Supporting Information

Tetraarylphosphonium Salt-Catalyzed Synthesis of Oxazolidinones from Isocyanates and Epoxides

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SI-X

General information

All reagents and solvents were commercial grade and purified prior to use when necessary. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2) and toluene were dried by passage through a column of activated alumina as described by Grubbs.[1] 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 Wako Pure Chemical Industries (Wakogel® C-300HG) or Fuji Silysia Chemical (PSQ60B, 60 μm). Products were visualized by ultraviolet (UV) light, iodine (I_2), and/or the use of Phosphomolybdic Acid (PMA), 4-Anisaldehyde (Anis), and potassium permanganate ($KMnO_4$) solutions were used. High-performance liquid chromatography (HPLC) was performed on a Jasco HPLC system using Daicel chiral columns (25 cm x 4.6 mm). Optical rotations were measured on a Jasco P-1010 polarimeter with a halogen lamp and are reported as follows; $[\alpha]^{T\,^\circ C}_D$ (*c* = g/100 mL, solvent). 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) or a Bruker Ascend 500 (500 MHz). Chemical shifts are measured relative to residual solvent peaks as an internal standard set to 7.26 and 77.0 for $CDCl_3$ (or 0.00 for TMS). Data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, br = broad, m = multiplet), coupling constants (Hz), and integration. Infrared (IR) spectra were recorded on a Jasco FT/IR-4200 spectrophotometer and are reported in wavenumbers (cm^{-1}). All compounds were analyzed as neat films on a potassium bromide (KBr) plate. Mass spectra were recorded on a Bruker micrOTOF II mass spectrometer by the ionization method noted. A post-acquisition gain correction was applied using sodium formate (HCO_2Na) as the lock mass.

Preparation of starting materials

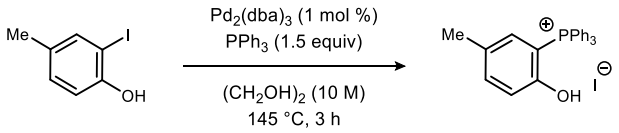
Epoxides; *rac*-**2a**, (*S*)-**2a**, **2b**, **2e**, **2f**, **2g**, **2i**, **2k**, and (*S*)-**2l** are commercially available. **2c**, **2d**, **2h**, and **2j** were prepared according to the reported procedure.[2] Isocyanates; **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, **3h**, **3i**, **3j**, and **5a-d** are commercially available. **3g** was prepared using the literature procedure.[3]

4-Bromo-3-fluorophenyl isocyanate (3g).[4] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.4, 7.5 Hz, 1H), 6.88 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.80 (ddd, *J* = 8.4, 2.4, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2 (d, *J* = 249 Hz, C), 134.1 (d, *J* = 8 Hz, C), 134.0 (d, *J* = 2 Hz, CH), 121.9 (d, *J* = 4 Hz, CH), 113.3 (d, *J* = 25 Hz, CH), 106.0 (d, *J* = 21 Hz, C); ^{19}F NMR (282 MHz, $CDCl_3$) δ -104.4.

Catalyst synthesis

Phosphonium salt **9** is commercially available. The synthetic procedures and spectroscopic data for TAPS **1a**, **1b**, **7a**, **8b**, and **8c** have been already reported.[2]

The improved method for the preparation of **1b**:



(2-Hydroxy-5-methylphenyl)triphenylphosphonium iodide (1b). To a test tube equipped with a stir bar was added 2-iodo-4-methylphenol (351.1 mg, 1.50 mmol), PPh_3 (590.1 mg, 2.25 mmol), and ethylene glycol (0.15 mL). $Pd_2(dba)_3$ (13.7 mg, 15 μmol) was added and the atmosphere was replaced with argon (x 3), and the reaction mixture was then stirred at 145 °C for 3 h. After cooling to rt, the mixture was treated with THF, and the solid was collected by vacuum filtration and washed with THF to give a white solid (667 mg, 74%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.51 (br s, 1H, OH), 8.06 (dd, *J* = 8.1, 6.9 Hz, 1H, H_C), 7.80-7.74 (m, 3H, ArH), 7.67-7.56 (m, 12H, ArH), 7.44 (ddd, *J* = 8.1, 1.2, 0.6 Hz, 1H, H_B), 6.60 (dd, *J* = 15.0, 1.2 Hz, 1H, H_A), 2.19 (s, 3H, Me). These protons were assigned by H-H COSY and NOESY experiments shown in Figure S1.

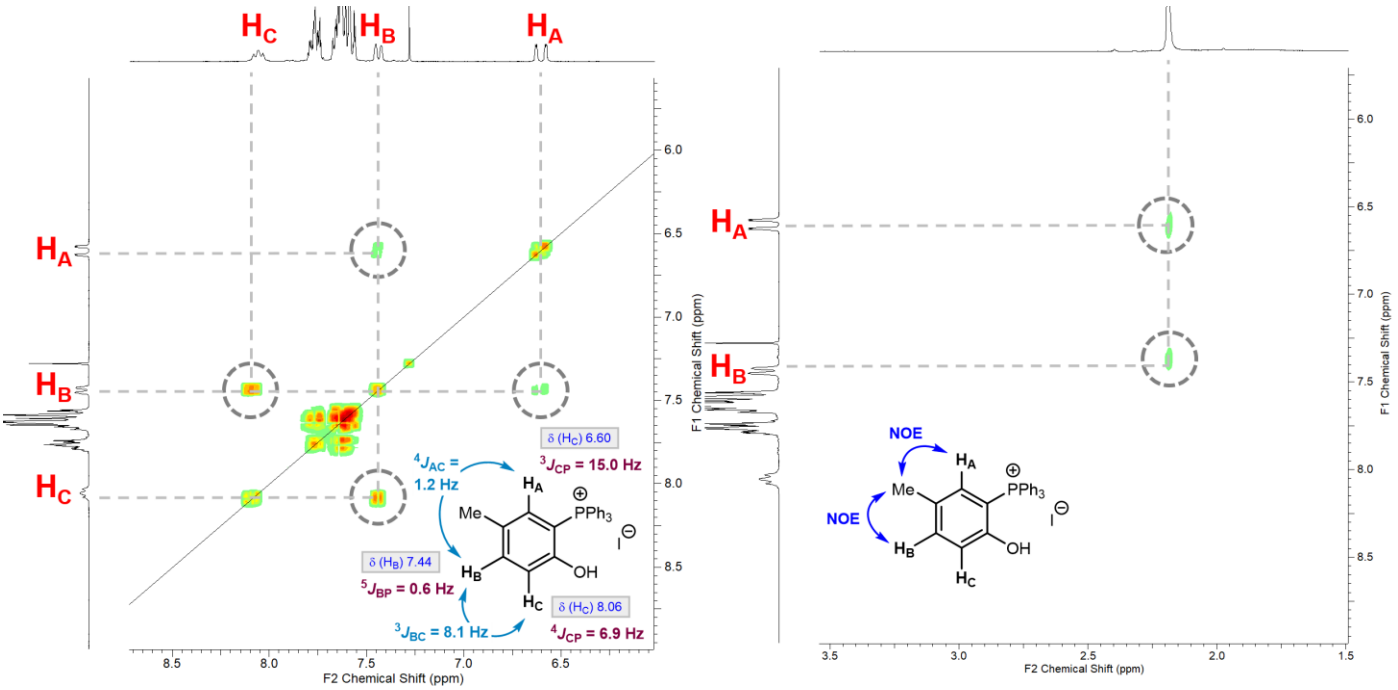
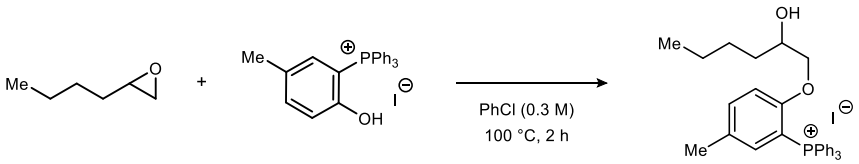
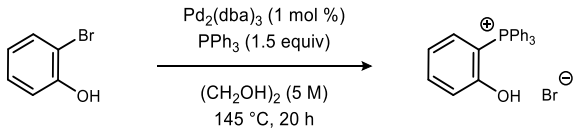


Figure S1. (a) H-H COSY spectrum of **1b**. (b) NOESY spectrum of **1b**.



(2-(2-Hydroxyhexyloxy)-5-methylphenyl)triphenylphophonium iodide (7b). A solution of epoxide **2i** (6.0 mg, 0.06 mmol) and TAPS **1b** (24.9 mg, 0.05 mmol) in PhCl (0.17 mL) was heated at 100 °C for 2 h. After cooling to rt, the mixture was concentrated, and then purified by flash column chromatography (SiO_2, 10% MeOH in $CHCl_3$) to give a viscous oil (29.7 mg, 97%). R_f = 0.1 (10% MeOH/$CHCl_3$) visualized with $KMnO_4$; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88-7.82 (m, 3H), 7.79-7.73 (m, 6H), 7.70-7.59 (m, 7H), 7.41 (dd, *J* = 8.7, 6.3 Hz, 1H), 6.73 (dd, *J* = 15.3, 1.5 Hz, 1H), 4.06 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.94 (dd, *J* = 9.6, 4.5 Hz, 1H), 3.32-3.23 (m, 1H), 2.61 (d, *J* = 5.4 Hz, 1H), 2.26 (s, 3H), 1.19-0.82 (m, 6H), 0.74 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2 (d, *J* = 2 Hz, C), 139.5 (d, *J* = 2 Hz, CH), 135.5 (d, *J* = 9 Hz, CH), 135.0 (d, *J* = 3 Hz, CH), 133.7 (d, *J* = 11 Hz, CH), 132.2 (d, *J* = 13 Hz, C), 130.4 (d, *J* = 13 Hz, CH), 118.3 (d, *J* = 92 Hz, C), 114.6 (d, *J* = 7 Hz, CH), 104.1 (d, *J* = 93 Hz, C), 73.5 (CH_2), 68.4 (CH), 32.4 (CH_2), 27.2 (CH_2), 22.3 (CH_2), 20.5 (CH_3), 13.8 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.0; IR (KBr) 3362, 2927, 1603, 1486, 1438, 1289, 1253, 1106, 999, 723, 690 cm^{-1}; HRMS (ESI) Exact mass calcd for $C_{31}H_{34}O_2P$ $[M\text{-}I]^+$ 469.2291, found 469.2305. The structure was confirmed by 2D NMR analysis.

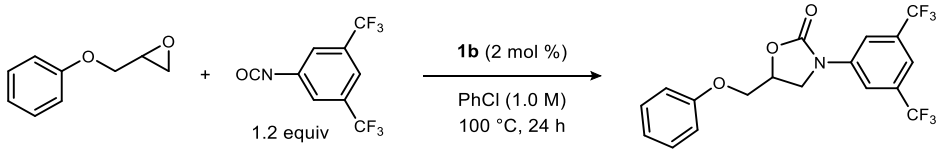


(2-Hydroxyphenyl)triphenylphosphonium bromide (8a). To a test tube equipped with a stir bar was added 2-bromophenol (519 mg, 3.0 mmol), PPh_3 (1.18 g, 4.5 mmol) and ethylene glycol (0.6 mL). $Pd_2(dba)_3$ (55 mg, 60 μmol) was added and the atmosphere was replaced with argon (x 3), and the reaction mixture was then stirred at 145 °C for 20 h. After cooling to rt, the mixture was treated with H_2O, and the aqueous layer was extracted with CH_2Cl_2 (x 2). The organic layers were combined, washed with H_2O (x 2), dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography (SiO_2, 1-10% MeOH in

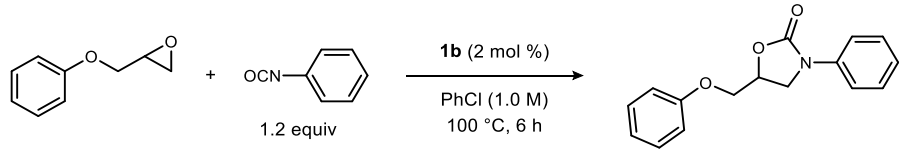
$CHCl_3$), and the solid obtained was triturated with a CH_2Cl_2/Et_2O (1/20) mixture to give a white solid (542 mg, 42%). R_f = 0.3 (10% MeOH/$CHCl_3$) visualized with $KMnO_4$; Mp 259-260 °C; ^{1}H NMR (300 MHz, CD_3OD) δ 7.91-7.83 (m, 3H), 7.79-7.71 (m, 13H), 7.12-7.01 (m, 3H); ^{13}C NMR (75 MHz, CD_3OD) δ 164.2 (d, *J* = 3 Hz, C), 139.4 (d, *J* = 2 Hz, CH), 136.8 (d, *J* = 10 Hz, CH), 135.9 (d, *J* = 3 Hz, CH), 135.5 (d, *J* = 11 Hz, CH), 131.3 (d, *J* = 13 Hz, CH), 121.6 (d, *J* = 13 Hz, CH), 120.8 (d, *J* = 92 Hz, C), 119.1 (d, *J* = 7 Hz, CH), 104.7 (d, *J* = 94 Hz, C); ^{31}P NMR (121 MHz, CD_3OD) δ 21.7; IR (KBr) 3422, 2773, 1587, 1438, 1342, 1295, 1106, 761, 716, 689 cm^{-1}; HRMS (ESI) Exact mass calcd for $C_{24}H_{20}OP$ $[M-Br]^+$ 355.1246, found 356.1280.

General procedure for TAPS-catalyzed [3+2] coupling reaction of isocyanates and epoxides

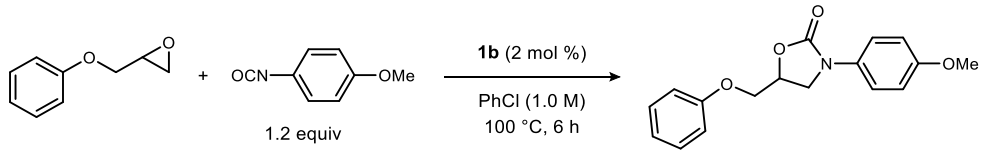
To a flame-dried test tube equipped with a stir bar was added epoxide **2** (1.0 equiv), TAPS **1b** (cat.), PhCl (1.0 M), and isocyanate **3** (1.2 equiv). The reaction mixture was stirred at 100 °C for 6-24 h under argon atmosphere, cooled to rt, and then concentrated. Flash column chromatography (SiO_2: Wakogel® C-300HG) yielded the product.



3-(3,5-Bis(trifluoromethyl)phenyl)-5-(phenoxymethyl)oxazolidin-2-one (4a). Prepared according to the general procedure using epoxide **2a** (90.1 mg, 0.60 mmol), isocyanate **3a** (125 µL, 0.72 mmol), and TAPS **1b** (6.0 mg, 12 µmol). Flash column chromatography (SiO_2, 100% $CHCl_3$) yielded a white solid (228.0 mg, 94%). R_f = 0.5 (100% $CHCl_3$) visualized with $KMnO_4$; Mp 129 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.64 (s, 1H), 7.31-7.27 (m, 2H), 7.01-6.98 (m, 1H), 6.90-6.88 (m, 2H), 5.05 (dddd, *J* = 8.7, 6.0, 4.8, 3.9 Hz, 1H), 4.26 (dd, *J* = 10.5, 4.8 Hz, 1H), 4.25 (t, *J* = 8.7 Hz, 1H), 4.22 (dd, *J* = 10.5, 3.9 Hz, 1H), 4.15 (dd, *J* = 8.7, 6.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.8 (C), 153.9 (C), 139.6 (C), 132.5 (q, *J* = 34 Hz, C), 129.7 (CH), 123.0 (q, *J* = 273 Hz, C), 121.1 (CH), 117.5 (q, *J* = 4 Hz, CH), 117.2 (sept, *J* = 4 Hz, CH), 114.5 (CH), 70.8 (CH), 67.5 (CH_2), 46.8 (CH_2); ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.9; IR (KBr) 1747, 1479, 1416, 1386, 1281, 1207, 1128, 899, 768, 750, 693 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{18}H_{13}F_6NNaO_3$ $[M+Na]^+$ 428.0692, found 428.0693.

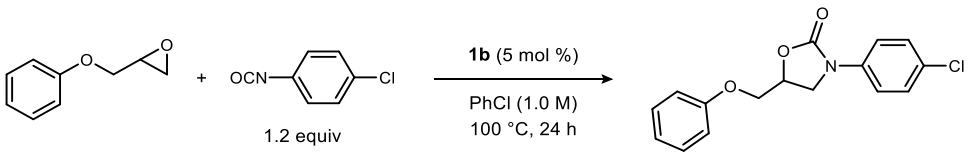


5-(Phenoxymethyl)-3-phenyloxazolin-2-one (4b).[5] Prepared according to the general procedure using epoxide **2a** (90.3 mg, 0.60 mmol), isocyanate **3b** (78 µL, 0.72 mmol), and TAPS **1b** (6.4 mg, 12 µmol). Flash column chromatography (SiO_2, 100% $CHCl_3$) yielded a white solid (144.5 mg, 90%). R_f = 0.3 ($CHCl_3$) visualized with Anis; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.55 (m, 2H), 7.43-7.36 (m, 2H), 7.33-7.26 (m, 2H), 7.18-7.13 (m, 1H), 7.03- 6.97 (m, 1H), 6.93-6.88 (m, 2H), 4.98 (dddd, *J* = 9.0, 6.0, 6.0, 4.5 Hz, 1H), 4.24 (dd, *J* = 10.2, 4.5 Hz, 1H), 4.21 (dd, *J* = 10.2, 6.0 Hz,1H), 4.20 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.07 (dd, *J* = 9.0, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9 (C), 154.4 (C), 138.1 (C), 129.6 (CH), 129.0 (CH), 124.1 (CH), 121.7 (CH), 118.2 (CH), 114.5 (CH), 70.3 (CH), 67.8 (CH_2), 47.3 (CH_2). Characterization data matched the literature.

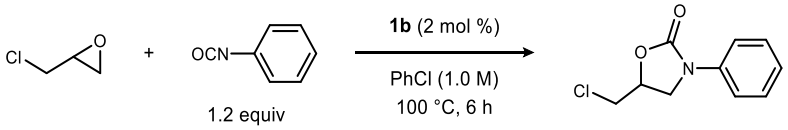


3-(4-Methoxyphenyl)-5-(phenoxymethyl)oxazolidin-2-one (4c).[6] Prepared according to the general procedure using epoxide **2a** (90.3 mg, 0.60 mmol), isocyanate **3c** (93 µL, 0.72 mmol), and TAPS **1b** (6.0 mg, 12 µmol). Flash column chromatography (SiO_2, 100% CH_2Cl_2) yielded a white solid (153.7 mg, 86%). R_f =

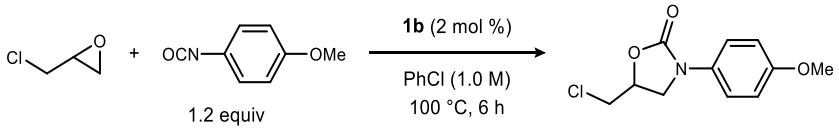
0.4 (20% EtOAc/hexane) visualized with $KMnO_4$; Mp 149-151 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.43 (m, 2H), 7.33-7.26 (m, 2H), 7.02-6.97 (m, 1H), 6.94-6.88 (m, 4H), 4.95 (dddd, *J* = 9.0, 6.0, 5.4, 4.5 Hz, 1H), 4.23 (dd, *J* = 10.2, 4.5 Hz, 1H), 4.19 (dd, *J* = 10.2, 5.4 Hz, 1H), 4.15 (t, *J* = 9.0 Hz, 1H), 4.01 (dd, *J* = 9.0, 6.0 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0 (C), 156.5 (C), 154.7 (C), 131.3 (C), 129.6 (CH), 121.7 (CH), 120.4 (CH), 114.6 (CH), 114.3 (CH), 70.3 (CH), 67.9 (CH_2), 55.5 (CH_3), 47.9 (CH_2); IR (KBr) 1736, 1598, 1520, 1440, 1251, 1147, 1093, 1042 821, 757 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{17}H_{17}NNaO_4$ $[M+Na]^+$ 322.1050, found 322.1055.



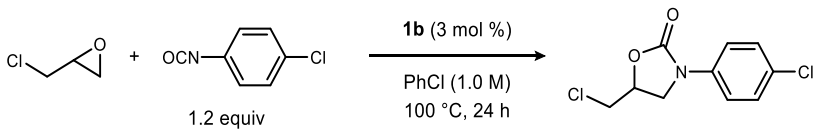
3-(4-Chlorophenyl)-5-(phenoxymethyl)oxazolidin-2-one (4d).[6] Prepared according to the general procedure using epoxide **2a** (90.2 mg, 0.60 mmol), isocyanate **3d** (92 µL, 0.72 mmol), and TAPS **1b** (14.9 mg, 30 µmol). Flash column chromatography (SiO_2, 100% CH_2Cl_2) yielded a white solid (145.0 mg, 80%). R_f = 0.5 (20% EtOAc/hexane) visualized with $KMnO_4$; Mp 148-150 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.49 (m, 2H), 7.36-7.26 (m, 3H), 7.03-6.97 (m, 1H), 6.92-6.87 (m, 2H), 4.98 (ddt, *J* = 9.0, 6.0, 4.5 Hz, 1H), 4.22 (d, *J* = 4.5 Hz, 2H), 4.16 (t, *J* = 9.0 Hz, 1H), 4.04 (dd, *J* = 9.0, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9 (C), 154.2 (C), 136.7 (C), 129.7 (CH), 129.4 (C), 129.1 (CH), 121.8 (CH), 119.4 (CH), 114.6 (CH), 70.4 (CH), 67.8 (CH_2), 47.3 (CH_2); IR (KBr) 1738, 1499, 1252, 758 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{16}H_{14}ClNNaO_3$ $[M+Na]^+$ 326.0554, found 326.0555.



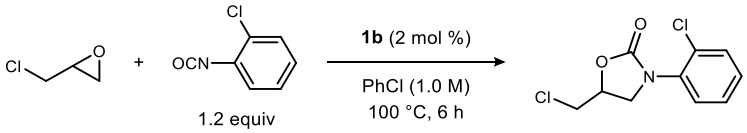
5-(Chloromethyl)-3-phenyloxazolidin-2-one (4e).[5] Prepared according to the general procedure using epoxide **2b** (55.6 mg, 0.60 mmol), isocyanate **3b** (78 µL, 0.72 mmol), and TAPS **1b** (6.0 mg, 12 µmol). Flash column chromatography (SiO_2, 100% $CHCl_3$) yielded a white solid (111.6 mg, 88%). R_f = 0.2 ($CHCl_3$) visualized with Anis; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.52 (m, 2H), 7.42-7.36 (m, 2H), 7.19-7.13 (m, 1H), 4.87 (dddd, *J* = 9.0, 6.6, 5.7, 4.2 Hz, 1H), 4.17 (dd, *J* = 9.3, 9.0 Hz, 1H), 3.97 (dd, *J* = 9.3, 5.7 Hz, 1H), 3.80 (dd, *J* = 11.7, 4.2 Hz,1H), 3.74 (dd, *J* = 11.7, 6.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9 (C), 137.8 (C), 129.1 (CH), 124.4 (CH), 118.3 (CH), 70.8 (CH), 48.2 (CH_2), 44.5 (CH_2). Characterization data matched the literature.



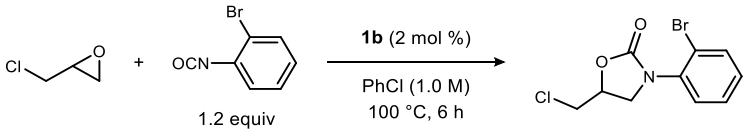
5-(Chloromethyl)-3-(4-methoxyphenyl)oxazolidin-2-one (4f).[5a] Prepared according to the general procedure using epoxide **2b** (55.5 mg, 0.60 mmol), isocyanate **3c** (93 µL, 0.72 mmol), and TAPS **1b** (6.0 mg, 12 µmol). Flash column chromatography (SiO_2, 100% $CHCl_3$) yielded a white solid (135.2 mg, 93%). R_f = 0.3 (20% EtOAc/hexane) visualized with Anis; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 9.3 Hz, 2H), 6.92 (d, *J* = 9.3 Hz, 2H), 4.85 (dddd, *J* = 8.7, 6.3, 5.7 4.2 Hz, 1H), 4.14 (dd, *J* = 9.0, 8.7 Hz, 1H), 3.92 (dd, *J* = 9.0, 5.7 Hz, 1H), 3.80 (s, 3H), 3.79 (dd, *J* = 11.4, 4.2 Hz, 1H), 3.74 (dd, *J* = 11.4, 6.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6 (C), 154.2 (C), 130.9 (C), 120.5 (CH), 114.3 (CH), 70.8 (CH), 55.5 (CH_3), 48.7 (CH_2), 44.6 (CH_2). Characterization data matched the literature.



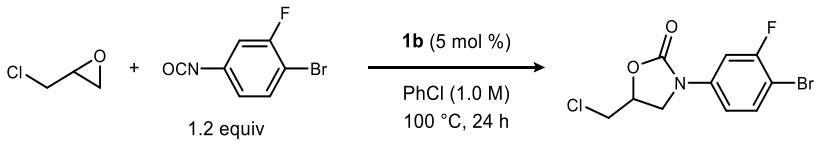
5-(Chloromethyl)-3-(4-chlorophenyl)oxazolidin-2-one (4g).[5a] Prepared according to the general procedure using epoxide **2b** (55.7 mg, 0.60 mmol), isocyanate **3d** (92 µL, 0.72 mmol), and TAPS **1b** (8.9 mg, 18 µmol). Flash column chromatography (SiO_2, 100% CH_2Cl_2) yielded a white solid (106.9 mg, 72%). R_f = 0.4 (20% EtOAc/hexane) visualized with $KMnO_4$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, *J* = 9.3 Hz, 2H), 7.34 (d, *J* = 9.3 Hz, 2H), 4.88 (dddd, *J* = 9.0, 6.0, 5.7, 4.2 Hz, 1H), 4.15 (dd, *J* = 9.3, 9.0 Hz, 1H), 3.93 (dd, *J* = 9.3, 5.7 Hz, 1H), 3.80 (dd, *J* = 11.7, 4.2 Hz, 1H), 3.75 (dd, *J* = 11.7, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7 (C), 136.4 (C), 129.6 (C), 129.1 (CH), 119.4 (CH), 70.8 (CH), 48.0 (CH_2), 44.5 (CH_2). Characterization data matched the literature.



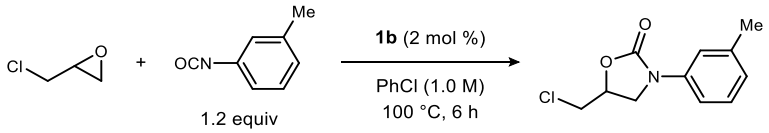
5-(Chloromethyl)-3-(2-chlorophenyl)oxazolidin-2-one (4h). Prepared according to the general procedure using epoxide **2b** (55.6 mg, 0.60 mmol), isocyanate **3e** (87 µL, 0.72 mmol), and TAPS **1b** (6.0 mg, 12 µmol). Flash column chromatography (SiO_2, 5-15% hexane/$CHCl_3$) yielded a colorless oil (143.0 mg, 97%). R_f = 0.3 (33% EtOAc/hexane) visualized with $KMnO_4$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.28 (m, 4H), 4.93 (dddd, *J* = 8.7, 6.0, 5.4, 4.8 Hz, 1H), 4.14 (dd, *J* = 9.0, 8.7 Hz, 1H), 3.92 (dd, *J* = 9.0, 5.4 Hz, 1H), 3.83 (dd, *J* = 11.7, 6.0 Hz, 1H), 3.79 (dd, *J* = 11.7, 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5 (C), 134.3 (C), 132.3 (C), 130.6 (CH), 129.6 (CH), 129.4 (CH), 128.0 (CH), 72.1 (CH), 49.7 (CH_2), 44.2 (CH_2); IR (KBr) 1759, 1488, 1415, 1232, 1142, 756 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{10}H_{10}Cl_2NO_2$ $[M+H]^+$ 246.0083, found 246.0097.



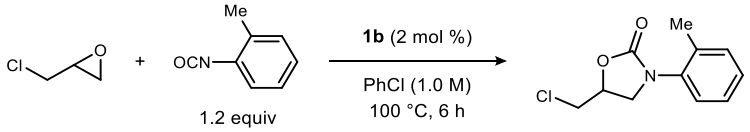
3-(2-Bromophenyl)-5-(chloromethyl)oxazolidin-2-one (4i). Prepared according to the general procedure using epoxide **2b** (55.5 mg, 0.60 mmol), isocyanate **3f** (74 µL, 0.72 mmol), and TAPS **1b** (6.0 mg, 12 µmol). Flash column chromatography (SiO_2, 2-5% EtOAc/toluene) yielded a colorless oil (147.6 mg, 85%). R_f = 0.3 (20% EtOAc/hexane) visualized with $KMnO_4$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.42-7.36 (m, 2H), 7.29-7.20 (m, 1H), 4.92 (dddd, *J* = 8.8, 6.3, 5.4, 4.8 Hz, 1H), 4.14 (dd, *J* = 9.0, 8.7 Hz, 1H), 3.92 (dd, *J* = 9.0, 5.4 Hz, 1H), 3.85 (dd, *J* = 11.4, 6.3 Hz, 1H), 3.80 (dd, *J* = 11.4, 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3 (C), 135.8 (C), 133.8 (CH), 130.1 (CH), 129.7 (CH), 128.8 (CH), 122.4 (C), 72.2 (CH), 49.9 (CH_2), 44.4 (CH_2); IR (KBr) 1759, 1484, 1233, 1141, 755 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{10}H_9BrClNNaO_2$ $[M+Na]^+$ 311.9397, found 311.9404.



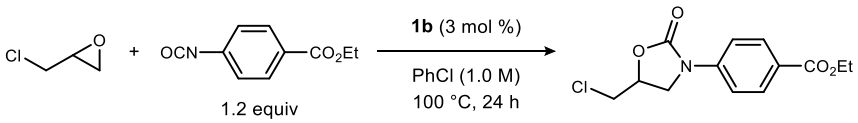
3-(4-Bromo-3-fluorophenyl)-5-(chloromethyl)oxazolidin-2-one (4j). Prepared according to the general procedure using epoxide **2b** (55.5 mg, 0.60 mmol), isocyanate **3g** (155.6 mg, 0.72 mmol), and TAPS **1b** (14.9 mg, 30 µmol). Flash column chromatography (SiO_2, 1-2% EtOAc/toluene) yielded a white solid (144.9 mg, 78%). R_f = 0.3 (5% EtOAc/toluene) visualized with $KMnO_4$; Mp 95-97 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65-7.49 (m, 2H), 7.14 (ddd, *J* = 8.7, 2.7, 0.9 Hz, 1H), 4.91 (dddd, *J* = 9.0, 5.7, 5.4, 4.5 Hz, 1H), 4.14 (t, 9.0 Hz, 1H), 3.93 (dd, *J* = 9.0, 5.7 Hz, 1H), 3.81 (dd, *J* = 11.7, 4.5 Hz, 1H), 3.77 (dd, *J* = 11.7, 5.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1 (d, *J* = 246.5 Hz, C), 153.4 (C), 138.5 (d, *J* = 9.3 Hz, C), 133.5 (d, *J* = 1.5 Hz, CH), 114.4 (d, *J* = 3.3 Hz, CH), 106.7 (d, *J* = 27.9 Hz, CH), 103.5 (d, *J* = 21.0 Hz, C), 70.8 (CH), 47.8 (CH_2), 44.5 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ -104.6; IR (KBr) 1753, 1603, 1580, 1496, 1482, 1410, 1365, 1327, 1208, 1119, 1046, 745 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{10}H_8BrClFNNaO_2$ $[M+Na]^+$ 329.9303, found 329.9293.



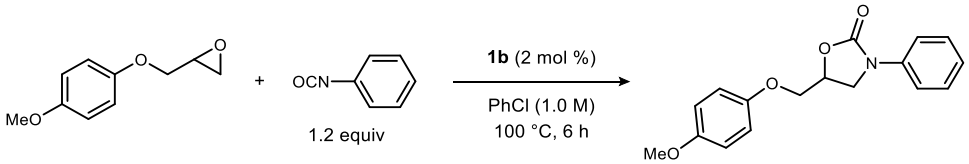
5-(Chloromethyl)-3-*m*-tolyloxazolidin-2-one (4k). Prepared according to the general procedure using epoxide **2b** (55.7 mg, 0.60 mmol), isocyanate **3h** (93 µL, 0.72 mmol), and TAPS **1b** (6.0 mg, 12 µmol). Flash column chromatography (SiO_2, 100% $CHCl_3$) yielded a white solid (125.9 mg, 93%). R_f = 0.5 (20% EtOAc/hexane) visualized with $KMnO_4$; Mp 64-65 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.33-7.24 (m, 2H), 6.98 (d, *J* = 7.2 Hz, 1H), 4.86 (dddd, *J* = 8.7, 6.6, 5.7, 4.2 Hz, 1H), 4.16 (dd, *J* = 9.0, 8.7 Hz, 1H), 3.95 (dd, *J* = 9.0, 5.7 Hz, 1H), 3.80 (dd, *J* = 11.7, 4.2 Hz, 1H), 3.73 (dd, *J* = 11.7, 6.6 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9 (C), 139.1 (C), 137.7 (C), 128.9 (CH), 125.2 (CH), 119.1 (CH), 115.5 (CH), 70.8 (CH), 48.3 (CH_2), 44.5 (CH_2), 21.6 (CH_3); IR (KBr) 1737, 1604, 1493, 1417, 1354, 1302, 1230, 1128, 1038, 889, 774, 748, 688 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{11}H_{12}ClNNaO_2$ $[M+Na]^+$ 248.0449, found 248.0441.



5-(Chloromethyl)-3-*o*-tolyloxazolidin-2-one (4l).[7] Prepared according to the general procedure using epoxide **2b** (55.6 mg, 0.60 mmol), isocyanate **3i** (89 µL, 0.72 mmol), and TAPS **1b** (6.0 mg, 12 µmol). Flash column chromatography (SiO_2, 100% $CHCl_3$) yielded a white solid (122.7 mg, 91%). R_f = 0.5 (20% EtOAc/hexane) visualized with $KMnO_4$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.23 (m, 4H), 4.93 (dddd, *J* = 8.7, 6.0, 5.7, 4.2 Hz, 1H), 4.07 (dd, *J* = 9.0, 8.7 Hz, 1H), 3.86 (dd, *J* = 9.0, 5.7 Hz, 1H), 3.84 (dd, *J* = 11.7, 6.0 Hz, 1H), 3.79 (dd, *J* = 11.7, 4.2 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4 (C), 136.0 (C), 135.5 (C), 131.4 (CH), 128.4 (CH), 127.0 (CH), 126.6 (CH), 71.6 (CH), 50.4 (CH_2), 44.9 (CH_2), 17.8 (CH_3). Characterization data matched the literature.

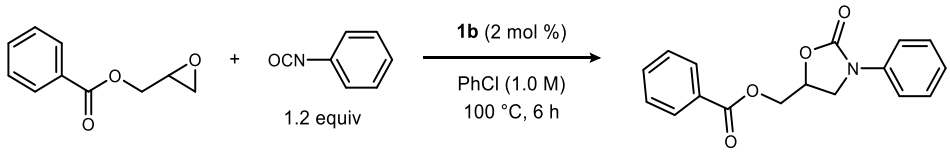


Ethyl 4-(5-(chloromethyl)-2-oxooxazolidin-3-yl)benzoate (4m). Prepared according to the general procedure using epoxide **2b** (55.5 mg, 0.60 mmol), isocyanate **3j** (137.8 mg, 0.72 mmol), and TAPS **1b** (8.9 mg, 18 µmol). Flash column chromatography (SiO_2, 100% $CHCl_3$) yielded a white solid (144.5 mg, 85%). R_f = 0.2 (100% $CHCl_3$) visualized with $KMnO_4$; Mp 95-97 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 9.0 Hz, 2H), 7.62 (d, *J* = 9.0 Hz, 2H), 4.91 (dddd, *J* = 9.0, 6.0, 5.7, 4.2 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.20 (dd, *J* = 9.3, 9.0 Hz, 1H), 4.00 (dd, *J* = 9.3, 5.7 Hz, 1H), 3.81 (dd, *J* = 11.7, 4.2 Hz, 1H), 3.76 (dd, *J* = 11.7, 6.0 Hz, 1H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9 (C), 153.5 (C), 141.6 (C), 130.7 (CH), 126.0 (C), 117.2 (CH), 70.9 (CH), 61.0 (CH_2), 47.9 (CH_2), 44.4 (CH_2), 14.3 (CH_3); IR (KBr) 1762, 1690, 1610, 1408, 1287, 1226, 1114, 770 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{13}H_{14}ClNNaO_4$ $[M+Na]^+$ 306.0504, found 306.0497.

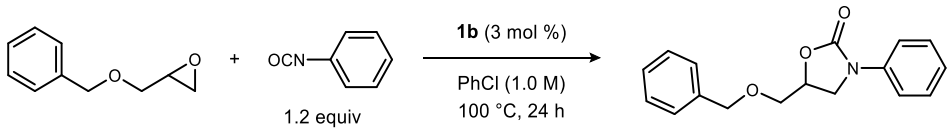


5-((4-Methoxyphenoxy)methyl)-3-phenyloxazolin-2-one (4n). Prepared according to the general procedure using epoxide **2c** (108.1 mg, 0.60 mmol), isocyanate **3b** (78 µL, 0.72 mmol), and TAPS **1b** (6.2 mg, 12 µmol). Flash column chromatography (SiO_2, 100% $CHCl_3$) yielded a white solid (163.5 mg, 91%). R_f = 0.2 (100% $CHCl_3$) visualized with $KMnO_4$; Mp 149-150 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.55 (m, 2H), 7.42-7.35 (m, 2H), 7.17-7.12 (m, 1H), 6.87- 6.80 (m, 4H), 4.94 (dddd, *J* = 8.7, 6.0, 5.1, 4.2 Hz, 1H), 4.18 (dd, *J* = 10.2, 4.2 Hz, 1H), 4.17 (dd, *J* = 9.0, 8.7 Hz, 1H), 4.14 (dd, *J* = 10.2, 5.1 Hz, 1H), 4.05 (dd, *J* = 9.0, 6.0 Hz, 1H),

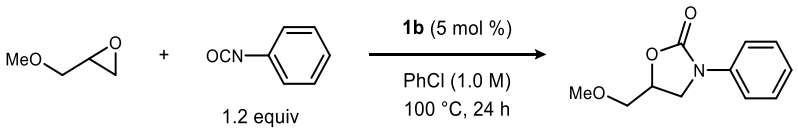
3.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5 (C), 154.4 (C), 152.2 (C), 138.1 (C), 129.1 (CH), 124.1 (CH), 118.3 (CH), 115.7 (CH), 114.7 (CH), 70.5 (CH), 68.8 (CH_2), 55.7 (CH_3), 47.3 (CH_2); IR (KBr) 1738, 1507, 1409, 1245, 1143, 1093, 1047, 830, 752 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{17}H_{17}NNaO_4$ $[M+Na]^+$ 322.1050, found 322.1056.



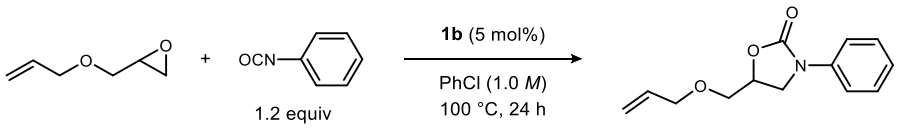
(2-Oxo-3-phenyloxazolidin-5-yl)methyl benzoate (4o). Prepared according to the general procedure using epoxide **2d** (106.9 mg, 0.60 mmol), isocyanate **3b** (78 µL, 0.72 mmol), and TAPS **1b** (6.0 mg, 12 µmol). Flash column chromatography (SiO_2, 20-25% hexane/CH_2Cl_2) and crystallization ($CHCl_3$/hexane = 0.5/1.0 mL) yielded a white solid (119.5 mg, 68%). R_f = 0.4 (33% EtOAc/hexane) visualized with $KMnO_4$; Mp 117-119 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03-7.99 (m, 2H), 7.60-7.53 (m, 3H), 7.44-7.35 (m, 4H), 7.18-7.13 (m, 1H), 5.01 (dddd, *J* = 9.0, 6.0, 4.8, 3.9 Hz, 1H), 4.63 (dd, *J* = 12.3, 3.9 Hz, 1H), 4.55 (dd, *J* = 12.3, 4.8 Hz, 1H), 4.23 (t, *J* = 9.0 Hz, 1H), 3.94 (dd, *J* = 9.0, 6.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0 (C), 154.2 (C), 137.9 (C), 133.4 (CH), 129.7 (C), 129.04 (CH), 128.99 (C), 128.4 (CH), 124.2 (CH), 118.2 (CH), 70.1 (CH), 65.0 (CH_2), 47.1 (CH_2); IR (KBr) 1745, 1711, 1598, 1496, 1420, 1278, 1232, 1116, 759, 713 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{17}H_{15}NNaO_4$ $[M+Na]^+$ 320.0893, found 320.0887.



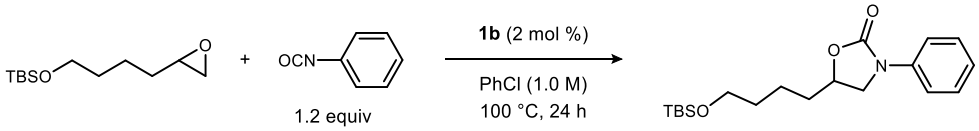
5-(Benzyloxymethyl)-3-phenyloxazolidin-2-one (4p).[8] Prepared according to the general procedure using epoxide **2e** (98.9 mg, 0.60 mmol), isocyanate **3b** (78 µL, 0.72 mmol), and TAPS **1b** (9.1 mg, 18 µmol). Flash column chromatography (SiO_2, 100% $CHCl_3$, 20% EtOAc/hexane) yielded a colorless oil (153.2 mg, 90%). R_f = 0.2 ($CHCl_3$) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.51 (m, 2H), 7.40-7.25 (m, 7H), 7.15-7.10 (m, 1H), 4.76 (ddt, *J* = 9.0, 6.3, 4.5 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.04 (dd, *J* = 9.0, 8.7 Hz, 1H), 3.91 (dd, *J* = 8.7, 6.3 Hz, 1H), 3.71 (d, *J* = 4.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154. 6 (C), 138.2 (C), 137.3 (C), 129.0 (CH), 128.5 (CH), 128.0 (CH), 127.7 (CH), 124.0 (CH), 118.2 (CH), 73.7 (CH_2), 71.2 (CH), 70.0 (CH_2), 47.3 (CH_2); IR (film) 1752, 1599, 1500, 1411, 1311, 1225, 1133, 756, 695. Characterization data matched the literature.



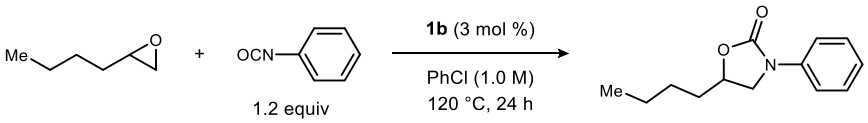
5-(Methoxymethyl)-3-phenyloxazolidin-2-one (4q).[5b] Prepared according to the general procedure using epoxide **2f** (52.9 mg, 0.60 mmol), isocyanate **3b** (78 µL, 0.72 mmol), and TAPS **1b** (14.9 mg, 30 µmol). Flash column chromatography (SiO_2, 10-20% EtOAc/hexane) yielded a colorless oil (116.1 mg, 92%). R_f = 0.2 (20% EtOAc/hexane) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.51 (m, 2H), 7.40-7.25 (m, 7H), 7.15-7.10 (m, 1H), 4.76 (ddt, *J* = 9.0, 6.3, 4.5 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.04 (dd, *J* = 9.0, 8.7 Hz, 1H), 3.91 (dd, *J* = 8.7, 6.3 Hz, 1H), 3.71 (d, *J* = 4.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154. 6 (C), 138.2 (C), 137.3 (C), 129.0 (CH), 128.5 (CH), 128.0 (CH), 127.7 (CH), 124.0 (CH), 118.2 (CH), 73.7 (CH_2), 71.2 (CH), 70.0 (CH_2), 47.3 (CH_2); IR (film) 1752, 1599, 1500, 1411, 1311, 1225, 1133, 756, 695. Characterization data matched the literature.



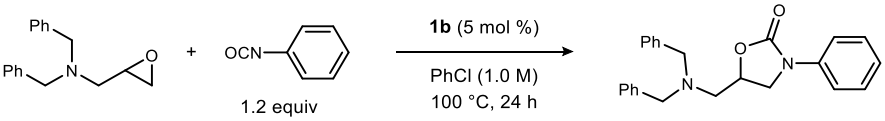
5-(Allyloxymethyl)-3-phenyloxazolidin-2-one (4r).[5b] Prepared according to the general procedure using epoxide **2g** (68.6 mg, 0.60 mmol), isocyanate **3b** (78 µL, 0.72 mmol), and TAPS **1b** (15.3 mg, 30 µmol). Flash column chromatography (SiO_2, 100% $CHCl_3$, 25% EtOAc/hexane) yielded a colorless oil (128.3 mg, 91%). R_f = 0.2 ($CHCl_3$) visualized with Anis; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58-7.53 (m, 2H), 7.41-7.34 (m, 2H), 7.16-7.11 (m, 1H), 5.89 (ddt, *J* = 17.4, 10.4, 5.7 Hz, 1H), 5.28 (dq, *J* = 17.4, 1.5 Hz, 1H), 5.21 (dq, *J* = 10.5, 1.5 Hz, 1H), 4.77 (dddd, *J* = 8.7, 6.3, 4.8, 4.5 Hz, 1H), 4.08 (dt, *J* = 5.7, 1.5 Hz, 2H), 4.07 (t, *J* = 8.7 Hz, 1H), 3.94 (dd, *J* = 8.7, 6.3 Hz, 1H), 3.72 (dd, *J* = 10.5, 4.5 Hz, 1H), 3.68 (dd, *J* = 10.5, 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5 (C), 138.2 (C), 133.9 (CH), 128.9 (CH), 123.9 (CH), 118.1 (CH), 117.6 (CH_2), 72.5 (CH_2), 71.2 (CH), 69.9 (CH_2), 47.1 (CH_2). Characterization data matched the literature.



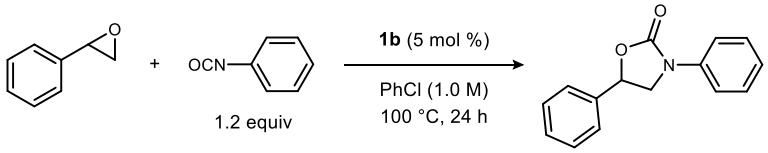
5-(4-(*tert*-Butyldimethylsilyloxy)butyl-3-phenyloxazolidin-2-one (4s). Prepared according to the general procedure using epoxide **2h** (138.6 mg, 0.60 mmol), isocyanate **3b** (78 µL, 0.72 mmol), and TAPS **1b** (6.2 mg, 12 µmol). Flash column chromatography (SiO_2, 5-10% EtOAc/hexane) yielded a white solid (160.6 mg, 77%). R_f = 0.3 (10% EtOAc/hexane) visualized with Anis; Mp 51-52 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.51 (m, 2H), 7.40-7.34 (m, 2H), 7.16-7.10 (m, 1H), 4.69-4.60 (m, 1H), 4.08 (t, *J* = 8.7 Hz, 1H), 3.69-3.62 (m, 3H), 1.95-1.70 (m, 2H), 1.65-1.47 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9 (C), 138.4 (C), 129.0 (CH), 123.9 (CH), 118.2 (CH), 73.0 (CH), 62.7 (CH_2), 50.5 (CH_2), 34.8 (CH_2), 32.3 (CH_2), 25.9 (CH_3), 21.1 (CH_2), 18.3 (C), 5.31 (CH_3); IR (KBr) 2930, 1735, 1602, 1507, 1417, 1092, 835, 754, 690 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{19}H_{31}NNaO_3Si$ $[M+Na]^+$ 372.1965, found 372.1976.



