Supporting information for:

Access to valuable building blocks by selective ring-opening of itaconic anhydride using lipase catalysis.

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1. Materials and methods:

1.1. Chemicals and Materials

All reagents purchased from: Aldrich, were used as received. Alcohols **[1-18]** and **[20-21]** are commercially available. All used lipases are commercially available and used as purchased without any pre-treatment Lipase from *pseudomonas cepacia* (*Amano Lipase Ps, from burkhoderia cepacia) (PCL;* Specific activity up to 30000 U/g*), Candida rugosa* lipase (*CRL;* LA= 1170 U/mg) and the *Candida antarctica* lipase fraction B immobilized on acrylic resin (*CAL-B;* LA > 10000 U/g). Reactions were monitored by thin-layer chromatography (TLC) carried out on Silica gel $60F_{254}$ plates type *MERCK* 5179, 250 *mesh*, using UV light (254 nm) the visualizing agent sing ultraviolet light (254 nm) as the visualizing agent and $KMnO_4$ solution as developing agents. The separation of the resulting alcohols and the remaining acetates was performed by liquid-liquid extraction.

1.2. Instrumentations

NMR spectra were recorded on Bruker spectrometers (300 MHz for ^1H, 75 MHz for ^{13}C) instrument and calibrated using residual deuterated solvent as an internal reference (peak at 7.26 ppm in ^1H NMR and 3 peaks at 77 ppm in ^{13}C NMR in the case of $CDCl_3$ and DMSO. The following abbreviations were used to designate multiplicities: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br: broad signal, dd=double-doublet. Chemical shifts were expressed in ppm and coupling constant (*J*) in Hz. The enantiomeric excesses were measured by a chiral stationary phase HPLC: *Chiralpak* OJ-H, *Chiralpak IA* or *Chiralpak IB* columns (4.6 × 250 mm). Retention times are reported in minutes. Mass spectra were taken by a MicrOTOF-Q Bruker spectrometer using electrospray ionization (ESI) analysis.

2. Synthesis of racemic alcohols [19, 22-25]:

The racemic alcohols **[19, 22-25]** were prepared from the corresponding commercial ketones using the following procedure: to solution of THF / H_2O (4/1, *v/v*), 6 equivalent of sodium borohydride (18 mmol) are added, and stirred at 0°C. 3 mmoles of the corresponding alcohol diluted in 20 mL of THF are added by drops. After consumption the ketone, the mixture was neutralized by addition of a solution of (HCl, 1N). Then the organic layer was removed, and the aqueous layer was extracted with ethyl acetate (3 x 80 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated to give the corresponding alcohols with good yields. The ^1H and ^{13}C NMR spectra of these products were in good agreement with the literature.

1,2-dihydroacenaphthylen-1-ol (rac-19)

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 2 (s, O**H**), 3.26 (d, *J* = 17.7Hz, 1H), 3.82 (dd, *J* = 17.7, 7.1Hz, 1H), 5.74 (dd, *J* = 7.1, 2.1Hz, 1H), 7.32- 7.79 (m, H_{arm}). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 41.9, 74.4, 119.8, 120.3, 122.7, 125, 128, 128.5, 131.2, 137.1, 141.5, 145.7.

Chiral HPLC: Chiralpak IA**.** ***Eluent (v,v)*** **:** Hexane/ iPrOH. **Flow rate :** 0.5 mL/min. **Retention time :** t_R = 25.81 min, t_S = 27.71 min.

6-methyl-2,3-dihydro-1H-inden-1-ol (rac-22)

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.95 (m, 1H), 2.2 (s, O**H**), 2.41 (s, 3H), 2.49 (m, 1H), 2.79 (m, 1H), 3.03 (m, 1H); 5.21 (t, 1H), 7.09- 7.25 (m, H_{arm}). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 21.2, 29.3, 36.1, 77, 124.6, 124.7, 129.1, 136.3, 140.2, 145.1.

Chiral HPLC: Chiralpak IA**.** ***Eluent (v,v) :*** Hexane/ iPrOH. **Flow rate*:*** 0.5 mL/min. **Retention time :** t_S = 17.63 min, t_R = 18.96 min.

6-methoxy-2,3-dihydro-1H-inden-1-ol (rac-23)

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.71 (s, OH), 1.96 (m, 1H), 2.5 (m, 1H), 2.77 (m, 1H), 3 (m, 1H), 3.83 (s, 3H), 5.23 (t, *J* = 6.2 Hz, 1H), 6.83-7.15(m, H_{arm}). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 28.9, 36.6, 55.5, 77.4, 108.8, 115, 125.5, 135, 146.3, 159.

Chiral HPLC: Chiralpak IA**.** ***Eluent (v,v) :*** Hexane/ iPrOH. **Flow rate*:*** 0.5 mL/min. **Retention time :** t_S = 30.60 min, t_R = 32.87 min.

6-chloro-2,3-dihydro-1H-inden-1-ol (rac-24)

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.94 (m, 1H), 2.3 (s, OH), 2.5 (m, 1H), 2.77 (m, 1H), 3 (m, 1H), 5.19 (t, *J* = 6.3Hz, 1H), 7.15- 7.36 (m, H_{arm}). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 29.2 ; 36.2, 76, 124.4, 125.9, 128.3, 132.3, 141.6, 146.9.

Chiral HPLC: Chiralpak IA**.** ***Eluent (v,v) :*** Hexane/ iPrOH. **Flow rate*:*** 0.5 mL/min. **Retention time*:*** t_S = 18.55 min, t_R = 21.85 min.

6-(trifluoromethyl)-2,3-dihydro-1H-inden-1-ol (rac-25)

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.98 (m, 1H), 2.2 (s, OH), 2.5 (m, 1H), 3.03 (m, 2H), 5.26 (t, *J* = 6.3Hz, 1H), 7.34- 7.67 (m, H_{arm}). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 29.7, 35.9, 75.8, 121.2, 121.3, 125.2, 125.32, 125.37, 145.6, 147.3.

Chiral HPLC: Chiralpak IA**.** ***Eluent (v,v) :*** Hexane/ iPrOH. **Flow rate*:*** 0.5 mL/min. **Retention time*:*** t_S = 14.35 min, t_R = 16.31 min.

3. PCL-catalyzed regioselective ring-opening of IAn using several primary alcohols*:*

To equimolecular mixture of itaconic anhydride and the appropriate alcohol **[1-15]** diluted in 5 mL of TBME, the adequate amount of lipase is added. After 24 hours of stirring at room temperature, the lipase was removed by filtration. The no reacted alcohol was removed by liquid-liquid extraction. The obtained monoesters recovered pure after re-crystallization. Complete experimental data have been provided (NMR spectra and HRMS).

4-ethoxy-2-methylene-4-oxobutanoic acid **(*2e*).** White crystalline. mp 45 °C. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ** 09.88 (s, 1H, OH), 6.48 (s, 1H, C=C$\underline{H}_2$), 5.84 (s, 1H, C=C$\underline{H}_2$), 4.18 (q, 2H, J=7.1 Hz, C$\underline{H}_2$CH$_3$), 3.35 (s, 1H, CH$_2$-C=), 1.27 (t, 3H, J=7.1 Hz, CH$_2$C$\underline{H}_3$,). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 171.5, 170.6, 133.3, 130.78, 61.08, 37.36, 14.1. **HRMS (ESI) m/z calcd for $C_7H_{10}O_4$ [M + Na^+]:**181.04**, Found:** 181.048.

4-isobutoxy-2-methylene-4-oxobutanoic acid (3e). White crystalline. mp 47 °C. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ** 11.2 (s, 1H, OH), 6.46 (s, 1H, C=C$\underline{H}_2$), 5.83 (s, 1H, C=C$\underline{H}_2$), 3.88 (d, 2H, *J* = 6.7 Hz, O-C$\underline{H}_2$CH), 3.35 (s, 2H, OOC-C$\underline{H}_2$-C=), 1.93 (m, 1H), 0.91 (d, 6H, *J* = 6.7 Hz, 2CH$_3$). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 171.7, 170.6, 133.4, 130.6, 71.1, 37.3, 27.6, 18.9. **HRMS (ESI) m/z calcd for $C_9H_{14}O_4$ [M + Na^+]:** 209.19, **Found:** 209.0792.

4-(3- Methylbutanoxy)-2-methylene-4-oxobutanoic acid (1e). Gummy liquid · **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ** 10 (s, 1H, OH), 6.45 (s, 1H, C=C$\underline{H}_2$), 5.82 (s, 1H, C=C$\underline{H}_2$), 4.13 (d, *J* = 6.8 Hz, 2H, O-C$\underline{H}_2$CH), 3.34 (d, 2H, *J* = 5.4 Hz, OOC-C$\underline{H}_2$-C=), 1.67 (m, 1H, CH$_2$-C$\underline{H}$(CH$_3$)$_2$), 1.51 (q, 2H, *J* = 13.5, 6.7 Hz, CH-C$\underline{H}_2$-CH$_2$,), 0.90 (d, 6H, *J* = 6.5 Hz, C$\underline{H}_3$-CH-C$\underline{H}_3$). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 171.4, 170.7, 133.4, 130.5, 63.7, 37.3, 37.1, 34.04, 24.9, 22.3. 16.2, 11.1 **HRMS (ESI) m/z calcd for $C_{10}H_{16}O_4$ [M + Na^+]:**223.08**, Found:** 223.095.

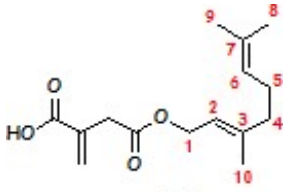
4-(hexyloxy)-2-methylene-4-oxobutanoic acid (4e). White crystalline. mp 42 °C. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ** 09 (s, 1H, OH), 6.45 (s, 1H, C=C$\underline{H}_2$), 5.82 (s, 1H, C=C$\underline{H}_2$), 4.15 (t, 2H, J = 6.7 Hz, O-C$\underline{H}_2$CH$_2$), 3.34 (s, 2H, OOC-C$\underline{H}_2$-C=), 1.36 (m, 2H, O-CH$_2$-C$\underline{H}_2$-(CH$_2$)$_3$-CH$_3$), 1.28 (m, 6H, CH$_2$-(C$\underline{H}_2$)$_3$-CH$_3$), 0.90 (m, 3H, CH$_2$C$\underline{H}_3$). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 171.4, 170.7, 133.4, 130.5, 65.2, 37.3, 31.3, 28.4, 25.4, 22.4, 13.9. **HRMS (ESI) m/z calcd for $C_{11}H_{18}O_4$ [M + Na^+]:**237.100**, Found:** 237.1102.

4-(heptyloxy)-2-methylene-4-oxobutanoic acid (5e). White crystalline. mp 53 °C. **^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ** 8.3 (s, 1H, OH), 6.47 (s, 1H, C=C$\underline{H}_2$), 5.84 (s, 1H, C=C$\underline{H}_2$), 4.11 (t, 2H, *J* = 6.7 Hz, O-C$\underline{H}_2$CH$_2$), 3.35 (s, 2H, CH$_2$-C=), 1.6 (m, 2H,C$\underline{H}_2$-CH$_2$-O), 1.30 (m, 8H, O-CH$_2$-(C$\underline{H}_2$)$_4$-CH$_3$), 0.89 (t, 3H, *J* = 9.2 Hz, CH$_2$C$\underline{H}_3$). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 171.5, 170.6, 133.3, 130.6, 65.2,

37.3, 31.7, 28.8, 28.5, 25.7, 22.5, 14.07. **HRMS (ESI) m/z calcd for $C_{12}H_{20}O_4$ [M + Na^+]:**251.120**, Found:** 251.259.

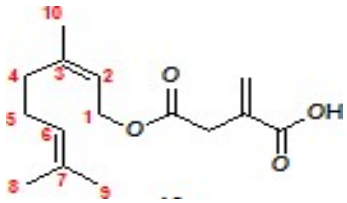
4-(decyloxy)-2-methylene-4-oxobutanoic acid (6e) .White crystalline. mp 67 °C. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ** 6.48 (s, 1H, C=C$\underline{H}_2$), 5.84 (s, 1H, C=C$\underline{H}_2$), 4.12 (t, 2H, *J* = 6.7 Hz, O-C$\underline{H}_2$CH_2), 3.35 (s, 2H, OOCC$\underline{H}_2$-C=), 1.6 (m, 2H, C$\underline{H}_2$-CH_2-O), 1.30 (m, 14H, OCH_2-CH_2-(C$\underline{H}_2$)-CH_3), 0.8 (t, 3H, *J* = 6.7 Hz, CH_2C$\underline{H}_3$). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 171.3, 170.6, 133.3, 130.5, 65.2, 37.3, 31.8, 29.5, 29.4, 29.29, 29.21, 25.8, 22.6, 14.09. **HRMS (ESI) m/z calcd for $C_{15}H_{26}O_4$ [M + Na^+]:** 293.16**, Found:** 293.1730.

(E)-4-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-2-methylene-4-oxobutanoic acid (Mono 4-geranyl Itaconate)(7e) :



Gummy liquid. **^{1}HNMR (300 MHz, $CDCl_3$, 25 °C) δ** 9.2 (s, 1H, OH), 6.48 (s, 1H, C=C$\underline{H}_2$), 5.84 (s, 1H, C=C$\underline{H}_2$), 5.35 (m, 1H, CH=C$^2\underline{H}$-CH_2), 5.33 (m, 1H, C=C$^6\underline{H}$-CH_2), 4.64 (d, 2H, *J* = 7.1 Hz, O-C$^1\underline{H}_2$CH), 3.35 (s, 2H, C$\underline{H}_2$-C=), 2(m, 4H,C$^4\underline{H}_2$-C$^5\underline{H}_2$), 1.7 (s, 6H,C$^9H_3$, C$^{10}H_3$),1.61 (s, 3H, =CC$^8\underline{H}_3$). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 170.7, 170.6, 142.5, 133.4, 131.8, 130.4, 123.7, 117.9, 61.9, 39.5, 37.3, 26.2, 25.6, 17.6, 16.4. **HRMS (ESI) m/z calcd for $C_{15}H_{22}O_4$ [M + Na^+]:** 289.13**, Found:** 289.1408.

(Z)-4-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-2-methylene-4-oxobutanoic acid (Mono 4-Néronyl Itaconate)(8e):



Gummy liquid. **^{1}HNMR (300 MHz, $CDCl_3$, 25 °C) δ** 6.48 (s, 1H, C=C$\underline{H}_2$), 5.84 (s, 1H, C=C$\underline{H}_2$), 5.35 (m, 1H, CH=C$^2\underline{H}$-CH_2), 5.1 (m, 1H, C=C$^6\underline{H}$-CH_2), 4.61 (d, 2H, *J* = 7.2 Hz, O-C$^1\underline{H}_2$CH), 3.35 (s, 2H, C$\underline{H}_2$-C=), 2.11 (m, 4H, C$^4\underline{H}_2$-C$^5\underline{H}_2$), 1.78 (s, 3H, C$^{10}H_3$), 1.69 (s, 3H, =CC$^9\underline{H}_3$), 1.61 (s, H, =CC$^8\underline{H}_3$). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 171.2, 170.5, 142.8, 133.3, 132.1, 130.6, 123.5, 118.9, 61.6, 37.2, 32.1, 26.6, 25.6, 23.4, 17.6. **HRMS (ESI) m/z calcd for $C_{15}H_{22}O_4$ [M + Na^+]:** 289.13**, Found:** 289.1408.

***4-(benzyloxy)-2-methylene-4-oxobutanoic acid* (*9e)*.** White crystalline. mp 80 °C. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ** 10.3 (s, 1H, COO$\underline{H}$), 7.37 (m, 5H, H_{arm}), 6.51 (s, 1H, C$\underline{H}_2$=C), 5.86 (s, 1H, C$\underline{H}_2$=C), 5.19 (s, 2H, -COO-C$\underline{H}_2$), 3.43 (s, 2H, -C$\underline{H}_2$-COO).**^{13}C NMR (75 MHz, $CDCl_3$) δ** 171.5, 170.4, 135.6, 133.2, 130.9, 128.5, 128.2, 128.1, 66.8, 37.3. **HRMS (ESI) m/z calcd for $C_{12}H_{12}O_4$ [M + Na^+]:** 243.05**, Found:** 243.0641.

4-(2-phenylethoxy)-2-methylene-4-oxobutanoic acid (10e). White crystalline. mp 83 °C. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ** 7.25 (m, 5H, H_{arm}), 6.48 (s, 1H, C$\underline{H_2}$=C), 5.82 (s, 1H, C$\underline{H_2}$=C), 4.34 (t, 2H, *J* = 7 Hz, COO-C$\underline{H_2}$-CH_2-Ar), 3.35 (s, 2H, -C$\underline{H_2}$-COO), 2.96 (t, 2H, *J* = 7.2 Hz, -CH_2-Ar). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 171.3, 170.2, 137.5, 133.1, 130.9, 128.9, 128.5, 126.5, 65.5, 37.2, 34.9. **HRMS (ESI) m/z calcd for $C_{13}H_{14}O_4$ [M + Na^+]:** 257.07**, Found:** 257.0787

***4-(3-phenylethoxy)-2-methylene-4-oxobutanoic* acid (11e)**. White crystalline. mp 86 °C **^{1}HNMR (300 MHz, $CDCl_3$, 25 °C) δ** 8.6 (s, 1H, OH), 7.25 (m, 5H, H_{arm}), 6.49 (s, 1H, C$\underline{H_2}$=C), 5.85 (s, 1H, C$\underline{H_2}$=C), 4.15 (t, 2H, *J* = 6.5 Hz, COO-C$\underline{H_2}$-$(CH_2)_2$-Ar), 3.37 (s, 2H, -C$\underline{H_2}$-COO), 2.7 (m, 2H, CH_2-C$\underline{H_2}$-Ar), 1.98 (m, 2H, -C$\underline{H_2}$-CH_2-Ar). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 171.4, 170.7, 141.1, 133.3, 130.7, 128.4, 126.0, 64.3, 37.3, 32.0, 30.1. **HRMS (ESI) m/z calcd for $C_{14}H_{16}O_4$ [M + Na^+]:** 271.08**, Found:** 271.0940.

4-(cinnamyloxy)-2-methylene-4-oxobutanoic acid (12e). White crystalline. mp 87 °C. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ** 7.36 (m, 5H, H_{arm}), 6.6 (d, 1H, *J*= 15.9 Hz, CH=C$\underline{H}$-Ph), 6.49 (s, 1H, CH_2=C), 6.31 (m, 1H, C$\underline{H}$=CH-Ph), 5.87 (s, 1H, C$\underline{H_2}$=C), 4.7 (dd, 2H, *J* = 6.4, 1 Hz, COO-C$\underline{H_2}$-CH=CH-Ar), 3.4 (s, 2H, -C$\underline{H_2}$-COO). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 171.3, 170.4, 136.1, 134.3, 133.1, 130.9, 128.6, 128.0, 126.6, 122.8, 65.6, 37.3, 29.7. **HRMS (ESI) m/z calcd for $C_{14}H_{14}O_4$ [M + Na^+]:** 269.07**, Found:** 269.0781

4-([1,1'-biphenyl]-4-ylmethoxy)-2-methylene-4-oxobutanoic acid (13e). White crystalline. mp 98 °C. **^{1}H NMR *(300 MHz, $CDCl_3$)* δ** 3.4 (s, 2H, -CH_2-COO); 5.21 (s, 2H, COO-CH_2-Ph), 5.84 (s, lH, CH_2=C); 6.48 (s, 1H, CH_2=C), 7.47-7.68 (m, 9H, H_{arm}). **^{13}C NMR *(75 MHz, $CDCl_3$)* δ** 170.7, 170.2, 140.8, 140.6, 139.7, 128.8, 128.7, 127.5, 127.3, 127.1, 66.5, 65.0, 37.5. **HRMS (ESI) m/z calcd for $C_{18}H_{16}O_4$ [M + Na^+]:** 319.08**, Found:** 319.0928.

4-(furan-2-ylmethoxy)-2-methylene-4-oxobutanoic acid (14e). White crystalline. mp 75 °C. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ** 10 (s, 1H, OH), 7.43 (, 1H, CH=C$\underline{H}$-O), 6.49 (s, 1H, CH_2=C), 6.42 (m, 1H, C$\underline{H}$=CH), 6.37 (m, 1H, C$\underline{H}$=CH) 5.85(s, 1H, CH_2=C), 5.12(s, 2H, COO-C$\underline{H_2}$-CH=), 3.38 (s, 2H, -C$\underline{H_2}$-COO). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 171.4, 170.3, 149.1, 143.3, 133.03, 131.07, 110.8, 110.5, 58.7, 37.1. **HRMS (ESI) m/z calcd for $C_{10}H_{10}O_5$ [M + Na^+]:**233.03**, Found:** 233.0421.

4. Crystallographic data and structure refinement details for monoesters itaconates: 2e, 6e and 9e .

X-ray diffraction data for compounds (**6e**: **mo_v463), (2e: mo_v468)** & **(9e: mo_v471)**were collected by using a VENTURE PHOTON100 CMOS Bruker diffractometer with Micro-focus IuS source Mo Kα radiation (ƛ = 0.71073 Å). Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. For compounds, the temperature of the crystal was maintained at the selected value by means of a N-Helix Cryostream cooling device to within an accuracy of ±1K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97[1] and refined against F^2 by full-matrix least-squares techniques using SHELXL-2018[2] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX[3].

The crystal data collection and refinement parameters are given in Table 3.

