Supporting Information

Cyano(ethoxycarbonothioylthio)methyl benzoate:

A Novel One-Carbon Radical Equivalent

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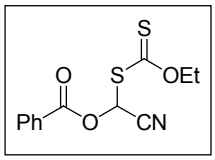
Contents:

General experimental methods. Anhydrous acetone was obtained by refluxing over potassium carbonate for one hour followed by distillation under nitrogen. Anhydrous dichloromethane was obtained by refluxing over calcium hydride for one hour followed by distillation under nitrogen. Anhydrous THF was obtained by refluxing over sodium-benzophenone for one hour followed by distillation under argon. Anhydrous DMF was obtained by stirring over calcium sulphate followed by distillation under nitrogen. Petroleum ether 40-60 refers to the fraction of light petroleum ether boiling between 40-60°C. All reagents were used as obtained from commercial sources unless otherwise stated and were purified in accordance with the instructions in D.D. Perrin and W.L.F. Armarego, "Purification of Laboratory Chemicals", Fourth edition, The Bath Press, Bath, 2002. All reactions were carried out under dry, oxygen free argon or nitrogen. Flash chromatography was performed on silica gel (SDS 60 C. C. 40-63) as the stationery phase. Thin layer chromatography (TLC) was performed on aluminium plates pre-coated with silica (Merck silica gel 60 F_{254} 1.05554), which were visualized by the quenching of UV fluorescence (λ_{max} = 254nm), and/or by staining with *p*-anisaldehyde solution in acidic ethanol, vanillin solution in acidic ethanol or 1% w/v $KMnO_4$ in 0.5M aq. K_2CO_3, followed by heating. Retention factors (R_f) are reported to ± 0.05. Boiling points were obtained by short path distillation and both boiling points (bp) and melting points (mp) are uncorrected. Infrared (IR) spectra were recorded as thin films between NaCl plates or as solutions in CCl_4. Absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}) and only selected peaks are reported. Magnetic resonance spectra were recorded at ambient temperature. Proton magnetic resonance spectra (^{1}H NMR) were recorded at 400 MHz. Coupling constants (*J*) are reported to ± 0.5 Hz. Carbon magnetic resonance spectra (^{13}C NMR) were recorded at 100.6 MHz. Chemical shifts (δ_H, δ_C) are quoted in parts per million (ppm) and are referenced to the residual solvent peak. Low-resolution mass spectra (*m/z*) were recorded using HP 5989B, JMS-GCmateII and Micromass Autospec mass spectrometers and only report molecular species (M^+, $[M+H]^+$, $[M+Na]^+$, $[M+NH_4]^+$) and other major fragments, with intensities quoted as percentages

of the base peak. High-resolution mass spectra were recorded by electron impact ionization (EI) on a JMS-GCmateII mass spectrometer. The quoted masses are accurate to ± 5 ppm.

Experimental Procedures.

(±)-Acyl radical equivalent xanthate (3)



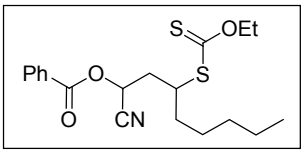
To a stirred solution of benzoic acid (7.5 g, 61 mmol, 1 eq) in DCM (123 mL) at 0°C and under nitrogen, was added triethylamine (17.1 mL, 122 mmol, 2 eq) followed by chloroacetonitrile (5.8 mL, 92 mmol, 1.5 eq) and the resulting mixture heated under reflux for 14 h overnight. The mixture was then cooled to rt and the organic layer washed with 1M aq. HCl (2 × 100 mL), sat. aq. $NaHCO_3$ (100 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Distillation under reduced pressure (110°C, 1mmHg, lit.[1] 152-154°C/11mmHg) gave the corresponding benzoic acid cyanomethylester **1** as a viscous clear oil (8.2 g, 51 mmol), which was split into two portions (4.1 g each) that were brominated in the subsequent step independently in order to permit efficient irradiation. A mixture of ester **1** (4.1 g, 25 mmol, 1 eq) and *N*-bromosuccinmide (5.0 g, 28 mmol, 1.1 eq) in CCl_4 (50 mL) in a flask fitted with a reflux condenser under nitrogen, was irradiated simultaneously with a 500W tungsten lamp and 50-150W halogen lamp for 12 h. The mixture was then cooled to rt, filtered through a pad of Celite® and concentrated *in vacuo*. The following day the crude product was re-dissolved in CCl_4, a fresh portion of *N*-bromosuccinmide added and the resulting mixture irradiated for a further 10 h. The crude product was cooled to rt, filtered through a pad of Celite® and concentrated *in vacuo* to afford a mixture of bromide **2** and ester **1** in a 4.5:1 ratio as a brown oil (6.75g, overall combined mass from both portions = 13.5 g). To a solution of the combined crude product mixture (13.5 g, 56 mmol) in acetone (240 mL) at 0ºC under nitrogen was added portionwise potassium *O*-ethylxanthate (9.9 g, 62 mmol, 1.1 eq) and the

resulting mixture stirred for 1 h. The solution was then allowed to warm to rt, concentrated under reduced pressure and diluted with water (150 mL) and Et_2O (150 mL). The aqueous layer was extracted with Et_2O (3 × 150 mL), and the organic layers were combined, washed with water (250 mL), brine (250 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification by flash chromatography (petroleum ether 40-60: Et_2O 95:5) gave xanthate **3** as a pale yellow oil (7.2 g, 42% over 3 steps); R_f 0.2 (petroleum ether 40-60: Et_2O 95:5); ν_{max}(film)/cm^{-1} 3065w, 2984s, 1739s, 1600m, 1257s, 1112s, 733s; δ_H(400MHz, $CDCl_3$) 1.47 (3H, t, *J* 7.0 Hz), 4.72 (2H, q, *J* 7.0 Hz), 7.26 (1H, s), 7.49 (2H, t, *J* 8.0 Hz), 7.65 (1H, t, *J* 8.0 Hz), 8.05 (2H, d, *J* 8.0 Hz); δ_C(100.6MHz, $CDCl_3$) 13.7 (CH_3), 65.2 (CH), 72.0 (CH_2), 113.7 (C), 127.3(C), 128.9 (2CH), 130.3 (2CH), 134.7 (CH), 163.9 (C), 205.6 (C); *m/z*(CI) 299[MNH_4^+,7%], 282[MH^+, 100%]; HRMS: found 281.0188 (M^+). $C_{12}H_{11}O_3NS_2$ requires 281.0181.

General procedure for the preparation of xanthate adducts 6a-m

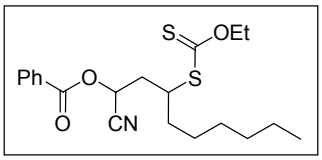
A solution of xanthate **3** (1 mmol) and the desired olefin (2 mmol) in 1,2-dichloroethane (DCE) (1 mL) was refluxed for 15 min under nitrogen. Lauroyl peroxide (DLP) (5% mol) was then added to the refluxing solution, followed by additional portions (5% mol) every 1.5 h until xanthate **3** was completely consumed. The mixture was then cooled to rt, concentrated under reduced pressure and purified by flash chromatography (silica gel). A small layer of basic alumina was placed on top of the silica to remove any lauric acid present.

(±)-Adduct 6a



Obtained from xanthate **3** as a pale yellow oil (93%) (petroleum ether 40-60: Et_2O 95:5) and as a mixture of 2 diastereomers in a 1.1:1 ratio which were not separated; R_f 0.45 (petroleum ether 40-60: Et_2O 8:2); ν_{max}(film)/cm^{-1} 3065w, 2929s, 2860s, 2255w, 1735s, 1601m, 1261s, 1098s, 1051s, 710s; δ_H(400MHz, $CDCl_3$) 0.88-0.97 (6H, m), 1.24-1.64 (12H, m), 1.38 (3H, t, *J* 7.0 Hz), 1.46 (3H, t, *J* 7.0 Hz), 1.69-1.92 (4H, m), 2.37-2.66 (4H, m), 3.96-4.11 (2H, m), 4.53-4.74 (4H, m), 5.72 (1H, dd, *J* 9.5, 4.5 Hz), 5.77 (1H, t, *J* 7.0 Hz), 7.48-7.56 (4H, m), 7.63-7.70 (2H, m), 8.07-8.14 (4H, m); δ_C(100.6MHz, $CDCl_3$) 13.7 (CH_3), 13.8 (CH_3), 14.0 (CH_3), 14.1 (CH_3), 22.5 ($2CH_2$), 26.4 ($2CH_2$), 31.4 ($2CH_2$), 33.9 (CH_2), 34.5 (CH_2), 37.5 (CH_2), 37.6 (CH_2), 46.8 (CH), 47.1 (CH), 59.5 (CH), 60.1 (CH), 70.4 ($2CH_2$), 116.8 (2C), 128.1 (C), 128.2 (C), 128.7 (4CH), 130.1 (4CH), 134.1 (CH), 134.2 (CH), 164.7 (C), 164.8 (C), 212.7 (C), 212.9 (C); *m/z*(CI) 380[MH^+,90%]; *m/z*(EI) 379[M^+,100%], 346[40]; HRMS: found 379.1273 (M^+). $C_{19}H_{25}O_3NS_2$ requires 379.1276.

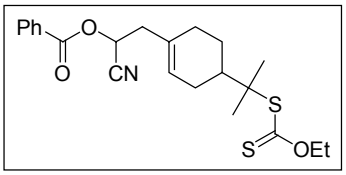
(±)-Xanthate adduct 6b



Obtained from xanthate **3** as a pale yellow oil (85%) (petroleum ether 40-60: Et_2O 98:2) and as a mixture of 2 diastereomers in a 1.2:1 ratio which were not separated; R_f 0.4 (petroleum ether 40-60: Et_2O 9:1); ν_{max}(film)/cm^{-1} 2928s, 2856s, 1733s, 1602m, 1262s, 1049s, 710s; δ_H(400MHz, $CDCl_3$) 0.89-0.94 (6H, m), 1.20-1.58 (16H, m), 1.34 (3H, t, *J* 7.0 Hz), 1.41 (3H, t, *J* 7.0 Hz), 1.65-1.85 (4H, m), 2.33-

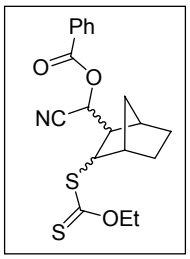
2.60 (4H, m), 3.92-4.04 (2H, m), 4.49-4.67 (4H, m), 5.66-5.74 (2H, m), 7.42-7.50 (4H, m), 7.59-7.65 (2H, m), 8.04-8.07 (4H, m); δ_C(100.6MHz, $CDCl_3$) 13.7 (CH_3), 13.8 (CH_3), 14.1 ($2CH_3$), 22.6 ($2CH_2$), 26.6 (CH_2), 26.7 (CH_2), 28.9 ($2CH_2$), 31.6 ($2CH_2$), 33.9 (CH_2), 34.6 (CH_2), 37.6 ($2CH_2$), 46.8 (CH), 47.0 (CH), 59.5 (CH), 60.1 (CH), 70.3 (CH_2), 70.4 (CH_2), 116.7 (2C), 128.1 (C), 128.3 (C), 128.7 (4CH), 130.1 (4CH), 134.1 (2CH), 164.7 (C), 164.8 (C), 212.7 (C), 212.9 (C); *m/z*(CI) 411[MNH_4^+,100%], 394[MH^+,31%]; HRMS: found 393.1441 (M^+). $C_{20}H_{27}O_3NS_2$ requires 393.1433.

(±)-Xanthate adduct 6c



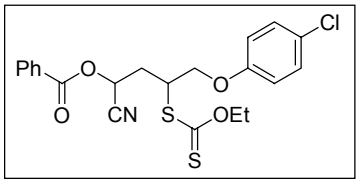
Obtained from xanthate **3** as a pale yellow oil (90%) (petroleum ether 40-60: Et_2O 8:2) and as a mixture of 2 diastereomers in a 1.1:1 ratio which were not separated; R_f 0.35 (petroleum ether 40-60: Et_2O 7:3); ν_{max}(film)/cm^{-1} 2924s, 1732s, 1601m, 1259s, 1068s, 711s; δ_H(400MHz, $CDCl_3$) 1.28-1.38 (2H, m), 1.40 (3H, t, *J* 7.0 Hz), 1.44 (3H, t, *J* 7.0 Hz), 1.47 (3H, s), 1.48 (3H, s), 1.50 (6H, s), 1.86-2.30 (12H, m), 2.71 (4H, d, *J* 7.0 Hz), 4.60-4.74 (4H, m), 5.69-5.75 (4H, m), 7.48-7.53 (4H, m), 7.62-7.68 (2H, m), 8.04-8.08 (4H, m); δ_C(100.6MHz, $CDCl_3$) 13.7 (CH_3), 13.8 (CH_3), 24.5 ($2CH_2$), 24.9 ($2CH_3$), 25.0 (CH_3), 25.1 (CH_3), 27.4 ($2CH_2$) 29.7 (CH_2), 29.8 (CH_2), 40.3 ($2CH_2$), 42.1 (CH), 42.2 (CH), 58.8 (2C), 60.7 (2CH), 69.4 ($2CH_2$), 116.8 (C), 116.9 (C), 127.2 (CH), 127.3 (CH), 128.3 (2C), 128.7 (4CH), 129.9 (4CH), 130.2 (C), 130.3 (C), 134.1 (2CH), 164.7 (2C), 214.0 (2C); *m/z*(CI) 418[MH^+,14%], 311[MH^+,100%]; HRMS: found 417.1419 (M^+). $C_{22}H_{27}O_3NS_2$ requires 417.1433.

(±)-Xanthate adduct 6d



Obtained from xanthate **3** as a clear oil (86%) (petroleum ether 40-60: Et_2O 97:3) and as a mixture of 4 diastereomers in a 1.3:1.3:1:1 ratio which were not separated; R_f 0.4 (petroleum ether 40-60: Et_2O 8:2); ν_{max}(film)/cm^{-1} 2958s, 2874s, 1732s, 1600m, 1090s, 710s; δ_H(400MHz, $CDCl_3$) 1.21-2.13 (38H, m), 2.48-2.61 (4H, m), 2.65-2.80 (6H, m), 3.88-4.18 (4H, m), 4.23-4.76 (8H, m), 5.48-5.66 (4H, m), 7.45-7.56 (8H, m), 7.61-7.69 (4H, m), 8.03-8.12 (8H, m); δ_C(100.6MHz, $CDCl_3$) see ^{13}C NMR spectrum in supporting information; *m/z*(CI) 393[MNH_4^+,100%], 376[MH^+,70%]; HRMS: found 375.0956 (M^+). $C_{19}H_{21}O_3NS_2$ requires 375.0963.

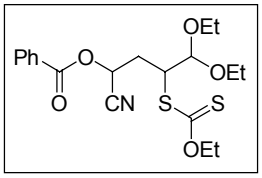
(±)-Xanthate adduct 6e



Obtained from xanthate **3** as a pale yellow oil (84%) (petroleum ether 40-60: EtOAc 93:7 to 90:10) and as a mixture of 2 diastereomers in a 1.1:1 ratio which were not separated; R_f 0.25 (petroleum ether 40-60: EtOAc 95:5); ν_{max}(CCl_4)/cm^{-1} 3065m, 2985s, 2938s, 1741s, 1601m, 1259s, 1090s, 1067s; δ_H(400MHz, $CDCl_3$) 1.38 (3H, t, *J* 7.0 Hz), 1.43 (3H, t, *J* 7.0 Hz), 2.53 (1H, ddd, *J* 15.0, 9.5, 4.0 Hz), 2.63 (1H, dt, *J* 15.0, 7.5 Hz), 2.76-2.90 (2H, m), 4.11-4.17 (2H, m), 4.34 (2H, dd, *J* 9.5, 3.0 Hz), 4.40-4.48 (2H, m), 4.60 (2H, dq, *J* 7.0, 2.5 Hz), 4.67 (2H, dq, *J* 7.0, 1.0 Hz), 5.75 (1H, dd, *J* 10.0, 4.0 Hz),

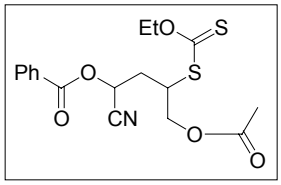
5.83 (1H, t, *J* 7.0 Hz), 6.81-6.85 (2H, m), 6.87-6.91 (2H, m), 7.20-7.24 (2H, m), 7.24-7.28 (2H, m), 7.42-7.50 (4H, m), 7.60-7.66 (2H, m), 7.99-8.03 (4H, m); δ_C(100.6MHz, $CDCl_3$) 13.7 (CH_3), 13.8 (CH_3), 34.1 ($2CH_2$), 45.6 (2CH), 59.1 (CH), 60.0 (CH), 69.0 (CH_2), 70.0 (CH_2), 70.9 (CH_2), 71.0 (CH_2), 115.8 (2CH), 116.1 (2CH), 116.4 (C), 116.5 (C), 126.5 (C), 126.6 (C), 127.8 (C), 127.9 (C), 128.7 (4CH), 129.4 (2CH), 129.5 (2CH), 130.0 (4CH), 134.1 (2CH), 156.4 (C), 156.5 (C), 164.6 (C), 164.7 (C), 211.6 (C), 211.7 (C); *m/z*(CI) 469[MNH_4^+,34%], 467[MNH_4^+,100%], 452[MH^+,13%], 450 [MH^+,30%].

(±)-Xanthate adduct 6f



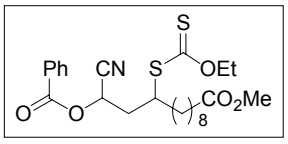
Obtained from xanthate **3** as a pale yellow oil (65%) (petroleum ether 40-60: Et_2O 97:3) and as a mixture of 2 diastereomers in a 1.2:1 ratio which were not separated; R_f 0.4 (petroleum ether 40-60: Et_2O 8:2); ν_{max}(film)/cm^{-1} 2977s, 1735s, 1602m, 1263s, 1093s, 711s; δ_H(400MHz, $CDCl_3$) 1.16-1.34 (12H, m), 1.39 (3H, t, *J* 7.0 Hz), 1.44 (3H, t, *J* 7.0 Hz), 2.40-2.52 (2H, m), 2.78-2.88 (2H, m), 3.42-3.83 (8H, m), 4.27-4.34 (2H, m), 4.53-4.70 (6H, m), 5.80-5.90 (2H, m), 7.46-7.53 (4H, m), 7.61-7.68 (2H, m), 8.07 (2H, d, *J* 7.0 Hz), 8.11 (2H, d, *J* 7.0 Hz); δ_C(100.6MHz, $CDCl_3$) 13.7 (CH_3), 13.8 (CH_3), 15.1 (CH_3), 15.2 ($2CH_3$), 15.3 (CH_3), 31.5 (CH_2), 31.8 (CH_2), 49.3 (CH), 49.5 (CH), 59.9 (CH), 60.4 (CH), 64.4 ($2CH_2$), 65.1 (CH_2), 65.3 (CH_2), 70.7 ($2CH_2$), 103.7 (CH), 103.9 (CH), 116.9 (C), 117.0 (C), 128.3 (C), 128.4 (C), 128.6 (2CH), 128.7 (2CH), 130.0 (4CH), 134.0 (2CH), 164.7 (2C), 212.9 (C), 213.0 (C); *m/z*(CI) 429[MNH_4^+,12%], 363[100]; HRMS: found 411.1191 (M^+). $C_{19}H_{25}O_5NS_2$ requires 411.1174.

(±)-Xanthate adduct 6g



Obtained from xanthate **3** as a pale yellow oil (69%) (petroleum ether 40-60: Et_2O 7:3) and as a mixture of 2 diastereomers in a 1.1:1 ratio which were not separated; R_f 0.2 (petroleum ether 40-60: Et_2O 7:3); ν_{max}(film)/cm^{-1} 2978s, 1738s, 1602m, 1232s, 1048s, 711s; δ_H(400MHz, $CDCl_3$) 1.35 (3H, t, *J* 7.0 Hz), 1.42 (3H, t, *J* 7.0 Hz), 2.06 (3H, s), 2.11 (3H, s), 2.38-2.73 (4H, m), 4.23-4.47 (6H, m), 4.51-4.70 (4H, m), 5.70-5.85 (2H, m), 7.45-7.53 (4H, m), 7.60-7.67 (2H, m), 8.02-8.10 (4H, m); δ_C(100.6MHz, $CDCl_3$) 12.6 (CH_3), 12.7 (CH_3), 19.6 (CH_3), 19.7 (CH_3), 33.1 ($2CH_2$), 44.1 (CH), 44.3 (CH), 58.1 (CH), 58.8 (CH), 64.0 (CH_2), 64.4 (CH_2), 69.8 ($2CH_2$), 115.3 (C), 115.4 (C), 126.9 (C), 127.0 (C), 127.7 (4CH), 129.0 (4CH), 133.1 (CH), 133.2 (CH), 163.5 (C), 163.6 (C), 169.3 (2C), 210.0 (C), 210.2 (C); *m/z*(CI) 399[MNH_4^+,100%], 382[MH^+,12%]; HRMS: found 381.0690 (M^+). $C_{17}H_{19}O_5NS_2$ requires 381.0705.

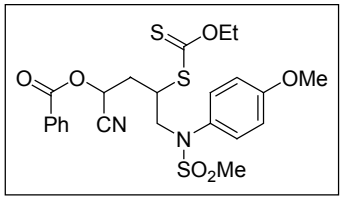
(±)-Xanthate adduct 6h



Obtained from xanthate **3** as a pale yellow oil (89%) (petroleum ether 40-60: Et_2O: DCM 85:5:10) and as a mixture of 2 diastereomers in a 1.1:1 ratio which were not separated; R_f 0.25 (petroleum ether 40-60: Et_2O: DCM 8:1:1); ν_{max}(film)/cm^{-1} 2930s, 2856s, 1734s, 1601m, 1263s, 1092s, 711s; δ_H(400MHz, $CDCl_3$) 1.12-1.48 (26H, m), 1.47-1.59 (4H, m), 1.59-1.82 (4H, m), 2.16-2.27 (4H, m), 2.27-2.55 (4H, m), 3.58 (6H, s), 3.88-4.01 (2H, m), 4.41-4.63 (4H, m), 5.59-5.69 (2H, m), 7.38-7.44 (4H, m), 7.52-7.59

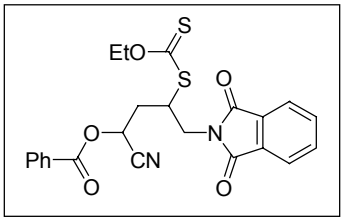
(2H, m), 7.96-8.03 (4H, m); δ_C(100.6MHz, $CDCl_3$) 13.7 ($2CH_3$), 24.9 ($2CH_2$), 26.6 ($2CH_2$), 29.0 ($2CH_2$), 29.1 ($6CH_2$), 33.7 (CH_2), 34.0 ($2CH_2$), 34.5 (CH_2), 37.4 (CH_2), 37.5 (CH_2), 46.7 (CH), 47.0 (CH), 51.3 (CH_3), 51.4 (CH_3), 59.4 (CH), 60.0 (CH), 70.3 ($2CH_2$), 116.7 (2C), 128.1 (C), 128.2 (C), 128.7 (4CH), 130.0 (4CH), 134.0 (CH), 134.1 (CH), 164.6 (C), 164.7 (C), 174.0 (2C), 212.6 (C), 212.8 (C); *m/z*(CI) 497[MNH_4^+,100%], 480[MH^+,12%]; HRMS: found 479.1786 (M^+). $C_{24}H_{33}O_5NS_2$ requires 479.1800.

(±)-Xanthate adduct 6i



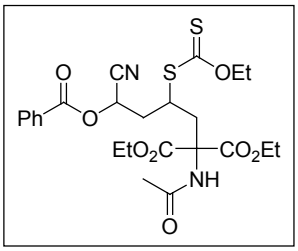
Obtained from xanthate **3** as a pale yellow foam (88%) (petroleum ether 40-60: EtOAc 75:25) and as a mixture of 2 diastereomers in a 1.2:1 ratio which were not separated; R_f 0.1 (petroleum ether 40-60: EtOAc 75:25); ν_{max}(film)/cm^{-1} 3066m, 2934s, 2841s, 2257w, 1732s, 1604m, 1250s, 1047s, 714s; δ_H(400MHz, $CDCl_3$) 1.22 (3H, t, *J* 7.0 Hz), 1.30 (3H, t, *J* 7.0 Hz), 2.23-2.48 (2H, m), 2.80-3.12 (2H, m), 2.91 (6H, s), 3.77 (3H, s), 3.79 (3H, s), 3.83-4.14 (6H, m), 4.40-4.60 (4H, m), 5.65-5.80 (2H, m), 6.91 (4H, d, *J* 8.5 Hz), 7.29-7.40 (4H, m), 7.41-7.53 (4H, m), 7.59-7.69 (2H, m), 7.88 (2H, d, *J* 7.5 Hz), 8.03 (2H, d, *J* 7.5 Hz); δ_C(100.6MHz, $CDCl_3$) 13.5 (CH_3), 13.6 (CH_3), 33.1 (CH_2), 33.4 (CH_2), 36.9 (CH_3), 37.1 (CH_3), 44.2 (CH), 44.5 (CH), 53.5 (CH_2), 53.6 (CH_2), 55.5 (CH_3), 55.6 (CH_3), 58.8 (CH), 59.8 (CH), 70.7 (CH_2), 70.8 (CH_2), 114.9 (2CH), 115.0 (2CH), 116.5 (C), 116.7 (C), 127.9 (C), 128.0 (C), 128.7 (4CH), 130.0 (2CH), 130.1 (4CH), 130.2 (2CH), 130.4 (C), 130.5 (C), 134.2 (2CH), 159.7 (C), 159.8 (C), 164.6 (C), 164.7 (C), 210.7 (C), 210.9 (C); *m/z*(EI) 522[M^+,100%]; HRMS: found 522.0939 (M^+). $C_{23}H_{26}O_6N_2S_3$ requires 522.0953.

