Electronic Supplementary Information

Use of Trichloroacetonitrile as a Hydrogen Chloride Generator for Ring-Opening Reactions of Aziridines

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ESI-X

General information

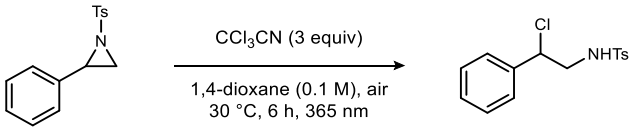
All reagents and solvents were commercial grade and purified prior to use when necessary. Tetrahydrofuran (THF), diethyl ether (Et_2O), and dichloromethane (CH_2Cl_2) were dried by passage through a column of activated alumina as described by Grubbs.[1] Thin layer chromatography (TLC) was performed using TLC aluminum sheets from Merck (silica gel 60 F_{254}, 200 μm), and flash chromatography utilized silica gel from Fuji Silysia Chemical (PSQ60B, 60 μm). Products were visualized by ultraviolet (UV) light, iodine (I_2), and/or a TLC stain (phosphomolybdic acid (PMA), 4-anisaldehyde (AA), potassium permanganate ($KMnO_4$)). 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). 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 aziridines

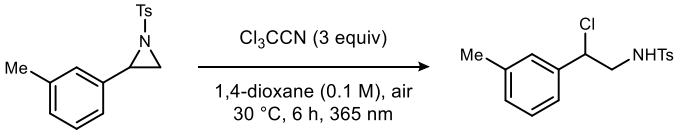
1a was prepared according to the reported procedure.[2] The procedure was applied to the synthesis of **1b**-**1j**, and their characterization data matched the literature.[3-6] (*R*)-**1a** was prepared according to the reported procedure.[6]

General procedure for HCl addition reactions

To an oven-dried test tube equipped with a stir bar was added aziridine **1** (0.20 mmol, 1.0 equiv), 1,4-dioxane (2.0 mL, 0.1 M), and trichloroacetonitrile (60 μL, 0.60 mmol, 3.0 equiv). The mixture was stirred with UV irradiation (365 nm, 4 W x 2) under air atmosphere at 30 °C for 6 h. The mixture was treated with satd $NaHCO_3$ aq, and the aqueous layer was extracted with Et_2O (x 3). The organic layers were combined, washed with H_2O (x 2), dried over Na_2SO_4, and concentrated. Flash column chromatography (SiO_2: 9 g) yielded product **2**.

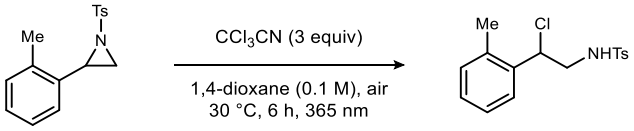


***N*-(2-Chloro-2-phenylethyl)-4-methylbenzenesulfonamide (2a).** Prepared according to the general procedure using aziridine **1a** (54.6 mg, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 10/1) yielded a white solid (57.6 mg, 93%). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75-7.71 (m, 2H), 7.36-7.25 (m, 7H), 4.94 (t, *J* = 6.6 Hz, 1H), 4.87 (dd, *J* = 8.1, 6.0 Hz, 1H), 3.52-3.36 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8 (C), 137.8 (C), 136.9 (C), 129.9 (CH), 129.1 (CH), 128.9 (CH), 127.2 (CH), 127.0 (CH), 61.6 (CH), 50.3 (CH_2), 21.5 (CH_3). Chiral HPLC analysis (Chiralcel OJ, Hexane/^{i}PrOH = 90/10, 1.0 mL/min, t_r(*major*) = 16.4 min, t_r(*minor*) = 18.7 min, 220 nm, 35 °C). Characterization data matched the literature.[7,8]

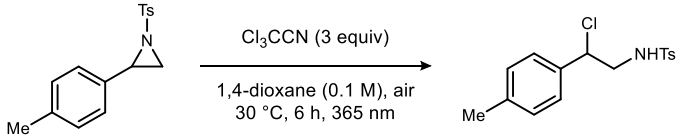


***N*-(2-Chloro-2-*m*-tolylethyl)-4-methylbenzenesulfonamide (2b).** Prepared according to the general procedure using aziridine **1b** (57.5 mg, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 10/1)

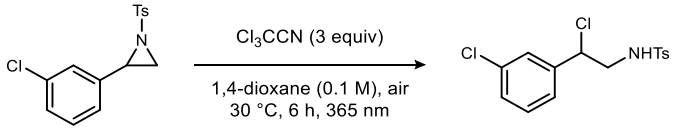
yielded a white solid (58.9 mg, 91%). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.70 (m, 2H), 7.32-7.29 (m, 2H), 7.24-7.05 (m, 4H), 5.02 (t, *J* = 6.6 Hz, 1H), 4.83 (dd, *J* = 7.8, 6.3 Hz, 1H), 3.51-3.36 (m, 2H), 2.43 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7 (C), 138.6 (C), 137.7 (C), 136.9 (C), 129.8 (CH x 2), 128.7 (CH), 127.8 (CH), 127.0 (CH), 124.2 (CH), 61.6 (CH), 50.2 (CH_2), 21.5 (CH_3), 21.3 (CH_3). Characterization data matched the literature.[9]



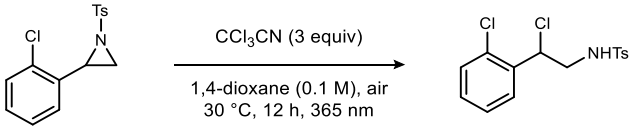
***N*-(2-Chloro-2-*o*-tolylethyl)-4-methylbenzenesulfonamide (2c).** Prepared according to the general procedure using aziridine **1c** (57.5 mg, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 10/1) yielded a white solid (59.2 mg, 91%). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76-7.72 (m, 2H), 7.34-7.30 (m, 3H), 7.24-7.13 (m, 3H), 5.16 (dd, *J* = 8.7, 5.4 Hz, 1H), 4.83 (dd, *J* = 7.5, 5.7 Hz, 1H), 3.55-3.37 (m, 2H), 2.43 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8 (C), 137.0 (C), 135.9 (C), 135.8 (C), 130.8 (CH), 129.8 (CH), 128.8 (CH), 127.0 (CH), 126.7 (CH), 126.4 (CH), 58.2 (CH), 49.4 (CH_2), 21.5 (CH_3) , 19.0 (CH_3). Characterization data matched the literature.[9]



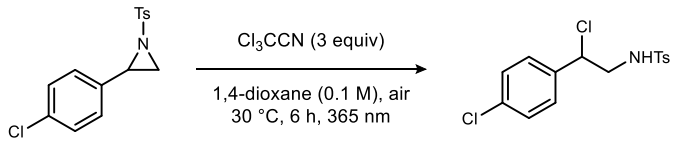
***N*-(2-Chloro-2-*p*-tolylethyl)-4-methylbenzenesulfonamide (2d).** Prepared according to the general procedure using aziridine **1d** (57.5 mg, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 10/1) yielded a white solid (60.1 mg, 93%). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.70 (m, 2H), 7.31-7.28 (m, 2H), 7.17-7.11 (m, 4H), 5.00 (t, *J* = 6.6 Hz, 1H), 4.84 (dd, *J* = 7.8, 6.3 Hz, 1H), 3.50-3.35 (m, 2H), 2.43 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7 (C), 139.0 (C), 136.9 (C), 134.8 (C), 129.8 (CH), 129.5 (CH), 127.04 (CH), 126.97 (CH), 61.5 (CH), 50.2 (CH_2), 21.5 (CH_3), 21.1 (CH_3). Characterization data matched the literature.[7]



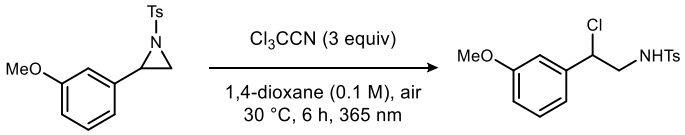
***N*-(2-Chloro-2-(3-chlorophenyl)ethyl)-4-methylbenzenesulfonamide (2e).** Prepared according to the general procedure using aziridine **1e** (61.6 mg, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 10/1) yielded a white solid (64.2 mg, 95%). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.71 (m, 2H), 7.34-7.26 (m, 5H), 7.18 (dd, *J* = 6.6, 1.8 Hz, 1H), 4.87-4.82 (m, 2H), 3.51-3.35 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9 (C), 139.8 (C), 136.7 (C), 134.6 (C), 130.1 (CH), 129.9 (CH), 129.1 (CH), 127.4 (CH), 126.9 (CH), 125.5 (CH), 60.6 (CH), 50.1 (CH_2), 21.5 (CH_3). Characterization data matched the literature.[9]



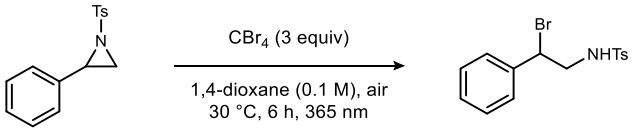
***N*-(2-Chloro-2-(2-chlorophenyl)ethyl)-4-methylbenzenesulfonamide (2f).** Prepared according to the general procedure using aziridine **1f** (61.6 mg, 0.20 mmol) at 30 °C for 12 h. Flash column chromatography (Hexane/EtOAc = 10/1) yielded a white solid (63.8 mg, 93%, 4% of regioisomer was included). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77-7.72 (m, 2H), 7.52-7.46 (m, 1H), 7.37-7.22 (m, 5H), 5.37 (dd, *J* = 8.7, 4.8 Hz, 1H), 5.03 (dd, *J* = 8.1, 5.1 Hz, 1H), 3.59 (ddd, *J* = 14.1, 8.1, 4.8 Hz, 1H), 3.36 (ddd, *J* = 14.1, 8.7, 5.1 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8 (C), 136.9 (C), 135.1 (C), 132.8 (C), 130.0 (CH), 129.83 (CH), 128.79 (CH), 128.7 (CH), 127.4 (CH), 127.1 (CH), 57.9 (CH), 49.1 (CH_2), 21.5 (CH_3). Characterization data matched the literature.[8,9]



***N*-(2-Chloro-2-(4-chlorophenyl)ethyl)-4-methylbenzenesulfonamide (2g).** Prepared according to the general procedure using aziridine **1g** (61.7 mg, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 10/1) yielded a white solid (67.4 mg, 98%). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.68 (m, 2H), 7.31-7.20 (m, 6H), 5.11 (t, *J* = 6.6 Hz, 1H), 4.87 (dd, *J* = 7.5, 6.6 Hz, 1H), 3.49-3.34 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9 (C), 136.8 (C), 136.4 (C), 134.9 (C), 129.8 (CH), 129.0 (CH), 128.6 (CH), 127.0 (CH), 60.7 (CH), 50.2 (CH_2), 21.5 (CH_3). Characterization data matched the literature.[7,8]



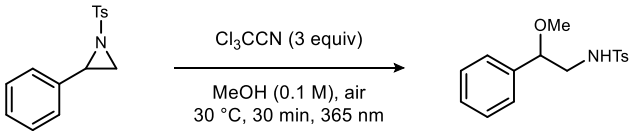
***N*-(2-Chloro-2-(3-methoxyphenyl)ethyl)-4-methylbenzenesulfonamide (2h).** Prepared according to the general procedure using aziridine **1h** (60.6 mg, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 10/1) yielded a white solid (61.9 mg, 91%). R_f = 0.2 (Hexane/EtOAc = 4/1) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.70 (m, 2H), 7.32-7.20 (m, 3H), 6.87-6.81 (m, 3H), 4.96 (t, *J* = 6.6 Hz, 1H), 4.83 (dd, *J* = 7.8, 6.3 Hz, 1H), 3.78 (s, 3H), 3.54-3.36 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8 (C), 143.7 (C), 139.2 (C), 136.9 (C), 129.9 (CH), 129.8 (CH), 127.0 (CH), 119.3 (CH), 114.4 (CH), 112.9 (CH), 61.4 (CH), 55.3 (CH_3), 50.2 (CH_2), 21.5 (CH_3). Characterization data matched the literature.[9]



***N*-(2-Bromo-2-phenylethyl)-4-methylbenzenesulfonamide (4).** Prepared according to the general procedure using aziridine **1a** (54.6 mg, 0.20 mmol) and tetrabromomethane (199.0 mg, 0.60 mmol). Flash column chromatography (Hexane/EtOAc = 10/1) yielded a white solid (66.5 mg, 94%). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75-7.71 (m, 2H), 7.35-7.26 (m, 7H), 4.91 (dd, *J* = 7.5, 6.9 Hz, 1H), 4.85 (t, *J* = 6.6 Hz, 1H), 3.65-3.49 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8 (C), 138.1 (C), 136.9 (C), 129.9 (CH), 129.2 (CH), 129.0 (CH), 127.6 (CH), 127.0 (CH), 52.6 (CH), 50.1 (CH_2), 21.5 (CH_3). Characterization data matched the literature.[9]

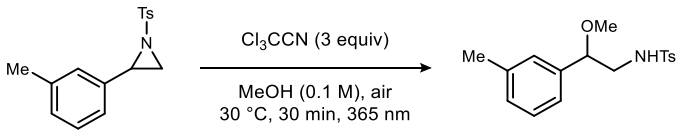
General procedure for methanol addition reactions

To an oven-dried test tube equipped with a stir bar was added aziridine **1** (0.20 mmol, 1.0 equiv), methanol (2.0 mL, 0.1 M), and trichloroacetonitrile (60 μL, 0.60 mmol, 3.0 equiv). The mixture was then stirred with UV irradiation (365 nm, 4 W x 2) under air atmosphere at 30 °C for 30 minutes. The resulting mixture was concentrated and purified by flash column chromatography (SiO_2: 7 g) to give product **3**.

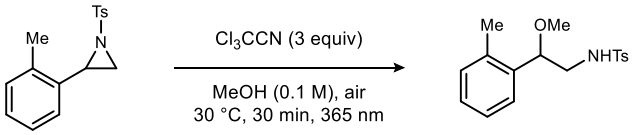


***N*-(2-Methoxy-2-phenylethyl)-4-methylbenzenesulfonamide (3a).** Prepared according to the general procedure using aziridine **1a** (54.5 mg, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 4/1) yielded a white solid (59.6 mg, 98%). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75-7.72 (m, 2H), 7.36-7.27 (m, 5H), 7.21-7.18 (m, 2H), 5.18-5.15 (m, 1H), 4.19 (dd, *J* = 9.3, 3.6 Hz, 1H), 3.25-3.16 (m, 4H), 2.97 (ddd, *J* = 12.9, 9.3, 3.3 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3 (C), 138.2 (C), 137.0 (C), 129.6 (CH), 128.6 (CH), 128.3 (CH), 127.0 (CH), 126.5 (CH), 82.0

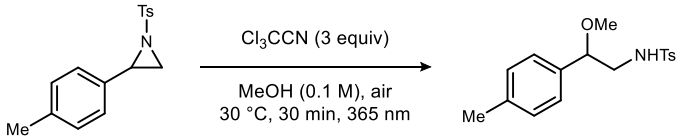
(CH), 56.7 (CH_3), 49.2 (CH_2), 21.4 (CH_3). Chiral HPLC analysis (Chiralcel OJ, Hexane/^{i}PrOH = 90/10, 1.0 mL/min, t_r(*major*) = 10.3 min, t_r(*minor*) = 14.2 min, 254 nm, 35 °C), $[\alpha]_D^{27}$ +112.1 (*c* = 0.52, $CHCl_3$ for 96% ee). Characterization data matched the literature.[10,11]



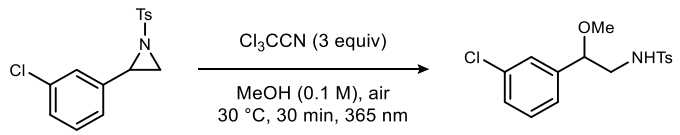
***N*-(2-Methoxy-2-*m*-tolylethyl)-4-methylbenzenesulfonamide (3b).** Prepared according to the general procedure using aziridine **1b** (57.5 mg, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 4/1) yielded a white solid (61.3 mg, 96%). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; Mp 71-72 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75-7.72 (m, 2H), 7.30-7.18 (m, 3H), 7.11-7.08 (m, 1H), 7.01-6.98 (m, 1H), 5.16 (dd, *J* = 8.7, 3.3 Hz, 1H), 4.16 (dd, *J* = 9.3, 3.6 Hz, 1H), 3.24-3.16 (m, 4H), 2.96 (ddd, *J* = 12.9, 9.3, 3.3 Hz, 1H), 2.41 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3 (C), 138.3 (C), 138.2 (C), 136.9 (C), 129.6 (CH), 129.0 (CH), 128.5 (CH), 127.2 (CH), 127.0 (CH), 123.6 (CH), 82.0 (CH), 56.7 (CH_3), 49.3 (CH_2), 21.4 (CH_3), 21.3 (CH_3); IR (KBr) 3269, 2921, 1420, 1331, 1164, 1081 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{17}H_{21}NNaO_3S$ $[M+Na]^+$ 342.1134, found 342.1143.



***N*-(2-Methoxy-2-*o*-tolylethyl)-4-methylbenzenesulfonamide (3c).** Prepared according to the general procedure using aziridine **1c** (57.5 mg, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 4/1) yielded a colorless oil (61.0 mg, 95%). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; Mp 80-81 °C;^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76-7.73 (m, 2H), 7.30-7.28 (m, 2H), 7.25-7.10 (m, 4H), 5.27-5.24 (m, 1H), 4.45 (dd, *J* = 9.3, 3.6 Hz, 1H), 3.24-3.14 (m, 4H), 2.87 (ddd, *J* = 12.6, 9.3, 3.0 Hz, 1H), 2.41 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3 (C), 137.1 (C), 136.1 (C), 135.7 (C), 130.6 (CH), 129.6 (CH), 127.8 (CH), 127.0 (CH), 126.3 (CH), 125.5 (CH), 78.7 (CH), 56.6 (CH_3), 48.2 (CH_2), 21.4 (CH_3), 18.8 (CH_3); IR (KBr) 3267, 2921, 1415, 1327, 1161, 1114 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{17}H_{21}NNaO_3S$ $[M+Na]^+$ 342.1134, found 342.1135.

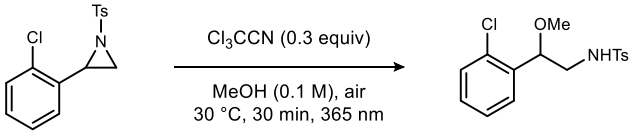


***N*-(2-Methoxy-2-*p*-tolylethyl)-4-methylbenzenesulfonamide (3d).** Prepared according to the general procedure using aziridine **1d** (57.3 mg, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 4/1) yielded a white solid (60.2 mg, 90%). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; Mp 75-76 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.71 (m, 2H), 7.30-7.27 (m, 2H), 7.14-7.07 (m, 4H), 5.14 (dd, *J* = 8.7, 3.3 Hz, 1H), 4.16 (dd, *J* = 9.3, 3.9 Hz, 1H), 3.22-3.14 (m, 4H), 2.96 (ddd, *J* = 12.9, 9.3, 3.3 Hz, 1H), 2.41 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3 (C), 138.1 (C), 137.0 (C), 135.2 (C), 129.6 (CH), 129.2 (CH), 127.0 (CH), 126.5 (CH), 81.8 (CH), 56.5 (CH_3), 49.3 (CH_2), 21.4 (CH_3), 21.0 (CH_3); IR (KBr) 3252, 2923, 1411, 1332, 1164, 1116, 1086 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{17}H_{21}NNaO_3S$ $[M+Na]^+$ 342.1134, found 342.1153.

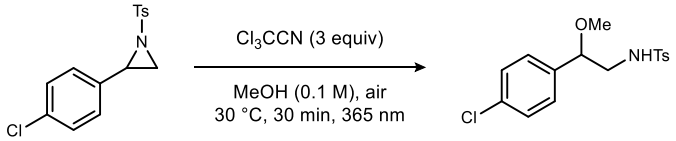


***N*-(2-(3-Chlorophenyl)-2-methoxyethyl)-4-methylbenzenesulfonamide (3e).** Prepared according to the general procedure using aziridine **1e** (61.6 mg, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 4/1) yielded a white solid (53.9 mg, 80%). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; Mp 98-99 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.71 (m, 2H), 7.31-7.26 (m, 4H), 7.20-7.18 (m, 1H), 7.12-7.08 (m,

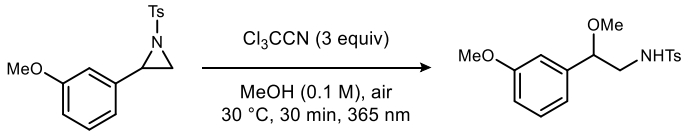
1H), 5.14-5.10 (m, 1H), 4.18 (dd, *J* = 9.0, 3.6 Hz, 1H), 3.24-3.15 (m, 4H), 2.93 (ddd, *J* = 12.6, 9.0, 3.3 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5 (C), 140.5 (C), 136.8 (C), 134.6 (C), 130.0 (CH), 129.7 (CH), 128.5 (CH), 127.0 (CH), 126.6 (CH), 124.8 (CH), 81.5 (CH), 56.9 (CH_3), 49.1 (CH_2), 21.5 (CH_3); IR (KBr) 3272, 2921, 1420, 1330, 1165, 1080 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{16}H_{18}ClNNaO_3S$ $[M+Na]^+$ 362.0588, found 362.0563.



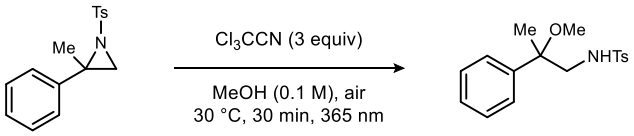
***N*-(2-(2-Chlorophenyl)-2-methoxyethyl)-4-methylbenzenesulfonamide (3f).** Prepared according to the general procedure using aziridine **1f** (61.6 mg, 0.20 mmol) and trichloroacetonitrile (6 μL, 0.06 mmol, 0.3 equiv). Flash column chromatography (Hexane/EtOAc = 4/1) yielded a white solid (64.2 mg, 94%, a trace amount of **2f** was contaminating). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78-7.74 (m, 2H), 7.34-7.18 (m, 6H), 5.26-5.24 (m, 1H), 4.61 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.38 (ddd, *J* =12.3, 9.3, 3.3 Hz, 1H), 3.16 (s, 3H), 2.88 (ddd, *J* = 12.3, 9.0, 3.3 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5 (C), 140.5 (C), 136.8 (C), 134.6 (C), 130.0 (CH), 129.7 (CH), 128.5 (CH), 127.0 (CH), 126.6 (CH), 124.8 (CH), 81.5 (CH), 56.9 (CH_3), 49.1 (CH_2), 21.5 (CH_3); IR (KBr) 3262, 2987, 2923, 1598, 1418, 1325, 911 cm^{-1}. Characterization data matched the literature.[10]



***N*-(2-(4-Chlorophenyl)-2-methoxyethyl)-4-methylbenzenesulfonamide (3g).** Prepared according to the general procedure using aziridine **1g** (61.6 mg, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 4/1) yielded a white solid (64.0 mg, 94%). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; Mp 87-88 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73-7.70 (m, 2H), 7.30-7.27 (m, 4H), 7.16-7.13 (m, 2H), 5.24-5.21 (m, 1H), 4.19 (dd, *J* = 9.0, 3.9 Hz, 1H), 3.23-3.14 (m, 4H), 2.94 (ddd, *J* = 12.9, 9.0, 3.6 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4 (C), 136.8 (C), 134.0 (C), 129.6 (CH), 128.7 (CH), 127.9 (CH), 126.9 (CH), 81.3 (CH), 56.7 (CH_3), 49.1 (CH_2), 21.4 (CH_3); IR (KBr) 3269, 2930, 1400, 1332, 1167, 1087 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{16}H_{18}ClNNaO_3S$ $[M+Na]^+$ 362.0588, found 362.0561.

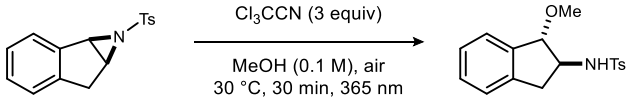


***N*-(2-Methoxy-2-(3-methoxyphenyl)ethyl)-4-methylbenzenesulfonamide (3h).** Prepared according to the general procedure using aziridine **1h** (61.2 mg, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 4/1) yielded a white solid (65.8 mg, 97%). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.71 (m, 2H), 7.30-7.21 (m, 3H), 6.85-6.74 (m, 3H), 5.16-5.12 (m, 1H), 4.17 (dd, *J* = 9.3, 3.6 Hz, 1H), 3.78 (s, 3H), 3.25-3.16 (m, 4H), 2.96 (ddd, *J* = 12.9, 9.3, 3.3 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8 (C), 143.3 (C), 139.9 (C), 136.9 (C), 129.6 (CH x 2), 127.0 (CH), 118.9 (CH), 113.7 (CH), 111.9 (CH), 81.9 (CH), 56.7 (CH_3), 55.1 (CH_3), 49.2 (CH_2), 21.4 (CH_3); IR (KBr) 3257, 2912, 1595, 1331, 1164, 1081 cm^{-1}. Characterization data matched the literature.[10]

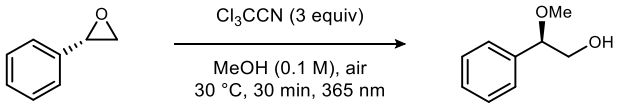


***N*-(2-Methoxy-2-phenylpropyl)-4-methylbenzenesulfonamide (3i).** Prepared according to the general procedure using aziridine **1i** (57.4 mg, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 4/1) yielded a colorless oil (62.9 mg, 98%). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; ^{1}H NMR (300

MHz, $CDCl_3$) δ 7.67-7.64 (m, 2H), 7.35-7.23 (m, 7H), 4.91-4.87 (m, 1H), 3.10 (dd, *J* = 12.0, 8.1 Hz, 1H), 3.03-2.98 (m, 4H), 2.39 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1 (C), 141.8 (C), 136.8 (C), 129.6 (CH), 128.4 (CH), 127.6 (CH), 126.9 (CH), 126.1 (CH), 78.2 (C), 53.5 (CH_2), 50.3 (CH_3), 21.4 (CH_3), 20.3 (CH_3); IR (KBr) 3279, 2936, 1447, 1332, 1167, 1093 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{17}H_{21}NNaO_3S$ $[M+Na]^+$ 342.1134, found 342.1125.

