Supporting Information

Preparation of One–Carbon Homologated Amides from Aldehydes or Primary Alcohols

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General Information

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker instruments at 360 or 500 MHz, 125.4 MHz, and 338 MHz, respectively. Mass spectra were recorded on an AutoSpec-Ultima_NT mass spectrometer using electron ionization (EI) at 70 eV and an EBE sector mass analyzer. Melting points were determined with a Mel-Temp 1001D capillary melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO FT/IR-4100 instrument. Optical rotations were measured with a Rudolph AUTOPOL IV/6W polarimeter. TLC visualization was achieved by UV light (254 nm) or $KMnO_4$ staining. Dess−Martin periodinane was prepared by the method of Boeckman, et al.[1] All reagents were used directly as obtained from commercial sources unless otherwise noted.

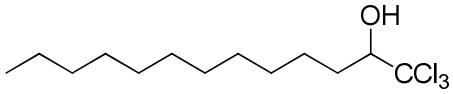
General Procedures for the Preparation of Trichloromethyl Carbinols (3a-3j)

Method A: Trichloromethyl carbinols in entries (**3a**–**3j)** were prepared by the method of Corey and Link[2] from the respective aldehydes. Yields and reaction times are unoptimized. The following serves as a general procedure. To a solution of aldehyde (1.0 mmol) in 1.35 mL of anhydrous DMF was added trichloroacetic acid (1.5 mmol) then sodium trichloroacetate (1.5 mmol) with stirring at room temperature. Initially, rapid evolution of CO_2 was observed. After 6–8 h, the mixture was monitored by TLC. If starting material remained, one equivalent of sodium trichloroacetate and one equivalent of trichloroacetic acid were added. After an additional 4–8 h, the mixture was diluted with 5 mL of diethyl ether and washed with saturated aqueous sodium bicarbonate. Precipitated solids were filtered and washed three times with diethyl ether. The filtrate was washed two more times with sodium bicarbonate solution and once with brine. The organic phase was dried with sodium sulfate, and the solvent was evaporated under reduced pressure. The resulting residue was eluted through a plug of silica gel with hexanes/ethyl acetate to afford the corresponding trichloromethyl carbinol.

Method B: To a solution of primary alcohol **2a**-**2j** (1.0 mmol) in anhydrous $CHCl_3$ (1.5 mL) was added Dess–Martin periodinane (509 mg, 1.2 mmol) at 0 ^{o}C under an argon atmosphere. The reaction mixture was brought to room temperature and allowed to stir until the starting alcohol was consumed as determined by TLC analysis (typically 4-8 hours). 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) (446 mg, 3.2 mmol) was added in three portions and stirred very rapidly at 0 ^{o}C. After 6-8 h, the mixture was monitored by TLC. If corresponding aldehyde remained, one equivalent of TBD was added with vigorous stirring. After completion of the reaction, as indicated by TLC, the mixture was diluted with saturated aqueous $NaHCO_3$ (5 mL) and CH_2Cl_2 (5 mL). The precipitated solids were filtered on a bed of diatomaceous earth and the filter cake was rinsed with CH_2Cl_2. The filtrate was separated, and the aqueous layer was extracted with dichloromethane (3 x 5 mL). The combined organic layers were dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The resulting residue was eluted through a plug of silica gel using indicated ratios of ethyl acetate/hexanes to afford the corresponding trichloromethyl carbinols **3**.

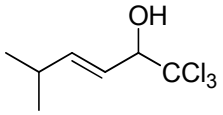
Full characterization data for compounds **3a**–**3d, 3f-3h,** and **3j** were reported previously.[3] Characterization data for new compounds **3e** and **3i** are provided below.

1,1,1–Trichlorotridecan–2–ol (3e).



The crude material was purified by flash chromatography through a plug of silica gel, using 95:5 hexane/EtOAc as the eluent. The indicated compound was obtained as a colorless oil in 88% yield (267.3 mg); IR (film): 3579, 2927, 2856, 1461, 1265, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz): δ 4.0 (ddd, 1H, *J* = 9.4, 5.3, 1.7 Hz), 2.65 (d, 1H, *J* = 5.3 Hz), 2.16 – 1.91 (m, 1H), 1.70 – 1.55 (m, 2H), 1.53 – 1.40 (m, 1H), 1.36 – 1.17 (m, 16H), 0.88 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 104.4, 83.0, 31.9, 31.5, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 26.1, 22.7, 14.1; HRMS *m/z* calcd for $C_{12}H_{25}O$ [M–CCl_3]$^+$, 185.1905; found 185.1901.

(*E*)–1,1,1–Trichloro–5–methylhex–3–en–2–ol (3i).

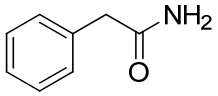


The crude material was purified by flash chromatography through a plug of silica gel, using 95:5 hexane/EtOAc as the eluent. The indicated compound was obtained as a colorless oil in 93% yield (202.3 mg); IR (film): 3366, 2964, 2871, 1643, 1266, 972, 739 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz): δ 5.99 (ddd, 1H, *J* = 15.5, 6.7, 1.0 Hz), 5.59 (ddd, 1H, *J* = 15.5, 6.7, 1.4 Hz), 4.52 (t, 1H, *J* = 6.0 Hz), 2.78 (dd, 1H, *J* = 6.0, 2.9 Hz), 2.44 – 2.33 (m, 1H), 1.05 (s, 3H), 1.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.1, 121.0, 103.1, 83.5, 31.1, 21.8, 21.8; HRMS *m/z* calcd for $C_6H_{11}O$ [M–CCl_3]$^+$, 99.0810; found 99.0807.

General Procedure for the Preparation of One–Carbon Homologated Primary Amides (6a-6j) from Trichloromethyl Carbinols

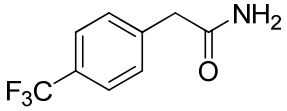
Diphenyldiselenide (1.3 mmol, 406 mg) was added to a 50 mL dry pressure tube temporarily fit with a rubber septum and equipped with a magnetic stir bar. Ammonia saturated absolute ethanol (4 mL) was added followed by the rapid addition of $NaBH_4$ (2.8 mmol, 106 mg) under argon. Shortly after the addition, the initial yellow solution turned colorless, indicating complete reduction of diphenyldiselenide. The solution stirred at room temperature for 30 minutes, then neat trichloromethyl carbinol **3** (1.0 mmol) was added, followed by the addition of freshly powdered NaOH (2.5 mmol, 100.0 mg) under argon. The rubber septum was quickly replaced with a Teflon screw cap and the solution was heated in a 55 °C oil bath for 24–36 hours. After completion of the reaction as indicated by TLC, the system was cooled to rt, and the ethanolic ammonia was removed by rotary evaporation. The amorphous solids were dissolved in 5 mL ethyl acetate and 5 mL H_2O. The resulting solution was cooled to 0 °C and adjusted to pH 1 with 1 N HCl. The product was extracted with ethyl acetate (5 × 10 mL), dried with anhydrous sodium sulfate, and then concentrated by rotary evaporation. The crude material was purified by flash chromatography through a small plug of silica using the specified eluent indicated below, affording the corresponding primary amide.

2–Phenylacetamide (6a).[4]



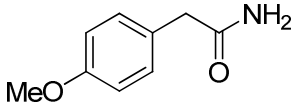
The crude material was purified by flash chromatography through a plug of silica gel using 1:9 EtOAc/hexane to remove diphenyldiselenide then 95:5 EtOAc/MeOH as the eluent. The indicated product was obtained as an off–white solid in 88% yield (119.1 mg); m.p. 156–157 °C; IR (solid): ν 3349, 3163, 3031, 2923, 2804, 1633, 1411, 1285, 1181, 742 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.41 – 7.33 (m, 2H), 7.33 – 7.26 (m, 3H), 5.68 (brs, 1H), 5.39 (brs, 1H), 3.59 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.6, 134.8, 129.4, 129.0, 127.4, 43.3; HRMS *m/z* calcd for C_8H_9NO, 135.0684; found 135.0689.

2–{4–(Trifluoromethyl)phenyl}acetamide (6b).



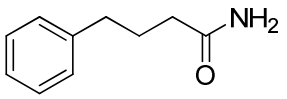
The crude material was purified by flash chromatography through a plug of silica gel, using 1:9 EtOAc/hexane to remove diphenyldiselenide then 95:5 EtOAc/MeOH as the eluent. The indicated compound was obtained as a white solid in 90% yield (183.7 mg); m.p. 148–150 °C; IR (solid): ν 3352, 3166, 2924, 2806, 1634, 1413, 1323, 1132, 1064, 1019, 815 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.62 (d, 2H, J = 8.0 Hz), 7.41 (d, 2H, J = 8.0 Hz), 5.69 (brs, 1H), 5.40 (brs, 1H), 3.64 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.1, 138.7, 129.9 (q, J = 32.4 Hz), 129.7, 125.8 (q, J = 3.7 Hz), 122.9 (q, J = 276.3 Hz), 42.8; ^{19}F NMR ($CDCl_3$, 360 MHz): δ –62.6; HRMS *m/z* calcd for $C_9H_8F_3NO$, 203.0558; found 203.0556.

2–(4–Methoxyphenyl)acetamide (6c).



The crude material was purified by flash chromatography through a plug of silica gel, using 1:9 EtOAc/hexane to remove diphenyldiselenide then 95:5 EtOAc/MeOH as the eluent. The indicated compound was obtained as a white solid in 86% yield (142.2 mg); m.p. 189–190 °C; IR (solid): ν 3345, 3168, 2972, 2940, 2807, 1631, 1509, 1411, 1298, 1204, 1180, 1023, 811, 772 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.19 (d, 2H, J = 8.6 Hz), 6.89 (d, 2H, J = 8.6 Hz), 5.37 (brs, 2H), 3.81 (s, 3H), 3.53 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.7, 159.0, 130.5, 126.9, 114.5, 55.3, 42.4; HRMS *m/z* calcd for $C_9H_{11}NO_2$, 165.0790; found 165.0793.

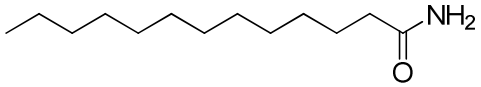
4–Phenylbutanamide (6d).[5]



The crude material was purified by flash chromatography through a plug of silica gel, using 1:9 EtOAc/hexane to remove diphenyldiselenide then 95:5 EtOAc/MeOH as the eluent. The indicated compound was obtained as an off–white solid in 85% yield (138.7 mg); m.p. 80–81 °C; IR (solid): ν 3380, 3198, 3023, 2944, 2861, 1645, 1418, 755 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.32 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 6.0 (brs, 1H), 5.55 (brs, 1H), 2.66 (t, 2H, J = 7.5 Hz), 2.20 (t, 2H, J = 7.5 Hz), 2.00 – 1.92 (m, 2H); ^{13}C

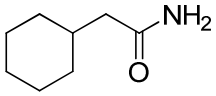
NMR ($CDCl_3$, 125 MHz): δ 175.4, 141.3, 128.4, 128.3, 125.9, 35.0, 34.9, 26.8; HRMS *m/z* calcd for $C_{10}H_{13}NO$, 163.0997; found 163.0998.

Tridecanamide (6e).



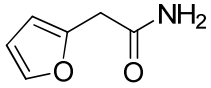
The crude material was purified by flash chromatography through a plug of silica gel, using 1:9 EtOAc/hexane to remove diphenyldiselenide then 95:5 EtOAc/MeOH as the eluent. The indicated compound was obtained as a white solid in 80% yield (170.5 mg); m.p. 93–95 °C; IR (solid): ν 3356, 3188, 2916, 2849, 1631, 1466, 1416, 1136, 791 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.68 (brs, 1H), 5.46 (brs, 1H), 2.21 (t, 2H, *J* = 7.5 Hz), 1.63 (dd, 2H, *J* = 14.8, 7.5 Hz), 1.40 – 1.18 (m, 18H), 0.88 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 175.7, 36.0, 31.9, 29.6, 29.6, 29.6, 29.6, 29.5, 29.3, 29.2, 25.5, 22.7, 14.1; HRMS *m/z* calcd for $C_{13}H_{27}NO$, 213.2093; found 213.2100.

2–Cyclohexylacetamide (6f).[4]



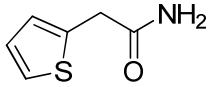
The crude material was purified by flash chromatography through a plug of silica gel, using 1:9 EtOAc/hexane to remove diphenyldiselenide then 95:5 EtOAc/MeOH as the eluent. The indicated compound was obtained as a white solid in 92% yield (130.4 mg); m.p. 160–162 °C; IR (solid): ν 3349, 3183, 2922, 2846, 1623, 1410 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.44 (brs, 1H), 5.39 (brs, 1H), 2.08 (d, 2H, *J* = 6.7 Hz), 1.89 – 1.60 (m, 6H), 1.38 – 1.21 (m, 2H), 1.21 – 1.06 (m, 1H), 0.96 (qd, 2H, *J* = 13.0, 3.1 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.7, 44.0, 35.2, 33.1, 26.2, 26.0; HRMS *m/z* calcd for $C_8H_{15}NO$, 141.1154; found 141.1152.

2–(Furan–2–yl)acetamide (6g).



The crude material was purified by flash chromatography through a plug of silica gel, using 1:9 EtOAc/hexane to remove diphenyldiselenide then 95:5 EtOAc/MeOH as the eluent. The indicated compound was obtained as a grey solid in 75% yield (93.8 mg); m.p. 108–109 °C; IR (solid): ν 3351, 3175, 2808, 1641, 1406, 1288, 1143, 1072, 1011, 945, 903, 775 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.38 (d, 1H, *J* = 1.5 Hz), 6.35 (dd, 1H, *J* = 3.1, 1.5 Hz), 6.24 (d, 1H, *J* = 3.1 Hz), 5.97 (brs, 1H), 5.71 (brs, 1H), 3.61 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.2, 148.6, 142.5, 110.8, 108.5, 35.8; HRMS *m/z* calcd for $C_6H_7NO_2$, 125.0477; found 125.0480.

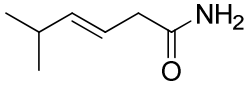
2–(Thiophen–2–yl)acetamide (6h).



The crude material was purified by flash chromatography through a plug of silica gel, using 1:9 EtOAc/hexane to remove diphenyldiselenide then 95:5 EtOAc/MeOH as the eluent. The indicated compound was obtained as a grey solid in 90% yield (127.6 mg). m.p. 150–151 °C; IR (solid): ν 3348, 3164, 2909, 2812, 1634, 1407, 1284, 1134, 822 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.26 (dd, 1H, *J* = 5.1, 1.2 Hz), 7.00 (dd, 1H, *J* = 5.1, 3.5 Hz), 6.97 (dd, 1H, *J* = 3.5, 1.2 Hz), 5.88 (brs, 1H), 5.65 (brs, 1H), 3.79 (s, 2H); ^{13}C NMR

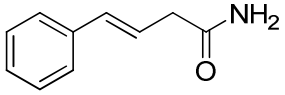
($CDCl_3$, 125 MHz): δ 172.3, 136.1, 127.4, 125.6, 37.0; HRMS *m/z* calcd for C_6H_7NOS, 141.0248; found 141.0250.

(*E*)–5–Methylhex–3–enamide (6i).



The crude material was purified by flash chromatography through a plug of silica gel, using 1:9 EtOAc/hexane to remove diphenyldiselenide then 95:5 EtOAc/MeOH as the eluent. The indicated compound was obtained as a white solid in 86% yield (109.4 mg); m.p. 87–88 °C; IR (solid): ν 3349, 3177, 2958, 2868, 2805, 1630, 1409, 967, 813 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.87 (brs, 1H), 5.64 (dd, 1H, *J* = 15.3, 6.4 Hz), 5.63 (brs, 1H), 5.55 – 5.42 (m, 1H), 2.94 (d, 2H, *J* = 6.9 Hz), 2.33 (dq, 1H, *J* = 13.4, 6.9 Hz), 1.00 (d, 6H, *J* = 6.7 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.2, 143.4, 119.6, 39.9, 31.0, 22.2; HRMS *m/z* calcd for $C_7H_{13}NO$, 127.0997; found 127.1002.

(*E*)–4–Phenylbut–3–enamide (6j).

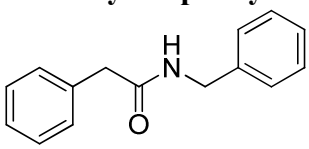


The crude material was purified by flash chromatography through a plug of silica gel, using 1:9 EtOAc/hexane to remove diphenyldiselenide then 95:5 EtOAc/MeOH as the eluent. The indicated compound was obtained as a white solid in 74% yield (119.3 mg) in 9:1 isomeric ratio. Characteristic data of major product; m.p. 105–106 °C; IR (solid): ν 3378, 3191, 3032, 2912, 2848, 1641, 1410, 1259, 963, 741 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.50 – 7.10 (m, 5H), 6.55 (d, 1H, *J* = 15.8 Hz), 6.28 (dt, 1H, *J* = 15.8, 7.2 Hz), 5.90 (brs, 1H), 5.72 (brs, 1H), 3.17 (d, 2H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.3, 136.5, 134.7, 128.6, 127.8, 126.3, 122.2, 40.2; HRMS *m/z* calcd for $C_{10}H_{11}NO$, 161.0841; found 161.0842.

General Procedure for the Preparation of One–Carbon Homologated Secondary Amides (6k-6t) from Trichloromethyl Carbinols

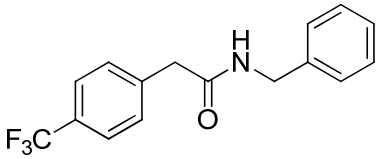
Diphenyldiselenide (1.3 mmol, 406 mg) was added to a dry round–bottom flask equipped with stir bar under a blanket of argon. Deoxygenated absolute ethanol (purged for 30 minutes with argon) (4 mL) was then added, followed by the rapid addition of $NaBH_4$ (2.8 mmol, 106 mg). Shortly after the addition, the initial yellow solution turned colorless, indicating complete reduction of diphenyldiselenide. The solution stirred at room temperature for 30 minutes, then neat trichloromethyl carbinol **3** (1.0 mmol) was added, followed by the additions of freshly powdered NaOH (2.5 mmol, 100 mg) and benzylamine (1.1 mmol, 118 mg) under argon. The mixture was heated in a 55°C oil bath and allowed to react at this temperature for 24–36 hours while monitoring by TLC for consumption of starting material and 2-phenylselanylamide **14**. After completion of the reaction as indicated by TLC, ethanol was removed by rotary evaporation and the amorphous solids were dissolved in 5 mL saturated aqueous NH_4Cl, and the solution was extracted with ethyl acetate (5 × 10 mL). The combined organic layers were dried with anhydrous sodium sulfate and concentrated by rotary evaporation. The crude material was purified by flash chromatography through a small plug of silica using the specified eluent, affording the corresponding pure secondary amide.

***N*–Benzyl–2–phenylacetamide (6k).**[6]



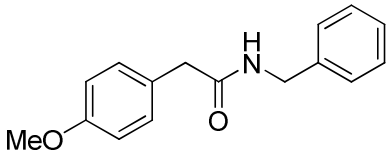
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated compound was obtained as an off–white solid in 89% yield (200.5 mg); m.p. 116–117 °C; IR (solid): ν 3284, 2925, 1637, 1549, 1489, 1448, 1025, 727 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40 – 7.20 (m, 8H), 7.16 (d, 2H, *J* = 7.6 Hz), 5.79 (brs, 1H), 4.39 (d, 2H, *J* = 5.8 Hz), 3.61 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 138.1, 134.8, 129.4, 129.0, 128.6, 127.4, 127.4, 127.3, 43.8, 43.5; HRMS *m/z* calcd for $C_{15}H_{15}NO$, 225.1154; found 225.1160.

***N*–Benzyl–2–(4–(trifluoromethyl)phenyl)acetamide (6l).**



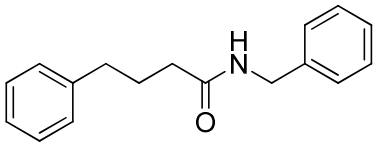
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated product was obtained as a white solid in 95% yield (278.6 mg); m.p. 135–136 ^{o}C; IR (solid): ν 3241, 3066, 2929, 2856, 1626, 1554, 1330, 1124, 1068, 1015, 822, 749 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.58 (d, 2H, *J* = 8.0 Hz), 7.39 (d, 2H, *J* = 8.0 Hz), 7.34 – 7.22 (m, 3H), 7.19 (d, 2H, *J* = 6.9 Hz), 5.90 (brs, 1H), 4.40 (d, 2H, *J* = 5.8 Hz), 3.61 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.7, 138.9, 137.9, 129.7, 129.5 (q, *J* = 32.5 Hz), 128.7, 127.6, 127.6, 125.8 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.0 Hz), 43.8, 43.3; ^{19}F NMR ($CDCl_3$, 360 MHz): δ –62.5; (HRMS *m/z* calcd for $C_{16}H_{14}F_3NO$, 293.1027; found 293.1028.

***N*–Benzyl–2–(4–methoxyphenyl)acetamide (6m).**[7]



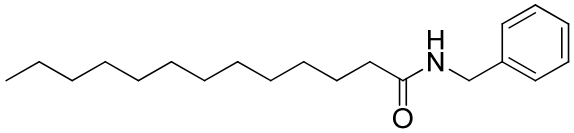
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated product was obtained as an off–white solid in 87% yield (222.4 mg); m.p. 132–133 ^{o}C; IR (solid): ν 3288, 3069, 3032, 2840, 1633, 1584, 1508, 1459, 1298, 1241, 1180, 1029, 809, 738 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.36 – 7.21 (m, 3H), 7.16 (d, 4H, *J* = 8.4 Hz), 6.87 (d, 2H, *J* = 8.4 Hz), 5.73 (brs, 1H), 4.40 (d, 2H, *J* = 5.8 Hz), 3.79 (s, 3H), 3.56 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.2, 158.9, 138.2, 130.5, 128.6, 127.5, 127.4, 126.7, 114.5, 55.3, 43.5, 42.9; HRMS *m/z* calcd for $C_{16}H_{17}NO_2$, 255.1259; found 255.1264.

***N*–Benzyl–4–phenylbutanamide (6n).**[8]



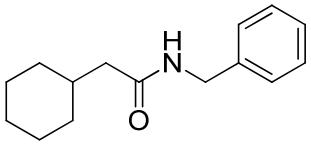
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated compound was obtained as an off–white solid in 85% yield (215.3 mg); m.p. 75–76 °C; IR (solid): ν 3285, 3066, 3025, 2920, 2868, 1639, 1543, 1453, 1266, 1209, 1076, 1025, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.37 – 7.20 (m, 7H), 7.19 – 7.09 (m, 3H), 5.96 (brs, 1H), 4.37 (d, 2H, *J* = 5.6 Hz), 2.62 (t, 2H, *J* = 7.4 Hz), 2.17 (t, 2H, *J* = 7.4 Hz), 2.09 – 1.79 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.5, 141.4, 138.3, 128.6, 128.4, 128.3, 127.7, 127.4, 125.9, 43.4, 35.7, 35.1, 27.0; HRMS *m/z* calcd for $C_{17}H_{19}NO$, 253.1467; found 253.1470.

***N*–Benzyltridecanamide (6o).**[9]



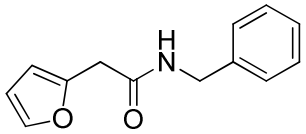
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated compound was obtained as a white solid in 96% yield (291.3 mg); m.p. 80–81 °C; IR (solid): ν 3295, 3073, 3032, 2916, 2848, 1637, 1550, 1457, 1238, 1029, 725 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40 – 7.30 (m, 2H), 7.29 – 7.24 (m, 3H), 5.74 (brs, 1H), 4.44 (d, 2H, *J* = 5.6 Hz), 2.20 (t, 2H, *J* = 7.5 Hz), 1.70 – 1.60 (m, 2H), 1.25 (m, 18H), 0.88 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.9, 138.5, 128.7, 127.8, 127.5, 43.6, 36.8, 31.9, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 29.3, 25.8, 22.7, 14.1; HRMS *m/z* calcd for $C_{20}H_{33}NO$, 303.2562; found 303.2570.

N–Benzyl–2–cyclohexylacetamide (6p).



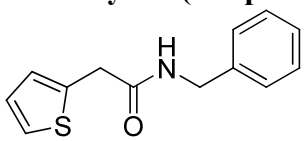
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated compound was obtained as a white solid in 93% yield (214.8 mg); m.p. 132–134 °C; IR (solid): ν 3276, 3065, 2923, 1639, 1450, 1265, 738 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.37 – 7.30 (m, 2H), 7.30 – 7.24 (m, 3H), 5.70 (brs, 1H), 4.44 (d, 2H, *J* = 5.7 Hz), 2.07 (d, 2H, *J* = 7.1 Hz), 1.89 – 1.80 (m, 1H), 1.78 – 1.72 (m, 2H), 1.72 – 1.61 (m, 3H), 1.34 – 1.22 (m, 2H), 1.19 – 1.07 (m, 1H), 0.99 – 0.89 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.2, 138.5, 128.7, 127.8, 127.5, 44.9, 43.6, 35.4, 33.2, 26.2, 26.1; HRMS *m/z* calcd for $C_{15}H_{21}NO$, 231.1623; found 231.1624.

***N*–Benzyl–2–(furan–2–yl)acetamide (6q).**[10]



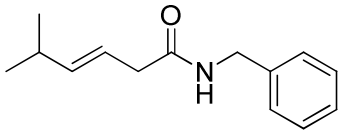
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated compound was obtained as an off–white solid in 83% yield (178.2 mg); m.p. 88–89 °C; IR (solid): ν 3279, 3069, 3028, 2934, 2885, 1645, 1545, 1247, 1073, 1007, 727 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.36 (dd, 1H, *J* = 1.8, 0.6 Hz), 7.33 – 7.28 (m, 2H), 7.28 – 7.23 (m, 1H) 7.23 – 7.16 (m, 2H), 6.33 (dd, 1H, *J* = 3.0, 1.9 Hz), 6.22 (dd, 1H, *J* = 3.0, 0.5 Hz), 6.10 (brs, 1H), 4.42 (d, 2H, *J* = 5.8 Hz), 3.64 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.4, 148.6, 142.4, 138.0, 128.6, 127.4, 127.4, 110.7, 108.5, 43.5, 36.2; HRMS *m/z* calcd for $C_{13}H_{13}NO_2$, 215.0946; found 215.0950.

***N*–Benzyl–2–(thiophen–2–yl)acetamide (6r).**



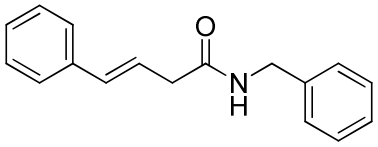
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated compound was obtained as an off–white solid in 92% yield (212.8 mg); m.p. 102–103 °C; IR (solid): ν 3268, 3073, 3024, 2919, 1645, 1550, 1410, 1352, 1254, 1025, 840, 731 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.36 – 7.27 (m, 2H), 7.27 – 7.18 (m, 4H), 6.96 (dd, 1H, *J* = 5.1, 3.5 Hz), 6.92 (dd, 1H, *J* = 3.5, 0.9 Hz), 6.06 (brs, 1H), 4.41 (d, 2H, *J* = 5.8 Hz), 3.80 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.7, 137.9, 136.0, 128.6, 127.5, 127.4, 127.4, 127.3, 125.6, 43.6, 37.5; HRMS *m/z* calcd for $C_{13}H_{13}NOS$, 231.0718; found 231.0727.

(*E*)–*N*–Benzyl–5–methylhex–3–enamide (6s).



The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated product was obtained as a grey solid in 96% yield (208.6 mg); m.p. 36–37 °C; IR (solid): ν 3298, 3069, 3034, 2958, 2930, 2868, 1638, 1545, 1456, 1323, 1246, 1026, 968, 732 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.35 – 7.30 (m, 2H), 7.29 – 7.23 (m, 3H), 5.96 (brs, 1H), 5.59 (dd, 1H, *J* = 15.4, 6.7 Hz), 5.53 – 5.46 (m, 1H), 4.43 (d, 2H, *J* = 5.7 Hz), 2.97 (d, 2H, *J* = 6.7 Hz), 2.31 (dq, 1H, *J* = 13.4, 6.7 Hz), 0.98 (d, 6H, *J* = 6.7 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.2, 143.4, 138.3, 128.7, 127.6, 127.4, 119.6, 43.5, 40.4, 31.0, 22.2; HRMS *m/z* calcd for $C_{14}H_{19}NO$, 217.1467; found 217.1472.

(*E*)–*N*–Benzyl–4–phenylbut–3–enamide (6t).

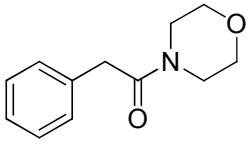


The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated product was obtained as an off–white solid in 82% yield (205.8 mg) as 9:1 isomeric ratio. Characteristic data of major compound; m.p. 113–114 °C; IR (solid): ν 3246, 3063, 3028, 2930, 2822, 1629, 1551, 1448, 1349, 1242, 1066, 1022, 963, 745 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.37 – 7.20 (m, 10H), 6.51 (d, 1H, J = 15.9 Hz), 6.29 (dt, 1H, J = 15.9, 7.2 Hz), 6.09 (brs, 1H), 4.43 (d, 2H, J = 5.8 Hz), 3.17 (dd, 2H, J = 7.2, 1.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.5, 138.0, 136.5, 134.6, 128.6, 128.5, 127.7, 127.4, 126.3, 122.3, 43.6, 40.7; HRMS *m/z* calcd for $C_{17}H_{17}NO$, 251.1310; found 251.1311.

General Procedure for the Preparation of One–Carbon Homologated Tertiary Amides (6u-6cc) from Trichloromethyl Carbinols

Diphenyldiselenide (1.3 mmol, 406 mg) was added to a dry round–bottom flask equipped with stir bar under a blanket of argon. Deoxygenated absolute ethanol (purged for 30 minutes with argon) (4 mL) was then added, followed by the rapid addition of $NaBH_4$ (2.8 mmol, 106 mg). Shortly after the addition, the initial yellow solution turned colorless, indicating complete reduction of diphenyldiselenide. The solution stirred at room temperature for 30 minutes, then neat trichloromethyl carbinol **3** (1.0 mmol) was added, followed by the additions of freshly powdered NaOH (2.5 mmol, 100 mg) and morpholine (1.1 mmol, 95.8 mg) under argon. The mixture was heated in a 55°C oil bath and allowed to react at this temperature for 24–36 hours while monitoring by TLC for consumption of starting material and 2-phenylselanylamide **14**. After completion of the reaction, as indicated by TLC, ethanol was removed by rotary evaporation and the amorphous solids were dissolved in 5 mL saturated aqueous NH_4Cl, and the solution was extracted with ethyl acetate (5 × 10 mL). The combined organic layers were dried with anhydrous sodium sulfate and concentrated by rotary evaporation. The crude material was purified by flash chromatography through a small plug of silica using the specified eluent, affording the corresponding pure tertiary amide.

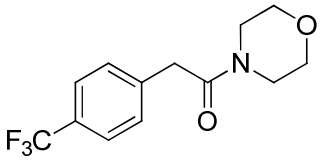
1–Morpholino–2–phenylethanone (6u).[11]



The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated compound was obtained as an off–white solid in 88% yield (180.1 mg); m.p. 62–63 °C; IR (solid): ν 3028, 2961, 2896, 2850, 1642, 1433, 1272, 1227, 1111, 1033, 960, 848, 733 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.36 – 7.29 (m, 2H), 7.28 – 7.21 (m,

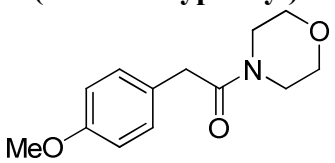
3H), 3.73 (s, 2H), 3.64 (s, 4H), 3.51 – 3.38 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.5, 134.7, 128.7, 128.4, 126.8, 66.7, 66.3, 46.4, 42.0, 40.7; HRMS *m/z* calcd for $C_{12}H_{15}NO_2$, 205.1103; found 205.1099.

1–Morpholino–2–(4–(trifluoromethyl)phenyl)ethanone (6v).[12]



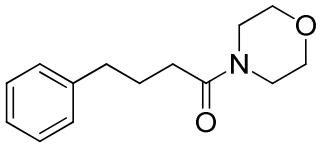
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated compound was obtained as a yellow oil in 88% yield (240.5 mg); IR (film): ν 2916, 2248, 1644, 1461, 1327, 1117, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz): δ 7.59 (d, 2H, *J* = 8.0 Hz), 7.36 (d, 2H, *J* = 8.0 Hz), 3.77 (s, 2H), 3.70 – 3.62 (m, 4H), 3.59 – 3.53 (m, 2H), 3.49 – 3.42 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.7, 138.9, 129.4 (q, *J* = 32.5 Hz), 129.2, 125.7 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.4 Hz), 66.8, 66.4, 46.5, 42.2, 40.2; ^{19}F ($CDCl_3$, 360 MHz): δ –62.5; HRMS *m/z* calcd for $C_{13}H_{14}F_3NO_2$, 273.0977; found 273.0977.

2–(4–Methoxyphenyl)–1–morpholinoethanone (6w).



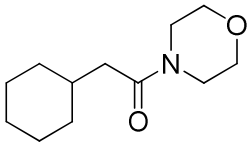
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated compound was obtained as a colorless oil in 81% yield (190.6 mg); IR (film): ν 2964, 2911, 2857, 1634, 1513, 1459, 1362, 1247, 1178, 1114, 1035, 964, 787, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.15 (d, 2H, *J* = 8.8 Hz), 6.86 (d, 2H, *J* = 8.8 Hz), 3.79 (s, 3H) 3.66 (s, 2H), 3.63 (s, 4H), 3.49 – 3.44 (m, 2H), 3.44 – 3.35 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): 169.9, 158.4, 129.5, 126.7, 114.1, 66.7, 66.4, 55.2, 46.4, 42.0, 39.8; HRMS *m/z* calcd for $C_{13}H_{17}NO_3$, 235.1208; found 235.1217.

1–Morpholino–4–phenylbutan–1–one (6x).



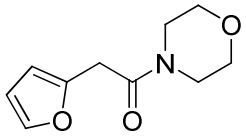
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated compound was obtained as a colorless oil in 84% yield (196.7 mg); IR (film): ν 3024, 2962, 2922, 2857, 1642, 1436, 1361, 1237, 1116, 1068, 745 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30 – 7.25 (m, 2H), 7.20 – 7.16 (m, 3H), 3.67 – 3.56 (m, 6H), 3.35 (t, 2H, *J* = 4.8 Hz), 2.67 (t, 2H, *J* = 7.4 Hz), 2.28 (t, 2H, *J* = 7.4 Hz), 2.02 – 1.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.3, 141.5, 128.4, 128.3, 125.8, 66.8, 66.5, 45.8, 41.8, 35.1, 32.0, 26.4; HRMS *m/z* calcd for $C_{14}H_{19}NO_2$, 233.116; found 233.118.

2–Cyclohexyl–1–morpholinoethanone (6y).



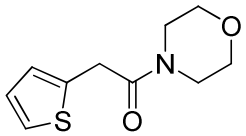
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated compound was obtained as a white solid in 95% yield (200.7 mg); m.p. 64–65 °C; IR (solid): ν 2920, 2849, 1632, 1427, 1274, 1229, 1112, 1032, 973, 898, 795, 736 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 3.62 – 3.52 (m, 6H), 3.41 (d, 2H, *J* = 4.1 Hz), 2.21 (t, 2H, *J* = 6.4 Hz), 1.78 – 1.55 (m, 6H), 1.28 – 1.16 (m, 2H), 1.13 – 1.02 (m, 1H), 0.96 (q, 2H, *J* = 11.8 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.9, 66.8, 66.6, 46.2, 41.7, 40.3, 34.9, 33.2, 26.1, 26.0; HRMS *m/z* calcd for $C_{12}H_{21}NO_2$, 211.1572; found 211.1579.

2–(Furan–2–yl)–1–morpholinoethanone (6z).



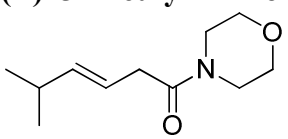
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 3:7 hexanes/EtOAc as the eluent. The indicated compound was obtained as a light yellow oil in 75% yield (146.6 mg); IR (film): ν 3031, 2924, 2858, 1655, 1547, 1245, 1014, 907, 735 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz): δ 7.35 (dd, 1H, *J* = 1.8, 0.7 Hz), 6.33 (dd, 1H, *J* = 3.1, 1.8 Hz)), 6.19 (dd, 1H, *J* = 3.1, 0.7 Hz)), 3.77 (s, 2H), 3.67 – 3.62 (m, 4H), 3.61 (t, 2H, *J* = 5.0 Hz), 3.53 (t, 2H, *J* = 5.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.2, 148.5, 141.8, 110.6, 107.6, 66.7, 66.6, 46.6, 42.3, 33.9; HRMS *m/z* calcd for $C_{10}H_{13}NO_3$, 195.0895; found 195.0903.

1–Morpholino–2–(thiophen–2–yl)ethanone (6aa).



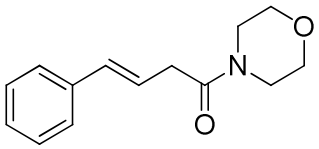
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated compound was obtained as an off–white solid in 91% yield (192.5 mg); m.p. 59–60 °C; IR (solid): ν 2961, 2896, 2853, 1641, 1438, 1270, 1227, 1110, 1066, 1030, 957, 784 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.20 (dd, 1H, *J* = 5.1, 1.0 Hz), 6.95 (dd, 1H, *J* = 5.1, 3.5 Hz), 6.89 (dd, 1H, *J* = 2.2, 1.0 Hz), 3.88 (s, 2H), 3.65 (s, 4H), 3.56 (t, 2H, *J* = 4.7 Hz), 3.49 (t, 2H, *J* = 4.7 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.4, 136.2, 126.8, 125.9, 124.7, 66.6, 66.3, 46.5, 42.2, 34.8; HRMS *m/z* calcd for $C_{10}H_{13}NO_2S$, 211.0667; found 211.0659.

(*E*)–5–Methyl–1–morpholinohex–3–en–1–one (6bb).



The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated compound was obtained as a colorless oil in 82% yield (161.4 mg); IR (flim): ν 2959, 2863, 1645, 1433, 1272, 1116 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.51 – 5.47 (m, 2H), 3.68 – 3.63 (m, 4H), 3.61 (t, 2H, *J* = 4.7 Hz), 3.45 (t, 2H, *J* = 4.7 Hz), 3.07 (d, 2H, *J* = 4.7 Hz), 2.34 – 2.26 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.2, 141.2, 119.6, 66.9, 66.7, 46.2, 41.9, 37.6, 31.1, 22.3; HRMS *m/z* calcd for $C_{11}H_{19}NO_2$, 197.1416; found 197.1414.

(*E*)–1–Morpholino–4–phenylbut–3–en–1–one (6cc).

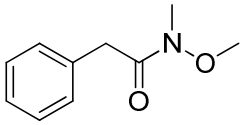


The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated compound was obtained as a white solid in 78% yield (180.1 mg); m.p.: 92–93 °C; IR (solid): ν 3443, 2856, 1636, 1437, 1115 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.39 – 7.19 (m, 5H), 6.48 (d, 1H, *J* = 16.0 Hz), 6.32 (dt, 1H, *J* = 16.0, 6.6 Hz), 3.72 – 3.62 (m, 6H), 3.54 – 3.48 (m, 2H), 3.30 (dd, 2H, *J* = 6.6, 1.4 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.5, 136.8, 133.0, 128.5, 127.5, 126.2, 122.7, 66.9, 66.6, 46.3, 42.1, 37.7; HRMS *m/z* calcd for $C_{14}H_{17}NO_2$, 231.1259; found 231.1259.

General Procedure for the Preparation of One–Carbon Homologated Weinreb Amide Derivatives (7a-7e) from Trichloromethyl Carbinols

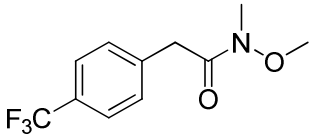
Diphenyldiselenide (1.3 mmol, 406 mg) was added to a dry round–bottom flask equipped with stir bar under a blanket of argon. Deoxygenated absolute ethanol (purged for 30 minutes with argon) (4 mL) was then added, followed by the rapid addition of $NaBH_4$ (2.8 mmol, 106 mg). Shortly after the addition, the initial yellow solution turned colorless, indicating complete reduction of diphenyldiselenide. The solution stirred at room temperature for 30 minutes, then neat trichloromethyl carbinol **3** (1.0 mmol) was added, followed by the additions of freshly powdered NaOH (3.3 mmol, 132 mg) and *N*,*O*–dimethylhydroxylamine hydrochloride (1.1 mmol, 107.3 mg) under argon. The mixture was heated in a 55 °C oil bath and allowed to react at this temperature for 20-24 hours while monitoring by TLC for consumption of starting material and 2-phenylselanylamide **14**. After completion of the reaction, as indicated by TLC, ethanol was removed by rotary evaporation and the amorphous solids were dissolved in 5 mL saturated aqueous NH_4Cl, and the solution was extracted with ethyl acetate (5 × 10 mL). The combined organic layers were dried with anhydrous sodium sulfate and concentrated by rotary evaporation. The crude material was purified by flash chromatography through a small plug of silica using the specified eluent, affording the corresponding pure Weinreb amide derivative.

***N*–Methoxy–*N*–methyl–2–phenylacetamide (7a).[13]**



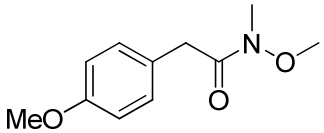
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 1:9 hexanes/EtOAc as the eluent. The indicated compound was obtained as a colorless oil in 83% yield (148.7 mg); IR (film): ν 3031, 2938, 2856, 1644, 1456, 1383, 1292, 1175, 1103, 1004, 934, 776 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.34 – 7.25 (m, 4H), 7.25 – 7.20 (m, 1H), 3.76 (s, 2H), 3.58 (s, 3H), 3.18 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.3, 134.9, 129.2, 128.4, 126.6, 61.1, 39.3, 32.1; HRMS *m/z* calcd for $C_{10}H_{13}NO_2$, 179.0946; found 179.0942.

_N_–Methoxy–_N_–methyl–2–(4–(trifluoromethyl)phenyl)acetamide (7b).



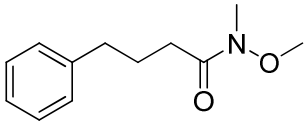
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 1:9 hexanes/EtOAc as the eluent. The indicated compound was obtained as a white solid in 89% yield (219.7 mg); m.p. 34–35 °C; IR (solid): ν 2974, 3944, 2833, 1661, 1414, 1382, 1322, 1109, 1062, 867, 822, 793, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.57 (d, 2H, J = 8.0 Hz), 7.41 (d, 2H, J = 8.0 Hz), 3.82 (s, 2H), 3.65 (s, 3H), 3.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.4, 139.0, 129.7, 129.2 (q, J = 32.5 Hz), 125.3 (q, J = 3.7 Hz), 123.1 (q, J = 264.3 Hz), 61.3, 39.0, 32.3; ^{19}F ($CDCl_3$, 360 MHz): δ –62.5; HRMS *m/z* calcd for $C_{11}H_{12}F_3NO_2$, 247.0820; found 247.0822.

_N_–Methoxy–2–(4–methoxyphenyl)–_N_–methylacetamide (7c).



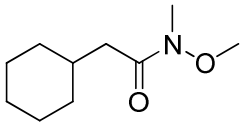
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 1:9 hexanes/EtOAc as the eluent. The indicated compound was obtained as a colorless oil in 76% yield (159.3 mg); IR (film): ν 2970, 2941, 2838, 1648, 1513, 1437, 1384, 1297, 1248, 1177, 1031, 787 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.21 (d, 2H, J = 8.7 Hz), 6.85 (d, 2H, J = 8.7 Hz), 3.78 (s, 3H), 3.70 (s, 2H), 3.61 (s, 3H), 3.18 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.7, 158.4, 130.2, 126.9, 113.9, 61.2, 55.2, 38.4, 32.2; HRMS *m/z* calcd for $C_{11}H_{15}NO_3$, 209.1052; found 209.1053.

_N_–Methoxy–_N_–methyl–4–phenylbutanamide (7d).



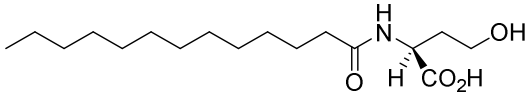
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 1:9 hexanes/EtOAc as the eluent. The indicated compound was obtained as a colorless oil in 87% yield (180.3 mg); IR (film): ν 3027, 2938, 2866, 1637, 1189, 746 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz): δ 7.31 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 3.62 (s, 3H), 3.17 (s, 3H), 2.68 (t, 2H, J = 7.5 Hz), 2.42 (t, 2H, J = 7.5 Hz), 2.02 – 1.93 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.4, 141.8, 128.5, 128.3, 125.8, 61.1, 35.3, 32.2, 31.2, 26.0; HRMS *m/z* calcd for $C_{12}H_{17}NO_2$, 207.1259; found 207.1265.

2–Cyclohexyl–*N*–methoxy–*N*–methylacetamide (7e).



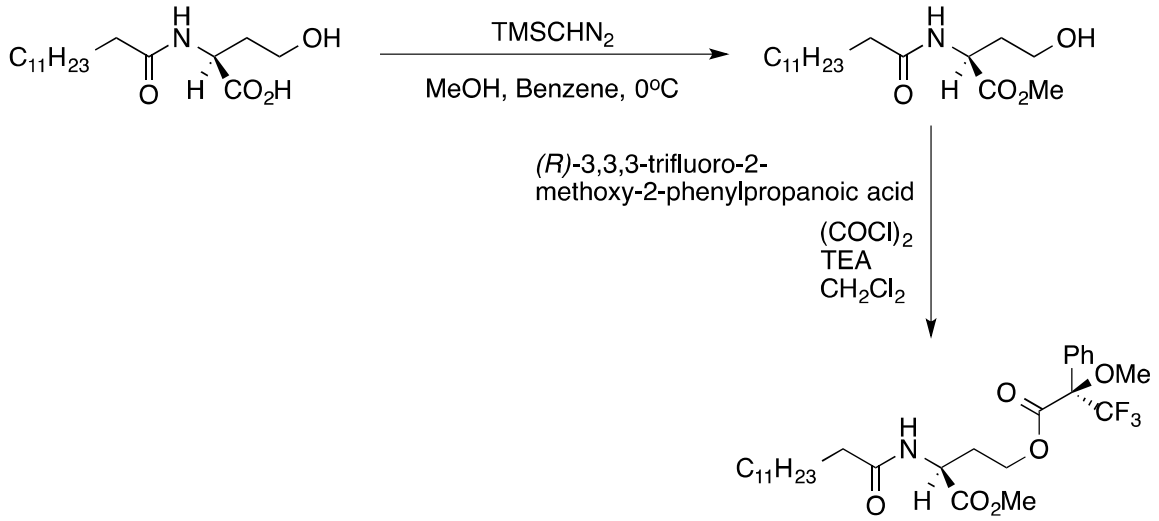
The crude material was purified by flash chromatography through a plug of silica gel, using hexane to remove diphenyldiselenide then 1:9 hexanes/EtOAc as the eluent. The indicated compound was obtained as a colorless oil in 75% yield (139.1 mg); IR (film): ν 2980, 2928, 2855, 1652, 1375, 1243, 1046 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz): δ 3.64 (s, 3H), 3.14 (s, 3H), 2.26 (d, 2H, J = 6.6 Hz), 1.84 – 1.71 (m, 1H), 1.70 – 1.53 (m, 5H), 1.32 – 1.06 (m, 3H), 1.00 – 0.85 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.0, 61.1, 39.3, 34.4, 33.3, 26.2, 26.1, 26.0; HRMS *m/z* calcd for $C_{10}H_{19}NO_2$, 185.1416; found 185.1416.

Preparation of *N*–Tridecanoyl–L–homoserine (9) from L–homoserine.