CCDC 2088738-2088740 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

5. PCL-catalyzed regioselective and enantioselective opening ring of (IAn) using a set of arylalkyl carbinols as chiral nucleophiles:

To equimolecular mixture of itaconic anhydride and the appropriate alcohol **(*rac*-16-25)** diluted in 5mL of TBME, the adequate amount of lipase is added. After 24 hours of stirring at room temperature, the lipase was removed by filtration. The obtained monoester itaconate and the remained alcohols were easily separated by a simple alkaline washing. The two components were recovered by liquid–liquid extraction, the remaining (*S*)-alcohol was recovered in the organic layer and the monoester itaconate in the aqueous phase and then the chemical isolated yield was determined. The proportions of the isomeric mixture of the (α / β) mono esters itaconates recovered were checked by ^{1}H NMR analysis. Their quantifications were based on the chemical shifts of the double bond protons. The enantiomeric excesses of the (*R*)-monoesters itaconates are measured by chiral HPLC after saponification and obtaining the corresponding (*R*)-alcohols.

(R)-4-((1,2-dihydroacenaphthylen-1-yl)oxy)-2-methylene-4-oxobutanoic acid (19e)

White powder. mp 140°C. **^{1}HNMR (300 MHz, $CDCl_3$, 25°C) δ** 09.5 (s, 1H, OH), 7.56 (m, 6H, ar), 6.67 (dd, 1H, *J* = 7.1 Hz, 2.3 Hz, $CH_2OOCC\underline{\mathbf{H}}$), 6.48 (s, 1H, C=C$\underline{\mathbf{H}_2}$***),*** 5.84 (s, 1H, C=C$\underline{\mathbf{H}_2}$***),*** , 3.84

[1] Sheldrick, G. M. SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997.

[2] G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112-122

[3] Farrugia, L. J. J. Appl. Cryst., 1999, 32, 837.

(dd, 1H, *J* = 18 Hz ***),*** 3.39 (s, 2H, , C**H**$_2$OOC), 3.31 (m, 1H ***)***. **^{13}C NMR (75 MHz, CDCl$_3$): δ** 171.58, 170.81, 141.67, 141.09, 137.89, 133.25, 131.15, 131.06, 128.16, 128.12, 125.5, 122.95, 121.93, 119.86, 76.4, 38.64, 37.56. **HRMS (ESI) m/z calcd for C$_{17}$H$_{13}$O$_4$ [M -1]:**281.09**, Found** 281.081.

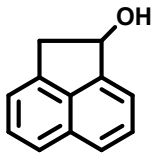
(R)-4-((2,3-dihydro-1H-inden-1-yl)oxy)-2-methylene-4-oxobutanoic acid (21e)

White powder. mp 106°C. **^{1}H NMR (300 MHz, CDCl$_3$, 25°C) δ** 7.42 (d, *J* = 7.4 Hz, 1H, H$_{arm}$), 7.29 (m, 2H, H$_{arm}$), 6.48 (s, 1H, C=C**H$_2$**), 6.26 (dd, *J* = 7,4 Hz, 1H, CHOCO***),*** 5.85 (s, 1H, C=C**H$_2$**), 3.37 (S, 2H, ***),*** 3.13 (m, 1H,***),*** 2.9 (m, 1H,***),*** 2.52 (m, 1H,***),*** 2.13 (m, 1H,***)***. **^{13}C NMR (75 MHz, CDCl$_3$) δ** 171.15, 170.61, 144.41, 140.76, 133.32, 130.68, 129, 126.74, 125.59, 124.79, 79.07, 37.59, 32.17, 30.19. **HRMS (ESI) m/z calcd for C$_{14}$H$_{14}$O$_4$ [M -1]:**245.09**, Found** 245.816.

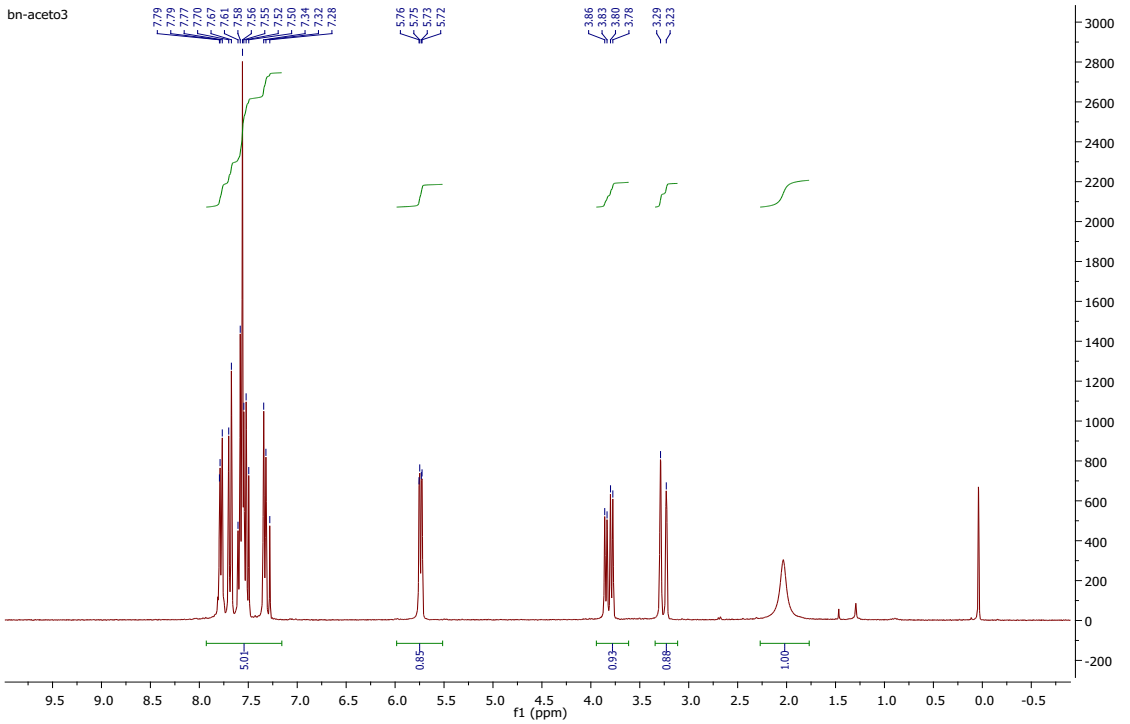
(R)-4-((6-methoxy-2,3-dihydro-1H-inden-1-yl)oxy)-2-methylene-4-oxobutanoic acid (23e)

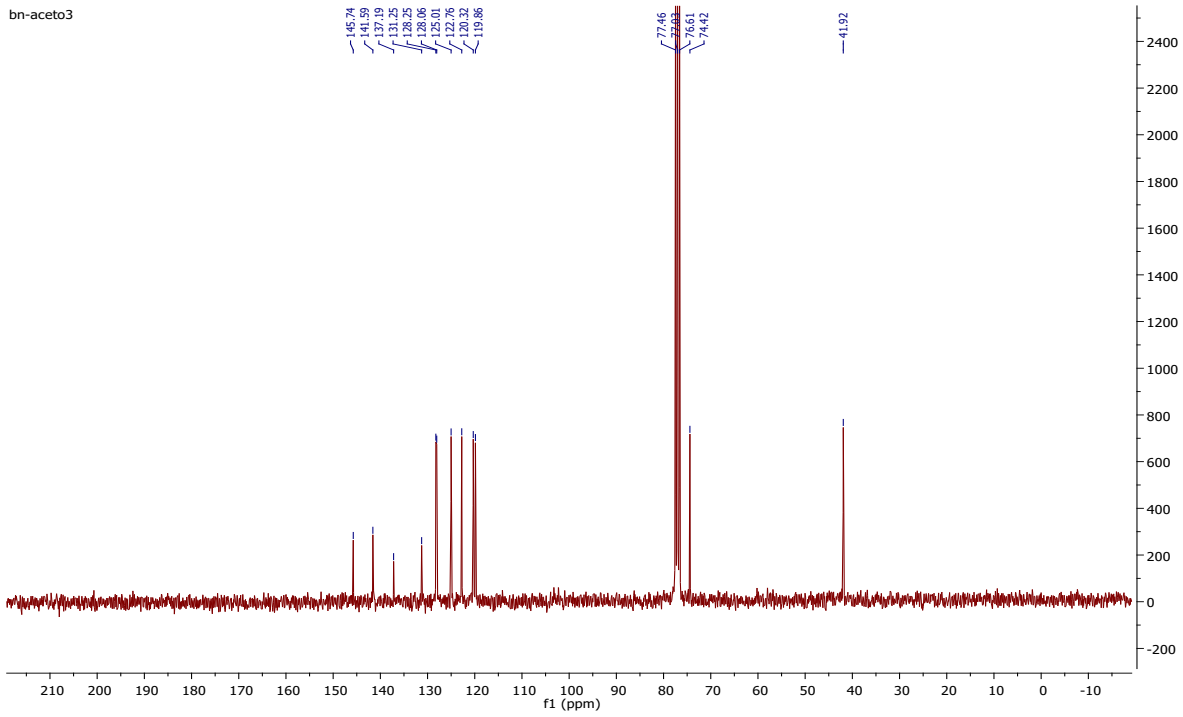
White powder. mp110°C .**^{1}HNMR (300 MHz, CDCl$_3$, 25°C) δ** 7.17 (d, *J* = 8.3 Hz, 1H, H$_{arm}$), 6.9 (m, 2H, H$_{arm}$), 6.48 (s, 1H, C=C**H$_2$**), 6.23 (dd, 1H, *J* = 7, 4 Hz, CHOCO***),*** 5.85 (s, 1H, C=C**H$_2$**), 3.8 (S, 3H, , C**H$_3$O**), 3.38 (S, 2H***),*** 3.05 (m, 1H***),*** 2.82 (m, 1H***),*** 2.54 (m, 1H***),*** 2.12 (m, 1H***)*** . **^{13}C NMR (75 MHz, CDCl$_3$) δ** 171.28, 170.57, 158.93, 142, 136.23, 130.71, 125.37, 116, 109.76, 79.18, 55.48, 37.56, 32.69, 29.33. **HRMS (ESI) m/z calcd for C$_{15}$H$_{16}$O$_5$ [M -1]:**275.10**, Found** 275.0924**.**

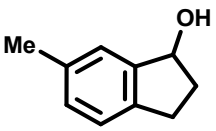
6. **NMR spectra of racemic alcohols [19, 22-25]:**



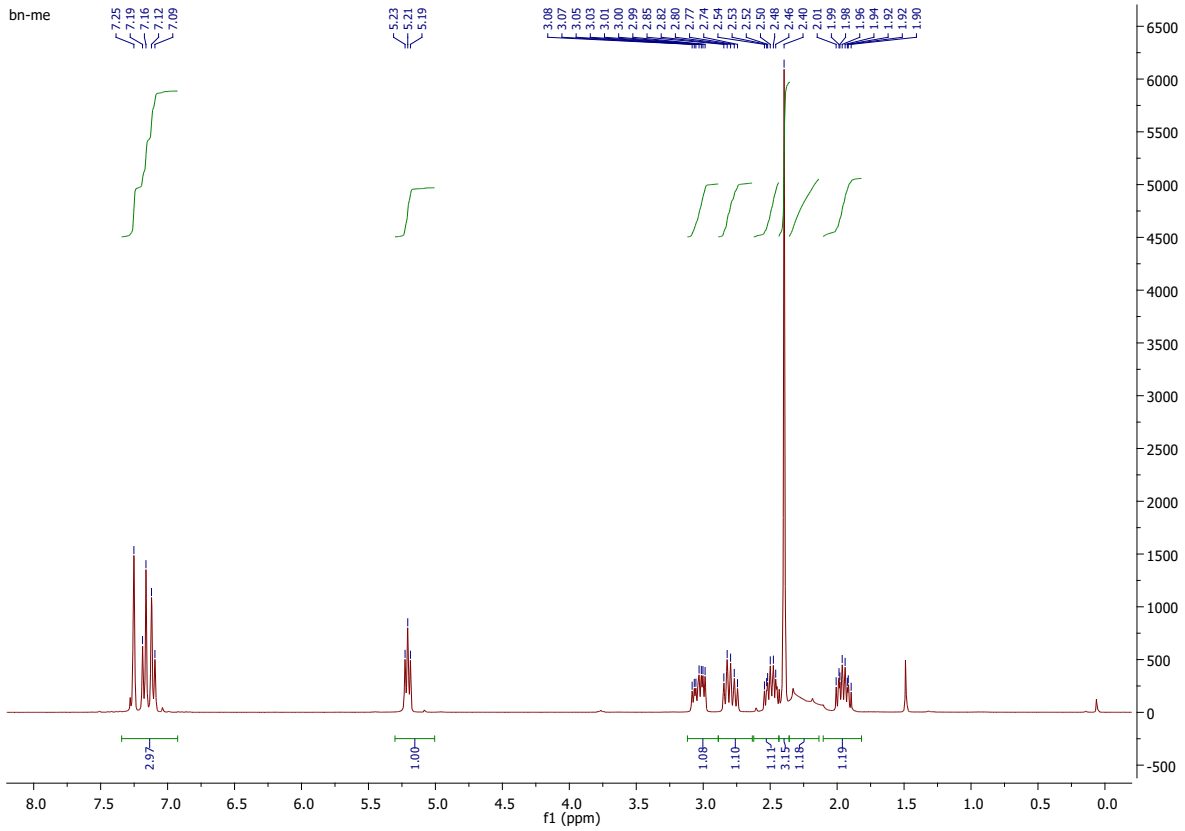
***rac*-19**

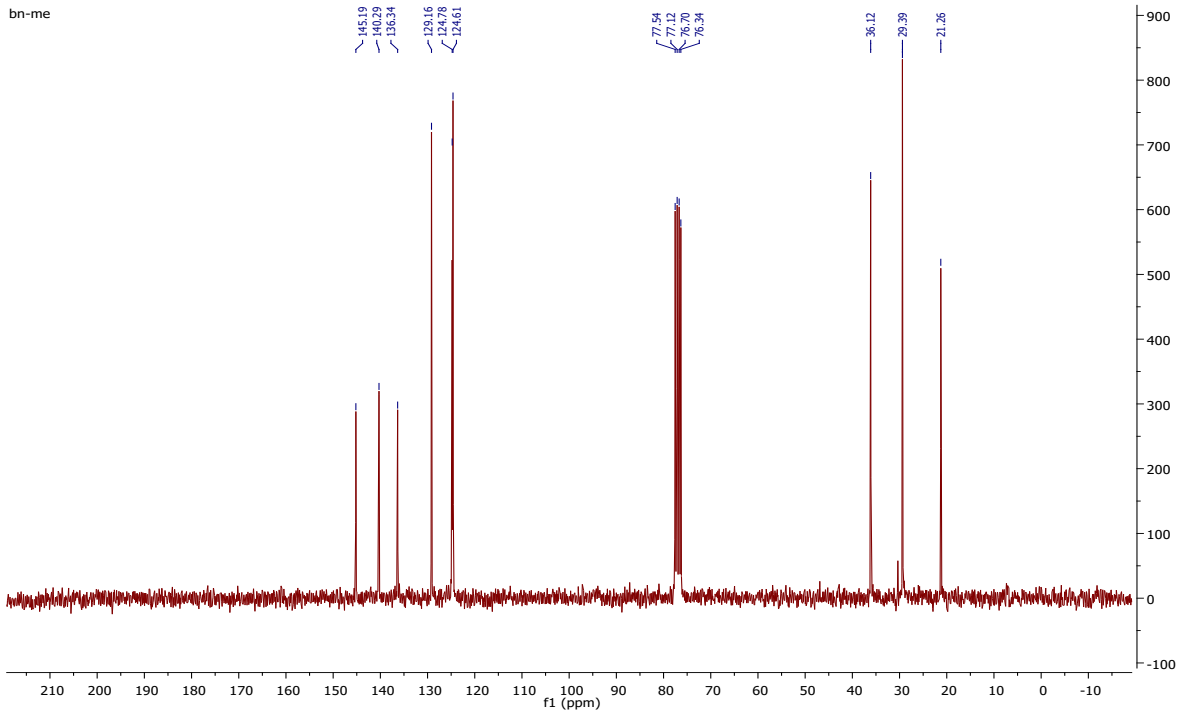

bn-aceto3
7.79
7.79
7.77
7.77
7.70
7.67
7.61
7.58
7.56
7.55
7.52
7.50
7.34
7.32
7.28
5.76
5.75
5.73
5.72
3.86
3.83
3.80
3.78
3.29
3.23
5.01
0.85
0.93
0.88
1.00
f1 (ppm)

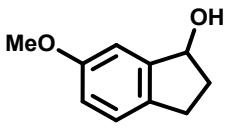

bn-aceto3
145.74
141.59
137.19
131.25
128.25
128.06
125.01
122.76
120.32
119.86
77.46
76.61
74.42
41.92
f1 (ppm)


OH
Me

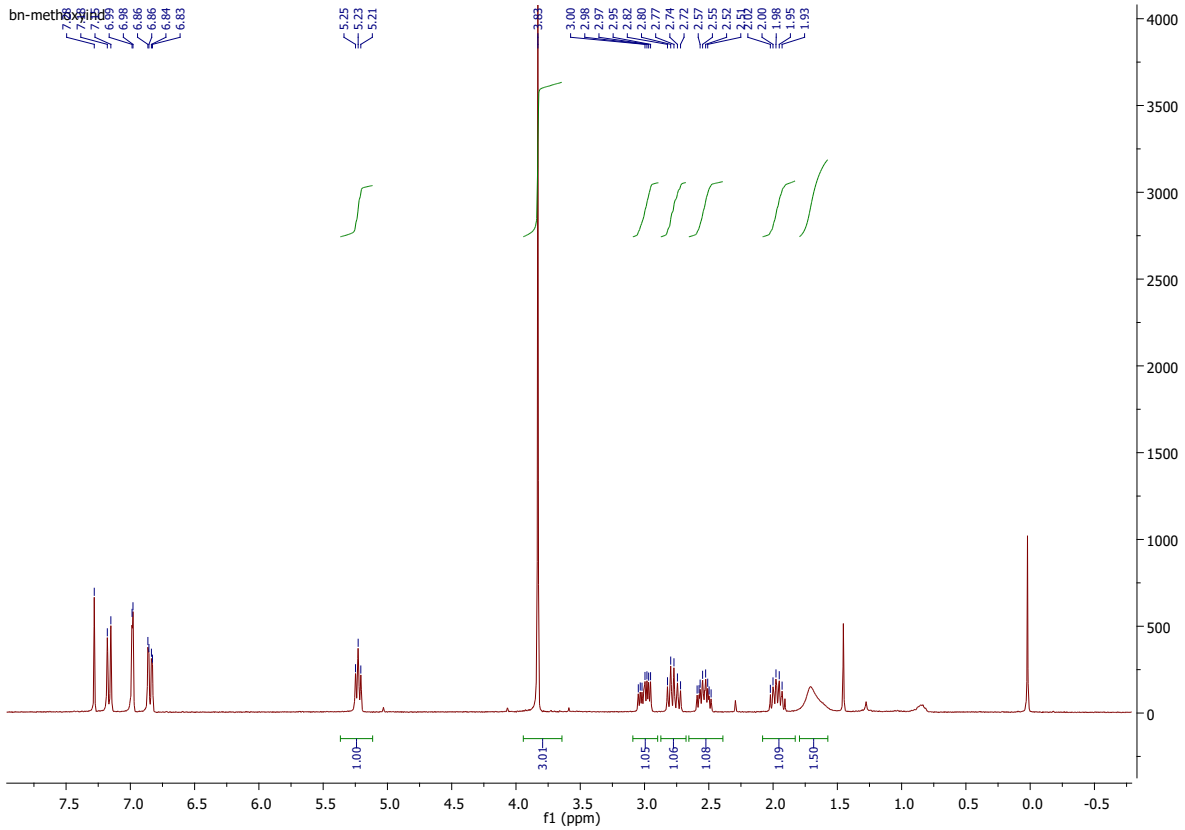
***rac*-22**

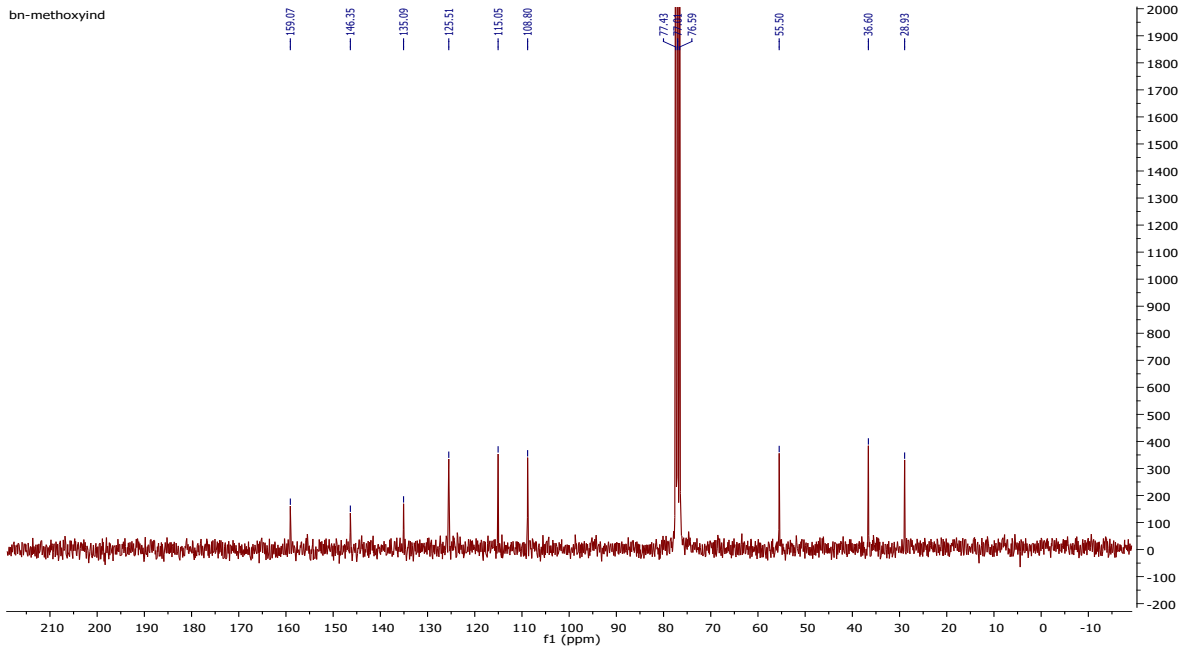

bn-me
7.25
7.19
7.16
7.12
7.09
5.23
5.21
5.19
3.08
3.07
3.05
3.03
3.01
3.00
2.99
2.85
2.82
2.80
2.77
2.74
2.54
2.53
2.52
2.50
2.48
2.46
2.40
2.01
1.99
1.98
1.96
1.94
1.92
1.92
1.90
2.97
1.00
1.08
1.10
1.11
3.15
1.18
1.19
f1 (ppm)