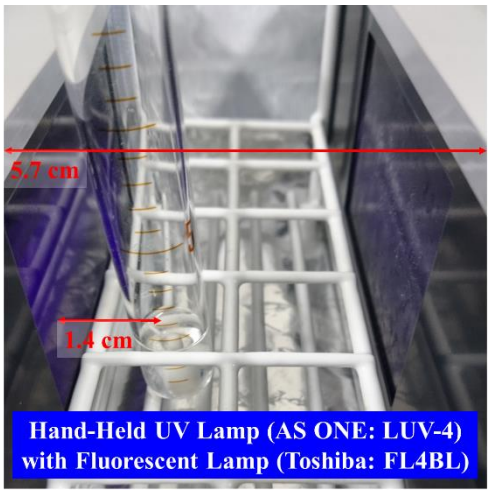


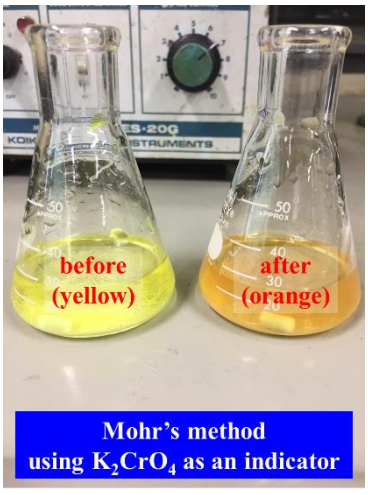
***N*-(1-Methoxy-2,3-dihydro-1*H*-inden-2-yl)-4-methylbenzenesulfonamide (3j).** Prepared according to the general procedure using aziridine **1j** (57.1 mg, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 4/1) yielded a yellowish solid (45.3 mg, 71%). R_f = 0.3 (Hexane/EtOAc = 4/1) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2H), 7.33-7.28 (m, 3H), 7.23-7.20 (m, 2H), 7.13-7.10 (m, 1H), 5.16 (d, *J* = 8.1 Hz, 1H), 4.60 (d, *J* = 4.5 Hz, 1H), 3.99-3.91 (m, 1H), 3.36 (s, 3H), 3.19 (dd, *J* = 16.2, 7.5 Hz, 1H), 2.57 (dd, *J* = 16.2, 5.4 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6 (C), 139.9 (C), 139.5 (C), 137.5 (C), 129.7 (CH), 129.0 (CH), 127.13 (CH), 127.08 (CH), 125.2 (CH), 125.0 (CH), 88.7 (CH), 59.1 (CH), 56.9 (CH_3), 37.6 (CH_2), 21.5 (CH_3); IR (KBr) 3199, 2924, 2361, 1598, 1460, 1331, 1164, 1092, 930 cm^{-1}. The *trans*-stereochemistry was postulated by the coupling constant of the methine protons. Characterization data matched the literature.[10]



(*R*)-2-Methoxy-2-phenylethanol (6). Prepared according to the general procedure using styrene oxide (*S*)-**1a** (22.8 μL, 0.20 mmol). Flash column chromatography (Hexane/EtOAc = 2/1) yielded a colorless oil (28.9 mg, 95%). R_f = 0.3 (Hexane/EtOAc = 2/1) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.28 (m, 5H), 4.31 (dd, *J* = 8.1, 3.9 Hz, 1H), 3.72-3.58 (m, 2H), 3.31 (s, 3H), 2.57 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2 (C), 128.5 (CH), 128.1 (CH), 126.8 (CH), 84.6 (CH), 67.3 (CH_2), 56.9 (CH_3). Chiral HPLC analysis (Chiralcel OD-3, Hexane/^{i}PrOH = 98/2, 0.7 mL/min, t_r(*major*) = 17.7 min, t_r(*minor*) = 19.1 min, 210 nm, 35 °C), $[\alpha]_D^{26}$ -111.7 (*c* = 0.40, $CHCl_3$ for 82% ee). Characterization data matched the literature.[12]

Mohr's method





UV irradiation was performed for a solution of trichloroacetonitrile (30 μL, 0.30 mmol) in 1,4-dioxane or methanol (1 mL). After the indicated time, the reaction mixture was poured into 100 mL Erlenmeyer flask,

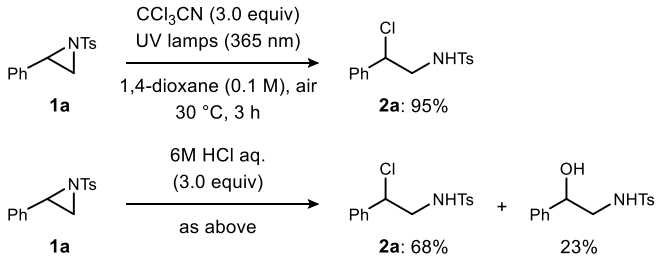
and diluted with dist H_2O (20 mL). The acidic solution was neutralized with Na_2CO_3 (30 mg), and then 5% K_2CrO_4 aq (5 mL) was added as an indicator. The resulting solution was titrated by a 0.1 M $AgNO_3$ aq (until the color changes from yellow to orange). This experiment was repeated three times.

in 1,4-dioxane for 30 min: 28.8 μmol (Cl^-)
1 h: 131.7 μmol (Cl^-)
3 h: 238.1 μmol (Cl^-)
12 h: 348.6 μmol (Cl^-)

in methanol for 30 min: 6.6 μmol (Cl^-)

Appendix

The following experiments were conducted in accordance with the reviewers' comments.



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(5) For **1d**, **1f**, **1g**, **1i**, and **1j**: Arenas, I.; Fuentes, M. A.; Álvarez, E.; Díaz, Y.; Caballero, A.; Castillón, S.; Pérez, P. J. *Inorg. Chem.* **2014**, *53*, 3991-3999.
(6) For **1e** and (*R*)-**1a**: Craig, R. A., II; O'Connor, N. R.; Goldberg, A. F. G.; Stoltz, B. M. *Chem. Eur. J.* **2014**, *20*, 4806-4813.
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^{1}H & ^{13}C NMR Spectra of 2a

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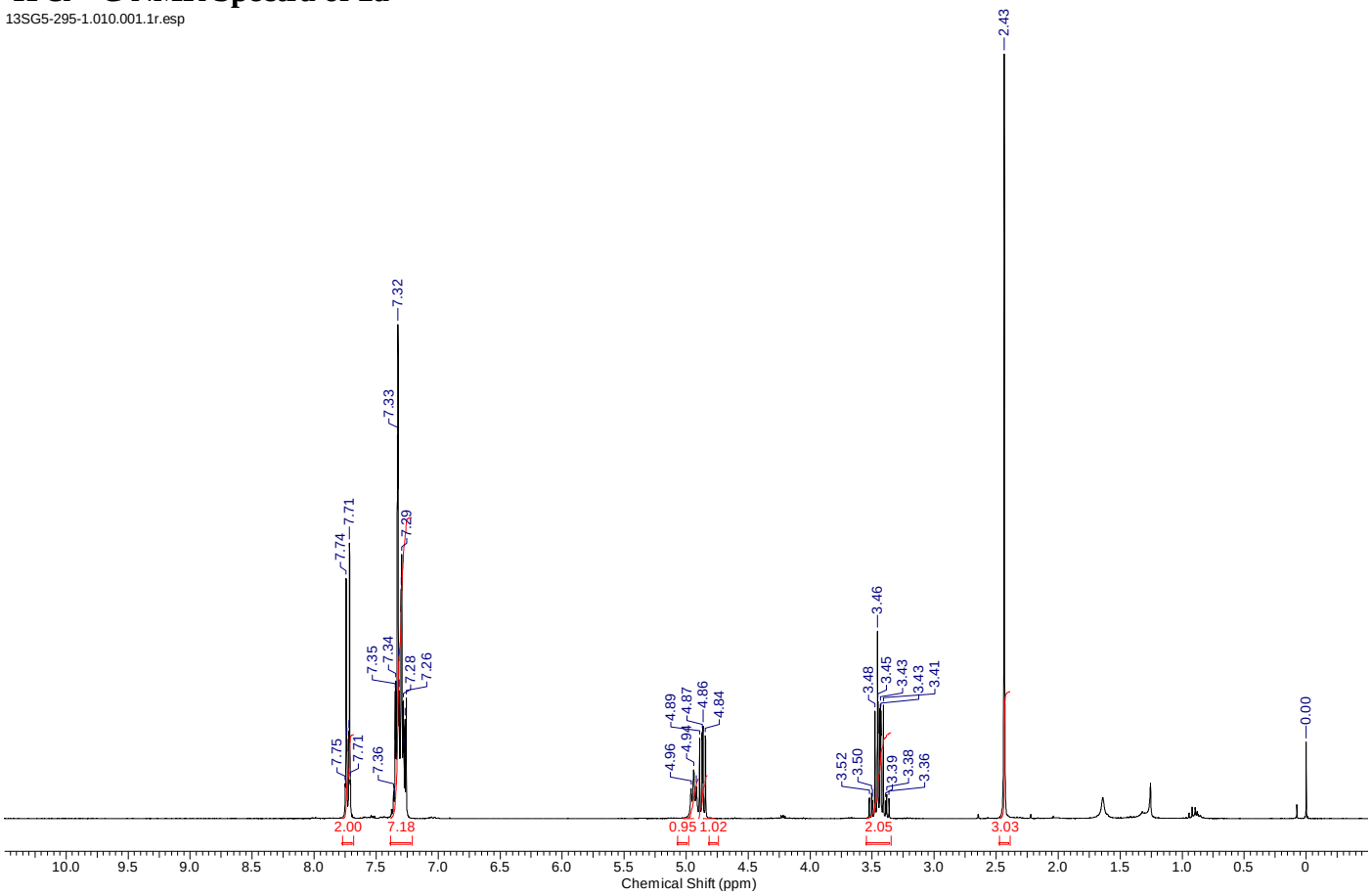

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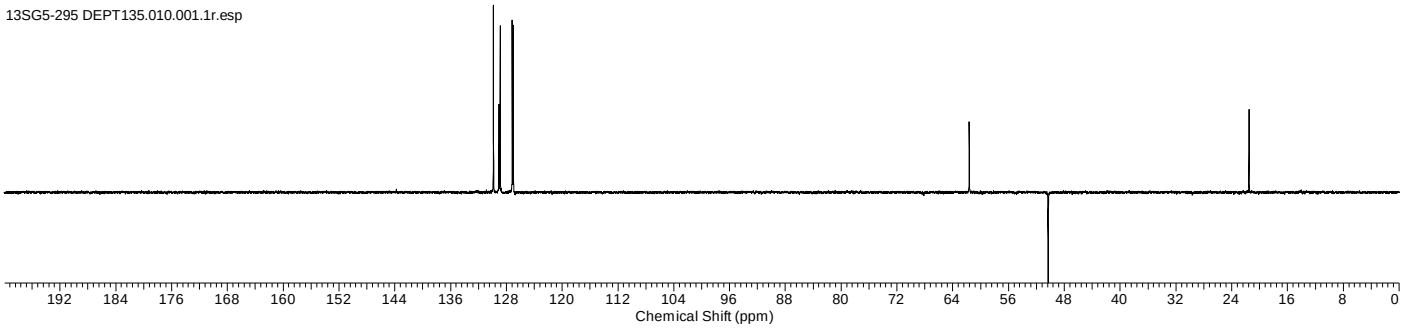

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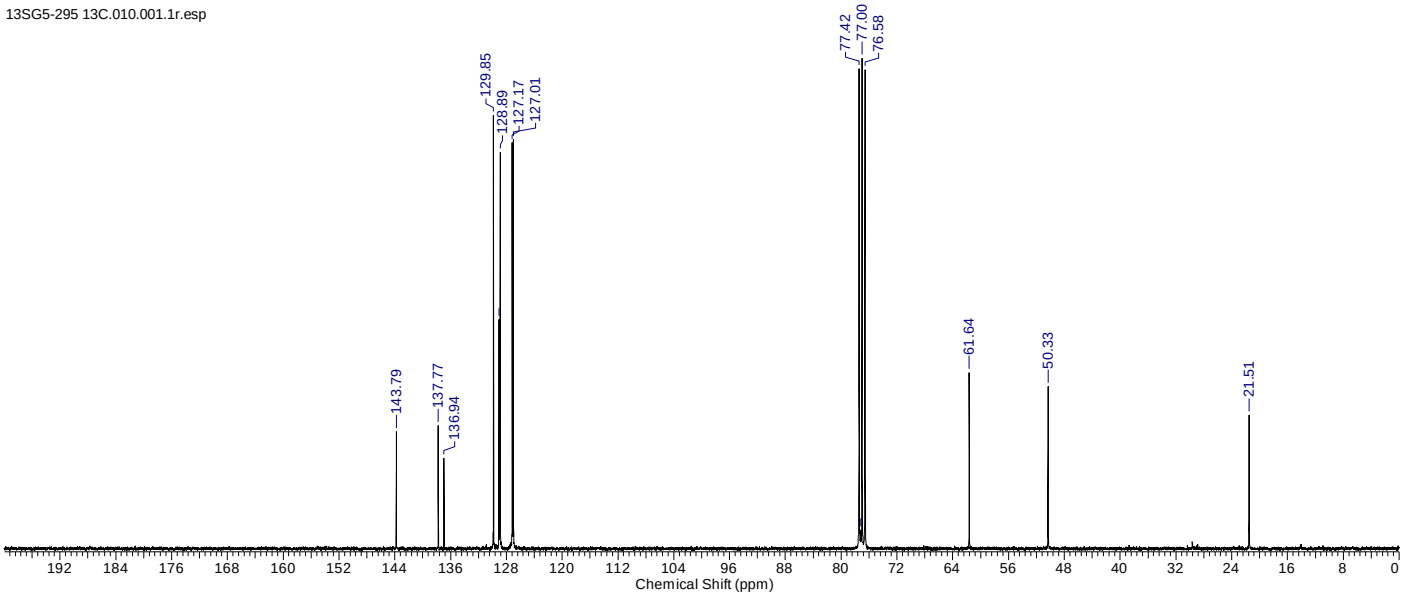

^{1}H & ^{13}C NMR Spectra of 2b

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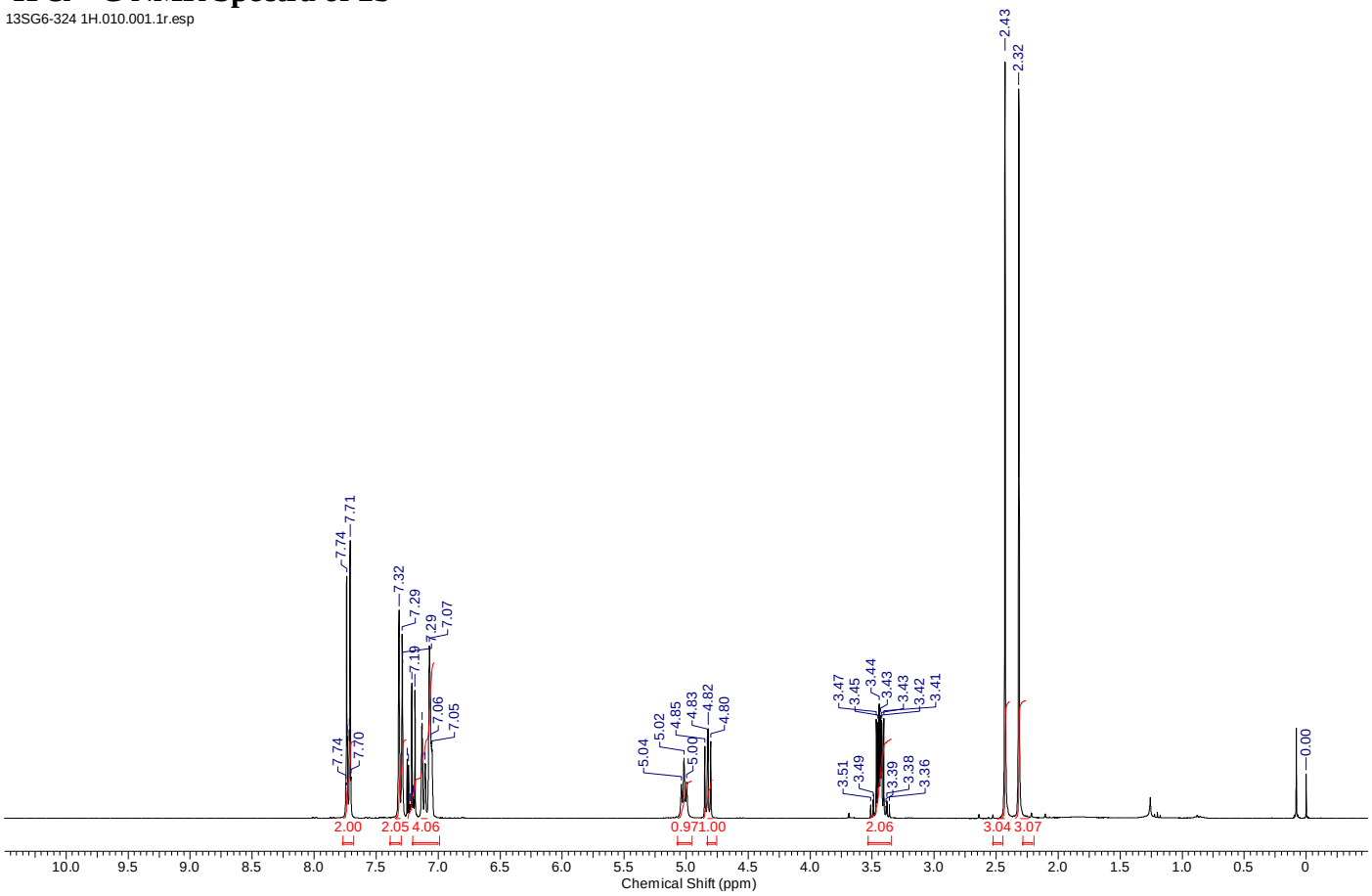

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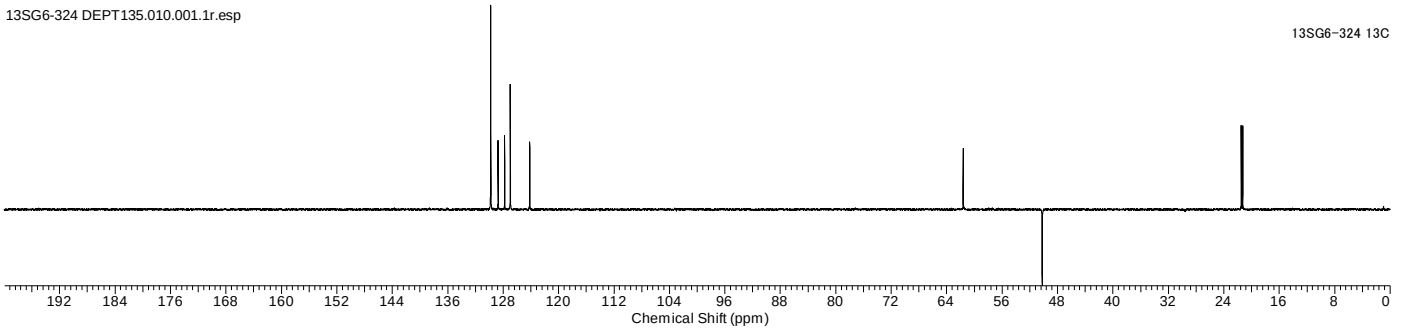
13SG6-324 13C



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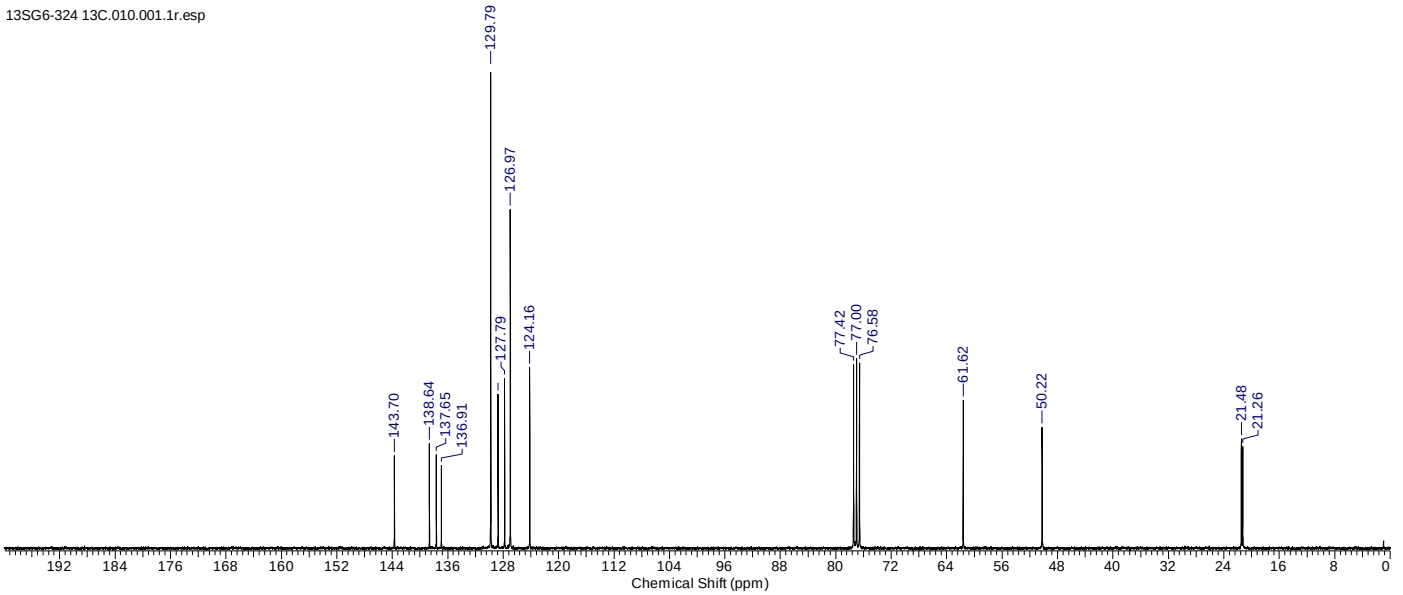

^{1}H & ^{13}C NMR Spectra of 2c

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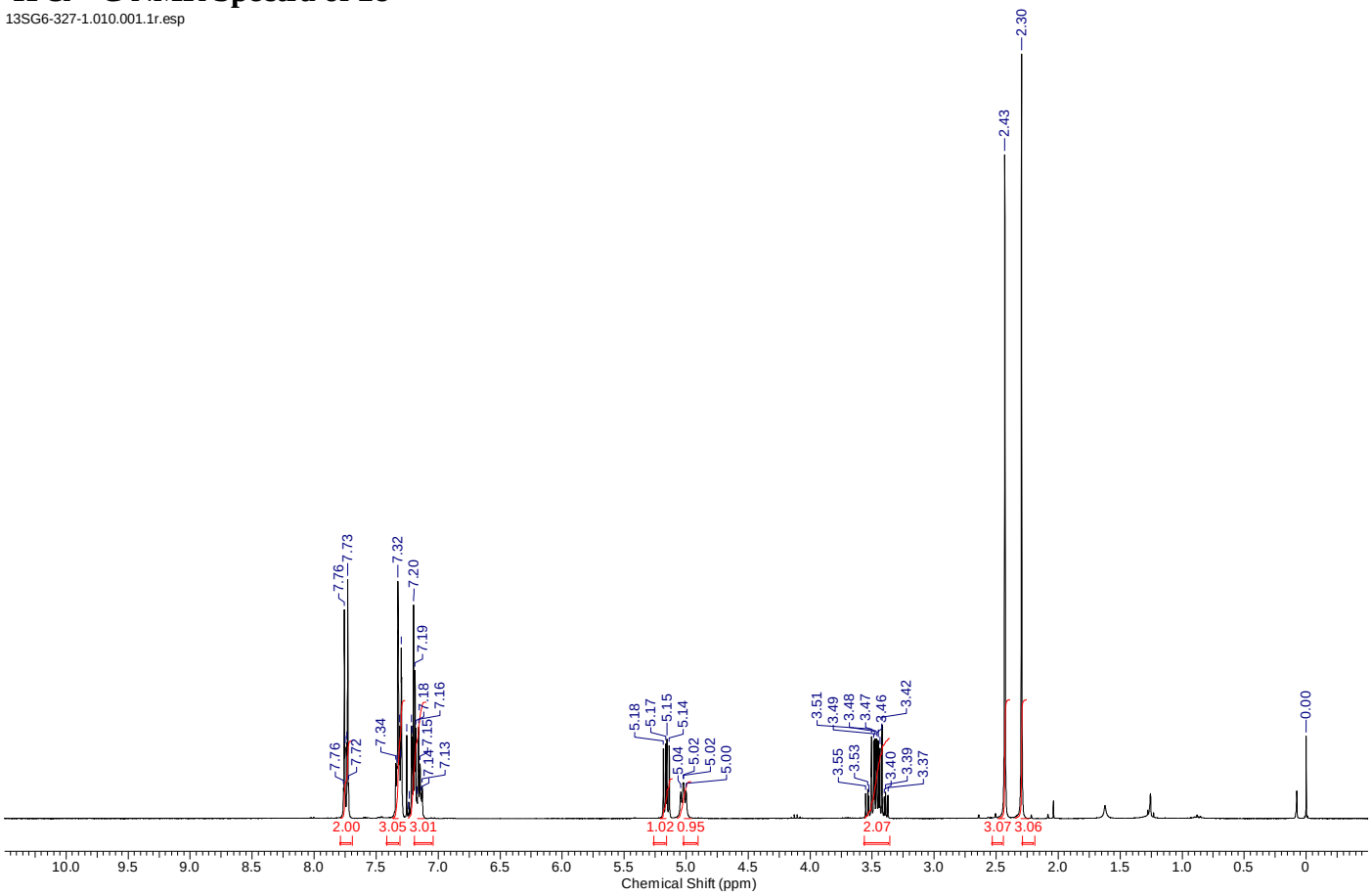

