Supplementary Information

Synthesis and Evaluation of Biocide and Cetane Number Improver Additives for Biodiesel from Chemical Changes in Triacylglycerides

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Spectroscopic data of the products

Soybean ethylene glycol esters (**1**)

^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (m, 3H, H_{18}), 1.27 (m, 14H, H_4, H_5, H_6, H_7, H_{15}, H_{16}, H_{17}), 1.61 (m, 2H, H_3), 2.03 (m, 5H, H_8, H_{14}, $OH_{2'}$), 2.33 (m, 2H, H_2), 2.77 (t, *J* 5.97 Hz, 2H, H_{11}), 3.81 (m, 2H, $H_{2'}$), 4.19 (m, 2H, $H_{1'}$), 5.32 (m, 4H, H_9, H_{10}, H_{12}, H_{13}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0 (C_{18}), 22.5 (C_{17}), 24.9 (C_3), 25.6 (C_{11}), 27.2 (C_4), 29.1 (C_{14}, C_8), 29.3 (C_5), 29.6 (C_6, C_{15}), 31.5 (C_7, C_{16}), 34.2 (C_2), 61.3 ($C_{2'}$), 65.9 ($C_{1'}$), 127.9 (C_{10}), 128.0 (C_{12}), 130.0 (C_9), 130.2 (C_{13}), 174.2 (C_1); IR (KBr) ν / cm^{-1} 3467 (νO–H), 3009 (νCsp^2–H), 1741 (νC=O).

Soybean ethylene glycol esters epoxidation product (**2**)

^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0 (C_{18}), 22.6 (C_{17}), 24.7 (C_3, C_{15}), 26.0 (C_7), 28.9 (C_4), 29.0 (C_5), 29.2 (C_6), 29.6 (C_{11}), 31.5 (C_8, C_{14}), 31.8 (C_{16}), 34.0 (C_2), 53.4 (C_9, C_{10}, C_{12}, C_{13}), 61.6 ($C_{2'}$), 65.8 ($C_{1'}$), 173.5 (C_1); IR (KBr) ν / cm^{-1} 3435 (νO–H), 2926 (νCsp^3–H), 1740 (νC=O).

Soybean ethylene glycol esters hydrolysis product (**3**)

^{1}H NMR (200 MHz, $CDCl_3$) δ 0.85 (m, 3H, H_{18}), 1.28 (m, 18H, H_4, H_5, H_6, H_7, H_8, H_{14}, H_{15}, H_{16}, H_{17}), 1.61 (br s, 4H, H_3, H_{11}), 2.31 (m, 2H, H_2), 3.38 (br s, 4H, H_9, H_{10}, H_{12}, H_{13}), 4.18 (m, 4H, $H_{1'}$, $H_{2'}$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1 (C_{18}), 22.6 (C_{17}), 24.6 (C_7, C_{15}), 24.8 (C_3), 28.9 (C_4), 29.2 (C_5), 29.6 (C_6), 31.8 (C_8, C_{11}, C_{14}, C_{16}), 33.9 (C_2), 62.1 ($C_{2'}$), 67.0 ($C_{1'}$), 71.4 (C_{10}, C_{12}), 74.5 (C_9, C_{13}), 173.3 (C_1); IR (KBr) ν / cm^{-1} 3436 (νO–H), 2926 (νCsp^3–H), 1737 (νC=O).

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†This paper is dedicated to the memory of professor Angelo da Cunha Pinto, who recently passed away.

Soybean ethylene glycol esters solvolysis product (**4**)

^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (m, 3H, H_{18}), 1.33 (m, 18H, H_4, H_5, H_6, H_7, H_8, H_{14}, H_{15}, H_{16}, H_{17}), 1.58 (m, 4H, H_3, H_{11}), 1.98 (br s, 3H, $OH_{2'}$, OH_{10}, OH_{12}), 2.28 (t, *J* 7.51 Hz, 2H, H_{11}), 2.55 (m, 2H, H_9, H_{13}), 3.37 (m, 2H, H_{10}, H_{12}), 3.62 (s, 6H, 2 OCH_3), 4.12 (m, 4H, $H_{1'}$, $H_{2'}$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0 (C_{18}), 22.6 (C_{17}), 24.8 (C_7, C_{15}), 25.5 (C_3), 28.9 (C_8, C_{14}), 29.4 (C_4, C_5), 31.8 (C_{11}, C_{16}), 34.0 (C_2), 51.4 (OC_9H_3, $OC_{13}H_3$), 74.4 (C_{10}, C_{12}), 80.2 (C_9, C_{13}), 174.3 (C_1).

Soybean ethylene glycol esters nitration product (**5**)

IR (KBr) ν / cm^{-1} 3469 (νOH), 3008 (νCsp^2–H), 2926 (νCsp^3–H), 1747 (νC=O), 1640 (νNO_2), 1279 (νNO_2).

Soybean hydroxylated ethylene glycol esters nitration product (**6**)

IR (KBr) ν / cm^{-1} 3478 (νOH), 2929 (νCsp^3–H), 1741 (νC=O), 1640 (νNO_2), 1556 (νNO_2), 1279 (νNO_2).

Ethylene glycol linoleate (**8**)

^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (m, 3H, H_{18}), 1.27 (m, 14H, H_4, H_5, H_6, H_7, H_{15}, H_{16}, H_{17}), 1.61 (m, 2H, H_3), 2.03 (m, 5H, H_8, H_{14}, $OH_{2'}$), 2.33 (m, 2H, H_2), 2.77 (t, *J* 5.97 Hz, 2H, H_{11}), 3.81 (m, 2H, $H_{2'}$), 4.19 (m, 2H, $H_{1'}$), 5.32 (m, 4H, H_9, H_{10}, H_{12}, H_{13}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0 (C_{18}), 22.5 (C_{17}), 24.9 (C_3), 25.6 (C_{11}), 27.2 (C_4), 29.1 (C_{14}, C_8), 29.3 (C_5), 29.6 (C_6, C_{15}), 31.5 (C_7, C_{16}), 34.2 (C_2), 61.3 ($C_{2'}$), 65.9 ($C_{1'}$), 127.9 (C_{10}), 128.0 (C_{12}), 130.0 (C_9), 130.2 (C_{13}), 174.2 (C_1); IR (KBr) ν / cm^{-1} 3458 (νO–H), 3009 (νCsp^2–H), 2928 (νCsp^3–H), 1740 (νC=O).

Ethylene glycol oleate (**9**)

^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (m, 3H, H_{18}), 1.26 (m, 20H, H_4, H_5, H_6, H_7, H_{12}, H_{13}, H_{14}, H_{15}, H_{16}, H_{17}), 1.61 (m, 2H, H_3), 2.01 (m, 5H, H_8, H_{11}, $OH_{2'}$), 2.32 (m, 2H, H_2), 3.71 (m, 2H, $H_{2'}$), 4.19 (m, 2H, $H_{1'}$), 5.33 (m, 2H, H_9, H_{10}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0 (C_{18}), 22.6 (C_{17}), 24.8 (C_3), 27.2 (C_8, C_{11}), 29.0 (C_4), 29.3 (C_{15}), 29.5 (C_5), 29.6 (C_6), 29.7 (C_7, C_{12}, C_{13}, C_{14}), 31.9 (C_{16}), 34.1 (C_2), 61.2 ($C_{2'}$), 65.9 ($C_{1'}$), 129.9 (C_9, C_{10}), 174.2 (C_1); IR (KBr) ν / cm^{-1} 3432 (νO–H), 3005 (νCsp^2–H), 2925 (νCsp^3–H), 1740 (νC=O).

Ethylene glycol stearate (**10**)

^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (m, 3H, H_{18}), 1.24 (m, 28H, H_4-H_7), 1.60 (m, 2H, H_3), 2.03 (s, 1H, $OH_{2'}$), 2.31 (m, 2H, H_2), 3.81 (m, 2H, $H_{2'}$), 4.20 (m, 2H, $H_{1'}$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0 (C_{18}), 22.6 (C_{17}), 24.9 (C_3), 29.0 (C_4), 29.4 (C_5, C_{15}), 29.6 (C_6-C_{14}), 31.9 (C_{16}), 34.1 (C_2), 61.2 ($C_{2'}$), 65.8 ($C_{1'}$), 174.2 (C_1); IR (KBr) ν / cm^{-1} 3463 (νO–H), 2919 (νCsp^3–H), 1740 (νC=O).

Ethylene glycol linoleate nitration product (**11**)

IR (KBr) ν / cm^{-1} 3457 (νOH), 2932 (νCsp^3–H), 1738 (νC=O), 1634 (νNO_2), 1556 (νNO_2), 1280 (νNO_2).

Ethylene glycol oleate nitration product (**12**)

IR (KBr) ν / cm^{-1} 3465 (νOH), 2929 (νCsp^3–H), 1740 (νC=O), 1640 (νNO_2), 1556 (νNO_2), 1279 (νNO_2).

Ethylene glycol stearate nitration product (**13**)

IR (KBr) ν / cm^{-1} 2925 (νCsp^3–H), 1744 (νC=O), 1644 (νNO_2), 1553 (νNO_2), 1279 (νNO_2).

Jatropha ethylene glycol esters (**14**)

^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (m, 3H, H_{18}), 1.26 (m, 20H, H_4, H_5, H_6, H_7, H_{12}, H_{13}, H_{14}, H_{15}, H_{16}, H_{17}), 1.61 (m, 2H, H_3), 2.03 (m, 5H, H_8, H_{11}, $OH_{2'}$), 2.32 (m, 2H, H_2), 3.82 (m, 2H, $H_{2'}$), 4.19 (m, 2H, $H_{1'}$), 5.35 (m, 2H, H_9, H_{10}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0 (C_{18}), 22.5 (C_{17}), 24.9 (C_3), 27.2 (C_8, C_{11}), 29.1 (C_4), 29.3 (C_5, C_{15}), 29.7 (C_6, C_7, C_{12}, C_{13}, C_{14}), 31.9 (C_{16}), 34.1 (C_2), 61.2 ($C_{2'}$), 65.9 ($C_{1'}$), 129.9 (C_9, C_{10}), 174.2 (C_1); IR (KBr) ν / cm^{-1} 3459 (νO–H), 3008 (νCsp^2–H), 2925 (νCsp^3–H), 1740 (νC=O).

Castor ethylene glycol esters (**15**)

^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (m, 3H, H_{18}), 1.26 (m, 16H, H_4, H_5, H_6, H_7, H_{14}, H_{15}, H_{16}, H_{17}), 1.44 (br s, 2H, H_{13}), 1.61 (m, 2H, H_3), 2.02 (m, 2H, OH_{12}, $OH_{2'}$), 2.19 (t, *J* 6.49 Hz, 2H, H_2), 2.32 (m, 2H, H_{11}), 3.60 (m, 1H, H_{12}), 3.80 (m, 2H, $H_{2'}$), 4.19 (m, 2H, $H_{1'}$), 5.44 (m, 2H, H_9, H_{10}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9 (C_{18}), 22.5 (C_{17}), 24.8 (C_{14}), 25.6 (C_3), 27.3 (C_8) 28.9 (C_4), 29.0 (C_5), 29.3 (C_{15}), 29.5 (C_6, C_7), 31.8 (C_{16}), 34.1 (C_2), 35.3 (C_{11}), 36.8 (C_{13}), 61.1 ($C_{2'}$), 65.8 ($C_{1'}$), 71.5 (C_{12}), 125.2 (C_9), 133.2 (C_{10}), 174.1 (C_1); IR (KBr) ν / cm^{-1} 3405 (νO–H), 3008 (νCsp^2–H), 2926 (νCsp^3–H), 1740 (νC=O).

Jatropha ethylene glycol esters nitration product (**16**)

IR (KBr) $\nu_{máx}$ / cm^{-1} 3469 (νOH), 2928 (νCsp^3–H), 1742 (νC=O), 1640 (νNO_2), 1557 (νNO_2), 1280 (νNO_2).

Castor ethylene glycol esters nitration product (**17**)

IR (KBr) ν / cm^{-1} 3468 (νOH), 2930 (νCsp^3–H), 1742 (νC=O), 1629 (νNO_2), 1556 (νNO_2), 1279 (νNO_2).

Soybean glycerol esters (**18**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (t, 3H, H_{18}), 1.27 (m, 14H, H_{4-7} and H_{15-17}), 1.58 (m, 2H, H_3), 1.93-2.04 (m, 4H, H_{14}, H_9), 2.30 (t, 2H, H_2), 2.73 (t, *J* 6.79 Hz, 2H, H_{11}), 3.55 (q, *J* 11.40 Hz, 2H, $H_{2'}$), 3.65 (q, *J* 1.00 Hz, 2H, $H_{3'}$), 4.07-4.21 (m, 1H, $H_{1'}$), 5.25-5.39 (m, 4H, H_9, H_{10}, H_{12} and H_{13}); ^{13}C NMR (50 MHz, $CDCl_3$) δ 173.8 (C_1), 130.1 (C_9, C_{12}), 127.8 (C_{10}, C_{13}), 70.2 ($C_{1'}$), 65.0 ($C_{2'}$), 64.9 ($C_{3'}$), 34.1 (C_2), 31.8 (C_8, C_{14}), 31.5 (C_{11}), 24.8 (C_4), 22.5-29.54 (C_{3-7}, $C_{15,16}$); IR (ATR) ν / cm^{-1} 3368 (νO–H), 3008 (νCsp^2–H), 1735 (νC=O), 1047 (νC–O).

Soybean glycerol esters nitration product (**19**)

IR (ATR) ν / cm^{-1} 3365 (νOH), 3008 (νCsp^2–H), 2927 (νCsp^3–H), 1738 (νC=O), 1555 (νNO_2), 1240 (νNO_2).

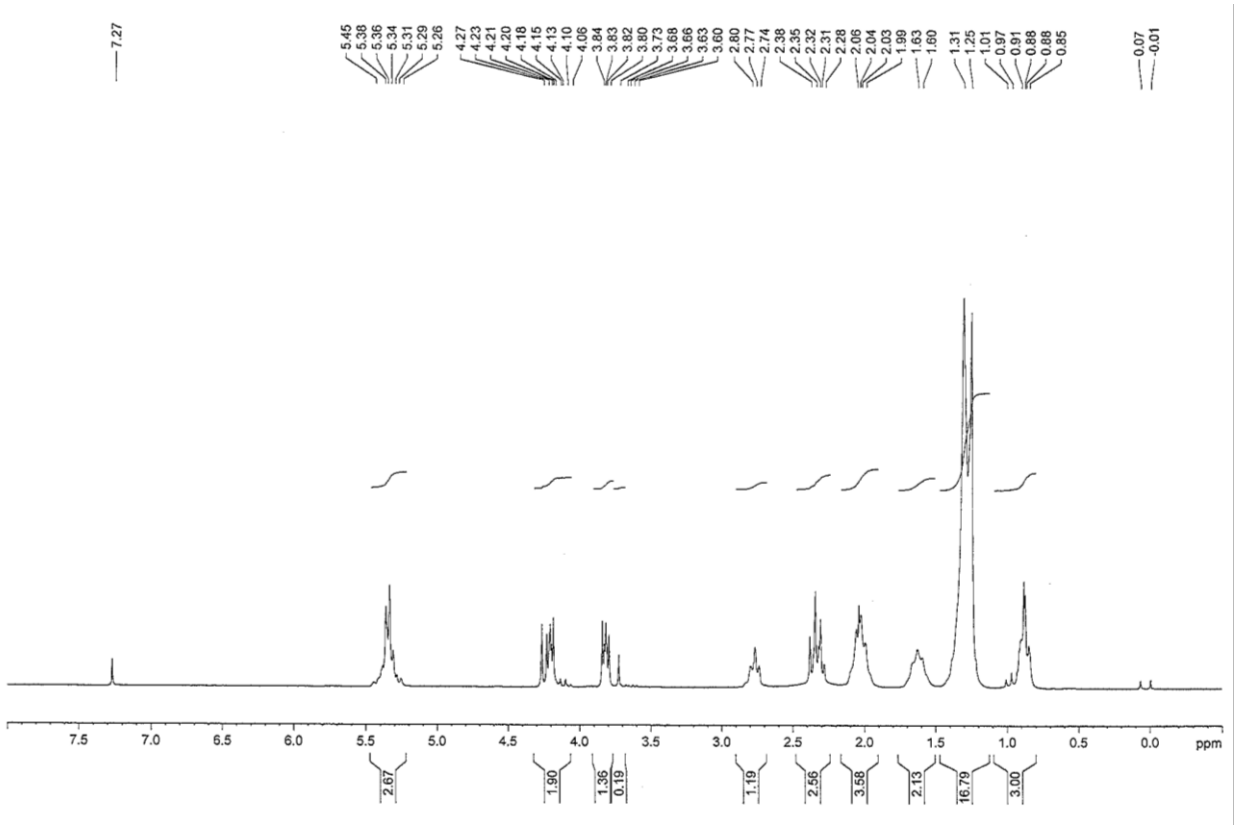

Figure S1. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of product **1**.

