Supplementary Information

A Simple Route to 1,4-Addition Reactions by Co-Catalyzed Reductive Coupling of Organic Tosylates and Triflates with Activated Alkenes

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General information:

All reagents were purchased from Sigma-Aldrich, Alfa-Aesar, TCI and Fisher-Acros, which were used without further purification unless otherwise noted. THF and Et_2O were distilled from sodium, and CH_3CN was distilled from CaH_2. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique. Flash column chromatography was performed using silica gel (230-400 mesh). Analytical thin layer chromatography (TLC) was performed on 60 F_{254} (0.25 mm) plates and visualization was accomplished with UV light (254 and 354 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on Bruck 400 or Varian 500 spectrometer with Me_4Si or solvent resonance as the internal standard (^{1}H NMR, Me_4Si at 0 ppm, $CDCl_3$ at 7.24 ppm; ^{13}C NMR, Me_4Si at 0 ppm, $CDCl_3$ at 77.0 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. IR spectral data were recorded on a Horiba Fourier Transform Infrared Spectroscopy FT-720. Melting points (mp) were determined using a SRS OptiMelt MPA100. GC-MS data were obtained from the HP 5890 Series II GC/HP 5972 GC MASS Spectrometer System. High Resolution Mass spectral data were obtained from JEOL JMS-700 by using EI method.

Synthesis of aryl triflates 1 and alkyl triflates 4:

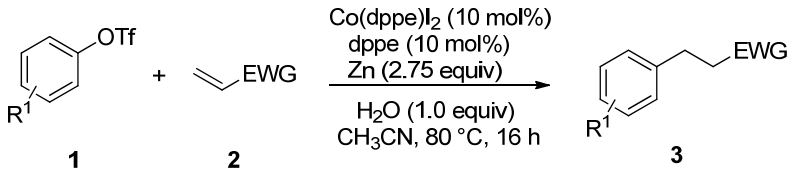
To a stirred solution of substituted phenols or alkyl alcohols (5.0 mmol) and triethylamine (7.5 mmol) in DCM (20 mL) at 0 °C was added dropwise trifluoromethanesulfonyl chloride (6.0 mmol). The mixture was slowly warmed to room temperature with continue stirring for 10 h, and then diluted with saturated sodium bicarbonate (10 mL), extracted with DCM (2 × 20 mL). The combined organic layer was washed with brine (2 × 10 mL), dried over $MgSO_4$ and then concentrated under reduced pressure.

The aryl triflates **1** was purified through a column chromatography by using hexane and ethyl acetate as eluent. The alkyl triflates **4** was purified by distillation under reduced pressure.

Synthesis of alkyl tosylates 6:

To a stirred solution of alkyl alcohols (5.0 mmol) and triethylamine (7.5 mmol) in DCM (20 mL) at 0 °C was added dropwise *p*-toluenesulfonyl chloride (6.0 mmol). The mixture was slowly warmed to room temperature with continue stirring for 10 h. The reaction mixture was then diluted with saturated sodium bicarbonate (10 mL) and extracted with DCM (2 × 20 mL), the combined organic layer was washed with brine (2 × 10 mL) and dried over $MgSO_4$ and concentrated under reduced pressure. The alkyl tosylates **6** was was purified by distillation under reduced pressure.

General procedure for Co-catalyzed 1,4-addition reaction of aryl triflates with activated alkenes:

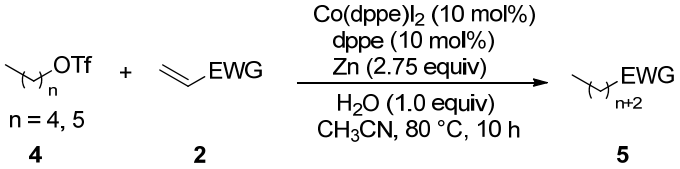


1 **2** **3**

A sealed tube containing Co(dppe)I_2 (36 mg, 0.05 mmol, 10 mol%), dppe (20 mg, 0.05 mmol, 10 mol%) and Zn (88 mg, 1.38 mmol, 2.75 equiv) was evacuated and purged with nitrogen

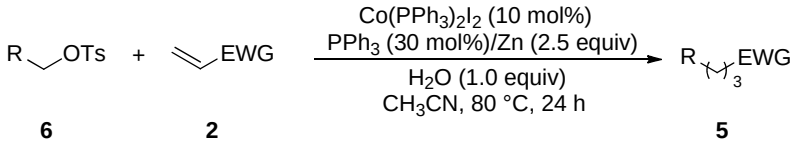
gas three times. Then, freshly distilled CH_3CN (2 mL), aromatic triflates **1** (0.5 mmol, 1.0 equiv), alkenes **2** (1.0 mmol, 2.0 equiv) and water (9.0 μL, 0.5 mmol, 1.0 equiv) were added to the sealed tube via syringe under nitrogen atmosphere. The reaction mixture was allowed to stir at 80 °C for 16 h and then cooled, diluted with dichloromethane. The mixture was filtered through a celite and silica gel pad. The filtrate was concentrated and the residue was purified through a column chromatography by using hexane and ethyl acetate as eluent to afford the desired product **3**.

General procedure for Co-catalyzed 1,4-addition reaction of alkyl triflates with activated alkenes:



A sealed tube containing $Co(dppe)I_2$ (36 mg, 0.05 mmol, 10 mol%), dppe (20 mg, 0.05 mmol, 10 mol%) and Zn (88 mg, 1.38 mmol, 2.75 equiv) was evacuated and purged with nitrogen gas three times. Then, freshly distilled CH_3CN (2 mL), aliphatic triflates **4** (0.5 mmol, 1.0 equiv), alkenes **2** (1.0 mmol, 2.0 equiv) and water (9.0 μL, 0.5 mmol, 1.0 equiv) were added to the sealed tube via syringe under nitrogen atmosphere. The reaction mixture was allowed to stir at 80 °C for 10 h and then cooled, diluted with dichloromethane. The mixture was filtered through a celite and silica gel pad. The filtrate was concentrated and the residue was purified through a column chromatography by using hexane and ethyl acetate as eluent to afford the desired product **5**.

General procedure for Co-catalyzed 1,4-addition reaction of alkyl tosylates with activated alkenes:

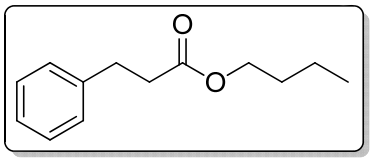


A sealed tube containing $Co(PPh_3)_2I_2$ (42 mg, 0.05 mmol, 10 mol%), PPh_3 (39 mg, 0.15 mmol, 30 mol%) and Zn (80 mg, 1.25 mmol, 2.5 equiv) was evacuated and purged with nitrogen gas three times. Then, freshly distilled CH_3CN (2 mL), aliphatic tosylates **6** (0.5 mmol, 1.0 equiv), alkenes **2** (2.0 mmol, 4.0 equiv) and water (9.0 μL, 0.5 mmol, 1.0 equiv) were added to the sealed tube via syringe under nitrogen atmosphere. The reaction mixture was allowed to stir at 80 °C for 24 h and then cooled, diluted with dichloromethane. The mixture was filtered through a celite and silica gel pad. The filtrate was concentrated and the residue was purified through a column chromatography by using hexane and ethyl acetate as eluent to afford the desired product **5**.

The spectral data and a copy of ^1H and ^{13}C NMR spectra of all products are listed below.

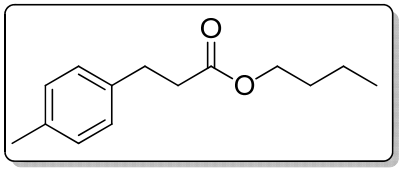
Spectral data for all products:

Butyl 3-phenylpropanoate (3a)



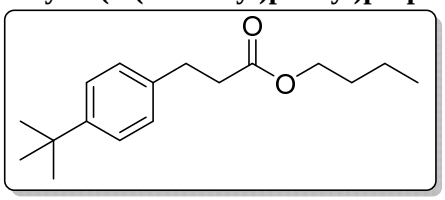
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.28 (m, 3H), 7.17–7.19 (m, 2H), 4.05 (t, 2H, *J* = 6.8 Hz), 2.93 (t, 2H, *J* = 7.6 Hz), 2.61 (t, 2H, *J* = 7.6 Hz), 1.54–1.59 (m, 2H), 1.29–1.34 (m, 2H), 0.89 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.0, 140.6, 128.5, 128.3, 126.2, 64.3, 35.9, 31.0, 30.6, 19.1, 13.7; IR (KBr): 2958, 1739, 1465, 1243, 1176 cm^{-1}; HRMS [(EI), M^+]: 206.1288 (calcd for $C_{13}H_{18}O_2$ 206.1307).

Butyl 3-(*p*-tolyl)propanoate (3b)



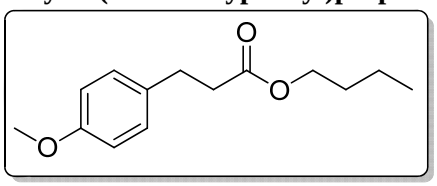
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (s, 4H), 4.05 (t, 2H, *J* = 6.8 Hz), 2.89 (t, 2H, *J* = 7.6 Hz), 2.58 (t, 2H, *J* = 7.6 Hz), 2.30 (s, 3H), 1.55–1.63 (m, 2H), 1.30–1.35 (m, 2H), 0.90 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 137.4, 135.6, 129.1, 128.1, 64.3, 36.0, 30.6, 30.5, 20.9, 19.1, 13.6; IR (KBr): 2869, 1728, 1596, 1249, 1025 cm^{-1}; HRMS [(EI), M^+]: 220.1465 (calcd for $C_{14}H_{20}O_2$ 220.1463).

Butyl 3-(4-(*tert*-butyl)phenyl)propanoate (3c)



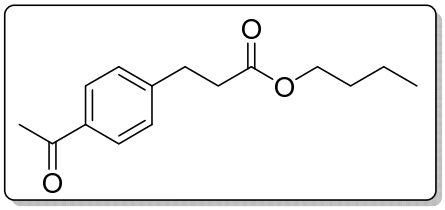
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, 2H, *J* = 8.4 Hz), 7.12 (d, 2H, *J* = 8.4 Hz), 4.05 (t, 2H, *J* = 6.8 Hz), 2.90 (t, 2H, *J* = 7.6 Hz), 2.60 (t, 2H, *J* = 7.6 Hz), 1.54–1.58 (m, 2H), 1.27–1.35 (m, 11H), 0.89 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 149.0, 137.5, 127.9, 125.3, 64.4, 35.9, 34.3, 31.3, 30.8, 30.4, 19.1, 13.7; IR (KBr): 2873, 1716, 1637, 1488, 1108 cm^{-1}; HRMS [(EI), M^+]: 262.1930 (calcd for $C_{17}H_{26}O_2$ 262.1933).

Butyl 3-(4-methoxyphenyl)propanoate (3d)



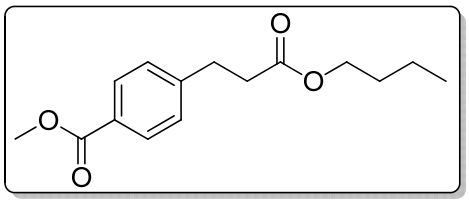
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, 2H, *J* = 6.4 Hz), 6.08 (d, 2H, *J* = 6.8 Hz), 4.04 (t, 2H, *J* = 6.8 Hz), 3.76 (s, 3H), 2.87 (t, 2H, *J* = 7.2 Hz), 2.56 (t, 2H, *J* = 7.6 Hz), 1.54–1.57 (m, 2H), 1.23–1.32 (m, 2H), 0.89 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.1, 158.0, 132.6, 129.2, 113.8, 64.3, 55.2, 36.2, 30.6, 30.1, 19.1, 13.7; IR (KBr): 2873, 1732, 1608, 1465, 1064 cm^{-1}; HRMS [(EI), M^+]: 236.1428 (calcd for $C_{14}H_{20}O_3$ 236.1412).

Butyl 3-(4-acetylphenyl)propanoate (3e)



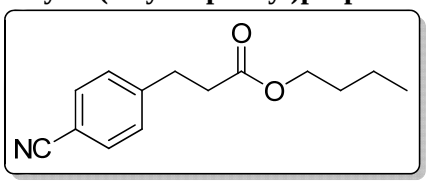
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, 2H, *J* = 8.0 Hz), 7.27 (d, 2H, *J* = 8.4 Hz), 4.03 (t, 2H, *J* = 6.8 Hz), 2.98 (t, 2H, *J* = 8.0 Hz), 2.62 (t, 2H, *J* = 8.0 Hz), 2.55 (s, 3H), 1.51–1.58 (m, 2H), 1.22–1.33 (m, 2H), 0.88 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.8, 172.6, 146.3, 135.4, 128.6, 128.5, 64.5, 35.3, 30.8, 30.6, 26.5, 19.0, 13.6; IR (KBr): 2873, 1739, 1682, 1313, 1280 cm^{-1}; HRMS [(EI), M$^+$]: 248.1425 (calcd for $C_{15}H_{20}O_3$ 248.1412).

Methyl 4-(3-butoxy-3-oxopropyl)benzoate (3f)



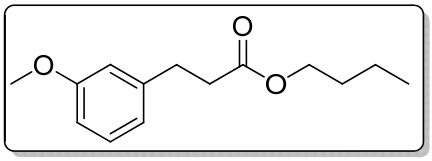
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, 2H, *J* = 6.8 Hz), 7.24 (d, 2H, *J* = 7.2 Hz), 4.03 (t, 2H, *J* = 6.8 Hz), 3.87 (s, 3H), 2.97 (t, 2H, *J* = 8.0 Hz), 2.61 (t, 2H, *J* = 8.0 Hz), 1.32–1.56 (m, 2H), 1.27–1.32 (m, 2H), 0.88 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.6, 167.0, 146.0, 129.8, 128.3, 64.5, 52.0, 35.4, 30.9, 30.6, 19.1, 13.7; IR (KBr): 2960, 1724, 1635, 1465, 1392 cm^{-1}; HRMS [(EI), M$^+$]: 264.1335 (calcd for $C_{15}H_{20}O_4$ 264.3169).

Butyl 3-(4-cyanophenyl)propanoate (3g)



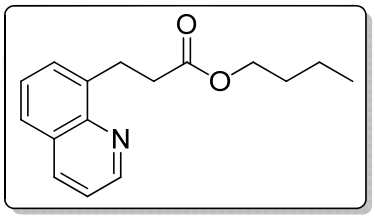
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, 2H, *J* = 8.0 Hz), 7.28 (d, 2H, *J* = 8.0 Hz), 4.02 (t, 2H, *J* = 6.8 Hz), 2.97 (t, 2H, *J* = 7.2 Hz), 2.61 (t, 2H, *J* = 7.2 Hz), 1.49–1.56 (m, 2H), 1.23–1.33 (m, 2H), 0.87 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.3, 146.1, 132.3, 129.2, 118.9, 110.2, 64.6, 35.1, 30.9, 30.6, 19.1, 13.6; IR (KBr): 2964, 1730, 1644, 1351, 1186 cm^{-1}; HRMS [(EI), M$^+$]: 231.1261 (calcd for $C_{14}H_{17}NO_2$ 231.1259).

Butyl 3-(3-methoxyphenyl)propanoate (3h)



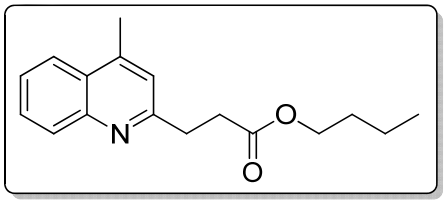
Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (t, 1H, *J* = 8.0 Hz), 6.77 (d, 2H, *J* = 7.5 Hz), 6.72 (s, 1H), 4.05 (t, 2H, *J* = 6.5 Hz), 3.77 (s, 3H), 2.90 (t, 2H, *J* = 7.5 Hz), 2.59 (t, 2H, *J* = 7.5 Hz), 1.53–1.61 (m, 2H), 1.30–1.34 (m, 2H), 0.89 (t, 3H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 159.7, 142.2, 129.4, 120.6, 114.0, 111.6, 64.4, 55.1, 35.8, 31.0, 30.6, 19.1, 13.7; IR (KBr): 1712, 1639, 1488, 1259, 1049 cm^{-1}; HRMS [(EI), M$^+$]: 236.1410 (calcd for $C_{14}H_{20}O_3$ 236.1412).

Butyl 3-(quinolin-8-yl)propanoate (3i)



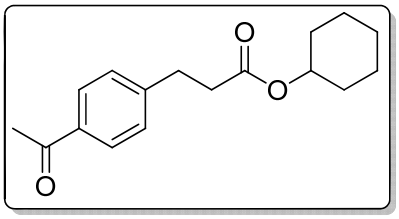
Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.91 (d, 1H, *J* = 5.5 Hz), 8.12 (d, 1H, *J* = 7.0 Hz), 7.67 (d, 1H, *J* = 8.0 Hz), 7.57 (d, 1H, *J* = 7.0 Hz), 7.44 (t, 1H, *J* = 7.0 Hz), 7.38 (t, 1H, *J* = 5.0 Hz), 4.03 (t, 2H, *J* = 7.0 Hz), 3.56 (t, 2H, *J* = 7.5 Hz), 2.84 (t, 2H, *J* = 7.5 Hz), 1.50–1.59 (m, 2H), 1.23–1.32 (m, 2H), 0.87 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.5, 149.3, 139.2, 136.4, 129.2, 128.4, 126.6, 126.3, 120.9, 64.2, 35.2, 30.6, 27.4, 19.1, 13.7; IR (KBr): 2962, 1733, 1511, 1457, 1241 cm^{-1}; HRMS [(EI), M$^+$]: 257.1425 (calcd for $C_{16}H_{19}NO_2$ 257.1416).

Butyl 3-(4-methylquinolin-2-yl)propanoate (3j)



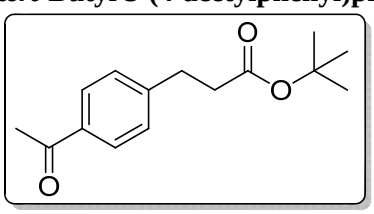
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, 1H, *J* = 8.4 Hz), 7.92 (d, 1H, *J* = 8.0 Hz), 7.64 (t, 1H, *J* = 8.0 Hz), 7.48 (t, 1H, *J* = 8.0 Hz), 7.14 (s, 1H), 4.05 (t, 2H, *J* = 6.8 Hz), 3.22 (t, 2H, *J* = 7.6 Hz), 2.88 (t, 2H, *J* = 7.6 Hz), 2.62 (s, 3H), 1.51–1.58 (m, 2H), 1.23–1.33 (m, 2H), 0.86 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.2, 160.1, 147.4, 144.6, 129.2, 129.2, 126.9, 125.7, 123.6, 122.2, 64.3, 33.4, 33.3, 30.6, 19.1, 18.7, 13.7; IR (KBr): 2931, 1737, 1465, 1392, 1278 cm^{-1}; HRMS [(EI), M$^+$]: 271.1560 (calcd for $C_{17}H_{21}NO_2$ 271.1572).

Cyclohexyl 3-(4-acetylphenyl)propanoate (3k)



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, 2H, *J* = 8.0 Hz), 7.27 (d, 2H, *J* = 8.4 Hz), 4.74–4.71 (m, 1H), 2.98 (t, 2H, *J* = 7.6 Hz), 2.61 (t, 2H, *J* = 7.6 Hz), 2.55 (s, 3H), 1.65–1.78 (m, 4H), 1.23–1.52 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.8, 171.9, 146.3, 135.3, 128.6, 128.5, 72.9, 35.6, 31.6, 30.9, 26.6, 25.3, 23.7; IR (KBr): 2933, 1730, 1677, 1455, 1292 cm^{-1}; HRMS [(EI), M$^+$]: 274.1570 (calcd for $C_{17}H_{22}O_3$ 274.1569).

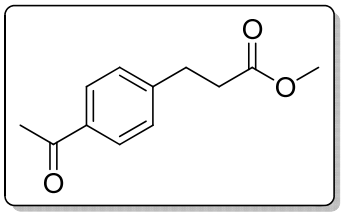
***tert*-Butyl 3-(4-acetylphenyl)propanoate (3l)**



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, 2H, *J* = 8.0 Hz), 7.27 (d, 2H, *J* = 8.0 Hz),

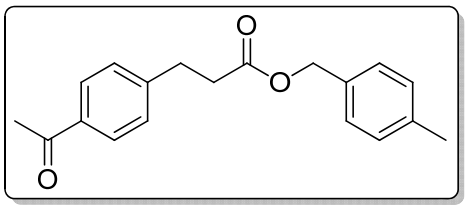
2.95 (t, 2H, J = 7.6 Hz), 2.56 (s, 3H), 2.55 (t, 2H, J = 6.8 Hz), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 171.8, 146.5, 135.4, 128.5, 80.6, 36.4, 31.0, 28.1, 26.5; IR (KBr): 2873, 1727, 1587, 1417, 1164 cm^{-1}; HRMS [(EI), M^+]: 248.1430 (calcd for $C_{15}H_{20}O_3$ 248.1412).

Methyl 3-(4-acetylphenyl)propanoate (3m)



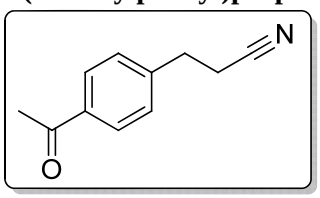
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, 2H, J = 8.0 Hz), 7.26 (d, 2H, J = 8.0 Hz), 3.64 (s, 3H), 2.98 (t, 2H, J = 7.6 Hz), 2.63 (t, 2H, J = 7.6 Hz), 2.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.8, 172.9, 146.1, 135.4, 128.6, 128.5, 51.7, 35.0, 30.8, 26.5; IR (KBr): 2873, 1733, 1679, 1417, 1311 cm^{-1}; HRMS [(EI), M^+]: 206.0940 (calcd for $C_{12}H_{14}O_3$ 206.0943).

4-Methylbenzyl 3-(4-acetylphenyl)propanoate (3n)



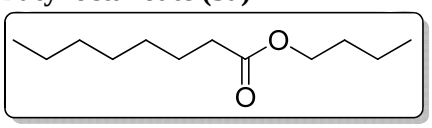
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, 2H, J = 6.8 Hz), 7.25 (d, 2H, J = 7.2 Hz), 7.12–7.19 (m, 4H), 5.04 (s, 2H), 3.00 (t, 2H, J = 7.6 Hz), 2.67 (t, 2H, J = 7.2 Hz), 2.56 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.8, 172.3, 146.1, 138.2, 135.4, 132.7, 129.2, 128.6, 128.5, 128.5, 66.4, 35.3, 30.8, 26.6, 21.2; IR (KBr): 2960, 1734, 1681, 1290, 1170 cm^{-1}; HRMS [(EI), M^+]: 296.1427 (calcd for $C_{19}H_{20}O_3$ 296.1412).

3-(4-Acetylphenyl)propanenitrile (3o)



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, 2H, J = 8.0 Hz), 7.32 (d, 2H, J = 8.0 Hz), 3.00 (t, 2H, J = 7.2 Hz), 2.64 (t, 2H, J = 7.2 Hz), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.7, 143.3, 136.3, 129.0, 128.6, 118.6, 31.4, 26.5, 18.9; IR (KBr): 2873, 1731, 1294, 1241, 1180 cm^{-1}; HRMS [(EI), M^+]: 173.0839 (calcd for $C_{11}H_{11}NO$ 173.0841).

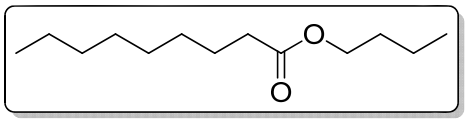
Butyl octanoate (5a)



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.04 (t, 2H, J = 6.8 Hz), 2.27 (t, 2H, J = 7.6 Hz), 1.55-1.59 (m, 4H), 1.23-1.35 (m, 10H), 0.91 (t, 3H, J = 7.6 Hz), 0.85 (t, 3H, J = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.0, 64.1, 34.4, 31.8, 30.6, 29.2, 29.1, 25.0, 18.9, 14.1, 13.7; IR

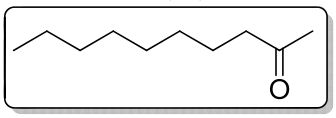
(KBr): 1736, 1519, 1347, 1255, 1166 cm^{-1}; HRMS [(EI), M^+]: 200.1772 (calcd for $C_{12}H_{24}O_2$ 200.1776).

Butyl nonanoate (5b)



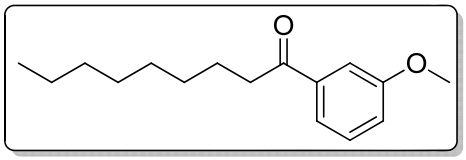
Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 4.04 (t, 2H, *J* = 6.8 Hz), 2.26 (t, 2H, *J* = 7.6 Hz), 1.56–1.61 (m, 4H), 1.32–1.38 (m, 2H), 1.24–1.31 (m, 10H), 0.91 (t, 3H, *J* = 7.2 Hz), 0.85 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 64.1, 34.4, 31.8, 30.7, 29.2, 29.1, 29.1, 25.0, 22.6, 19.2, 14.1, 13.7; IR (KBr): 1735, 1488, 1446, 1373, 1182 cm^{-1}; HRMS [(EI), M^+]: 214.1934 (calcd for $C_{13}H_{26}O_2$ 214.1933).

Decan-2-one (5c)



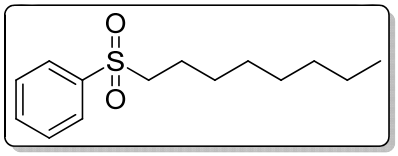
Colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 2.39 (t, 2H, *J* = 7.0 Hz), 2.11 (s, 3H), 1.55 (m, 4H), 1.25 (m, 8H), 0.86 (t, 3H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 209.5, 43.8, 31.8, 29.86, 29.4, 29.2, 29.1, 23.9, 22.6, 14.1; IR (KBr): 1731, 1421, 1240, 1213, 1170 cm^{-1}; HRMS [(EI), M^+]: 156.1513 (calcd for $C_{10}H_{20}O$ 156.1514).

1-(3-Methoxyphenyl)nonan-1-one (5d)



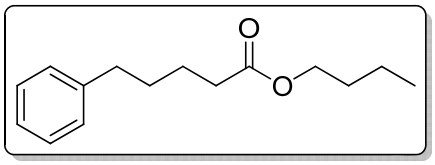
Yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, 1H, *J* = 6.0 Hz), 6.76 (d, 1H, *J* = 8.0 Hz), 6.62–6.67 (m, 2H), 3.97 (s, 3H), 2.54 (t, 2H, *J* = 7.6 Hz), 1.71–1.76 (m, 2H), 1.25–1.40 (m, 10H), 0.89 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.3, 160.4, 151.7, 129.8, 113.8, 111.6, 107.6, 55.4, 34.4, 31.8, 29.7, 29.2, 29.1, 24.9, 22.6, 14.1; IR (KBr): 2937, 1761, 1608, 1290, 1213 cm^{-1}; HRMS [(EI), M^+]: 248.1770 (calcd for $C_{16}H_{24}O_2S$ 248.1776).

(Octylsulfonyl)benzene (5e)



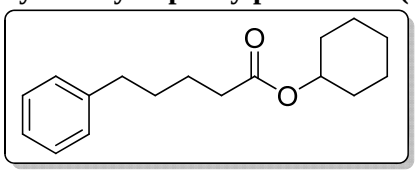
Yellow oil; ^1H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, 2H, *J* = 6.4 Hz), 7.63 (t, 1H, *J* = 6.0 Hz), 7.55 (t, 2H, *J* = 6.0 Hz), 3.05 (t, 2H, *J* = 6.4 Hz), 1.63–1.69 (m, 2H), 1.28–1.33 (m, 2H), 1.19 (m, 8H), 0.83 (t, 3H, *J* = 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ139.3, 133.6, 129.2, 128.0, 56.3, 31.6, 28.9, 28.8, 28.2, 22.6, 22.5, 14.0; IR (KBr): 2927, 1739, 1436, 1363, 1294 cm^{-1}; HRMS [(EI), M^+]: 254.1342 (calcd for $C_{14}H_{22}O_2S$ 254.1341).

Butyl 5-phenylpentanoate (5f)



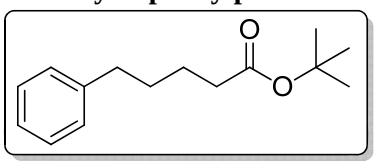
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.27 (m, 2H), 7.14–7.17 (m, 3H), 4.04 (t, 2H, *J* = 6.4 Hz), 2.60 (t, 2H, *J* = 6.8 Hz), 2.30 (t, 2H, *J* = 6.8 Hz), 1.61–1.67 (m, 4H), 1.54–1.58 (m, 2H), 1.32–1.39 (m, 2H), 0.91 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.8, 142.2, 128.4, 128.3, 125.7, 64.2, 35.6, 34.2, 30.9, 30.7, 24.6, 19.1, 13.7; IR (KBr): 1731, 1465, 1390, 1294, 1180 cm^{-1}; HRMS [(EI), M^+]: 234.1622 (calcd for $C_{15}H_{22}O_2$ 234.1620).

Cyclohexyl 5-phenylpentanoate (5g)



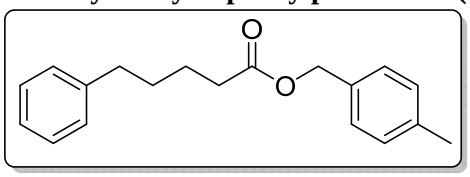
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.27 (m, 3H), 7.13–7.17 (m, 2H), 4.73 (m, 1H), 2.60 (t, 2H, *J* = 7.2 Hz), 2.28 (t, 2H, *J* = 7.2 Hz), 1.69–1.79 (m, 2H), 1.62–1.68 (m, 6H), 1.29–1.42 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.1, 142.2, 128.4, 128.3, 125.7, 72.4, 35.6, 34.6, 31.6, 30.9, 29.7, 25.4, 24.7, 23.7; IR (KBr): 2873, 1729, 1465, 1390, 1294 cm^{-1}; HRMS [(EI), M^+]: 260.1754 (calcd for $C_{17}H_{24}O_2$ 260.1776).

***tert*-Butyl 5-phenylpentanoate (5h)**



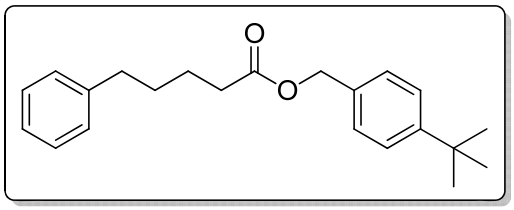
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.27 (m, 2H), 7.14–7.17 (m, 3H), 2.60 (t, 2H, *J* = 7.2 Hz), 2.21 (t, 2H, *J* = 7.2 Hz), 1.60–1.63 (m, 4H), 1.41 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.1, 142.3, 128.4, 128.3, 125.7, 80.0, 35.6, 35.4, 30.9, 28.1, 24.7; IR (KBr): 2873, 1700, 1455, 1311, 1199 cm^{-1}; HRMS [(EI), M^+]: 234.1605 (calcd for $C_{15}H_{22}O_2$ 234.1620).

4-Methylbenzyl 5-phenylpentanoate (5i)



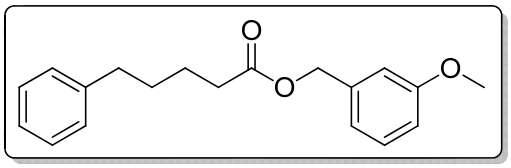
Yellow oil; ^{1}H NMR **(**400 MHz, $CDCl_3$): δ 7.20–7.26 (m, 5H), 7.11–7.16 (m, 4H), 5.04 (s, 2H), 2.58 (t, 2H, *J* = 6.4 Hz), 2.34 (t, 5H, *J* = 6.4 Hz), 1.61–1.66 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.5, 142.1, 138.0, 133.0, 129.2, 128.4, 128.3, 125.7, 66.1, 35.5, 34.2, 30.9, 24.6, 21.2; IR (KBr): 2856, 1744, 1509, 1292, 1157 cm^{-1}; HRMS [(EI), M^+]: 282.1611 (calcd for $C_{19}H_{22}O_2$ 282.1620).

