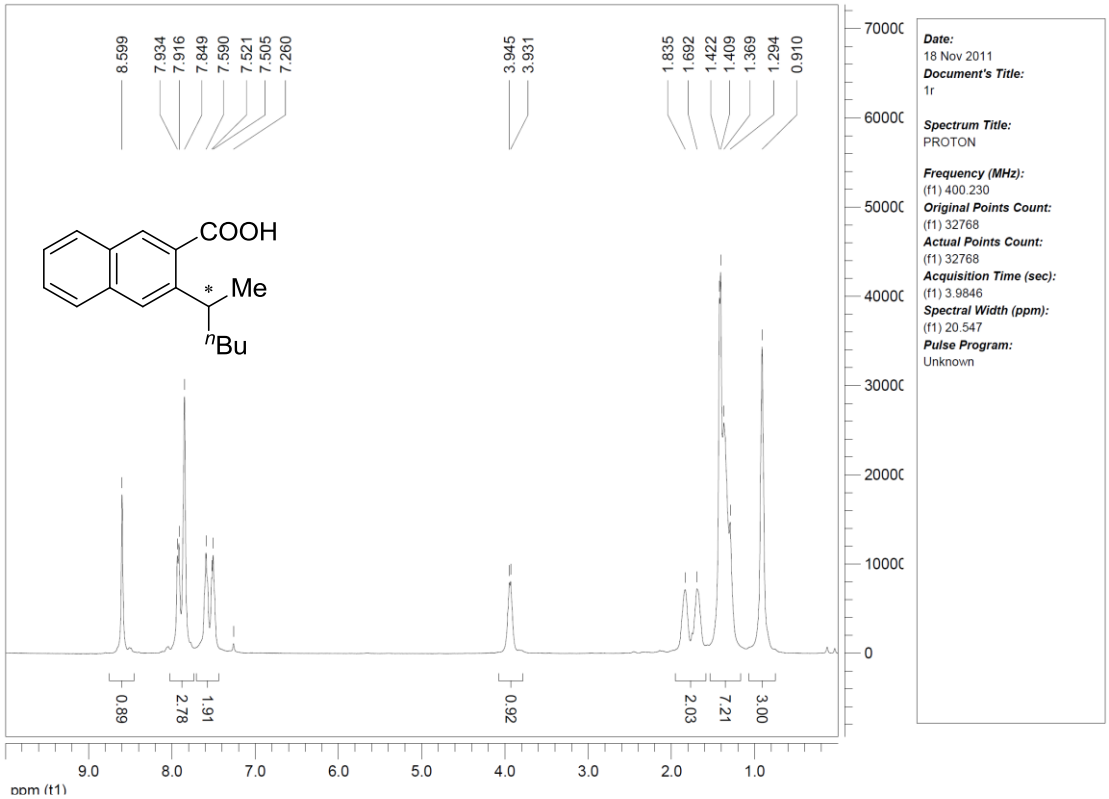


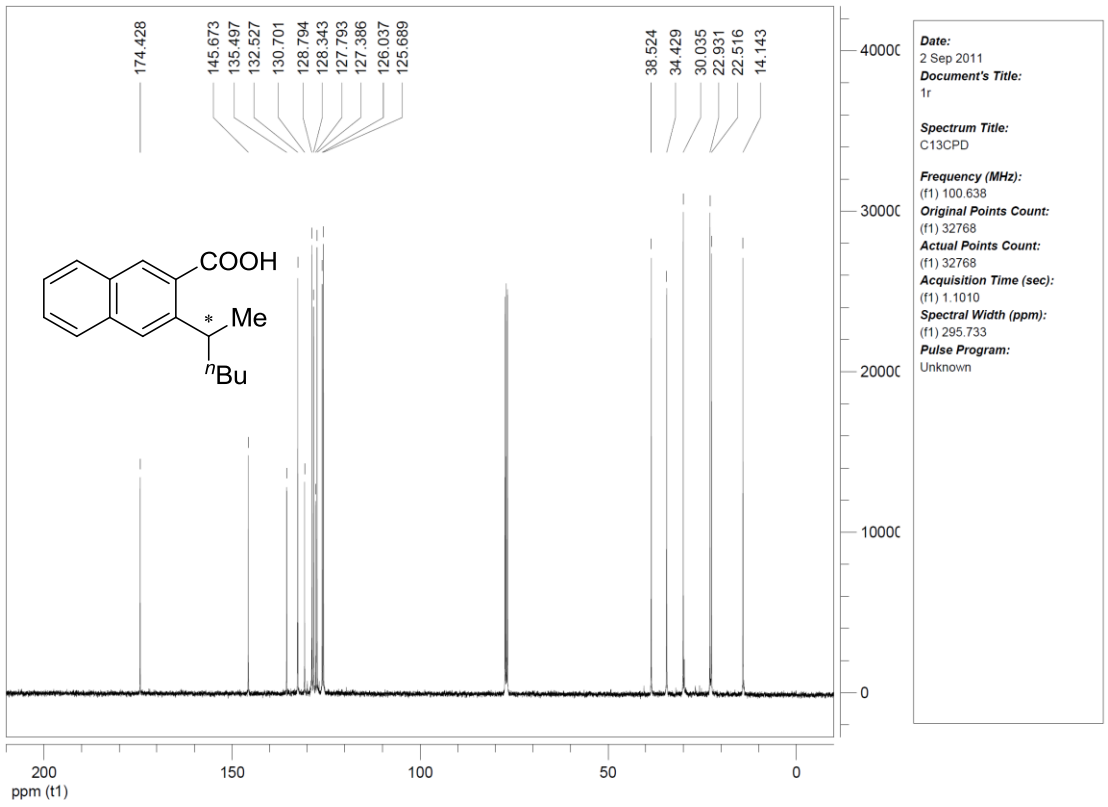
2-(5-Methoxypentan-2-yl)benzoic acid (3g)



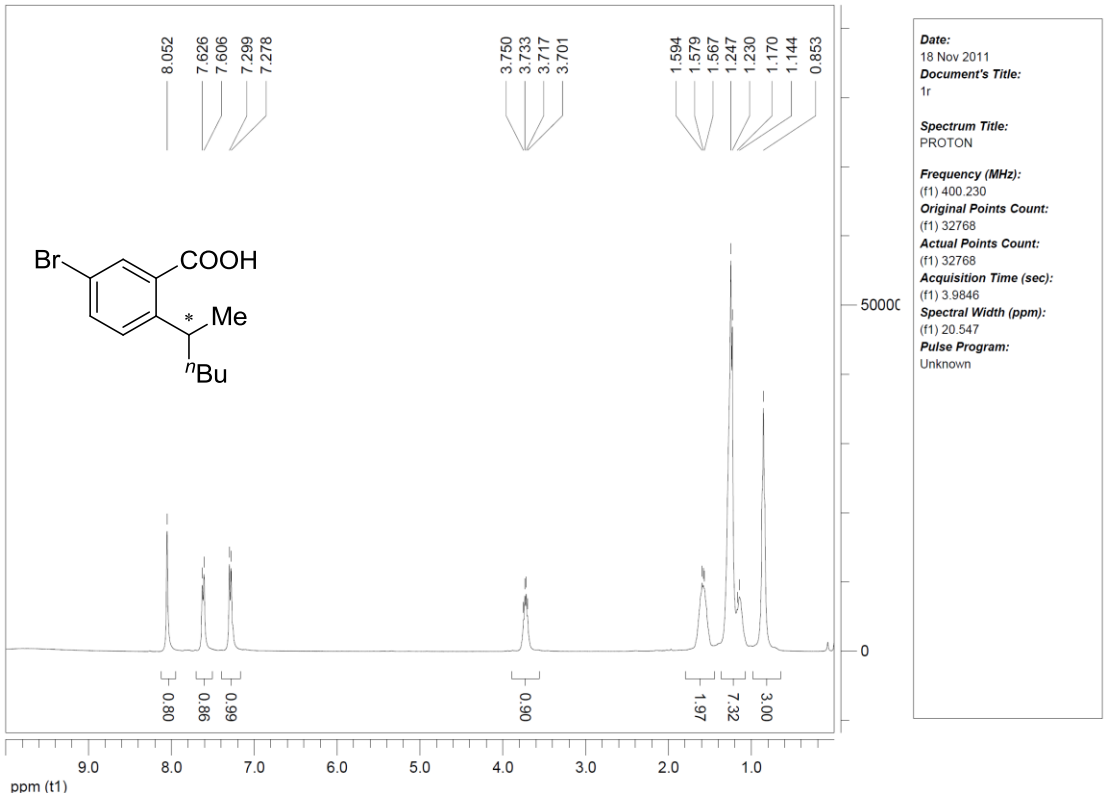


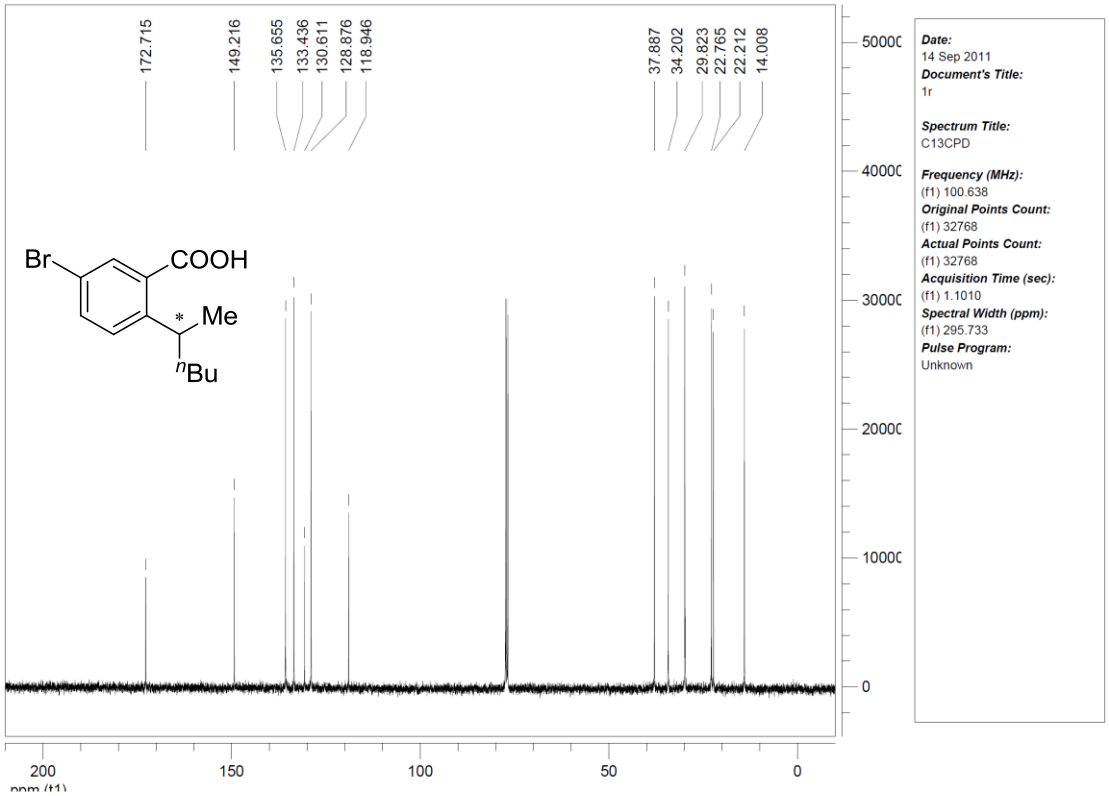
3-(Hexan-2-yl)-2-naphthoic acid (3h)



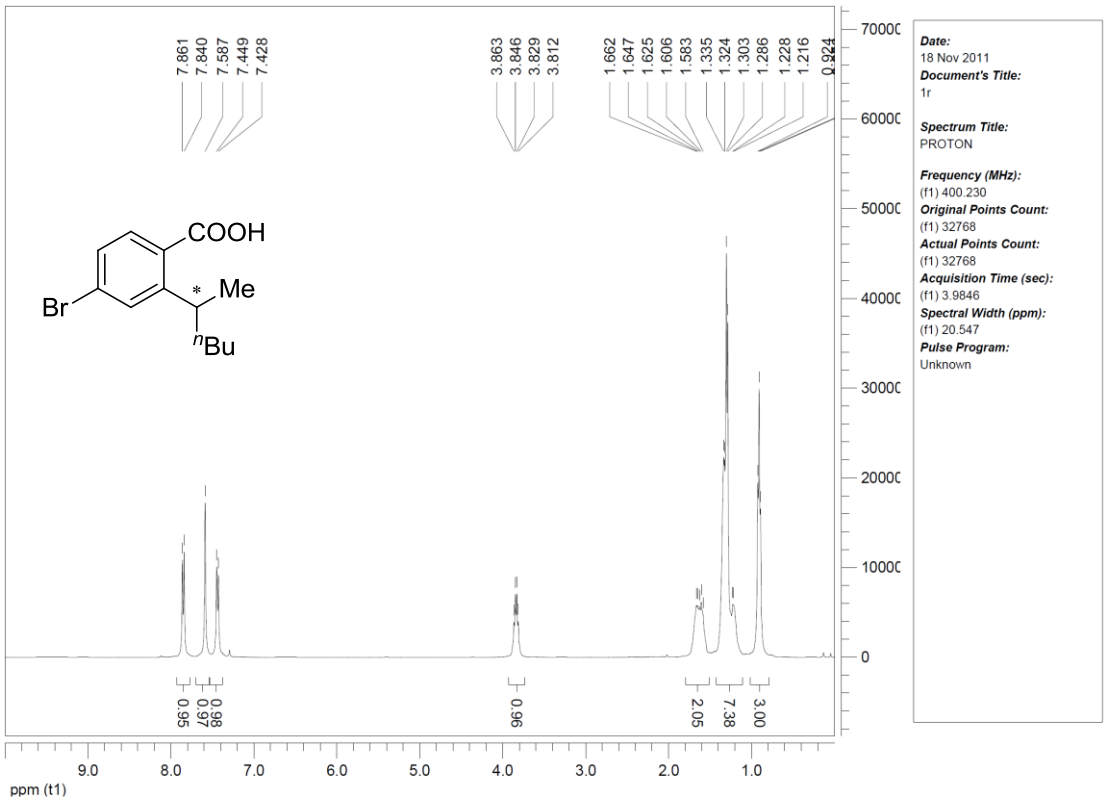


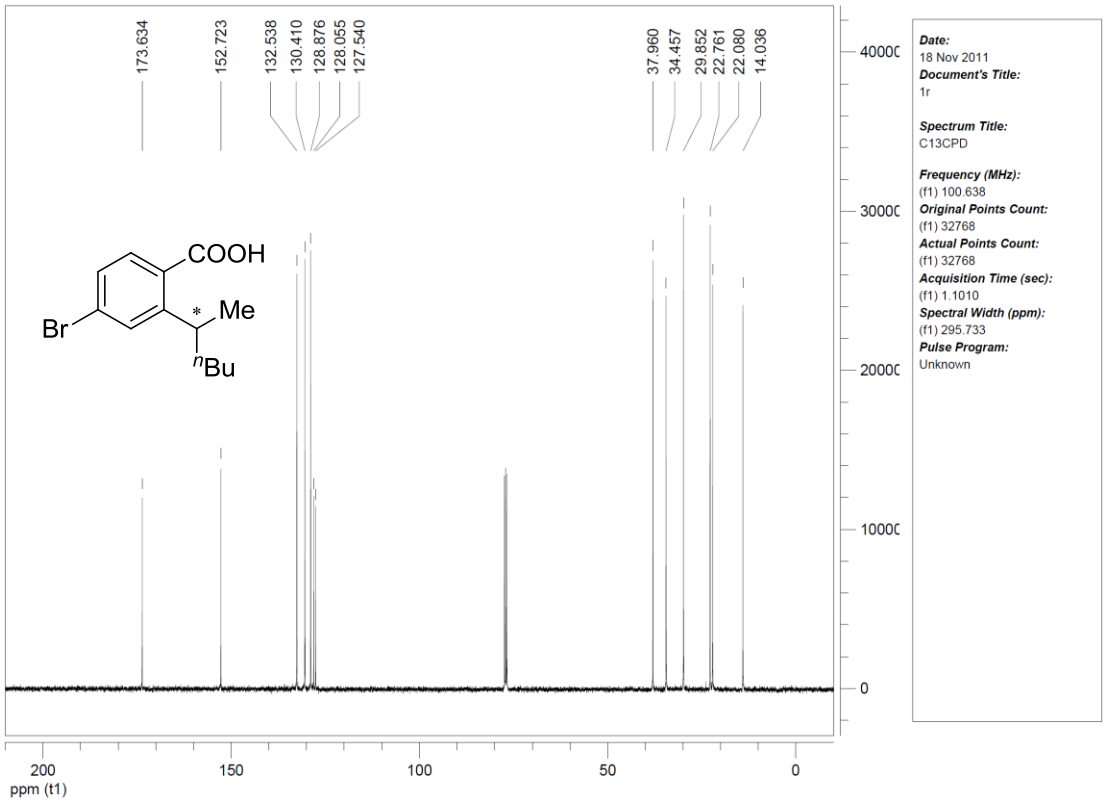
5-Bromo-2-(hexan-2-yl)benzoic acid (3i)



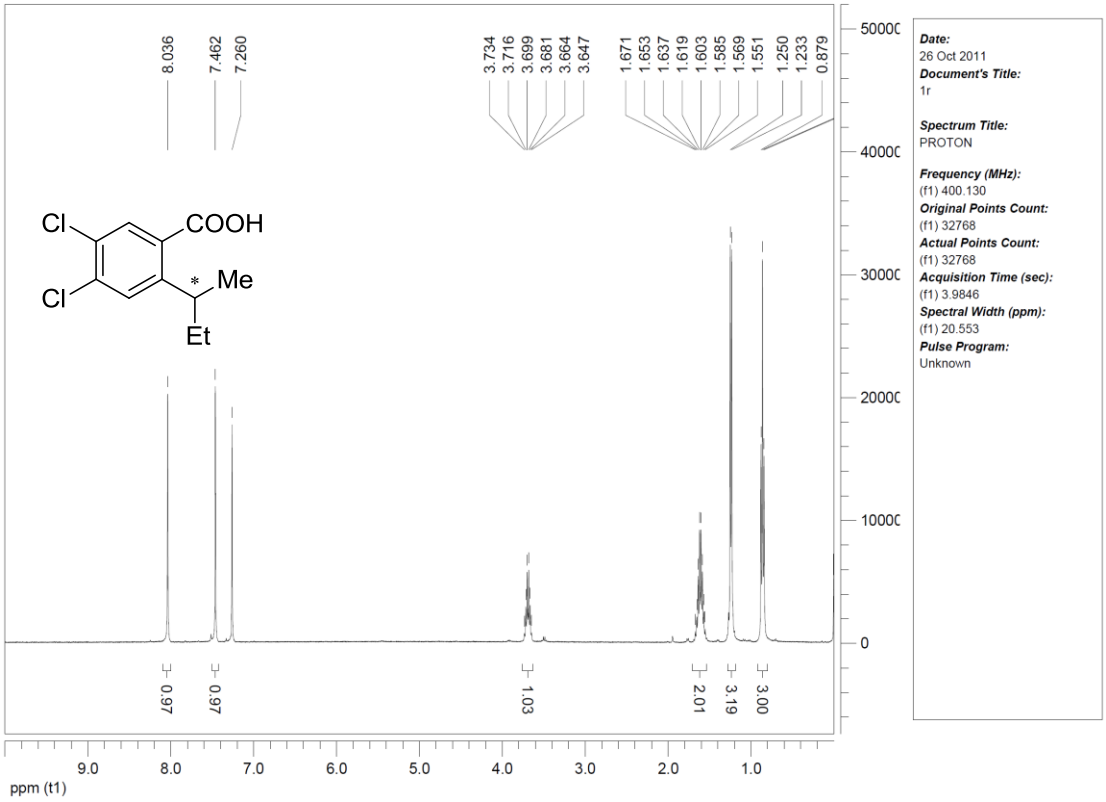


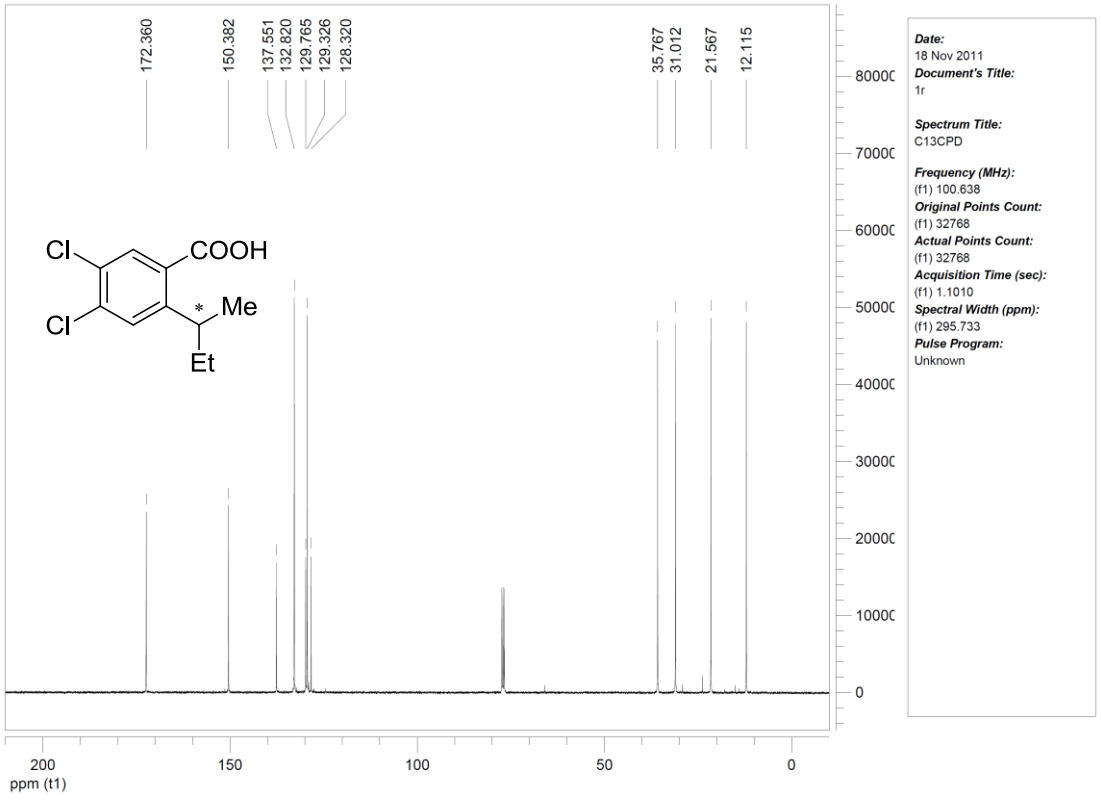
4-Bromo-2-(hexan-2-yl)benzoic acid (3j)