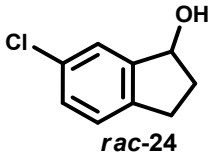

bn-me
145.19
140.29
136.34
129.16
124.78
124.61
77.54
77.12
76.70
76.34
36.12
29.39
21.26
f1 (ppm)


MeO
OH

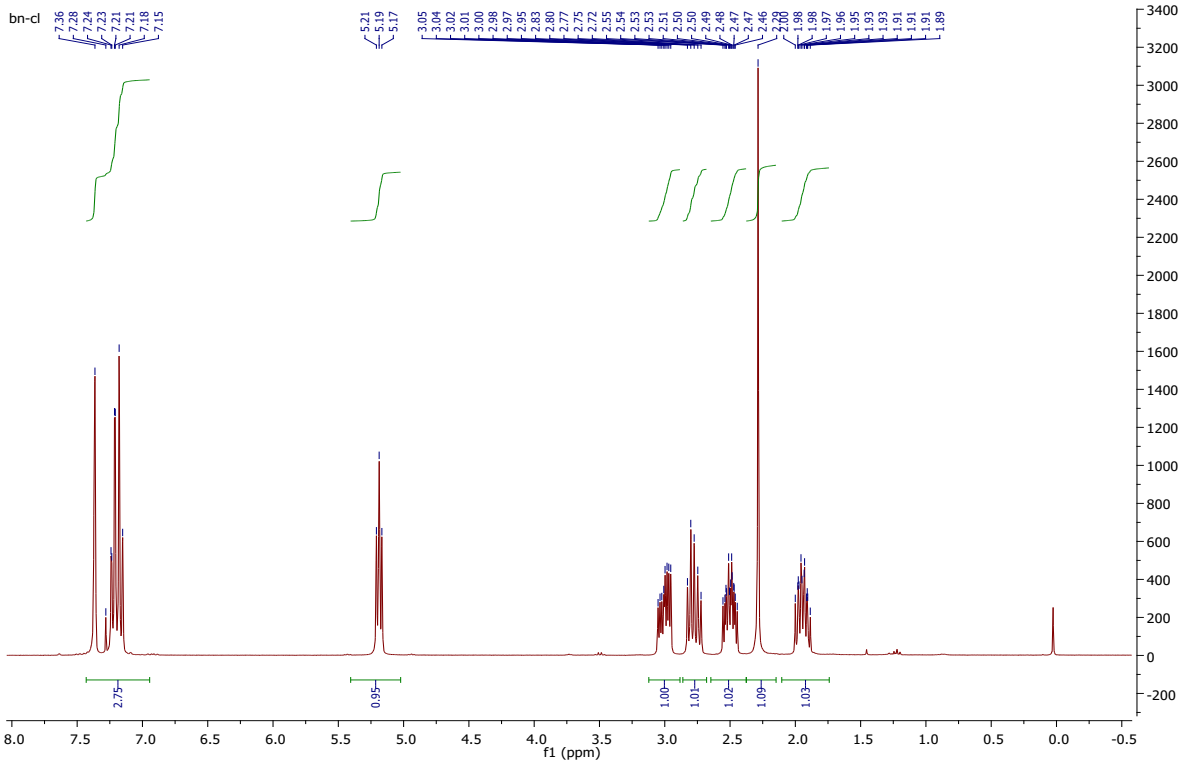
***rac*-23**

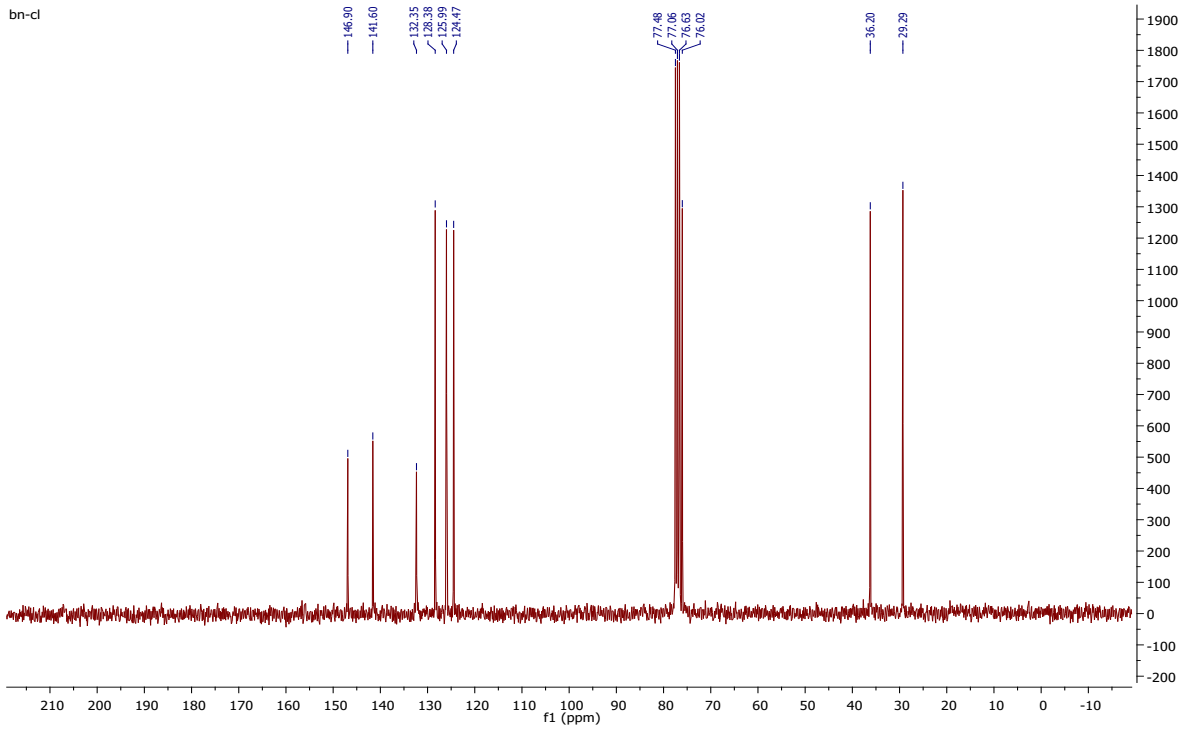

bn-methoxyind
f1 (ppm)

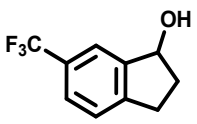

bn-methoxyind
159.07
146.35
135.09
125.51
115.05
108.80
77.43
77.01
76.59
55.50
36.60
28.93
f1 (ppm)


OH
Cl

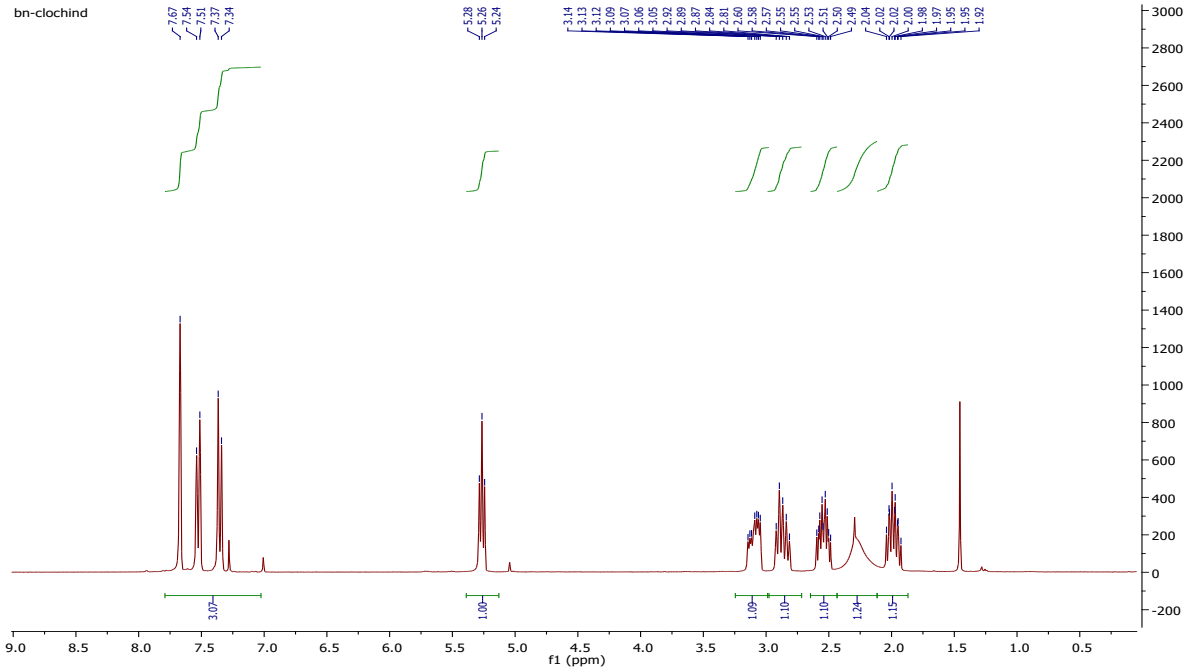
***rac*-24**

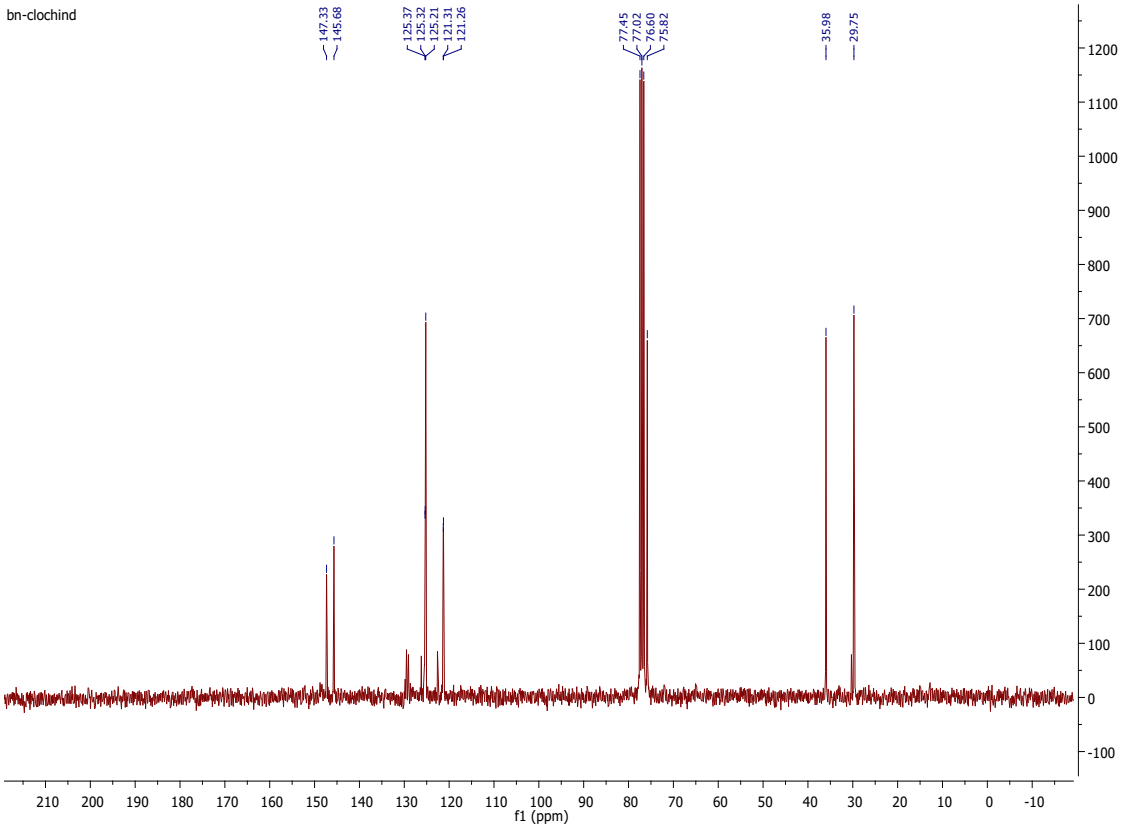




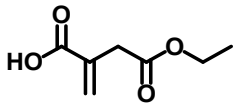


***rac*-25**

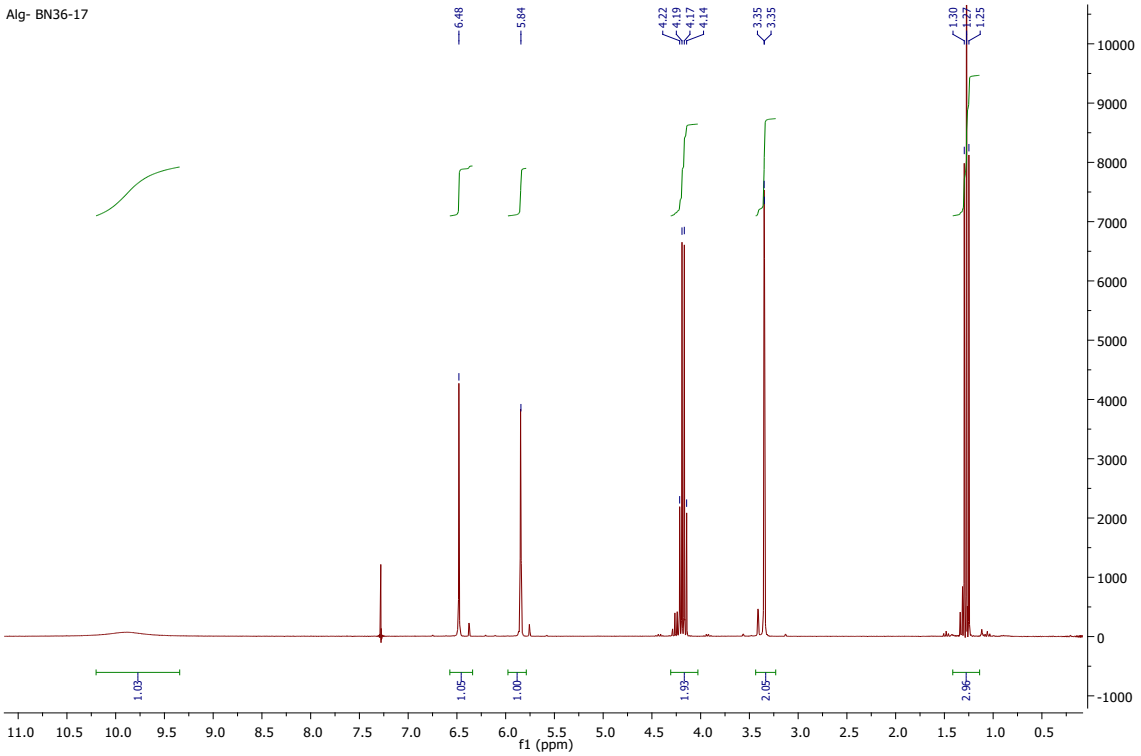


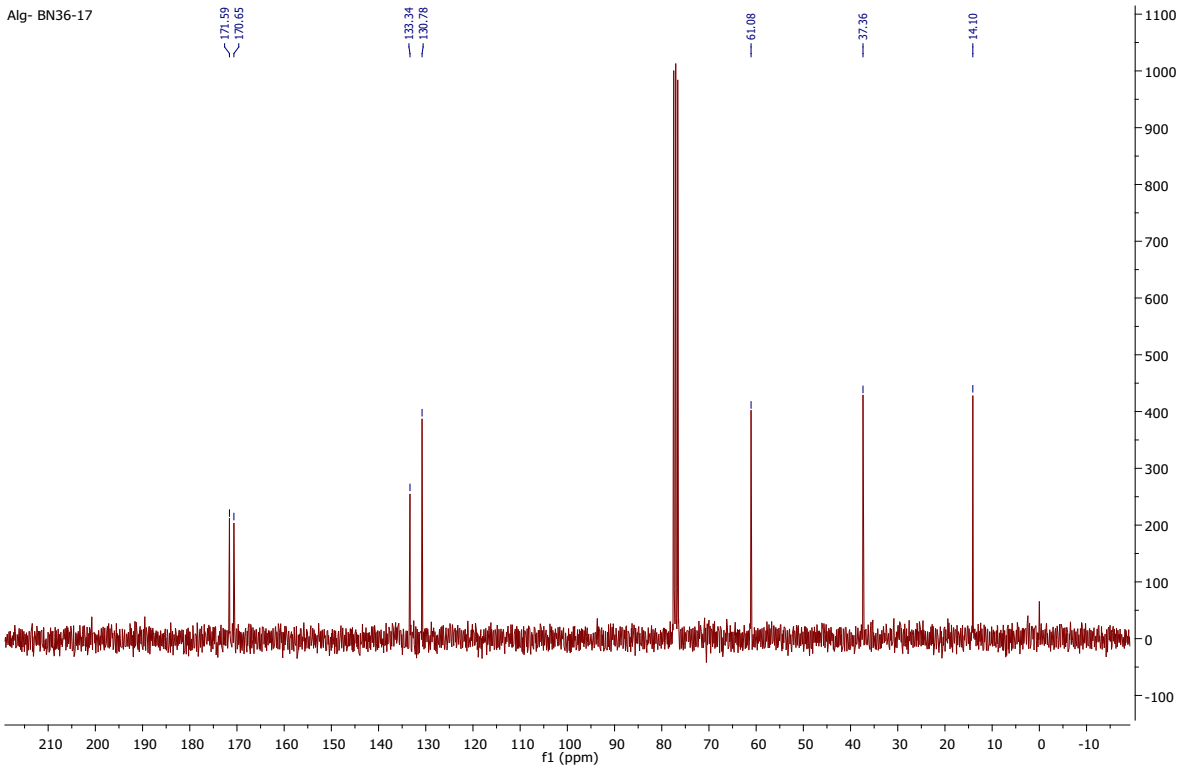


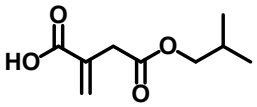
NMR spectra of all the monoesters itaconates:


HO
O
O
O

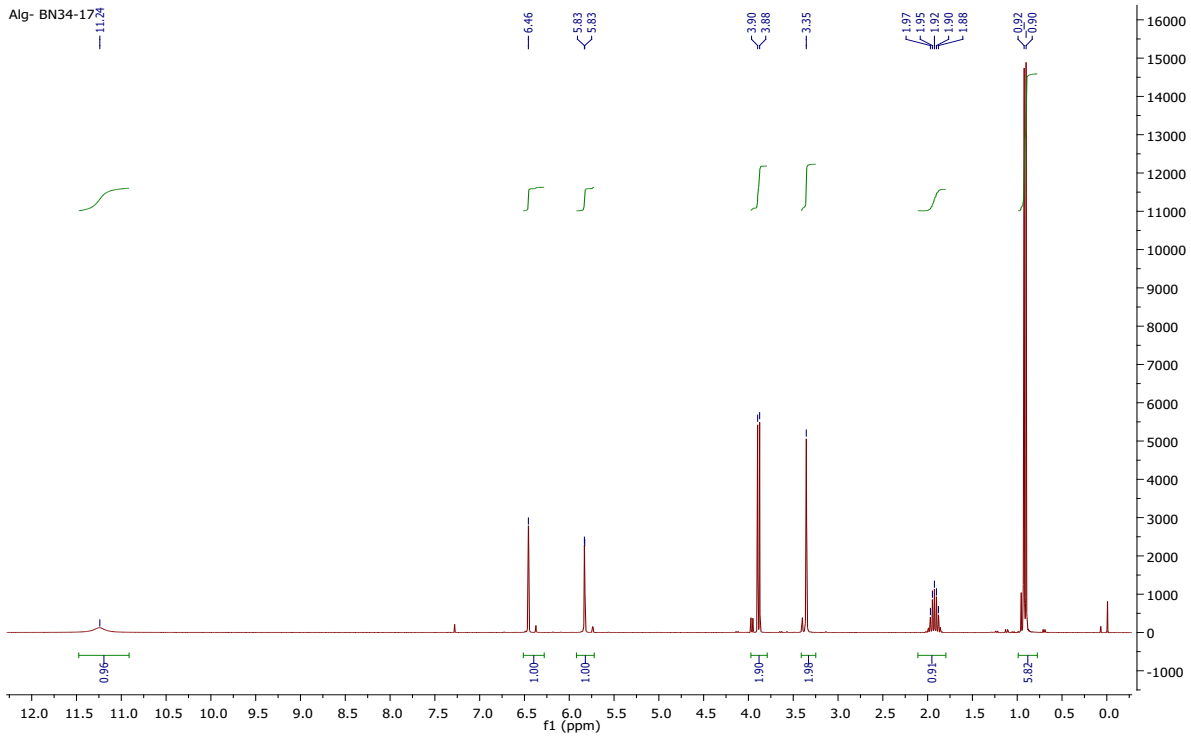
2e

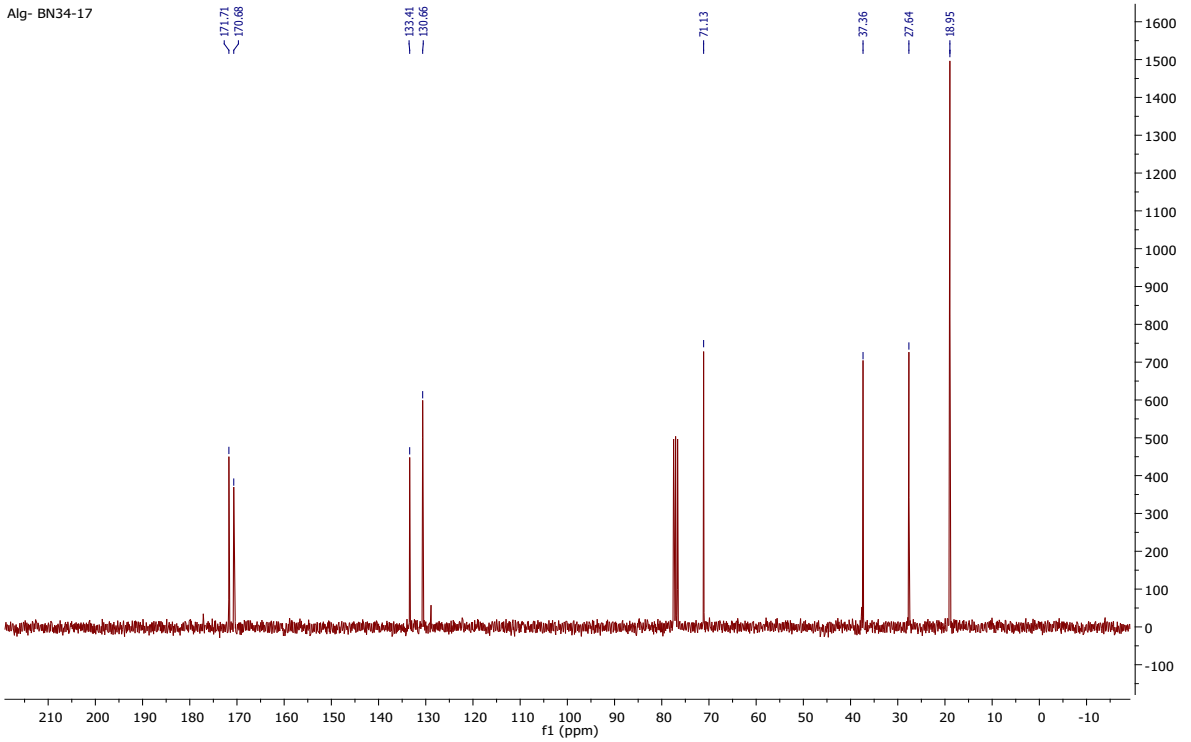

Alg- BN36-17
6.48
5.84
4.22
4.19
4.17
4.14
3.35
3.35
1.30
1.27
1.25
1.03
1.05
1.00
1.93
2.05
2.96
f1 (ppm)

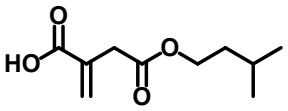

Alg- BN36-17
171.59
170.65
133.34
130.78
61.08
37.36
14.10
f1 (ppm)


HO
O
O
O

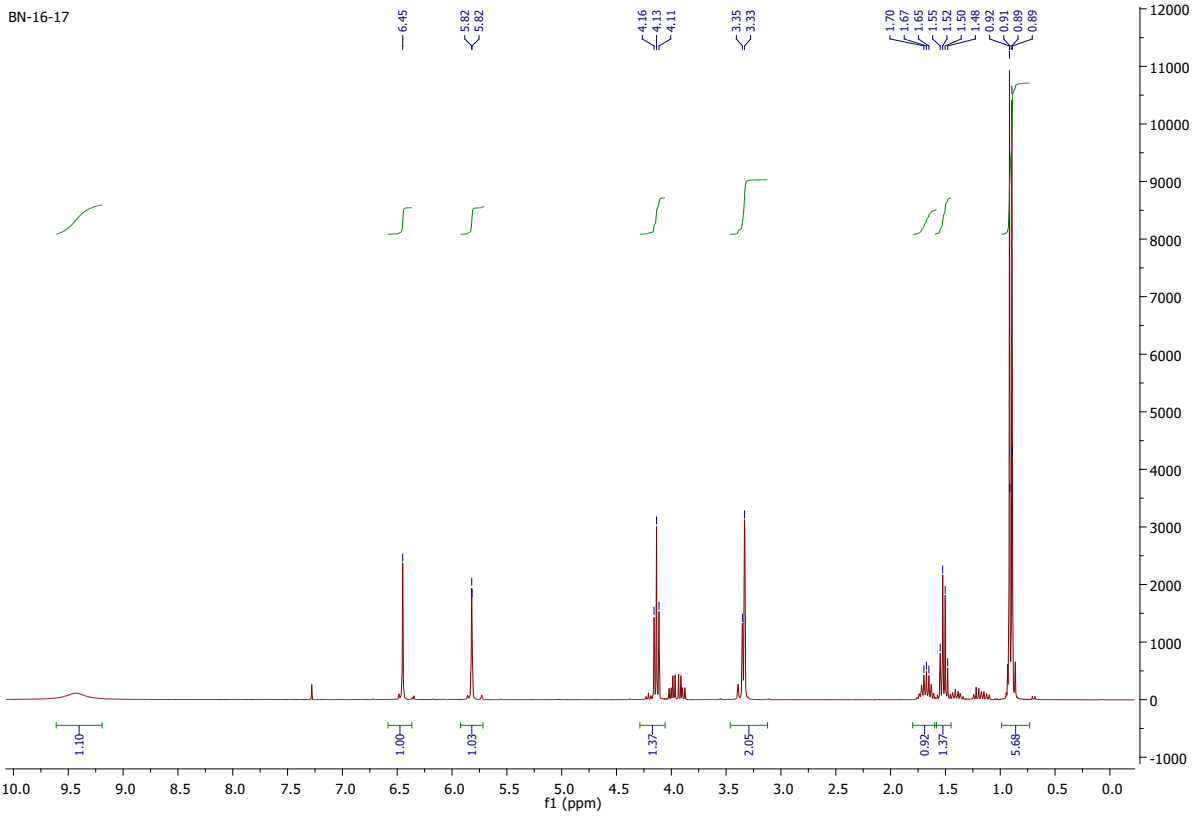
3e

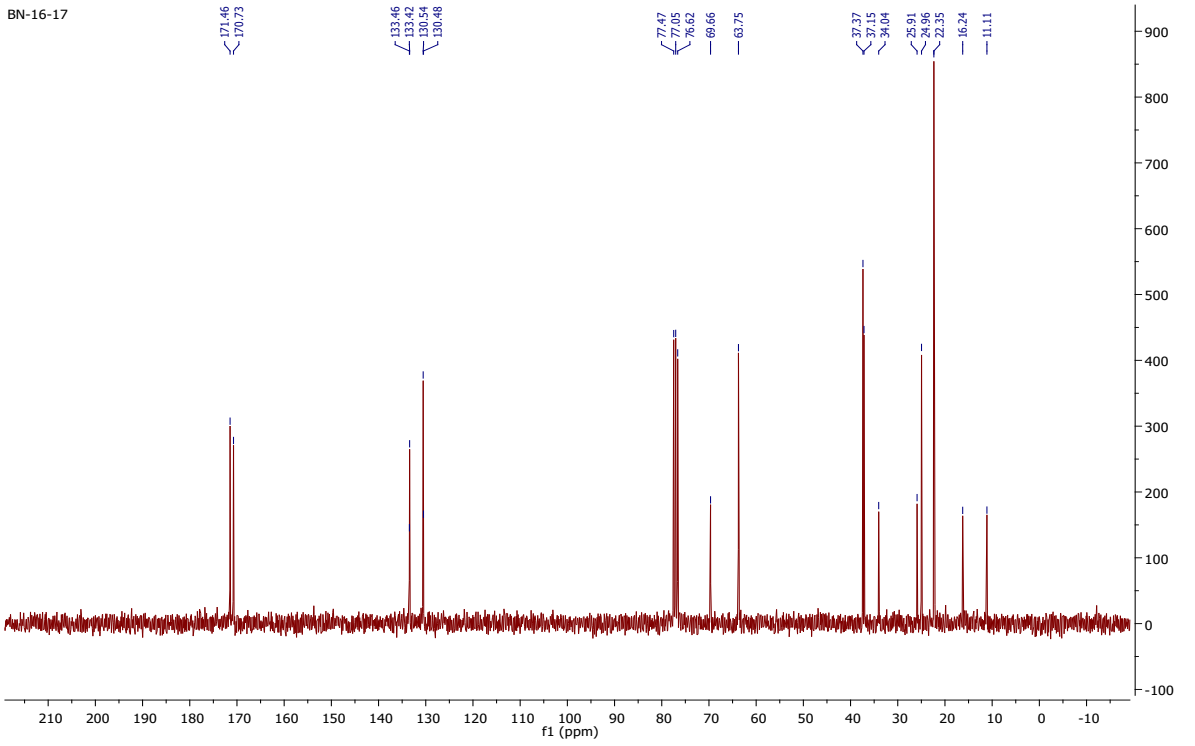

Alg- BN34-17
11.24
6.46
5.83
5.83
3.90
3.88
3.35
1.97
1.95
1.92
1.90
1.88
0.92
0.90
0.96
1.00
1.00
1.90
1.98
0.91
5.82
f1 (ppm)

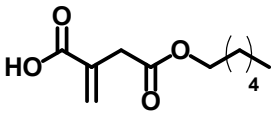

Alg- BN34-17
171.71
170.68
133.41
130.66
71.13
37.36
27.64
18.95
f1 (ppm)


HO
O
O
O

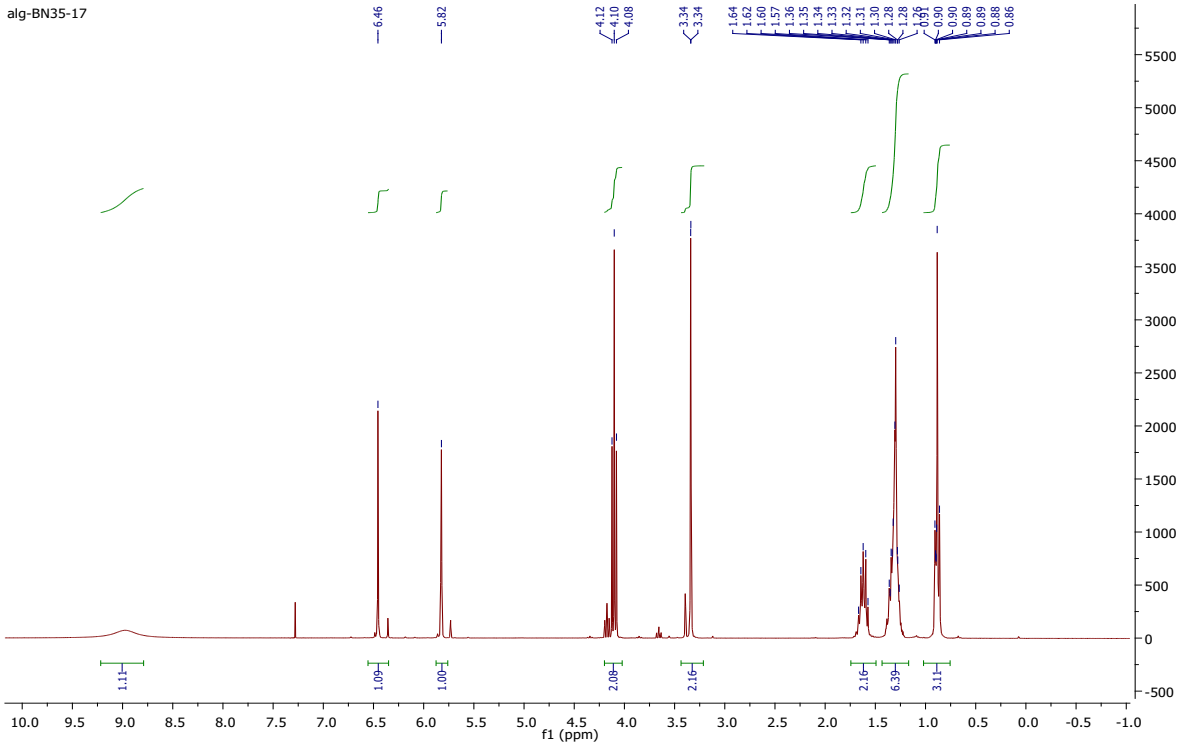
1e

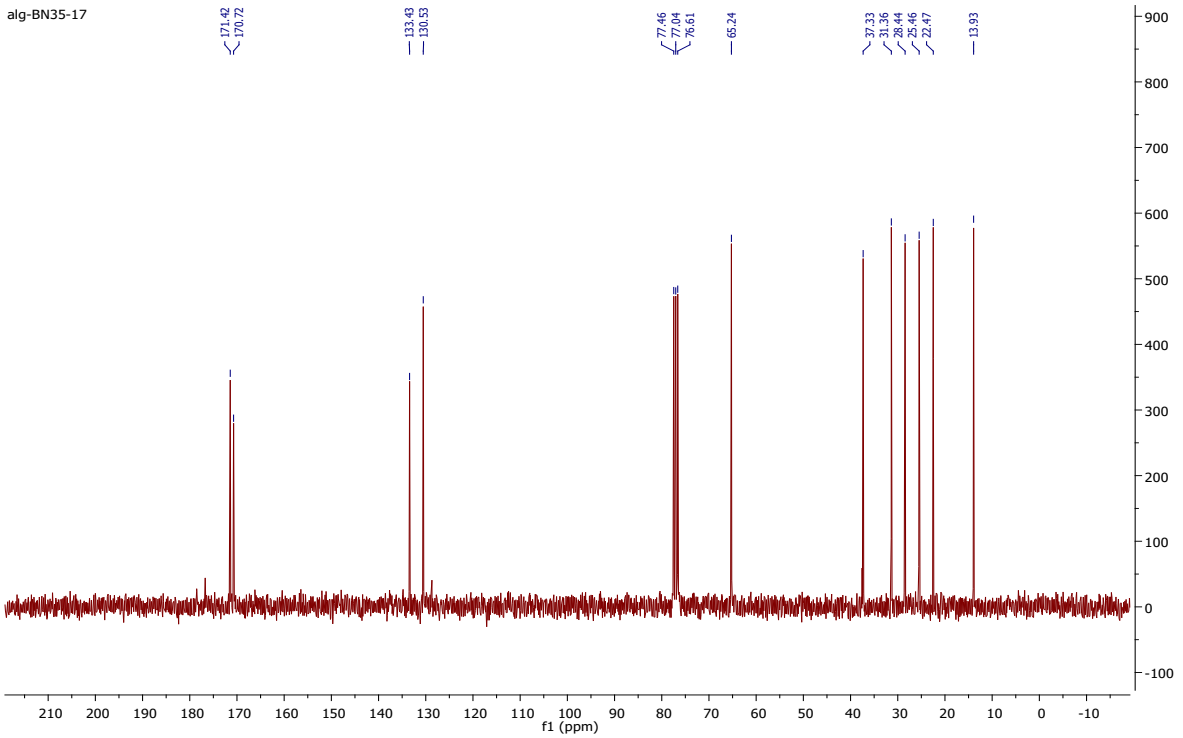

BN-16-17
6.45
5.82
5.82
4.16
4.13
4.11
3.35
3.33
1.70
1.67
1.65
1.55
1.52
1.50
1.48
0.92
0.91
0.89
0.89
1.10
1.00
1.03
1.37
2.05
0.92
1.37
5.68
f1 (ppm)

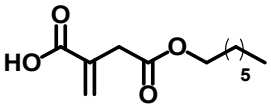

BN-16-17
171.46
170.73
133.46
133.42
130.54
130.48
77.47
77.05
76.62
69.66
63.75
37.37
37.15
34.04
25.91
24.96
22.35
16.24
11.11
f1 (ppm)


HO
O
O
O
4

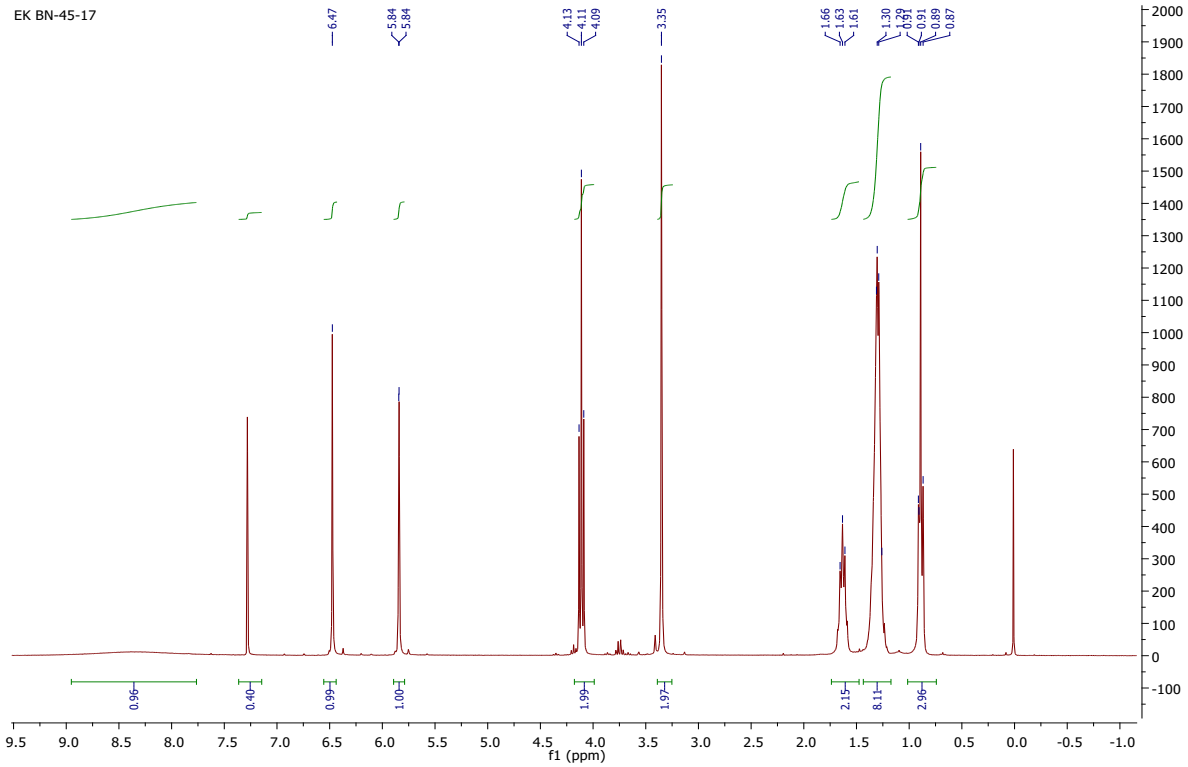
4e

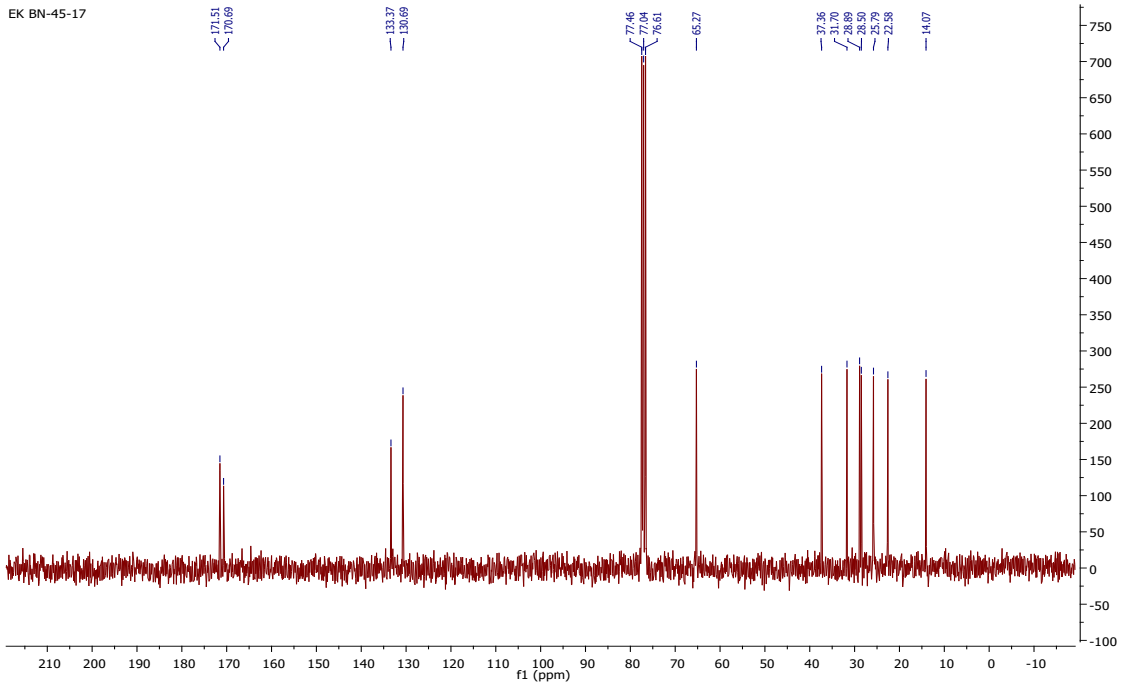

alg-BN35-17
6.46
5.82
4.12
4.10
4.08
3.34
3.34
1.64
1.62
1.60
1.57
1.36
1.35
1.34
1.33
1.32
1.31
1.30
1.28
1.28
0.91
0.90
0.90
0.89
0.89
0.88
0.86
1.11
1.09
1.00
2.08
2.16
2.16
6.39
3.11
f1 (ppm)