(±)-Xanthate adduct 6j



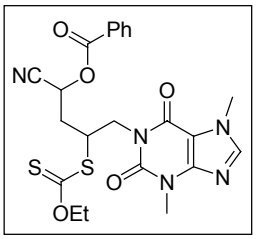
Obtained from xanthate **3** as a white foam (65%) (petroleum ether 40-60: Et_2O 1:1) and as a mixture of 2 diastereomers in a 1.2:1 ratio which were not separated; R_f 0.6 (petroleum ether 40-60: EtOAc 1:1); ν_{max}(film)/cm^{-1} 2934s, 1774s, 1715s, 1601m, 1244s, 1091s, 712s; δ_H(400MHz, $CDCl_3$) 1.36 (3H, t, *J* 7.0 Hz), 1.46 (3H, t, *J* 7.0 Hz), 2.40-2.75 (4H, m), 4.12 (2H, d, *J* 3.0 Hz), 4.14 (2H, d, *J* 2.5 Hz), 4.38-4.72 (6H, m), 5.80 (1H, dd, *J* 10.0, 4.0 Hz), 5.92 (1H, t, *J* 7.0 Hz), 7.49-7.56 (4H, m), 7.64-7.70 (2H, m), 7.75-7.83 (4H, m), 7.87-7.95 (4H, m), 8.06-8.13 (4H, m); δ_C(100.6MHz, $CDCl_3$) 13.6 (CH_3), 13.7 (CH_3), 34.9 (CH_2), 35.0 (CH_2), 40.5 (CH_2), 40.9 (CH_2), 45.4 (CH), 45.5 (CH), 58.9 (CH), 59.9 (CH), 70.8 ($2CH_2$), 116.3 (C), 116.4 (C), 123.7 (4CH), 128.0 (2C), 128.7 (4CH), 130.1 (4CH), 131.7 (4C), 134.1 (CH), 134.2 (CH), 134.4 (4CH), 164.6 (C), 164.7 (C), 168.0 (2C), 168.1 (2C), 210.5 (C), 210.6 (C); *m/z*(CI) 486[MNH_4^+,100%], 469[MH^+,21%]; HRMS: found 468.0795 (M^+). $C_{23}H_{20}O_5N_2S_2$ requires 468.0814.

(±)-Xanthate adduct 6k



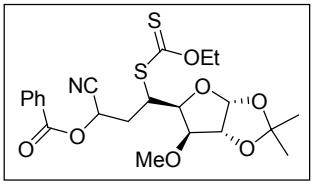
Obtained from xanthate **3** as a white foam (57%) (petroleum ether 40-60: Et_2O 1:1) and as a mixture of 2 diastereomers in a 1.2:1 ratio which were not separated; R_f 0.1 (petroleum ether 40-60: Et_2O 1:1); ν_{max}(film)/cm^{-1} 3399 br s, 2982s, 1738s, 1681s, 1602m, 1370s, 1047s, 713s; δ_H(400MHz, $CDCl_3$) 1.20-1.34 (12H, m), 1.40 (3H, t, *J* 7.0 Hz), 1.46 (3H, t, *J* 7.0 Hz), 1.94 (3H, s), 2.04 (3H, s), 2.41-2.66 (4H, m), 2.71-2.87 (2H, m), 3.09-3.20 (2H, m), 3.95-4.08 (2H, m), 4.17-4.36 (8H, m), 4.55-4.72 (4H, m), 5.59 (1H, dd, *J* 9.5, 5.0 Hz), 5.65 (1H, dd, *J* 8.0, 6.0 Hz), 6.88 (2H, br s) 7.48-7.56 (4H, m), 7.63-7.69 (2H, m), 8.09 (2H, d, *J* 7.5 Hz), 8.15 (2H, d, *J* 7.0 Hz); δ_C(100.6MHz, $CDCl_3$) 13.7 (CH_3), 13.8 ($3CH_3$), 13.9 (CH_3), 14.0 (CH_3), 22.9 (CH_3), 23.0 (CH_3), 35.5 (CH_2), 36.3 (CH_2), 39.2 (CH_2), 39.3 (CH_2), 42.3 (CH), 42.7 (CH), 59.0 (CH), 59.6 (CH), 62.8 ($2CH_2$), 63.4 ($2CH_2$), 65.1 (C), 65.3 (C), 70.8 (CH_2), 70.9 (CH_2), 116.4 (C), 116.5 (C), 128.0 (C), 128.3 (C), 128.7 (4CH), 130.1 (2CH), 130.2 (2CH), 134.0 (CH), 134.1 (CH), 164.6 (C), 164.7 (C), 167.1 (2C), 167.8 (2C), 169.6 (C), 169.7 (C), 211.7 (C), 211.9 (C); *m/z*(CI) 556[MNH_4^+,28%], 539[MH^+,100%]; HRMS: found 538.1454 (M^+). $C_{24}H_{30}O_8N_2S_2$ requires 538.1444.

(±)-Xanthate adduct 6l



Obtained from xanthate **3** as a pale yellow foam (79%) (petroleum ether 40-60: EtOAc: DCM 3:6:1) and as a mixture of 2 diastereomers in a 1.1:1 ratio which were not separated; R_f 0.2 (petroleum ether 40-60: Et_2O 1:1); ν_{max}(film)/cm^{-1} 2923s, 2843s, 1730s, 1705s, 1656s, 1600m, 1544m, 1259s, 1042s; δ_H(400MHz, $CDCl_3$) 1.34 (3H, t, *J* 7.0 Hz), 1.42 (3H, t, *J* 7.0 Hz), 2.45-2.72 (4H, m), 3.53 (3H, s), 3.57 (3H, s), 3.93 (3H, s), 3.99 (3H, s), 4.30-4.69 (10H, m), 5.76 (1H, dd, *J* 9.5, 4.0 Hz), 5.82 (1H, t, *J* 7.0 Hz), 7.44-7.52 (4H, m), 7.54 (1H, s), 7.56 (1H, s), 7.59-7.67 (2H, m), 8.03-8.11 (4H, m); δ_C(100.6MHz, $CDCl_3$) 13.6 (CH_3), 13.7 (CH_3), 29.8 ($2CH_3$), 33.6 (CH_3), 33.7 (CH_3), 35.2 (CH_2), 35.5 (CH_2), 43.0 (CH_2), 43.3 (CH_2), 44.7 (CH), 44.9 (CH), 59.2 (CH), 60.0 (CH), 70.5 ($2CH_2$), 107.4 (2C), 116.6 (2C), 128.1 (C), 128.2 (C), 128.6 (4CH), 130.1 (4CH), 134.0 (2CH), 142.0 (2CH), 149.1 (2C), 151.4 (2C), 154.9 (C), 155.0 (C), 164.6 (C), 164.7 (C), 211.5 (2C); *m/z*(CI) 519[MNH_4^+,17%], 502[MH^+,89%], 443[100]; HRMS: found 501.1121 (M^+). $C_{22}H_{23}O_5N_5S_2$ requires 501.1141.

Xanthate adduct 6m



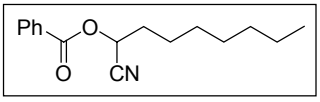
Obtained from xanthate **3** as a white foam (79%) (petroleum ether 40-60: Et_2O: DCM 8:1:1) and as a mixture of 4 diastereomers in a 2.2:2.2:1:1 ratio which were not separated; R_f 0.5 (petroleum ether 40-

60: Et_2O: DCM 7:2:1); ν_{max}(film)/cm^{-1} 2988s, 2935s, 1732s, 1602m, 1266s, 1091s, 712s; δ_H(400MHz, $CDCl_3$) 1.30-1.53 (54H, m), 2.41-2.63 (6H, m), 2.82-2.98 (6H, m), 3.38 (12H, s), 3.54 (6H, s), 3.82-3.86 (4H, m), 3.87-3.90 (2H, m), 4.25-4.70 (30H, m), 5.66-5.85 (6H, m), 5.92-6.03 (6H, m), 7.46-7.54 (12H, m), 7.61-7.68 (6H, m), 8.06-8.12 (12H, m); δ_C(100.6MHz, $CDCl_3$) see ^{13}C NMR spectrum in supporting information; *m/z*(CI) 499[MNH_4^+,100%], 482[MH^+,58%]; HRMS: found 481.1230 (M^+). $C_{22}H_{27}O_7NS_2$ requires 481.1229.

General procedure for the reduction of xanthate adducts 6 to 7

A solution of xanthate **6** (1 mmol) in propan-2-ol (10 mL) was refluxed for 15 min under nitrogen. Lauroyl peroxide (DLP) (0.2 mmol) was then added to the refluxing solution every hour until a total of 1.2 mmol had been added. After the final DLP addition the reaction mixture was refluxed for a further 1 h. The mixture was then cooled to rt, concentrated under reduced pressure and purified by flash chromatography (silica gel). A small layer of basic alumina was placed on top of the silica to remove any lauric acid present.

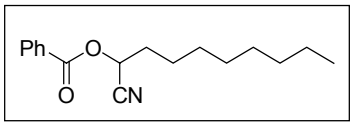
(±)-Benzoic acid 1-cyano-octyl ester (7a)[2]



Obtained from adduct **6a** by reduction using the general procedure as a colorless oil (80%) (petroleum ether 40-60: EtOAc 3:197 to 5:95); R_f 0.4 (petroleum ether 40-60: EtOAc 98:2); ν_{max}(CCl_4)/cm^{-1} 2957s, 2929s, 2359w, 1737s, 1602m, 1092s, 1068s, 1027s; δ_H(400MHz, $CDCl_3$) 0.90 (3H, t, *J* 7.0 Hz), 1.23-1.45 (8H, m), 1.56-1.63 (2H, m), 2.02-2.08 (2H, m), 5.59 (1H, t, *J* 7.0 Hz), 7.48 (2H, t, *J* 7.5 Hz), 7.62 (1H, t, *J* 7.5 Hz), 8.06 (2H, d *J* 7.5 Hz); δ_C(100.6MHz, $CDCl_3$) 14.0 (CH_3), 22.6 (CH_2), 24.6 (CH_2), 28.8

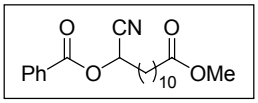
(CH_2), 28.9 (CH_2), 31.6 (CH_2), 32.4 (CH_2), 61.6 (CH), 117.0 (C), 128.3 (C), 128.6 (2CH), 129.9 (2CH), 133.9 (CH), 164.8 (C); *m/z*(CI) 277[MNH_4^+, 100%], 260[MH^+, 15%].

(±)-Benzoic acid 1-cyano-nonyl ester (7b)



Obtained from xanthate **6b** by reduction using the general procedure as a colorless oil (72%) (petroleum ether 40-60: DCM 7:3); R_f 0.35 (petroleum ether 40-60: Et_2O 95:5); ν_{max}(film)/cm^{-1} 2927s, 2856s, 1733s, 1602m, 1068s, 710s; δ_H(400MHz, $CDCl_3$) 0.93 (3H, t, *J* 7.0 Hz), 1.28-1.50 (10H, m), 1.60-1.70 (2H, m), 2.06-2.12 (2H, m), 5.63 (1H, t, *J* 6.5 Hz), 7.50-7.55 (2H, m), 7.64-7.70 (1H, m), 8.08-8.12 (2H, m); δ_C(100.6MHz, $CDCl_3$) 14.1 (CH_3), 22.6 (CH_2), 24.7 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 32.5 (CH_2), 61.7 (CH), 117.1 (C), 128.4 (C), 128.7 (2CH), 130.0 (2CH), 134.0 (CH), 164.8 (C); *m/z*(CI) 291[MNH_4^+,100%], 274[MH^+,17%]; HRMS: found 273.1719 (M^+). $C_{17}H_{23}O_2N$ requires 273.1729.

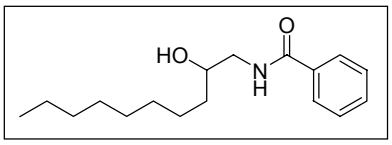
(±)-Benzoic acid 1-cyano-11-methoxycarbonyl-undecyl ester (7h)



Obtained from xanthate **6h** by reduction using the general procedure as a clear oil (79%) (petroleum ether 40-60: Et_2O: DCM 87:3:10); R_f 0.7 (petroleum ether 40-60: Et_2O: DCM 3:1:1); ν_{max}(film)/cm^{-1} 2928s, 2855s, 2345w, 1734s, 1601m, 1070s, 712s; δ_H(400MHz, $CDCl_3$) 1.21-1.48 (12H, m), 1.56-1.70 (4H, m), 2.04-2.12 (2H, m), 2.34 (2H, t, *J* 7.5 Hz), 3.70 (3H, s), 5.62 (1H, t, *J* 6.5 Hz), 7.52 (2H, t, *J* 8.0

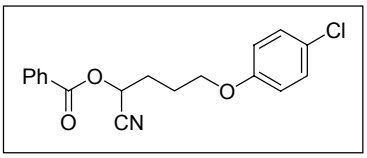
Hz), 7.63-7.69 (1H, m), 8.08-8.12 (2H, m); δ_C(100.6MHz, $CDCl_3$) 25.0 (CH_2), 25.3 (CH_2), 29.2 (CH_2), 29.5 (CH_2), 29.6 ($2CH_2$), 29.7 ($2CH_2$), 32.8 (CH_2), 34.5 (CH_2), 51.9 (CH_3), 62.0 (CH), 117.4 (C), 128.7 (C), 129.0 (2CH), 130.4 (2CH), 134.4 (CH), 165.2 (C), 174.7 (C); *m/z*(CI) 377[MNH_4^+,100%], 360[MH^+,38%]; HRMS: found 359.2104 (M^+). $C_{21}H_{29}O_4N$ requires 359.2097.

(±)-*N*-(2-Hydroxy-decyl)-benzamide (10b)



A mixture of **7b** (55 mg, 0.2 mmol), 10% palladium on carbon (61 mg) and methanol (4.9 mL) at rt was flushed three times with hydrogen (balloon). Methanolic hydrochloric acid (6.4 mL, 2.1 mmol, 0.33M HCl in MeOH) was then added *via* syringe and the resulting mixture stirred vigorously under an atmosphere of hydrogen for 48h. The catalyst was removed by filtration over Celite®, and the resulting acidic solution was basified using solid K_2CO_3 to pH 8/9. The basic solution was stirred for 15 min at rt and then re-acidified with methanolic HCl (0.33M HCl in MeOH) to pH 6/7. The solvent was removed by concentration *in vacuo* and the residue formed purified by flash chromatography (petroleum ether 40-60: EtOAc 7:3) to afford the title compound **10b** (22 mg, 40% over 2 steps) as a white solid; mp 83-85°C; (data for the major rotamer) R_f 0.2 (petroleum ether 40-60: EtOAc 7:3); ν_{max}(film)/cm^{-1} 3372br s, 2916s, 2845s, 1624s, 1459s, 1012s, 715s; δ_H(400MHz, $CDCl_3$) 0.93 (3H, t, *J* 7.0 Hz), 1.22-1.62 (14H, m), 2.50-2.90 (1H, br s), 3.36 (1H, ddd, *J* 14.0, 8.0, 5.0 Hz), 3.77 (1H, ddd, *J* 14.0, 6.5, 3.0 Hz), 3.84-3.92 (1H, m), 6.65-6.73 (1H, m), 7.45-7.58 (3H, m), 7.82-7.86 (2H, m); δ_C(100.6MHz, $CDCl_3$) 14.1 (CH_3), 22.7 (CH_2), 25.6 (CH_2), 29.3 (CH_2), 29.6 ($2CH_2$), 31.9 (CH_2), 35.2 (CH_2), 46.2 (CH_2), 71.5 (CH), 127.0 (2CH), 128.6 (2CH), 131.6 (CH), 134.4 (C), 168.4 (C); *m/z*(CI) 278[MH^+,100%]; HRMS: found 277.2038 (M^+). $C_{17}H_{27}O_2N$ requires 277.2042.

(±)-Benzoic acid 4-(4-chloro-phenoxy)-1-cyano-butyl ester (7e)

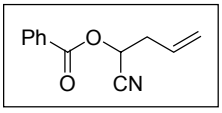


Method A: DLP/isopropanol

Reduction of **6e** using the general procedure (petroleum ether 40-60: Et_2O: DCM 87:3:10) afforded **7e** (60%) as a pale yellow oil and olefin **8e** (35%) as a pale yellow oil.

Data for 7e: R_f 0.1 (petroleum ether 40-60: EtOAc 9:1); $\nu_{max}(CCl_4)/cm^{-1}$ 3065m, 2949s, 1739s, 1601m, 1583m, 1390s, 1260s, 992s; δ_H(400MHz, $CDCl_3$) 2.07-2.14 (2H, m), 2.27-2.33 (2H, m), 4.04 (2H, t, *J* 6.0 Hz), 5.72 (1H, t, *J* 7.0 Hz), 6.81-6.85 (2H, m), 7.21-7.25 (2H, m), 7.45-7.51 (2H, m), 7.62-7.66 (1H, m), 8.02-8.08 (2H, m); δ_C(100.6MHz, $CDCl_3$) 24.6 (CH_2), 29.6 (CH_2), 61.4 (CH), 66.8 (CH_2), 115.7 (2CH), 116.8 (C), 125.9 (C), 128.2 (C), 128.7 (2CH), 129.4 (2CH), 130.0 (2CH), 134.1 (CH), 157.2 (C), 164.8 (C); *m/z*(CI) 349[MNH_4^+, 37%], 347[MNH_4^+, 100%], 332[MH^+, 50%], 330[MH^+, 8%].

Data for (±)-Benzoic acid 1-cyano-but-3-enyl ester (8e):

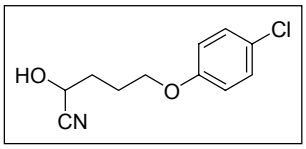


R_f 0.5 (petroleum ether 40-60: EtOAc 9:1); $\nu_{max}(CCl_4)/cm^{-1}$ 3074m, 2927s, 2855s, 1739s, 1645m, 1602m, 1586m, 1246s, 1091s, 988s; δ_H(400MHz, $CDCl_3$) 2.79-2.83 (2H, m), 5.31-5.39 (2H, m), 5.64 (1H, t, *J* 6.5 Hz), 5.90 (1H, ddt, *J* 17.0, 10.5, 7.0 Hz), 7.47-7.52 (2H, m), 7.62-7.66 (1H, m), 8.04-8.09 (2H, m); δ_C(100.6MHz, $CDCl_3$) 36.8 (CH_2), 61.1 (CH), 116.6 (C), 121.3 (CH_2), 128.3 (C), 128.7 (2CH), 129.6 (CH), 130.1 (2CH), 134.1 (CH), 164.7 (C); *m/z*(CI) 219[MNH_4^+, 100%].

Method B: AIBN/tributyltin hydride

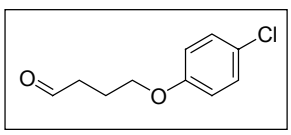
A solution of xanthate **6e** (160 mg, 0.36 mmol, 1 eq) in heptane (7 mL) was refluxed for 15 min under nitrogen. Tributyltin hydride (105 μL, 0.39 mmol, 1.1 eq) and 2,2'-azobisisobutyronitrile (AIBN) (6 mg, 40 μmol, 0.1 eq) were then added to the refluxing solution, and reflux continued for a further 2 h. The mixture was then cooled to rt and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether 40-60: EtOAc 23:2 to 1:3) gave **7e** (52 mg, 44%) as a pale yellow oil and a product derived from debenzoylation **7e'** (33 mg, 40%) as a pale yellow oil.

Data for debenzoylation product (±)-5-(4-Chloro-phenoxy)-2-hydroxy-pentanenitrile (7e'):



R_f 0.1 (petroleum ether 40-60: EtOAc 9:1); $\nu_{max}(CCl_4)/cm^{-1}$ 3449 br s, 2931s, 2873s, 1598m, 1390s, 1242s, 1050s, 984s; δ_H(400MHz, $CDCl_3$) 1.98-2.10 (4H, m), 3.52 (1H, br s), 3.96-4.04 (2H, m), 4.60 (1H, t, *J* 6.0 Hz), 6.80-6.84 (2H, m), 7.22-7.26 (2H, m); δ_C(100.6MHz, $CDCl_3$) 24.6 (CH_2), 32.2 (CH_2), 61.0 (CH), 67.0 (CH_2), 115.8 (2CH), 119.9 (C), 126.0 (C), 129.5 (2CH), 157.1 (C); *m/z*(CI) 245[MNH_4^+,34%], 243[MNH_4^+,100%].

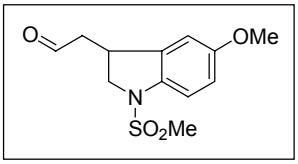
4-(4-Chloro-phenoxy)-butyraldehyde (9e)



To a solution of **7e** (52 mg, 0.16 mmol) and the debenzoylation product **7e'** (33 mg, 0.15 mmol) in a mixture of $CHCl_3$ and MeOH (32 mL, 1:1 v/v) at rt was added NaOH (26 mg, 0.62 mmol, 2 eq) and the

resulting mixture stirred for 22 h. An additional portion of NaOH (19 mg, 0.48 mmol) was then added and stirring continued for a further 3 h. The mixture was then poured into a solution of 5% aq. HCl (25 mL). The aqueous layer was extracted with $CHCl_3$ (2 × 15 mL) and the organic layers were combined, dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether: EtOAc 9:1) gave **9e** (44 mg, 71%) as a pale yellow oil; R_f 0.5 (petroleum ether: EtOAc 8:2); $\nu_{max}(CCl_4)/cm^{-1}$ 2935s, 2820s, 1731s, 1598m, 1243s, 1170s, 1062s, 987s; δ_H(400MHz, $CDCl_3$) 2.08-2.15 (2H, m), 2.67 (2H, dt, *J* 7.0, 1.0 Hz), 3.97 (2H, t, *J* 6.0 Hz), 6.78-6.82 (2H, m), 7.21-7.25 (2H, m), 9.84 (1H, t, *J* 1.0 Hz); δ_C(100.6MHz, $CDCl_3$) 22.0 (CH_2), 40.6 (CH_2), 67.0 (CH_2), 115.8 (2CH), 125.7 (C), 129.4 (2CH), 157.3 (C), 201.7 (CH); *m/z*(CI) 218[MNH_4^+, 34%], 216[MNH_4^+, 100%]; HRMS: found 198.0449 (M^+). $C_{10}H_{11}{}^{35}ClO_2$ requires 198.0448.

(±)-(1-Methanesulfonyl-5-methoxy-2,3-dihydro-1*H*-indol-3-yl)-acetaldehyde (9i)



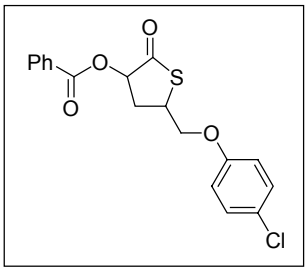
Indoline **11i** was obtained from xanthate **6i** by reduction using the general procedure as a pale yellow oil (73%) (petroleum ether 40-60: EtOAc 30:70 to 35:65) and as a mixture of 2 diastereomers in a 1.1:1 ratio which were not separated.

Data for 11i: R_f 0.6 (petroleum ether 40-60: EtOAc 3:2); δ_H(400MHz, $CDCl_3$) 2.31-2.38 (1H, m), 2.41-2.48 (1H, m), 2.52-2.65 (2H, m), 2.86 (3H, s), 2.88 (3H, s), 3.62-3.74 (2H, m), 3.78 (3H, s), 3.81 (3H, s), 3.84-3.90 (2H m), 4.12-4.22 (2H, m), 5.70-5.77 (2H, m), 6.76-6.86 (4H, m), 7.31-7.36 (2H, m), 7.49-7.53 (4H, m), 7.64-7.68 (2H, m), 8.04-8.08 (4H, m); δ_C(100.6MHz, $CDCl_3$) 34.0 (CH_3), 34.1 (CH_3), 36.7 (CH, CH_2), 36.8 (CH), 36.9 (CH_2), 55.6 (CH_3), 55.7 (CH_3), 56.1 ($2CH_2$), 59.9 (CH), 60.0 (CH), 110.7 (CH), 110.8 (CH), 113.7 (CH), 113.8 (CH), 114.7 (CH), 114.8 (CH), 116.5 (2C), 127.6 (2C),

128.7 (4CH), 129.9 (4CH), 133.9 (C), 134.1 (C), 134.2 (2CH), 134.8 (C), 134.9 (C), 156.7 (C), 156.8 (C), 164.6 (2C).

To a solution of **11i** (104 mg, 0.26 mmol, 1 eq) in a mixture of $CHCl_3$ and MeOH (26 mL, 1:1 v/v) at rt was added NaOH (42 mg, 1.04 mmol, 4 eq) and the resulting mixture stirred for 3.5 h. The mixture was then poured into a solution of 5% aq. HCl (35 mL). The aqueous layer was extracted with $CHCl_3$ (2 × 15 mL) and the organic layers were combined, dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash chromatography (MeOH-DCM, 0:100 to 2:98) afforded impure **9i** (68 mg) as a pale yellow oil. Further purification by flash chromatography (petroleum ether: EtOAc 1:1) gave pure **9i** (48 mg, 67%) pale yellow oil; R_f 0.5 (DCM: MeOH 95:5); $\nu_{max}(CCl_4)/cm^{-1}$ 3002m, 2953s, 2892s, 1729s, 1596m, 1489m, 1361s, 1320s, 1230s, 1199s; δ_H(400MHz, $CDCl_3$) 2.84 (1H, dd, *J* 19.0, 8.0 Hz), 2.85 (3H, s), 3.00 (1H, dd, *J* 19.0, 5.0 Hz), 3.59 (1H, dd *J* 11.0, 6.0 Hz), 3.78 (3H, s), 3.82-3.89 (1H, m), 4.19 (1H, dd, *J* 11.0, 9.0 Hz), 6.74-6.79 (2H, m), 7.33 (1H, d, *J* 8.5 Hz), 9.86 (1H, s); δ_C(100.6MHz, $CDCl_3$) 34.1 (CH_3), 34.4 (CH), 48.9 (CH_2), 55.8 (CH_3), 56.6 (CH_2), 111.0 (CH), 113.4 (CH), 114.9 (CH), 135.1 (2C), 156.9 (C), 199.7 (CH); *m/z*(CI) 287 [MNH_4^+,100%], 270[MH^+,15%], 191[28]. HRMS: found 269.0721 (M^+). $C_{12}H_{15}NO_4S$ requires 269.0722.

