**Electronic Supplementary Information**

# Chemoselective Synthesis of Cyclic Carbamates by Atmospheric Carbon Dioxide Fixation

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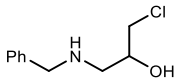
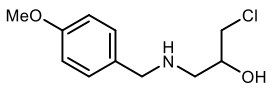
## General Information

All reagents and solvents were commercial grade and purified prior to use when necessary. Thin-layer chromatography (TLC) was performed using TLC aluminum sheets from Merck (silica gel 60 $F_{254}$, 200 μm), and flash chromatography was performed using silica gel from Fuji Silysia Chemical (PSQ60B, 60 μm). Products were visualized by ultraviolet (UV) light and TLC stains. Melting points were measured on a Yanaco micro melting point apparatus and were not corrected. Nuclear magnetic resonance (NMR) spectra were acquired on a Bruker Fourier 300 spectrometer. Chemical shifts were measured relative to residual solvent peaks as an internal standard set to 0.00 ($^{1}$H) for TMS and 77.0 ($^{13}C\{^{1}H\}$) for $CDCl_3$. $^{13}C\{^{1}H\}$ NMR peak assignments were confirmed by the DEPT135 program. Data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sext = sextet, sept = septet, br = broad, and m = multiplet), coupling constants (Hz), and integration. Infrared (IR) spectra were recorded on a Jasco FT/IR-4200 spectrophotometer and are reported in wavenumbers ($cm^{-1}$). All compounds were analyzed as neat films on a potassium bromide (KBr) plate. Mass spectra were recorded on a Bruker micrOTOF II mass spectrometer by the ionization method noted. A post-acquisition gain correction was applied using sodium formate ($HCO_2Na$) as the lock mass.

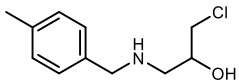
## Preparation of Starting Materials



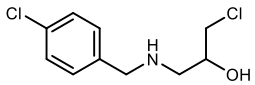

1-(Benzylamino)-3-chloropropan-2-ol (**1a**) was prepared according to the literature.[1] $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.37-7.24 (m, 5H), 3.92-3.76 (m, 3H), 3.58 (dd, *J* = 11.4, 5.1 Hz, 1H), 3.54 (dd, *J* = 11.4, 5.7 Hz, 1H), 2.84 (dd, *J* = 12.3, 4.2 Hz, 1H), 2.72 (dd, *J* = 12.3, 7.8 Hz, 1H), 2.41 (br s, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 139.0 (C), 128.6 (CH), 128.2 (CH), 127.4 (CH), 69.3 ($CH_2$), 53.6 ($CH_2$), 51.4 ($CH_2$), 47.3 ($CH_2$); HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_{15}ClNO$ 200.0837, found 200.0831.



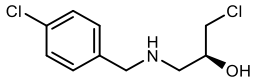
**1-Chloro-3-[(4-methoxybenzyl)amino]propan-2-ol (1b).** To a solution of epichlorohydrin (196 μL, 2.5 mmol) in $^{i}$PrOH (7.5 mL) was added 4-methoxybenzylamine (388 μL, 3.0 mmol, 1.2 equiv) at 0 °C. After stirring at room temperature for 18 h, the mixture was concentrated. Flash column chromatography ($SiO_2$: 20 g, Hexane:EtOAc = 6:1–EtOAc) yielded a white solid (288.3 mg, 50%). $R_f$ = 0.35 (EtOAc:MeOH = 4:1) visualized with $KMnO_4$; mp 73-74 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.25-7.20 (m, 2H), 6.89-6.84 (m, 2H), 3.91-3.83 (m, 1H), 3.80 (s, 3H), 3.77 (d, *J* = 13.2 Hz, 1H), 3.72 (d, *J* = 13.2 Hz, 1H), 3.56 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.53 (dd, *J* = 11.1, 6.0 Hz, 1H), 2.82 (dd, *J* = 12.3, 3.9 Hz, 1H), 2.70 (dd, *J* = 12.3, 7.8 Hz, 1H), 2.41 (br s, 2H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 158.8 (C), 131.7 (C), 129.3 (CH), 113.9 (CH), 69.4 (CH), 55.3 ($CH_3$), 53.1 ($CH_2$), 51.3 ($CH_2$), 47.4 ($CH_2$); IR (KBr) 3275, 3262, 2837, 1516, 1254, 1034, 811, 736 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{16}ClNNaO_2$ 252.0762, found 252.0761.



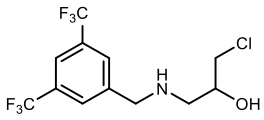

**1-Chloro-3-[(4-methylbenzyl)amino]propan-2-ol (1c).** To a solution of epichlorohydrin (196 μL, 2.5 mmol) in $^{i}$PrOH (7.5 mL) was added 4-methylbenzylamine (379 μL, 3.0 mmol, 1.2 equiv) at 0 °C. After stirring at room temperature for 18 h, the mixture was concentrated. Flash column chromatography ($SiO_2$: 20 g, Hexane:EtOAc = 6:1–1:1) yielded a white solid (264.5 mg, 50%). $R_f$ = 0.40 (EtOAc:MeOH = 10:1) visualized with $KMnO_4$; mp 102-103 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.21-7.13 (m, 4H), 3.91-3.83 (m, 1H), 3.79 (d, *J* = 13.2 Hz, 1H), 3.74 (d, *J* = 13.2 Hz, 1H), 3.57 (dd, *J* = 11.1, 5.1 Hz, 1H), 3.53 (dd, *J* = 11.1, 5.7 Hz, 1H), 2.82 (dd, *J* = 12.3, 4.2 Hz, 1H), 2.70 (dd, *J* = 12.3, 7.8 Hz, 1H), 2.34 (s, 3H), 2.27 (br s, 2H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 136.9 (C), 136.6 (C), 129.2 (CH), 128.0 (CH), 69.4 (CH), 53.4 ($CH_2$), 51.4 ($CH_2$), 47.4 ($CH_2$), 21.1 ($CH_3$); IR (KBr) 3286, 3019, 2906, 2856, 2670, 1342, 1074, 884, 813, 753 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_{11}H_{17}ClNO$ 214.0993, found 214.1004.



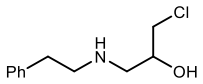

**1-Chloro-3((4-chlorobenzyl)amino)propan-2-ol (1d).** To a solution of epichlorohydrin (196 μL, 2.5 mmol) in $^{i}$PrOH (7.5 mL) was added 4-chlorobenzylamine (364 μL, 3.0 mmol, 1.2 equiv) at 0 °C. After stirring at room temperature for 18 h, the mixture was concentrated. Flash column chromatography ($SiO_2$: 20 g, Hexane:EtOAc = 6:1–1:1) yielded a white solid (238.7 mg, 41%). $R_f$ = 0.50 (EtOAc:MeOH = 10:1) visualized with $KMnO_4$; mp 94-95 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.33-7.29 (m, 2H), 7.27-7.22 (m, 2H), 3.93-3.85 (m, 1H), 3.81 (d, *J* = 13.5 Hz, 1H), 3.76 (d, *J* = 13.5 Hz, 1H), 3.59 (dd, *J* = 11.4, 5.1 Hz, 1H), 3.55 (dd, *J* = 11.4, 5.7 Hz, 1H), 2.82 (dd, *J* = 12.3, 3.9 Hz, 1H), 2.71 (dd, *J* = 12.3, 7.8 Hz, 1H), 2.35 (br s, 2H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 138.1 (C), 133.0 (C), 129.4 (CH), 128.6 (CH), 69.6 (CH), 53.0 ($CH_2$), 51.4 ($CH_2$), 47.4 ($CH_2$); IR (KBr) 3410, 3285, 2855, 1491, 1089, 753 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_{14}Cl_2NO$ 234.0430, found 234.0447.



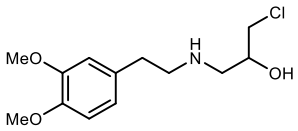

(*S*)-**1d**. To a solution of (*S*)-epichlorohydrin (196 μL, 2.5 mmol, 99% ee) in $^{i}$PrOH (7.5 mL) was added 4-chlorobenzylamine (364 μL, 3.0 mmol, 1.2 equiv) at 0 °C. After stirring at room temperature for 18 h, the mixture was concentrated. Flash column chromatography ($SiO_2$: 23 g, Hexane:EtOAc = 20:1– EtOAc) yielded a white solid (333.4 mg, 57%). The product was determined to be 99% ee by chiral HPLC analysis (Chiralpak AD-3, Hexane:EtOH = 95:5, 1.0 mL/min, $t_r$(*minor*) = 22.9 min, $t_r$(*major*) = 24.6 min, 220 nm, 35 °C); $[\alpha]_D^{24}$ -17.4 (*c* 0.50, $CHCl_3$, 99% ee). The absolute configuration was determined according to the literature.[2]



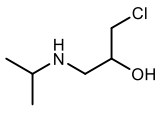
**1-{[3,5-bis(trifluoromethyl)benzyl]amino}-3-chloropropan-2-ol (1e).** To a solution of epichlorohydrin (196 μL, 2.5 mmol) in $^{i}$PrOH (7.5 mL) was added 3,5-bis(trifluoromethyl)benzylamine (728.6 mg, 3.0 mmol, 1.2 equiv) at 0 °C. After stirring at room temperature for 18 h, the mixture was concentrated. Flash column chromatography ($SiO_2$: 20 g, Hexane:EtOAc = 7:1–4:1) yielded a white solid (266.4 mg, 32%). $R_f$ = 0.40 (hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 65-66 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.81 (s, 2H), 7.79 (s, 1H), 4.00-3.91 (m, 3H), 3.64 (dd, *J* = 11.4, 5.1 Hz, 1H), 3.60 (dd, *J* = 11.4, 6.0 Hz, 1H), 2.86 (dd, *J* = 12.3, 4.2 Hz, 1H), 2.76 (dd, *J* = 12.3, 7.2 Hz, 1H), 1.77 (br s, 2H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 142.5 (C), 131.8 (q, *J* = 33.2 Hz, C), 128.1 (m, CH), 123.3 (q, *J* = 272.5 Hz, C), 121.2 (sept, *J* = 3.9 Hz, CH), 70.0 (CH), 52.9 ($CH_2$), 51.7 ($CH_2$), 47.5 ($CH_2$); $^{19}$F{$^1$H} NMR (470 MHz, $CDCl_3$) δ -62.8; IR (KBr) 3281, 3056, 2857, 1378, 1174, 1136, 903, 710 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{13}ClF_6NO$ 336.0584, found 336.0569.



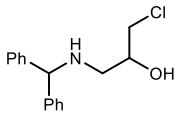

**1-Chloro-3-[(2-phenylethyl)amino]propan-2-ol (1f).** To a solution of epichlorohydrin (196 μL, 2.5 mmol) in $^{i}$PrOH (7.5 mL) was added phenethylamine (328 μL, 3.0 mmol, 1.2 equiv) at 0 °C. After stirring at room temperature for 72 h, the mixture was concentrated. Flash column chromatography ($SiO_2$: 14 g, Hexane:EtOAc = 6:1–EtOAc) yielded a pale yellow oil (286.2 mg, 54%). $R_f$ = 0.40 (EtOAc:MeOH = 4:1) visualized with $KMnO_4$; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.33-7.18 (m, 5H), 3.89-3.81 (m, 1H), 3.54 (d, *J* = 5.4 Hz, 2H), 2.96-2.78 (m, 5H), 2.70 (dd, *J* = 12.4, 8.1 Hz, 1H), 2.33 (br s, 2H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 139.5 (C), 128.7 (CH), 128.5 (CH), 126.3 (CH), 69.2 (CH), 51.8 ($CH_2$), 50.8 ($CH_2$), 47.3 ($CH_2$), 36.2 ($CH_2$); IR (KBr) 3303, 2948, 2844, 1455, 1117, 1080, 912 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_{11}H_{17}ClNO$ 214.0993, found 214.0970.



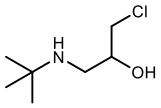

**1-Chloro-3-{[2-(3,4-dimethoxyphenyl)ethyl]amino}propan-2-ol (1g).** To a solution of epichlorohydrin (196 μL, 2.5 mmol) in $^{i}$PrOH (7.5 mL) was added homoveratrylamine (525 μL, 3.0 mmol, 1.2 equiv) at 0 °C. After stirring at room temperature for 18 h, the mixture was concentrated. Flash column chromatography ($SiO_2$: 15 g, Hexane:EtOAc = 1:1–EtOAc) yielded a white solid (307.1 mg, 45%). $R_f$ = 0.30 (EtOAc:MeOH = 4:1) visualized with $KMnO_4$; mp 65-66 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 6.82-6.73 (m, 3H), 3.90-3.83 (m, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.55 (d, *J* = 5.4 Hz, 2H), 2.93-2.68 (m, 6H), 2.40 (br s, 2H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 149.0 (C), 147.5 (C), 132.0 (C), 120.5 (CH), 111.9 (CH), 111.3 (CH), 69.2 (CH), 55.9 ($CH_3$), 55.8 ($CH_3$), 51.8 ($CH_2$), 51.0 ($CH_2$), 47.3 ($CH_2$), 35.7 ($CH_2$); IR (KBr) 3078, 2836, 1519, 1266, 1238, 1158, 1023, 834 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{21}ClNO_3$ 274.1204, found 274.1197.



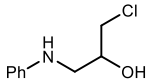

**1-Chloro-3-(propan-2-ylamino)propan-2-ol (1h).** To a solution of epichlorohydrin (392 μL, 5.0 mmol) in $^{i}$PrOH (15 mL) was added isopropylamine (516 μL, 6.0 mmol, 1.2 equiv) at 0 °C. After stirring at room temperature for 18 h, the mixture was concentrated. Flash column chromatography ($SiO_2$: 8 g, EtOAc) yielded a white solid (427.1 mg, 56%). $R_f$ = 0.10 (EtOAc:MeOH = 4:1) visualized with $KMnO_4$; mp 44-45 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 3.86-3.78 (m, 1H), 3.58 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.54 (dd, *J* = 11.1, 5.7 Hz, 1H), 2.86-2.74 (m, 2H), 2.66 (dd, *J* = 12.3, 7.8 Hz, 1H), 2.12 (br s, 2H), 1.08 (d, *J* = 6.3 Hz, 6H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 69.6 (CH), 49.5 ($CH_2$), 48.9 (CH), 47.4 ($CH_2$), 23.1 ($CH_3$), 23.0 ($CH_3$); IR (KBr) 3278, 3096, 2977, 2831, 1471, 1380, 1253, 1172, 1076, 914, 739 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_6H_{15}ClNO$ 152.0837, found 152.0861.



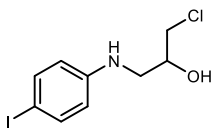
**1-Chloro-3-[(diphenylmethyl)amino]propan-2-ol (1i).**[3] To a solution of epichlorohydrin (196 μL, 2.5 mmol) in $^{i}$PrOH (7.5 mL) was added benzhydrylamine (514 μL, 3.0 mmol, 1.2 equiv) at 0 °C. After stirring at room temperature for 18 h, the mixture was concentrated. Flash column chromatography ($SiO_2$: 20 g, Hexane:EtOAc = 4:1) yielded a white solid (330.1 mg, 48%). $R_f$ = 0.25 (Hexane:EtOAc = 4:1) visualized with $KMnO_4$; mp 66-67 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.38-7.19 (m, 10H), 4.83 (s, 1H), 3.93-3.85 (m, 1H), 3.58 (d, *J* = 5.4 Hz, 2H), 2.79 (dd, *J* = 12.3, 4.2 Hz, 1H), 2.69 (dd, *J* = 12.3, 7.2 Hz, 1H), 2.10 (br s, 2H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 143.4 (C), 143.3 (C), 128.6 (CH), 127.3 (CH), 127.2 (CH), 70.1 (CH), 67.2 (CH), 50.5 ($CH_2$), 47.7 ($CH_2$); IR (KBr) 3372, 3323, 3026, 2835, 1493, 1452, 1028, 762, 705 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{18}ClNNaO$ 298.0969, found 298.0969.



**1-(*tert*-Butylamino)-3-chloropropan-2-ol (1j).** To a solution of epichlorohydrin (392 μL, 5.0 mmol) in $^{i}$PrOH (15 mL) was added *tert*-butylamine (636 μL, 6.0 mmol, 1.2 equiv) at 0 °C. After stirring at room temperature for 18 h, the mixture was concentrated. Flash column chromatography ($SiO_2$: 7 g, EtOAc) yielded a white solid (442.0 mg, 53%). $R_f$ = 0.10 (EtOAc:MeOH = 4:1) visualized with $KMnO_4$; mp 42-44 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 3.83-3.75 (m, 1H), 3.58 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.53 (dd, *J* = 11.1, 6.0 Hz, 1H), 2.81 (dd, *J* = 12.0, 4.2 Hz, 1H), 2.67 (br s, 2H), 2.62 (dd, *J* = 12.0, 7.8 Hz, 1H), 1.11 (s, 9H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 69.7 (CH), 50.6 (C), 47.2 ($CH_2$), 44.9 ($CH_2$), 28.9 ($CH_3$); IR (KBr) 3108, 2969, 1474, 1369, 1229, 1093, 850, 741 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_7H_{17}ClNO$ 166.0993, found 166.0985.

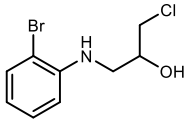


**1-Chloro-3-(phenylamino)propan-2-ol (1k).**[4] To a mixture of aniline (456 μL, 5.0 mmol, 1.0 equiv) and epichlorohydrin (394 μL, 5.0 mmol) was added LiBr (21.2 mg, 0.25 mmol, 5 mol %) at room temperature. After stirring at room temperature for 4 h, the resulting mixture was directly purified by flash column chromatography ($SiO_2$: 24 g, Hexane:EtOAc = 10:1–8:1) to give a white solid (572.7 mg, 62%). $R_f$ = 0.25 (Hexane:EtOAc = 4:1); mp 39-40 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.23-7.16 (m, 2H), 6.78-6.73 (m, 1H), 6.68-6.64 (m, 2H), 4.12-4.04 (m, 1H), 3.69 (dd, *J* = 11.1, 4.5 Hz, 1H), 3.64 (dd, *J* = 11.1, 6.0 Hz, 1H), 3.38 (dd, *J* = 13.2, 4.5 Hz, 1H), 3.24 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.54 (br, s, 2H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 147.7 (C), 129.4 (CH), 118.2 (CH), 113.3 (CH), 69.8 (CH), 47.7 ($CH_2$), 47.1 ($CH_2$); HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_9H_{13}ClNO$ 186.0680, found 186.0686.

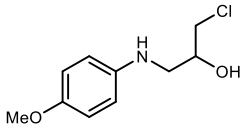


**1-Chloro-3-[(4-iodophenyl)amino]propan-2-ol (1l).** To a mixture of 4-iodoaniline (547.6 mg, 2.5 mmol, 1.0 equiv) and epichlorohydrin (196 μL, 2.5 mmol) was added LiBr (10.8 mg, 0.125 mmol, 5 mol %) at room temperature. After stirring at room temperature for 4 h, the resulting mixture was directly purified by flash column chromatography ($SiO_2$: 12 g, Hexane:EtOAc = 12:1–10:1) to give a white solid (415.5 mg, 52%). $R_f$ = 0.50 (Hexane:EtOAc = 4:1) visualized with $KMnO_4$; mp 69-70 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.46-7.41 (m, 2H), 6.46-6.41 (m, 2H), 4.10-4.02 (m, 2H), 3.68 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.62 (dd, *J* = 11.4, 6.0 Hz,

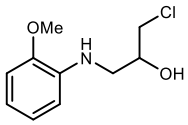
1H), 3.34 (dd, *J* = 13.2, 4.5 Hz, 1H), 3.19 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.44 (br s, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 147.4 (C), 137.9 (CH), 115.4 (CH), 78.9 (C), 69.8 (CH), 47.6 ($CH_2$), 46.8 ($CH_2$); IR (KBr) 3315, 3146, 1591, 1488, 1245, 1073, 810 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_9H_{12}ClINO$ 311.9647, found 311.9674.



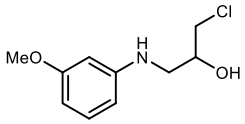

**1-[(2-Bromophenyl)amino]-3-chloropropan-2-ol (1m).** To a mixture of 2-bromoaniline (430.1 mg, 2.5 mmol, 1.0 equiv) and epichlorohydrin (196 μL, 2.5 mmol) was added LiBr (21.7 mg, 0.25 mmol, 10 mol %) at room temperature. After stirring at 50 °C for 4 h, the resulting mixture was directly purified by flash column chromatography ($SiO_2$: 14 g, Hexane:EtOAc = 30:1–3:1) to give a yellow oil (352.7 mg, 53%). $R_f$ = 0.36 (Hexane:EtOAc = 4:1) visualized with $KMnO_4$; $^{1}H$ NMR (300 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.18 (ddd, *J* = 8.1, 7.2, 1.5 Hz, 1H), 6.68 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.60 (ddd, *J* = 7.8, 7.2, 1.5 Hz, 1H), 4.63 (br s, 1H), 4.13-4.06 (m, 1H) 3.70 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.64 (dd, *J* = 11.4, 6.0 Hz, 1H), 3.45-3.40 (m, 1H), 3.29 (dd, *J* = 13.2, 6.9 Hz, 1H), 2.52 (br s, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 144.6 (C), 132.6 (CH), 128.5 (CH), 118.6 (CH), 111.6 (CH), 110.3 (C), 69.7 (CH), 47.5 ($CH_2$), 46.8 ($CH_2$); IR (KBr) 3405, 3063, 2952, 2911, 2855, 1596, 1509, 1458, 1320, 1090, 1019, 744 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_9H_{12}BrClNO$ 263.9785, found 263.9787.



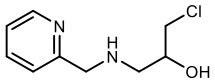

**1-Chloro-3-[(4-methoxyphenyl)amino]propan-2-ol (1n).** To a mixture of 4-methoxyaniline (307.8 mg, 2.5 mmol, 1.0 equiv) and epichlorohydrin (196 μL, 2.5 mmol) was added LiBr (10.8 mg, 0.125 mmol, 5 mol %) at room temperature. After stirring at room temperature for 4 h, the resulting mixture was directly purified by flash column chromatography ($SiO_2$: 14 g, Hexane:EtOAc = 7:1–EtOAc) to give a brownish solid (327.3 mg, 61%). $R_f$ = 0.30 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 43-44 °C; $^{1}H$ NMR (300 MHz, $CDCl_3$) δ 6.82-6.77 (m, 2H), 6.67-6.61 (m, 2H), 4.10-4.02 (m, 1H), 3.75 (s, 3H), 3.69 (dd, *J* = 11.1, 4.5 Hz, 1H), 3.63 (dd, *J* = 11.1, 6.0 Hz, 1H), 3.34 (dd, *J* = 13.2, 4.2 Hz, 1H), 3.18 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.68 (br s, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 152.7 (C), 141.8 (C), 114.9 (CH), 114.8 (CH), 69.8 (CH), 55.8 ($CH_3$), 48.2 ($CH_2$), 47.6 ($CH_2$); IR (KBr) 3255, 3082, 2832, 1514, 1246, 1038, 828 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_{15}ClNO_2$ 216.0786, found 216.0795.



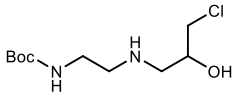

**1-Chloro-3-[(2-methoxyphenyl)amino]propan-2-ol (1o).** To a mixture of 2-methoxyaniline (282 μL, 2.5 mmol, 1.0 equiv) and epichlorohydrin (196 μL, 2.5 mmol) was added LiBr (10.8 mg, 0.125 mmol, 5 mol %) at room temperature. After stirring at room temperature for 4 h, the resulting mixture was directly purified by flash column chromatography ($SiO_2$: 14 g, Hexane:EtOAc = 15:1–5:1) to give a brownish oil (323.0 mg, 60%). $R_f$ = 0.45 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; $^{1}H$ NMR (300 MHz, $CDCl_3$) δ 6.87 (td, *J* = 7.5, 1.5 Hz, 1H), 6.78 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.74-6.64 (m, 2H), 4.12-4.05 (m, 1H), 3.84 (s, 3H), 3.69 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.65 (dd, *J* = 11.4, 6.0 Hz, 1H), 3.38 (dd, *J* = 13.5, 4.8 Hz, 1H), 3.26 (dd, *J* = 13.5, 6.9 Hz, 1H), 2.82 (br s, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 147.1 (C), 137.6 (C), 121.2 (CH), 117.4 (CH), 110.3 (CH), 109.6 (CH), 69.9 (CH), 55.4 ($CH_3$), 47.6 ($CH_2$), 46.9 ($CH_2$); IR (KBr) 3411, 2943, 2835, 1603, 1514, 1458, 1250, 1223, 1028, 741 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_{15}ClNO_2$ 216.0786, found 216.0787.



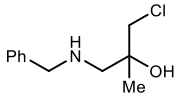
**1-Chloro-3-[(3-methoxyphenyl)amino]propan-2-ol (1p).** To a mixture of 3-methoxyaniline (280 μL, 2.5 mmol, 1.0 equiv) and epichlorohydrin (196 μL, 2.5 mmol) was added LiBr (10.8 mg, 0.125 mmol, 5 mol %) at room temperature. After stirring at room temperature for 4 h, the resulting mixture was directly purified by flash column chromatography ($SiO_2$: 14 g, Hexane:EtOAc = 20:1–EtOAc) to give a brownish oil (346.3 mg, 64%). $R_f$ = 0.40 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.09 (t, *J* = 8.1 Hz, 1H), 6.32 (ddd, *J* = 8.1, 2.4, 0.9 Hz, 1H), 6.27 (ddd, *J* = 8.1, 2.4, 0.9 Hz, 1H), 6.21 (t, *J* = 2.4 Hz, 1H), 4.10-4.02 (m, 1H), 3.77 (s, 3H), 3.67 (dd, *J* = 11.1, 4.5 Hz, 1H), 3.61 (dd, *J* = 11.1, 6.0 Hz, 1H), 3.36 (dd, *J* = 13.5, 4.5 Hz, 1H), 3.20 (dd, *J* = 13.5, 7.2 Hz, 1H), 3.10 (br s, 2H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 160.8 (C), 149.1 (C), 130.1 (CH), 106.3 (CH), 103.3 (CH), 99.4 (CH), 69.8 (CH), 55.1 ($CH_3$), 47.6 ($CH_2$), 47.0 ($CH_2$); IR (KBr) 3406, 2952, 2837, 1615, 1513, 1497, 1211, 1164, 1047, 830, 760, 689 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_{15}ClNO_2$ 216.0786, found 216.0783.



**1-Chloro-3-[(pyridin-2-ylmethyl)amino]propan-2-ol (1q).** To a solution of epichlorohydrin (196 μL, 2.5 mmol) in $^i$PrOH (7.5 mL) was added 2-picolylamine (300 μL, 3.0 mmol, 1.2 equiv) at 0 °C. After stirring at room temperature for 60 h, the mixture was concentrated. Flash column chromatography ($SiO_2$: 20 g, Hexane:EtOAc = 1:1–EtOAc–EtOAc:MeOH = 4:1) yielded a pale yellow oil (267.1 mg, 53%). $R_f$ = 0.30 (EtOAc:MeOH = 3:1) visualized with $KMnO_4$; $^1$H NMR (300 MHz, $CDCl_3$) δ 8.56 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.67 (td, *J* = 7.8, 1.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.20 (ddd, *J* = 7.8, 4.8, 0.9 Hz, 1H), 4.04-3.90 (m, 5H), 3.56 (d, *J* = 5.7 Hz, 2H), 2.91 (dd, *J* = 12.3, 3.6 Hz, 1H), 2.79 (dd, *J* = 12.3, 8.1 Hz, 1H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 158.4 (C), 149.2 (CH), 136.8 (CH), 122.5 (CH), 122.3 (CH), 69.4 (CH), 54.2 ($CH_2$), 51.9 ($CH_2$), 47.1 ($CH_2$); IR (KBr) 3306, 2952, 2911, 2846, 1595, 1436, 761 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_9H_{14}ClN_2O$ 201.0789, found 201.0791.



***tert*-Butyl {2-[(3-chloro-2-hydroxypropyl)amino]ethyl}carbamate (1r).** To a solution of epichlorohydrin (196 μL, 2.5 mmol) in $^i$PrOH (7.5 mL) was added *N*-Boc-ethylenediamine (400.5 mg, 2.5 mmol, 1.0 equiv) at 0 °C. After stirring at room temperature for 30 h, the mixture was concentrated. Flash column chromatography ($SiO_2$: 20 g, Hexane:EtOAc = 1:1–EtOAc–EtOAc:MeOH = 4:1) yielded a yellow solid (420.1 mg, 66%). $R_f$ = 0.35 (EtOAc:MeOH = 4:1) visualized with $KMnO_4$; mp 57-59 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 5.31 (br s, 1H), 3.89-3.84 (m, 1H), 3.50 (d, *J* = 5.5 Hz, 2H), 3.37 (br s, 2H), 3.20-3.17 (m, 2H), 2.77-2.63 (m, 4H), 1.38 (s, 9H); $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$) δ 156.2 (C), 79.2 (C), 69.5 (CH), 51.9 ($CH_2$), 49.1 ($CH_2$), 47.2 ($CH_2$), 39.9 ($CH_2$), 28.3 ($CH_3$); IR (KBr) 3359, 3273, 2985, 2897, 2847, 1684, 1535, 1295, 1272, 1180, 1119, 1102, 1058, 984, 968, 938, 802 694 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{21}ClN_2NaO_3$ 275.1133, found 275.1113.

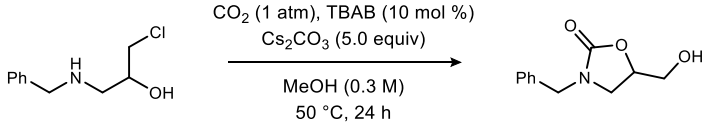


**1-(Benzylamino)-3-chloro-2-methylpropan-2-ol (1s).** To a solution of 2-(chloromethyl)-2-methyloxirane (240 μL, 2.5 mmol) in $^i$PrOH (7.5 mL) was added benzylamine (327 μL, 3.0 mmol, 1.2 equiv) at 0 °C. After stirring at room temperature for 18 h, the mixture was concentrated. Flash column chromatography ($SiO_2$: 23 g, Hexane:EtOAc = 10:1–1:2) yielded a yellow oil (276.4 mg, 52%). $R_f$ = 0.35 (Hexane:EtOAc = 1:2)

visualized with $KMnO_4$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.37-7.24 (m, 5H), 3.84 (s, 2H), 3.52 (d, *J* = 11.1 Hz, 1H), 3.46 (d, *J* = 11.1 Hz, 1H), 2.90 (d, *J* = 12.6 Hz, 1H), 2.55 (d, *J* = 12.6 Hz, 1H), 2.29 (br s, 2H), 1.25 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 139.8 (C), 128.5 (CH), 128.0 (CH), 127.2 (CH), 71.3 (C), 55.0 ($CH_2$), 54.4 ($CH_2$), 51.0 ($CH_2$), 23.5 ($CH_3$); IR (KBr) 3408, 2975, 2934, 2839, 1454, 1110, 789, 737, 699 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_{11}H_{17}ClNO$ 214.0993, found 214.0990.

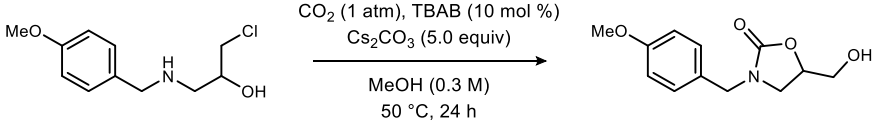
**General Procedure for the Oxazolidinone Synthesis**

To an oven-dried 10 mL test tube equipped with a stir bar was added **1** (0.30 mmol, 1.0 equiv), TBAB (9.7 mg, 0.03 mmol, 10 mol %), $Cs_2CO_3$ (488.7 mg, 1.5 mmol, 5.0 equiv), and MeOH (1.0 mL, 0.3 M). The atmosphere was replaced with $CO_2$ (× 3) using a diaphragm pump. After stirring at 50 °C for 24 h, the mixture was filtrated by Celite® with $CH_2Cl_2$ (20 mL). Flash column chromatography yielded oxazolidinone **2**.

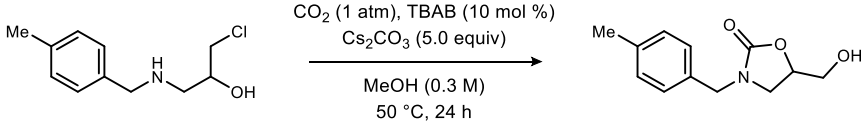



**3-Benzyl-5-(hydroxymethyl)-1,3-oxazolidin-2-one (2a).**[5] Prepared according to the general procedure using **1a** (59.9 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 7 g, Hexane:EtOAc = 1:1–EtOAc) yielded a white solid (59.0 mg, 95%). $R_f$ = 0.30 (EtOAc:Hexane = 2.5:1) visualized with $KMnO_4$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.38-7.26 (m, 5H), 4.61-4.53 (m, 1H), 4.48 (d, *J* = 15.0 Hz, 1H), 4.36 (d, *J* = 15.0 Hz, 1H), 3.84 (ddd, *J* = 12.6, 6.6, 3.3 Hz, 1H), 3.60 (ddd, *J* = 12.6, 6.6, 4.5 Hz, 1H), 3.44 (t, *J* = 8.7 Hz, 1H), 3.35 (dd, *J* = 8.7, 6.6 Hz, 1H), 3.25-3.21 (t, *J* = 6.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 158.1 (C), 135.5 (C), 128.8 (CH), 128.0 (CH), 127.9 (CH), 73.6 (CH), 62.9 ($CH_2$), 48.2 ($CH_2$), 45.1 ($CH_2$); HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{13}NNaO_3$ 230.0788, found 230.0776.

**Procedure for a gram-scale reaction:** To an oven-dried 50 mL round-bottom flask equipped with a stir bar was added **1a** (1.20 g, 6.0 mmol), TBAB (193 mg, 0.60 mmol, 10 mol %), $Cs_2CO_3$ (9.80 g, 30 mmol, 5.0 equiv), and MeOH (20 mL, 0.3 M). The atmosphere was replaced with $CO_2$ (× 3) using a diaphragm pump. After stirring at 50 °C for 24 h, the mixture was filtrated by Celite® with $CH_2Cl_2$ (60 mL). Flash column chromatography ($SiO_2$: 16 g, Hexane:EtOAc = 1:1–EtOAc) yielded **2a** (1.13 g, 91%).

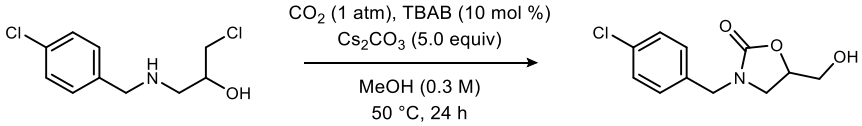



**5-(Hydroxymethyl)-3-(4-methoxylbenzyl)-1,3-oxazolidin-2-one (2b).** Prepared according to the general procedure using **1b** (68.9 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 13 g, Hexane:EtOAc = 2:1–1:2) yielded a white solid (70.2 mg, 98%). $R_f$ = 0.30 (EtOAc) visualized with $KMnO_4$; mp 93-94 °C; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.23-7.18 (m, 2H), 6.90-6.85 (m, 2H), 4.56 (dddd, *J* = 8.7, 6.6, 4.5, 3.3 Hz, 1H), 4.42 (d, *J* = 14.7 Hz, 1H), 4.31 (d, *J* = 14.7 Hz, 1H), 3.83 (dd, *J* = 12.6, 3.3 Hz, 1H), 3.80 (s, 3H), 3.60 (dd, *J* = 12.6, 4.5 Hz, 1H), 3.42 (t, *J* = 8.7 Hz, 1H), 3.31 (dd, *J* = 8.7, 6.6 Hz, 1H), 2.73 (br s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 159.3 (C), 157.9 (C), 129.4 (CH), 127.6 (C), 114.2 (CH), 73.5 (CH), 63.1 ($CH_2$), 55.3 ($CH_3$), 47.7 ($CH_2$), 45.0 ($CH_2$); IR (KBr) 3354, 2919, 1718, 1519, 1459, 1256, 1182, 1100, 1035, 837, 762 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{15}NNaO_4$ 260.0893, found 260.0910.

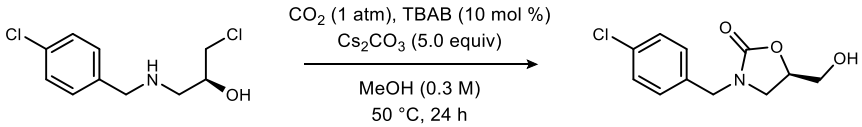



**5-(Hydroxymethyl)-3-(4-methylbenzyl)-1,3-oxazolidin-2-one (2c).** Prepared according to the general procedure using **1c** (64.1 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 13 g, Hexane:EtOAc = 2:1–

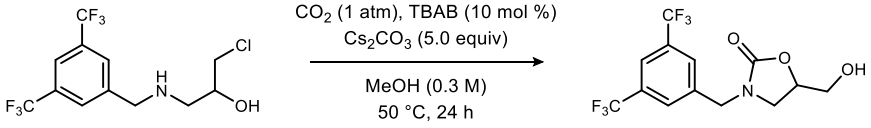
1:2) yielded a white solid (63.2 mg, 95%). $R_f$ = 0.40 (EtOAc) visualized with $KMnO_4$; mp 78-80 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.19-7.13 (m, 4H), 4.56 (dddd, *J* = 8.7, 6.6, 4.5, 3.3 Hz, 1H), 4.44 (d, *J* = 14.7 Hz, 1H), 4.33 (d, *J* = 14.7 Hz, 1H), 3.84 (ddd, *J* = 12.6, 6.3, 3.3 Hz, 1H), 3.61 (ddd, *J* = 12.6, 6.3, 4.5 Hz, 1H), 3.42 (t, *J* = 8.7 Hz, 1H), 3.31 (dd, *J* = 8.7, 6.6 Hz, 1H), 2.63 (t, *J* = 6.3 Hz, 1H), 2.34 (s, 3H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 157.9 (C), 137.7 (C), 132.5 (C), 129.5 (CH), 128.1 (CH), 73.5 (CH), 63.1 ($CH_2$), 48.0 ($CH_2$), 45.0 ($CH_2$), 21.1 ($CH_3$); IR (KBr) 3418, 2946, 2920, 1725, 1708, 1460, 1269, 1105, 992, 766 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{15}NNaO_3$ 244.0944, found 244.0933.



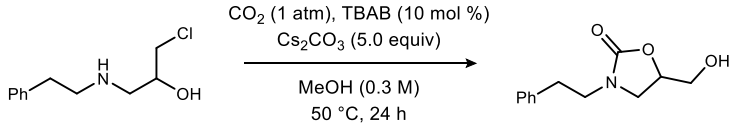

**3-(4-Chlorobenzyl)-5-(hydroxymethyl)-1,3-oxazolidin-2-one (2d).** Prepared according to the general procedure using **1d** (70.2 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 13 g, Hexane:EtOAc = 2:1–1:2) yielded a white solid (69.2 mg, 95%). $R_f$ = 0.35 (EtOAc) visualized with $KMnO_4$; mp 82-83 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.35-7.31 (m, 2H), 7.25-7.20 (m, 2H), 4.59 (dddd, *J* = 8.7, 6.6, 3.9, 3.3 Hz, 1H), 4.43 (d, *J* = 15.0 Hz, 1H), 4.37 (d, *J* = 15.0 Hz, 1H), 3.86 (dd, *J* = 12.6, 3.0 Hz, 1H), 3.60 (dd, *J* = 12.6, 3.9 Hz, 1H), 3.44 (t, *J* = 8.7 Hz, 1H), 3.36 (dd, *J* = 8.7, 6.6 Hz, 1H), 2.82 (br s, 1H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 158.0 (C), 134.1 (C), 133.9 (C), 129.4 (CH), 129.0 (CH), 73.5 (CH), 62.9 ($CH_2$), 47.6 ($CH_2$), 45.1 ($CH_2$); IR (KBr) 3363, 2909, 1724, 1711, 1492, 1282, 1102, 814 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{12}ClNNaO_3$ 264.0398, found 264.0416.



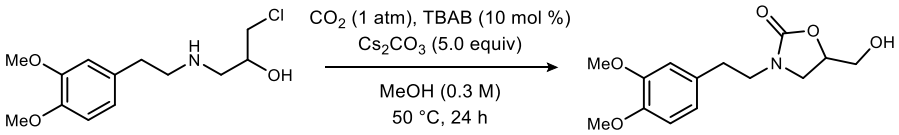

(*S*)-**2d**. Prepared according to the general procedure using (*S*)-**1d** (70.2 mg, 0.30 mmol, 99% ee). Flash column chromatography ($SiO_2$: 13 g, Hexane:EtOAc = 2:1–1:2) yielded a white solid (71.3 mg, 98%). The product was determined to be 99% ee by chiral HPLC analysis (Chiralpak AD-3, Hexane:EtOH = 70:30, 1.0 mL/min, $t_r$(*minor*) = 12.0 min, $t_r$(*major*) = 15.3 min, 220 nm, 35 °C); $[\alpha]_D^{24}$ -40.9 (*c* 0.50, $CHCl_3$, 99% ee). The absolute configuration was determined according to the literature.[6]



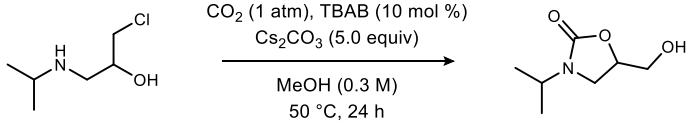

**3-[3,5-Bis(trifluoromethyl)benzyl]-5-(hydroxymethyl)-1,3-oxazolidin-2-one (2e).** Prepared according to the general procedure using **1e** (100.7 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 13 g, Hexane:EtOAc = 3:1–1:2) yielded a white solid (95.1 mg, 92%). $R_f$ = 0.35 (Hexane:EtOAc = 1:3) visualized with $KMnO_4$; mp 129-131 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.77 (s, 2H), 4.70-4.63 (m, 1H), 4.63 (d, *J* = 15.9 Hz, 1H), 4.52 (d, *J* = 15.9 Hz, 1H), 3.96 (d, *J* = 12.6, 1.2 Hz, 1H), 3.62 (d, *J* = 12.6 Hz, 1H), 3.53 (t, *J* = 8.4 Hz, 1H), 3.47 (dd, *J* = 8.4, 6.6 Hz, 1H), 2.63 (br s, 1H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 158.1 (C), 138.5 (C), 132.3 (q, *J* = 33.6 Hz, C), 127.9 (q, *J* = 2.8 Hz, CH), 123.1 (q, *J* = 272.7 Hz, C), 122.0 (sept, *J* = 3.9 Hz, CH), 73.6 (CH), 62.8 ($CH_2$), 47.6 ($CH_2$), 45.2 ($CH_2$); $^{19}$F{$^1$H} NMR (470 MHz, $CDCl_3$) δ -62.9; IR (KBr) 3390, 2943, 1731, 1349, 1283, 1167, 1119, 707, 682 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{11}F_6NNaO_3$ 366.0535, Found 366.0532.



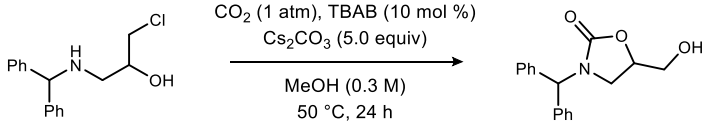

**5-(Hydroxymethyl)-3-(2-phenylethyl)-1,3-oxazolidin-2-one (2f).** Prepared according to the general procedure using **1f** (64.1 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 7 g, EtOAc) yielded a white solid (55.8 mg, 84%). $R_f$ = 0.40 (EtOAc) visualized with $KMnO_4$; mp 85-87 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.32-7.20 (m, 5H), 4.54-4.46 (m, 1H), 3.76 (dd, *J* = 12.3, 3.0 Hz, 1H), 3.59-3.31 (m, 6H), 2.86 (t, *J* = 7.5 Hz, 2H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 157.9 (C), 138.2 (C), 128.6 (CH), 128.5 (CH), 126.5 (CH), 73.5 (CH), 62.7 ($CH_2$), 46.0 ($CH_2$), 45.3 ($CH_2$), 33.7 ($CH_2$); IR (KBr) 3362, 2937, 2878, 1712, 1464, 1268, 1102, 1039, 776, 759, 709 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{15}NNaO_3$ 244.0944, found 244.0939.



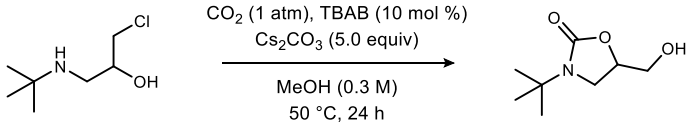

**3-[2-(3,4-Dimethoxyphenyl)ethyl]-5-(hydroxymethyl)-1,3-oxazolidin-2-one (2g).** Prepared according to the general procedure using **1g** (82.1 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 7 g, Hexane:EtOAc = 1:2) yielded a white solid (75.7 mg, 90%). $R_f$ = 0.25 (EtOAc) visualized with $KMnO_4$; mp 82-84 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 6.82-6.74 (m, 3H), 4.55-4.47 (m, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.77 (dd, *J* = 12.6, 3.3 Hz, 1H), 3.62-3.35 (m, 6H), 2.82 (t, *J* = 7.2 Hz, 2H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 157.9 (C), 148.9 (C), 147.6 (C), 130.6 (C), 120.5 (CH), 111.7 (CH), 111.2 (CH), 73.5 (CH), 62.7 ($CH_2$), 55.8 ($CH_3$), 46.0 ($CH_2$), 45.3 ($CH_2$), 33.3 ($CH_2$); IR (KBr) 3420, 2948, 2832, 1727, 1516, 1451, 1264, 1158, 1034, 767 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{19}NNaO_5$ 304.1155, found 304.1152.



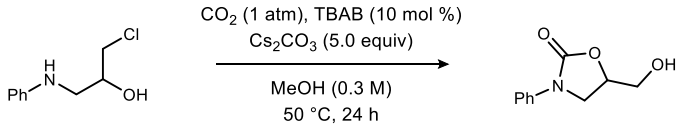

**5-(Hydroxymethyl)-3-(propan-2-yl)-1,3-oxazolidin-2-one (2h).** Prepared according to the general procedure using **1h** (45.5 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 7 g, Hexane:EtOAc = 1:1) yielded a white solid (43.1 mg, 90%). $R_f$ = 0.30 (EtOAc) visualized with $KMnO_4$; mp 54-55 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 4.63-4.55 (m, 1H), 4.07 (sept, *J* = 6.9 Hz, 1H), 3.84 (dd, *J* = 12.0, 4.2 Hz, 1H), 3.82 (br s, 1H), 3.66 (dd, *J* = 12.0, 3.3 Hz, 1H), 3.53 (t, *J* = 8.7 Hz, 1H), 3.43 (dd, *J* = 8.7, 6.6 Hz, 1H), 1.183 (d, *J* = 6.9 Hz, 3H), 1.177 (d, *J* = 6.9 Hz, 3H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 157.3 (C), 73.6 (CH), 62.8 ($CH_2$), 44.7 (CH), 40.8 ($CH_2$), 19.7 ($CH_3$), 19.4 ($CH_3$); IR (KBr) 3357, 2974, 2934, 2875, 1716, 1455, 1266, 1078, 1058, 762 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_7H_{13}NNaO_3$ 182.0788, found 182.0794.



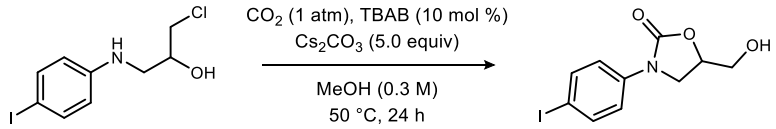

**3-(Diphenylmethyl)-5-(hydroxymethyl)-1,3-oxazolidin-2-one (2i).** Prepared according to the general procedure using **1i** (82.7 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 7 g, Hexane:EtOAc = 3:1) yielded a white solid (76.0 mg, 90%). $R_f$ = 0.40 (Hexane:EtOAc = 1:2) visualized with $KMnO_4$; mp 138-140 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.40-7.20 (m, 10H), 6.34 (s, 1H), 4.61-4.54 (m, 1H), 3.86 (dd, *J* = 12.6, 3.0 Hz, 1H), 3.60 (dd, *J* = 12.6, 3.9 Hz, 1H), 3.37 (dd, *J* = 8.7, 6.9 Hz, 1H), 3.33 (t, *J* = 8.7 Hz, 1H), 2.65 (br s, 1H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 157.9 (C), 138.1 (C), 137.9 (C), 128.69 (CH), 128.65 (CH), 128.6 (CH), 128.04 (CH), 127.95 (CH), 127.6 (CH), 73.9 (CH), 62.9 ($CH_2$), 60.8 (CH), 43.0 ($CH_2$); IR (KBr) 3376, 2916, 1705, 1477, 1262, 712 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{17}NNaO_3$ 306.1101, found 306.1107.



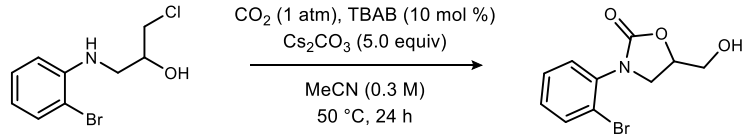

**3-*tert*-Butyl-5-(hydroxymethyl)-1,3-oxazolidin-2-one (2j).**[5] Prepared according to the general procedure using **1j** (49.7 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 7 g, Hexane:EtOAc = 1:1) yielded a white solid (44.1 mg, 85%). $R_f$ = 0.45 (EtOAc) visualized with $KMnO_4$; mp 53-54 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 4.52-4.44 (m, 1H), 3.82 (dt, *J* = 12.0, 4.2 Hz, 1H), 3.68-3.51 (m, 4H), 1.39 (s, 9H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 156.9 (C), 72.3 (CH), 62.7 ($CH_2$), 53.4 (C), 44.5 ($CH_2$), 27.3 ($CH_3$). Characterization data matched the literature.




**5-(Hydroxymethyl)-3-phenyl-1,3-oxazolidin-2-one (2k).**[5] Prepared according to the general procedure using **1k** (54.8 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 15 g, Hexane:EtOAc = 3:1) yielded a white solid (54.0 mg, 93%). $R_f$ = 0.25 (Hexane:EtOAc = 1:2) visualized with $KMnO_4$; mp 138-139 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.56-7.52 (m, 2H), 7.41-7.34 (m, 2H), 7.17-7.12 (m, 1H), 4.78-4.70 (m, 1H), 4.05 (t, *J* = 8.7 Hz, 1H), 4.00 (dd, *J* = 8.7, 7.1 Hz, 1H), 3.96 (br s, 1H), 3.78-3.74 (m, 1H), 2.52. (br s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 154.9 (C), 138.0 (C), 129.0 (CH), 124.2 (CH), 118.3 (CH), 72.9 (CH), 62.7 ($CH_2$), 46.3 ($CH_2$); IR (KBr) 3390, 2953, 2926, 2867, 1713, 1601, 1497, 1430, 1383, 1310, 1233, 1146, 1005, 767 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{11}NNaO_3$ 216.0631, found 216.0630.

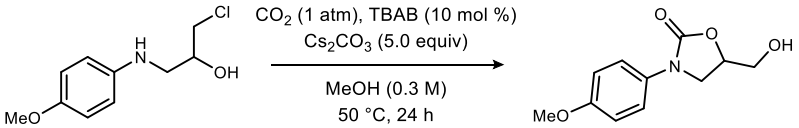



**5-(Hydroxymethyl)-3-(4-iodophenyl)-1,3-oxazolidin-2-one (2l).**[5] Prepared according to the general procedure using **1l** (93.5 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 15 g, Hexane:EtOAc = 2:1–1:2) yielded a white solid (84.8 mg, 89%). $R_f$ = 0.30 (Hexane:EtOAc = 1:2) visualized with $KMnO_4$; mp 114-115 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.68-7.63 (m, 2H), 7.34-7.29 (m, 2H), 4.78-4.70 (m, 1H), 4.03-3.94 (m, 3H), 3.74 (d, *J* = 12.4 Hz, 1H), 2.65 (br s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 154.6 (C), 137.93 (CH), 137.88 (C), 120.0 (CH), 87.6 (C), 72.9 (CH), 62.6 ($CH_2$), 46.0 ($CH_2$); IR (KBr) 3385, 2962, 1743, 1726, 1494, 1428, 1233, 1083, 811, 754 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{10}INNaO_3$ 341.9598, found 341.9597.

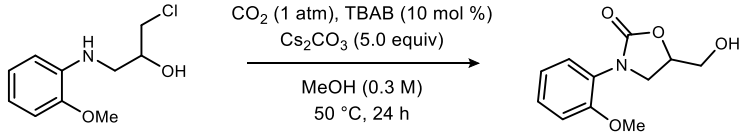



**3-(2-Bromophenyl)-5-(hydroxymethyl)-1,3-oxazolidin-2-one (2m).** Prepared according to the general procedure using **1m** (79.4 mg, 0.30 mmol) in MeCN (1.0 mL, 0.3 M). Flash column chromatography ($SiO_2$: 13 g, Hexane:EtOAc = 2:1–1:2) yielded a white solid (71.1 mg, 87%). $R_f$ = 0.20 (Hexane:EtOAc = 1:3) visualized with $KMnO_4$; mp 93-94 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.43-7.35 (m, 2H), 7.24 (ddd, *J* = 8.1, 6.9, 2.4 Hz, 1H), 4.82 (dddd, *J* = 8.7, 6.6, 4.5, 3.3 Hz, 1H), 4.04 (t, *J* = 8.7 Hz, 1H), 3.98 (dd, *J* = 12.6, 3.3 Hz, 1H), 3.90 (dd, *J* = 8.7, 6.6 Hz, 1H), 3.80 (dd, *J* = 12.6, 4.5 Hz, 1H), 2.77 (br s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 156.3 (C), 136.2 (C), 133.7 (CH), 130.0 (CH), 129.8 (CH),

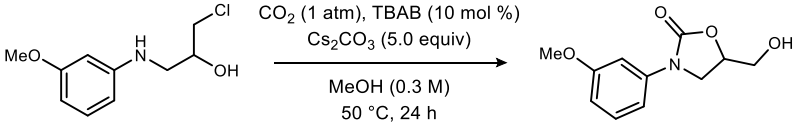
128.7 (CH), 122.5 (C), 74.3 (CH), 63.0 ($CH_2$), 48.3 ($CH_2$); IR (KBr) 3395, 2915, 2874, 1714, 1487, 1236, 1146, 758 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{10}BrNNaO_3$ 293.9736, found 293.9758.



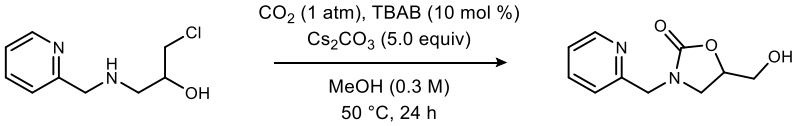

**5-(Hydroxymethyl)-3-(4-methoxyphenyl)-1,3-oxazolidin-2-one (2n).**[2] Prepared according to the general procedure using **1n** (64.7 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 13 g, Hexane:EtOAc = 3:1–2:1) yielded a white solid (65.7 mg, 97%). $R_f$ = 0.30 (Hexane:EtOAc = 1:2) visualized with $KMnO_4$; mp 138-140 °C; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.47-7.41 (m, 2H), 6.94-6.88 (m, 2H), 4.77-4.69 (m, 1H), 4.04-3.93 (m, 3H), 3.80 (s, 3H), 3.76 (dd, *J* = 12.6, 4.2 Hz, 1H), 2.30 (br s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 156.5 (C), 155.0 (C), 131.2 (C), 120.4 (CH), 114.3 (CH), 72.8 (CH), 62.9 ($CH_2$), 55.5 ($CH_3$), 46.9 ($CH_2$); IR (KBr) 3419, 2930, 1718, 1517, 1445, 1237, 1037, 826 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{13}NNaO_4$ 246.0737, found 246.0746.




**5-(Hydroxymethyl)-3-(2-methoxyphenyl)-1,3-oxazolidin-2-one (2o).** Prepared according to the general procedure using **1o** (64.7 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 15 g, Hexane:EtOAc = 3:1–1:2) yielded a white solid (59.2 mg, 88%). $R_f$ = 0.20 (Hexane:EtOAc = 1:3) visualized with $KMnO_4$; mp 69-70 °C; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.36-7.33 (m, 1H), 7.31-7.26 (m, 1H), 7.00-6.94 (m, 2H), 4.78-4.70 (m, 1H), 3.99 (t, *J* = 8.7 Hz, 1H), 3.92-3.80 (m, 5H), 3.75 (dd, *J* = 12.6, 4.8 Hz, 1H), 3.07 (br s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 157.0 (C), 154.9 (C), 129.0 (CH), 128.4 (CH), 125.7 (C), 120.9 (CH), 112.0 (CH), 74.1 (CH), 63.2 ($CH_2$), 55.6 ($CH_3$), 48.2 ($CH_2$); IR (KBr) 3376, 2957, 1719, 1512, 1437, 1247, 1023, 758 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{13}NNaO_4$ 246.0737, found 246.0729.

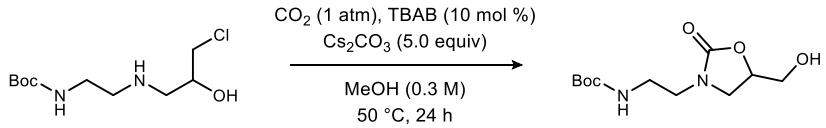



**5-(Hydroxymethyl)-3-(3-methoxyphenyl)-1,3-oxazolidin-2-one (2p).**[2] Prepared according to the general procedure using **1p** (64.7 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 13 g, Hexane:EtOAc = 2:1–1:2) yielded a white solid (59.8 mg, 90%). $R_f$ = 0.25 (Hexane:EtOAc = 1:3) visualized with $KMnO_4$; mp 120-121 °C; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 7.04 (ddd, *J* = 8.1, 2.1, 0.9 Hz, 1H), 6.70 (ddd, *J* = 8.4, 2.4, 0.9 Hz, 1H), 4.77-4.69 (m, 1H), 4.06-3.94 (m, 3H), 3.82 (s, 3H), 3.76 (dd, *J* = 12.6, 3.9 Hz, 1H), 2.36 (br s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 160.2 (C), 154.6 (C), 139.3 (C), 129.8 (CH), 110.4 (CH), 109.8 (CH), 104.5 (CH), 72.8 (CH), 62.8 ($CH_2$), 55.4 ($CH_3$), 46.4 ($CH_2$); IR (KBr) 3409, 2967, 1718, 1499, 1415, 1250, 1014, 779 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{13}NNaO_4$ 246.0737, found 246.0737.

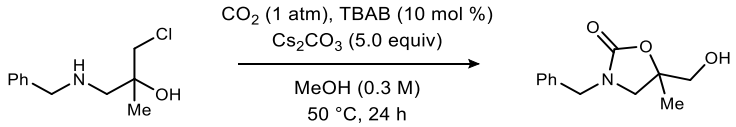



**5-(Hydroxymethyl)-3-(pyridin-2-ylmethyl)-1,3-oxazolidin-2-one (2q).** Prepared according to the general procedure using **1q** (40.0 mg, 0.20 mmol). Flash column chromatography ($SiO_2$: 7 g, EtOAc:MeOH = 200:1–20:1) yielded a pale yellow oil (35.5 mg, 86%). $R_f$ = 0.40 (EtOAc:MeOH = 3:1) visualized with $KMnO_4$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.54 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.71 (td, *J* = 7.8, 1.8 Hz, 1H), 7.34 (d, *J* = 7.8

Hz, 1H), 7.26-7.21 (m, 1H), 4.68-4.61 (m, 2H), 4.52 (d, *J* = 15.9 Hz, 1H), 4.14 (br s, 1H), 3.89 (dd, *J* = 12.3, 3.2 Hz, 1H), 3.70-3.63 (m, 1H), 3.55 (dd, *J* = 8.7, 6.0 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 158.3 (C), 155.6 (C), 149.2 (CH), 137.3 (CH), 122.8 (CH), 122.1 (CH), 73.8 (CH), 63.1 ($CH_2$), 49.3 ($CH_2$), 45.9 ($CH_2$); IR (KBr) 3400, 2925, 1738, 1595, 1490, 1440, 1272, 1080, 763 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{12}N_2NaO_3$ 231.0740, found 231.0729.



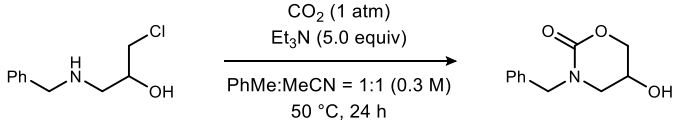

***tert*-Butyl {2-[5-(hydroxymethyl)-2-oxo-1,3-oxazolidin-3-yl]ethyl}carbamate (2r).** Prepared according to the general procedure using **1r** (50.5 mg, 0.20 mmol). Flash column chromatography ($SiO_2$: 7 g, EtOAc:MeOH = 200:1–20:1) yielded a pale yellow oil (45.3 mg, 87%). $R_f$ = 0.45 (EtOAc:MeOH = 10:1) visualized with $KMnO_4$; $^{1}H$ NMR (500 MHz, $CDCl_3$) δ 5.12 (br s, 1H), 4.62-4.57 (m, 1H), 3.87-3.84 (m, 2H), 3.69-3.64 (m, 2H), 3.57 (dd, *J* = 8.2, 6.3 Hz, 1H), 3.40-3.30 (m, 5H), 1.42 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 158.5 (C), 155.4 (C), 79.6 (C), 73.7 (CH), 62.9 ($CH_2$), 45.6 ($CH_2$), 44.1 ($CH_2$), 37.9 ($CH_2$), 28.3 ($CH_3$); IR (KBr) 3370, 2978, 2934, 1737, 1693, 1525, 1454, 1366, 1254, 1171, 763 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{20}N_2NaO_5$ 283.1264, found 283.1257.




**3-Benzyl-5-(hydroxymethyl)-5-methyl-1,3-oxazolidin-2-one (2s).** Prepared according to the general procedure using **1s** (64.1 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 15 g, Hexane:EtOAc = 4:1–1:2) yielded a white solid (64.9 mg, 98%). $R_f$ = 0.45 (EtOAc) visualized with $KMnO_4$; mp 78-79 °C; $^{1}H$ NMR (300 MHz, $CDCl_3$) δ 7.38-7.25 (m, 5H), 4.50 (d, *J* = 15.0 Hz, 1H), 4.38 (d, *J* = 15.0 Hz, 1H), 3.66 (d, *J* = 12.0 Hz, 1H), 3.50 (d, *J* = 8.4 Hz, 1H), 3.43 (d, *J* = 12.0 Hz, 1H), 3.04 (d, *J* = 8.4 Hz, 1H), 2.98 (br s, 1H), 1.35 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 157.6 (C), 135.7 (C), 128.8 (CH), 127.89 (CH), 127.85 (CH), 79.6 (C), 67.0 ($CH_2$), 51.1 ($CH_2$), 48.1 ($CH_2$), 22.7 ($CH_3$); IR (KBr) 3328, 2920, 1716, 1496, 1453, 1324, 1080, 963, 762, 698 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{15}NNaO_3$ 244.0944, found 244.0937.

## General Procedure for the Oxazinanone Synthesis

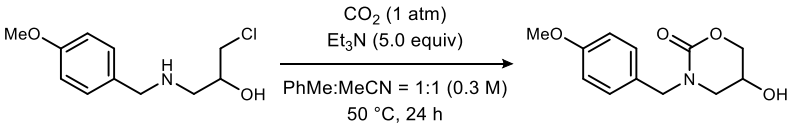
To an oven-dried 10 mL test tube equipped with a stir bar was added **1** (0.30 mmol, 1.0 equiv), a 1:1 mixture of PhMe/MeCN (v/v, 1.0 mL, 0.3 M), and $Et_3N$ (0.21 mL, 1.5 mmol, 5.0 equiv). The atmosphere was replaced with $CO_2$ (× 3) using a diaphragm pump. After stirring at 50 °C for 24 h, the mixture was directly purified by flash column chromatography to obtain oxazinanone **3**.



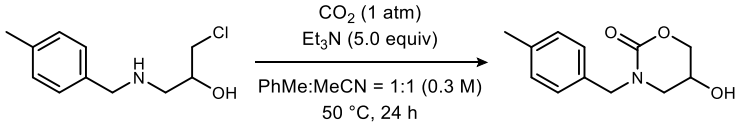

**3-Benzyl-5-hydroxy-1,3-oxazinan-2-one (3a).**[6] Prepared according to the general procedure using **1a** (59.9 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 8 g, EtOAc:$Et_3N$ = 250:1) yielded a white solid (57.7 mg, 93%). $R_f$ = 0.30 (EtOAc) visualized with $KMnO_4$; $^{1}H$ NMR (300 MHz, $CDCl_3$) δ 7.36-7.25 (m, 5H), 4.65 (d, *J* = 15.0 Hz, 1H), 4.43 (d, *J* = 15.0 Hz, 1H), 4.28-4.18 (m, 2H) 4.15-4.10 (m, 1H), 3.84 (br s, 1H), 3.40 (dd, *J* = 12.3, 3.9 Hz, 1H), 3.22-3.16 (m, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 153.8 (C), 136.1 (C), 128.7 (CH), 127.9 (CH), 127.7 (CH), 70.5 ($CH_2$), 60.9 (CH), 52.7 ($CH_2$), 51.3 ($CH_2$); $^{1}H$ NMR (300 MHz, $CD_3OD$) δ 7.38-7.25 (m, 5H), 4.57 (d, *J* = 15.3 Hz, 1H), 4.52 (d, *J* = 15.3 Hz, 1H), 4.32 (dddd, *J* = 11.4, 1.8, 0.6, 0.6 Hz, 1H), 4.18 (ddd, *J* = 11.4, 3.3, 2.7 Hz, 1H), 4.12-4.08 (m, 1H), 3.49 (ddd, *J* = 12.3, 3.9, 0.6 Hz, 1H), 3.15

(dddd, $J$ = 12.3, 2.7, 2.7, 0.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CD_3OD$) δ 156.0 (C), 137.9 (C), 129.7 (CH), 128.9 (CH), 128.7 (CH), 71.9 ($CH_2$), 61.9 (CH), 53.5 ($CH_2$), 52.5 ($CH_2$); IR (KBr) 3294, 2921, 1668, 1504, 1264, 730 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{13}NNaO_3$ 230.0788, found 230.0801.

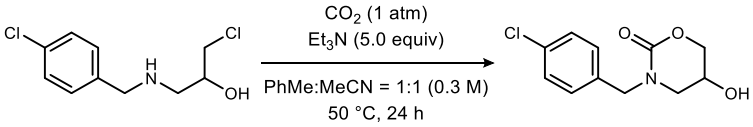
**Procedure for a gram-scale reaction:** To an oven-dried 50 mL round-bottom flask equipped with a stir bar was added **1a** (1.20 g, 6.0 mmol), a 1:1 mixture of PhMe/MeCN (v/v, 20 mL, 0.3 M), and $Et_3N$ (4.2 mL, 30 mmol, 5.0 equiv). The atmosphere was replaced with $CO_2$ (× 3) using a diaphragm pump. After stirring at 50 °C for 24 h, the mixture was concentrated. Flash column chromatography ($SiO_2$: 25 g, EtOAc:$Et_3N$ = 250:1) yielded **3a** (1.10 g, 89%).



