Experimental Supporting Information

FDA Certified Food Dyes as Organocatalysts in the Visible-Light Promoted Chlorination of Aromatics and Heteroaromatics

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Materials and Instrumentation:

All reagents and solvents were purchased from commercial sources and used without further purification. Fast Green FCF (CAS # 2353-45-9; FW = 808.86), Brilliant Blue FCF (CAS # 3844-45-9; FW = 792.84), and Indigo Carmine (CAS # 860-22-0; FW = 466.36) were purchased from Alfa Aesar. Erythrosine B (CAS # 16423-68-0; FW = 879.86) and Tartrazine (CAS # 1934-21-0; FW = 534.36) were purchased from Spectrum. Allura Red AC (CAS # 25956-17-6; FW = 496.42) and Sunset Yellow FCF (CAS # 2783-94-0; FW = 452.36) were purchased from TCI America. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 400/100 (400 MHz) spectrometer in deuterated chloroform ($CDCl_3$), dimethyl sulfoxide (DMSO), or methanol (CD_3OD) with the solvent residual peak as internal reference unless otherwise stated ($CDCl_3$: ^{1}H = 7.26 ppm, ^{13}C = 77.02 ppm; DMSO: ^{1}H = 2.50 ppm, ^{13}C = 39.52 ppm; CD_3OD: ^{1}H = 3.31 ppm, ^{13}C = 49.00 ppm). Data are reported in the following order: Chemical shifts (δ) are reported in ppm, and spin-spin coupling constants (*J*) are reported in Hz, while multiplicities are abbreviated by s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublets), t (triplet), dt (double of triplets), td (triplet of doublets), m (multiplet), q (quartet). Infrared spectra were recorded on a Nicolet iS50 FT-IR spectrometer, and peaks are reported in reciprocal centimeters (cm^{-1}). Melting points (m.p.) were recorded on a Mel-Temp II (Laboratory Devices, USA) and were uncorrected. Nominal MS (EI) were obtained using a Shimadzu GC-2010 Plus with GCMS-QP2010. Relative intensity (in percentage) is shown in parentheses following the fragment peak where appropriate.

Construction of LED Chambers:

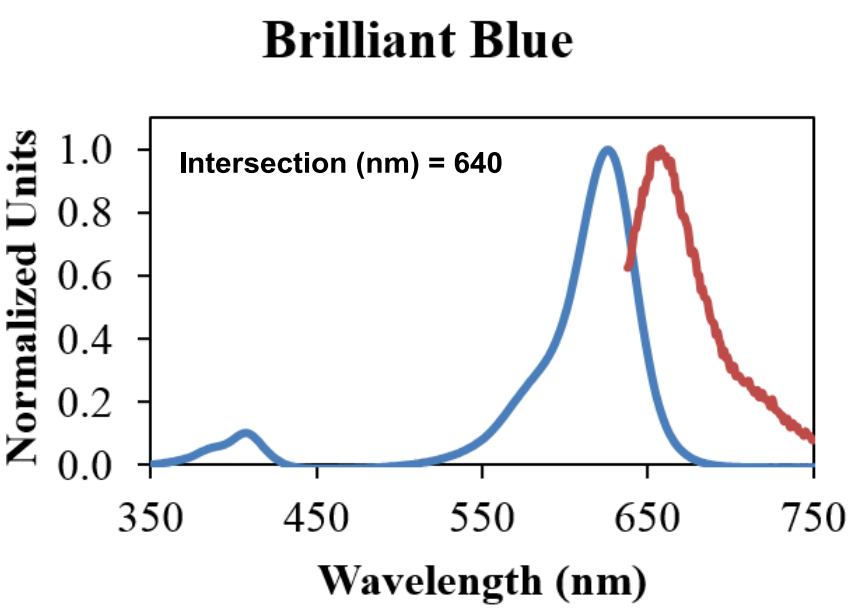
Visible-light photocatalytic reactions were set up in a light bath which was constructed in our laboratory by coiling LED strips around an evaporating dish according to our previous reports:[1-5]

Waterproof 5050 LED strips (12V with power adapter, 18 LEDs/foot, approximately 0.24 Watt per LED – 72 Watt per strip) are coiled around the interior of evaporating dish (170mm x 90mm) using the adhesive backing of the LED strip. A Petri dish (150 x 20 mm) is placed upside down at the bottom of the dish to serve as an elevated glass "floor" to ensure that a round-bottom flask receives maximum light exposure. The ambient temperature inside the dish is monitored and is generally maintained (air-cooled) between 19-22 ^{o}C (the temperature has not been observed above 25 ^{o}C).

Determination of photoexcited energy via fluorescence emission:

Excitation energy ($E_{0,0}$) was determined by calculating the energy of the wavelength (in nm) that the substrate's UV-Vis absorption and fluorescence emission spectra overlap. The energy converter on the following website was used to convert wavelength (nM) to eV: https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/cnvcalc.htm

Procedure: UV-vis spectroscopy was performed using a Shimadzu UV-1800 spectrometer using a 3D printed vial adaptor[6] for convenience while fluorescence measurements were performed using a Tecan Safire spectrometer with a clear-bottom 96 well plate. Solutions were prepared by saturating a pure ACN solution or a 7:1 ACN:water solution with the dye of interest, centrifuging the sample at 1500 rpm for 2 minutes, then analyzing the supernatant. In most cases the solution was diluted for UV-vis measurements to keep the absorbance value below 1.5. For fluorescence measurements, excitation was performed at 15 nm below the peak absorption value to determine overlap with the absorbance spectra. The wavelength of this emission and absorbance spectra was used in combination with the reduction potential determined in the electrochemical analysis to determine the excited state reduction potential as has been previously reported in the literature.[7]

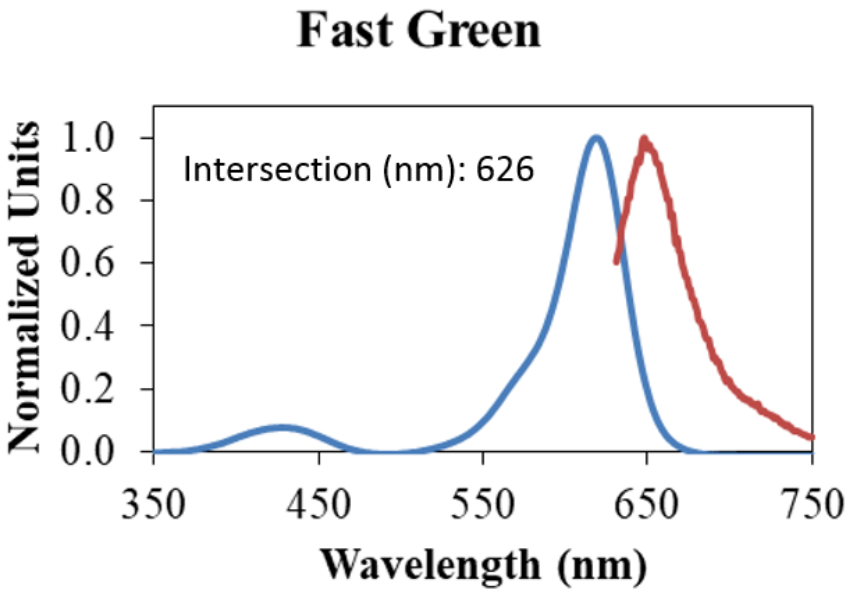


Absorbance λ_{max} = 626 nm

Emission λ_{max} = 658 nm

$E_{0,0}$ = 1.94 eV

Figure S1. Fluorescence emission spectrum of Brilliant Blue FCF. (Blue = Absorbance; Red = Emission)

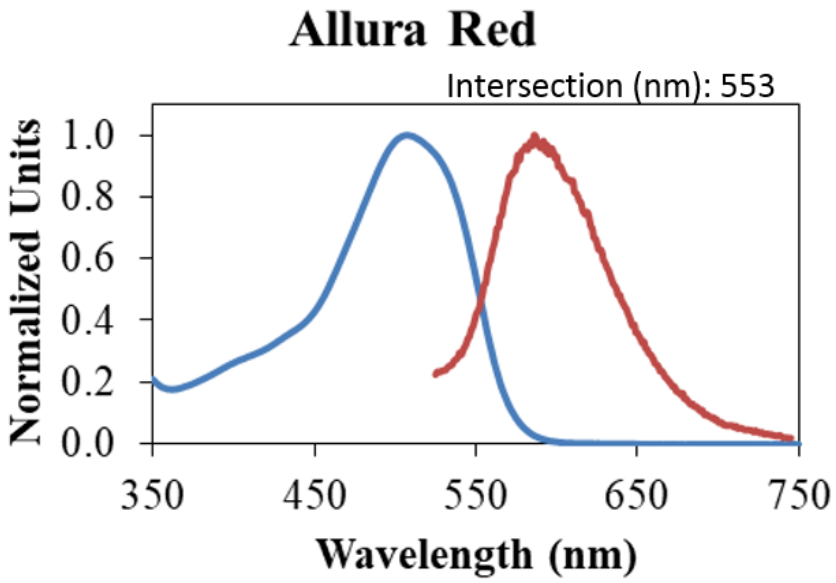


Absorbance λ_{max} = 619 nm

Emission λ_{max} = 648 nm

$E_{0,0}$ = 1.98 eV

Figure S2. Fluorescence emission spectrum of Fast Green FCF. (Blue = Absorbance; Red = Emission)

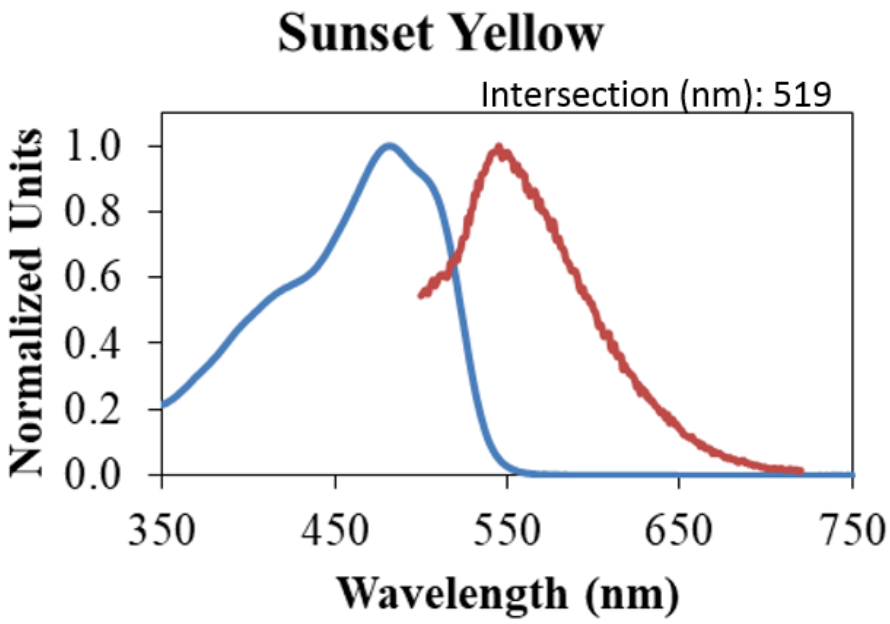


Absorbance λ_{max} = 507 nm

Emission λ_{max} = 586 nm

$E_{0,0}$ = 2.24 eV

Figure S3. Fluorescence emission spectrum of Allura Red AC. (Blue = Absorbance; Red = Emission)

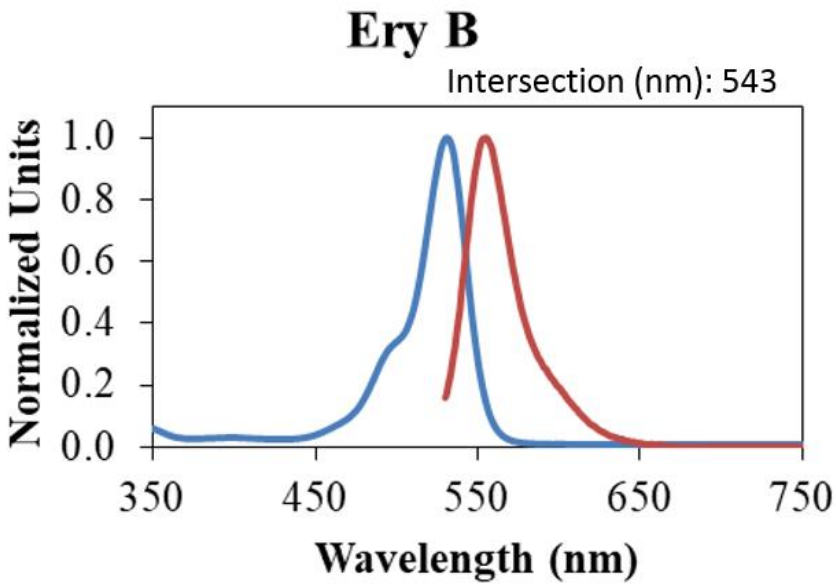


Absorbance λ_{max} = 482 nm

Emission λ_{max} = 545 nm

$E_{0,0}$ = 2.39 eV

Figure S4. Fluorescence emission spectrum of Sunset Yellow FCF. (Blue = Absorbance; Red = Emission)