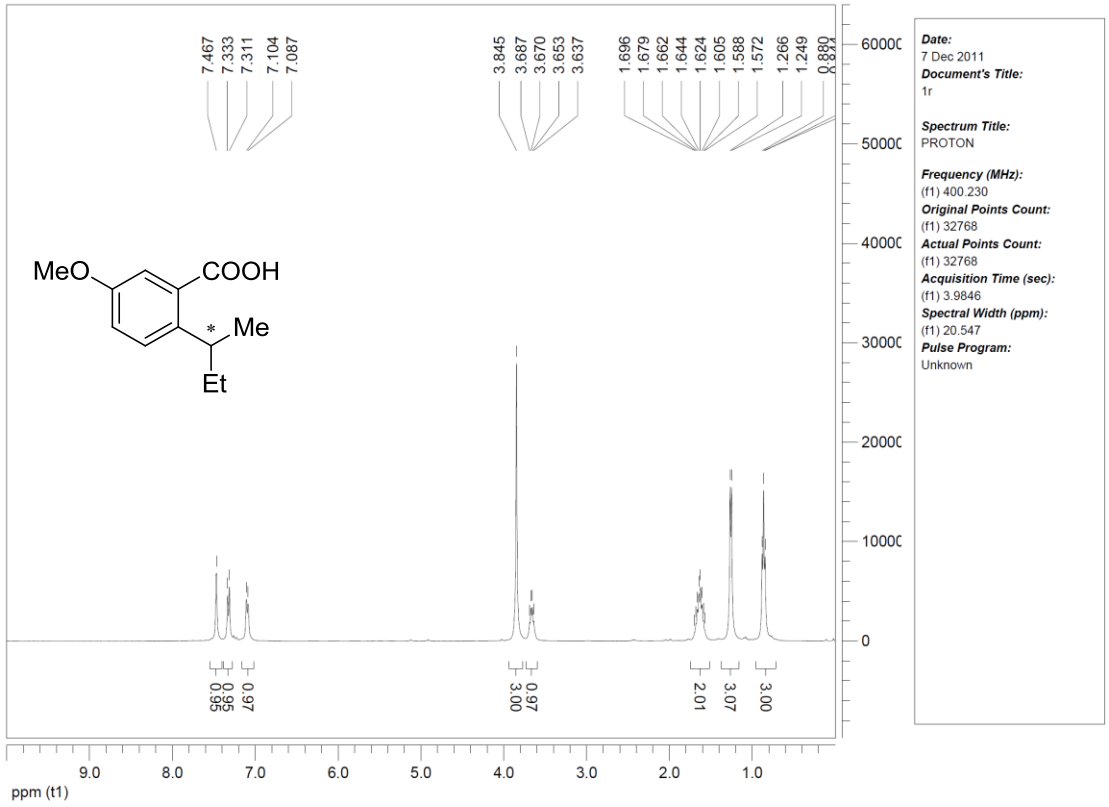


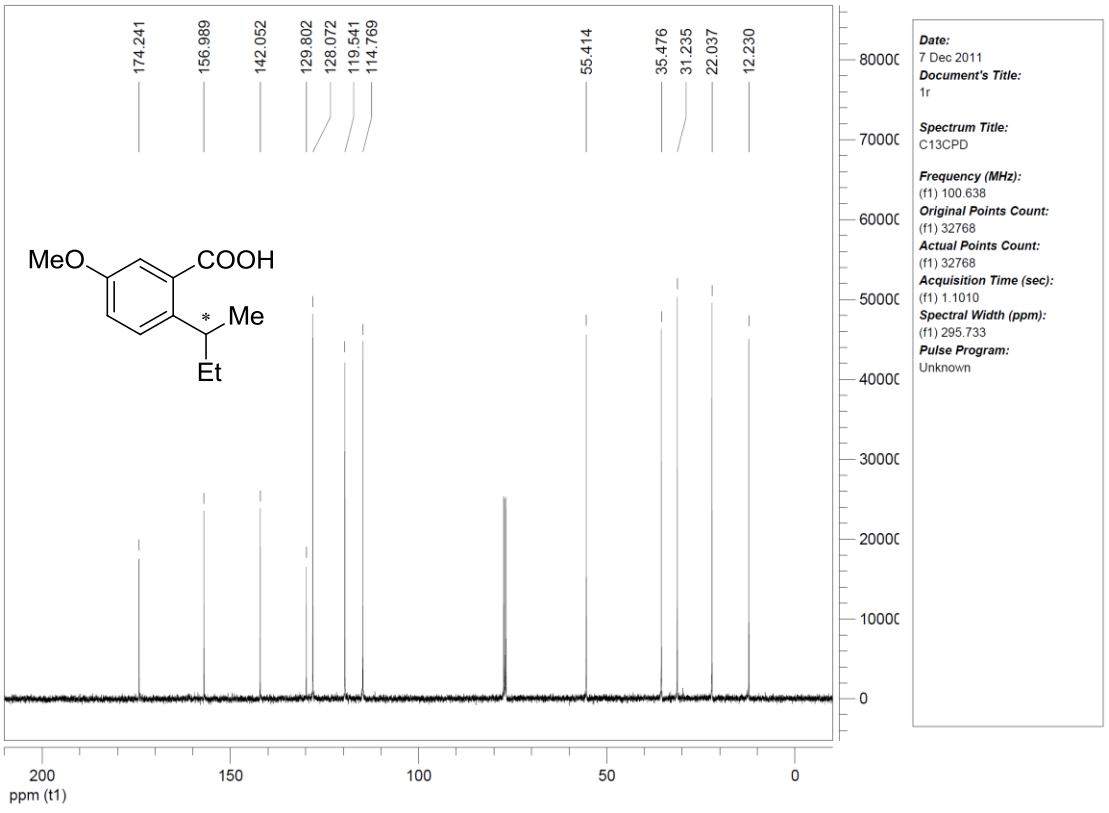
2-*sec*-Butyl-4,5-dichlorobenzoic acid (3k)



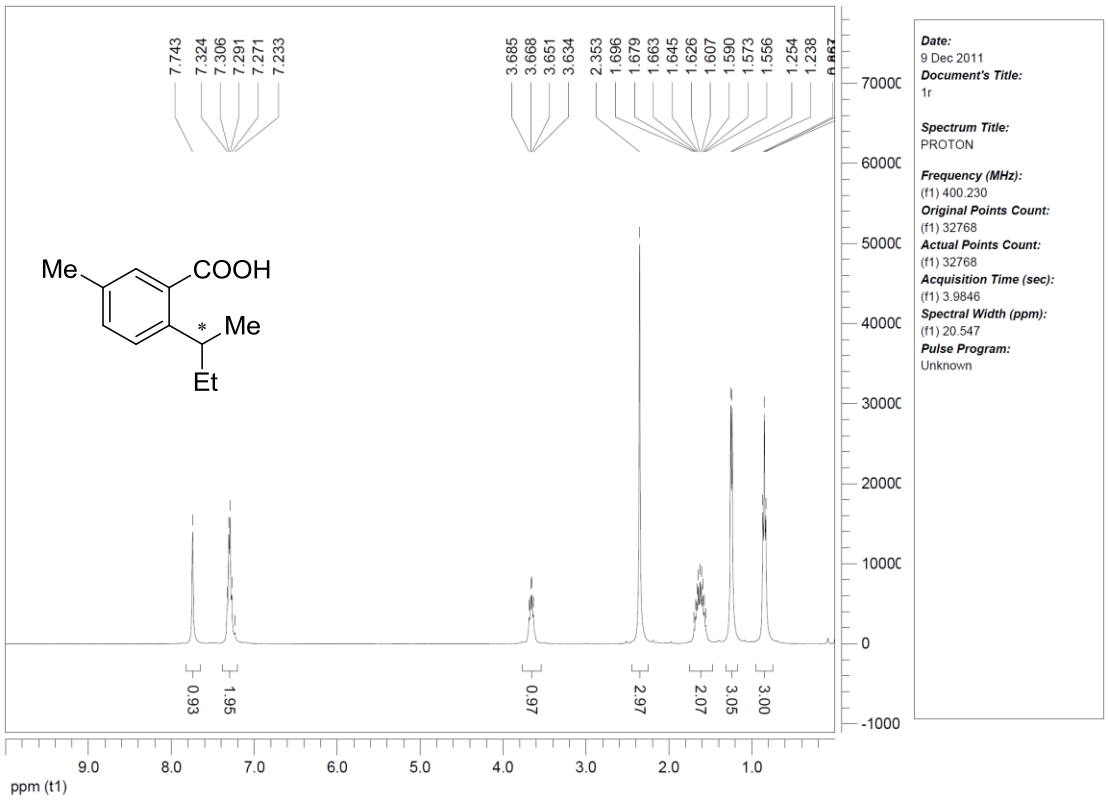


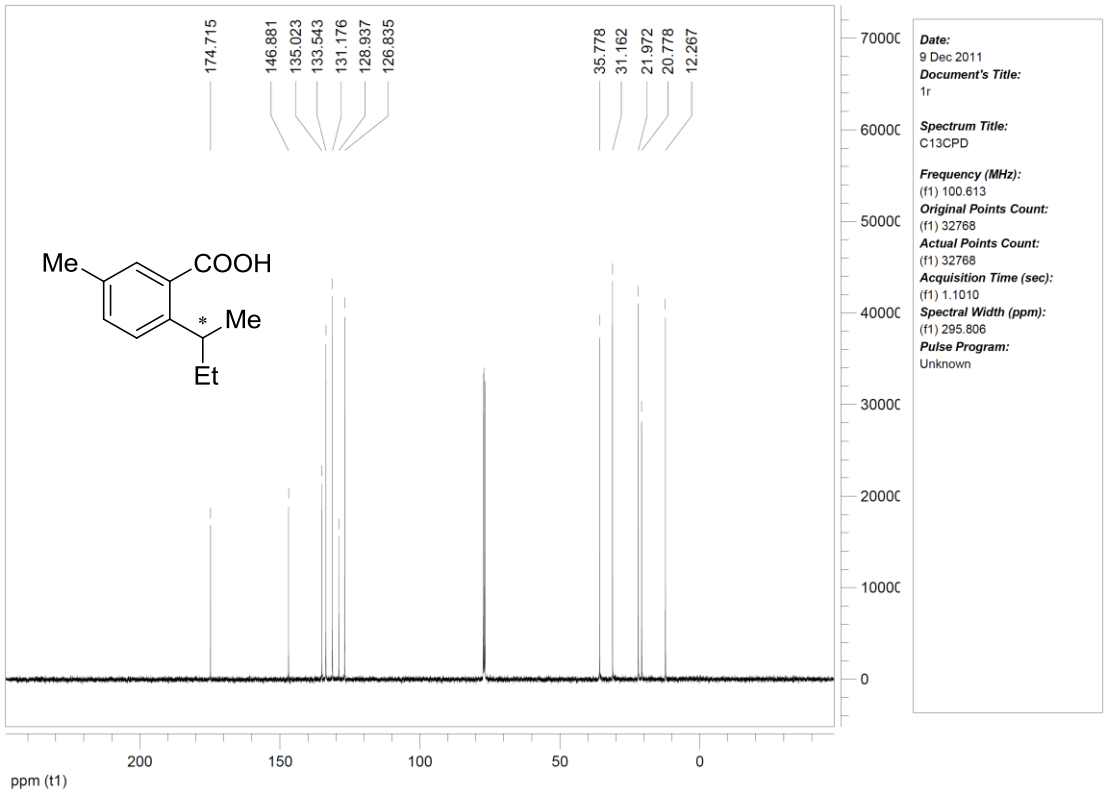
2-*sec*-Butyl-5-methoxybenzoic acid (3l)



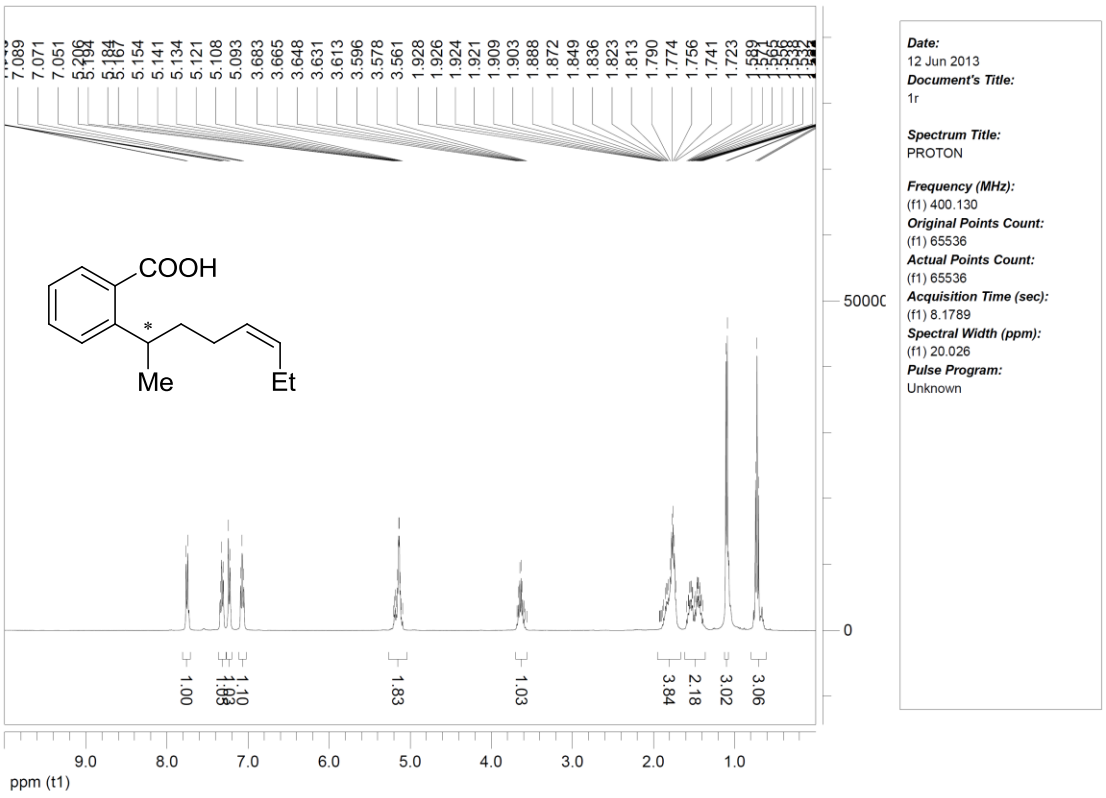


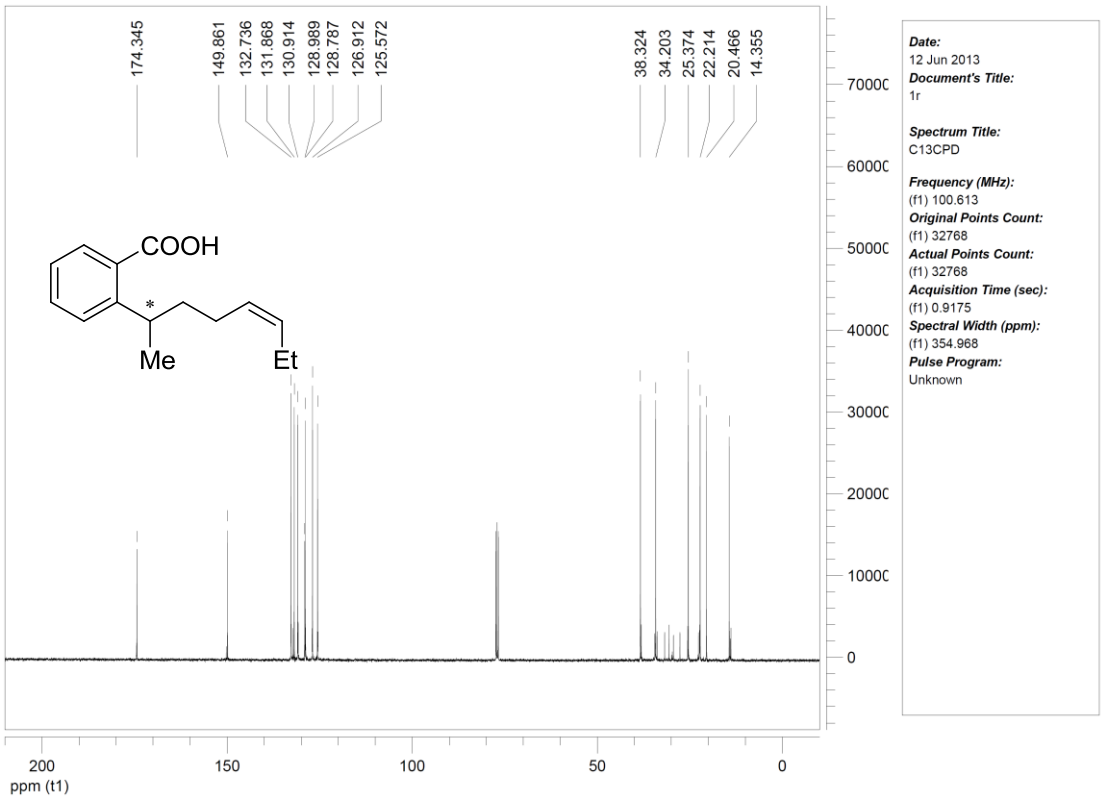
2-*sec*-Butyl-5-methylbenzoic acid (3m)



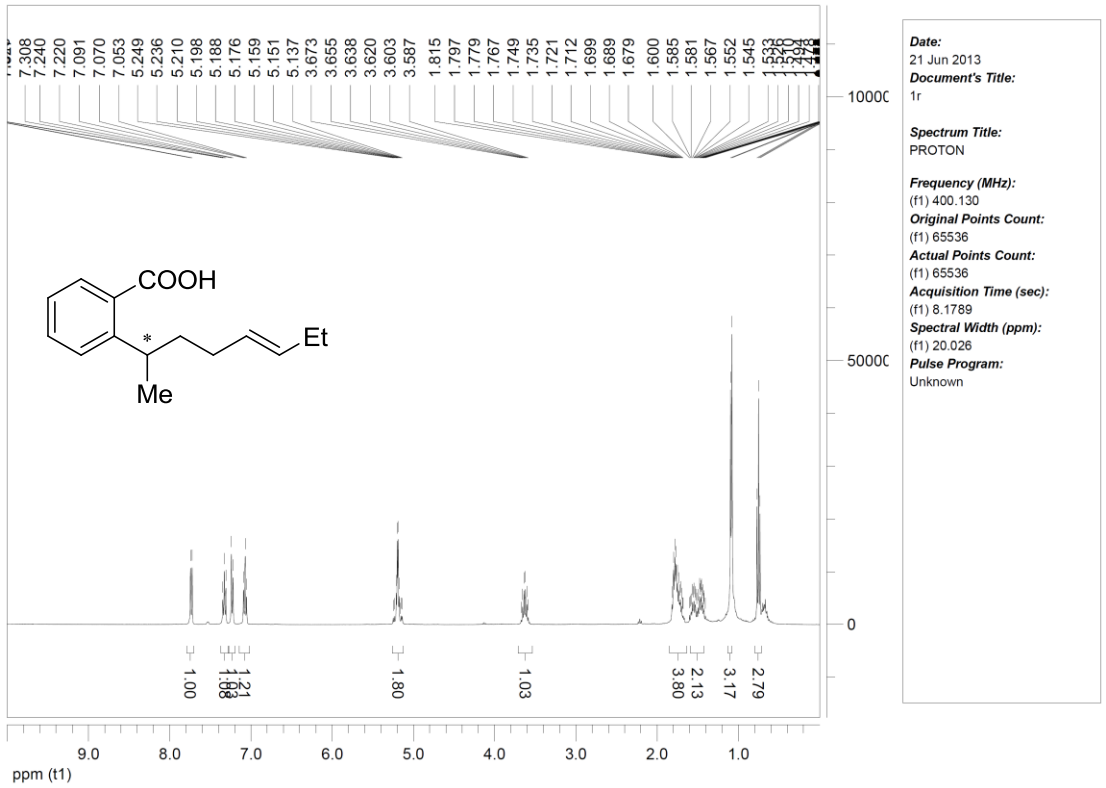


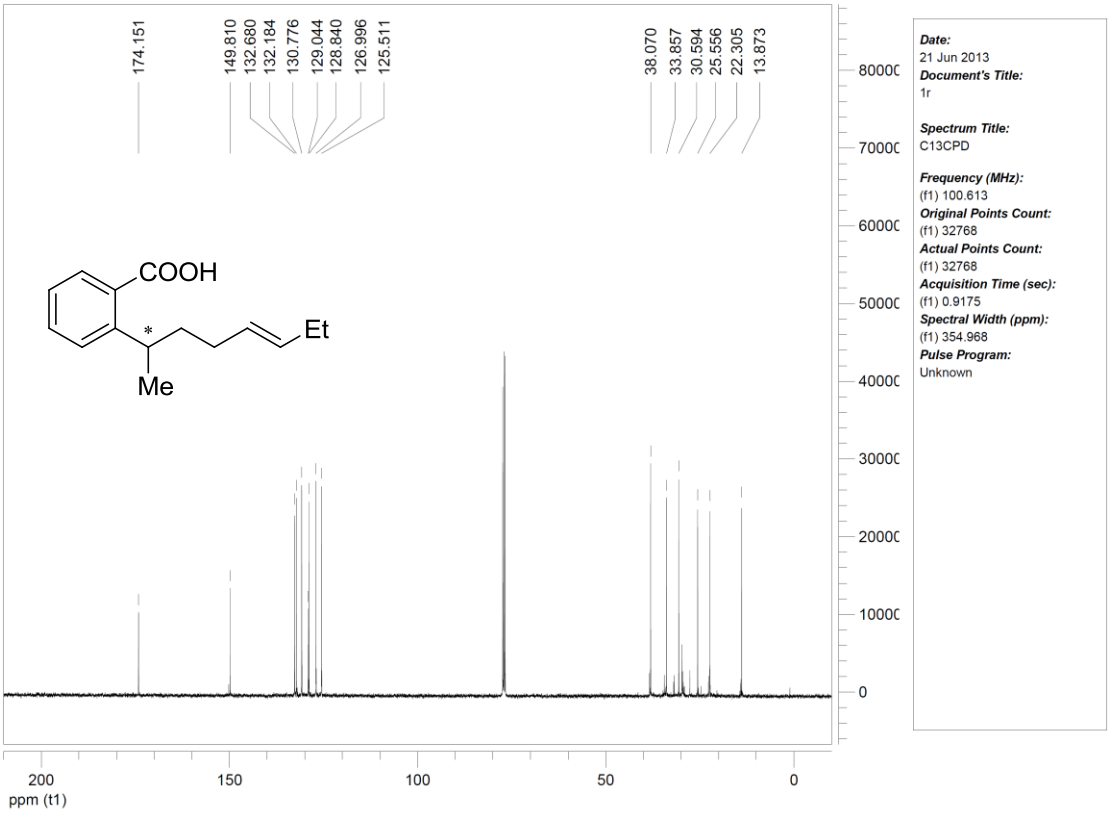
(Z)-2-(Oct-5-en-2-yl)benzoic acid (3n)