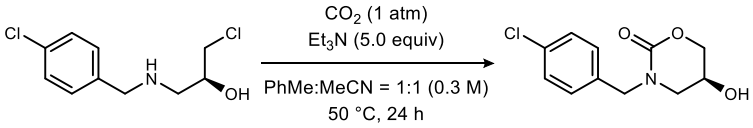

**5-Hydroxy-3-(4-methoxylbenzyl)-1,3-oxazinan-2-one (3b).** Prepared according to the general procedure using **1b** (68.9 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 7 g, EtOAc:$Et_3N$ = 250:1) yielded a white solid (61.3 mg, 86%). $R_f$ = 0.15 (EtOAc) visualized with $KMnO_4$; mp 97-99 °C; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.25-7.20 (m, 2H), 6.88-6.84 (m, 2H), 4.58 (d, $J$ = 14.7 Hz, 1H), 4.38 (d, $J$ = 14.7 Hz, 1H), 4.27-4.17 (m, 2H), 4.14-4.10 (m, 1H), 3.79 (s, 3H), 3.47 (br s, 1H), 3.38 (dd, $J$ = 12.3, 3.9 Hz, 1H), 3.20-3.15 (m, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 159.1 (C), 153.7 (C), 129.4 (CH), 128.2 (C), 114.0 (CH), 70.5 ($CH_2$), 60.8 (CH), 55.2 ($CH_3$), 52.1 ($CH_2$) 51.0 ($CH_2$); IR (KBr) 3512, 3376, 2936, 1686, 1516, 1493, 1248, 1027, 811 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{15}NNaO_4$ 260.0893, found 260.0893.




**5-Hydroxy-3-(4-methylbenzyl)-1,3-oxazinan-2-one (3c).** Prepared according to the general procedure using **1c** (64.1 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 7 g, EtOAc:$Et_3N$ = 250:1) yielded a white solid (58.7 mg, 88%). $R_f$ = 0.20 (EtOAc) visualized with $KMnO_4$; mp 109-110 °C; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.19-7.11 (m, 4H), 4.62 (d, $J$ = 15.0 Hz, 1H), 4.35 (d, $J$ = 15.0 Hz, 1H), 4.25-4.16 (m, 2H), 4.13-4.08 (m, 1H), 4.01 (br s, 1H), 3.37 (dd, $J$ = 12.3, 3.9 Hz, 1H), 3.19-3.14 (m, 1H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 153.7 (C), 137.4 (C), 133.1 (C) 129.4 (CH), 128.0 (CH), 70.5 ($CH_2$), 61.0 (CH), 52.5 ($CH_2$), 51.2 ($CH_2$), 21.1 ($CH_3$); IR (KBr) 3420, 2923, 1671, 1496, 1250, 1153, 760 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{15}NNaO_3$ 244.0944, found 244.0939.




**3-(4-Chlorobenzyl)-5-hydroxy-1,3-oxazinan-2-one (3d).** Prepared according to the general procedure using **1d** (70.1 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 7 g, EtOAc:$Et_3N$ = 250:1) yielded a white solid (64.0 mg, 88%). $R_f$ = 0.20 (EtOAc) visualized with $KMnO_4$; mp 131-132 °C; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.27-7.23 (m, 2H), 4.55 (d, $J$ = 15.0 Hz, 1H), 4.49 (d, $J$ = 15.0 Hz, 1H), 4.31-4.21 (m, 2H), 4.18-4.14 (m, 1H), 3.43 (dd, $J$ = 12.3, 3.9 Hz, 1H), 3.22-3.16 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 153.3 (C), 134.7 (C), 133.7 (C), 129.4 (CH), 128.9 (CH), 70.5 ($CH_2$), 61.3 (CH), 52.1 ($CH_2$), 51.5 ($CH_2$); IR (KBr) 3296, 2919, 1665, 1493, 1282, 1160, 1012, 836, 757 $cm^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{12}ClNNaO_3$ 264.0398, found 264.0420.




(*S*)-**3d**. Prepared according to the general procedure using (*S*)-**1d** (70.1 mg, 0.30 mmol, 99% ee). Flash column chromatography ($SiO_2$: 7 g, EtOAc:$Et_3N$ = 250:1) yielded a white solid (63.4 mg, 88%). The product was determined to be 99% ee by chiral HPLC analysis (Chiralcel OZ-3, Hexane:EtOH = 80:20, 1.0 mL/min, $t_r$(*minor*) = 11.3 min, $t_r$(*major*) = 14.4 min, 220 nm, 35 °C); $[\alpha]_D^{23}$ -34.9 (*c* 0.50, $CHCl_3$, 99% ee). The absolute configuration was determined to be (*S*) by X-ray crystallographic analysis. The crystal was grown from EtOAc under hexane atmosphere. The data has been deposited with the Cambridge Crystallographic Data Centre (CCDC2082859).

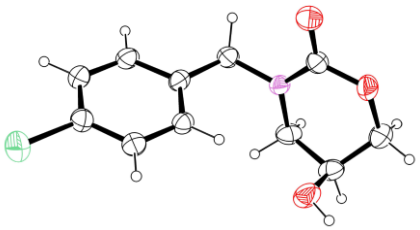
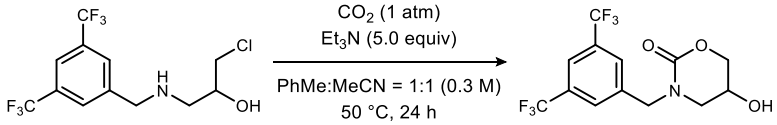
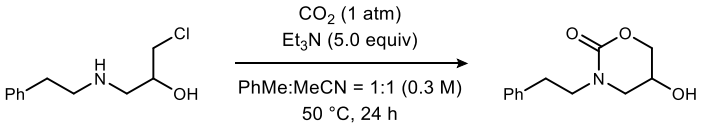


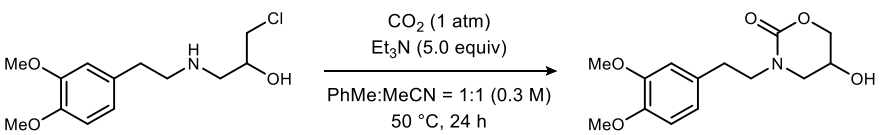
**Figure S1.** ORTEP drawing of (*S*)-**3d** (30% probability ellipsoids).



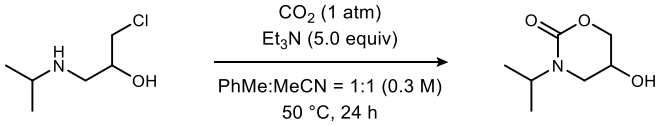

**3-[3,5-Bis(trifluoromethyl)benzyl]-5-hydroxy-1,3-oxazinan-2-one (3e).** Prepared according to the general procedure using **1e** (100.7 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 7 g, Hexane:EtOAc:$Et_3N$ = 150:50:1–EtOAc) yielded a white solid (89.5 mg, 87%). $R_f$ = 0.30 (EtOAc) visualized with $KMnO_4$; mp 143-145 °C; $^1$H NMR (300 MHz, $CD_3OD$) δ 7.99 (s, 2H), 7.88 (s, 1H), 4.89 (d, *J* = 15.9 Hz, 1H), 4.51 (d, *J* = 15.9, Hz, 1H), 4.41 (dd, *J* = 11.4, 1.8 Hz, 1H), 4.25 (dt, *J* = 11.4, 3.0 Hz, 1H), 4.17-4.13 (m, 1H), 3.67 (dd, *J* = 12.3, 3.0 Hz, 1H), 3.22 (dt, *J* = 12.3, 2.7 Hz, 1H); $^{13}$C{$^1$H} NMR (75 MHz, $CD_3OD$) δ 156.0 (C), 141.8 (C), 133.0 (q, *J* = 33.3 Hz, C), 129.2 (q, *J* = 2.7 Hz, CH), 124.8 (q, *J* = 271.8 Hz, C), 122.3 (sept, *J* = 3.9 Hz, CH), 72.3 ($CH_2$), 61.8 (CH), 53.1 ($CH_2$), 52.5 ($CH_2$); $^{19}$F{$^1$H} NMR (470 MHz, $CD_3OD$) δ -64.3; IR (KBr) 3289, 2930, 1657, 1508, 1281, 1167, 1126, 1015, 837, 763, 683 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{11}F_6NNaO_3$ 366.0535, found 366.0524.



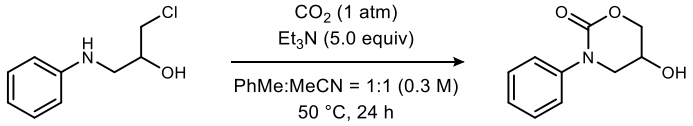

**5-Hydroxy-3-(2-phenylethyl)-1,3-oxazinan-2-one (3f).** Prepared according to the general procedure using **1f** (64.1 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 7 g, EtOAc) yielded a white solid (51.0 mg, 77%). $R_f$ = 0.40 (EtOAc:MeOH = 10:1) visualized with $KMnO_4$; mp 120-121 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.31-7.17 (m, 5H), 4.32 (br s, 1H), 4.19-4.12 (m, 2H), 4.09-4.05 (m, 1H), 3.61 (ddd, *J* = 13.8, 8.7, 6.2 Hz, 1H), 3.41 (ddd, *J* = 13.8, 8.4, 6.9 Hz, 1H), 3.31 (dd, *J* = 12.3, 3.9 Hz, 1H), 3.18-3.13 (m, 1H), 2.97-2.81 (m, 2H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 153.3 (C), 138.5 (C), 128.8 (CH), 128.5 (CH), 126.5 (CH), 70.4 ($CH_2$), 60.8 (CH), 52.7 ($CH_2$), 51.3 ($CH_2$), 33.3 ($CH_2$); IR (KBr) 3298, 2941, 1660, 1494, 1284, 1147, 759 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{15}NNaO_3$ 244.0944, found 244.0954.



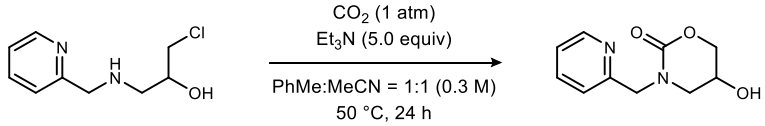
**3-[2-(3,4-Dimethoxyphenyl)ethyl]-5-hydroxy-1,3-oxazinan-2-one (3g).** Prepared according to the general procedure using **1g** (82.1 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 7 g, EtOAc) yielded a white solid (71.9 mg, 85%). $R_f$ = 0.30 (EtOAc:MeOH = 10:1) visualized with $KMnO_4$; mp 124-125 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 6.80-6.73 (m, 3H), 4.31 (br s, 1H), 4.17-4.16 (m, 2H), 4.11-4.07 (m, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.63-3.54 (m, 1H), 3.46-3.39 (m, 1H), 3.34 (dd, *J* = 12.0, 3.9 Hz, 1H), 3.20-3.15 (m, 1H), 2.92-2.76 (m, 2H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 153.2 (C), 148.8 (C), 147.5 (C), 131.0 (C), 120.7 (CH), 112.1 (CH), 111.3 (CH), 70.4 ($CH_2$), 60.8 (CH), 55.8 ($2CH_3$), 52.6 ($CH_2$), 51.3 ($CH_2$), 32.8 ($CH_2$); IR (KBr) 3301, 2921, 1656, 1498, 1291, 1239, 1149, 1031, 852, 810, 763 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{19}NNaO_5$ 304.1155, found 304.1160.



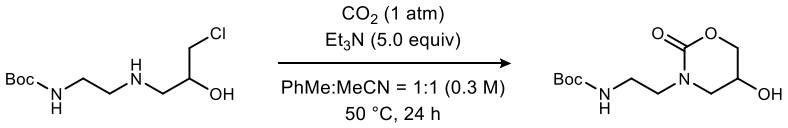

**5-Hydroxy-3-(propan-2-yl)-1,3-oxazinan-2-one (3h).** Prepared according to the general procedure using **1h** (45.5 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 7 g, EtOAc) yielded a white solid (14.8 mg, 31%). $R_f$ = 0.25 (EtOAc:MeOH = 10:1) visualized with $KMnO_4$; mp 111-112 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 4.52 (sept, *J* = 6.9 Hz, 1H), 4.25-4.15 (m, 3H), 4.08 (br s, 1H), 3.37-3.31 (m, 1H), 3.23-3.17 (m, 1H), 1.16 (d, *J* = 6.9 Hz, 3H), 1.15 (d, *J* = 6.9 Hz, 3H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 152.9 (C), 70.0 ($CH_2$), 60.9 (CH), 47.4 (CH), 45.0 ($CH_2$), 19.2 ($CH_3$), 18.9 ($CH_3$); IR (KBr) 3336, 2925, 1661, 1490, 1289, 1202, 1142, 827, 762, 648 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_7H_{13}NNaO_3$ 182.0788, found 182.0781.



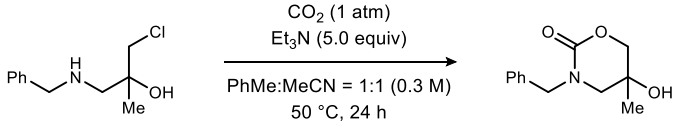

**5-Hydroxy-3-phenyl -1,3-oxazinan-2-one (3k).**[7] Prepared according to the general procedure using **1k** (54.8 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 7 g, Hexane:EtOAc = 20:1) yielded a white solid (10.2 mg, 18%). $R_f$ = 0.25 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 113-114 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.25-7.17 (m, 2H), 6.82-6.76 (m, 1H), 6.67-6.62 (m, 2H), 4.96-4.88 (m, 1H), 4.54 (t, *J* = 8.4 Hz, 1H), 4.29 (dd, *J* = 8.4, 6.9 Hz, 1H), 3.97 (br s, 1H) 3.56-3.40 (m, 2H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 154.6 (C), 146.9 (C), 129.5 (CH), 118.9 (CH), 113.2 (CH), 75.3 (CH), 67.0 ($CH_2$) 45.9 ($CH_2$); IR (KBr) 3405, 3034, 2991, 2925, 1782, 1602, 1524, 1172, 1032, 749 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{11}NNaO_3$ 216.0631, found 216.0636.




**5-Hydroxy-3-(pyridin-2-ylmethyl)-1,3-oxazinan-2-one (3q).** Prepared according to the general procedure using **1q** (40.0 mg, 0.20 mmol). Flash column chromatography ($SiO_2$: 7 g, EtOAc:MeOH:$Et_3N$ = 200:1:1-200:10:1) yielded a pale yellow oil (39.3 mg, 95%). $R_f$ = 0.30 (EtOAc:MeOH = 3:1) visualized with $KMnO_4$; $^1$H NMR (300 MHz, $CDCl_3$) δ 8.48 (ddd, *J* = 5.1, 1.8, 0.9 Hz. 1H), 7.71 (td, *J* = 7.8, 1.8 Hz, 1H), 7.29-7.21 (m, 2H), 5.13 (d, *J* = 16.8 Hz, 1H), 4.41-4.32 (m, 2H), 4.22 (d, *J* = 16.8 Hz, 1H), 4.17 (qui, *J* = 2.7 Hz, 1H), 3.79 (dd, *J* = 12.6, 2.7 Hz, 1H), 3.46 (dtd, *J* = 12.6, 2.7, 1.2 Hz, 1H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 155.8 (C), 153.2 (C), 148.5 (CH), 137.4 (CH), 122.7 (CH), 122.2 (CH), 72.7 ($CH_2$), 61.5 (CH), 52.33 ($CH_2$), 52.28 ($CH_2$); IR (KBr) 3369, 2924, 1677, 1596, 1491, 1439, 1263, 1158, 1109, 1011, 841, 762 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{12}N_2NaO_3$ 231.0740, found 231.0729.



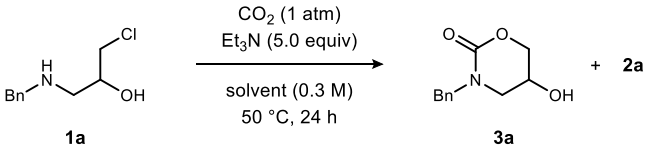

***tert*-Butyl [2-(5-hydroxy-2-oxo-1,3-oxazinan-3-yl)ethyl]carbamate (3r).** Prepared according to the general procedure using **1r** (50.5 mg, 0.20 mmol). Flash column chromatography ($SiO_2$: 7 g, EtOAc:MeOH = 100:1-5:1) yielded a white solid (44.1 mg, 85%). $R_f$ = 0.40 (EtOAc:MeOH = 10:1) visualized with $KMnO_4$; mp 103-105 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 5.35 (t, *J* = 5.5 Hz. 1H), 4.27-4.23 (m, 2H), 4.15-4.13 (m, 1H), 3.71 (ddd, *J* = 12.5, 7.5, 3.5 Hz, 1H), 12.5 (dd, *J* = 12.5, 3.5 Hz, 1H), 3.47-3.40 (m, 1H), 3.26-3.14 (m, 1H), 1.41 (s, 9H); $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$) δ 157.2 (C), 153.7 (C), 79.8 (C), 70.9 ($CH_2$), 61.0 (CH), 51.6 ($CH_2$), 49.1 ($CH_2$), 37.7 ($CH_3$); IR (KBr) 3371, 2979, 2942, 1680, 1521, 1487, 1368, 1254, 1174 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{20}N_2NaO_5$ 283.1264, found 283.1279.




**3-Benzyl-5-hydroxy-5-methyl-1,3-oxazinan-2-one (3s).** Prepared according to the general procedure using **1s** (64.1 mg, 0.30 mmol). Flash column chromatography ($SiO_2$: 15 g, Hexane:EtOAc = 10:1– EtOAc) yielded a white solid (27.2 mg, 41%). $R_f$ = 0.25 (EtOAc) visualized with $KMnO_4$; mp 145-146 °C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.38-7.27 (m, 5H), 4.64 (d, *J* = 15.0 Hz, 1H), 4.48 (d, *J* = 15.0 Hz, 1H), 4.10 (d, *J* = 11.1 Hz, 1H), 4.04 (dd, *J* = 11.1, 2.7 Hz, 1H), 3.21 (d, *J* = 12.0 Hz, 1H), 3.10 (ddd, *J* = 12.0, 2.7, 0.6 Hz, 1H), 2.73 (br s, 1H), 1.25 (s, 3H); $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 153.1 (C), 136.2 (C), 128.8 (CH), 128.1 (CH), 127.8 (CH), 74.3 ($CH_2$), 64.8 (C), 56.2 ($CH_2$), 52.8 ($CH_2$), 22.5 ($CH_3$); IR (KBr) 3386, 3250, 2929, 1685, 1486, 1231, 1107, 752, 703 cm$^{-1}$; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{15}NNaO_3$ 244.0944, found 244.0945.

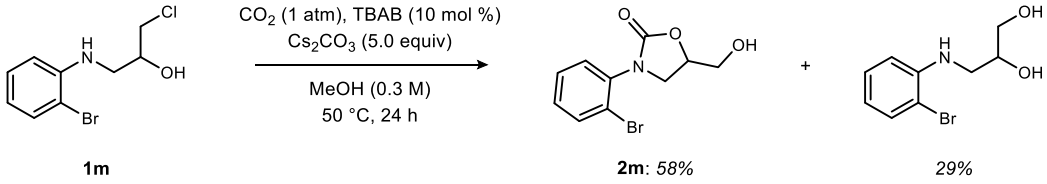
## Appendix

**Table S1.** Solvent Effect[a]




| entry | solvent | conv. (%)[b] | yield of **3a** (%)[c] | selectivity **3a**/**2a**[b] |
|---|---|---|---|---|
| 1 | MeCN | >98 | 88 | 11:1 |
| 2 | MeOH | >98 | 85 | 14:1 |
| 3 | acetone | 14 | 13 | >20:1 |
| 4 | THF | 20 | 24 | >20:1 |
| 5 | PhCN | >98 | 91 | >20:1 |
| 6 | $PhCF_3$ | 73 | 71 | >20:1 |
| 7 | PhCl | 64 | 64 | >20:1 |
| 8 | toluene | 21 | 17 | >20:1 |
| 9 | MeCN/toluene | >98 | 93 | >20:1 |

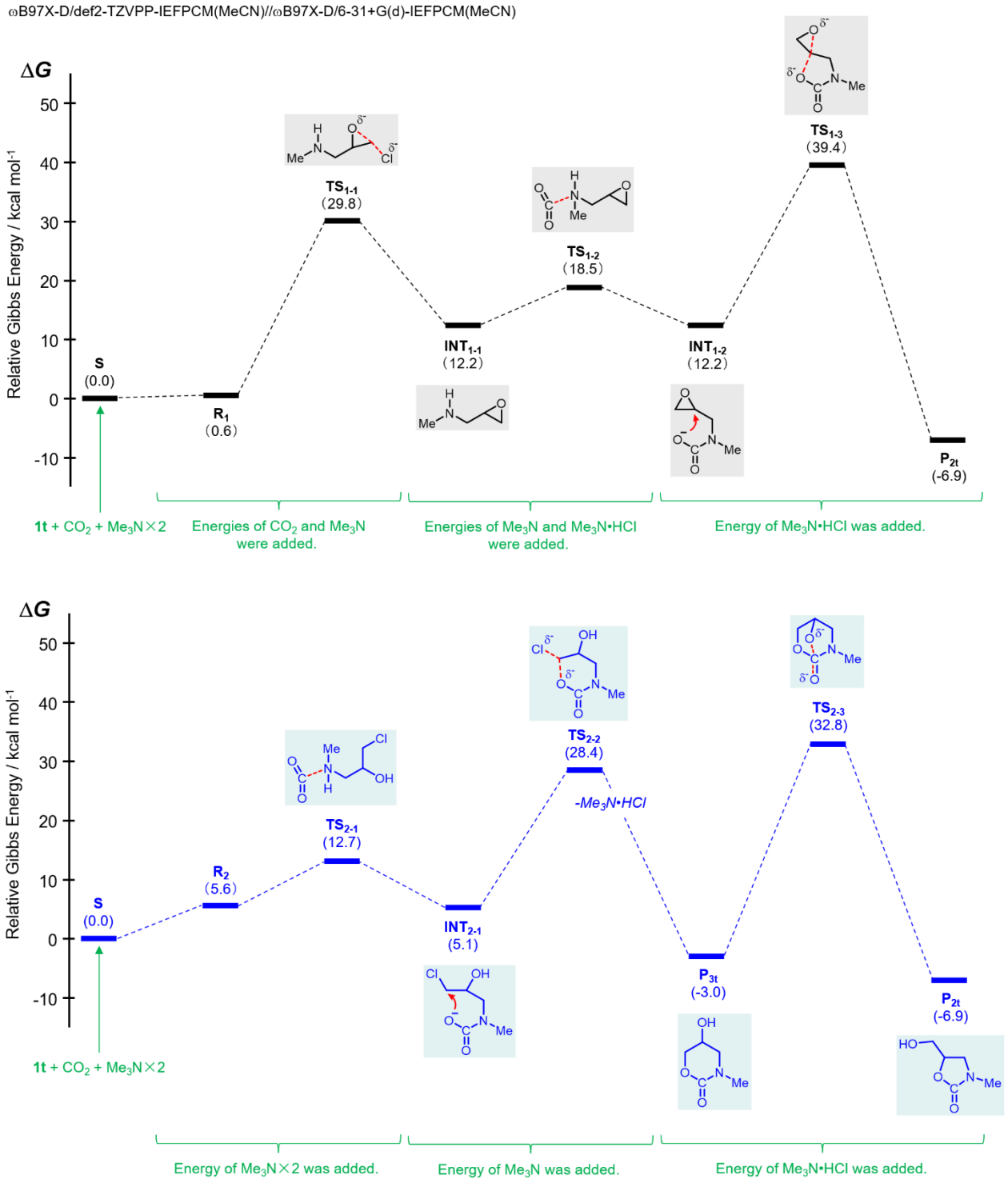
[a]Unless otherwise noted, all reactions were carried out with **1a** (0.3 mmol) and $Et_3N$ (1.5 mmol) under a balloon of $CO_2$ in 0.3 M solution at 50 °C for 24 h. [b]Determined by $^1H$ NMR. [c]Isolated yield.




**Scheme S1.** Reaction of **1m** in MeOH.

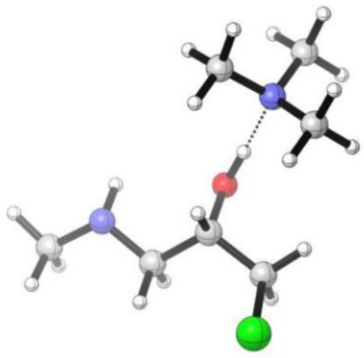
## DFT Studies

Quantum mechanical calculations were performed using Gaussian 16 (Revision B.01).[8] All geometries were optimized using the ωB97X-D density functional,[9] the 6-31+G(d) basis set, and an ultrafine integration grid within the IEFPCM model in acetonitrile.[10] Single point energies were calculated using ωB97X-D, the polarized, triple-ζ valence quality def2-TZVPP basis set of Weigend and Ahlrichs[11] and an ultrafine integration grid within the IEFPCM model in acetonitrile. The resulting energies were used to correct the energies obtained from the ωB97X-D optimizations. The free energy corrections were calculated at 1 atm and 298.15 K.



**$R_1$**

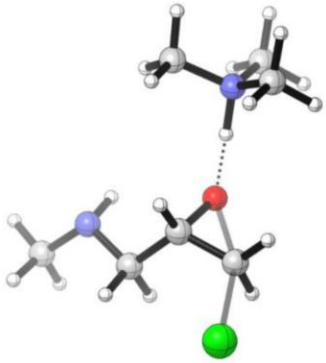
| basis set | 6-31+G(d) | def2-TZVPP |
|---|---|---|
| $E$ (a.u.) | -922.965385 | -923.167079 |
| $G$_corr (a.u.) | 0.22688 | - |
| $G$ (a.u.) | -922.738504 | -922.940199 |
| freq ($cm^{-1}$) | 22.81 | - |



| | | | |
|---|---|---|---|
| C, | -0.369985539, | -0.2914183652, | -0.3424117094 |
| H, | 0.7257685586, | -0.2395641112, | -0.4233450678 |
| C, | -0.9762532944, | 0.9655609405, | -0.9684961391 |
| H, | -0.7029304908, | 1.8448488883, | -0.3846314092 |
| C, | -0.8471554447, | -1.5762474605, | -1.0022749794 |
| H, | -0.5983407424, | -1.5580062575, | -2.0695183662 |
| H, | -1.9502083038, | -1.6228841122, | -0.9213385495 |
| O, | -0.7561379532, | -0.3191579287, | 1.0175935333 |
| N, | -0.1990084872, | -2.7275649635, | -0.3931788548 |
| C, | -0.6870709162, | -3.9906985995, | -0.9322077797 |
| H, | -0.221081094, | -4.822306538, | -0.3957546418 |
| H, | -0.4078095618, | -4.0696617928, | -1.9888126285 |
| H, | -1.783301145, | -4.1005343803, | -0.8625368293 |
| N, | 1.2870367278, | 1.0123271092, | 2.2862633996 |
| C, | 0.8671535045, | 1.3553953508, | 3.6424606564 |
| H, | 1.6710769352, | 1.8586065506, | 4.2059911141 |
| H, | 0.5815923541, | 0.4456251614, | 4.1785142085 |
| H, | 0.0002280839, | 2.0211557193, | 3.5999669206 |
| C, | 2.4052720386, | 0.0727636378, | 2.3062876039 |
| H, | 2.1080077085, | -0.8383015492, | 2.8335925242 |
| H, | 3.2907193439, | 0.4988716475, | 2.8078829106 |
| H, | 2.6802793294, | -0.1941175999, | 1.2815570014 |
| C, | 1.6230484872, | 2.2119306117, | 1.5245141138 |
| H, | 2.4696013947, | 2.759675822, | 1.972212654 |
| H, | 0.7570200545, | 2.8798340785, | 1.4906787736 |
| H, | 1.8921343893, | 1.93610751, | 0.5001203387 |
| H, | -0.063446122, | 0.1829559867, | 1.5336702271 |
| H, | -2.0636039021, | 0.8929732513, | -1.0310563602 |
| Cl, | -0.3667434945, | 1.2600903275, | -2.6479893799 |
| H, | -0.3841641292, | -2.6934885646, | 0.6062111149 |

**$TS_{1\text{-}1}$**

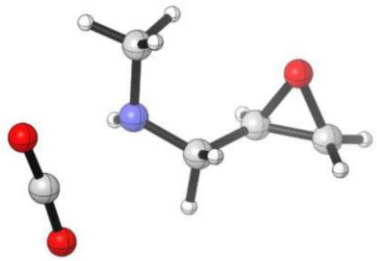
| basis set | 6-31+G(d) | def2-TZVPP |
|---|---|---|
| $E$ (a.u.) | -922.924430 | -923.120226 |
| $G$_corr (a.u.) | 0.226611 | - |
| $G$ (a.u.) | -922.697818 | -922.940199 |
| freq ($cm^{-1}$) | -541.73 | - |



| | | | |
|---|---|---|---|
| C, | -0.6407321807, | 0.0010249641, | -1.3053233349 |
| H, | 0.4310808886, | 0.1084913635, | -1.522576277 |
| C, | -1.4408382521, | 1.1833081346, | -1.620712852 |
| H, | -0.9961398063, | 2.1555722869, | -1.4656820439 |
| C, | -1.1438969053, | -1.3559281687, | -1.7489891454 |
| H, | -0.9162106855, | -1.4991620865, | -2.8121909614 |
| H, | -2.2436807764, | -1.3881533203, | -1.6354238825 |
| O, | -0.9875408663, | 0.3368222946, | 0.0138685479 |
| N, | -0.4758824854, | -2.3933947343, | -0.975869089 |
| C, | -0.9578413256, | -3.7302860757, | -1.3006568064 |
| H, | -0.4768068665, | -4.4628624343, | -0.6460135319 |
| H, | -0.6909214203, | -3.9725657115, | -2.3352834303 |
| H, | -2.0519162212, | -3.8358506059, | -1.1994572839 |
| N, | 0.9687137676, | 1.2124138685, | 1.4923816265 |
| C, | 0.4022585791, | 1.2559961471, | 2.8624447632 |
| H, | 1.1727685606, | 1.5784279787, | 3.5662813452 |
| H, | 0.0469048134, | 0.2594940591, | 3.1271251326 |
| H, | -0.4325015914, | 1.9576106751, | 2.8752804159 |
| C, | 2.0576291819, | 0.2112051103, | 1.3842446017 |
| H, | 1.6611493492, | -0.768497816, | 1.6531978115 |
| H, | 2.8729967982, | 0.4836199884, | 2.0581123077 |
| H, | 2.4176013091, | 0.1892284637, | 0.3551336511 |
| C, | 1.4065590781, | 2.5546926964, | 1.0398420032 |
| H, | 2.2016148156, | 2.9187879945, | 1.6943692894 |
| H, | 0.5536035361, | 3.2332456957, | 1.0762213957 |
| H, | 1.7732347392, | 2.4817701167, | 0.015356193 |
| H, | 0.1650827539, | 0.8837021004, | 0.8370272445 |
| H, | -2.5168317146, | 1.0977489107, | -1.5592771329 |
| Cl, | -1.5069990214, | 1.509307613, | -3.9333583217 |
| H, | -0.6504580718, | -2.205768499, | 0.0089277441 |

**$INT_{1-1}$**

| basis set | 6-31+G(d) | def2-TZVPP |
|---|---|---|
| *E* (a.u.) | -476.221987 | -476.404205 |
| *G*_corr (a.u.) | 0.106032 | - |
| *G* (a.u.) | -476.115955 | -476.298173 |
| freq ($cm^{-1}$) | 9.10 | - |



| | | | |
|---|---|---|---|
| C, | 1.4454344154, | 0.6426035078, | 1.4886652351 |
| H, | 1.1612859894, | 0.3083250429, | 2.4879403035 |
| C, | 2.5866685302, | 1.5523243697, | 1.3721741379 |
| H, | 3.1045896989, | 1.889365098, | 2.2673338467 |
| C, | 0.3367739193, | 0.6348373177, | 0.4582525596 |
| H, | 0.7721275056, | 0.8538217835, | -0.5255562043 |
| H, | -0.3592426772, | 1.4480821017, | 0.6956518416 |
| O, | 2.7321932273, | 0.1605066712, | 1.0761822569 |
| N, | -0.4340805435, | -0.5970547839, | 0.359997844 |
| C, | 0.3538353519, | -1.7804669797, | 0.0323709483 |
| H, | -0.3167454804, | -2.6384634741, | -0.0689760647 |
| H, | 1.1271623607, | -2.0250105505, | 0.7760449606 |
| H, | 0.8492616953, | -1.6219222014, | -0.9316329724 |
| C, | -2.2770655501, | -0.1329028177, | -1.6299816894 |
| O, | -2.5476040962, | 0.9201093359, | -1.2070717178 |
| O, | -2.0802404279, | -1.1653536718, | -2.1351163227 |
| H, | 2.6553347728, | 2.2118516596, | 0.5082837275 |
| H, | -0.9446507915, | -0.7508662789, | 1.2253607495 |

**$TS_{1-2}$**

| basis set | 6-31+G(d) | def2-TZVPP |
|---|---|---|
| *E* (a.u.) | -476.219154 | -476.397951 |
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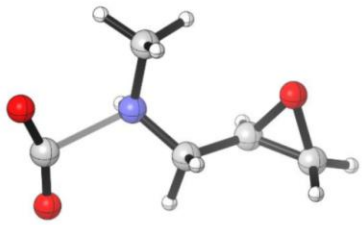
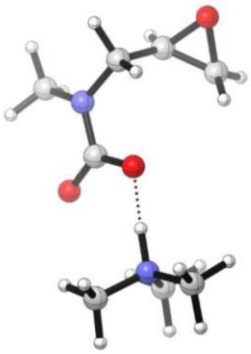
| *G* (a.u.) | -476.109399 | -476.288196 |
| freq ($cm^{-1}$) | -176.26 | - |



| | | | |
|---|---|---|---|
| C, | 1.4808001942, | 1.2457539197, | -0.0547491742 |
| H, | 1.0746289053, | 0.9890633862, | 0.9244885875 |
| C, | 2.6910122594, | 2.0679200749, | -0.1008404938 |
| H, | 3.1406626792, | 2.4160250331, | 0.8260274668 |
| C, | 0.486029083, | 1.2626978708, | -1.1894903742 |
| H, | 1.0138988916, | 1.4238601486, | -2.1361298878 |
| H, | -0.2044521684, | 2.0995579998, | -1.0428790526 |
| O, | 2.759598182, | 0.6551748742, | -0.3142967426 |
| N, | -0.318979734, | 0.0450914069, | -1.3164204415 |
| C, | 0.4463213499, | -1.1691245738, | -1.6045995579 |
| H, | -0.2496440703, | -1.9975218257, | -1.7502244718 |
| H, | 1.1477668334, | -1.4229270992, | -0.8019263823 |
| H, | 1.0090413057, | -1.020135575, | -2.5300060295 |
| C, | -1.8405218442, | 0.3693111289, | -2.7594423527 |
| O, | -2.2281239913, | 1.4491847538, | -2.460545086 |
| O, | -1.8162154199, | -0.6315327254, | -3.3920536398 |
| H, | 2.8915104066, | 2.6728944722, | -0.9834478979 |
| H, | -0.8617440122, | -0.08825144, | -0.4648120996 |

**$INT_{1-2}$**

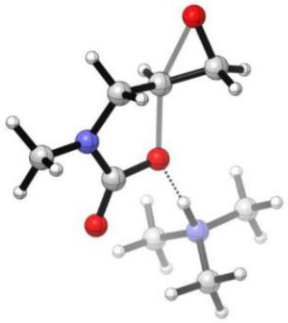
| basis set | 6-31+G(d) | def2-TZVPP |
|---|---|---|
| *E* (a.u.) | -650.683139 | -650.919629 |
| *G*_corr (a.u.) | 0.227098 | - |
| *G* (a.u.) | -650.456040 | -650.692531 |
| freq ($cm^{-1}$) | 15.77 | - |



| | | | |
|---|---|---|---|
| N, | -0.2325011217, | 1.7241474411, | 0.8350028864 |
| C, | -1.204601811, | 2.7924776918, | 0.6856350606 |
| H, | -0.8244184982, | 3.689048237, | 1.1843920352 |
| H, | -2.1482888632, | 2.5050936634, | 1.1517784156 |
| H, | -1.4051711399, | 3.0398906389, | -0.3667006174 |
| C, | 1.1720787568, | 2.0877778349, | 0.8203306857 |
| H, | 1.75834516, | 1.2632173952, | 1.2291997466 |
| H, | 1.3130298417, | 2.9618310519, | 1. 4678149555 |
| C, | 1.6763373044, | 2.4153756015, | -0.5703826809 |
| H, | 1.1638485861, | 3.2302020596, | -1.0828900167 |
| C, | 2.3571352424, | 1.4126544731, | -1.389477641 |
| O, | 3.0981805778, | 2.4488016752, | -0.7282645369 |
| C, | -0.6210907706, | 0.41323366, | 0.5765818871 |
| O, | -1.8367493329, | 0.1739542176, | 0.3699236047 |
| O, | 0.3041651642, | -0.4753428348, | 0.5923651328 |
| H, | -0.3506486354, | -1.8318311979, | 0.2714143244 |
| N, | -0.7768966639, | -2.7989026403, | 0.0253463304 |
| C, | -1.3568119842, | -2.673718581, | -1.3322806712 |
| H, | -1.8200750519, | -3.6199463261, | -1.6217767417 |
| H, | -0.5595774756, | -2.4197080888, | -2.0323763551 |
| H, | -2.0954863982, | -1.8723033723, | -1.3109799048 |
| C, | 0.3211829826, | -3.7912477128, | 0.0688957047 |
| H, | 0.7498656548, | -3.7993612928, | 1.0718160825 |
| H, | 1.0862932071, | -3.5020957032, | -0.6528385509 |
| H, | -0.0686891531, | -4.7816408798, | -0.1772019243 |
| H, | -2.2990715471, | -4.0385525741, | 0.812084724 |
| C, | -1.8214736852, | -3.0819800502, | 1.0371832995 |
| H, | -1.3543606872, | -3.1207455078, | 2.0223671866 |
| H, | -2.5476013715, | -2.2694885894, | 1.0077679688 |
| H, | 2.5016520875, | 0.4151635392, | -0.9810817467 |
| H, | 2.3358482655, | 1.491878581, | -2.4743011936 |

**$TS_{1-3}$**

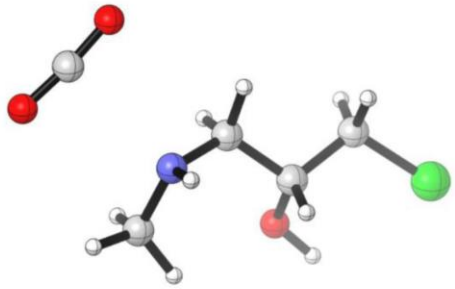
| basis set | 6-31+G(d) | def2-TZVPP |
|---|---|---|
| *E* (a.u.) | -650.643269 | -650.877007 |
| *G*_corr (a.u.) | 0.227719 | - |
| *G* (a.u.) | -650.415550 | -650.649288 |
| freq ($cm^{-1}$) | -594.16 | - |



| | | | |
|---|---|---|---|
| N, | -0.2262828359, | 0.6958316118, | 0.2202373057 |
| C, | -1.091130856, | 1.6593170512, | 0.863799425 |
| H, | -0.7971861088, | 1.8313089669, | 1.9091976665 |
| H, | -2.1160168755, | 1.2877910934, | 0.8412301878 |
| H, | -1.0439080818, | 2.6114128993, | 0.3264059229 |
| C, | 1.1781949779, | 1.0275548606, | 0.0595435368 |
| H, | 1.6744057149, | 1.1440717656, | 1.0352343553 |
| H, | 1.2634785672, | 1.9737062546, | -0.4808093743 |
| C, | 1.839510191, | -0.0836070289, | -0.7226406896 |
| H, | 1.5794990597, | -0.1799132385, | -1.7696144453 |
| C, | 3.1675195326, | -0.5555196628, | -0.3454835267 |
| O, | 3.6118146194, | 0.6220350843, | -0.9366725711 |
| C, | -0.5020778737, | -0.6486655453, | 0.2335092079 |
| O, | -1.5996949414, | -1.1203678447, | 0.5714665823 |
| O, | 0.5095431677, | -1.3626068115, | -0.1783738361 |
| H, | 0.0617951281, | -2.9569665615, | -0.2805368893 |
| N, | -0.2771622587, | -3.9523637339, | -0.3453827109 |
| C, | -1.4167590899, | -3.9481467272, | -1.2985341056 |
| H, | -1.8245112424, | -4.957847764, | -1.37424939 |
| H, | -1.0577012311, | -3.6142062578, | -2.2725407191 |
| H, | -2.1685619346, | -3.2542637456, | -0.9223516052 |
| C, | 0.8534108136, | -4.7818255803, | -0.8327379136 |
| H, | 1.6778861064, | -4.7049466021, | -0.1234330409 |
| H, | 1.1690521563, | -4.407243761, | -1.8069410903 |
| H, | 0.5268239597, | -5.8198992124, | -0.9170063209 |
| H, | -1.1017211733, | -5.3669224875, | 0.988769818 |
| C, | -0.712942546, | -4.3472794813, | 1.0186160761 |
| H, | 0.1438330304, | -4.291362973, | 1.6907187325 |
| H, | -1.4836346618, | -3.6477308525, | 1.3421037994 |
| H, | 3.3335769704, | -0.6344440796, | 0.7421188925 |
| H, | 3.4893186458, | -1.4894697464, | -0.8332284797 |

**R2**

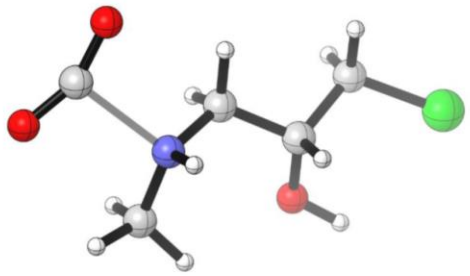
| basis set | 6-31+G(d) | def2-TZVPP |
|---|---|---|
| *E* (a.u.) | -937.052241 | -937.270273 |
| *G*_corr (a.u.) | 0.115098 | - |
| *G* (a.u.) | -936.937143 | -937.155175 |
| freq ($cm^{-1}$) | 2.87 | - |



| | | | |
|---|---|---|---|
| C, | 1.0003121964, | 0.0901408576, | 0.7008 478668 |
| H, | 0.6822746497, | -0.3957006853, | 1.635057682 |
| C, | 1.4446406783, | 1.5152593637, | 1.0103083311 |
| H, | 0.6492068259, | 2.0792425514, | 1.4985080571 |
| C, | -0.1872609489, | 0.1300617825, | -0.2747518894 |
| H, | 0.2113145771, | 0.2921548569, | -1.2842967283 |
| H, | -0.8150567173, | 0.995125312, | -0.0337626225 |
| O, | 2.0433144954, | -0.6582824044, | 0.0958742349 |
| N, | -1.0587210893, | -1.0331737382, | -0.3016731931 |
| C, | -0.4407193628, | -2.2939206117, | -0.6977570465 |
| H, | -1.2220201232, | -3.0551186793, | -0.7832148327 |
| H, | 0.3323447166, | -2.6533022956, | -0.0046936055 |
| H, | 0.0210967156, | -2.1695088658, | -1.6829500716 |
| C, | -3.0559413044, | -0.4669755365, | -2.101592876 |
| O, | -2.9819436085, | 0.6813616043, | -1.9096295313 |
| O, | -3.2134621154, | -1.5910224952, | -2.3697889115 |
| H, | 2.7490282213, | -0.7890234339, | 0.744323731 |
| H, | 1.7700079338, | 2.0323232237, | 0.1057541888 |
| Cl, | 2.854347548, | 1.5340279976, | 2.1475601879 |
| H, | -1.5145811983, | -1.1401517937, | 0.6002678089 |

**TS2-1**

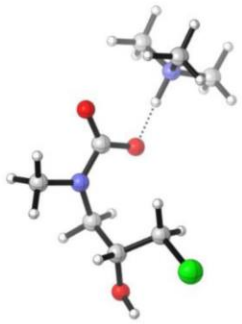
| basis set | 6-31+G(d) | def2-TZVPP |
|---|---|---|
| *E* (a.u.) | -937.049459 | -937.264178 |
| *G*_corr (a.u.) | 0.120359 | - |
| *G* (a.u.) | -936.929100 | -937.143819 |
| freq ($cm^{-1}$) | -163.00 | - |



| | | | |
|---|---|---|---|
| C, | 1.7782261088, | 1.1635363128, | -0.112 5197469 |
| H, | 1.2927930638, | 0.8779793027, | 0.8322457906 |
| C, | 2.3614691667, | 2.5656154034, | 0.0392400484 |
| H, | 1.5909907159, | 3.2870492785, | 0.3128620817 |
| C, | 0.731322242, | 1.1816247005, | -1.2286386654 |
| H, | 1.2379836264, | 1.2633514506, | -2.1966232741 |
| H, | 0.1001634878, | 2.0674857233, | -1.1077772355 |
| O, | 2.7755854091, | 0.2167651031, | -0.4526276871 |
| N, | -0.1663348289, | 0.0279939425, | -1.2808206149 |
| C, | 0.4213119798, | -1.2360036474, | -1.7320067428 |
| H, | -0.3806715988, | -1.9685575937, | -1.8444296577 |
| H, | 1.1765867688, | -1.6159643969, | -1.0387827541 |
| H, | 0.8865214861, | -1.0782660183, | -2.7087755805 |
| C, | -1.8665365864, | 0.5208186574, | -2.4550250986 |
| O, | -2.02867497, | 1.6645096824, | -2.1869337342 |
| O, | -2.1152346124, | -0.5053661259, | -2.99200414 |
| H, | 3.376938728, | 0.1131208215, | 0.2978978187 |
| H, | 2.8659947952, | 2.883472263, | -0.8747255167 |
| Cl, | 3.6004061414, | 2.6146310887, | 1.3558908687 |
| H, | -0.5978565736, | -0.1045365381, | -0.3677202195 |

**$INT_{2\text{-}1}$**

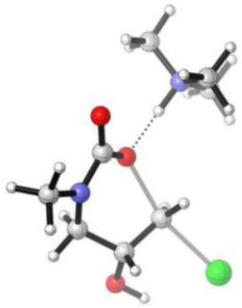
| basis set | 6-31+G(d) | def2-TZVPP |
|---|---|---|
| *E* (a.u.) | -1111.517467 | -1111.789632 |
| *G*_corr (a.u.) | 0.239225 | - |
| *G* (a.u.) | -1111.278242 | -1111.550407 |
| freq ($cm^{-1}$) | 18.46 | - |



| | | | |
|---|---|---|---|
| C, | -2.3424854537, | -0.9177145269, | -1.1130180505 |
| H, | -2.6949960522, | -0.3084047217, | -1.9575455381 |
| C, | -2.3018974842, | -0.0536656619, | 0.1369653736 |
| H, | -1.6069367519, | 0.7766120966, | 0.0192626223 |
| C, | -0.9444224191, | -1.4616667663, | -1.4334886034 |
| H, | -1.0520564822, | -2.1809499754, | -2.2547171572 |
| H, | -0.5556653918, | -1.9958110031, | -0.5641784624 |
| O, | -3.1811564597, | -2.0498386563, | -0.9473793697 |
| N, | -0.0100026967, | -0.427480486, | -1.8228712952 |
| C, | 0.0484414804, | -0.0926404321, | -3.2330560293 |
| H, | 0.5059108601, | 0.8880894462, | -3.3601606994 |
| H, | -0.9652859552, | -0.0623944515, | -3.6446472958 |
| H, | 0.631263358, | -0.8297566611, | -3.804903499 |
| C, | 0.9873645711, | 0.004723599, | -0.9574115646 |
| O, | 0.8992089564, | -0.3989073903, | 0.2578547566 |
| O, | 1.8866012944, | 0.7647721678, | -1.3942136806 |
| N, | 2.7603353611, | 0.8058817242, | 1.6646753264 |
| C, | 4.0823144678, | 0.3898159744, | 1.1415164038 |
| H, | 4.132765809, | 0.6678234535, | 0.0887159379 |
| H, | 4.1741961778, | -0.6927372511, | 1.2402490771 |
| H, | 4.8727334102, | 0.8848420594, | 1.7106454086 |
| C, | 2.542546845, | 2.2617901703, | 1.4948081659 |
| H, | 2.616212013, | 2.4913661732, | 0.4316867964 |
| H, | 3.2939660676, | 2.8135011358, | 2.0645891679 |
| H, | 1.5432019452, | 2.5106368483, | 1.8550705495 |
| C, | 2.5592231339, | 0.3751638854, | 3.0671834926 |
| H, | 3.297201235, | 0.8607276751, | 3.7098060329 |
| H, | 2.6723424057, | -0.7083008791, | 3.1227153117 |
| H, | 1.5521695294, | 0.6538943135, | 3.3803728403 |
| H, | 2.0098974299, | 0.3068287943, | 1.0627427807 |
| H, | -4.0901261763, | -1.7480928324, | -0.8132928792 |
| H, | -2.0362464239, | -0.642003236, | 1.0156128546 |
| Cl, | -3.9315883741, | 0.6734679442, | 0.4744541456 |

**$TS_{2\text{-}2}$**

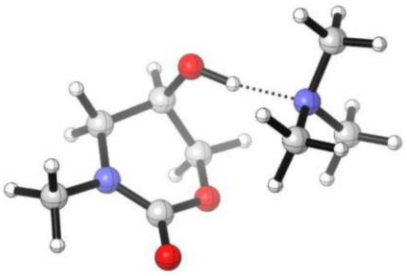
| basis set | 6-31+G(d) | def2-TZVPP |
|---|---|---|
| *E* (a.u.) | -1111.485459 | -1111.754567 |
| *G*_corr (a.u.) | 0.241413 | - |
| *G* (a.u.) | -1111.244046 | -1111.513154 |
| freq ($cm^{-1}$) | -512.68 | - |



| | | | |
|---|---|---|---|
| C, | -2.6105729248, | -0.9160733452, | -0.7909826713 |
| H, | -3.1823734716, | -0.1139956801, | -1.2740150603 |
| C, | -1.9392928739, | -0.3304242031, | 0.4352040109 |
| H, | -1.6762778298, | 0.7133162793, | 0.4720160121 |
| C, | -1.6107881272, | -1.4822552018, | -1.8094234282 |
| H, | -2.1818539339, | -1.7861980885, | -2.6895915131 |
| H, | -1.1494848179, | -2.3779800017, | -1.3771445336 |
| O, | -3.452638329, | -1.9989438654, | -0.4554680096 |
| N, | -0.609852258, | -0.5207293501, | -2.2164120932 |
| C, | -0.4221407482, | -0.2427984937, | -3.6276967797 |
| H, | 0.2280482138, | 0.6251746078, | -3.7352872559 |
| H, | -1.3887318108, | -0.0222198033, | -4.0895618087 |
| H, | 0.0345854709, | -1.0929241287, | -4.151718252 |
| C, | 0.3382496589, | -0.1723389619, | -1.2887665023 |
| O, | 0.0497961957, | -0.5583624818, | -0.0763557928 |
| O, | 1.3643686568, | 0.4665803895, | -1.5853065319 |
| N, | 1.7641925429, | 0.6990429969, | 1.5852465065 |
| C, | 3.1256160965, | 0.1947317669, | 1.2751259721 |
| H, | 3.3250519237, | 0.3885177599, | 0.221281118 |
| H, | 3.1531361433, | -0.878731561, | 1.4654830042 |
| H, | 3.8524268807, | 0.7069560358, | 1.908480367 |
| C, | 1.6415312875, | 2.1501657402, | 1.29599798 |
| H, | 1.8897520312, | 2.3090999806, | 0.2467833819 |
| H, | 2.3229058817, | 2.704132019, | 1.9447484451 |
| H, | 0.6127369852, | 2.4602744595, | 1.4833905445 |
| C, | 1.3521903535, | 0.3749428271, | 2.973084199 |
| H, | 2.0208326194, | 0.8784550172, | 3.6739222161 |
| H, | 1.4063229907, | -0.7048664867, | 3.113681455 |
| H, | 0.3271824238, | 0.7151017303, | 3.1240806714 |
| H, | 1.0984732186, | 0.1987178801, | 0.9310784118 |
| H, | -4.0902985629, | -1.6629189949, | 0.1963923677 |
| H, | -1.6838258271, | -0.967555732, | 1.2674642681 |
| Cl, | -3.9092680495, | 0.2461068696, | 1.5562693009 |

**$P_3$**

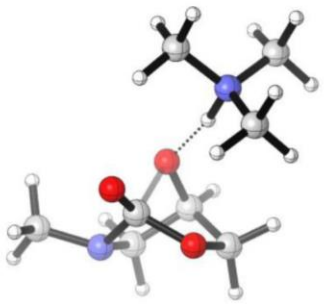
| basis set | 6-31+G(d) | def2-TZVPP |
|---|---|---|
| $E$ (a.u.) | -650.709407 | -650.948322 |
| $G$_corr (a.u.) | 0.231554 | - |
| $G$ (a.u.) | -650.477852 | -650.716768 |
| freq ($cm^{-1}$) | 18.30 | - |



| | | | |
|---|---|---|---|
| C, | 1.8487528128, | 0.0959958368, | 0.1391459951 |
| H, | 2.8503200025, | -0.0186624746, | 0.5727933057 |
| C, | 1.2212319376, | -1.2789690152, | 0.0293925831 |
| H, | 1.0219289627, | -1.7214693462, | 1.0067261128 |
| C, | 1.9965678687, | 0.6341777232, | -1.274485194 |
| H, | 2.8435609922, | 0.1542244401, | -1.7809566906 |
| H, | 2.1904616464, | 1.7106461051, | -1.2321758853 |
| O, | 1.0953494654, | 0.9910626521, | 0.9238821399 |
| N, | 0.7780840846, | 0.4187901095, | -2.0533816014 |
| C, | 0.6228386092, | 1.2583926851, | -3.2304260494 |
| H, | 0.3155722133, | 2.2722386279, | -2.9475523394 |
| \|H, | -0.1244645469, | 0.8292475605, | -3.8961624984 |
| H, | 1.5824145959, | 1.3127992539, | -3.752739153 |
| C, | -0.2336774187, | -0.402103393, | -1.691143591 |
| O, | -0.0560991807, | -1.2020866394, | -0.6160950428 |
| O, | -1.3103071642, | -0.469869989, | -2.2775566856 |
| N, | -1.2282554879, | 0.164712433, | 2.1414359437 |
| C, | -2.2945454027, | 0.6059454182, | 1.2463563419 |
| H, | -2.2821519139, | -0.0024484557, | 0.3383427556 |
| H, | -2.1284030045, | 1.6509804954, | 0.9674282521 |
| H, | -3.2880197684, | 0.5221499416, | 1.7198156626 |
| C, | -1.384573521, | -1.2451251274, | 2.4826517848 |
| H, | -1.3949476721, | -1.8425720904, | 1.5670197088 |
| H, | -2.3219530171, | -1.4317774249, | 3.0346538425 |
| H, | -0.5454267032, | -1.5682038993, | 3.1068124106 |
| C, | -1.1813351207, | 0.9895581959, | 3.3454754184 |
| H, | -0.3486071846, | 0.6678938724, | 3.9780096529 |
| H, | -2.1151238908, | 0.9190886097, | 3.9293158384 |
| H, | -1.0222394626, | 2.0357182883, | 3.0674210211 |
| H, | 0.2821351922, | 0.5644036882, | 1.3183274697 |
| H, | 1.8733296467, | -1.9497251218, | -0.5402686688 |

**$TS_{2\text{-}3}$**

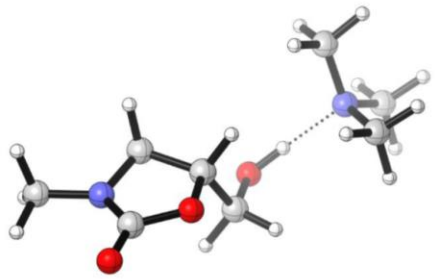
| basis set | 6-31+G(d) | def2-TZVPP |
|---|---|---|
| $E$ (a.u.) | -650.662773 | -650.896118 |
| $G$_corr (a.u.) | 0.236319 | - |
| $G$ (a.u.) | -650.426454 | -650.659799 |
| freq ($cm^{-1}$) | -207.20 | - |



| | | | |
|---|---|---|---|
| C, | 1.9334869726, | 0.1753975907, | -0.2501814256 |
| H, | 2.5784465832, | 0.6980413636, | 0.4592901902 |
| C, | 1.8185910906, | -1.3330114149, | -0.0192676111 |
| H, | 1.6621900084, | -1.5779148203, | 1.0387247996 |
| C, | 2.2998427729, | 0.3984452749, | -1.7242381016 |
| H, | 3.2035956337, | -0.1423655009, | -2.0263442293 |
| H, | 2.4520128264, | 1.4690377803, | -1.9128144254 |
| O, | 0.593590124, | 0.5973335551, | -0.2031566199 |
| N, | 1.099364113, | -0.0822808831, | -2.4293388319 |
| C, | 0.5731199433, | 0.8702284687, | -3.3929927383 |
| H, | 0.2850970419, | 1.8291131987, | -2.9293584202 |
| H, | -0.3010969724, | 0.4472272912, | -3.891126774 |
| H, | 1.3423436942, | 1.0681065534, | -4.1461790091 |
| C, | 0.1345698145, | -0.497345669, | -1.4254211038 |
| O, | 0.6402489808, | -1.6636342491, | -0.7511304769 |
| O, | -1.0883167073, | -0.5033852233, | -1.6693008799 |
| N, | -1.2804264176, | 0.056725665, | 1.617722347 |
| C, | -2.3960868278, | 0.8716514949, | 1.0730516352 |
| H, | -2.569752358, | 0.5501604088, | 0.0455792737 |
| H, | -2.1018830831, | 1.921780298, | 1.0876893281 |
| H, | -3.2857686651, | 0.7219605127, | 1.6884345161 |
| C, | -1.6108328534, | -1.3901621942, | 1.5974169364 |
| H, | -1.835708484, | -1.6682587302, | 0.5684784839 |
| H, | -2.466320542, | -1.5710025033, | 2.2518931026 |
| H, | -0.7453490913, | -1.9537111918, | 1.9471643888 |
| C, | -0.8625015234, | 0.5128641241, | 2.9649858426 |
| H, | -0.0193060801, | -0.0944204907, | 3.2964336289 |
| H, | -1.6979288295, | 0.4030340995, | 3.6593890817 |
| H, | -0.5617571509, | 1.5594119916, | 2.9056614525 |
| H, | -0.461318341, | 0.2097205384, | 0.9566003211 |
| H, | 2.6806203874, | -1.8949771387, | -0.3959673813 |

**$P_2$**

| basis set | 6-31+G(d) | def2-TZVPP |
|---|---|---|
| *E* (a.u.) | -650.713449 | -650.952645 |
| *G*_corr (a.u.) | 0.229629 | - |
| *G* (a.u.) | -650.483820 | -650.723016 |
| freq ($cm^{-1}$) | 23.69 | - |



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| C, | 1.6771843296, | -1.6085591252, | 0.1875495651 |
| H, | 1.2507614398, | -2.1246559329, | -0.6803432467 |
| C, | 1.9101468912, | 0.46723666, | -1.2978218913 |
| H, | 2.6318099447, | -0.1922327535, | -1.7880220563 |
| H, | 2.350651907, | 1.4675378904, | -1.2019496909 |
| O, | 0.0187200771, | 0.1469480773, | 0.0600971166 |
| N, | 0.657412623, | 0.522307267, | -2.0269879142 |
| C, | 0.5742381651 | 1.0156511769, | -3.3827539908 |
| H, | 0.9026215698, | 2.0607404484, | -3.4391782944 |
| H, | -0.4608097239, | 0.9458556204, | -3.7199591578 |
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| C, | -0.4056781878, | 0.4532053954, | -1.193063828 |
| O, | 3.0531832486, | -1.8999508772, | 0.2338886729 |
| O, | -1.5858837032, | 0.6179576897, | -1.4539555752 |
| N, | 3.8976820523, | -1.1611260766, | 2.7643396399 |
| C, | 4.8380971181, | -2.1973356514, | 3.1836576342 |
| H, | 5.6767990578, | -2.2366694253, | 2.4824801064 |
| H, | 4.3365251051, | -3.1694865184, | 3.1807764703 |
| H, | 5.2339402277, | -2.0075354559, | 4.1958470223 |
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| H, | 3.0196097084, | -0.8734920488, | 4.6875116853 |
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| H, | 3.3900278833, | -1.6329920573, | 1.1344236539 |
| H, | 1.1549223959, | -1.9670383655, | 1.085406437 |

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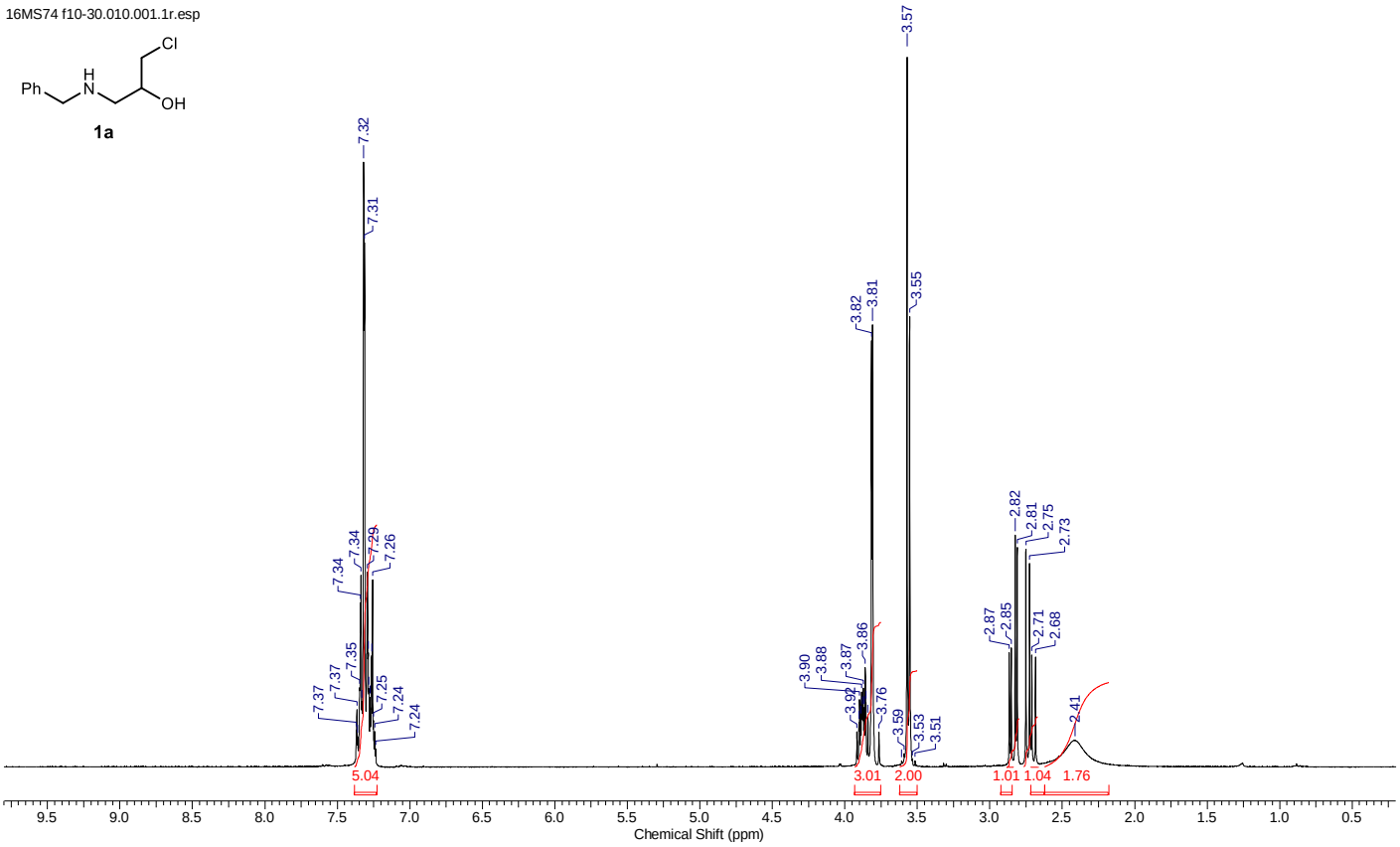
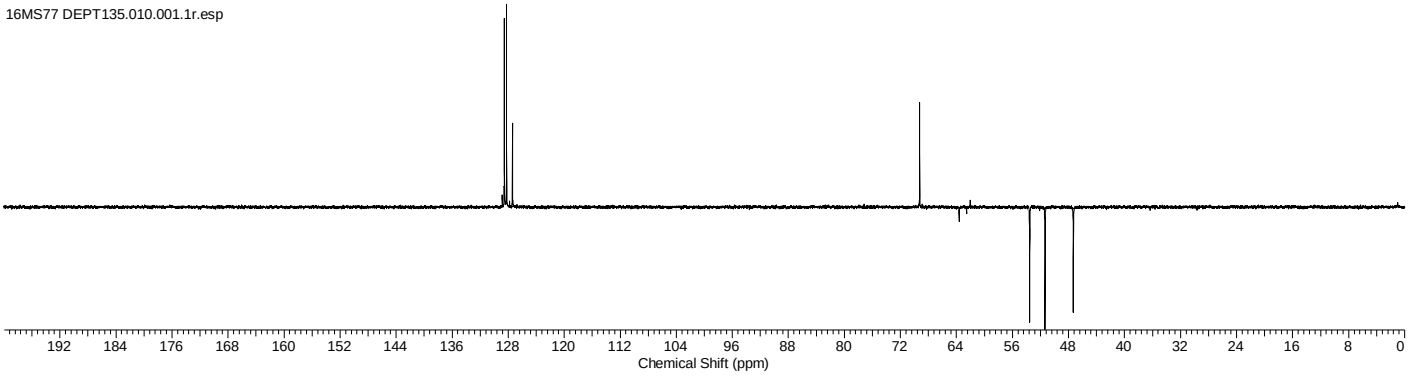
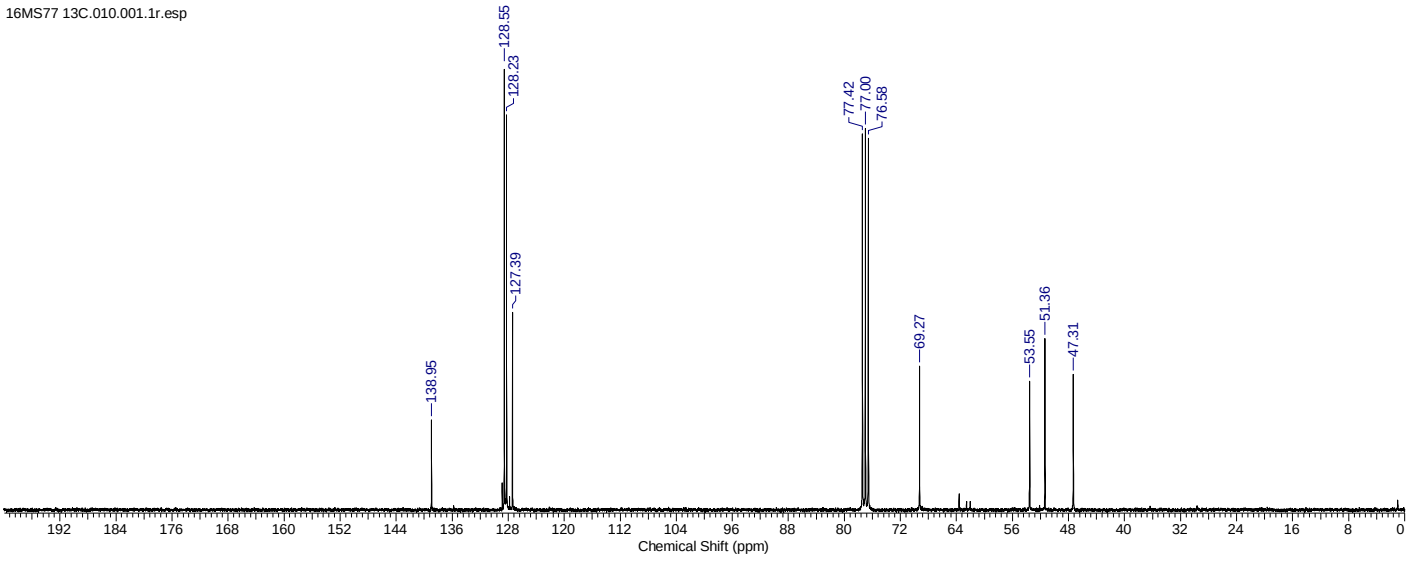
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 1a



