Supporting Information for

Highly Enantioselective Oxidation of Non-activated Aliphatic C-H Bonds with Hydrogen Peroxide Catalyzed by Manganese Complexes

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1. Experimental Section

1.1 Materials

Reagents and solvents used were of commercially available reagent quality unless stated otherwise. Solvents were purchased from SDS and Scharlab. Solvents were purified and dried by passing through an activated alumina purification system (M-Braun SPS-800) or by conventional distillation techniques.

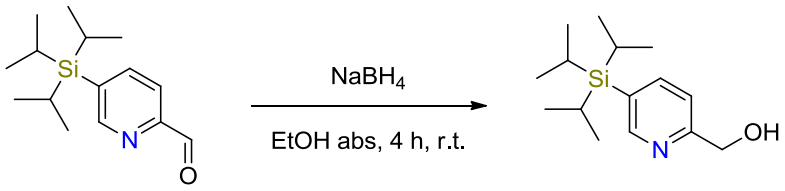
1.2 Instrumentation

Oxidation products were identified by comparison of their GC retention times and GC/MS with those of authentic compounds, and/or by ^{1}H and $^{13}C\{^{1}H\}$-NMR analyses. IR spectra were taken in a Mattson-Galaxy Satellite FT-IR spectrophotometer using a MKII Golden Gate single reflection ATR system. Elemental analyses were performed using a CHNS-O EA-1108 elemental analyzer from Fisons. NMR spectra were taken on BrukerDPX300 and DPX400 spectrometers using standard conditions. Electrospray ionization mass spectrometry (ESI-MS) experiments were performed on a Bruker Daltonics Esquire 3000 Spectrometer using a 1 mM solution of the analyzed compound. High resolution mass spectra (HRMS) were recorded on a Bruker MicroTOF-Q IITM instrument with a ESI source at Serveis Tècnics of the University of Girona. Samples were introduced into the mass spectrometer ion source by direct infusion through a syringe pump and were externally calibrated using sodium formate. Chromatographic resolution of enantiomers was performed on an AgilentGC-7820-A chromatograph using a CYCLOSIL-B column and HPLC 1200 series Agilent technologies using CHIRALPAK-IA and CHIRALPAK-IC columns. The configuration of the major enantiomer was determined by chemical correlation.

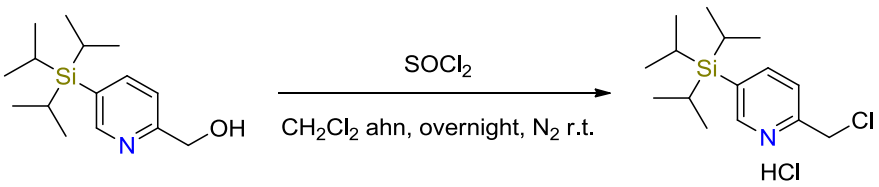
2. Synthesis of the complexes

2.1 Synthesis of the pyridine synthons

Pyridine synthons **^{TIPS}PyCHO**[1] and **5-(2,6-bis(trifluoromethyl)phenyl)-2-(chloromethyl)pyridine)**[2] were synthetized following previously described procedure.



^{TIPS}PyCH$_2$OH: ^{TIPS}PyCHO (5 g, 19 mmol) was dissolved in absolute ethanol (45 ml) and $NaBH_4$ (2 eq., 38 mmol) was directly added as a solid in little portions. The reaction mixture was stirred for 4 hours at room temperature and then 10 ml of water were slowly added. After 10 minutes of stirring, the solvent was removed under reduced pressure and 10 ml of water were added. The mixture was extracted with 3 x 20 ml of CH_2Cl_2, the combined organic phases were dried with anhydrous $MgSO_4$ and the solvent was removed under reduced pressure to yield the desired product, (2.57 g, 9.68 mmol, 51% yield). ^{1}H-NMR (400 MHz, $CDCl_3$, 300 K) δ, ppm 8.62 (dd, *J* = 1.7, 1.0 Hz, 1H), 7.78 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.28 (dd, *J* = 7.7, 0.9 Hz, 1H), 4.78 (s, 2H), 1.42 (hept, *J* = 7.4 Hz, 3H), 1.08 (d, *J* = 7.5 Hz, 18H).^{13}C{^{1}H}-NMR 159.3, 154.1, 143.7, 128.3, 120.1, 64.2, 18.4, 10.9, 10.6. HRMS(ESI-MS) *m/z* calculated for $C_{15}H_{27}NOSi$[M+H]+ 266.1935, found 266.1941.

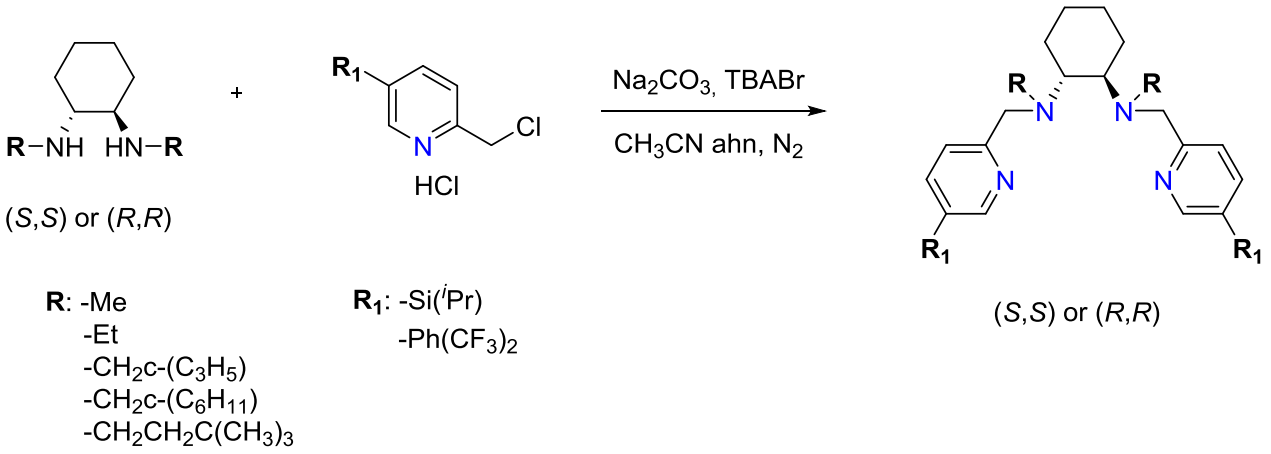


^{TIPS}PyCH$_2$Cl·HCl: ^{TIPS}PyCH$_2$OH (2.50 g, 9.42 mmol) was dissolved in 167 ml of anhydrous CH_2Cl_2 and a solution of $SOCl_2$ (5 equiv., 47.1 mmol) in anhydrous CH_2Cl_2 (20 ml) was slowly added at 0°C under inert atmosphere. The reaction mixture was stirred overnight at room temperature and then the solvent was removed at reduced pressure to yield the desired product, (2.95 g, 9.2 mmol, 98% yield). ^{1}H-NMR (400 MHz, $CDCl_3$, 300 K) δ, ppm 8.61 (s, 1H), 8.19 (d, *J* = 7.2 Hz, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 5.03 (s, 2H), 1.47 (hept, *J* = 7.4 Hz, 3H), 1.10 (d, *J* = 7.4 Hz, 18H). ^{13}C{^{1}H}-NMR 152.6,

151.3, 144.6, 136.3, 126.2, 39.5, 18.3, 18.2, 18.1, 10.7, 10.4, 10.1. HRMS(ESI-MS) *m/z* calculated for $C_{15}H_{26}NOSiCl$[M+H]+ 284.1596, found 284.1591.

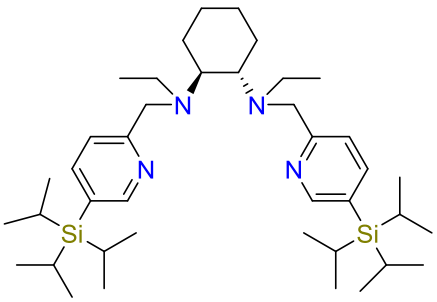
2.2 Synthesis of the ligands

***N,N*-1,2-cyclohexanediamine** derivatives were prepared according to the reported procedures.[3] **^{TIPS}mcp** and **^{TIPS}pdp** ligand was prepared according to the reported procedures.[1]



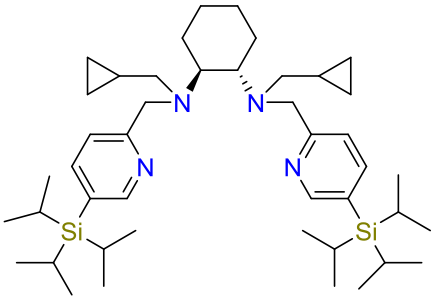
R: -Me
-Et
-CH_2c-(C_3H_5)
-CH_2c-(C_6H_{11})
-$CH_2CH_2C(CH_3)_3$

R_1: -Si(^{i}Pr)
-Ph(CF_3)$_2$

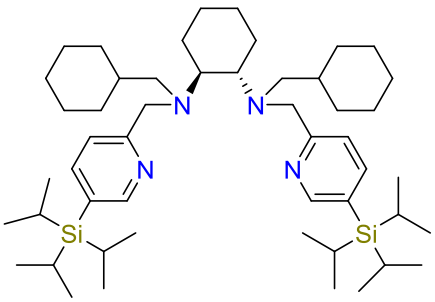


(*S,S*)-^{TIPS}ecp: (*S,S*)-*N,N*-Diethyl-1,2-cyclohexanediamine (0.5 g, 2.9 mmol), **^{TIPS}PyCH$_2$Cl·HCl** (2.08 g, 6.5 mmol), Na_2CO_3 (11 g, 104 mmol) and TBABr (10 mg) was dissolved in anhydrous CH_3CN (100 ml). The reaction mixture was refluxed overnight under N_2. At this point, the crude reaction was filtered and the solvent was evaporated under reduced pressure. NaOH (50 ml) was added and the organic layer was separated from the basic aqueous layer. The aqueous layer was extracted with CH_2Cl_2 (3x) and the organic layer were combined and dried over Na_2SO_4. The obtained brown oil was purified by silica column (CH_2Cl_2:MeOH:NH_3 95:4:1) and the collected fractions were removed under reduced pressure to provide 1.1 g (1.65 mmol, yield 57%) of a brown-yellow oil that turns solid after drying under vacuum. ^{1}H-NMR (400 MHz, $CDCl_3$, 300 K) δ, ppm: 8.45 (t, *J* = 1.3 Hz, 2H),

7.58 (d, *J* = 7.7 Hz, 2H), 7.52 (dd, *J* = 7.8, 1.8 Hz, 2H), 3.83 (d, *J* = 15.2 Hz, 2H), 3.55 (d, *J* = 15.2 Hz, 2H), 2.65 (d, *J* = 7.3 Hz, 2H), 2.49 (ddt, *J* = 20.1, 12.8, 6.6 Hz, 4H), 1.97 (d, *J* = 10.2 Hz, 2H), 1.67 (m, 3H), 1.59 (m, 2H), 1.37-1.24 (m, 6H), 1.00 (dd, *J* = 7.5, 1.1 Hz, 36H), 0.92 (t, *J* = 7.1 Hz, 6H). $^{13}C\{^{1}H\}$-NMR 165.5, 154.1, 142.83, 142.75, 127.2, 126.7, 122.7, 122.6, 60.8, 56.4, 53.4, 44.1, 26.1, 25.9, 18.4, 14.3, 10.9, 10.6, 10.4. HRMS(ESI-MS) *m/z* calculated for $C_{40}H_{72}N_4Si_2$[M+H]+ 665.5368, found 665.5366.

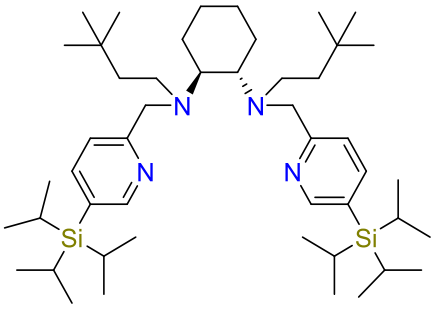


(*S*,*S*)-^{TIPS}cpcp: Following the previous conditions, the crude mixture was purified by flash chromatography over silica using CH_2Cl_2:MeOH:NH_3 96:3:1 and the product was concentrated to dryness. The product was isolated as a yellow oil (0.230 g, 61% yield). ^{1}H-NMR (400 MHz, $CDCl_3$, 300 K) δ, ppm: 8.49 (d, *J* = 1.6 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.58 (dd, *J* = 7.8, 1.8 Hz, 2H), 4.05 (d, *J* = 15.1 Hz, 2H), 3.59 (d, *J* = 15.1 Hz, 2H), 2.95 (d, *J* = 7.3 Hz, 2H), 2.63 (dd, *J* = 13.0, 5.4 Hz, 2H), 2.24 (dd, *J* = 13.0, 7.5 Hz, 2H), 2.06 (d, *J* = 10.4 Hz, 2H), 1.75 (d, *J* = 10.4 Hz, 2H), 1.36 (q, *J* = 7.4 Hz, 6H), 1.18 (d, *J* = 11.8 Hz, 4H), 1.05 (d, *J* = 7.8 Hz, 36H), 0.76 (qd, *J* = 8.0, 6.7, 3.8 Hz, 2H), 0.36 (tt, *J* = 8.8, 4.6 Hz, 2H), 0.24 (tt, *J* = 8.9, 4.6 Hz, 2H), 0.02 (dq, *J* = 9.5, 4.9 Hz, 2H), 0.09 (dq, *J* = 9.5, 4.9 Hz, 2H). $^{13}C\{^{1}H\}$-NMR 162.4, 154.1, 142.6, 126.6, 122.9, 61.2, 56.3, 55.6, 26.1, 25.5, 18.5, 10.6, 5.5, 2.8. HRMS(ESI-MS) *m/z* calculated for $C_{44}H_{76}N_4Si_2$[M+H]+ 717.5681, found 717.5676.

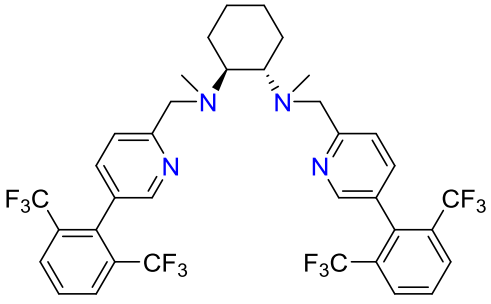


(*S*,*S*)-^{TIPS}chcp: Following the previous conditions, the crude mixture was purified by flash chromatography over silica using CH_2Cl_2:MeOH:NH_3 95:4:1 and the product was concentrated to dryness. The product was isolated as a yellow oil (0.130 g, 41% yield). ^{1}H-NMR (400 MHz, $CDCl_3$,

300 K) δ, ppm: 8.53 (s, 2H), 7.67 (d, *J* = 1.5 Hz, 4H), 4.03 (d, *J* = 15.2 Hz, 2H), 3.63 (d, *J* = 15.2 Hz, 2H), 2.85 – 2.72 (m, 2H), 2.42 (dd, *J* = 6.8, 3.2 Hz, 4H), 2.14 – 2.05 (m, 2H), 1.76 (m, 4H), 1.65 – 1.48 (m, 8H), 1.40 (p, *J* = 7.5 Hz, 6H), 1.34 – 1.21 (m, 6H), 1.08 (d, *J* = 7.4 Hz, 36H), 1.04 – 0.95 (m, 6H), 0.66 (dtd, *J* = 23.5, 11.8, 8.6 Hz, 4H).$^{13}C\{^1H\}$-NMR 162.4, 154.2, 142.7, 126.6, 122.6, 61.9, 58.9, 36.3, 32.14, 32.09, 26.7, 26.3, 26.2, 26.0, 18.4, 10.6. HRMS(ESI-MS) *m/z* calculated for $C_{50}H_{88}N_4Si_2$[M+H]+ 801.6620, found 801.6605.



(*S*,*S*)-^{TIPS}tBucp: Following the previous conditions, the crude mixture was purified by flash chromatography over silica using CH_2Cl_2:MeOH:NH_3 95:4:1 and the product was concentrated to dryness. The product was isolated as a brown-yellow oil (0.170 g, 23% yield). ^{1}H-NMR (400 MHz, $CDCl_3$, 300 K) δ, ppm: 8.53 (s, 2H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.60 (dd, *J* = 7.8, 1.8 Hz, 2H), 3.96 (d, *J* = 15.2 Hz, 2H), 3.64 (d, *J* = 15.2 Hz, 2H), 2.76 (d, *J* = 7.7 Hz, 2H), 2.61 – 2.44 (m, 4H), 2.15 – 2.00 (m, 2H), 1.80 – 1.77 (m, 2H) 1.46 – 1.38 (m, 6H), 1.36 – 1.22 (m, 4H), 1.07 (d, *J* = 7.4 Hz, 36H), 1.02 – 0.94 (m, 4H), 0.74 (s, 18H). $^{13}C\{^1H\}$-NMR 162.4, 154.1, 142.7, 126.7, 122.7, 61.3, 56.5, 46.8, 42.8, 29.8, 29.4, 26.3, 26.2, 18.4, 10.6. HRMS(ESI-MS) *m/z* calculated for $C_{48}H_{88}N_4Si_2$[M+H]+ 777.6620, found 777.6603.

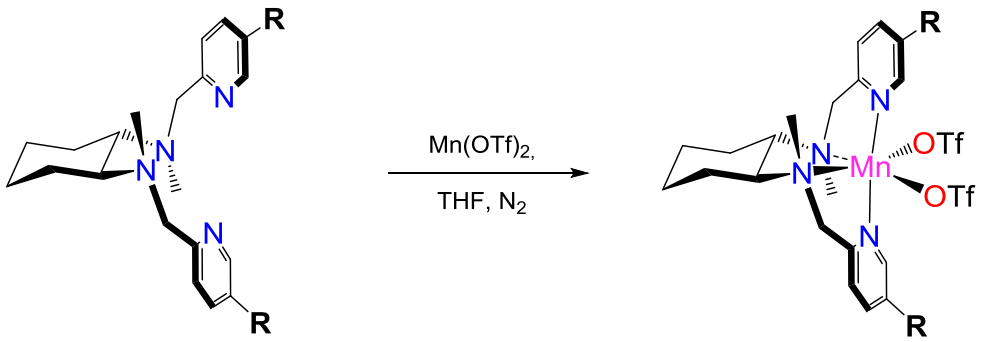


(*S*,*S*)-^{CF3}mcp: Following the previous conditions, the crude mixture was purified by flash chromatography over silica using CH_2Cl_2:MeOH:NH_3 97:2:1 and the product was concentrated to dryness. The product was isolated as a yellow oil (0.210 g, 44% yield). ^{1}H-NMR (400 MHz, $CDCl_3$, 300 K) δ, ppm: 8.39 (s, 2H), 7.99 (dd, *J* = 8.1, 3.7 Hz, 4H), 7.68 (q, *J* = 7.9 Hz, 4H), 7.55 – 7.45 (m,

2H), 4.04 (d, *J* = 14.5 Hz, 2H), 3.87 (d, *J* = 14.5 Hz, 2H), 2.70 (d, *J* = 9.1 Hz, 2H), 2.35 (s, 6H), 2.05 (d, *J* = 12.3 Hz, 2H), 1.81 (d, *J* = 8.6 Hz, 2H), 1.41 – 1.27 (m, 2H), 1.20 (m, 2H). $^{13}C\{^{1}H\}$-NMR 161.6, 148.5, 137.6, 137.0, 131.9, 129.3, 128.5, 127.9, 124.4, 121.3, 64.3, 60.0, 36.8, 25.8, 25.4. HRMS(ESI-MS) *m/z* calculated for $C_{36}H_{32}F_{12}N_4$ [M+H]+ 749.2508, found 749.2518.

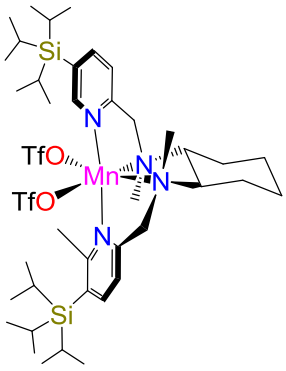
2.3 Synthesis of the complexes

[Fe(CF_3SO_3)$_2$(mcp)],[4] **[Fe(CF_3SO_3)$_2$(pdp)]**,[5] **[Fe(CF_3SO_3)$_2$(^{TIPS}mcp)]**,[1] **[Fe(CF_3SO_3)$_2$(^{TIPS}pdp)]**,[1] **[Mn(CF_3SO_3)$_2$(mcp)]**,[6] **[Mn(CF_3SO_3)$_2$(pdp)]**,[7] **[Mn(CF_3SO_3)$_2$(^{dMM}mcp)]**,[8] **[Mn(CF_3SO_3)$_2$(^{Me2N}pdp)]**[8] and **[Mn(CF_3SO_3)$_2$(^{BzIm}pdp)]**[9] complexes were prepared according to the reported procedures.



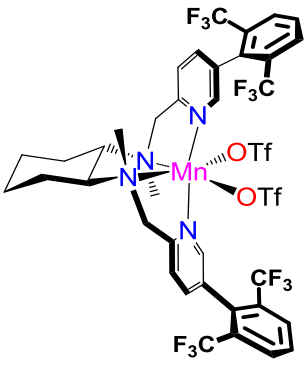
(*S*,*S*) or (*R*,*R*)

R: -Si(^{i}Pr)$_3$
-Ph(CF_3)$_2$

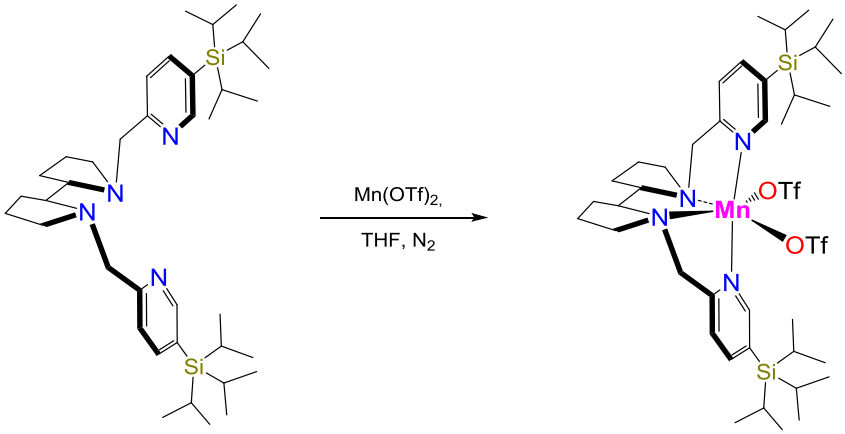


(*R*,*R*)-[Mn(CF_3SO_3)$_2$(^{TIPS}mcp)]: Under N_2 atmosphere, a suspension of $Mn(CF_3SO_3)_2$ (83.1 mg, 0.24 mmol) in anhydrous THF (1 mL) was added drop-wise to a vigorously stirred solution of **(*R*,*R*)-^{TIPS}mcp** (150 mg, 0.24 mmol) in THF (1 mL). After a few seconds the solution became cloudy and a white precipitate appeared. After stirring for 4 hours the solution was filtered off and the resultant white solid dried under vacuum. This solid was dissolved in

CH_2Cl_2 (3 mL) and the solution filtered off through Celite©. Slow diethyl ether diffusion over the resultant solution afforded, in a few days, white crystals (158 mg, 0.16 mmol, 67% yield). Anal. Calcd for $C_{40}H_{68}F_6MnN_4O_6S_2Si_2$: C, 48.52; H, 6.92; N, 5.66 Found: C, 48.65; H, 6.95; N, 5.76 %. FT-IR (ATR) v, cm^{-1}: 2943 – 2866 (C-H)sp^3, 1592, 1459, 1311, 1233, 1211, 1164, 1026, 882, 701, 635, 567, 514. ESI-HRMS calcd. for $C_{38}H_{68}N_4Si_2MnCF_3SO_3$ [M-OTf]+: 840.3878, found: 840.3888.

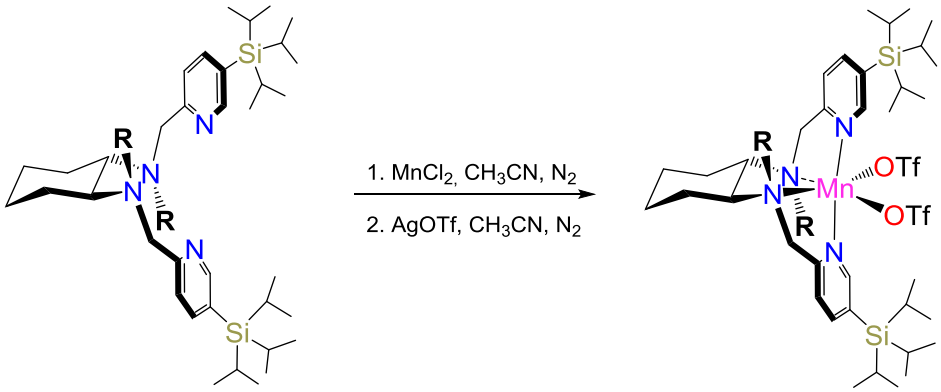


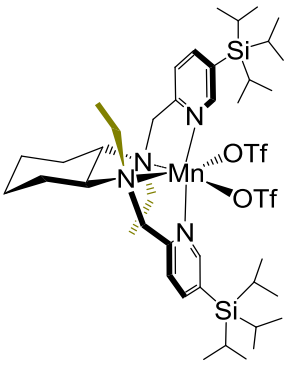
(*S,S*)-[Mn(CF_3SO_3)$_2$(^{CF3}mcp)]: Following the previous conditions, white crystals were obtained after slow diethyl ether diffusion in CH_2Cl_2. (286 mg, 0.26 mmol, 68% yield). Anal. Calcd for $C_{38}H_{32}F_{18}MnN_4O_6S_2$: C, 41.43 H, 2.93; N, 5.09 Found: C, 41.20; H, 2.91; N, 4.84 %. FT-IR (ATR) v, cm^{-1}: 3458 – 2945 (C-H)sp^3, 1612, 1459, 1293, 1127, 1067, 1030, 822, 761, 677, 635, 513. ESI-HRMS calcd. for $C_{36}H_{32}N_4F_{12}MnCF_3SO_3$ [M-OTf]+: 952.1331, found: 952.1346.



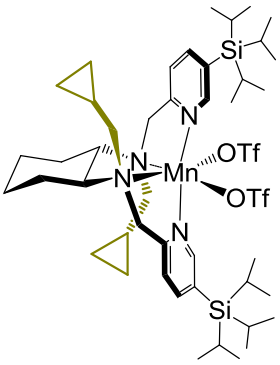
(*S,S*)-[Mn(CF_3SO_3)$_2$(^{TIPS}pdp)]: Under N_2 atmosphere, a suspension of Mn(CF_3SO_3)$_2$ (86.5 mg, 0.25 mmol) in anhydrous THF (1 mL) was added drop-wise to a vigorously stirred solution of **(*S,S*)-^{TIPS}pdp** (159 mg, 0.25 mmol) in THF (1 mL). After a few seconds the solution became cloudy and a white precipitate appeared. After stirring for 4 hours the solution was filtered off and the resultant white solid dried under vacuum. This solid was dissolved in CH_2Cl_2 (3 mL) and the solution filtered off through Celite©. Slow diethyl ether diffusion over the resultant solution afforded, in a few days, white crystals (155 mg, 0.16 mmol, 64% yield). Anal. Calcd for $C_{40}H_{66}F_6MnN_4O_6S_2Si_2$: C, 48.62;

H, 6.73; N, 5.67 Found: C, 48.83; H, 7.05; N, 5.81 %. FT-IR (ATR) ν, cm^{-1}: 2944 – 2866 (C-H)sp^3, 1593, 1463, 1307, 1229, 1030, 983, 882, 760, 682, 636, 514. ESI-HRMS calcd. for $C_{38}H_{66}N_4Si_2MnCF_3SO_3$ [M-OTf]+: 838.3721, found: 838.3723.

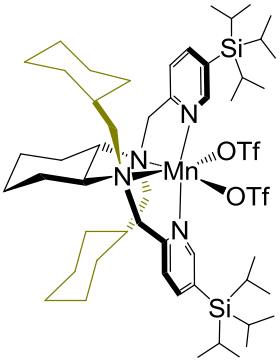




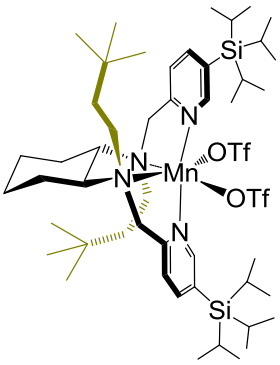
(*S,S*)-[Mn(CF_3SO_3)$_2$(^{TIPS}ecp)]: Under N_2 atmosphere, a suspension of $MnCl_2$ (30.5 mg, 0.24 mmol) in anhydrous CH_3CN (1 mL) was added drop-wise to a vigorously stirred solution of **(*S,S*)-^{TIPS}ecp** (161 mg, 0.24 mmol) in CH_3CN (1 mL). After 4 hours 2 equiv. of $AgCF_3SO_3$ (123.3 mg, 0.48 mmol) were added to the solution. After 2 hours, the reaction mixture was filtered through Celite© and dried under vacuum. The solid was crystallized by layering CH_2Cl_2 solution of the complex with hexane to yield the desired white/brown complex (163 mg, 0.16 mmol, 68% yield). Anal. Calcd for $C_{42}H_{72}F_6MnN_4O_6S_2Si_2$: C, 49.54; H, 7.13; N, 5.5 %. Found: C, 49.71; H, 7.35; N, 5.80 %. FT-IR (ATR) ν, cm^{-1}: 2944 – 2866 (C-H)sp^3, 1592, 1462, 1309, 1211, 1163, 1111, 1028, 882, 683, 636, 568, 514. ESI-HRMS calcd. for $C_{40}H_{72}N_4Si_2MnCF_3SO_3$ [M-OTf]+: 868.4191, found: 868.4200.



(*S*,*S*)-[Mn(CF_3SO_3)$_2$(^{TIPS}cpcp)]: Following the previous conditions, white crystals were obtained by layering CH_2Cl_2 solution of the complex with hexane. (153 mg, 0.14 mmol, 48% yield). Anal. Calcd for $C_{46}H_{76}F_6MnN_4O_6S_2Si_2$: C, 51.62; H, 7.16; N, 5.23 %. Found: C, 51.32; H, 7.06; N, 5.29 %. FT-IR (ATR) ν, cm^{-1}: 2944 – 2866 (C-H)sp^3, 1592, 1462, 1311, 1233, 1210, 1163, 1025, 882, 704, 682, 634, 569, 513. ESI-HRMS calcd. for $C_{44}H_{76}N_4Si_2MnCF_3SO_3$ [M-OTf]+: 920.4504, found: 920.4482.



(*S*,*S*)-[Mn(CF_3SO_3)$_2$(^{TIPS}chcp)]: Following the previous conditions, white crystals were obtained by layering CH_2Cl_2 solution of the complex with hexane. (127 mg, 0.11 mmol, 51% yield). Anal. Calcd for $C_{52}H_{88}F_6MnN_4O_6S_2Si_2$: C, 54.10; H, 7.68; N, 4.85 %. Found: C, 49.71; H, 7.50; N, 4.98 %. FT-IR (ATR) ν, cm^{-1}: 2944 – 2866 (C-H)sp^3, 1592, 1462, 1311, 1233, 1210, 1163, 1025, 882, 704, 682, 634, 569, 513. ESI-HRMS calcd. for $C_{50}H_{88}N_4Si_2MnCF_3SO_3$ [M-OTf]+: 1004.5443, found: 1004.5470.



(*S*,*S*)-[Mn(CF_3SO_3)$_2$(^{TIPS}*t*Bucp)]: Following the previous conditions, white/ brown crystals were obtained by layering CH_2Cl_2 solution of the complex with hexane. (98 mg, 0.087 mmol, 41% yiel). Anal. Calcd for $C_{50}H_{88}F_6MnN_4O_6S_2Si_2$: C, 53.12; H, 7.85; N, 4.96 %. Found: C, 53.50; H, 8.05; N, 4.91 %. FT-IR (ATR) ν, cm^{-1}: 2944 – 2866 (C-H)sp^3, 1592, 1463, 1311, 1209, 1165, 1025, 881, 682, 635, 569, 514. ESI-HRMS calcd. for $C_{49}H_{88}N_4Si_2MnCF_3SO_3$ [M-OTf]+: 980.5448, found: 980.5451.

3. Synthesis of the substrates

The following substrates were prepared according to the reported procedures. All the remaining ones are commercially available.

S2[10]

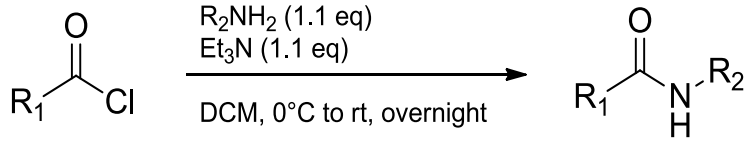
S3[11]

S8, **S9**, **S10**, **S11**, **S12**, **S13, S15**[12]

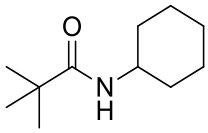
S18[13]

S19[14]

S20, S21, S22[15]

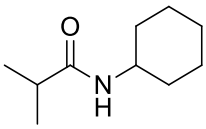


A round-bottom flask equipped with a septum and kept under nitrogen was charged with a 0.20 M solution of the amine (1.1 equiv) in dichloromethane and cooled to 0 °C. Triethylamine (1.1 equiv) was added to the reaction flask. The acyl chloride (1.0 equiv) was added dropwise and the reaction was stirred overnight at room temperature. At this point, a saturated aqueous Na_2CO_3 solution was added until pH~10-11 and then diluted with dichloromethane. The organic layer was separated from the basic aqueous layer. The aqueous layer was extracted with dichloromethane (2x) and the organic layers were combined. The organic layer was washed with 1N HCl and dried over anhydrous sodium sulfate (Na_2SO_4). The organic layer was evaporated to dryness and the crude amine was purified by flash chromatography over silica gel.



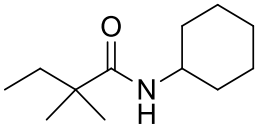
***N*-Cyclohexylpivalamide (S8):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.38 g, 79% yield).

^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.46 (bs, 1H), 3.75 - 3.73 (m, 1H), 1.92 - 1.86 (m, 2H), 1.73 - 1.57 (m, 3H), 1.44 - 1.30 (m, 3H), 1.18 (s, 9H), 1.14 – 1.04 (m, 2H). ^{13}C-NMR 177.4, 47.9, 38.5, 33.1, 27.6, 25.6, 24.9 HRMS(ESI+) *m/z* calculated for $C_{11}H_{21}NO$ [M+Na]+ 206.1515, found 206.1512.

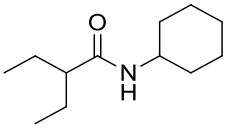


***N*-Cyclohexylisobutyramide (S9):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.43 g, 83% yield).

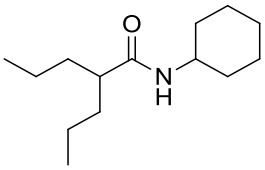
^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.34 (bs, 1H), 3.82 - 3.70 (m, 1H), 2.35 - 2.28 (q, 1H), 1.94 - 1.88 (m, 2H), 1.74 - 1.60 (m, 3H), 1.43 – 1.31 (m, 2H), 1.23 – 1.21 (m, 1H), 1.15 (d, 6H), 1.10 - 1.0 (m, 2H). ^{13}C-NMR 176.0, 47.8, 35.8, 33.2, 25.6, 24.9, 19.7. HRMS(ESI+) *m/z* calculated for $C_{10}H_{19}NO$ [M+Na]+ 192.1359, found 192.1358.



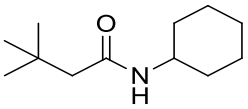
***N*-(cyclohexyl)-2,2-dimethylbutanamide (S10):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.56 g, 97% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.45 (bs, 1H), 3.86 – 3.66 (m, 1H), 1.96 – 1.80 (m, 2H), 1.75 – 1.55 (m, 4H), 1.51 (q, *J* = 7.5 Hz, 2H), 1.44 – 1.27 (m, 2H), 1.22 – 1.14 (m, 1H), 1.12 (s, 6H), 1.10 – 1.02 (m, 1H), 0.82 (t, *J* = 7.5 Hz, 3H) .^{13}C-NMR 176.6, 47.9, 42.1, 33.9, 33.2, 25.6, 25.0, 24.9, 9.1. HRMS(ESI+) *m/z* calculated for $C_{12}H_{23}NO$ [M+Na]+ 220.1672, found 220.1673.



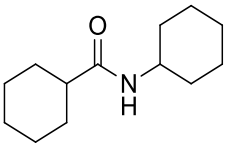
***N*-(cyclohexyl)-2-ethylbutanamide (S11):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.65 g, 84% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.62 (bs, 1H), 3.78 (tdt, *J* = 10.7, 8.1, 3.9 Hz, 1H), 1.87 (dd, *J* = 12.5, 3.8 Hz, 2H), 1.79 (tt, *J* = 9.3, 5.1 Hz, 1H), 1.67 (dt, *J* = 13.2, 3.6 Hz, 2H), 1.62 – 1.50 (m, 3H), 1.46 – 1.26 (m, 4H), 1.18 – 1.05 (m, 3H), 0.88 – 0.80 (t, *J* = 7.4 Hz, 6H). ^{13}C-NMR 174.6, 51.4, 47.8, 33.3, 25.8, 25.5, 24.9, 12.0. HRMS(ESI+) *m/z* calculated for $C_{12}H_{23}NO$ [M+Na]+ 220.1672, found 220.1673.



***N*-(cyclohexyl)-2-propylbutanamide (S12):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.53 g, 80% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.39 (bs, 1H), 3.90 – 3.70, (m, 1H), 2.04 – 1.81 (m, 3H), 1.76 – 1.51 (m, 5H), 1,45 – 1.19 (m, 8H), 1.12 (ddd, *J* = 23.0, 12.1, 3.4 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 6H). ^{13}C-NMR 174.9, 47.9, 47.8, 35.4, 33.4, 25.6, 24.9, 20.8, 14.1 HRMS(ESI+) *m/z* calculated for $C_{14}H_{27}NO$ [M+Na]+ 248.1985, found 248.1981.

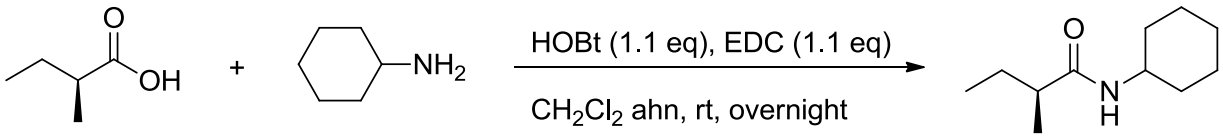


***N*-(cyclohexyl)-3,3-dimethylbutanamide (S13):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.75 g, 85% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.26 (bs, 1H), 3.84 - 3.77 (m, 1H), 2.02 (s, 2H), 1.99 - 1.86 (m, 2H), 1.77 - 1.55 (m, 3H), 1.47 - 1.28 (m, 2H), 1.25 – 1.07 (m, 3H), 1.04 (s, 9H). ^{13}C-NMR 170.6, 50.9, 48.0, 33.3, 30.8, 29.8, 25.6, 24.9 HRMS(ESI+) *m/z* calculated for $C_{12}H_{23}NO$ [M+Na]+ 220.1672, found 220.1667.



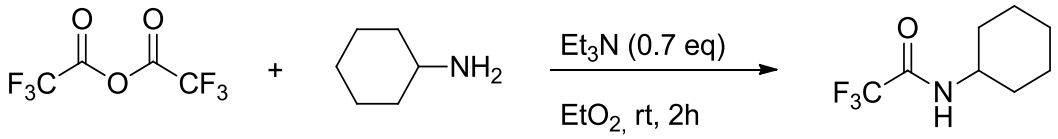
***N*-Cyclohexylcyclohexanecarboxamide (S15):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.32 g, 53% yield).

^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.34 (bs, 1H), 3.85 - 3.64 (m, 1H), 2.02 (tt, *J* = 11.7, 3.4 Hz 1H), 1.93 - 1.58 (m, 10H), 1.47 - 1.03 (m, 10H). ^{13}C-NMR 175.1, 47.7, 45.7, 33.3, 30.9, 29.7, 26.5, 25.8, 24.9 HRMS(ESI+) *m/z* calculated for $C_{13}H_{23}NO$ [M+Na]+ 232.1672, found 232.1678.

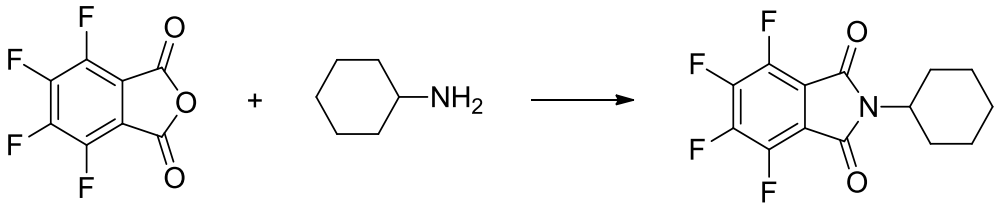


***N*-(cyclohexyl)-(S)-(+)-2-methylbutanamide (S14):** Following the traditional methodology used for peptide synthesis, the product was isolated as a white solid (0.85 g, 85% yield).

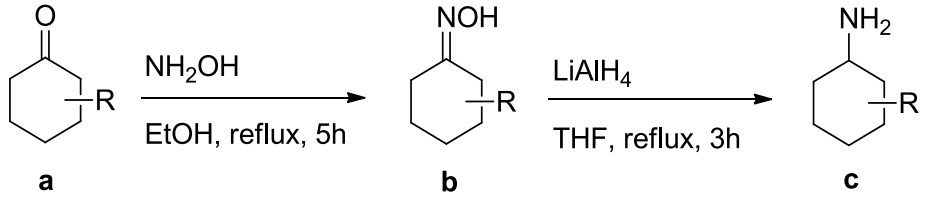
^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.41 (bs, 1H), 3.79 (tdt, *J* = 12.2, 8.1, 3.9 Hz, 1H), 2.02 (dq, *J* = 13.5, 6.8 Hz, 1H), 1.92-1.88 (m, 2H), 1.73 - 1.56 (m, 4H), 1.49 – 1.28 (m, 4H), 1.21-1.17 (m, 2H), 1.12 (dd, *J* = 12.4, 7.9 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR 175.4, 47.8, 43.3, 33.4, 27.4, 25.6, 24.9, 17.6, 11.9. HRMS(ESI+) *m/z* calculated for $C_{11}H_{21}NO$ [M+Na]+ 206.1515, found 206.1517.



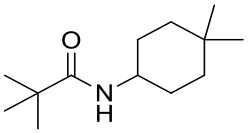
***N*-Cyclohexyltrifluoroacetamide (S17):** A round-bottom flask equipped with a septum and kept under nitrogen was charged with cyclohexylamine (1.0 equiv, 0.24 g, 2.4 mmol) and solubilized in diethylether (1.4 M). Triethylamine (0.7 equiv) was added to the reaction flask. Trifluoroacetic anhydride (1.0 equiv, 0.5 g, 2.4 mmol) in diethylether (1.4 M) was added dropwise and the reaction was stirred for 2 hours at room temperature. At this point H_2O was added and the basic aqueous layer was separated. The organic layer was extracted with $NaHCO_3$, saturated with NH_4Cl and dried over anhydrous sodium sulfate (Na_2SO_4). The organic layer was evaporated to dryness and the crude amine was purified by flash chromatography over silica gel using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.25 g, 1.3 mmol 54% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 6.24 (bs, 1H), 3.94 - 3.69 (m, 1H), 2.08 – 1.88 (m, 2H), 1.87 - 1.59 (m, 3H), 1.52 – 1.08 (m, 5H). ^{13}C-NMR 156.5, 117.8, 113.9, 100.0, 49.2, 32.4, 25.2, 24.6 HRMS(ESI+) *m/z* calculated for $C_8H_{12}F_3NO$ [M+Na]+ 218.0763, found 218.0762.



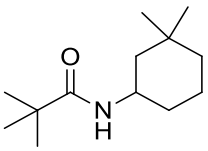
***N*-Cyclohexyltetrafluorophthalimide (S19):** Tetrafluorophthalic anhydride (0.5 g, 2.3 mmol, 1.2 eq.) was added to a solution of cyclohexylamine (0.19 g, 1.9 mmol, 1.0 eq.) in glacial acetic acid and refluxed overnight. The solvent was removed under reduced pressure and the reaction mixture was refluxed in acetic anhydride for 12 h. The solvent was evaporated and the crude amide was purified by flash chromatography over silica gel with hexane:ethyl acetate 3:1 and the product was concentrated to dryness. The product was isolated as a yellow solid (0.24 g, 82% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 4.08 (t, *J* = 12.4 Hz, 1H), 2.26 – 2.06 (m, 2H), 1.87 (d, *J* = 13.0 Hz, 2H), 1.70 (d, *J* = 12.0 Hz, 3H), 1.47 – 1.13 (m, 3H). ^{13}C-NMR 162.5, 146.2, 144.5, 143.5, 141.9, 113.8, 51.9, 29.6, 25.9, 24.9. HRMS(ESI+) *m/z* calculated for $C_{14}H_{11}F_4NO_2(CH_3OH)$ [M+Na]+ 356.0880, found 356.0885.



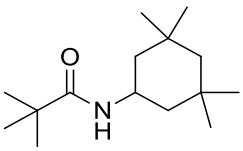
Hydroxylamine hydrochloride (1.2 equiv) followed by pyridine (3.0 equiv) was added to a solution of ketone (**a**) (1.0 equiv) in absolute ethanol and the reaction mixture was heated to reflux temperature under stirring for 5 hours. The reaction was then quenched with water and the product extracted with ethyl acetate (2 x 50 mL). The organic fractions were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to obtain the oxime (**b**) that was used in the next step without further purification. To a stirred solution of lithium aluminium hydride (0.5 equiv) in anhydrous THF under N_2, was added a solution of intermediate **b** drop wise. The reaction was slowly heated to reflux temperature for 3 hours. After this, the reaction mixture was quenched with 1M NaOH solution at 5°C. After filtration through Celite© and extraction with ethyl acetate (2 x 50 mL) the organic fractions were dried over anhydrous $MgSO_4$, the solvent removed under vacuum and the obtained intermediate **c** was used in the next acylation step without further purification to give the corresponding amide.



***N*-(4,4-dimethylcyclohexyl)pivalamide (S20):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.39 g, 94% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.49 (s, 1H), 3.68 (tt, *J* = 9.2, 4.8 Hz, 1H), 1.75-1.72 (m, 2H), 1.38 – 1.17 (m, 6H), 1.17 (s, 9H), 0.91 (s, 6H).^{13}C-NMR 177.6, 48.1, 38.5, 37.6, 31.5, 29.5, 28.7, 27.6, 25.1. HRMS(ESI+) *m/z* calculated for $C_{13}H_{25}NO$ [M+Na]+ 234.1828, found 234.1822.



***N*-(3,3-dimethylcyclohexyl)pivalamide (S21):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.38 g, 70% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.32 (d, *J* = 7.0 Hz, 1H), 3.88 (tdt, *J* = 12.0, 8.0, 4.1 Hz, 1H), 1.95 – 1.92 (m, 1H), 1.64 – 1.46 (m, 4H), 1.35 – 1.31 (m, 1H), 1.15 (s, 9H), 1.09 – 0.99 (m, 2H), 0.94 (s, 3H), 0.91 (s, 3H), 0.88-0.84 (m, 1H).^{13}C-NMR 177.5, 46.0, 45.2, 38.53, 38.46, 33.3, 33.0, 31.7, 27.6, 24.7, 21.3. HRMS(ESI+) *m/z* calculated for $C_{13}H_{25}NO$ [M+Na]+ 234.1828, found 234.1826.



***N*-(3,3,5,5-tetramethylcyclohexyl)pivalamide (S22):** Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.41 g, 55% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.35 (d, *J* = 7.5 Hz, 1H), 4.07 (dtd, *J* = 12.0, 8.2, 3.9 Hz, 1H), 1.70 (dddd, *J* = 11.4, 3.7, 2.2, 1.3 Hz, 2H), 1.36 – 1.19 (m, 2H), 1.18 (s, 9H), 1.07 (s, 6H), 0.91 (s, 6H), 0.84 (d, *J* = 12.0 Hz, 2H).^{13}C-NMR 177.6, 51.7, 46.1, 43.3, 38.5, 35.1, 32.2, 27.6, 27.3. HRMS(ESI+) *m/z* calculated for $C_{15}H_{29}NO$ [M+Na]+ 262.2141, found 262.2139.

4. Oxidation reactions

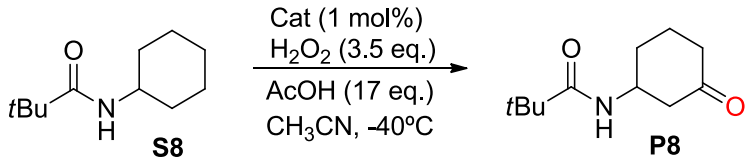
Hydrogen peroxide solutions employed in the oxidation reactions were prepared by diluting commercially available hydrogen peroxide (30% H_2O_2 solution in water, Aldrich) in acetonitrile to achieve a 1.5 M. Commercially available glacial acetic acid (99-100%) purchased from Riedel-de-Haën was employed. The purity of the amide substrates synthetized as described above was in all cases >99%. Carboxylic acids were purchased from Acros and Aldrich.

4.1 Reaction protocol for catalysis

An acetonitrile solution (400 µL) of the substrate (0.25 M) and the corresponding complex (2.5 mM) was prepared in a vial (10 mL) equipped with a stir bar cooled at -40 ºC, in a CH_3CN/N_2(liq) bath. 98 µL (neat, 17 equiv.) of acetic acid were added directly to the solution. Then, 236 µL of a 1.5 M hydrogen peroxide solution in CH_3CN (3.5 equiv.) were added by syringe pump over a period of 30 min. At this point, an internal standard (biphenyl) was added and the solution was quickly filtered through a basic alumina plug, which was subsequently rinsed with 2 x 1 mL AcOEt. GC analysis of the solution provided substrate conversions and product yields relative to the internal standard integration. Isomer ratio was determined by GC or ^{1}H-NMR. Commercially unavailable products were identified by a combination of ^{1}H, ^{13}C{^{1}H}-NMR analysis, and HRMS. The oxidized products were identified by comparison to the GC retention time of racemate products.

Attempts to trap the alcohol product were performed by carrying out catalytic reactions in the presence of acetic anhydride or trifluoroacetic anhydride. Unfortunately, under these conditions oxidation did not take place. Reactions performed using substoichiometric amounts of oxidant, providing low conversion of the substrate did not result in the accumulation of the alcohol, indicating that this initial product is much more reactive against oxidation than the starting material, and can not accumulate in solution.

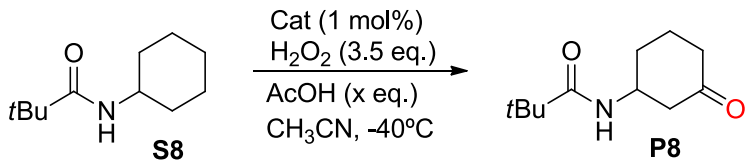
Table S1. Oxidation of N-(cyclohexyl)pivalamide (S8) with (*S,S*)-[Mn(CF_3SO_3)$_2$(^{TIPS}cpcp)], (*S,S*)-[Mn(CF_3SO_3)$_2$ (^{TIPS}chcp)] and (*S,S*)-[Mn(CF_3SO_3)$_2$ (^{TIPS}tBucp)]



Entry	Cat.	Conv (%)[a]	Yield (%)[a]	Ee %
1	**Mn(^{TIPS}cpcp)**	85	60	80
2	**Mn(^{TIPS}chcp)**	22	10	86
3	**Mn(^{TIPS}tBucp)**	31	20	56

[a]Conversions and yields determined from crude reaction mixtures by GC.
Ee's determined by GC with chiral stationary phase

Table S2. Oxidation of N-(cyclohexyl)pivalamide (S8) with (*R,R*)-[Mn(CF_3SO_3)$_2$ (^{TIPS}mcp)] using different equivalents of acetic acid



Entry	x (equiv)	Conv (%)[a]	Yield K_3 (%)[a]	Ee %
1	**50**	>99	90	72
2	**25**	>99	90	73
3	**17**	>99	90	79
4	**13**	>99	84	79
5	**10**	80	74	74
6	**8**	86	74	78
7	**5**	33	28	75

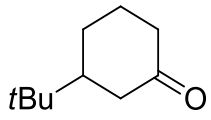
[a]Conversions and yields determined from crude reaction mixtures by GC.
Ee's determined by GC with chiral stationary phase

4.2 General Procedure for product isolation

A 25 mL round bottom flask was charged with: catalyst (6 µmol, 1.0 mol%), substrate (1 equiv.), CH_3CN (3.3 mL) and a magnetic stir bar. The carboxylic acid of choice was the added (17 equiv.) and the mixture was cooled at -40 ºC in an CH_3CN/N_2(liq) bath under magnetic stirring. Then, 1.4 mL of a 1.5 M hydrogen peroxide solution in CH_3CN (3.5 equiv.) were added by syringe pump over a period of 30 min at -40°C. At this point, 15 mL of an aqueous $NaHCO_3$ saturated solution were added to the mixture. The resultant solution was extracted with CH_2Cl_2 (3 x 10 mL). Organic fractions were combined, dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the oxidized product. This residue was filtered by silica gel column to obtain the pure product.

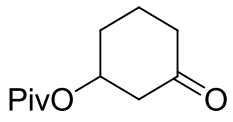
5. Characterization of the isolated products

The oxidation products obtained after oxidation of substrates **S1**, **S3**, **S4**, **S5**, **S6**, **S18** and **S19** (**P1**, **P3**, **P4**, **P5**, **P6, P18, P19**, respectively) were collected as mixtures of C3 and C4 oxidation products.



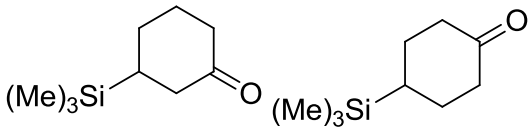
3-*tert*-butylcyclohexanone (P1 (K_3), Scheme 4) purification by flash chromatography (SiO_2; hexane:AcOEt 5:1) gave the product as a white solid (50% total yield (K_3+K_4), 64% ee K_3); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 2.45-2.43 (m, 1H), 2.37-2.35 (m, 1H), 2.23 (dt, J = 6.0, 13.5 Hz, 1H), 2.12-2.08 (m, 1H), 2.04 (t, J = 12.0 Hz, 1H), 1.96-1.91 (m, 1H), 1.59-1.45 (m, 2H), 1.32 (qd, J = 3.6, 12.8 Hz, 1H), 0.89 (s, 9H). HRMS(ESI+) *m/z* calculated for $C_{10}H_{18}O$ [M+Na]+ 177.1250, found 177.1250. Chiral GC analysis with CYCLOSIL-B. Spectroscopic data are in agreement with a previous literature report.[16]

4-*tert*-butylcyclohexanone (P1 (K_4)) ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 2.41-2.39 (m, 1H), 2.33-2.31 (m, 1H), 2.23 (dt, J = 6.0, 13.5 Hz, 1H), 2.12-2.08 (m, 1H), 2.04 (t, J = 12.0 Hz, 1H), 1.96-1.91 (m, 1H), 1.59-1.45 (m, 2H), 1.32 (qd, J = 3.6, 12.8 Hz, 1H), 0.89 (s, 9H). ^{13}C-NMR 212.9, 49.4, 43.6, 41.3, 32.7, 27.2, 26.2, 25.6. Spectroscopic data are in agreement with a previous literature report.[16]



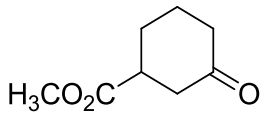
3-oxocyclohexylpivalate (P2 (K_3), Scheme 4) purification by flash chromatography (SiO_2; hexane:AcOEt 5:1) gave the product as a white solid (36% yield, 61% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.18 (tt, *J* = 5.7, 3.0 Hz, 1H), 2.57 (ddd, *J* = 15.8, 10.2, 6.1 Hz, 2H), 2.42 – 2.36 (m, 2H), 2.19 – 2.02 (m, 4H), 1.26 (s, 9H). ^{13}C-NMR 209.9, 177.8, 68.0, 39.0, 37.2, 30.4, 27.2. HRMS(ESI+) *m/z* calculated for $C_{11}H_{18}O_3$ [M+Na]+ 221.1148, found 221.1146. $[\alpha]_D^{24}$ +9.3 ($CHCl_3$, *c* 0.333). Chiral GC analysis with CYCLOSIL-B.