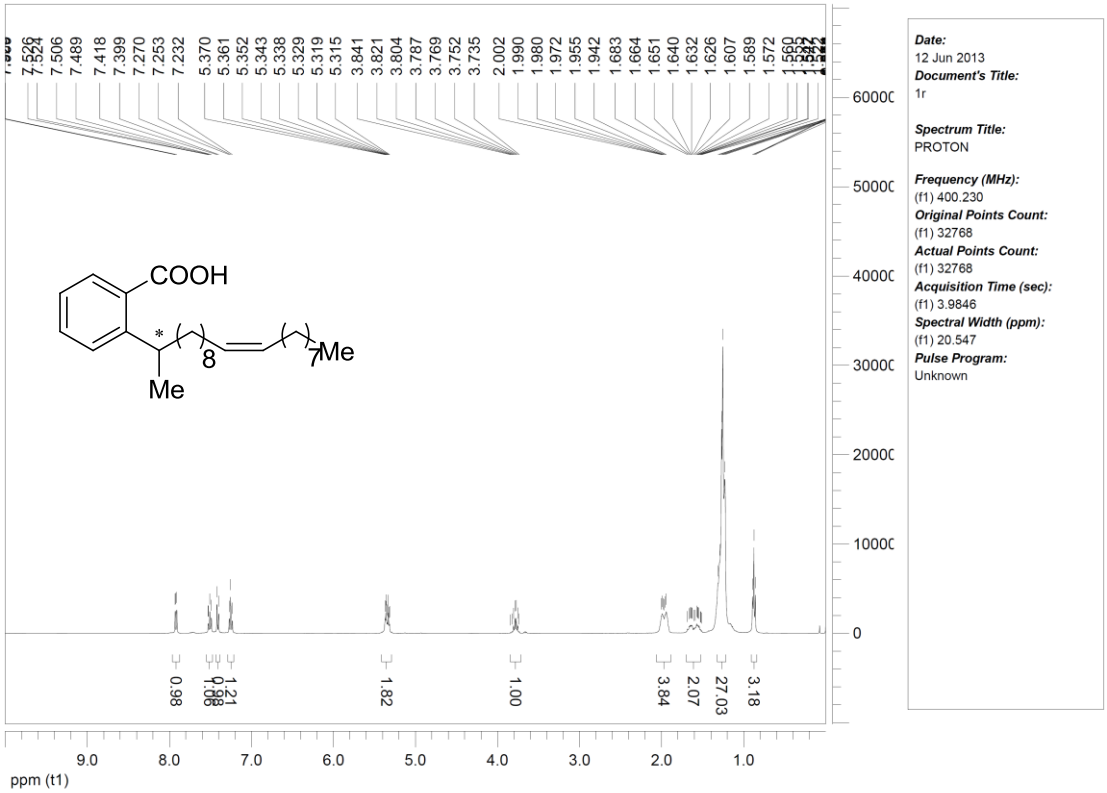


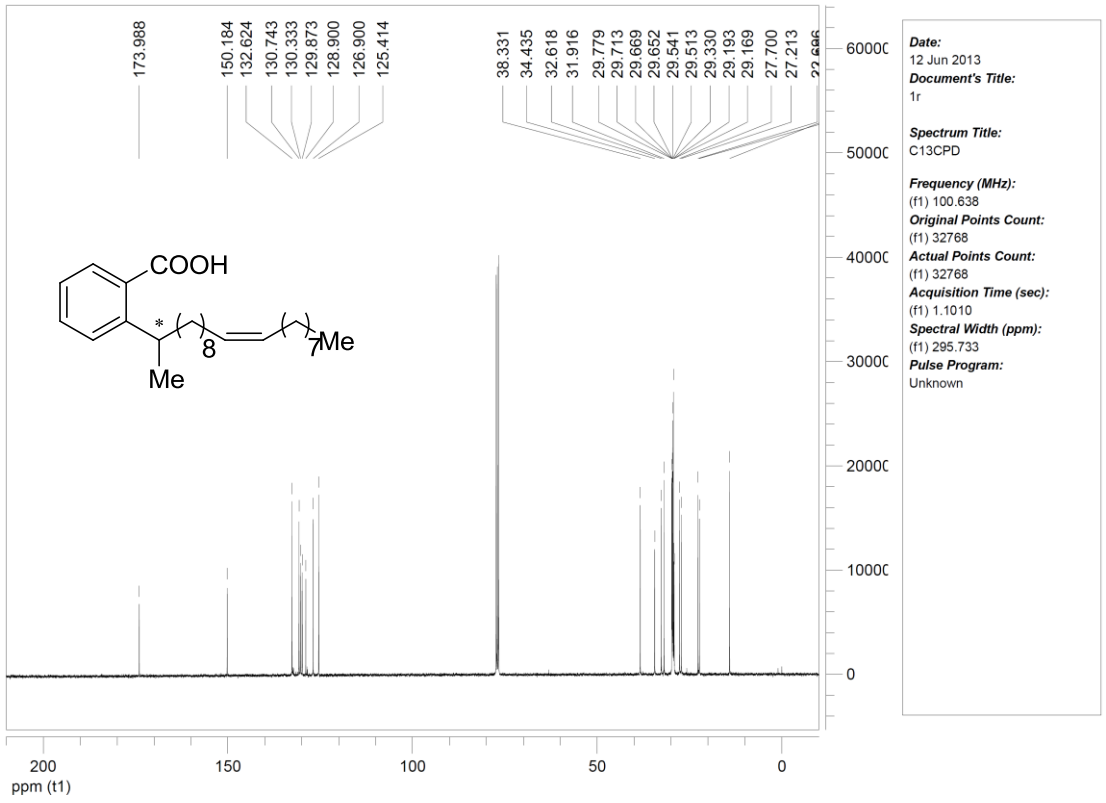
(*E*)-2-(Oct-5-en-2-yl)benzoic acid (3o)



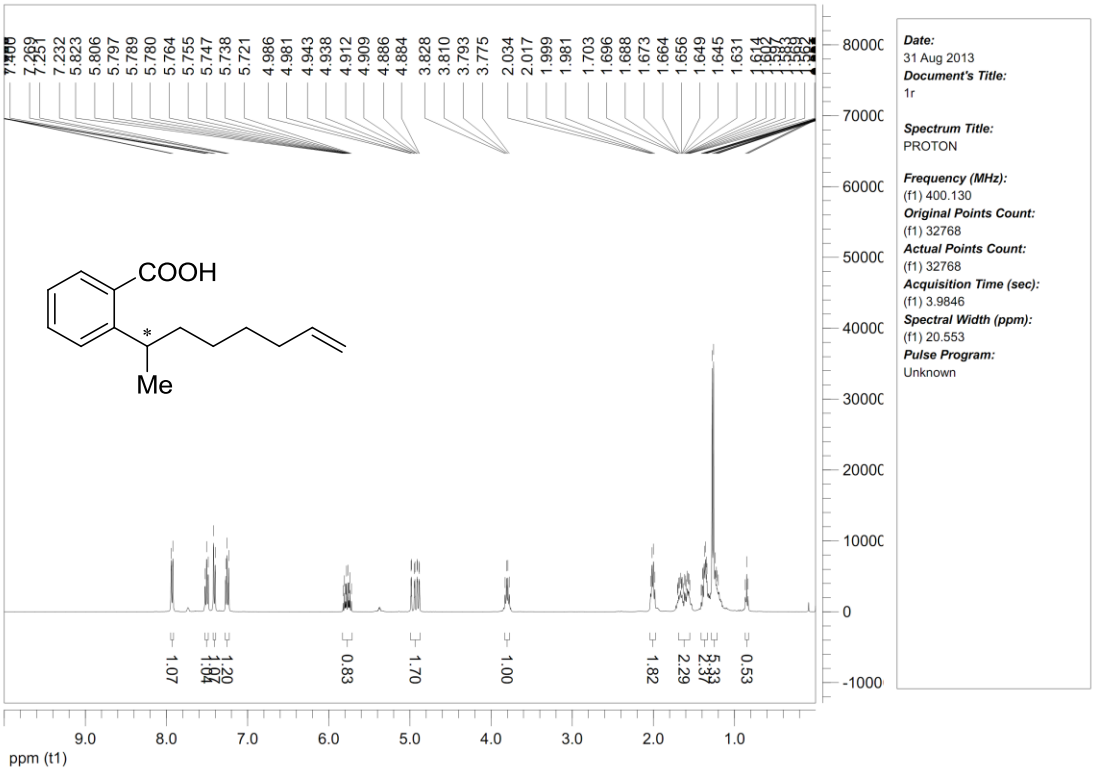


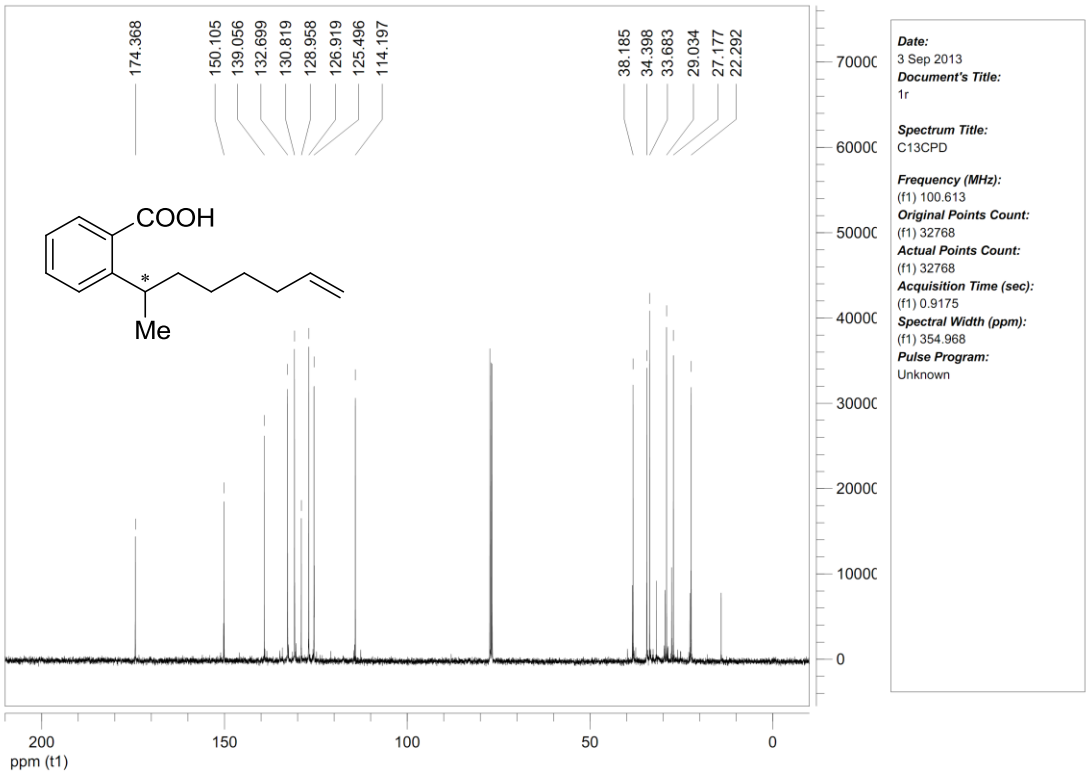
(*Z*)-2-(Icos-11-en-2-yl)benzoic acid (3p)



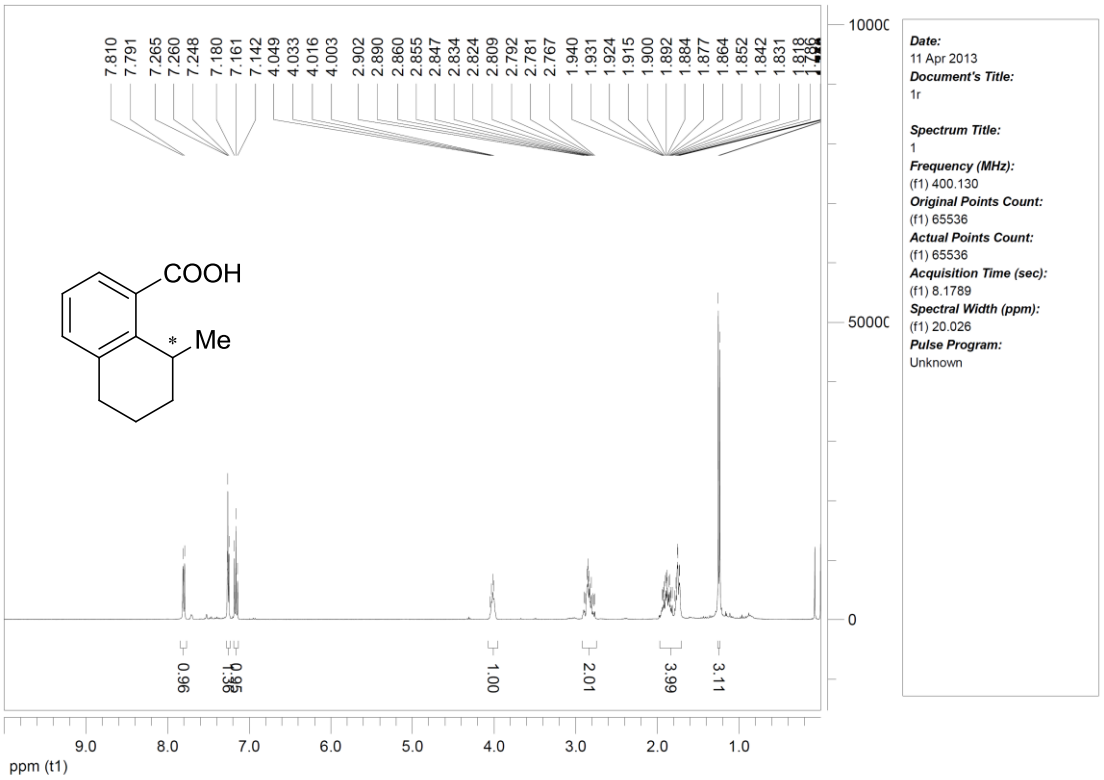


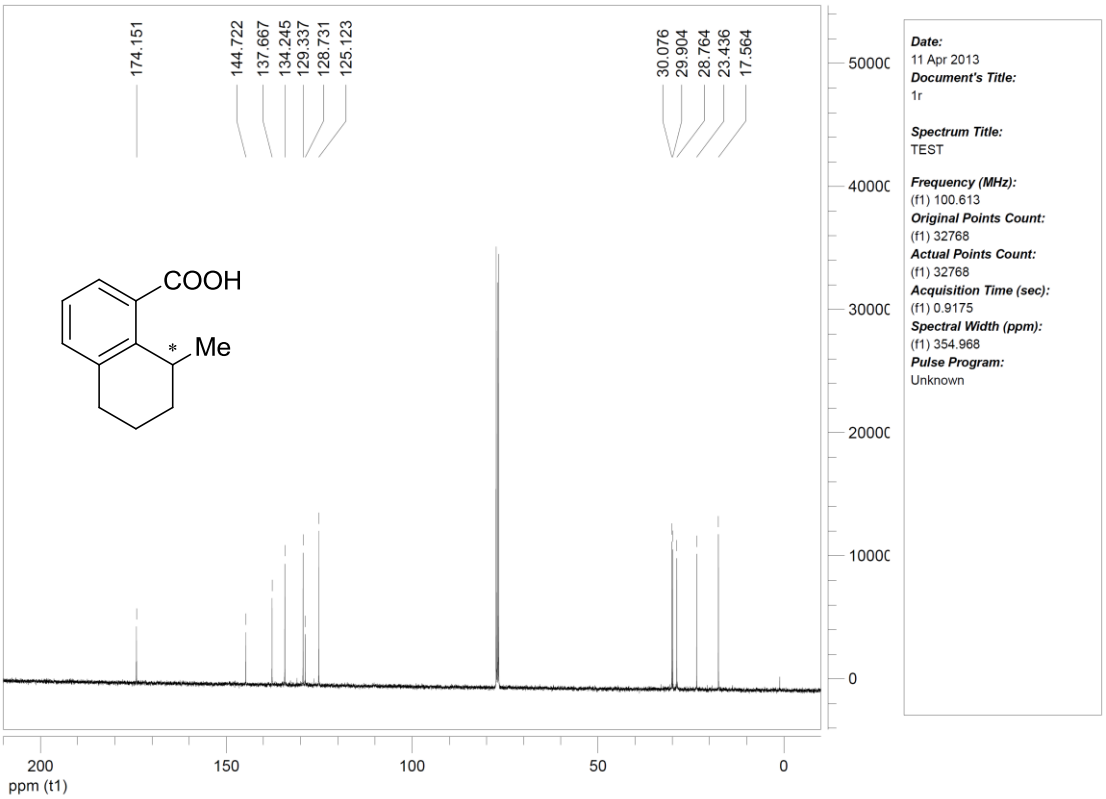
2-(Oct-7-en-2-yl)benzoic acid (3q) (with 13% over hydrogenation product)



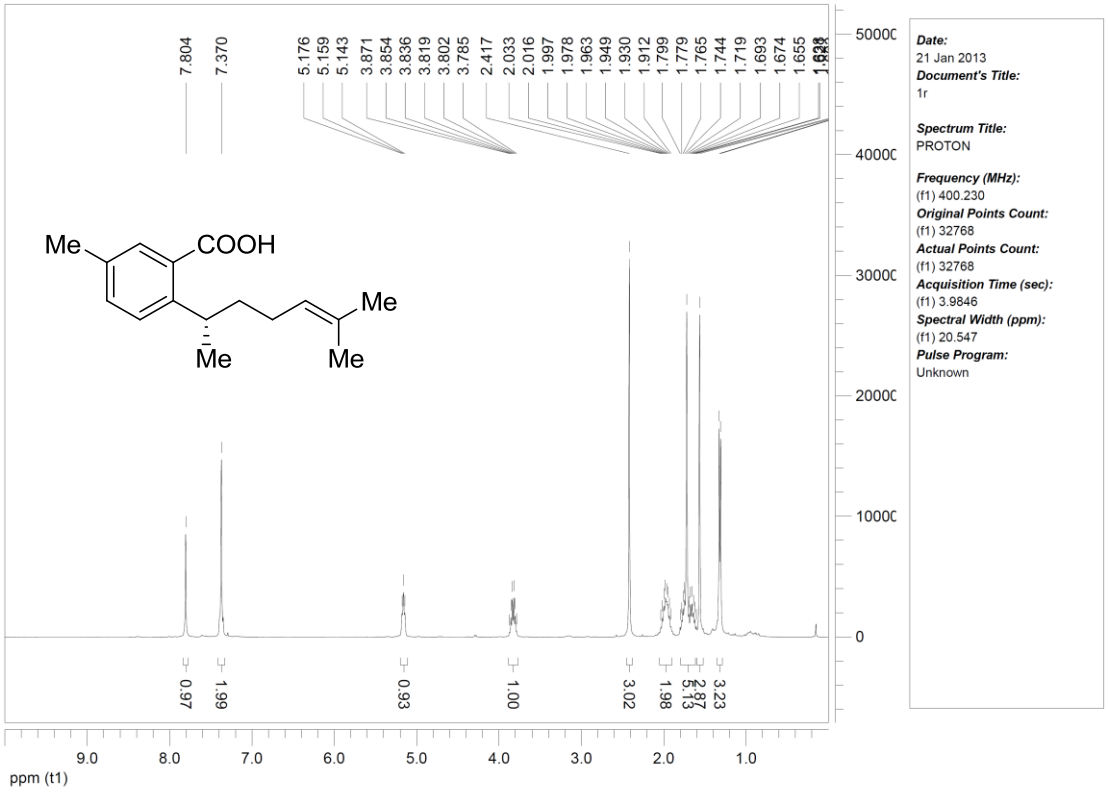


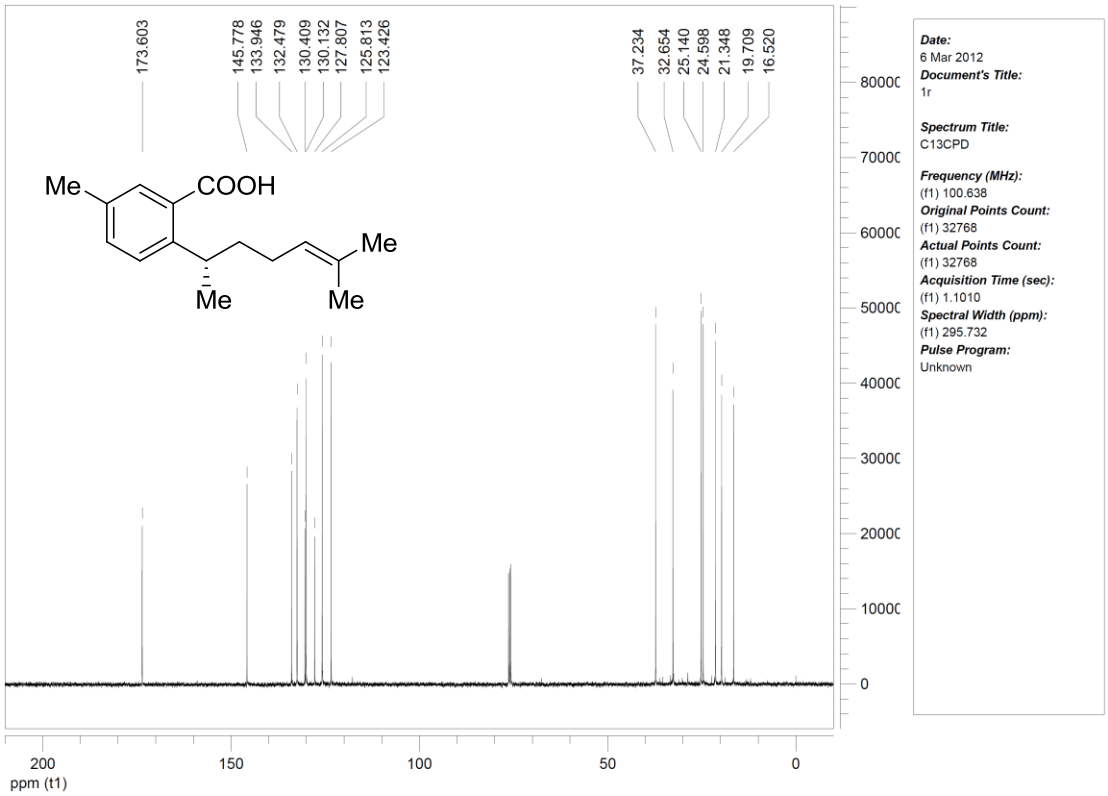
8-Methyl-5,6,7,8-tetrahydronaphthalene-1-carboxylic acid (3r)