4-(*tert*-Butyl)benzyl 5-phenylpentanoate (5j)



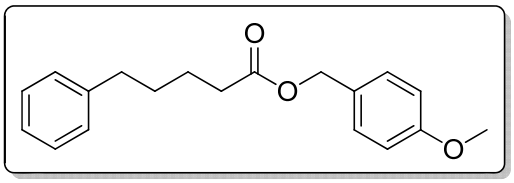
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.38 (m, 2H), 7.23–7.27 (m, 4H), 7.13–7.16 (m, 3H), 5.06 (s, 2H), 2.06 (t, 2H, *J* = 7.2 Hz), 2.36 (t, 2H, *J* = 7.2 Hz), 1.63–1.68 (m, 4H), 1.30 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.5, 151.2, 142.1, 133.0, 128.4, 128.3, 128.1, 125.7, 125.5, 66.0, 42.6, 35.5, 34.6, 34.1, 31.3, 30.9; IR (KBr): 2856, 1730, 1292, 1222, 1157 cm^{-1}; HRMS [(EI), M^{+}]: 324.2092 (calcd for $C_{22}H_{28}O_2$ 324.2089).

3-Methoxybenzyl 5-phenylpentanoate (5k)



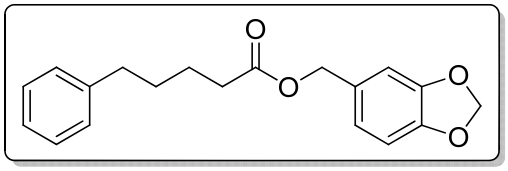
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.27 (m, 3H), 7.12–7.17 (m, 2H), 6.83–6.91 (m, 4H), 5.06 (s, 2H), 3.78 (s, 3H), 2.60 (t, 2H, *J* = 7.2 Hz), 2.73 (t, 2H, *J* = 7.2 Hz), 1.62–1.70 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.4, 159.7, 142.1, 137.5, 129.6, 128.4, 128.3, 125.7, 120.3, 113.7, 113.6, 66.0, 55.2, 35.5, 34.1, 30.9, 24.6; IR (KBr): 2960, 1739, 1455, 1292, 1178 cm^{-1}; HRMS [(EI), M^{+}]: 298.1563 (calcd for $C_{19}H_{22}O_3$ 298.1569).

4-Methoxybenzyl 5-phenylpentanoate (5l)



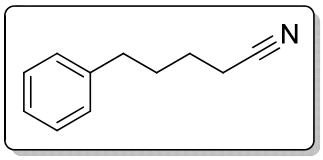
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.27 (m, 4H), 7.11–7.17 (m, 3H), 6.85–6.87 (d, 2H, *J* = 8.8 Hz), 5.02 (s, 2H), 3.78 (s, 3H), 2.59 (t, 2H, *J* = 6.8 Hz), 2.33 (t, 2H, J = 6.8 Hz), 1.61–1.66 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.5, 159.6, 142.1, 130.1, 128.4, 128.3, 128.2, 125.7, 113.9, 65.9, 55.3, 35.5, 34.2, 30.8, 24.6; IR (KBr): 2933, 1730, 1488, 1359, 1253 cm^{-1}; HRMS [(EI), M^{+}]: 298.1560 (calcd for $C_{19}H_{22}O_3$ 298.1569).

Benzo[*d*][1,3]dioxol-5-ylmethyl 5-phenylpentanoate (5m)



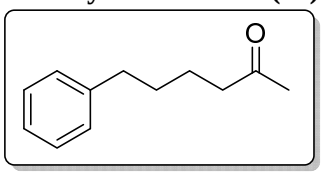
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.26 (m, 2H), 7.12–7.17 (m, 3H), 6.76–6.81 (m, 3H), 5.93 (s, 2H), 4.98 (s, 2H), 2.59 (t, 2H, *J* = 6.8 Hz), 2.34 (t, 2H, *J* = 6.8 Hz), 1.61–1.66 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.4, 147.8, 147.6, 142.1, 129.8, 128.4, 128.3, 125.7, 122.2, 109.0, 108.2, 101.1, 66.1, 35.5, 34.1, 30.8, 24.6; IR (KBr): 2869, 1740, 1511, 1357, 1241 cm^{-1}; HRMS [(EI), M^{+}]: 312.1346 (calcd for $C_{19}H_{20}O_4$ 312.1362).

5-Phenylpentanenitrile (5n)



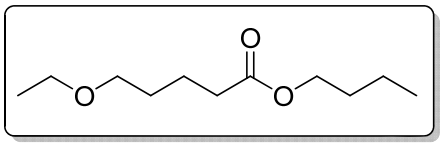
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.29 (m, 2H), 7.14–7.20 (m, 3H), 2.64 (t, 2H, *J* = 7.6 Hz), 2.32 (t, 2H, *J* = 7.4 Hz), 1.73–1.79 (m, 2H), 1.64–1.70 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.2, 128.4, 128.3, 126.0, 119.6, 34.9, 30.2, 24.8, 17.0; IR (KBr): 2960, 1606, 1587, 1417, 1164 cm^{-1}; HRMS [(EI), M^+]: 159.1053 (calcd for $C_{11}H_{13}N$ 159.1048).

6-Phenylhexan-2-one (5o)



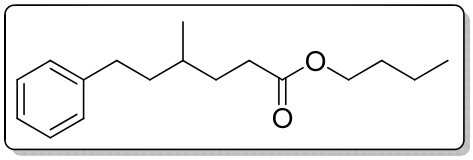
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.27 (m, 2H), 7.13–7.17 (m, 3H), 2.59 (t, 2H, *J* = 6.8 Hz), 2.42 (t, 2H, *J* = 6.8 Hz), 2.09 (s, 3H), 1.56–1.61 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 209.0, 142.2, 128.4, 128.3, 125.7, 43.6, 35.7, 30.9, 29.9, 23.4; IR (KBr): 2958, 1715, 1602, 1490, 1153 cm^{-1}; HRMS [(EI), M^+]: 176.1201 (calcd for $C_{12}H_{16}O$ 176.1201).

Butyl 5-ethoxypentanoate (5p)



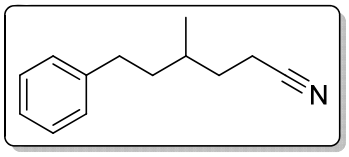
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.04 (t, 2H, *J* = 6.8 Hz), 3.38–3.46 (m, 4H), 2.30 (t, 2H, *J* = 7.2 Hz), 1.58–1.67 (m, 6H), 1.32–1.38 (m, 2H), 1.17 (t, 3H, *J* = 7.2 Hz), 0.90 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.8, 70.1, 66.1, 64.2, 34.1, 30.7, 29.2, 21.8, 19.1, 15.2, 13.7; IR (KBr): 2962, 1735, 1457, 1288, 1172 cm^{-1}; HRMS [(EI), M^+]: 202.1567 (calcd for $C_{11}H_{22}O_3$ 202.1569).

Butyl 4-methyl-6-phenylhexanoate (5q)



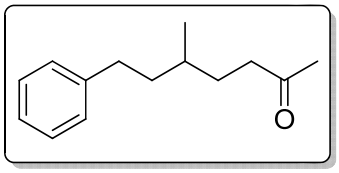
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.29 (m, 2H), 7.15–7.18 (m, 3H), 4.04 (t, 2H, *J* = 7.6 Hz), 2.56–2.72 (m, 2H), 2.24–2.40 (m, 2H), 1.25–1.70 (m, 9H), 0.91–0.96 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.1, 142.7, 128.3, 128.3, 125.6, 64.2, 38.6, 33.3, 32.1, 32.1, 31.8, 30.7, 19.2, 19.1, 13.7; IR (KBr): 2958, 1742, 1602, 1455, 1261 cm^{-1}; HRMS [(EI), M^+]: 262.1916 (calcd for $C_{17}H_{26}O_2$ 262.1933).

4-Methyl-6-phenylhexanenitrile (5r)



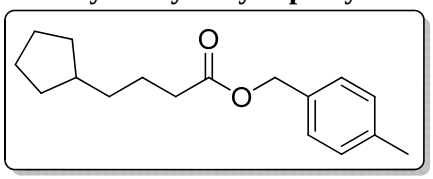
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.30 (m, 2H), 7.16–7.20 (m, 3H), 2.56–2.76 (m, 2H), 2.28–2.44 (m, 2H), 1.65–1.72 (m, 1H), 1.59–1.64 (m, 2H), 1.46–1.55 (m, 2H), 0.98 (d, 3H, J = 6.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.2, 128.4, 128.3, 125.8, 119.9, 38.2, 33.2, 32.2, 31.8, 18.7, 14.9; IR (KBr): 2873, 1735, 1490, 1263, 1153 cm^{-1}; HRMS [(EI), M^+]: 187.1359 (calcd for $C_{13}H_{17}N$ 187.1361).

5-Methyl-7-phenylheptan-2-one (5s)



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.27 (m, 2H), 7.13–7.16 (m, 3H), 2.55–2.64 (m, 2H), 2.37–2.43 (m, 2H), 2.11 (s, 3H), 1.59–1.68 (m, 2H), 1.38–1.46 (m, 3H), 0.92 (d, 3H, J = 6.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 209.4, 142.7, 128.3, 128.3, 125.6, 41.4, 38.6, 33.3, 32.0, 30.5, 29.9, 19.3; IR (KBr): 2958, 1716, 1602, 1465, 1176 cm^{-1}; HRMS [(EI), M^+]: 204.1514 (calcd for $C_{14}H_{20}O$ 204.1514).

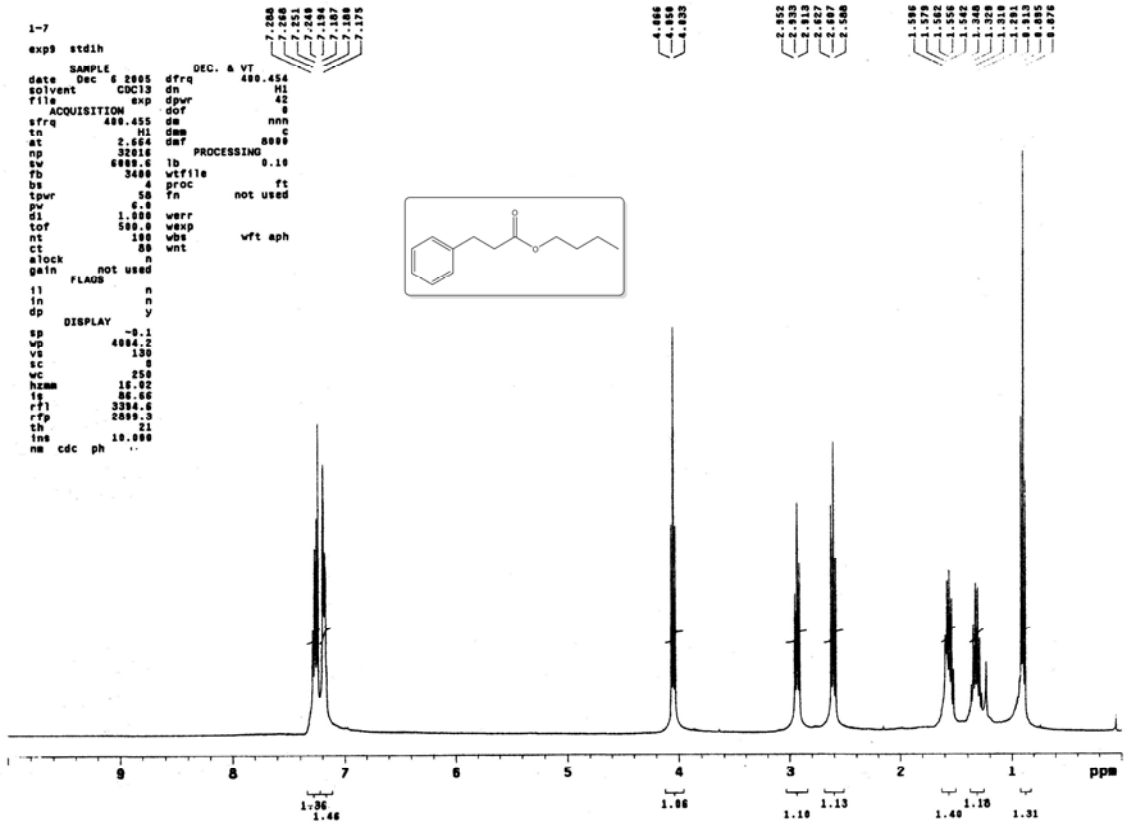
4-Methylbenzyl 4-cyclopentylbutanoate (7)

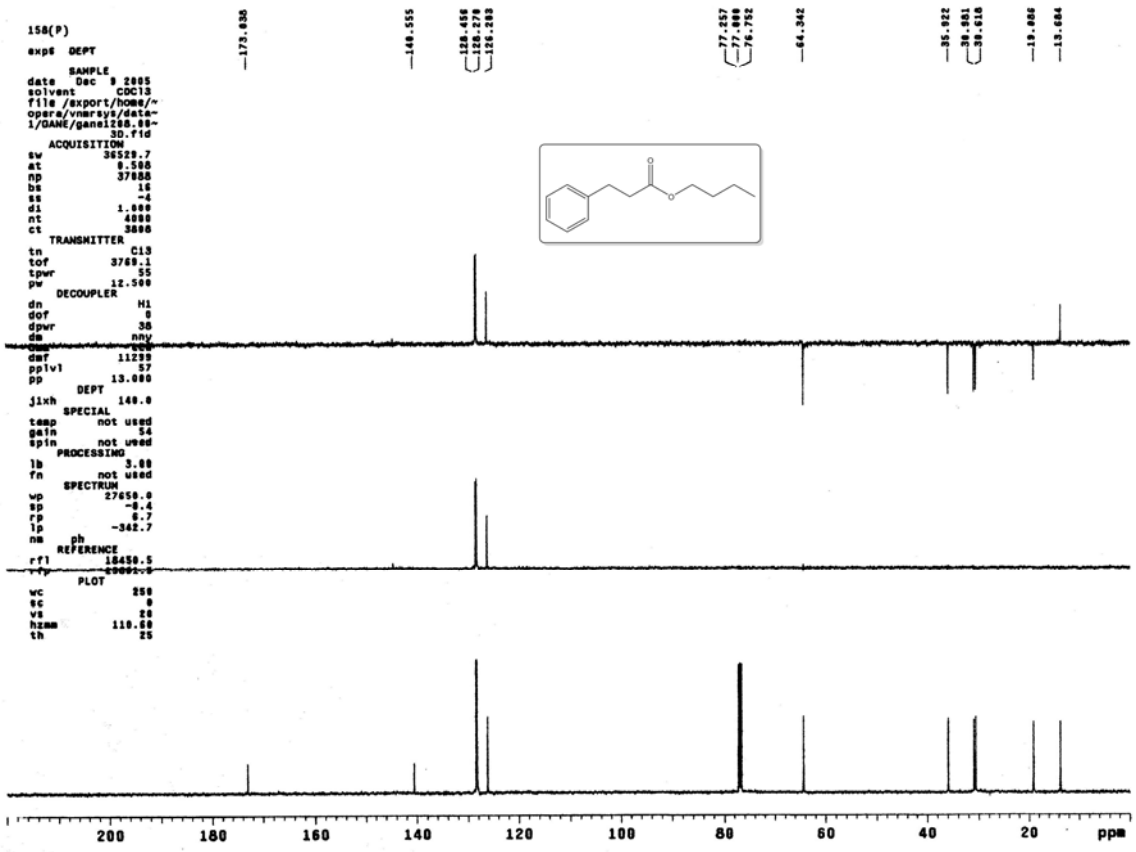


Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 7.6 Hz, 2H), 5.06 (s, 2H), 2.34–2.30 (m, 5H), 1.67–1.48 (m, 9H), 1.32–1.04 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.8, 138.0, 133.1, 129.2, 128.4, 66.0, 39.8, 35.6, 34.6, 32.6, 25.1, 24.2, 21.2; IR (KBr): 2958, 1735, 1602, 1465, 1243, cm^{-1}; HRMS [(EI), M^+]: 260.1774 (calcd for $C_{17}H_{24}O_2$ 260.1776).

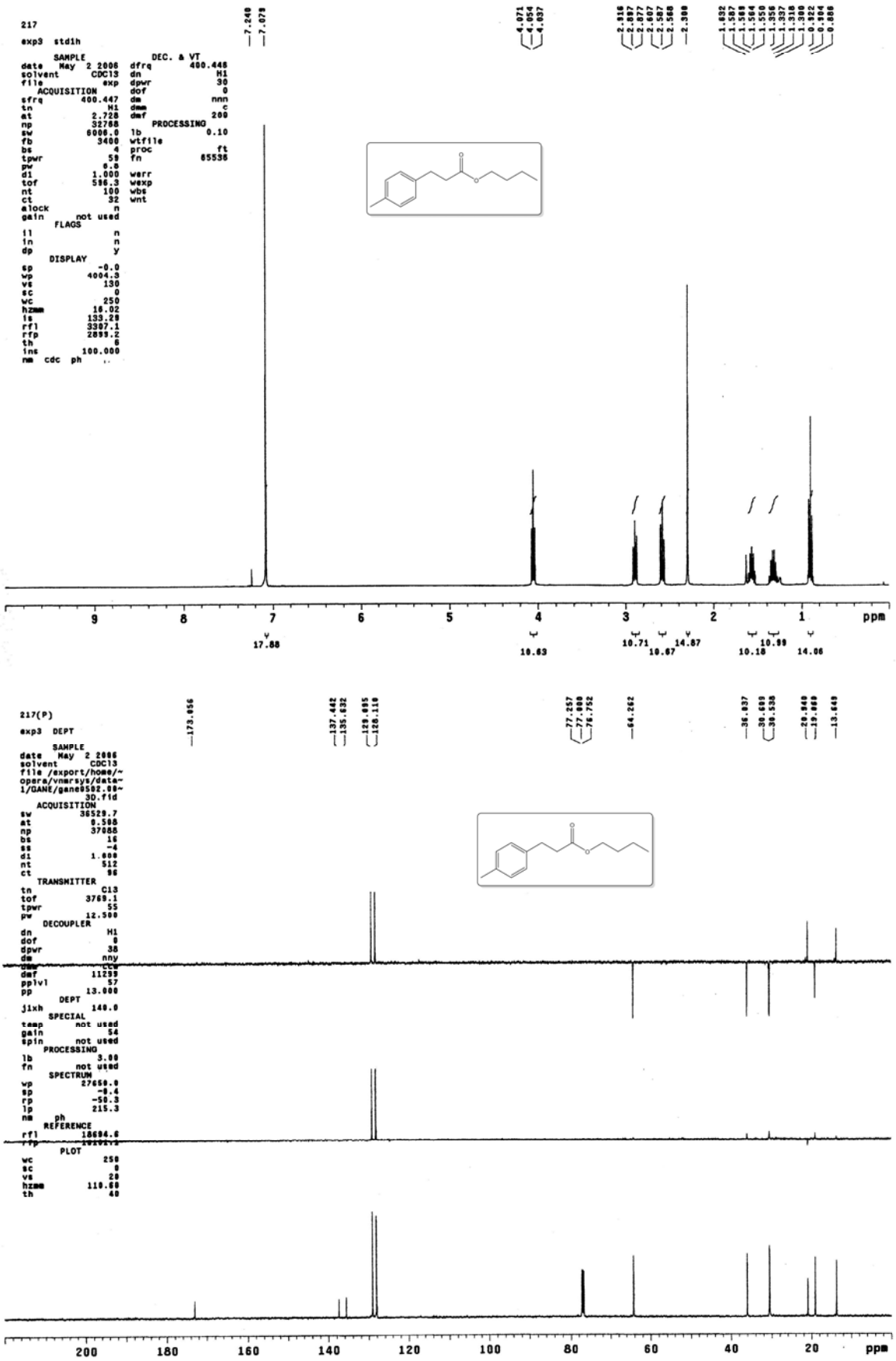
^{1}H NMR and ^{13}C NMR Spectra for Products (400 or 500 MHz)

Butyl 3-phenylpropanoate (3a) ($CDCl_3$)

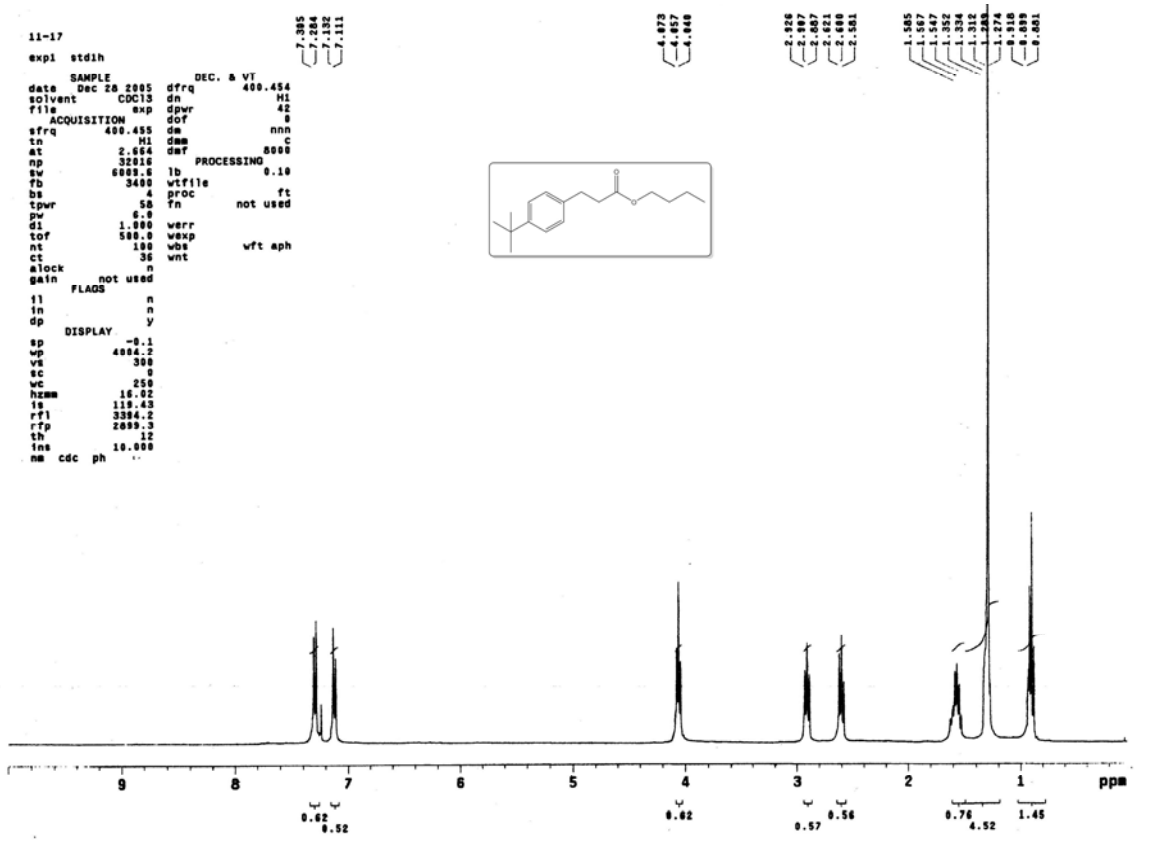


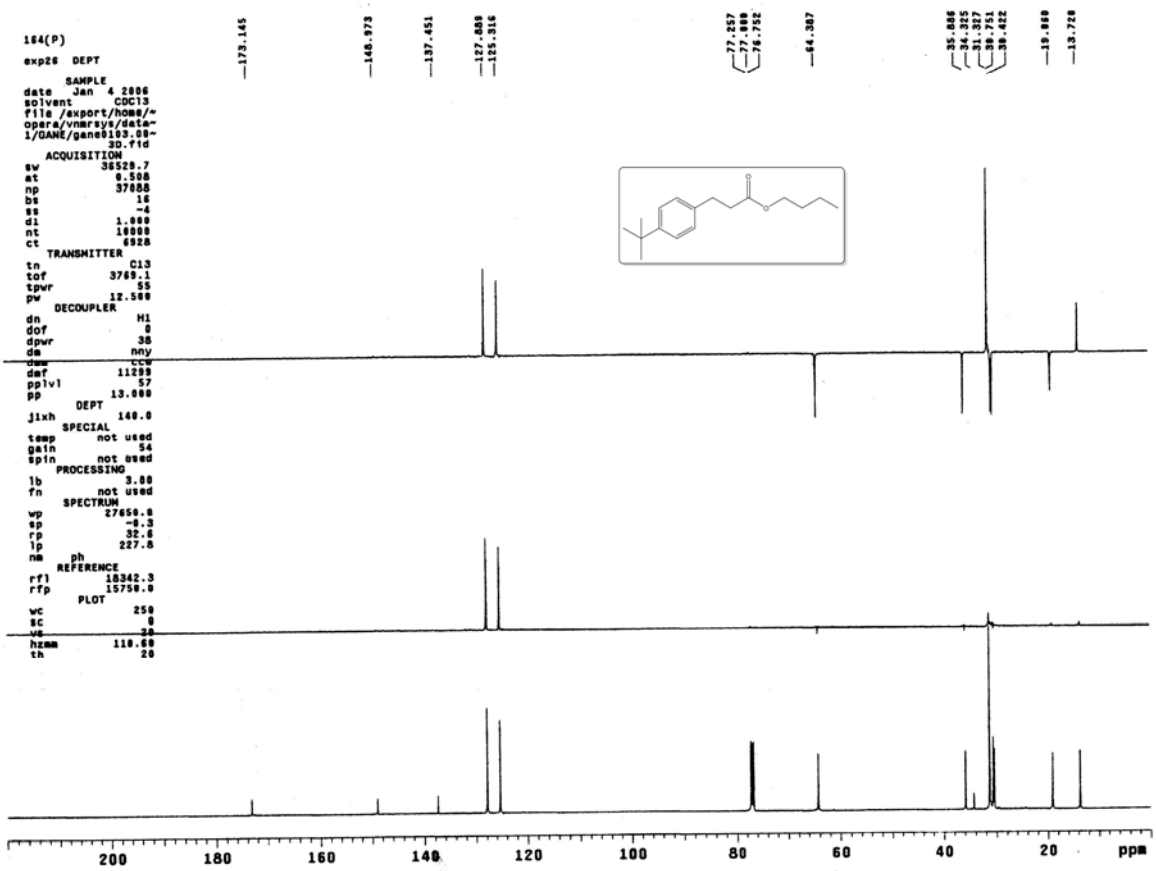


Butyl 3-(*p*-tolyl)propanoate (3b) ($CDCl_3$)

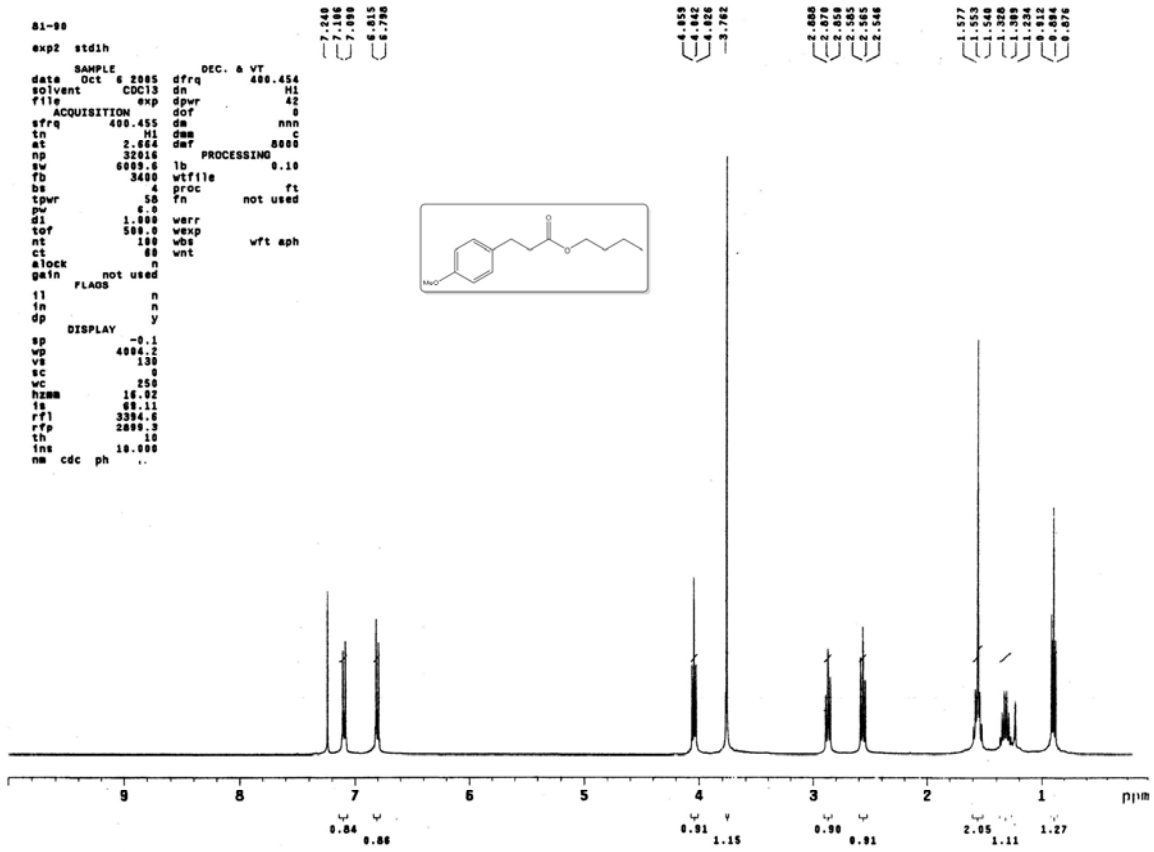


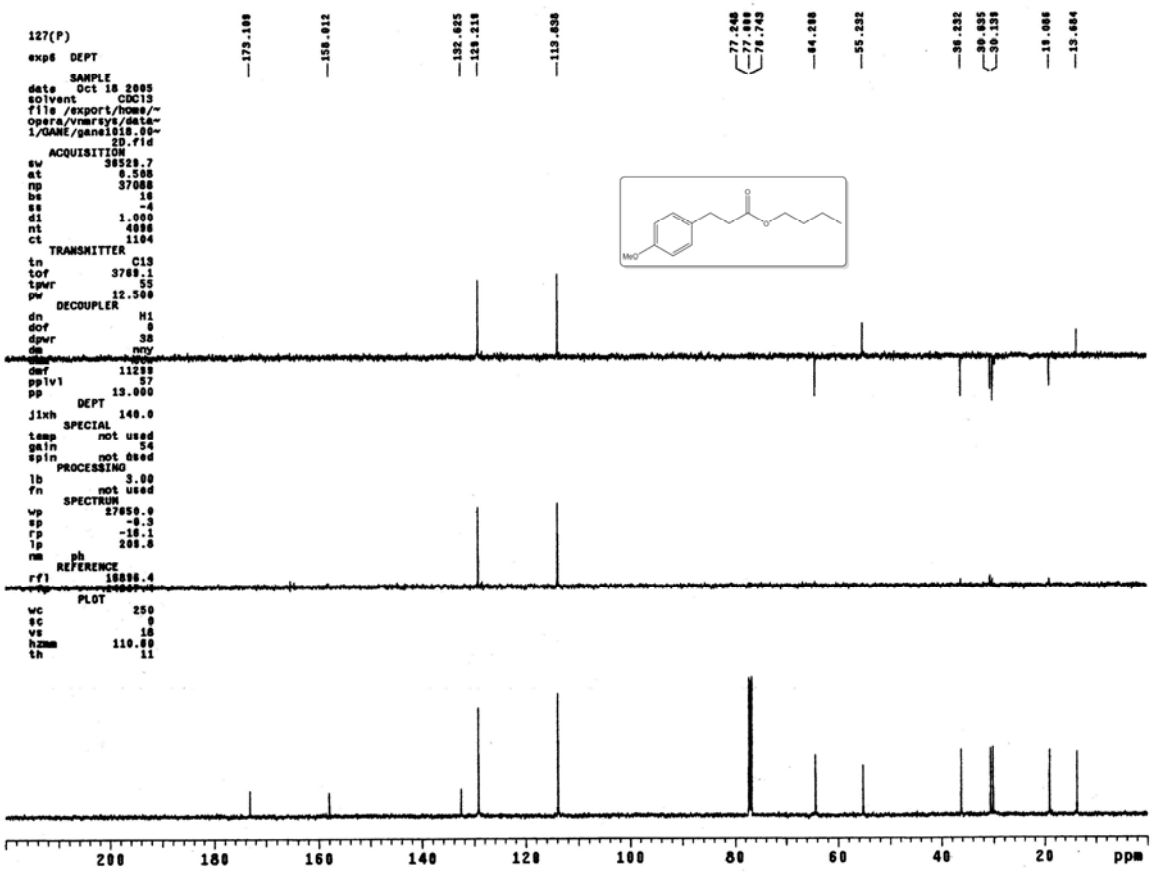
Butyl 3-(4-(*tert*-butyl)phenyl)propanoate (3c) ($CDCl_3$)