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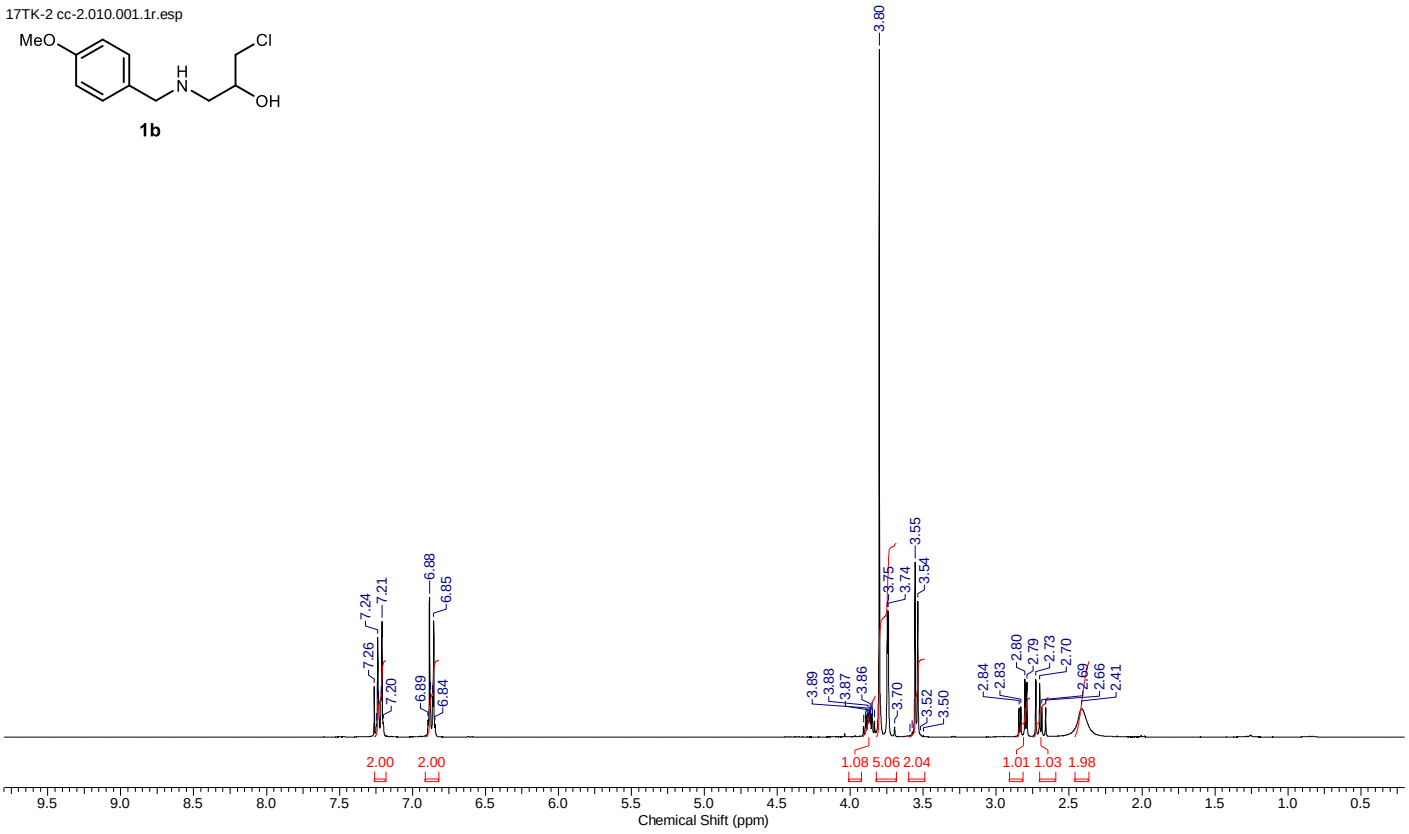


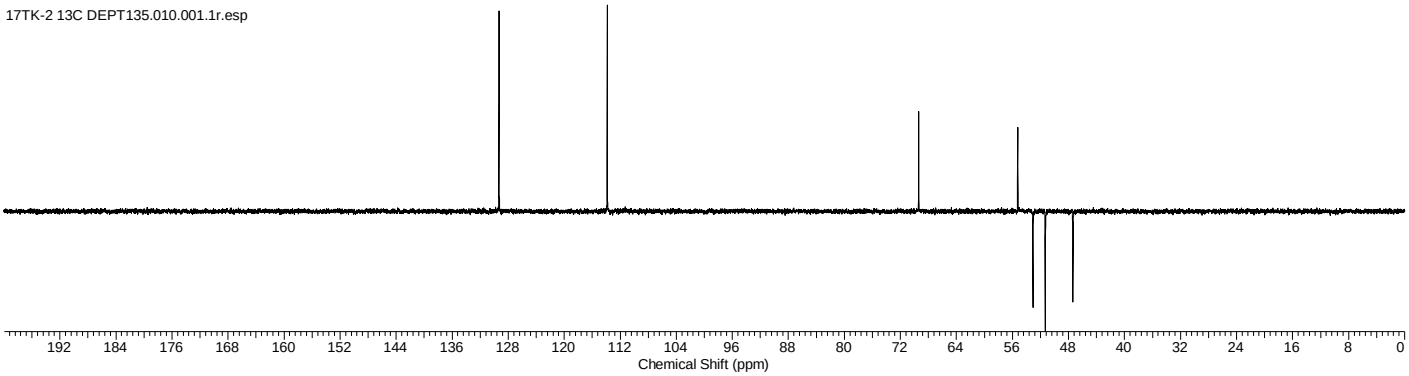


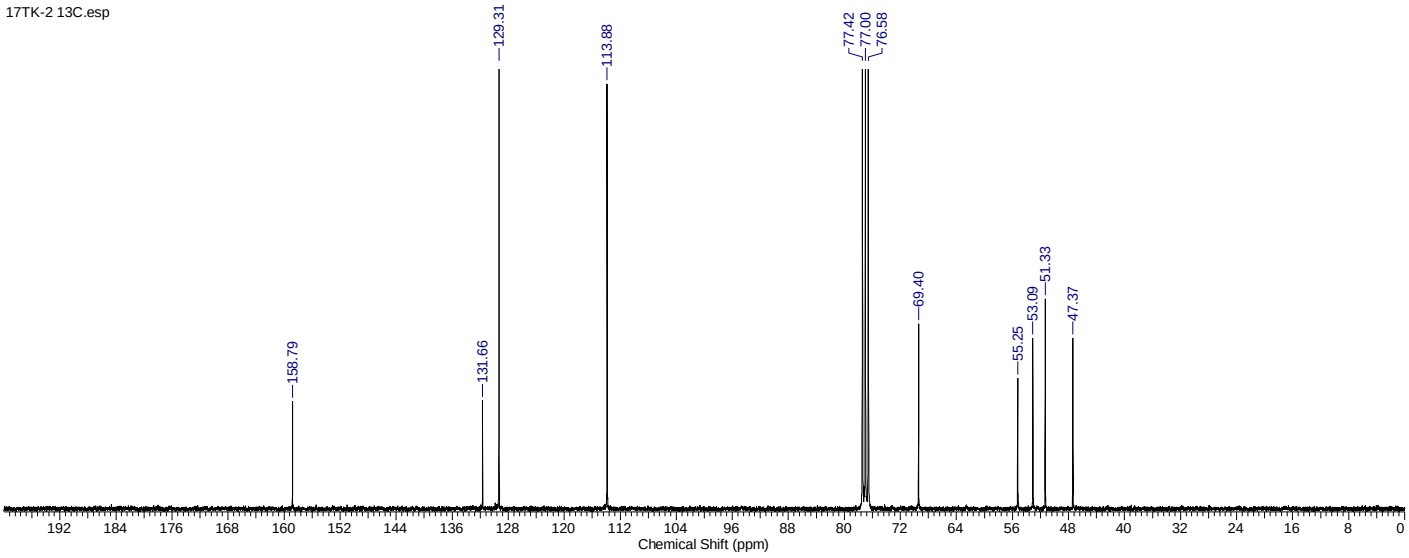

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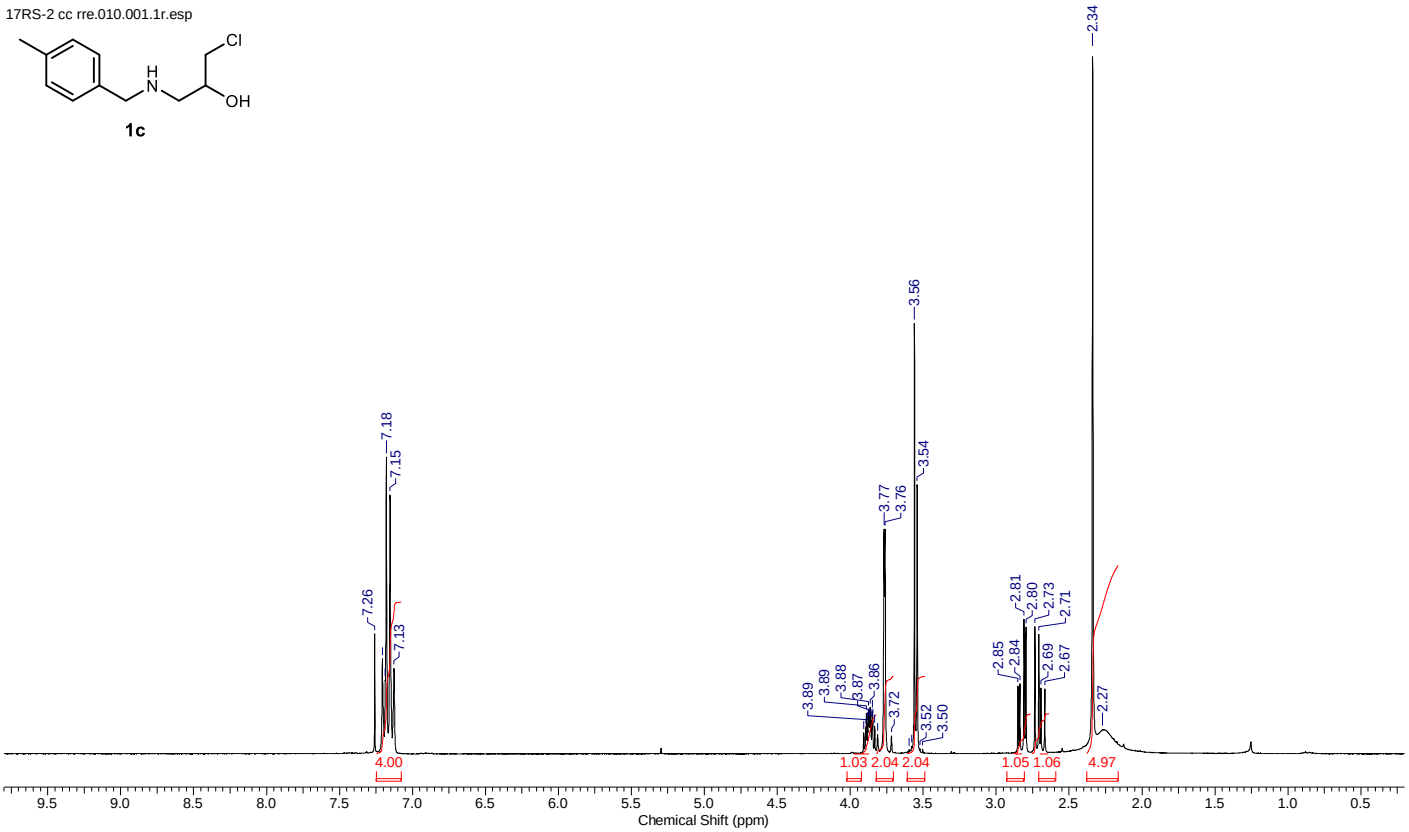


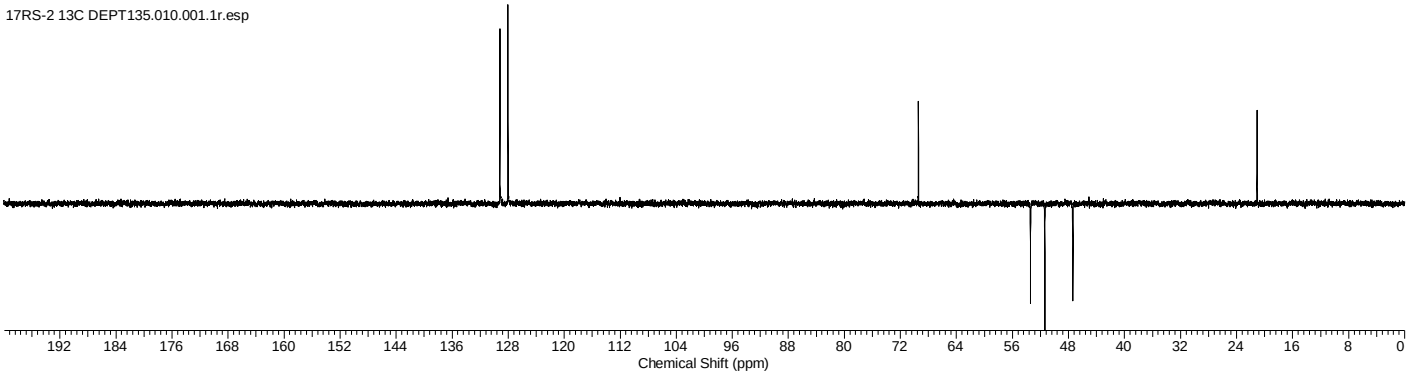


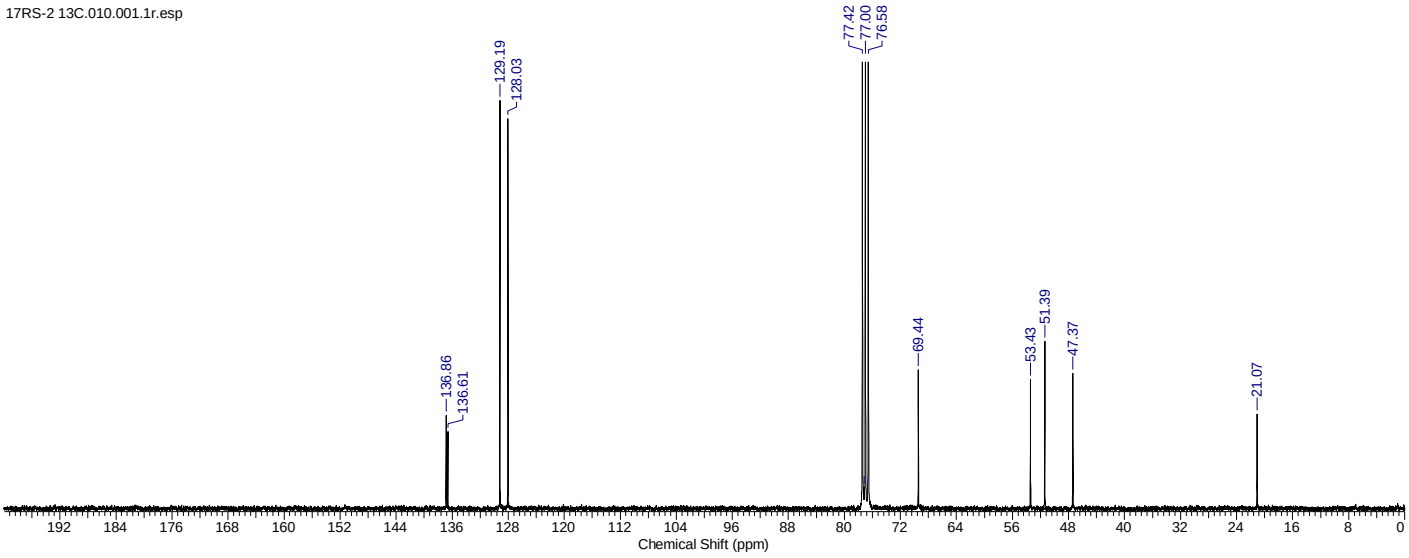

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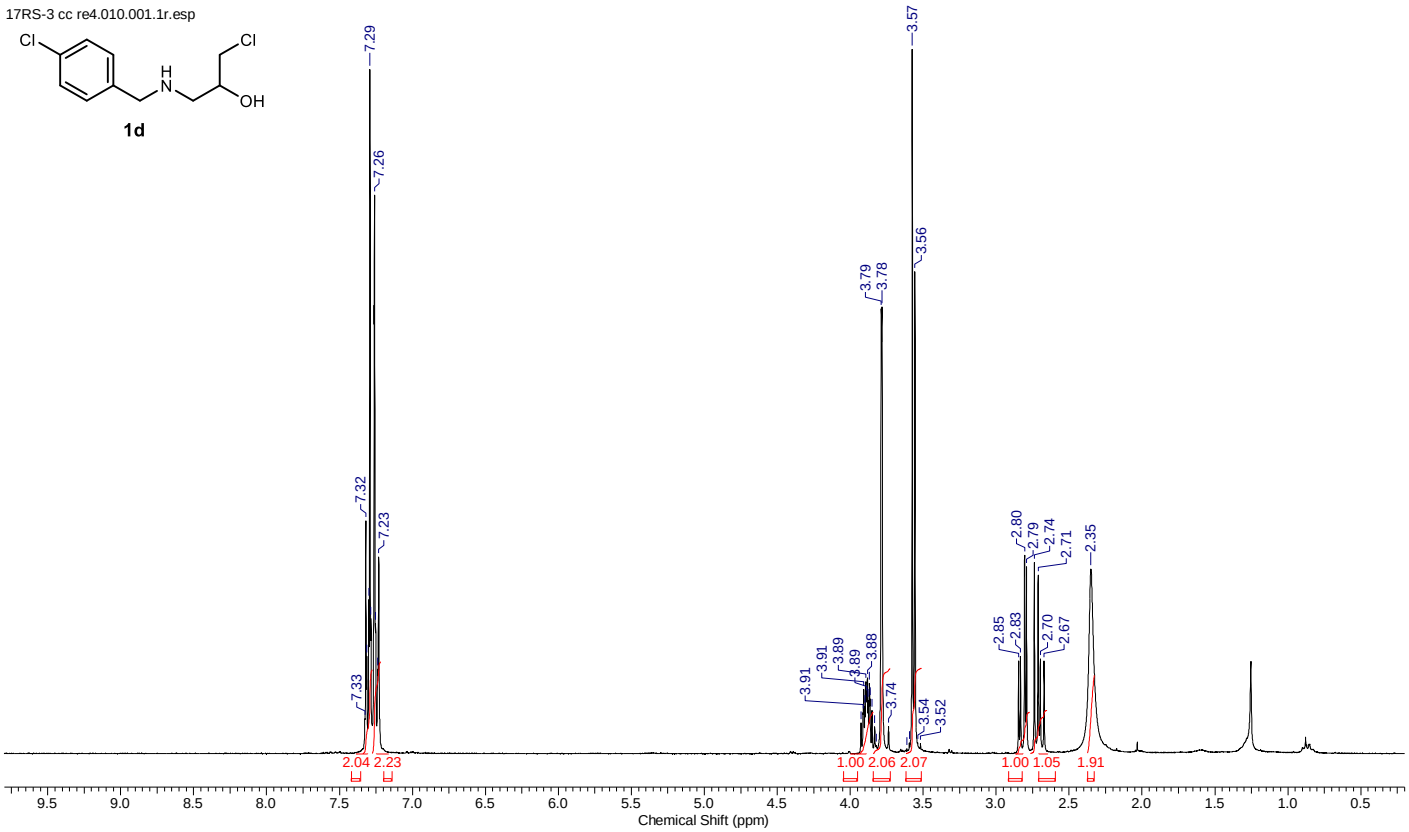


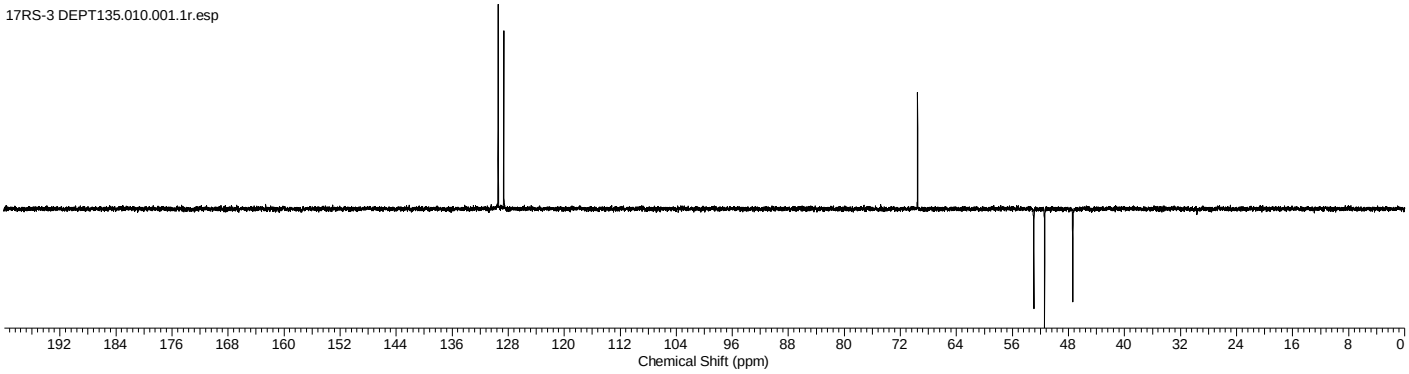


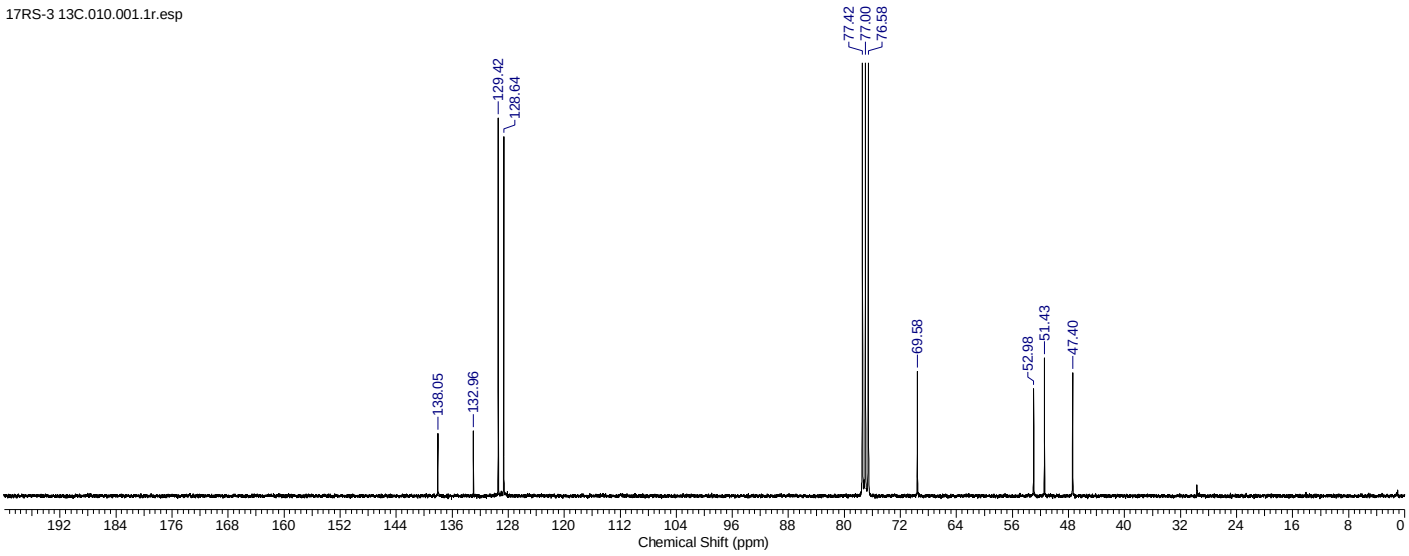

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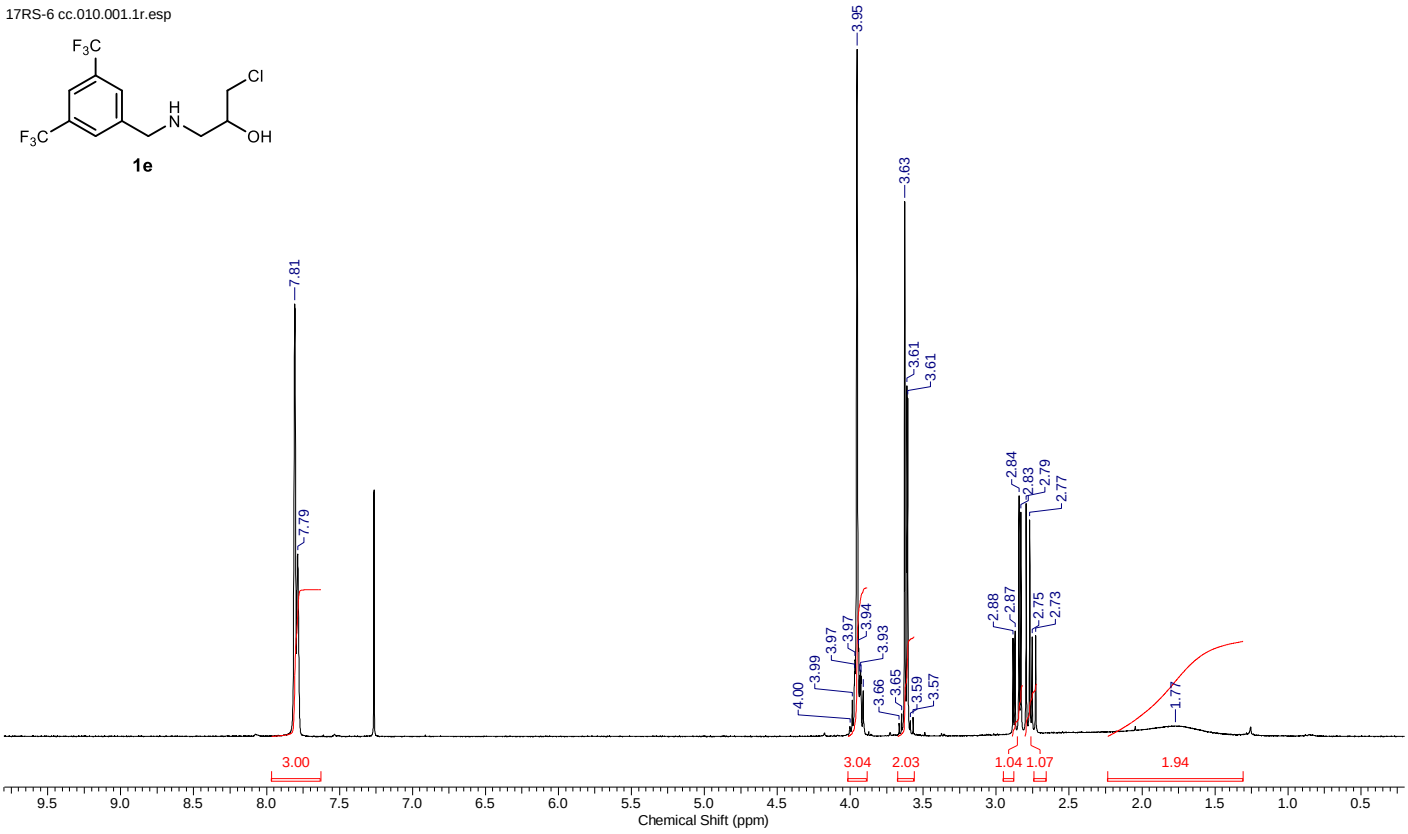


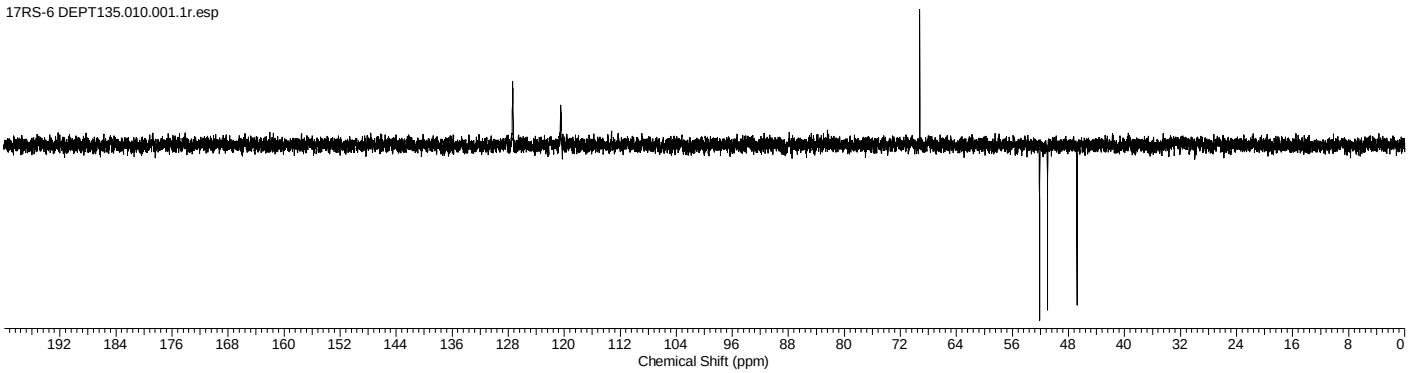


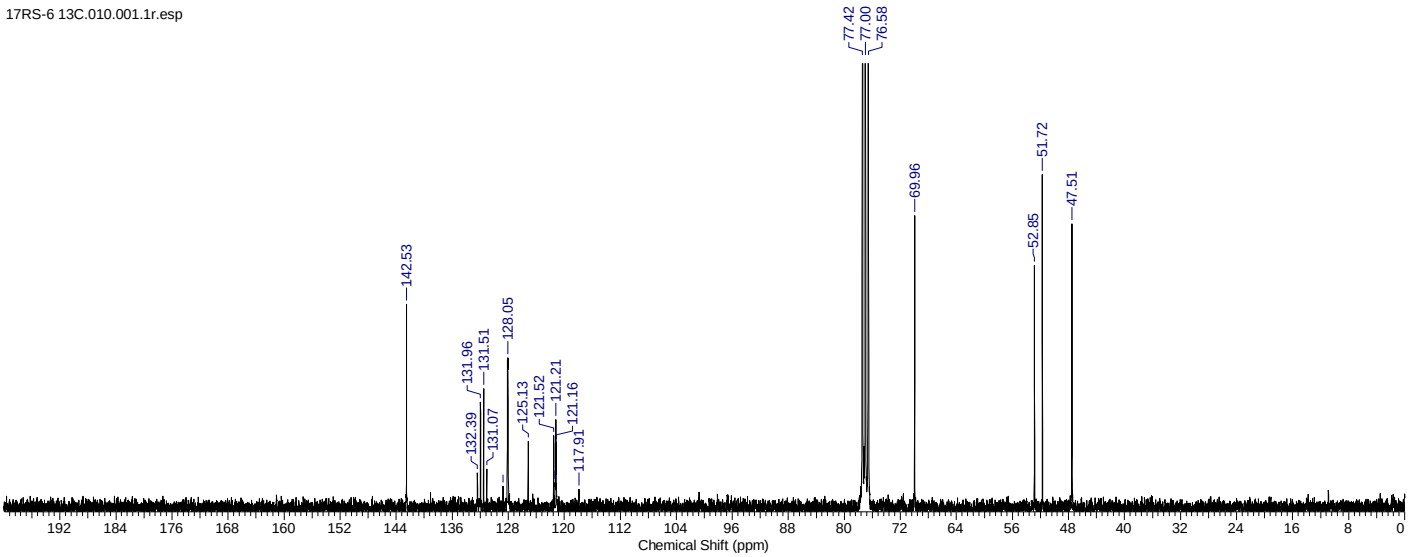

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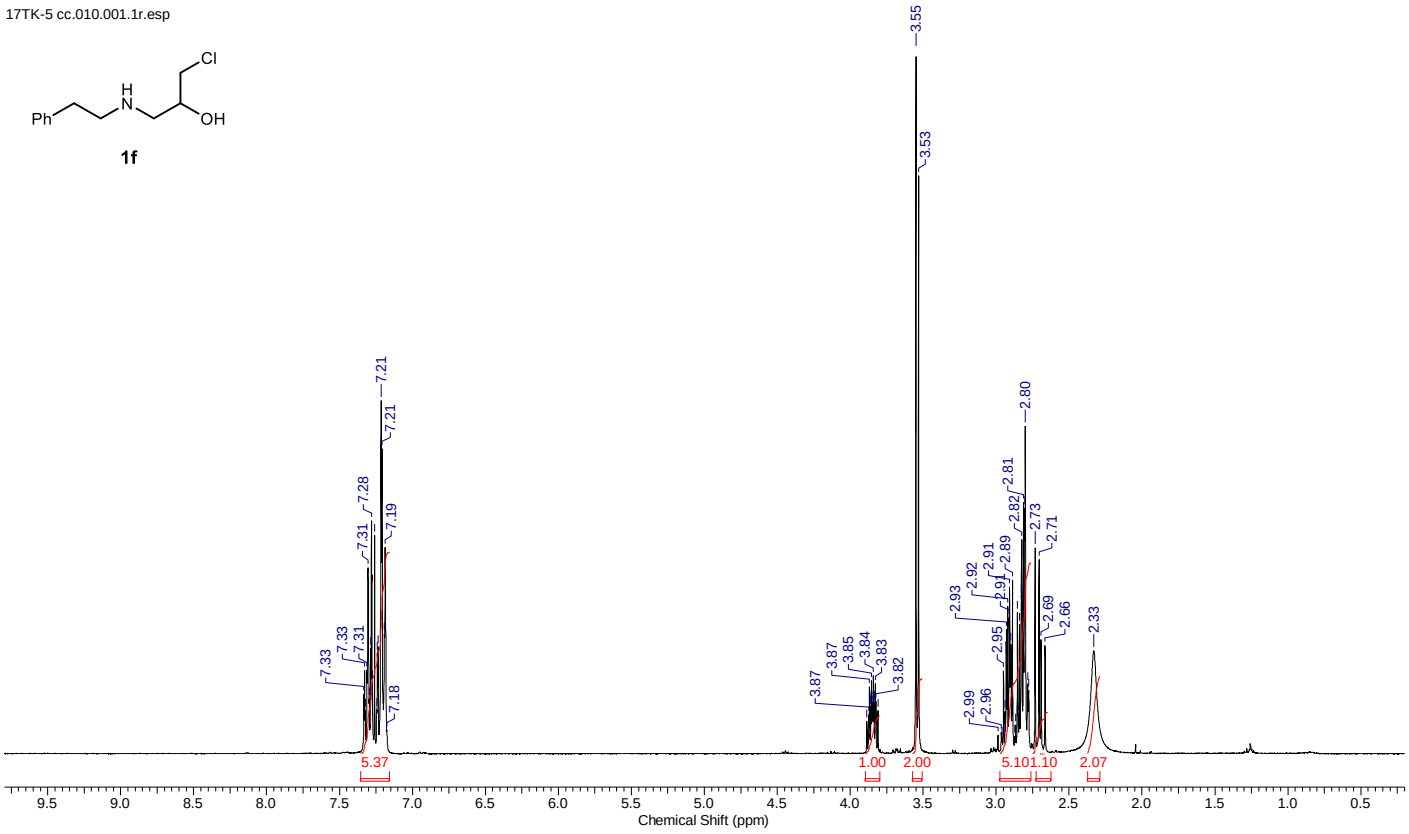


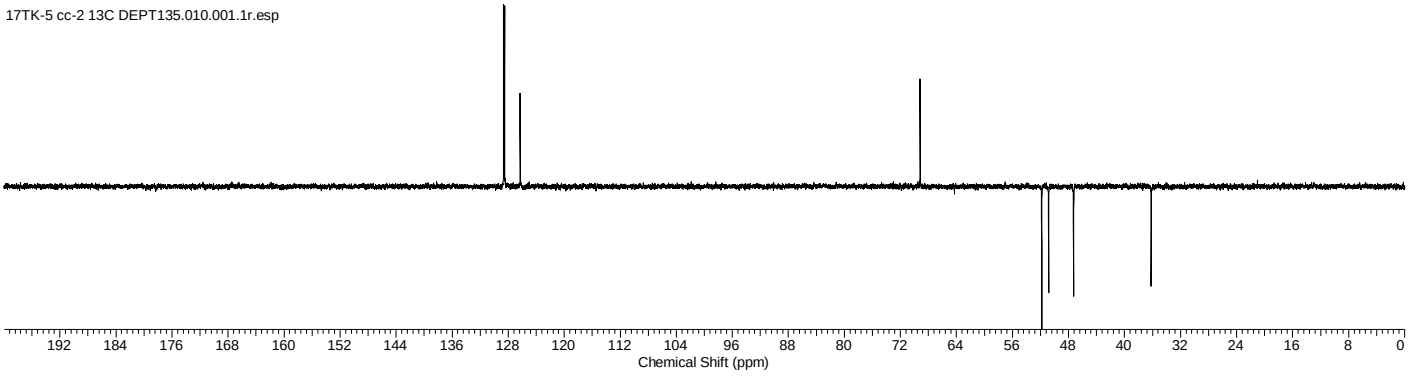


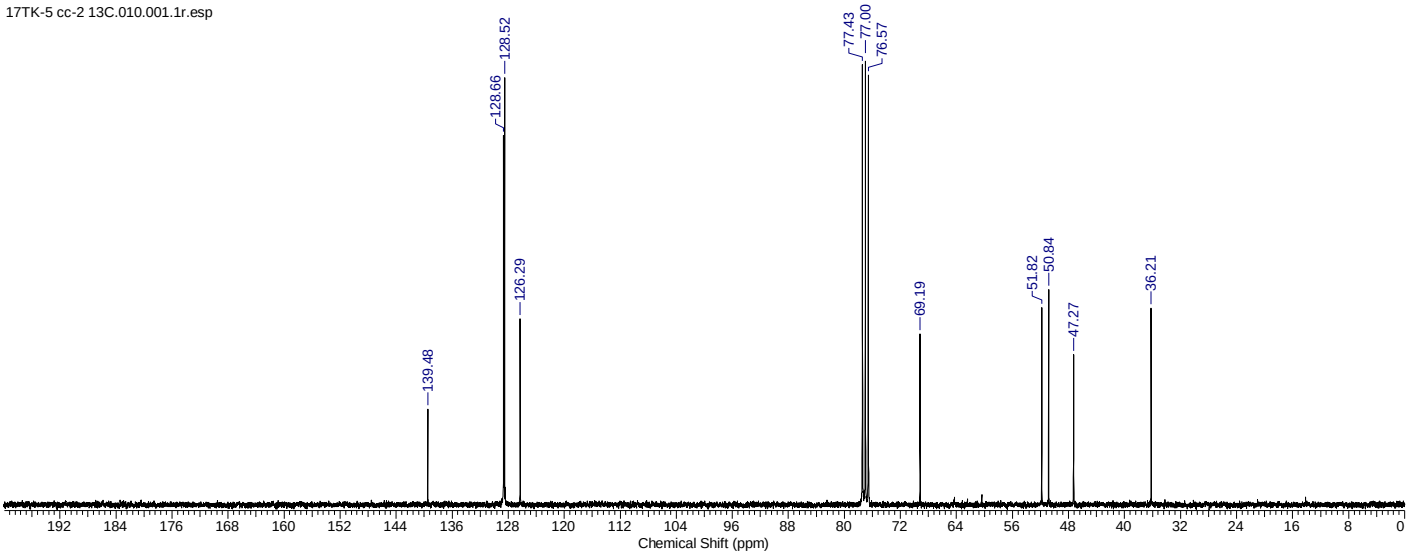

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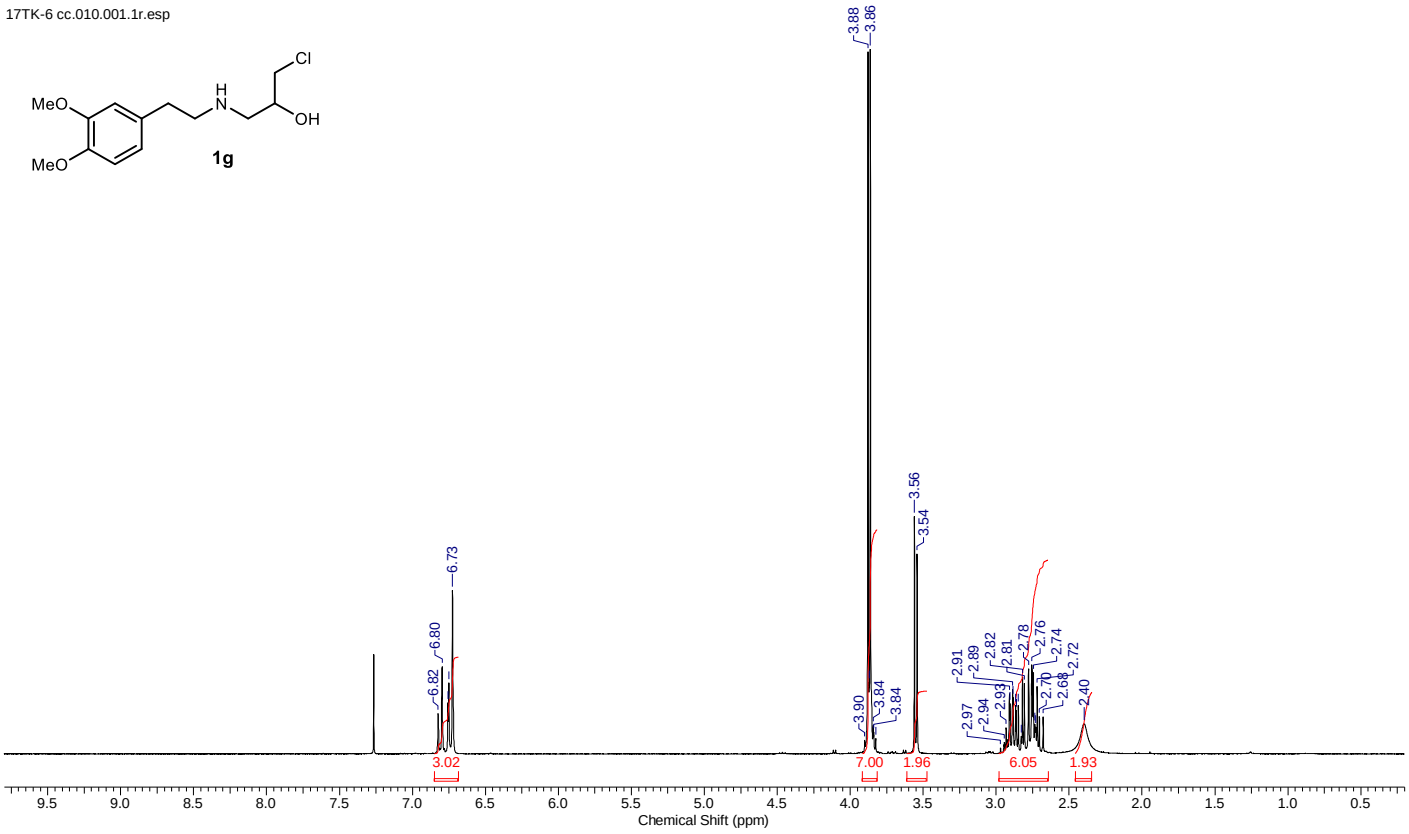


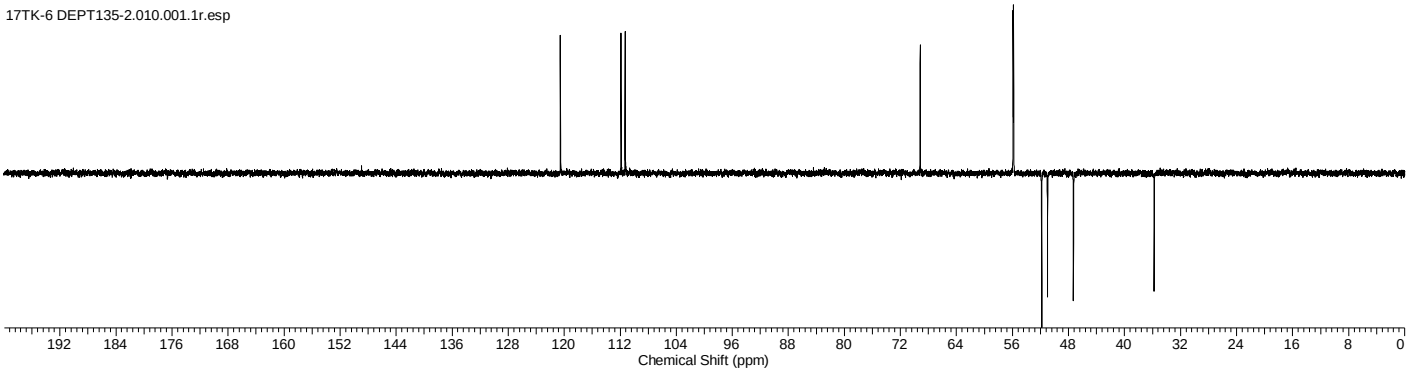


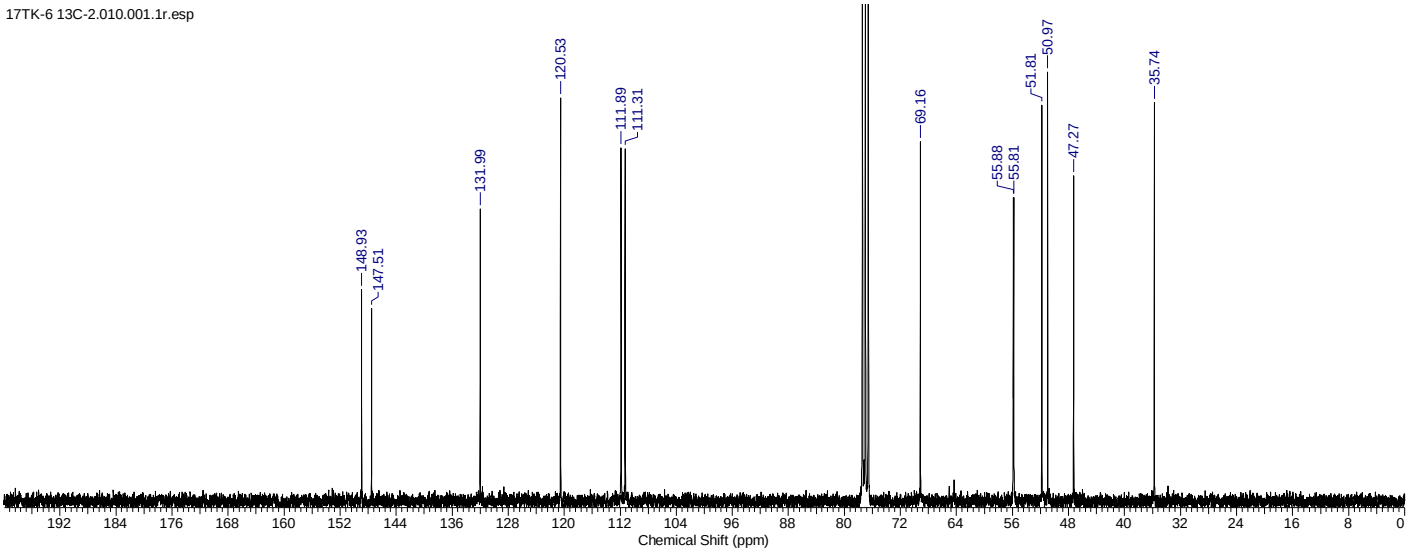

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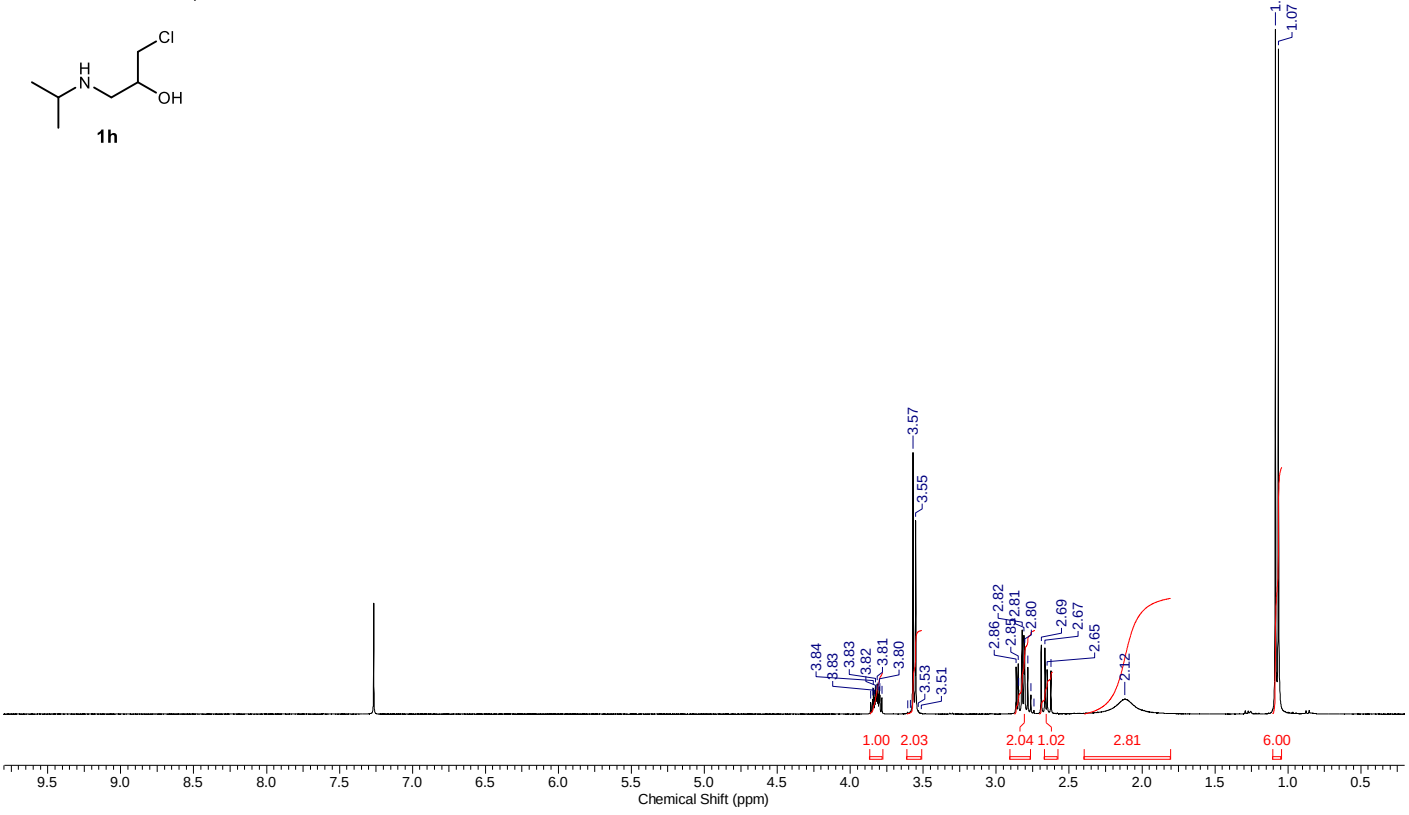


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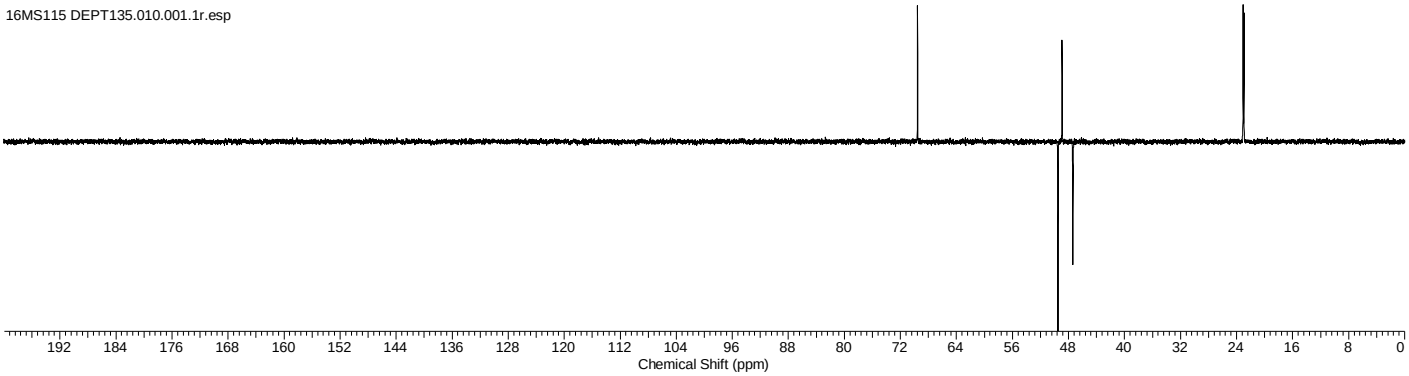


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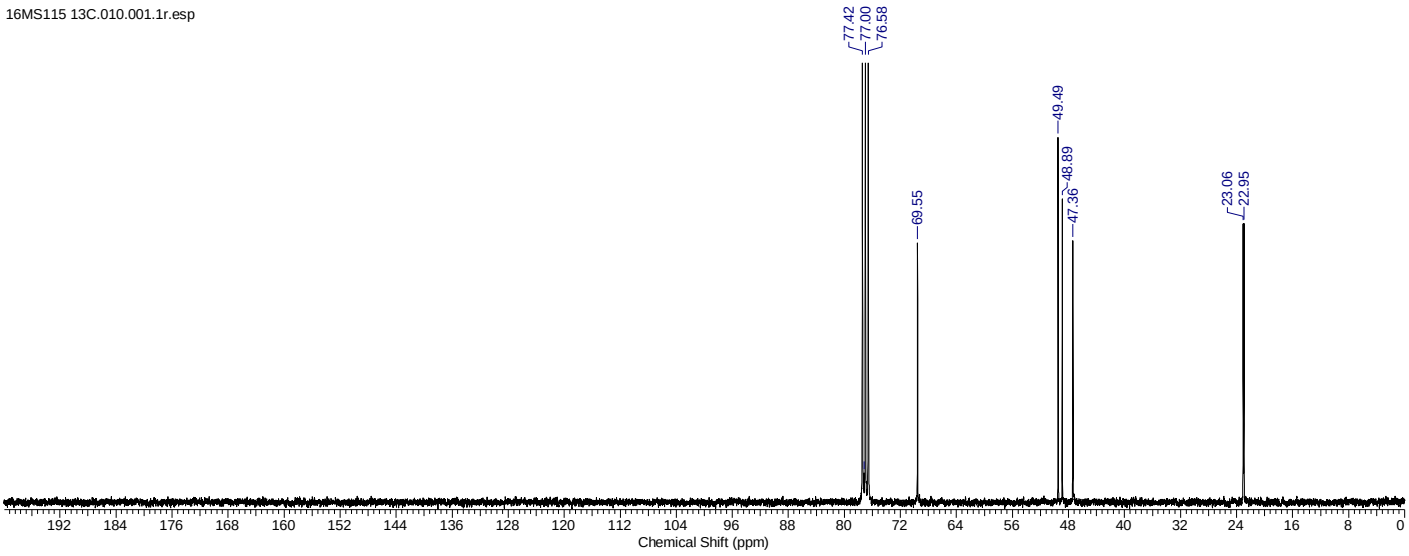

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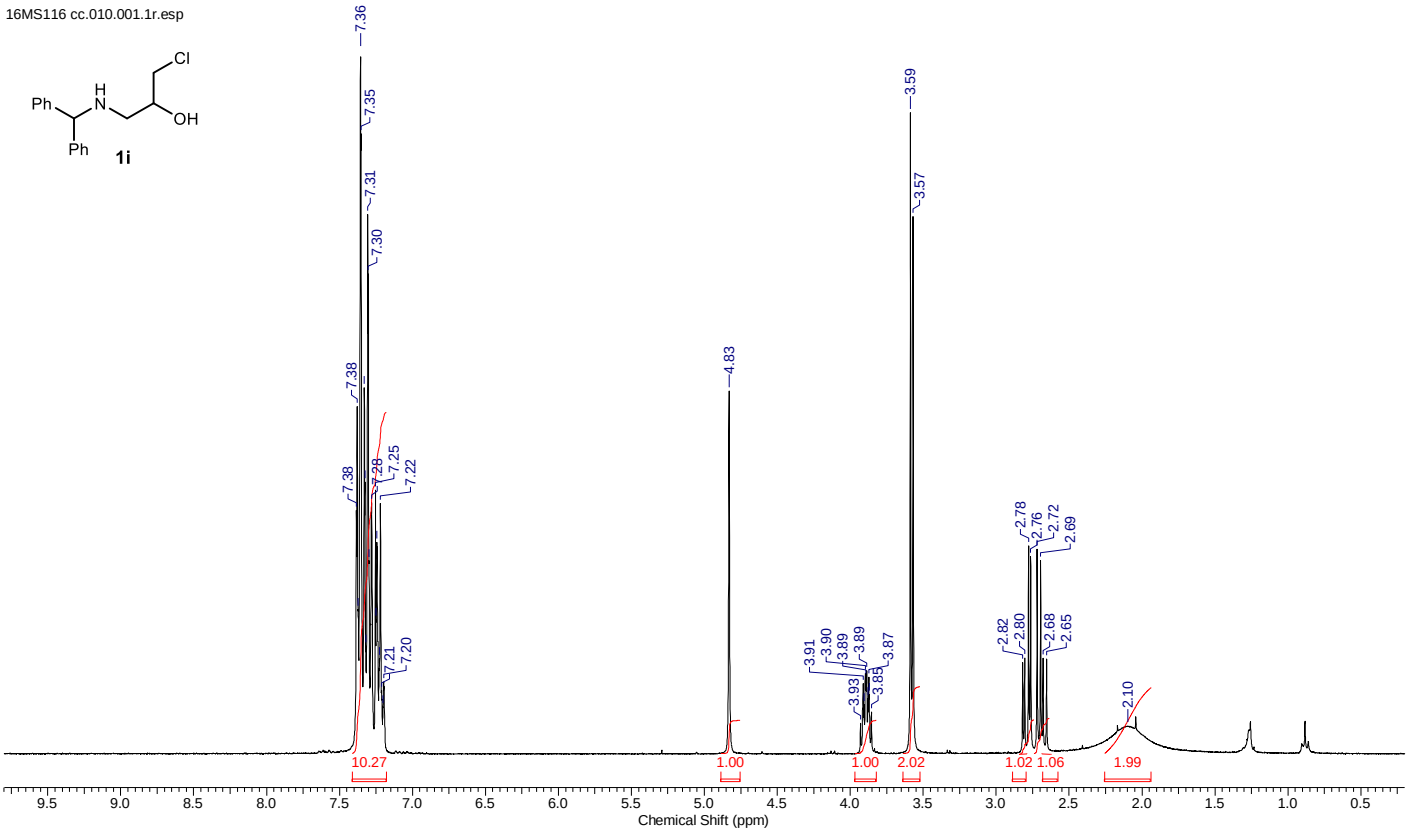


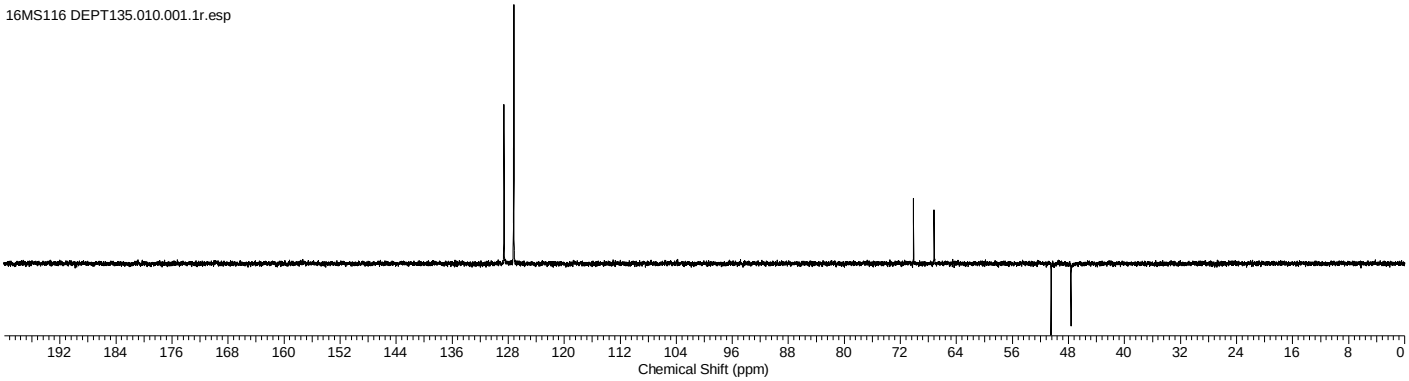


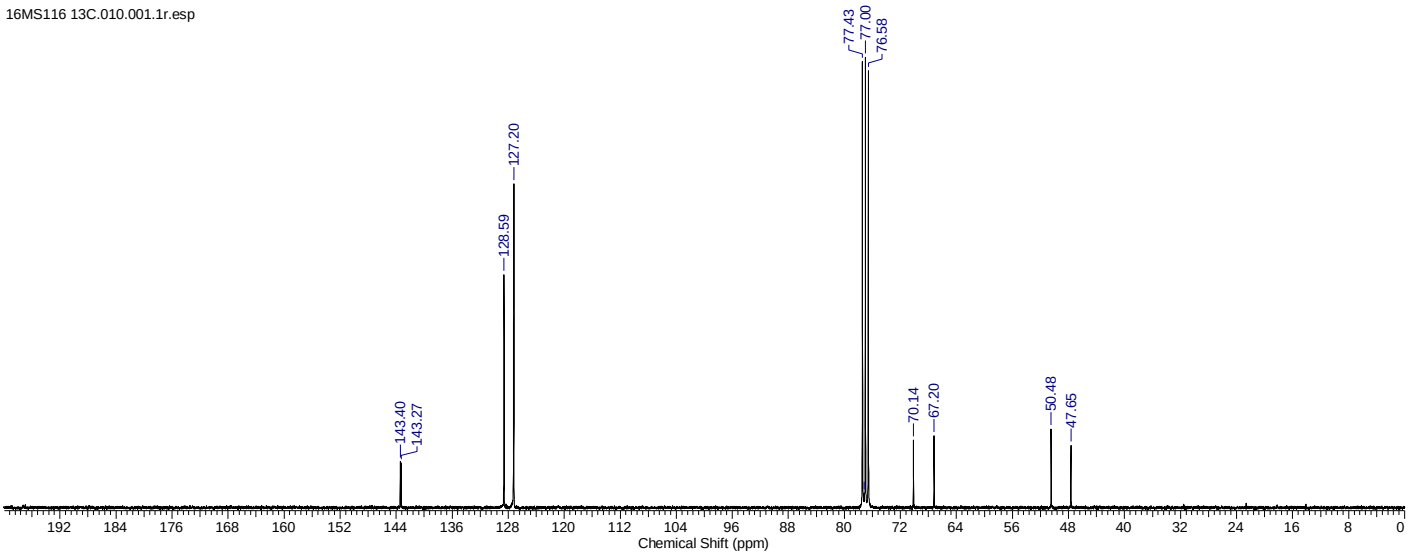

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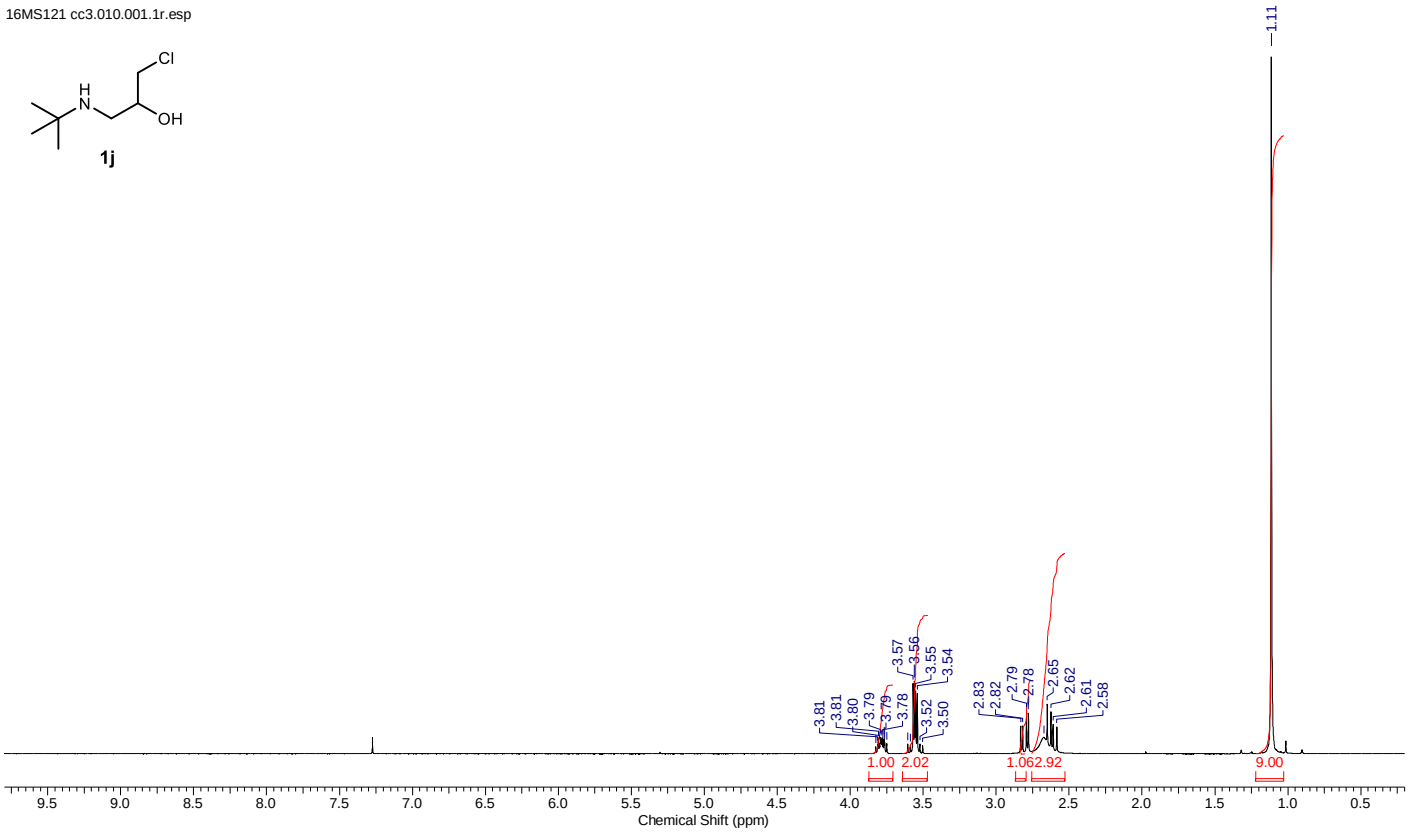