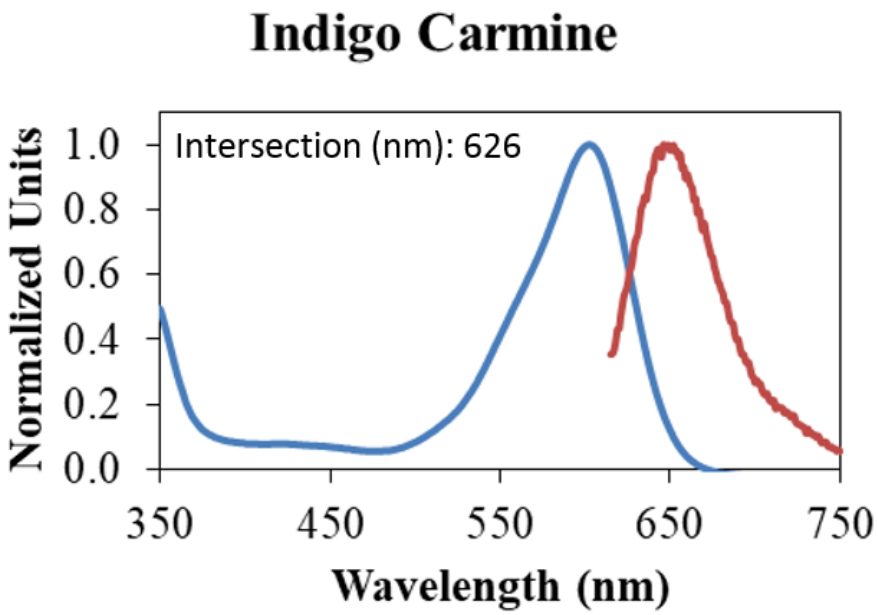


Absorbance λ_{max} = 531 nm

Emission λ_{max} = 562 nm

$E_{0,0}$ = 2.28 eV

Figure S5. Fluorescence emission spectrum of Erythrosine B. (Blue = Absorbance; Red = Emission)

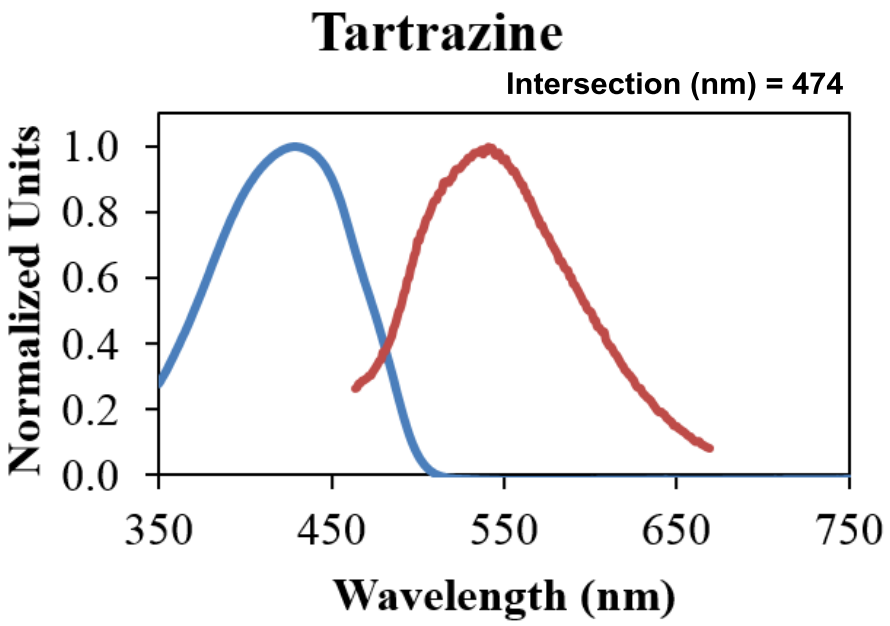


Absorbance λ_{max} = 602 nm

Emission λ_{max} = 646 nm

$E_{0,0}$ = 1.98 eV

Figure S6. Fluorescence emission spectrum of Indigo Carmine. (Blue = Absorbance; Red = Emission)



Absorbance λ_{max} = 429 nm

Emission λ_{max} = 535 nm

$E_{0,0}$ = 2.62 eV

Figure S7. Fluorescence emission spectrum of Tartrazine. (Blue = Absorbance; Red = Emission)

Determination of Ground State Dye Reduction Potential:

Electrochemical experiments were performed using a Biologic SP300 Potentiostat with a glassy carbon working electrode (3 mm diameter), a platinum counter electrode (2 mm diameter), and a Ag/AgCl reference electrode. All voltage data was adjusted to SCE by adding 0.045 V to the experimental data. The electrolyte consisted of a 7:1 ACN:water solution, 1 mM tetrabutylammonium hexafluorophosphate, and saturated with the dye of interest. Cyclic voltammetry was performed at a scan rate of 100 mV/s, starting at the open circuit potential and scanning across the voltage range displayed.

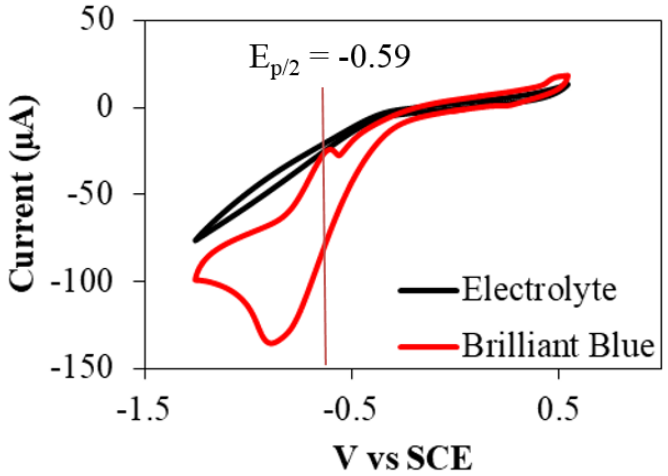


Figure S8. Cyclic voltammogram of Brilliant Blue FCF.

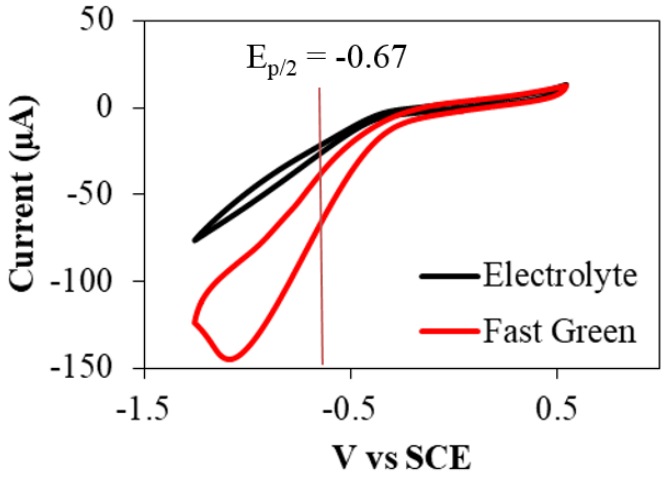


Figure S9. Cyclic voltammogram of Fast Green FCF.

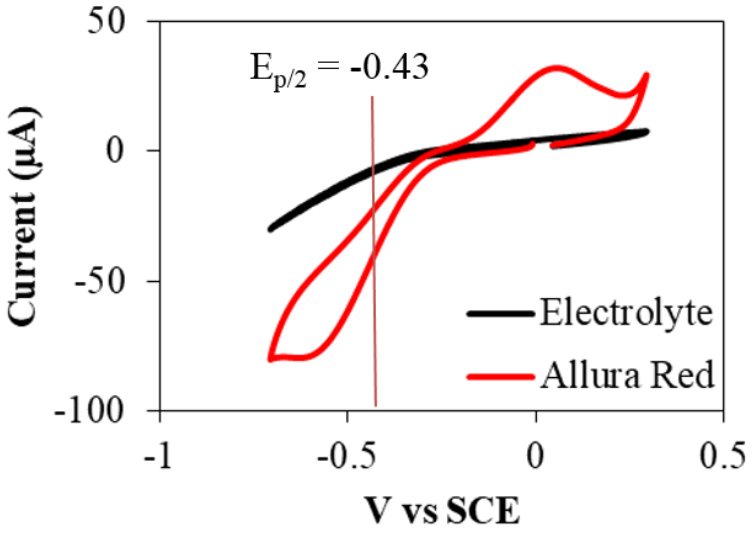


Figure S10. Cyclic voltammogram of Allura Red AC.

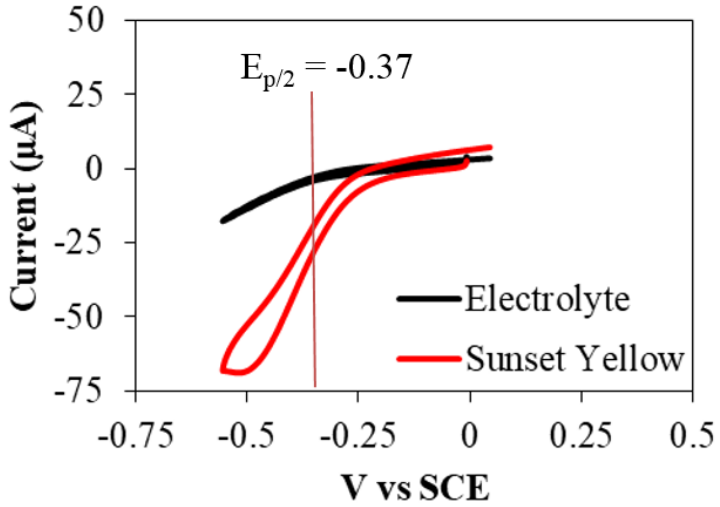


Figure S11. Cyclic voltammogram of Sunset Yellow FCF.

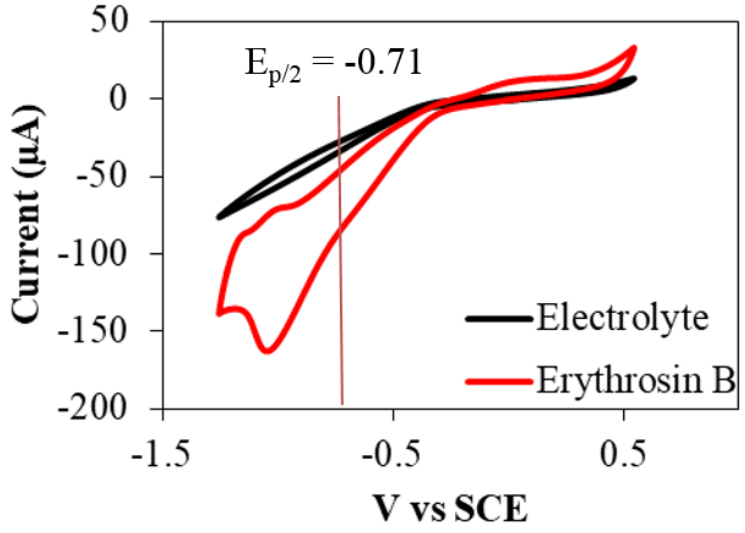


Figure S12. Cyclic voltammogram of Erythrosine B.

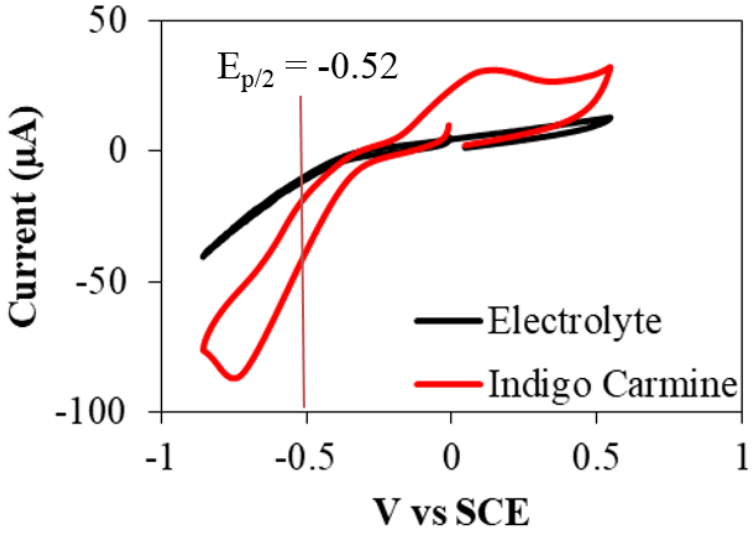


Figure S13. Cyclic voltammogram of Indigo Carmine.

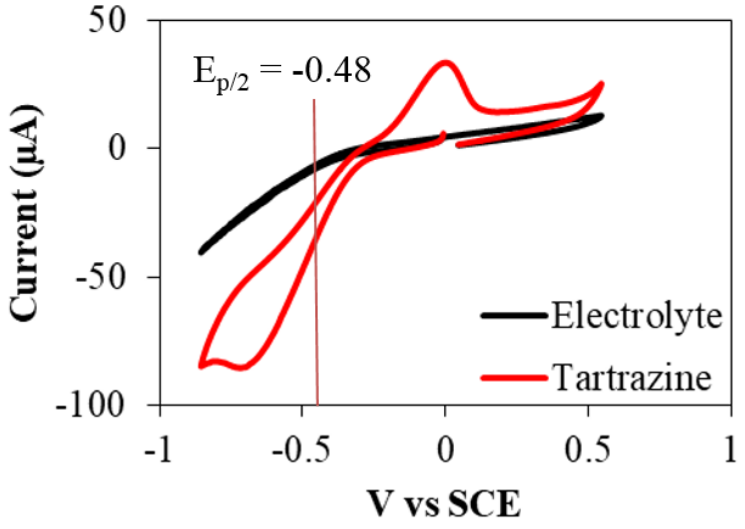


Figure S14. Cyclic voltammogram of Tartrazine.