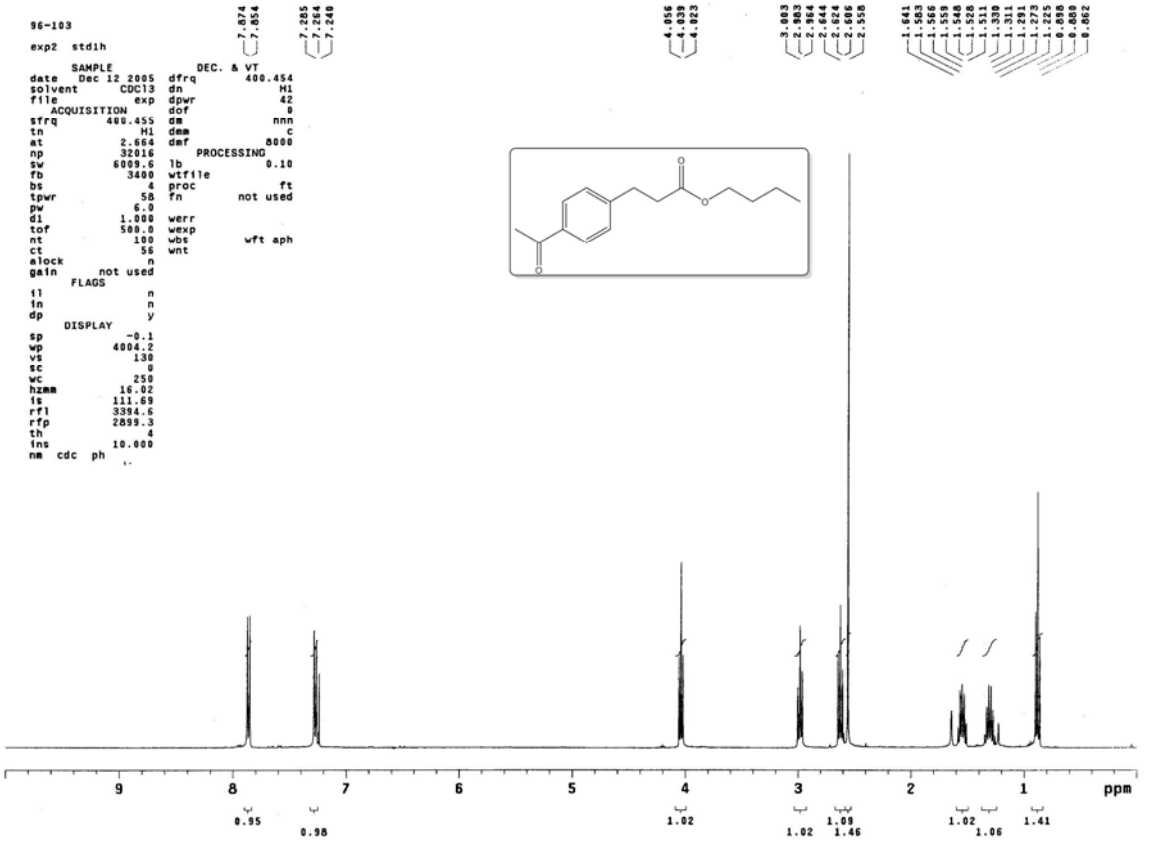


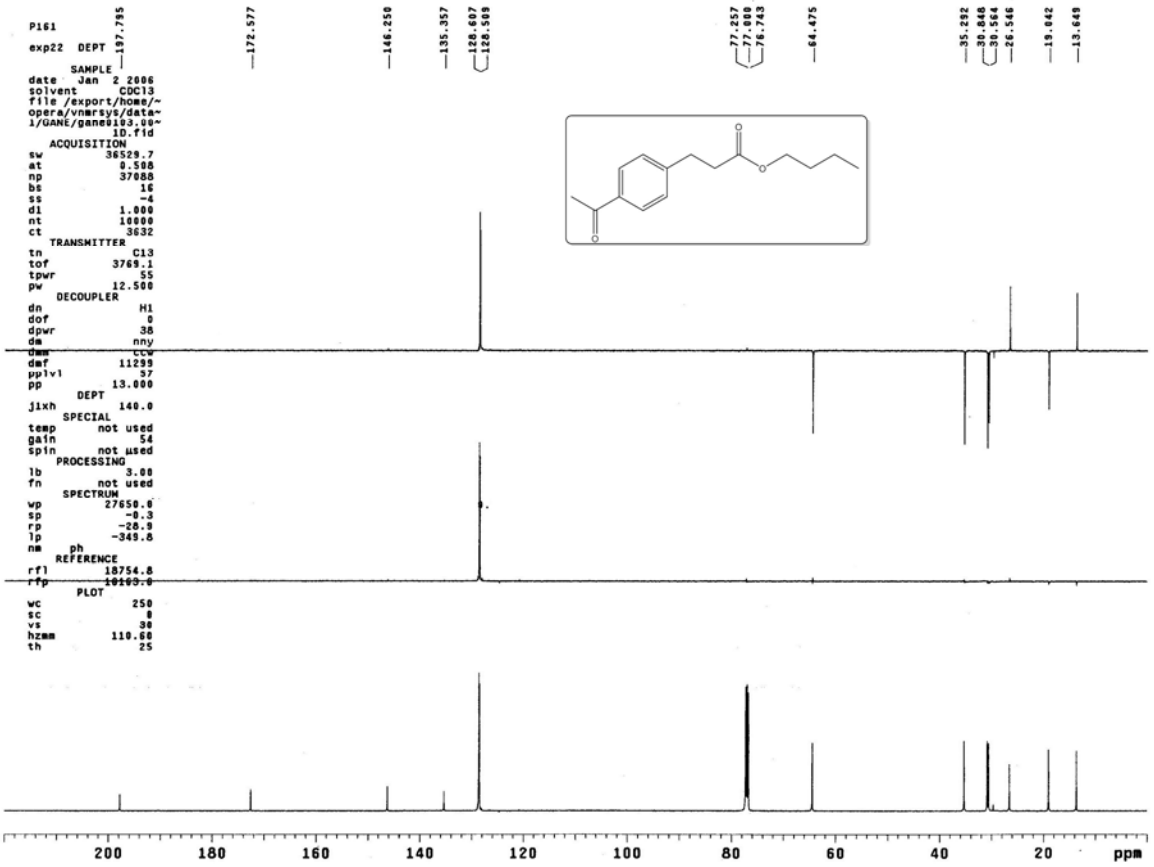
Butyl 3-(4-methoxyphenyl)propanoate (3d) ($CDCl_3$)



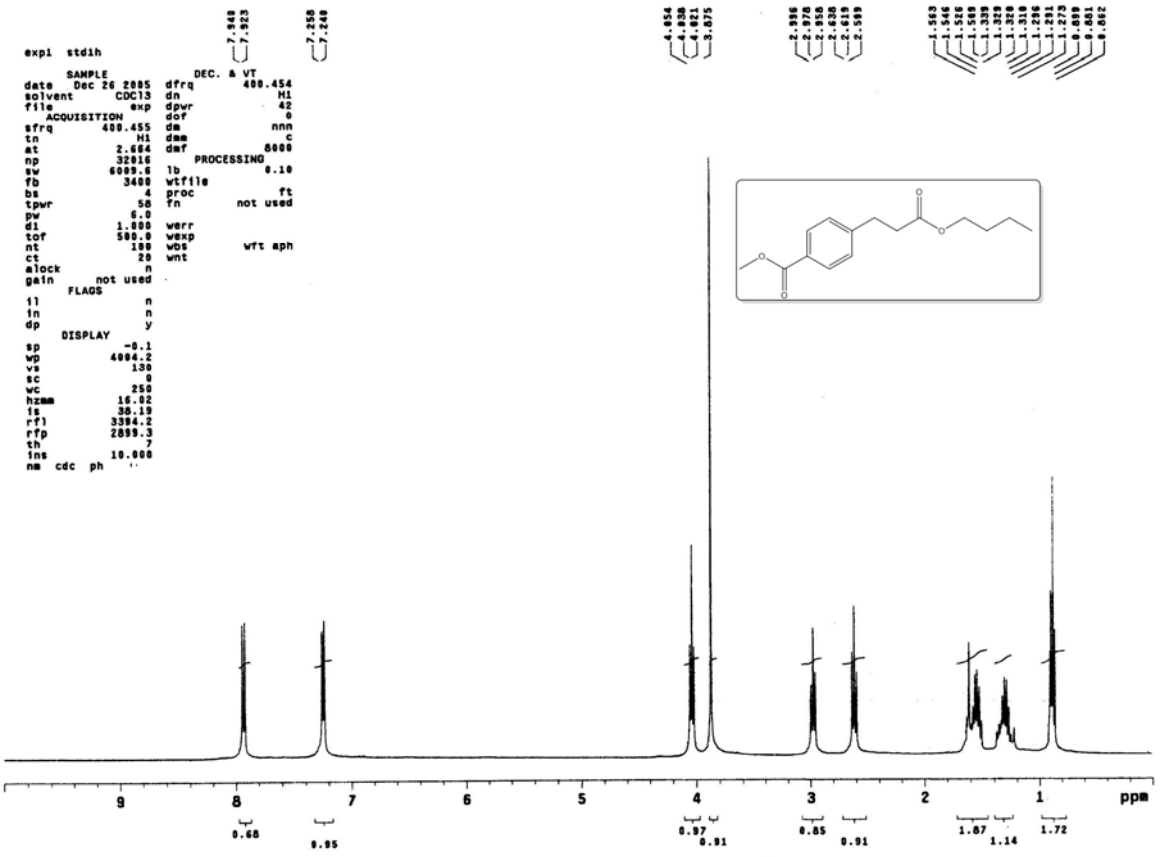


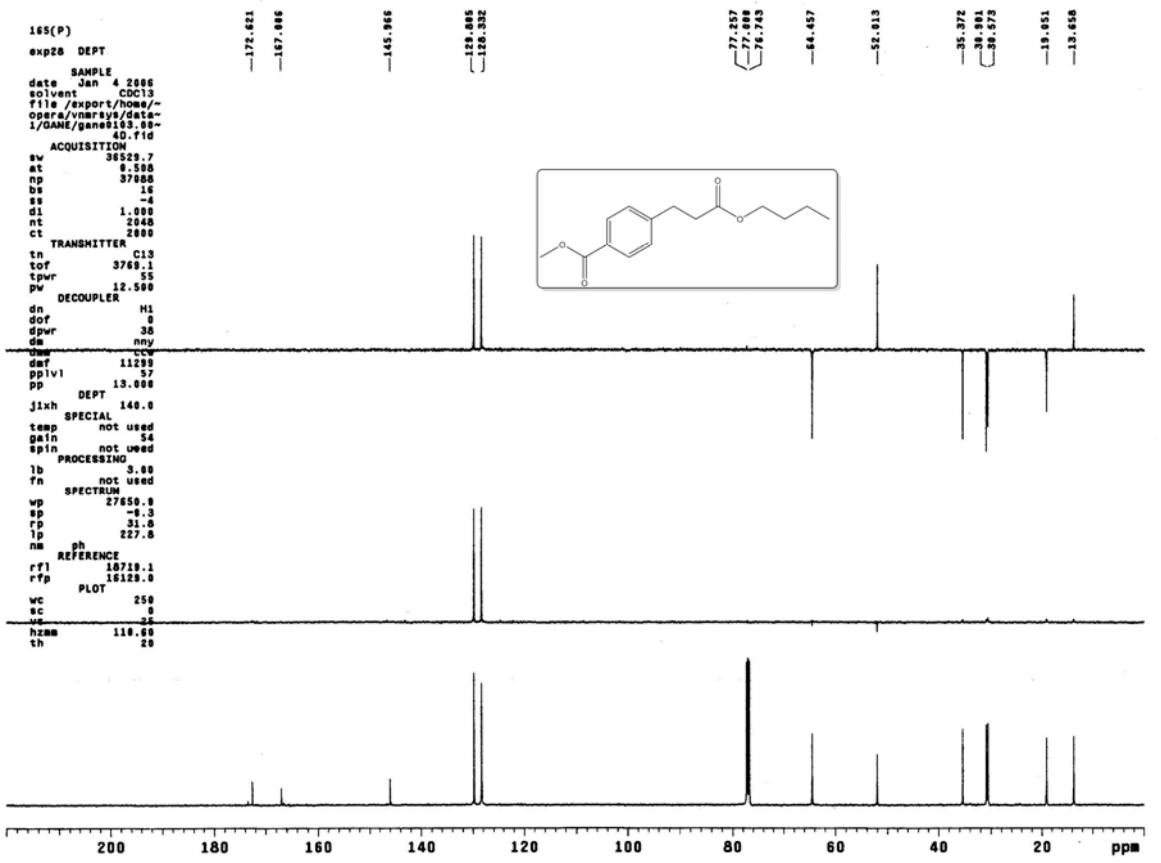
Butyl 3-(4-acetylphenyl)propanoate (3e) ($CDCl_3$)



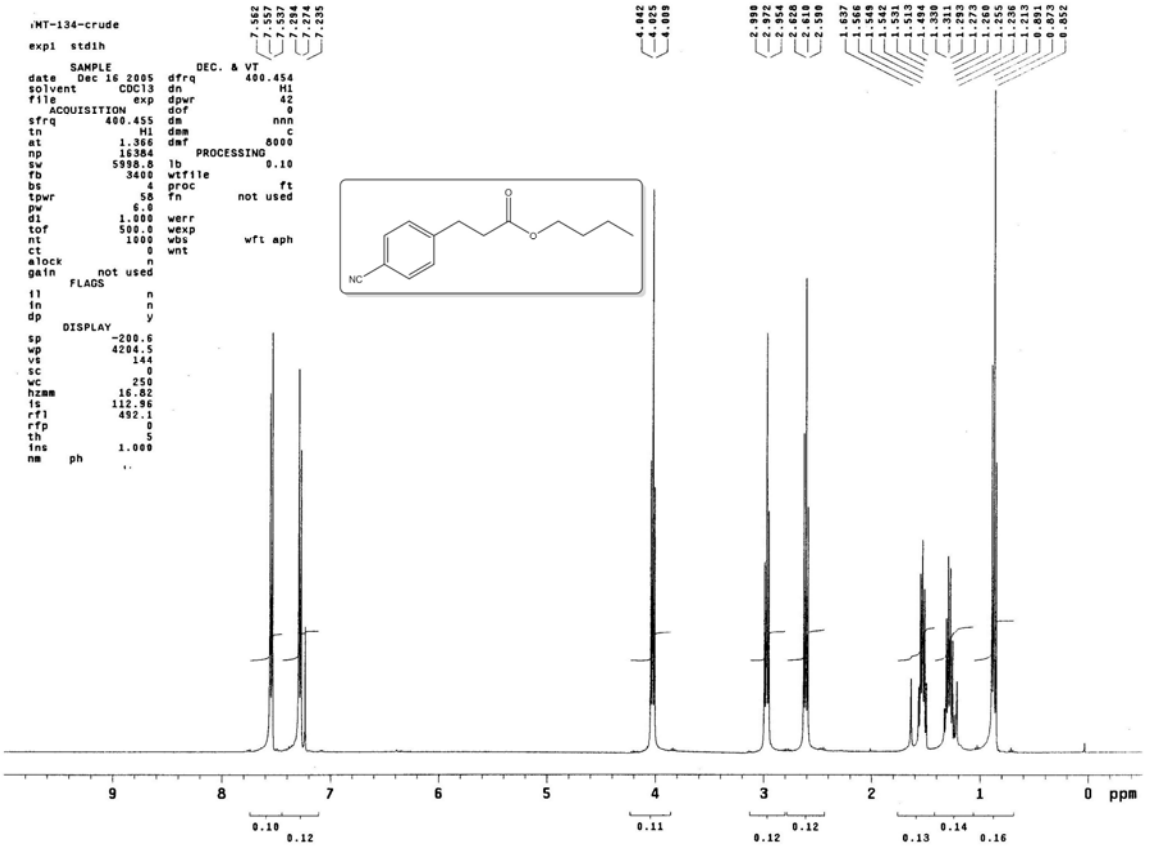


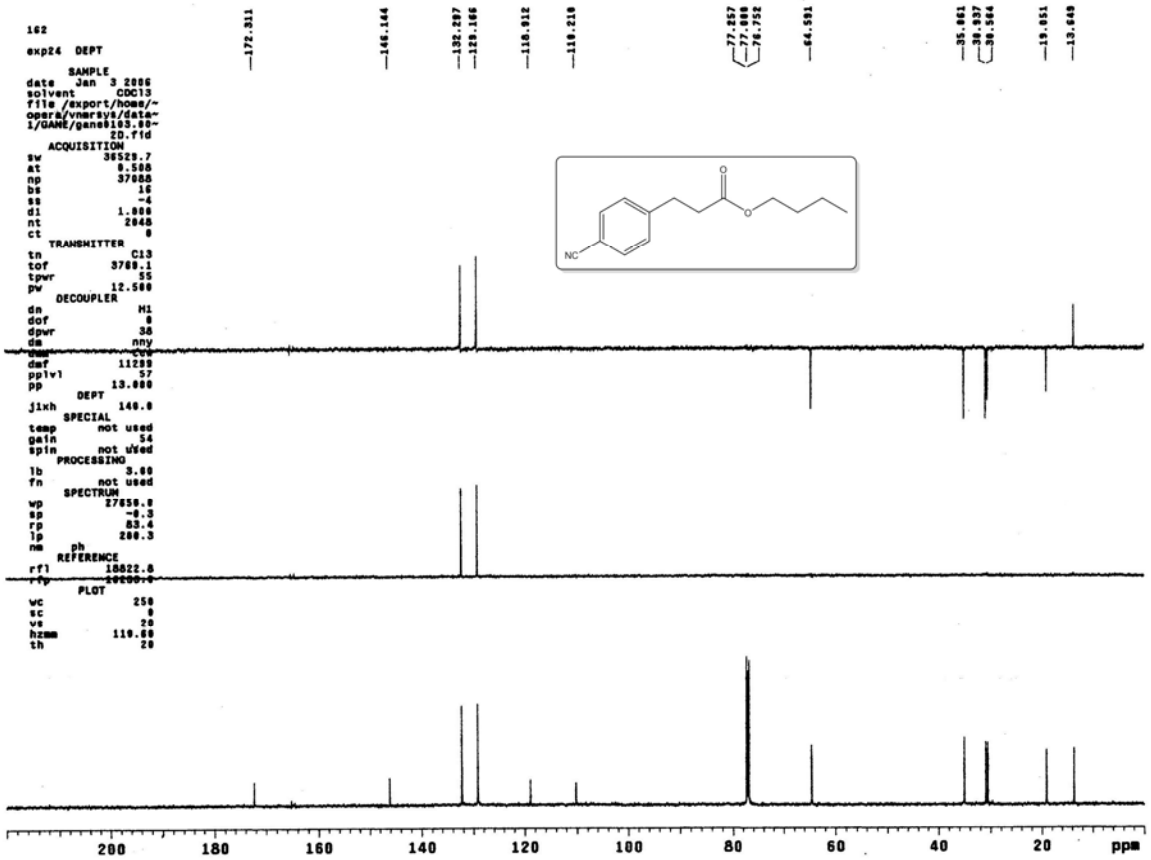
Methyl 4-(3-butoxy-3-oxopropyl)benzoate (3f) ($CDCl_3$)



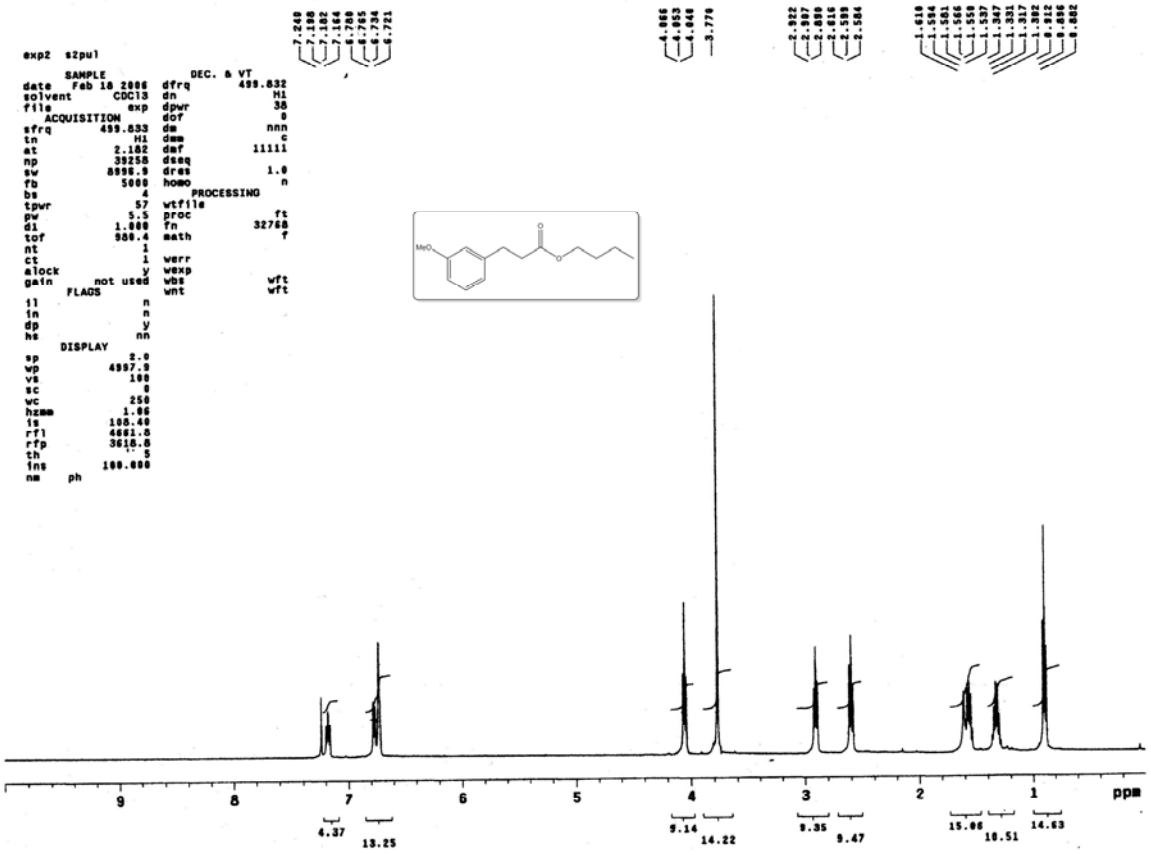


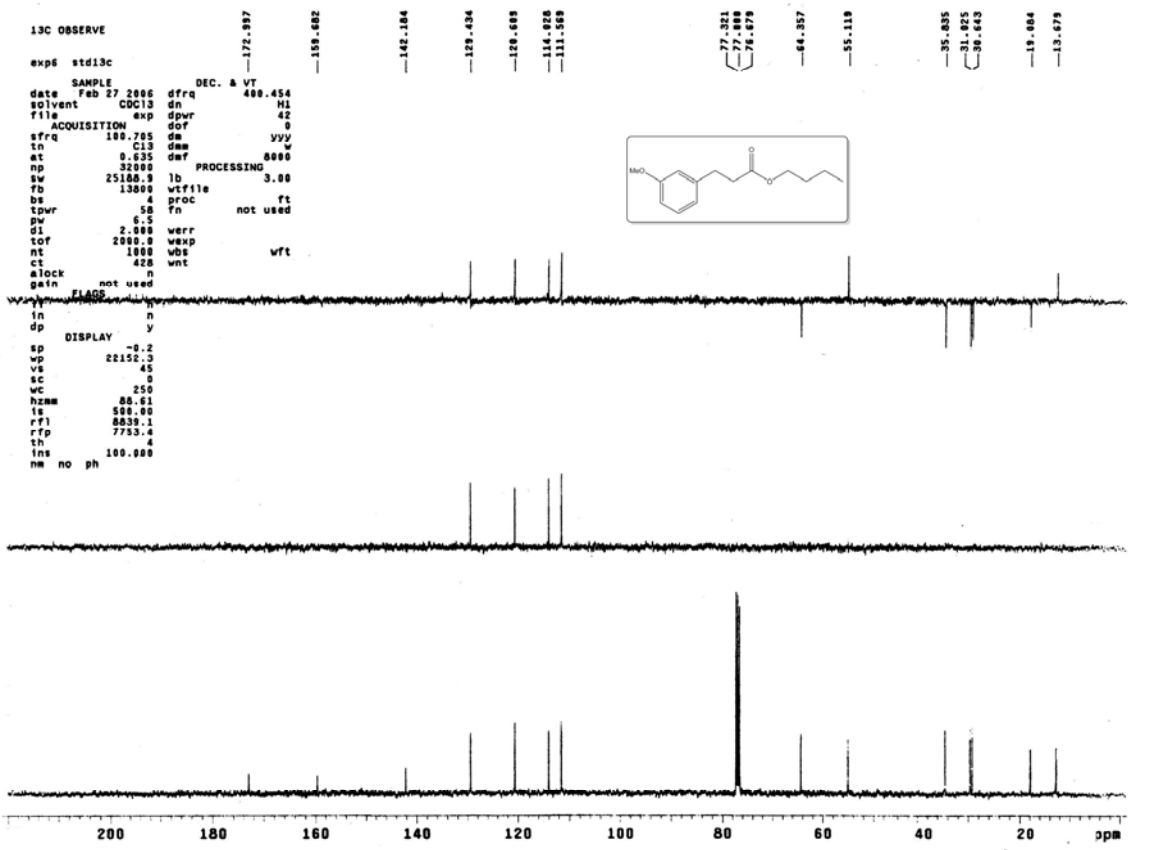
Butyl 3-(4-cyanophenyl)propanoate (3g) ($CDCl_3$)



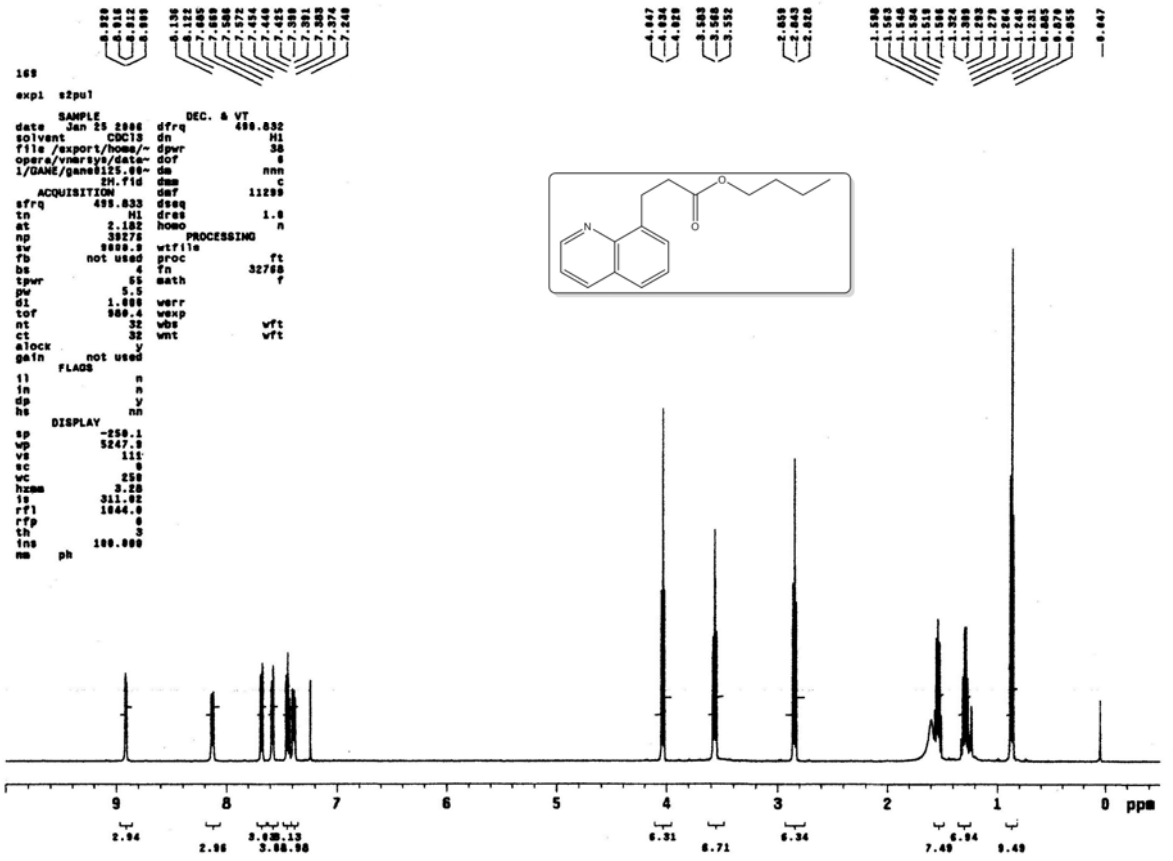


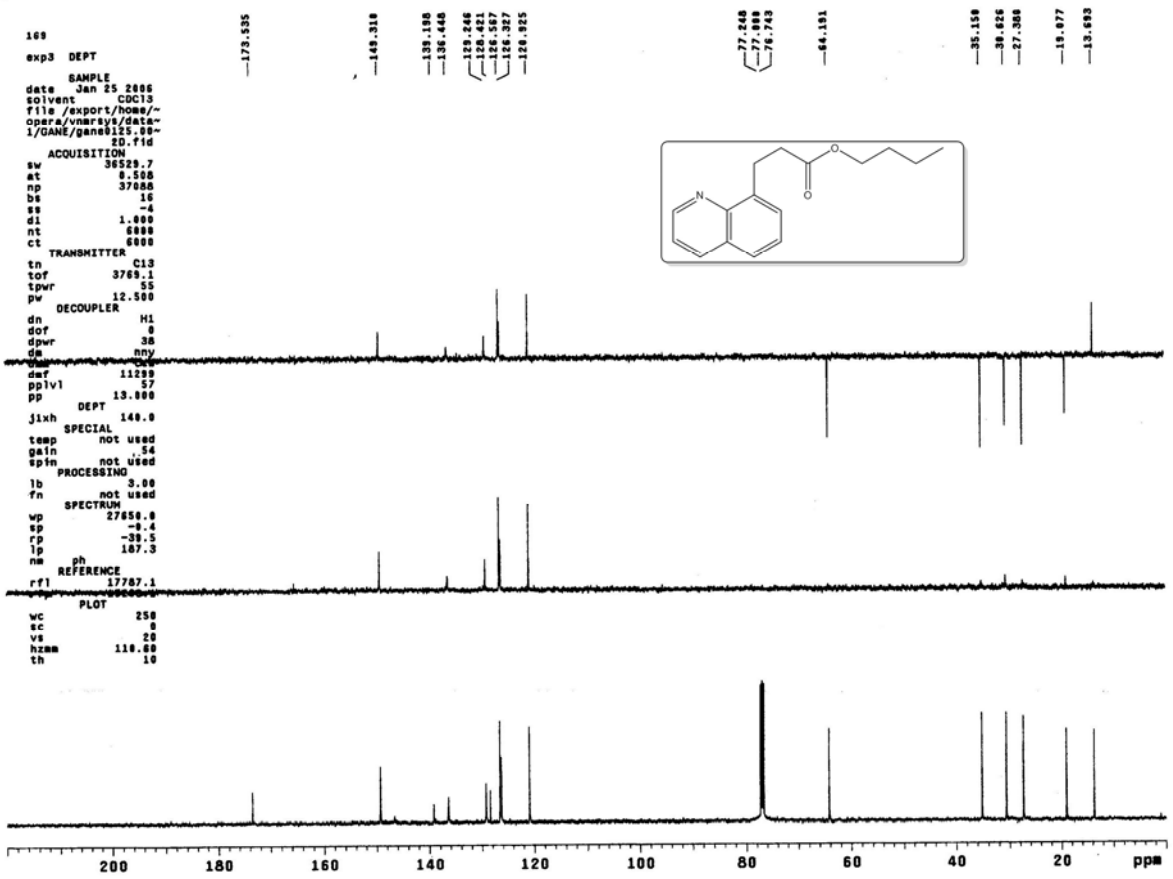
Butyl 3-(3-methoxyphenyl)propanoate (3h) ($CDCl_3$)