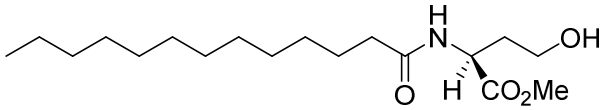


Diphenyldiselenide (1.3 mmol, 406 mg) was added to a dry round–bottom flask equipped with stir bar under a blanket of argon. Deoxygenated absolute ethanol (purged for 30 minutes with argon) (4 mL) was then added, followed by the rapid addition of $NaBH_4$ (2.8 mmol, 106 mg). Shortly after the addition, the initial yellow solution turned colorless, indicating complete reduction of diphenyldiselenide. The solution stirred at room temperature for 30 minutes, then neat trichloromethyl carbinol **3** (1.0 mmol) was added, followed by the additions of freshly powdered NaOH (3.3 mmol, 132 mg) and L–homoserine (1.1 mmol, 131 mg) under argon. The mixture was heated in a 55 °C oil bath and allowed to react at this temperature for 36 hours while monitoring by TLC for consumption of starting material and 2-phenylselanylamide **14**. After completion of the reaction, as indicated by TLC, ethanol was removed by rotary evaporation and the amorphous solids were dissolved in 5 mL ethyl acetate and 5 mL H_2O. The resulting solution was cooled to 0 °C and adjusted to pH 1 with 1 N HCl. The product was extracted with ethyl acetate (5 × 10 mL), dried with anhydrous sodium sulfate, and then concentrated by rotary evaporation. The crude material was purified by flash chromatography through a plug of silica gel, using 1:9 EtOAc/hexane to remove diphenyldiselenide then 95:5 EtOAc/MeOH as the eluent. The indicated product was obtained as a white solid in 89% yield (280.7 mg); m.p. 103–104 °C; $[\alpha]_D^{21} = -23.1^o$ cm^3 g^{-1} dm^{-1} (c = 1.0 in CH_3OH); IR (solid): ν 3394, 3310, 2915, 2850, 1701, 1650, 1539, 1290 cm^{-1}; ^1H NMR (DMSO d_6, 500 MHz): δ 12.40 (brs, 1H), 7.96 (d, 1H, J = 7.6 Hz), 4.25 (ddd, 1H, J = 12.3, 9.1, 4.4 Hz), 3.48 – 3.36 (m, 2H), 2.09 (t, 2H, J = 7.5 Hz), 1.89 – 1.80 (m, 1H), 1.74 – 1.64 (m, 1H), 1.47 (t, 2H, J = 6.2 Hz), 1.29 – 1.21 (m, 19H), 0.86 (t, 3H, J = 6.8 Hz); ^{13}C NMR (DMSO d_6, 125 MHz): δ 174.0, 172.4, 57.3, 49.0, 35.0, 34.1, 31.3, 29.0, 29.0, 29.0, 29.0, 28.8, 28.7, 28.6, 25.2, 22.1, 13.9; HRMS *m/z* calcd for $C_{17}H_{31}NO_3$, 297.2304; found 297.2302 which corresponds to [M–H_2O].

Scheme 1. Conversion of **9** to the corresponding methyl ester and subsequently the Mosher's ester derivative.



General Procedure for the Formation of Methyl Ester of 9



To a chilled stirred solution of **9** (0.16 mmol, 50 mg) in 0.30 mL methanol and 1.1 mL benzene was added $TMSCHN_2$ (0.19 mmol, 95 μL) at 0 °C. The ice bath was removed, and the mixture was stirred at rt for 5 min. At that point, the reaction was complete, as indicated by TLC, and the solvents were removed by rotary evaporation. The crude reaction mixture was purified by flash chromatography through a plug of pyridine-saturated silica gel, using 1:1 EtOAc/hexane as the eluent. The methyl ester was obtained as a white solid in 75% yield (39 mg); m.p. 71–72 °C; $[\alpha]_D^{20} = +3.63^o$ cm^3 g^{-1} dm^{-1} (*c* = 1.1 in CH_2Cl_2); IR (solid): ν 3419, 3314, 2915, 2848, 1730, 1647, 1539, 1216 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.34 (d, 1H, *J* = 7.5 Hz), 4.76 (ddd, 1H, *J* = 11.0, 7.7, 3.7 Hz), 3.78 (s, 3H), 3.69 (s, 1H), 3.62 – 3.46 (m, 2H), 2.35 – 2.22 (m, 2H), 2.22 – 2.14 (m, 1H), 1.68 – 1.55 (m, 4H), 1.31 – 1.22 (m, 19H), 0.88 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.3, 173.3, 58.1, 52.6, 49.4, 36.5, 36.1, 31.9, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 29.2, 25.6, 22.7, 14.1; HRMS *m/z* calcd for $C_{18}H_{35}NO_4$, 329.2566; found 329.2567.

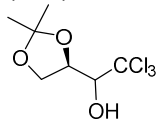
General Procedure for the Mosher's Ester Formation from the Methyl Ester of 9.[18]

Dry benzene (2 mL) was added to a round bottom flask containing 40 mg (0.17 mmol) of *(R)*-3,3,3-trifluoro-2-methoxy-2-phenylpropanoic acid. This solution was then concentrated under reduced pressure. To the dried residue was added CH_2Cl_2 (1 mL), 19 μL (0.22 mmol) of oxalyl chloride and 2 μL (0.026 mmol) of anhydrous *N*,*N*-dimethylformamide. This solution was stirred under argon at rt for 20 minutes, then transferred to an ice bath and stirred for 10 minutes. The solution was stirred under reduced pressure at 0 °C for 30 minutes to remove the volatile components. To the residue was added CH_2Cl_2 (1 mL), and this clear solution was cannulated into another round bottom flask containing the methyl ester from **9** (0.05 mmol), 40 μL (0.28 mmol) of triethylamine, and 2 mg (0.016 mmol) of DMAP in CH_2Cl_2 (0.5 mL) at 0 °C. The ice bath was then removed, and the reaction progress was monitored by TLC analysis. When

the starting material was consumed, the reaction mixture was diluted with CH_2Cl_2, then washed successively with sat. NH_4Cl (2 x 10 mL), sat. $NaHCO_3$ (2 x 10 mL), and H_2O (10 mL). The organic layer was dried with anhydrous sodium sulfate and then concentrated under reduced pressure. The crude material was purified by flash chromatography through a plug of silica gel using 2:8 EtOAc/hexane as the eluent to afford the desired Mosher's ester as a white solid in 92% yield (25 mg). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53 – 7.49 (m, 2H), 7.44 – 7.40 (m, 3H), 6.03 (d, 1H, *J* = 7.7 Hz), 4.73 – 4.67 (m, 1H), 4.41 – 4.30 (m, 2H), 3.72 (s, 3H), 3.54 (d, 3H, *J* = 0.9 Hz), 2.31 – 2.21 (m, 1H), 2.17 – 2.07 (m, 3H), 1.62 – 1.54 (m, 2H), 1.32 – 1.21 (m, 18H), 0.88 (t, 3H, *J* = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.1, 171.9, 166.4, 132.0, 129.8, 128.5, 127.4, 123.1 (q, *J* = 288 Hz), 84.7 (q, *J* = 27.6 Hz), 63.0, 55.5, 52.6, 49.7, 36.4, 31.9, 30.9, 29.6, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 29.2, 25.5, 22.7, 14.1; ^{19}F ($CDCl_3$, 360 MHz): δ –71.49.

No racemization was indicated in the NMR spectra of the corresponding Mosher derivative; see spectra on pages S64–S65.

Preparation of (*R*)–2,2,2–trichloro–1–((*R*)–2,2–dimethyl–1,3–dioxolan–4–yl)ethanol (12a) and its (*R*,*S*)–diastereomer (12b):



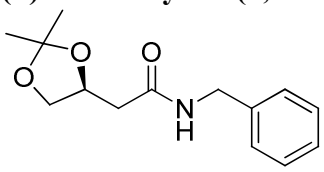
(*R*)–Isopropylidine–D–mannitol was purchased from Sigma–Aldrich and used without further purification. (*R*)–2,2–dimethyl–1,3–dioxolane–4–carbaldehyde **10** was prepared according to procedures reported by Schmid and Bryant.[14]

To a 0 °C solution of sodium trichloroacetate (245 mg, 1.5 mmol) and trichloroacetic acid (278 mg, 1.5 mmol) in 2 mL of DMF was added **10** (130 mg, 1.0 mmol) dissolved in 1 mL of DMF. After stirring for 15 min., the mixture was warmed to room temperature then stirred rapidly for 12 hours while monitoring by TLC for consumption of starting material. After judged complete, the mixture was diluted with 5 mL of EtOAc and washed with saturated aqueous $NaHCO_3$. Precipitated solids were filtered and rinsed three times with EtOAc. The combined organic phase was dried with sodium sulfate, and the EtOAc was evaporated under reduced pressure. The crude material was purified by flash chromatography through a plug of silica gel, using 9:1 hexanes/EtOAc as eluent. The (*R*,*R*)–isomer was obtained as a white solid in 45% yield (112 mg), and the (*R*,*S*)–diastereomer was obtained as a colorless oil in 23% yield (57 mg). The physical and analytical data for both isomers were identical to that previously reported.[15] (*R*)–2,2,2–Trichloro–1–((*R*)–2,2–dimethyl–1,3–dioxolan–4–yl)ethanol (**12a**): m.p. 81–82 °C, (lit m.p. 82–83 °C)[4]; $[\alpha]_D^{20}$ = +21.3 $cm^3\ g^{-1}\ dm^{-1}$ (*c* = 3.8 g cm^{-3} in $CHCl_3$); IR (solid): ν 3371, 2985, 1375, 1150, 1042 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.62 – 4.56 (m, 1H), 4.36 (dd, 1H, *J* = 4.0, 3.5 Hz), 4.27 (dd, 1H, *J* = 8.7, 6.3 Hz), 4.09 (dd, 1H, *J* = 8.7, 6.3 Hz), 3.10 (dd, 1H, *J* = 4.0, 3.5 Hz), 1.48 (s, 3H), 1.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 109.2, 100.6, 82.4, 75.1, 64.7, 26.3, 25.3; HRMS *m/z* calcd for $C_6H_8Cl_3O$, 232.2539; found 232.9546 which corresponds to $[M–CH_3]^+$.

(*S*)–2,2,2–Trichloro–1–((*R*)–2,2–dimethyl–1,3–dioxolan–4–yl)ethanol (**12b**): $[\alpha]_D^{20}$ = +10.5 $cm^3\ g^{-1}\ dm^{-1}$ (*c* = 2.0 in $CHCl_3$); IR (film): ν 3446, 2987, 2934, 1374, 1025 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.57 (ddd, *J* = 2.5, 6.5, 6.5 Hz, 1H), 4.25 (dd, *J* = 6.5, 8.5 Hz,

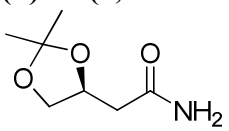
1H), 3.98 (dd, J = 2.5, 8.5 Hz, 1H), 3.91 (dd, J = 7, 8.5 Hz, 1H), 3.72 (d, J = 8.5 Hz, 1H), 1.49 (s, 3H), 1.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 110.9, 101.3, 81.1, 73.2, 68.4, 26.1, 25.7; HRMS *m/z* calcd for $C_7H_{11}Cl_3O_3$, 246.9696; found 246.9701.

(*S*)–*N*–Benzyl–2–(2,2–dimethyl–1,3–dioxolan–4–yl)acetamide (13a).



Diphenyldiselenide (1.3 mmol, 406 mg) was added to a dry round–bottom flask equipped with stir bar under a blanket of argon. Deoxygenated absolute ethanol (purged for 30 minutes with argon) (4 mL) was then added, followed by the rapid addition of $NaBH_4$ (2.8 mmol, 106 mg). Shortly after the addition, the initial yellow solution turned colorless, indicating complete reduction of diphenyldiselenide. The solution stirred at room temperature for 30 minutes, then a mixture of diastereomers **12a** and **12b** (1 mmol) was added, followed by the additions of freshly powdered NaOH (2.5 mmol, 100 mg) and benzylamine (1.1 mmol, 118 mg) under argon. The mixture was heated in a 55°C oil bath and allowed to react at this temperature for 36 hours while monitoring by TLC for consumption of starting material and 2-phenylselanylamide **14**. After completion of the reaction, ethanol was removed by rotary evaporation and the amorphous solids were dissolved in 5 mL satd NH_4Cl and extracted with ethyl acetate (5 × 10 mL). The combined organic layers were dried with anhydrous sodium sulfate, and then concentrated by rotary evaporation. The crude material was purified by flash chromatography through a plug of pyridine-saturated silica gel, using hexane to remove diphenyldiselenide then 2:8 hexanes/EtOAc as the eluent. The indicated compound was obtained as an off–white solid in 80% yield (199.3 mg); m.p. 38–39 °C; $[\alpha]_D^{24}$ = –9.6^o cm^3 g^{-1} dm^{-1} (c = 3.3 in CH_2Cl_2); IR (solid): ν 3276, 3084, 3032, 2984, 2871, 1637, 1567, 1369, 1217, 1154 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35 – 7.30 (m, 2H), 7.29 – 7.25 (m, 3H), 6.43 (brs, 1H), 4.45 (d, 2H, J = 5.7 Hz), 4.44 – 4.40 (m, 1H), 4.12 (dd, 1H, J = 8.1, 6.1 Hz), 3.63 (dd, 1H, J = 8.1, 7.0 Hz), 2.57 – 2.46 (m, 2H), 1.38 (s, 3H), 1.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.8, 138.2, 128.6, 127.6, 127.4, 109.3, 72.5, 69.1, 43.4, 40.5, 26.8, 25.5; EIMS (*m/z*): 249.1, 234.1, 191.1, 174.1, 149.1, 119.1, 106.1, 91; HRMS *m/z* calcd for $C_{14}H_{19}NO_3$, 249.1365; found 249.1372.

(*S*)–2–(2,2–Dimethyl–1,3–dioxolan–4–yl)acetamide (13b)



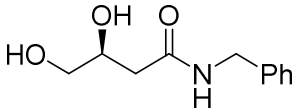
Diphenyldiselenide (1.3 mmol, 406 mg) was added to a 50 mL dry pressure tube temporarily fit with a rubber septum and equipped with a magnetic stir bar. Ammonia saturated absolute ethanol (4 mL) was added followed by the rapid addition of $NaBH_4$ (2.8 mmol, 106 mg) under argon. Shortly after the addition, the initial yellow solution turned colorless, indicating complete reduction of diphenyldiselenide. The solution stirred at room temperature for 30 minutes, then a mixture of diastereomers **12a** and **12b** (1 mmol) was added, followed by the addition of freshly powdered NaOH (2.5 mmol, 100.0 mg) under argon. The rubber septum was quickly replaced with a Teflon screw cap and the solution was heated in a 55 °C oil bath for 36 hours. After completion of the reaction as indicated by TLC, the ethanolic ammonia was removed by rotary evaporation

and the amorphous solids were dissolved in 5 mL ethyl acetate and 5 mL saturated aqueous NH_4Cl. The resulting solution was cooled to 0 °C and adjusted to pH 4 with 1 N HCl and then saturated with solid NaCl. The product was extracted with ethyl acetate (5 × 10 mL), dried with anhydrous sodium sulfate, and then concentrated by rotary evaporation. The crude material was purified by flash chromatography through a small plug of pyridine-saturated silica gel, using hexane to remove diphenyldiselenide then 95:5 EtOAc/MeOH as the eluent. The indicated compound was obtained as a white solid in 75% yield (119.4 mg); m.p. 105–106 °C, (lit[16] m.p. 106–108 °C); $[\alpha]_D^{24} = -15.0^o$ cm^3 g^{-1} dm^{-1} (*c* = 0.4 in CH_2Cl_2), (lit[5] $[\alpha]_D^{24} = -15.4^o$ cm^3 g^{-1} dm^{-1} (*c* = 1.0 in $CHCl_3$); IR (solid): ν 3364, 3192, 2993, 1640, 1252, 1156, 1061 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz): δ 6.14 (brs, 1H), 5.83 (brs, 1H), 4.46 – 4.38 (m, 1H), 4.14 (dd, 1H, *J* = 8.3, 6.1 Hz), 3.63 (dd, 1H, *J* = 8.3, 6.8 Hz), 2.55 (dd, 1H, *J* = 15.3, 7.7 Hz), 2.46 (dd, 1H, *J* = 15.3, 4.8 Hz), 1.42 (s, 3H), 1.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.5, 109.4, 72.3, 69.1, 40.1, 26.9, 25.5; HRMS *m/z* calcd for $C_6H_{10}NO_3$, 144.0661; found 144.0664 which corresponds to $[M–CH_3]^+$.

General Procedure for the Diol Deprotection of Dioxolanes 13a and 13b to Form the Corresponding 3,4–Dihydroxyamides (13aa and 13bb)

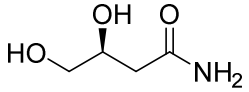
The isopropylidine was cleaved following the procedure reported by Lavallee et al.[17] Yields and reaction times are unoptimized. A solution of homologated amide **13a** or **13b** (1 mmol) in 1.1 mL of 80% AcOH in H_2O was heated to 40^{o}C (bath temperature) under argon. When the starting material was consumed, as indicated by TLC, saturated aqueous $NaHCO_3$ was *slowly* added to quench the reaction. All solvents were evaporated under reduced pressure at 45 ^{o}C, and the resulting solid was rinsed with acetone and filtered. The filtrate was concentrated to obtain the corresponding diols. No further purification was necessary. The characterization data for compounds **13aa**, **13bb** are given below.

(*S*)-*N*-benzyl-3,4-dihydroxybutanamide (13aa)



The indicated compound was obtained as a white solid in 98% yield (204.9 mg). m.p. 114–115 °C; $[\alpha]_D^{20} = -12.5^o$ cm^3 g^{-1} dm^{-1} (*c* = 1.7 in acetone); IR (solid): ν 3299, 3084, 2920, 1634, 1095, 734 cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$, 500 MHz): δ 7.66 (brs, 1H), 7.33 – 7.27 (m, 4H), 7.25 – 7.20 (m, 1H), 4.41 (d, 2H, *J* = 5.9 Hz), 4.31 (brs, 1H), 4.03 – 3.96 (m, 1H), 3.74 (brs, 1H), 3.48 (d, 2H, *J* = 5.5 Hz), 2.48 (dd, 1H, *J* = 14.8, 4.1 Hz), 2.36 (dd, 1H, *J* = 14.8, 8.2 Hz); ^{13}C NMR ($(CD_3)_2CO$, 125 MHz): δ 172.5, 140.5, 129.2, 128.3, 127.7, 70.3, 66.8, 43.4, 40.4; HRMS *m/z* calcd for $C_{11}H_{15}NO_3$, 209.1052; found 209.1061.

(*S*)-3,4-dihydroxybutanamide (13bb)



The indicated compound was obtained as a colorless oil in 42% yield (42.5 mg). $[\alpha]_D^{21} = -6.8^o$ cm^3 g^{-1} dm^{-1} (*c* = 1.07 in acetone); IR (film): ν 3369, 2925, 1666, 1409, 867 cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$, 500 MHz): δ 6.92 (brs, 1H), 6.31 (brs, 1H), 4.31 (d, 1H, *J* = 3.0 Hz), 3.98 – 3.90 (m, 1H), 3.71 – 3.64 (m, 1H), 3.46 (t, 1H, *J* = 4.8 Hz), 2.41 (dd, 1H, *J* = 15.1, 4.1 Hz), 2.29 (dd, 1H, *J* = 15.1, 8.3 Hz); ^{13}C NMR ($(CD_3)_2CO$, 125 MHz): δ 173.9,

69.2, 65.8, 38.7; HRMS *m/z* calcd for $C_4H_7NO_2$, 101.0477; found 101.0477 which corresponds to [M–H_2O]

General Procedure for the Formation of Mosher's Diesters of 13aa and 13bb.[18]

Dry benzene (2 mL) was added to a round bottom flask containing 80 mg (0.34 mmol) of *(R)*-3,3,3-trifluoro-2-methoxy-2-phenylpropanoic acid. This solution was then concentrated under reduced pressure. To the dried residue was added CH_2Cl_2 (1 mL), 40 μL (0.47 mmol) of oxalyl chloride and 4 μL (0.055 mmol) of anhydrous *N*,*N*-dimethylformamide. This solution was stirred under argon at rt for 20 minutes, then transferred to an ice bath and stirred for 10 minutes. The solution was stirred under reduced pressure at 0 ^oC for 30 minutes to remove the volatile components. To the resulting residue was added CH_2Cl_2 (1 mL), and this clear solution was cannulated into another round bottom flask containing **13aa** or **13bb** (0.05 mmol), 80 μL (0.56 mmol) of triethylamine, and 4 mg (0.032 mmol) of DMAP in CH_2Cl_2 (0.5 mL) at 0 ^oC. The ice bath was then removed and the reaction progress was monitored by TLC analysis. When the starting material was consumed, the reaction mixture was diluted with CH_2Cl_2, and washed successively with sat. NH_4Cl (2 x 10 mL), sat. $NaHCO_3$ (2 x 10 mL), and H_2O (10 mL). The organic layer was dried with anhydrous sodium sulfate and then concentrated under reduced pressure. The crude material was purified by flash chromatography through a plug of silica gel, using 2:8 EtOAc/hexane as the eluent to afford the desired Mosher's diesters as colorless oils.

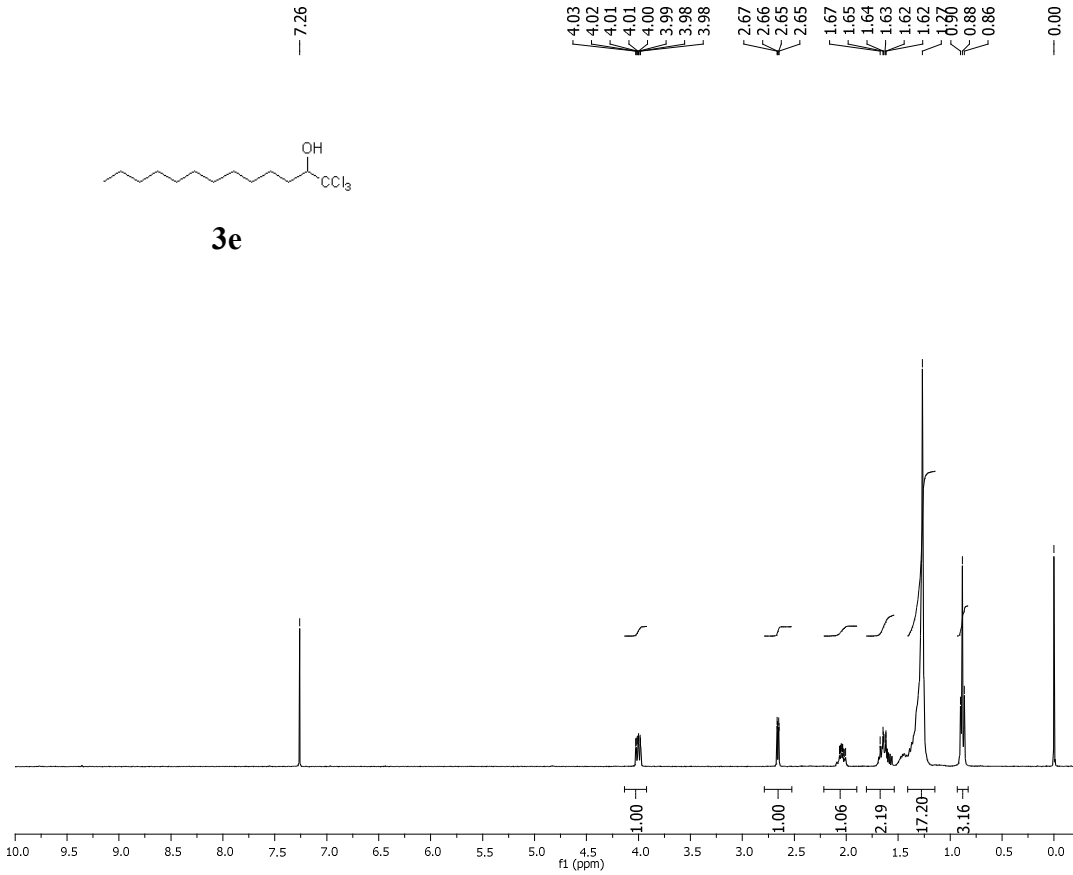
The Mosher's diester of **13aa** was obtained as a colorless oil in 91% yield (29 mg). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.55 – 7.16 (m, 15H), 5.80 – 5.74 (m, 1H), 5.62 (t, 1H, *J* = 5.0 Hz), 4.72 (dd, 1H, *J* = 12.6, 2.5 Hz), 4.43 – 4.29 (m, 3H), 3.41 (s, 3H), 3.39 (s, 3H), 2.54 (dd, 1H, *J* = 15.3, 7.4 Hz), 2.49 (dd, 1H, *J* = 15.3, 6 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.5, 166.0, 165.8, 137.5, 131.9, 131.7, 129.7, 129.7, 128.8, 128.5, 128.5, 127.9, 127.8, 127.4, 127.3, 124.3, 124.3, 122.0, 122.0, 70.8, 65.5, 55.4, 55.3, 43.8, 36.7; ^{19}F ($CDCl_3$, 360 MHz): δ –71.42, –71.58.
By means of comparison, the Mosher's diester of ***rac*-13aa** shows four peaks in its ^{19}F NMR spectrum: ^{19}F ($CDCl_3$, 360 MHz): δ –71.42, –71.47, –71.58, –71.58.

The Mosher's diester of **13bb** was obtained as a colorless oil in 85% yield (23 mg). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.53 – 7.33 (m, 10H), 5.79 – 5.72 (m, 1H), 5.27 (brs, 2H), 4.70 (dd, 1H, *J* = 12.5, 2.7 Hz), 4.40 (dd, 1H, *J* = 12.5, 3.7 Hz), 3.45 (d, 3H, *J* = 0.9 Hz), 3.40 (d, 3H, *J* = 0.9 Hz), 2.59 (dd, 1H, *J* = 15.5, 7.5 Hz), 2.51 (dd, 1H, *J* = 15.5, 5.9 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.6, 165.8, 165.6, 139.4, 131.9, 131.7, 129.7, 129.7, 128.5, 128.5, 127.4, 127.3, 124.3, 122.8, 107.7, 70.5, 65.5, 55.4, 55.4, 35.9; ^{19}F ($CDCl_3$, 360 MHz): δ –71.48, –71.55.
By means of comparison, the Mosher's diester of ***rac*-13bb** shows four peaks in its ^{19}F NMR spectrum: ^{19}F ($CDCl_3$, 360 MHz): δ –71.44, –71.48, –71.55, –71.60.

No racemization was indicated in the NMR spectra of the corresponding Mosher diester derivatives of **13aa** or **13bb**; see spectra on pages S73–S80.

References

(1) Boeckman Jr., R. K.; Shao, P.; Mullins, J. J. *Organic Syntheses;* Wiley & Sons: New York, 2004; p. 696.
(2) Corey, E. J.; Link, J. O.; Shao, Y. *Tetrahedron Lett.* **1992,** *33*, 3435.
(3) (a) Cafiero, L. R.; Snowden, T. S. *Org. Lett.* **2008,** *10*, 3853; (b) Gupta, M. K.; Li, Z.; Snowden, T. S. *J. Org. Chem.* **2012,** *77*, 4854.
(4) Bonne, D.; Dekhane, M.; Zhu, J. *J. Am. Chem. Soc.* **2005,** *127*, 6926.
(5) Salaun, A.; Favre, A.; Le Grel, B.; Potel, M.; Le Grel, P. *J. Org. Chem.* **2006,** *71*, 150.
(6) Chen, Z.–W.; Jiang, H.–F.; Pan, X.–Y.; He, Z.–J. *Tetrahedron* **2011,** *67*, 5920.
(7) Ghosh, S. C.; Hong, S. H. *Eur. J. Org. Chem.* **2010,** *22*, 4266.
(8) Maki, T.; Ishihara, K.; Yamamoto, H. *Org. Lett.* **2006,** *8*, 1431.
(9) Sudrik, S. G.; Chavan, S. P.; Chandrakumar, R. S.; Pal, S.; Date, S. K.; Chavan, S. P.; Sonawane, H. R. *J. Org. Chem.* **2002,** *67*, 1574.
(10) Arjona, O.; Csaky, A. G.; Murcia, M. C.; Plumet, J. *Helv. Chim. Acta.* **2001,** *84*, 3667.
(11) Motoyama, Y.; Aoki, M.; Takaoka, N.; Aoto, R.; Nagashima, H. *Chem. Commun.* **2009,** 1574.
(12) Hama, T.; Culkin, D. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006,** *128*, 4976.
(13) Mordant, C. *Tetrahedron* **2007,** *63,* 6115.
(14) Schmid, C. R.; Bryant, J. D. *Organic Syntheses Coll. Vol. 9*, **1998**, 450.
(15) Oliver, J. E.; Schmidt, W. F. *Tetrahedron: Asymmetry* **1998,** *9,* 1723.
(16) Wang, G.; Hollingsworth, R. I. *J. Org. Chem.* **1999,** *64*, 1036.
(17) Lavallee, P.; Ruel, R.; Grenier, L.; Bissonnette, M. *Tetrahedron Lett.* **1986,** *27*, 679.
(18) For preparation of Mosher ester derivatives, see: Myers, A. G.; Bryant, H. Y.; Chen, H. *Organic Syntheses*; Wiley & Sons: New York, 2004; p. 509.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1.67
1.65
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1.62
1.62
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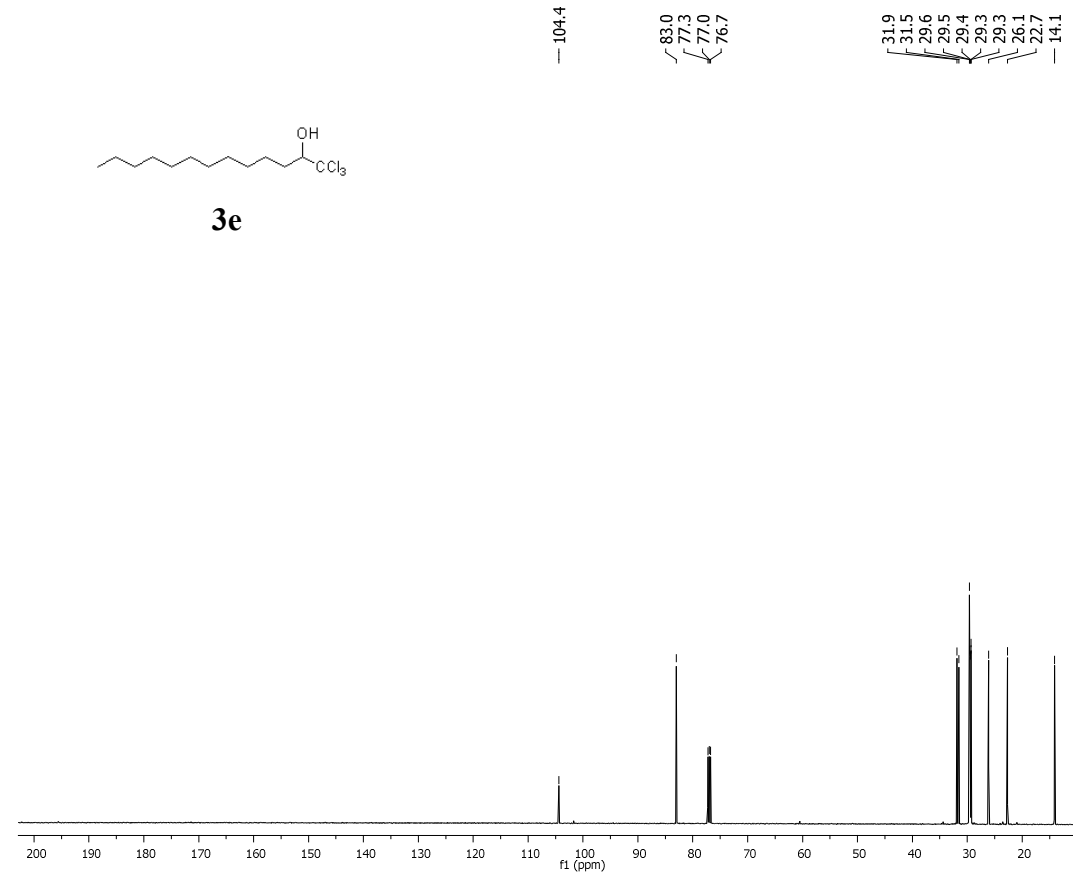
f1 (ppm)

3e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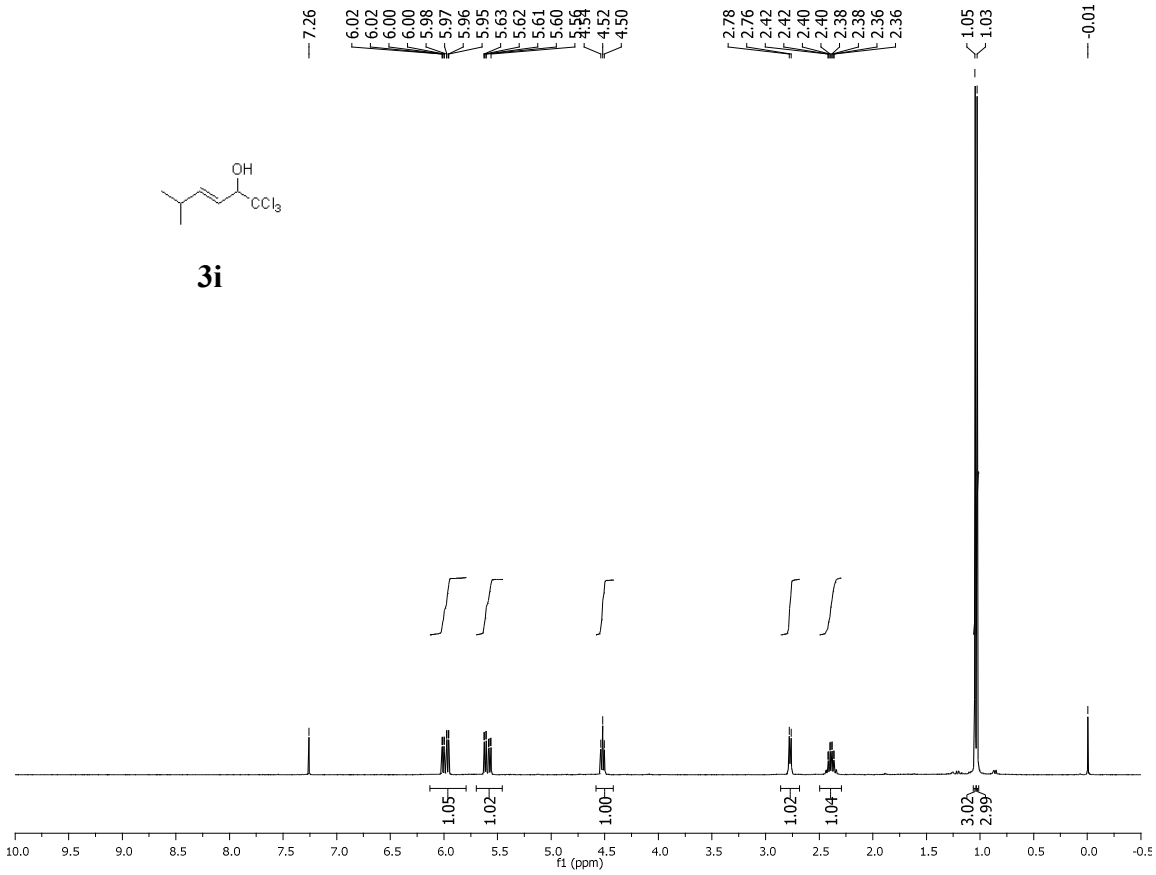
14.1
OH
CCl3
f1 (ppm)

3e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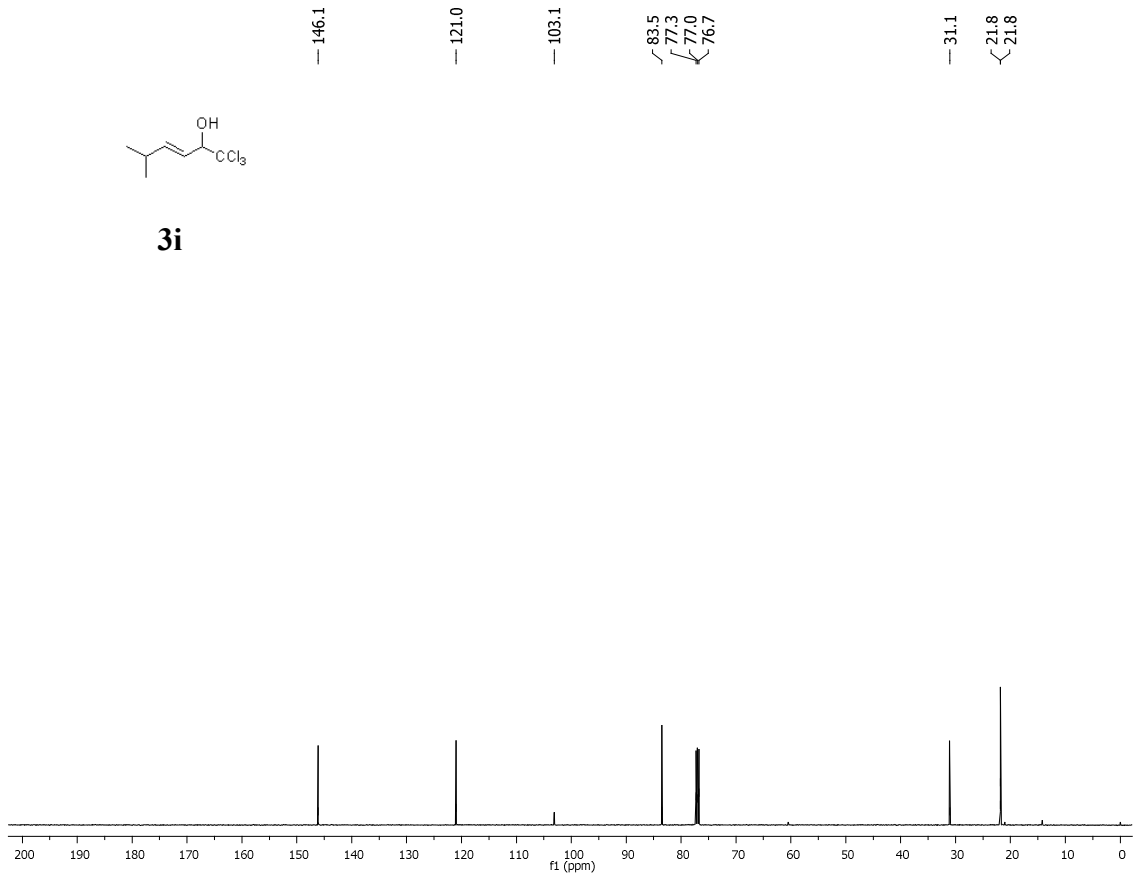
f1 (ppm)

3i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OH
CCl3
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3i


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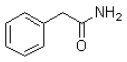
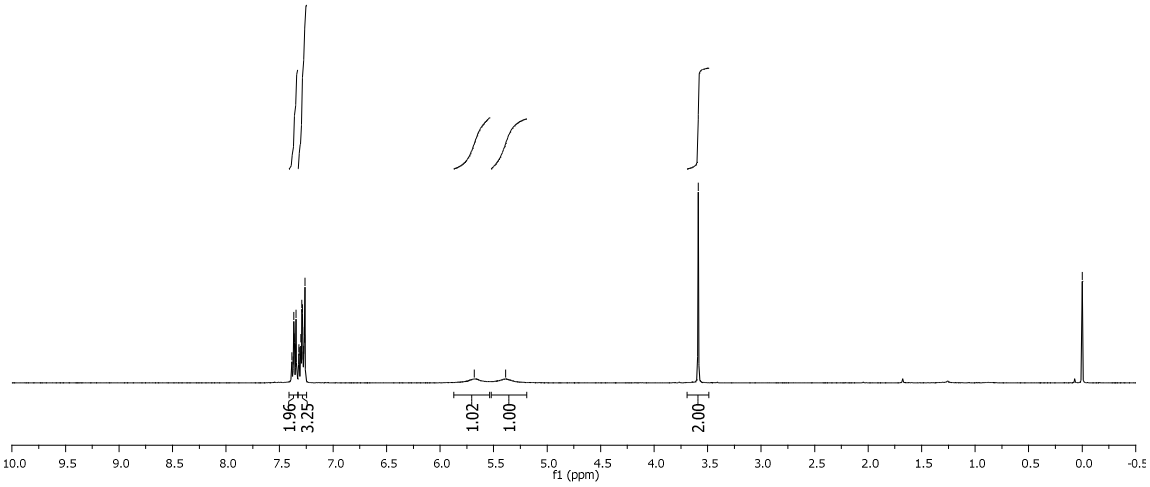

NH2
O

6a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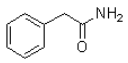
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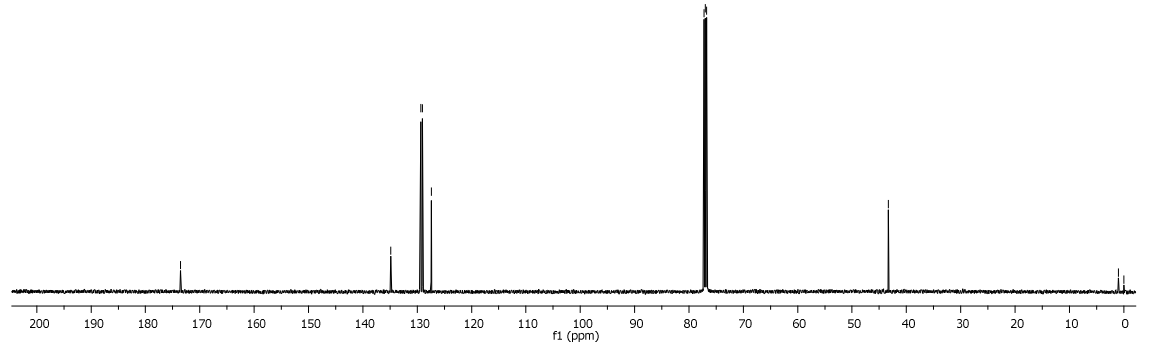
O

6a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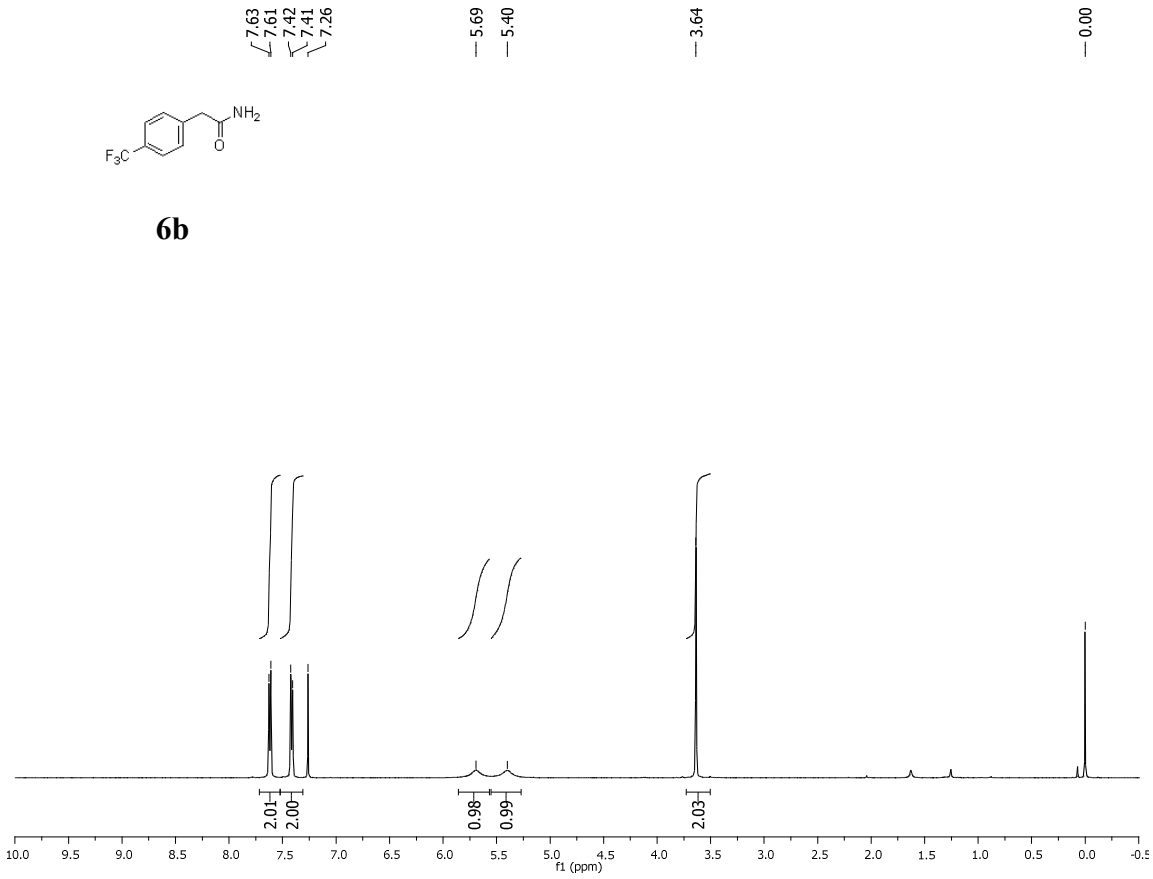
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f1 (ppm)

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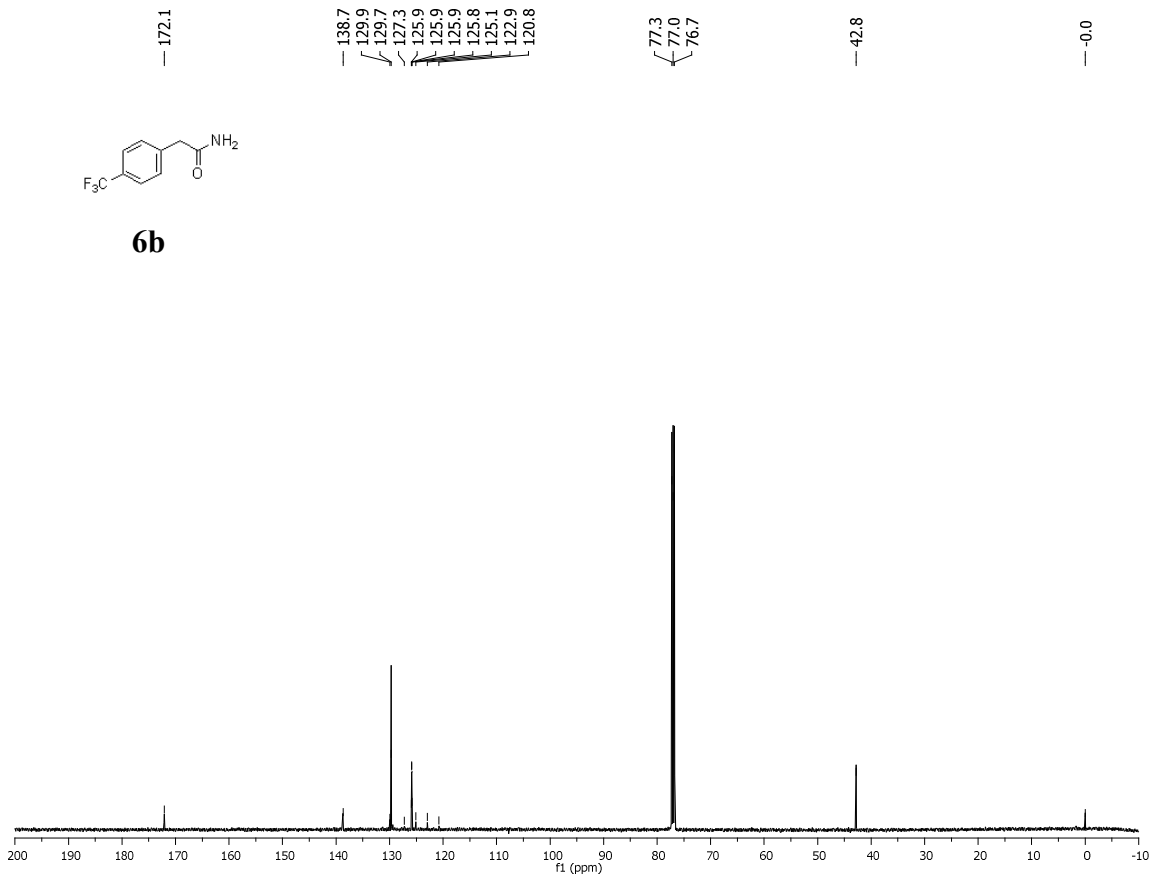
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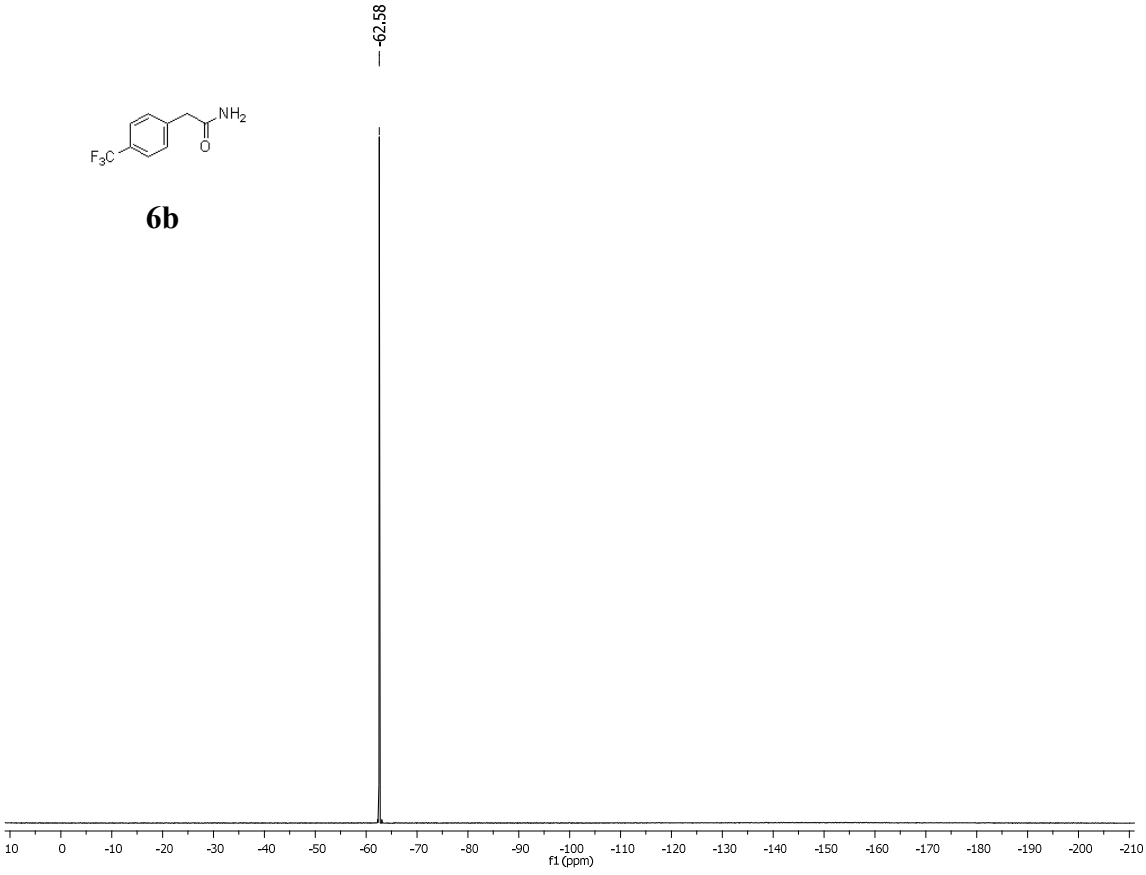
f1 (ppm)