Determination of excited state reduction potentials ($E_{p/2}$*)

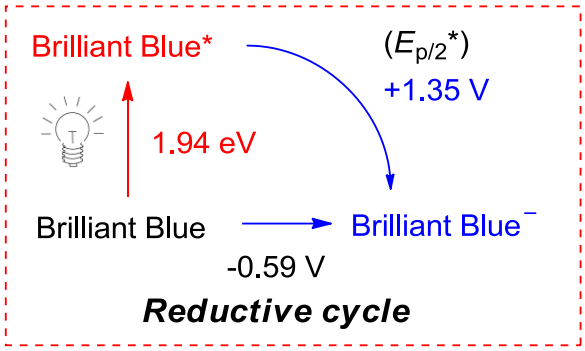


Figure S15. Excited state reduction potential of Brilliant Blue FCF.

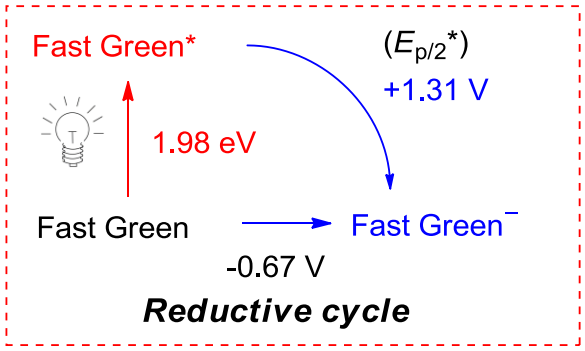


Figure S16. Excited state reduction potential of Fast Green FCF.

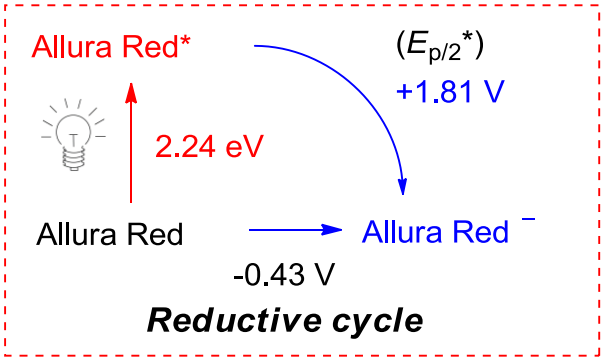


Figure S17. Excited state reduction potential of Allura Red AC.

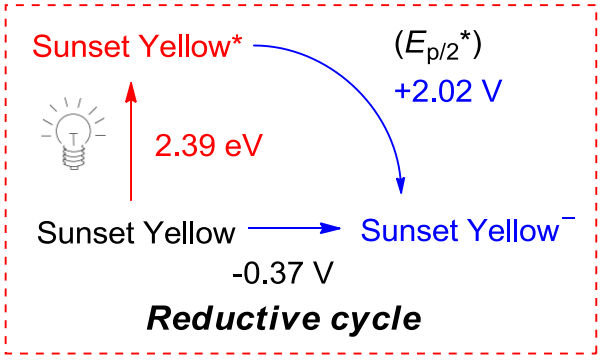


Figure S18. Excited state reduction potential of Sunset Yellow FCF.

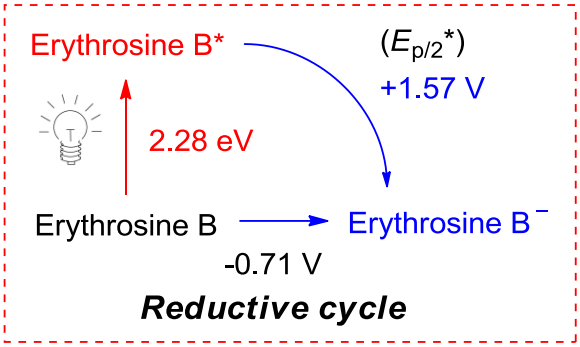


Figure S19. Excited state reduction potential of Erythrosine B.

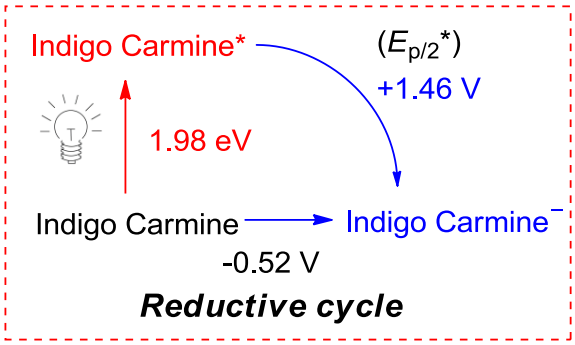


Figure S20. Excited state reduction potential of Indigo Carmine.

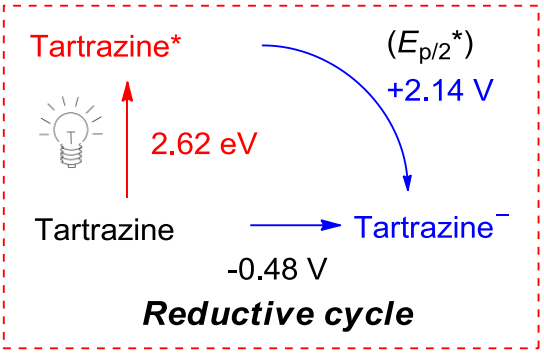


Figure S21. Excited state reduction potential of Indigo Carmine.

General Procedure A for Light-Promoted (Fast Green/NCS) Chlorination of Aromatics/Heteroaromatics:

To an oven-dried flask was added a magnetic stir bar, Fast Green FCF (8.1 mg, 0.02 equiv, 0.01 mmol), arene/heteroarene (1 equiv, 0.5 mmol), acetonitrile (2.5 mL), and then N-chlorosuccinimide (73.4 mg, 1.1 equiv, 0.55 mmol). The reaction mixture was stirred open to air at room temperature (20 °C) in a white LED chamber for 24 hours. For substrates that produced a mixture of mono- and di-brominated products upon full conversion, 2.2 equivalents (1.1 mmol) of N-chlorosuccinimide was employed. Upon completion of the reaction, the crude mixture was evaporated under pressure and the chlorinated product was isolated via column chromatography on silica gel.

General Procedure B for Brilliant Blue/DCDMH Chlorination of Aromatics/Heteroaromatics:

To an oven-dried flask was added a magnetic stir bar, Brilliant Blue FCF (15.9 mg, 0.04 equiv, 0.02 mmol), arene/heteroarene (1 equiv, 0.5 mmol), acetonitrile (2.5 mL), and then DCDMH (108.4 mg, 1.1 equiv, 0.55 mmol). The reaction mixture was stirred open to air at room temperature (20 °C) for 24 hours. Upon completion of the reaction, the crude mixture was evaporated under pressure and the chlorinated product was isolated via column chromatography on silica gel.

Procedure for light-dependent chlorination of naphthalene:

Using visible-light photochambers assembled in our laboratory, the yield of product **1** was calculated using GC integration with adamantane as internal standard according to the following procedure as described in the product characterization of 1-chloronaphthalene (page S-14). Experiments were conducted in a visible-light photochamber that has been protected from any external background light (inside a light-proof chamber constructed in our laboratory) for 24 h. The crude was analyzed after extraction by GC and a yield was calculated in comparison to internal standard curve.[8] Reactions were run in triplicate and the three trials for each LED photochamber were averaged. For the dark reaction, the reaction flask was wrapped in aluminum foil and the reaction was shielded from light in a darkened laboratory with a light-proof chamber constructed in our laboratory.

Iodide Test to Detect Formation of Hydrogen Peroxide

Test solution preparation: 0.100g KI dissolved in 10 mL glacial acetic acid.

Control test: Three drops of 3% H_2O_2 solution were added by pipette to the KI/AcOH test solution in a 4 dram vial. The vial was capped and shaken, resulting in an opaque red-brown color (photo below).

Figure S22A - On the left: Fresh KI test solution

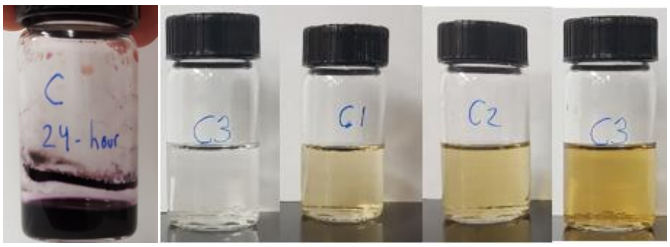
Figure S22B - On the right: Test solution with 3 drops 3 wt% H_2O_2

0-minute test: A test test was loaded following the general procedure using naphthalene as substrate. After addition of all reagents, the test tube was lightly shaken to mix contents. Three drops of the crude reaction mixture was immediately transferred via pipette to a freshly prepared KI/AcOH test solution in a 4-dram vial. The vial was capped and shaken, and appeared as a green color (no I_2 formation).

Figure S22C - On the left: Crude reaction mixture at *t* = 0 h

Figure S22D - On the right: 3 drops of crude rxn at *t* = 0 h added to KI test solution (green)

24-hour test: A test tube was loaded following the general procedure using naphthalene as substrate. After addition of all reagents, the test tube was equipped with a stir bar and allowed to react open to air in a white LED photochamber for 24 hours. At *t* = 24 h, 3, 9, and 15 drops of the dark purple crude reaction mixture were immediately transferred via pipette to three separate, freshly prepared KI/AcOH test solutions in 4-dram vials. The vials were capped and shaken, converting to a faint yellow color. We believe that this indicates that I_2 is forming via the presence of a small amount of hydrogen peroxide. Oxygen appears to play a role in the oxidation of the excited state of the photocatalyst, though not as large a role as in other systems we've observed.[4-5]



E F G H I

Figure S22E - Crude reaction after *t* = 24 h

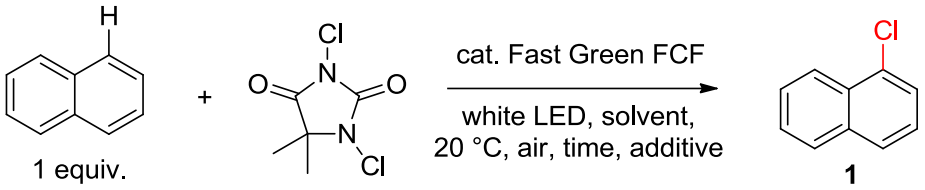
Figure S22F - Fresh KI/HOAc test solution

Figure S22G - 3 drops of crude in test solution

Figure S22H - 9 drops of crude in test solution

Figure S22I - 15 drops of crude in test solution

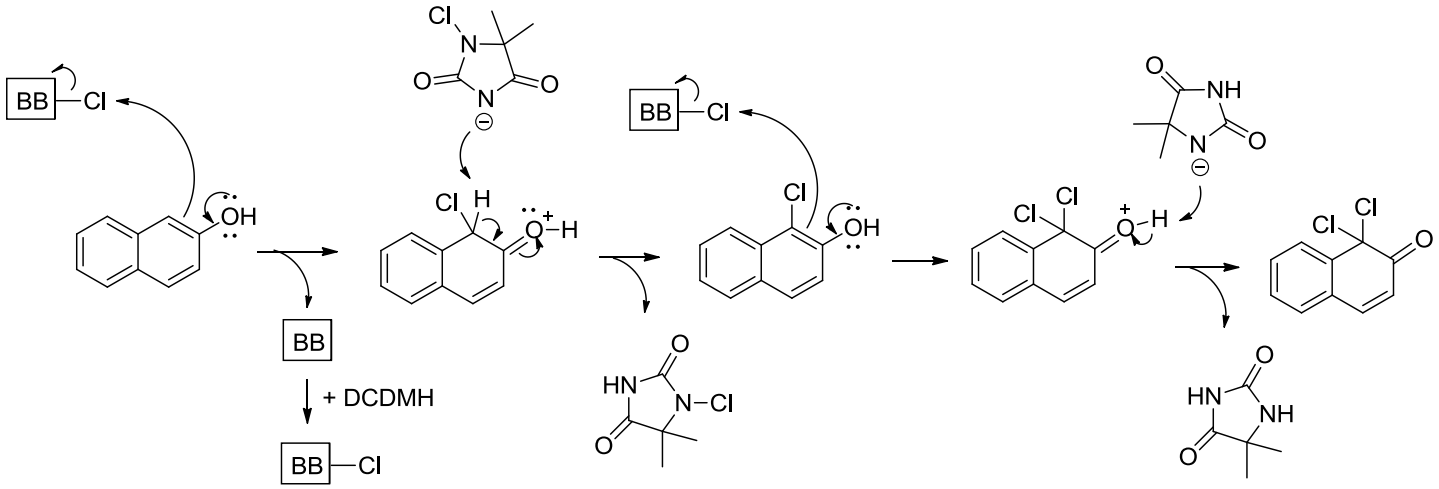
Figure S22. Iodide Test for Detection of Hydrogen Peroxide Formation (all photos in Figure S22 were taken by a co-author, David Rogers, and are free domain).



Entry	DCDMH (equiv.)	solvent (0.1 M)	catalyst (mol %)	time (hours)	additive (equiv.)	Yield **1** (%)[a]
1	1.1	MeCN	4	24	-	91
2	0.55	MeCN	4	24	-	70
3	1.1	MeCN	1	24	-	52
4	1.1	MeCN	10	24	-	92
5	1.1	MeCN (0.2M)	4	24	-	73
6	1.1	MeCN (0.05M)	4	24	-	66

a) Gas chromatography (GC) yields calculated using adamantane as internal standard.

