Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2022

Electronic Supplementary Information

Tetraarylphosphonium salts-catalyzed formal [3+2] cycloaddition between epoxides and trichloroacetonitrile for the synthesis of β-amino alcohol derivatives

Yasunori Toda, Ryota Shiokawa, Masaya Iwasaki, Daisuke Yamaguchi, Keisuke Kawamura, Kimiya Sukegawa, and Hiroyuki Suga

Department of Materials Chemistry, Faculty of Engineering
Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

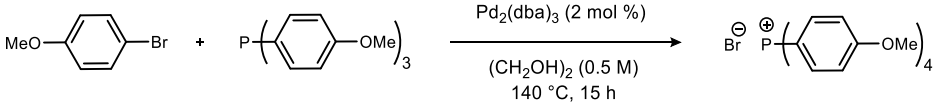
E-mail: ytoda@shinshu-u.ac.jp (Y.T.)

General information

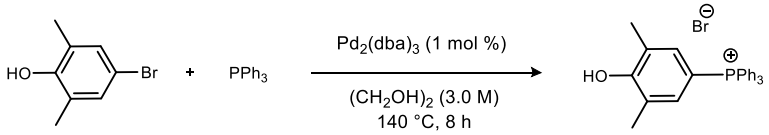
All reagents and solvents were commercial grade and purified prior to use when necessary. Thin layer chromatography (TLC) was performed using TLC aluminum sheets from Merck (silica gel 60 F_{254}, 200 μm), and flash chromatography utilized silica gel from Fuji Silysia Chemical (PSQ60B, 60 μm). Products were visualized by ultraviolet (UV) light and/or 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 (300 MHz). Chemical shifts are 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 DEPT135. 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. X-ray diffraction data were collected at 93 K using a Bruker SMART APEX2 diffractometer [Mo Kα radiation (λ = 0.71073 Å)].

Preparation of tetraarylphosphonium salts

$Ph_4P^+Br^-$ is commercially available. TAPA **A-C** were prepared according to the reported procedure.[1,2]

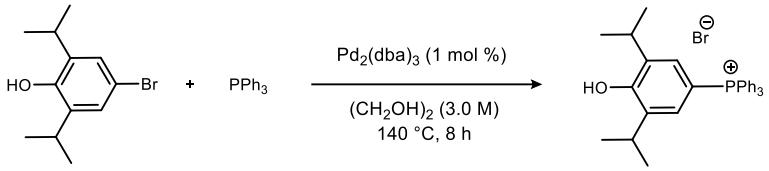


(4-MeOC$_6$H$_4$)$_4$P$^+$Br$^-$. To an oven-dried test tube equipped with a stir bar was added 4-bromoanisole (188.1 mg, 1.0 mmol), tris(4-methoxyphenyl)phosphine (352.4 mg, 1.0 mmol), ethylene glycol (2.0 mL), and $Pd_2(dba)_3$ (18.2 mg, 20 μmol). The atmosphere was replaced with argon (×3) using a diaphragm pump. After stirring at 140 °C for 15 h, the mixture was treated with H_2O (20 mL), and the aqueous layer was extracted with CH_2Cl_2 (15 mL×3). The organic layers were combined, washed with H_2O (30 mL×2), dried over Na_2SO_4, and concentrated. The crude material was triturated with THF (20 mL) to give a brownish powder (71.7 mg, 13%). R_f = 0.30 (CH_2Cl_2:MeOH = 10:1) visualized with $KMnO_4$; mp 249-250 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.45 (m, 8H), 7.26-7.21 (m, 8H), 3.97 (s, 12H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 164.8 (d, *J* = 2.8 Hz, C), 136.0 (d, *J* = 12.1 Hz, CH), 116.2 (d, *J* = 14.3 Hz, CH), 109.0 (d, *J* = 97.9 Hz, C), 56.1 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 20.5; IR (KBr) 3055, 1592, 1567, 1503, 1304, 1267, 1190, 1111, 1020, 836, 804 cm^{-1}; HRMS (ESI/TOF) m/z: $[M-Br]^+$ calcd for $C_{28}H_{28}O_4P$ 459.1720, found 459.1732.

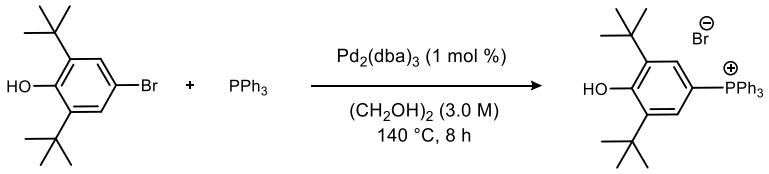


TAPS D. To an oven-dried test tube equipped with a stir bar was added 4-bromo-2,6-dimethylphenol (201.2 mg, 1.0 mmol), triphenylphosphine (394.1 mg, 1.5 mmol), ethylene glycol (0.33 mL), and $Pd_2(dba)_3$ (9.2 mg,

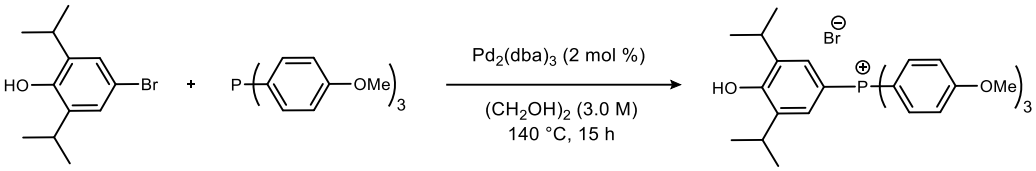
10 μmol). The atmosphere was replaced with argon (×3) using a diaphragm pump. After stirring at 140 °C for 8 h, the mixture was treated with H_2O (15 mL), and the aqueous layer was extracted with $CHCl_3$ (15 mL×3). The organic layers were combined, washed with H_2O (30 mL×2), dried over Na_2SO_4, and concentrated. The crude material was triturated with THF (25 mL) to give TAPS **D** as a white powder (253.2 mg, 59%, 5% of THF was included). R_f = 0.40 (CH_2Cl_2:MeOH = 10:1) visualized with $KMnO_4$; mp 255-256 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91-7.85 (m, 3H), 7.77-7.71 (m, 6H), 7.63-7.55 (m, 6H), 6.99 (d, *J* = 12.9 Hz, 2H), 2.42 (s, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 161.6 (d, *J* = 3.3 Hz, C), 135.2 (d, *J* = 2.8 Hz, CH), 134.2 (d, *J* = 9.9 Hz, CH), 134.1 (d, *J* = 11.0 Hz, CH), 130.4 (d, *J* = 12.7 Hz, CH), 128.7 (d, *J* = 14.9 Hz, C), 119.1 (d, *J* = 89.7 Hz, C), 102.7 (d, *J* = 96.8 Hz, C), 18.1 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.3; IR (KBr) 3386, 2988, 1587, 1483, 1437, 1306, 1278, 1204, 1118, 909, 724, 691 cm^{-1}; HRMS (ESI/TOF) m/z: [M-Br]$^+$ calcd for $C_{26}H_{24}OP$ 383.1599, found 383.1572.



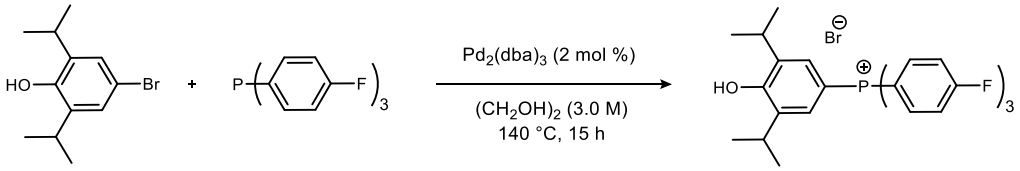
TAPS E. To an oven-dried test tube equipped with a stir bar was added 4-bromo-2,6-diisopropylphenol (257.2 mg, 1.0 mmol),[3] triphenylphosphine (394.1 mg, 1.5 mmol), ethylene glycol (0.33 mL), and $Pd_2(dba)_3$ (9.2 mg, 10 μmol). The atmosphere was replaced with argon (×3) using a diaphragm pump. After stirring at 140 °C for 8 h, the mixture was treated with H_2O (15 mL), and the aqueous layer was extracted with $CHCl_3$ (15 mL×3). The organic layers were combined, washed with H_2O (30 mL×2), dried over Na_2SO_4, and concentrated. The crude material was triturated with THF (25 mL) to give TAPS **E** as a white powder (397.2 mg, 76%). R_f = 0.25 (CH_2Cl_2:MeOH = 10:1) visualized with $KMnO_4$; mp 288-290 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93-7.87 (m, 3H), 7.79-7.72 (m, 6H), 7.64-7.56 (m, 6H), 7.06 (d, *J* = 13.4 Hz, 2H), 3.79 (sept d, *J* = 6.8, 1.1 Hz, 2H), 1.86 (br s, 1H), 1.10 (d, *J* = 6.8 Hz, 12H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 159.1 (d, *J* = 3.3 Hz, C), 138.8 (d, *J* = 13.8 Hz, C), 135.2 (d, *J* = 2.8 Hz, CH), 133.9 (d, *J* = 10.5 Hz, CH), 130.3 (d, *J* = 12.7 Hz, CH), 129.6 (d, *J* = 11.6 Hz CH), 118.9 (d, *J* = 89.7 Hz, C), 103.2 (d, *J* = 96.3 Hz, C), 27.0 (CH), 22.5 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.0; IR (KBr) 3393, 3087, 2965, 1593, 1567, 1503, 1464, 1442, 1296, 1266, 1187, 1151, 1111, 1019, 836, 804 cm^{-1}; HRMS (ESI/TOF) m/z: [M-Br]$^+$ calcd for $C_{30}H_{32}OP$ 439.2185, found 439.2203. A single crystal was grown in CH_2Cl_2/Hexane at 4 °C for X-ray crystallographic analysis.



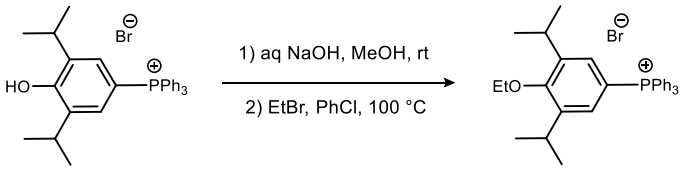
TAPS F. To an oven-dried test tube equipped with a stir bar was added 4-bromo-2,6-di-*tert*-butylphenol (285.4 mg, 1.0 mmol), triphenylphosphine (394.1 mg, 1.5 mmol), ethylene glycol (0.33 mL), and $Pd_2(dba)_3$ (9.2 mg, 10 μmol). The atmosphere was replaced with argon (×3) using a diaphragm pump. After stirring at 140 °C for 8 h, the mixture was treated with H_2O (15 mL), and the aqueous layer was extracted with $CHCl_3$ (15 mL×3). The organic layers were combined, washed with H_2O (30 mL×2), dried over Na_2SO_4, and concentrated. The crude material was triturated with THF (25 mL) to give TAPS **F** as a white powder (342.6 mg, 63%). R_f = 0.25 (CH_2Cl_2:MeOH = 10:1) visualized with $KMnO_4$; mp 283-284 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.90 (m, 3H), 7.85-7.78 (m, 6H), 7.66-7.59 (m, 6H), 7.28 (d, *J* = 13.8 Hz, 2H), 1.37 (s, 18H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 160.4 (d, *J* = 3.3 Hz, C), 139.1 (d, *J* = 13.2 Hz, C), 135.6 (d, *J* = 3.3 Hz, CH), 134.2 (d, *J* = 10.5 Hz, CH), 131.5 (d, *J* = 12.7 Hz, CH), 130.7 (d, *J* = 12.7 Hz, CH), 118.4 (d, *J* = 89.7 Hz, C), 105.4 (d, *J* = 96.3 Hz, C), 34.8 (C), 29.8 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.4; IR (KBr) 3429, 2951, 1442, 1427, 1150, 1106, 723, 694 cm^{-1}; HRMS (ESI/TOF) m/z: [M-Br]$^+$ calcd for $C_{32}H_{36}OP$ 467.2498, found 467.2516.



TAPS G. To an oven-dried test tube equipped with a stir bar was added 4-bromo-2,6-diisopropylphenol (257.2 mg, 1.0 mmol), tris(4-methoxyphenyl)phosphine (352.5 mg, 1.0 mmol), ethylene glycol (0.33 mL), and $Pd_2(dba)_3$ (18.3 mg, 20 μmol). The atmosphere was replaced with argon (×3) using a diaphragm pump. After stirring at 140 °C for 15 h, the mixture was treated with H_2O (15 mL), and the aqueous layer was extracted with CH_2Cl_2 (15 mL×3). The organic layers were combined, washed with H_2O (30 mL×2), dried over Na_2SO_4, and concentrated. The crude material was triturated with EtOAc/Hexane (0.5 mL/20 mL) and THF (15 mL) to give TAPS **G** as a white powder (362.1 mg, 59%). R_f = 0.40 (CH_2Cl_2:MeOH = 10:1) visualized with $KMnO_4$; mp 216-217 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.41 (m, 6H), 7.21-7.16 (m, 6H), 7.06 (d, *J* = 13.3 Hz, 2H), 3.96 (s, 9H), 3.72 (sept d, *J* = 6.9, 0.9 Hz, 2H), 2.04 (br s, 1H), 1.12 (d, *J* = 6.9 Hz, 12H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 164.6 (d, *J* = 2.8 Hz, C), 158.5 (d, *J* = 3.3 Hz, C), 138.4 (d, *J* = 13.2 Hz, C), 135.9 (d, *J* = 12.1 Hz, CH), 129.3 (d, *J* = 12.1 Hz, CH), 115.9 (d, *J* = 13.8 Hz CH), 110.0 (d, *J* = 97.4 Hz, C), 105.7 (d, *J* = 97.9 Hz, C), 56.0 (CH_3), 27.0 (CH), 22.7 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.0; IR (KBr) 3393, 3087, 2965, 1593, 1567, 1503, 1464, 1442, 1296, 1266, 1187, 1151, 1111, 1019, 836, 804 cm^{-1}; HRMS (ESI/TOF) m/z: [M-Br]$^+$ calcd for $C_{33}H_{38}O_4P$ 529.2502, found 529.2530.

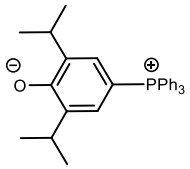


TAPS H. To an oven-dried test tube equipped with a stir bar was added 4-bromo-2,6-diisopropylphenol (128.9 mg, 0.50 mmol), tris(4-fluorophenyl)phosphine (158.6 mg, 0.50 mmol), ethylene glycol (0.17 mL), and $Pd_2(dba)_3$ (9.2 mg, 10 μmol). The atmosphere was replaced with argon (×3) using a diaphragm pump. After stirring at 140 °C for 15 h, the mixture was treated with H_2O (15 mL), and the aqueous layer was extracted with CH_2Cl_2 (15 mL×3). The organic layers were combined, washed with H_2O (30 mL×2), dried over Na_2SO_4, and concentrated. The crude material was triturated with EtOAc/Hexane (0.2 mL/15 mL) and THF (15 mL) to give TAPS **H** as a white powder (77.7 mg, 27%). R_f = 0.30 (CH_2Cl_2:MeOH = 10:1) visualized with $KMnO_4$; mp 245-247 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75-7.64 (m, 6H), 7.52-7.44 (m, 6H), 7.02 (d, *J* = 13.5 Hz, 2H), 3.72 (sept d, *J* = 6.6, 1.2 Hz, 2H), 1.92 (br s, 1H), 1.11 (d, *J* = 6.6 Hz, 12H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 166.8 (dd, *J* = 261.9, 3.6 Hz, C), 159.6 (d, *J* = 3.3 Hz, C), 139.2 (d, *J* = 13.8 Hz, C), 137.1 (dd, *J* = 12.1, 9.9 Hz, CH), 129.5 (d, *J* = 12.1 Hz, CH), 118.5 (dd, *J* = 22.0, 14.3 Hz, CH), 114.7 (dd, *J* = 94.6, 3.3 Hz, C), 102.9 (d, *J* = 97.9 Hz, C), 27.1 (CH), 22.6 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 21.7; IR (KBr) 3402, 2964, 1590, 1497, 1242, 1164, 1110, 831 cm^{-1}; HRMS (ESI/TOF) m/z: [M-Br]$^+$ calcd for $C_{30}H_{29}F_3O_4P$ 493.1903, found 493.1919.



TAPS I. To a solution of TAPS **E** (155.8 mg, 0.30 mmol) in MeOH (0.6 mL) was added 10 wt% NaOH aq (0.4 mL), and the mixture was then stirred at rt for 0.5 h. The mixture was treated with H_2O (5 mL), and the aqueous layer was extracted with CH_2Cl_2 (5 mL×3). The organic layers were combined, washed with H_2O (15 mL×2), dried over Na_2SO_4, filtered, and concentrated. The crude material was triturated with CH_2Cl_2/Hexane (1 mL/20 mL) to give betaine **S1** as a yellowish solid (110.5 mg). To an oven-dried test tube equipped with a stir bar was added **S1** (44.6 mg), PhCl (2.0 mL), MS4A (100 mg), and bromoethane (0.4 mL). The mixture

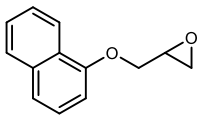
was then stirred at rt for 30 min. After stirring at 100 °C for 12 h, the resulting mixture was filtered by celite with CH_2Cl_2 (15 mL) and concentrated. The crude material was triturated with THF (5 mL) to give TAPS **I** as a white powder (36.4 mg, 66%). R_f = 0.25 ($CHCl_3$:MeOH = 30:1) visualized with $KMnO_4$; mp 202-203 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98-7.92 (m, 3H), 7.87-7.80 (m, 6H), 7.68-7.60 (m, 6H), 7.21 (d, *J* = 13.2 Hz, 2H), 3.96 (q, *J* = 6.9 Hz, 2H), 3.36 (septd, *J* = 6.9, 1.5 Hz, 2H), 1.51 (t, *J* = 6.9 Hz, 3H), 1.13 (d, *J* = 6.9 Hz, 12H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 160.2 (d, *J* = 3.9 Hz, C), 145.5 (d, *J* = 13.2 Hz, C), 135.8 (d, *J* = 2.8 Hz, CH), 134.2 (d, *J* = 9.9 Hz, CH), 130.8 (d, *J* = 12.7 Hz, CH), 130.6 (d, *J* = 11.0 Hz, CH), 117.9 (d, *J* = 89.7 Hz, C), 111.8 (d, $J_{C\text{-}P}$ = 91.3 Hz, C), 71.3 (CH_2), 26.9 (CH), 23.6 (CH_3), 15.8 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 23.1; IR (KBr) 3036, 2962, 2928, 2871, 1439, 1264, 1108, 1071, 1020, 758, 725, 693 cm^{-1}; HRMS (ESI/TOF) m/z: $[M\text{-}Br]^+$ calcd for $C_{32}H_{36}OP$ 467.2498, found 467.2484.



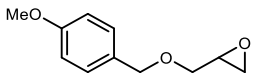
S1. 81% (3% of CH_2Cl_2 was included); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78-7.69 (m, 3H), 7.67-7.57 (m, 12H), 6.78 (d, *J* = 12.6 Hz, 2H), 3.53 (septd, *J* = 6.9, 0.9 Hz, 2H), 1.05 (d, *J* = 6.9 Hz, 12H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 174.9 (d, *J* = 1.7 Hz, C), 139.6 (d, *J* = 13.8 Hz, C), 134.0 (d, *J* = 9.9 Hz, CH), 133.7 (d, *J* = 3.3 Hz, CH), 129.4 (d, *J* = 12.1 Hz, CH), 128.2 (d, *J* = 12.7 Hz, CH), 123.0 (d, *J* = 89.1 Hz, C), 78.8 (d, *J* = 108.4 Hz, C), 26.6 (CH), 22.7 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 20.8; IR (KBr) 3057, 2952, 2861, 1581, 1504, 1436, 1136, 1104, 1071, 749, 723, 693 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_{30}H_{32}OP$ 439.2185, found 439.2186.

Preparation of epoxides

All epoxides are commercially available or prepared according to the reported procedure except for below.[1]

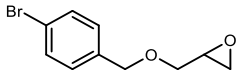


Glycidyl 1-naphthyl ether.[4] To a solution of 1-naphthol (721.0 mg, 5.0 mmol) in DMF (10 mL) was added NaH (60% dispersion in mineral oil, 132.1 mg, 5.5 mmol) at 0 °C. After stirring at 0 °C for 30 min, epichlorohydrin (771 µL, 10 mmol) was added and the reaction was allowed to warm up to rt. After stirring at rt for 12 h, the reaction was quenched with H_2O. The resulting mixture was extracted with Et_2O (30 mL×3). The organic layers were combined, washed with H_2O (40 mL×2) and brine (40 mL×1), dried over Na_2SO_4, and concentrated. Flash column chromatography (SiO_2 50 g, Hexane:EtOAc = 10:1-4:1) yielded a yellowish oil (732.0 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33-8.27 (m, 1H), 7.82-7.76 (m, 1H), 7.52-7.43 (m, 3H), 7.35 (dd, *J* = 8.1, 7.5 Hz, 1H), 6.80 (dd, *J* = 7.5, 0.9 Hz, 1H), 4.38 (dd, *J* = 11.1, 3.3 Hz, 1H), 4.13 (dd, *J* = 11.1, 5.7 Hz, 1H), 3.48 (dddd, *J* = 5.7, 4.2, 3.3, 2.7 Hz, 1H), 2.95 (dd, *J* = 4.8, 4.2 Hz, 1H), 2.84 (dd, *J* = 4.8, 2.7 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 154.2 (C), 134.5 (C), 127.4 (CH), 126.5 (CH), 125.7 (CH), 125.6 (C), 125.3 (CH), 122.0 (CH), 120.8 (CH), 105.0 (CH), 68.9 (CH_2), 50.2 (CH), 44.7 (CH_2).



Glycidyl 4-methoxylbenzyl ether.[5] To a solution of 4-methoxybenzyl alcohol (4.145 g, 30 mmol) and TBAB (0.485 g, 1.5 mmol, 5 mol %) in 40 wt% NaOH aq (40 mL) was added epichlorohydrin (9.41 mL, 120 mmol) at 0 °C. After stirring at 0 °C for 24 h, the resulting mixture was extracted with Et_2O (30 mL×3). The organic layers were combined, dried over Na_2SO_4, and concentrated. Flash column chromatography (SiO_2 50 g, Hexane:EtOAc = 10:1-3:1) yielded a colorless oil (2.006 g, 34%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 6.91-6.86 (m, 2H), 4.55 (d, *J* = 11.4 Hz, 1H), 4.49 (d, *J* = 11.4 Hz, 1H), 3.81 (s, 3H), 3.73 (dd, *J* =

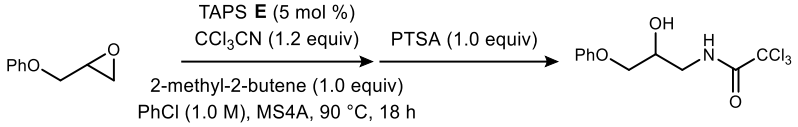
11.4, 3.0 Hz, 1H), 3.42 (dd, *J* = 11.4, 5.7 Hz, 1H), 3.19 (ddt, *J* = 5.7, 4.2, 3.0 Hz, 1H), 2.80 (dd, *J* = 5.1, 4.2 Hz, 1H), 2.61 (dd, *J* = 5.1, 3.0 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 159.2 (C), 129.9 (C), 129.4 (CH), 113.8 (CH), 72.9 (CH_2), 70.5 (CH_2), 55.2 (CH_3), 50.8 (CH), 44.3 (CH_2).



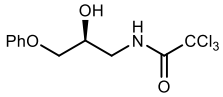
4-Bromobenzyl glycidyl ether.[6] To a solution of 4-bromobenzyl alcohol (5.621 g, 30 mmol) and TBAB (0.485 g, 1.5 mmol, 5 mol %) in 40 wt% NaOH aq (40 mL) was added epichlorohydrin (9.41 mL, 120 mmol) at 0 °C. After stirring at 0 °C for 24 h, the resulting mixture was extracted with Et_2O (30 mL×3). The organic layers were combined, dried over Na_2SO_4, and concentrated. Flash column chromatography (SiO_2 50 g, Hexane:EtOAc = 8:1-5:1) yielded a colorless oil (2.411 g, 33%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.45 (m, 2H), 7.25-7.20 (m, 2H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 3.79 (dd, *J* = 11.4, 2.7 Hz, 1H), 3.41 (dd, *J* = 11.4, 6.0 Hz, 1H), 3.19 (ddt, *J* = 6.0, 4.2, 2.7 Hz, 1H), 2.81 (dd, *J* = 5.1, 4.2 Hz, 1H), 2.62 (dd, *J* = 5.1, 2.7 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 136.9 (C), 131.5 (CH), 129.3 (CH), 121.6 (CH), 72.5 (CH_2), 70.9 (CH_2), 50.8 (CH), 44.1 (CH_2).

General procedure for [3+2] reactions followed by hydrolysis

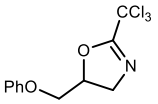
To an oven-dried 10 mL test tube equipped with a stir bar was added epoxide **1** (1.5 mmol, 1.0 equiv), TAPS **E** (39.0 mg, 75 μmol, 5 mol %), PhCl (1.5 mL, 1.0 M), MS4A (150 mg), trichloroacetonitrile (182 μL, 1.8 mmol, 1.2 equiv), and 2-methyl-2-butene (159 μL, 1.5 mmol). The atmosphere was replaced with argon (×3) using a diaphragm pump. After stirring at 90 °C for 18 h, the mixture was filtered through a pad of celite with $CHCl_3$ (40 mL) and then the filtered solution was concentrated. The unpurified material in a 50 mL round-bottom flask was diluted with PhCl (15 mL). *p*-TsOH•H_2O (285.4 mg, 1.5 mmol) was added into the flask at rt. After stirring at rt for 3 h, the mixture was treated with satd aq $NaHCO_3$ (30 mL). The aqueous layer was extracted with $CHCl_3$ (30 mL×3). The organic layers were combined, washed with H_2O (100 mL), dried over Na_2SO_4, filtered, and concentrated. Flash column chromatography yielded β-amino alcohol **4**.



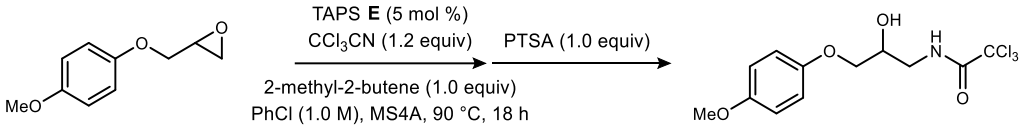
2,2,2-Trichloro-*N*-(2-hydroxy-3-phenoxypropyl)acetamide (4a). Prepared according to the general procedure using glycidyl phenyl ether (225.4 mg, 1.5 mmol). Flash column chromatography (SiO_2 24 g, Hexane:EtOAc = 8:1-5:1) yielded a white solid (348.8 mg, 74%). R_f = 0.25 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 75-77 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.27 (m, 3H), 7.02-6.97 (m, 1H), 6.92-6.88 (m, 2H), 4.27-4.20 (m, 1H), 4.07 (dd, *J* = 9.6, 3.9 Hz, 1H), 3.97 (dd, *J* = 9.6, 6.3 Hz, 1H), 3.75 (ddd, *J* = 14.1, 6.3, 3.9 Hz, 1H), 3.55 (ddd, *J* = 14.1, 6.6, 5.1 Hz, 1H), 2.86 (br s, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 162.6 (C), 158.0 (C), 129.7 (CH), 121.6 (CH), 114.5 (CH), 92.4 (C), 69.5 (CH_2), 68.6 (CH), 43.8 (CH_2); IR (KBr) 3407, 3278, 3047, 2918, 2867, 1686, 1601, 1535, 1497, 1335, 1236, 1120, 887, 822, 745, 689, 665 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{12}Cl_3NNaO_3$ 333.9775, found 333.9762.



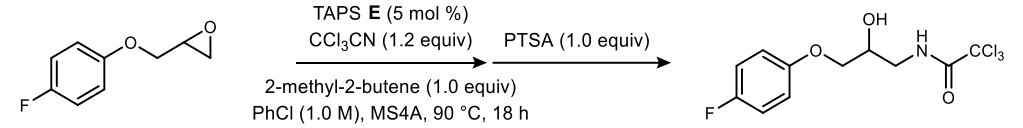
(*S*)-4a. Prepared according to the general procedure using epoxide (*S*)-**1a** (90.1 mg, 0.60 mmol). Flash column chromatography (SiO_2 24 g, Hexane:EtOAc = 8:1-5:1) yielded a white solid (133.1 mg, 71%). The product was determined to be 99% ee by chiral HPLC analysis (Chiralpak AD-3, Hexane:^{i}PrOH = 95:5, 1.0 mL/min, t_r(*minor*) = 29.7 min, t_r(*major*) = 34.2 min, 220 nm, 35 °C); $[\alpha]_D^{27}$ -3.9 (*c* 0.30, $CHCl_3$). The absolute configuration was confirmed by X-ray crystallographic analysis.



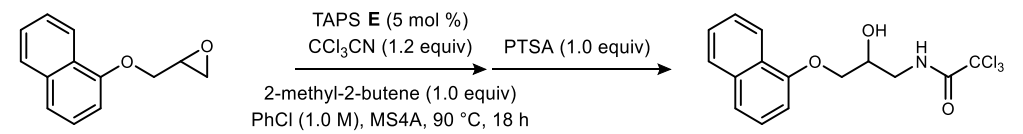
5-(Phenoxymethyl)-2-(trichloromethyl)-4,5-dihydro-1,3-oxazole (2a). R_f = 0.40 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 53-55 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.27 (m, 2H), 7.02-6.96 (m, 1H), 6.94-6.89 (m, 2H), 5.28-5.20 (m, 1H), 4.25 (dd, *J* = 15.3, 9.9 Hz, 1H), 4.19 (dd, *J* = 10.5, 3.9 Hz, 1H), 4.13 (dd, *J* = 10.5, 4.2 Hz, 1H), 4.11 (dd, *J* = 15.3, 7.2 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.5 (C), 158.2 (C), 129.6 (CH), 121.6 (CH), 114.6 (CH), 86.4 (C), 81.4 (CH), 68.2 (CH_2), 57.1 (CH_2); IR (KBr) 2970, 1666, 1600, 1491, 1447, 1227, 1060, 1014, 872, 826, 801, 762, 659 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{10}Cl_3NNaO_2$ 315.9669, found 315.9661.



2,2,2-Trichloro-*N*-[2-hydroxy-3-(4-methoxyphenoxy)propyl]acetamide (4b). Prepared according to the general procedure using glycidyl 4-methoxyphenyl ether (270.4 mg, 1.5 mmol). Flash column chromatography (SiO_2 24 g, Hexane:EtOAc = 8:1-2:1) yielded a white solid (346.4 mg, 67%). R_f = 0.25 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 54-55 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (br s, 1H), 6.87-6.80 (m, 4H), 4.25-4.16 (m, 1H), 4.02 (dd, *J* = 9.6, 4.2 Hz, 1H), 3.92 (dd, *J* = 9.6, 6.3 Hz, 1H), 3.77 (s, 3H), 3.73 (ddd, *J* = 13.8, 6.3, 3.9 Hz, 1H), 3.53 (ddd, *J* = 13.8, 6.6, 5.4 Hz, 1H), 2.90 (d, *J* = 4.5 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.6 (C), 154.4 (C), 152.2 (C), 115.5 (CH), 114.8 (CH), 92.4 (C), 70.4 (CH_2), 68.6 (CH), 55.7 (CH_3), 43.9 (CH_2); IR (KBr) 3456, 3391, 2939, 2839, 1684, 1512, 1231, 1032, 824, 734 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{14}Cl_3NNaO_4$ 363.9881, found 363.9869.

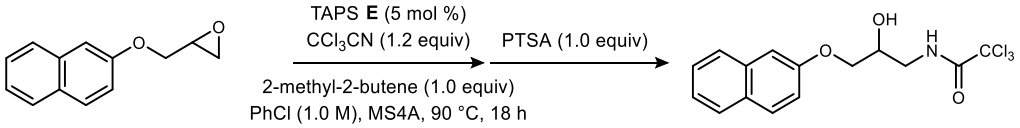


2,2,2-Trichloro-*N*-[2-hydroxy-3-(4-fluorophenoxy)propyl]acetamide (4c). Prepared according to the general procedure using 4-fluorophenyl glycidyl ether (252.5 mg, 1.5 mmol). Flash column chromatography (SiO_2 24 g, Hexane:EtOAc = 8:1-2:1) yielded a yellowish oil (311.6 mg, 63%). R_f = 0.25 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (br s, 1H), 7.03-6.95 (m, 2H), 6.88-6.81 (m, 2H), 4.27-4.19 (m, 1H), 4.03 (dd, *J* = 9.6, 3.9 Hz, 1H), 3.93 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.74 (ddd, *J* = 14.1, 6.3, 3.9 Hz, 1H), 3.54 (ddd, *J* = 14.1, 6.6, 5.4 Hz, 1H), 2.82 (d, *J* = 4.2 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.7 (C), 157.7 (d, *J* = 239.3 Hz, C), 154.2 (d, *J* = 2.2 Hz, C), 116.0 (d, *J* = 23.1 Hz, CH), 115.6 (d, *J* = 7.7 Hz, CH), 92.4 (C), 70.3 (CH_2), 68.6 (CH), 43.8 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ -122.7; IR (KBr) 3419, 3355, 2926, 1700, 1507, 1248, 1211, 825, 762 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{11}Cl_3FNNaO_3$ 351.9681, found 351.9670.

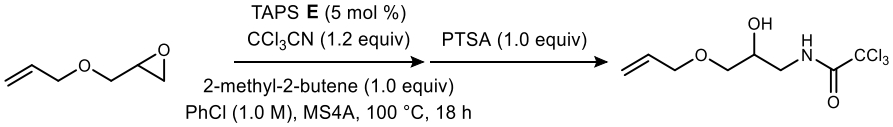


2,2,2-Trichloro-*N*-[2-hydroxy-3-(naphthalen-1-yloxy)propyl]acetamide (4d). Prepared according to the general procedure using glycidyl 1-naphthyl ether (300.5 mg, 1.5 mmol). Flash column chromatography (SiO_2 24 g, Hexane:EtOAc = 8:1-2:1) yielded a white solid (368.7 mg, 68%). R_f = 0.25 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 77-78 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24-8.17 (m, 1H), 7.85-7.77 (m, 1H), 7.54-7.45 (m, 3H), 7.37 (dd, *J* = 8.1, 7.8 Hz, 1H), 7.30 (br s, 1H), 6.81 (dd, *J* = 7.5, 0.6 Hz, 1H), 4.42-4.34 (m, 1H), 4.22 (dd, *J* = 9.6, 4.2 Hz, 1H), 4.14 (dd, *J* = 9.6, 6.3 Hz, 1H), 3.83 (ddd, *J* = 14.1, 6.3, 3.6 Hz, 1H), 3.63

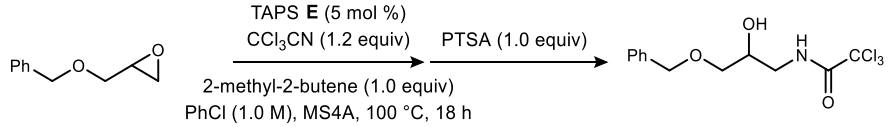
(ddd, *J* = 14.1, 7.2, 5.4 Hz, 1H), 2.91 (br d, *J* = 4.2 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 162.7 (C), 153.7 (C), 134.5 (C), 127.7 (CH), 126.6 (CH), 125.7 (CH), 125.5 (CH), 125.3 (C), 121.4 (CH), 121.3 (CH), 105.1 (CH), 92.4 (C), 69.7 (CH_2), 68.9 (CH), 43.9 (CH_2); IR (KBr) 3407, 3319, 3052, 2937, 1688, 1523, 1394, 1273, 1107, 822, 769 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{14}Cl_3NNaO_3$ 383.9931, found 383.9912.



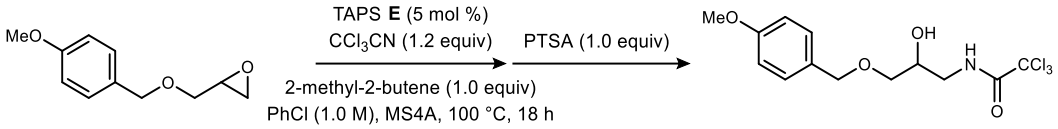
2,2,2-Trichloro-*N*-[2-hydroxy-3-(naphthalen-2-yloxy)propyl]acetamide (4e). Prepared according to the general procedure using glycidyl 2-naphthyl ether (300.4 mg, 1.5 mmol). Flash column chromatography (SiO_2 24 g, Hexane:EtOAc = 8:1-2:1) yielded a white solid (350.6 mg, 64%). R_f = 0.25 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 95-96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.72 (m, 3H), 7.46 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.36 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.33-7.29 (m, 1H), 7.16-7.12 (m, 2H), 4.34-4.26 (m, 1H), 4.18 (dd, *J* = 9.6, 3.9 Hz, 1H), 4.08 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.79 (ddd, *J* = 14.1, 6.3, 3.9 Hz, 1H), 3.58 (ddd, *J* = 14.1, 6.6, 5.4 Hz, 1H), 2.85 (d, *J* = 3.9 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 162.7 (C), 155.9 (C), 134.3 (C), 129.7 (CH), 129.3 (C), 127.7 (CH), 126.8 (CH), 126.6 (CH), 124.1 (CH), 118.3 (CH), 107.0 (CH), 92.4 (C), 69.6 (CH_2), 68.6 (CH), 43.9 (CH_2); IR (KBr) 3492, 3295, 3055, 2931, 2872, 1692, 1628, 1600, 1514, 1391, 1262, 1215, 1183, 1036, 839, 824, 749, 662 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{14}Cl_3NNaO_3$ 383.9931, found 383.9939.



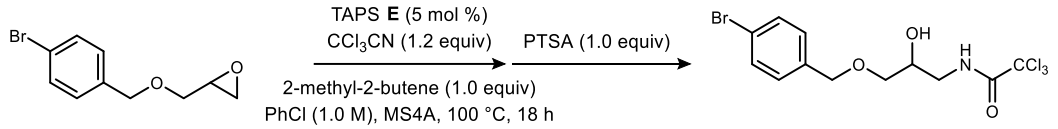
2,2,2-Trichloro-*N*-[2-hydroxy-3-(prop-2-en-1-yloxy)propyl]acetamide (4f). Prepared according to the general procedure using allyl glycidyl ether (171.3 mg, 1.5 mmol) at 100 °C for 18 h. Flash column chromatography (SiO_2 24 g, CH_2Cl_2-CH_2Cl_2:EtOAc = 70:1) yielded a white solid (218.8 mg, 53%). R_f = 0.35 (CH_2Cl_2:EtOAc = 2:1) visualized with $KMnO_4$; mp 44-45 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (br s, 1H), 5.90 (ddt, *J* = 17.1, 10.5, 5.7 Hz, 1H), 5.29 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.23 (dq, *J* = 10.5, 1.5 Hz, 1H), 4.05-3.97 (m, 3H), 3.64 (ddd, *J* = 13.8, 6.3, 3.9 Hz, 1H), 3.57 (dd, *J* = 9.6, 3.9 Hz, 1H), 3.45 (dd, *J* = 9.6, 6.3 Hz, 1H), 3.40 (ddd, *J* = 13.8, 6.3, 4.8 Hz, 1H), 2.72 (d, *J* = 4.5 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 162.4 (C), 133.9 (CH), 117.9 (CH_2), 92.5 (C), 72.5 (CH_2), 71.8 (CH_2), 68.5 (CH), 44.1 (CH_2); IR (KBr) 3422, 3278, 2852, 1687, 1676, 1535, 1430, 1333, 1229, 1119, 821, 743, 662 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_8H_{12}Cl_3NNaO_3$ 297.9775, found 297.9775.



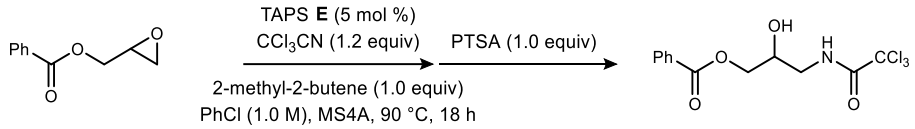
***N*-[3-(Benzyloxy)-2-hydroxypropyl]-2,2,2-trichloroacetamide (4g).** Prepared according to the general procedure using benzyl glycidyl ether (246.4 mg, 1.5 mmol) at 100 °C for 18 h. Flash column chromatography (SiO_2 24 g, Hexane:EtOAc = 8:1-5:1) yielded a white solid (287.5 mg, 57%). R_f = 0.40 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 45-46 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.28 (m, 6H), 4.57 (d, *J* = 11.7 Hz, 1H), 4.53 (d, *J* = 11.7 Hz, 1H), 4.04-3.97 (m, 1H), 3.62 (ddd, *J* = 13.8, 6.3, 4.2 Hz, 1H), 3.59 (dd, *J* = 9.6, 3.9 Hz, 1H), 3.49 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.40 (ddd, *J* = 13.8, 6.3, 5.1 Hz, 1H), 2.79 (br s, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 162.4 (C), 137.2 (C), 128.6 (CH), 128.1 (CH), 127.9 (CH), 92.4 (C), 73.7 (CH_2), 71.9 (CH_2), 68.5 (CH), 44.1 (CH_2); IR (KBr) 3424, 3282, 2882, 2857, 2798, 1689, 1679, 1536, 1335, 1111, 820, 741, 697, 662 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{14}Cl_3NNaO_3$ 347.9931, found 347.9906.



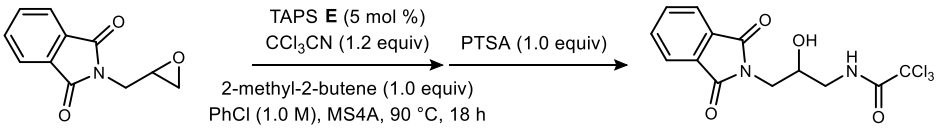
2,2,2-Trichloro-*N*-{2-hydroxy-3-[(4-methoxybenzyl)oxy]propyl}acetamide (4h). Prepared according to the general procedure using glycidyl 4-methoxybenzyl ether (299.5 mg, 1.5 mmol) at 100 °C for 18 h. Flash column chromatography (SiO_2 24 g, Hexane:EtOAc = 7:1-4:1) yielded a white solid (297.4 mg, 56%). R_f = 0.30 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 51-52 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.23 (m, 3H), 6.91-6.87 (m, 2H), 4.51 (d, *J* = 11.4 Hz, 1H), 4.47 (d, *J* = 11.4 Hz, 1H), 4.04-3.95 (m, 1H), 3.81 (s, 3H), 3.62 (ddd, *J* = 13.8, 6.3, 4.2 Hz, 1H), 3.57 (dd, *J* = 9.6, 3.9 Hz, 1H), 3.46 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.39 (ddd, *J* = 13.8, 6.3, 4.8 Hz, 1H), 2.59 (br s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.4 (C), 159.5 (C), 129.6 (CH), 129.3 (C), 114.0 (CH), 92.5 (C), 73.4 (CH_2), 71.5 (CH_2), 68.5 (CH), 55.3 (CH_3), 44.1 (CH_2); IR (KBr) 3416, 3004, 2867, 2839, 1712, 1515, 1363, 1249, 1224, 1035, 823 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{16}Cl_3NNaO_4$ 378.0037, found 347.0056.



***N*-{3-[(4-Bromobenzyl)oxy]-2-hydroxypropyl}-2,2,2-trichloroacetamide (4i).** Prepared according to the general procedure using 4-bromobenzyl glycidyl ether (364.7 mg, 1.5 mmol) at 100 °C for 18 h. Flash column chromatography (SiO_2 24 g, Hexane:EtOAc = 7:1-4:1) yielded a white solid (312.0 mg, 51%). R_f = 0.25 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 59-60 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7. 51-7.46 (m, 2H), 7.27 (br s, 1H), 7.22-7.18 (m, 2H), 4.52 (d, *J* = 12.4 Hz, 1H), 4.48 (d, *J* = 12.4 Hz, 1H), 4.05-3.97 (m, 1H), 3.62 (ddd, *J* = 13.8, 6.3, 4.2 Hz, 1H), 3.58 (dd, *J* = 9.6, 3.9 Hz, 1H), 3.48 (dd, *J* = 9.6, 6.3 Hz, 1H), 3.40 (ddd, *J* = 13.8, 6.6, 5.1 Hz, 1H), 2.76 (d, *J* = 3.6 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.4 (C), 136.3 (C), 131.7 (CH), 129.5 (CH), 122.0 (C), 92.4 (C), 72.9 (CH_2), 71.9 (CH_2), 68.6 (CH), 44.0 (CH_2); IR (KBr) 3446, 3326, 2916, 2888, 2866, 1678, 1531, 1338, 1140, 1112, 1091, 819, 801, 652 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{13}BrCl_3NNaO_3$ 425.9037, found 425.9033.

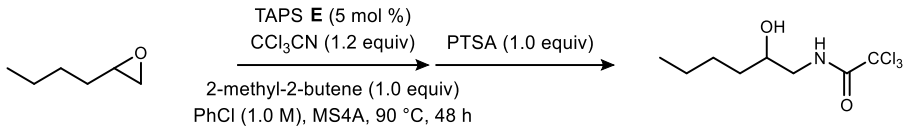


2-Hydroxy-3-[(trichloroacetyl)amino]propyl benzoate (4j). Prepared according to the general procedure using glycidyl benzoate (267.3 mg, 1.5 mmol). Flash column chromatography (SiO_2 24 g, Hexane:EtOAc = 8:1-5:1) yielded a white solid (380.5 mg, 74%). R_f = 0.35 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 86-87 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07-8.04 (m, 2H), 7.63-7.57 (m, 1H), 7.49-7.43 (m, 2H), 7.39-7.35 (m, 1H, NH), 4.46 (dd, *J* = 11.7, 4.8 Hz, 1H), 4.40 (dd, *J* = 11.7, 5.4 Hz, 1H), 4.24-4.18 (m, 1H), 3.70 (ddd, *J* = 14.1, 6.6, 4.2 Hz, 1H), 3.49 (ddd, *J* = 14.1, 6.9, 5.4 Hz, 1H), 3.07 (br s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 167.0 (C), 162.8 (C), 133.6 (CH), 129.8 (CH), 129.2 (C), 128.5 (CH), 92.3 (C), 68.7 (CH), 66.3 (CH_2), 43.7 (CH_2); IR (KBr) 3384, 3311, 2955, 1724, 1704, 1680, 1530, 1282, 1119, 820, 710 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{12}Cl_3NNaO_4$ 361.9724, found 361.9707.

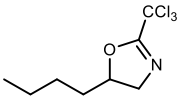


2,2,2-Trichloro-*N*-[3-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)-2-hydroxypropyl]acetamide (4k). Prepared according to the general procedure using glycidyl phthalimide (304.5 mg, 1.5 mmol). Flash column

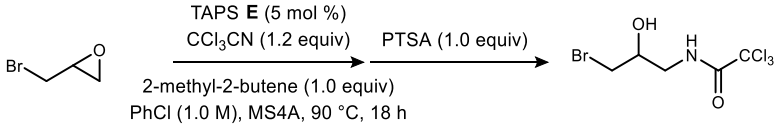
chromatography (SiO_2 24 g, Hexane:EtOAc = 8:1-2:1) yielded a white solid (345.5 mg, 63%). R_f = 0.25 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; mp 185-186 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.98 (t, *J* = 5.7 Hz, 1H), 7.90-7.81 (m, 4H), 5.30 (d, *J* = 5.4 Hz, 1H), 4.04-3.93 (m, 1H), 3.60 (dd, *J* = 13.8, 8.1 Hz, 1H), 3.51 (dd, *J* = 13.8, 4.8 Hz, 1H), 3.28 (dd, *J* = 13.8, 5.7 Hz, 1H), 3.22 (dd, *J* = 13.8, 5.7 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6) δ 168.0 (C), 161.7 (C), 134.3 (CH), 131.8 (C), 123.0 (CH), 92.8 (C), 66.0 (CH), 45.0 (CH_2), 42.1 (CH_2); IR (KBr) 3476, 3330, 2572, 2474, 1774, 1698, 1434, 1398, 1359, 1038, 840, 727 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{11}Cl_3N_2NaO_4$ 386.9677, found 386.9665.