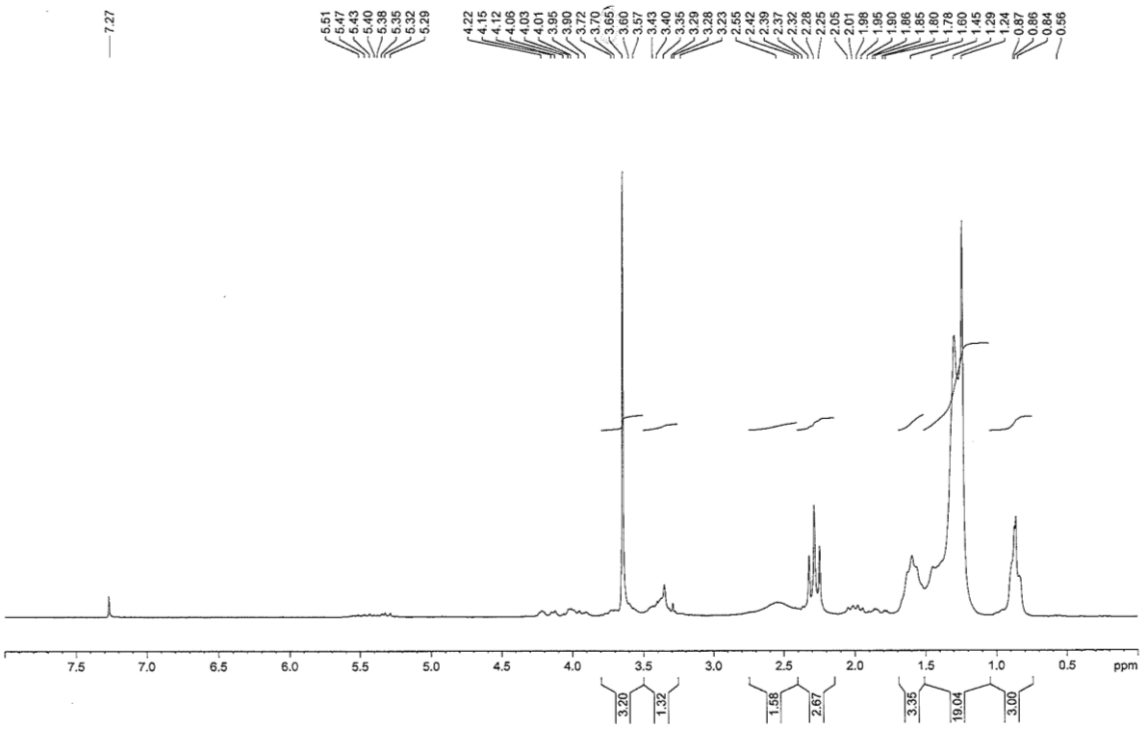

Figure S2. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of product **4**.

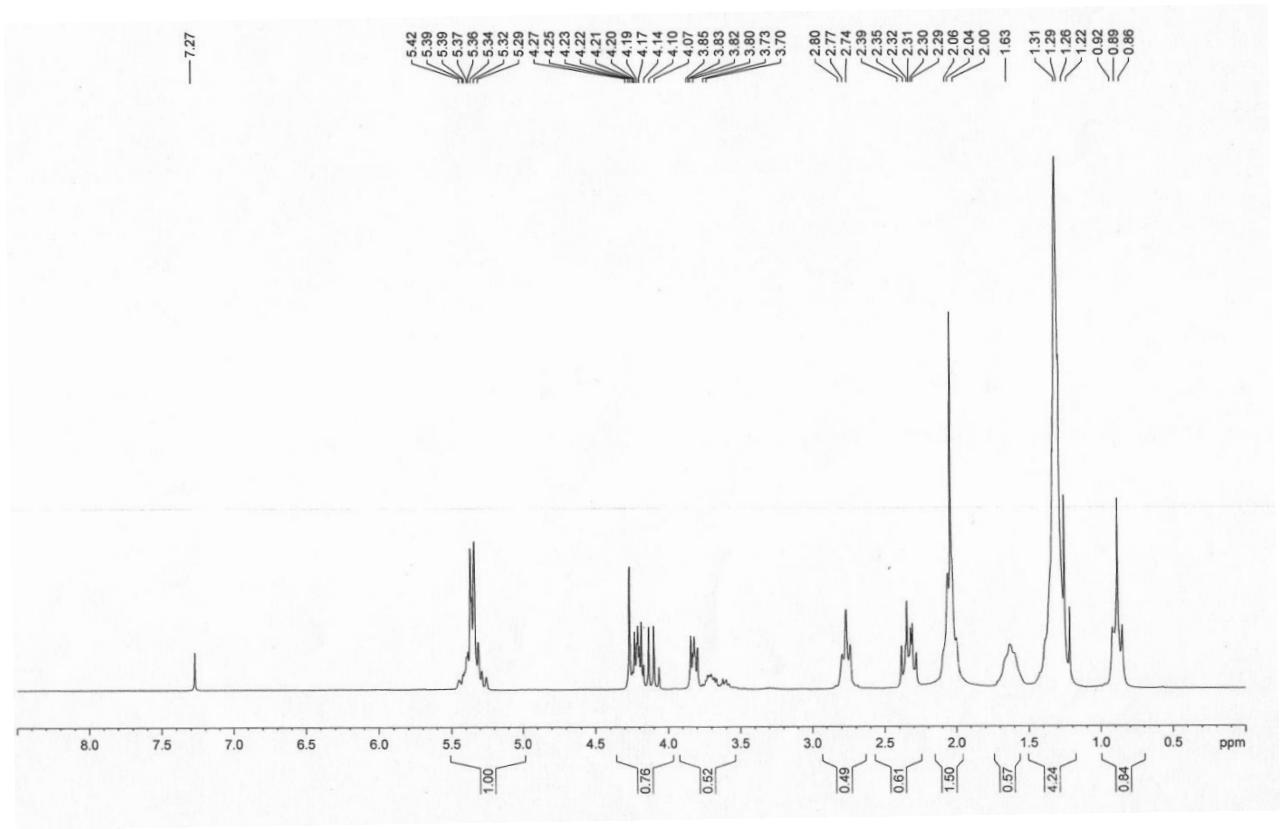

Figure S3. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of product **8**.

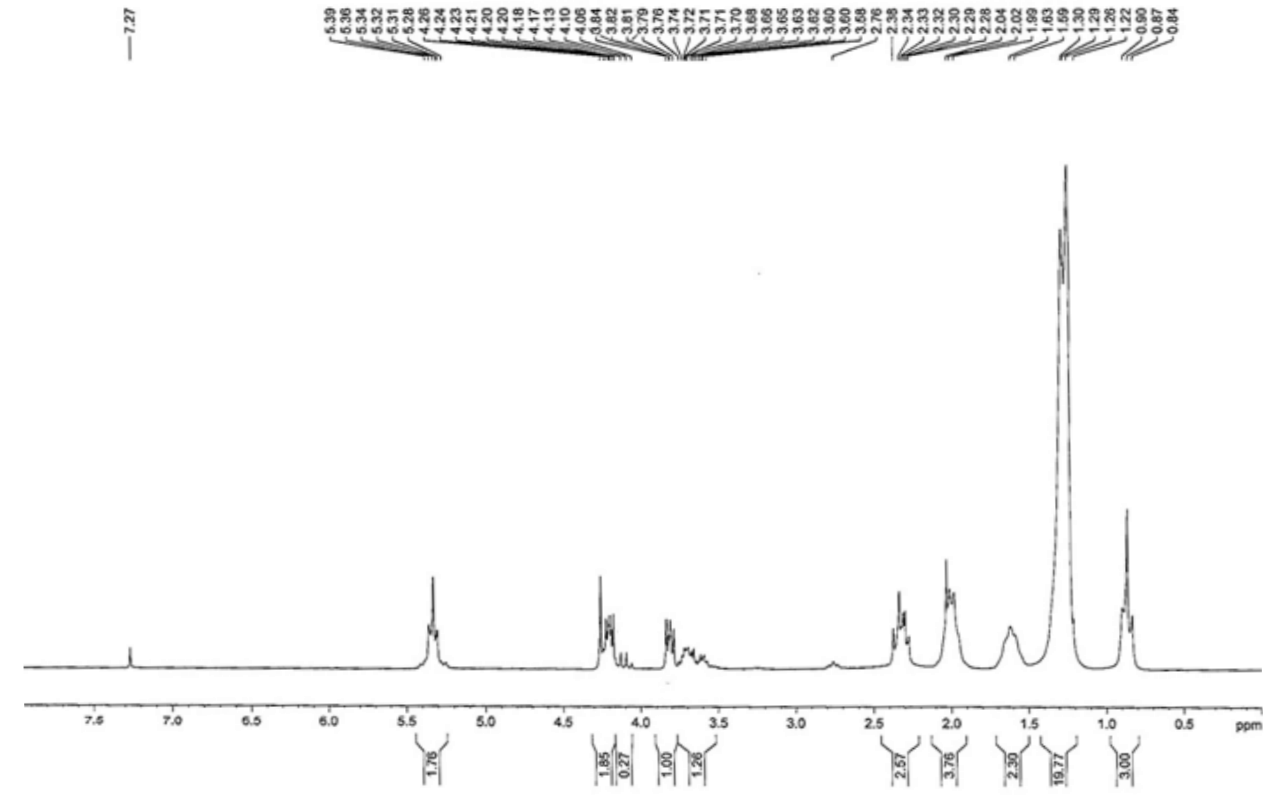

Figure S4. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of product **9**.

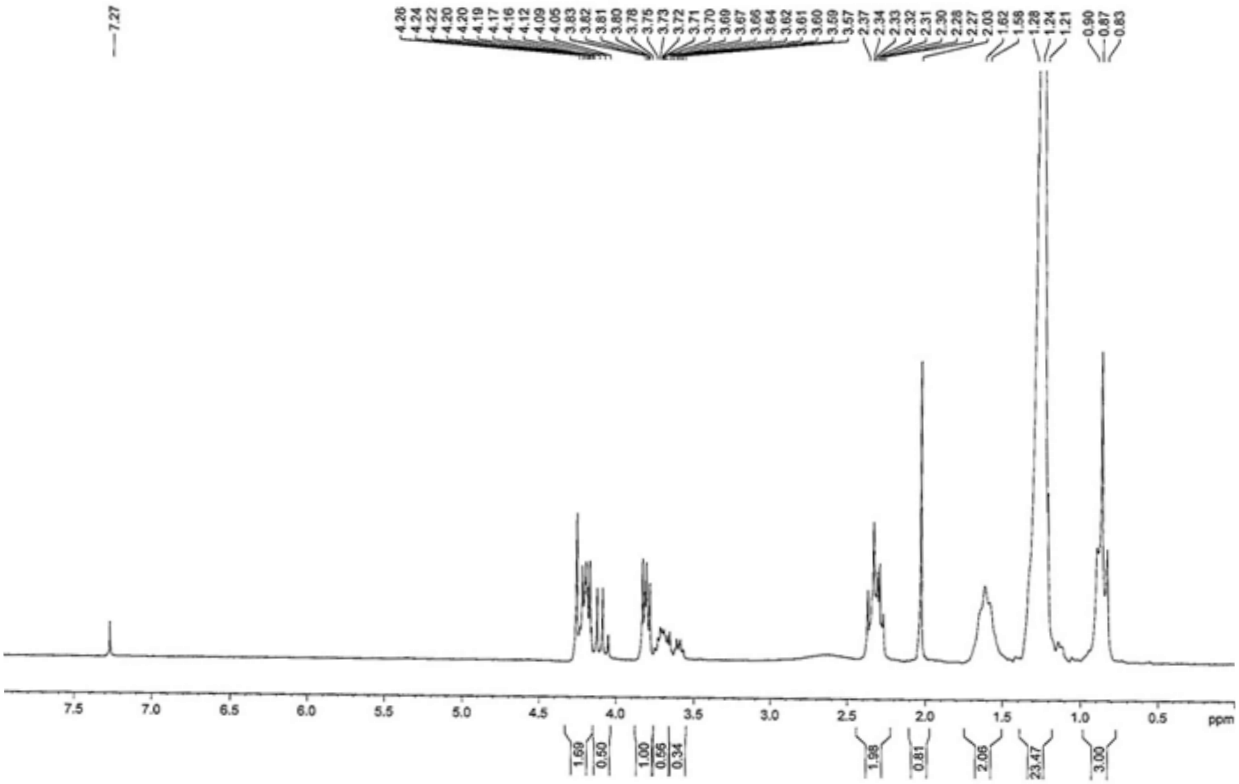

Figure S5. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of product **10**.

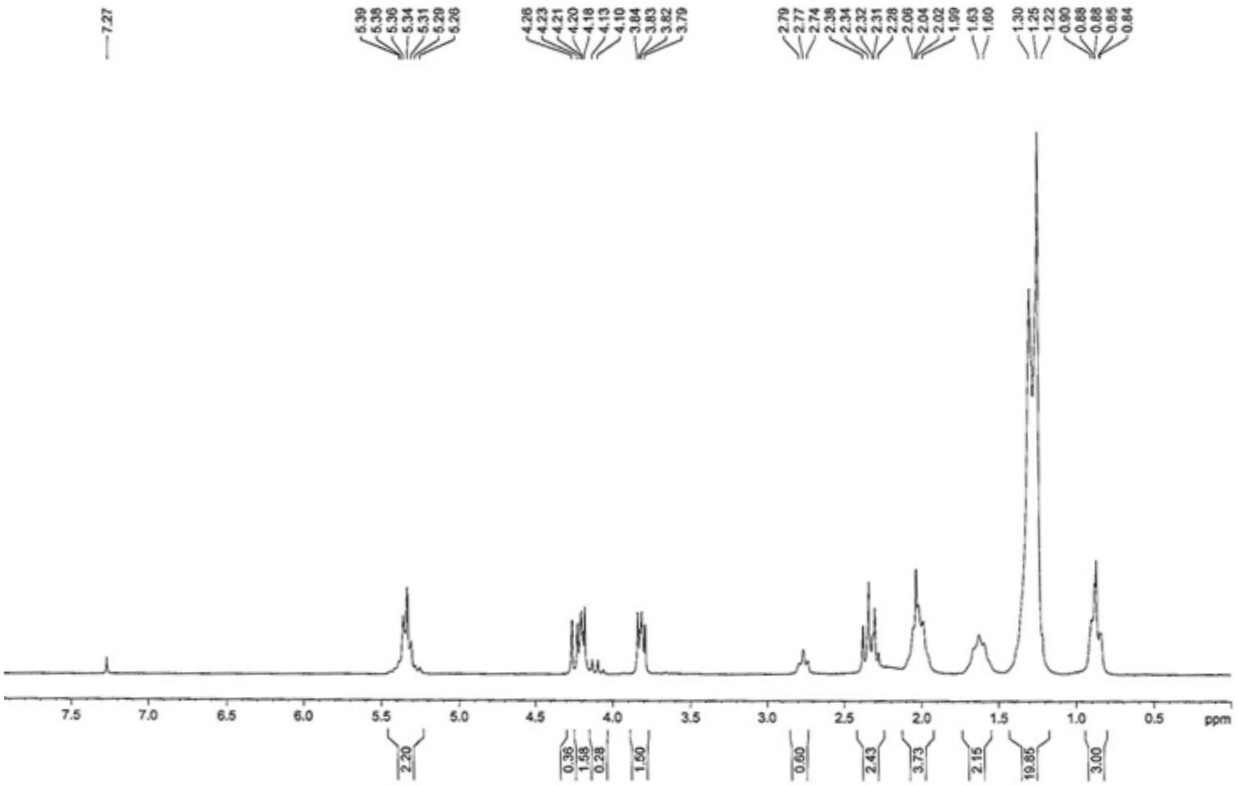

Figure S6. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of product **14**.