(±)-Benzoic acid 5-(4-chloro-phenoxymethyl)-2-oxo-tetrahydro-thiophen-3-yl ester (13e)



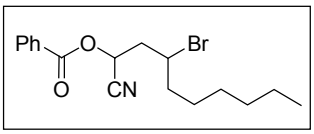
To a solution of **6e** (117 mg, 0.26 mmol, 1 eq) in dry THF (0.5 mL) at rt was added *n*-$BuNH_2$ (26 µL, 0.26 mmol, 1 eq) and the resulting yellow solution was stirred at rt for 45 min. A mixture of TFA and water (50 µL 1:1 v/v) was then added and stirring continued for a further 3 h. Sat. aq. $NaHCO_3$ (10 mL)

was added and the mixture extracted with DCM (3 × 10 mL). The organic layers were combined, dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether: EtOAc 85:15) gave the title compound **13e** (43 mg, 46%) as a pale yellow oil, and as a mixture of 2 diastereomers in a 1.3:1 ratio which were not separated; R_f 0.25 (petroleum ether 40-60: EtOAc 9:1); $\nu_{max}(CCl_4)/cm^{-1}$ 3069m, 2926s, 2865s, 1729s, 1596m, 1493s, 1261s, 1116s, 1097s, 821s; δ_H(400MHz, $CDCl_3$) 2.23-2.32 (1H, m), 2.61-2.68 (1H, m), 2.81-2.86 (1H, m), 2.98 (1H, ddd, *J* 12.0, 7.0, 5.0 Hz), 4.20-4.34 (6H, m), 5.84 (1H, dd, *J* 12.0, 7.0 Hz), 5.99 (1H, dd, *J* 10.0, 7.0 Hz), 6.87-6.94 (4H, m), 7.29-7.34 (4H, m), 7.48-7.52 (4H, m), 7.63-7.67 (2H, m), 8.12 (4H, d, *J* 8.0 Hz); δ_C(100.6MHz, $CDCl_3$) 32.6 (CH_2), 32.8 (CH_2), 41.6 (CH), 42.6 (CH), 71.0 (CH_2), 71.0 (CH_2), 75.7 (CH), 77.0 (CH), 116.0 (4CH), 127.7 (C), 126.7 (C), 128.6 (4CH), 128.8 (C), 129.0 (C), 129.6 (4CH), 130.0 (4CH), 133.7 (2CH), 156.6 (2C), 165.3 (C), 165.4 (C), 200.3 (C), 201.4 (C); *m/z*(CI) 382[MNH_4^+,40%], 380[MNH_4^+,100%], 365[MH^+,6%], 363[MH^+, 18%]. HRMS: found 362.0376 (M^+). $C_{18}H_{15}{}^{35}ClO_4S$ requires 362.0380.

General procedure for conversion of adducts 6 into bromides 14

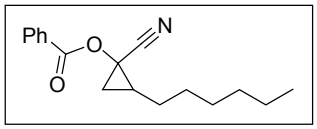
Bromides **14** were prepared *via* minor modification of the general procedure described by Barbier *et al*.[3] A solution of xanthate **6** (1 mmol) and ethyl-2-bromo-2-methylpropionate (5 mmol) in chlorobenzene (14 mL) was refluxed for 3-5 min under nitrogen. Cumyl peroxide (0.5 mmol) was then added to the refluxing solution every 2 h until a total of 1.5 mmol had been added. After the final cumyl peroxide addition the reaction mixture was refluxed for a further 2 h. The mixture was then cooled to rt and left under a flow of nitrogen overnight in order to remove chlorobenzene and excess ethyl-2-bromo-2-methylpropionate. The residue obtained was then purified by flash chromatography (silica gel).

(±)-Benzoic acid 3-bromo-1-cyano-nonyl ester (14b)



Obtained from xanthate **6b** as a colorless oil (86%) (petroleum ether 40-60: DCM 7:3) and as a mixture of 2 diastereomers in a 1.2:1 ratio which were not separated; R_f 0.2, 0.15 (petroleum ether 40-60: DCM 7:3); ν_{max}(film)/cm^{-1} 2929s, 2857s, 1736s, 1602m, 1452s, 1265s, 1092s; δ_H(400MHz, $CDCl_3$) 0.91-0.98 (6H, m), 1.27-1.72 (16H, m), 1.89-2.06 (4H, m), 2.46-2.78 (4H, m), 4.11-4.29 (2H, m), 5.88 (1H, dd, *J* 10.0, 3.5 Hz), 5.94 (1H, dd, *J* 9.0, 6.0 Hz), 7.50-7.57 (4H, m), 7.65-7.72 (2H, m), 8.08-8.12 (4H, m); δ_C(100.6MHz, $CDCl_3$) 14.0 ($2CH_3$), 22.5 (CH_2), 22.6 (CH_2), 27.2 (CH_2), 27.3 (CH_2), 28.5 ($2CH_2$), 31.6 ($2CH_2$), 38.9 (CH_2), 39.0 (CH_2), 41.2 (CH_2), 41.6 (CH_2), 49.8 (CH), 50.3 (CH), 60.0 (CH), 61.4 (CH), 116.3 (C), 116.6 (C), 128.1 (2C), 128.7 (2CH), 128.8 (2CH), 130.0 (4CH), 134.2 (2CH), 164.5 (C), 164.6 (C); *m/z*(CI) 371[MNH_4^+,100%], 369[MNH_4^+,100%], 354[MH^+,15%], 352[MH^+,15%]; HRMS: found 351.0818 (M^+). $C_{17}H_{22}O_2N^{79}Br$ requires 351.0834.

(±)-Benzoic acid 1-cyano-2-hexyl-cyclopropyl ester (15b)



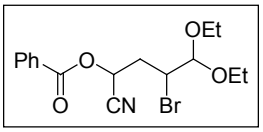
To a solution of bromide **14b** (22 mg, 62 μmol, 1eq) in dry THF (0.62 mL) at 0°C was added sodium bis(trimethylsilyl)amide (62 μL of a 1M solution in THF, 62 μmol, 1 eq) and the resulting solution stirred at 0°C for 1 h. Sat. aq. NH_4Cl (1 mL) was then added and the mixture allowed to warm to rt. The mixture was then extracted with Et_2O (3 × 10 mL), and the organic layers combined, dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether: EtOAc

98:2) gave the title compound **15b** (12 mg, 71%) as a pale yellow oil, and as a mixture of 2 separable diastereomers in a 1.8:1 ratio.

Data for least polar diastereomer: R_f 0.25 (petroleum ether 40-60: EtOAc 98:2); $\nu_{max}(CCl_4)/cm^{-1}$ 2929s, 2859s, 1749s, 1600m, 1271s, 1088s, 1066s, 910s; δ_H(400MHz, $CDCl_3$) 0.91 (3H, t, *J* 7.0 Hz), 1.25-1.44 (7H, m), 1.51-1.76 (6H, m), 7.47 (2H, t, *J* 8.0 Hz), 7.60-7.64 (1H, m), 8.01 (2H, dd, *J* 8.0, 1.0 Hz); δ_C(100.6MHz, $CDCl_3$) 14.1 (CH_3), 21.5 (CH_2), 22.7 (CH_2), 27.1 (CH), 28.1 (CH_2), 29.0 (CH_2), 30.2 (CH_2), 31.7 (CH_2), 49.9 (C), 117.0 (C), 128.5 (C), 128.7 (2CH), 130.0 (2CH), 134.0 (CH), 165.5 (C); *m*/*z*(EI) 271[M^+,51%]; HRMS: found 271.1566 (M^+). $C_{17}H_{21}NO_2$ requires 271.1572.

Data for most polar diastereomer: R_f 0.2 (petroleum ether 40-60: EtOAc 98:2); $\nu_{max}(CCl_4)/cm^{-1}$ 2929s, 2859s, 1749s, 1600m, 1271s, 1179s, 1088s, 1066s, 910s; δ_H(400MHz, $CDCl_3$) 0.89 (3H, t, *J* 7.0 Hz), 1.08 (1H, t, *J* 13.0 Hz), 1.22-1.39 (7H, m), 1.48-1.69 (3H, m), 1.72-1.81 (2H, m), 7.48 (2H, t, *J* 8.0 Hz), 7.63 (1H, t, *J* 8.0 Hz), 8.02 (2H, dd, *J* 8.0, 1.0 Hz); δ_C(100.6MHz, $CDCl_3$) 14.1 (CH_3), 20.5 (CH_2), 22.6 (CH_2), 26.8 (CH), 27.2 (CH_2), 28.7 (CH_2), 29.0 (CH_2), 31.7 (CH_2), 47.6 (C), 118.7 (C), 128.4 (C), 128.8 (2CH), 130.0 (2CH), 134.1 (CH), 165.5 (C); *m*/*z*(EI) 271[M^+,51%]; HRMS: found 271.1566 (M^+). $C_{17}H_{21}NO_2$ requires 271.1572.

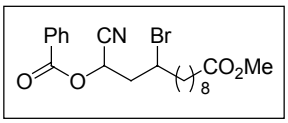
(±)-Benzoic acid 3-bromo-1-cyano-4,4-diethoxy-butyl ester (14f)



Obtained from xanthate **6f** *via* the general bromination procedure. However, for removal of impurities that were difficult to separate by flash chromatography bromide **14f** was heated at 60ºC for 1 h under a flow of nitrogen prior to or after purification by flash chromatography (petroleum ether 40-60: Et_2O: DCM 8.5:0.5:1). This protocol afforded the title compound **14f** as a colorless oil (56%) and as a

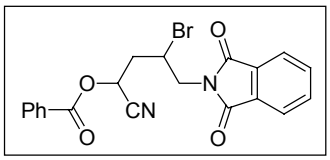
mixture of 2 diastereomers in a 1.1:1 ratio, which were not separated. R_f 0.4 (petroleum ether 40-60: Et_2O: DCM 8:1:1); ν_{max}(film)/cm^{-1} 2979s, 1732s, 1602m, 1265s, 1093s, 712s; δ_H(400MHz, $CDCl_3$) 1.23-1.35 (12H, m), 2.50-2.70 (2H, m), 2.82-3.01 (2H, m), 3.55-3.92 (8H, m), 4.09-4.24 (2H, m), 4.64-4.72 (2H, m), 5.84-5.95 (2H, m), 7.48-7.58 (4H, m), 7.63-7.73 (2H, m), 8.05-8.17 (4H, m); δ_C(100.6MHz, $CDCl_3$) 15.2 ($2CH_3$), 15.3 ($2CH_3$), 35.1 (CH_2), 35.5 (CH_2), 47.3 (CH), 48.0 (CH), 59.9 (CH), 61.2 (CH), 64.1 (CH_2), 64.3 (CH_2), 65.2 (CH_2), 65.4 (CH_2), 104.0 (CH), 104.1 (CH), 116.4 (C), 116.7 (C), 128.1 (C), 128.2 (C), 128.7 (4CH), 130.0 (4CH), 134.1 (CH), 134.2 (CH), 164.6 (2C); *m/z*(CI) 389[MNH_4^+,100%], 387[MNH_4^+,100%], 326[17], 324[18]; HRMS: found 369.0586 (M^+). $C_{16}H_{20}O_4N^{79}Br$ requires 369.0576.

(±)-Benzoic acid 3-bromo-1-cyano-11-methoxycarbonyl-undecyl ester (14h)



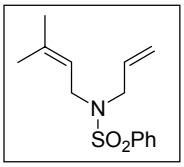
Obtained from xanthate **6h** as a colorless oil (90%) (petroleum ether 40-60: Et_2O: DCM 83:7:10) and as a mixture of 2 diastereomers in a 1.2:1 ratio which were not separated; R_f 0.45 (petroleum ether 40-60: Et_2O: DCM 7:2:1); ν_{max}(film)/cm^{-1} 2930s, 2856s, 1732s, 1602m, 1176s, 1026s, 712s; δ_H(400MHz, $CDCl_3$) 1.30-1.70 (24H, m), 1.89-1.99 (4H, m), 2.34, (4H, t, *J* 7.5 Hz), 2.46-2.75 (4H, m), 3.71 (6H, s), 4.07-4.27 (2H, m), 5.87 (1H, dd, *J* 10.5, 3.5 Hz), 5.93 (1H, dd, *J* 9.0, 6.0 Hz), 7.50-7.55 (4H, m), 7.65-7.70 (2H, m), 8.08-8.10 (4H, m); δ_C(100.6MHz, $CDCl_3$) 24.9 ($2CH_2$), 27.2 (CH_2), 27.3 (CH_2), 28.8 ($2CH_2$), 29.1 ($2CH_2$), 29.2 ($2CH_2$), 29.3 ($2CH_2$), 34.1 ($2CH_2$), 38.9 (CH_2), 39.0 (CH_2), 41.1 (CH_2), 41.6 (CH_2), 49.7 (CH), 50.3 (CH), 51.5 ($2CH_3$), 60.0 (CH), 61.4 (CH), 116.2 (C), 116.6 (C), 128.0 (2C), 128.7 (2CH), 128.8 (2CH), 130.0 (4CH), 134.2 (2CH), 164.5 (C), 164.6 (C), 174.3 (2C); *m/z*(CI) 457[MNH_4^+,100%], 455[MNH_4^+,100%], 440[MH^+,8%], 438[MH^+,8%]; HRMS: found 437.1211 (M^+). $C_{21}H_{28}O_4N^{79}Br$ requires 437.1202.

(±)-Benzoic acid 3-bromo-1-cyano-4-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-butyl ester (14j)



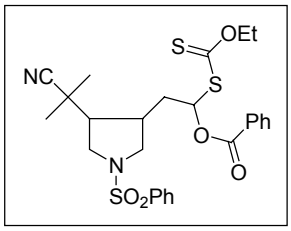
Obtained from xanthate **6j** as a white foam (82%) (petroleum ether 40-60: Et_2O: DCM 7:2:1) and as a mixture of 2 diastereomers in a 1.1:1 ratio which were not separated; R_f 0.2 (petroleum ether 40-60: Et_2O: DCM 6:3:1); ν_{max}(film)/cm^{-1} 2924s, 2849s, 2355w, 1774s, 1718s, 1601m, 1467m, 1091s, 712s; δ_H(400MHz, $CDCl_3$) 2.49-2.87 (4H, m), 4.10-4.30 (4H, m), 4.50-4.62 (2H, m), 5.86 (1H, dd, *J* 10.5, 3.0 Hz), 5.96 (1H, dd, *J* 9.0, 6.0 Hz), 7.49-7.57 (4H, m), 7.64-7.71 (2H, m), 7.76-7.84 (4H, m), 7.90-7.97 (4H, m), 8.05-8.11 (4H, m); δ_C(100.6MHz, $CDCl_3$) 38.6 (CH_2), 38.8 (CH_2), 44.0 ($2CH_2$), 44.2 (CH), 44.6 (CH), 59.5 (CH), 60.9 (CH), 115.8 (C), 116.2 (C), 123.8 (4CH), 127.8 (C), 127.9 (C), 128.8 (4CH), 130.1 (4CH), 131.7 (4C), 134.2 (CH), 134.3 (CH), 134.5 (4CH), 164.4 (C), 164.6 (C), 167.8 (4C); *m/z*(CI) 446[MNH_4^+,100%], 444[MNH_4^+,100%]; HRMS: found 426.0235 (M^+). $C_{20}H_{15}O_4N_2{}^{79}Br$ requires 426.0215.

***N*-Allyl-*N*-(3-methyl-but-2-enyl)-benzenesulfonamide (22)**



To a flask containing sodium hydroxide (1.2 g, 30 mmol, 1.2 eq) at 0°C under nitrogen was added water (13 mL) followed by Et_2O (13 mL) and then allylamine (1.9 mL, 25 mmol, 1 eq). Benzenesulfonyl chloride (3.5 mL, 27.4 mmol, 1.1 eq) was then added dropwise and the reaction mixture stirred at rt for 3 h. The organic layer was separated, dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification by flash chromatography (petroleum ether 40-60: Et_2O 8:2) gave *N*-allyl-benzenesulfonamide (5.0 g). To a flask containing *N*-allyl-benzenesulfonamide (5.0 g, 25 mmol, 1 eq) at rt under nitrogen was added dry DMF (30 mL) and the solution stirred for 5 min. The solution was then cooled to 0°C, NaH (1.22 g, 60% dispersion in mineral oil, 1.2 eq) added portionwise and the resulting mixture stirred at rt for 1 h. 1-Bromo-3-methylbut-2-ene (90% purity, 4.2 mL, 33 mmol, 1.3 eq) was then added and stirring continued for a further 20 h. The mixture was poured into ice-water (360 mL) and the aqueous layer was extracted with DCM (3 × 200 mL). The organic layers were combined, dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residual oil was dissolved in Et_2O (50 mL), washed with water (3 × 100 mL) and then dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification by flash chromatography (petroleum ether 40-60: DCM 6:4) gave the title compound **22** as a colorless oil (6.4 g, 97% over 2 steps); R_f 0.3 (petroleum ether 40-60: Et_2O 9:1); ν_{max}(film)/cm^{-1} 3067m, 2972s, 2916s, 1673m, 1643m, 1344s, 1161s, 768s; δ_H(400MHz, $CDCl_3$) 1.63 (3H, s), 1.69 (3H, s), 3.82-3.87 (4H, m), 4.97-5.03 (1H, m), 5.15-5.22 (2H, m), 5.64-5.75 (1H, m), 7.51-7.57 (2H, m), 7.58-7.63 (1H, m), 7.84-7.89 (2H, m); δ_C(100.6MHz, $CDCl_3$) 17.8 (CH_3), 25.7 (CH_3), 44.5 (CH_2), 49.3 (CH_2), 118.4 (CH_2), 118.7 (CH), 127.1 (2CH), 129.0 (2CH), 132.4 (CH), 133.1 (CH), 136.9 (C), 140.6 (C); *m/z*(CI) 283[MNH_4^+,6%], 266[MH^+, 100%]; HRMS: found 265.1130 (M^+). $C_{14}H_{19}O_2NS$ requires 265.1137.

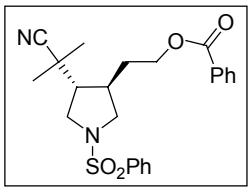
Addition of 3 to diene 22: (±)-(1,5) Nitrile translocation product (24)



A solution of xanthate **3** (260 mg, 0.92 mmol, 1 eq) and diene **22** (490 mg, 1.85 mmol, 2 eq) in 1,2-dichloroethane (DCE) (0.92 mL) was refluxed for 15 min under nitrogen. Lauroyl peroxide (DLP) (18.4 mg, 46 μmol, 0.05 eq) was then added to the refluxing solution, followed by additional portions (18.4 mg, 46 μmol, 0.05 eq) every 1.5 h until **3** was completely consumed. The mixture was then cooled to rt, concentrated under reduced pressure and purified by flash chromatography (petroleum ether 40-60: Et_2O: DCM 6:3:1). A small layer of basic alumina was placed on top of the silica to remove any lauric acid present. This procedure afforded adduct **24** (226 mg, 45%) as a white foam and as a mixture of 4 diastereomers in a 3:3:1:1 ratio and adduct **23** (45 mg, 9%) as a yellow oil and as a mixture of 4 diastereomers.

Data for adduct 24: white foam (226 mg, 45%); R_f 0.15 (petroleum ether 40-60: Et_2O: DCM 6:3:1); ν_{max}(film)/cm^{-1} 2979s, 2933s, 2232w, 1728s, 1599m, 1347s, 1248s, 1168s, 1091s; δ_H(400MHz, $CDCl_3$) 1.25-1.50 (72H, m), 1.98-2.50 (32H, m), 2.83-3.80 (32H, m), 4.60-4.73 (16H, m), 6.68-6.88 (8H, m), 7.34-8.11 (80H, m); δ_C(100.6MHz, $CDCl_3$) see ^{13}C NMR spectrum in supporting information; *m/z*(CI) 564[MNH_4^+,12%], 547[MH^+, 3%], 443[100]; HRMS: found 546.1330 (M^+). $C_{26}H_{30}O_5N_2S_3$ requires 546.1317.

(±)-Benzoic acid 2-[1-benzenesulfonyl-4-(cyano-dimethyl-methyl)-pyrrolidin-3-yl]-ethyl ester (25)



A solution of xanthate **24** (83 mg, 0.15 mmol, 1 eq) in toluene (1.5 mL) was refluxed for 15 min under nitrogen. Tributyltin hydride (46.3 μL, 0.17 mmol, 1.1 eq) and 2,2'-azobisisobutyronitrile (AIBN) (2.5 mg, 15 μmol, 0.1 eq) were then added to the refluxing solution, and reflux continued for a further 2 h. The mixture was then cooled to rt, concentrated under reduced pressure and the residue obtained dissolved in MeCN (20 mL) and washed with petroleum ether 40-60 (3 × 20 mL) to remove tin-based residues. The MeCN layer was then concentrated under reduced pressure and purified by flash chromatography (petroleum ether 40-60: Et_2O: DCM 7:2:1) to afford the reduced compounds as a white foam (31.4 mg, 49%) and as a 3(*trans*): 1(*cis*), mixture of diastereomers. Further purification by preparative chromatography (petroleum ether 40-60: Et_2O: DCM 55:35:10) allowed the pure major *(trans)* diastereomer **25a** to be isolated.

Data for major diastereomer 25a: clear oil (23.6 mg, 37%); R_f 0.29 (petroleum ether 40-60: Et_2O: DCM 5:4:1); ν_{max}(film)/cm^{-1} 3064m, 2977s, 2233w, 1717s, 1602m, 1585m, 1347s, 1167s, 1070s, 692s; δ_H(400MHz, $CDCl_3$) 1.33 (3H, s), 1.40 (3H, s), 1.83-1.93 (1H, m), 2.02-2.15 (2H, m), 2.32-2.42 (1H, m), 3.01 (1H, dd, *J* 10.0, 7.0 Hz), 3.15 (1H, dd, *J* 10.0, 5.0 Hz), 3.37 (1H, dd, *J* 10.0, 7.5 Hz), 3.53 (1H, dd, *J* 10.0, 8.5 Hz), 4.35-4.40 (2H, m), 7.49-7.54 (2H, m), 7.56-7.69 (4H, m), 7.83-7.86 (2H, m), 8.04-8.08 (2H, m); δ_C(100.6MHz, $CDCl_3$) 24.4 (CH_3), 25.6 (CH_3), 34.4 (CH_2), 35.3 (C), 38.1 (CH), 49.8 (CH_2), 52.0 (CH), 53.2 (CH_2), 62.9 (CH_2), 123.3 (C), 127.9 (2CH), 128.5 (2CH), 129.2 (2CH), 129.6 (2CH), 129.9 (C), 133.2 (CH), 133.3 (CH), 134.8 (C), 166.4 (C); *m/z*(CI) 444[MNH_4^+,100%], 427[MH^+, 33%]; HRMS: found 426.1629 (M^+). $C_{23}H_{26}O_4N_2S$ requires 426.1613.

References

(1) Dinizo, S. E.; Freerksen, R. W.; Pabst, E.; Watt, D. S. *J. Org. Chem.* **1976**, *41*, 2846.

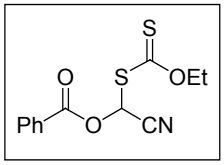
(2) Tanji, K.-I.; Sato, S.; Kanamaru, Y.; Lijima, C.; Miyashita, A.; Higashino, T. *Chem. Pharm. Bull*. **1992**, *40*, 512.

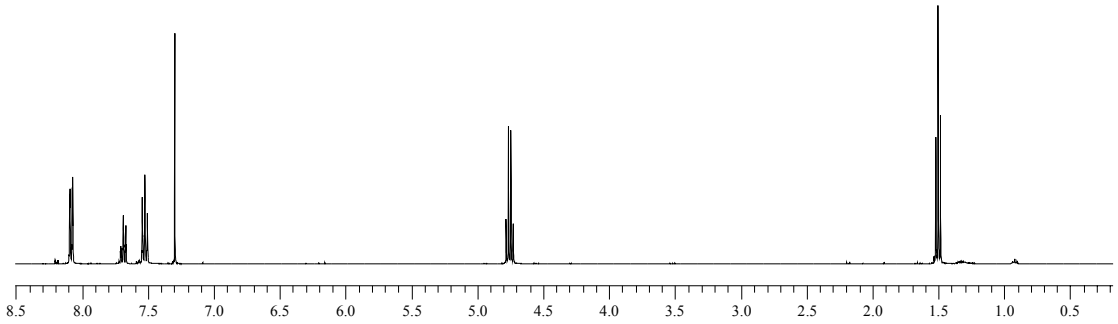
(3) Barbier, F.; Pautrat, F.; Quiclet-Sire, B.; Zard, S. Z. *Synlett* **2002**, *5*, 811.