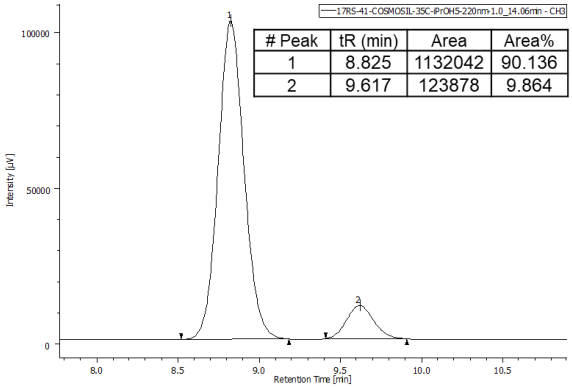
2,2,2-Trichloro-*N*-(2-hydroxyhexyl)acetamide (4l). Prepared according to the general procedure using 1,2-epoxyhexane (150.4 mg, 1.5 mmol) at 90 °C for 48 h. Flash column chromatography (SiO_2 24 g, Hexane:EtOAc = 8:1-5:1) yielded a white solid (106.1 mg, 33%). R_f = 0.35 (Hexane:EtOAc = 2:1) visualized with anisaldehyde; mp 35-36 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (br s, 1H), 3.87-3.79 (m, 1H), 3.61 (ddd, *J* = 13.8, 6.6, 3.0 Hz, 1H), 3.23 (ddd, *J* = 13.8, 7.8, 4.8 Hz, 1H), 1.87 (br s, 1H), 1.56-1.23 (m, 6H), 0.94-0.90 (m, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.3 (C), 92.6 (C), 70.4 (CH), 46.7 (CH_2), 34.6 (CH_2), 27.4 (CH_2), 22.5 (CH_2), 13.9 (CH_3); IR (KBr) 3454, 3359, 2960, 2934, 2859, 1697, 1529, 1461, 1269, 1095, 823, 670 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_8H_{14}Cl_3NNaO_2$ 283.9982, found 283.9978.

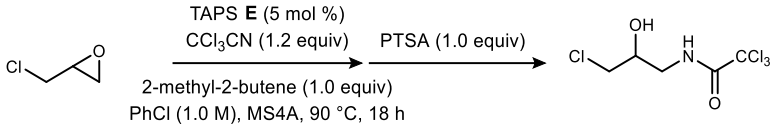


5-Butyl-2-(trichloromethyl)-4,5-dihydro-1,3-oxazole (2l). R_f = 0.22 (Hexane:EtOAc = 10:1) visualized with anisaldehyde; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.99-4.89 (m, 1H), 4.14 (dd, *J* = 15.0, 9.6 Hz, 1H), 3.71 (dd, *J* = 15.0, 7.2 Hz, 1H), 1.86-1.60 (m, 2H), 1.49-1.33 (m, 4H), 0.96-0.90 (m, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.6 (C), 86.9 (C), 84.5 (CH), 59.8 (CH_2), 34.6 (CH_2), 26.6 (CH_2), 22.4 (CH_2), 13.9 (CH_3); IR (KBr) 2959, 2933, 2873, 1716, 1660, 1516, 1467, 1332, 1233, 1116, 1014, 969, 853, 794, 657 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_8H_{12}Cl_3NNaO$ 265.9877, found 265.9867.

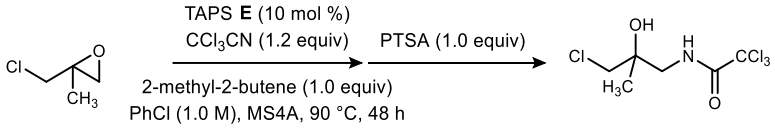


2,2,2-Trichloro-*N*-(3-bromo-2-hydroxypropyl)acetamide (4m). Prepared according to the general procedure using epibromohydrin (205.5 mg, 1.5 mmol). Flash column chromatography (SiO_2 24 g, Hexane:EtOAc = 8:1-5:1) yielded a white solid (269.3 mg, 64%, 6% of **4n** was included). R_f = 0.30 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 41-42 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (br s, 1H), 4.11-4.03 (m, 1H), 3.72 (ddd, *J* = 14.1, 6.3, 3.6 Hz, 1H), 3.53 (dd, *J* = 10.5, 4.5 Hz, 1H), 3.48 (ddd, *J* = 14.1, 5.4, 1.8 Hz, 1H), 3.43 (dd, *J* = 10.5, 6.9 Hz, 1H), 2.94-2.91 (m, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.7 (C), 92.2 (C), 69.5 (CH), 44.9 (CH_2), 35.9 (CH_2); IR (KBr) 3454, 3274, 3065, 2948, 2916, 1698, 1534, 1433, 1254, 1074, 827, 667 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_5H_7BrCl_3NNaO_2$ 319.8618, found 319.8612. The ratio of **4m** and **4n** was determined by HPLC analysis (COSMOSIL 5SL-II, Hexane:^{i}PrOH = 95:5, 1.0 mL/min, t_r(**4m**) = 8.8 min, t_r(**4n**) = 9.6 min, 220 nm, 35 °C).

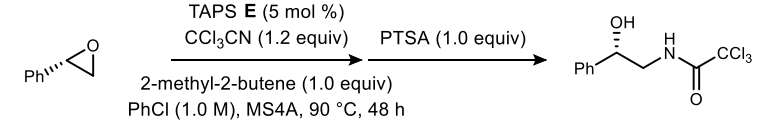




2,2,2-Trichloro-*N*-(3-chloro-2-hydroxypropyl)acetamide (4n). Prepared according to the general procedure using epichlorohydrin (138.8 mg, 1.5 mmol). Flash column chromatography (SiO_2 24 g, Hexane:EtOAc = 8:1-5:1) yielded a white solid (284.0 mg, 74%). R_f = 0.30 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 52-53 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (br s, 1H), 4.11-4.04 (m, 1H), 3.74-3.64 (m, 2H), 3.55 (dd, *J* = 11.4, 6.9 Hz, 1H), 3.47 (ddd, *J* = 14.1, 7.2, 5.4 Hz, 1H), 2.73 (br s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.8 (C), 92.2 (C), 69.9 (CH), 47.0 (CH_2), 44.2 (CH_2); IR (KBr) 3417, 3338, 2952, 1699, 1526, 1433, 1263, 1110, 823, 754, 669 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_5H_7Cl_4NNaO_2$ 275.9123, found 275.9102.
HPLC analysis (Chiralpak AD-3, Hexane:^{i}PrOH = 95:5, 1.0 mL/min, t_r(*minor*) = 19.0 min, t_r(*major*) = 20.4 min, 220 nm, 35 °C); $[\alpha]_D^{23}$ -5.3 (*c* 1.1, $CHCl_3$ for 28% ee).

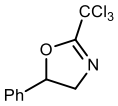


2,2,2-Trichloro-*N*-(3-chloro-2-hydroxy-2-methylpropyl)acetamide (4o). Prepared according to the general procedure using methyl epichlorohydrin (160.0 mg, 1.5 mmol) and TAPS **E** (78.0 mg, 150 μmol, 10 mol %) at 90 °C for 48 h. Flash column chromatography (SiO_2 24 g, Hexane:EtOAc = 8:1-5:1) yielded a yellowish solid (93.3 mg, 23%). R_f = 0.40 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 43-44 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (br s, 1H), 3.57-3.53 (m, 4H), 2.55 (br s,1H), 1.353 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.8 (C), 92.4 (C), 72.3 (C), 51.5 (CH_2), 48.1 (CH_2), 23.2 (CH_3); IR (KBr) 3410, 3305, 2956, 1694, 1530, 1129, 822, 671 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_6H_9Cl_4NNaO_2$ 289.9280, found 289.9278.

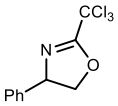


(*R*)-2,2,2-Trichloro-*N*-(2-hydroxy-2-phenylethyl)acetamide (4q). Prepared according to the general procedure using epoxide (*S*)-styrene oxide (72.0 mg, 0.60 mmol) at 90 °C for 48 h. Flash column chromatography (SiO_2 24 g, Hexane:EtOAc = 8:1-5:1, CH_2Cl_2:EtOAc = 80:1-60:1) yielded a white solid (54.4 mg, 32%). The product was determined to be 91% ee by chiral HPLC analysis (Chiralpak AD-3, Hexane:^{i}PrOH = 95:5, 1.0 mL/min, t_r(*minor*) = 22.7 min, t_r(*major*) = 24.7 min, 220 nm, 35 °C); $[\alpha]_D^{25}$ +35.3 (*c* 1.1, $CHCl_3$). R_f = 0.50 (Hexane:EtOAc = 2:1) visualized with anisaldehyde; mp 59-60 °C; ^{1}H NMR (300

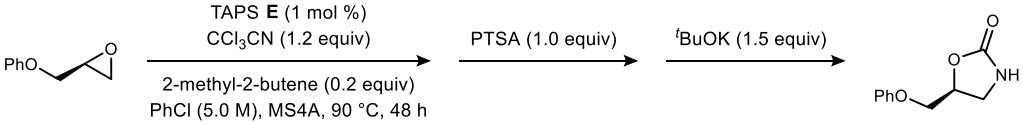
MHz, $CDCl_3$) δ 7.42-7.30 (m, 5H), 7.18 (br s, 1H), 4.92 (dt, *J* = 8.1, 3.6 Hz, 1H), 3.78 (ddd, *J* = 13.8, 7.2, 3.6 Hz, 1H), 3.43 (ddd, *J* = 13.8, 8.1, 4.5 Hz, 1H), 2.52 (br s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 162.3 (C), 140.7 (C), 128.8 (CH), 128.5 (CH), 125.8 (CH), 92.5 (C), 72.5 (CH), 48.1 (CH_2); IR (KBr) 3410, 3033, 2871, 1696, 1524, 1269, 1073, 818, 700 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{10}Cl_3NNaO_2$ 303.9669, found 303.9645.



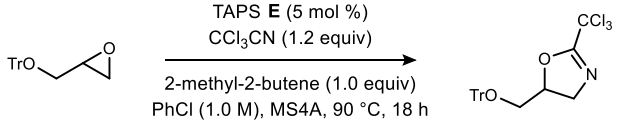
5-Phenyl-2-(trichloromethyl)-4,5-dihydro-1,3-oxazole (2q). R_f = 0.37 (Hexane:CH_2Cl_2 = 1:1) visualized with PMA; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45-7.32 (m, 5H), 5.87 (dd, *J* = 10.2, 7.8 Hz, 1H), 4.53 (dd, *J* = 15.3, 7.8 Hz, 1H), 4.05 (dd, *J* = 15.3, 10.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 162.4 (C), 139.3 (C), 129.0 (CH), 128.9 (CH), 125.7 (CH), 86.6 (C), 85.0 (CH), 63.0 (CH_2); IR (KBr) 3033, 2942, 2880, 1715, 1662, 1496, 1453, 1320, 1228, 1208, 973, 845, 793, 758, 698, 656 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_9Cl_3NO$ 263.9744, found 263.9736.



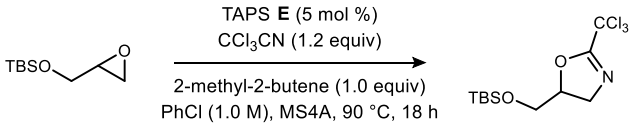
4-Phenyl-2-(trichloromethyl)-4,5-dihydro-1,3-oxazole (2q').[7] ^1H NMR (300 MHz, $CDCl_3$) δ 7.42-7.30 (m, 3H), 7.28-7.25 (m, 2H), 5.43 (dd, *J* = 10.2, 8.1 Hz, 1H), 5.00 (dd, *J* = 10.2, 8.4 Hz, 1H), 4.52 (dd, *J* = 8.4, 8.1 Hz, 1H).



(5*S*)-5-(Phenoxymethyl)-1,3-oxazolidin-2-one (5). To an oven-dried 10 mL test tube equipped with a stir bar was added (*S*)-glycidyl phenyl ether (1.127 g, 7.5 mmol, 1.0 equiv), TAPS **E** (39.2 mg, 75 μmol, 1 mol %), PhCl (1.5 mL, 5.0 M), MS4A (150 mg), trichloroacetonitrile (0.91 mL, 9.0 mmol, 1.2 equiv), and 2-methyl-2-butene (159 μL, 1.5 mmol). The atmosphere was replaced with argon (×3) using a diaphragm pump. After stirring at 90 °C for 48 h, the mixture was filtered through a pad of celite with $CHCl_3$ (40 mL) and then the filtered solution was concentrated. The unpurified material in a 200 mL round-bottom flask was diluted with PhCl (75 mL). *p*-TsOH•H_2O (1.427 g, 7.5 mmol) was added into the flask at rt. After stirring at rt for 3 h, the mixture was treated with satd aq $NaHCO_3$ (90 mL). The aqueous layer was extracted with $CHCl_3$ (50 mL×3). The organic layers were combined, washed with H_2O (200 mL), dried over Na_2SO_4, filtered, and concentrated. Flash column chromatography (SiO_2 45 g, Hexane:EtOAc = 5:1 – EtOAc) yielded the corresponding oxazolidinone as a white solid (0.934 g, 64%). The product was determined to be 99% ee by chiral HPLC analysis (Chiralcel OD-3, Hexane:EtOH = 80:20, 1.0 mL/min, t_r(*minor*) = 10.3 min, t_r(*major*) = 11.6 min, 220 nm, 35 °C); $[\alpha]_D^{23}$ +8.2 (*c* 0.3, $CHCl_3$). R_f = 0.35 (EtOAc) visualized with $KMnO_4$; mp 109-110 °C (rac); ^1H NMR (300 MHz, $CDCl_3$) δ 7.33-7.26 (m, 2H), 7.02-6.96 (m, 1H), 6.93-6.89 (m, 2H), 6.16 (br s, 1H), 5.01-4.93 (m, 1H), 4.16 (dd, *J* = 10.5, 4.8 Hz, 1H), 4.13 (dd, *J* = 10.5, 5.4 Hz, 1H), 3.78 (td, *J* = 8.7, 0.6 Hz, 1H), 3.62 (ddd, *J* = 8.7, 6.3, 0.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 159.6 (C), 158.1 (C), 129.6 (CH), 121.6 (CH), 114.6 (CH), 74.2 (CH), 67.9 (CH_2), 42.7 (CH_2); IR (KBr) 3281, 3159, 2925, 1742, 1602, 1491, 1252, 1239, 1091, 965, 760, 734, 695 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{11}NNaO_3$ 216.0631, found 216.0653.



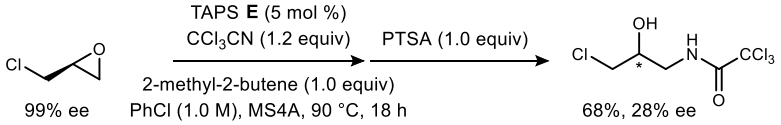
2-(Trichloromethyl)-5-[(trityloxy)methyl]-4,5-dihydro-1,3-oxazole (S2). To an oven-dried 10 mL test tube equipped with a stir bar was added glycidyl trityl ether (189.7 mg, 0.60 mmol), TAPS **E** (15.6 mg, 30 μmol, 5 mol %), PhCl (0.6 mL, 1.0 M), MS4A (120 mg), trichloroacetonitrile (73 μL, 0.72 mmol, 1.2 equiv), and 2-methyl-2-butene (64 μL, 0.60 mmol). The atmosphere was replaced with argon (×3) using a diaphragm pump. After stirring at 90 °C for 18 h, the mixture was filtered through a pad of celite with $CHCl_3$ (40 mL) and then the filtered solution was concentrated. Flash column chromatography (SiO_2 25 g, Hexane:EtOAc = 15:1-5:1) yielded **S2** as a white solid (123.8 mg, 45%). R_f = 0.35 (Hexane:EtOAc = 10:1) visualized with $KMnO_4$; mp 158-159 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.44 (m, 6H), 7.33-7.21 (m, 9H), 5.08-4.99 (m, 1H), 4.08 (dd, *J* = 15.0, 9.9 Hz, 1H), 3.95 (dd, *J* = 15.0, 7.5 Hz, 1H), 3.47 (dd, *J* = 10.8, 3.0 Hz, 1H), 3.17 (dd, *J* = 10.8, 4.5 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.6 (C), 143.4 (C), 128.6 (CH), 127.9 (CH), 127.2 (CH), 86.8 (C), 86.7 (C), 82.9 (CH), 64.2 (CH_2), 56.9 (CH_2); IR (KBr) 3067, 2977, 2922, 1662, 1491, 1448, 1232, 1119, 1015, 913, 851, 790, 749, 708, 647, 632 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{24}H_{20}Cl_3NNaO_2$ 482.0452, found 482.0458.



2-(Trichloromethyl)-5-[(*tert*-butyldimethylsilyloxy)methyl]-4,5-dihydro-1,3-oxazole (S3). To an oven-dried 10 mL test tube equipped with a stir bar was added *tert*-butyldimethylsilyl glycidyl ether (113.1 mg, 0.60 mmol), TAPS **E** (15.6 mg, 30 μmol, 5 mol %), PhCl (0.6 mL, 1.0 M), MS4A (120 mg), trichloroacetonitrile (73 μL, 0.72 mmol, 1.2 equiv), and 2-methyl-2-butene (64 μL, 0.60 mmol). The atmosphere was replaced with argon (×3) using a diaphragm pump. After stirring at 90 °C for 18 h, the mixture was filtered through a pad of celite with $CHCl_3$ (40 mL) and then the filtered solution was concentrated. Flash column chromatography (SiO_2 25 g, Hexane:EtOAc = 40:1-10:1, Toluene:EtOAc = 100:1-50:1) yielded **S3** as a colorless oil (61.1 mg, 31%). R_f = 0.40 (Hexane:EtOAc = 10:1) visualized with $KMnO_4$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.96 (dddd, *J* = 9.6, 7.5, 3.9, 3.6 Hz, 1H), 4.09 (dd, *J* = 15.0, 9.6 Hz, 1H), 4.00 (dd, *J* = 15.0, 7.5 Hz, 1H), 3.88 (dd, *J* = 11.4, 3.6 Hz, 1H), 3.72 (dd, *J* = 11.4, 3.9 Hz, 1H), 0.89 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.6 (C), 86.7 (C), 83.8 (CH), 63.4 (CH_2), 56.4 (CH_2), 25.7 (CH_3), 18.2 (C), -5.45 (CH_3), -5.54 (CH_3); IR (KBr) 2962, 2936, 2875, 1722, 1371, 1253, 1166, 1053, 840 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{20}Cl_3NNaO_2Si$ 354.0221, found 354.0204.

Appendix

The reaction using (*S*)-epichlorohydrin (99% ee) provided the product with deteriorated optical purity, which indirectly supports the proposed mechanism.



Due to the effect of the phenyl group, lower regioselectivity (ca. 6:1) was observed in the reaction using styrene oxide.

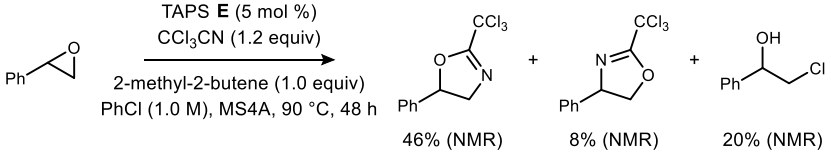
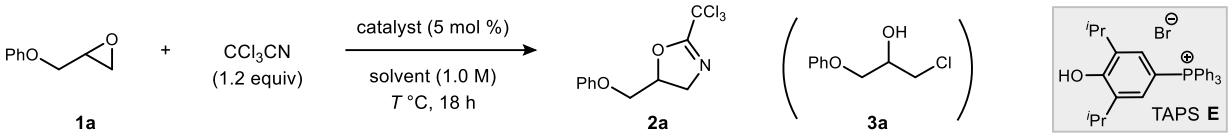


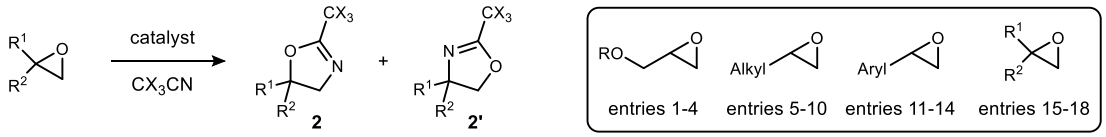
Table S1. Optimization of reaction conditions



entry	catalyst	*T* (°C)	solvent (1.0 M)	conv. (%)[a]	**2a** (%)[a]	**3a** (%)[a]
1	$Ph_4P^+I^-$	100	PhCl	>95	50	15
2	$Ph_4P^+Cl^-$	100	PhCl	58	43	10
3	$Ph_4P^+Br^-$	100	PhCl	>95	67	24
4	$Ph_4P^+Br^-$	80	PhCl	93	53	15
5	$Ph_4P^+Br^-$	90	PhCl	>95	69	22
6[b,c]	$Ph_4P^+Br^-$	90	PhCl	>95	72	10
7	$Ph_4P^+Br^-$	90	$PhCH_3$	34	21	<5
8	$Ph_4P^+Br^-$	90	$PhCF_3$	>95	64	15
9	$^nBu_4P^+Br^-$	90	PhCl	64	33	28
10	$^nBu_4N^+Br^-$	90	PhCl	89	60	11
11	DMAP	90	PhCl	79	35	18
12	TAPS **E**	90	PhCl	>95	75	13
13[b]	TAPS **E**	90	PhCl	>95	77	10
14[c]	TAPS **E**	90	PhCl	>95	76	12
15[b,c]	TAPS **E**	90	PhCl	>95	79	9

[a]Estimated by ^{1}H NMR analysis using $(CHCl_2)_2$ as an internal standard. [b]MS 4A (100 mg/mmol) was added. [c]2-Methyl-2-butene was added.

Table S2. Comparison of regioselectivity[8]



entry	epoxide	CX_3CN	catalyst (mol %)	yield (%)	**2:2'**
1[a]	$R^1 = CH_2O^nC_6H_{13}$, $R^2 = H$	X = H	HF (1000)	91	73:27
2[a]	$R^1 = CH_2O^nC_6H_{13}$, $R^2 = H$	X = H	TfOH (100)	0	-
3[a]	$R^1 = CH_2O^nC_6H_{13}$, $R^2 = H$	X = H	$AlCl_3$ (100)	39	>99:1
4	$R^1 = CH_2OBn$, $R^2 = H$	X = Cl	TAPS **E** (5)	57[b]	>99:1
5[a]	$R^1 = {}^nC_6H_{13}$, $R^2 = H$	X = H	HF (1000)	68	27:73
6[a]	$R^1 = {}^nC_6H_{13}$, $R^2 = H$	X = H	TfOH (100)	47	26:74
7[a]	$R^1 = {}^nC_6H_{13}$, $R^2 = H$	X = H	$AlCl_3$ (100)	45	48:52
8[c]	$R^1 = {}^nC_4H_9$, $R^2 = H$	X = Cl	TfOH (5)	0[d]	-
9[c]	$R^1 = {}^nC_4H_9$, $R^2 = H$	X = Cl	$AlCl_3$ (5)	0[d]	-
10[c]	$R^1 = {}^nC_4H_9$, $R^2 = H$	X = Cl	TAPS **E** (5)	37[d]	>99:1
11[a]	$R^1 = C_6F_5$, $R^2 = H$	X = H	HF (1000)	74	<1:99
12[a]	$R^1 = C_6F_5$, $R^2 = H$	X = H	TfOH (100)	67	<1:99
13[a]	$R^1 = C_6F_5$, $R^2 = H$	X = H	$AlCl_3$ (100)	18	<1:99
14	$R^1 = C_6H_5$, $R^2 = H$	X = Cl	TAPS **E** (5)	42[d]	88:12
15[a]	$R^1 = {}^nC_4H_9$, $R^2 = CH_3$	X = H	HF (1000)	0	-
16[a]	$R^1 = {}^nC_4H_9$, $R^2 = CH_3$	X = H	TfOH (100)	45	<1:99
17[a]	$R^1 = {}^nC_4H_9$, $R^2 = CH_3$	X = H	$AlCl_3$ (100)	66	<1:99
18	$R^1 = CH_2Cl$, $R^2 = CH_3$	X = Cl	TAPS **E** (5)	23[b]	>99:1

[a]Reported by Umezawa *et al.*, see ref 9b in the main text. [b]Isolated yield of a trichloroacetylated amino alcohol after hydrolysis of oxazoline. [c]PhCl (1.0 M), 90 °C, 18 h. [d]NMR yield of oxazoline.

DFT studies

Quantum mechanical calculations were performed using Gaussian 16 (Revision B.01).[9] All geometries were optimized using the M06-2X density functional, the 6-31G(d) basis set (C, H, N, O, P, and Cl), the LanL2DZ basis set (Br), and an ultrafine integration grid within the IEFPCM model in chlorobenzene.[10,11] Single point energies were calculated using the M06-2X density functional, the triple-zeta valence with polarization quality def2-TZVPP basis set, and an ultrafine integration grid within the IEFPCM model in chlorobenzene.[12] The resulting energies were used to correct the energies obtained from the M06-2X/6-31G(d) + LanL2DZ optimizations. The free energy corrections were calculated at 1 atm and 298.15 K.

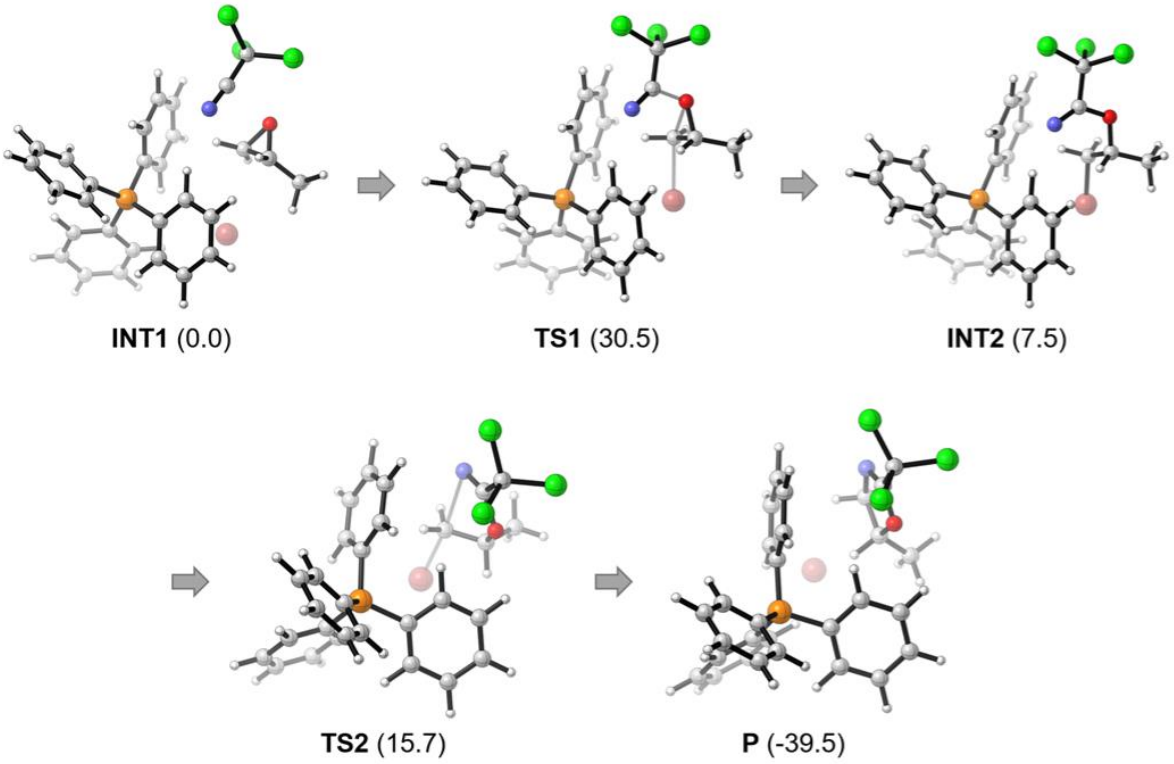


Figure S1. Path A: 3D view of DFT results. Relative free energies based on **INT1** are shown (kcal mol^{-1}).

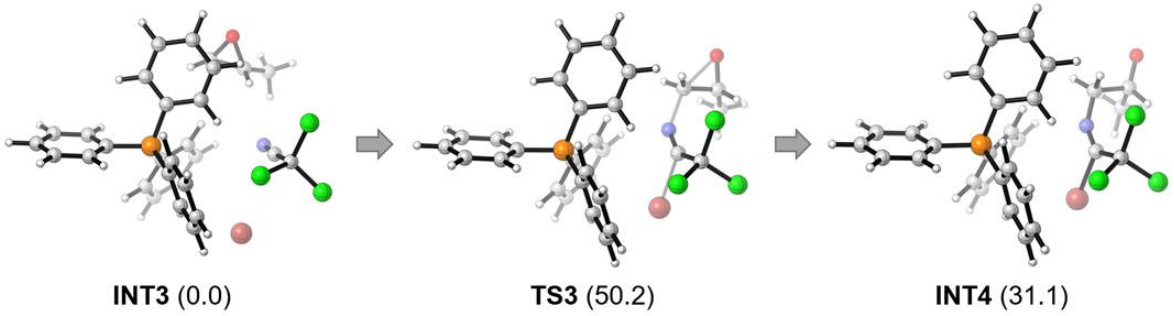


Figure S2. Path B: 3D view of DFT results. Relative free energies based on **INT3** are shown (kcal mol^{-1}).

INT1

Optimization: IEFPCM(PhCl)-M06-2X/6-31G(d) + LanL2DZ

E(RM062X) = -2985.03173632 Hartree

Thermal correction to Gibbs Free Energy = 0.405293 Hartree

Sum of electronic and thermal Free Energies = -2984.626444 Hartree

The lowest frequency = 18.8447 cm^{-1}

Number of imaginary frequencies = 0

Single-point calculation: IEFPCM(PhCl)-M06-2X/def2-TZVPP

E(RM062X) = -5546.75156560 Hartree

P	-0.3617081175	2.3041559379	-0.4565433394
C	-1.9673942467	2.9605376135	0.0481877422
C	-4.4051137054	4.0721556132	0.7943000478
C	-2.1243997935	3.4997524553	1.3328688623
C	-3.0306001744	2.9765726204	-0.8588044648
C	-4.2495476958	3.533881164	-0.4802125234
C	-3.3441666977	4.0561286047	1.7002006184
H	-1.3015005219	3.4801612966	2.0427336277
C	-0.5900841859	1.2820939273	-1.9195377717
C	-1.0918915428	-0.2758705269	-4.1601379548
C	-0.456059465	1.8406657688	-3.1948382609
C	-0.9811819161	-0.0510824854	-1.7596870057
C	-1.23561959	-0.8243734437	-2.8869655432
C	-0.7040053141	1.0531254318	-4.3144826308
H	-0.1490408486	2.8749575489	-3.3153449334
H	-1.0855414463	-0.4899337219	-0.7706928372
H	-1.5450892215	-1.8578880404	-2.7710206938
H	-0.5884766887	1.4775711109	-5.305761002
H	-1.2812290701	-0.8877311608	-5.036022492
C	0.2875913992	1.3268506439	0.9154439138
C	1.283575851	-0.2037519703	3.0120512045
C	-0.5978159434	0.6569416776	1.7713933415
C	1.6706443277	1.2148886844	1.0968033812
C	2.1620044573	0.4492089558	2.1501428063
C	-0.0938855168	-0.1075446666	2.8189365277
H	-1.6717360896	0.7303359632	1.6261986643
H	2.3625267823	1.697946074	0.4153366469
H	3.2338484049	0.3600047555	2.2893907396
H	-0.7785253398	-0.6268870813	3.482372221
H	1.6731343609	-0.7963048123	3.8337111713
C	0.7377260784	3.6804174026	-0.8453022941
C	2.4792757394	5.7714857576	-1.4072685169
C	0.4098855349	4.9821169529	-0.4490618157
C	1.9307992807	3.4215983294	-1.534129441
C	2.7983803805	4.4747426125	-1.8069110107
C	1.2868603807	6.0249356202	-0.7324534139
H	-0.5215073705	5.187702148	0.0681586151
H	2.1891906257	2.4089895657	-1.8506942354
H	3.7244127376	4.2747727945	-2.3355243613
H	1.0344247112	7.0351389055	-0.4285467479
H	3.1594572495	6.5884116807	-1.6260180532
H	-2.9112346916	2.5535322229	-1.8515006729
H	-3.4679558989	4.4727116438	2.6938857701
H	-5.3568257373	4.5036989617	1.0863835359

H	-5.076572771	3.542626665	-1.1818267248
N	-1.7911840568	-2.2934640875	0.8062562834
C	-1.4133160496	-3.1334608151	1.5027223588
Br	3.1625061594	0.0307348202	-2.1076202752
C	-1.0553882072	-4.186547986	2.4628685037
Cl	-0.8149885882	-5.7199797206	1.6099030354
Cl	0.3993400013	-3.7170331123	3.3594501658
Cl	-2.4268596267	-4.3435934908	3.6003917985
O	1.0569403787	-3.5761412896	0.3923488118
C	1.3565171755	-2.219054264	0.0516938793
H	2.4113564719	-1.9634636423	0.0058473856
H	0.7044190041	-1.4770606514	0.5099154073
C	0.8135583852	-3.1404433195	-0.9463933104
H	-0.2501214995	-3.0574095337	-1.1734806348
C	1.682018658	-3.7334288985	-2.0187684584
H	1.3610847277	-4.7496166515	-2.2678816497
H	1.630996966	-3.1151491443	-2.9193150585
H	2.7226620592	-3.7613998143	-1.6848582392

TS1

Optimization: IEFPCM(PhCl)-M06-2X/6-31G(d) + LanL2DZ

E(RM062X) = -2984.98914613 Hartree

Thermal correction to Gibbs Free Energy = 0.405231 Hartree

Sum of electronic and thermal Free Energies = -2984.583915 Hartree

The lowest frequency = -568.9710 cm^{-1}

Number of imaginary frequencies = 1

Single-point calculation: IEFPCM(PhCl)-M06-2X/def2-TZVPP

E(RM062X) = -5546.70289312 Hartree

P	-3.228547387	5.9114971747	5.2692378717
C	-4.7993534276	6.6230096648	5.806803485
C	-7.1773524989	7.8175857778	6.6104083447
C	-4.9374388491	7.0831688143	7.1229947107
C	-5.851202544	6.7578997421	4.8957760172
C	-7.0402557817	7.3564004588	5.3033616576
C	-6.1280647399	7.6823165501	7.5192281116
H	-4.1236996241	6.9687047313	7.8339098793
C	-3.5192653505	4.9052410537	3.806643004
C	-4.1059260681	3.3818323021	1.5621447159
C	-3.4169090874	5.4794089925	2.5344755623
C	-3.9167668836	3.5744699819	3.962410186
C	-4.2156195003	2.8202956649	2.8325142859
C	-3.7064724589	4.7088337545	1.412945262
H	-3.1040322295	6.512557539	2.4163868966
H	-3.9898561117	3.096618998	4.937151206
H	-4.5298233044	1.7884038799	2.9555316384
H	-3.6176380974	5.1454962231	0.4240475399
H	-4.3302136644	2.7845254799	0.6842828296
C	-2.5827687623	4.933165816	6.6392582153
C	-1.6109904532	3.3879655456	8.7353525527
C	-3.4565102252	4.1067184836	7.3593962161
C	-1.2231283633	4.9830422416	6.9655798652
C	-0.743164923	4.2100443108	8.0184467826
C	-2.9638378482	3.3319021684	8.4042725557

H	-4.5118165878	4.0551324506	7.1059576729
H	-0.5425034141	5.6116133188	6.4018670761
H	0.3104774348	4.2474267462	8.272849782
H	-3.6371716248	2.6769689768	8.9482037632
H	-1.2314225035	2.7827668582	9.5521946946
C	-2.0852025957	7.2427853769	4.8547449132
C	-0.2793075229	9.2632529776	4.2442612495
C	-2.3557638975	8.5567517666	5.2495460083
C	-0.9140137164	6.9349601154	4.1473978442
C	-0.0136337105	7.9523463048	3.8490654604
C	-1.4469041893	9.565233328	4.9411617319
H	-3.2682553951	8.7962530142	5.7862713197
H	-0.7070528374	5.9092671849	3.8432109547
H	0.8949719293	7.7185026246	3.3047122177
H	-1.6551524242	10.5860177823	5.2429204174
H	0.4256560556	10.0527949312	4.0048782874
H	-5.7474922841	6.3909693645	3.8791886104
H	-6.2385825677	8.0371994682	8.5381339705
H	-8.1069751244	8.2802379895	6.9252030888
H	-7.8598705039	7.455934954	4.6000863675
N	-4.3026839735	1.2193130221	6.1740649772
C	-3.5557953927	0.4547423845	6.703222113
Br	-0.1342576046	3.2525664197	3.9299212027
C	-3.5848642768	-0.4702564574	7.9061863636
Cl	-3.4721960199	-2.1787201402	7.3819401487
Cl	-2.2375244961	-0.1273848416	9.0374498272
Cl	-5.1189316664	-0.2400531387	8.7779228176
O	-2.0149077794	0.1285447077	6.1643937385
C	-1.1709109812	1.611841756	5.6106508113
H	-0.1865382186	1.4459087041	6.0254447763
H	-1.7979707678	2.3964175092	6.0163002507
C	-1.8036728529	0.5670576547	4.8206574971
H	-2.7435142474	0.8784743807	4.3588307885
C	-0.9710241768	-0.3808584101	4.001728997
H	-1.5352764254	-1.2944913028	3.7970752776
H	-0.7062302615	0.0954917297	3.0543518118
H	-0.0526072859	-0.6433200604	4.533684389

INT2

Optimization: IEFPCM(PhCl)-M06-2X/6-31G(d) + LanL2DZ

E(RM062X) = -2985.02420107 Hartree

Thermal correction to Gibbs Free Energy = 0.409763 Hartree

Sum of electronic and thermal Free Energies = -2984.614438 Hartree

The lowest frequency = 18.0449 cm^{-1}

Number of imaginary frequencies = 0

Single-point calculation: IEFPCM(PhCl)-M06-2X/def2-TZVPP

E(RM062X) = -5546.75156560 Hartree

P	-0.4540294681	2.3164176143	-0.4605817962
C	-2.0165772003	3.0263736318	0.097235194
C	-4.3811449335	4.2199700481	0.9369874632
C	-2.1462870639	3.4544786583	1.4247815171
C	-3.0698205725	3.1910192656	-0.807459542
C	-4.2522408252	3.7891994511	-0.3815075634

C	-3.3307035986	4.0539193875	1.8390666594
H	-1.3319131865	3.3138551483	2.1300507859
C	-0.7455416636	1.3156709933	-1.9282520157
C	-1.3258628811	-0.188518477	-4.1891481677
C	-0.6791994002	1.9121867012	-3.1949588058
C	-1.1020903437	-0.028892235	-1.7854999657
C	-1.395756401	-0.7713618768	-2.9265269654
C	-0.9671886865	1.1527508178	-4.3238888223
H	-0.3999824743	2.9563590712	-3.3023214496
H	-1.1472178271	-0.5484740816	-0.8247285243
H	-1.6743299501	-1.8142559957	-2.8101279277
H	-0.9099135068	1.6084237299	-5.3066246981
H	-1.5494210094	-0.7776285803	-5.0728849248
C	0.2270792348	1.3491795154	0.8981535123
C	1.2509017503	-0.192710936	2.9711770909
C	-0.6095715433	0.4579725921	1.5817589987
C	1.5767502083	1.4720213763	1.2536817045
C	2.0828034841	0.6986028081	2.2927937275
C	-0.0899525644	-0.3144517461	2.6158278929
H	-1.6504394937	0.3317122947	1.2993629633
H	2.2274352127	2.161813147	0.7263826201
H	3.1278347075	0.7897639103	2.5689073723
H	-0.7331589156	-1.0286570605	3.1188043874
H	1.6517807559	-0.8039989521	3.7734497947
C	0.6879127189	3.6463578738	-0.8880290799
C	2.5115775723	5.6539699772	-1.4958115256
C	0.4474846548	4.9546934195	-0.4596211512
C	1.8403856211	3.3400555467	-1.6258074789
C	2.7501841594	4.3479142979	-1.9243685029
C	1.3642618813	5.9568829812	-0.7672337543
H	-0.4490429327	5.1942007575	0.1035887525
H	2.021804386	2.321775476	-1.9620075
H	3.6427902966	4.1139934624	-2.4943275718
H	1.1777818039	6.9737309454	-0.4393258751
H	3.2225163462	6.4381459479	-1.73456696
H	-2.9729309135	2.8458235507	-1.8323602574
H	-3.4356886073	4.3837478061	2.8669162148
H	-5.3062078641	4.681888892	1.2659378468
H	-5.0738085071	3.9114484762	-1.0788482605
N	-1.412500121	-2.2594302248	0.4124835579
C	-0.6908016035	-3.153102319	0.8208787934
Br	2.5015623468	-0.5821177143	-1.7359497778
C	-0.8946634393	-4.0223743256	2.1075314529
Cl	-1.008879148	-5.7771280604	1.7113521192
Cl	0.4880022938	-3.8091329244	3.2555779968
Cl	-2.3835064364	-3.5489898427	2.9536556424
O	0.5413714501	-3.675863299	0.3026517147
C	1.7330079088	-1.7479679595	-0.2702896902
H	2.5827406648	-1.9984390632	0.3647327759
H	1.021651439	-1.10896613	0.2489744961
C	1.0456123942	-2.9891865177	-0.8232106241
H	0.2145801379	-2.6721094799	-1.4640662213
C	1.9796904189	-3.9379371438	-1.5526393272

H	1.4314487698	-4.8385435662	-1.8393791215
H	2.3901559628	-3.4731361578	-2.4523528067
H	2.8072561116	-4.2312527033	-0.8985482823

TS2

Optimization: IEFPCM(PhCl)-M06-2X/6-31G(d) + LanL2DZ

E(RM062X) = -2985.01641394 Hartree

Thermal correction to Gibbs Free Energy = 0.410021 Hartree

Sum of electronic and thermal Free Energies = -2984.606393 Hartree

The lowest frequency = -318.6370 cm^{-1}

Number of imaginary frequencies = 1

Single-point calculation: IEFPCM(PhCl)-M06-2X/def2-TZVPP

E(RM062X) = -5546.73134687 Hartree

P	1.3567654462	1.7610543143	0.0350615667
C	-0.2392117664	2.3721697067	0.6150520206
C	-2.659098222	3.4138421853	1.4990578985
C	-0.3349648614	2.9114659959	1.9046690469
C	-1.3536515755	2.3495923546	-0.2288363752
C	-2.5634546096	2.8724773712	0.2191203085
C	-1.5474901295	3.4342250982	2.3409721246
H	0.5287242925	2.9166588537	2.5640549051
C	1.0976250425	0.5896200843	-1.3094596763
C	0.5324504615	-1.1884348454	-3.3701219017
C	0.9101173947	1.0718675749	-2.6123310541
C	1.0140947721	-0.779327675	-1.0420092693
C	0.7254798059	-1.6654647949	-2.0761535813
C	0.6280334027	0.1773174354	-3.6388801331
H	0.9906075257	2.1341745495	-2.825663247
H	1.1827093125	-1.1793106187	-0.0468731146
H	0.6707425705	-2.7255533243	-1.8492044559
H	0.4875433637	0.5467951091	-4.6489473736
H	0.3133351232	-1.8814888829	-4.1758479575
C	2.1780551413	0.9669816746	1.4229963729
C	3.4420078721	-0.4276680956	3.4640107794
C	1.4489866084	0.0484206901	2.1969541114
C	3.5284564721	1.2054928739	1.6874413602
C	4.1538231575	0.5084969234	2.7203792038
C	2.0890286743	-0.6571075401	3.2057854944
H	0.3939490265	-0.1259561182	2.0013716625
H	4.0935241281	1.9125659285	1.0890435029
H	5.2044416997	0.684823923	2.9240961536
H	1.5449217306	-1.4058467736	3.7711492288
H	3.9413477939	-0.9995757958	4.238443572
C	2.3401301178	3.1368832369	-0.5850154335
C	3.9224388735	5.2265347391	-1.5017413437
C	1.9989728808	4.4547195669	-0.2661480493
C	3.4696844048	2.8596007253	-1.3677565641
C	4.2595905573	3.910896708	-1.8199363191
C	2.7957916234	5.4983315738	-0.7290307259
H	1.1180783313	4.6681636307	0.3311743379
H	3.7313998272	1.8323896878	-1.613357
H	5.1364056148	3.7013397715	-2.4229643235
H	2.5328076031	6.5225050753	-0.487726977

H	4.5399355035	6.0432953792	-1.8610490392
H	-1.2831638723	1.9189743208	-1.2229950807
H	-1.6254677384	3.8503504983	3.3394574481
H	-3.6050415994	3.8169370726	1.845489346
H	-3.4314192839	2.8503939307	-0.4307771669
N	3.1557649884	-3.4119914777	2.213078832
C	2.1932360565	-3.672809537	1.5013135602
Br	4.9480744213	-0.7055606511	-1.1228296125
C	0.8098665604	-4.2286303941	1.9289658355
Cl	-0.4943845207	-3.0497874109	1.4981121263
Cl	0.4467775112	-5.7809617337	1.0976332096
Cl	0.7518517573	-4.4967933979	3.6806664772
O	2.0849423594	-3.4890952467	0.0994296754
C	4.042023906	-2.0934691059	0.3717800079
H	4.9505673454	-2.3391637195	0.9008371051
H	3.405771495	-1.3702368432	0.8636363999
C	3.3532469038	-3.1654870376	-0.4602420099
H	3.1054637017	-2.748608951	-1.4384450895
C	4.2252634158	-4.4004718665	-0.6361857379
H	3.7010919498	-5.1425862098	-1.2435626624
H	5.1584977232	-4.1301351828	-1.1404801373
H	4.458788518	-4.8337538634	0.3391892285

P

Optimization: IEFPCM(PhCl)-M06-2X/6-31G(d) + LanL2DZ

E(RM062X) = -2985.11112386 Hartree

Thermal correction to Gibbs Free Energy = 0.412511 Hartree

Sum of electronic and thermal Free Energies = -2984.698613 Hartree

The lowest frequency = 17.6350 cm^{-1}

Number of imaginary frequencies = 0

Single-point calculation: IEFPCM(PhCl)-M06-2X/def2-TZVPP

E(RM062X) = -5546.82171128 Hartree

P	-0.630334252	2.0698959881	-0.292357658
C	-2.1987449477	2.8026123589	0.2128735861
C	-4.5724627972	4.0321744995	0.9714753478
C	-2.2752421748	3.4678315623	1.4441752374
C	-3.3086018861	2.7501135514	-0.6350380712
C	-4.4958517996	3.3673848899	-0.2499034988
C	-3.4646100932	4.0832045082	1.8177993966
H	-1.414502238	3.4986202699	2.1069690292
C	-0.9160109155	0.8689403735	-1.606111123
C	-1.4280294506	-0.9845962449	-3.6106428588
C	-0.978628678	1.2908410912	-2.9404893872
C	-1.105665682	-0.4754609375	-1.2760695689
C	-1.3579582503	-1.4022245957	-2.2833200217
C	-1.2404458916	0.3586172151	-3.9387409324
H	-0.8137454102	2.3333733581	-3.1976416288
H	-1.0333955605	-0.8131402476	-0.246983686
H	-1.4806586557	-2.448119199	-2.0215036749
H	-1.2857637326	0.6787335973	-4.973982681
H	-1.6204385948	-1.708349547	-4.3959465617
C	0.089352427	1.235850006	1.1335290822
C	1.1847481541	-0.2139904624	3.2393232687