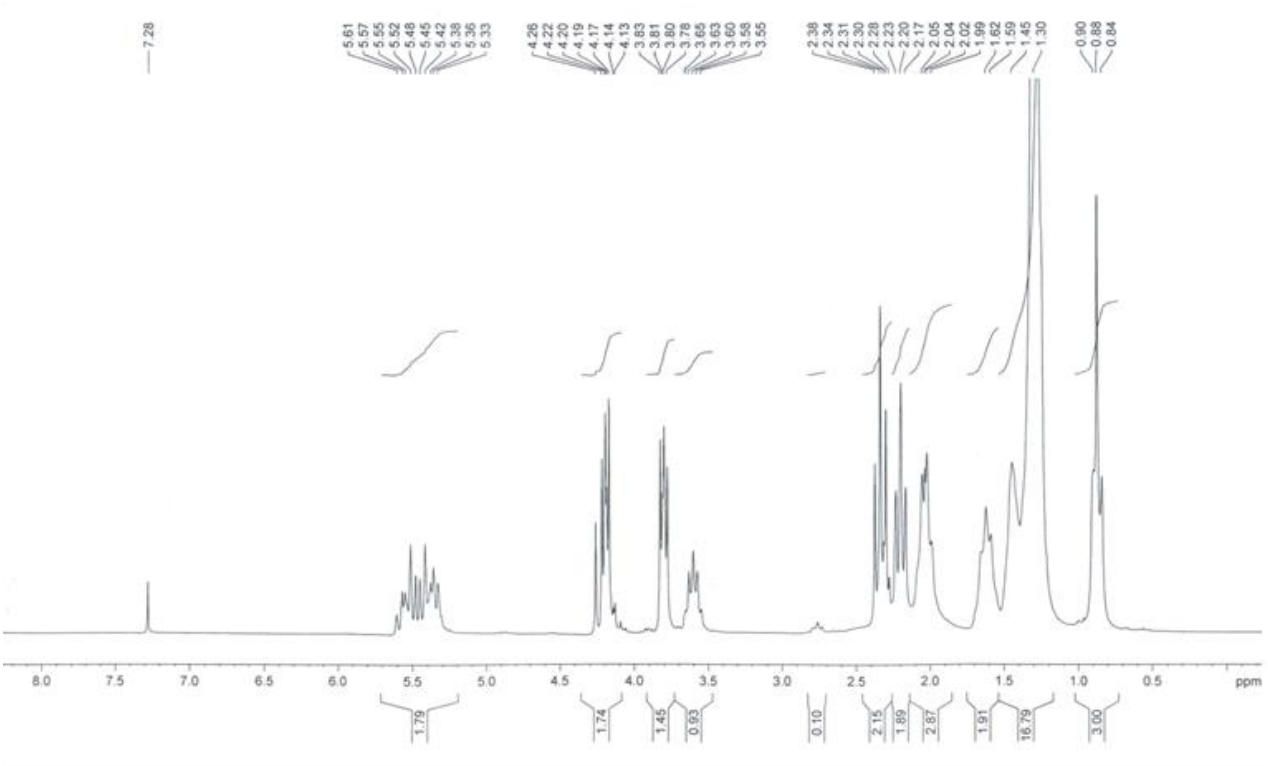

Figure S7. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of product **15**.

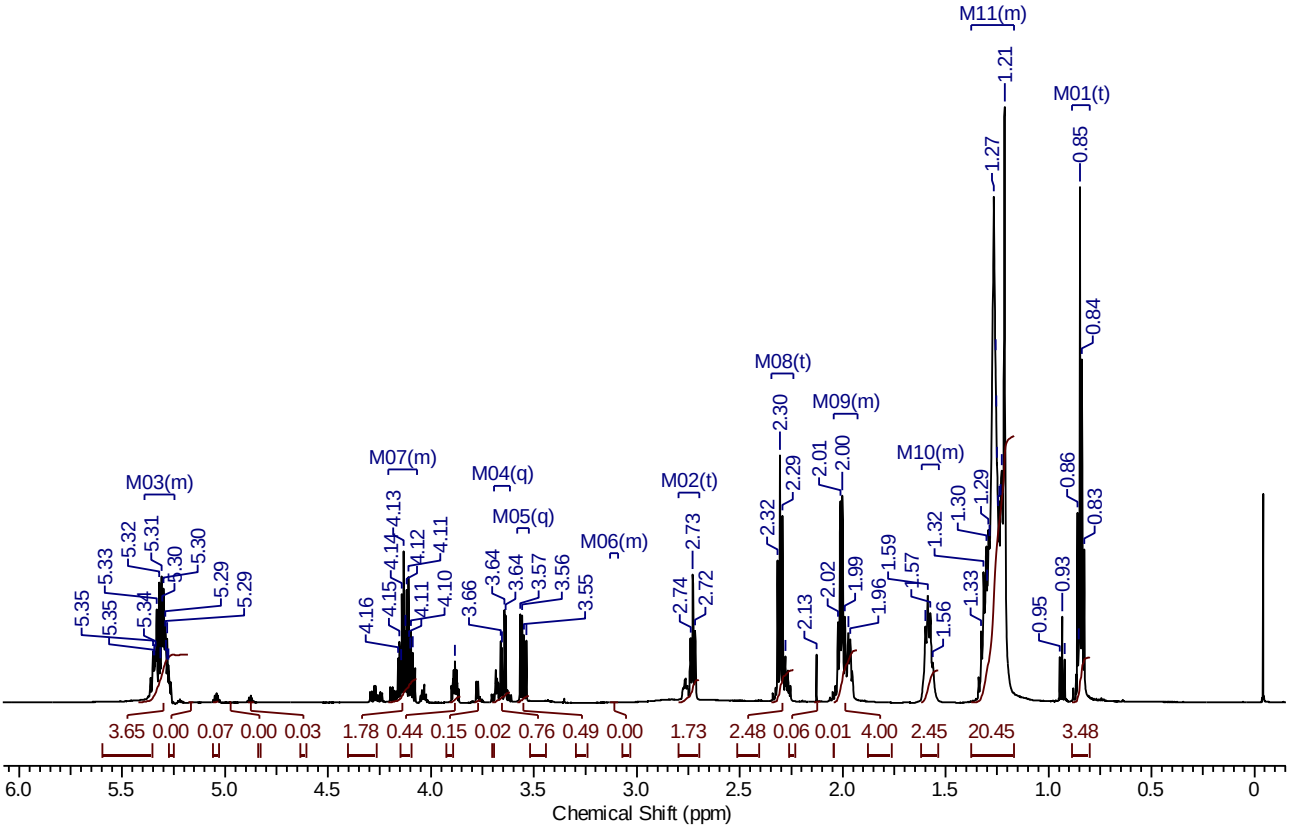

Figure S8. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of product **18**.

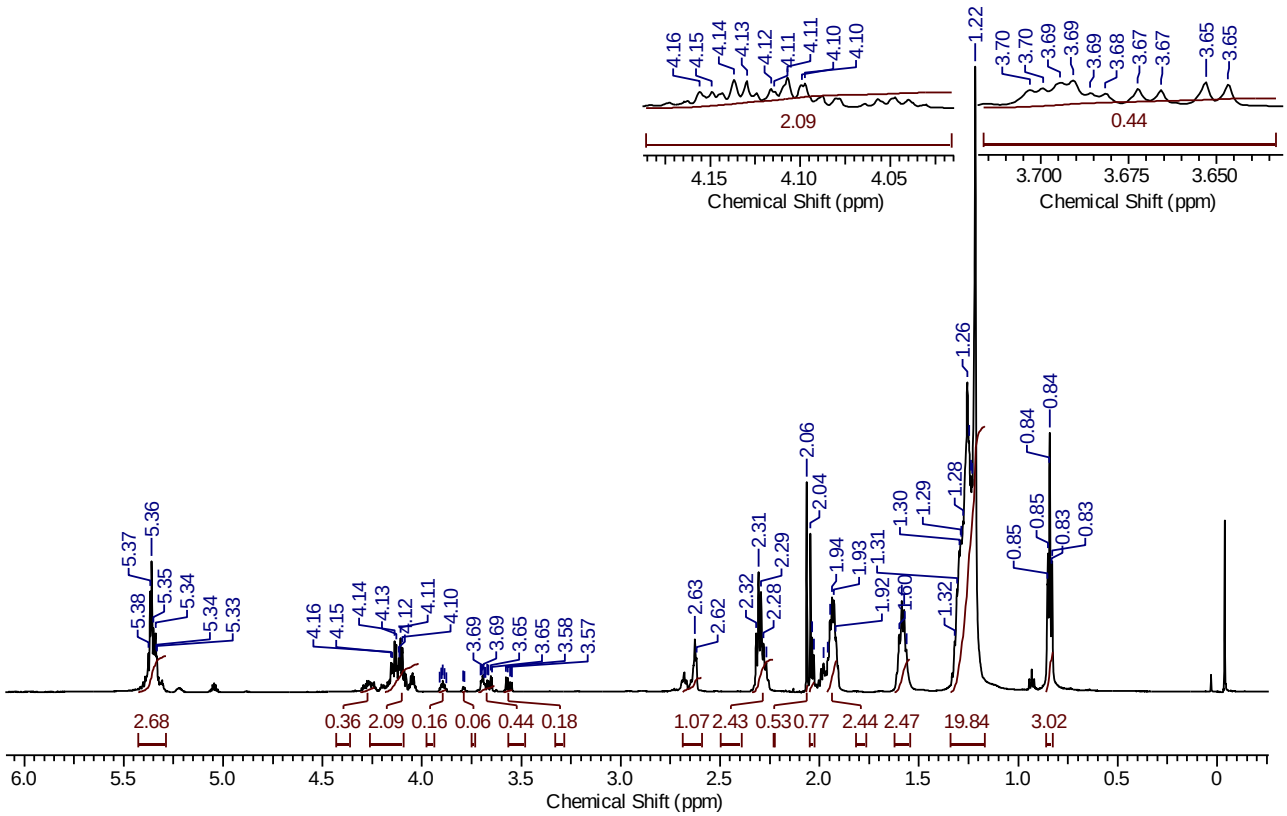

Figure S9. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of product **19**.

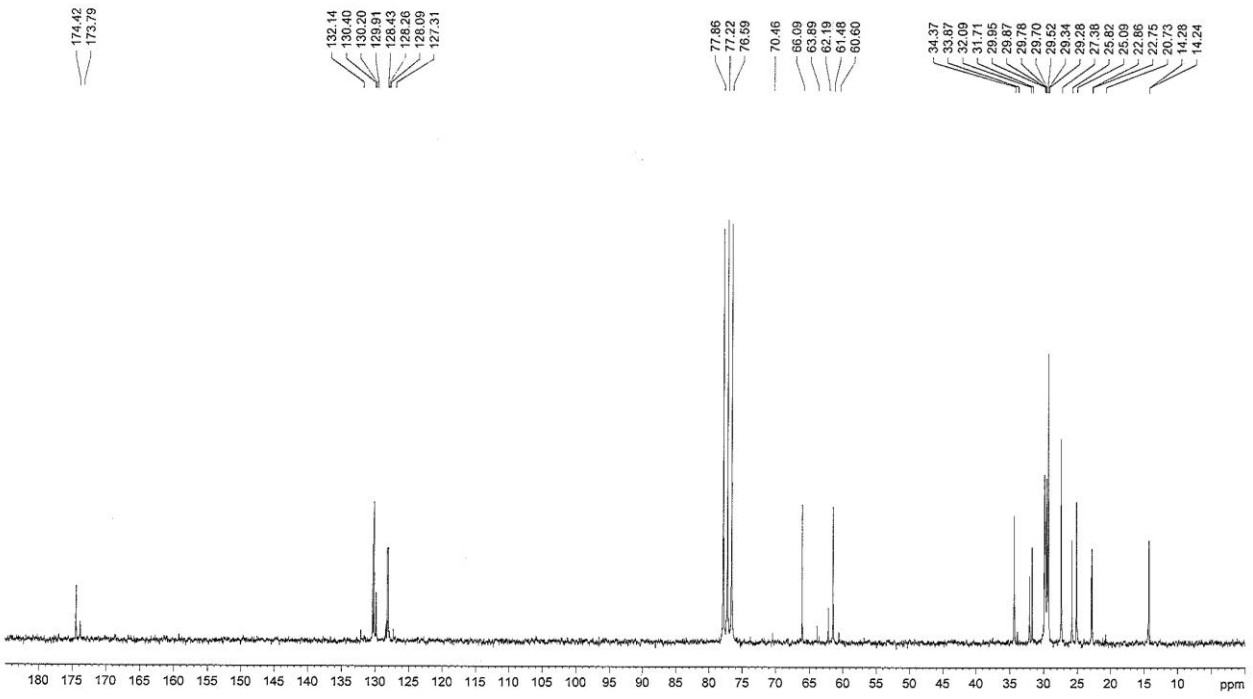

Figure S10. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of product **1**.

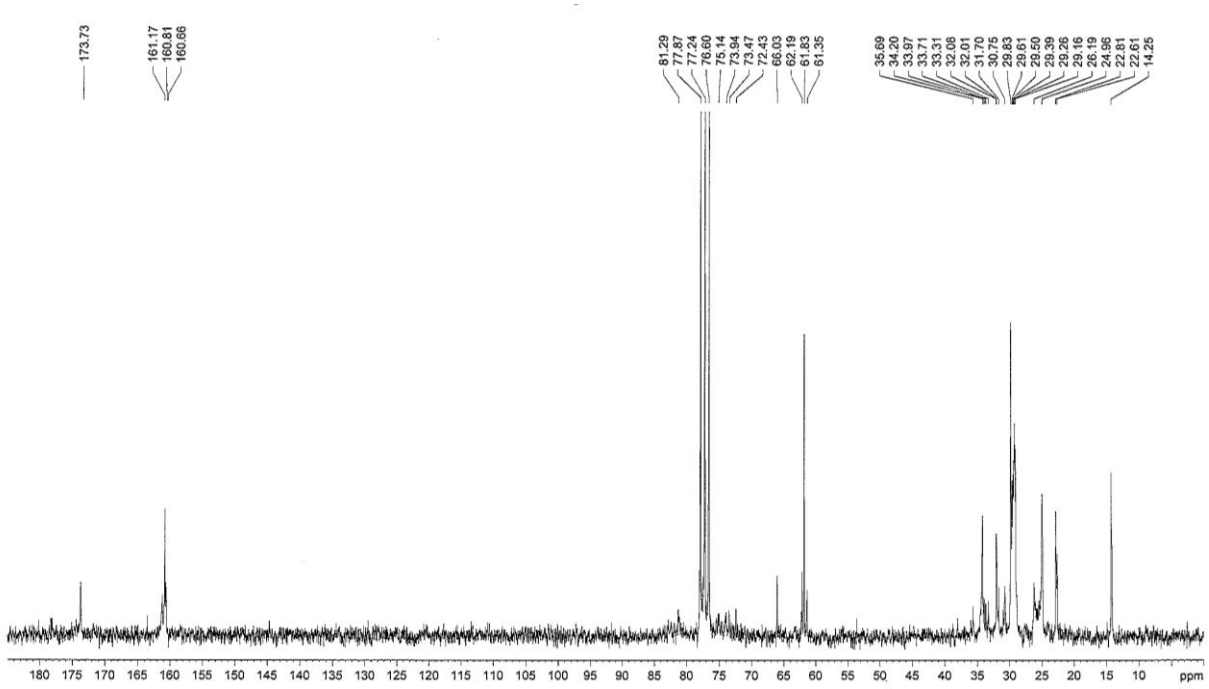

Figure S11. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of product **2**.