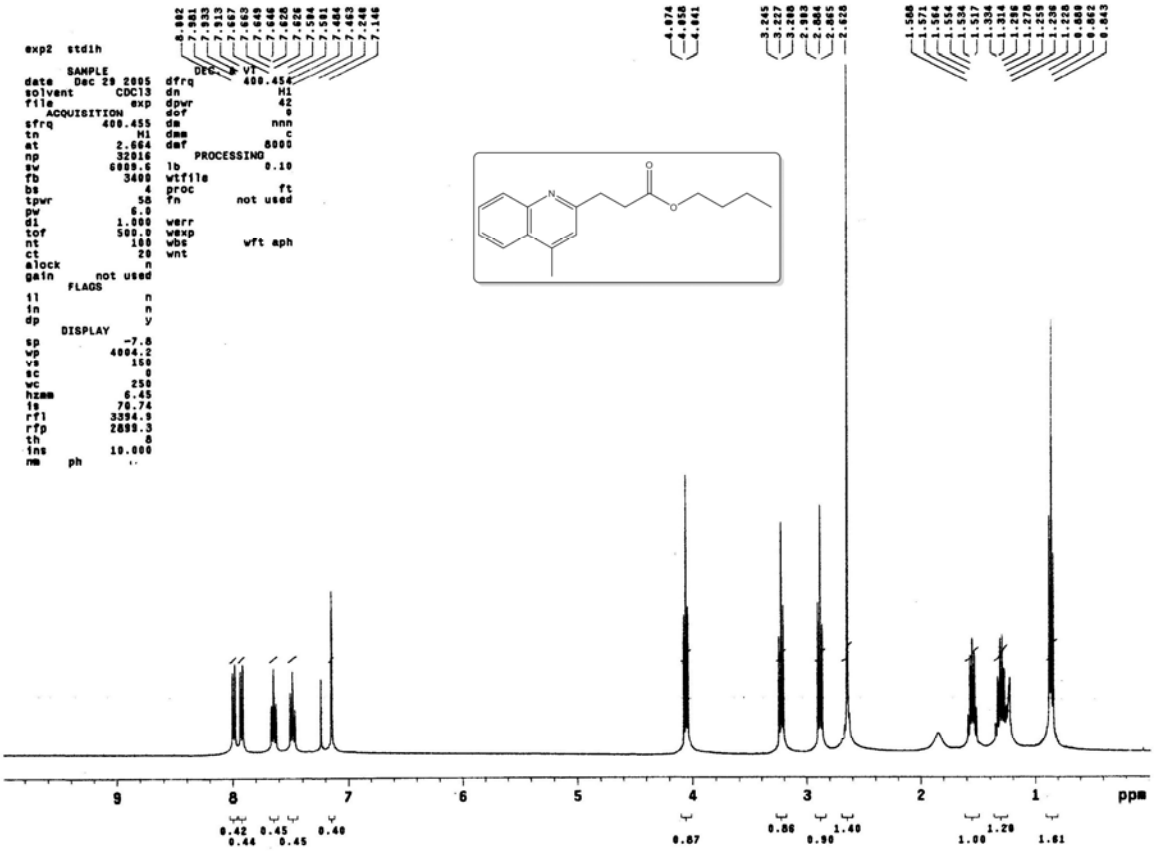


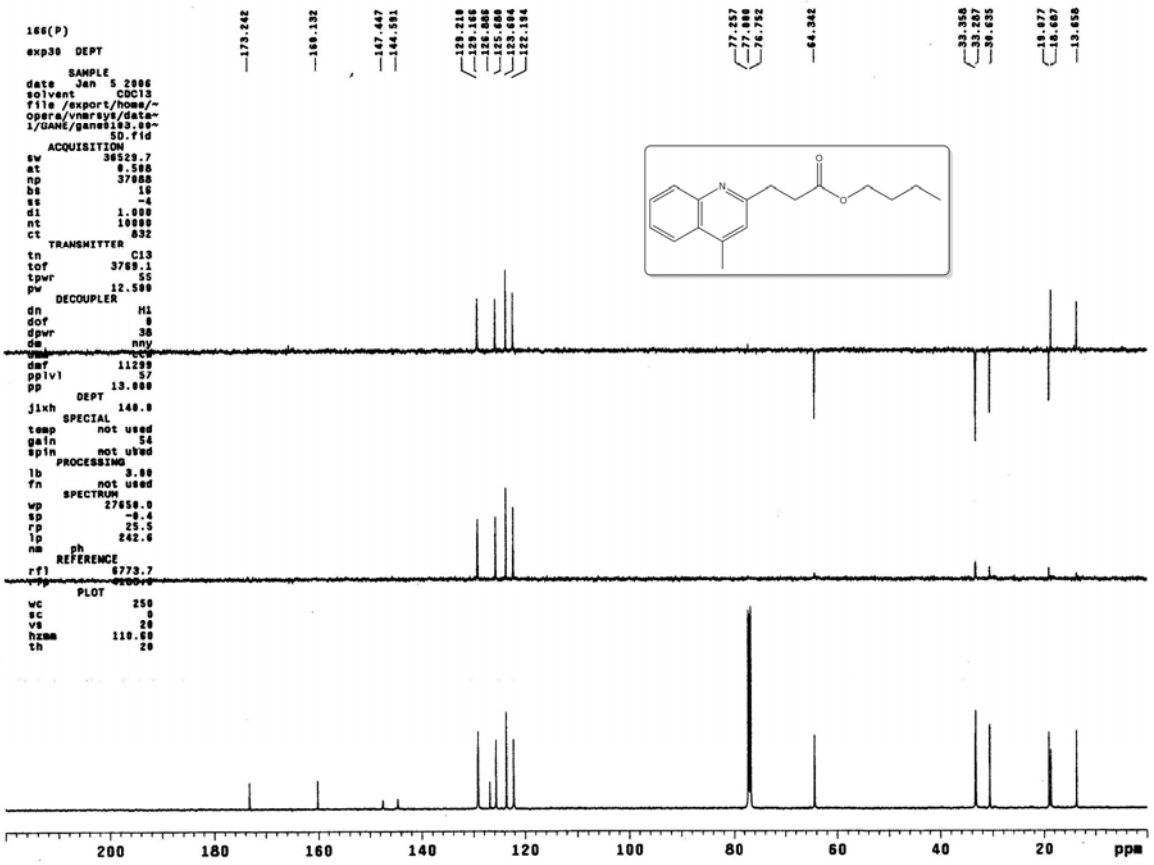
Butyl 3-(quinolin-8-yl)propanoate (3i) ($CDCl_3$)



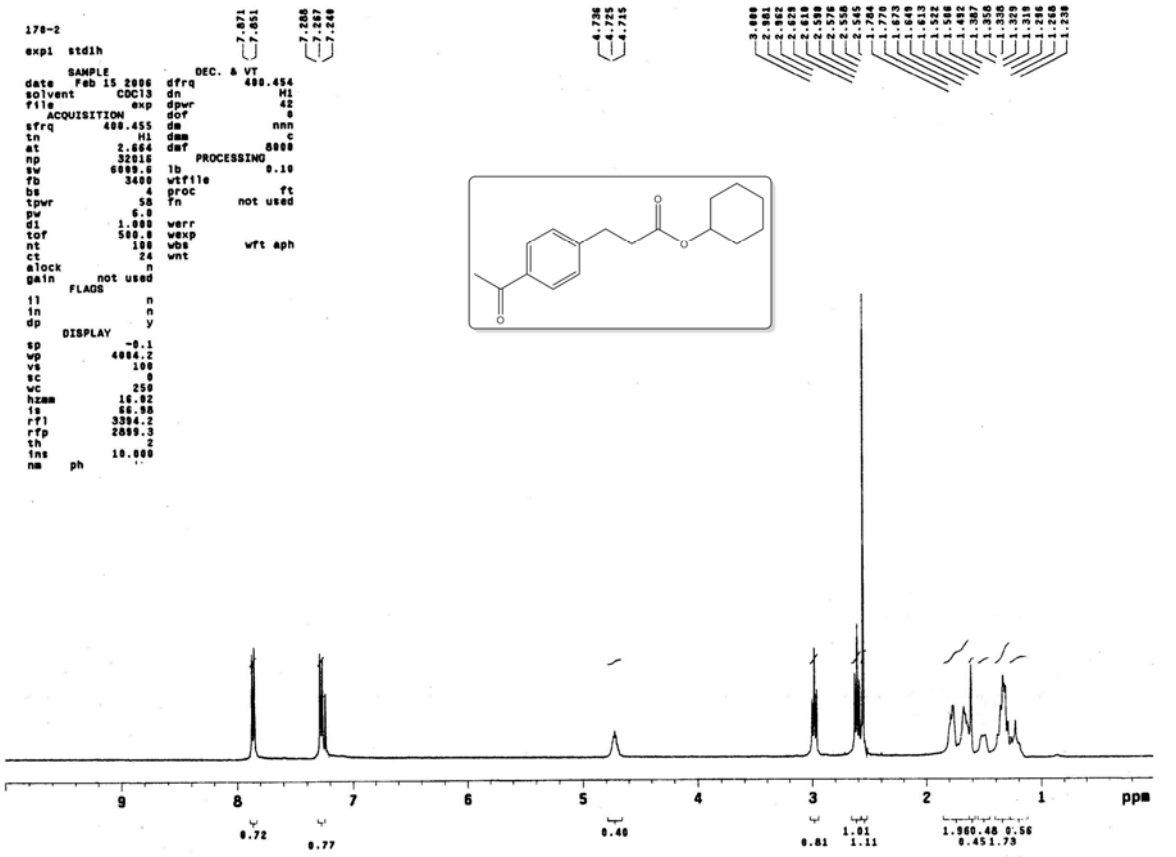


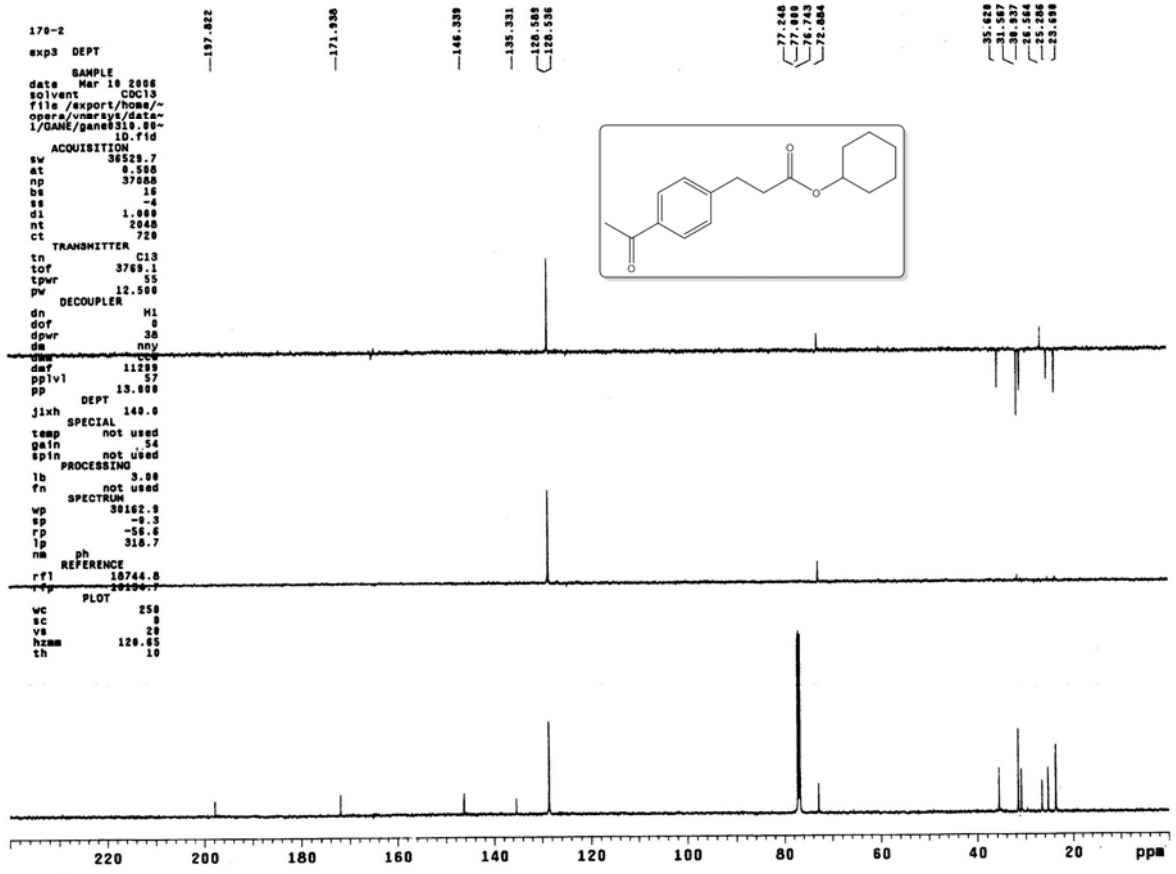
Butyl 3-(4-methylquinolin-2-yl)propanoate (3j) ($CDCl_3$)



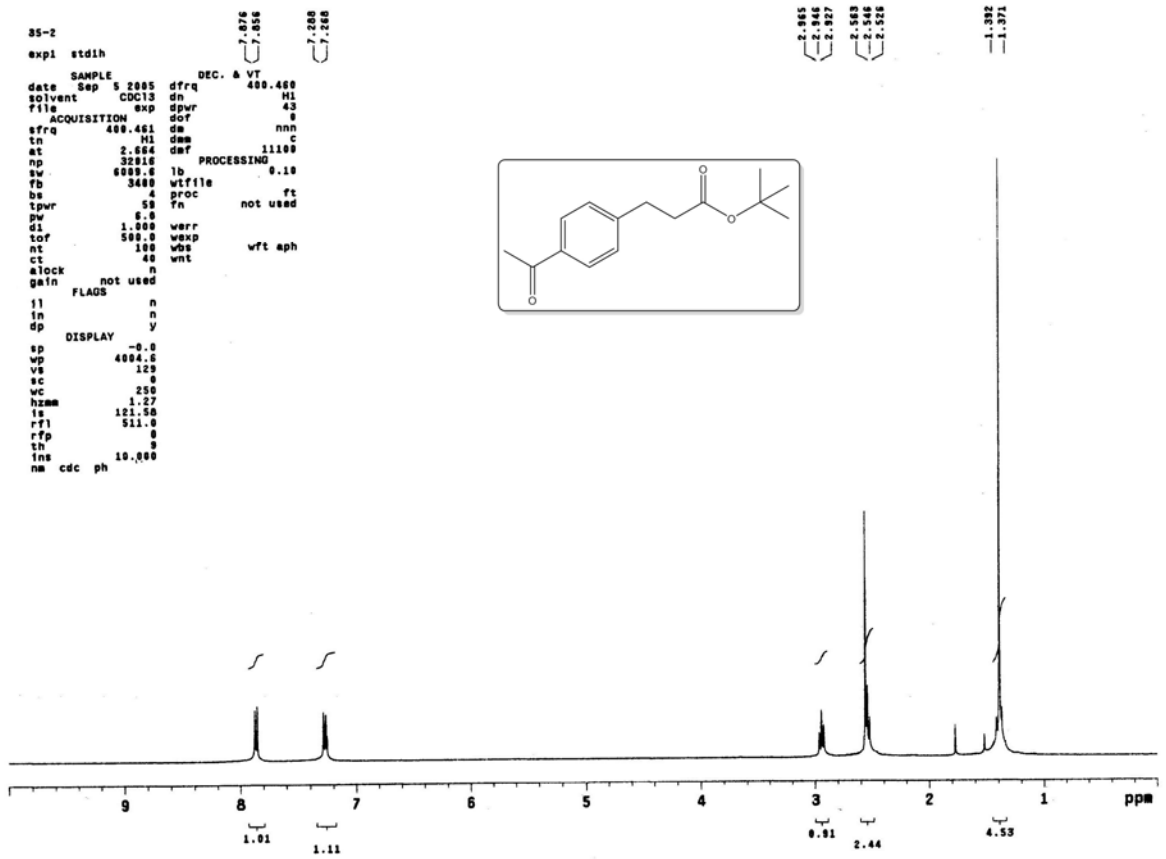


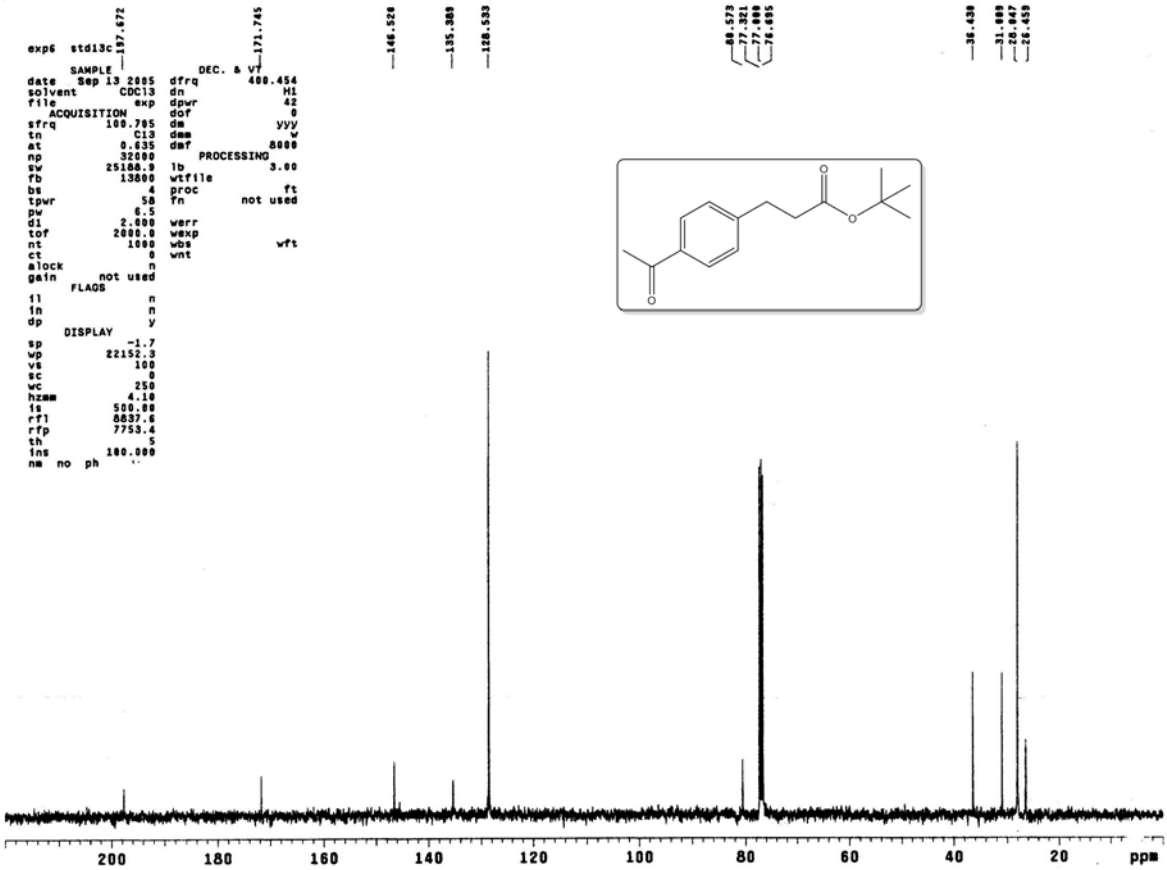
Cyclohexyl 3-(4-acetylphenyl)propanoate (3k) ($CDCl_3$)



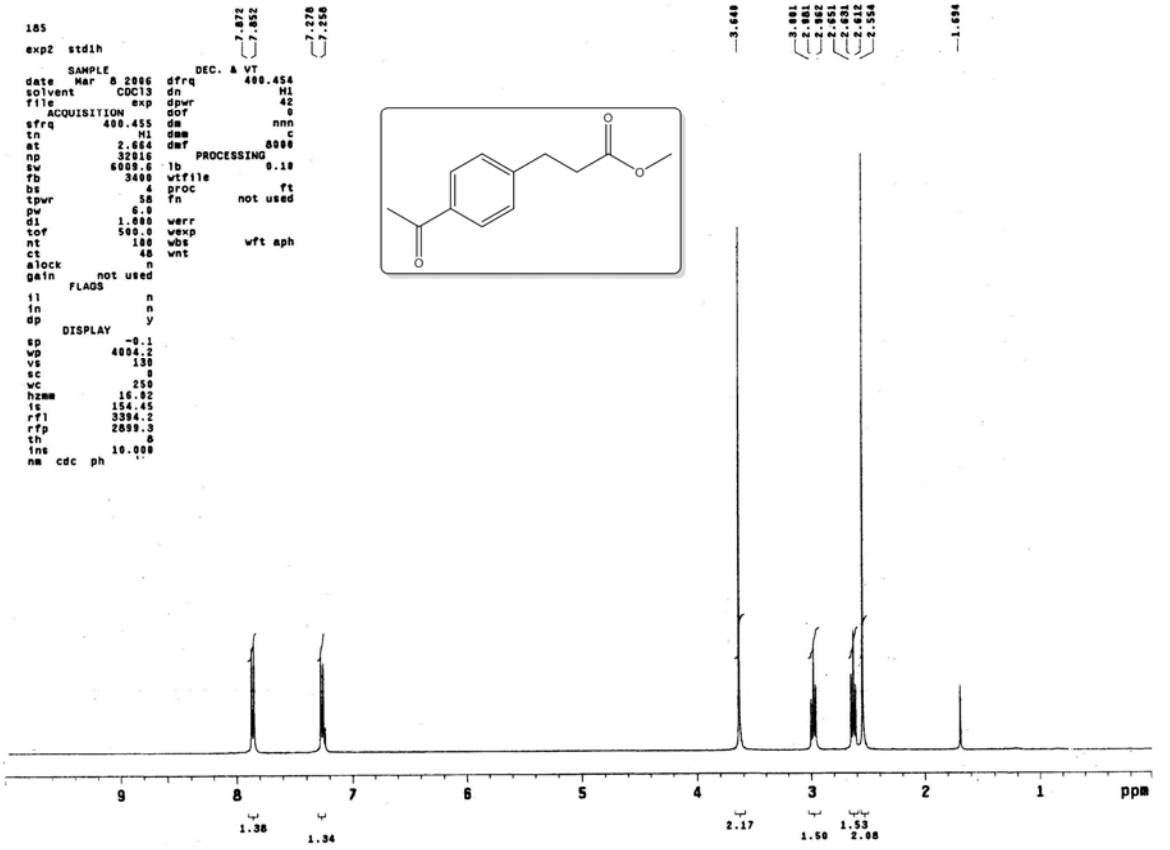


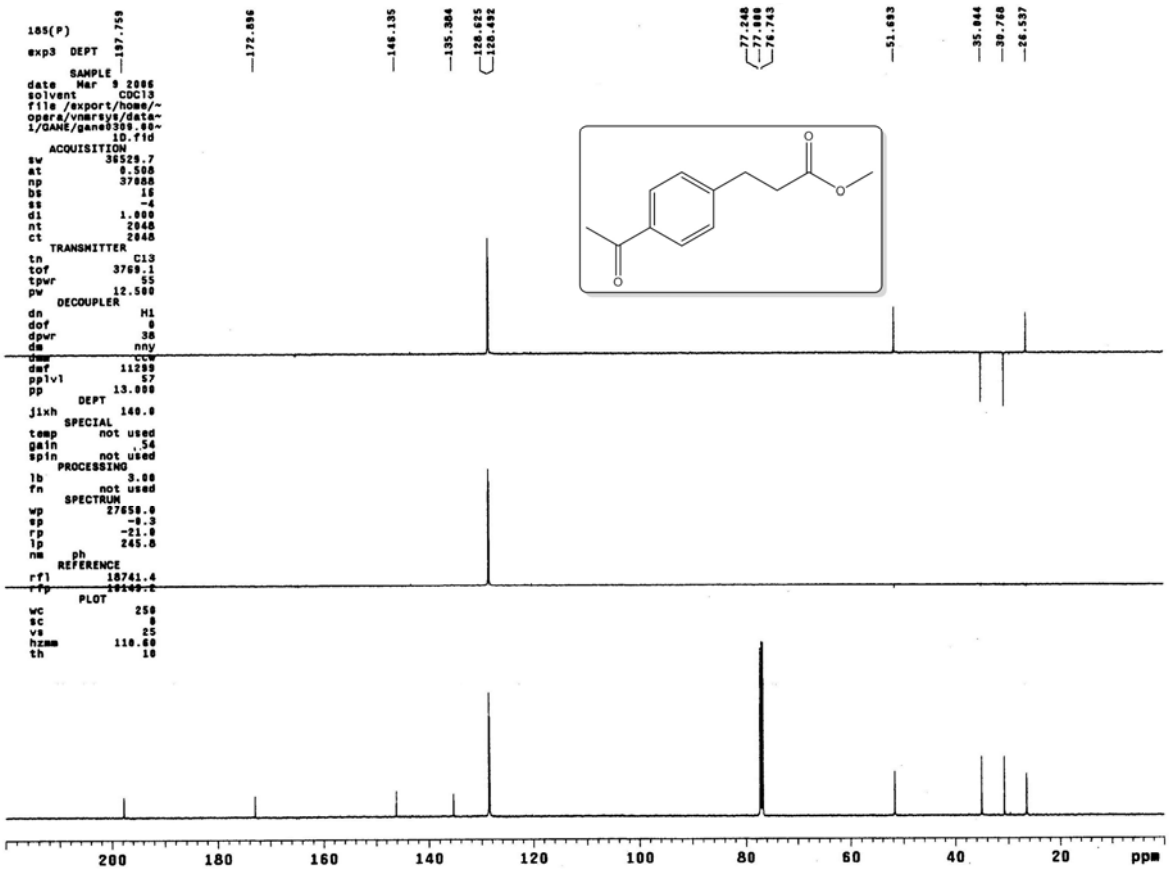
tert-Butyl 3-(4-acetylphenyl)propanoate (3l) ($CDCl_3$)



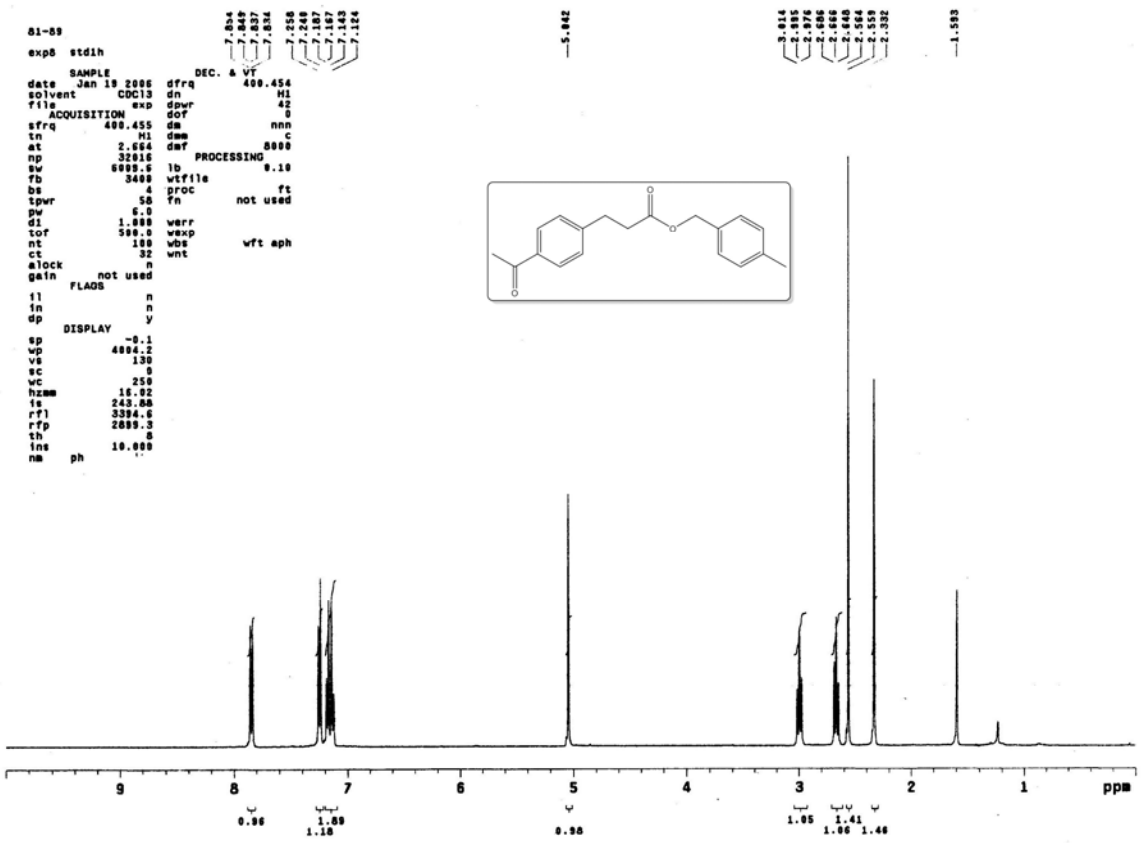


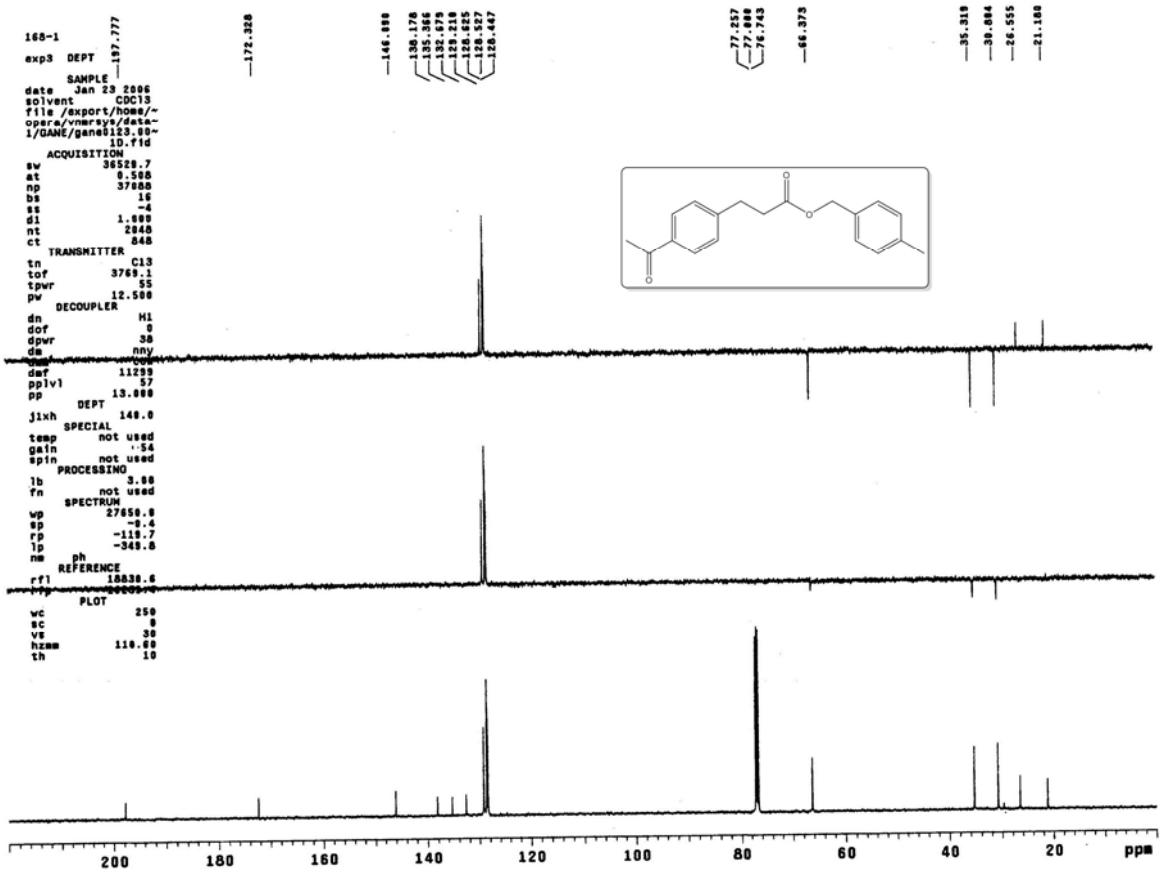
Methyl 3-(4-acetylphenyl)propanoate (3m) ($CDCl_3$)