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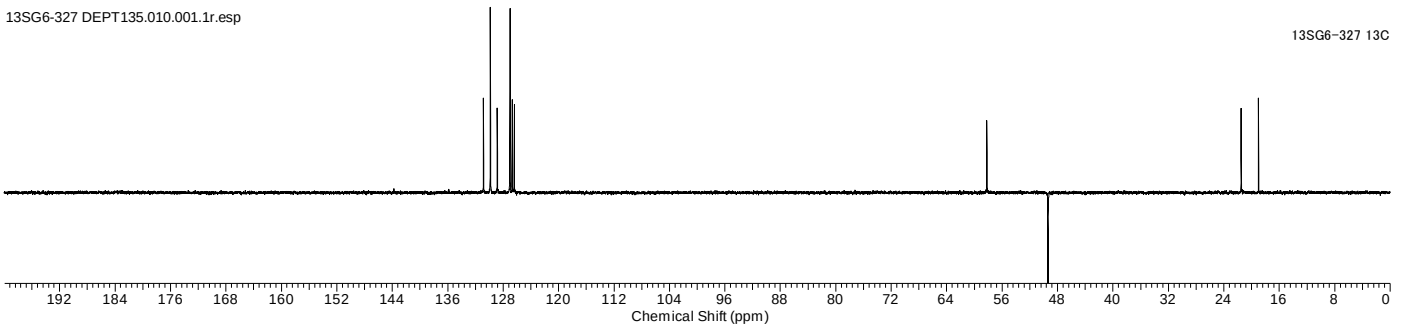
13SG6-327 13C



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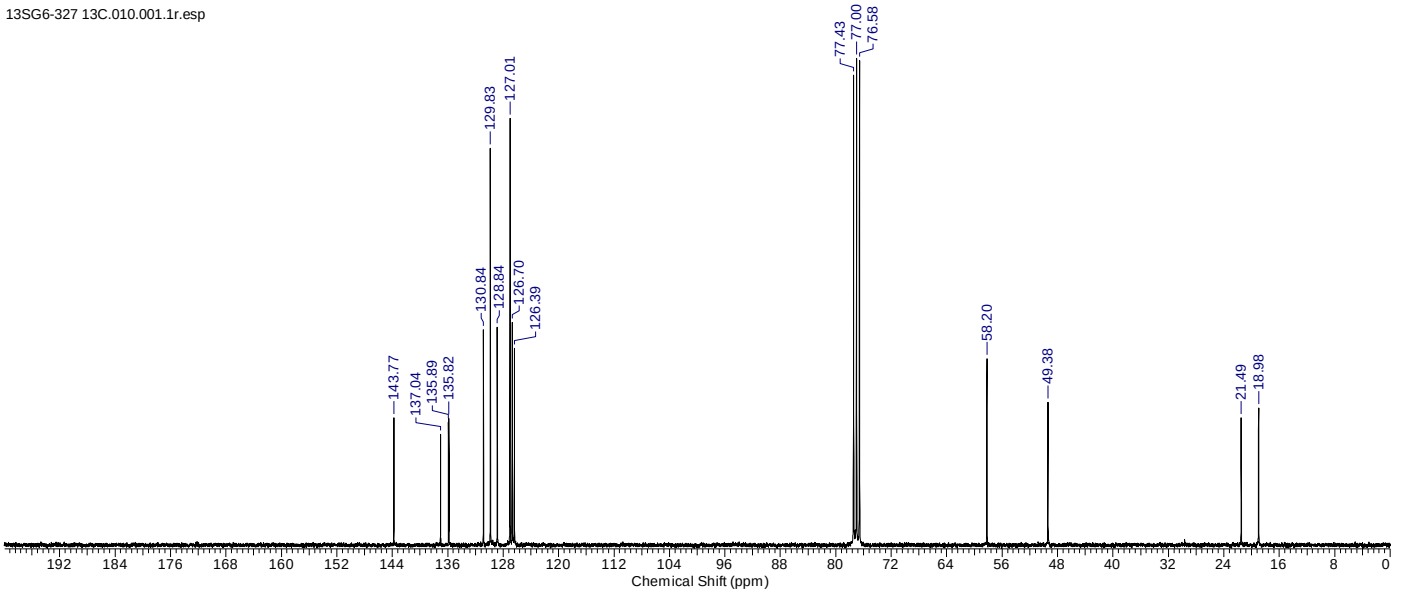
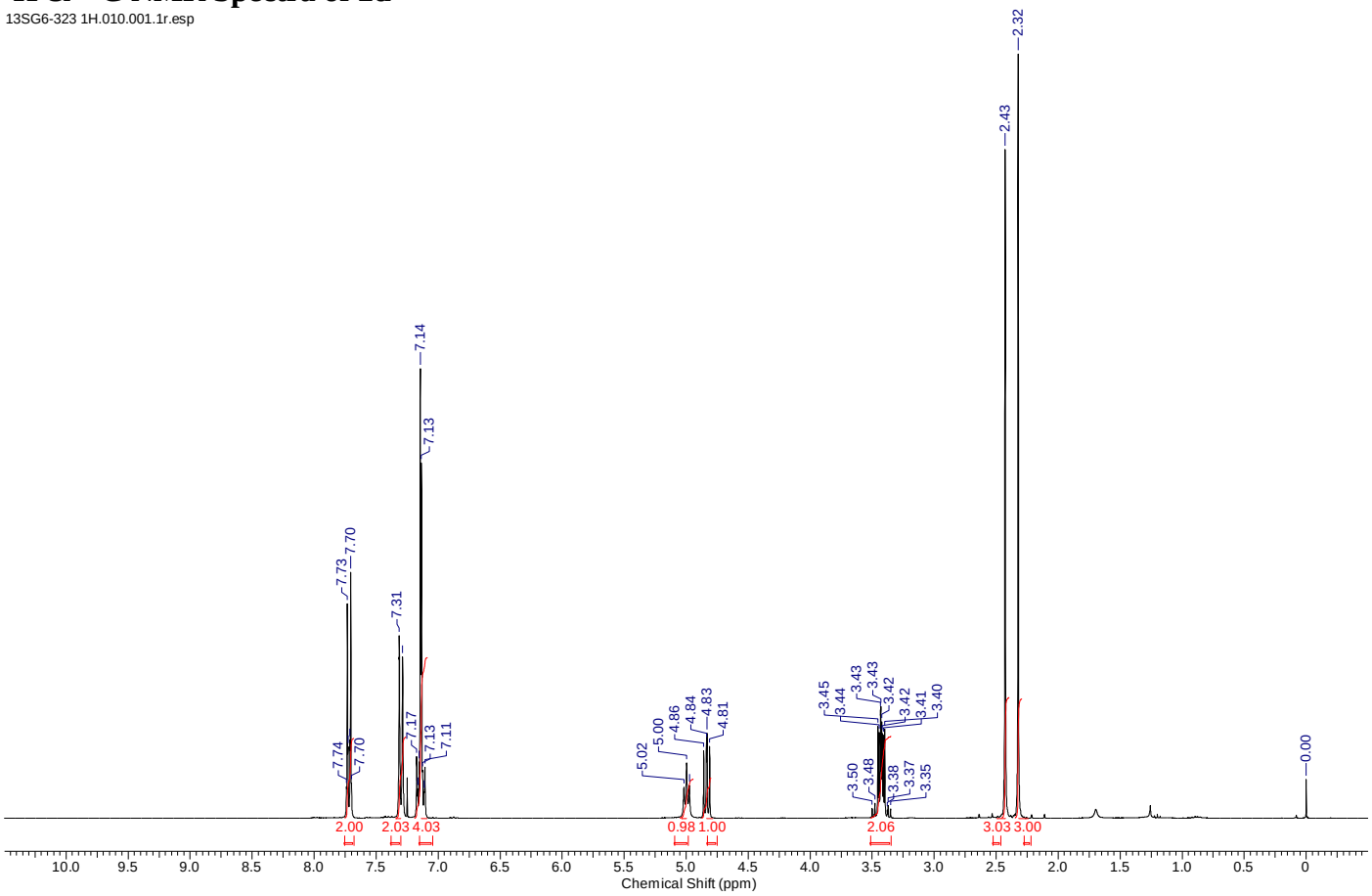
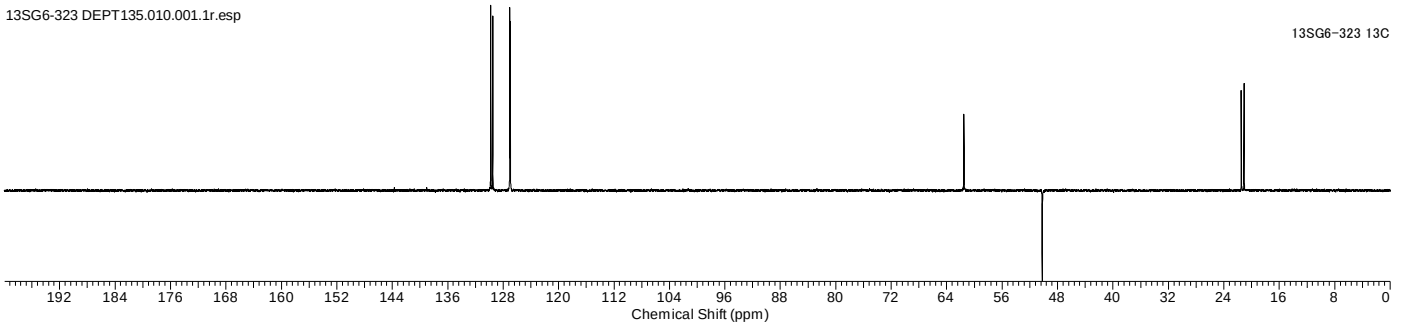
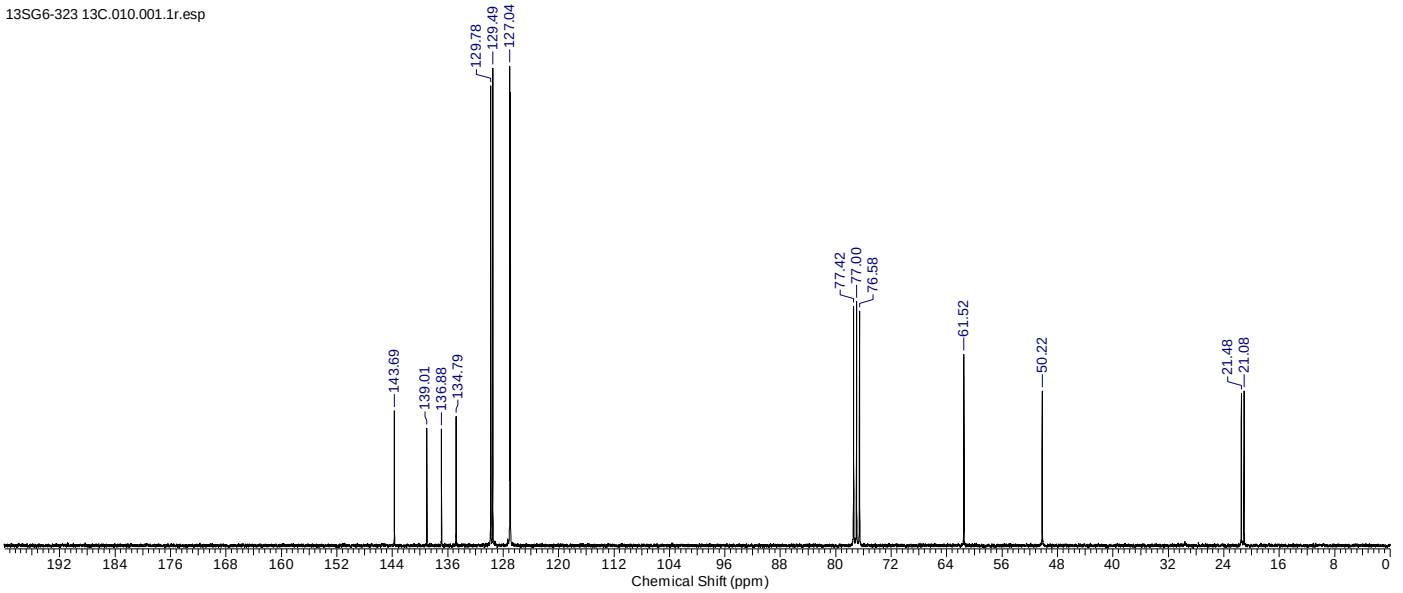


^{1}H & ^{13}C NMR Spectra of 2d







^{1}H & ^{13}C NMR Spectra of 2e

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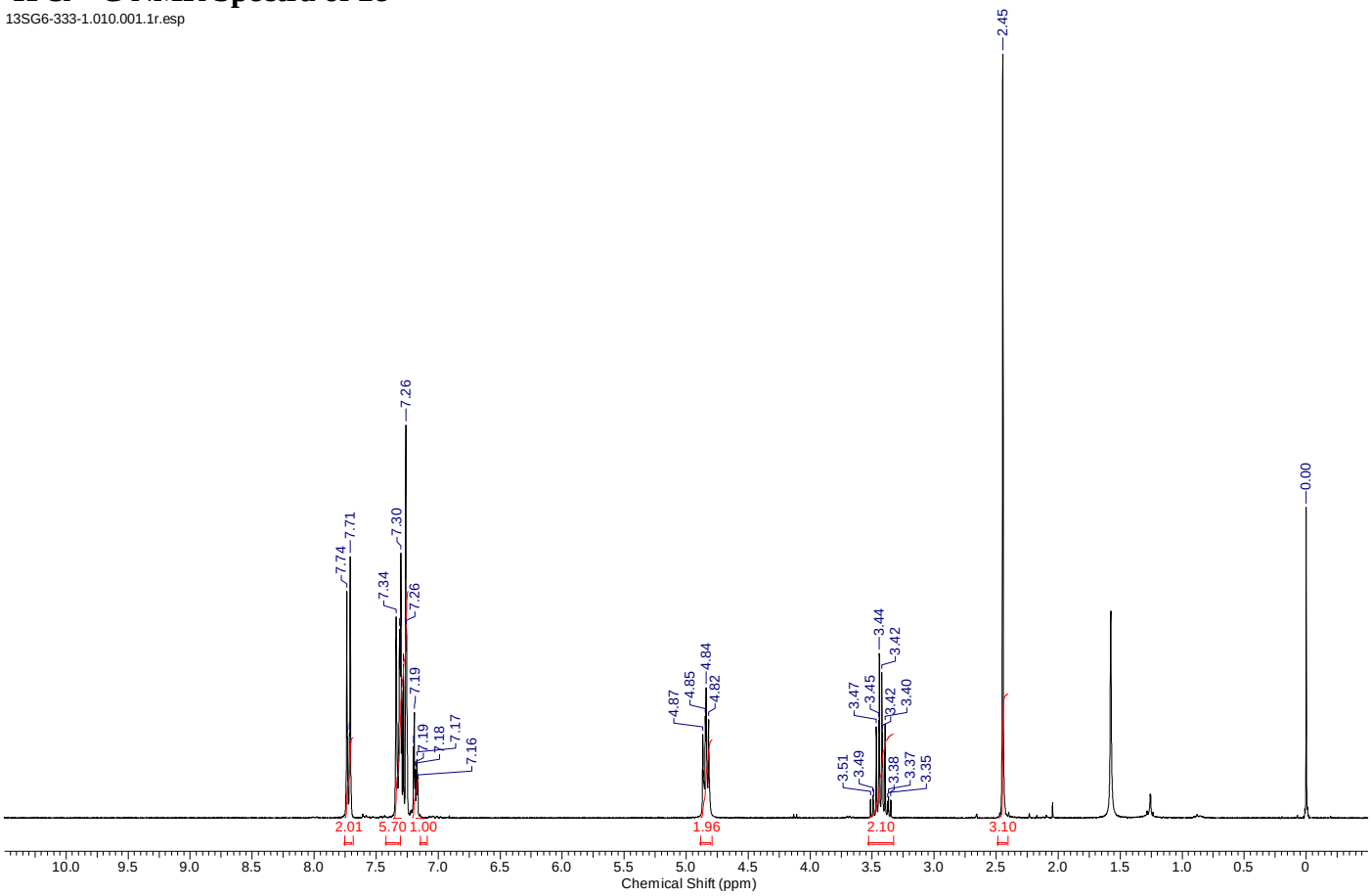

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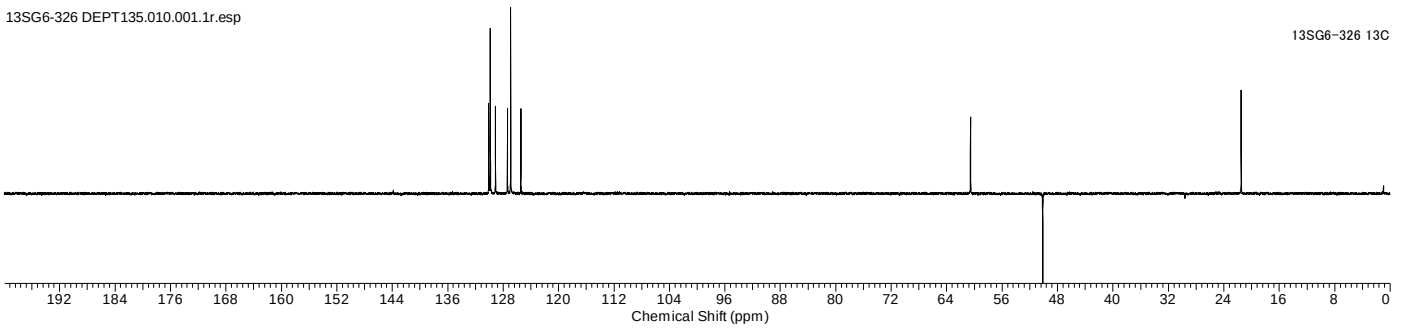
13SG6-326 13C



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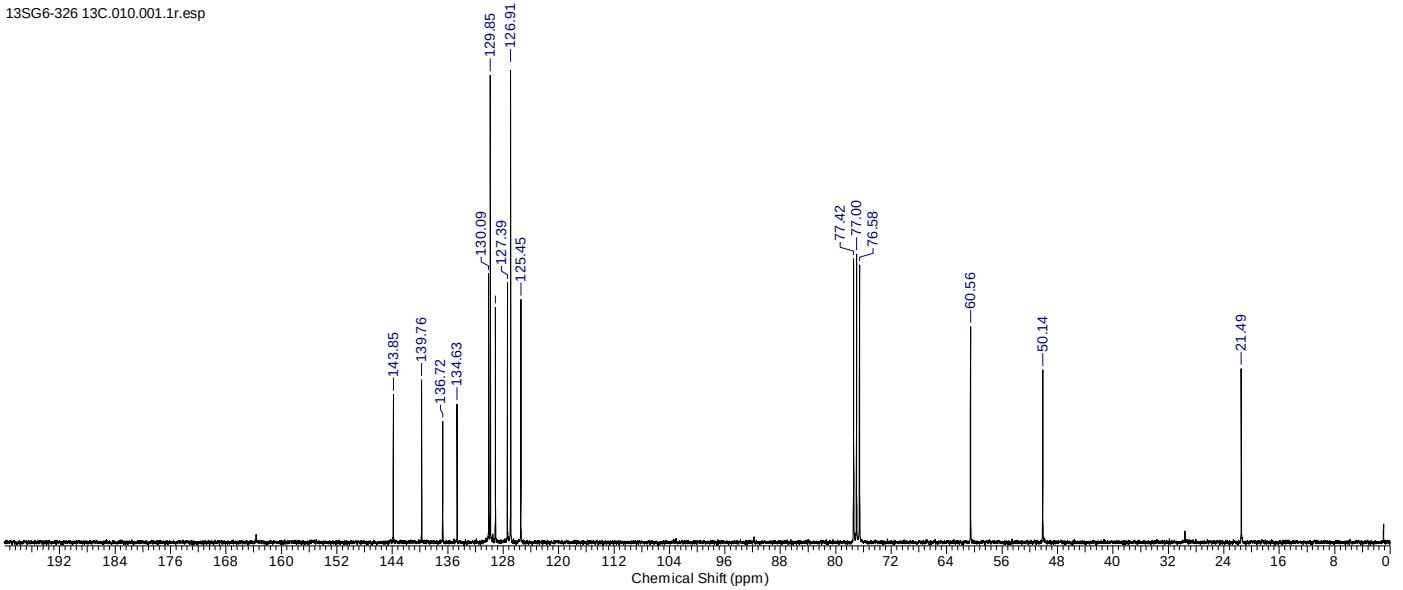

^{1}H & ^{13}C NMR Spectra of 2f

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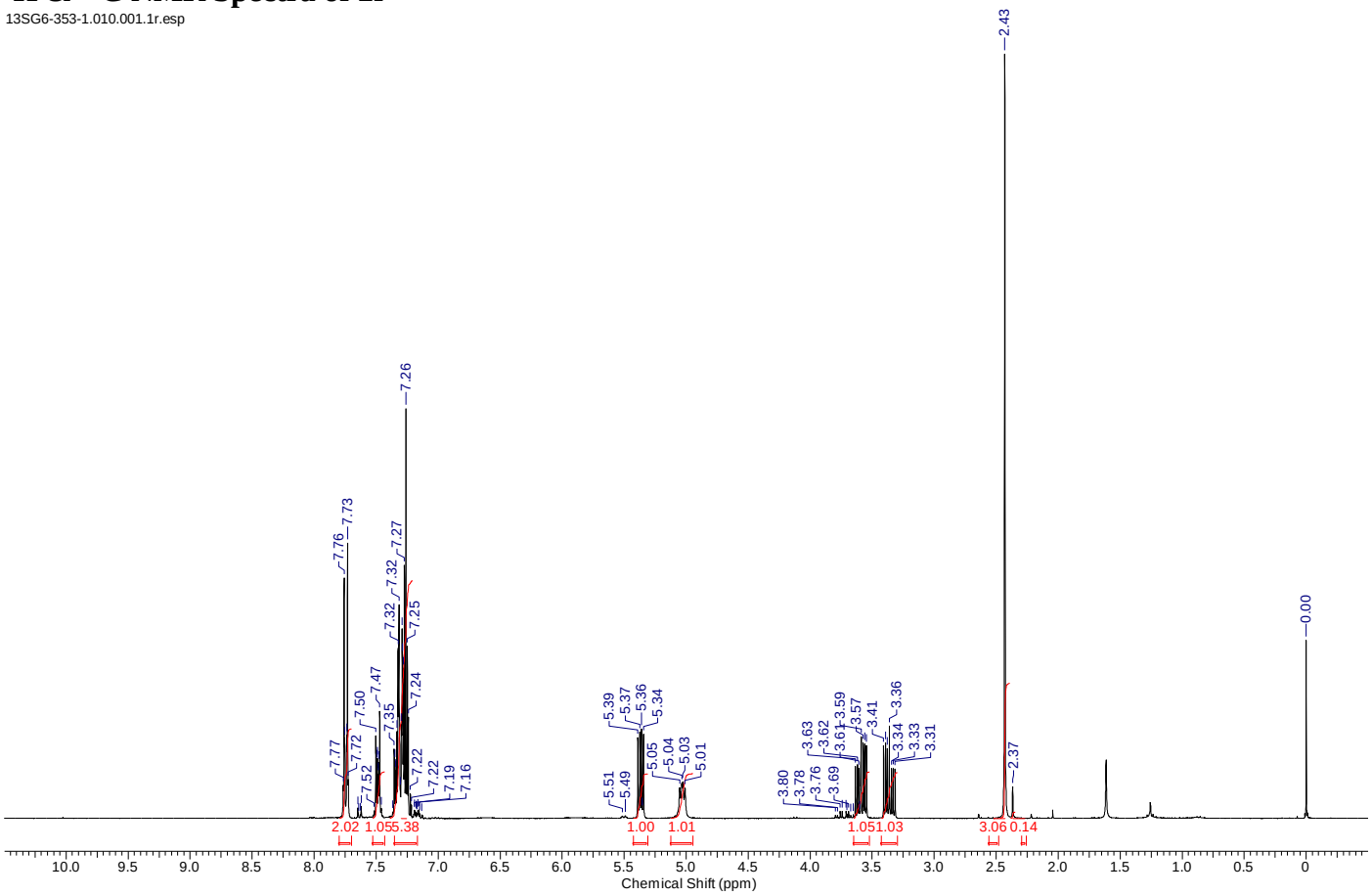

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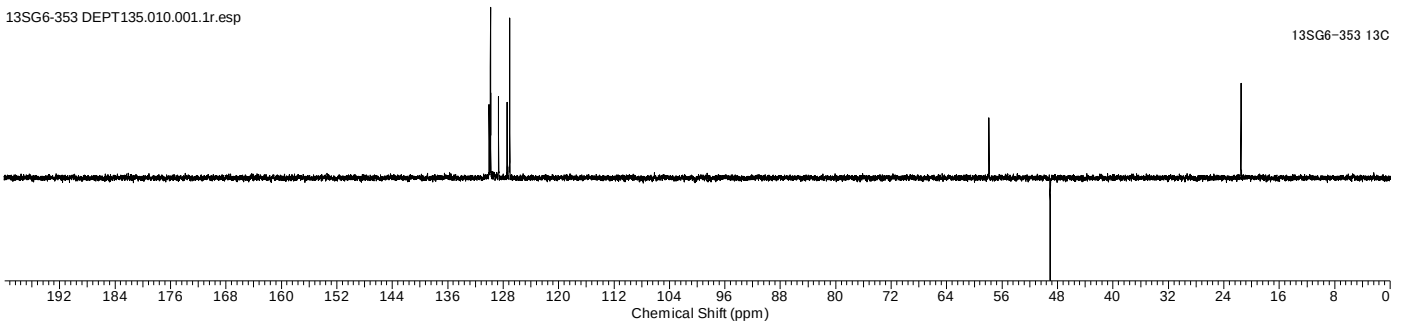