C	-0.7540274442	0.5602666873	2.0287065287
C	1.4778267227	1.1883919843	1.2937319494
C	2.0182718173	0.4619478314	2.3521580649
C	-0.2008794095	-0.1624136478	3.0792147525
H	-1.8335276972	0.5959207734	1.9062927346
H	2.1520901463	1.6757818916	0.5966893094
H	3.0971018679	0.4212757104	2.462509259
H	-0.851422594	-0.6903440093	3.7690141352
H	1.6113344698	-0.7936504306	4.0514418496
C	0.4637662715	3.350538516	-0.9239751486
C	2.2229127198	5.2805098144	-1.8649088684
C	0.1580439173	4.7052526608	-0.7543328821
C	1.6418940107	2.957608961	-1.5722053144
C	2.5246492587	3.9294750368	-2.0293669794
C	1.042238482	5.6676459183	-1.2327011113
H	-0.7595406807	5.008353163	-0.259964831
H	1.9036559288	1.908285808	-1.6968271983
H	3.4486870104	3.6179928232	-2.5045502276
H	0.8085813059	6.7195532752	-1.1086464102
H	2.9114944451	6.0362060823	-2.2288790965
H	-3.2510978621	2.2267366901	-1.5845833896
H	-3.5280303541	4.5977507107	2.7704126826
H	-5.5000499165	4.510115554	1.2688864987
H	-5.3602124276	3.324192961	-0.9035424124
N	1.7701087194	-2.9806033536	1.7889768299
C	0.6324310145	-3.1245123047	1.2625246317
Br	4.1378017822	0.4057978739	-1.0099315337
C	-0.5690906121	-3.7494689716	1.9437426923
Cl	-2.0370023843	-2.7904543307	1.6015946624
Cl	-0.7875359921	-5.3885567589	1.2645197881
Cl	-0.3250297456	-3.8525364925	3.6908671649
O	0.4220286058	-2.7884855613	-0.0211282279
C	2.6265469519	-2.4593887778	0.7113050489
H	3.369759439	-3.2243340574	0.4561334761
H	3.1605563969	-1.5619833037	1.0283351657
C	1.6721986081	-2.1625148903	-0.4626670198
H	1.4787409575	-1.087326375	-0.5405136173
C	2.081417661	-2.7348604955	-1.7977465038
H	1.3206738747	-2.5350902745	-2.5577565351
H	3.0157098955	-2.2545870535	-2.1009138514
H	2.2353452584	-3.8156074435	-1.7186773712

INT3

Optimization: IEFPCM(PhCl)-M06-2X/6-31G(d) + LanL2DZ

E(RM062X) = -2985.02453126 Hartree

Thermal correction to Gibbs Free Energy = 0.404058 Hartree

Sum of electronic and thermal Free Energies = -2984.620473 Hartree

The lowest frequency = 15.3063 cm^{-1}

Number of imaginary frequencies = 0

Single-point calculation: IEFPCM(PhCl)-M06-2X/def2-TZVPP

E(RM062X) = -5546.74639708 Hartree

P	-0.0366750291	0.7433312428	-1.913164834
C	-1.7003698416	0.5785283909	-1.2350097256
C	-4.2262303963	0.3500518668	-0.0916618172
C	-1.9195893297	-0.3476872163	-0.2041407456
C	-2.7479561716	1.3776301235	-1.7012550332
C	-4.0113930455	1.2582593603	-1.1249002604
C	-3.1829841115	-0.4564966783	0.3646475765
H	-1.1084429176	-0.9842426735	0.1425627225
C	-0.1153945825	1.5858036118	-3.507063161
C	-0.333272213	2.9105320892	-5.9411542863
C	-0.2483741537	2.9809960067	-3.5317446872
C	-0.0829671842	0.8565647466	-4.6990539392
C	-0.1919855745	1.5252423466	-5.9155098029
C	-0.361150215	3.6383270881	-4.7516698681
H	-0.2553953424	3.5494578305	-2.6056391093
H	0.0375991592	-0.2220650254	-4.682120631
H	-0.1605153319	0.9621283036	-6.84182509
H	-0.4635548536	4.7177968161	-4.7735088792
H	-0.415709622	3.4274345582	-6.8915536959
C	0.6458395886	-0.9080171599	-2.1103378686
C	1.6910949463	-3.4546330623	-2.4593660187
C	-0.1762126878	-1.9332751972	-2.6065684242
C	1.9761322654	-1.1582065257	-1.7707398681
C	2.4946015157	-2.440025927	-1.9500182667
C	0.3535186038	-3.2044409066	-2.7830965232
H	-1.2206713855	-1.7415646349	-2.8385637768
H	2.6002864568	-0.3994536812	-1.3087726648
H	3.5159044524	-2.6376826091	-1.6439967476
H	-0.2755126847	-4.0026916542	-3.1621697308
H	2.0967901895	-4.4528855171	-2.5889108106
C	0.98646203	1.735861431	-0.8159048919
C	2.6181067549	3.2214749403	0.871081245
C	0.6270230791	1.9071941409	0.5224750648
C	2.1682766175	2.3032712173	-1.3140989365
C	2.9819682591	3.0410800839	-0.4640786369
C	1.4466946628	2.6547100126	1.3633815681
H	-0.2805564549	1.4631949463	0.9184588836
H	2.4475930665	2.1727832346	-2.3561805016
H	3.9001805429	3.4759095597	-0.8432254974
H	1.1695869731	2.7736917911	2.4051642554
H	3.2584057066	3.7981562937	1.5301031776
H	-2.5864170735	2.0835222201	-2.5098849991
H	-3.3524220942	-1.1667756013	1.1672939174
H	-5.2067465843	0.2693116768	0.364393881
H	-4.8253986663	1.8778706685	-1.4851408752
N	0.592641349	-0.0652395134	2.9576112975
C	0.6572695021	-1.1947989626	2.7276901622
Br	3.8054878184	-0.9416638683	1.2288796744
C	0.5746997563	-2.6480219649	2.526888631
Cl	-1.0501999468	-3.1469171458	3.101847693
Cl	0.7361018813	-3.049293266	0.8095299199
Cl	1.8204091016	-3.4599416794	3.485044854
O	-3.6476820084	1.72595707	2.691156589

C	-2.6165072741	2.4751160421	2.0608815285
H	-2.547395055	3.5173252545	2.3684500605
H	-2.4970374107	2.2866294373	0.9944551757
C	-2.2995792986	1.4250156796	3.037777383
H	-1.9530026784	0.4679947486	2.6462913132
C	-1.8802314509	1.7529802693	4.443692972
H	-2.2710335071	1.0089180709	5.1441689757
H	-0.7896352823	1.7529272159	4.5199011146
H	-2.2611501897	2.7364303031	4.7328884086

TS3

Optimization: IEFPCM(PhCl)-M06-2X/6-31G(d) + LanL2DZ

E(RM062X) = -2984.94270715 Hartree

Thermal correction to Gibbs Free Energy = 0.405310 Hartree

Sum of electronic and thermal Free Energies = -2984.537397 Hartree

The lowest frequency = -656.4359 cm^{-1}

Number of imaginary frequencies = 1

Single-point calculation: IEFPCM(PhCl)-M06-2X/def2-TZVPP

E(RM062X) = -5546.66763568 Hartree

P	2.7035590996	3.2917853741	0.8719530205
C	0.9766552387	3.2322371478	1.387092271
C	-1.6387015403	3.2485067818	2.32711565
C	0.5719457741	2.2808152761	2.3323000385
C	0.0733436649	4.1879429587	0.9103450249
C	-1.2344946534	4.192918167	1.385389987
C	-0.739465001	2.2919972101	2.7964732214
H	1.2716751917	1.53290444	2.6960940814
C	2.8258267846	4.0147222925	-0.7798485986
C	2.9072941017	5.1623270868	-3.3118692156
C	2.8789874564	5.4085500971	-0.912251402
C	2.8220865352	3.1968469523	-1.9144244997
C	2.8629020038	3.7760567295	-3.1790009355
C	2.9158505438	5.9775562349	-2.1811548415
H	2.8998521185	6.0445061883	-0.0316947222
H	2.8003309234	2.1161900957	-1.8164396169
H	2.8657778767	3.1426670226	-4.0593766964
H	2.9581337465	7.0562826318	-2.2850531389
H	2.9416570954	5.6093912233	-4.2998864163
C	3.3465925439	1.6087100997	0.8512256304
C	4.3393273001	-0.9843118193	0.7262207972
C	2.5489376404	0.5814203976	0.3240721863
C	4.6309947202	1.3354182231	1.3277595694
C	5.1239856743	0.0344783977	1.2588440625
C	3.050186612	-0.7130243037	0.2624975373
H	1.5401330188	0.7878512871	-0.0235915595
H	5.2300194643	2.11390121	1.7865052743
H	6.1140198775	-0.1810657021	1.6456335927
H	2.4344270402	-1.5100577299	-0.1398669891
H	4.7253342081	-1.9975738595	0.6819543821
C	3.6258338614	4.3400862847	2.0030817931
C	5.0833382122	5.887007917	3.787536519
C	3.0370214619	4.759039118	3.1968276255
C	4.9415010267	4.7106956735	1.6863147793

C	5.6669312457	5.4805487175	2.5855390463
C	3.7742938169	5.5305840754	4.0906709376
H	2.0190131642	4.4769513313	3.4404190086
H	5.3916890675	4.4058159101	0.7449450577
H	6.6864177235	5.7656528841	2.349508594
H	3.3225436969	5.8377398278	5.0279676614
H	5.6575550195	6.4834222502	4.4888893237
H	0.3842180192	4.9204011997	0.1712725548
H	-1.0581006207	1.5495216892	3.5208181136
H	-2.6594674788	3.2543633313	2.6945577849
H	-1.9372608117	4.9321077086	1.0168484785
N	2.0241256018	2.8027857347	5.300471168
C	2.6391500809	1.7949030536	5.2089538533
Br	4.9810087398	2.0026694028	4.8062468688
C	2.4257089891	0.298913379	5.3086700415
Cl	0.6661145823	0.0275483133	5.5159208597
Cl	2.9326480156	-0.5285326567	3.8187813002
Cl	3.2764570737	-0.3661504748	6.7146711946
O	-0.631351453	3.6593607229	7.7047746104
C	0.5379404978	3.3644642699	6.1374485499
H	0.6006756116	4.4127735697	5.8723749532
H	-0.1895368128	2.7803254069	5.5866651081
C	0.6029512319	3.1024461894	7.5997380473
H	0.6697492351	2.0125145318	7.8106145244
C	1.7371209993	3.818307476	8.3265408706
H	1.5845363645	3.745376942	9.4082813942
H	2.7156707463	3.3892670492	8.0807700513
H	1.7338450616	4.8799429012	8.0544880918

INT4

Optimization: IEFPCM(PhCl)-M06-2X/6-31G(d) + LanL2DZ

E(RM062X) = -2984.96777136 Hartree

Thermal correction to Gibbs Free Energy = 0.406059 Hartree

Sum of electronic and thermal Free Energies = -2984.561712 Hartree

The lowest frequency = 20.6974 cm^{-1}

Number of imaginary frequencies = 0

Single-point calculation: IEFPCM(PhCl)-M06-2X/def2-TZVPP

E(RM062X) = -5546.69879039 Hartree

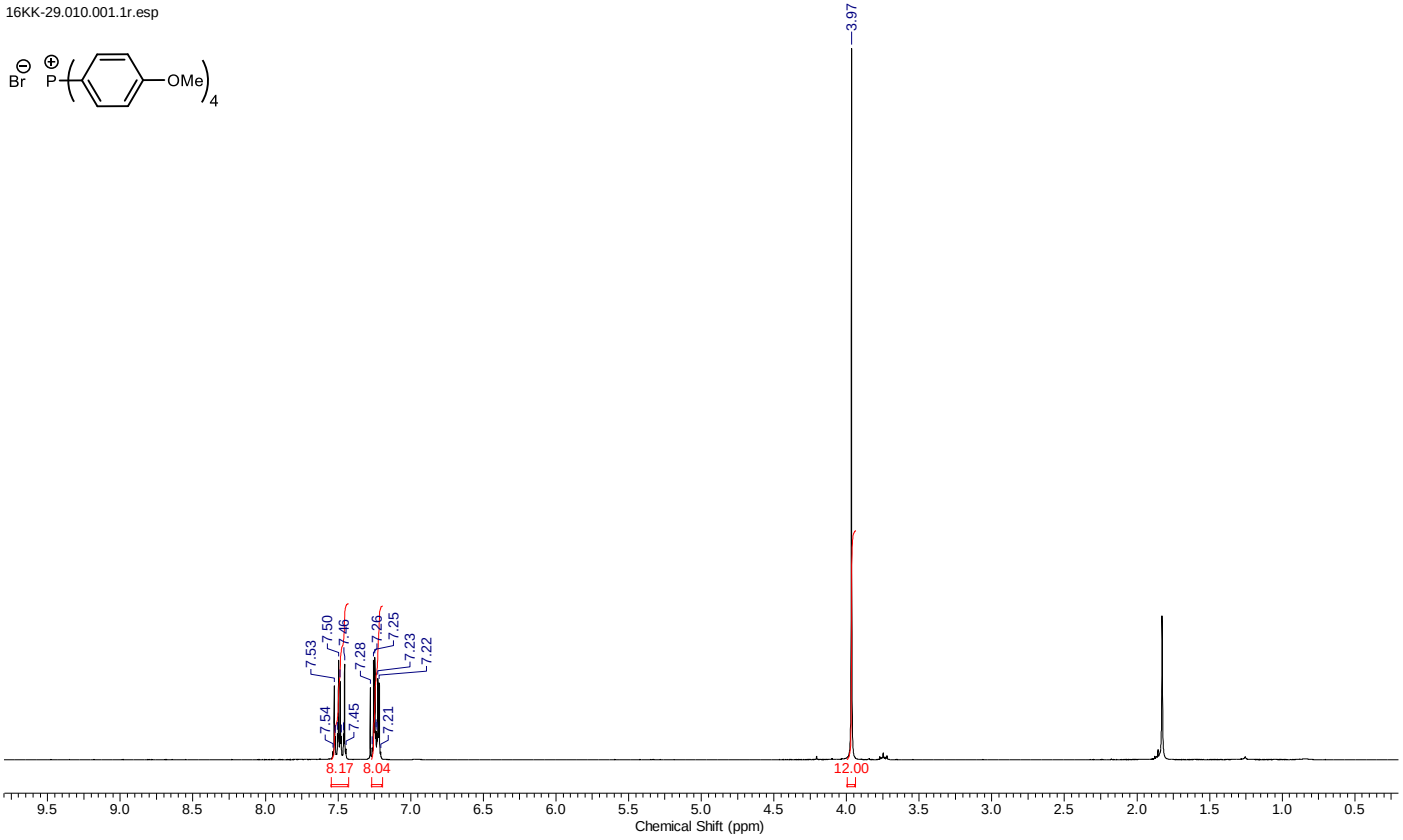
P	-0.0292898908	0.8360978073	-2.1182024993
C	-1.7711756921	0.7625135714	-1.6654405485
C	-4.4231133633	0.7382742166	-0.8383794783
C	-2.179935574	-0.1333343785	-0.6676181693
C	-2.6877157059	1.6413539638	-2.2507685234
C	-4.0152214122	1.6249111971	-1.8322760092
C	-3.5086982846	-0.1407695336	-0.2582335007
H	-1.4688382896	-0.8245325817	-0.2203871713
C	0.1570992036	1.5811304076	-3.7520082925
C	0.3339794517	2.7613539497	-6.2622114866
C	0.1899836939	2.9774217223	-3.8639671689
C	0.2213760767	0.7767816623	-4.8943286743
C	0.3098117846	1.3728653983	-6.1486443588
C	0.2747051712	3.56274754	-5.1228545276
H	0.1565167644	3.6018518533	-2.9755439637

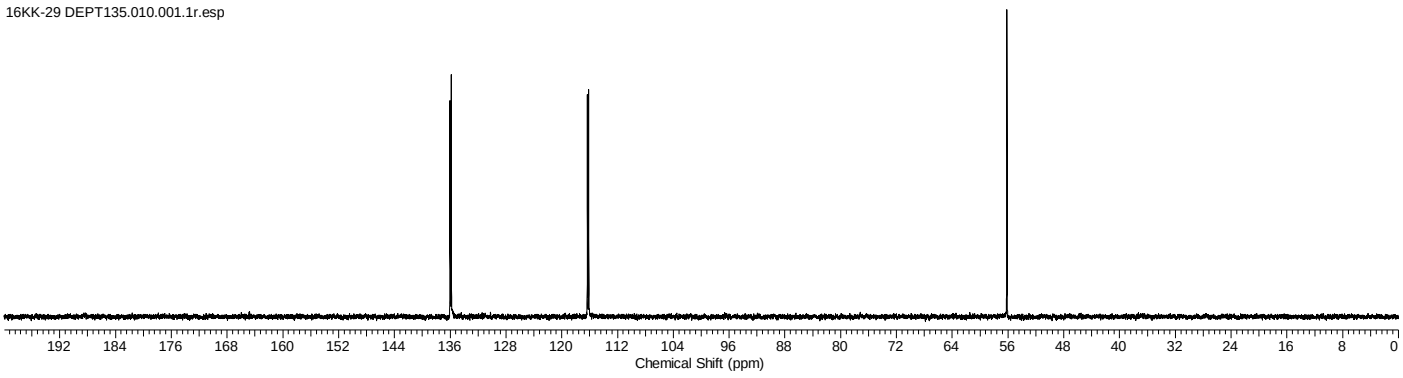
H	0.2127371189	-0.3053267972	-4.8081614121
H	0.3646211587	0.7513157357	-7.0356865602
H	0.3005576323	4.643257875	-5.2124088217
H	0.4049215884	3.2216704373	-7.242148526
C	0.6138311845	-0.848246869	-2.1445233982
C	1.6128265668	-3.4374385	-2.3122832984
C	-0.1964388771	-1.8767718955	-2.6468317823
C	1.9169700846	-1.1183375727	-1.717579236
C	2.4127355056	-2.416007651	-1.8057745693
C	0.3083915158	-3.1695936656	-2.7298934999
H	-1.2173752585	-1.6740482148	-2.9591020441
H	2.5342346823	-0.3339982824	-1.2935397296
H	3.4189801487	-2.6287165268	-1.4616658039
H	-0.3178766526	-3.9677130329	-3.113413536
H	2.0013709331	-4.4487711749	-2.3730973821
C	0.8552134476	1.8615821846	-0.9356406089
C	2.2579215154	3.3578054262	0.935679272
C	0.2276597507	2.2576335985	0.2461968703
C	2.1820924697	2.2358493657	-1.1991992403
C	2.8794340356	2.9801576542	-0.2572681843
C	0.9375557972	3.001890616	1.1850660124
H	-0.8032304574	1.9841908096	0.4435967987
H	2.6611420828	1.955728149	-2.1340063853
H	3.9063544603	3.2689869213	-0.4530829932
H	0.4546031243	3.2864152103	2.114454951
H	2.8106335455	3.9334449795	1.6708282324
H	-2.3721715653	2.3297687378	-3.0288406967
H	-3.8285878316	-0.8352419168	0.5114390799
H	-5.4583366172	0.7289609987	-0.5141715888
H	-4.7294267794	2.3036491973	-2.2853818853
N	-0.5991989251	0.3036919744	2.3556848195
C	0.0497188097	-0.7154908408	2.2170822465
Br	2.0939763725	-0.4989822189	1.8405234667
C	-0.2926256854	-2.2033653421	2.2702454573
Cl	-2.0512881001	-2.3863479032	2.4835419115
Cl	0.1610038971	-3.010878765	0.7381620119
Cl	0.5413653127	-2.9978903897	3.6293486059
O	-2.9883238704	1.1569263445	4.9367605728
C	-1.8254197578	0.7956302282	2.8603036662
H	-1.9511367349	1.8441241958	2.5734926246
H	-2.6900729923	0.2053698687	2.553924463
C	-1.8260771226	0.7585533878	4.503468598
H	-1.5479829942	-0.3257384347	4.6819684277
C	-0.619326061	1.6008461337	4.9731442317
H	-0.5695769033	1.5649935794	6.066896478
H	0.3395962194	1.2574767693	4.5638162985
H	-0.7783322771	2.6468351994	4.6815838887

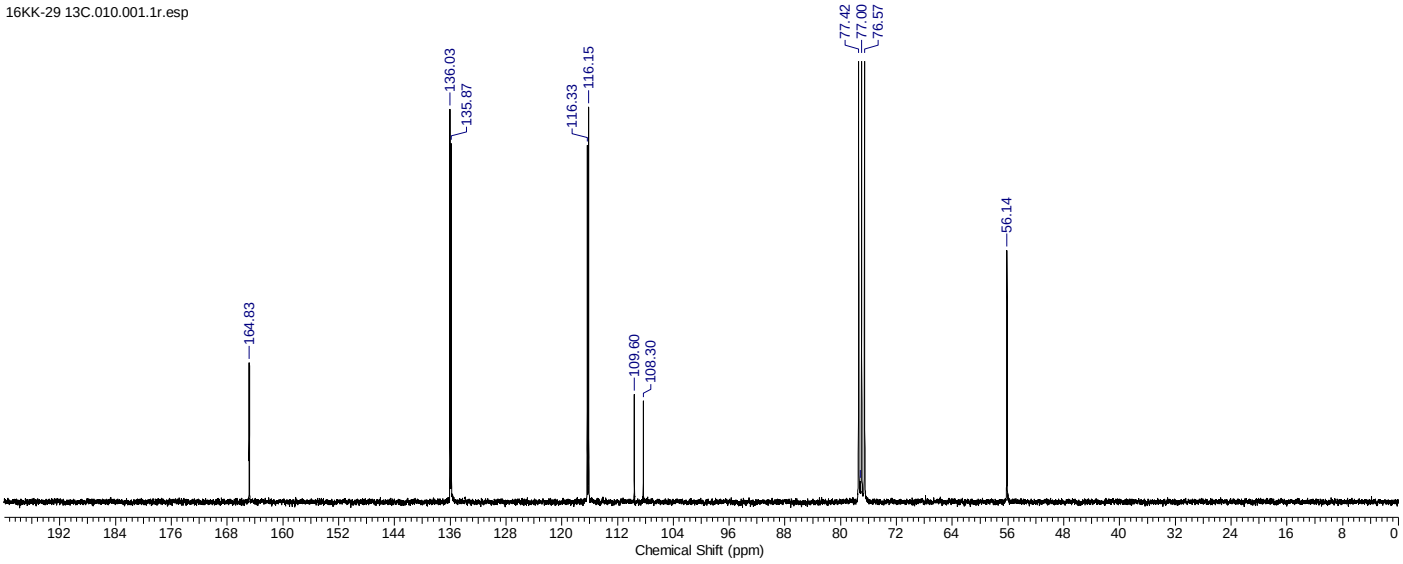
References

(1) Toda, Y.; Komiyama, Y.; Kikuchi, A.; Suga, H. Tetraarylphosphonium Salt-Catalyzed Carbon Dioxide Fixation at Atmospheric Pressure for the Synthesis of Cyclic Carbonates. *ACS Catal.* **2016**, *6*, 6906.
(2) Toda, Y.; Gomyou, S.; Shoya, T.; Komiyama, Y.; Kikuchi, A.; Suga, H. Tetraarylphosphonium Salt-Catalyzed Synthesis of Oxazolidinones from Isocyanates and Epoxides. *Org. Lett.* **2017**, *19*, 5786.
(3) Novakova, V.; Miletin, M.; Filandrová, T.; Lenčo, J.; Růžička, A.; Zimcik, P. Role of Steric Hindrance in the Newman-Kwart Rearrangement and in the Synthesis and Photophysical Properties of Arylsulfanyl Tetrapyrazinoporphyrazines. *J. Org. Chem.* **2014**, *79*, 2082.
(4) Seth, K.; Roy, S. R.; Pipaliya, B. V.; Chakraborti, A. K. Synergistic dual activation catalysis by palladium nanoparticles for epoxide ring opening with phenols. *Chem. Commun.* **2013**, *49*, 5886.
(5) Nicolaou, K. C.; Fylaktakidou, K. C.; Monenschein, H.; Li, Y.; Weyershausen, B.; Mitchell, H. J.; Wei, H.; Guntupalli, P.; Hepworth, D.; Sugita, K. Total Synthesis of Apoptolidin: Construction of Enantiomerically Pure Fragments. *J. Am. Chem. Soc.* **2003**, *125*, 15433.
(6) Smith, A. B., III; Lin, Q.; Doughty, V. A.; Zhuang, L.; McBriar, M. D.; Kerns, J. K.; Boldi, A. M.; Murase, N.; Moser, W. H.; Brook, C. S.; Bennett, C. S.; Nakayama, K.; Sobukawa, M.; Trout, R. E. L. Spongipyran synthetic studies. Total synthesis of (+)-spongistatin 2. *Tetrahedron* **2009**, *65*, 6470.
(7) Wappes, E. A.; Nakafuku, K. M.; Nagib, D. A. Directed β C−H Amination of Alcohols via Radical Relay Chaperones. *J. Am. Chem. Soc.* **2017**, *139*, 10204.
(8) Umezawa, J.; Takahashi, O.; Furuhashi, K.; Nohira, H. Synthesis of Optically Active Oxazolines from Optically Active Epoxides. *Tetrahedron: Asymmetry* **1994**, *5*, 491.
(9) Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
(10) (a) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215. (b) Zhao, Y.; Truhlar, D. G. Density Functionals with Broad Applicability in Chemistry. *Acc. Chem. Res.* **2008**, *41*, 157.
(11) Tomasi, J.; Mennucci, B.; Cammi, R. Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* **2005**, *105*, 2999.
(12) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

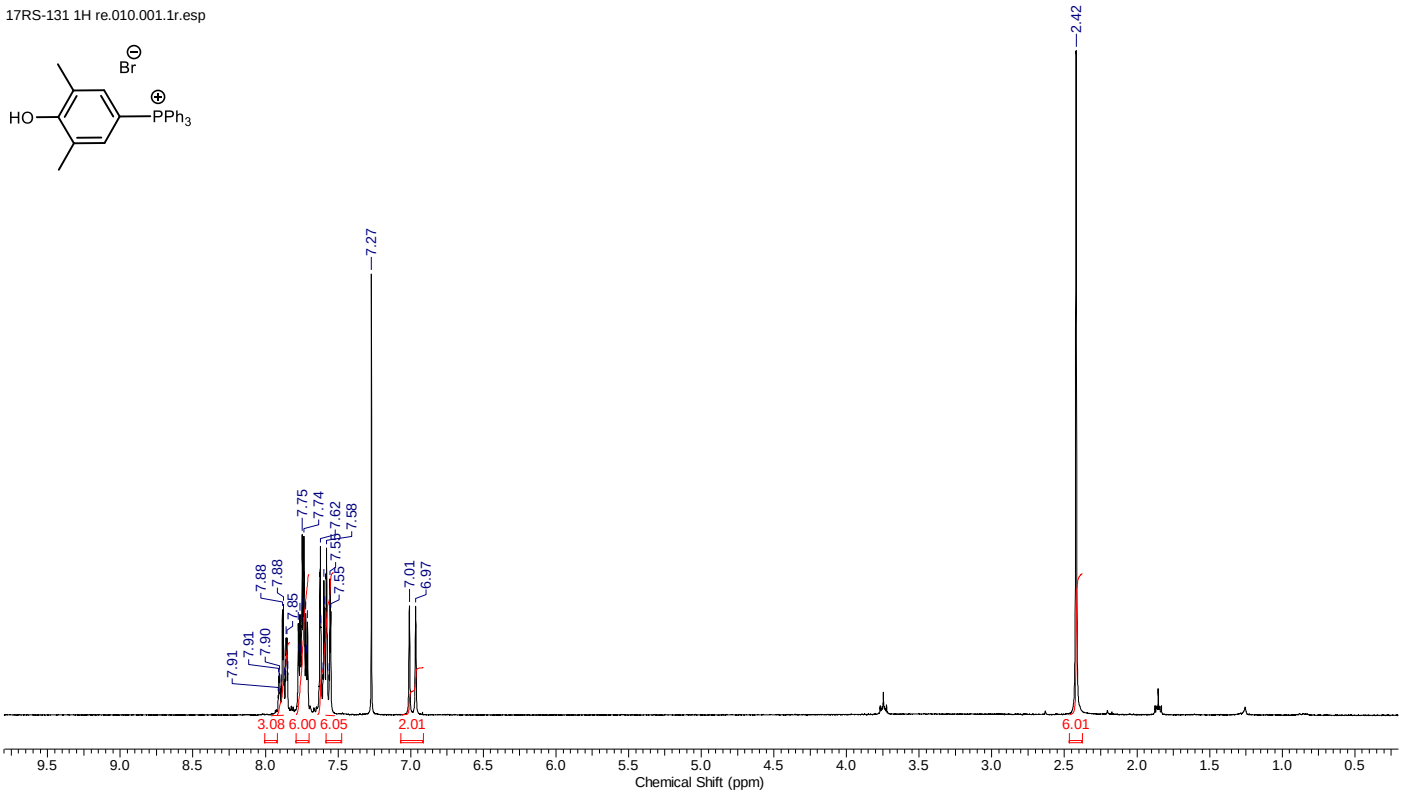
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of $(4\text{-}MeOC_6H_4)_4P^+Br^-$

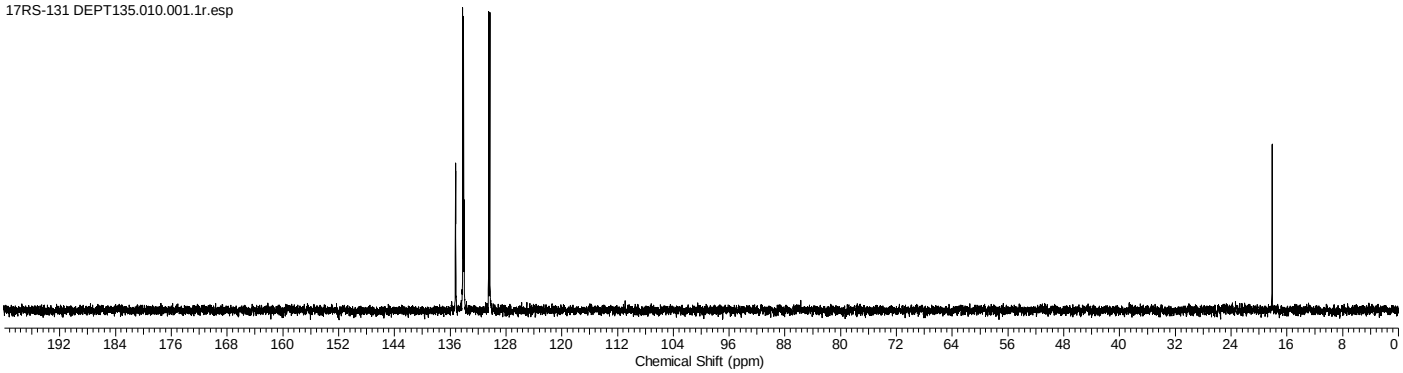


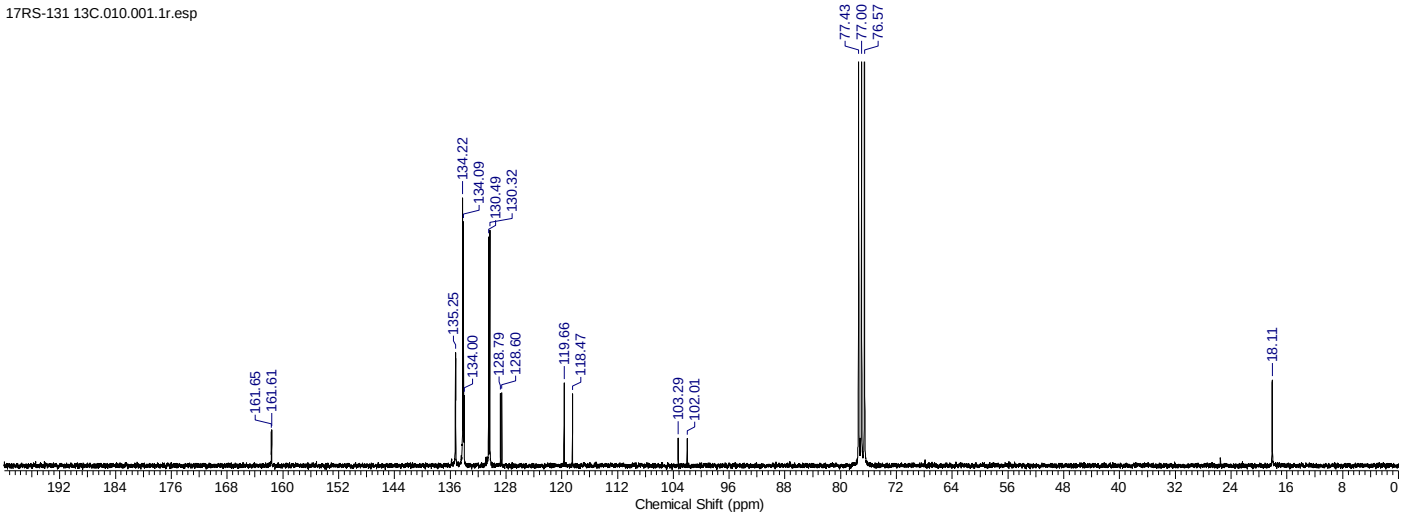




^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of TAPS D

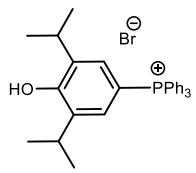




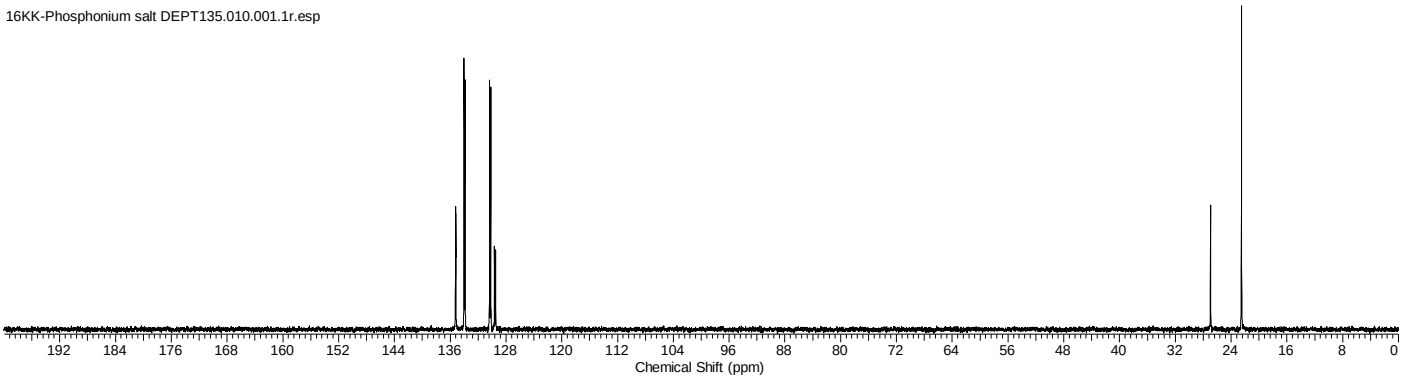


^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of TAPS E

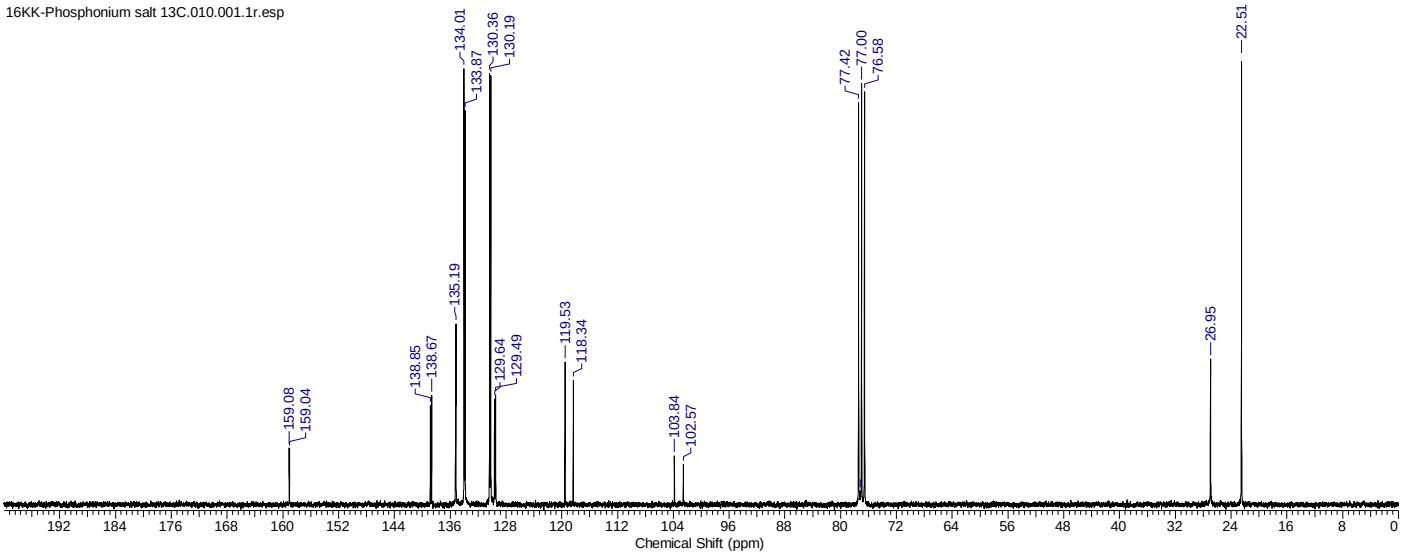
16KK-Phosphonium salt 1H.010.001.1r.esp



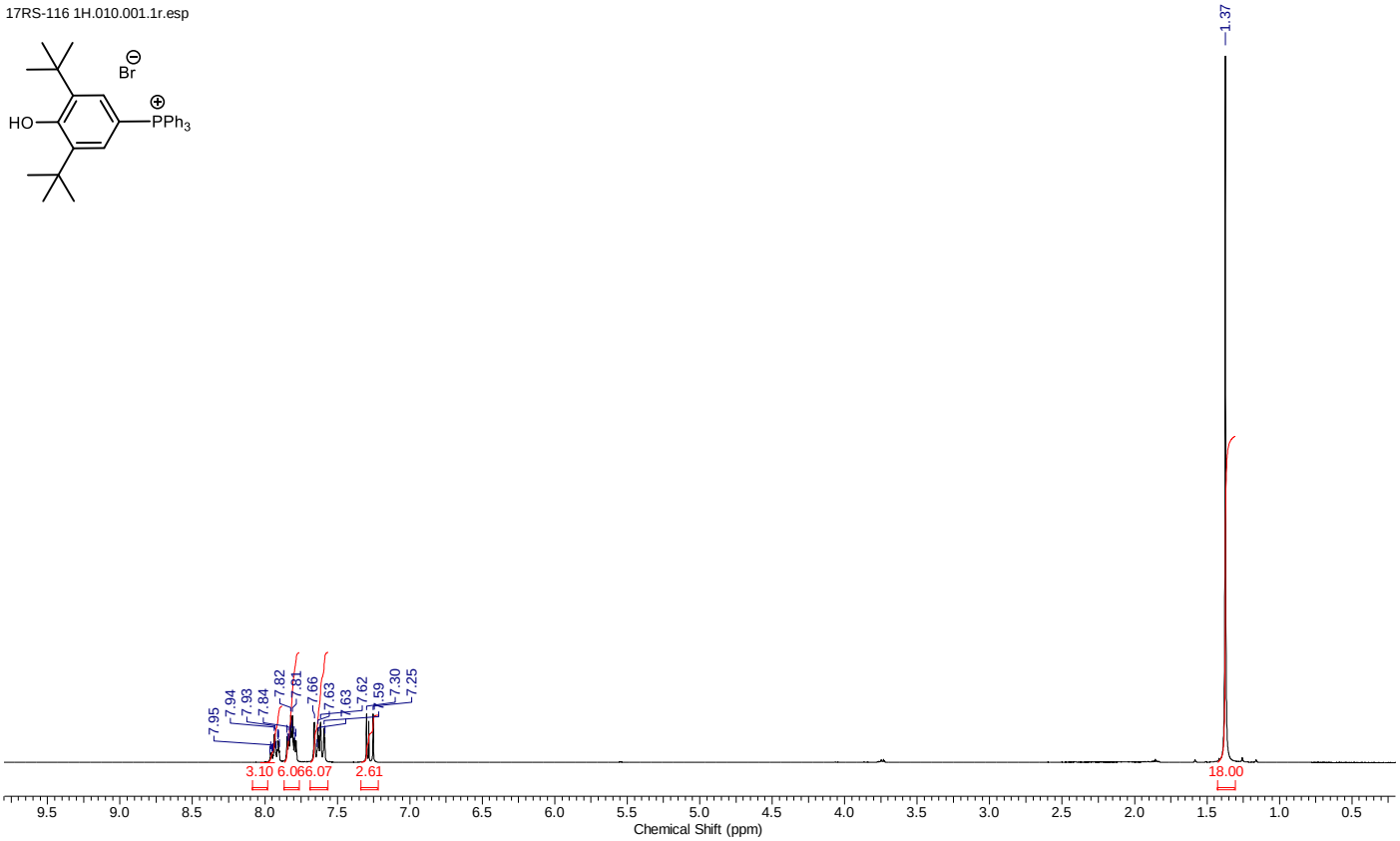
16KK-Phosphonium salt DEPT135.010.001.1r.esp

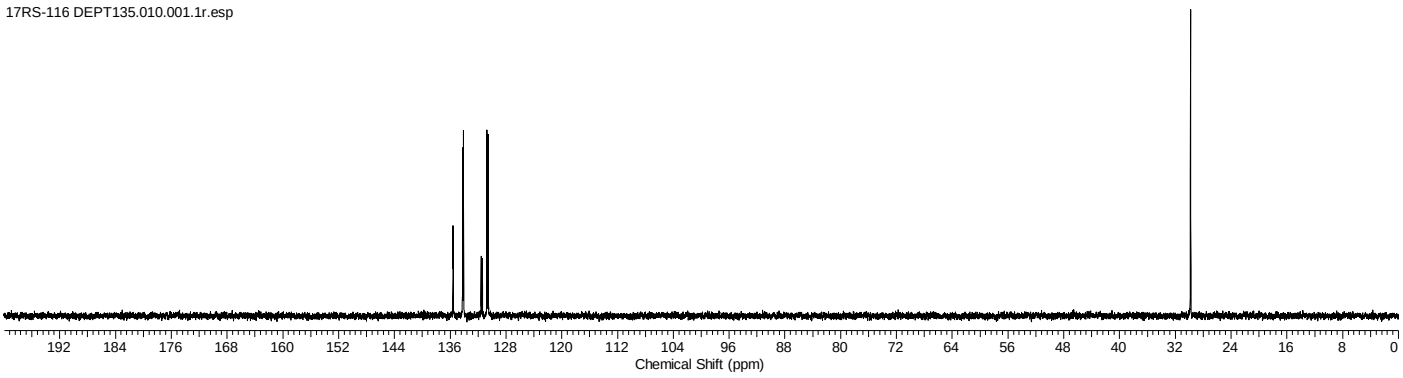


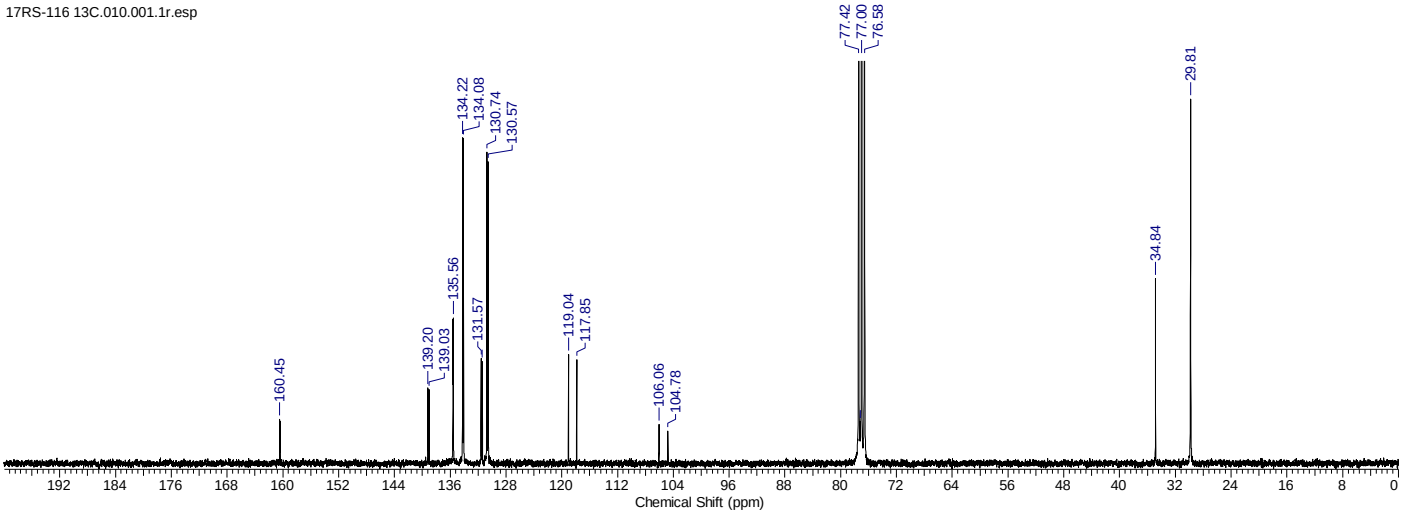
16KK-Phosphonium salt 13C.010.001.1r.esp



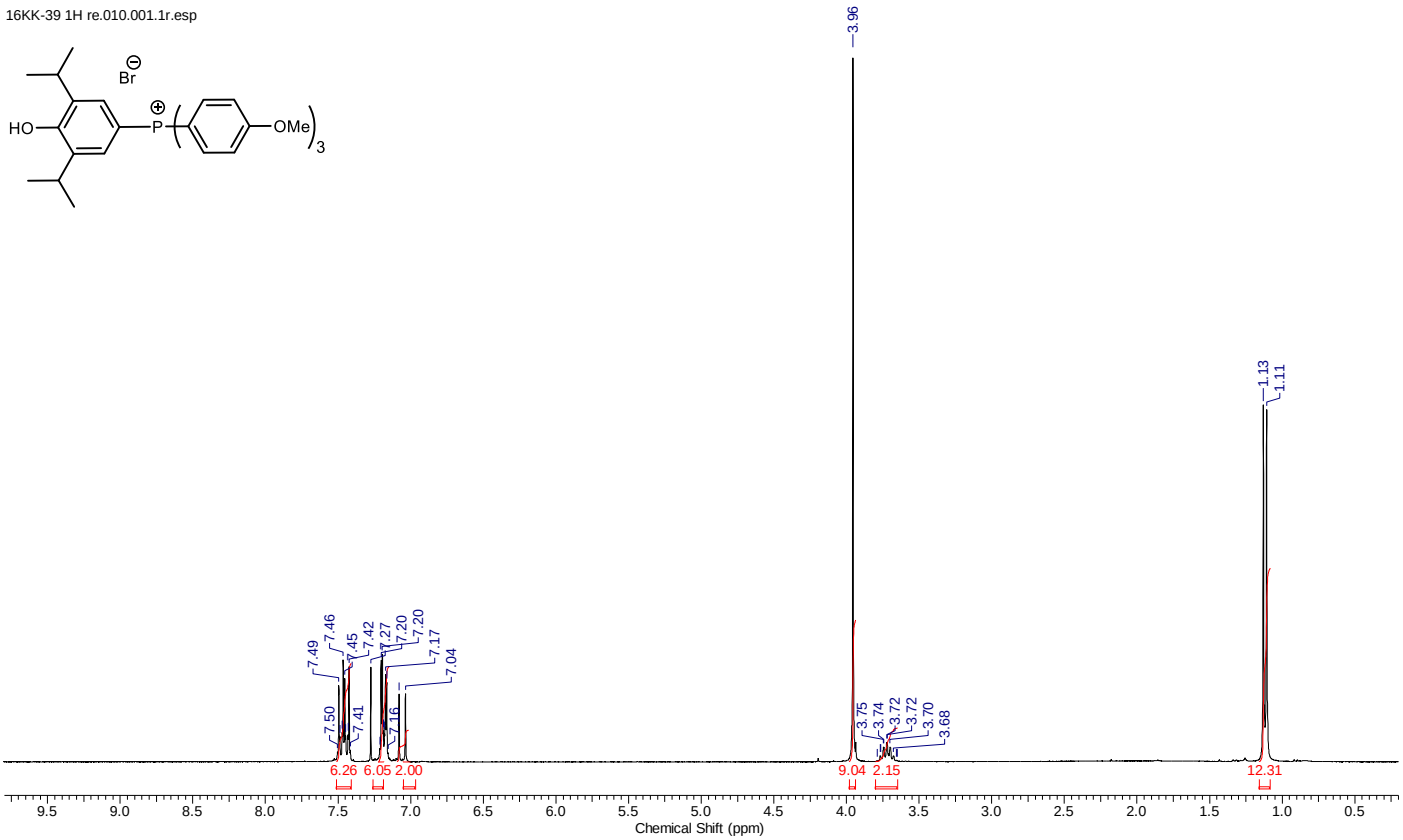
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of TAPS F