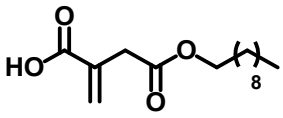

alg-BN35-17
171.42
170.72
133.43
130.53
77.46
77.04
76.61
65.24
37.33
31.36
28.44
25.46
22.47
13.93
f1 (ppm)



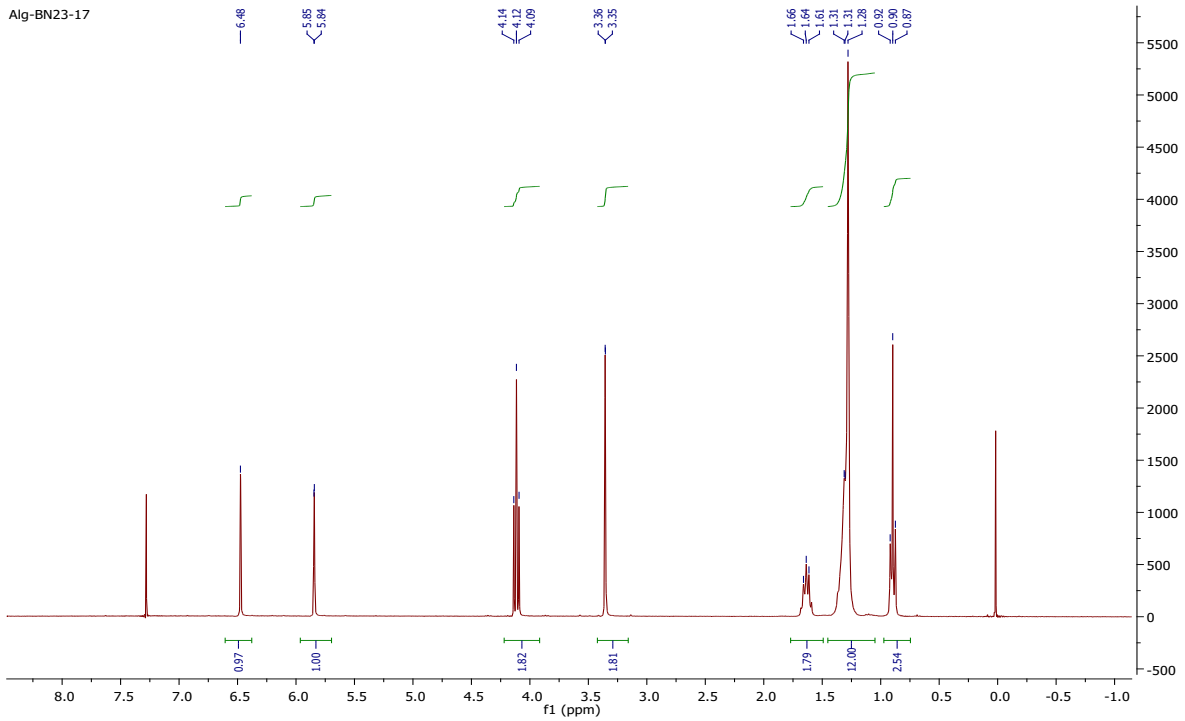
5e

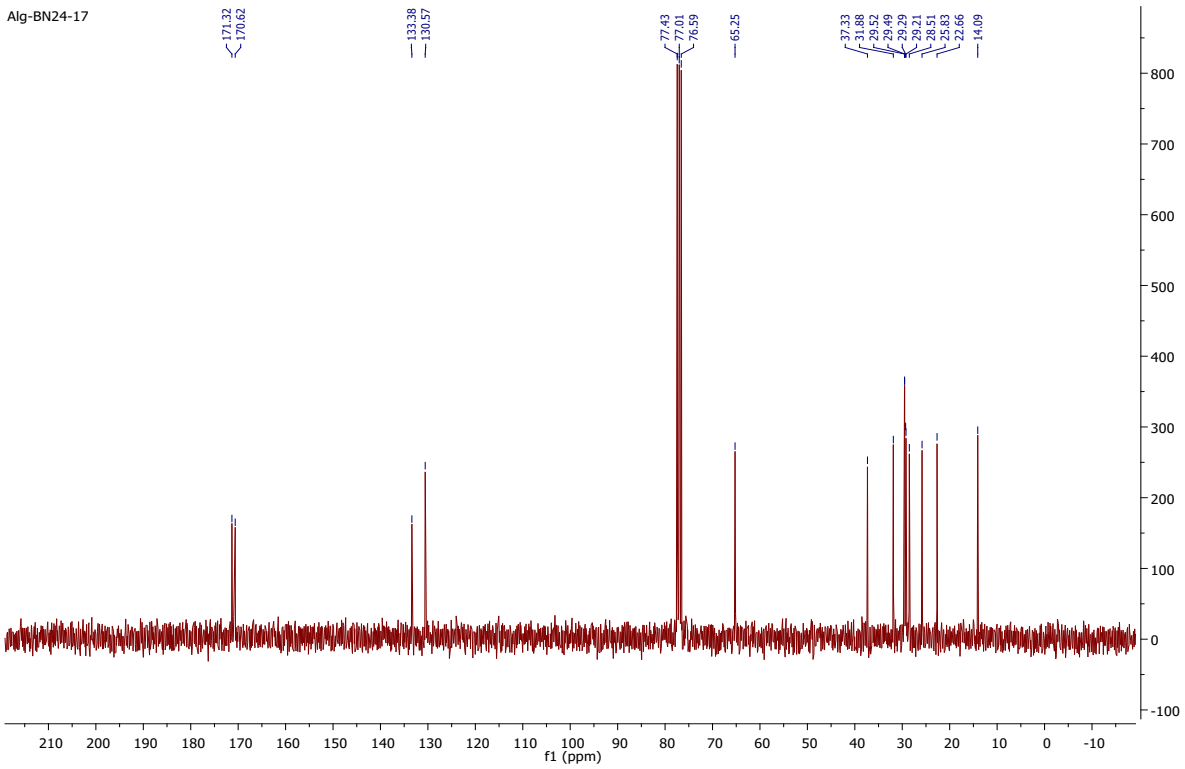

EK BN-45-17
6.47
5.84
5.84
4.13
4.11
4.09
3.35
1.66
1.63
1.61
1.30
1.29
0.91
0.89
0.87
0.96
0.40
0.99
1.00
1.99
1.97
2.15
8.11
2.96
f1 (ppm)

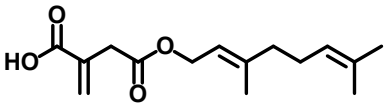

EK BN-45-17
171.51
170.69
133.37
130.69
77.46
77.04
76.61
65.27
37.36
31.70
28.89
28.50
25.79
22.58
14.07
f1 (ppm)


HO
O
O
O
8

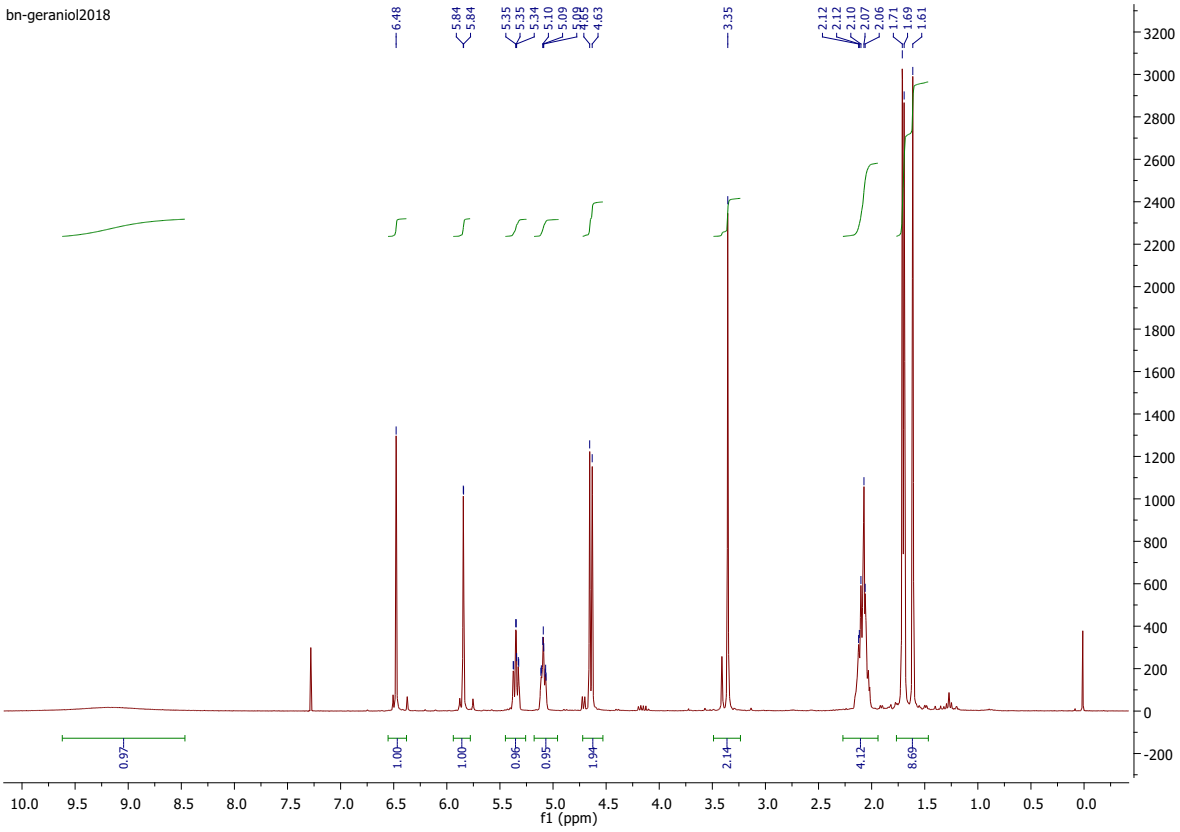
6e

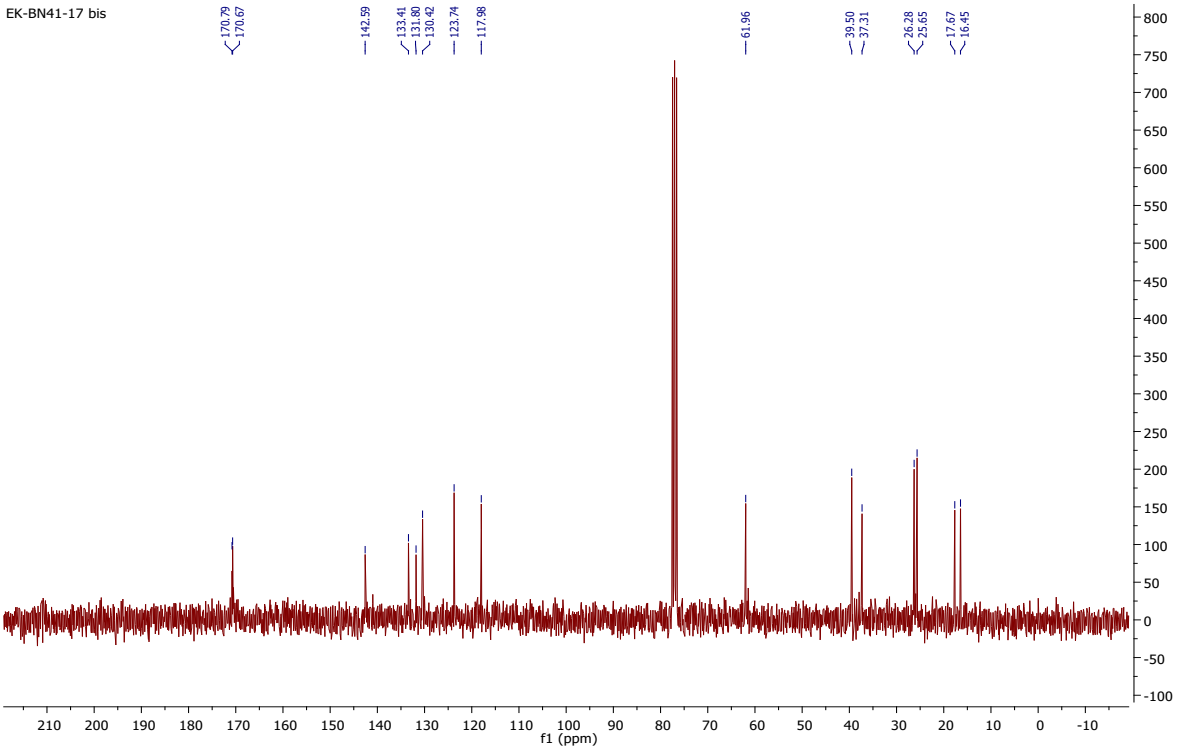

Alg-BN23-17
6.48
5.85
5.84
4.14
4.12
4.09
3.36
3.35
1.66
1.64
1.61
1.31
1.31
1.28
0.92
0.90
0.87
0.97
1.00
1.82
1.81
1.79
12.00
2.54
f1 (ppm)

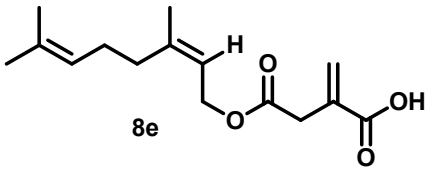

Alg-BN24-17
171.32
170.62
133.38
130.57
77.43
77.01
76.59
65.25
37.33
31.88
29.52
29.49
29.29
29.21
28.51
25.83
22.66
14.09
f1 (ppm)



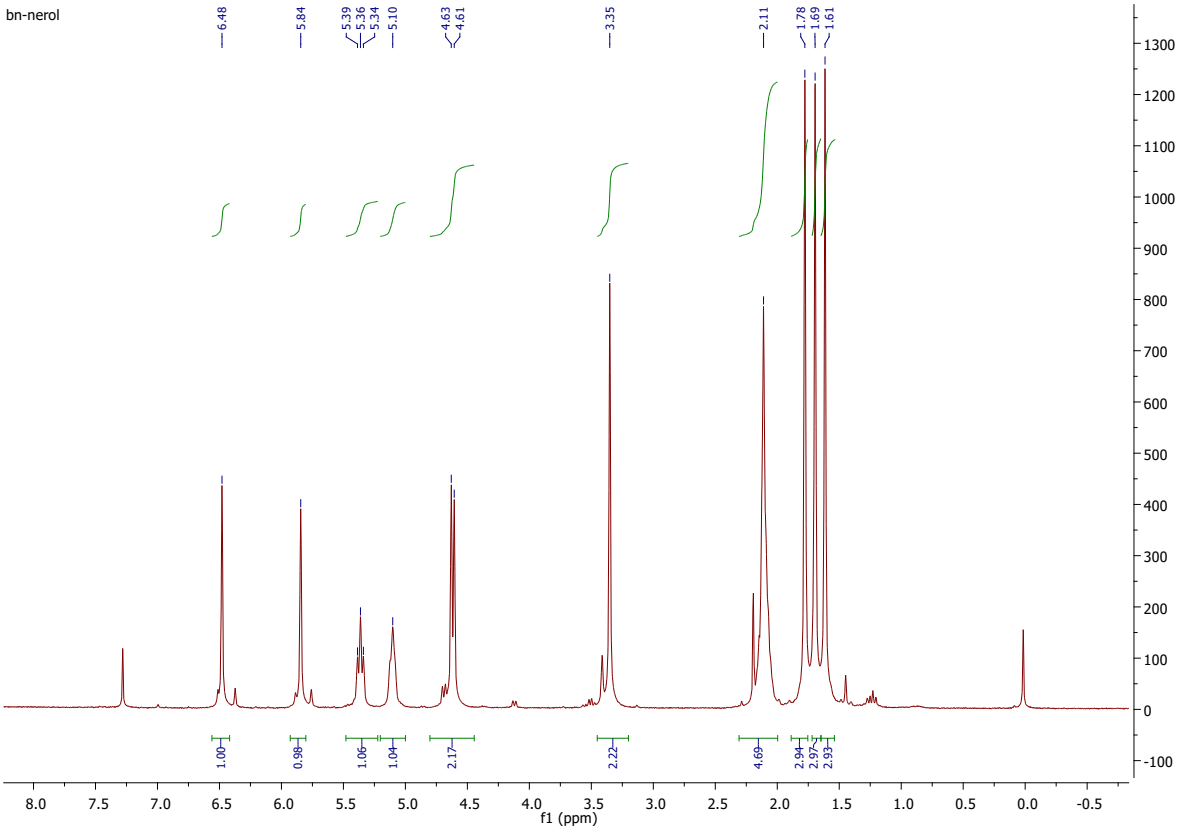
7e

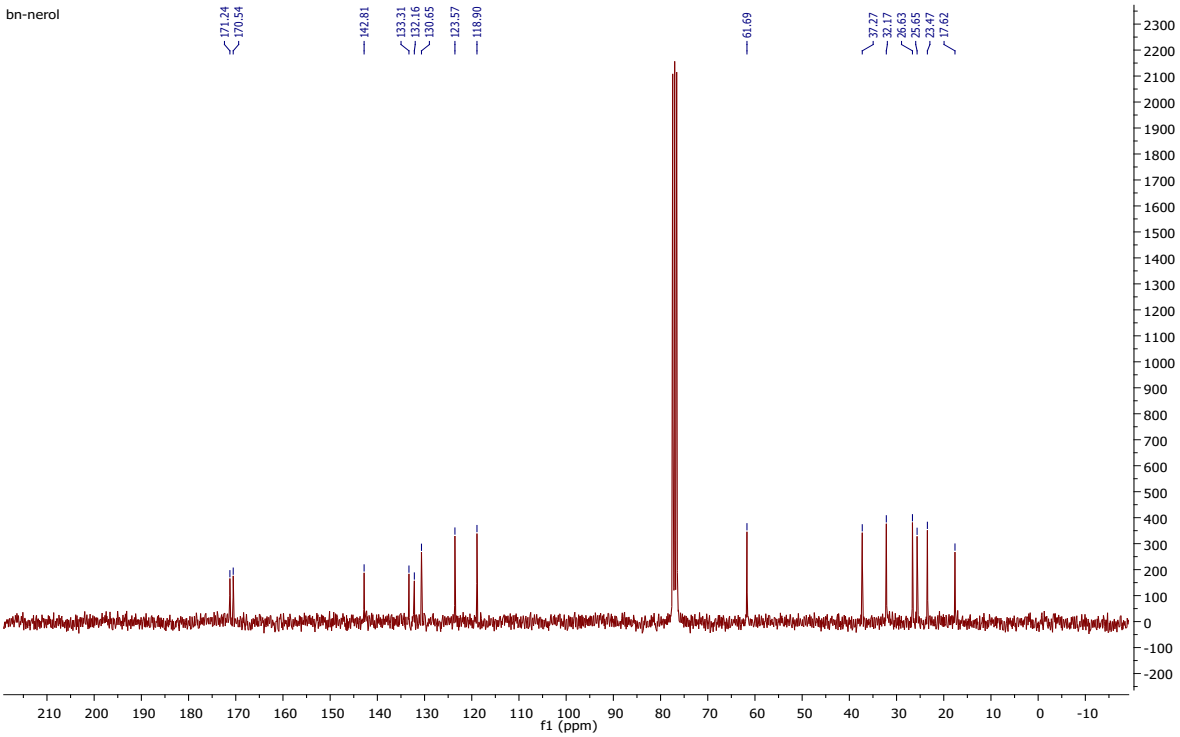

bn-geraniol2018
6.48
5.84
5.84
5.35
5.35
5.34
5.10
5.09
4.63
3.35
2.12
2.12
2.10
2.07
2.06
1.71
1.69
1.61
0.97
1.00
1.00
0.96
0.95
1.94
2.14
4.12
8.69
f1 (ppm)

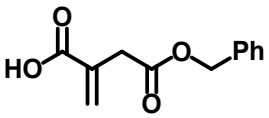

EK-BN41-17 bis
170.79
170.67
142.59
133.41
131.80
130.42
123.74
117.98
61.96
39.50
37.31
26.28
25.65
17.67
16.45
f1 (ppm)