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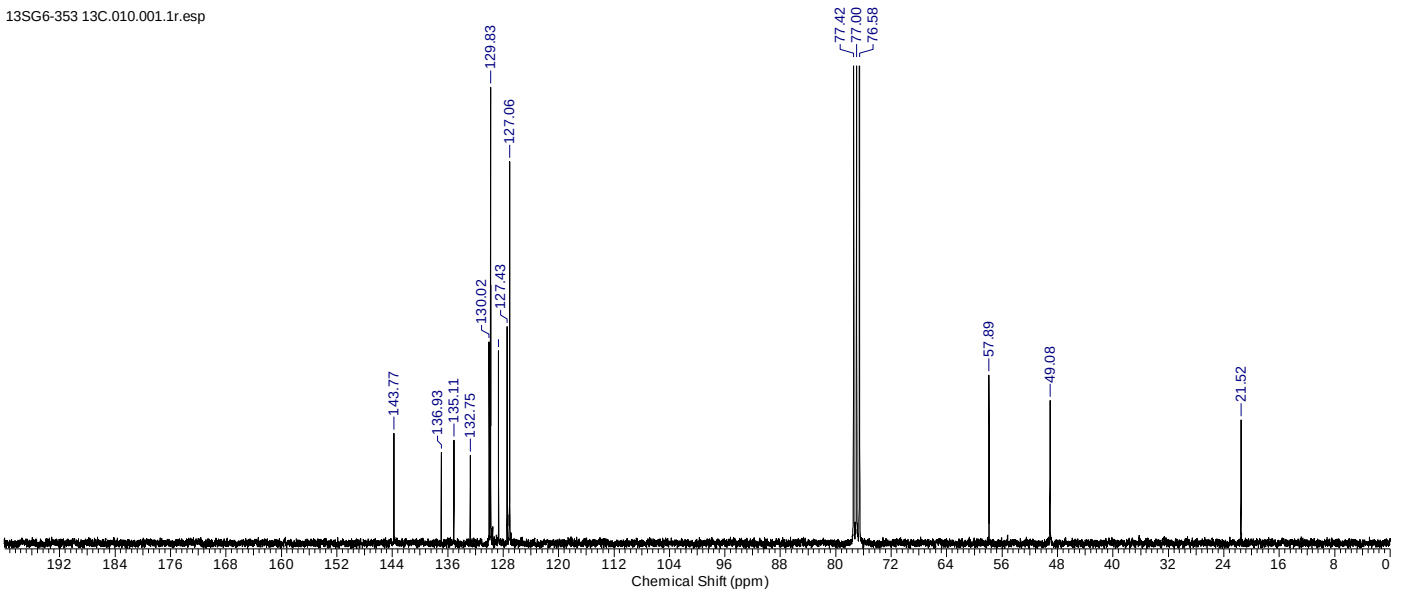

^{1}H & ^{13}C NMR Spectra of 2g

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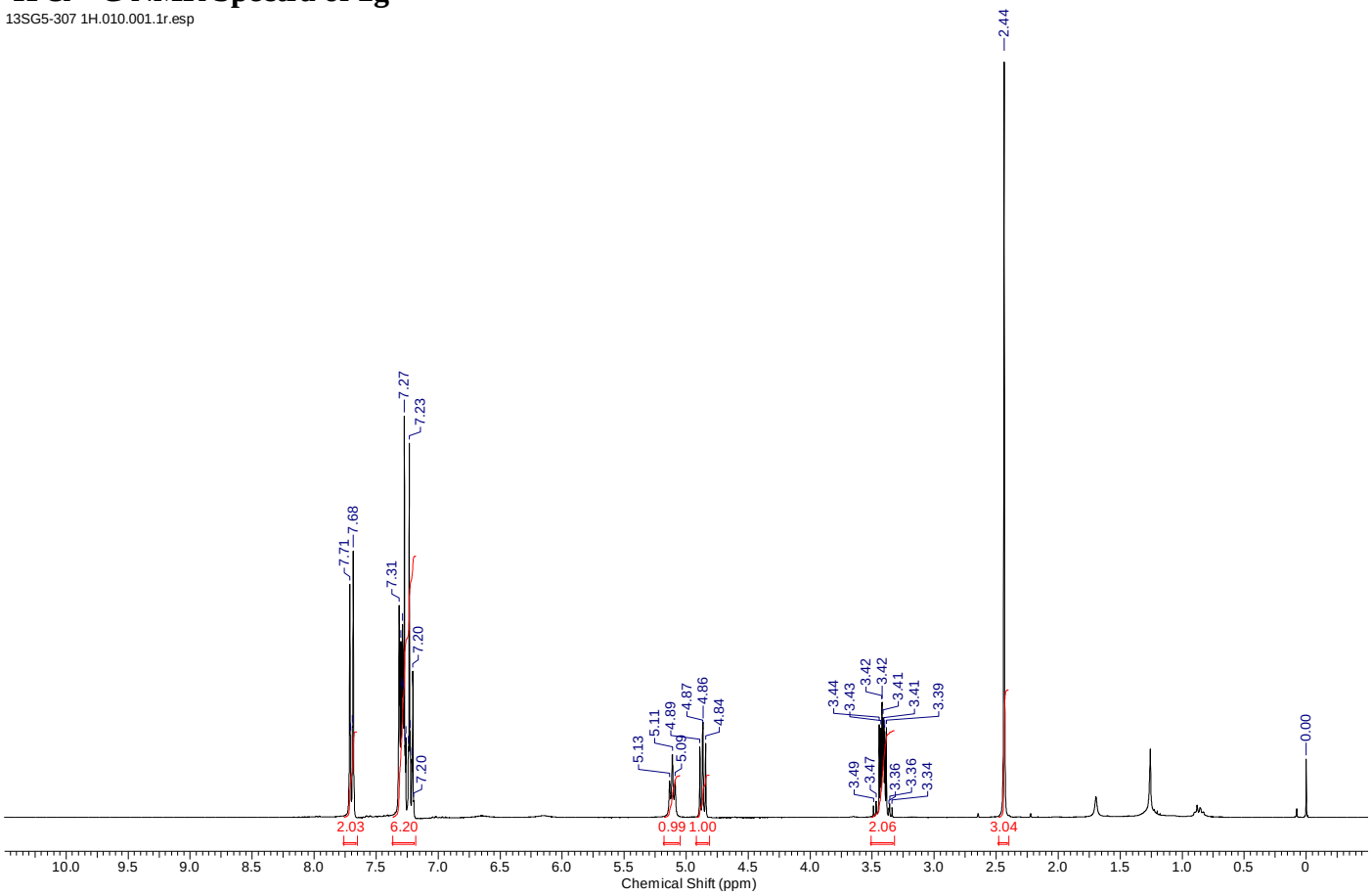

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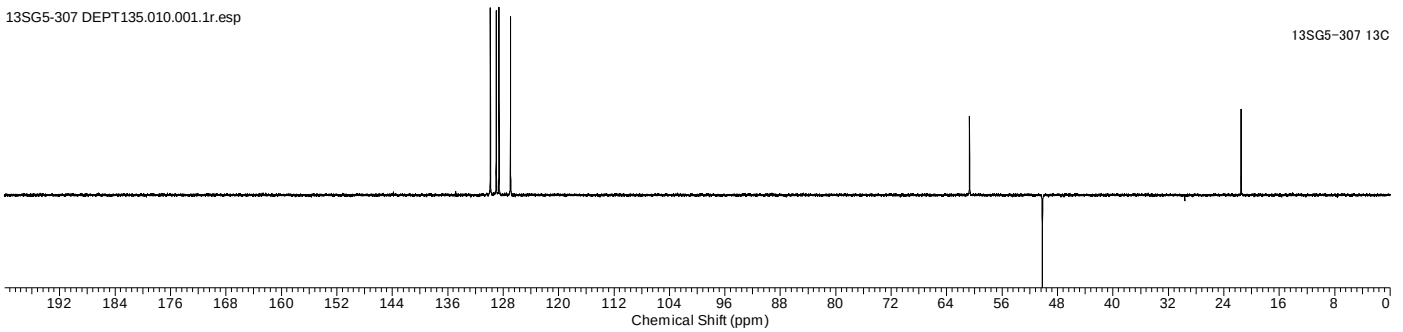

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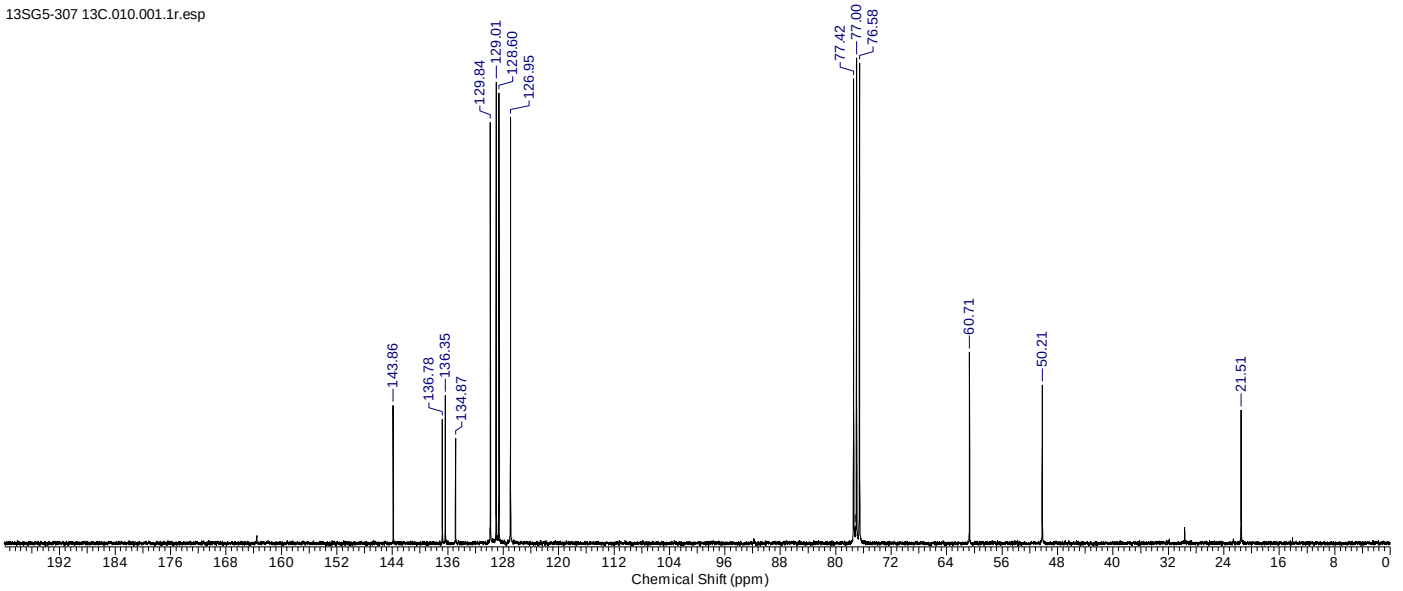
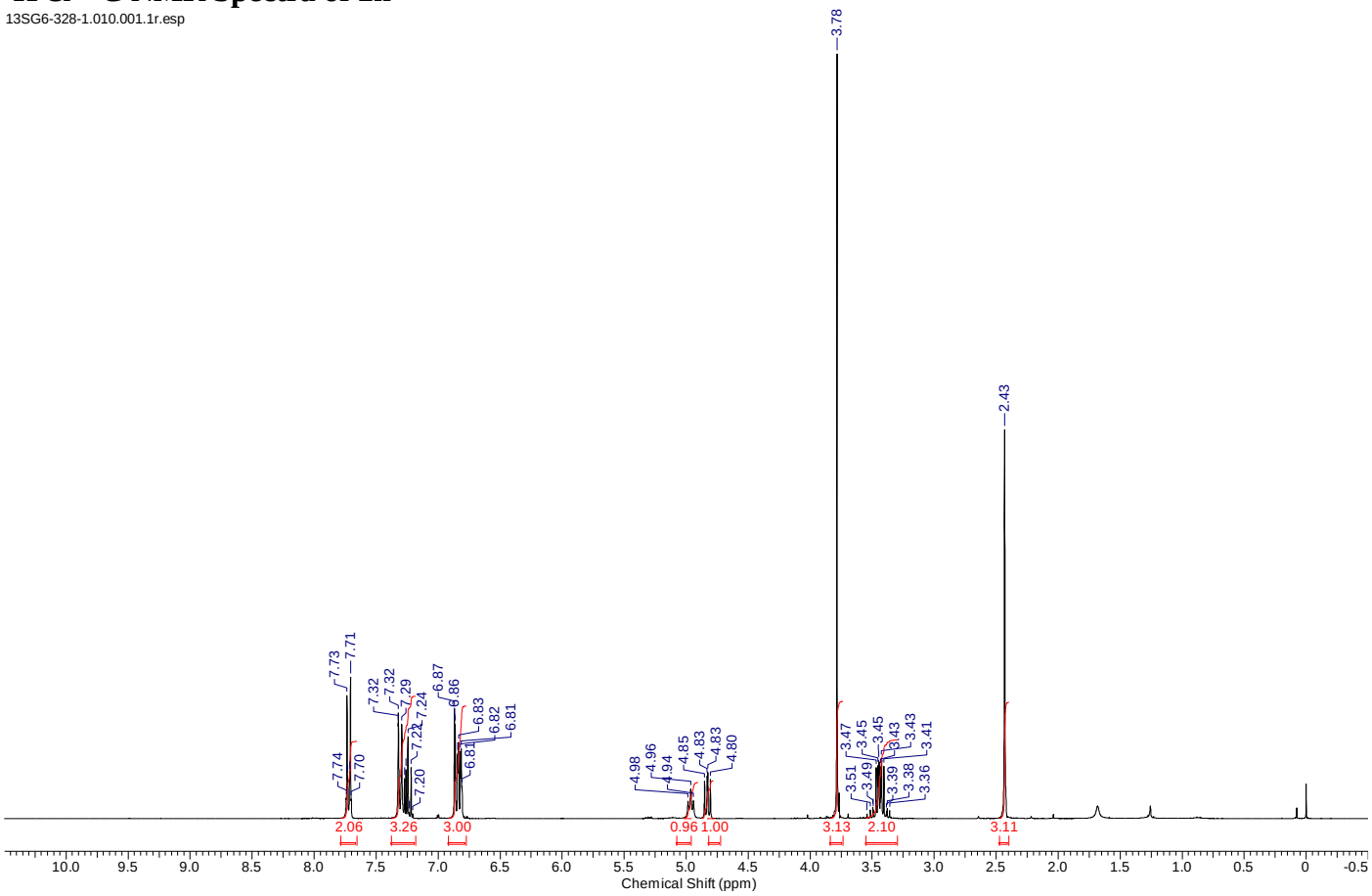
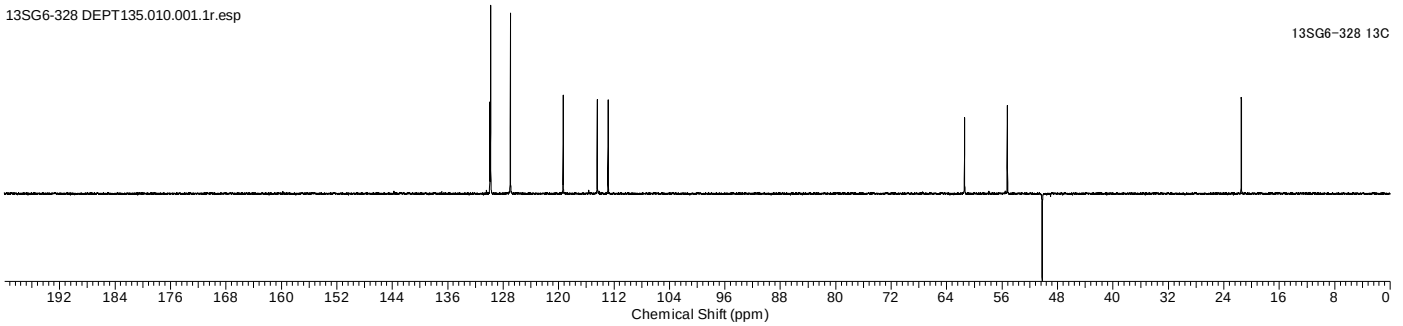
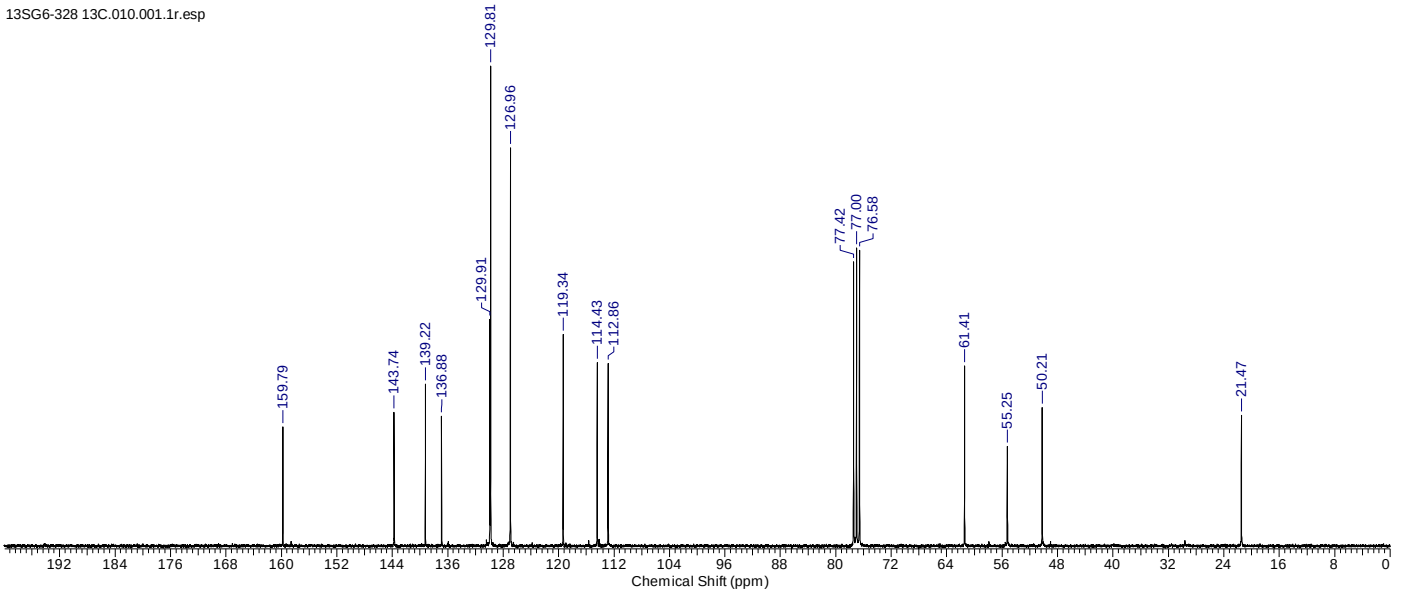