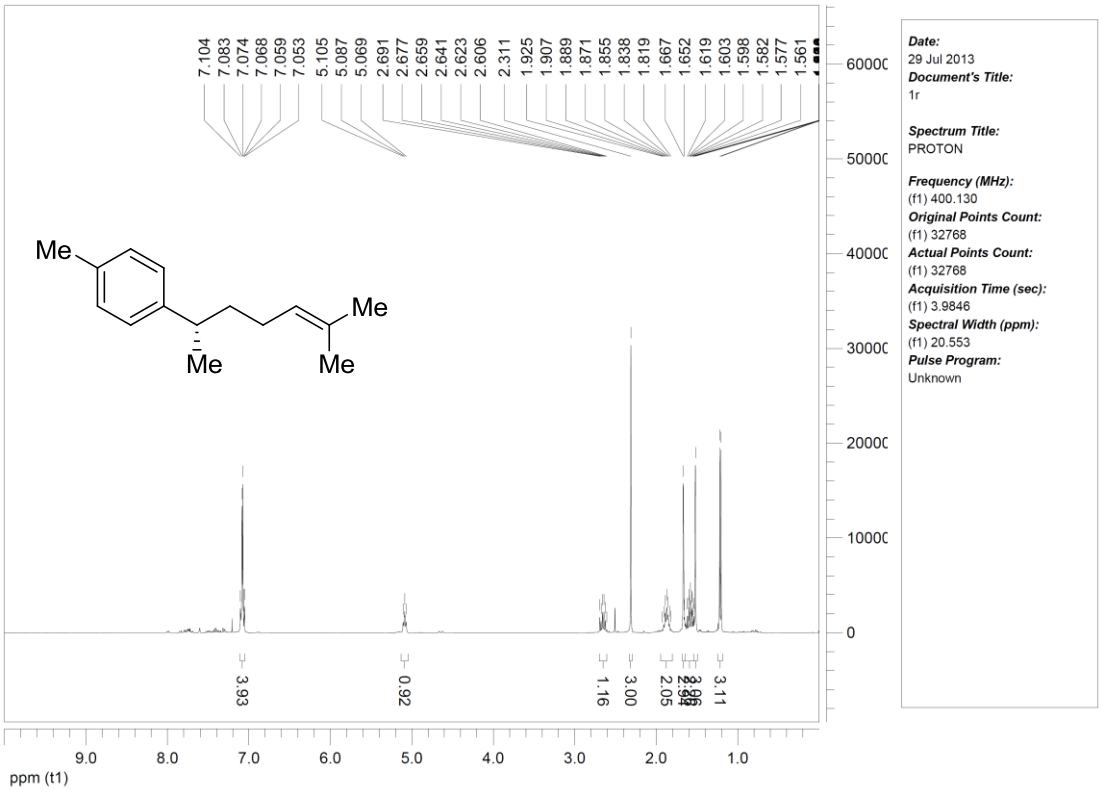


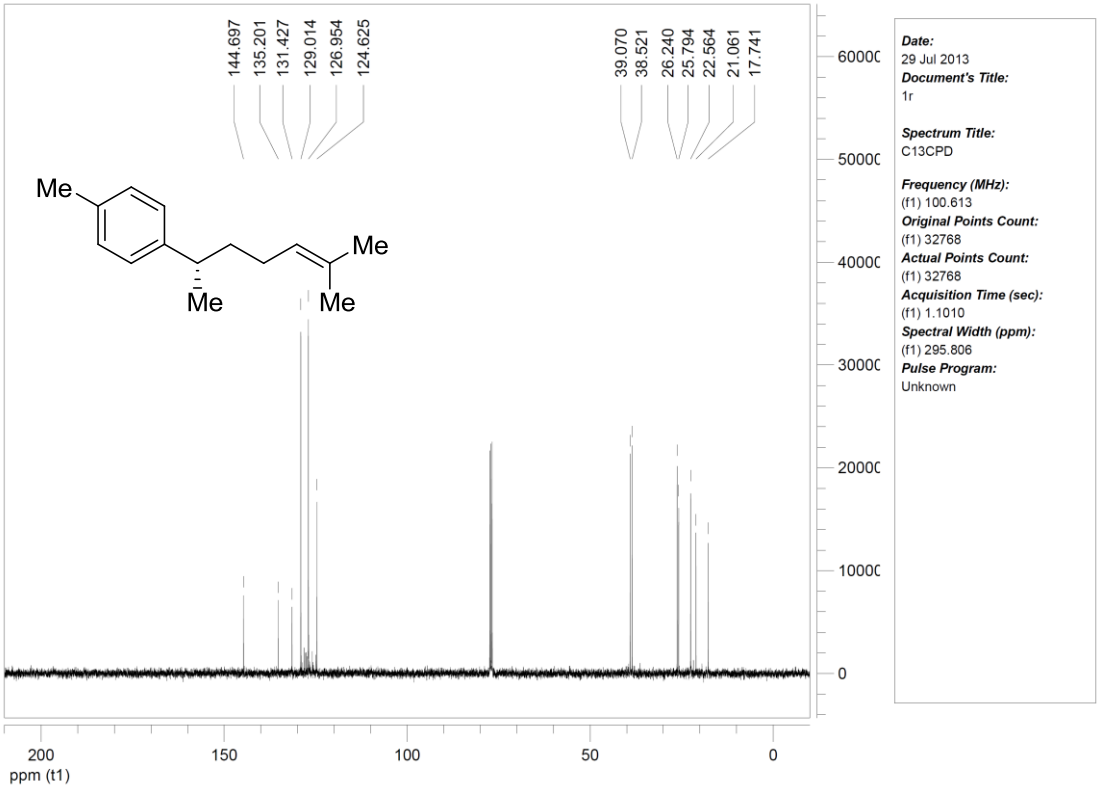
(*S*)-5-Methyl-2-(6-methylhept-5-en-2-yl)benzoic acid (10)



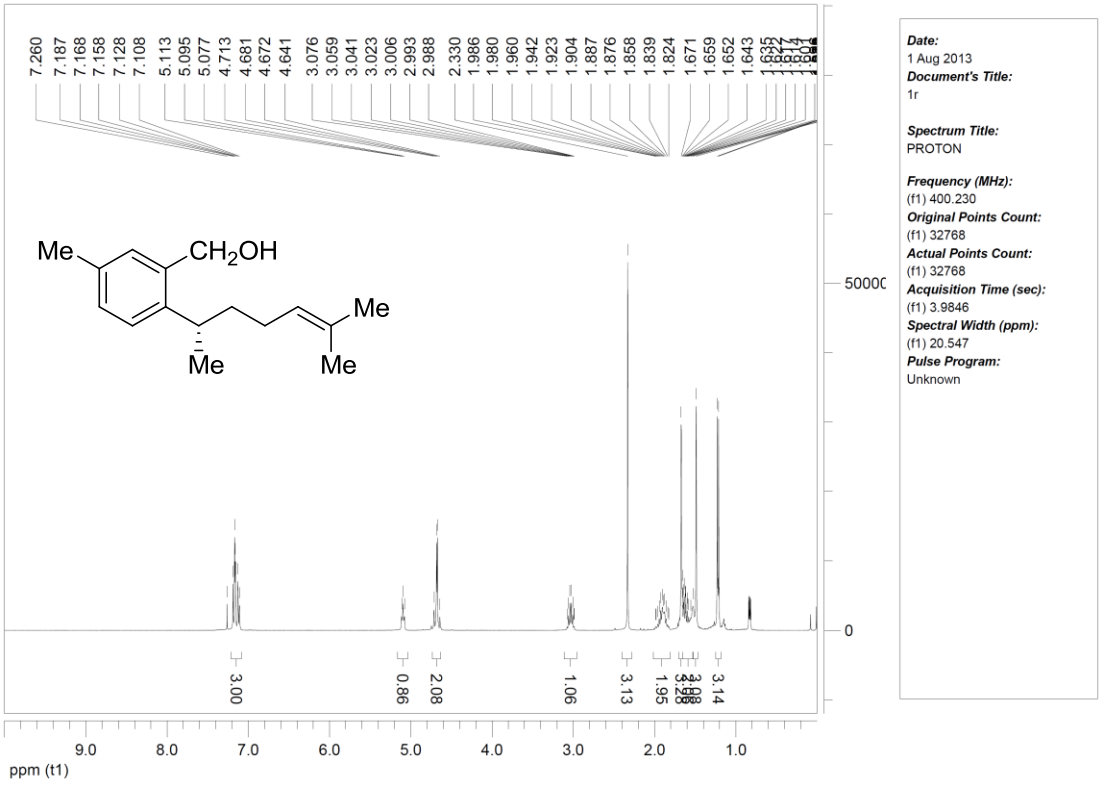


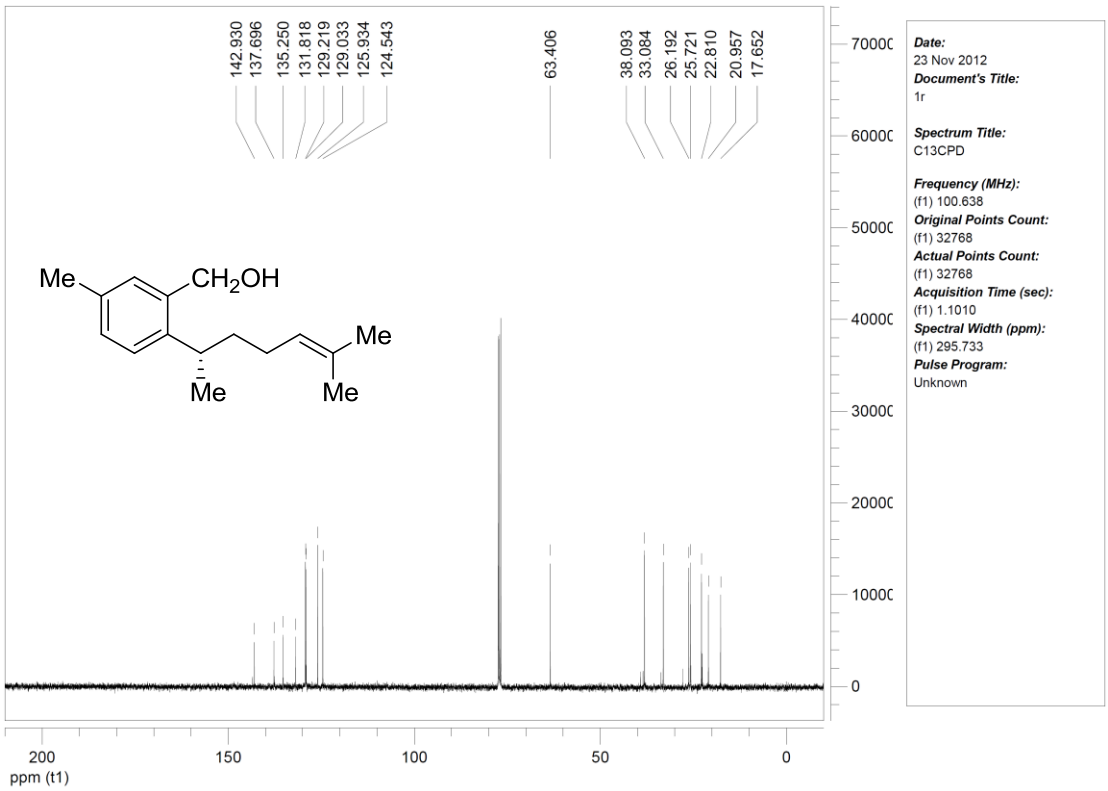
(*S*)-Curcumene


7.104
7.083
7.074
7.068
7.059
7.053
5.105
5.087
5.069
2.691
2.677
2.659
2.641
2.623
2.606
2.311
1.925
1.907
1.889
1.871
1.855
1.838
1.819
1.667
1.652
1.619
1.603
1.598
1.582
1.577
1.561
Me
Me
Me
3.93
0.92
1.16
3.00
2.05
3.11
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
Date:
29 Jul 2013
Document's Title:
1r
Spectrum Title:
PROTON
Frequency (MHz):
(f1) 400.130
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.553
Pulse Program:
Unknown

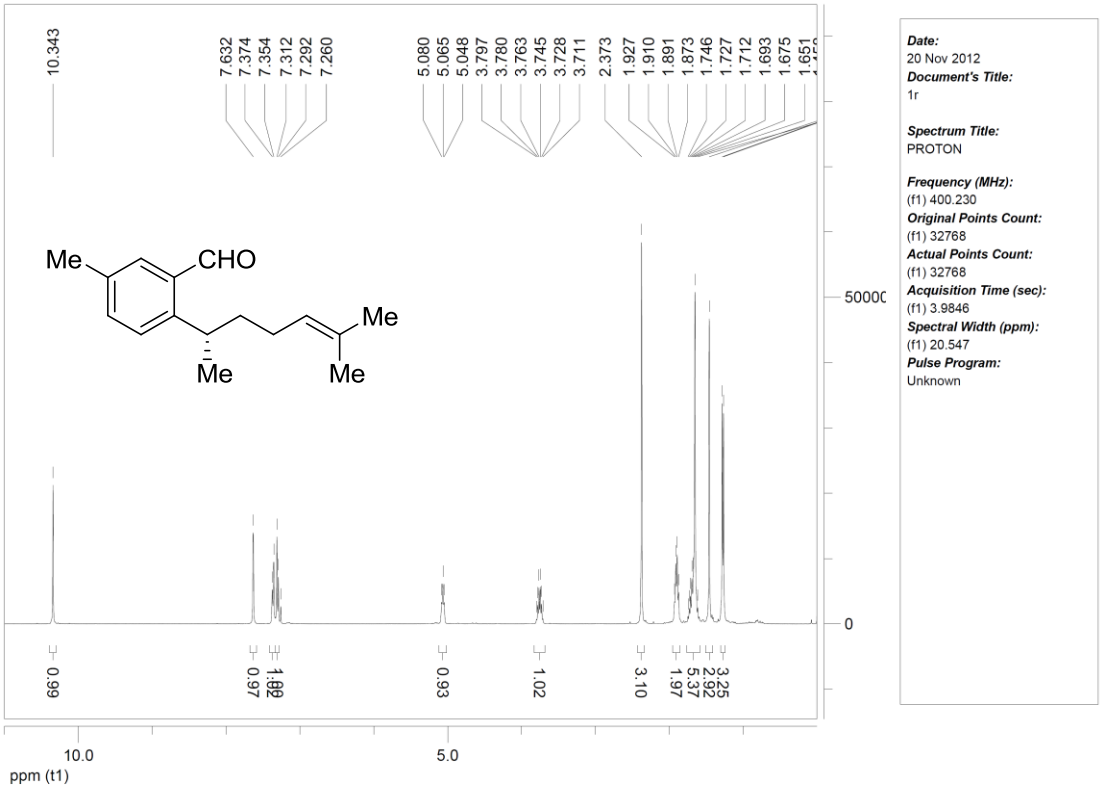

144.697
135.201
131.427
129.014
126.954
124.625
39.070
38.521
26.240
25.794
22.564
21.061
17.741
Me
Me
Me
Me
200
150
100
50
0
ppm (t1)
Date:
29 Jul 2013
Document's Title:
1r
Spectrum Title:
C13CPD
Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.1010
Spectral Width (ppm):
(f1) 295.806
Pulse Program:
Unknown

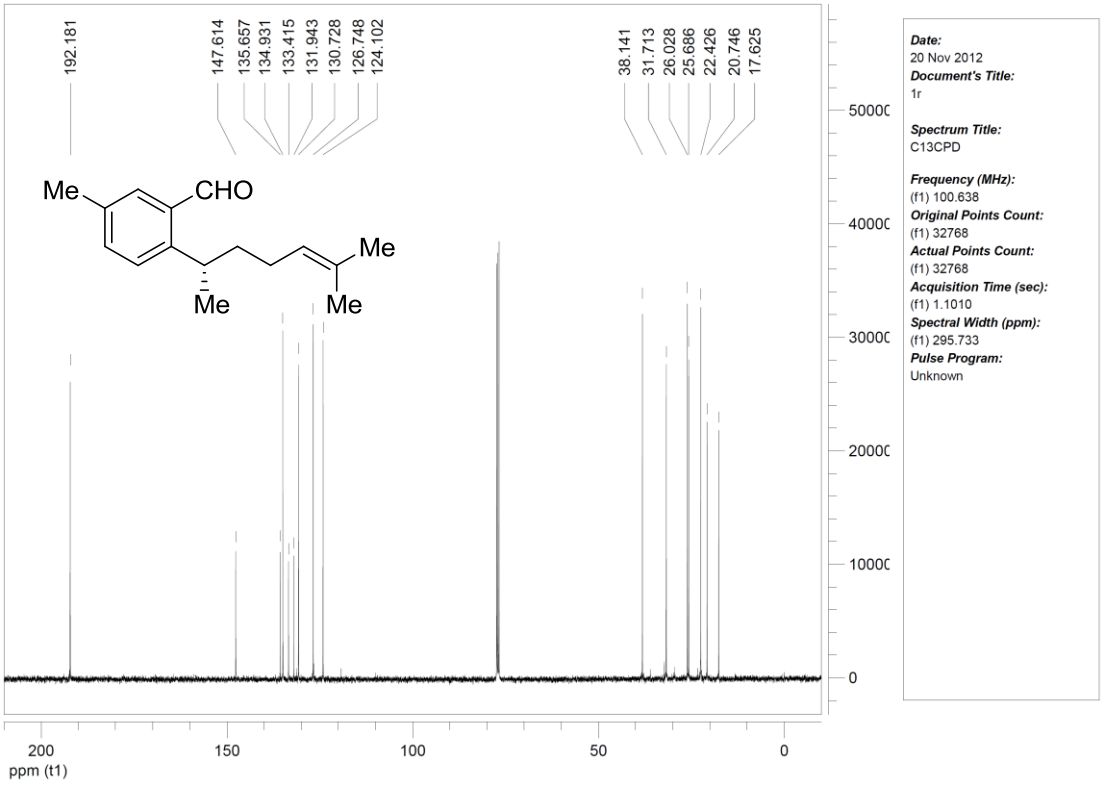
(*S*)-(5-Methyl-2-(6-methylhept-5-en-2-yl)phenyl)methanol



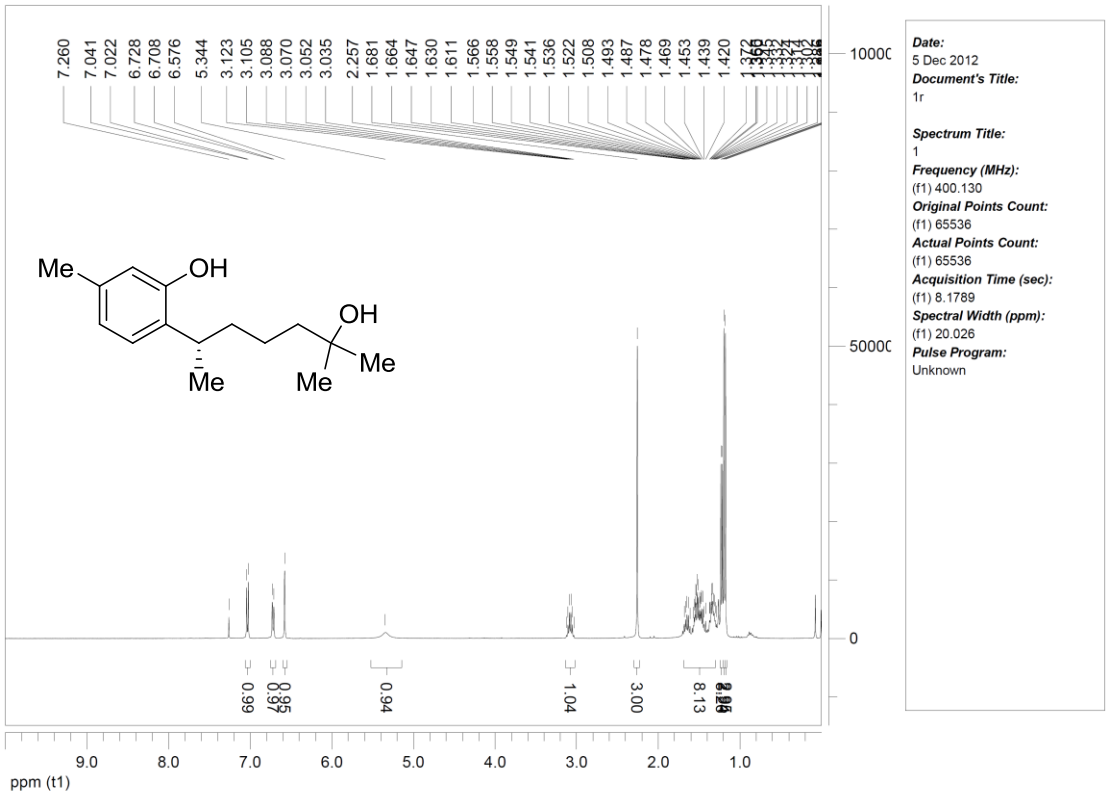


(*S*)-5-Methyl-2-(6-methylhept-5-en-2-yl)benzaldehyde (11)