H
O
O
OH
O

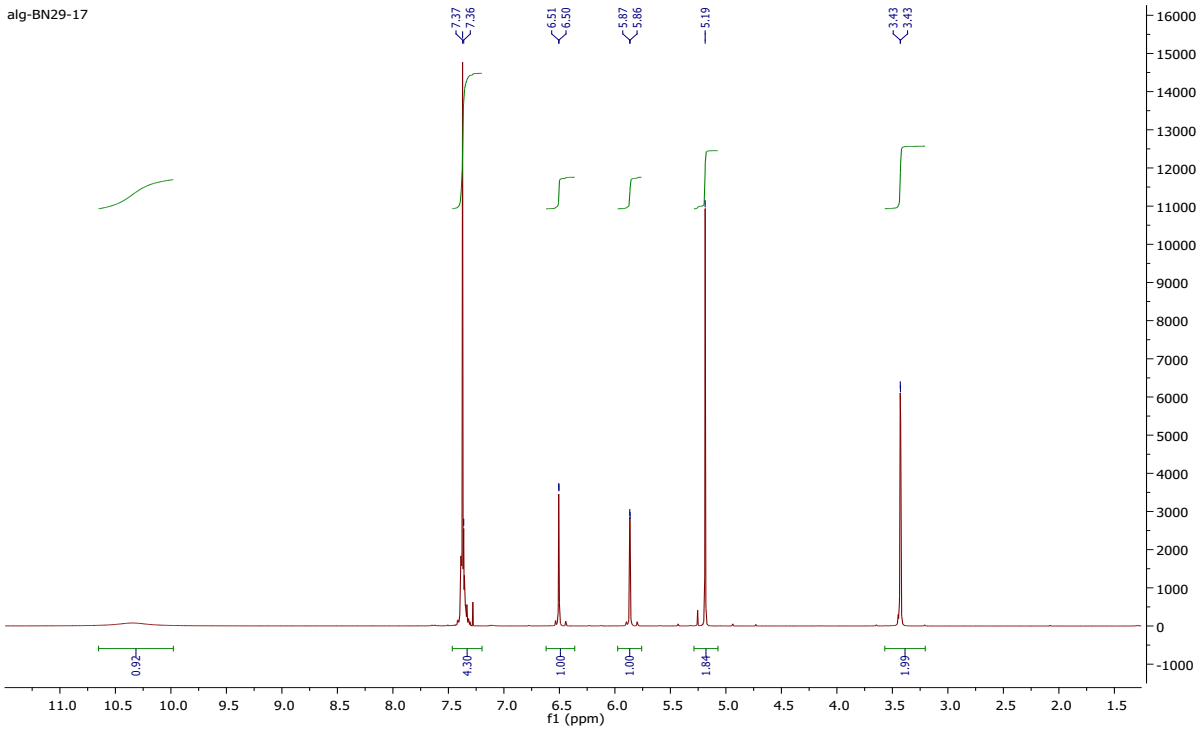
8e

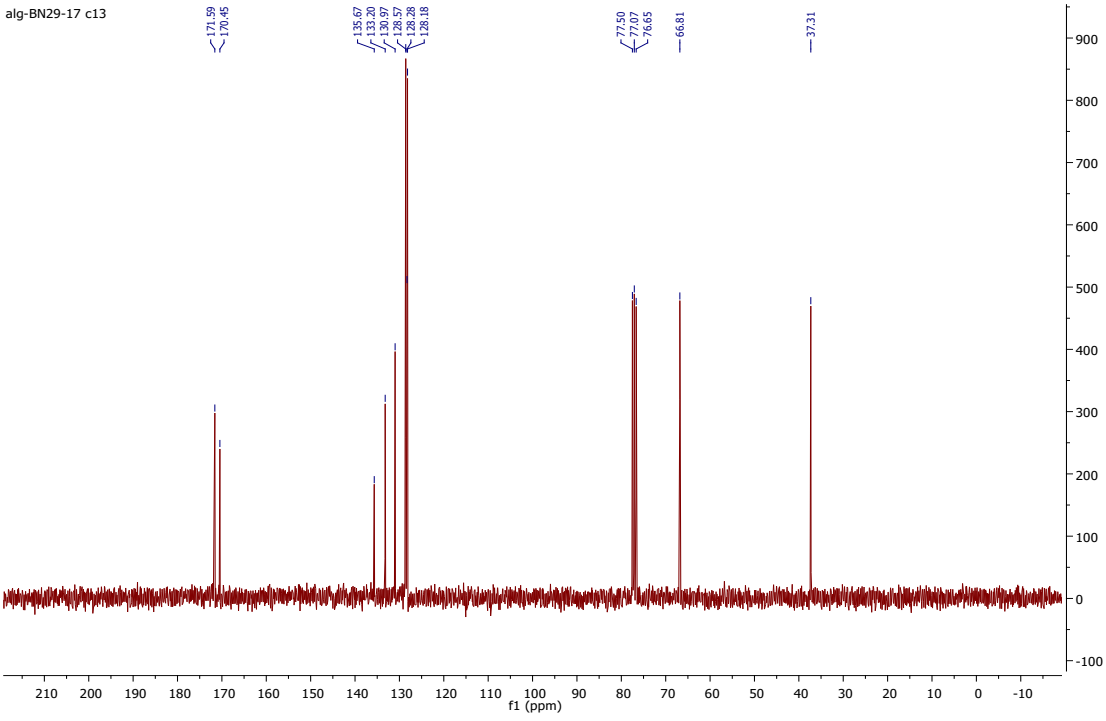

bn-nerol
6.48
5.84
5.39
5.36
5.34
5.10
4.63
4.61
3.35
2.11
1.78
1.69
1.61
1.00
0.98
1.06
1.04
2.17
2.22
4.69
2.94
2.97
2.93
f1 (ppm)

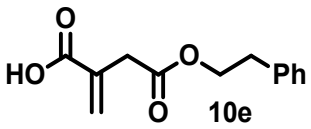

bn-nerol
171.24
170.54
142.81
133.31
132.16
130.65
123.57
118.90
61.69
37.27
32.17
26.63
25.65
23.47
17.62
f1 (ppm)


HO
O
O
O
Ph

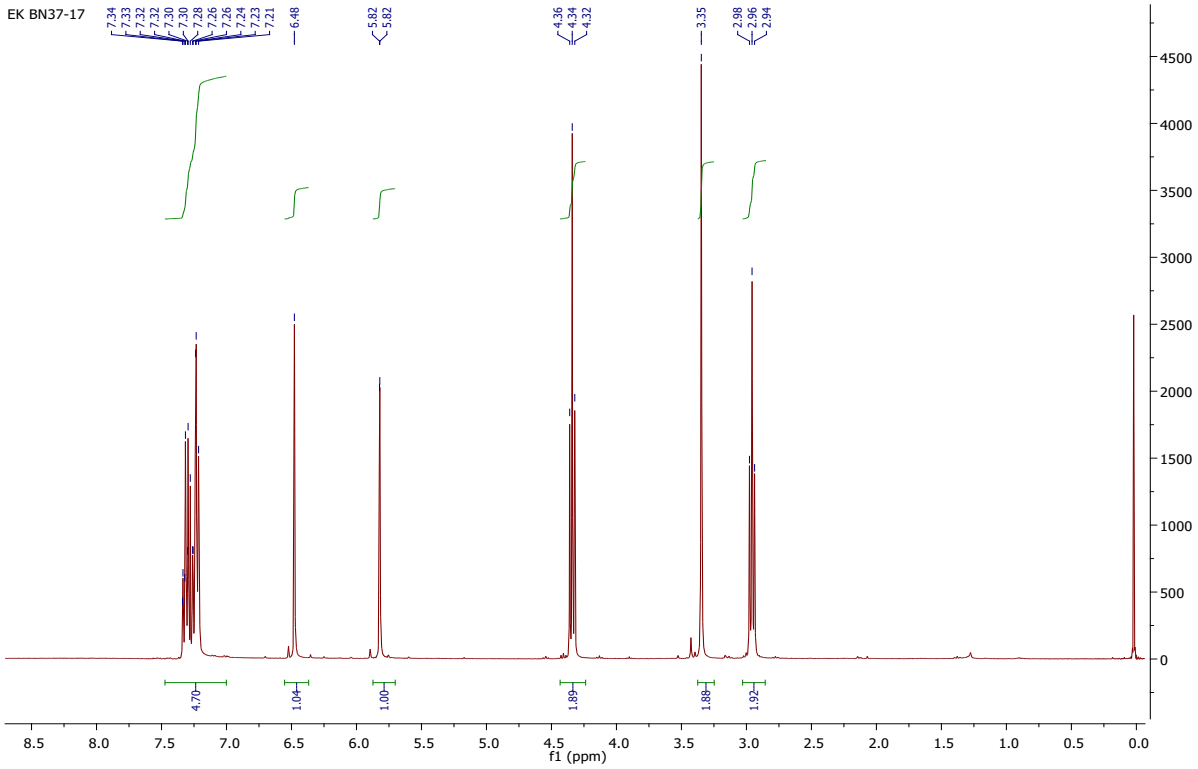
9e

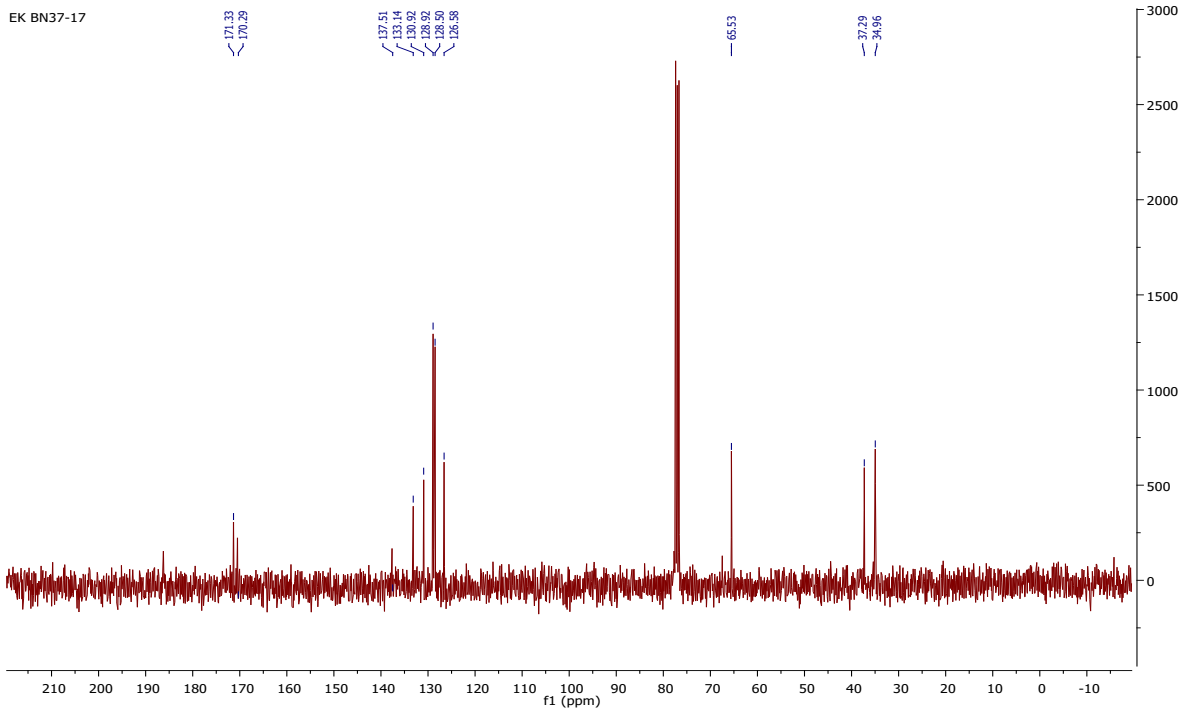

alg-BN29-17
7.37
7.36
6.51
6.50
5.87
5.86
5.19
3.43
3.43
0.92
4.30
1.00
1.00
1.84
1.99
f1 (ppm)

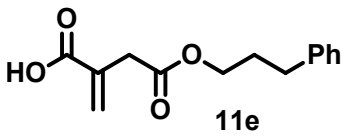

alg-BN29-17 c13
171.59
170.45
135.67
133.20
130.97
128.57
128.28
128.18
77.50
77.07
76.65
66.81
37.31
f1 (ppm)


HO
O
O
O
Ph

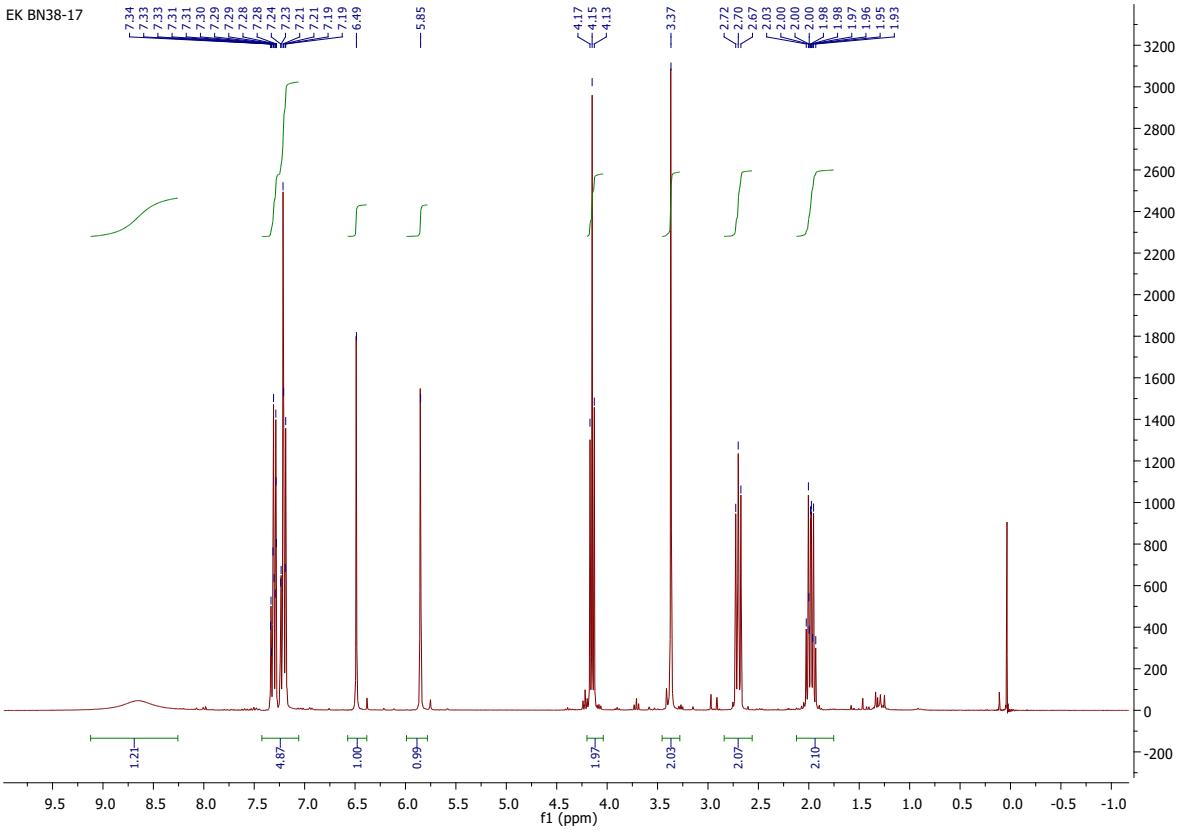
10e

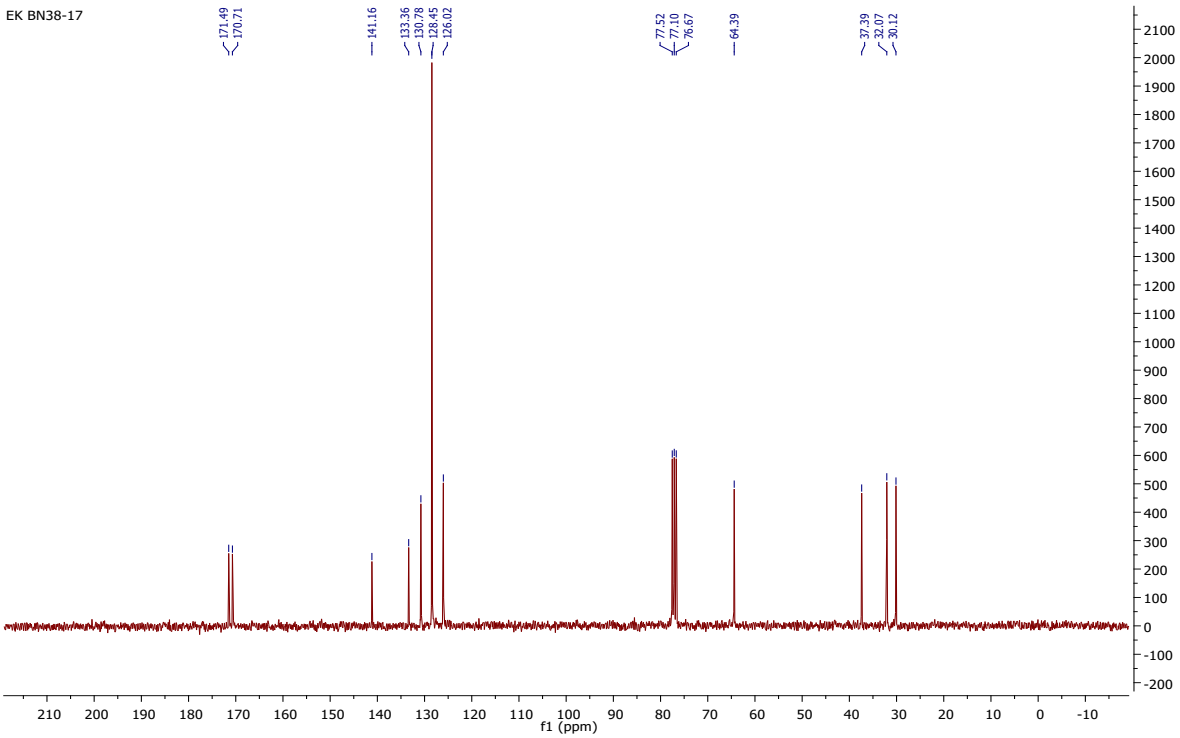

EK BN37-17
7.34
7.33
7.32
7.32
7.30
7.30
7.28
7.26
7.26
7.24
7.23
7.21
6.48
5.82
5.82
4.36
4.34
4.32
3.35
2.98
2.96
2.94
4.70
1.04
1.00
1.89
1.89
1.92
f1 (ppm)

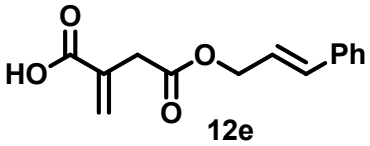

EK BN37-17
171.33
170.29
137.51
133.14
130.92
128.92
128.50
126.58
65.53
37.29
34.96
f1 (ppm)


O
HO
O
O
Ph

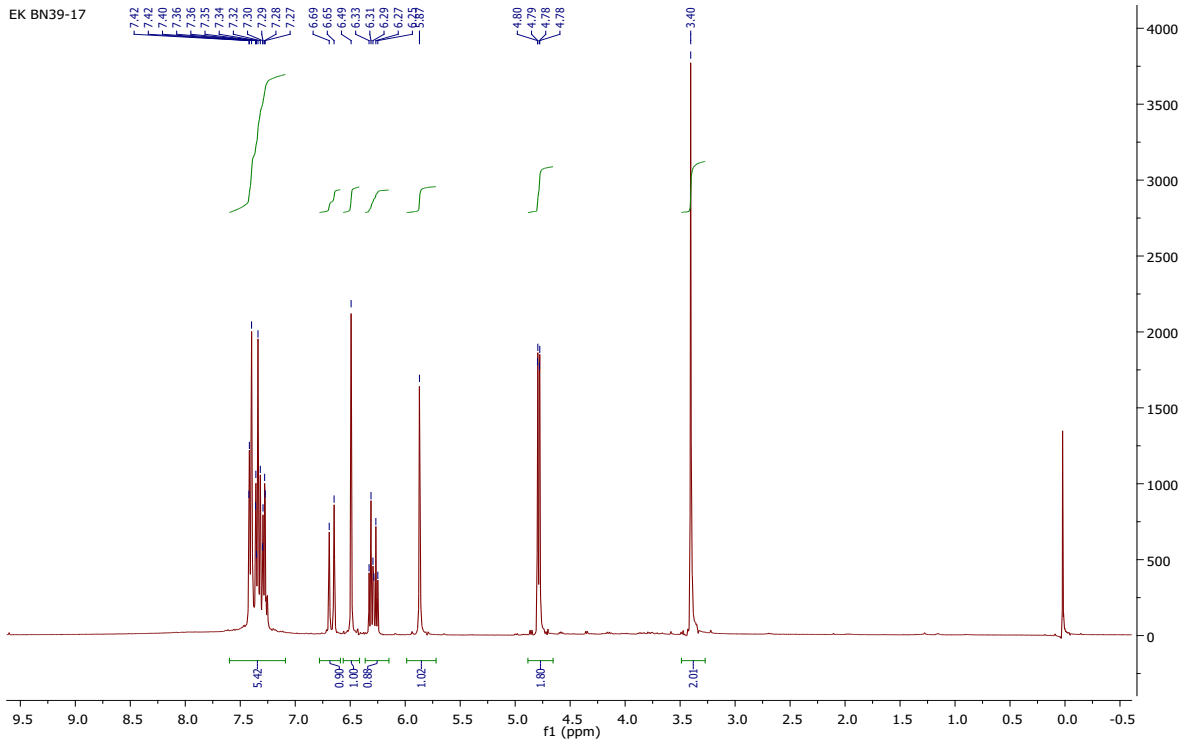
11e

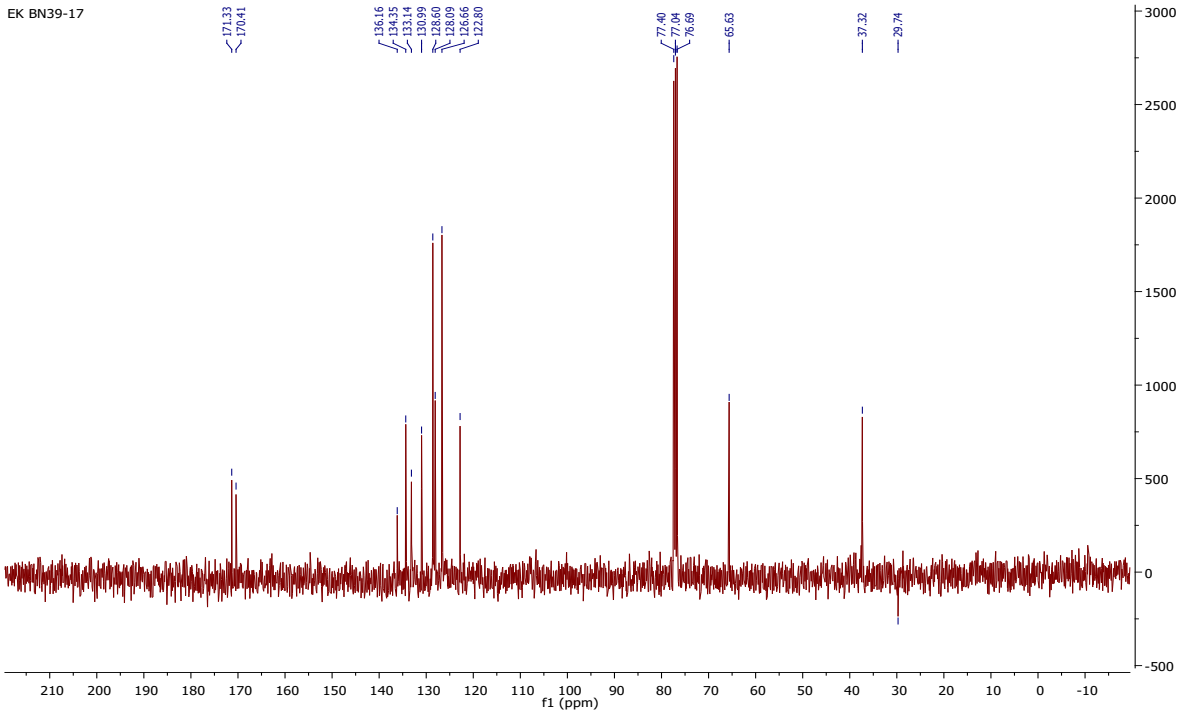

EK BN38-17
7.34
7.33
7.33
7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.24
7.23
7.21
7.21
7.19
7.19
6.49
5.85
4.17
4.15
4.13
3.37
2.72
2.70
2.67
2.03
2.00
2.00
2.00
1.98
1.97
1.96
1.95
1.93
1.21
4.87
1.00
0.99
1.97
2.03
2.07
2.10
f1 (ppm)