^{1}H & ^{13}C NMR Spectra of 2h

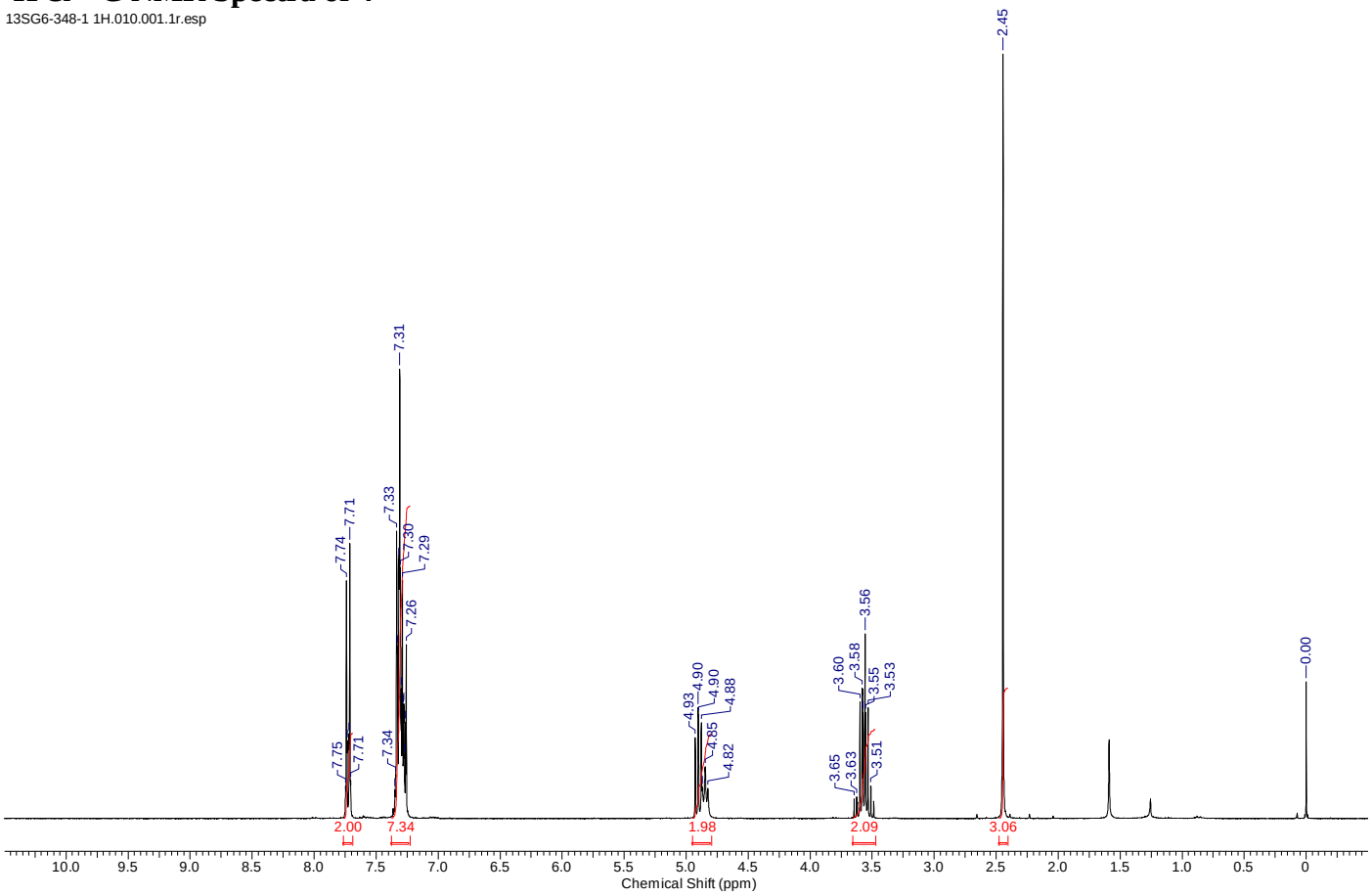






^{1}H & ^{13}C NMR Spectra of 4

13SG6-348-1 1H.010.001.1r.esp



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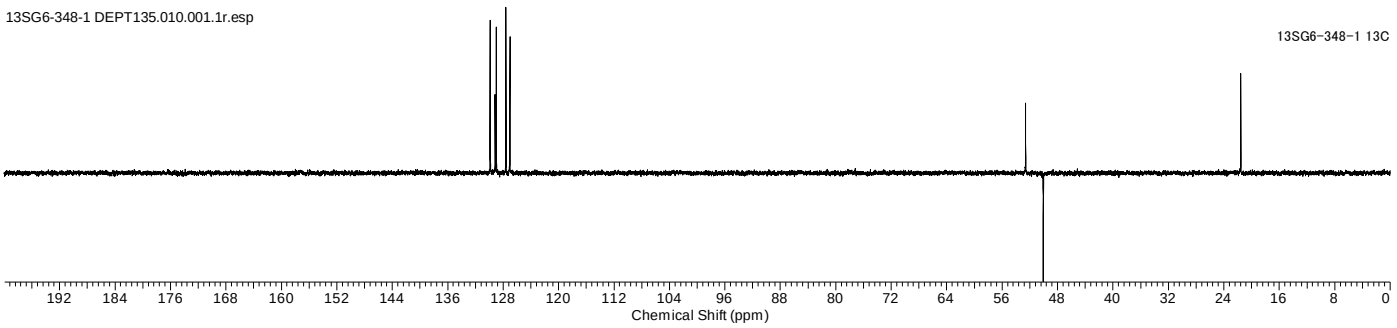
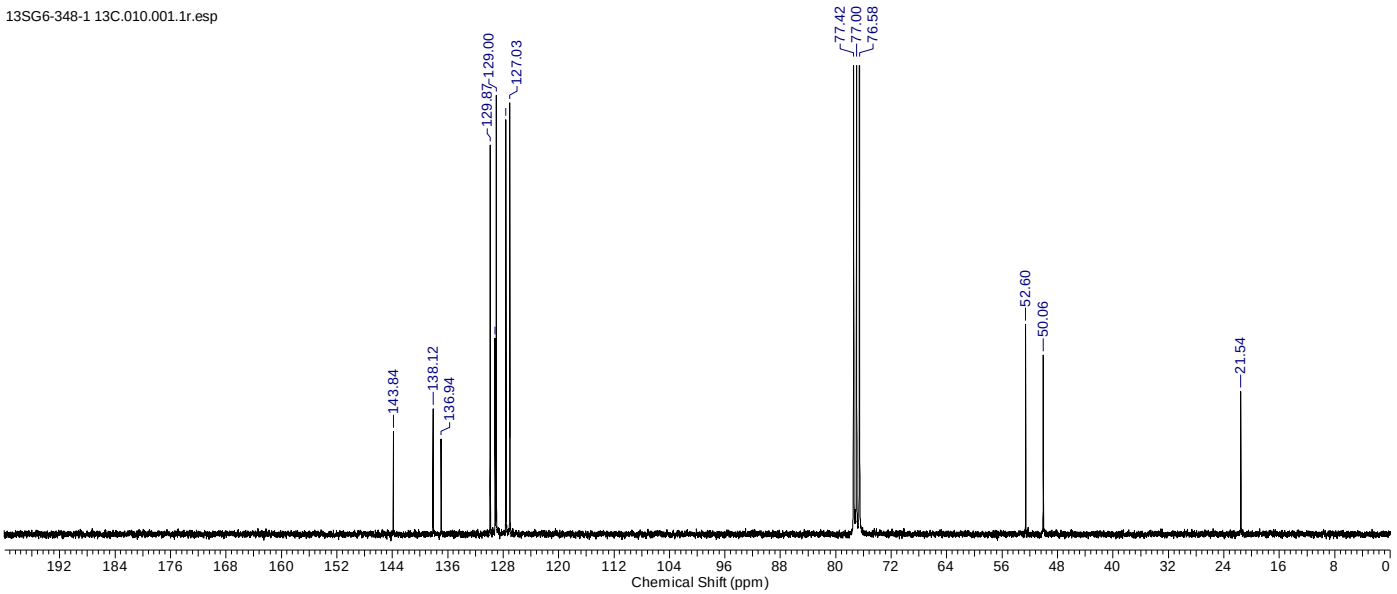
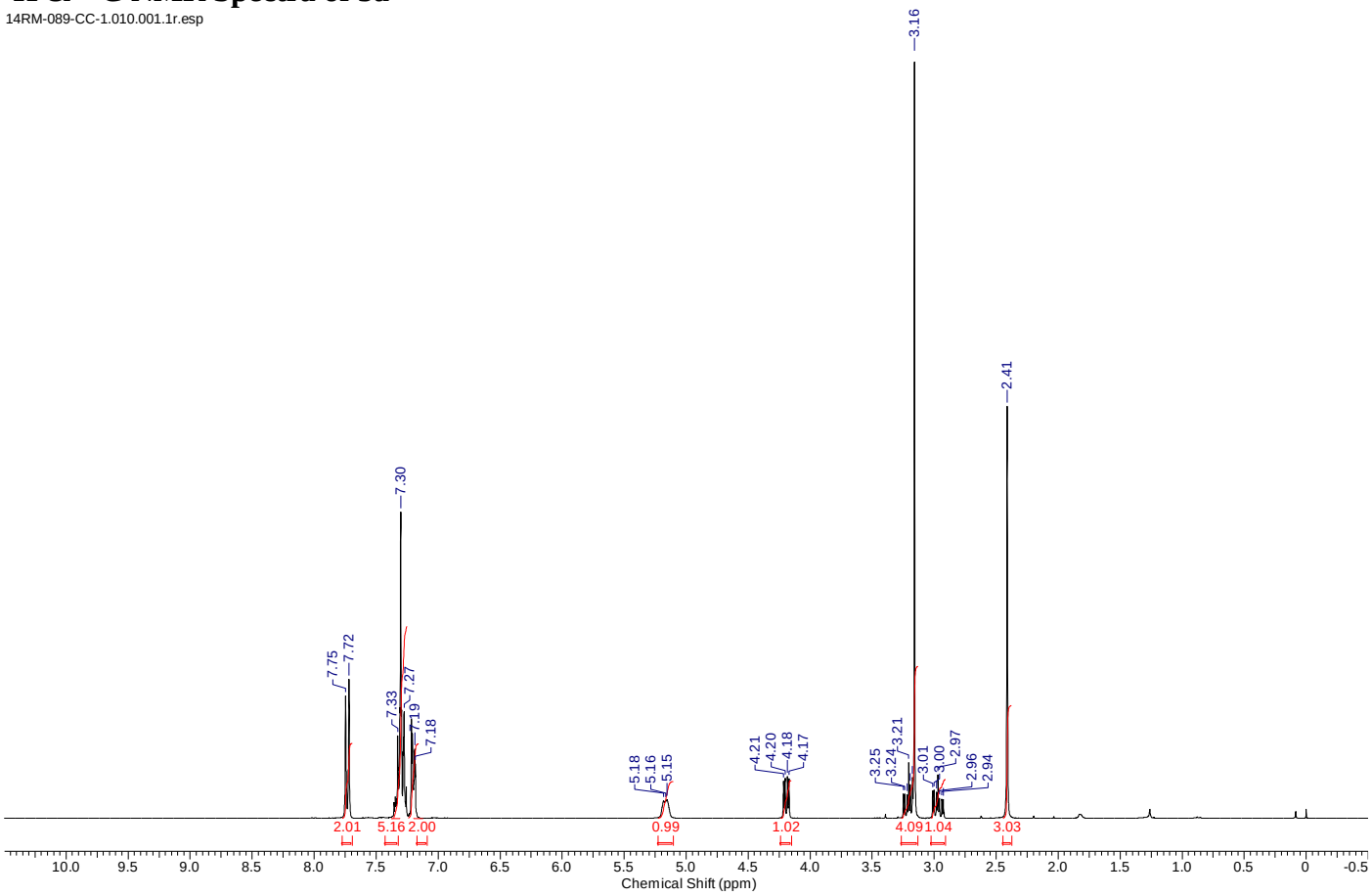


13SG6-348-1 13C.010.001.1r.esp



^{1}H & ^{13}C NMR Spectra of 3a

14RM-089-CC-1.010.001.1r.esp



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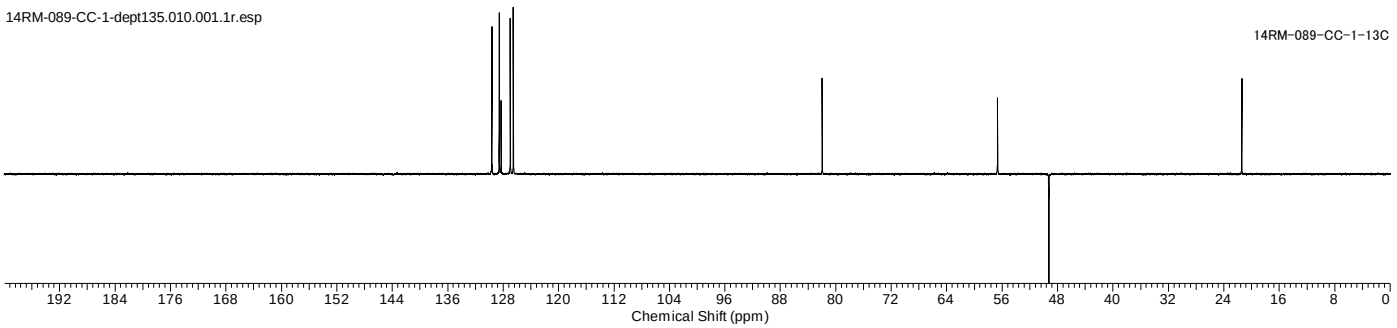

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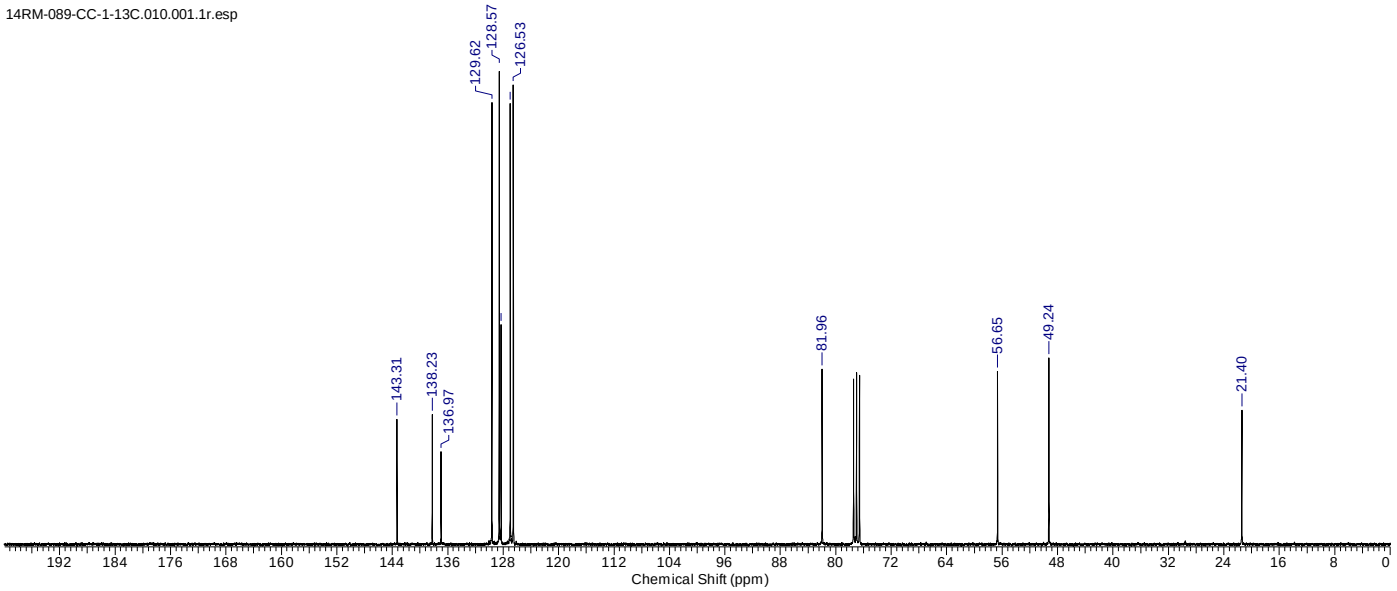
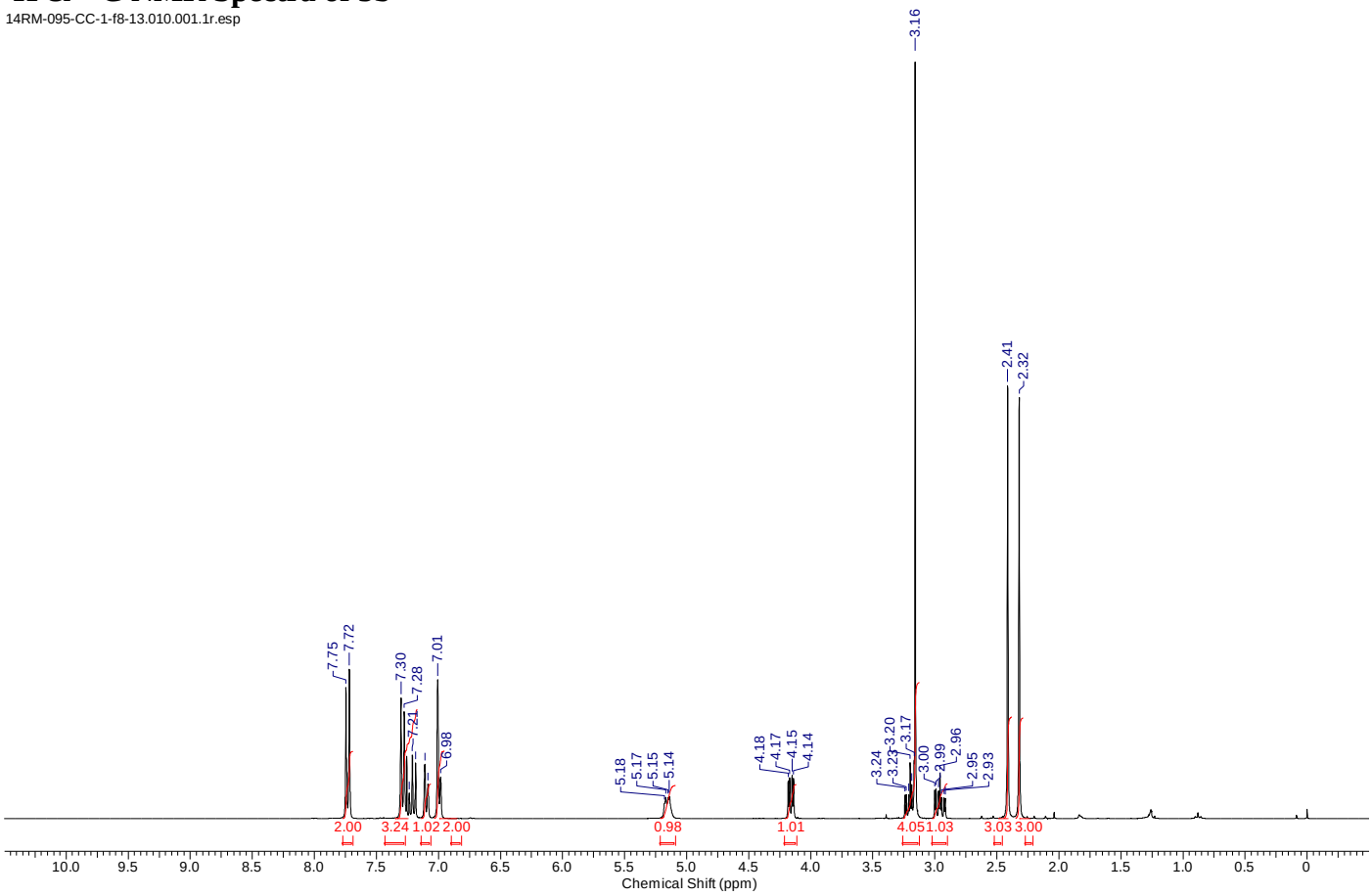


^{1}H & ^{13}C NMR Spectra of 3b

14RM-095-CC-1-f8-13.010.001.1r.esp



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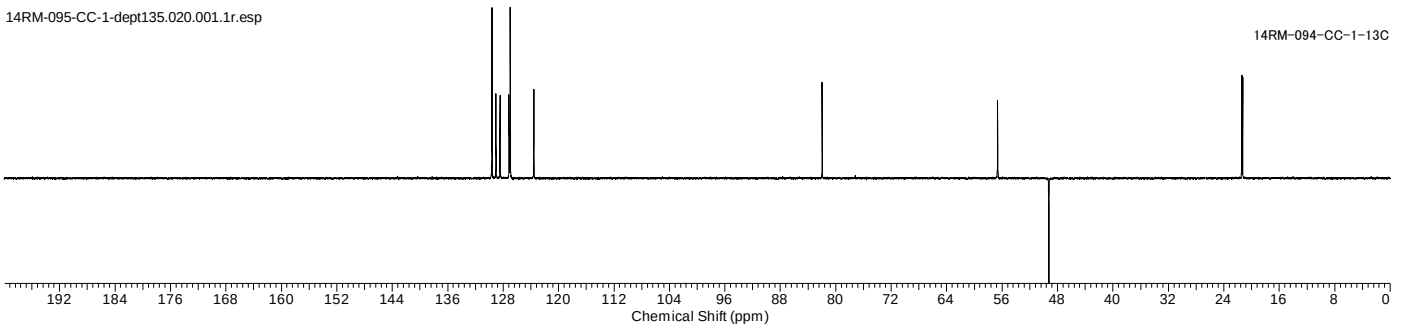
14RM-094-CC-1-13C



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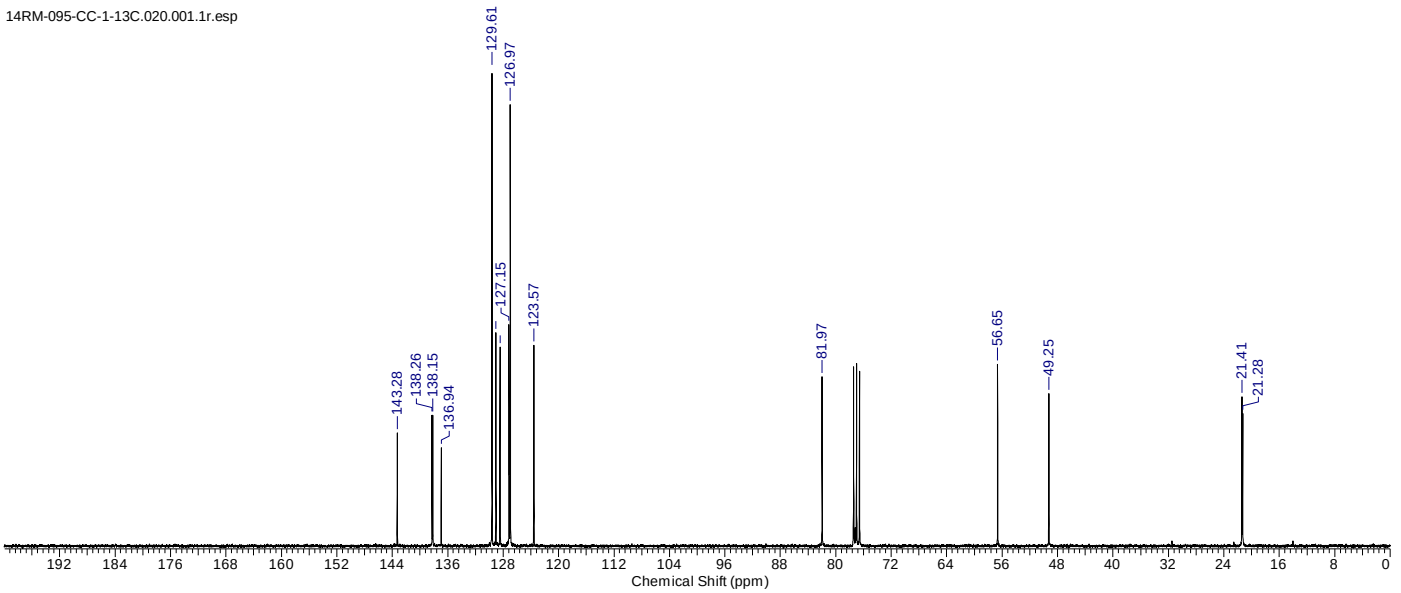
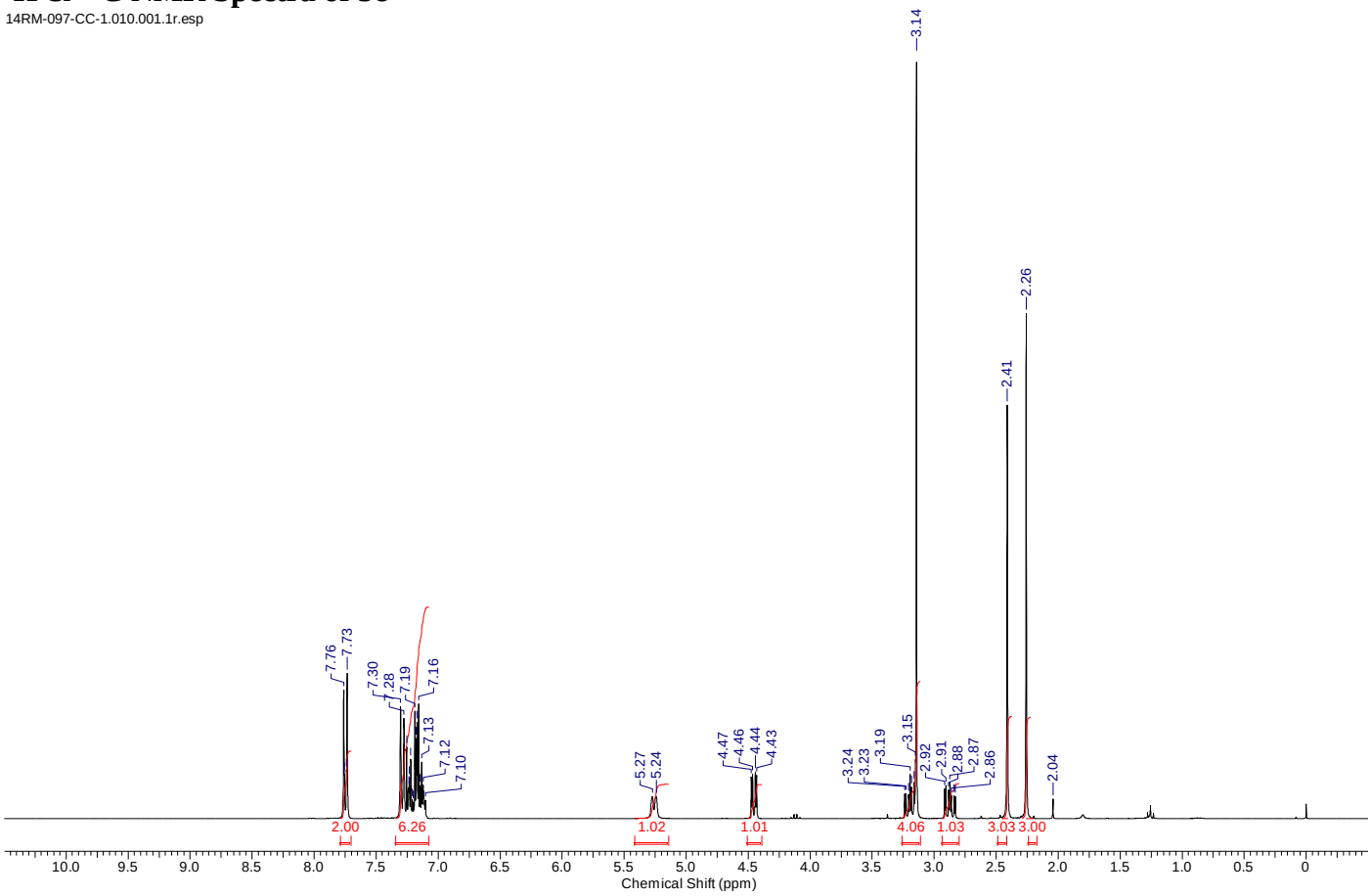


^{1}H & ^{13}C NMR Spectra of 3c

14RM-097-CC-1.010.001.1r.esp



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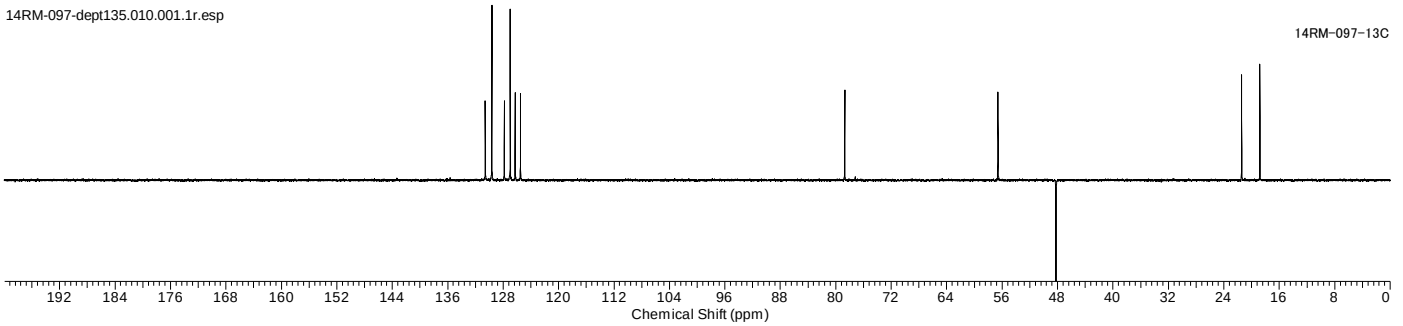

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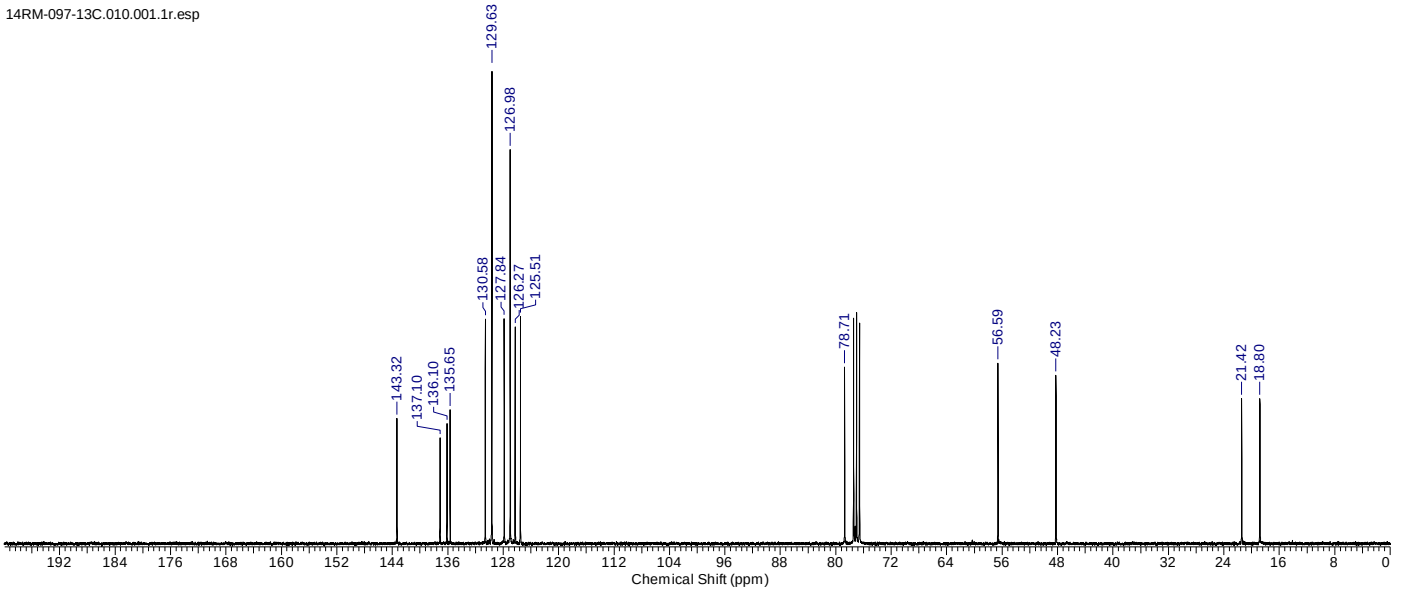
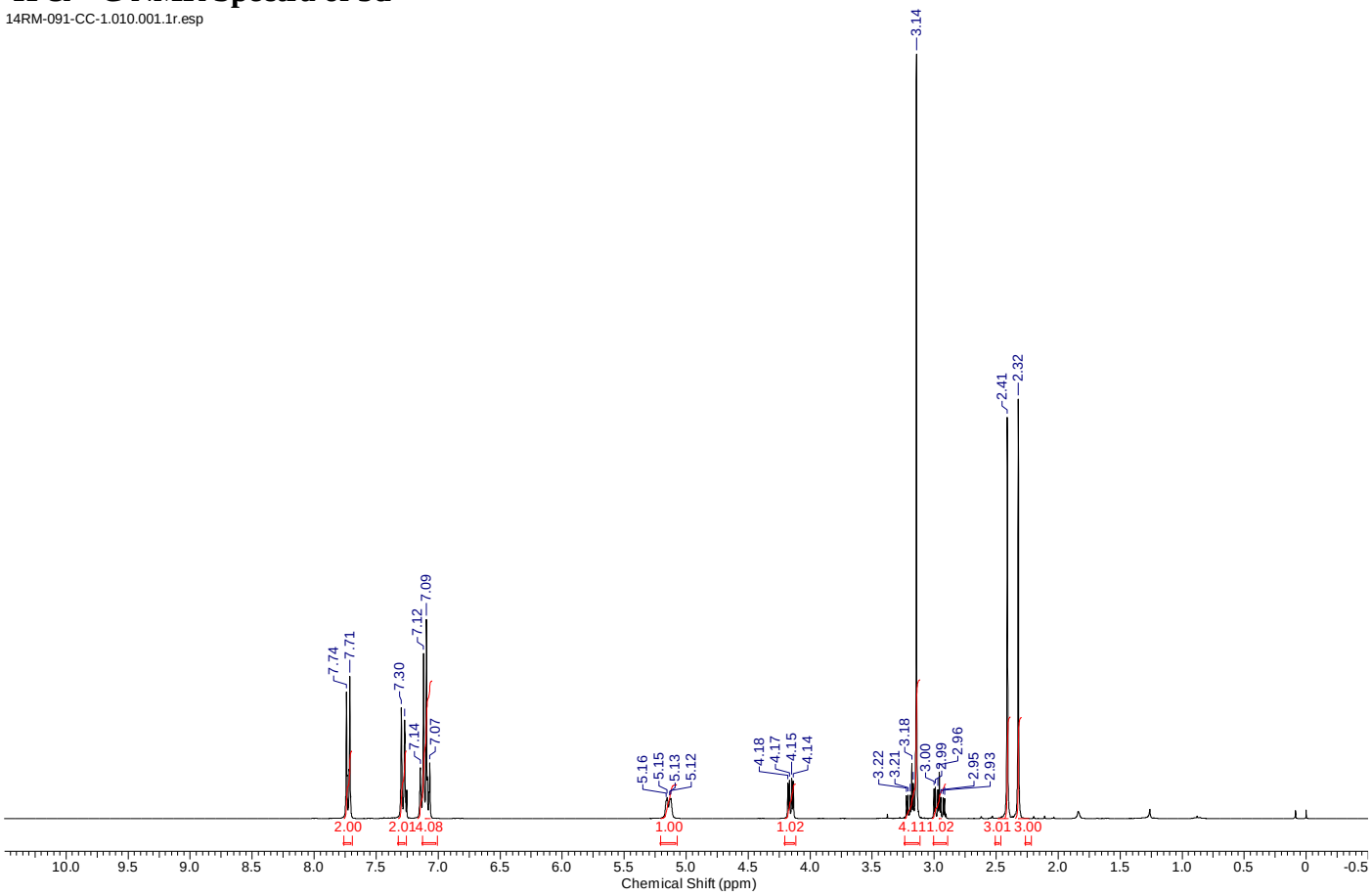