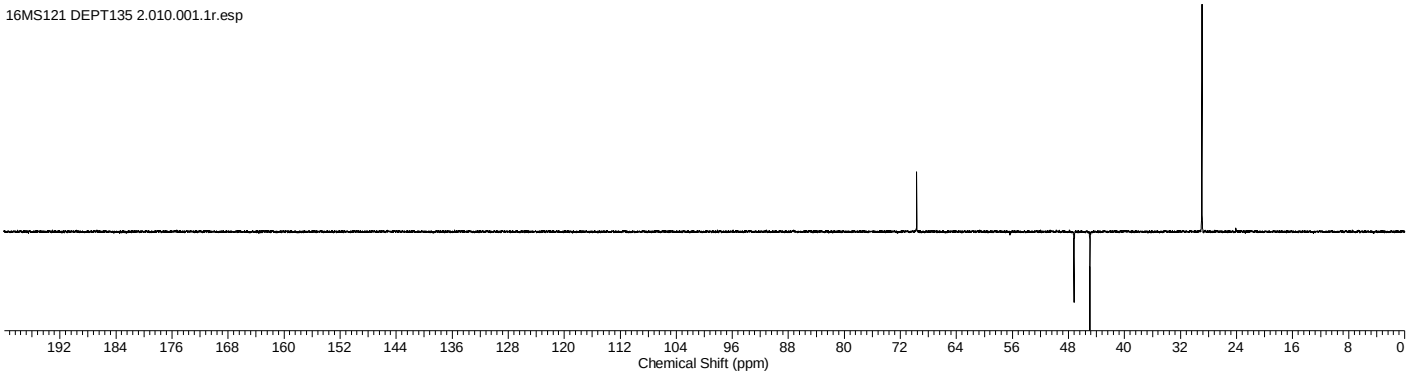


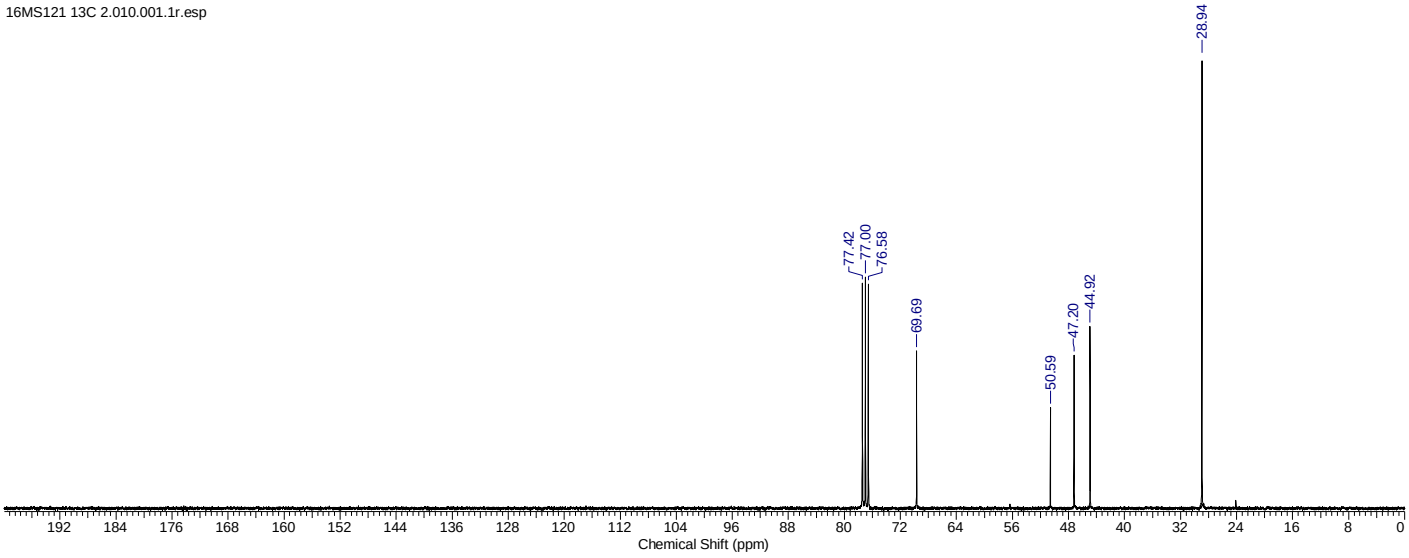

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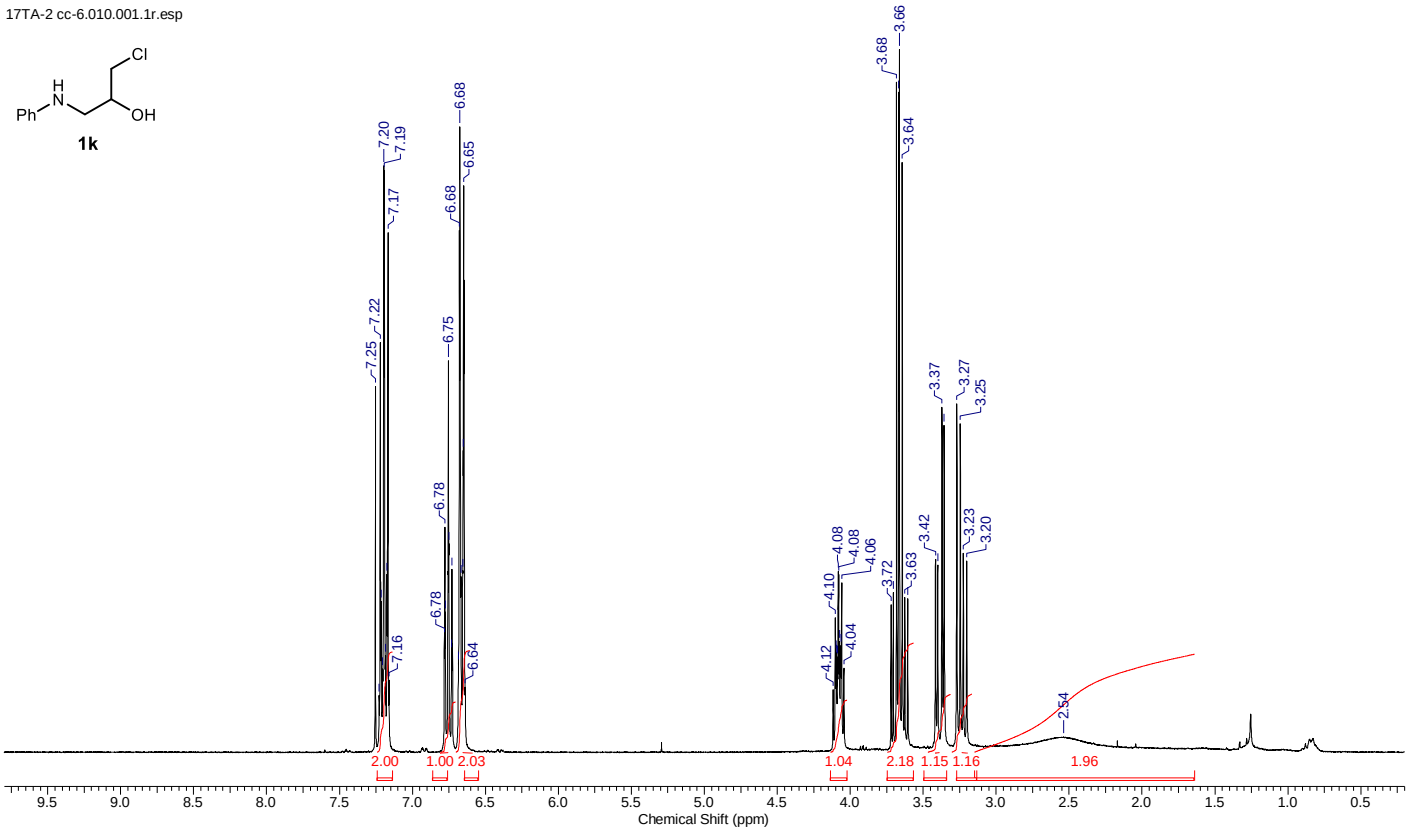


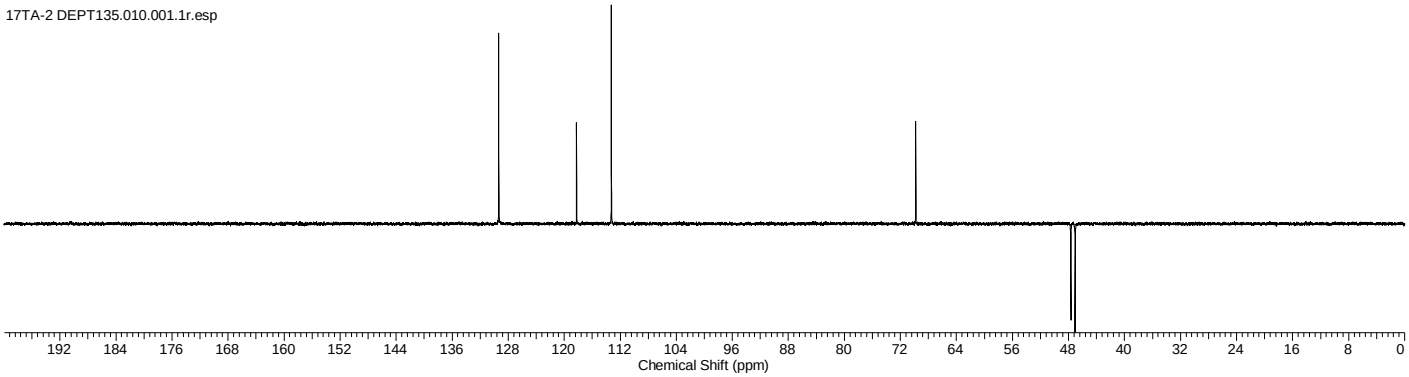


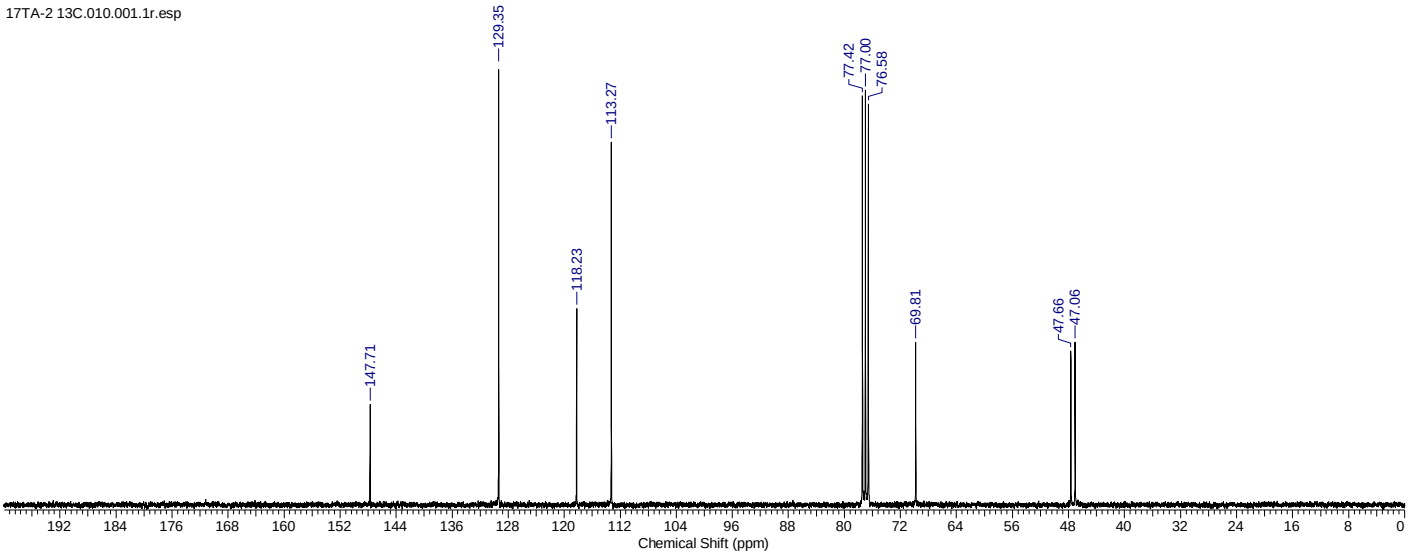

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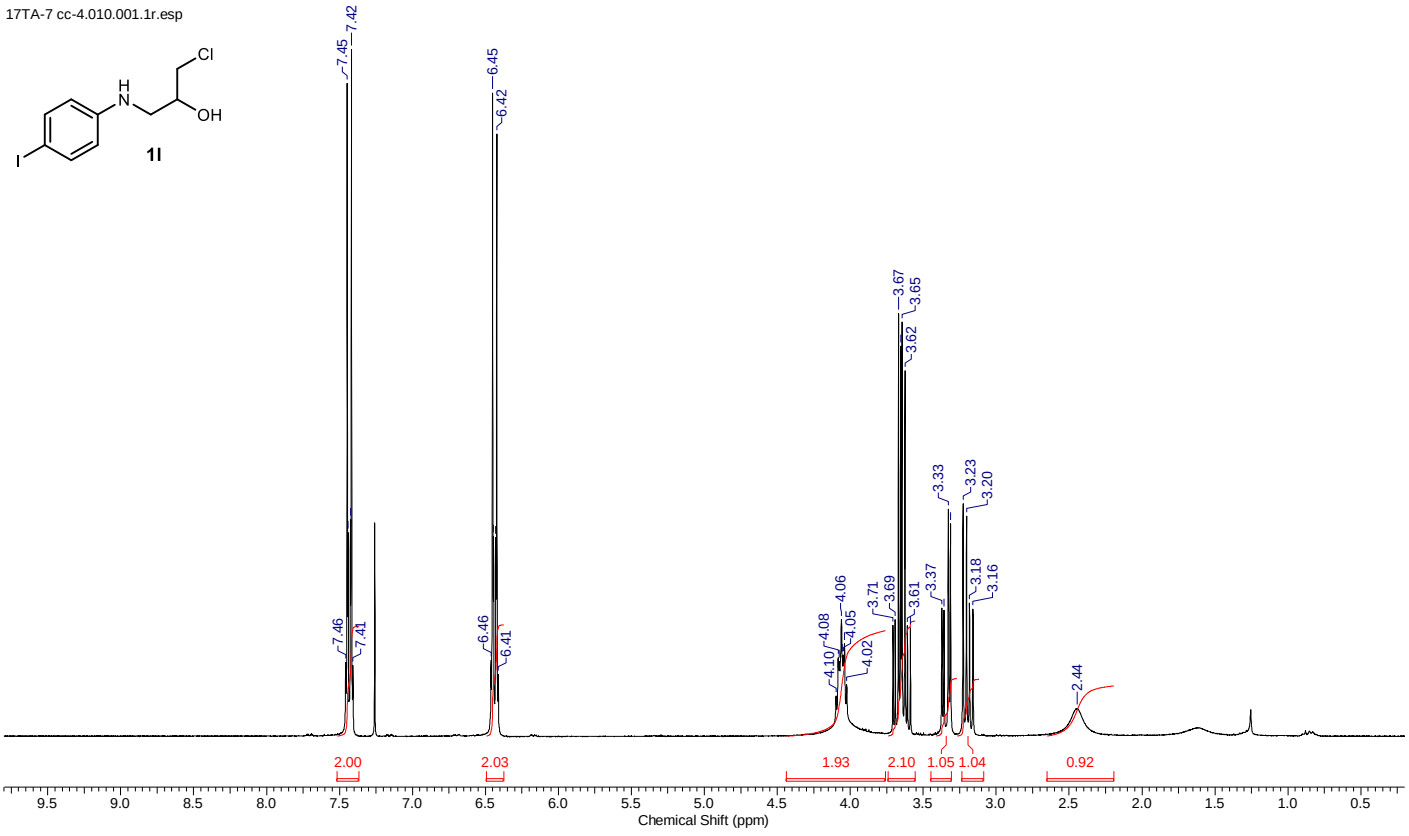


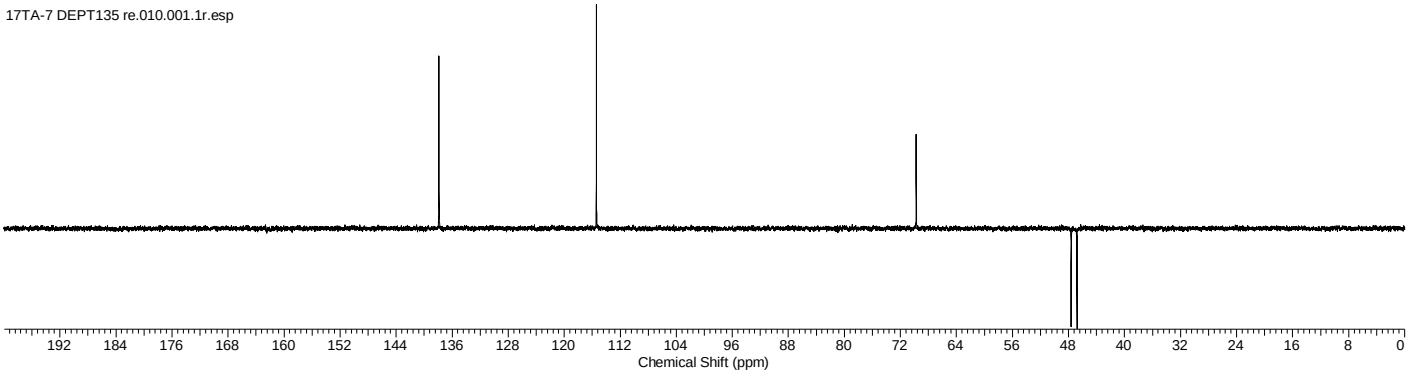


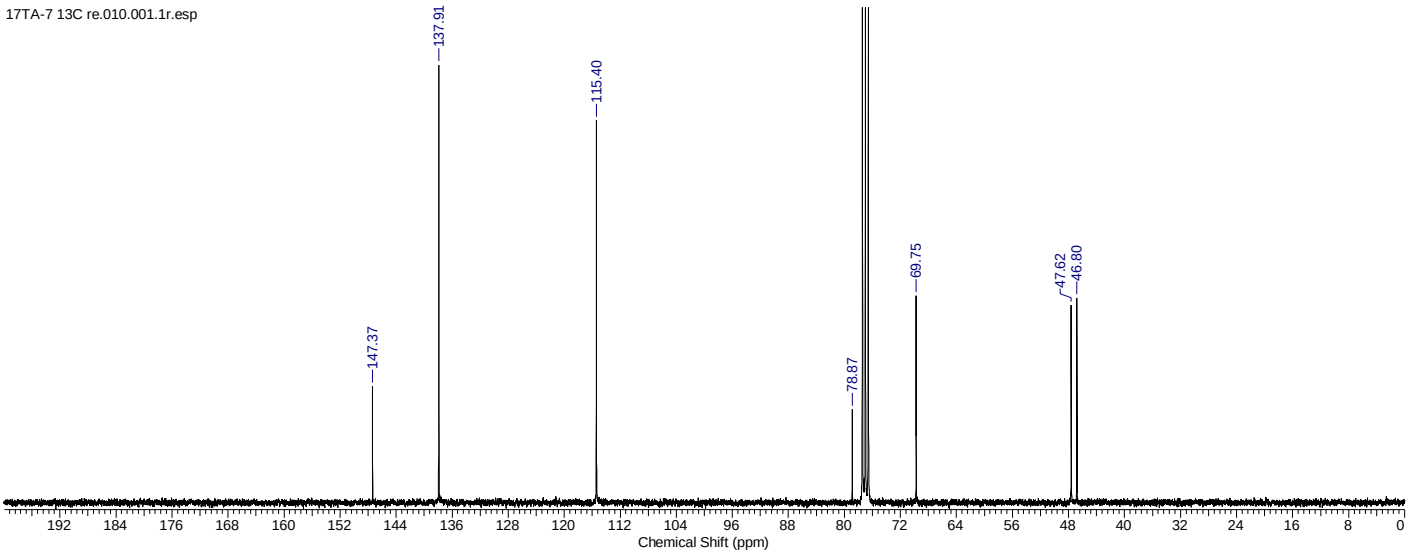

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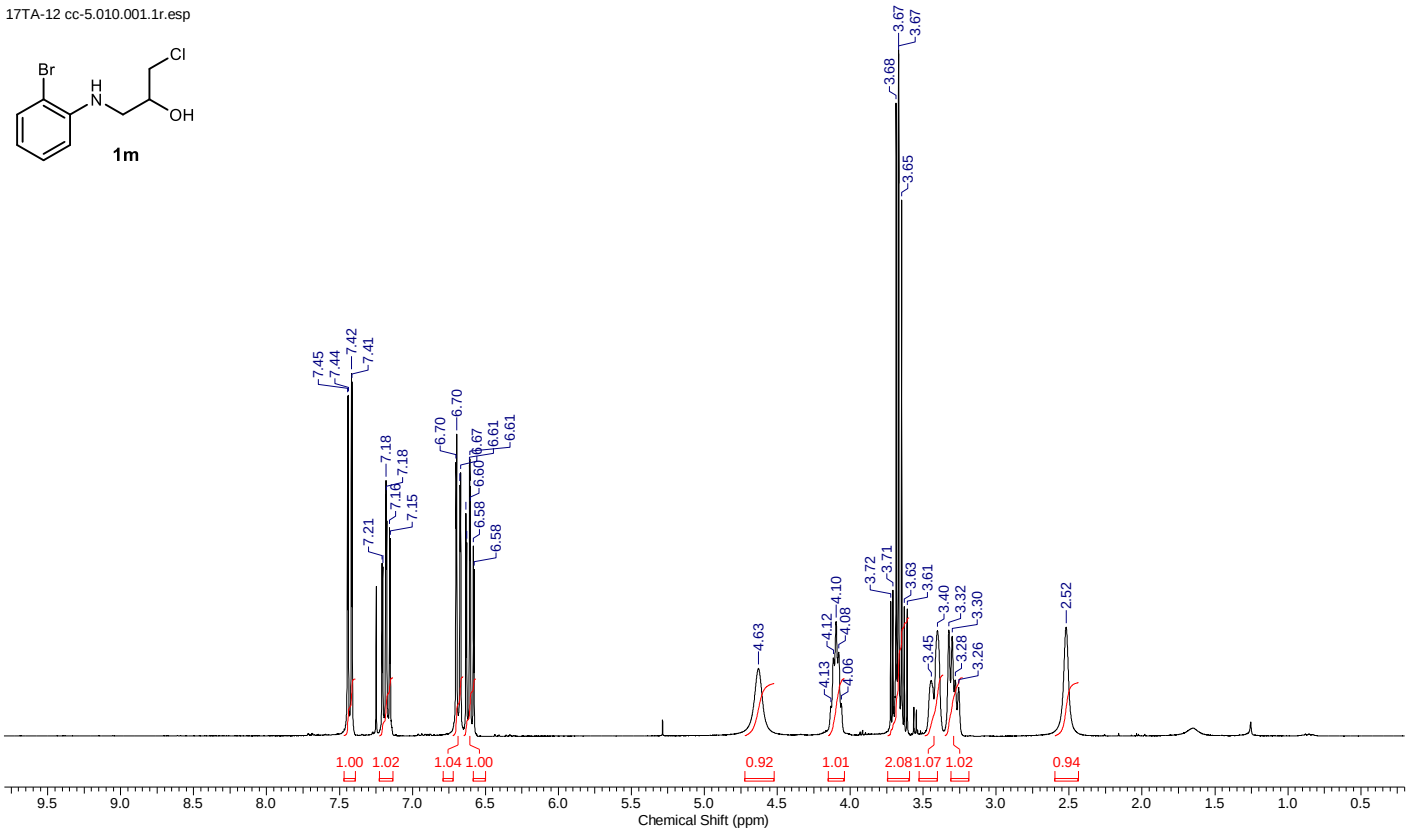
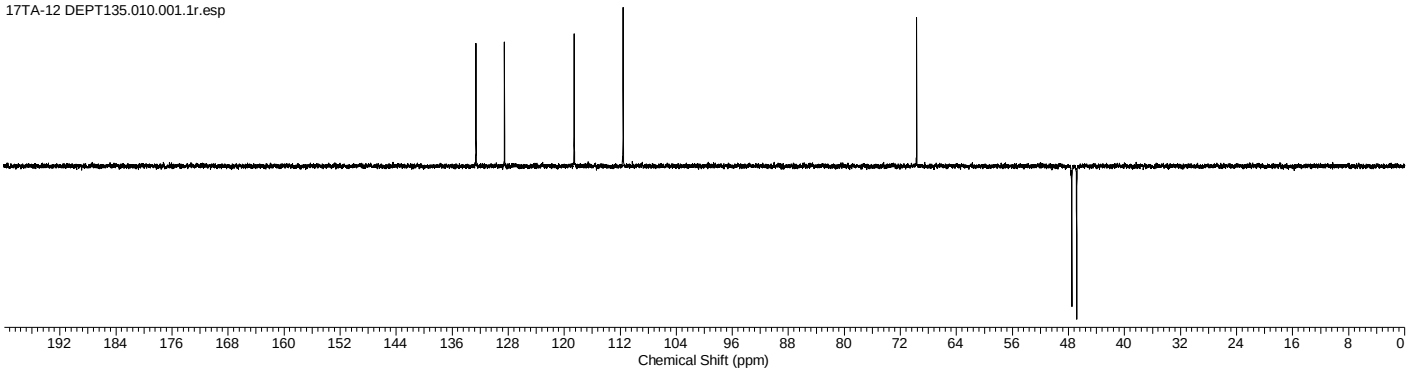
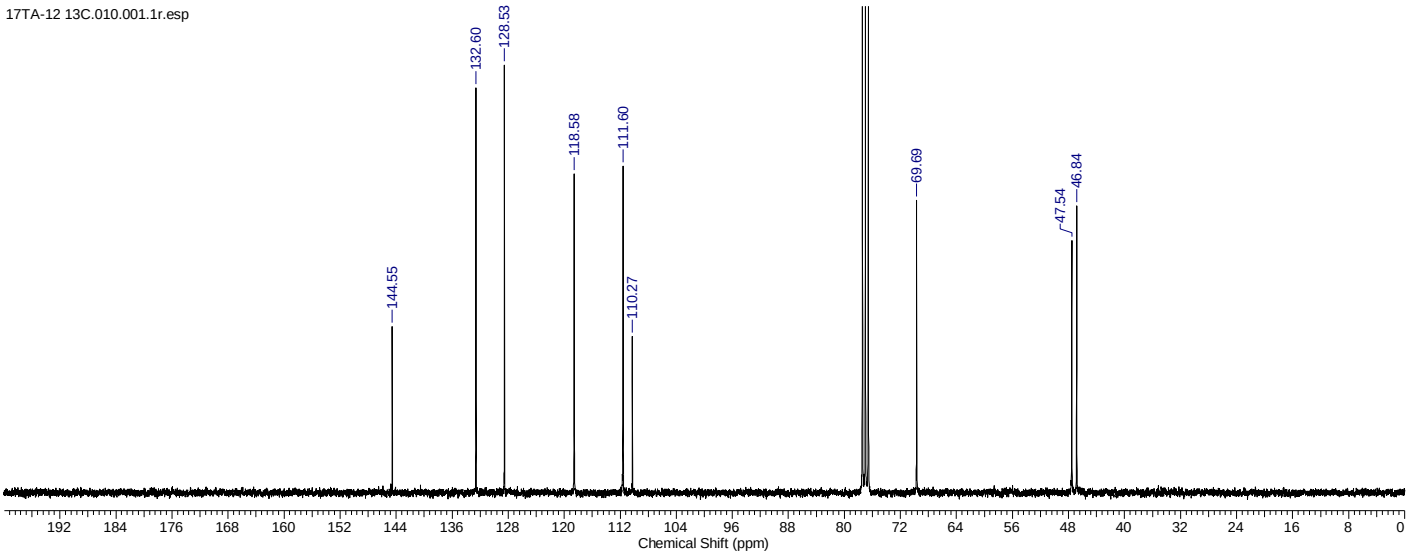
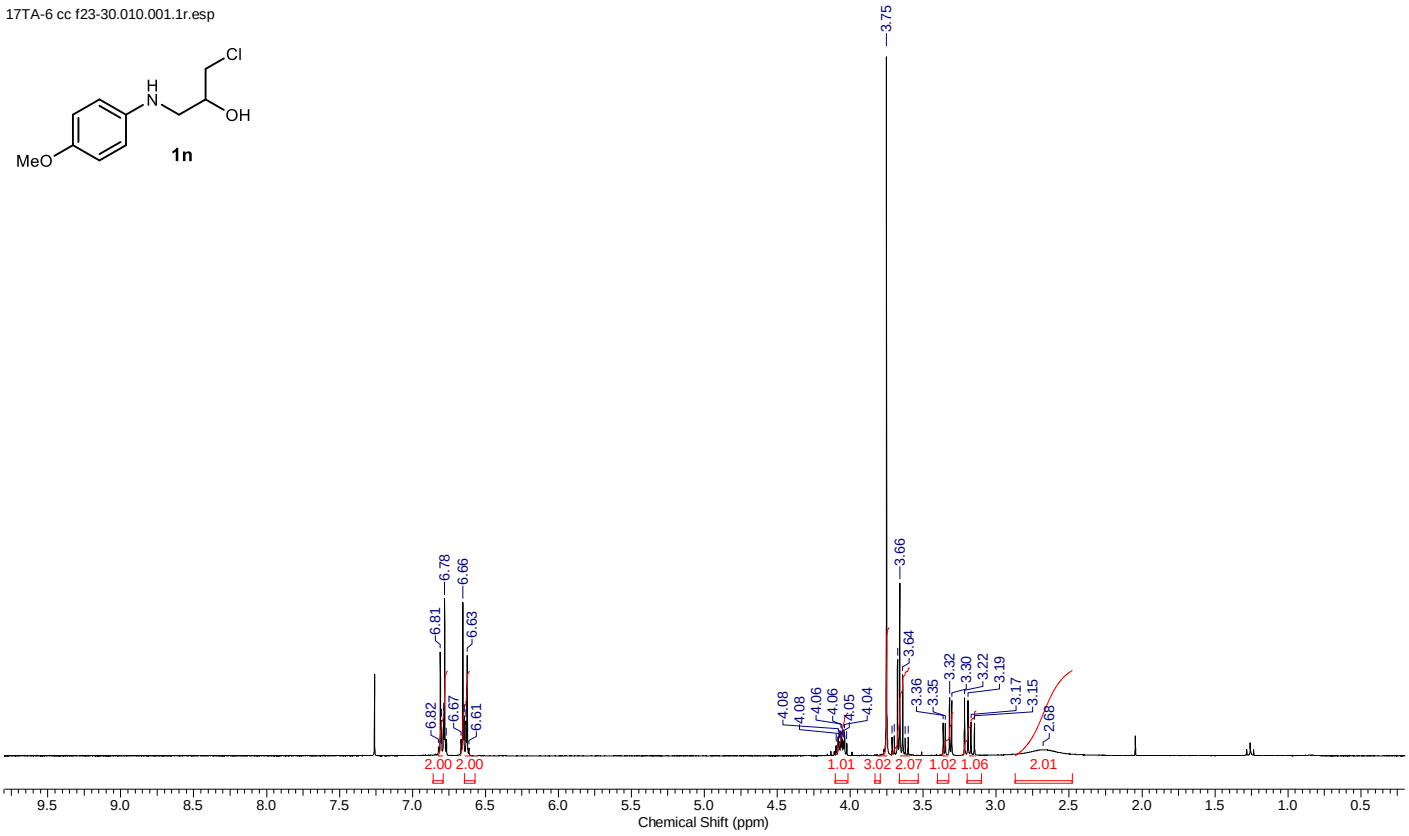
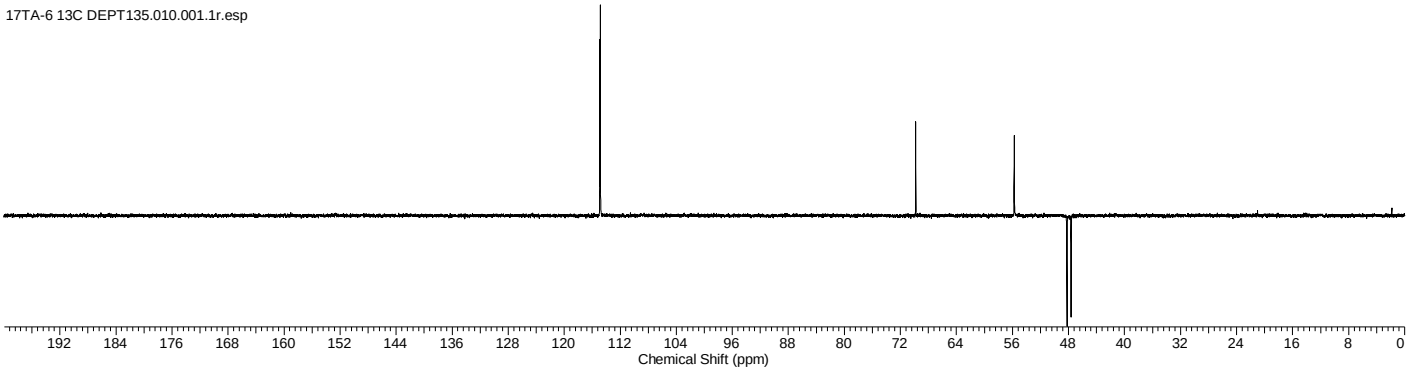


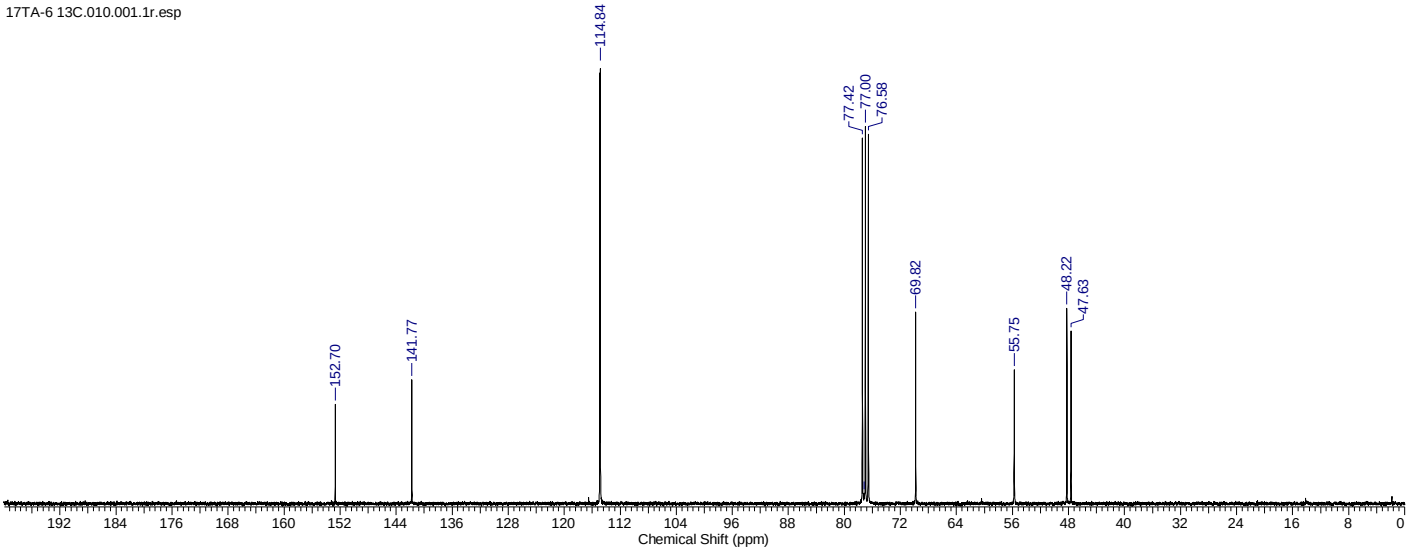



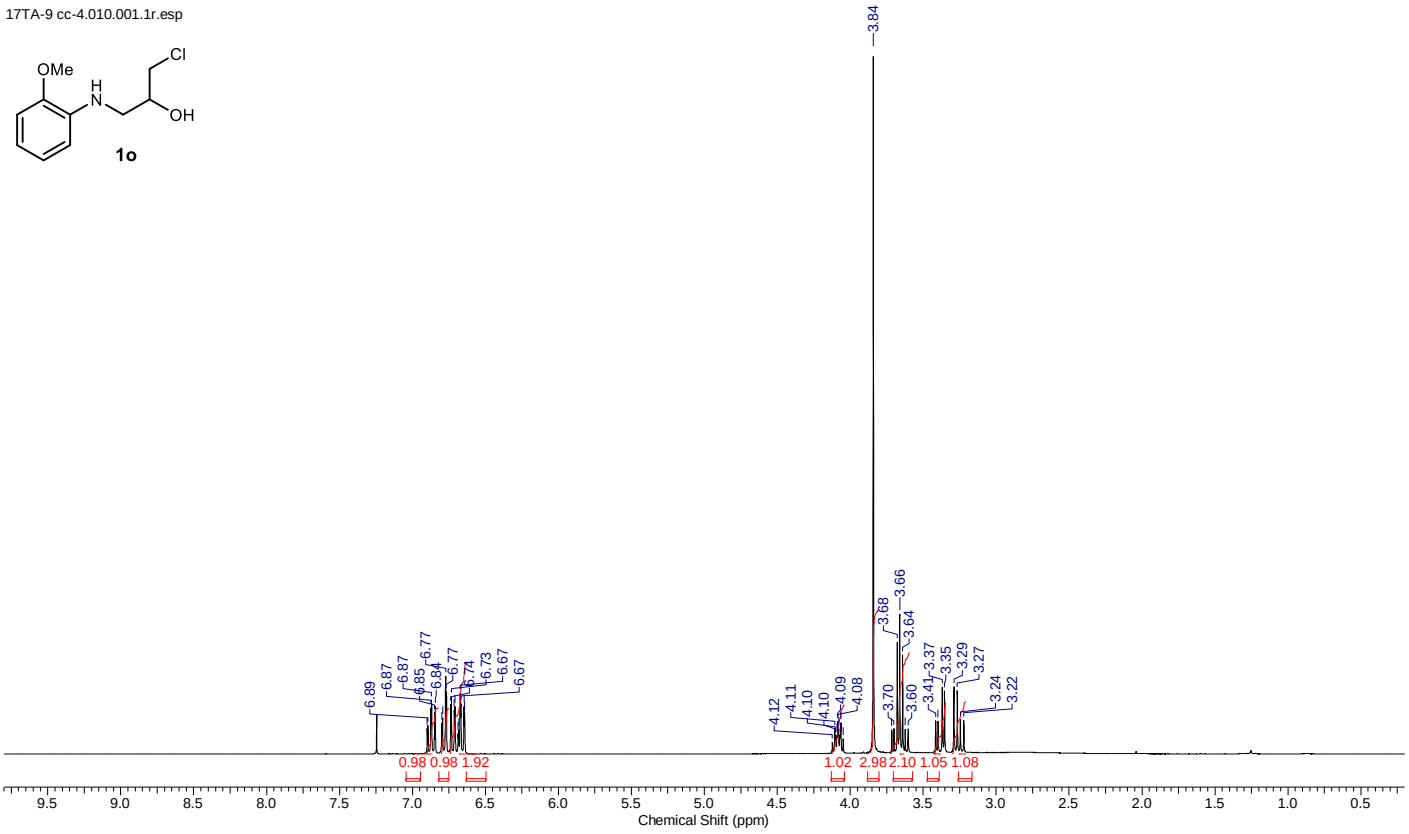
# $^{1}H$ (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 1n

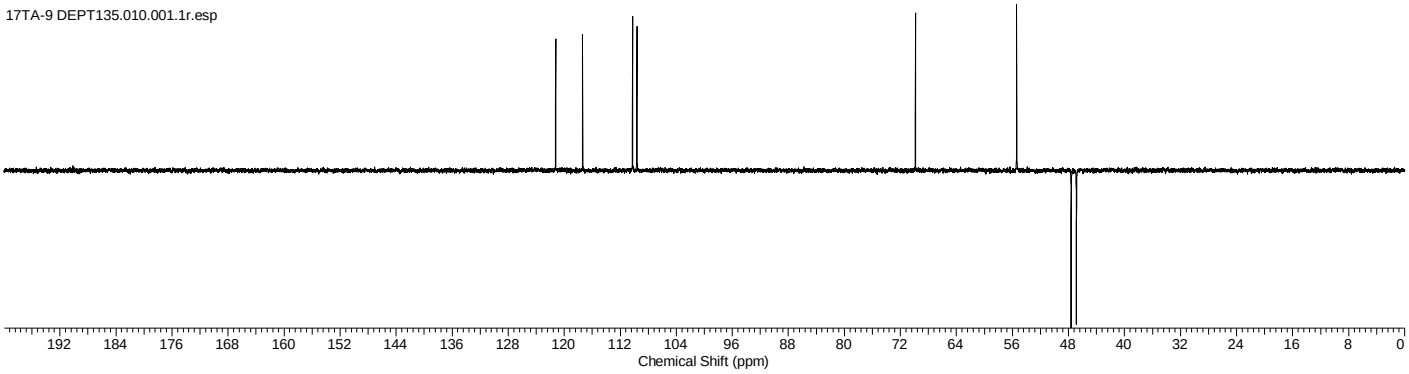


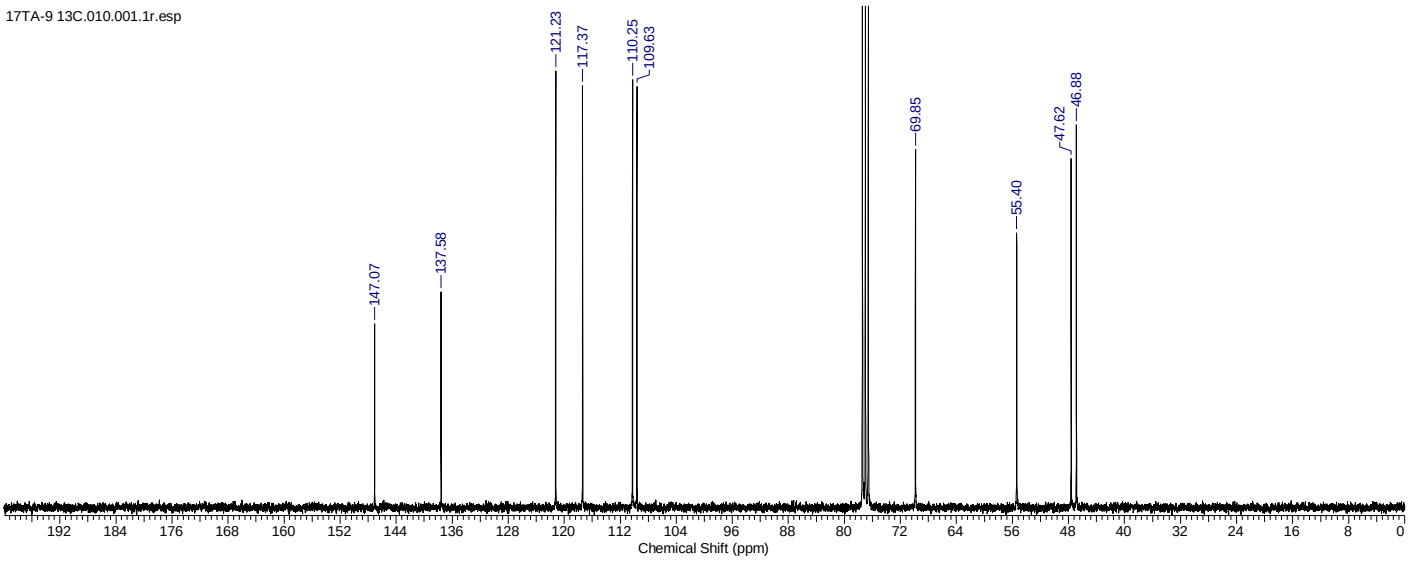



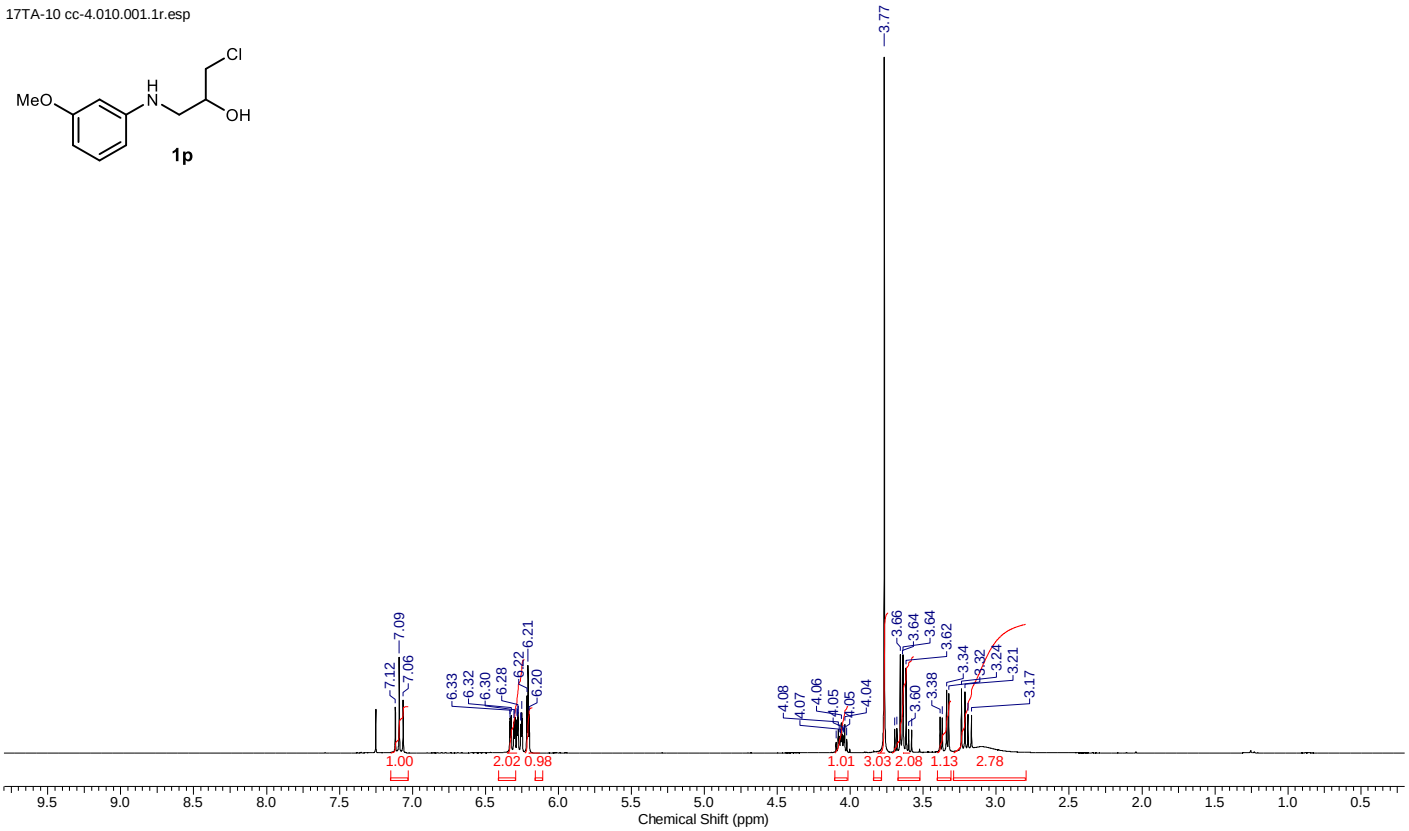
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 1o

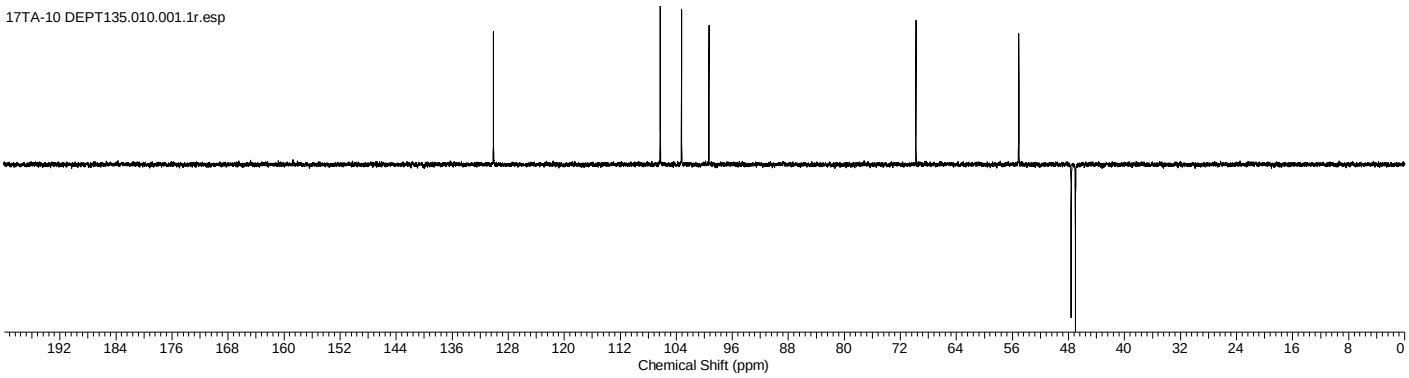


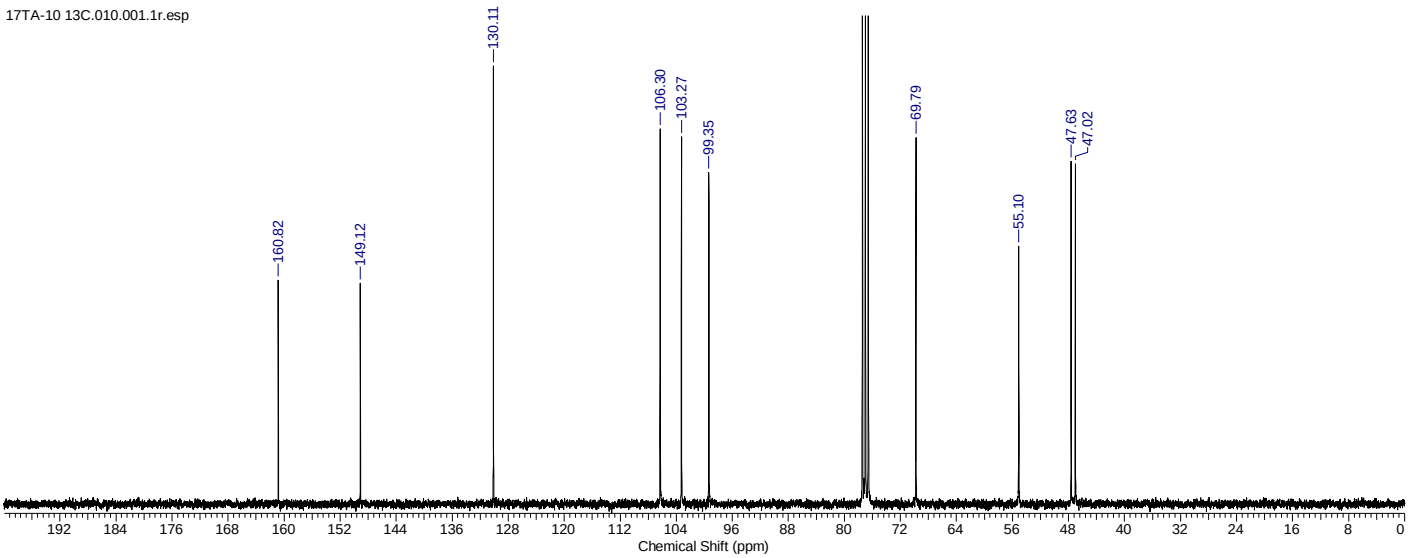



# $^{1}H$ (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 1p

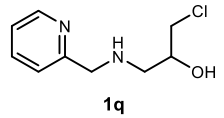


# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 1q

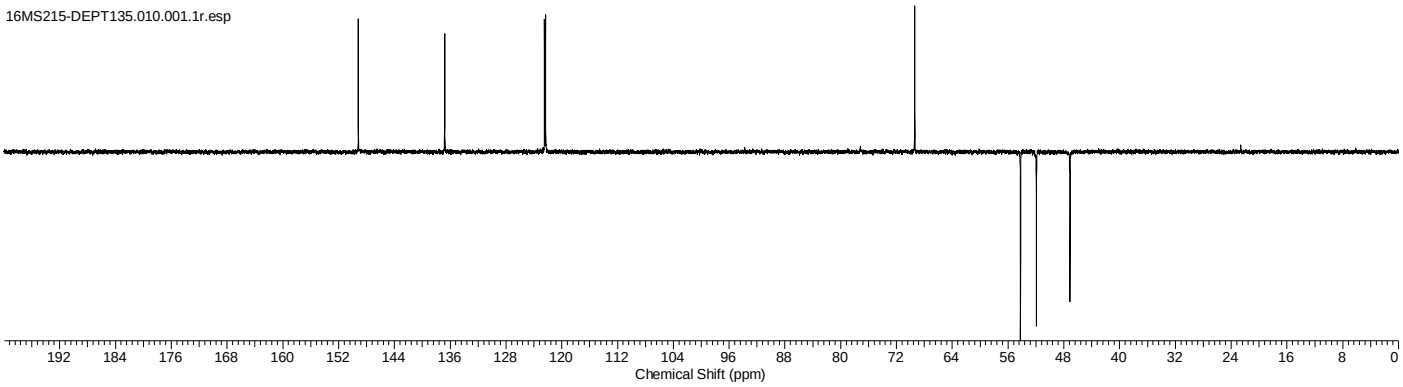
16MS215-1H.010.001.1r.esp




1q




16MS215-DEPT135.010.001.1r.esp

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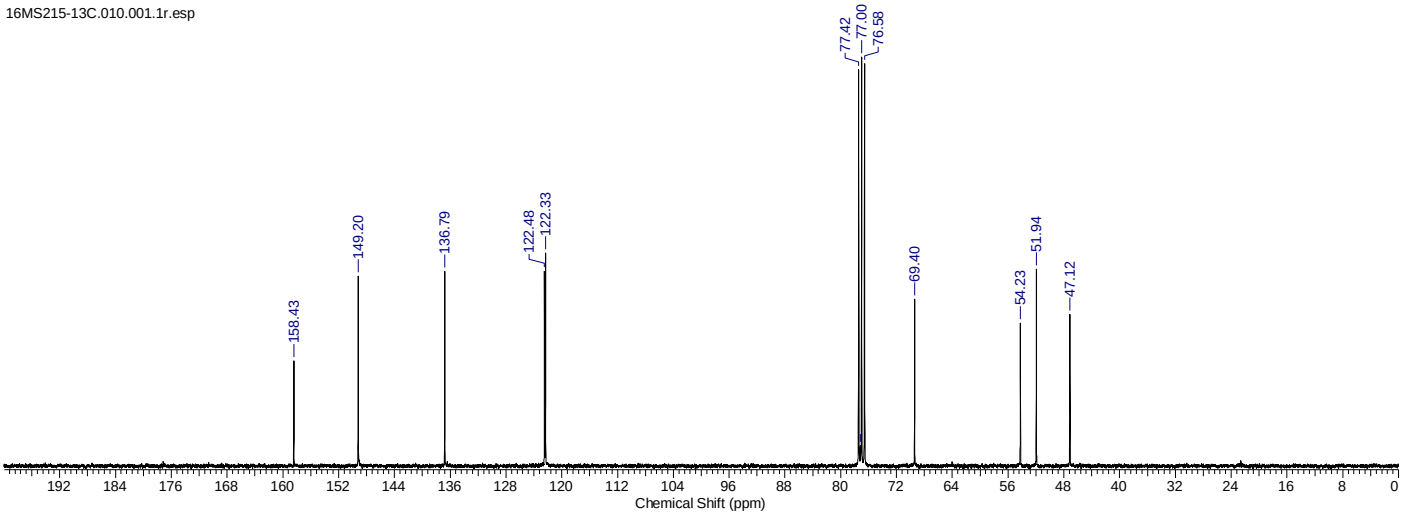
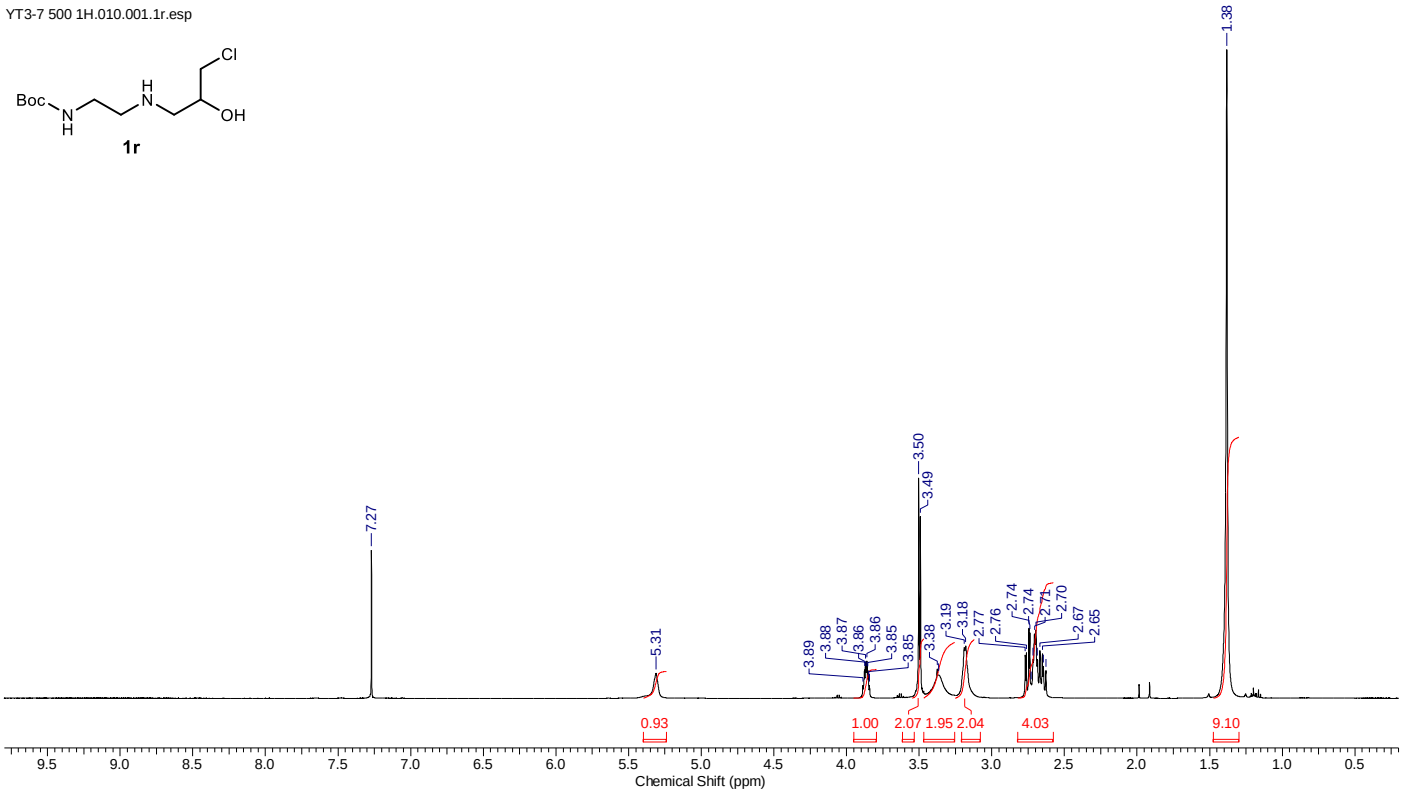
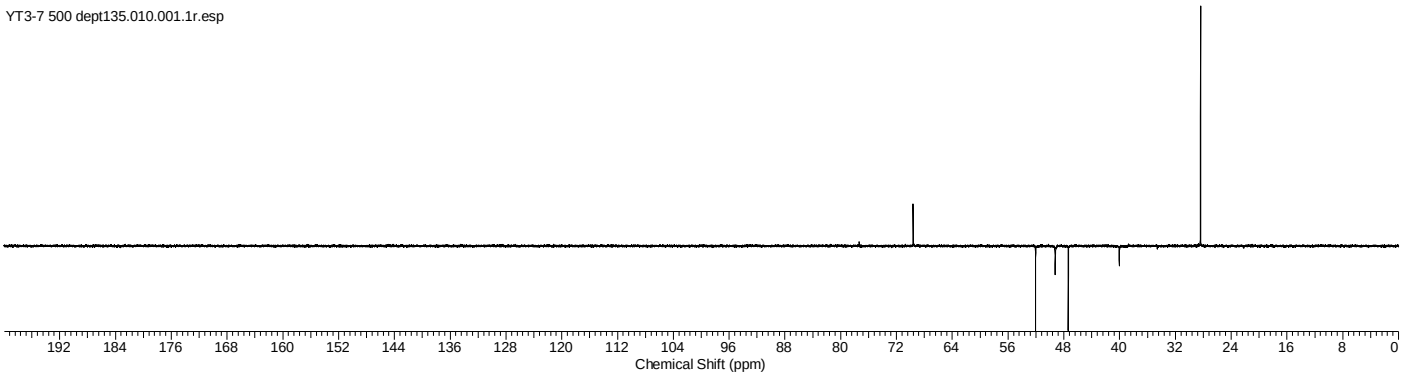
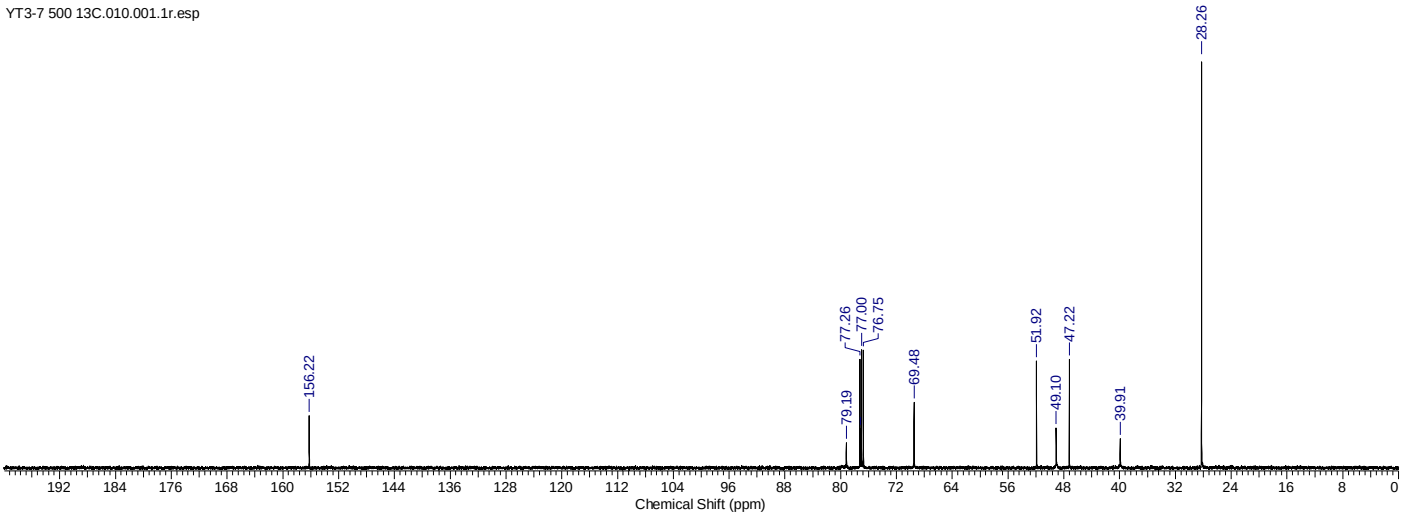


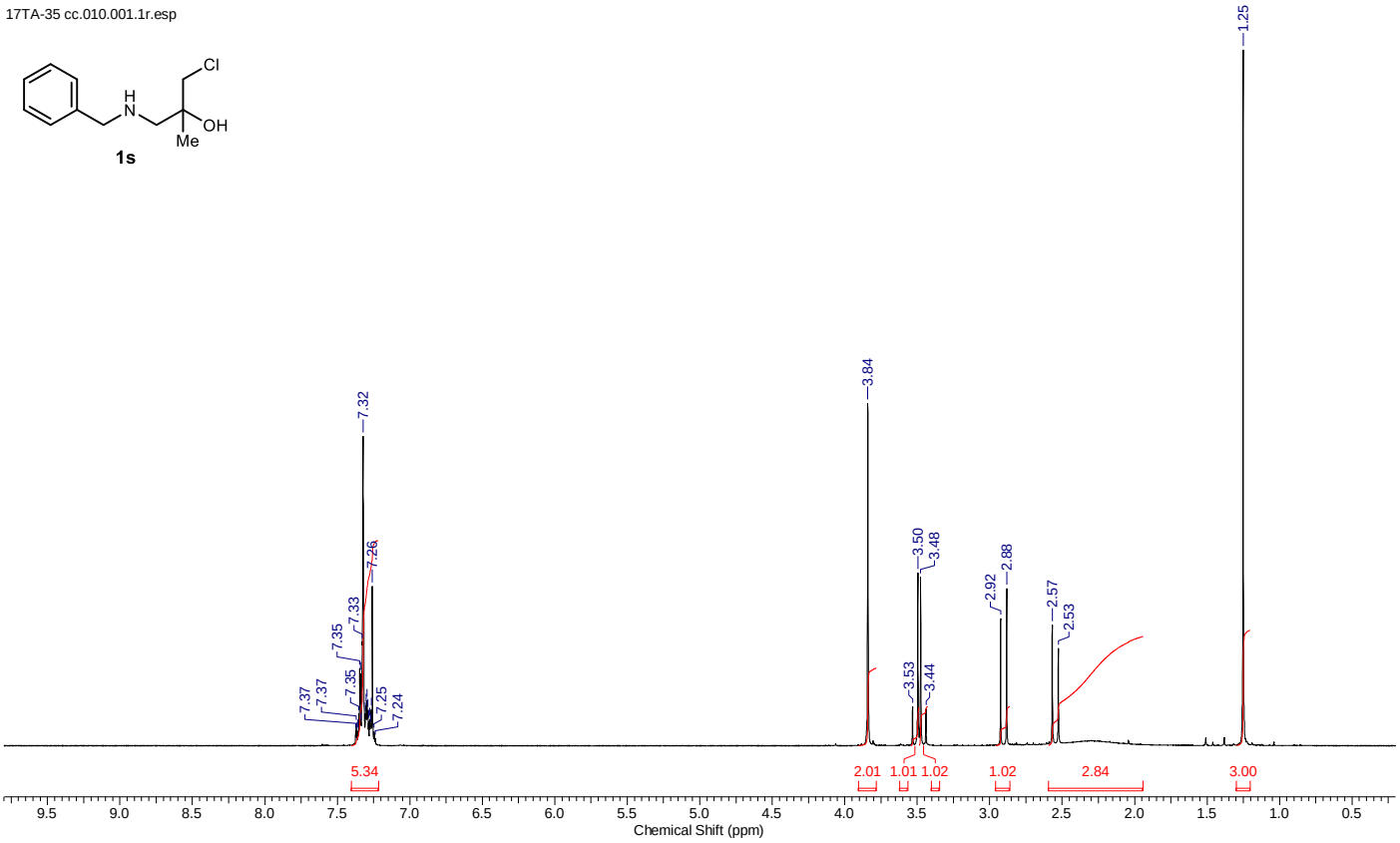
# $^{1}H$ (500 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) Spectra of 1r