Table S1. Optimization of Brilliant Blue/DCDMH chlorination of naphthalene.



Scheme S1. Plausible mechanism for the formation of **30**.

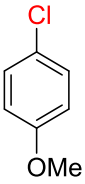
Product Characterization:

All chloroarenes were isolated according to general procedure unless otherwise noted and display the characterizational data shown below.

1-Chloronaphthalene **(1)**[8]

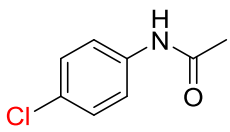
The title compound was prepared according to general procedure A or B and quantified using gas chromatography with adamantane as an internal standard. A standard curve of 1-chloronaphthalene was prepared in 6 separate reaction vessels by adding varying amounts of 1-chloronaphthalene (between 0 and 0.25 mmol) to 3 mL of acetonitrile.[8] To each of the 3 mL acetonitrile solutions was added 8 mL of hexanes and 0.156 mmol (20 mg) of adamantane. The acetonitrile solution was extracted with the hexanes, and 1 mL of the hexanes portion was removed for gas chromatography injection. Gas chromatography was performed using a Shimadzu GC-2010 Plus with GCMS-QP2010 with a Restek Rtx-5MS capillary column (30m; 0.25 mmID; 0.25 um df; Crossbond – 5% diphenyl/95% dimethyl pilosiloxane). The GC method was as follows: 40 °C for 5 minutes, then increase at 10 °C/minute for 16 minutes (up to 200 °C). 200 °C is maintained for 10 additional minutes. The title compound 1-chloronaphthalene is observed at 16.8 minutes,[8] and confirmed by MS (EI) *m/z* 164 (M+2, 30), 162 (M+, 100), 127 (48), 74, (36), 63 (56).

4-chloroanisole and 2-chloroanisole **(2)**[9-10]



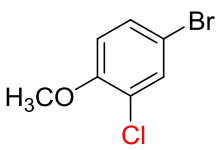
The title compounds were prepared according to general procedure A or B and characterizational spectra was consistent with literature values. A mixture (according to ^{1}H NMR integration) of para/ortho isomers was isolated, and data regarding the para (major) isomer is reported below. Clear oil (Procedure A: 44.9 mg, 63% yield total, 8:1 para/ortho; Procedure B: 46.3 mg, 65% yield total, 20:1 para/ortho). Purification (6 mL of 4M NaOH was added to the crude reaction mixture and extraction using EtOAc (3 x 10 mL) was performed, followed by drying with sodium sulfate). ^{1}H NMR (400 MHz, $CDCl_3$) from product of Procedure A – peaks reported correspond to major (para) isomer: δ = 7.23 (d, *J* = 6.9 Hz, 2H), 6.83 (d, *J* = 6.9 Hz, 2H), 3.78 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) from product of Procedure A – peaks reported correspond to major (para) isomer: δ = 158.2, 129.3, 125.5, 115.2, 55.5. MS (EI): m/z 144(M+2, 30), 142(M+, 84), 127(60), 99(100), 75(40), 73(40), 63(52).

4-chloroacetanilide **(3)**[8]



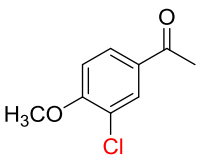
The title compound was prepared according to general procedure A and characterizational spectra was consistent with literature values. White solid (39.8 mg, 47% yield). m.p. 178-181 °C. Purification (6 mL of 4M NaOH was added to the crude reaction mixture and extraction using EtOAc (3 x 10 mL) was performed, followed by drying with sodium sulfate. Column chromatography using a 4:1 hexanes:EtOAc eluent resulted in pure compound). R_f = 0.13. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.21 (bs, 1H), 2.17 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 136.4, 129.3, 129.0, 121.0, 24.6. MS (EI): m/z 171(M+2, 3), 169(M+, 11), 129(23), 127(75), 65(10), 63(11), 43(100), 39(12).

***4-bromo-3-chloroanisole* (4)[5]**



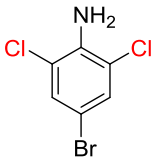
The title compound was prepared according to general procedure A and characterizational spectra was consistent with literature values. Clear oil (60.0 mg, 54% yield). Purification (6 mL of 4M NaOH was added to the crude reaction mixture and extraction using EtOAc (3 x 10 mL) was performed, followed by drying with sodium sulfate. Column chromatography using a 95:5 hexanes:EtOAc eluent resulted in pure compound). R_f = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 2.4 Hz, 1H), 7.33 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 3.88 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 132.7, 130.5, 123.6, 113.3, 112.5, 56.3. MS (EI): m/z 224(M+4, 16), 222(M+2, 56), 220(M+, 53), 207(51), 205(42), 179(45), 177(37), 75(36), 63(100), 62(40), 50(36).

***3-chloro-4-methoxyacetophenone* (5)[11]**



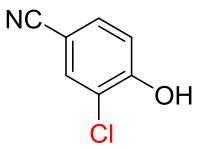
The title compound was prepared according to general procedure A and characterizational spectra was consistent with literature values. White solid (32.2 mg, 34% yield). m.p. 73-76 °C. Purification (Hexanes:DCM = 30:70). R_f = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 2.0 Hz, 1H), 7.86 (dd, J_1 = 8.6 Hz, J_2 = 2.0 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 3.96 (s, 3H), 2.55 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.7, 158.7, 130.7, 130.6, 128.8, 122.8, 111.2, 56.4, 26.3. MS (EI): m/z 186(M+2, 11), 184(M+, 31), 171(20), 169(100), 141(15), 77(40), 75(15), 63(42), 62(12), 43(76).

***4-bromo-2,6-dichloroaniline* (6)[5]**



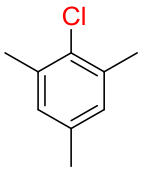
The title compound was prepared according to general procedure A with 2.2 equivalents of NCS and characterizational spectra was consistent with literature values. Red solid (85.3 mg, 70% yield). m.p. 77-80 °C. Purification (Hexanes:EtOAc = 95:5). R_f = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (s, 2H), 4.45 (bs, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.4, 130.2, 120.0, 107.9. MS (EI): m/z 243(M+4, 41), 242(M+3, 40), 241(M+2, 100), 239(M+, 55), 162(17), 160(27), 124(37), 63(50), 62(62), 61(35), 52(32).

***3-chloro-4-hydroxyphenol* (7)[8]**



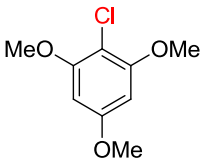
The title compound was prepared according to general procedure A and characterizational spectra was consistent with literature values. White solid (16.2 mg, 21% yield). m.p. 158-160 °C. Purification (Hexanes:DCM = 1:3). R_f = 0.10. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 2.0 Hz, 1H), 7.50 (dd, J_1 = 8.2 Hz, J_2 = 2.0 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.23 (bs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 133.1, 132.8, 120.8, 117.7, 117.2, 104.9. MS (EI): m/z 155(M+2, 32), 153(M+, 100), 89(53), 63(52), 62(68), 38(73), 37(54).

***2-chloromesitylene* (8)**[12]



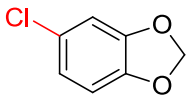
The title compound was prepared according to general procedure A or B and characterizational spectra was consistent with literature values. Clear oil (Procedure A: 48.0 mg, 62% yield; Procedure B: 51.8 mg, 67% yield). Purification (6 mL of 4M NaOH was added to the crude reaction mixture and extraction using EtOAc (3 x 10 mL) was performed, followed by drying with sodium sulfate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.89 (s, 2H), 2.34 (s, 6H), 2.25 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.8, 135.5, 131.5, 129.1, 20.7, 20.6. MS (EI): m/z 190(M+2, 25), 188(M+, 31), 155(40), 153(100), 117(30), 115(60), 91(30).

***2-chloro-1,3,5-trimethoxybenzene* (9)**[13]



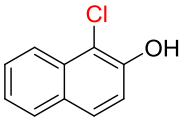
The title compound was prepared according to general procedure A and characterizational spectra was consistent with literature values. White solid (73.3 mg, 73% yield). m.p. 91-94 °C. Purification (Hexanes:EtOAc = 80:20). R_f = 0.52. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.18 (s, 2H), 3.87 (s, 6H), 3.81 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 156.5, 102.6, 91.5, 56.3, 55.5. MS (EI): m/z 204(M+2, 32), 202(M+, 100), 173(32), 159(32), 144(15), 139(17), 138(33), 137(16), 69(29), 59(30).

***3,4-methylenedioxychlorobenzene* (10)**[8]



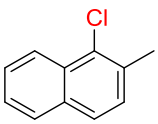
The title compound was prepared according to general procedure A and characterizational spectra was consistent with literature values. Clear oil (70.7 mg, 90% yield). Purification (Hexanes:EtOAc = 90:10). R_f = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84-6.77 (m, 2H), 6.72 (dd, J_1 = 8.0 Hz, J_2 = 0.4 Hz, 1H), 5.97 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.3, 146.4, 126.2, 121.3, 109.6, 108.9, 101.7. MS (EI): m/z 157(M+2, 34), 155(M+, 87), 65(23), 63(100), 62(36).

***1-chloro-2-naphthol* (11)**[5]



The title compound was prepared according to general procedure A and characterizational spectra was consistent with literature values. Yellow solid (85.9 mg, 94% yield). m.p. 65-68 °C. Purification (Hexanes:EtOAc = 80:20). R_f = 0.24. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J_1 = 8.6 Hz, 1H), 7.80 (d, J_1 = 8.2 Hz, 1H), 7.71 (d, J = 9.0 Hz, d, 1H), 7.59 (ddd, J_1 = 8.6 Hz, J_2 = 7.0 Hz, J_3 = 1.2 Hz, 1H), 7.41 (ddd, J_1 = 8.2 Hz, J_2 = 7.0 Hz, J_3 = 1.2 Hz, 1H), 7.28 (d, J = 9.0 Hz, 1H), 5.93 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.3, 131.0, 129.4, 128.4, 128.2, 127.6, 124.1, 122.7, 117.2, 113.3. MS (EI): m/z 180(M+2, 33), 178(M+, 100), 115(33), 114(80), 113(22), 89(25), 63(28), 57(49).

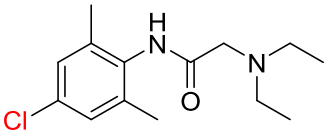
***1-chloro-2-methylnaphthalene* (12)**[5]



The title compound was prepared according to general procedure A or B and characterizational spectra was consistent with literature values. Clear oil (Procedure A: 79.4 mg, 90% yield; Procedure B: 73.2 mg, 84%). Purification (Hexanes). R_f = 0.55. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.60 (ddd, J_1 = 8.2 Hz, J_2 = 7.0 Hz, J_3 = 1.2 Hz, 1H), 7.50 (ddd, J_1 = 8.2 Hz, J_2 = 7.0 Hz, J_3 =

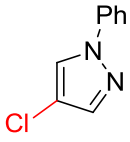
1.2 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 2.62 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.4, 133.0, 131.1, 130.6, 128.7, 128.0, 127.0, 126.4, 125.6, 124.1, 20.8. MS (EI): m/z 178(M+2, 17), 176(M+, 52), 141(100), 139(28), 115(24), 70(72).

N-(4-chloro-2,6-dimethylphenyl)-2-(diethylamino)acetamide **(13)**[5]



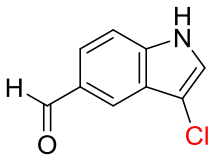
The title compound was prepared according to general procedure A or B and characterizational spectra was consistent with literature values. White solid (Procedure A: 28.9 mg, 22% yield; Procedure B: 68.5 mg, 51% yield). m.p. 33-36 °C. Purification (Hexanes:EtOAc = 1:1 with 2% NEt_3). R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.92 (bs, 1H), 7.09 (s, 2H), 3.22 (s, 2H), 2.69 (q, J_1 = 7.0 Hz, 4H), 2.23 (s, 6H), 1.14 (t, J_1 = 7.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 135.1, 134.0, 128.2, 127.1, 57.5, 49.0, 18.6, 12.7. MS (EI): m/z 234(1), 134(1), 132(1), 120(1), 86(100), 58(14), 42(9).

4-chloro-1-phenylpyrazole **(14)**[14]



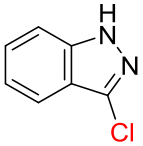
The title compound was prepared according to general procedure A and characterizational spectra was consistent with literature values. White solid (80.1 mg, 90% yield). m.p. 58-60 °C. Purification (Hexanes:EtOAc 85:15). R_f = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 0.6 Hz, 1H), 7.65-7.61 (m, 3H), 7.45 (m, 2H), 7.34-7.31 (tt, J_1 = 7.4 Hz, J_2 = 1.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.7, 139.4, 129.5, 127.0, 124.8, 118.9, 112.4. MS (EI): m/z 180(M+2, 21), 178(M+, 73), 152(18), 143(17), 116(21), 89(29), 77(71), 51(100).