^{1}H & ^{13}C NMR Spectra of 3d

14RM-091-CC-1.010.001.1r.esp



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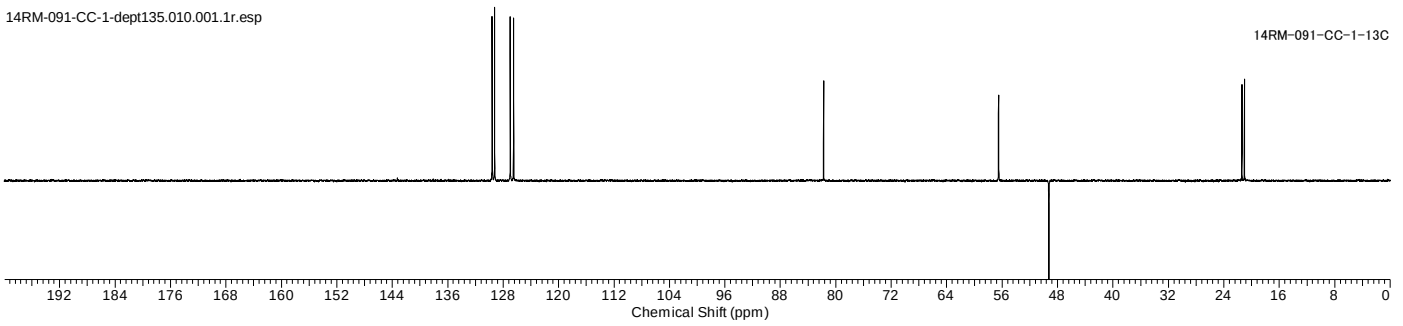

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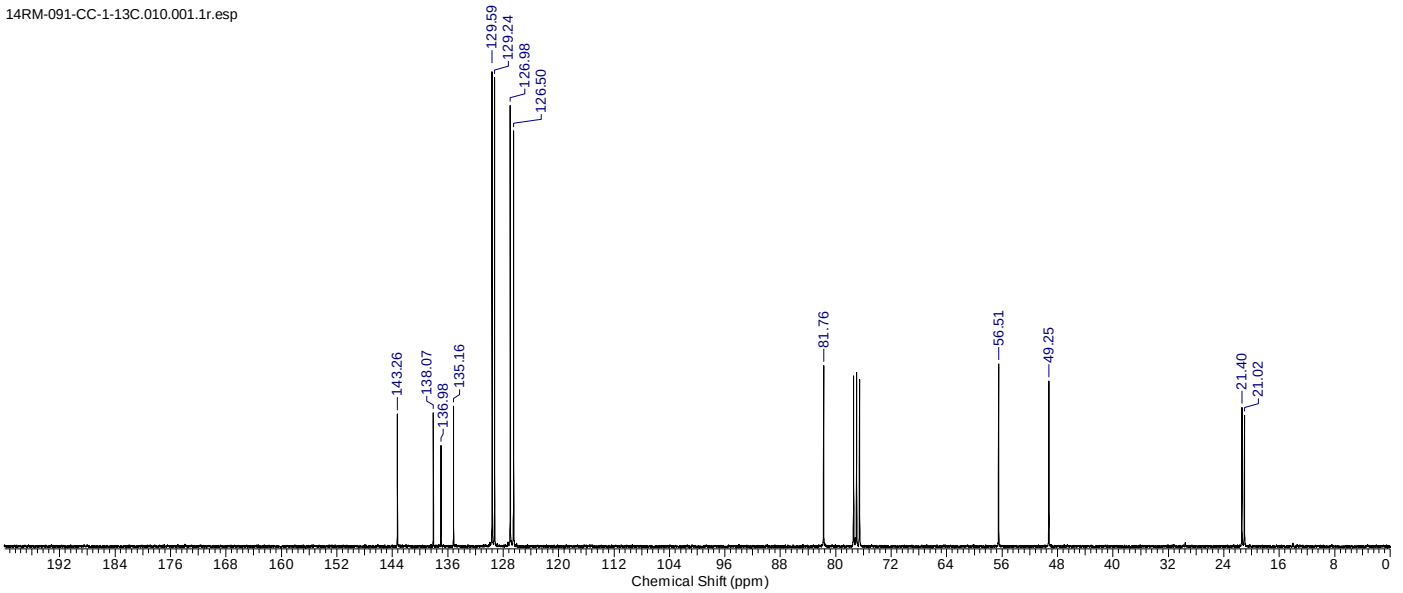

^{1}H & ^{13}C NMR Spectra of 3e

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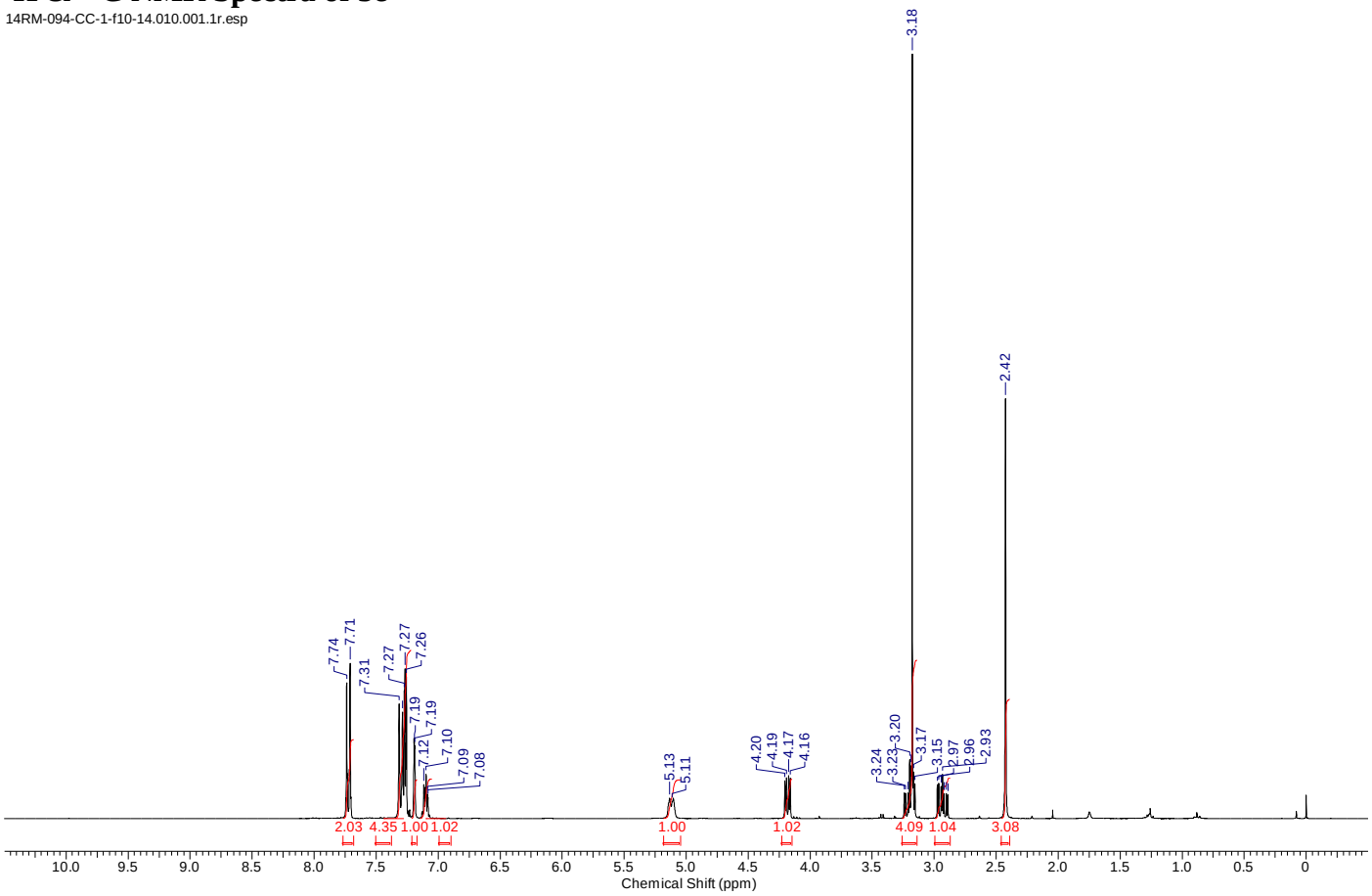

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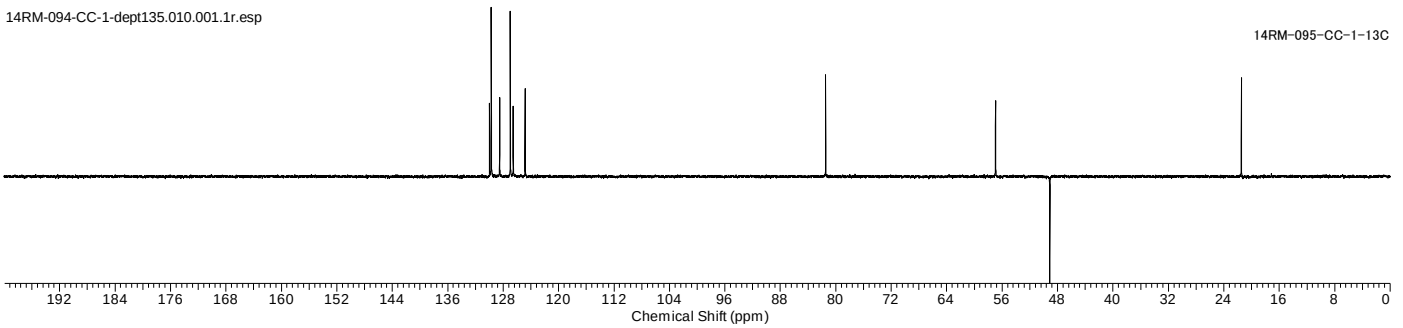

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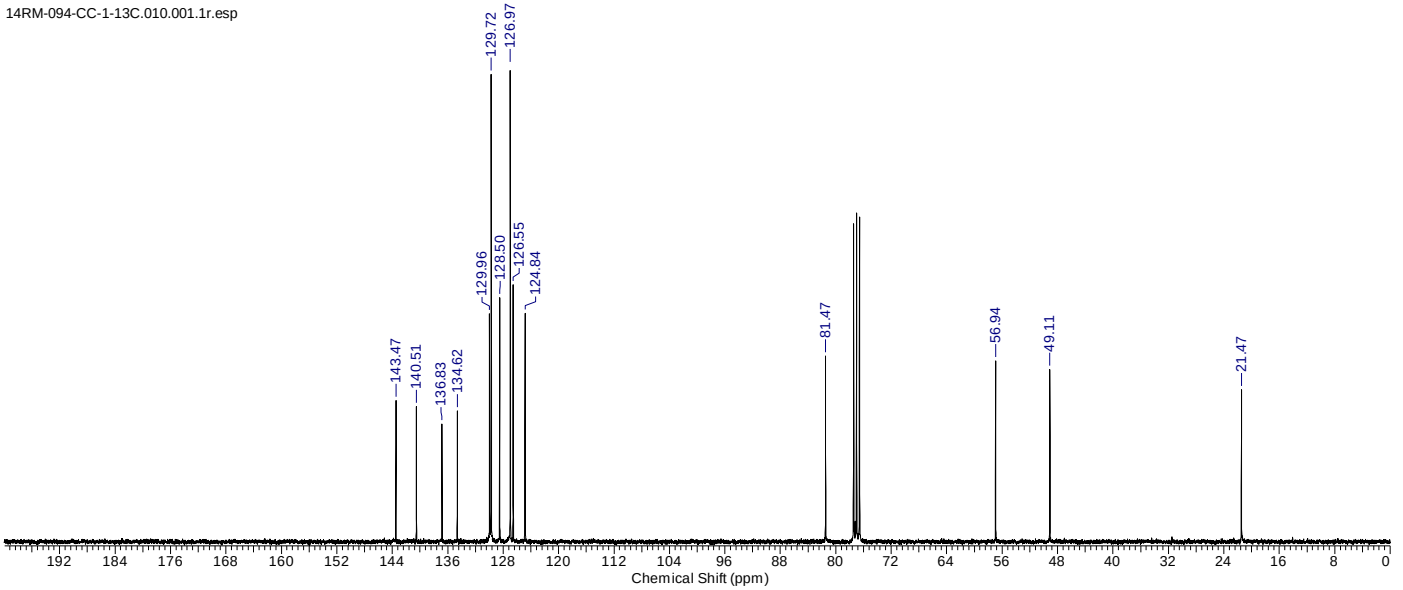
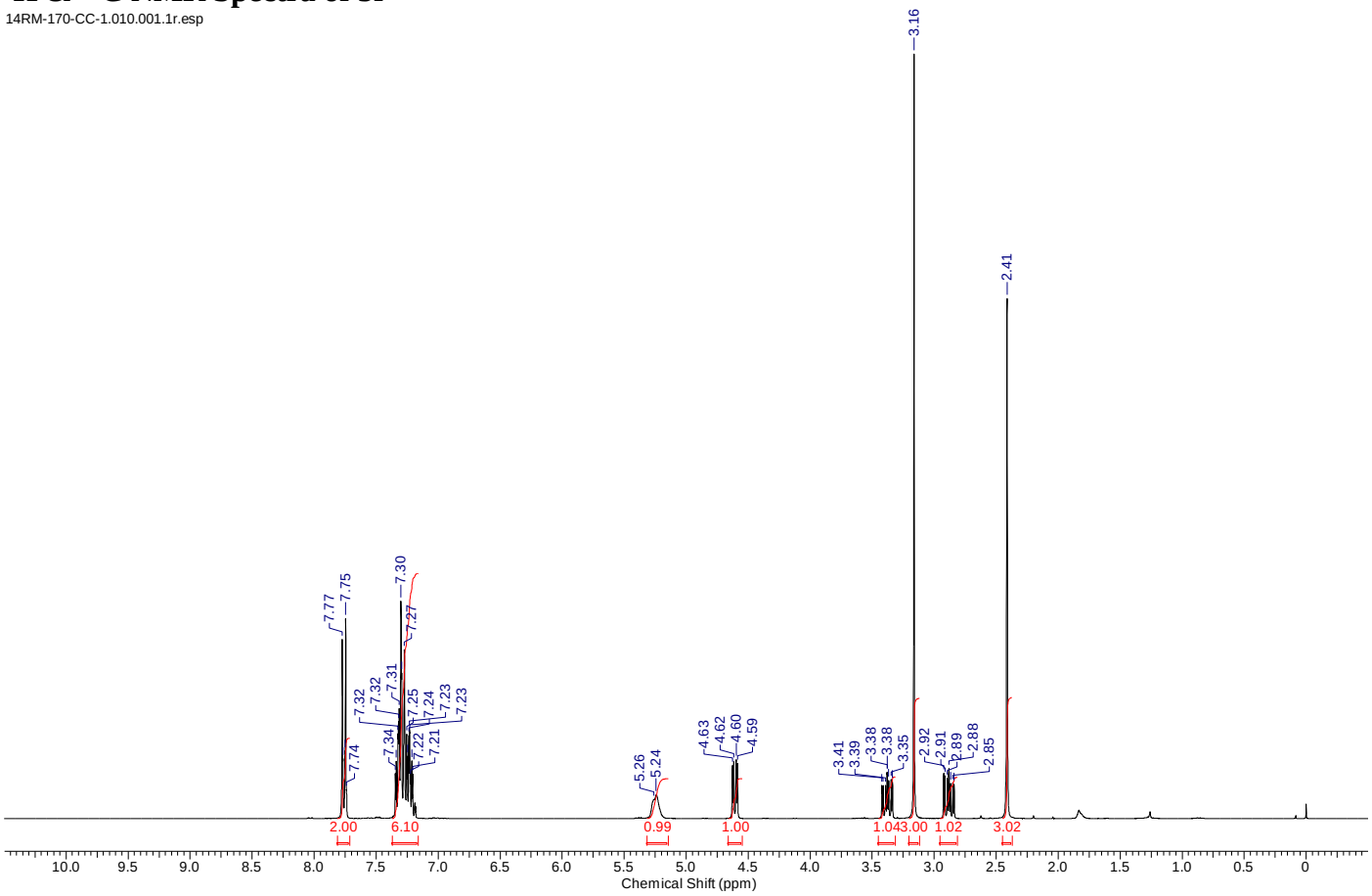


^{1}H & ^{13}C NMR Spectra of 3f

14RM-170-CC-1.010.001.1r.esp



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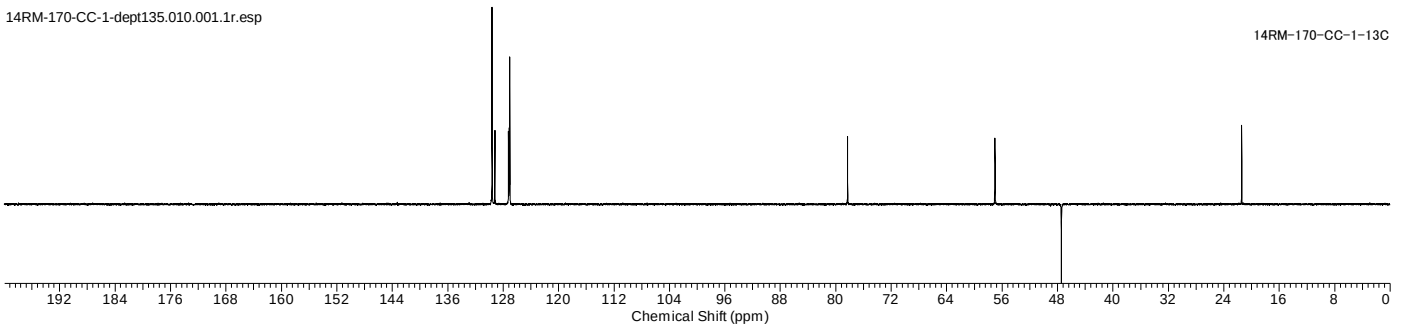

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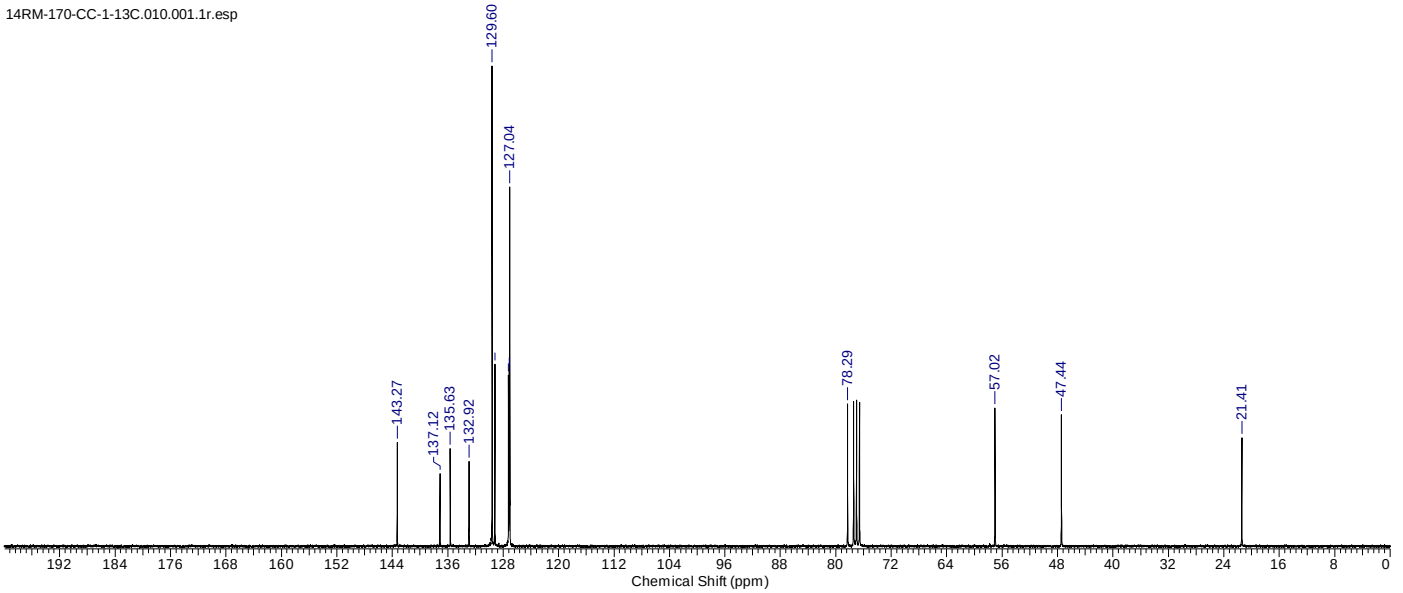
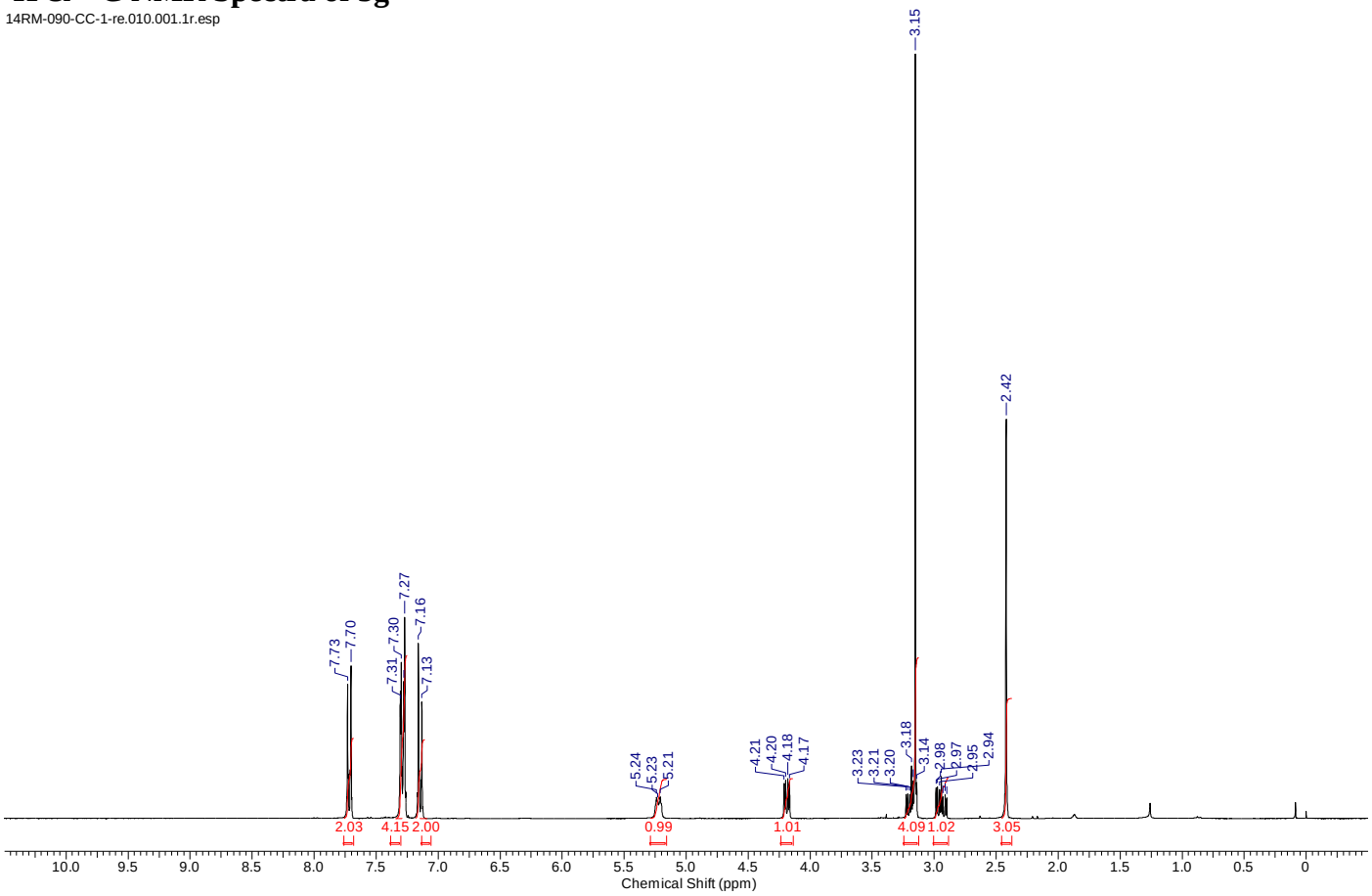