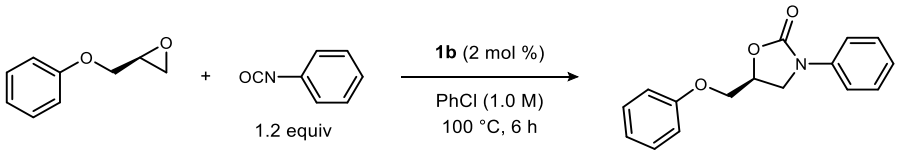
5-Butyl-3-phenyloxazolidin-2-one (4t).[5b] Prepared according to the general procedure using epoxide **2i** (60.1 mg, 0.60 mmol), isocyanate **3b** (78 µL, 0.72 mmol), and TAPS **1b** (8.9 mg, 18 µmol). Flash column chromatography (SiO_2, 10-20% EtOAc/hexane) yielded a white solid (115.2 mg, 88%). R_f = 0.5 (20% EtOAc/hexane) visualized with Anis; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.51 (m, 2H), 7.40-7.33 (m, 2H), 7.15-7.10 (m, 1H), 4.63 (tdd, *J* = 8.4, 7.2, 5.7 Hz, 1H), 4.07 (t, *J* = 8.7 Hz, 1H), 3.65 (dd, *J* = 8.7, 7.2 Hz, 1H), 1.92-1.67 (m, 2H), 1.59-1.33 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9 (C), 138.4 (C), 129.0 (CH), 123.9 (CH), 118.1 (CH), 73.1 (CH), 50.5 (CH_2), 34.7 (CH_2), 26.6 (CH_2), 22.3 (CH_2), 13.9 (CH_3). Characterization data matched the literature.



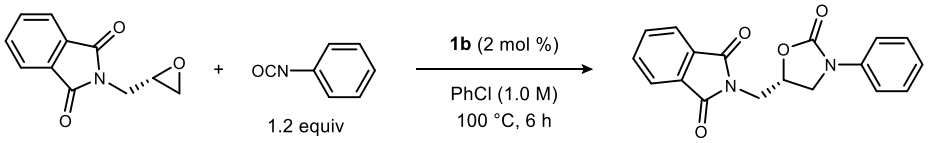
5-((Dibenzylamino)methyl)-3-phenyloxazolidin-2-one (4u). Prepared according to the general procedure using epoxide **2j** (152.0 mg, 0.60 mmol), isocyanate **3b** (78 µL, 0.72 mmol), and TAPS **1b** (14.9 mg, 30 µmol). Flash column chromatography (SiO_2, 10% EtOAc/hexane) yielded a white solid (173.1 mg, 77%). R_f = 0.4 (20% EtOAc/hexane) visualized with I_2; Mp 86-87 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.21 (m, 14H), 7.14-7.08 (m, 1H), 4.56 (dtd, *J* = 8.7, 6.6, 5.4 Hz, 1H), 3.79 (t, *J* = 8.7 Hz, 1H), 3.75 (d, *J* = 13.5 Hz, 2H), 3.65 (d, *J* = 13.5 Hz, 2H), 3.50 (dd, *J* = 8.7, 6.6 Hz, 1H), 2.87 (dd, *J* = 13.5, 5.4 Hz, 1H), 2.81 (dd, *J* = 13.5, 6.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7 (C), 138.8 (C), 138.2 (C), 129.0 (CH), 128.9 (CH), 128.4 (CH), 127.4 (CH), 123.9 (CH), 118.3 (CH), 71.3 (CH), 59.9 (CH_2), 56.3 (CH_2), 48.7 (CH_2); IR (KBr) 2895, 2812, 1752, 1598, 1495, 1409, 1323, 1218, 1138, 1050, 757, 703 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{24}N_2NaO_2$ $[M+Na]^+$ 395.1730, found 395.1729.



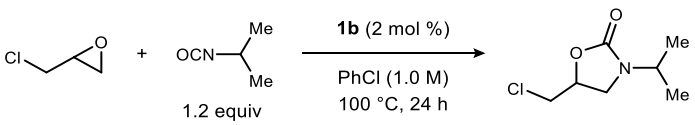
3,5-Diphenyloxazolidin-2-one (4v).[5] Prepared according to the general procedure using epoxide **2k** (72.2 mg, 0.60 mmol), isocyanate **3b** (78 µL, 0.72 mmol), and TAPS **1b** (15.1 mg, 30 µmol). Flash column chromatography (SiO_2, 10% EtOAc/hexane) yielded a white solid (70.3 mg, 49%). R_f = 0.5 (20% EtOAc/hexane) visualized with Anis; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.51 (m, 2H), 7.42-7.33 (m, 7H), 7.16-7.10 (m, 1H), 5.60 (dd, *J* = 8.4, 7.8 Hz, 1H), 4.34 (t, *J* = 8.7 Hz, 1H), 3.92 (dd, *J* = 8.7, 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6 (C), 138.08 (C), 138.05 (C), 129.02 (CH), 128.95 (CH), 125.6 (CH), 124.1 (CH), 118.2 (2CH), 74.0 (CH), 52.6 (CH_2). Characterization data matched the literature.



(*S*)-5-(Phenoxymethyl)-3-phenyloxazolin-2-one ((*S*)-4b). Prepared according to the general procedure using epoxide (*S*)-**2a** (90.2 mg, 0.60 mmol), isocyanate **3b** (78 µL, 0.72 mmol), and TAPS **1b** (6.4 mg, 12 µmol). Flash column chromatography (SiO_2, 100% $CHCl_3$, 30% EtOAc/hexane) yielded a white solid (145.2 mg, 89%). The product was determined to be 99% ee by chiral HPLC analysis (Chiralpak IC, 10% EtOH/hexane, 0.5 mL/min, t_r(*minor*) = 38.8 min, t_r(*major*) = 42.6 min, 254 nm, 35 °C); $[\alpha]_D^{26}$ +53.0 (*c* 1.0, $CHCl_3$). The absolute configuration was determined by analogy with (*S*)-**4w**.

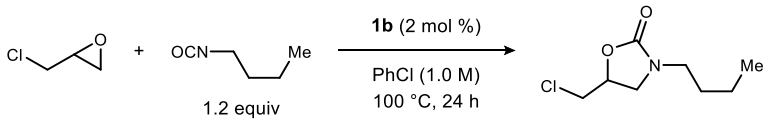


(*S*)-2-((2-Oxo-3-phenyloxazolidin-5-yl)methyl)isoindoline-1,3-dione ((*S*)-4w).[9] To a flame-dried test tube equipped with a stir bar was added epoxide (*S*)-**2l** (121.9 mg, 0.60 mmol), TAPS **1b** (5.9 mg, 12 µmol, 2 mol%), PhCl (1.0 M), and isocyanate **3b** (78 µL, 0.72 mmol). The reaction mixture was stirred at 100 °C for 6 h under argon atmosphere, cooled to rt, and then concentrated. The crude was triturated with EtOH (6.5 mL) to give a white solid (145.2 mg, 87%). The product was determined to be 99% ee by chiral HPLC analysis (Chiralpak IC, 20% EtOH/hexane, 0.5 mL/min, t_r(*minor*) = 49.1 min, t_r(*major*) = 53.4 min, 220 nm, 35 °C); $[\alpha]_D^{27}$ -66.3 (*c* 0.1, $CHCl_3$). R_f = 0.2 (33% EtOAc/hexane) visualized with Anis; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.86 (m, 2H), 7.78-7.74 (m, 2H), 7.53-7.51 (m, 2H), 7.39-7.35 (m, 2H), 7.16-7.13 (m, 1H), 4.99 (ddt, *J* = 9.0, 7.0, 6.0 Hz, 1H), 4.16 (dd, *J* = 14.0, 7.0 Hz, 1H), 4.14 (t, *J* = 9.0 Hz, 1H), 3.98 (dd, *J* = 14.0, 6.0 Hz, 1H), 3.92 (dd, *J* = 9.0, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0 (C), 153.9 (C), 137.9 (C), 134.4 (CH), 131.7 (C), 129.1 (CH), 124.3 (CH), 123.7 (CH), 118.4 (CH), 69.6 (CH), 48.4 (CH_2), 40.8 (CH_2). Characterization data matched the literature. The absolute configuration was determined by X-ray crystallographic analysis after derivatization to (*S*)-**4y**.

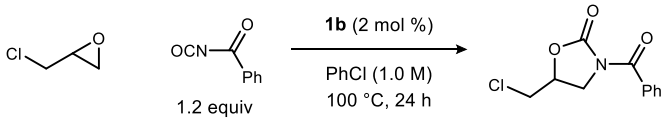


5-(Chloromethyl)-3-isopropyloxazolidin-2-one (6a). Prepared according to the general procedure using epoxide **2b** (55.5 mg, 0.60 mmol), isocyanate **5a** (71 µL, 0.72 mmol), and TAPS **1b** (6.0 mg, 12 µmol). The crude material was treated with K_2CO_3 (166 mg) in MeOH (0.6 mL) at rt for 4 h, and the mixture was filtered through Celite, and then concentrated. Flash column chromatography (SiO_2, 25% EtOAc/hexane, 100% $CHCl_3$) yielded a colorless oil (85.1 mg, 80%). R_f = 0.2 (50% EtOAc/hexane) visualized with $KMnO_4$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.68 (dddd, *J* = 8.7, 6.0, 5.7, 4.2 Hz, 1H), 4.07 (sept, *J* = 6.9 Hz, 1H), 3.68 (dd, *J* = 11.7, 4.2 Hz, 1H), 3.62 (dd, *J* = 11.7, 6.0 Hz, 1H), 3.60 (dd, *J* = 9.0, 8.7 Hz, 1H), 3.38 (dd, *J* = 9.0, 5.7 Hz,

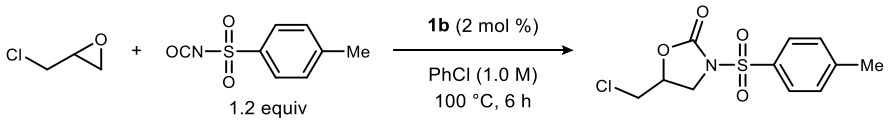
1H), 1.16 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2 (C), 71.3 (CH), 44.84 (CH_2), 44.81 (CH), 42.6 (CH_2), 19.6 (CH_3), 19.5 (CH_3); IR (KBr) 2977, 1746, 1437, 1257, 1038, 759 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_7H_{12}ClNNaO_2$ $[M+Na]^+$ 200.0449, found 200.0438.



3-Butyl-5-(chloromethyl)oxazolidin-2-one (6b). Prepared according to the general procedure using epoxide **2b** (55.5 mg, 0.60 mmol), isocyanate **5b** (80 µL, 0.72 mmol), and TAPS **1b** (6.0 mg, 12 µmol). The crude material was treated with K_2CO_3 (166 mg) in MeOH (0.6 mL) at rt for 4 h, and the mixture was filtered through Celite, and then concentrated. Flash column chromatography (SiO_2, 20% EtOAc/hexane) yielded a colorless oil (83.5 mg, 73%). R_f = 0.3 (30% EtOAc/hexane) visualized with $KMnO_4$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.71 (dddd, *J* = 9.0, 6.6, 5.7, 4.2 Hz, 1H), 3.71 (dd, *J* = 11.4, 4.2 Hz, 1H), 3.68 (t, *J* = 9.0 Hz, 1H), 3.64 (dd, *J* = 11.4, 6.6 Hz, 1H), 3.46 (dd, *J* = 9.0, 5.7 Hz, 1H), 3.34-3.20 (m, 2H), 1.60-1.50 (m, 2H), 1.42-1.29 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0 (C), 71.2 (CH), 47.5 (CH_2), 44.7 (CH_2), 43.8 (CH_2), 29.3 (CH_2), 19.8 (CH_2), 13.6 (CH_3); IR (KBr) 2961, 1752, 1449, 1266, 1046 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_8H_{15}ClNO_2$ $[M+H]^+$ 192.0786, found 192.0791.

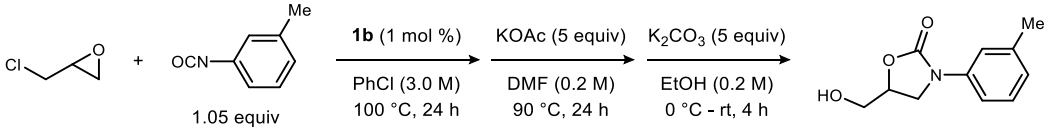


3-Benzoyl-5-(chloromethyl)oxazolidin-2-one (6c).[10] Prepared according to the general procedure using epoxide **2b** (55.5 mg, 0.60 mmol), isocyanate **5c** (90.5 mg, 0.72 mmol), and TAPS **1b** (6.0 mg, 12 µmol). Flash column chromatography (SiO_2, 10% EtOAc/hexane) yielded a white solid (114.1 mg, 79%). R_f = 0.3 (30% EtOAc/hexane) visualized with $KMnO_4$; Mp 96-98 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.63 (m, 2H), 7.58-7.52 (m, 1H), 7.46-7.40 (m, 2H), 4.90 (dddd, *J* = 9.0, 5.7, 5.1, 3.9 Hz, 1H), 4.28 (dd, *J* = 11.4, 9.0 Hz, 1H), 4.08 (dd, *J* = 11.4, 5.7 Hz, 1H), 3.82 (dd, *J* = 12.0, 5.1 Hz, 1H), 3.75 (dd, *J* = 12.0, 3.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4 (C), 152.1 (C), 132.5 (CH), 132.4 (C), 129.0 (CH), 127.9 (CH), 71.7 (CH), 46.4 (CH_2), 44.6 (CH_2); IR (KBr) 1793, 1678, 1325, 1208, 716 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{11}H_{10}ClNaNO_3$ $[M+Na]^+$ 262.0241, found 262.0234. Characterization data matched the literature.

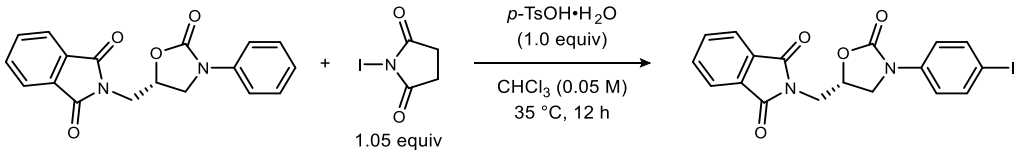


5-(Chloromethyl)-3-tosyloxazolidin-2-one (6d).[11] Prepared according to the general procedure using epoxide **2b** (55.7 mg, 0.60 mmol), isocyanate **5d** (110 µL, 0.72 mmol), and TAPS **1b** (6.0 mg, 12 µmol). Flash column chromatography (SiO_2, 20% EtOAc/hexane) yielded a white solid (168.3 mg, 97%). R_f = 0.2 (20% EtOAc/hexane) visualized with $KMnO_4$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 4.79 (dddd, *J* = 8.7, 5.7, 5.1, 4.2 Hz, 1H), 4.18 (dd, *J* = 9.6, 8.7 Hz, 1H), 3.96 (dd, *J* = 9.6, 5.7 Hz, 1H), 3.70 (dd, *J* = 12.0, 5.1 Hz), 3.64 (dd, *J* = 12.0, 4.2 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.9 (C), 145.9 (C), 133.8 (C), 129.9 (CH), 128.2 (CH), 71.7 (CH), 46.9 (CH_2), 44.1 (CH_2), 21.7 (CH_3). Characterization data matched the literature.

Synthetic applications



5-(Hydroxymethyl)-3-*m*-tolyloxazolidin-2-one (4x).[12] (i) To a round-bottom flask equipped with a stir bar was added epoxide **2b** (1.11 g, 12.0 mmol), TAPS **1b** (0.060 g, 0.12 mmol), PhCl (4.0 mL), and isocyanate **3h** (1.62 mL, 12.6 mmol). The reaction mixture was stirred at 100 °C for 24 h under argon atmosphere, cooled to rt, and then concentrated. Short column chromatography (SiO_2: 20% EtOAc/hexane) yielded oxazolidinone **4k** in nearly pure form. (ii) The oxazolidinone was dissolved in DMF (60 mL), and KOAc (5.89 g, 60.0 mmol) was added to the solution. After stirring the mixture at 90 °C for 24 h, H_2O (30 mL) and Et_2O (50 mL) were added, and then the aqueous layer was extracted with Et_2O (x 4). The organic layers were combined, washed with H_2O and brine, dried over Na_2SO_4 and concentrated. The material was employed for the next step without further purification. (iii) The material was dissolved in EtOH (60 mL), and K_2CO_3 (8.29 g, 60.0 mmol) was added to the solution at 0 °C. After stirring the mixture at 0 °C for 4 h, H_2O (60 mL) and EtOAc (50 mL) were added, and then the aqueous layer was extracted with EtOAc (x 2). The organic layers were combined, washed with H_2O and brine, dried over Na_2SO_4 and concentrated. Short column chromatography (SiO_2: 50% EtOAc/hexane) yielded oxazolidinone **4x** as a white solid (1.43 g, 58%). R_f = 0.2 (50% EtOAc/hexane) visualized with $KMnO_4$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.33-7.22 (m, 2H), 6.96 (d, *J* = 7.5 Hz, 1H), 4.76-4.68 (m, 1H), 4.05-3.92 (m, 3H), 3.75 (m, 1H), 2.66 (t, *J* = 6.6 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8 (C), 139.0 (C), 138.0 (C), 128.9 (CH), 125.0 (CH), 119.1 (CH), 115.5 (CH), 72.8 (CH), 62.8 (CH_2), 46.5 (CH_2), 21.6 (CH_3). Characterization data matched the literature.



(*S*)-2-((3-(4-Iodophenyl)-2-oxooxazolidin-5-yl)methyl)isoindoline-1,3-dione (4y). To a round-bottom flask equipped with a stir bar was added oxazolidinone (*S*)-**4w** (99% ee, 96.8 mg, 300 µmol), *p*-TsOH•H_2O (57.3 mg, 300 µmol), and $CHCl_3$ (6.0 mL). *N*-Iodosuccinimide (71.1 mg, 315 µmol) was added, and the reaction mixture was then stirred at 35 °C for 12 h. The mixture was treated with aq Na_2SO_3 (until the pink solution turned colorless), and the aqueous layer was extracted with $CHCl_3$ (x 2). The organic layers were combined, washed with H_2O (x 3), dried over Na_2SO_4 and concentrated. The crude material was washed with Et_2O (1 mL) and hexane (15 mL) to give a white solid (130.6 mg, 97%). The product was determined to be 99% ee by chiral HPLC analysis (Chiralpak IC, 20% EtOH/hexane, 0.5 mL/min, t_r(*major*) = 53.3 min, t_r(*minor*) = 48.4 min, 220 nm, 35 °C); $[\alpha]_D^{18}$ -58.8 (*c* 0.1, $CHCl_3$). R_f = 0.15 (100% $CHCl_3$) visualized with I_2; Mp 200-201 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92-7.86 (m, 2H), 7.80-7.74 (m, 2H), 7.69-7.64 (m, 2H), 7.33-7.28 (m, 2H), 4.99 (ddt, *J* = 9.0, 6.6, 6.0 Hz, 1H), 4.15 (dd, *J* = 14.1, 6.6 Hz, 1H), 4.10 (t, *J* = 9.0 Hz, 1H), 3.98 (dd, *J* = 14.1, 6.0 Hz, 1H), 3.89 (dd, *J* = 9.0, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0 (C), 153.6 (C), 138.0 (CH), 137.8 (C), 134.5 (CH), 131.7 (C), 123.7 (CH), 120.1 (CH), 87.8 (C), 69.6 (CH), 48.2 (CH_2), 40.7 (CH_2); IR (KBr) 1760, 1717, 1491, 1396, 1307, 1213, 1128, 1013, 966, 822, 738, 719 cm^{-1}; HRMS (ESI) Exact mass calcd for $C_{18}H_{13}N_2NaO_4$ $[M+Na]^+$ 470.9812, found 470.9799.

The absolute configuration was determined to be (*S*) by X-ray crystallographic analysis (see, CIF), and a crystal of **4y** was grown from $CHCl_3$ under hexane atmosphere.

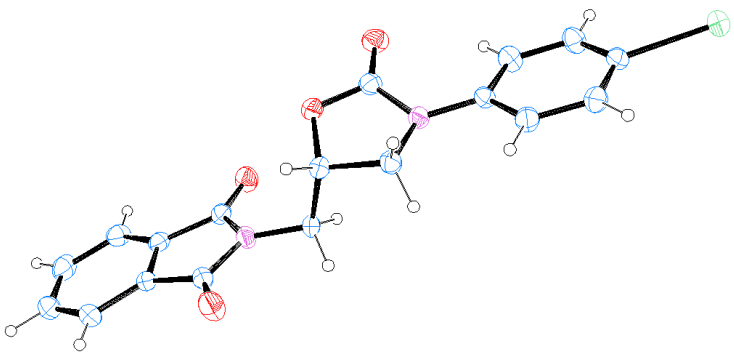


Figure S2. ORTEP drawing of (*S*)-**4y** (30% probability ellipsoids).

Mechanistic studies

^{1}H NMR experiments in $CDCl_3$ at 25 °C to monitor the behavior of the catalysts were conducted (Figure S3). When TAPS **1b** was mixed with a stoichiometric amount of epoxide **2i**, the Ar-H protons on the cresol moiety significantly shifted upfield. It should be emphasized that iodohydrin **11** was observed within 10 minutes upon the addition of **2i**. At the period of 60 minutes, the aromatic protons gave sharp signals, indicating the generation of the corresponding ylide **10**.

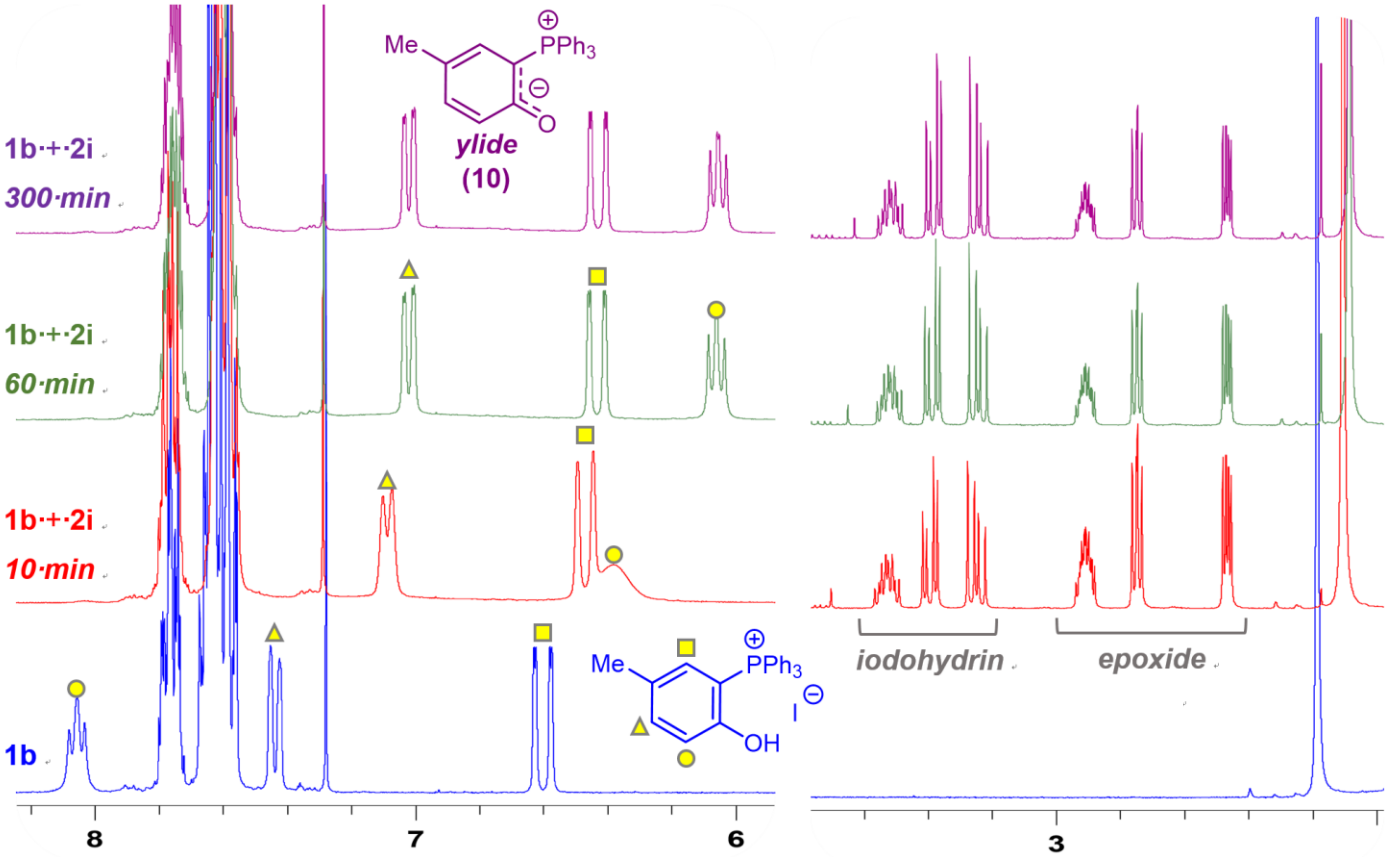
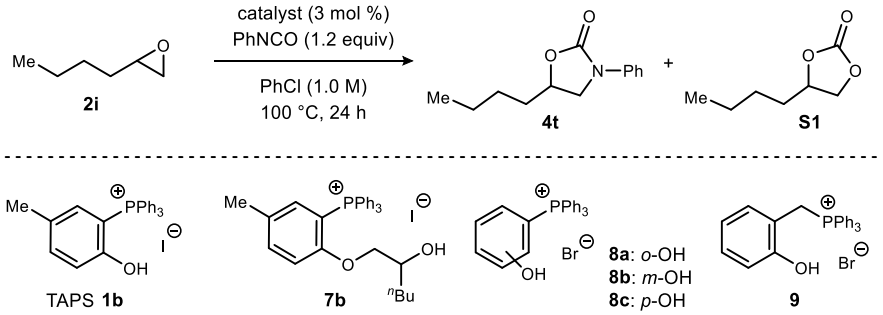


Figure S3. ^{1}H NMR spectra recorded in $CDCl_3$ (the range of 3.8-5.9 ppm were omitted).

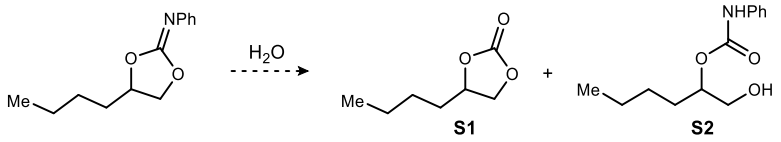
***Evaluation of TAPS catalysis for [3+2] coupling reaction in Table 3*:**

Table S1. Screening of catalysts[a]

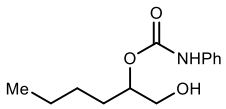


entry	catalyst	conv. (%)[a]	**4t** (%)[a]	**S1** (%)[a]
1	TAPS **1b**	>99	74	26
2	**7b**	28	24	3
3	**8a**	80	44	32
4	**8b**	54	40	10
5	**8c**	15	8	4
6	**9**	7	<1	<1

[a]All reactions were carried out on a 0.60 mmol scale. [b]Determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard

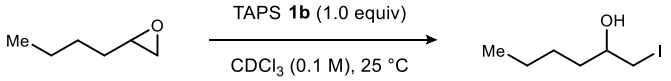


The reaction using epoxide **2i** afforded not only oxazolidinone **4t** but also cyclic carbonate **S1**. This carbonate would be derived from *O*-cyclization followed by hydrolysis (The hydrolysis may arise from a small amount of H_2O in the solution). By-product **S2** (4%) was observed in the case of catalyst **8a**, which is an evidence of hydrolysis of the *O*-cyclized product.



1-Hydroxyhexan-2-yl phenylcarbamate (S2). R_f = 0.2 (20% EtOAc/hexane) visualized with Anis; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.28 (m, 5H), 7.10-7.04 (m, 1H), 6.70 (br s, 1H), 4.90 (tdd, *J* = 7.2, 6.3, 3.0 Hz, 1H), 3.80 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.68 (dd, *J* = 12.0, 6.3 Hz, 1H), 1.69-1.30 (m, 6H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.0 (C), 137.7 (C), 129.1 (CH), 123.6 (CH), 118.8 (CH), 76.9 (CH), 65.2 (CH_2), 30.4 (CH_2), 27.5 (CH_2), 22.6 (CH_2), 13.9 (CH_3); IR (KBr) 3320, 2929, 1706, 1603, 1544, 1444, 1315, 1230, 1063, 753 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{13}H_{19}NNaO_3$ $[M+Na]^+$ 260.1257, found 260.1258.

***Representative procedure for ^{1}H NMR experiments in Figure 2a, 2b, and Scheme 2a*:**



To a NMR sample tube was added epoxide **2i** (5.0 mg, 50 μmol), TAPS **1b** (24.8 mg, 50 μmol), and $CDCl_3$ (500 μL). The mixture was placed in the water-bath at 25 °C. ^{1}H NMR experiments were performed at the period of 10 min, 60 min, and 300 min, and the conversions were estimated based on the integration of epoxide **2i** and iodohydrin **11**.

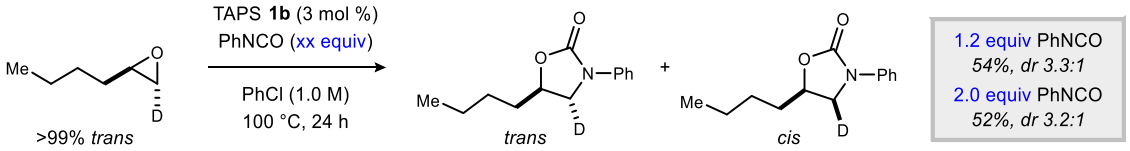
1-Iodohexan-2-ol (11).[13] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.56-3.47 (m, 1H), 3.40 (dd, *J* = 10.2, 3.3 Hz, 1H), 3.23 (dd, *J* = 10.2, 6.9 Hz, 1H), 1.92 (m, 1H), 1.60-1.26 (m, 6H), 0.92 (t, *J* = 6.9 Hz, 3H).

1-Bromohexan-2-ol (11').[14] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.82-3.72 (m, 1H), 3.53 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.40 (dd, *J* = 10.2, 6.6 Hz, 1H), 1.57-1.31 (m, 6H), 0.92 (t, *J* = 7.2 Hz, 3H).

***trans*-1-Deuterio-1,2-hexane oxide (*trans-D*-2i).**[15] A mixture of DIBAL-H (1.02 *M* in hexane, 19.6 mL, 20 mmol) in 1-hexyne (7.0 mL, 60 mmol) was stirred at 45 °C for 4.5 h, and then concentrated under vacuum at 50 °C. D_2O (1.8 mL, 100 mmol) was added at 0 °C dropwise over 1 h, and the mixture was allowed to warm to rt for 12 h. The resulting mixture was passed through a Celite pad and washed with CH_2Cl_2 (20 mL) to afford a solution of *trans*-deuterated 1-hexene in CH_2Cl_2. This solution was employed for the next step without further purification. To the solution obtained was added $NaHCO_3$ (3.4 g, 40 mmol) at rt, and *m*-CPBA (ca. 77%, 5.4 g, 24 mmol) at 0 °C portionwise. After stirring at rt for 12 h, the reaction mixture was treated with aq $Na_2S_2O_3$, and the aqueous layer was extracted with CH_2Cl_2 (x 2). The organic layers were combined, washed with aq $Na_2S_2O_3$ (x 2), NaOH (1%), and H_2O, which was dried over Na_2SO_4 and concentrated. Kugelrohr distillation (125 mmHg, 90 °C) yielded a colorless oil (559 mg, 28% over 2 steps, *97% deuterated*). R_f = 0.5 (20% EtOAc/hexane) visualized with $KMnO_4$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.90 (td, *J* = 5.4, 2.7 Hz, 1H), 2.45 (d, *J* = 2.7 Hz, 1H), 1.56-1.34 (m, 6H), 0.92 (t, *J* = 6.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.3 (CH), 46.8 (t, *J* = 27 Hz, CHD), 32.1 (CH_2), 28.1 (CH_2), 22.5 (CH_2), 14.0 (CH_3). Characterization data matched the literature.

***TAPS-catalyzed [3+2] coupling reaction with the use of trans-deuterated epoxide*:**

trans-Deuterated epoxide, *trans-D*-**2i**, was employed for the [3+2] reaction with phenyl isocyanate (1.2 equiv) to see whether the stereochemistry at the β-carbon is maintained or not. As a result, a mixture of the *trans*/*cis* oxazolidinones (dr 3.3:1) were obtained in both reactions, revealing that halide ion substitution occurs under the optimized conditions. No significant change of the diastereomeric ratio of the product was observed even when 2.0 equivalents of the isocyanate was employed. These results seem to imply that (a) formation of the carbamate intermediate would proceed quickly and (b) the final step, intramolecular cyclization to afford oxazolidinones, would be a rate-determining step.



5-Butyl-4-deuterio-3-phenyloxazolidin-2-one (*D*-4t). To a flame-dried test tube equipped with a stir bar was added *trans-D*-**2i** (>99% *trans*, 30.4 mg, 0.30 mmol), TAPS **1b** (4.5 mg, 9.0 μmol), PhCl (0.6 mL), and phenyl isocyanate (39 μL, 0.36 mmol). The reaction mixture was stirred at 100 °C for 24 h under argon atmosphere, cooled to rt, and then concentrated. Flash column chromatography (SiO_2, 0-10% EtOAc in hexane) to give a white solid (35.6 mg, 54%). The product was determined to be 3.3:1 *trans*/*cis* by ^{1}H NMR analysis. R_f = 0.5 (20% EtOAc/hexane) visualized with $KMnO_4$; Mp 57-58 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.52 (m, 2H), 7.40-7.34 (m, 2H), 7.16-7.10 (m, 1H), 4.66-4.60 (m, 1H), 4.07 (d, *J* = 8.4 Hz, 0.23H, *cis*), 3.64 (d, *J* = 7.2 Hz, 0.77H, *trans*), 1.91-1.67 (m, 2H), 1.57-1.34 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8 (C), 138.3 (C), 128.9 (CH), 123.7 (CH), 118.0 (CH), 72.9 (CH), 50.04 (t, *J* = 23 Hz, CH, *trans*), 50.00 (t, *J* = 21 Hz, CH, *cis*), 34.6 (CH_2, *trans*), 34.5 (CH_2, *cis*), 26.5 (CH_2), 22.2 (CH_2), 13.8 (CH_3); IR (KBr) 2955, 2926, 2856, 1739, 1724, 1602, 1505, 1460, 1412, 1232, 1148, 750 cm^{-1}; HRMS (ESI) Exact mass calcd for $C_{13}H_{16}DNNaO_2$ $[M+Na]^+$ 243.1214, found 243.1213. The relative configuration was determined by a NOESY experiment, see Figure S4.

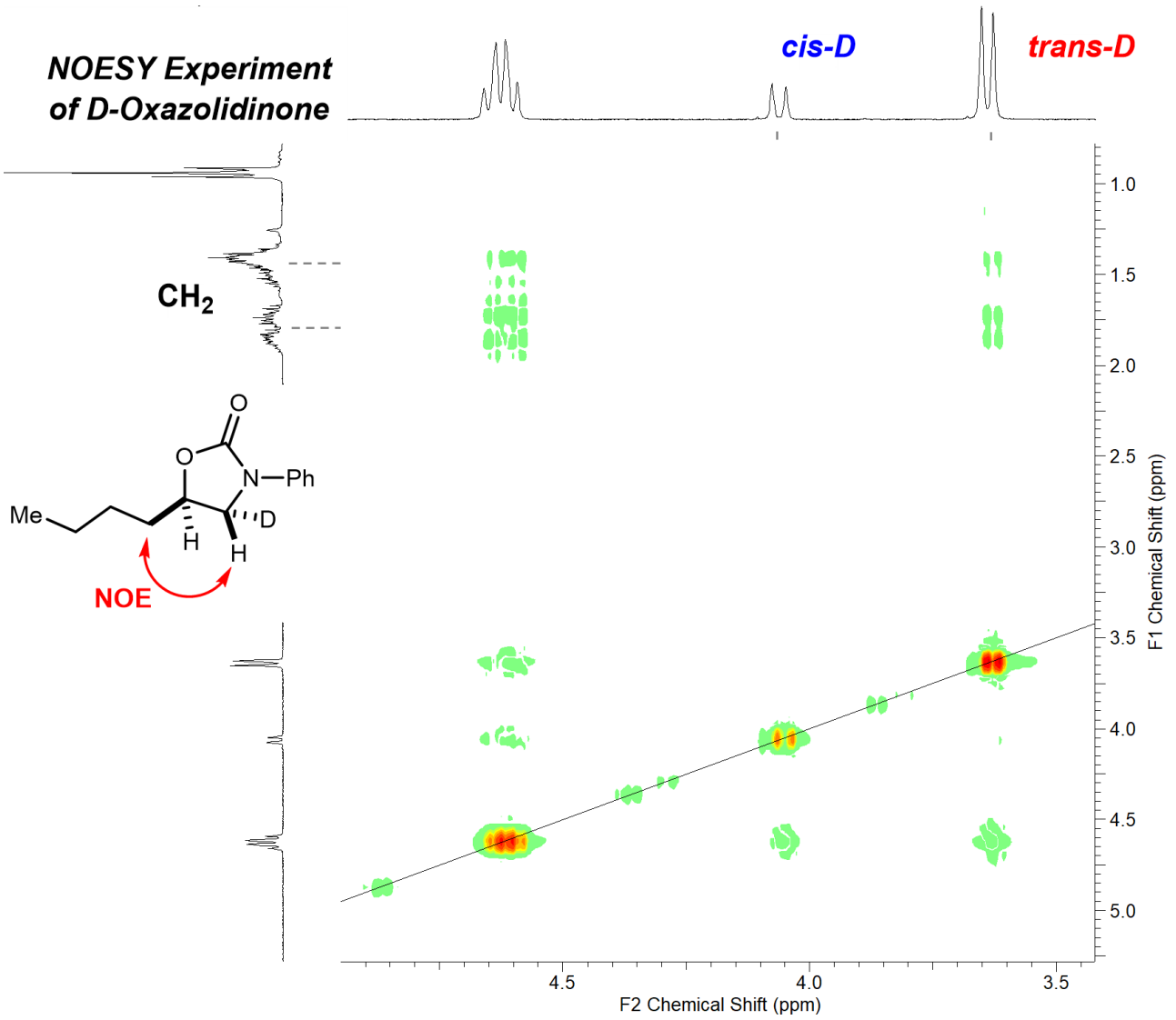
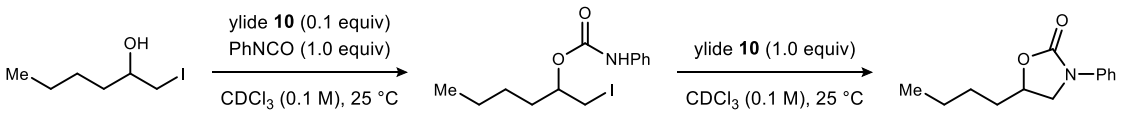


Figure S4. NOESY spectrum of *D*-**4t**.

***Representative procedure for ^{1}H NMR experiments in Scheme 2b and 2c*:**

Phosphonium ylide **10** was prepared according to the literature procedure.[16]

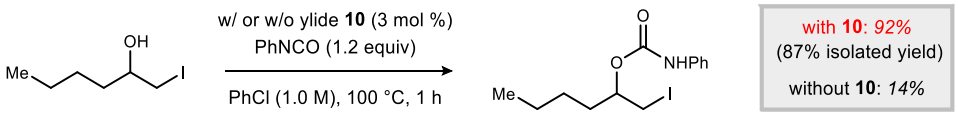


Step 1. To a NMR sample tube was added iodohydrin **11** (11.4 mg, 50 μmol), ylide **10** (1.8 mg, 5.0 μmol), $CDCl_3$ (500 μL), and phenyl isocyanate (5.4 μL, 50 μmol). The mixture was placed in the water-bath at 25 °C for 5 h. CH_2Cl_2 was used as an internal standard to see the conversions.

Step 2. To a NMR sample tube was added carbamate **12** (17.4 mg, 50 μmol), ylide **10** (18.4 mg, 50 μmol), $CDCl_3$ (500 μL). The mixture was placed in the water-bath at 25 °C for 24 h. CH_2Cl_2 was used as an internal standard to see the conversions.

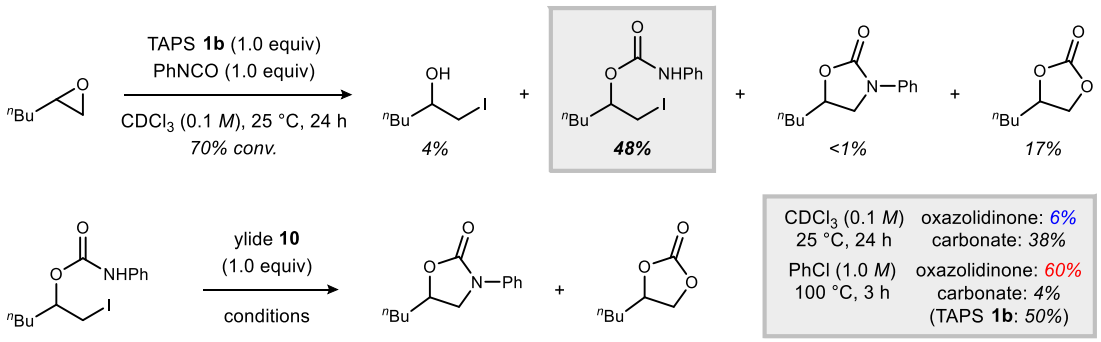
***Mechanistic experiments on carbamate formation and oxazolidinone formation*:**

The reactions in the presence and in the absence of ylide were performed under heating conditions (PhCl, 100 °C). As shown in the scheme below, it is obvious that the ylide effectively catalyzes carbamate formation from iodohydrins and isocyanates. Notably, any cyclized-products including the corresponding oxazolidinone were not observed at all in these reactions.



1-Iodohexan-2-yl phenylcarbamate (12). To a flame-dried test tube equipped with a stir bar was added iodohydrin **11** (136.8 mg, 0.6 mmol), ylide **10** (6.6 mg, 18 μmol), phenyl isocyanate (78.2 μL, 0.72 mmol), and PhCl (0.6 mL). The reaction mixture was stirred at 100 °C for 1 h under argon atmosphere, cooled to rt, and then concentrated. The NMR yield was determined by ^{1}H NMR analysis of the unpurified material using 1,1,2,2-tetrachloroethane as an internal standard (92%). Flash column chromatography (SiO_2: PSQ60B, 10% EtOAc/hexane) yielded the product as a white solid (182.3 mg, 87%). R_f = 0.4 (10% EtOAc/hexane) visualized with Anis; Mp 48-49 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 2H), 7.31 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.74 (br s, 1H), 4.69-4.61 (m, 1H), 3.45 (dd, *J* = 10.8, 4.8 Hz, 1H), 3.33 (dd, *J* = 10.8, 4.8 Hz, 1H), 1.78-1.65 (m, 2H), 1.43-1.26 (m, 4H), 0.92 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7 (C), 137.6 (C), 129.0 (CH), 123.5 (CH), 118.6 (CH), 73.0 (CH), 34.0 (CH_2), 27.1 (CH_2), 22.3 (CH_2), 13.9 (CH_3), 9.1 (CH_2); IR (KBr) 3333, 2951, 2921, 2860, 1709, 1602, 1540, 1445, 1236, 1052, 740, 693 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{13}H_{18}INNaO_2$ $[M+Na]^+$ 370.0274, found 370.0278.

In order to confirm whether carbamate **12** is a key intermediate or not, control experiments shown below were conducted. The reaction of an epoxide (1.0 equiv) and an isocyanate (1.0 equiv) in the presence of TAPS (1.0 equiv) in $CDCl_3$ at 25 °C for 24 h provided the carbamate in 48% NMR yield while only trace amounts of an oxazolidinone was observed. It should be noted that a cyclic carbonate was obtained around ambient temperature presumably due to *O*-cyclization. Moreover, carbamate **12** was reacted with a stoichiometric ylide at 100 °C, leading to the formation of the corresponding oxazolidinone and TAPS. These results indicated that *O*-cyclization to yield a carbonate would be kinetically favored and *N*-cyclization to yield a oxazolidinone would be thermodynamically favored.



***[1]H NMR analysis of TAPS and ylide*:**

Depending on the ratio of TAPS **1b** and ylide **10**, the chemical shifts of aromatic protons change significantly. The spectra of a X:Y mixture of **1b**/**10** recorded in $CDCl_3$ are shown in Figure S5.

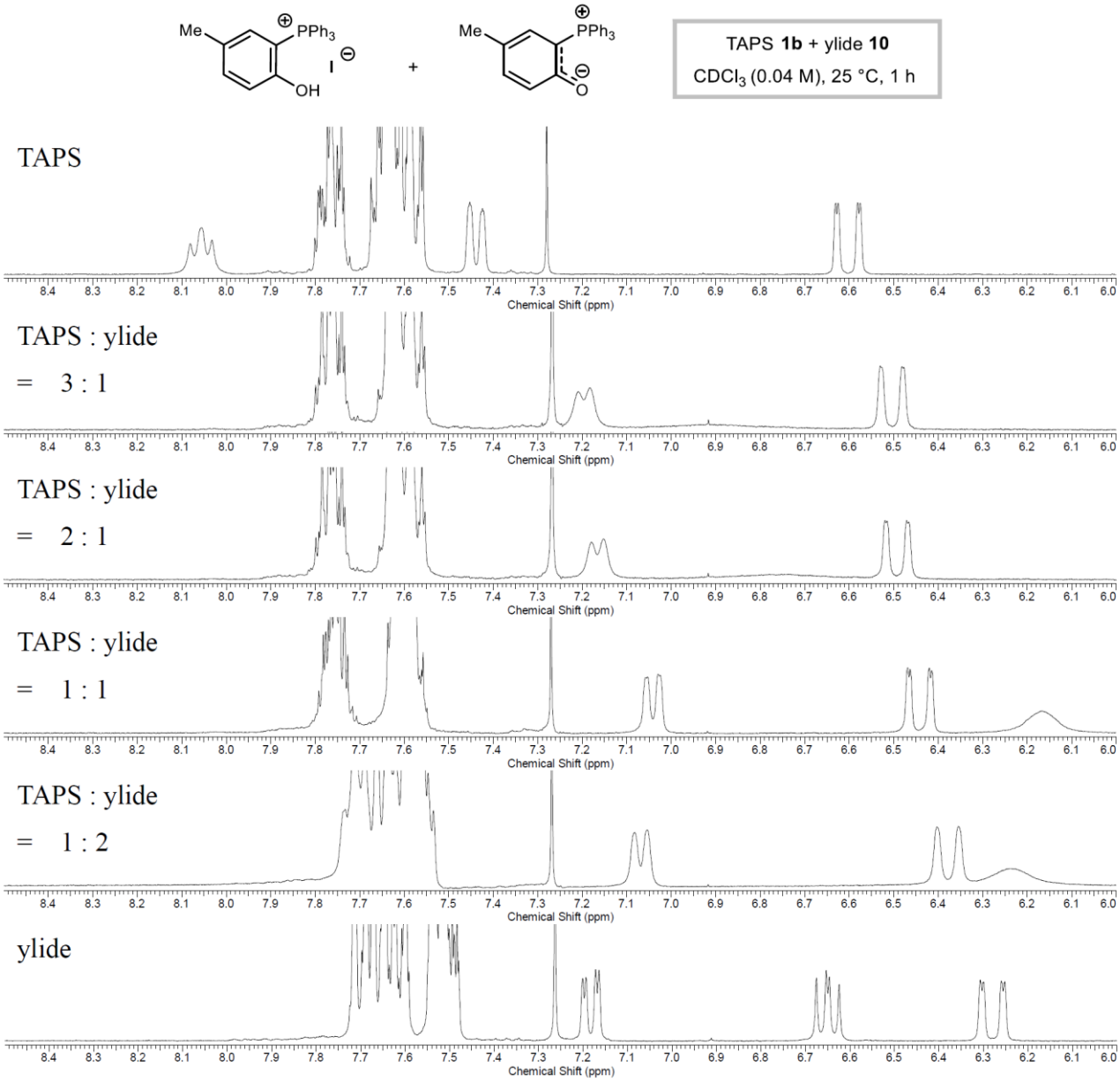
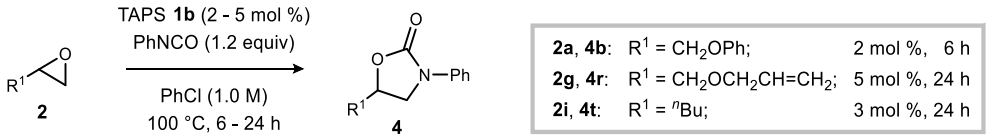


Figure S5. [1]H NMR spectra of a mixture of TAPS **1b** and ylide **10**.

Appendix

For a comparison of catalytic ability, other salts were examined for the [3+2] reaction. Reactivity of epoxides is different depending on the substituent of epoxides (R^1), three epoxides **4b**, **4r**, and **4t** were tested. As results shown in Table S2, TAPS exhibited wide applicability in a variety of epoxides. Although other catalysts were also effective in some cases (e.g. MgI_2 for **4t**), the activity of those salts is very specific.