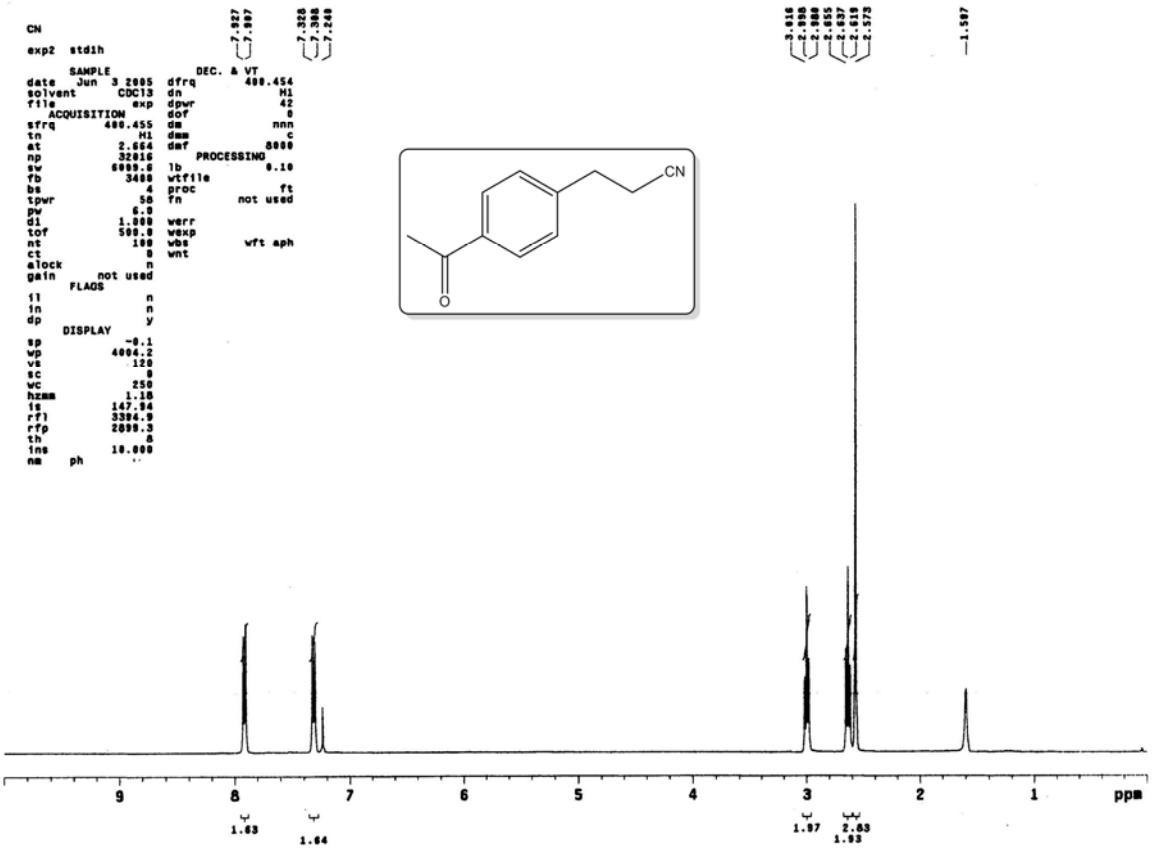


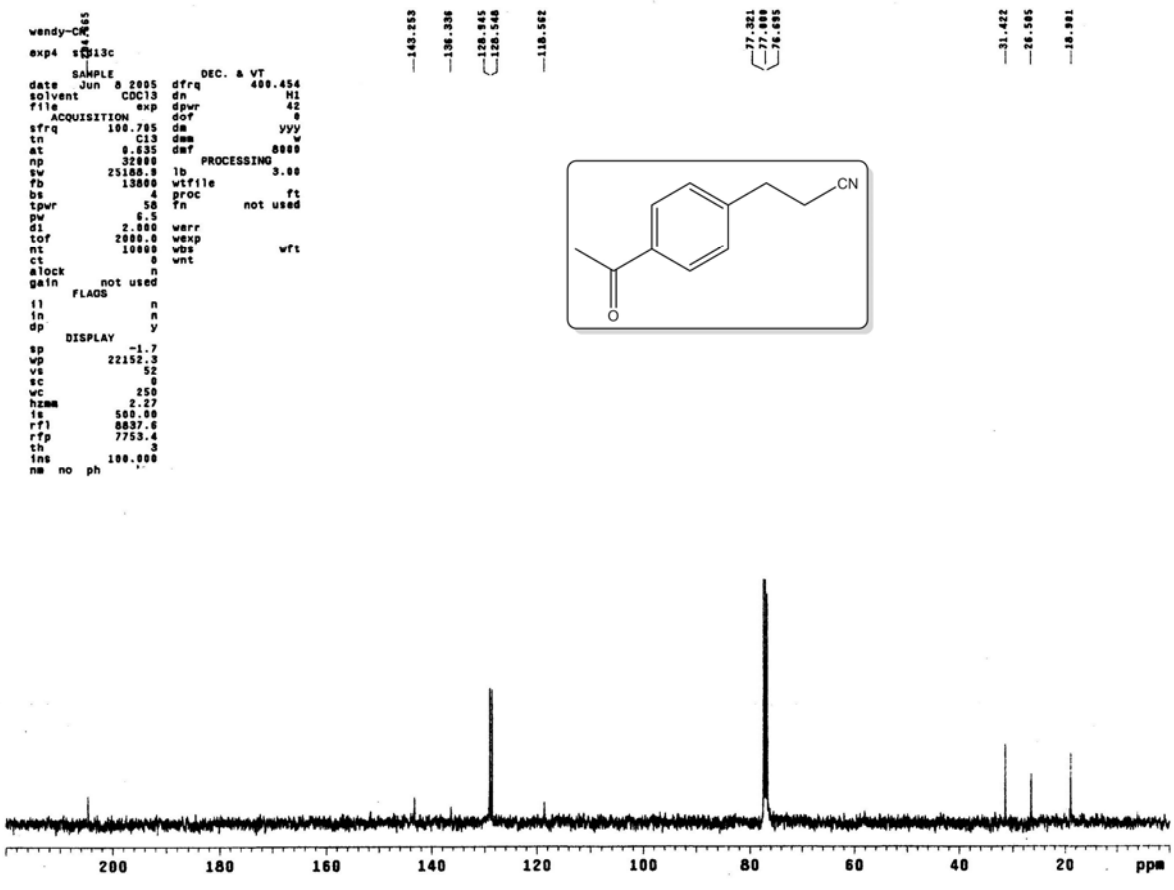
p-Tolyl 3-(4-acetylphenyl)propanoate (3n) ($CDCl_3$)



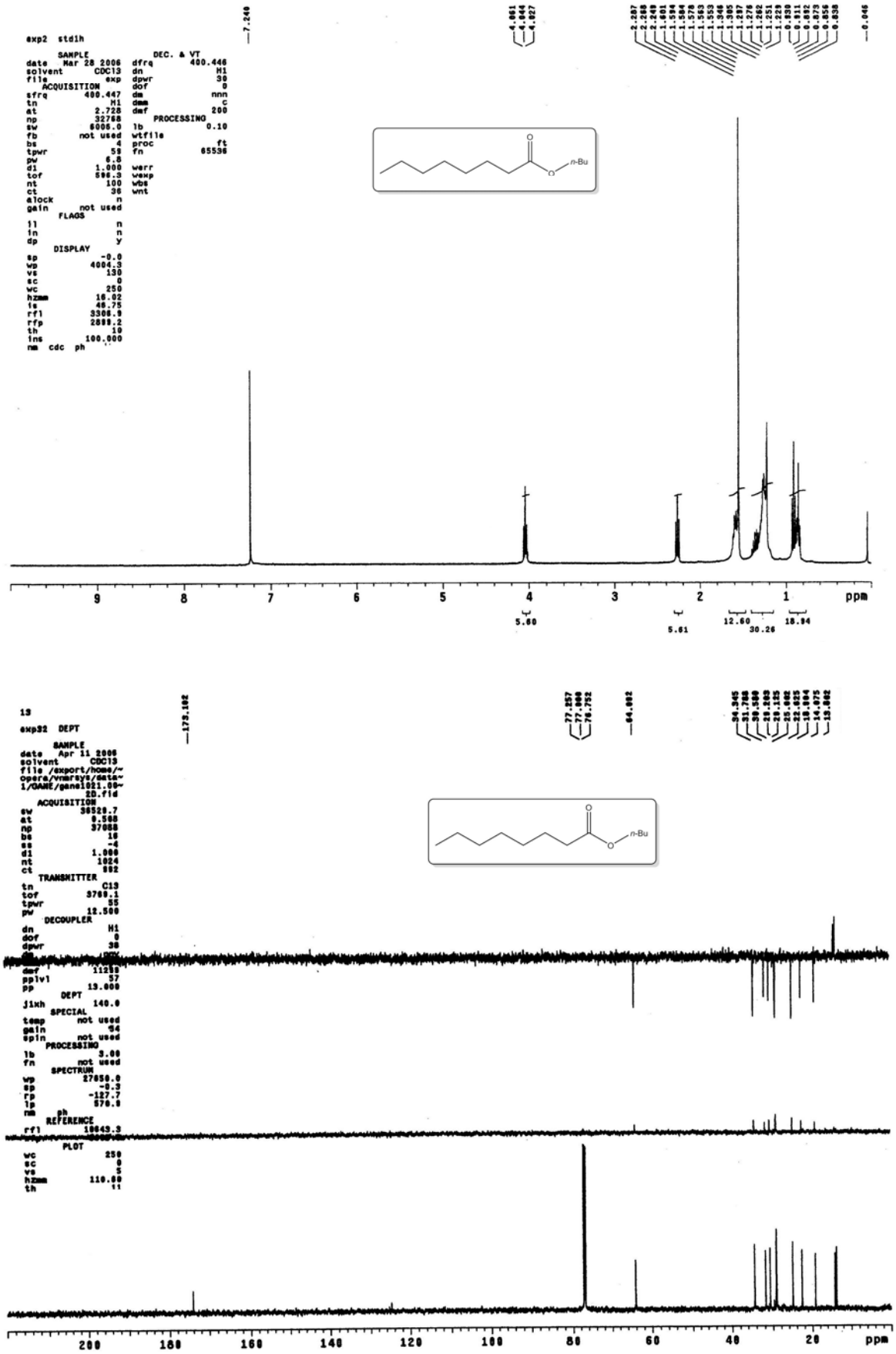


3-(4-Acetylphenyl)propanenitrile (3o) ($CDCl_3$)

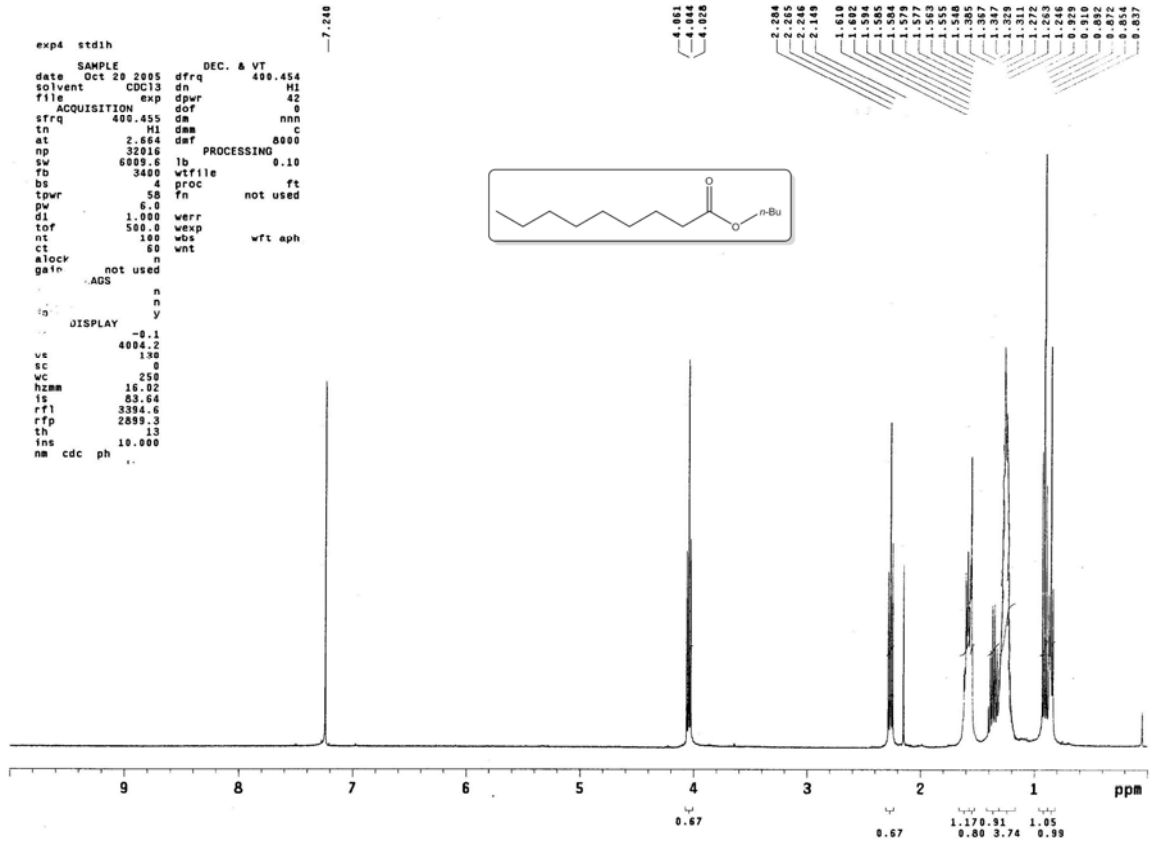


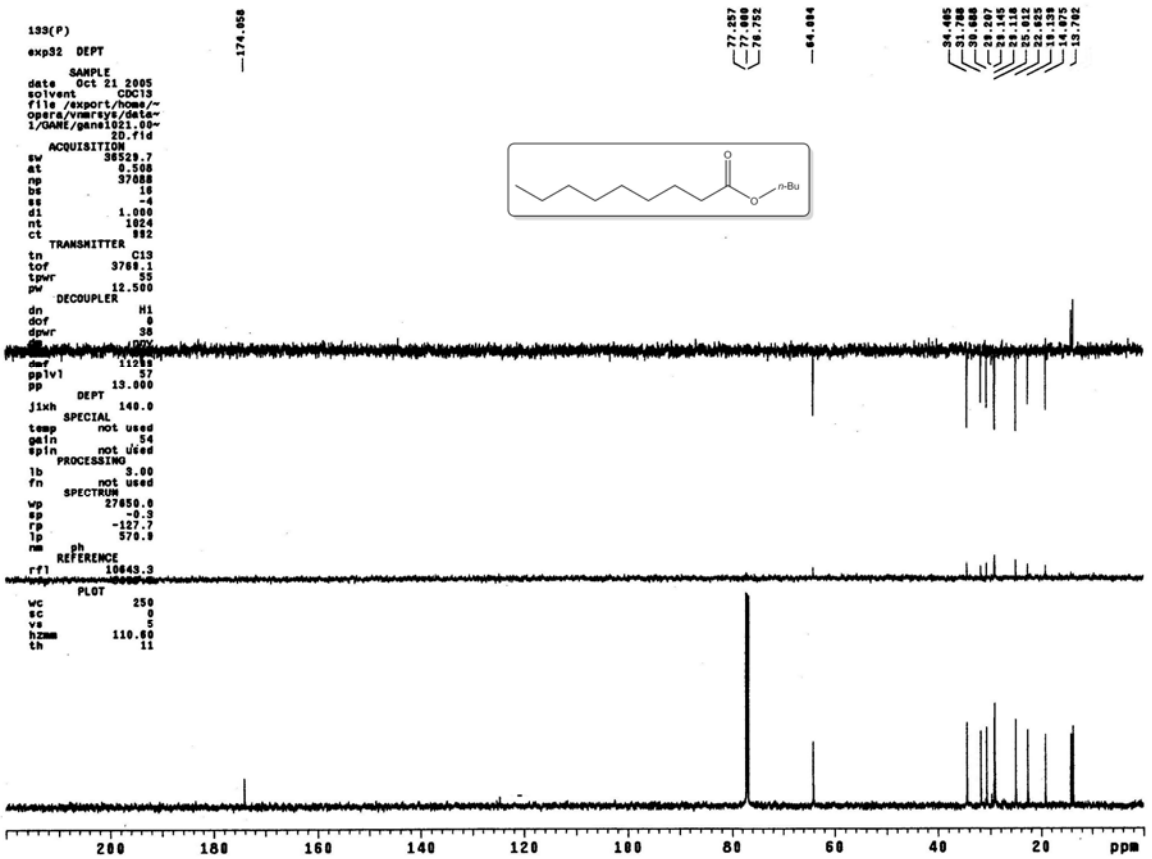


Butyl octanoate (5a) ($CDCl_3$)

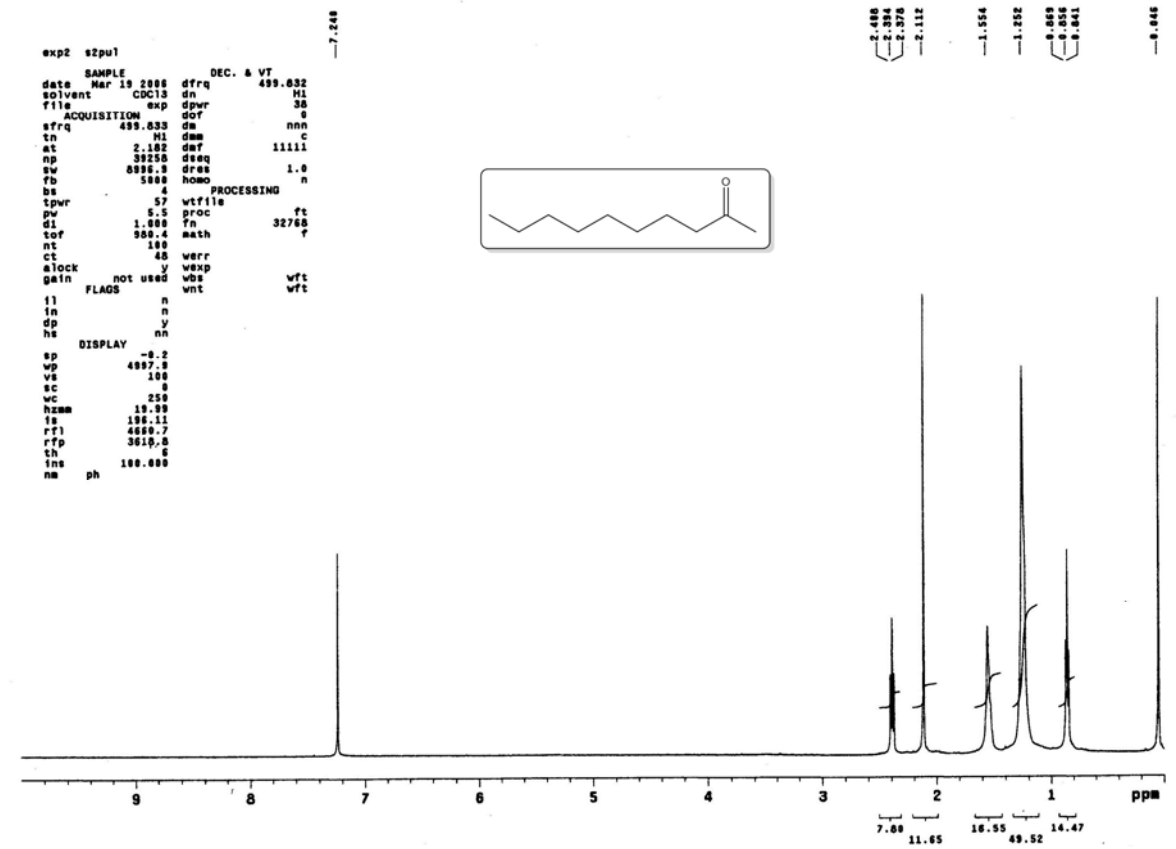


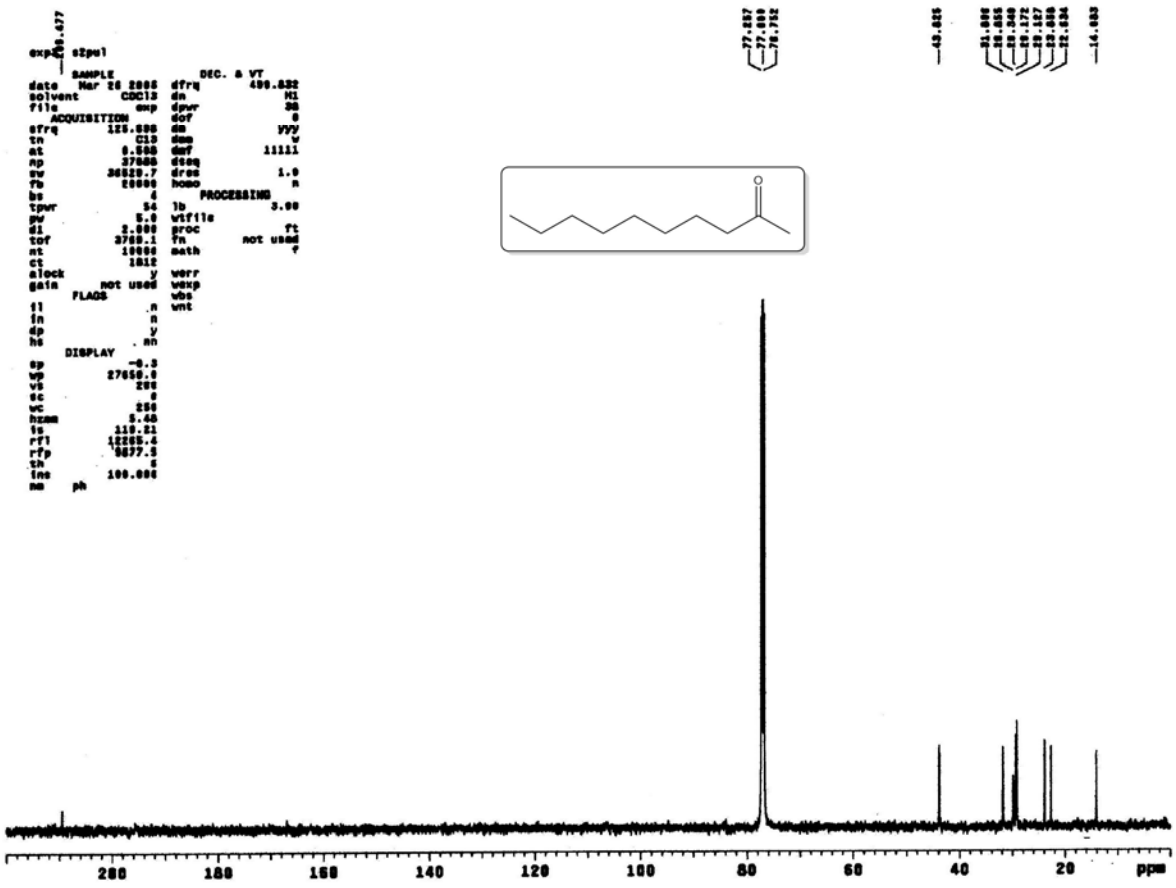
Butyl nonanoate (5b) ($CDCl_3$)



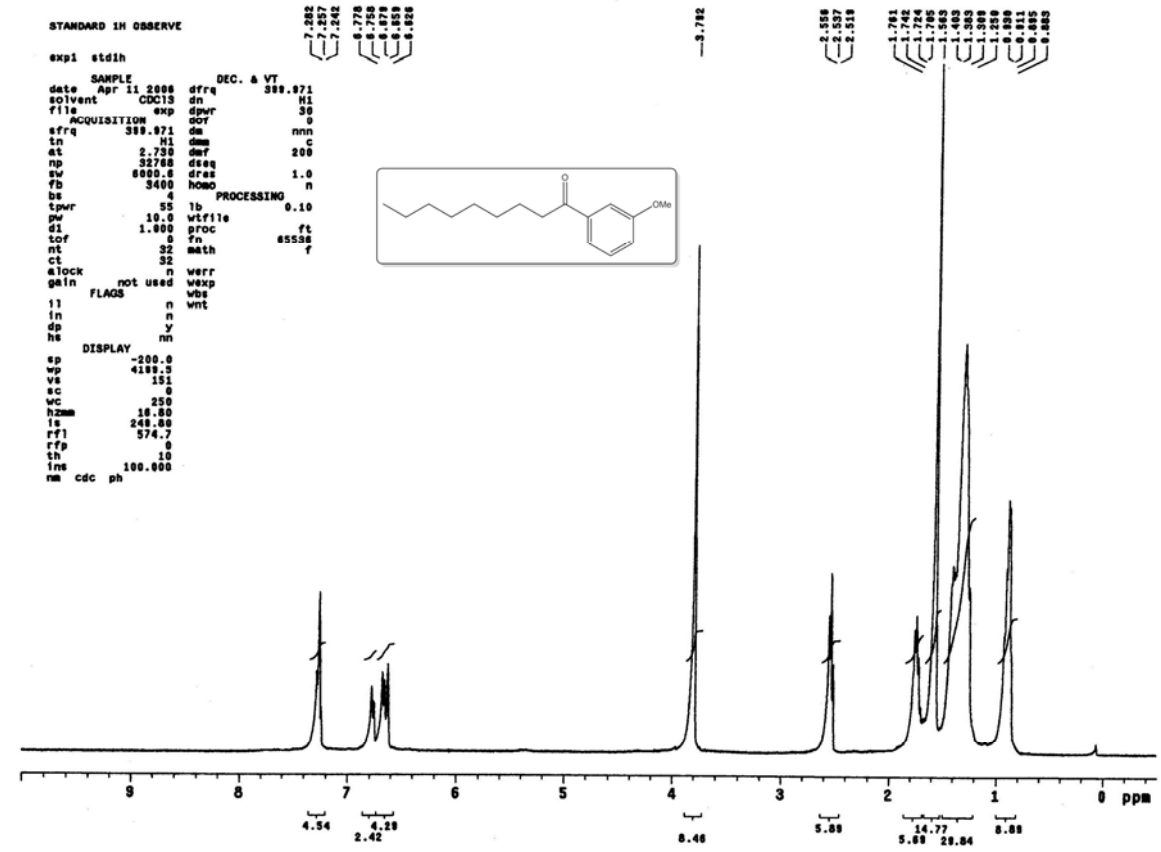


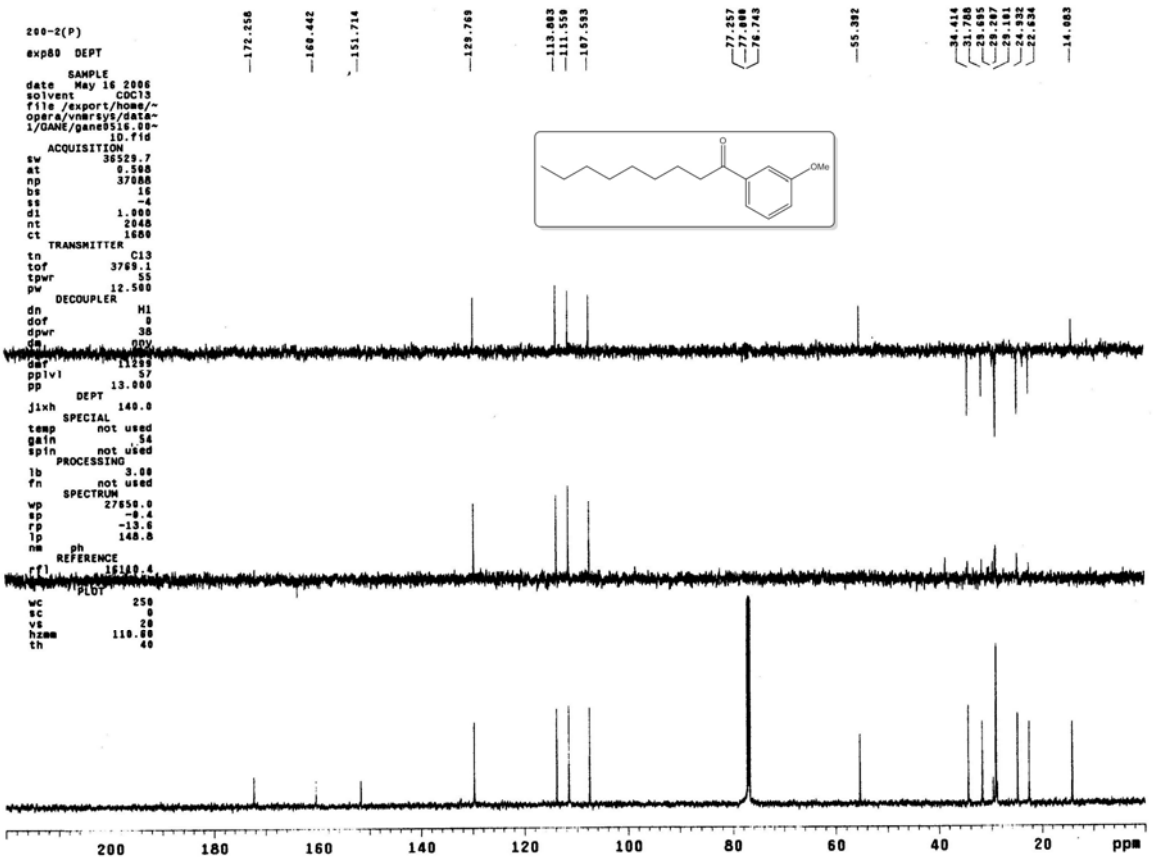
Decan-2-one (5c) ($CDCl_3$)