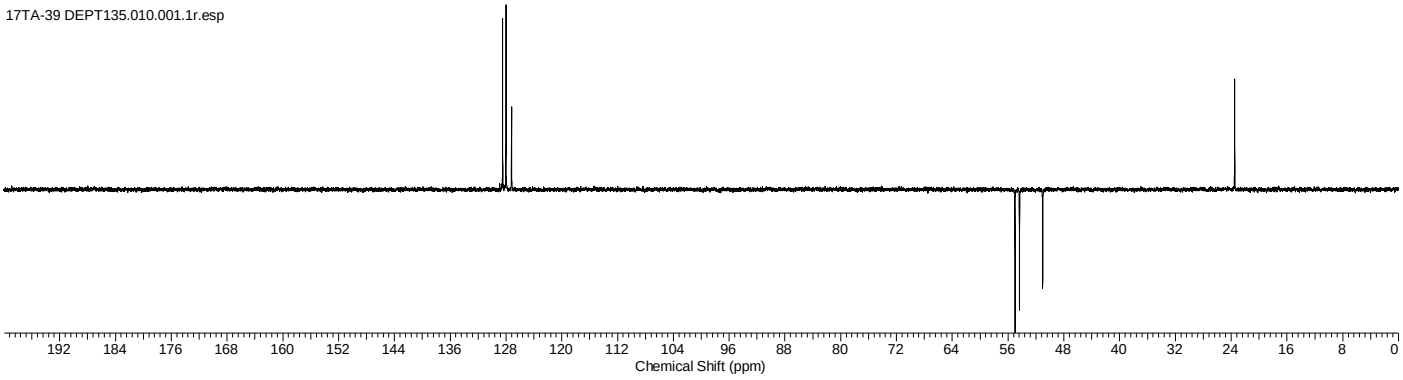


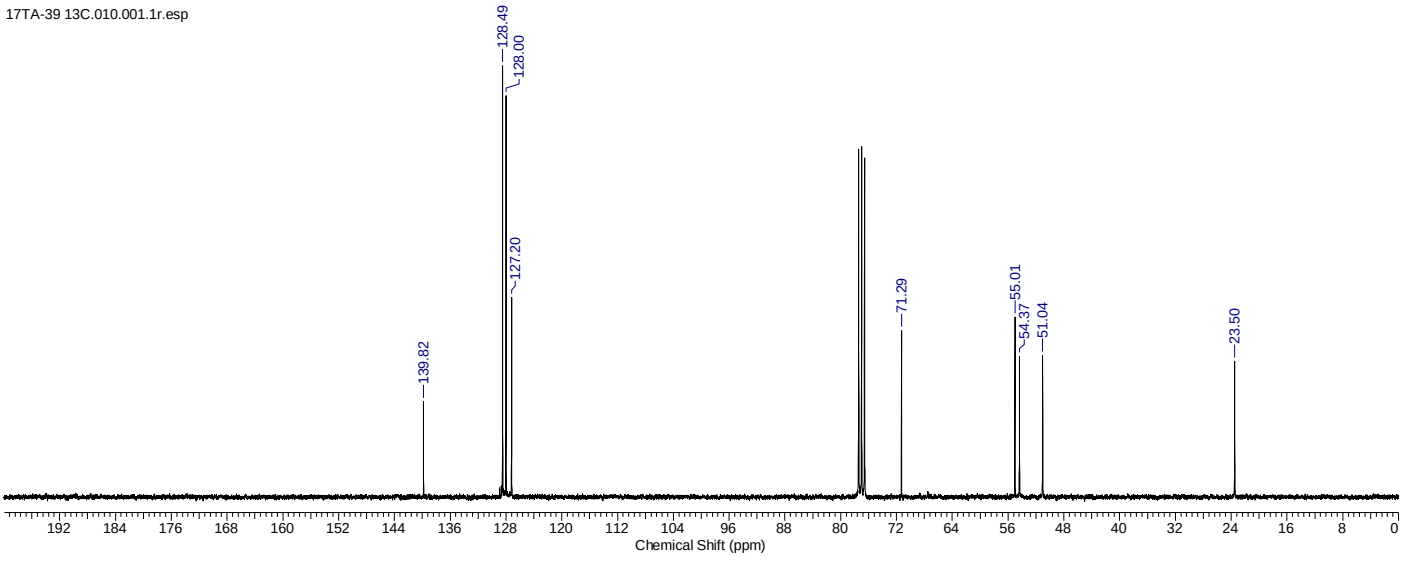



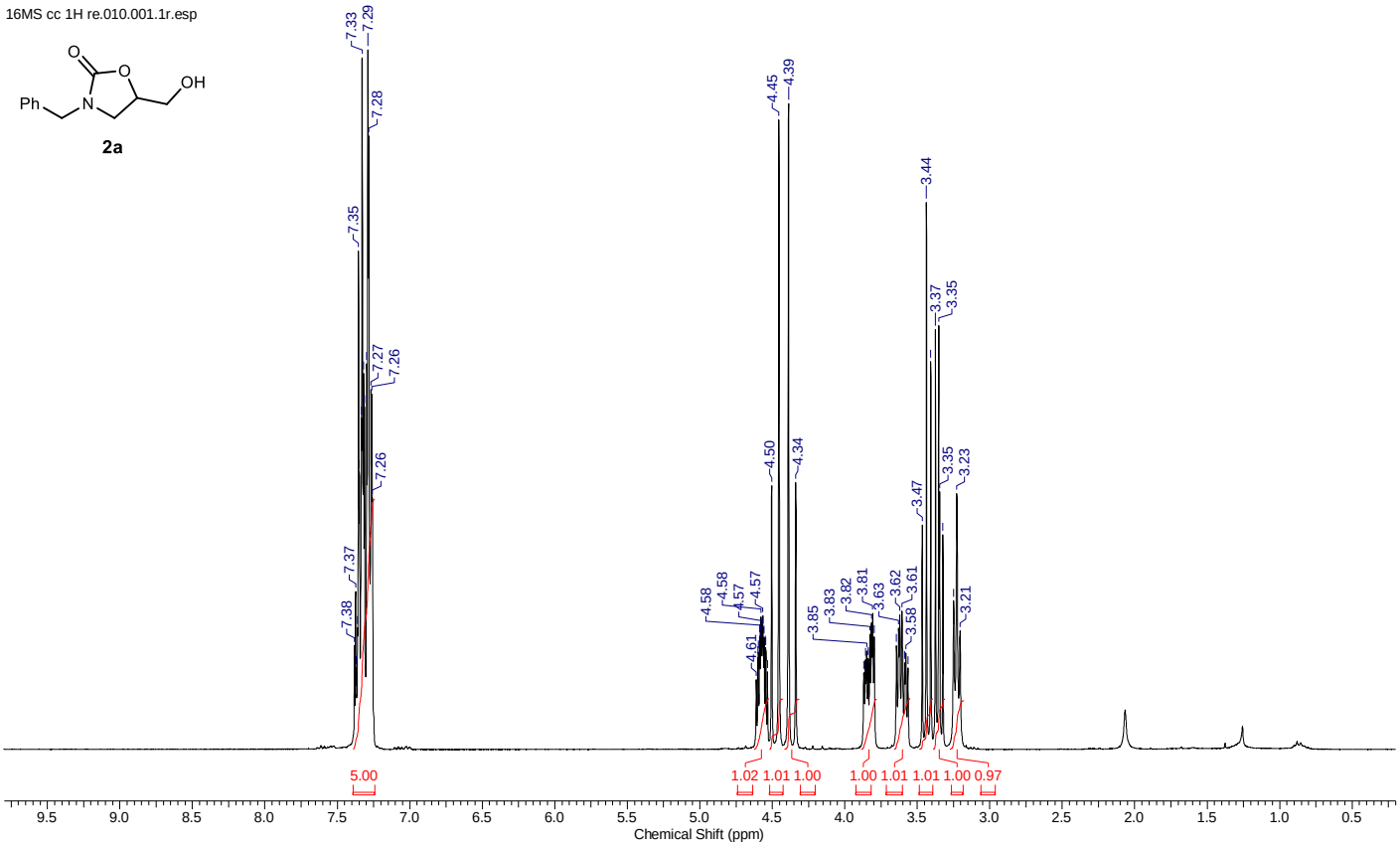
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 1s

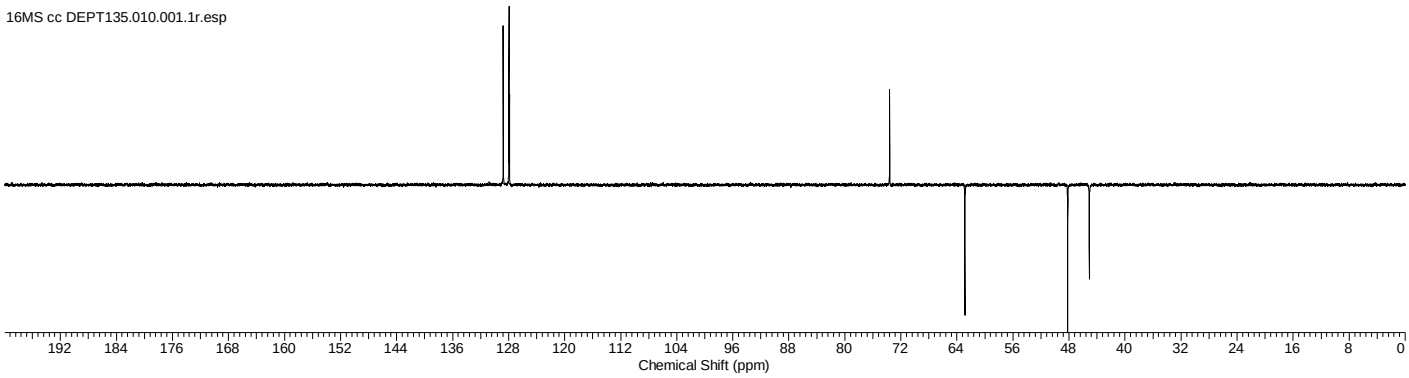


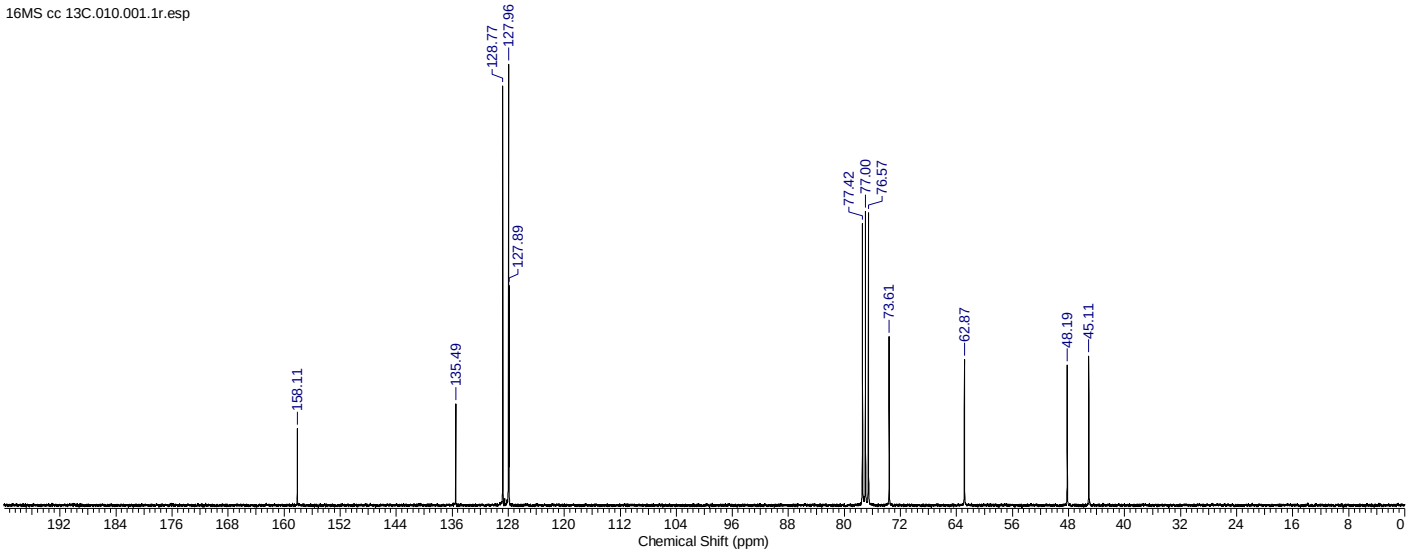



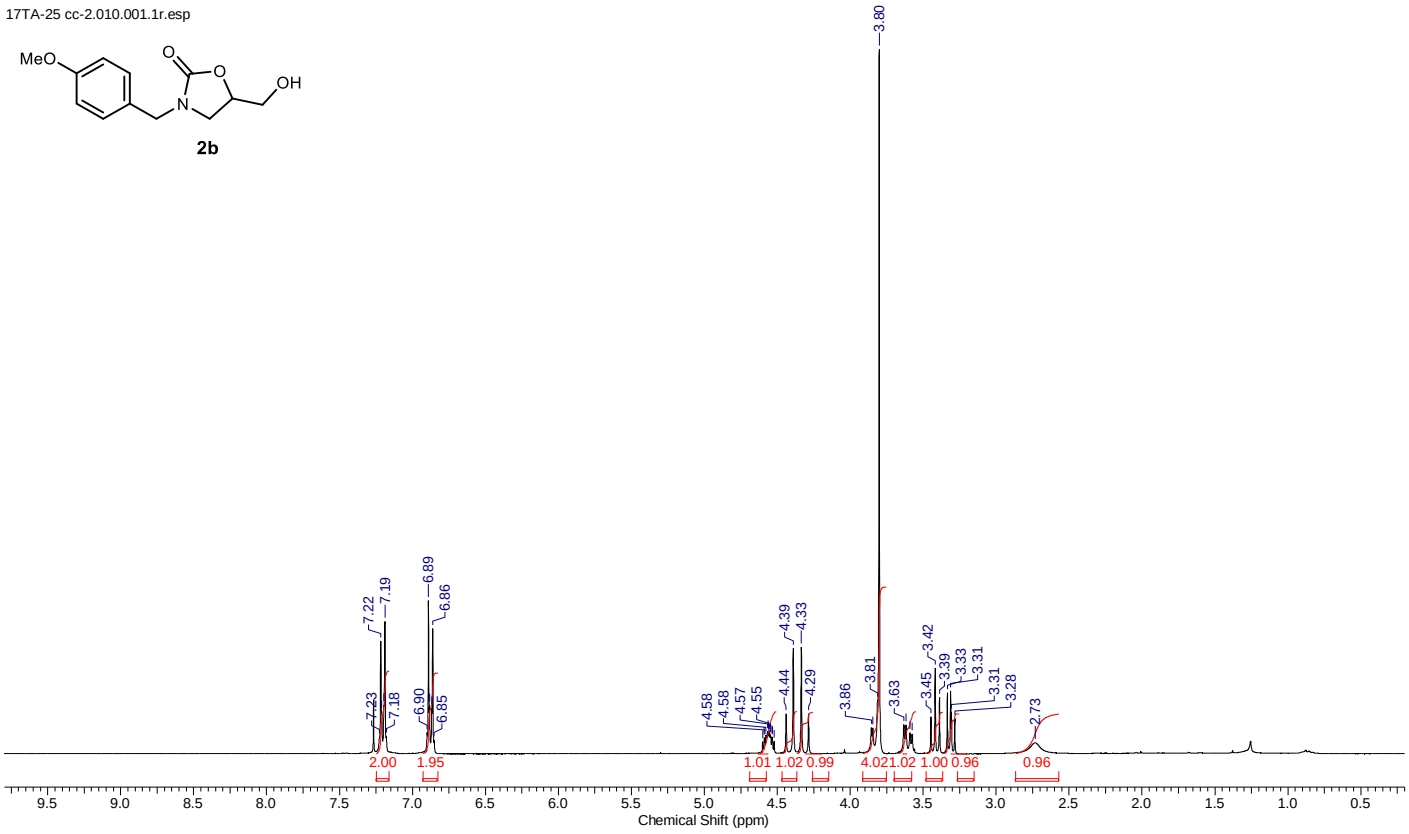
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2a

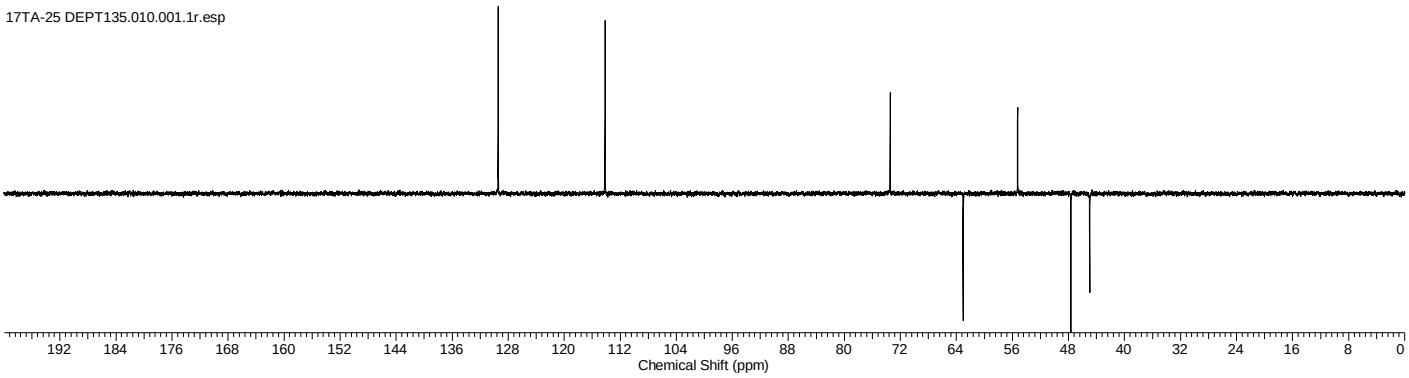


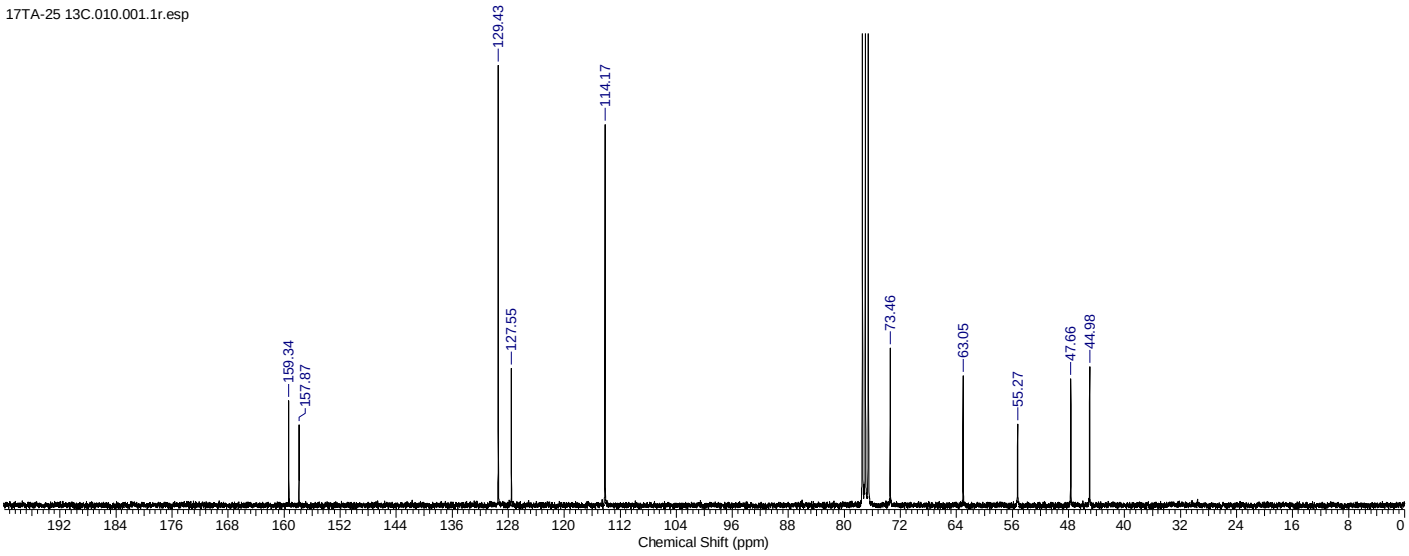



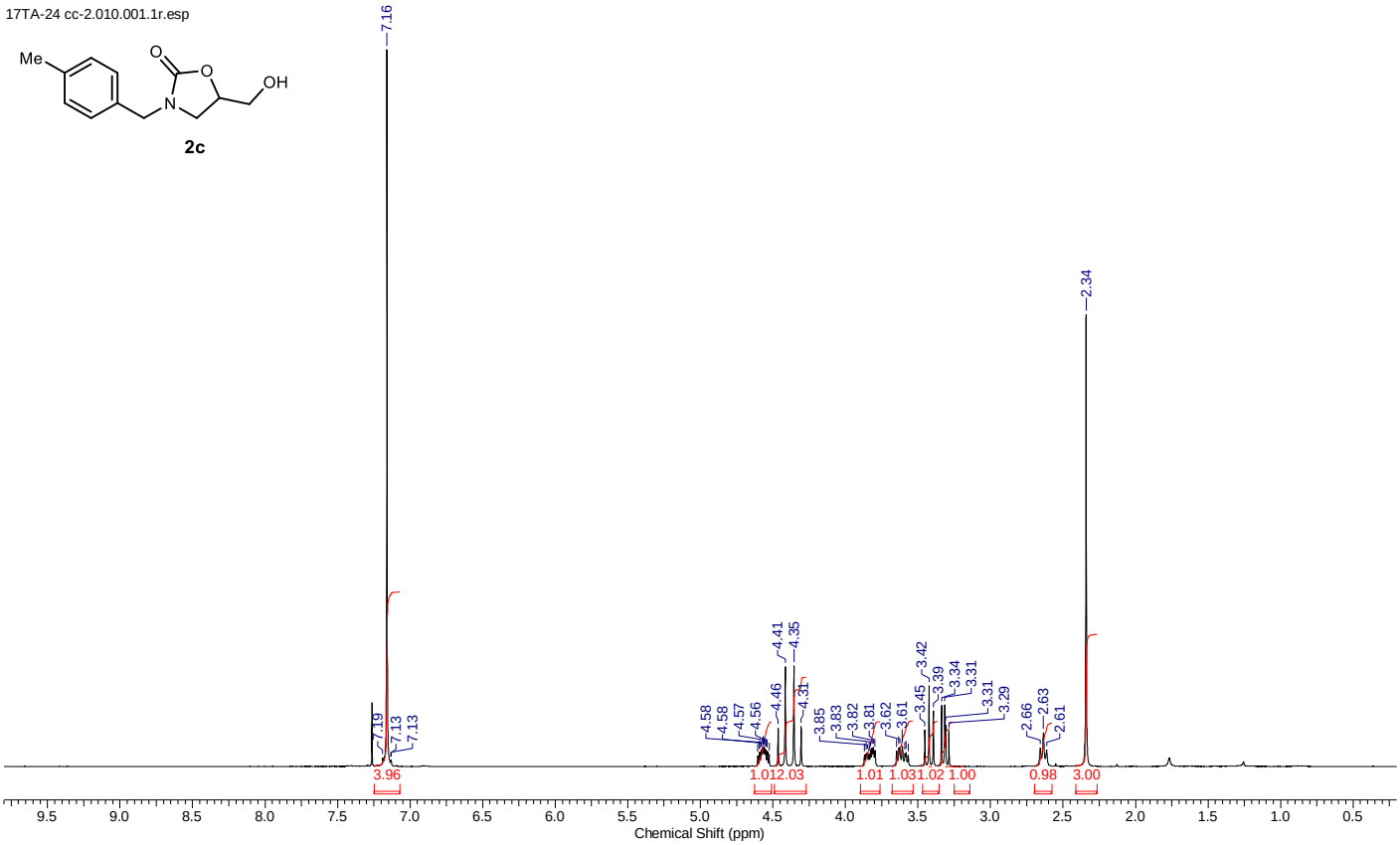
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2b

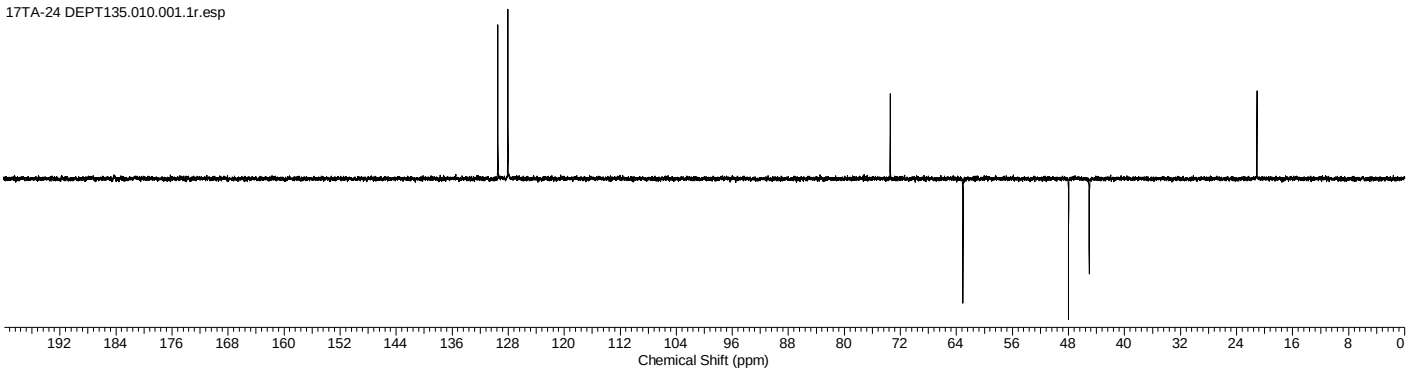


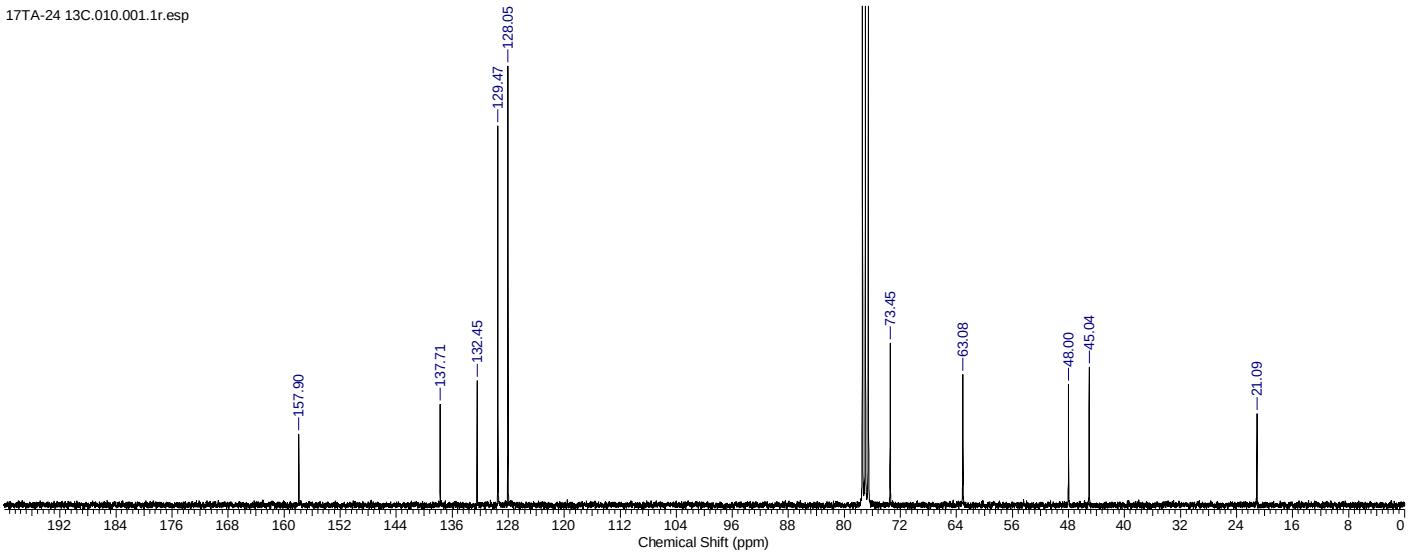



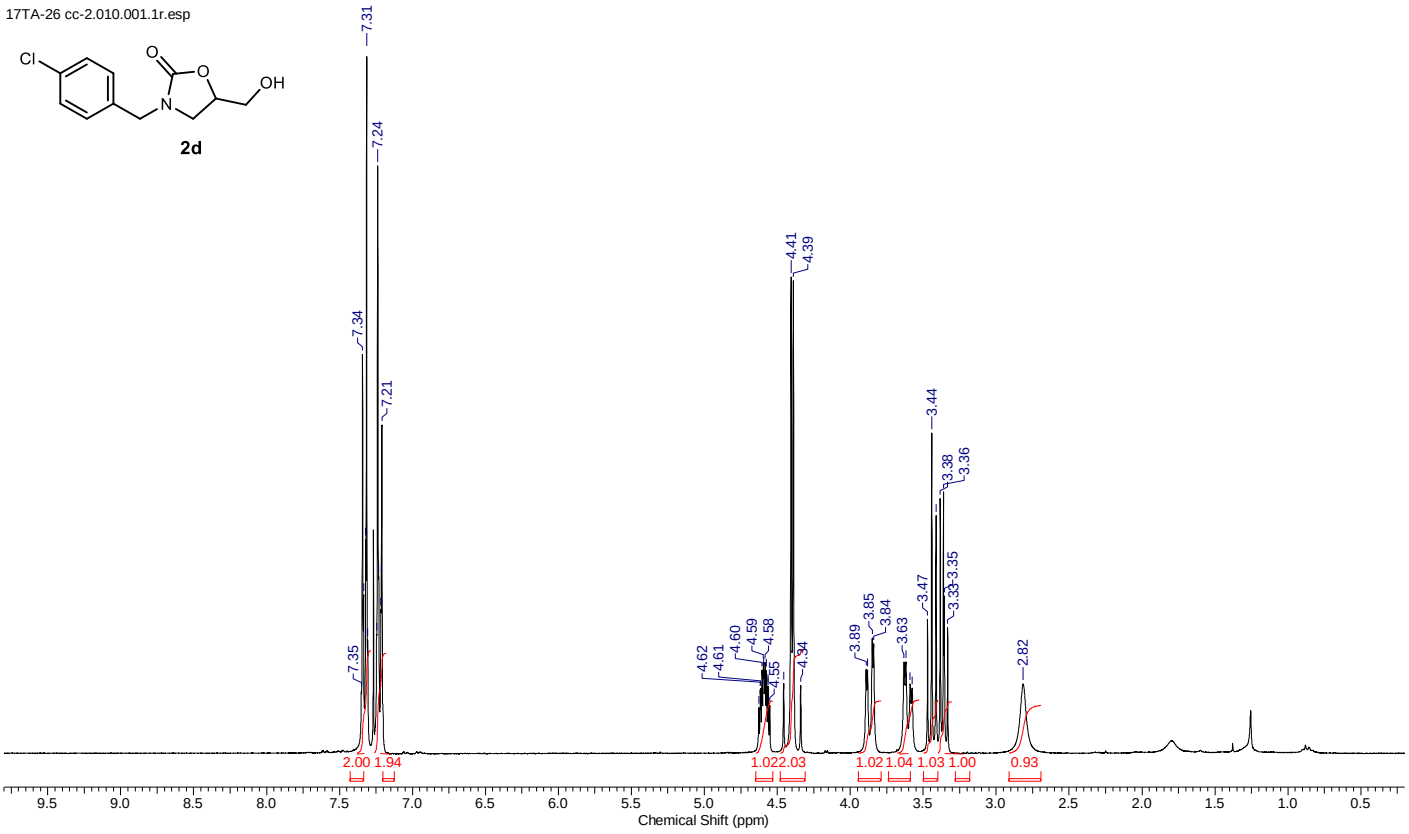
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2c

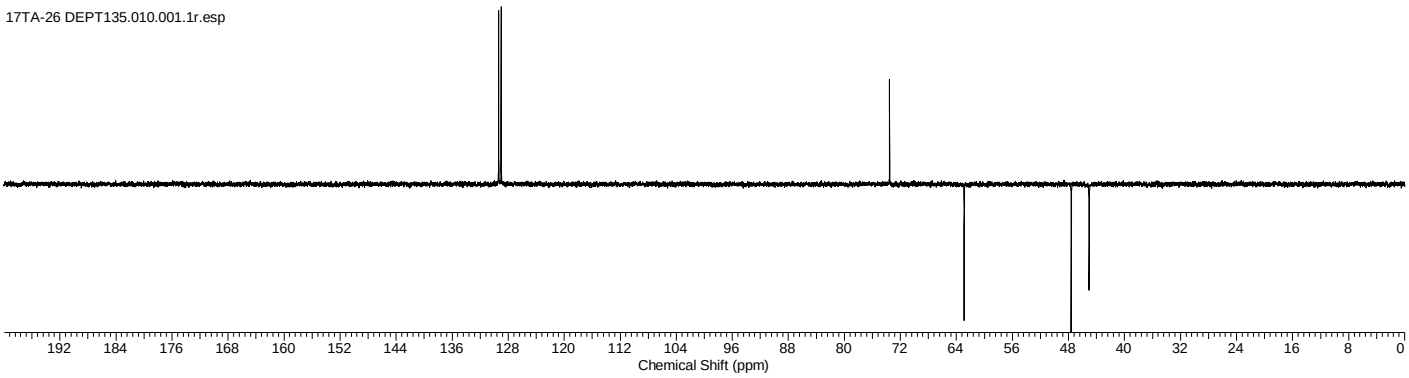


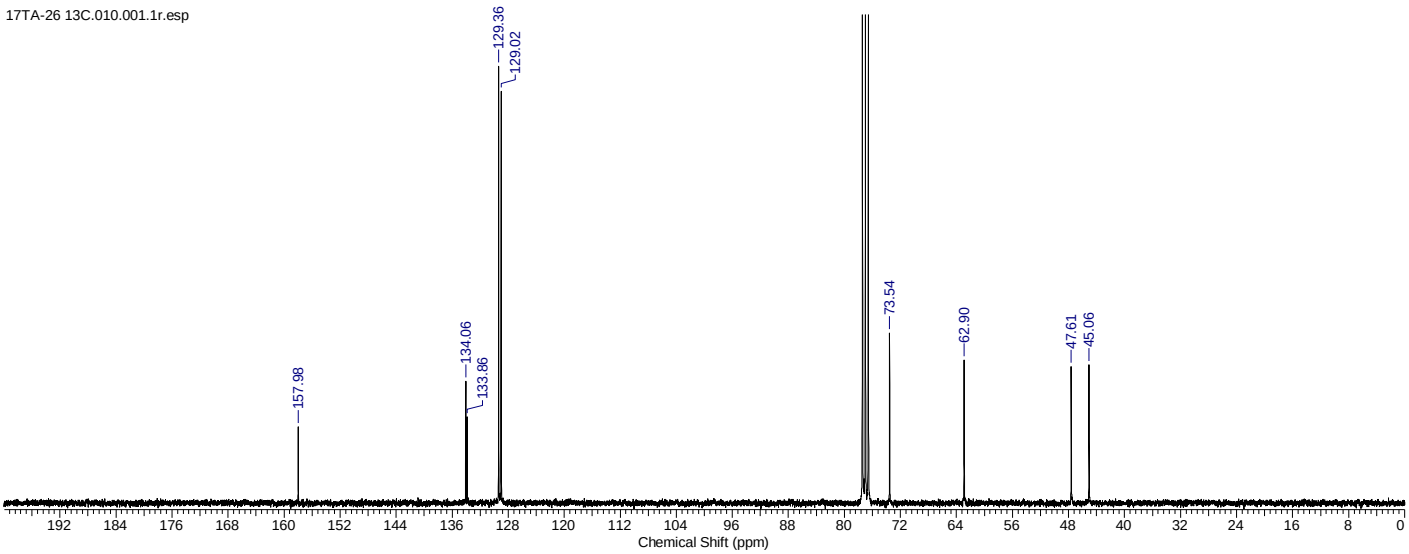



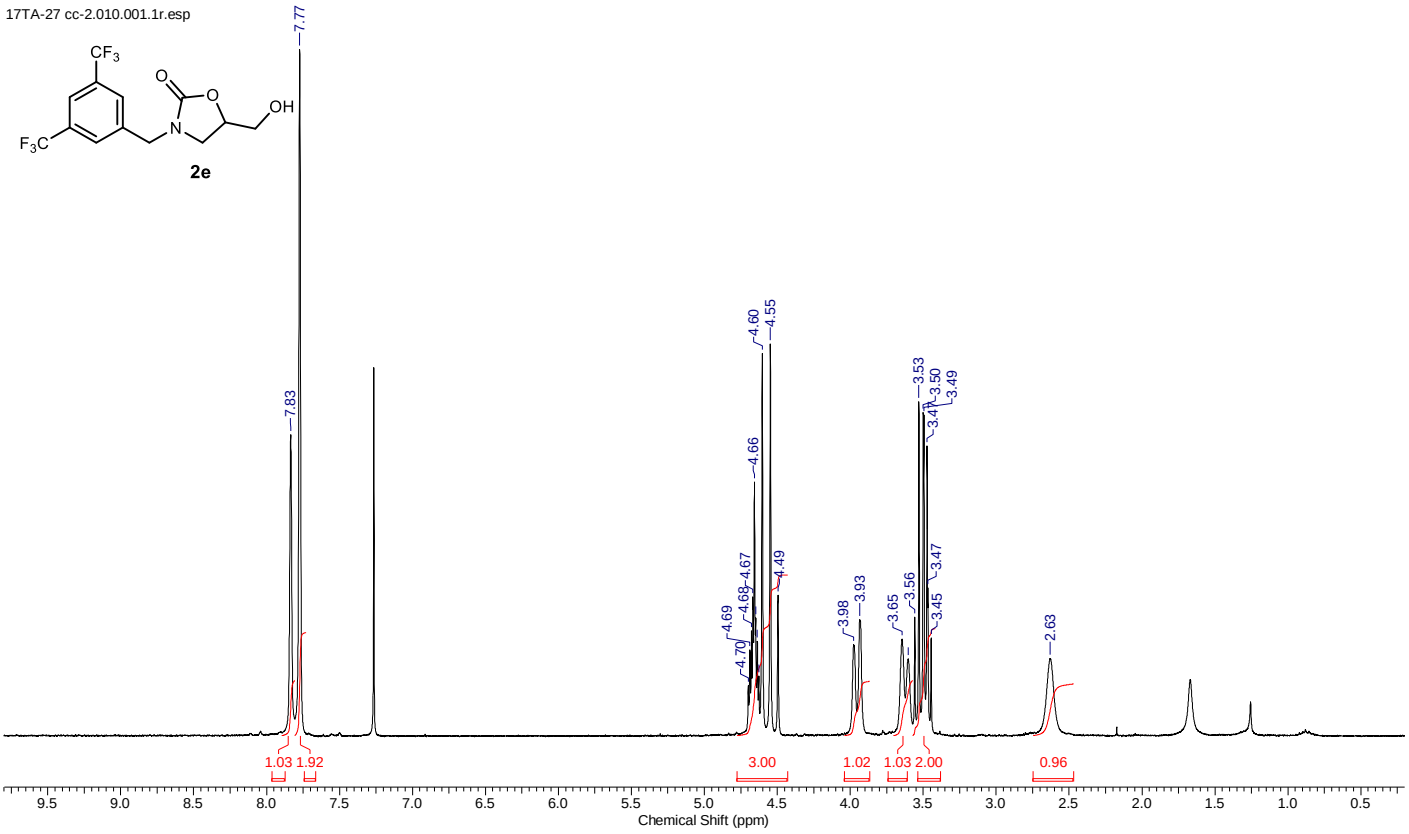
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2d

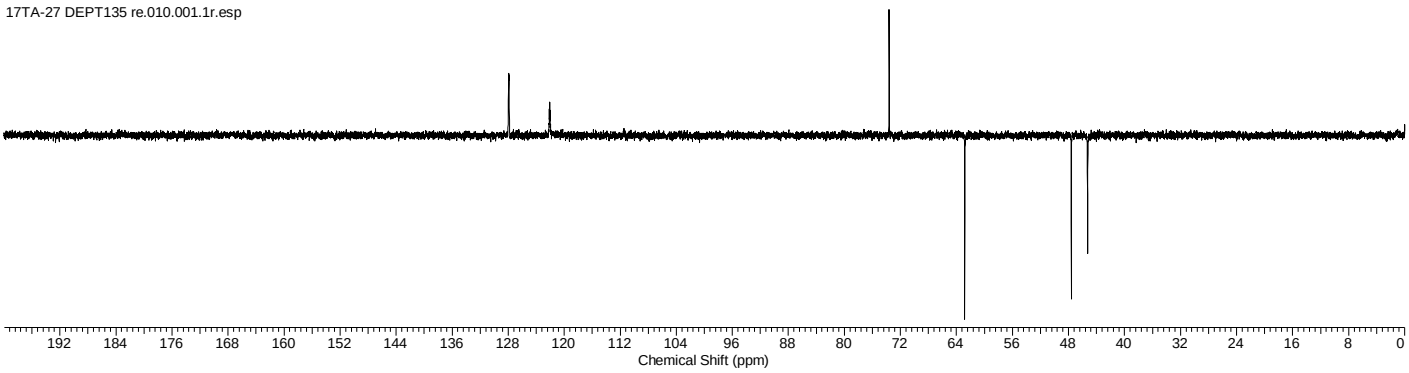


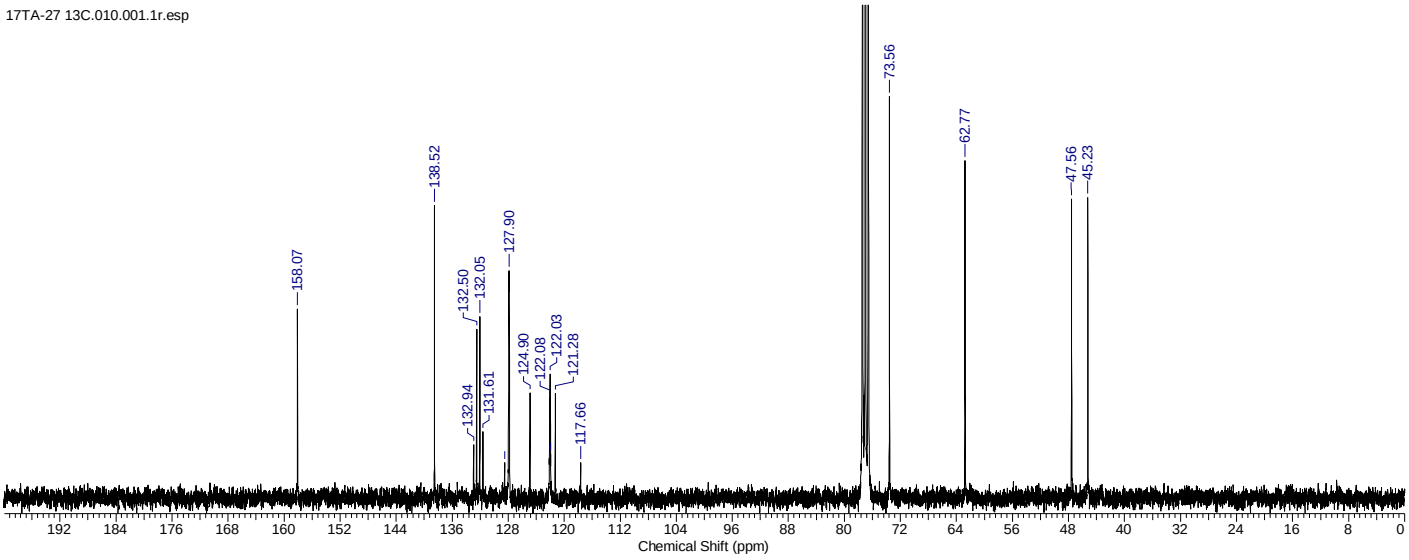



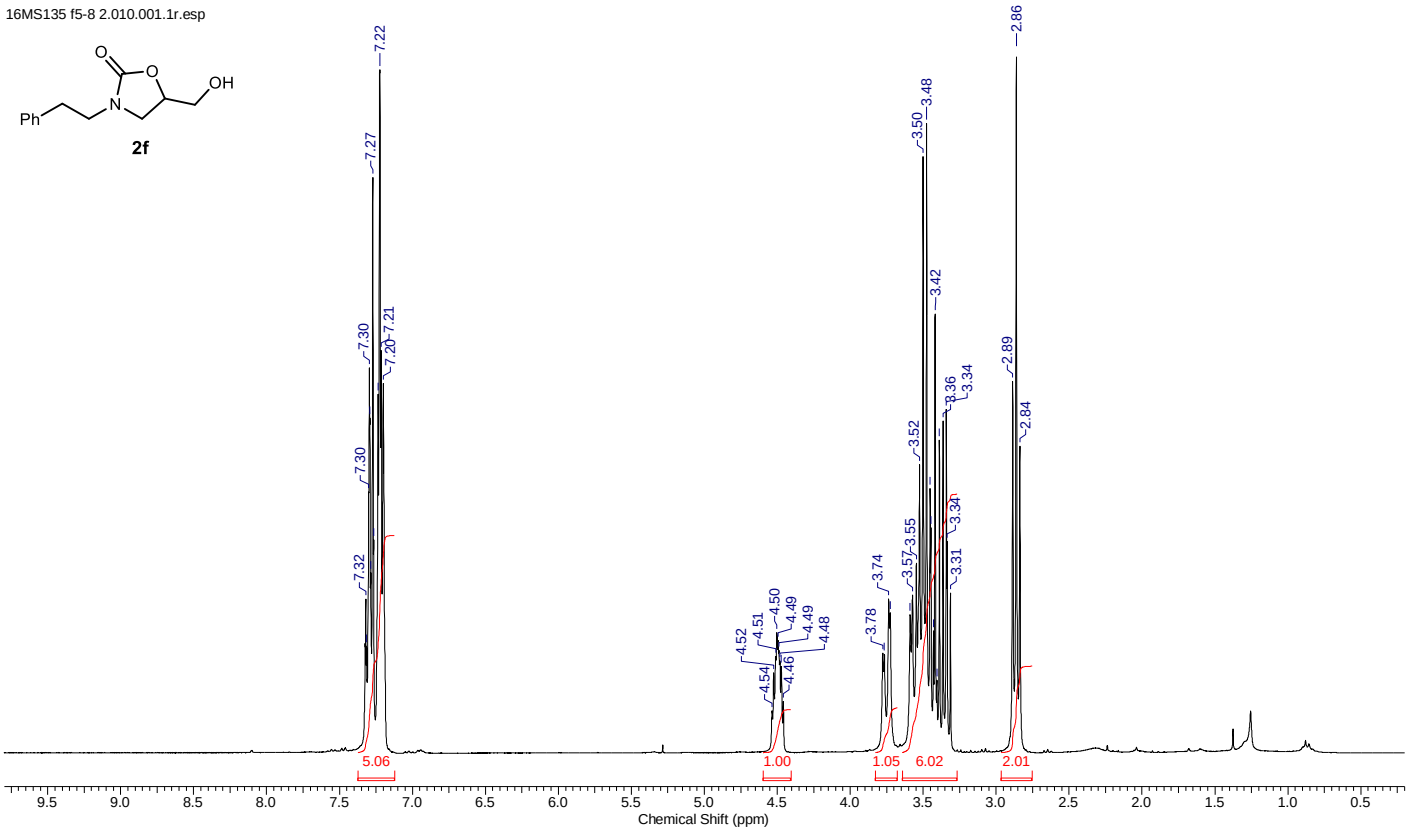
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2e

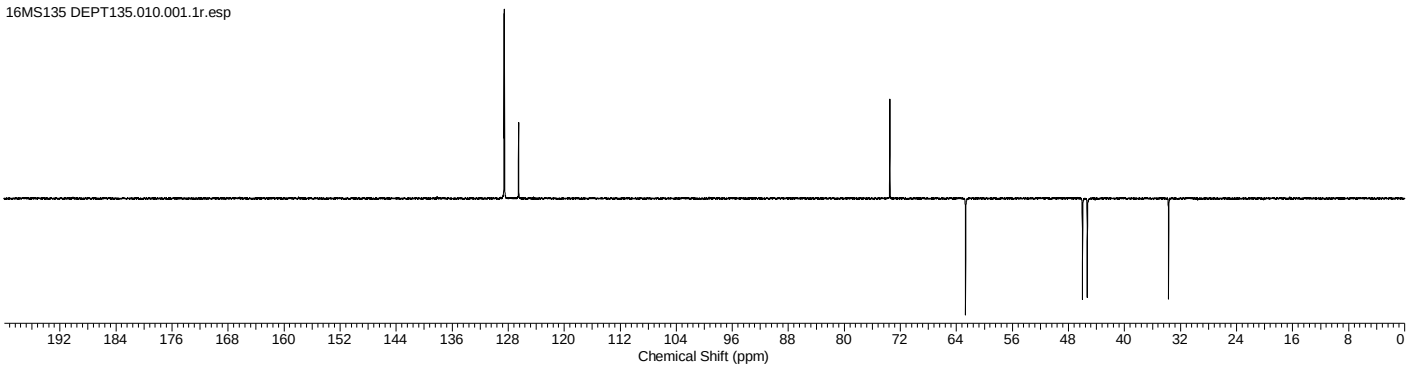


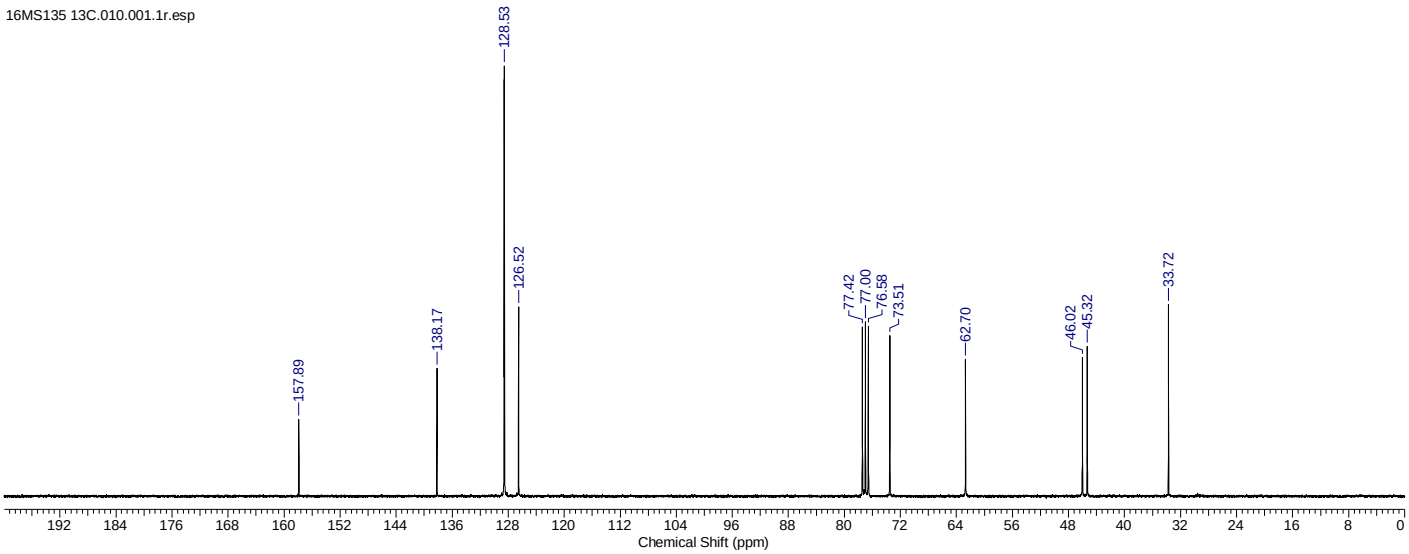



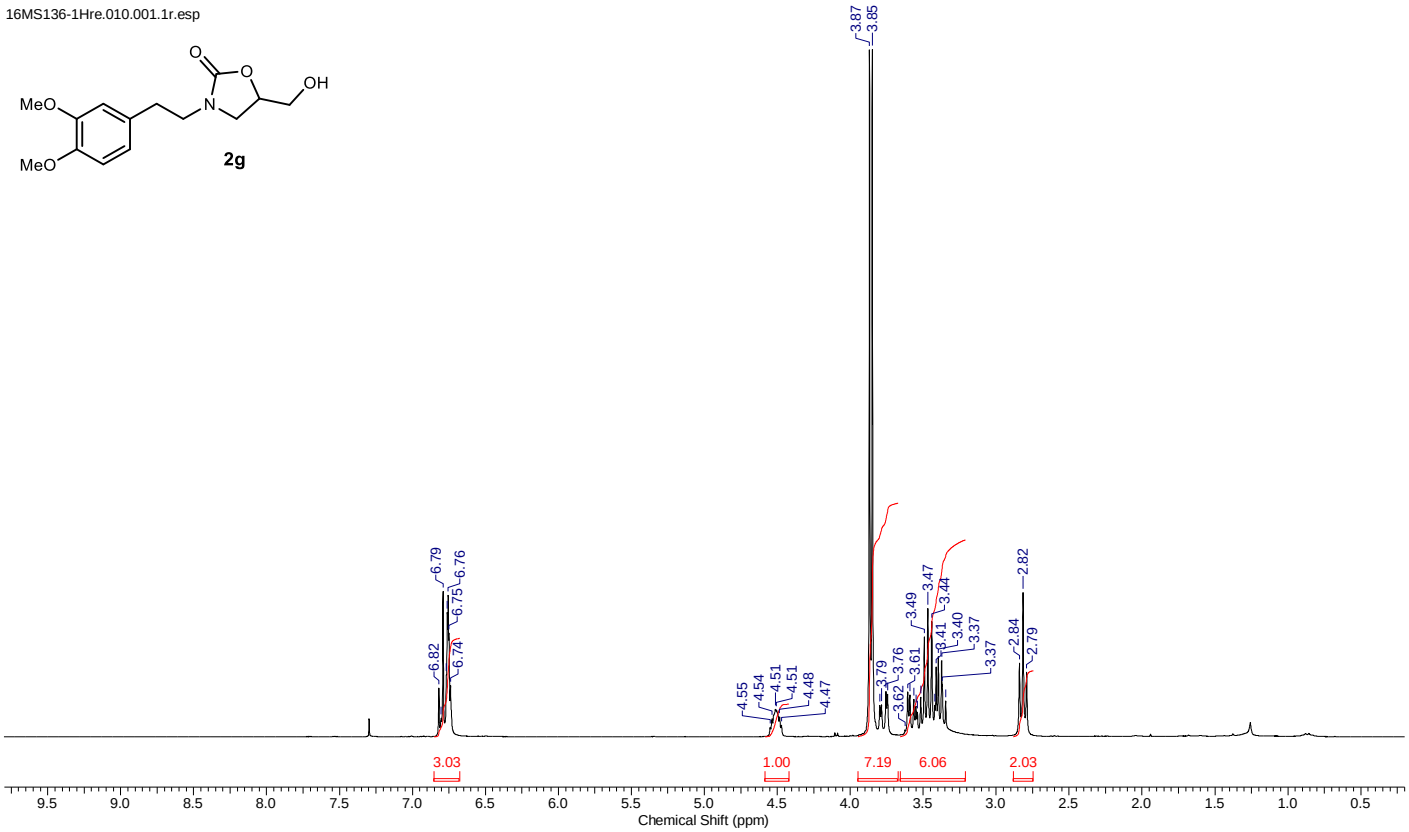
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2f

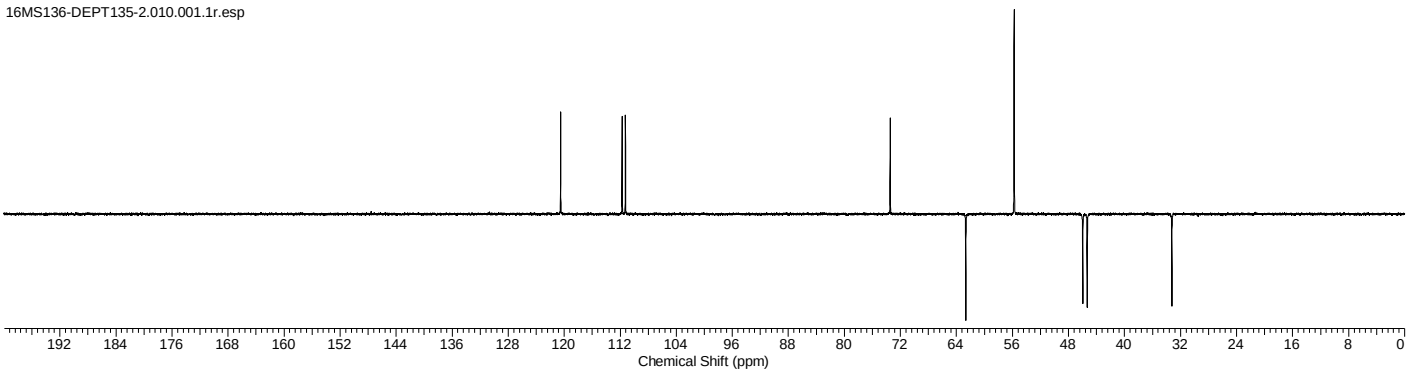


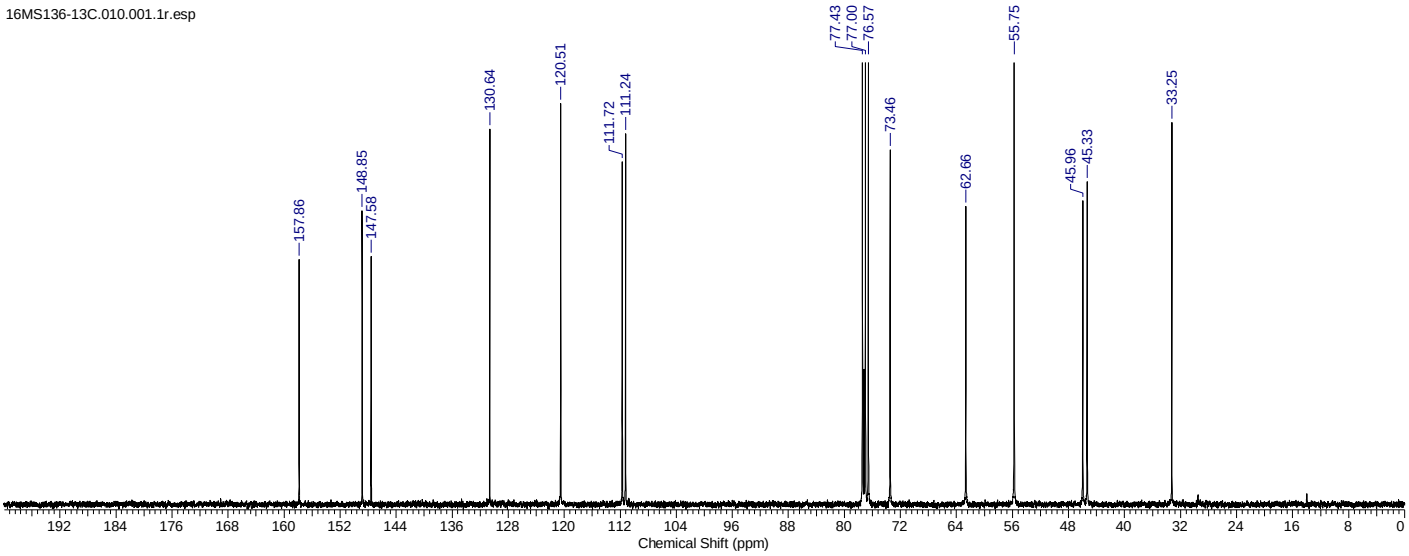



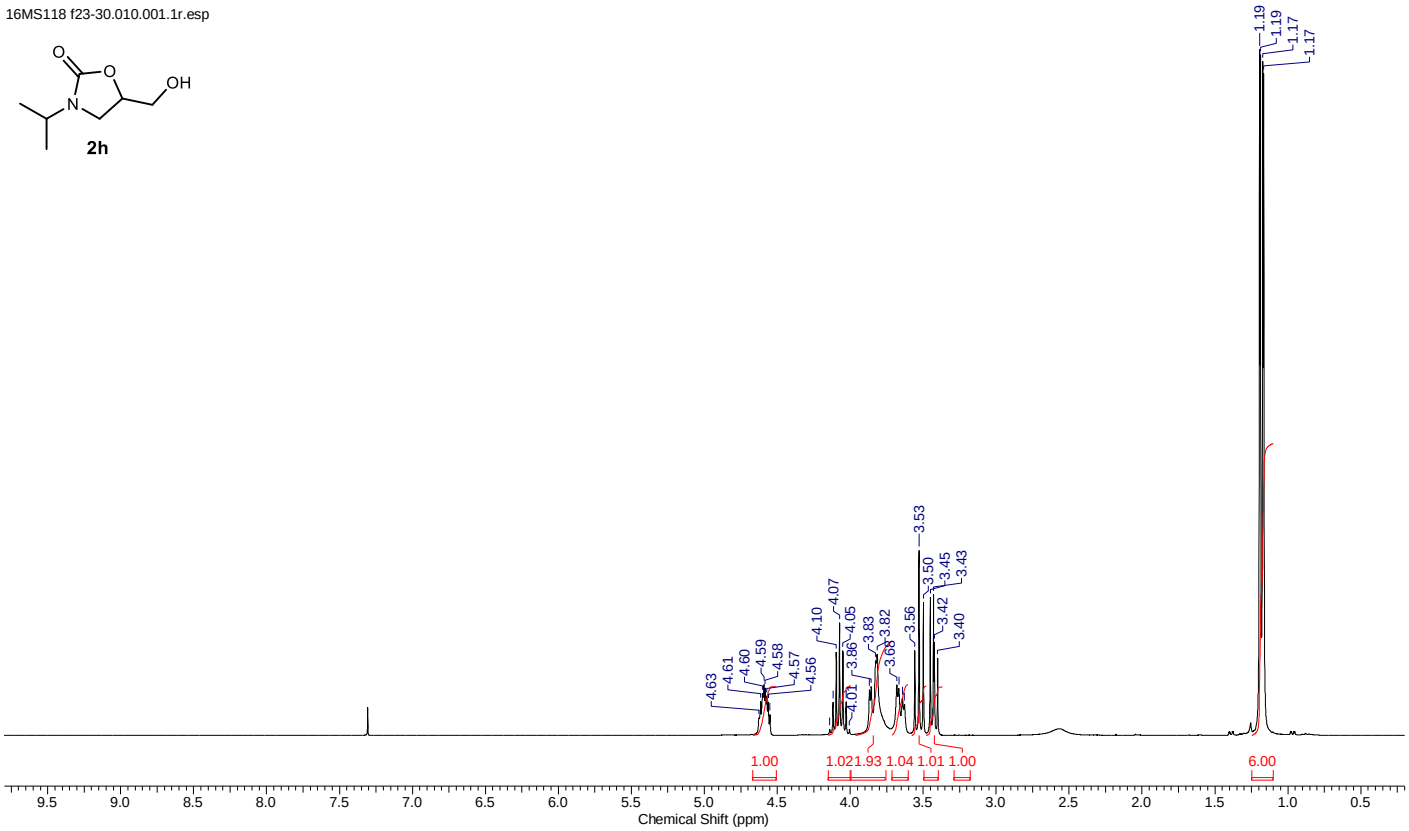
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2g

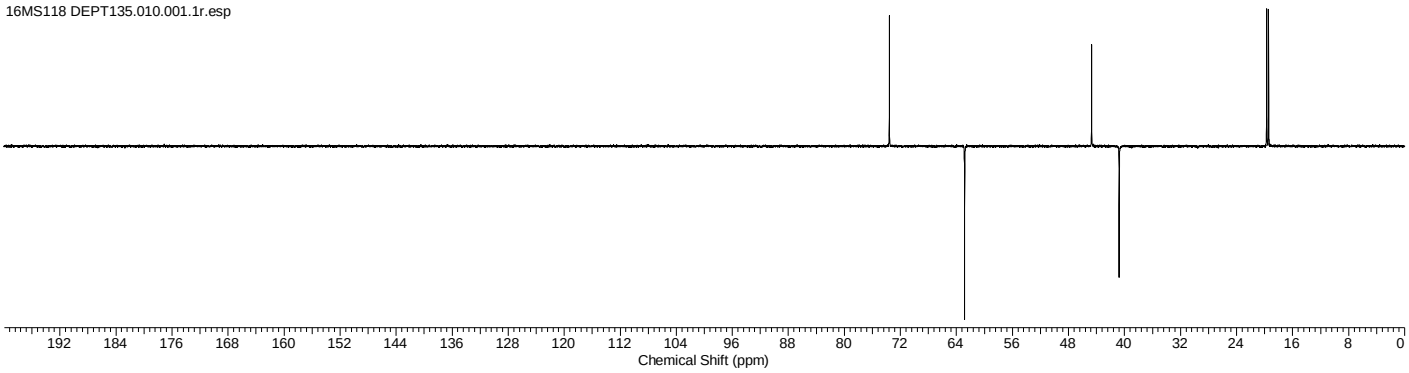


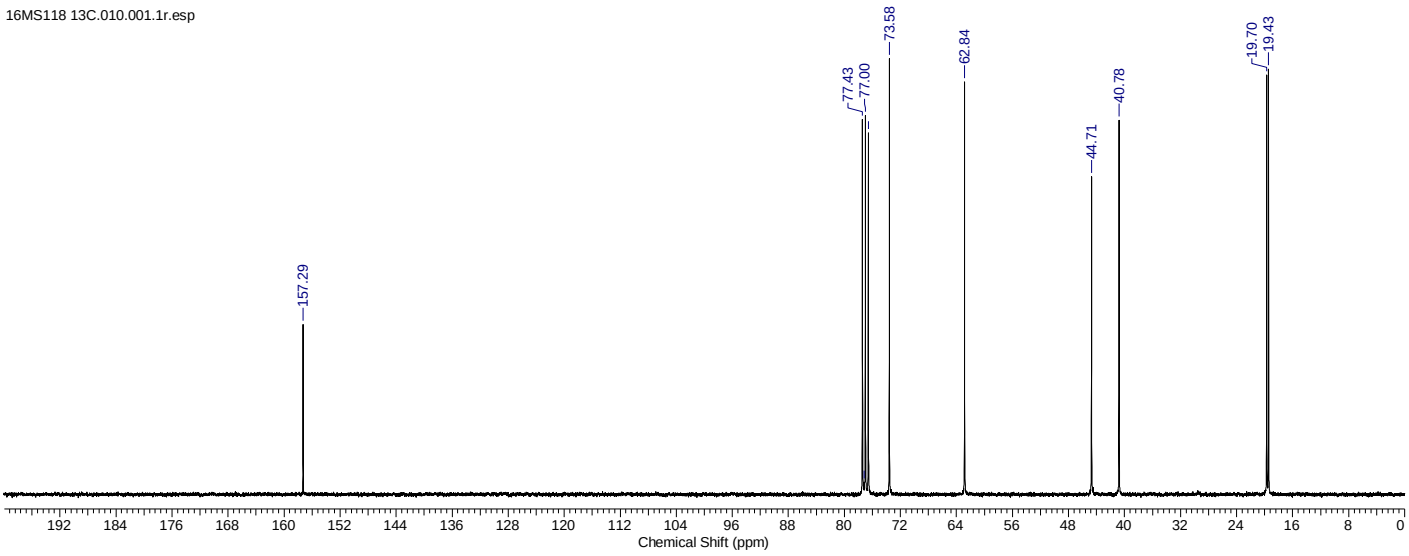



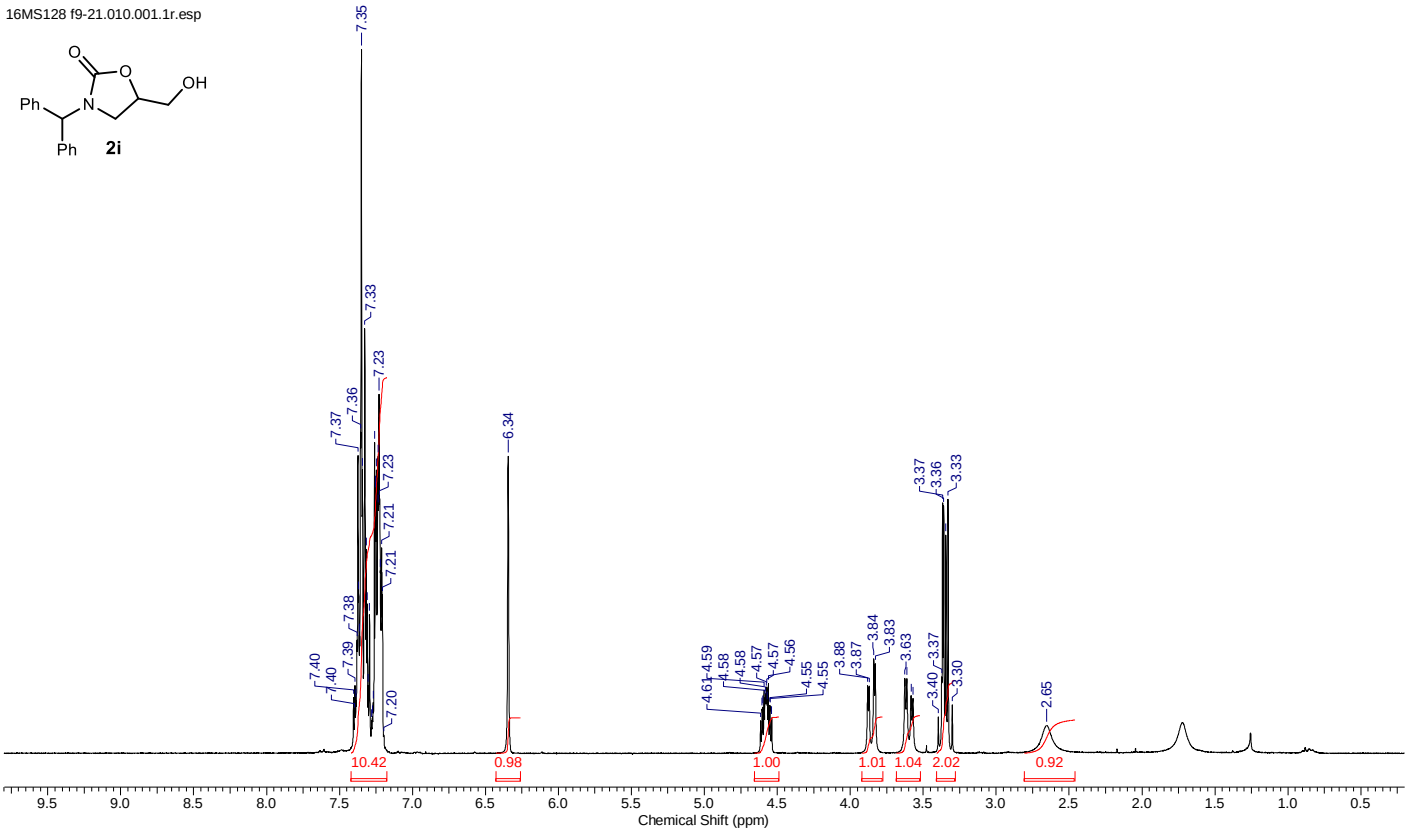
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2h