SPECTRAL DATA

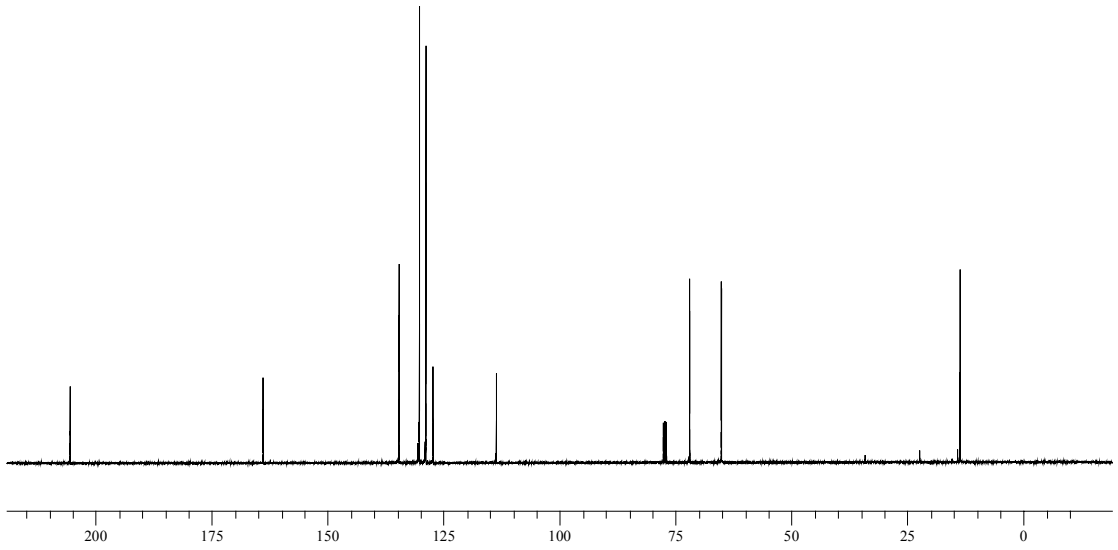
(±)-Acyl radical equivalent xanthate (3)

^{1}H NMR (400 MHz)





^{13}C NMR (100.6 MHz)



(±)-Adduct 6a

^{1}H NMR (400 MHz)

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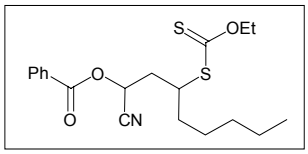
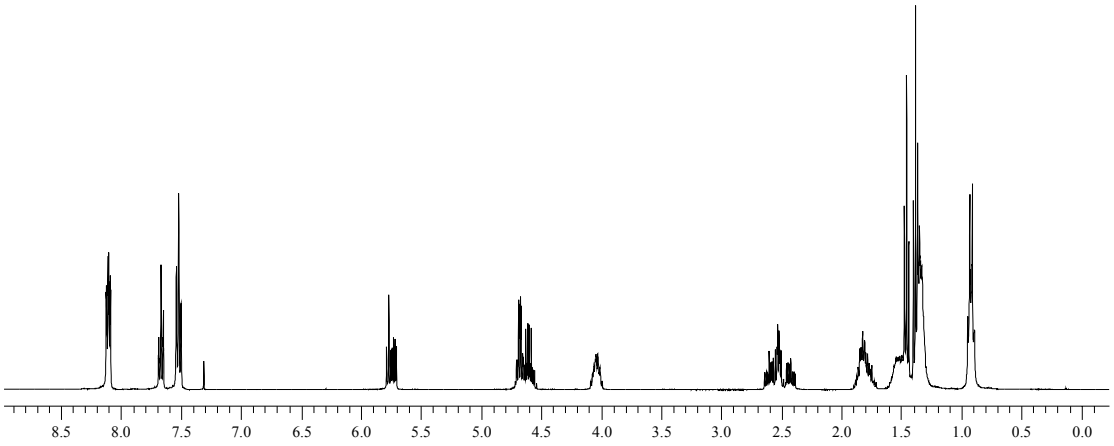
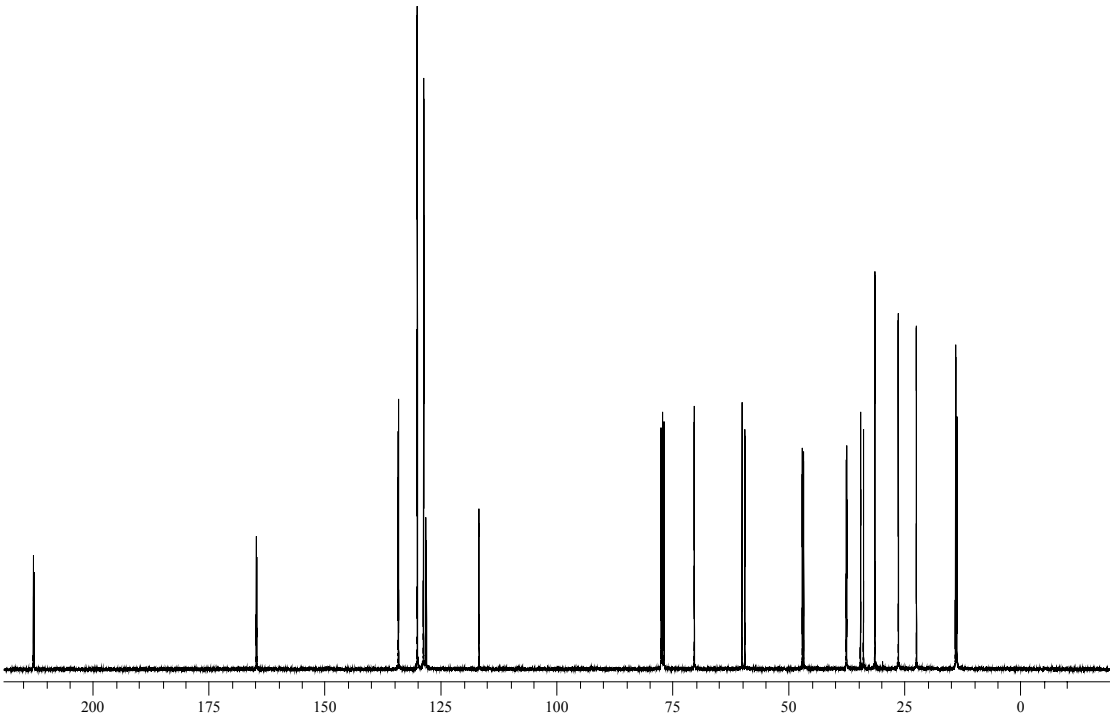




^{13}C NMR (100.6 MHz)



(±)-Adduct 6b

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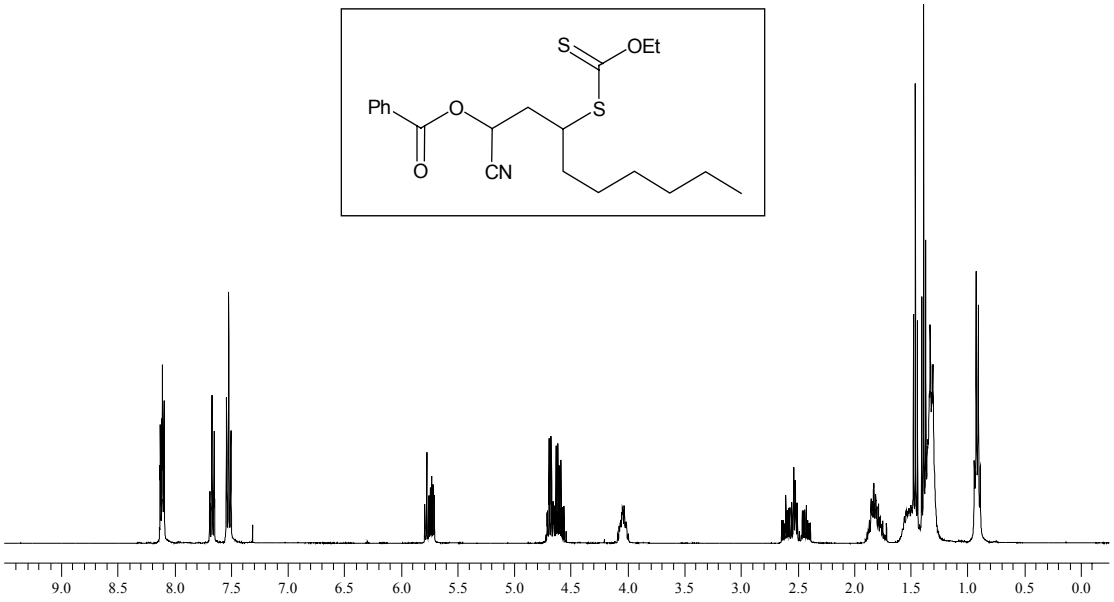
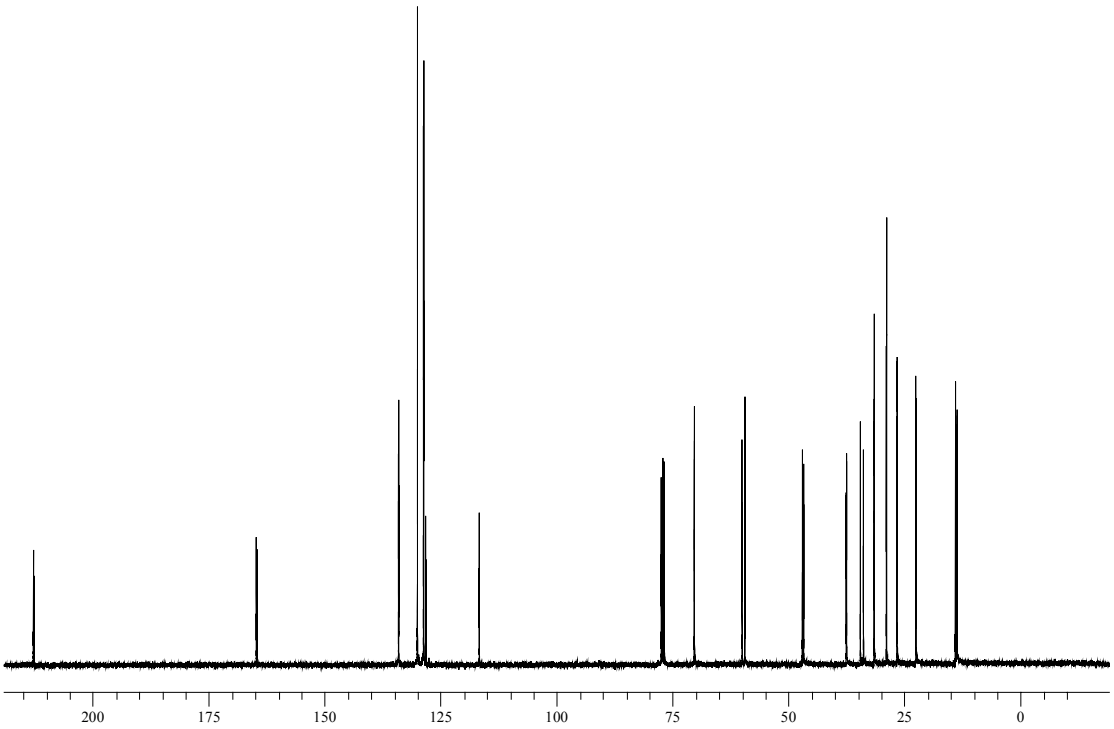


^{13}C NMR (100.6 MHz)



(±)-Adduct 6c

^{1}H NMR (400 MHz)

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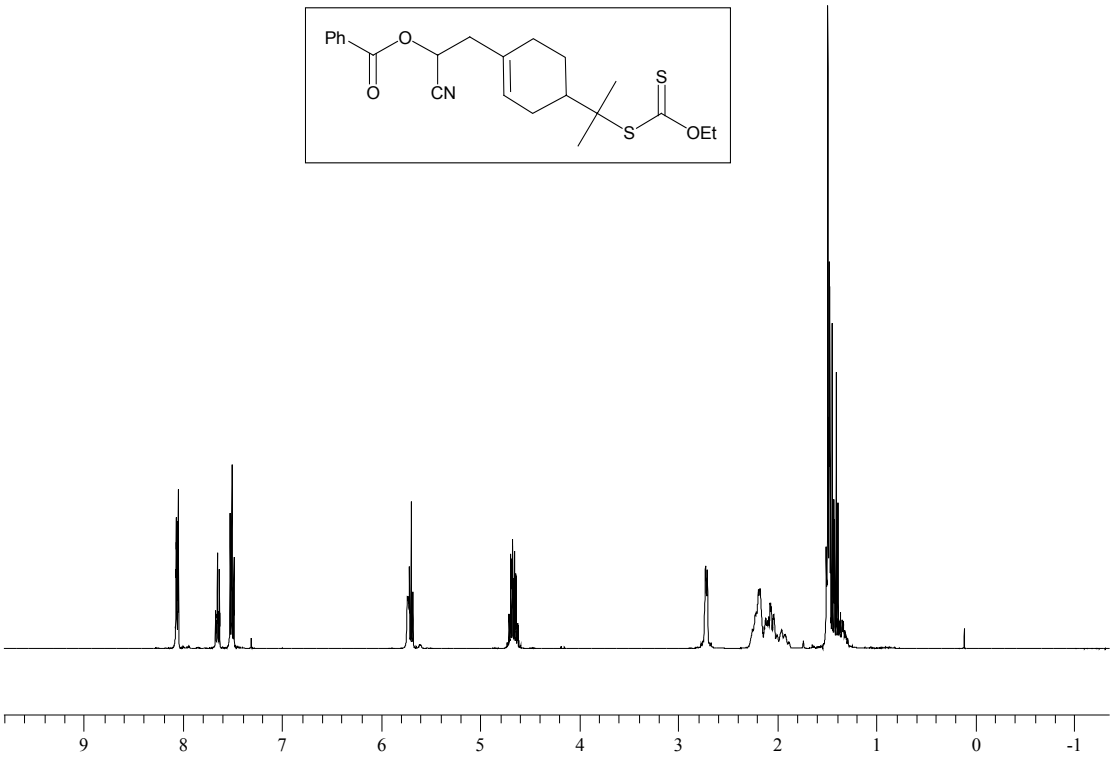
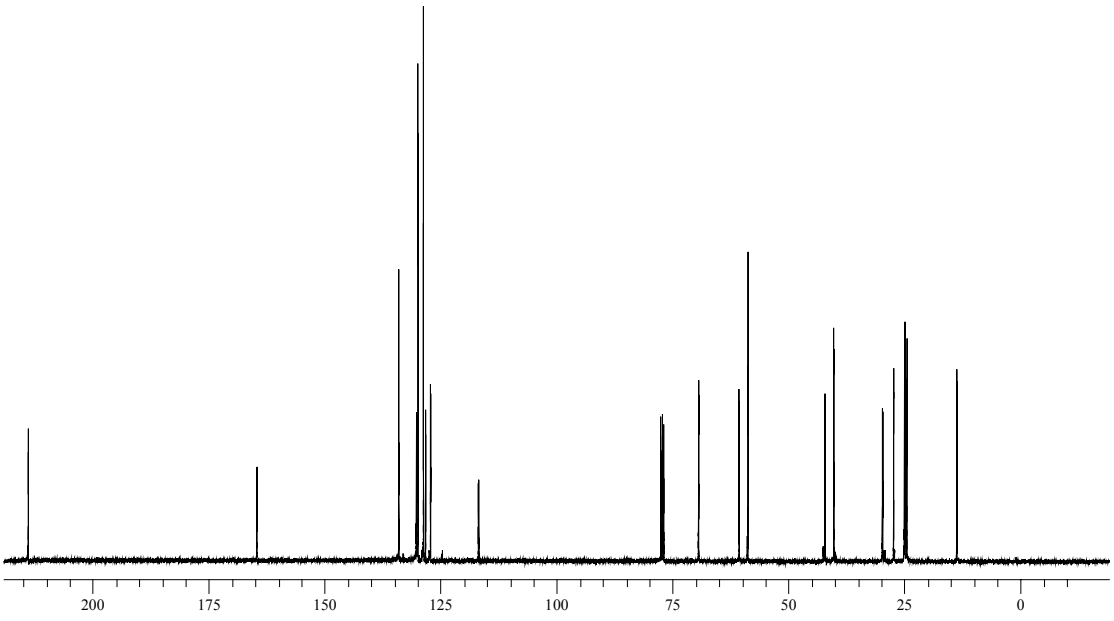


^{13}C NMR (100.6 MHz)



(±)-Adduct 6d

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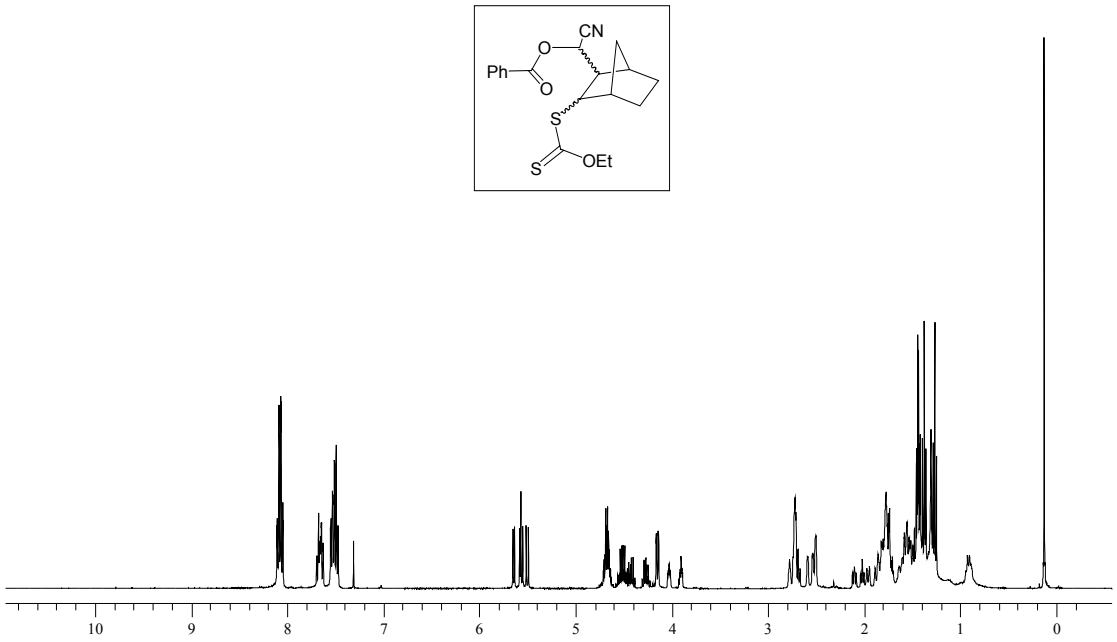
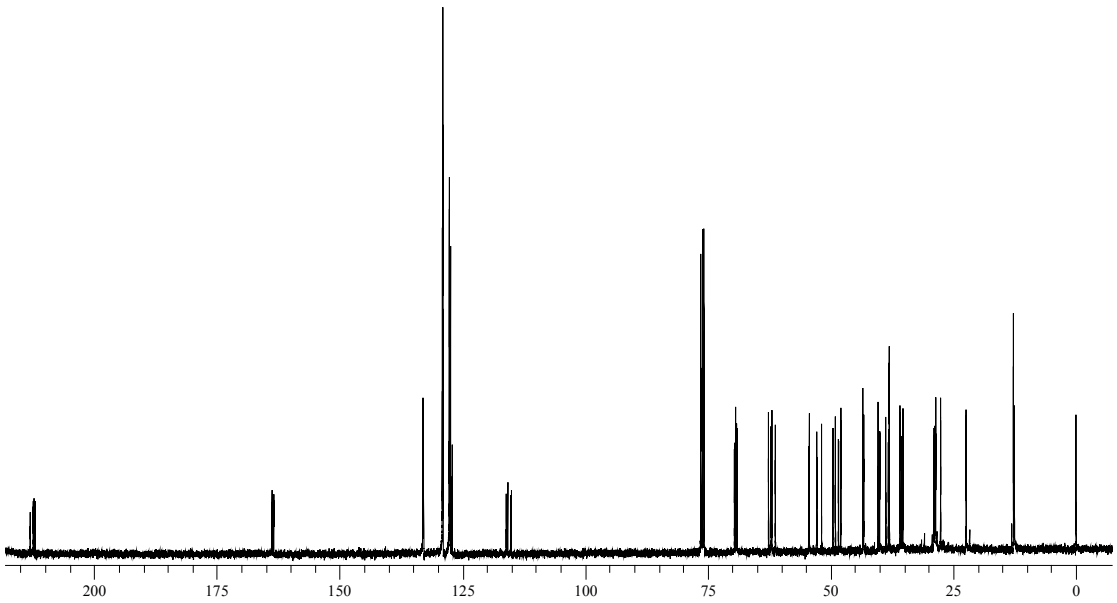


^{13}C NMR (100.6 MHz)



(±)-Adduct 6e

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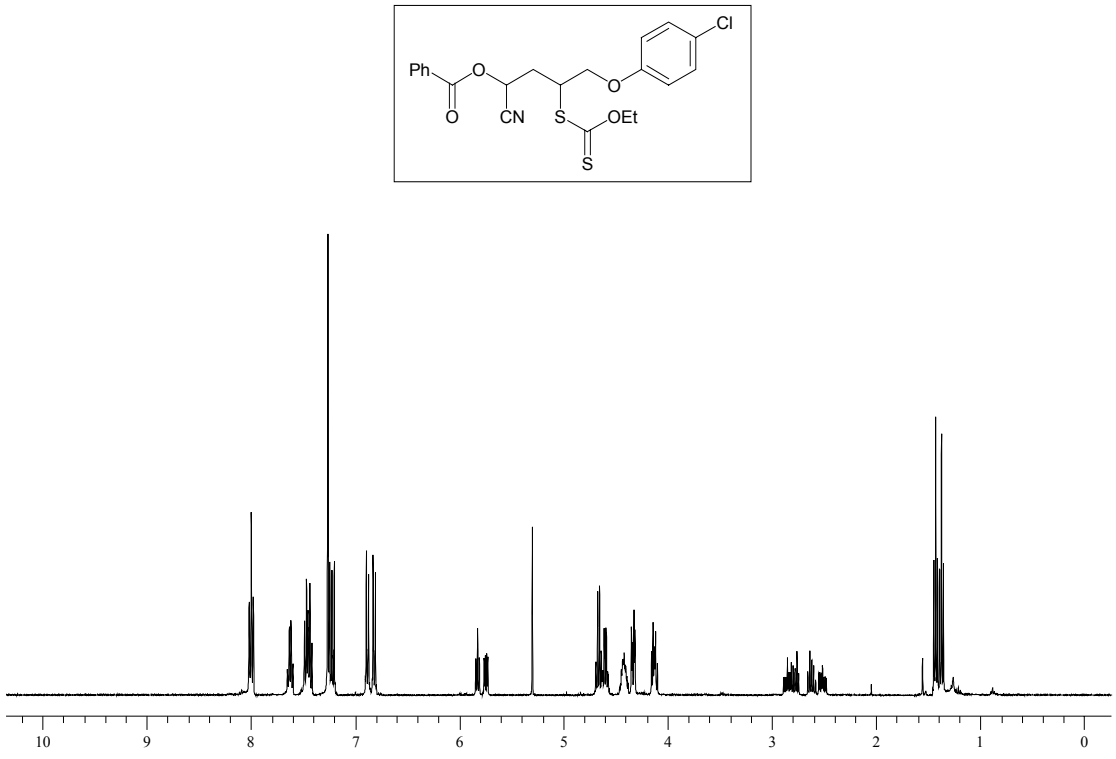

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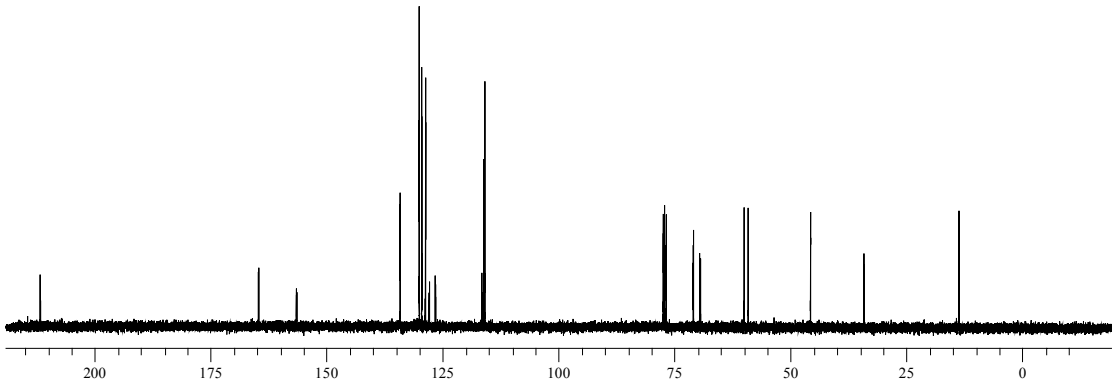

(±)-Adduct 6f

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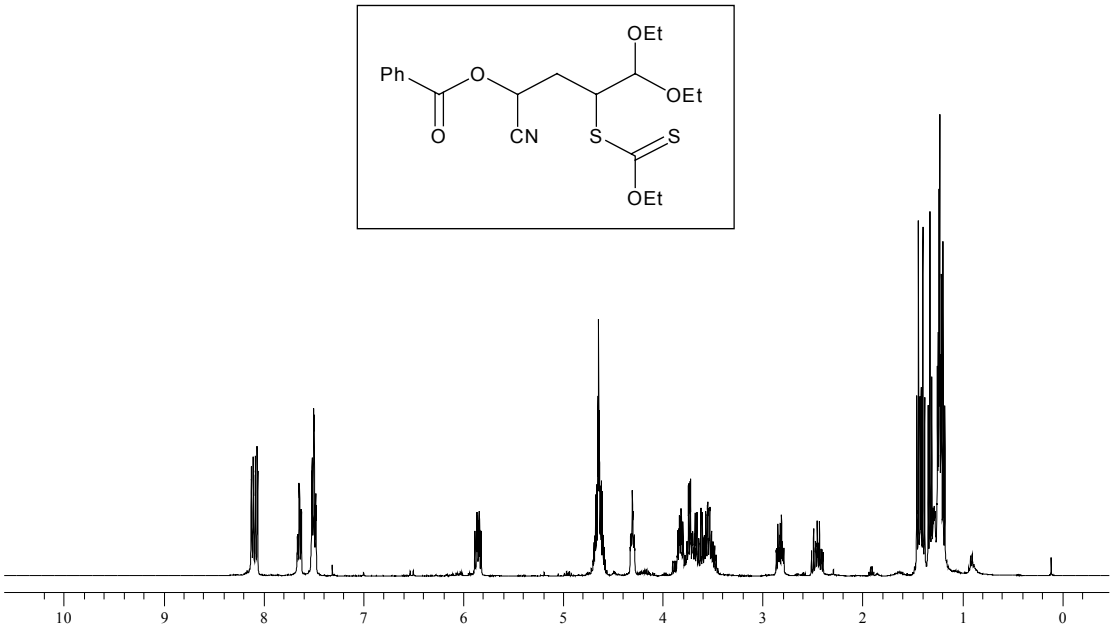
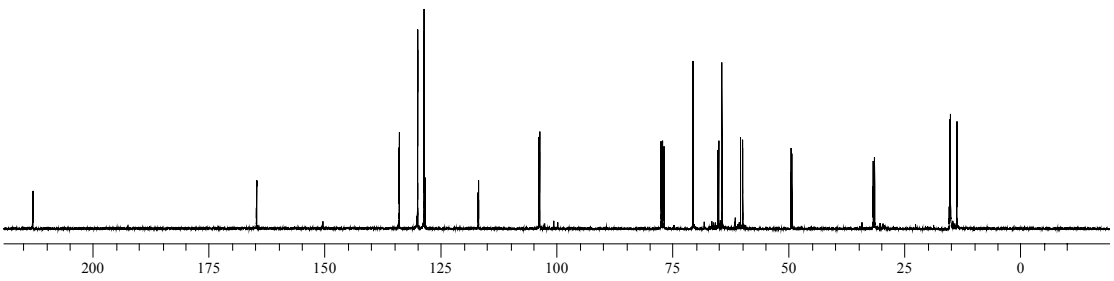


^{13}C NMR (100.6 MHz)



(±)-Adduct 6g

^{1}H NMR (400 MHz)