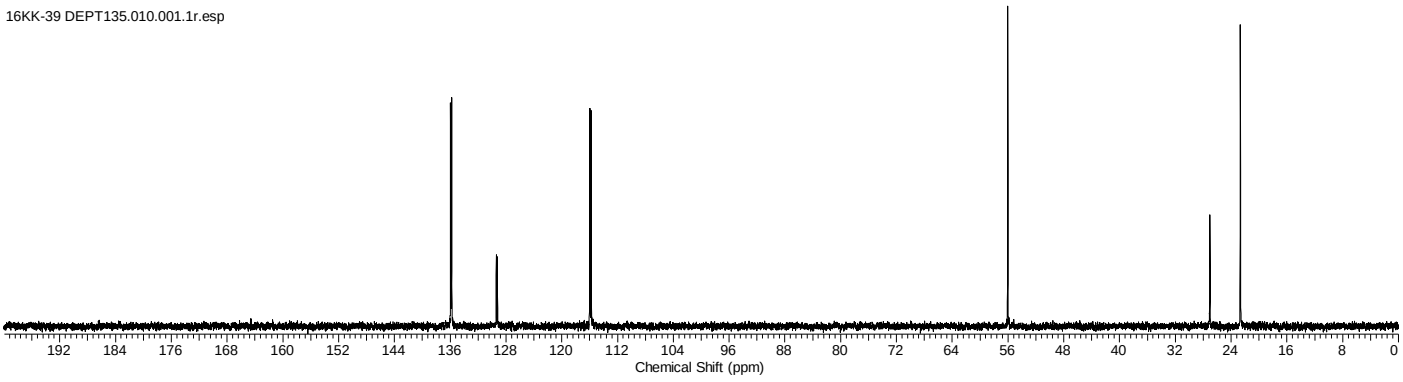


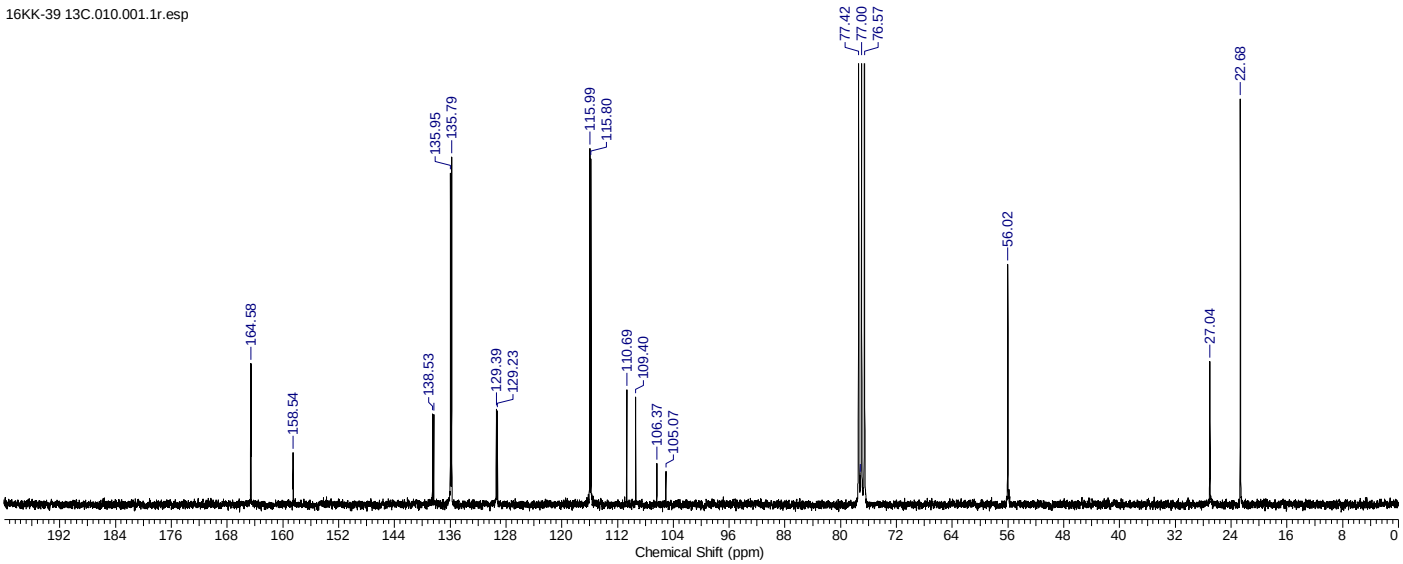




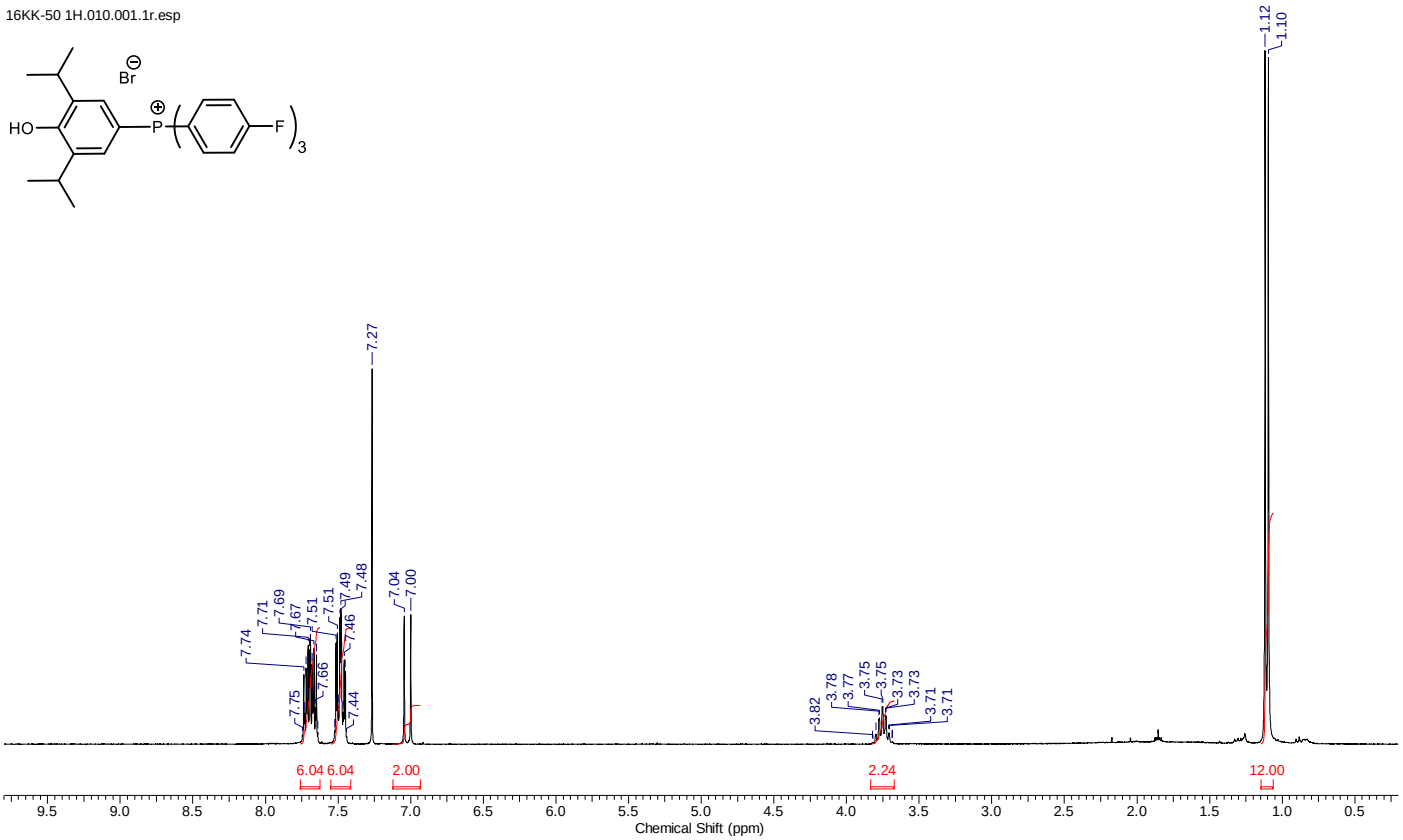
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of TAPS G

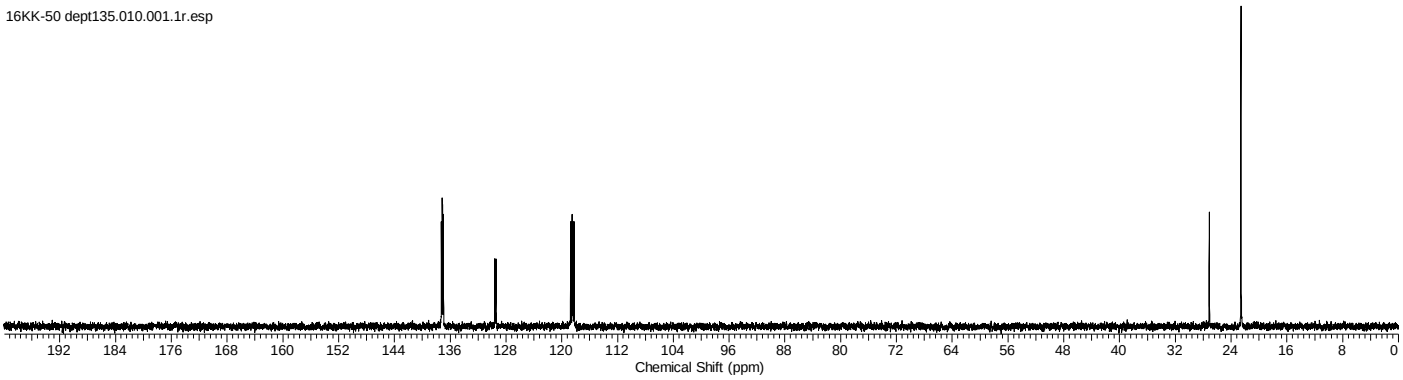


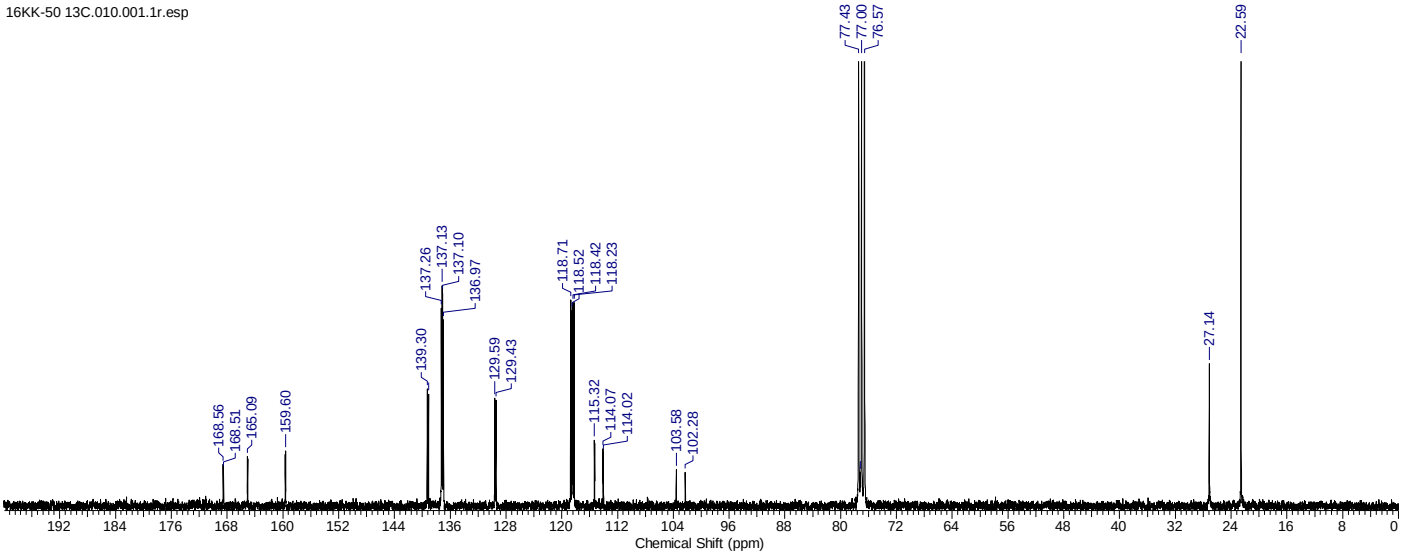




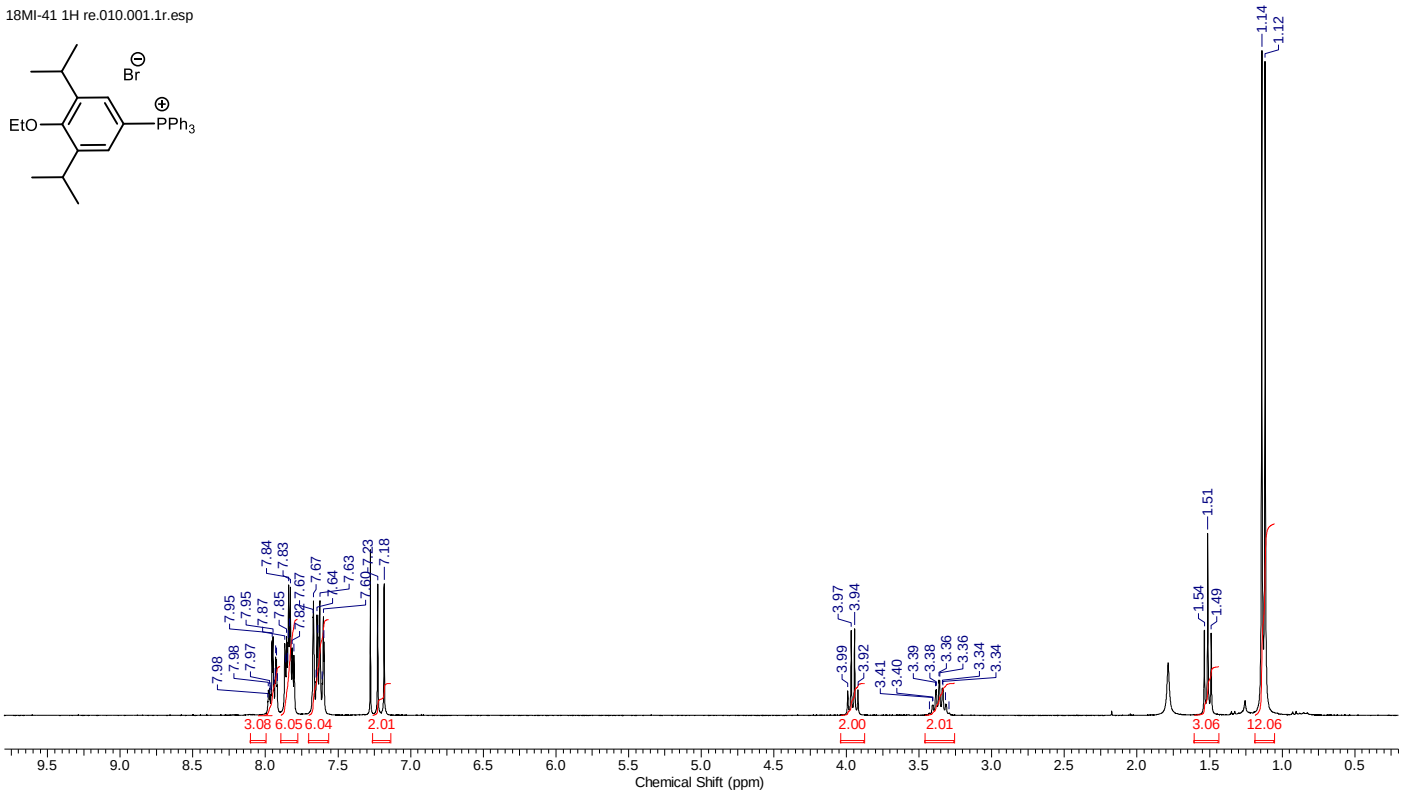
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of TAPS H

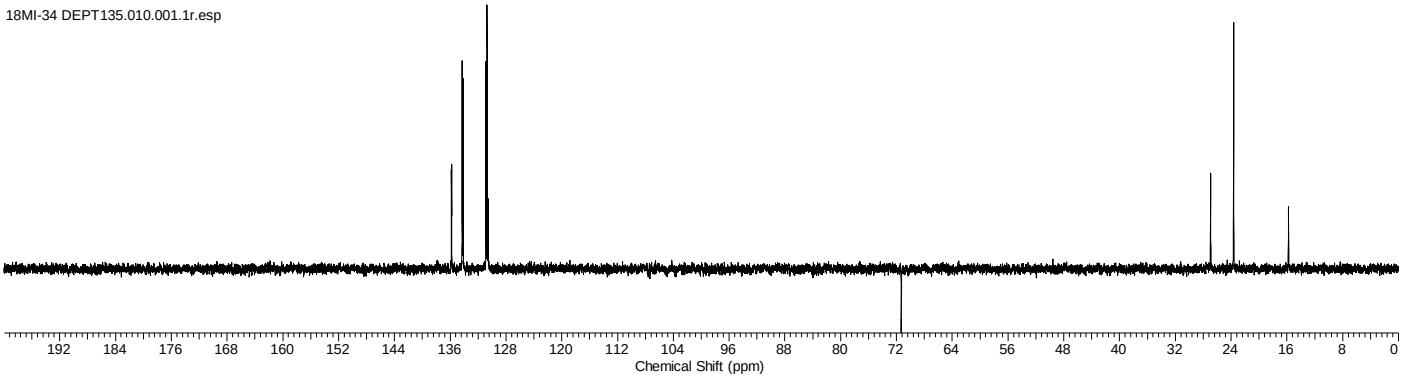


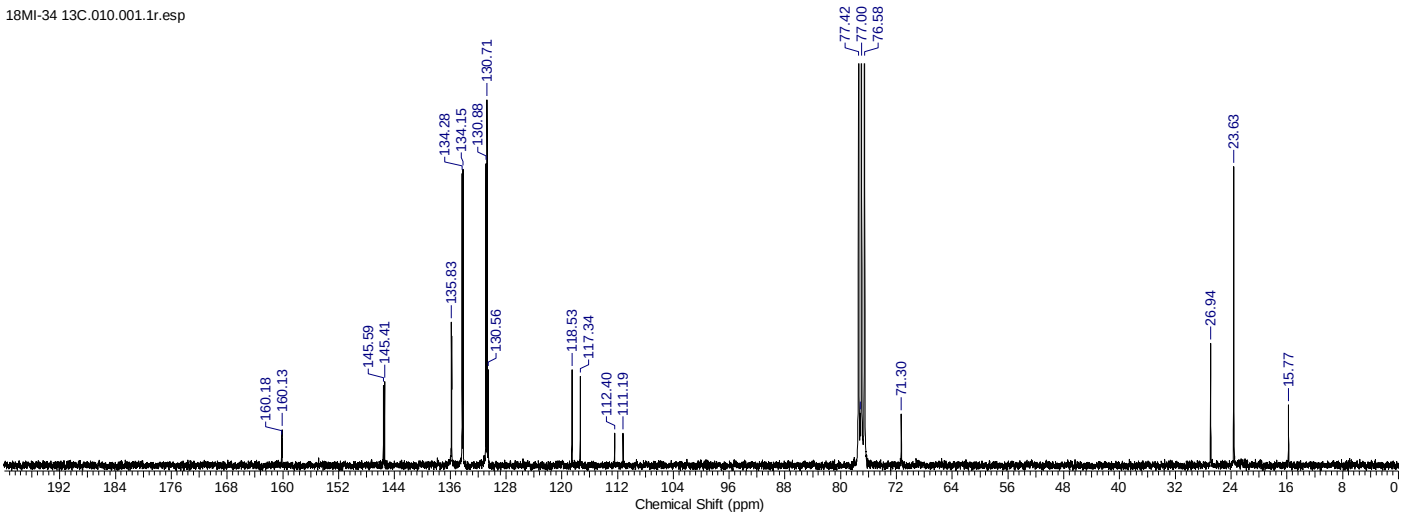




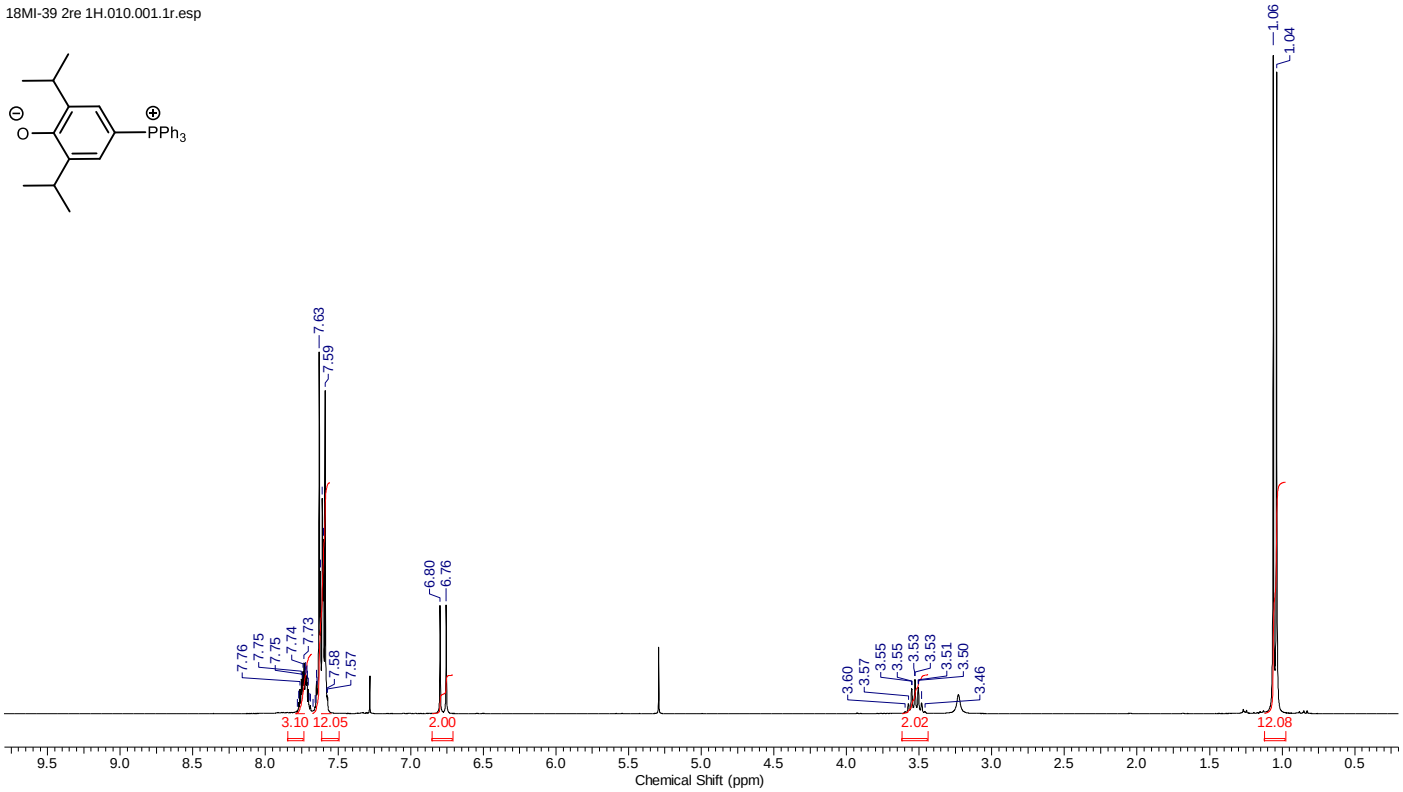
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of TAPS I

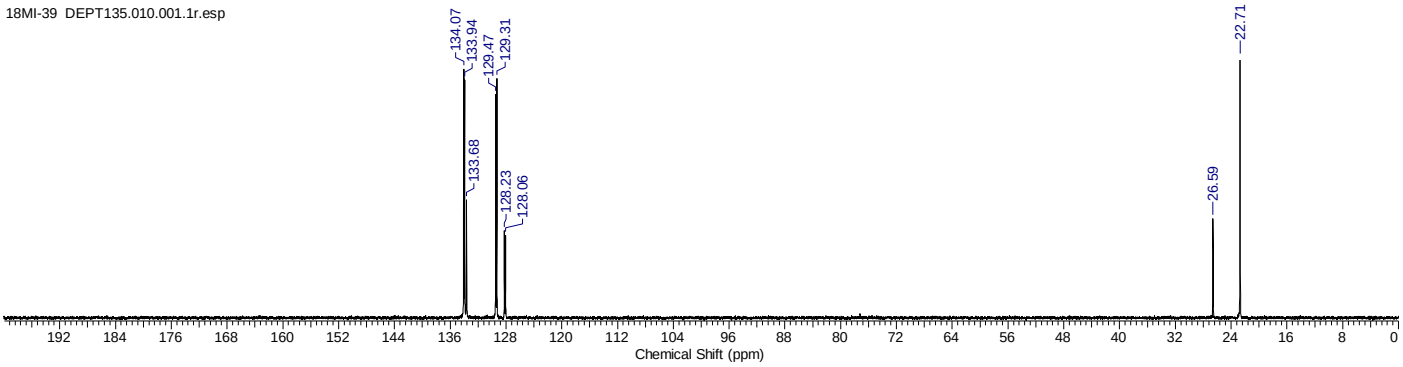


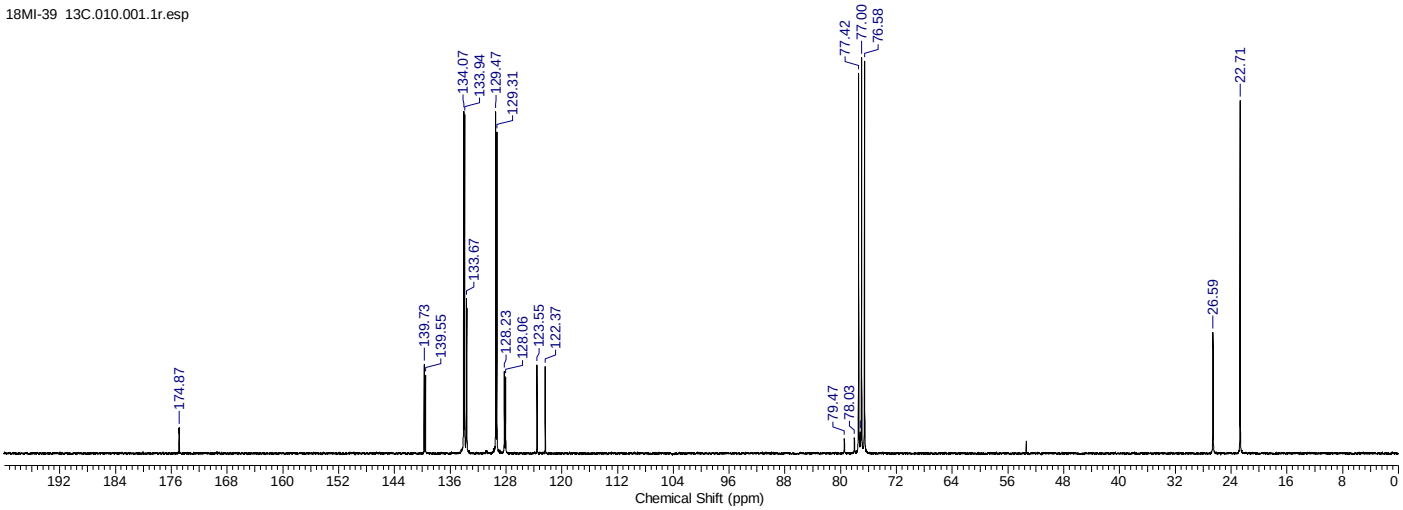




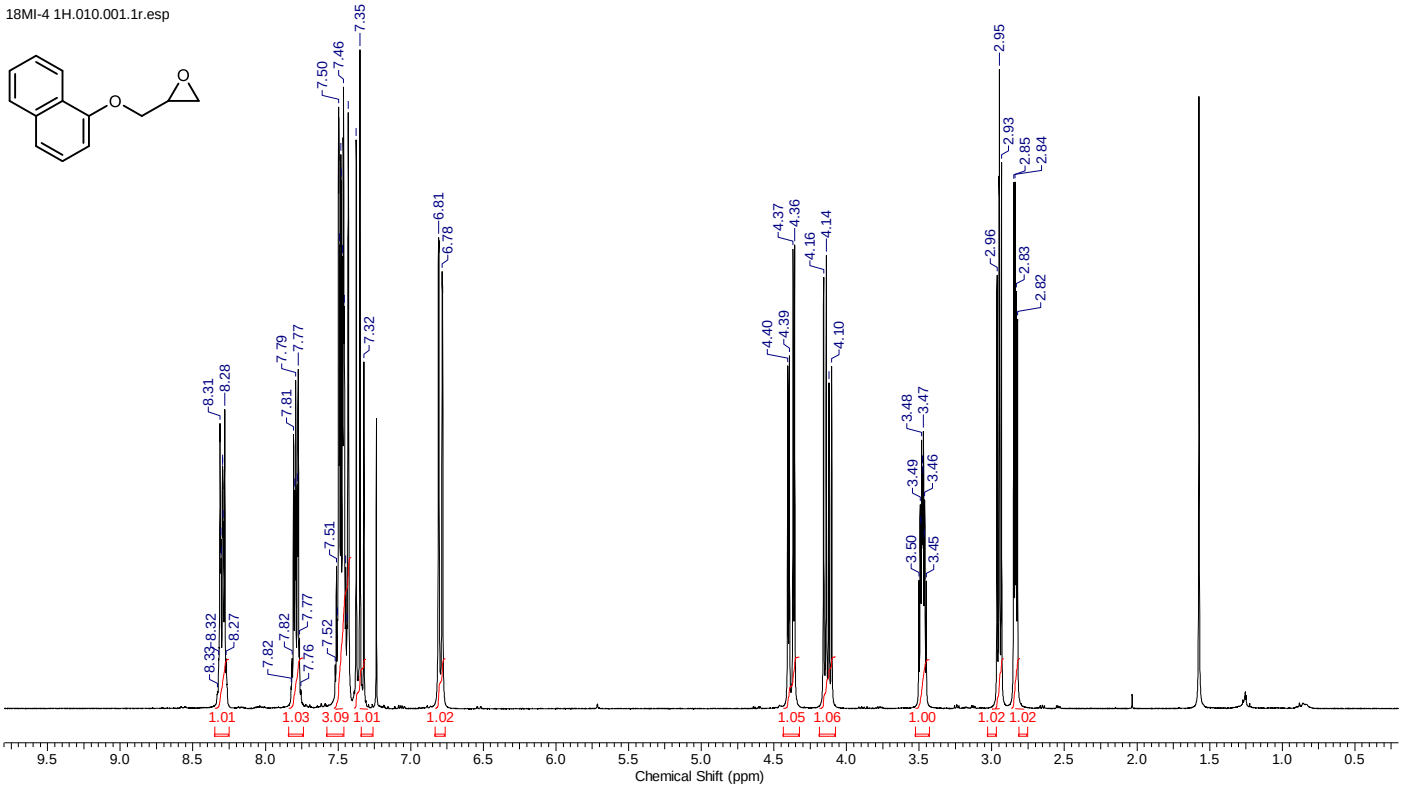
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of S1

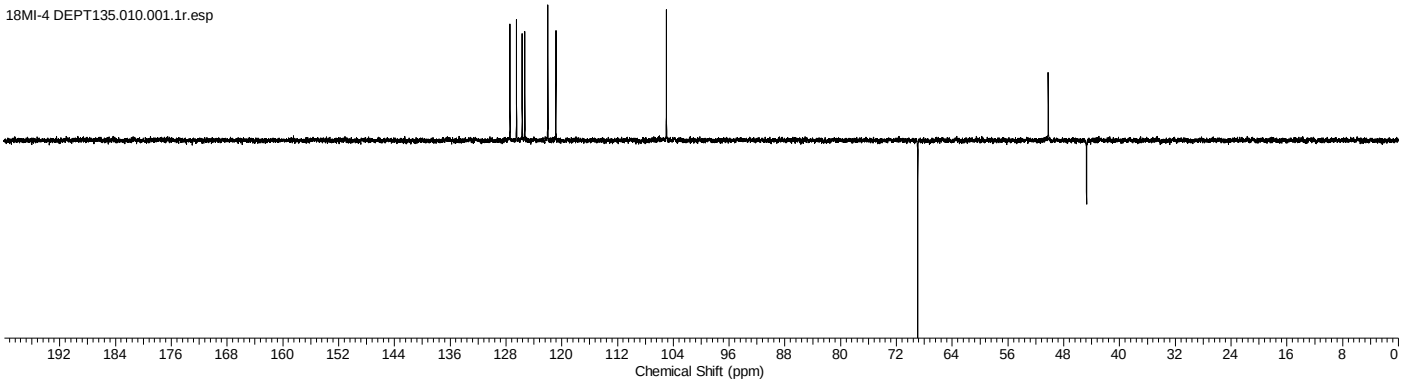


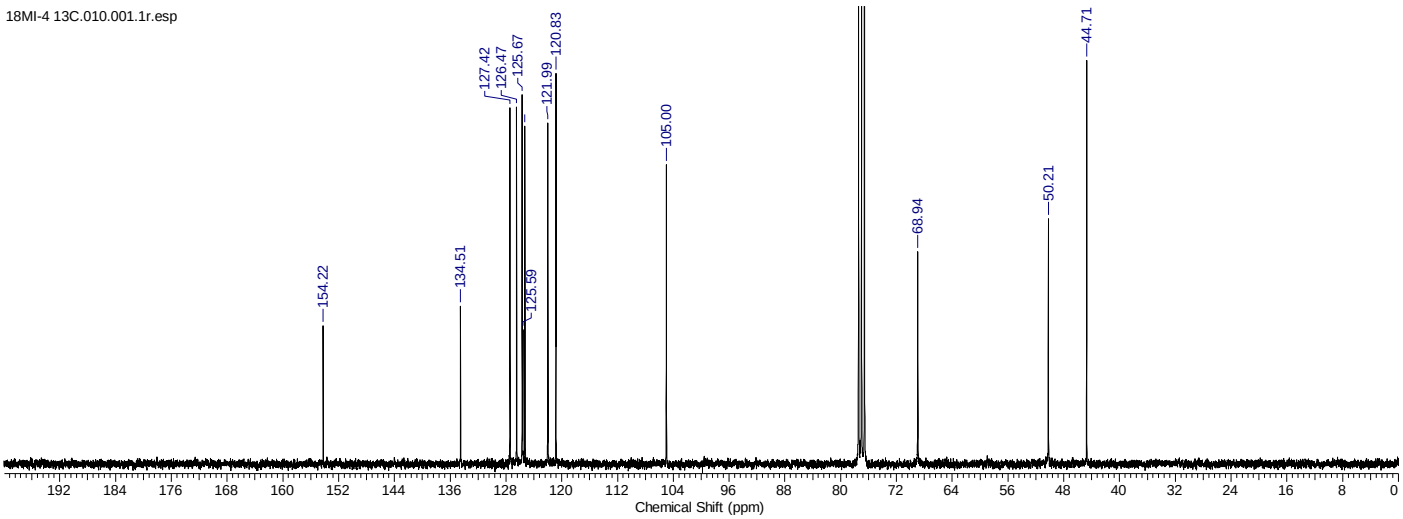




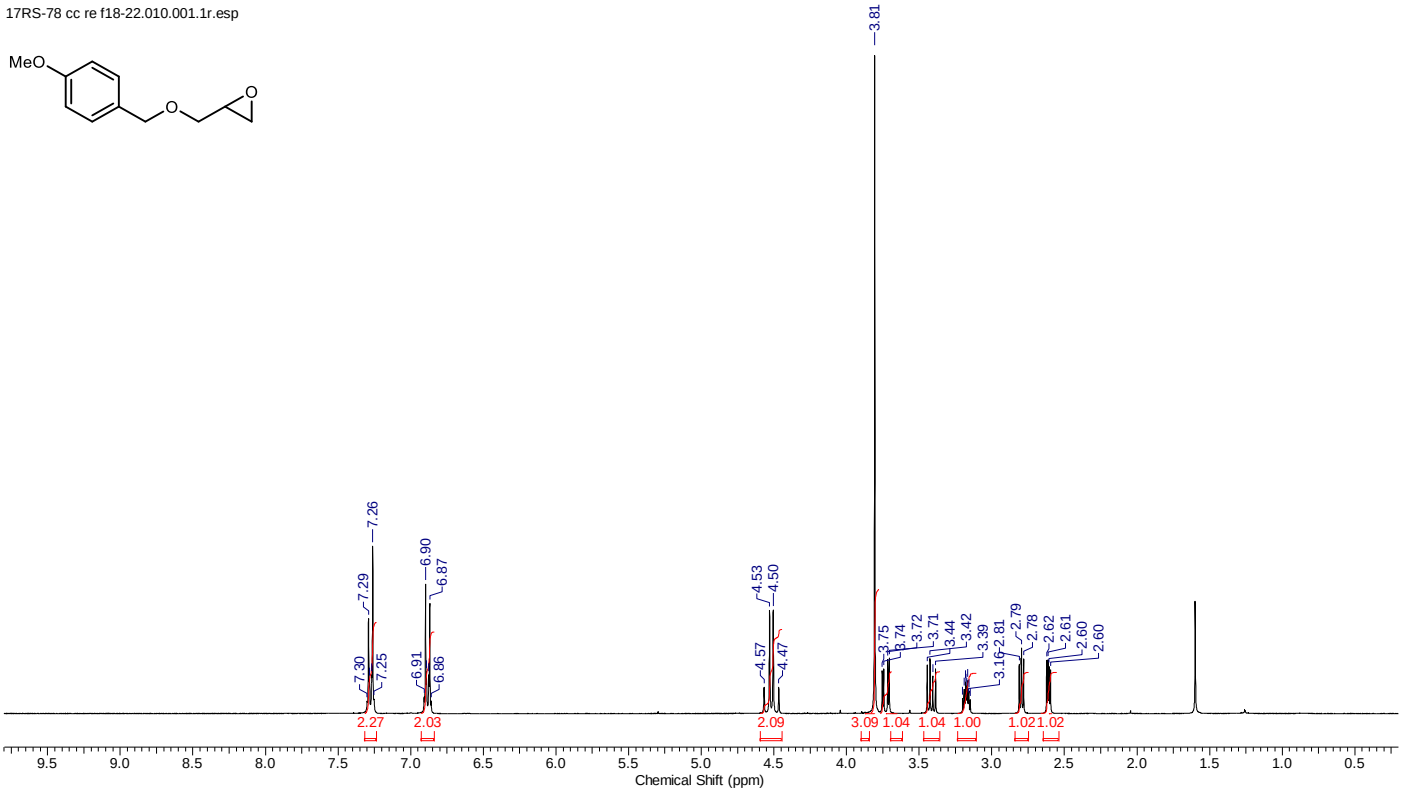
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of glycidyl 1-naphthyl ether

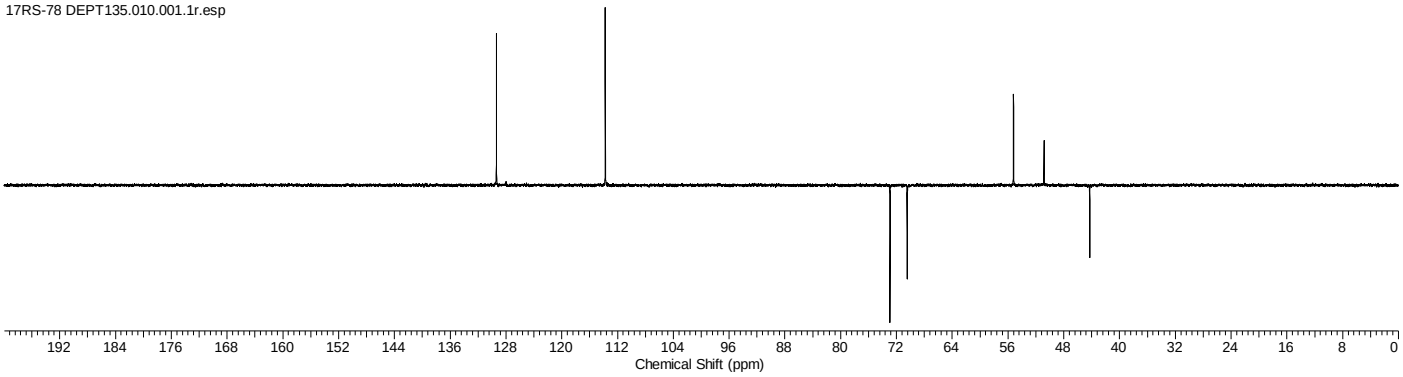


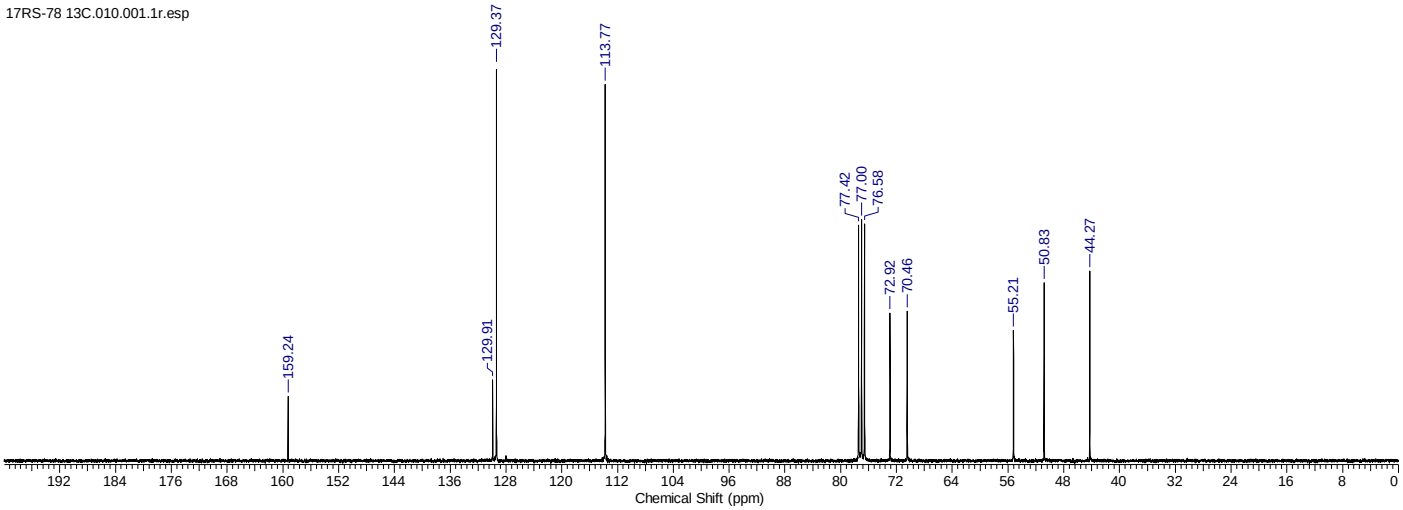




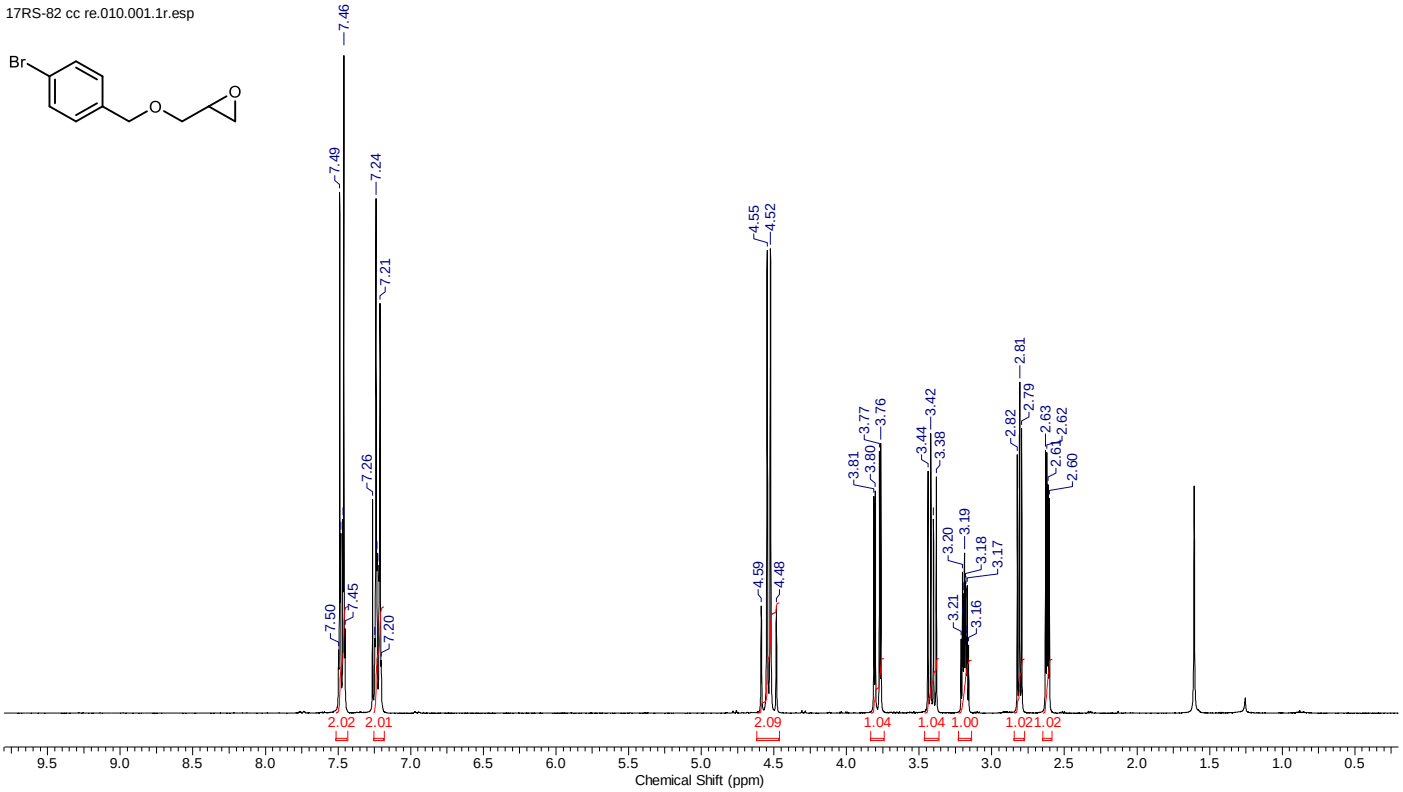
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of glycidyl 4-methoxylbenzyl ether