4-oxocyclohexylpivalate (P2 (K_4)) white solid product (9% yield); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.28 (tt, *J* = 5.5, 2.8 Hz, 1H), 2.64 (dd, *J* = 14.8, 4.2 Hz, 1H), 2.56 – 2.35 (m, 4H), 2.07 (dd, *J* = 11.3, 4.6 Hz, 1H), 1.98 (d, *J* = 7.9 Hz, 1H), 1.93 – 1.85 (m, 1H), 1.20 (s, 9H). ^{13}C-NMR 208.3, 177.5, 71.2, 46.4. 41.0, 29.7, 29.1, 27.1, 20.9. HRMS(ESI+) *m/z* calculated for $C_{11}H_{18}O_3$ [M+Na]+ 221.1148, found 221.1140.



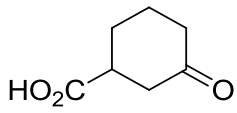
P3 (K_3) **P3 (K_4)**

(P3 (K_3+K_4), (*R*,*R*')-Mn-(^{TIPS}mcp) as catalyst and cyclopropanecarboxylic acid) purification by flash chromatography (SiO_2; hexane:AcOEt 3:1) gave the product as a white solid (49% total yield, 34% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 1.81 – 1.70 (m, 8H), 1.29 – 1.21 (m, 5H), 1.10 (q, *J* = 12.7 Hz, 4H), 0.67 – 0.48 (m, 1H), -0.03 (s, *J* = 0.7 Hz, 18H). ^{13}C-NMR 28.1, 27.4, 27.0, 26.2, -3.6. HRMS(ESI+) *m/z* calculated for $C_9H_{18}OSi$ [M+Na]+ 193.1019, found 193.1019. Chiral GC analysis with CYCLOSIL-B.

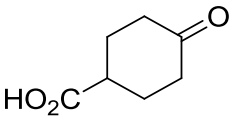


methyl-3-oxocyclohexanecarboxylate (P4 (K_3) Table 2, entry 4) purification by flash chromatography (SiO_2; hexane:AcOEt 4:1) gave the product as a white solid (52% total yield (K_3+K_4), 11% ee K_3); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 3.69 (s, 3H), 2.84-2.75 (m, 1H), 2.55 (d, J = 8.0 Hz, 2H), 2.40-2.29 (m, 2H), 2.13-2.02 (m, 2H), 1.87-1.81 (m, 1H), 1.77-1.69 (m, 1H). HRMS(ESI+) *m/z* calculated for $C_8H_{12}O_3$ [M+Na]+ 179.0679, found 179.0680. Chiral GC analysis with CYCLOSIL-B. Spectroscopic data are in agreement with a previous literature report.[17]

methyl-4-oxocyclohexanecarboxylate (P4 (K_4)) ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, 3.71 (s, 3H), 2.83- 2.75 (m, 1H), 2.50-2.46 (m, 2H), 2.40-2.29 (m, 2H), 2.23-2.19 (m, 2H), 2.13-2.02 (m, 2H). Spectroscopic data are in agreement with a previous literature report.[18]

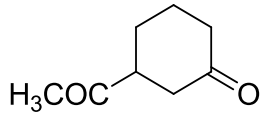


P5 (K_3)

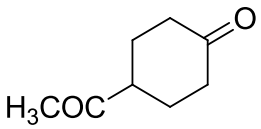


P5 (K_4)

(**P5 (K_3+K_4), Table 2, entry 5)** purification by flash chromatography (SiO_2; hexane:AcOEt 2:1) gave the product as a white solid (30% total yield, 9% ee K_3); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 2.93-2.80 (m, 2H), 2.61-2.58 (m, 2H), 2.56-2.50 (m, 2H), 2.44-2.36 (m, 4H), 2.30-2.23 (m, 2H), 2.22-2.16 (m, 1H), 2.14-2.03 (m, 3H), 1.96-1.87 (m, 1H), 1.84-1.74 (m, 1H). ^{13}C-NMR 209.9, 209.0, 180.4, 179.4, 42.9, 42.7, 40.9, 40.3, 39.6, 29.7, 28.2, 27.5, 24.3. HRMS(ESI+) *m/z* calculated for $C_7H_9O_3$ [M] 141.0546, found 141.0563. Chiral GC analysis with CYCLOSIL-B. Spectroscopic data are in agreement with a previous literature report.[19] The ee was determined after esterification following a reported procedure.[19]

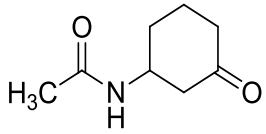


P6 (K_3)



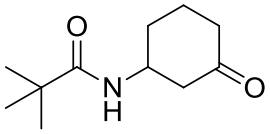
P6 (K_4)

(P6 (K_3+K_4), Table 2, entry 6) purification by flash chromatography (SiO_2; hexane:AcOEt 4:1) gave the product as a white solid (66% total yield, 8% ee K_3); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 2.90 – 2.80 (m, 1H), 2.79 – 2.72 (m, 1H), 2.47-2.36 (m, 3H), 2.34 – 2.22 (m, 4H), 2.17 (s, 3H), 2.14 (s, 3H), 2.07-1.97 (m, 3H), 1.89-1.79 (m, 1H), 1.75-1.59 (m, 2H). ^{13}C-NMR 210.0, 209.8, 209.7, 208.5, 50.8, 48.4, 42.3, 40.8, 39.7, 28.17, 28.15, 27.8, 27.1, 24.7. HRMS(ESI+) *m/z* calculated for $C_8H_{12}O_2$ [M+Na]+ 163.0730, found 163.0738. Chiral GC analysis with CYCLOSIL-B.

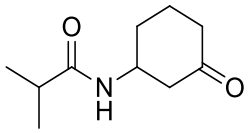


***N*-(3-oxocyclohexyl)acetamide (P7, Table 4, entry 1),** purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid; (61% yield, 78% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.79 (bs, 1H), 4.30 - 4.25 (m, 1H), 2.72-2.68 (m, 1H), 2.47-2.38 (m, 2H), 2.28 (m, 2H), 2.09 (m, 1H), 1.98 (s, 3H), 1.78 – 1.69 (m, 2H). ^{13}C-NMR 209.0, 169.4,

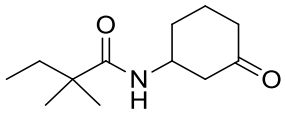
48.5, 47.6, 41.0, 30.8, 23.4, 22.1. HRMS(ESI+) *m/z* calculated for $C_8H_{13}NO_2$ [M+Na]+ 178.0838, found 178.0839. $[\alpha]_D^{24}$ -6.1 ($CHCl_3$, *c* 0.312). Chiral GC analysis with CYCLOSIL-B.



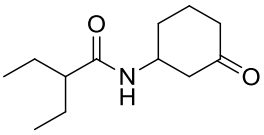
***N*-(3-oxocyclohexyl)pivalamide (P8, Table 4, entry 3),** purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid (84% yield, 91% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.60 (bs, 1H), 4.33 - 4.15 (m, 1H), 2.69 (ddt, *J* = 13.9, 4.8, 1.5 Hz, 1H), 2.49 - 2.20 (m, 3H), 2.14 – 1.97 (m, 1H), 1.99 – 1.59 (m, 3H), 1.18 (s, 6H). ^{13}C-NMR 209.0, 177.7, 48.4, 47.6, 41.0, 38.6, 30.7, 27.5, 22.2. HRMS(ESI+) *m/z* calculated for $C_{11}H_{19}NO_2$ [M+Na]+ 220.1308, found 220.1307. $[\alpha]_D^{24}$ -2.9 ($CHCl_3$, *c* 0.272). Chiral GC analysis with CYCLOSIL-B.



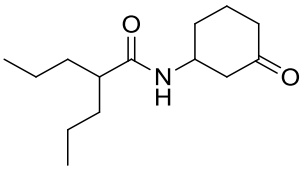
***N*-(3-oxocyclohexyl)isobutyramide (P9, Table 4, entry 2),** purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid (60% yield, 88% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.57 (bs, 1H), 4.35 - 4.17 (m, 1H), 2.69 (ddt, *J* = 13.9, 4.8, 1.4 Hz, 1H), 2.48 – 2.18 (m, 4H), 2.14 – 1.92 (m, 2H), 1.86 – 1.62 (m, 2H), 1.14 (dd, *J* = 6.9, 1.0 Hz, 6H). ^{13}C-NMR 209.0, 176.3, 48.2, 47.6, 41.0, 35.6, 30.7, 22.1, 19.6, 19.5 HRMS(ESI+) *m/z* calculated for $C_{10}H_{17}NO_2$ [M+Na]+ 206.1151, found 206.1152. $[\alpha]_D^{24}$ -6.5 ($CHCl_3$, *c* 0.232). Chiral GC analysis with CYCLOSIL-B.



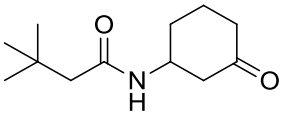
(*S*)-*N*-(3-oxocyclohexyl)-2,2-dimethylbutanamide (P10, Table 4, entry 4), purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid; (85% yield, 94% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.81 (d, *J* = 6.3 Hz, 1H), 4.25 - 4.08 (m, 1H), 2.60 (d, *J* = 13.6 Hz, 1H), 2.38 - 2.26 (m, 1H), 2.26 – 2.13 (m, 2H), 2.00 – 1.90 (m, 1H), 1.65 (q, *J* = 12.0, 10.7 Hz, 2H), 1.46 (q, *J* = 7.3 Hz, 2H), 1.07 (s, 6H), 0.76 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR 208.9, 176.9, 48.3, 47.6, 42.2, 40.8, 33.8, 30.8, 24.84, 24.82, 22.2, 9.1. HRMS(ESI+) *m/z* calculated for $C_{12}H_{21}NO_2$ [M+H]+ 234.1465, found 234.1464. $[\alpha]_D^{24}$ -5.2 ($CHCl_3$, *c* 0.302). Chiral GC analysis with CYCLOSIL-B. Structure was confirmed by X-Ray diffraction analysis.



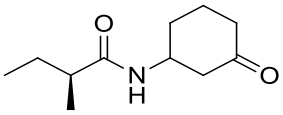
***N*-(3-oxocyclohexyl)-2-ethylbutanamide (P11, Table 4, entry 5),** purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid; (45% yield, 96% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.71 (d, *J* = 6.9 Hz, 1H), 4.31 (qt, *J* = 8.8, 4.4 Hz, 1H), 2.69 (dd, *J* = 14.1, 4.9 Hz, 1H), 2.45 - 2.22 (m, 2H), 2.12 – 1.93 (m, 2H), 1.83 (ddd, *J* = 14.1, 9.1, 5.1 Hz, 1H), 1.79 – 1.60 (m, 2H), 1.62 – 1.53 (m, 2H), 1.52 – 1.40 (m, 2H), 0.87 (td, *J* = 7.4, 3.4 Hz, 6H). ^{13}C-NMR 209.0, 175.0, 51.3, 48.3, 47.8, 40.9, 30.9, 25.8, 25.7, 22.1, 12.05, 12.02. HRMS(ESI+) *m/z* calculated for $C_{12}H_{21}NO_2$ [M+Na]+ 234.1465, found 234.1459. $[\alpha]_D^{24}$ -5.17 ($CHCl_3$, *c* 0.6). Chiral GC analysis with CYCLOSIL-B.



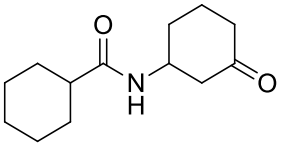
***N*-(3-oxocyclohexyl)-2-ethylbutanamide (P12, Table 4, entry 6),** purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid; (8% yield, 90% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.46 (d, *J* = 7.3 Hz, 1H), 4.32 (qt, *J* = 8.5, 4.3 Hz, 1H), 2.71 (dd, *J* = 14.1, 4.9 Hz, 1H), 2.46 - 2.37 (m, 1H), 2.30 (dt, *J* = 14.2, 7.9 Hz, 2H), 2.09 (dd, *J* = 12.8, 3.4, Hz, 1H), 1.98 (ddd, *J* = 12.7, 8.7, 5.1 Hz, 2H), 1.86 – 1.66 (m, 3H), 1.65 – 1.54 (m, 2H), 1.43 – 1.29 (m, 6H), 0.94 – 0.89 (m, 6H). ^{13}C-NMR 208.9, 175.3, 48.3, 47.77, 47.76, 41.0, 35.3, 35.2, 30.9, 29.7, 22.2, 20.8, 20.7, 14.1. HRMS(ESI+) *m/z* calculated for $C_{14}H_{25}NO_2$ [M+Na]+ 262.1778, found 262.1781. $[\alpha]_D^{24}$ -2.0 ($CHCl_3$, *c* 0.204). Chiral GC analysis with CYCLOSIL-B.



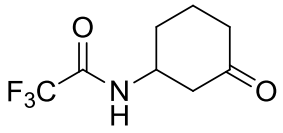
***N*-(3-oxocyclohexyl)-3,3-dimethylbutanamide (P13, Table 4, entry 7),** purification by flash chromatography (SiO_2; hexane:AcOEt 1:2) gave the product as a white solid (69% yield, 94% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 6.18 (d, *J* = 7.7 Hz, 1H), 4.21 – 4.12 (m, 1H), 2.59 (dd, *J* = 14.0, 4.8 Hz, 1H), 2.39 - 2.16 (m, 3H), 1.97 (s, 4H), 1.74 – 1.56 (m, 2H), 0.96 (s, 9H). ^{13}C-NMR 209.1, 171.0, 50.2, 48.2, 47.7, 40.8, 30.9, 30.8, 29.8, 22.1. HRMS(ESI+) *m/z* calculated for $C_{12}H_{21}NO_2$ [M+Na]+ 234.1465, found 234.1472. $[\alpha]_D^{24}$ -7.3 ($CHCl_3$, *c* 0.94). Chiral GC analysis with CYCLOSIL-B.



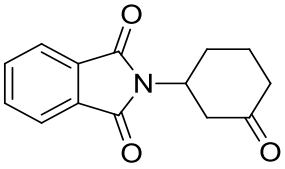
***N*-(3-oxocyclohexyl)-(S)-(+)-2-methylbutanamide (P14, Table 4, entry 8),** purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid; (50% yield, 91% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.97 (d, *J* = 7.2 Hz, 1H), 4.28 - 4.15 (m, 1H), 2.65 (dd, *J* = 14.1, 4.8 Hz, 1H), 2.36 (d, *J* = 14.6 Hz, 1H), 2.30 – 2.20 (m, 2H), 2.05 (dt, *J* = 16.4, 8.2 Hz, 2H), 1.97 – 1.94 (m, 1H), 1.74 – 1.67 (m, 2H), 1.65 – 1.58 (m, 1H), 1.43 – 1.36 (m, 1H), 1.08 (d, *J* = 6.9 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR 209.0, 175.8, 48.2, 47.8, 43.0, 40.9, 30.8, 27.3, 22.1, 17.5. 11.8. HRMS(ESI+) *m/z* calculated for $C_{11}H_{19}NO_2$ [M+Na]+ 220.1308, found 220.1303. $[\alpha]_D^{24}$ +9.5 ($CHCl_3$, *c* 0.508). Chiral GC analysis with CYCLOSIL-B.



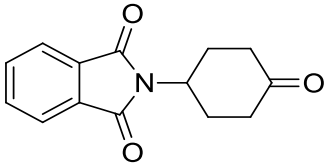
***N*-(3-oxocyclohexyl)cyclohexanecarboxamide (P15, Table 4, entry 9),** purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid (75% yield, 91% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.55 (d, *J* = 6.6 Hz, 1H), 4.31 – 4.23 (m, 1H), 2.69 (dd, *J* = 14.0, 4.8 Hz, 1H), 2.46 - 2.35 (m, 1H), 2.30 - 2.24 (m, 2H), 2.04 (t, *J* = 11.7 Hz, 2H), 1.79 (d, *J* = 13.8 Hz, 4H), 1.72 – 1.63 (m, 2H), 1.42 (dd, *J* = 22.9, 12.4 Hz, 2H), 1.25 (dd, *J* = 17.2, 10.9 Hz, 5H). ^{13}C-NMR 209.0, 175.4, 48.2, 47.7, 45.5, 41.0, 30.7, 29.7, 29.6, 25.68, 25.66, 22.16. HRMS(ESI+) *m/z* calculated for $C_{13}H_{21}NO_2$ [M+Na]+ 246.1465, found 246.1473. $[\alpha]_D^{24}$ -2.7 ($CHCl_3$, *c* 0.412). Chiral GC analysis with CYCLOSIL-B.



***N*-(3-oxocyclohexyl)trifluoroacetamide (P17, Table 4, entry 11),** purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid (65% yield, 65% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 7.19 (s, 1H), 4.21 (s, 1H), 2.69 (dd, *J* = 14.3, 4.9 Hz, 1H), 2.50 – 2.35 (m, 2H), 2.35 – 2.19 (m, 1H), 2.19 – 1.98 (m, 2H), 1.88 – 1.67 (m, 2H). ^{13}C-NMR 207.9, 156.8, 49.2, 46.5, 40.5, 38.8, 30.0, 21.8. HRMS(ESI+) *m/z* calculated for $C_{10}H_8F_3NO_2$ [M+H]+ 232.0580, found 232.0560. $[\alpha]_D^{24}$ -5.6 ($CHCl_3$, *c* 0.54). Chiral GC analysis with CYCLOSIL-B.

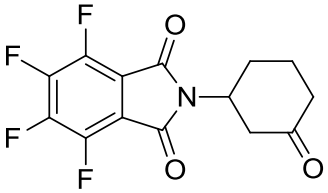


P18 (K_3)

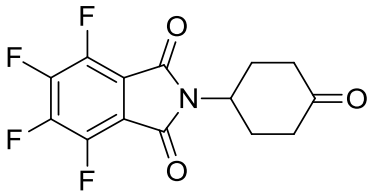


P18 (K_4)

***N*-(3-oxocyclohexyl)phthalimide (P18 (K_3+K_4), Table 4, entry 12),** purification by flash chromatography (SiO_2; hexane:AcOEt 3:1) gave the product as a white solid; (37% total yield, 62% ee K_3); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 7.90 – 7.80 (m, 3H), 7.78 – 7.67 (m, 3H), 4.64 (tt, *J* = 12.1, 4.1 Hz, 1H), 4.57 – 4.43 (m, 1H), 3.41 – 3.27 (m, 1H), 2.83 – 2.63 (m, 1H), 2.58 – 2.49 (m, 5H), 2.20 – 2.11 (m, 2H), 2.09 – 2.05 (m, 1H), 1.99 – 1.95 (m, 1H), 1.69 (ddddd, *J* = 17.5, 12.7, 10.4, 6.6, 3.5 Hz, 1H). ^{13}C-NMR 208.8, 207.8, 168.1, 167.9, 134.2, 134.1, 131.8, 131.7, 123.34, 123.26, 49.0, 48.3, 44.8, 40.4, 39.8, 28.6, 22.4. HRMS(ESI+) *m/z* calculated for $C_{14}H_{13}NO_3$ [M+Na]+ 266.0788, found 266.0783. HPLC analysis. Spectroscopic data are in agreement with a previous literature report.[20]

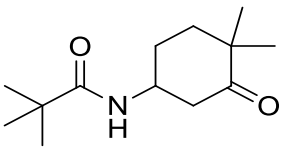


P19 (K_3)



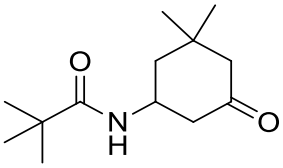
P19 (K_4)

***N*-(3-oxocyclohexyl)tetrafluorophthalimide (P19 (K_3+K_4), Table 4, entry 13)** purification by flash chromatography (SiO_2; hexane:AcOEt 3:1) gave the product as a white solid; (40% total yield); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 4.62 (tt, *J* = 12.1, 4.1 Hz, 1H), 4.53 – 4.44 (m, 1H), 3.28 (ddd, *J* = 13.5, 12.4, 0.9 Hz, 1H), 2.68 (qd, *J* = 12.7, 5.5 Hz, 2H), 2.57 – 2.37 (m, 8H), 2.20 – 2.00 (m, 1H), 2.13 – 2.03 (m, 2H), 1.96 (dtt, *J* = 12.9, 3.9, 2.2 Hz, 1H), 1.78 – 1.65 (m, 1H). ^{13}C-NMR 146.4, 144.8, 143.8, 142.1, 113.5, 49.8, 49.2, 44.4, 40.3, 39.6, 28.3, 22.2. HRMS(ESI+) *m/z* calculated for $C_{14}H_9F_4NO_3$ [M+Na]+ 338.0411, found 338.0417. HPLC analysis.



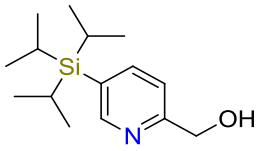
***N*-(4,4-dimethyl-3-oxocyclohexyl)pivalamide (P20, Scheme 4),** purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid; (52% yield, 76% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.57 (s, 1H), 4.22 – 4.13 (m, 1H), 2.70 (ddd, *J* =

14.1, 4.9, 1.5 Hz, 1H), 2.43 (dd, *J* = 14.1, 9.6 Hz, 1H), 2.03 (ddtd, *J* = 13.4, 8.0, 4.0, 2.0 Hz, 1H), 1.87 – 1.74 (m, 1H), 1.74 – 1.61 (m, 2H), 1.20 (s, 9H), 1.15 (d, *J* = 9.9 Hz, 6H). ^{13}C-NMR 213.0, 177.7, 49.0, 44.5, 43.9, 38.7, 36.6, 27.5, 27.3, 25.0, 24.7. HRMS(ESI+) *m/z* calculated for $C_{13}H_{23}NO_2$ [M+Na]+ 248.1621, found 248.1621. $[\alpha]_D^{24}$ +19.5 ($CHCl_3$, *c* 0.574). Chiral GC analysis with CYCLOSIL-B.

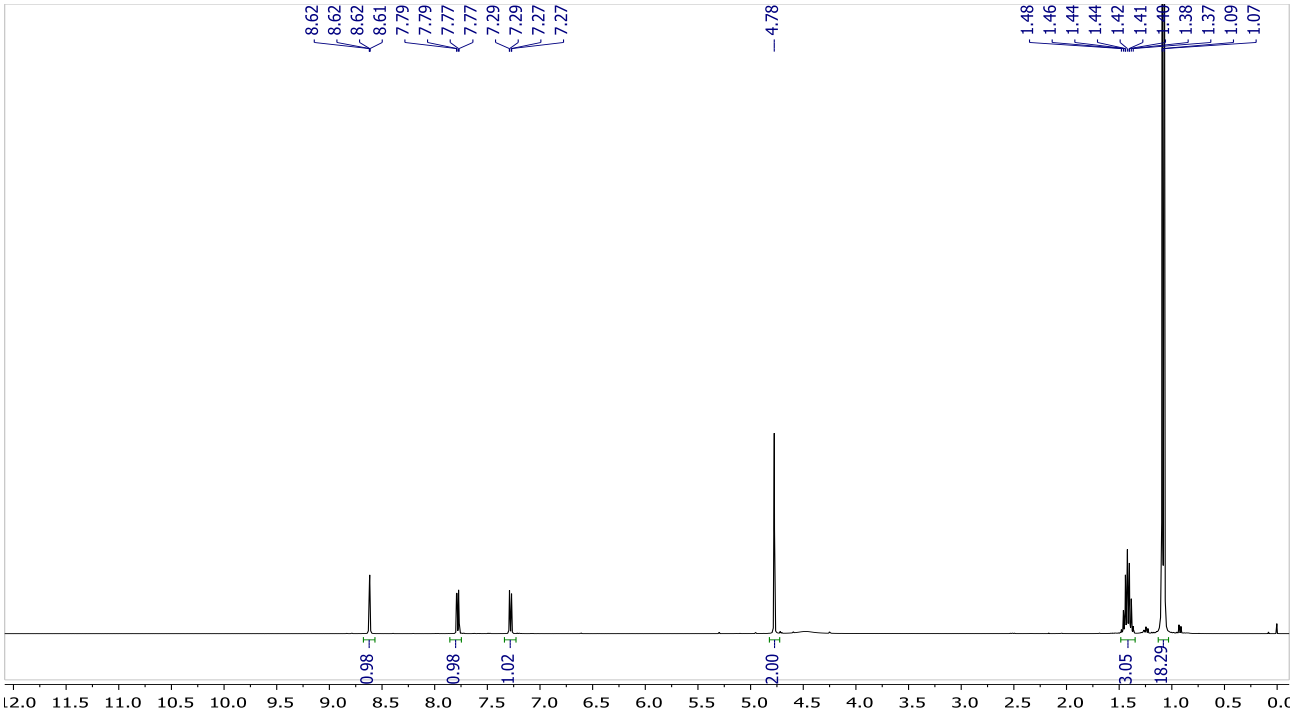


***N*-(5,5-dimethyl-3-oxocyclohexyl)pivalamide (P21, Scheme 4),** purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid; (39% yield, 55% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.47 (d, *J* = 7.6 Hz, 1H), 4.28 (tddd, *J* = 12.0, 7.8, 5.0, 4.3 Hz, 1H), 2.69 (ddt, *J* = 13.7, 5.1, 1.8 Hz, 1H), 2.36 – 2.07 (m, 3H), 1.90 (ddt, *J* = 12.9, 4.0, 1.9 Hz, 1H), 1.59 – 1.42 (m, 1H), 1.19 (s, 9H), 1.09 (s, 3H), 0.95 (s, 3H). ^{13}C-NMR 208.1, 177.7, 54.1, 47.1, 45.2, 44.7, 38.6, 33.5, 31.7, 27.5, 25.9. HRMS(ESI+) *m/z* calculated for $C_{13}H_{23}NO_2$ [M+Na]+ 248.1621, found 248.1627. $[\alpha]_D^{24}$ -12.0 ($CHCl_3$, *c* 0.366). Chiral GC analysis with CYCLOSIL-B

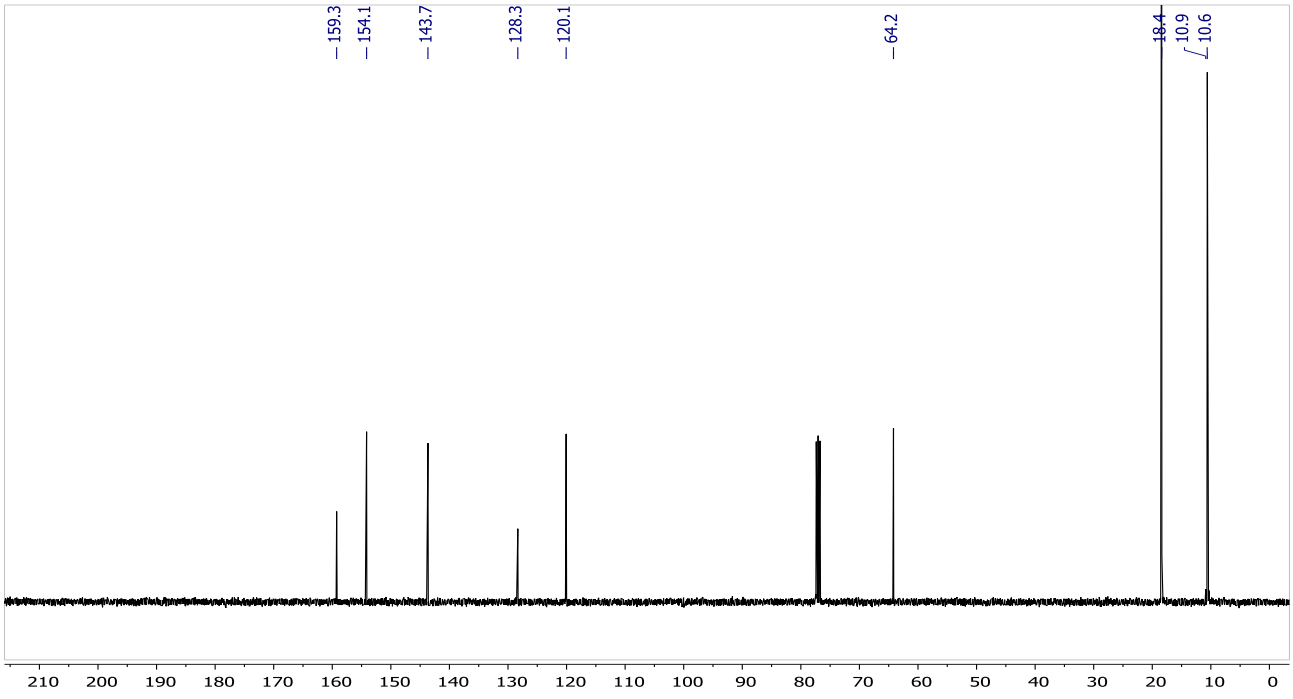
A1 ^{1}H and ^{13}C{^{1}H} NMR spectra of ligands

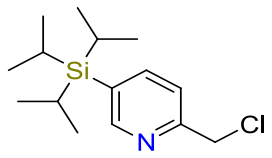


^{1}H-NMR of ^{TIPS}**PyOH** in $CDCl_3$



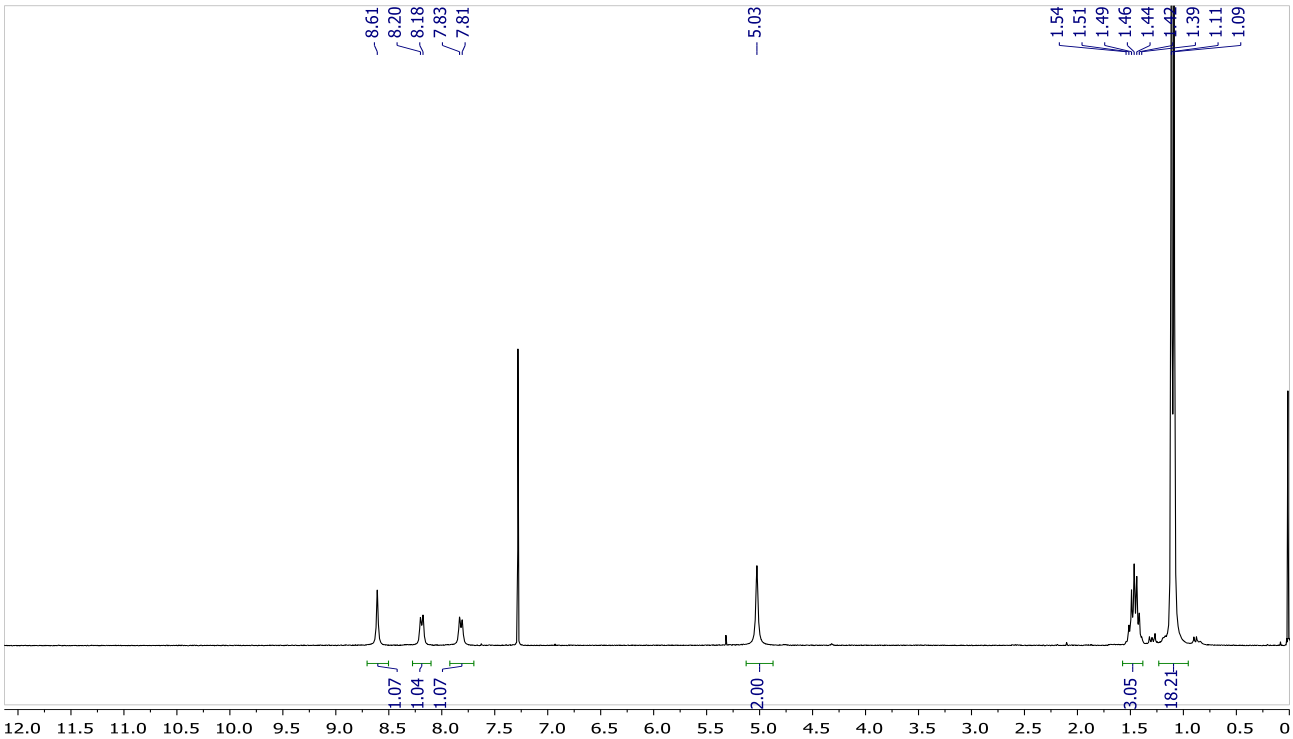
^{13}C{^{1}H}-NMR of ^{TIPS}**PyOH** in $CDCl_3$



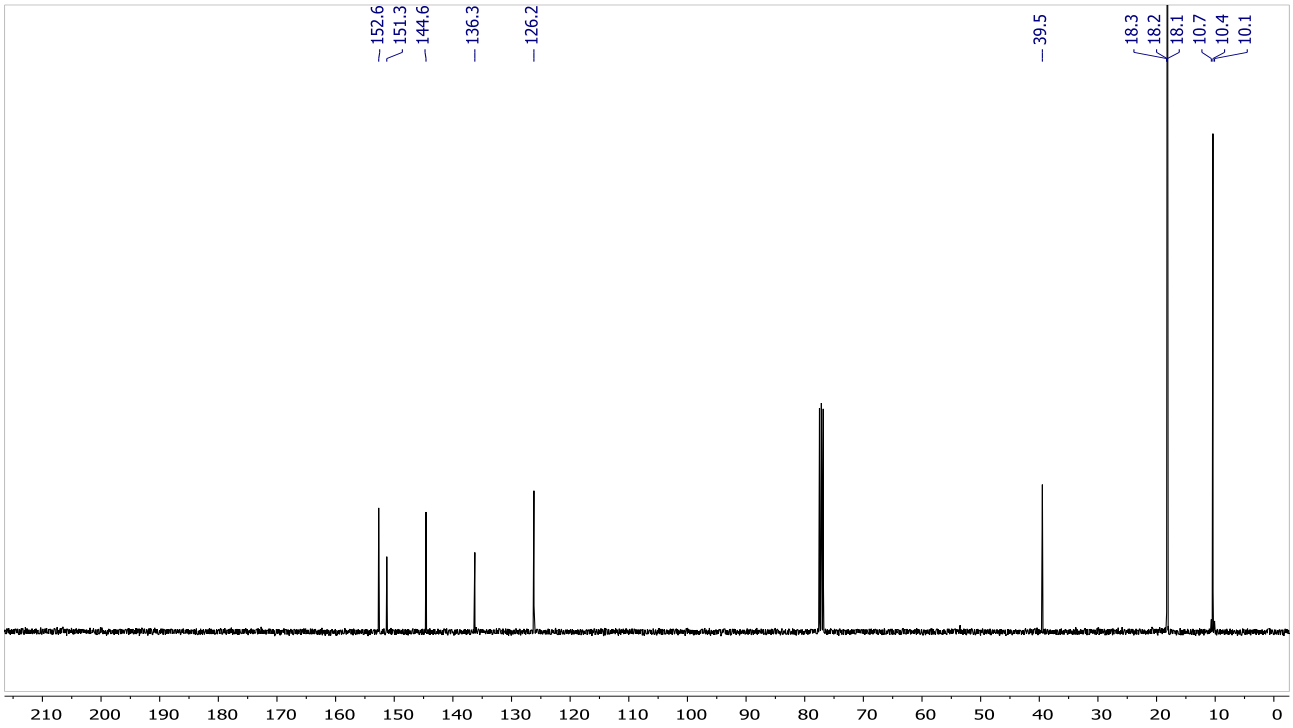


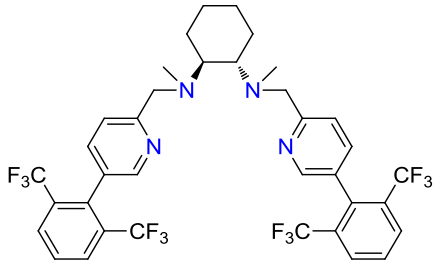
HCl

^{1}H-NMR of **^{TIPS}PyCl** in $CDCl_3$

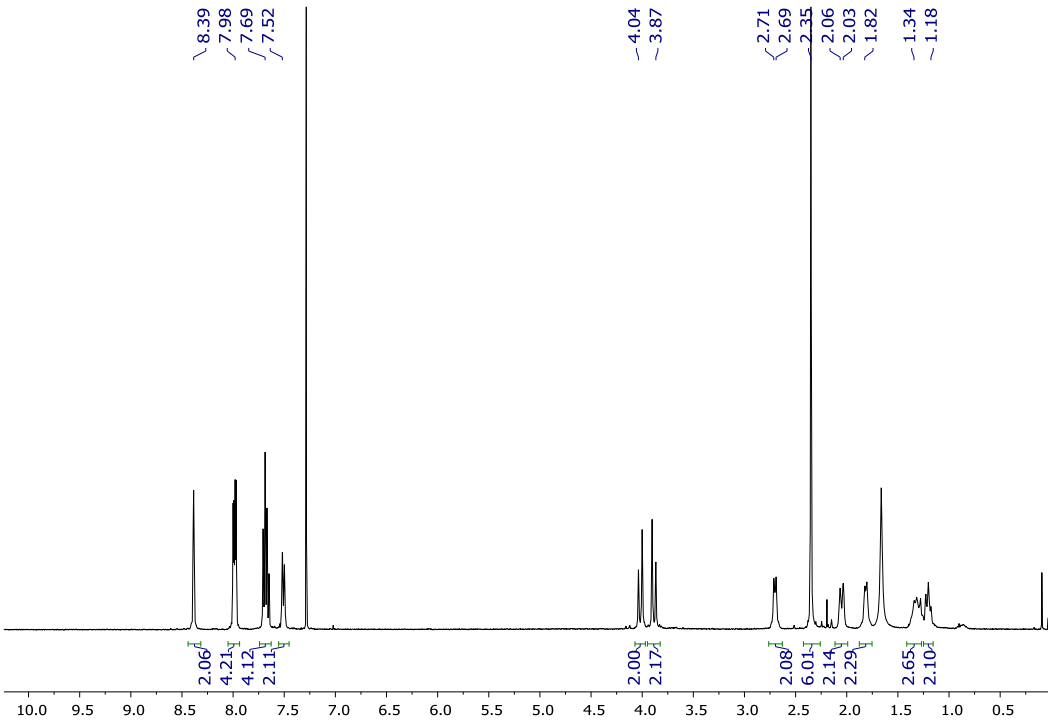


^{13}C{^{1}H}-NMR of **^{TIPS}PyCl** in $CDCl_3$

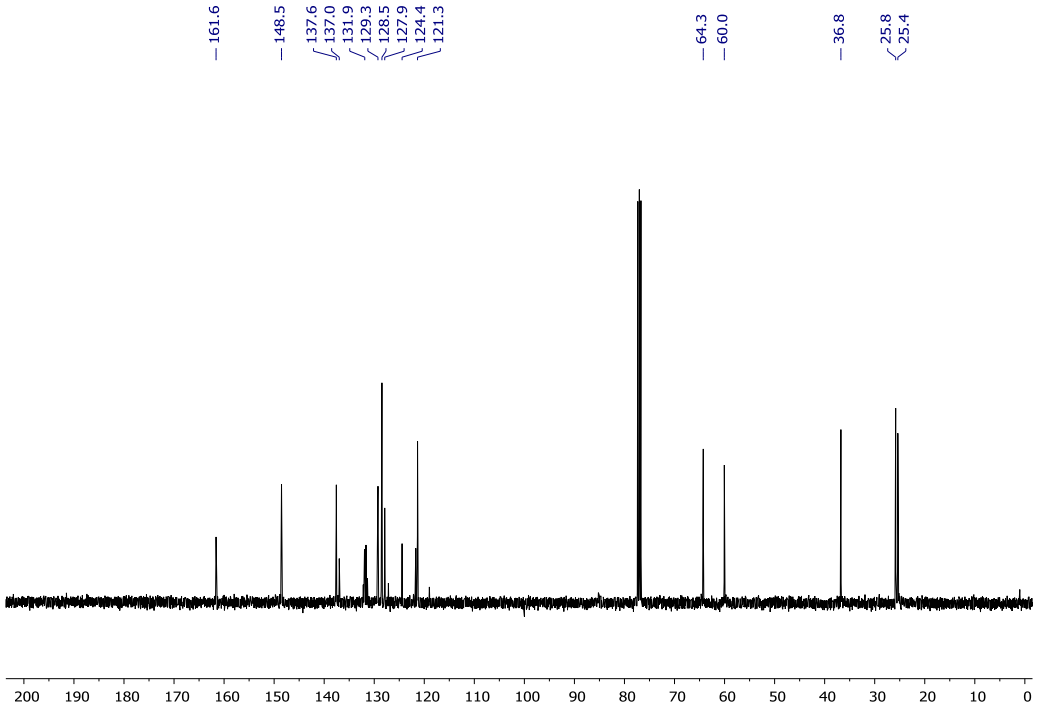


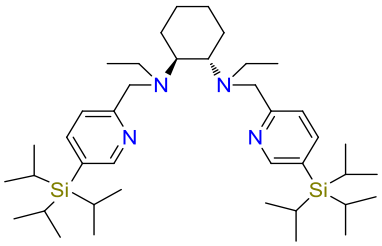


^{1}H-NMR of **^{CF3}mcp** in $CDCl_3$

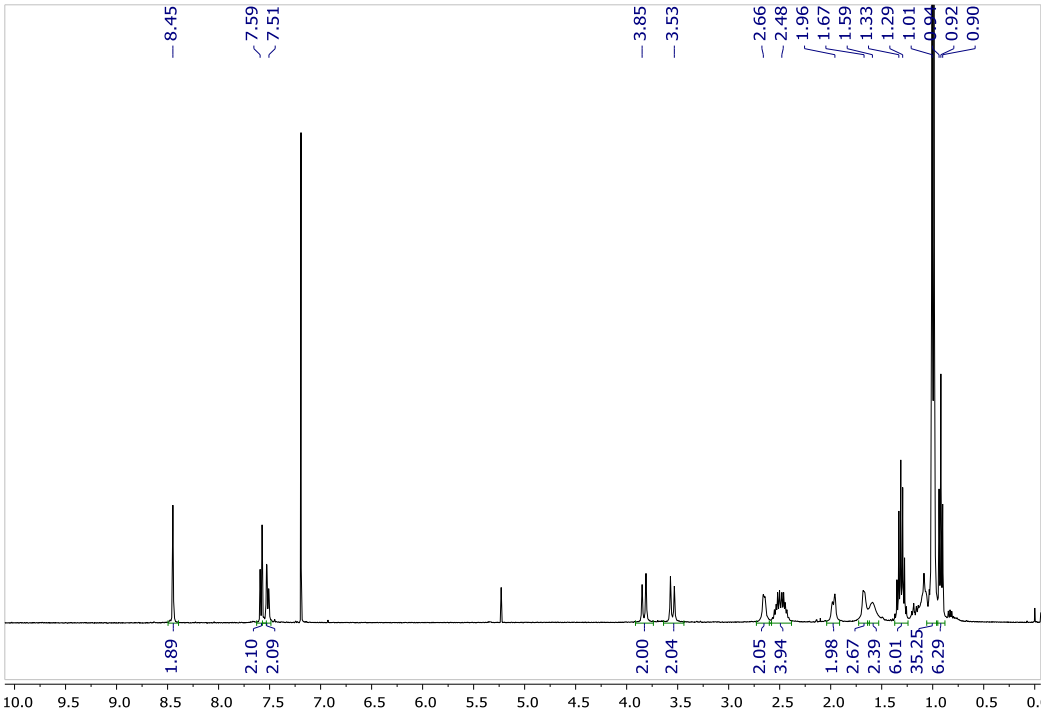


^{13}C{^{1}H}-NMR of **^{CF3}mcp** in $CDCl_3$

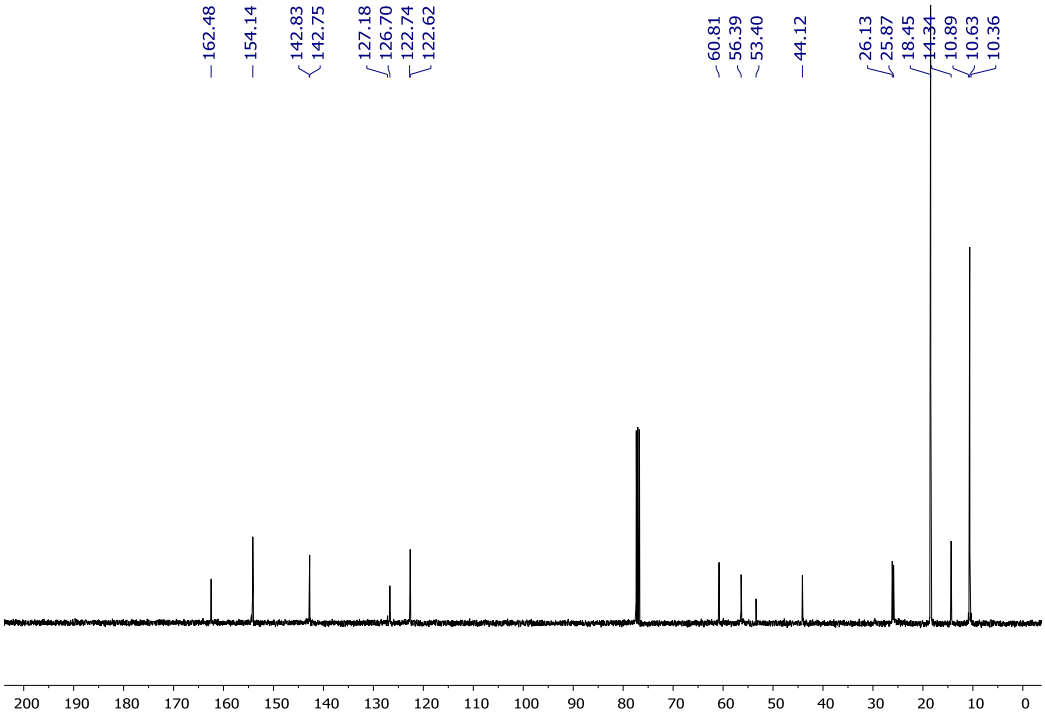


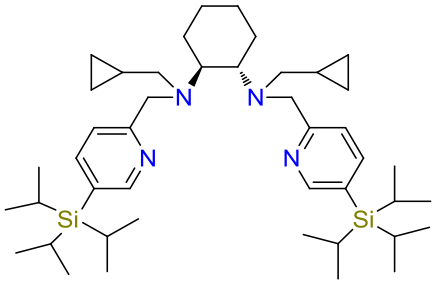


^{1}H-NMR of $^{\mathbf{TIPS}}$**ecp** in $CDCl_3$

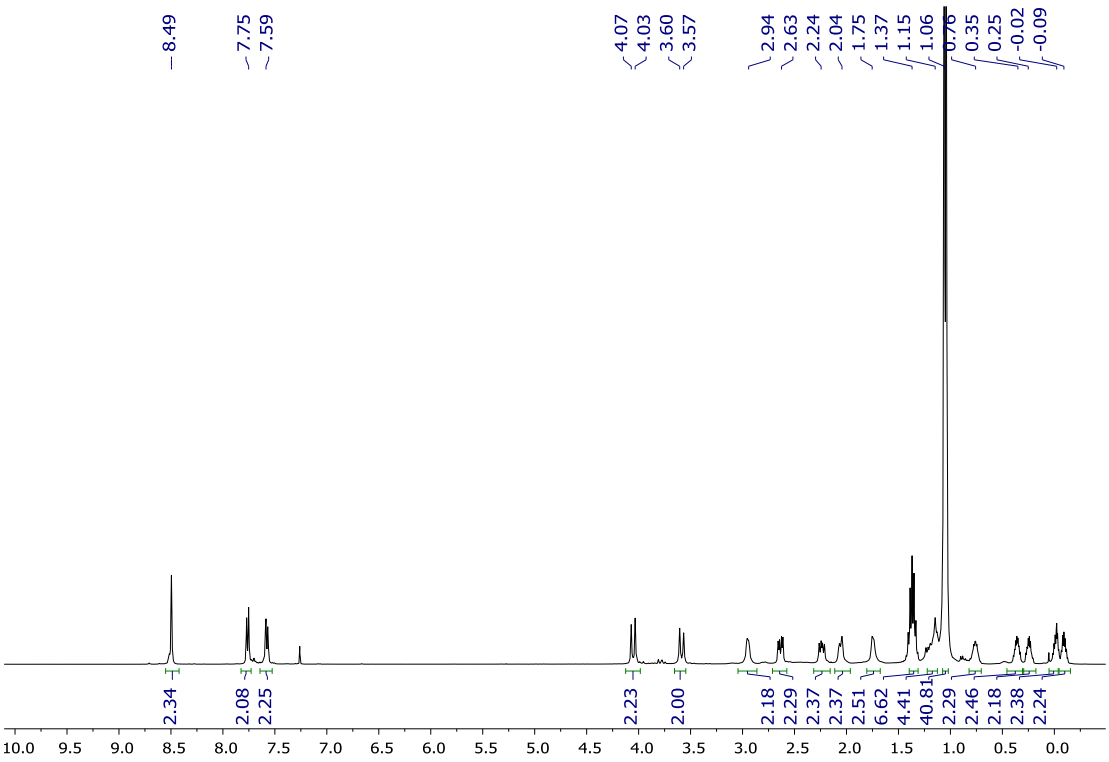


^{13}C{^{1}H}-NMR of $^{\mathbf{TIPS}}$**ecp** in $CDCl_3$

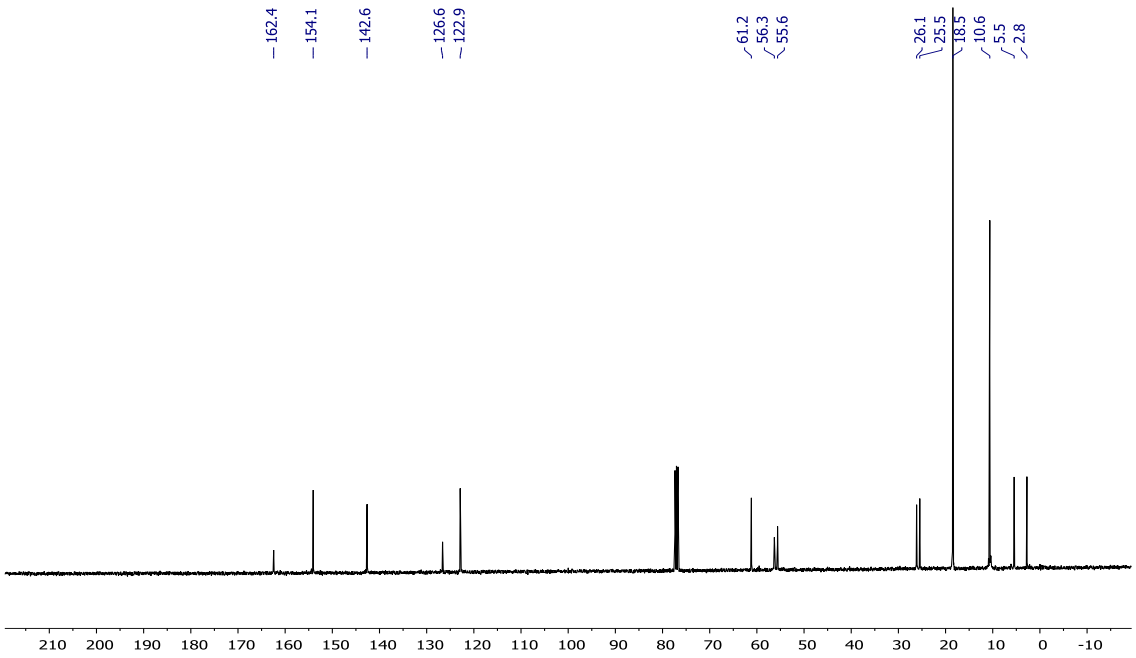


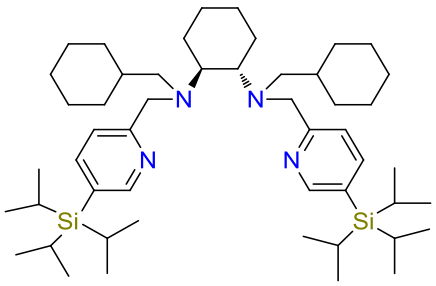


^{1}H-NMR of ^{TIPS}**cpcp** in $CDCl_3$

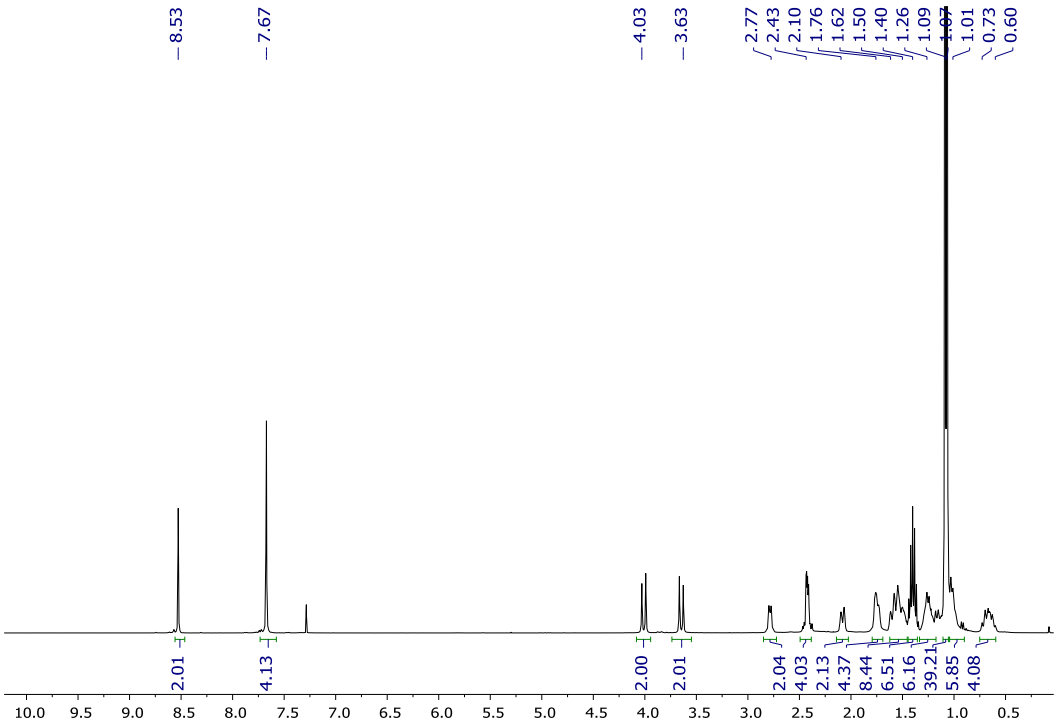


$^{13}C\{^{1}H\}$-NMR of **^{TIPS}cpcp** in $CDCl_3$

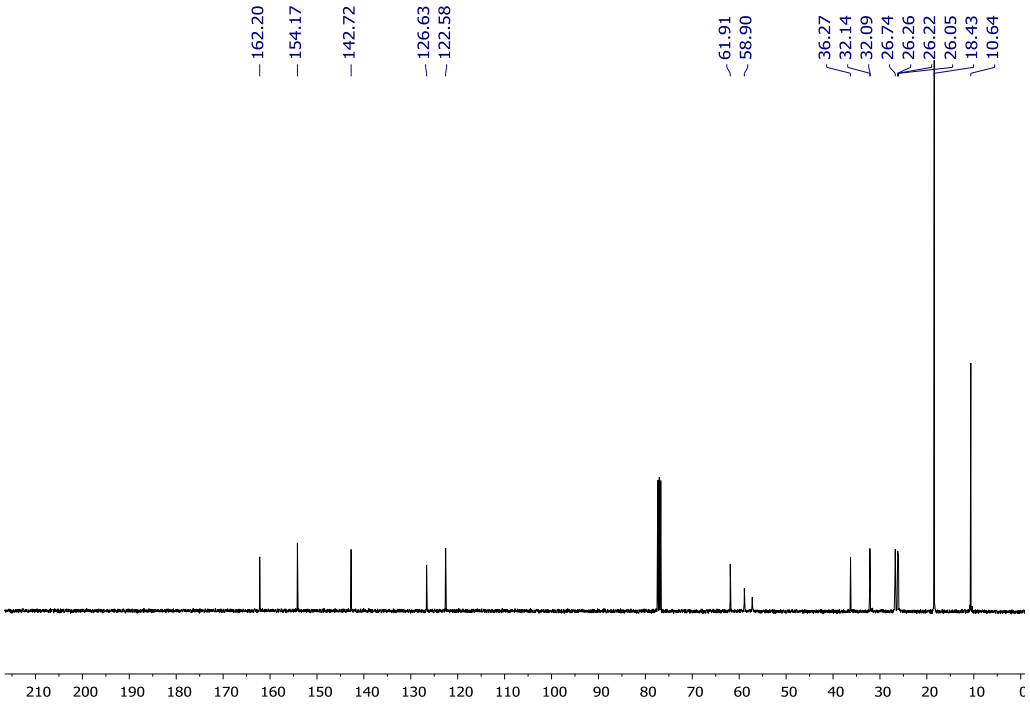


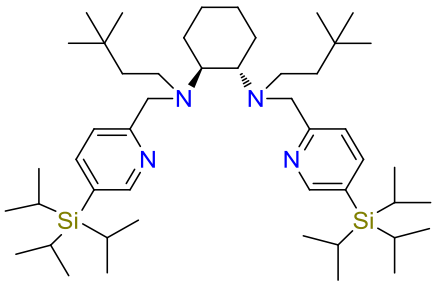


^{1}H-NMR of **^{TIPS}chcp** in $CDCl_3$

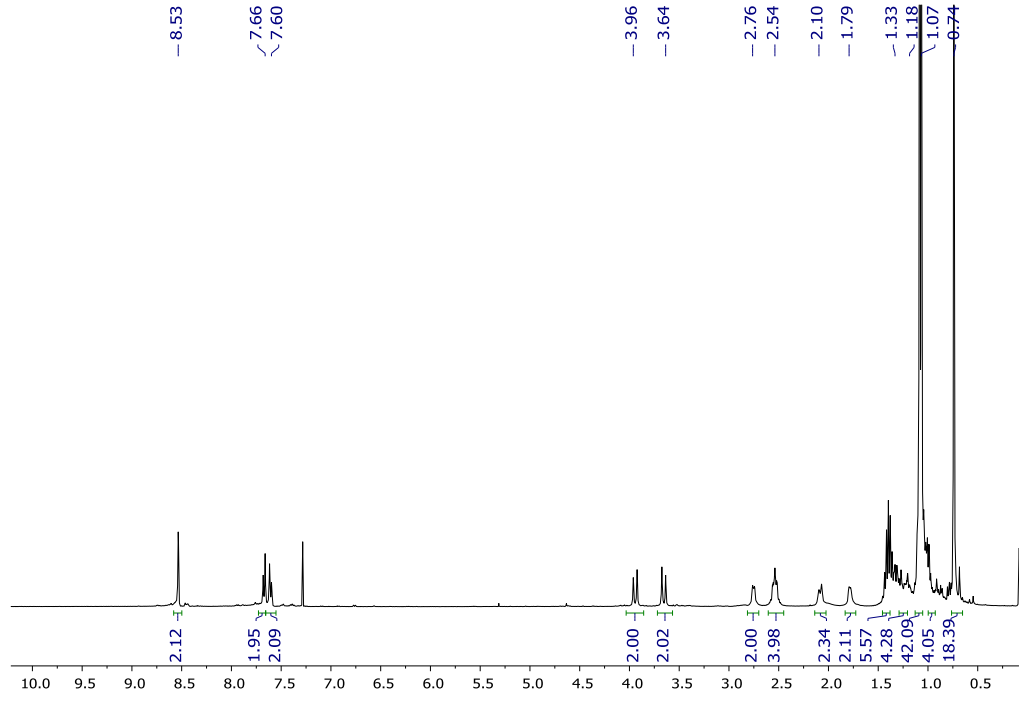


$^{13}C\{^{1}H\}$-NMR of **^{TIPS}chcp** in $CDCl_3$

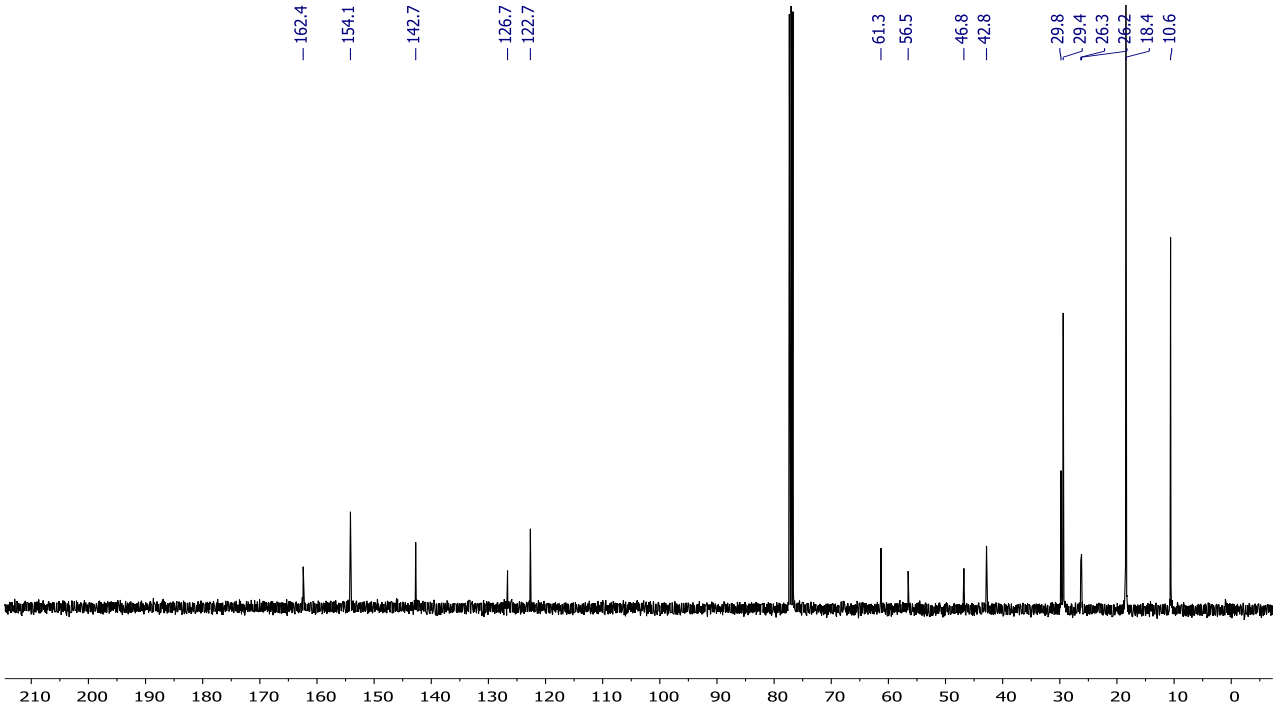




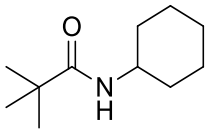
^{1}H-NMR of ^{TIPS}**tBucp** in $CDCl_3$