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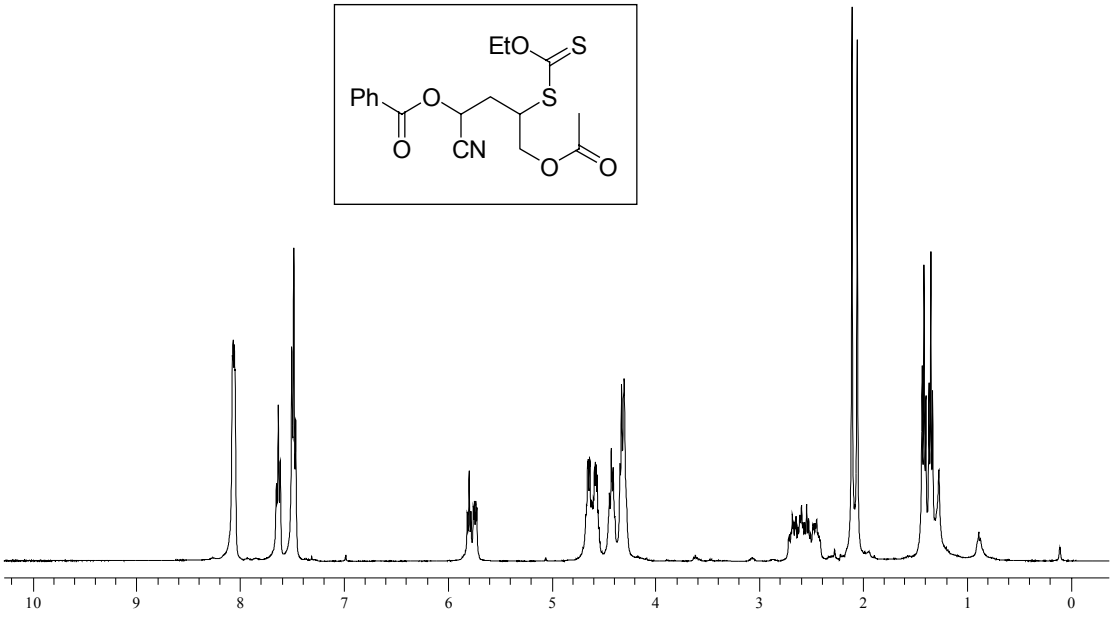
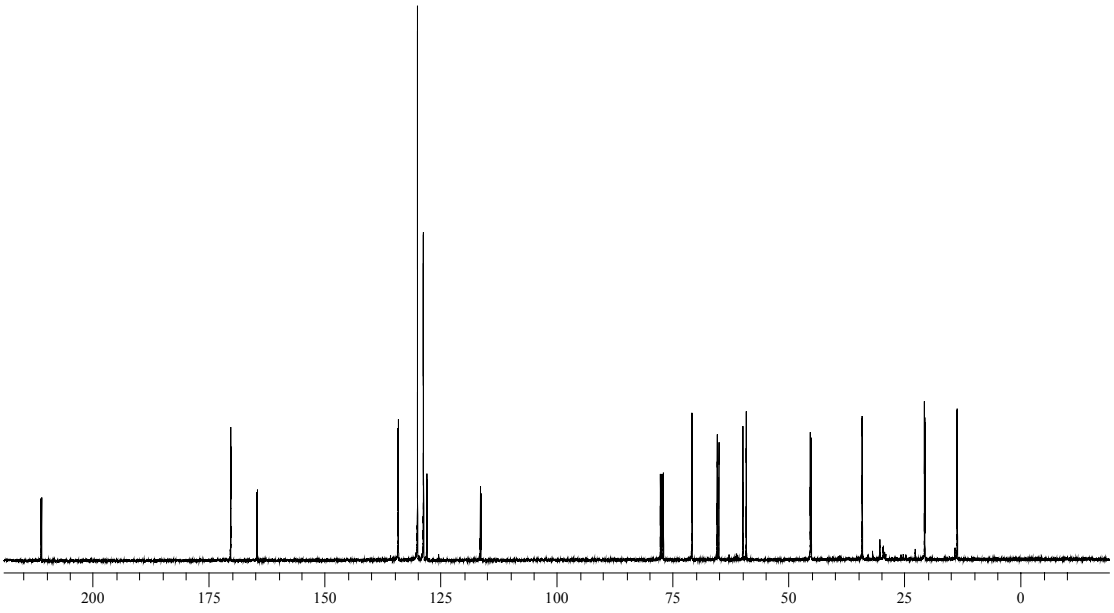


^{13}C NMR (100.6 MHz)



(±)-Adduct 6h

^{1}H NMR (400 MHz)

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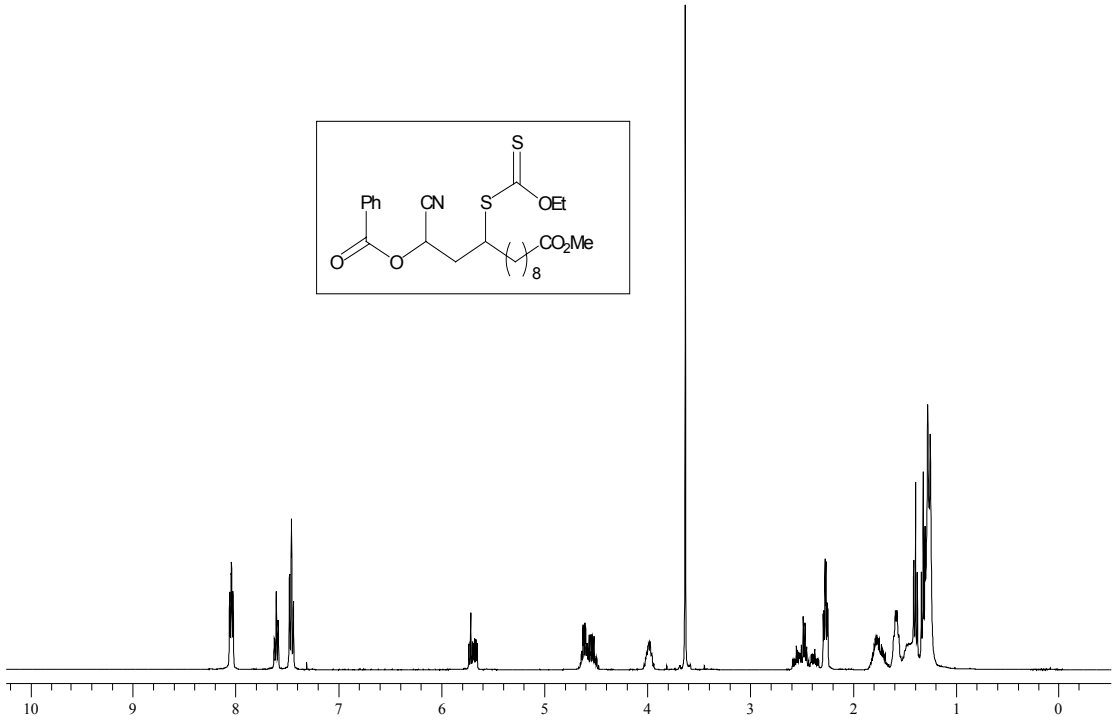

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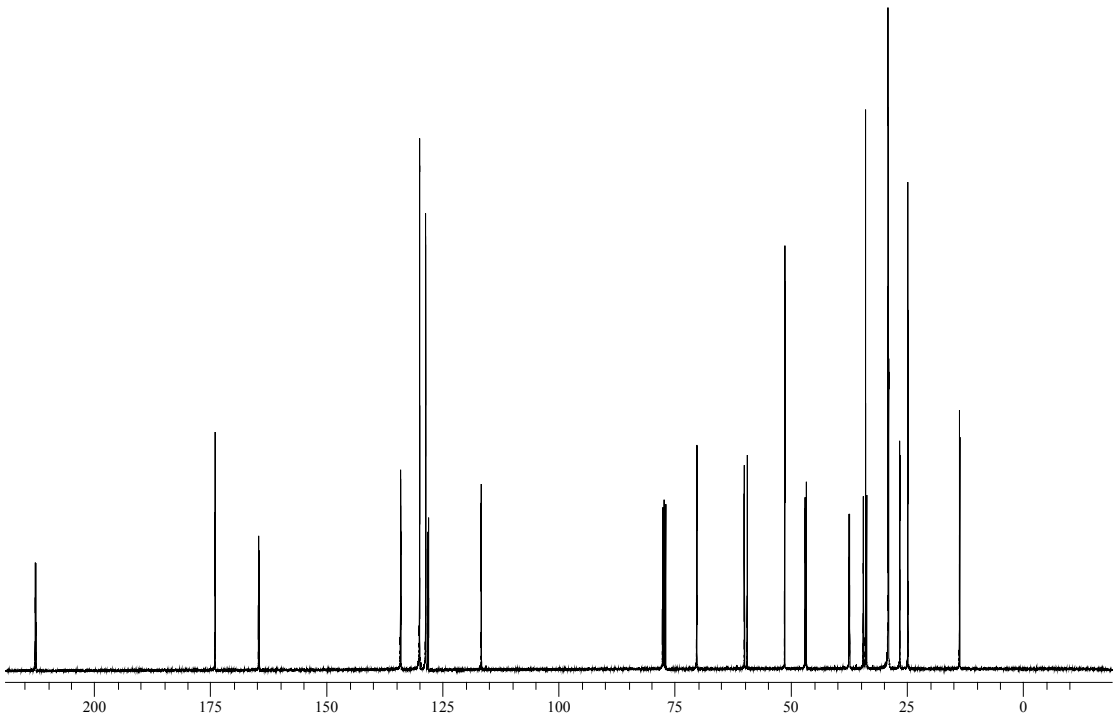

(±)-Adduct 6i

^{1}H NMR (400 MHz)

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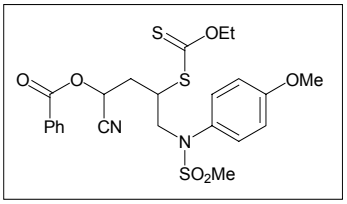
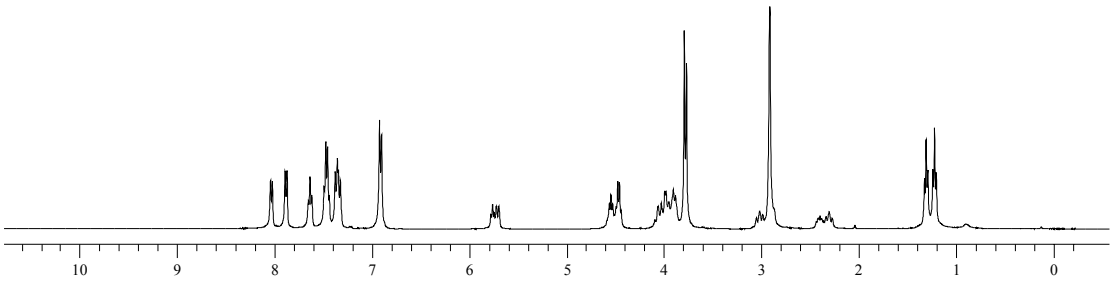
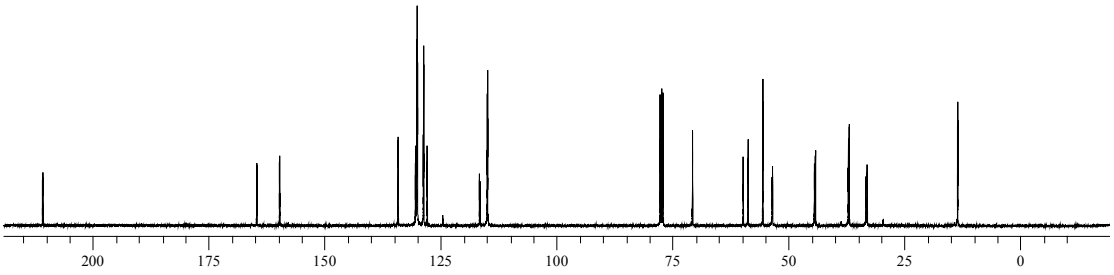




^{13}C NMR (100.6 MHz)



(±)-Adduct 6j

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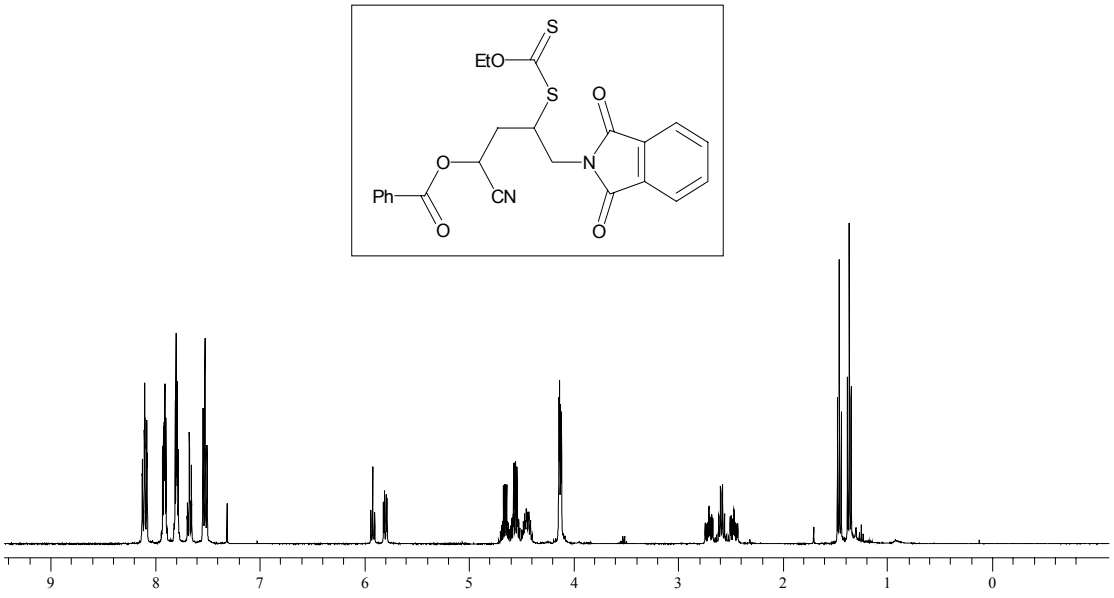

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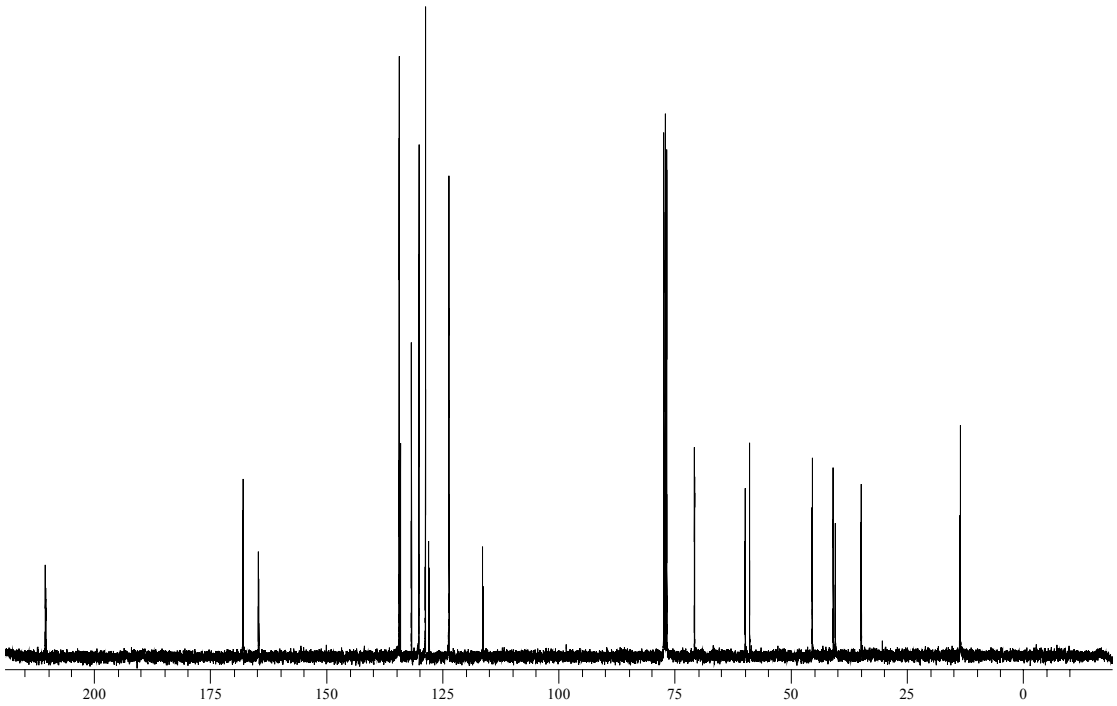

(±)-Adduct 6k

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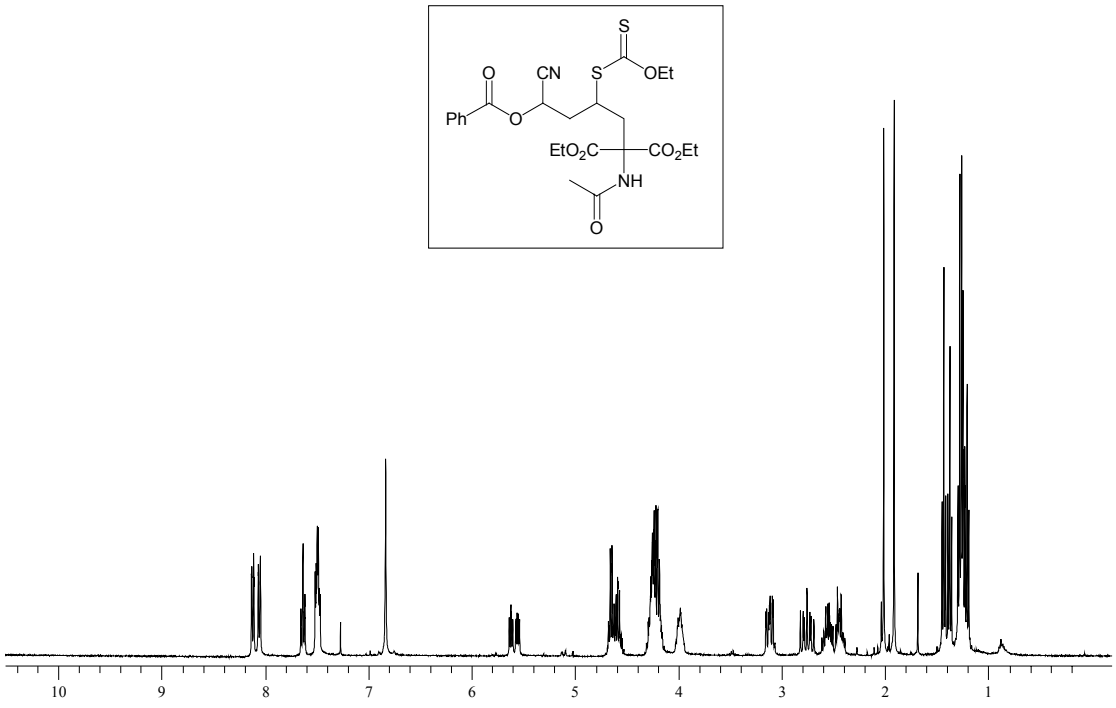
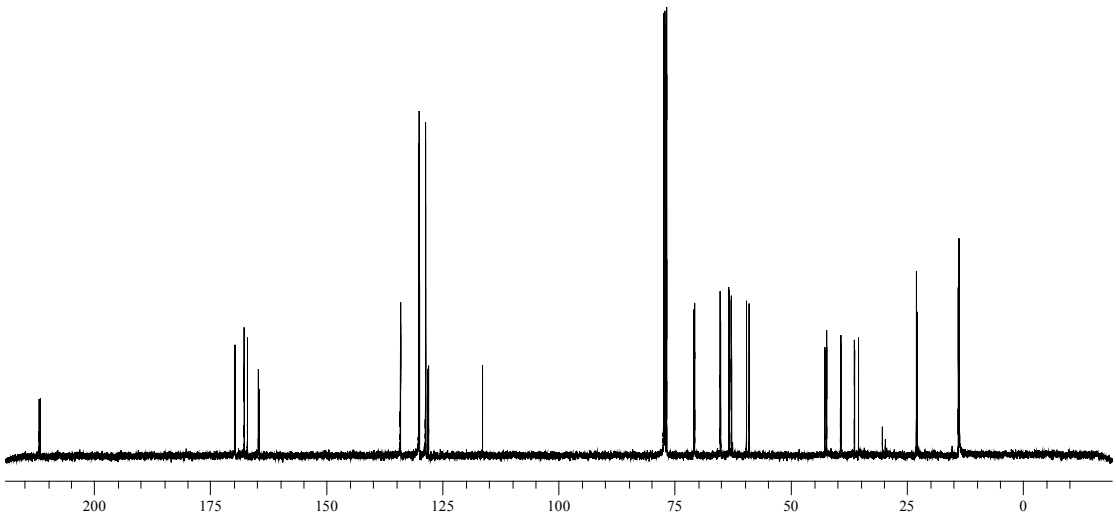


^{13}C NMR (100.6 MHz)



(±)-Adduct 6l

^{1}H NMR (400 MHz)

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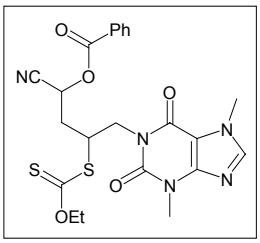
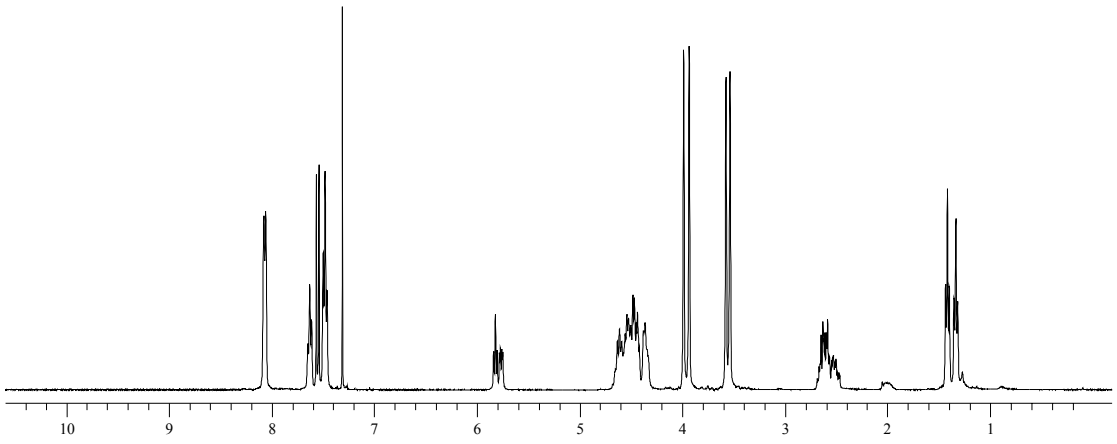
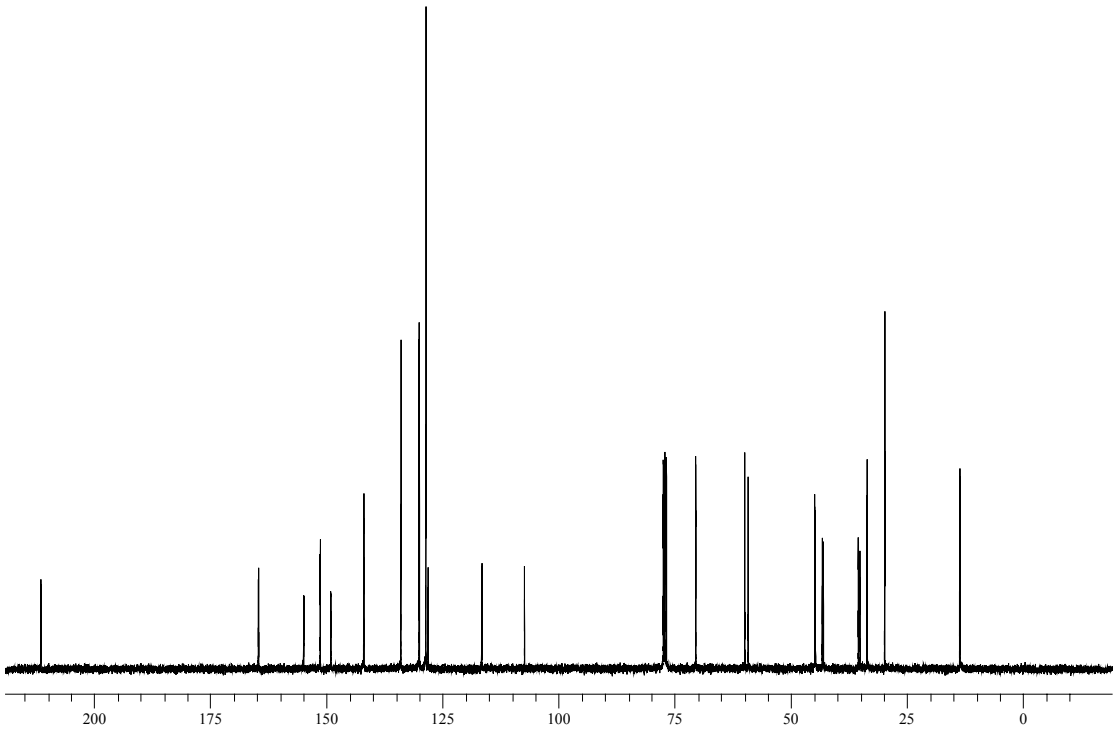




^{13}C NMR (100.6 MHz)



Adduct 6m

^{1}H NMR (400 MHz)