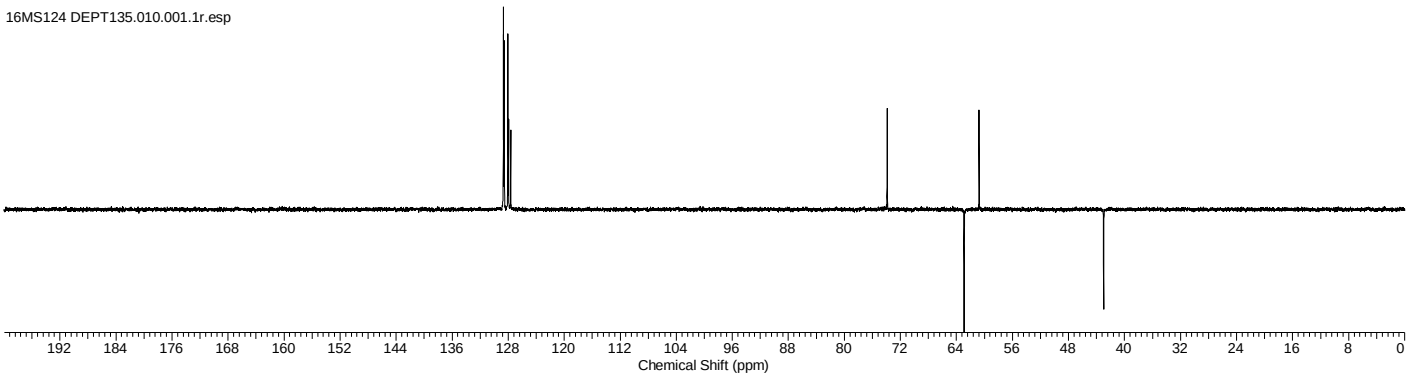


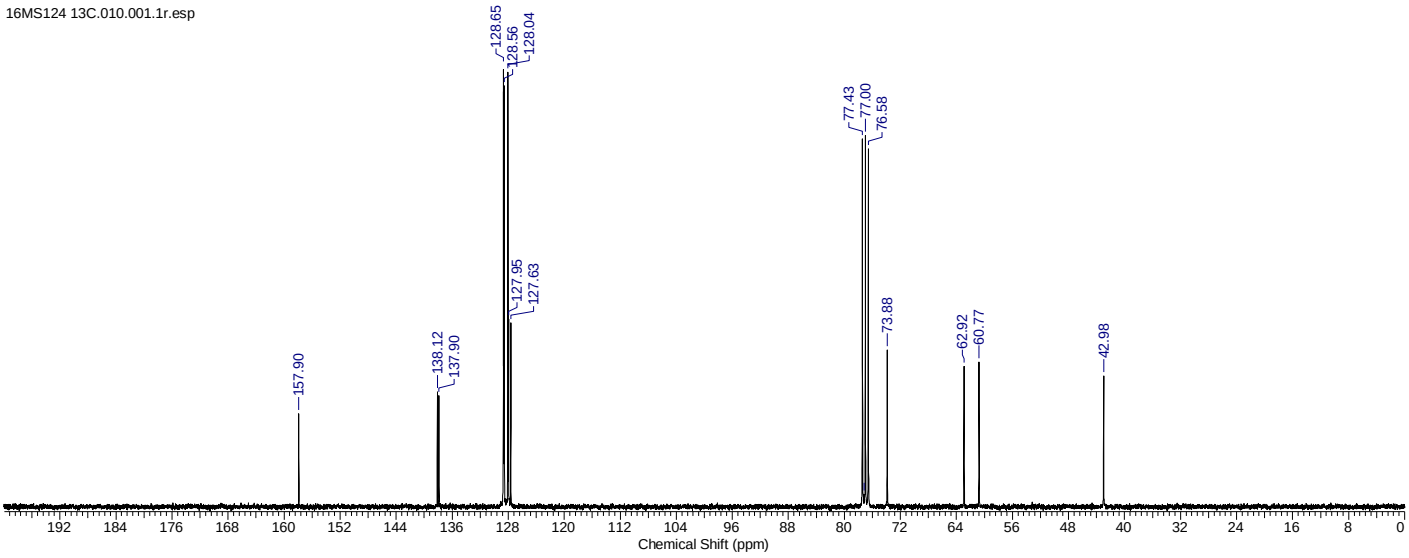



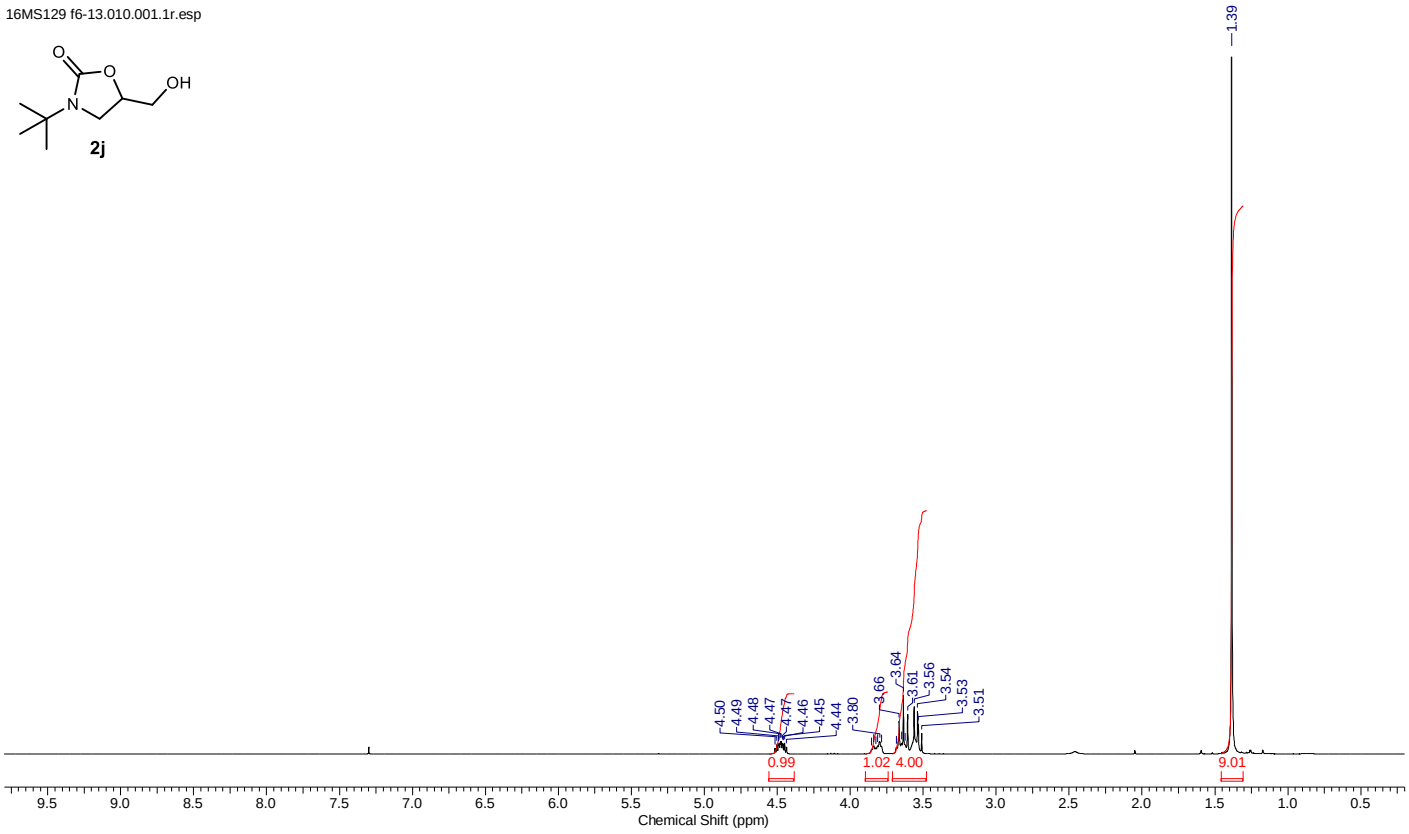
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2i

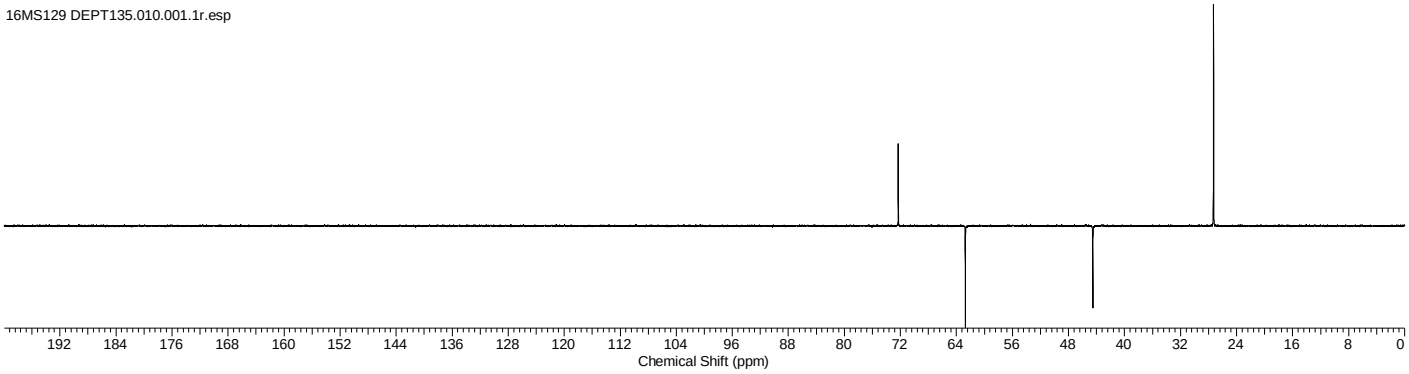


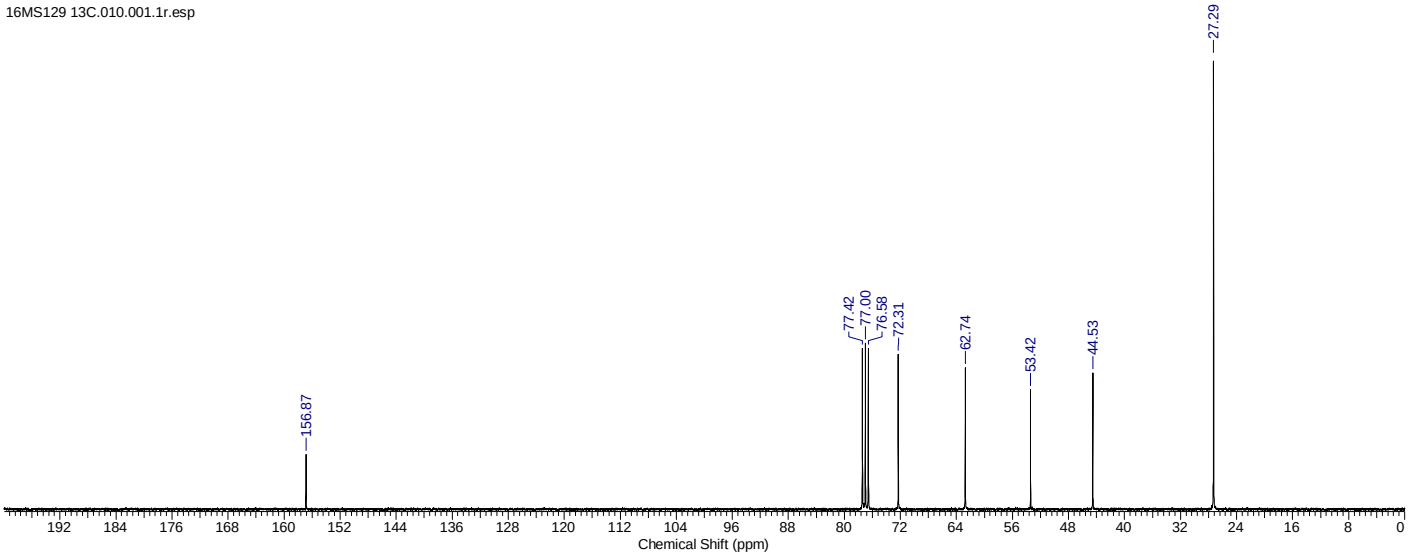



# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2j

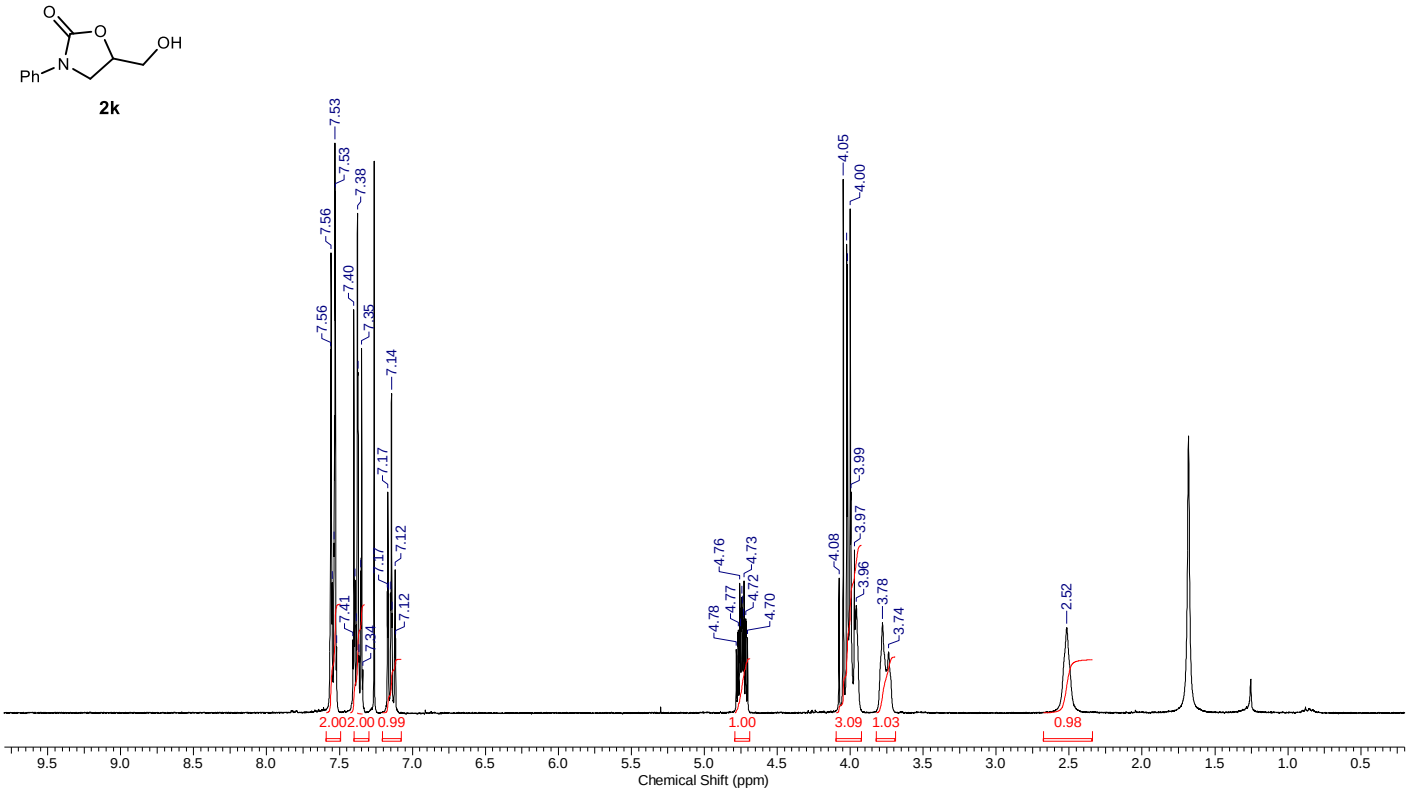


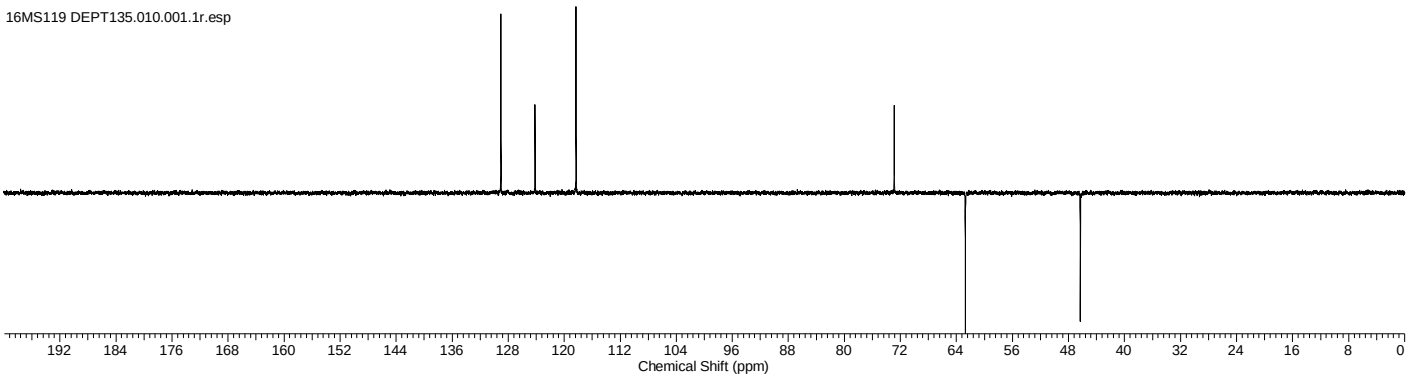



# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2k

16MS119 cc2 f20-28.010.001.1r.esp




16MS119 DEPT135.010.001.1r.esp

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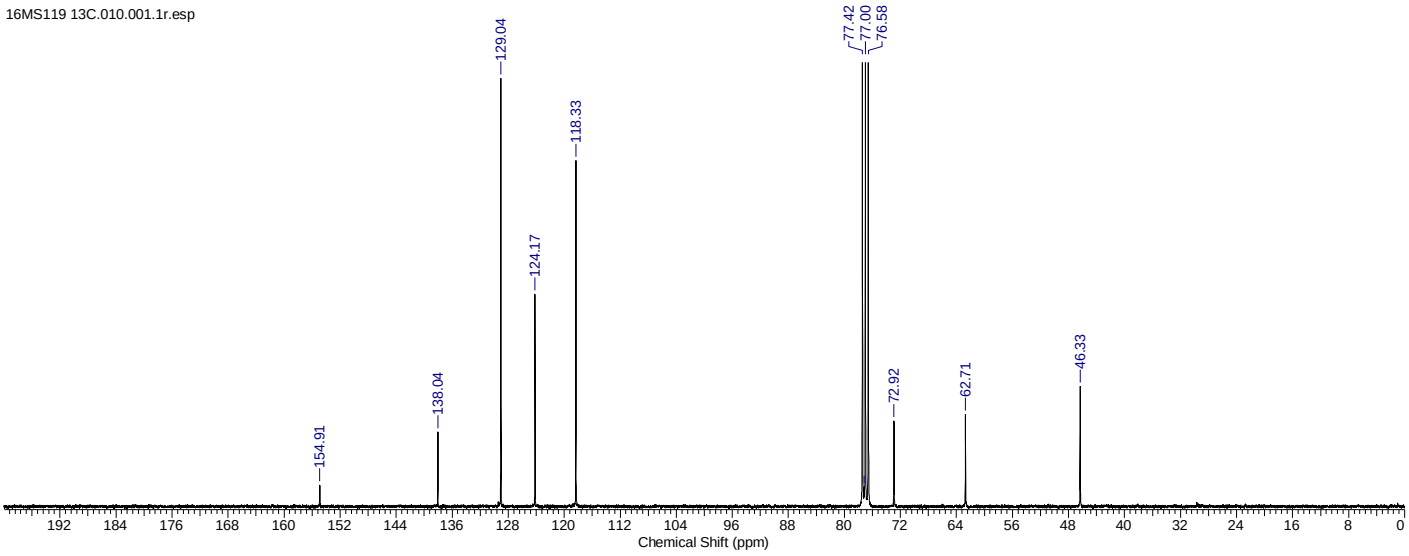
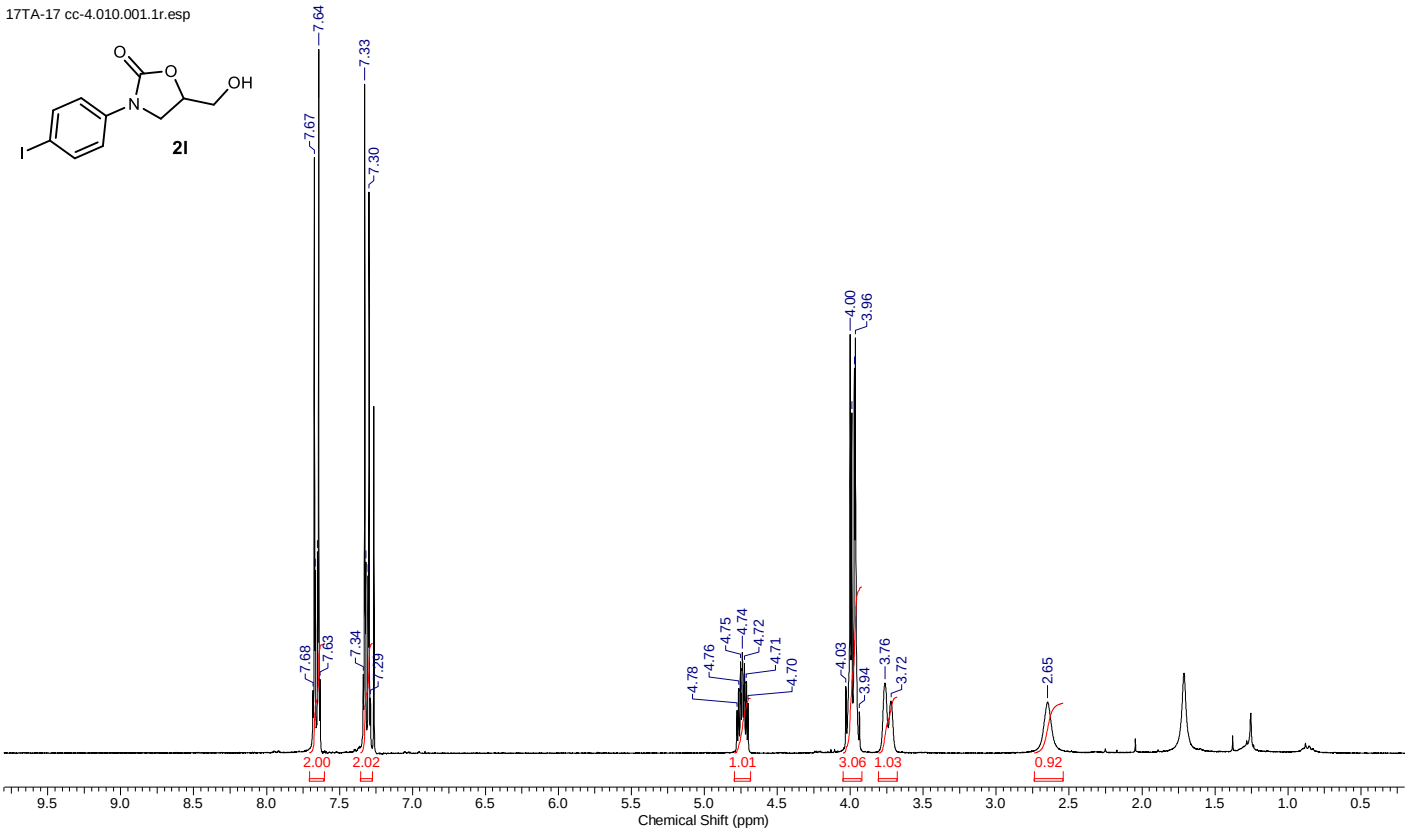
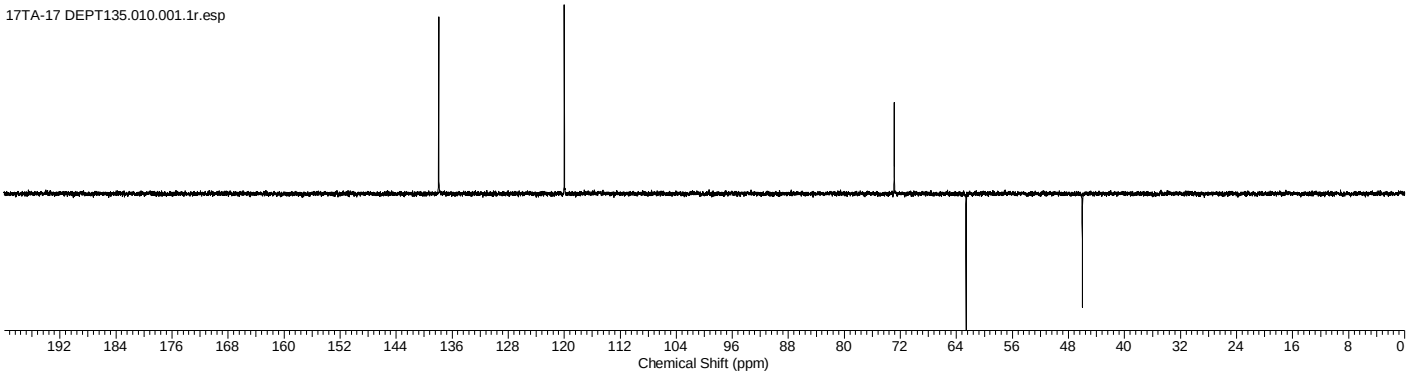
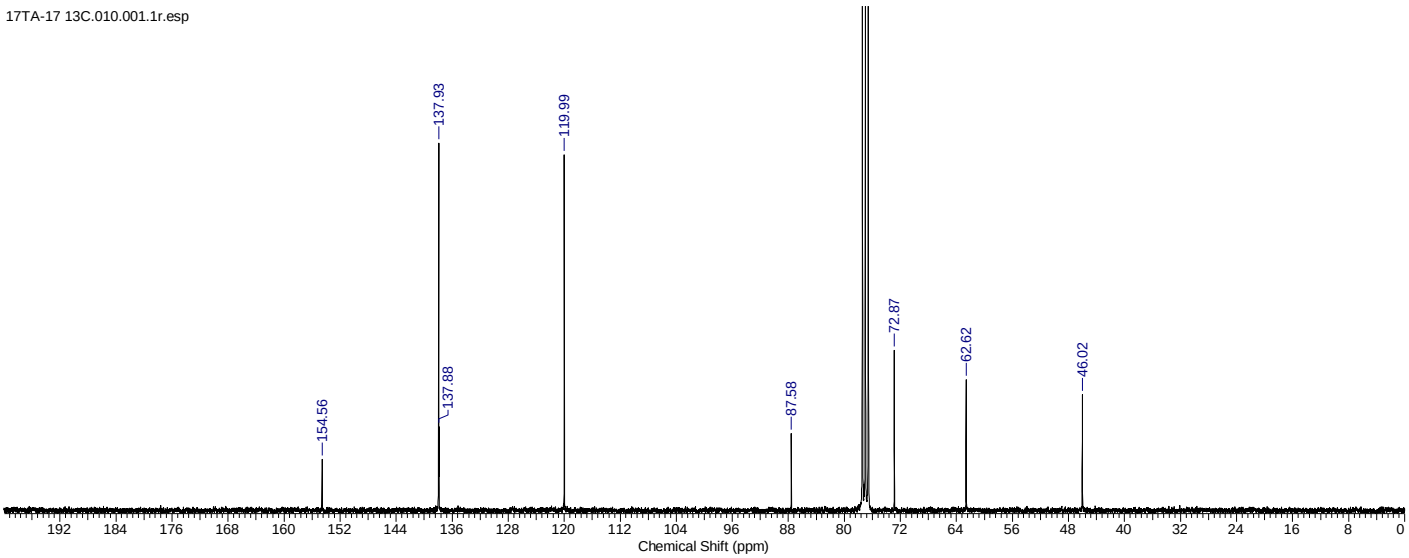


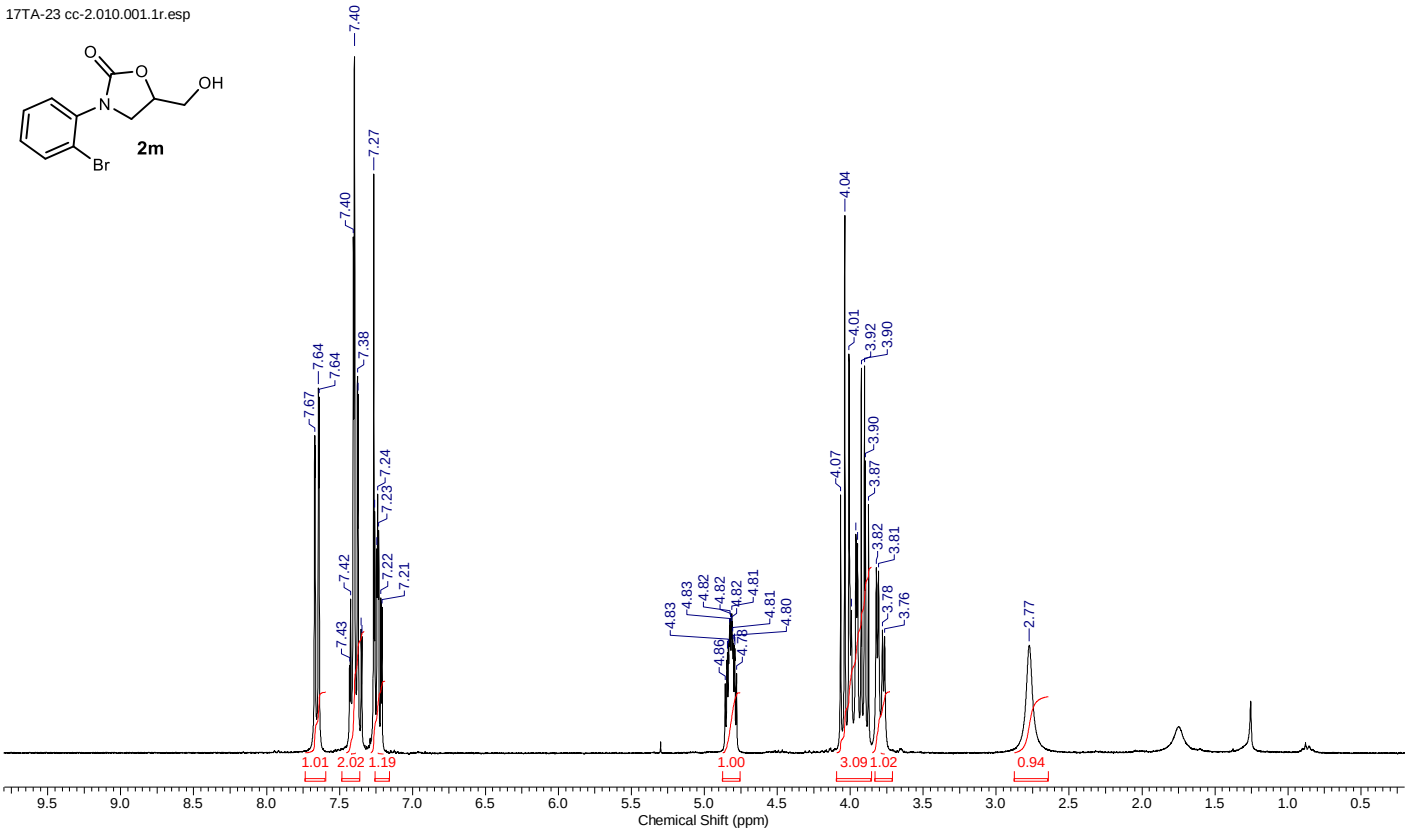
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2l

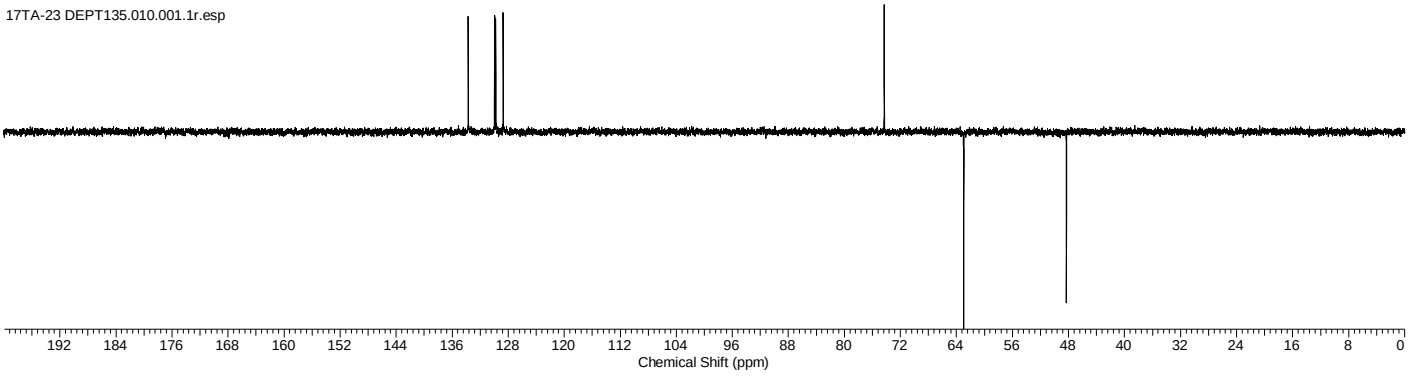


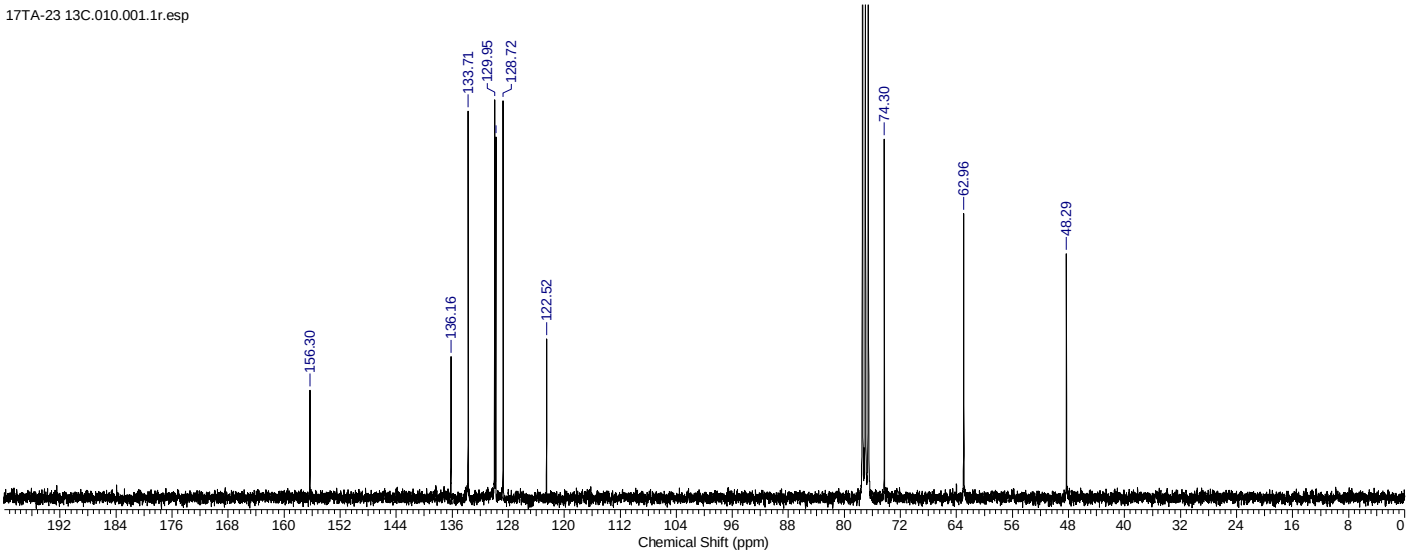



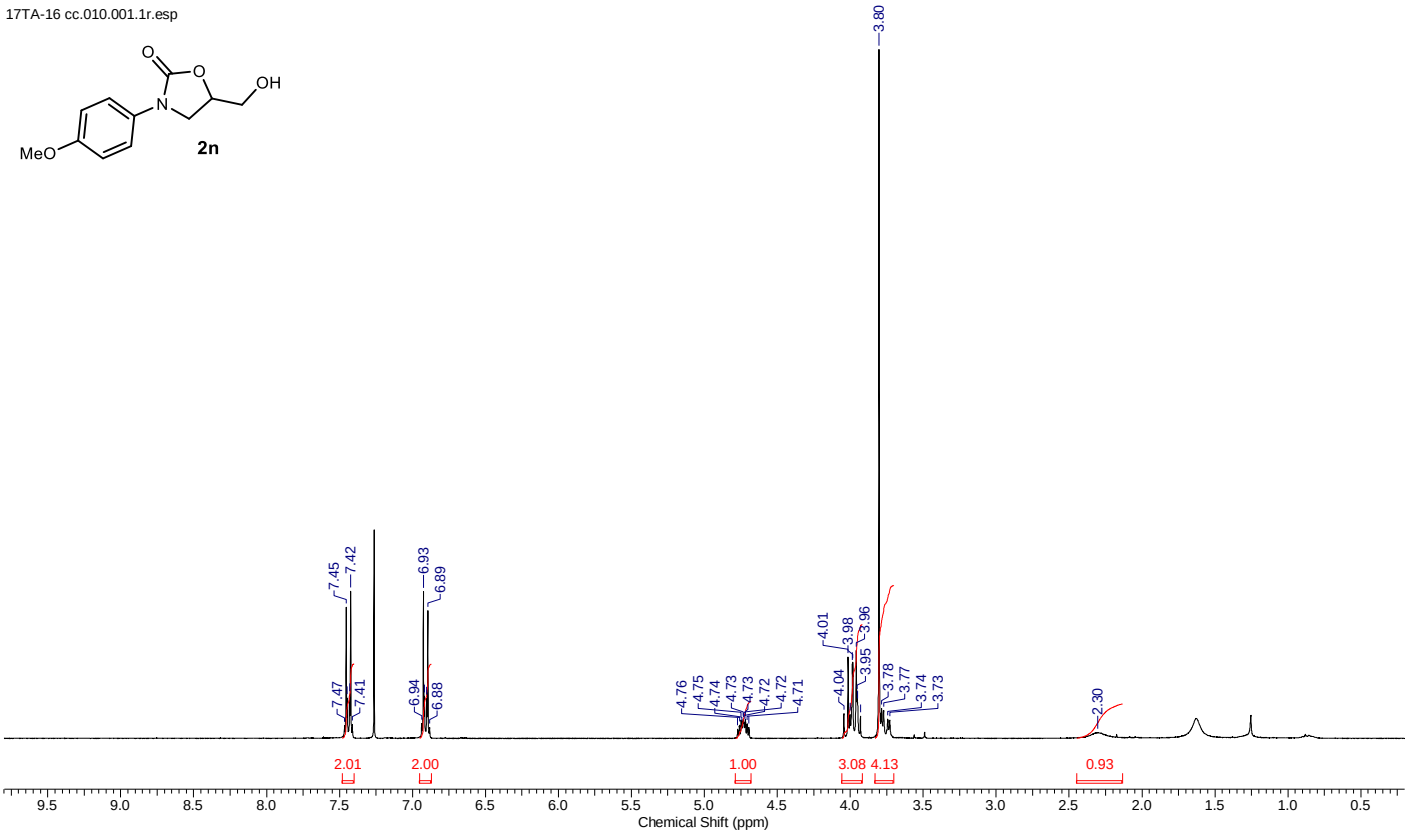
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2m

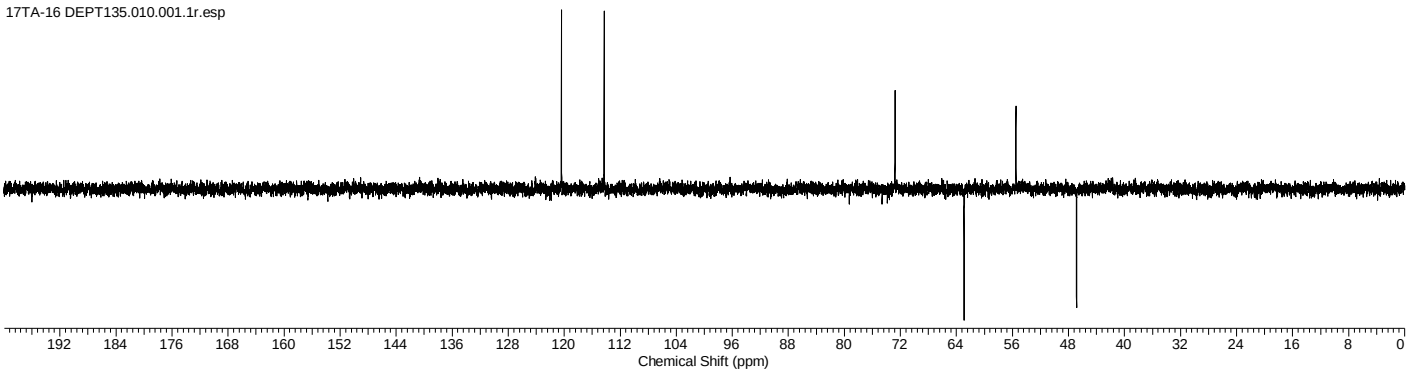


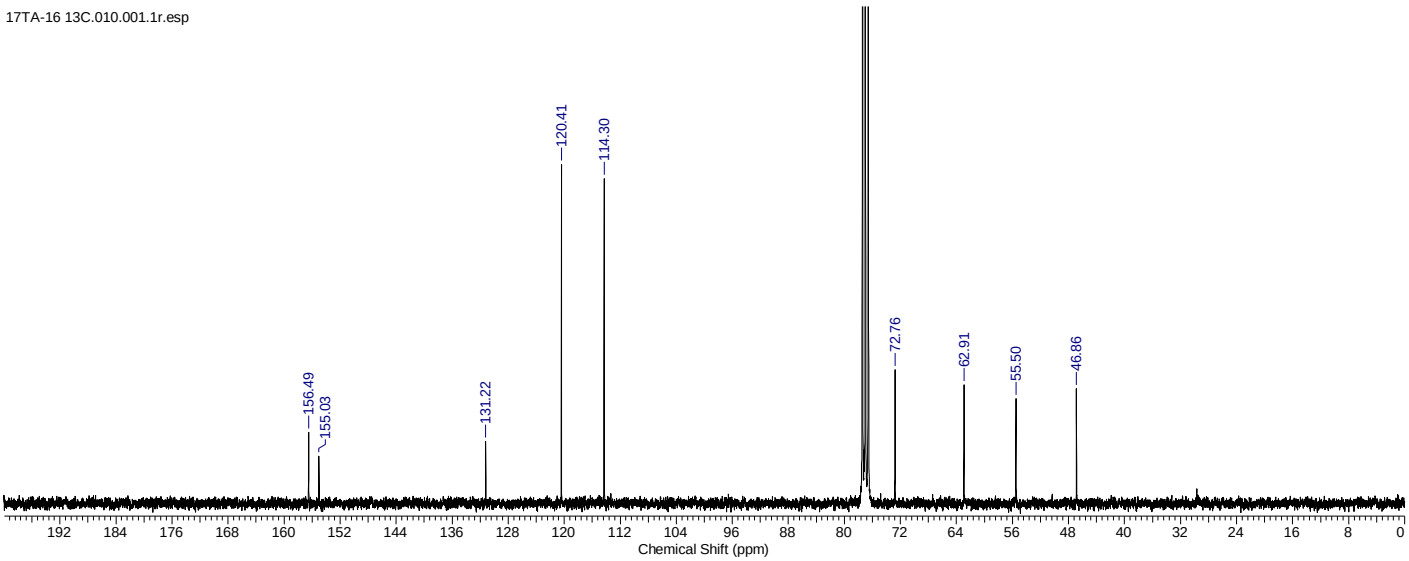



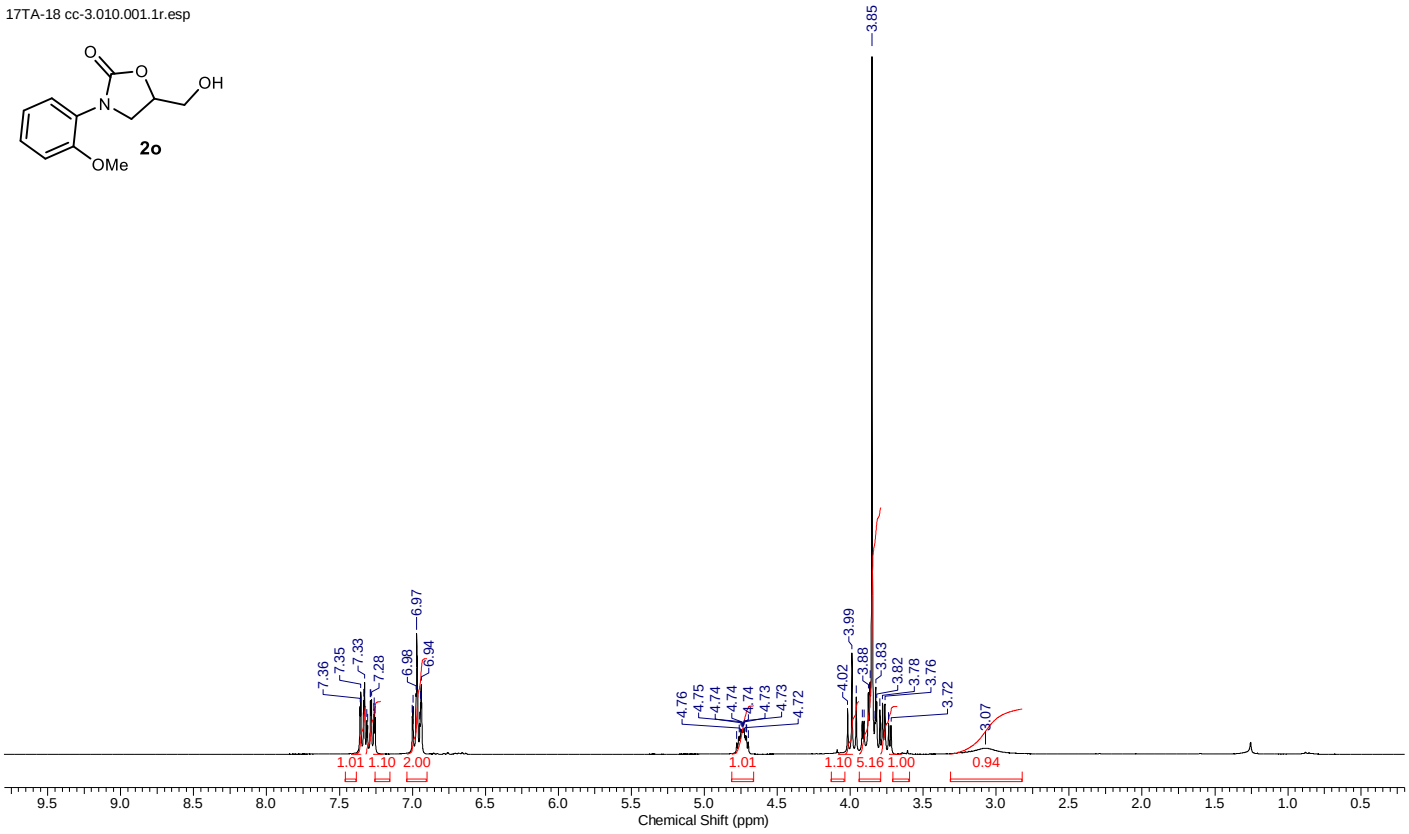
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2n

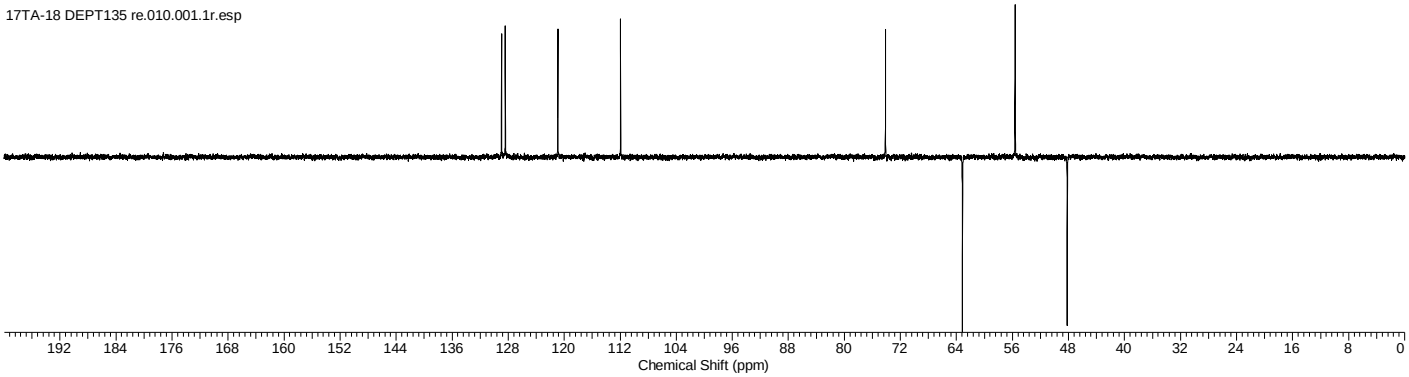


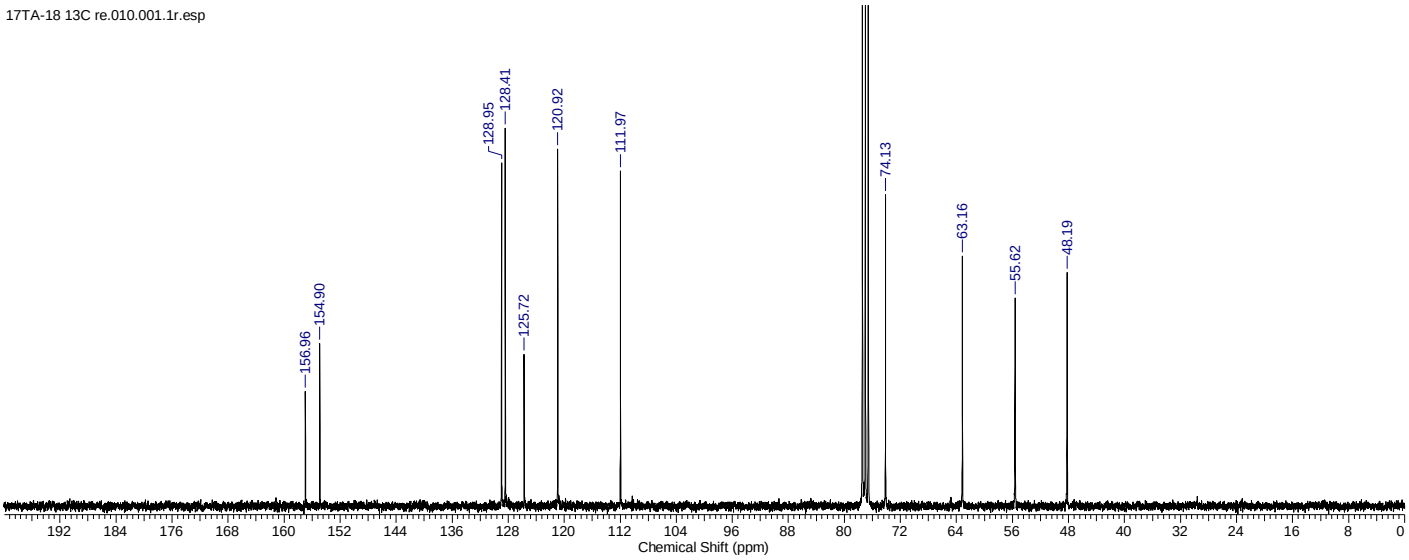



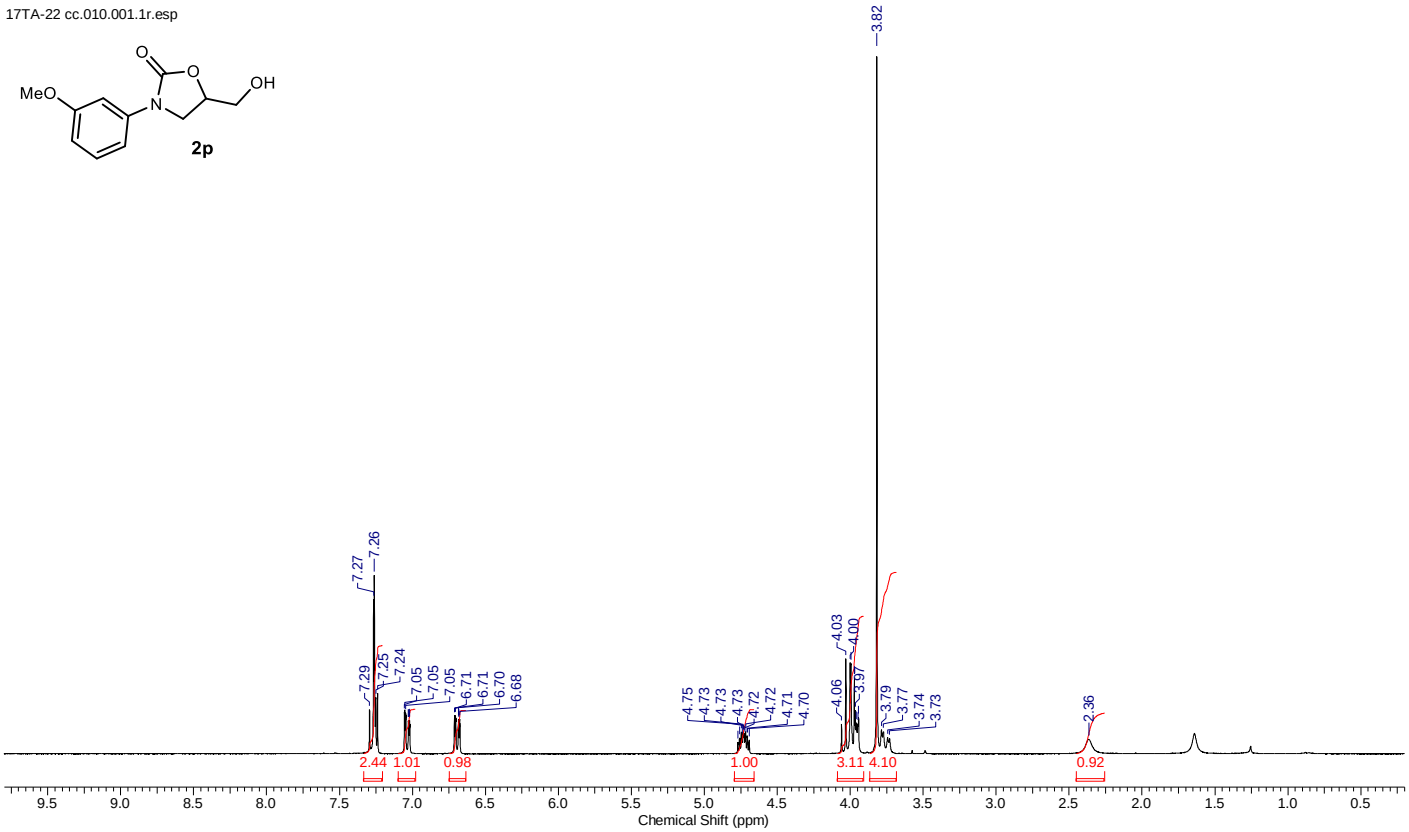
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2o

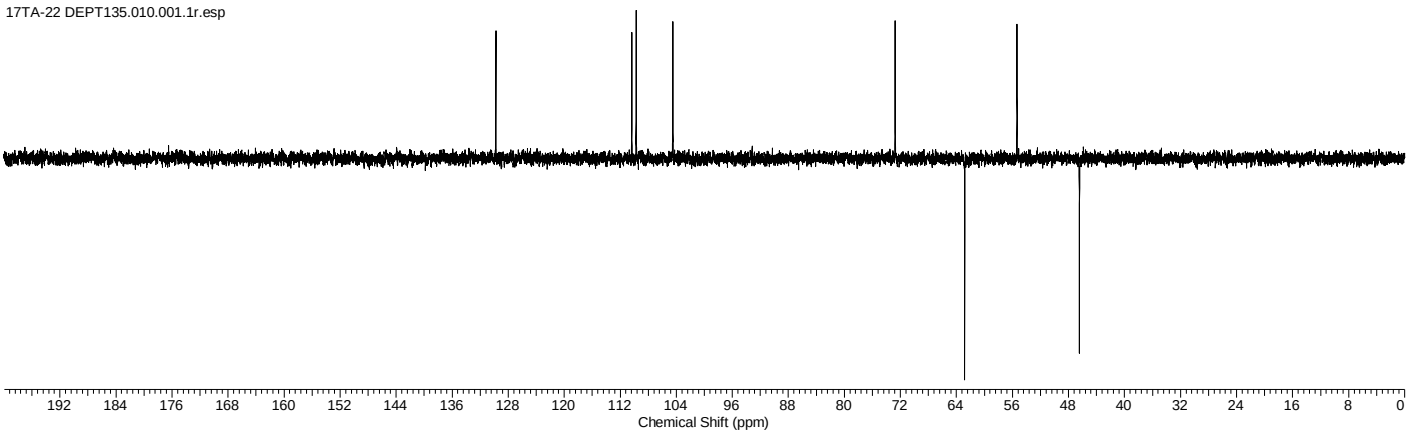


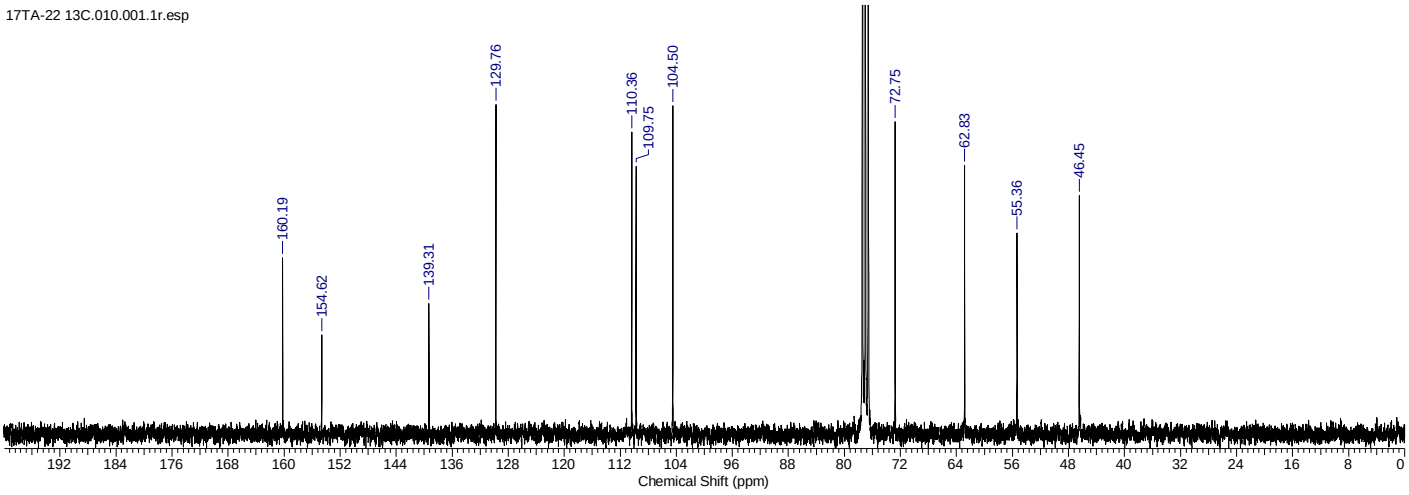



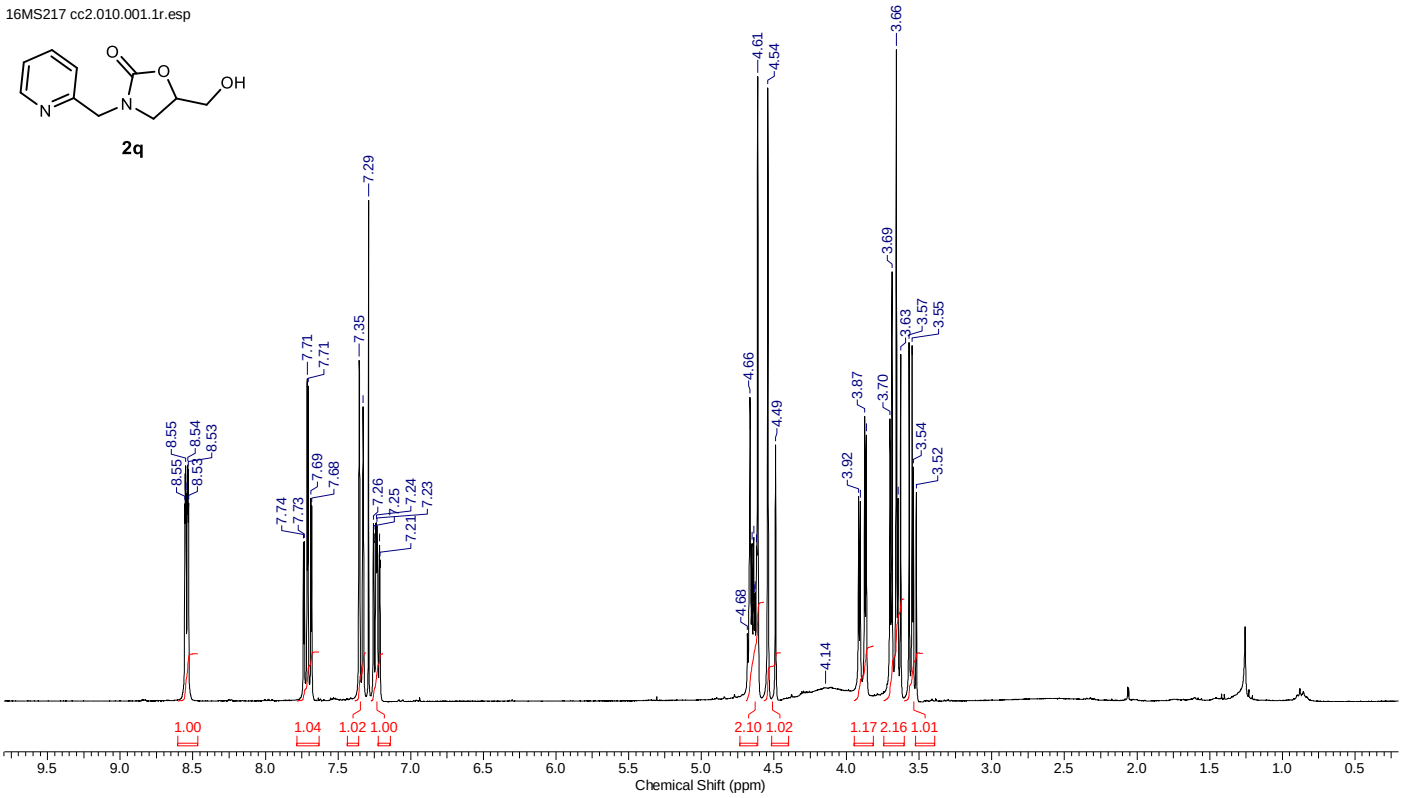
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2p