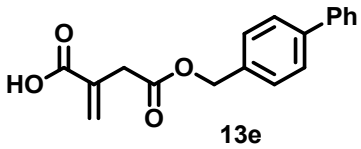

EK BN38-17
171.49
170.71
141.16
133.36
130.78
128.45
126.02
77.52
77.10
76.67
64.39
37.39
32.07
30.12
f1 (ppm)


HO
O
O
O
Ph

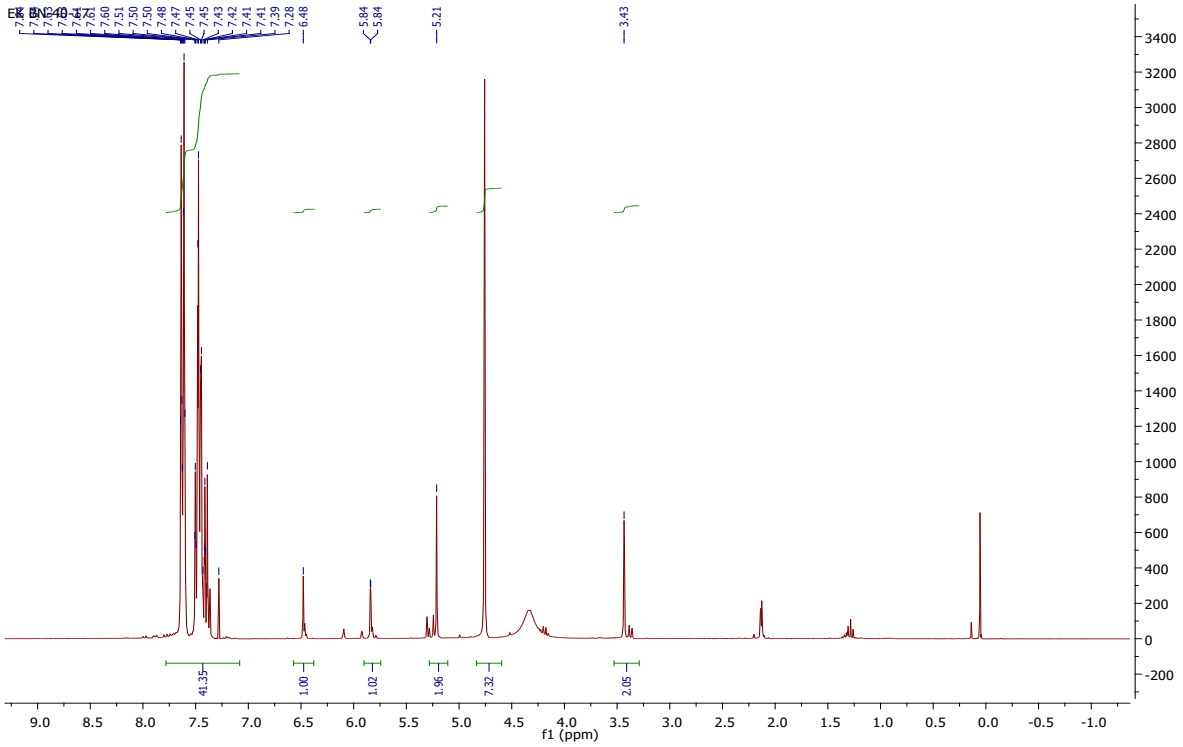
12e

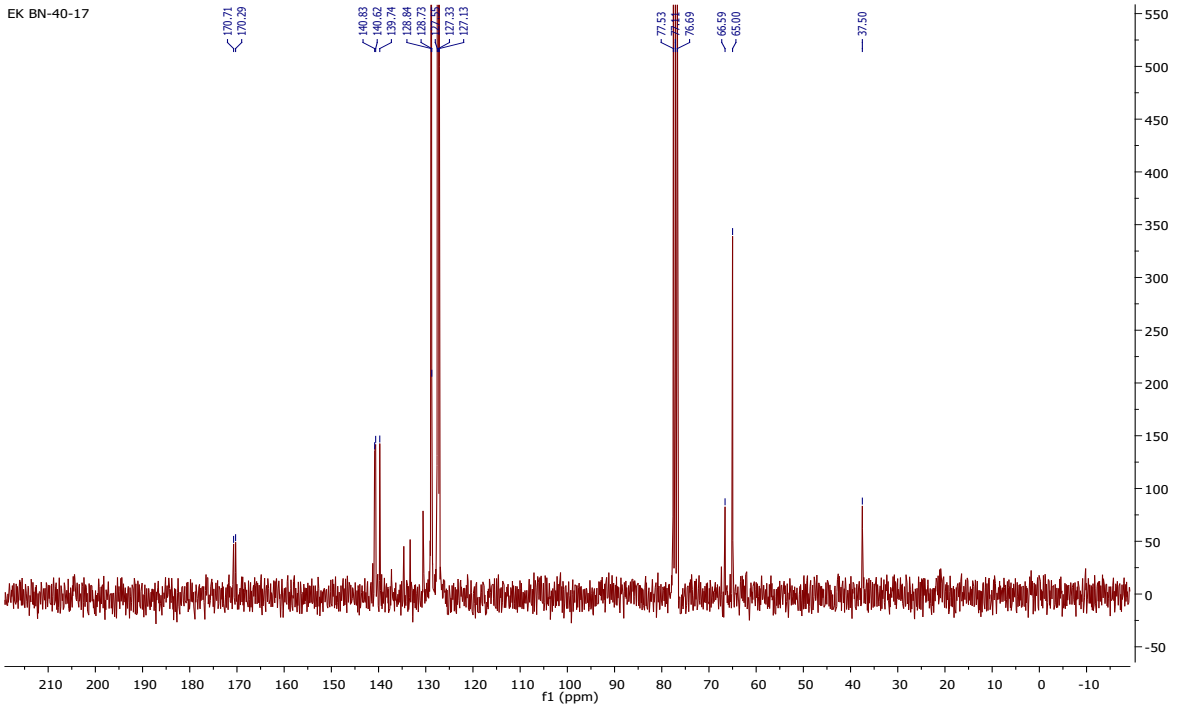

EK BN39-17
7.42
7.42
7.40
7.36
7.36
7.35
7.34
7.32
7.30
7.29
7.28
7.27
6.69
6.65
6.49
6.33
6.31
6.29
6.27
5.87
4.80
4.79
4.78
4.78
3.40
5.42
0.90
1.00
0.88
1.02
1.80
2.01
f1 (ppm)

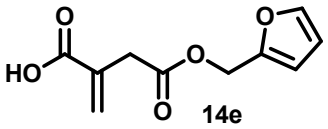

EK BN39-17
171.33
170.41
136.16
134.35
133.14
130.99
128.60
128.09
126.66
122.80
77.40
77.04
76.69
65.63
37.32
29.74
f1 (ppm)


Ph
O
HO
O
O

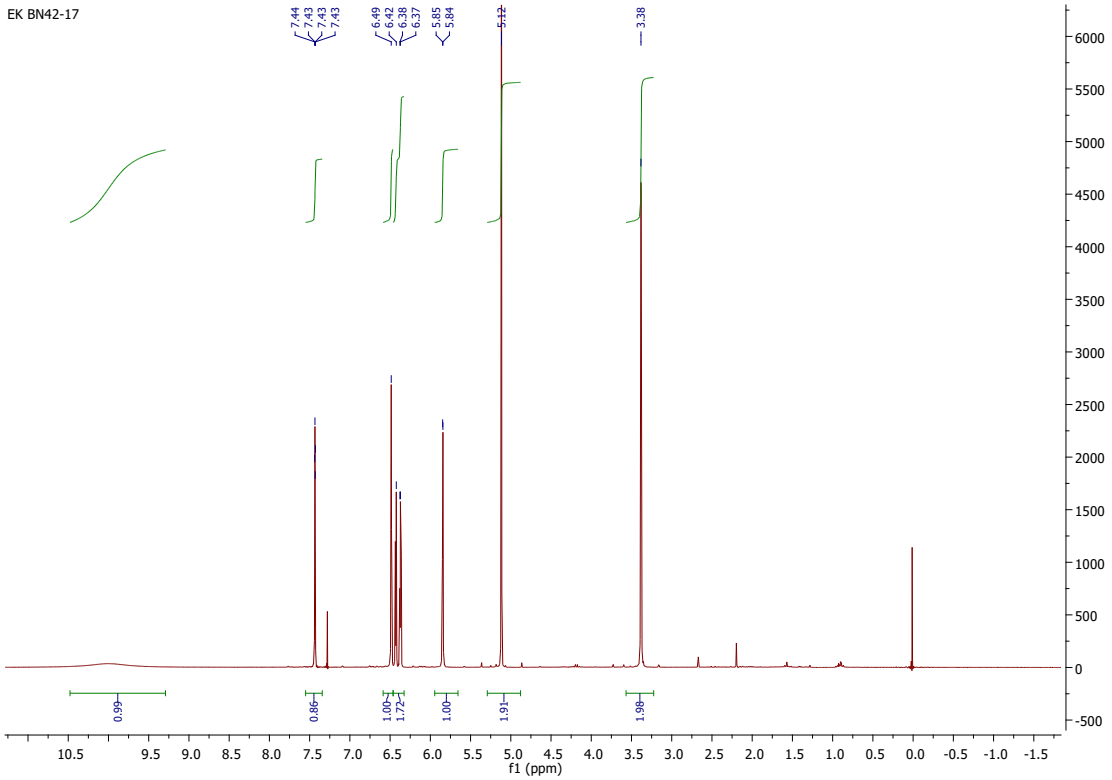
13e

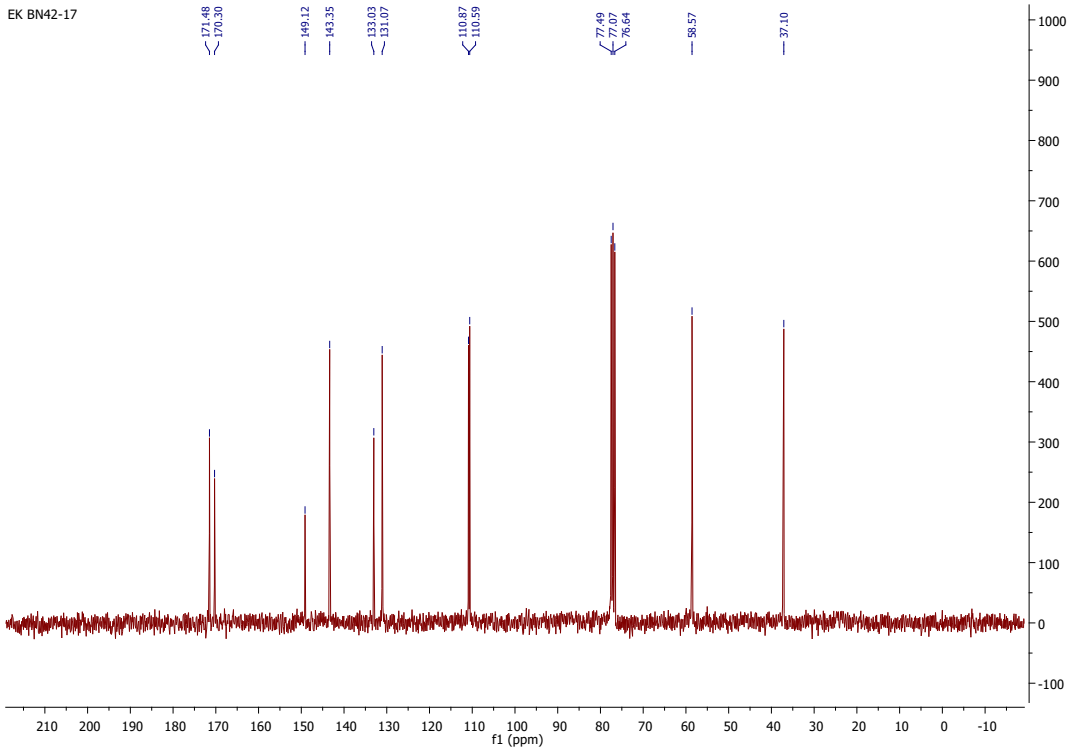

EK BN-40-1
7.64
7.63
7.62
7.61
7.60
7.51
7.50
7.50
7.48
7.47
7.45
7.45
7.43
7.42
7.41
7.41
7.39
7.28
6.48
5.84
5.84
5.21
3.43
41.35
1.00
1.02
1.96
7.32
2.05
f1 (ppm)

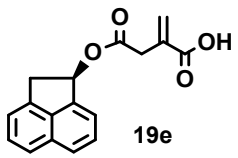

EK BN-40-17
170.71
170.29
140.83
140.62
139.74
128.84
128.73
127.33
127.13
77.53
77.21
76.69
66.59
65.00
37.50
f1 (ppm)


HO
O
O
O
O

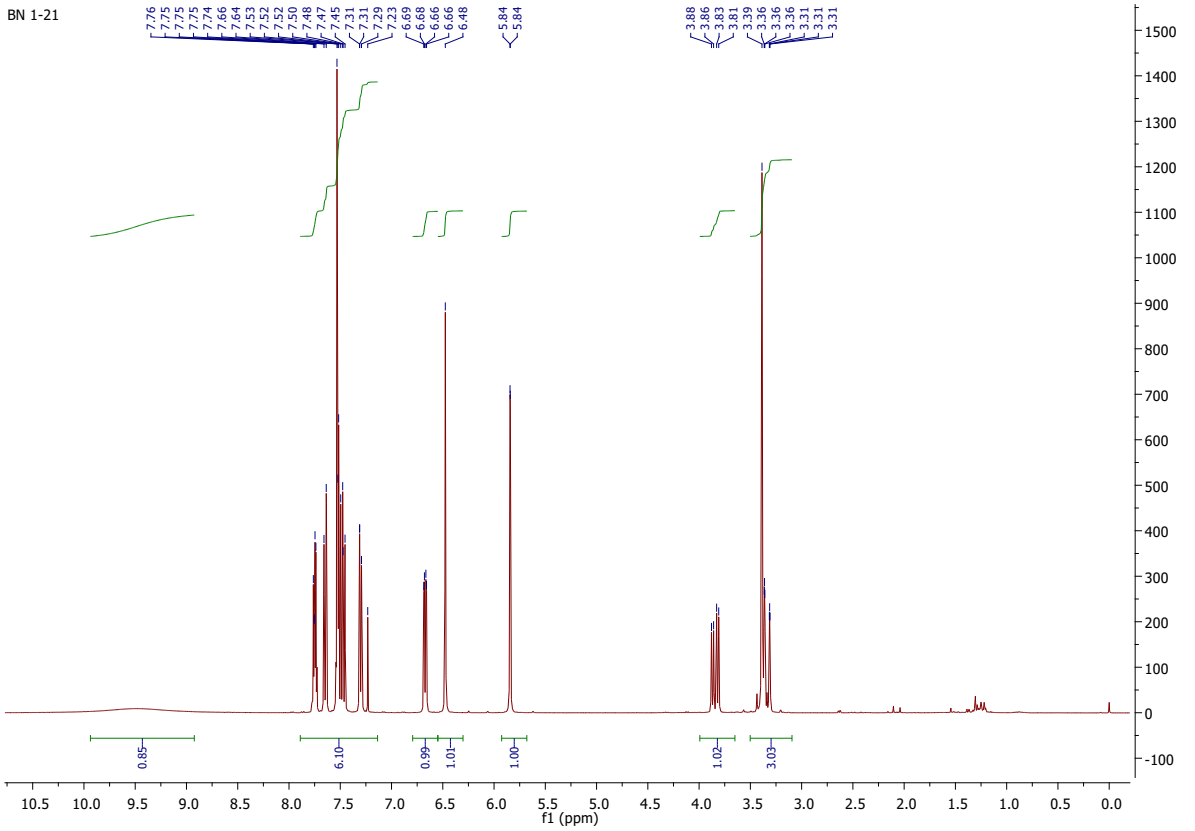
14e

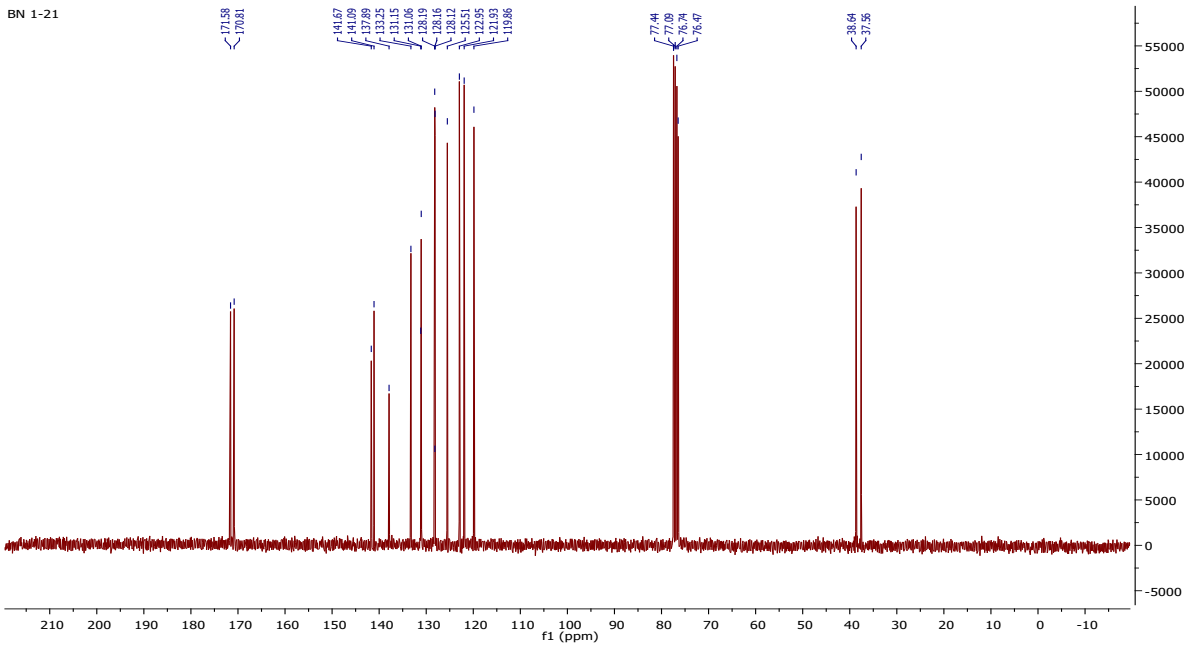

EK BN42-17
7.44
7.43
7.43
7.43
6.49
6.42
6.38
6.37
5.85
5.84
5.12
3.38
0.99
0.86
1.00
1.72
1.00
1.91
1.98
f1 (ppm)

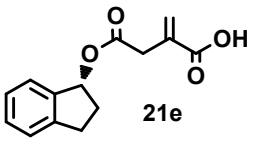

EK BN42-17
171.48
170.30
149.12
143.35
133.03
131.07
110.87
110.59
77.49
77.07
76.64
58.57
37.10
f1 (ppm)