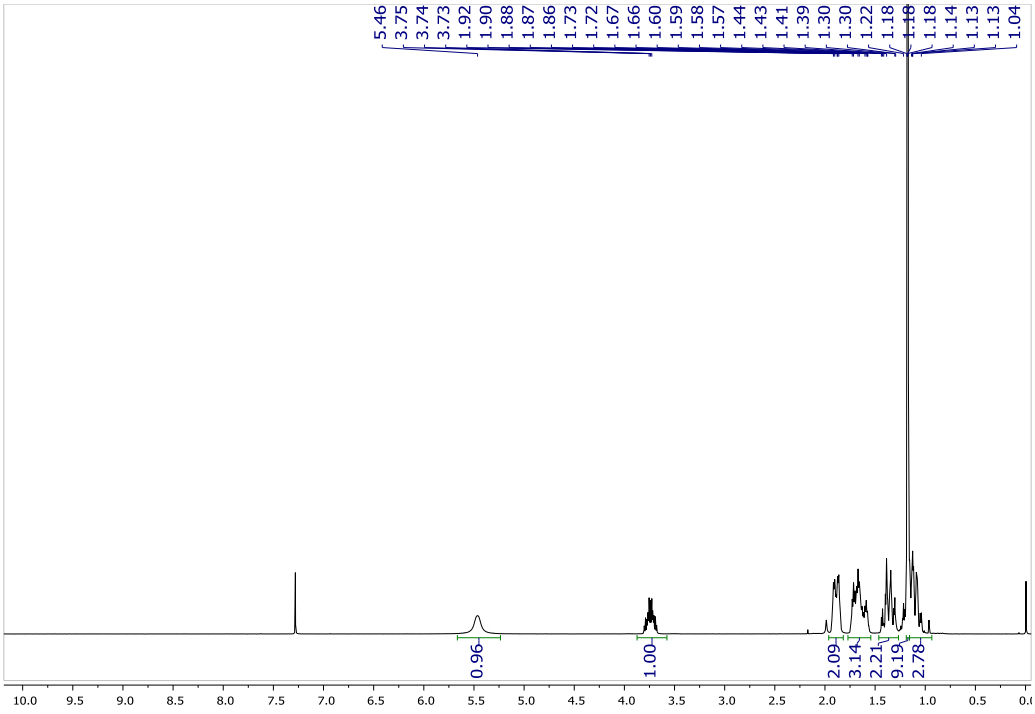
^{13}C{^{1}H}-NMR of ^{TIPS}**tBucp** in $CDCl_3$



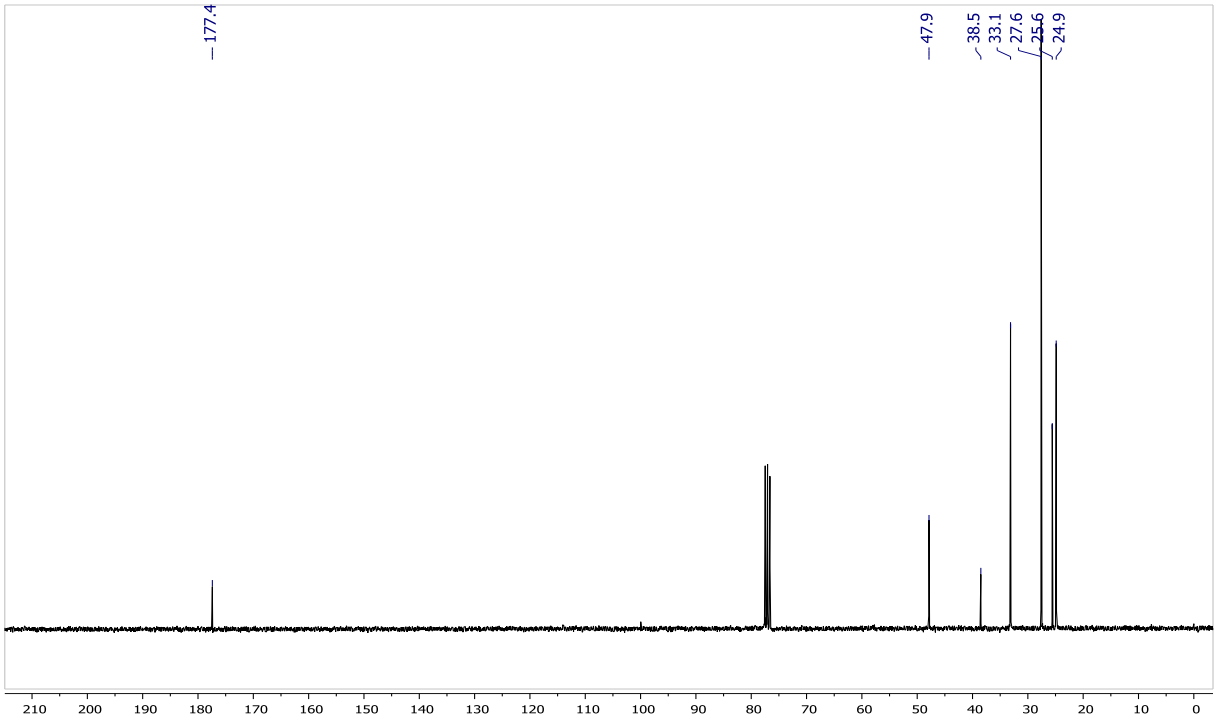
A2 ^{1}H and ^{13}C{^{1}H} NMR spectra of substrates

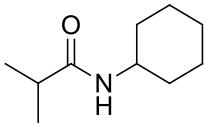


^{1}H-NMR of **S8** in $CDCl_3$

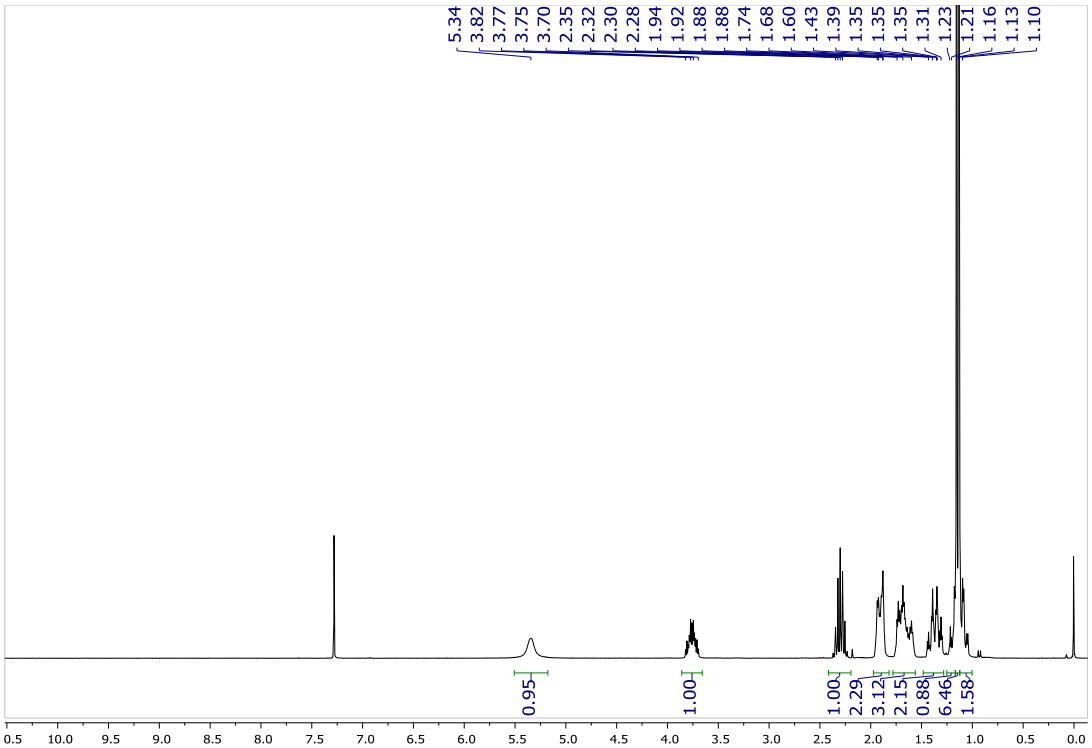


^{13}C{^{1}H}-NMR of **S8** in $CDCl_3$

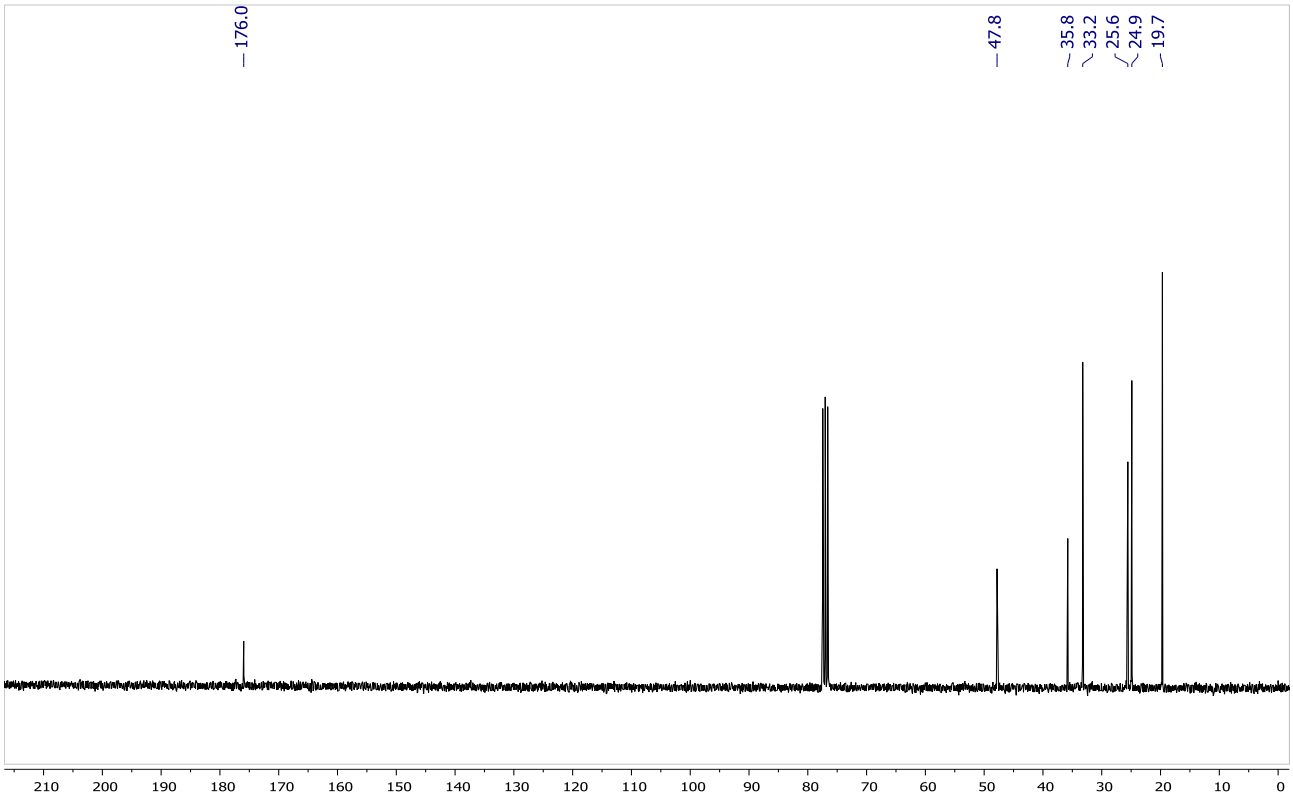


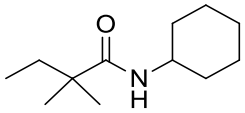


^{1}H-NMR of **S9** in $CDCl_3$

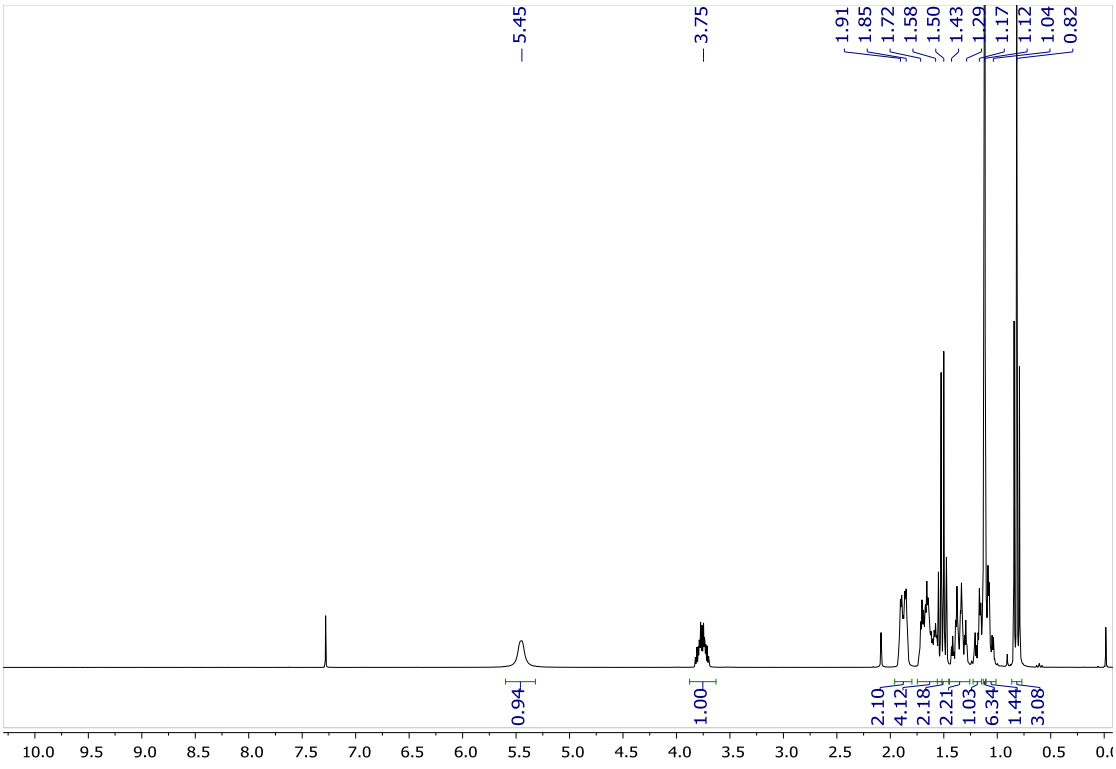


^{13}C{^{1}H}-NMR of **S9** in $CDCl_3$

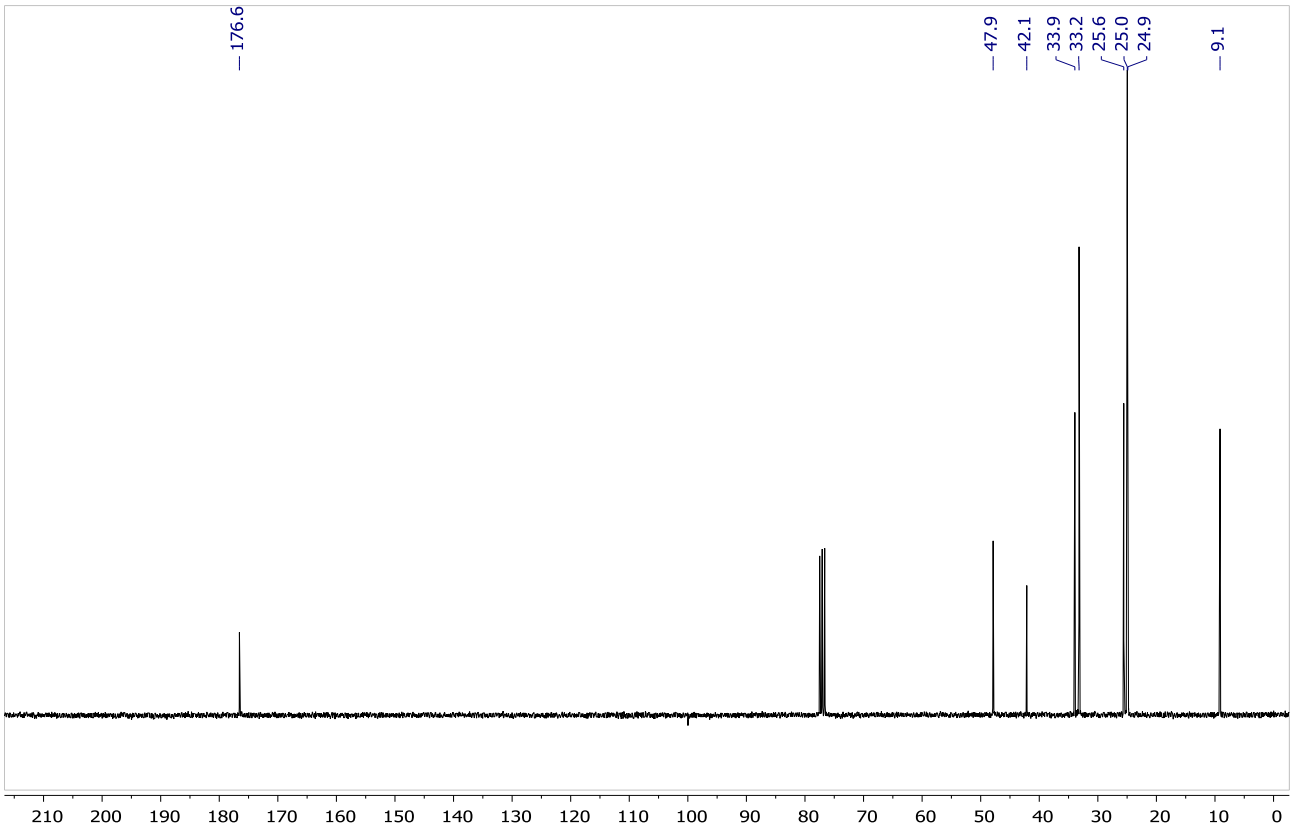


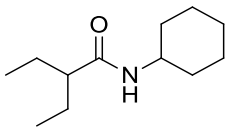


^{1}H-NMR of **S10** in $CDCl_3$

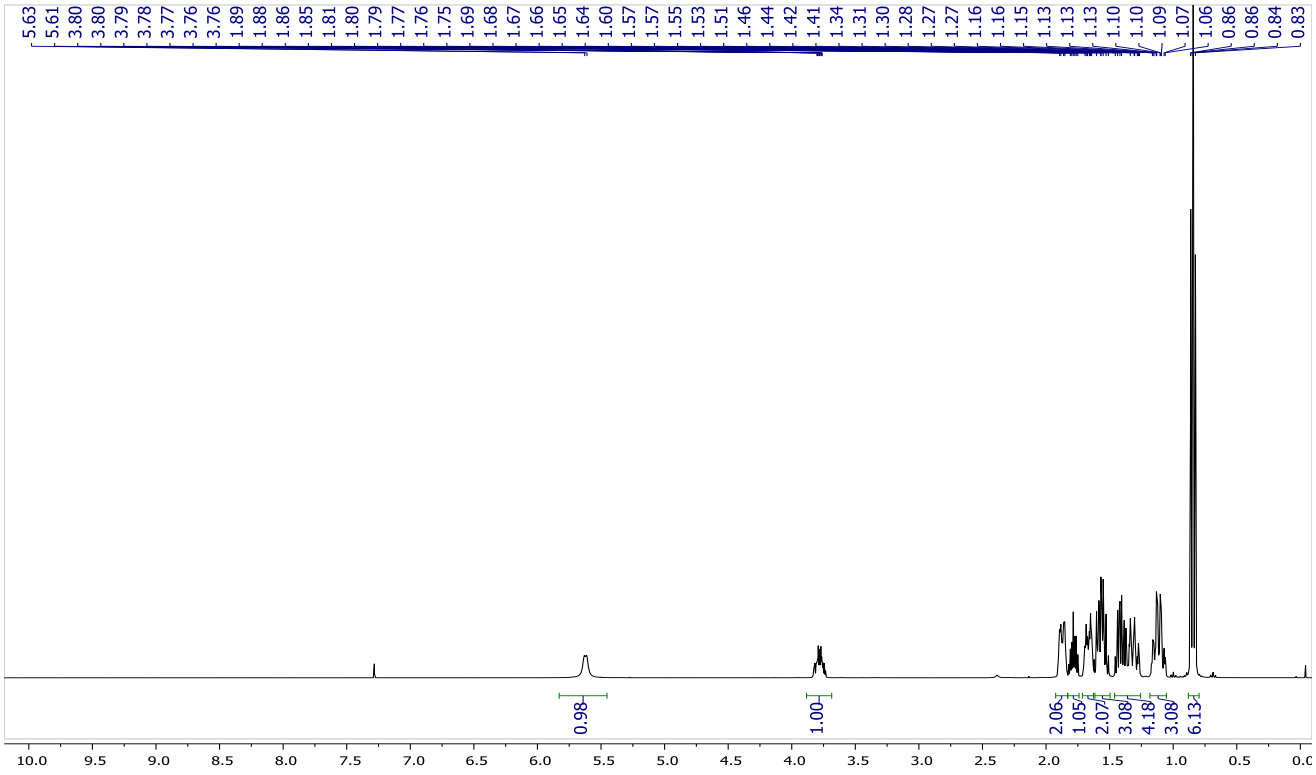


$^{13}C\{^{1}H\}$-NMR of **S10** in $CDCl_3$

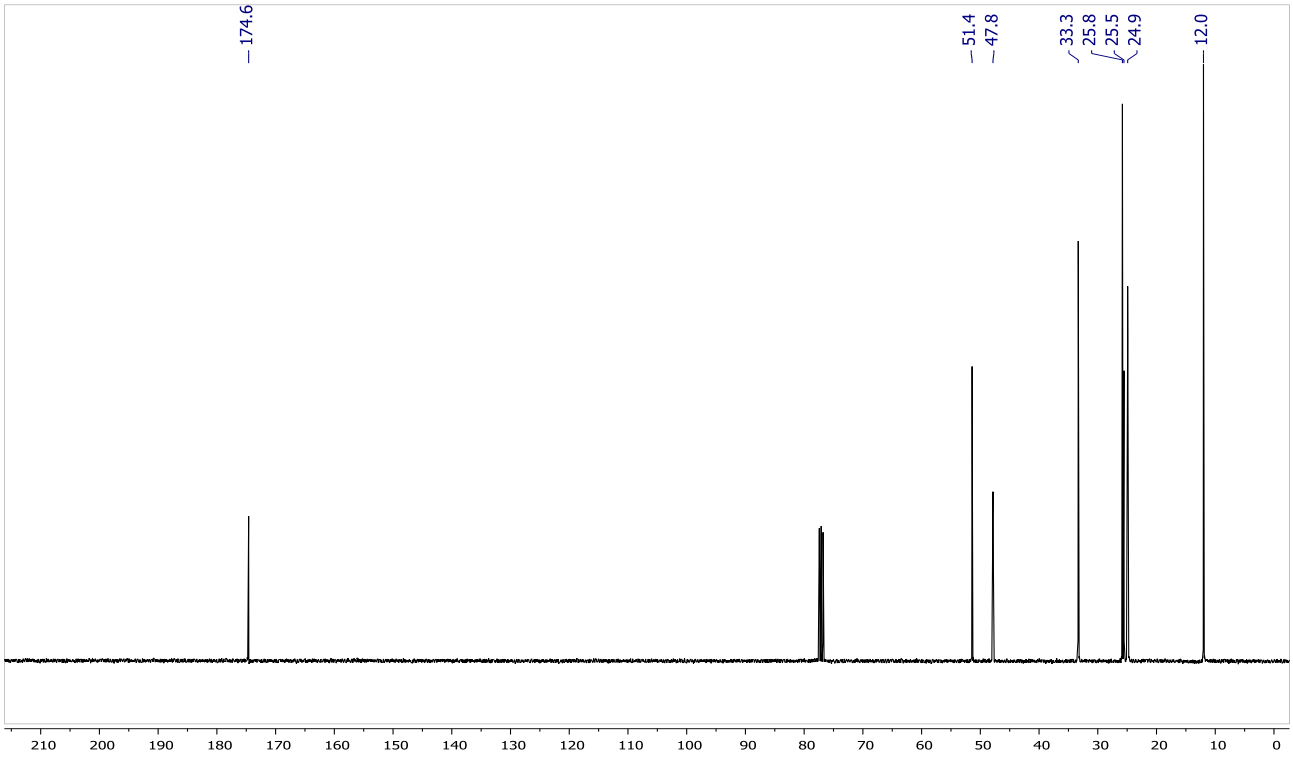


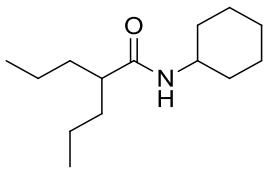


^{1}H-NMR of **S11** in $CDCl_3$

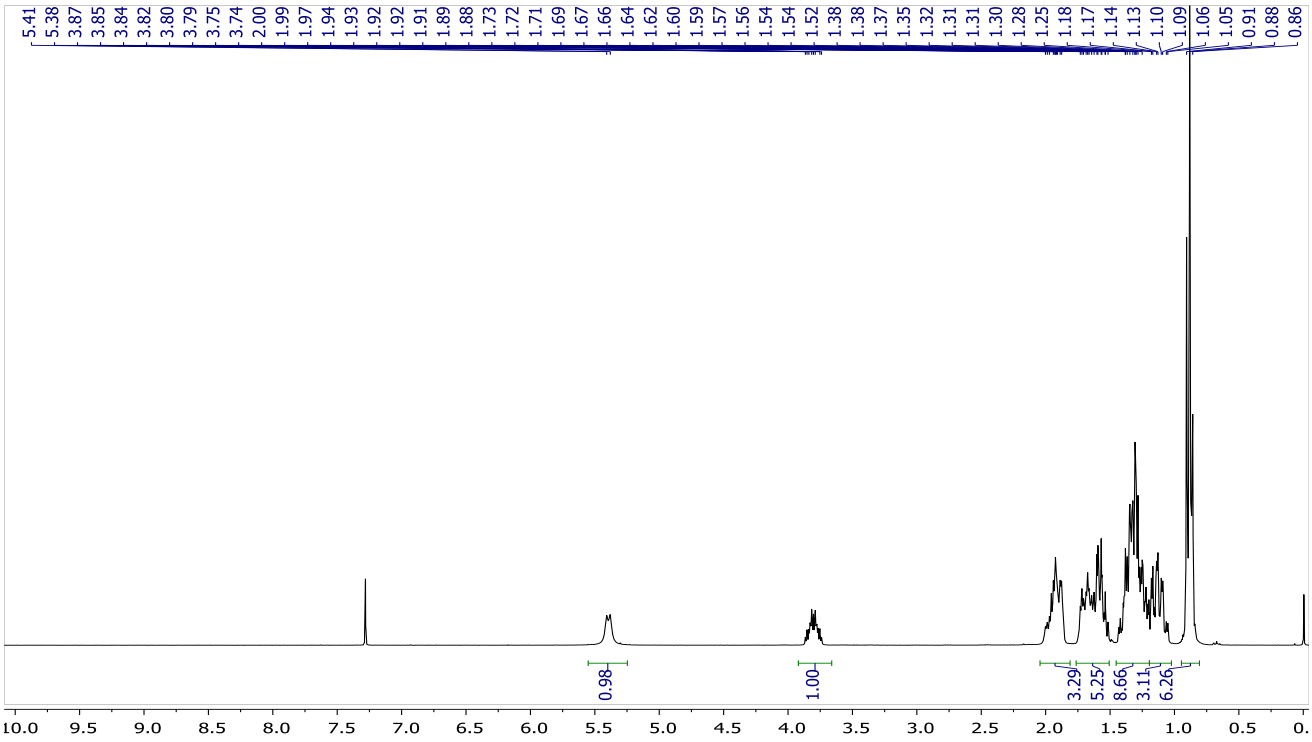


$^{13}C\{^{1}H\}$-NMR of **S11** in $CDCl_3$

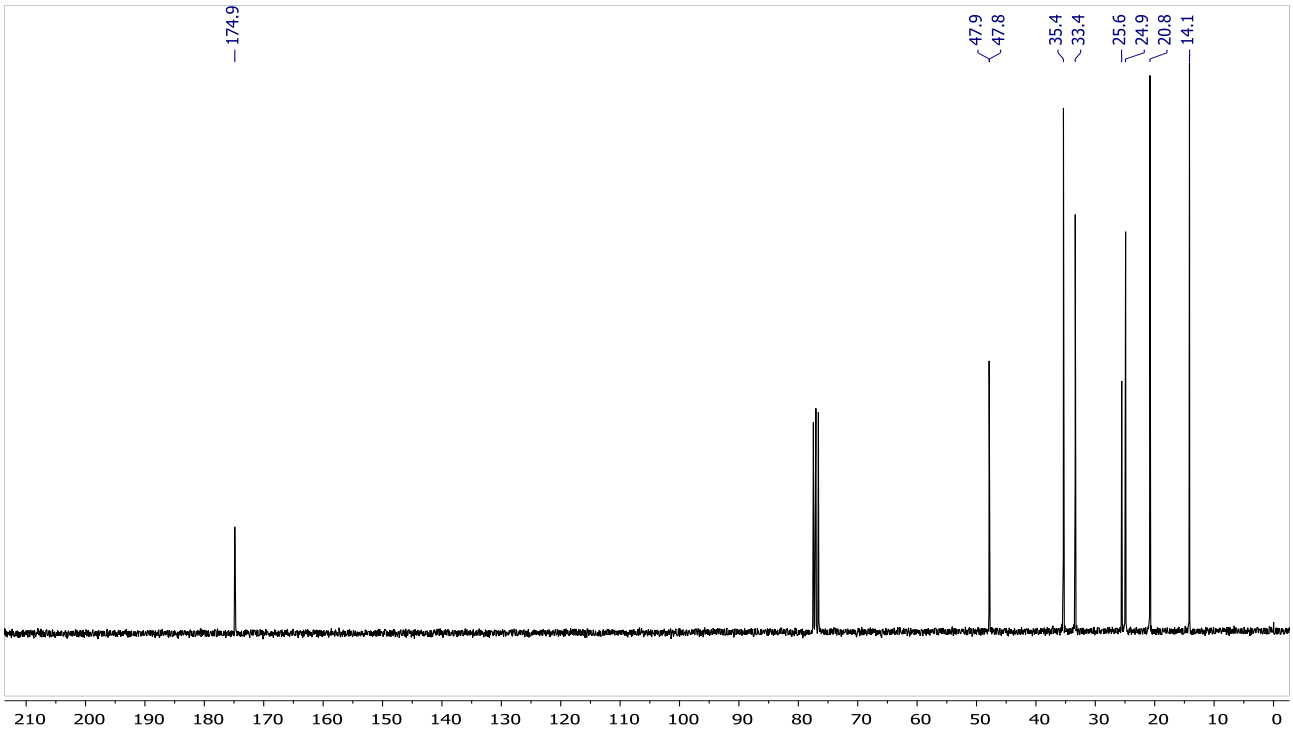


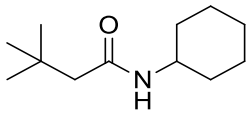


^{1}H-NMR of **S12** in $CDCl_3$

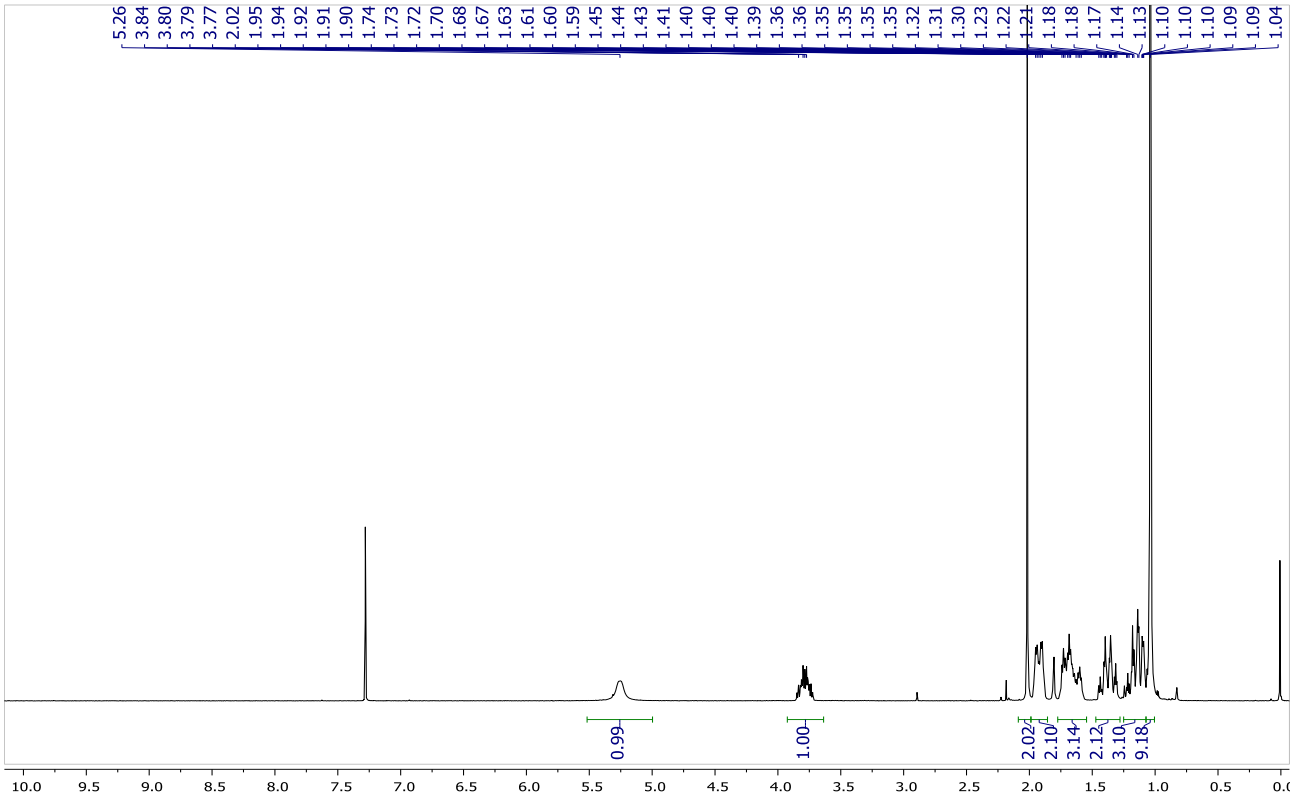


^{13}C{^{1}H}-NMR of **S12** in $CDCl_3$

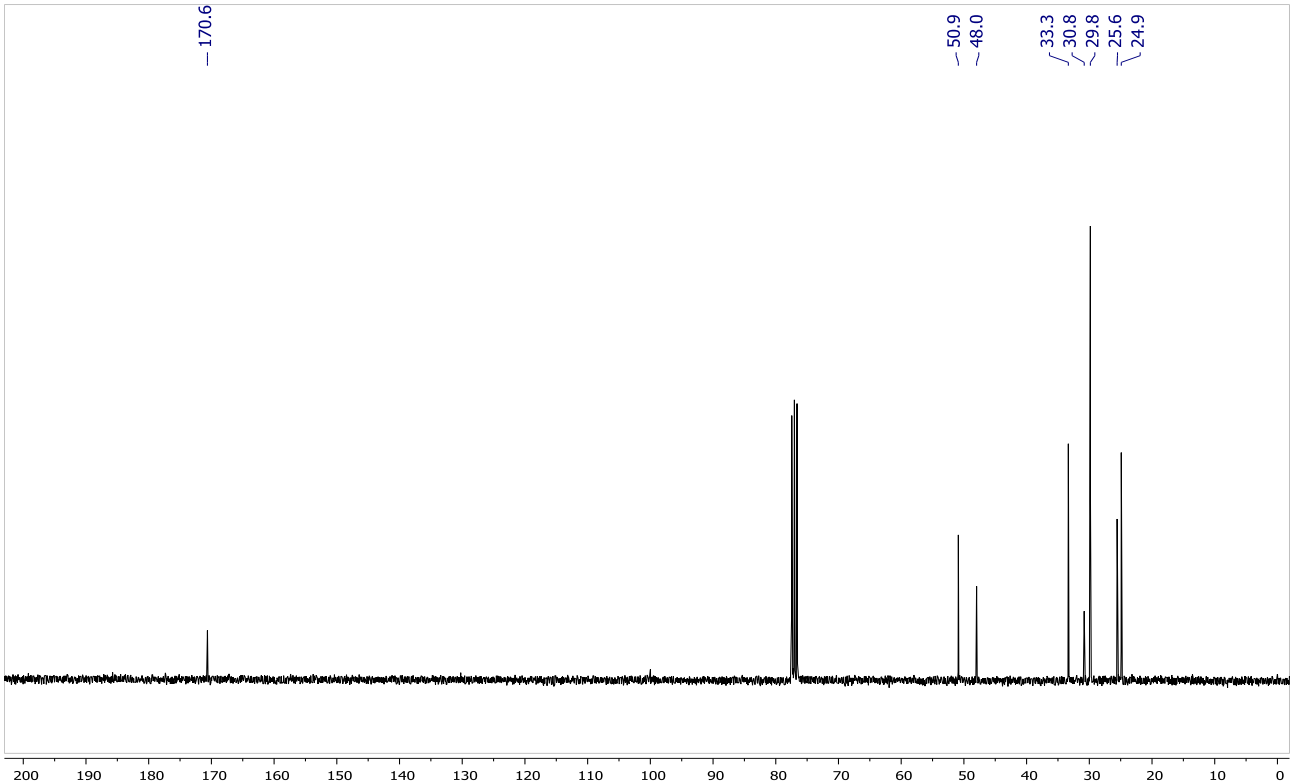


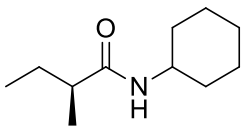


^{1}H-NMR of **S13** in $CDCl_3$

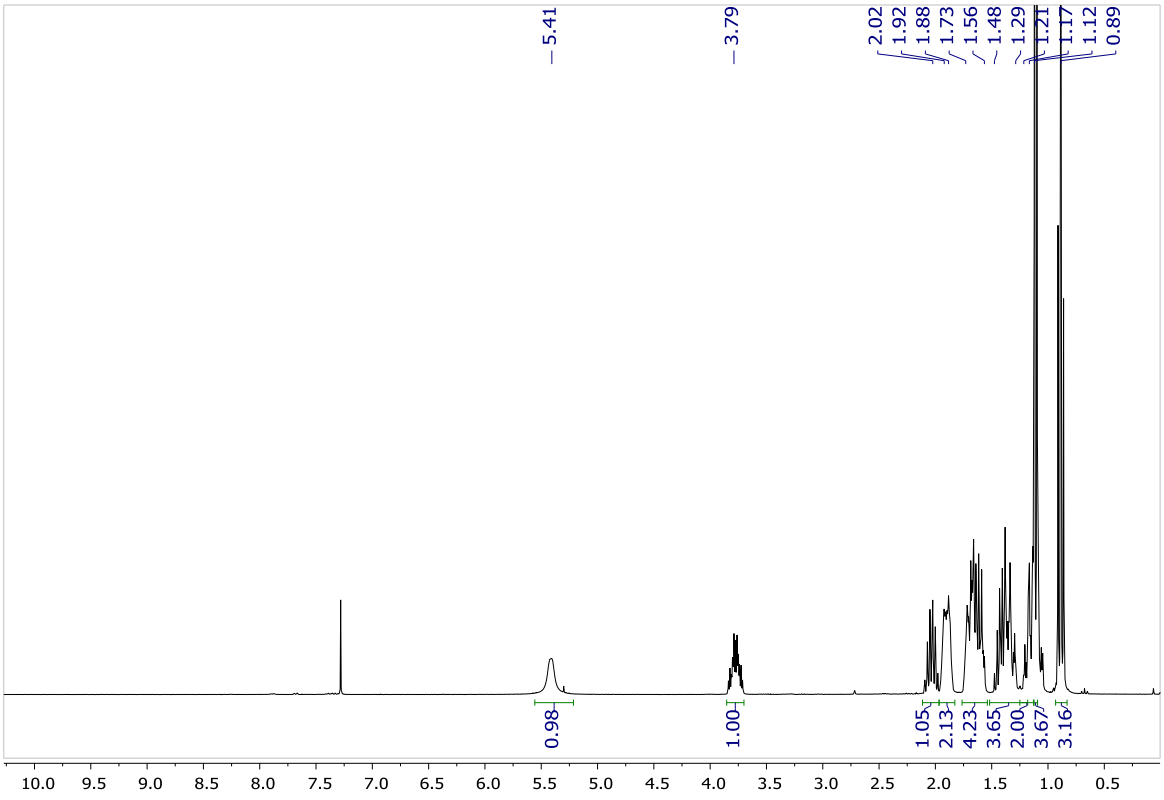


$^{13}C\{^{1}H\}$-NMR of **S13** in $CDCl_3$

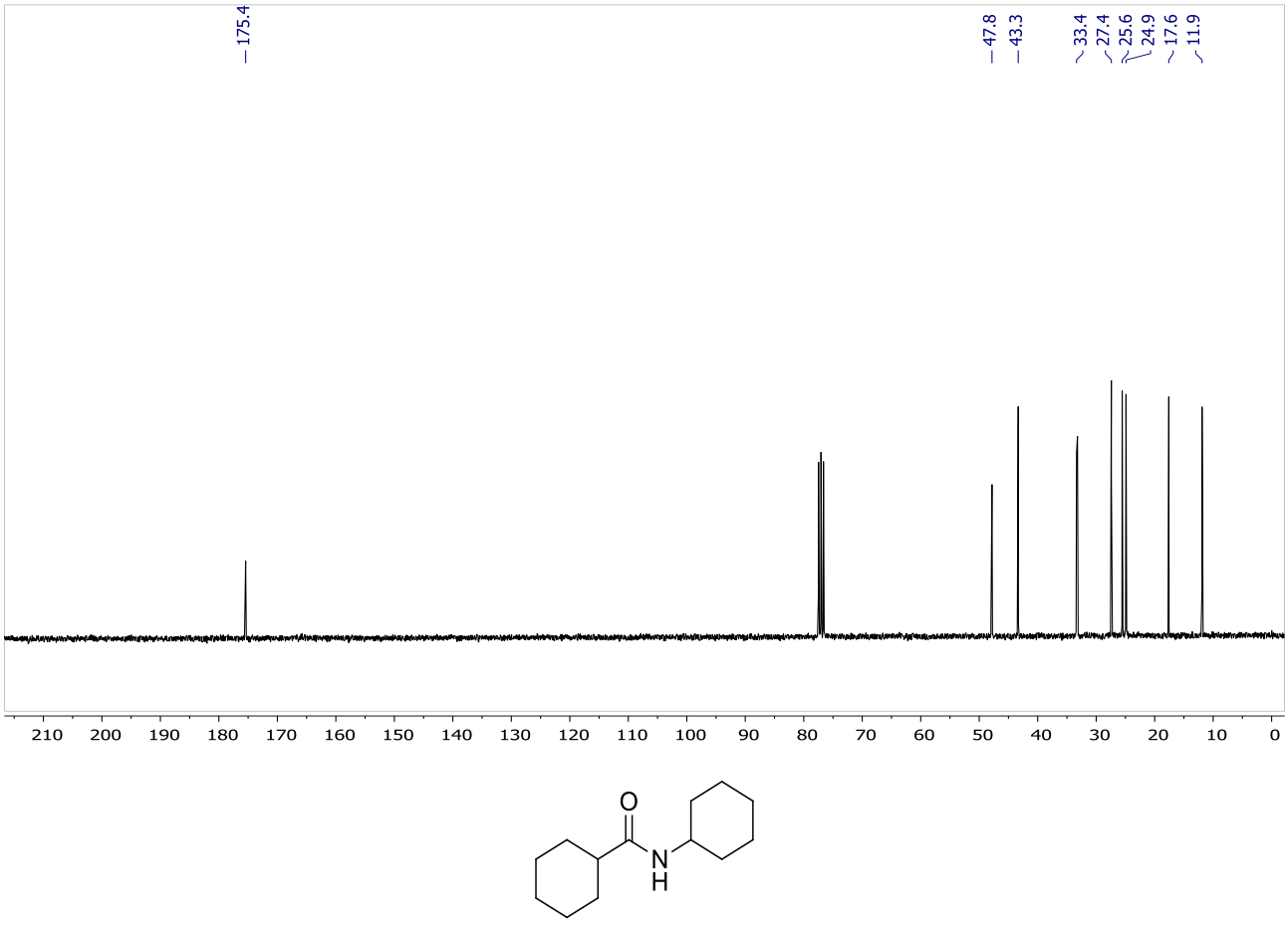




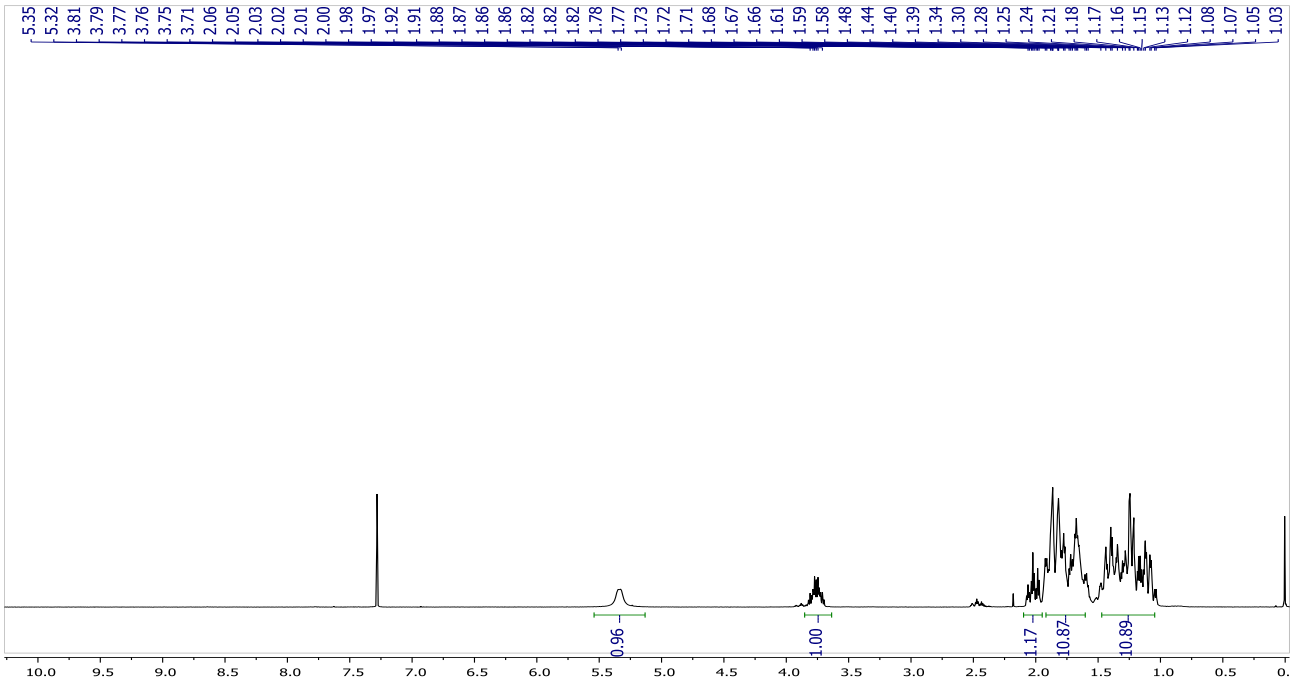
^{1}H-NMR of **S14** in $CDCl_3$



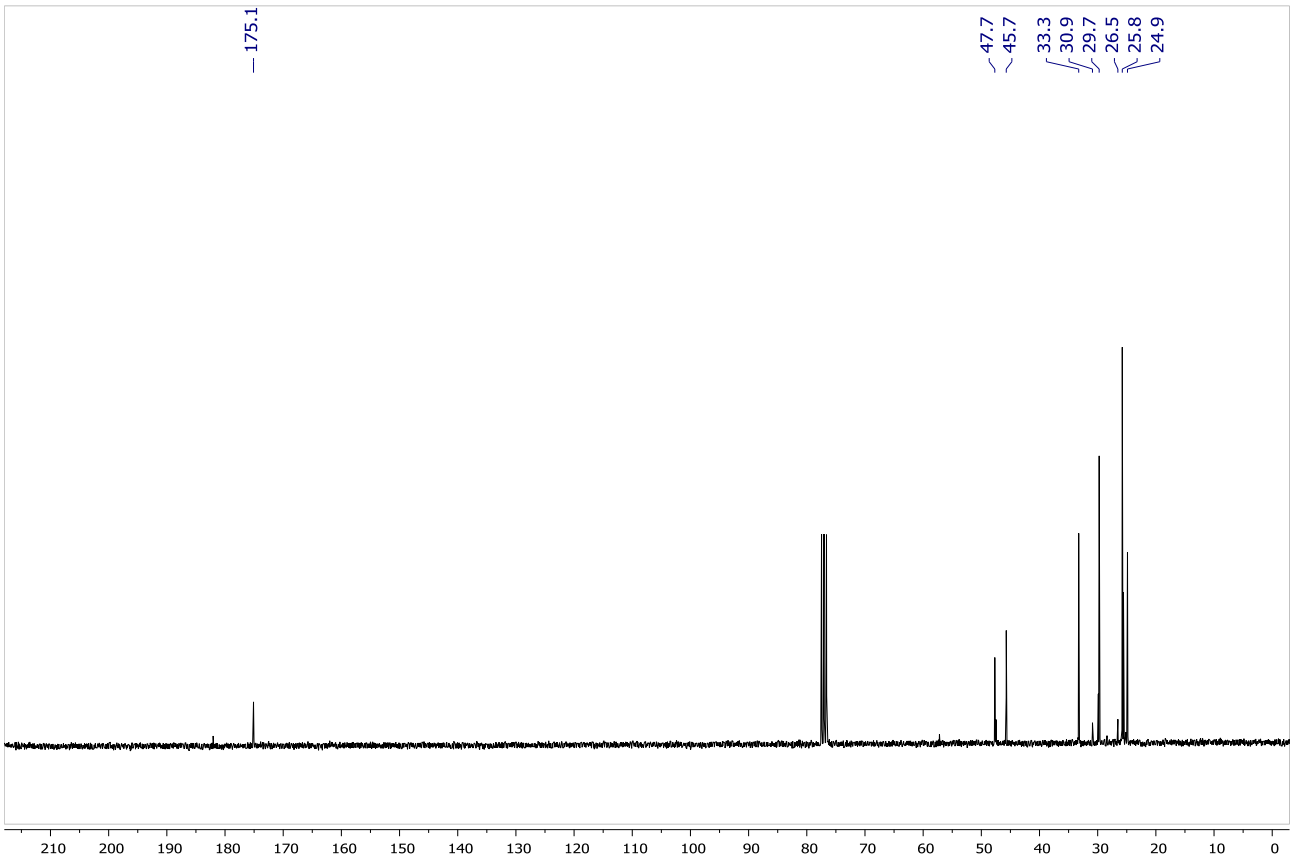
$^{13}C\{^{1}H\}$-NMR of **S14** in $CDCl_3$