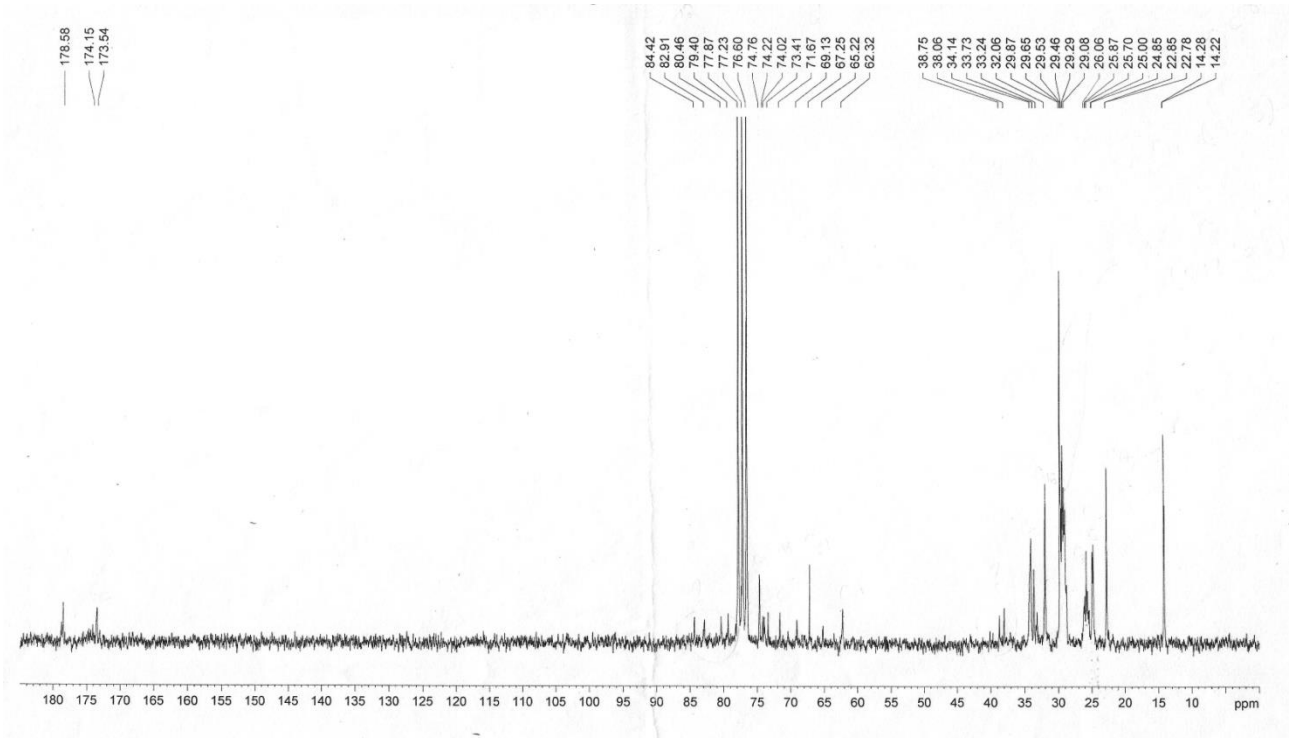

Figure S12. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of product **3**.

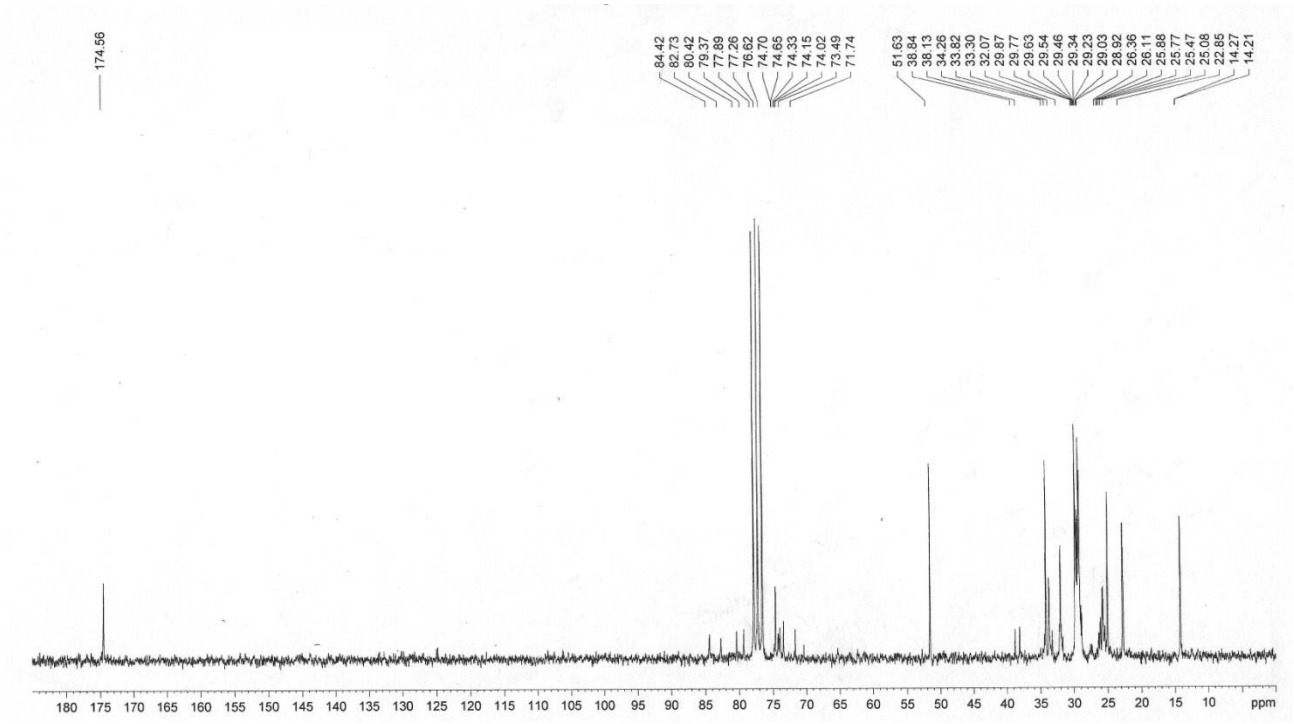

Figure S13. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of product **4**.

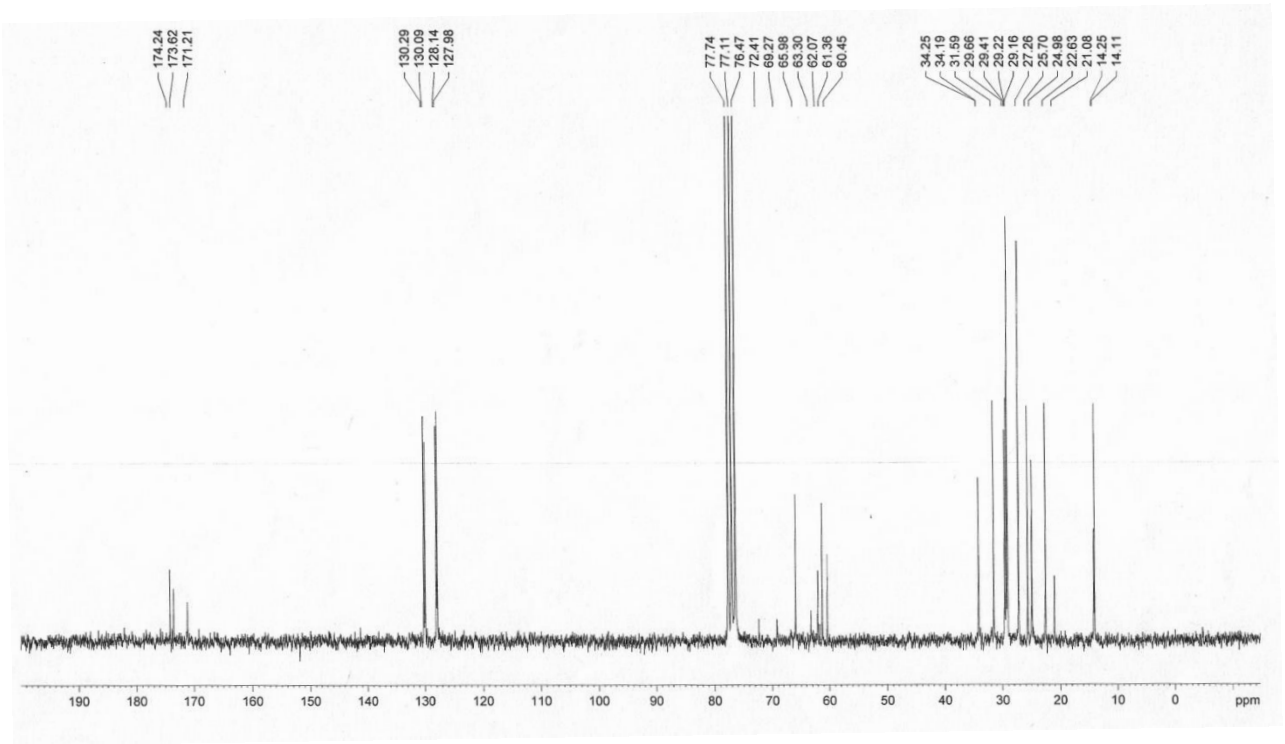

Figure S14. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of product **8**.

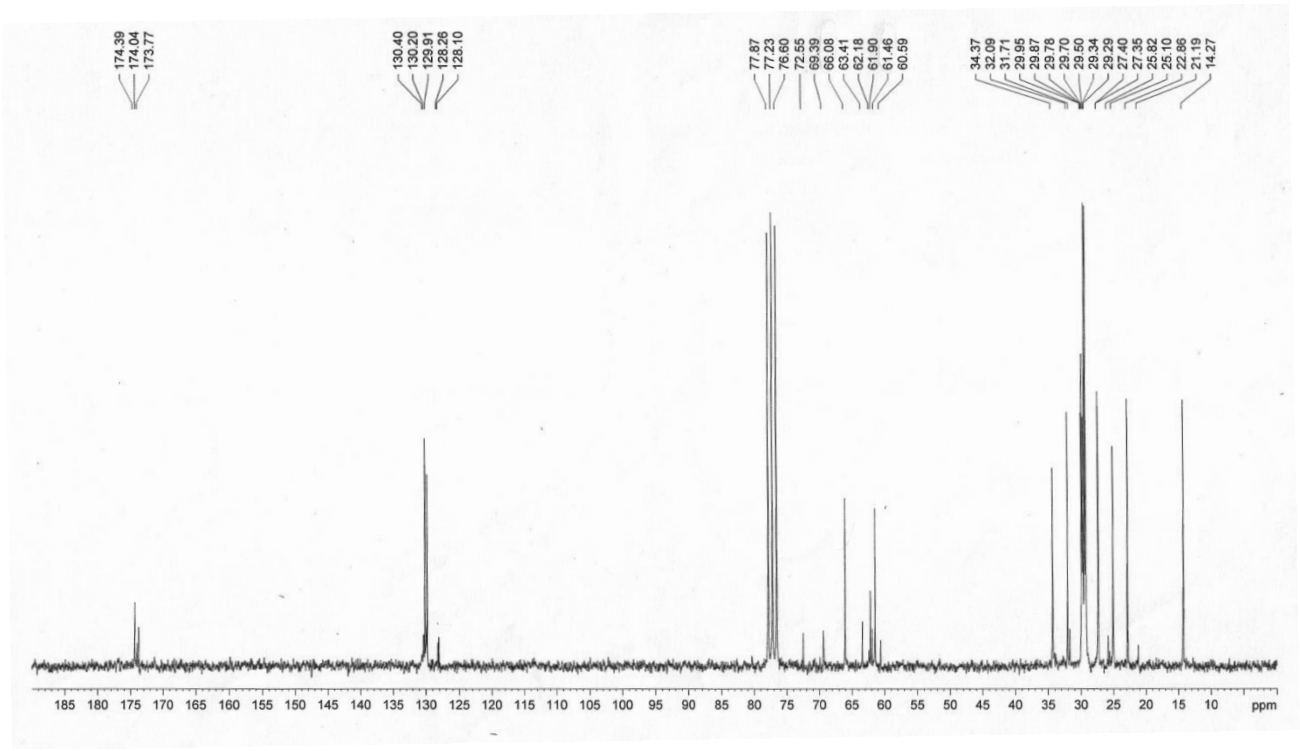

Figure S15. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of product **9**.

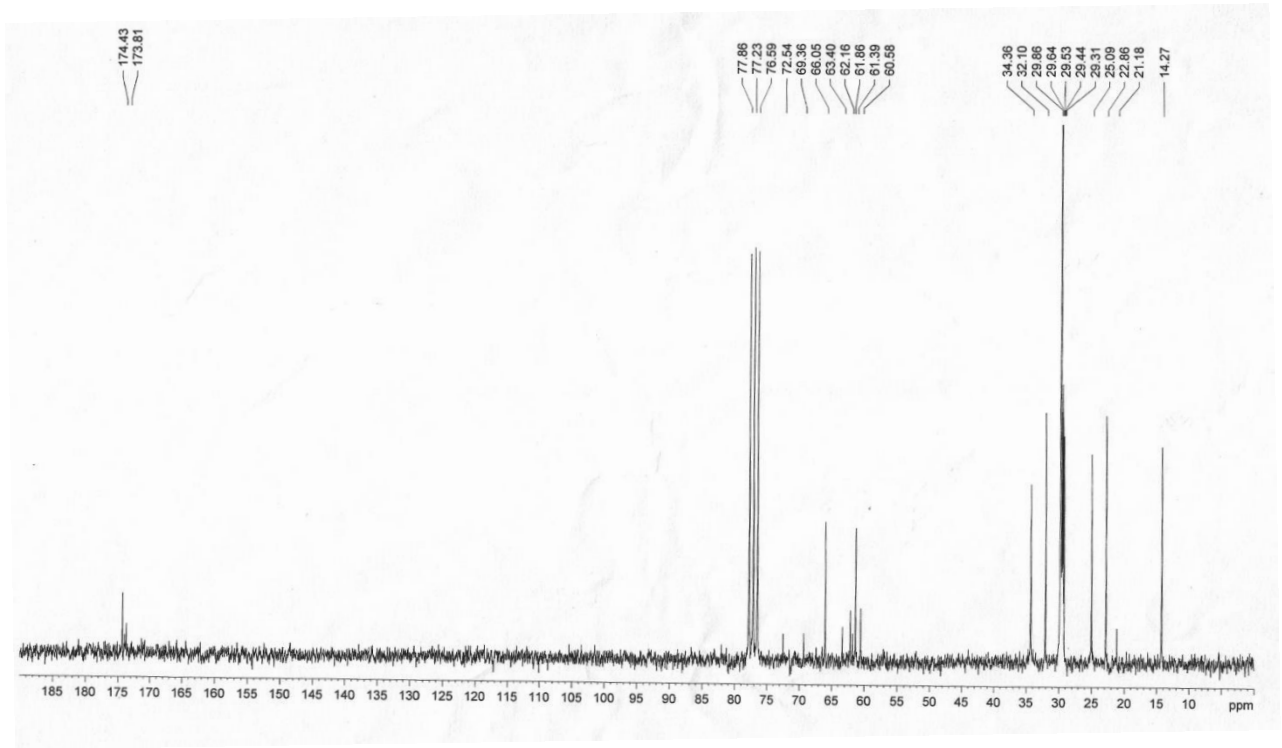

Figure S16. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of product **10**.