(*S*)-Curcudiol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7.041
7.022
6.728
6.708
6.576
5.344
3.123
3.105
3.088
3.070
3.052
3.035
2.257
1.681
1.664
1.647
1.630
1.611
1.566
1.558
1.549
1.541
1.536
1.522
1.508
1.493
1.487
1.478
1.469
1.453
1.439
1.420
Me
OH
OH
Me
Me
Me
0.99
0.97
0.95
0.94
1.04
3.00
8.13
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
Date:
5 Dec 2012
Document's Title:
1r
Spectrum Title:
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Frequency (MHz):
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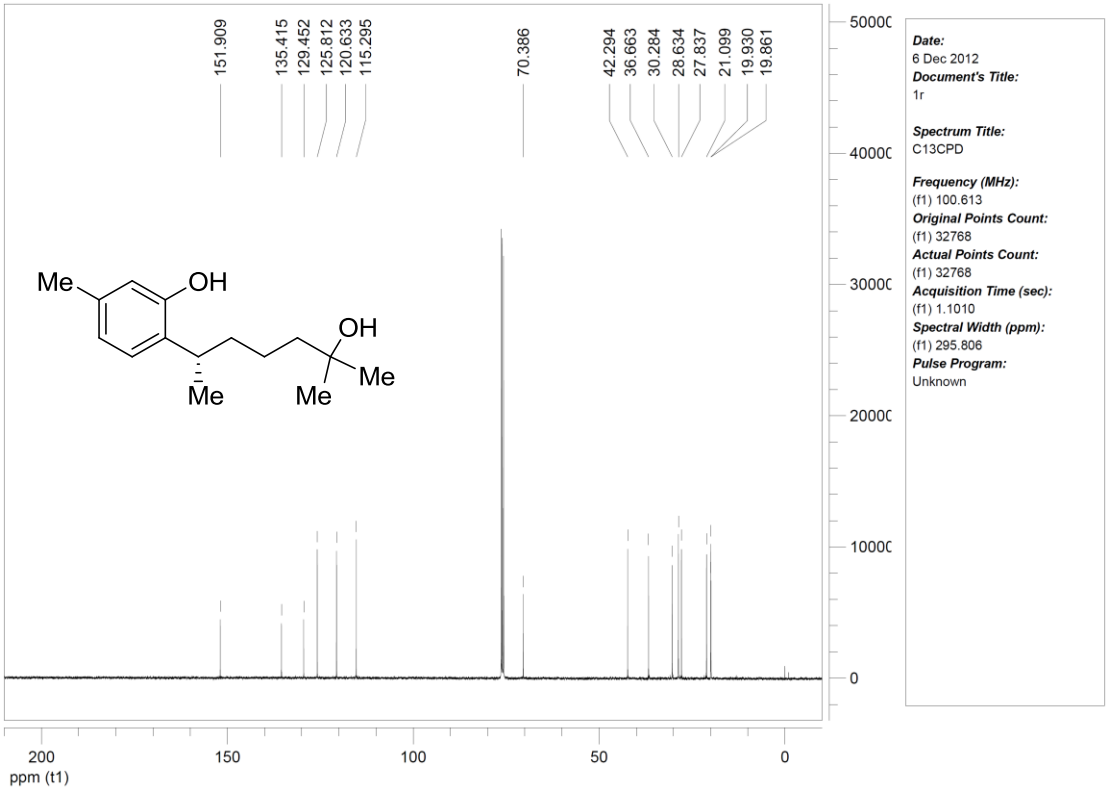
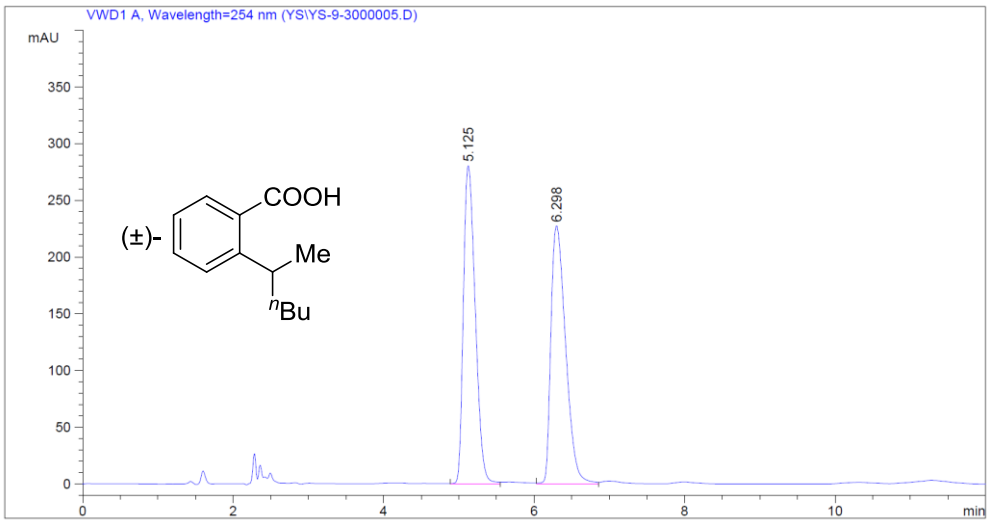
Original Points Count:
(f1) 65536
Actual Points Count:
(f1) 65536
Acquisition Time (sec):
(f1) 8.1789
Spectral Width (ppm):
(f1) 20.026
Pulse Program:
Unknown


151.909
135.415
129.452
125.812
120.633
115.295
70.386
42.294
36.663
30.284
28.634
27.837
21.099
19.930
19.861
Me
OH
OH
Me
Me
Me
200
150
100
50
0
ppm (t1)
Date:
6 Dec 2012
Document's Title:
1r
Spectrum Title:
C13CPD
Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.1010
Spectral Width (ppm):
(f1) 295.806
Pulse Program:
Unknown

(E) SFC Charts of Hydrogenation Product Derivatives

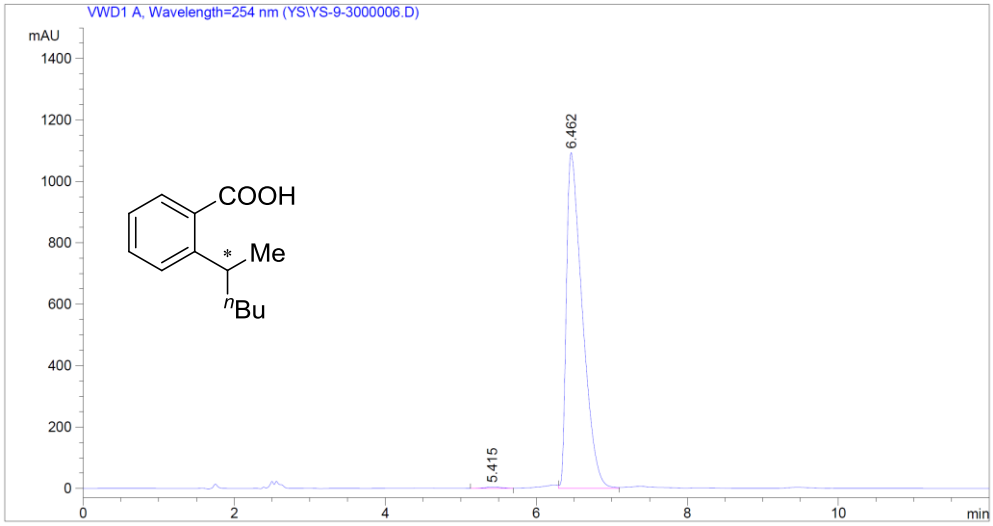
2-(Hexan-2-yl)benzoic acid (3a)



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %	Name
1	5.125	BV	0.1724	3057.36646	49.7568	?
2	6.298	VV	0.2138	3087.24902	50.2432	?

Totals : 6144.61548

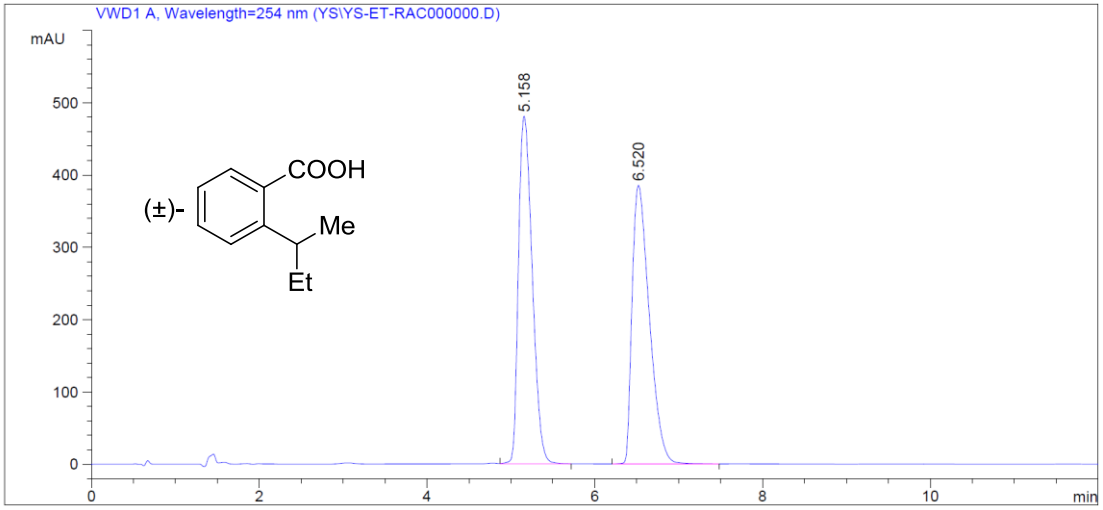


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %	Name
1	5.415	VV	0.2299	72.12315	0.4477	?
2	6.462	VV	0.2147	1.60368e4	99.5523	?

Totals : 1.61089e4

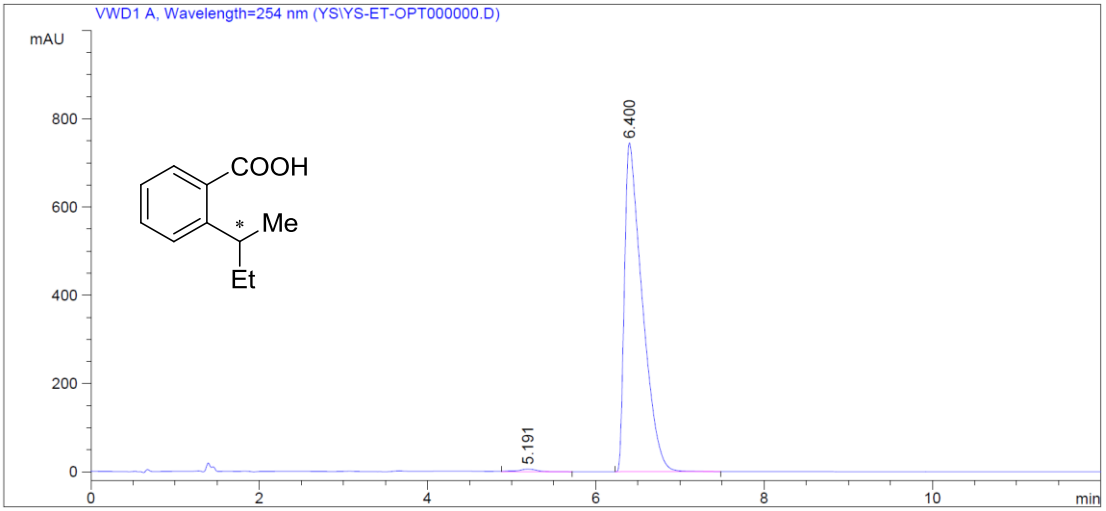
2-*sec*-Butylbenzoic acid (3b)



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %	Name
1	5.158	VB	0.1811	5478.37842	49.9374	?
2	6.520	BB	0.2217	5492.10791	50.0626	?

Totals : 1.09705e4

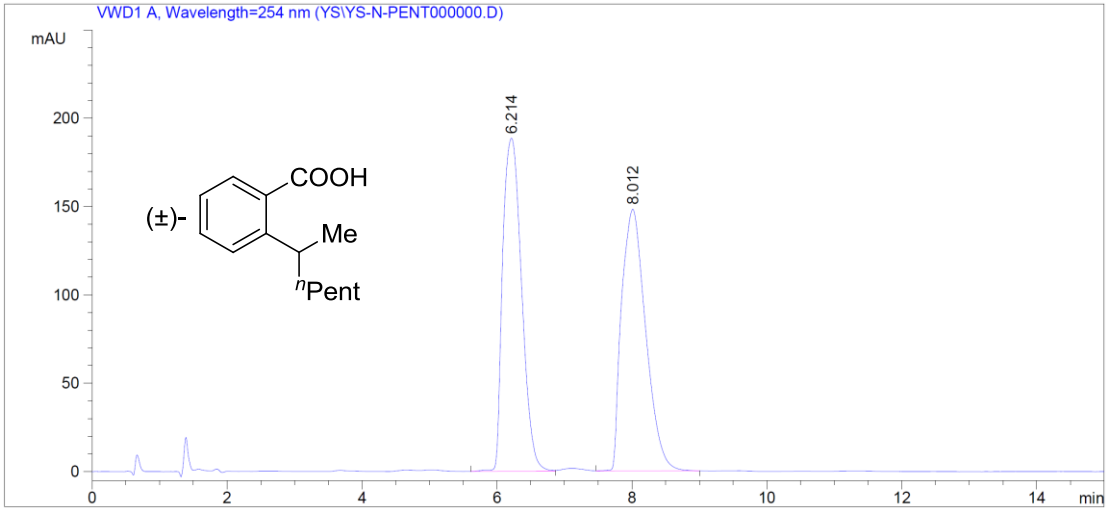


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %	Name
1	5.191	VV	0.2542	109.03738	0.9873	?
2	6.400	BB	0.2120	1.09355e4	99.0127	?

Totals : 1.10445e4

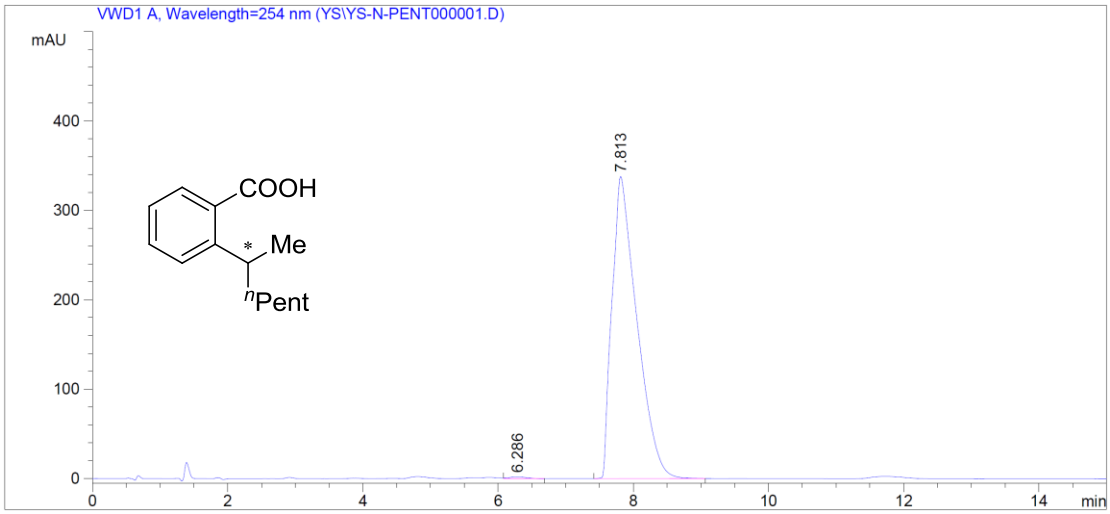
2-(Heptan-2-yl)benzoic acid (3c)



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	6.214	BB	0.3162	3674.57251	49.9630	?	
2	8.012	VB	0.4018	3680.00928	50.0370	?	

Totals : 7354.58179

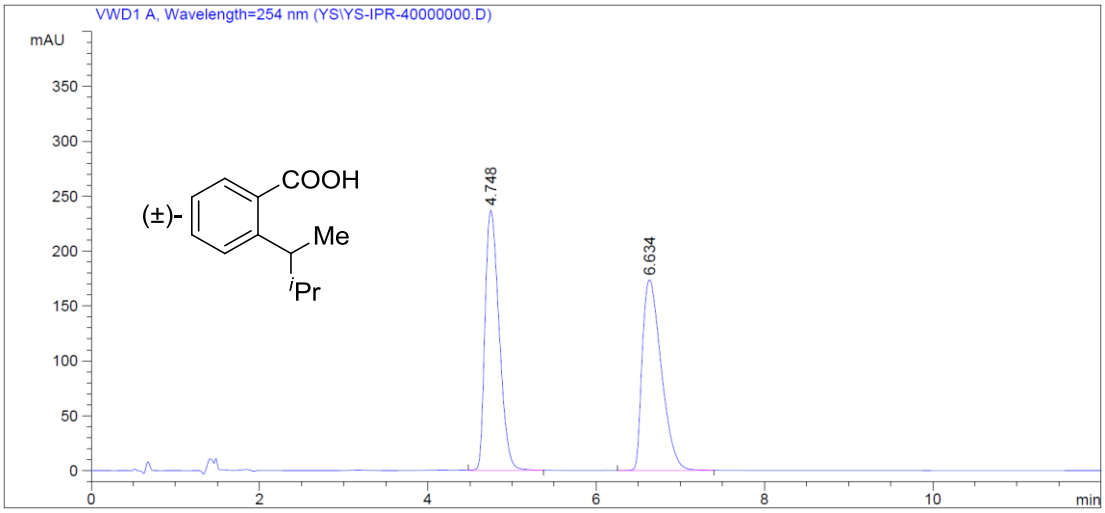


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	6.286	VV	0.3012	37.62837	0.4352	?	
2	7.813	BB	0.3497	8609.28711	99.5648	?	

Totals : 8646.91548

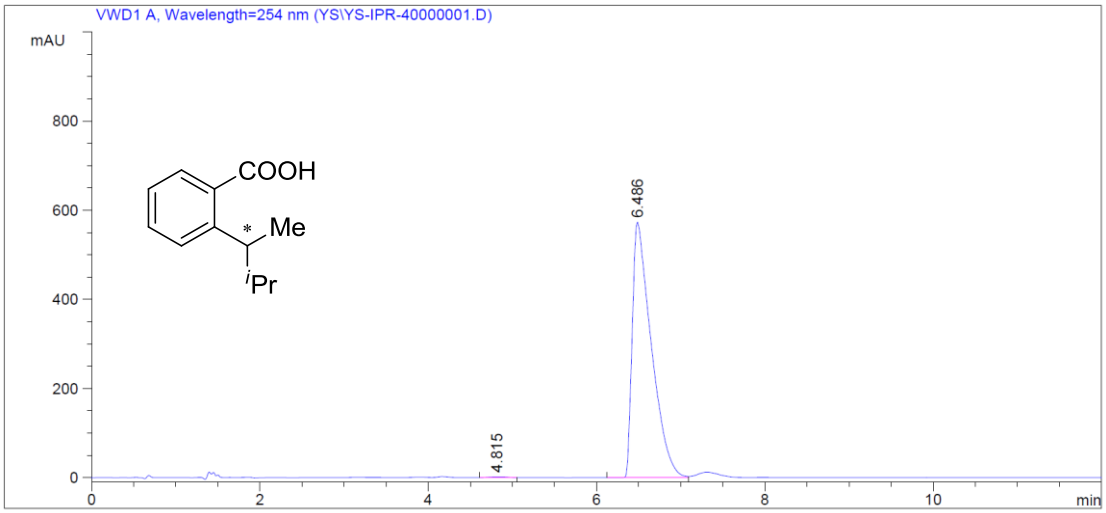
2-(3-Methylbutan-2-yl)benzoic acid (3d)



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	4.748	VB	0.1837	2752.78174	50.2841	?	
2	6.634	VB	0.2456	2721.67920	49.7159	?	

Totals : 5474.46094

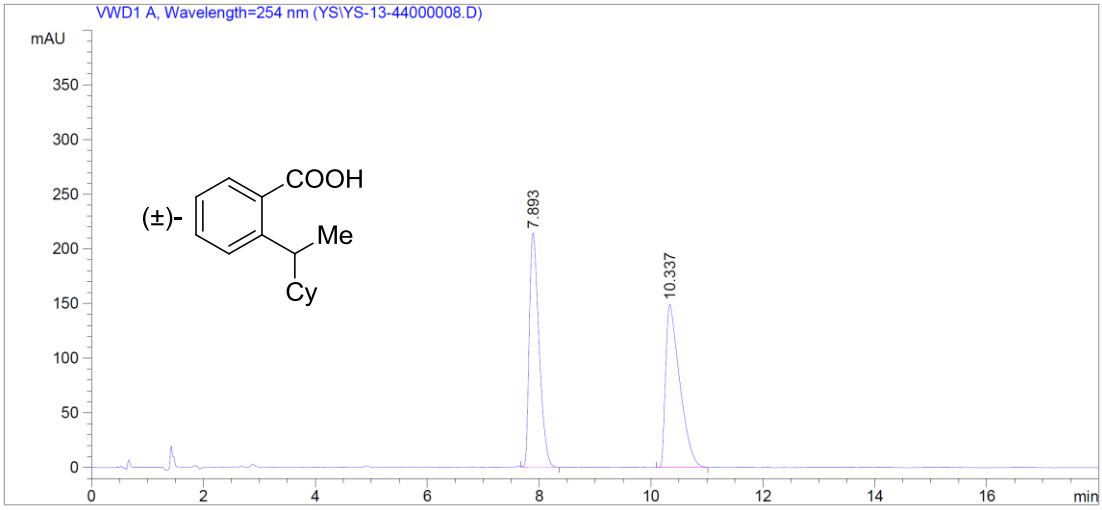


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	4.815	BV	0.1860	21.44241	0.2384	?	
2	6.486	BV	0.2264	8972.39453	99.7616	?	