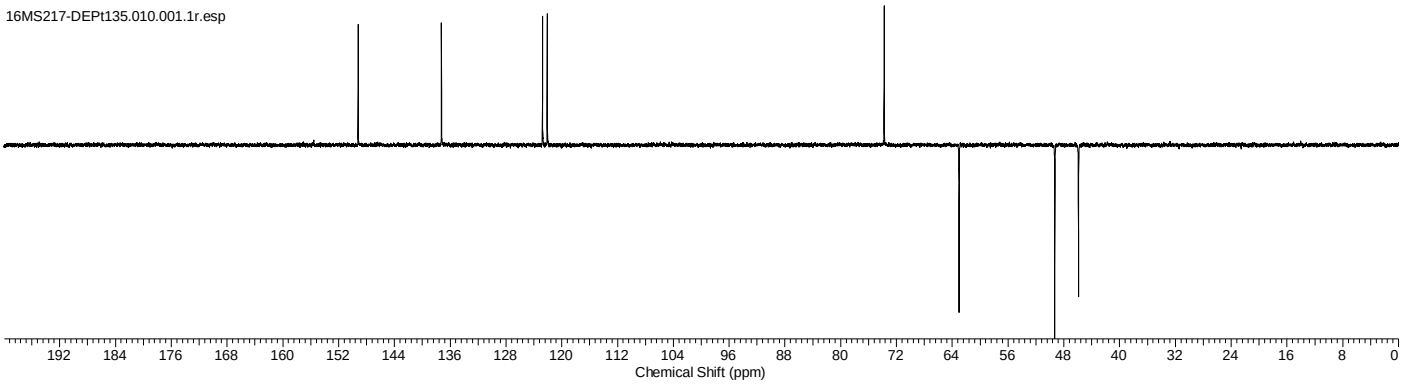


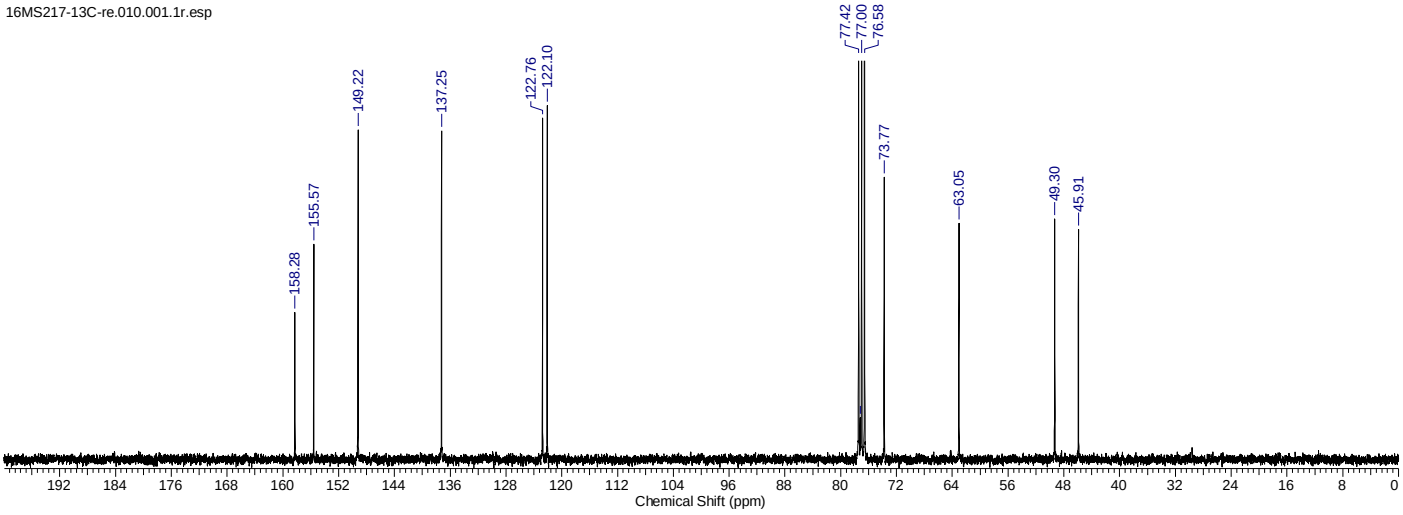



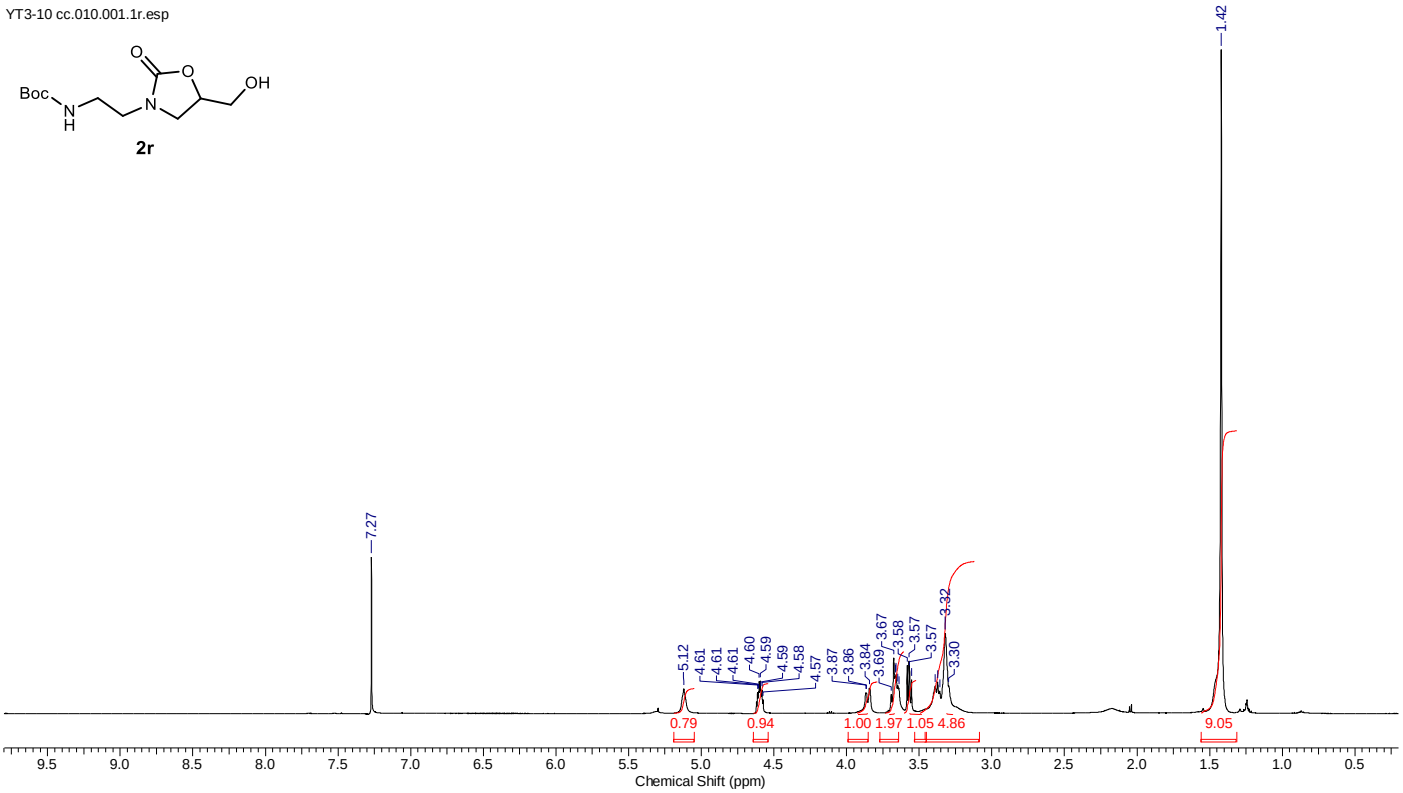
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2p

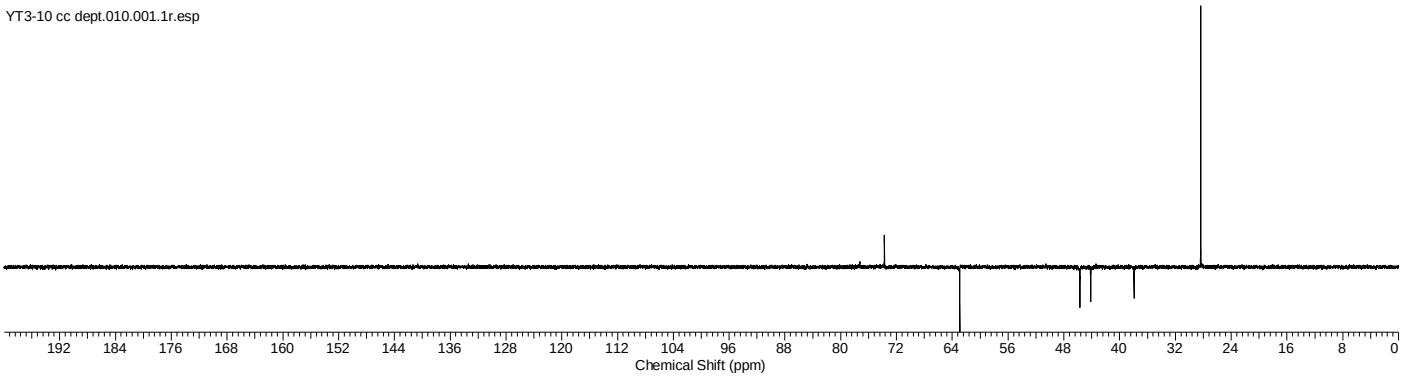


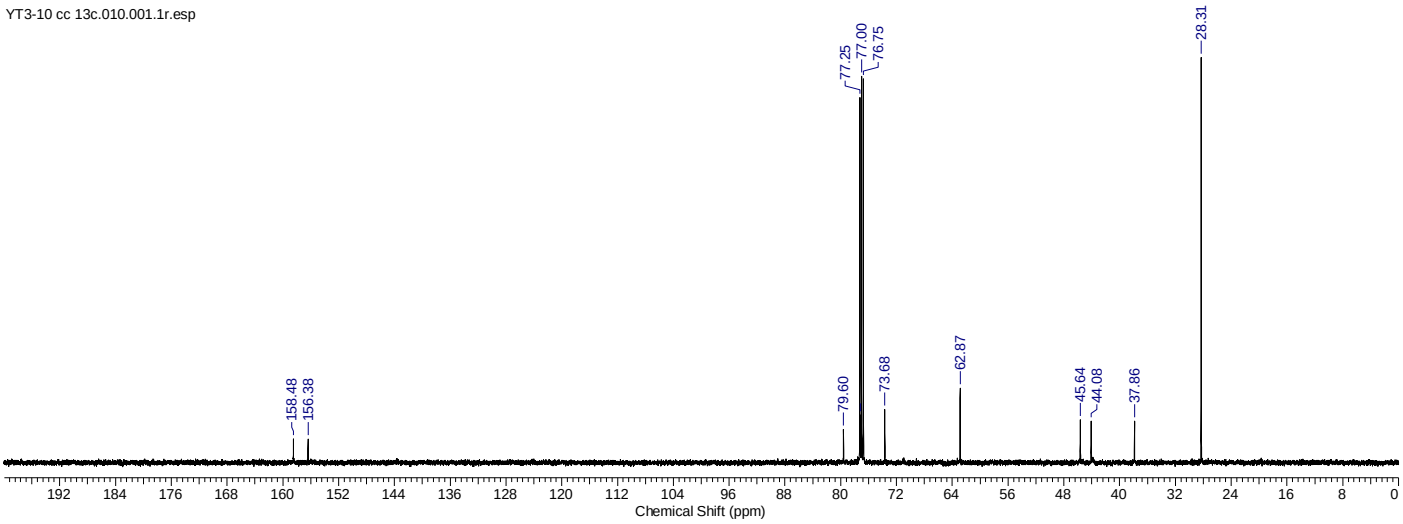



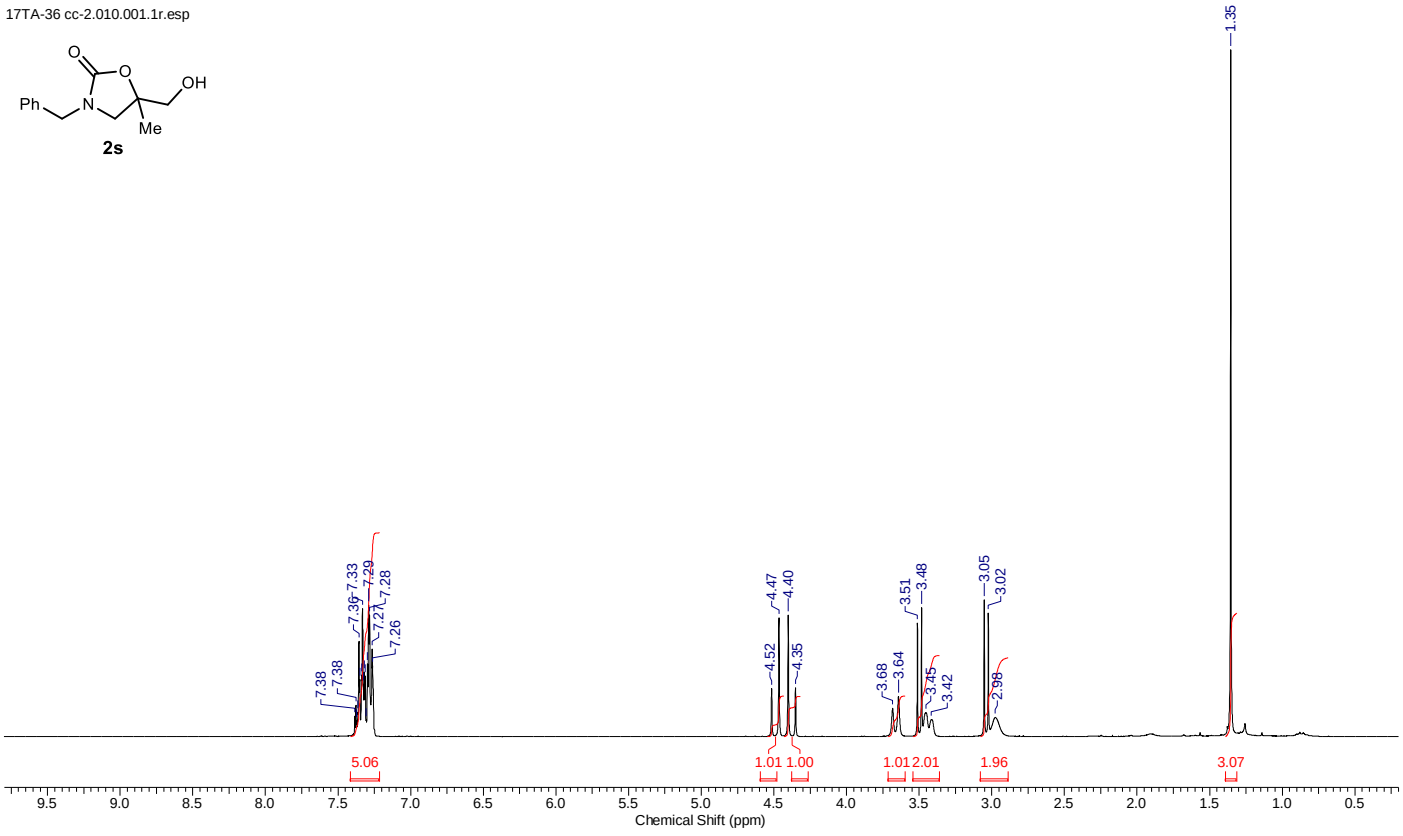
# $^{1}$H (500 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) Spectra of 2r

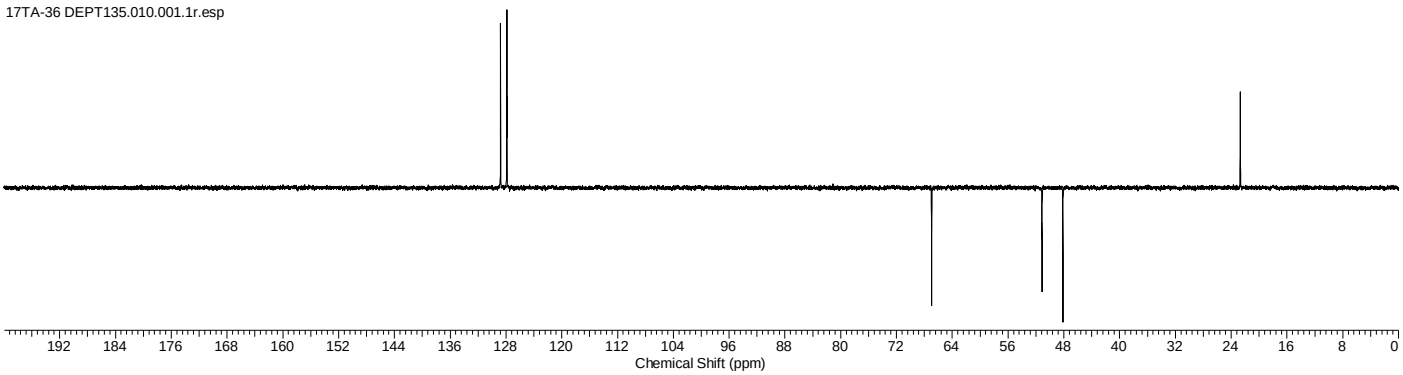


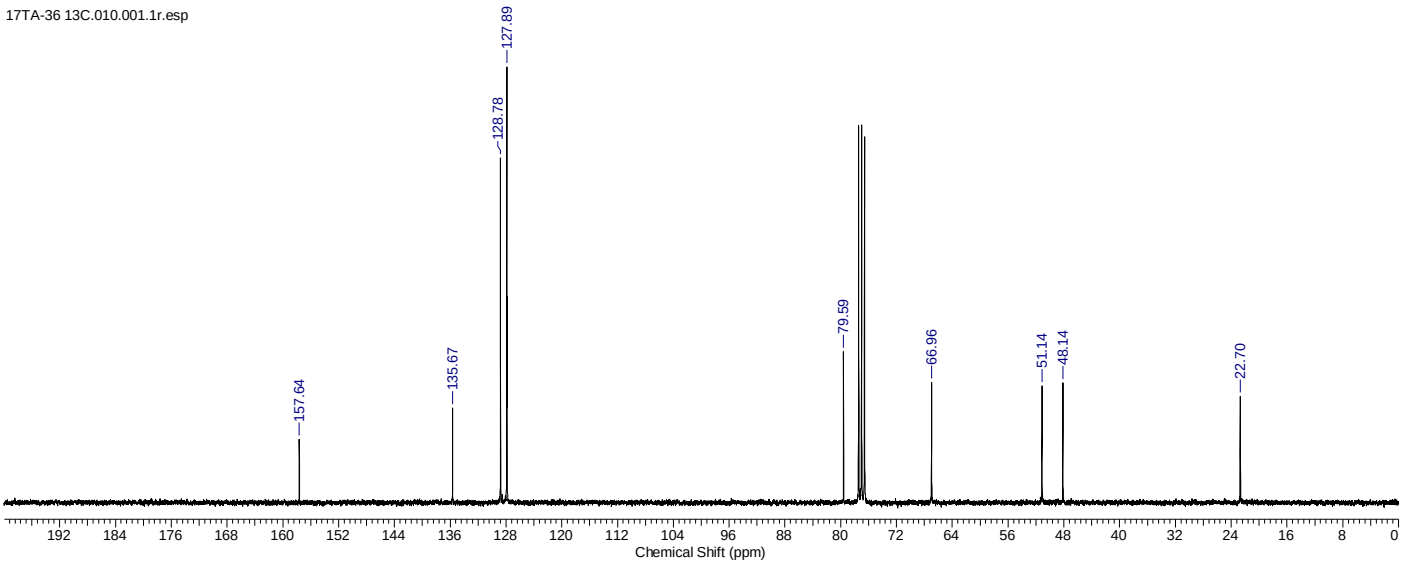



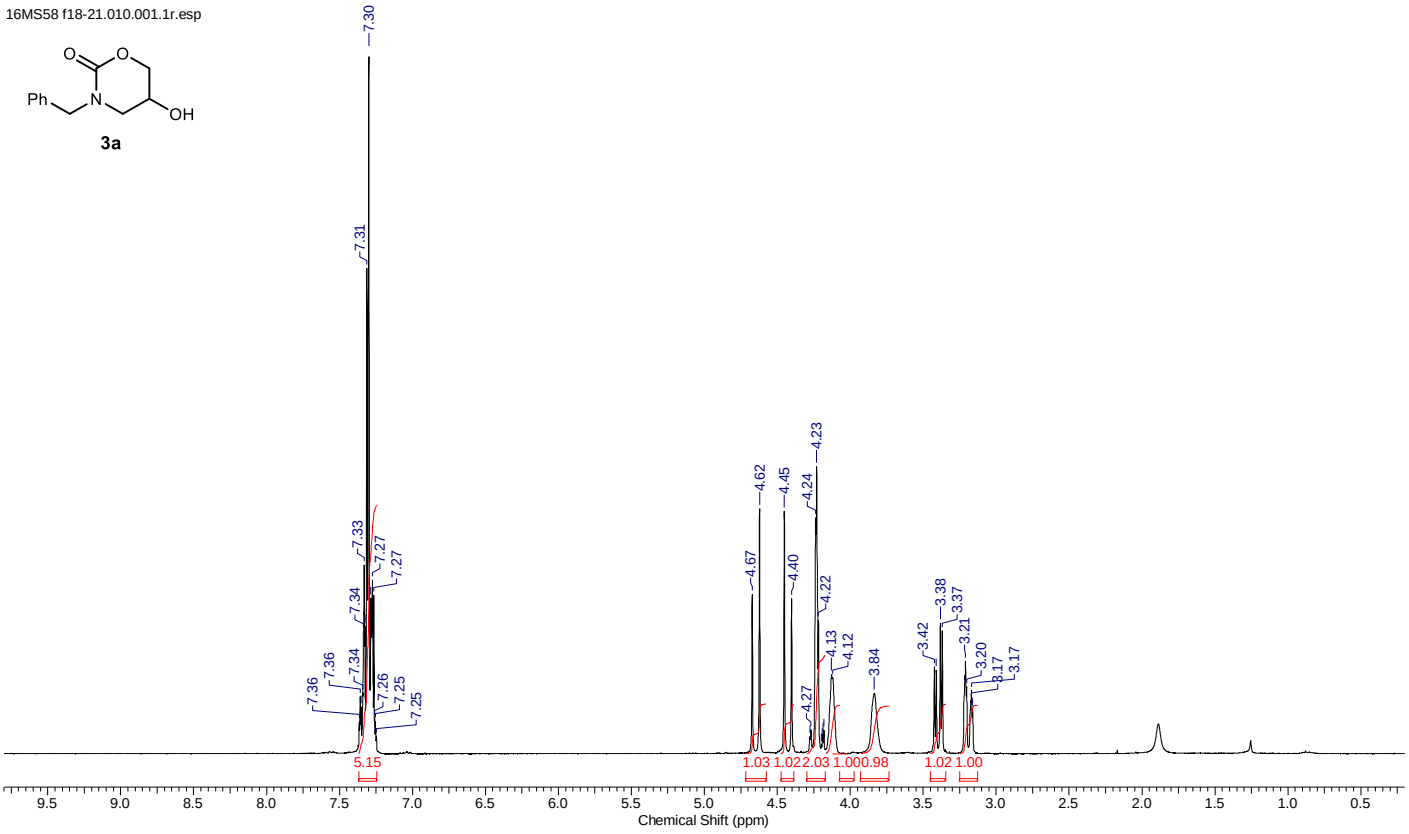
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2s

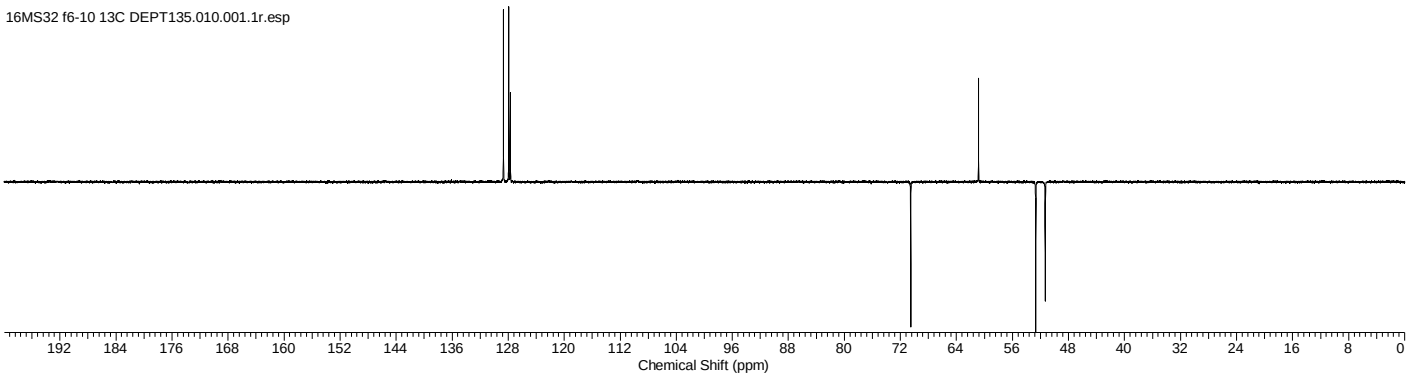


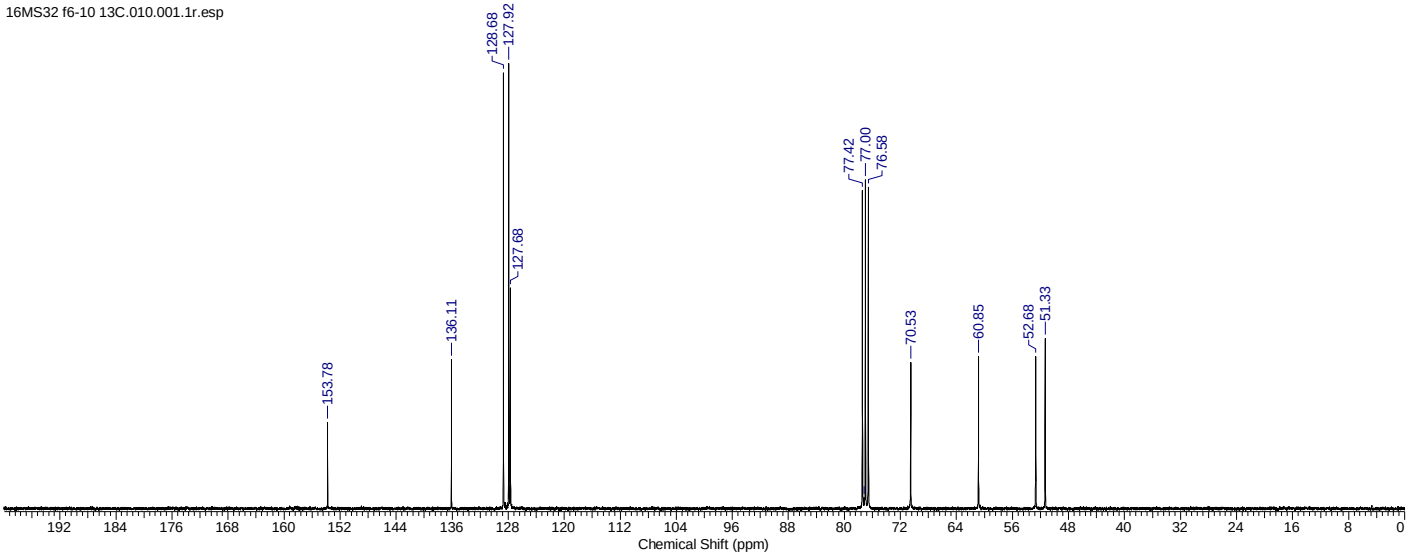



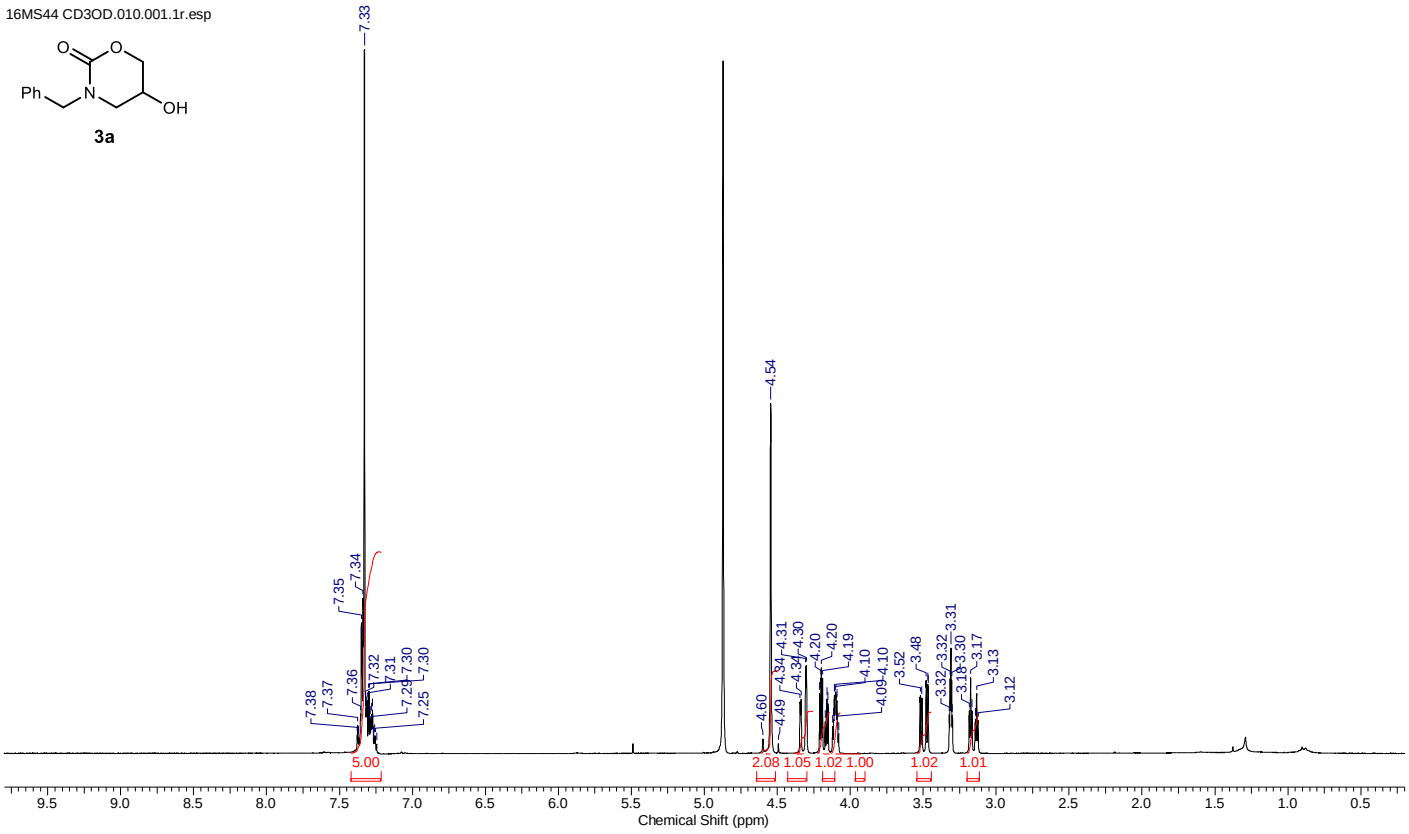
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3a

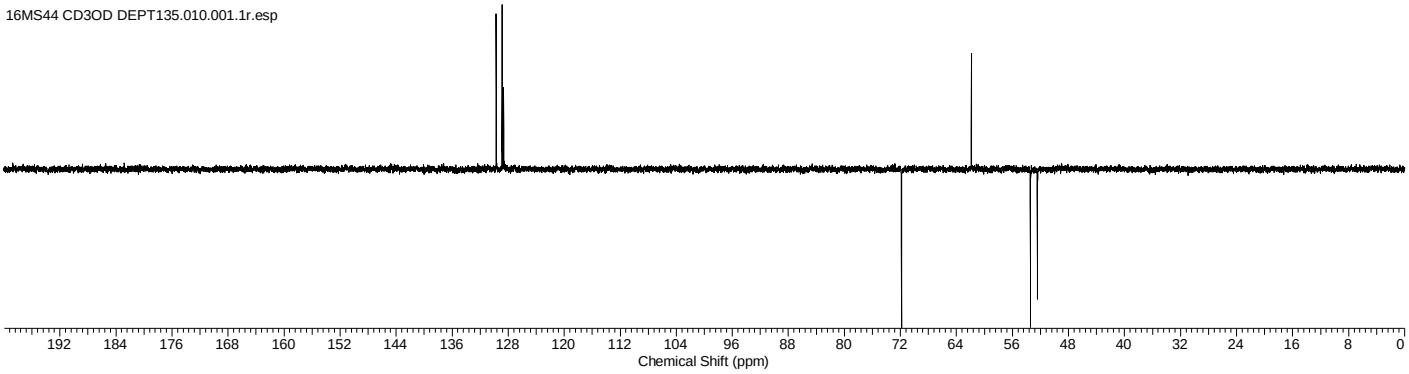


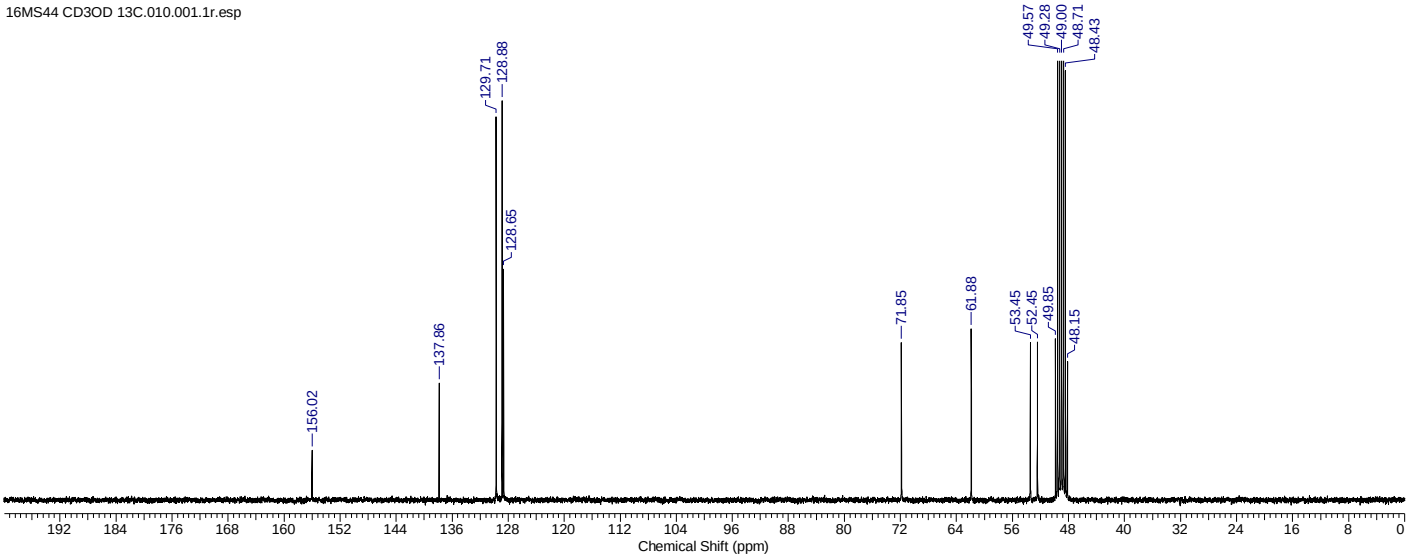



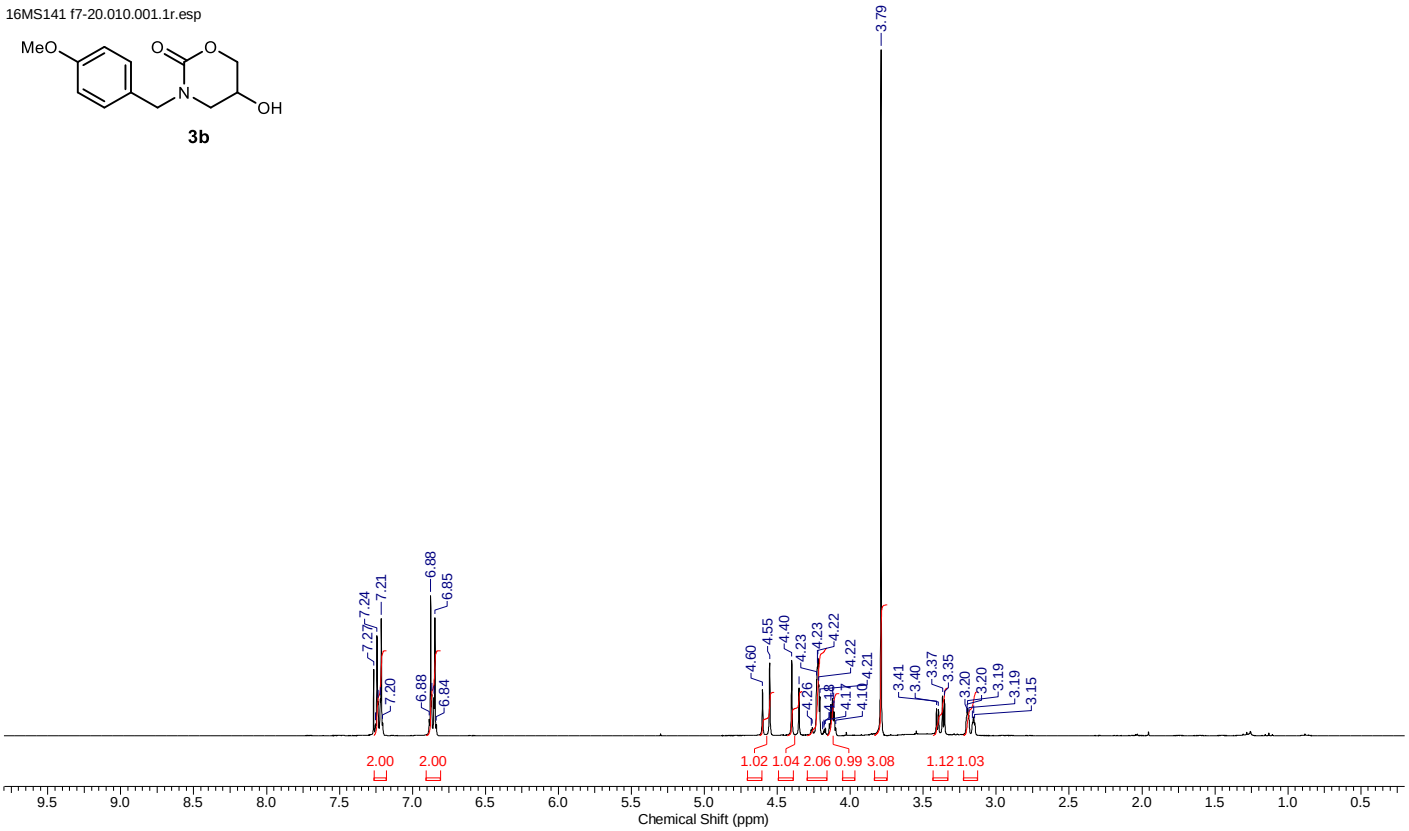
# $^{1}$H (300 MHz, CD$_3$OD) & $^{13}$C{$^{1}$H} NMR (75 MHz, CD$_3$OD) Spectra of 3a

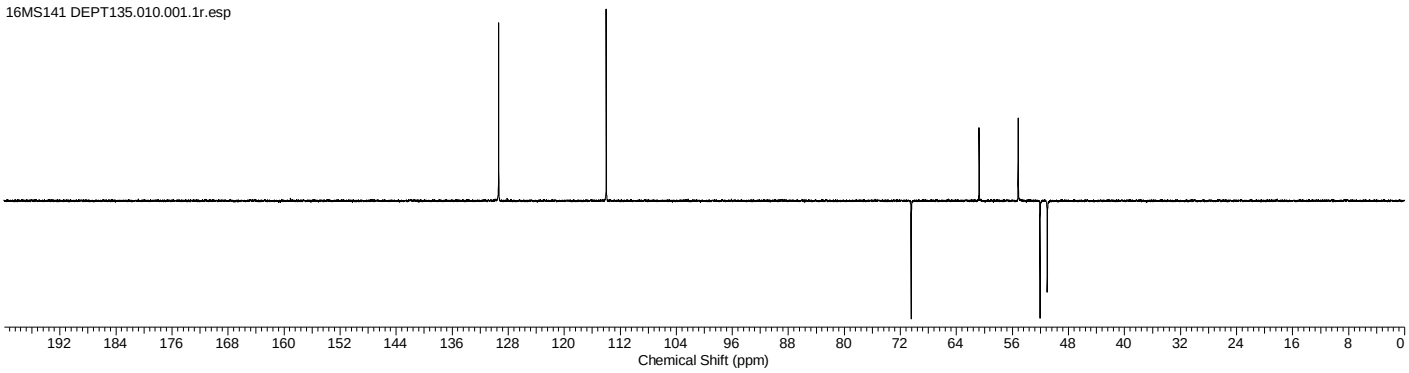


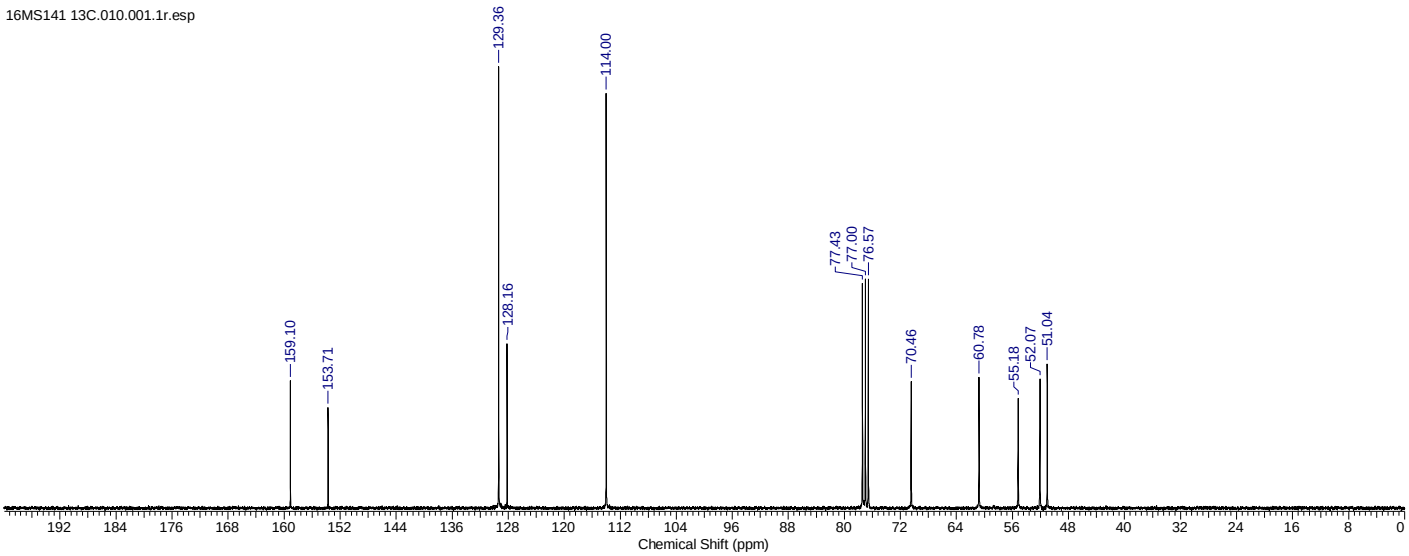



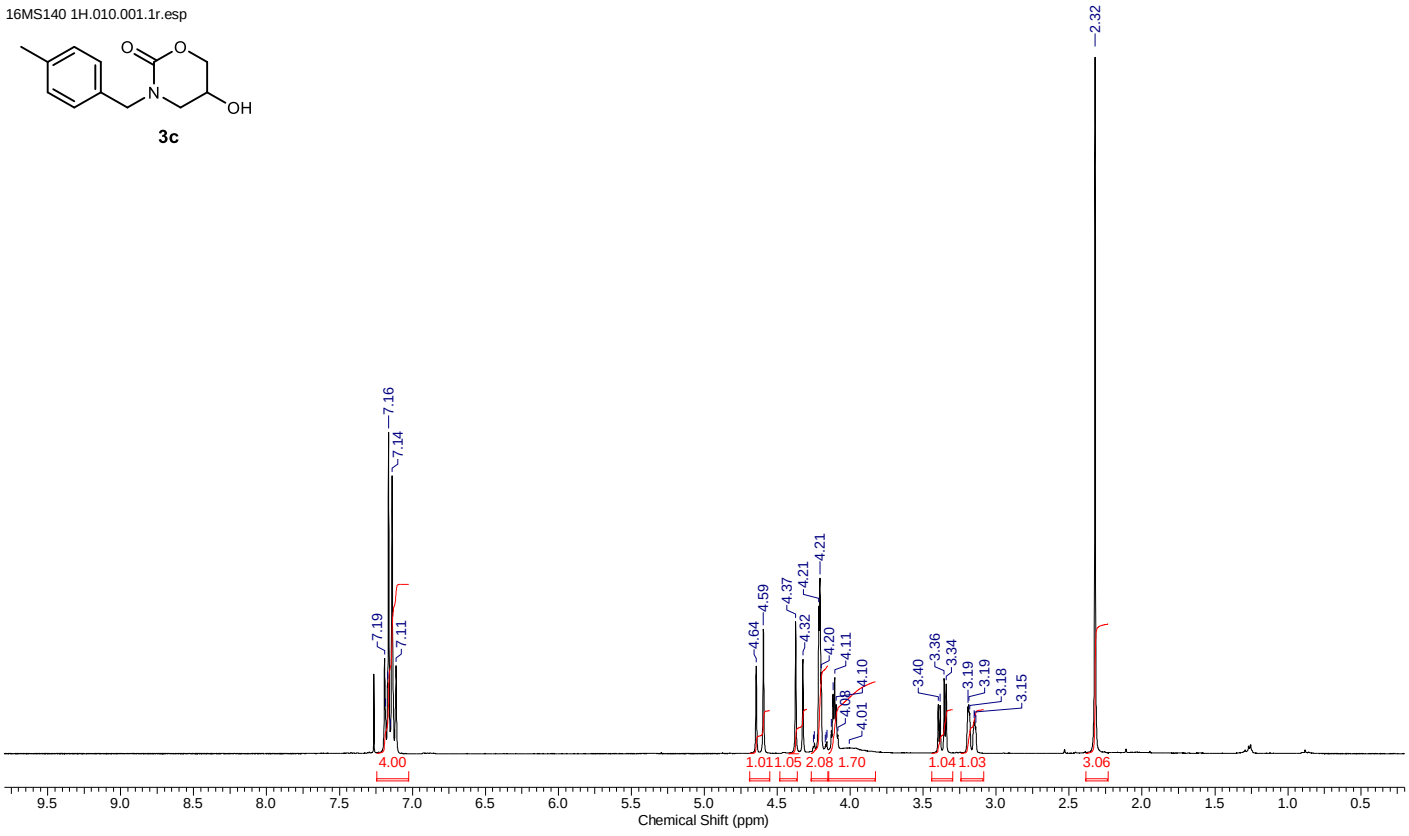
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3b

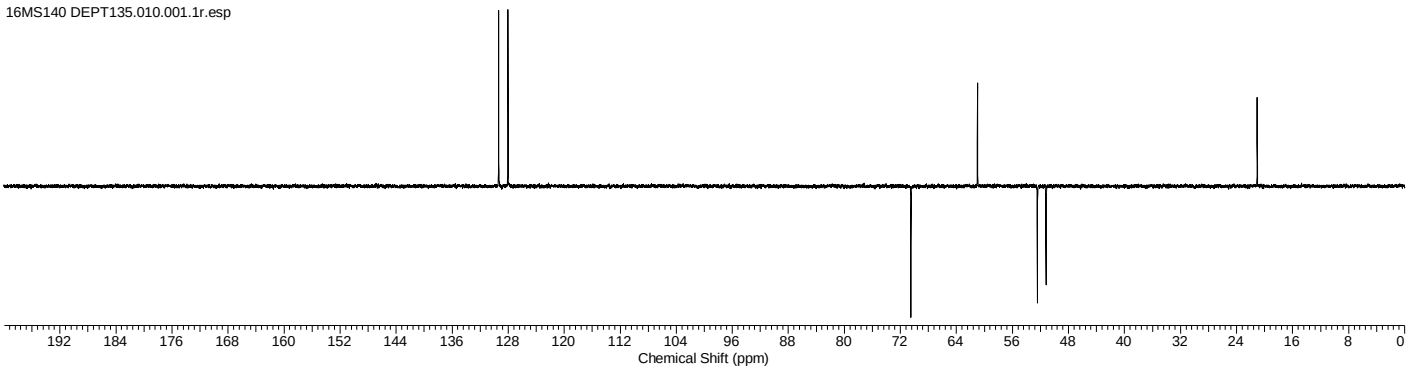


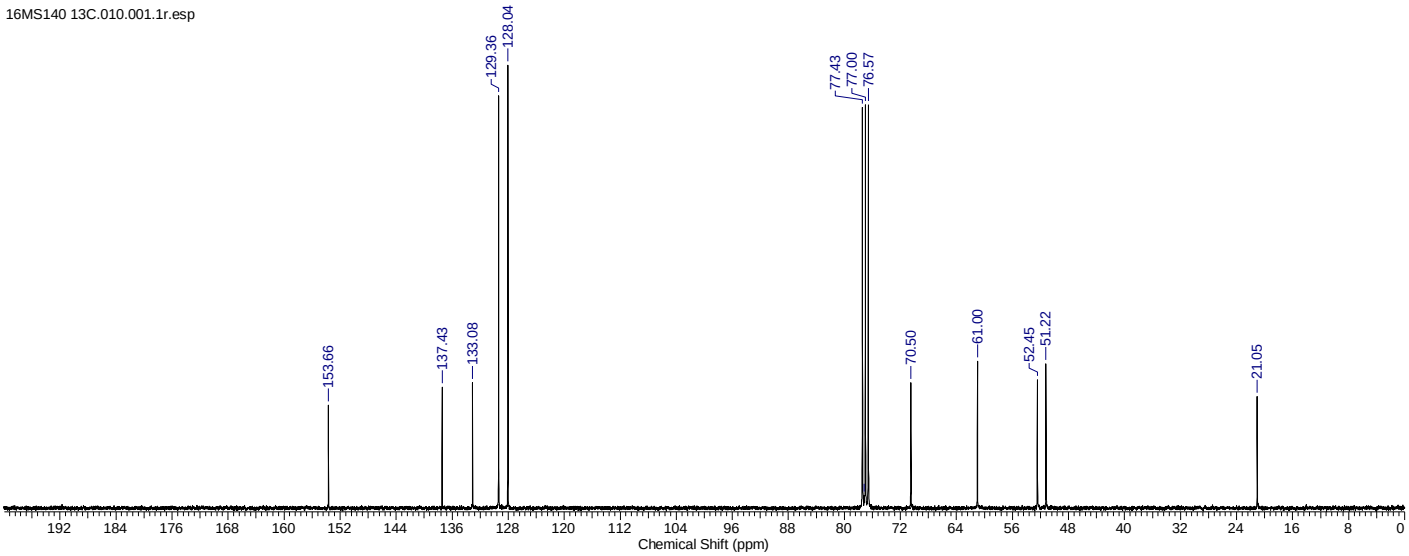



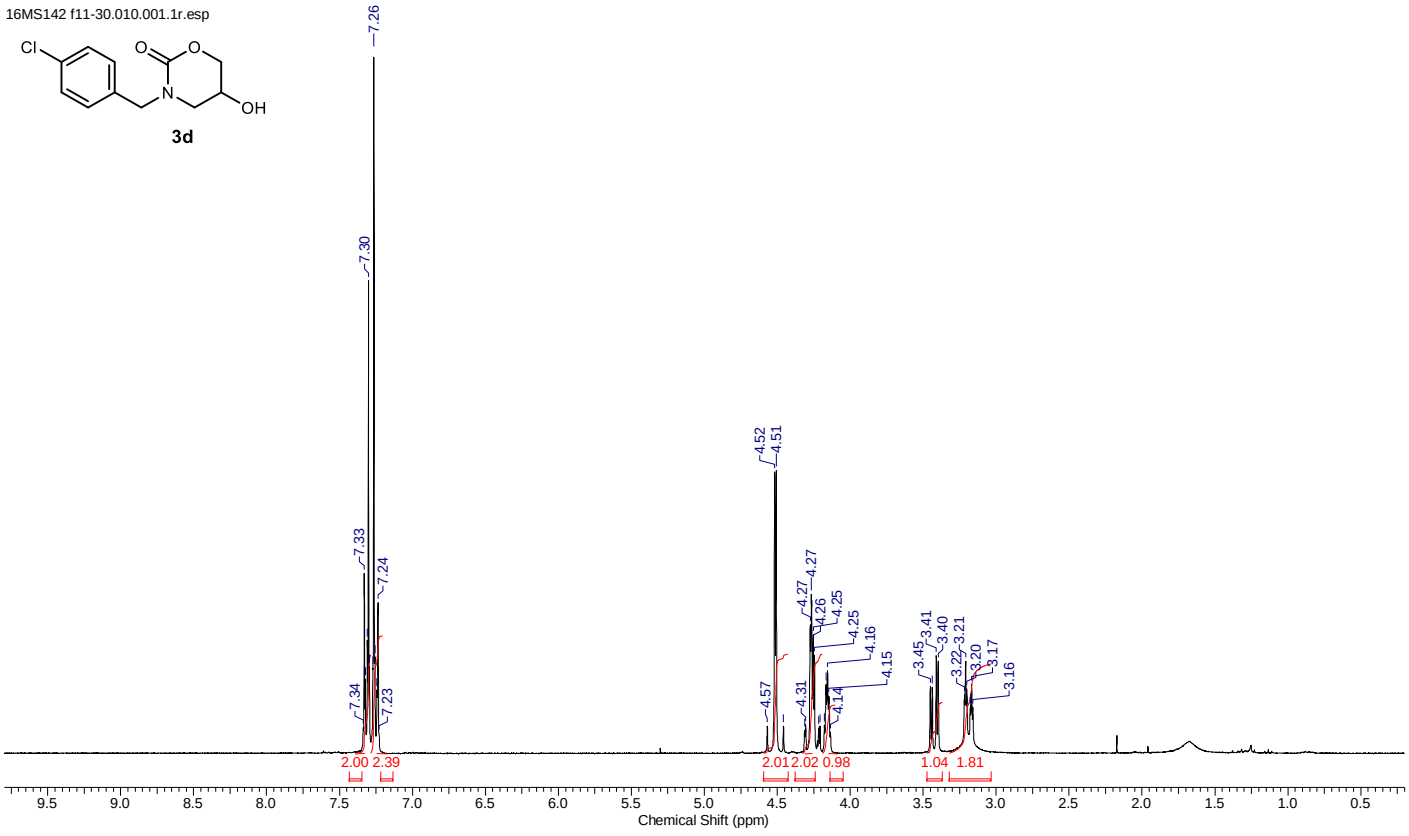
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3c

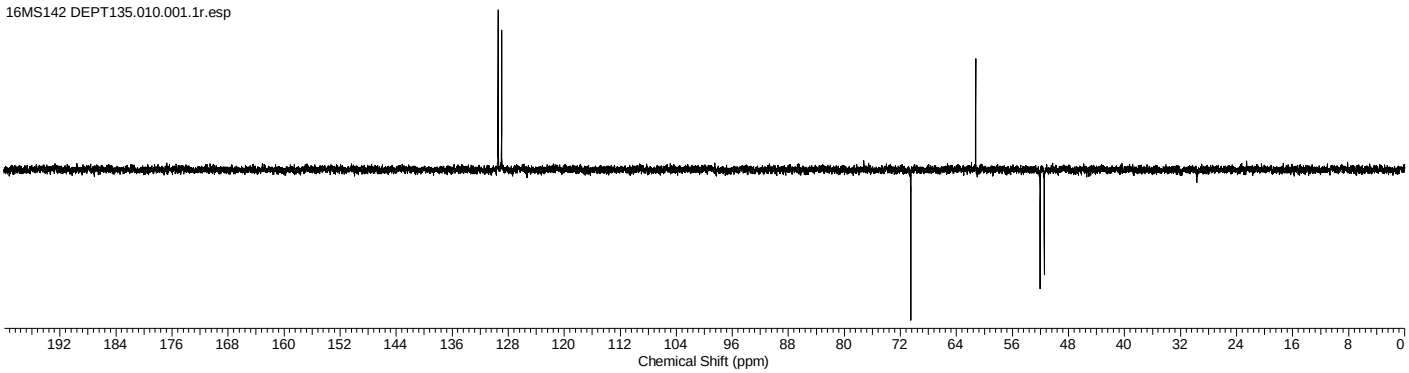


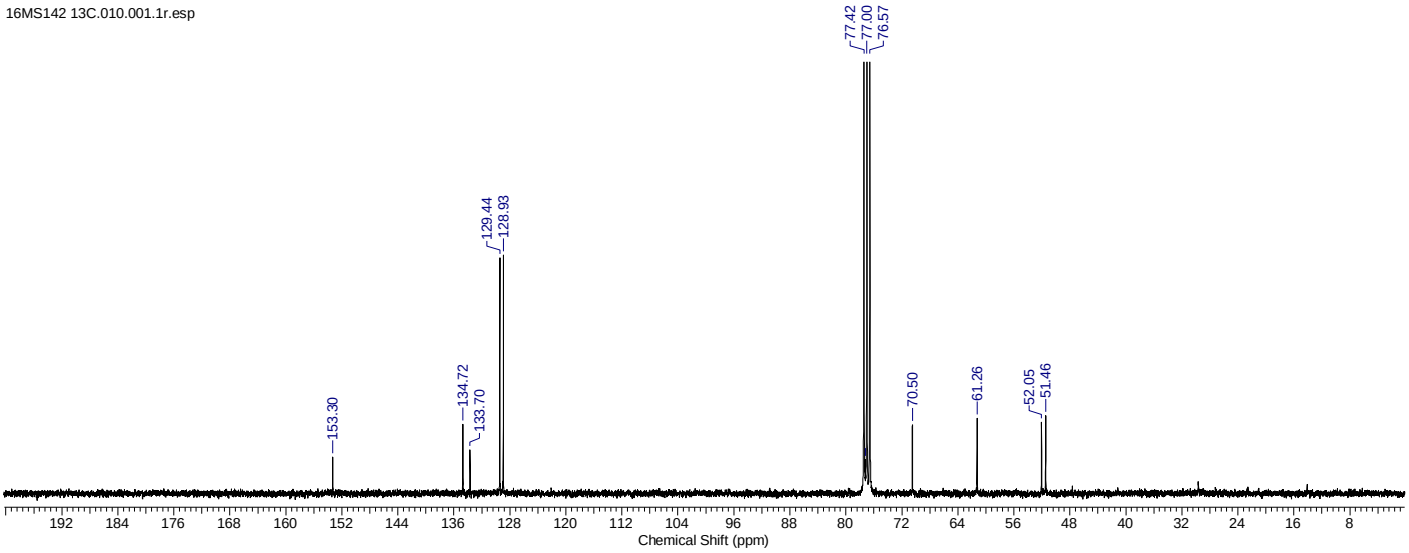



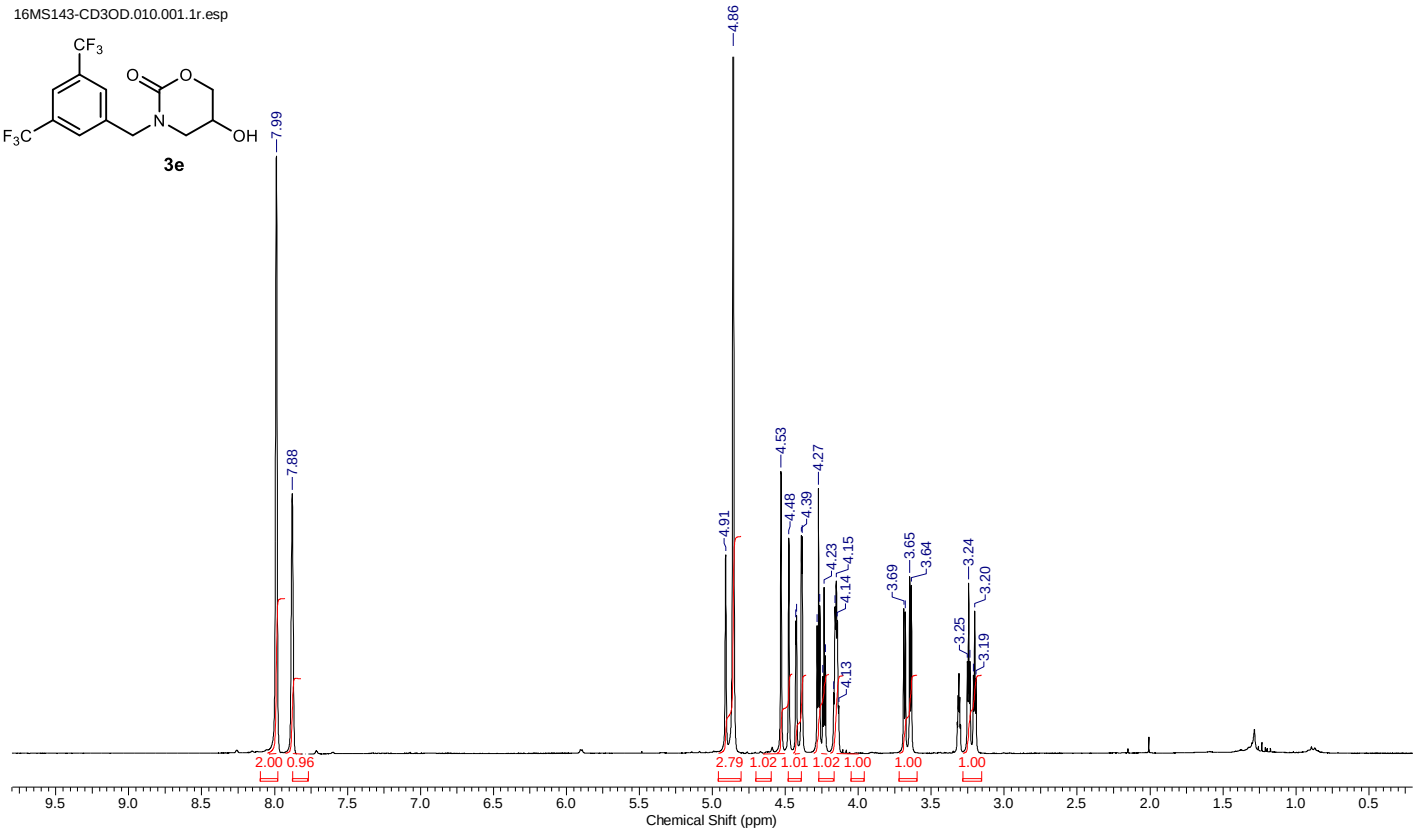
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3d

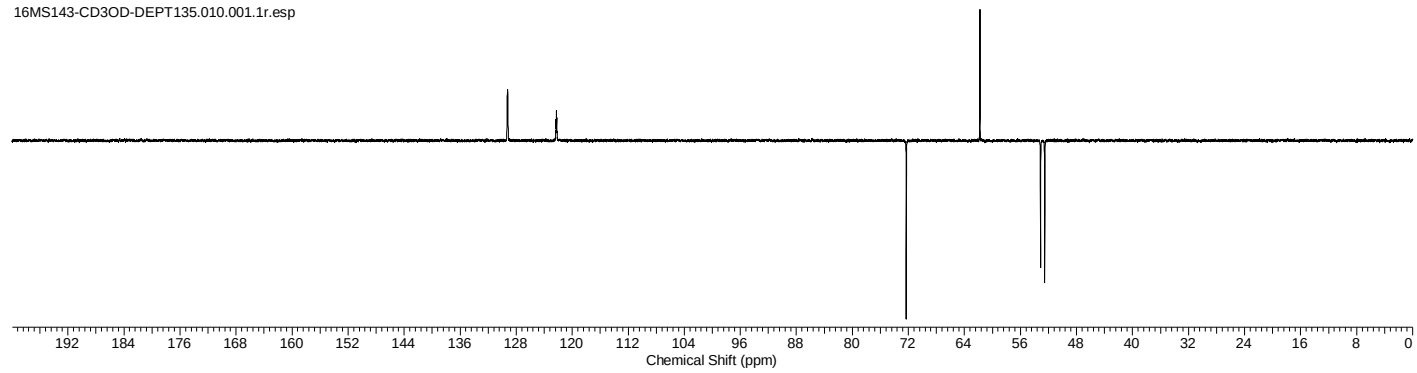


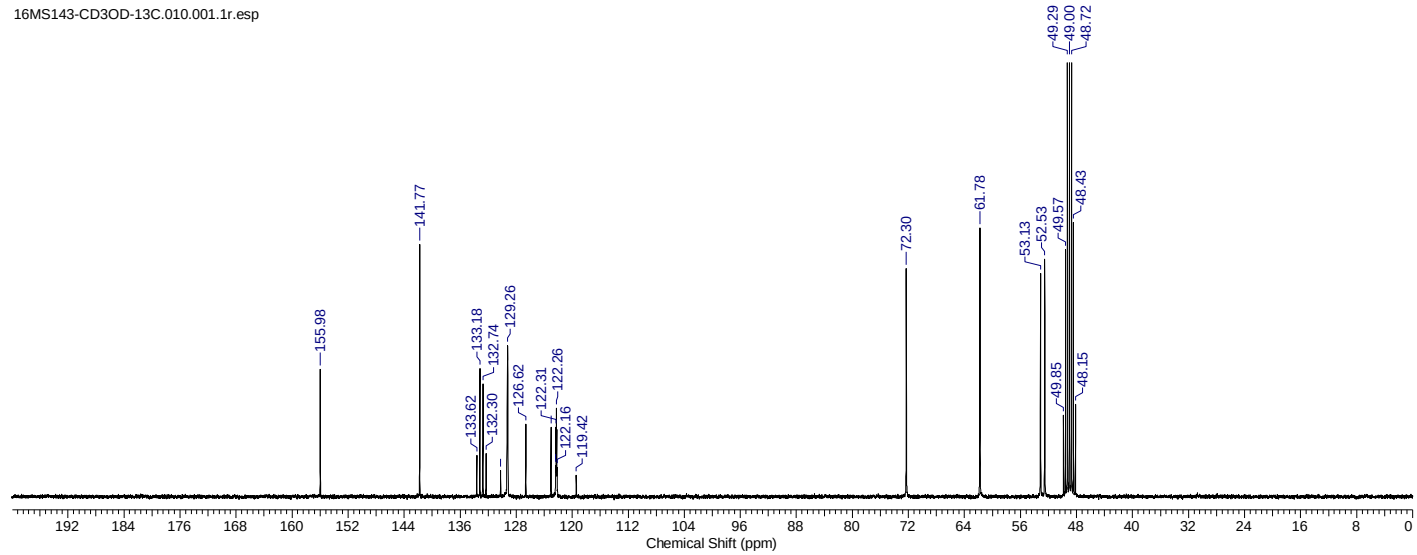



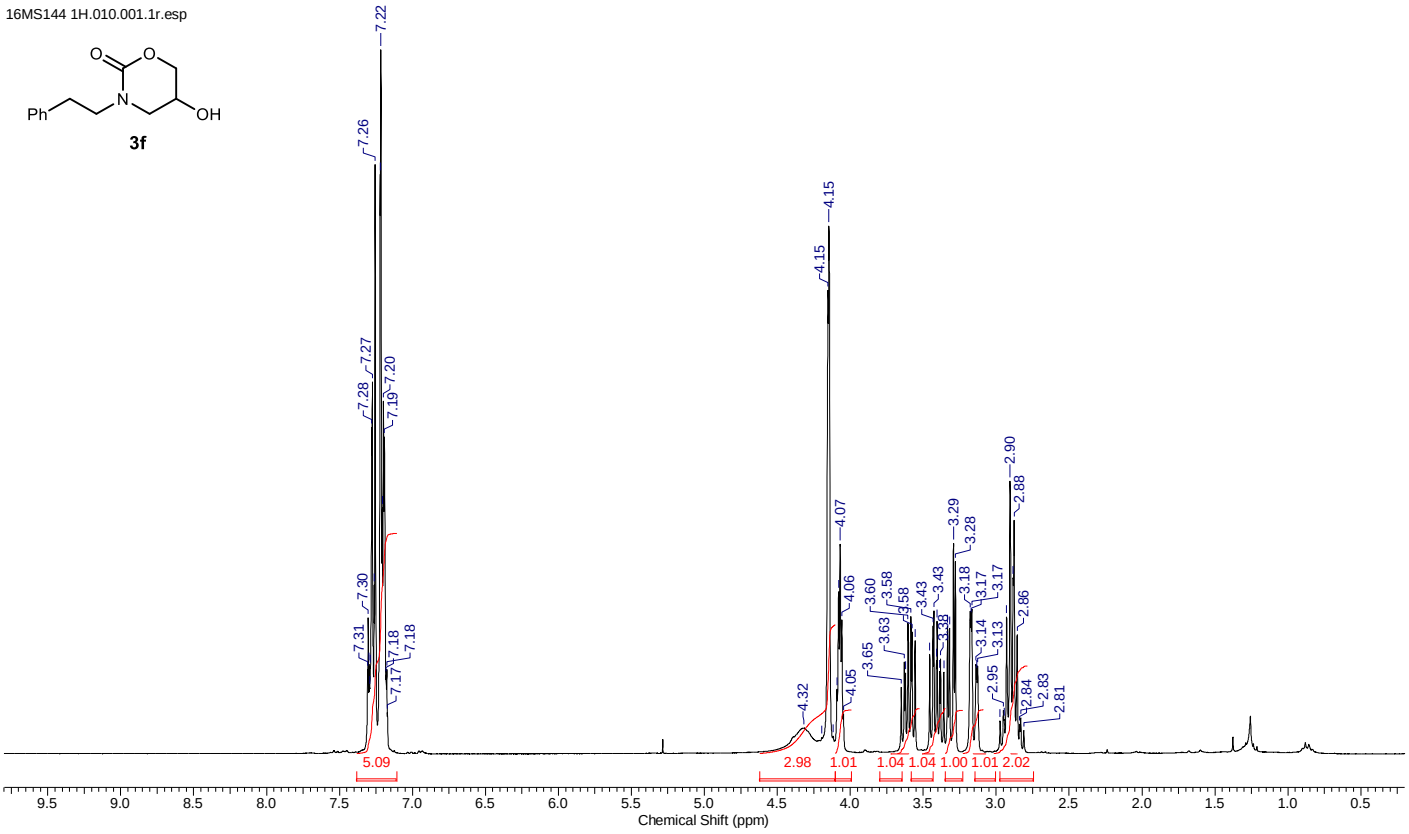
# $^{1}$H (300 MHz, $CD_3OD$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CD_3OD$) Spectra of 3e