O
O
OH
O

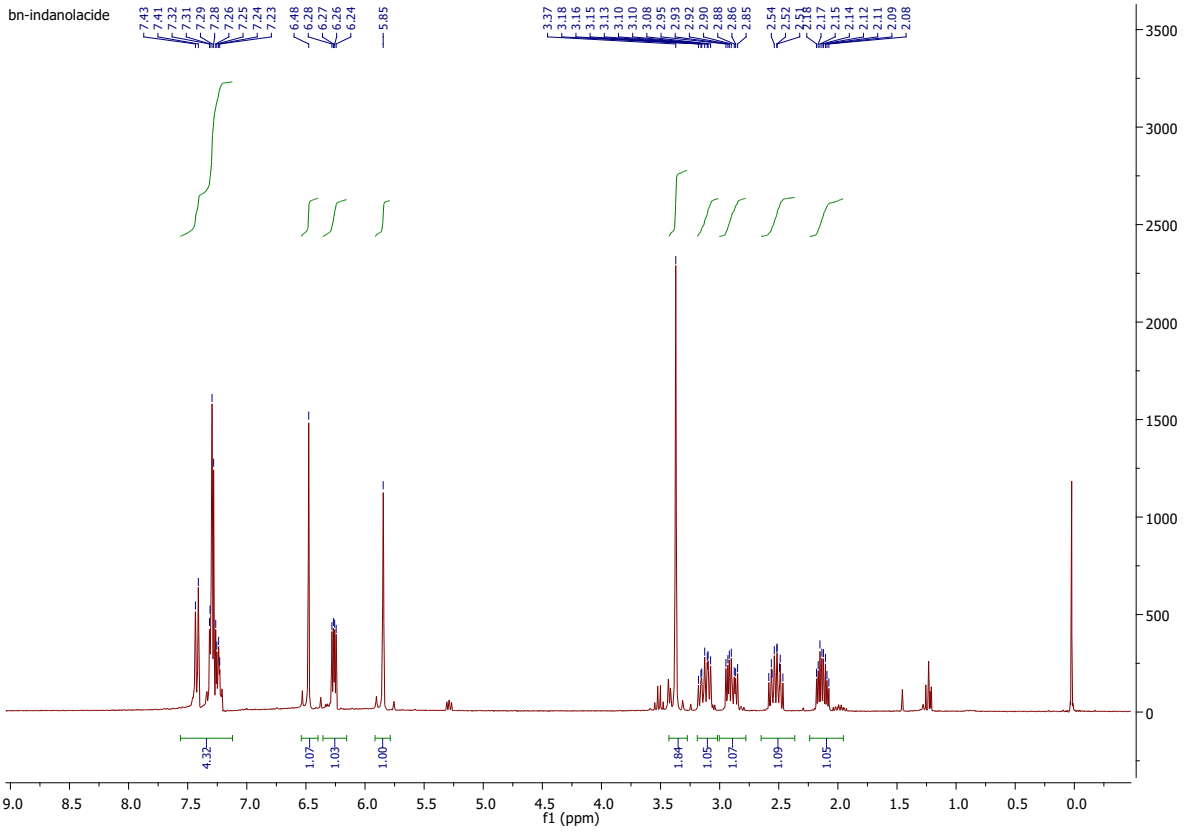
19e

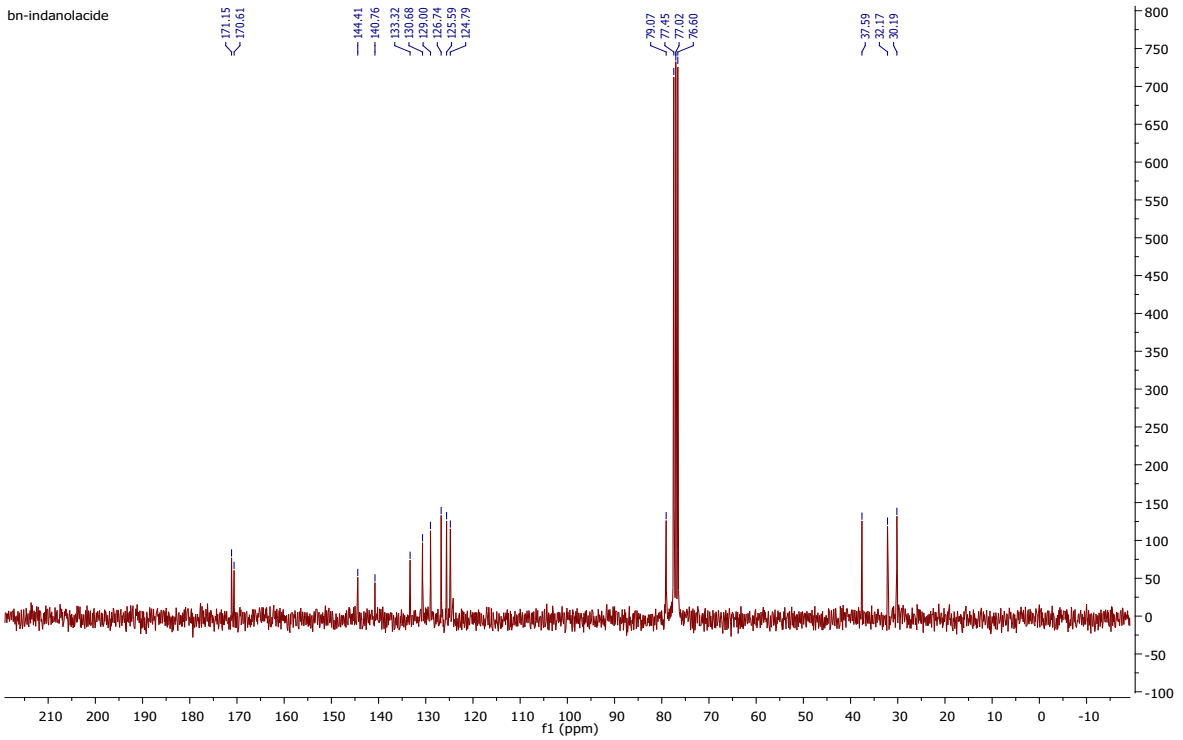

BN 1-21
7.76
7.75
7.75
7.75
7.74
7.66
7.64
7.53
7.52
7.52
7.50
7.48
7.47
7.45
7.31
7.31
7.29
7.23
6.69
6.68
6.66
6.66
6.48
5.84
5.84
3.88
3.86
3.83
3.81
3.39
3.36
3.36
3.36
3.31
3.31
3.31
0.85
6.10
0.99
1.01
1.00
1.02
3.03
f1 (ppm)

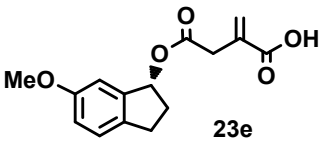

BN 1-21
171.58
170.81
141.67
141.09
137.89
133.25
131.15
131.06
128.19
128.16
128.12
125.51
122.95
121.93
119.86
77.44
77.09
76.74
76.47
38.64
37.56
f1 (ppm)


O
O
OH
O

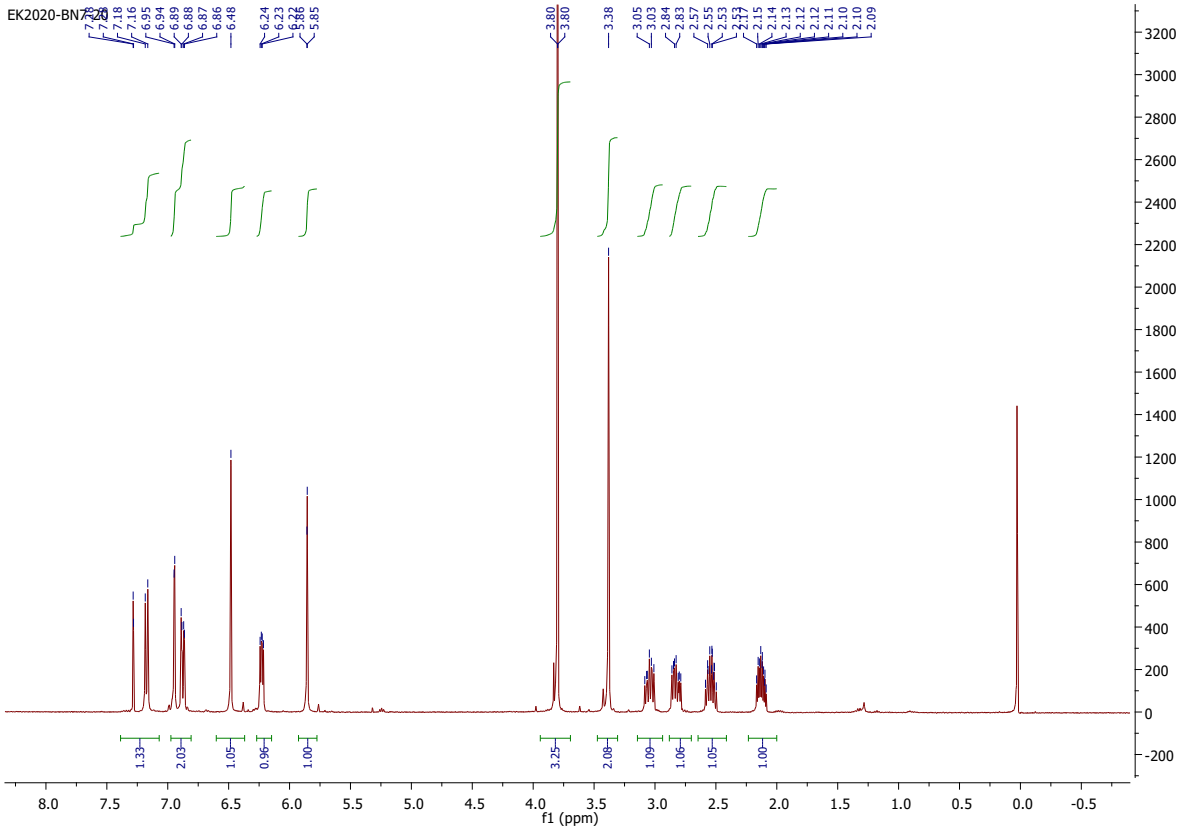
21e

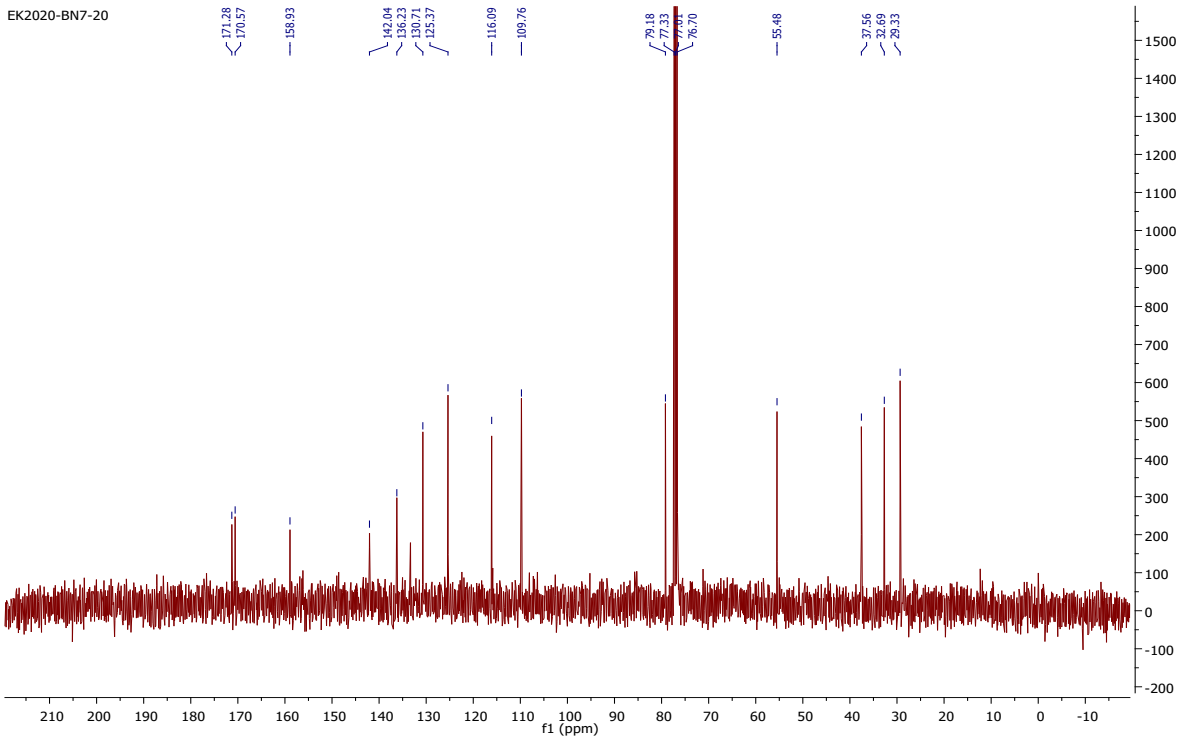

bn-indanolacide
7.43
7.41
7.32
7.31
7.29
7.28
7.26
7.25
7.24
7.23
6.48
6.28
6.27
6.26
6.24
5.85
3.37
3.18
3.16
3.15
3.13
3.10
3.10
3.08
2.95
2.93
2.92
2.90
2.88
2.86
2.85
2.54
2.52
2.17
2.15
2.14
2.12
2.11
2.09
2.08
4.32
1.07
1.03
1.00
1.84
1.05
1.07
1.09
1.05
f1 (ppm)


bn-indanolacide
171.15
170.61
144.41
140.76
133.32
130.68
129.00
126.74
125.59
124.79
79.07
77.45
77.02
76.60
37.59
32.17
30.19
f1 (ppm)

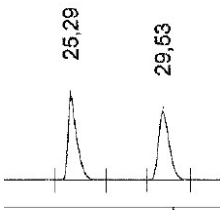
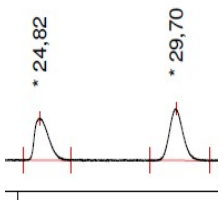
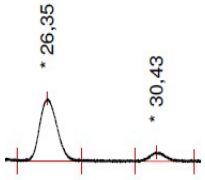
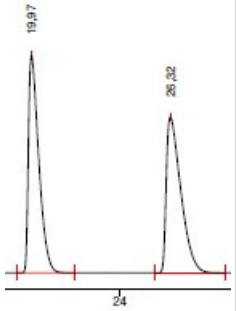
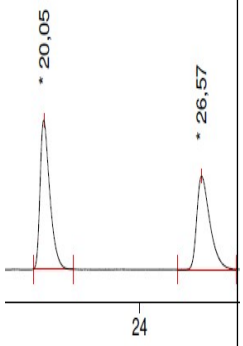
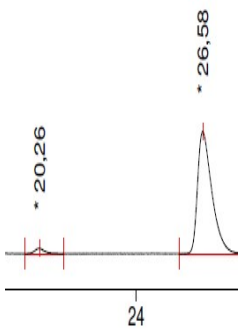
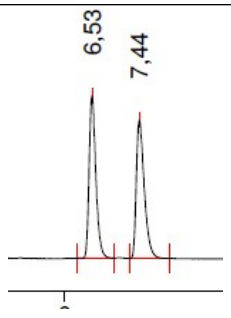
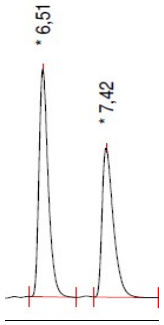
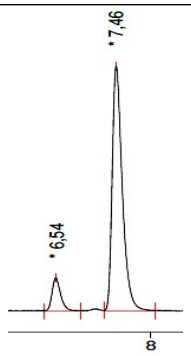
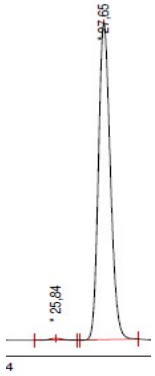
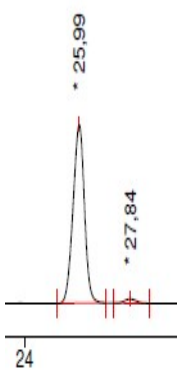


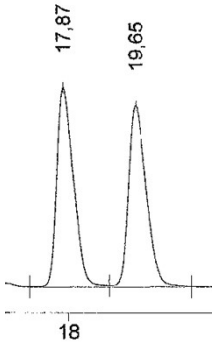
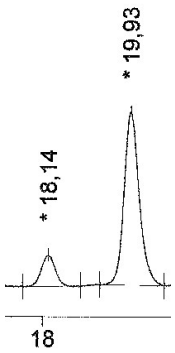
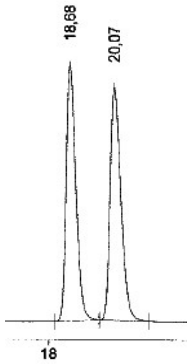
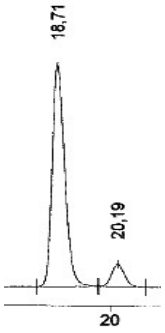
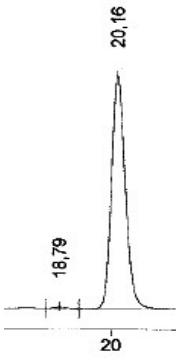
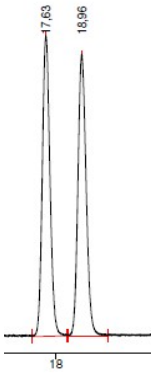
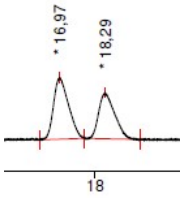
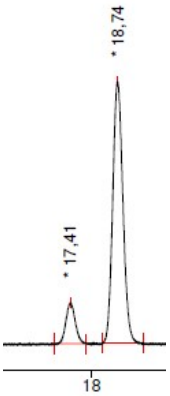
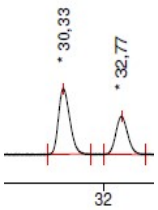
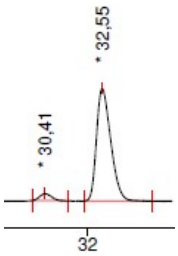
23e

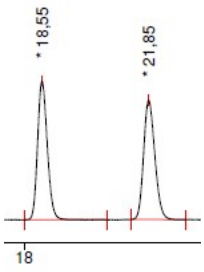
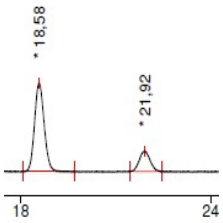
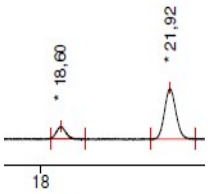




8 Chromatograms of PCL-catalyzed regio and enantioselective ring-opening of chiral secondary alcohol

Analysis's conditions	*racemic*	Unreacted alcohol $ee_{(S)}$	Reacted alcohol $ee_{(R)}$
rac-16 HPLC Chirale: colonne *Chiralpak* IB. t_S =25.29 min, t_R = 29.53min. Eluent (v,v): hexane/iPrOH: 98/02; Flow rate: 0.5mL/min. **ee_S = 8%** *(S)*-**16** **ee_p = 76%** (*R*)-**16**			
rac-17 HPLC Chirale: colonne *Chiralpak* OJ-H. t_S =19.97 min, t_R = 20.32 min. Eluent (v,v): hexane/iPrOH: 90/10; Flow rate: 0.8mL/min. **ee_S = 8.6%** *(S)*-**17** **ee_p = 94.6%** (*R*)-**17**			
rac-18 HPLC Chirale: colonne *Chiralpak IB.* t_S =6.53 min, t_R = 7.44 min. Eluent (v,v): hexane/iPrOH: 75/25; Flow rate: 0.8mL/min. **ee_S = 11%** *(S)*-**18** **ee_p = 79%** (*R*)-**18**			
rac 19 HPLC Chirale: colonne *Chiralpak IA.* t_R =25.81 min, t_S = 27.71min. Eluent (v,v): hexane/iPrOH: 95/05; Flow rate: 0.5mL/min. **ee_S = 99%** *(S)*-**19** **ee_p = 95%** (*R*)-**19**			

***rac*-20** HPLC Chirale: colonne *Chiralpak IA* $t_{S=}$17.87 min, $t_{R=}$ 19.65 min. Eluant (v,v): hexane/iPrOH: 95/05; Flow rate: 0.5mL/min. **ee_S = 3.4%** *(S)*-**20** **ee_p = 72%** (*R*)-**20**			
rac-21 HPLC Chirale: colonne *Chiralpak IA.* $t_{S=}$18.68 min, $t_{R=}$ 20.07 min. Eluant (v,v): hexane/iPrOH: 95/05; Flow rate: 0.5mL/min. **ee_S = 81%** *(S)*-**21** **ee_p = 98%** (*R*)-**21**			
rac-22 HPLC Chirale: colonne *Chiralpak IA* $t_{S=}$17.63 min, $t_{R=}$ 18.96 min. Eluant (v,v): hexane/iPrOH: 95/05; Flow rate: 0.5mL/min. **ee_S = 12%** *(S)*-**22** **ee_p = 75%** (*R*)-**22**			
rac-23 HPLC Chirale: colonne *Chiralpak IA.* $t_{S=}$30.6 min, $t_{R=}$ 32.87 min. Eluant (v,v): hexane/iPrOH: 95/05; Flow rate: 0.5mL/min. **ee_S = 24%** *(S)*-**23** **ee_p = 90%** (*R*)-**23**			

***rac*-24** HPLC Chirale: colonne *Chiralpak IA.* t_S = 18.55 min, t_R = 21.85 min. Eluant (v,v): hexane/iPrOH: 95/05; Flow rate: 0.5mL/min. **ee_S = 59%** *(S)*-**24** **ee_p = 71%** (*R*)-**24**			
rac-25 HPLC Chirale: colonne *Chiralpak IA.* t_S = 14.35 min, t_R = 16.31 min. Eluant (v,v): hexane/iPrOH: 95/05; Flow rate: 0.5mL/min. **ee_S = 45%** *(S)*-**25** **ee_p = 70%** (*R*)-**25**