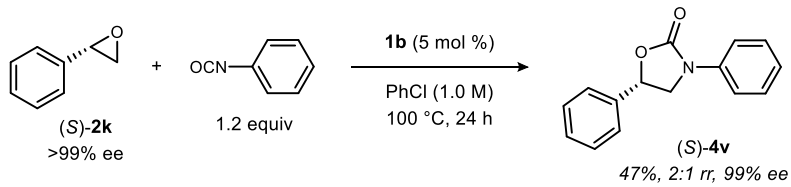
Table S2. TAPS *vs*. other catalysts[a]



catalyst	*conv.* (%)	**4b**	*conv.* (%)	**4r**	*conv.* (%)	**4t**
TAPS **1b**	>99	95	>99	96	>99 (>99)[b]	74 (92)[b]
Ph_4PI	85	83	49	42	23	23
$^nBu_4NI$	87	86	24	22	73	72
$^nBu_4NBr$	64	63	50	48	48	33
$Me_3S(O)I$	<1	0	2	<1	<1	<1
LiBr	4	3	93	85	72	66
MgI_2	4	4	56	13	>99	99

[a]Unless otherwise noted, all reactions were carried out on a 0.60 mmol scale. The conversions and chemical yields were determined by ^{1}H NMR. [b]120 °C

The reaction using enantio-enriched styrene oxide was carried out under the optimized conditions to see the change of the configuration at C5 position (methine carbon) during the oxazolidinone formation. As shown in the scheme below, no significant racemization was observed.



Chiral HPLC analysis (Chiralcel OD-H, 10% ^{i}PrOH/hexane, 0.5 mL/min, t_r(*major*) = 40.0 min, t_r(*minor*) = 45.9 min, 220 nm, 35 °C).[17]

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^{1}H & ^{13}C NMR Spectra of 4a

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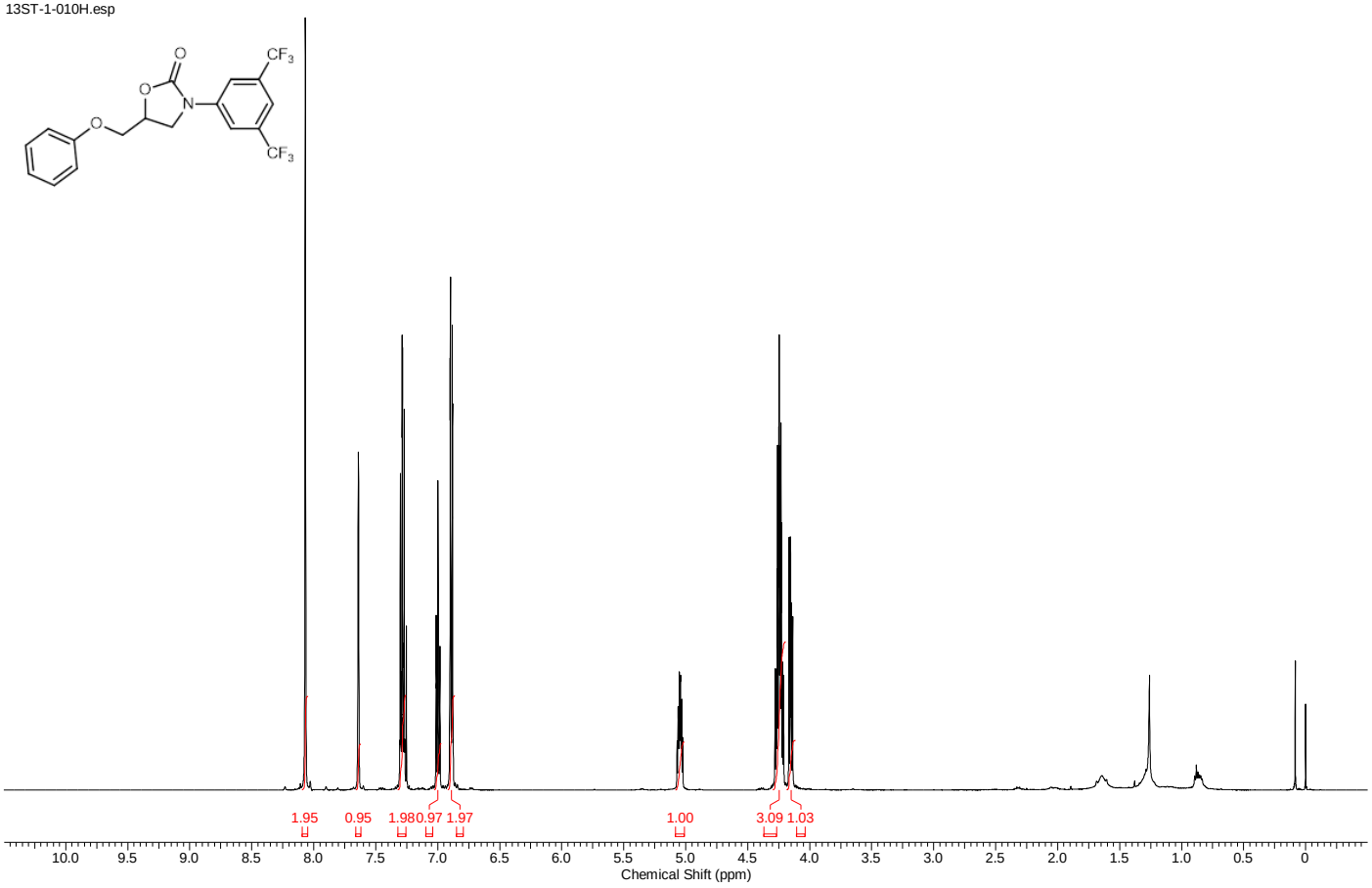

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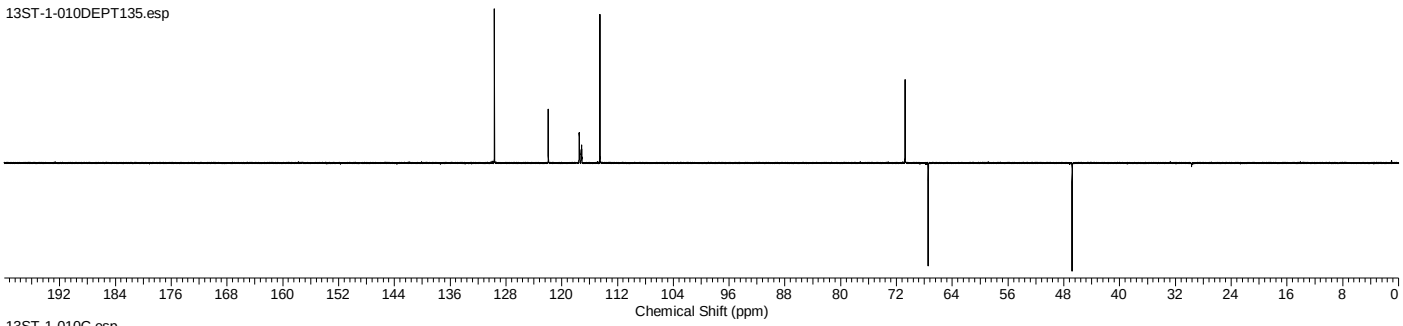

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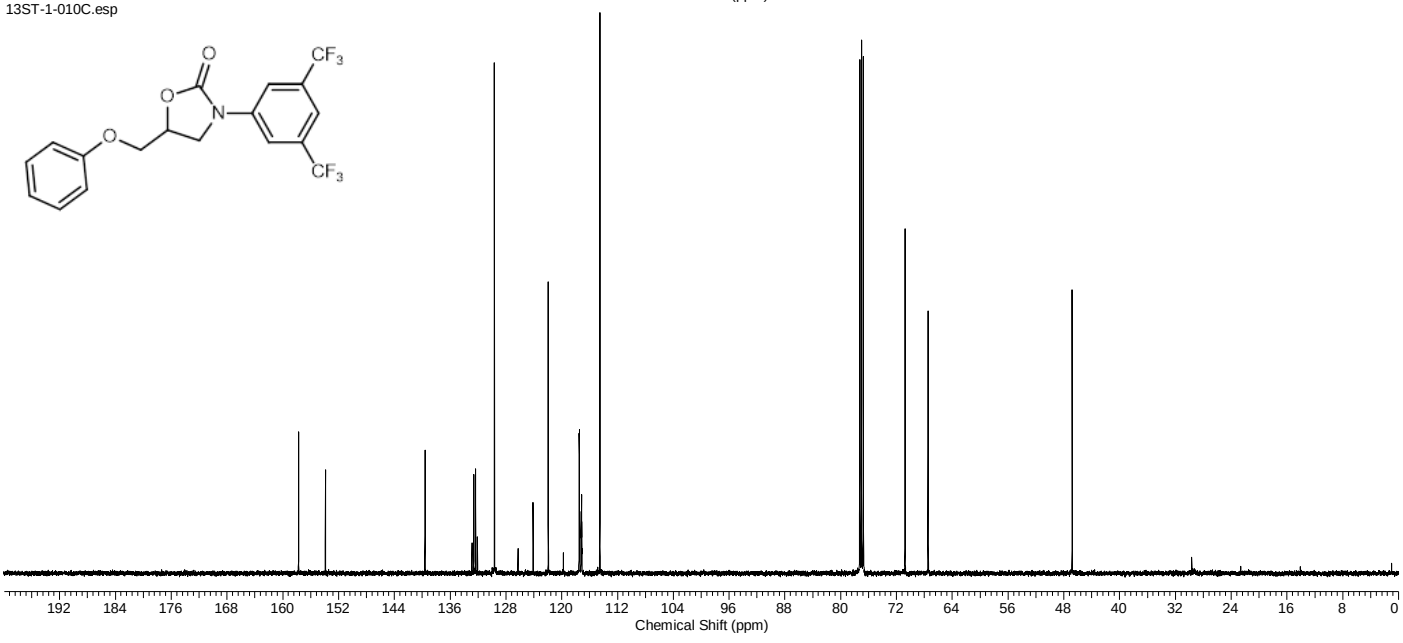

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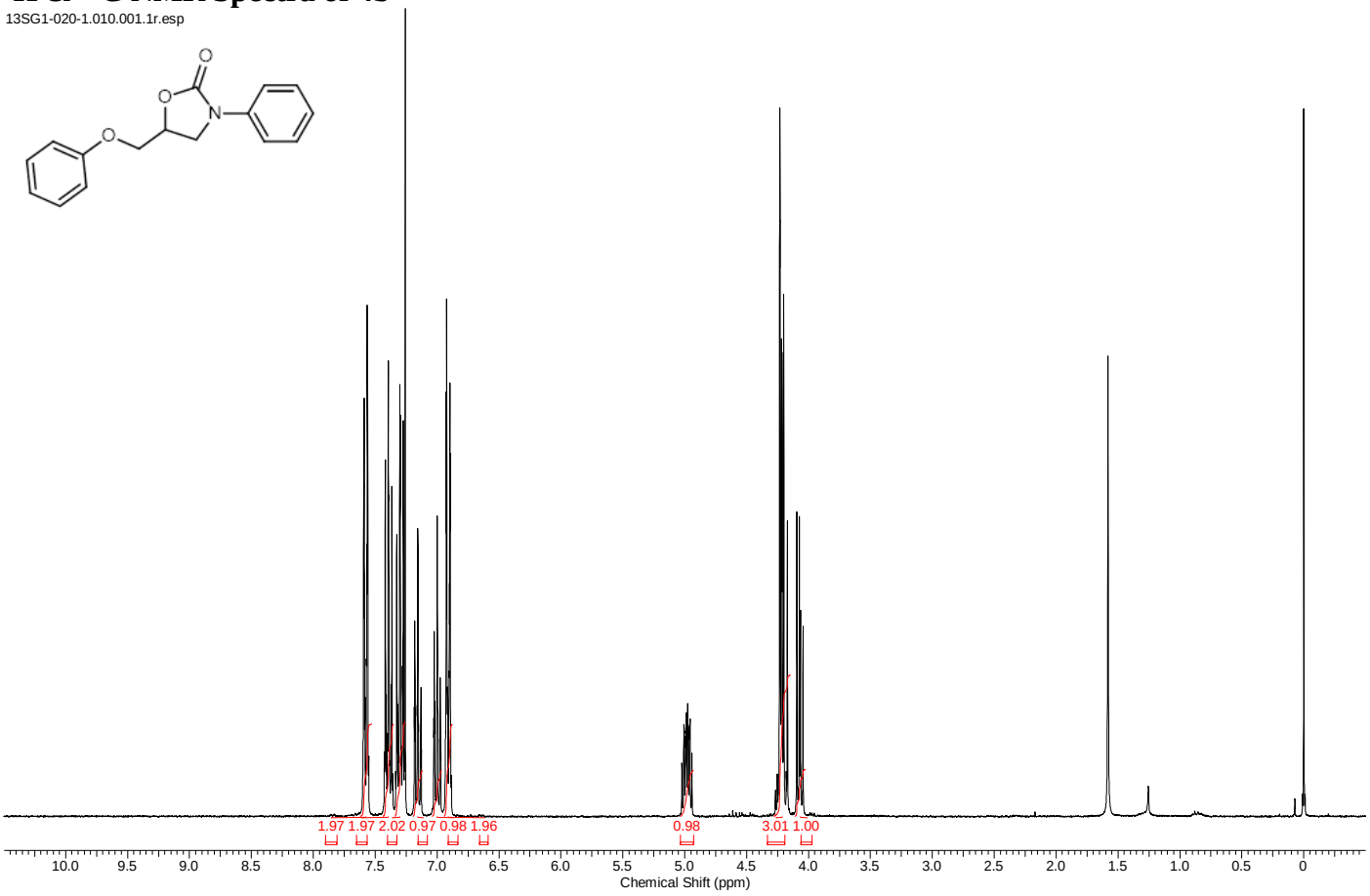

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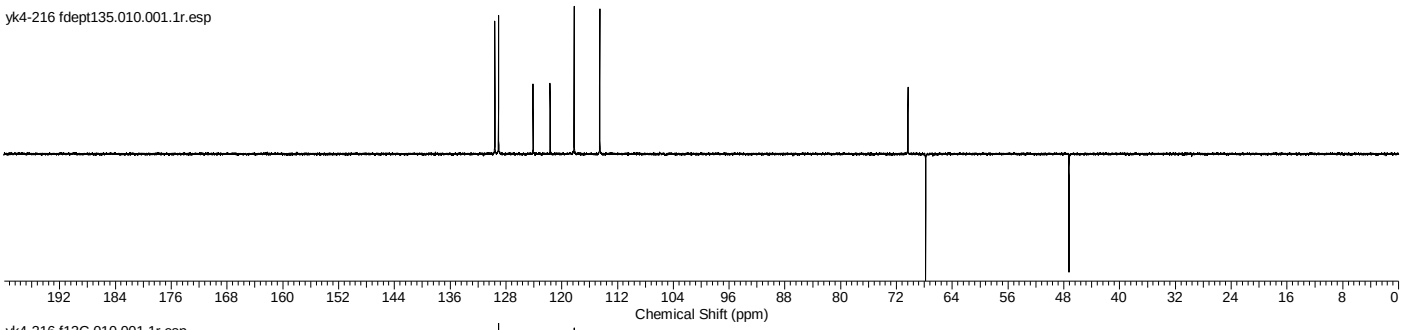

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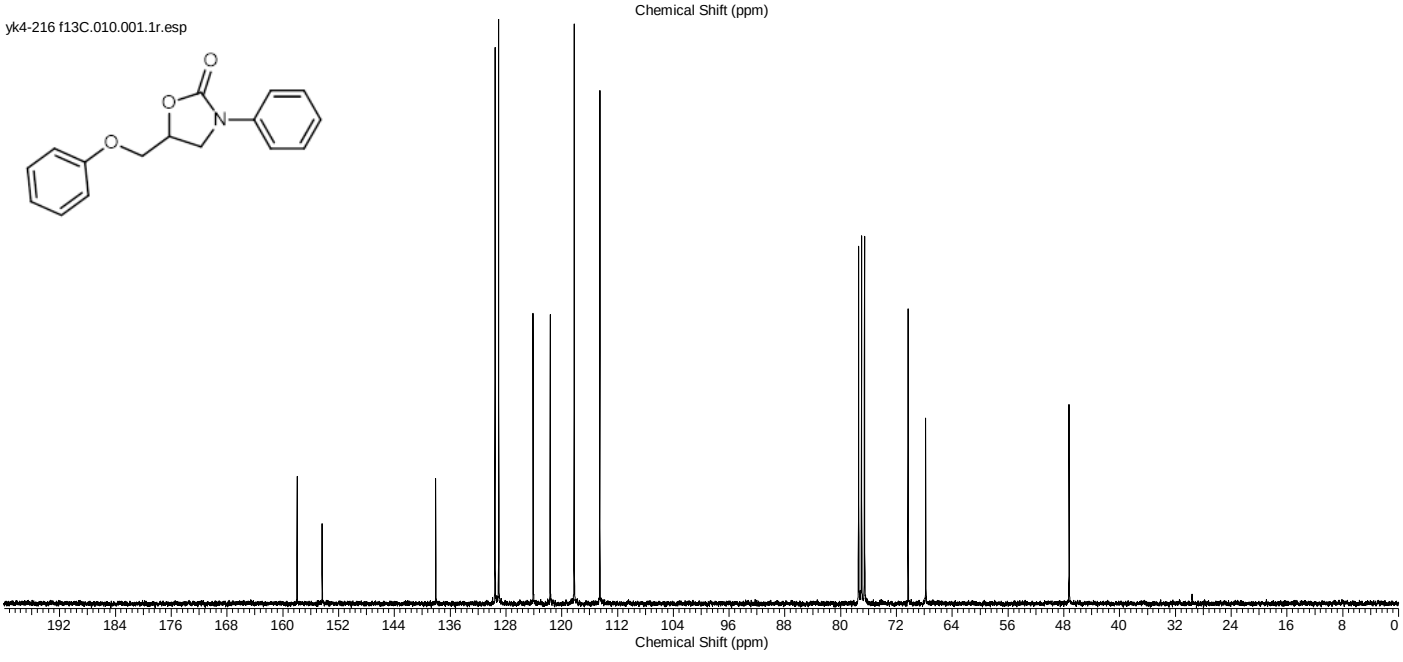

^{1}H & ^{13}C NMR Spectra of 4c

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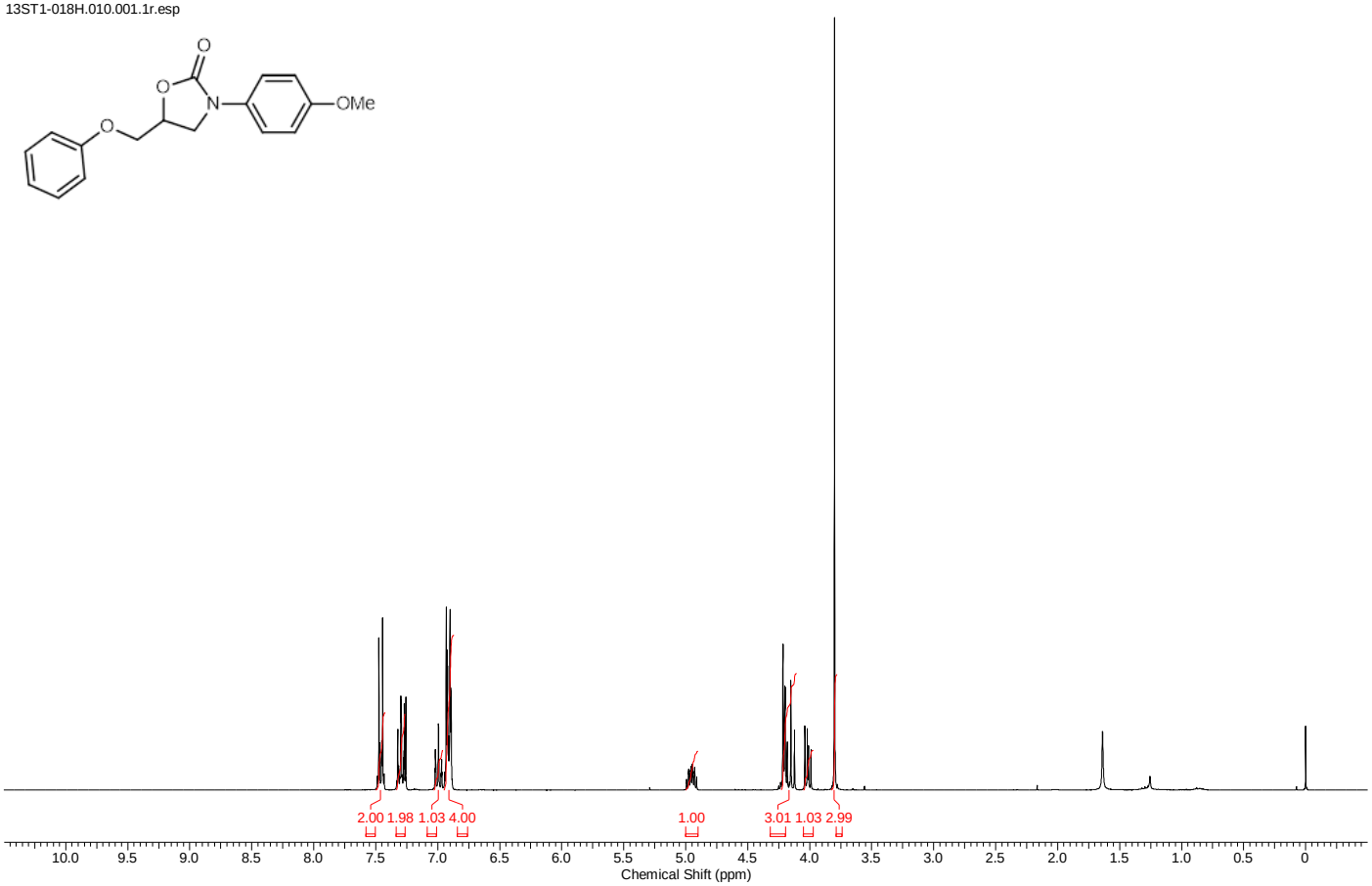

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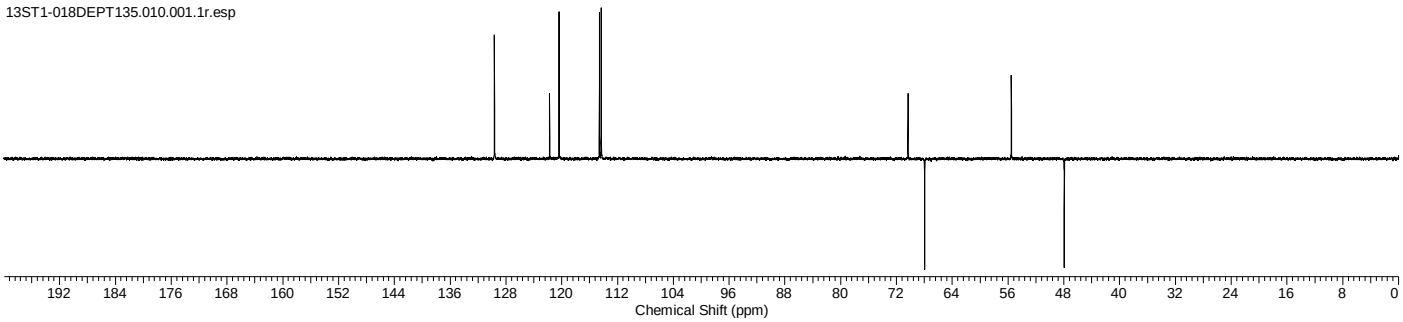

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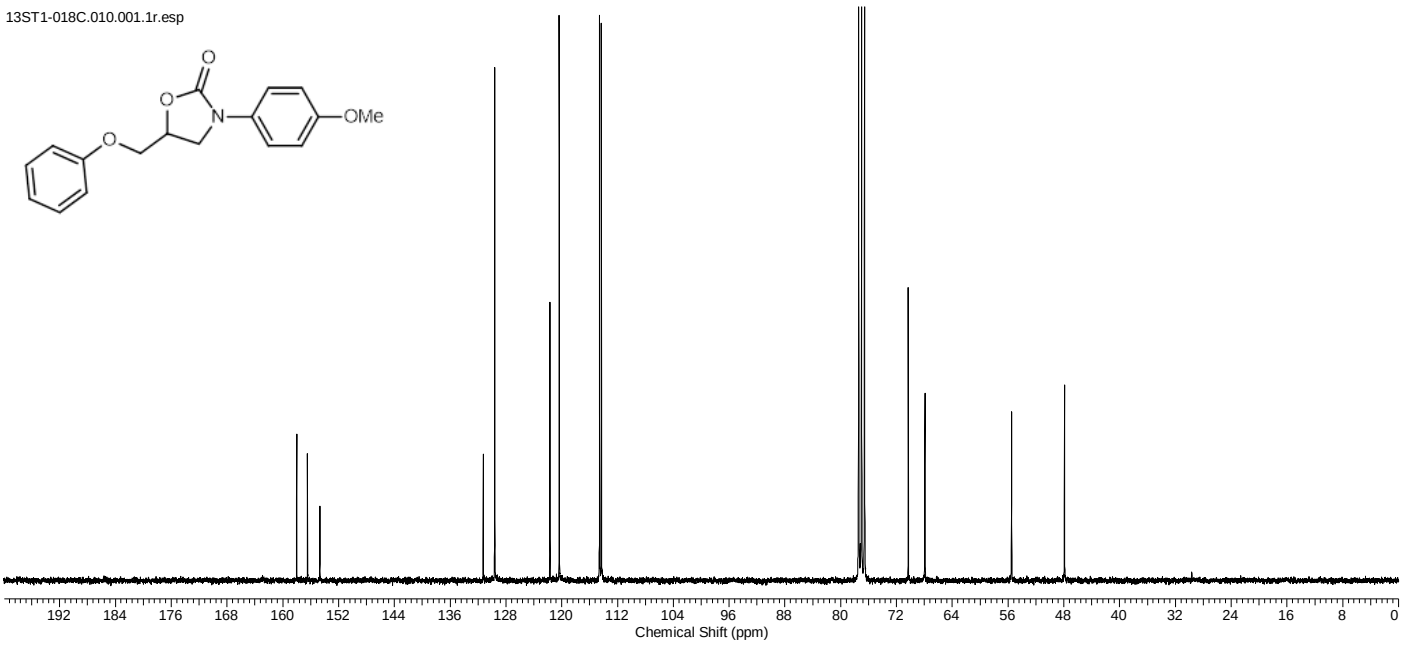
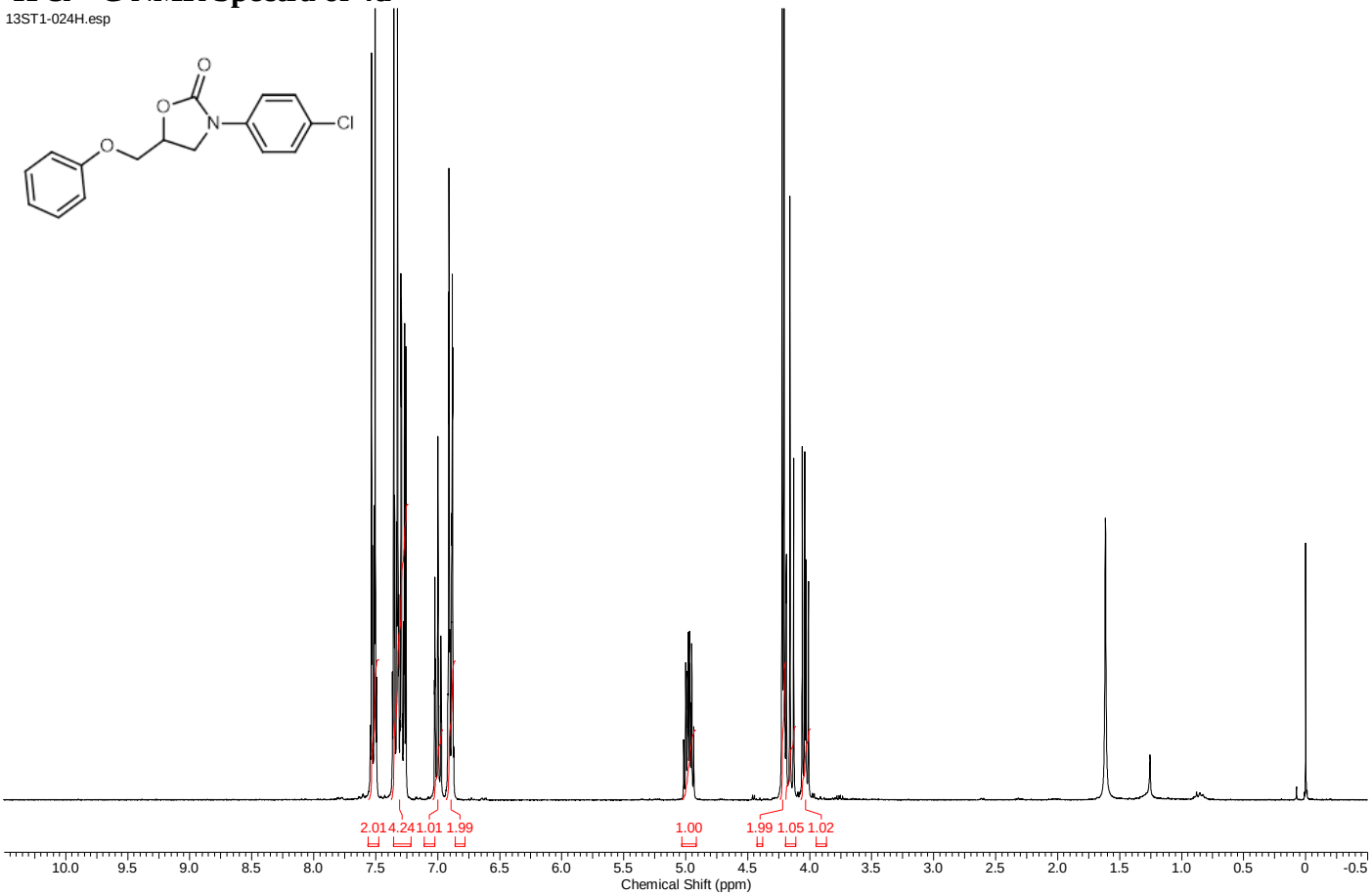
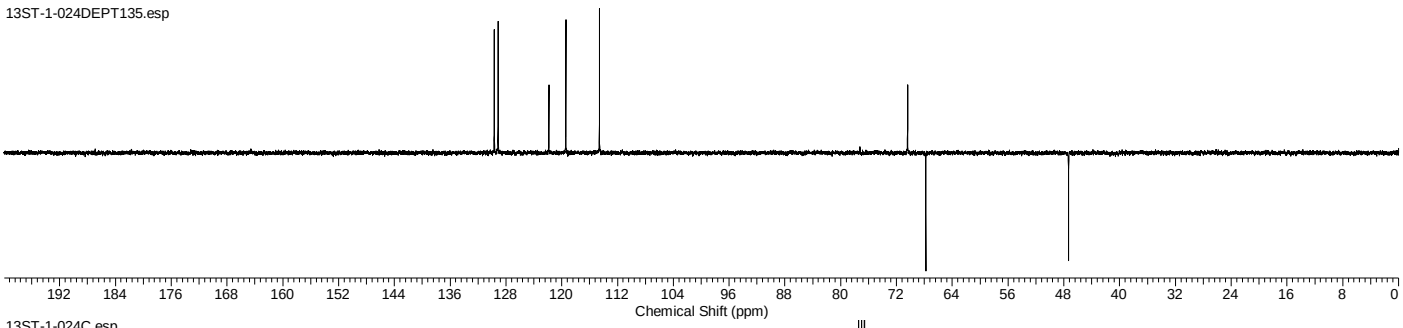
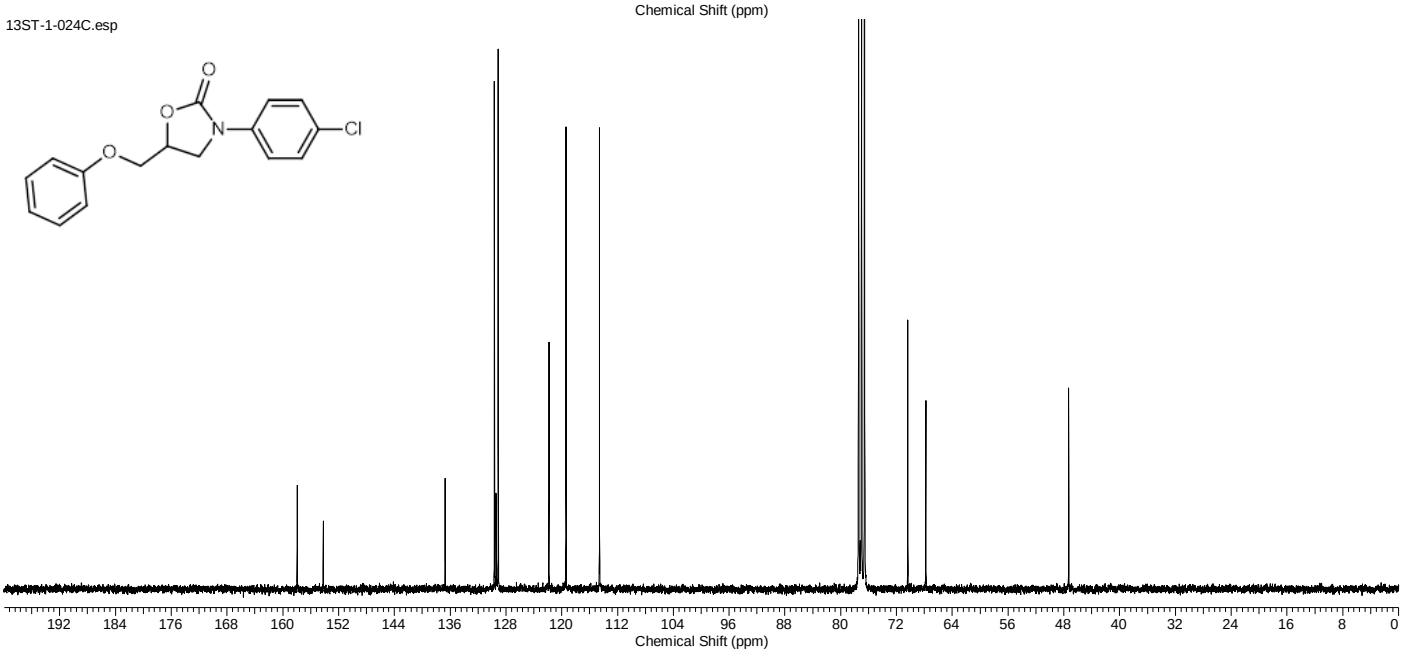


^{1}H & ^{13}C NMR Spectra of 4d

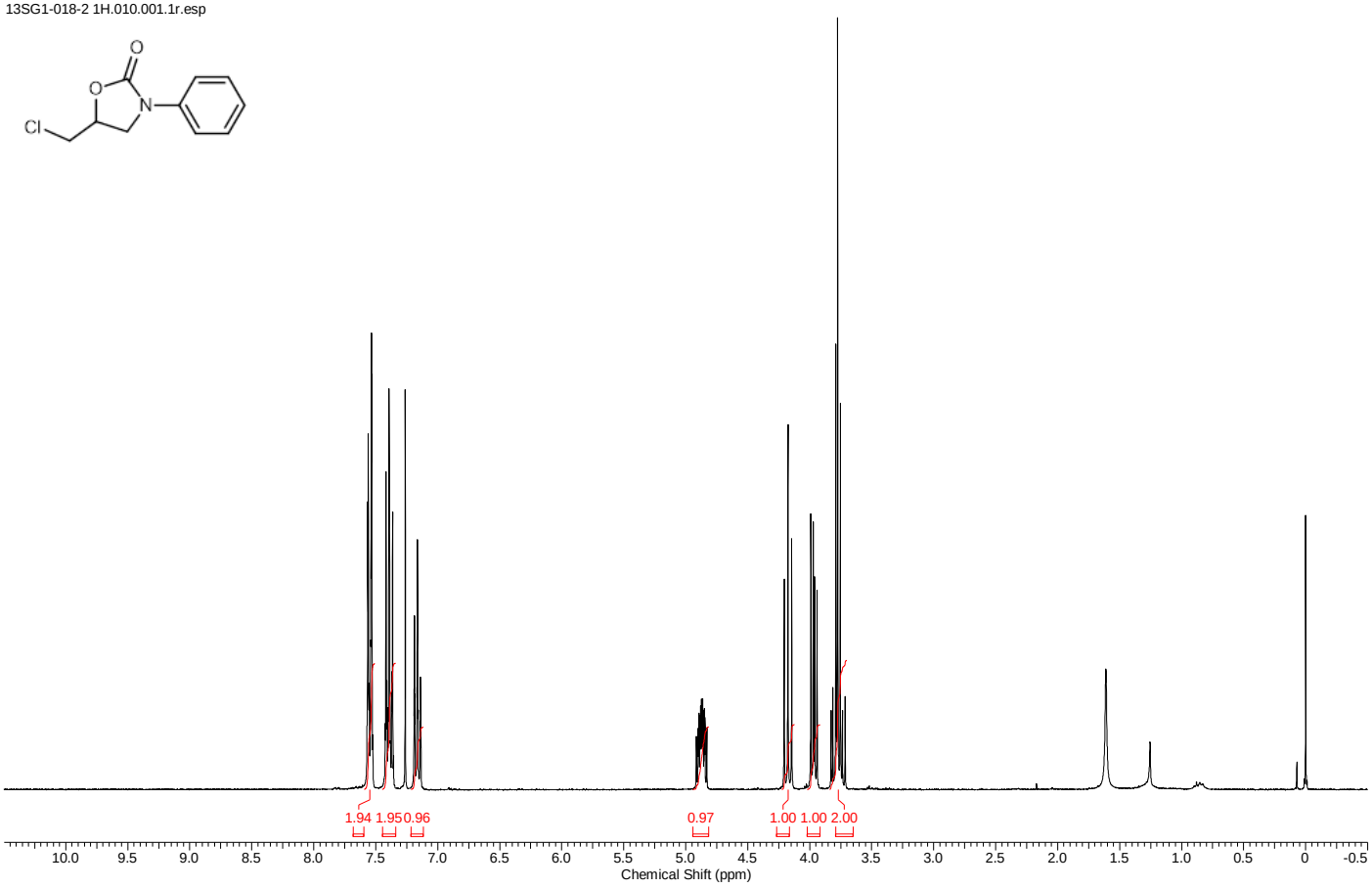






^{1}H & ^{13}C NMR Spectra of 4e

13SG1-018-2 1H.010.001.1r.esp



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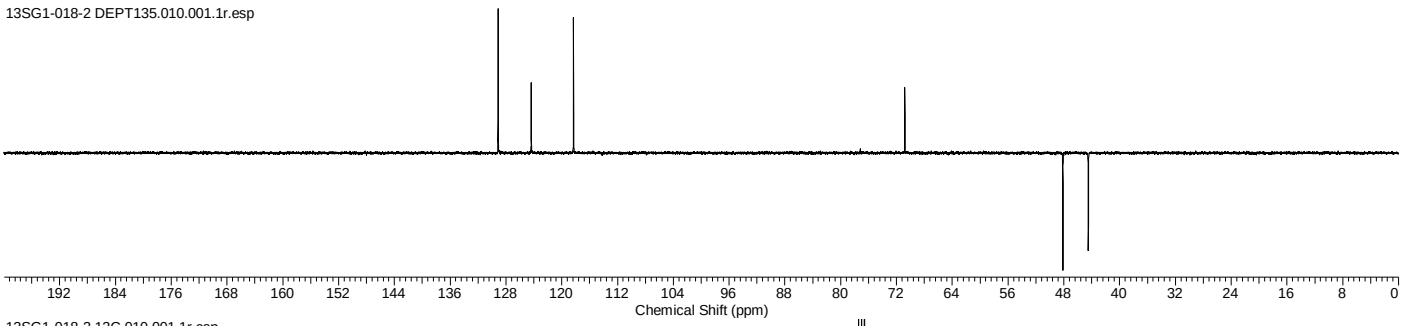

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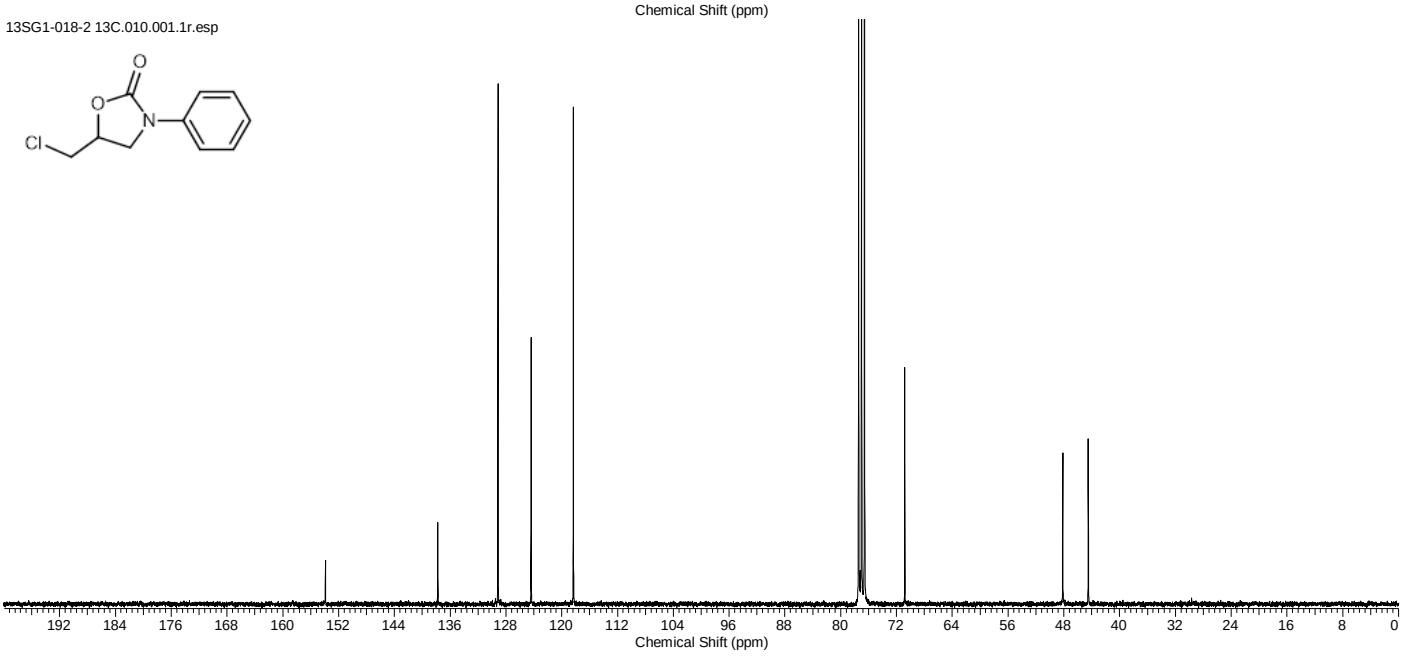
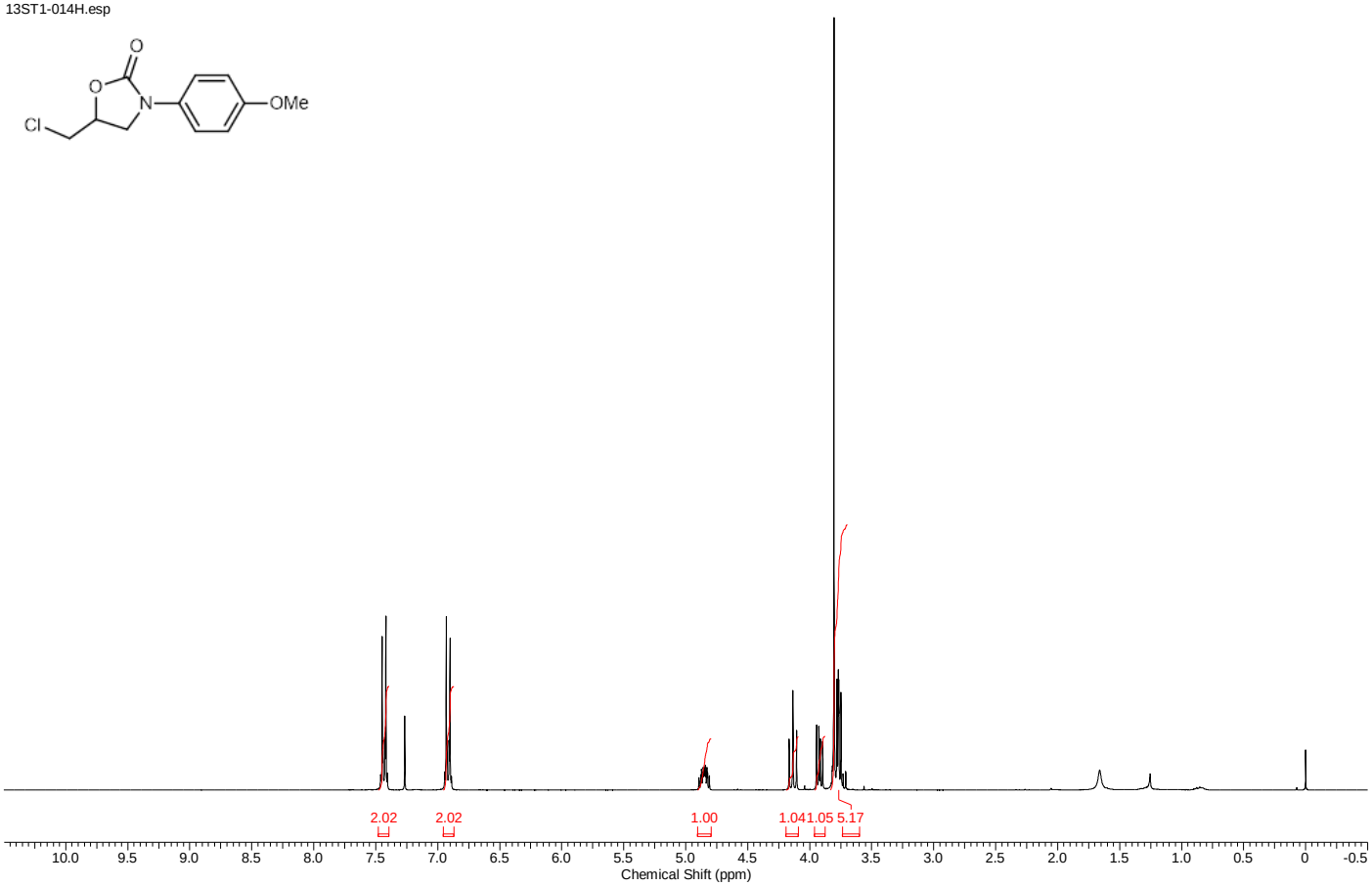
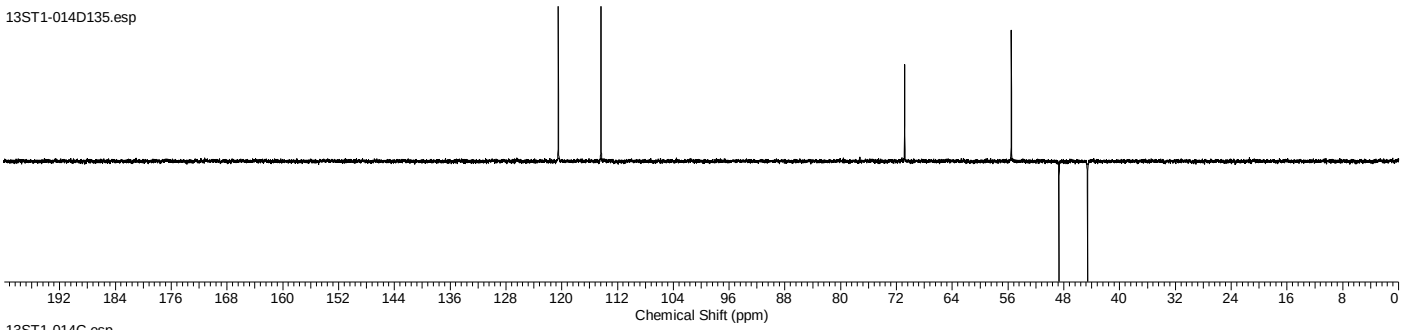