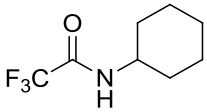


^{1}H-NMR of **S15** in $CDCl_3$

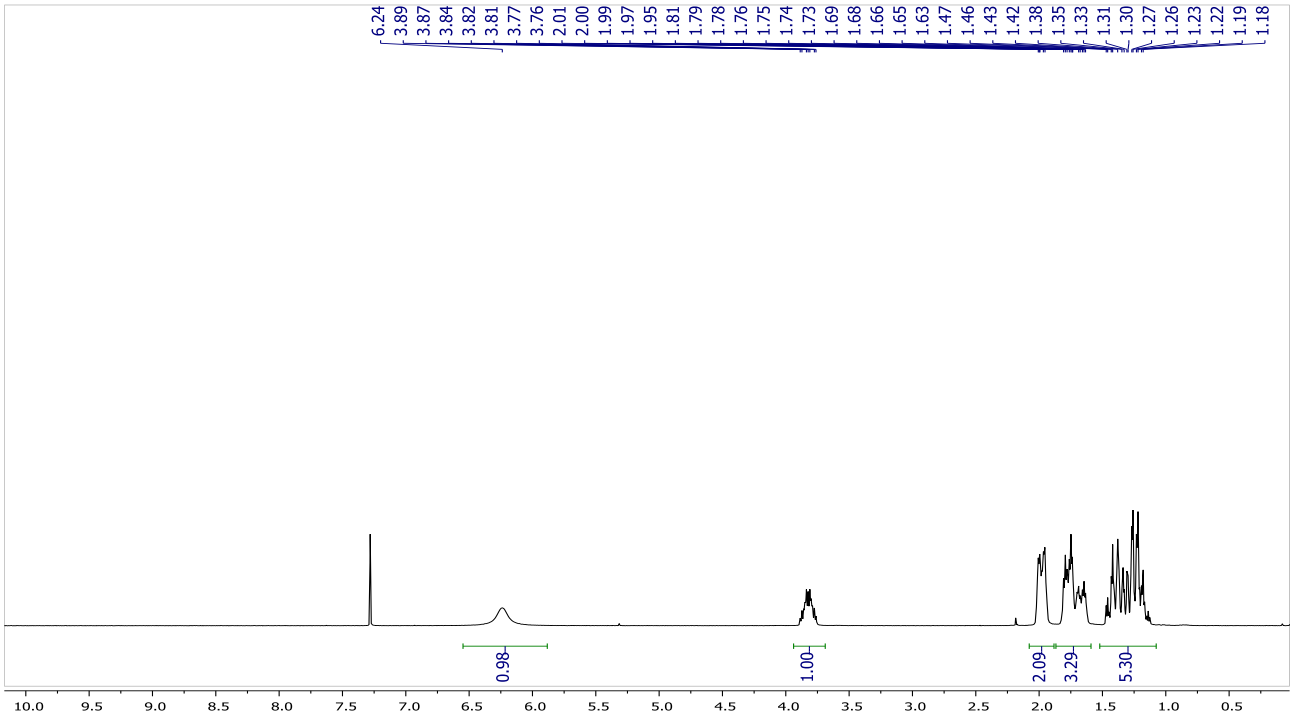


^{13}C{^{1}H}-NMR of **S15** in $CDCl_3$

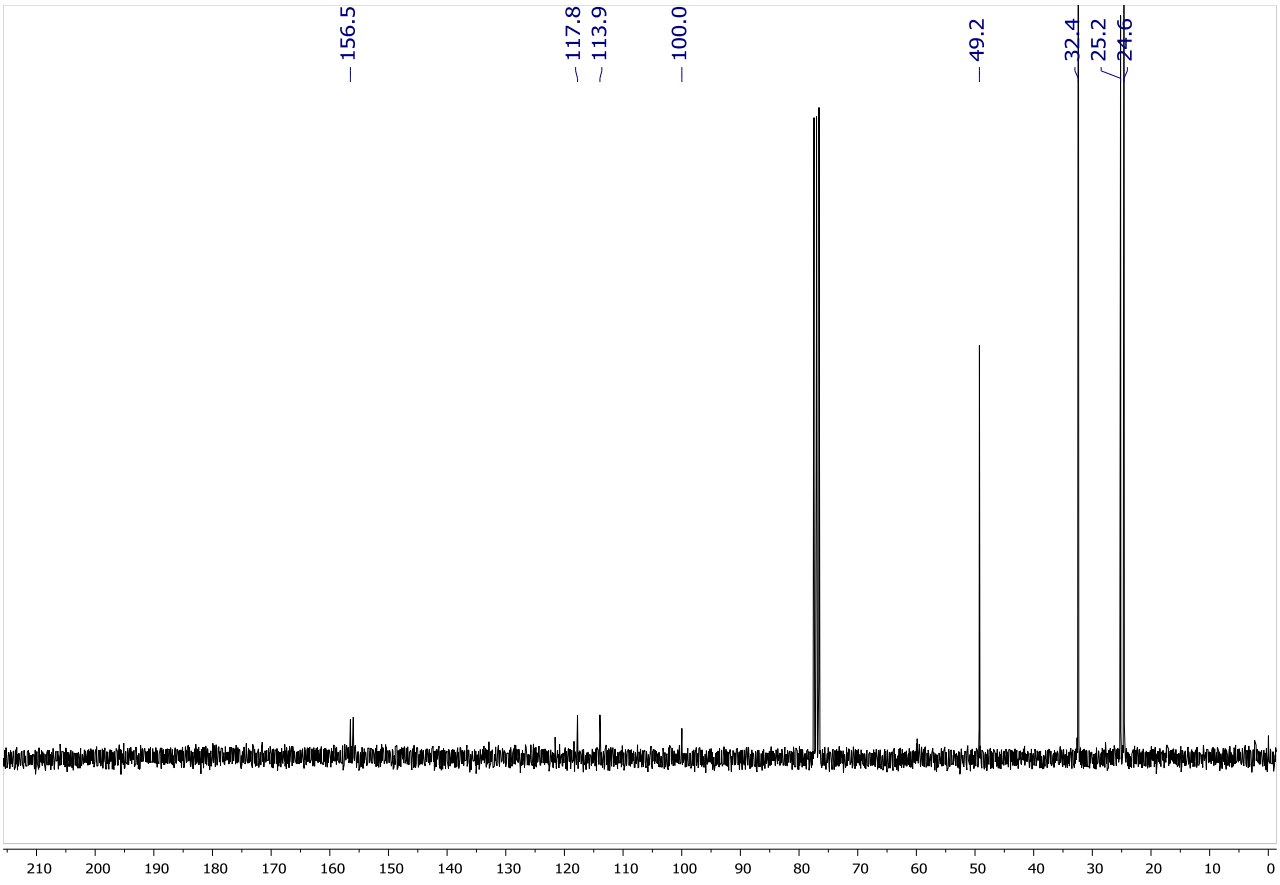


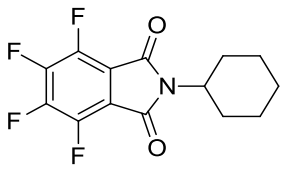


^{1}H-NMR of **S17** in $CDCl_3$

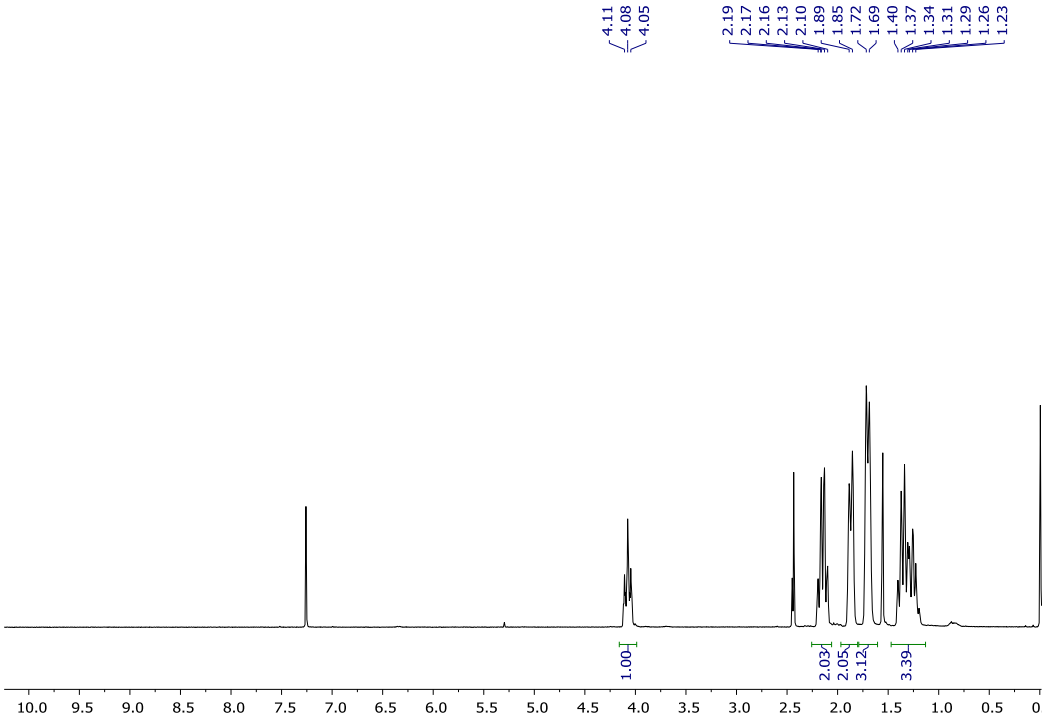


$^{13}C\{^{1}H\}$-NMR of **S17** in $CDCl_3$

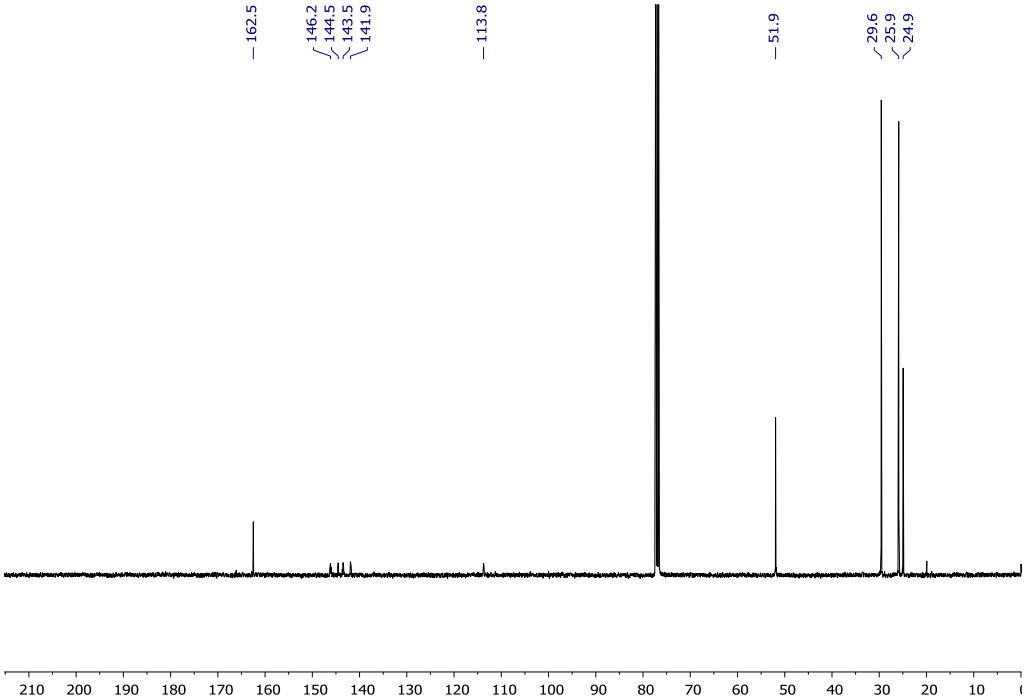


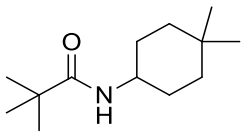


^{1}H-NMR of **S19** in $CDCl_3$

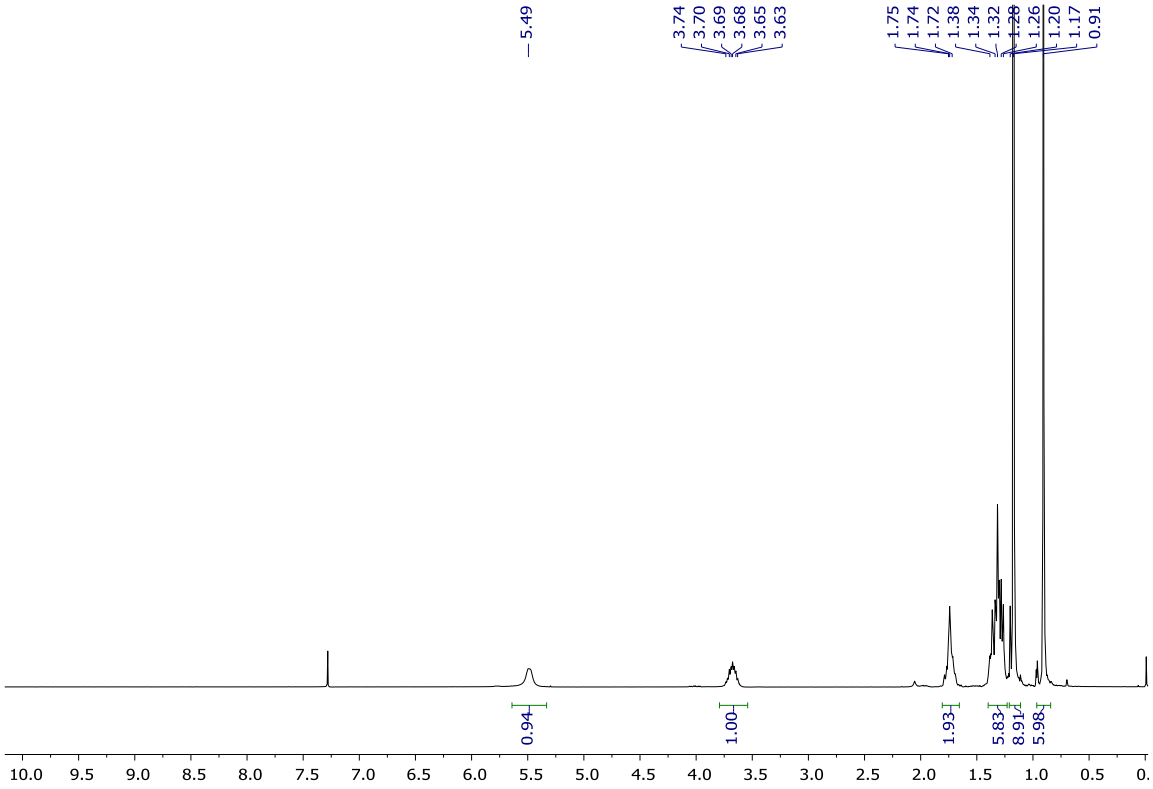


^{13}C{^{1}H}-NMR of **S19** in $CDCl_3$

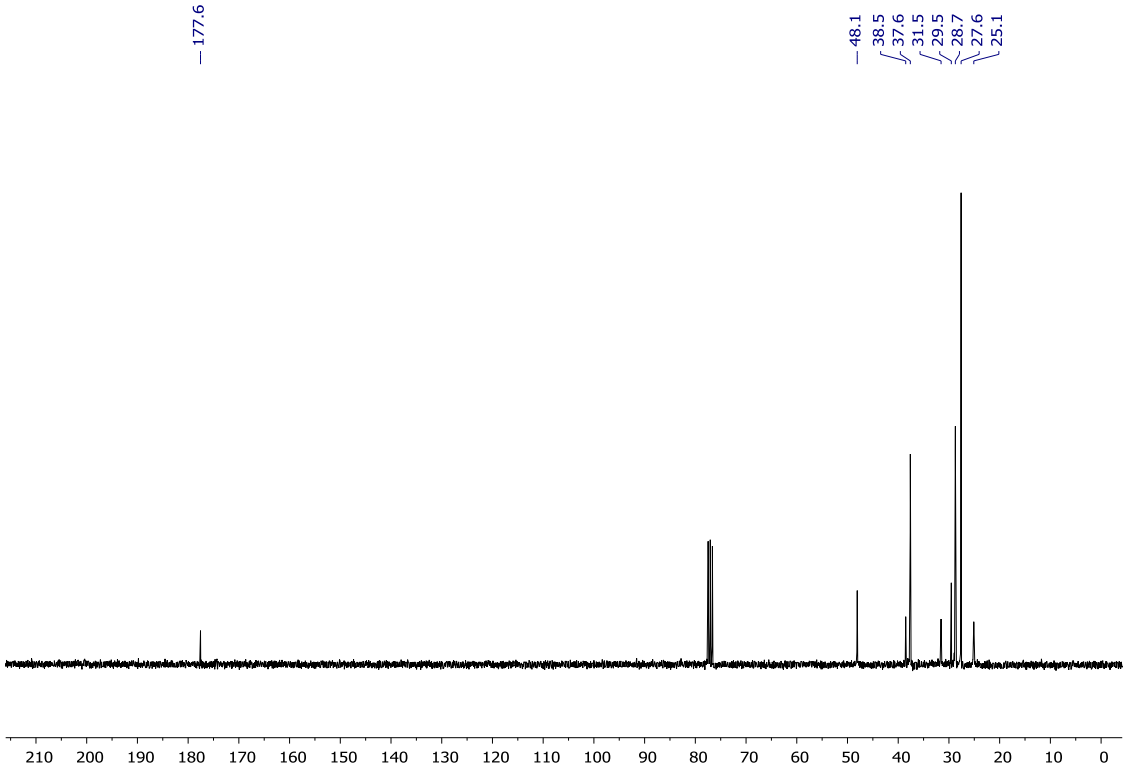


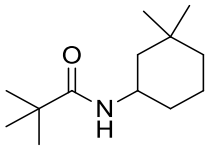


^{1}H-NMR of **S20** in $CDCl_3$

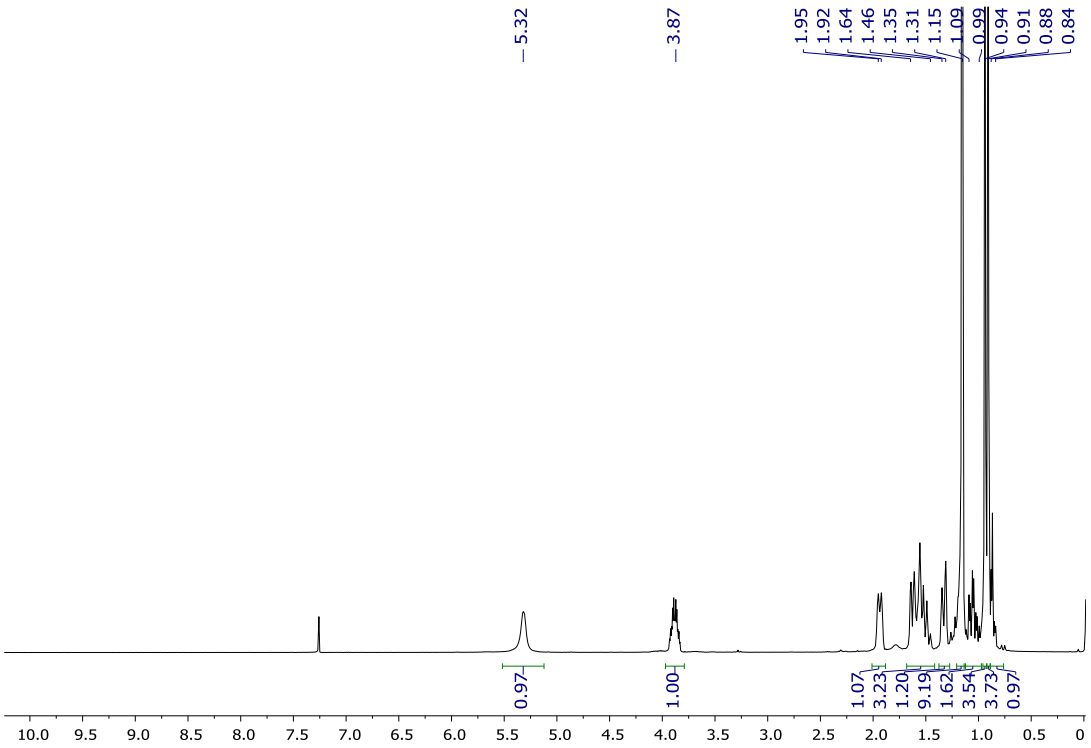


^{13}C{^{1}H}-NMR of **S20** in $CDCl_3$

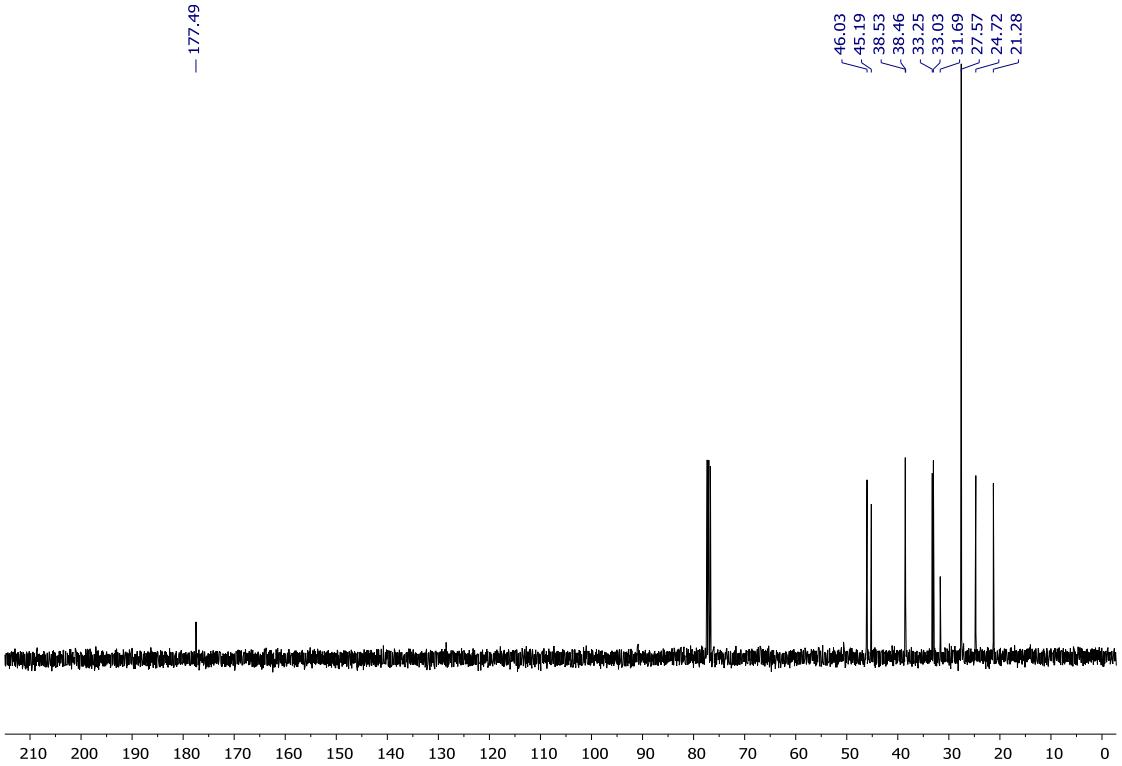


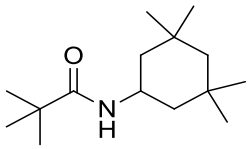


^{1}H-NMR of **S21** in $CDCl_3$

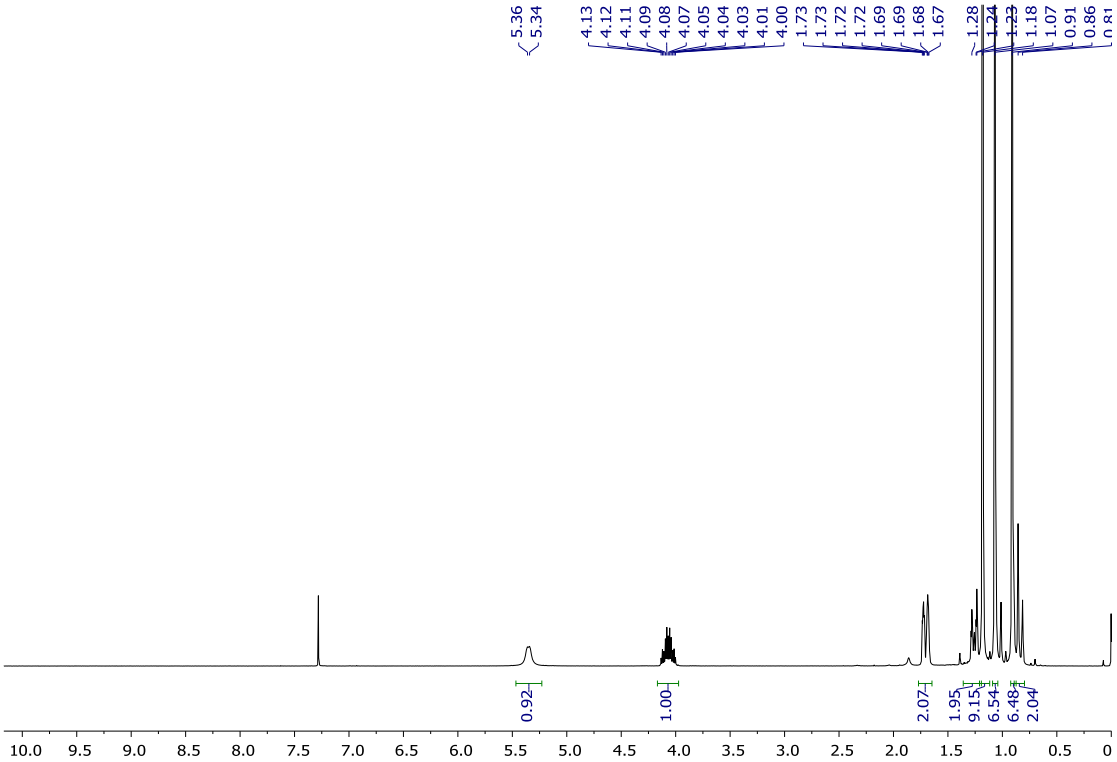


^{13}C{^{1}H}-NMR of **S21** in $CDCl_3$

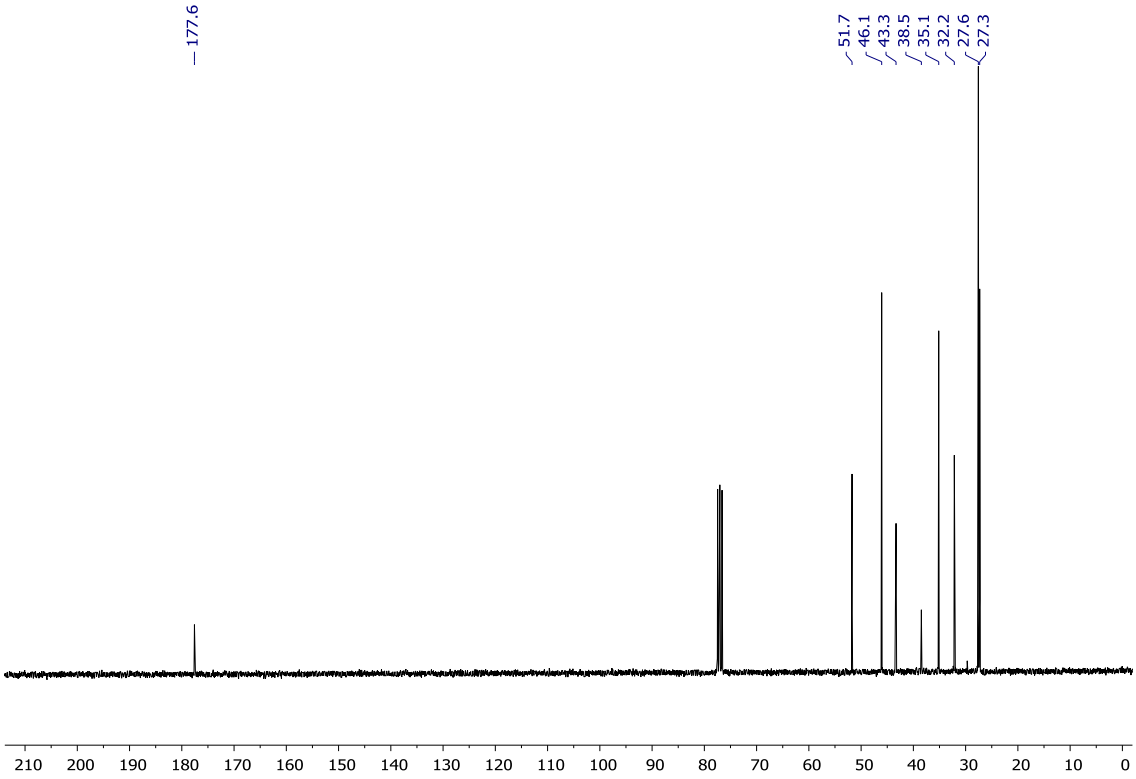




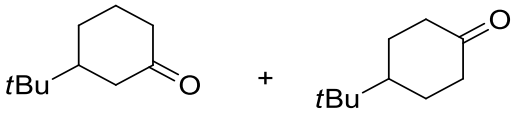
^{1}H-NMR of **S22** in $CDCl_3$



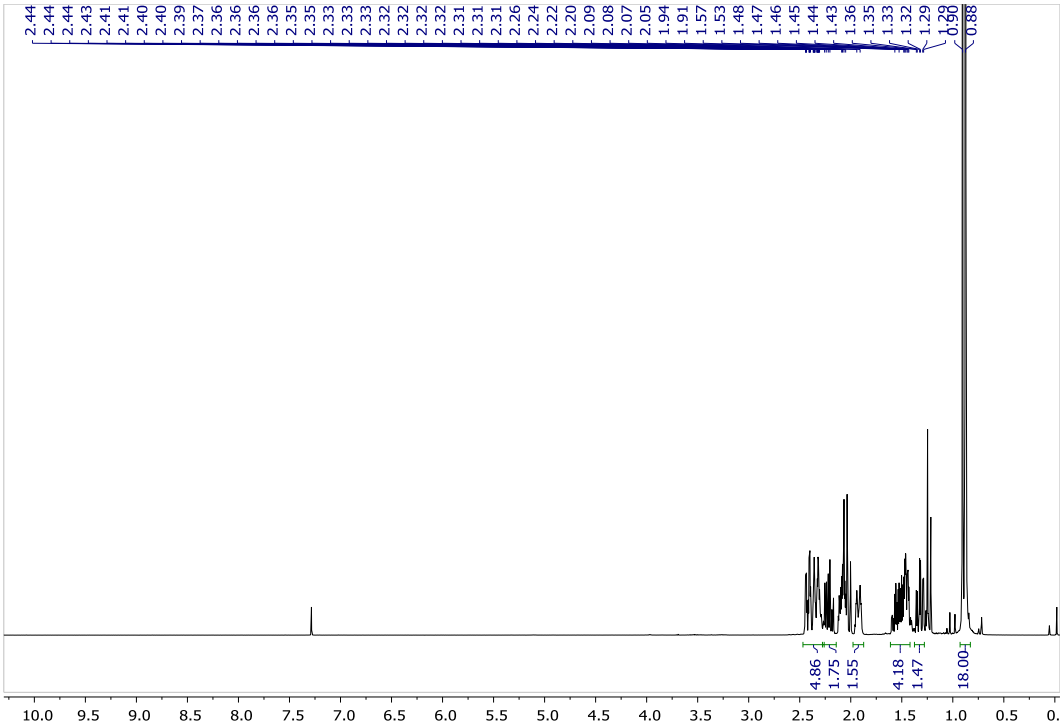
^{13}C{^{1}H}-NMR of **S22** in $CDCl_3$



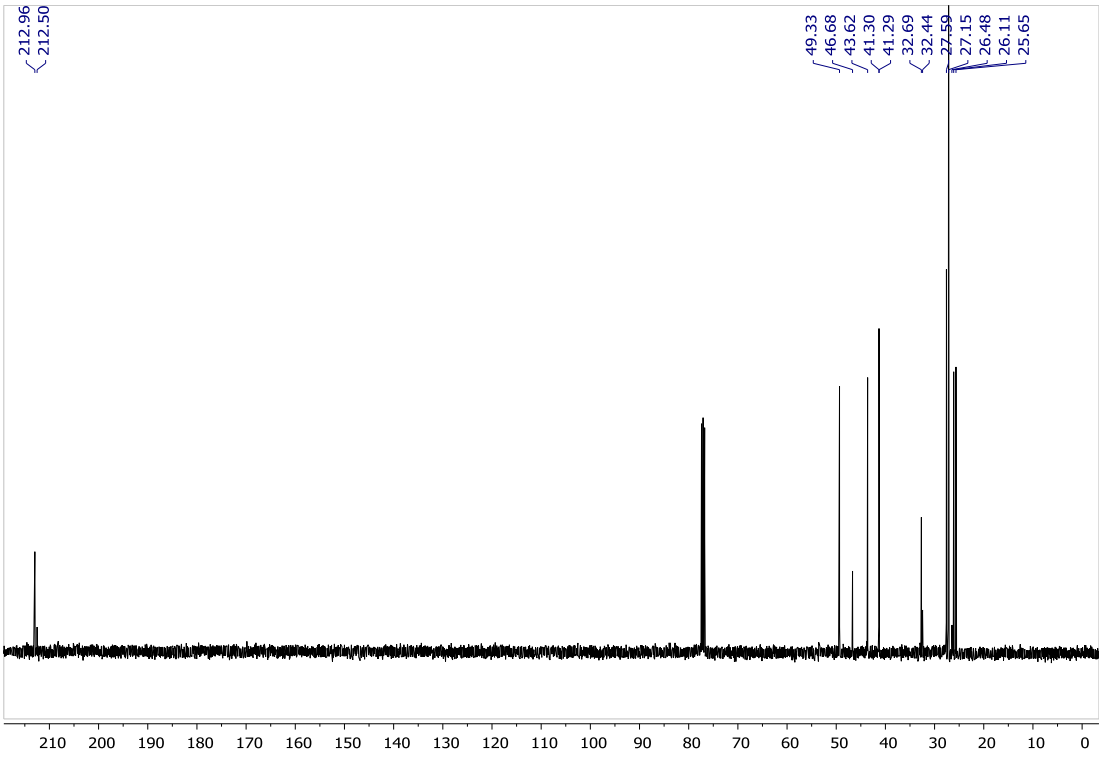
A3 ^{1}H and ^{13}C{^{1}H} NMR spectra of isolated products