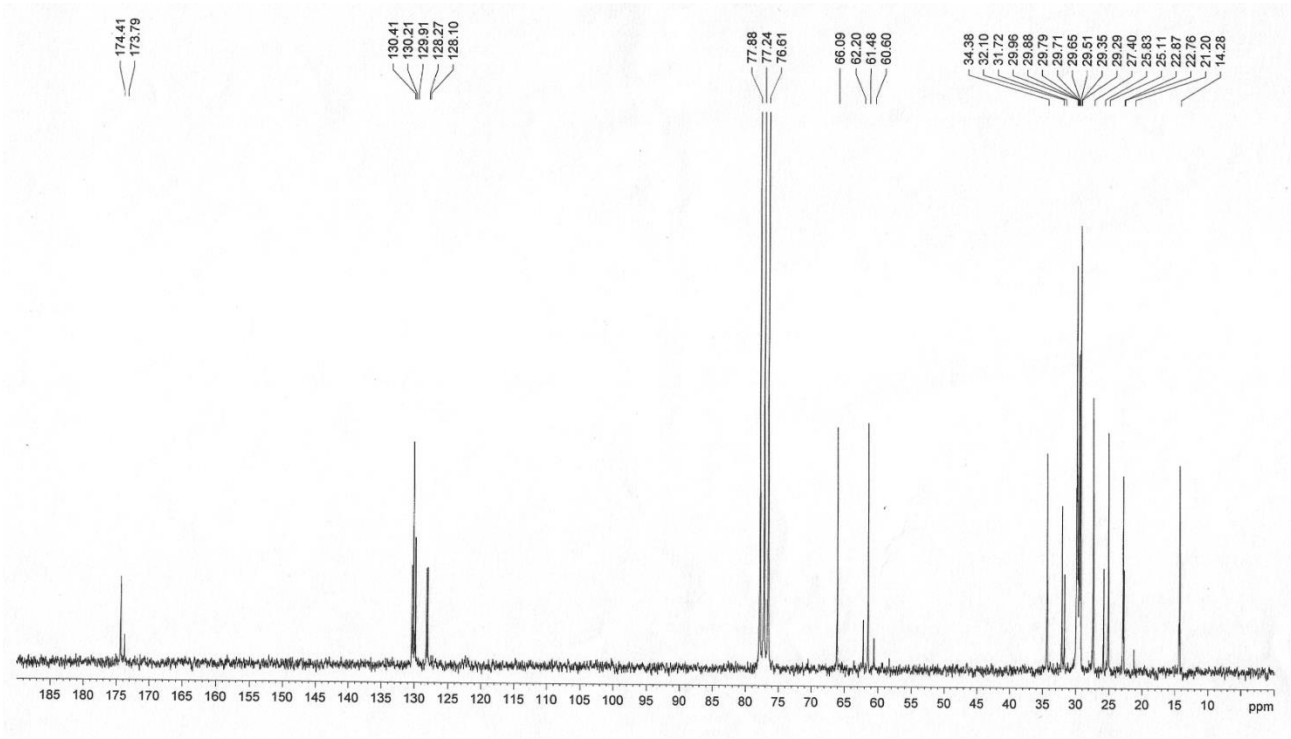

Figure S17. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of product **14**.

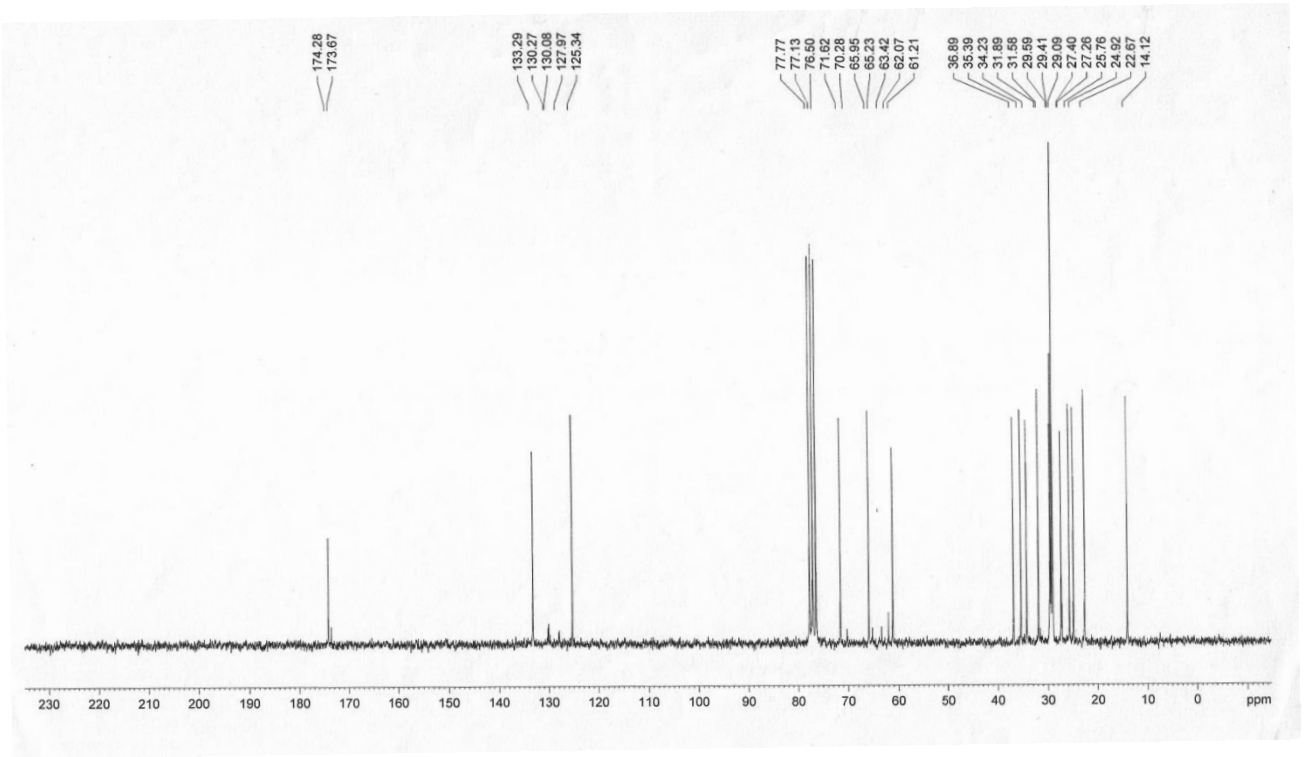

Figure S18. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of product **15**.

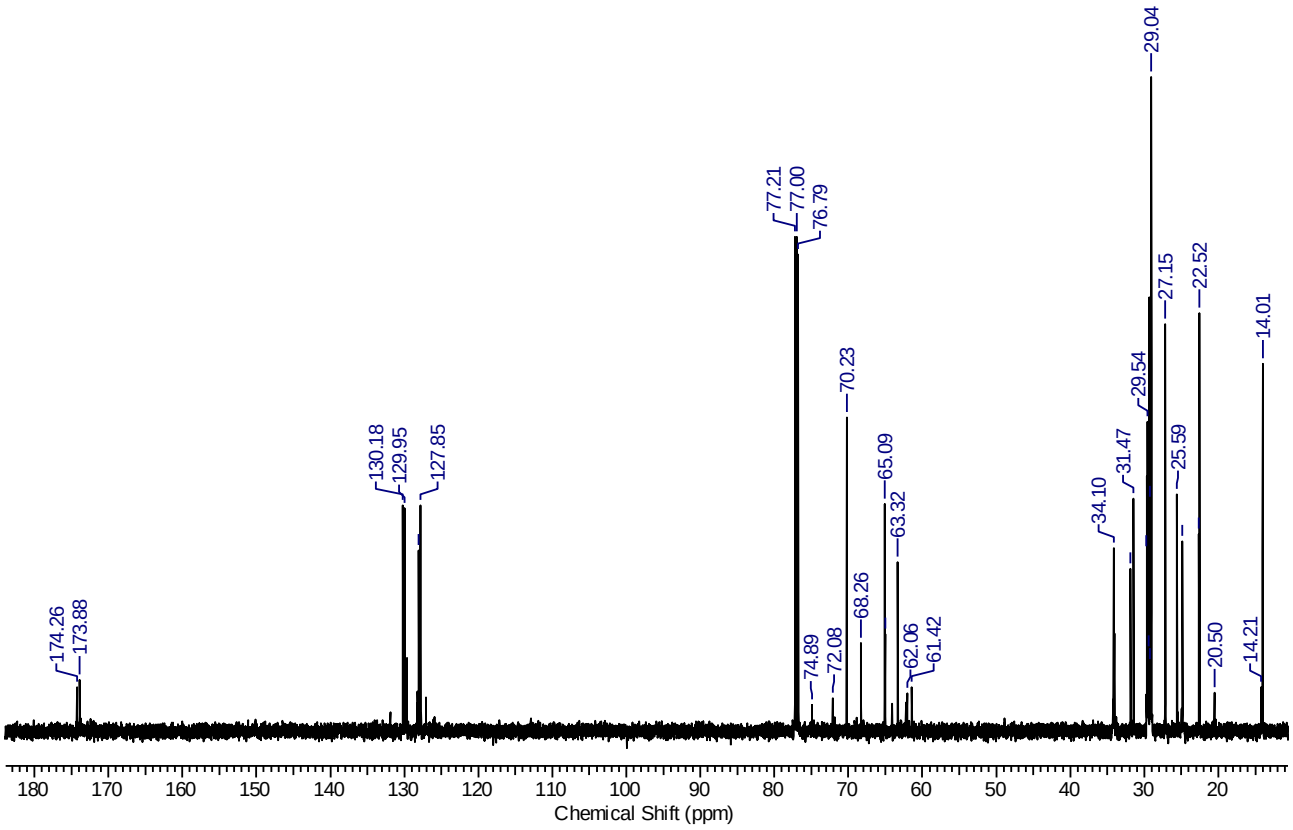

Figure S19. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of product **18**.

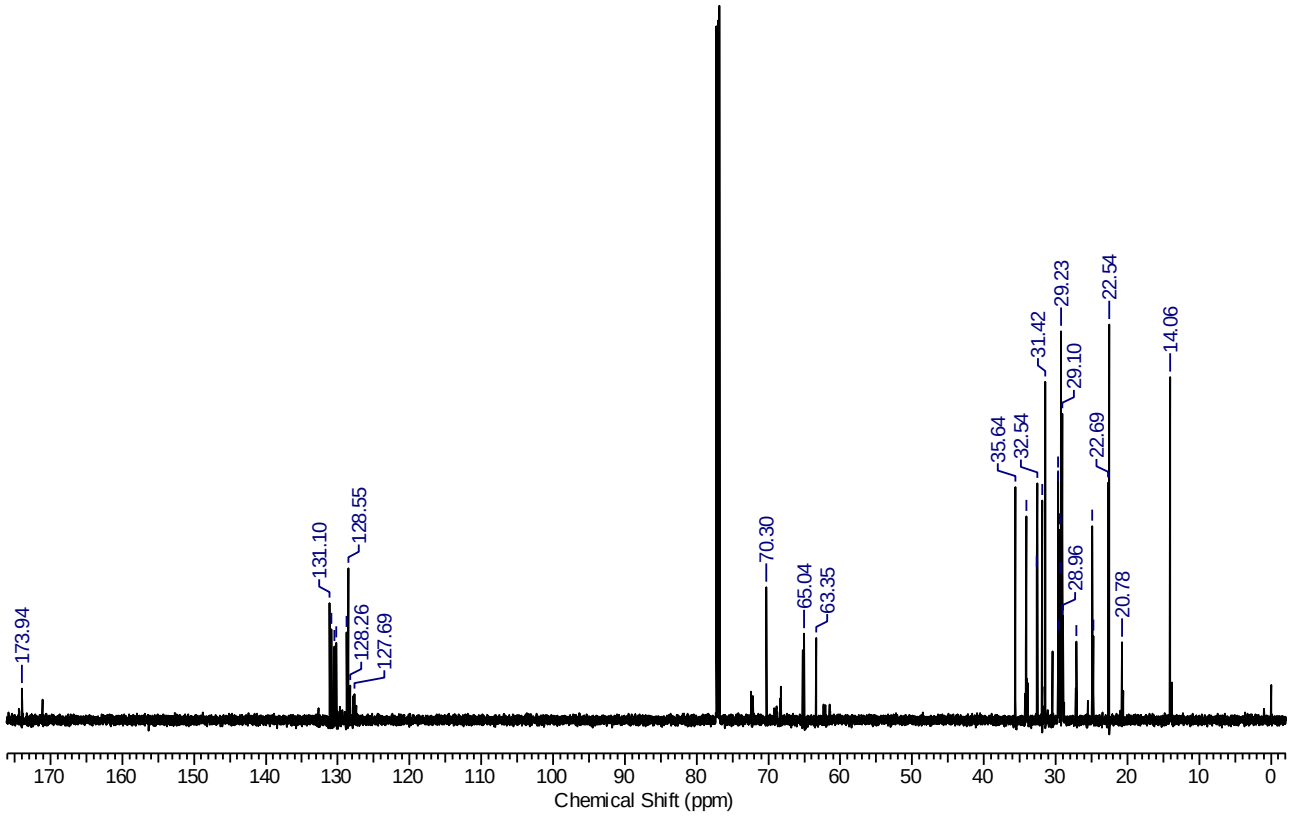

Figure S20. ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of product **19**.

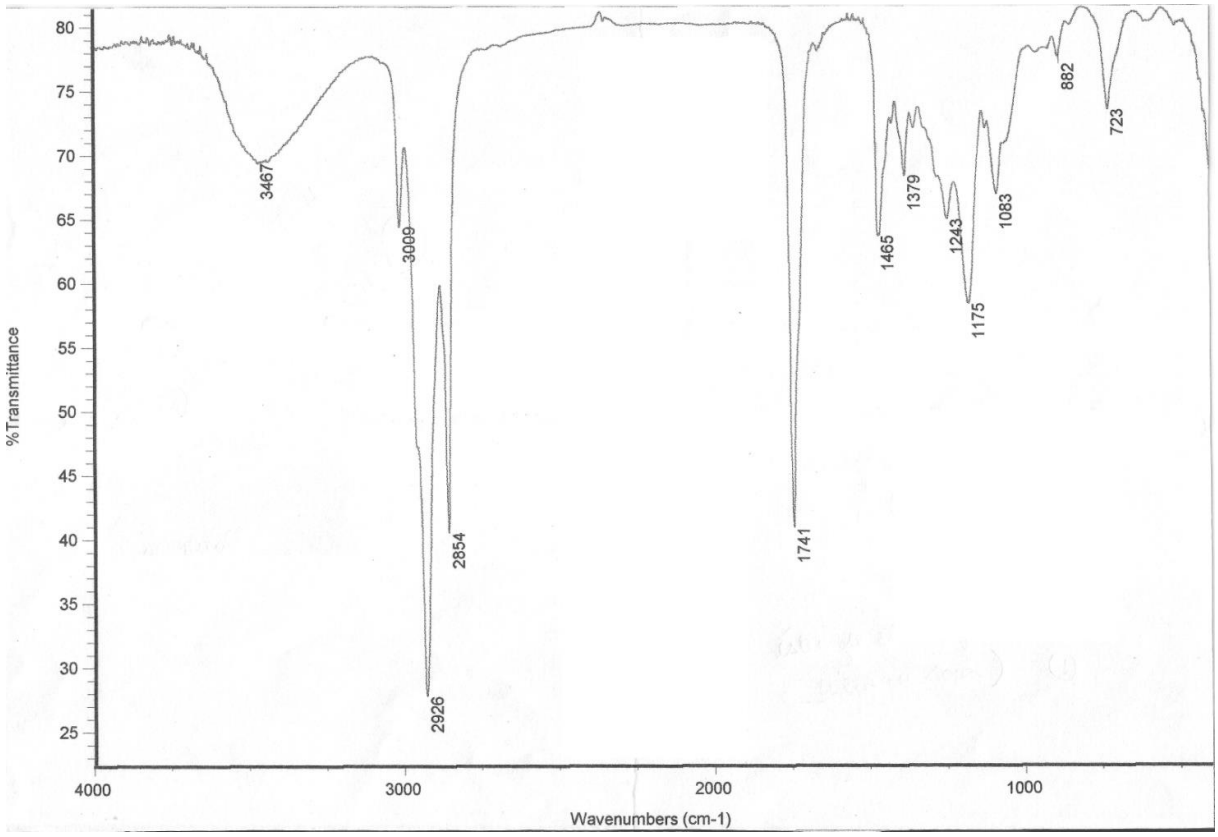

Figure S21. IR (KBr) spectrum of product **1**.