3-chloro-1H-indole-5-carboxaldehyde **(15)**[5]



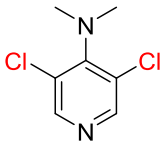
The title compound was prepared according to general procedure A on 0.25 mmol scale (5-formylindole) and characterizational spectra was consistent with literature values. Pale yellow solid (33.7 mg, 74% yield). m.p. 133-137 °C. Purification (Hexanes:EtOAc 60:40). R_f = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.08 (s, 1H), 8.66 (bs, 1H), 8.18 (s, 1H), 7.83 (dd, J_1 = 8.6 Hz, J_2 = 1.4 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.31 (d, *J* = 2.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 194.2, 140.2, 130.9, 126.4, 124.9, 124.4, 123.2, 113.6, 108.0. MS (EI): m/z 181(M+2, 10), 179(M+, 25), 159(60), 103(100).

3-chloro-1H-indazole **(16)**[15]



The title compound was prepared according to general procedure A and characterizational spectra was consistent with literature values. White solid (52.8 mg, 68% yield). m.p. 140-144 °C. Purification (Hexanes:EtOAc 80:20). R_f = 0.22. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.01 (bs, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.6 Hz, 1H), 7.47 (ddd, J_1 = 8.6 Hz, J_2 = 6.9 Hz, J_3 = 1.0 Hz, 1H), 7.25 (ddd, J_1 = 8.2 Hz, J_2 = 6.9 Hz, J_3 = 1.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.4, 135.1, 128.1, 121.7, 120.5, 119.6, 110.4. MS (EI): m/z 154(M+2, 26), 152(M+, 100), 117(54), 90(71), 64(32), 63(53), 62(33), 39(65), 38(46), 37(31).

***3,5-dichloro-4-(N,N-dimethylamino)pyridine* (17)[14]**

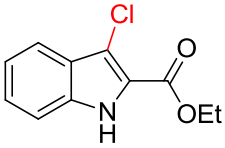


The title compound was prepared according to general procedure A using 2.2 equivalents NCS and characterizational spectra was consistent with literature values. Yellow oil (77.9 mg, 80% yield). Purification (Hexanes:EtOAc 2:1). R_f = 0.75. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (s, 2H), 3.01 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 149.1, 128.2, 42.6. MS (EI): m/z 194(M+4, 7), 193(M+3, 14), 192(M+2, 35), 191(69), 190(M+, 55), 189(100), 112(17), 59(15), 50(19), 44(20), 42(79).

***3-chloro-1H-indole* (18)[8]**

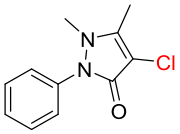
The title compound was prepared according to general procedure A and characterizational spectra was consistent with literature values. Brown solid (60.1 mg, 80% yield). m.p. 92-95 °C. Purification (Hexanes:EtOAc 70:30). R_f = 0.46. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (bs, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.22-7.11 (m, 2H), 7.07 (d, *J* = 1.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.9, 125.3, 123.1, 120.8, 120.4, 118.2, 111.5, 106.4. MS (EI): m/z 153(M+2, 29), 151(M+, 100), 116(21), 89(64), 63(25), 62(19), 57(18), 75(22).

***Ethyl-3-chloroindole-2-carboxylate* (19)[5]**



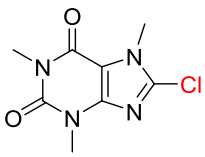
The title compound was prepared according to general procedure A or B and characterizational spectra was consistent with literature values. White solid (Procedure A: 25.6 mg, 23% yield; Procedure B: 31.3 mg, 28%). m.p. 148-150 °C. Purification (Hexanes:EtOAc 90:10). R_f = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.85 (bs, 1H), 7.72 (dd, J_1 = 7.4 Hz, J_2 = 1.0 Hz, 1H), 7.39 (m, 2H), 7.23 (m, 1H), 4.46 (q, *J* = 7.0 Hz, 2H), 1.45 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9, 134.6, 126.6, 126.2, 122.4, 121.3, 120.3, 112.5, 112.0, 61.4, 14.4. MS (EI): m/z 225(M+2, 8), 223(M+, 24), 179(30), 178(18), 177(100), 149(29), 123(21), 114(29).

***4-chloro-1,2-dihydro-1,5-dimethyl-2-phenyl- 3H-pyrazol-3-one* (20)[5]**



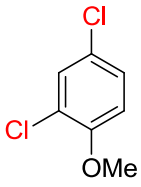
The title compound was prepared according to general procedure A or B and characterizational spectra was consistent with literature values. Light green solid (Procedure A: 102.3 mg, 92% yield; Procedure B: 87.8 mg, 79% yield). m.p. 117-121 °C. Purification (Hexanes:EtOAc 80:20). R_f = 0.20. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (m, 2H), 7.42 (m, 2H), 7.24 (m, 1H), 2.86 (s, 3H), 1.81 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 136.1, 129.2, 126.3, 120.7, 91.7, 86.0, 37.6, 20.2. MS (EI): m/z 191(61), 190(49), 189(95), 77(84), 43(82), 36(77), 51(56), 42(40), 38(39), 39(36).

***8-chlorocaffeine* (21)[5]**



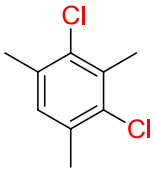
The title compound was prepared according to general procedure A and characterizational spectra was consistent with literature values. White solid (103.1 mg, 90% yield). m.p. 102-105 °C. Purification (Hexanes:EtOAc 1:1). R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3H), 3.50 (s, 3H), 3.35 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5, 151.2, 147.0, 138.9, 108.1, 32.6, 29.7, 27.9. MS (EI): m/z 230(M+2, 21), 228(M+, 63), 143(50), 82(33), 67(94), 55(100).

***2,4-dichloroanisole* (22)[16]**



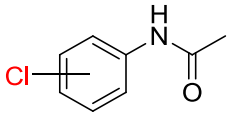
The title compound was prepared according to general procedure B and characterizational spectra was consistent with literature values. Clear oil (40.0 mg, 35% yield). Purification: 3 mL of 4M NaOH was added to the crude reaction mixture and extraction using EtOAc (3 x 10 mL) was performed, followed by drying with sodium sulfate, and chromatography (100% benzene). R_f = 0.90. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, J = 2.4 Hz, 1H), 7.19 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.84 (d, J = 8.8 Hz, 1H), 3.88 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.9, 130.0, 127.6, 125.6, 123.3, 112.8, 56.4. MS (EI): m/z 178(M+2, 50), 176(M+, 78), 163(62), 161(100), 135(40), 133(65), 75(26), 73(26).

***2,4-dichloro-1,3,5-trimethylbenzene* (23)[17-18]**



The title compound was prepared according to general procedure B. White solid (27.4 mg, 29% yield). m.p. 56-59 °C. Purification (Hexanes:EtOAc 9:1). R_f = 0.90. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.97 (s, 1H), 2.49 (s, 3H), 2.32 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.2, 134.0, 132.7, 129.8, 20.6, 18.4. MS (EI): m/z 190(M+2, 25), 188(M+, 32), 155(30), 153(100), 115(32), 57(43), 51(28).

***2-chloroacetanilide and 4-chloroacetanilide* (24)[8]**

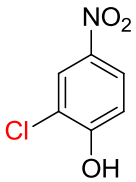


The title compounds were prepared according to general procedure B and characterizational spectra was consistent with literature values.

2-chloroacetanilide: White solid (59.4 mg, 70% yield). m.p. 86-89 °C. Purification (Hexanes:EtOAc 80:20). R_f = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, J = 9.0 Hz, 1H), 7.59 (bs, 1H), 7.36 (d, J = 2.3 Hz, 1H), 7.23 (dd, J_1 = 9.0 Hz, J_2 = 2.3 Hz, 1H), 2.23 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 133.4, 129.0, 128.7, 127.9, 122.9, 122.3, 24.9. MS (EI): m/z 171(M+2, 2), 169(M+, 7), 134(25), 129(25), 127(79), 43(100).

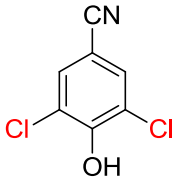
4-chloroacetanilide (**3**): White solid (16.3 mg, 20% yield). m.p. 174-177 °C. Purification (Hexanes:EtOAc 80:20). R_f = 0.10. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, J = 8.6 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 7.21 (bs, 1H), 2.17 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 136.4, 129.3, 129.0, 121.0, 24.6.

***2-chloro-4-nitrophenol* (25)[19]**



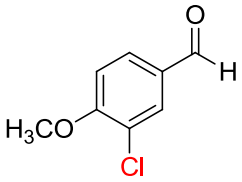
The title compound was prepared according to general procedure B and characterizational spectra was consistent with literature values. Yellow solid (50.3 mg, 58% yield). m.p. 103-105 °C. Purification: chromatography (100% DCM) followed by recrystallization with hexanes:EtOAc. R_f = 0.10. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, J = 2.7 Hz, 1H), 8.13 (dd, J_1 = 9.0 Hz, J_2 = 2.7 Hz, 1H), 7.14 (d, J = 9.0 Hz, 1H), 6.20 (bs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 125.3, 124.6, 124.3, 120.3, 116.3 ppm. MS (EI): m/z 175(M+2, 22), 173(M+, 68), 143(49), 99(56), 63(100), 53(67).

***3,5-dichloro-4-hydroxybenzonitrile* (26)[5]**



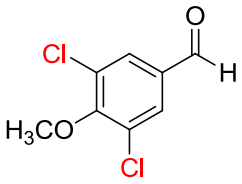
The title compound was prepared according to general procedure B and characterizational spectra was consistent with literature values. White solid (16.9 mg, 18% yield). m.p. 137-140 °C. Purification (Hexanes:EtOAc 80:20). R_f = 0.50. ^{1}H NMR (400 MHz, DMSO): δ = 11.57 (bs, 1H), 7.98 (s, 2H) ppm. ^{13}C NMR (100 MHz, DMSO): δ = 153.8, 132.7, 122.7, 117.1, 103.1.

***3-chloro-4-methoxybenzaldehyde* (27)[5]**



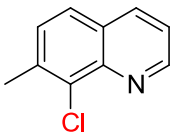
The title compound was prepared according to general procedure B and characterizational spectra was consistent with literature values. Red solid (58.8 mg, 69% yield). m.p. 51-56 °C. Purification (Hexanes:DCM 1:1). R_f = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.85 (s, 1H), 7.90 (d, J = 2.0 Hz, 1H), 7.77 (d, J_1 = 8.6 Hz, J_2 = 2.0 Hz, 1H), 7.04 (d, J = 8.6, 1H), 3.99 (s, 3H) ppm. ^{13}C NMR (100MHz, $CDCl_3$) δ 189.7, 159.8, 131.2, 130.6, 130.3, 123.7, 111.7, 56.5.

***3,5-dichloro-4-methoxybenzaldehyde* (28)[5]**



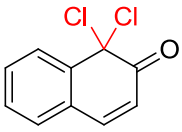
The title compound was prepared according to general procedure B and characterizational spectra was consistent with literature values. Red solid (18.5 mg, 18% yield). m.p. 58-63 °C. Purification (Hexanes:DCM 1:1). R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.87 (s, 1H), 7.82 (s, 2H), 3.99 (s, 3H) ppm. ^{13}C NMR (100MHz, $CDCl_3$) δ 188.7, 157.3, 133.1, 130.7, 130.1, 61.0.

***8-chloro-7-methylquinoline* (29)[5]**



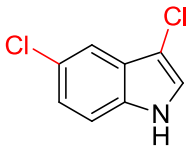
The title compound was prepared according to general procedure B and characterizational spectra was consistent with literature values. Yellow oily solid (27.5 mg, 31% yield). Purification (Hexanes:EtOAc 80:20). R_f = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.01 (dd, J_1 = 4.3 Hz, J_2 = 1.6 Hz, 1H), 8.10 (dd, J_1 = 8.2 Hz, J_2 = 1.6 Hz, 1H), 7.61 (d, J = 8.2 Hz, 1H), 7.39 (m, 2H), 2.61 (s, 3H) ppm. ^{13}C NMR (100MHz, $CDCl_3$) δ 150.8, 144.6, 137.7, 136.2, 132.1, 129.4, 127.7, 125.7, 120.9, 21.0. MS (EI) m/z 179(15), 177(54), 142(100), 141(25), 89(29), 75(23), 71(25), 57(26), 39(24).

***1,1-dichloronaphtalene-2(1H)-one* (30)[20]**



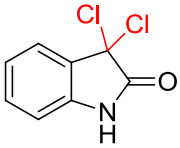
The title compound was prepared according to general procedure B and characterizational spectra was consistent with literature values. Red oil (92.4 mg, 88% yield). Purification (Hexanes:EtOAc 80:20). R_f = 0.58. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (dd, J_1 = 7.8 Hz, J_2 = 1.0 Hz, 1H), 7.53 (td, $J_{1,2}$ = 7.8 Hz, J_3 = 1.0 Hz, 1H), 7.47 (td, $J_{1,2}$ = 7.6 Hz, J_3 = 1.2 Hz, 1H), 7.45 (d, J = 10.0 Hz, 1H), 7.33 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 6.34 (d, J = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 144.9, 140.7, 131.2, 130.6, 129.54, 129.52, 126.9, 122.6, 80.4.

3,5-dichloro-1H-indole **(31)**[21]



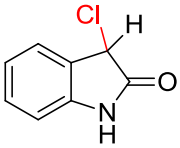
The title compound was prepared according to general procedure B and characterizational spectra was consistent with literature values. Red-brown solid (35.2 mg, 38% yield). m.p. 102-104 °C. Purification (Hexanes:EtOAc 80:20). R_f = 0.80. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (bs, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.26-7.16 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.2, 125.5, 123.4, 121.1, 120.0, 117.8, 110.8, 103.8. MS (EI): m/z 187(M+2, 64), 185(M+, 100), 152(28), 150(81), 123(32), 114(29), 92(28), 74(27), 61(25).