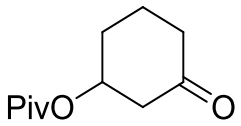


^{1}H-NMR of **P1 (K_3+K_4)** in $CDCl_3$

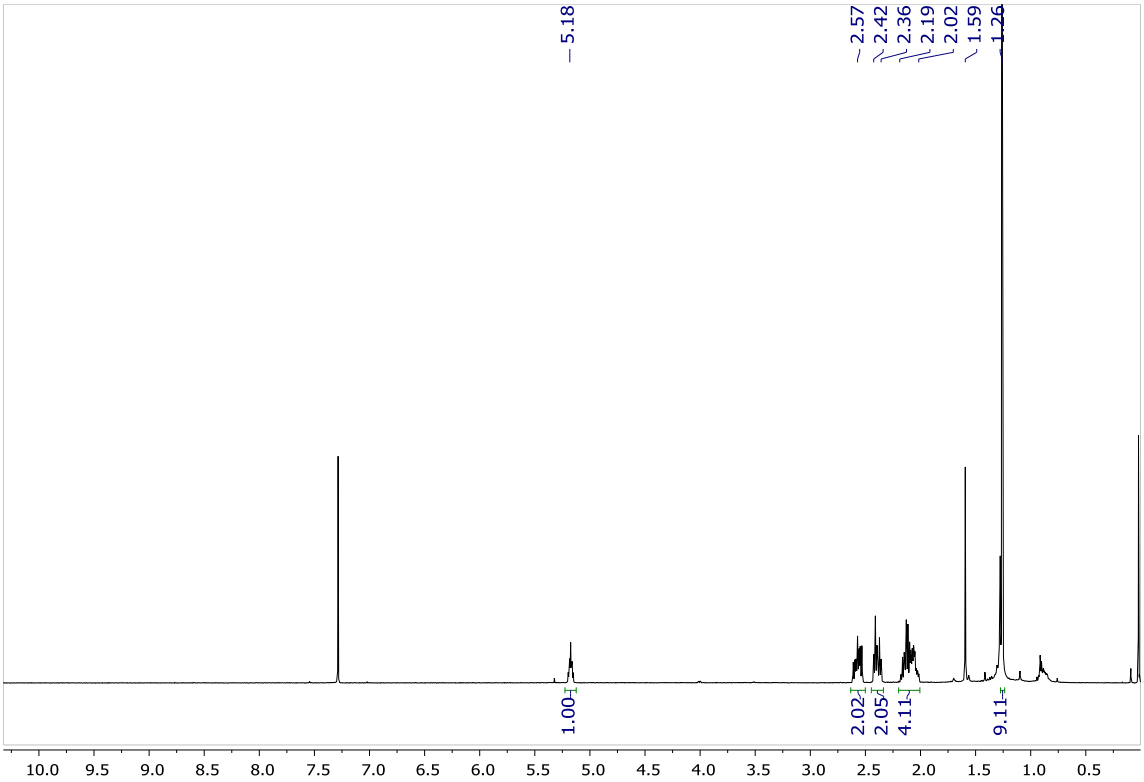


^{13}C{^{1}H}-NMR of **P1 (K_3+K_4)** in $CDCl_3$

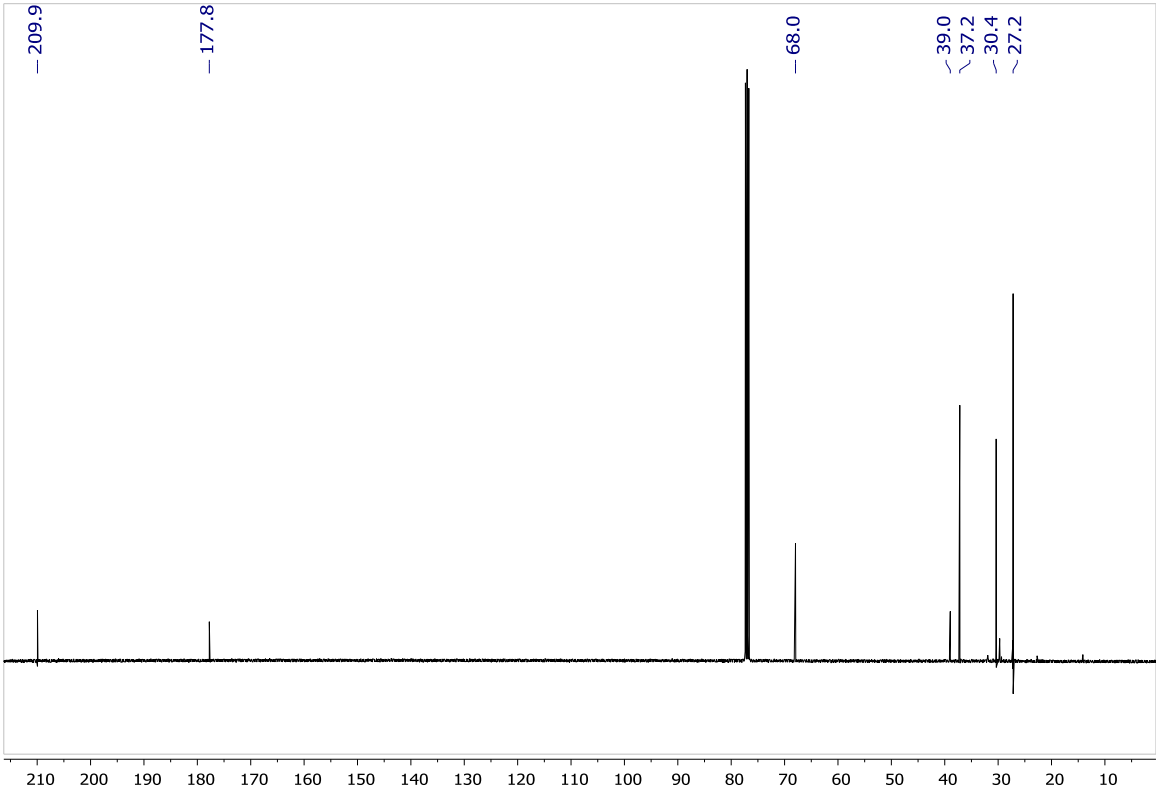


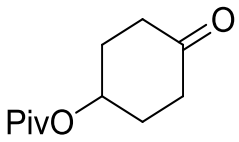


^{1}H-NMR of **P2 (K_3)** in $CDCl_3$

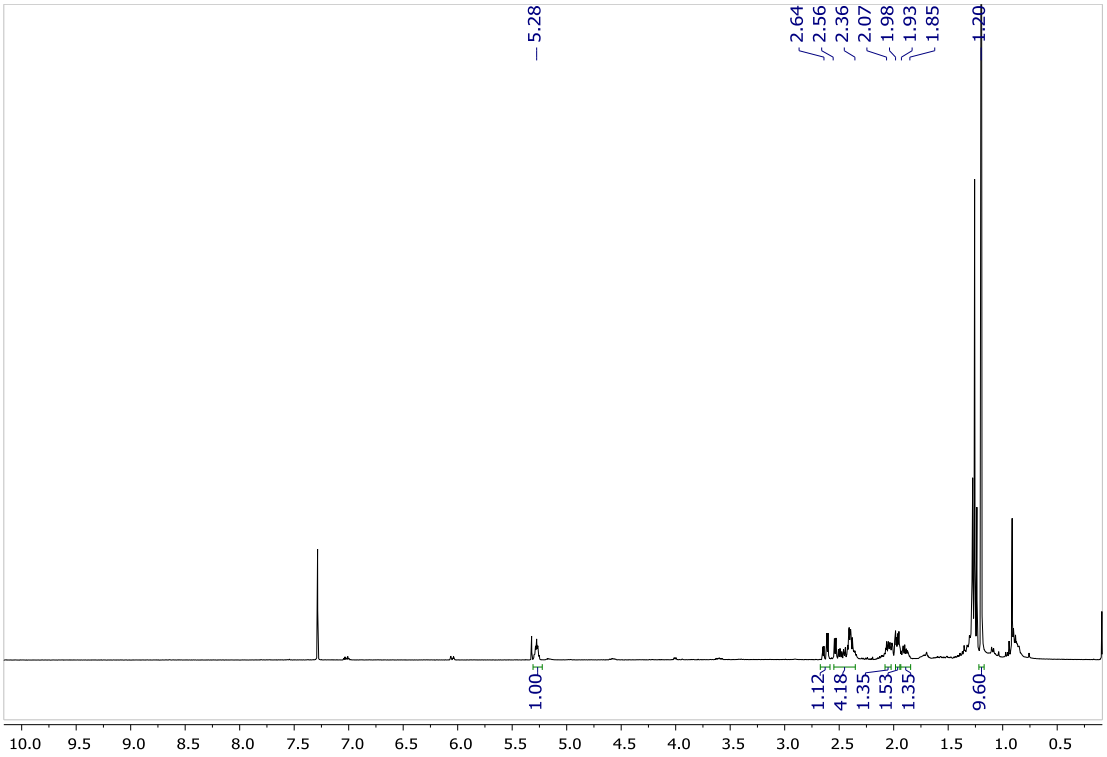


^{13}C{^{1}H}-NMR of **P2 (K_3)** in $CDCl_3$

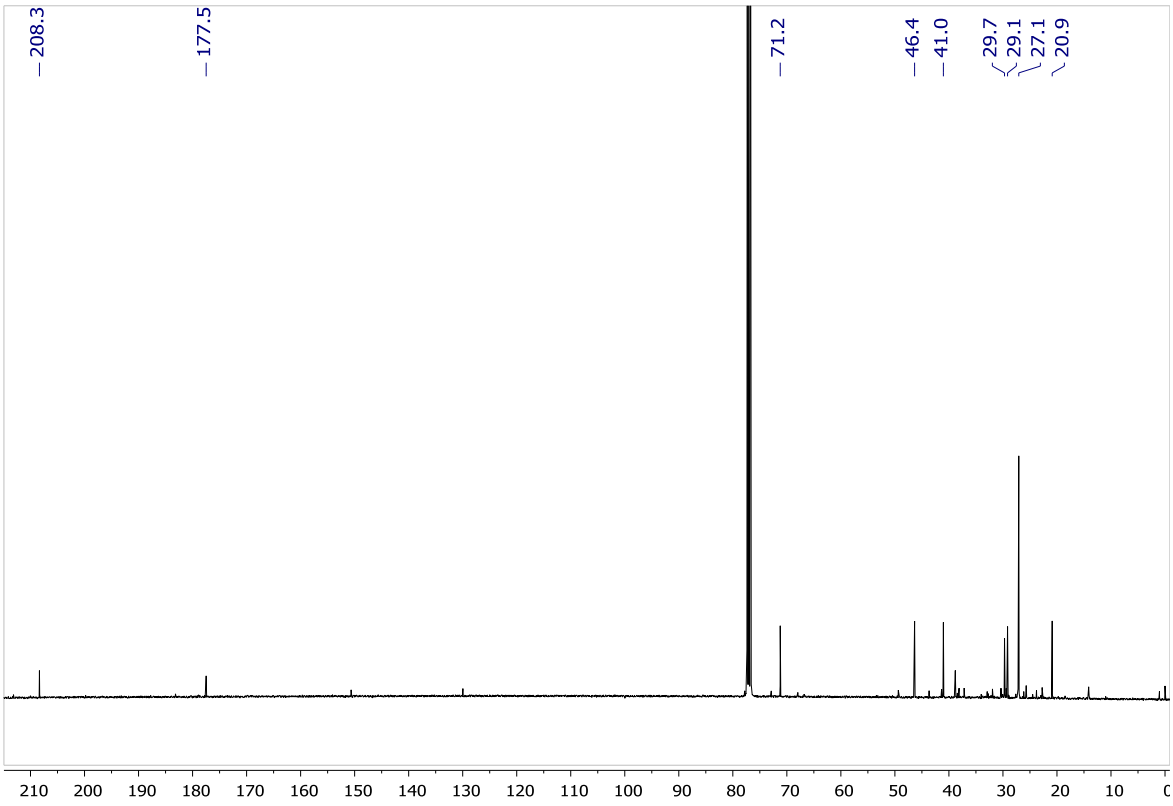


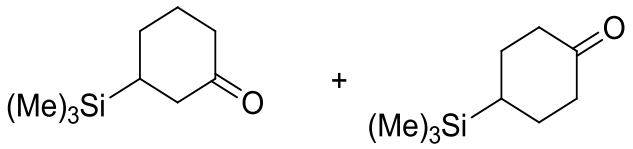


^{1}H-NMR of **P2 (K_4)** in $CDCl_3$

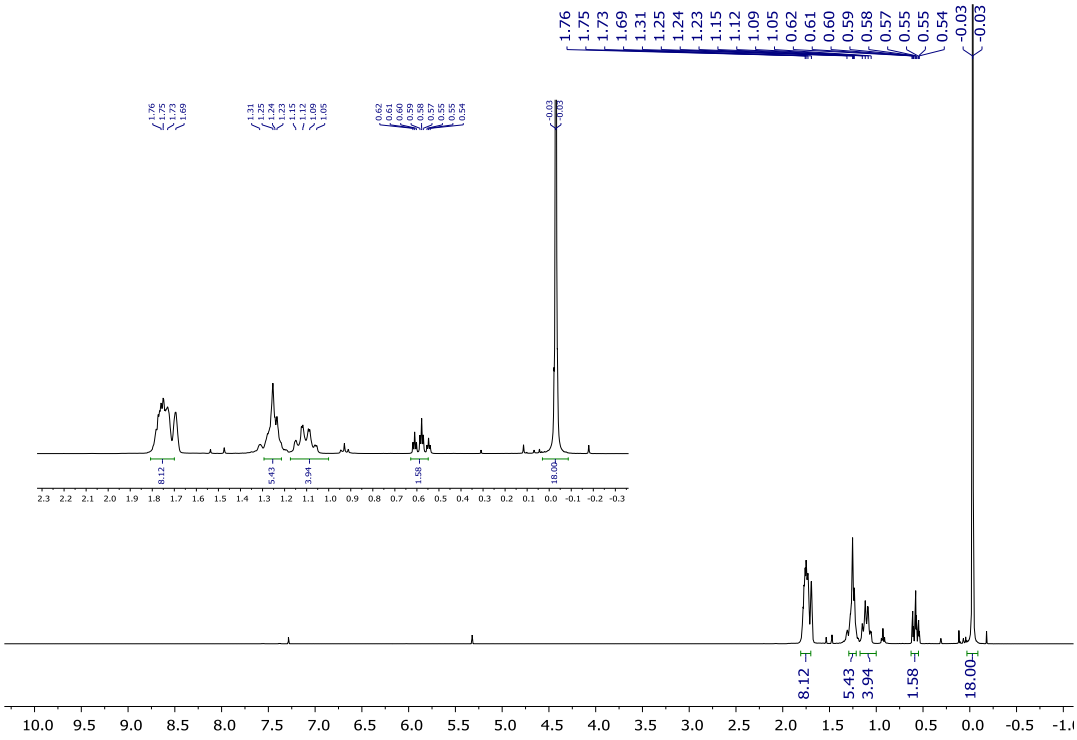


^{13}C{^{1}H}-NMR of **P2 (K_4)** in $CDCl_3$

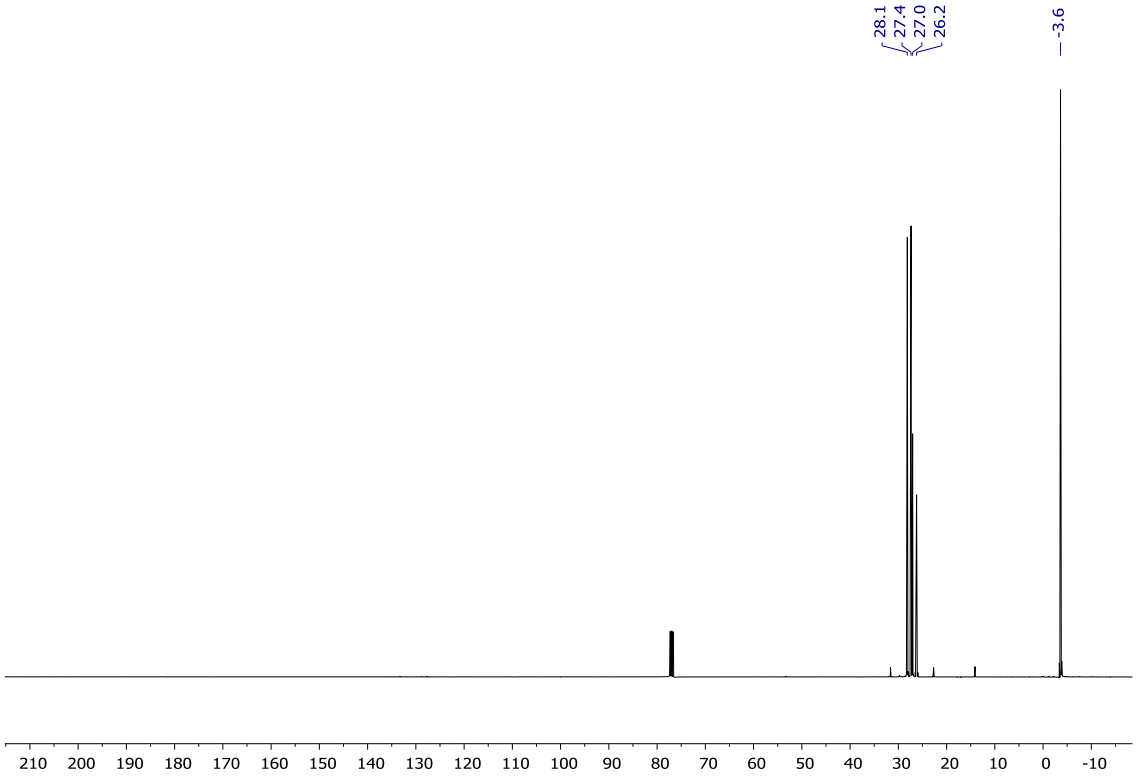


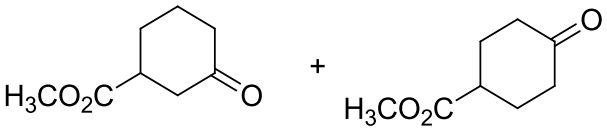


^{1}H-NMR of **P3 (K_3+K_4)** in $CDCl_3$

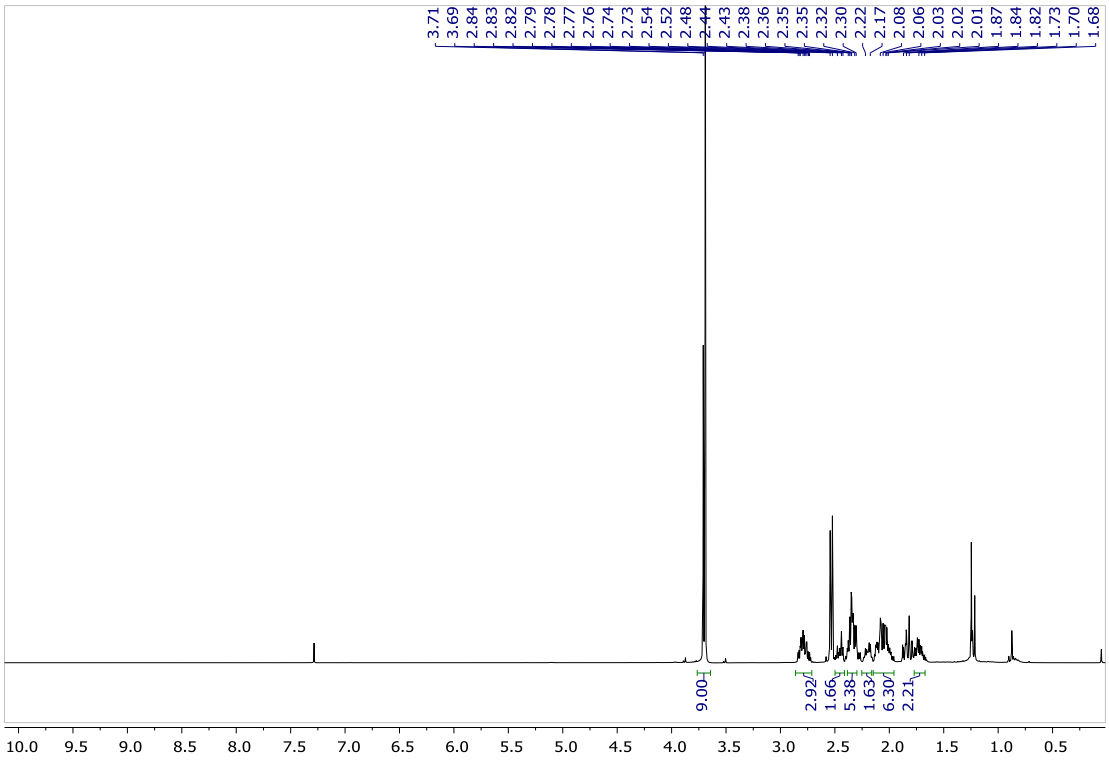


^{13}C{^{1}H}-NMR of **P3 (K_3+K_4)** in $CDCl_3$

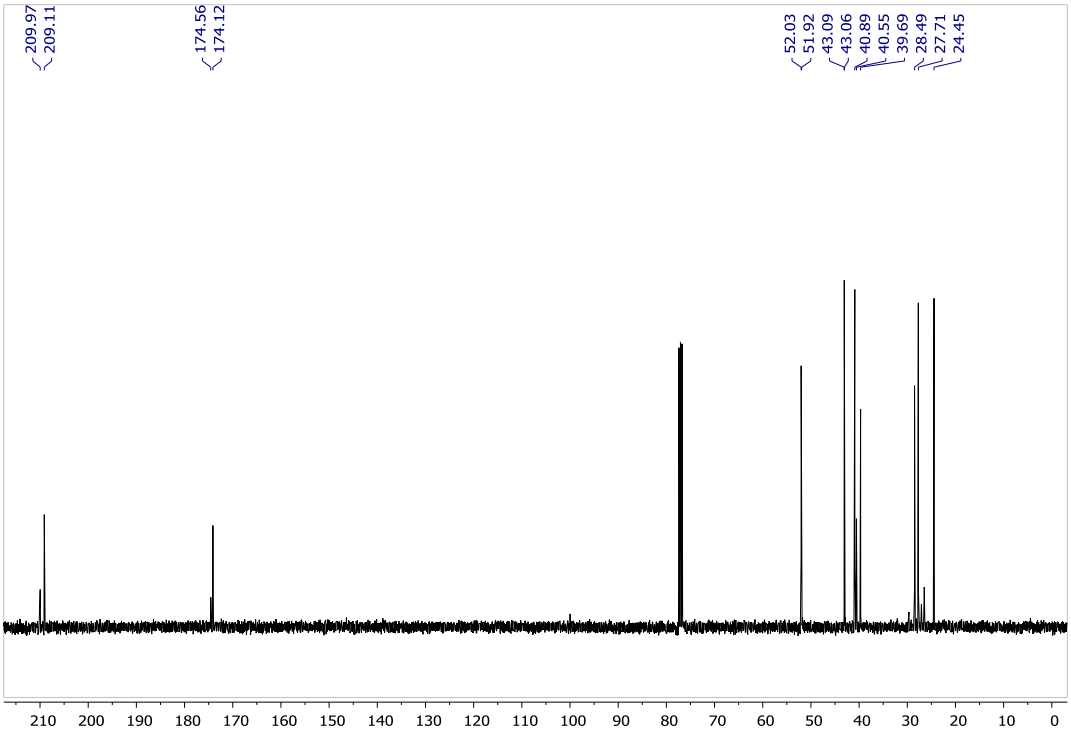


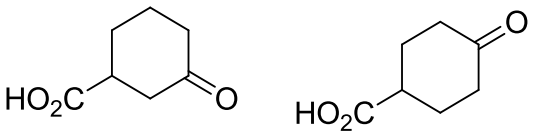


^{1}H-NMR of **P4 (K_3+K_4)** in $CDCl_3$

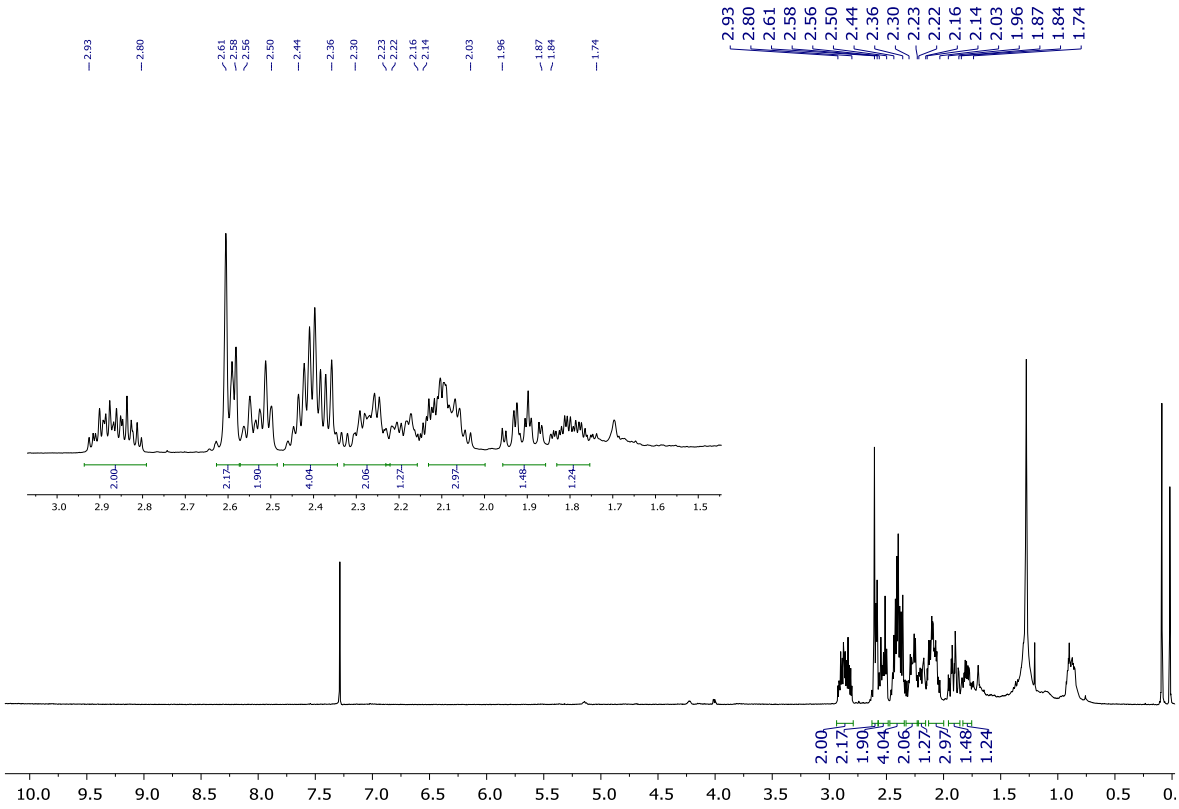


^{13}C{^{1}H}-NMR of **P4 (K_3+K_4)** in $CDCl_3$

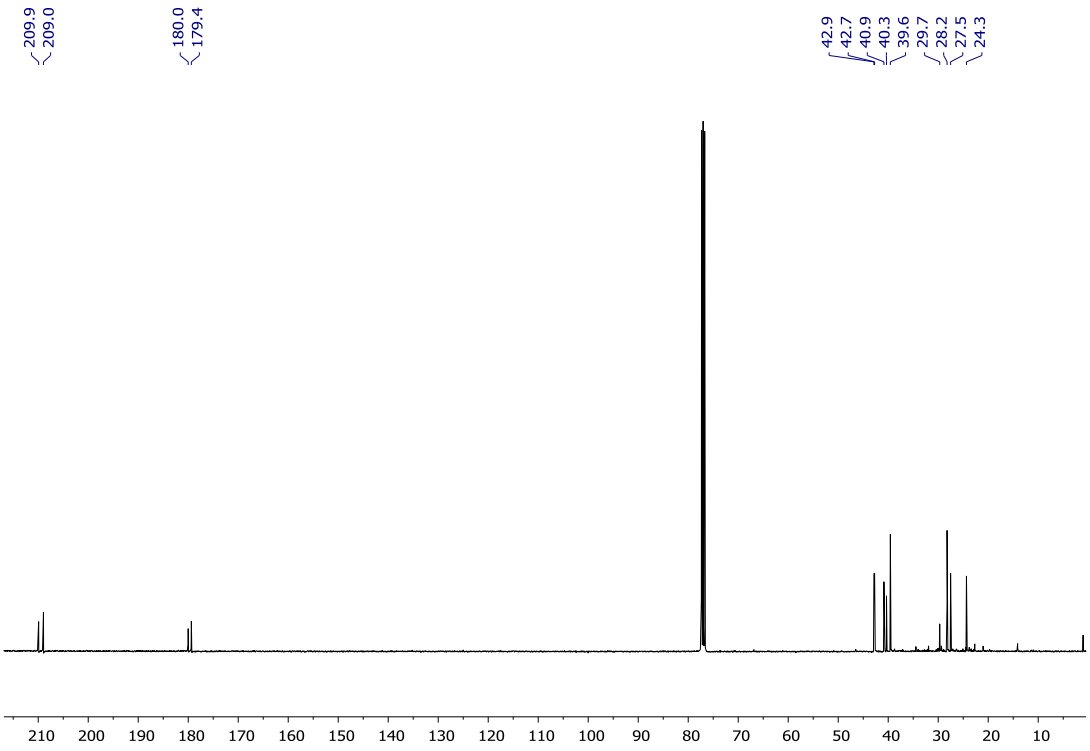


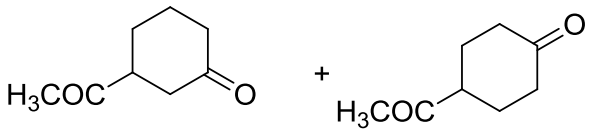


^{1}H-NMR of **P5 (K_3+K_4)** in $CDCl_3$

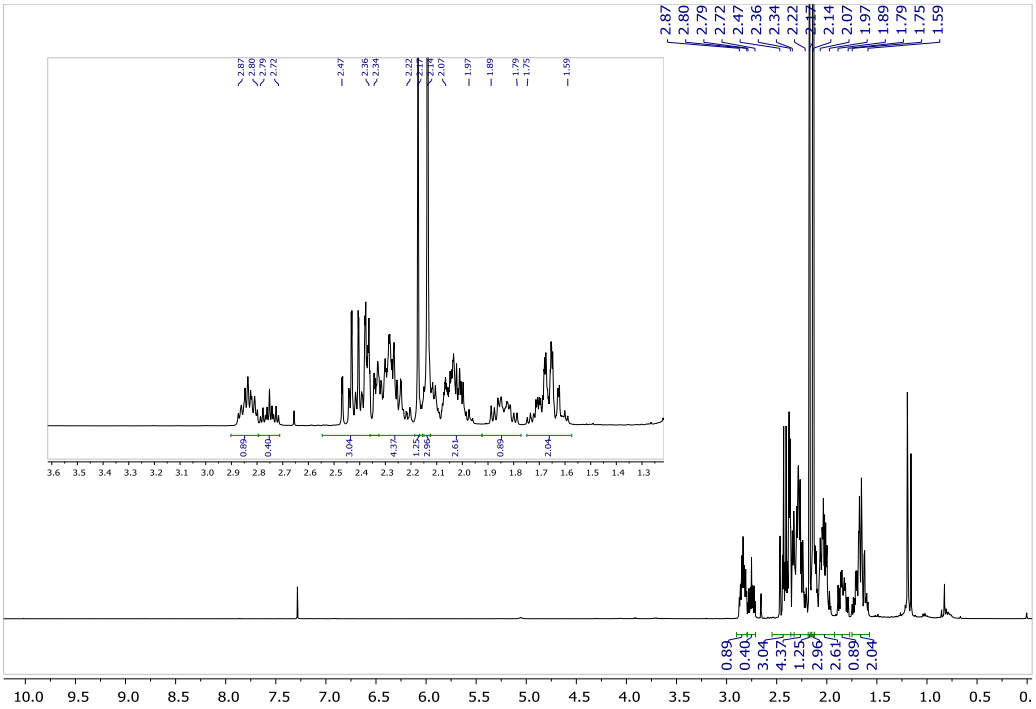


^{13}C{^{1}H}-NMR of **P5 (K_3+K_4)** in $CDCl_3$

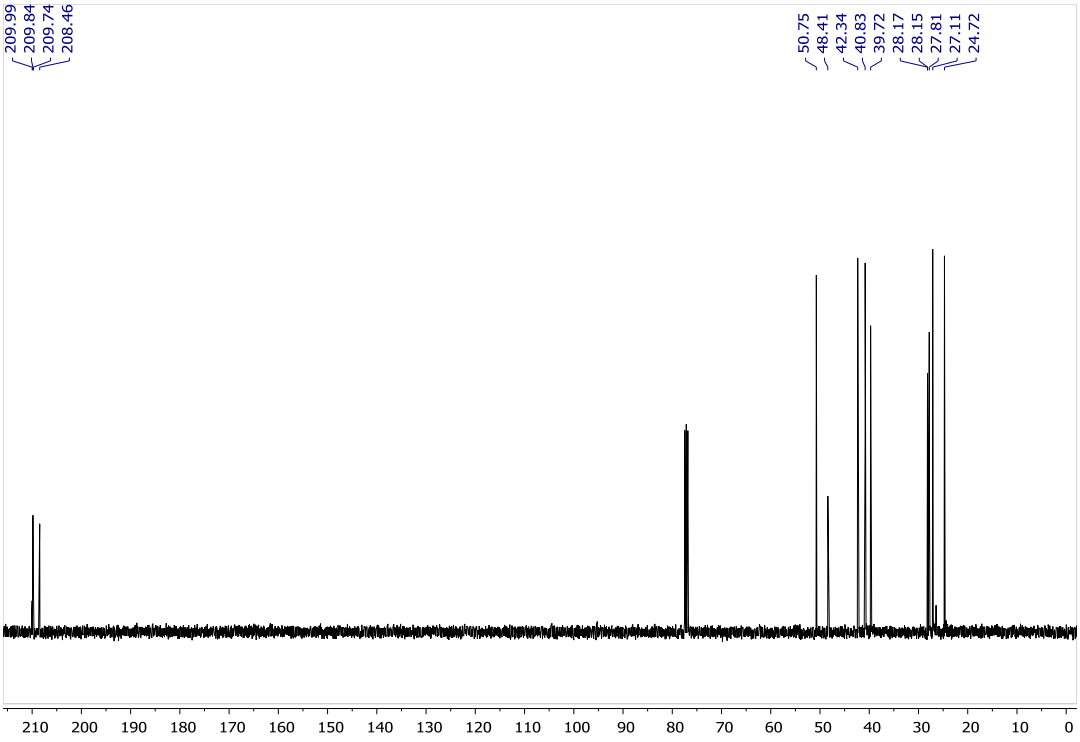


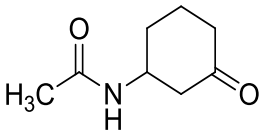


^{1}H-NMR of **P6 (K_3+K_4)** in $CDCl_3$

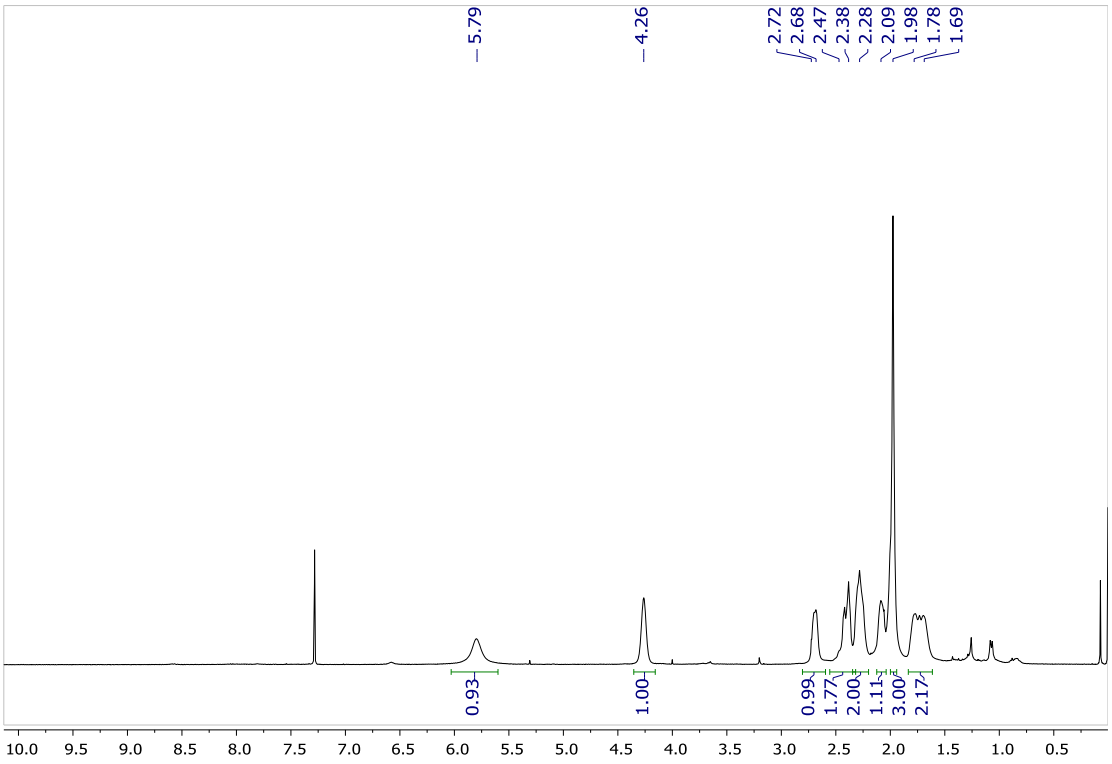


^{13}C{^{1}H}-NMR of **P6 (K_3+K_4)** in $CDCl_3$

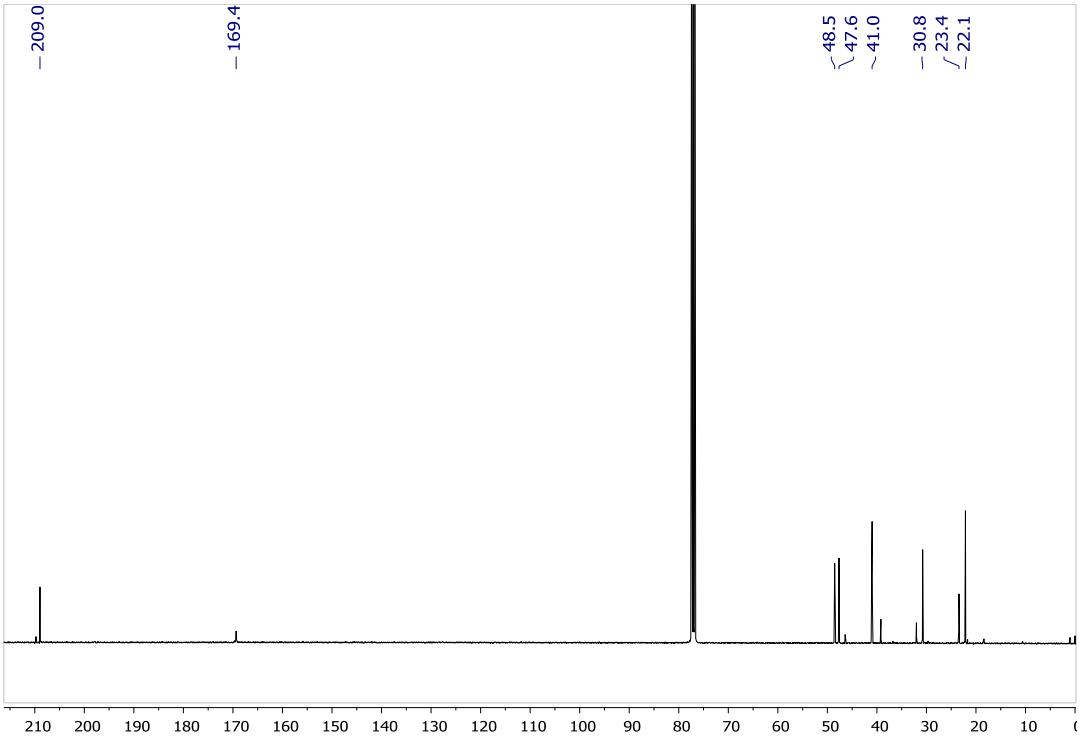


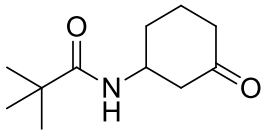


^{1}H-NMR of **P7** in $CDCl_3$

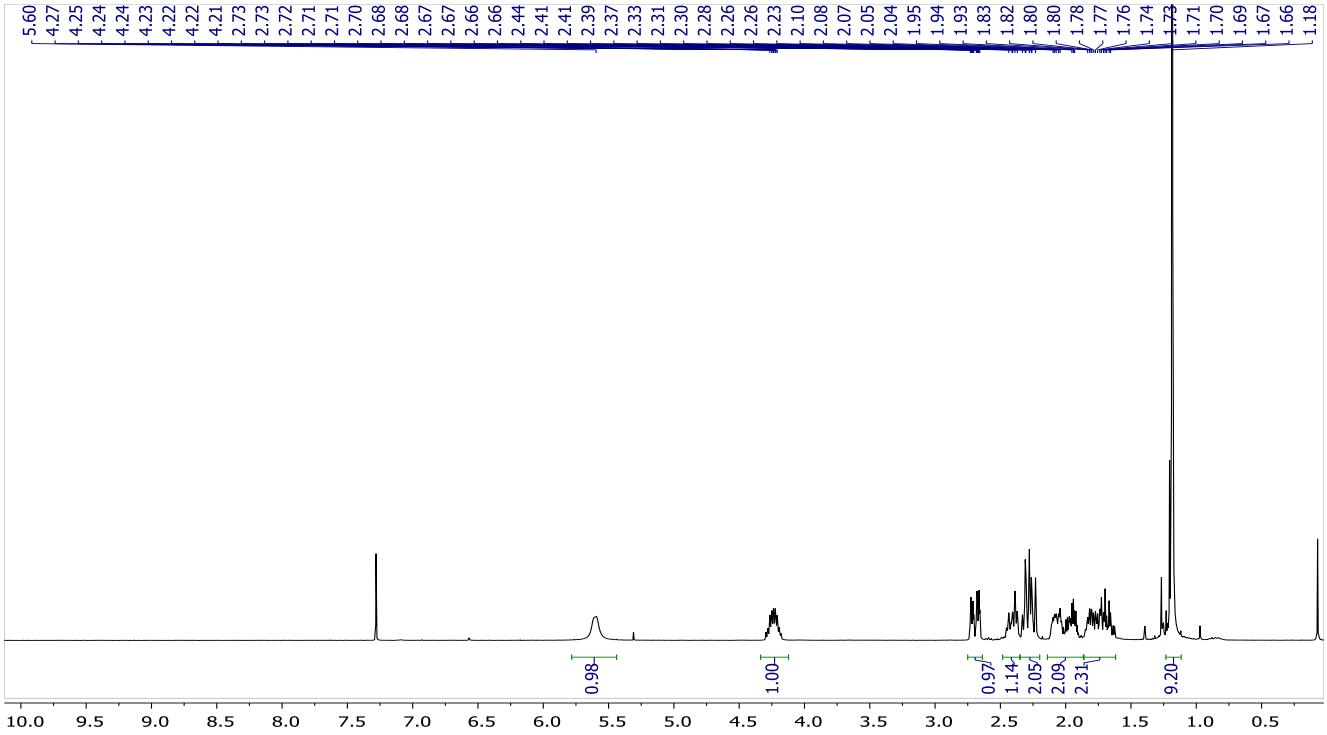


^{13}C{^{1}H}-NMR of **P7** in $CDCl_3$

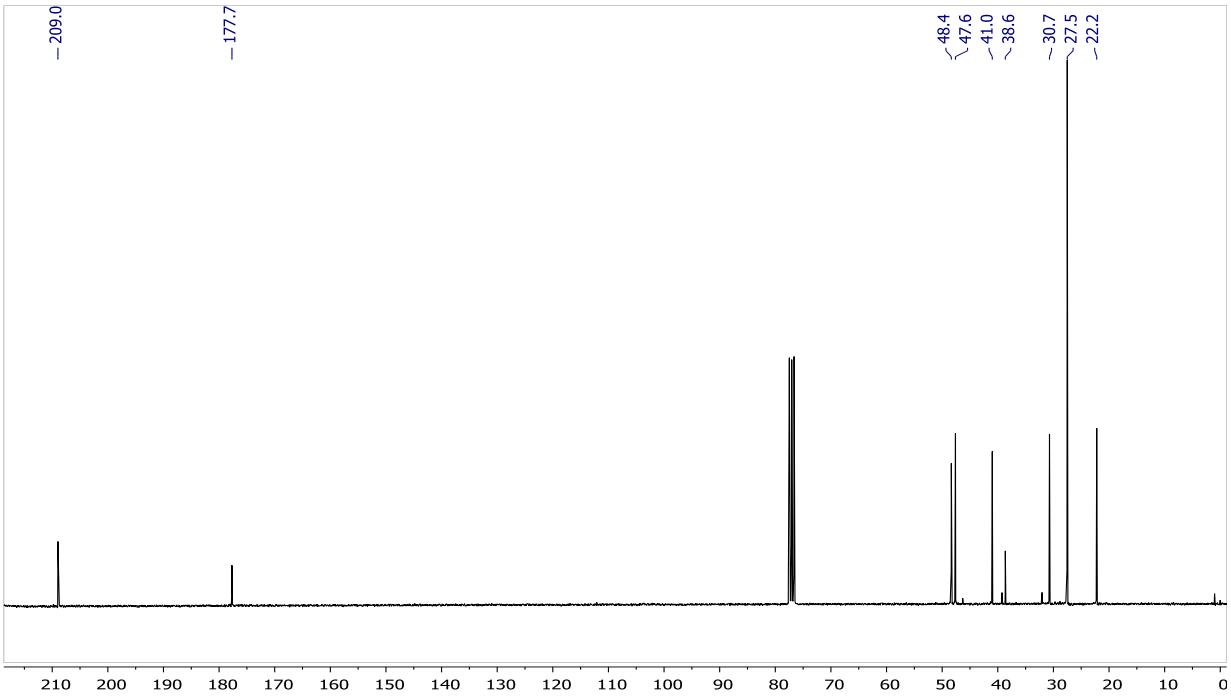


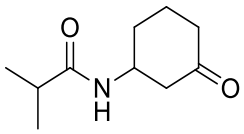


^{1}H-NMR of **P8** in $CDCl_3$

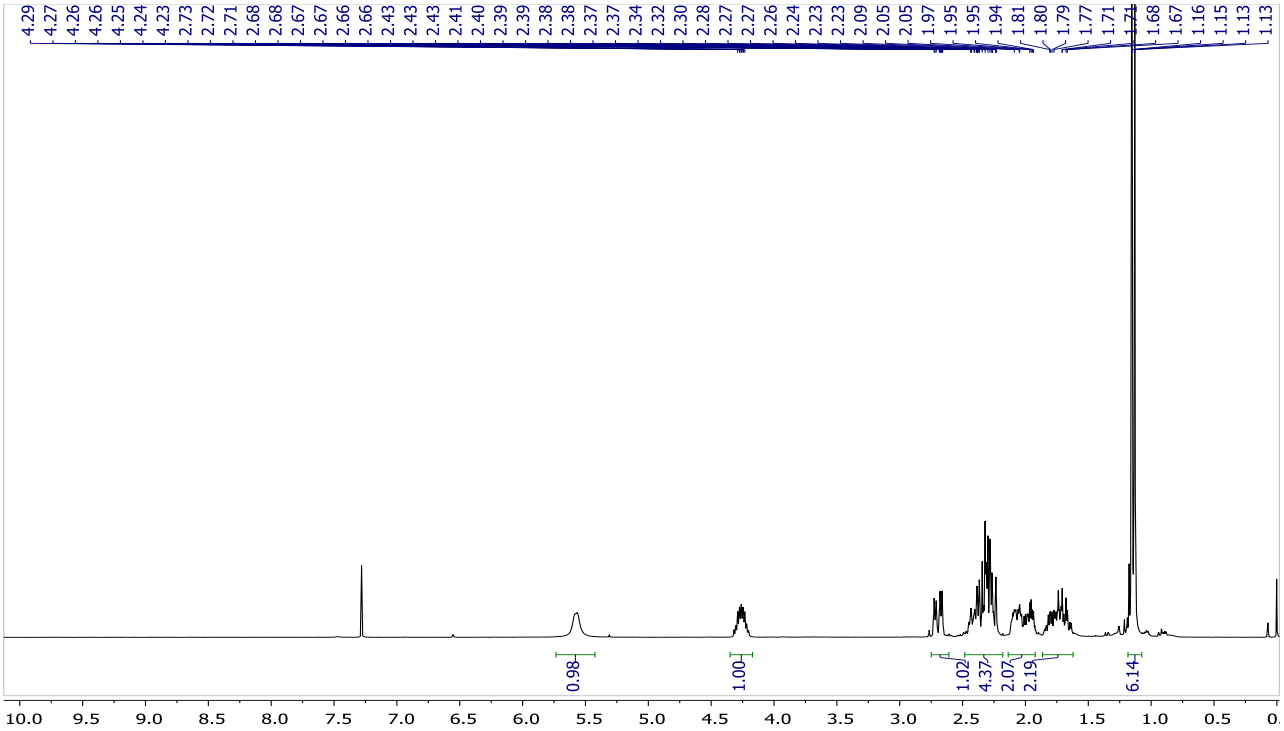


^{13}C{^{1}H}-NMR of **P8** in $CDCl_3$

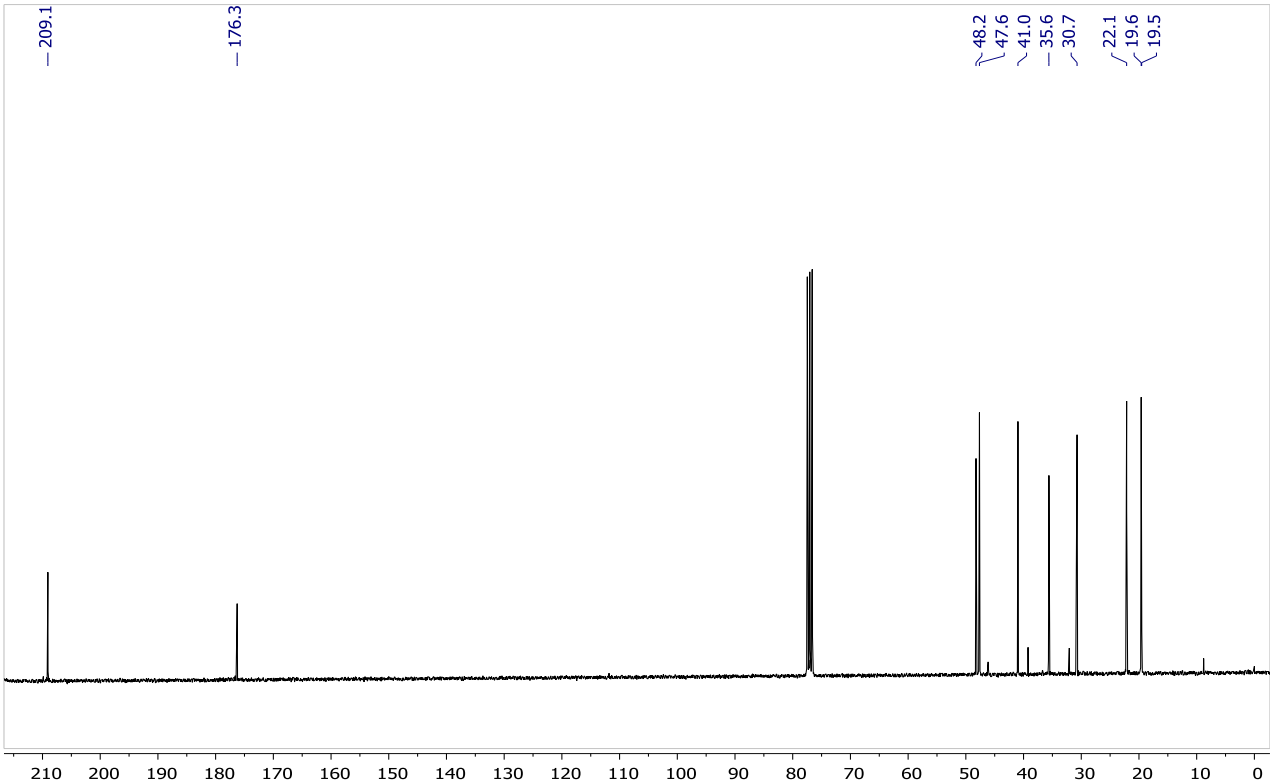


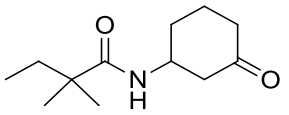


^{1}H-NMR of **P9** in $CDCl_3$

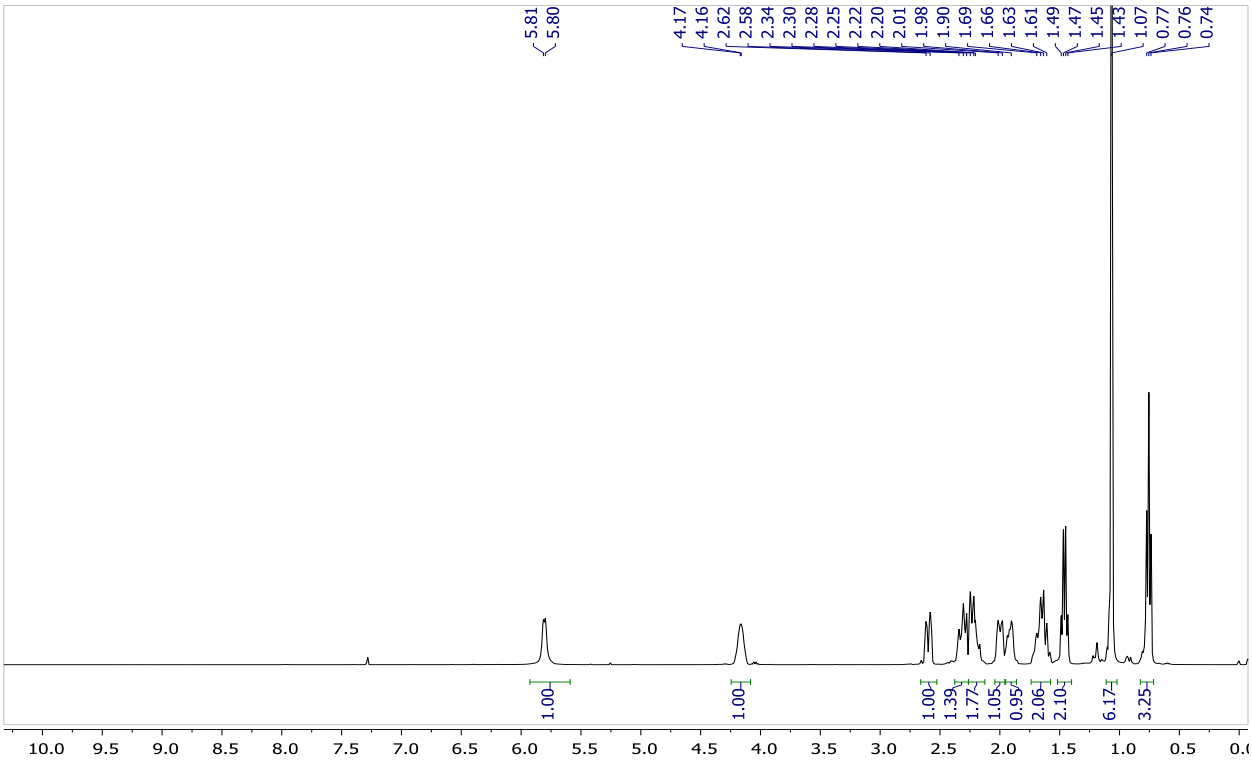


$^{13}C\{^{1}H\}$-NMR of **P9** in $CDCl_3$

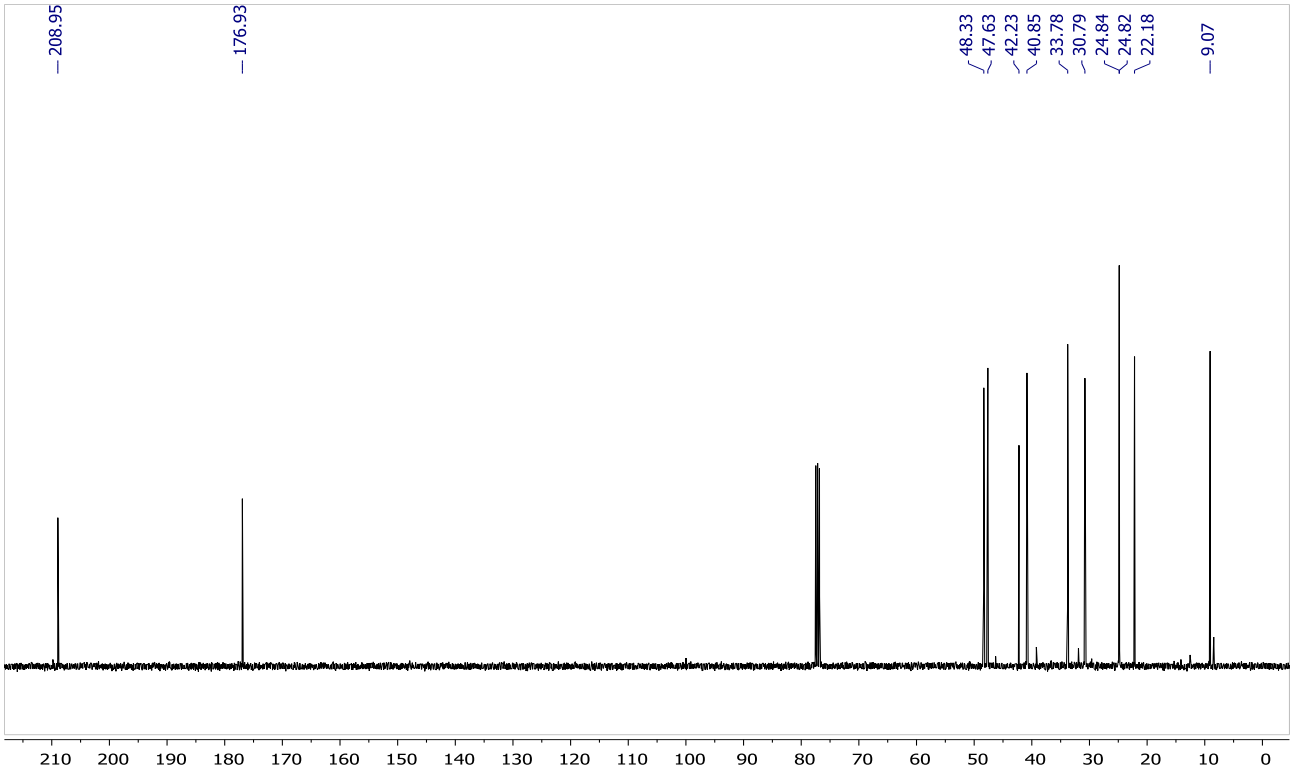


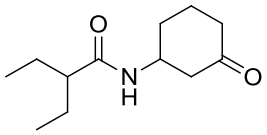


^{1}H-NMR of **P10** in $CDCl_3$

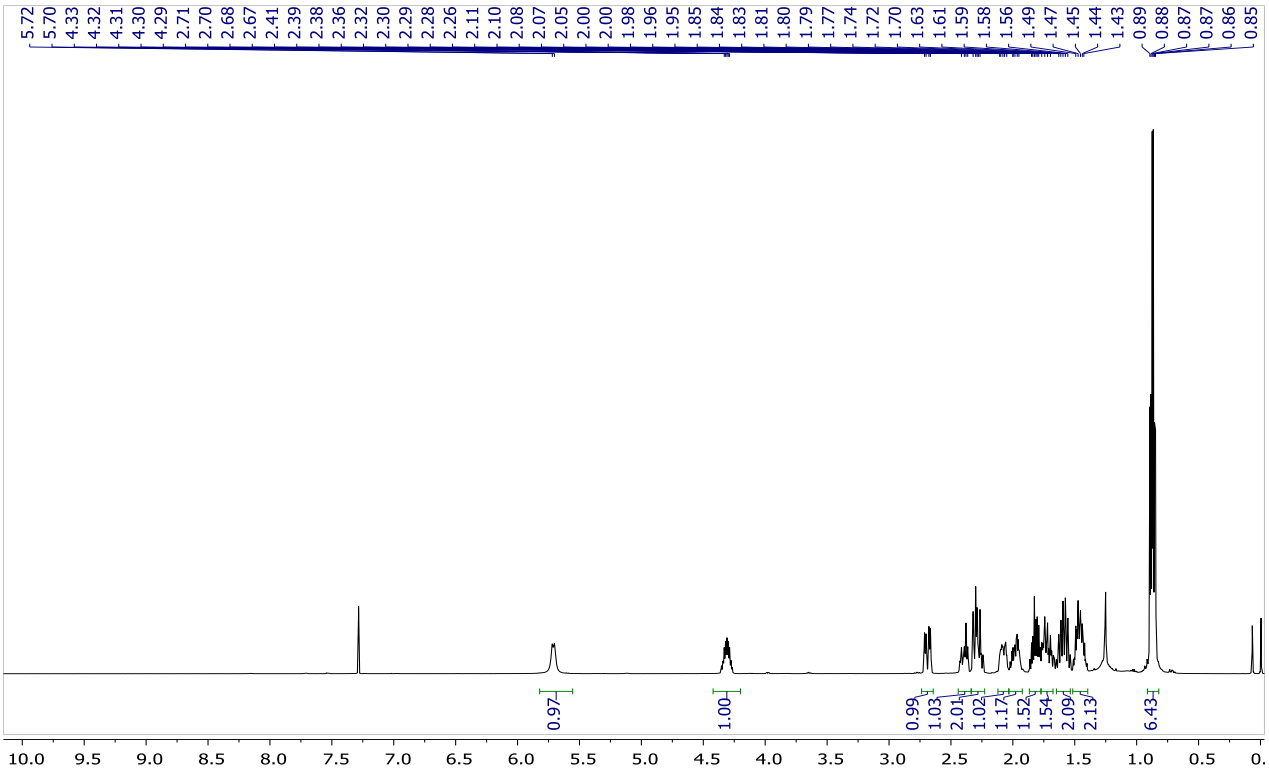


^{13}C{^{1}H}-NMR of **P10** in $CDCl_3$

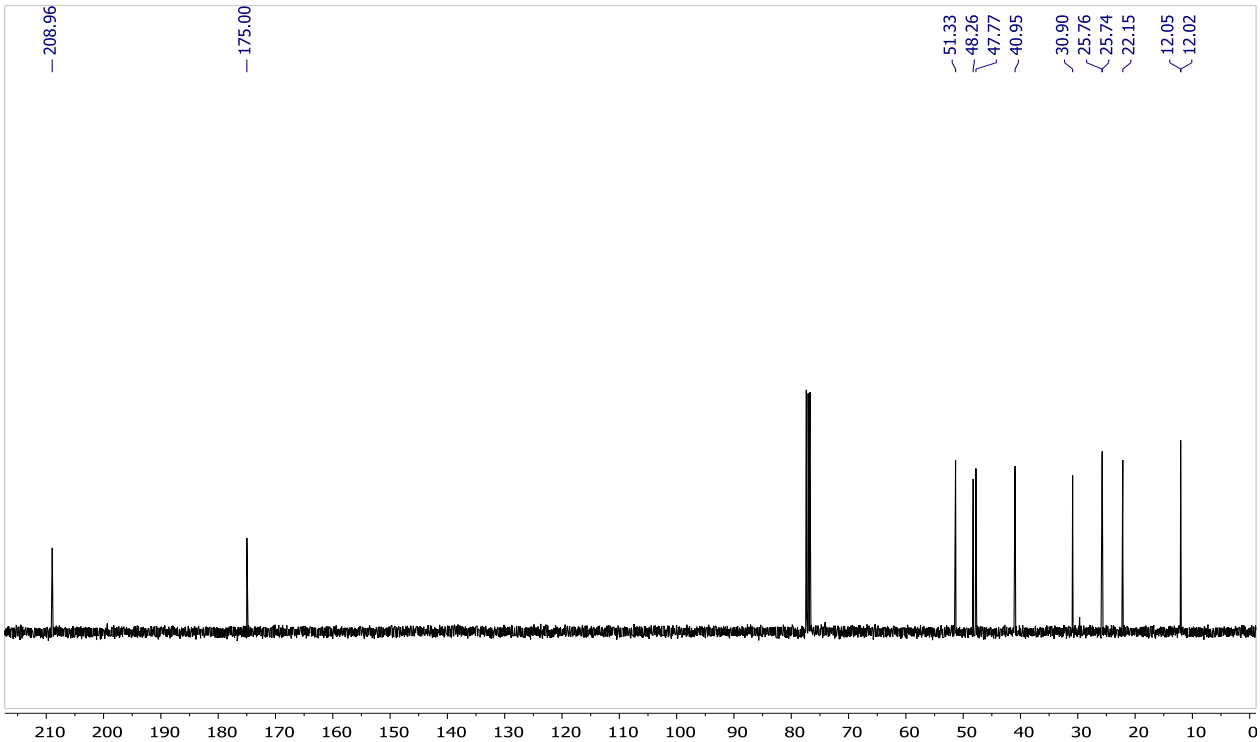


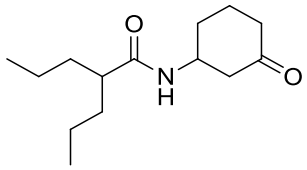


^{1}H-NMR of **P11** in $CDCl_3$

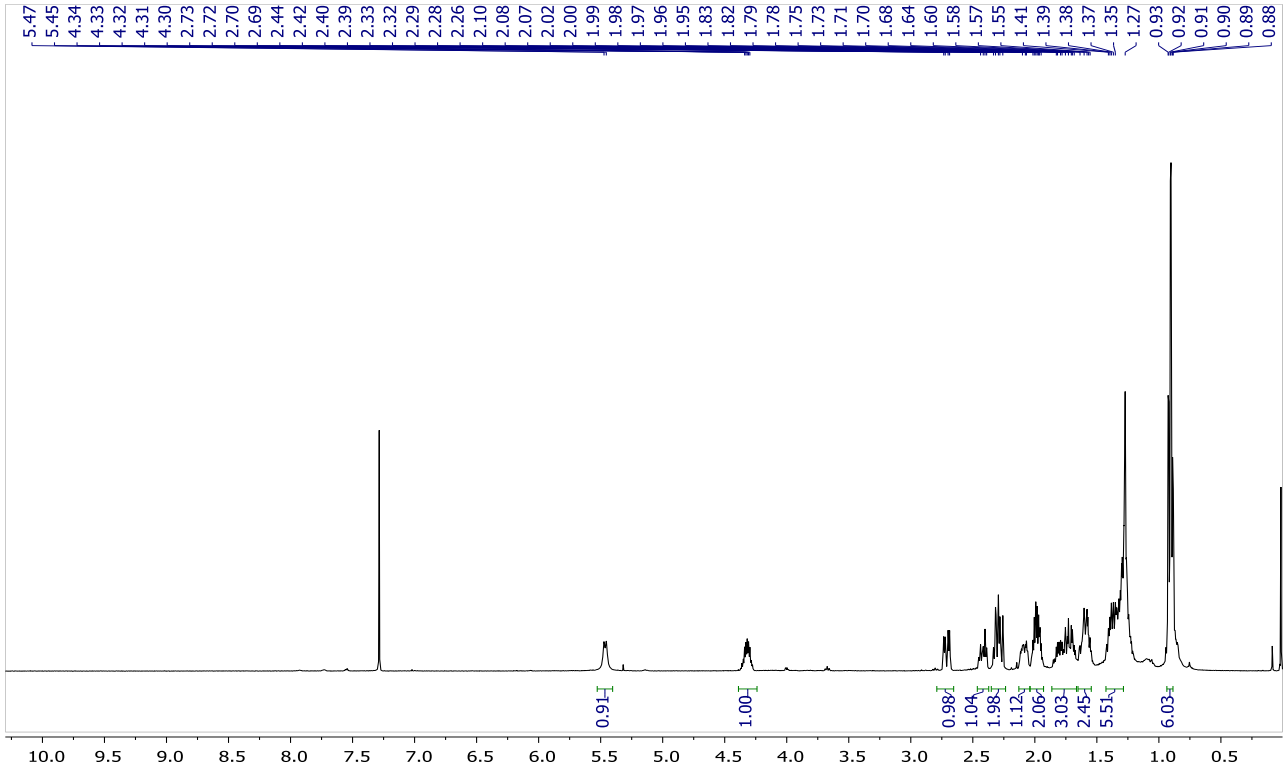


^{13}C{^{1}H}-NMR of **P11** in $CDCl_3$

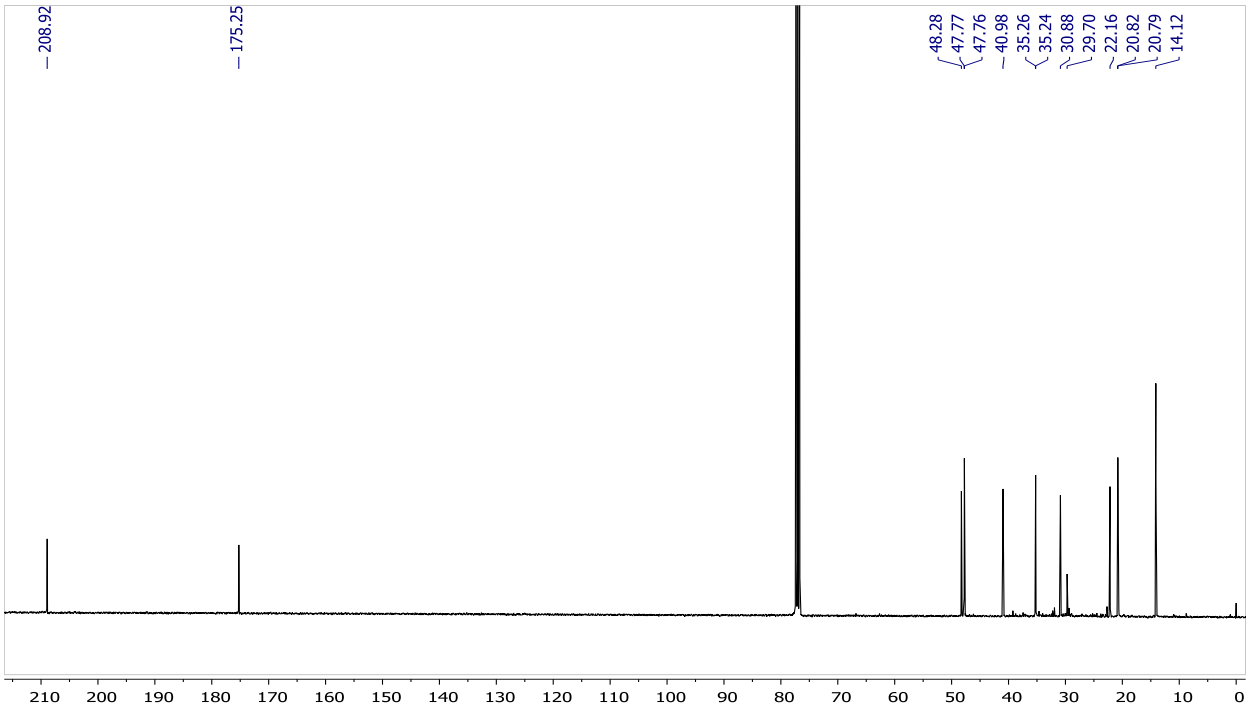