^{1}H & ^{13}C NMR Spectra of 4f

13ST1-014H.esp



13ST1-014D135.esp



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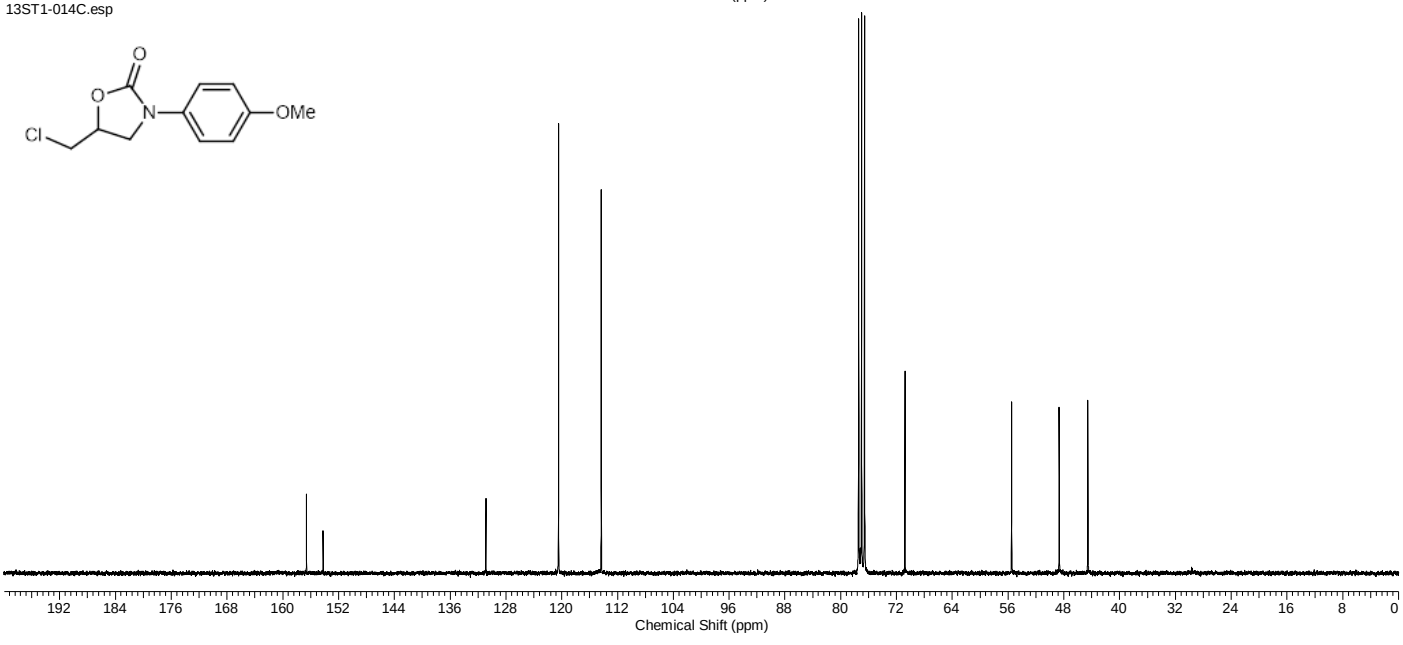
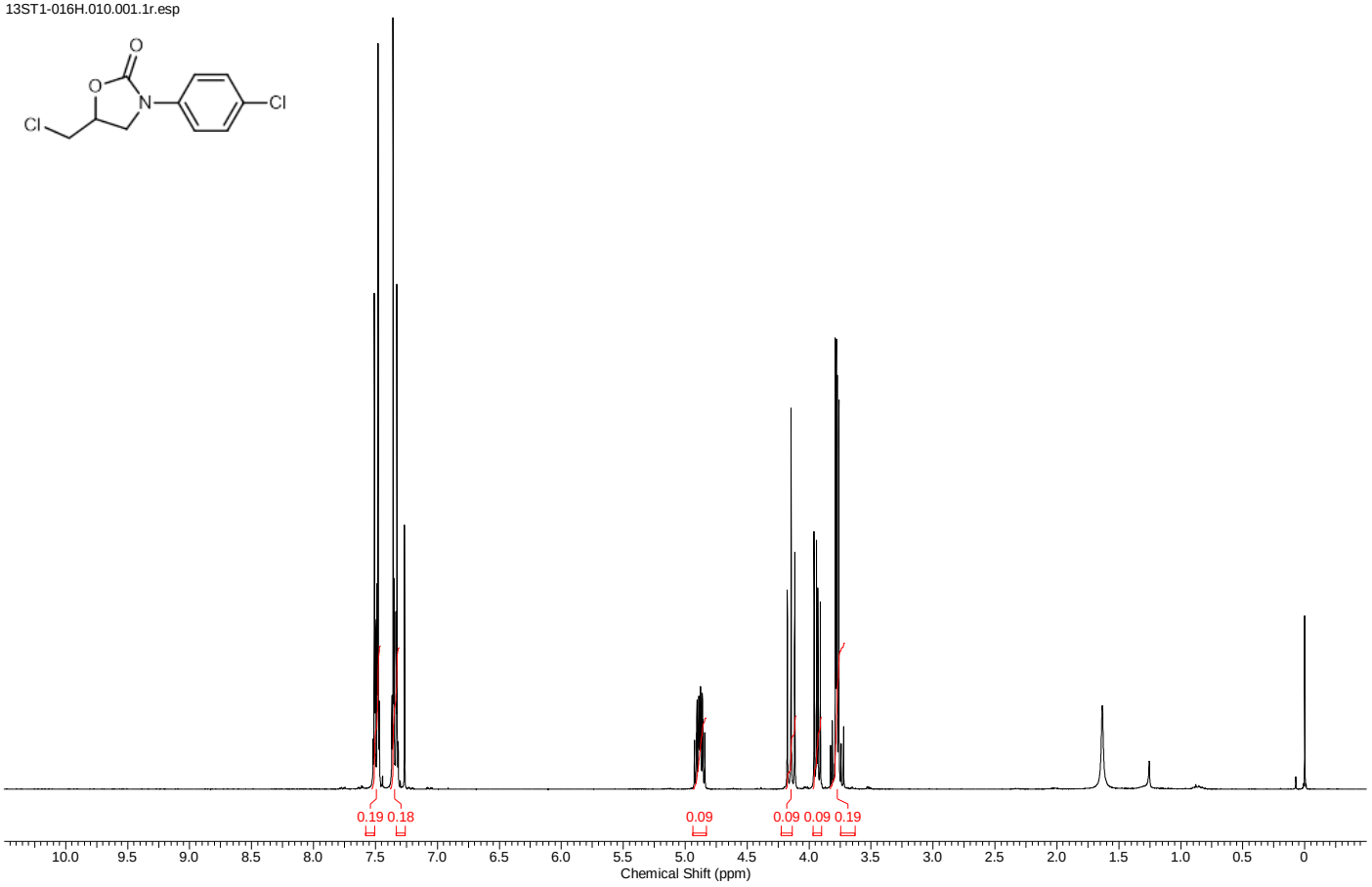


^{1}H & ^{13}C NMR Spectra of 4g

13ST1-016H.010.001.1r.esp



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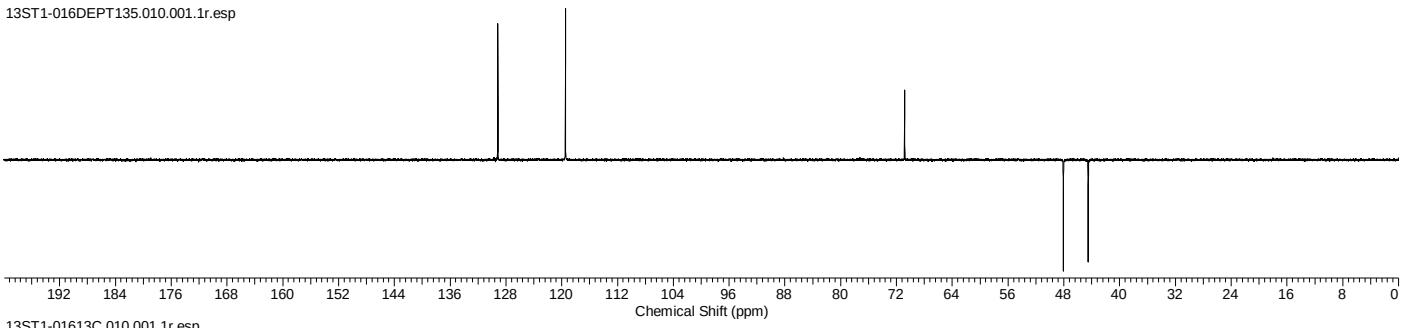
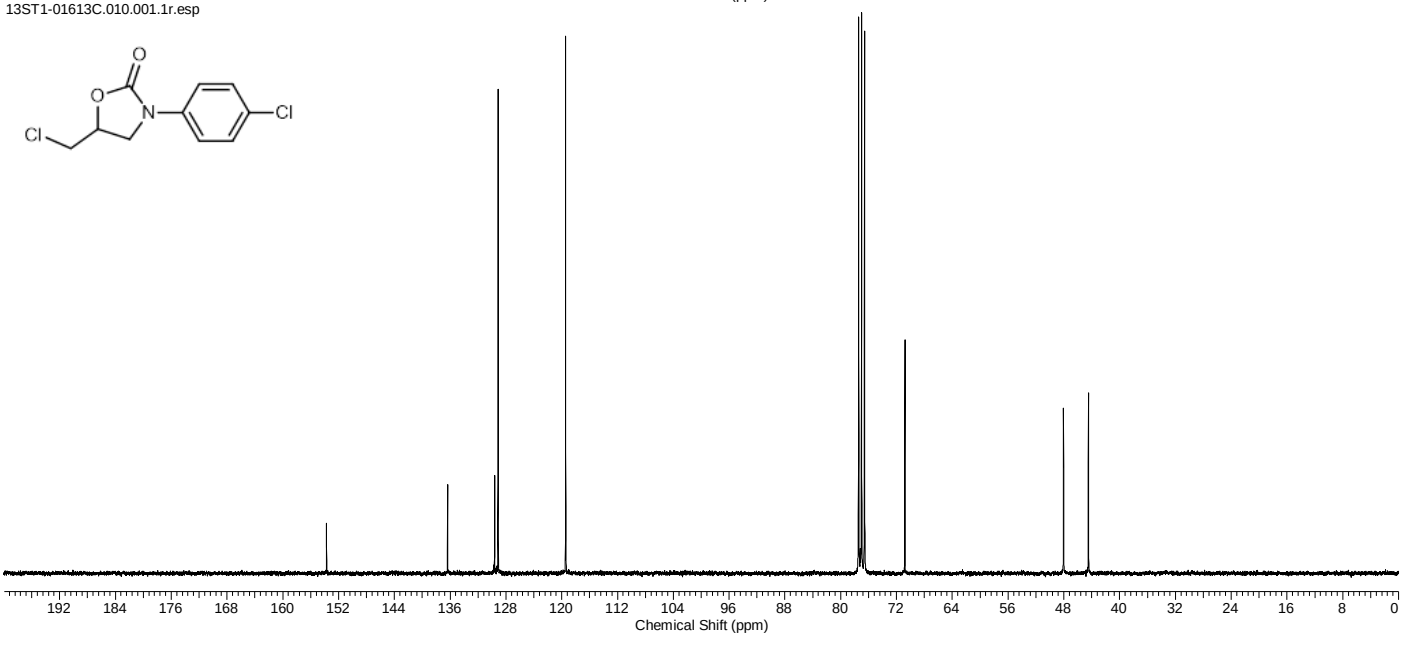
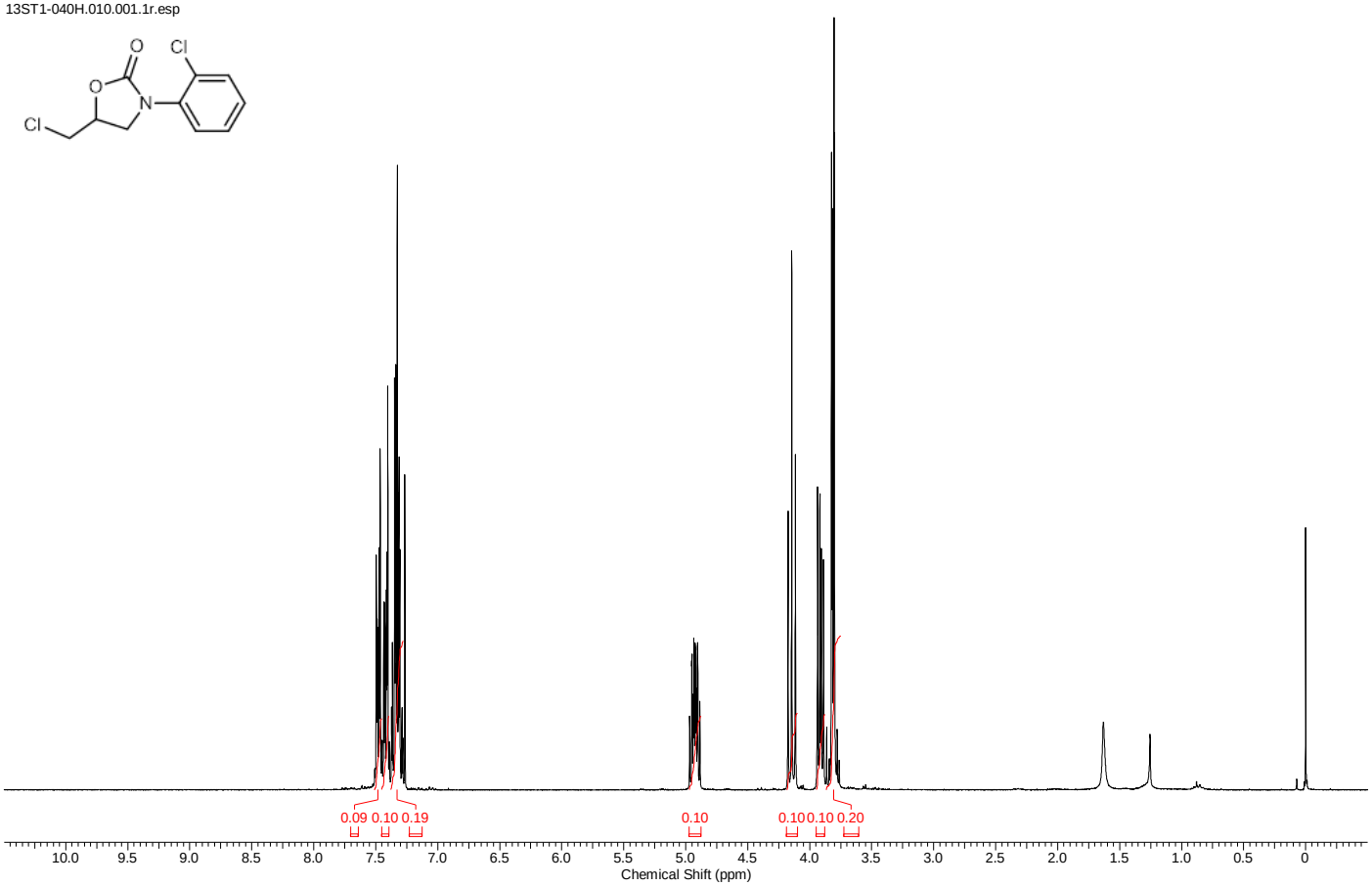


13ST1-01613C.010.001.1r.esp



^{1}H & ^{13}C NMR Spectra of 4h

13ST1-040H.010.001.1r.esp



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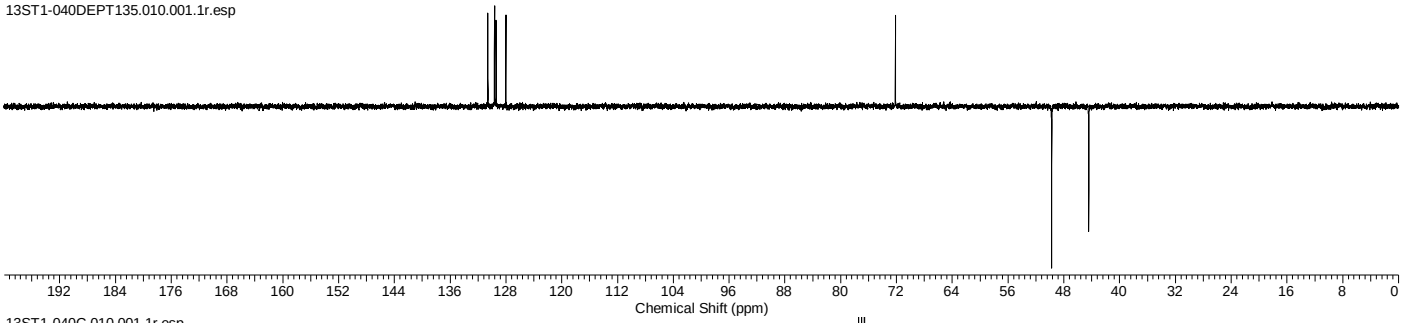

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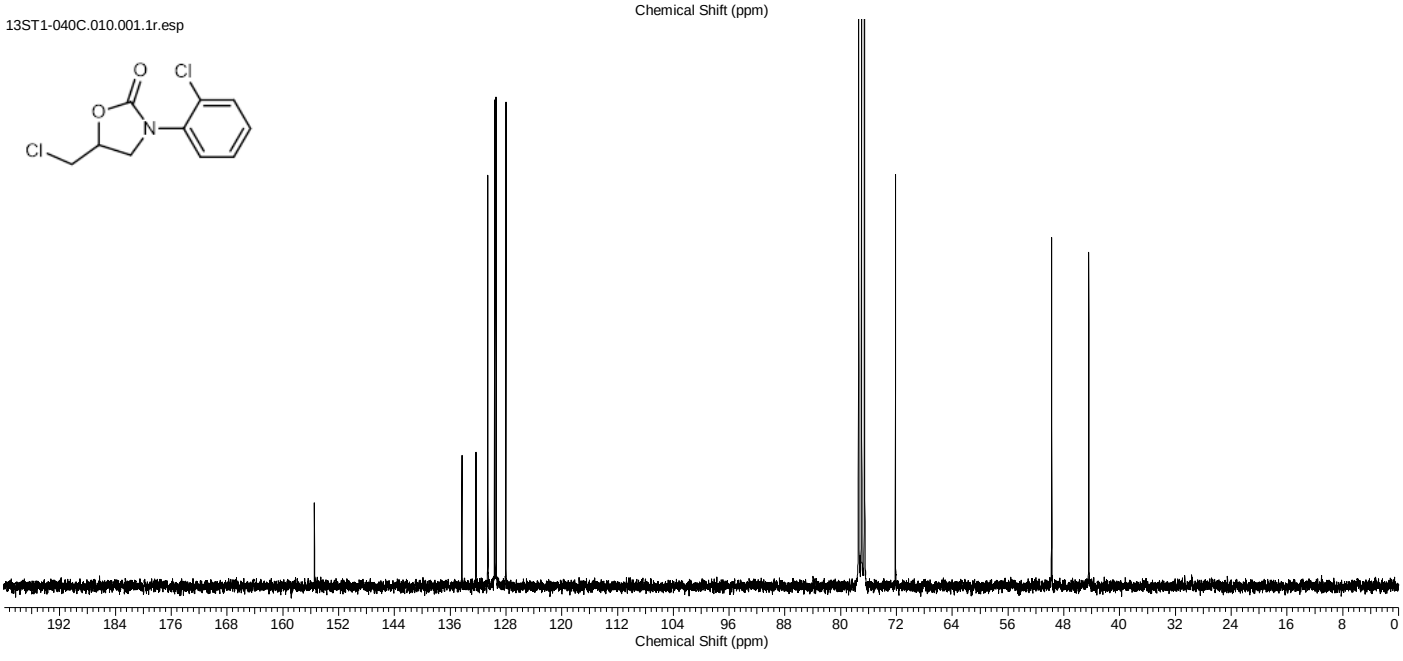
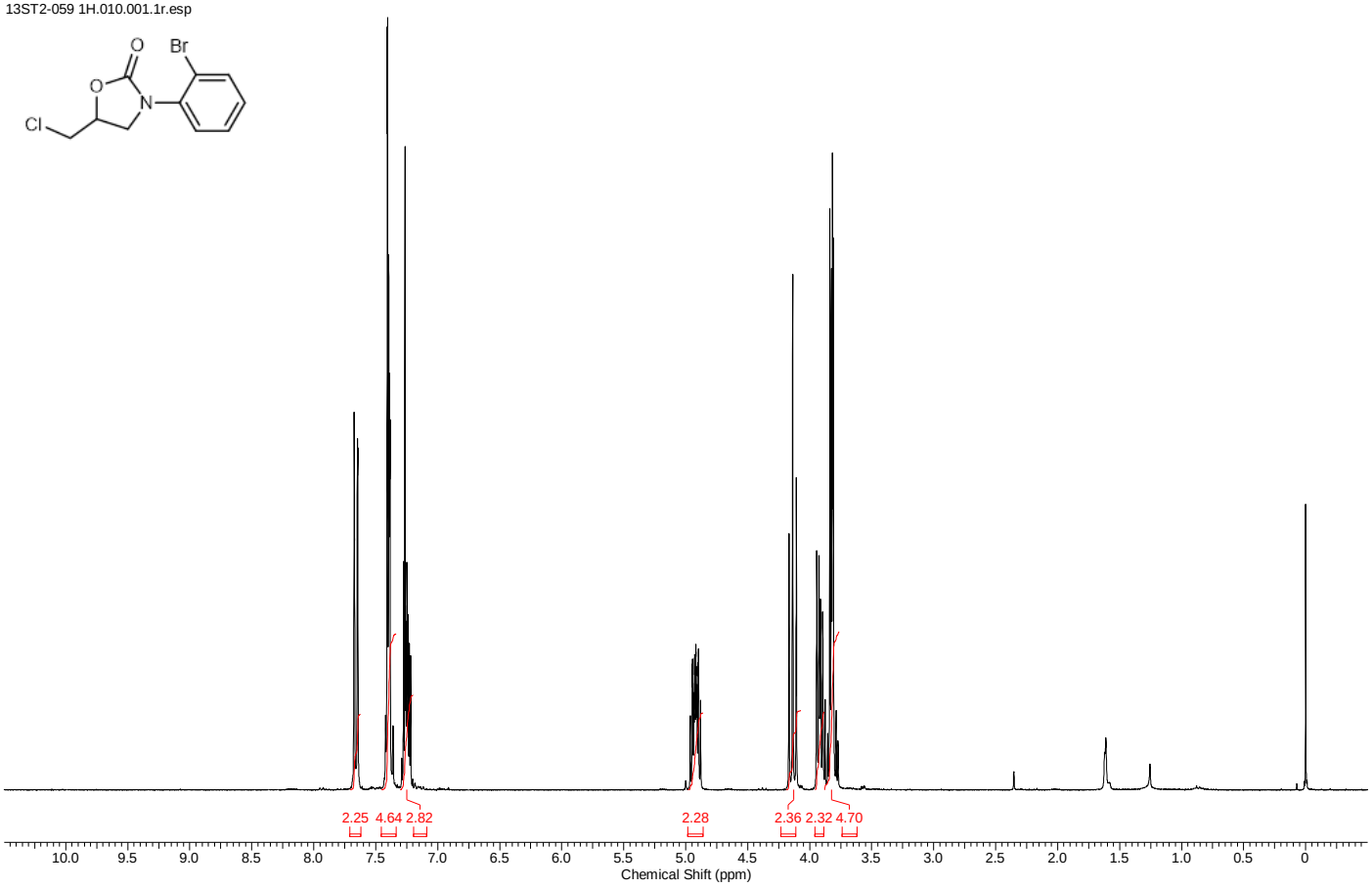
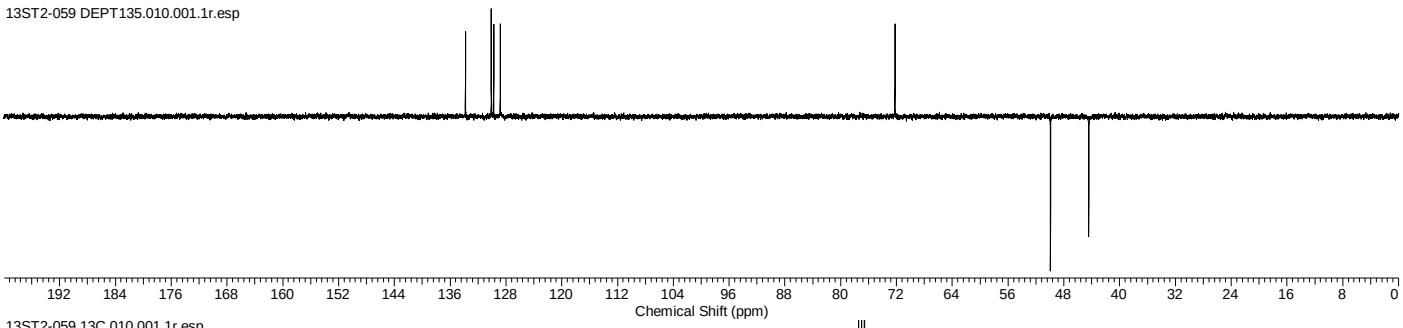


^{1}H & ^{13}C NMR Spectra of 4i

13ST2-059 1H.010.001.1r.esp



13ST2-059 DEPT135.010.001.1r.esp



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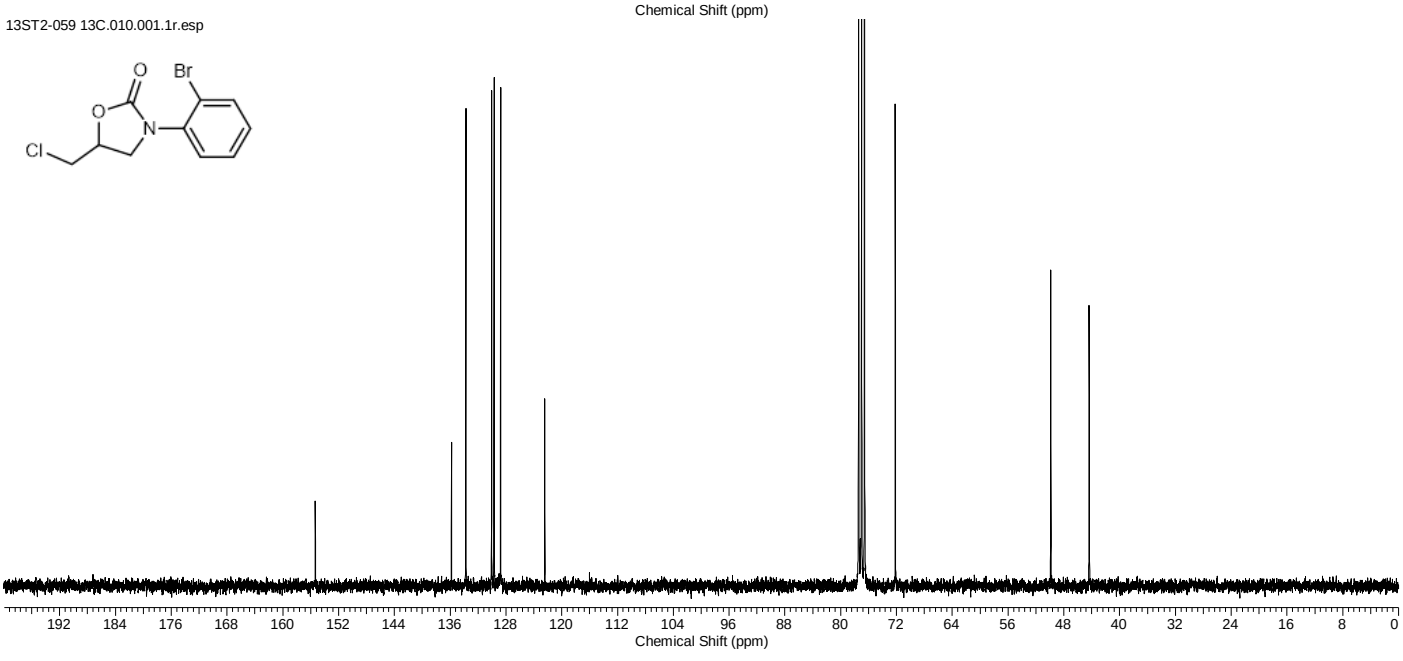
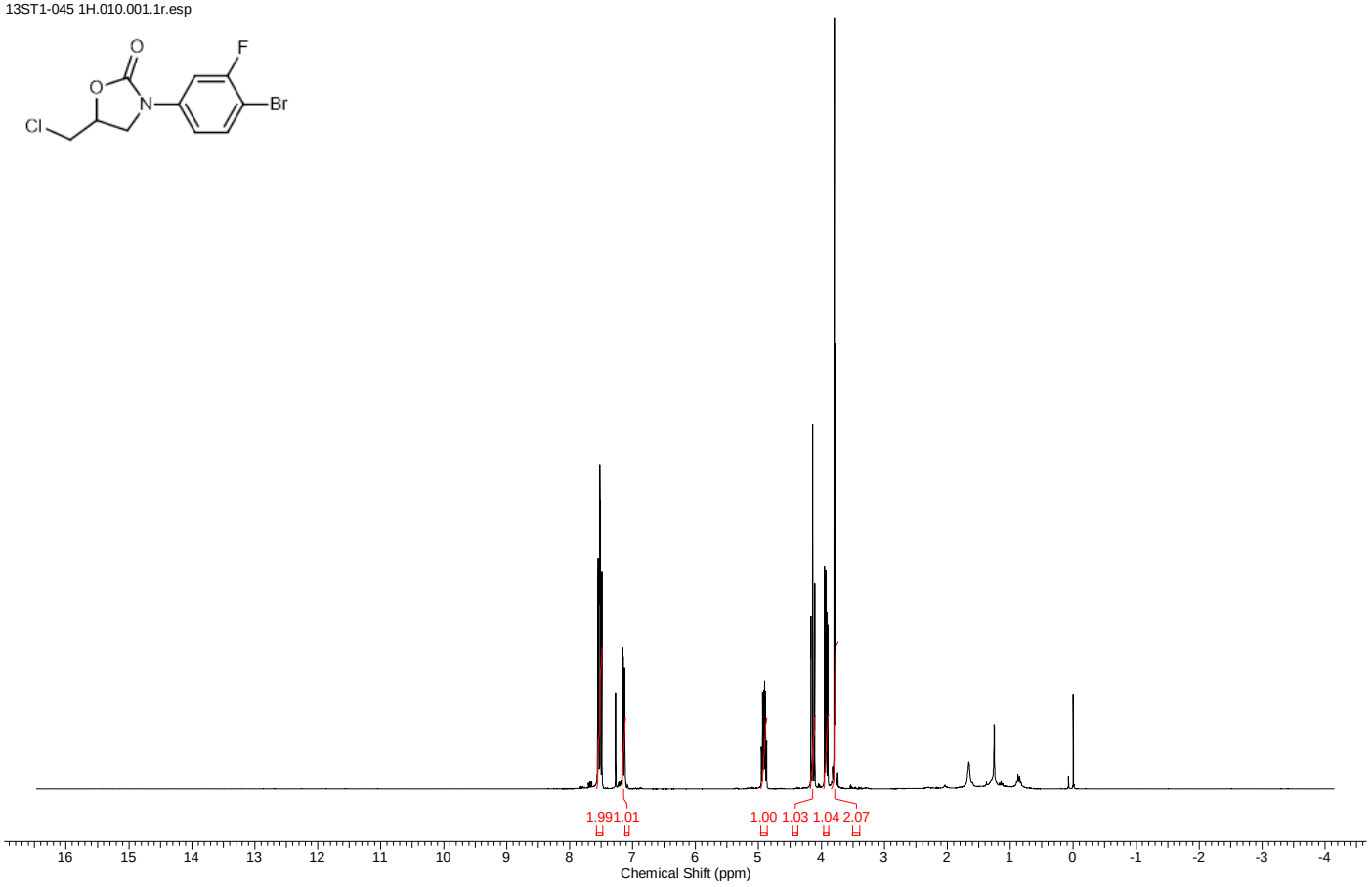


^{1}H & ^{13}C NMR Spectra of 4j

13ST1-045 1H.010.001.1r.esp



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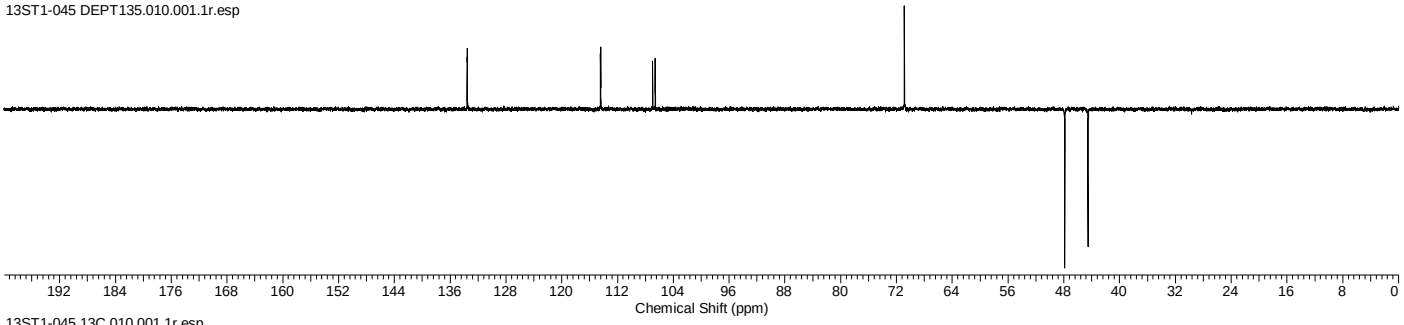

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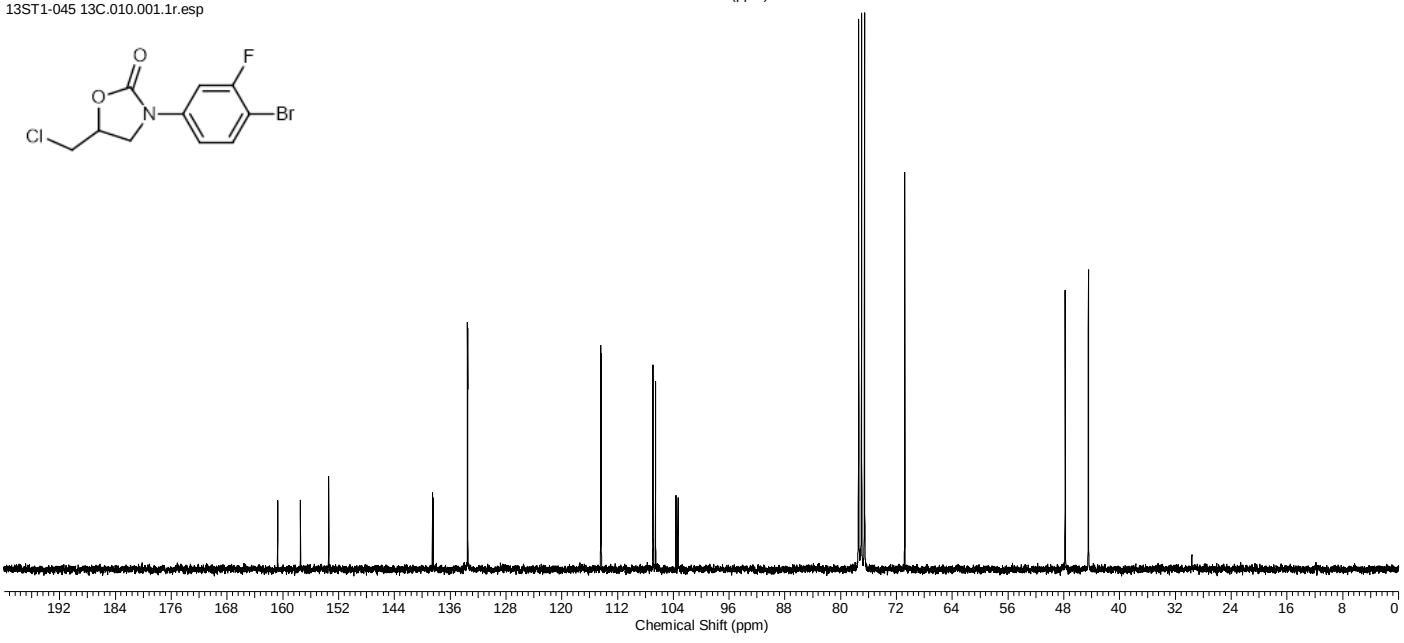
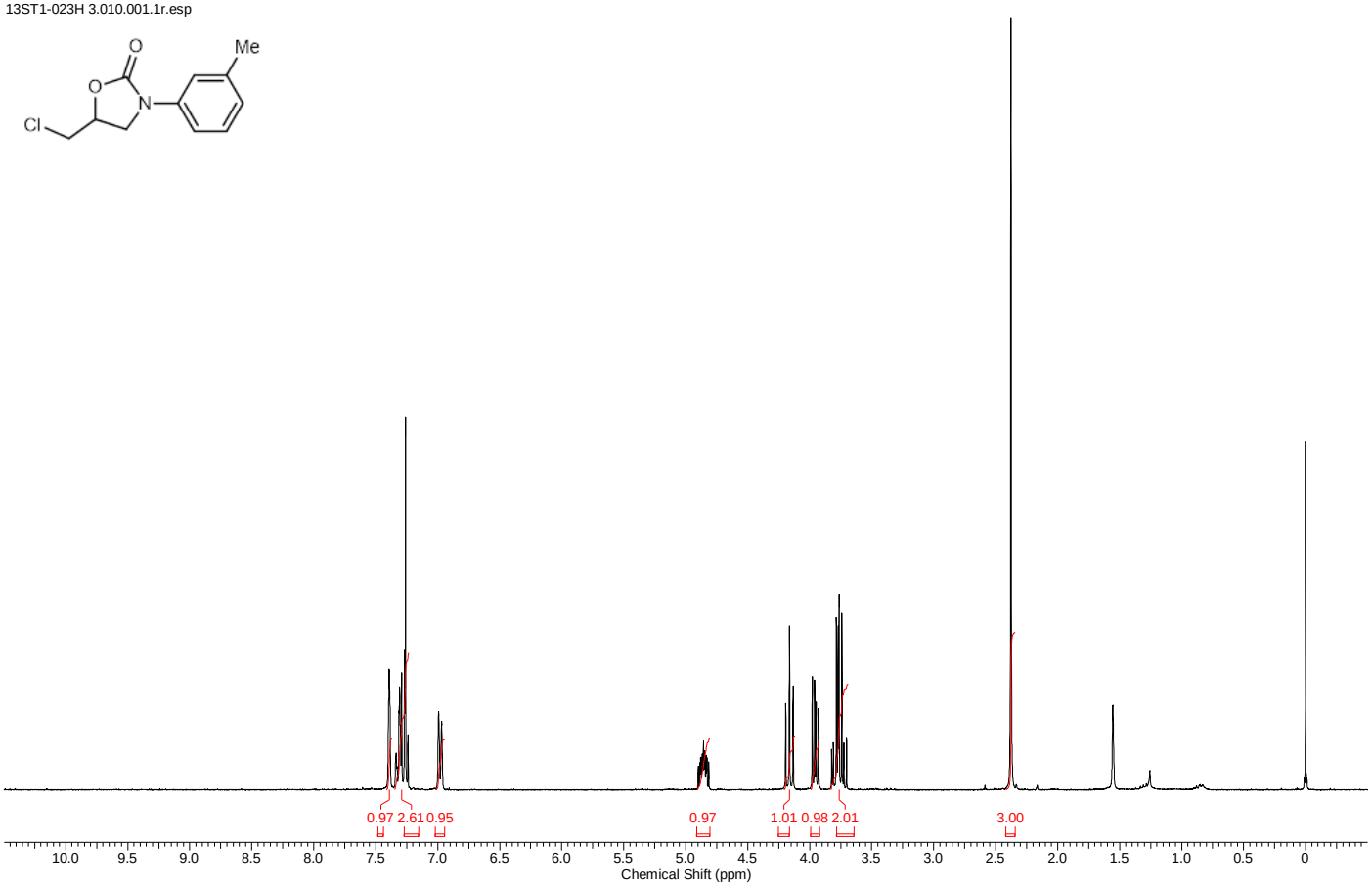


^{1}H & ^{13}C NMR Spectra of 4k

13ST1-023H 3.010.001.1r.esp



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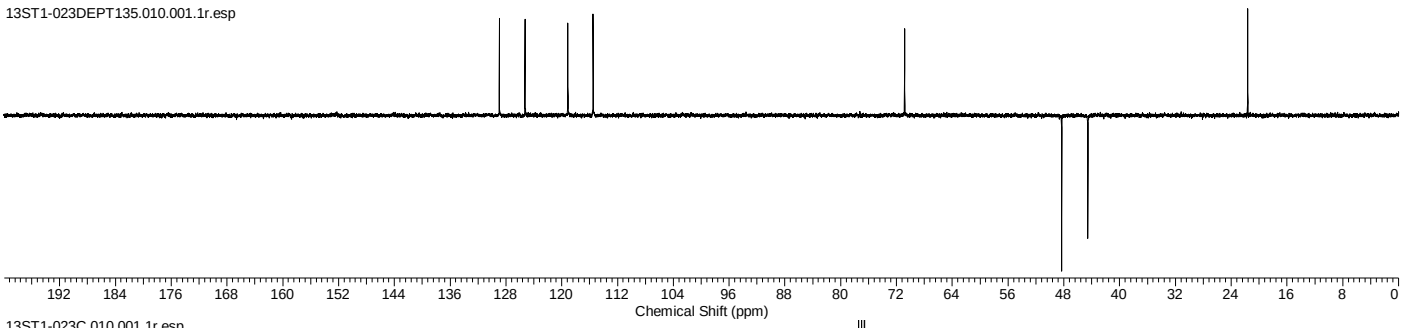

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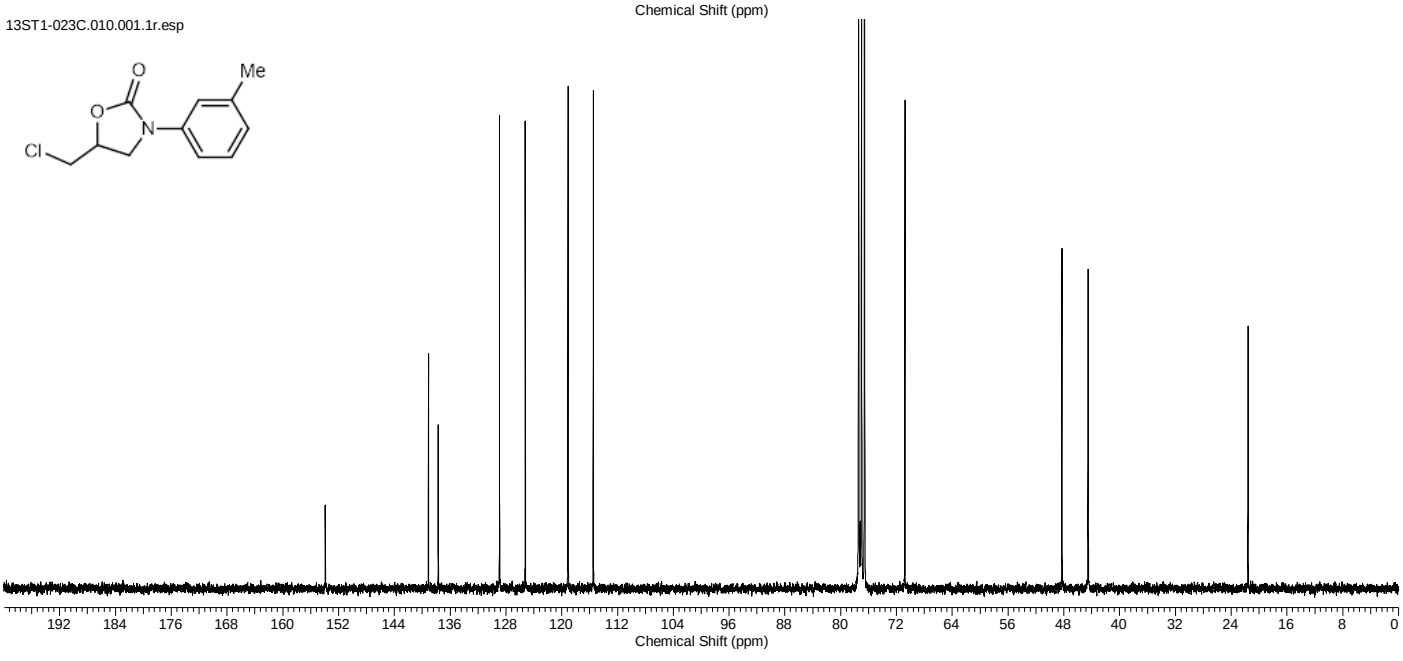
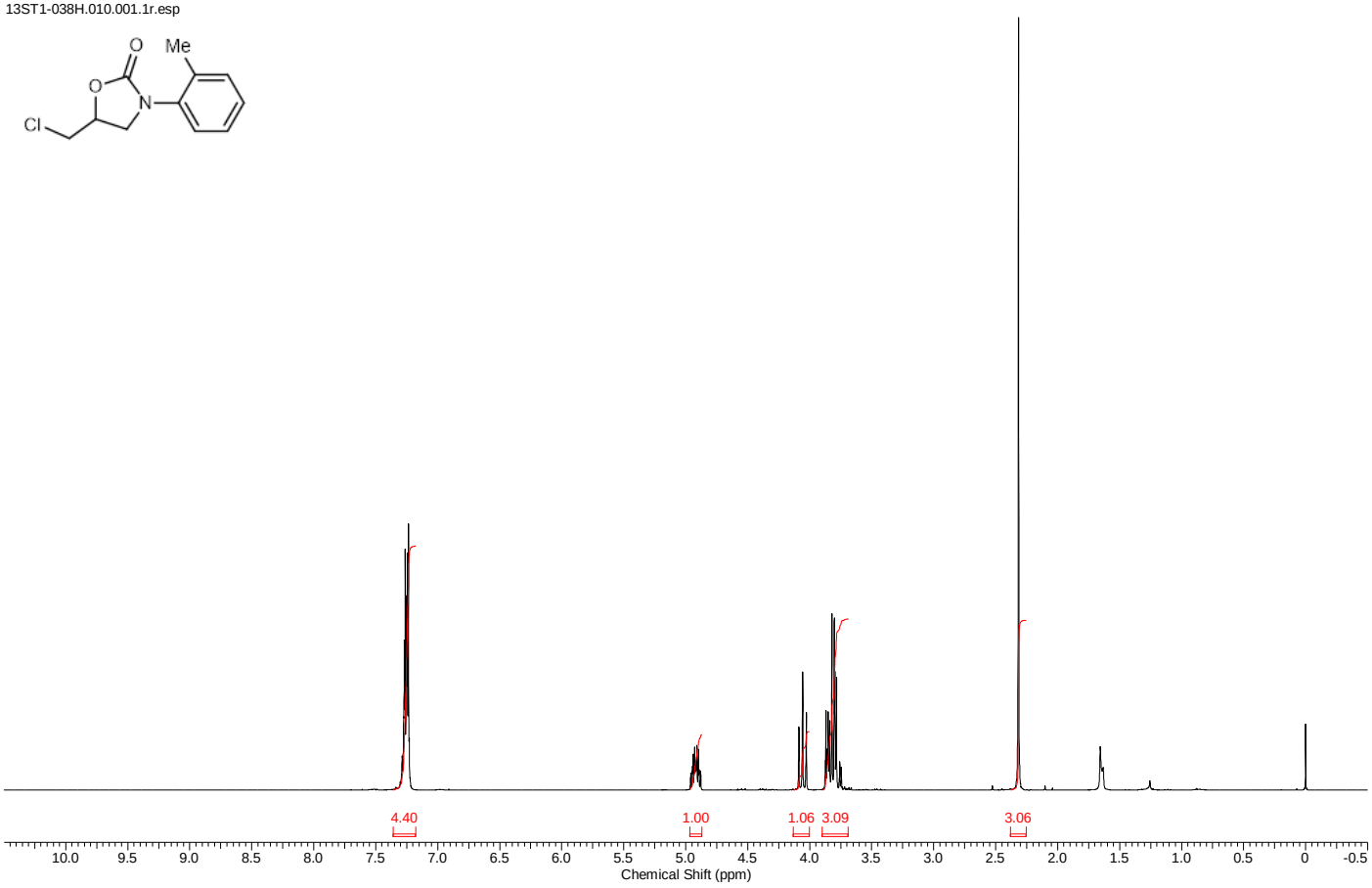


^{1}H & ^{13}C NMR Spectra of 4l

13ST1-038H.010.001.1r.esp



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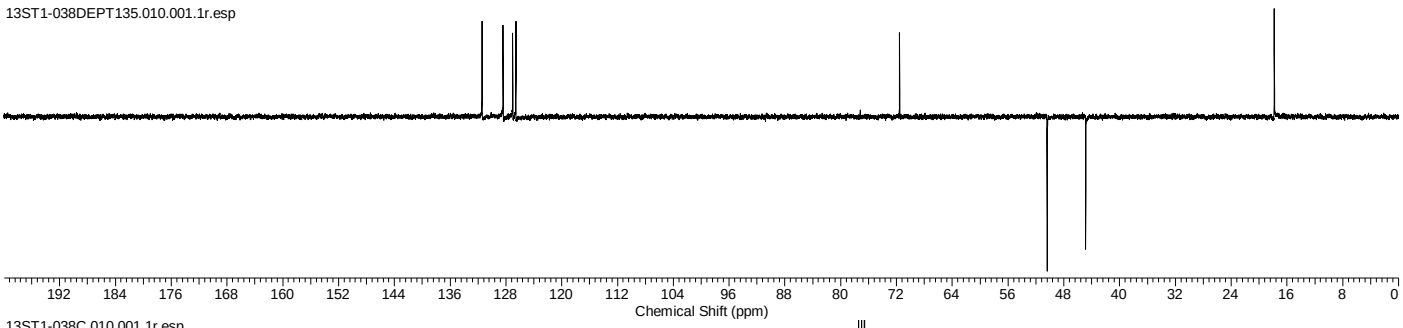