3,3-dichloro-2-oxindole **(32)**[22]



The title compound was prepared according to general procedure B and characterizational spectra was consistent with literature values. Brown solid (9.8 mg, 10% yield). m.p. 163-166 °C. Purification (Hexanes:EtOAc 80:20). R_f = 0.47. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.15 (bs, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.18 (t, J_1 = 7.6 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 137.8, 132.0, 129.7, 125.1, 124.4, 111.3, 74.6 ppm. FT-IR (neat, cm^{-1}): ν = 3146, 2940, 1730, 1681, 1621, 1486, 1469, 1396, 1206, 1188. MS (EI): m/z 169(M+2, 7), 167(M+, 26), 133(23), 132(100), 104(45), 77(39), 52(50), 51(81), 50(41), 38(24).

3-chloro-2-oxindole **(33)**[23]



The title compound was prepared according to general procedure B and characterizational spectra was consistent with literature values. Brown solid (15.1 mg, 18% yield). m.p. 156-158 °C. Purification (Hexanes:EtOAc 80:20). R_f = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (bs, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 5.16 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.2, 140.9, 130.6, 126.2, 126.0, 123.5, 110.5, 51.8.

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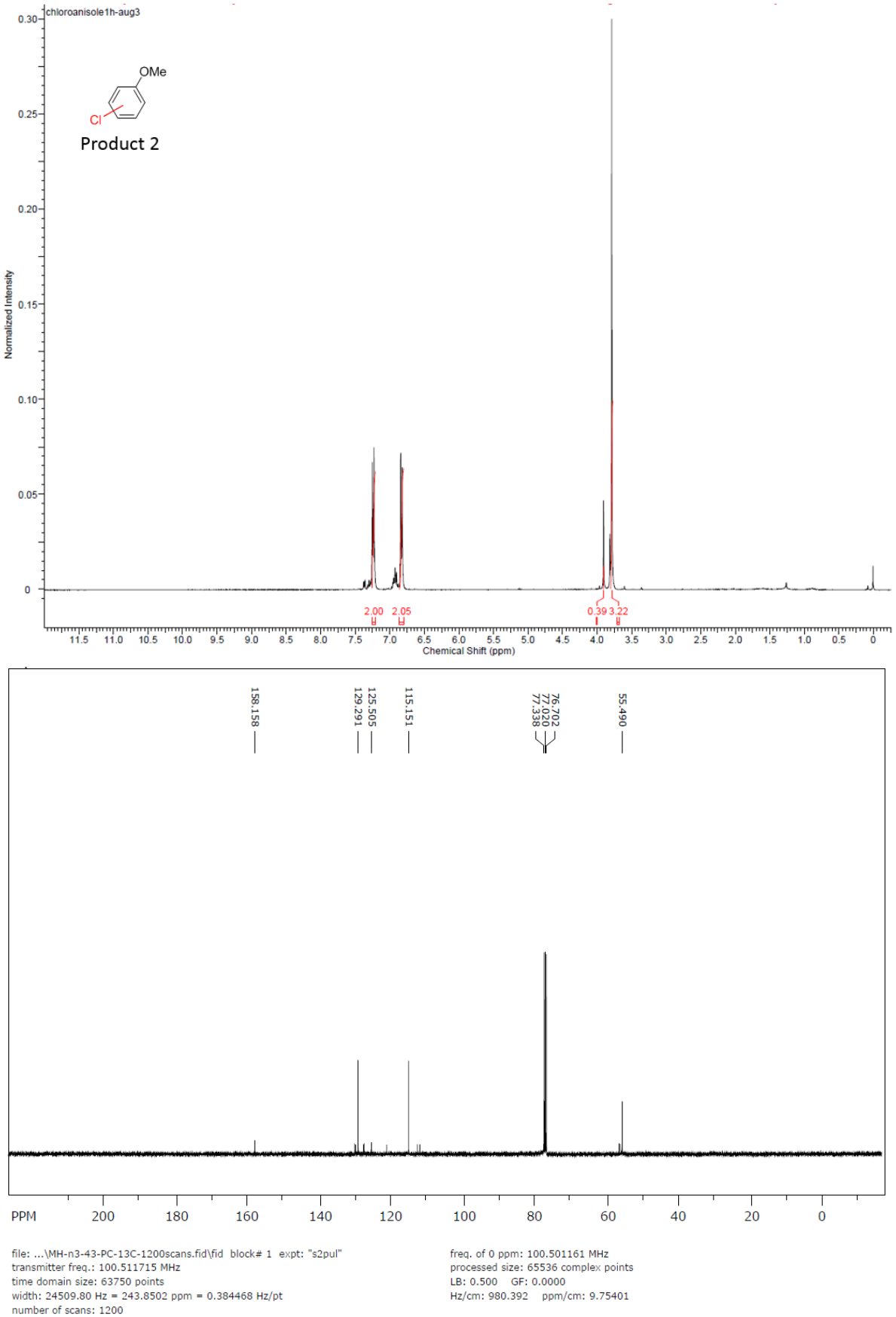


Figure S23. ^{1}H NMR and ^{13}C NMR of Product **2**.

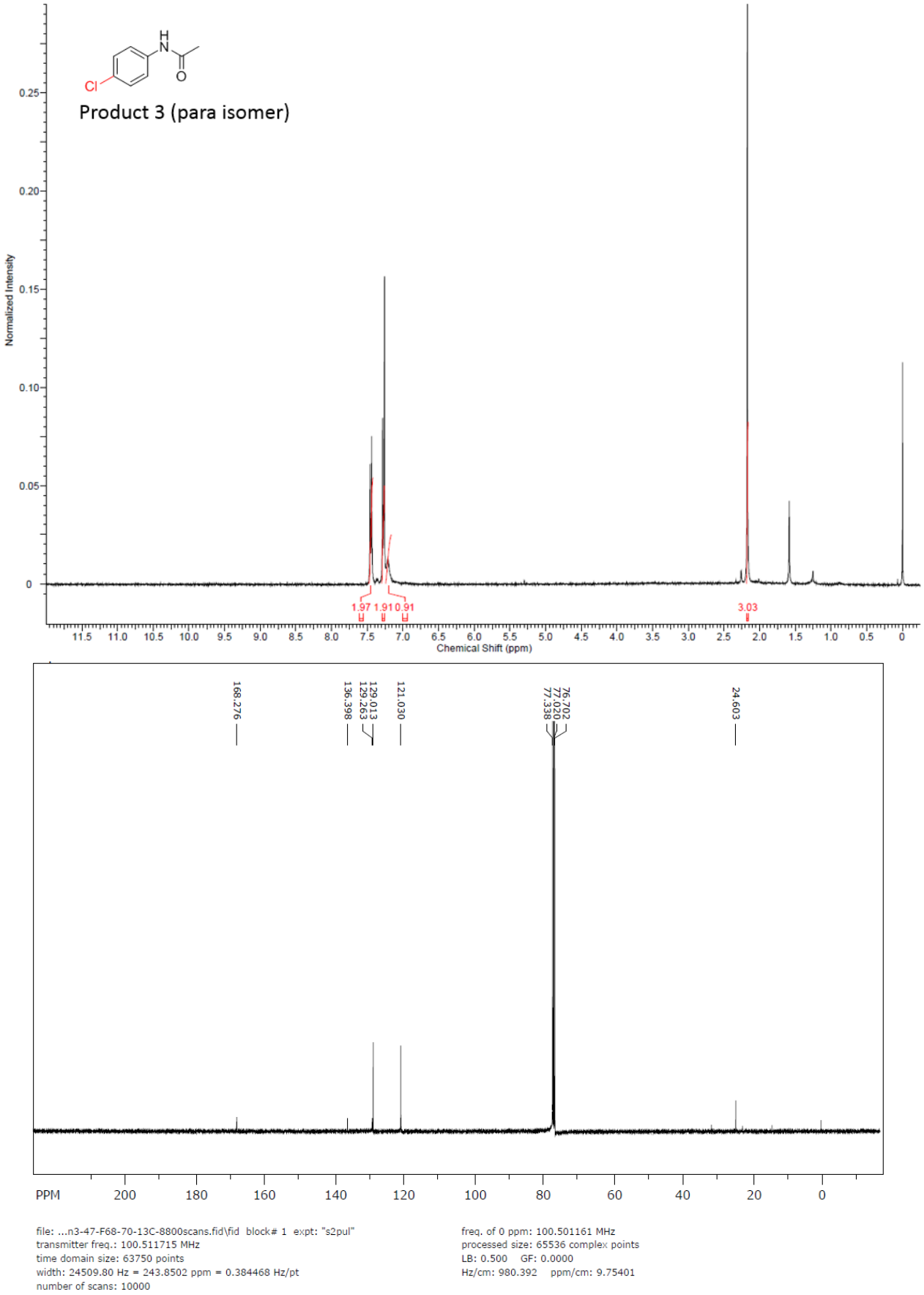


Figure S24. ^{1}H NMR and ^{13}C NMR of Product **3**.

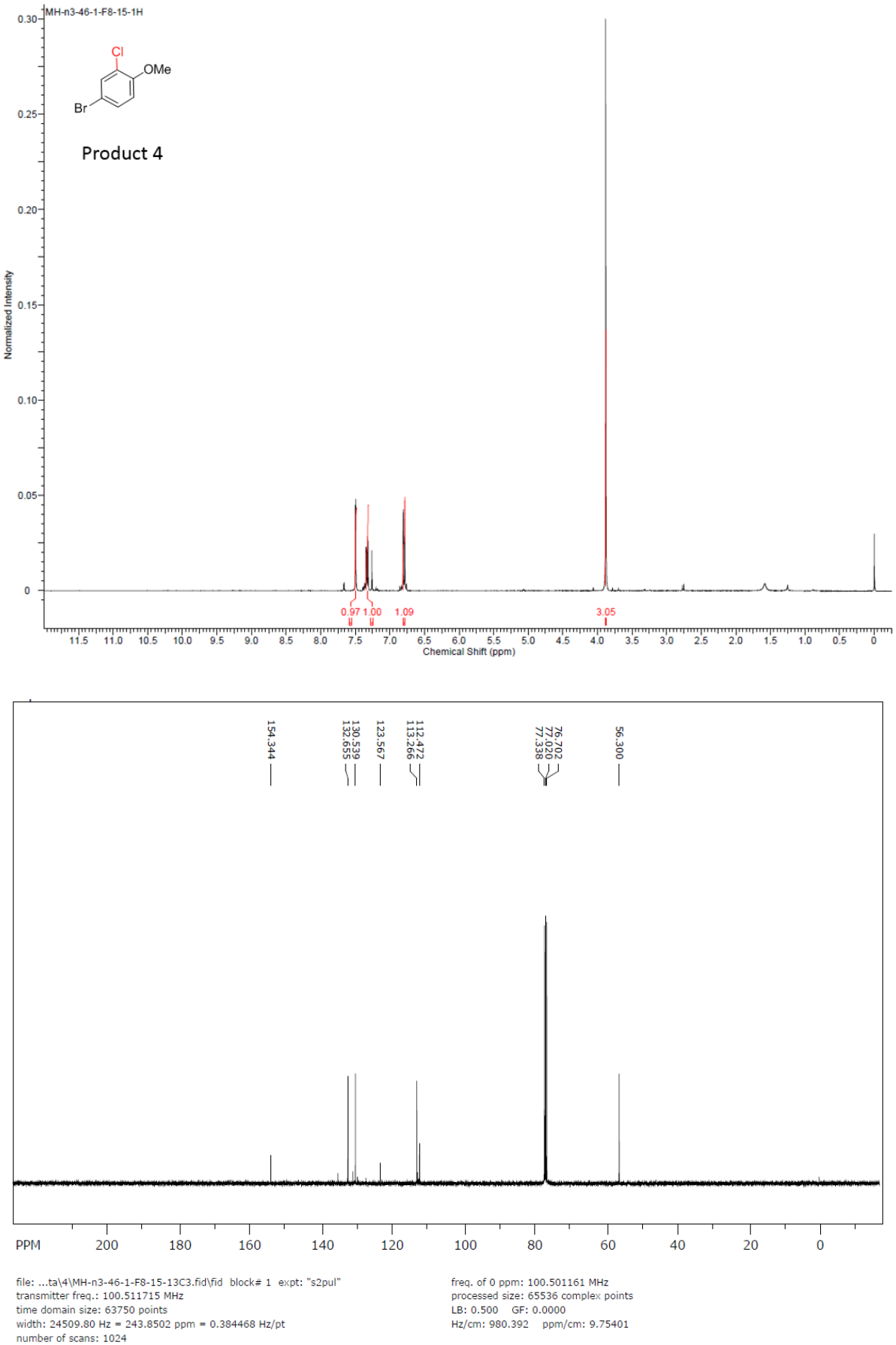


Figure S25. ^{1}H NMR and ^{13}C NMR of Product **4**.