6b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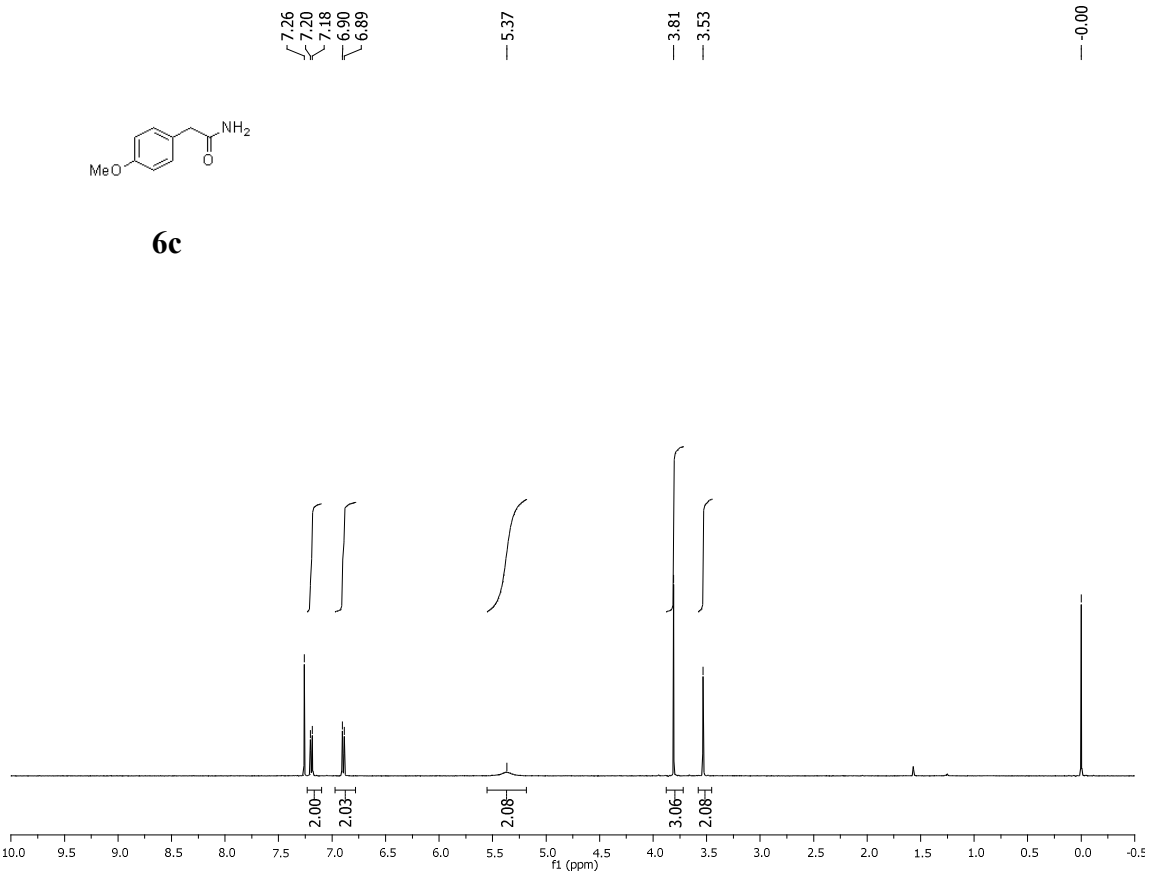
f1 (ppm)

6b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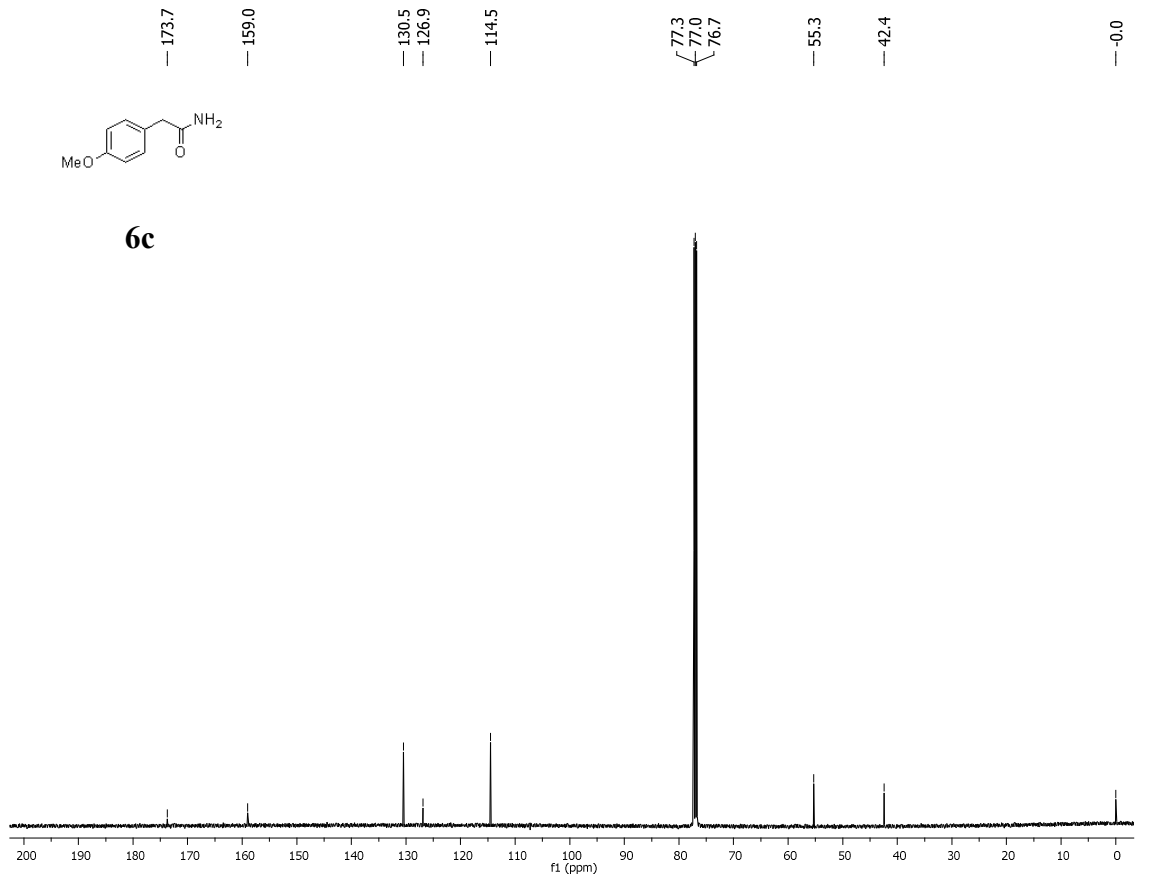
f1 (ppm)

6c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f1 (ppm)

6c


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NH2
O

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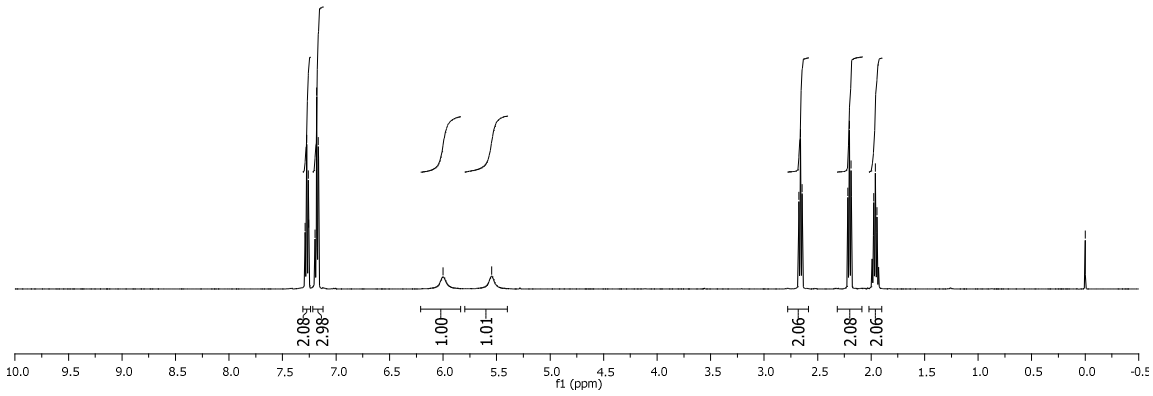
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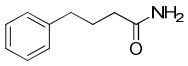
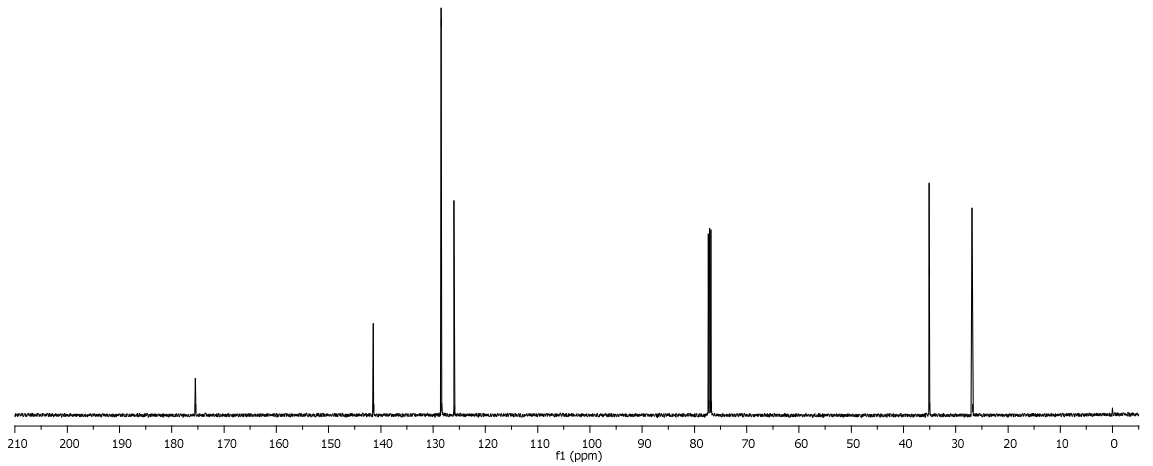
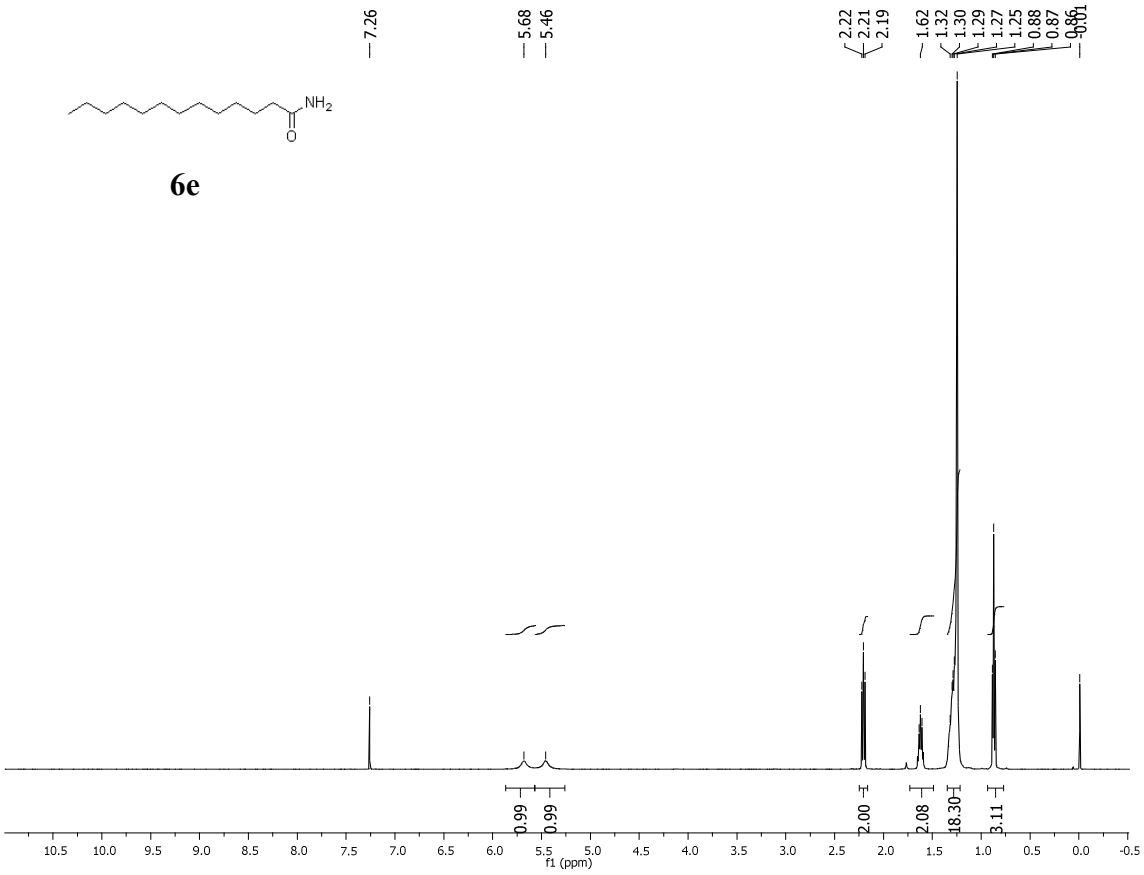
f1 (ppm)


175.4
141.3
128.4
128.3
125.9
77.3
77.0
76.7
35.0
34.9
26.8

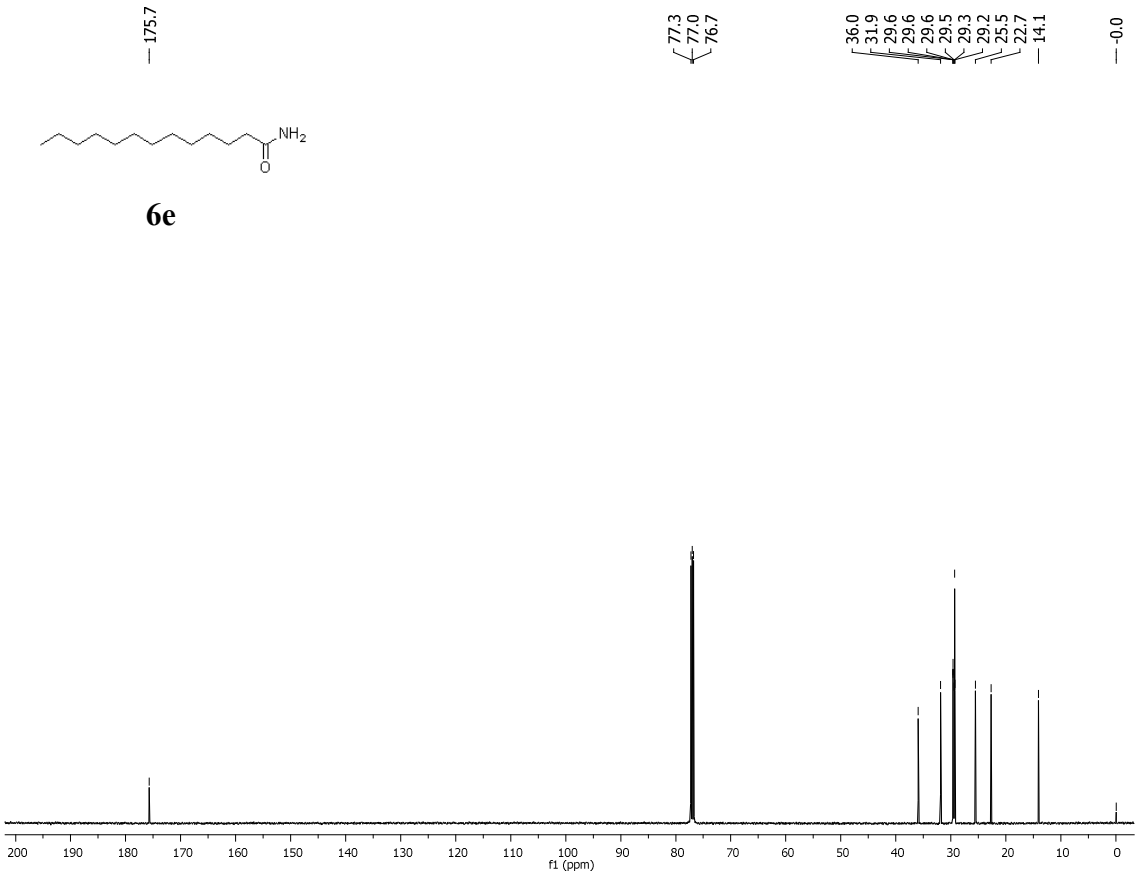

NH2
O

6d

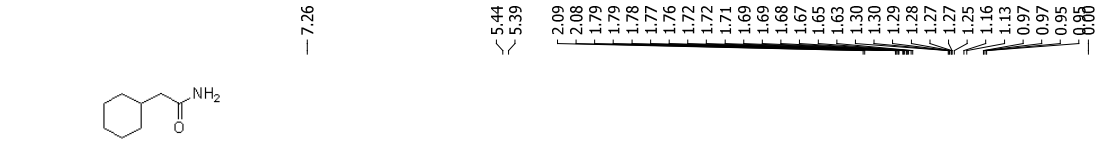

f1 (ppm)


7.26
5.68
5.46
2.22
2.21
2.19
1.62
1.32
1.30
1.29
1.27
1.25
0.88
0.87
0.86
0.01
NH2
O
0.99
0.99
2.00
2.08
18.30
3.11
f1 (ppm)

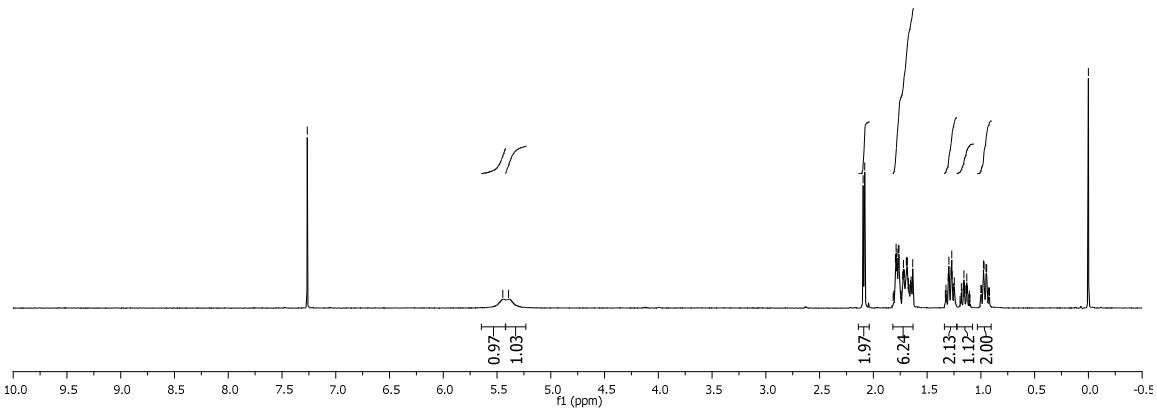
6e

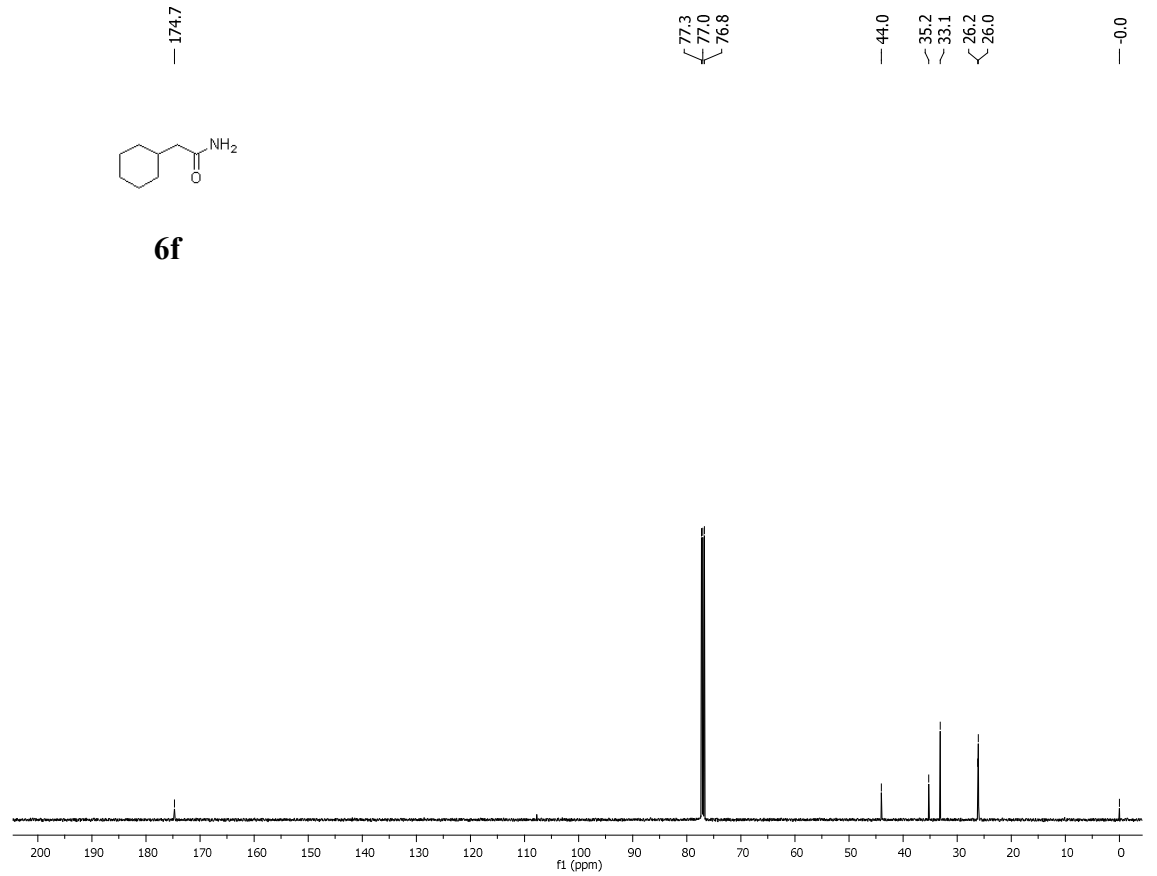

175.7
77.3
77.0
76.7
36.0
31.9
29.6
29.6
29.6
29.5
29.3
29.2
25.5
22.7
14.1
-0.0
NH2
O
f1 (ppm)

6e

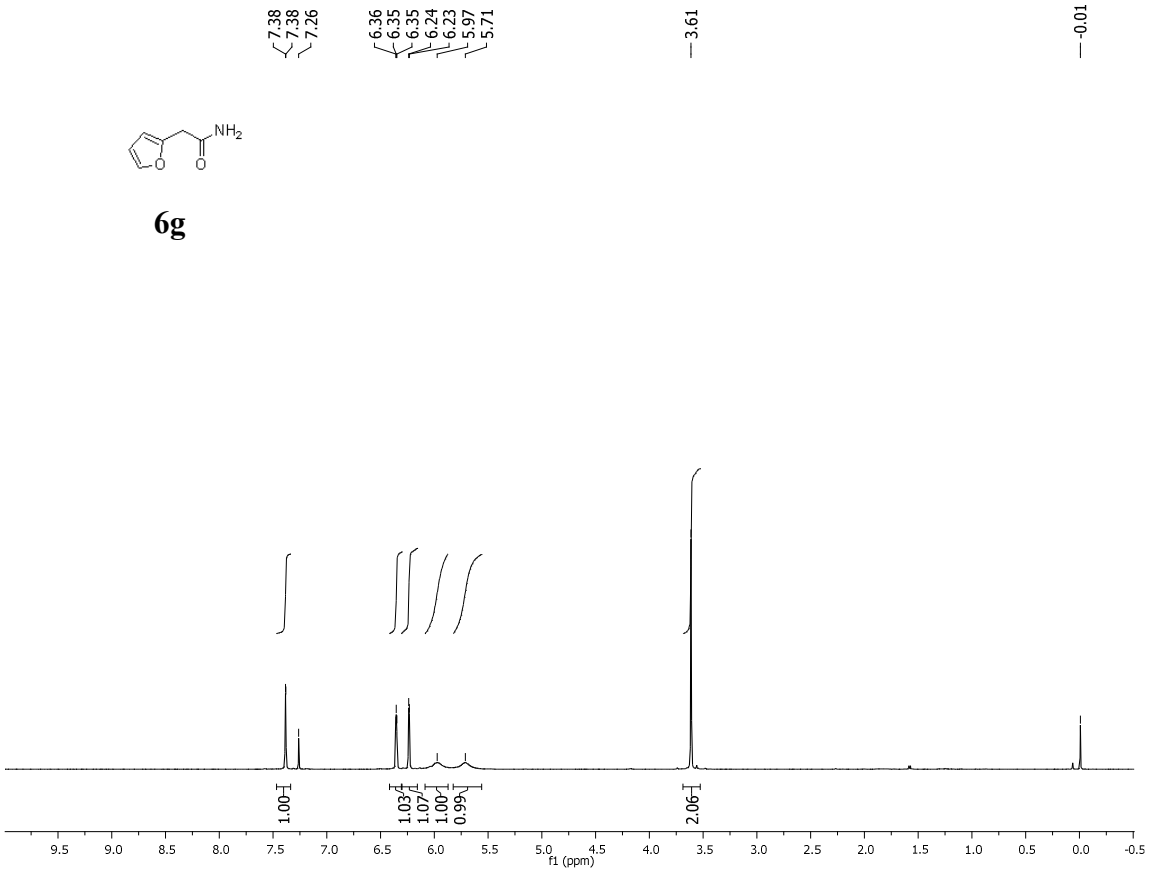

7.26
5.44
5.39
2.09
2.08
1.79
1.79
1.78
1.77
1.76
1.72
1.72
1.71
1.69
1.69
1.68
1.67
1.65
1.63
1.30
1.30
1.29
1.28
1.27
1.27
1.25
1.16
1.13
0.97
0.97
0.95
0.85
0.80
NH2
O

6f

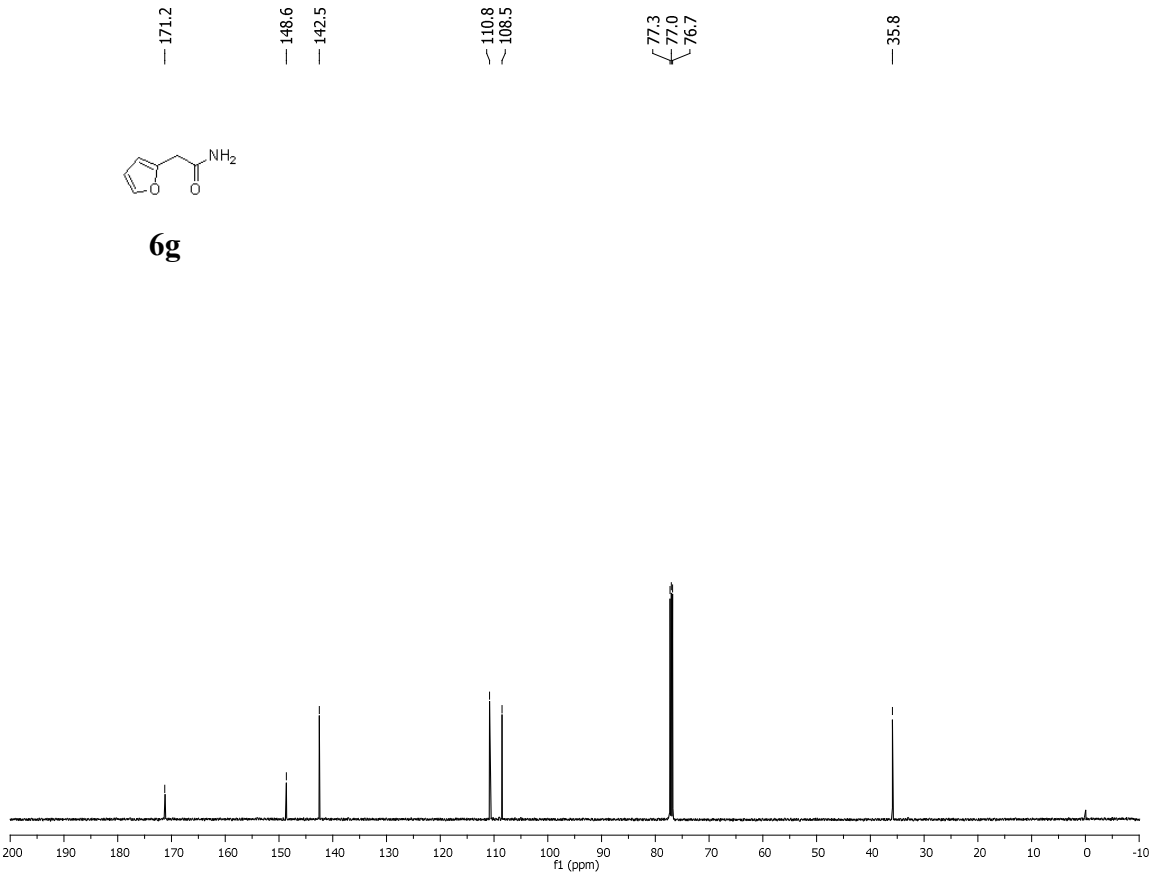

0.97
1.03
1.97
6.24
2.13
1.12
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


174.7
77.3
77.0
76.8
44.0
35.2
33.1
26.2
26.0
0.0
NH2
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

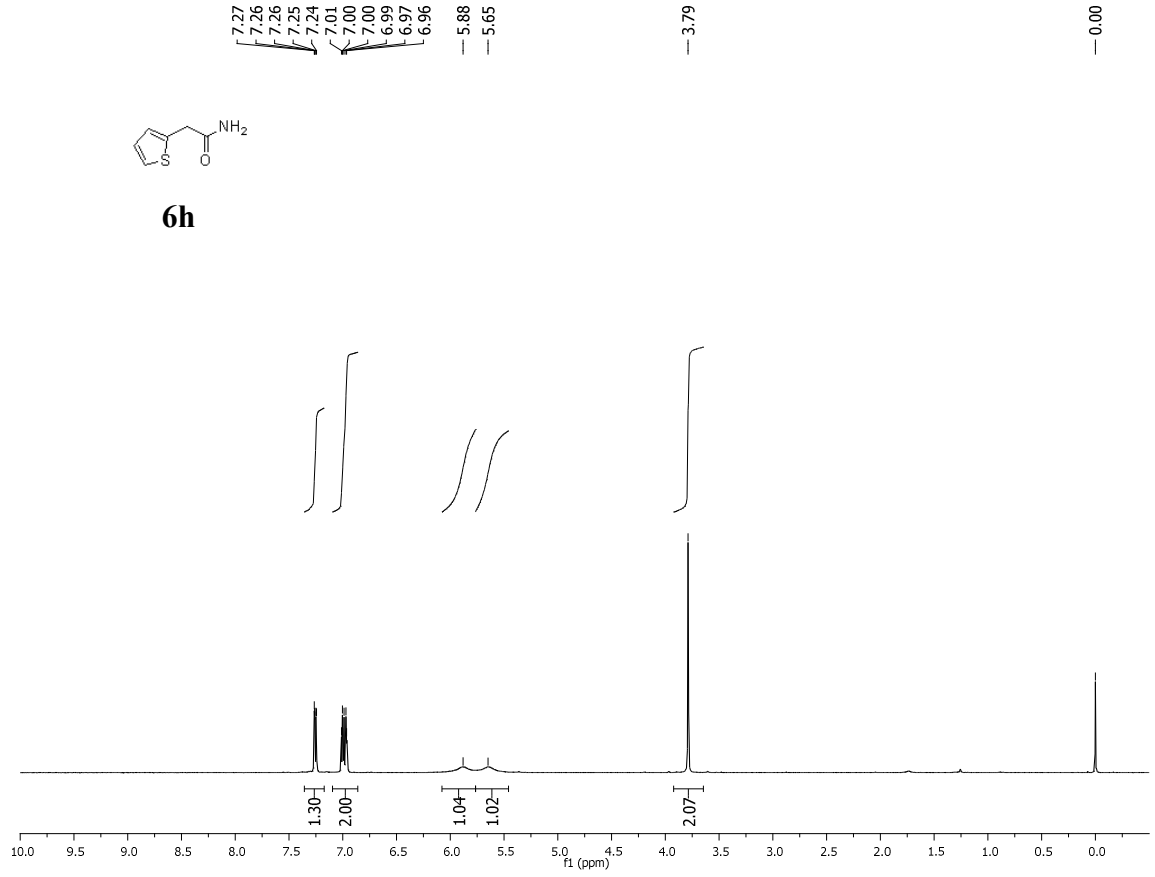
6f


7.38
7.38
7.26
6.36
6.35
6.35
6.24
6.23
5.97
5.71
3.61
-0.01
NH2
O
O
1.00
1.03
1.07
1.00
0.99
2.06
f1 (ppm)

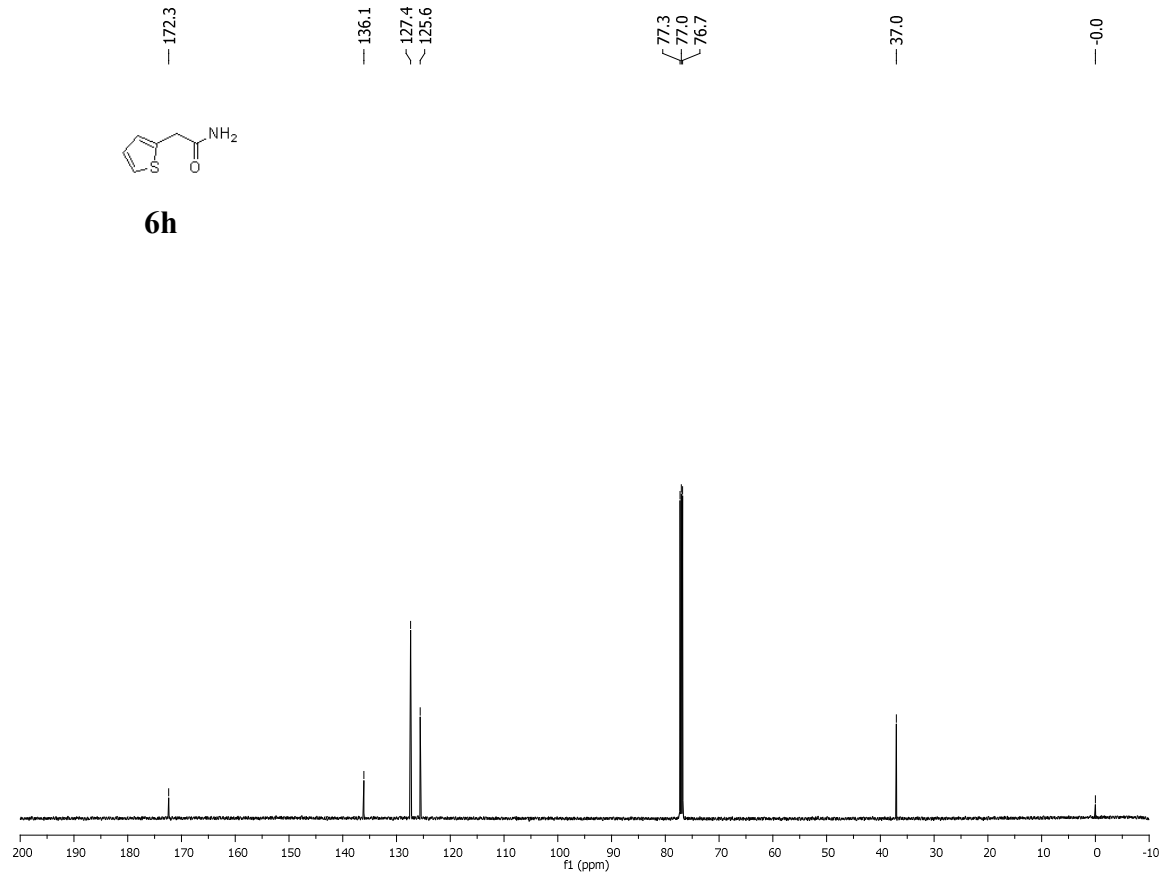
6g


171.2
148.6
142.5
110.8
108.5
77.3
77.0
76.7
35.8
NH2
O
O
f1 (ppm)

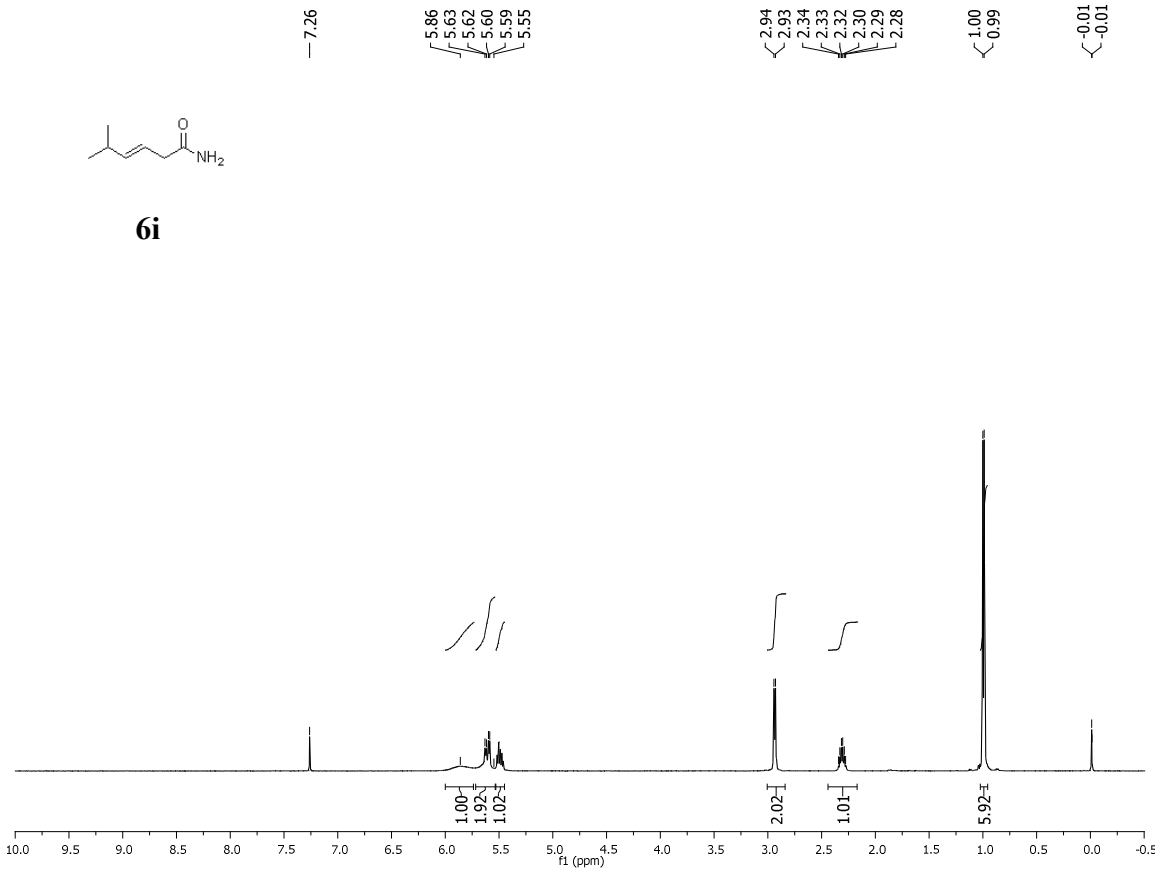
6g


7.27
7.26
7.26
7.25
7.24
7.01
7.00
7.00
6.99
6.97
6.96
5.88
5.65
3.79
0.00
NH2
O
S
1.30
2.00
1.04
1.02
2.07
f1 (ppm)

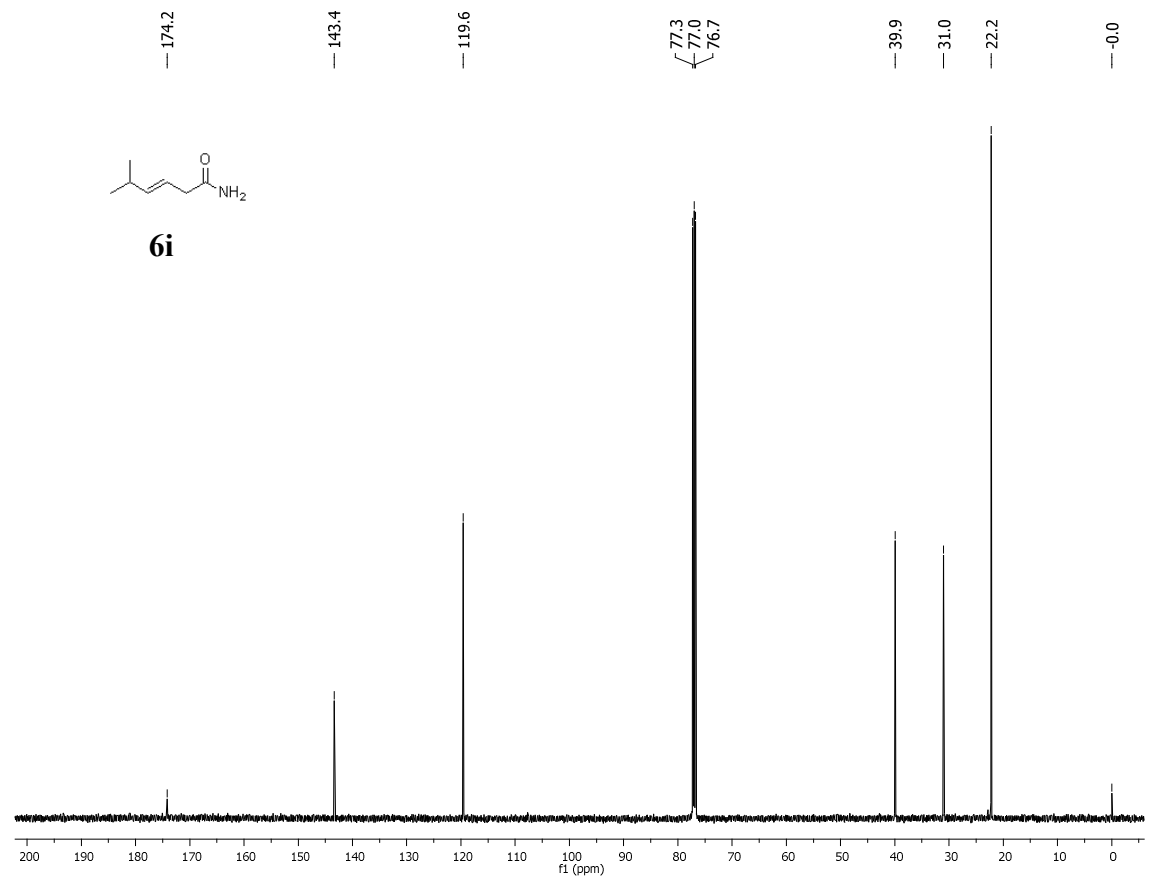
6h


172.3
136.1
127.4
125.6
77.3
77.0
76.7
37.0
-0.0
NH2
O
S
f1 (ppm)

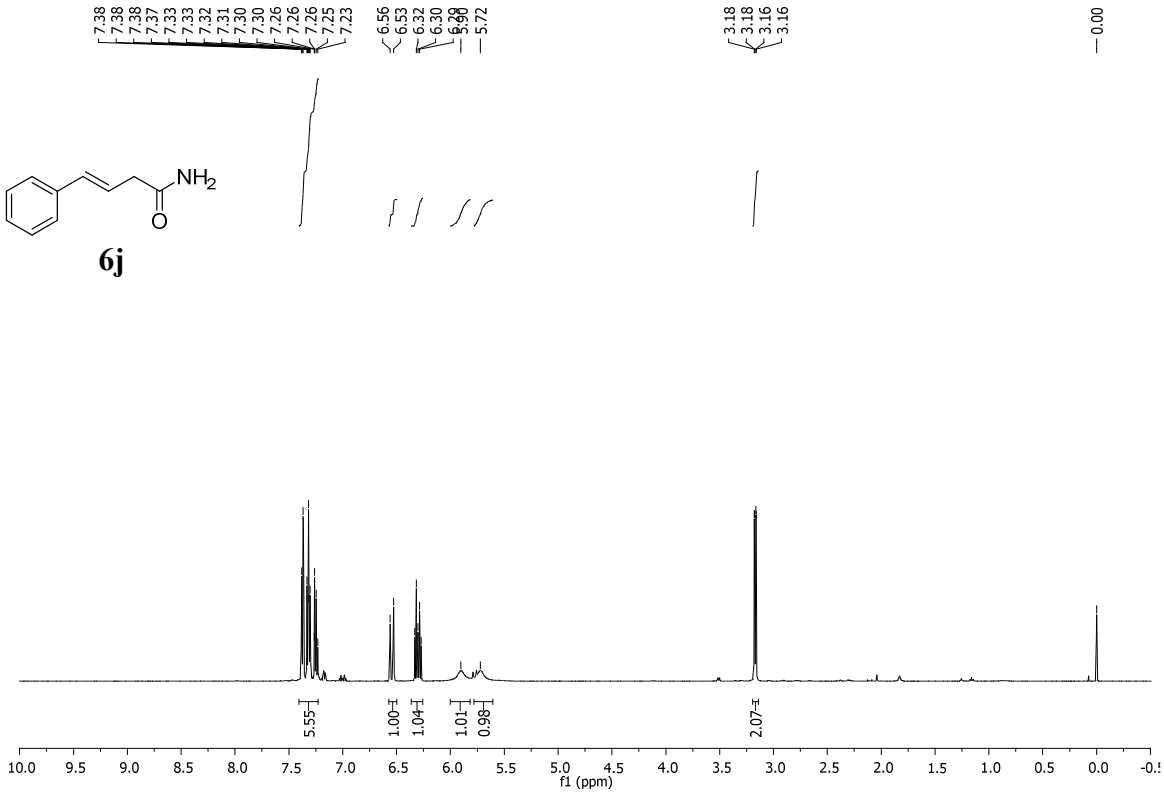
6h


7.26
5.86
5.63
5.62
5.60
5.59
5.55
2.94
2.93
2.34
2.33
2.32
2.30
2.29
2.28
1.00
0.99
-0.01
-0.01
O
NH2
1.00
1.92
1.02
2.02
1.01
5.92
f1 (ppm)