^{1}H & ^{13}C NMR Spectra of 3g

14RM-090-CC-1-re.010.001.1r.esp



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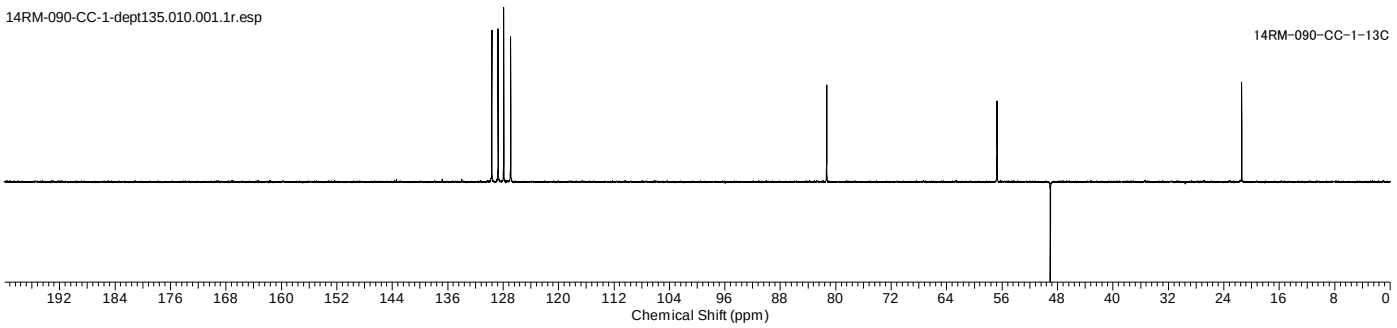

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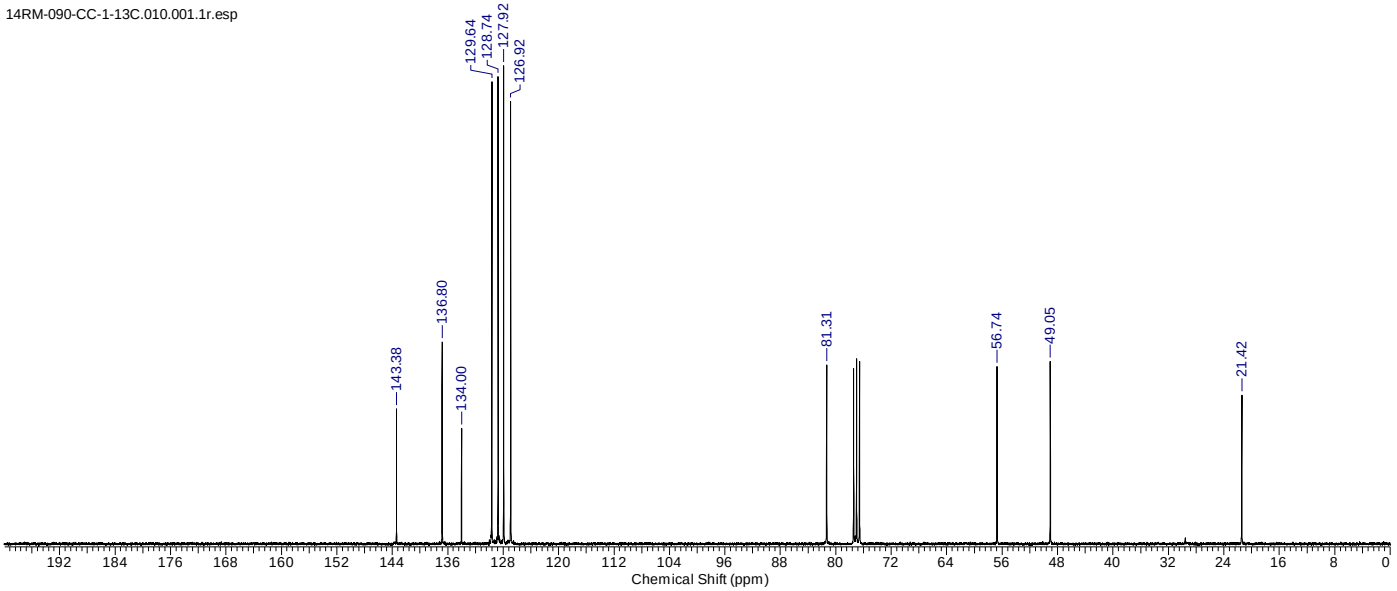
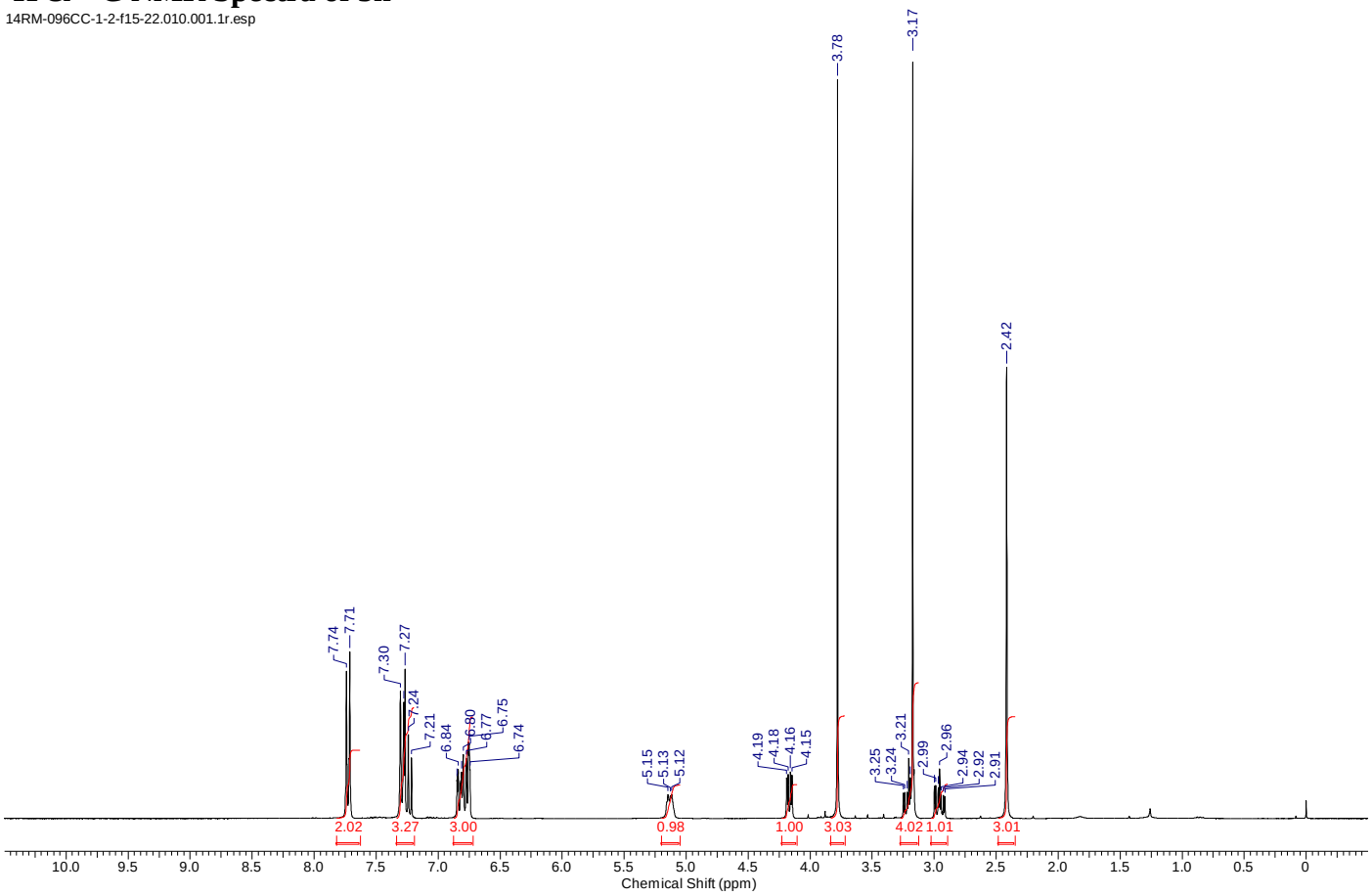


^{1}H & ^{13}C NMR Spectra of 3h

14RM-096CC-1-2-f15-22.010.001.1r.esp



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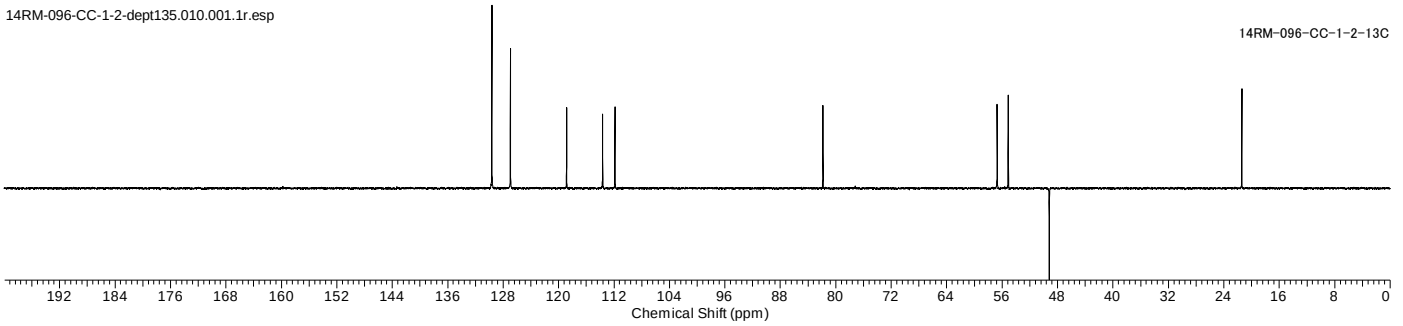

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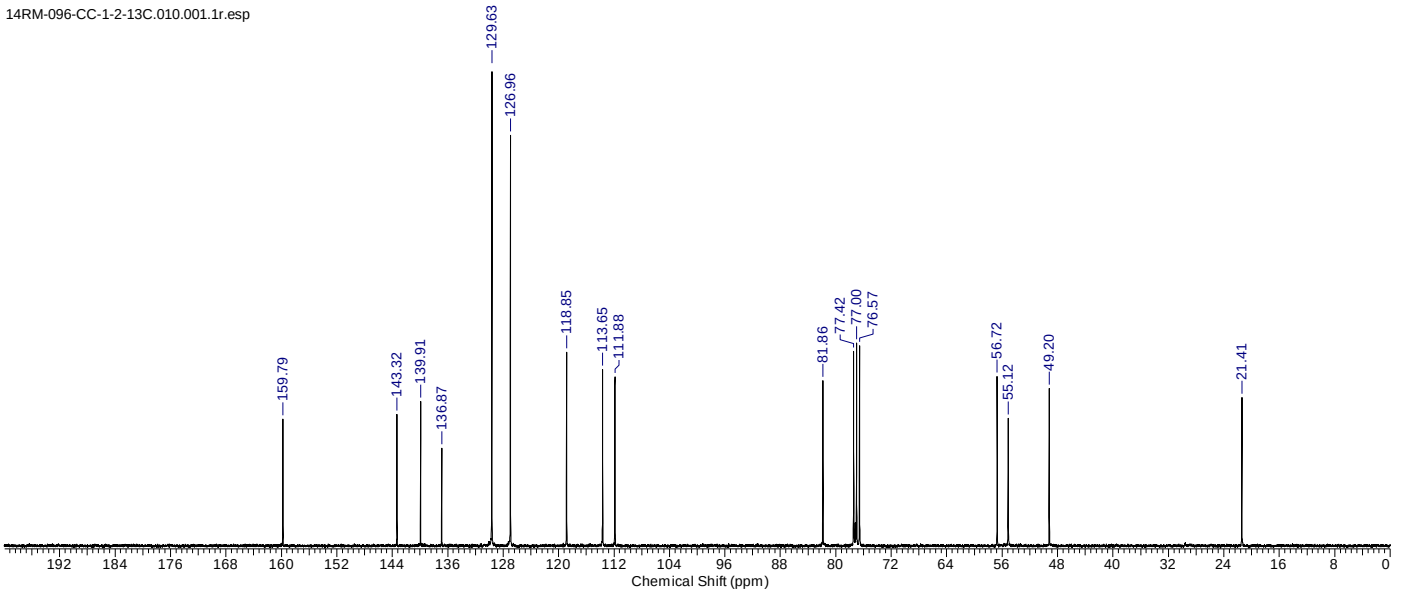
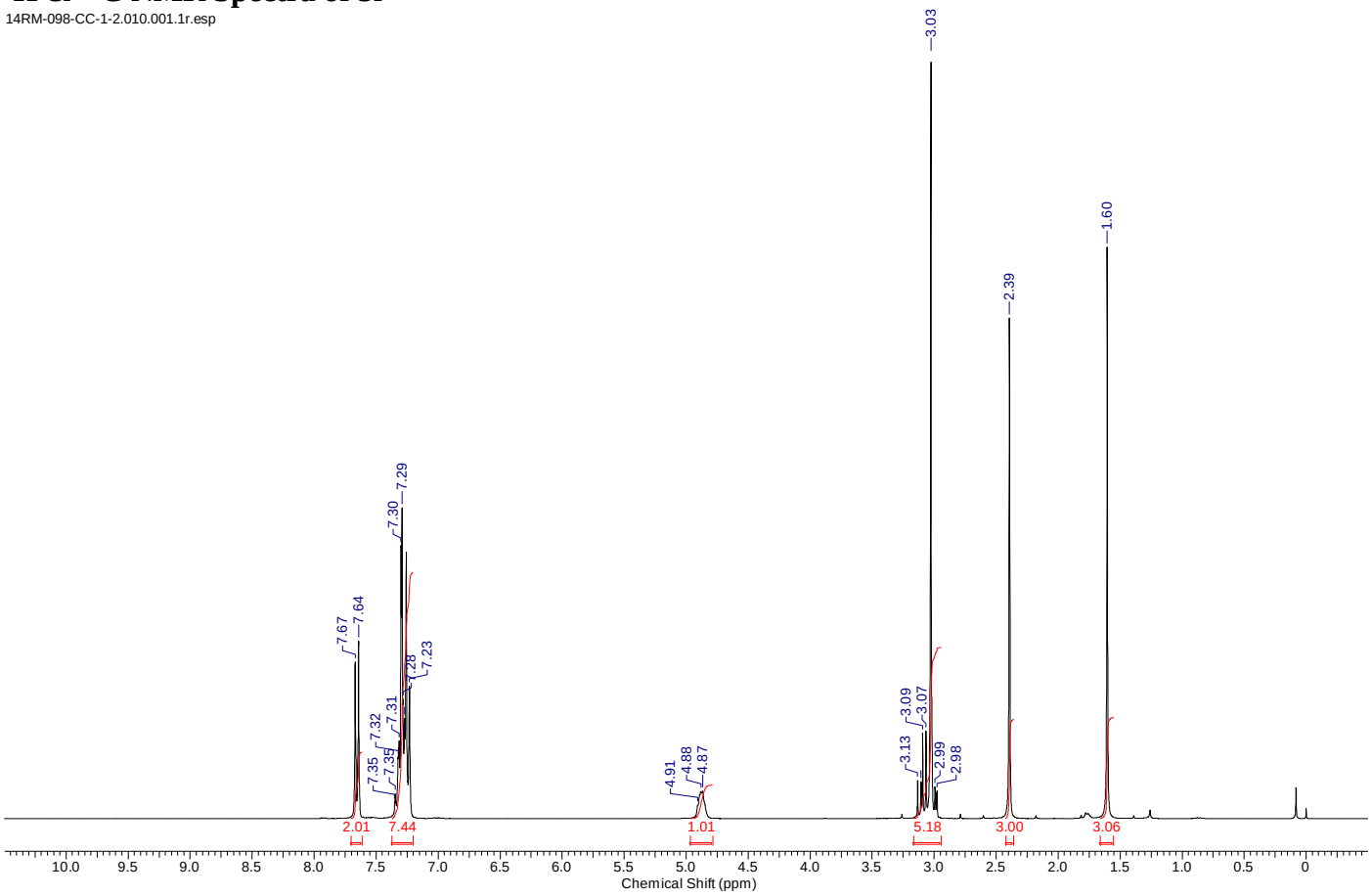
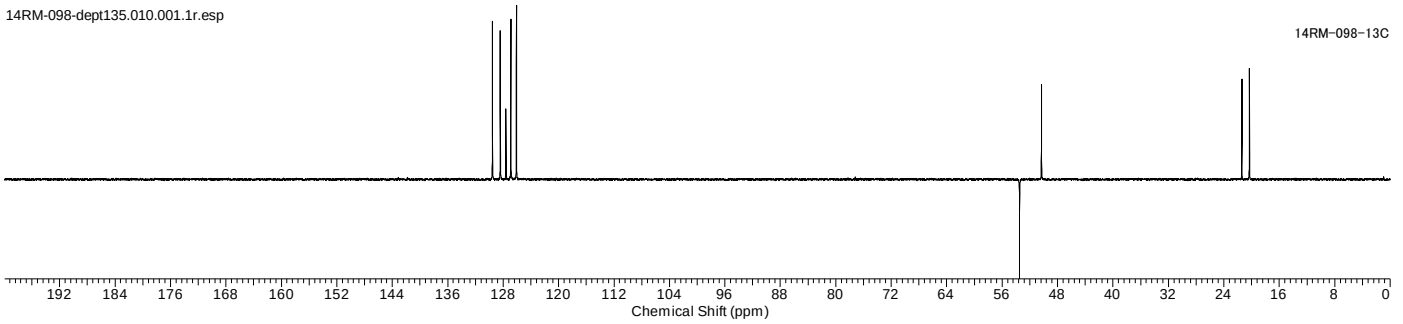
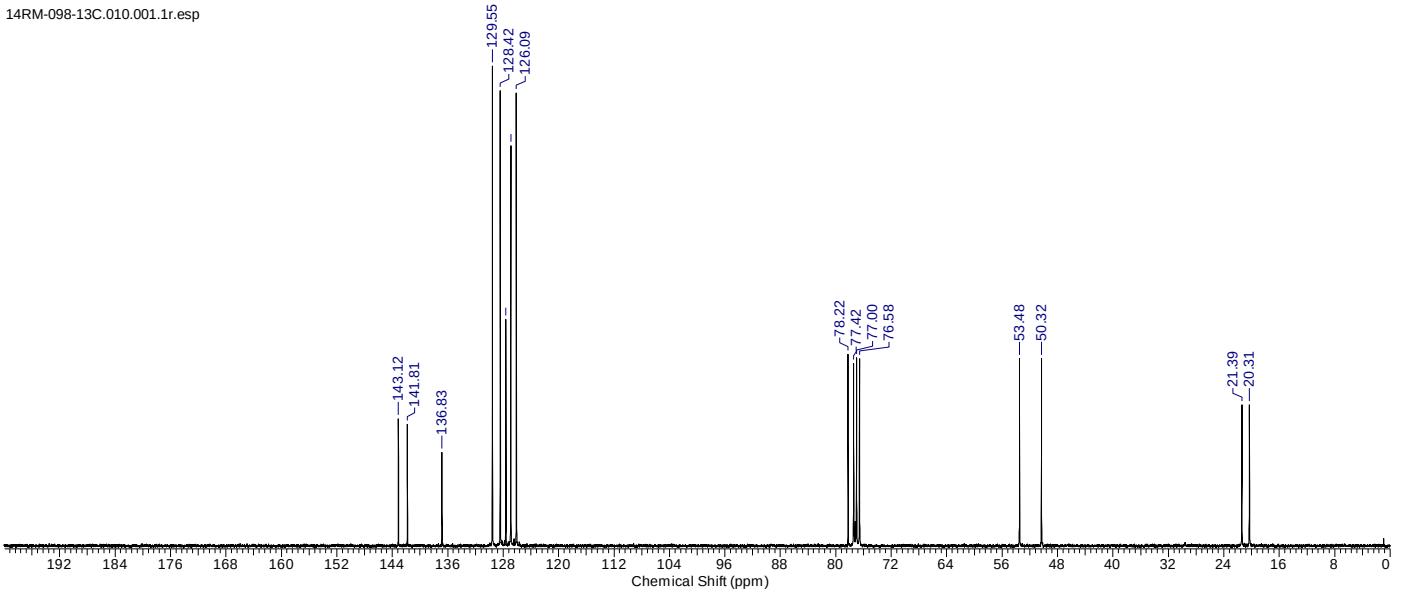


^{1}H & ^{13}C NMR Spectra of 3i

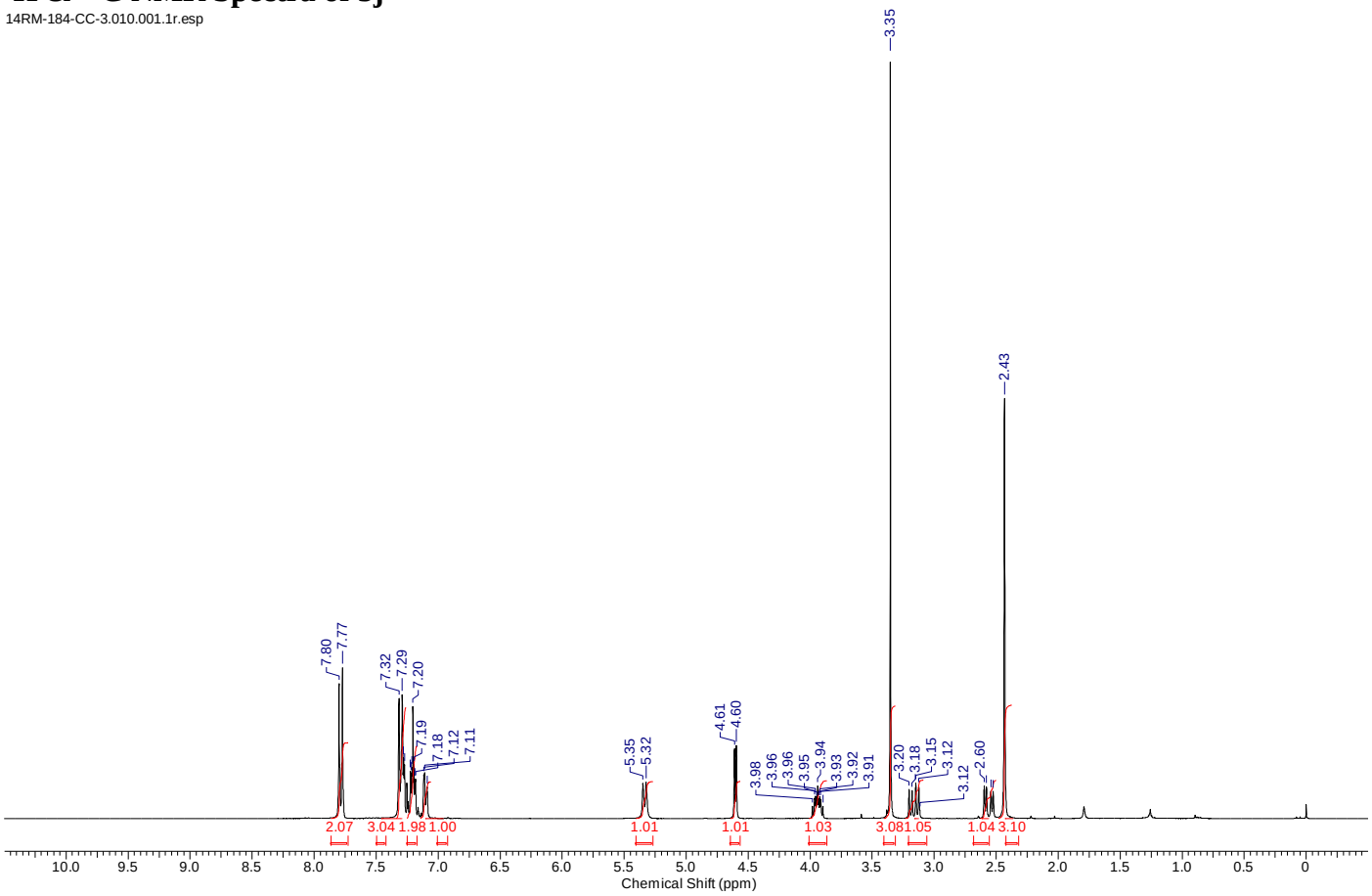






^{1}H & ^{13}C NMR Spectra of 3j

14RM-184-CC-3.010.001.1r.esp



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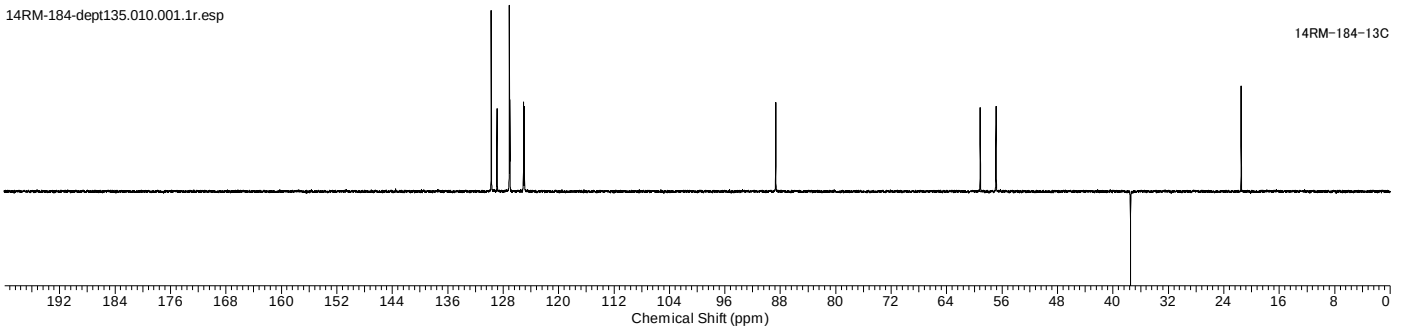