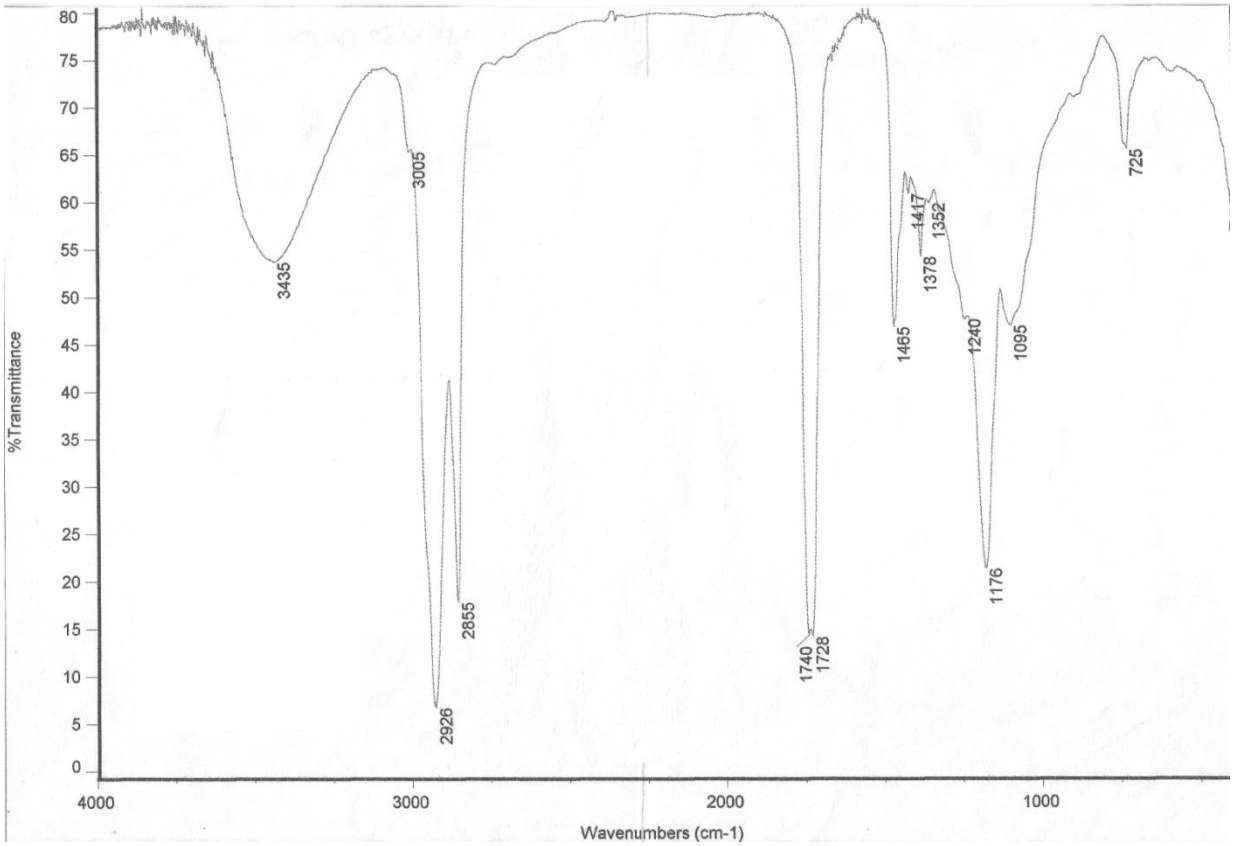

Figure S22. IR (KBr) spectrum of product **2**.

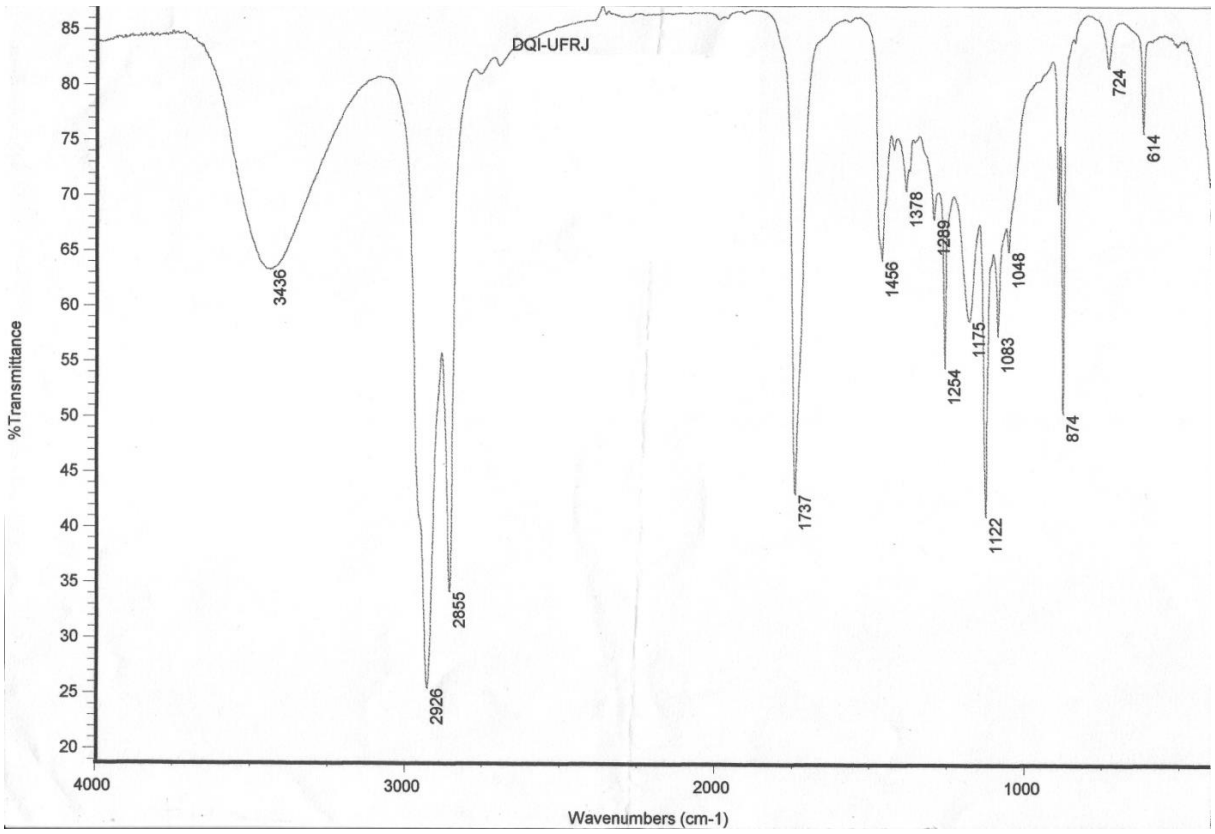

Figure S23. IR (KBr) spectrum of product **3**.

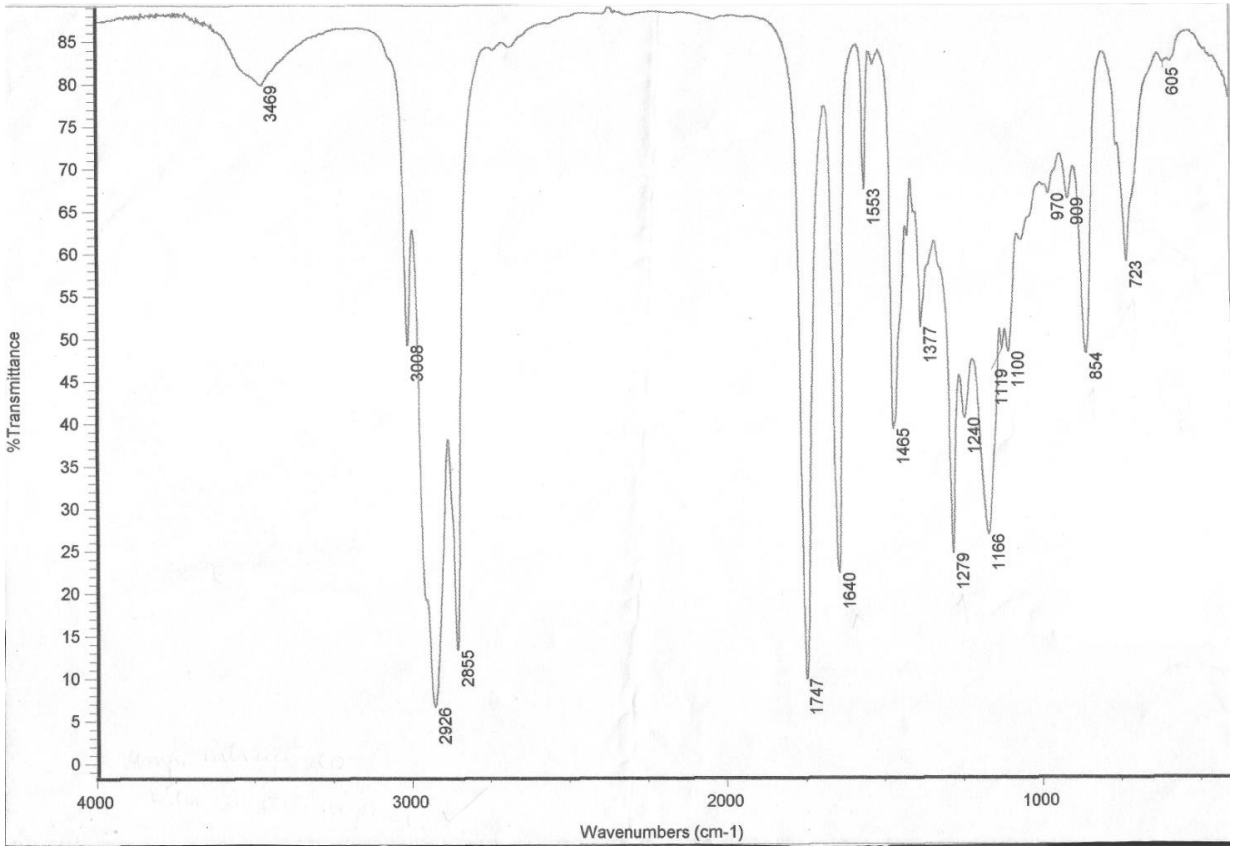

Figure S24. IR (KBr) spectrum of product **5**.

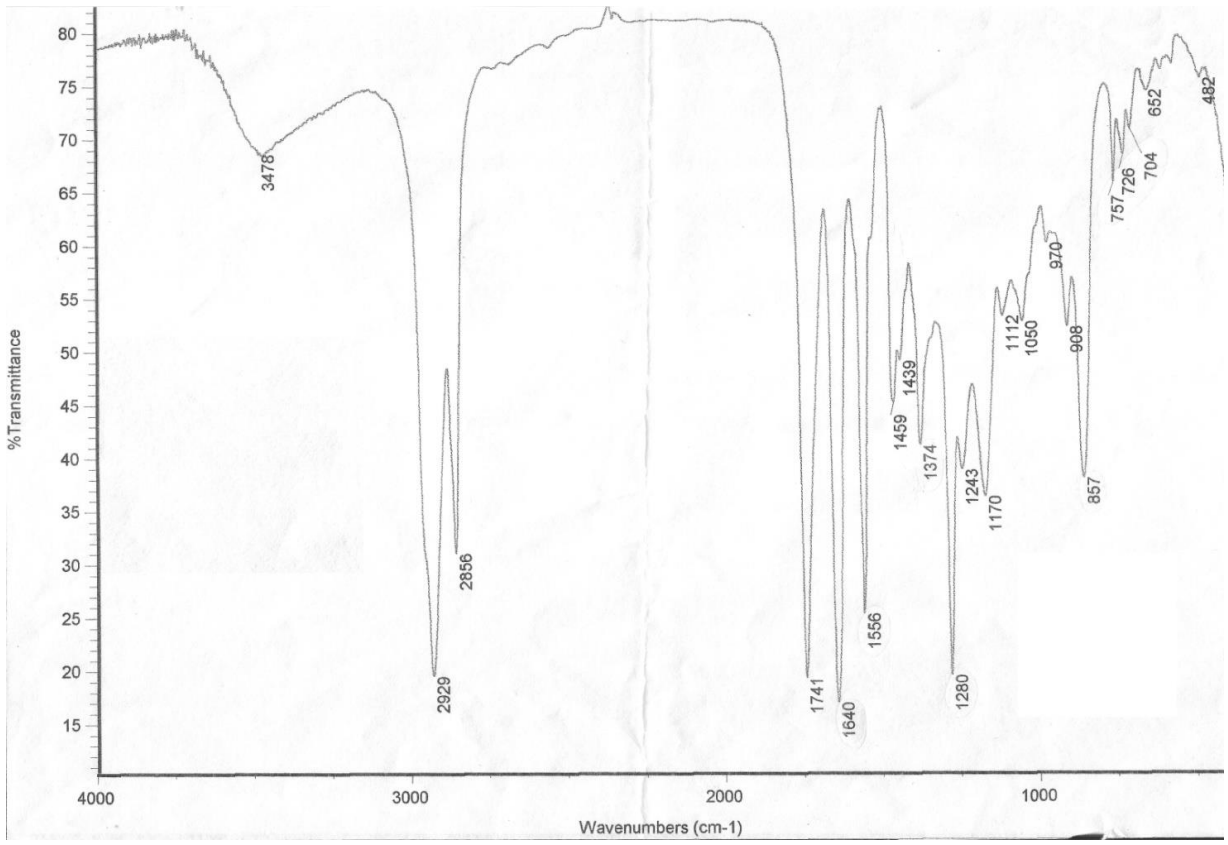

Figure S25. IR (KBr) spectrum of product **6**.

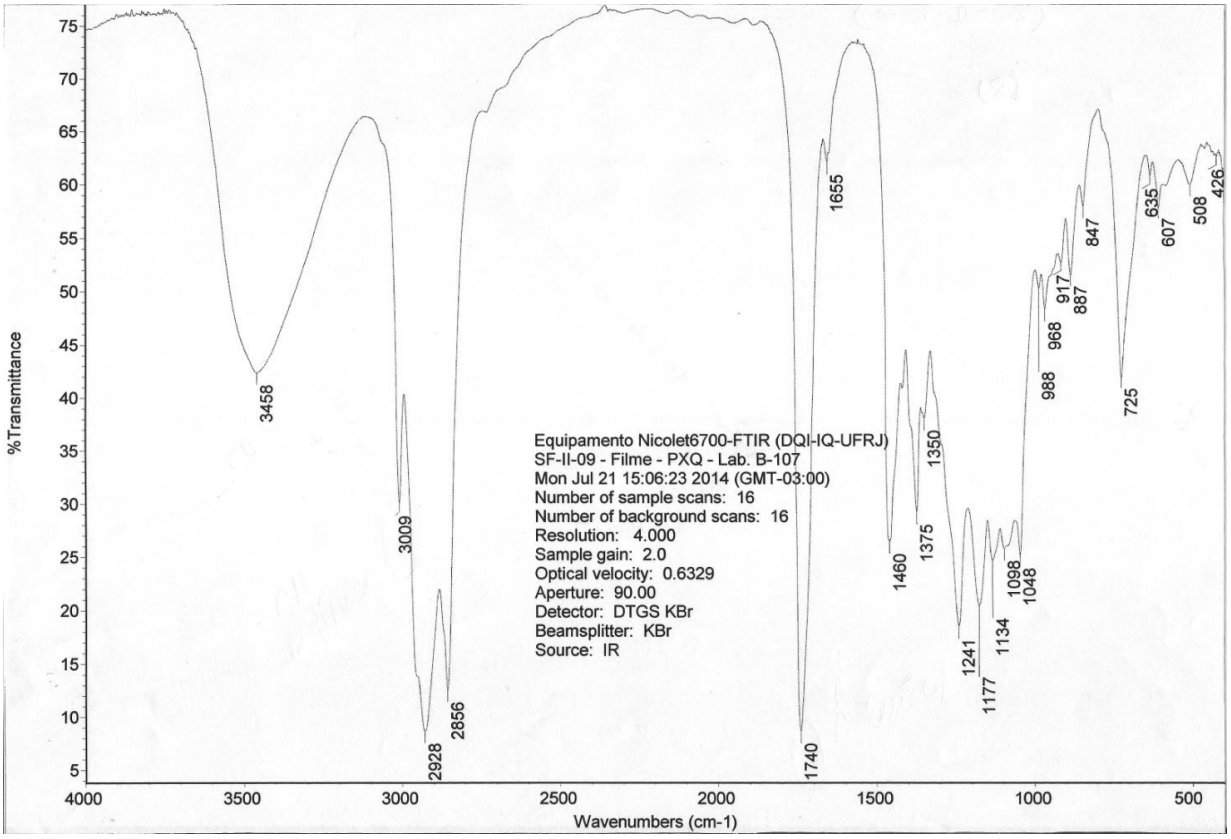

Figure S26. IR (KBr) spectrum of product **8**.