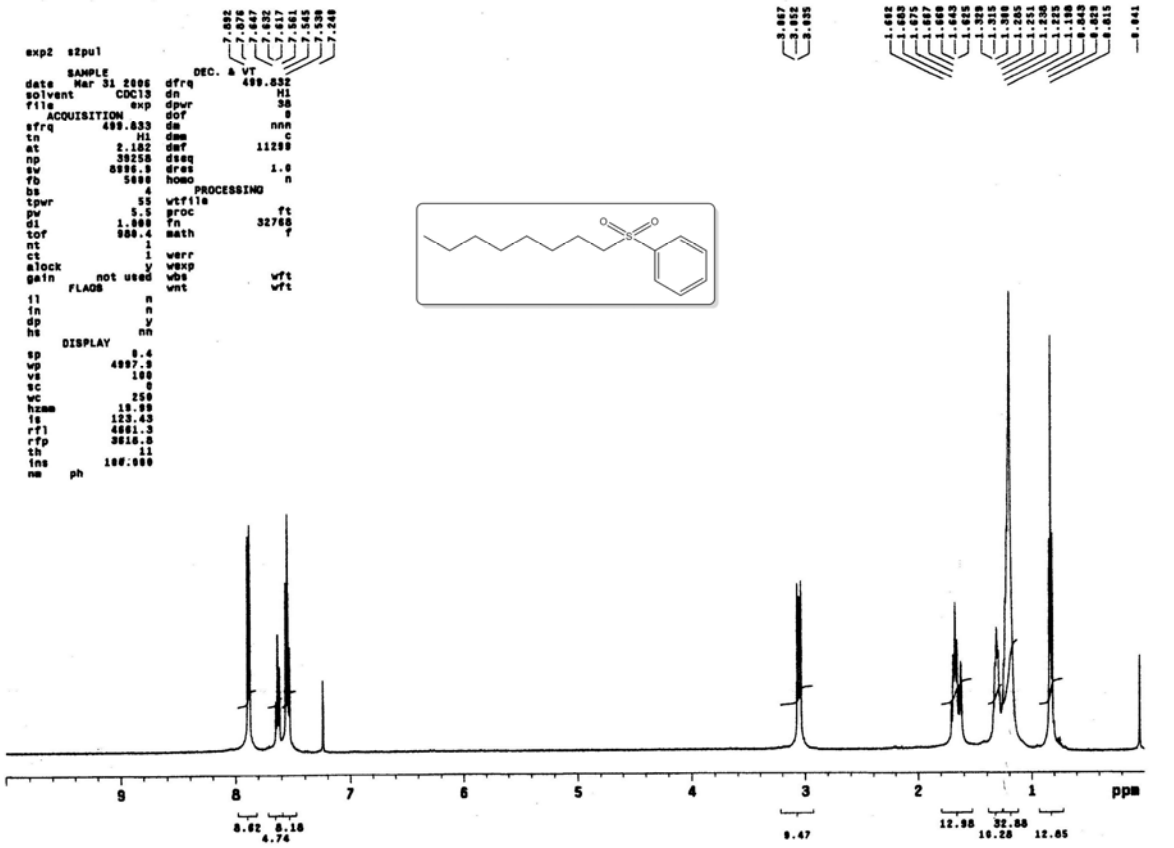


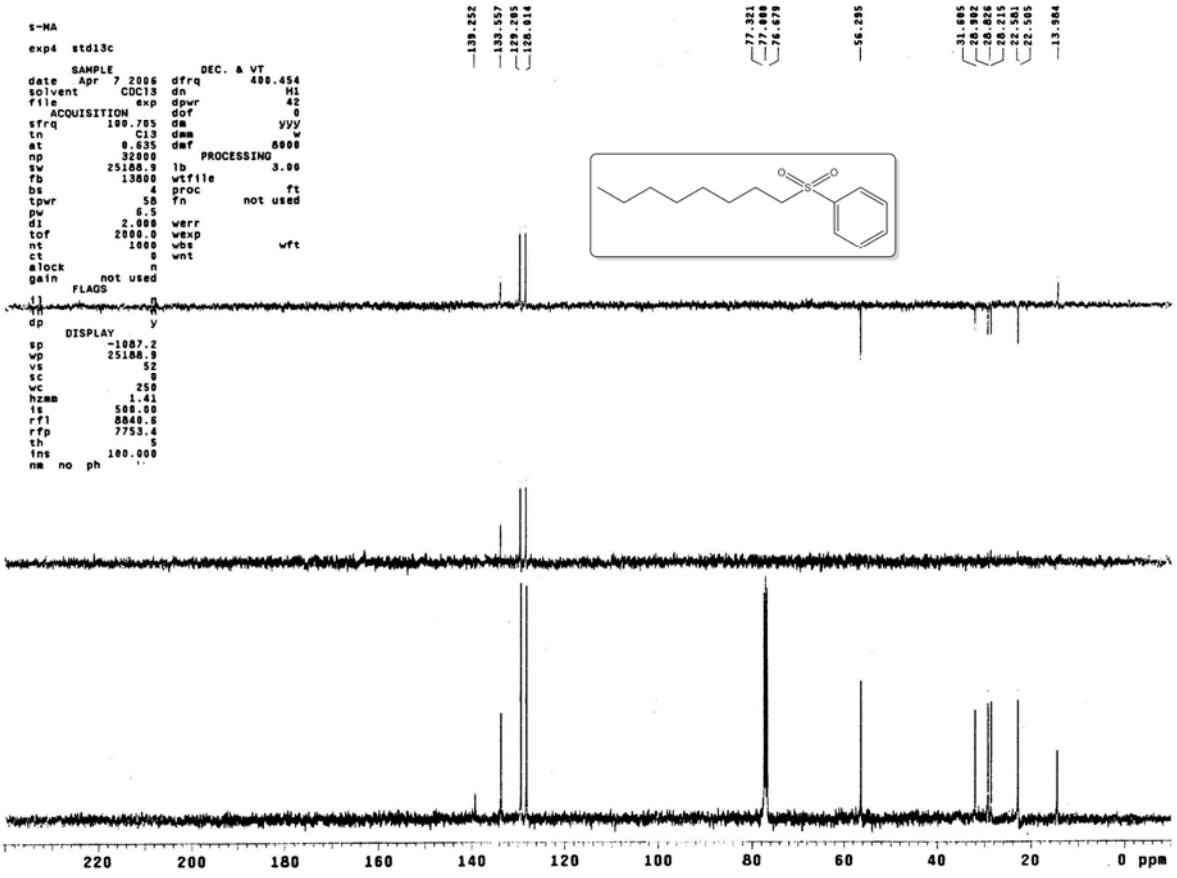
1-(3-Methoxyphenyl)nonan-1-one (5d) ($CDCl_3$)



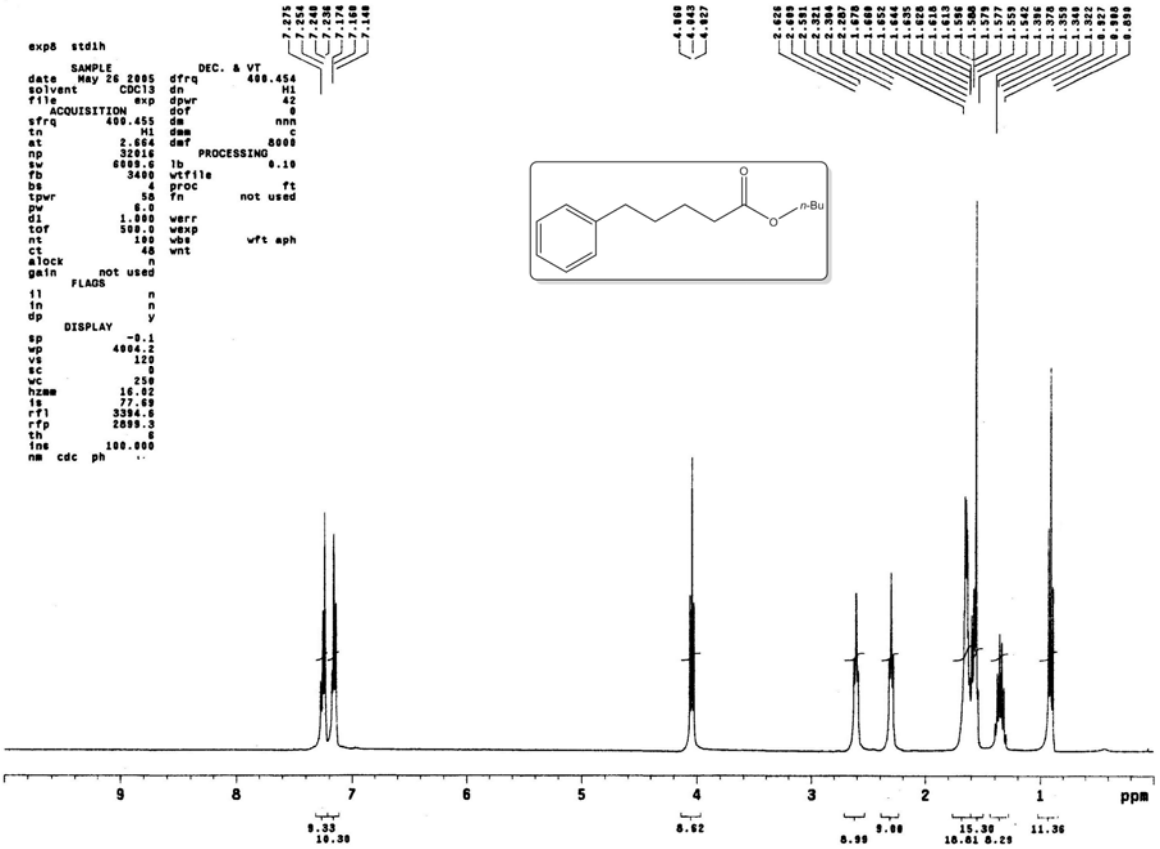


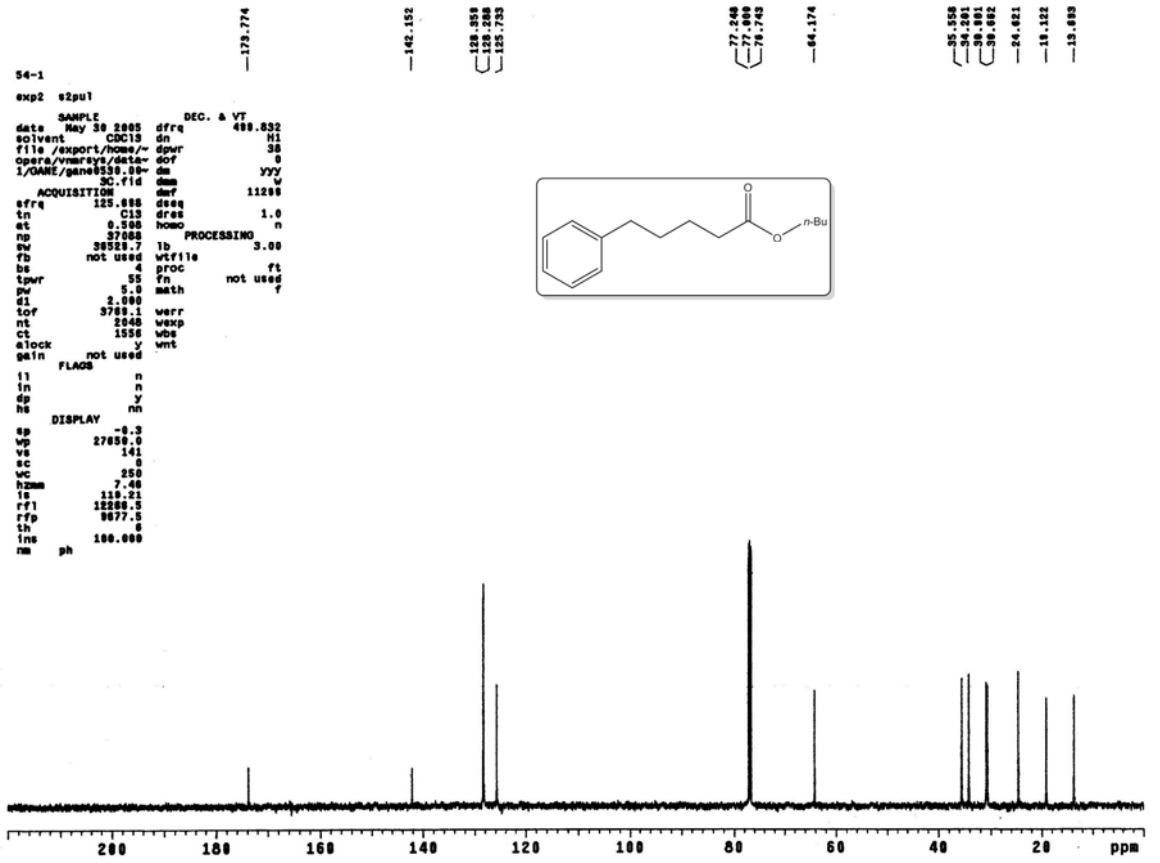
Octyl phenyl sulfone (5e) ($CDCl_3$)



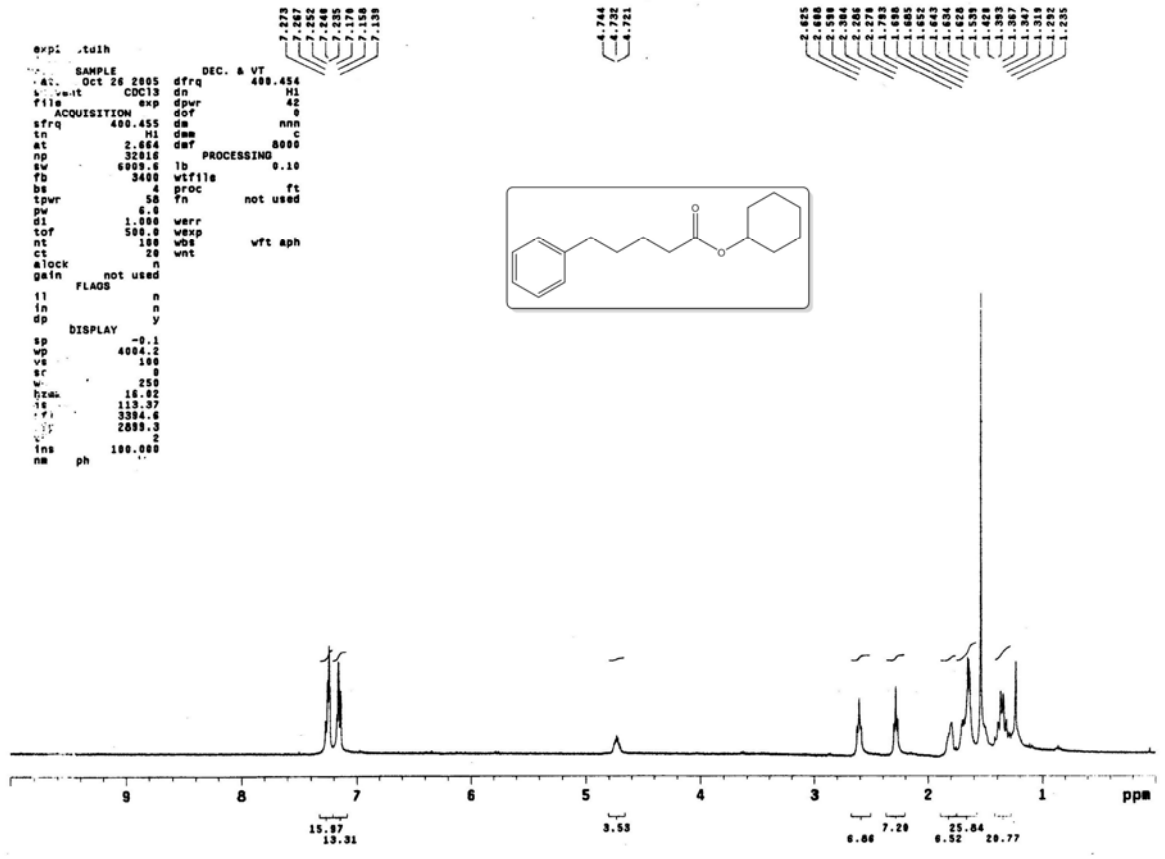


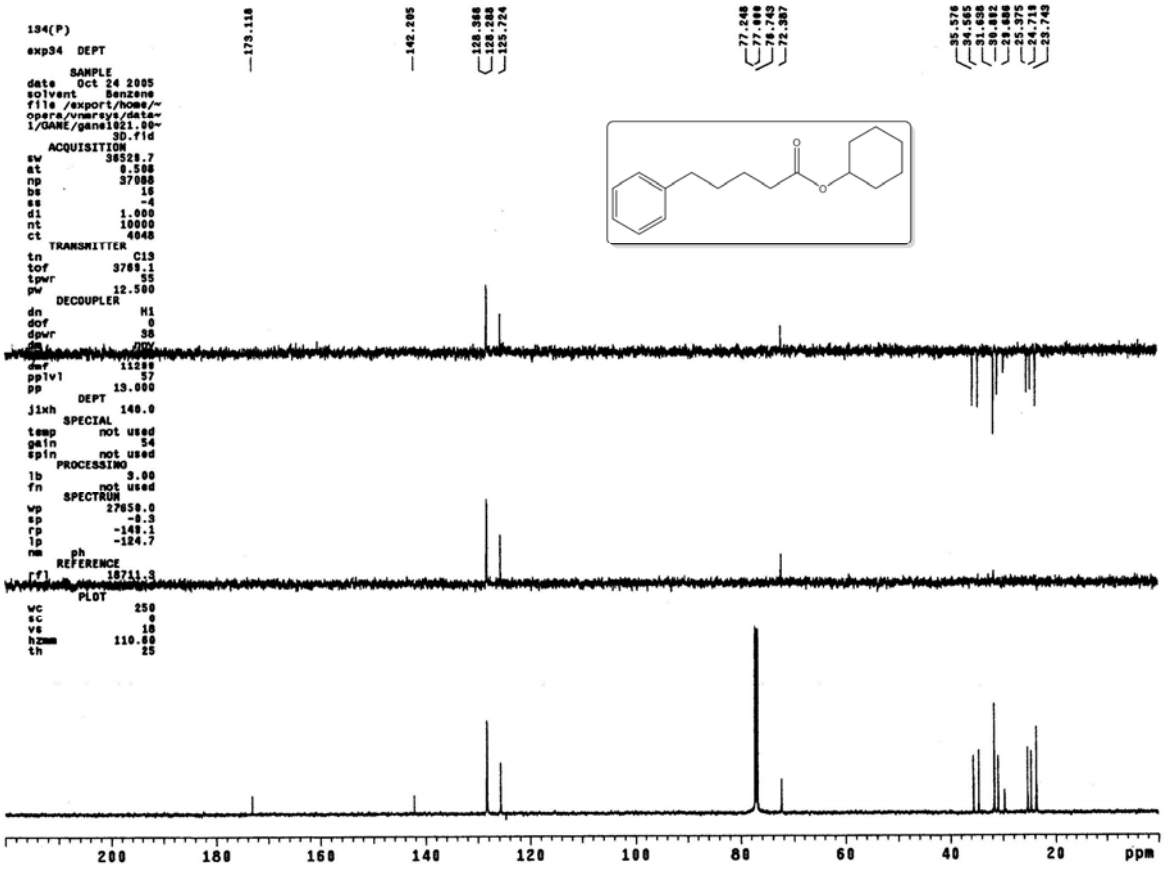
Butyl 5-phenylpentanoate (5f) ($CDCl_3$)



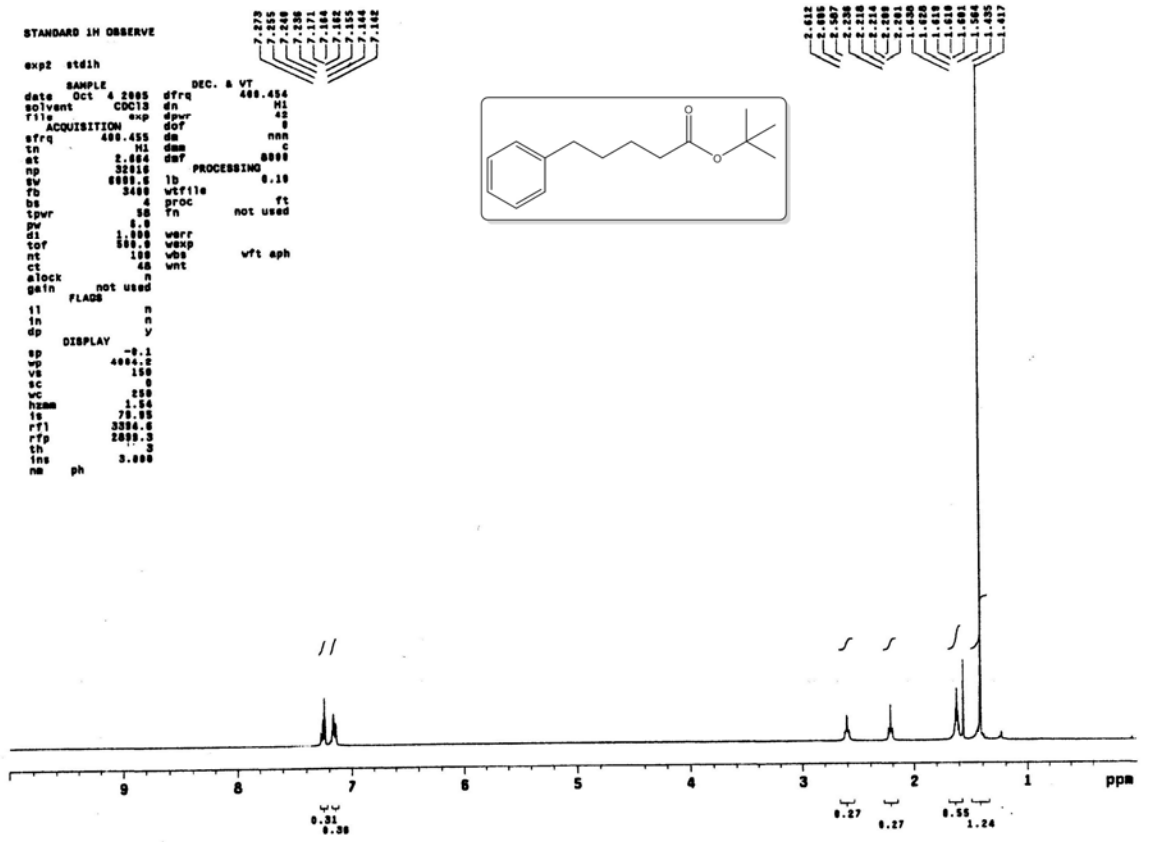


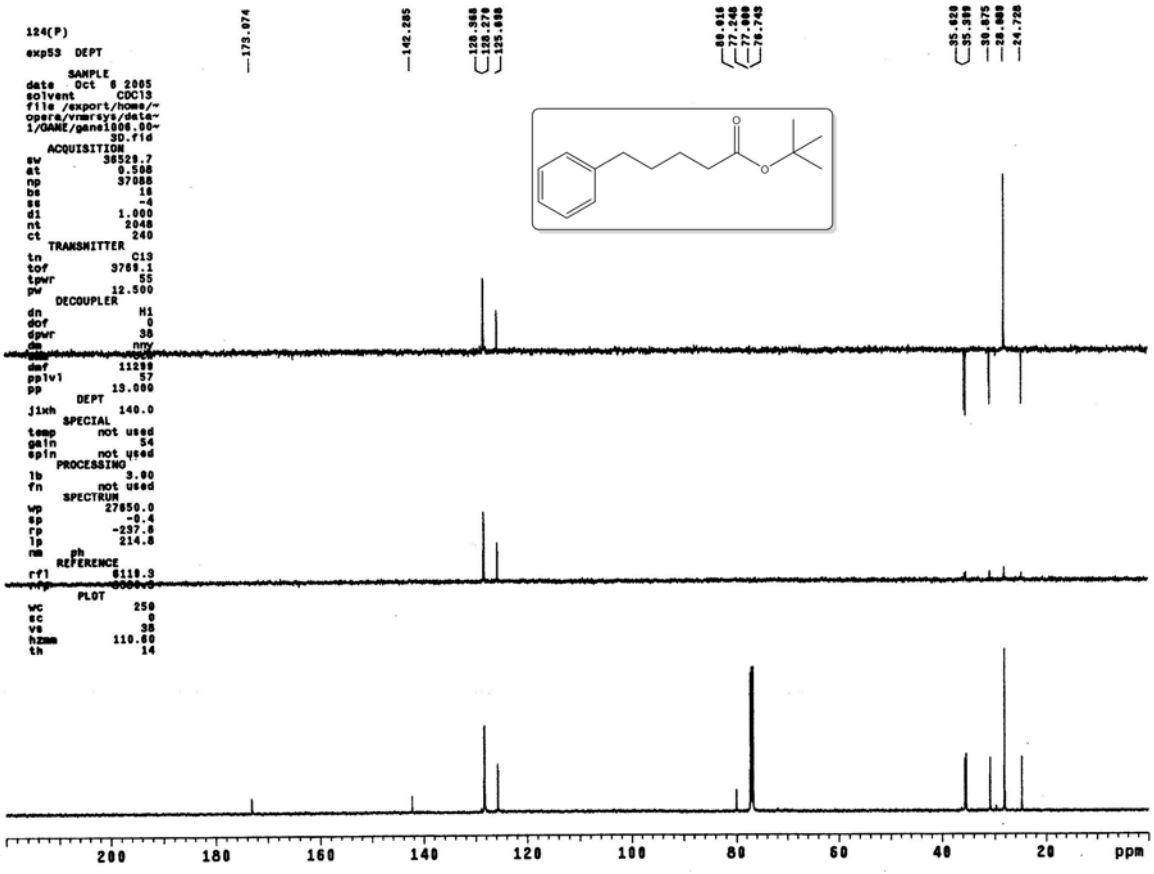
Cyclohexyl 5-phenylpentanoate (5g) ($CDCl_3$)



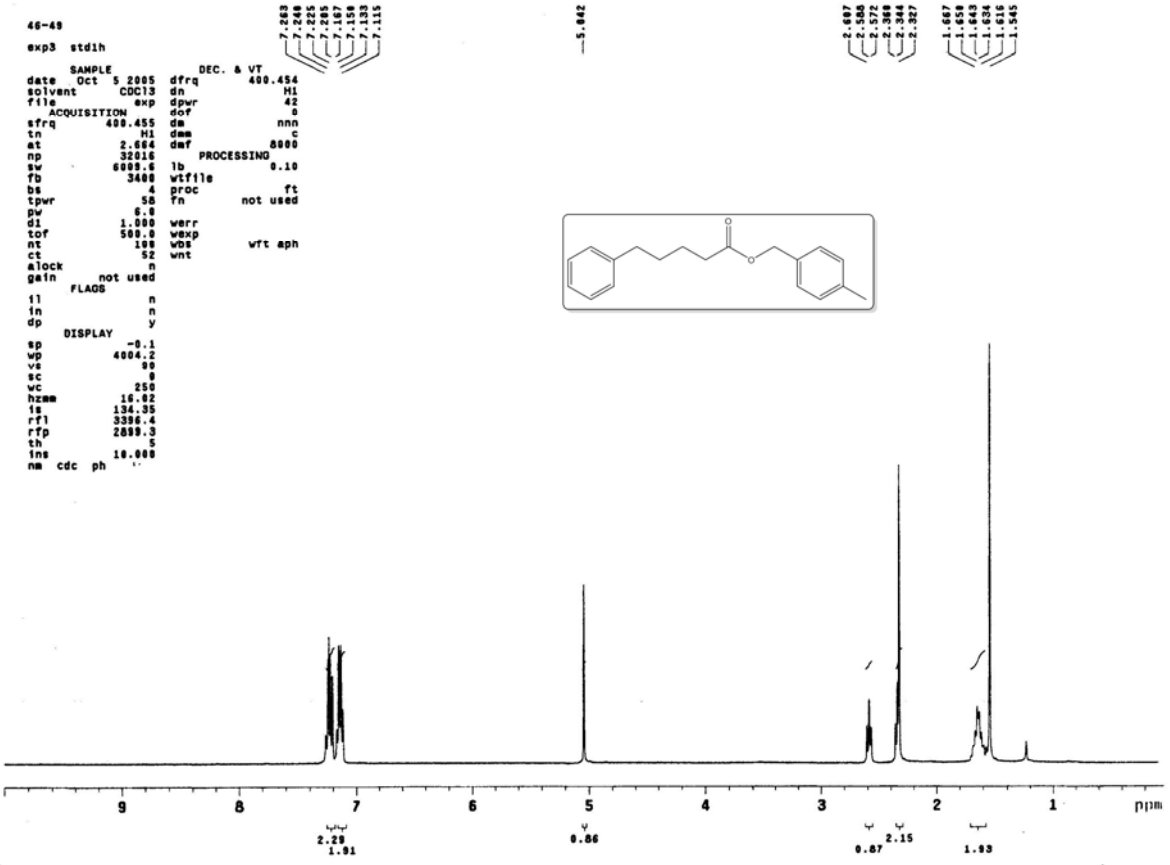


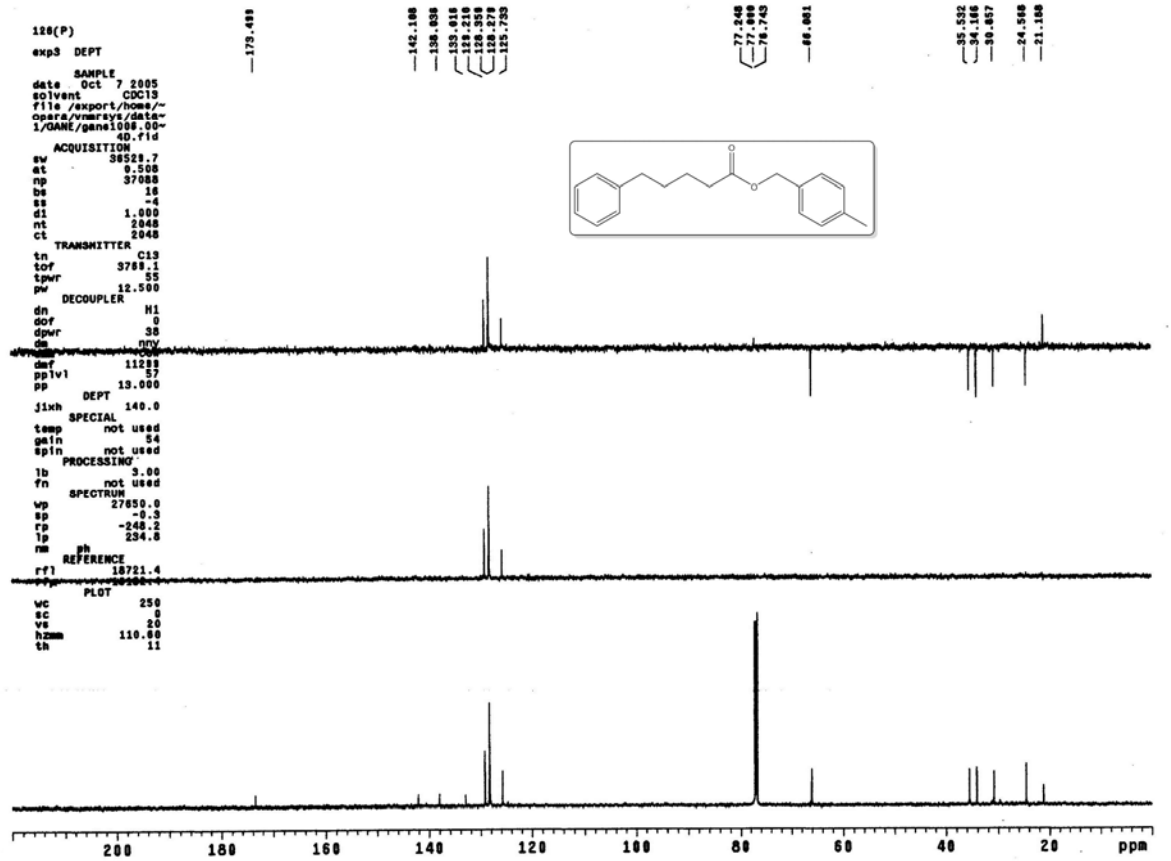
tert-Butyl 5-phenylpentanoate (5h) ($CDCl_3$)