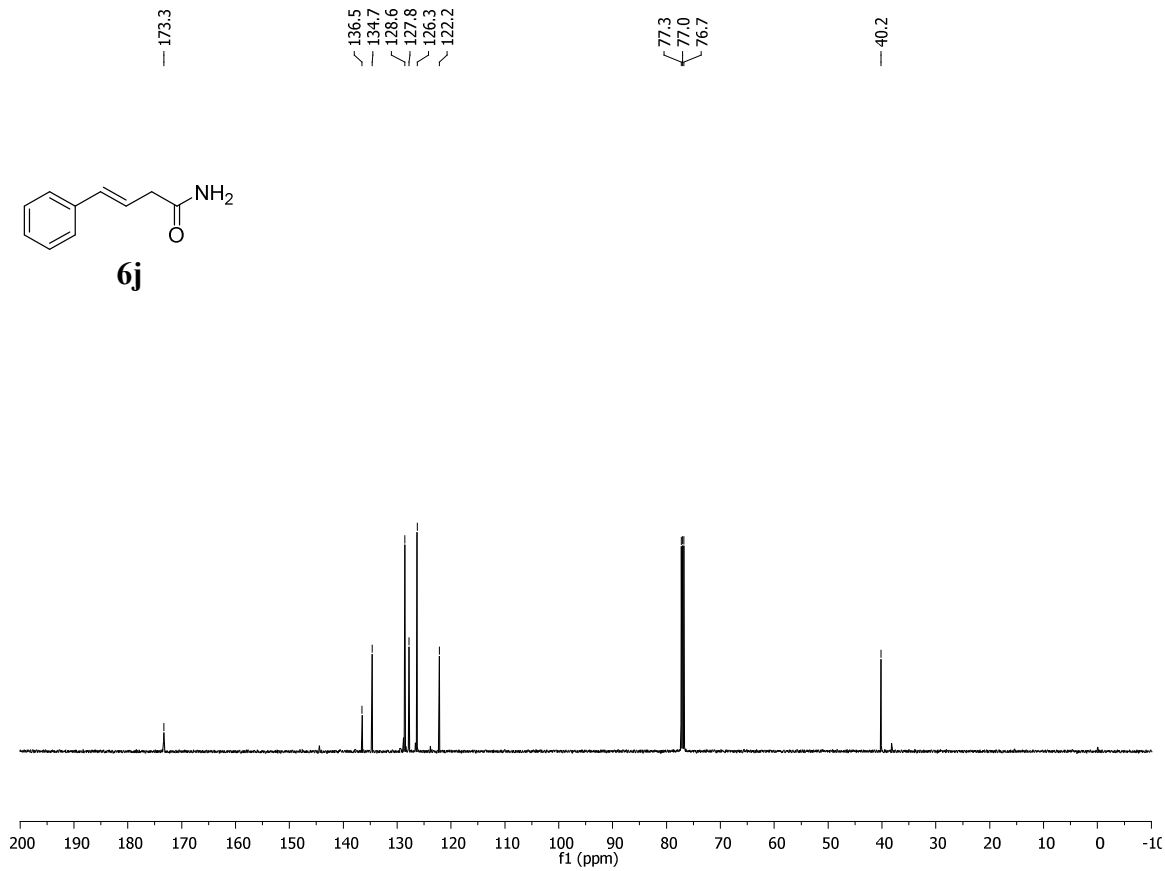
6i


174.2
143.4
119.6
77.3
77.0
76.7
39.9
31.0
22.2
-0.0
O
NH2
f1 (ppm)

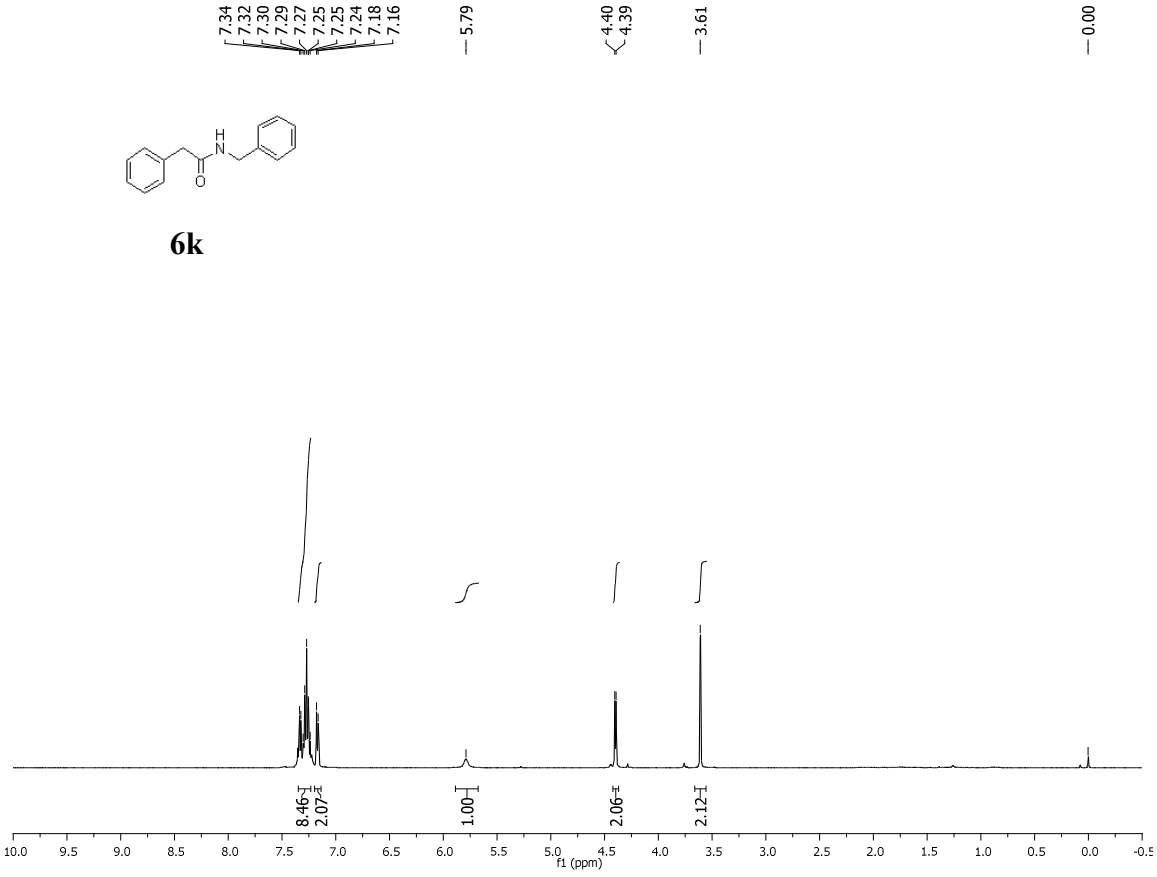
6i


7.38
7.38
7.38
7.37
7.33
7.33
7.32
7.31
7.30
7.30
7.26
7.26
7.26
7.25
7.23
6.56
6.53
6.32
6.30
6.28
5.90
5.72
3.18
3.18
3.16
3.16
0.00
NH2
O
5.55
1.00
1.04
1.01
0.98
2.07
f1 (ppm)

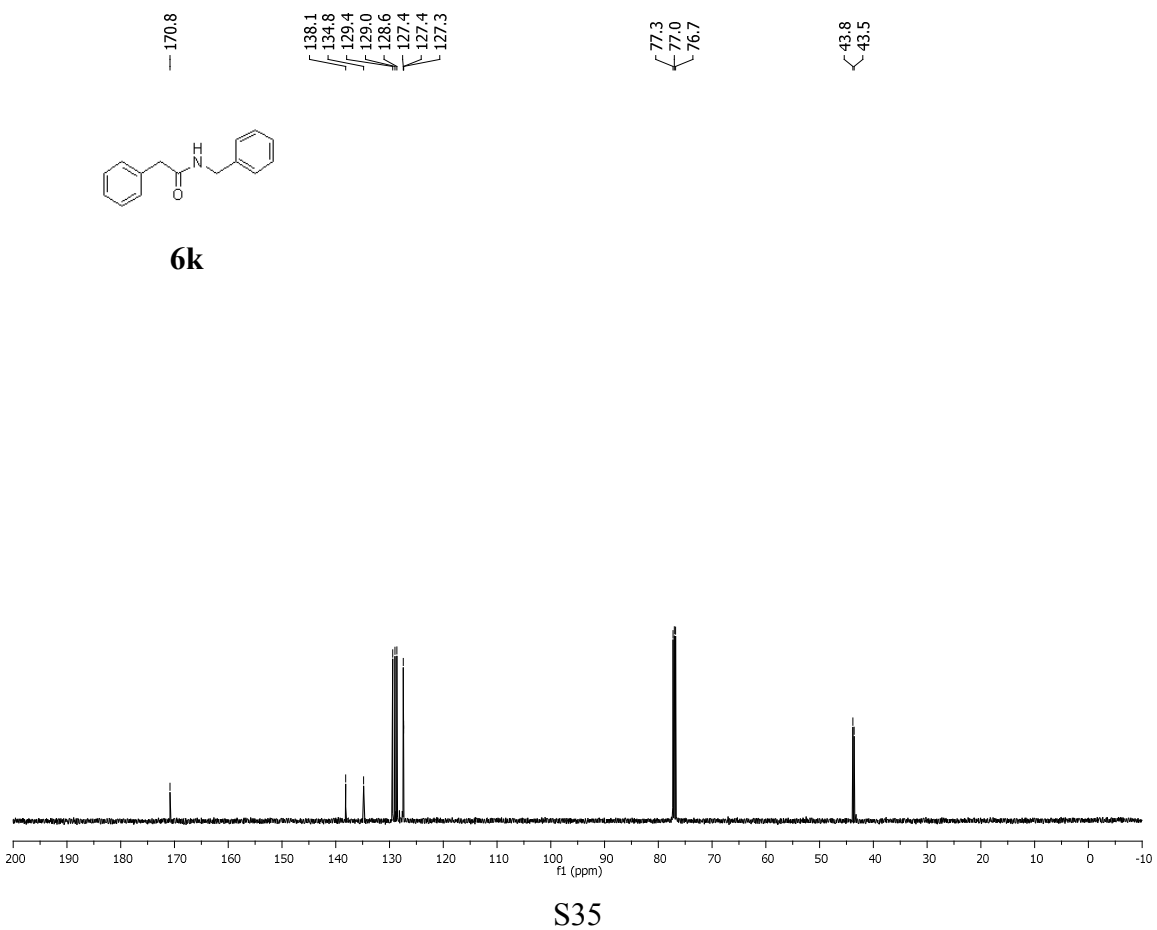
6j


173.3
136.5
134.7
128.6
127.8
126.3
122.2
77.3
77.0
76.7
40.2
NH2
O
f1 (ppm)

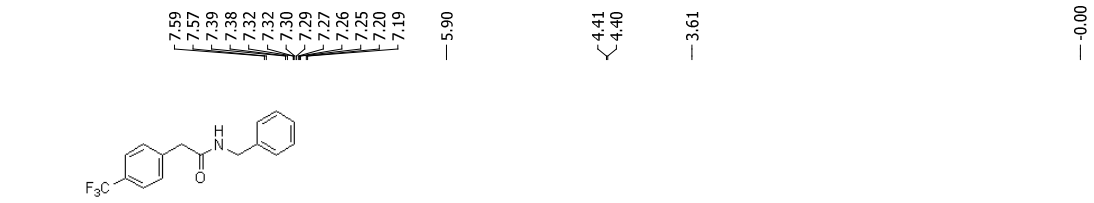
6j


7.34
7.32
7.30
7.29
7.27
7.25
7.25
7.24
7.18
7.16
5.79
4.40
4.39
3.61
0.00
8.46
2.07
1.00
2.06
2.12
f1 (ppm)

6k

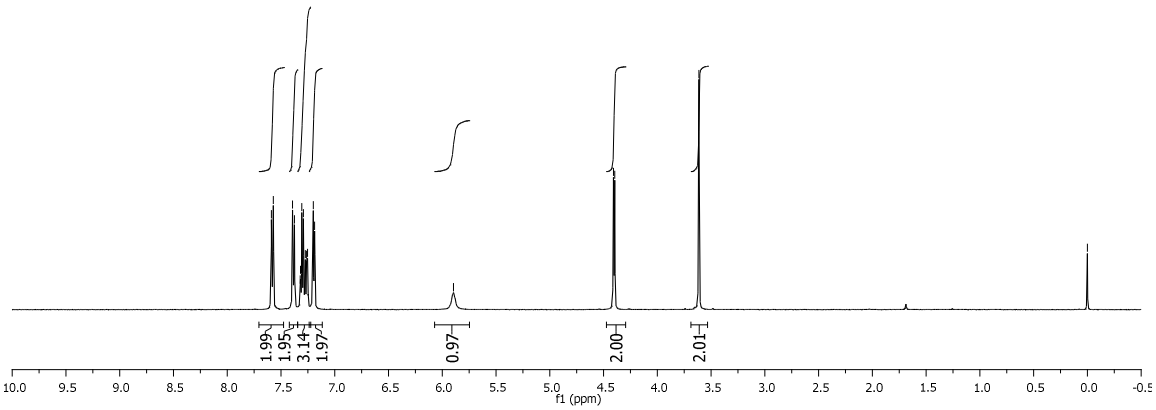

170.8
138.1
134.8
129.4
129.0
128.6
127.4
127.4
127.3
77.3
77.0
76.7
43.8
43.5
f1 (ppm)

6k

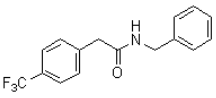

7.59
7.57
7.39
7.38
7.32
7.32
7.30
7.29
7.27
7.26
7.25
7.20
7.19
5.90
4.41
4.40
3.61
0.00

F3C
H
N
O

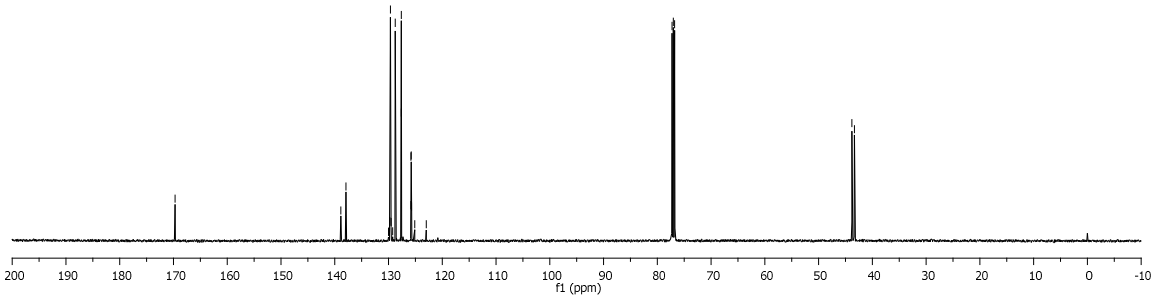
6l

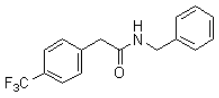

1.99
1.95
3.14
1.97
0.97
2.00
2.01
f1 (ppm)


169.7
138.9
137.9
130.0
129.7
129.6
129.5
129.2
128.7
127.6
127.6
125.8
125.8
125.8
125.7
125.1
123.0
77.3
77.0
76.7
43.8
43.3


F3C
H
N
O

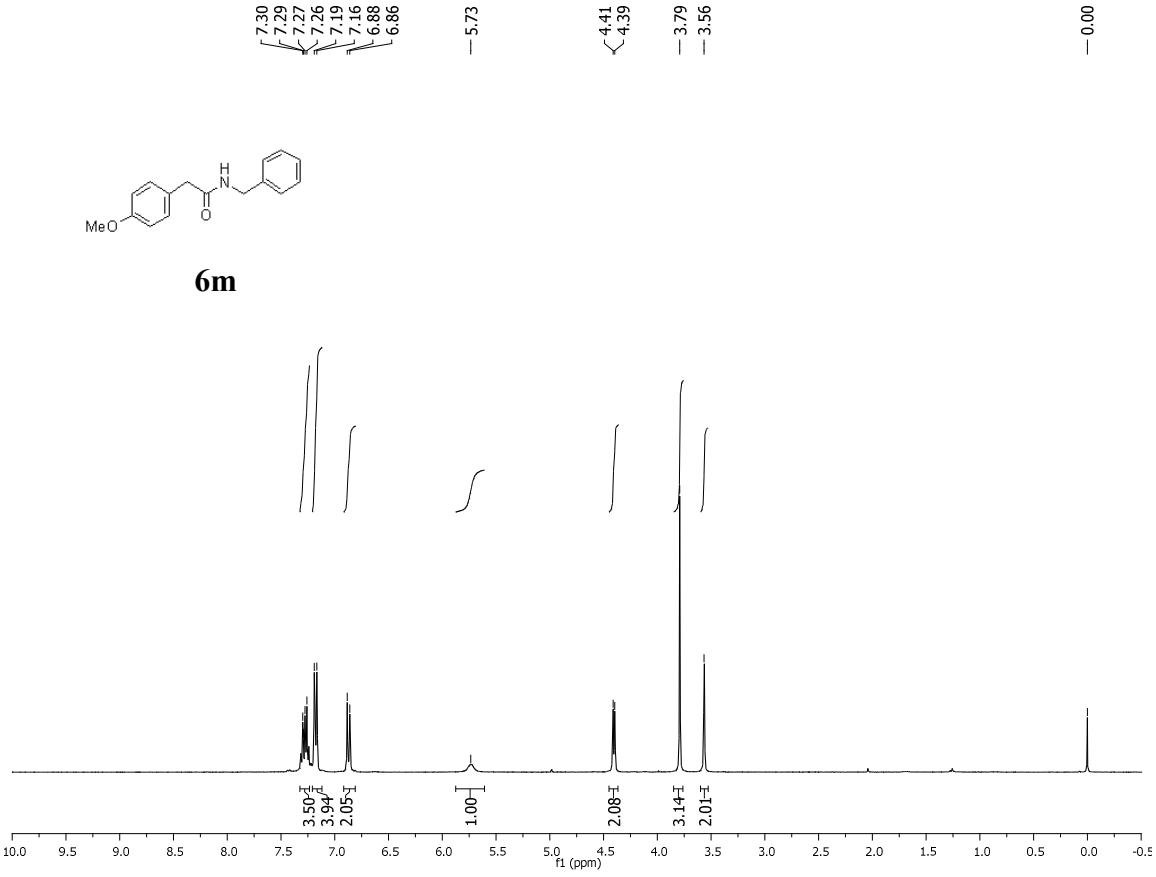
6l


f1 (ppm)

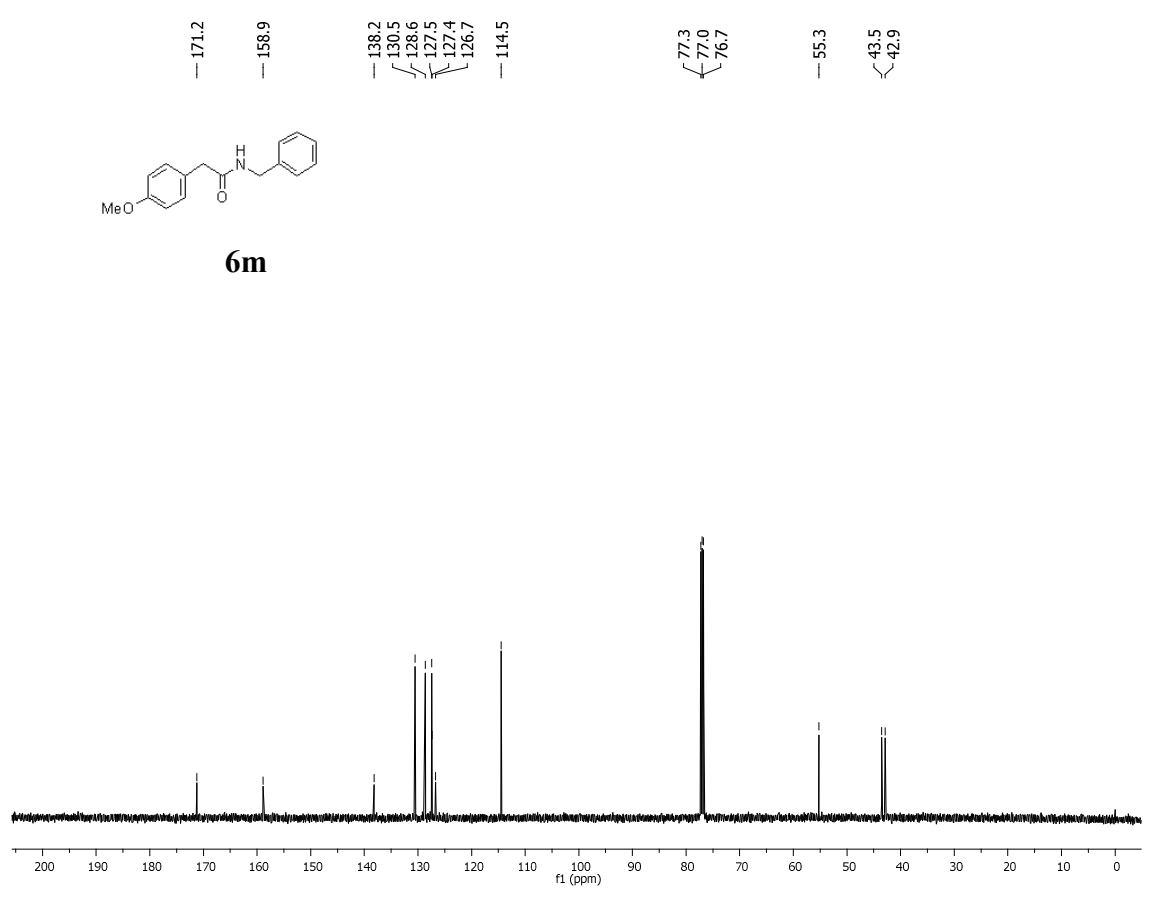

F3C
H
N
O

6l

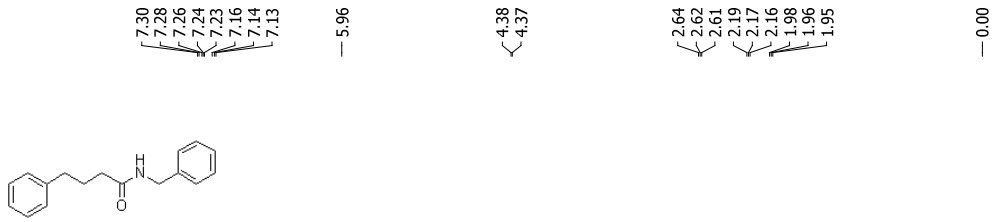
-62.52
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.30
7.29
7.27
7.26
7.19
7.16
6.88
6.86
5.73
4.41
4.39
3.79
3.56
0.00
MeO
H
N
O
3.50
3.94
2.05
1.00
2.08
3.14
2.01
f1 (ppm)

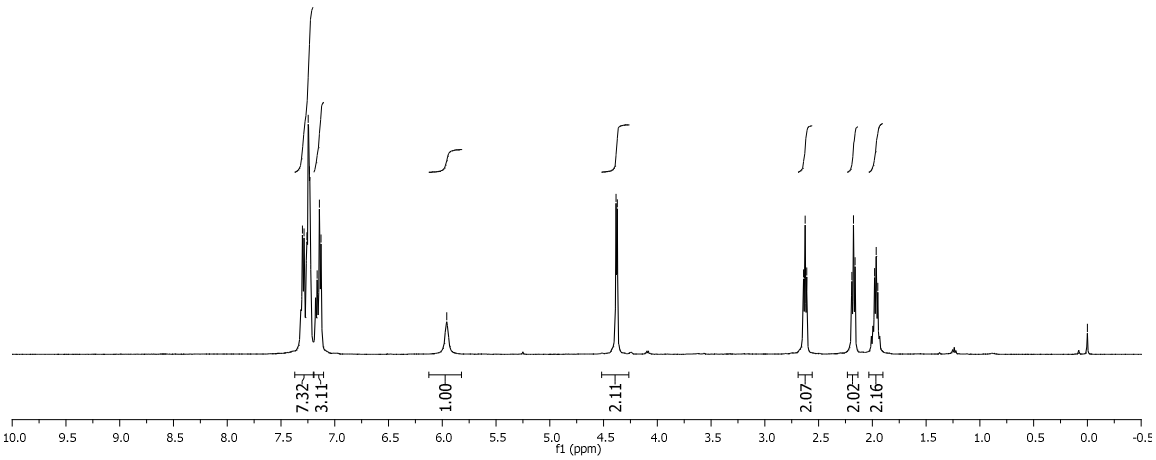
6m


171.2
158.9
138.2
130.5
128.6
127.5
127.4
126.7
114.5
77.3
77.0
76.7
55.3
43.5
42.9
MeO
H
N
O
f1 (ppm)

6m

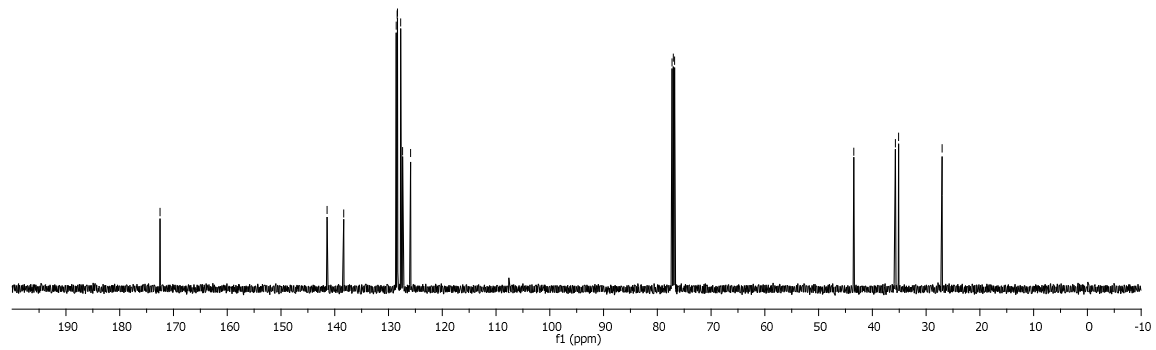

7.30
7.28
7.26
7.24
7.23
7.16
7.14
7.13
5.96
4.38
4.37
2.64
2.62
2.61
2.19
2.17
2.16
1.98
1.96
1.95
0.00

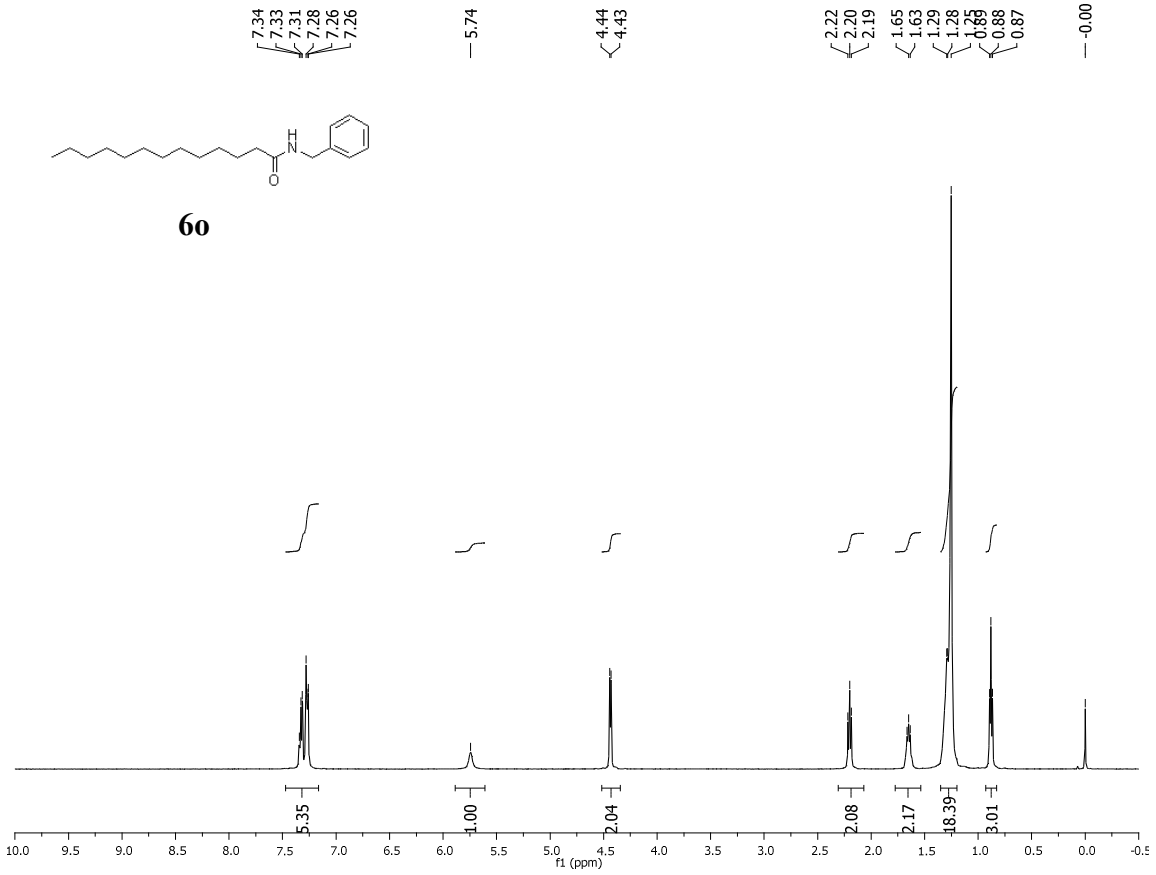
6n


7.32
3.11
1.00
2.11
2.07
2.02
2.16
f1 (ppm)

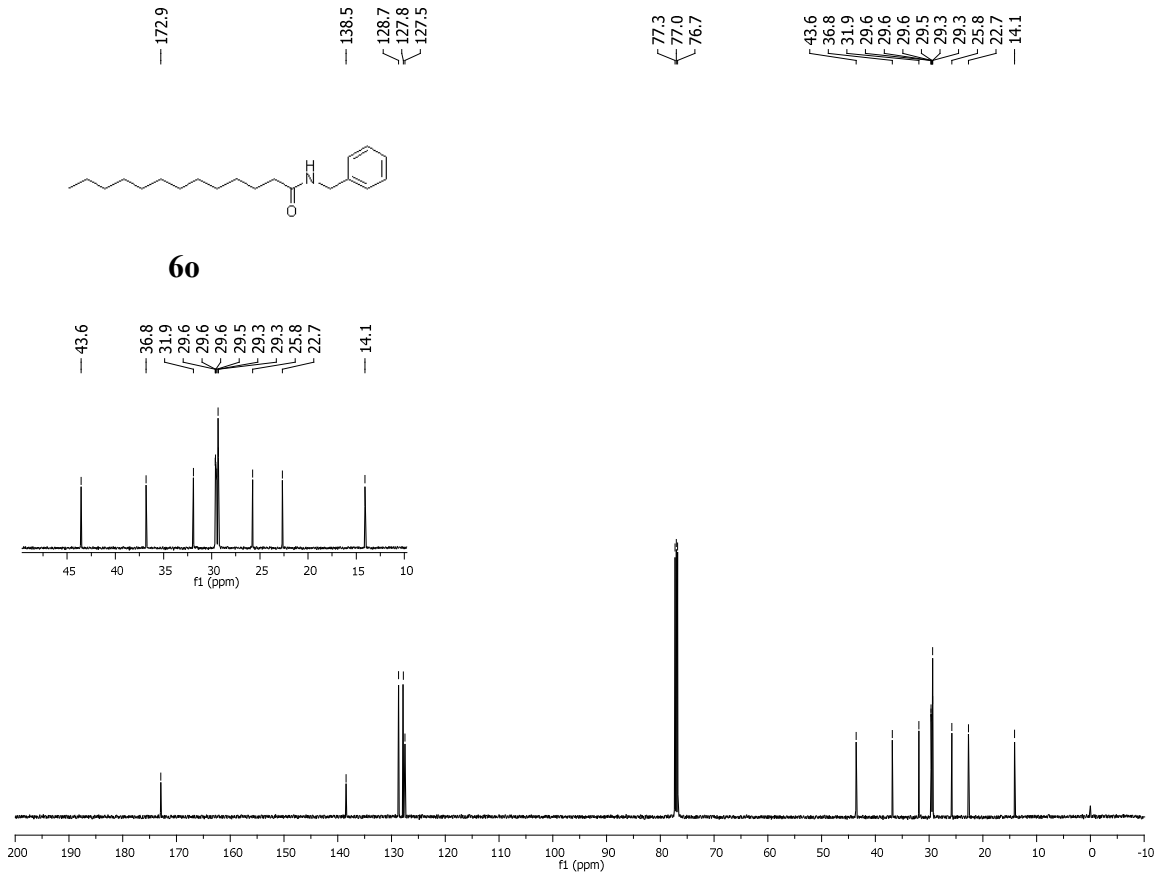

172.5
141.4
138.3
128.6
128.4
128.3
127.7
127.4
125.9
77.3
77.0
76.7
43.4
35.7
35.1
27.0

6n

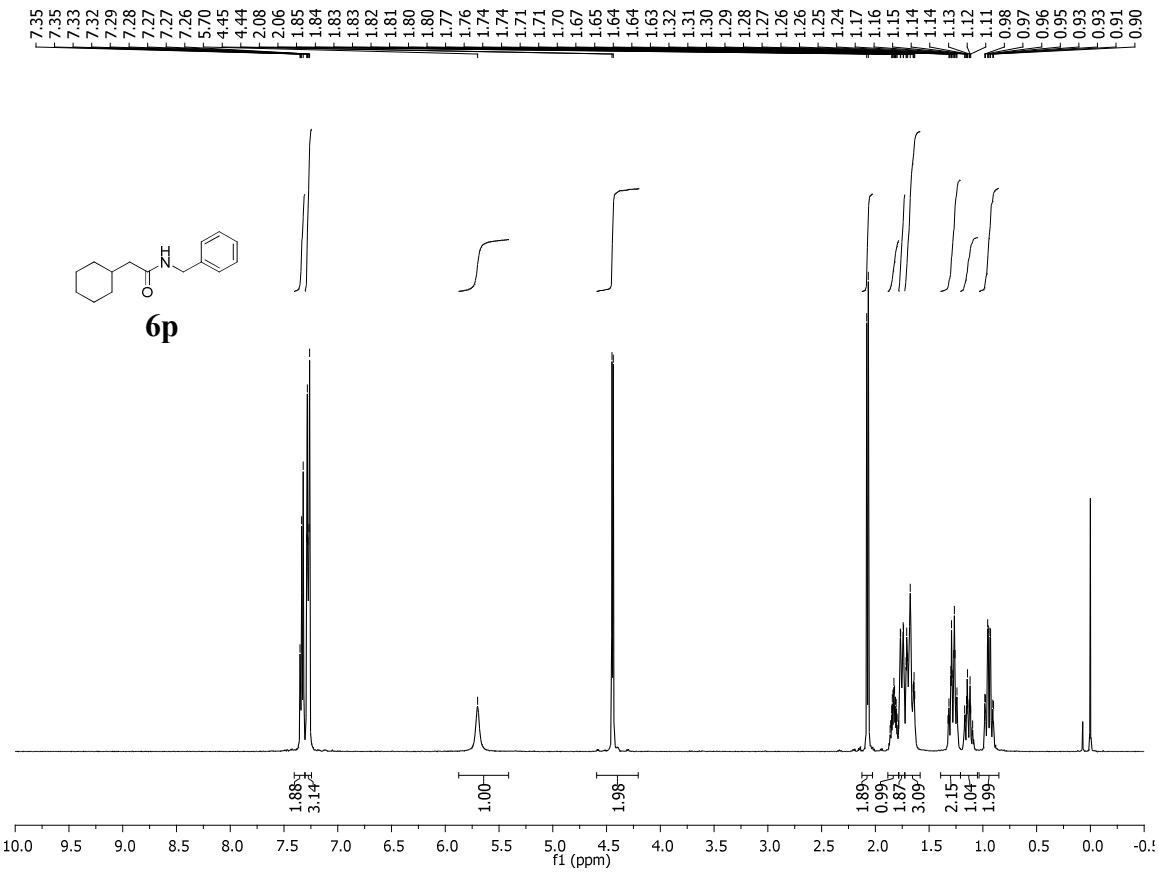

f1 (ppm)


7.34
7.33
7.31
7.28
7.26
7.26
5.74
4.44
4.43
2.22
2.20
2.19
1.65
1.63
1.29
1.28
0.89
0.88
0.87
0.00
5.35
1.00
2.04
2.08
2.17
18.39
3.01
f1 (ppm)

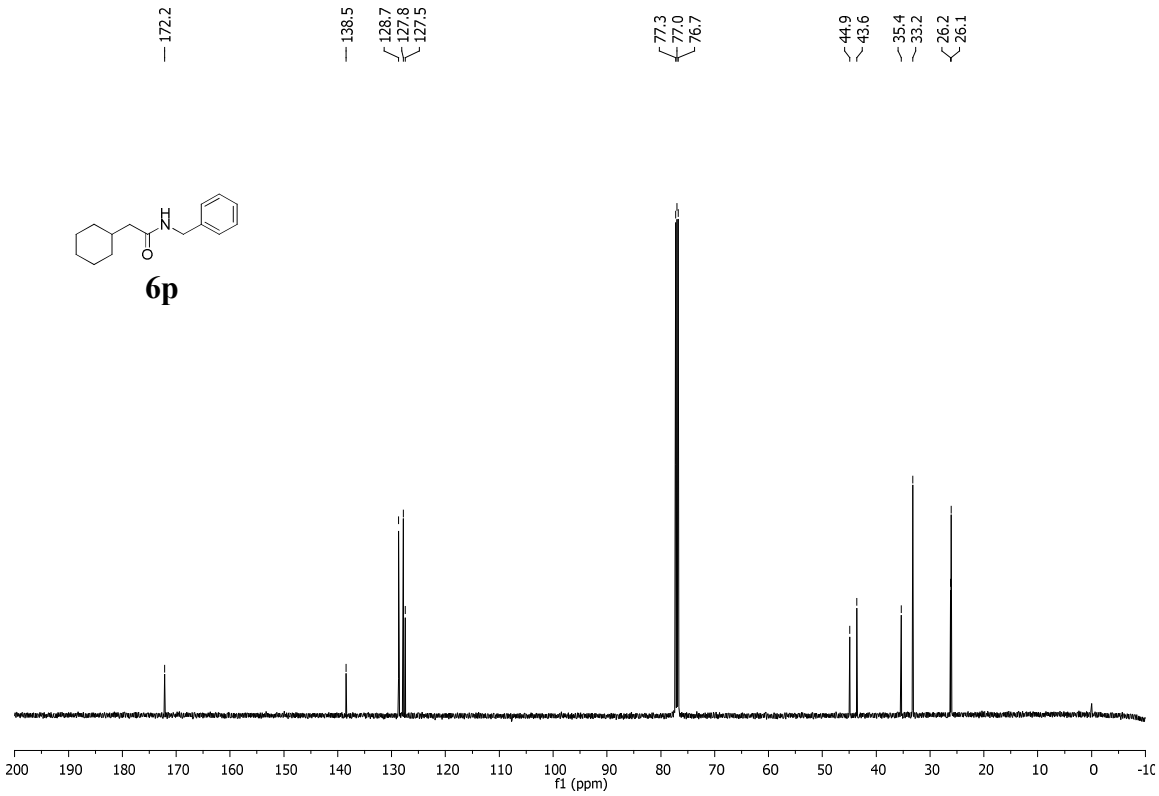
6o


172.9
138.5
128.7
127.8
127.5
77.3
77.0
76.7
43.6
36.8
31.9
29.6
29.6
29.6
29.5
29.3
29.3
25.8
22.7
14.1
f1 (ppm)

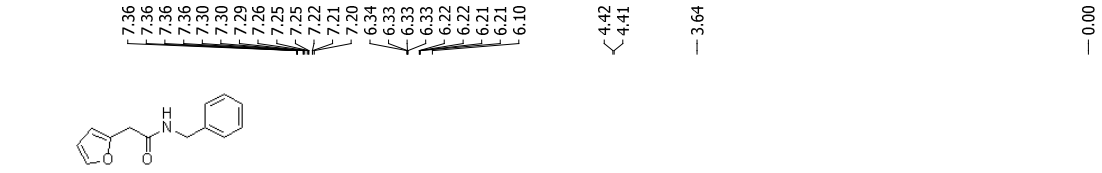
6o


7.35 7.35 7.33 7.32 7.29 7.28 7.27 7.27 7.26 5.70 4.45 4.44 2.08 2.06 1.85 1.84 1.83 1.83 1.82 1.81 1.80 1.80 1.77 1.76 1.74 1.74 1.71 1.71 1.70 1.67 1.65 1.64 1.64 1.63 1.32 1.31 1.30 1.29 1.28 1.27 1.26 1.26 1.25 1.24 1.17 1.16 1.15 1.14 1.14 1.13 1.12 1.11 0.98 0.97 0.96 0.95 0.93 0.93 0.91 0.90
1.88
3.14
1.00
1.98
1.89
0.99
1.87
3.09
2.15
1.04
1.99
f1 (ppm)

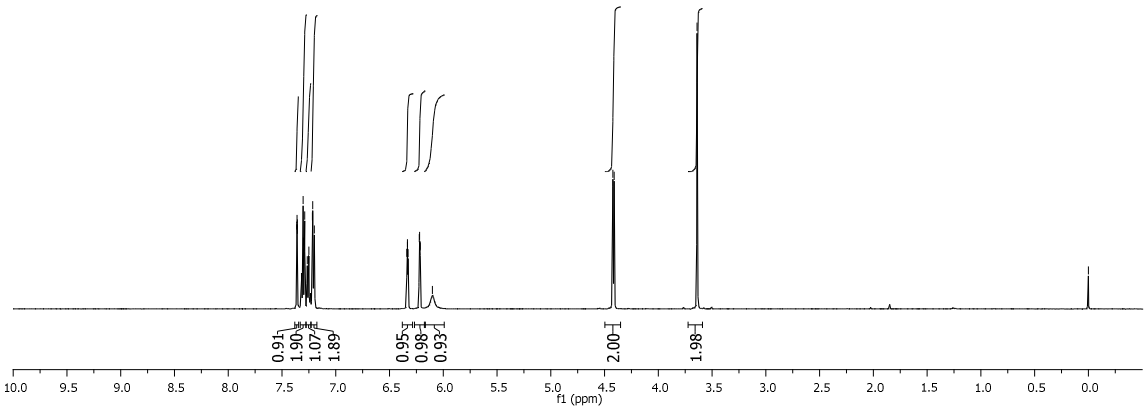
6p


172.2
138.5
128.7
127.8
127.5
77.3
77.0
76.7
44.9
43.6
35.4
33.2
26.2
26.1
f1 (ppm)

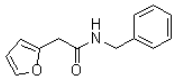
6p


7.36
7.36
7.36
7.36
7.30
7.30
7.29
7.26
7.25
7.25
7.22
7.21
7.20
6.34
6.33
6.33
6.33
6.22
6.22
6.21
6.21
6.10
4.42
4.41
3.64
0.00

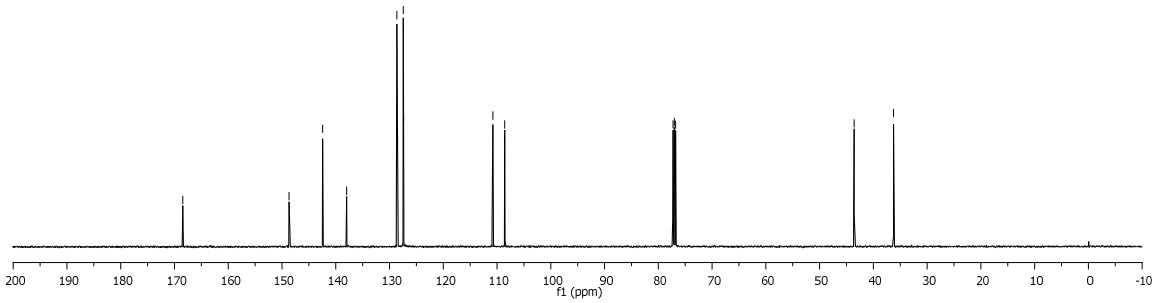
6q


0.91
1.90
1.07
1.89
0.95
0.98
0.93
2.00
1.98
f1 (ppm)

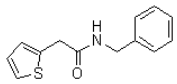

168.4
148.6
142.4
138.0
128.6
127.4
127.4
110.7
108.5
77.3
77.0
76.7
43.5
36.2



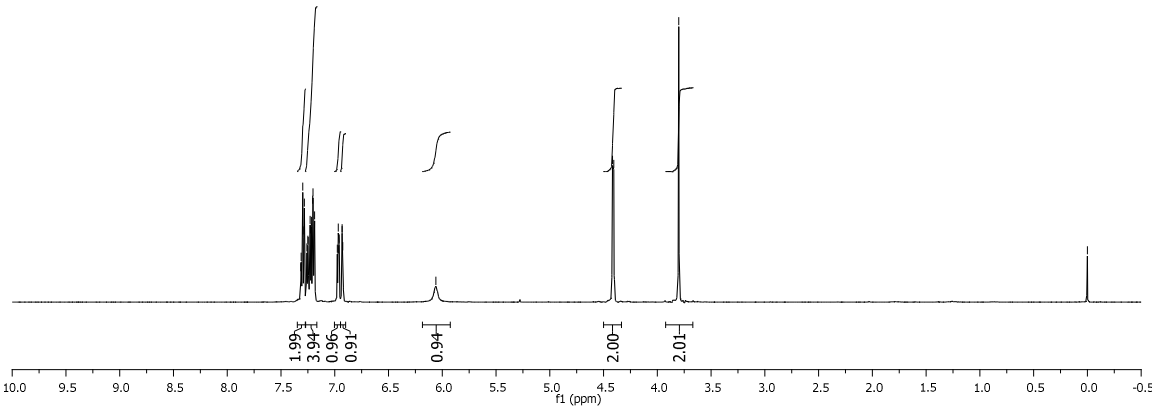
6q

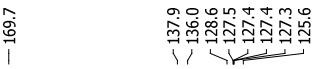

f1 (ppm)

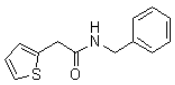

7.31
7.31
7.30
7.29
7.28
7.26
7.25
7.24
7.23
7.23
7.22
7.22
7.20
7.20
7.19
6.97
6.97
6.96
6.96
6.93
6.93
6.92
6.06
4.41
4.40
3.80
0.00



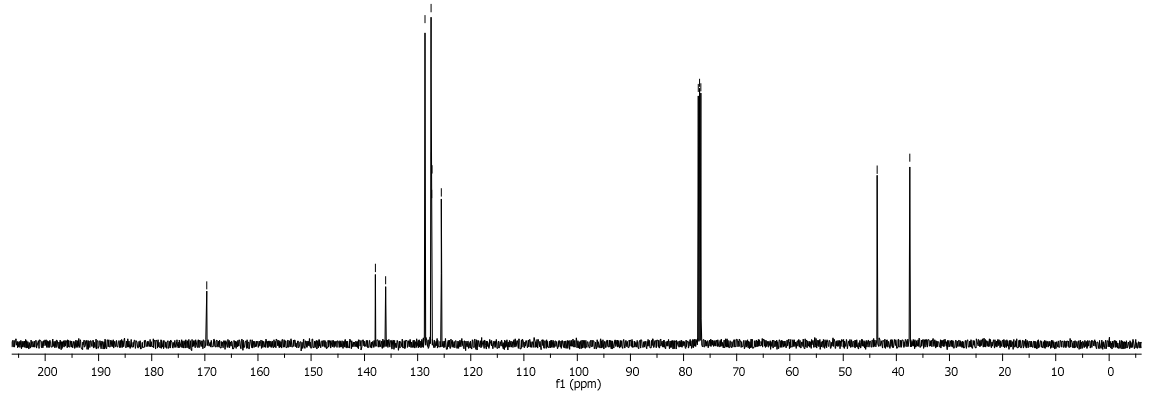
6r

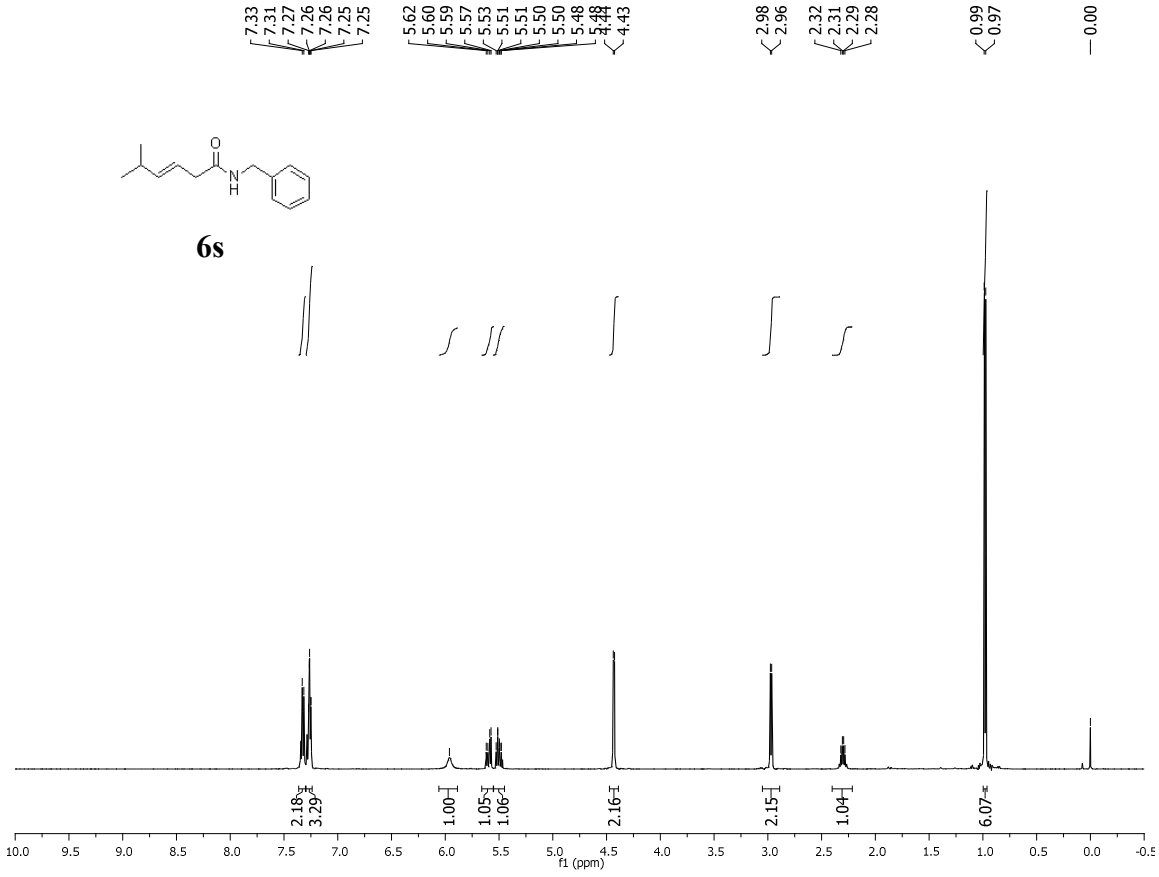

1.99
3.94
0.96
0.91
0.94
2.00
2.01
f1 (ppm)