Totals : 8993.83694

2-(1-Cyclohexylethyl)benzoic acid (3e)

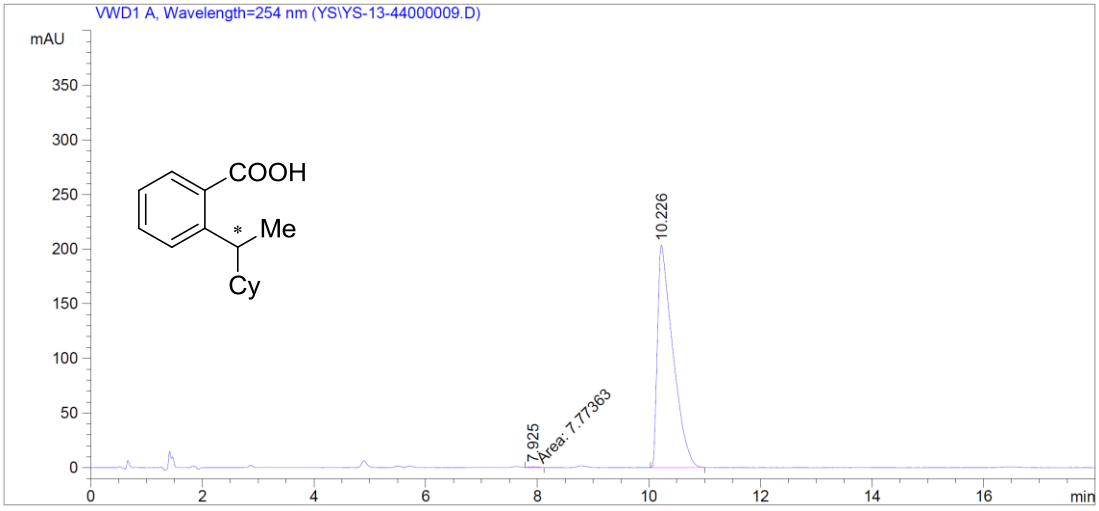


Signal 1: VWD1 A, Wavelength=254 nm

Uncalibrated Peaks:

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	7.893	BB	0.1878	2590.98511		49.8646	?
2	10.337	BB	0.2621	2605.05200		50.1354	?

Uncalib. totals : 5196.03711 100.0000



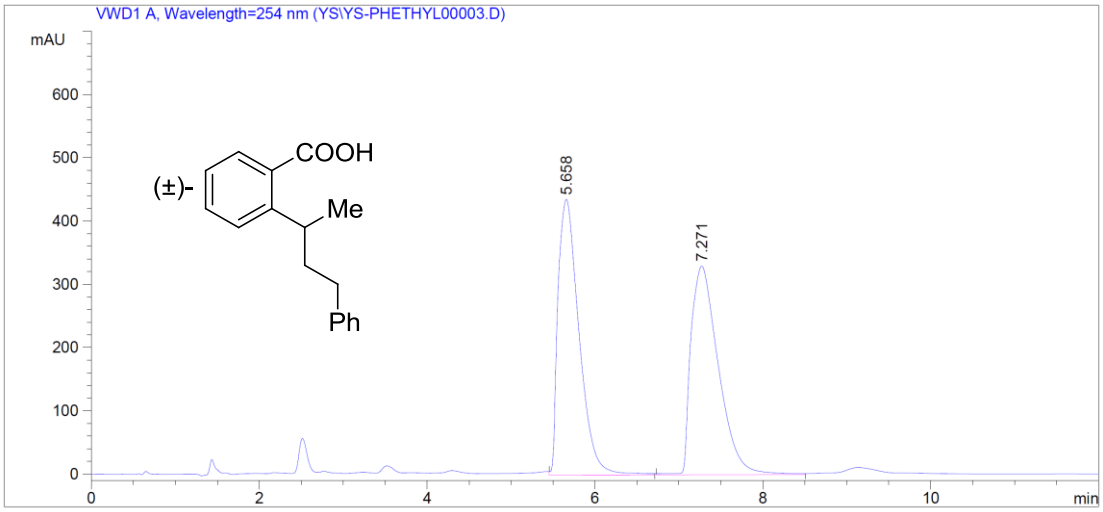
Signal 1: VWD1 A, Wavelength=254 nm

Uncalibrated Peaks:

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	7.925	MM	0.1703	7.77363		0.1989	?
2	10.226	BB	0.2731	3900.66846		99.8011	?

Uncalib. totals : 3908.44208 100.0000

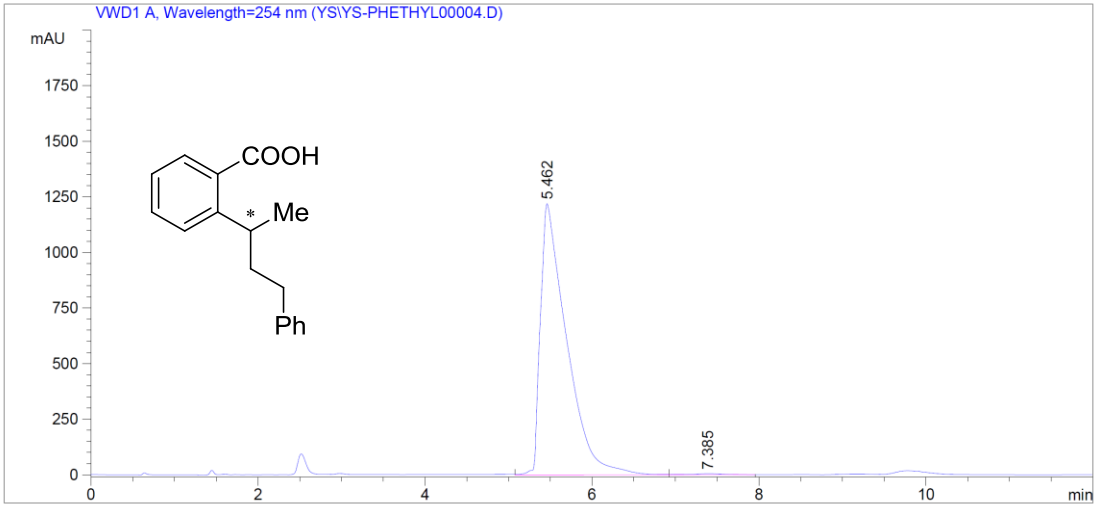
2-(4-Phenylbutan-2-yl)benzoic acid (3f)



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %	Name
1	5.658	VB	0.2697	7575.72461	50.1764	?
2	7.271	BB	0.3548	7522.47266	49.8236	?

Totals : 1.50982e4

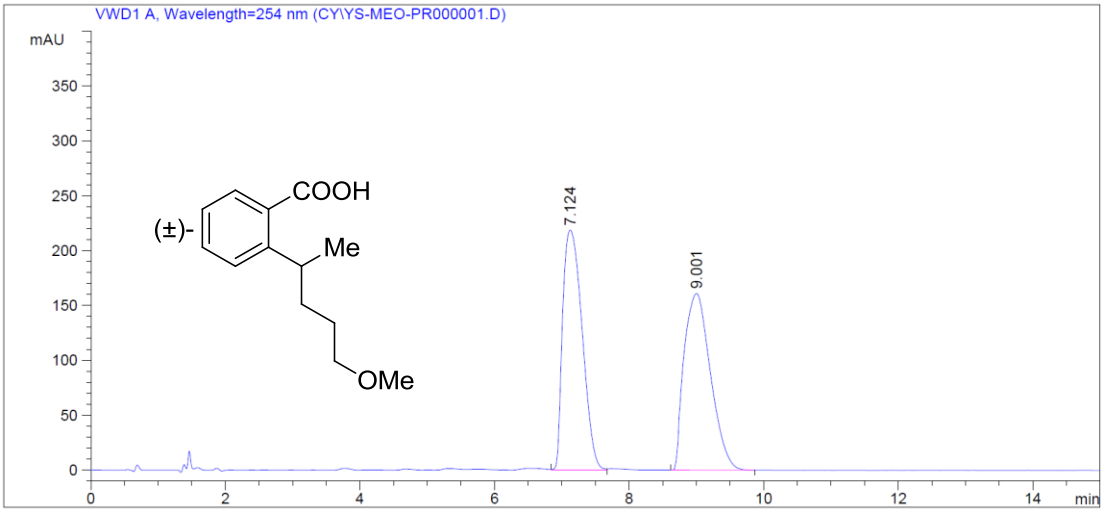


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %	Name
1	5.462	VV	0.2865	2.64569e4	99.5516	?
2	7.385	VV	0.3710	119.16550	0.4484	?

Totals : 2.65760e4

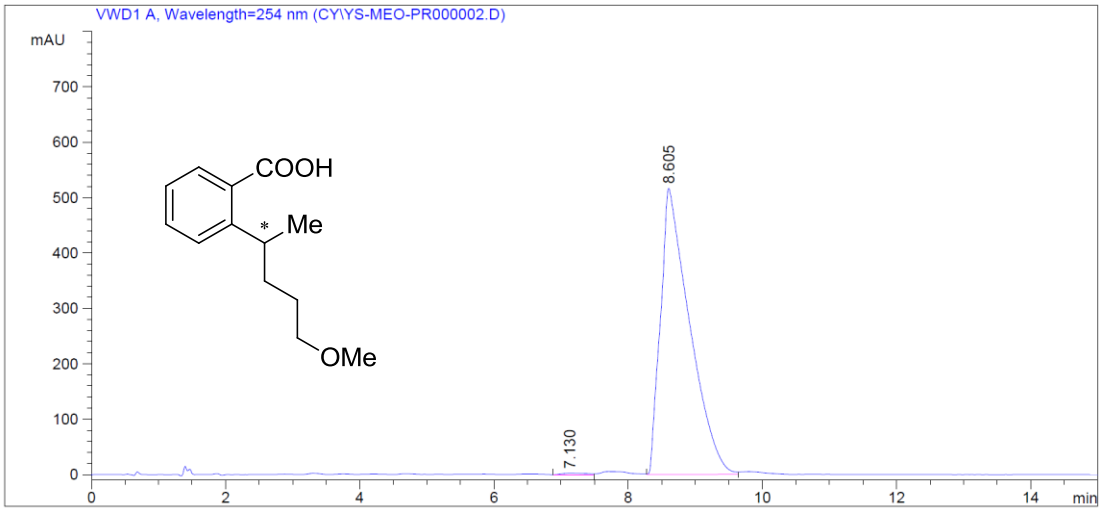
2-(5-Methoxypentan-2-yl)benzoic acid (3g)



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	7.124	VV	0.3336	4397.14941	50.1009	?	
2	9.001	BB	0.4413	4379.44336	49.8991	?	

Totals : 8776.59277

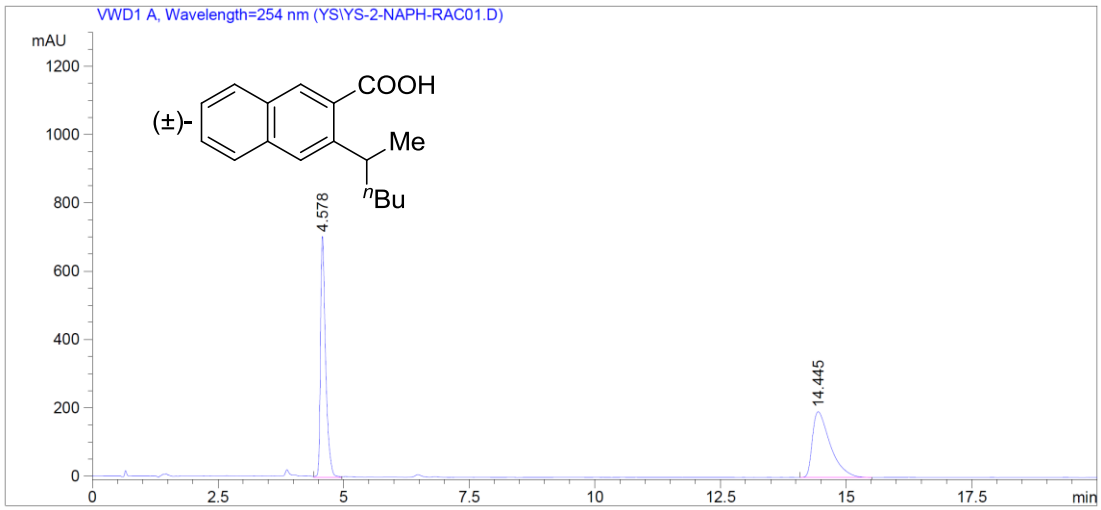


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	7.130	BV	0.2993	63.11938	0.4031	?	
2	8.605	VV	0.4018	1.55965e4	99.5969	?	

Totals : 1.56596e4

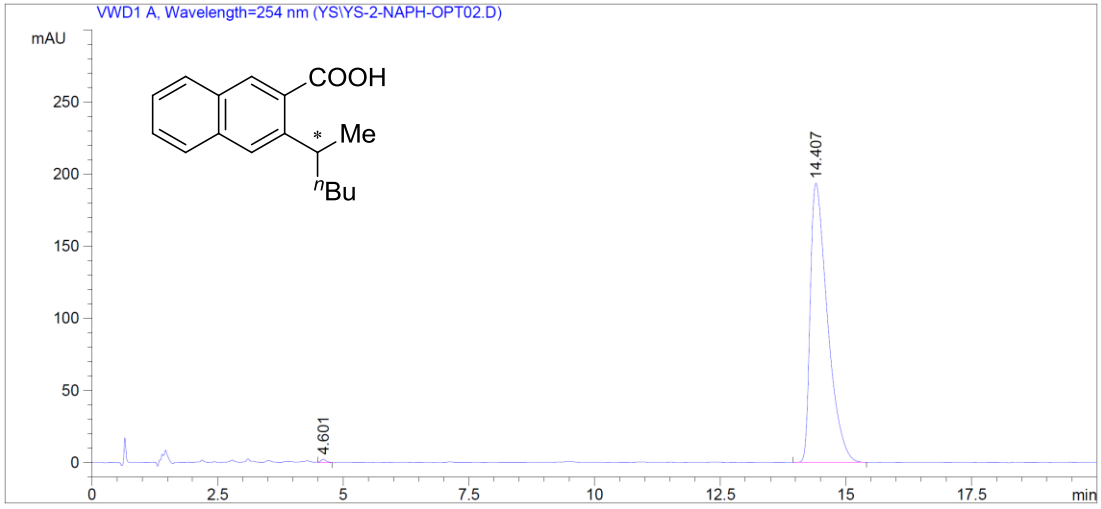
3-(Hexan-2-yl)-2-naphthoic acid (3h)



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	4.578	VV	0.1059	5004.74072	51.2803	?	
2	14.445	VV	0.3694	4754.82910	48.7197	?	

Totals : 9759.56982

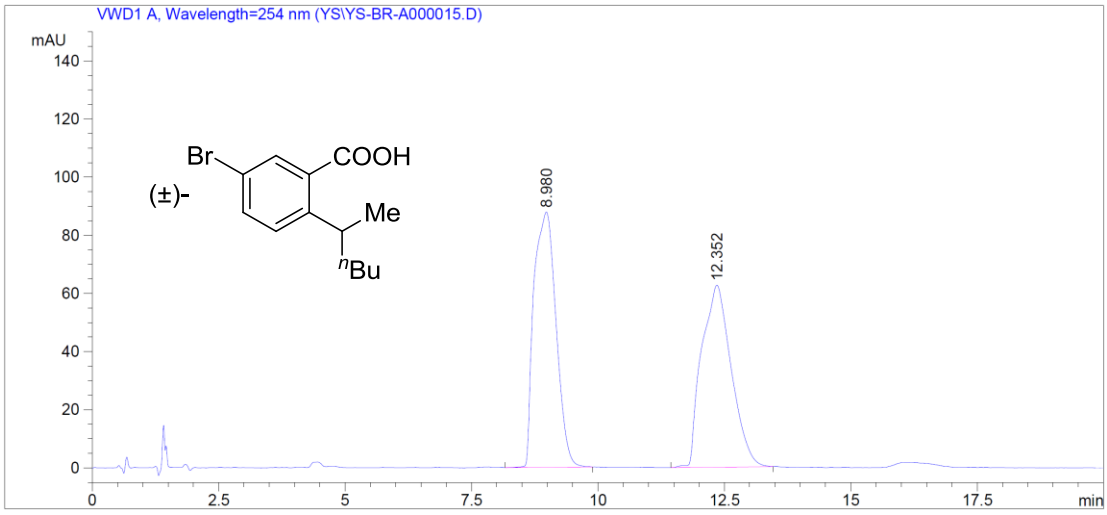


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	4.601	VV	0.1025	15.10795	0.3272	?	
2	14.407	VB	0.3604	4601.66650	99.6728	?	

Totals : 4616.77445

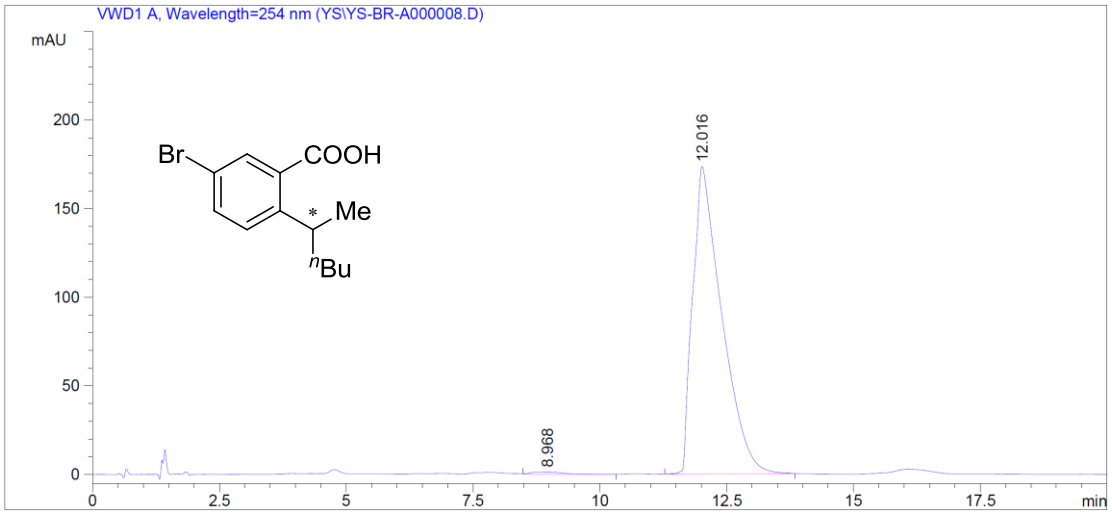
5-Bromo-2-(hexan-2-yl)benzoic acid (3i)



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %	Name
1	8.980	VB	0.4228	2677.66992	51.1677	?
2	12.352	BB	0.5564	2555.45435	48.8323	?

Totals : 5233.12427

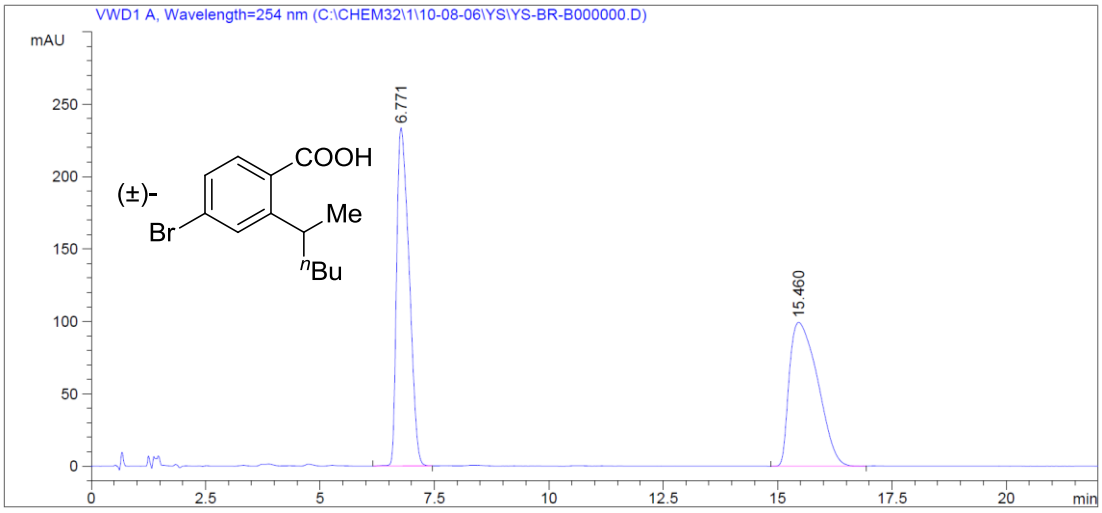


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %	Name
1	8.968	VV	0.4947	56.10809	0.8066	?
2	12.016	BB	0.5324	6899.94287	99.1934	?

Totals : 6956.05096

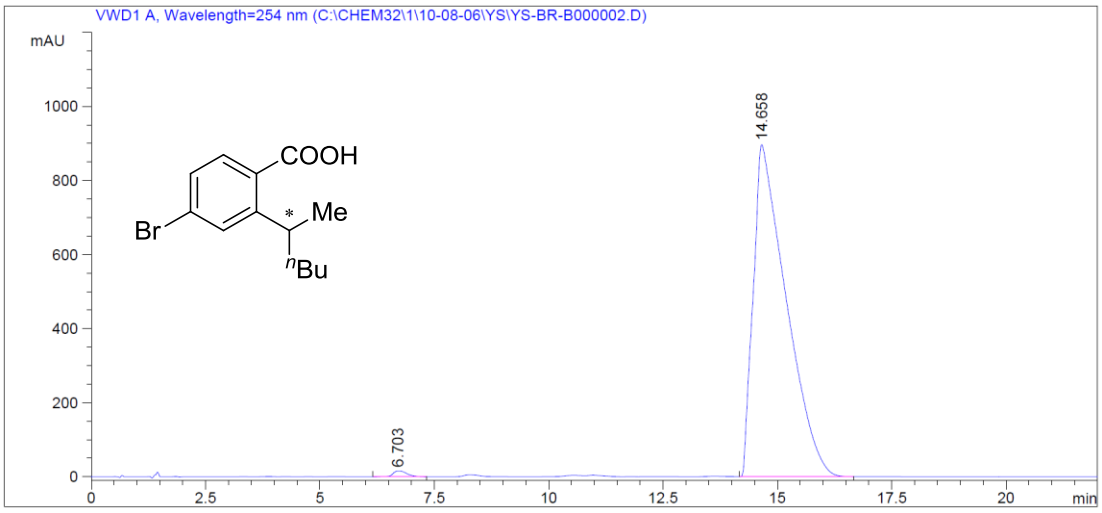
4-Bromo-2-(hexan-2-yl)benzoic acid (3j)



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %	Name
1	6.771	BB	0.3181	4413.39746	50.8186	?
2	15.460	BB	0.7231	4271.21924	49.1814	?