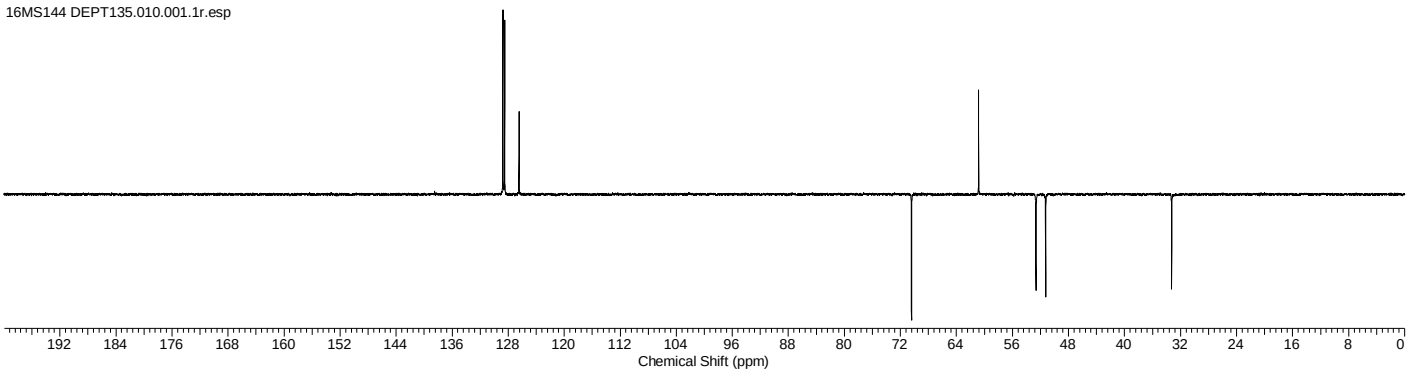


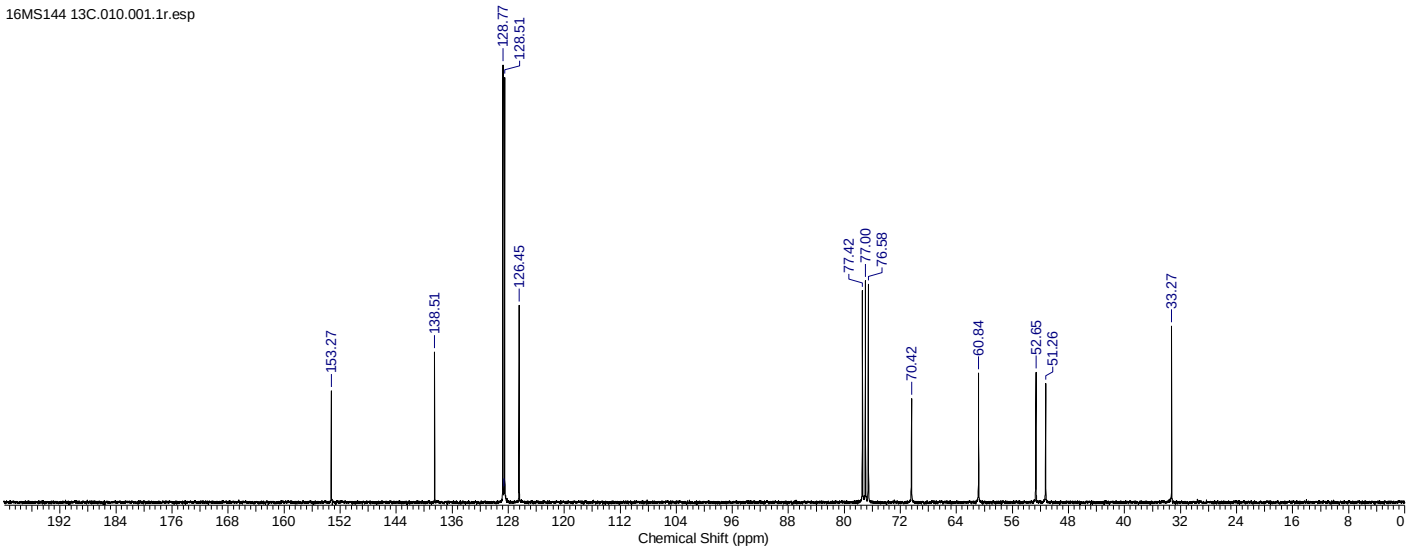



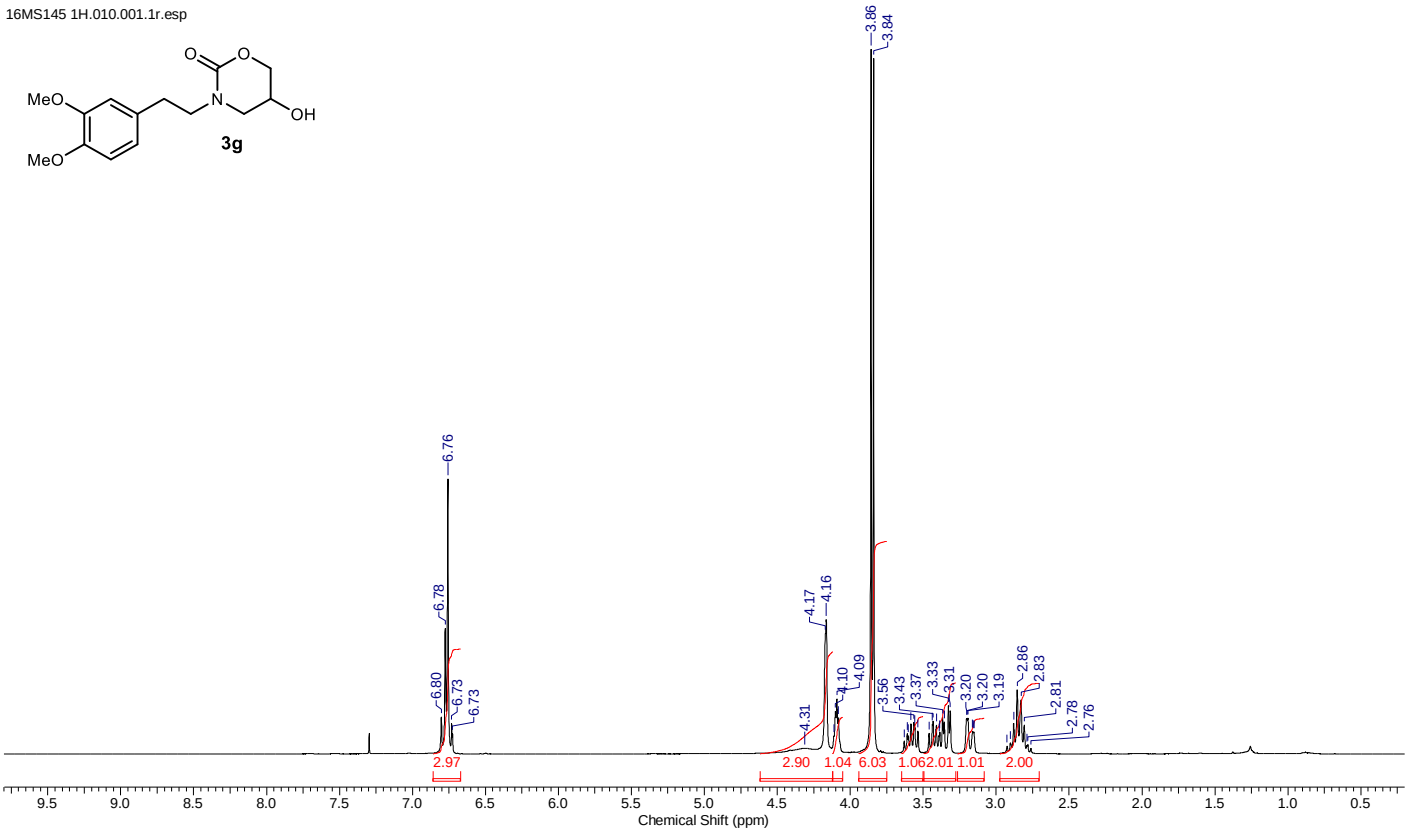
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3f

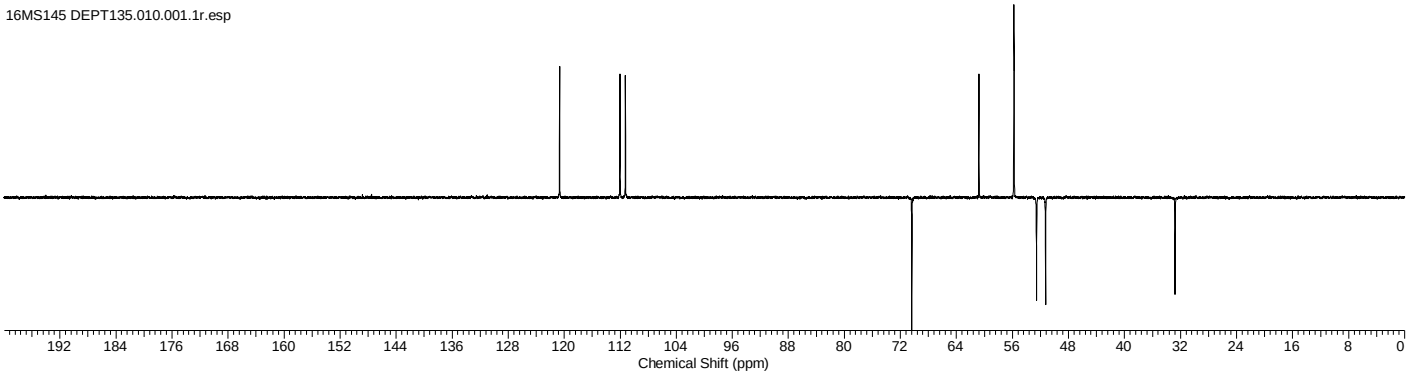


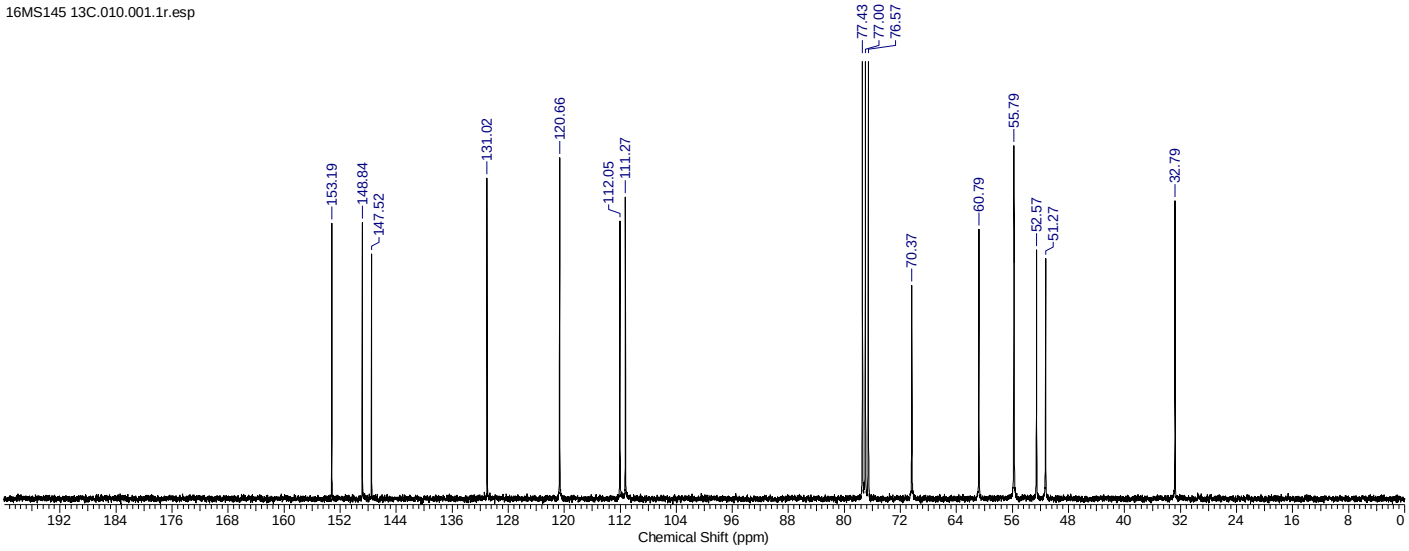



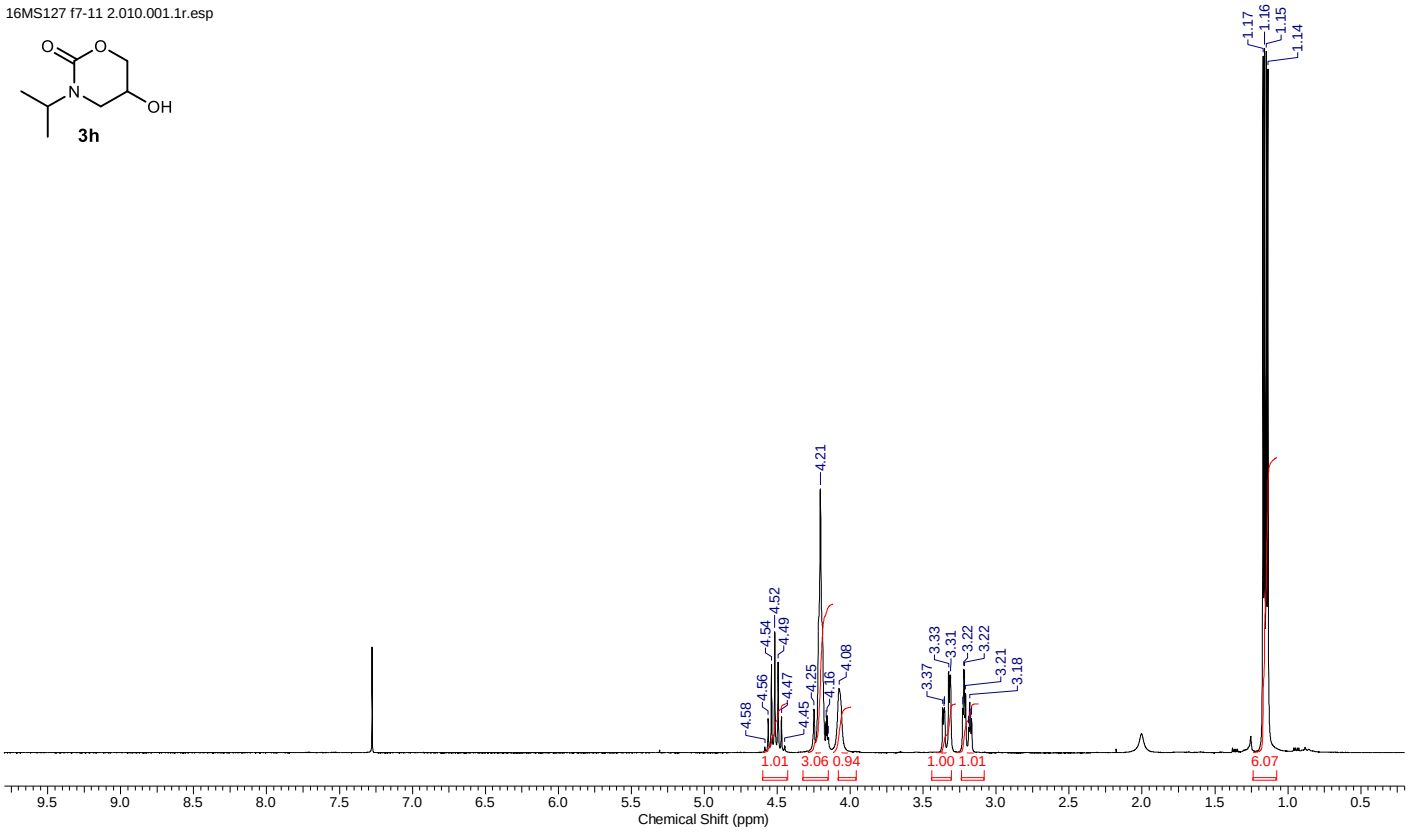
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3g

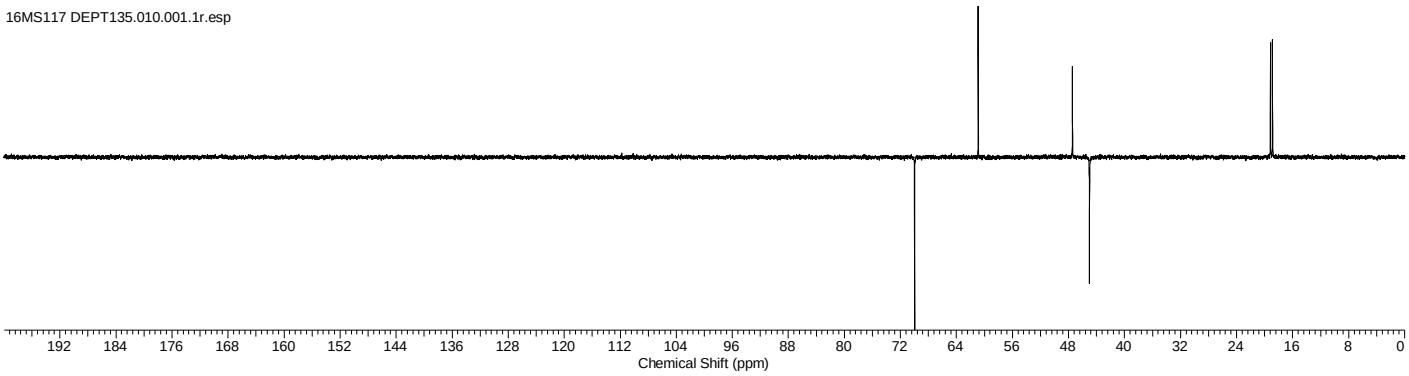


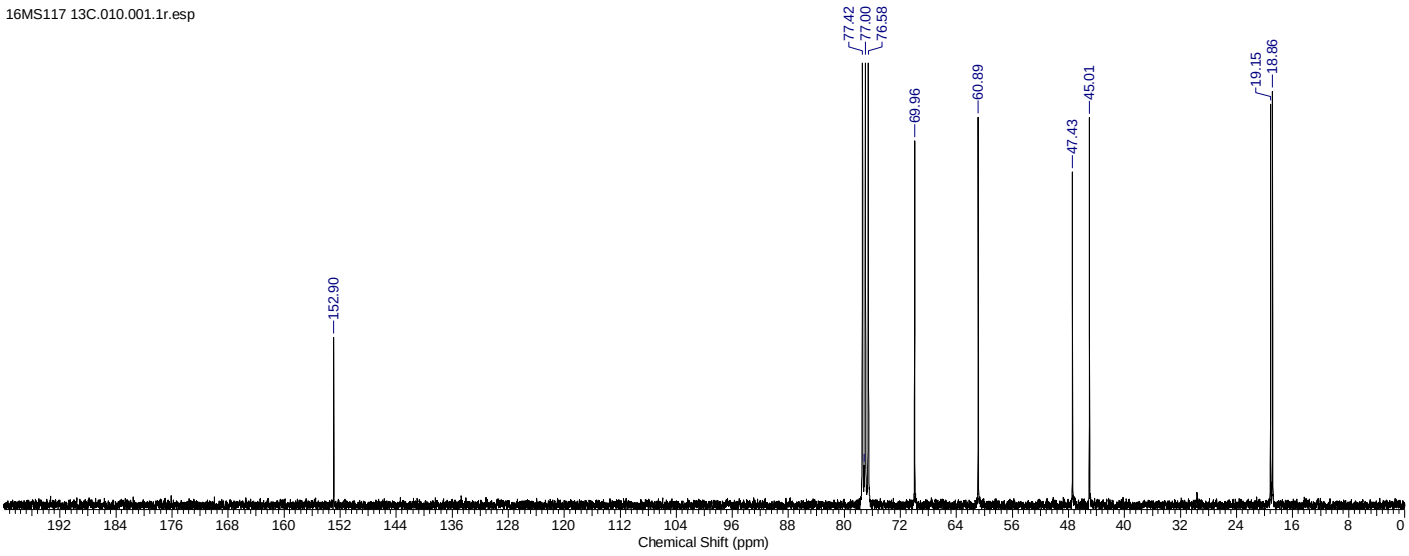



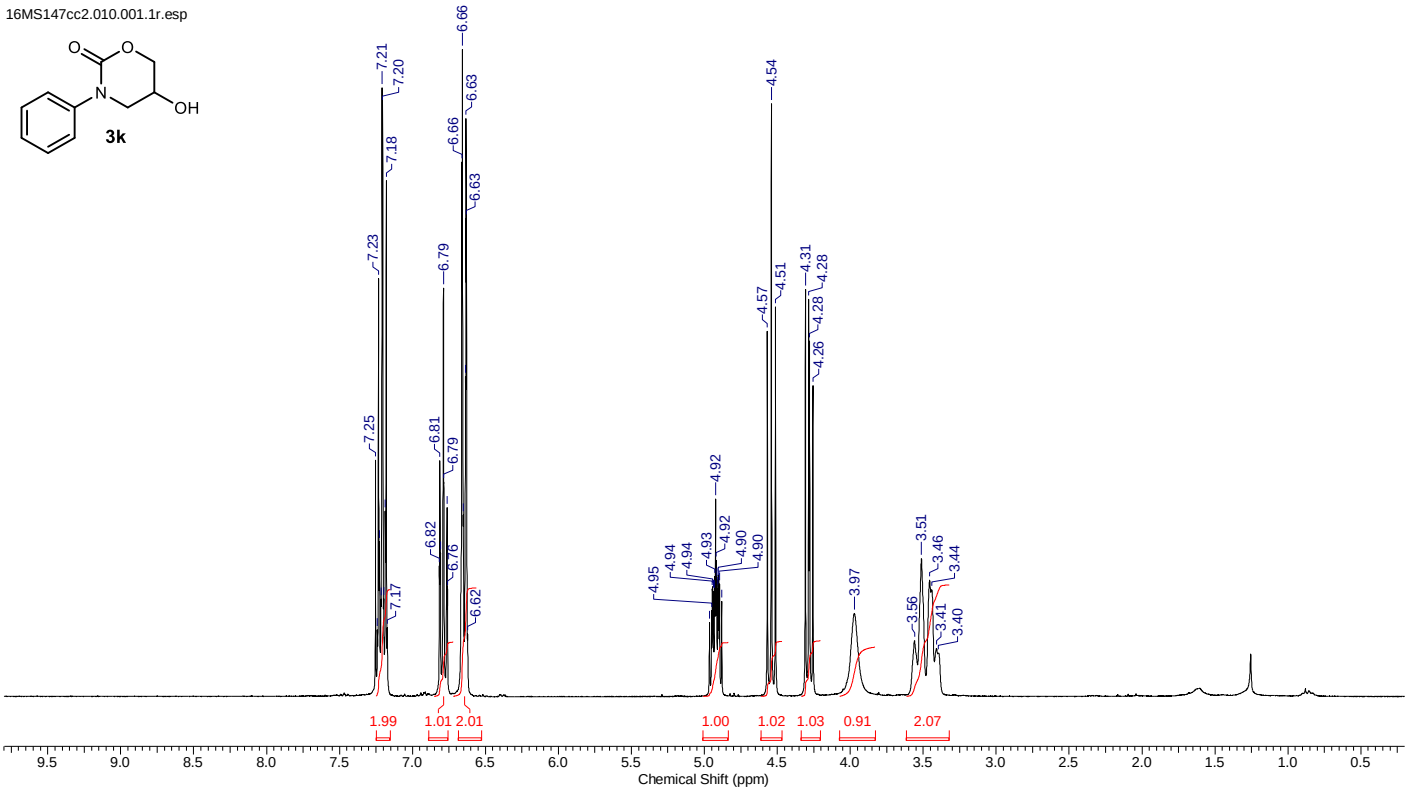
## $^{1}H$ (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3h

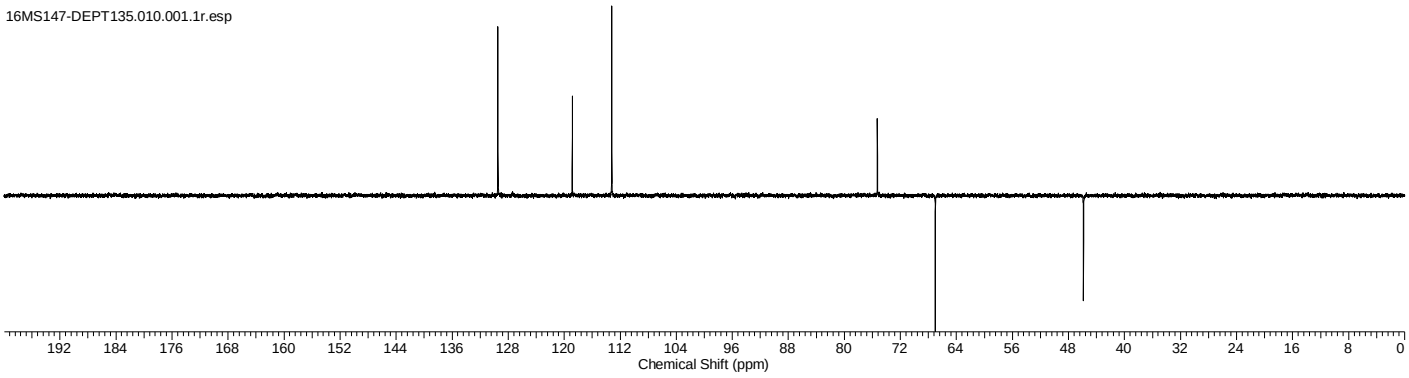


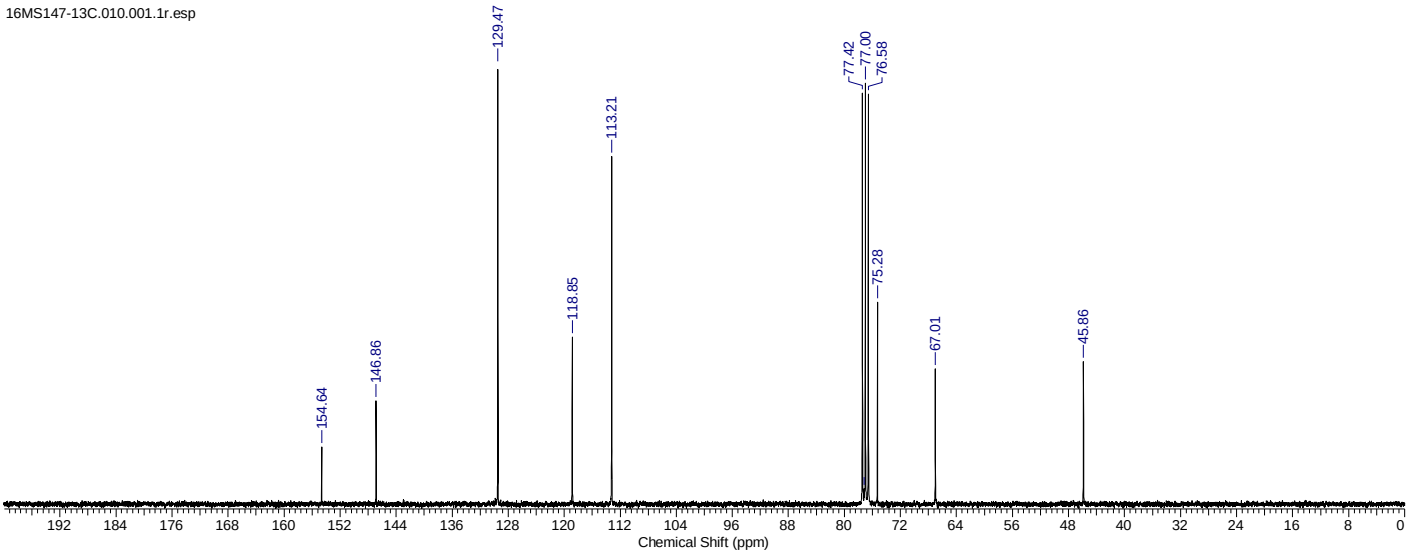



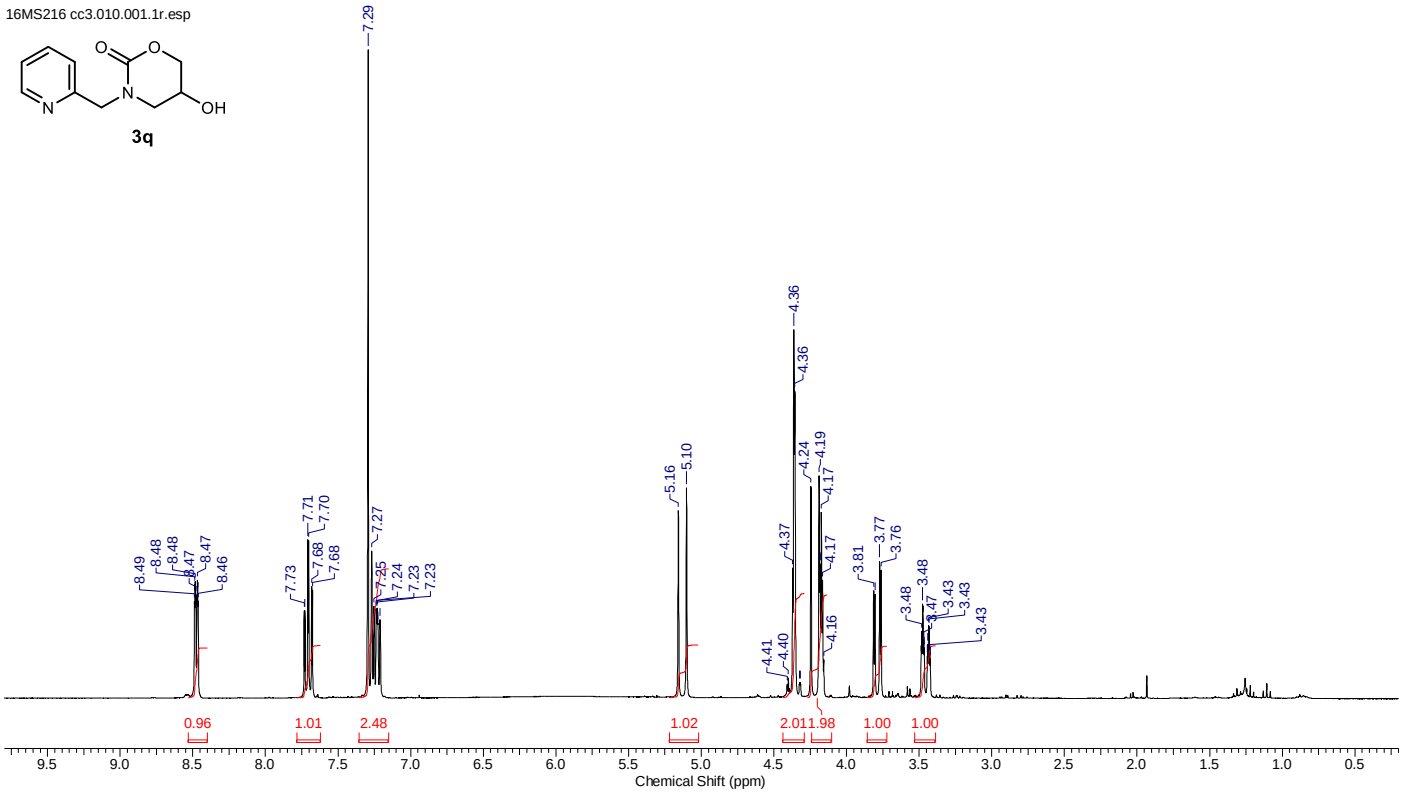
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3k

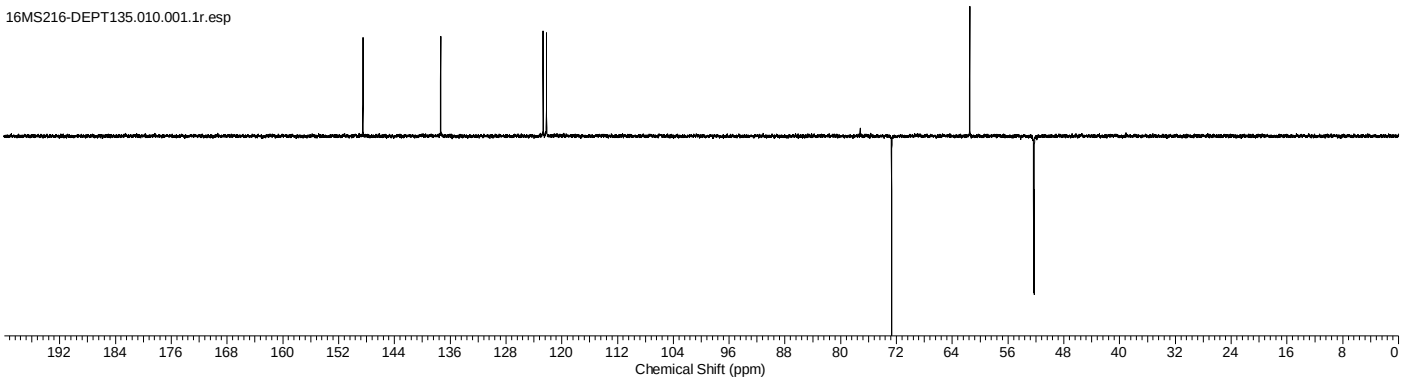


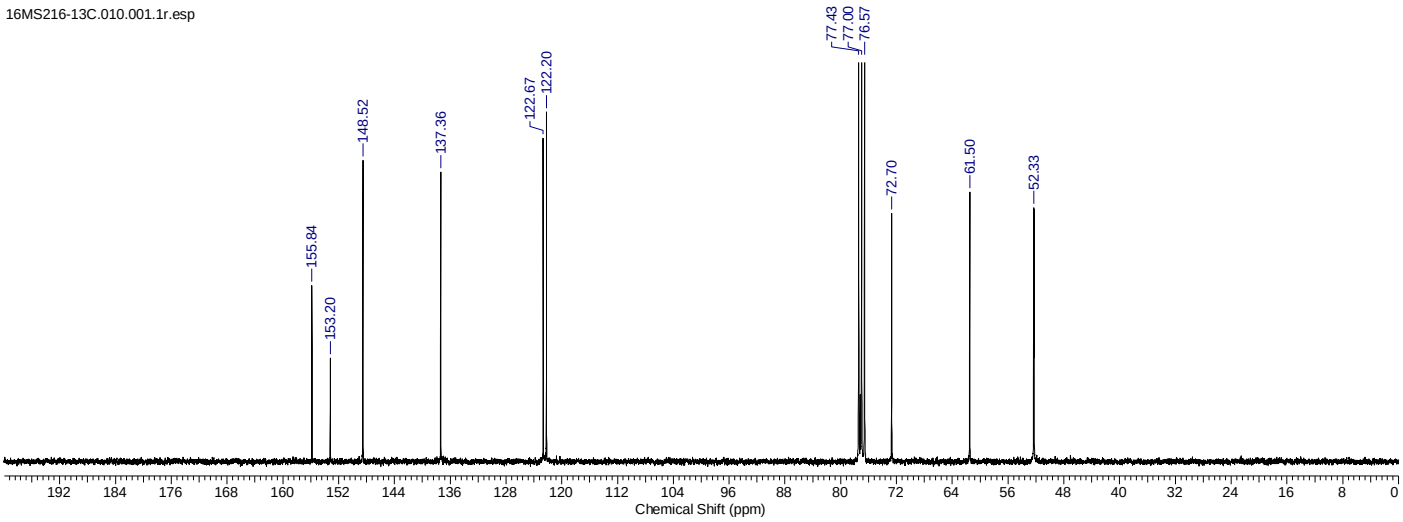



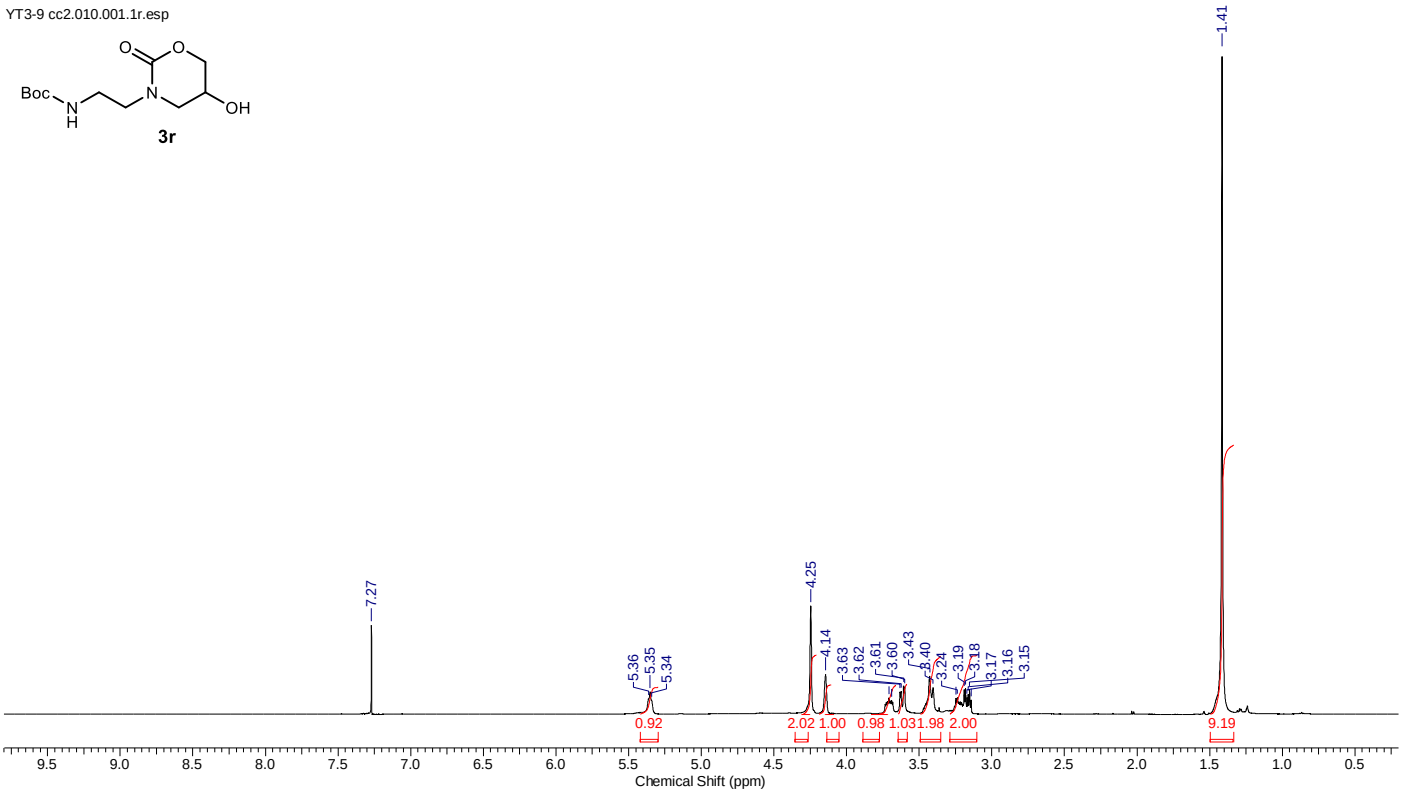
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3q

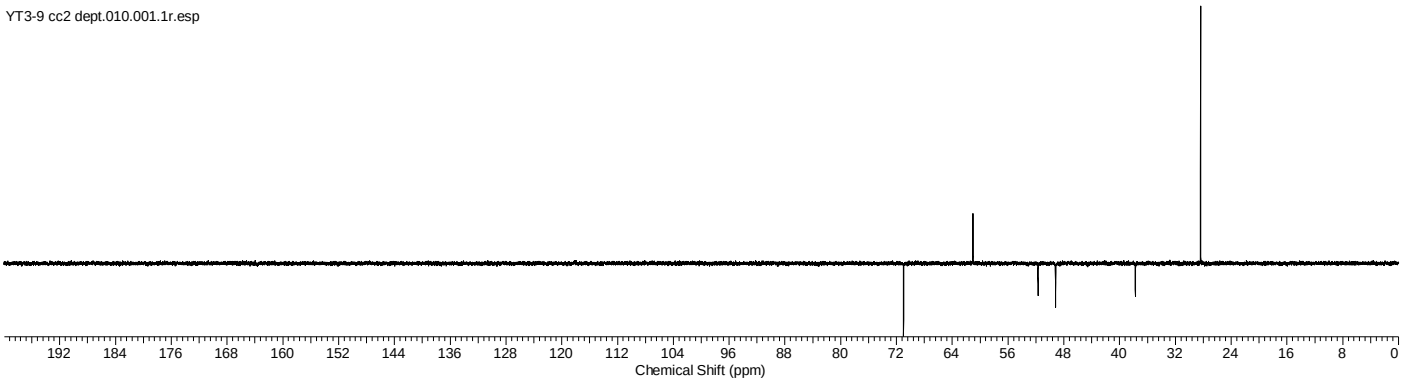


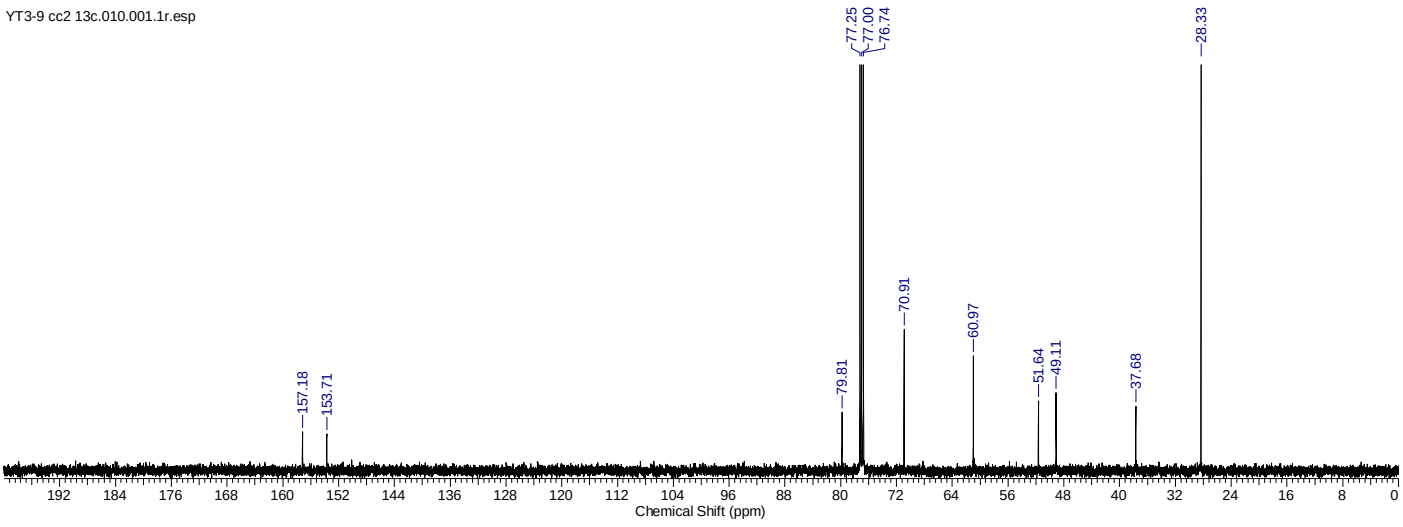



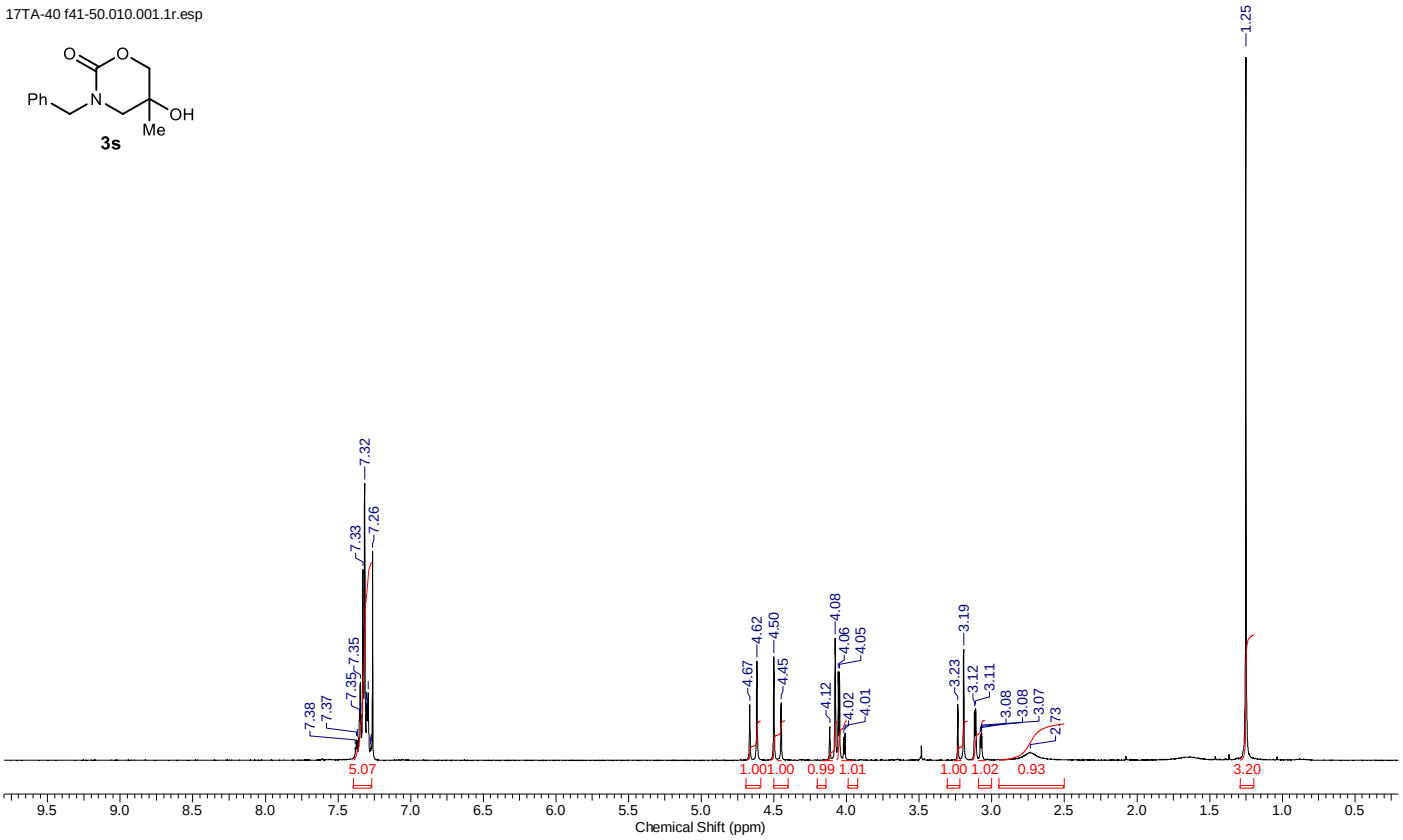
# $^{1}$H (500 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) Spectra of 3r

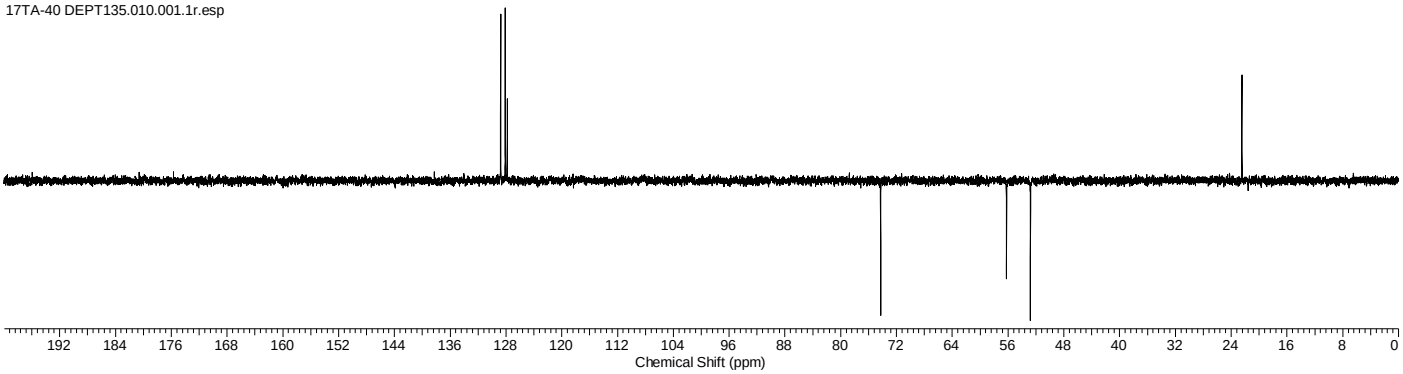


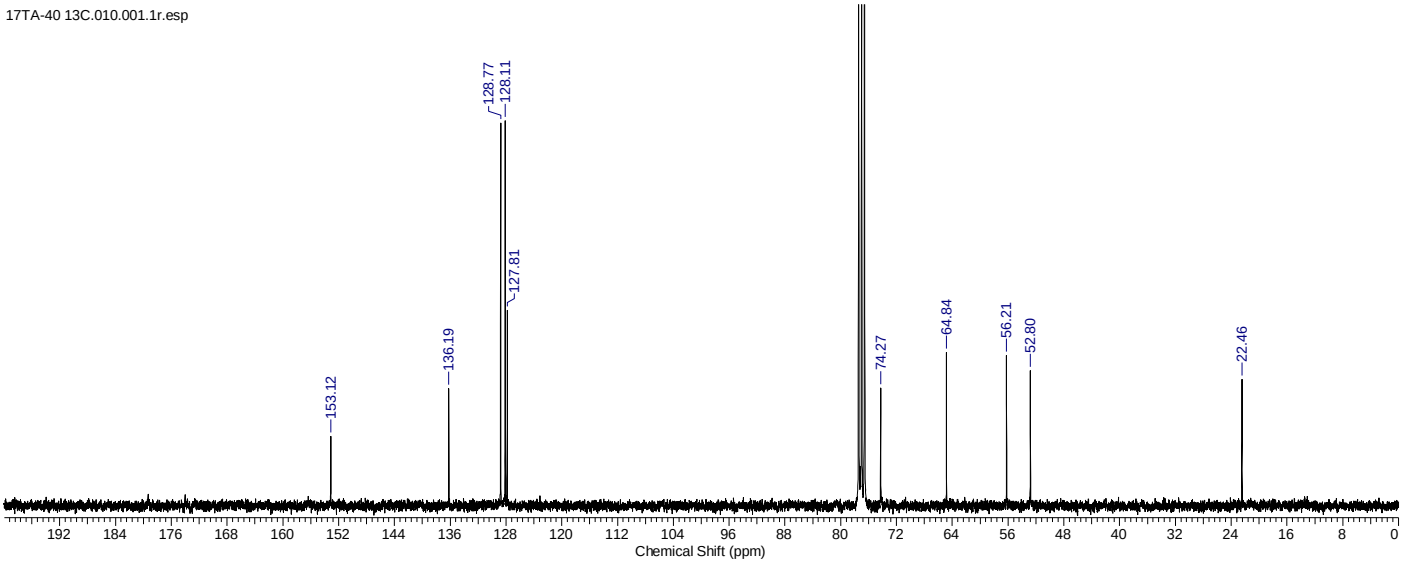



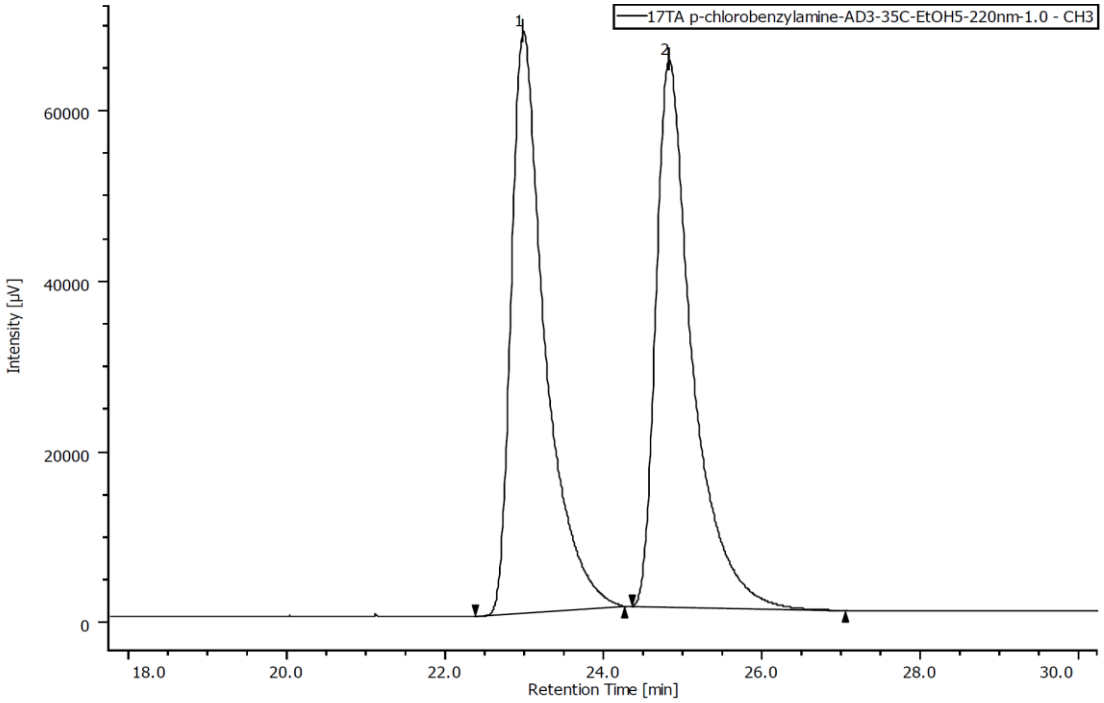
# $^{1}$H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3s



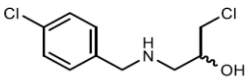



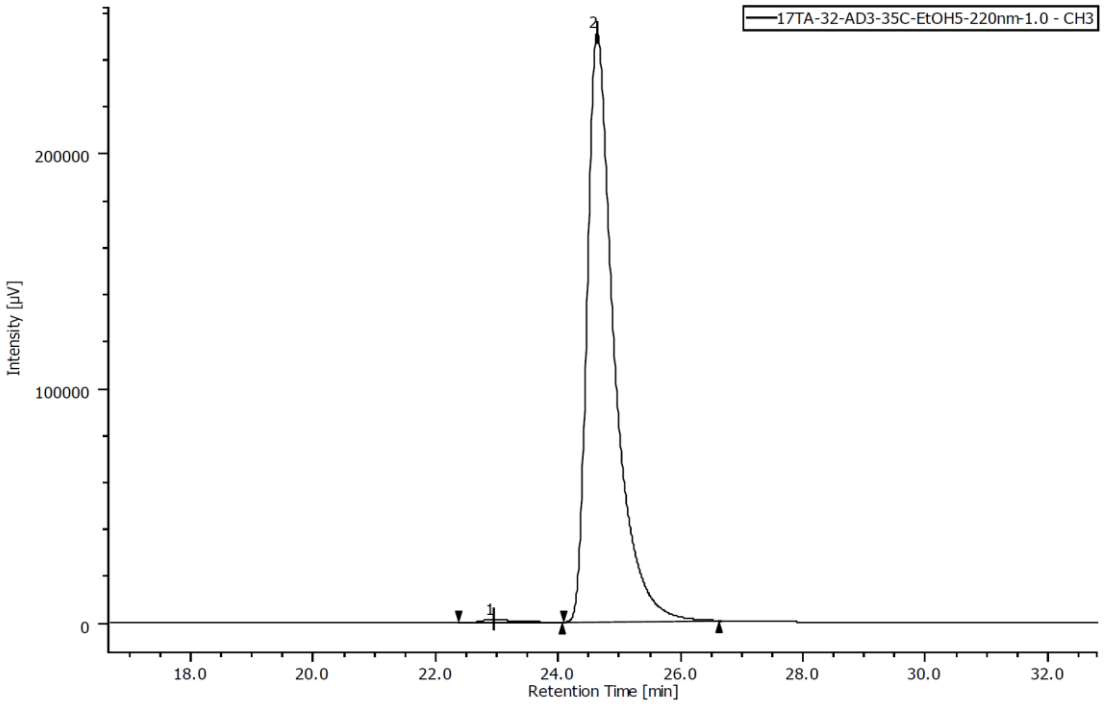



**HPLC Trace of 1d**

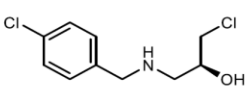



| # Peak | CH | tR (min) | Area | Height | Area% |
|---|---|---|---|---|---|
| 1 | 3 | 22.983 | 2014295 | 67989 | 49.702 |
| 2 | 3 | 24.825 | 2038429 | 64069 | 50.298 |

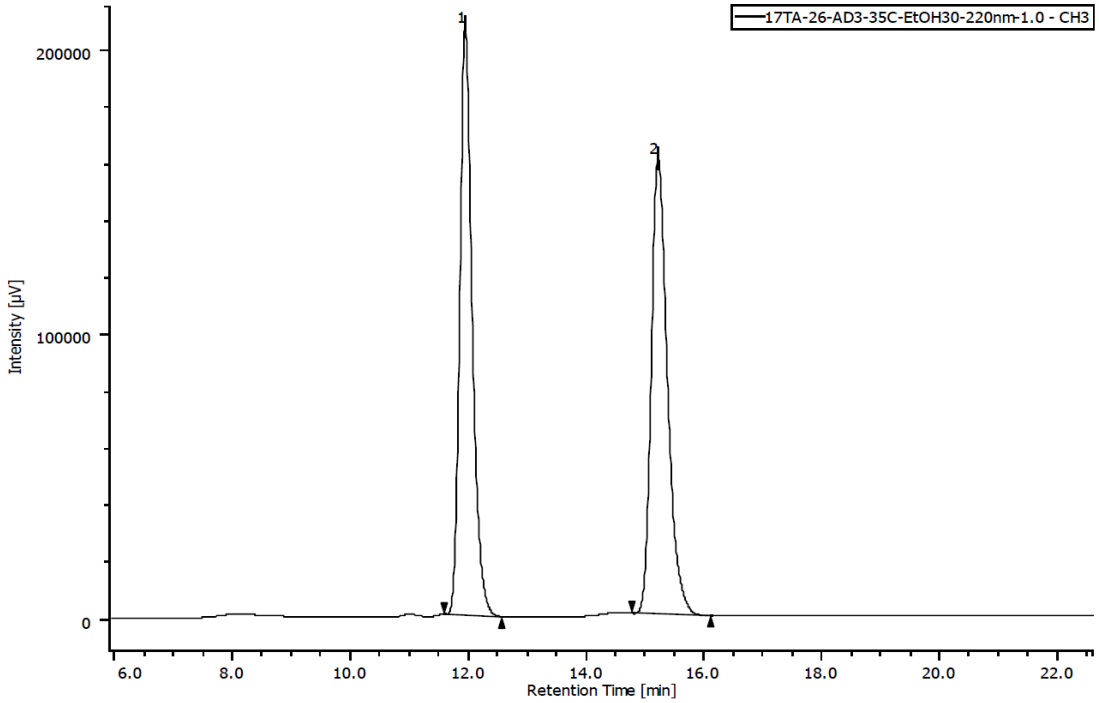




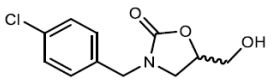

| # Peak | CH | tR (min) | Area | Height | Area% |
|---|---|---|---|---|---|
| 1 | 3 | 22.942 | 46612 | 1391 | 0.607 |
| 2 | 3 | 24.625 | 7634490 | 250387 | 99.393 |

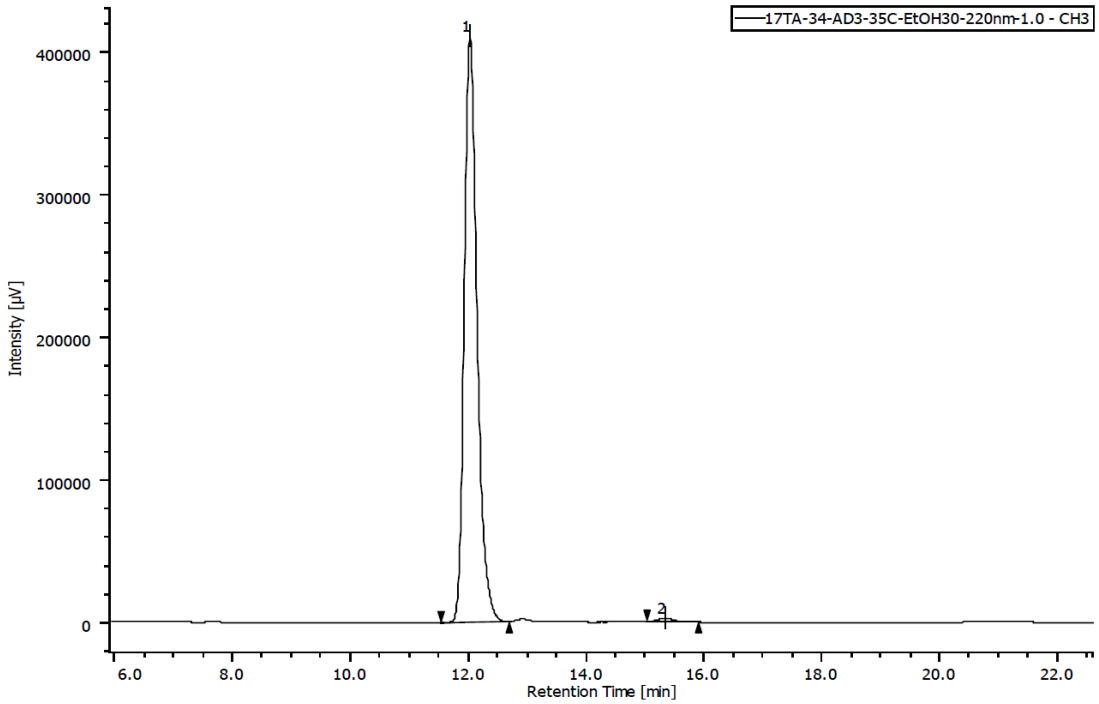


**HPLC Trace of 2d**

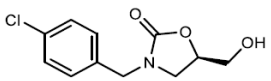



| # Peak | CH | tR (min) | Area | Height | Area% |
|---|---|---|---|---|---|
| 1 | 3 | 11.95 | 3043751 | 206182 | 50.018 |
| 2 | 3 | 15.217 | 3041582 | 159851 | 49.982 |

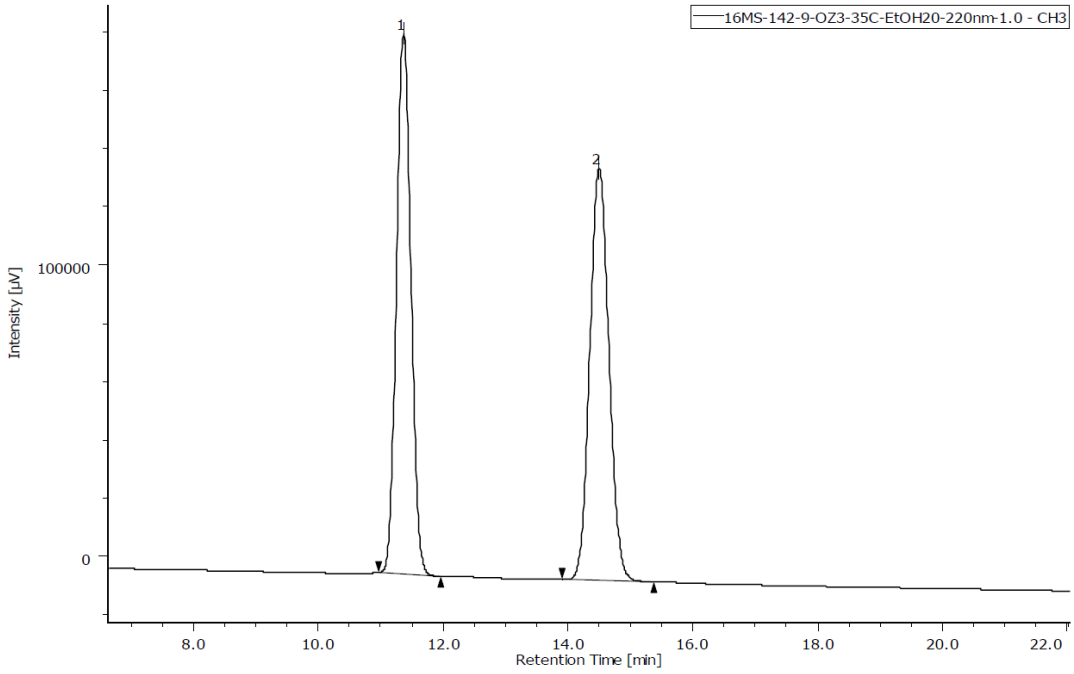




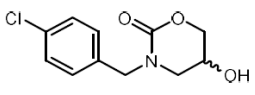

| # Peak | CH | tR (min) | Area | Height | Area% |
|---|---|---|---|---|---|
| 1 | 3 | 12.025 | 6194214 | 410128 | 99.314 |
| 2 | 3 | 15.333 | 42786 | 2396 | 0.686 |

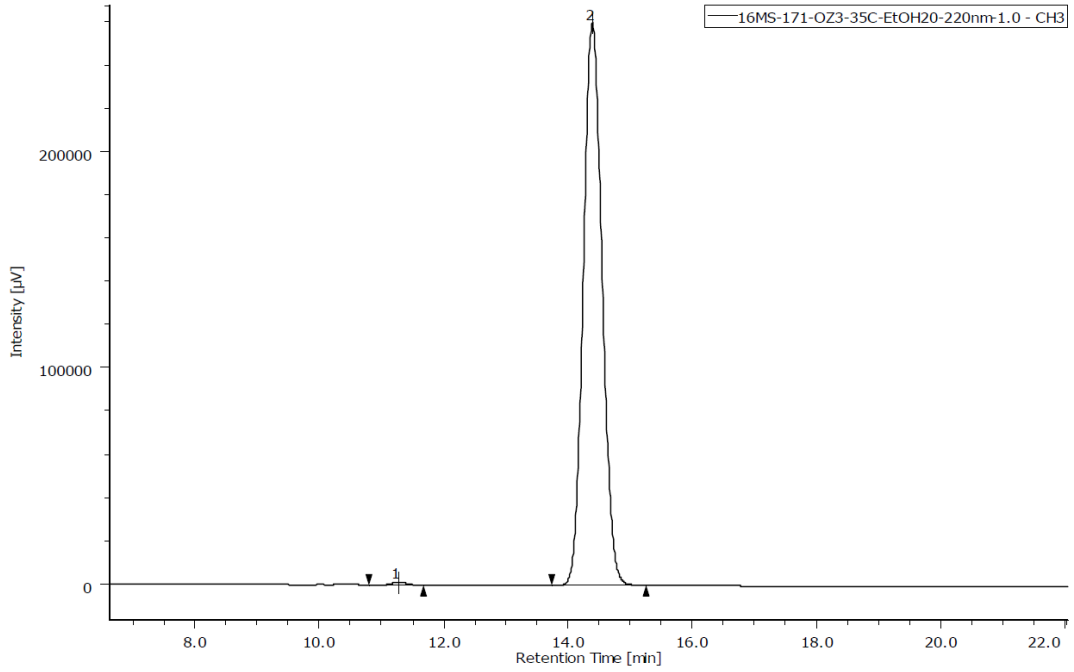


**HPLC Trace of 3d**




| # Peak | CH | tR (min) | Area | Height | Area% |
|---|---|---|---|---|---|
| 1 | 3 | 11.358 | 2979621 | 185292 | 49.764 |
| 2 | 3 | 14.483 | 3007880 | 141306 | 50.236 |




| # Peak | CH | tR (min) | Area | Height | Area% |
|---|---|---|---|---|---|
| 1 | 3 | 11.275 | 19257 | 1242 | 0.353 |
| 2 | 3 | 14.383 | 5436610 | 259632 | 99.647 |