169.7
137.9
136.0
128.6
127.5
127.4
127.4
127.3
125.6
77.3
77.0
76.7
43.6
37.5

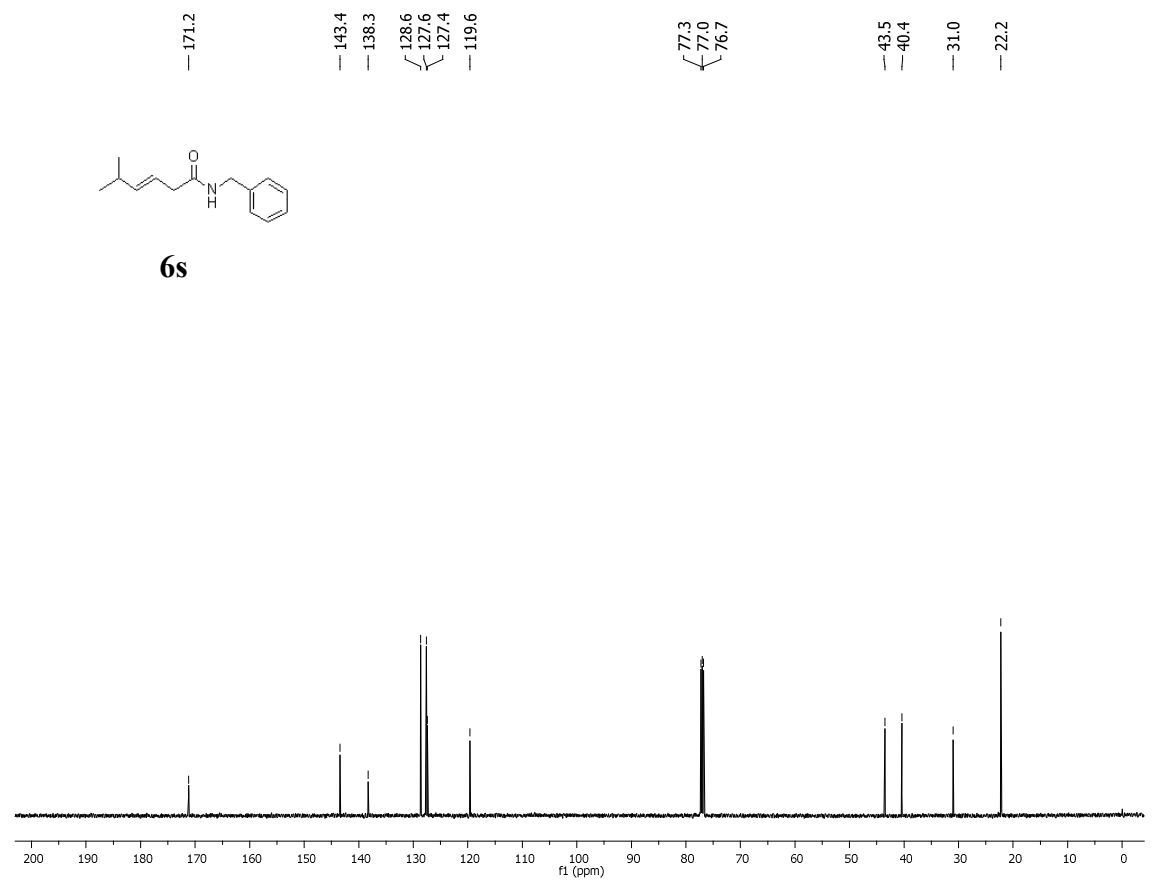


6r

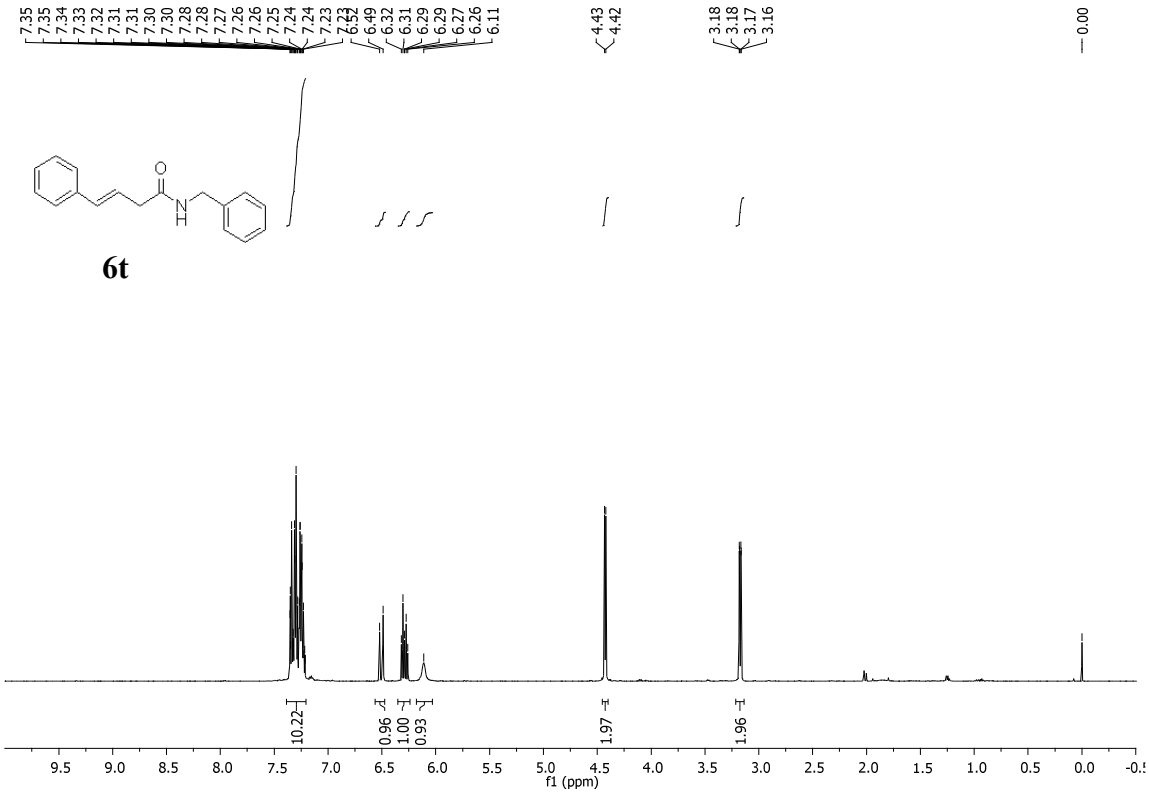

f1 (ppm)


7.33
7.31
7.27
7.26
7.26
7.25
7.25
5.62
5.60
5.59
5.57
5.53
5.51
5.51
5.50
5.50
5.48
4.43
2.98
2.96
2.32
2.31
2.29
2.28
0.99
0.97
0.00
2.18
3.29
1.00
1.05
1.06
2.16
2.15
1.04
6.07
f1 (ppm)

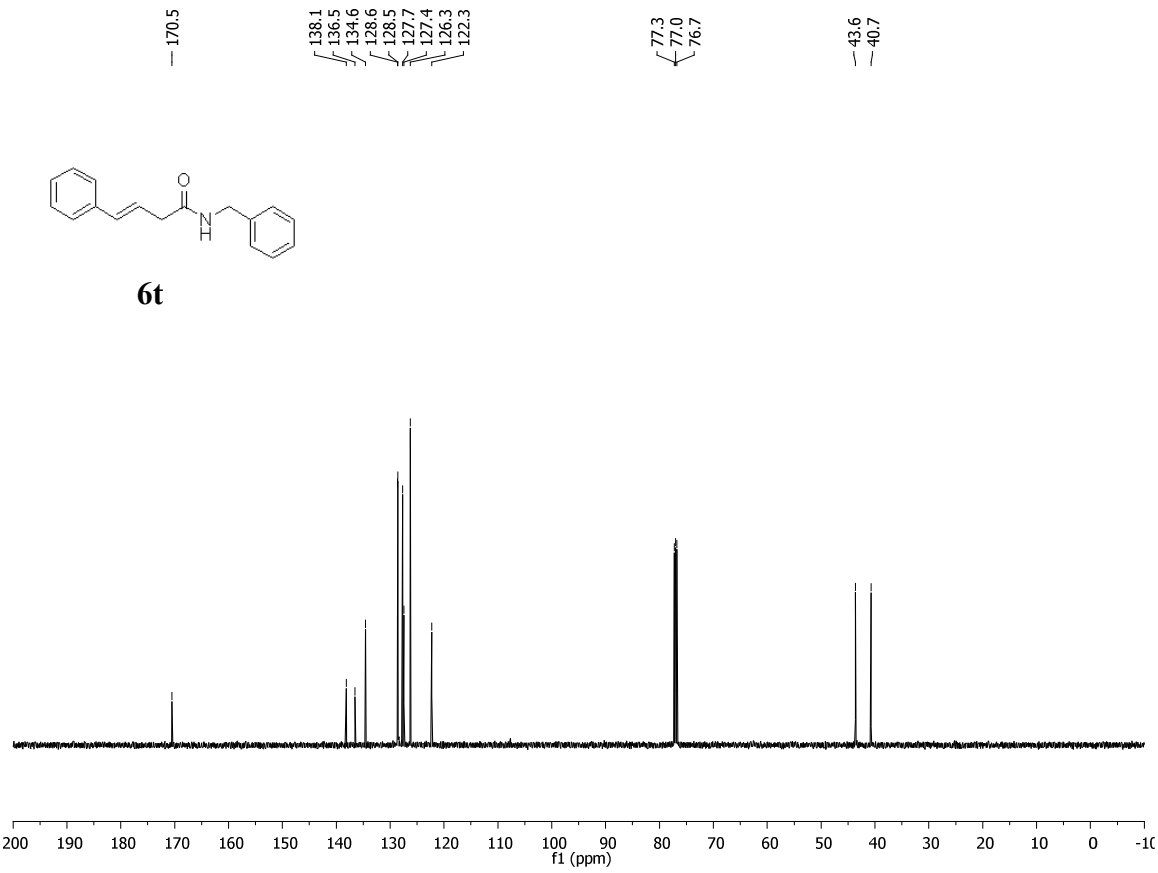
6s


171.2
143.4
138.3
128.6
127.6
127.4
119.6
77.3
77.0
76.7
43.5
40.4
31.0
22.2
f1 (ppm)

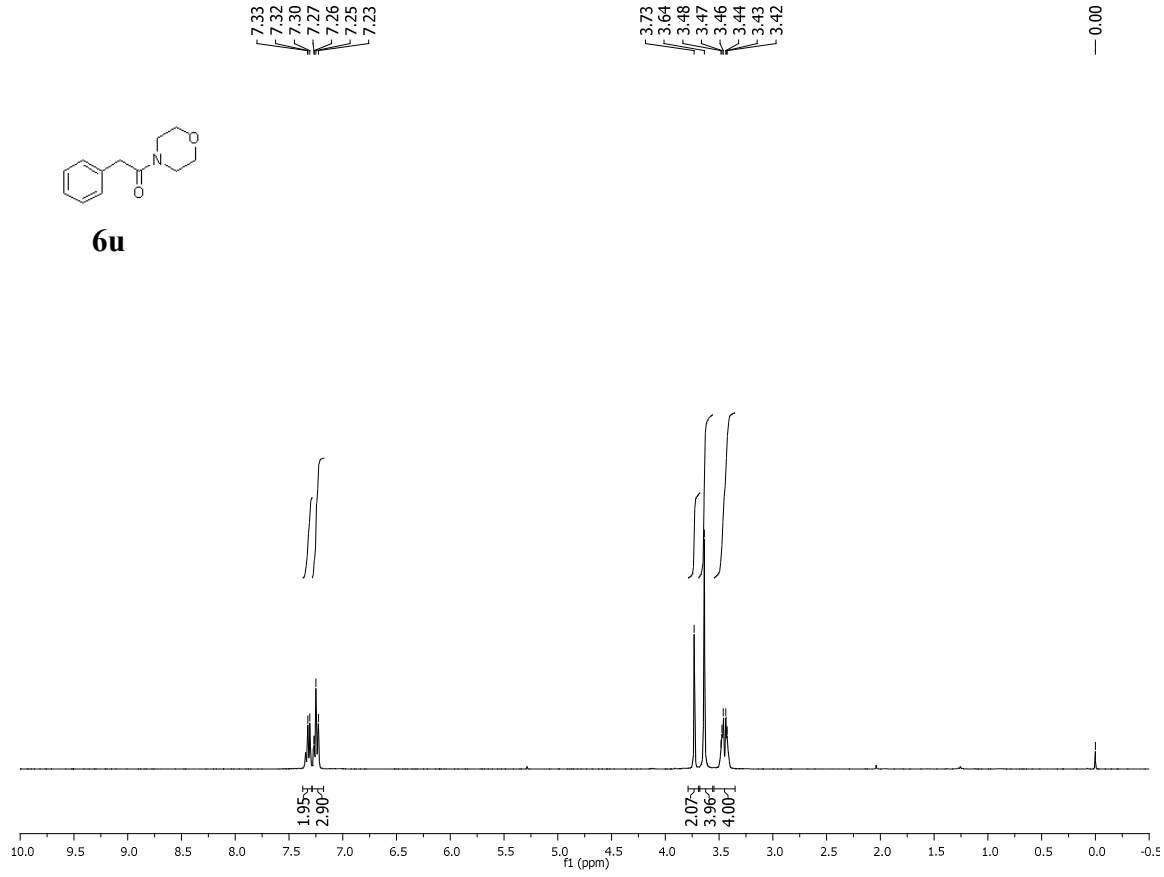
6s


7.35
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.30
7.28
7.28
7.27
7.26
7.26
7.25
7.24
7.24
7.23
6.49
6.32
6.31
6.29
6.29
6.27
6.26
6.11
4.43
4.42
3.18
3.18
3.17
3.16
0.00
10.22
0.96
1.00
0.93
1.97
1.96
f1 (ppm)

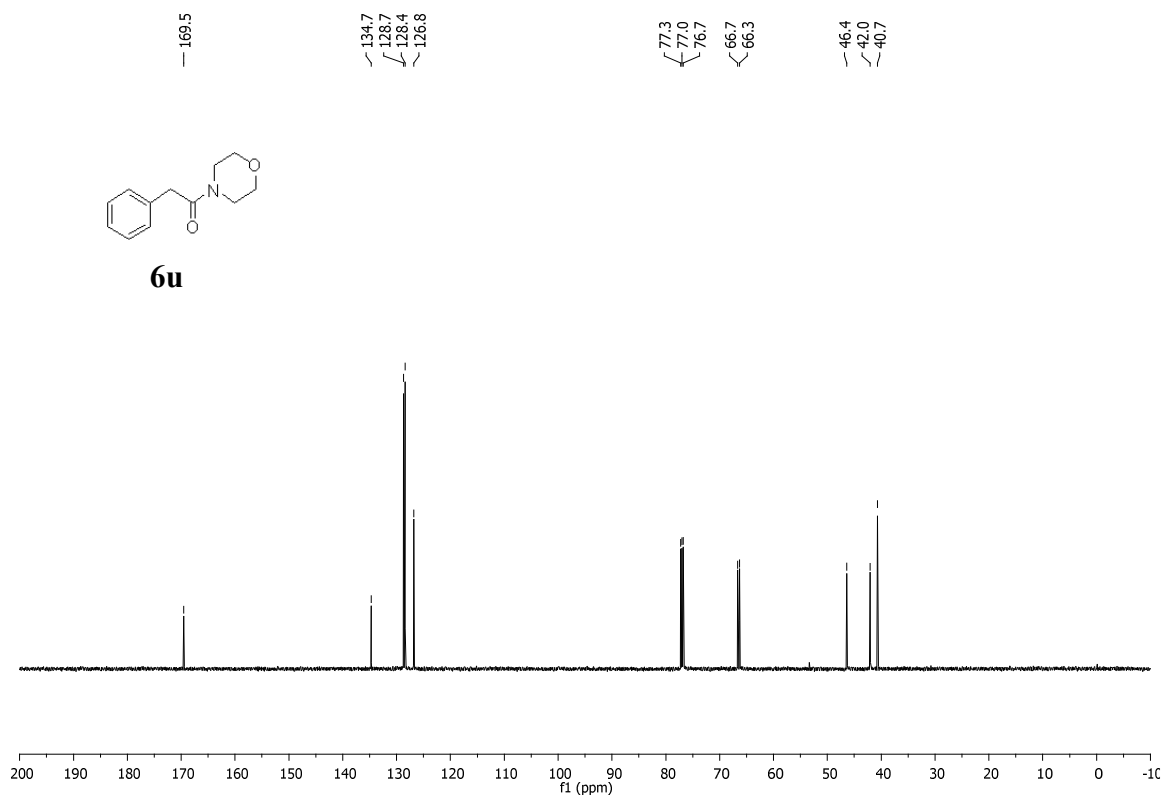
6t


170.5
138.1
136.5
134.6
128.6
128.5
127.7
127.4
126.3
122.3
77.3
77.0
76.7
43.6
40.7
f1 (ppm)

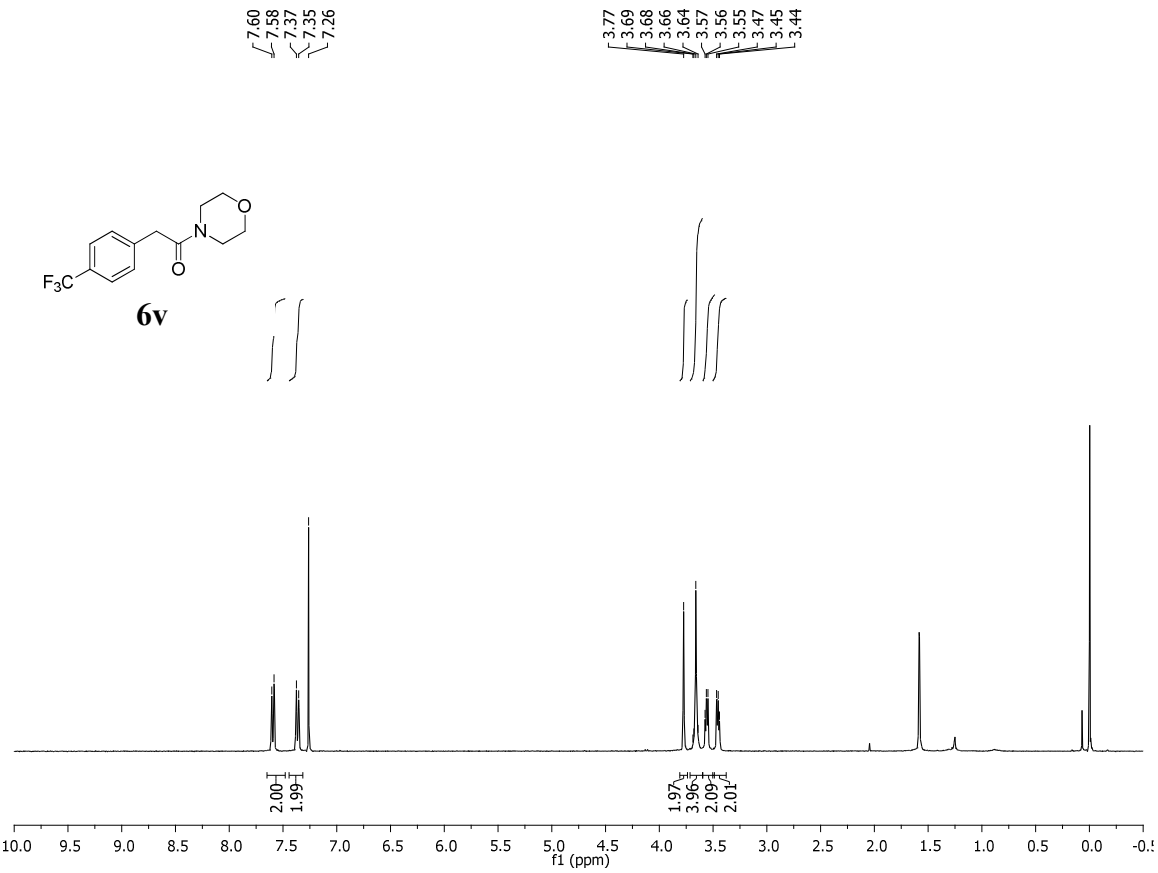
6t

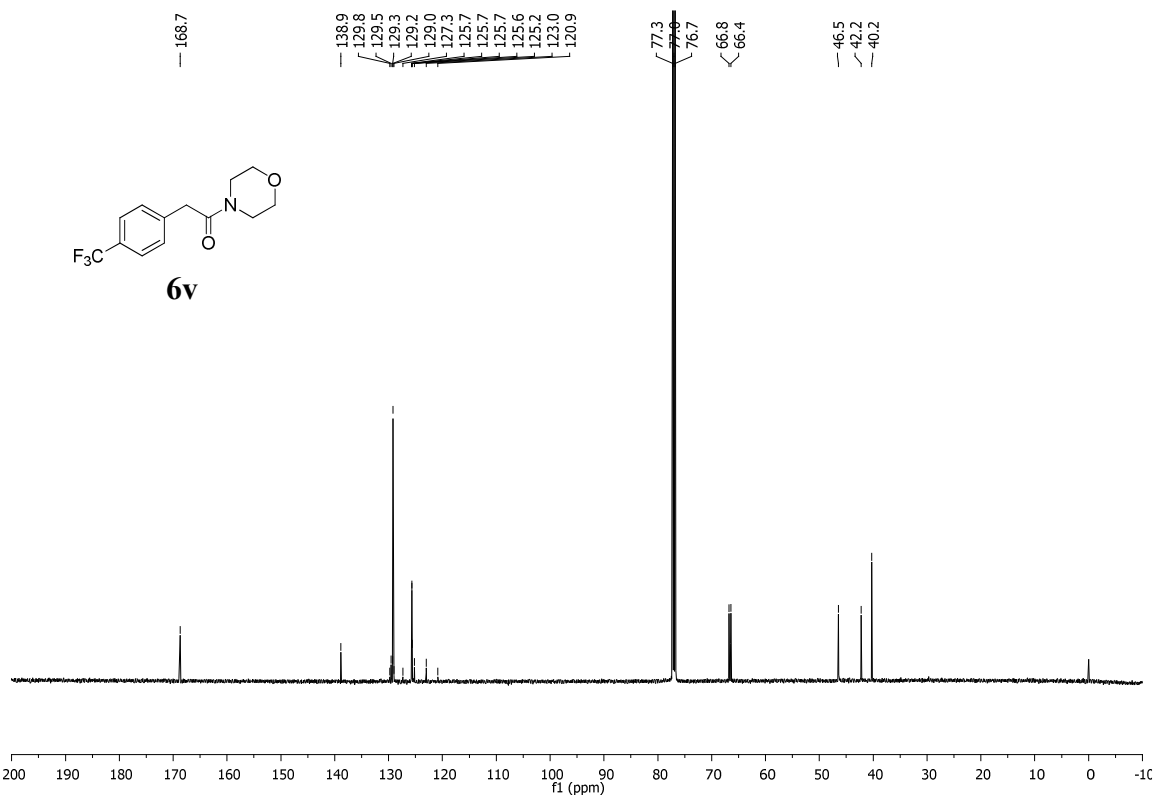

7.33
7.32
7.30
7.27
7.26
7.25
7.23
3.73
3.64
3.48
3.47
3.46
3.44
3.43
3.42
0.00
1.95
2.90
2.07
3.96
4.00
f1 (ppm)

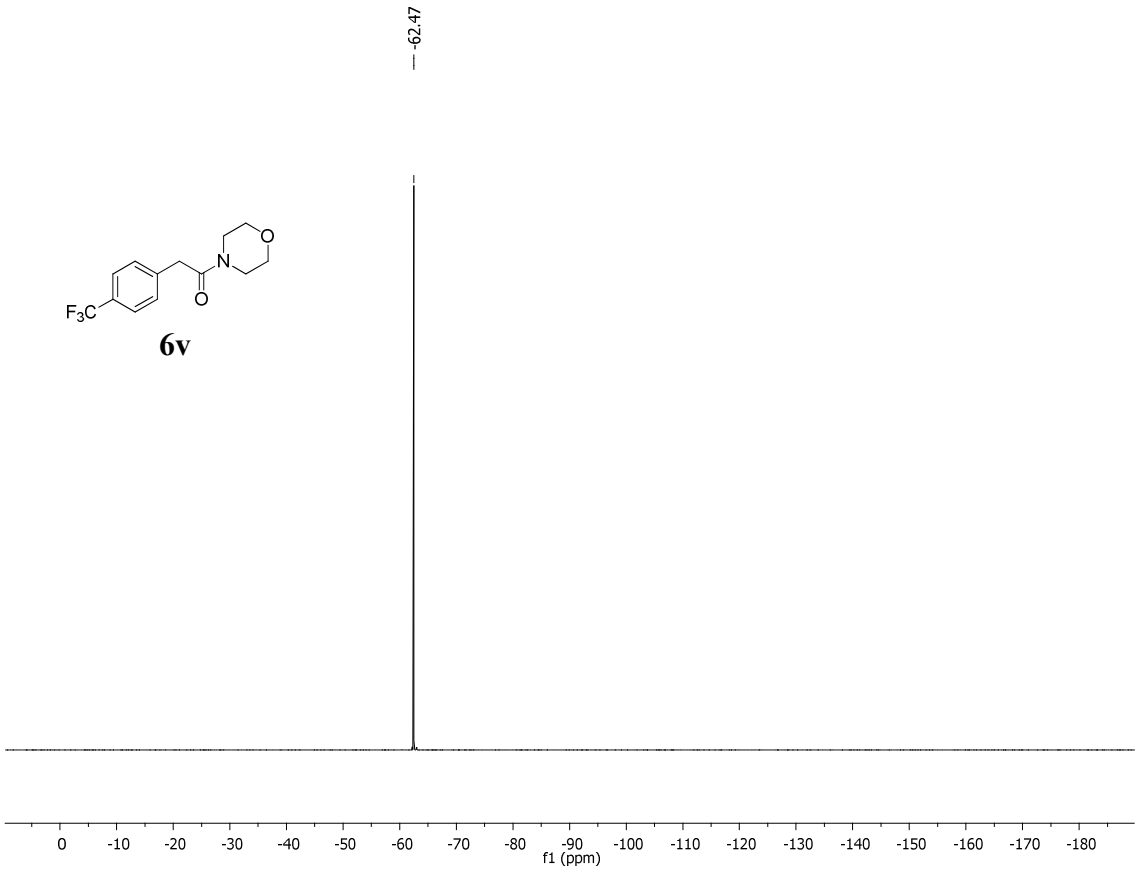
6u


169.5
134.7
128.7
128.4
126.8
77.3
77.0
76.7
66.7
66.3
46.4
42.0
40.7
f1 (ppm)

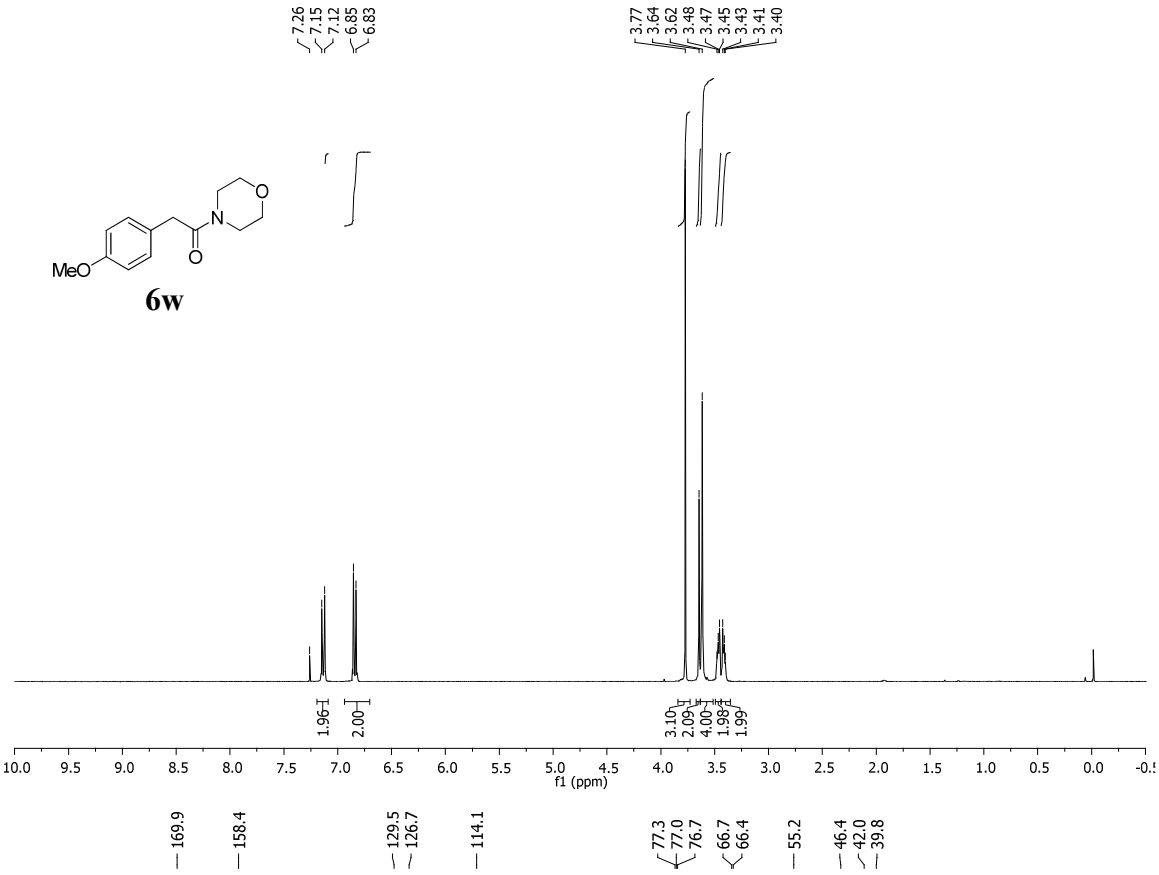
6u


7.60
7.58
7.37
7.35
7.26
3.77
3.69
3.68
3.66
3.64
3.57
3.56
3.55
3.47
3.45
3.44
O
N
O
F3C
6v
2.00
1.99
1.97
3.96
2.09
2.01
f1 (ppm)

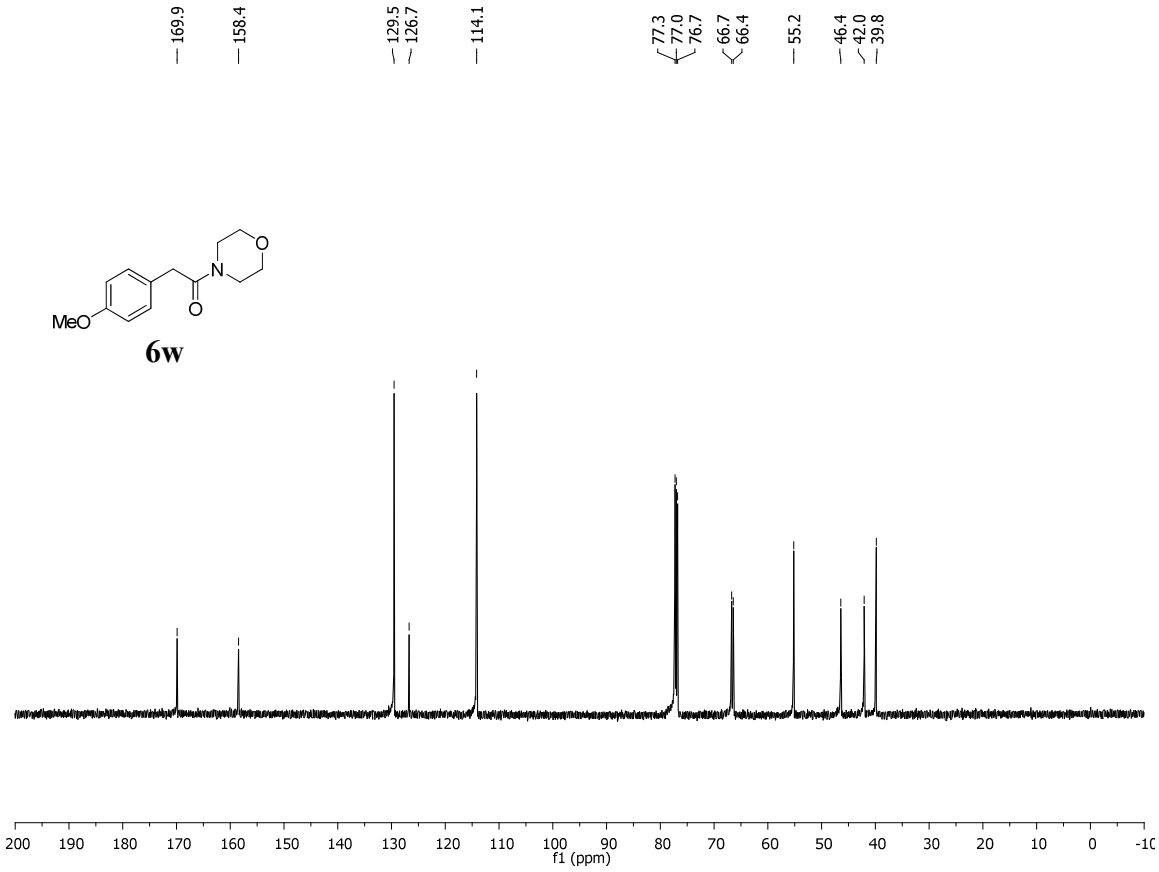

168.7
138.9
129.8
129.5
129.3
129.2
129.0
127.3
125.7
125.7
125.7
125.6
125.2
123.0
120.9
77.3
77.0
76.7
66.8
66.4
46.5
42.2
40.2
O
N
O
F3C
6v
f1 (ppm)


-62.47
O
N
O
F3C
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

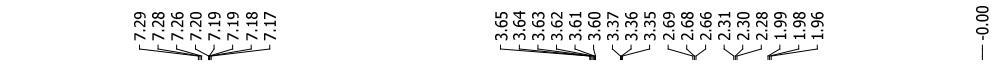
6v

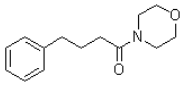

7.26
7.15
7.12
6.85
6.83
3.77
3.64
3.62
3.48
3.47
3.45
3.43
3.41
3.40
MeO
O
N
O
1.96
2.00
3.10
2.09
4.00
1.98
1.99
f1 (ppm)

6w

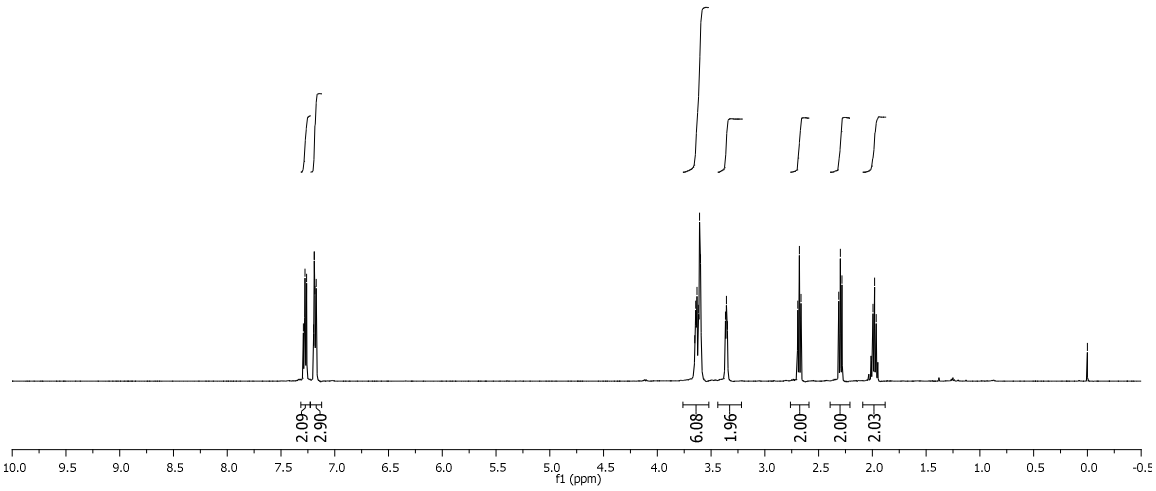

169.9
158.4
129.5
126.7
114.1
77.3
77.0
76.7
66.7
66.4
55.2
46.4
42.0
39.8
MeO
O
N
O
f1 (ppm)

6w

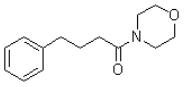

7.29
7.28
7.26
7.20
7.19
7.19
7.18
7.17
3.65
3.64
3.63
3.62
3.61
3.60
3.37
3.36
3.35
2.69
2.68
2.66
2.31
2.30
2.28
1.99
1.98
1.96
0.00



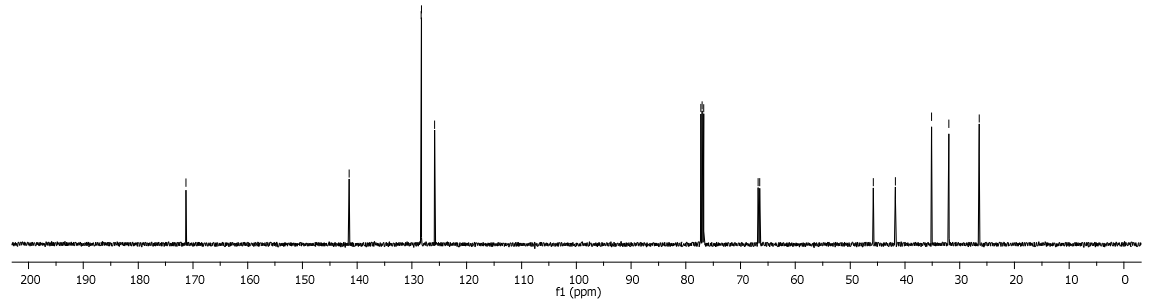
6x

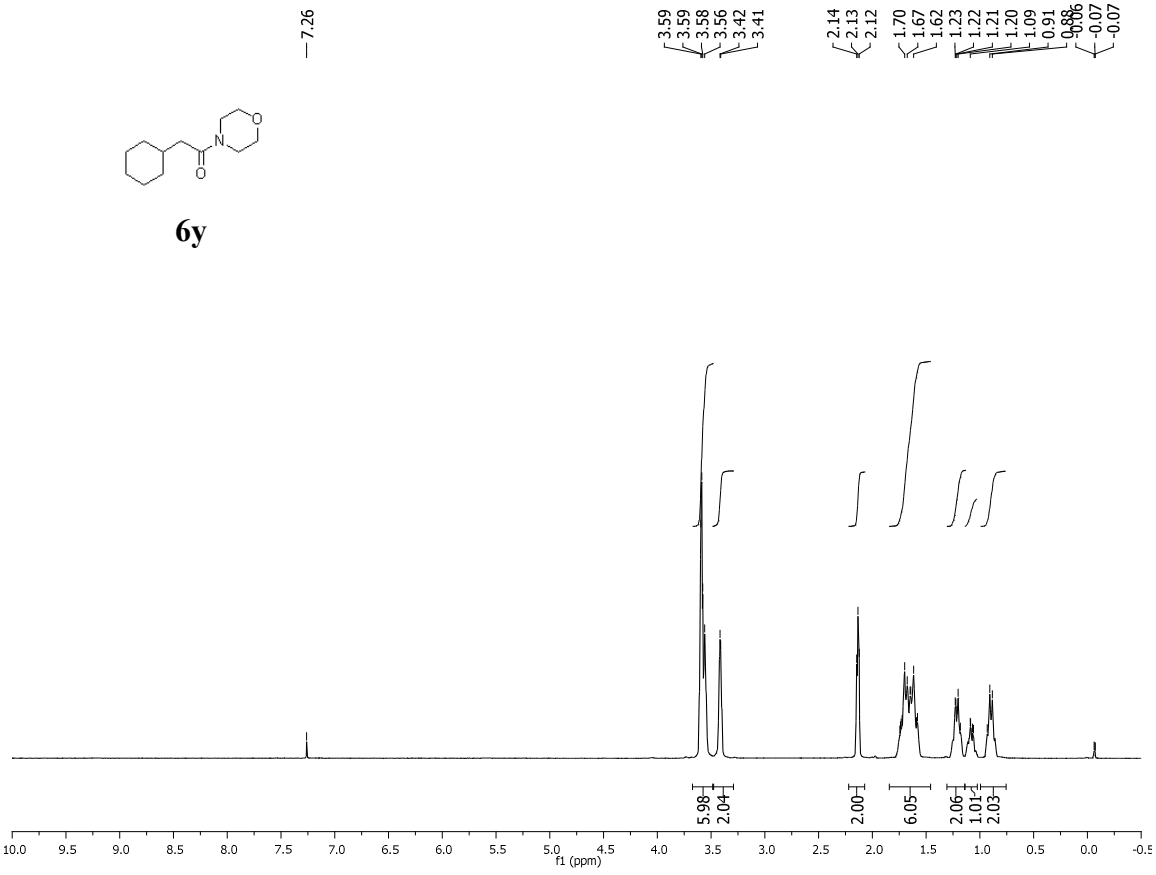

2.09
2.90
6.08
1.96
2.00
2.00
2.03
f1 (ppm)


171.3
141.5
128.4
128.3
125.8
77.3
77.0
76.7
66.8
66.5
45.8
41.8
35.1
32.0
26.4

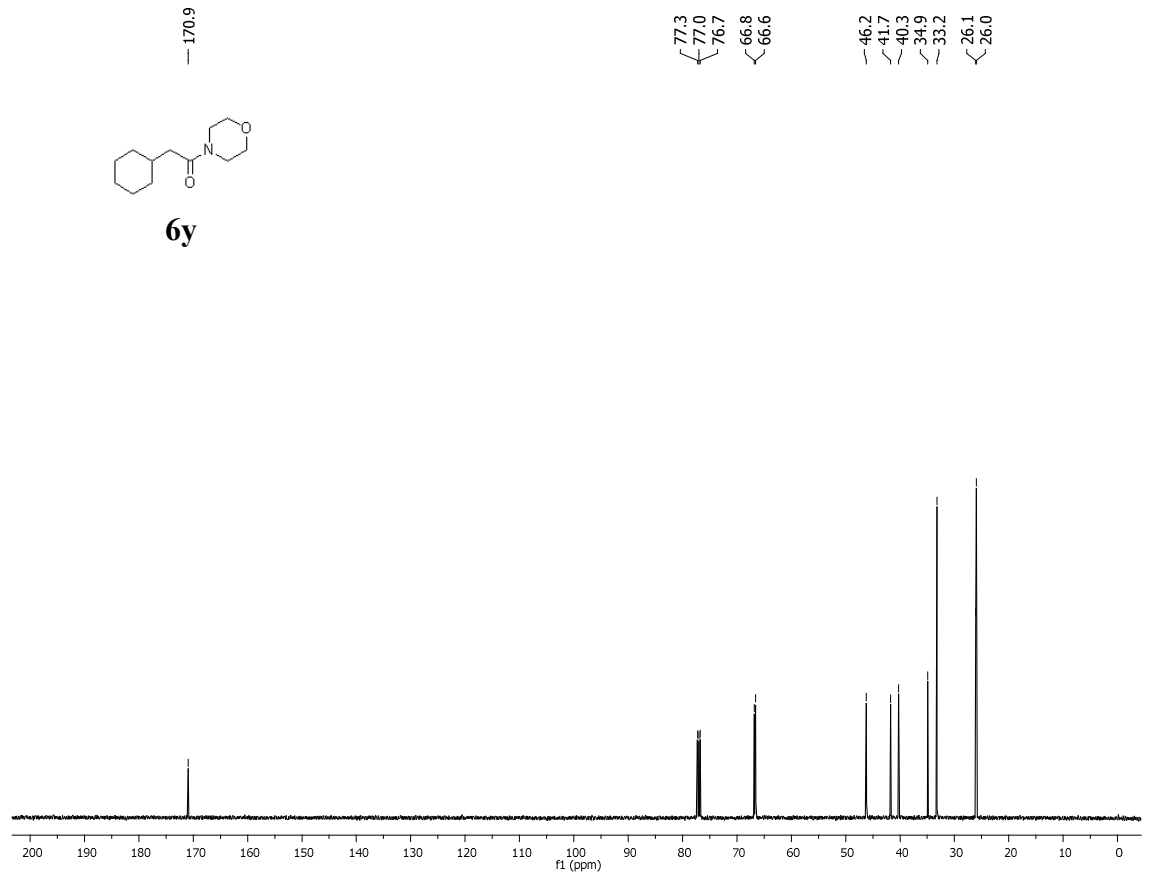


6x

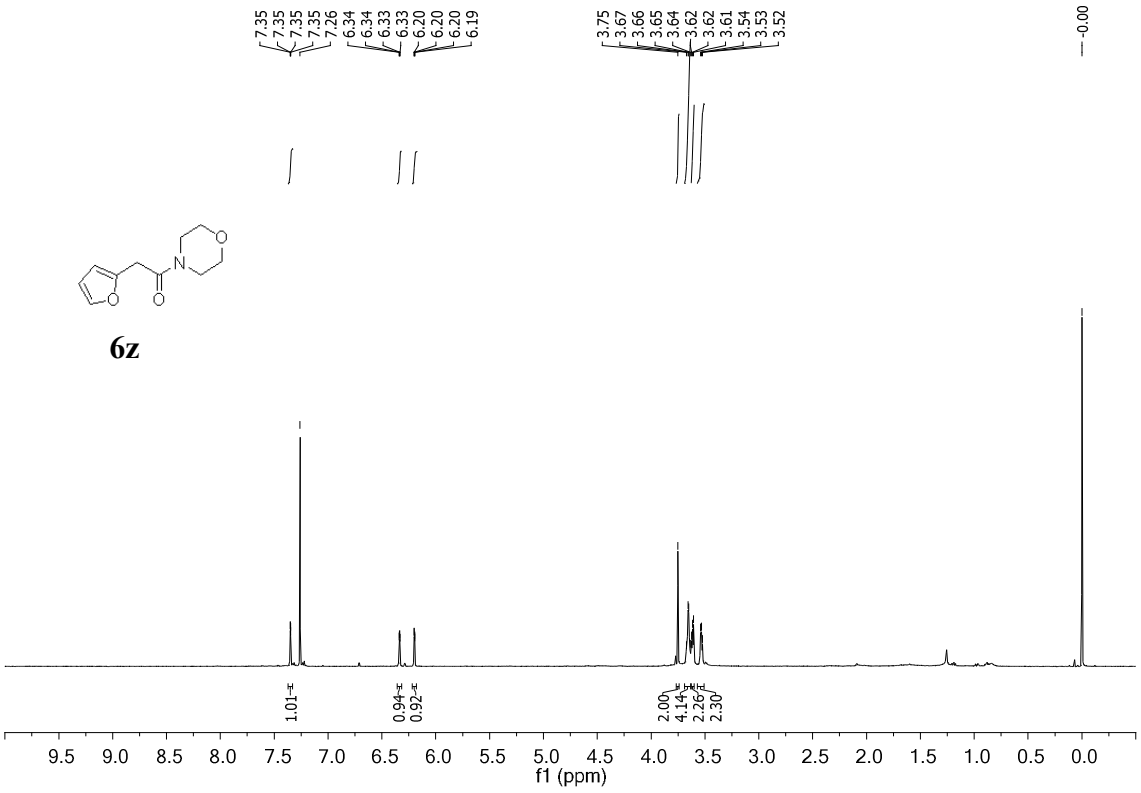

f1 (ppm)