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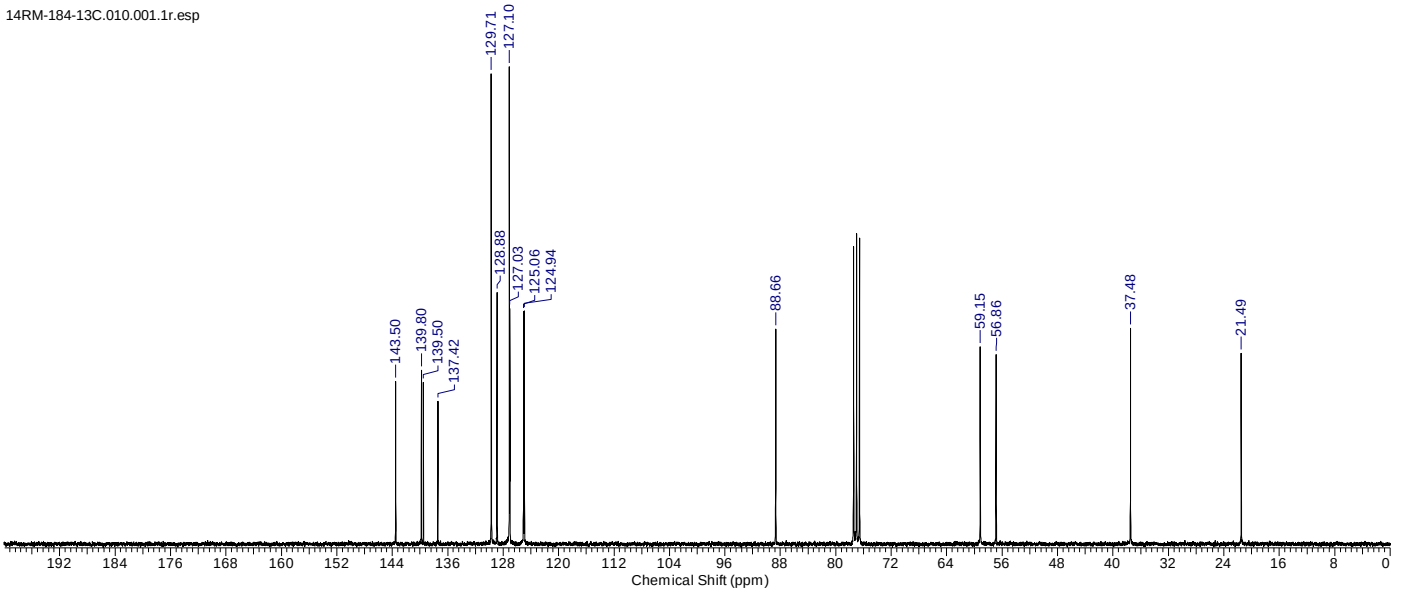
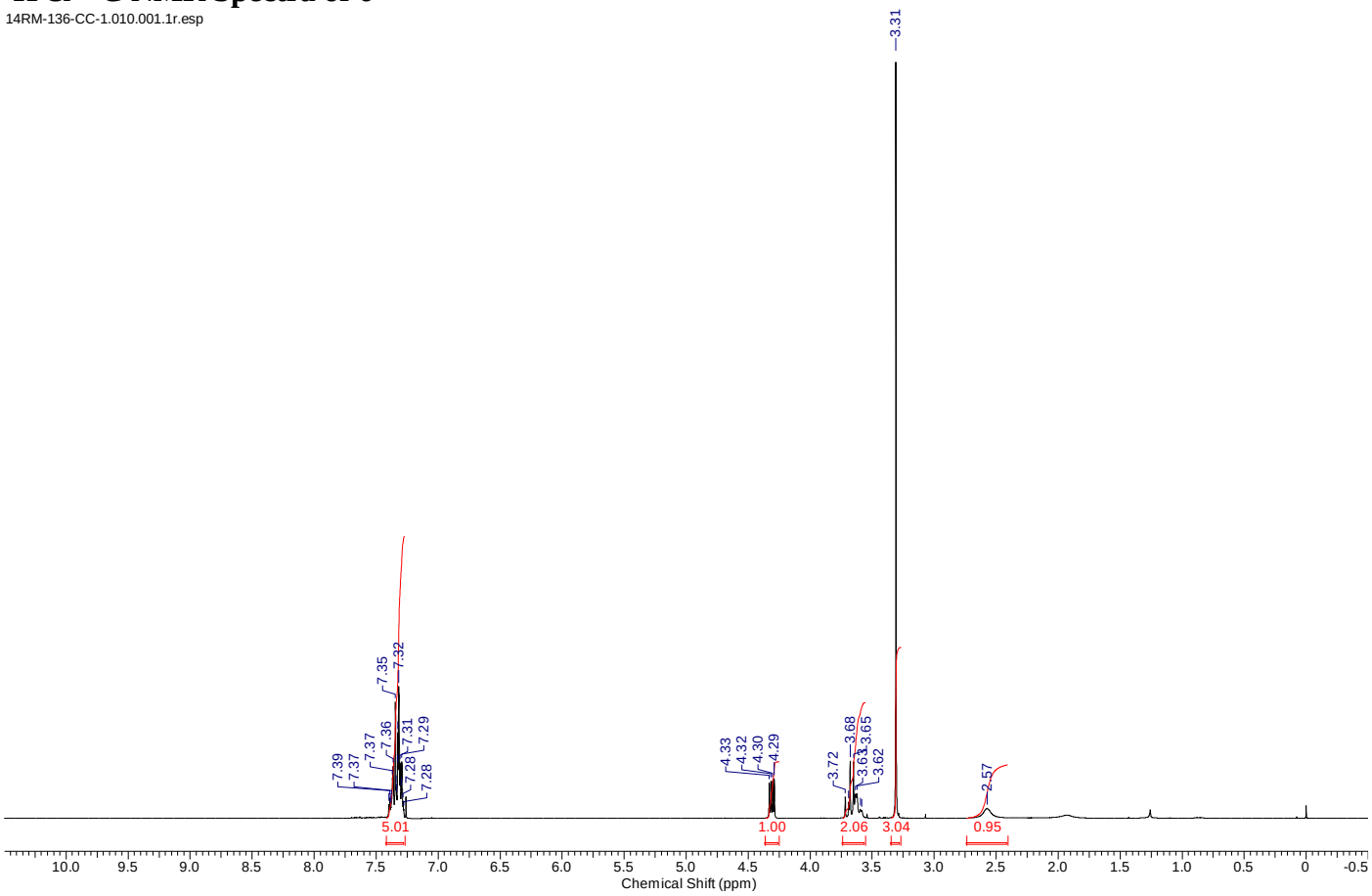


^{1}H & ^{13}C NMR Spectra of 6

14RM-136-CC-1.010.001.1r.esp



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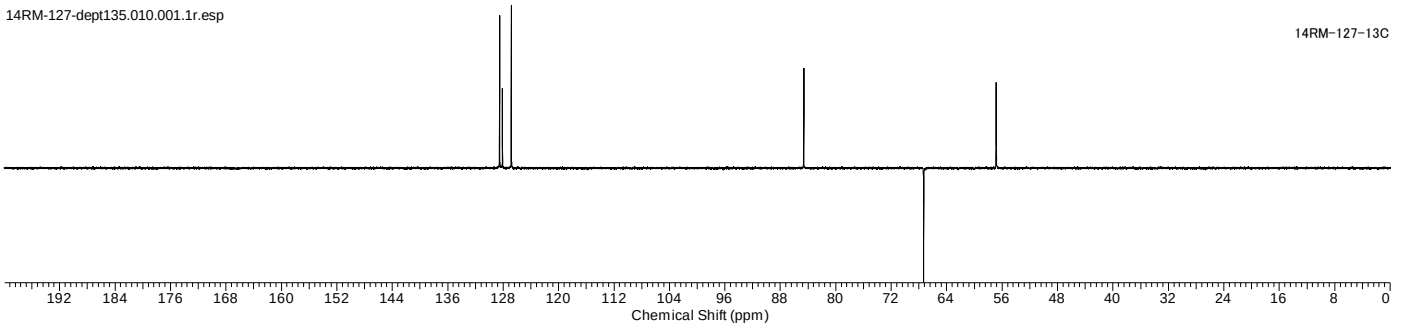

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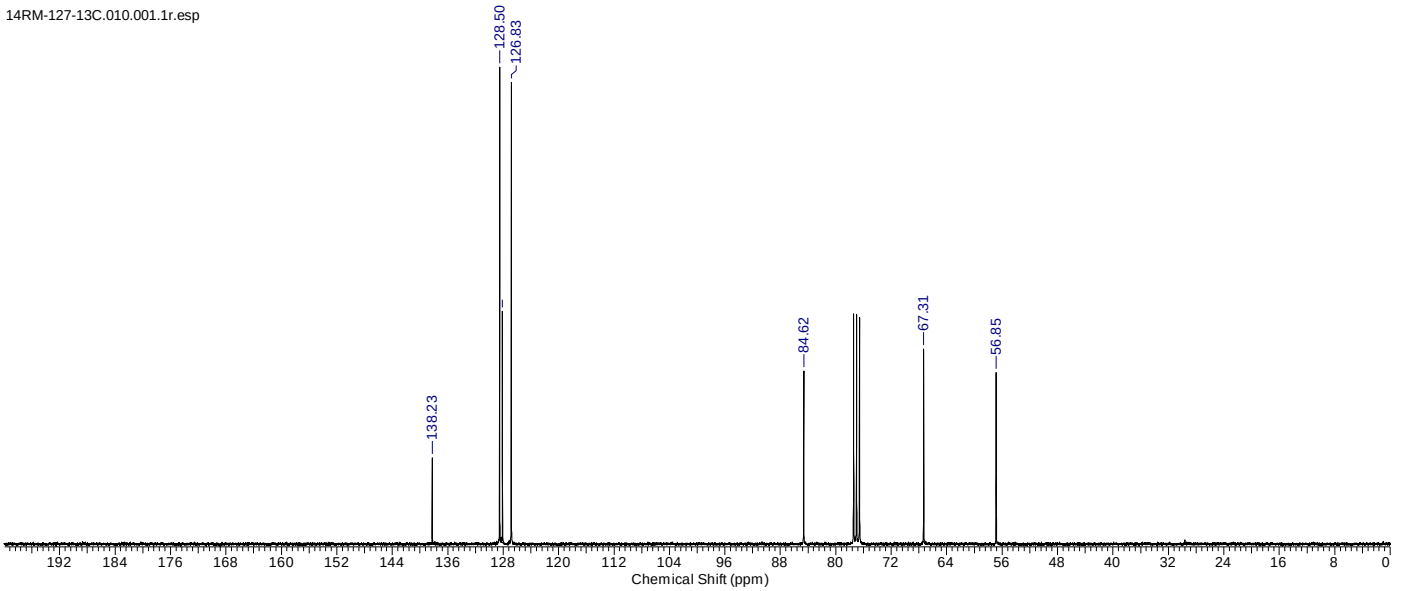
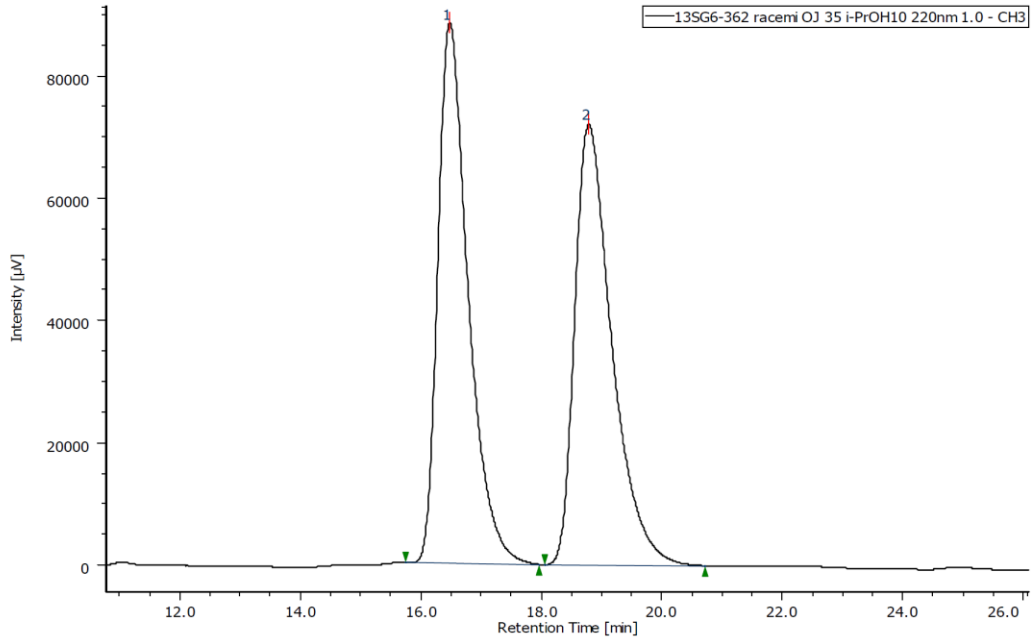
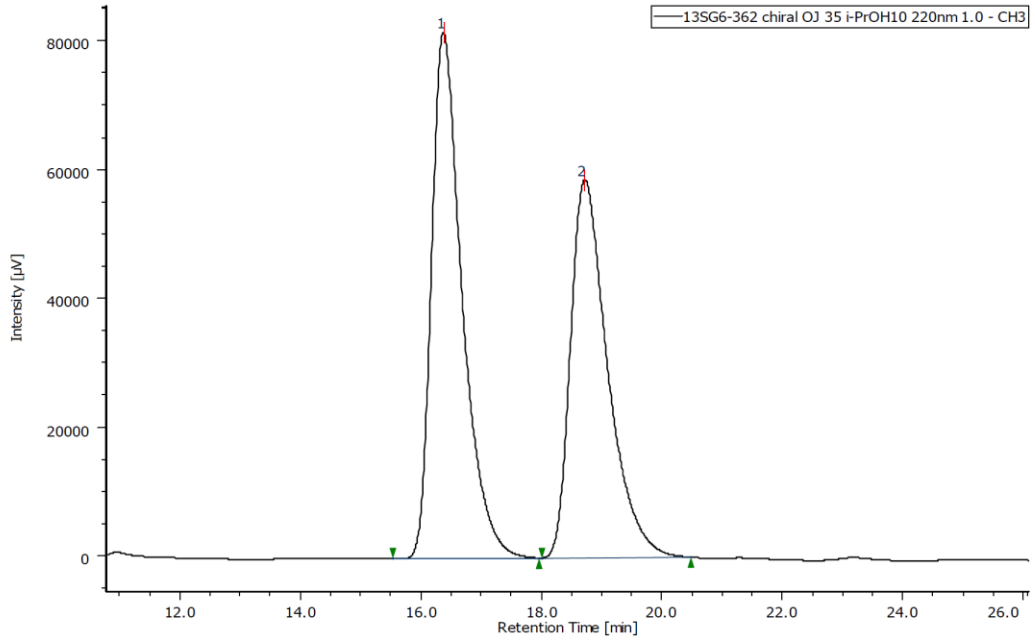


HPLC Trace of 2a

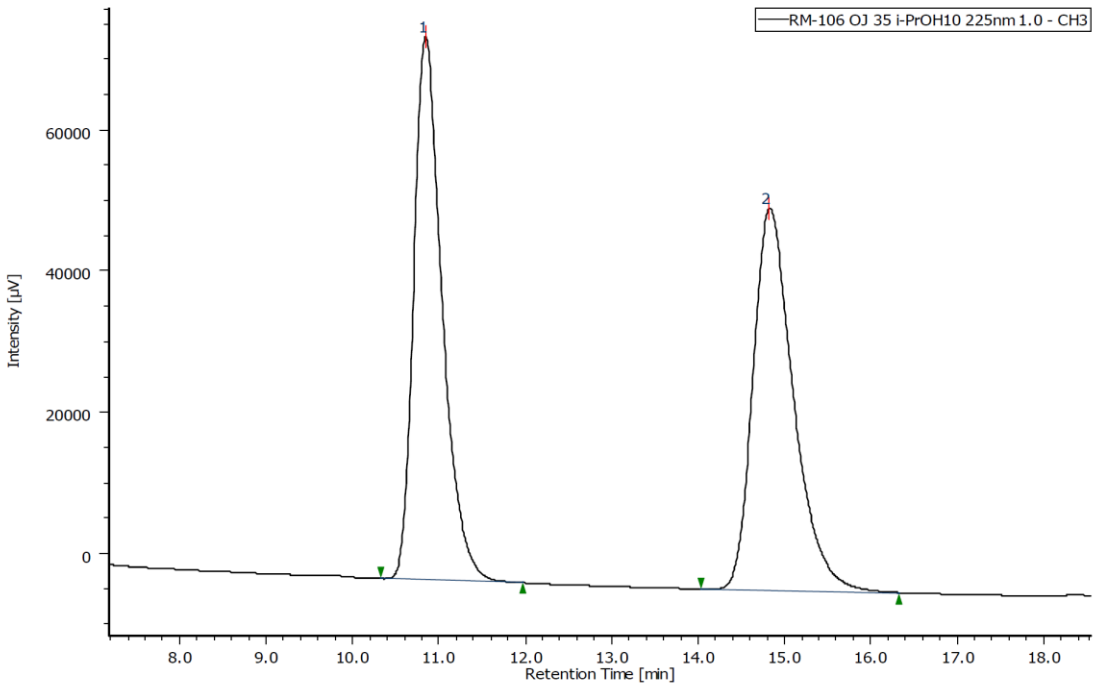


# Peak	CH	tR (min)	Area	Height	Area%
1	3	16.475	3070791	88095	50
2	3	18.775	3071442	71929	50

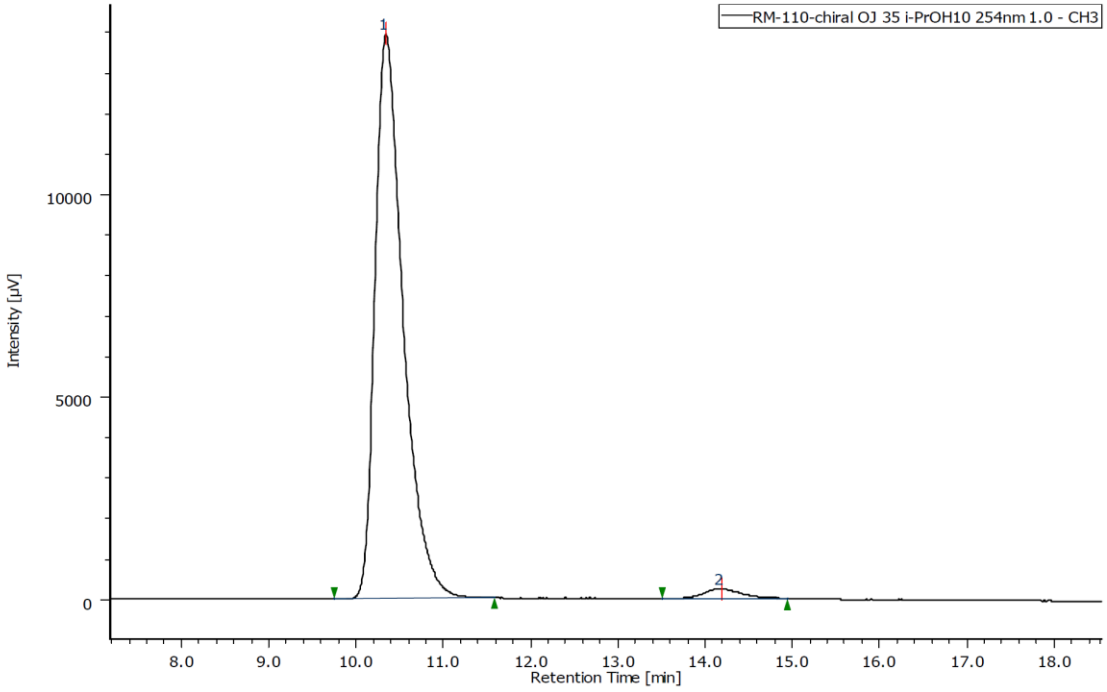


# Peak	CH	tR (min)	Area	Height	Area%
1	3	16.367	2868394	81461	53.4
2	3	18.708	2505263	58580	46.6

HPLC Trace of 3a

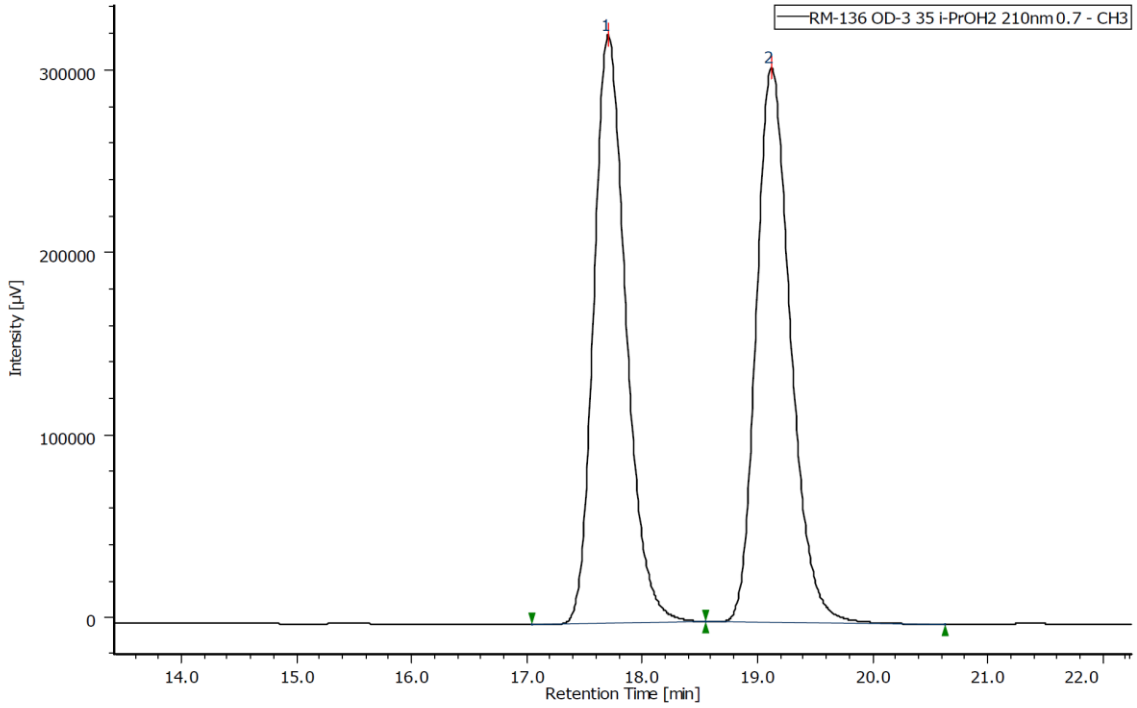


# Peak	CH	tR (min)	Area	Height	Area%
1	3	10.842	1749299	76783	50.013
2	3	14.817	1748386	53941	49.987

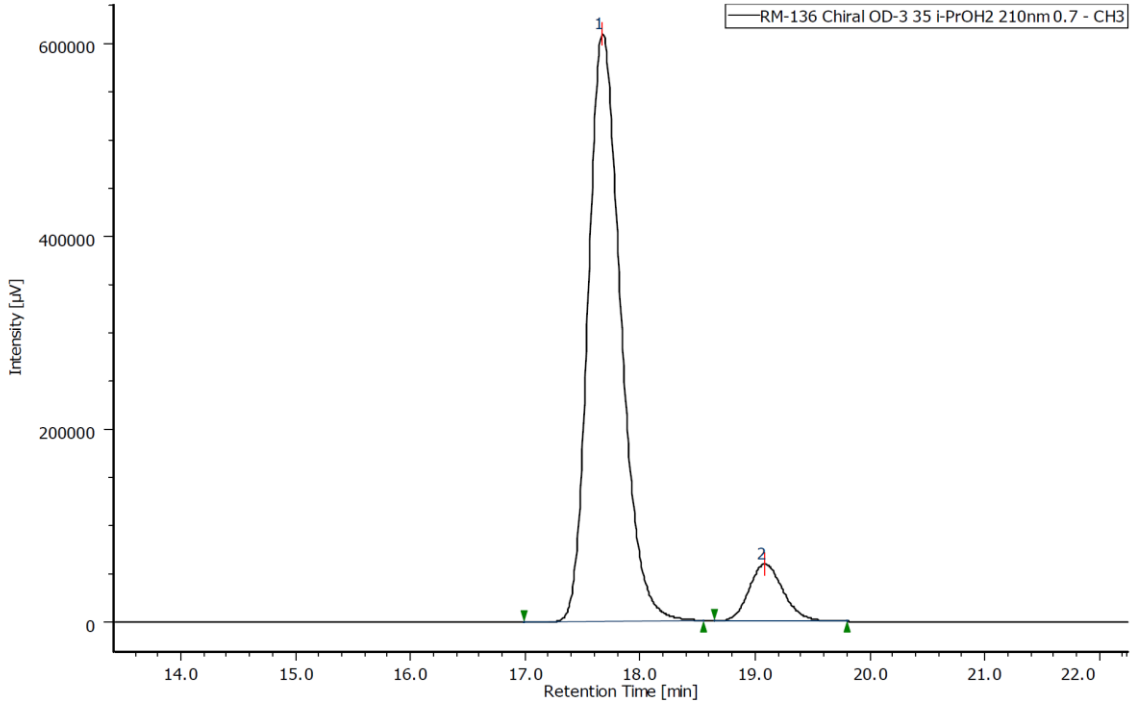


# Peak	CH	tR (min)	Area	Height	Area%
1	3	10.342	310460	13920	97.845
2	3	14.183	6837	236	2.155

HPLC Trace of 6



# Peak	CH	tR (min)	Area	Height	Area%
1	3	17.700	6253222	321956	49.908
2	3	19.117	6276179	303820	50.092



# Peak	CH	tR (min)	Area	Height	Area%
1	3	17.667	11937897	608842	90.800
2	3	19.075	1209518	59022	9.200