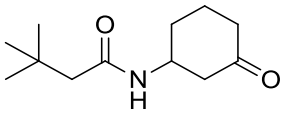


^{1}H-NMR of **P12** in $CDCl_3$

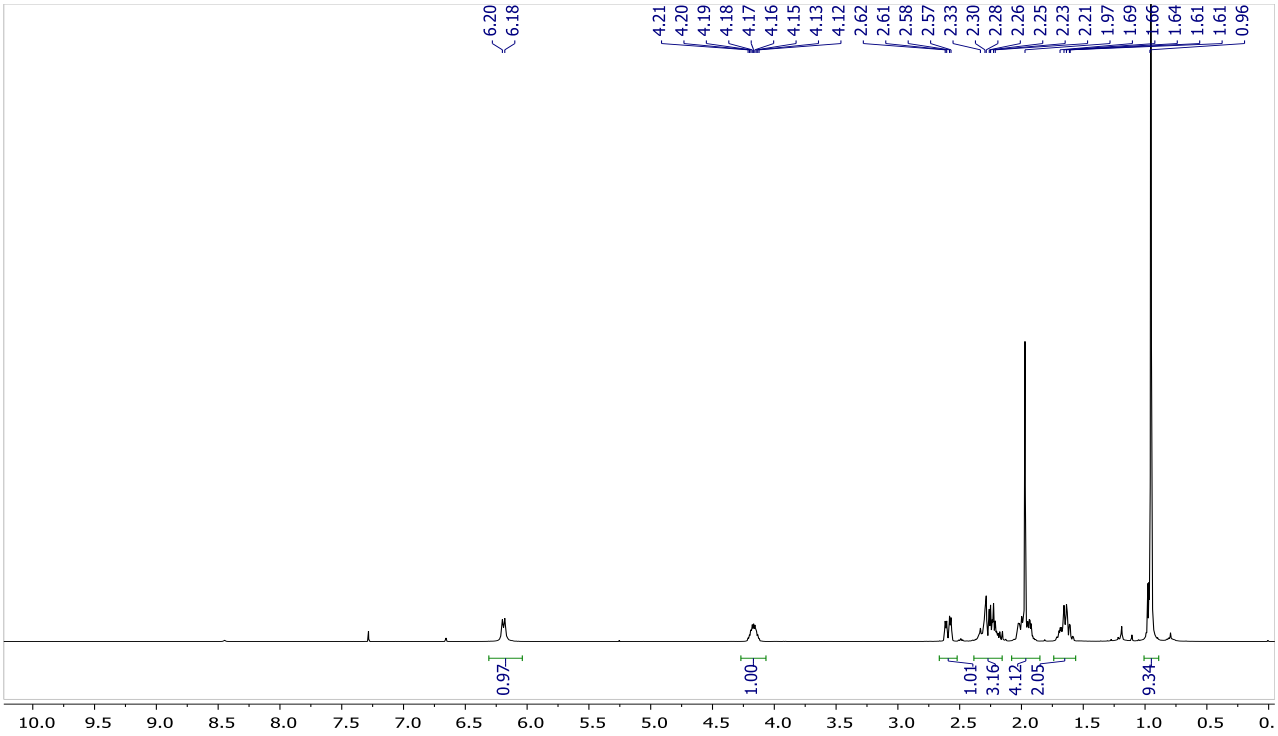


^{13}C{^{1}H}-NMR of **P12** in $CDCl_3$

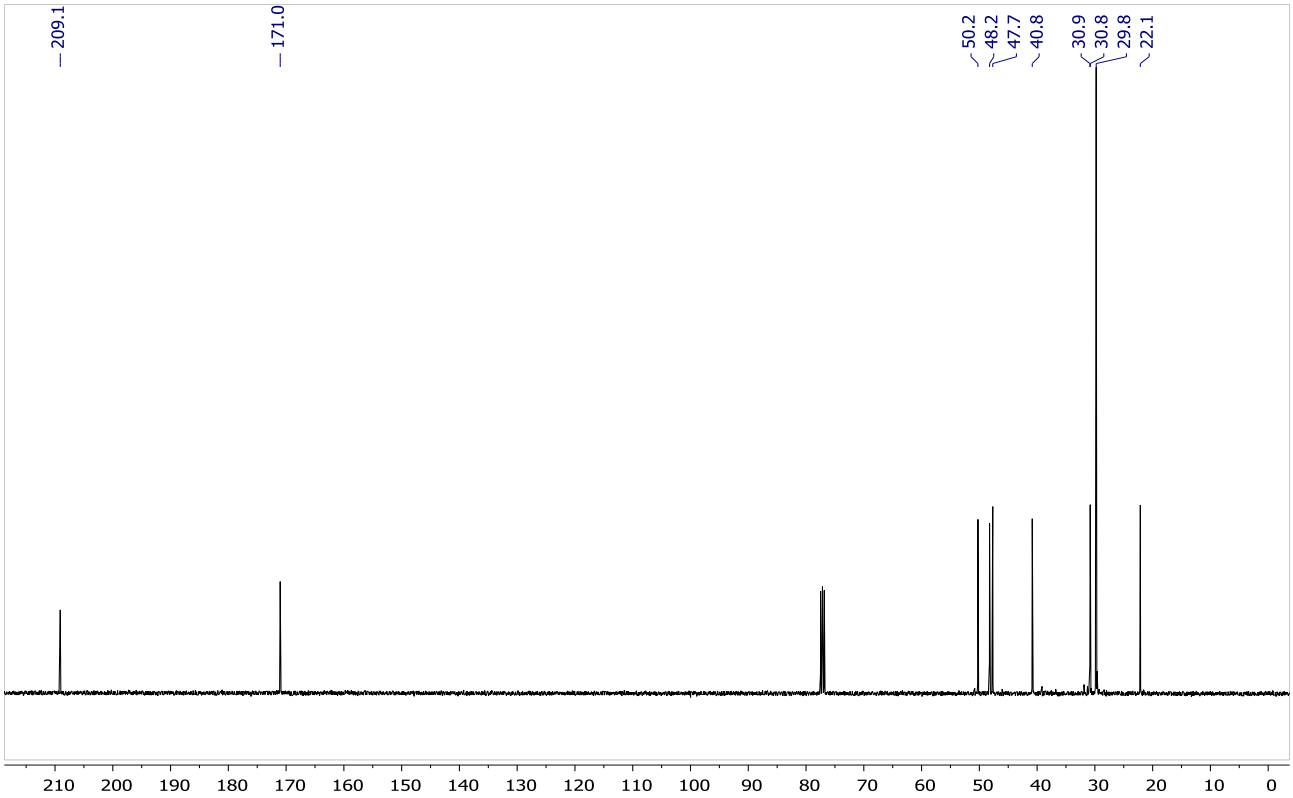


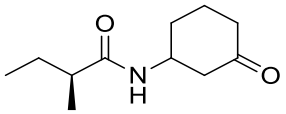


^{1}H-NMR of **P13** in $CDCl_3$

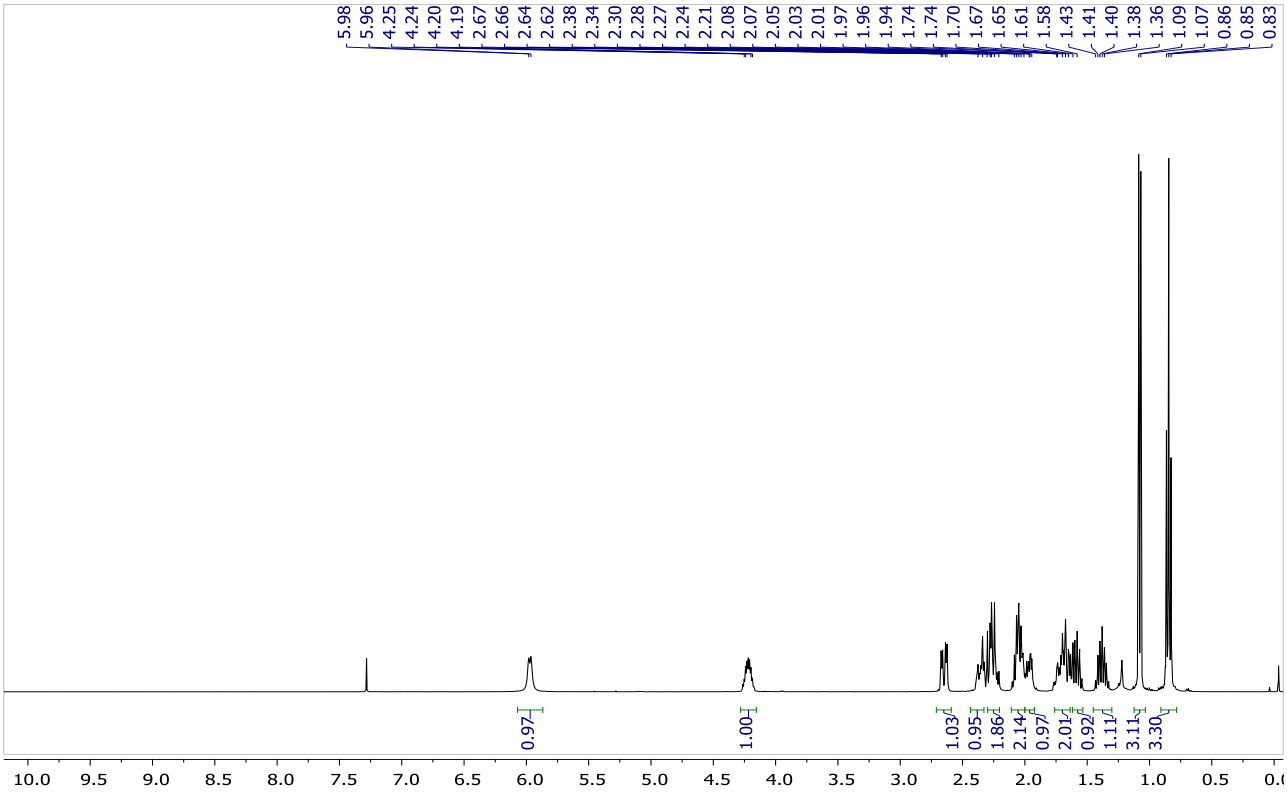


^{13}C{^{1}H}-NMR of **P13** in $CDCl_3$

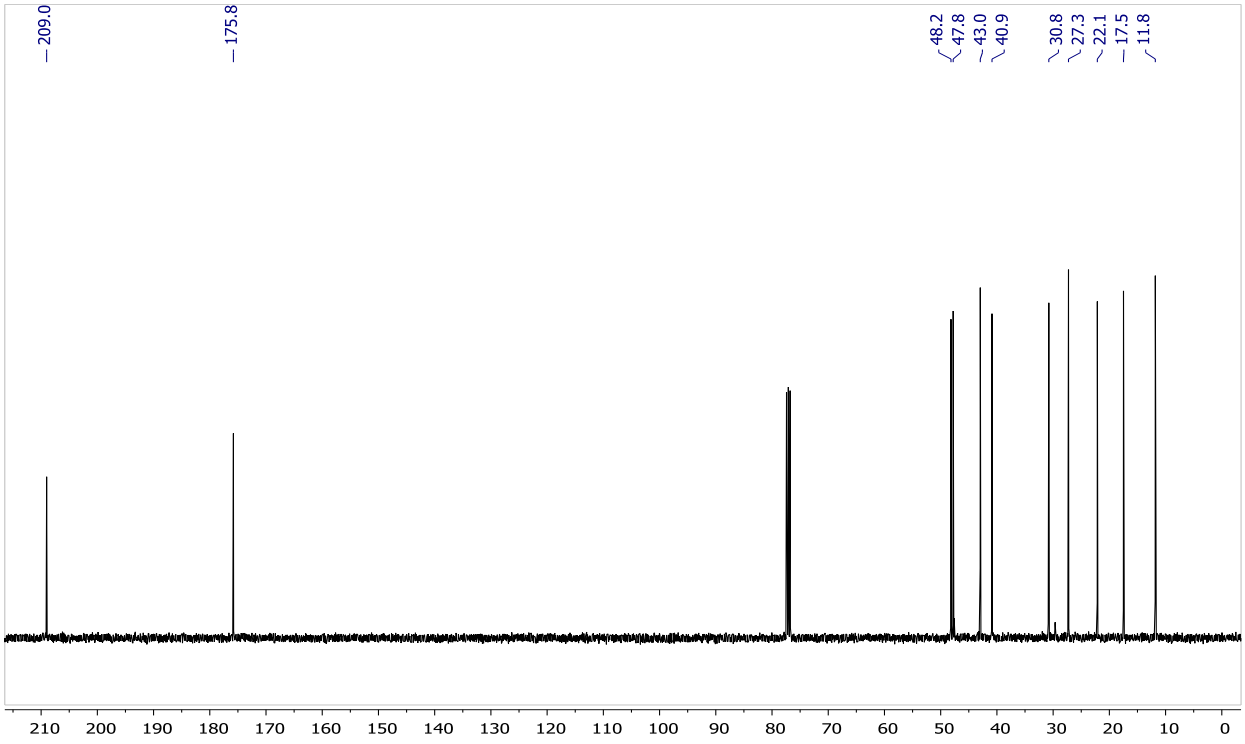


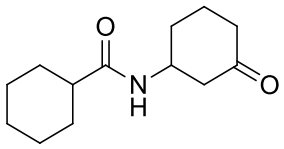


^{1}H-NMR of **P14** in $CDCl_3$

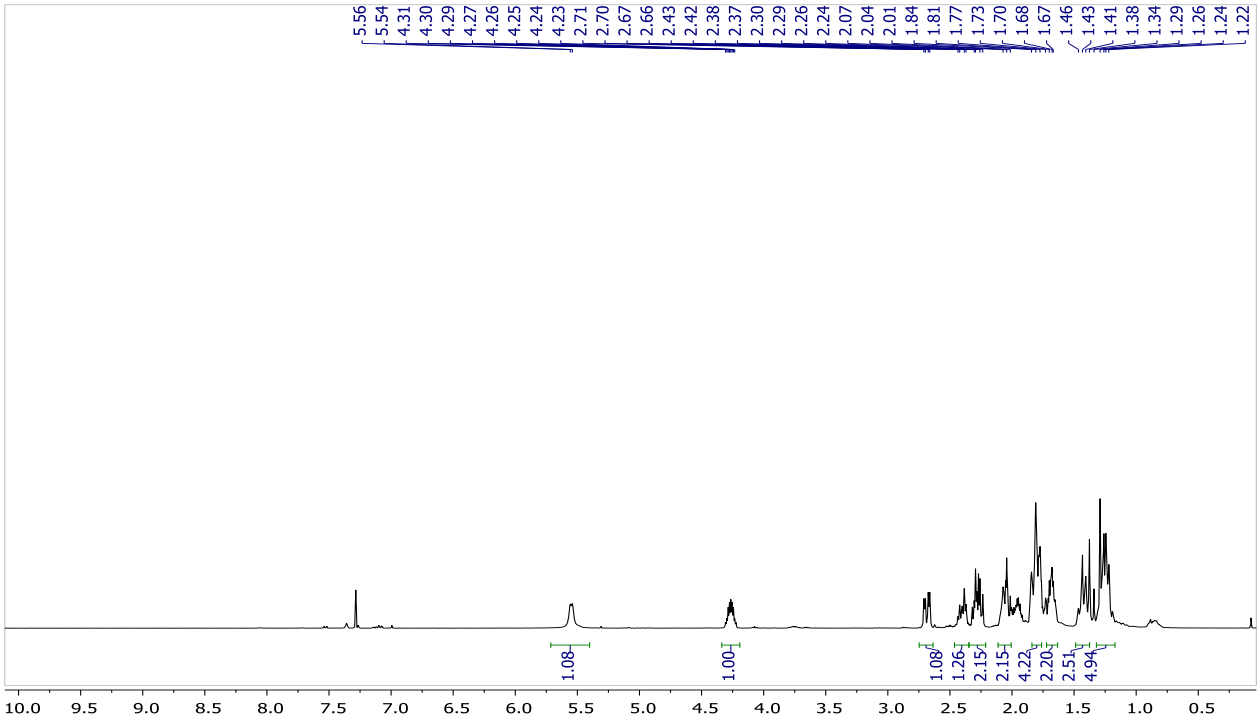


^{13}C{^{1}H}-NMR of **P14** in $CDCl_3$

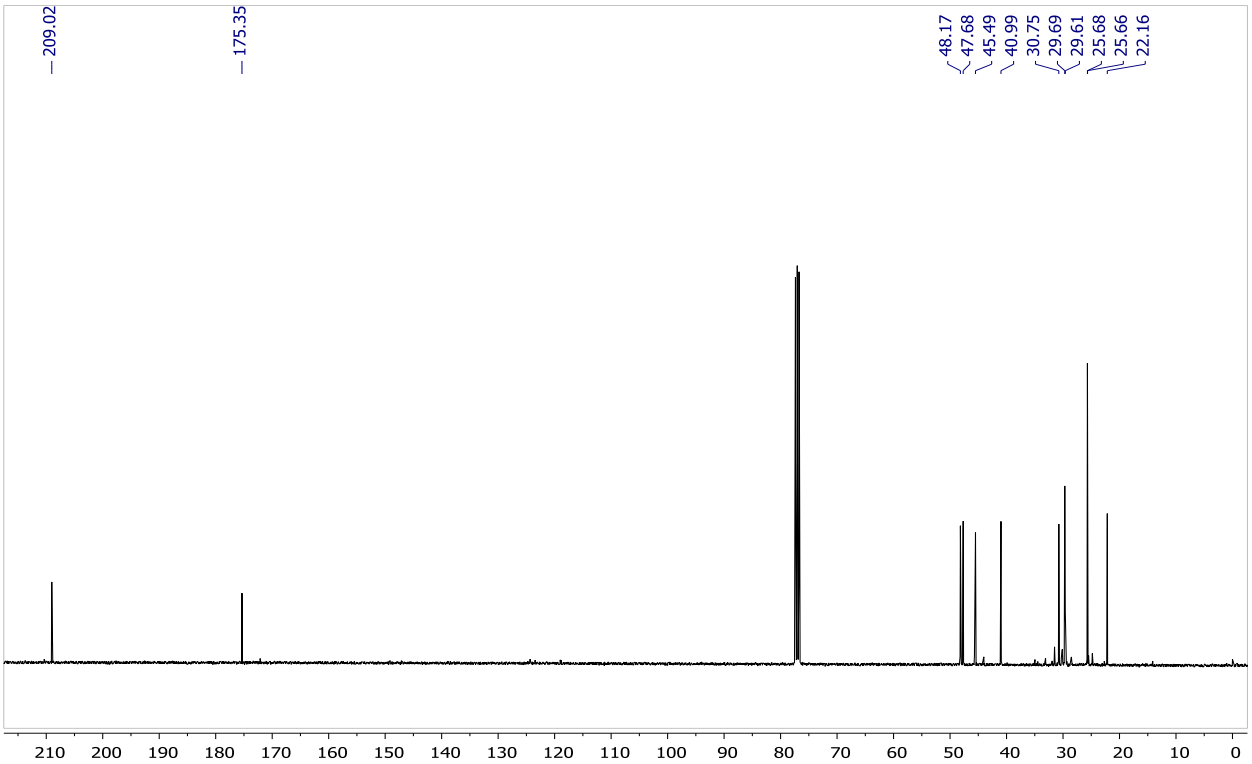


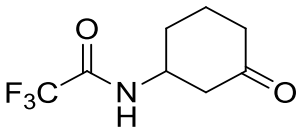


^{1}H-NMR of **P15** in $CDCl_3$

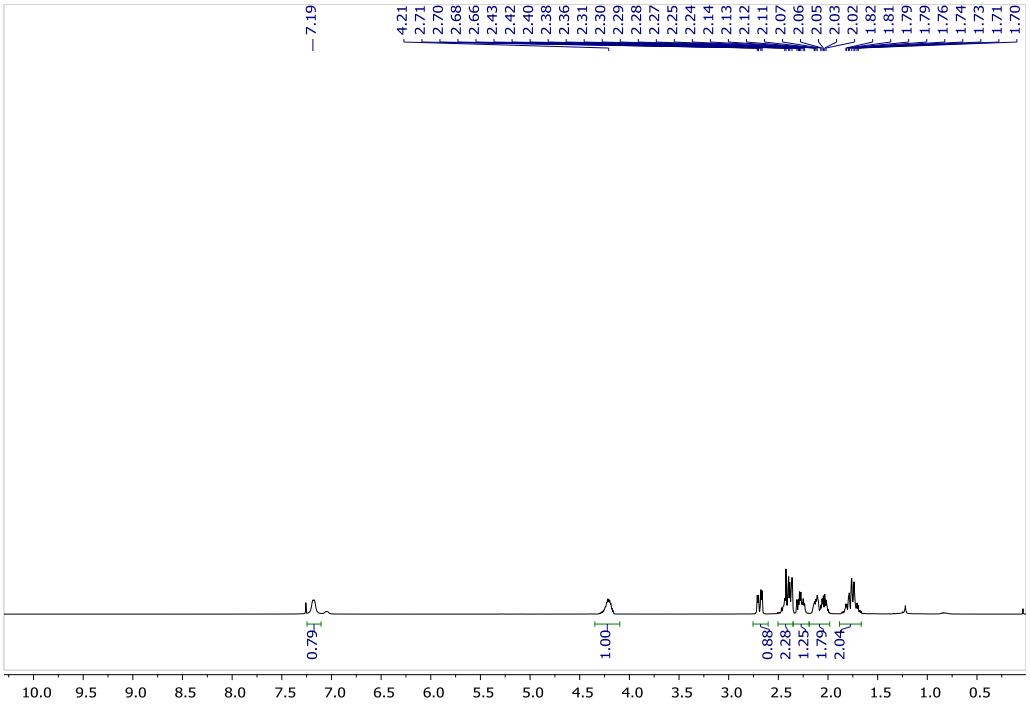


^{13}C{^{1}H}-NMR of **P15** in $CDCl_3$

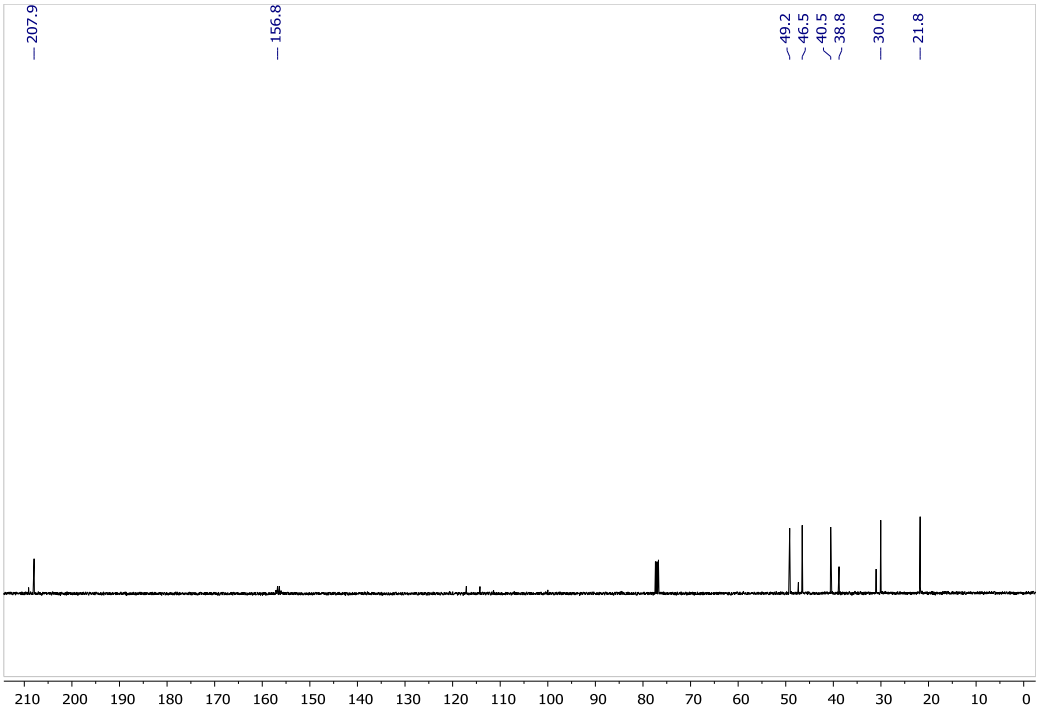


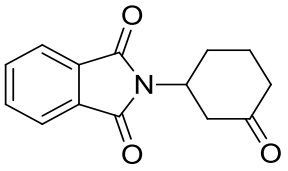


^{1}H-NMR of **P17** in $CDCl_3$

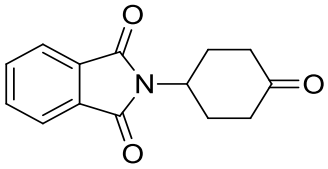


^{13}C{^{1}H}-NMR of **P17** in $CDCl_3$



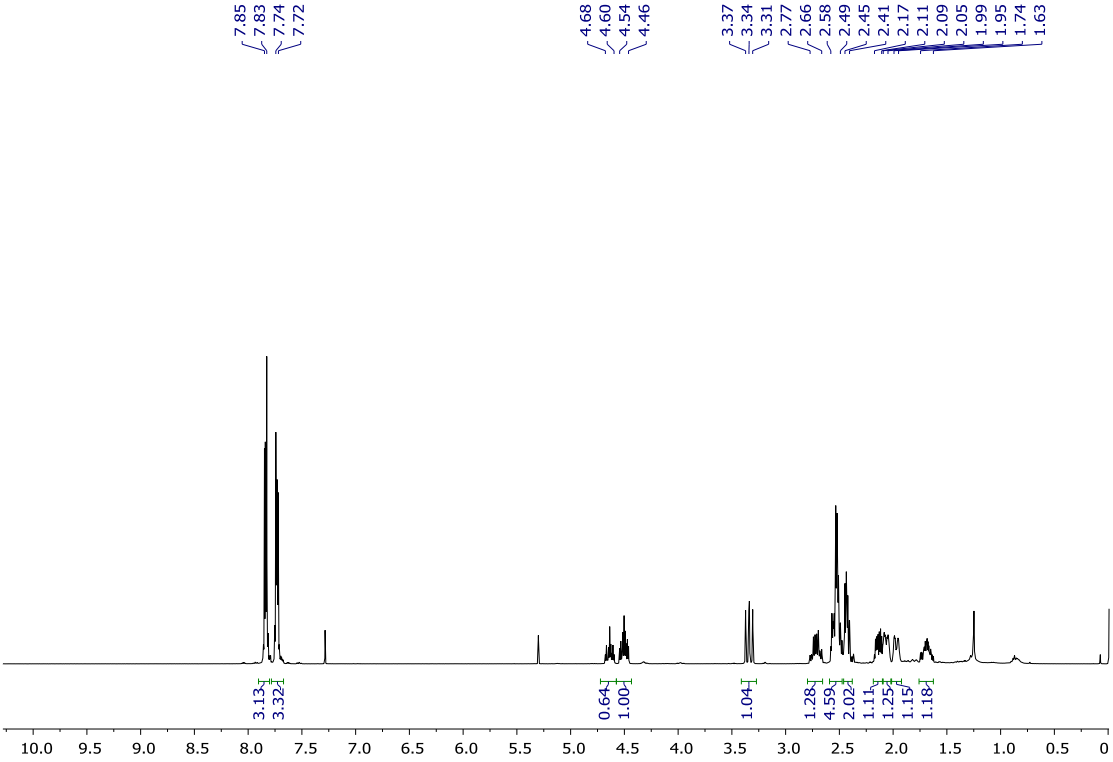


P18 (K_3)

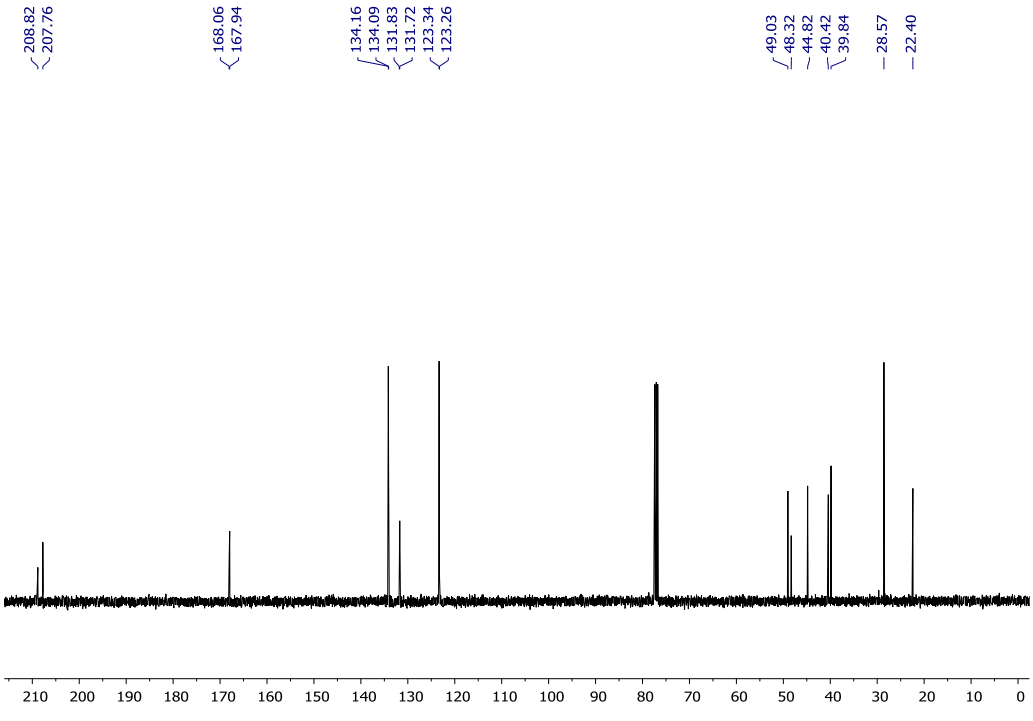


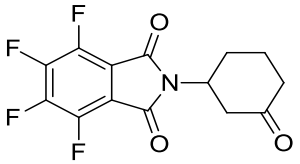
P18 (K_4)

^{1}H-NMR of **P18 (K_3+K_4)** in $CDCl_3$

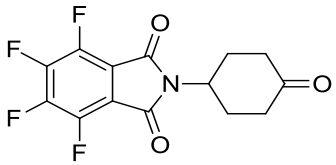


^{13}C{^{1}H}-NMR of **P18 (K_3+K_4)** in $CDCl_3$



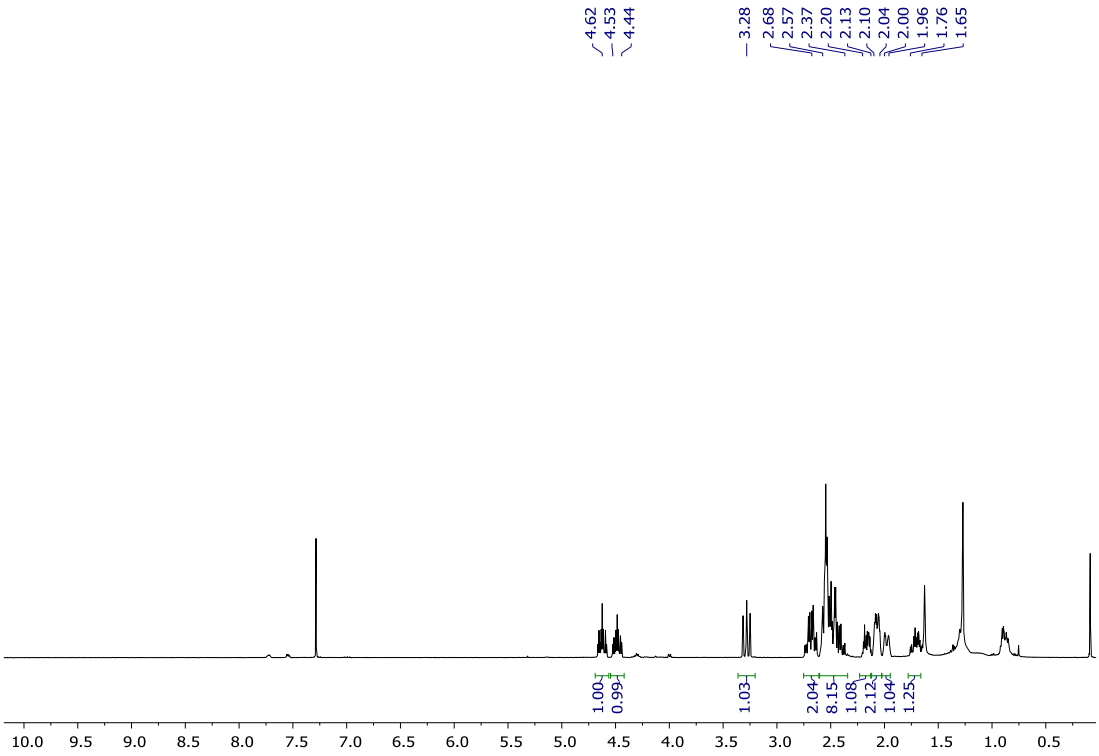


P19 (K_3)

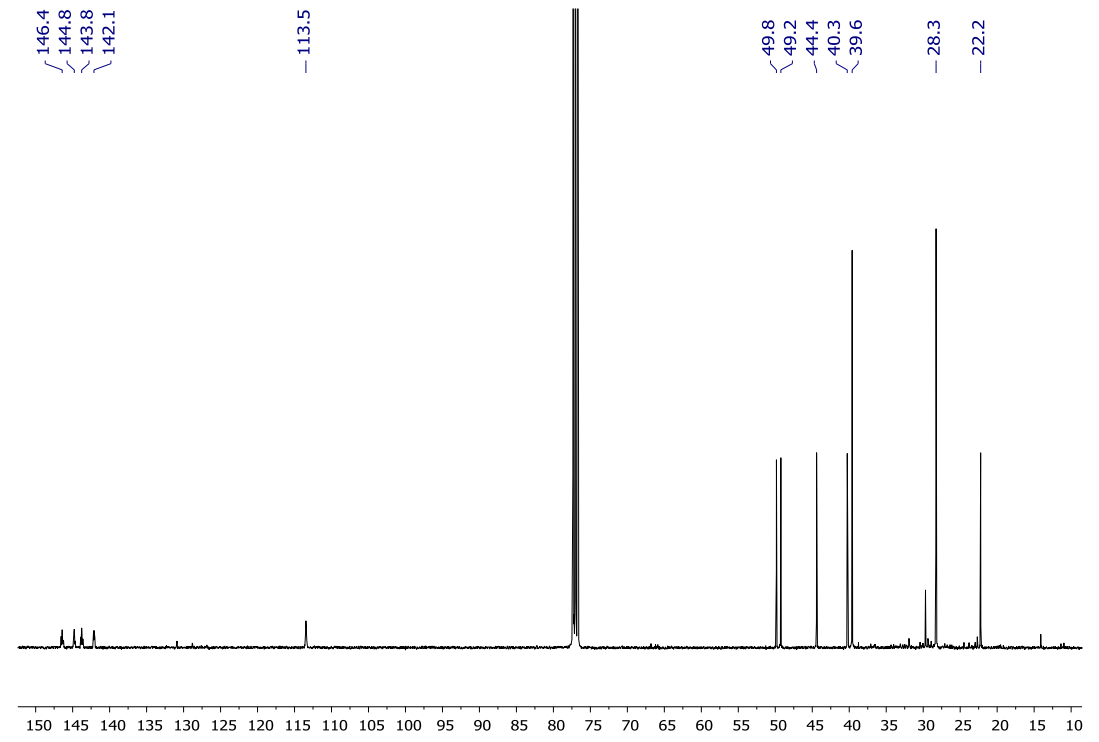


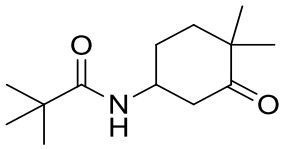
P19 (K_4)

^{1}H-NMR of **P19 (K_3+K_4)** in $CDCl_3$

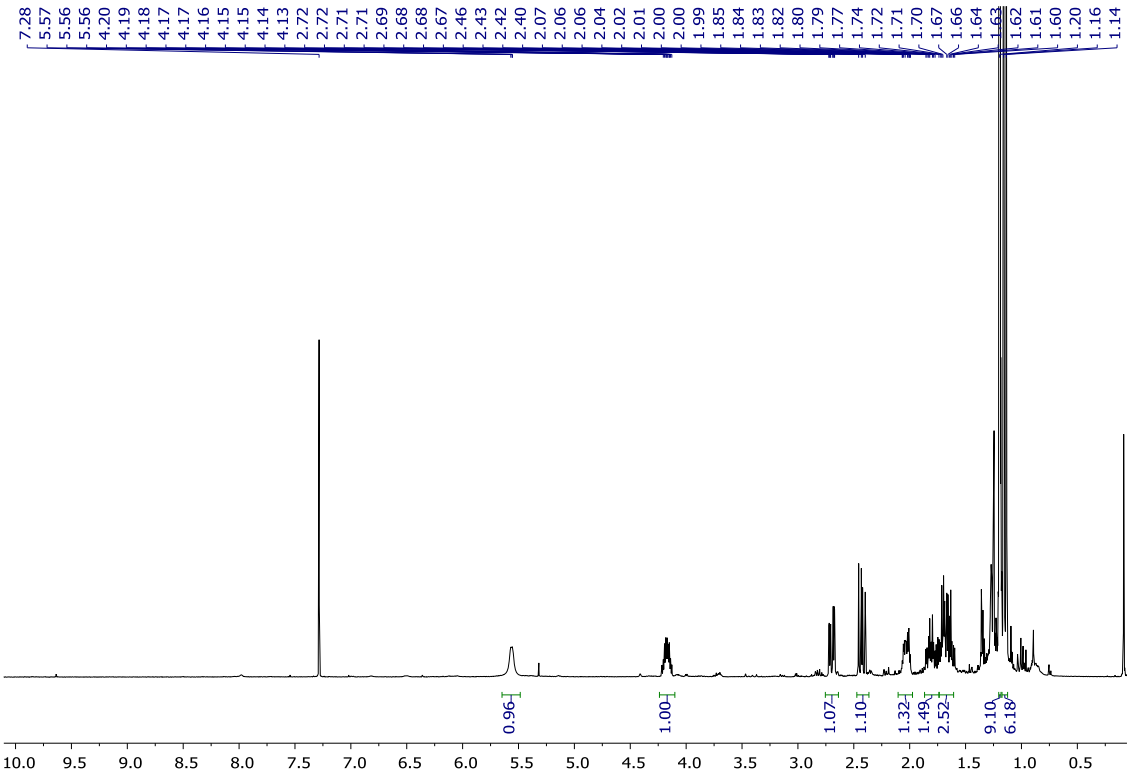


^{13}C{^{1}H}-NMR of **P19 (K_3+K_4)** in $CDCl_3$

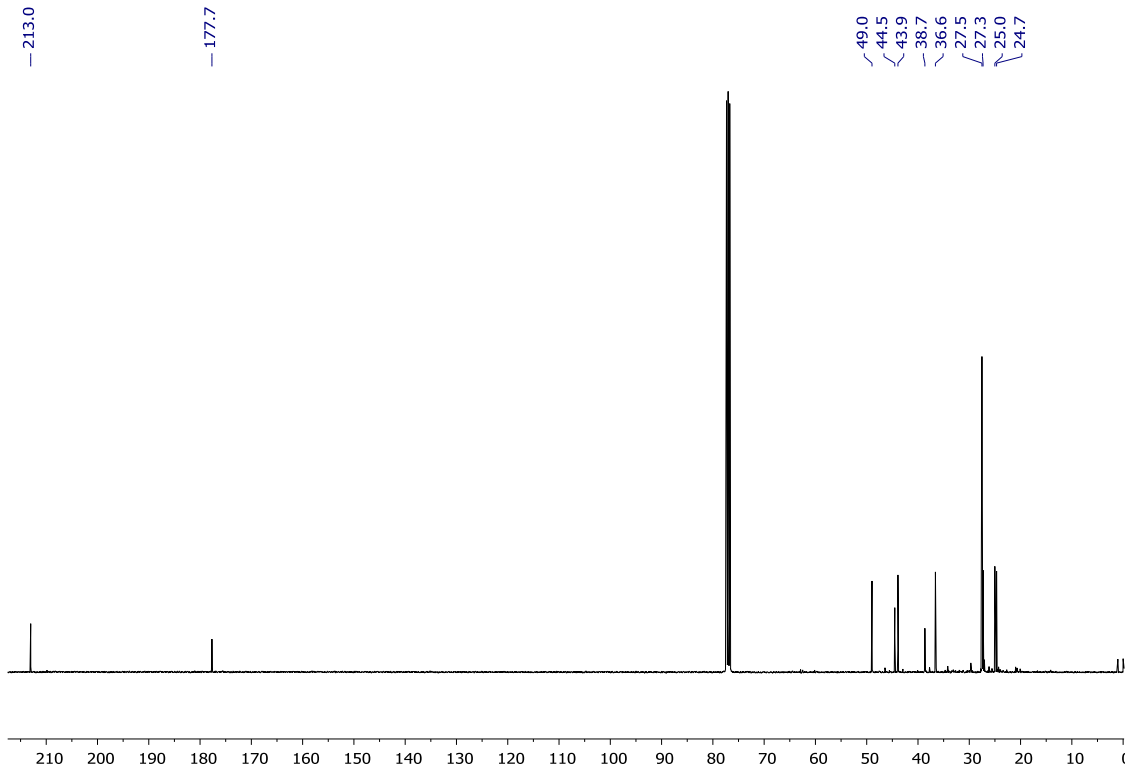


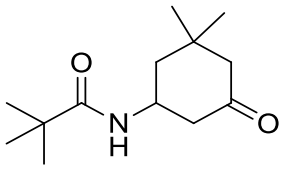


^{1}H-NMR of **P20** in $CDCl_3$

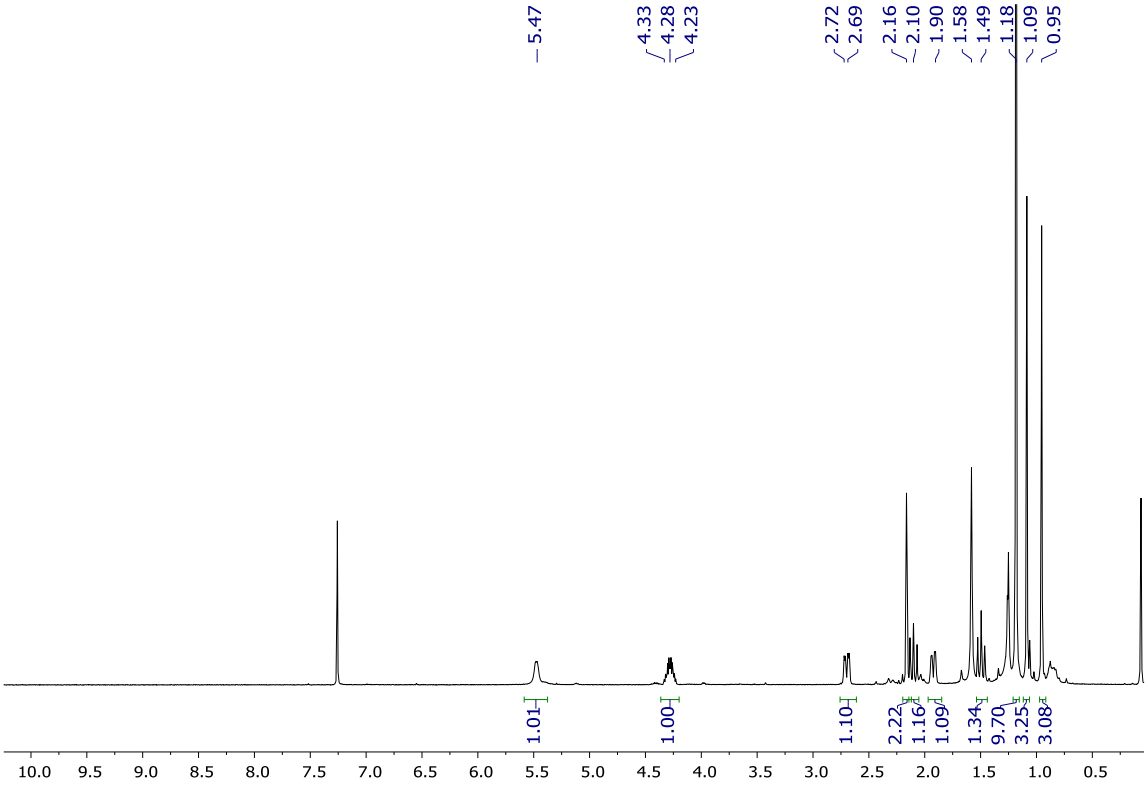


^{13}C{^{1}H}-NMR of **P20** in $CDCl_3$

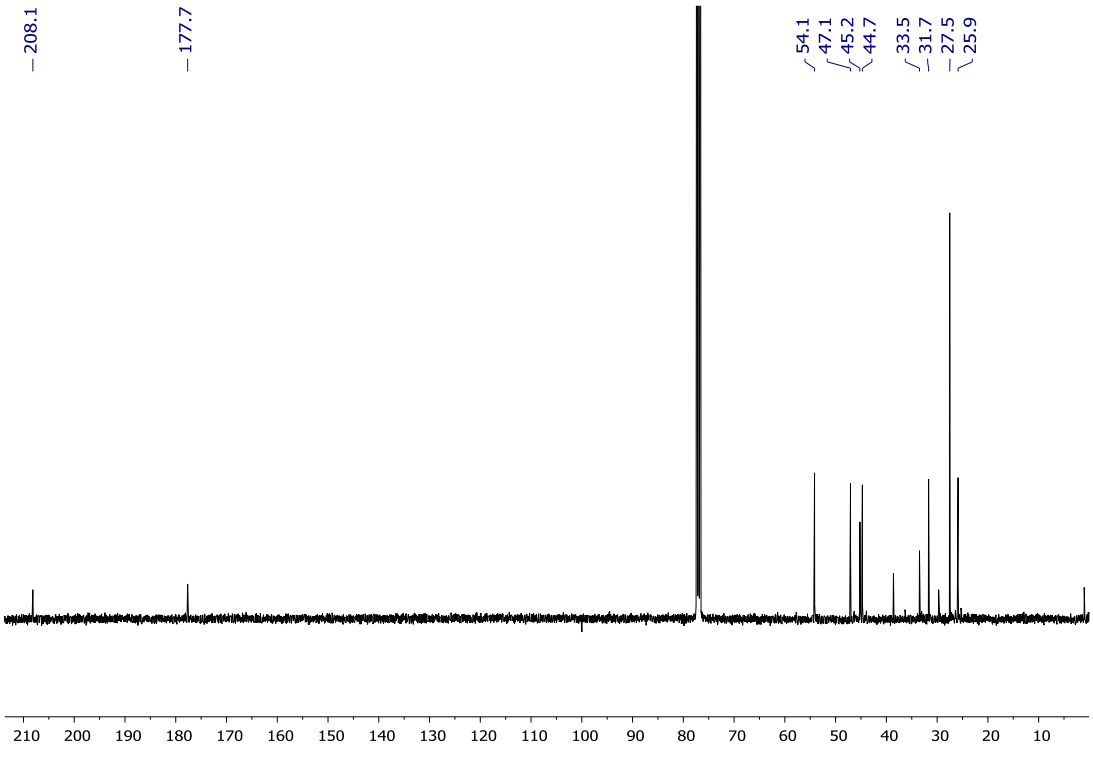




^{1}H-NMR of **P21** in $CDCl_3$

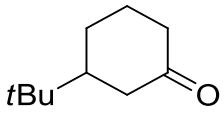


^{13}C{^{1}H}-NMR of **P21** in $CDCl_3$

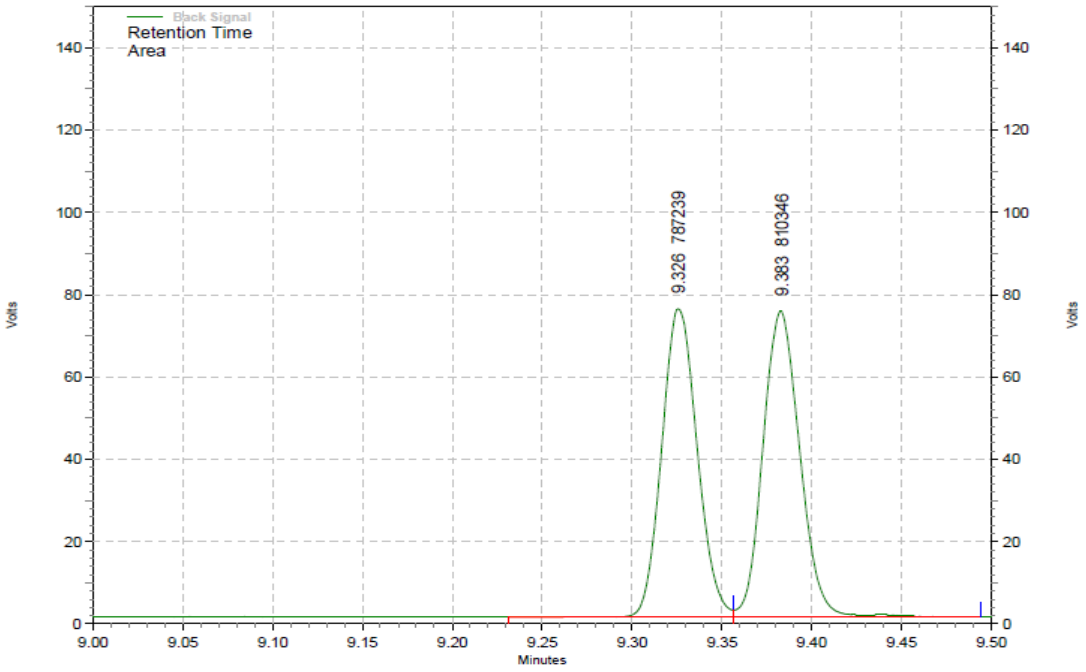


A4 HPLC and GC spectra of products

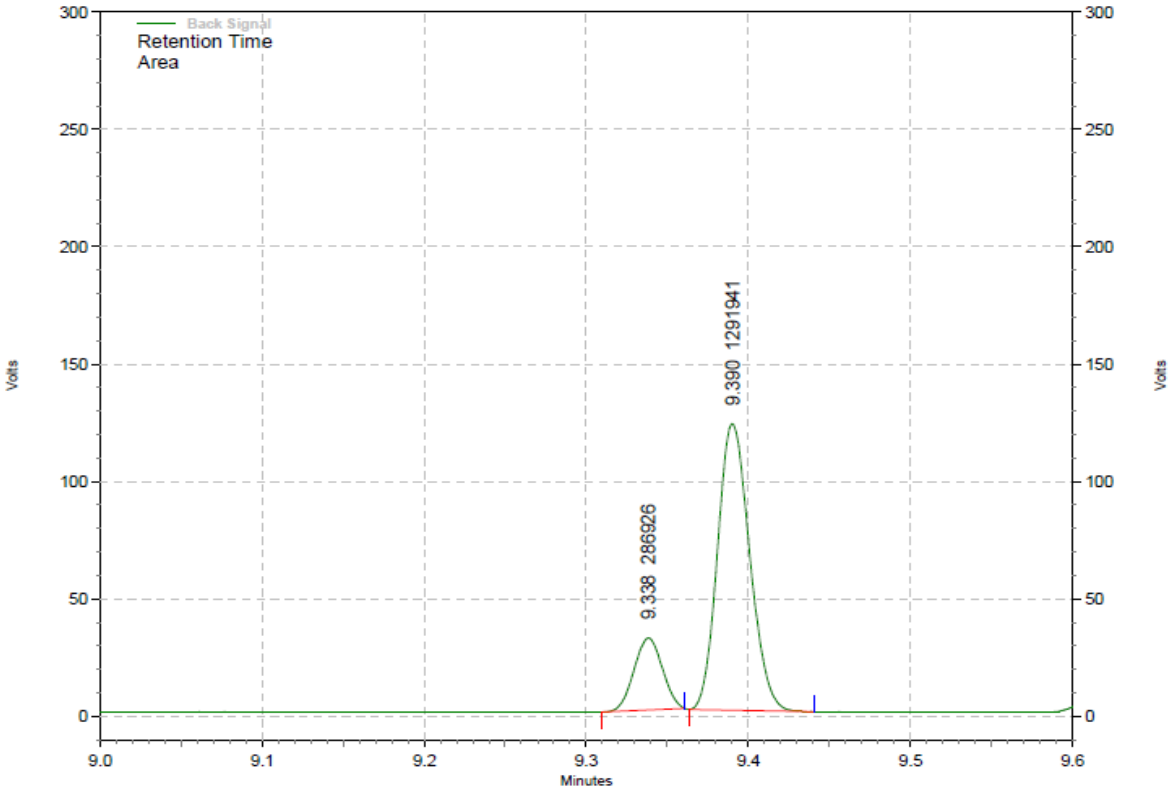
The racemic products were obtained by using the racemic **[Mn(CF$_3$SO$_3$)$_2$(^{TIPS}mcp)]** complex.

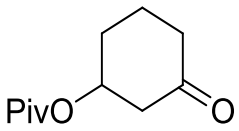


Rac

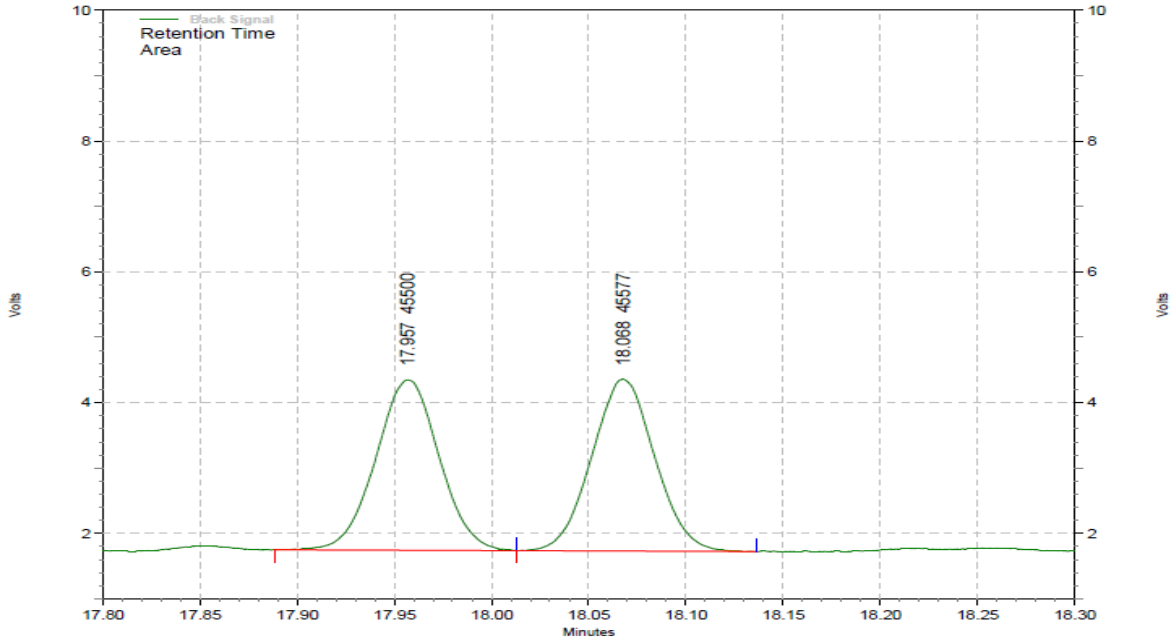


P1 (K_3)

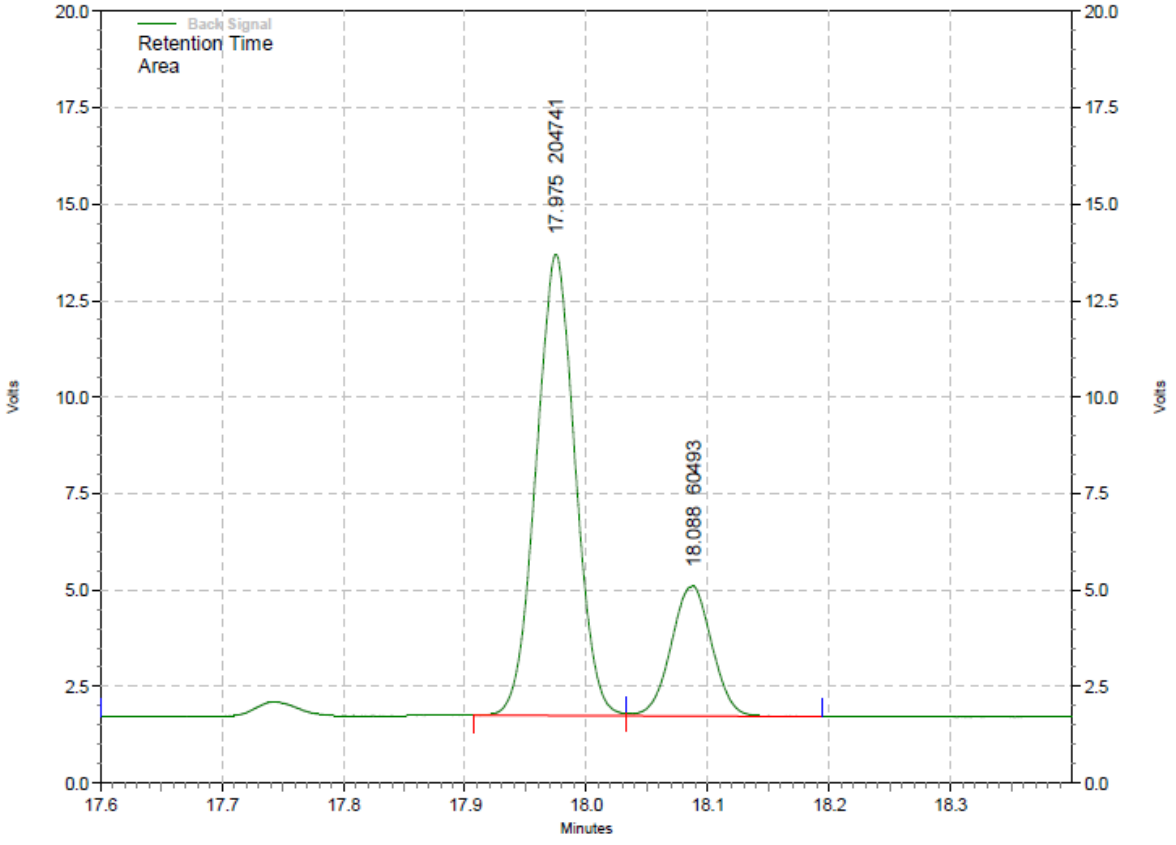



PivO
O

Rac


Back Signal
Retention Time
Area
17.957 45500
18.068 45577
Volts
Minutes

P2 (K_3)


Back Signal
Retention Time
Area
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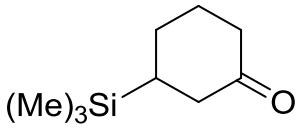
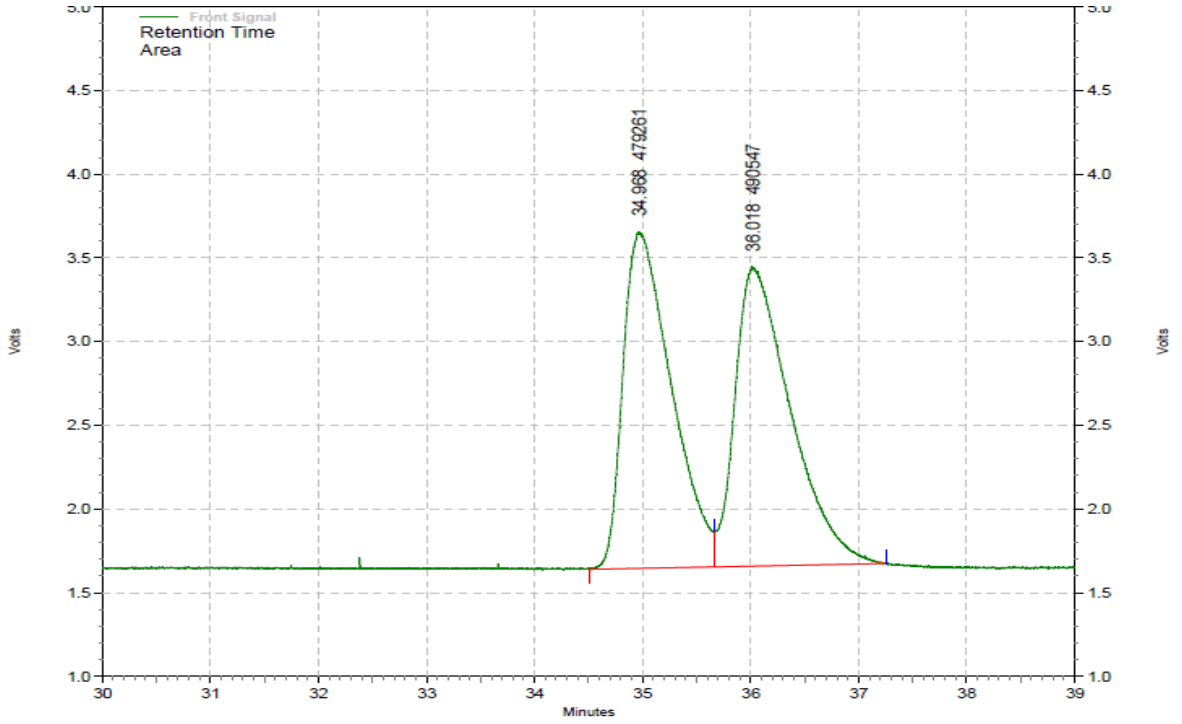
18.088 60493
Volts
Minutes