Totals : 8684.61670

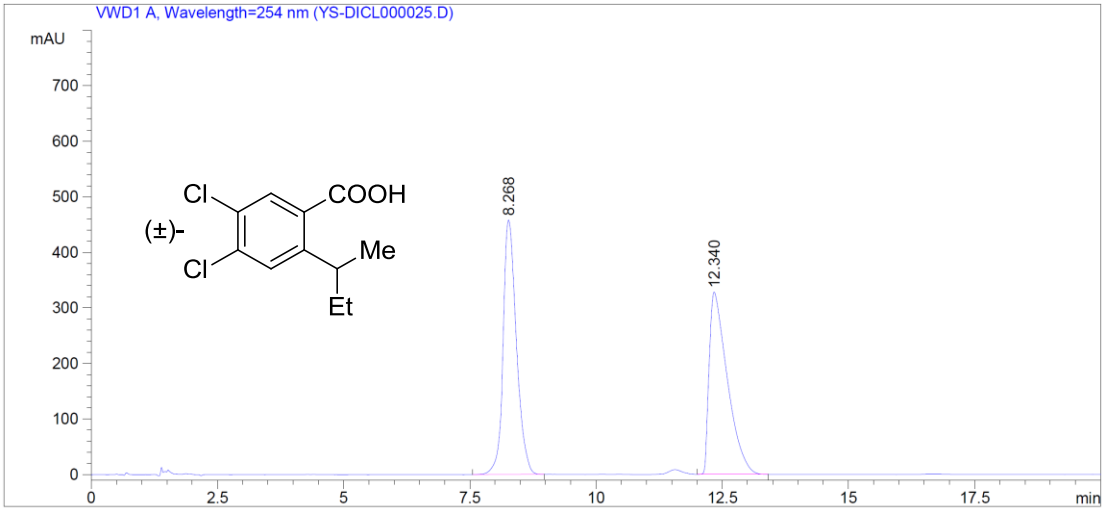


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %	Name
1	6.703	VB	0.2975	331.25906	0.7356	?
2	14.658	VB	0.6853	4.46996e4	99.2644	?

Totals : 4.50308e4

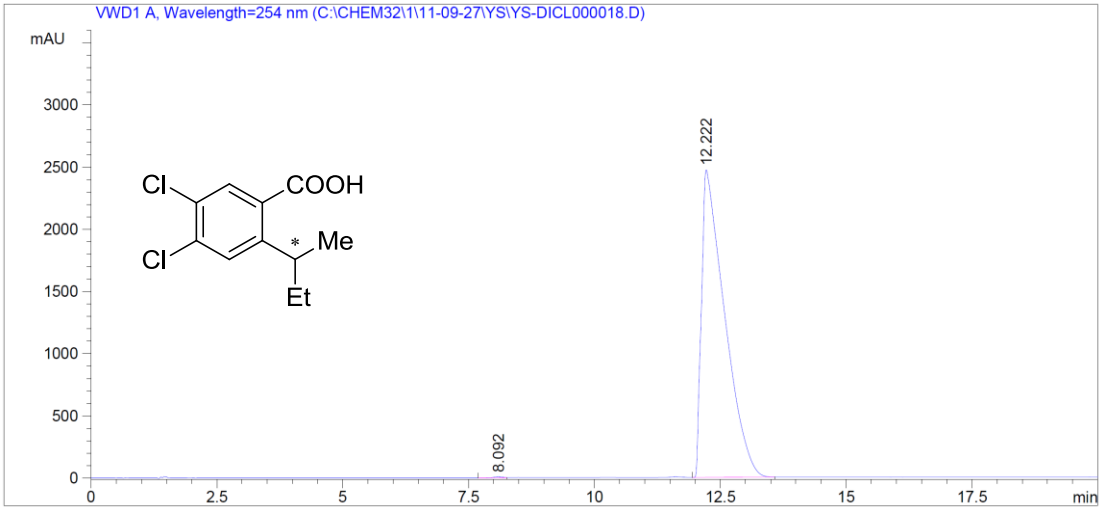
2-*sec*-Butyl-4,5-dichlorobenzoic acid (3k)



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	8.268	BB	0.2807	8389.72852	50.5023	?	
2	12.340	VB	0.3884	8222.82813	49.4977	?	

Totals : 1.66126e4

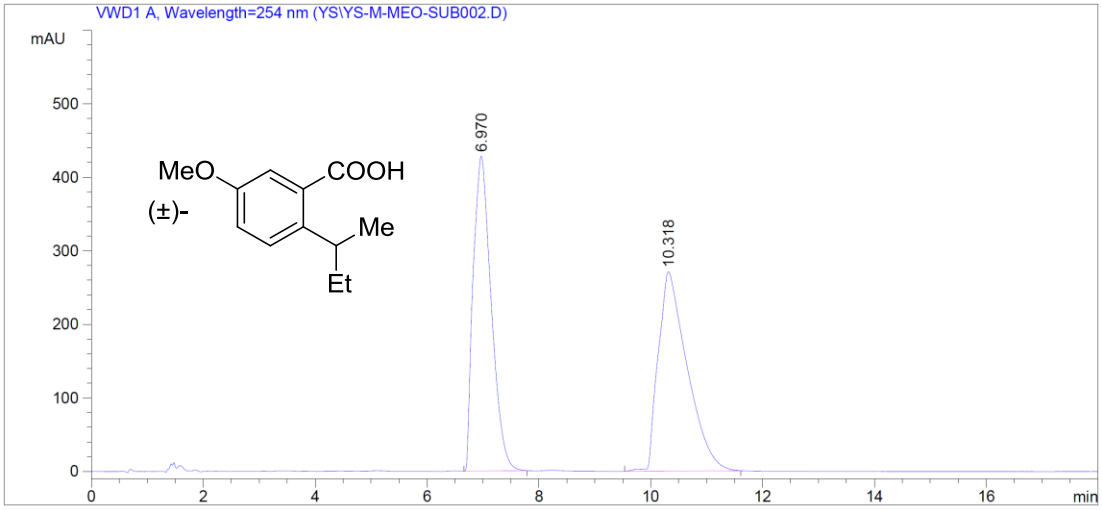


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	8.092	VV	0.1689	81.63694	0.1037	?	
2	12.222	VB	0.4294	7.86683e4	99.8963	?	

Totals : 7.87499e4

2-*sec*-Butyl-5-methoxybenzoic acid (3l)

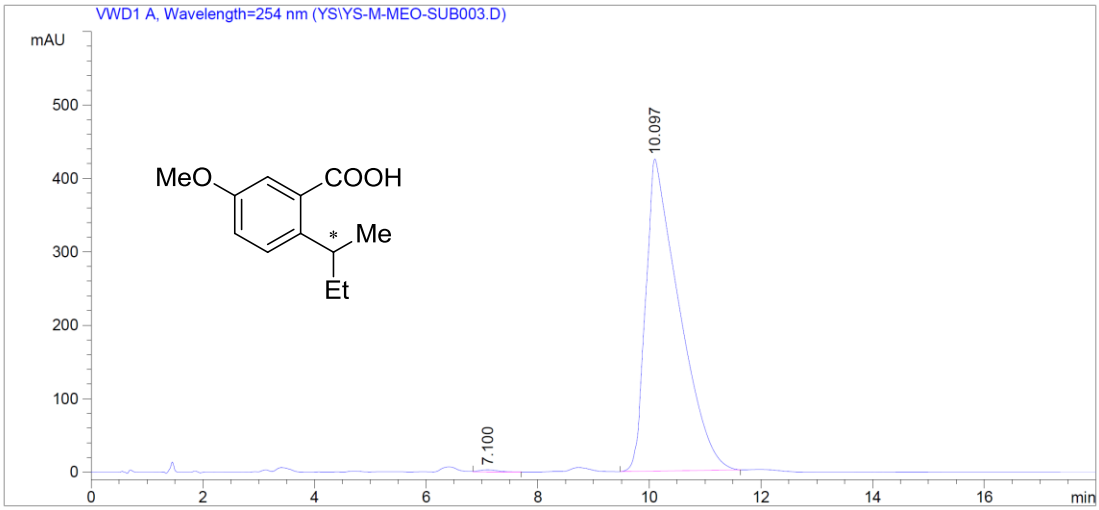


Signal 1: VWD1 A, Wavelength=254 nm

Uncalibrated Peaks:

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	6.970	BB	0.3604	9590.82422	49.5844	?	
2	10.318	BB	0.4907	9751.60742	50.4156	?	

Uncalib. totals : 1.93424e4 100.0000

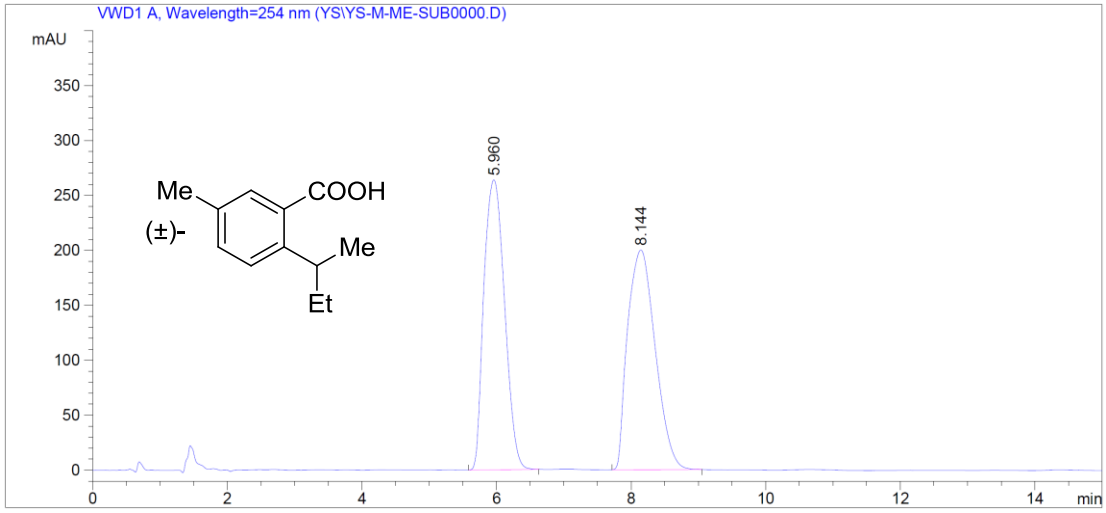


Signal 1: VWD1 A, Wavelength=254 nm

Uncalibrated Peaks:

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	7.100	VB	0.3649	65.08276	0.3667	?	
2	10.097	BB	0.5465	1.76832e4	99.6333	?	

2-*sec*-Butyl-5-methylbenzoic acid (3m)

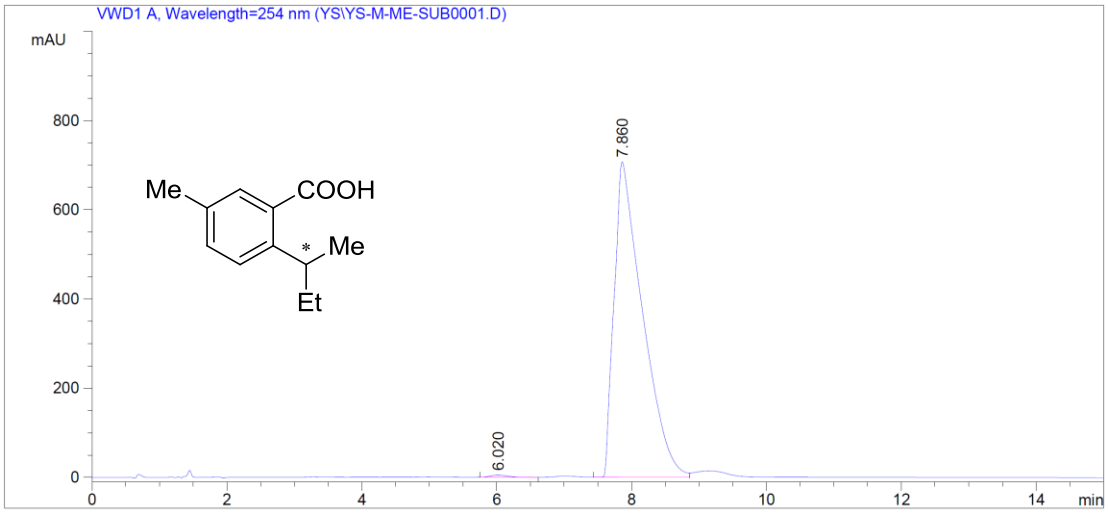


Signal 1: VWD1 A, Wavelength=254 nm

Uncalibrated Peaks:

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	5.960	BB	0.3502	5647.72266		49.7958	?
2	8.144	BB	0.4675	5694.04199		50.2042	?

Uncalib. totals : 1.13418e4 100.0000



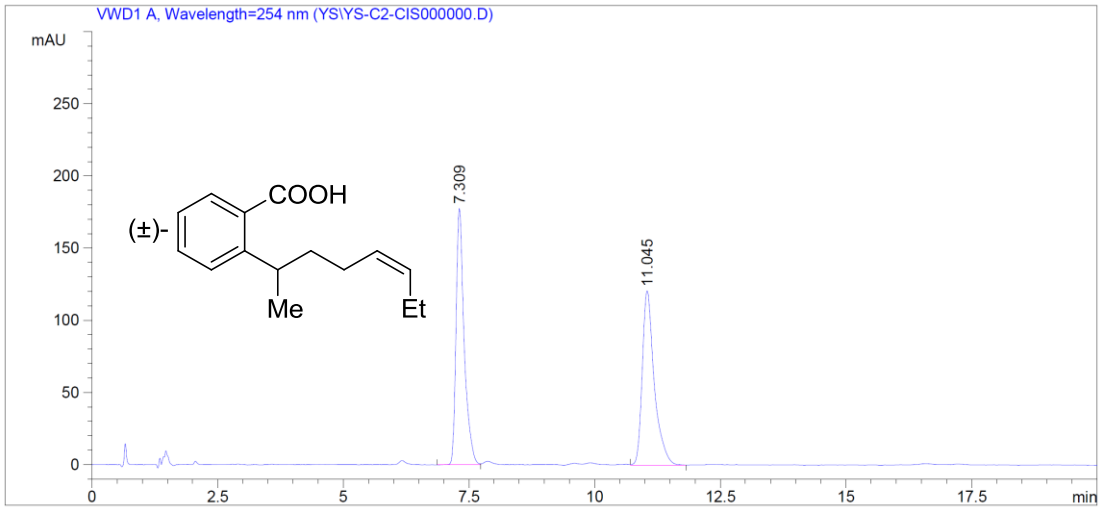
Signal 1: VWD1 A, Wavelength=254 nm

Uncalibrated Peaks:

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	6.020	BB	0.3026	89.23031		0.4300	?
2	7.860	VV	0.3876	2.06610e4		99.5700	?

Uncalib. totals : 2.07502e4 100.0000

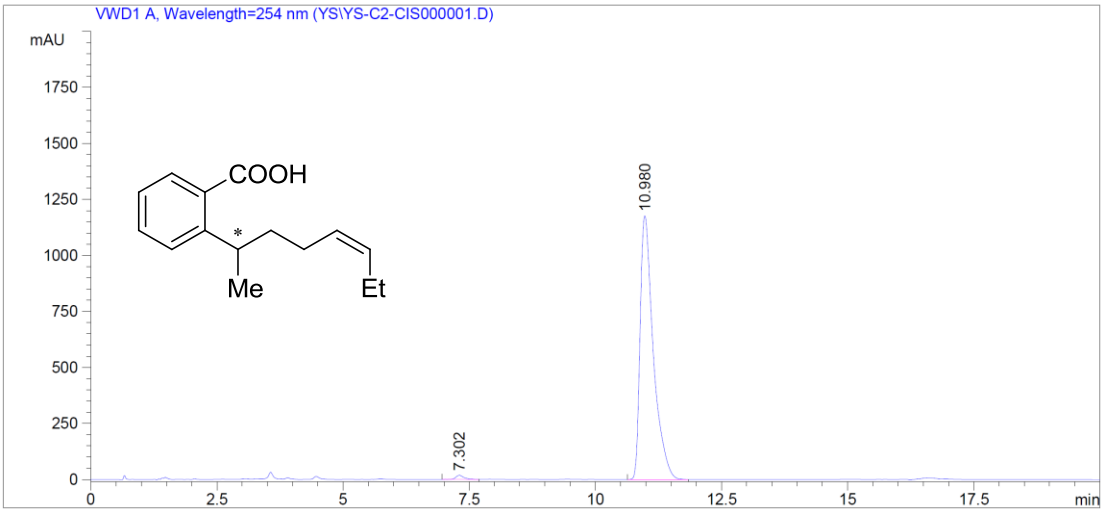
(Z)-2-(Oct-5-en-2-yl)benzoic acid (3n)



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %	Name
1	7.309	BV	0.1658	1993.92395	49.9590	?
2	11.045	VB	0.2471	1997.20044	50.0410	?

Totals : 3991.12439

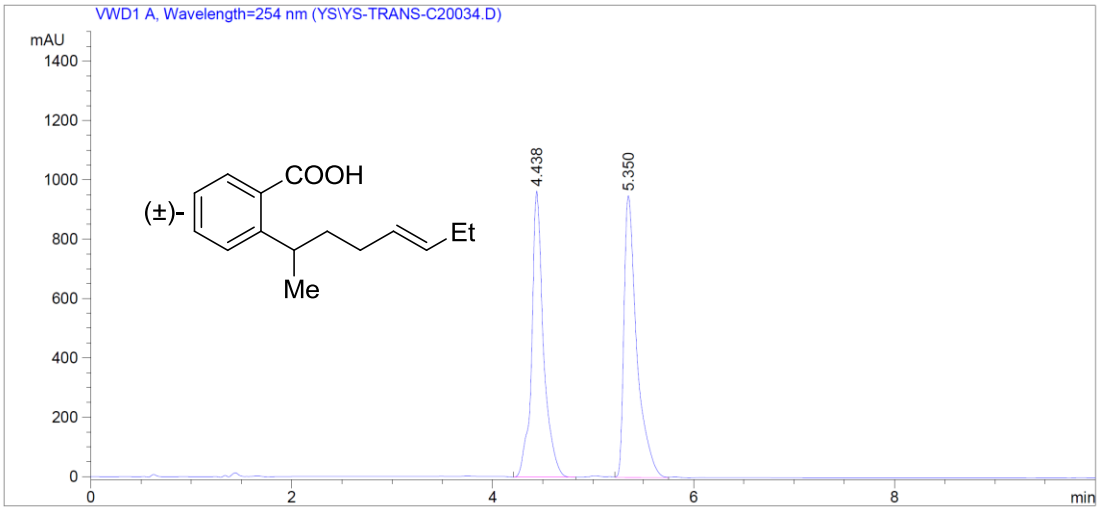


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %	Name
1	7.302	BV	0.1649	206.34799	0.9590	?
2	10.980	VV	0.2709	2.13112e4	99.0410	?