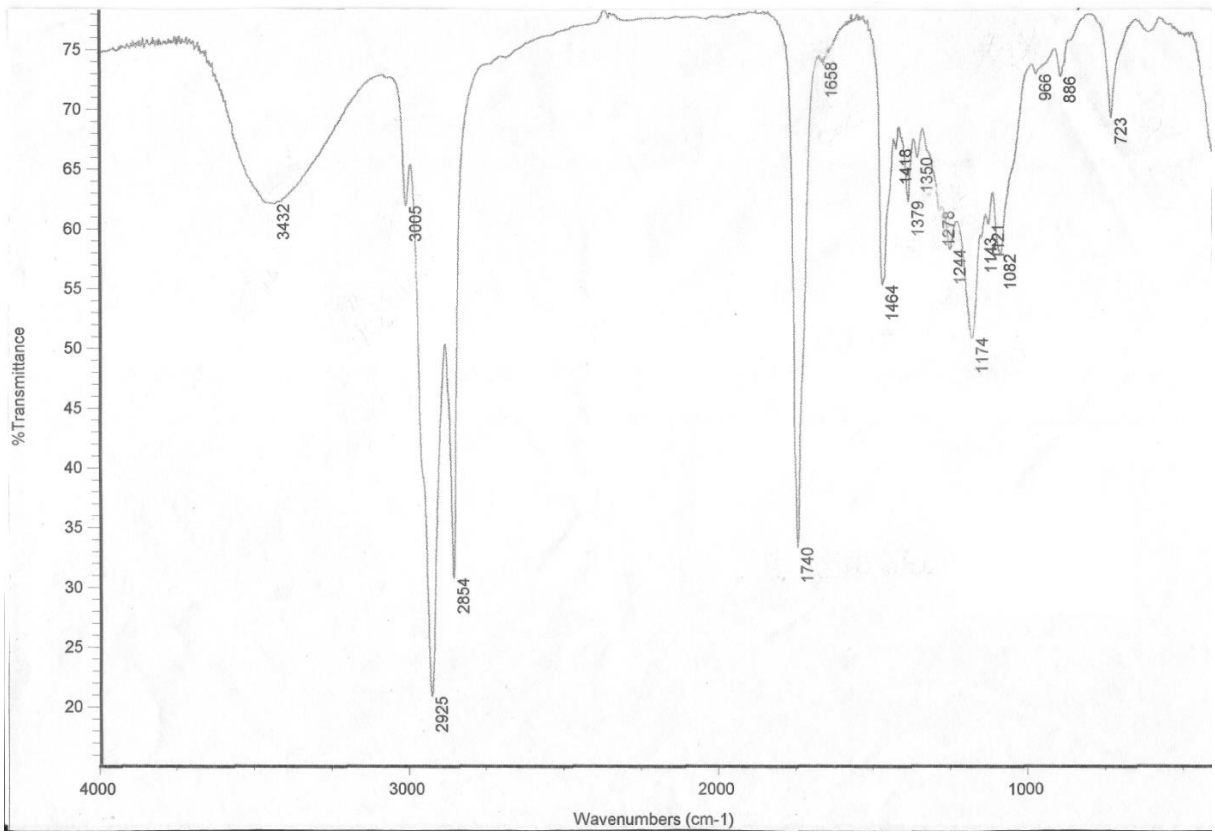

Figure S27. IR (KBr) spectrum of product **9**.

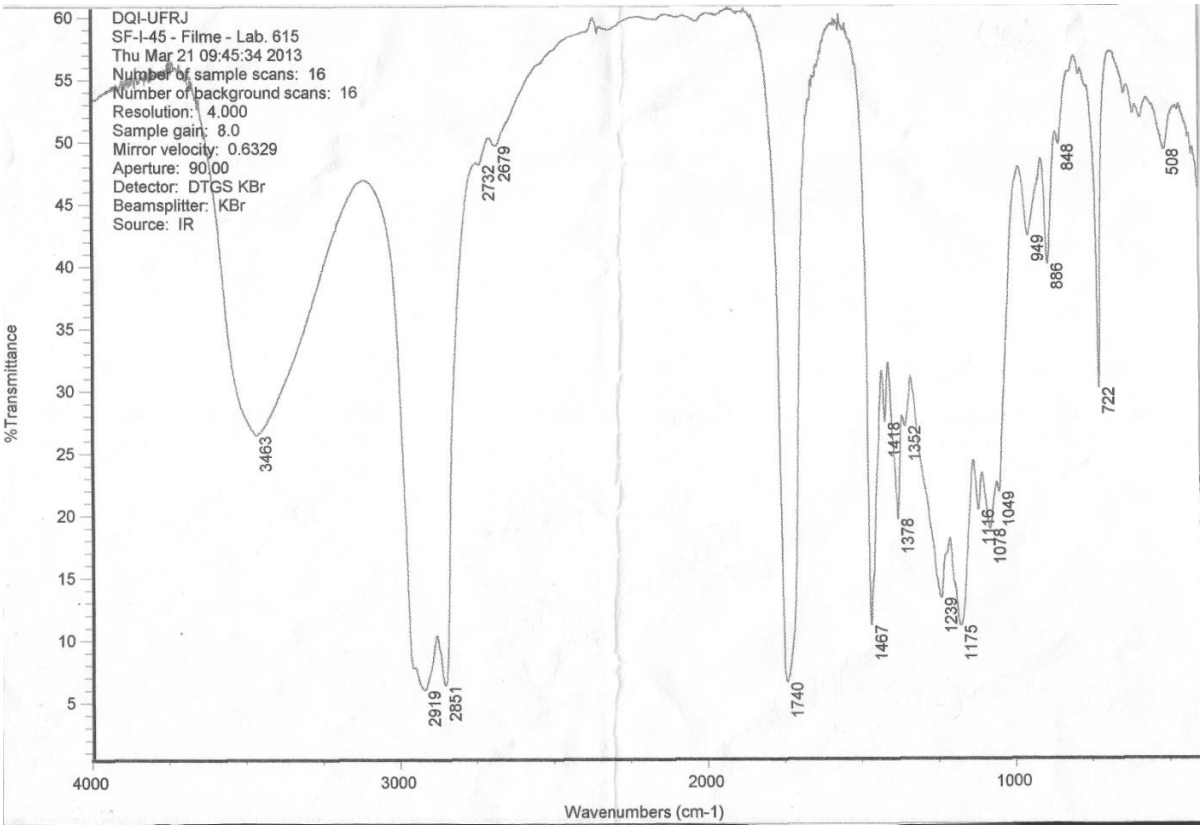

Figure S28. IR (KBr) spectrum of product **10**.

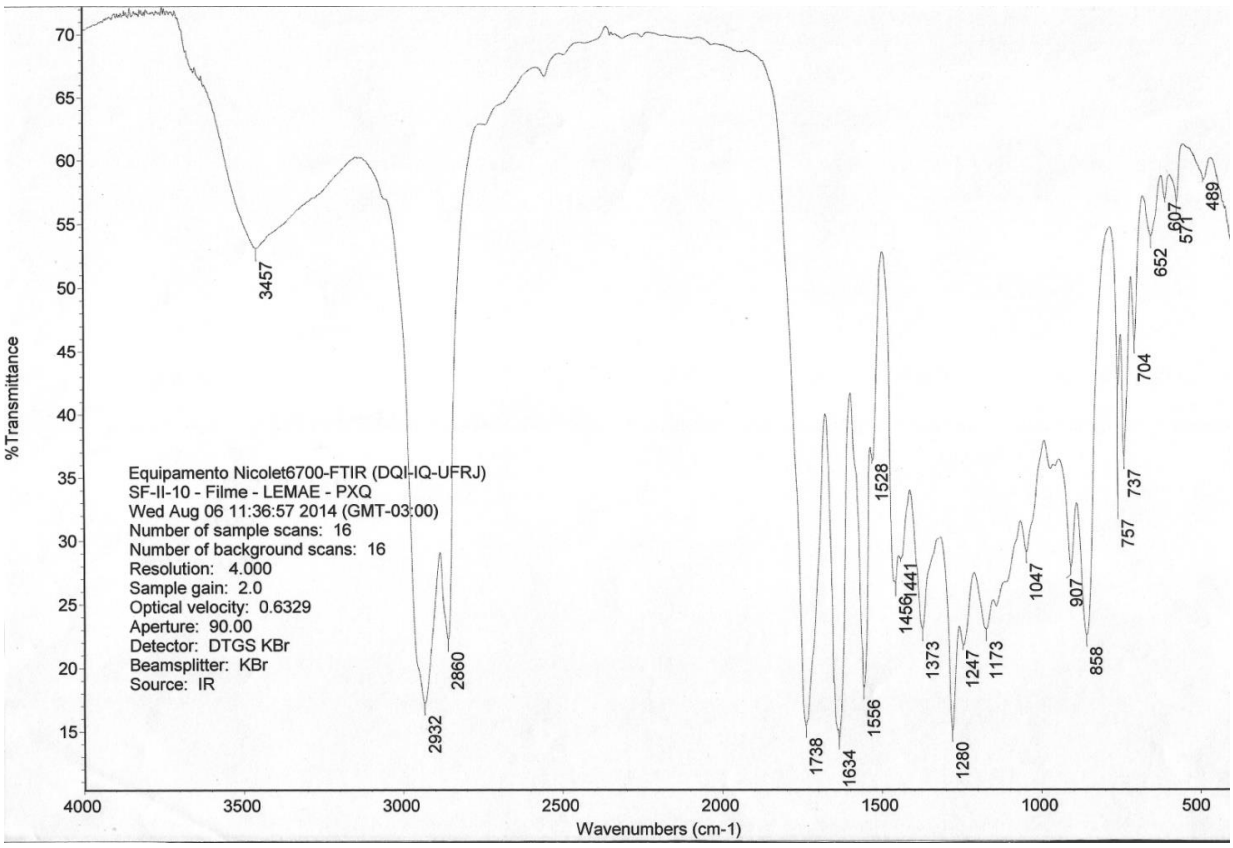

Figure S29. IR (KBr) spectrum of product **11**.

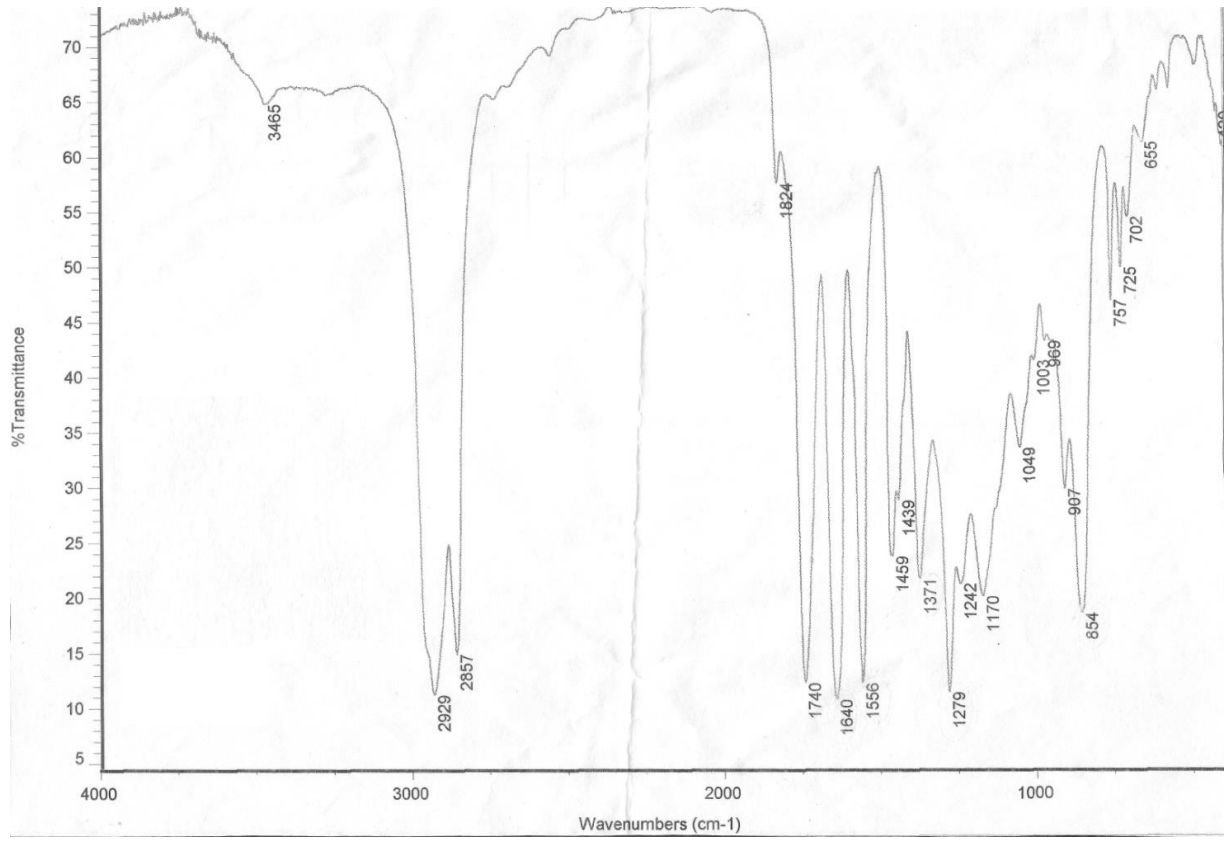

Figure S30. IR (KBr) spectrum of product **12**.

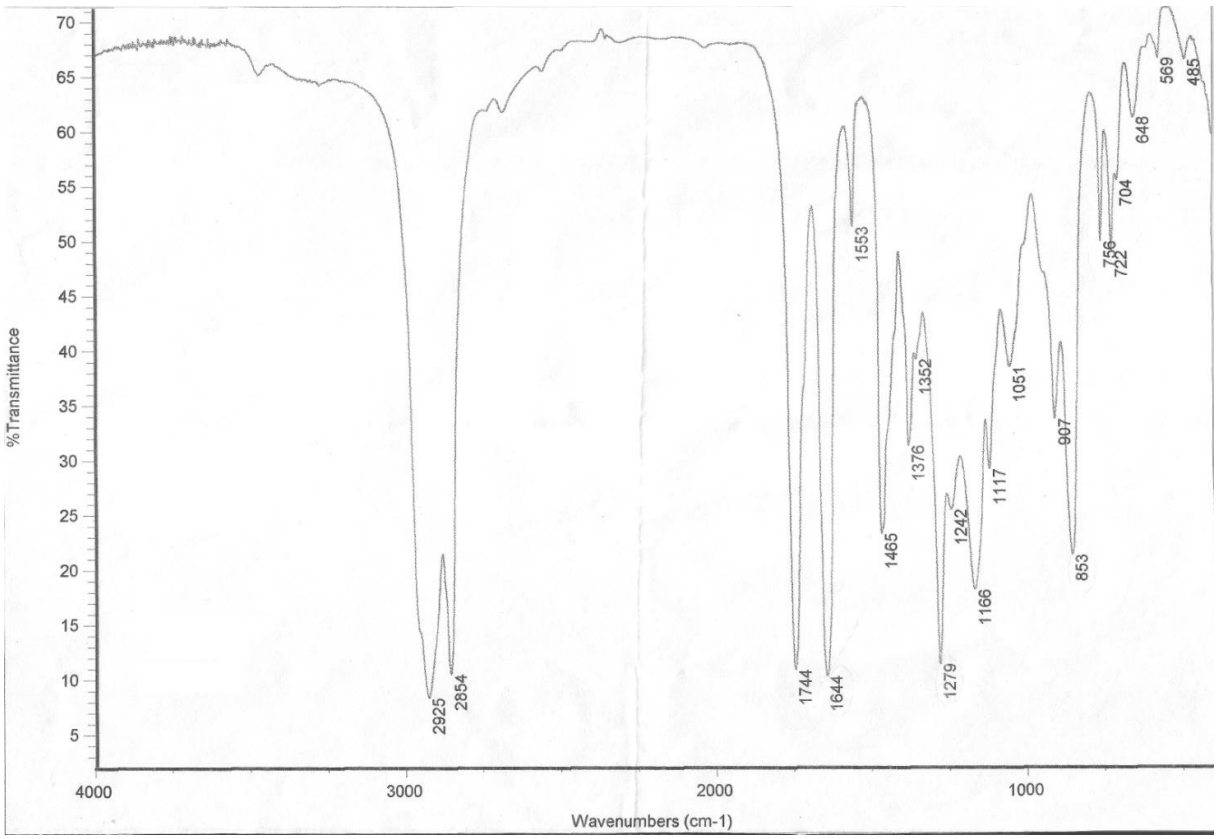

Figure S31. IR (KBr) spectrum of product **13**.