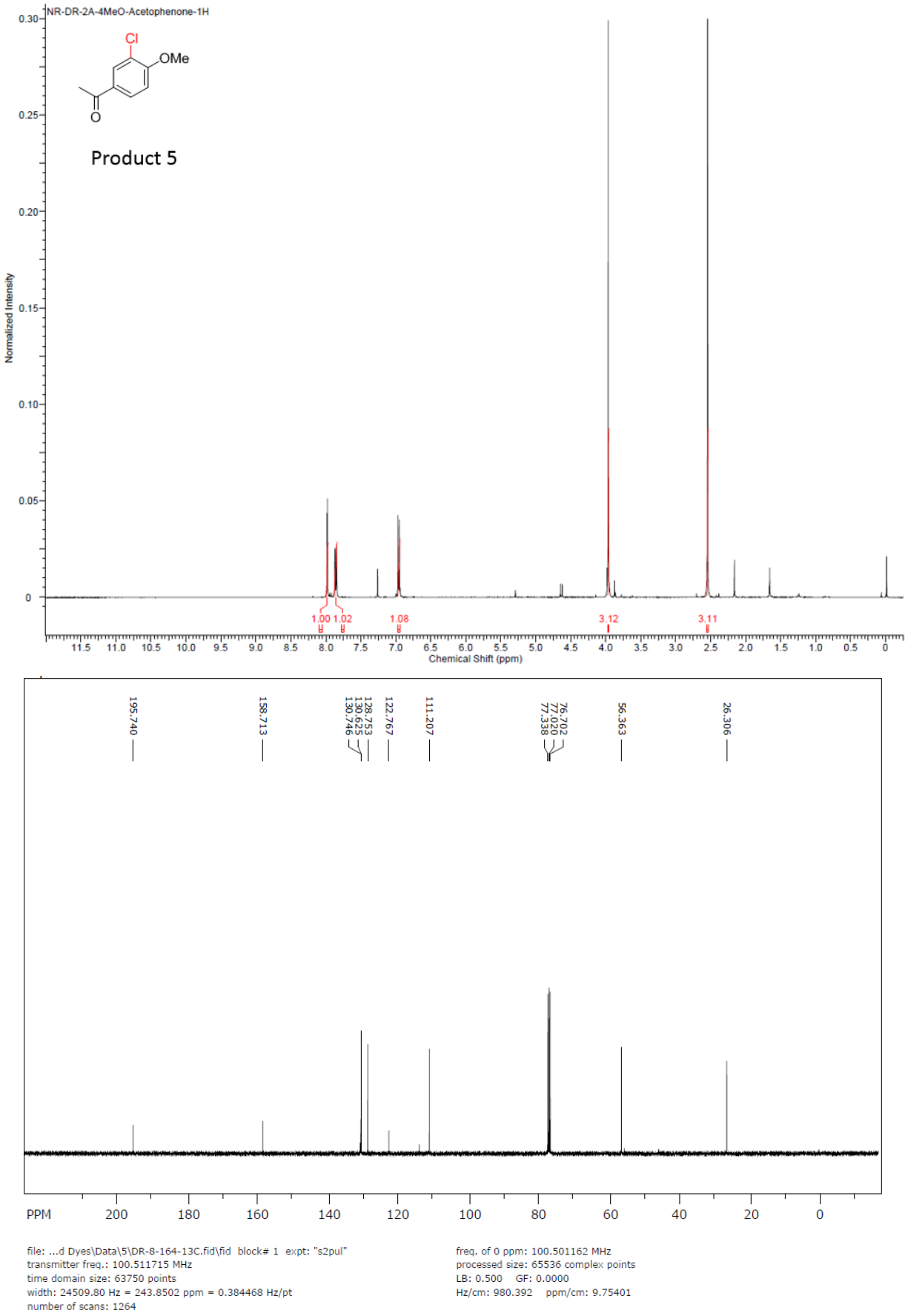


Figure S26. ^{1}H NMR and ^{13}C NMR of Product **5**.

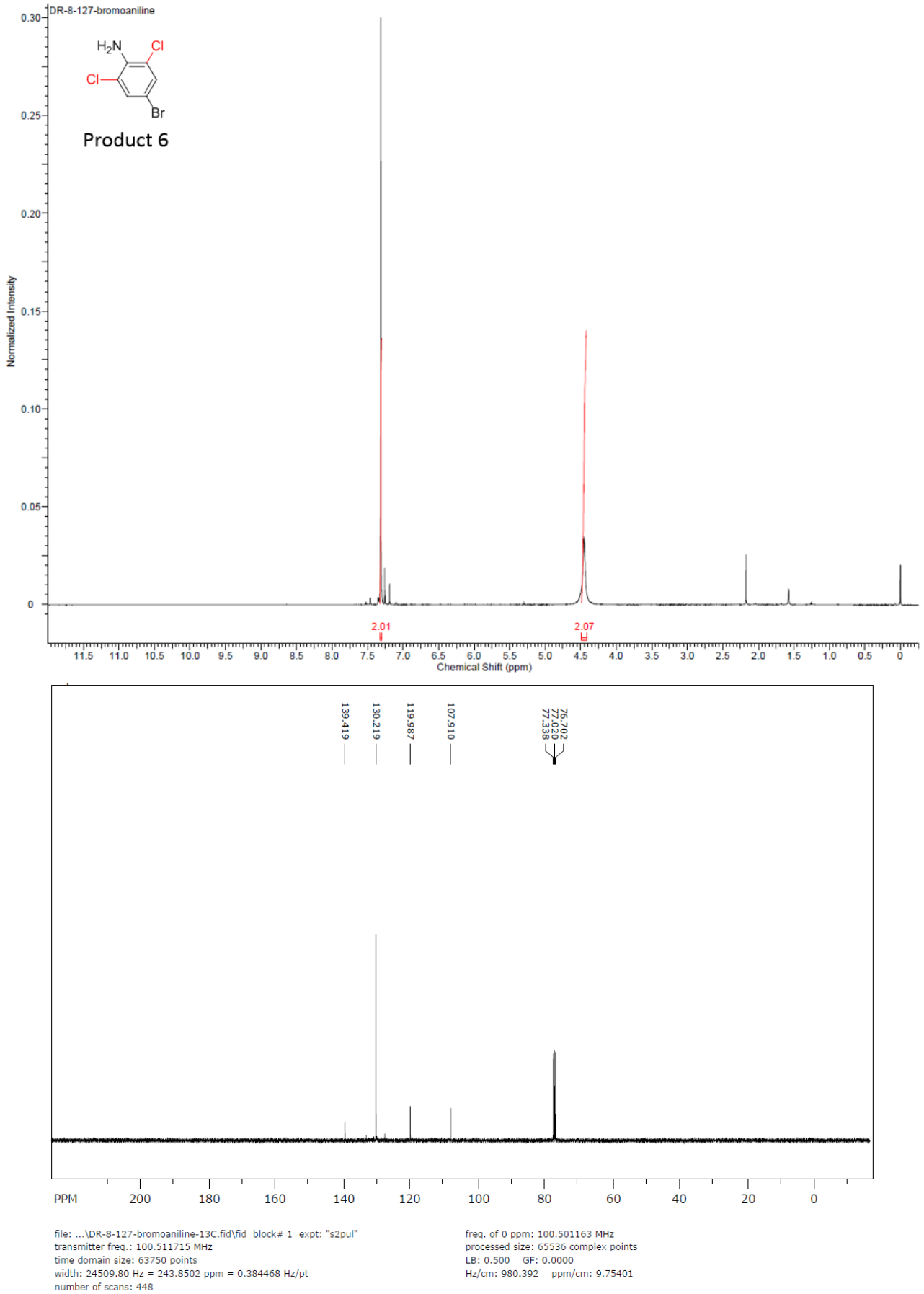


Figure S27. ^{1}H NMR and ^{13}C NMR of Product **6**.

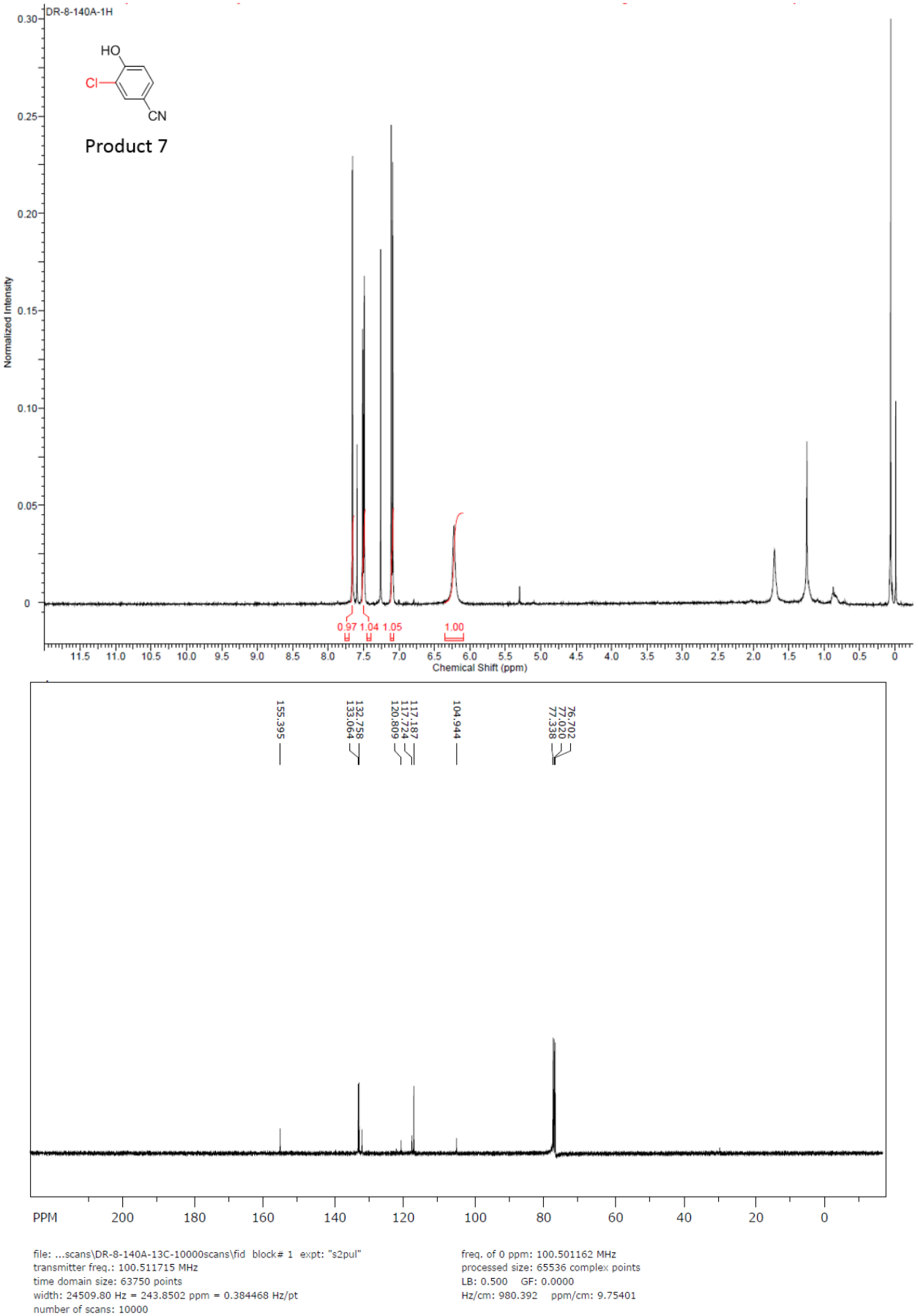


Figure S28. ^{1}H NMR and ^{13}C NMR of Product **7**.

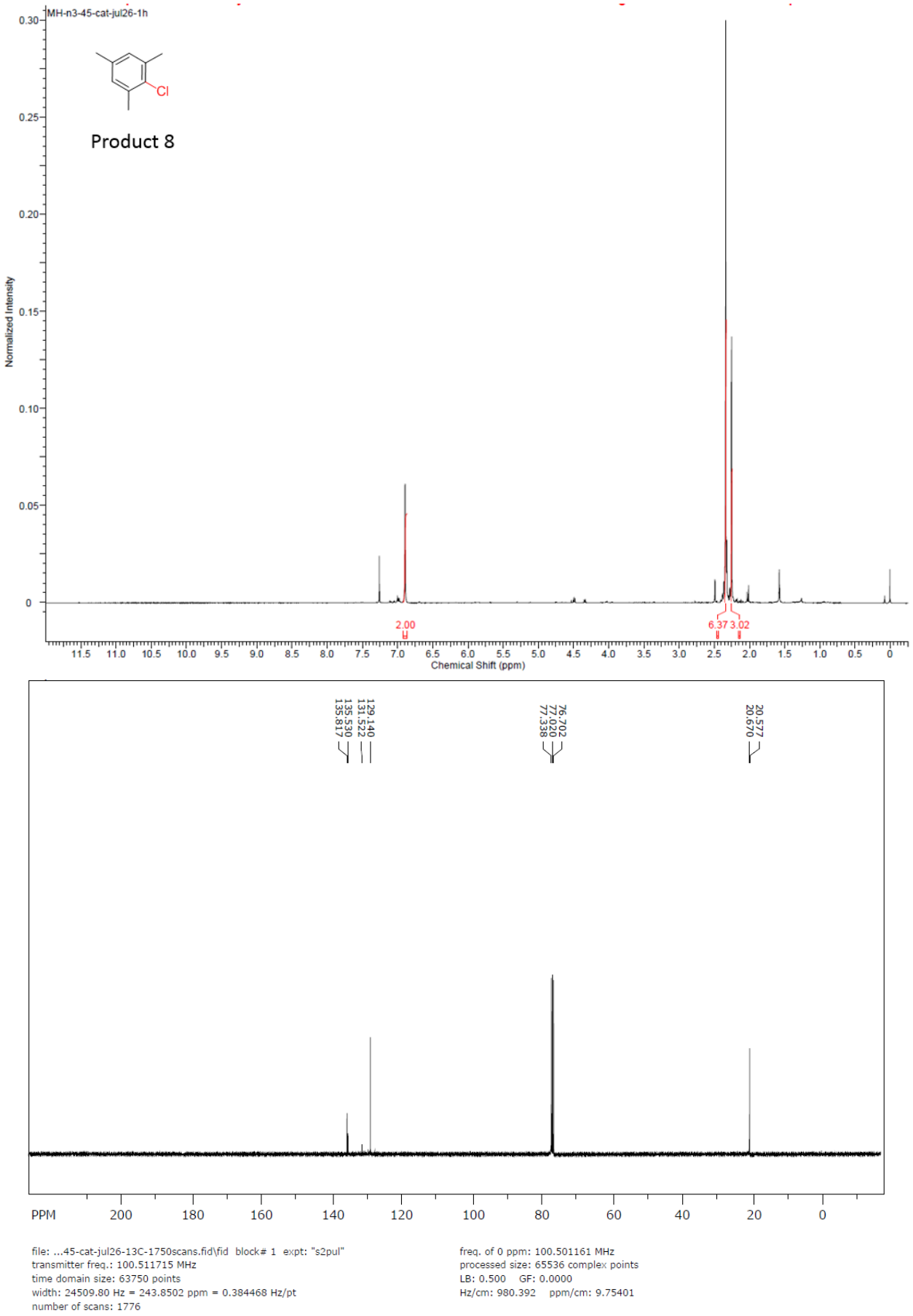


Figure S29. ^{1}H NMR and ^{13}C NMR of Product **8**.