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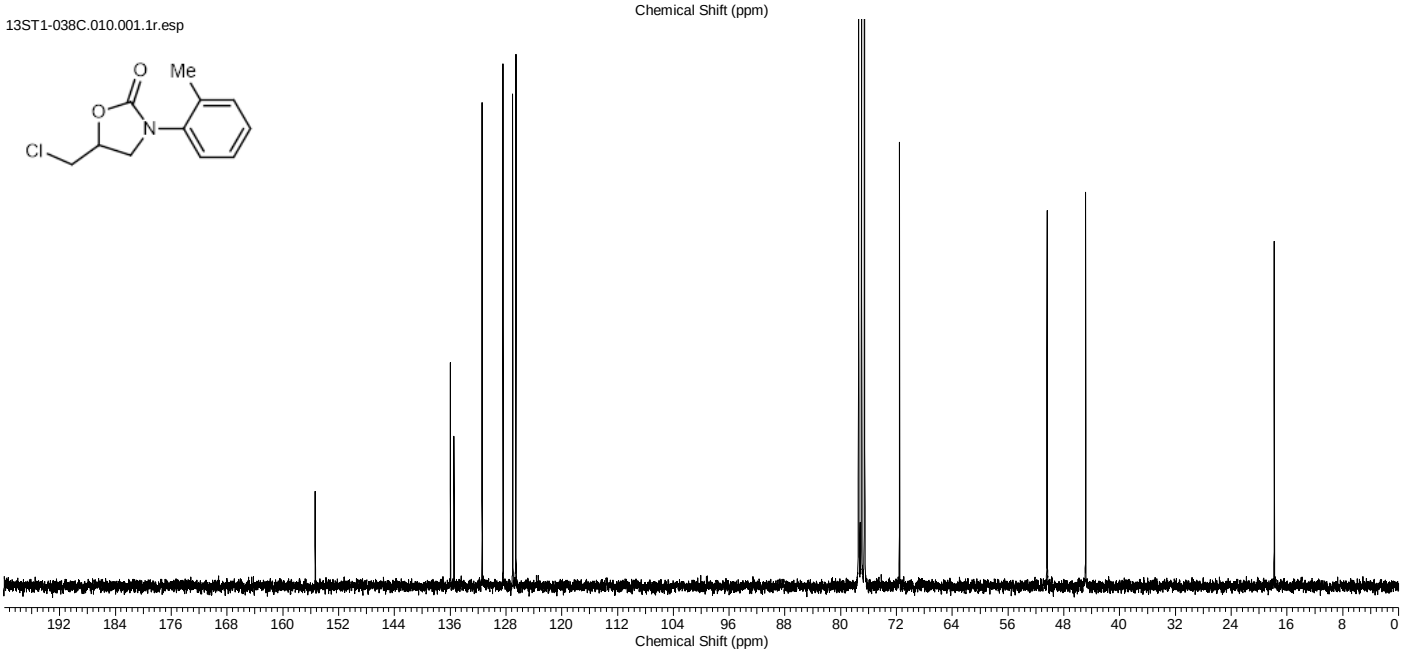
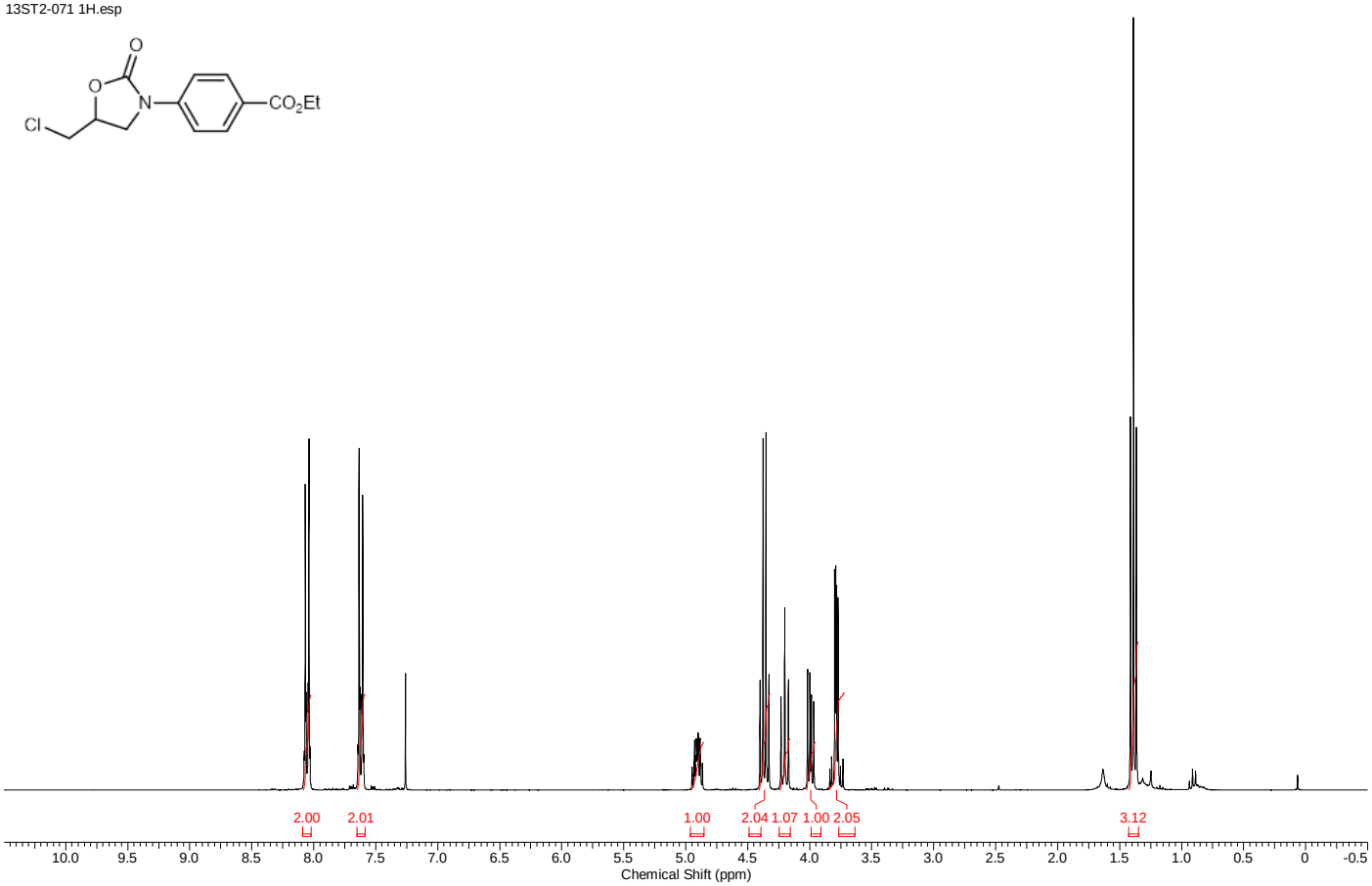
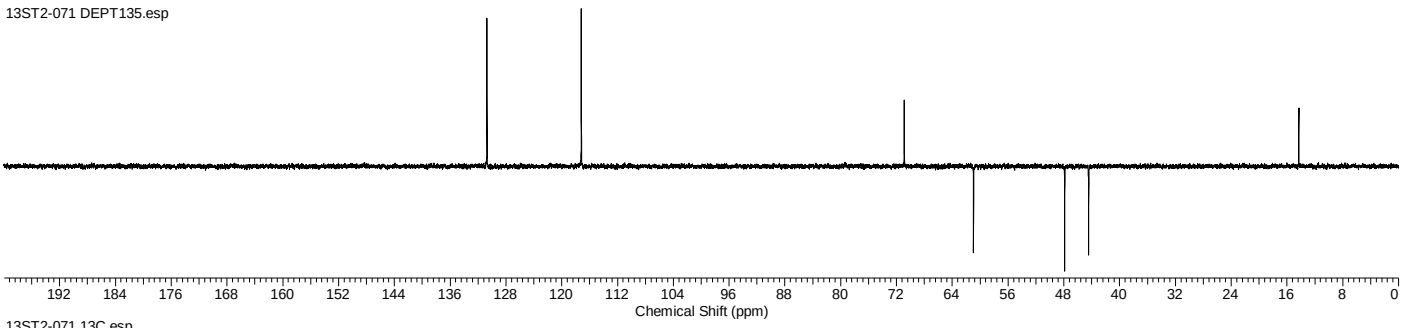


^{1}H & ^{13}C NMR Spectra of 4m

13ST2-071 1H.esp



13ST2-071 DEPT135.esp



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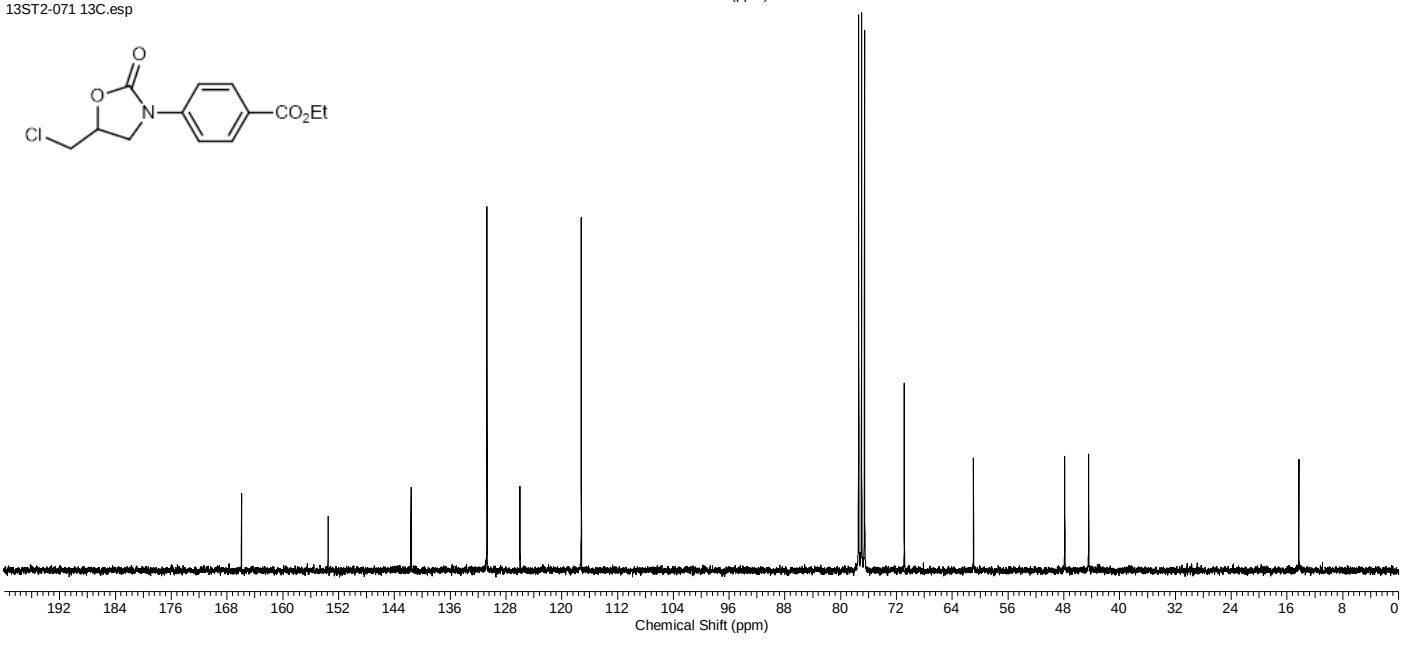
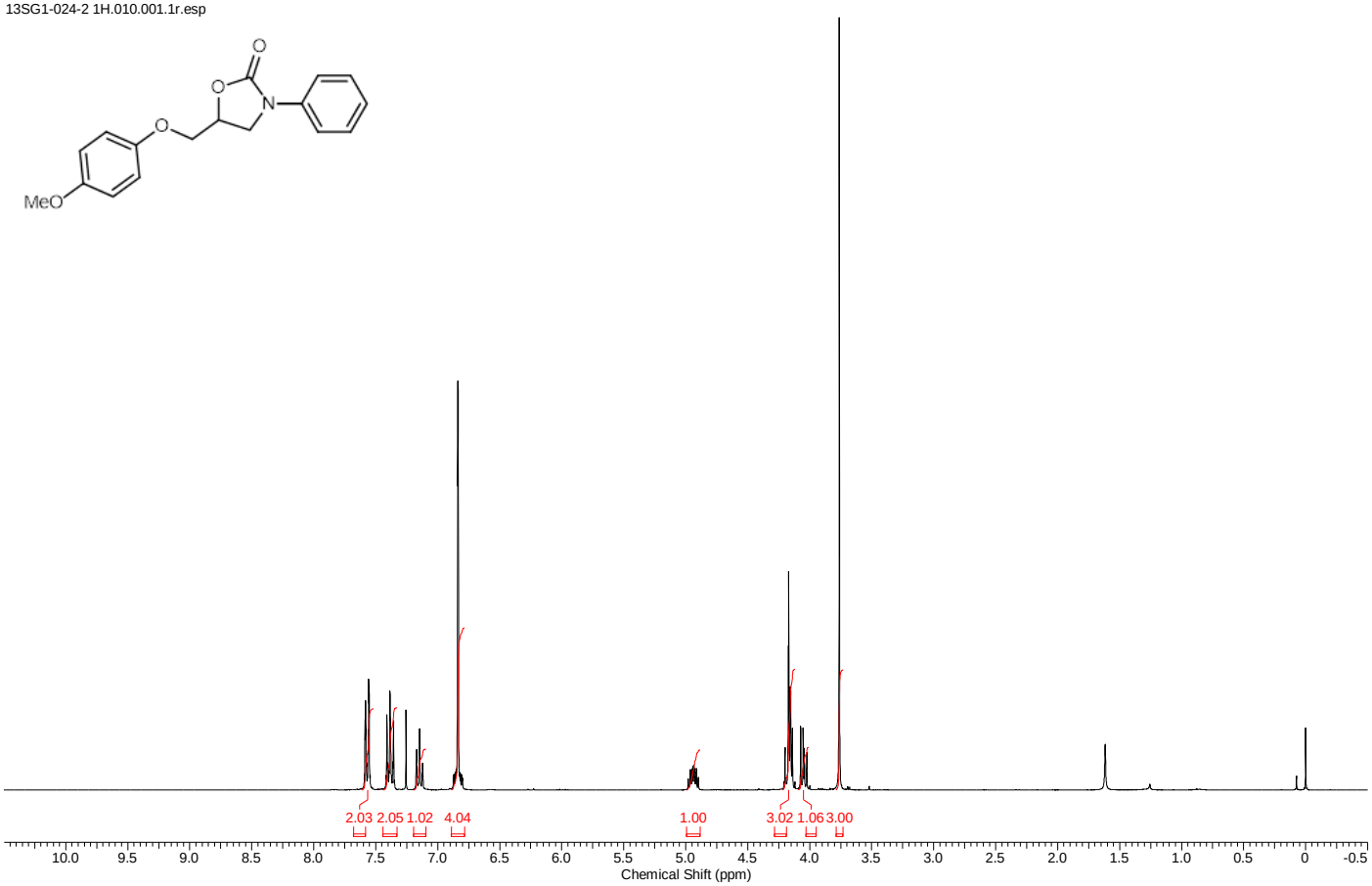


^{1}H & ^{13}C NMR Spectra of 4n

13SG1-024-2 1H.010.001.1r.esp



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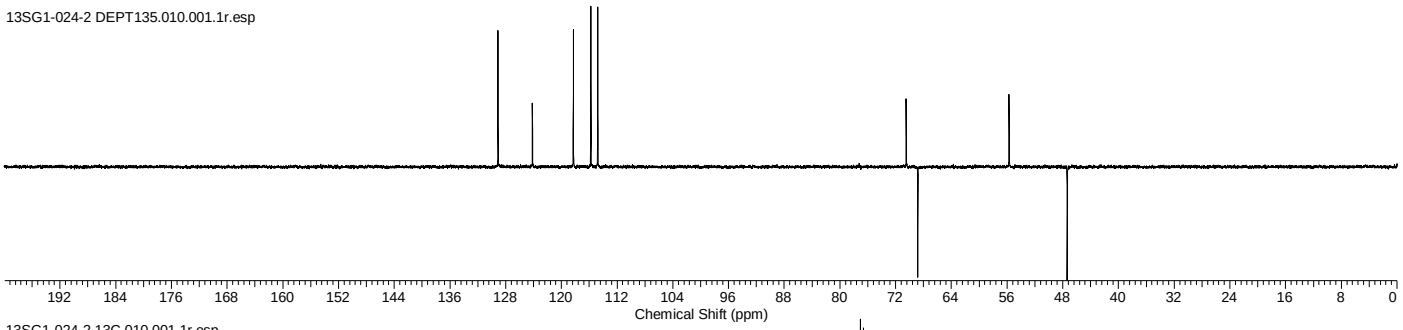

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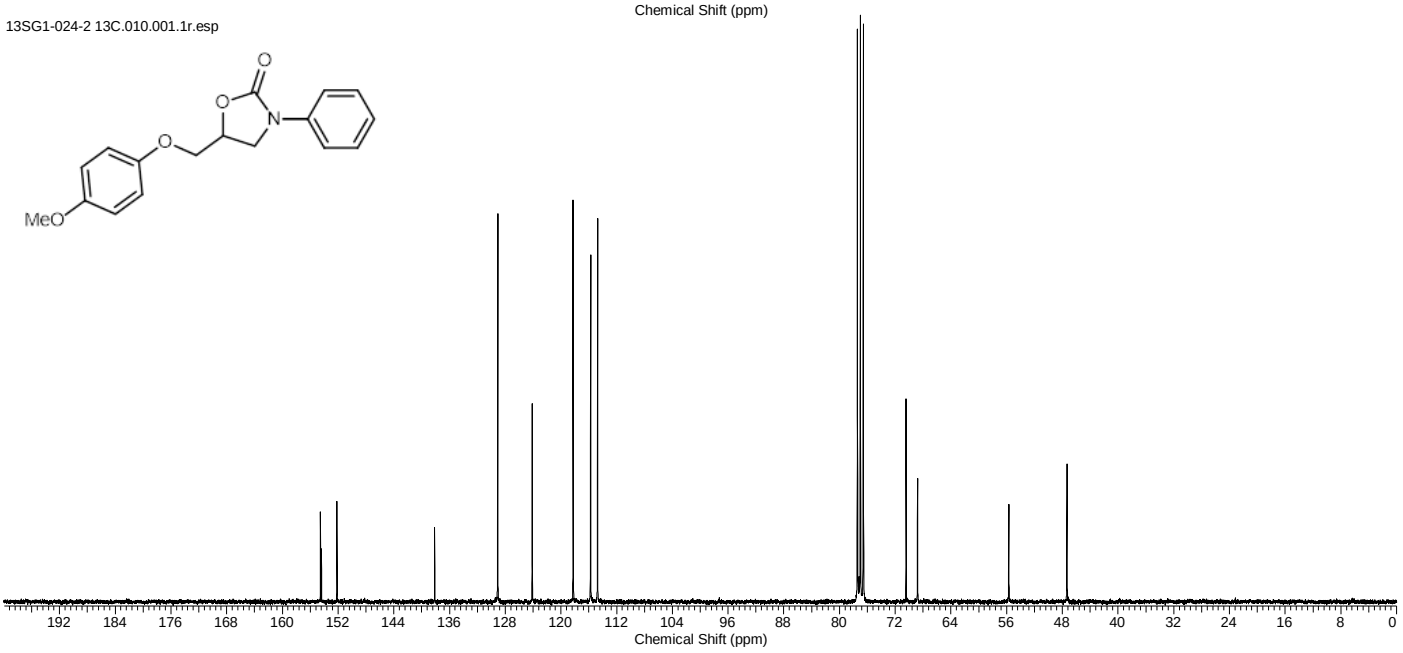
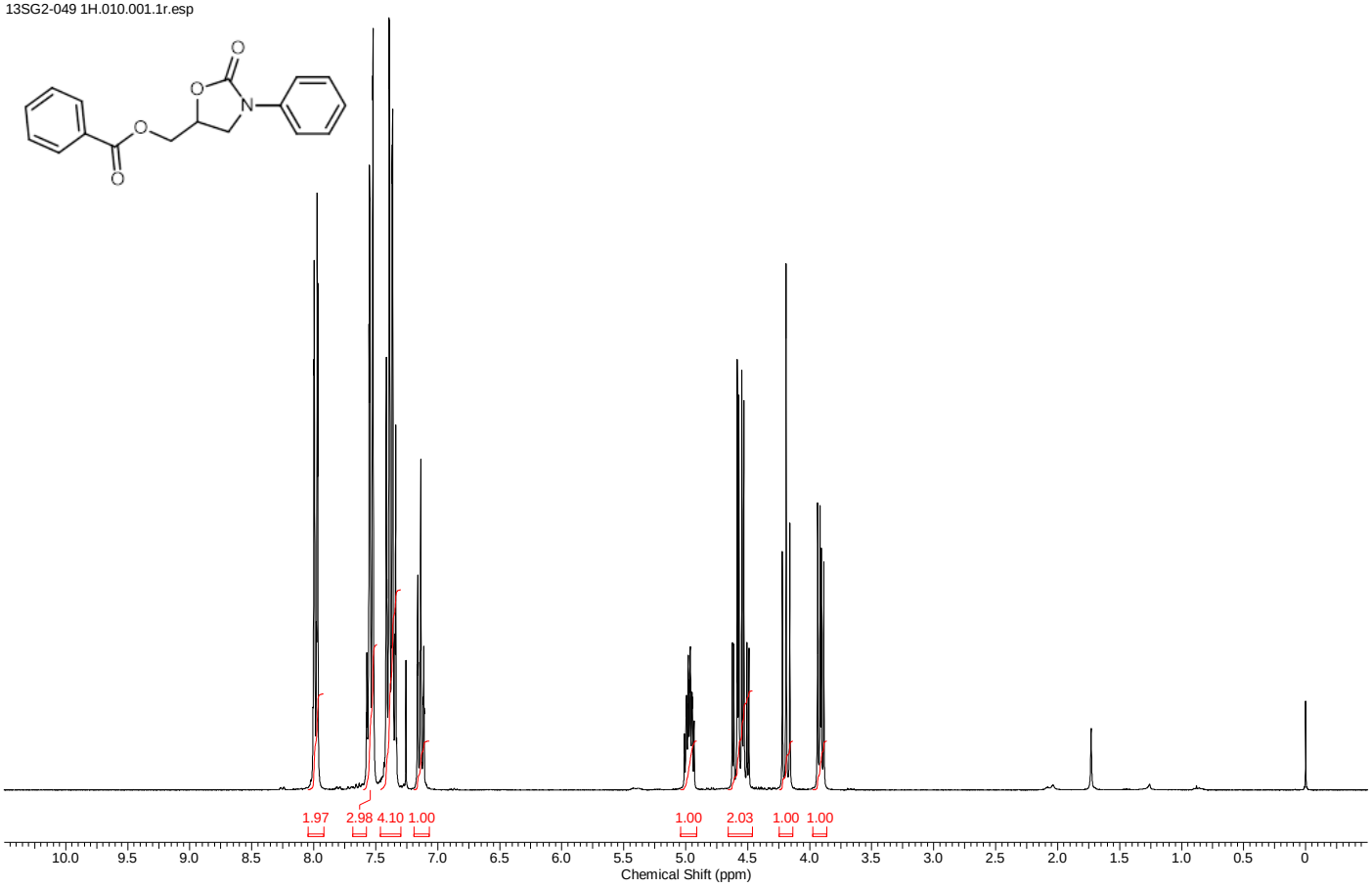


^{1}H & ^{13}C NMR Spectra of 4o

13SG2-049 1H.010.001.1r.esp



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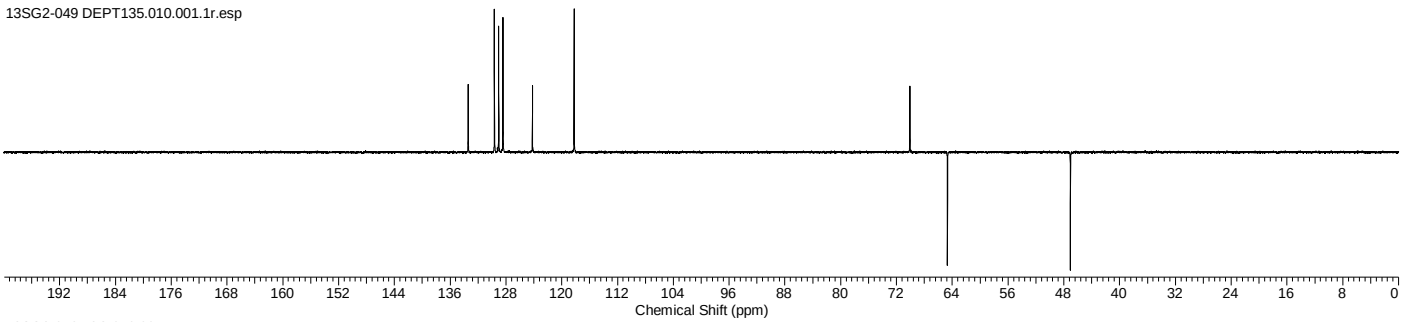

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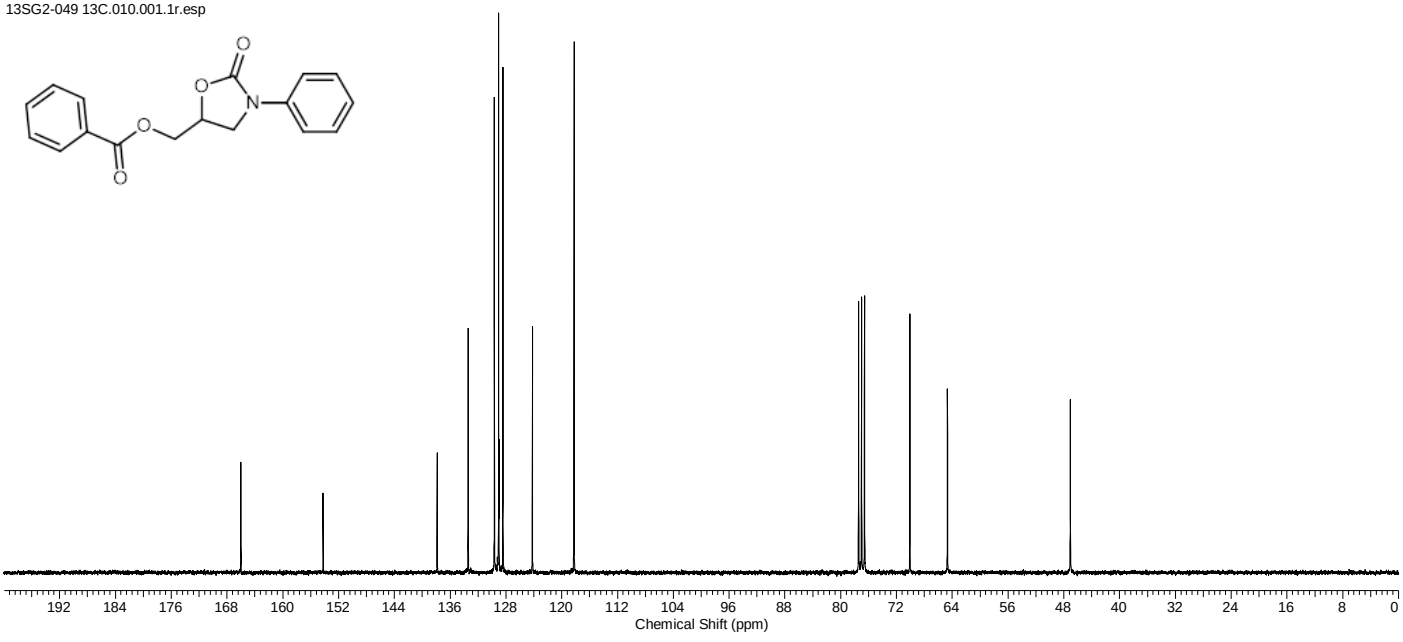
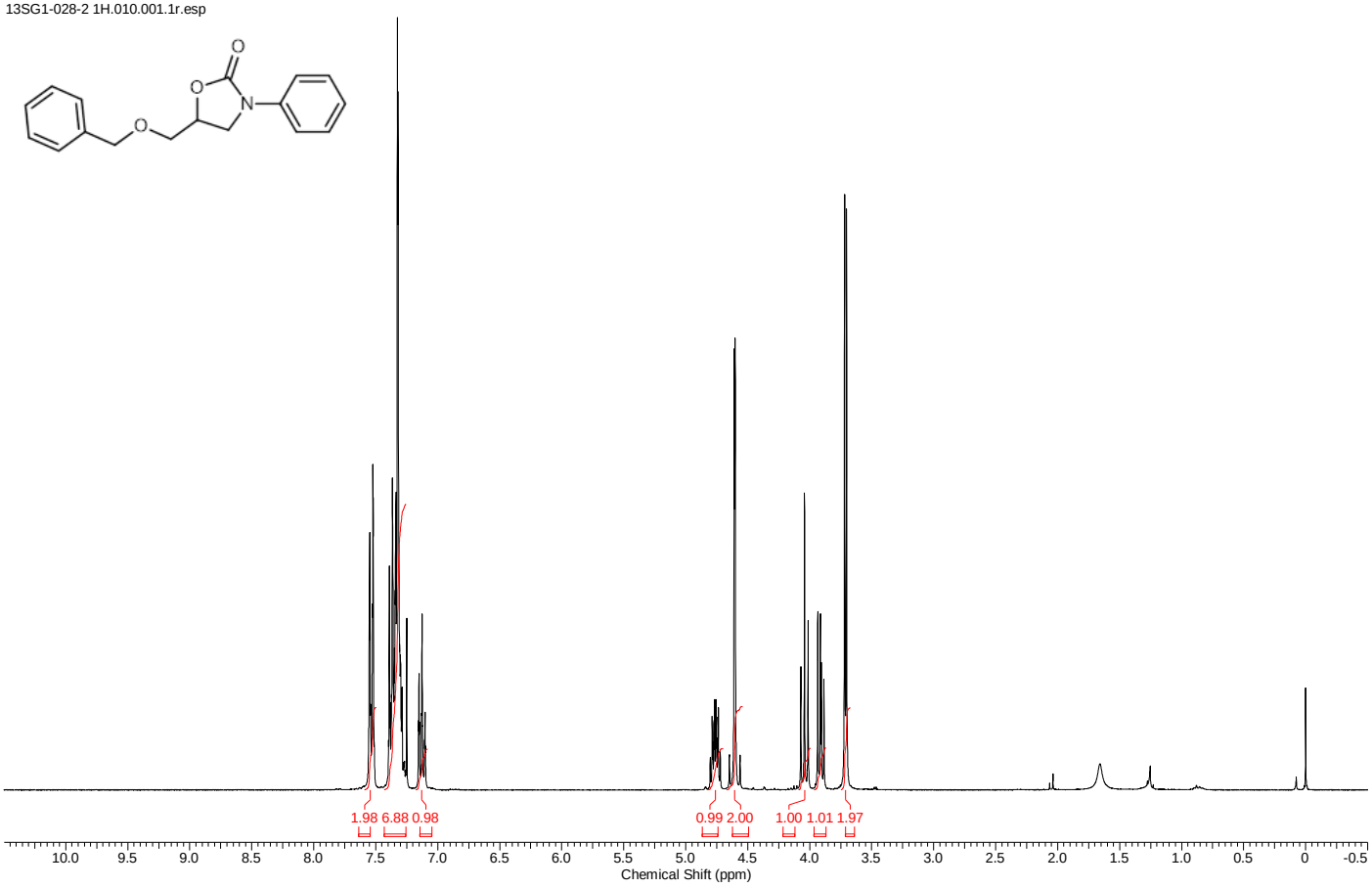


^{1}H & ^{13}C NMR Spectra of 4p

13SG1-028-2 1H.010.001.1r.esp



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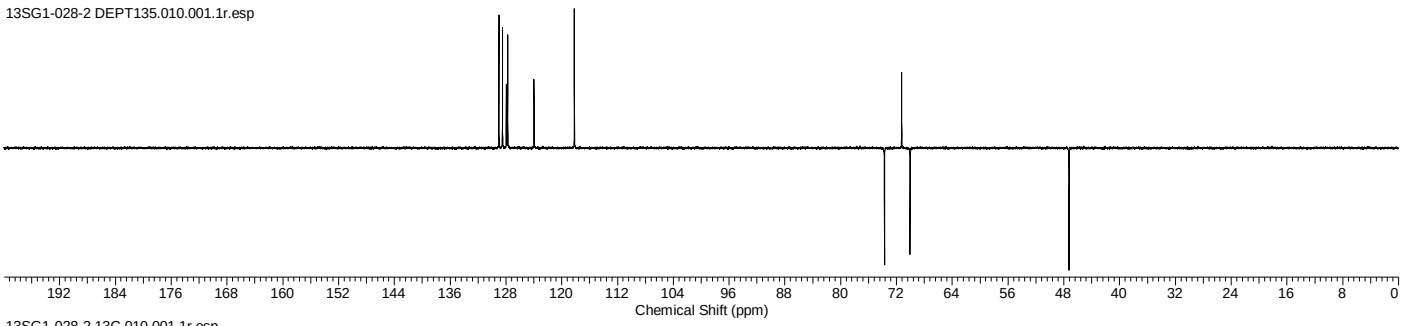

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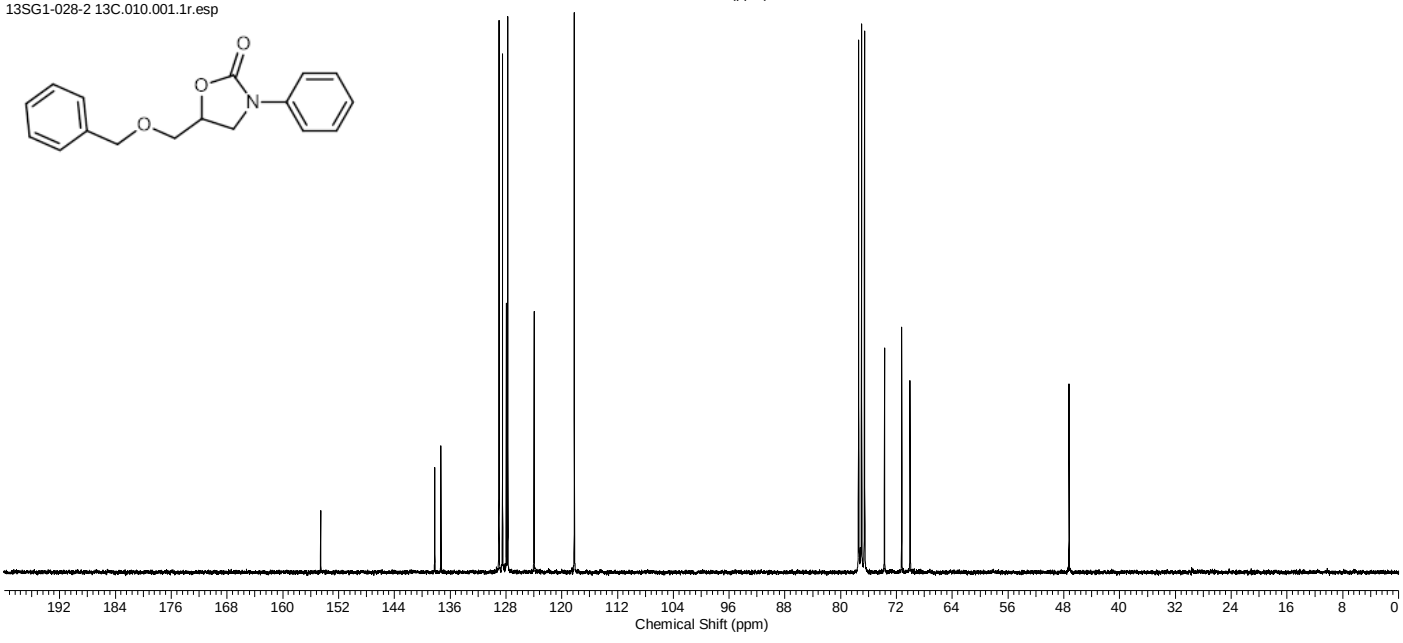
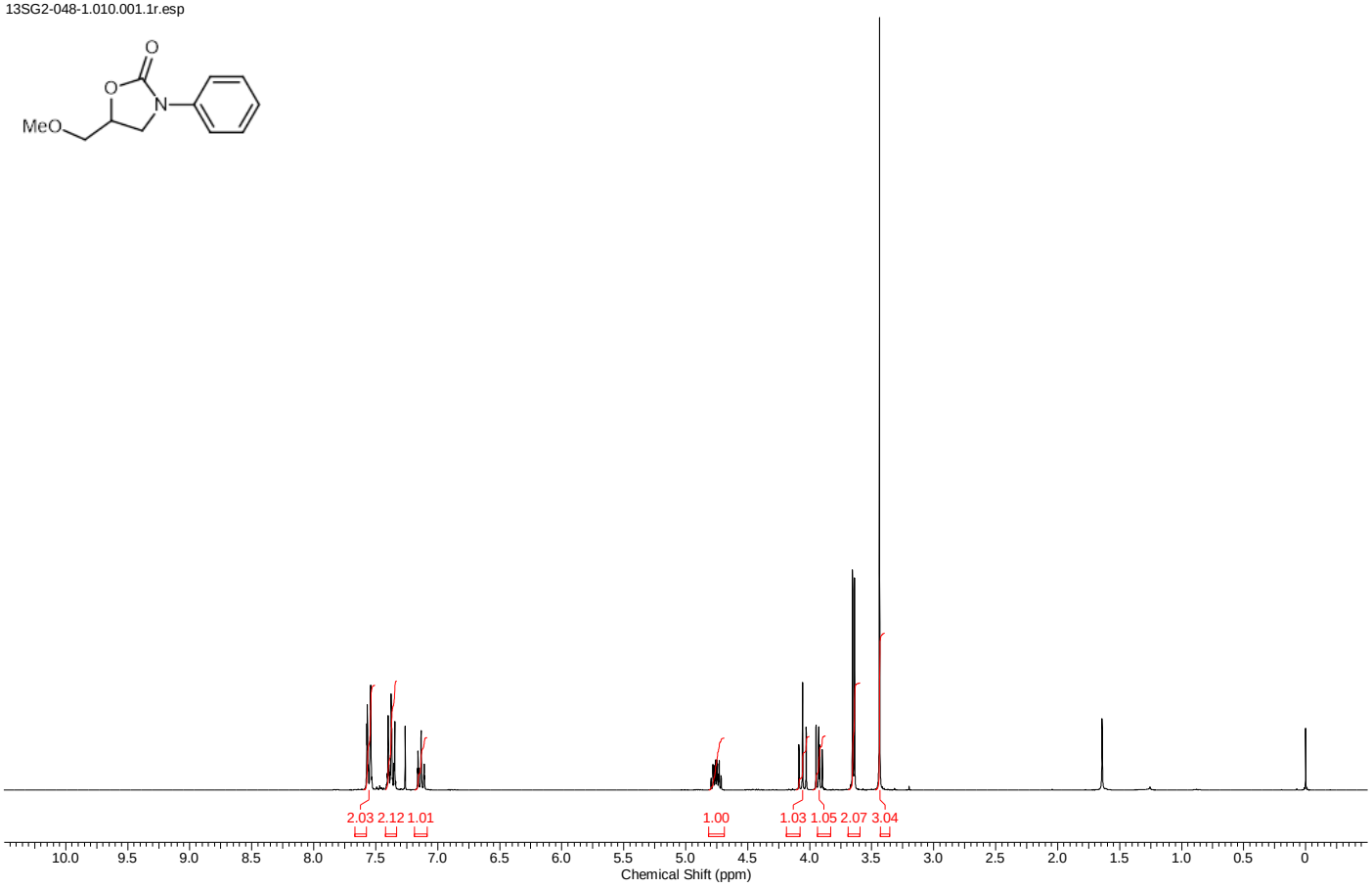


^{1}H & ^{13}C NMR Spectra of 4q

13SG2-048-1.010.001.1r.esp



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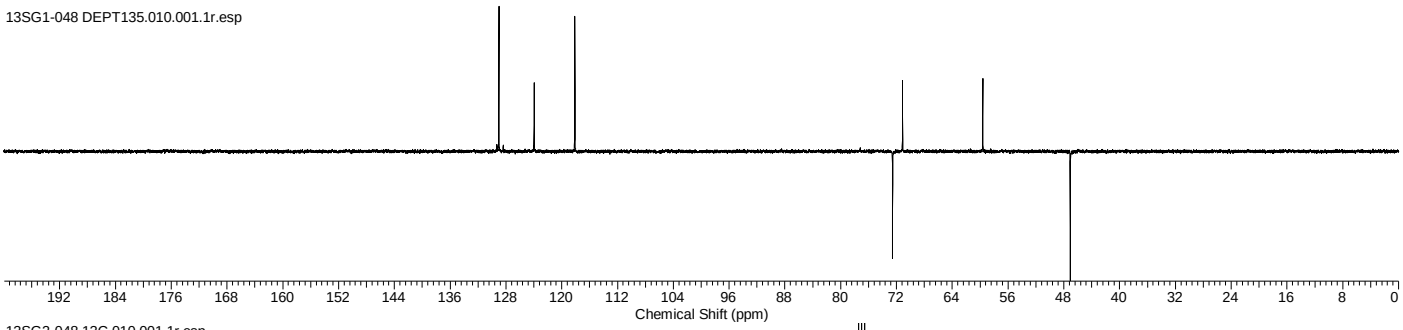

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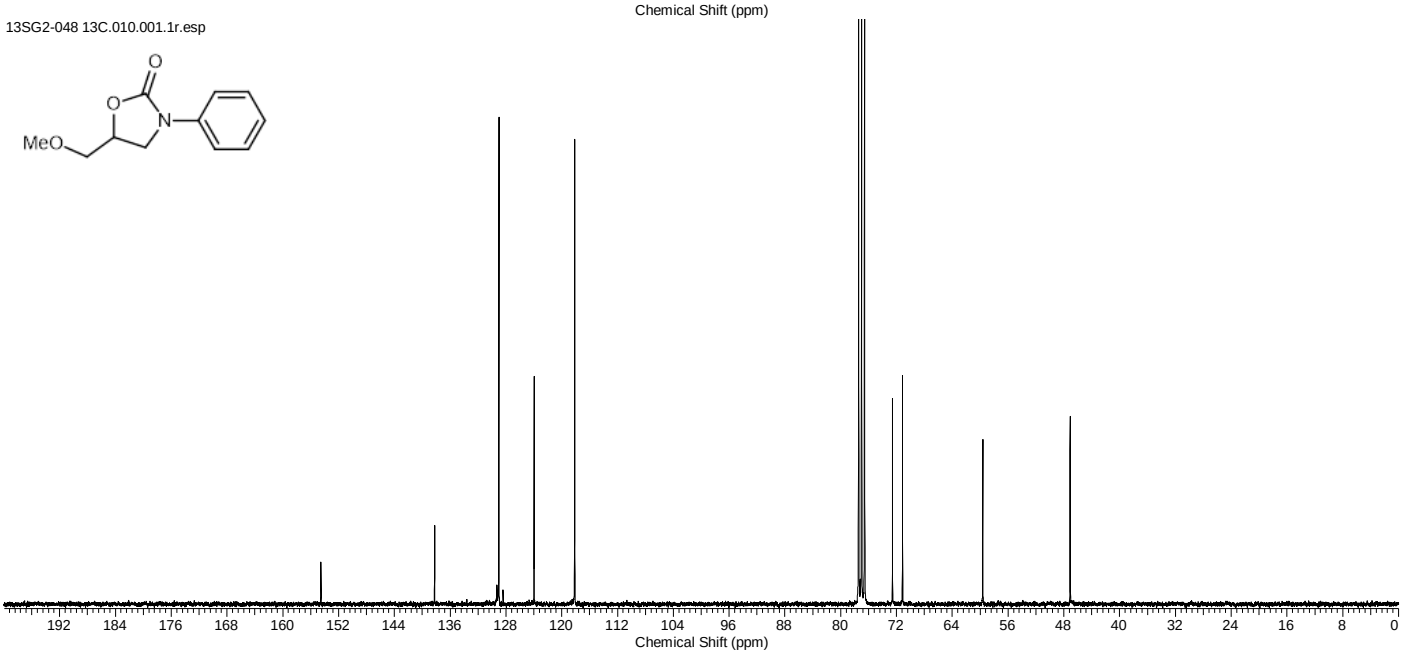
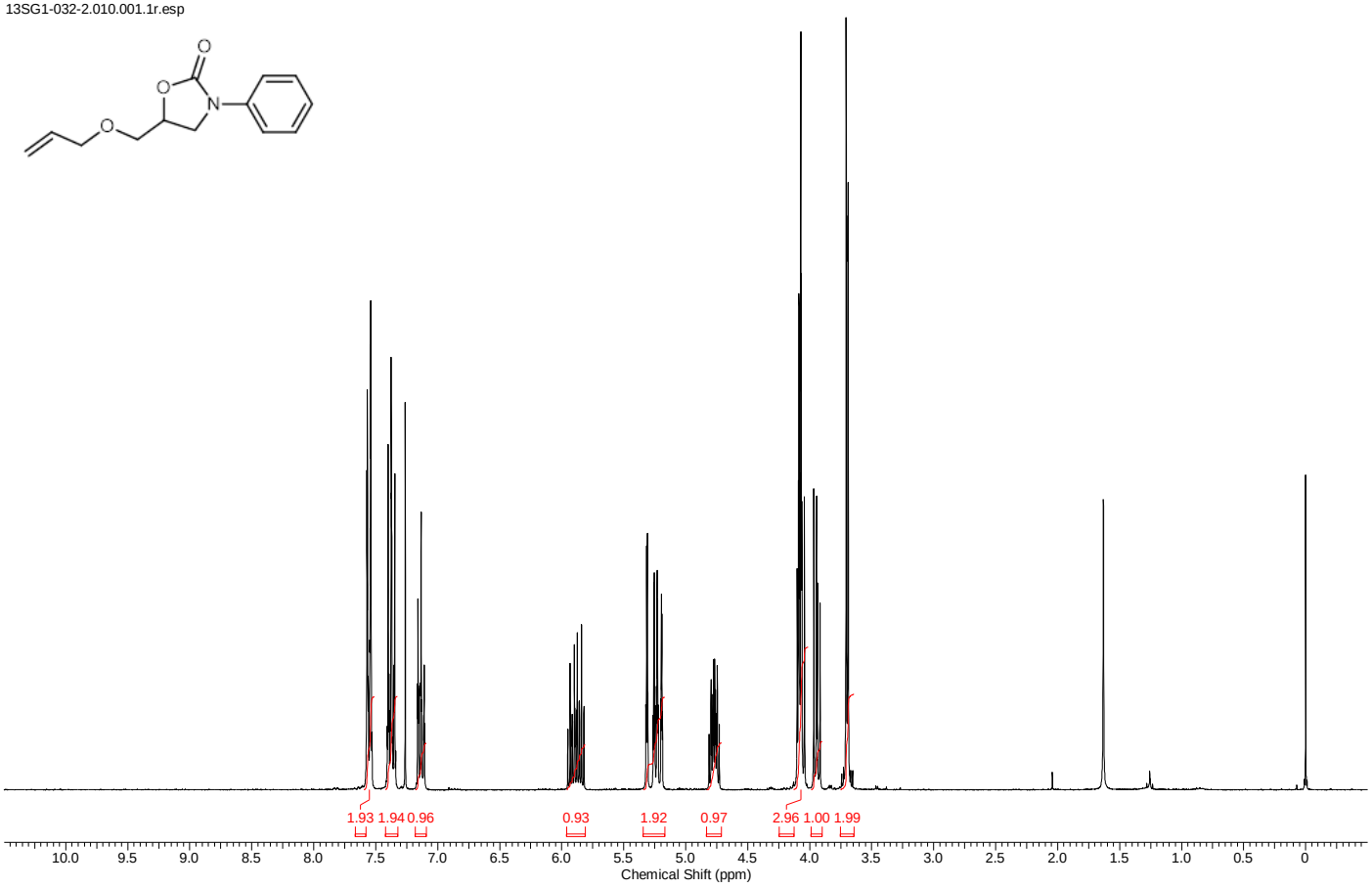