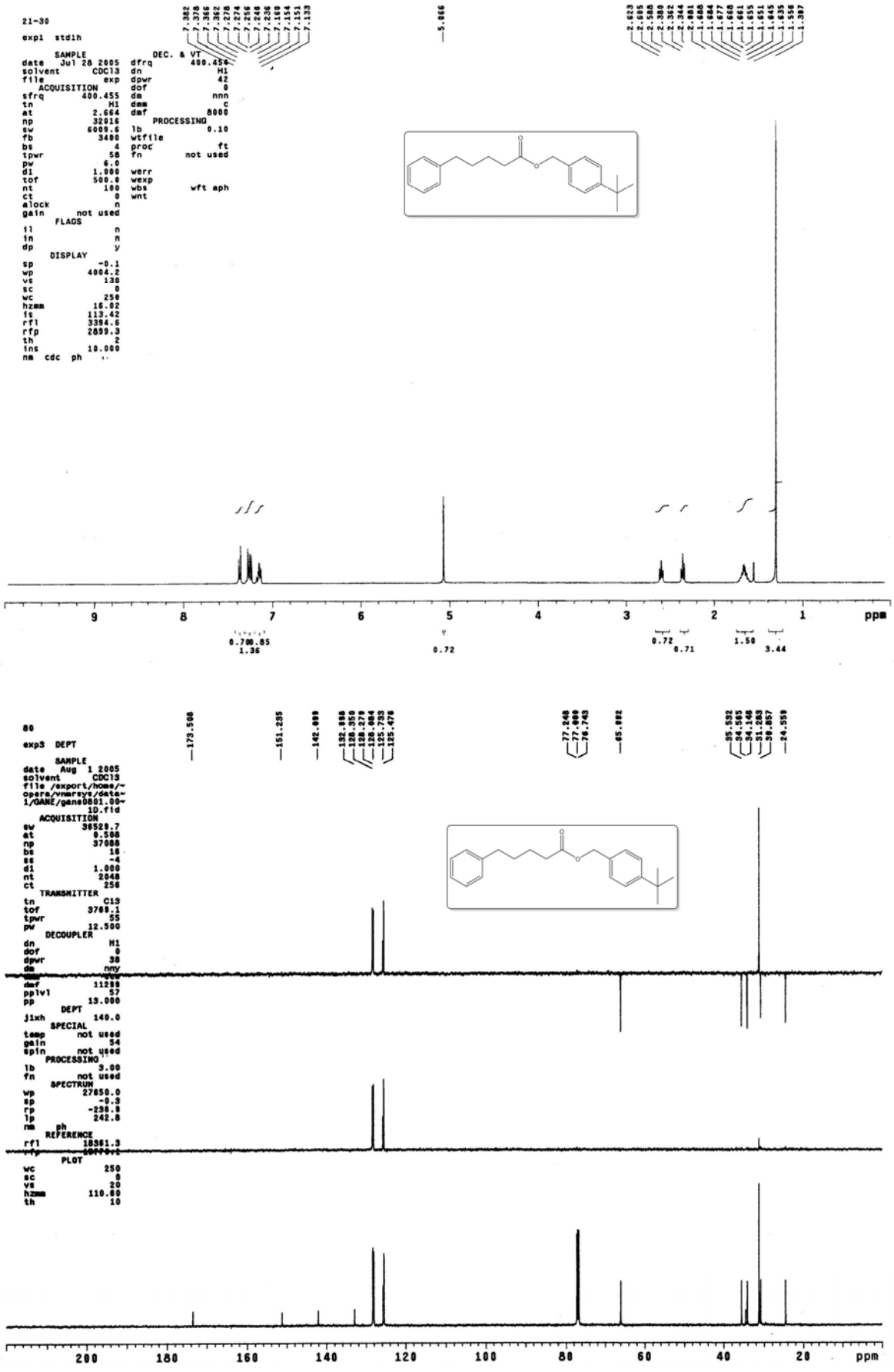


4-Methylbenzyl 5-phenylpentanoate (5i) ($CDCl_3$)

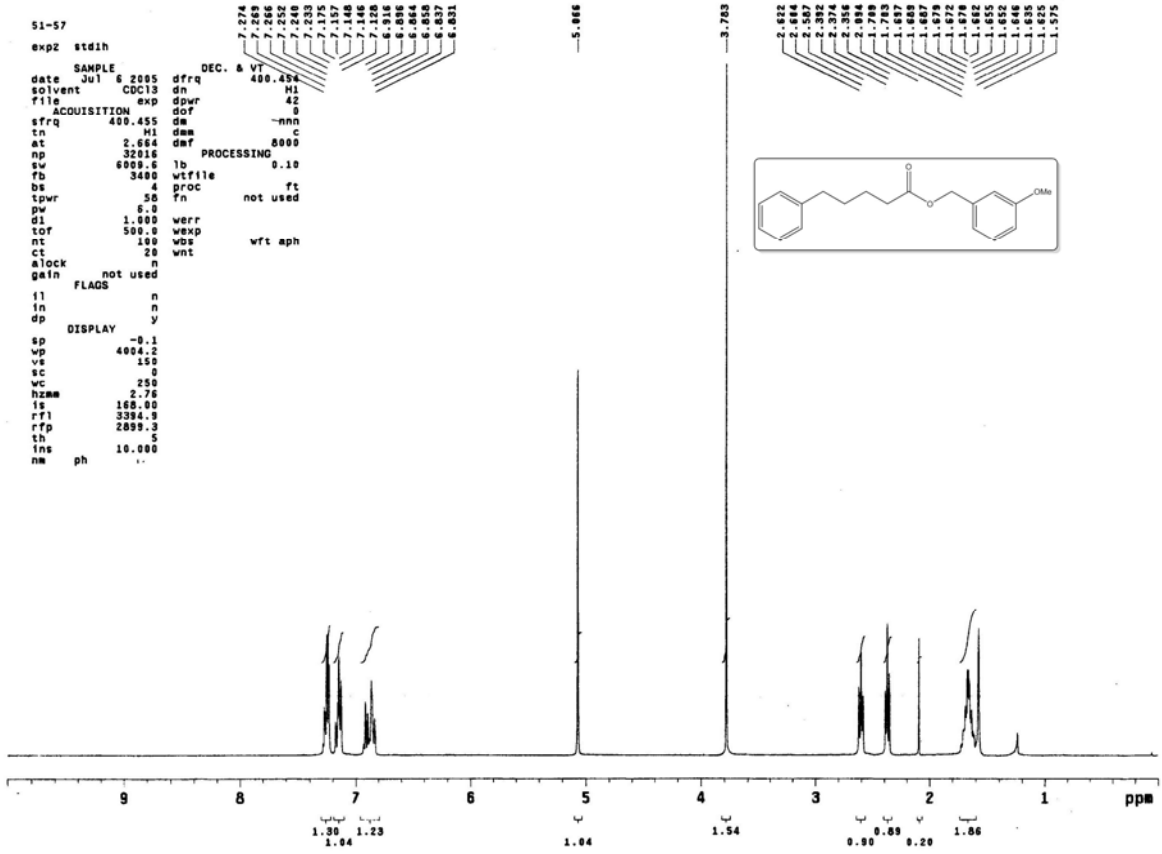


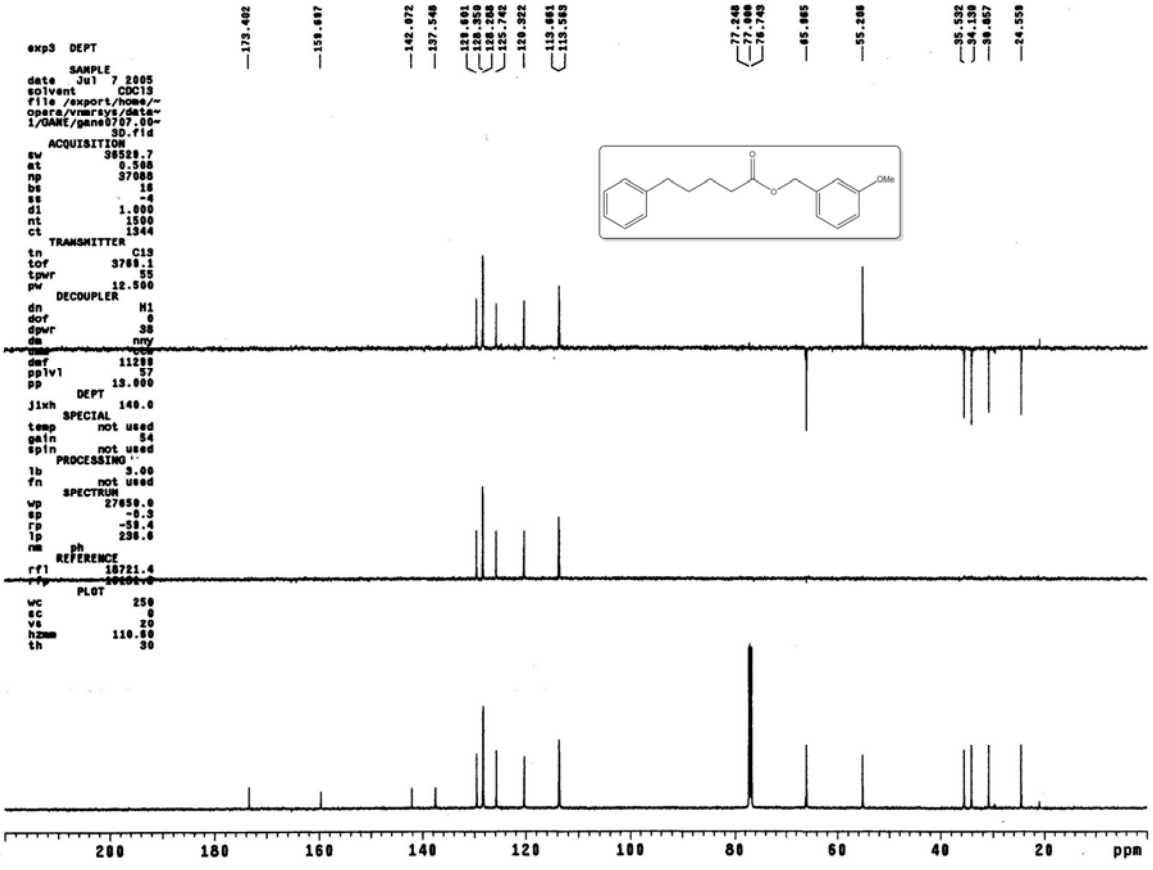


4-(*tert*-Butyl)benzyl 5-phenylpentanoate (5j) ($CDCl_3$)

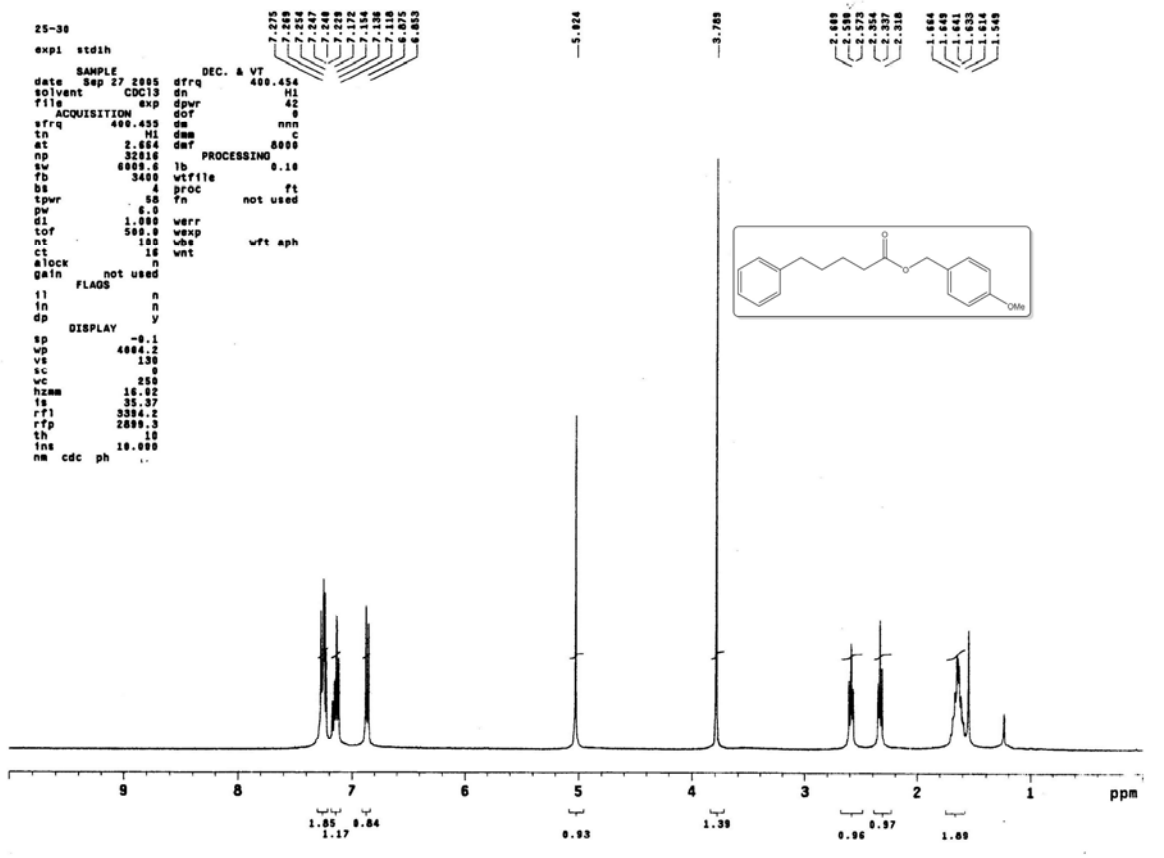


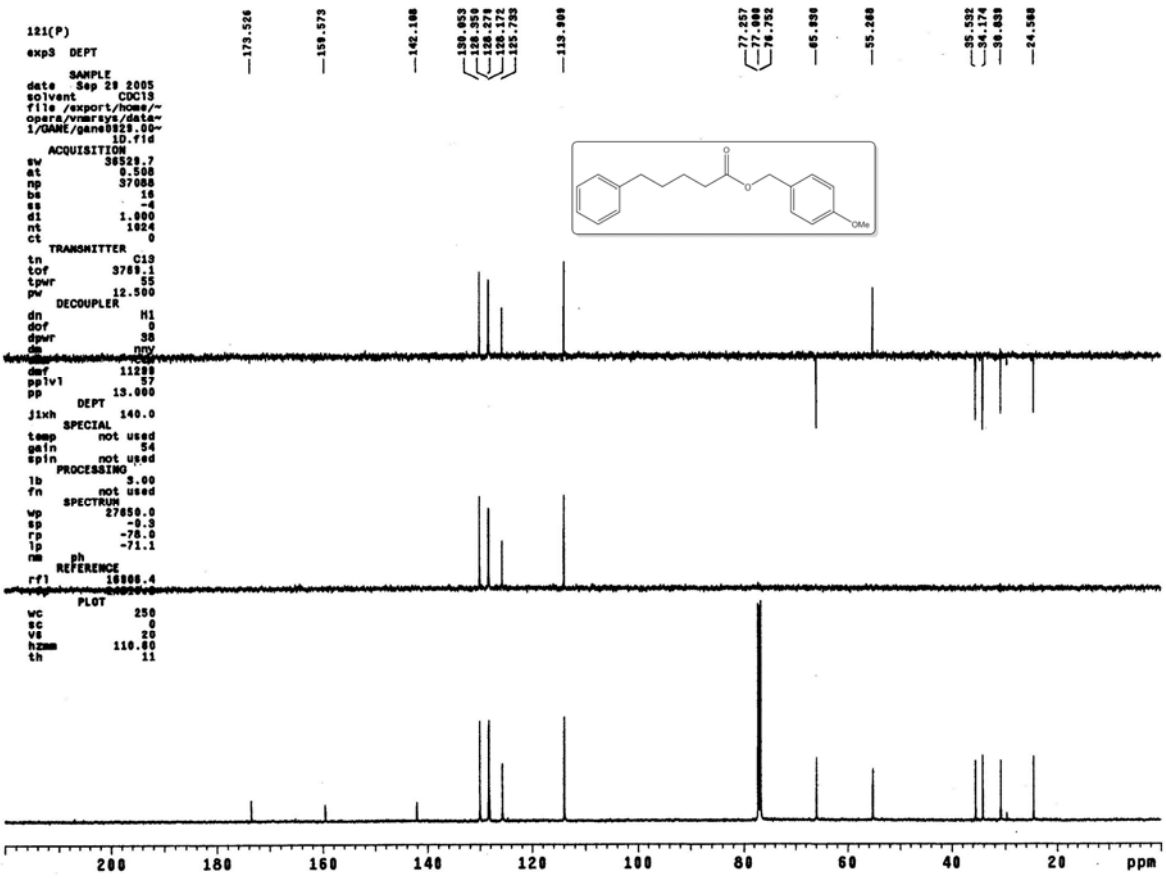
3-Methoxybenzyl 5-phenylpentanoate (5k) ($CDCl_3$)



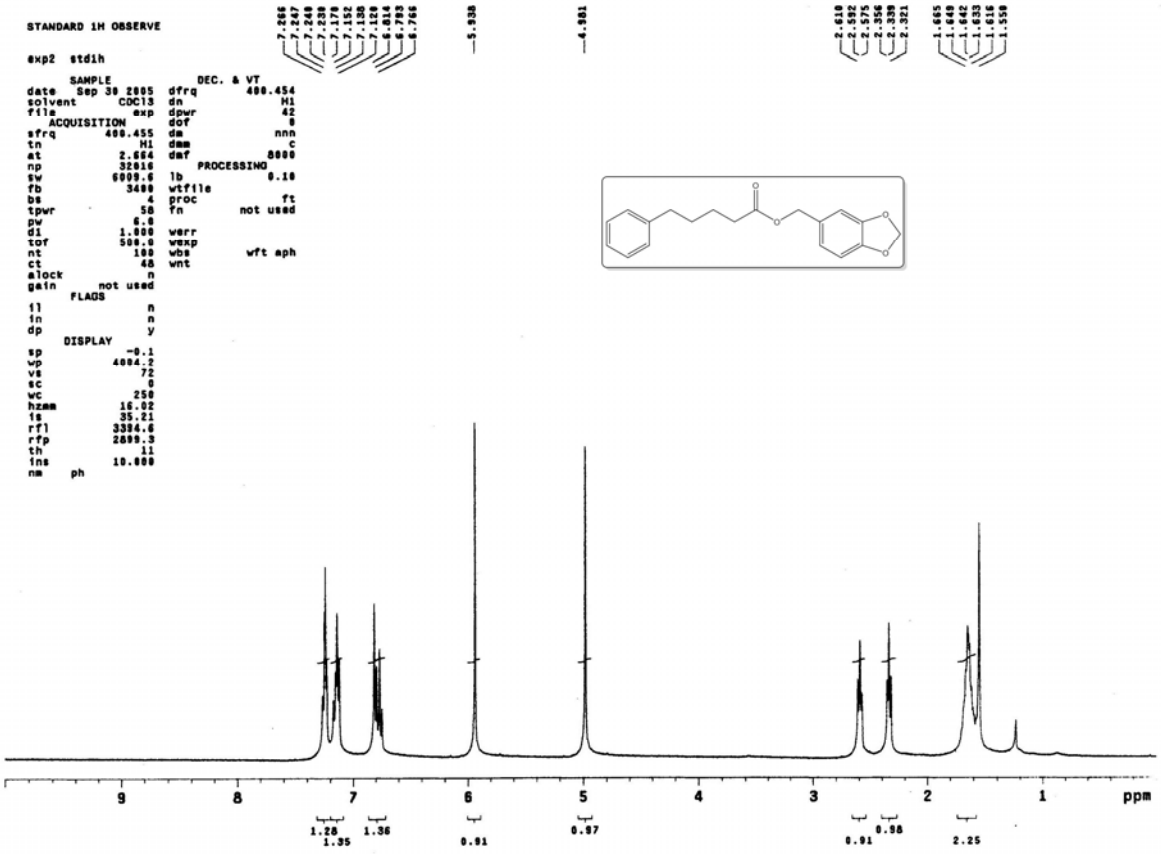


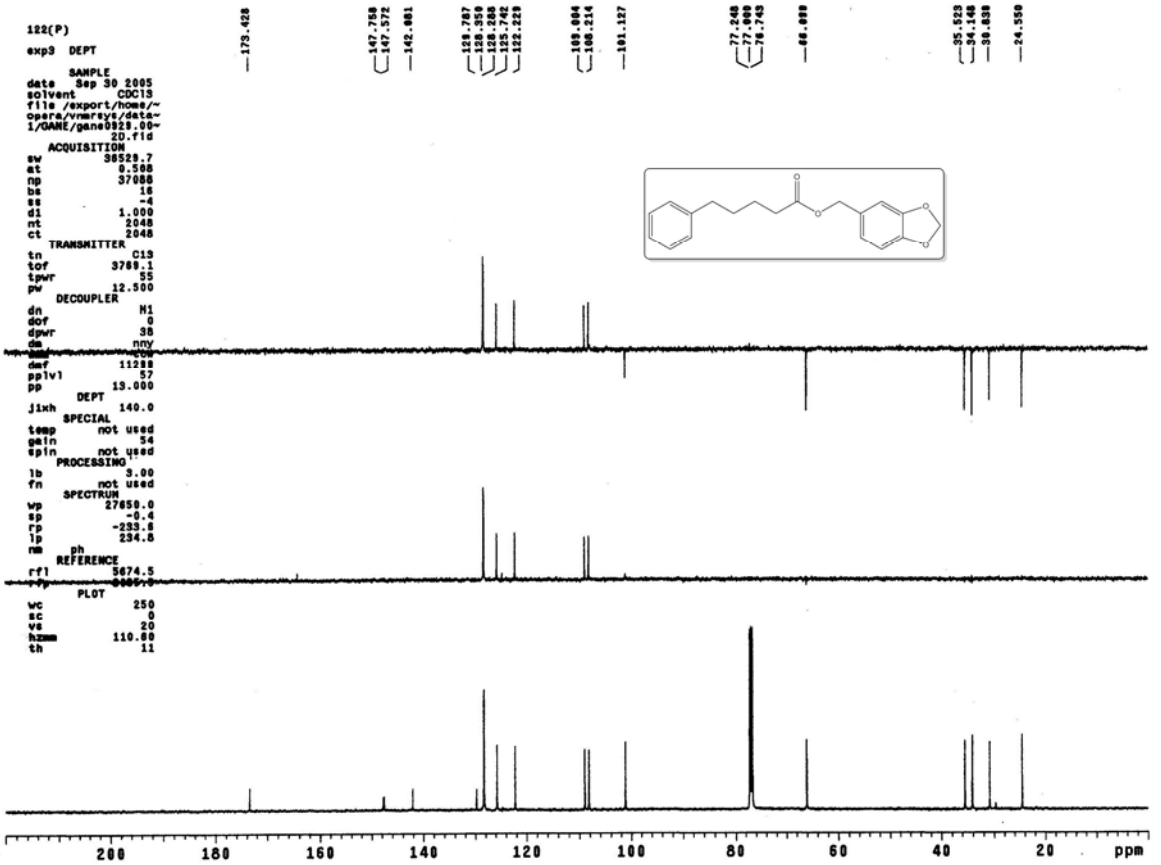
4-Methoxybenzyl 5-phenylpentanoate (5l) ($CDCl_3$)



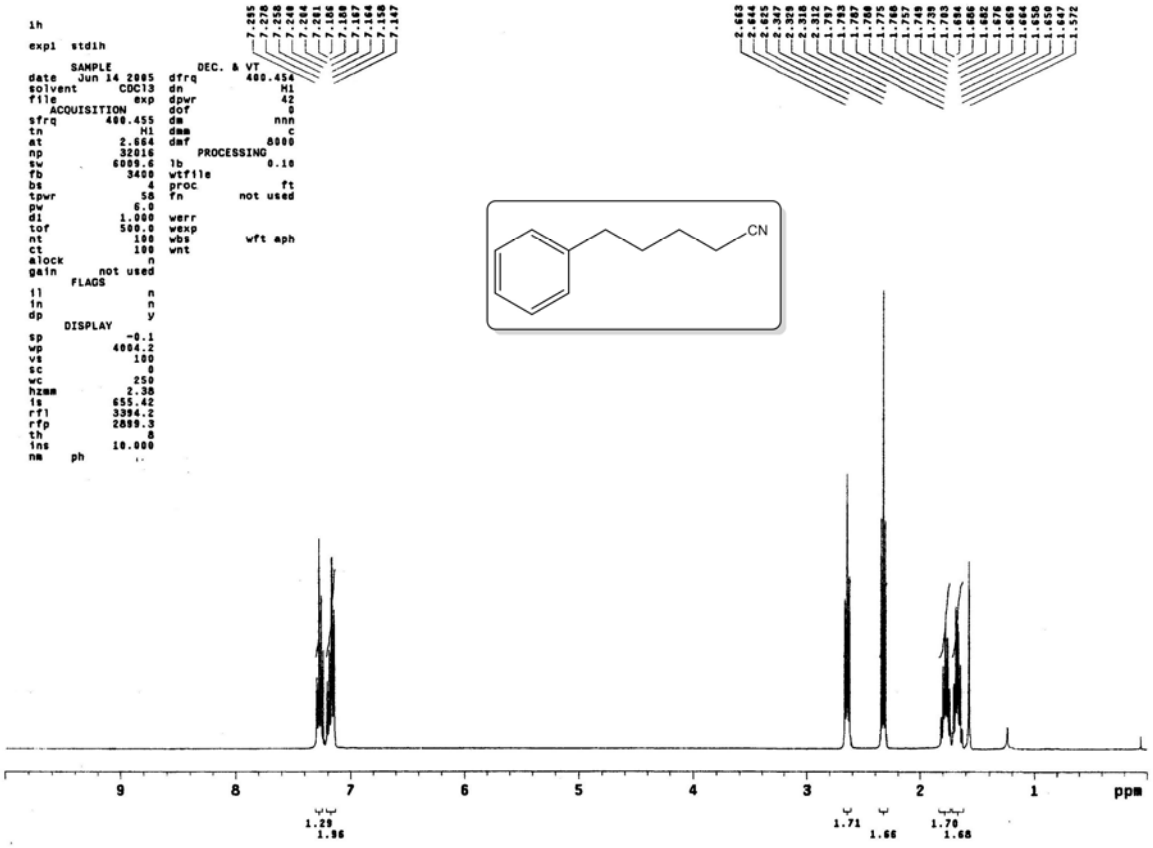


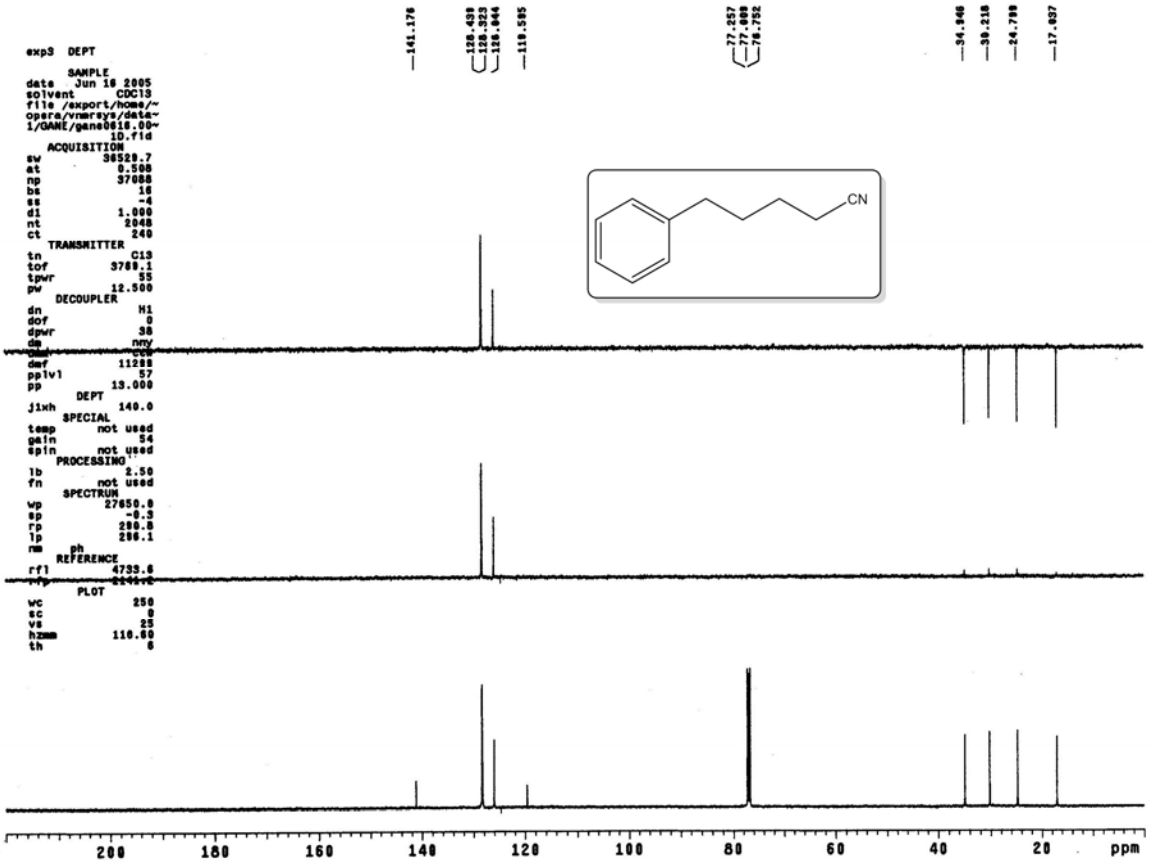
Benzo[*d*][1,3]dioxol-5-ylmethyl 5-phenylpentanoate (5m) ($CDCl_3$)