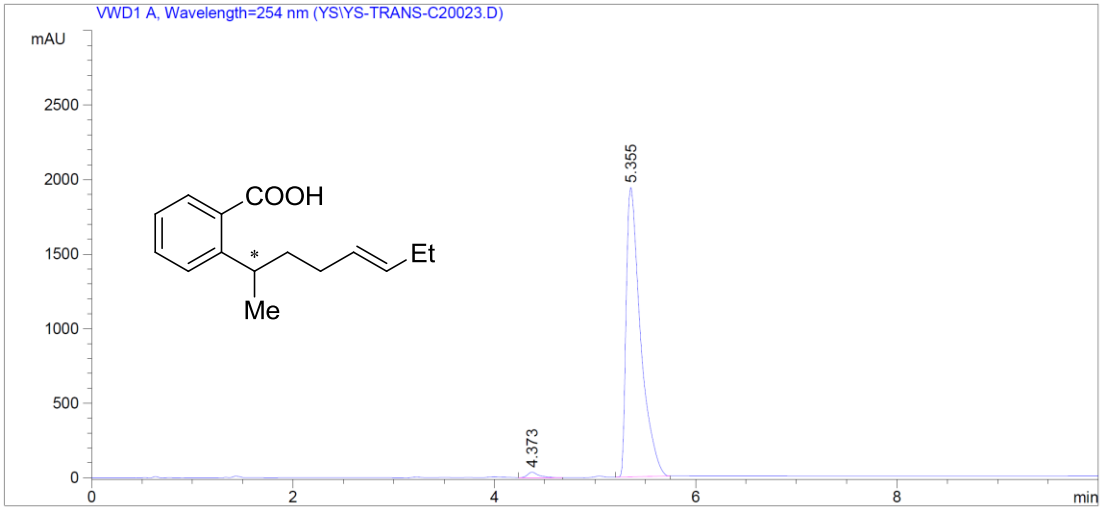
Totals : 2.15176e4

(*E*)-2-(Oct-5-en-2-yl)benzoic acid (3o)



Signal 1: VWD1 A, Wavelength=254 nm

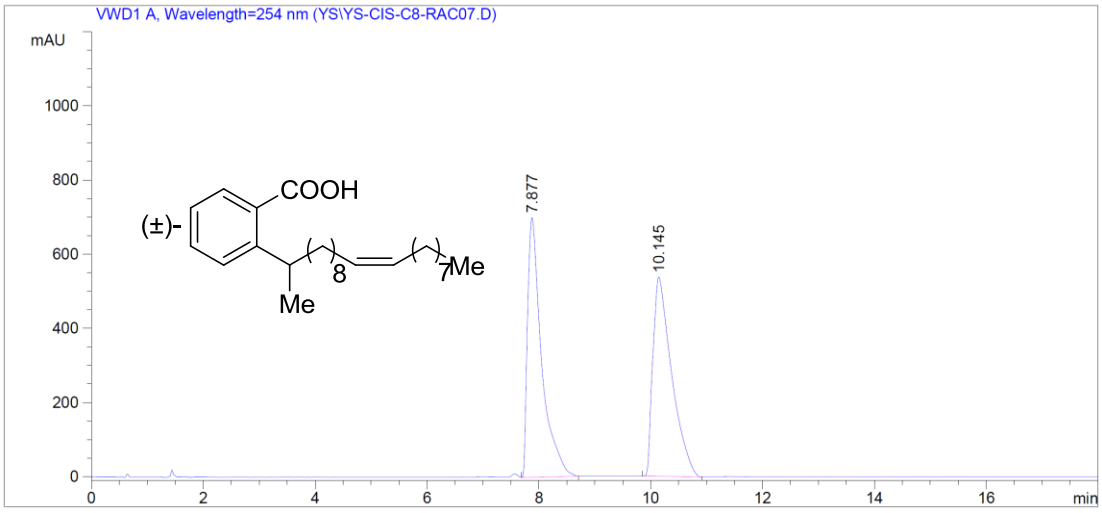
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Area %	Name
1	4.438	BB	0.1188	7902.92920	48.4847	?
2	5.350	VV	0.1322	8396.89551	51.5153	?
Totals :				1.62998e4		



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Area %	Name
1	4.373	VV	0.1143	287.70035	1.4762	?
2	5.355	VB	0.1475	1.92013e4	98.5238	?
Totals :				1.94890e4		

(*Z*)-2-(Icos-11-en-2-yl)benzoic acid (3p)

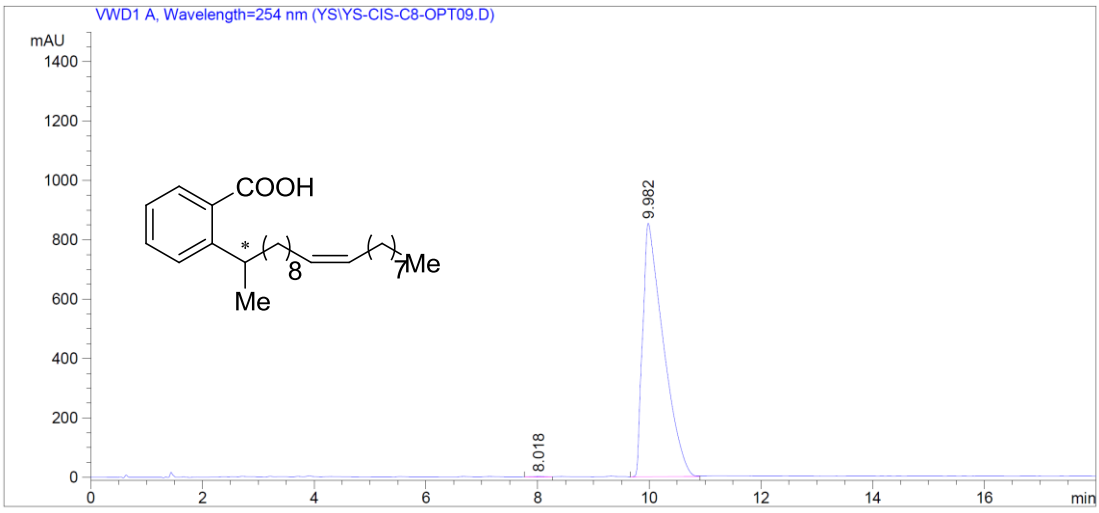


Signal 1: VWD1 A, Wavelength=254 nm

Uncalibrated Peaks:

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	7.877	VB	0.2620	1.22345e4	49.4278	?	
2	10.145	BB	0.3358	1.25178e4	50.5722	?	

Uncalib. totals : 2.47522e4 100.0000



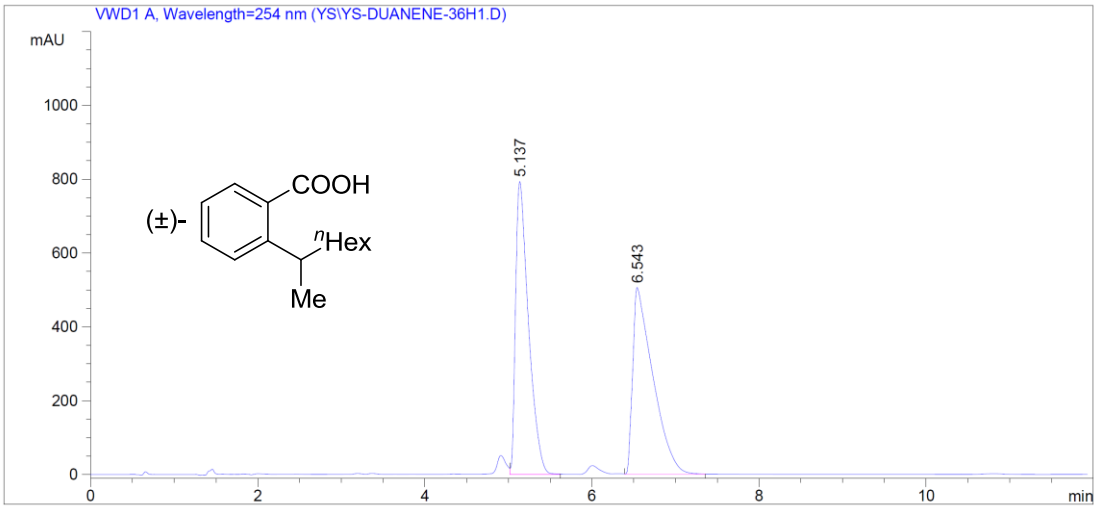
Signal 1: VWD1 A, Wavelength=254 nm

Uncalibrated Peaks:

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	8.018	BV	0.2641	35.68493	0.1626	?	
2	9.982	VB	0.3414	2.19112e4	99.8374	?	

Uncalib. totals : 2.19469e4 100.0000

2-(Octan-2-yl)benzoic acid (3q-H_2)

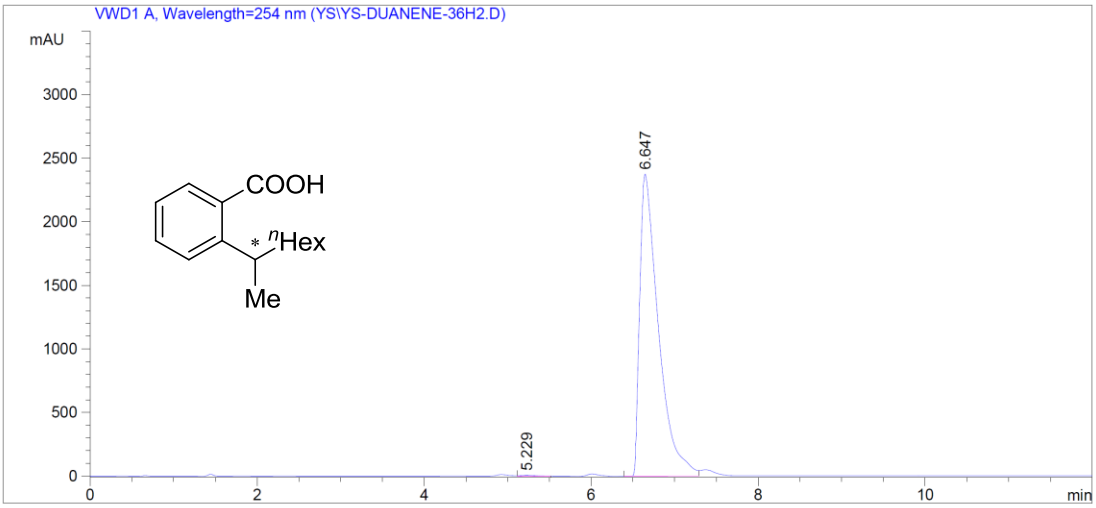


Signal 1: VWD1 A, Wavelength=254 nm

Uncalibrated Peaks:

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	5.137	VB	0.1630	8514.82324	50.0341	?	
2	6.543	BB	0.2396	8503.20605	49.9659	?	

Uncalib. totals : 1.70180e4 100.0000



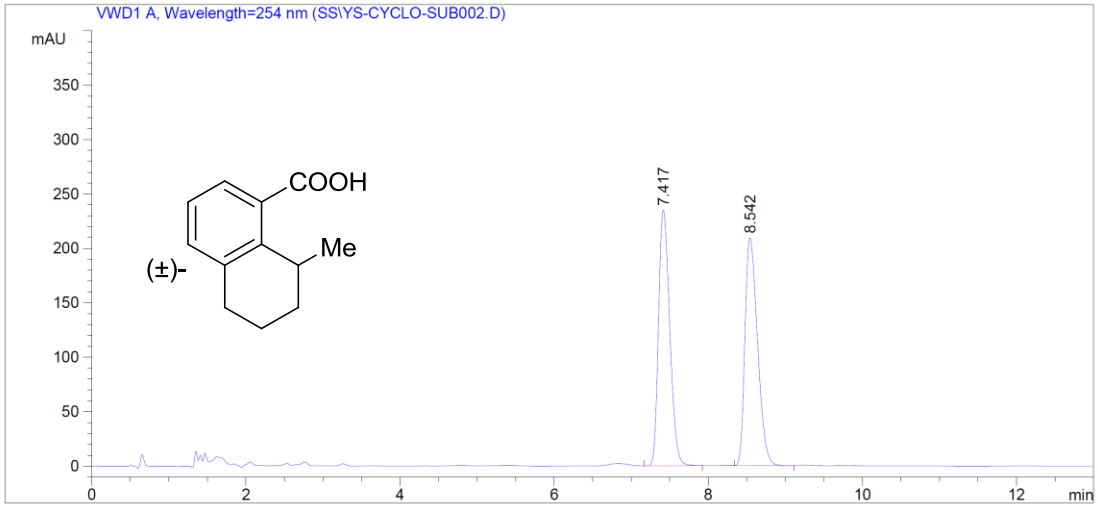
Signal 1: VWD1 A, Wavelength=254 nm

Uncalibrated Peaks:

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	5.229	VB	0.1690	78.47623	0.2126	?	
2	6.647	BV	0.2348	3.68358e4	99.7874	?	

Uncalib. totals : 3.69142e4 100.0000

8-Methyl-5,6,7,8-tetrahydronaphthalene-1-carboxylic acid (3r)

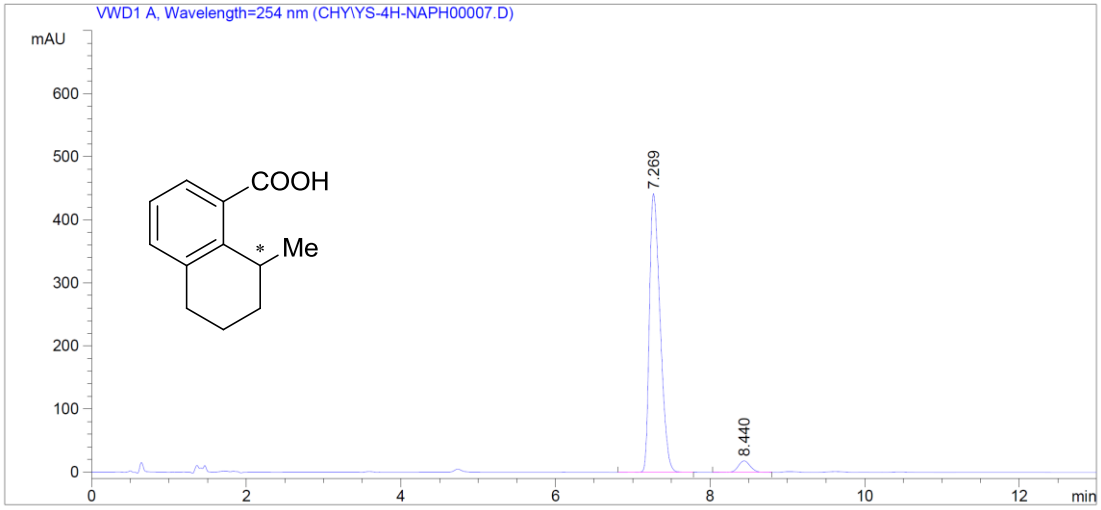


Signal 1: VWD1 A, Wavelength=254 nm

Uncalibrated Peaks:

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	7.417	VB	0.1588	2374.54614	50.0135	?	
2	8.542	BV	0.1787	2369.70630	49.9115	?	
3	14.333	VB	0.3094	3.55936	0.0750	?	

Uncalib. totals : 4747.81180 100.0000



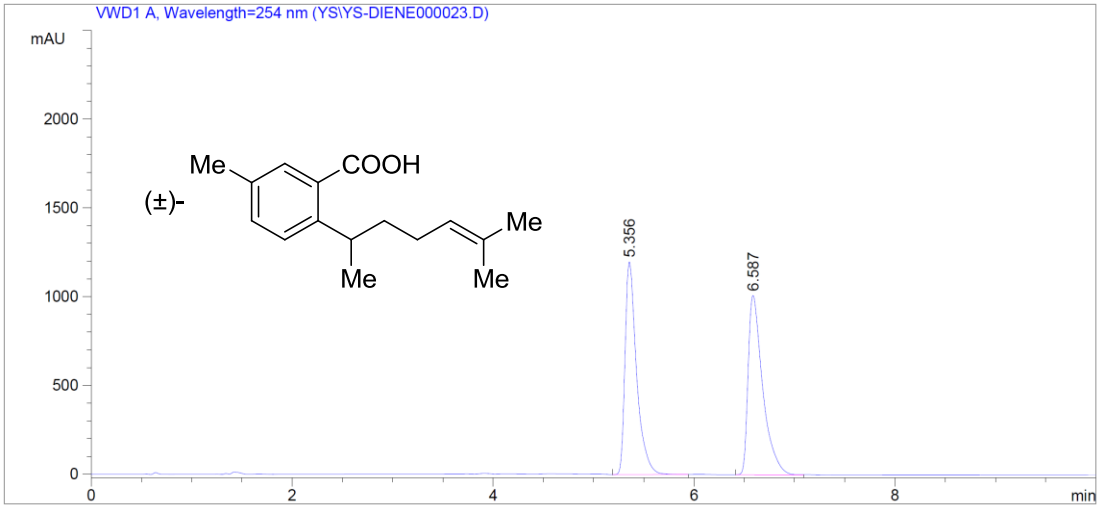
Signal 1: VWD1 A, Wavelength=254 nm

Uncalibrated Peaks:

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	7.269	VV	0.1520	4265.25244	95.6783	?	
2	8.440	VB	0.1665	192.65872	4.3217	?	

Uncalib. totals : 4457.91116 100.0000

(*S*)-5-Methyl-2-(6-methylhept-5-en-2-yl)benzoic acid (10)

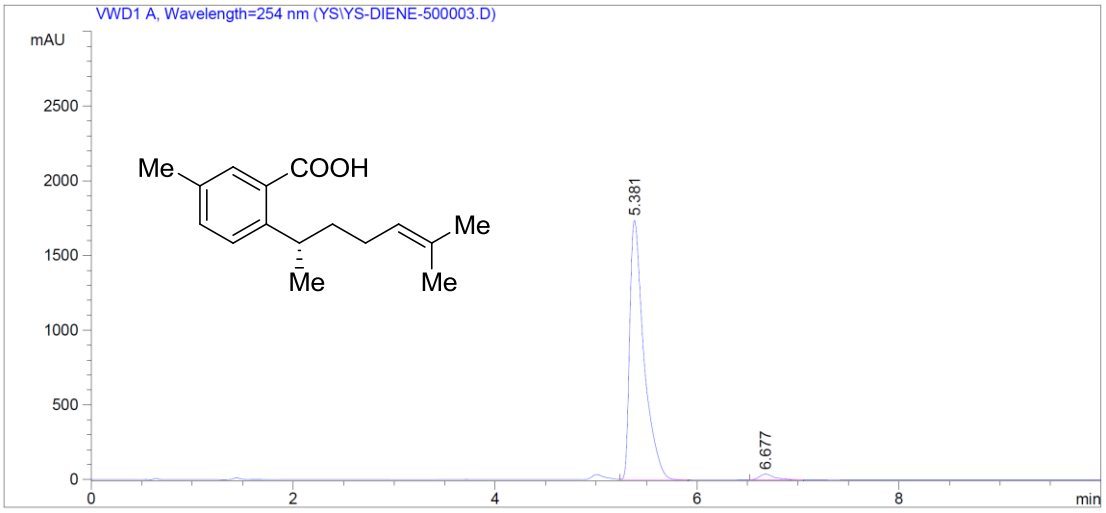


Signal 1: VWD1 A, Wavelength=254 nm

Uncalibrated Peaks:

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	5.356	VB	0.1209	9581.14941	48.5472	?	
2	6.587	BB	0.1507	1.01546e4	51.4528	?	

Uncalib. totals : 1.97358e4 100.0000

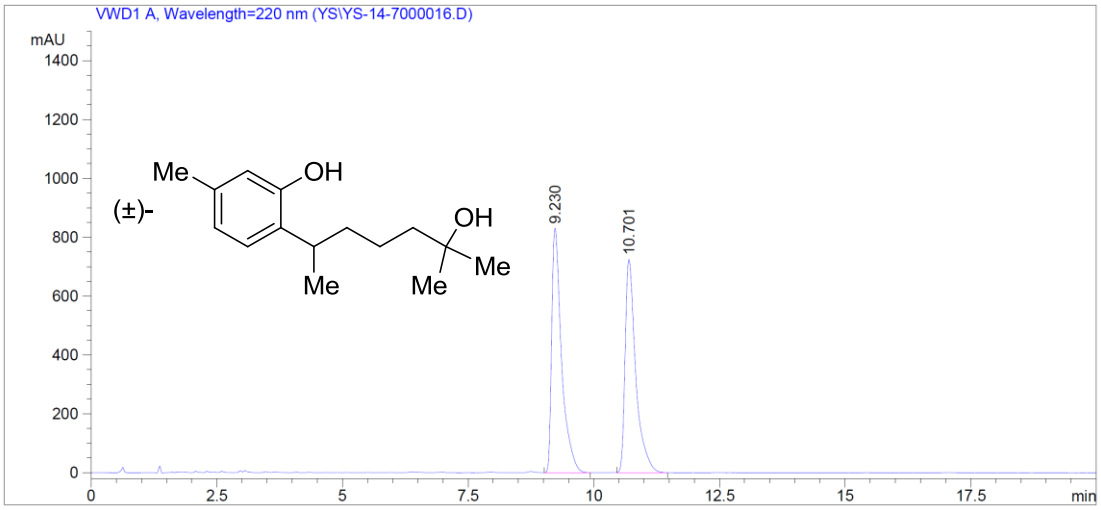


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %	Name
1	5.380	VV	0.1457	1.69125e4	97.7811	?	
2	6.676	VB	0.1496	383.79504	2.2189	?	

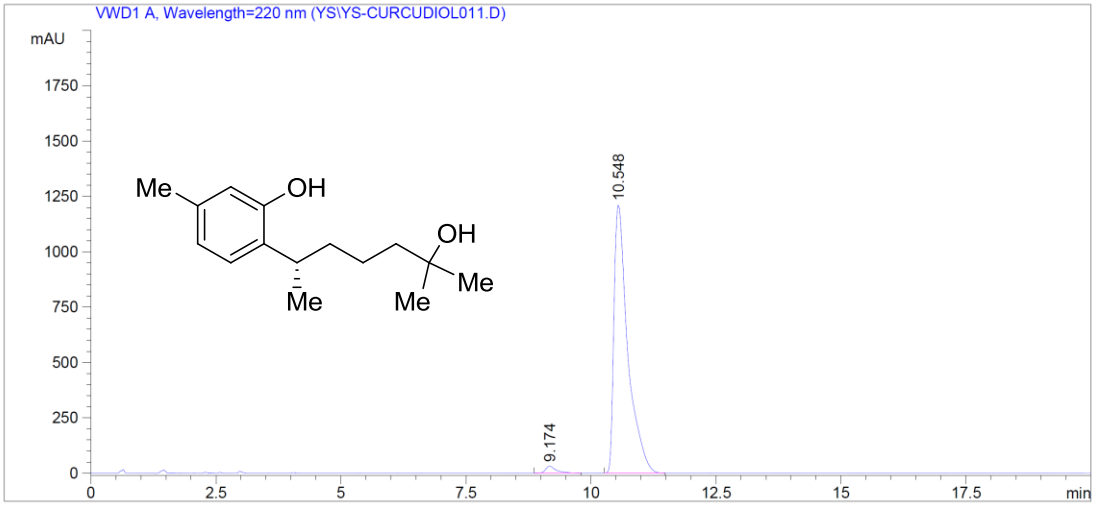
Totals : 1.72963e4

(*S*)-Curcudiol



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %	Name
1	9.230	BB	0.2038	1.12945e4	51.4722	?
2	10.701	BB	0.2196	1.06484e4	48.5278	?
Uncalib. totals :				2.19429e4	100.0000	



Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %	Name
1	9.174	VB	0.2140	460.19891	1.9449	?
2	10.548	VB	0.2848	2.32020e4	98.0551	?
Uncalib. totals :				2.36622e4	100.0000	

[1] J. D. Clark, J. M. Davis, D. Favor, L. K. Fay, L. Franklin, K. E. Henegar, D. S. Johnson, B. J. Nichelson, L. Ou, J. T. Repine, M. A. Walters, A. D. White and Z. Zhu, *US 2005/0043309 A1*.
[2] V. B. Phapale, M. Guisan-Ceinos, E. Bunuel and D. J. Cardenas, *Chem. Eur. J.*, 2009, **15**, 12681.
[3] T. Nishimura, Y. Yasuhara, T. Sawano and T. Hayashi, *J. Am. Chem. Soc.*, 2010, **132**, 7872.
[4] A. E. Wright, S. A. Pomponi, O. J. McConnell, S. Kohmoto and P. McCarthy, *J. Nat. Prod.*, 1987, **50**, 976.