7.26
3.59
3.59
3.58
3.56
3.42
3.41
2.14
2.13
2.12
1.70
1.67
1.62
1.23
1.22
1.21
1.20
1.09
0.91
0.88
0.06
-0.07
-0.07
5.98
2.04
2.00
6.05
2.06
1.01
2.03
f1 (ppm)

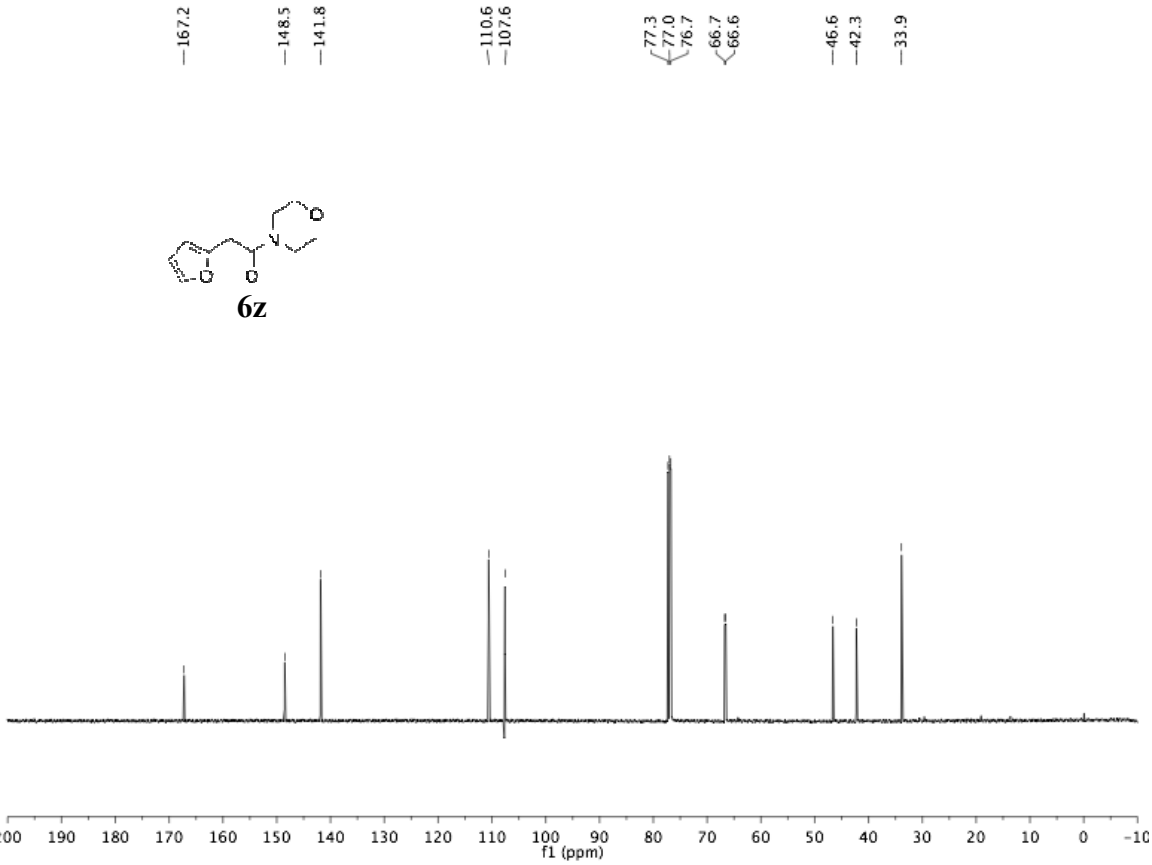
6y


170.9
77.3
77.0
76.7
66.8
66.6
46.2
41.7
40.3
34.9
33.2
26.1
26.0
f1 (ppm)

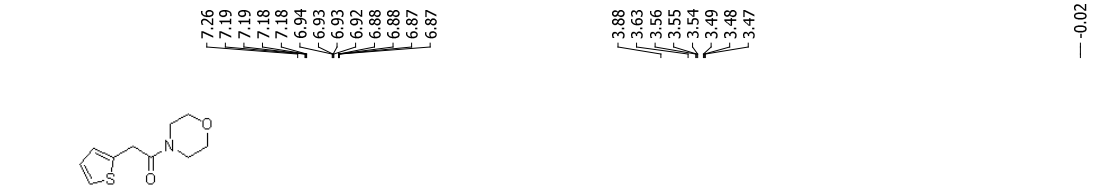
6y


7.35
7.35
7.35
7.35
7.26
6.34
6.34
6.33
6.33
6.20
6.20
6.20
6.19
3.75
3.67
3.66
3.65
3.64
3.62
3.62
3.61
3.54
3.53
3.52
0.00
1.01
0.94
0.92
2.00
4.14
2.26
2.30
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

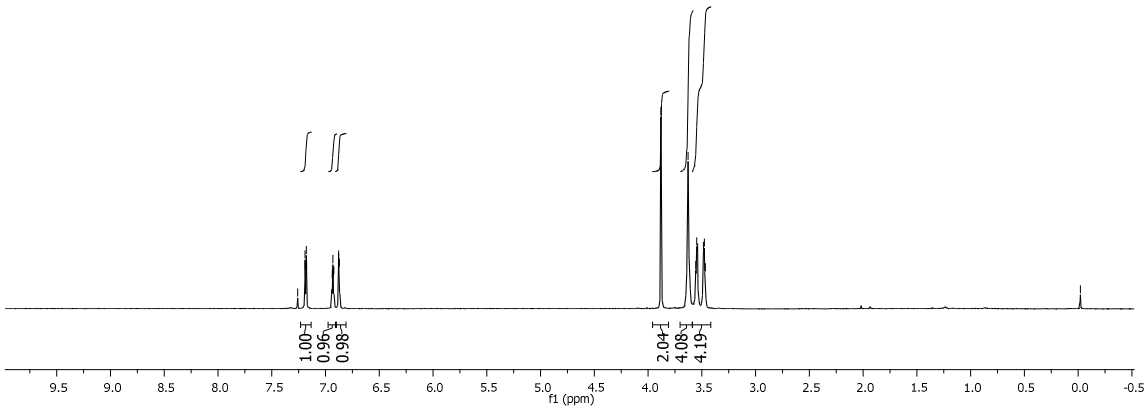
6z


167.2
148.5
141.8
110.6
107.6
77.3
77.0
76.7
66.7
66.6
46.6
42.3
33.9
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

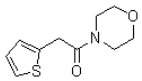
6z


7.26
7.19
7.19
7.18
7.18
6.94
6.93
6.93
6.92
6.88
6.88
6.87
6.87
3.88
3.63
3.56
3.55
3.54
3.49
3.48
3.47
-0.02

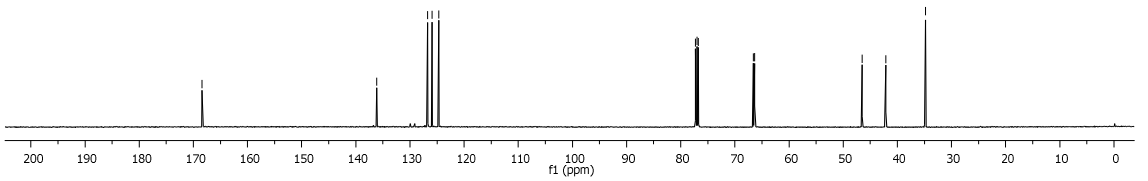
6aa

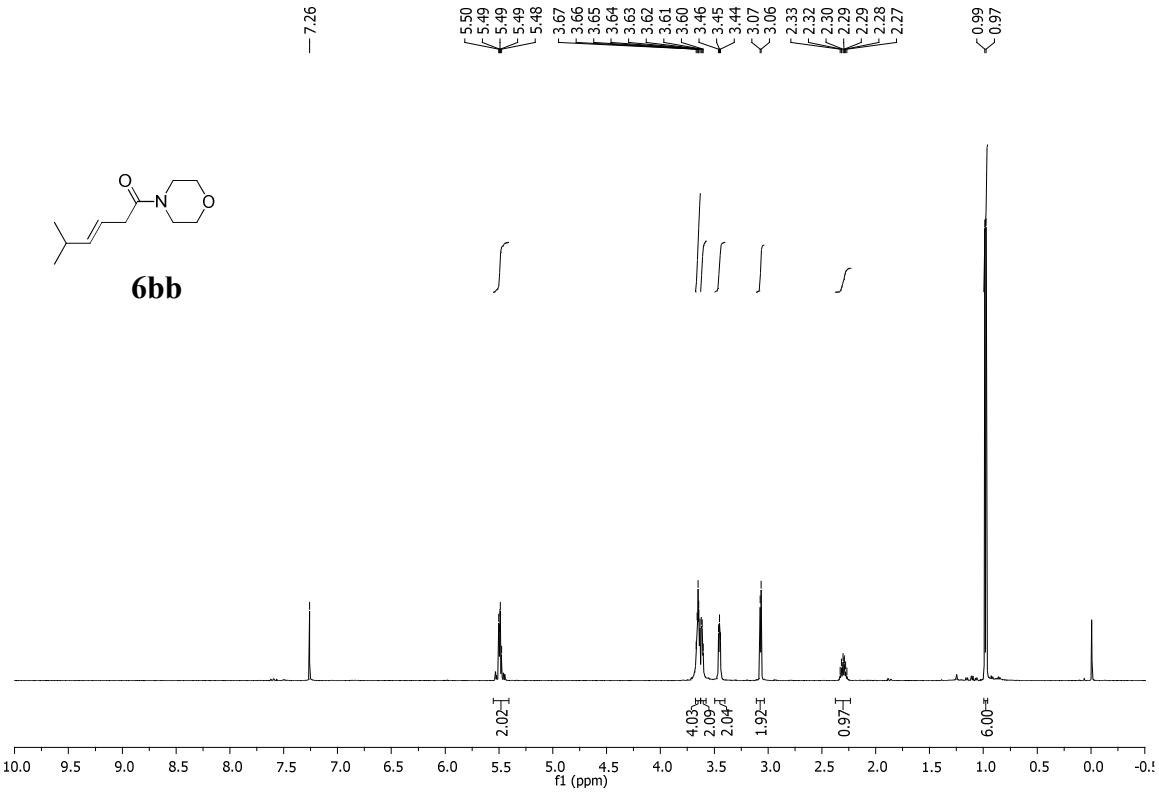

1.00
0.96
0.98
2.04
4.08
4.19
f1 (ppm)


168.4
136.2
126.8
125.9
124.7
77.3
77.0
76.7
66.6
66.3
46.5
42.2
34.8

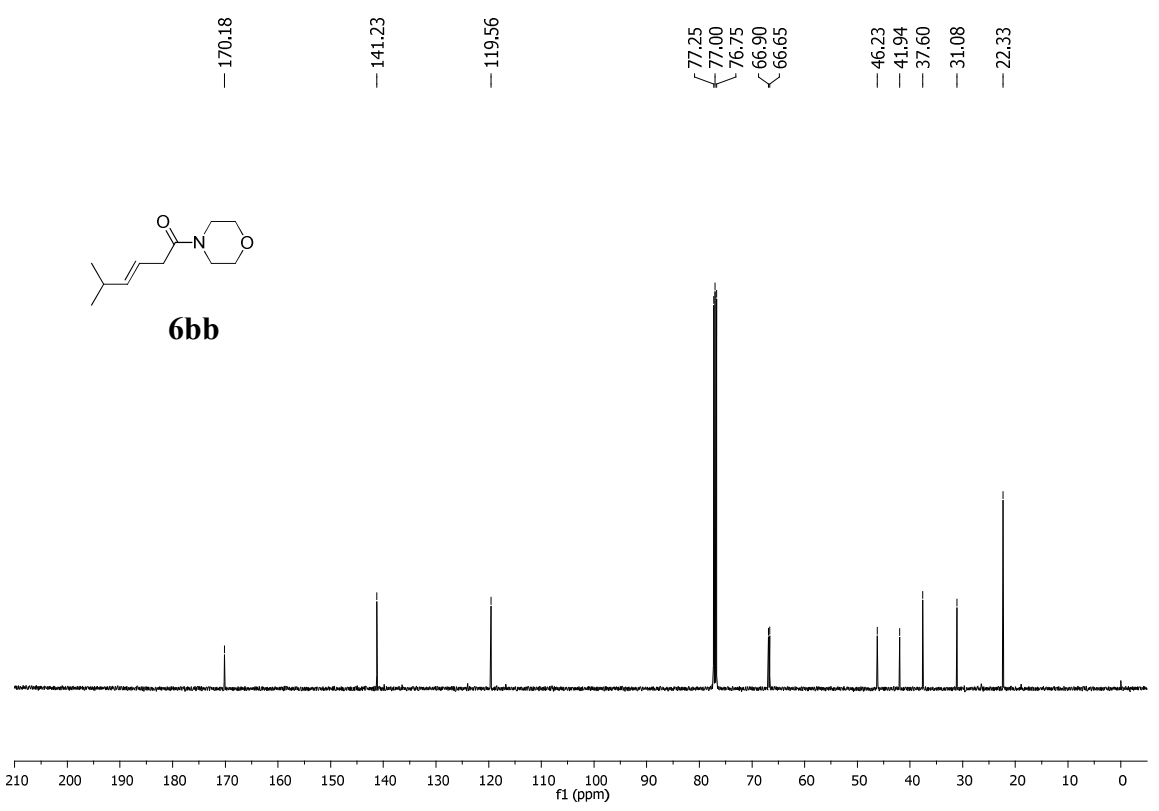


6aa


f1 (ppm)


7.26
5.50
5.49
5.49
5.49
5.48
3.67
3.66
3.65
3.64
3.63
3.62
3.61
3.60
3.46
3.45
3.44
3.07
3.06
2.33
2.32
2.30
2.29
2.29
2.28
2.27
0.99
0.97
2.02
4.03
2.09
2.04
1.92
0.97
6.00
f1 (ppm)

6bb


170.18
141.23
119.56
77.25
77.00
76.75
66.90
66.65
46.23
41.94
37.60
31.08
22.33
f1 (ppm)

6bb


7.37
7.37
7.36
7.32
7.31
7.29
7.26
7.24
7.23
7.22
6.50
6.46
6.35
6.34
6.33
6.32
6.31
6.30
3.69
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3.52
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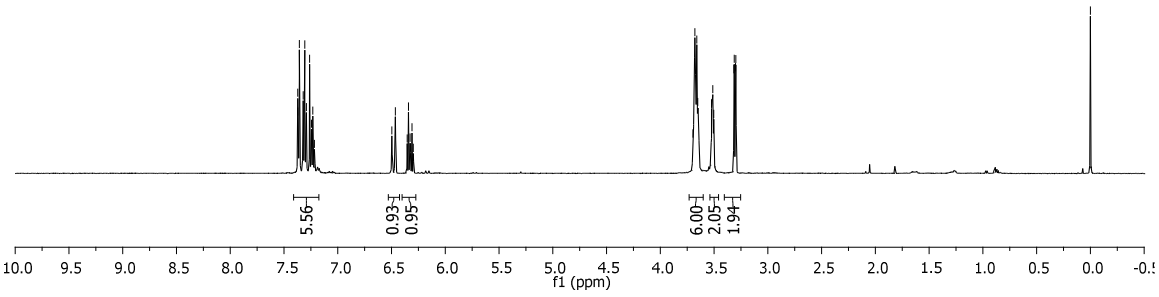
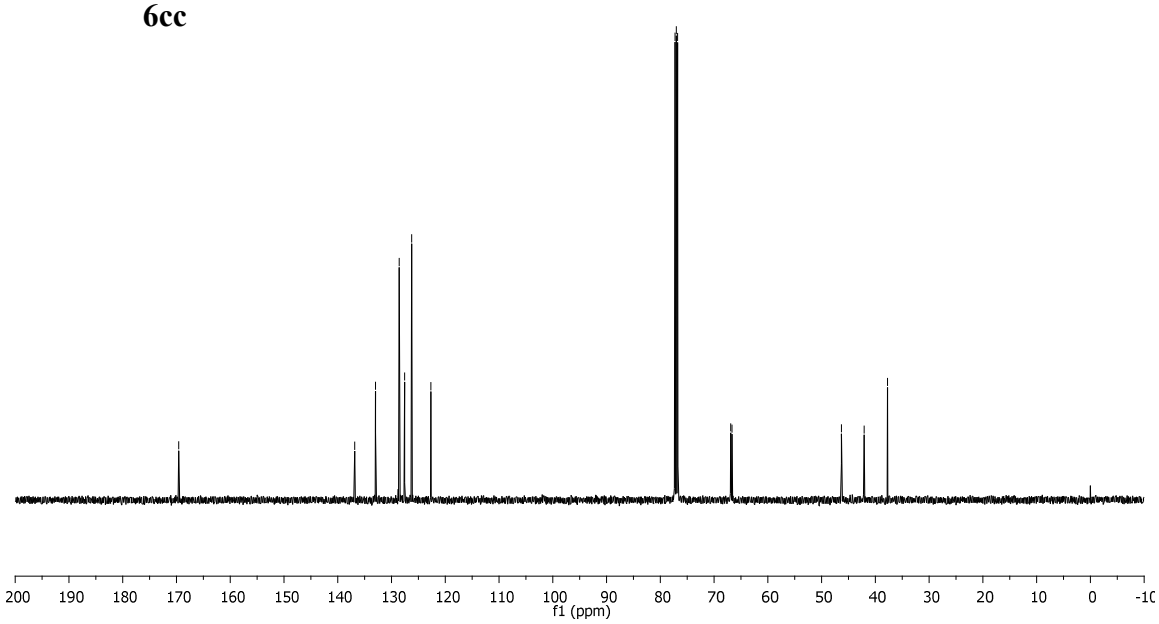
3.50
3.31
3.31
3.30
3.30
-0.00

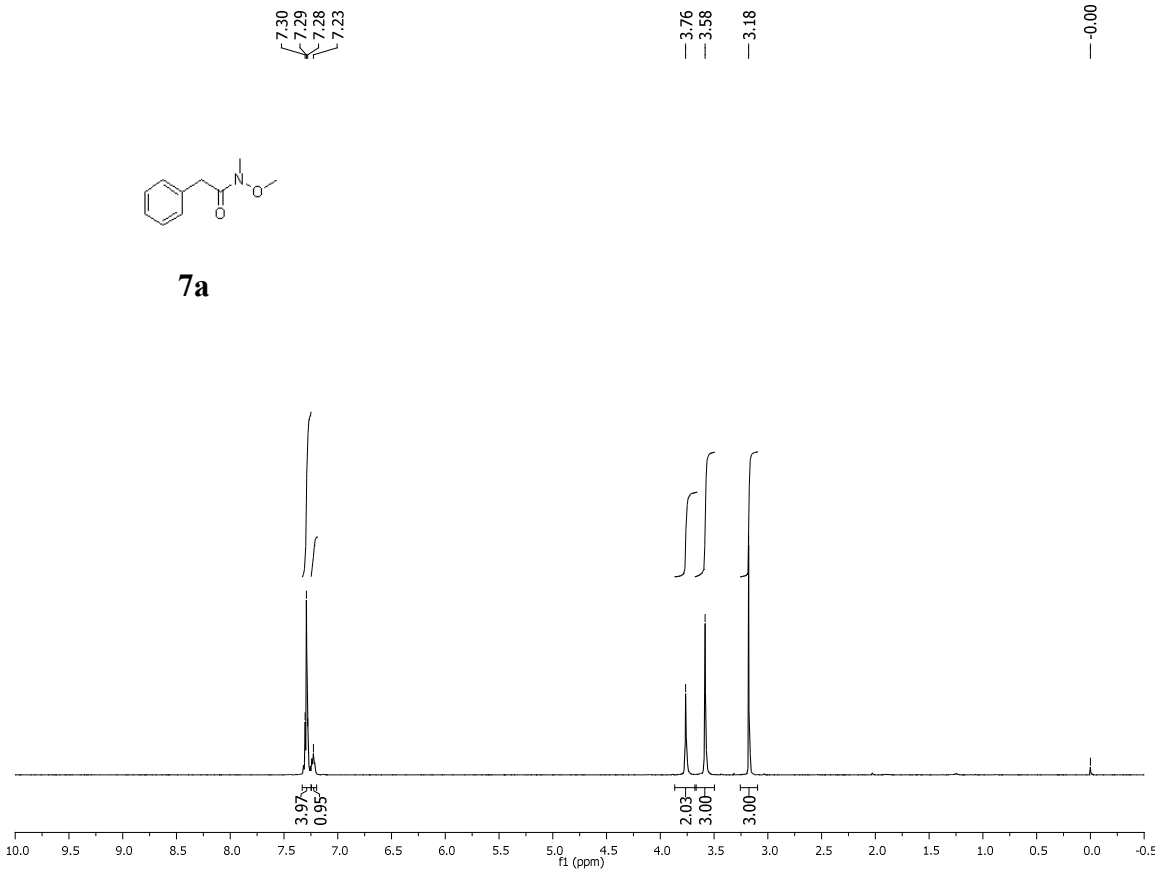
6cc


5.56
0.93
0.95
6.00
2.05
1.94
f1 (ppm)

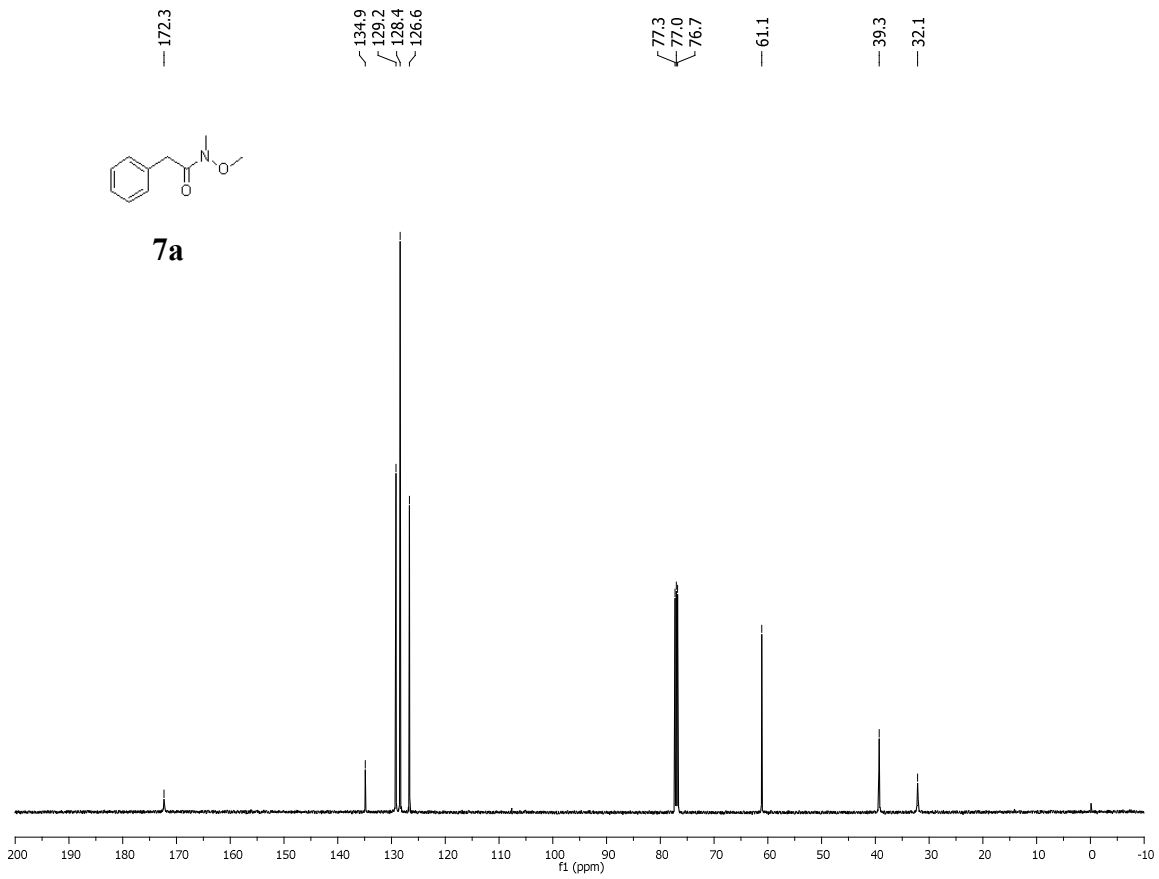

169.5
136.8
133.0
128.5
127.5
126.2
122.7
77.3
77.0
76.7
66.9
66.6
46.3
42.1
37.7

6cc

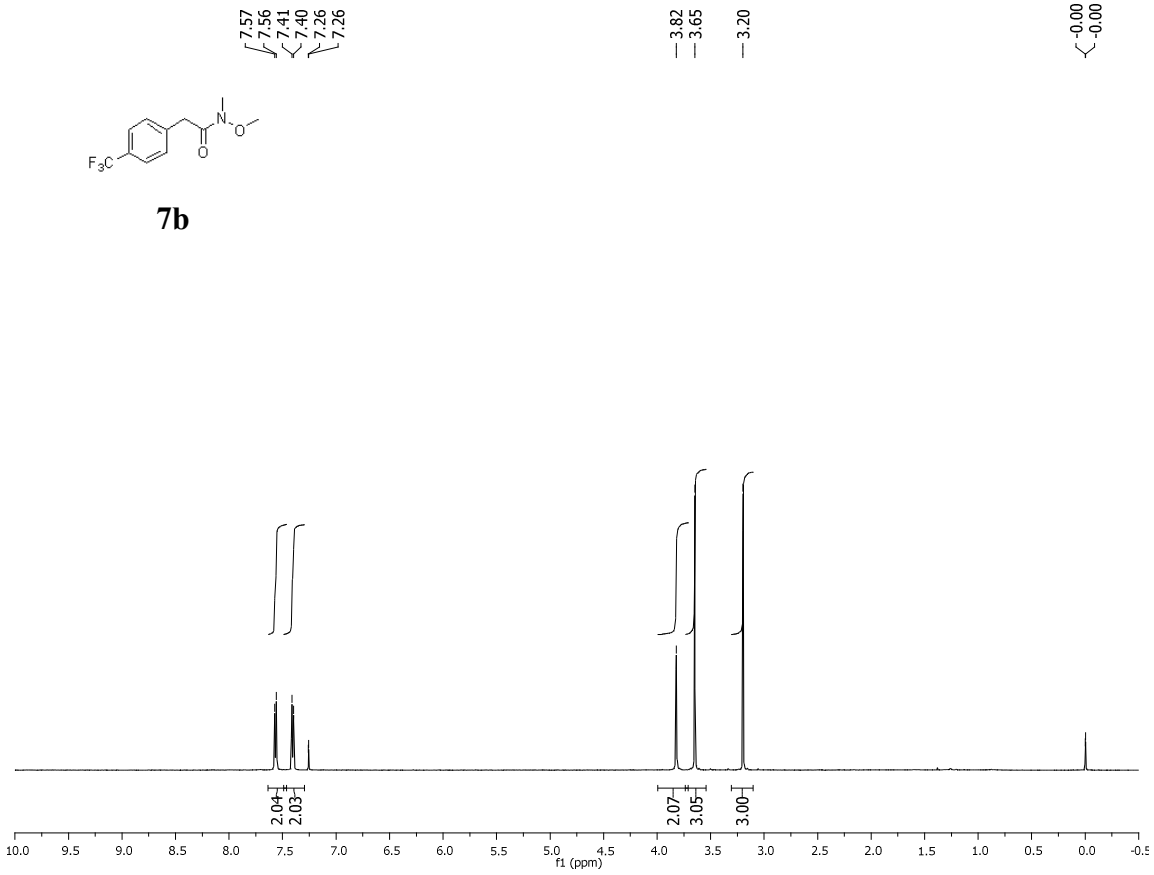

f1 (ppm)


7.30
7.29
7.28
7.23
3.76
3.58
3.18
-0.00
3.97
0.95
2.03
3.00
3.00
f1 (ppm)

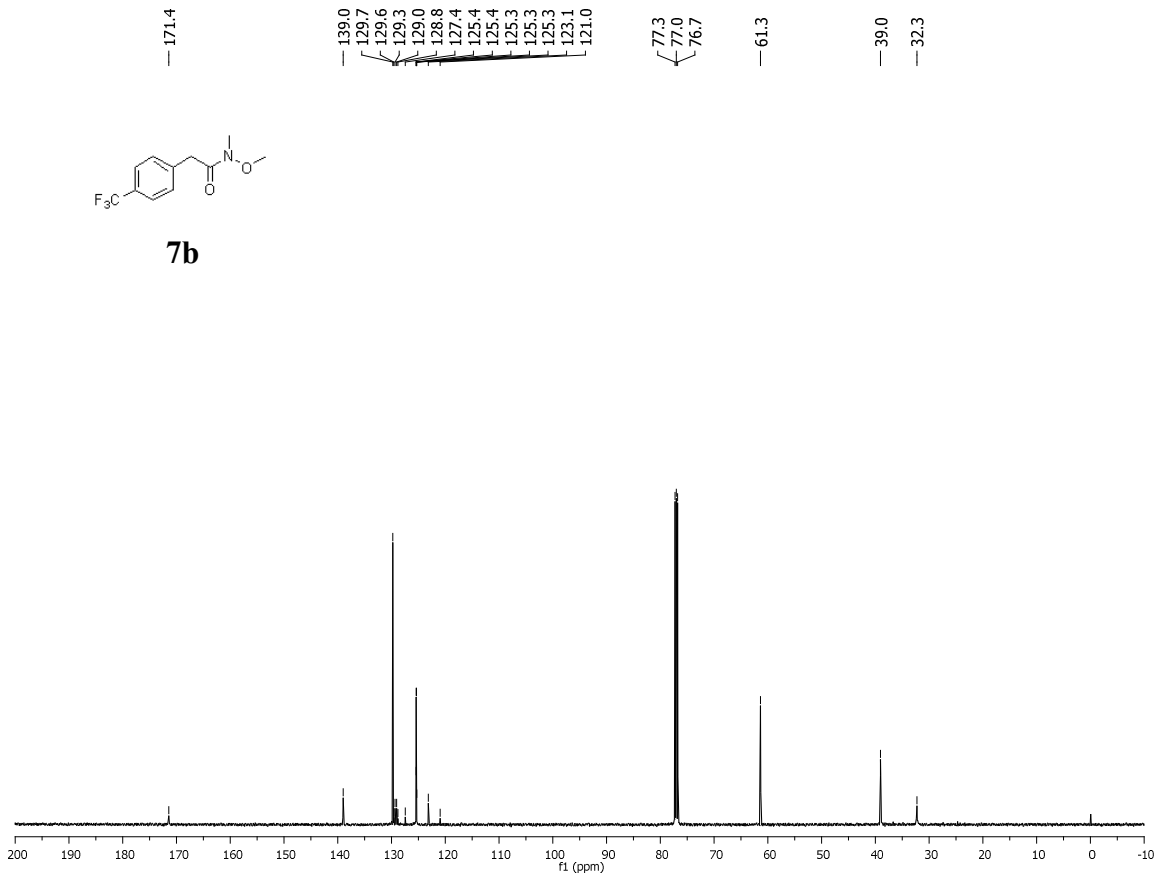
7a


172.3
134.9
129.2
128.4
126.6
77.3
77.0
76.7
61.1
39.3
32.1
f1 (ppm)

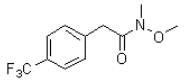
7a


7.57
7.56
7.41
7.40
7.26
7.26
3.82
3.65
3.20
-0.00
-0.00
2.04
2.03
2.07
3.05
3.00
f1 (ppm)

7b

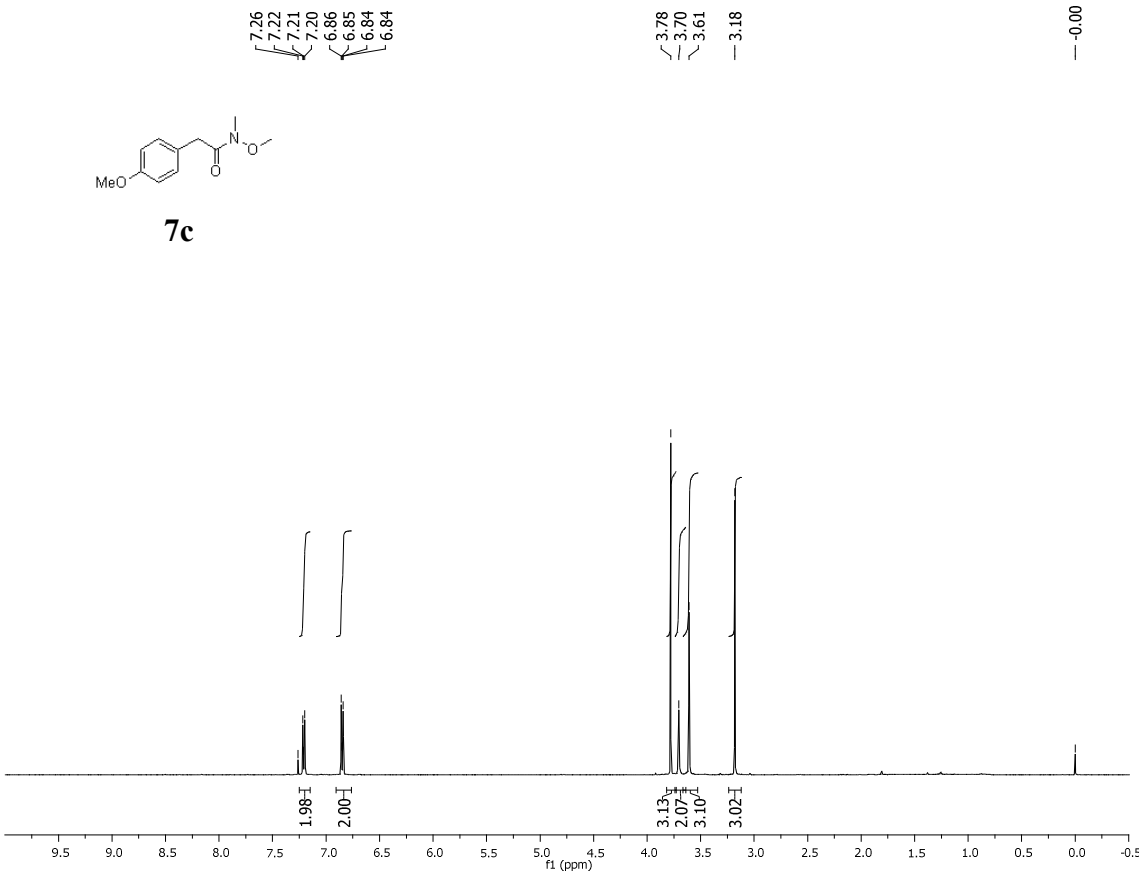

171.4
139.0
129.7
129.6
129.3
129.0
128.8
127.4
125.4
125.4
125.3
125.3
125.3
123.1
121.0
77.3
77.0
76.7
61.3
39.0
32.3
f1 (ppm)

7b

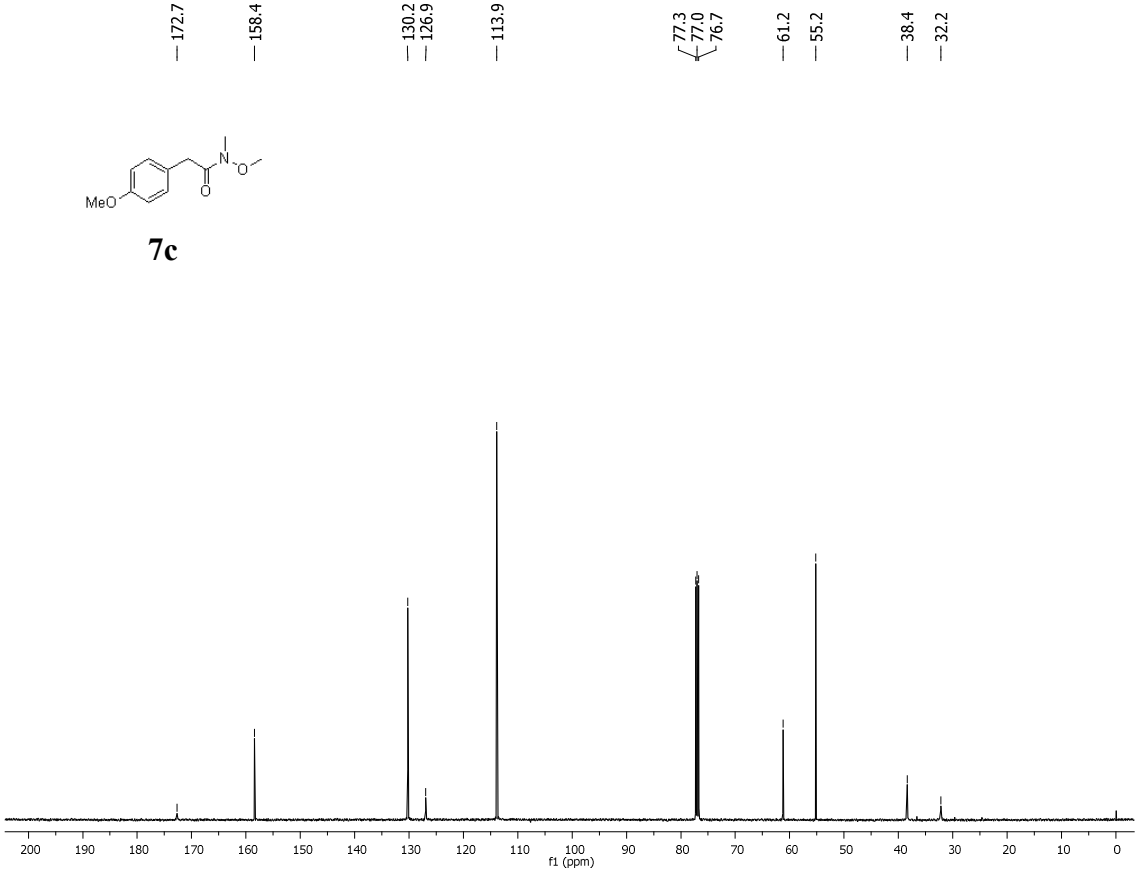


7b

-62.5
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

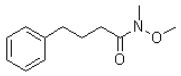

7.26
7.22
7.21
7.20
6.86
6.85
6.84
6.84
3.78
3.70
3.61
3.18
-0.00
MeO
N
O
O
1.98
2.00
3.13
2.07
3.10
3.02
f1 (ppm)

7c

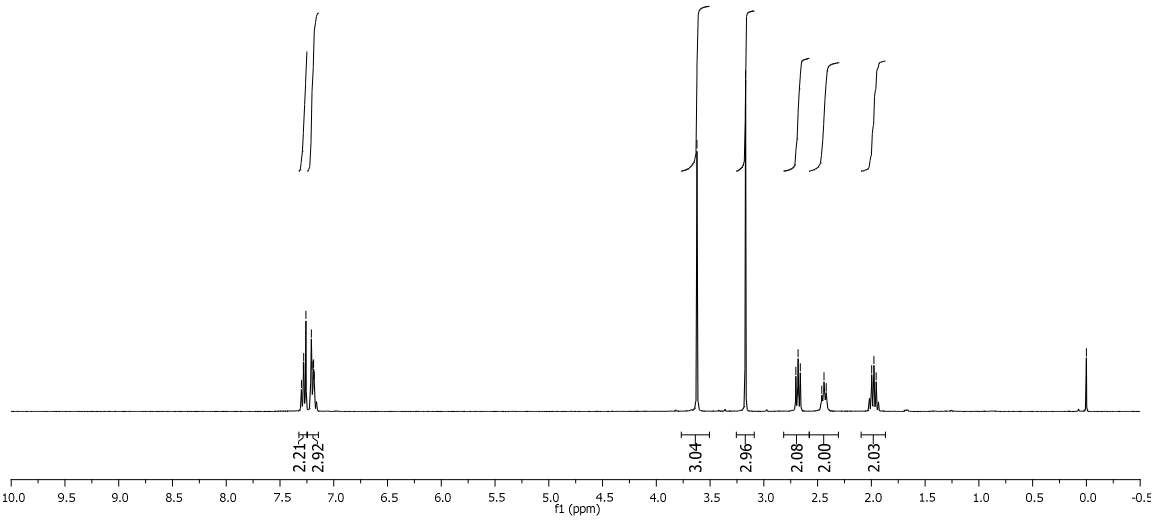

172.7
158.4
130.2
126.9
113.9
77.3
77.0
76.7
61.2
55.2
38.4
32.2
MeO
N
O
O
f1 (ppm)

7c

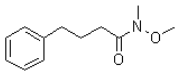

7.30
7.28
7.28
7.26
7.21
7.20
7.19
7.19
7.18
3.62
3.17
2.70
2.68
2.66
2.44
2.42
2.00
1.97
1.95
-0.00



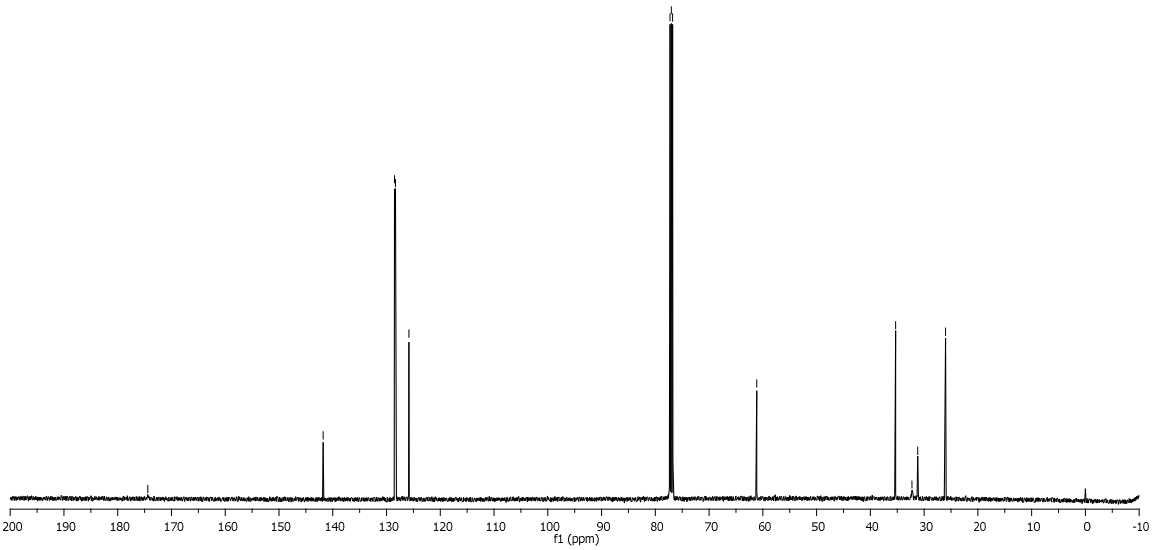
7d

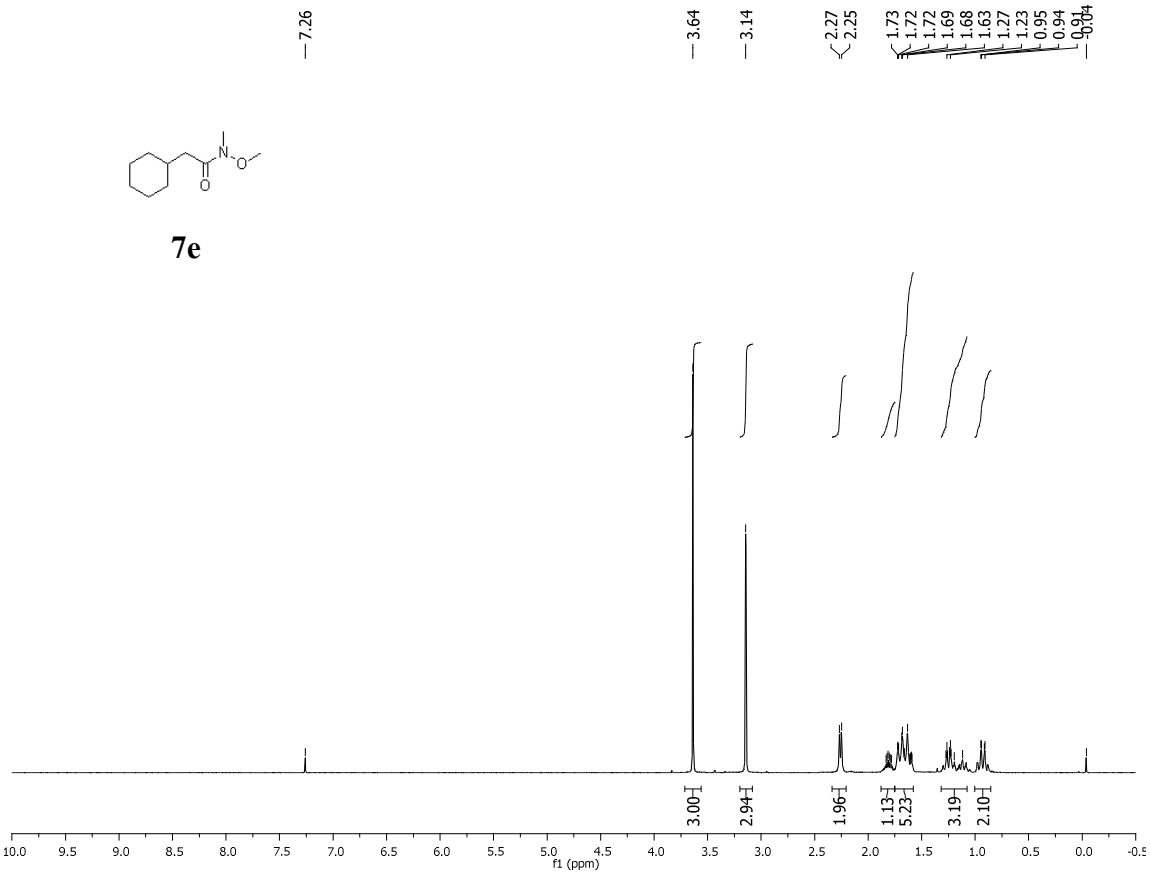

2.21
2.92
3.04
2.96
2.08
2.00
2.03
f1 (ppm)