^{1}H & ^{13}C NMR Spectra of 4r

13SG1-032-2.010.001.1r.esp



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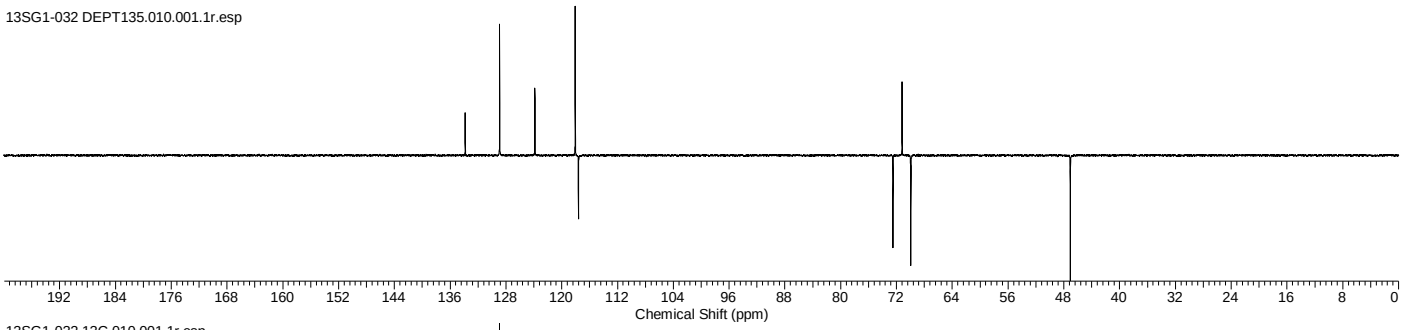

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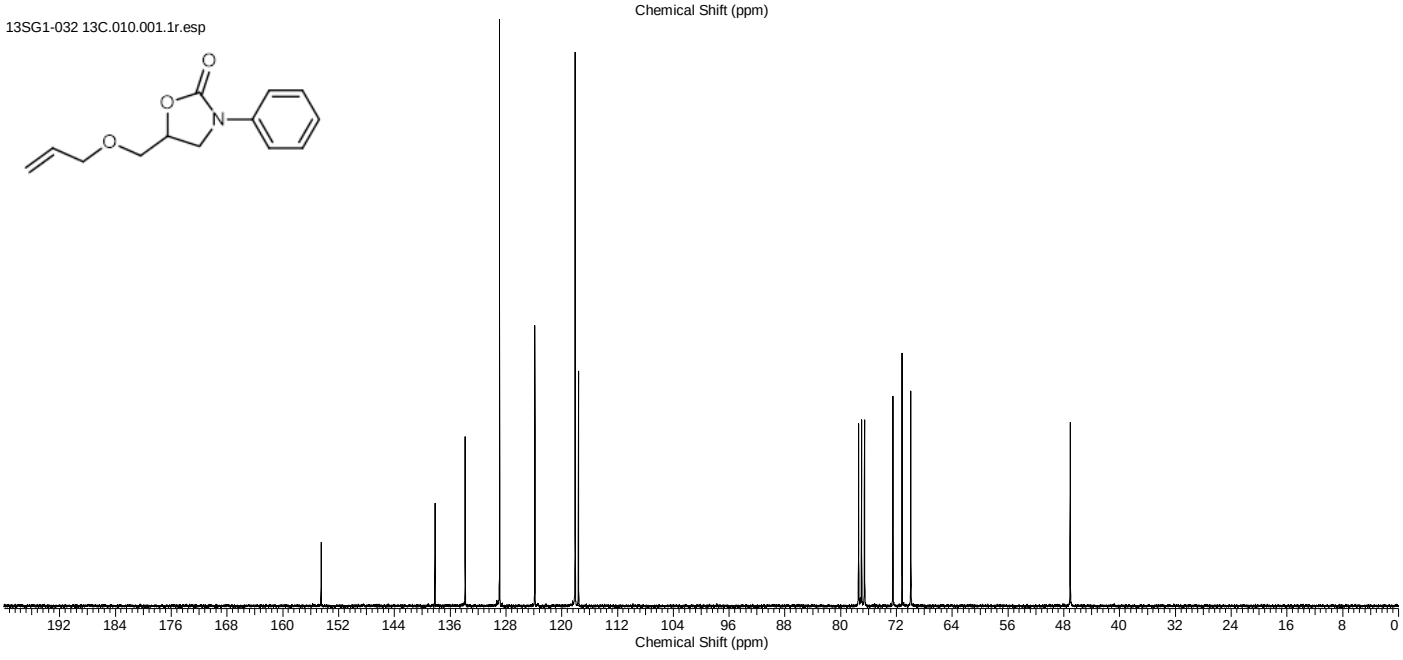
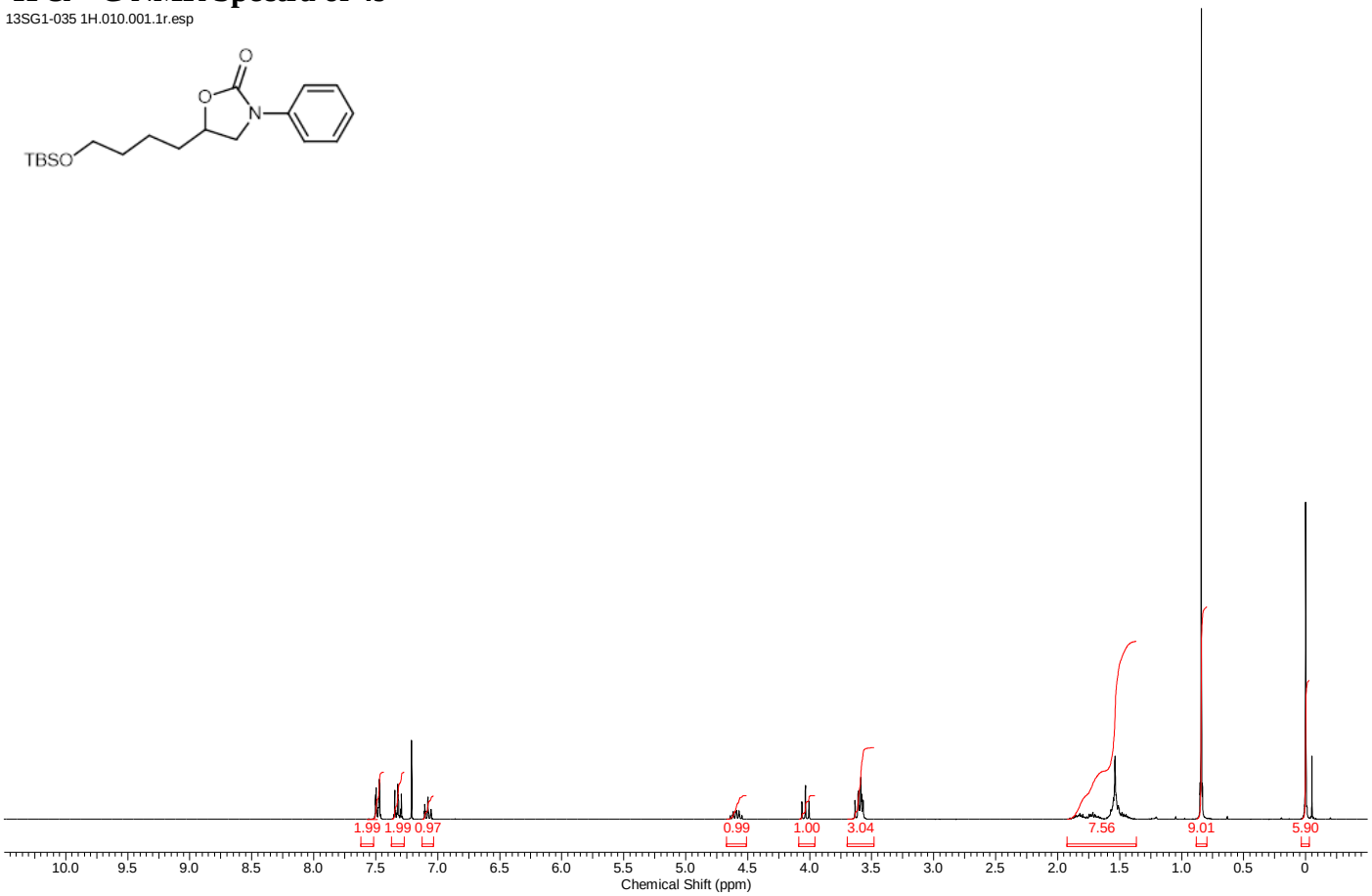


^{1}H & ^{13}C NMR Spectra of 4s

13SG1-035 1H.010.001.1r.esp



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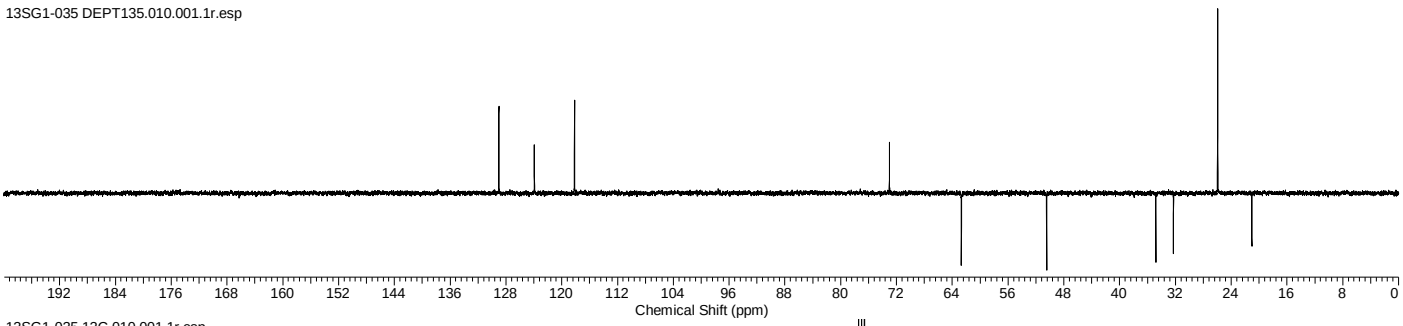
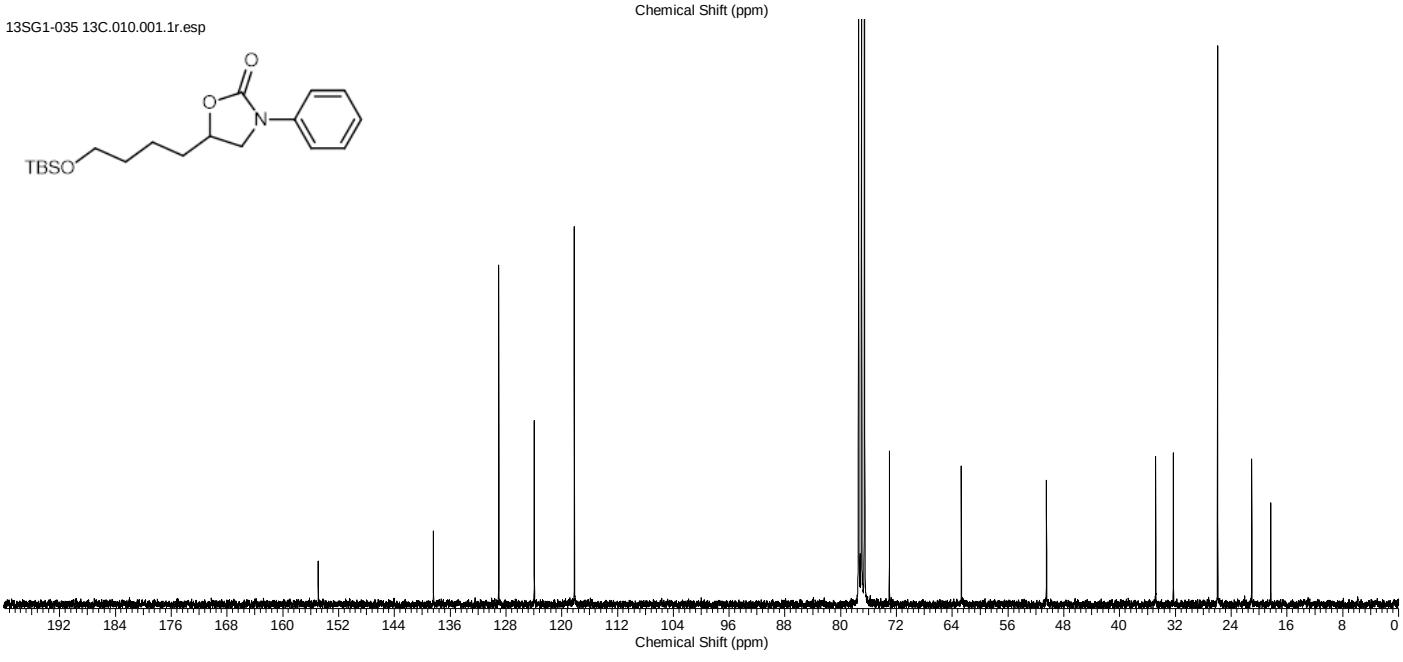
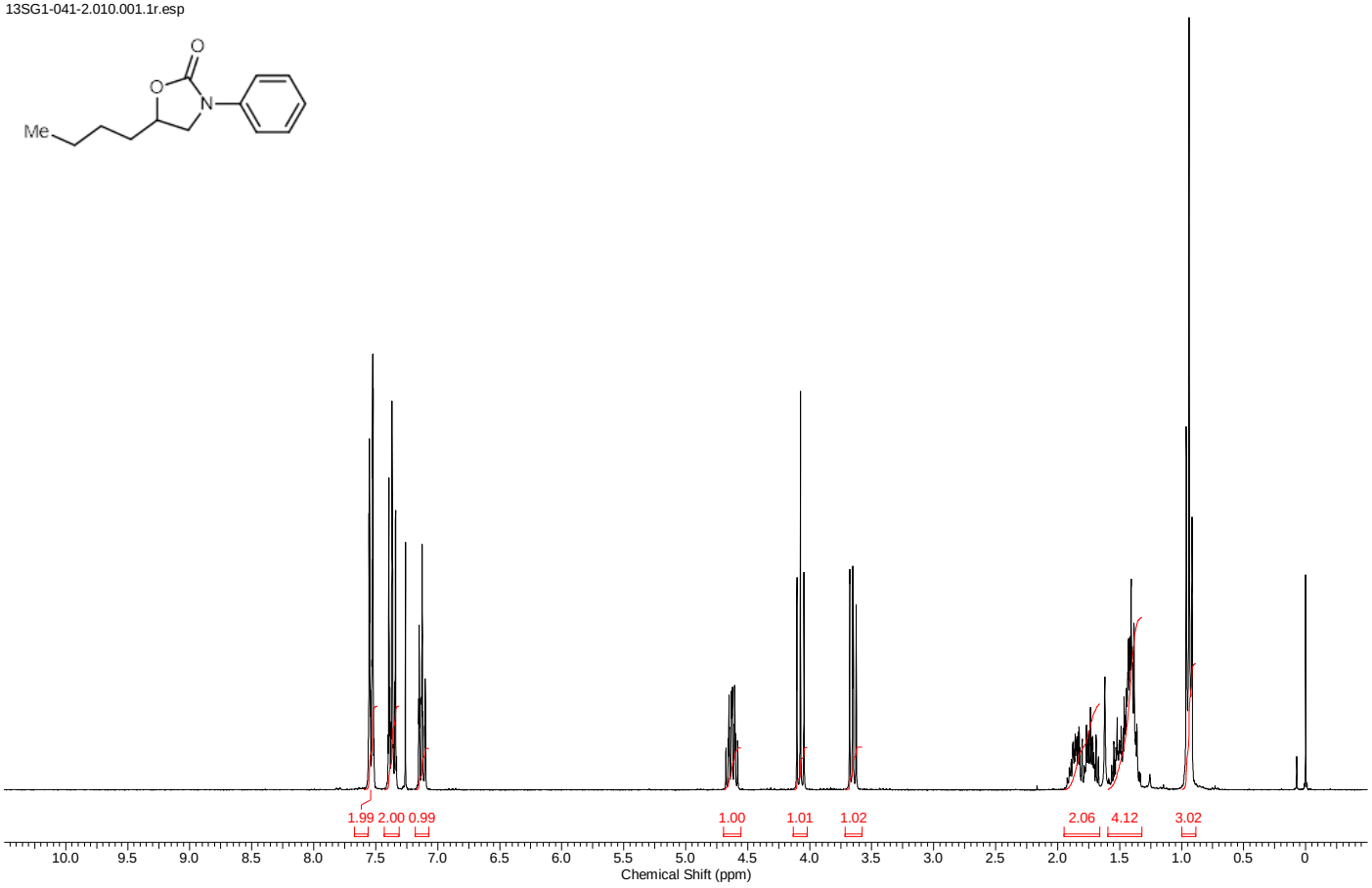


13SG1-035 13C.010.001.1r.esp



^{1}H & ^{13}C NMR Spectra of 4t

13SG1-041-2.010.001.1r.esp



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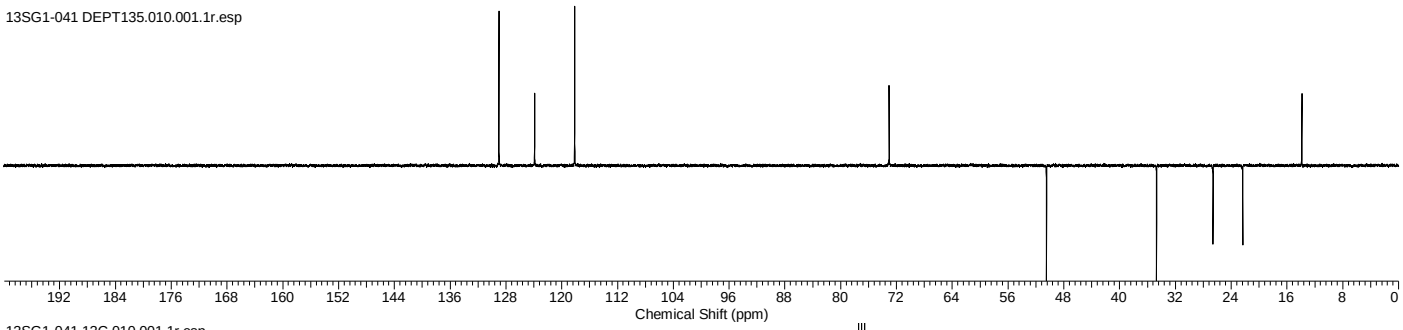

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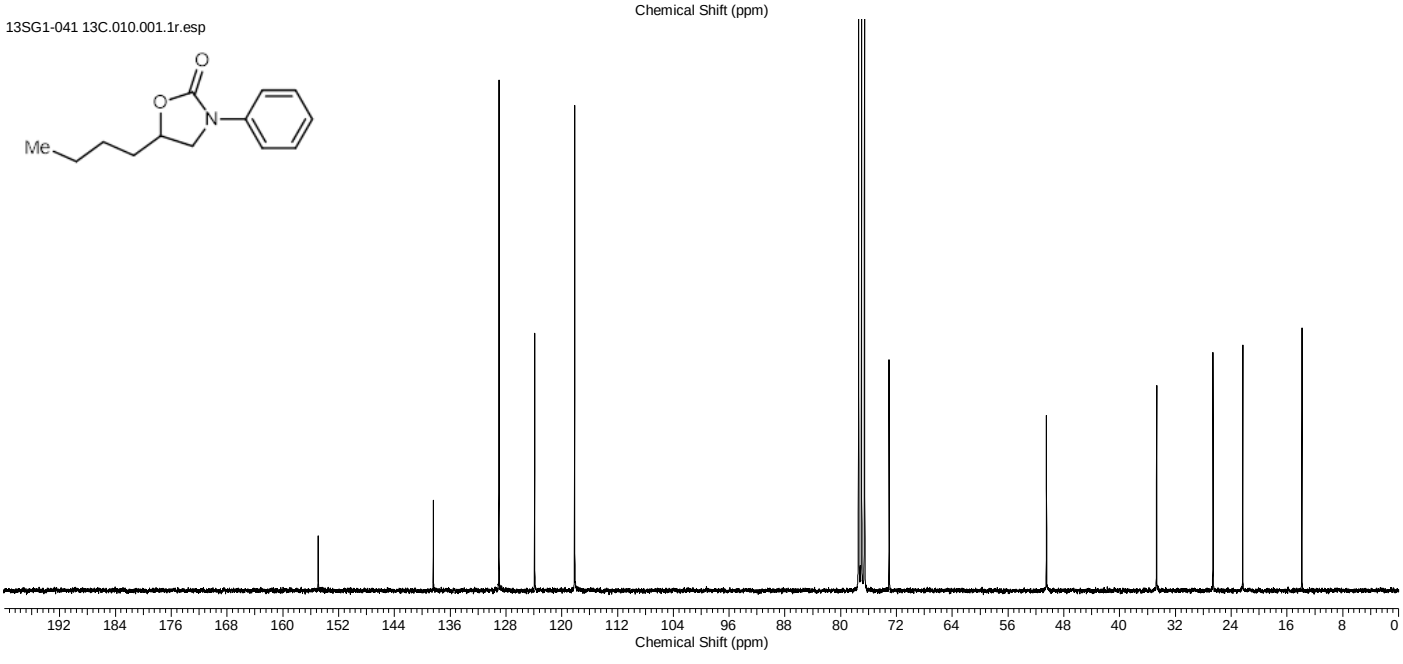
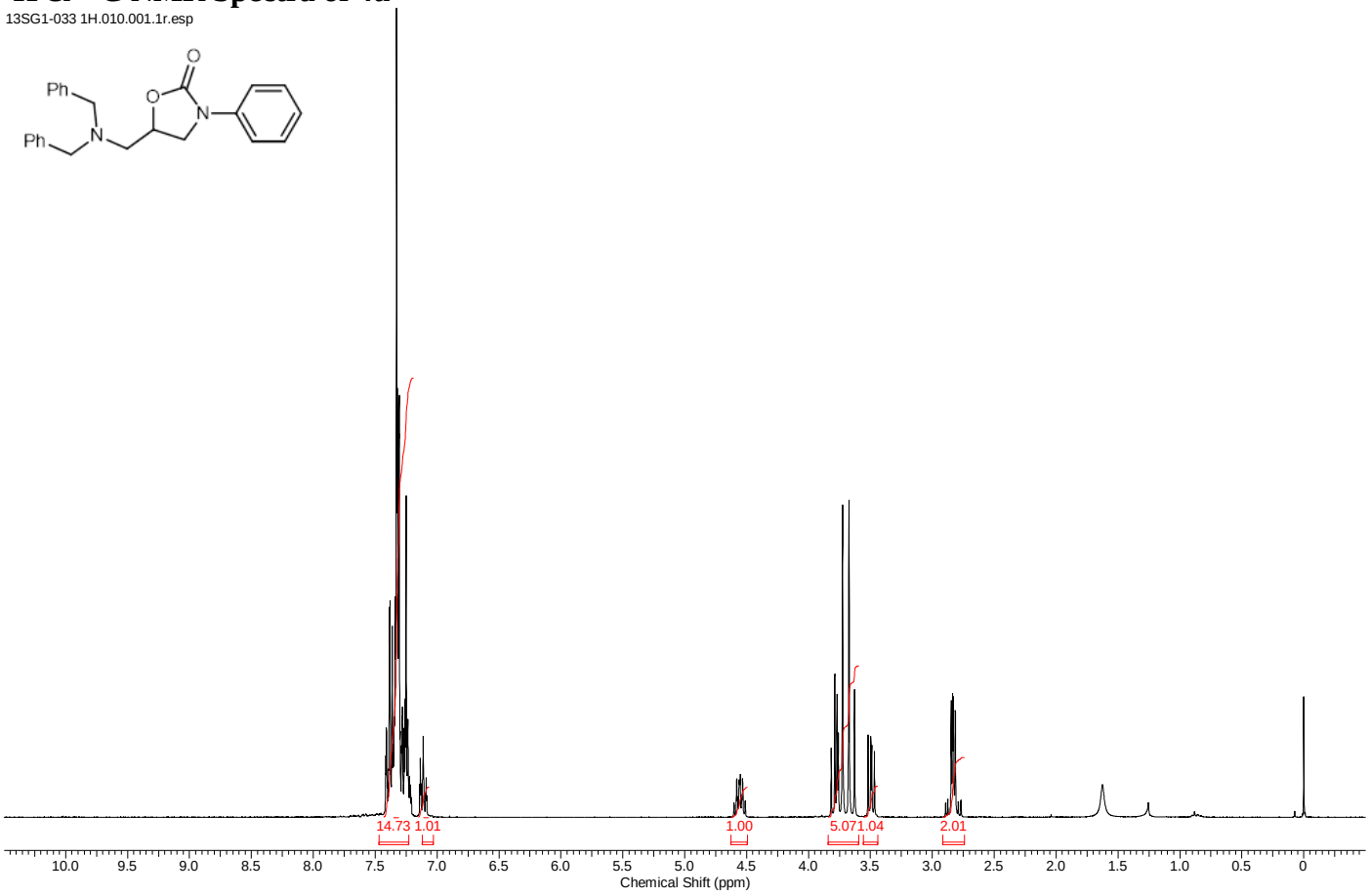
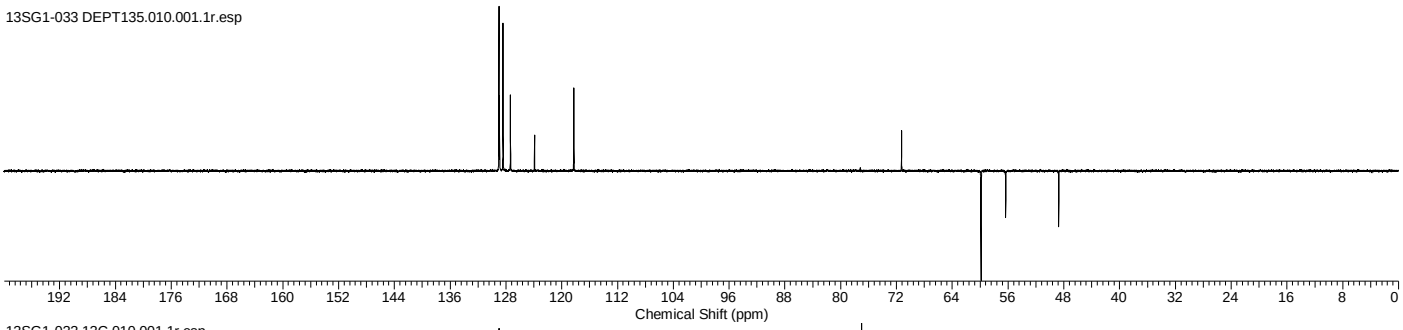