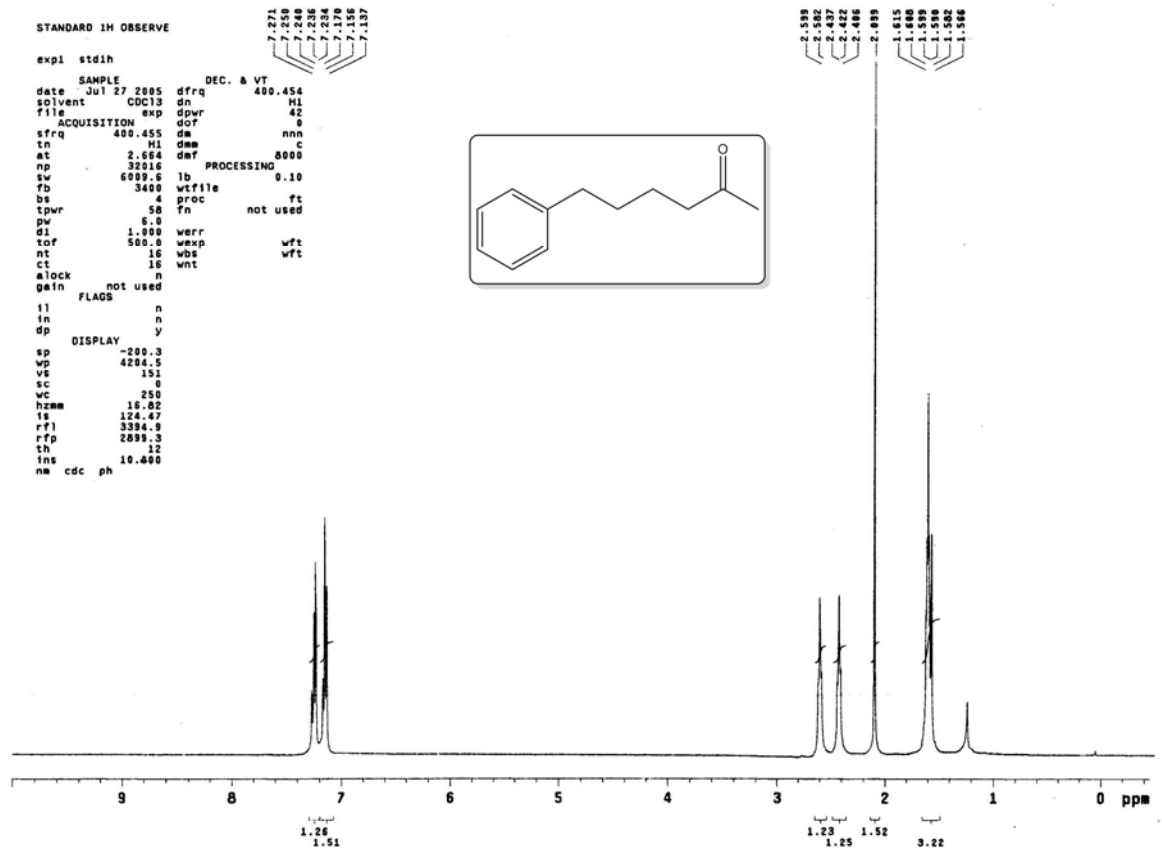


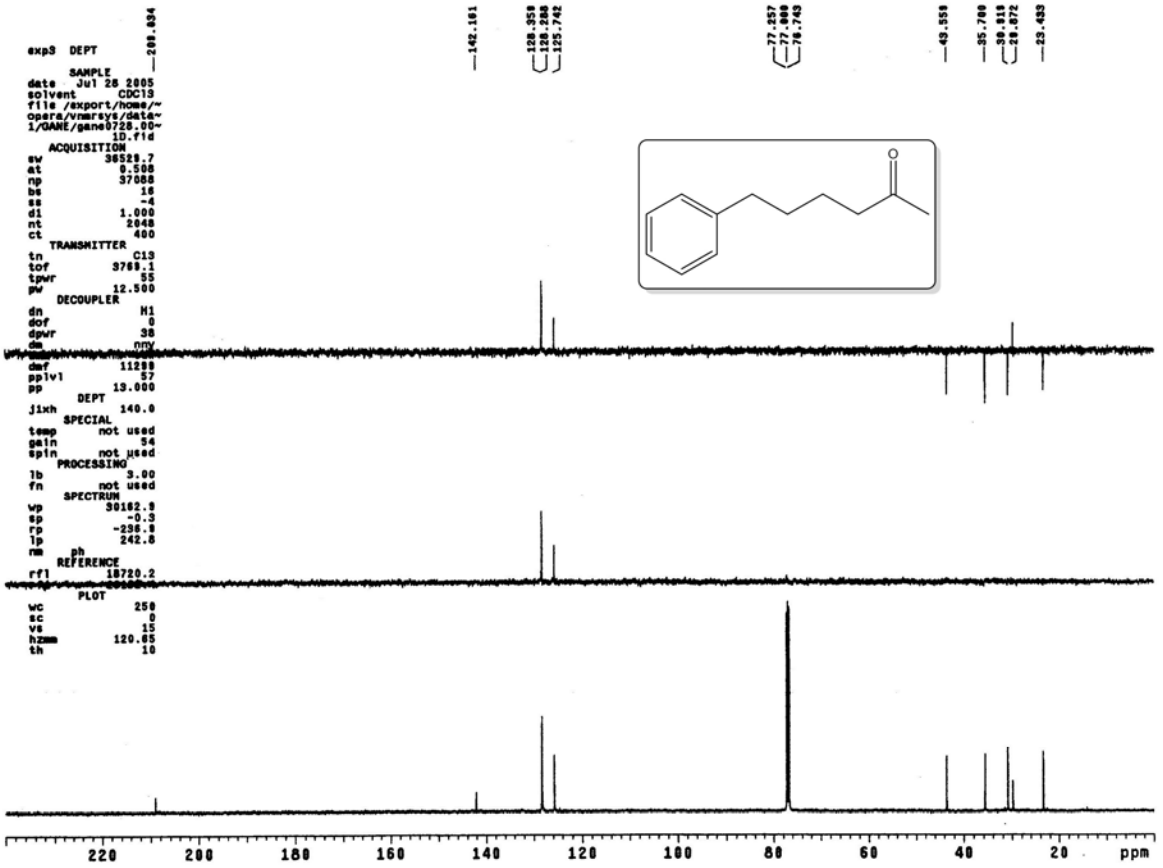
5-Phenylpentanenitrile (5n) ($CDCl_3$)



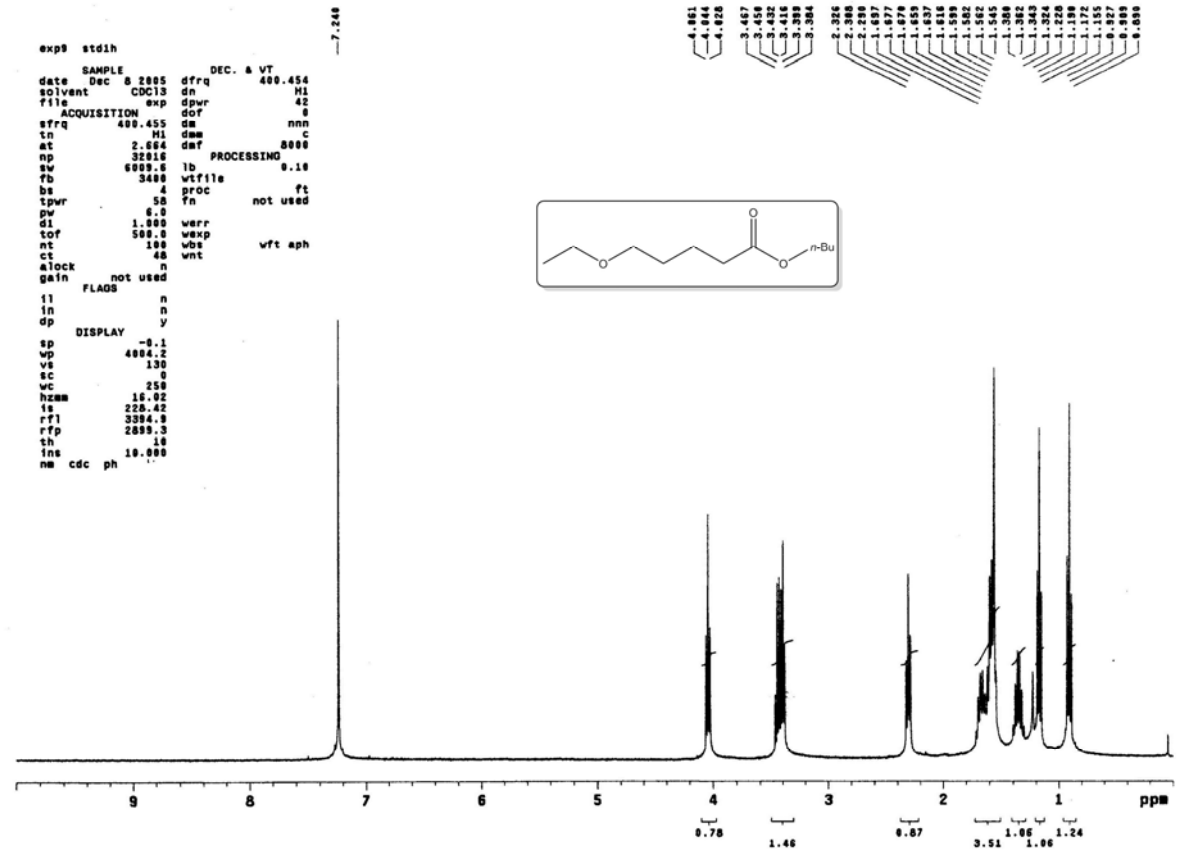


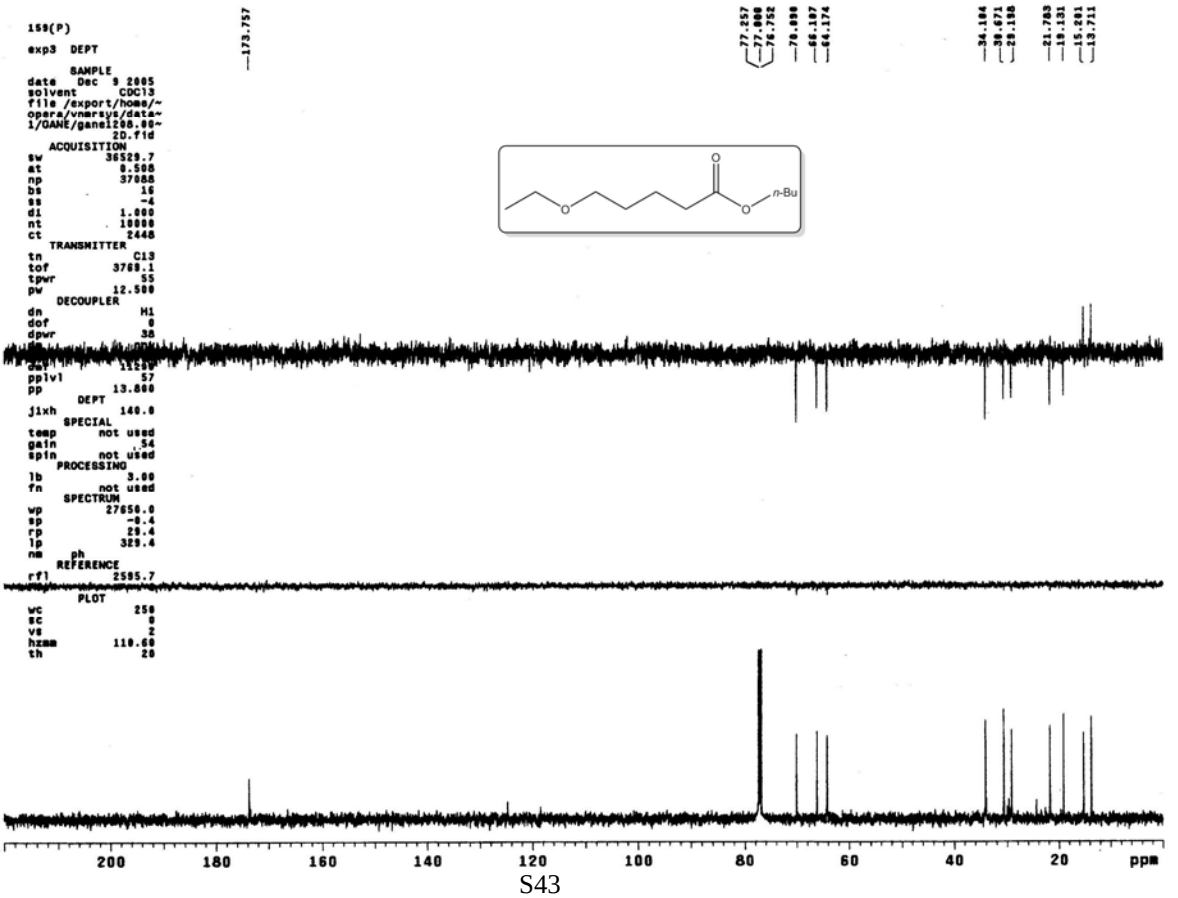
6-Phenylhexan-2-one (5o) ($CDCl_3$)



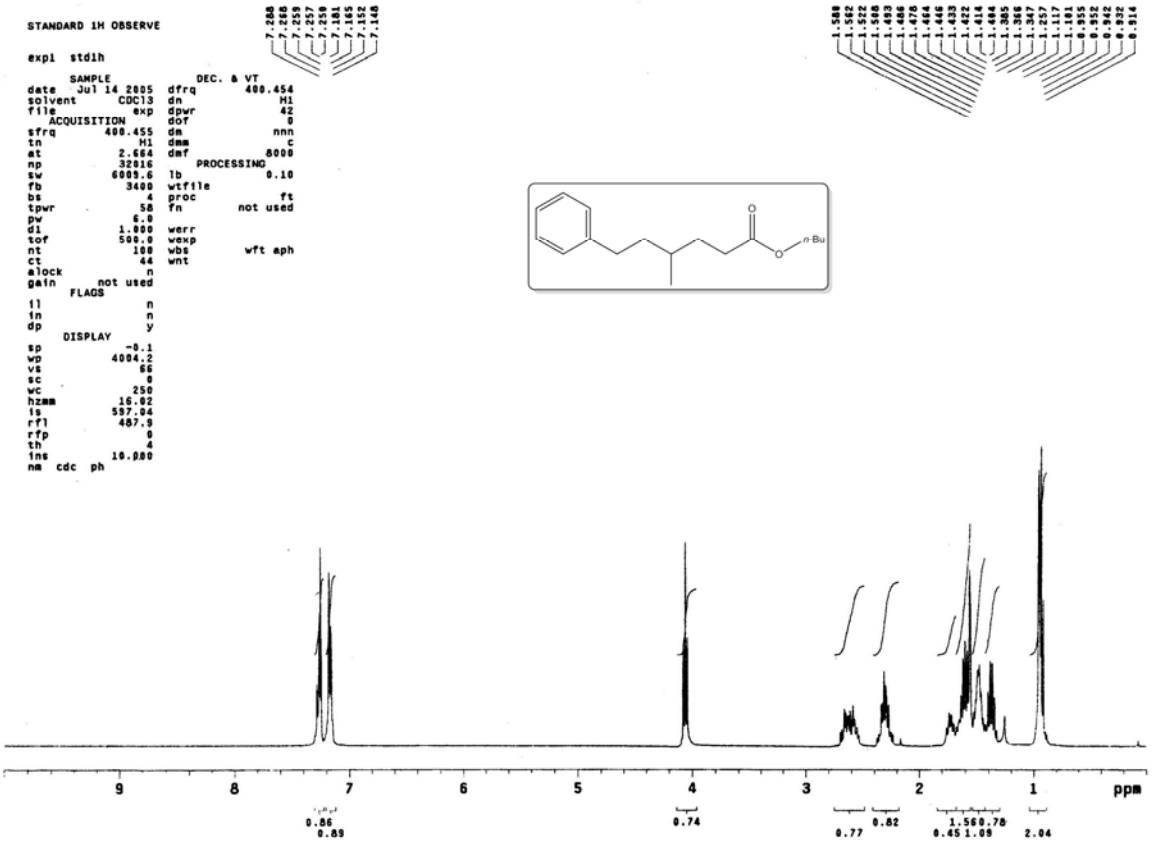


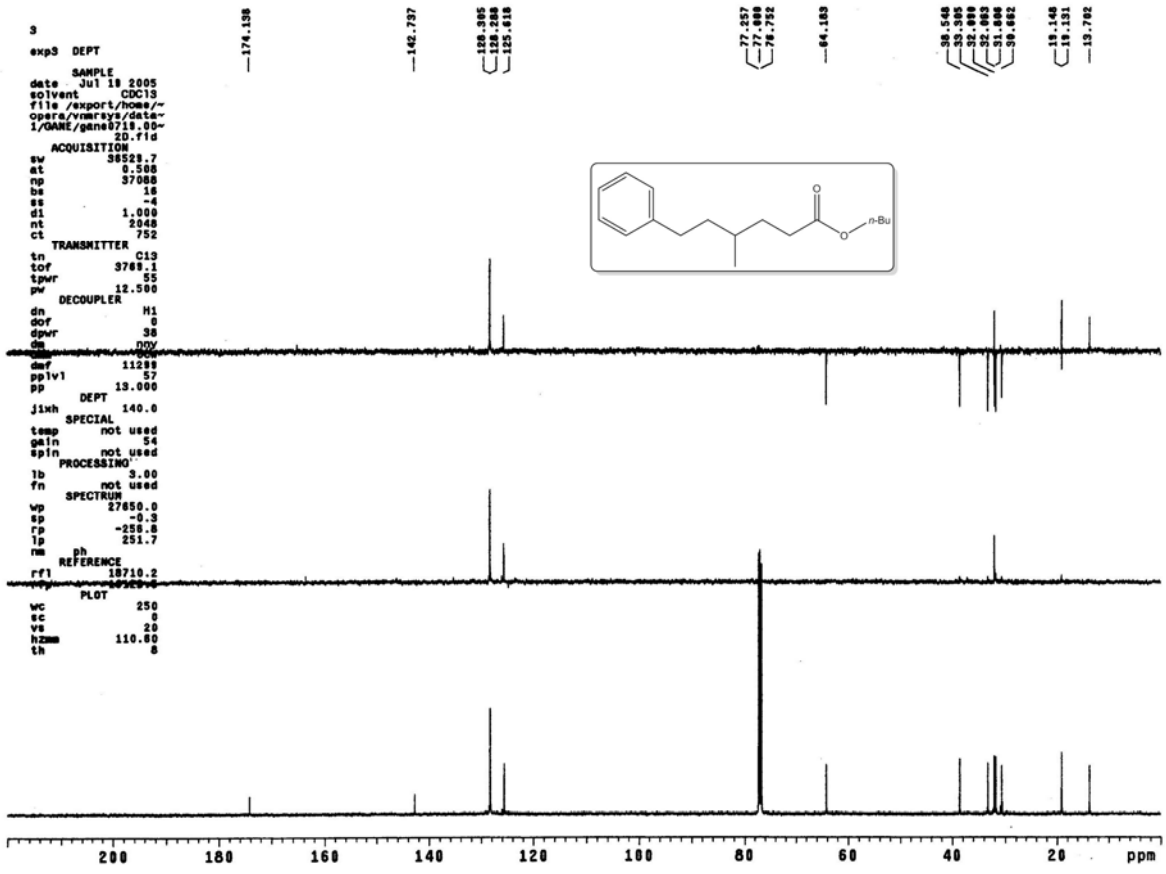
Butyl 5-ethoxypentanoate (5p) ($CDCl_3$)



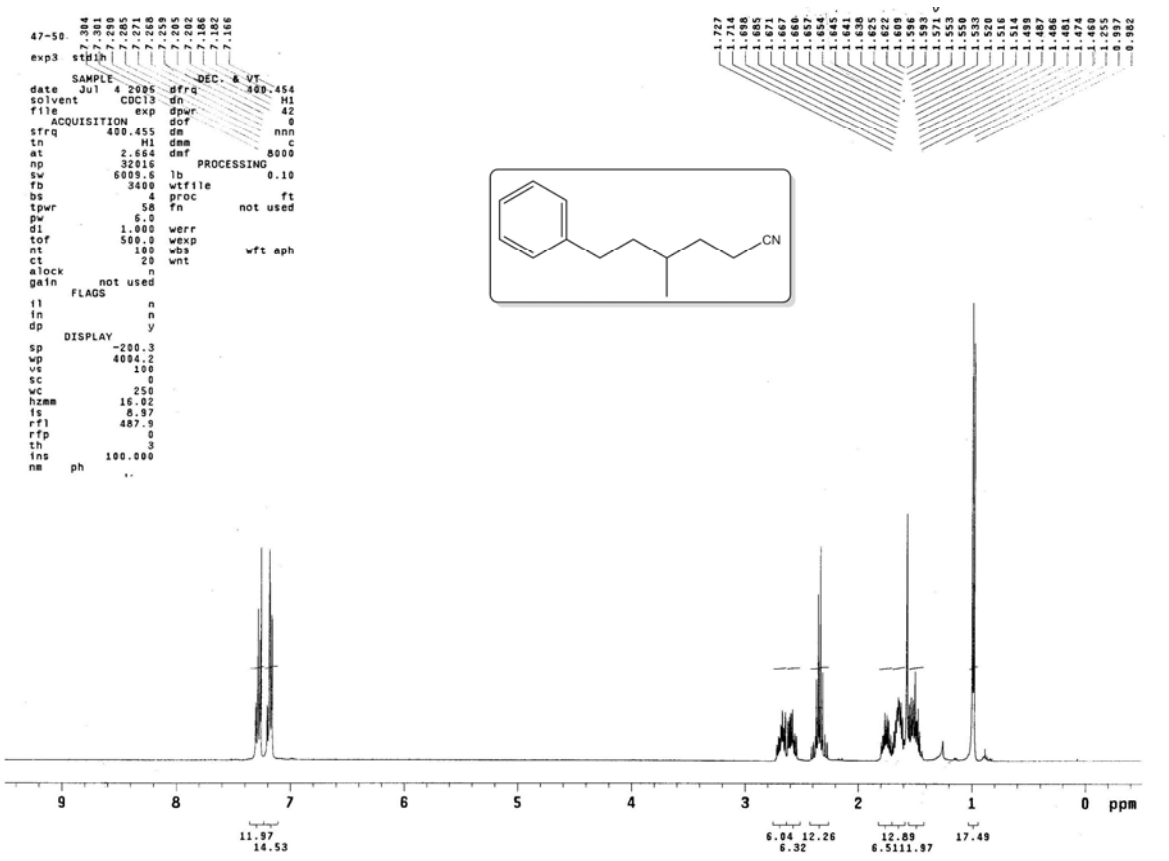


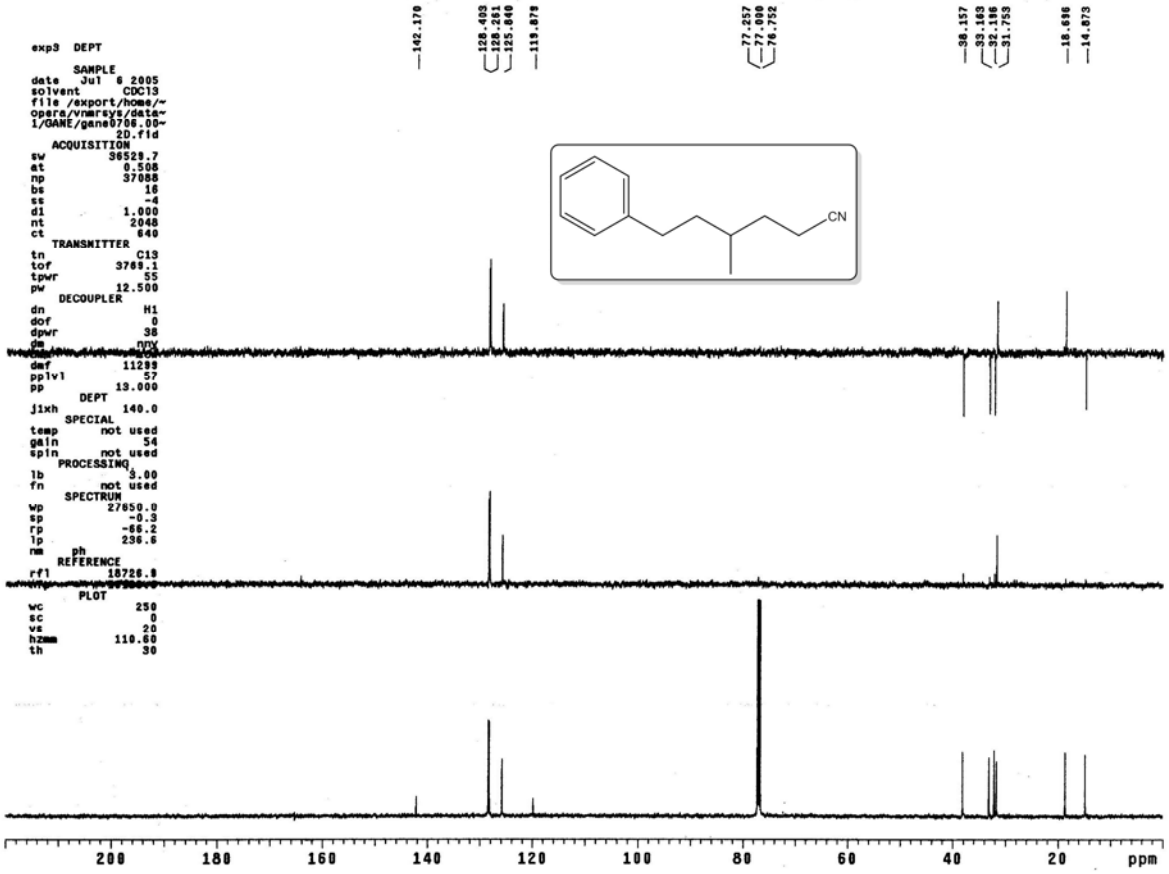
Butyl 4-methyl-6-phenylhexanoate (5q) ($CDCl_3$)



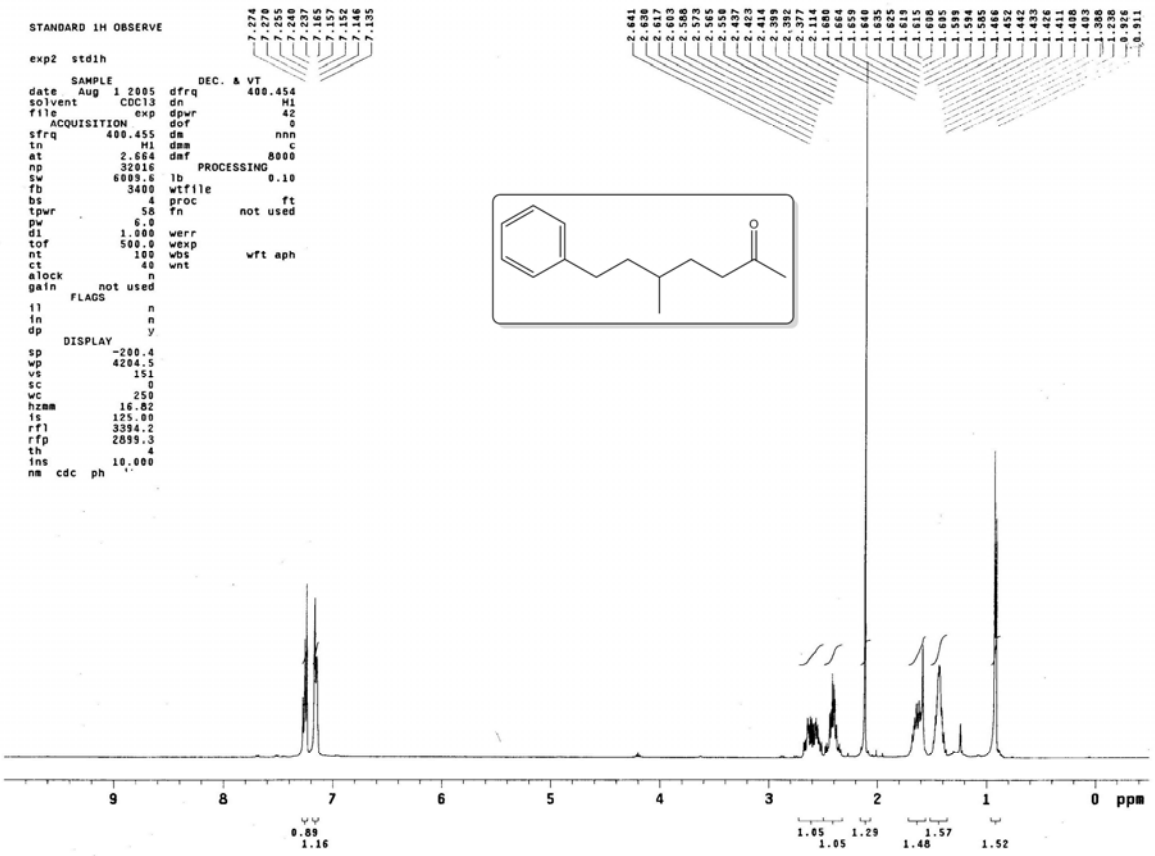


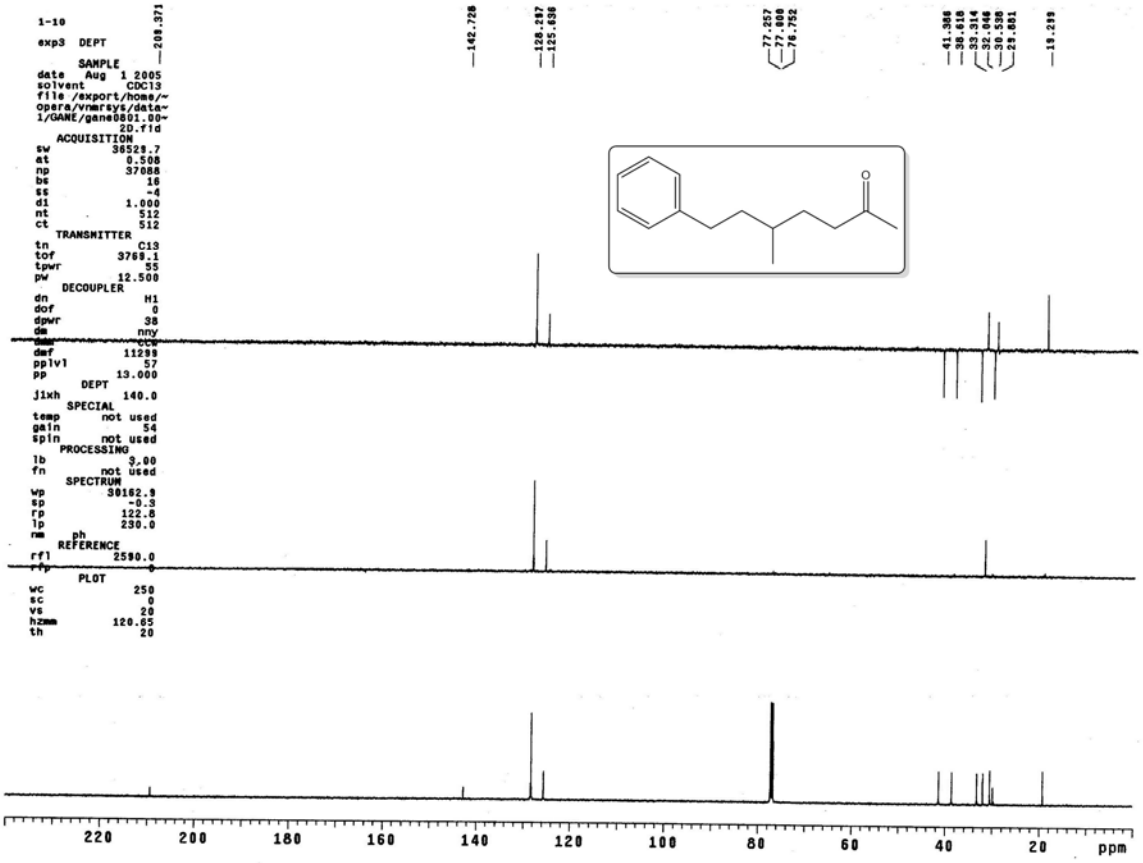
4-Methyl-6-phenylhexanenitrile (5r) ($CDCl_3$)





5-Methyl-7-phenylheptan-2-one (5s) ($CDCl_3$)





4-Methylbenzyl 4-cyclopentylbutanoate (7) ($CDCl_3$)