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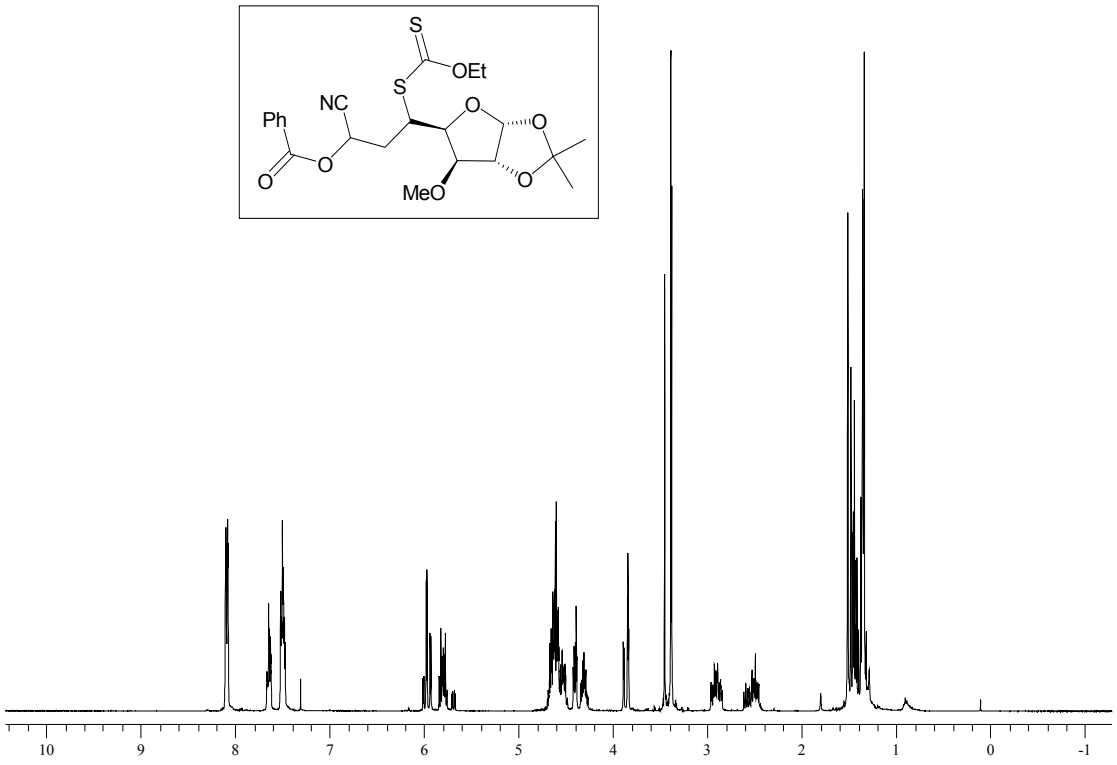
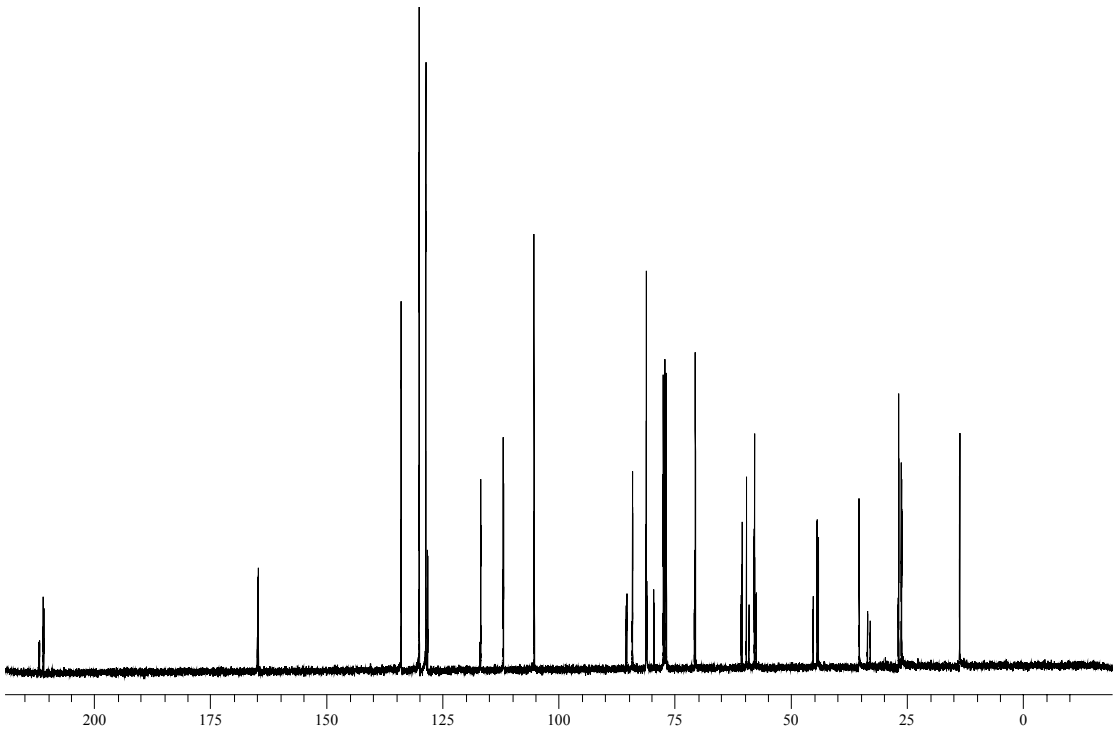
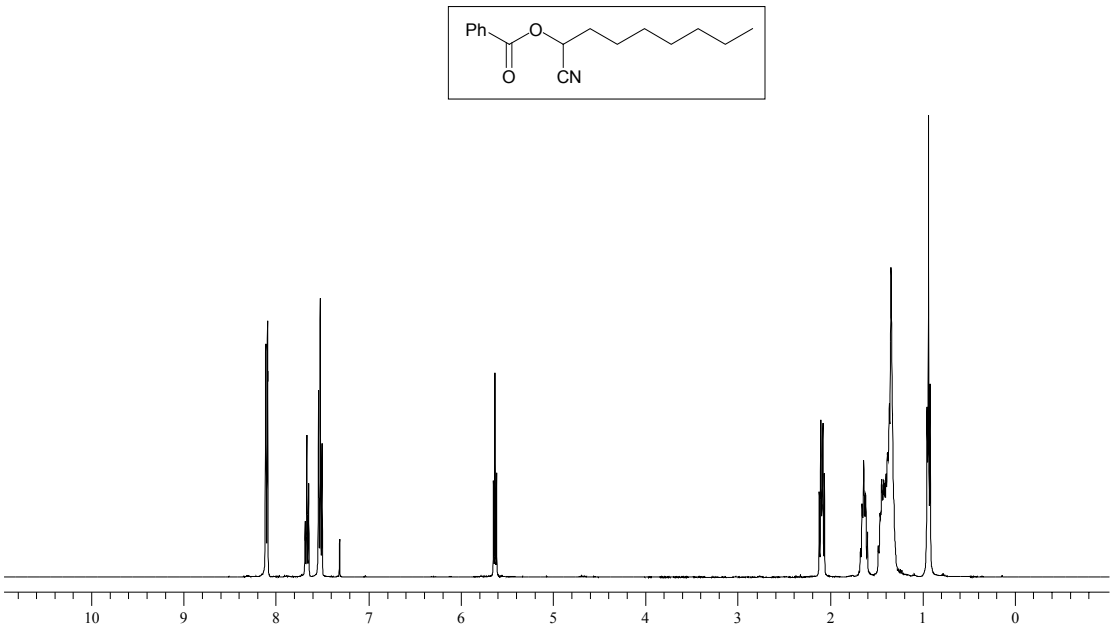


^{13}C NMR (100.6 MHz)

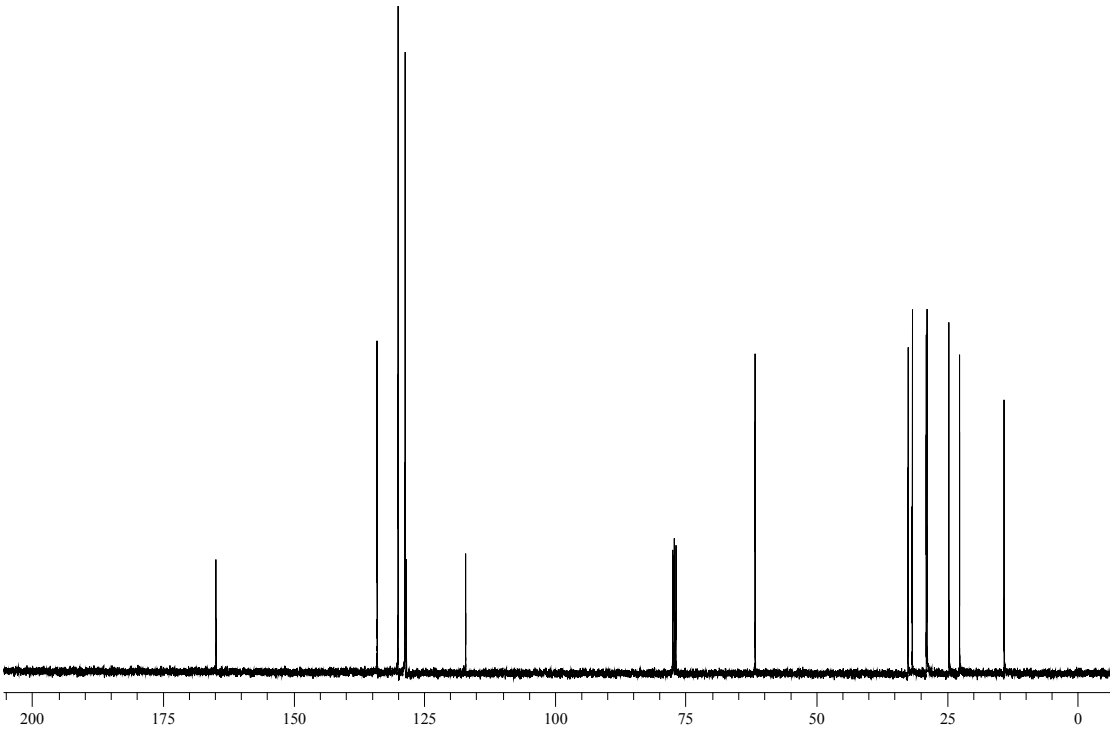


(±)-Benzoic acid 1-cyano-octyl ester (7a)

^{1}H NMR (400 MHz)

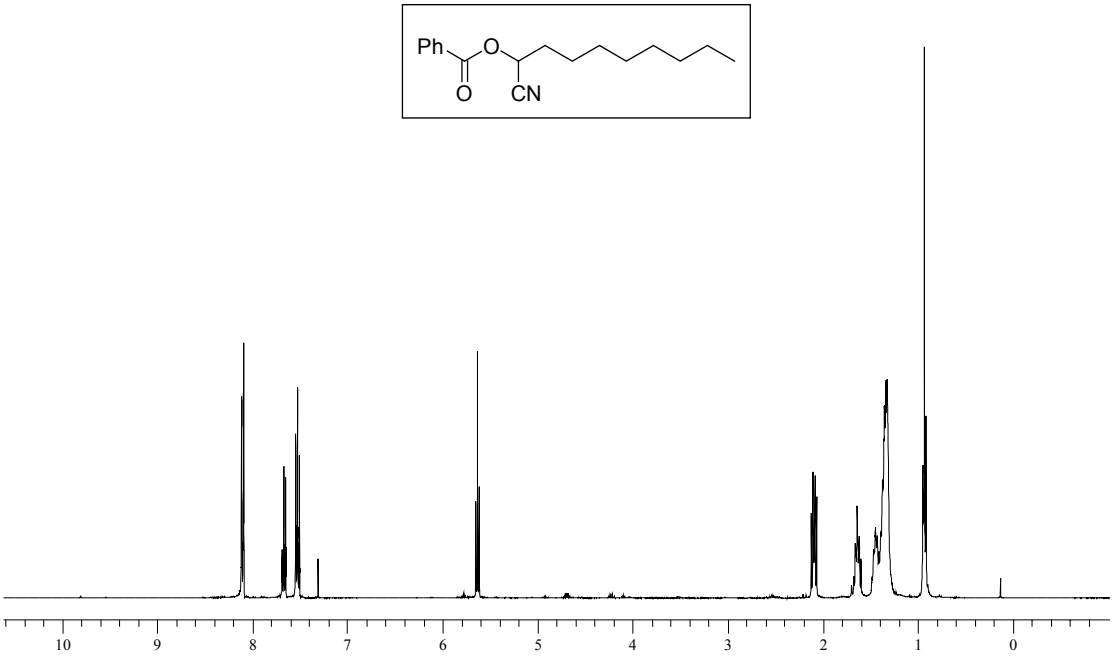


^{13}C NMR (100.6 MHz)

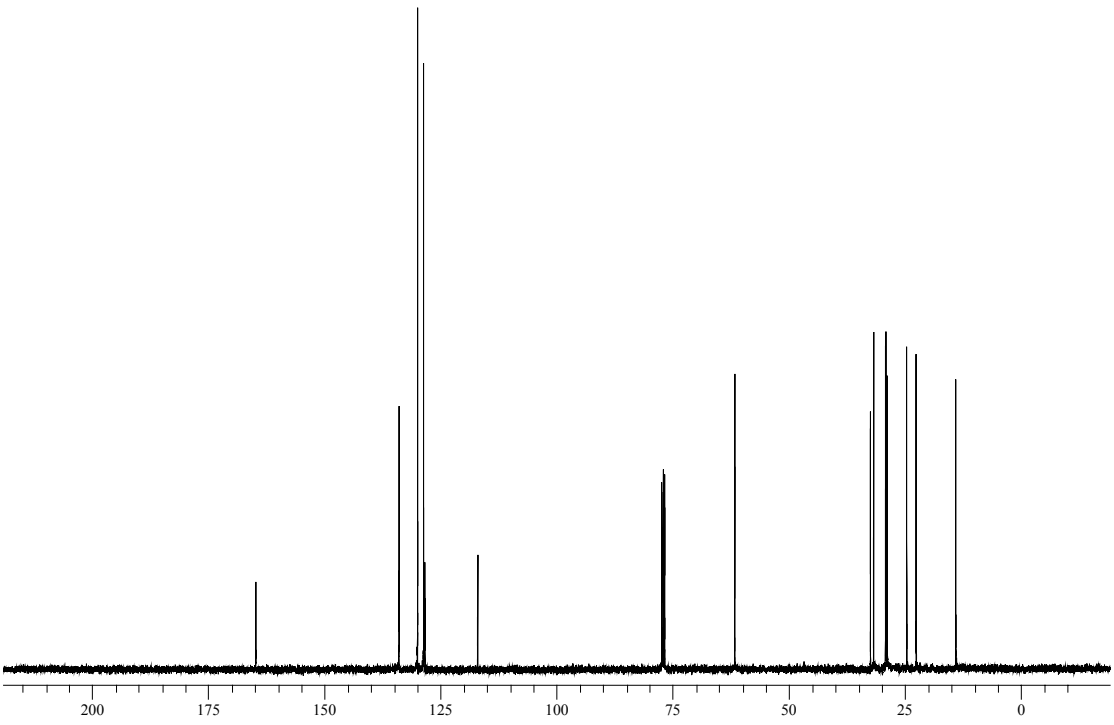


(±)-Benzoic acid 1-cyano-nonyl ester (7b)

^{1}H NMR (400 MHz)

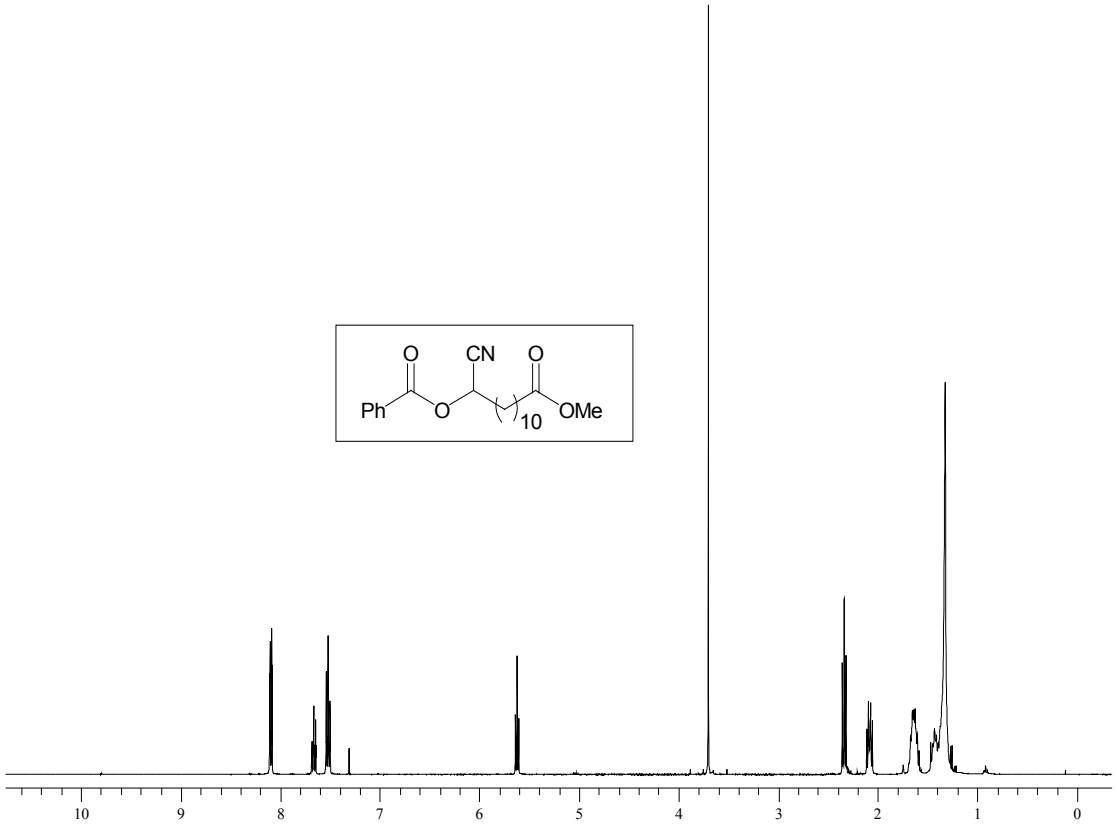


^{13}C NMR (100.6 MHz)

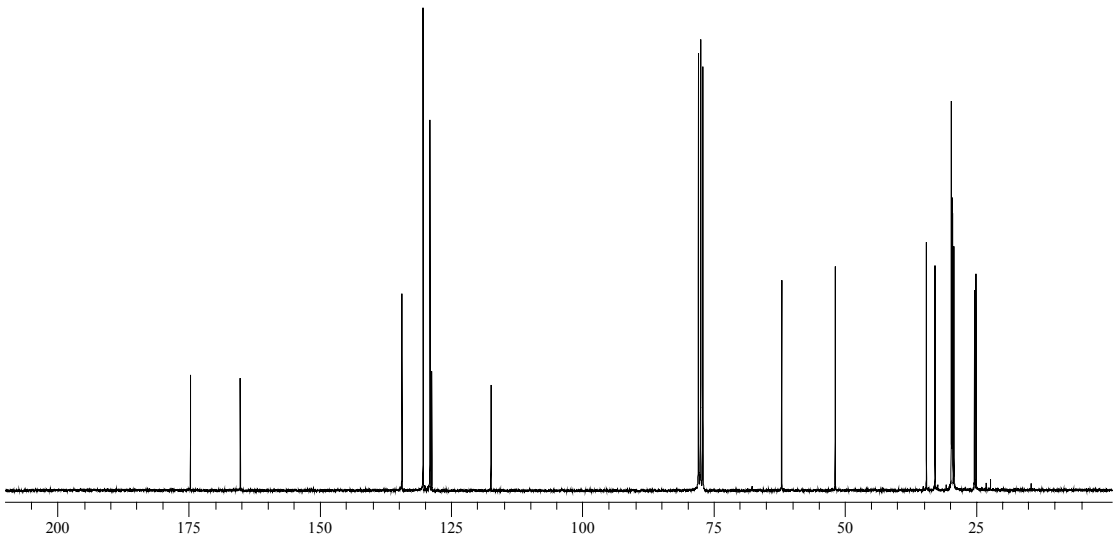


(±)-Benzoic acid 1-cyano-11-methoxycarbonyl-undecyl ester (7h)

^{1}H NMR (400 MHz)

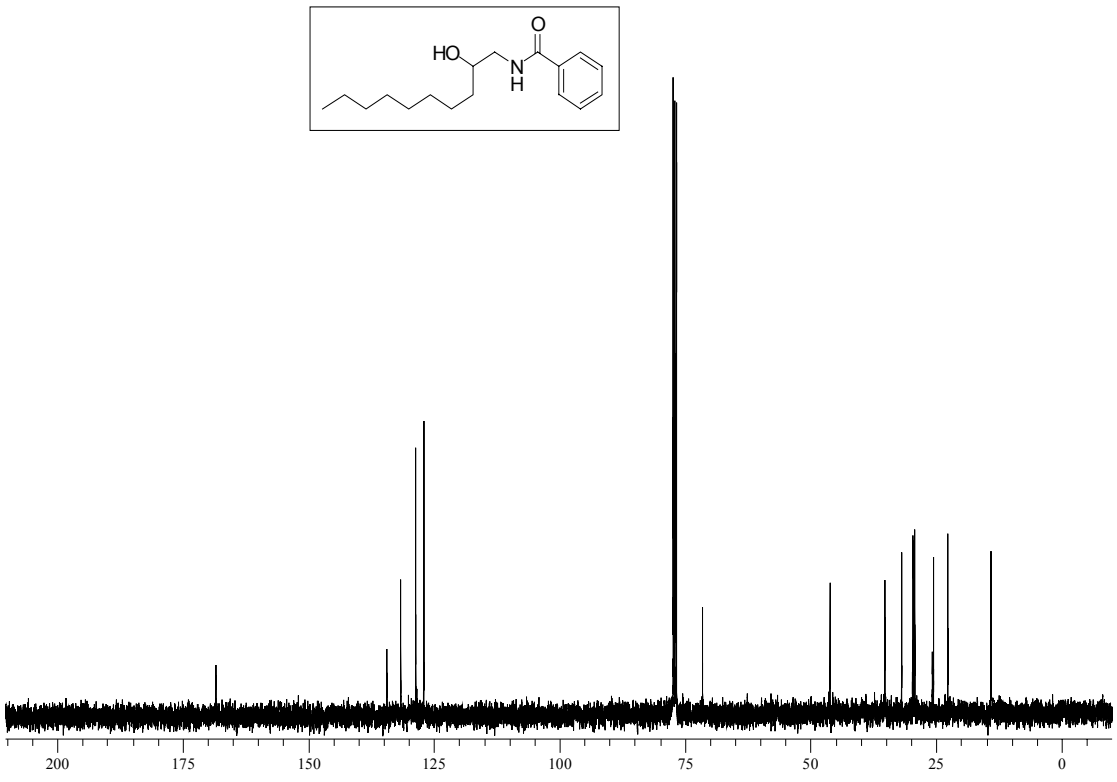


^{13}C NMR (100.6 MHz)



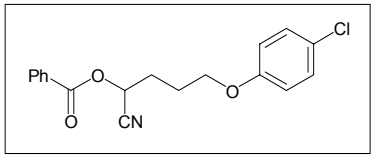
(±)-*N*-(2-Hydroxy-decyl)-benzamide (10b)

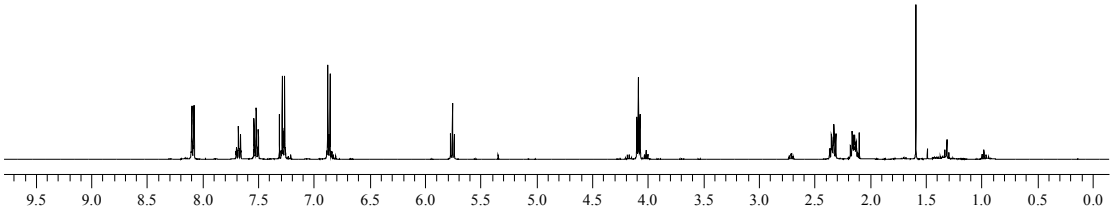
^{13}C NMR (100.6 MHz)



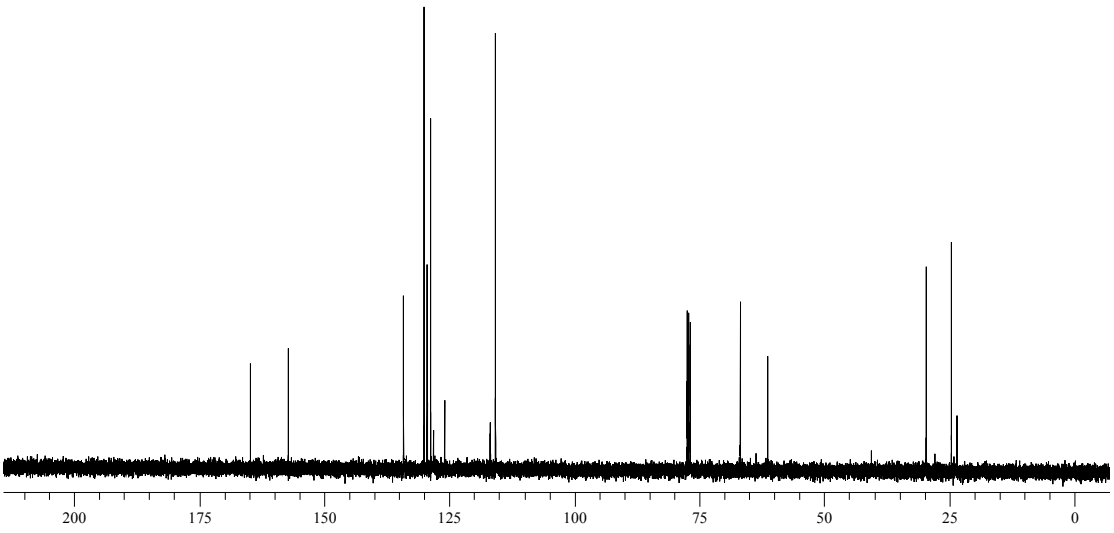
(±)-Benzoic acid 4-(4-chloro-phenoxy)-1-cyano-butyl ester (7e)

^{1}H NMR (400 MHz)



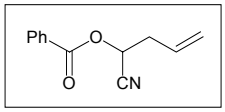


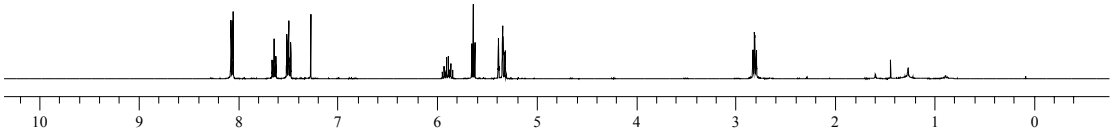
^{13}C NMR (100.6 MHz)



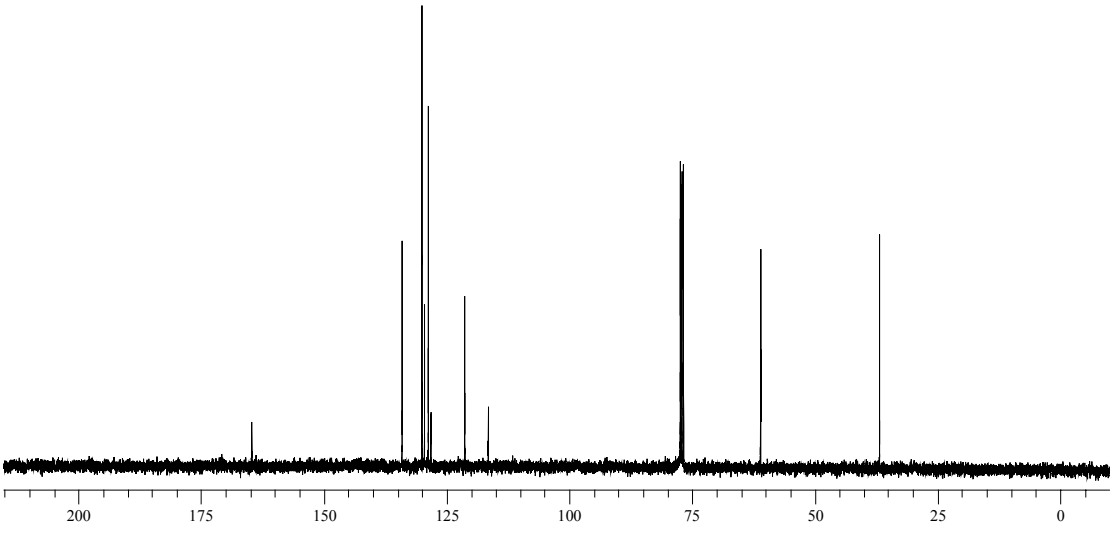
(±)-Benzoic acid 1-cyano-but-3-enyl ester (8e)

^{1}H NMR (400 MHz)