^{1}H & ^{13}C NMR Spectra of 4u

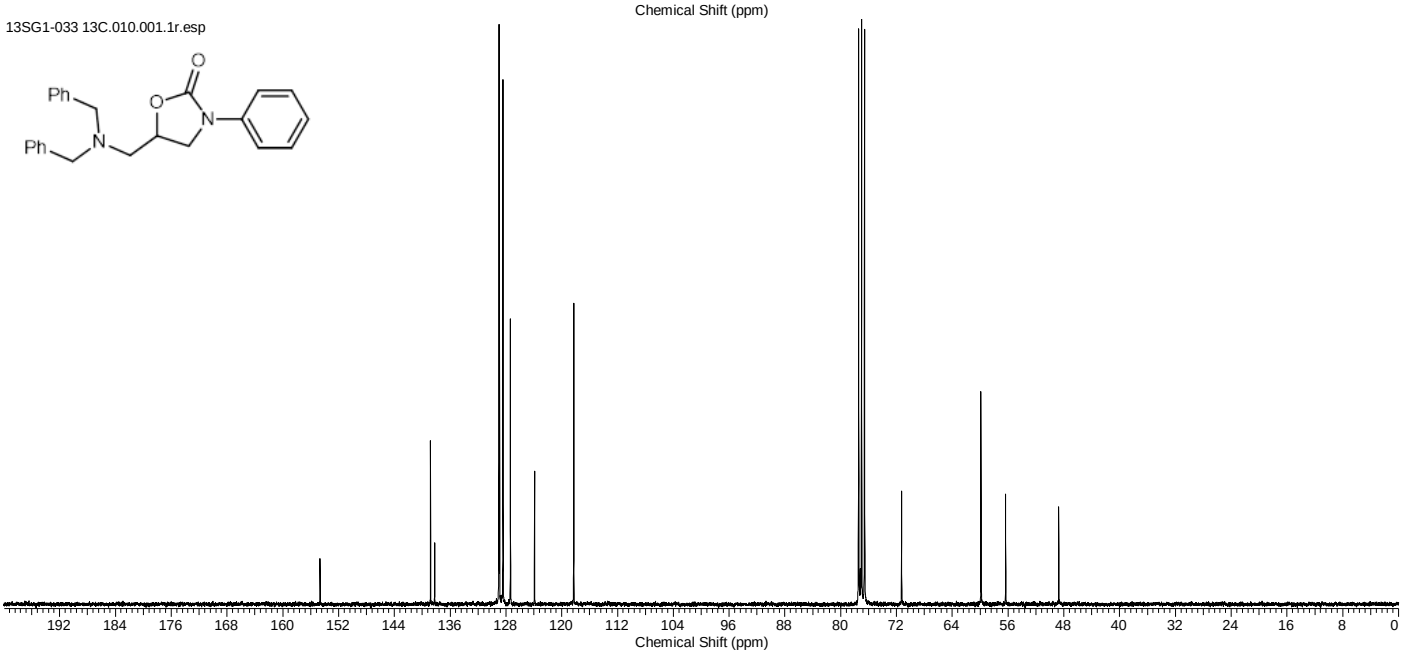
13SG1-033 1H.010.001.1r.esp



13SG1-033 DEPT135.010.001.1r.esp

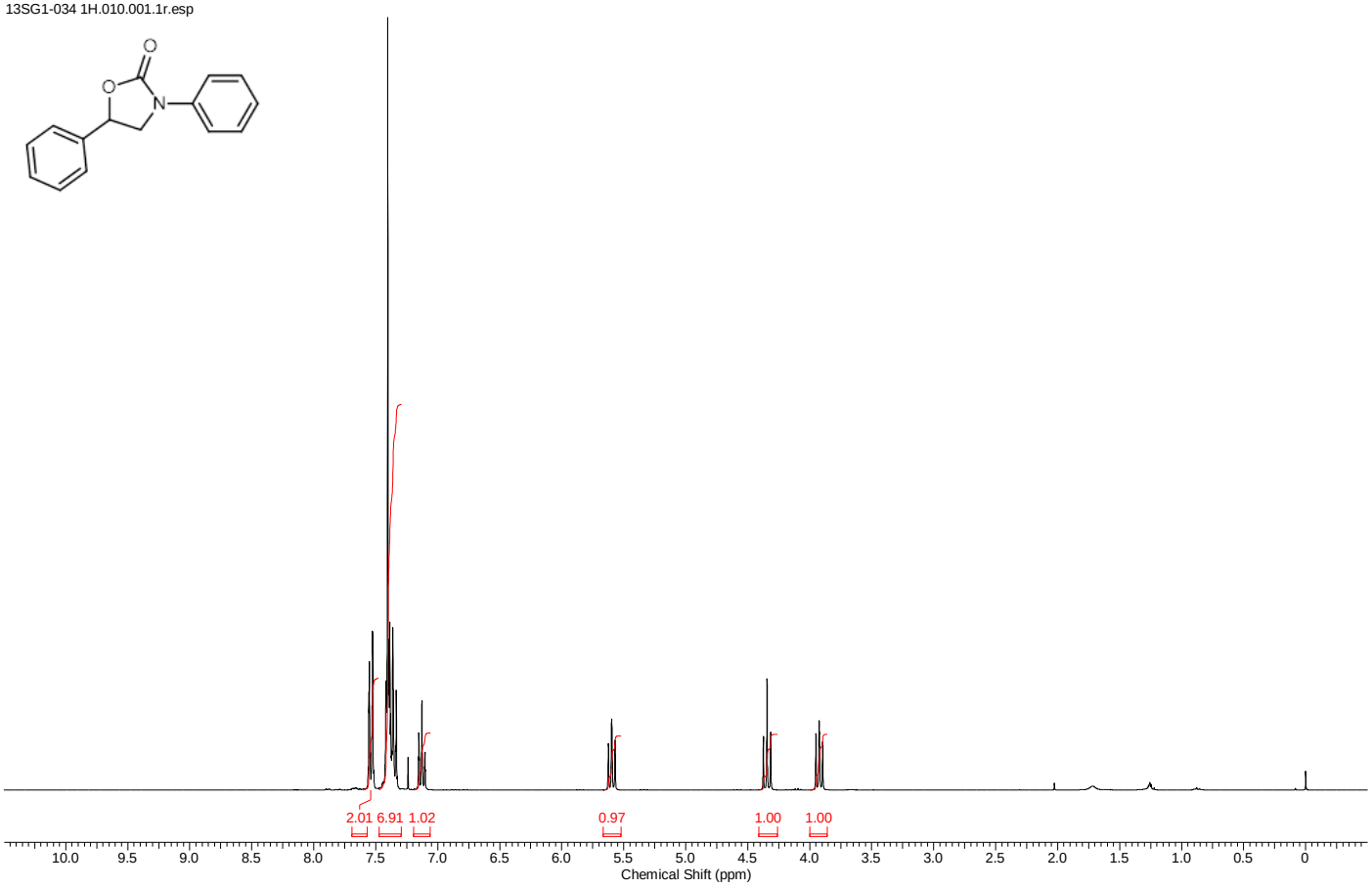


13SG1-033 13C.010.001.1r.esp

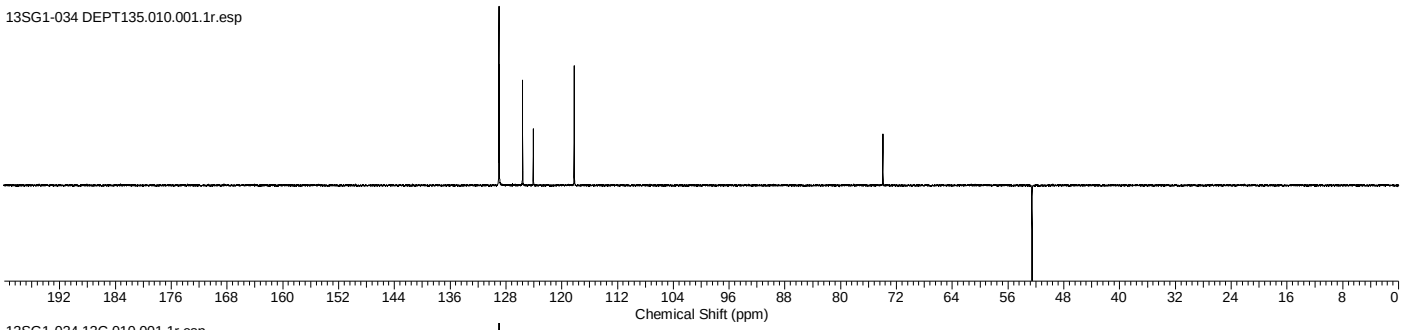


^{1}H & ^{13}C NMR Spectra of 4v

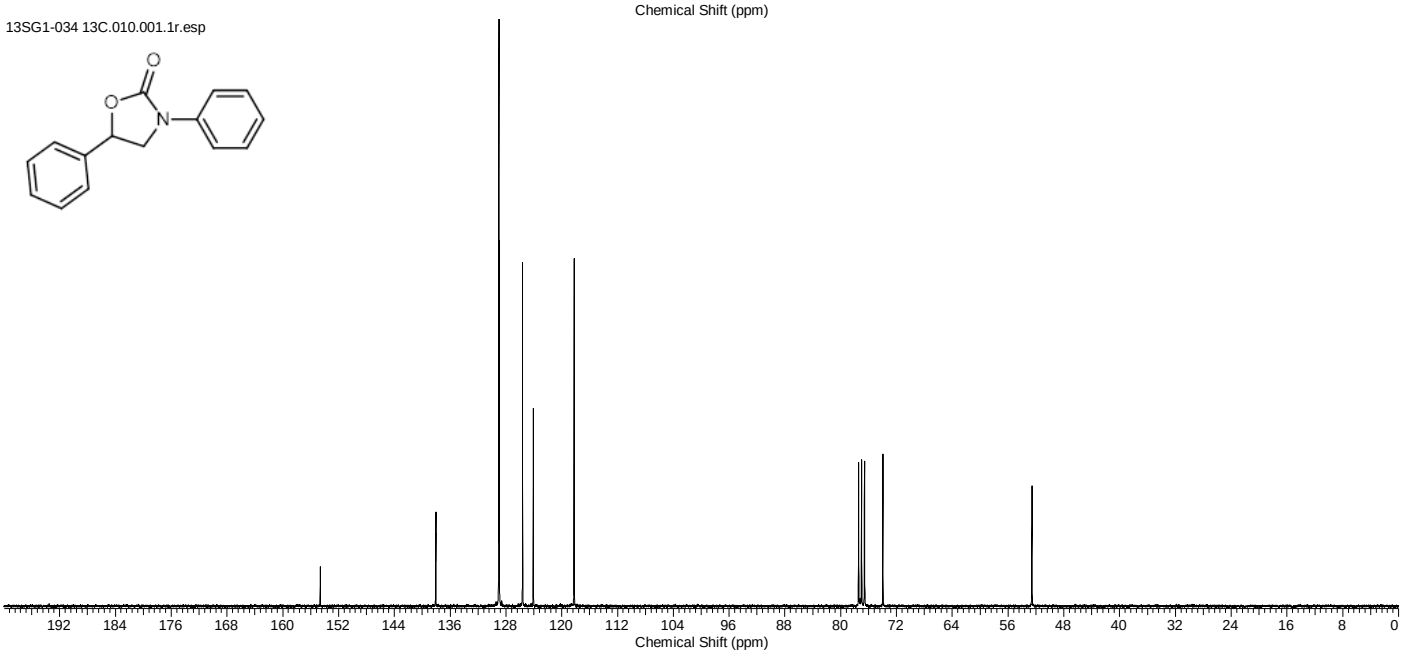
13SG1-034 1H.010.001.1r.esp



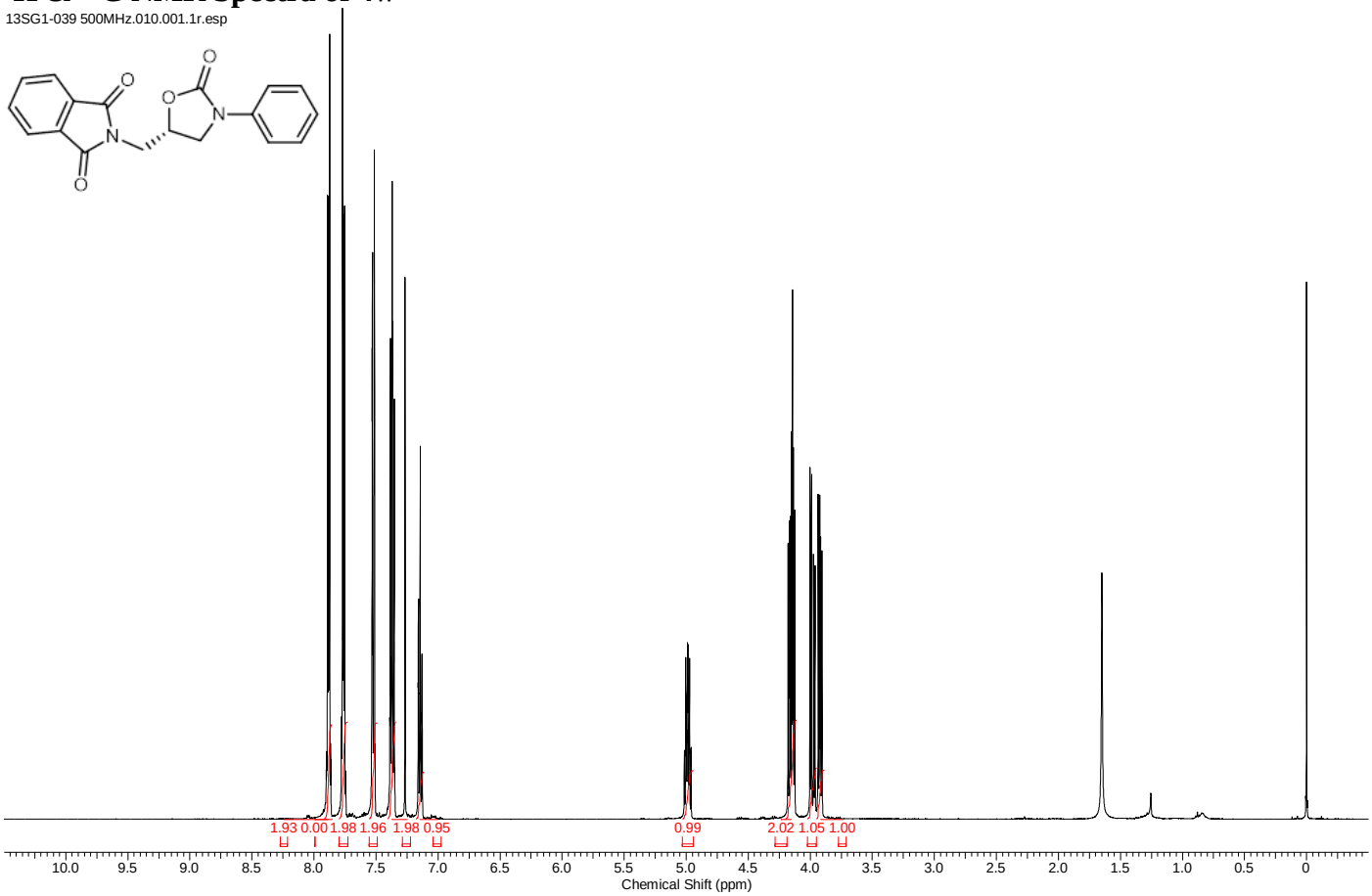
13SG1-034 DEPT135.010.001.1r.esp

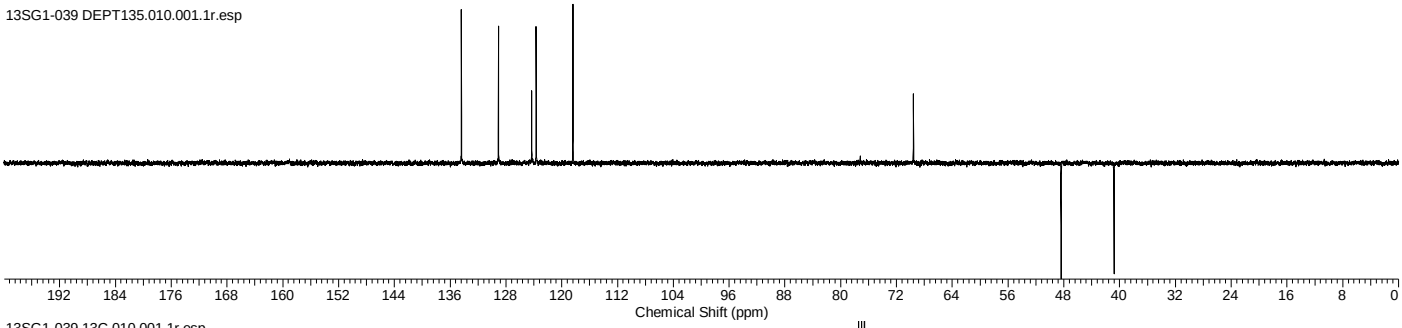


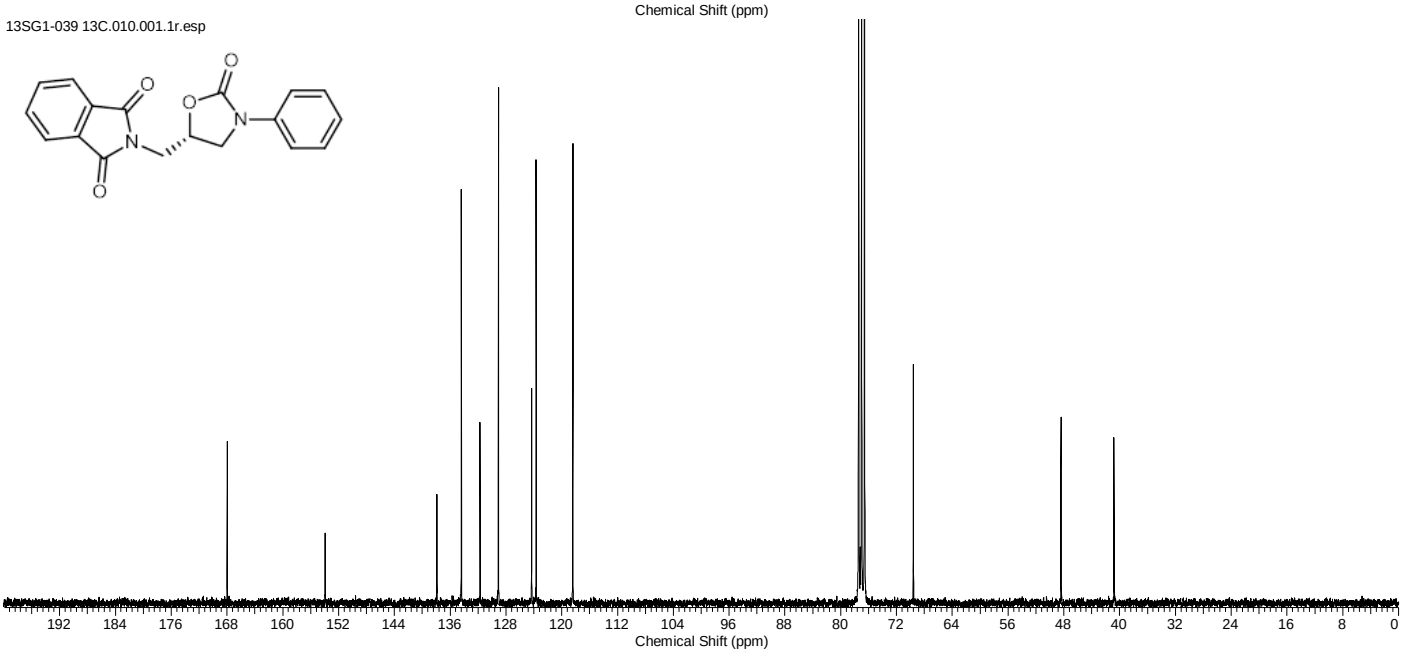
13SG1-034 13C.010.001.1r.esp



^{1}H & ^{13}C NMR Spectra of 4w

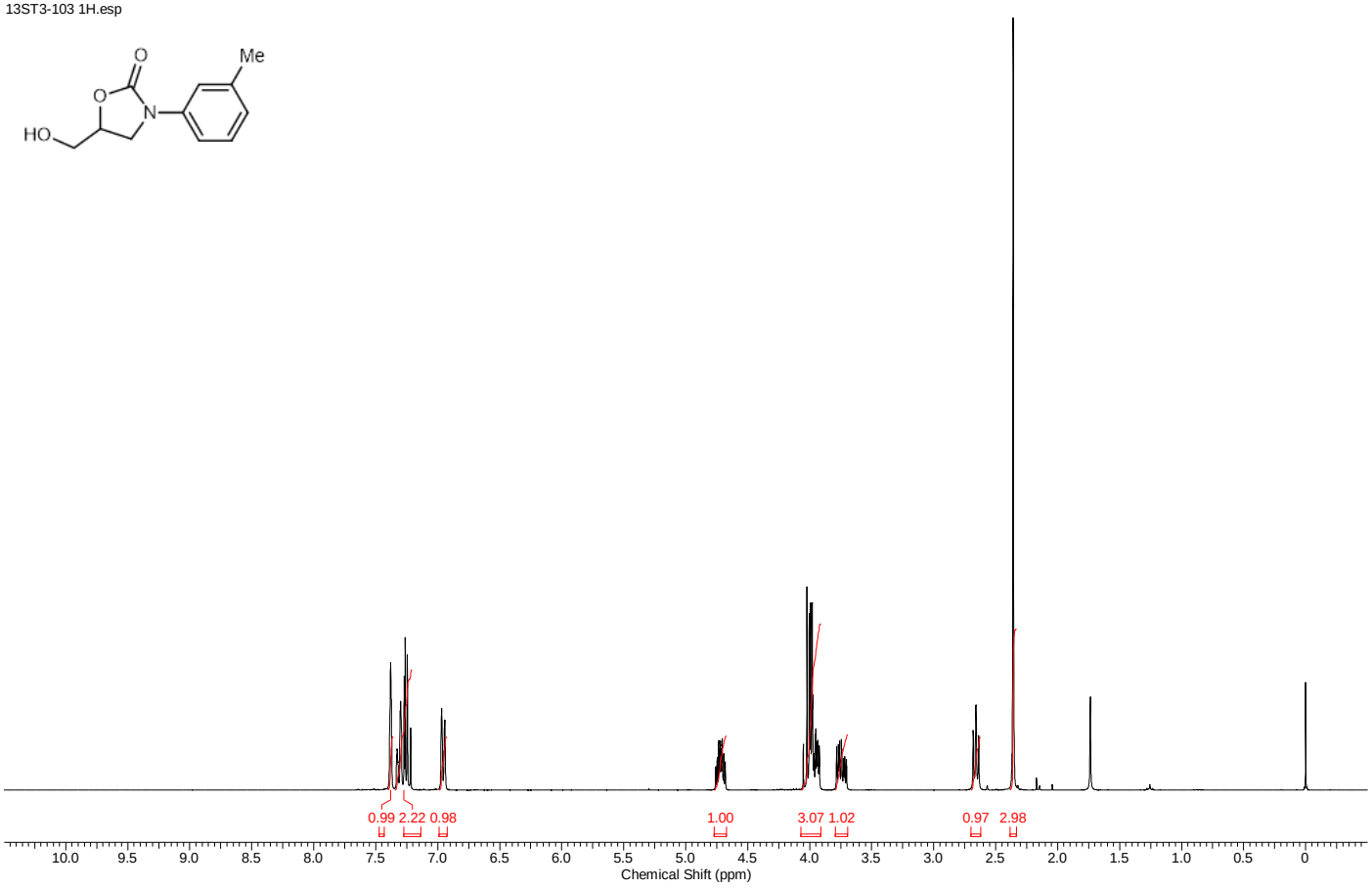




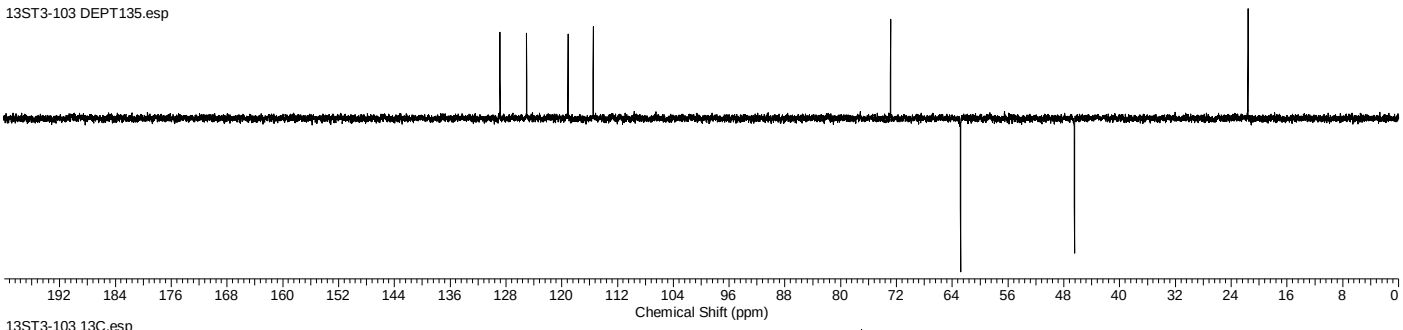


^{1}H & ^{13}C NMR Spectra of 4x

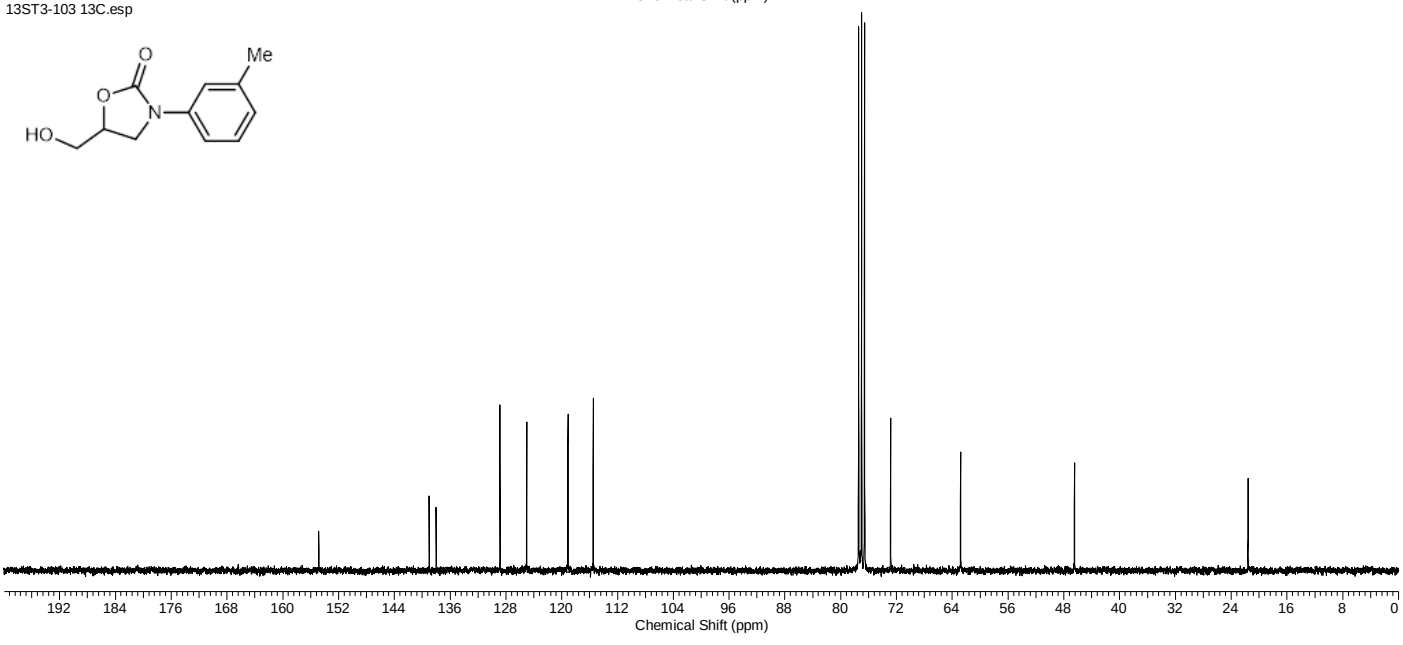
13ST3-103 1H.esp



13ST3-103 DEPT135.esp

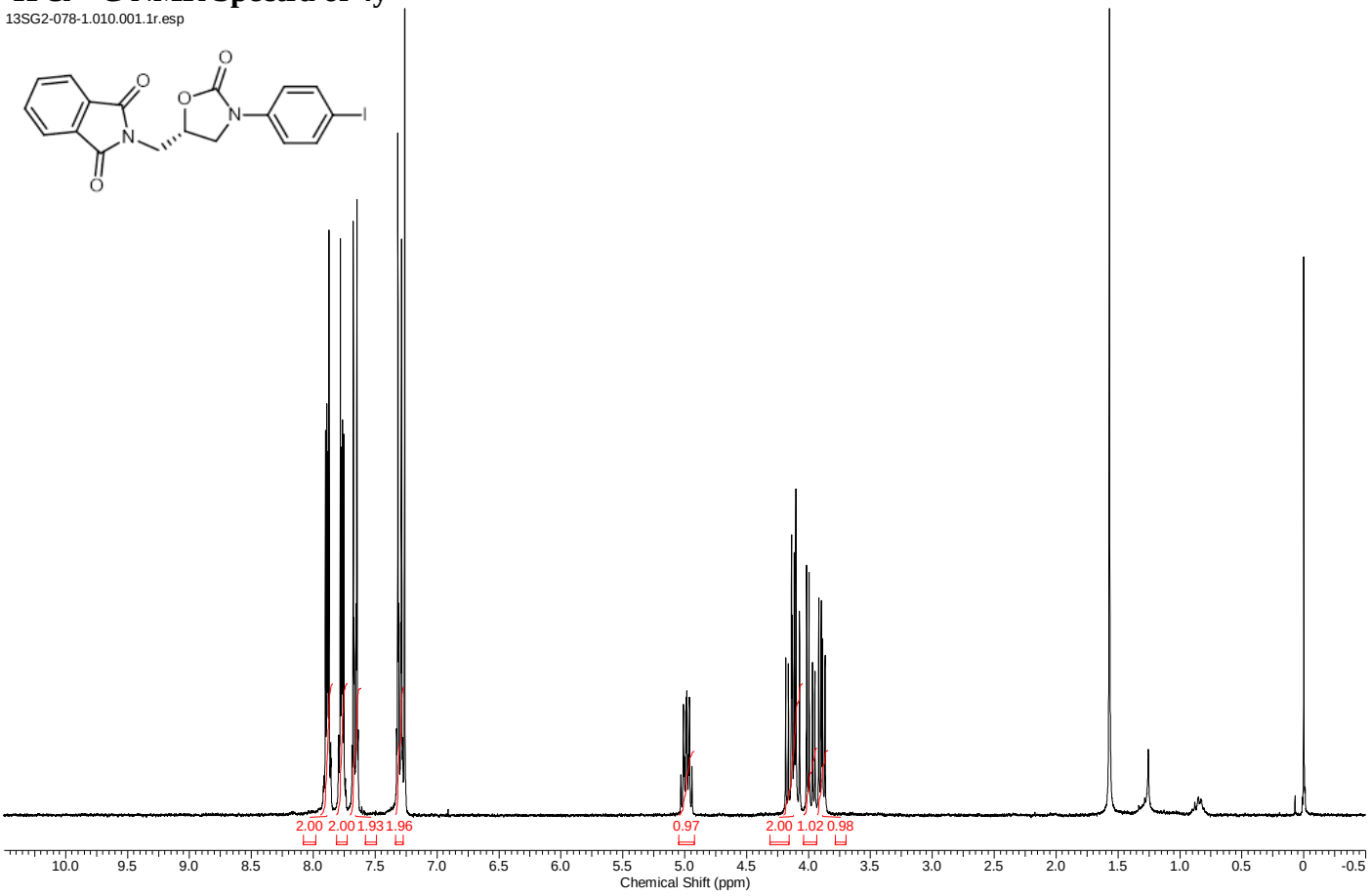


13ST3-103 13C.esp

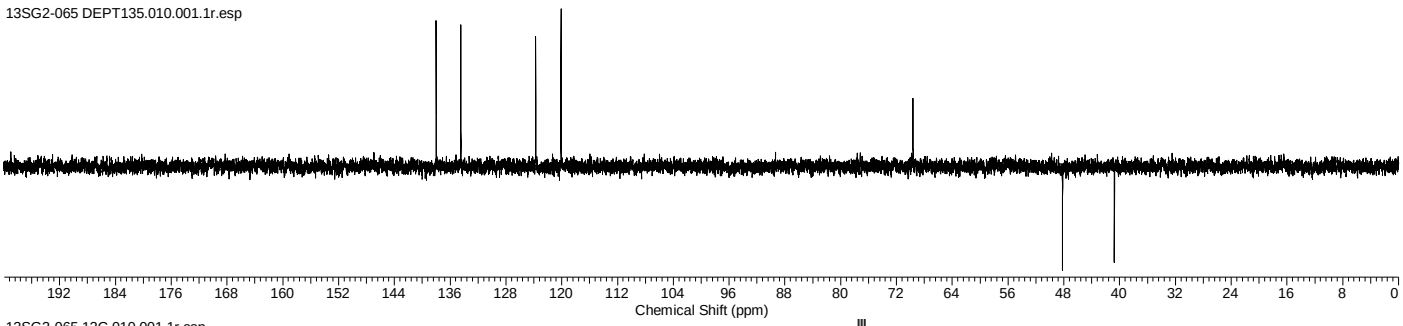


^{1}H & ^{13}C NMR Spectra of 4y

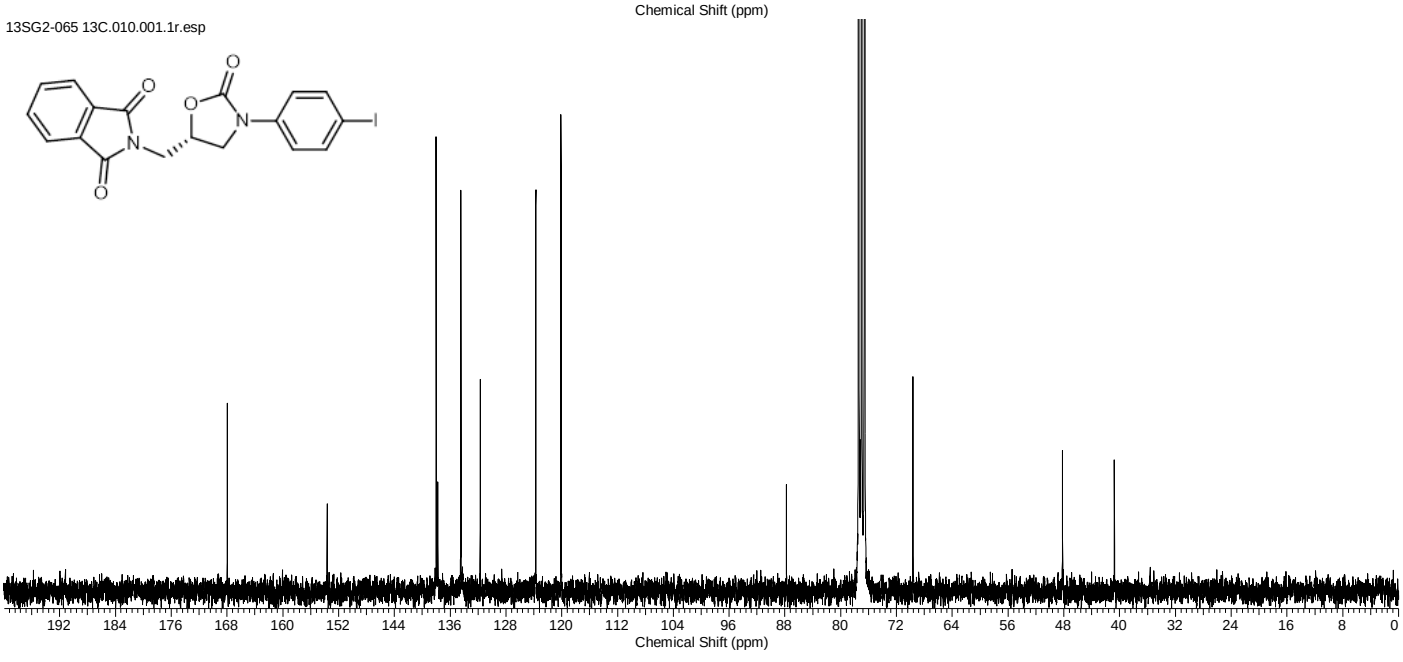
13SG2-078-1.010.001.1r.esp



13SG2-065 DEPT135.010.001.1r.esp

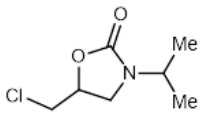


13SG2-065 13C.010.001.1r.esp

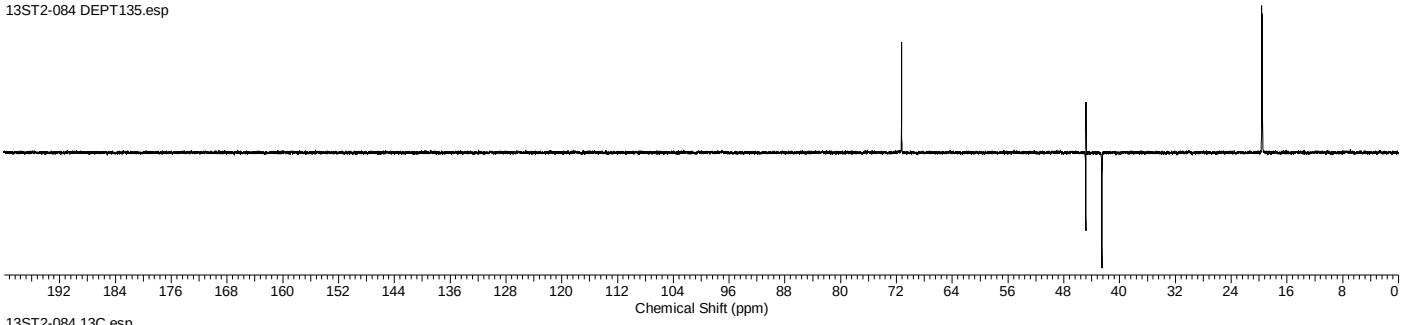


^{1}H & ^{13}C NMR Spectra of 6a

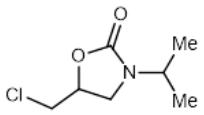
13ST2-084 1H.esp



13ST2-084 DEPT135.esp

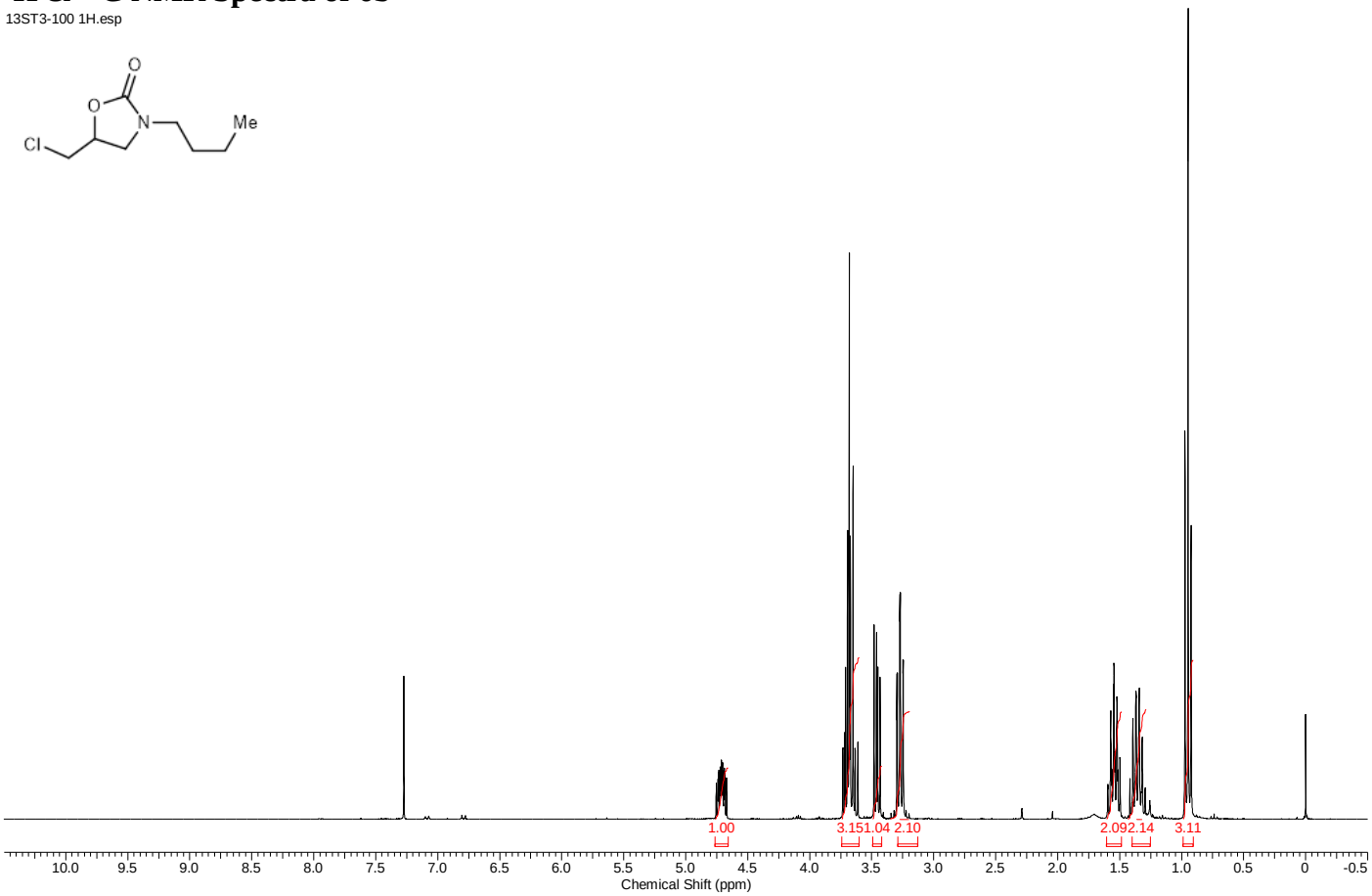


13ST2-084 13C.esp



^{1}H & ^{13}C NMR Spectra of 6b

13ST3-100 1H.esp



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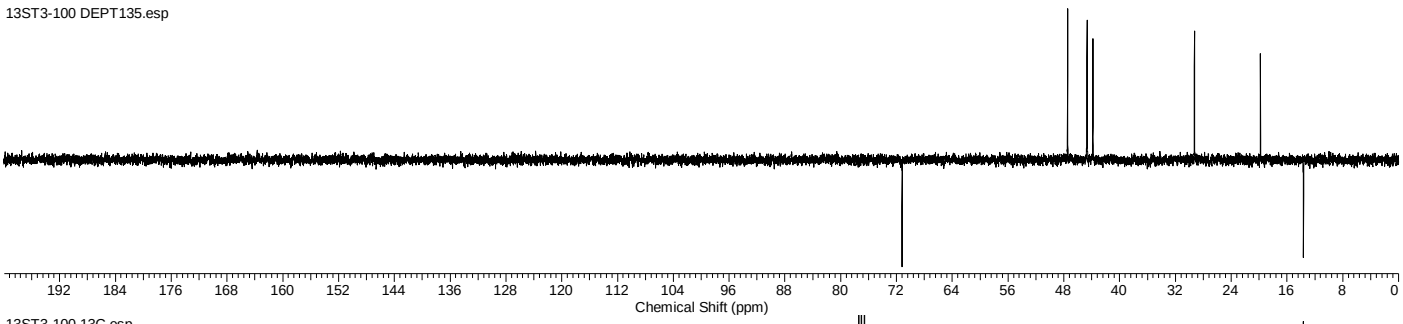
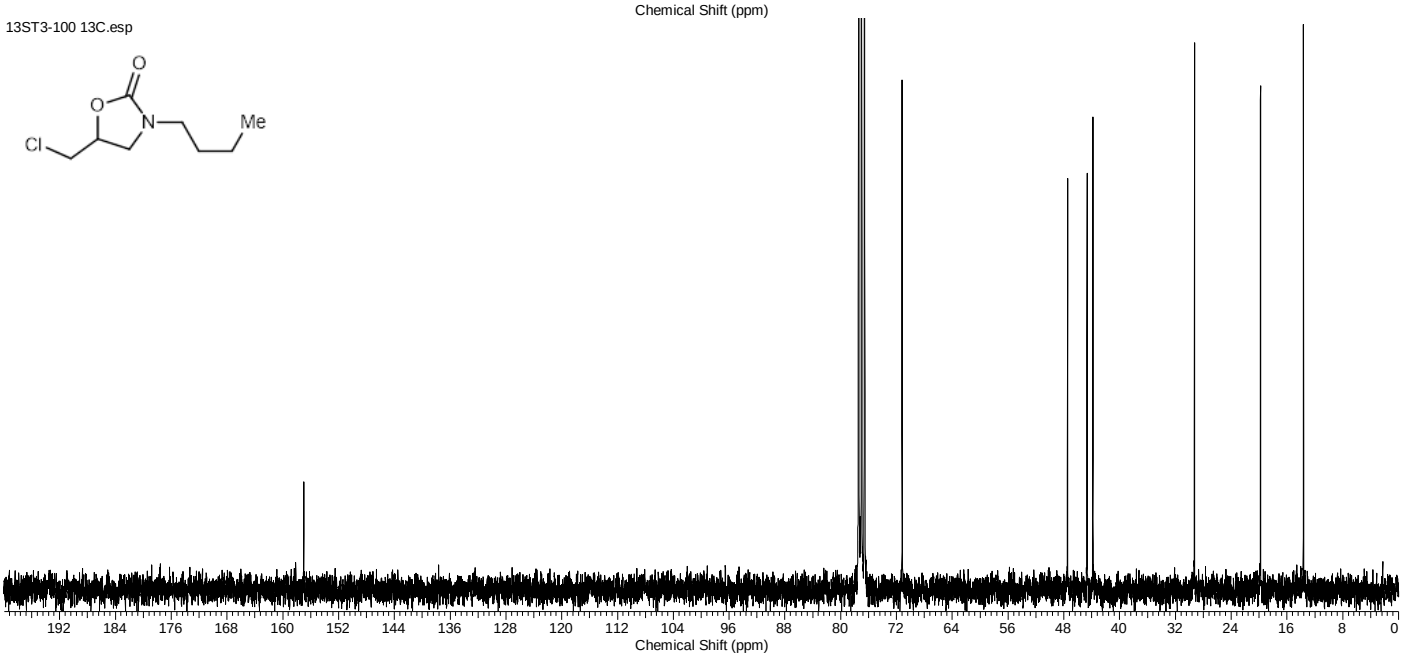
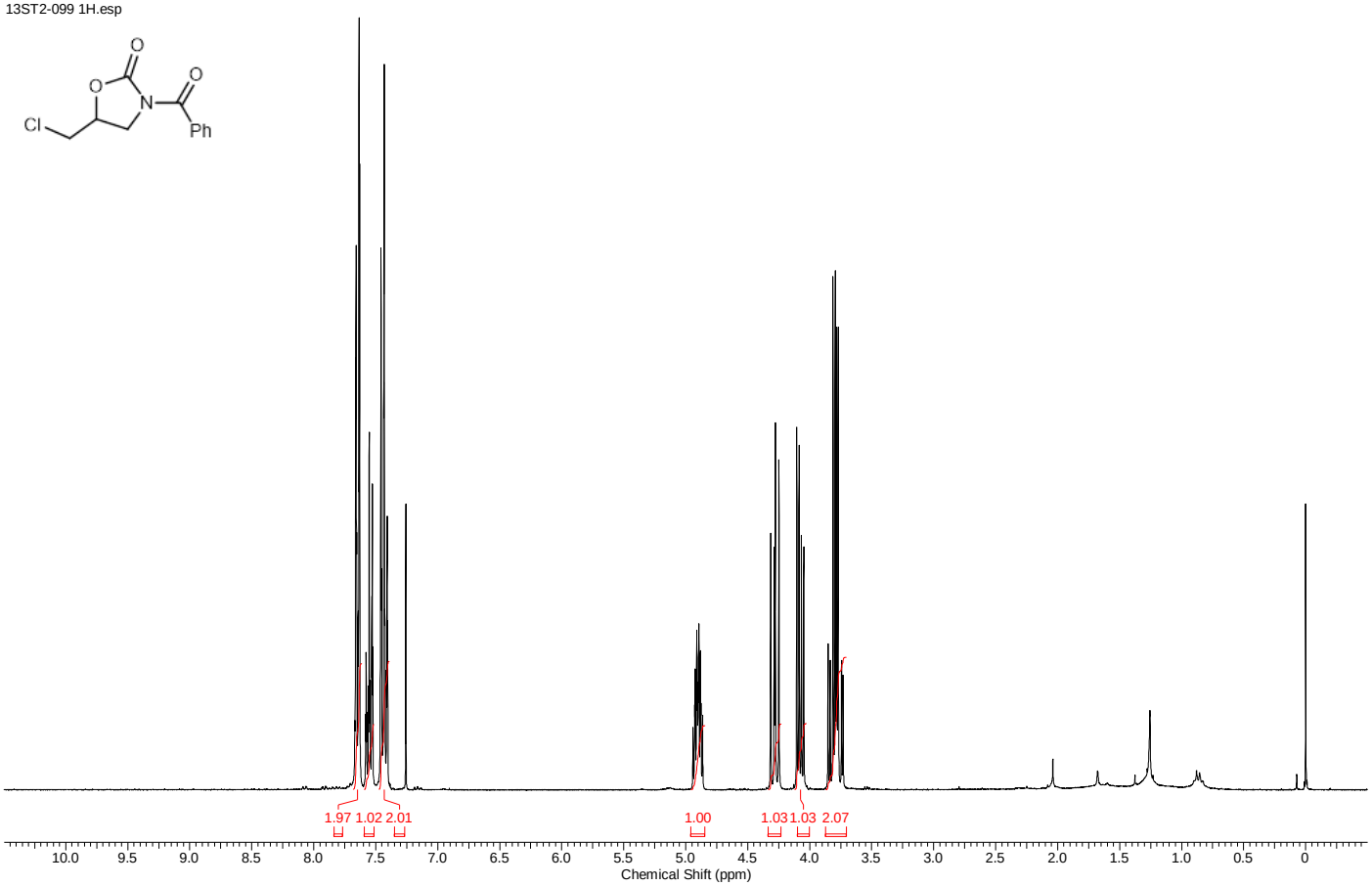


13ST3-100 13C.esp



^{1}H & ^{13}C NMR Spectra of 6c

13ST2-099 1H.esp



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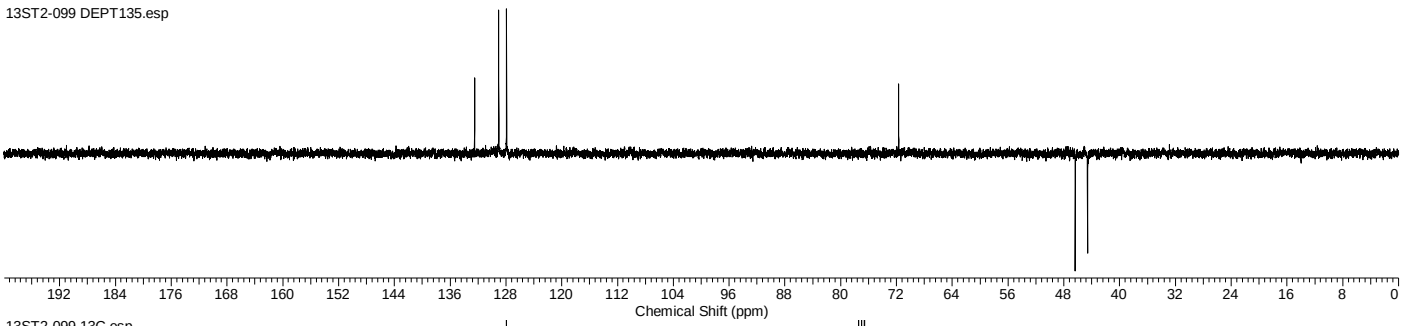
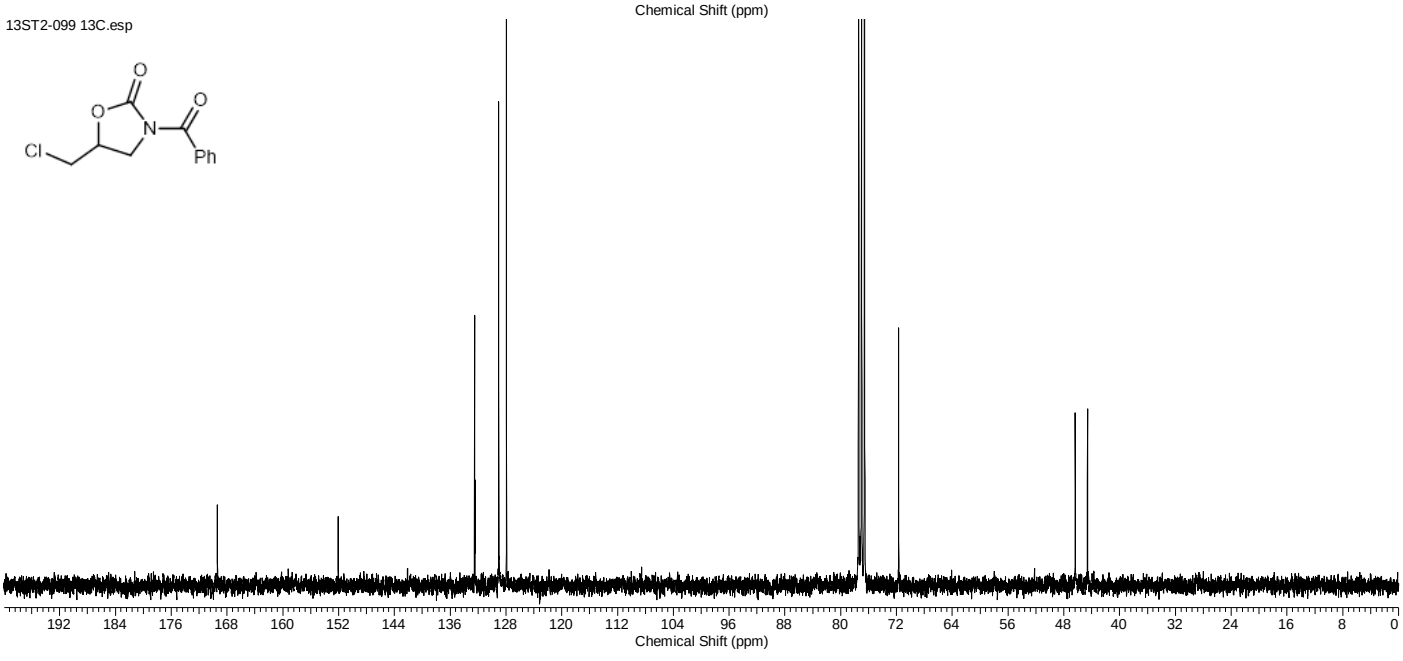
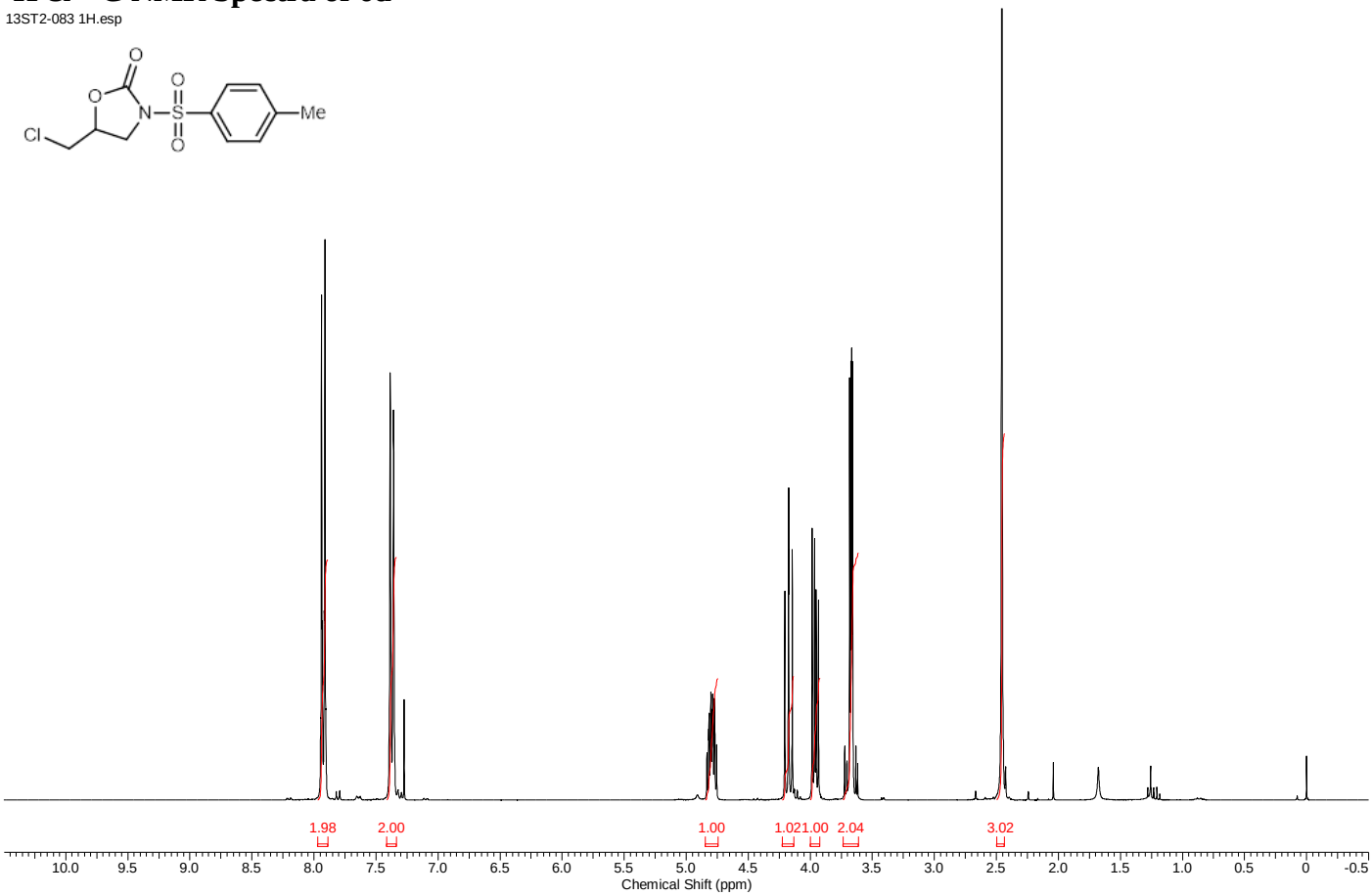


13ST2-099 13C.esp



^{1}H & ^{13}C NMR Spectra of 6d

13ST2-083 1H.esp



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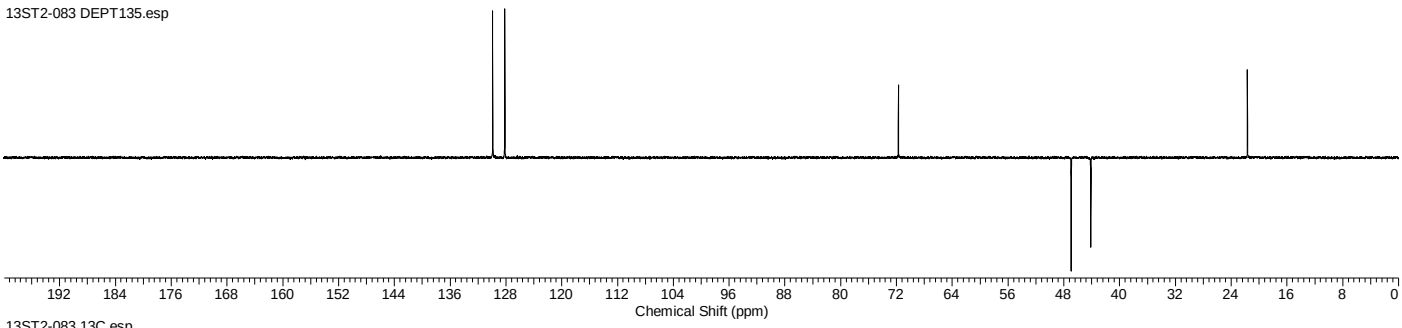

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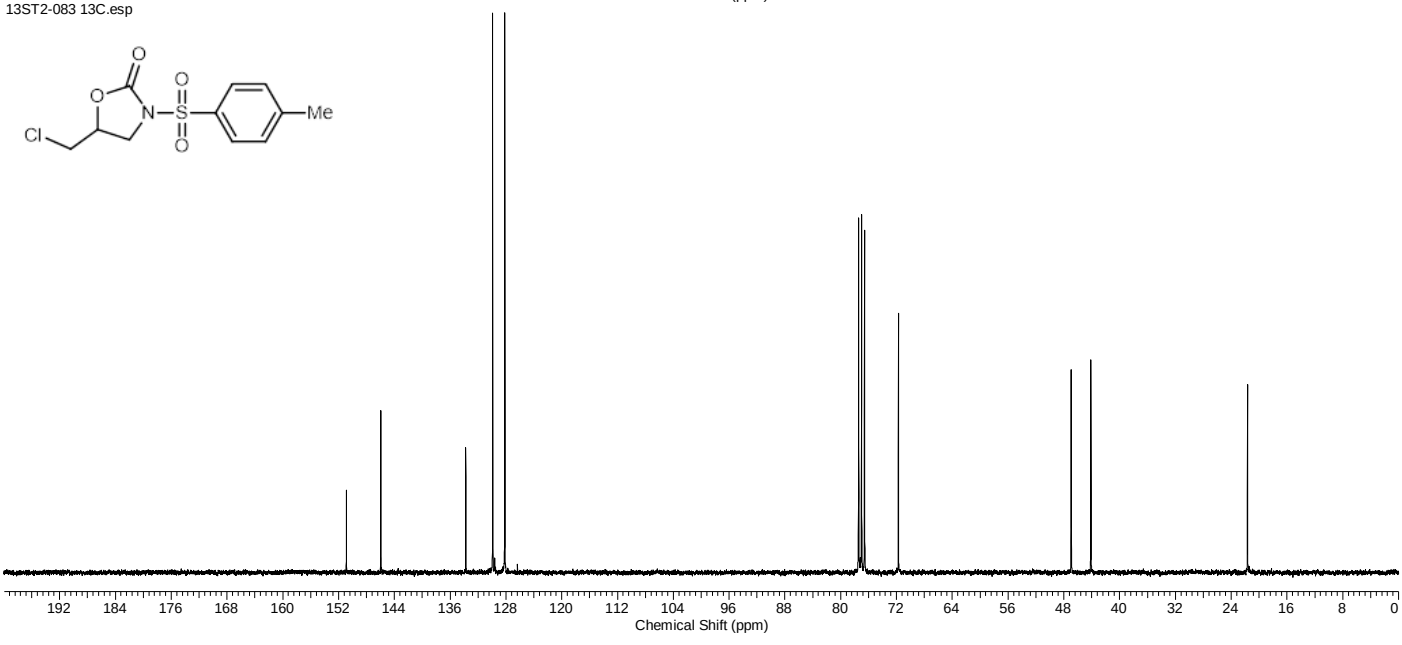
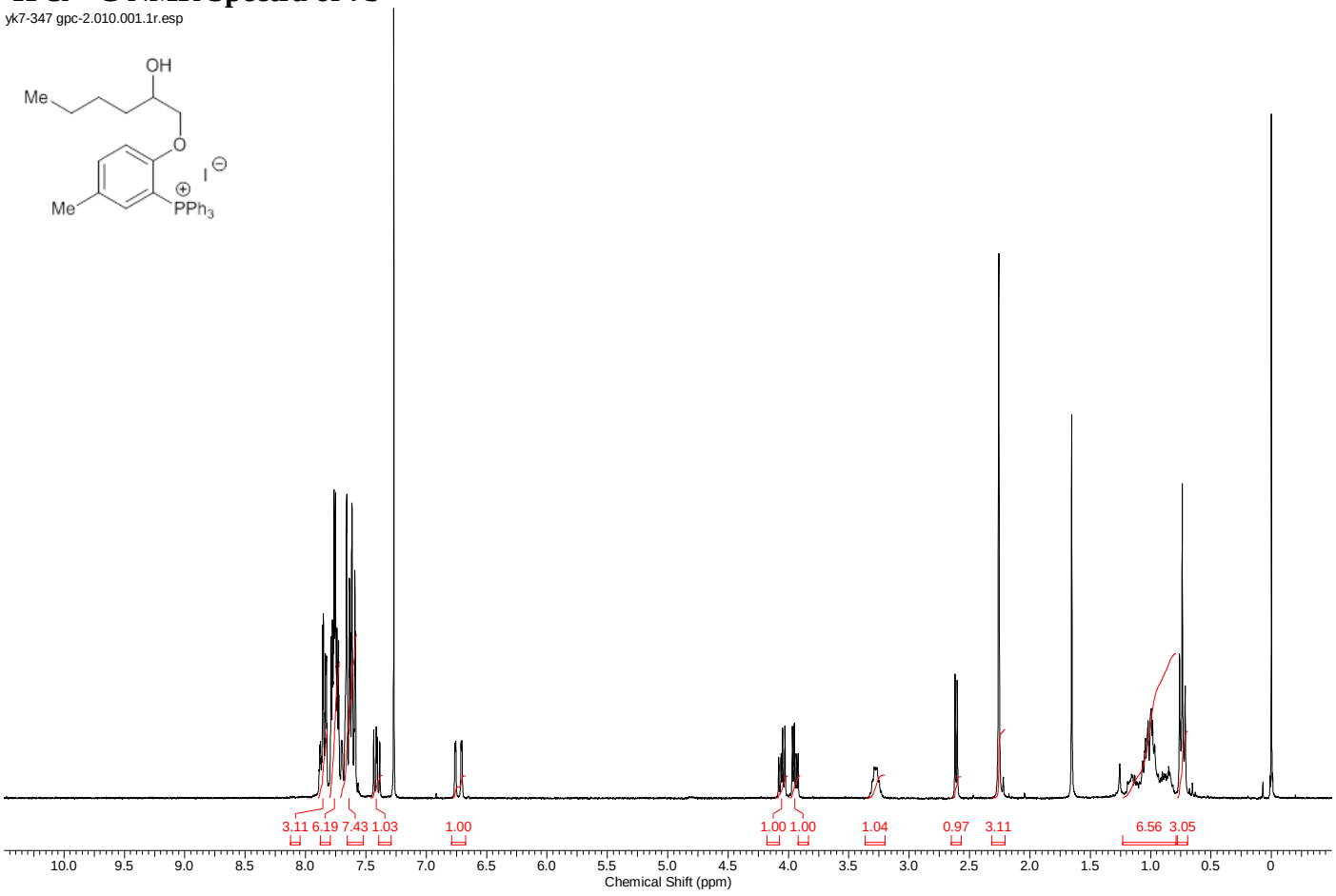
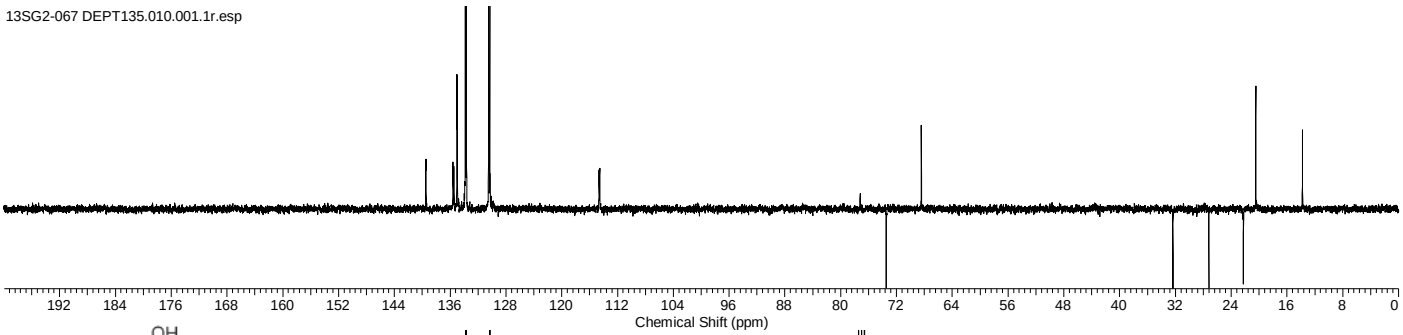