(Me)3Si
O

Rac


Front Signal
Retention Time
Area
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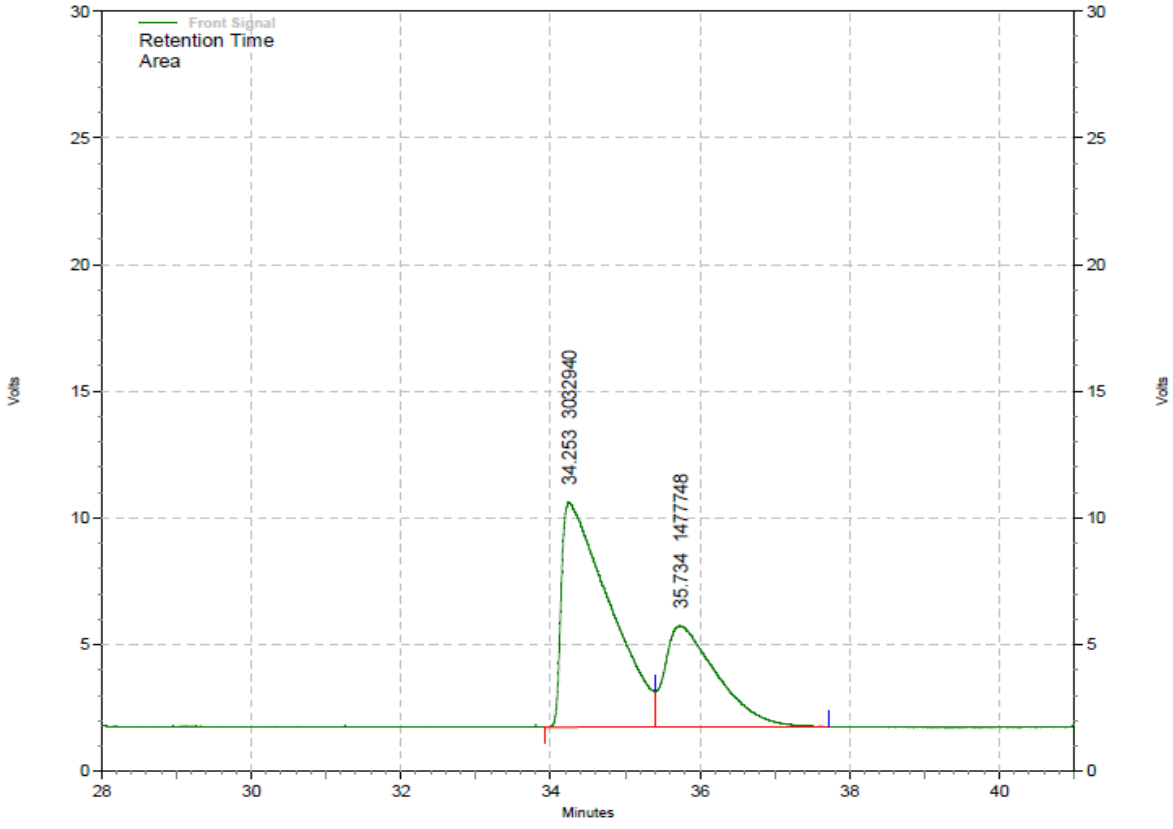
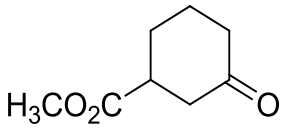
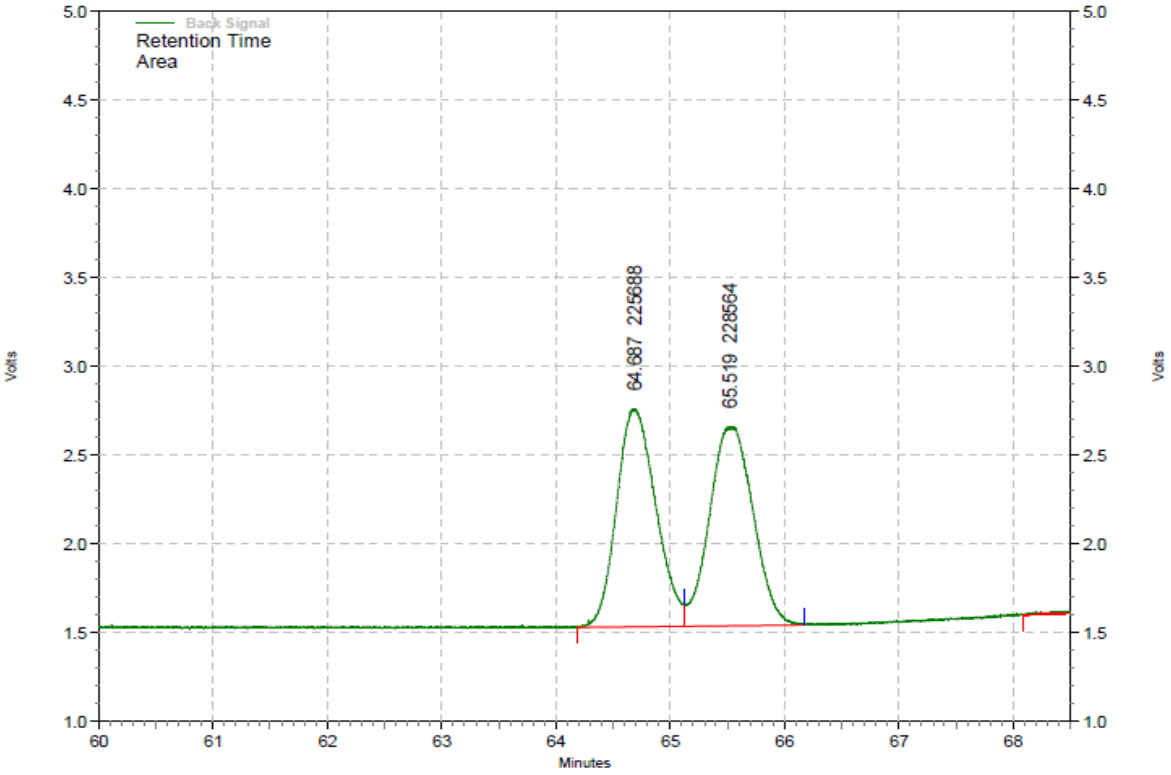
36.018 490547
Volts
Minutes

P3 (K_3)

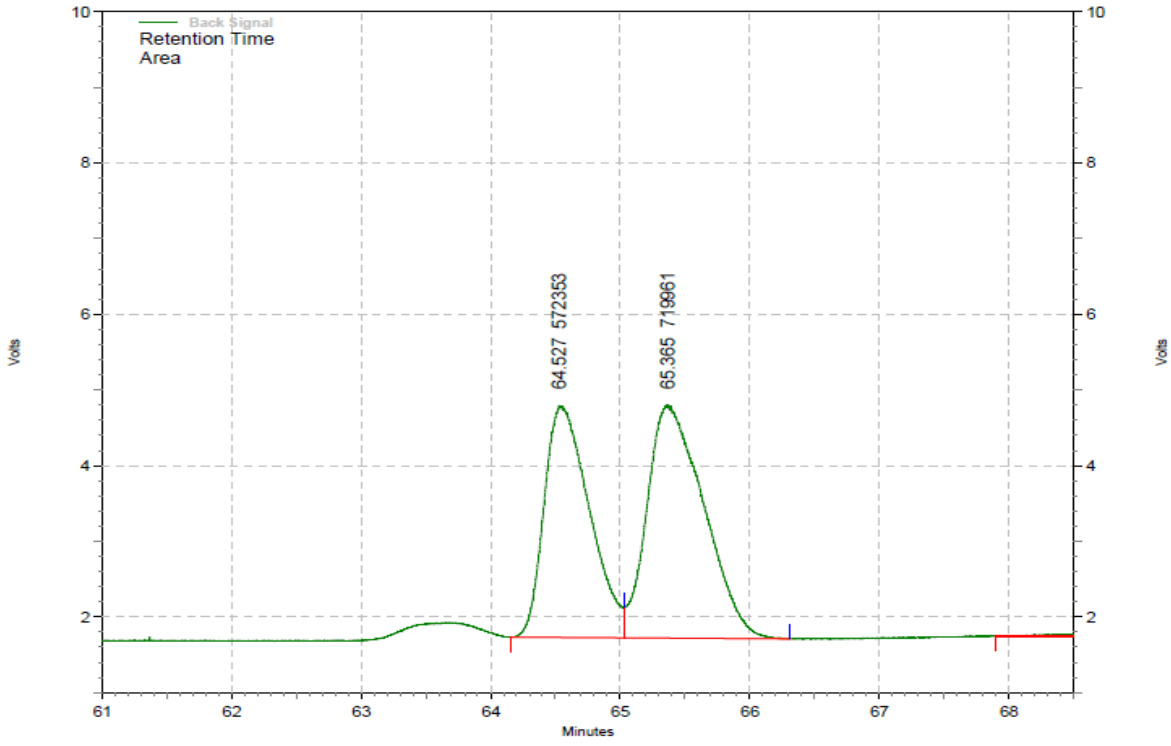

Front Signal
Retention Time
Area
34.253 3032940
35.734 1477748
Volts
Minutes

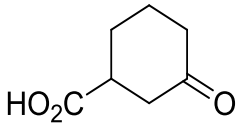

H_3CO_2C
O

Rac

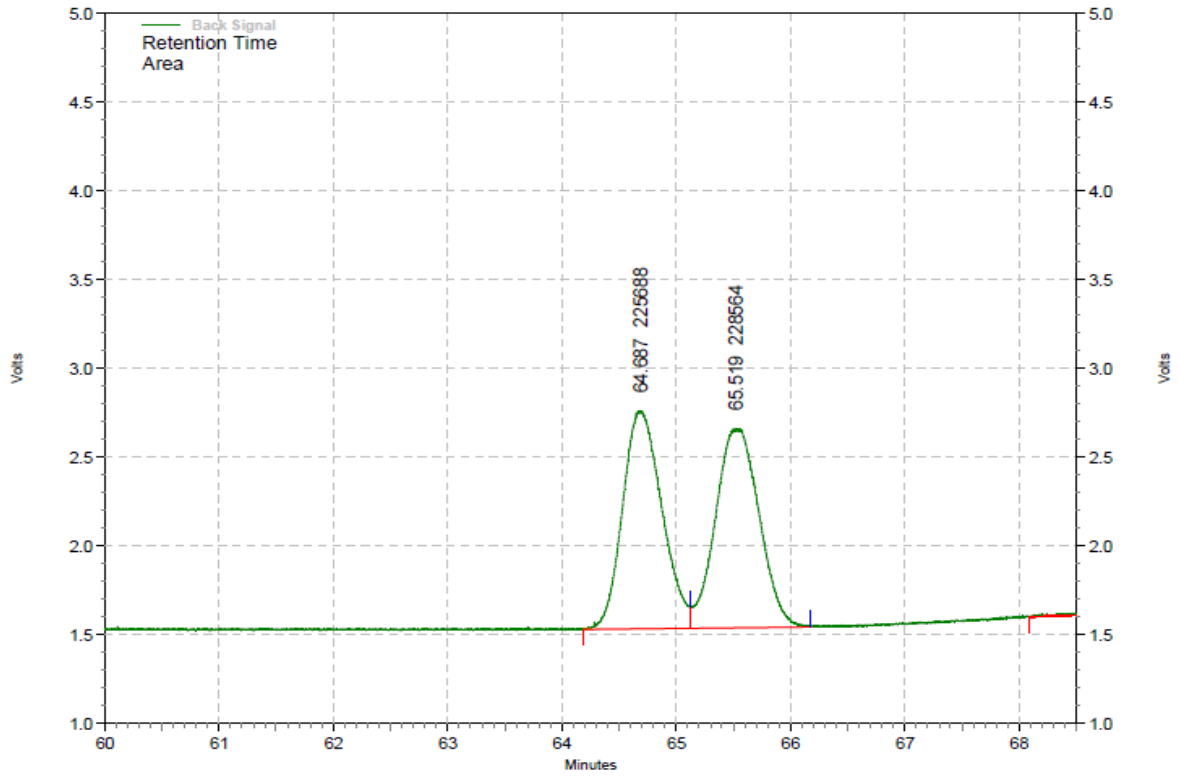

Back Signal
Retention Time
Area
64.687 225688
65.519 228564
Volts
Minutes

P4 (K_3)

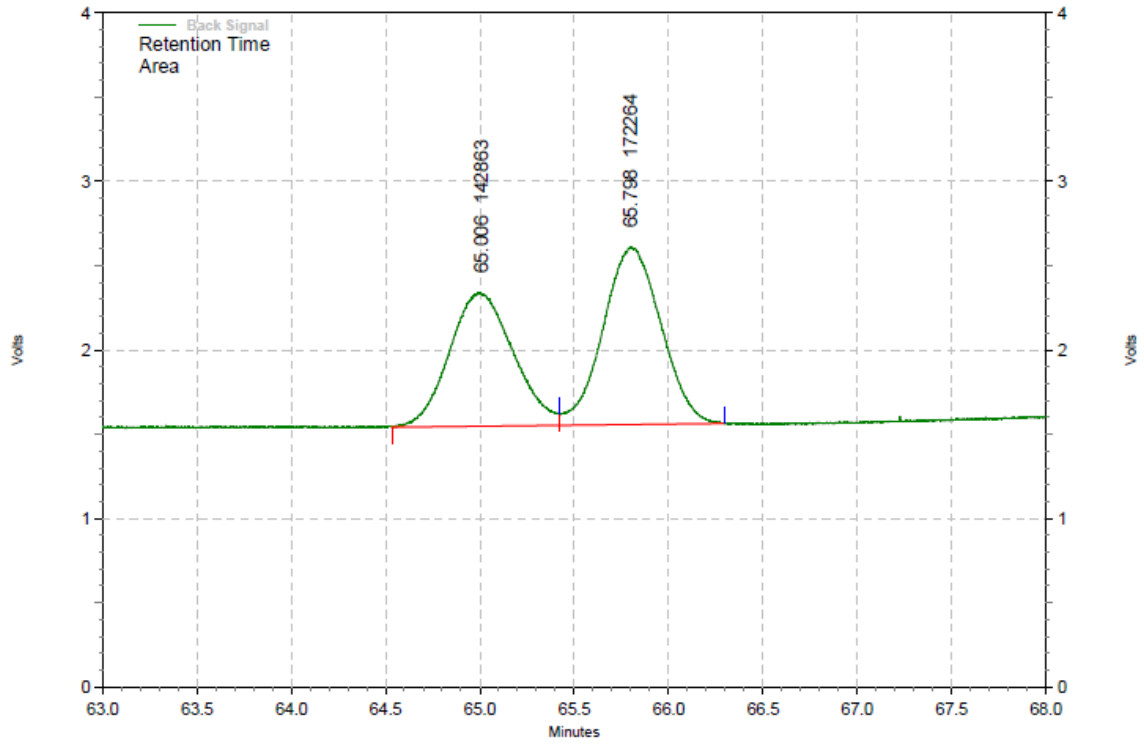

Back Signal
Retention Time
Area
64.527 572353
65.365 719961
Volts
Minutes

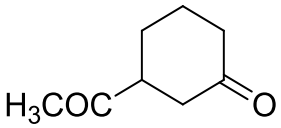


Rac

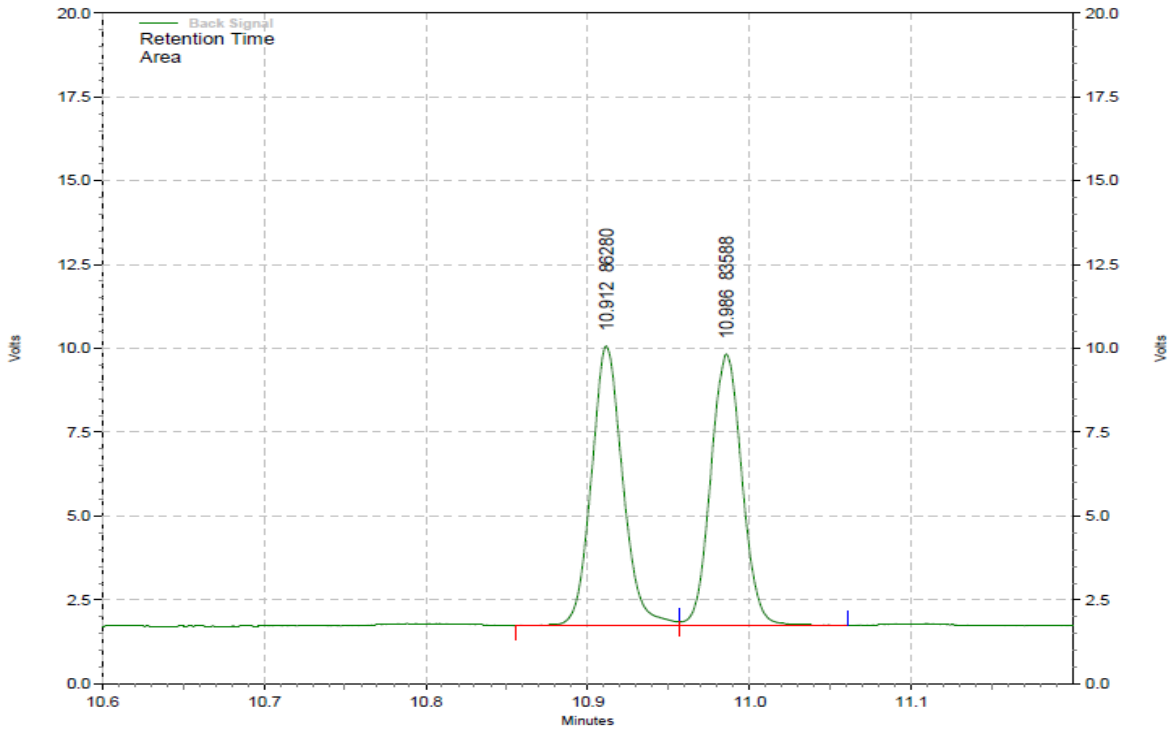


P5 (K_3) after esterification

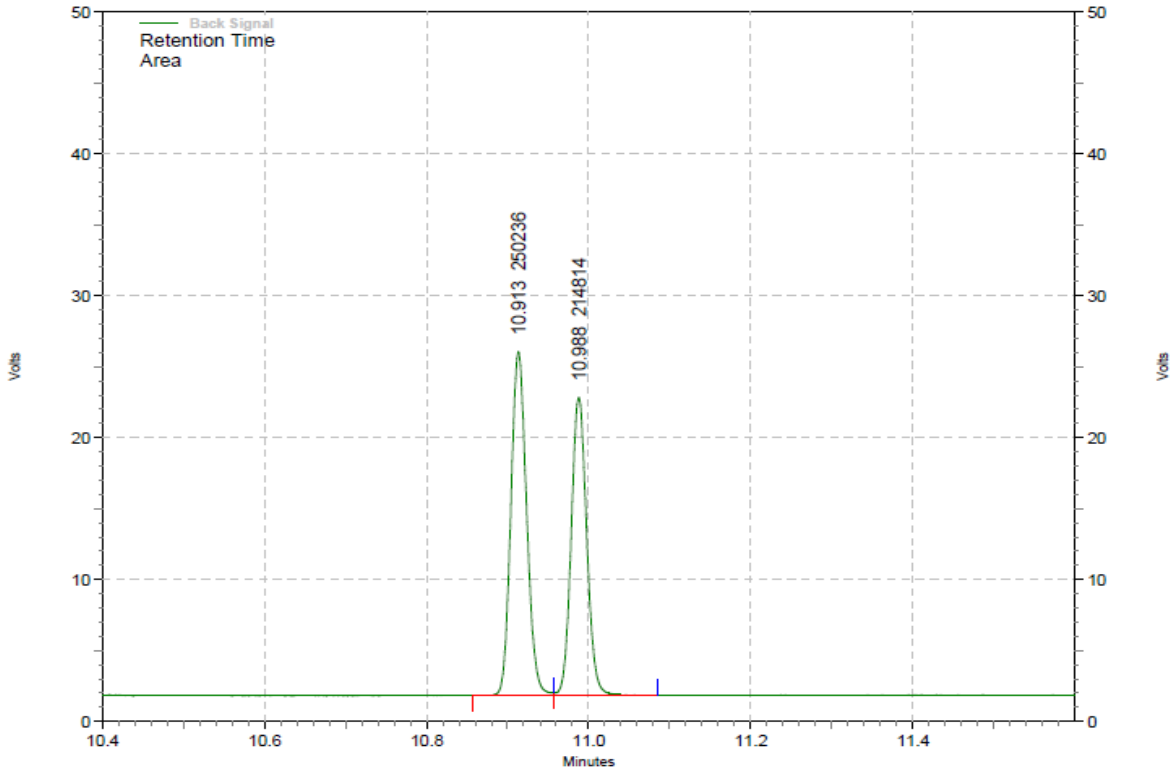


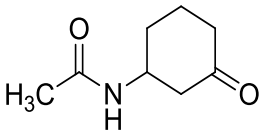

H3COC
O

Rac

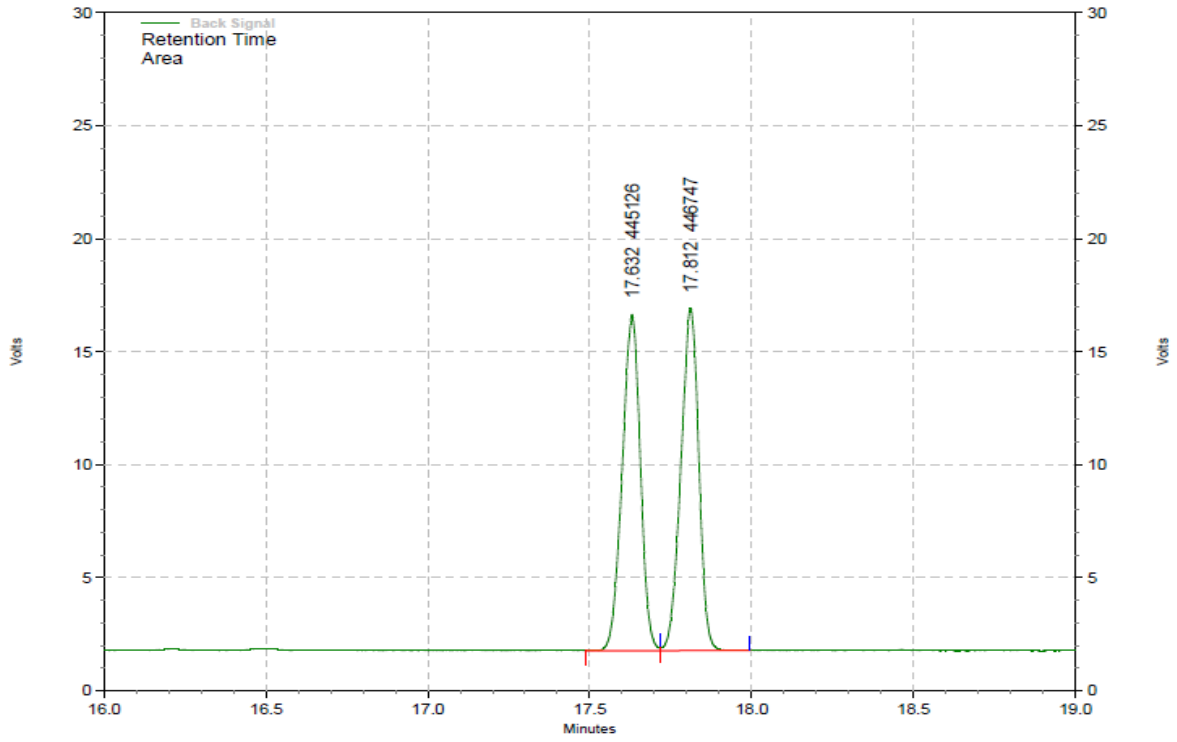

Back Signal
Retention Time
Area
10.912 86280
10.986 83588
Volts
Minutes

P6 (K_3)

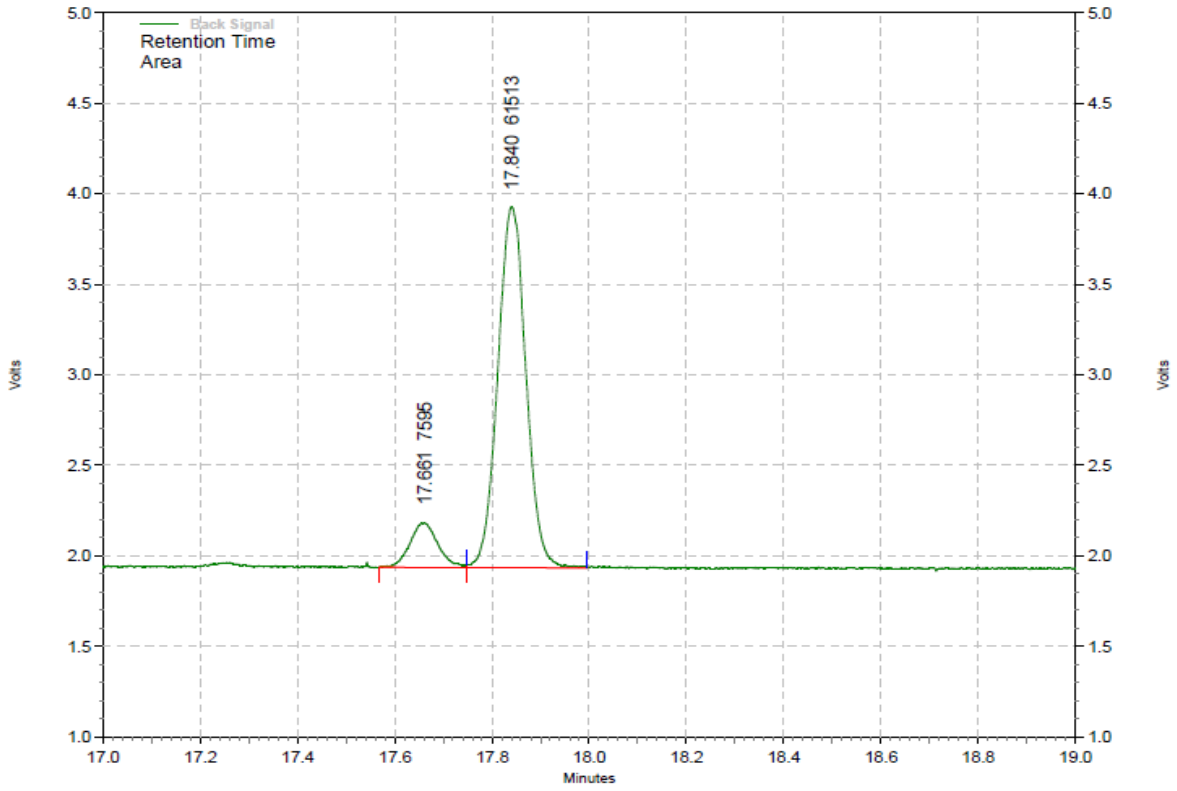

Back Signal
Retention Time
Area
10.913 250236
10.988 214814
Volts
Minutes

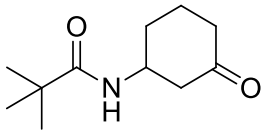

O
H3C
N
H
O

Rac

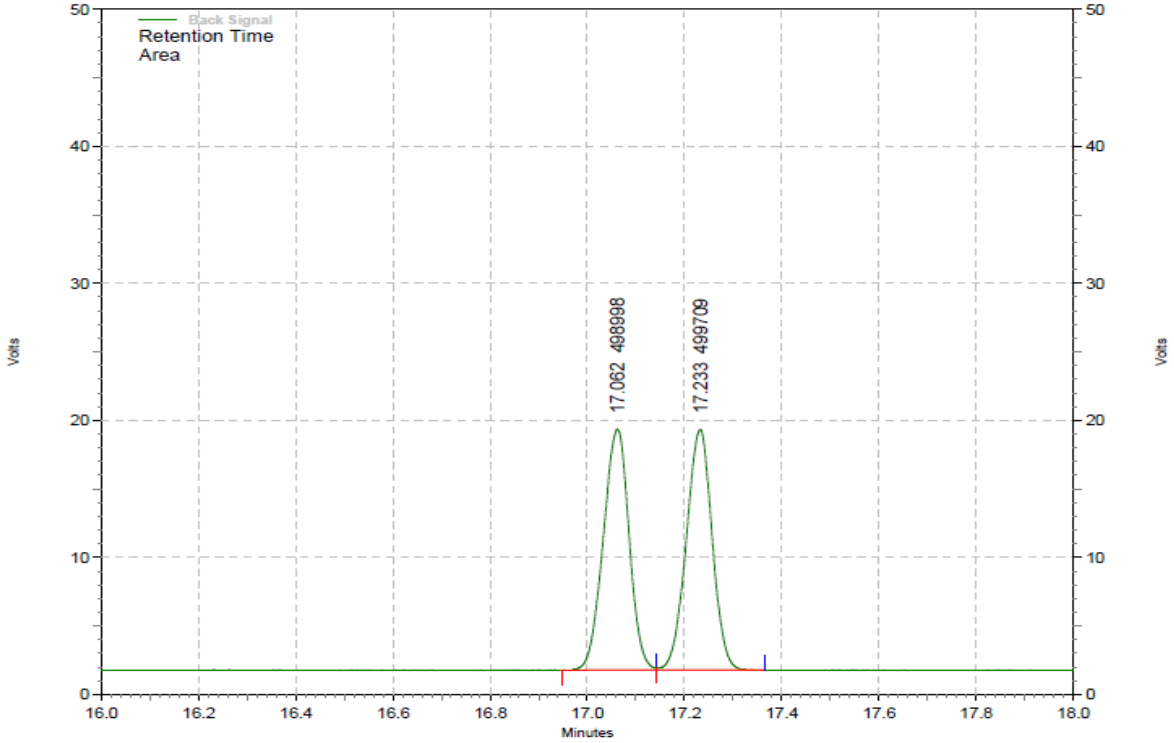

Back Signal
Retention Time
Area
17.632 445126
17.812 446747
Volts
Minutes
16.0
16.5
17.0
17.5
18.0
18.5
19.0
0
5
10
15
20
25
30

P7

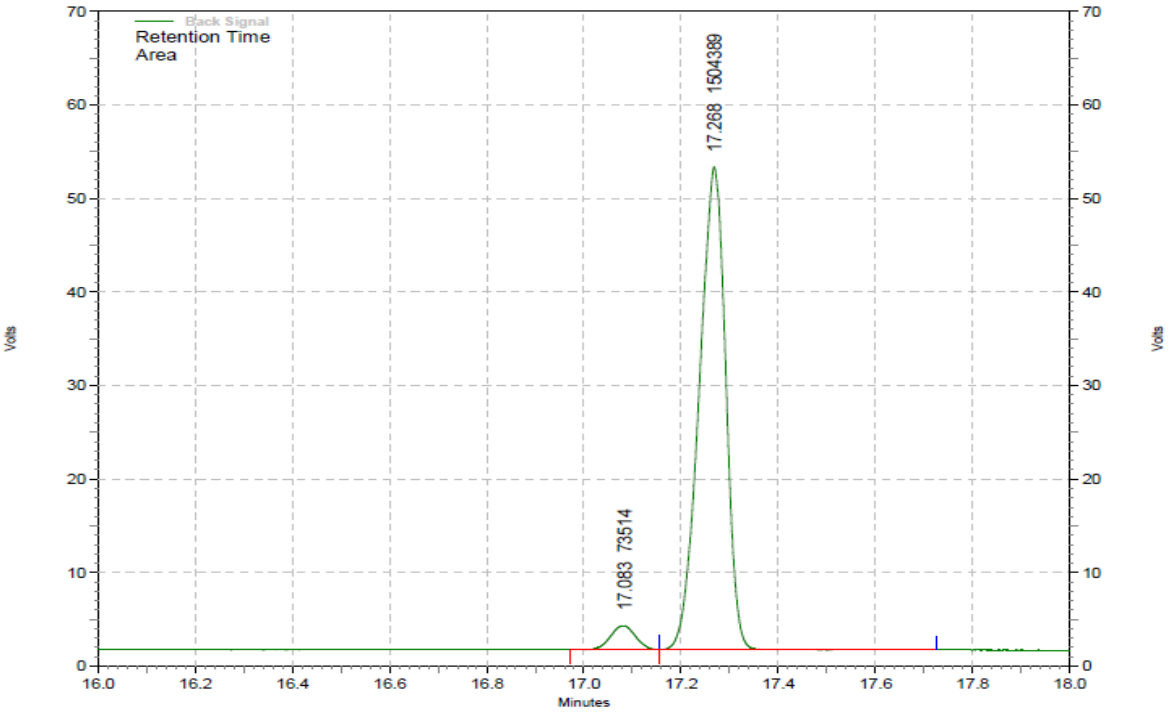

Back Signal
Retention Time
Area
17.661 7595
17.840 61513
Volts
Minutes
17.0
17.2
17.4
17.6
17.8
18.0
18.2
18.4
18.6
18.8
19.0
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0



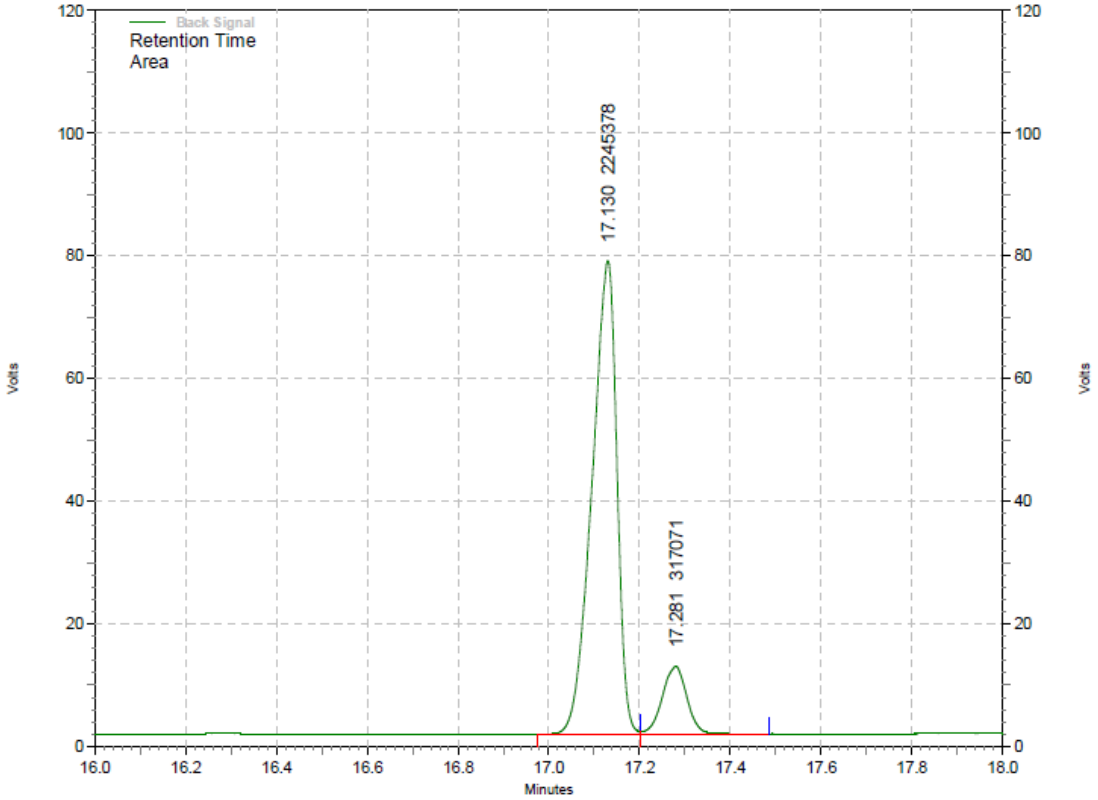
Rac



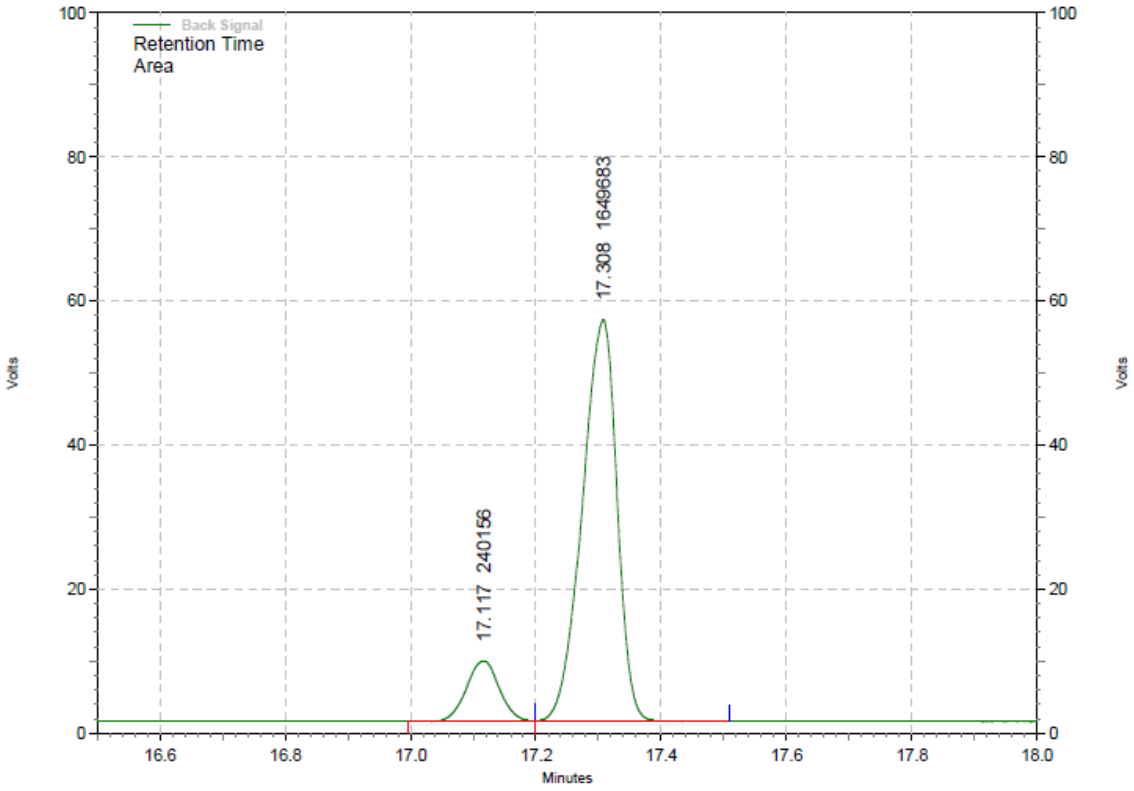
P8 (*S,S*)-(^{TIPS}ecp)

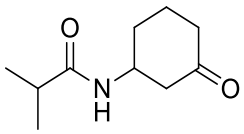


P8 (*R,R*)-(^{TIPS}mcp)

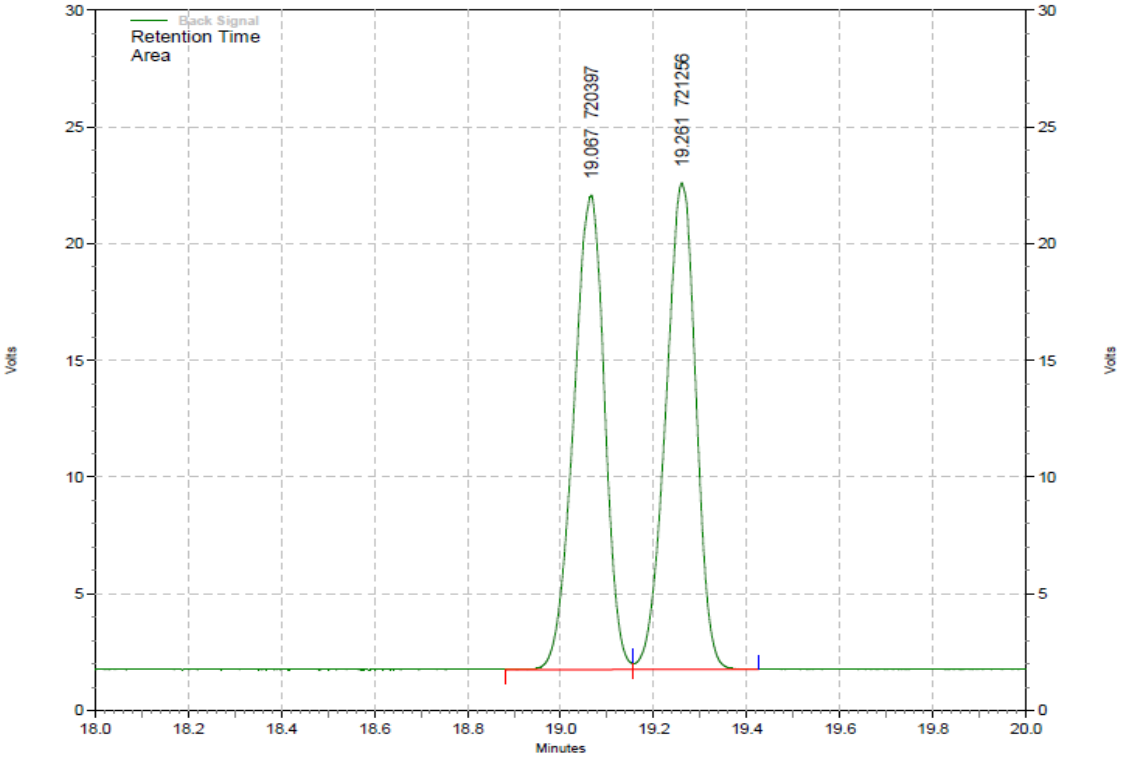


P8 (*S,S*)-(^{TIPS}mcp)

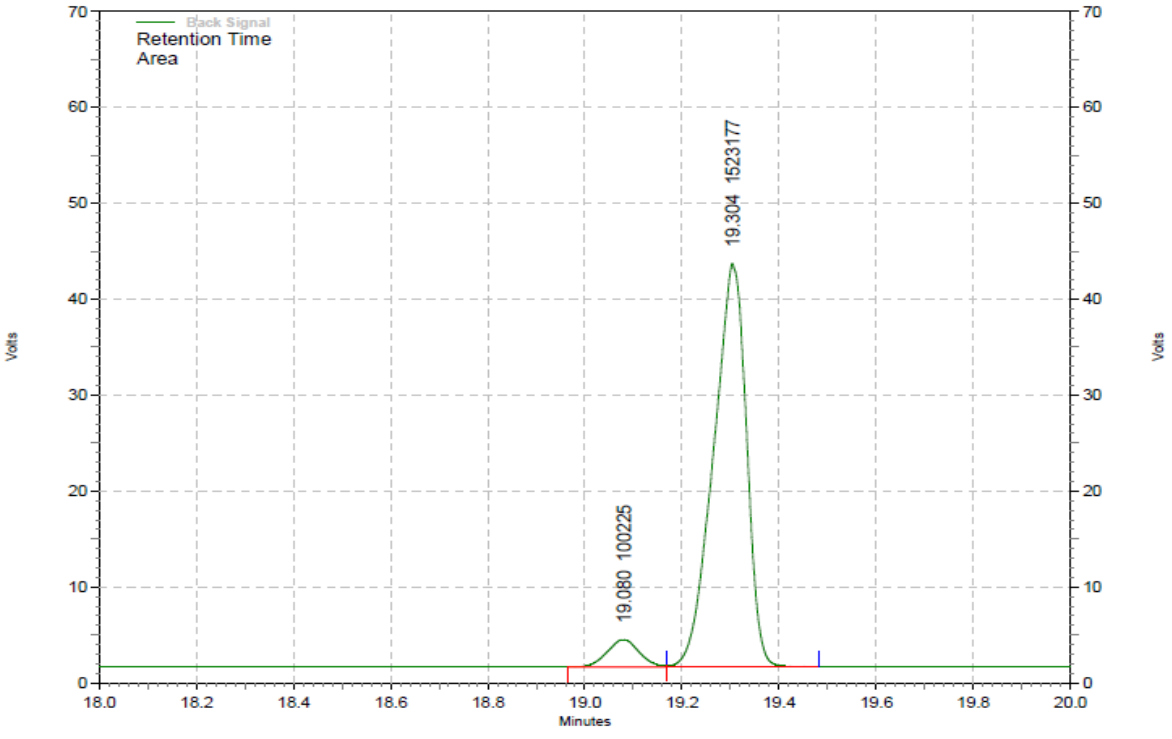


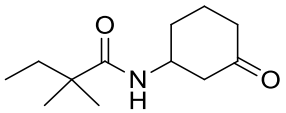

O
N
H
O

Rac

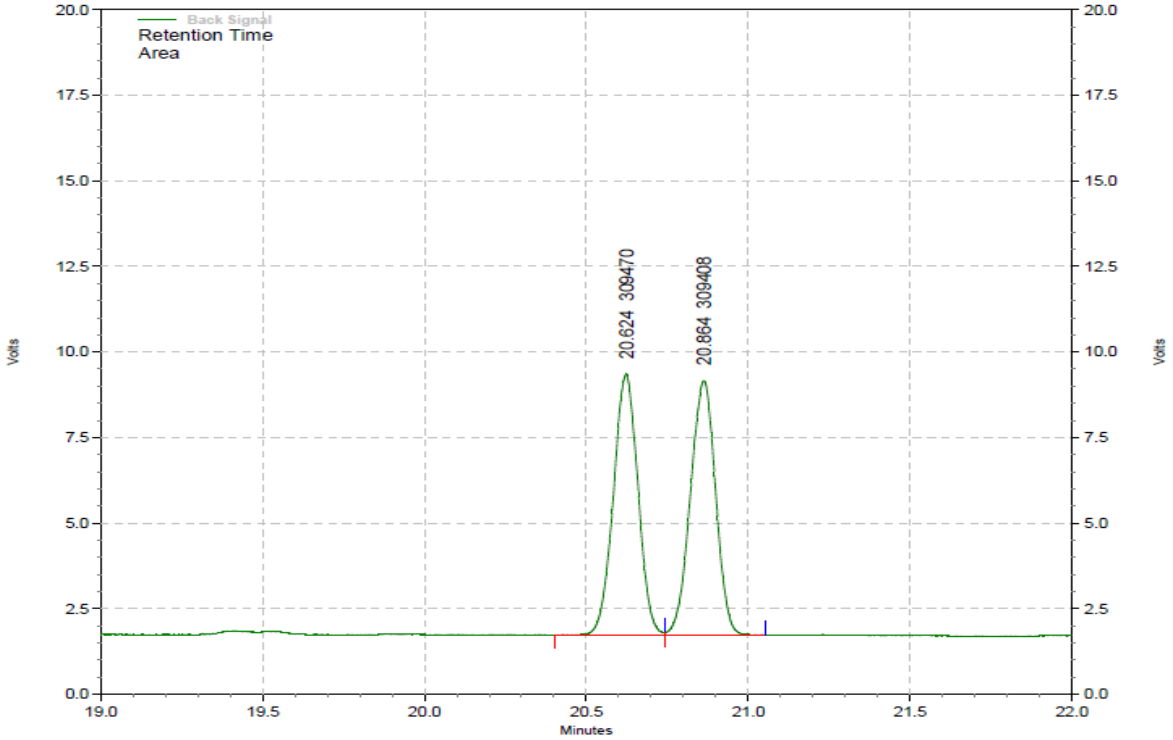

Back Signal
Retention Time
Area
19.067 720397
19.261 721256
Volts
Minutes
18.0
18.2
18.4
18.6
18.8
19.0
19.2
19.4
19.6
19.8
20.0
0
5
10
15
20
25
30

P9

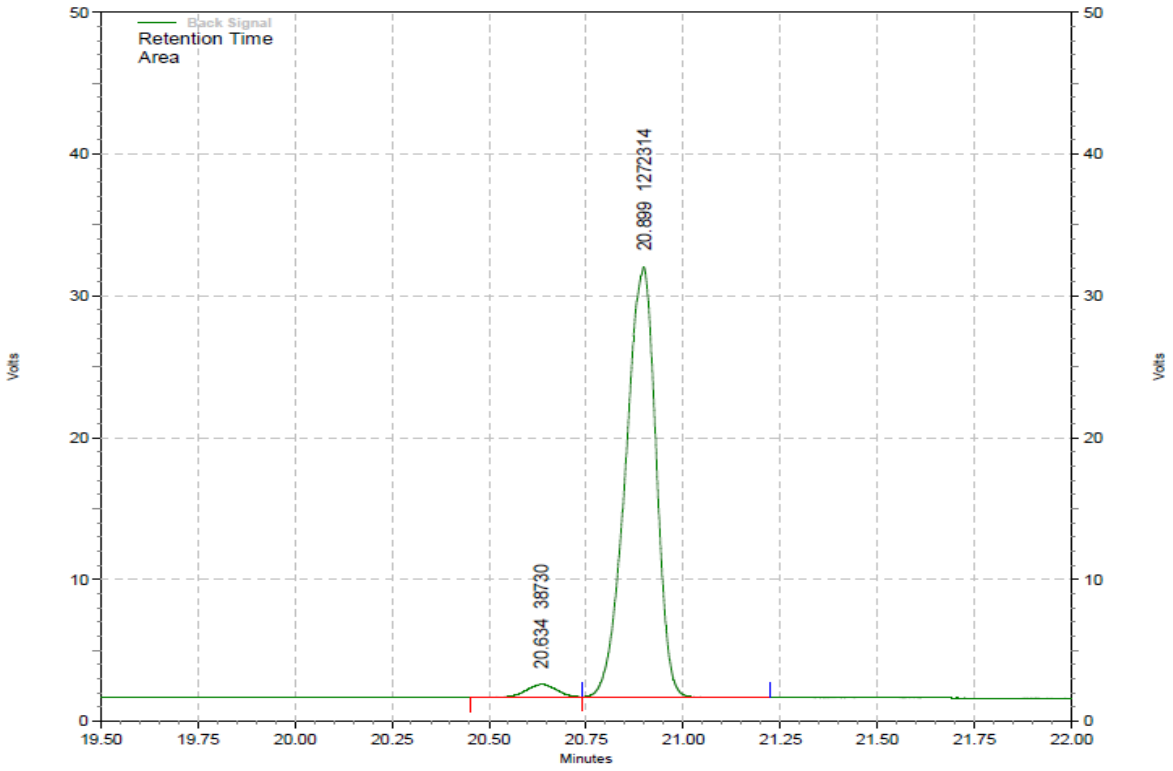

Back Signal
Retention Time
Area
19.080 100225
19.304 1523177
Volts
Minutes
18.0
18.2
18.4
18.6
18.8
19.0
19.2
19.4
19.6
19.8
20.0
0
10
20
30
40
50
60
70

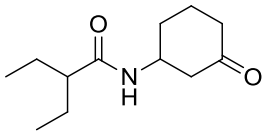

O
N
H
O

Rac

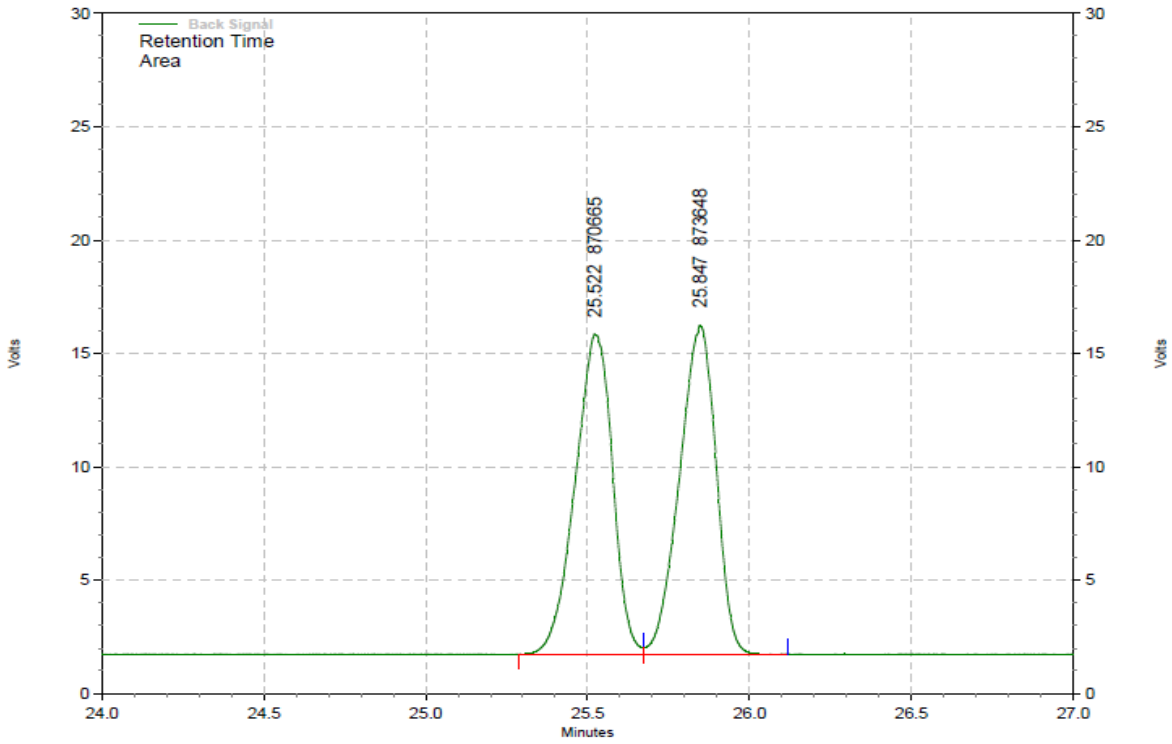

Back Signal
Retention Time
Area
20.624 309470
20.864 309408
Volts
Minutes

P10

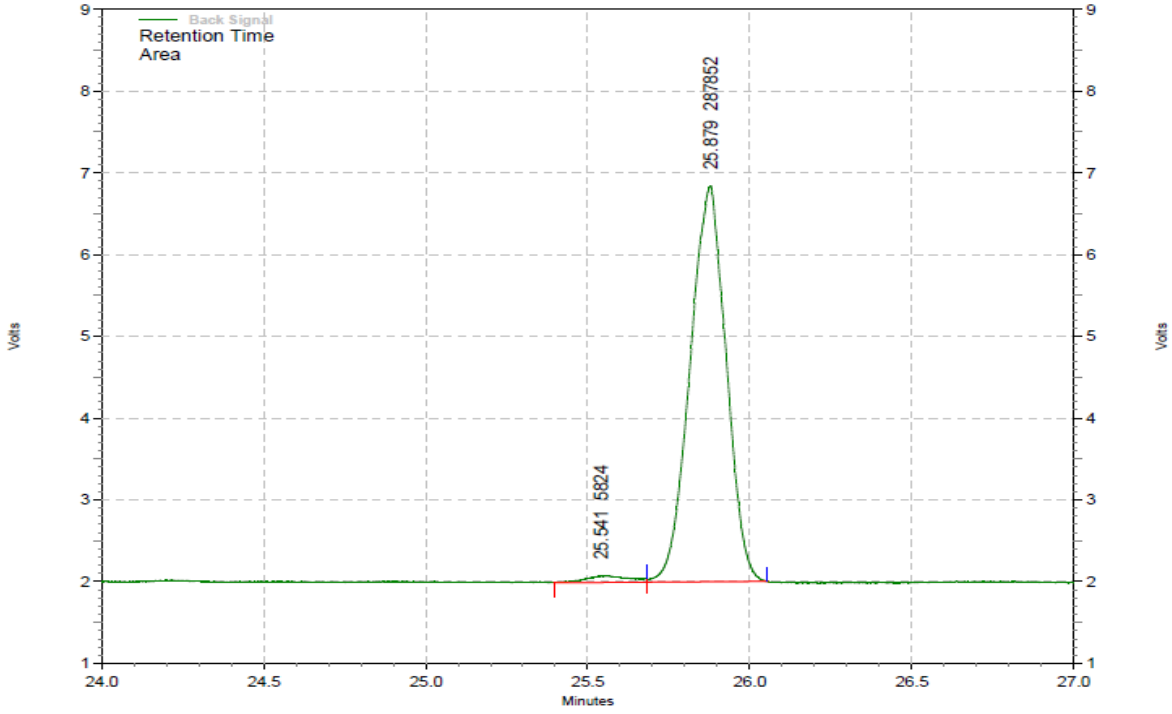

Back Signal
Retention Time
Area
20.634 38730
20.899 1272314
Volts
Minutes

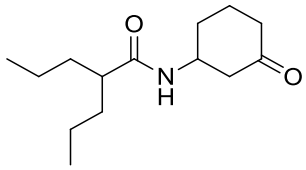

O
N
H
O

Rac

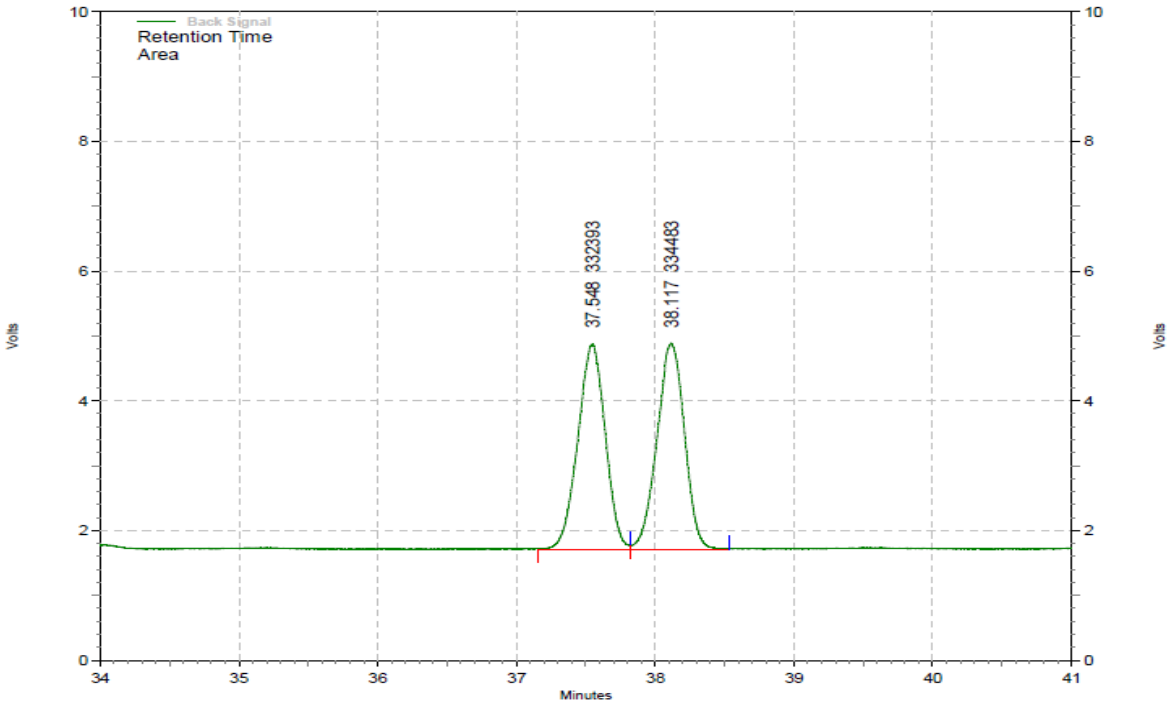

Back Signal
Retention Time
Area
25.522 870665
25.847 873648
Volts
Minutes
24.0
24.5
25.0
25.5
26.0
26.5
27.0