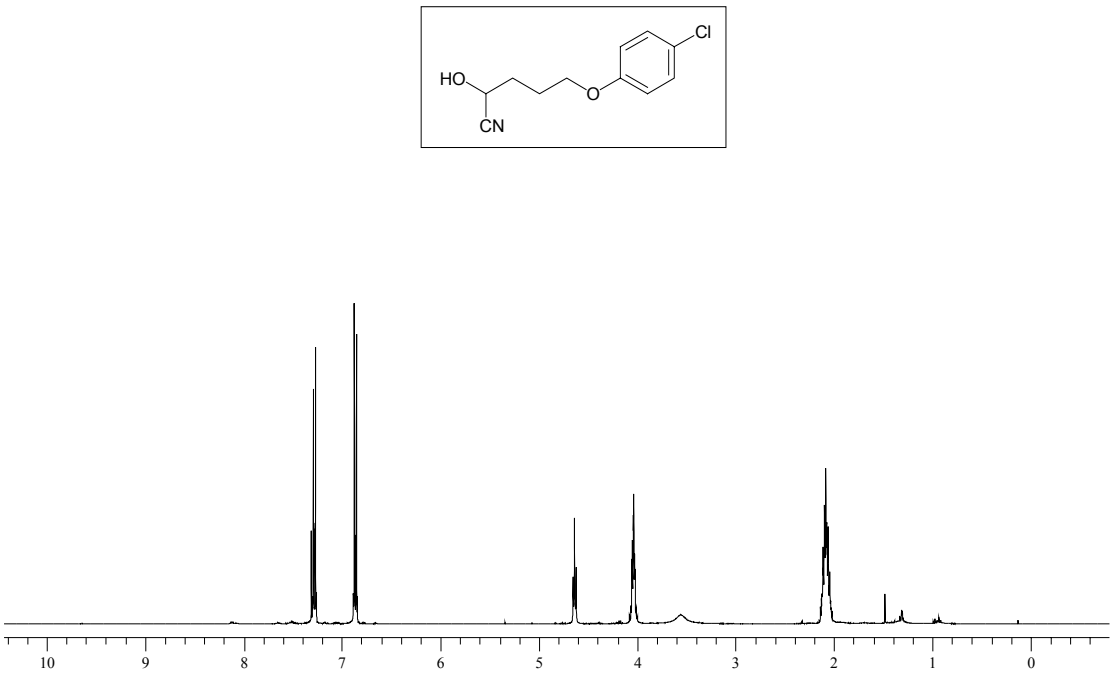


^{13}C NMR (100.6 MHz)

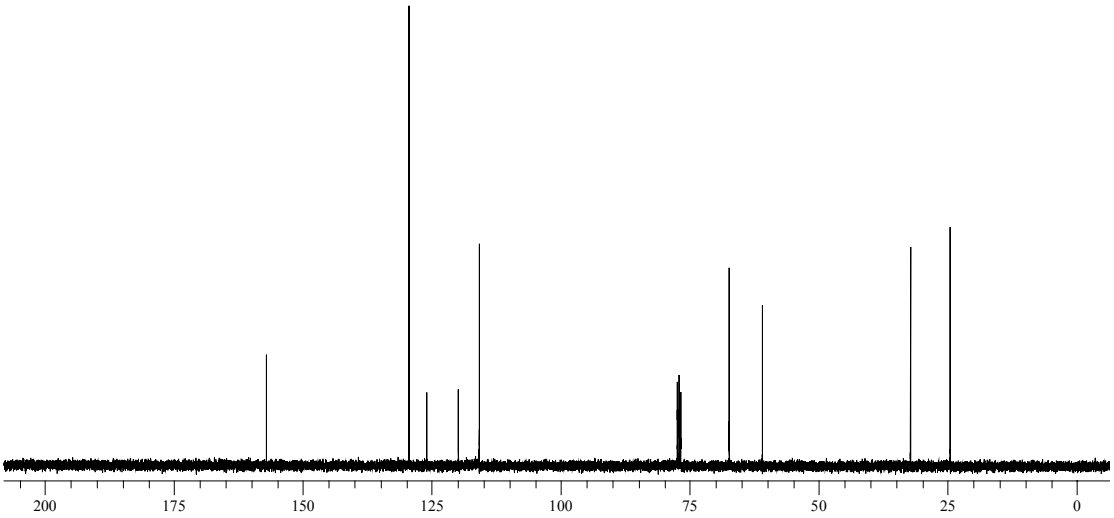


(±)-5-(4-Chloro-phenoxy)-2-hydroxy-pentanenitrile (7e')

^{1}H NMR (400 MHz)

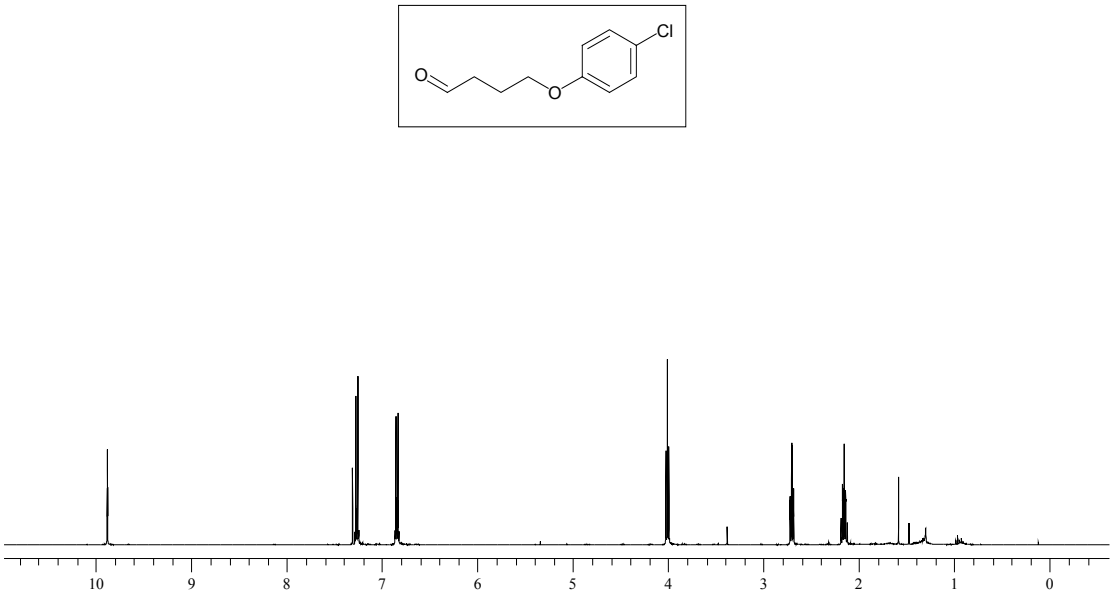


^{13}C NMR (100.6 MHz)

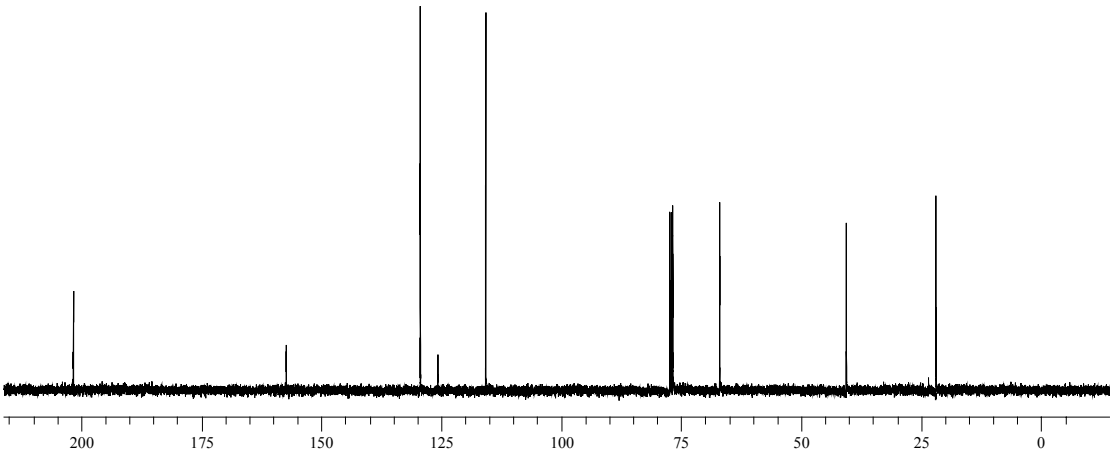


4-(4-Chloro-phenoxy)-butyraldehyde (9e)

^{1}H NMR (400 MHz)

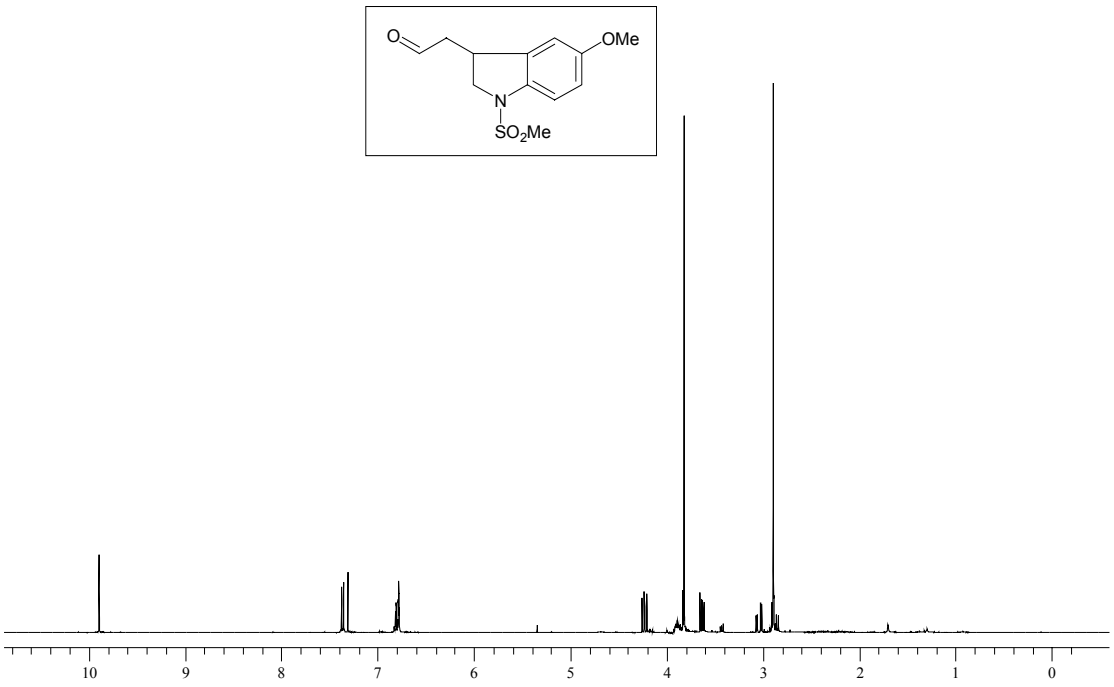


^{13}C NMR (100.6 MHz)

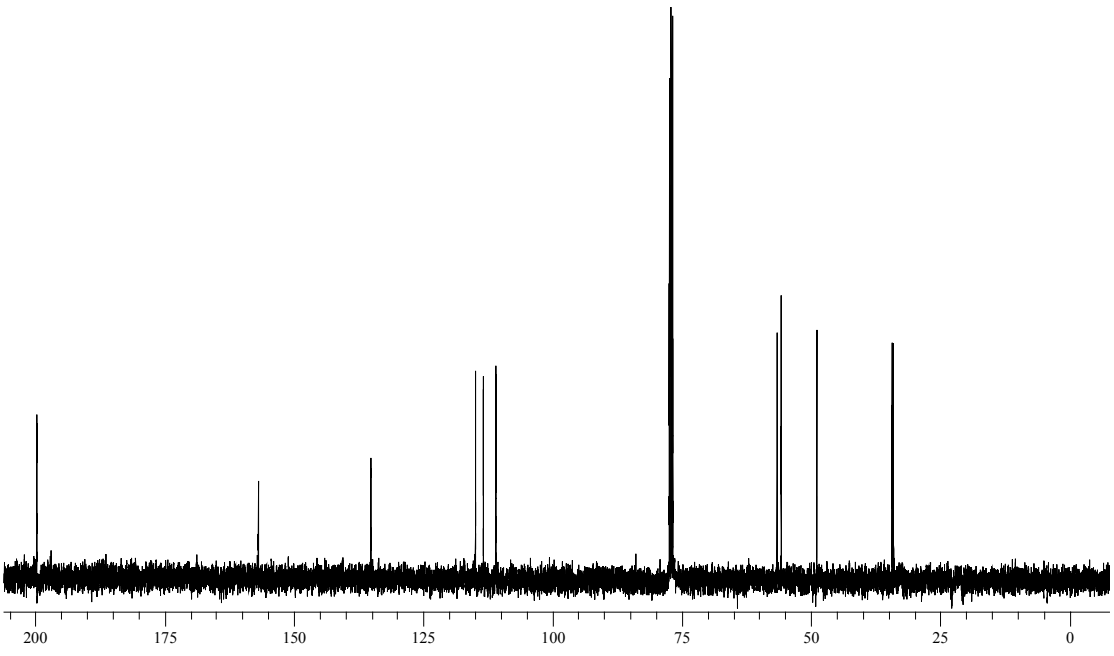


(±)-(1-Methanesulfonyl-5-methoxy-2,3-dihydro-1*H*-indol-3-yl)-acetaldehyde (9i)

^{1}H NMR (400 MHz)



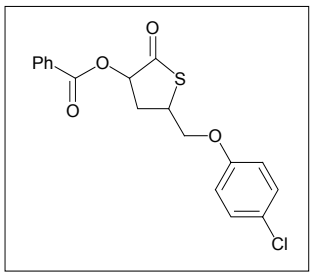
^{13}C NMR (100.6 MHz)

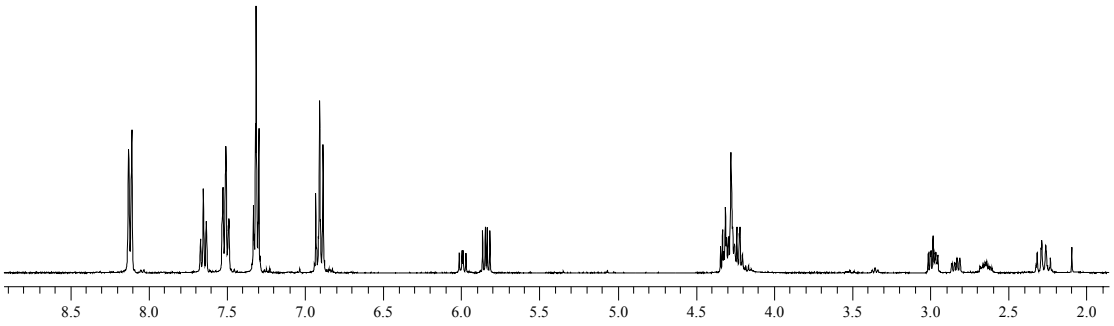


(±)-Benzoic acid 5-(4-chloro-phenoxymethyl)-2-oxo-tetrahydro-thiophen-3-yl ester (13e)

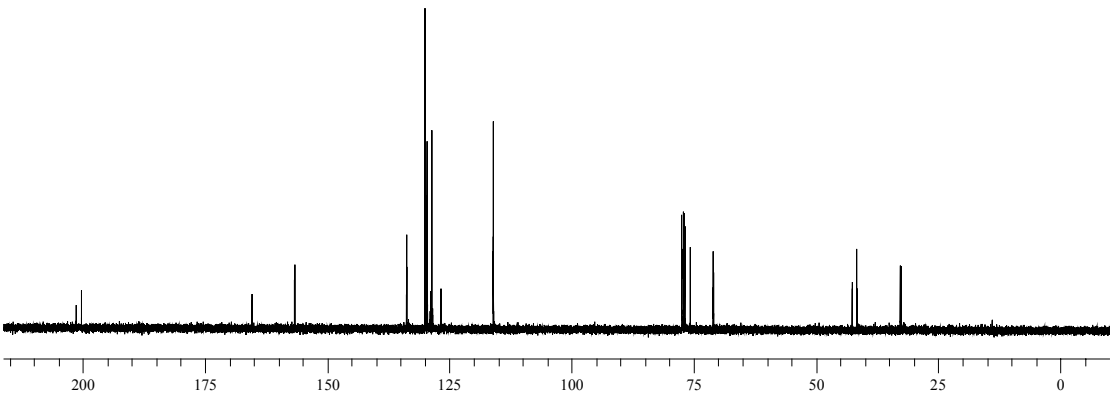
^{1}H NMR (400 MHz)

dr = 1.3:1





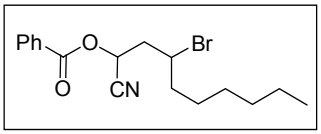
^{13}C NMR (100.6 MHz)

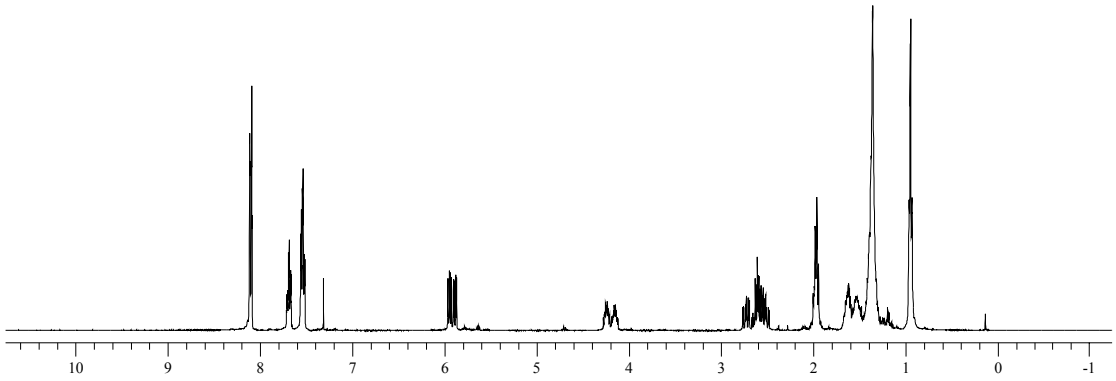


(±)-Benzoic acid 3-bromo-1-cyano-nonyl ester (14b)

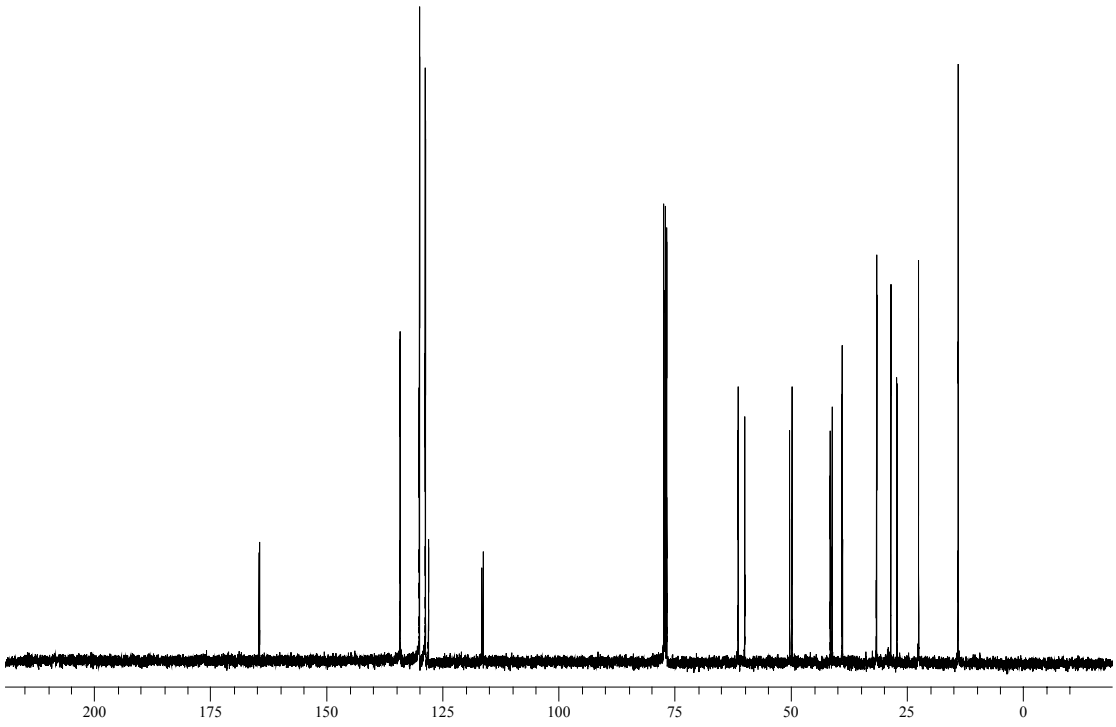
^{1}H NMR (400 MHz)

dr = 1.2:1





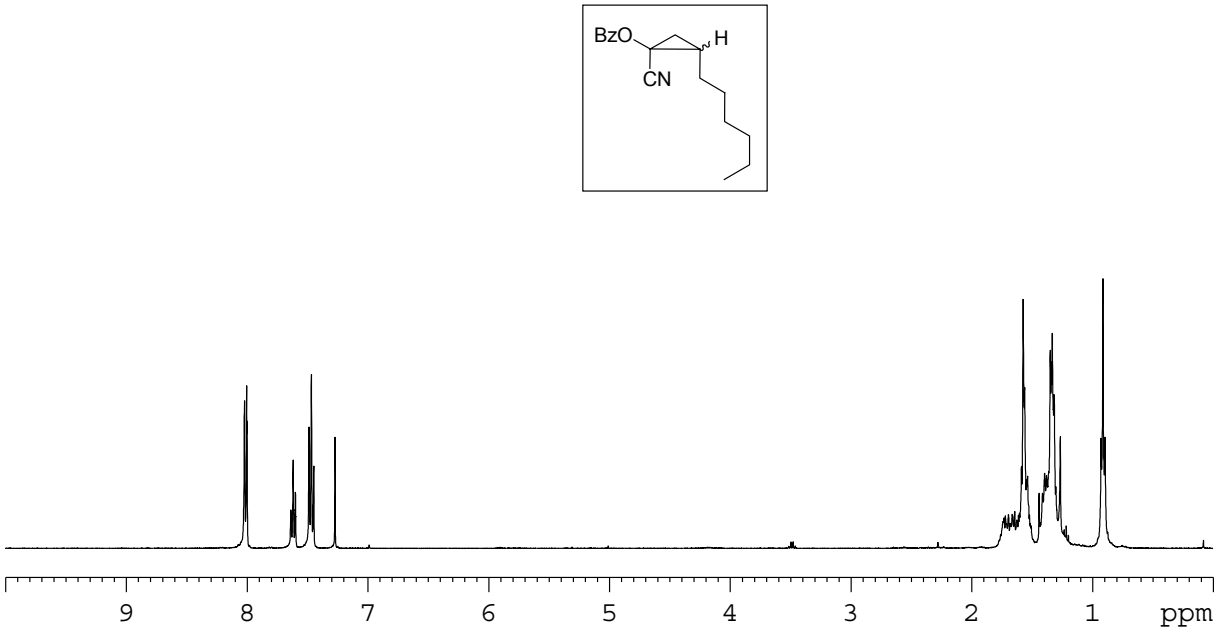
^{13}C NMR (100.6 MHz)



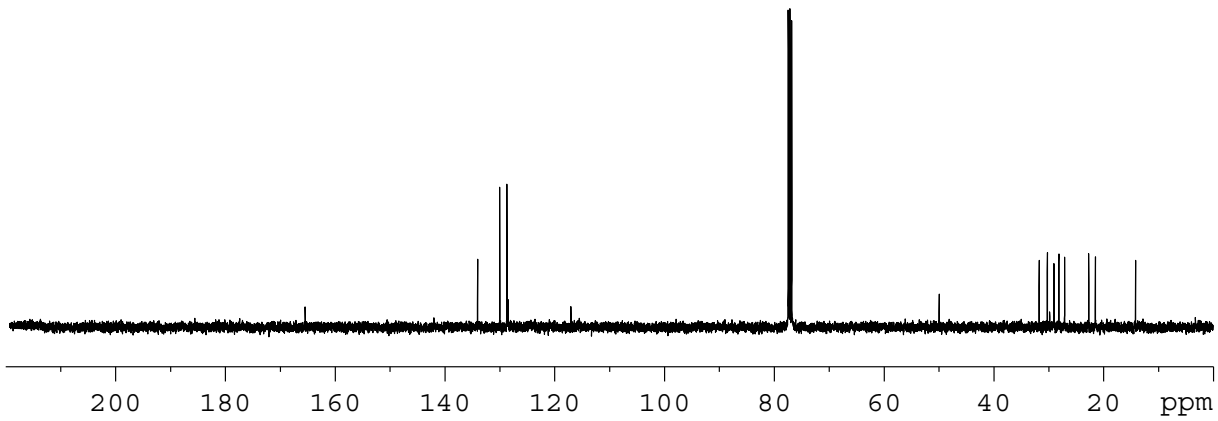
(±)-Benzoic acid 1-cyano-2-hexyl-cyclopropyl ester (15b)

Data for least polar diastereomer 15b:

^{1}H NMR (400 MHz)

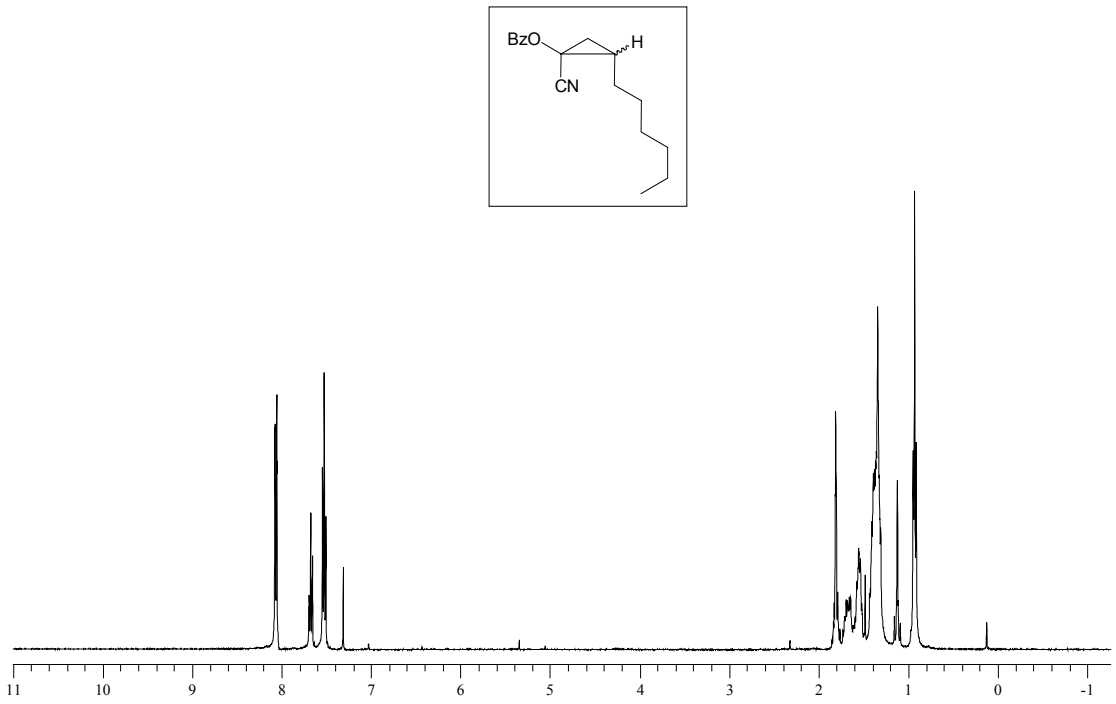


^{13}C NMR (100.6 MHz)