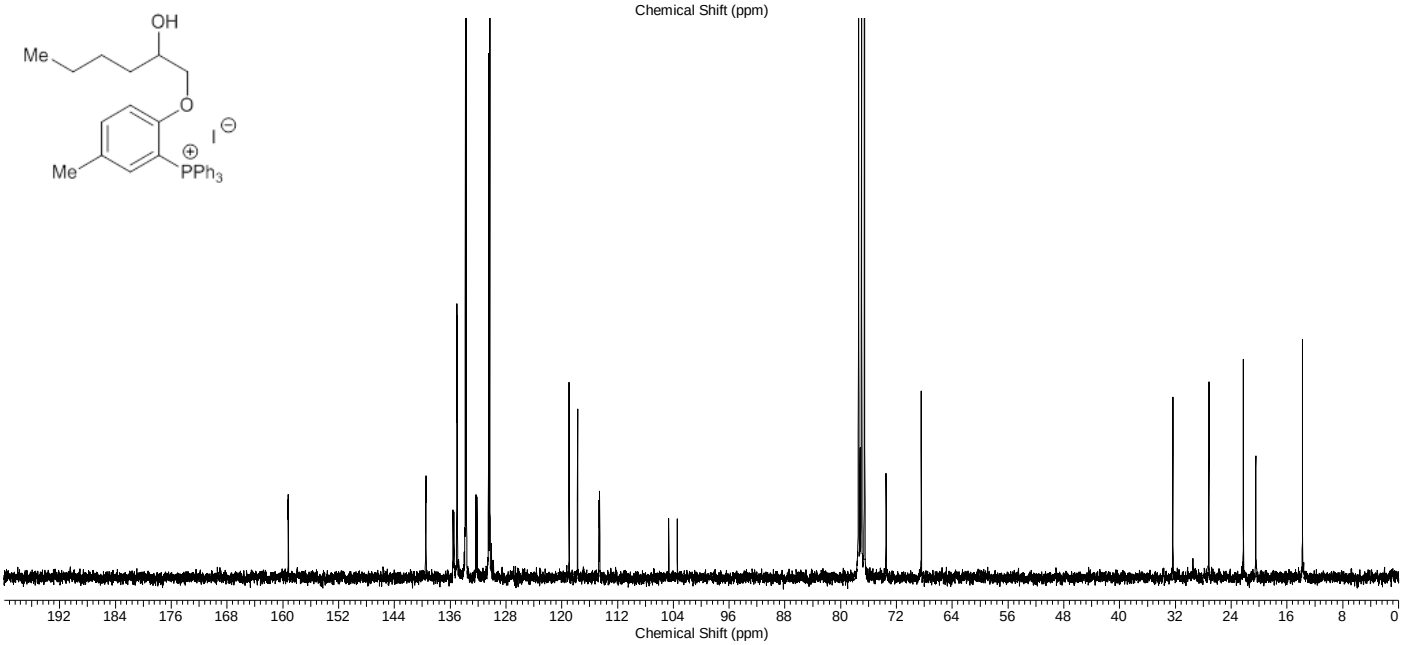
^{1}H & ^{13}C NMR Spectra of 7b

yk7-347 gpc-2.010.001.1r.esp



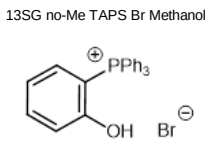
13SG2-067 DEPT135.010.001.1r.esp



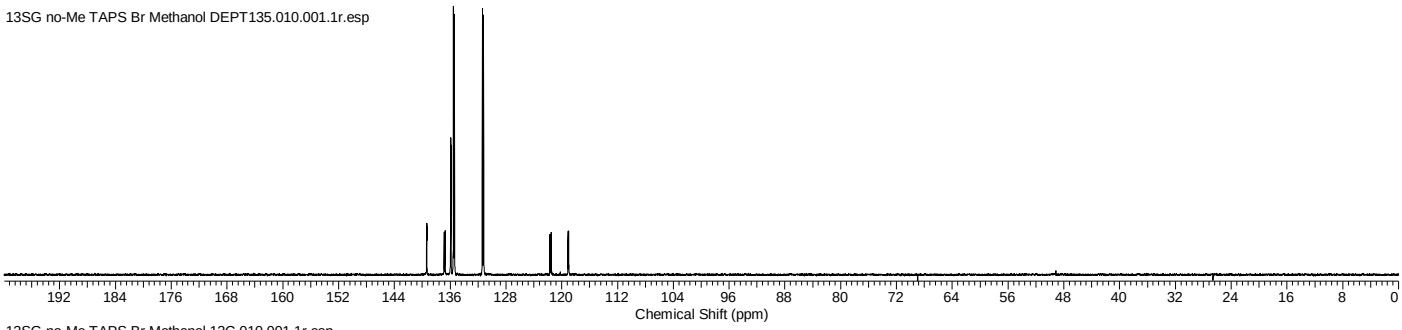


^{1}H & ^{13}C NMR Spectra of 8a

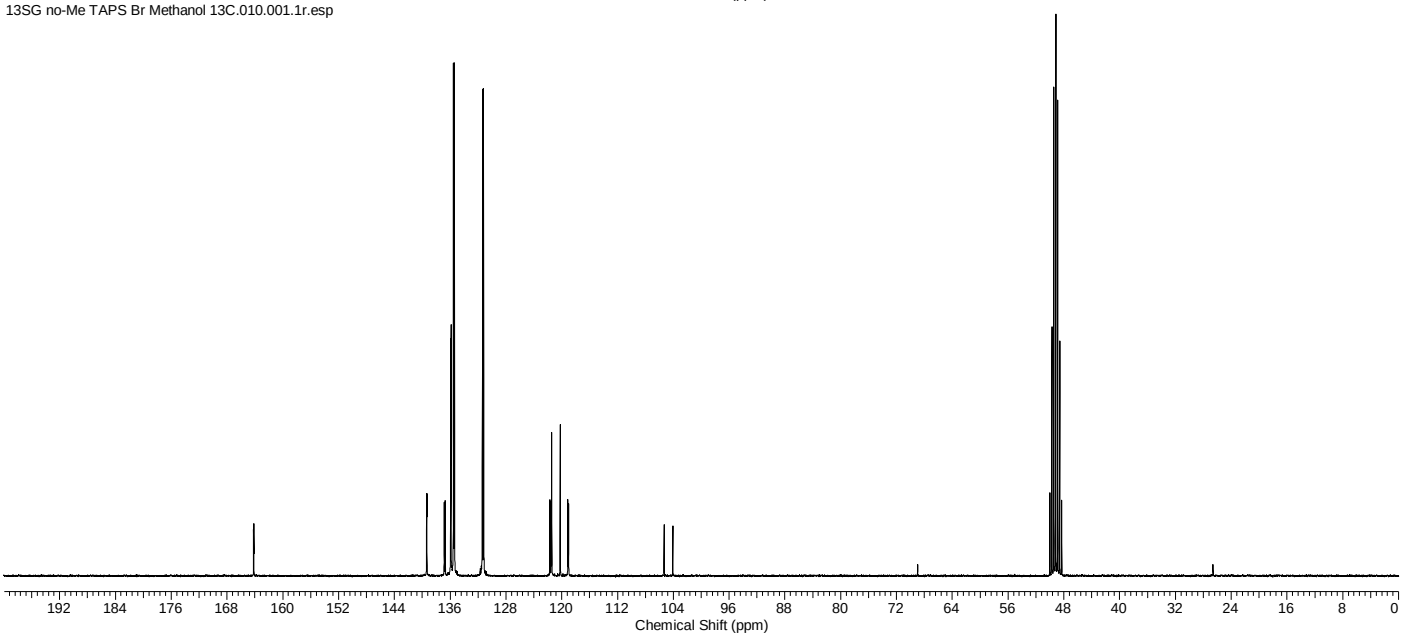
13SG no-Me TAPS Br Methanol 1H.010.001.1r.esp



13SG no-Me TAPS Br Methanol DEPT135.010.001.1r.esp

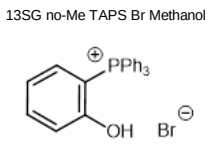


13SG no-Me TAPS Br Methanol 13C.010.001.1r.esp

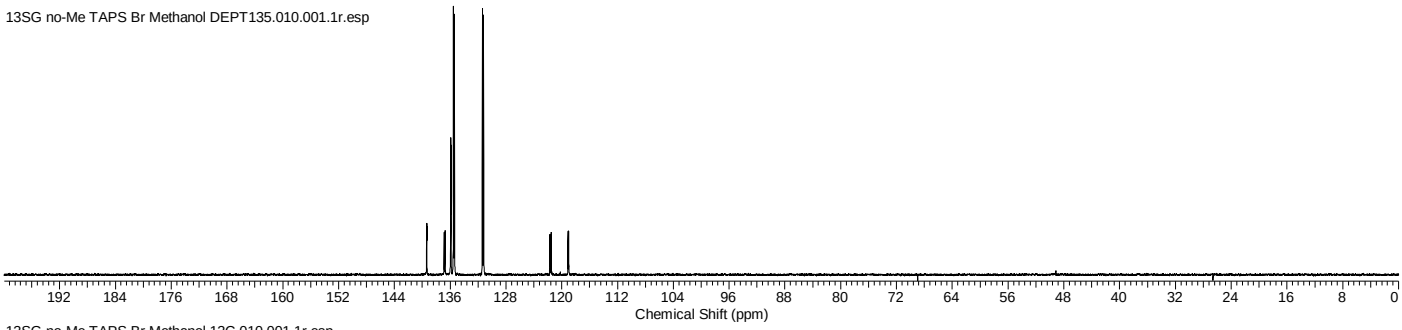


^{1}H & ^{13}C NMR Spectra of 8a

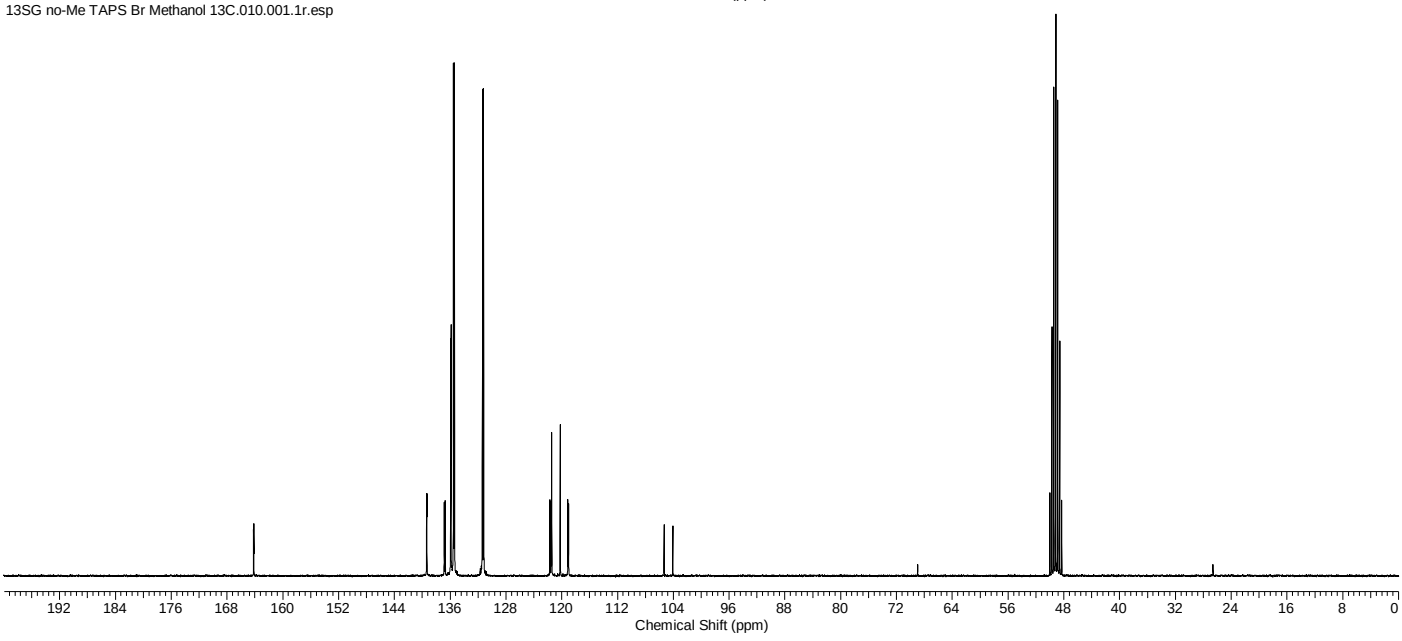
13SG no-Me TAPS Br Methanol 1H.010.001.1r.esp



13SG no-Me TAPS Br Methanol DEPT135.010.001.1r.esp

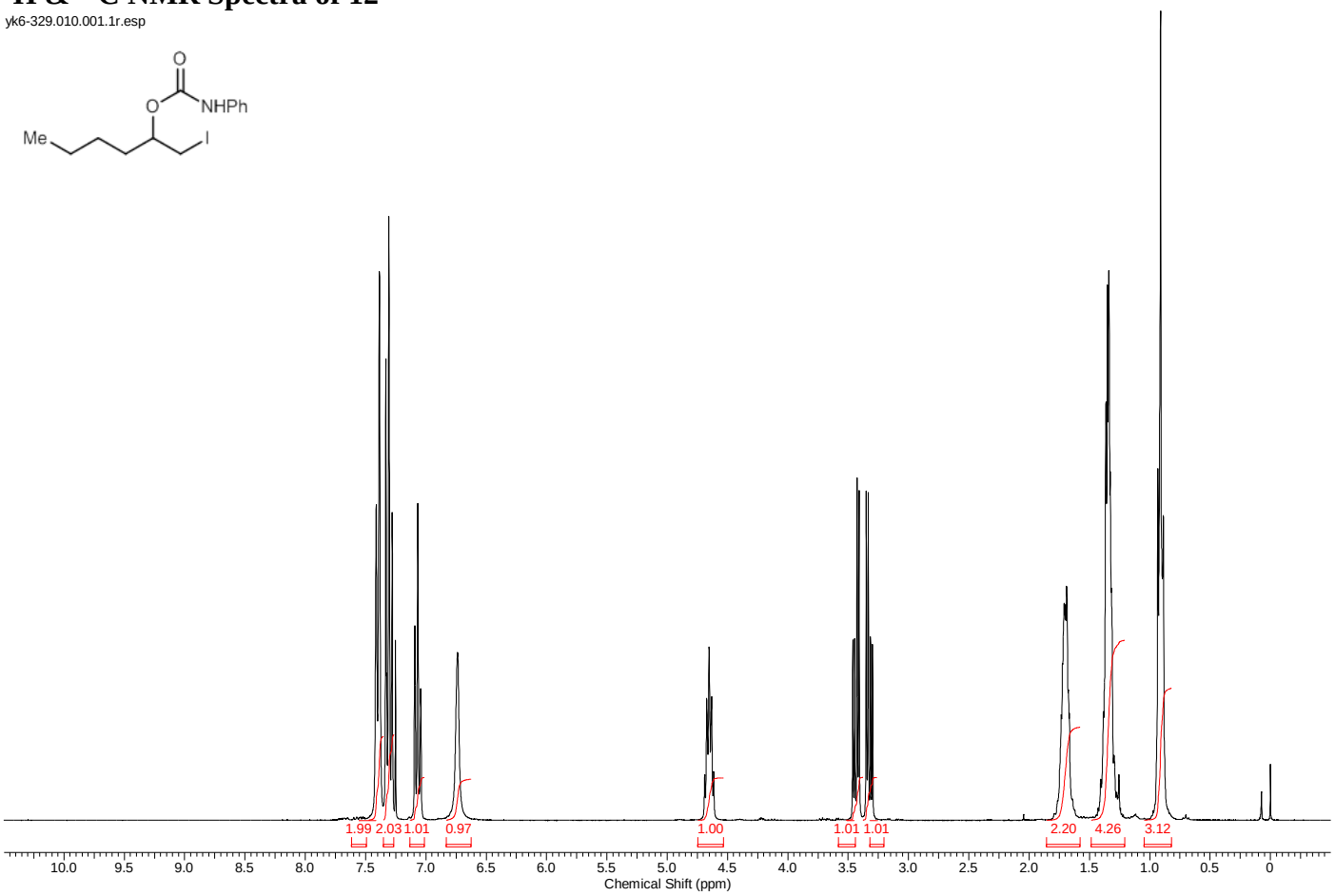


13SG no-Me TAPS Br Methanol 13C.010.001.1r.esp

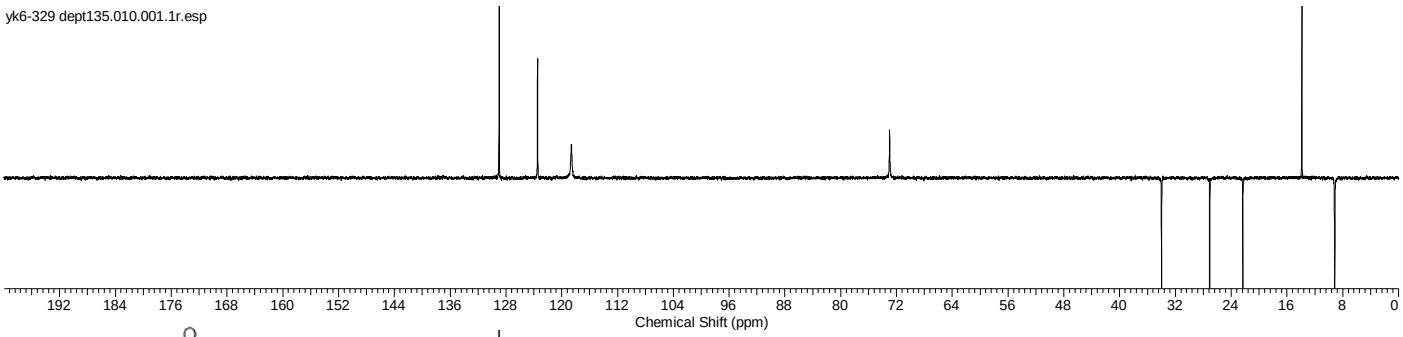


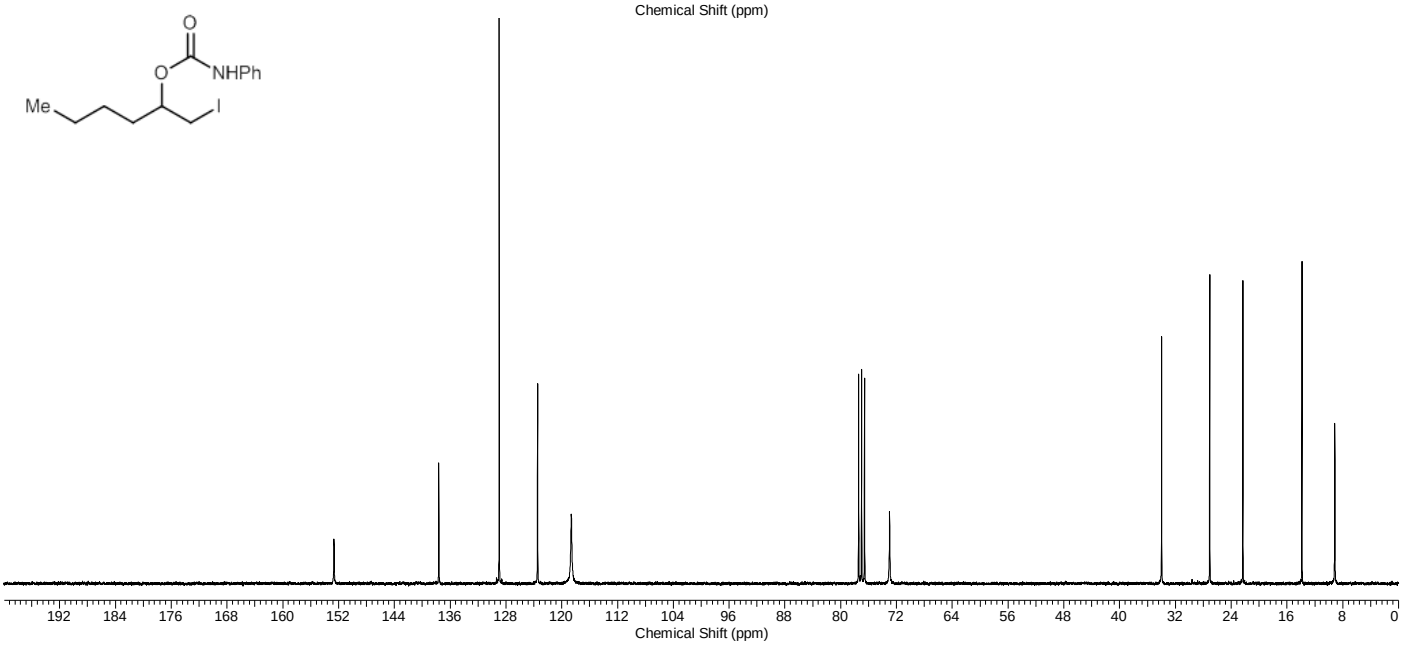
^{1}H & ^{13}C NMR Spectra of 12

yk6-329.010.001.1r.esp

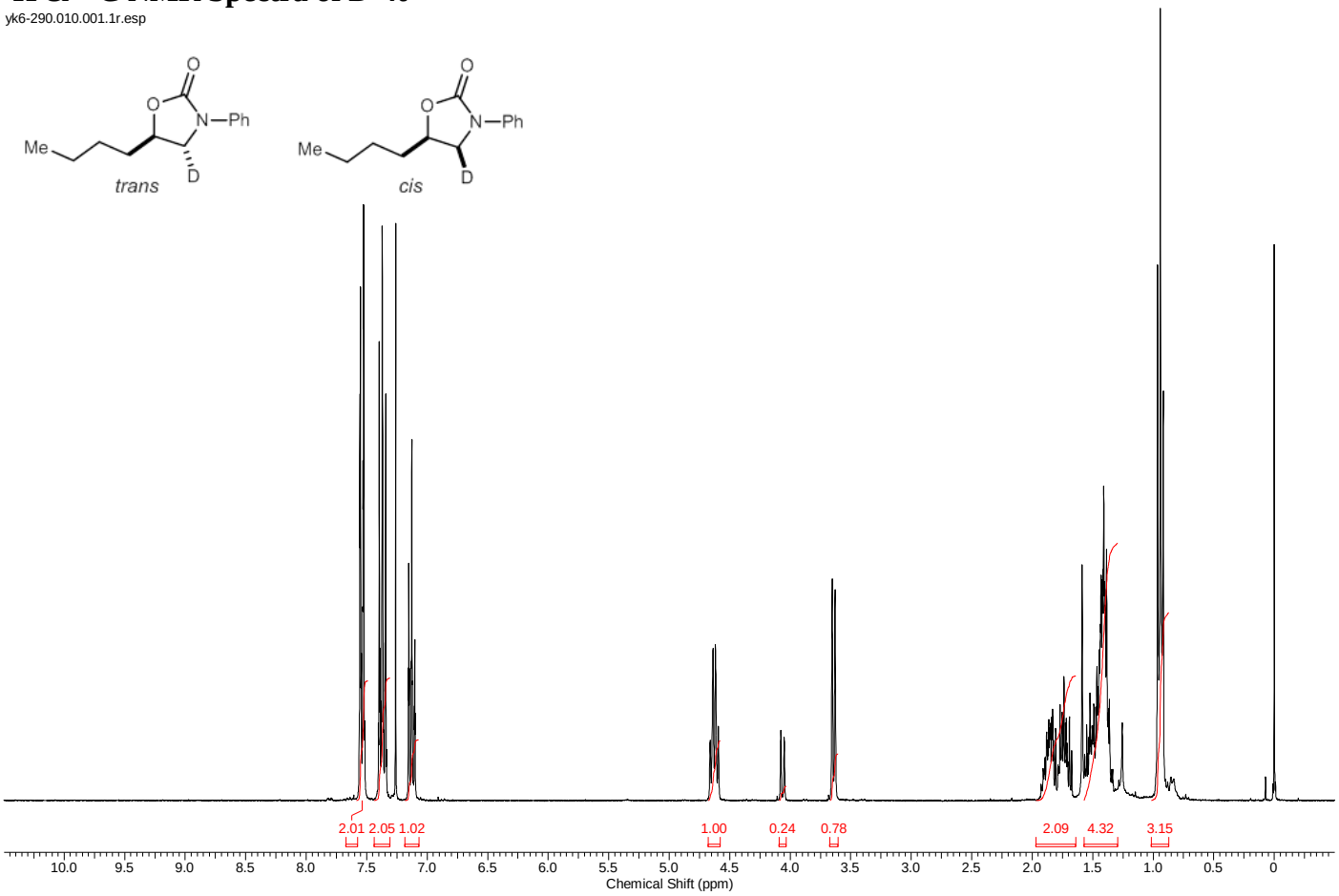


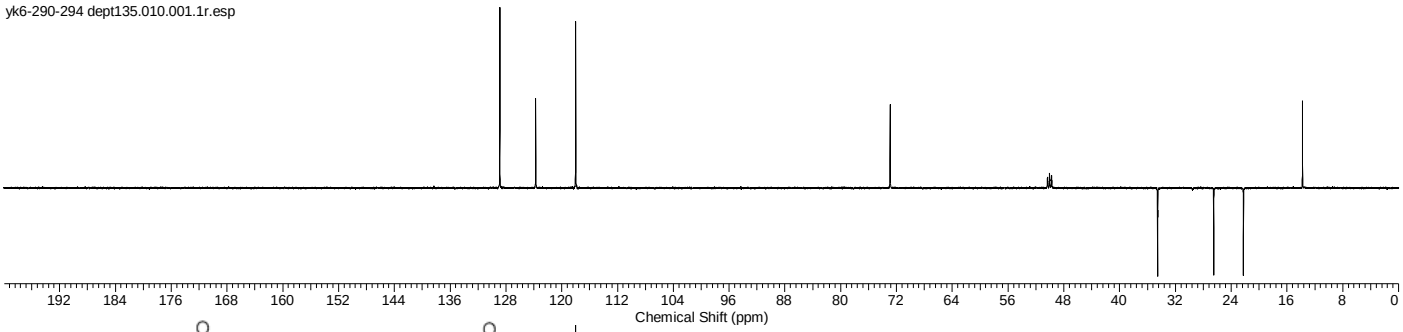
yk6-329 dept135.010.001.1r.esp

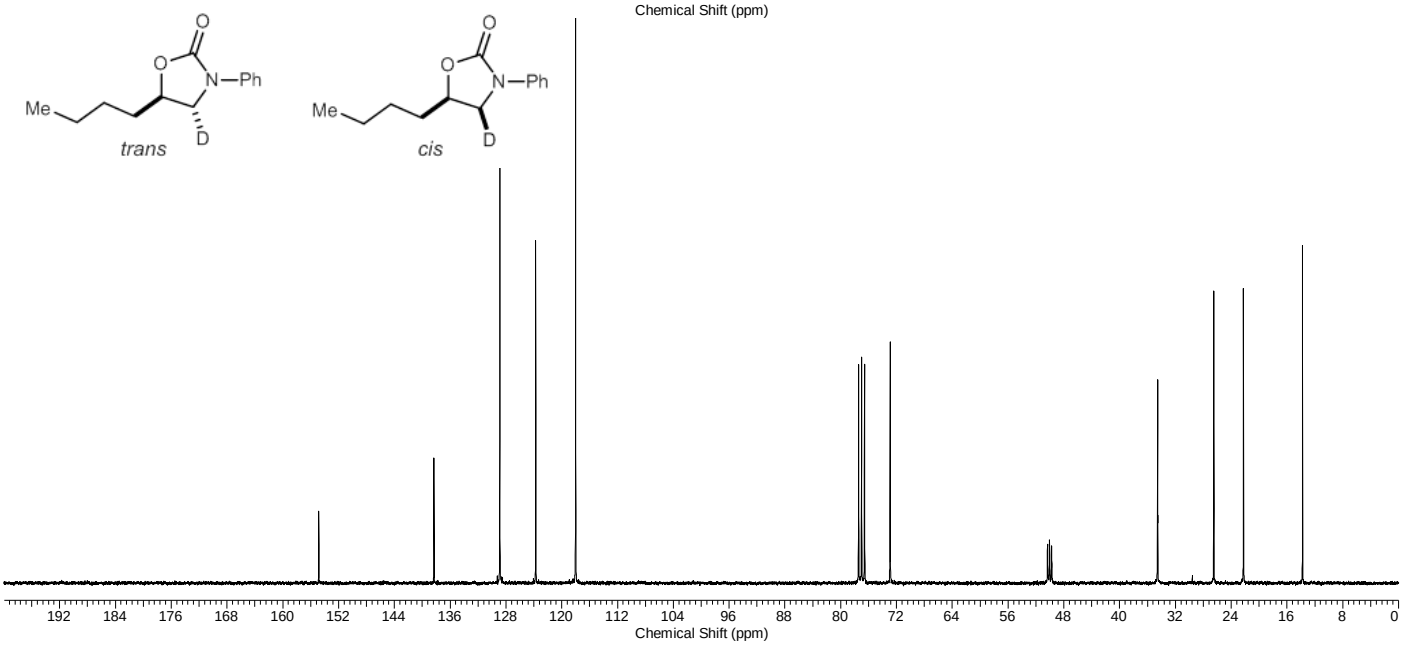




^{1}H & ^{13}C NMR Spectra of *D*-4t

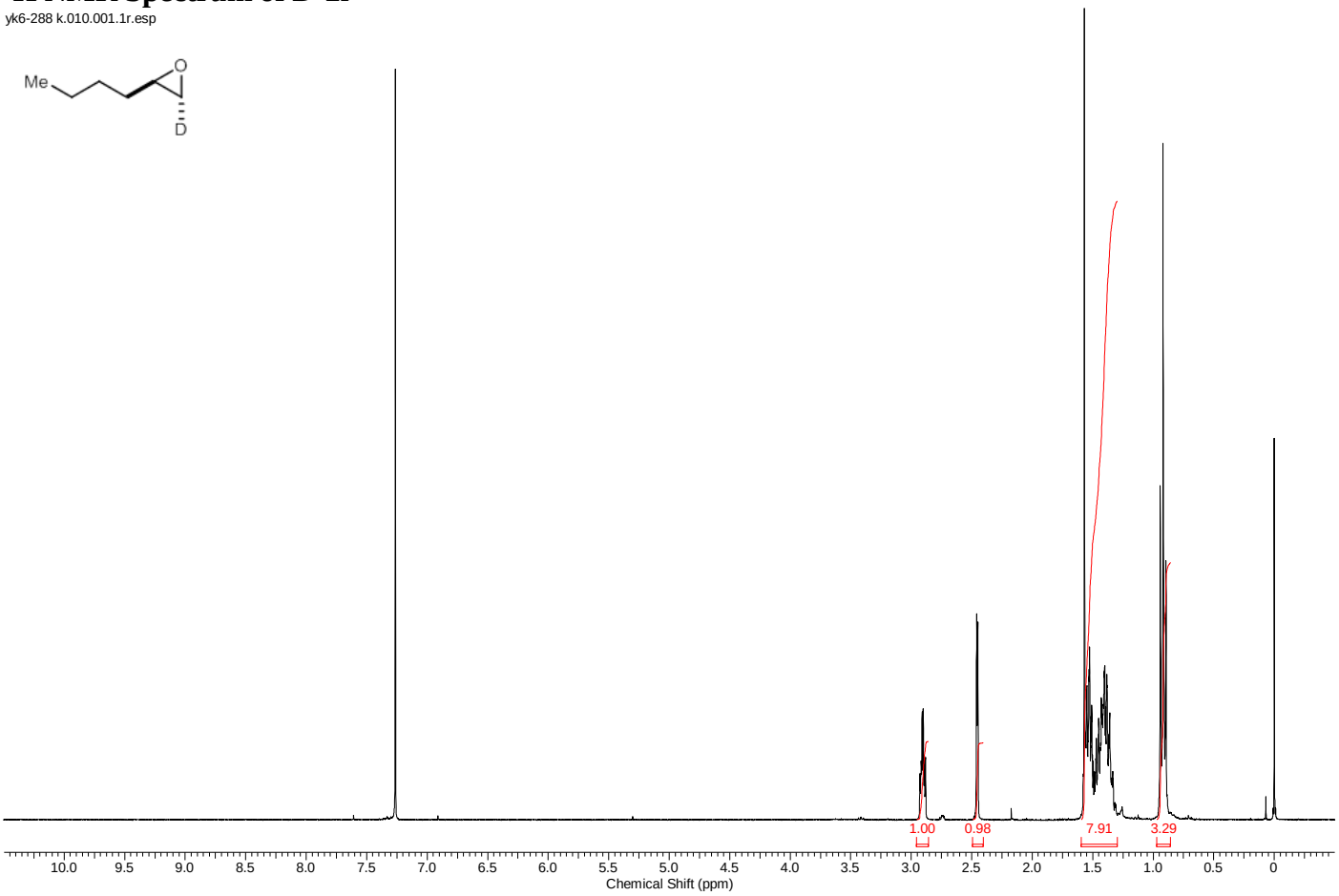






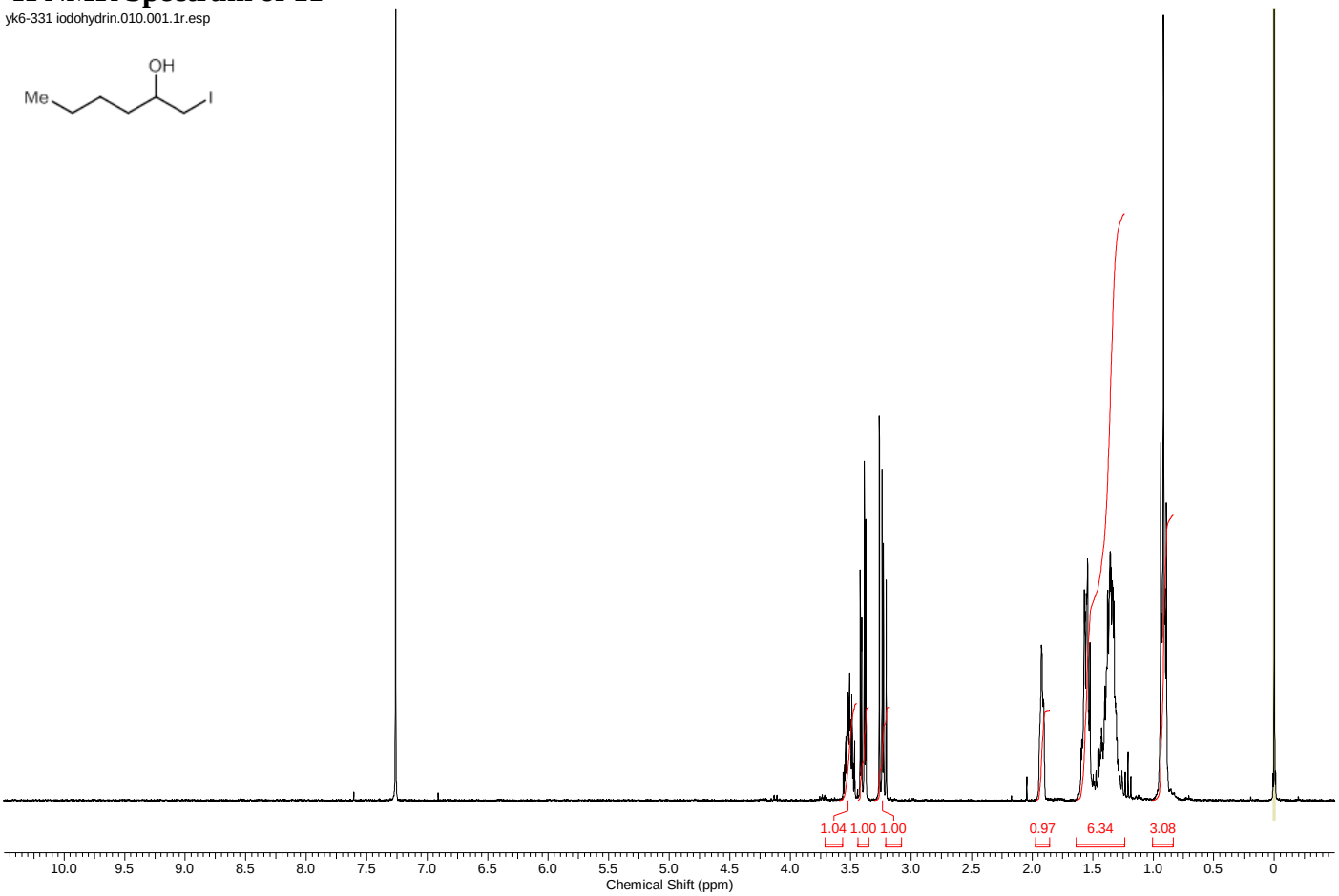
^{1}H NMR Spectrum of *D*-2i

yk6-288 k.010.001.1r.esp

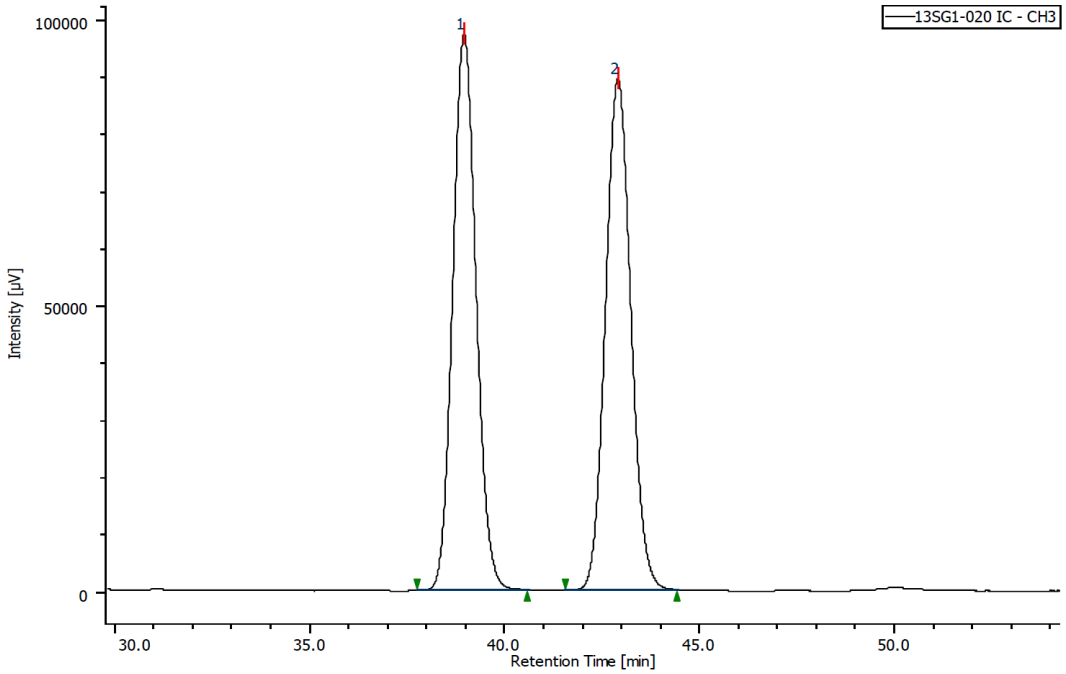


^{1}H NMR Spectrum of 11

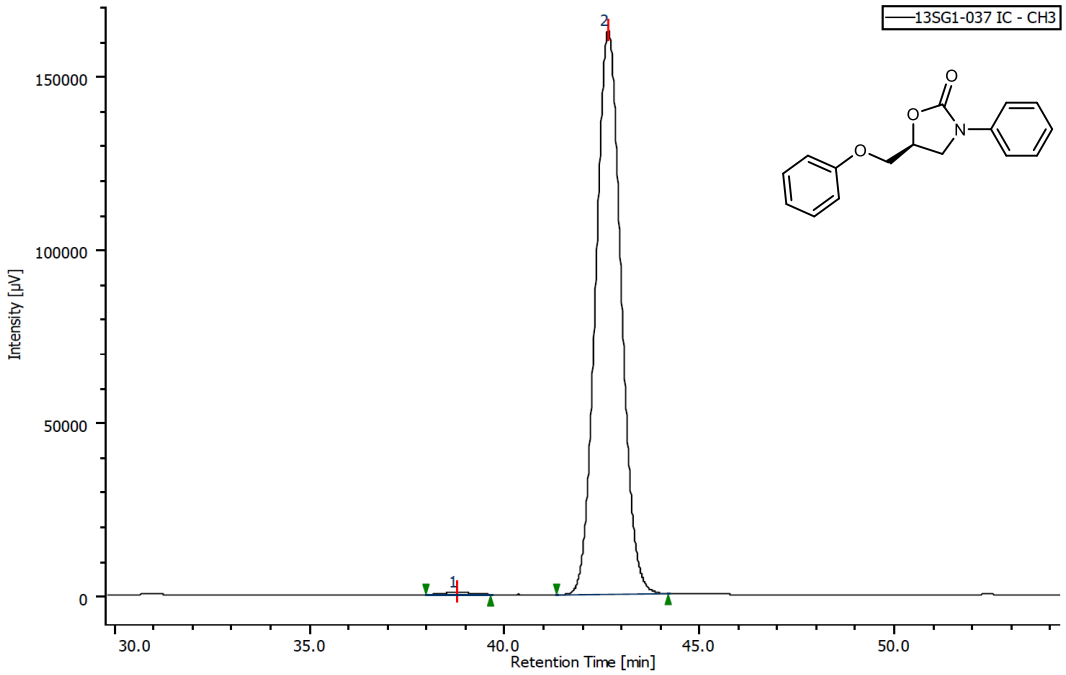
yk6-331 iodohydrin.010.001.1r.esp



HPLC Trace of 4b

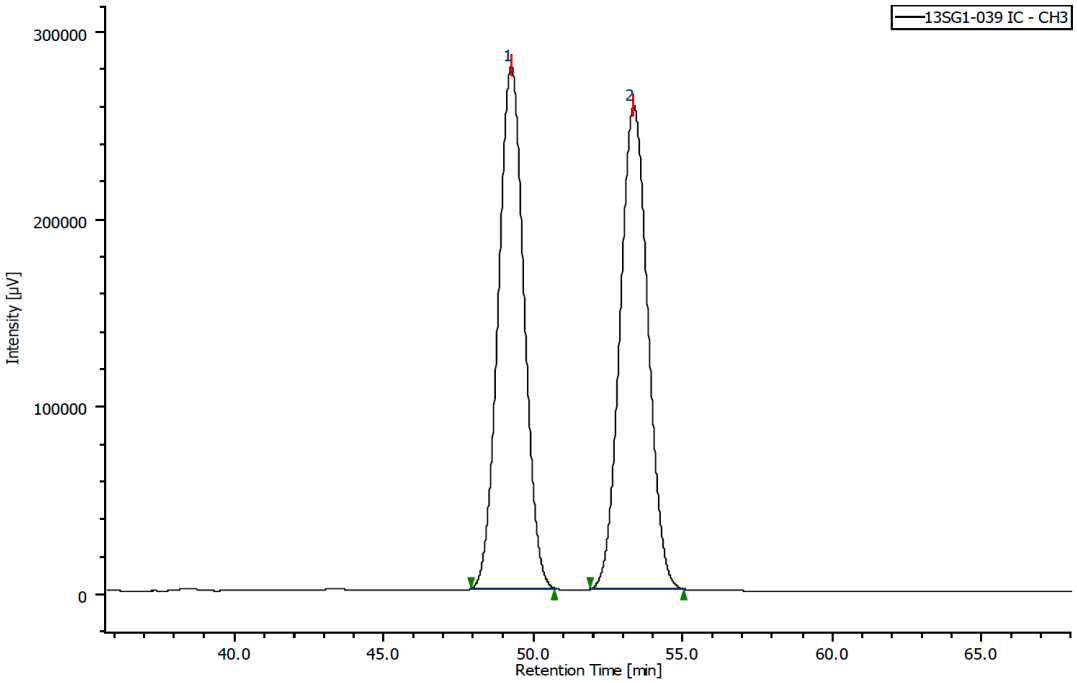


# Peak	tR (min)	Area	Height	Area%
1	38.950	4015545	97069	49.927
2	42.892	4027242	89249	50.073

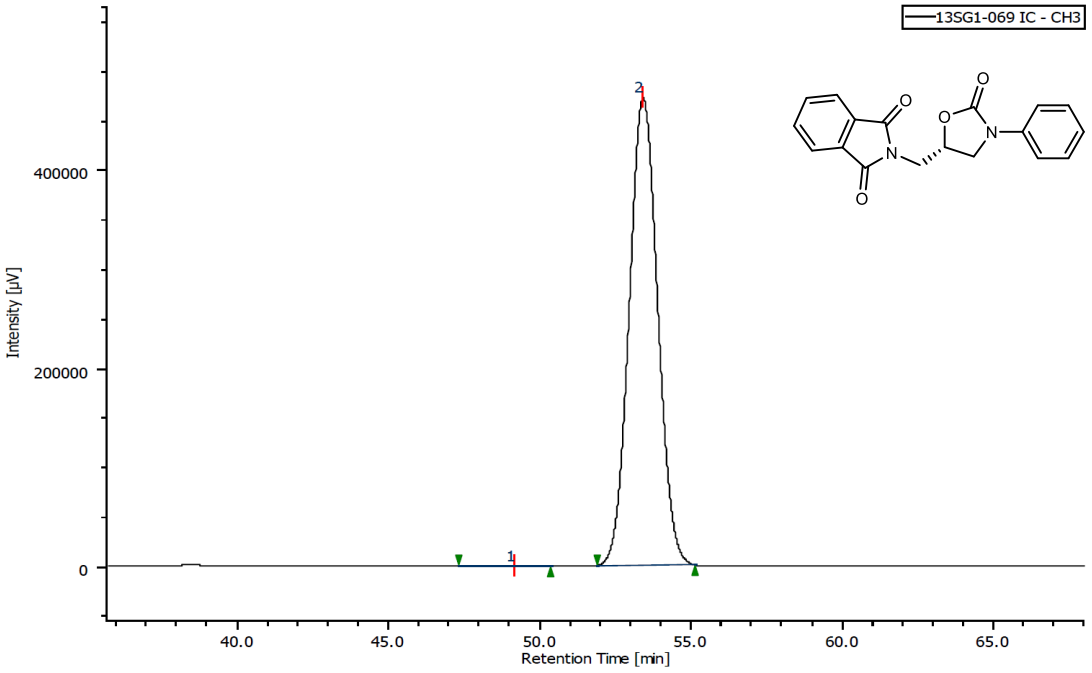


# Peak	tR (min)	Area	Height	Area%
1	38.783	29506	707	0.399
2	42.642	7356433	162344	99.601

HPLC Trace of 4w

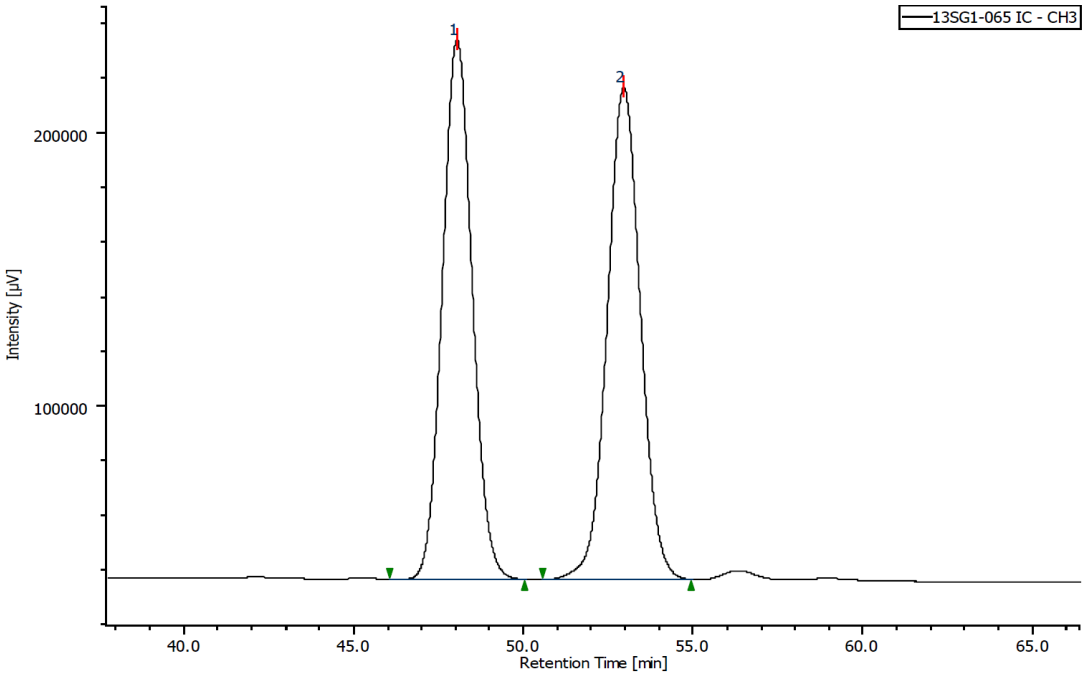


# Peak	tR (min)	Area	Height	Area%
1	49.250	16665616	277796	49.995
2	53.342	16668653	256995	50.005

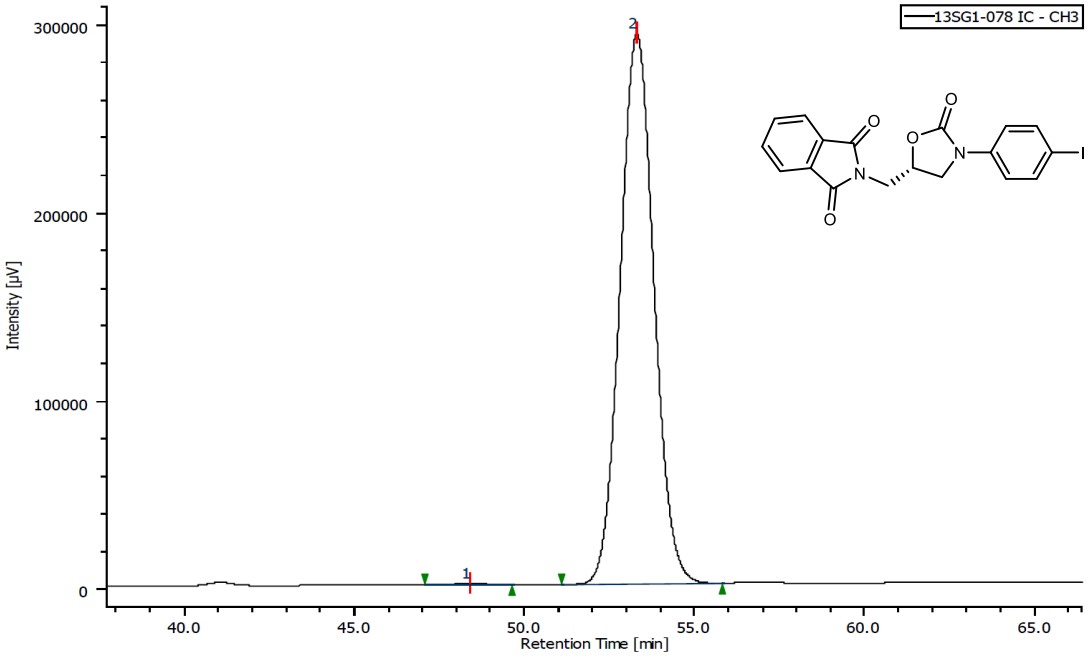


# Peak	tR (min)	Area	Height	Area%
1	49.133	14337	179	0.047
2	53.400	30751493	471047	99.953

HPLC Trace of 4y



# Peak	tR (min)	Area	Height	Area%
1	48.033	12013562	197208	49.556
2	52.933	12232936	179859	50.444



# Peak	tR (min)	Area	Height	Area%
1	48.400	32165	512	0.159
2	53.292	20148180	291868	99.841