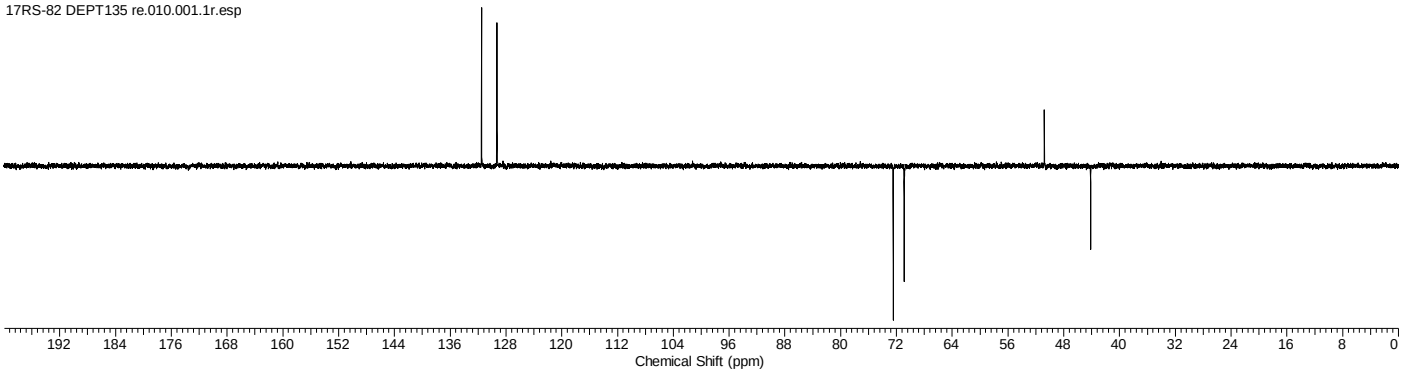


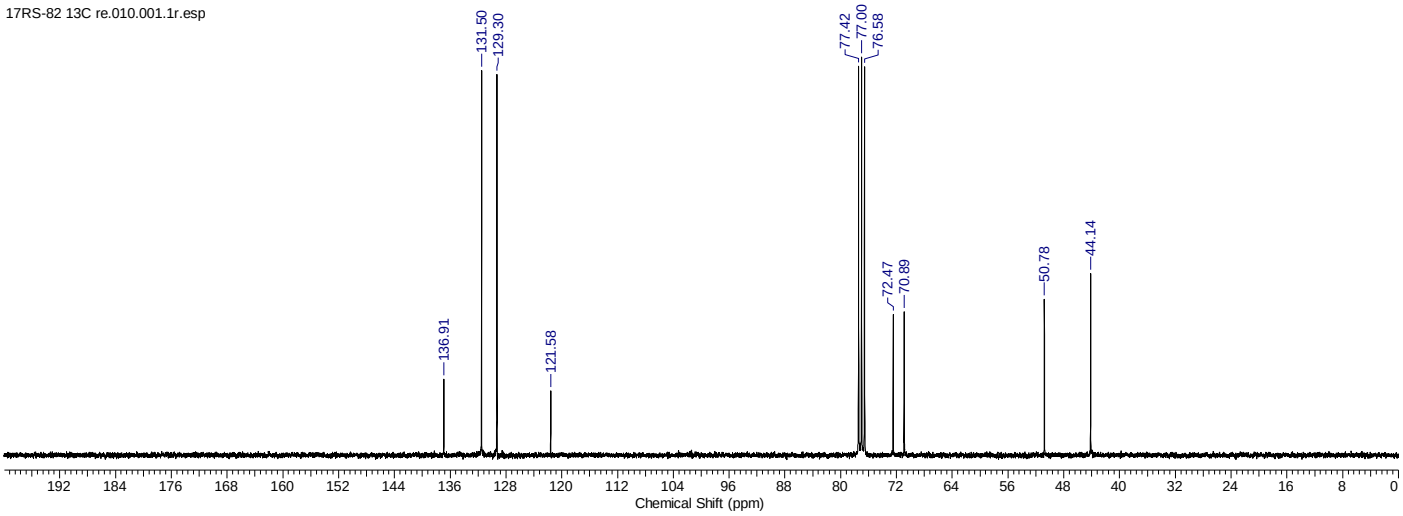




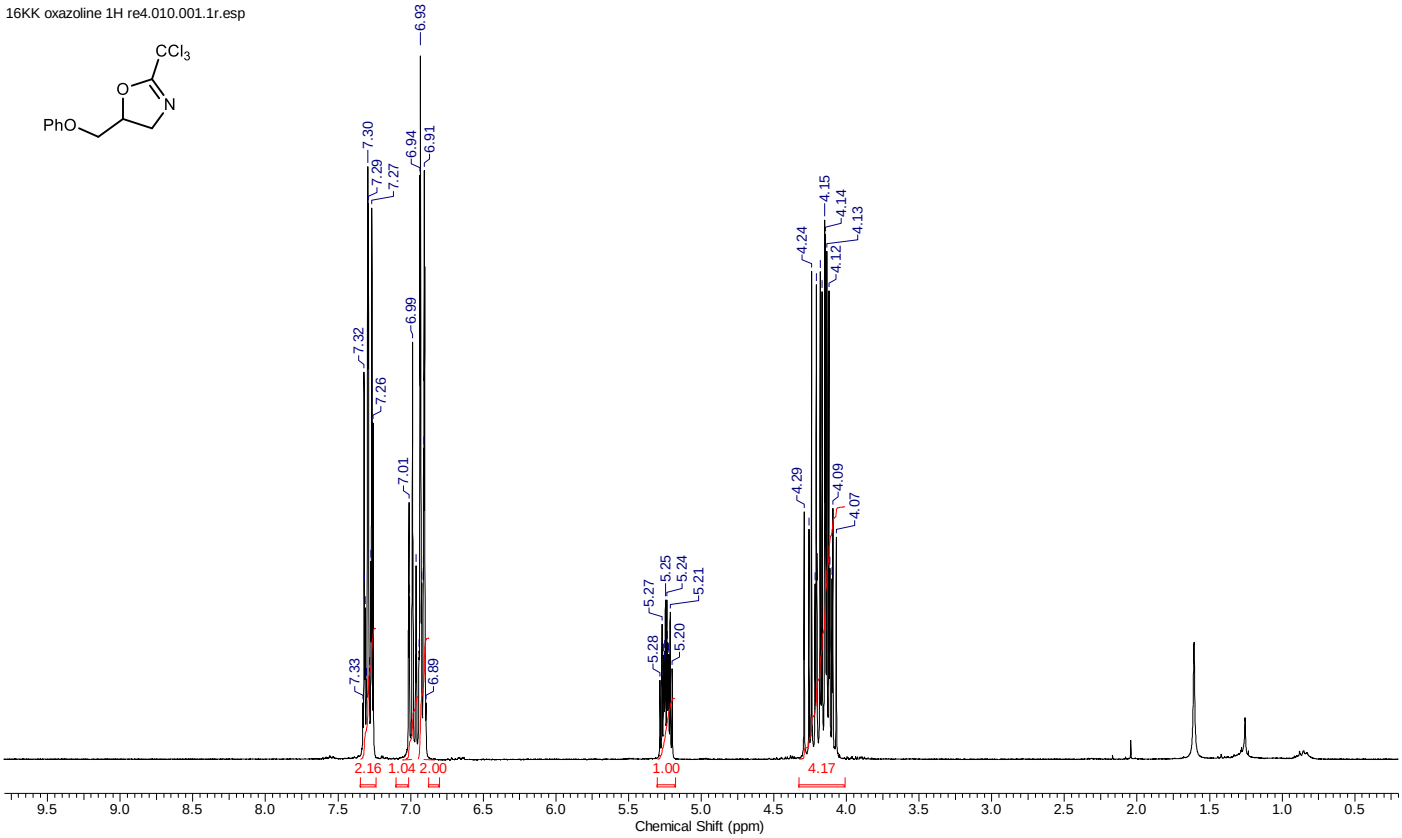
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4-bromobenzyl glycidyl ether

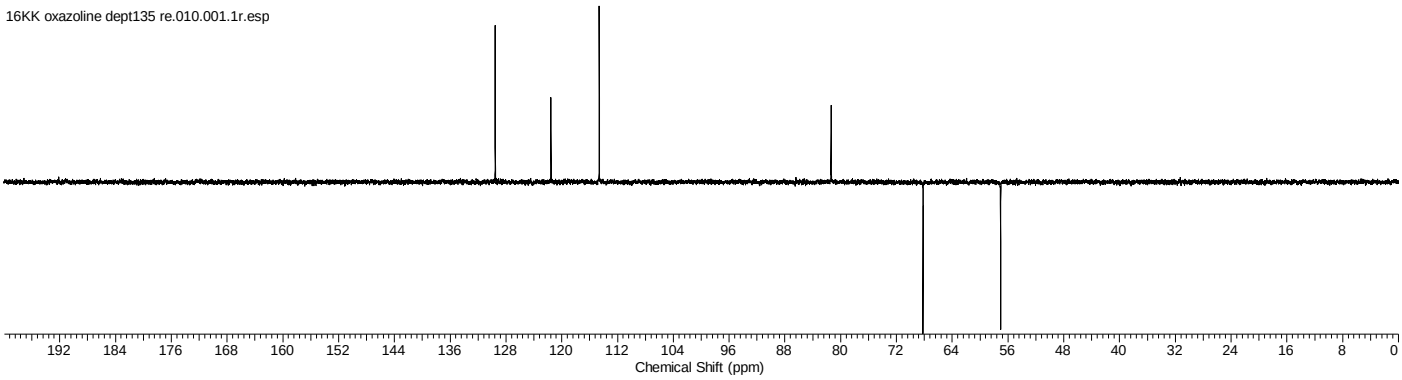


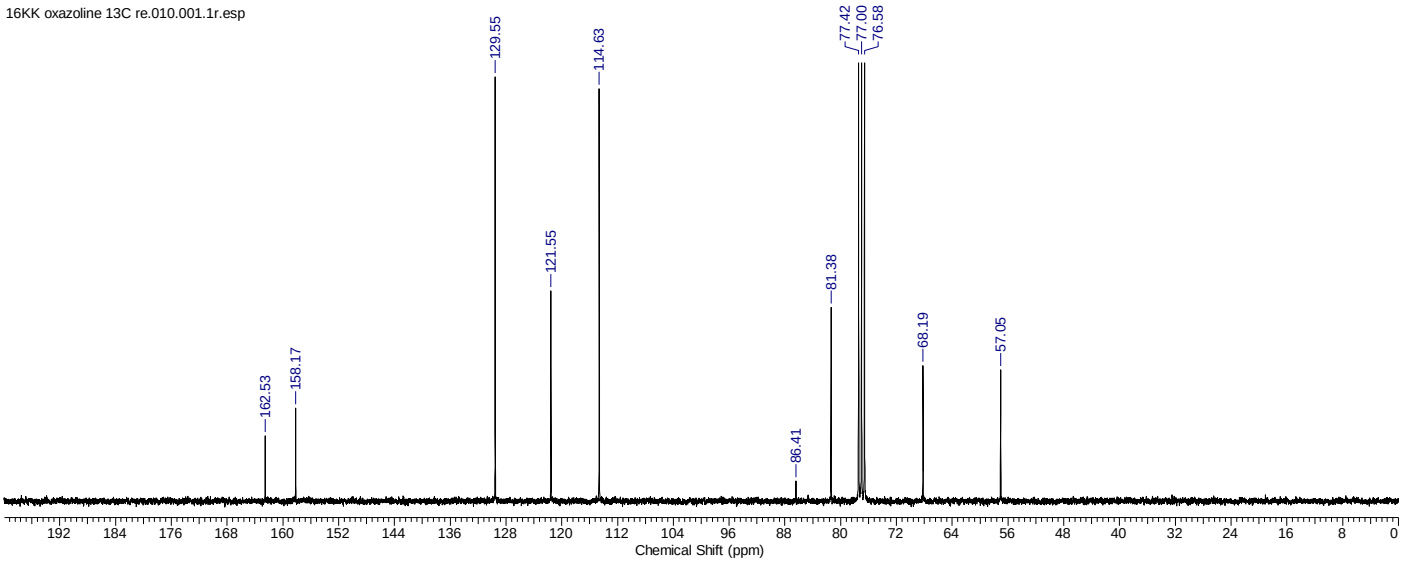




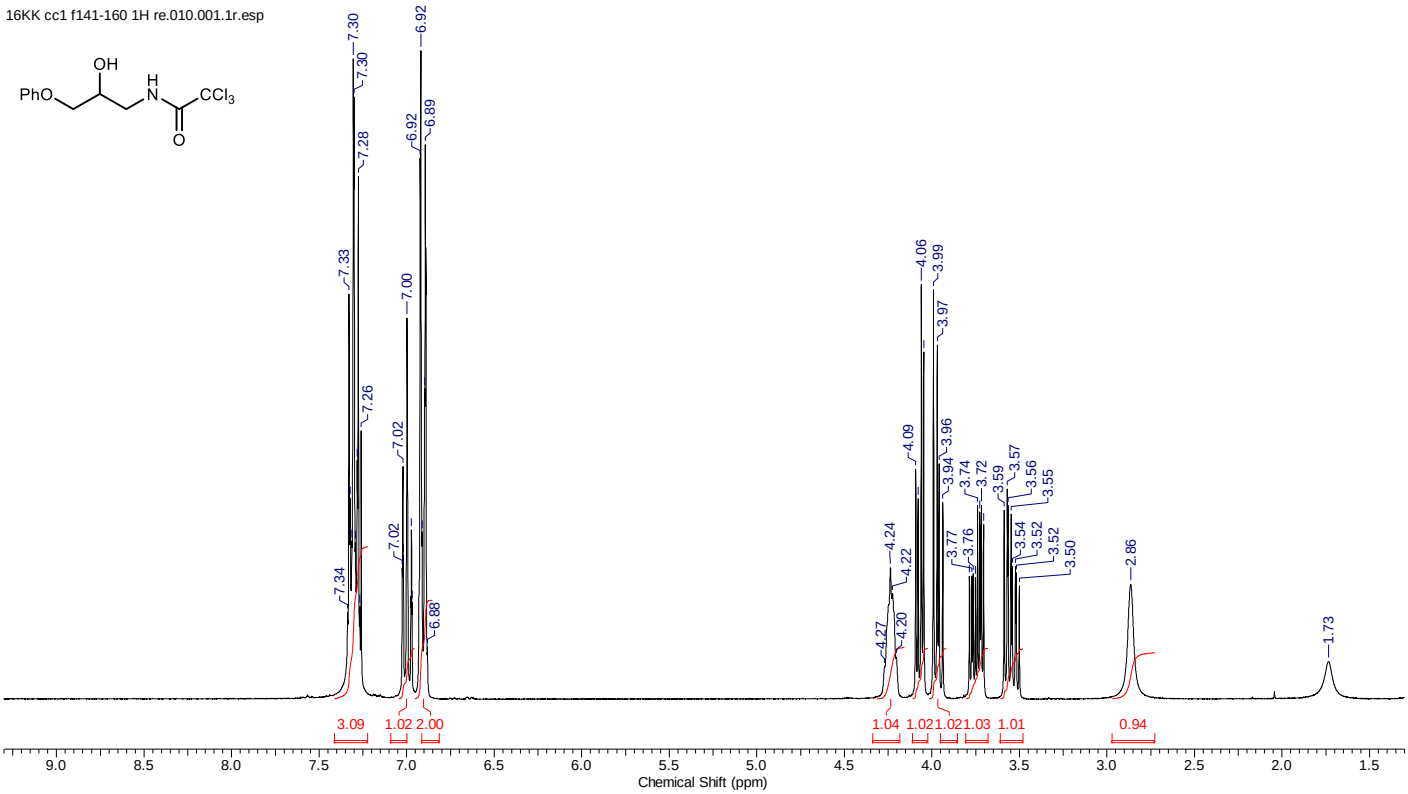
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 2a

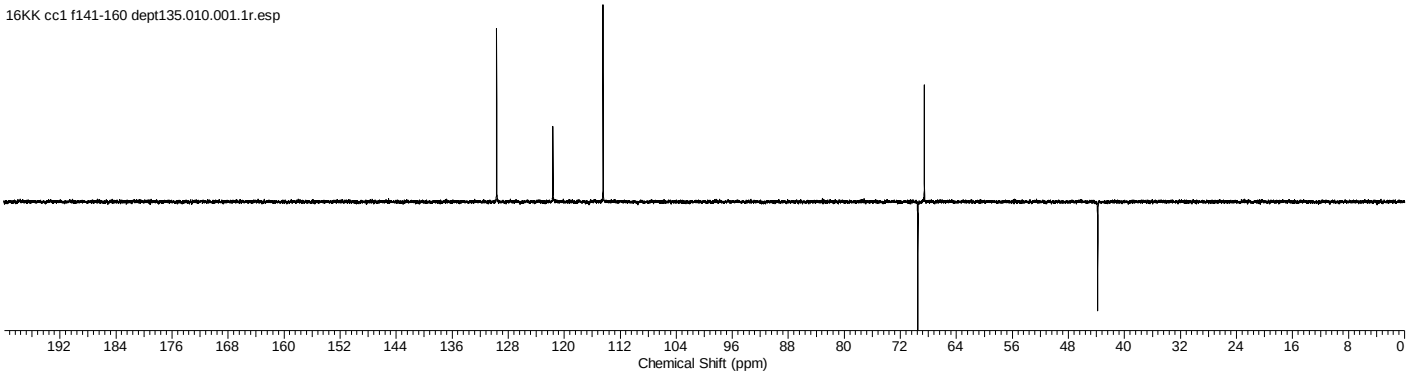


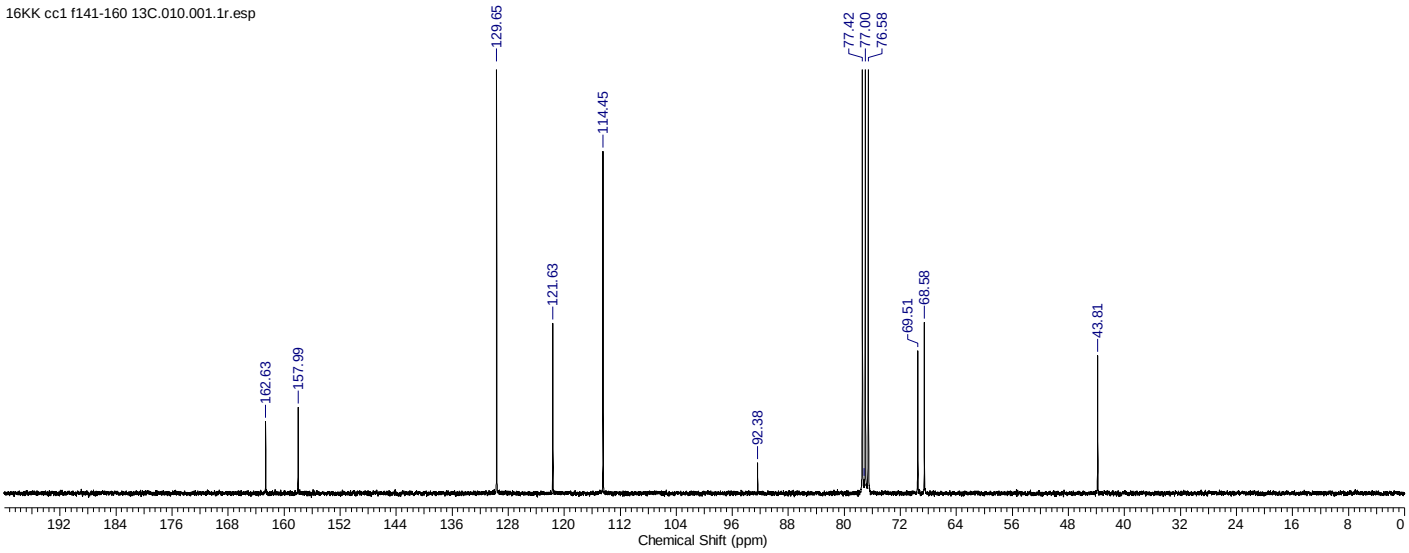




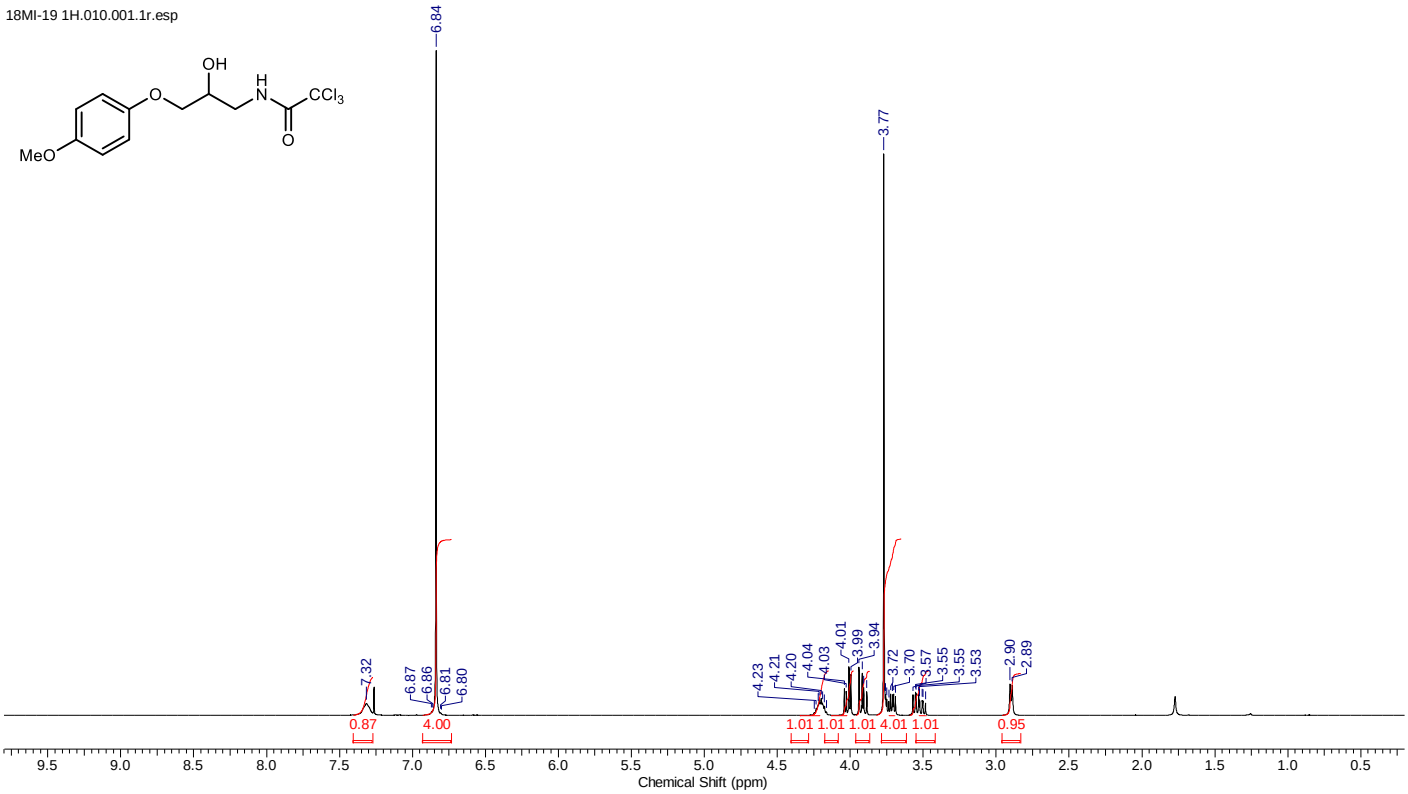
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4a

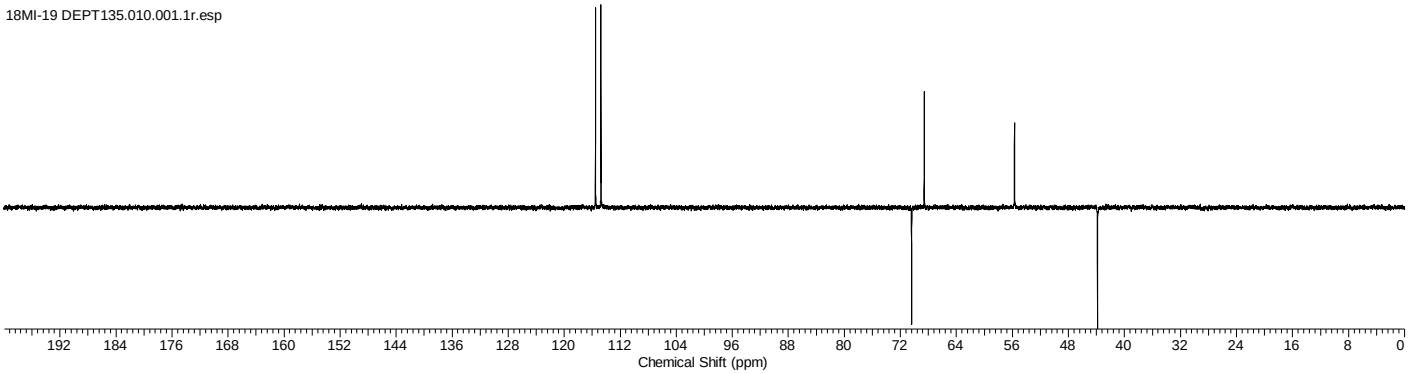


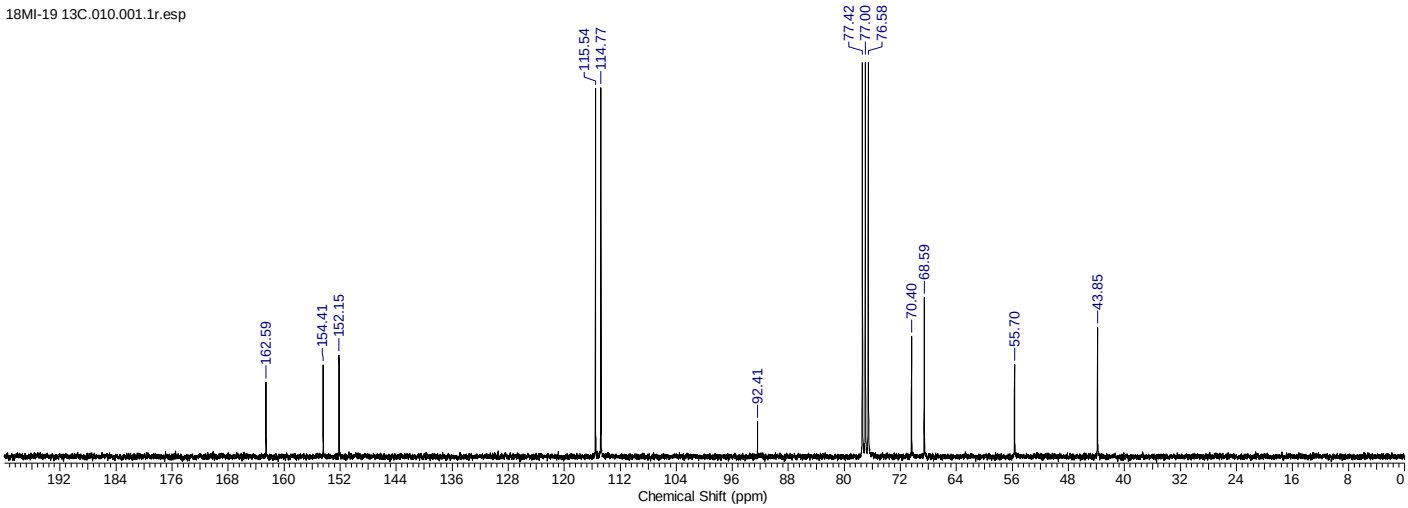




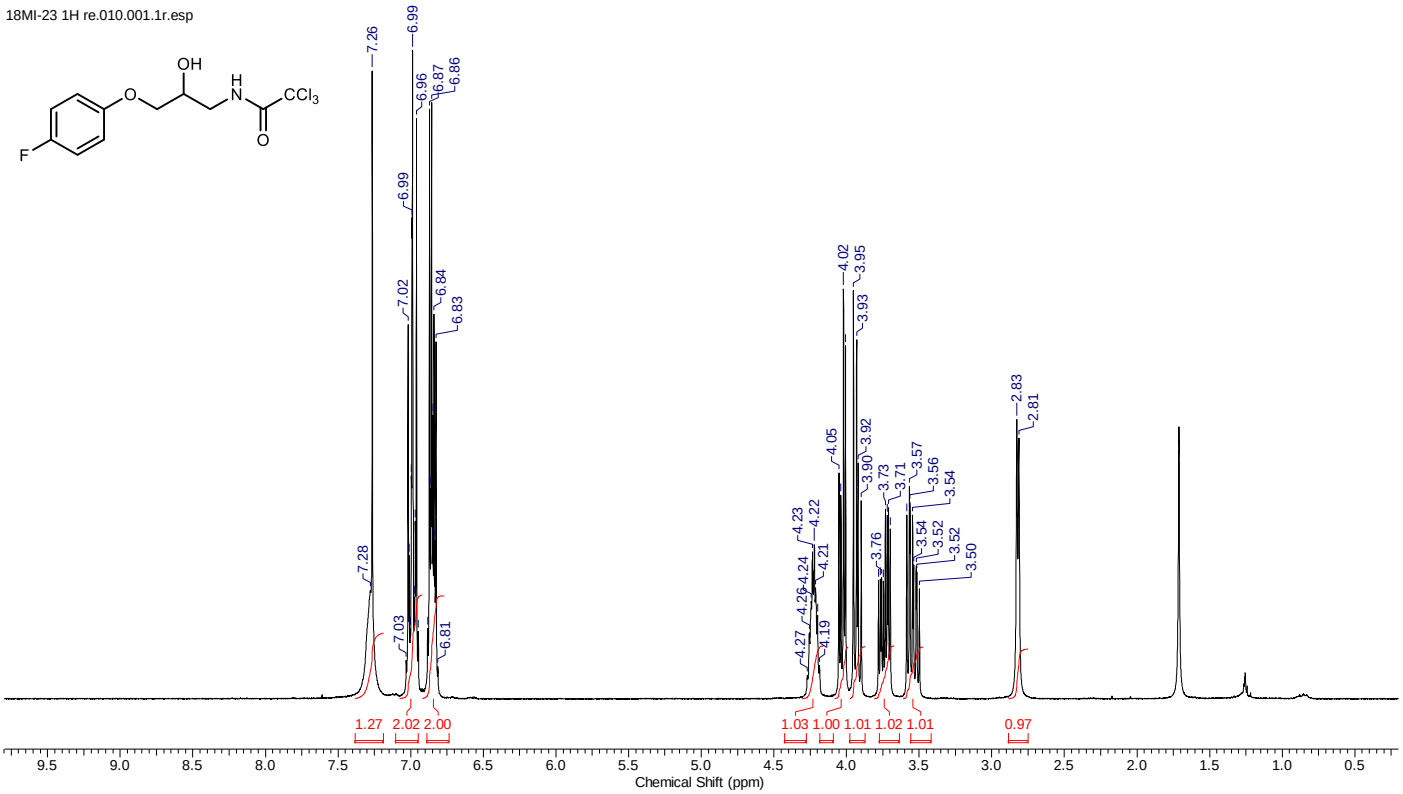
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4b

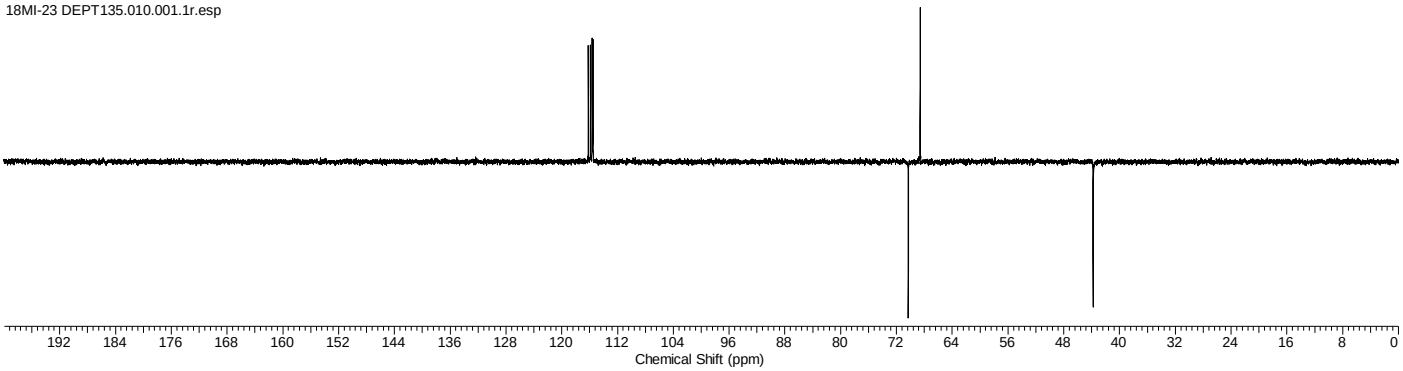


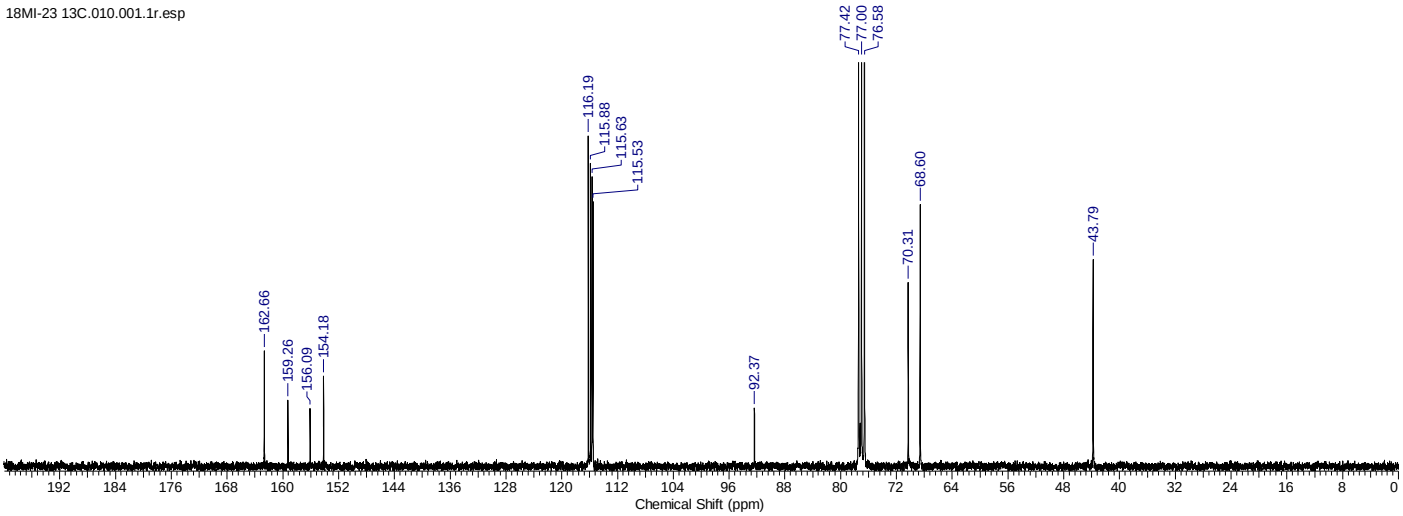




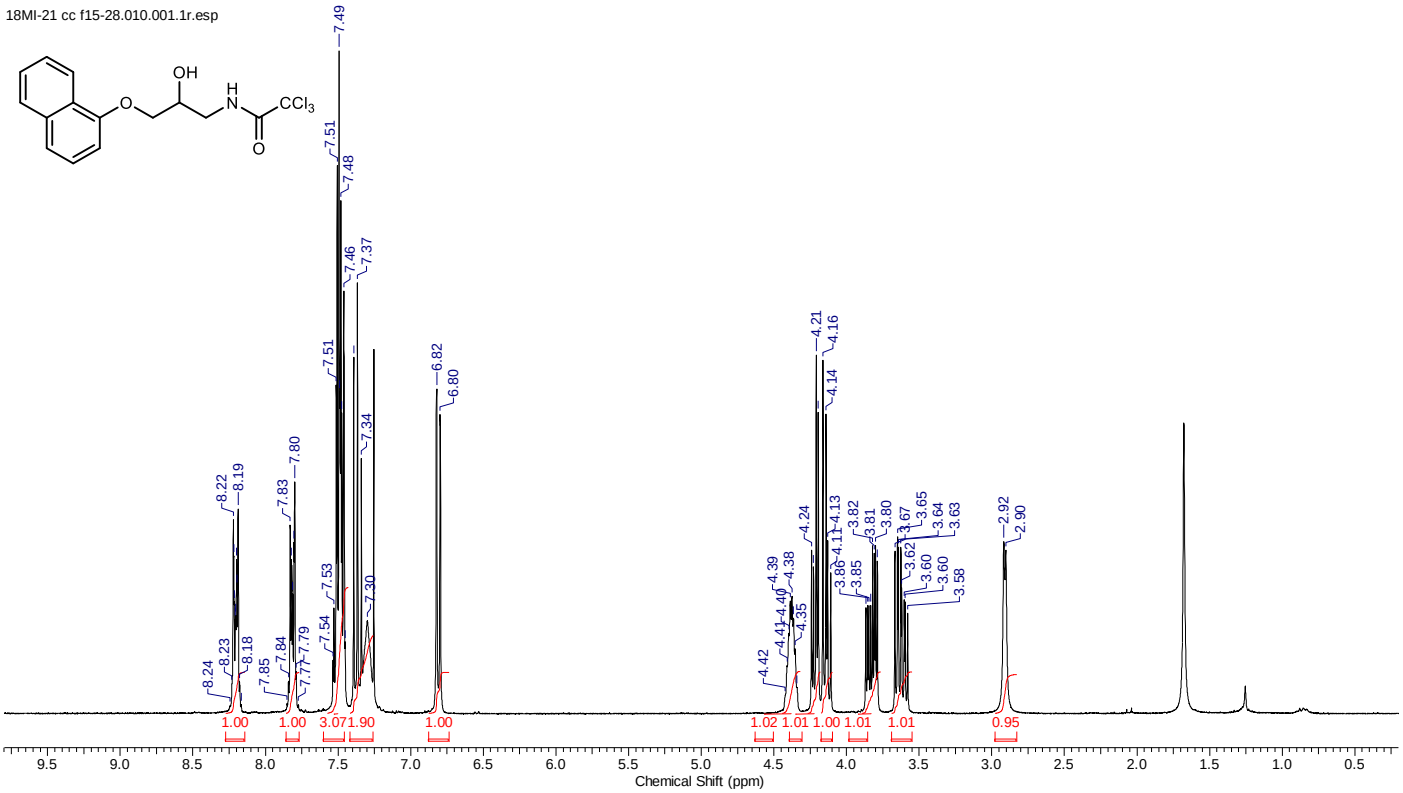
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4c

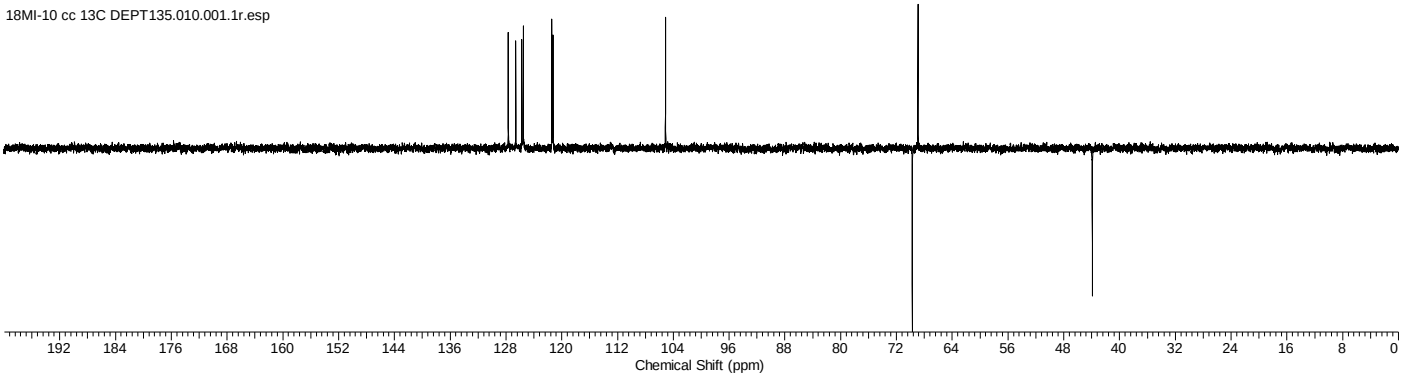


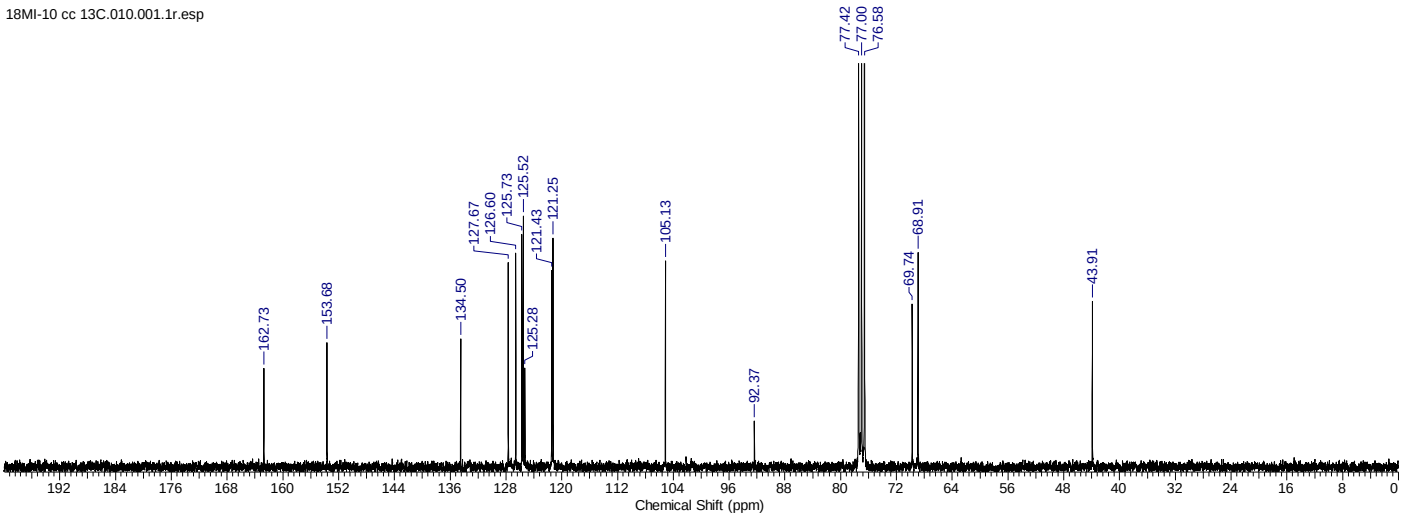




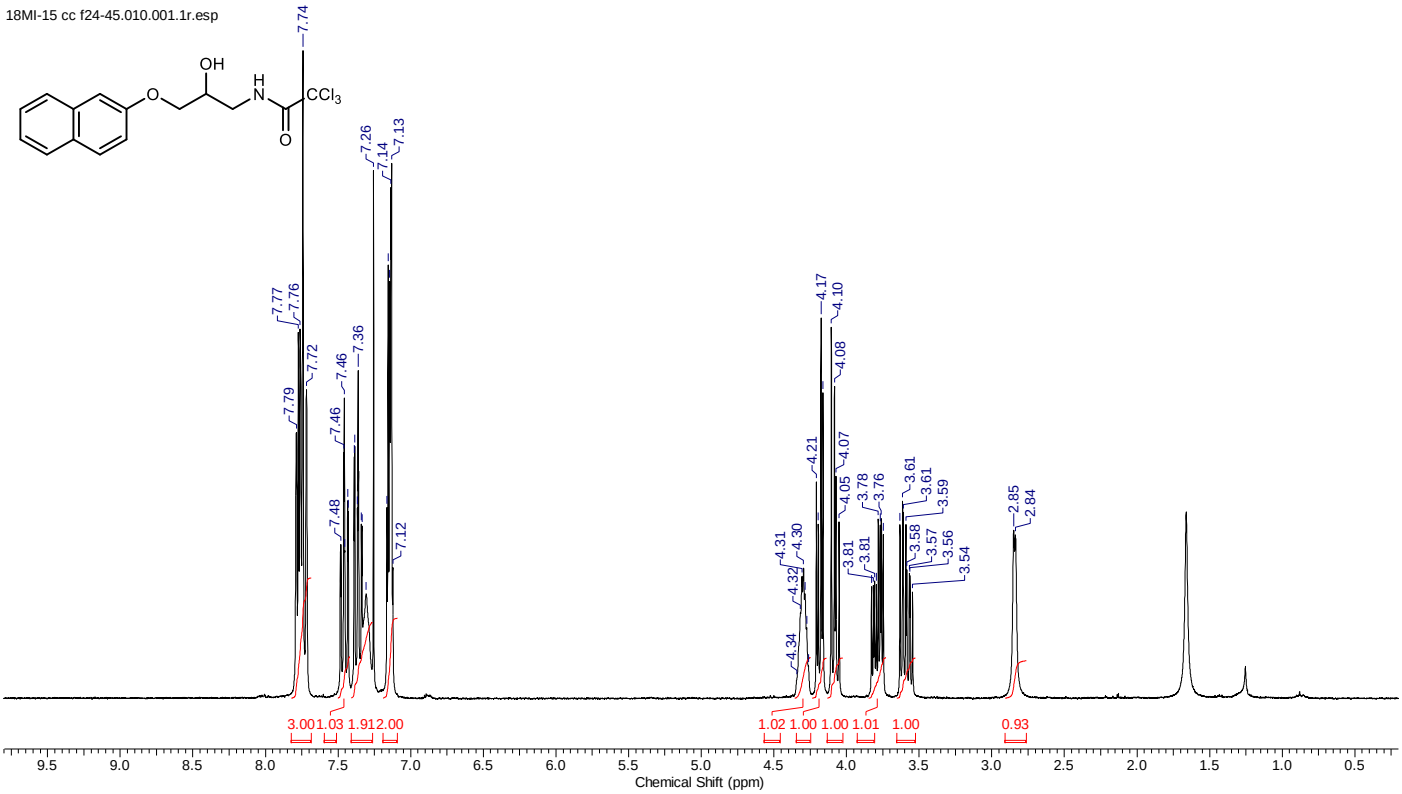
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4d