P11

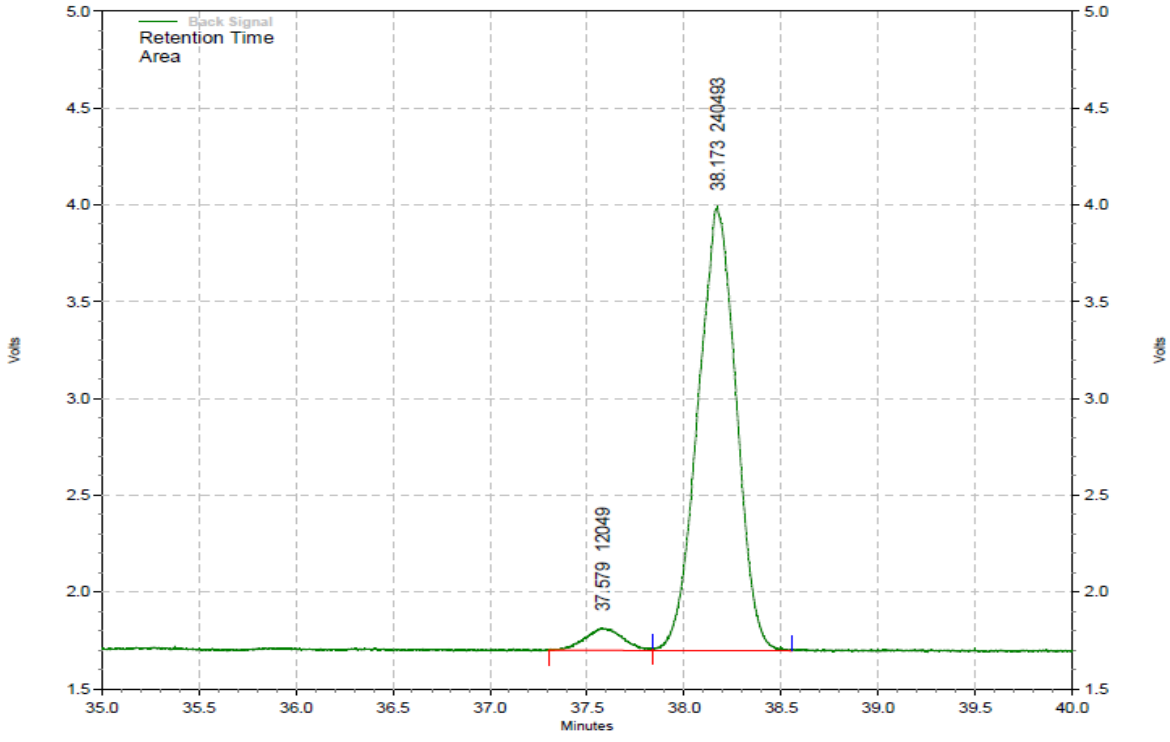

Back Signal
Retention Time
Area
25.541 5824
25.879 287852
Volts
Minutes
24.0
24.5
25.0
25.5
26.0
26.5
27.0

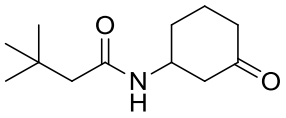

O
N
H
O

Rac

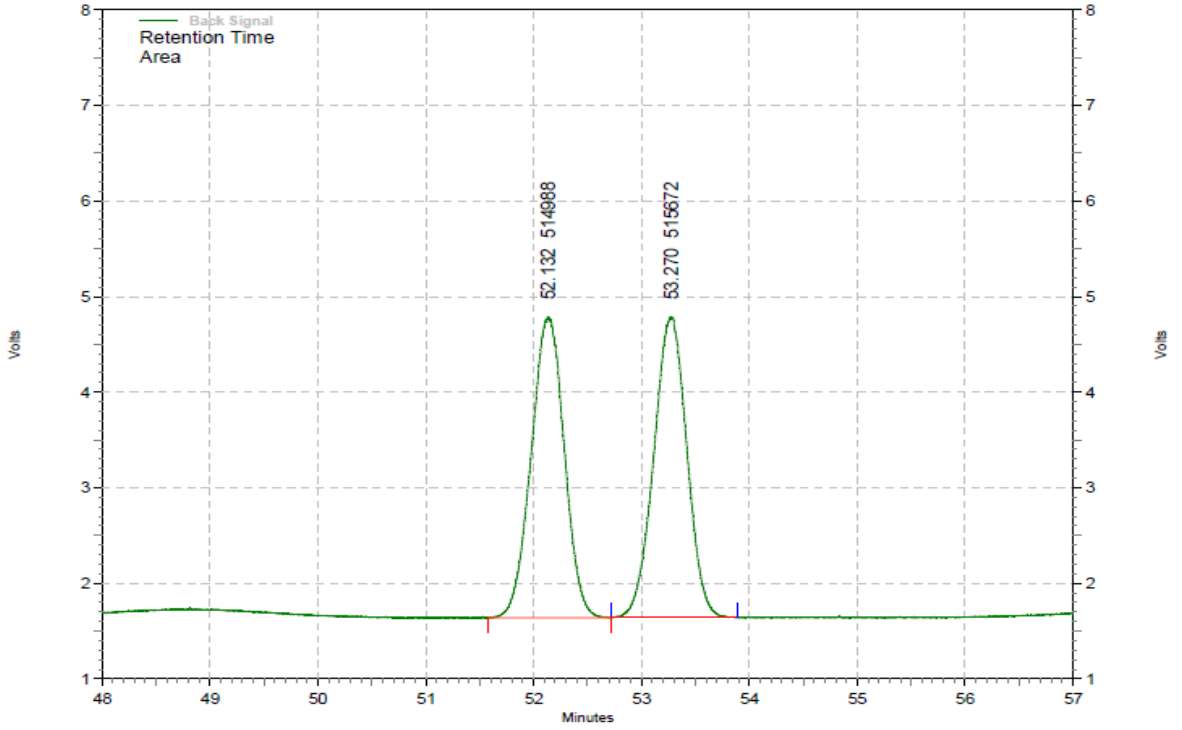

Back Signal
Retention Time
Area
37.548 332393
38.117 334483
Volts
Minutes

P12

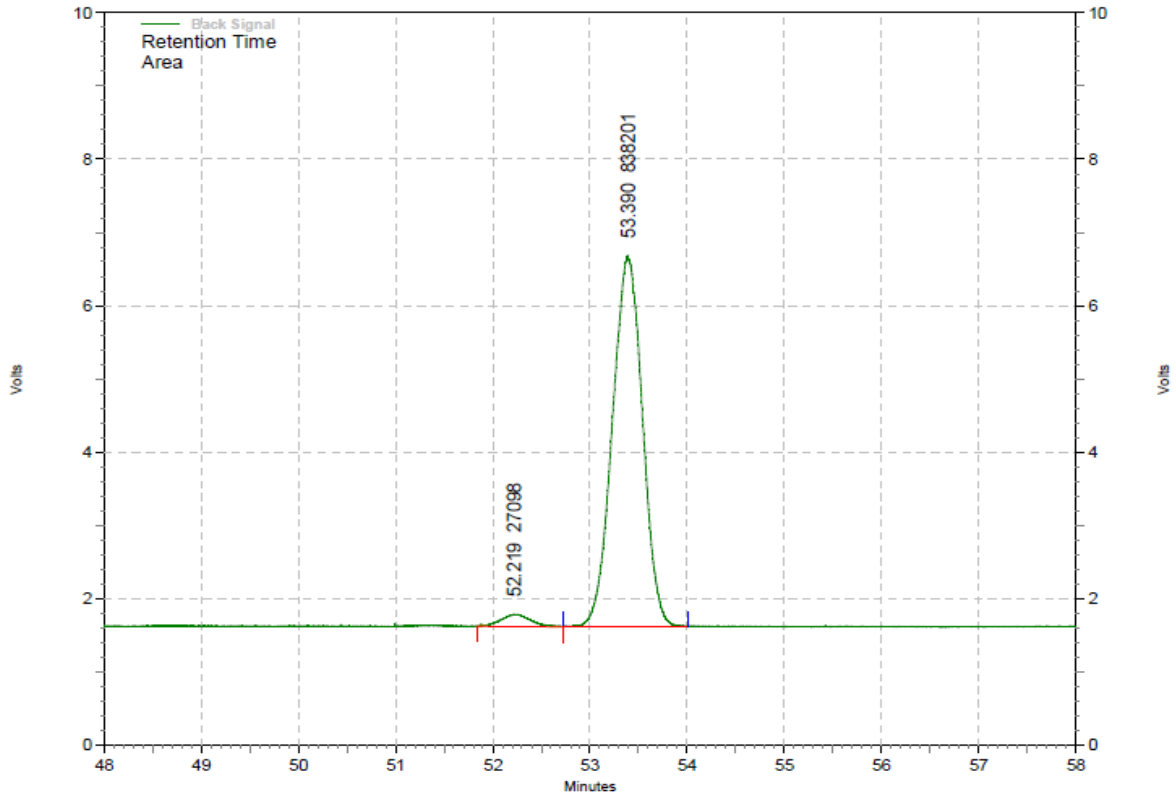

Back Signal
Retention Time
Area
38.173 240493
37.579 12049
Volts
Minutes

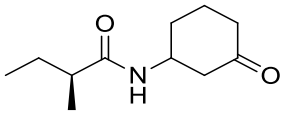

O
N
H
O

Rac

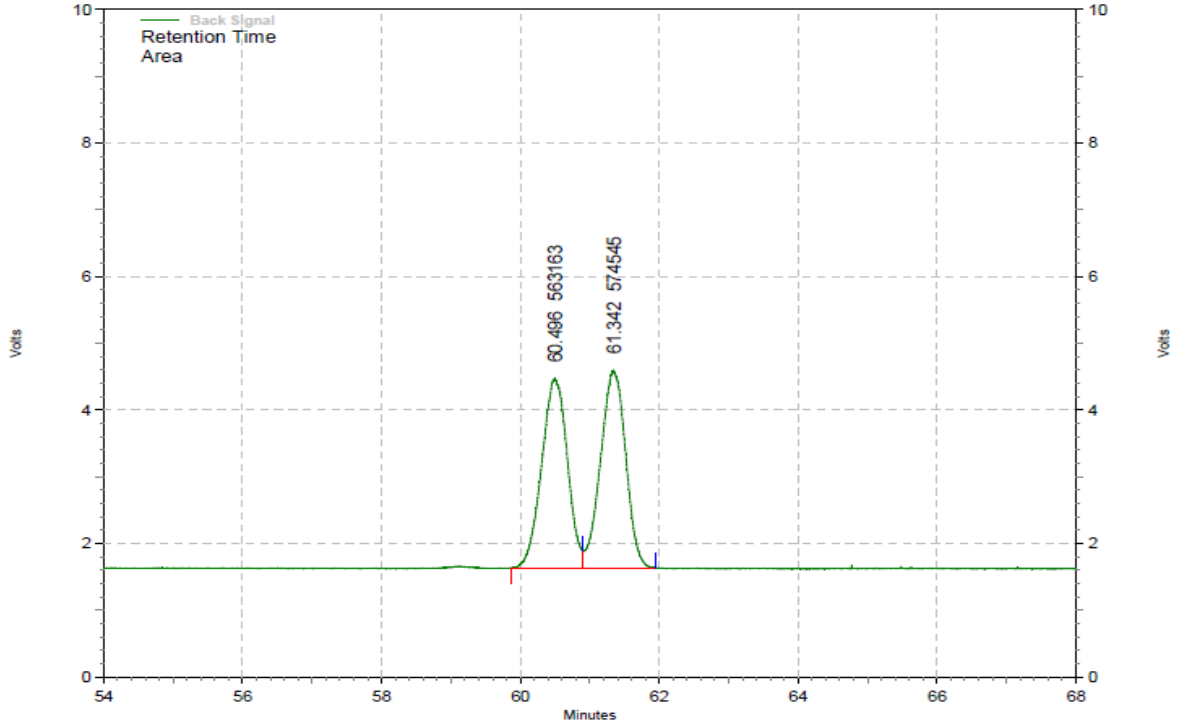

Back Signal
Retention Time
Area
52.132 514988
53.270 515672
Volts
Minutes

P13

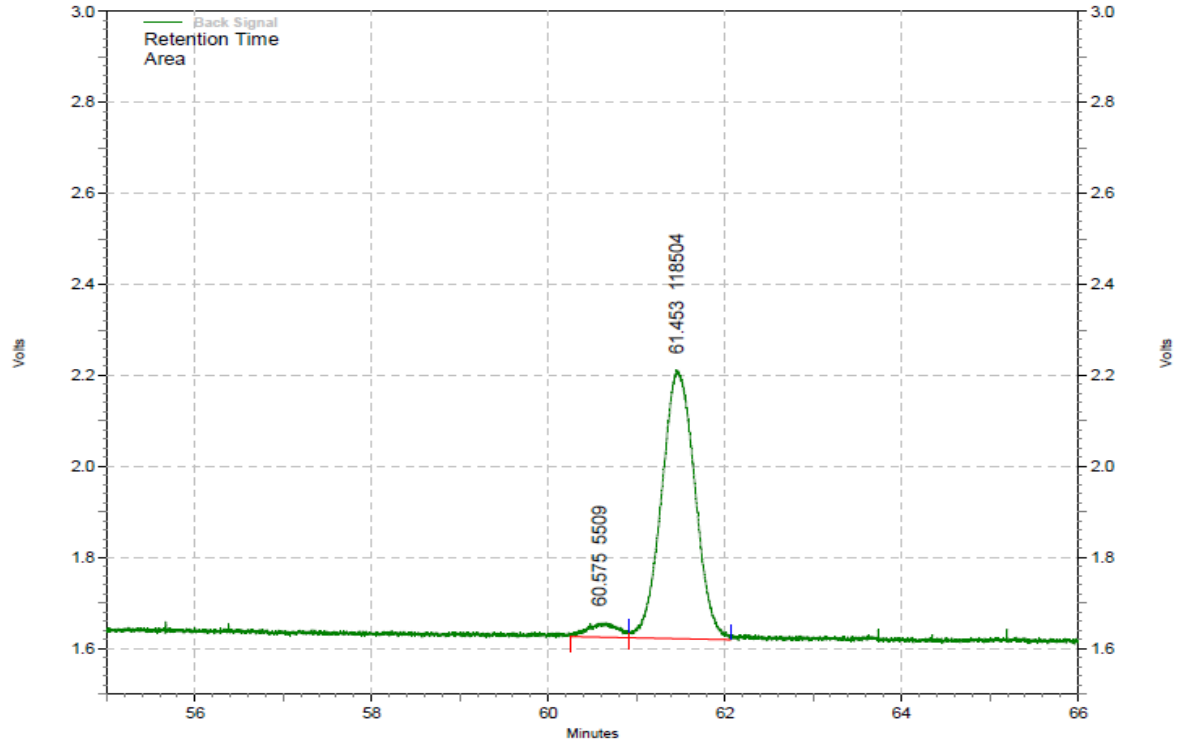

Back Signal
Retention Time
Area
53.390 838201
52.219 27098
Volts
Minutes

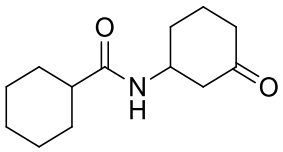


Rac

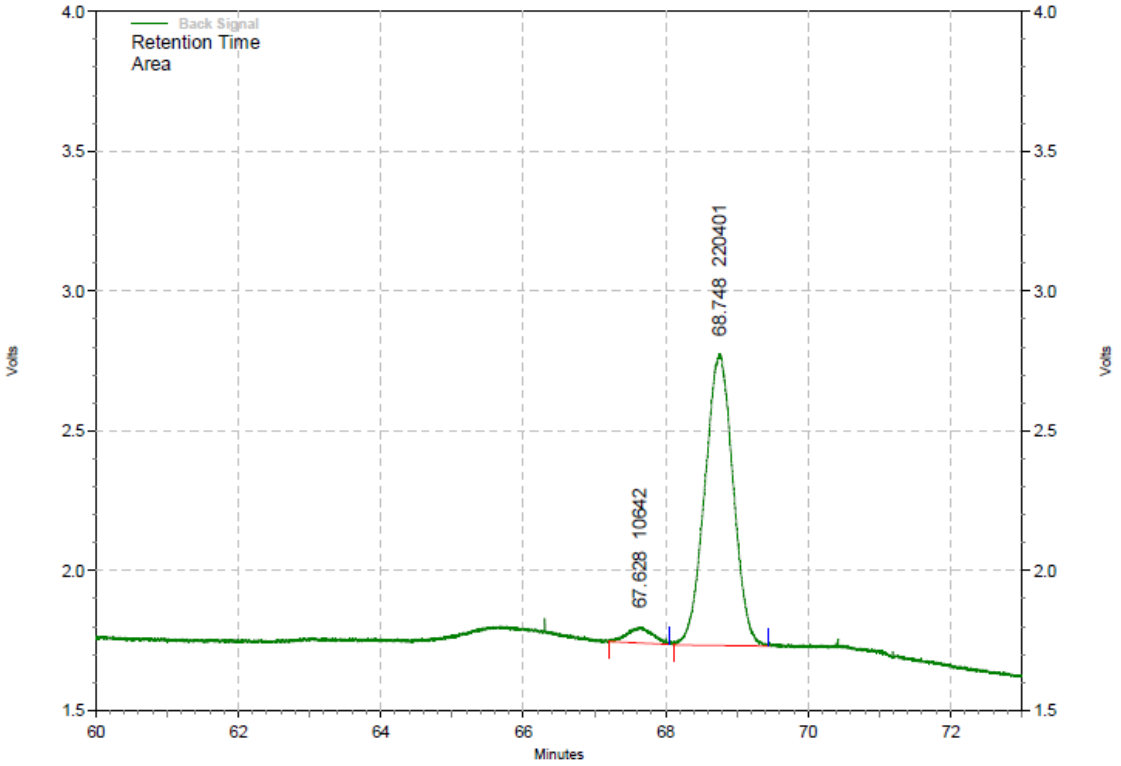

Back Signal
Retention Time
Area
60.496 563163
61.342 574545
Volts
Minutes

P14

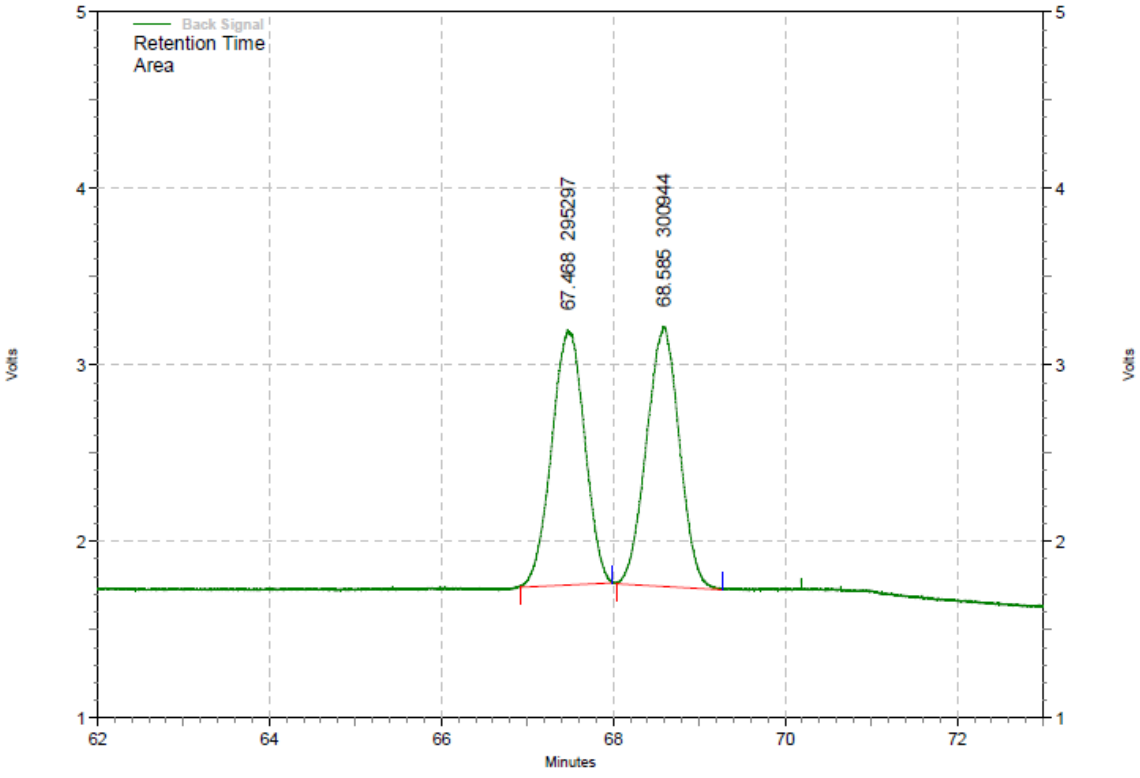

Back Signal
Retention Time
Area
60.575 5509
61.453 118504
Volts
Minutes

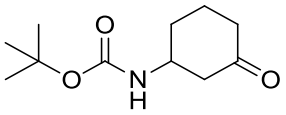

O
N
H
O

Rac

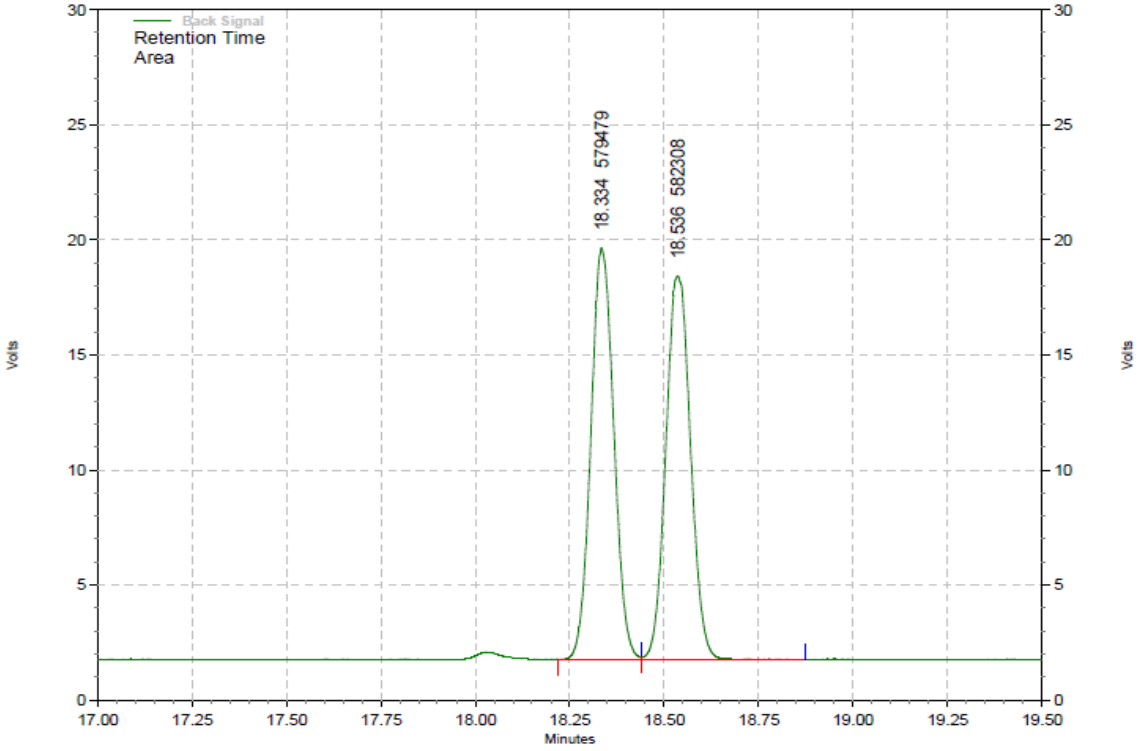

Back Signal
Retention Time
Area
68.748 220401
67.628 10642
Volts
Minutes
4.0
3.5
3.0
2.5
2.0
1.5
60
62
64
66
68
70
72

P15

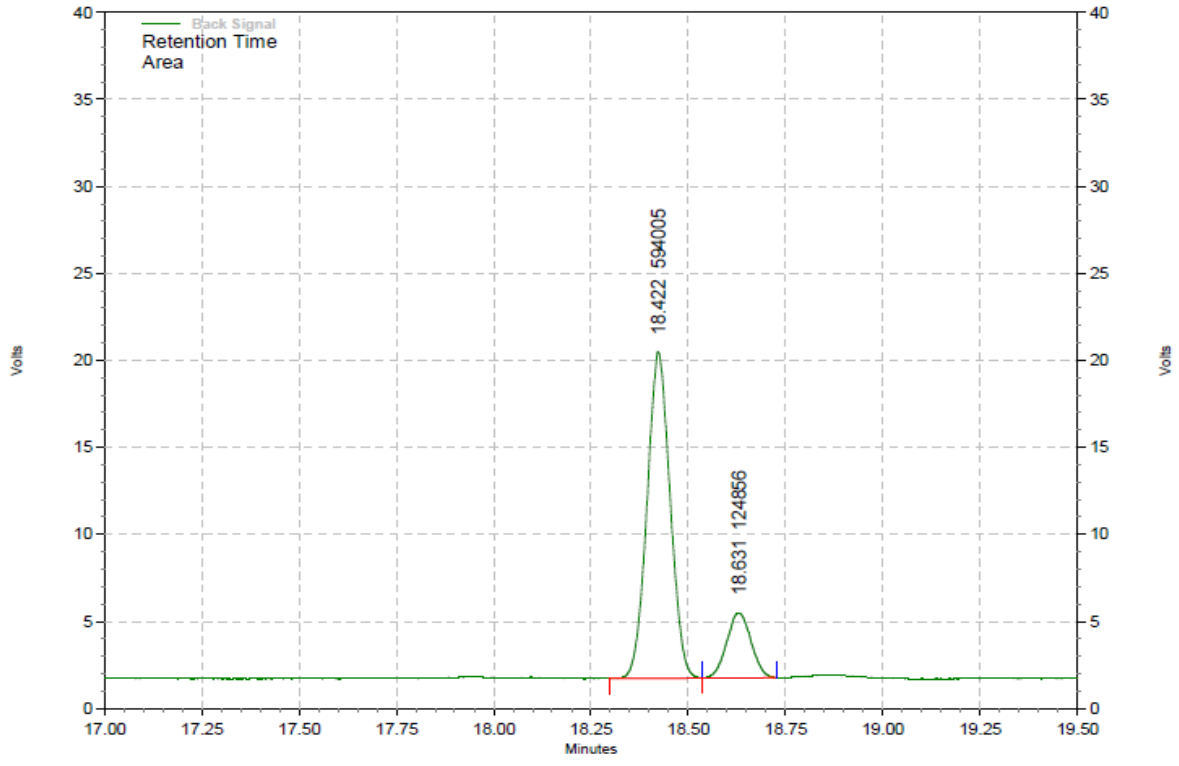

Back Signal
Retention Time
Area
67.468 295297
68.585 300944
Volts
Minutes
5
4
3
2
1
62
64
66
68
70
72

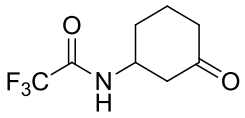


Rac

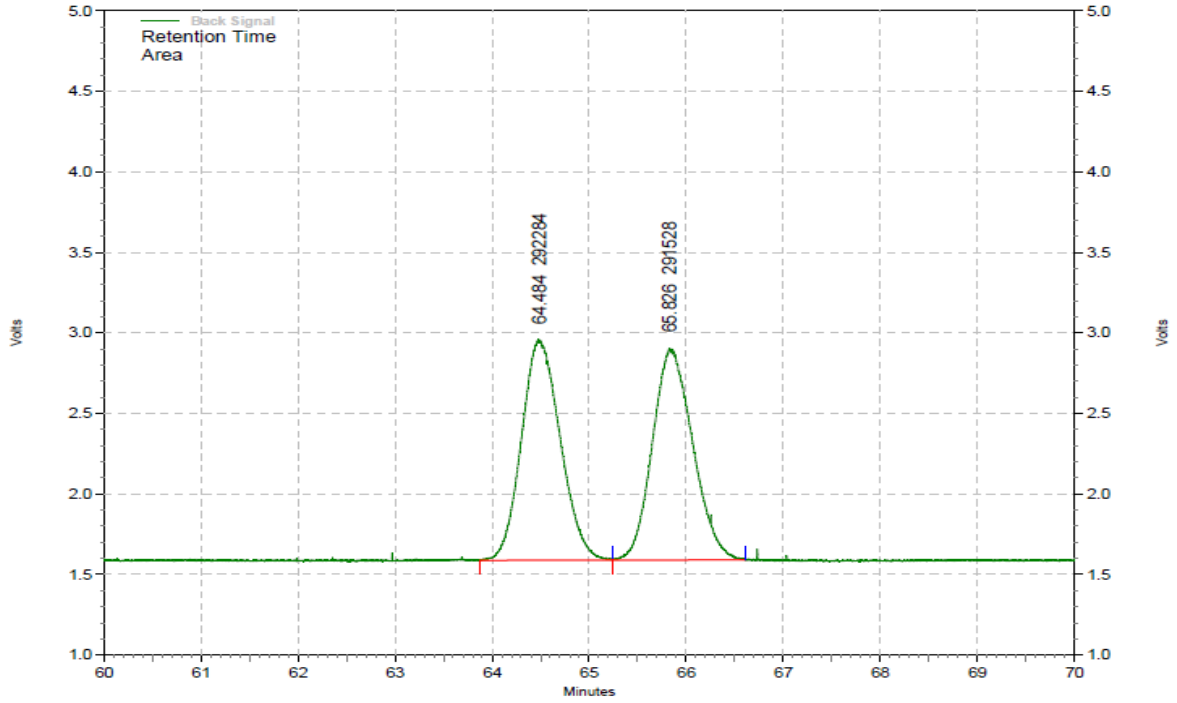

Back Signal
Retention Time
Area
18.334 579479
18.536 582308
Volts
Minutes

P16

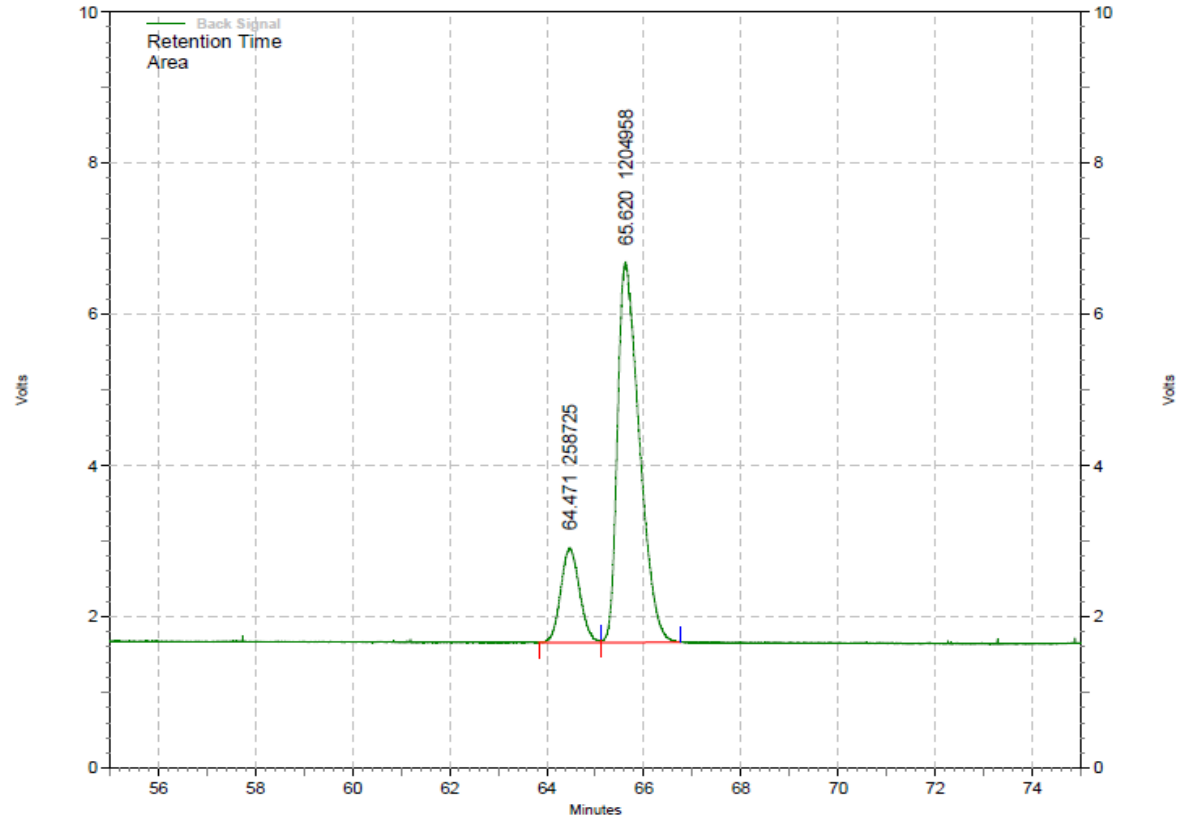

Back Signal
Retention Time
Area
18.422 594005
18.631 124856
Volts
Minutes


O
F3C
N
H
O

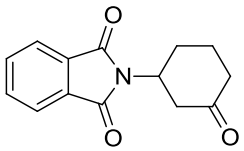
Rac


Back Signal
Retention Time
Area
64.484 292284
65.826 291528
Volts
Minutes

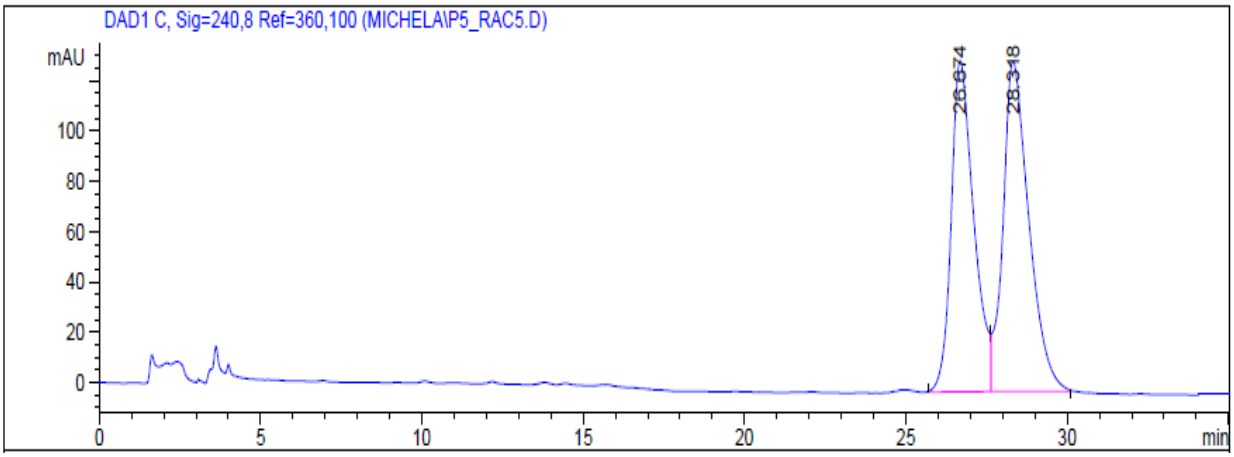
P17


Back Signal
Retention Time
Area
64.471 258725
65.620 1204958
Volts
Minutes

HPLC-separation conditions: Chiralpack IA 25ºC, 240.8 nm, 88/12 hexane/*i*-PrOH, 1.0 mL/min; r.t.(*minor*) = 26.166 min, r.t.(*major*) = 27.910 min.

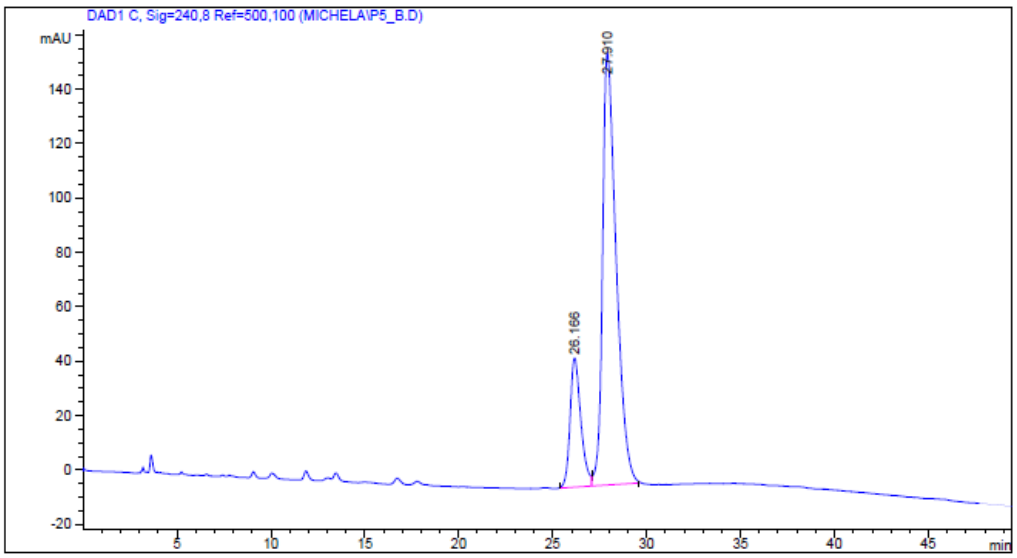


Rac

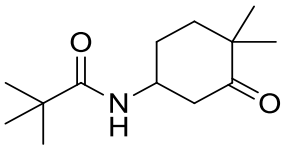


Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	26.674	1	BV	6397.72949	131.63432	46.6248
2	28.318	1	VB	7323.99268	131.42468	53.3752

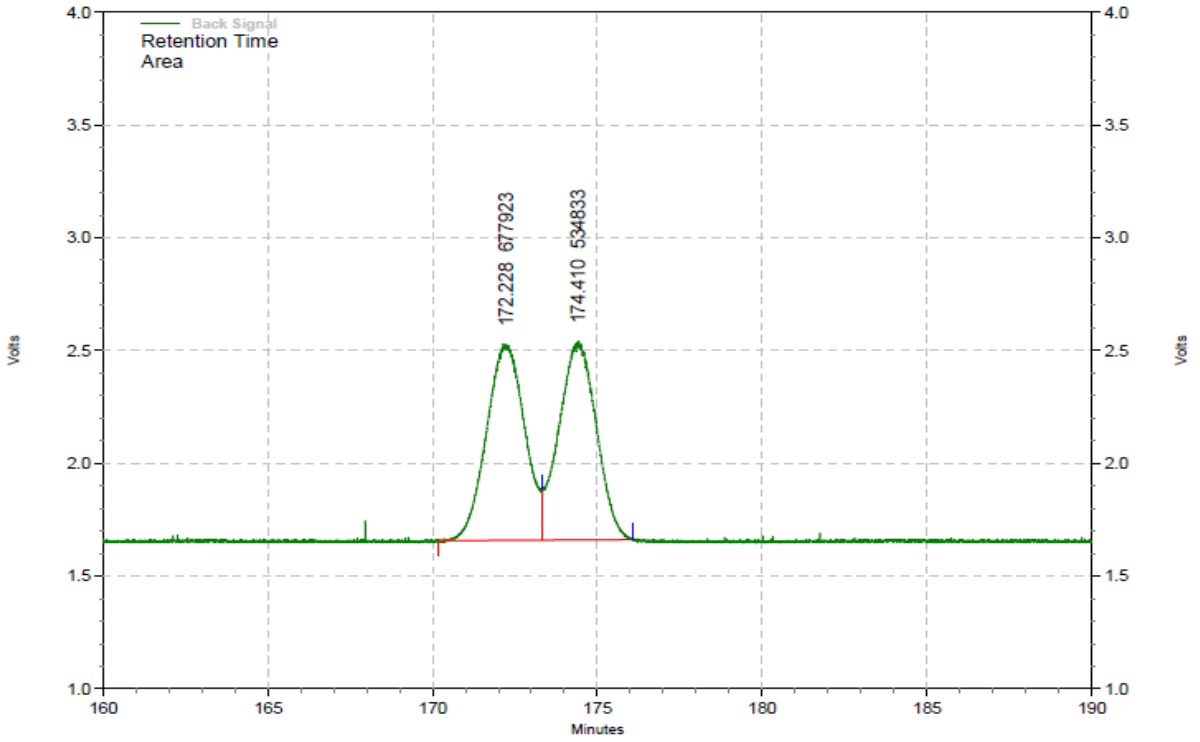
P18 (K_3)



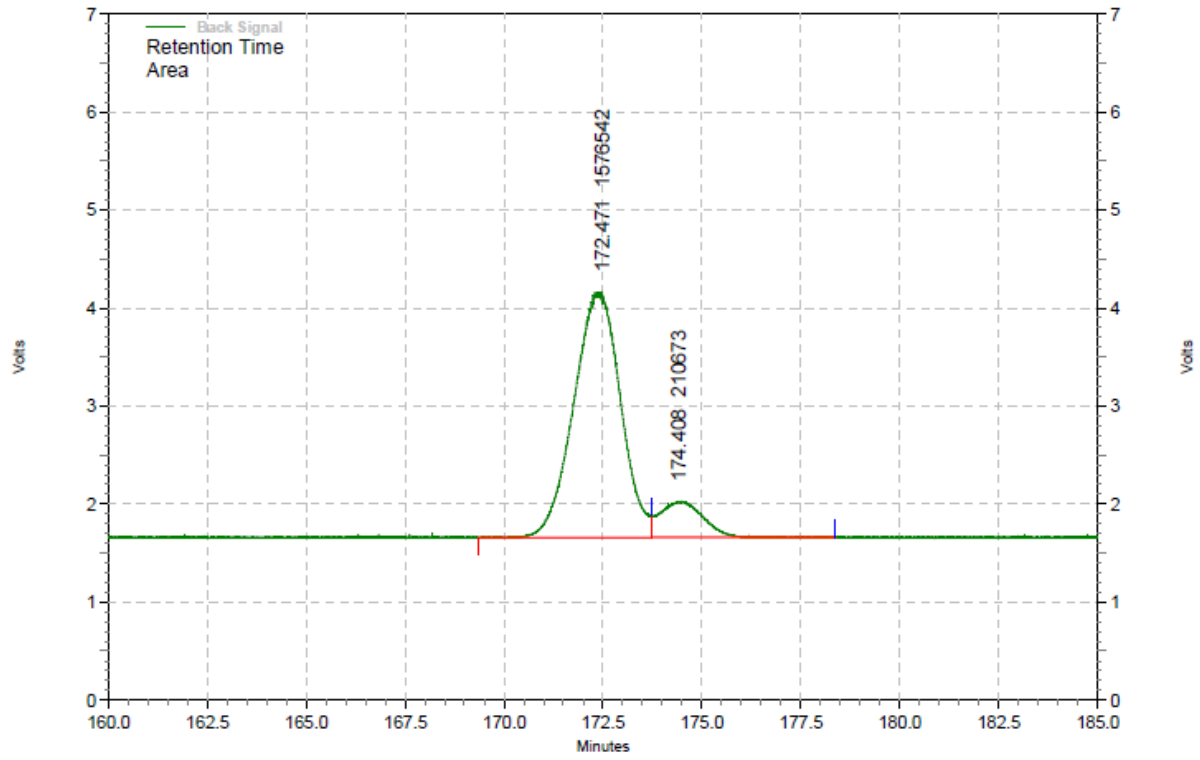
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.166	BV	0.5937	1895.62903	47.48789	19.1476
2	27.910	VB	0.7504	8004.47949	158.72383	80.8524

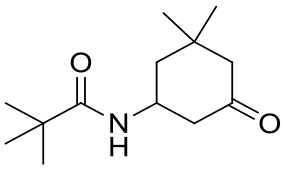

O
N
H
O

Rac

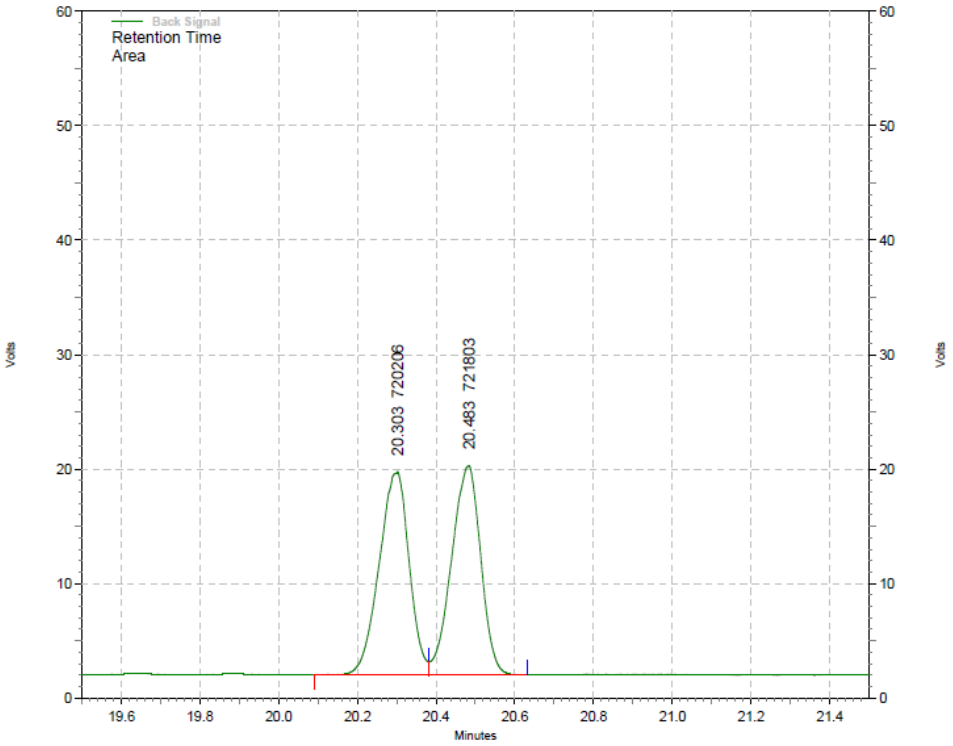

Back Signal
Retention Time
Area
172.228 677923
174.410 534833
Volts
Minutes
4.0
3.5
3.0
2.5
2.0
1.5
1.0
160
165
170
175
180
185
190

P20

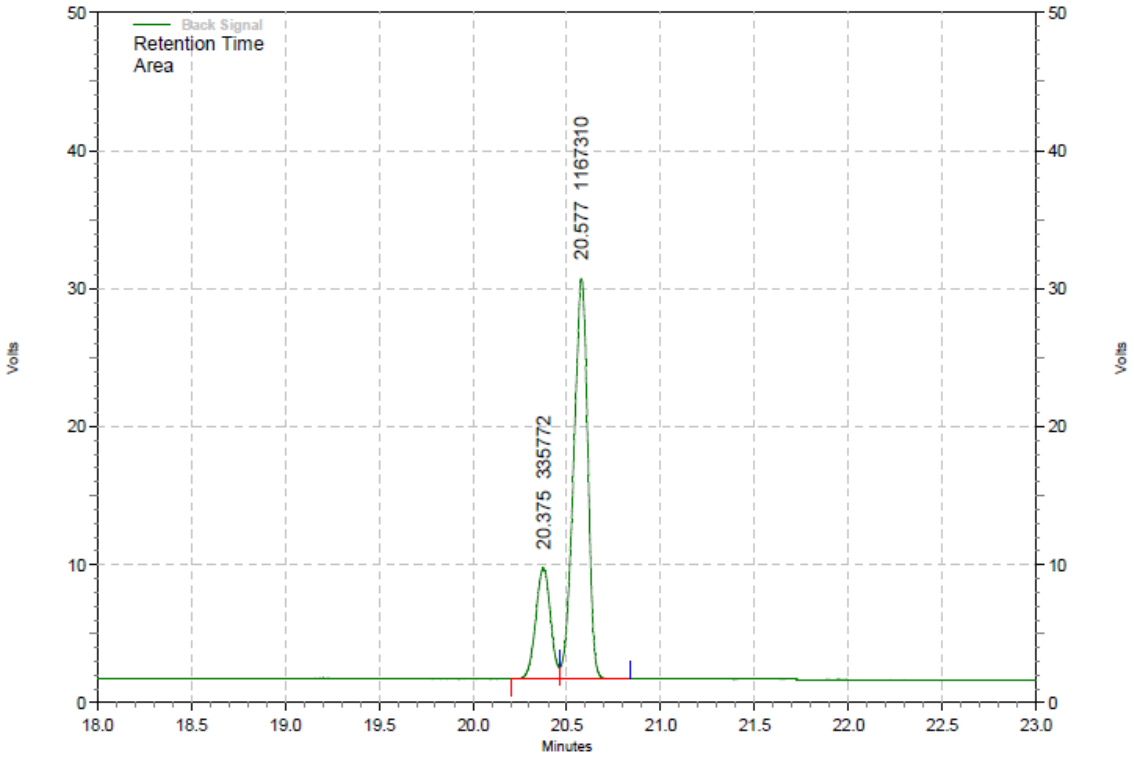

Back Signal
Retention Time
Area
172.471 1576542
174.408 210673
Volts
Minutes
7
6
5
4
3
2
1
0
160.0
162.5
165.0
167.5
170.0
172.5
175.0
177.5
180.0
182.5
185.0


O
N
H
O

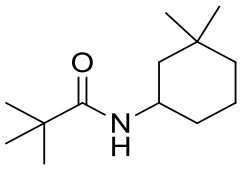
Rac


Back Signal
Retention Time
Area
20.303 720206
20.483 721803
Volts
Minutes

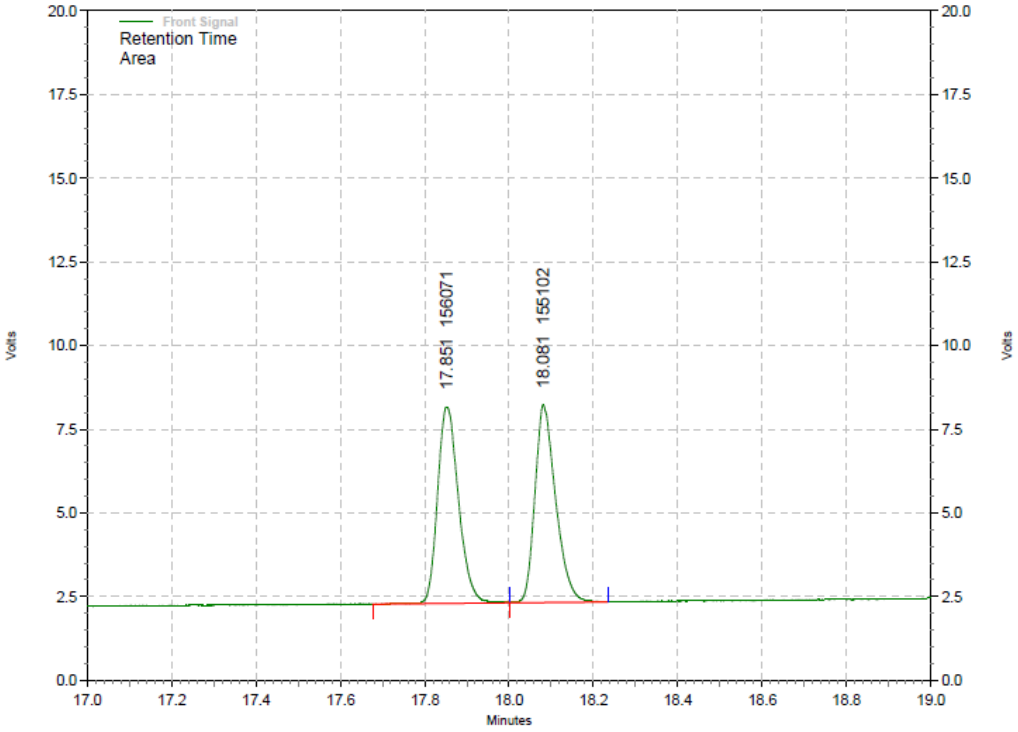
P21


Back Signal
Retention Time
Area
20.375 335772
20.577 1167310
Volts
Minutes

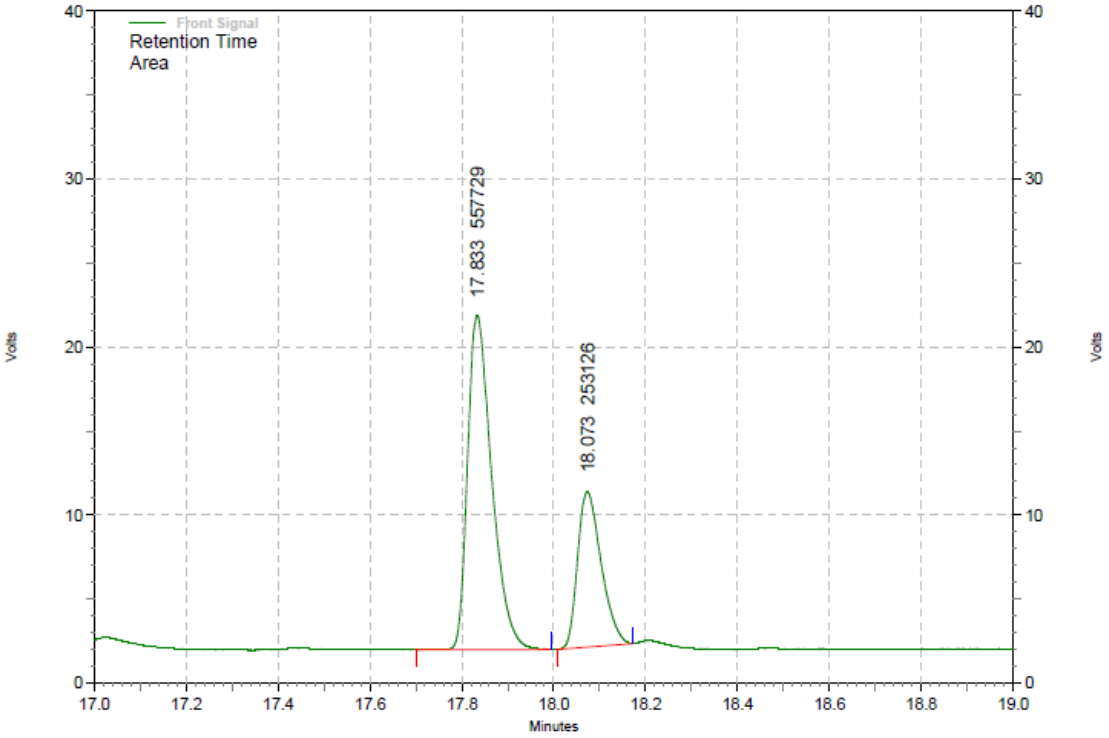
Chiral resolution of **S21:**



Rac



S21



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