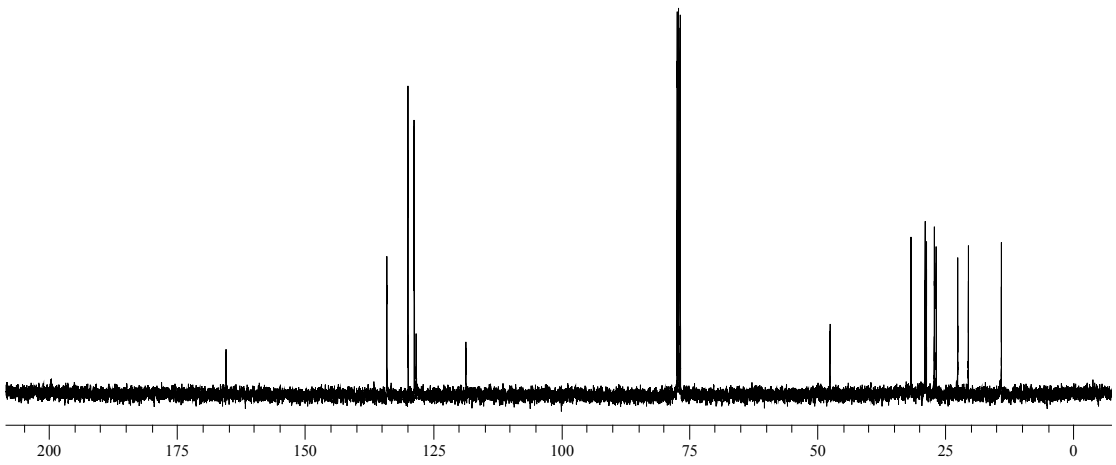


Data for most polar diastereomer 15b:

^{1}H NMR (400 MHz)



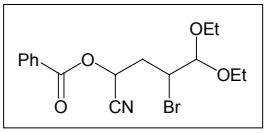
^{13}C NMR (100.6 MHz)

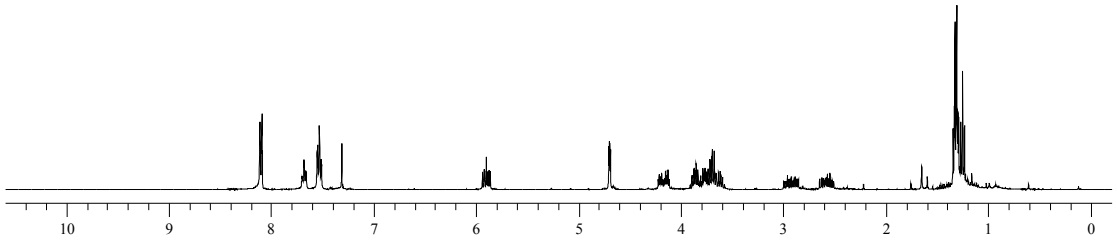


(±)-Benzoic acid 3-bromo-1-cyano-4,4-diethoxy-butyl ester (14f)

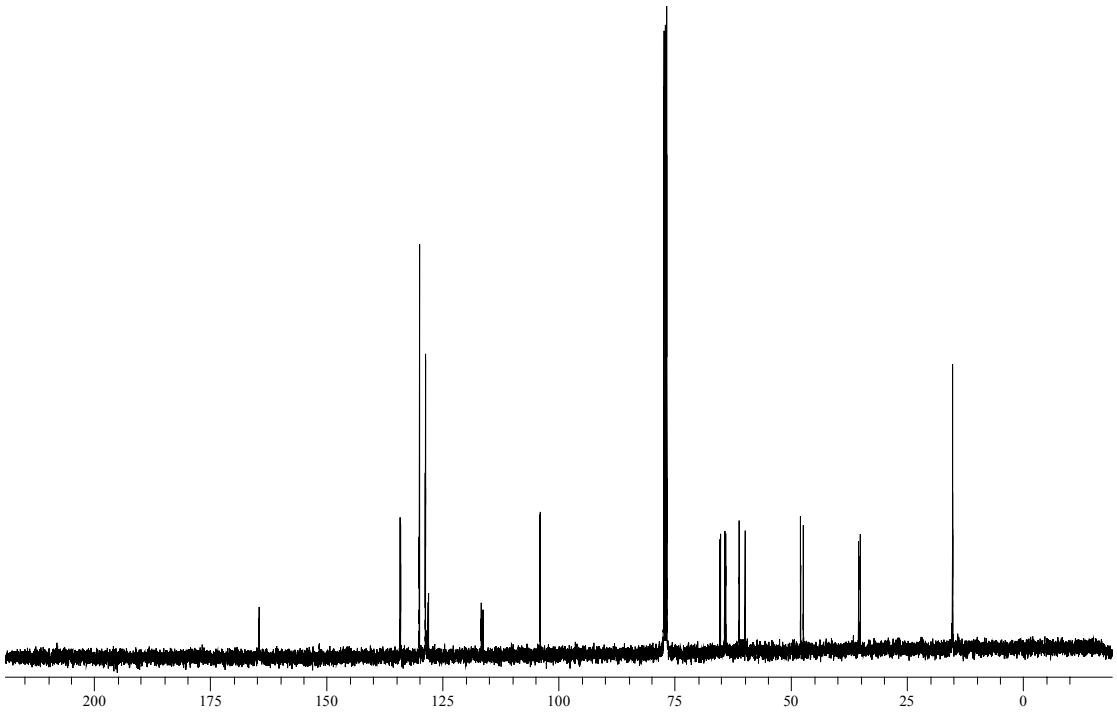
^{1}H NMR (400 MHz)

dr = 1.1:1





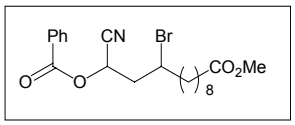
^{13}C NMR (100.6 MHz)

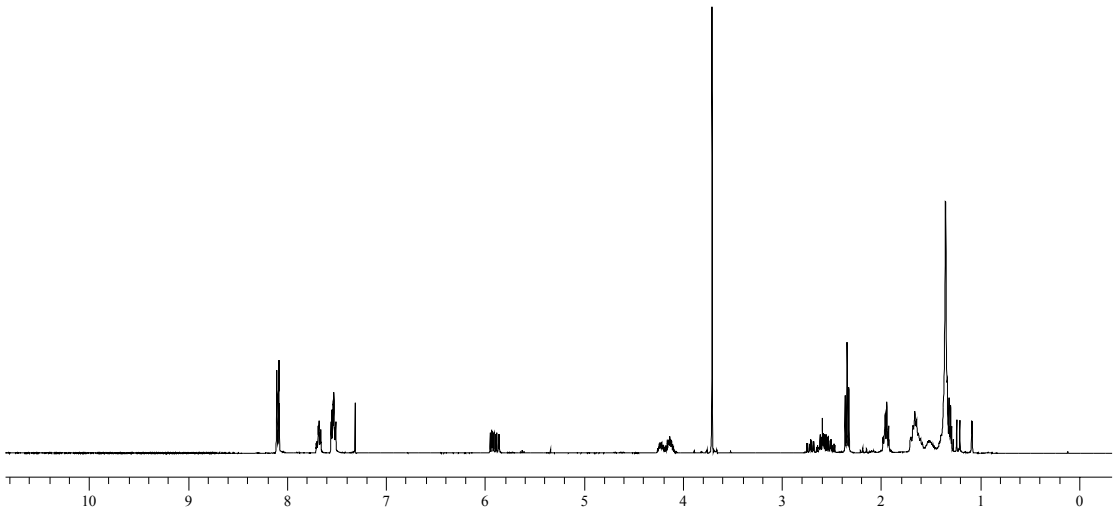


(±)-Benzoic acid 3-bromo-1-cyano-11-methoxycarbonyl-undecyl ester (14h)

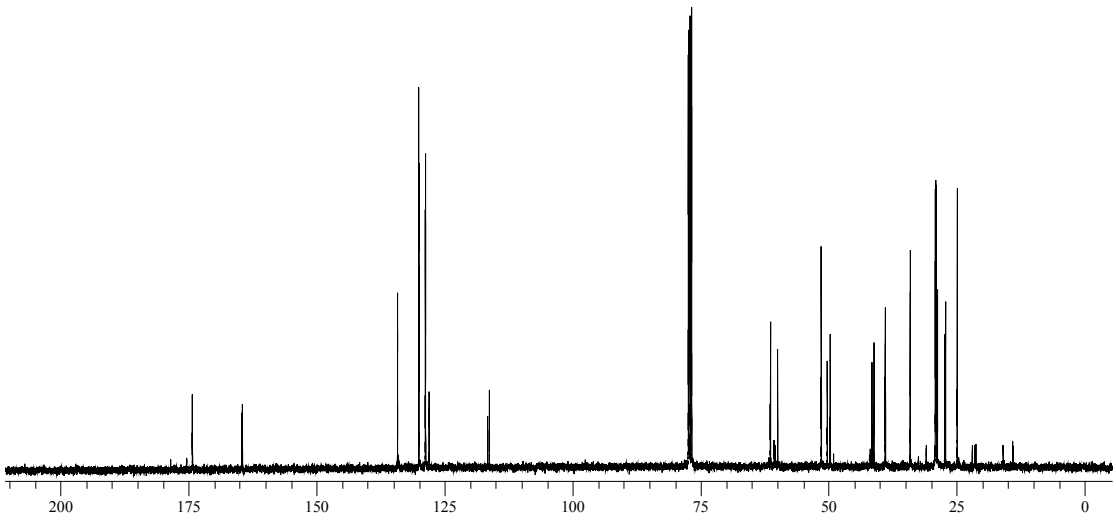
^{1}H NMR (400 MHz)

dr = 1.2:1





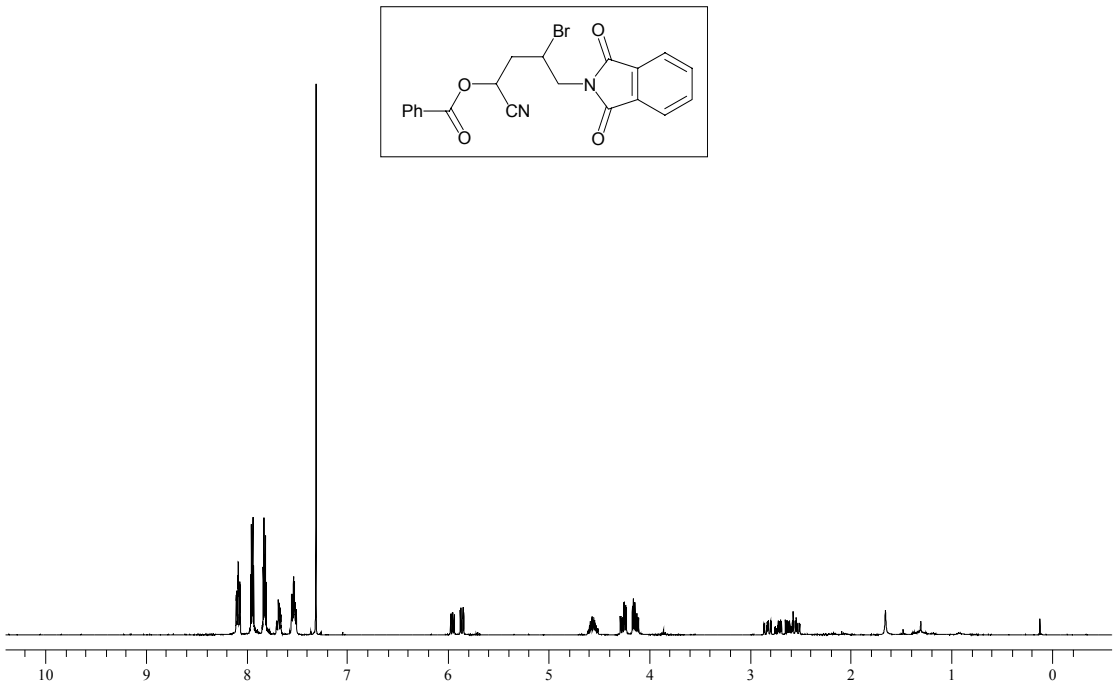
^{13}C NMR (100.6 MHz)



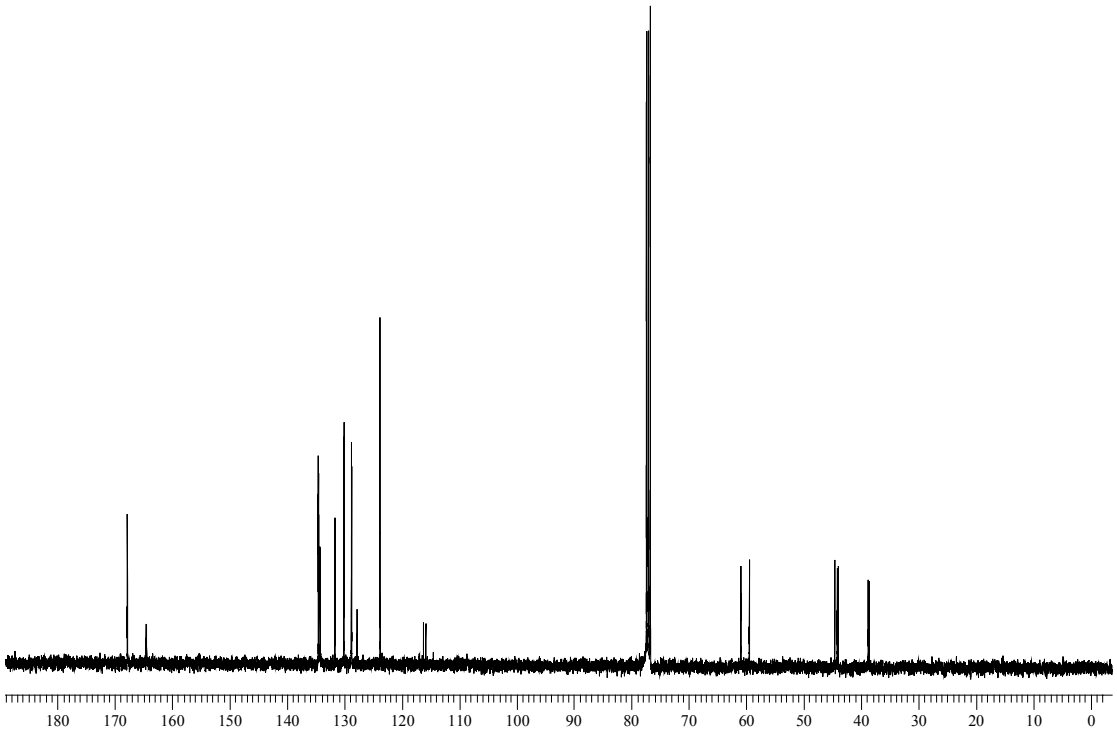
(±)-Benzoic acid 3-bromo-1-cyano-4-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-butyl ester (14j)

^{1}H NMR (400 MHz)

dr = 1.1:1

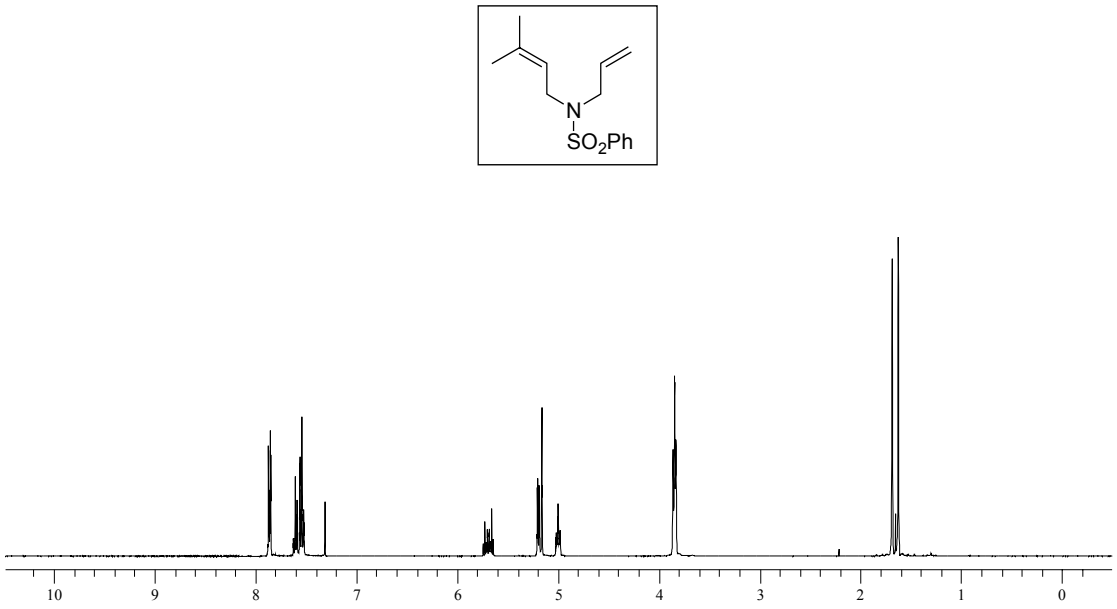


^{13}C NMR (100.6 MHz)

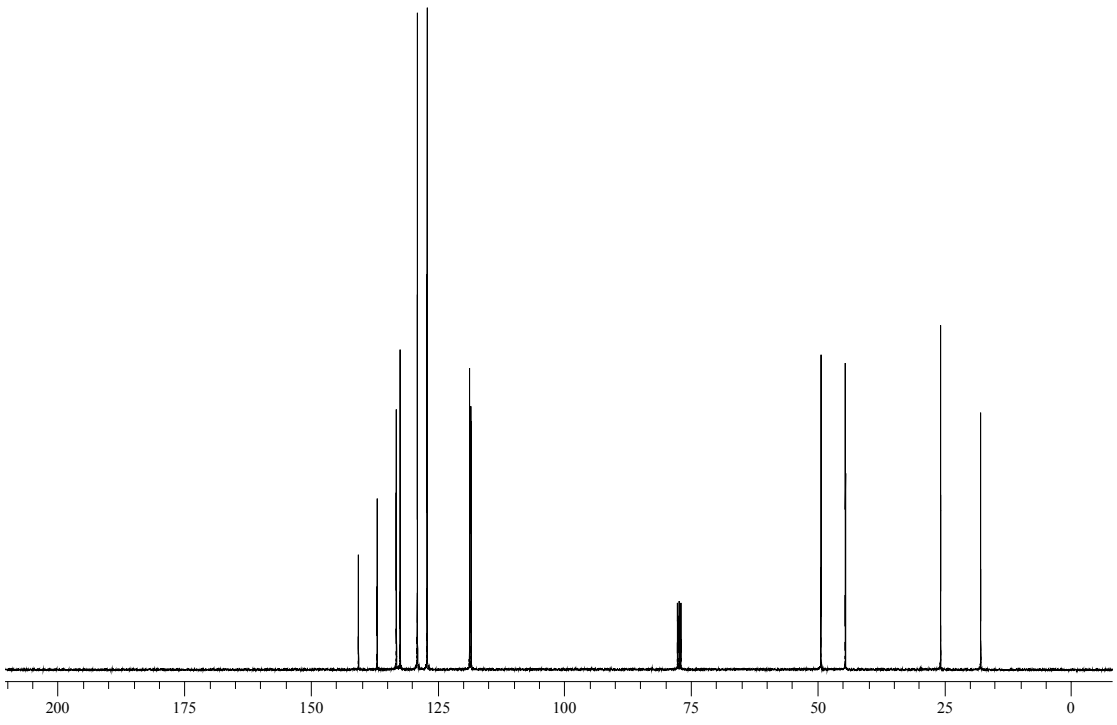


_N_-Allyl-_N_-(3-methyl-but-2-enyl)-benzenesulfonamide (22)

^{1}H NMR (400 MHz)



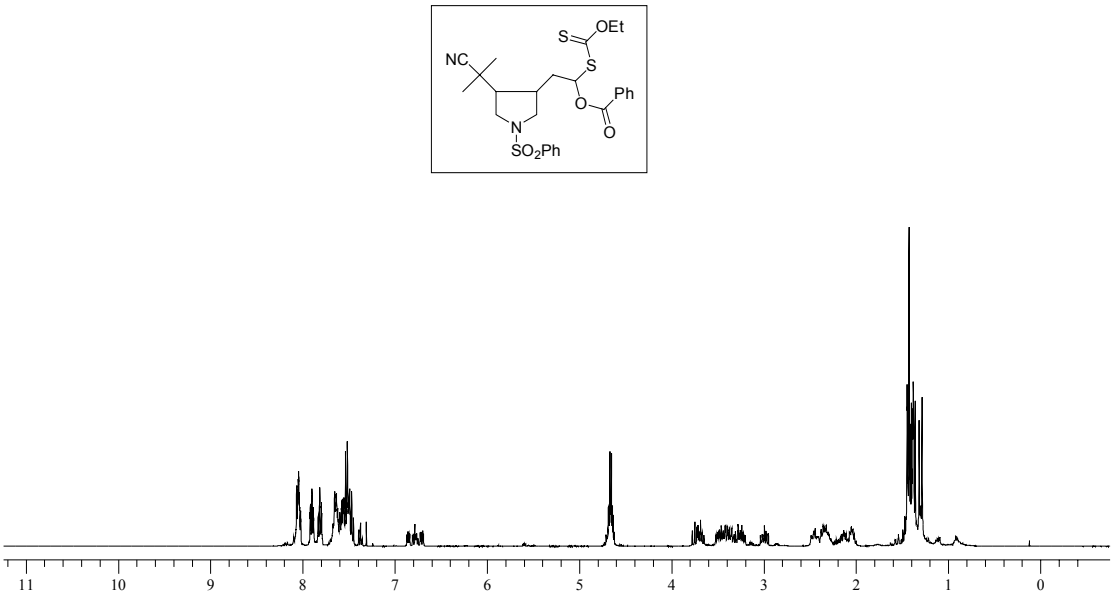
^{13}C NMR (100.6 MHz)



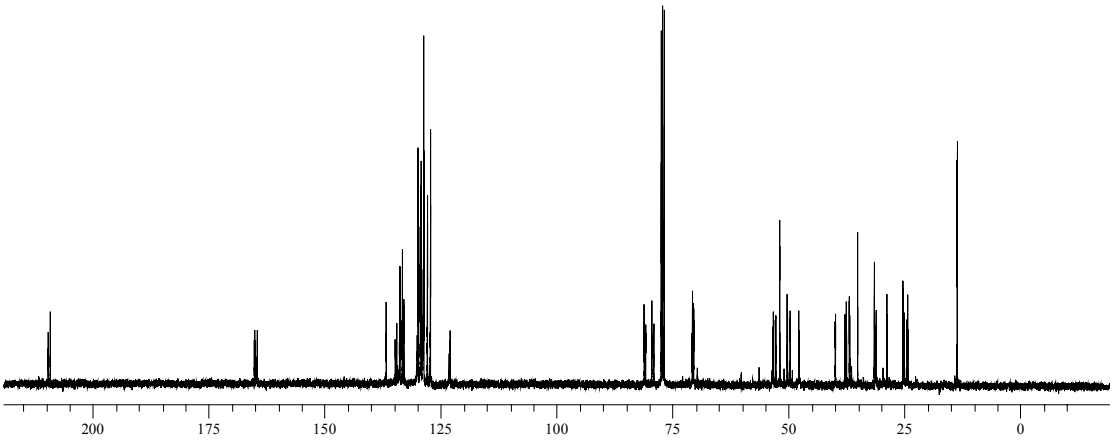
(±)- (1,5) Nitrile translocation product (24)

^{1}H NMR (400 MHz)

dr = 3:3:1:1

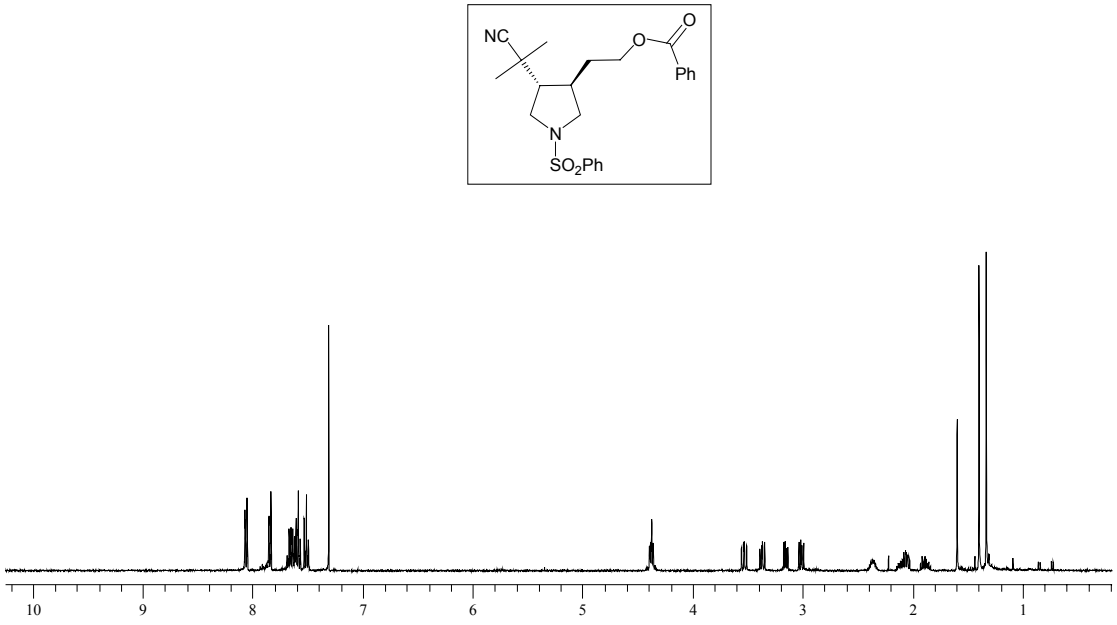


^{13}C NMR (100.6 MHz)



(±)-Benzoic acid 2-[1-benzenesulfonyl-4-(cyano-dimethyl-methyl)-pyrrolidin-3-yl]-ethyl ester (25a)

^{1}H NMR (400 MHz)



^{13}C NMR (100.6 MHz)