174.4
141.8
128.5
128.3
125.8
77.3
77.0
76.7
61.1
35.3
32.2
31.2
26.0

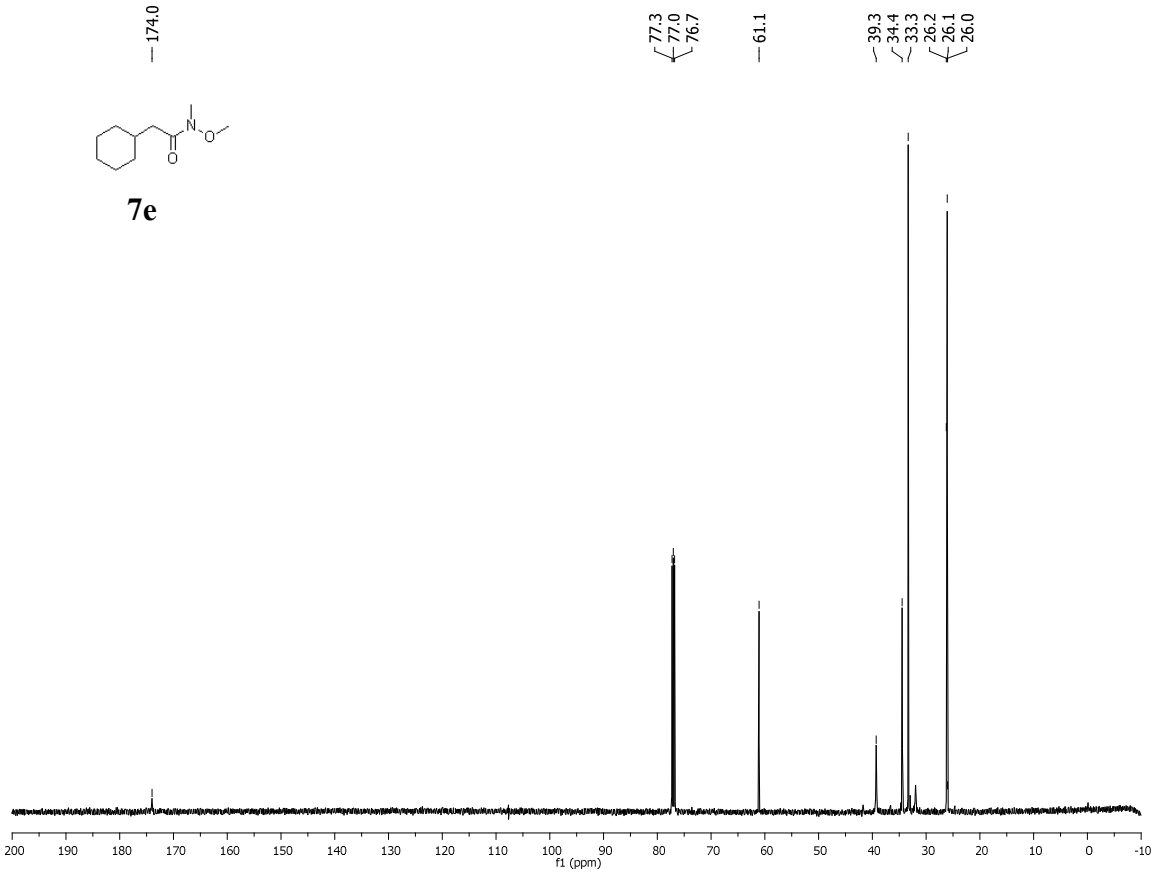


7d

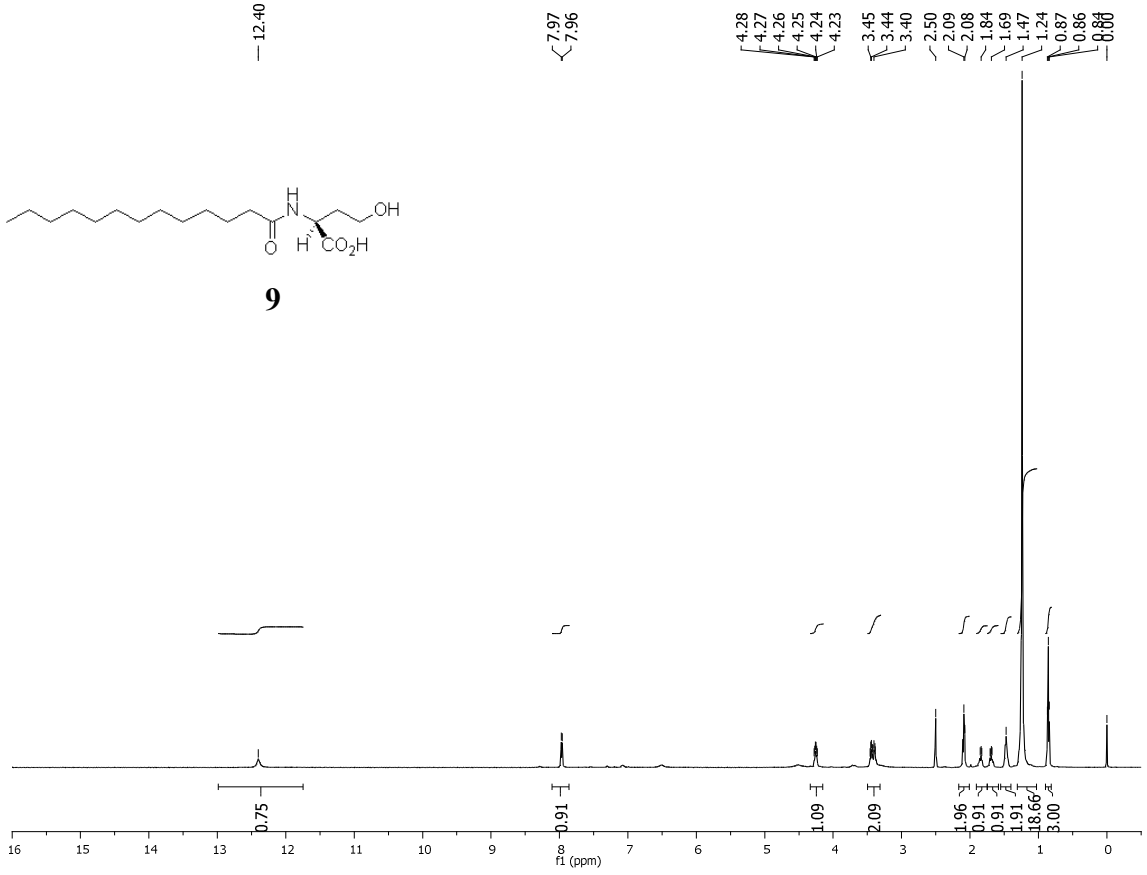

f1 (ppm)


7.26
3.64
3.14
2.27
2.25
1.73
1.72
1.72
1.69
1.68
1.63
1.27
1.23
0.95
0.94
0.91
0.04
3.00
2.94
1.96
1.13
5.23
3.19
2.10
f1 (ppm)

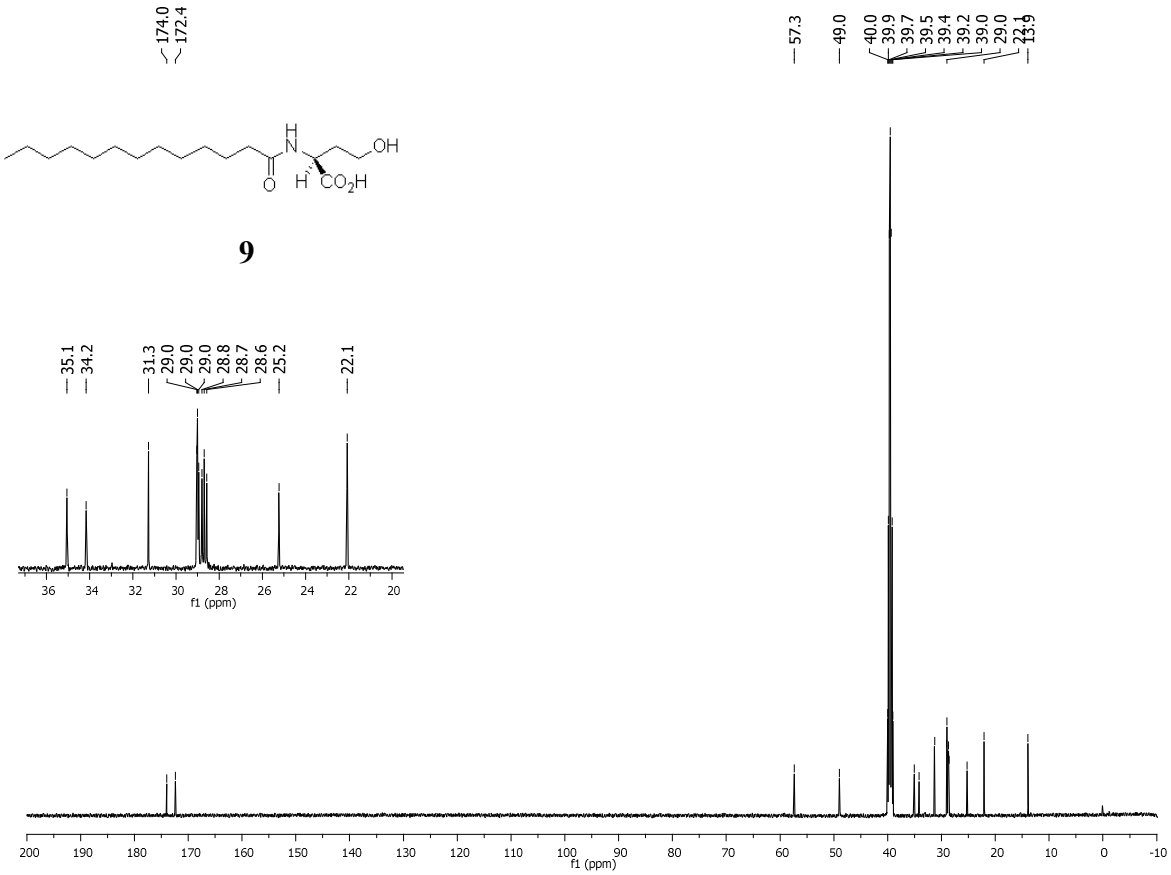
7e


174.0
77.3
77.0
76.7
61.1
39.3
34.4
33.3
26.2
26.1
26.0
f1 (ppm)

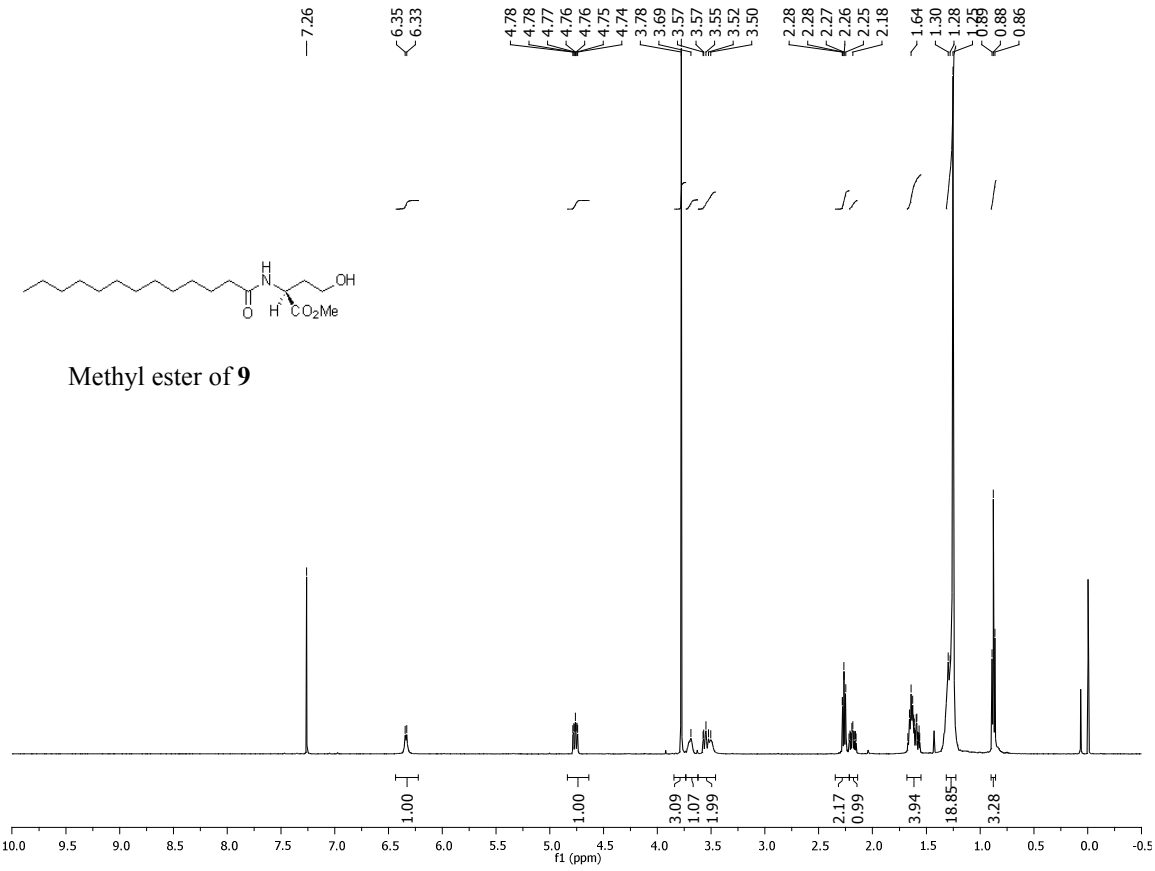
7e


12.40
7.97
7.96
4.28
4.27
4.26
4.25
4.24
4.23
3.45
3.44
3.40
2.50
2.09
2.08
1.84
1.69
1.47
1.24
0.87
0.86
0.84
0.00
OH
H
N
O
H
CO2H
0.75
0.91
1.09
2.09
1.96
0.91
0.91
1.91
18.66
3.00
f1 (ppm)

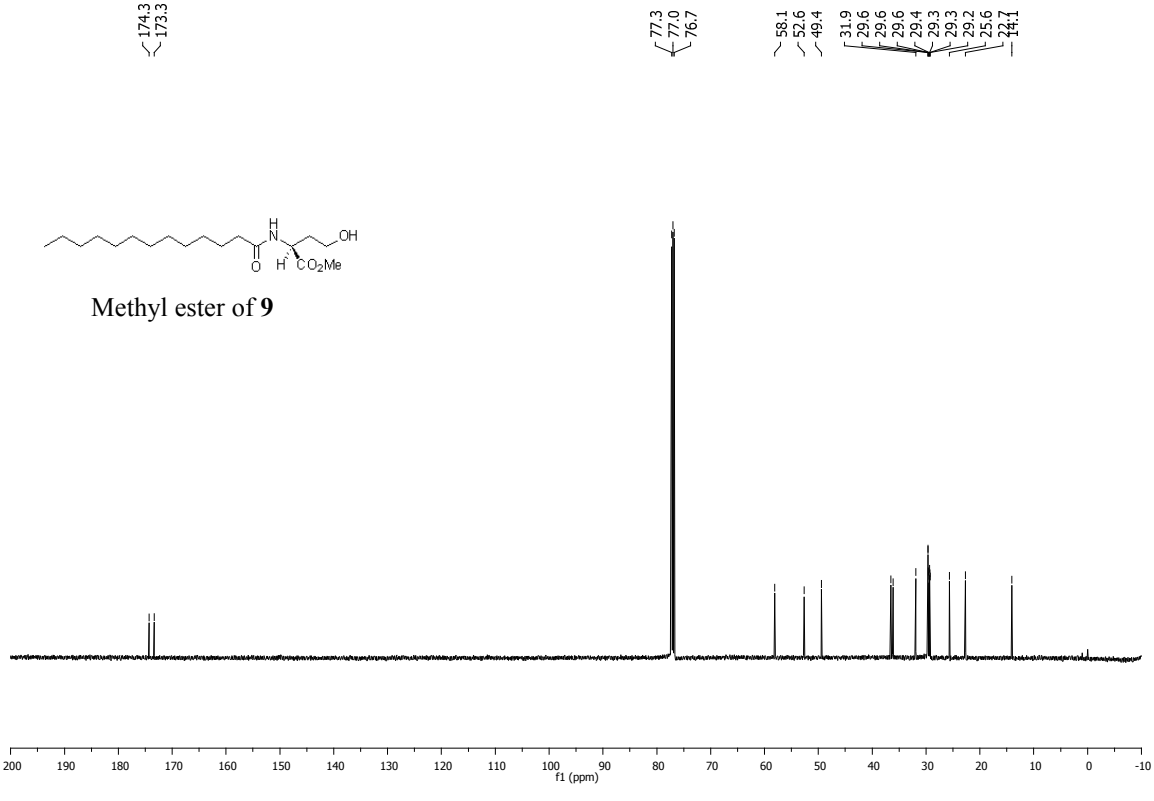
9


174.0
172.4
57.3
49.0
40.0
39.9
39.7
39.5
39.4
39.2
39.0
29.0
22.1
13.9
OH
H
N
O
H
CO2H
35.1
34.2
31.3
29.0
29.0
29.0
28.8
28.7
28.6
25.2
22.1
f1 (ppm)
f1 (ppm)

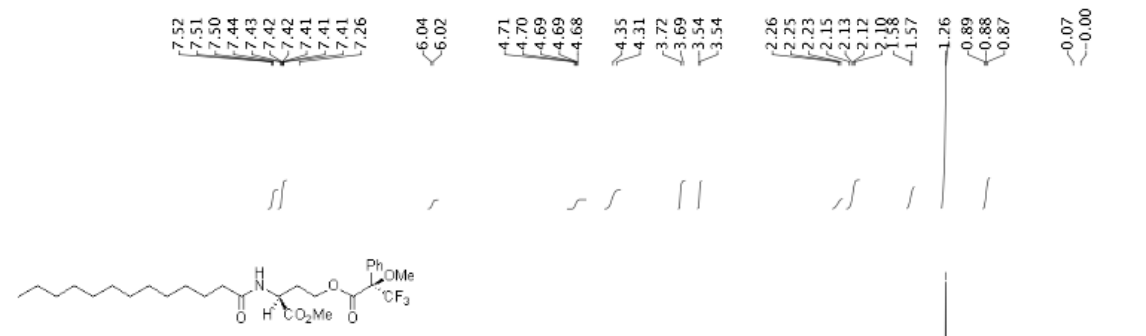
9



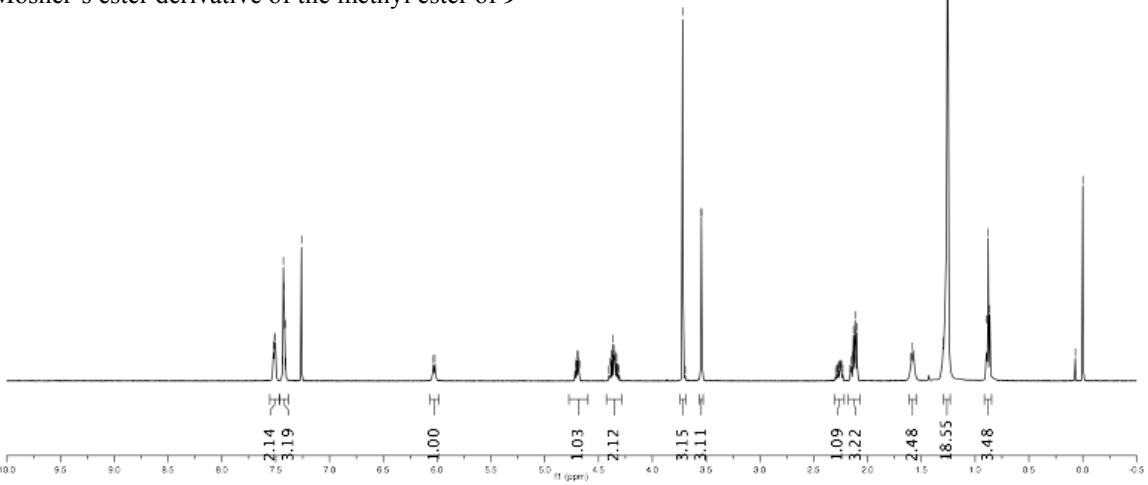
Methyl ester of **9**

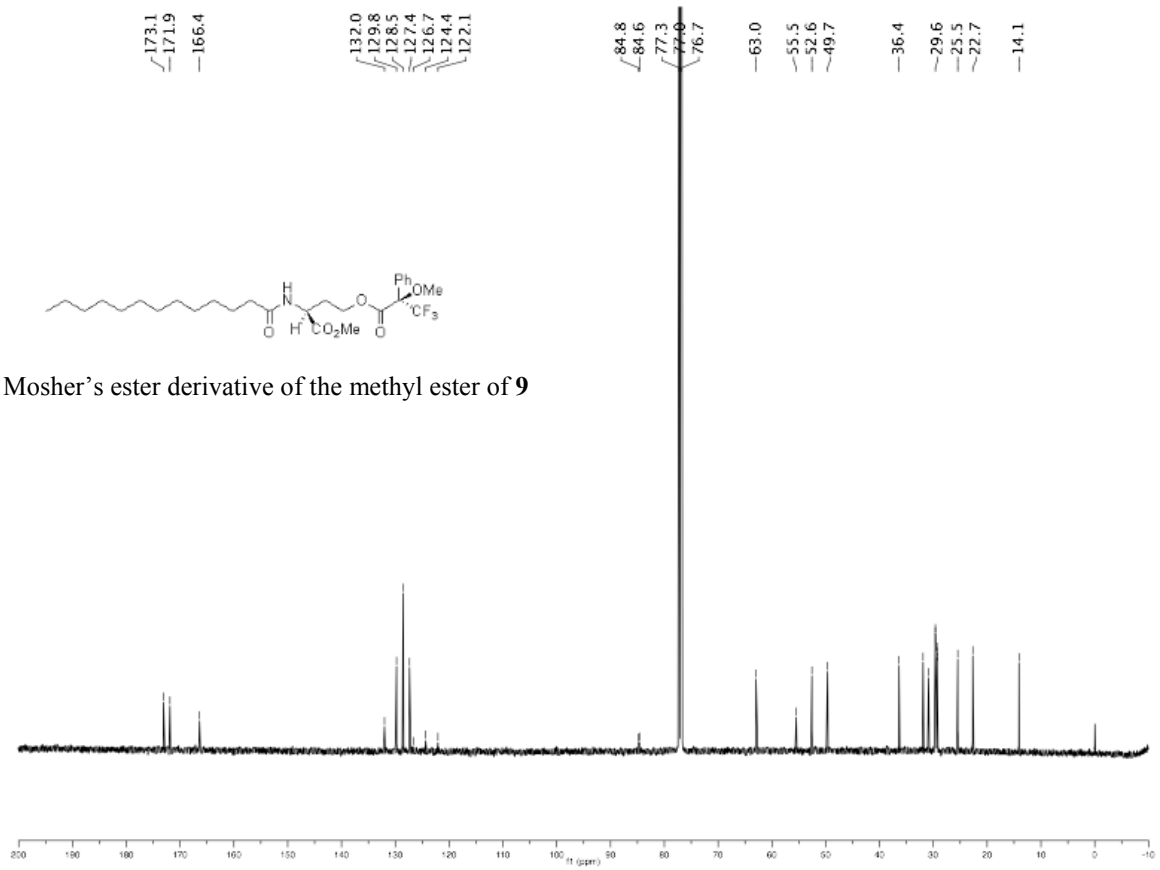


Methyl ester of **9**

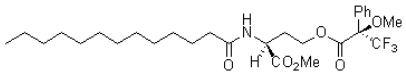


Mosher's ester derivative of the methyl ester of **9**

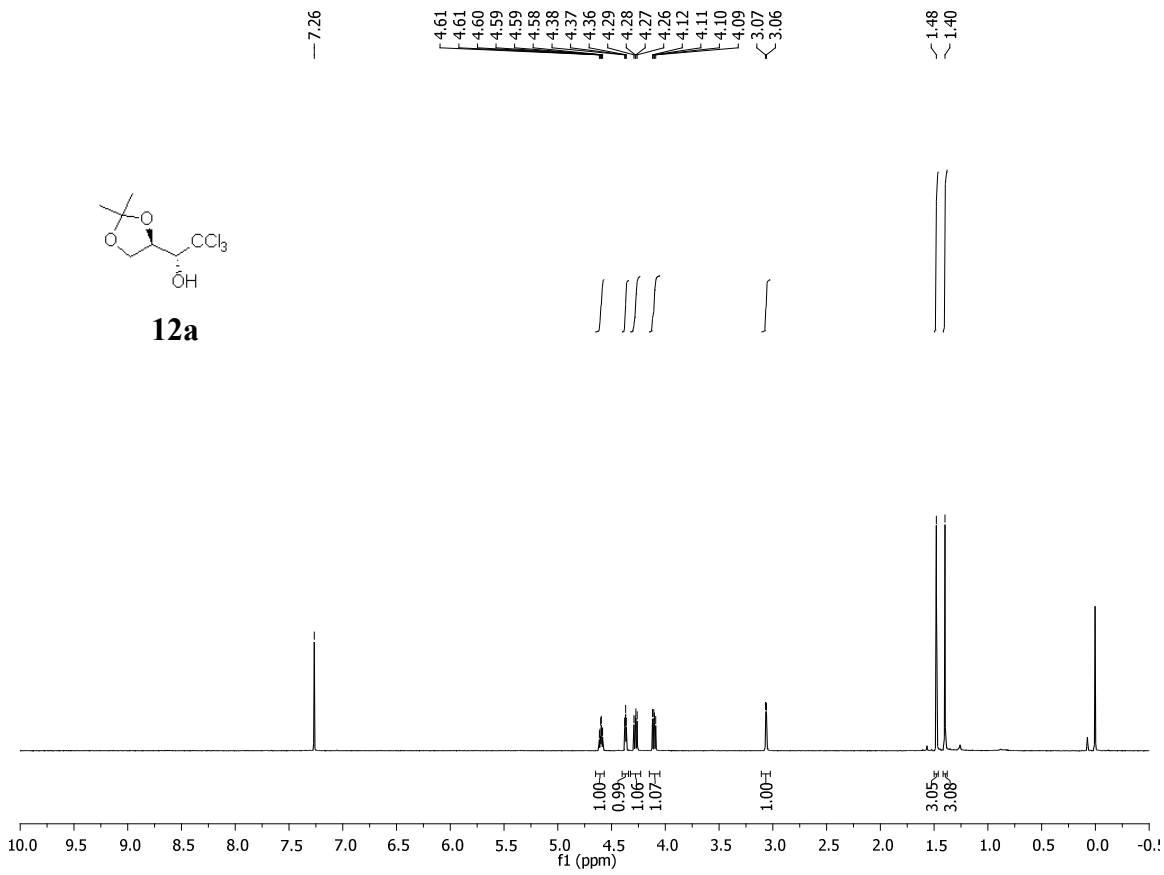




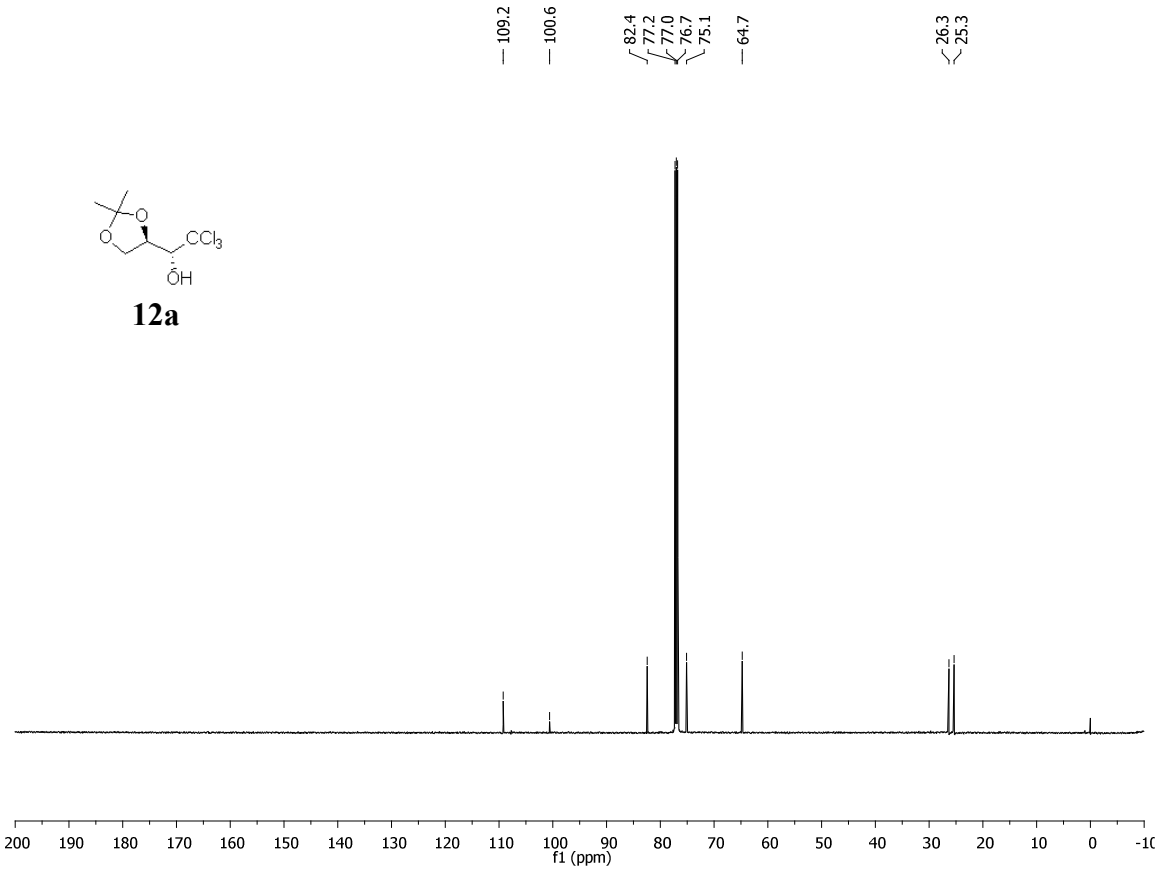
Mosher's ester derivative of the methyl ester of **9**



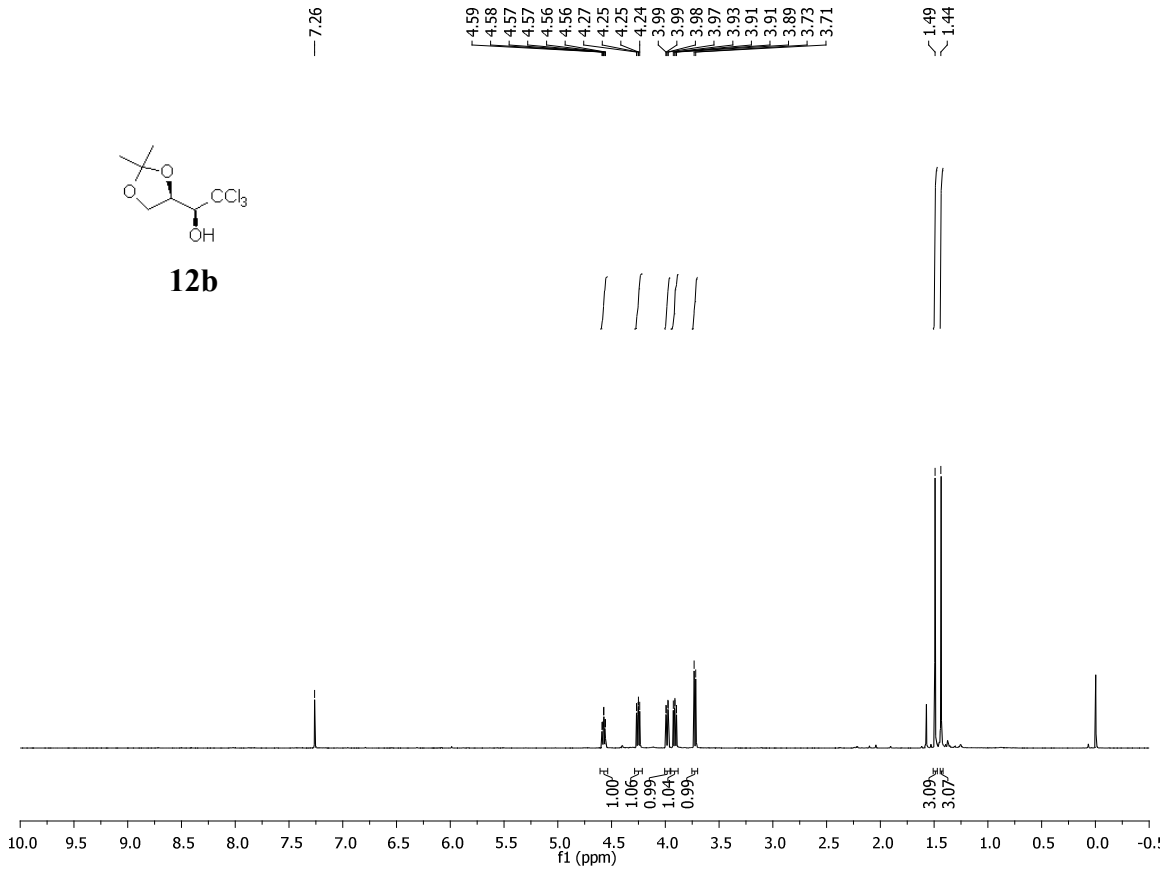
Mosher's ester derivative of the methyl ester of **9**


7.26
4.61
4.61
4.60
4.59
4.59
4.58
4.38
4.37
4.36
4.29
4.28
4.27
4.26
4.12
4.11
4.10
4.09
3.07
3.06
1.48
1.40
CCl3
OH
1.00
0.99
1.06
1.07
1.00
3.05
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

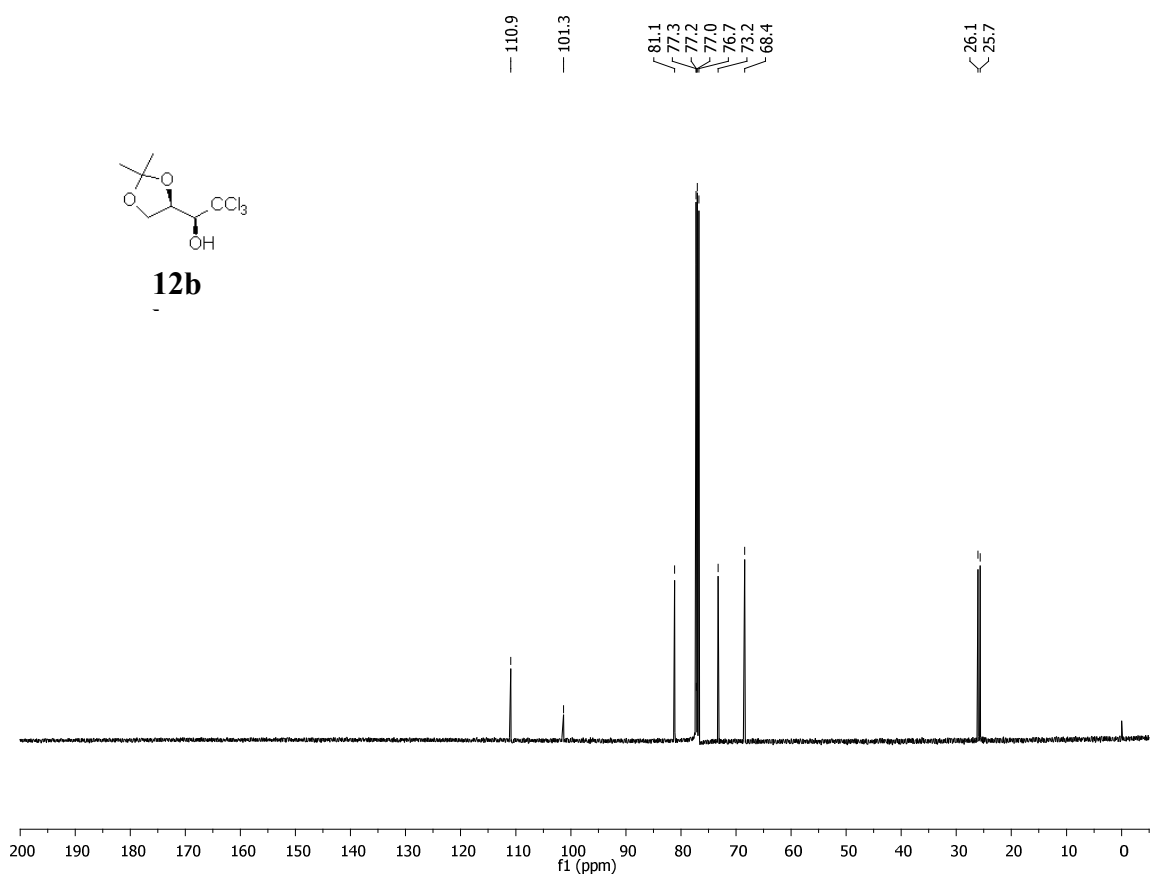
12a


109.2
100.6
82.4
77.2
77.0
76.7
75.1
64.7
26.3
25.3
O
O
CCl3
OH
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

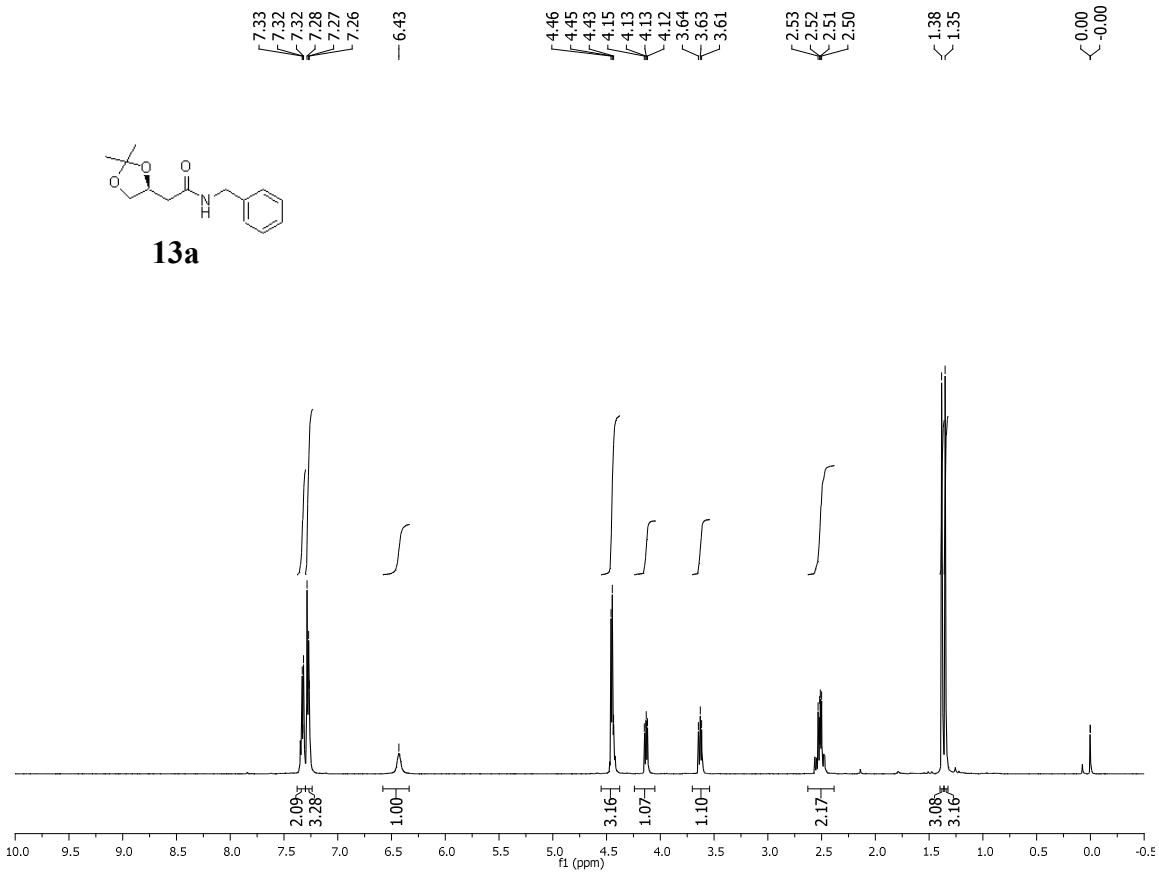
12a


7.26
4.59
4.58
4.57
4.57
4.56
4.56
4.27
4.25
4.25
4.24
3.99
3.99
3.98
3.97
3.93
3.91
3.91
3.89
3.73
3.71
1.49
1.44
CCl3
OH
1.00
1.06
0.99
1.04
0.99
3.09
3.07
f1 (ppm)

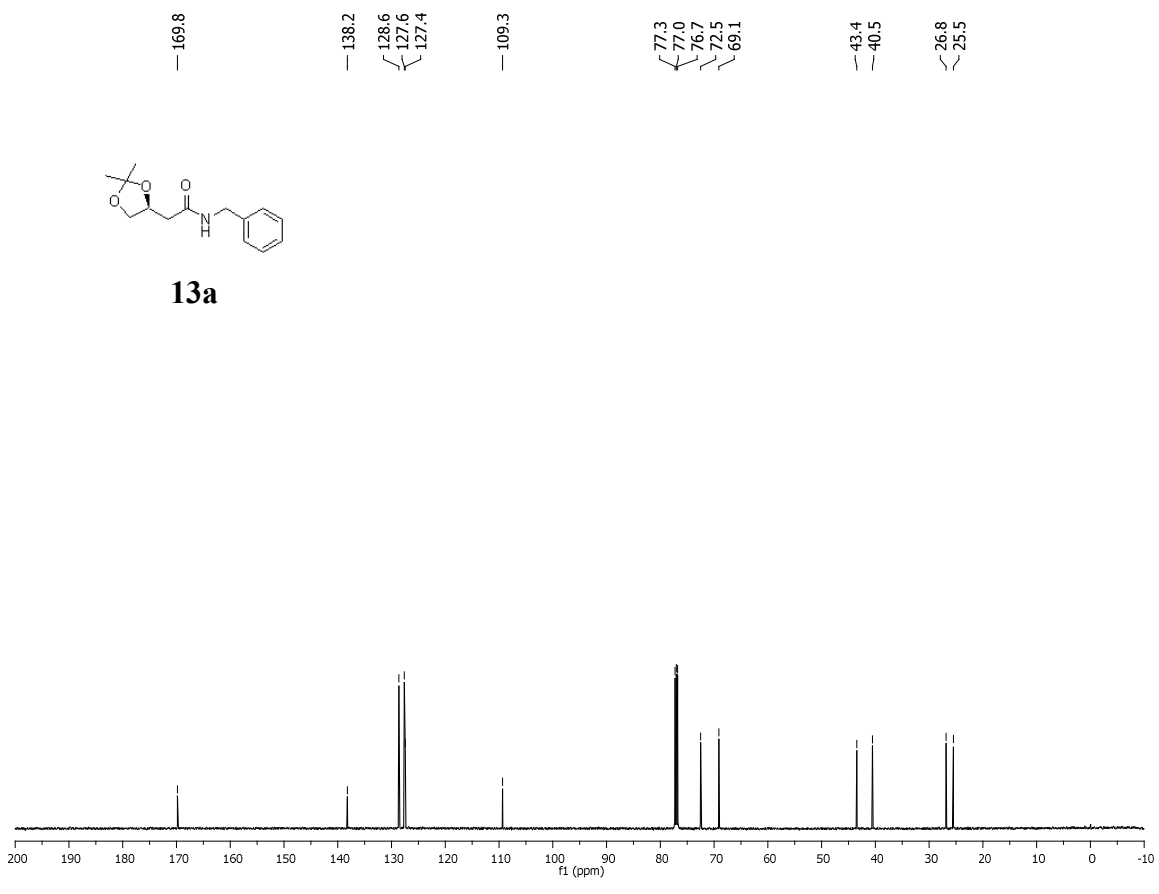
12b


110.9
101.3
81.1
77.3
77.2
77.0
76.7
73.2
68.4
26.1
25.7
CCl3
OH
f1 (ppm)

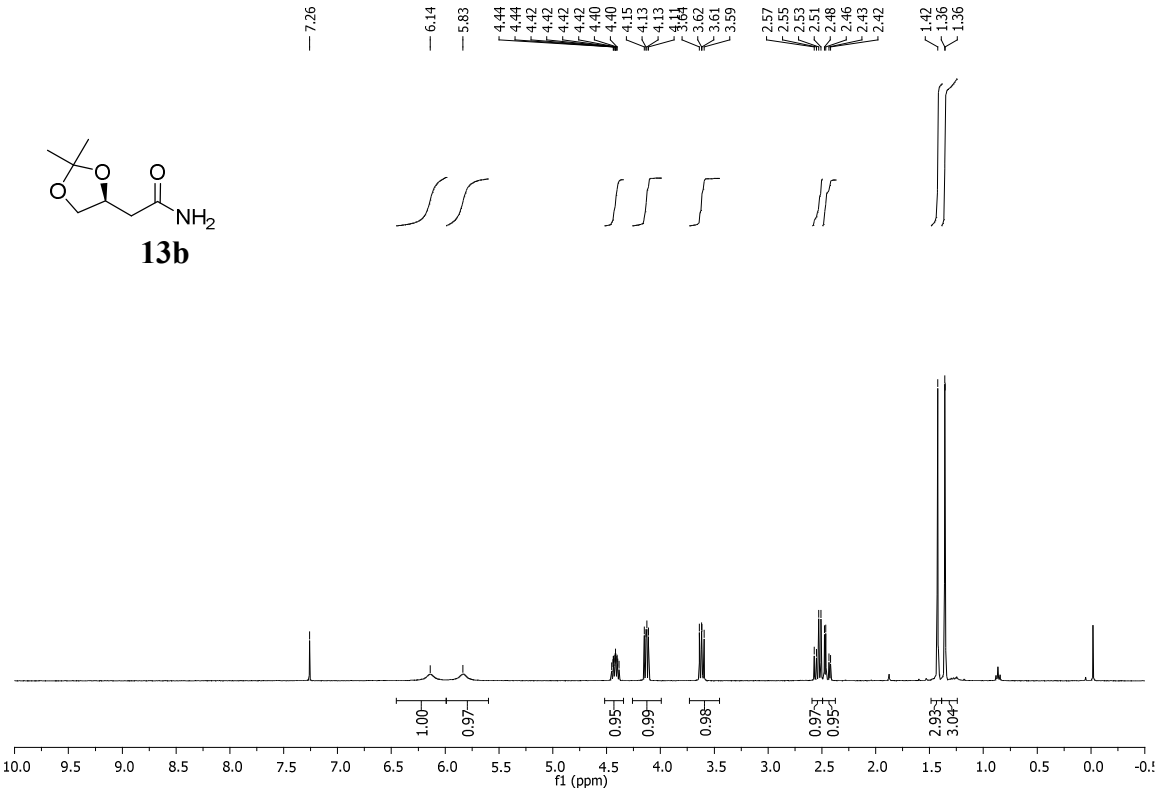
12b


7.33
7.32
7.32
7.28
7.27
7.26
6.43
4.46
4.45
4.43
4.15
4.13
4.13
4.12
3.64
3.63
3.61
2.53
2.52
2.51
2.50
1.38
1.35
0.00
-0.00
2.09
3.28
1.00
3.16
1.07
1.10
2.17
3.08
3.16
f1 (ppm)

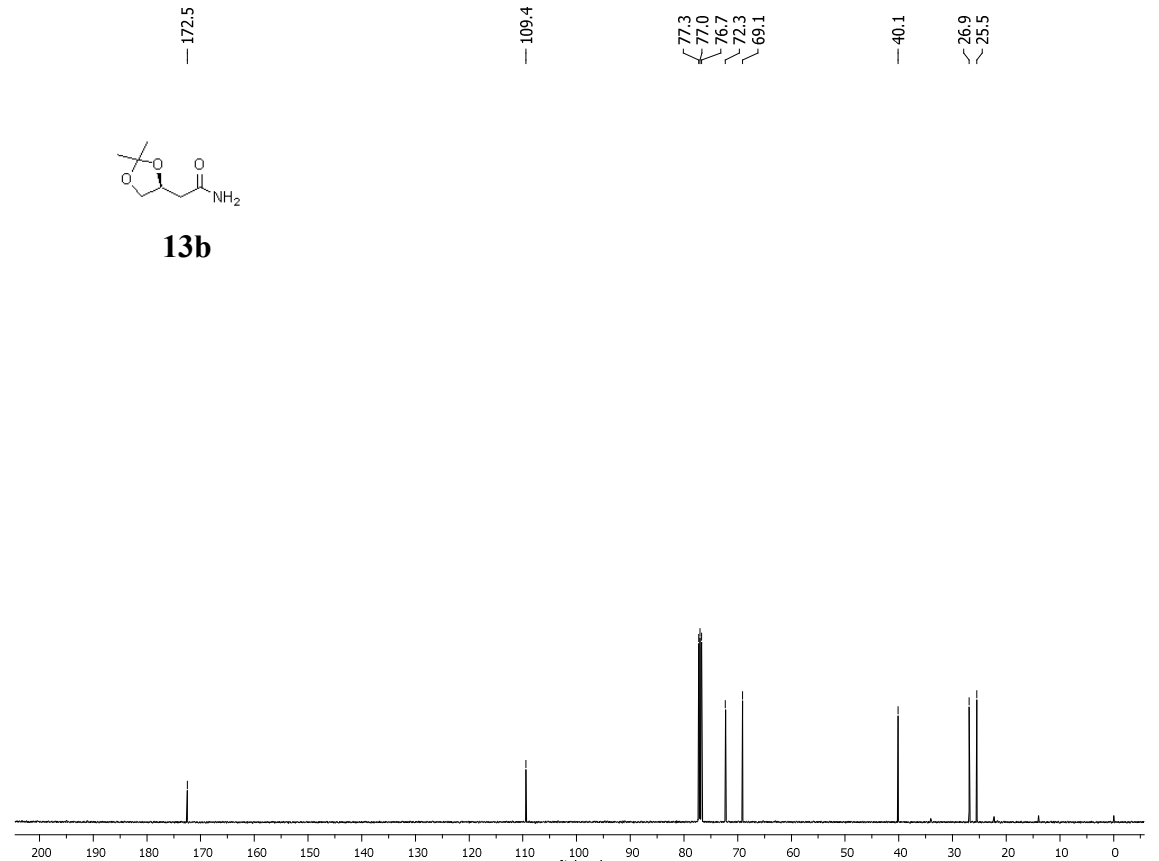
13a


169.8
138.2
128.6
127.6
127.4
109.3
77.3
77.0
76.7
72.5
69.1
43.4
40.5
26.8
25.5
f1 (ppm)