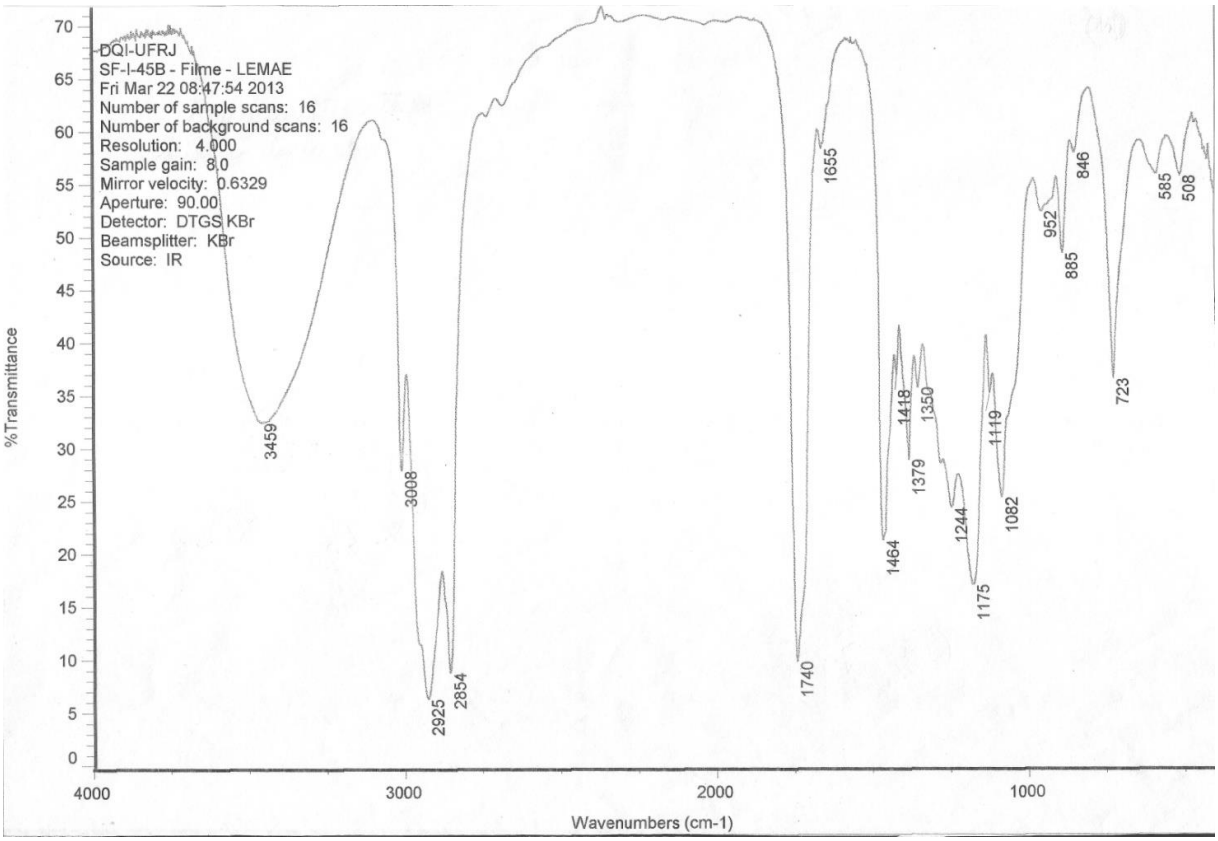

Figure S32. IR (KBr) spectrum of product **14**.

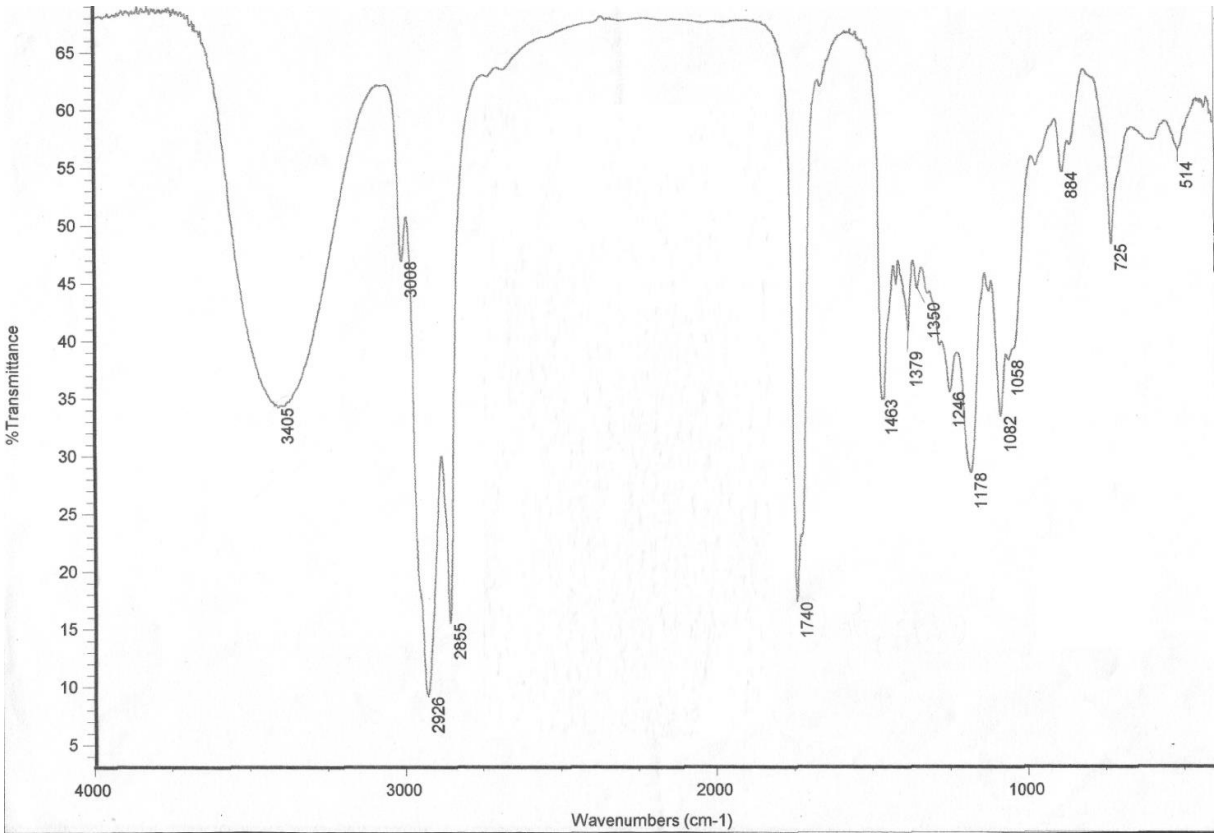

Figure S33. IR (KBr) spectrum of product **15**.

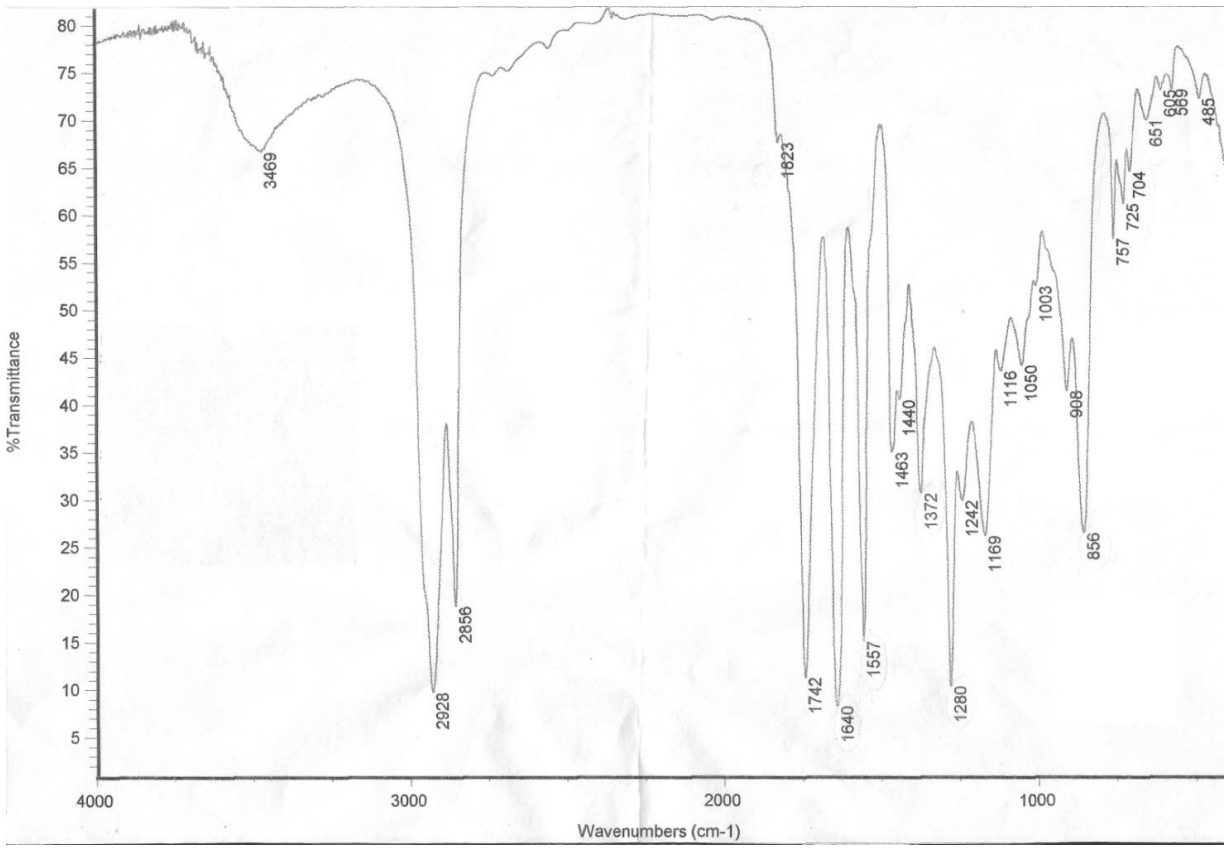

Figure S34. IR (KBr) spectrum of product **16**.

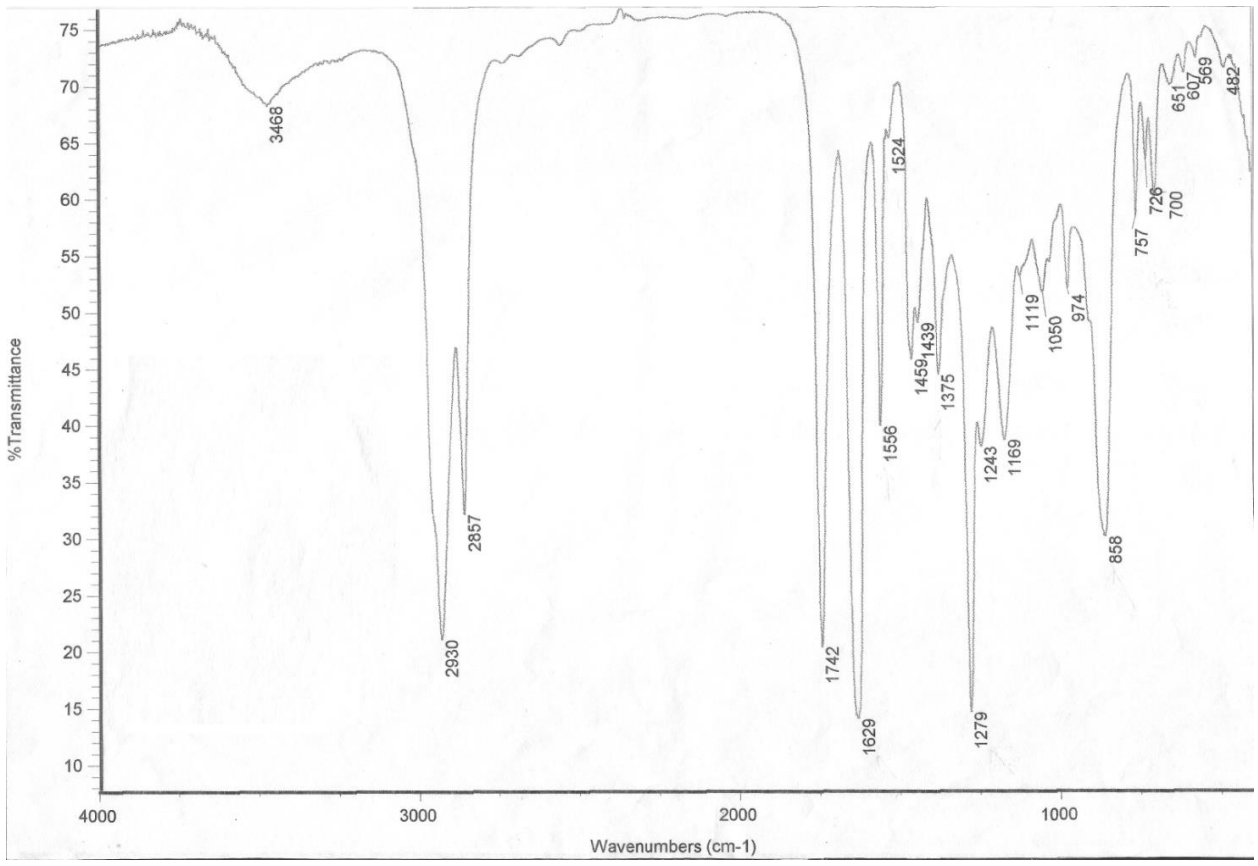

Figure S35. IR (KBr) spectrum of product **17**.

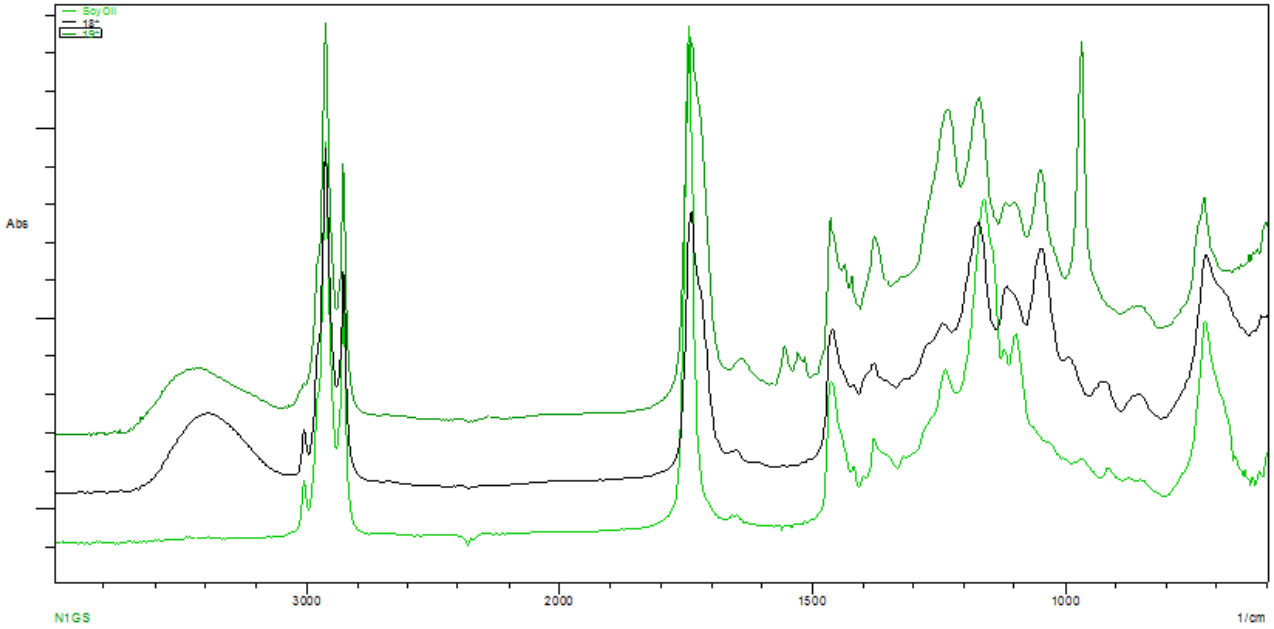

Figure S36. IR (ATR) spectra of soybean oil, products **18** and **19**.