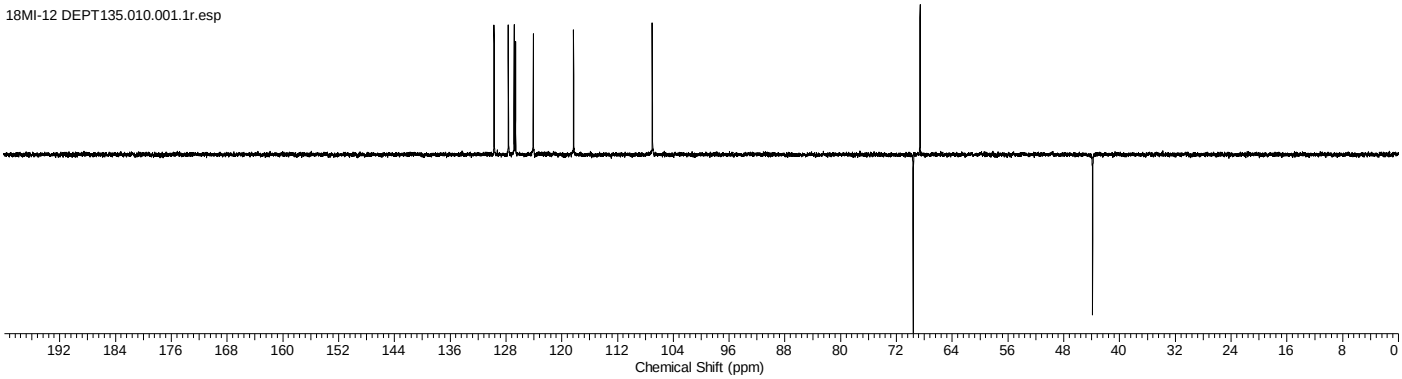


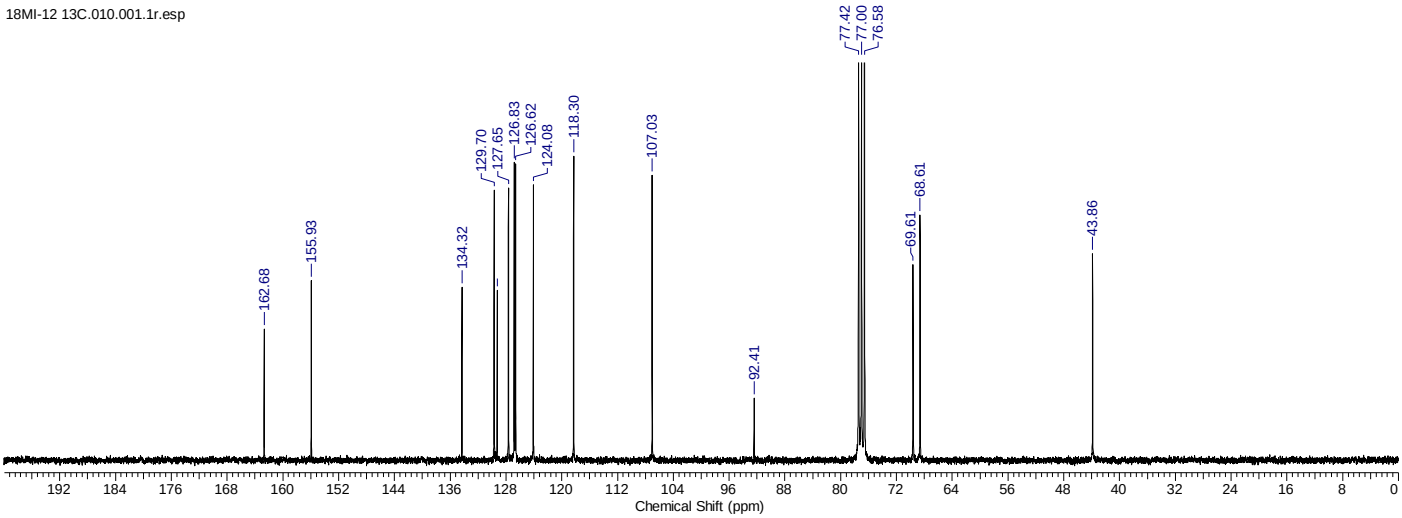




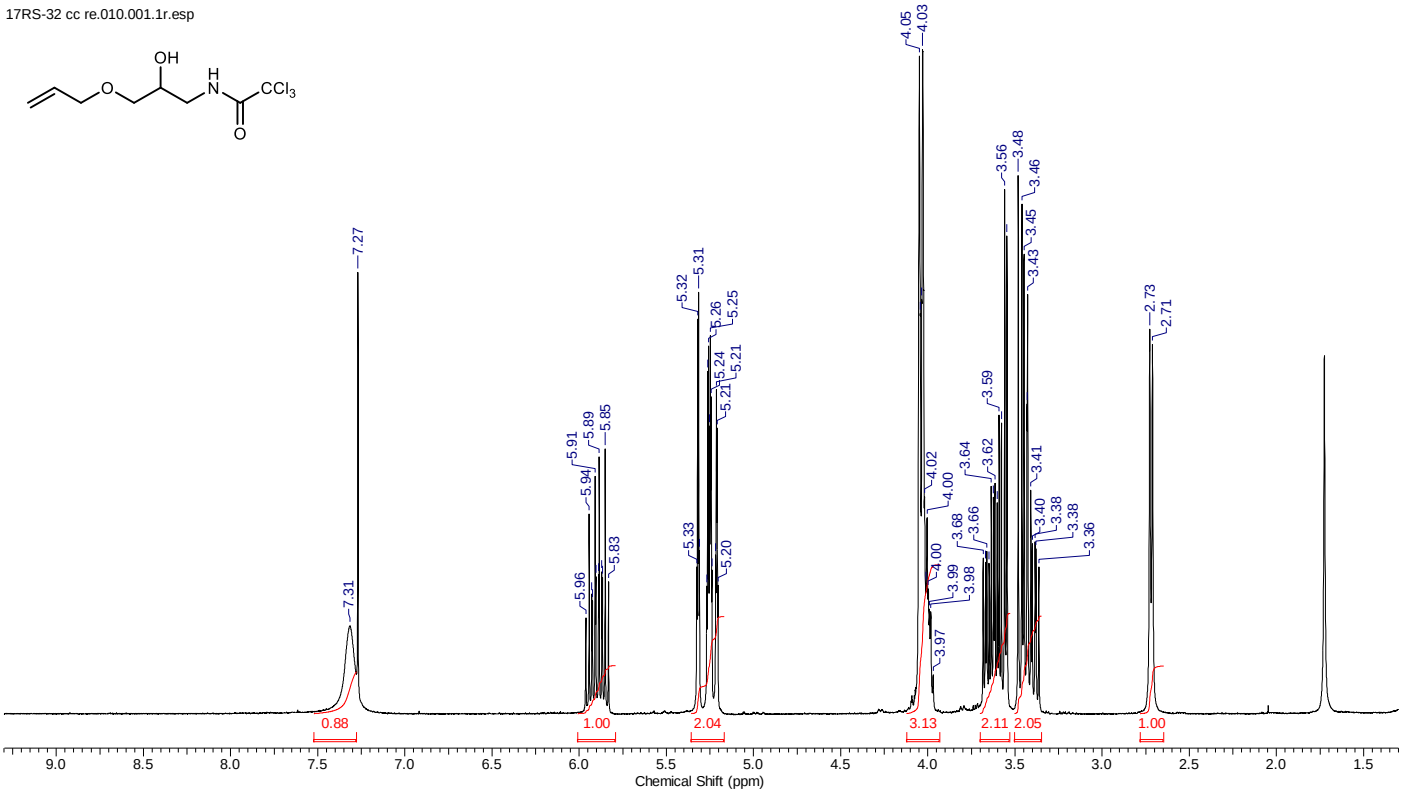
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4e

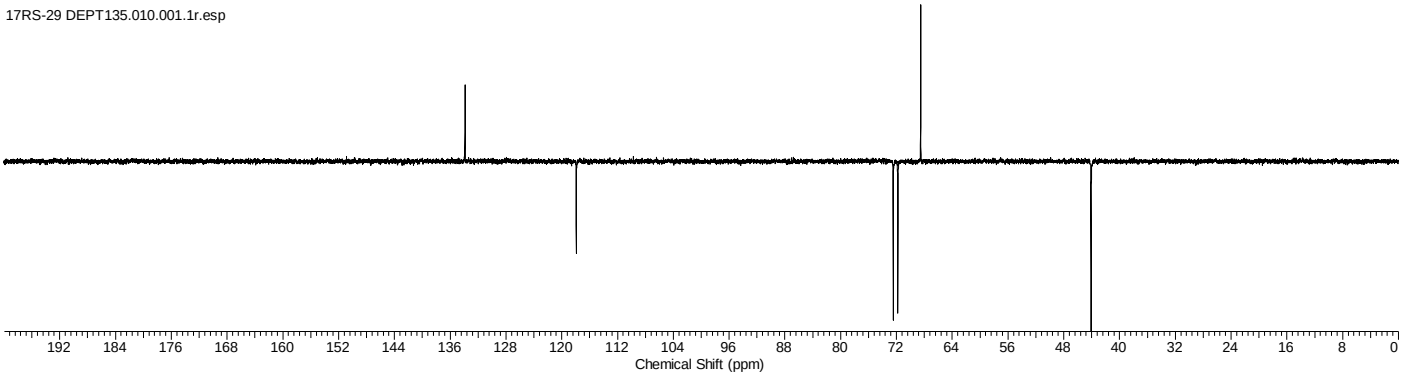


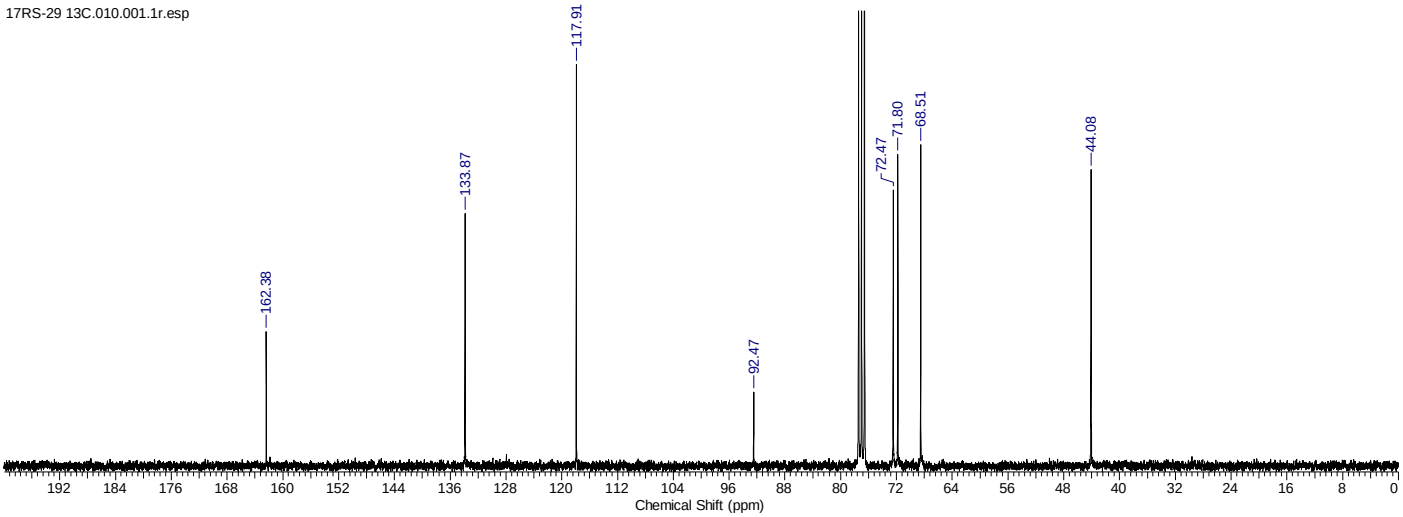




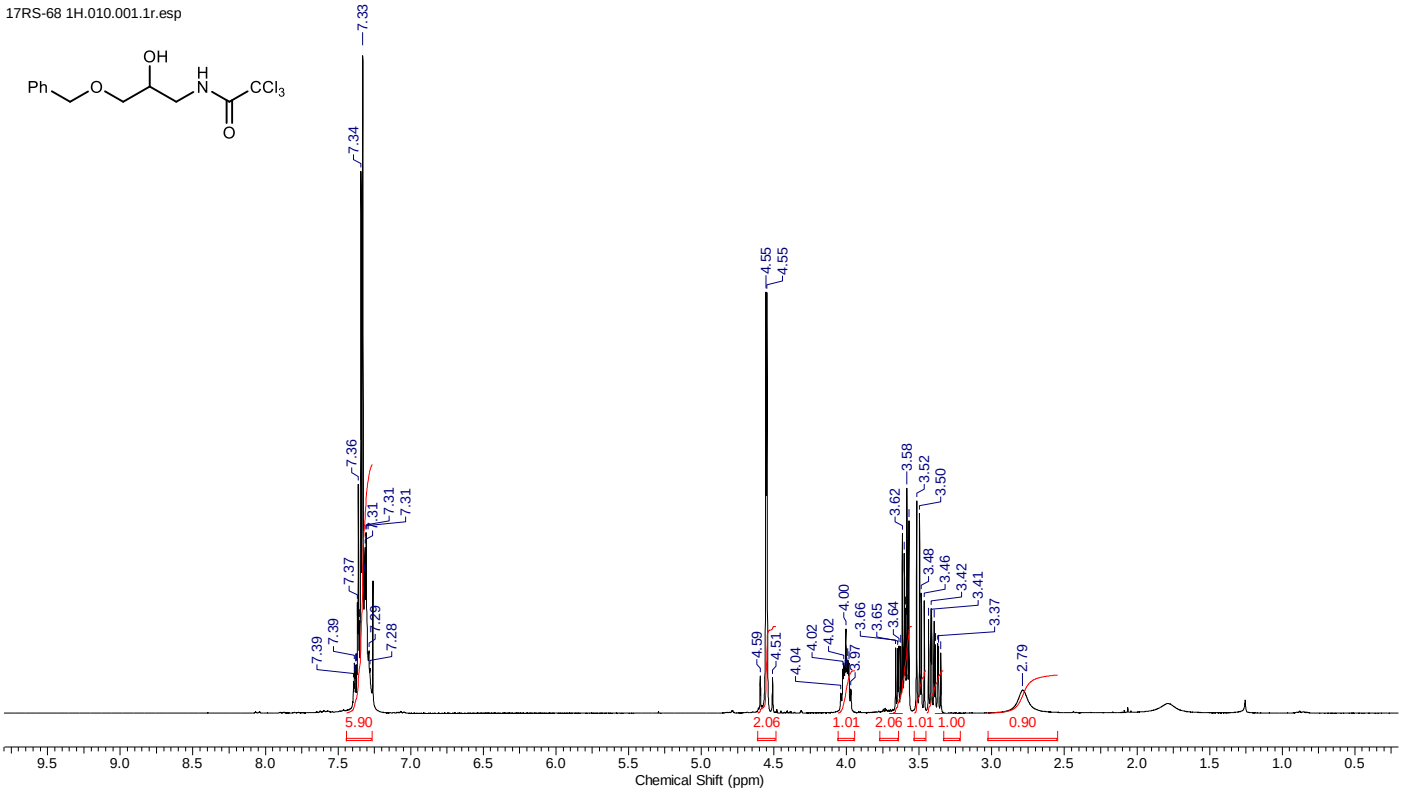
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4f

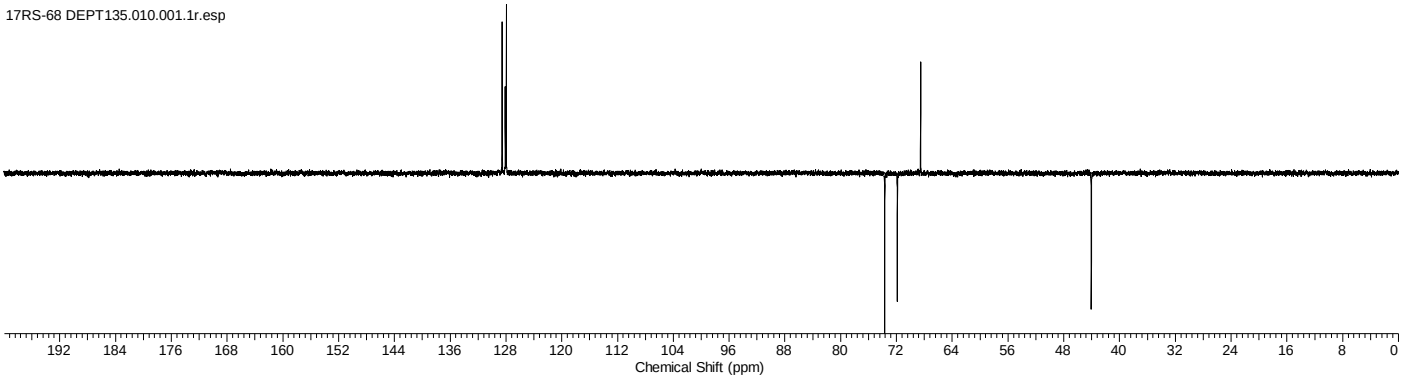


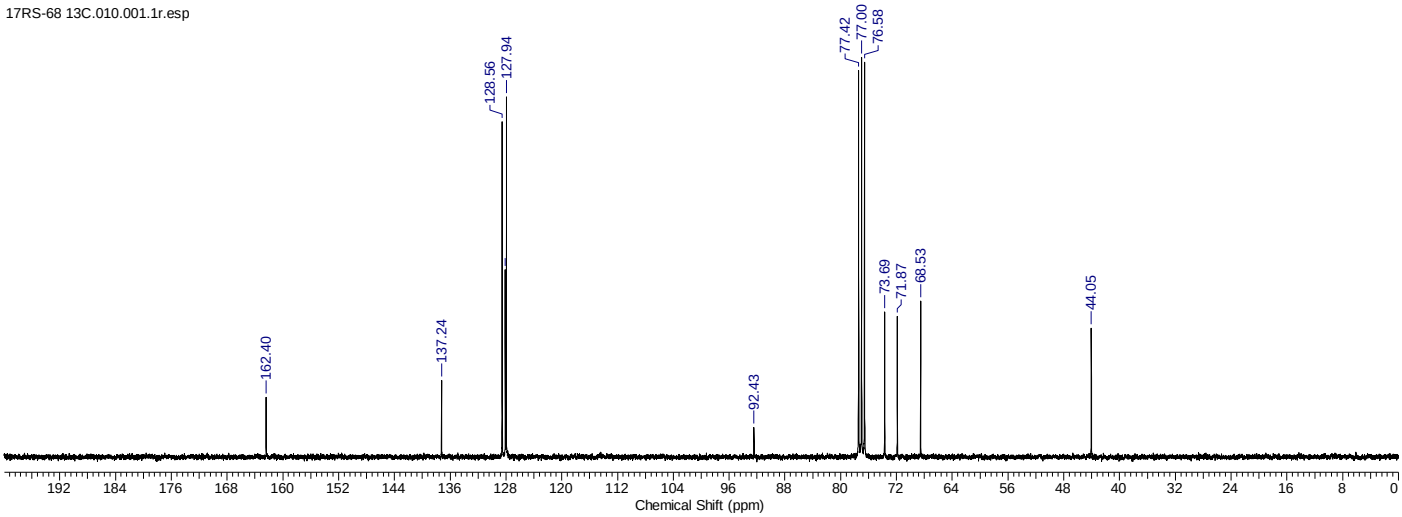




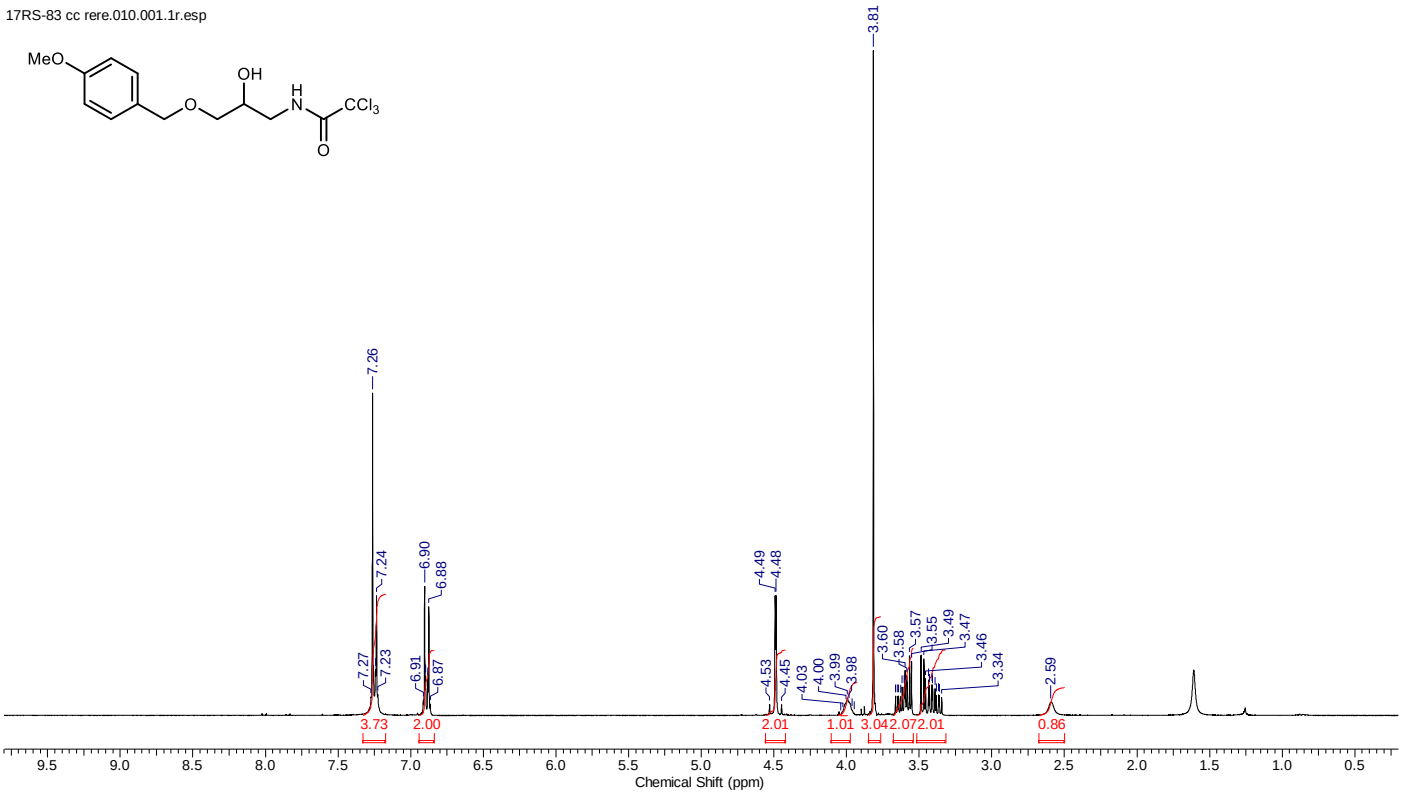
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4g

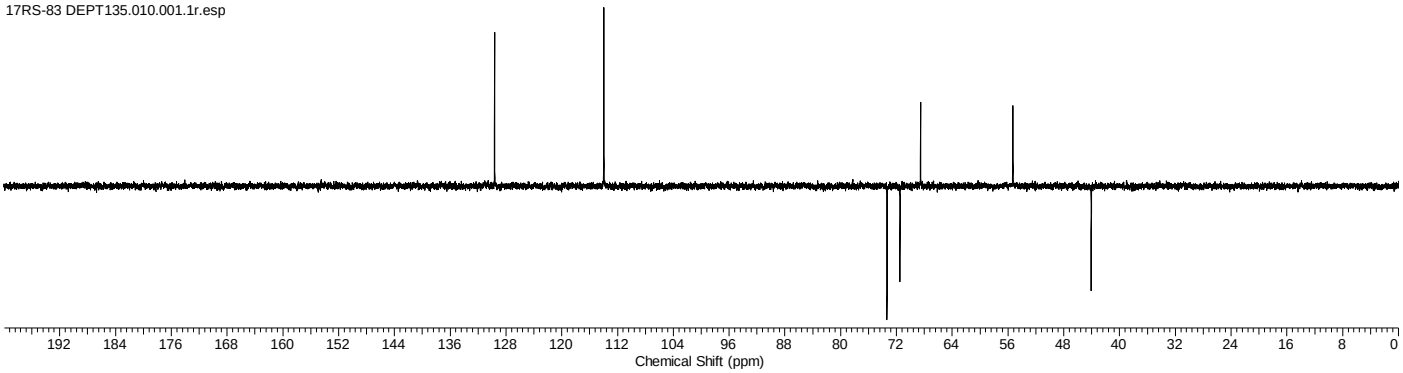


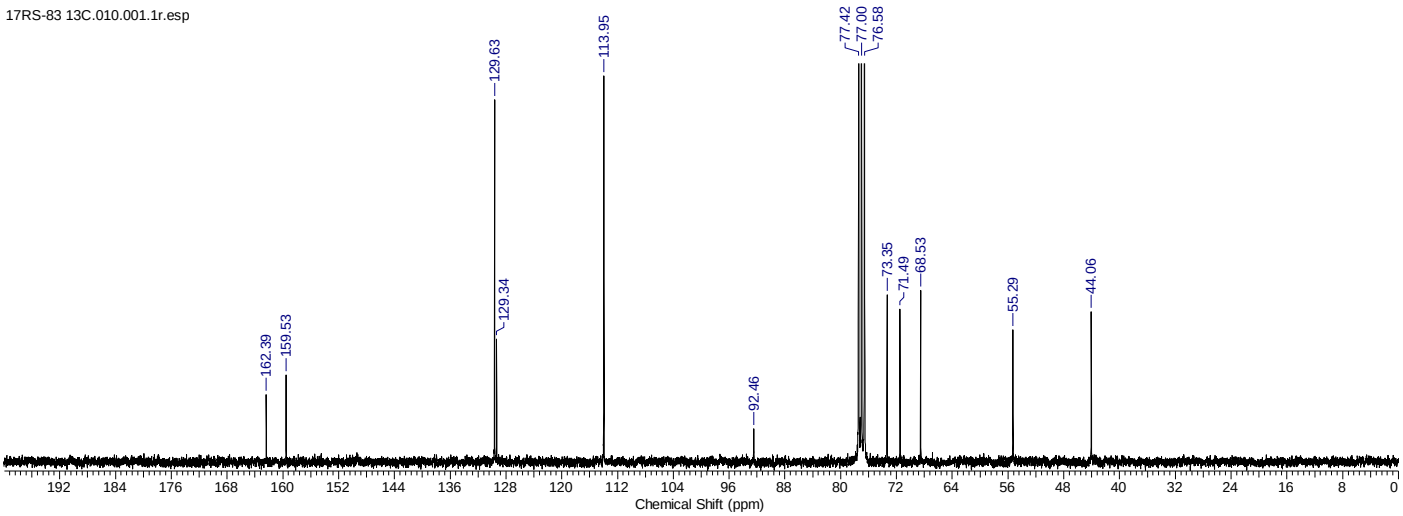




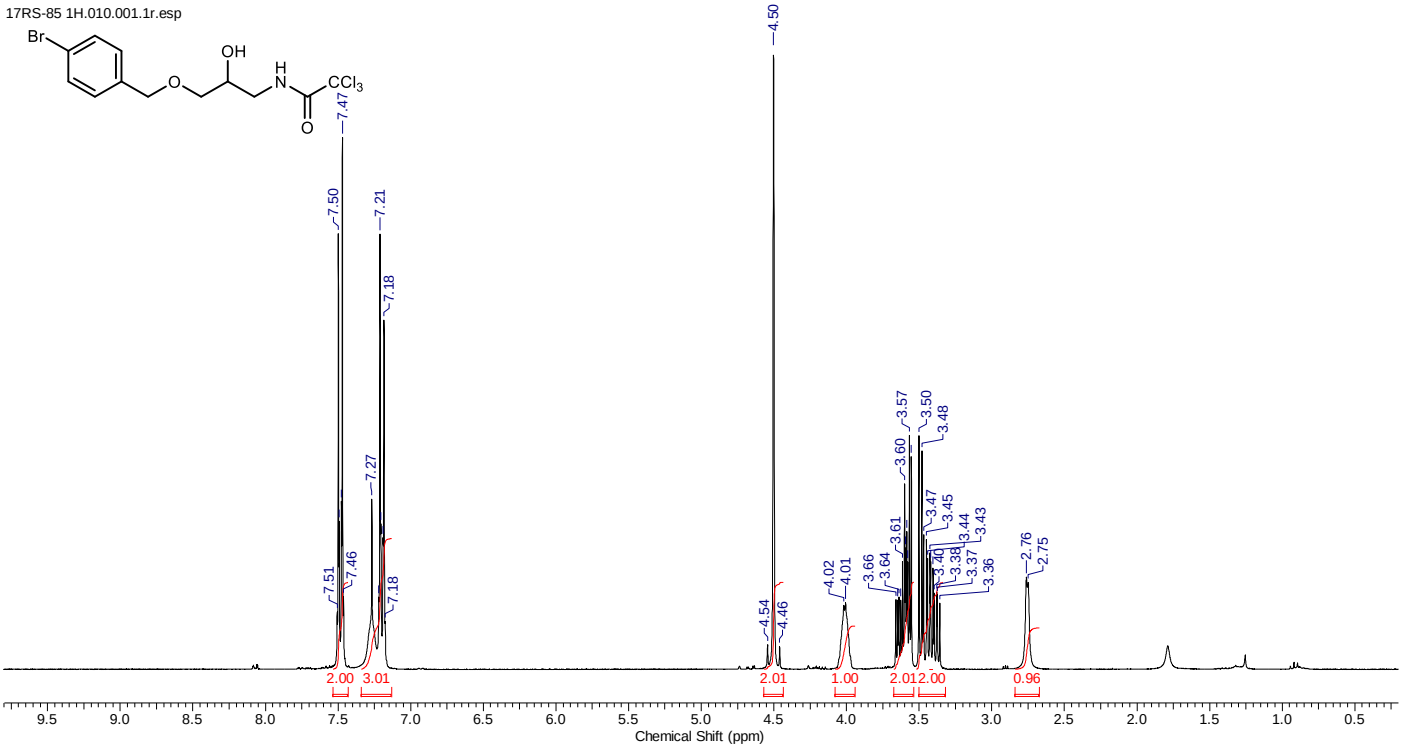
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4h

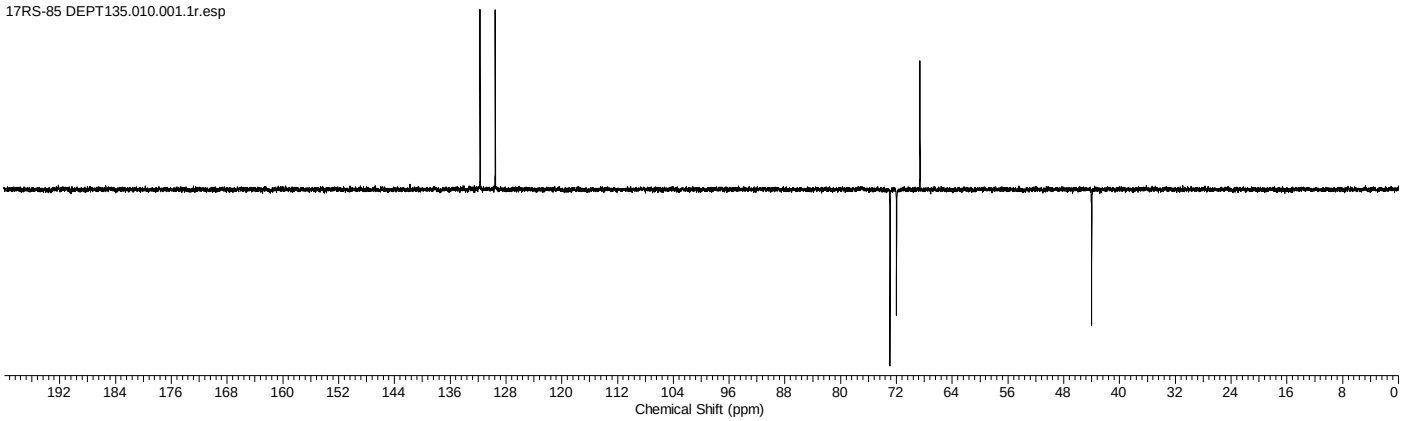


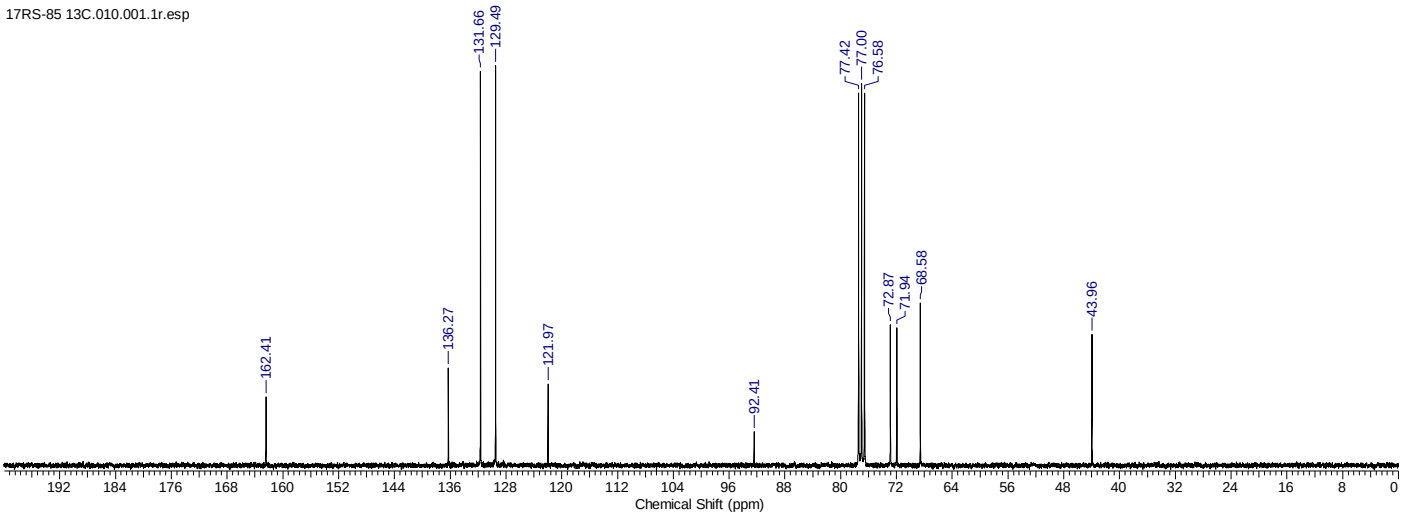




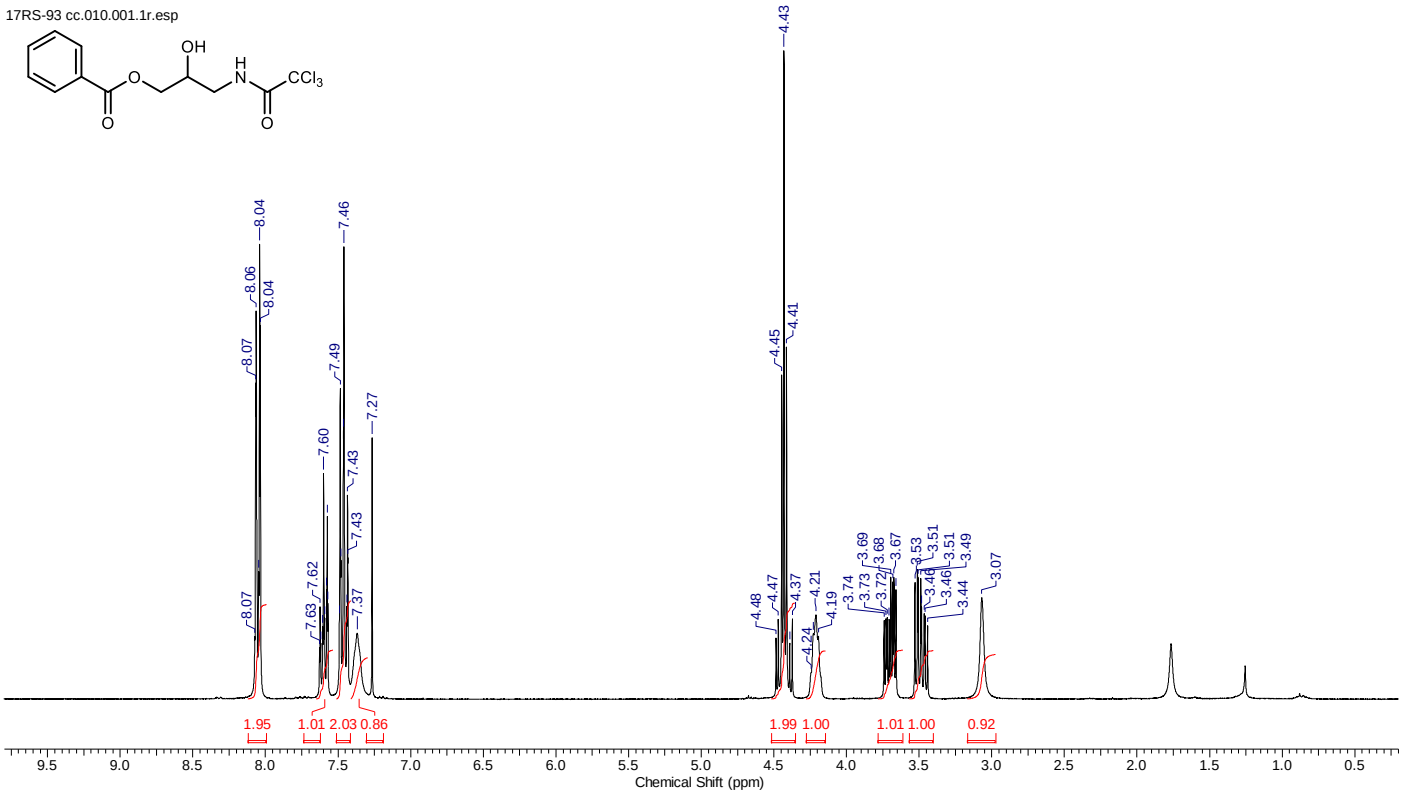
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4i

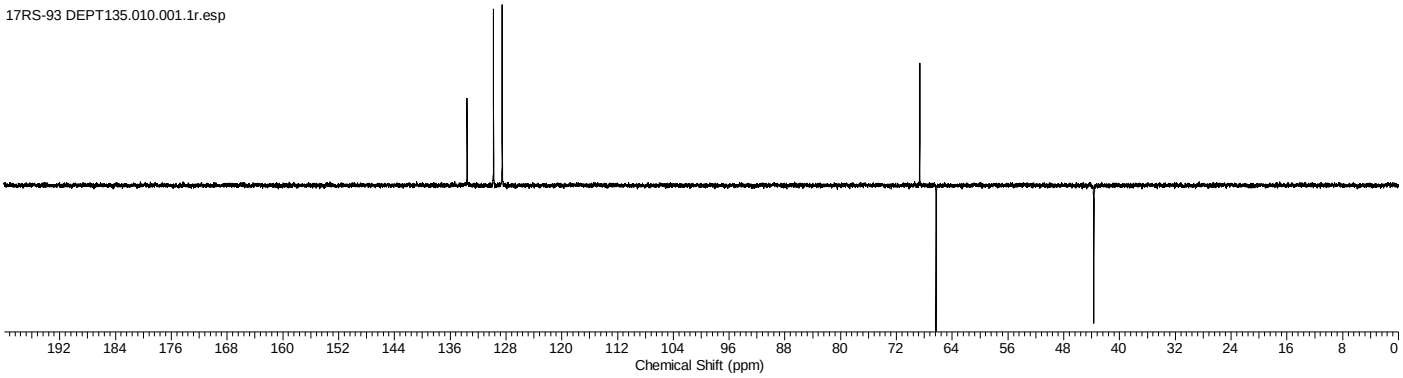


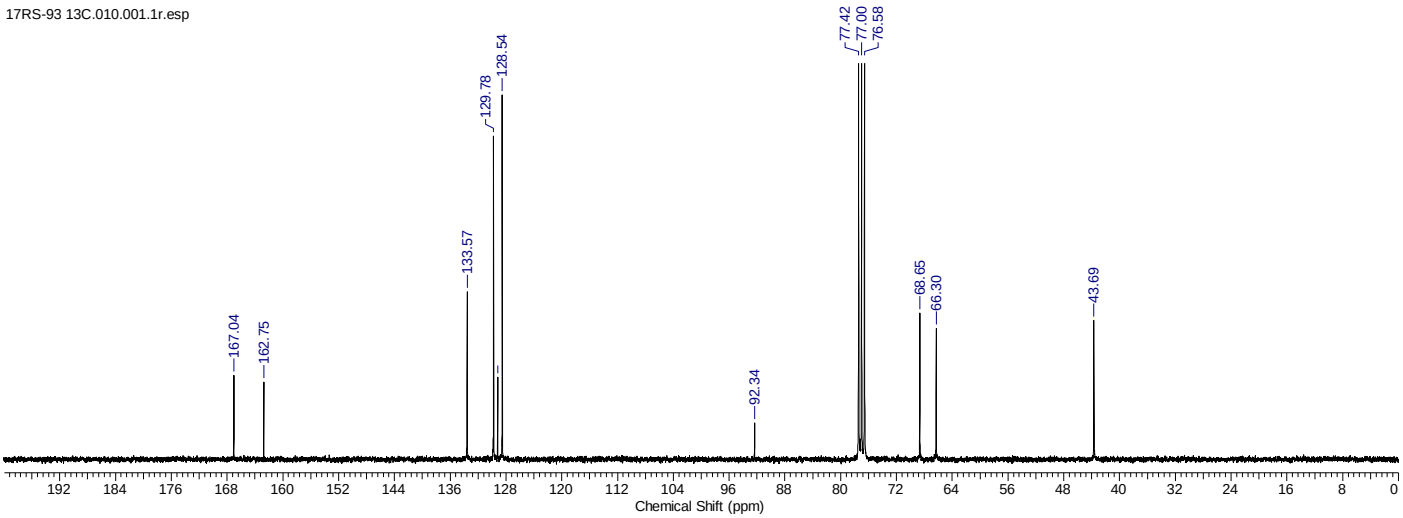




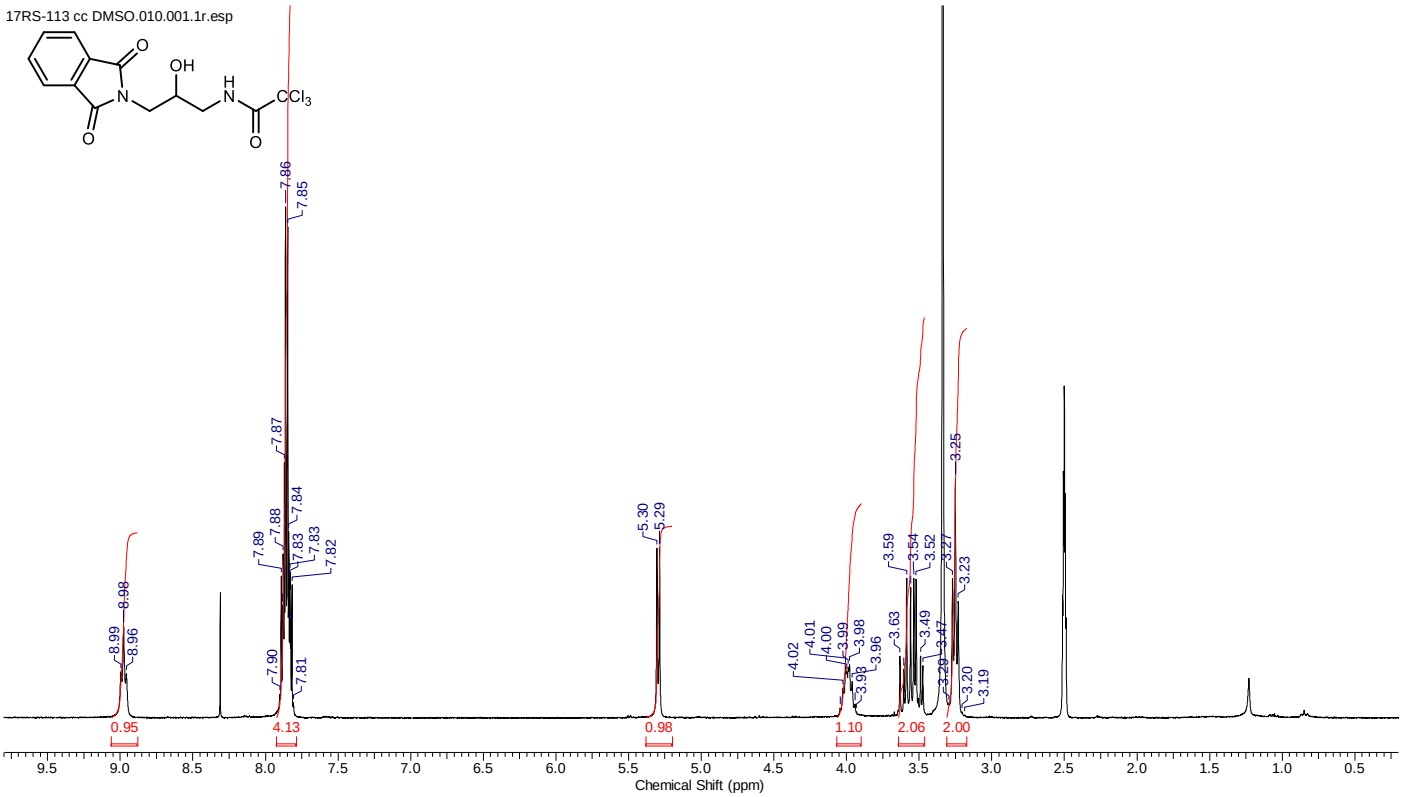
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4j

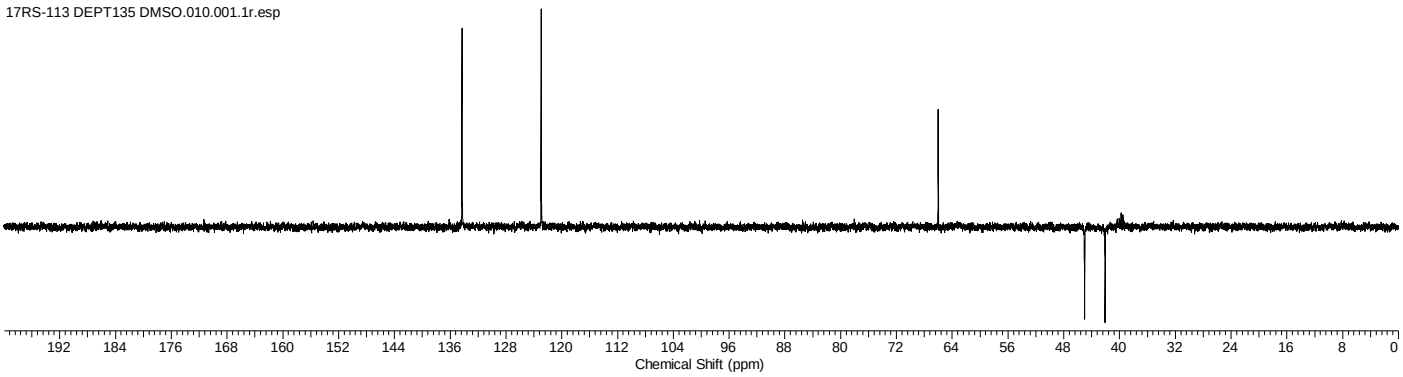


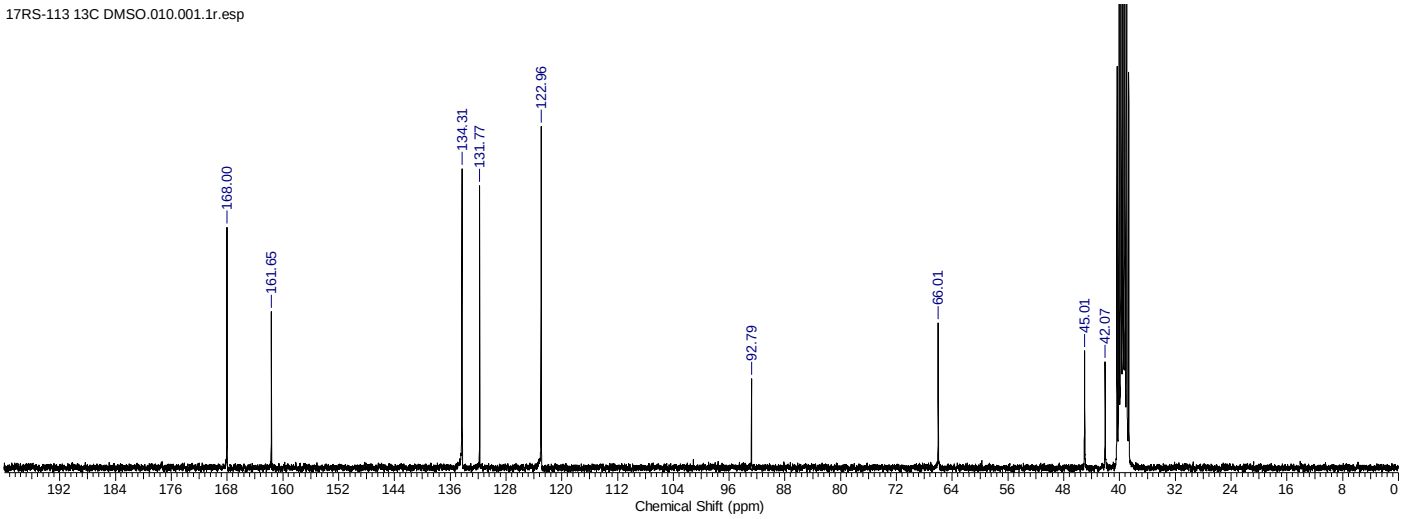




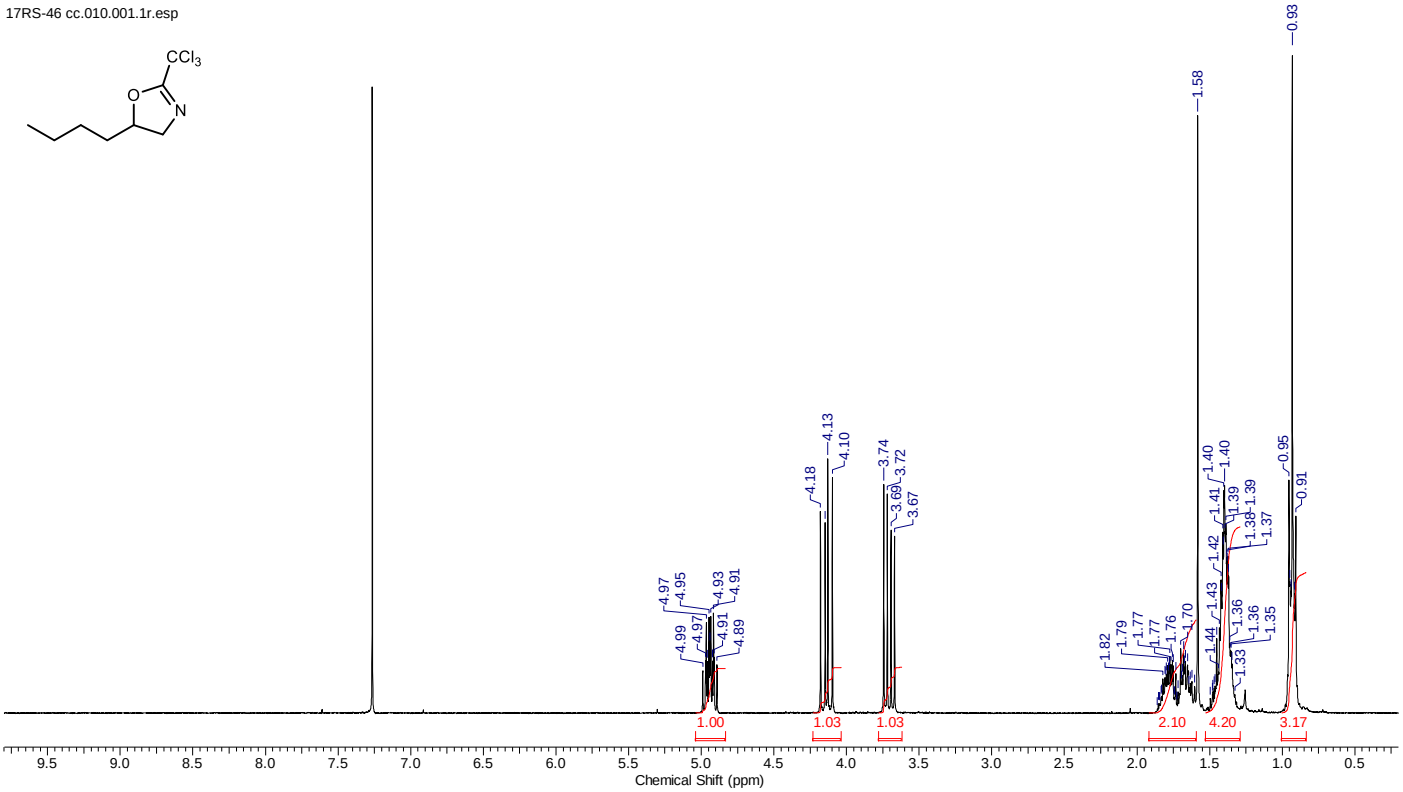
^{1}H (300 MHz, DMSO-*d*$_6$) & ^{13}C{^{1}H} NMR (75 MHz, DMSO-*d*$_6$) spectra of 4k