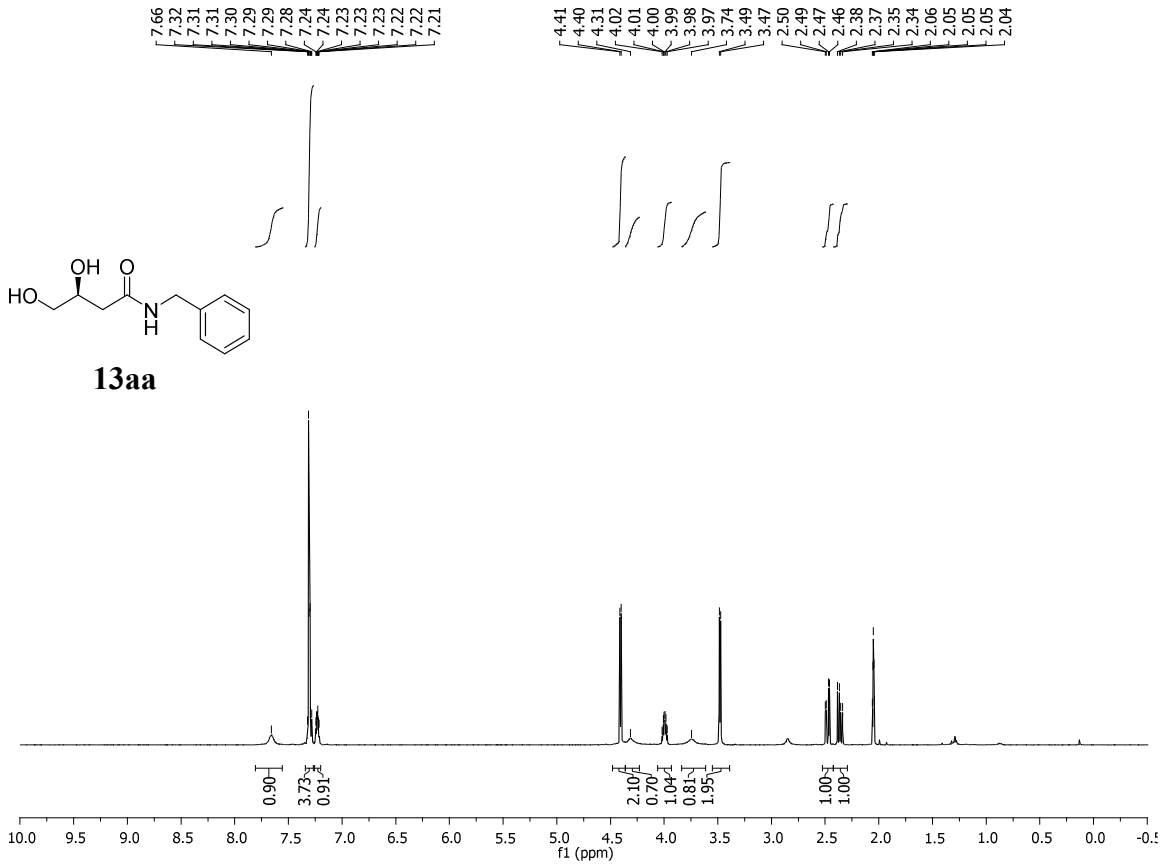
13a


7.26
6.14
5.83
4.44
4.44
4.42
4.42
4.42
4.42
4.40
4.40
4.15
4.13
4.13
3.64
3.62
3.61
3.59
2.57
2.55
2.53
2.51
2.48
2.46
2.43
2.42
1.42
1.36
1.36
O
O
O
NH2
1.00
0.97
0.95
0.99
0.98
0.97
0.95
2.93
3.04
f1 (ppm)

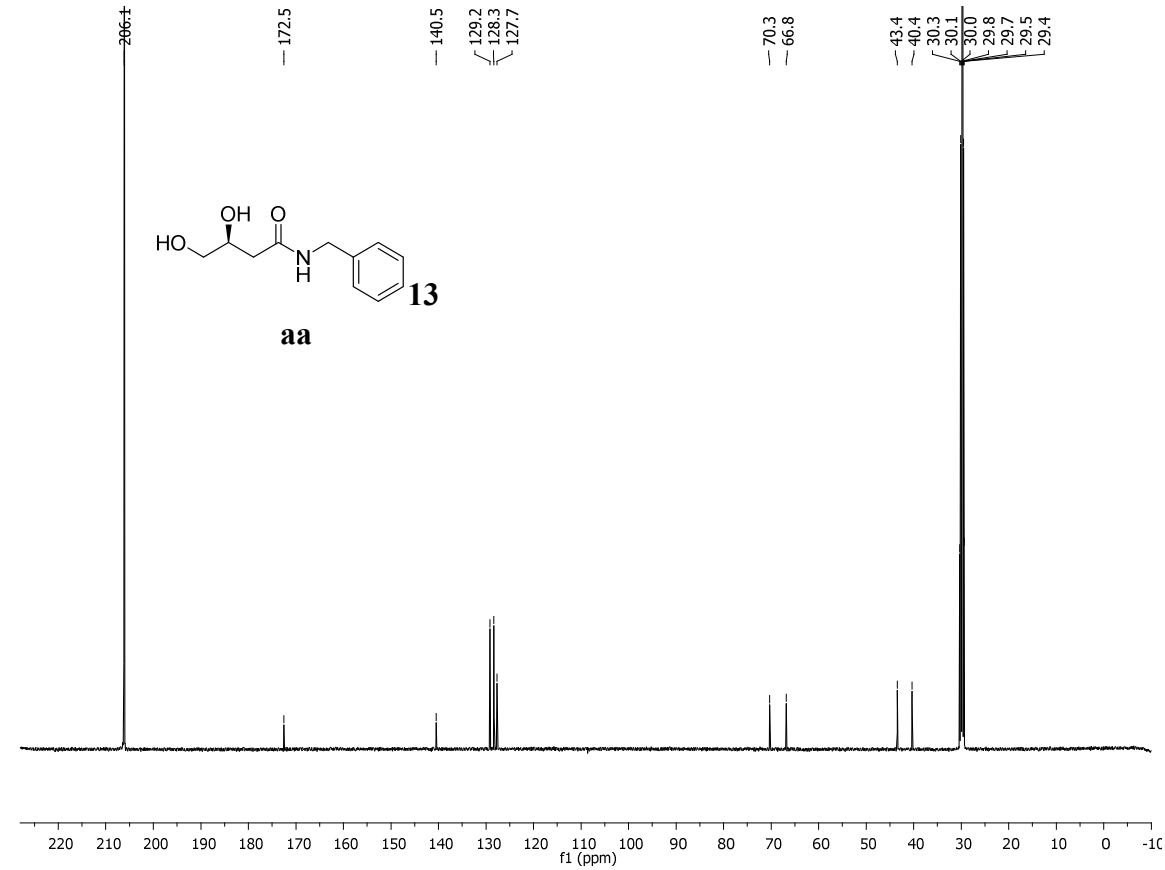
13b


172.5
109.4
77.3
77.0
76.7
72.3
69.1
40.1
26.9
25.5
O
O
O
NH2
f1 (ppm)

13b

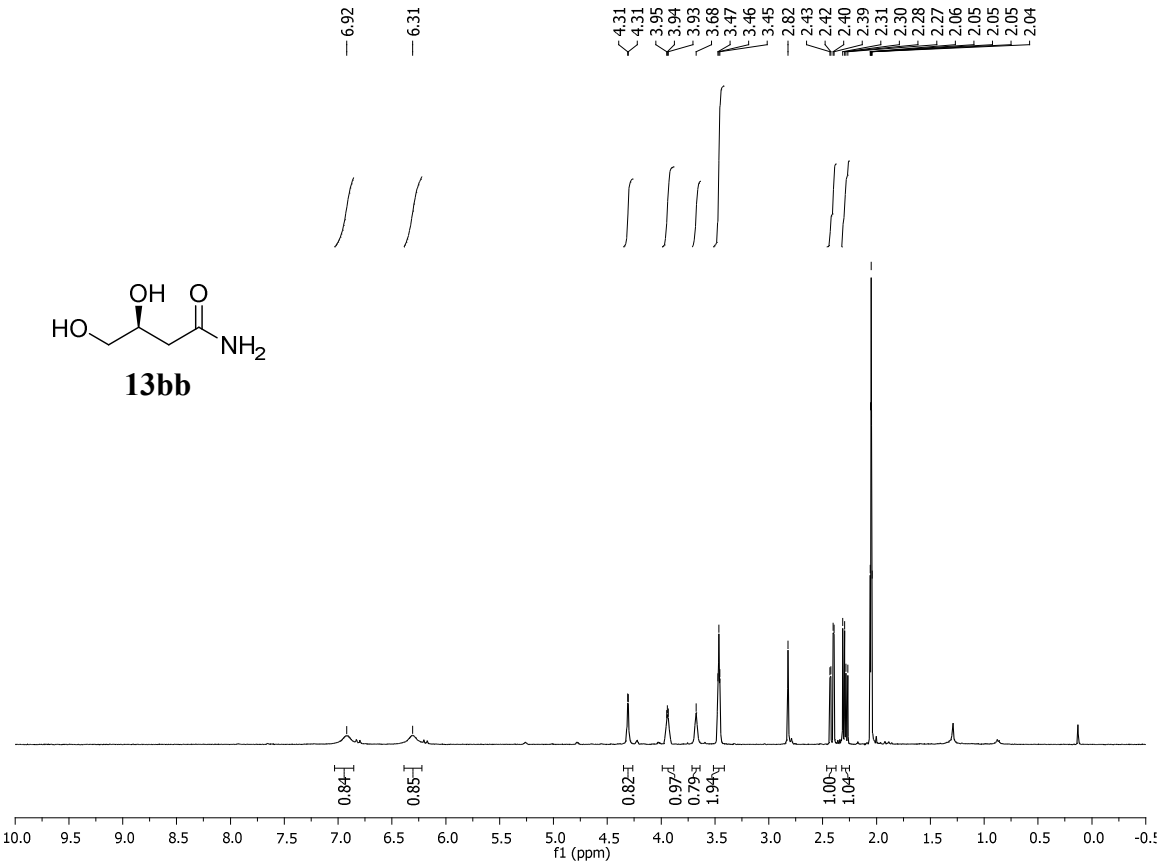

7.66
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.21
4.41
4.40
4.31
4.02
4.01
4.00
3.99
3.98
3.97
3.74
3.49
3.47
2.50
2.49
2.47
2.46
2.38
2.37
2.35
2.34
2.06
2.05
2.05
2.05
2.04
OH
O
HO
N
H
0.90
3.73
0.91
2.10
0.70
1.04
0.81
1.95
1.00
1.00
f1 (ppm)

13aa

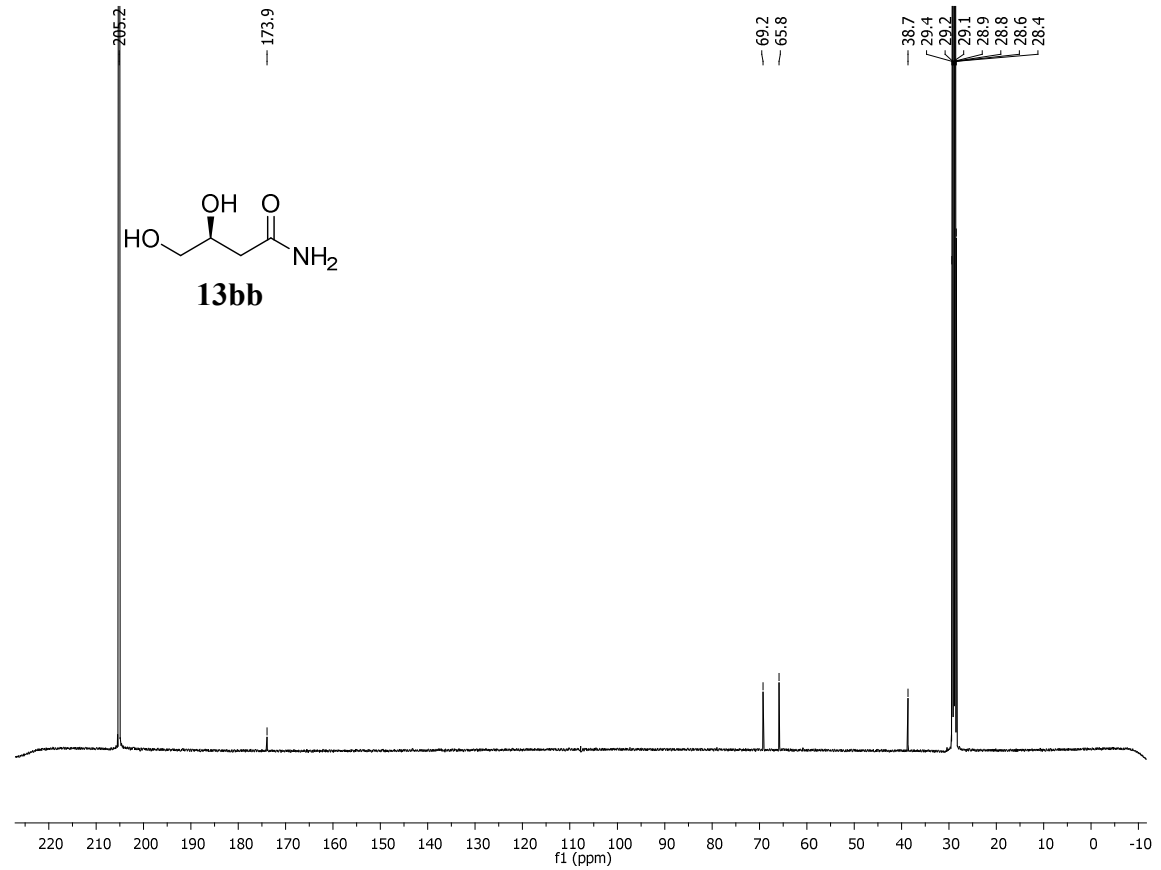

206.1
172.5
140.5
129.2
128.3
127.7
70.3
66.8
43.4
40.4
30.3
30.1
30.0
29.8
29.7
29.5
29.4
OH
O
HO
N
H
f1 (ppm)

13

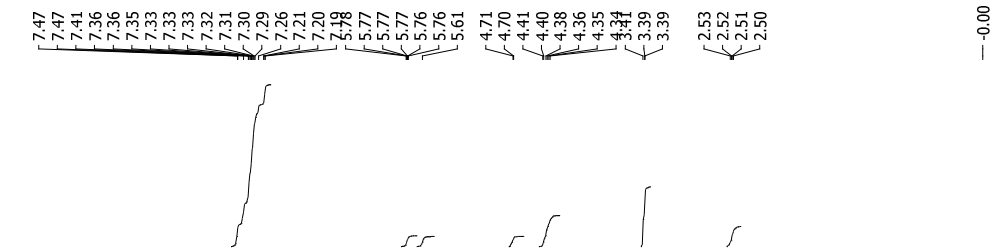
aa

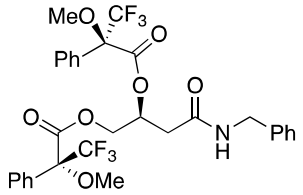

6.92
6.31
4.31
4.31
3.95
3.94
3.93
3.68
3.47
3.46
3.45
2.82
2.43
2.42
2.40
2.39
2.31
2.30
2.28
2.27
2.06
2.05
2.05
2.05
2.04
OH
O
HO
NH2
0.84
0.85
0.82
0.97
0.79
1.94
1.00
1.04
f1 (ppm)

13bb

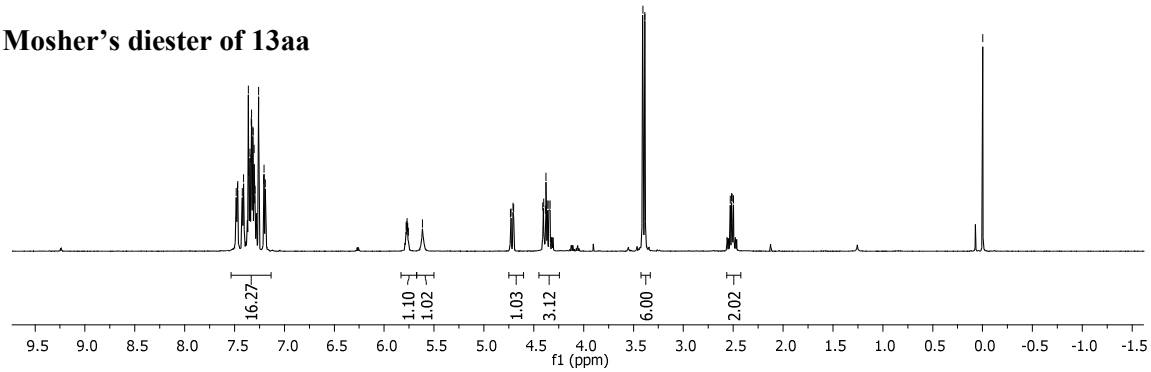

205.2
173.9
69.2
65.8
38.7
29.4
29.2
29.1
28.9
28.8
28.6
28.4
OH
O
HO
NH2
f1 (ppm)

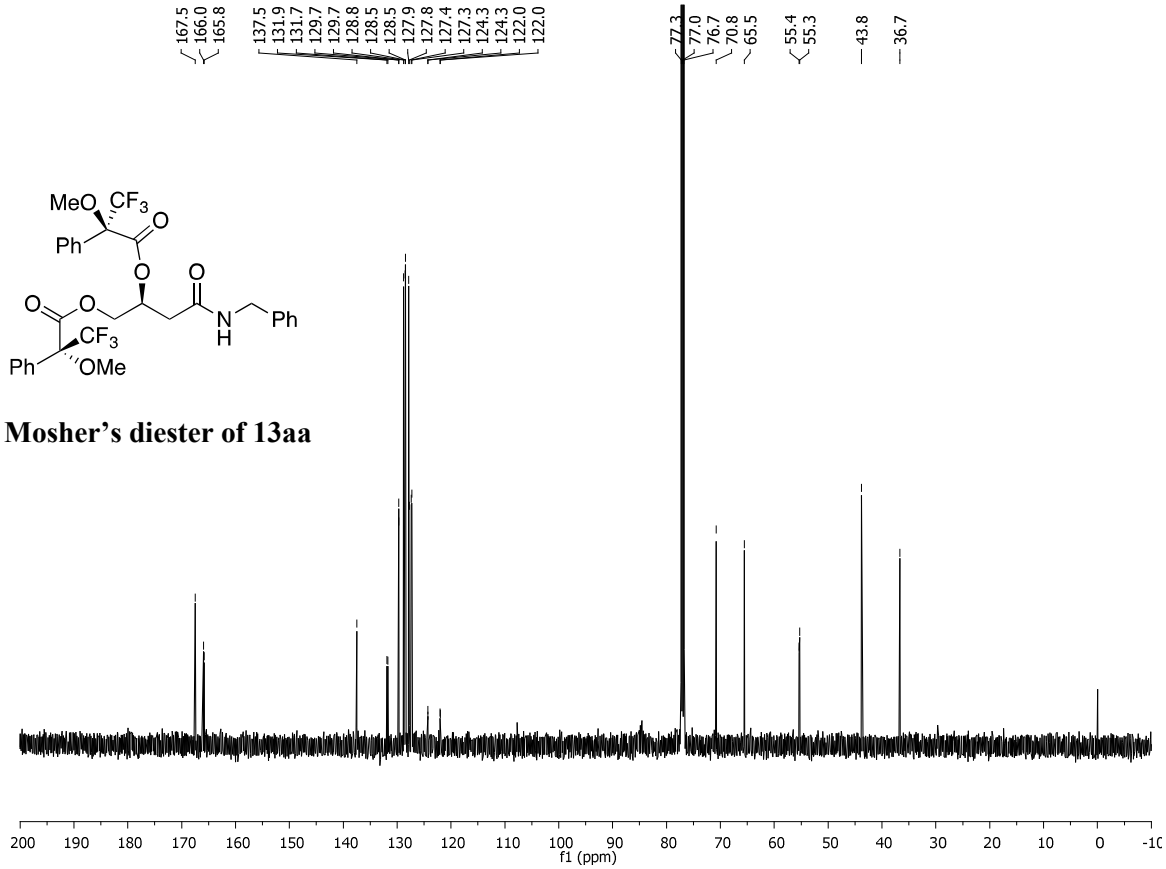
13bb



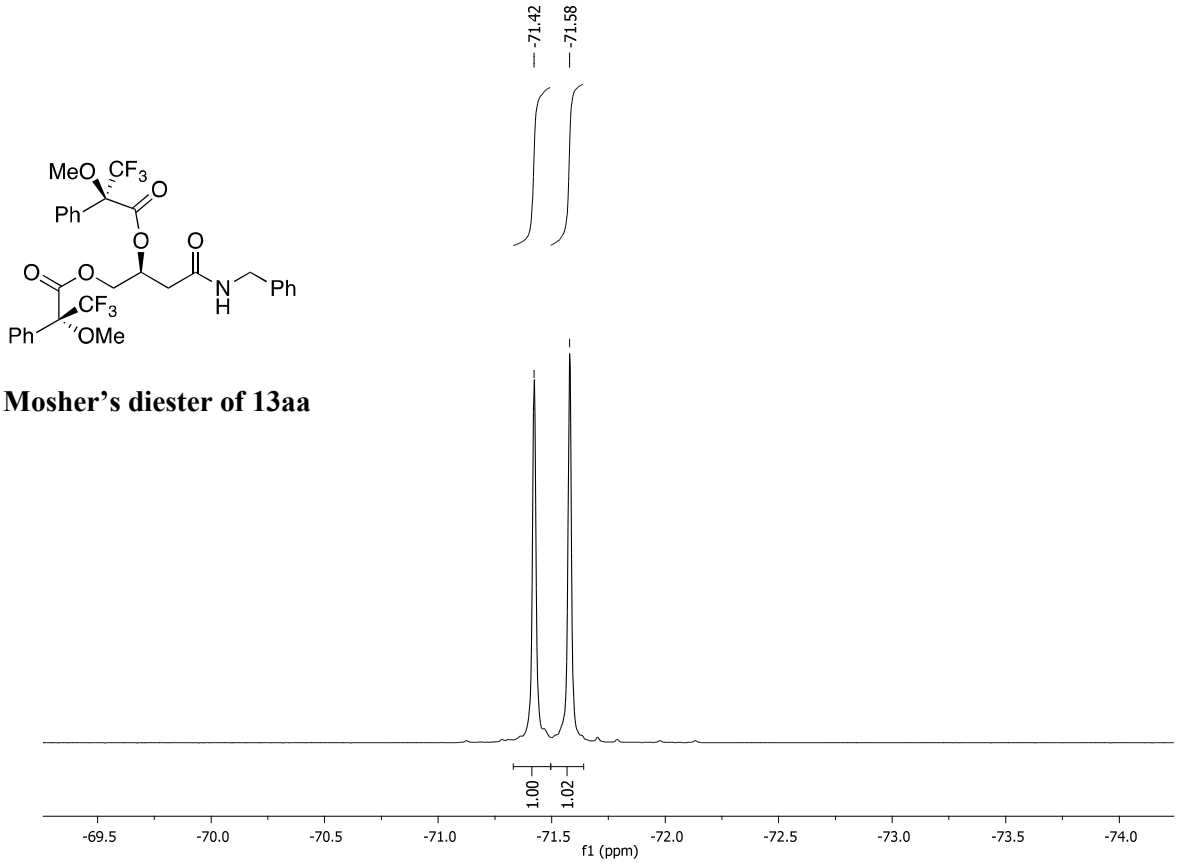


Mosher's diester of 13aa

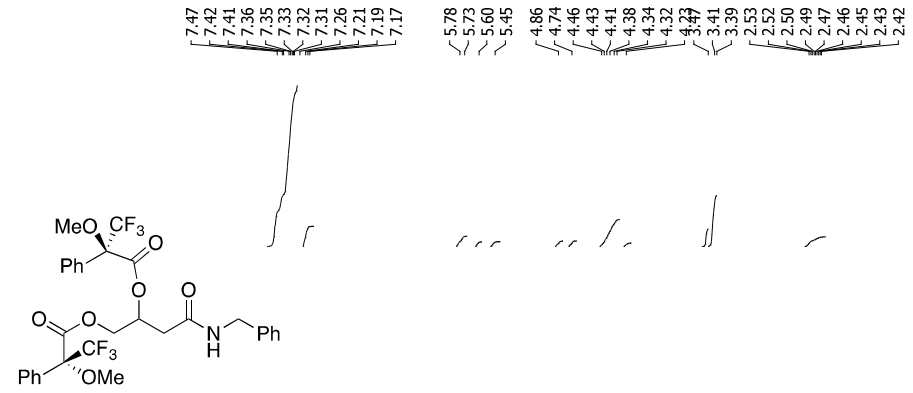




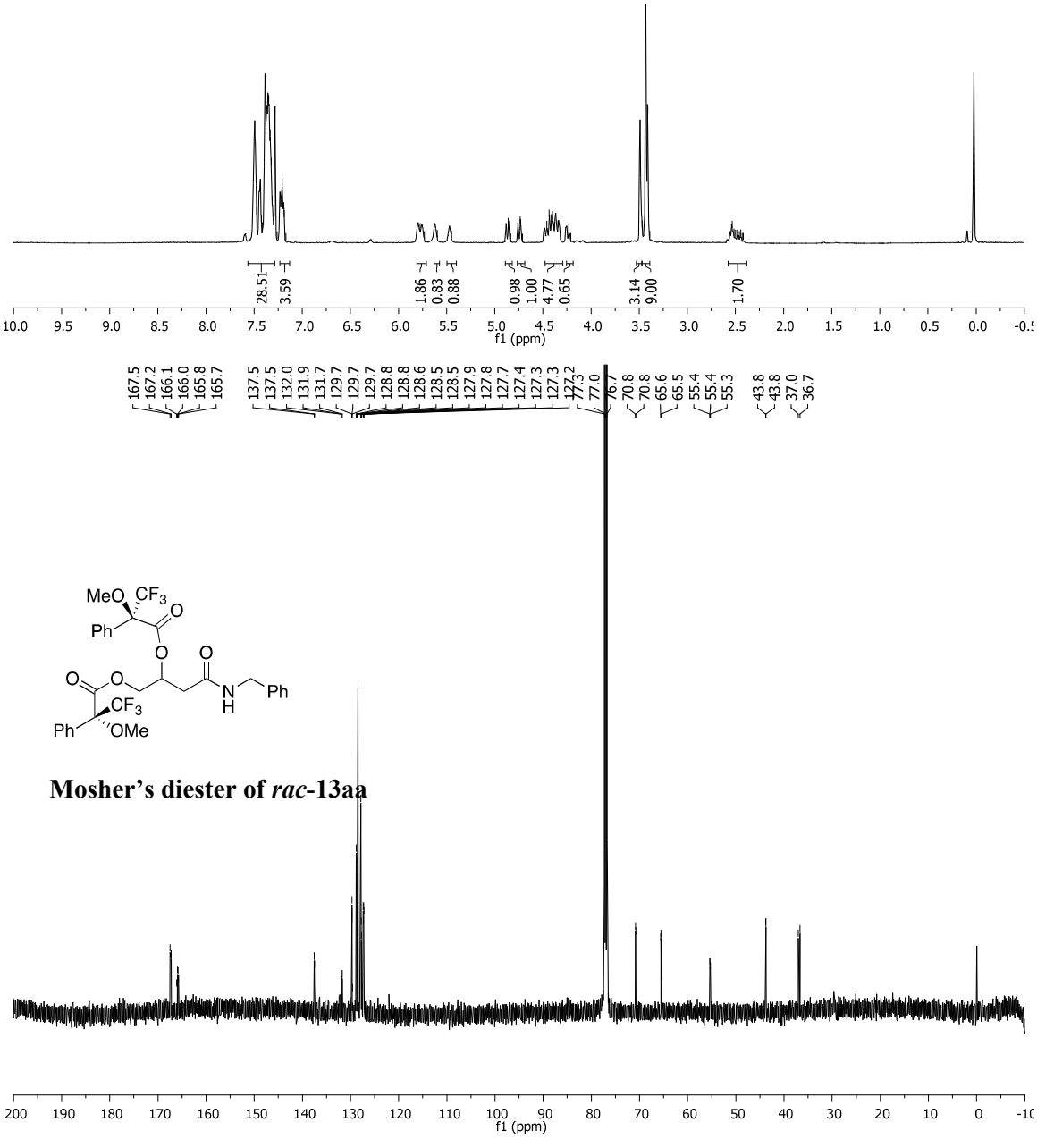
Mosher's diester of 13aa



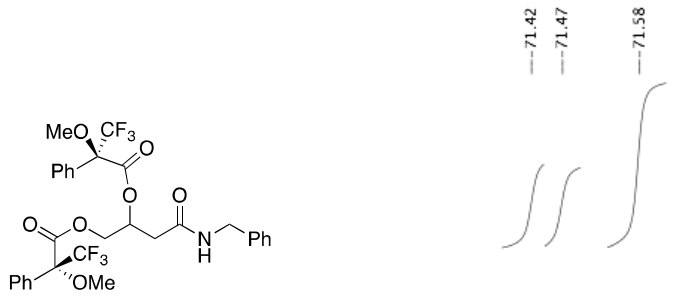
Mosher's diester of 13aa



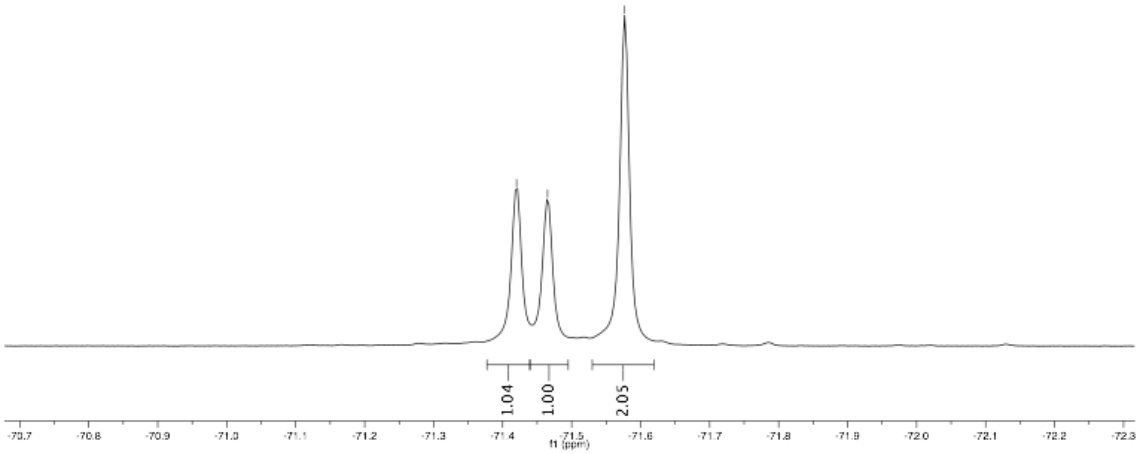
Mosher's diester of *rac*-13aa

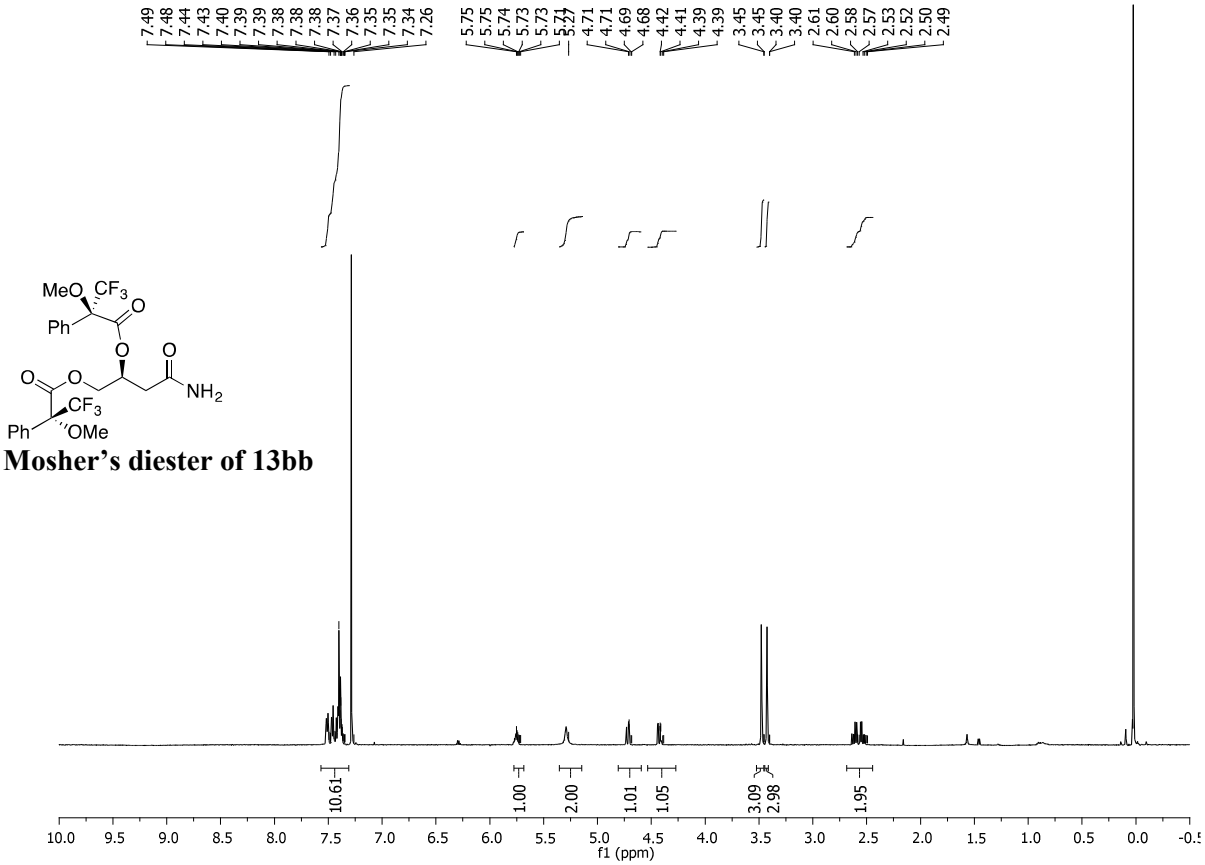


Mosher's diester of *rac*-13aa

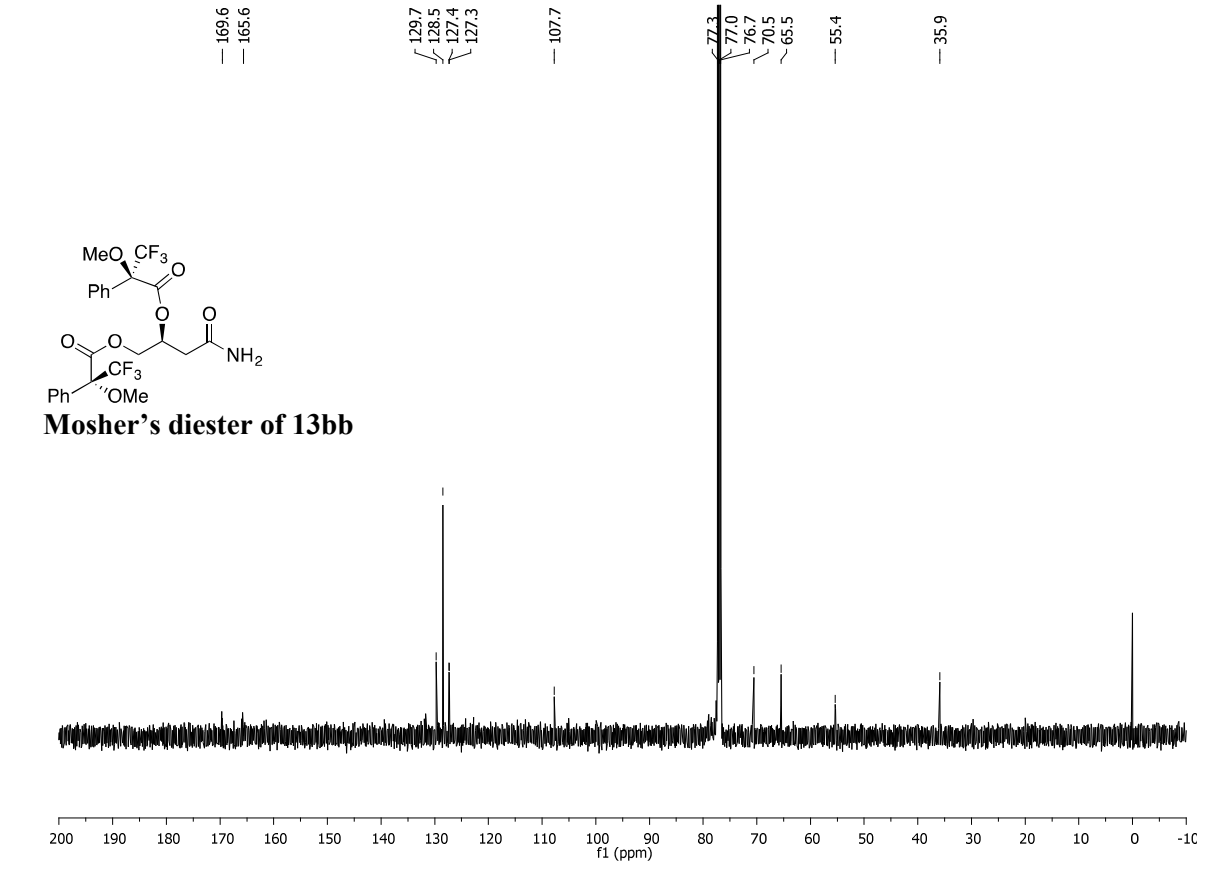


Mosher's diester of *rac*-13aa





Mosher's diester of 13bb



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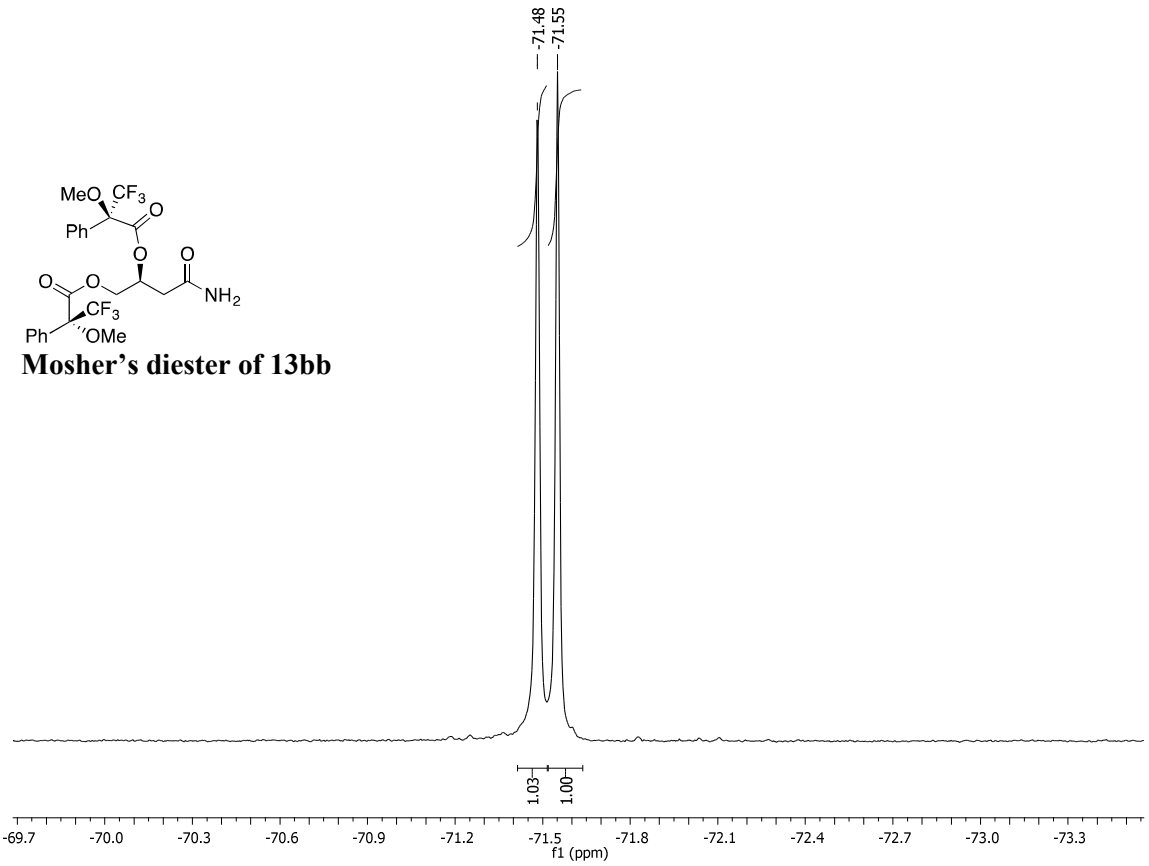

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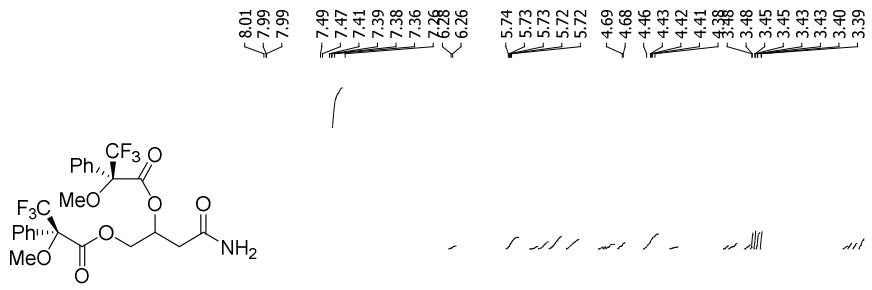
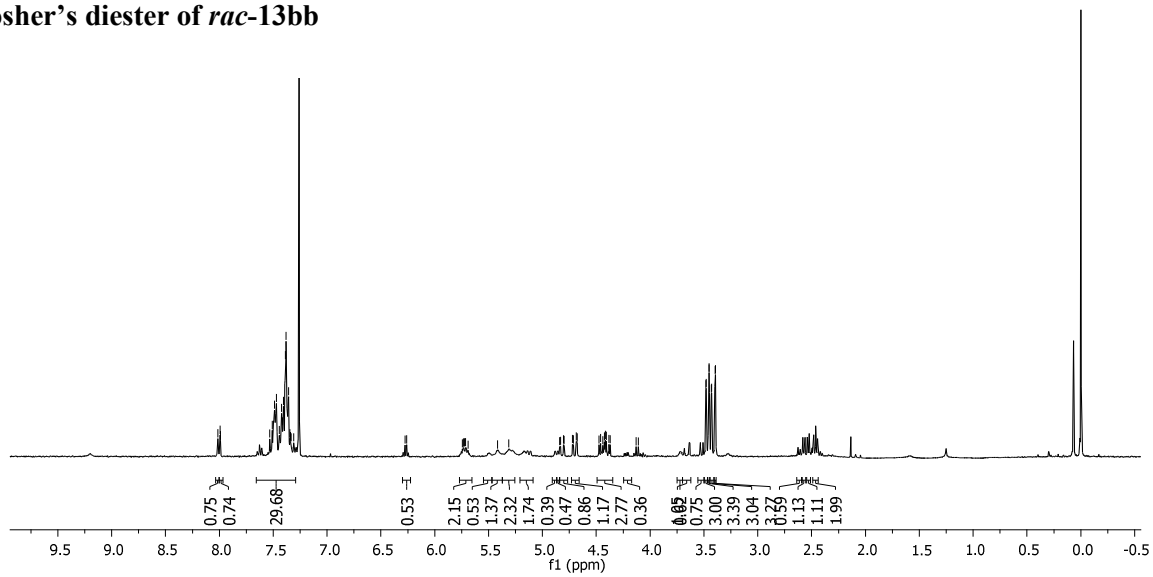
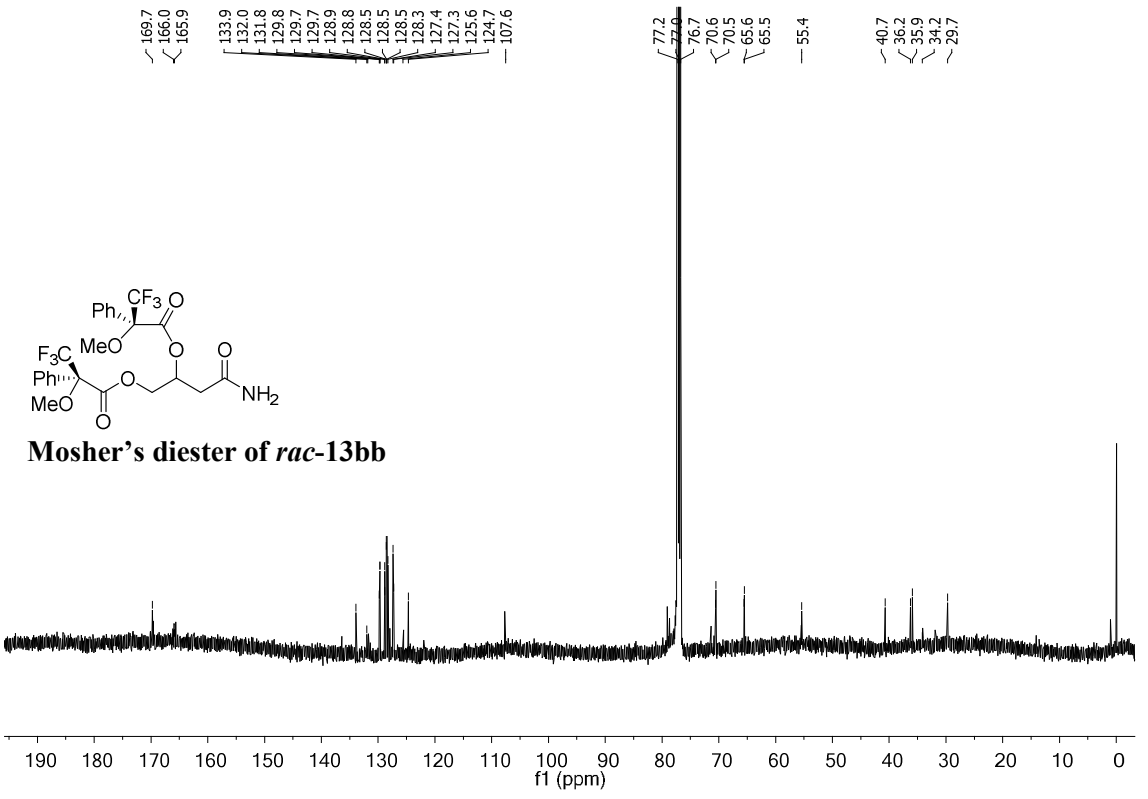
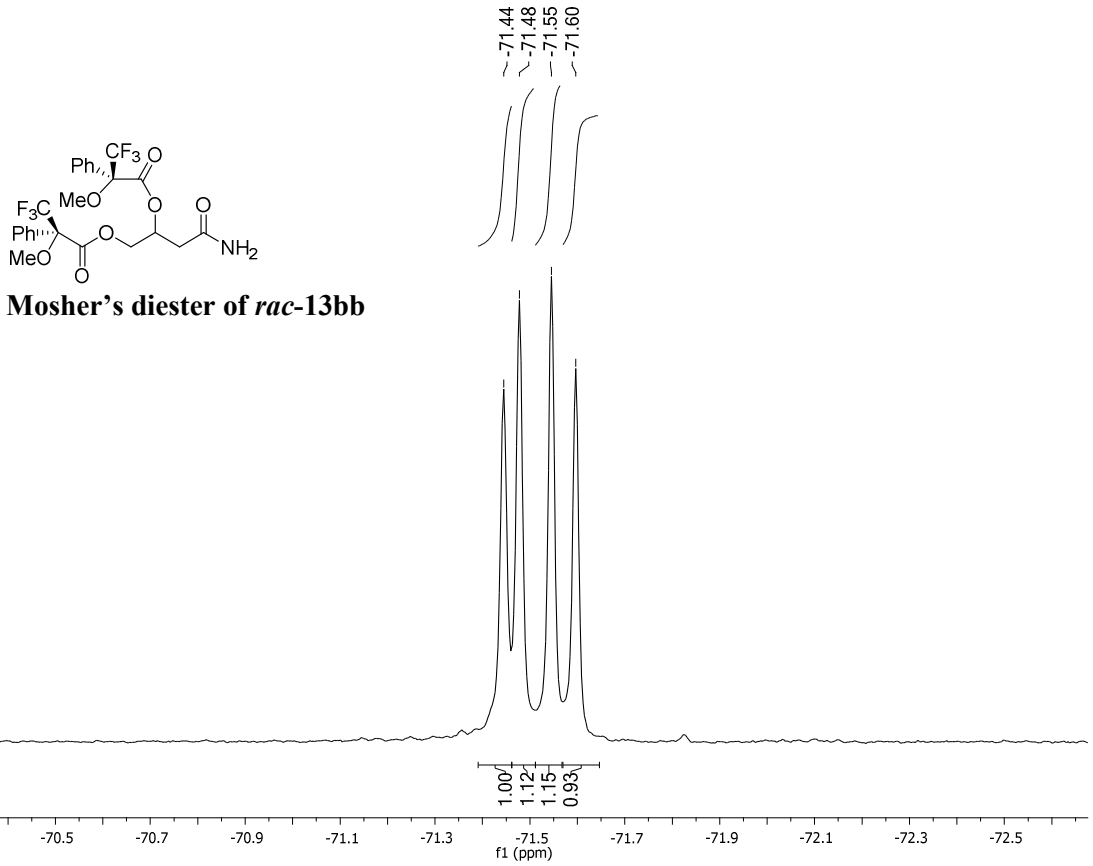


Mosher's diester of *rac*-13bb





Mosher's diester of *rac*-13bb



Mosher's diester of *rac*-13bb