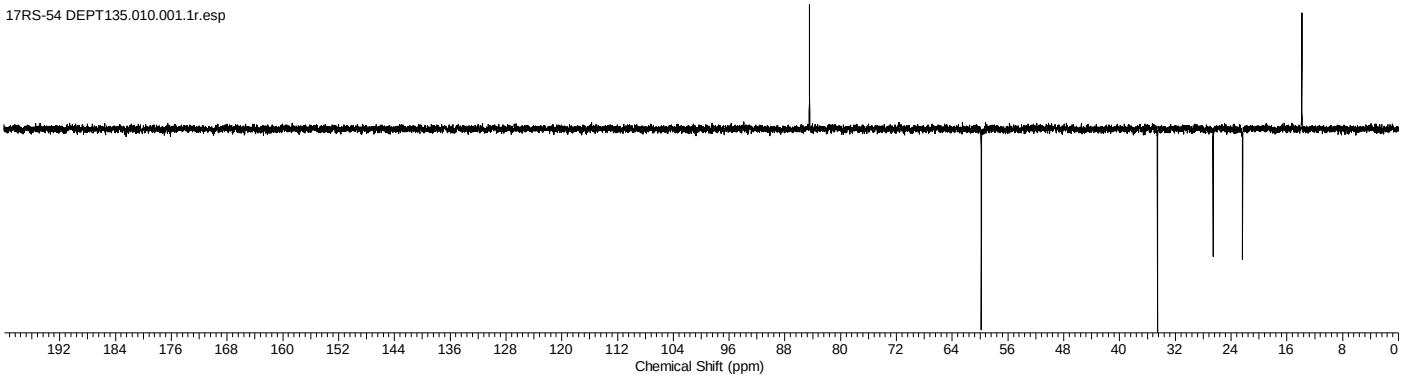


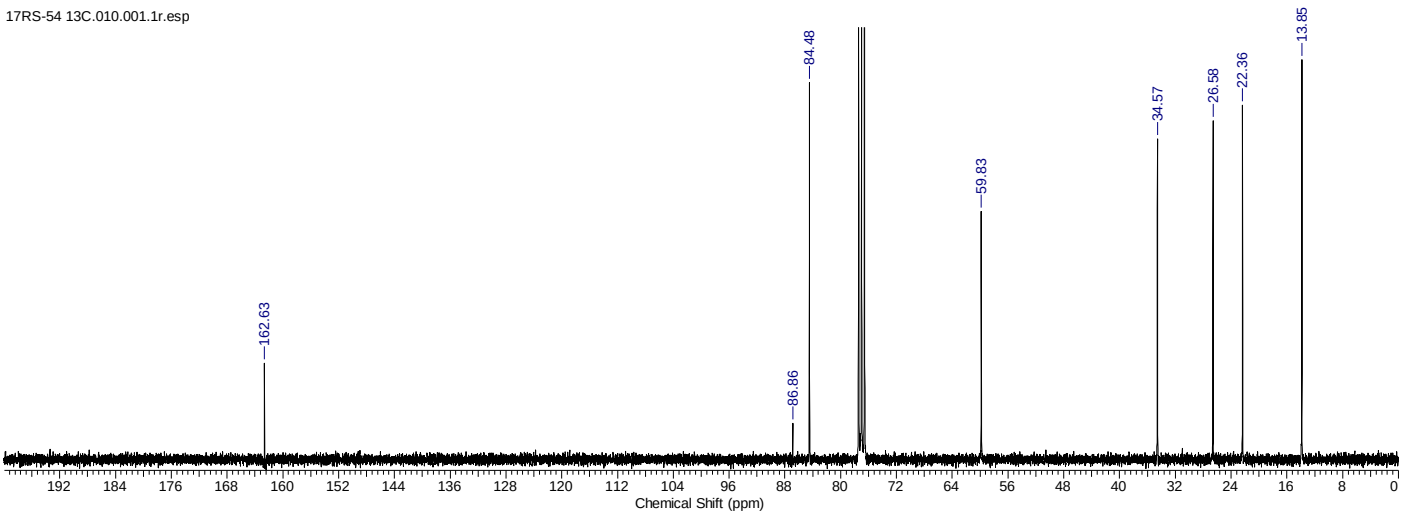




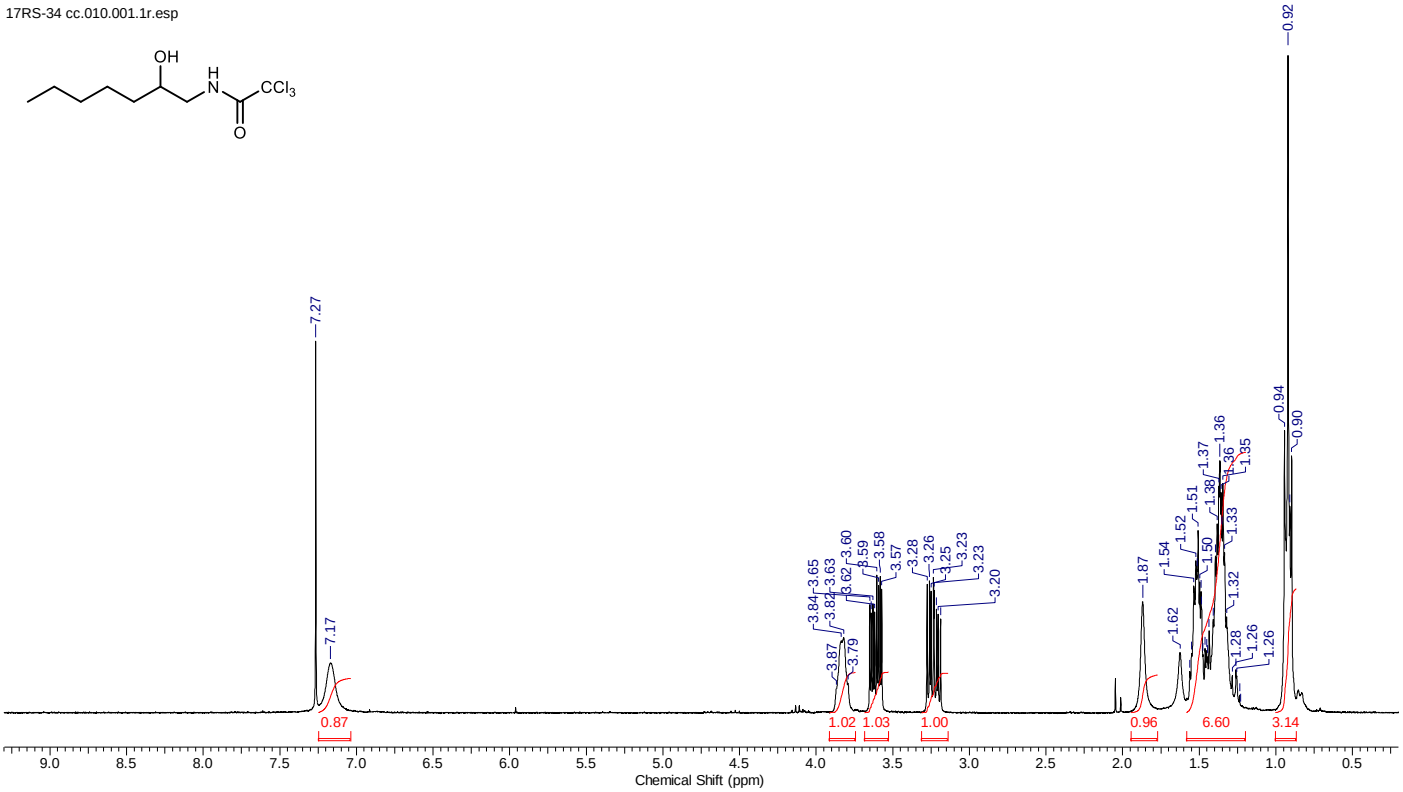
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 2l

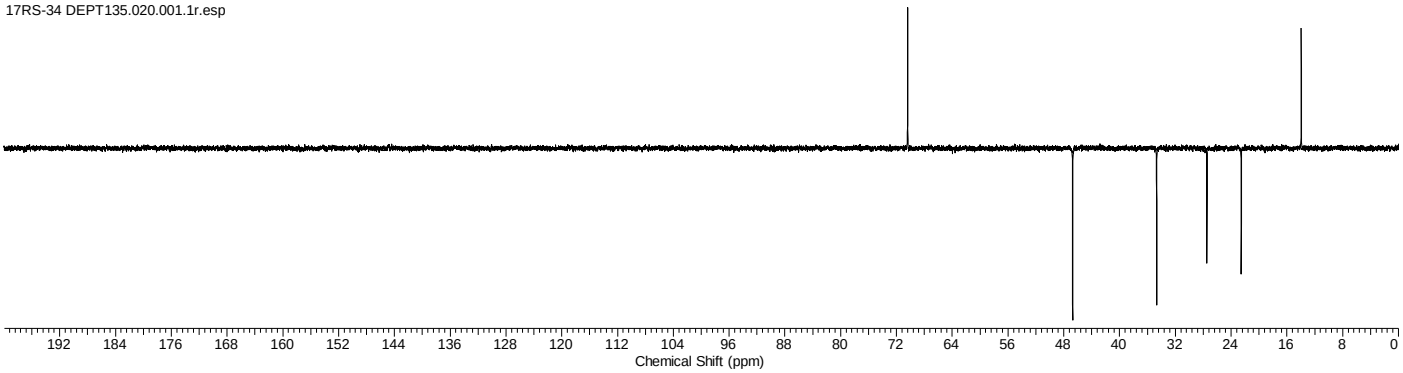


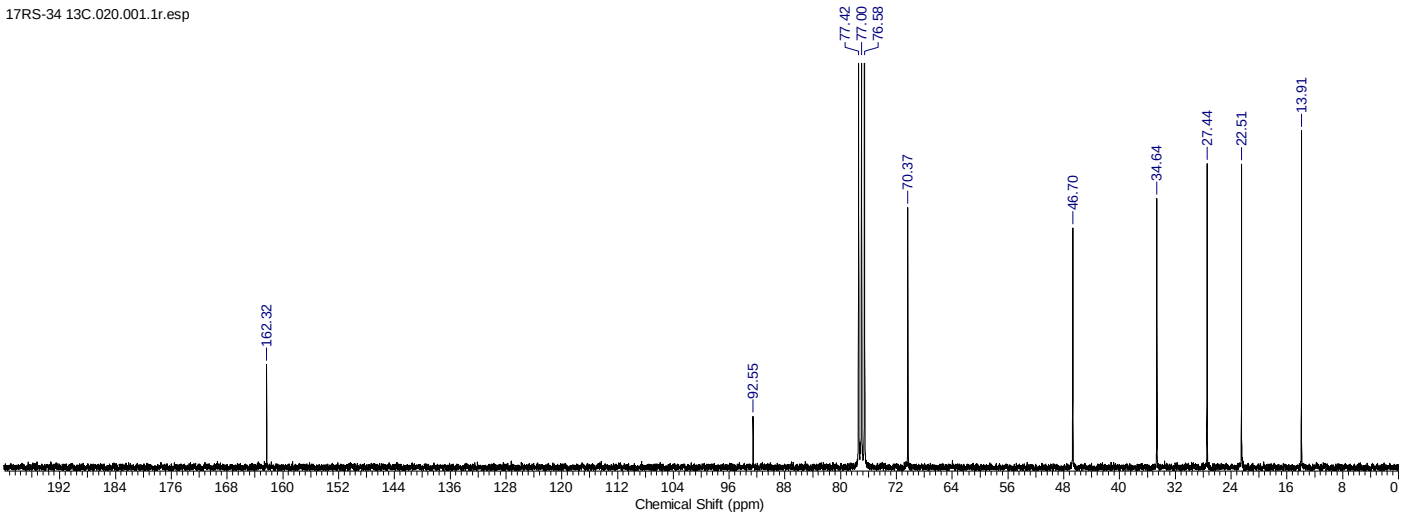




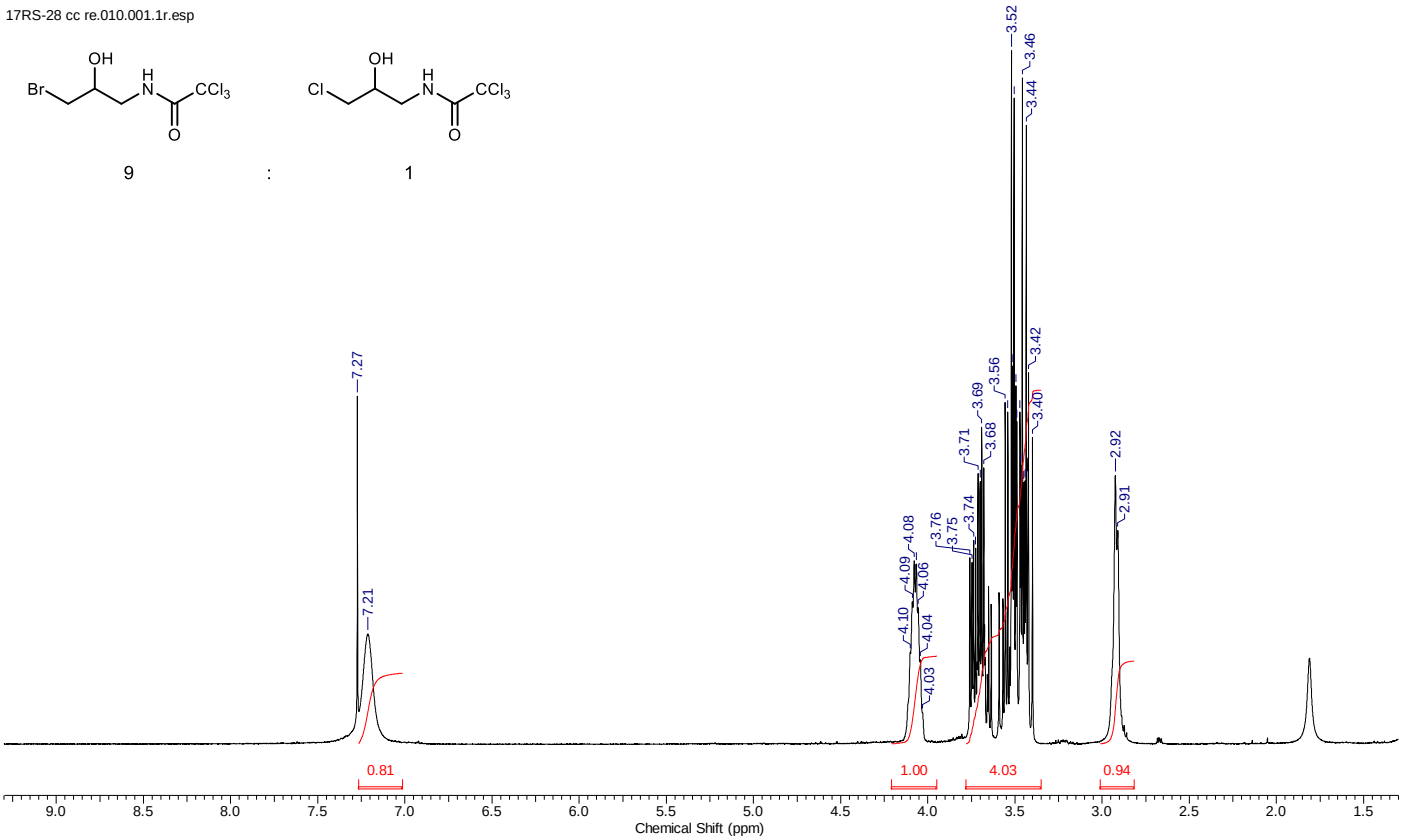
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4l

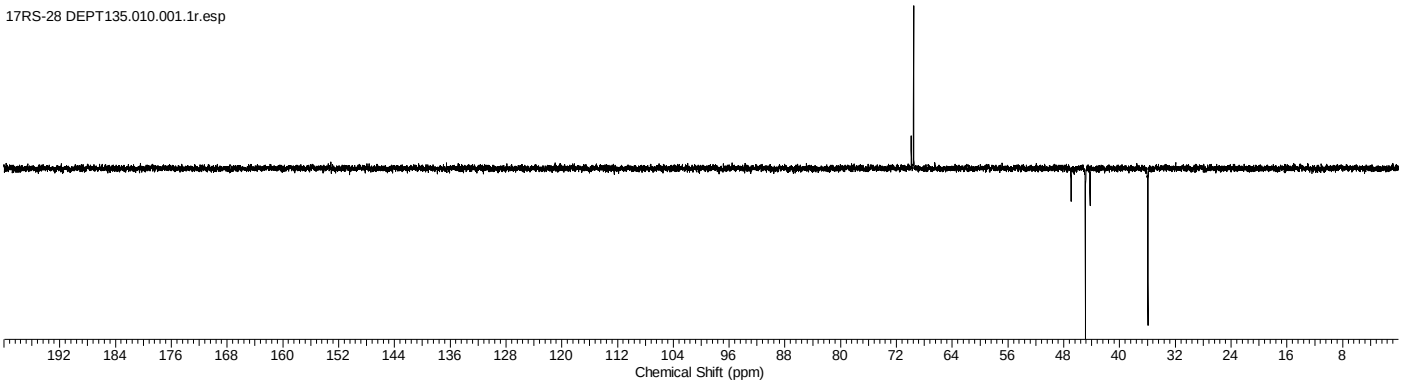


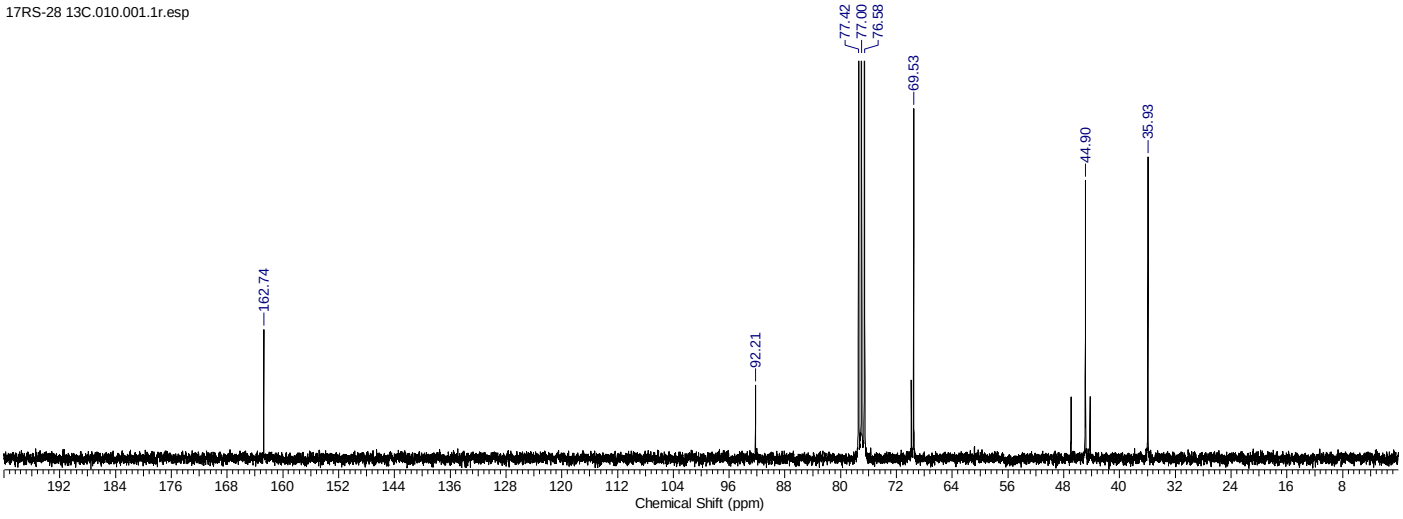




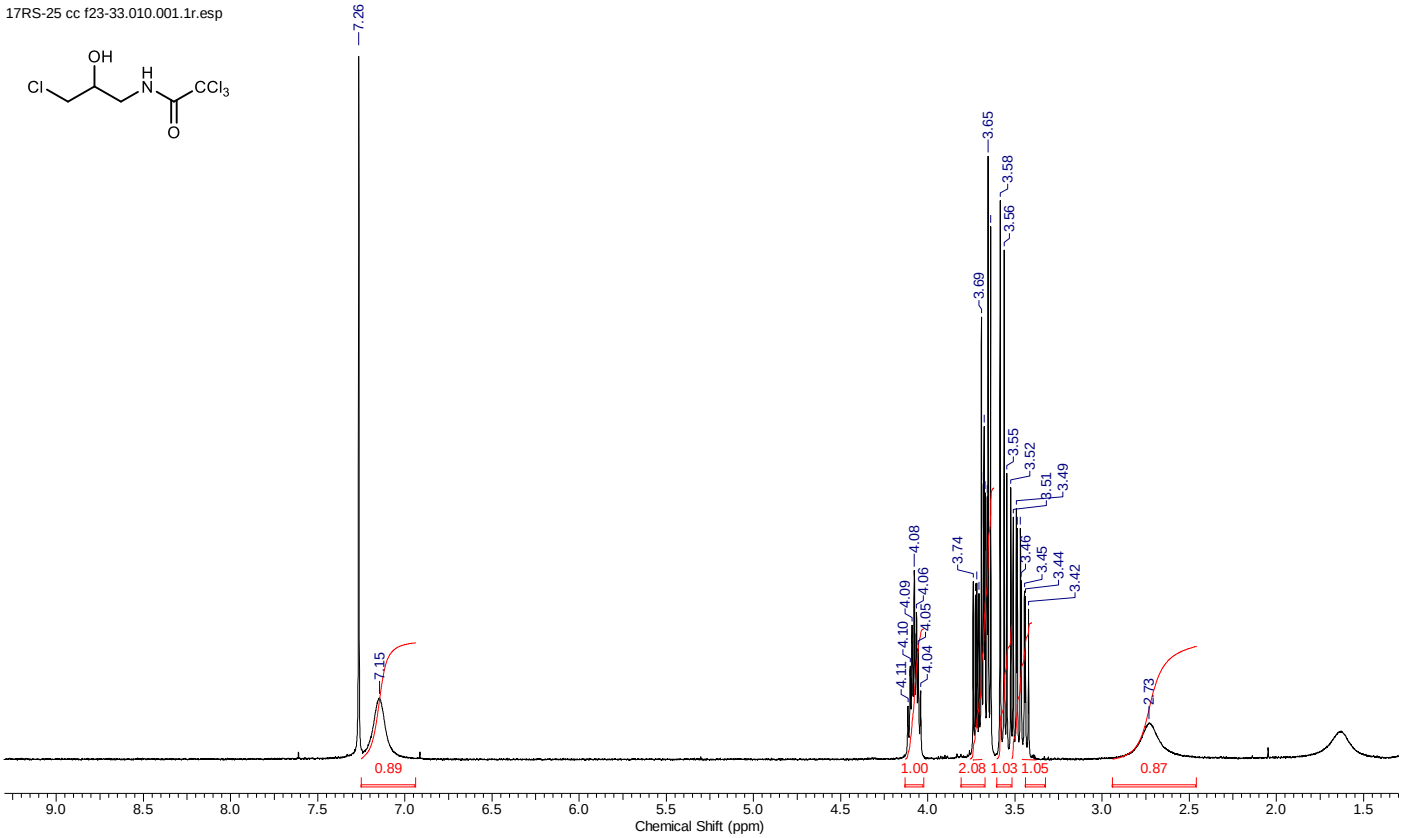
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4m

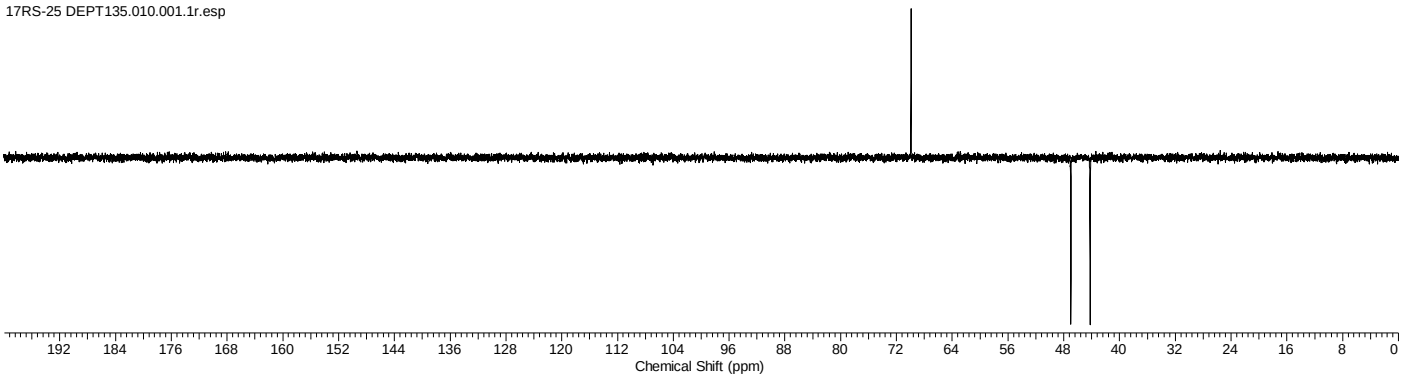


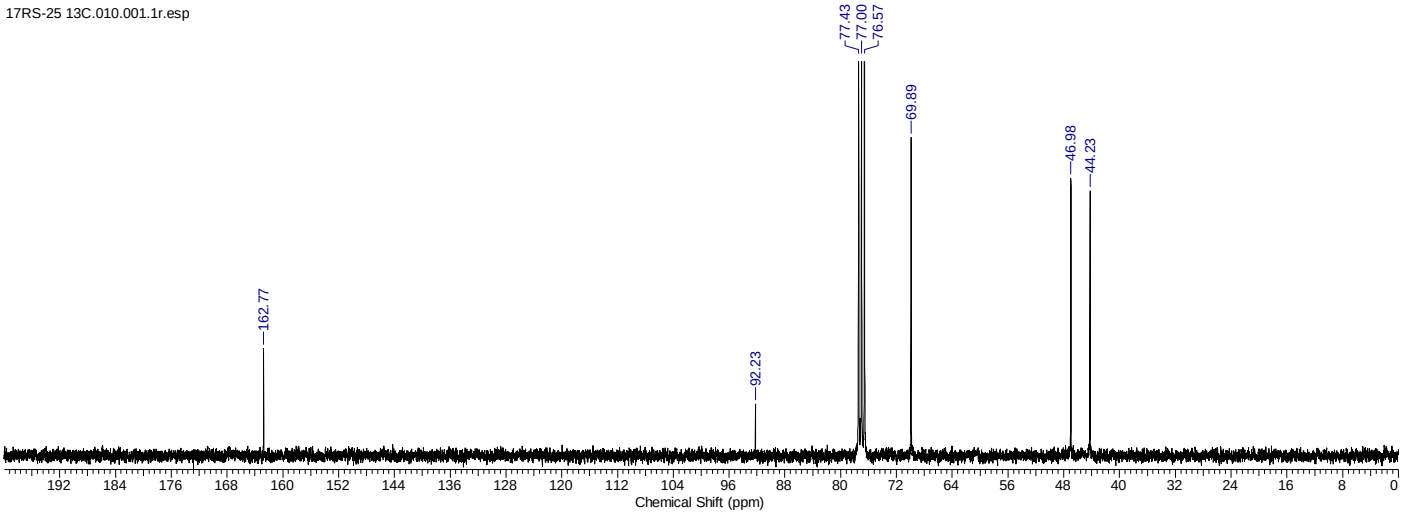




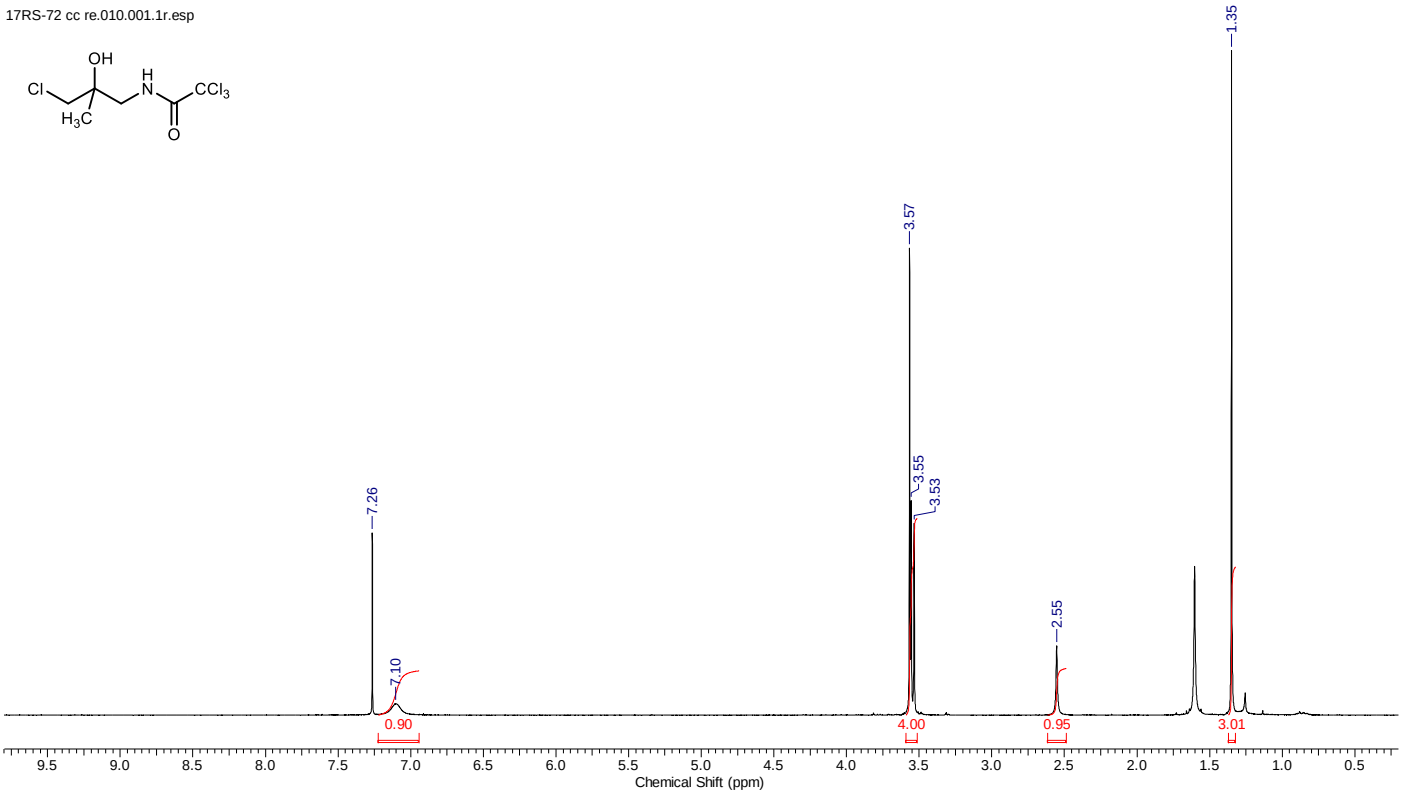
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4n

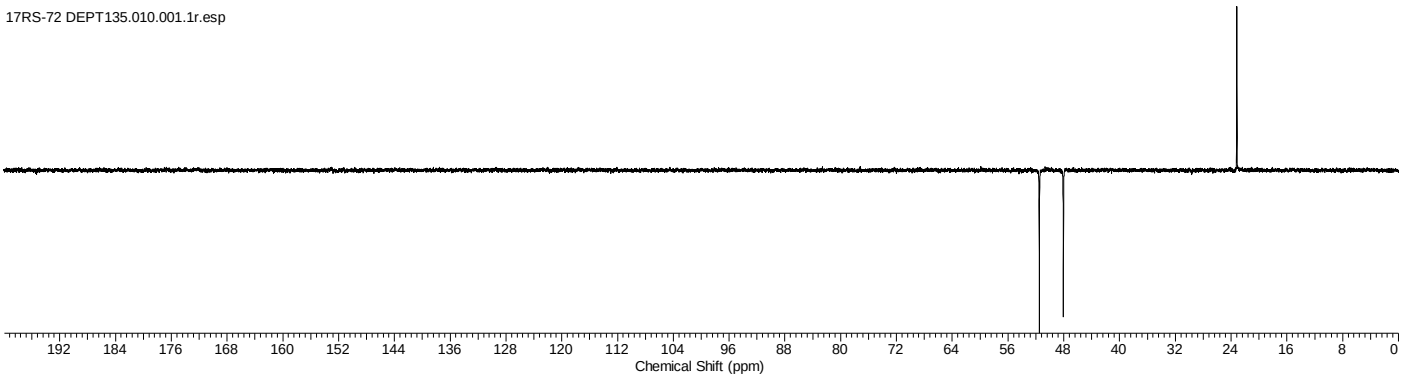


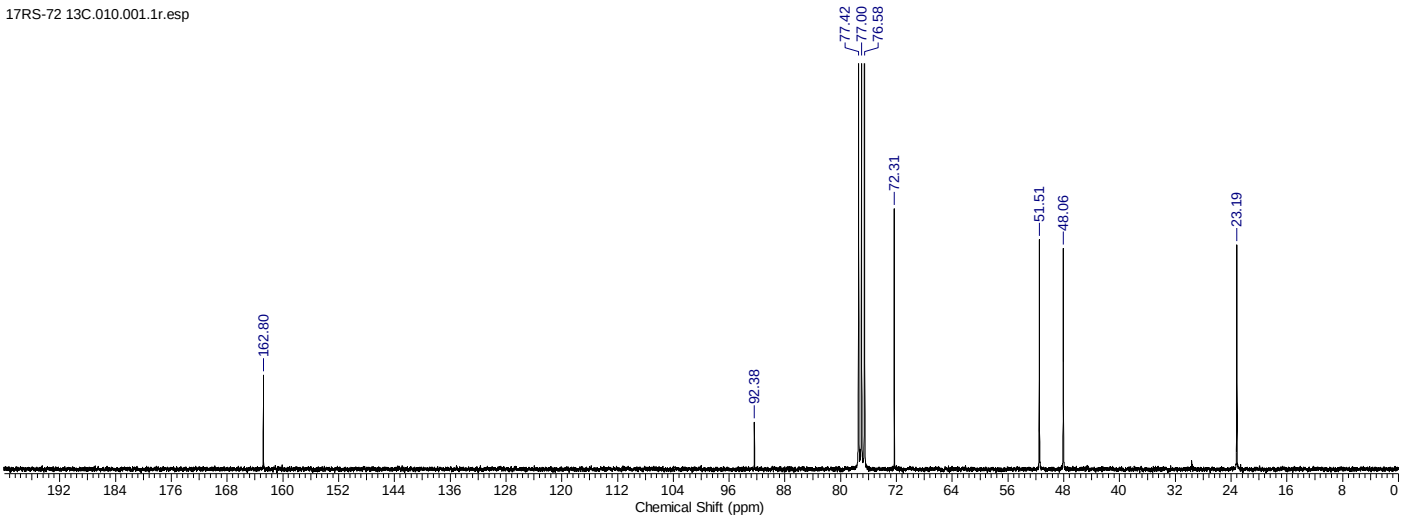




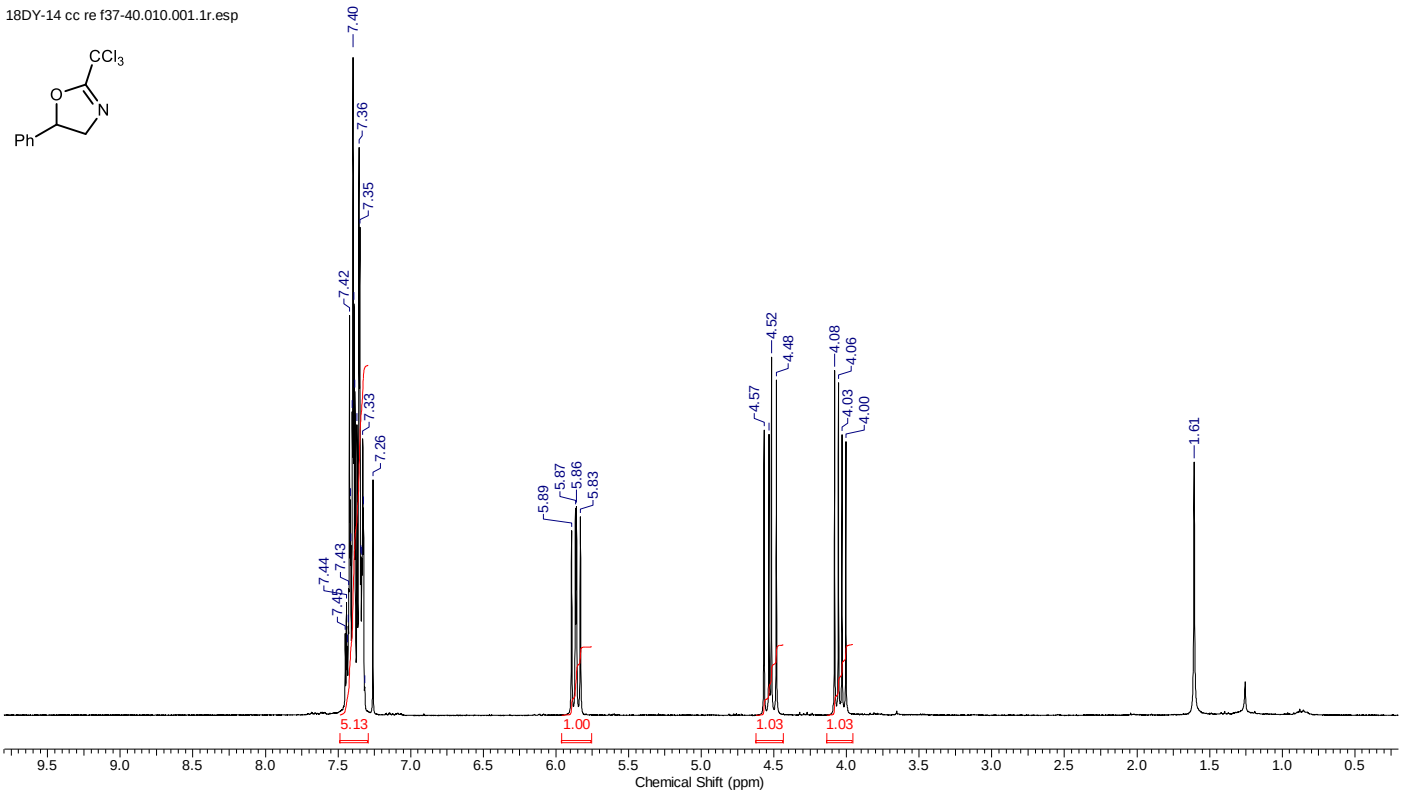
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4o

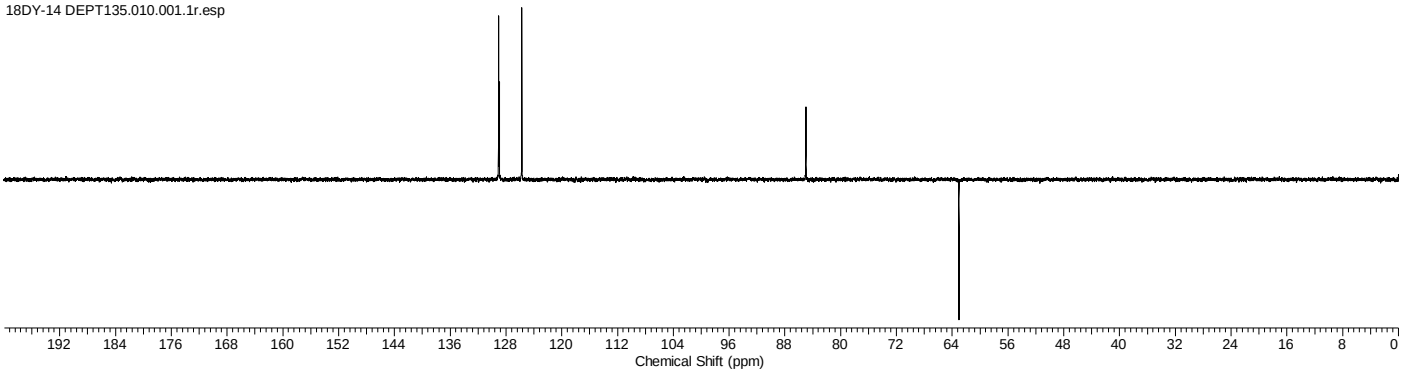


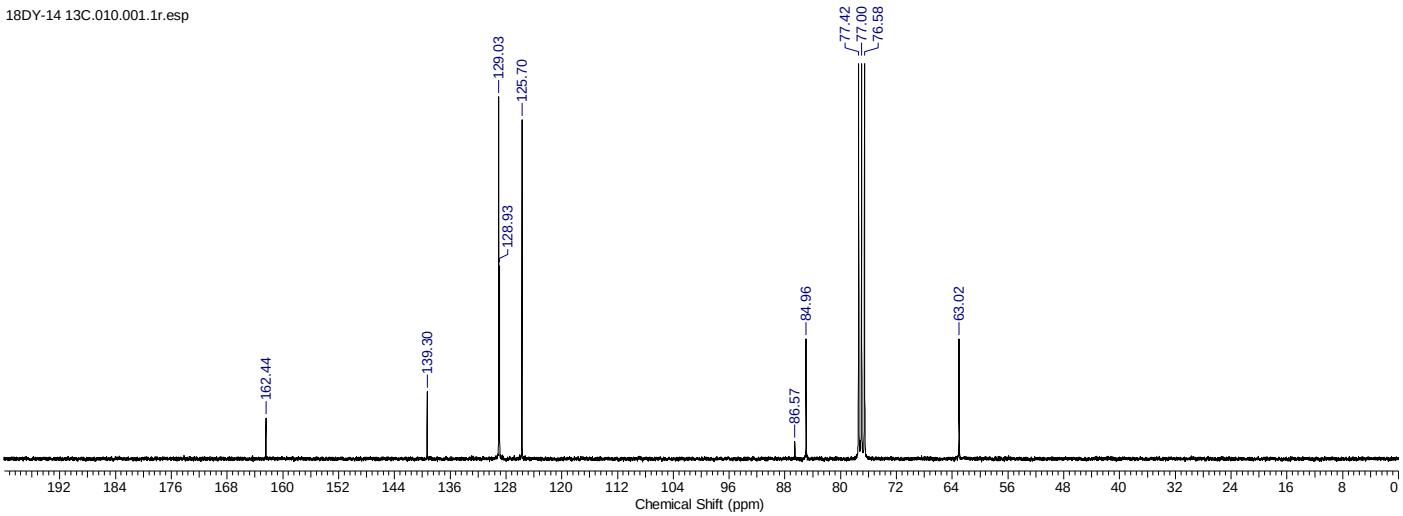




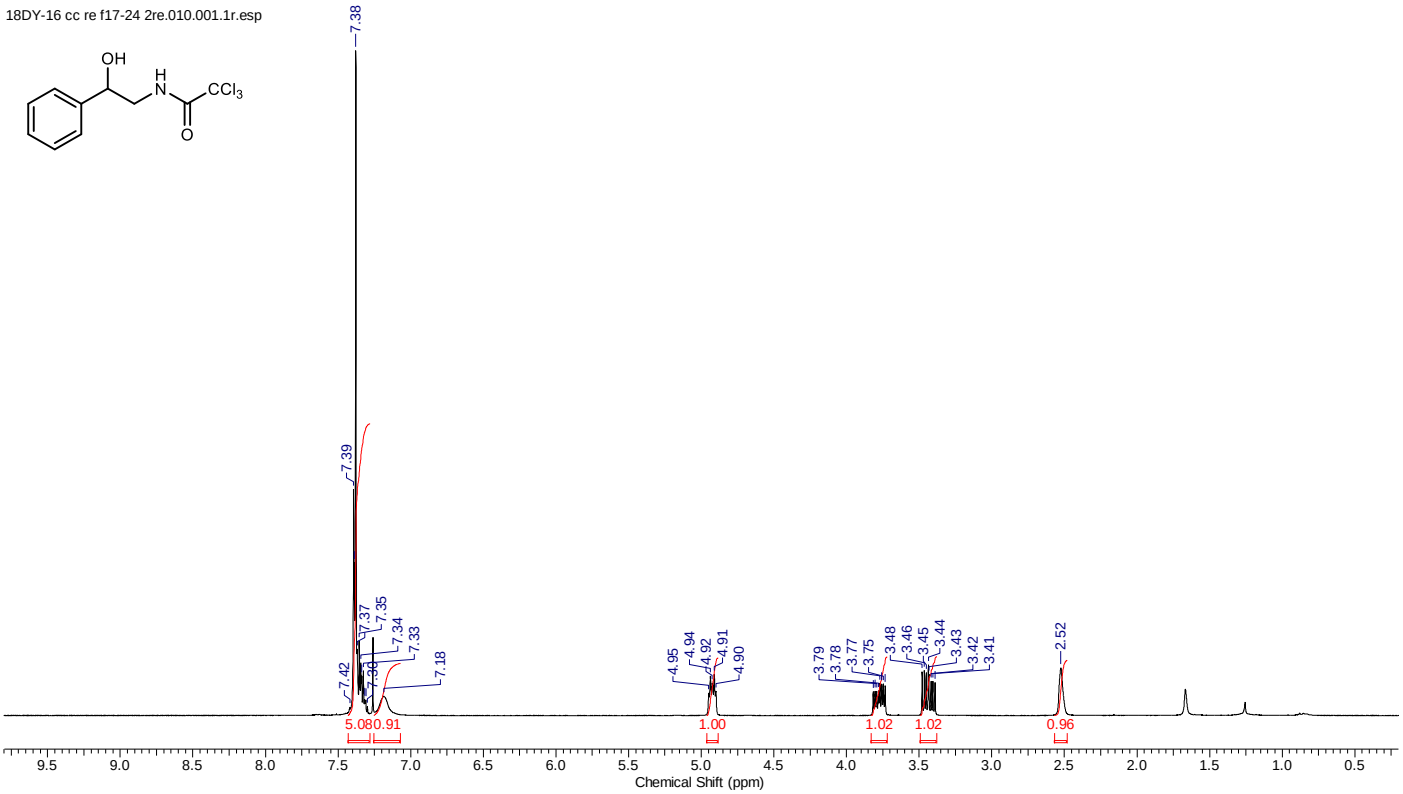
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 2q

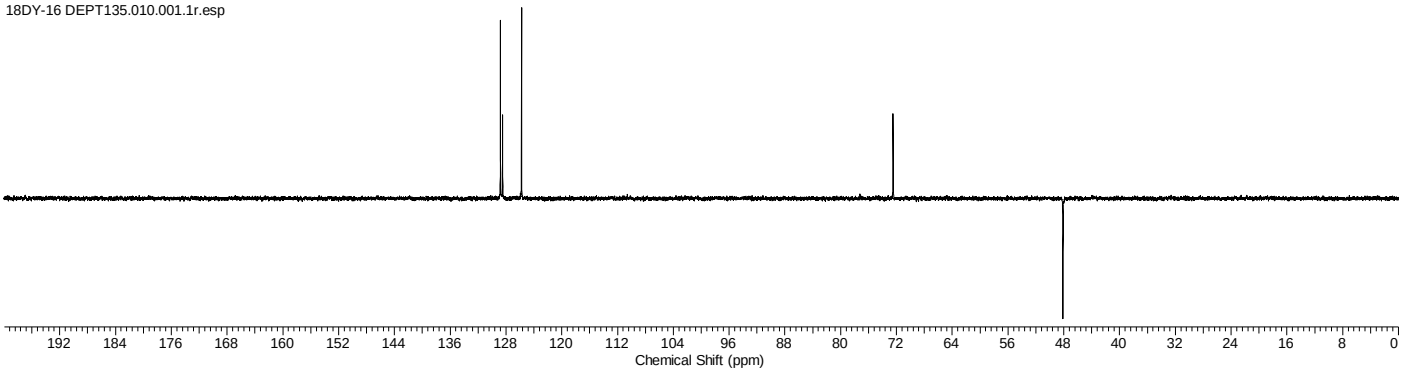


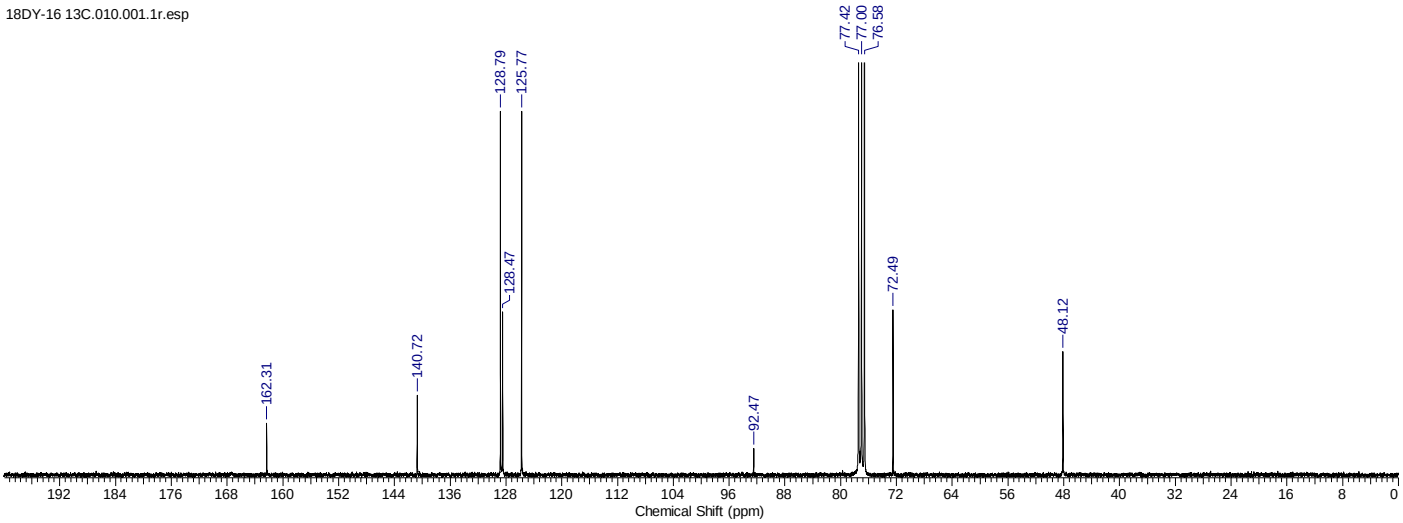




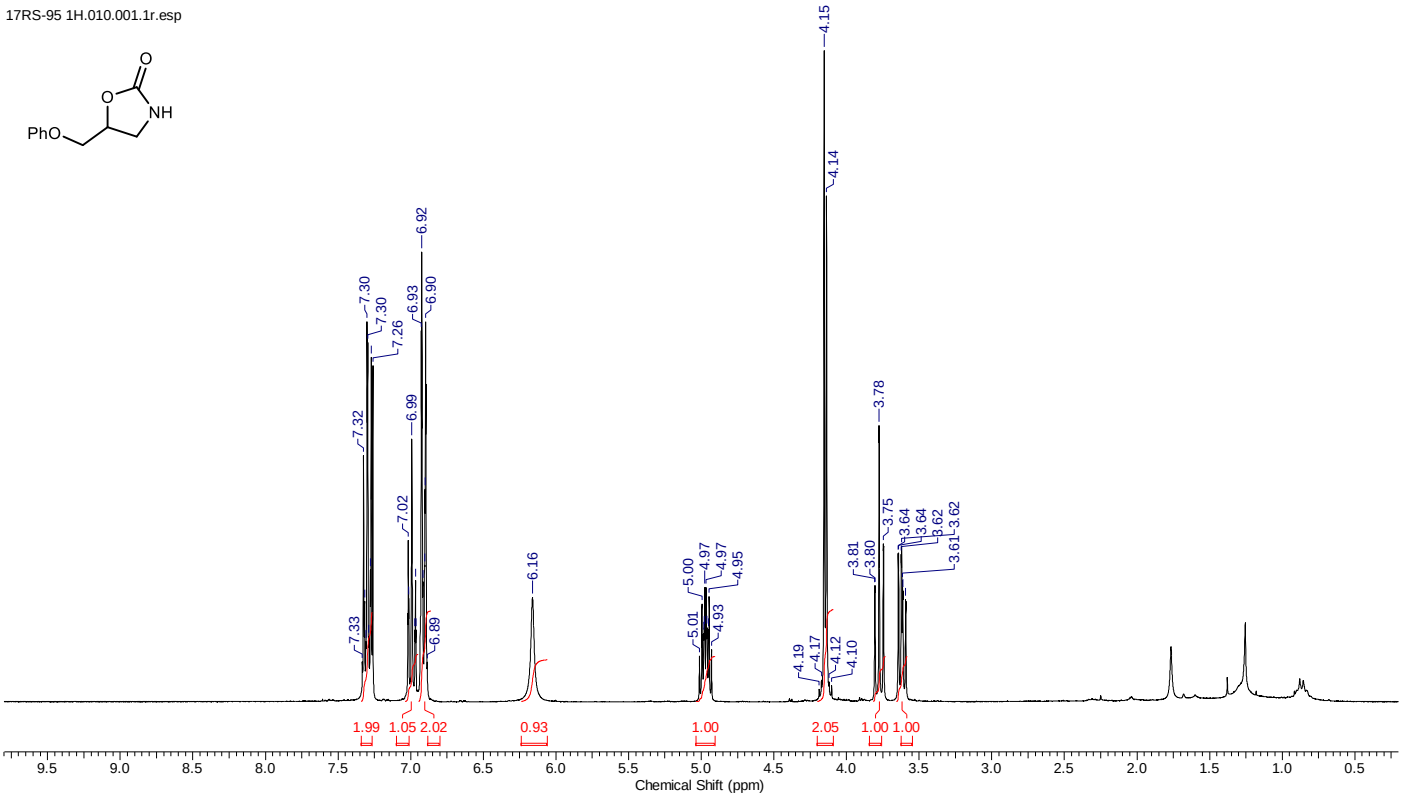
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 4q

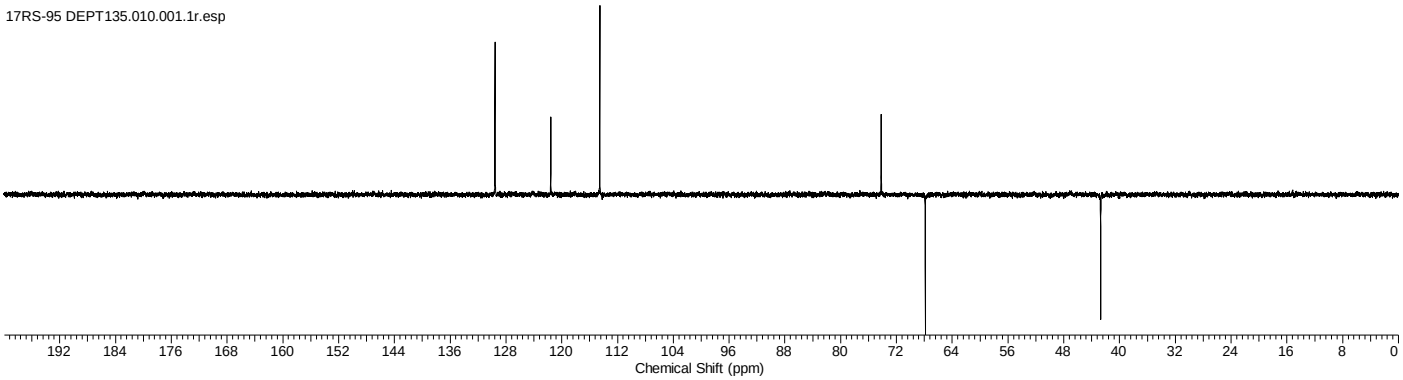


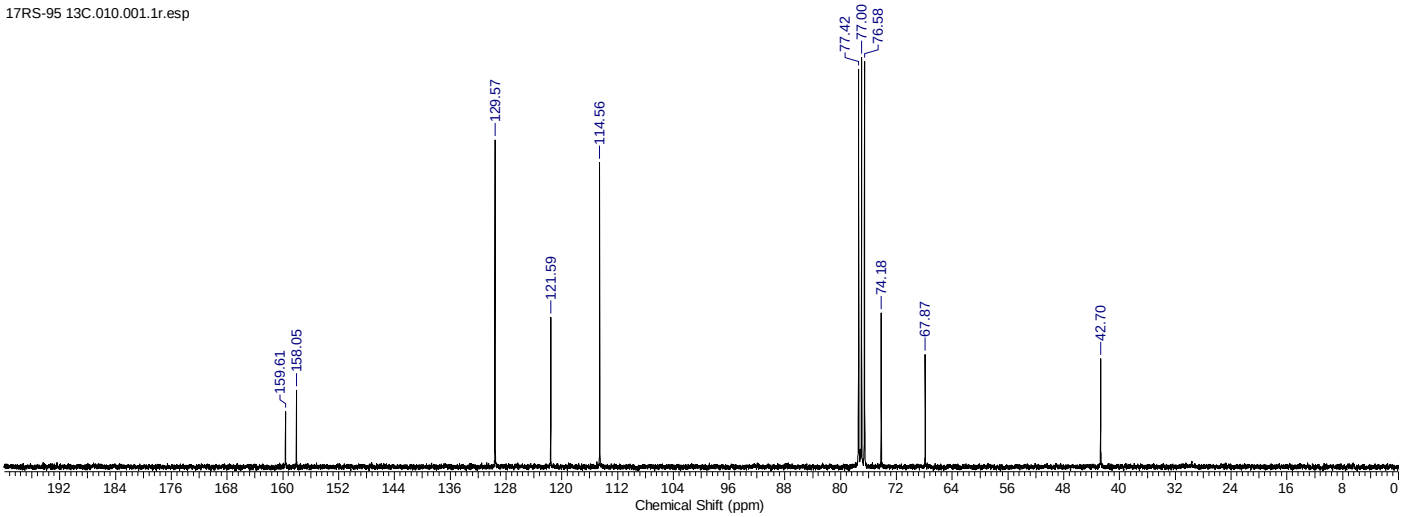




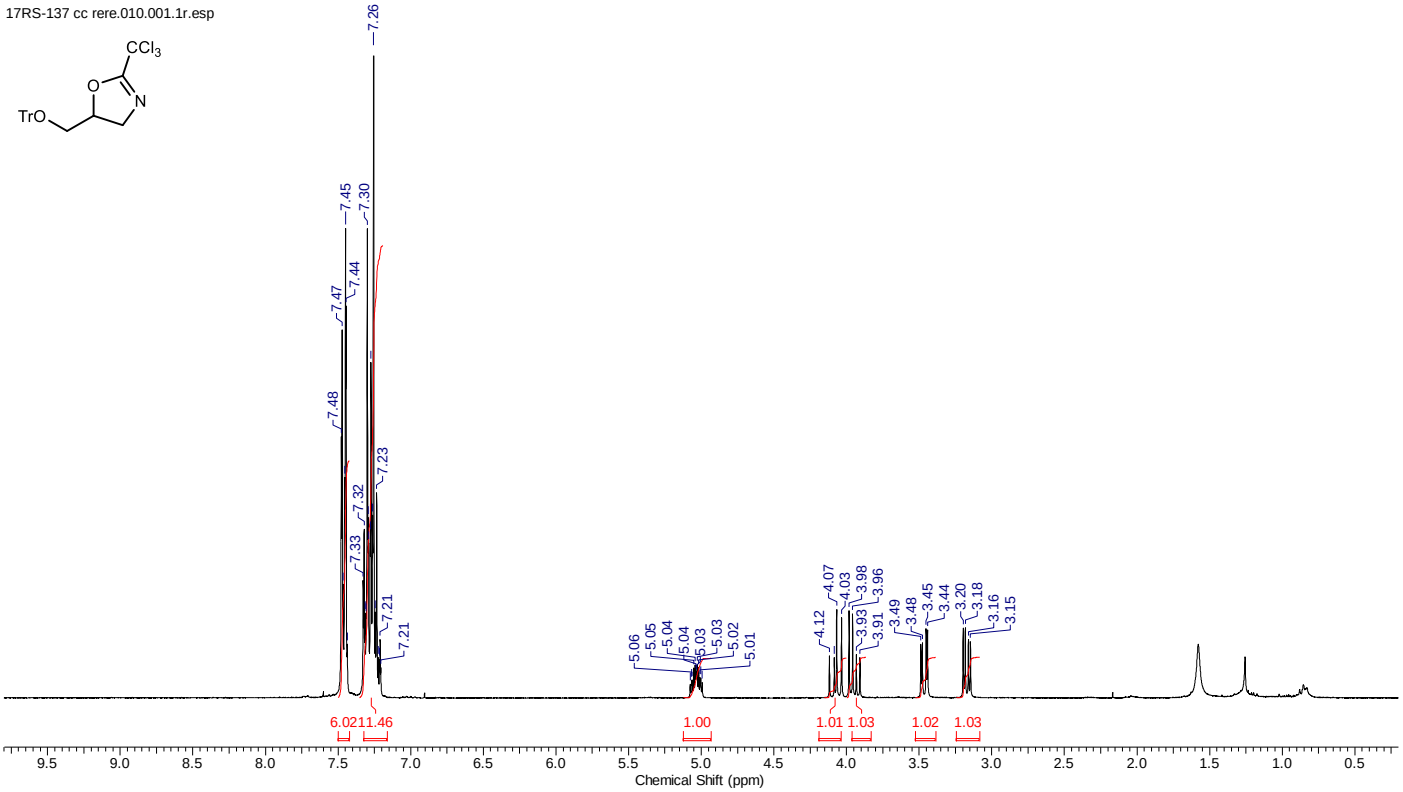
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of 5

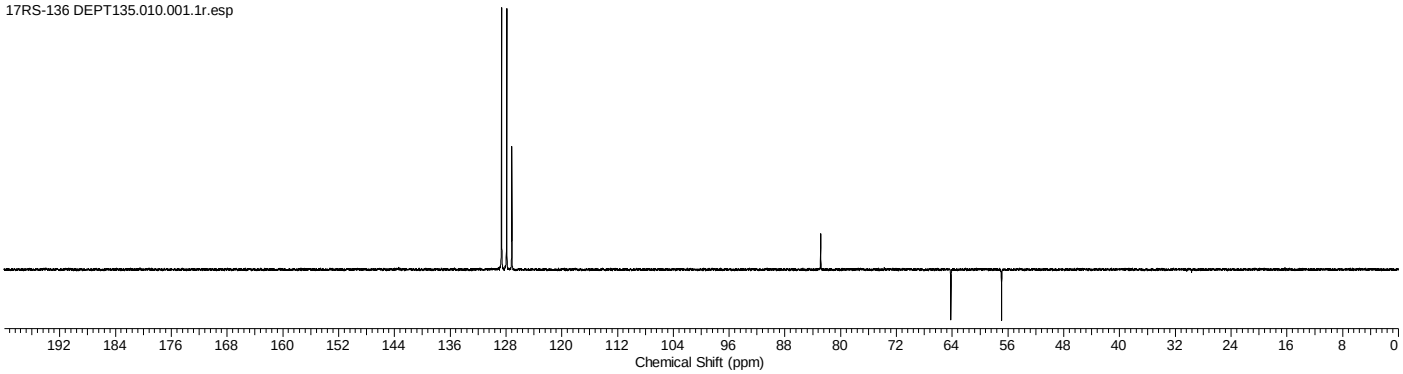


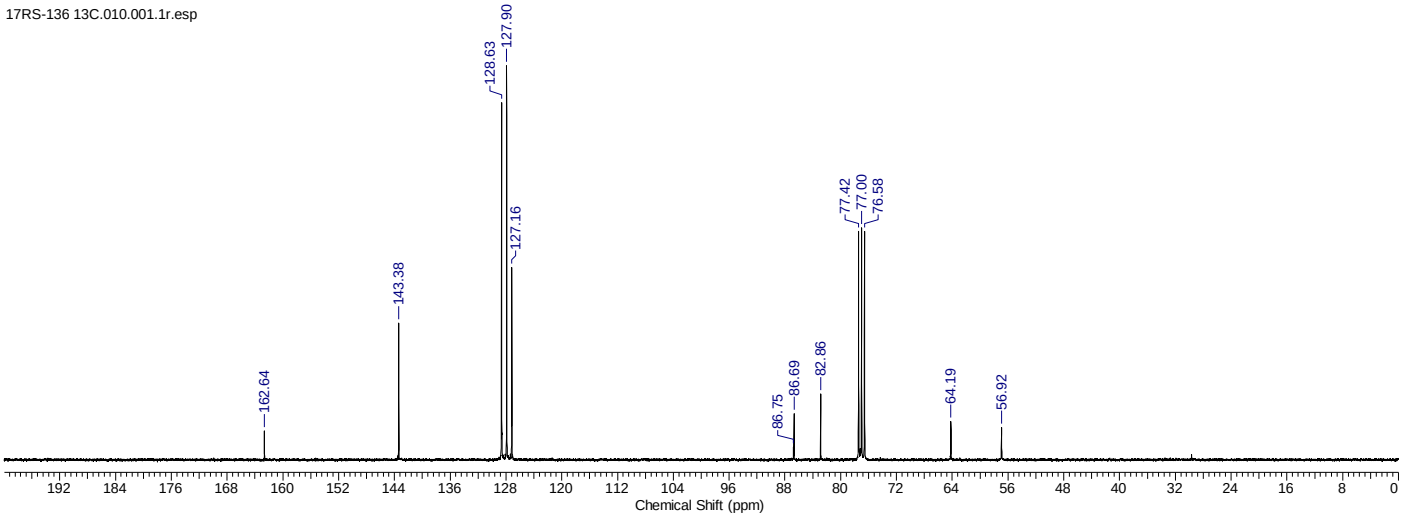




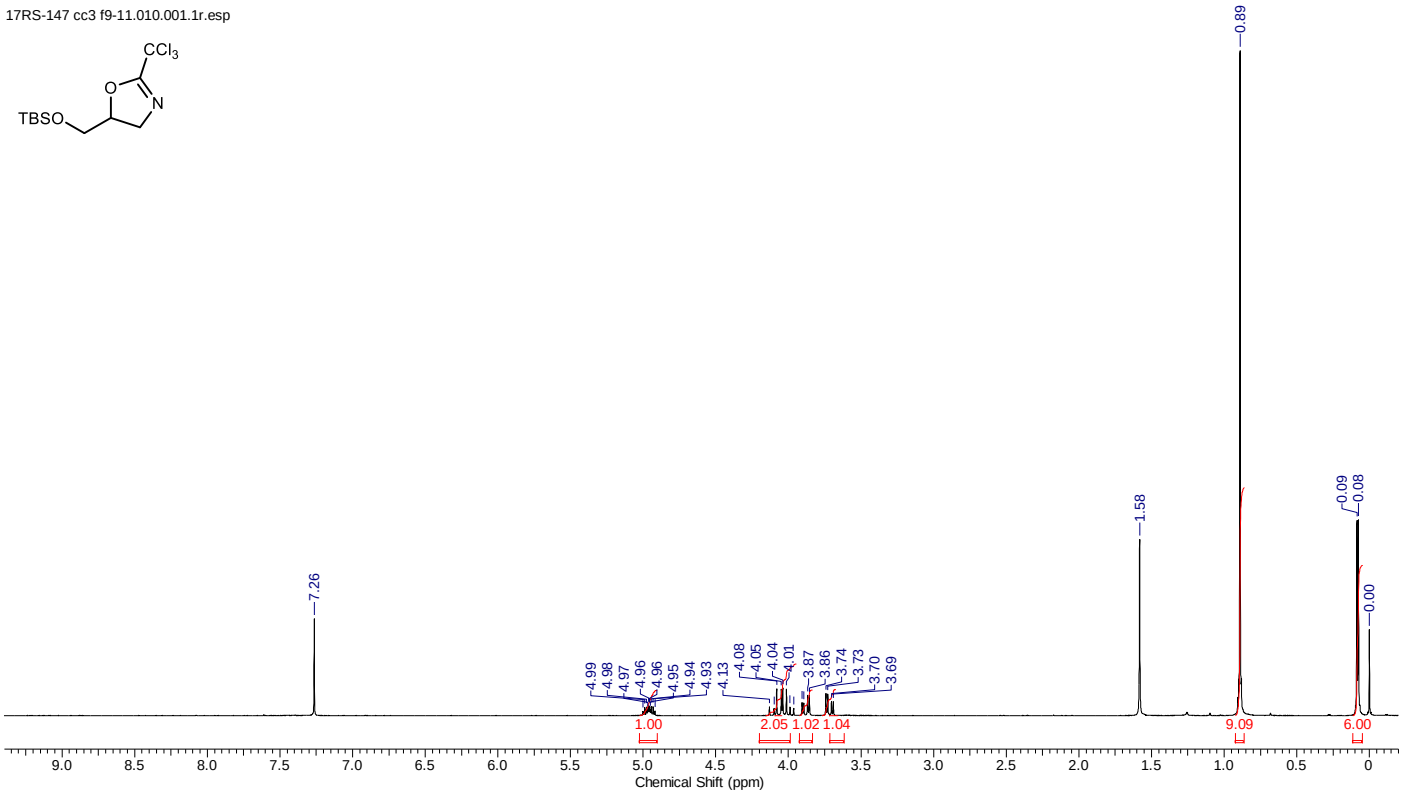
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of S2

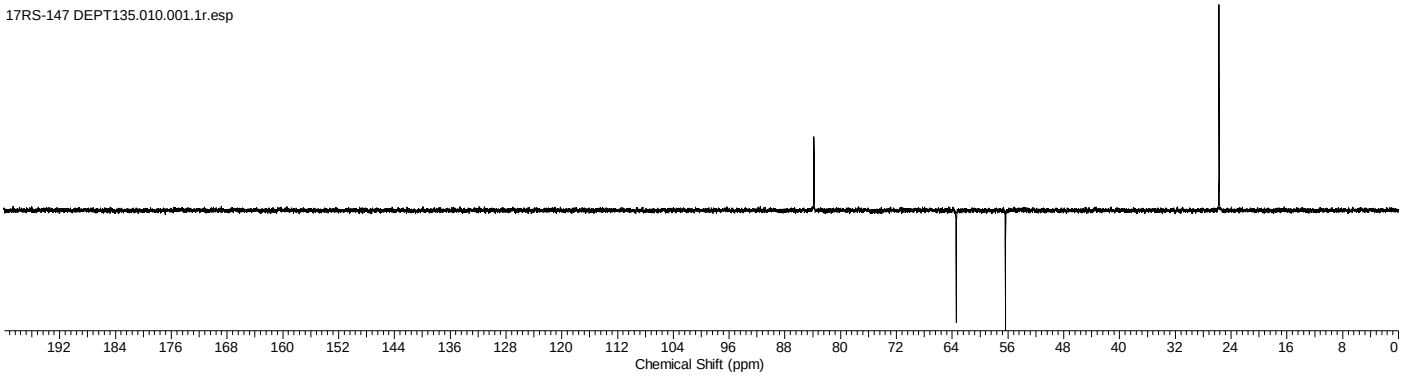


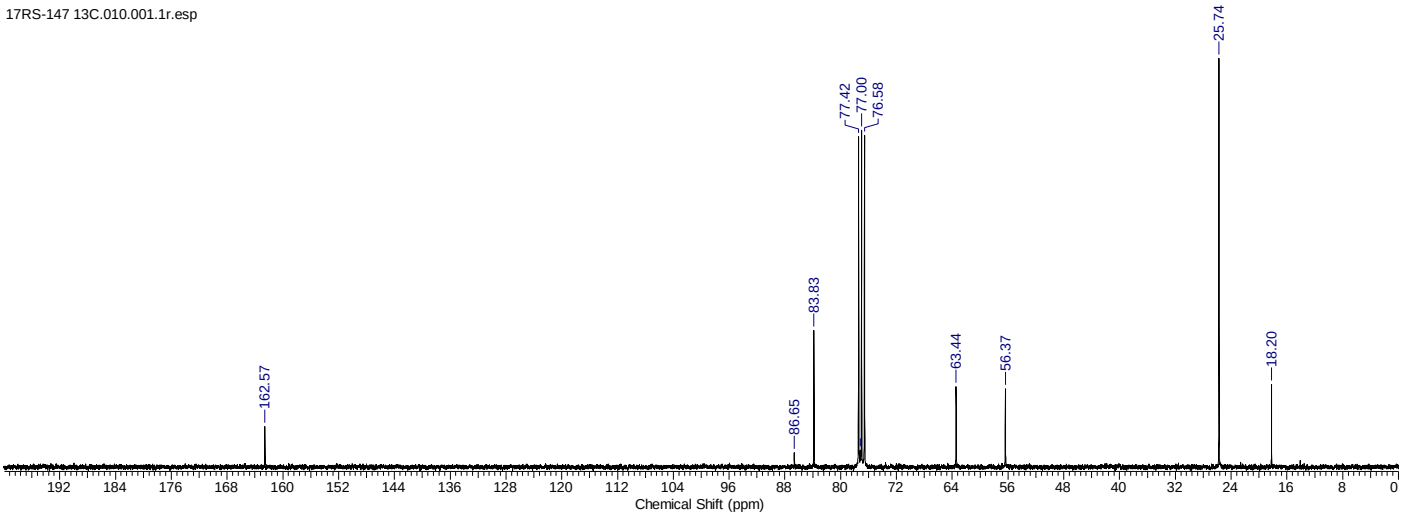




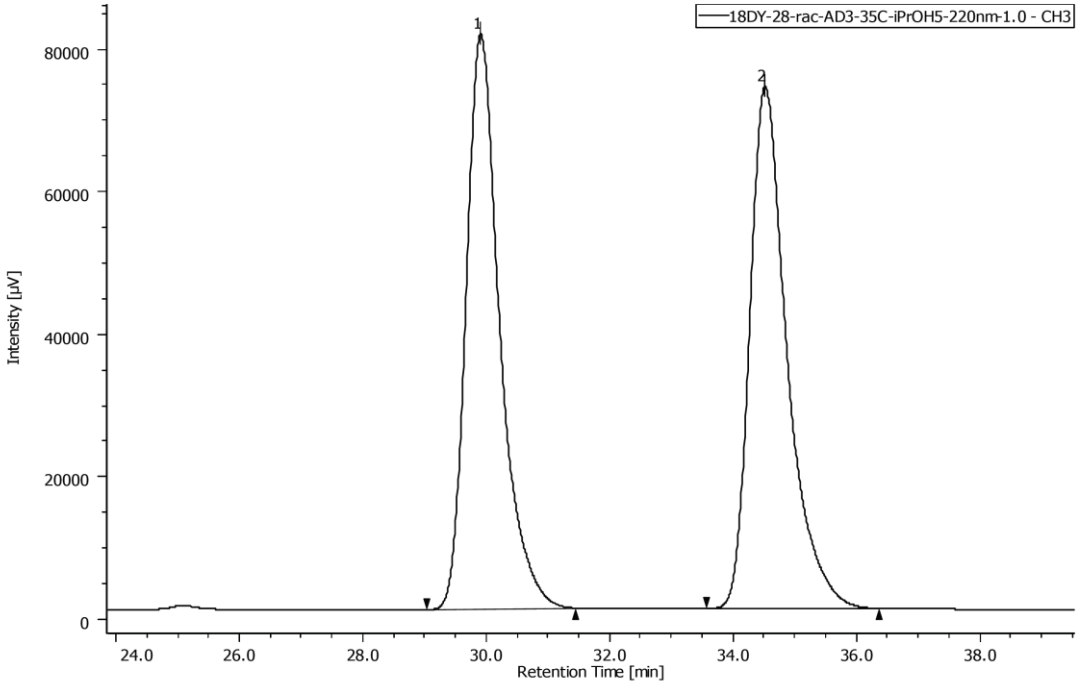
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of S3



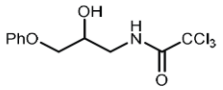


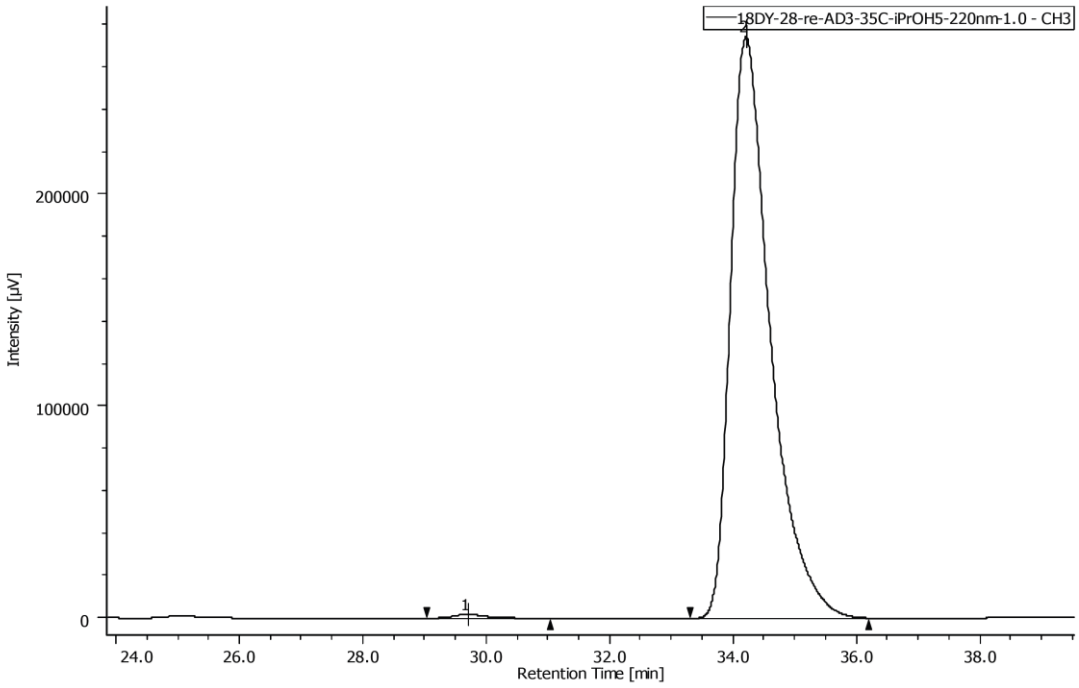


HPLC trace of 4a



# Peak	CH	tR (min)	Area	Height	Area%
1	3	29.908	3039635	80528	49.817
2	3	34.508	3061941	73109	50.183

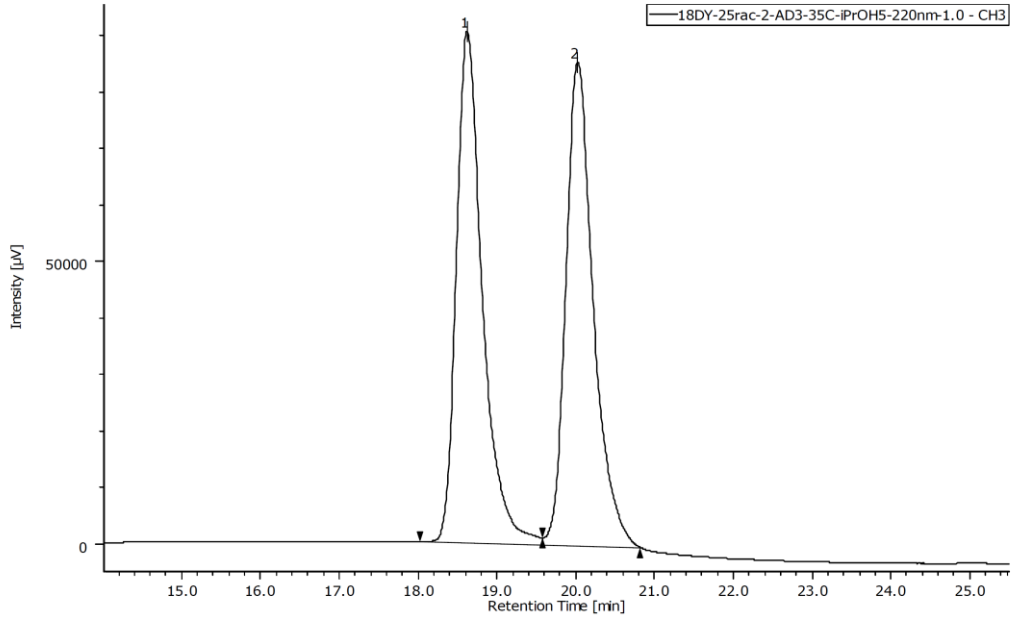




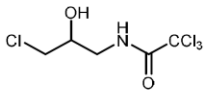
# Peak	CH	tR (min)	Area	Height	Area%
1	3	29.708	63666	1813	0.515
2	3	34.2	12288273	274049	99.485

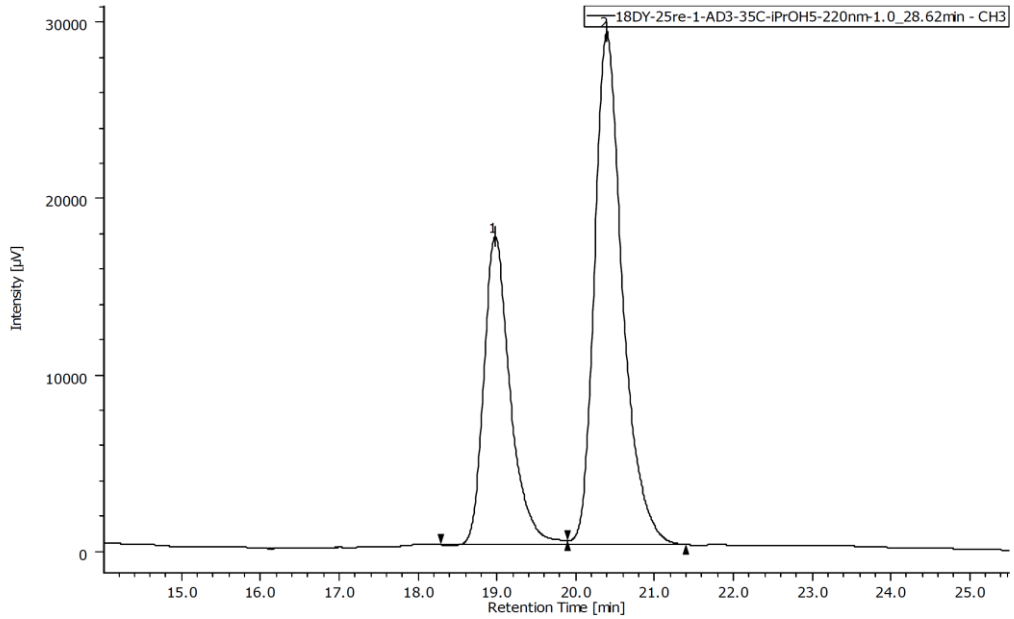
99% ee

HPLC trace of 4n



# Peak	CH	tR (min)	Area	Height	Area%
1	3	18.617	2076588	90485	50.149
2	3	20.017	2064285	85550	49.851

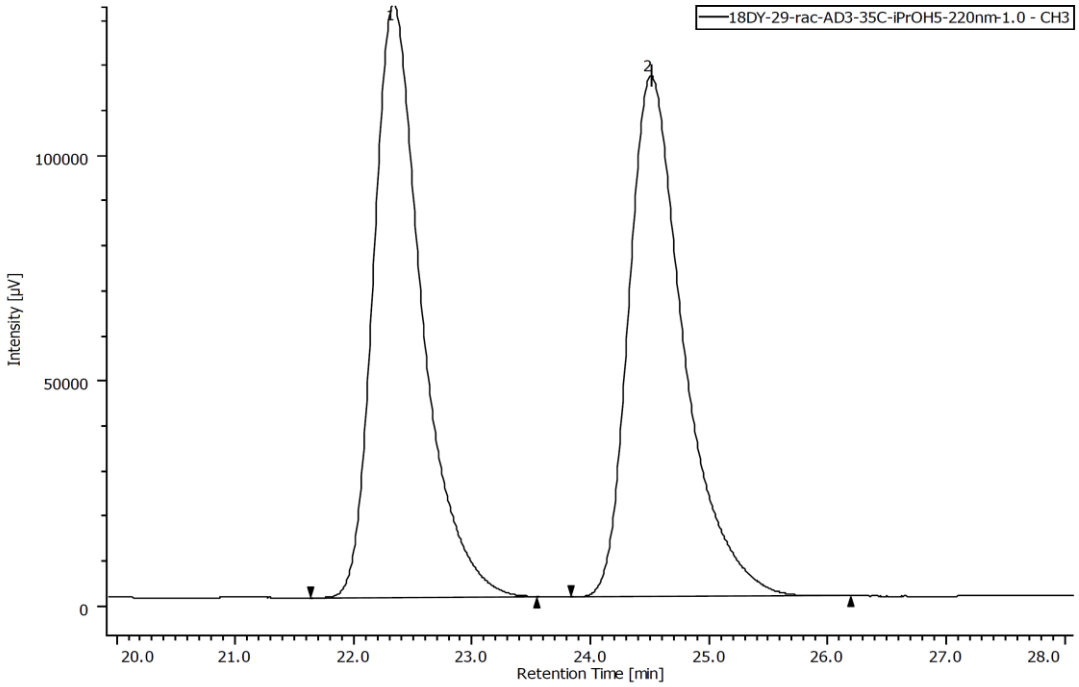




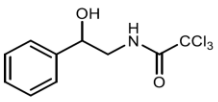
# Peak	CH	tR (min)	Area	Height	Area%
1	3	18.975	406712	17449	36.097
2	3	20.383	720020	29030	63.903

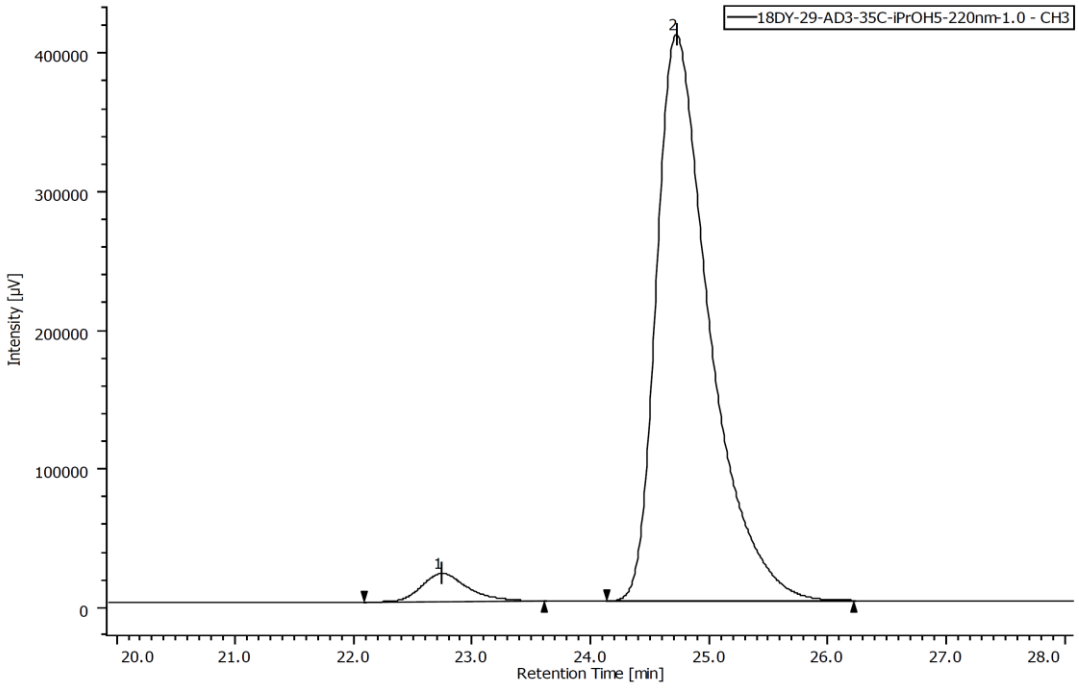
28% ee

HPLC trace of 4q



# Peak	CH	tR (min)	Area	Height	Area%
1	3	22.333	3722644	131394	50.061
2	3	24.508	3713599	115490	49.939

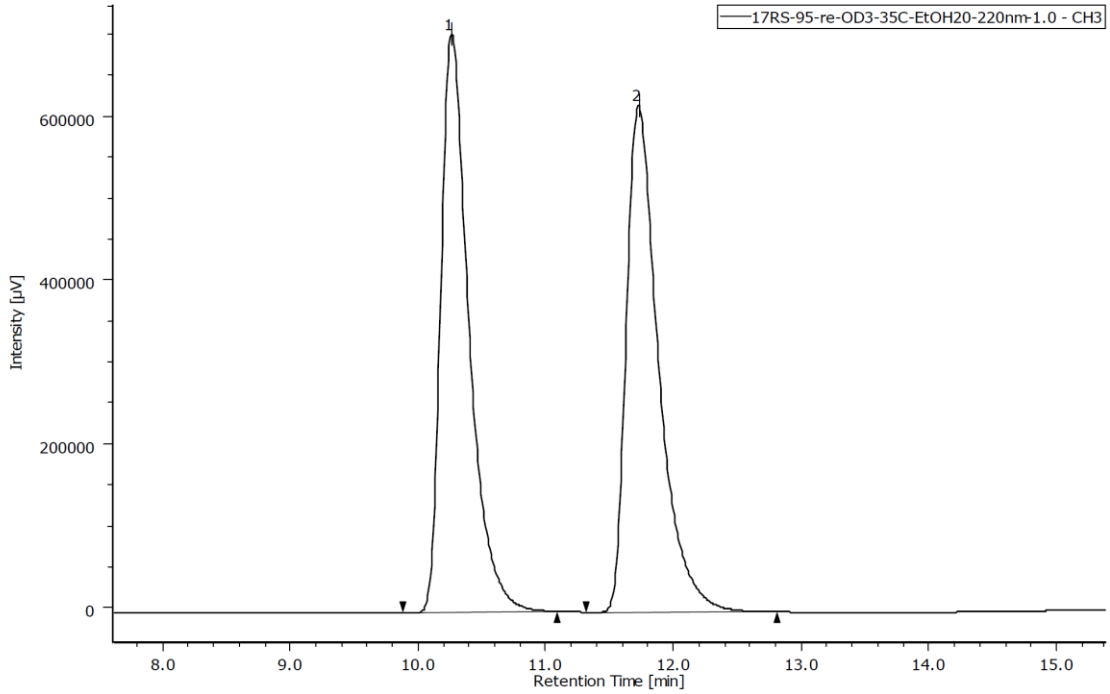




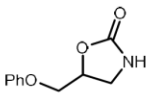
# Peak	CH	tR (min)	Area	Height	Area%
1	3	22.742	554979	20193	4.717
2	3	24.717	12654833	407867	95.799

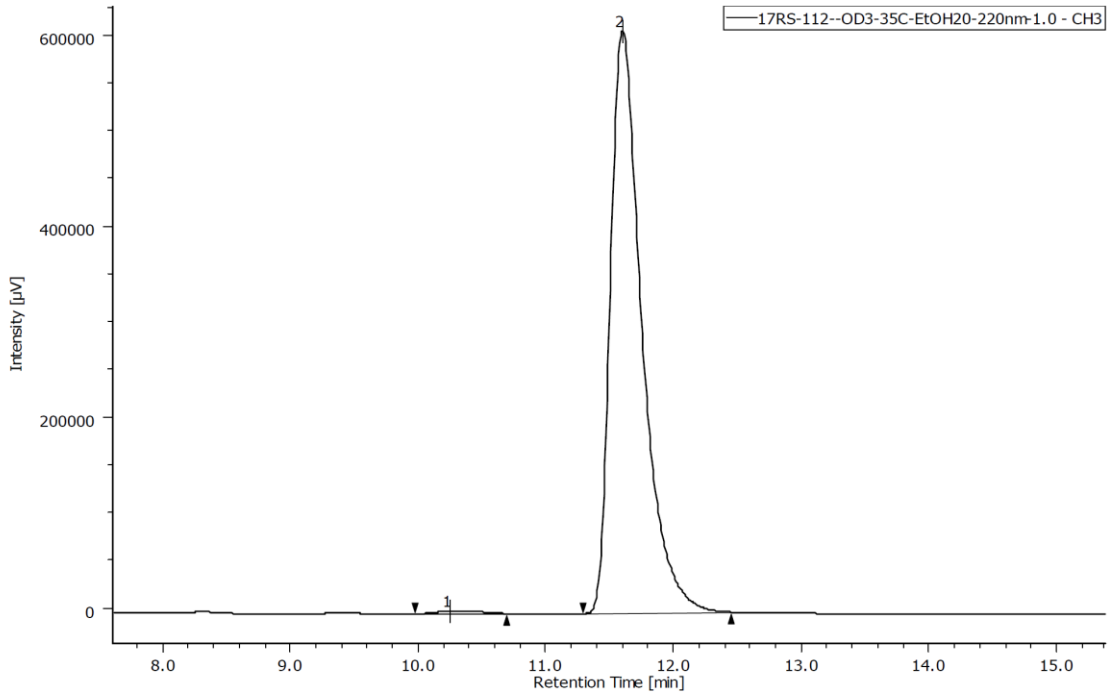
91% ee

HPLC trace of 5



# Peak	CH	tR	面積	高さ	面積%
1	3	10.258	10784021	704615	49.903
2	3	11.725	10826063	616547	50.097





# Peak	CH	tR (min)	Area	Height	Area%
1	3	10.25	61688	2912	0.59
2	3	11.6	10385183	608398	99.41

99% ee