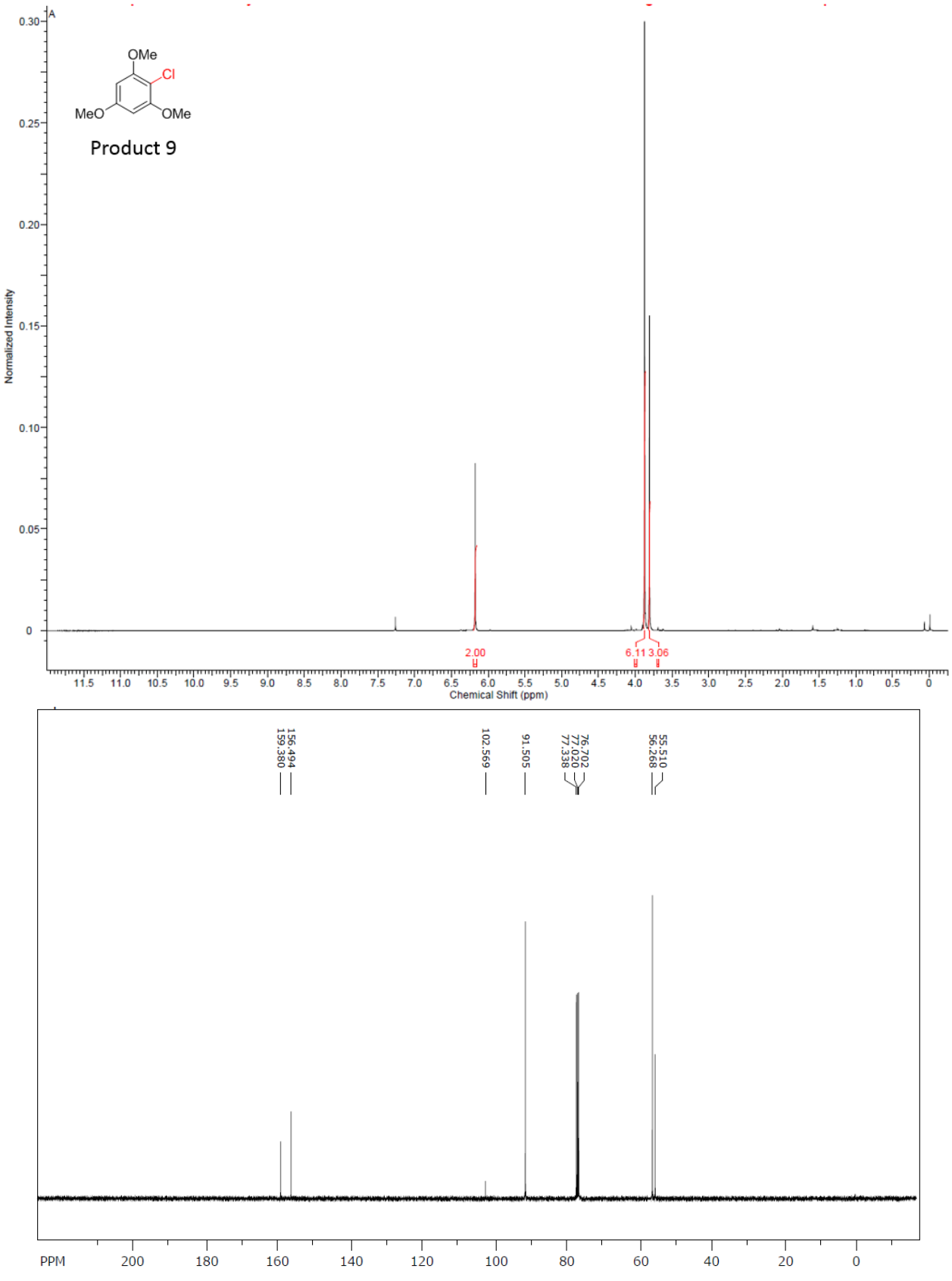


Figure S30. ^{1}H NMR and ^{13}C NMR of Product **9**.

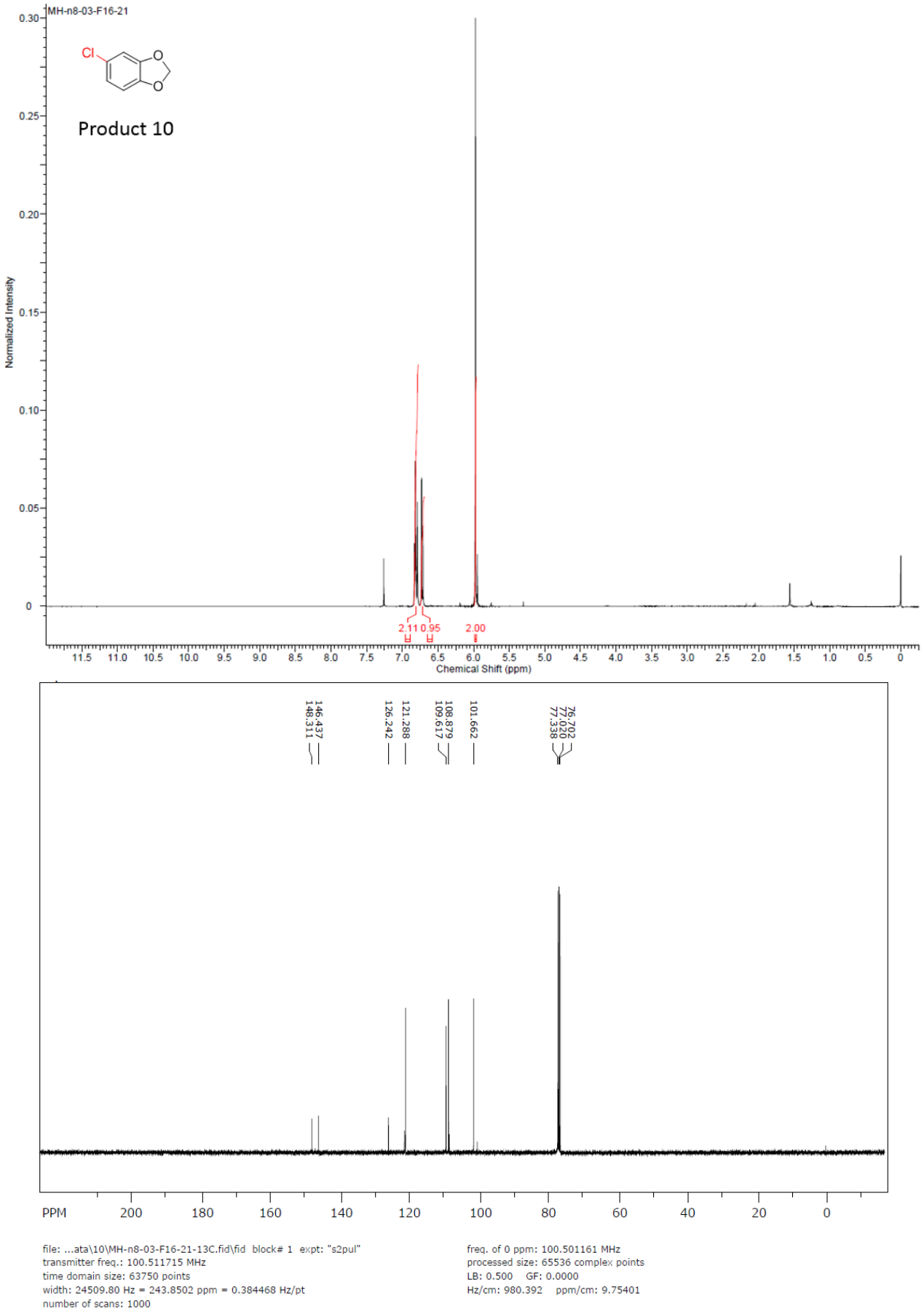


Figure S31. ^{1}H NMR and ^{13}C NMR of Product **10**.

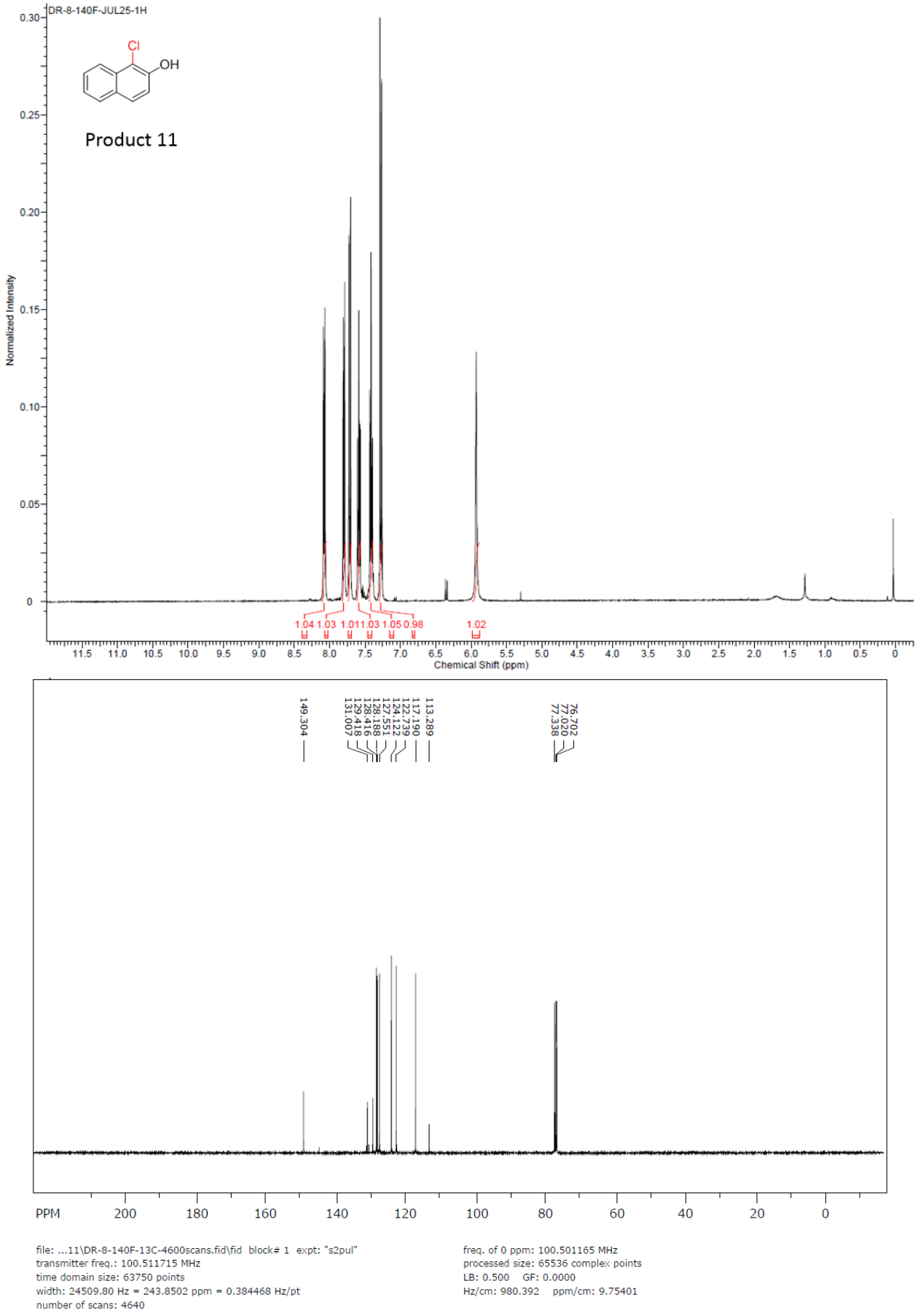


Figure S32. ^{1}H NMR and ^{13}C NMR of Product **11**.

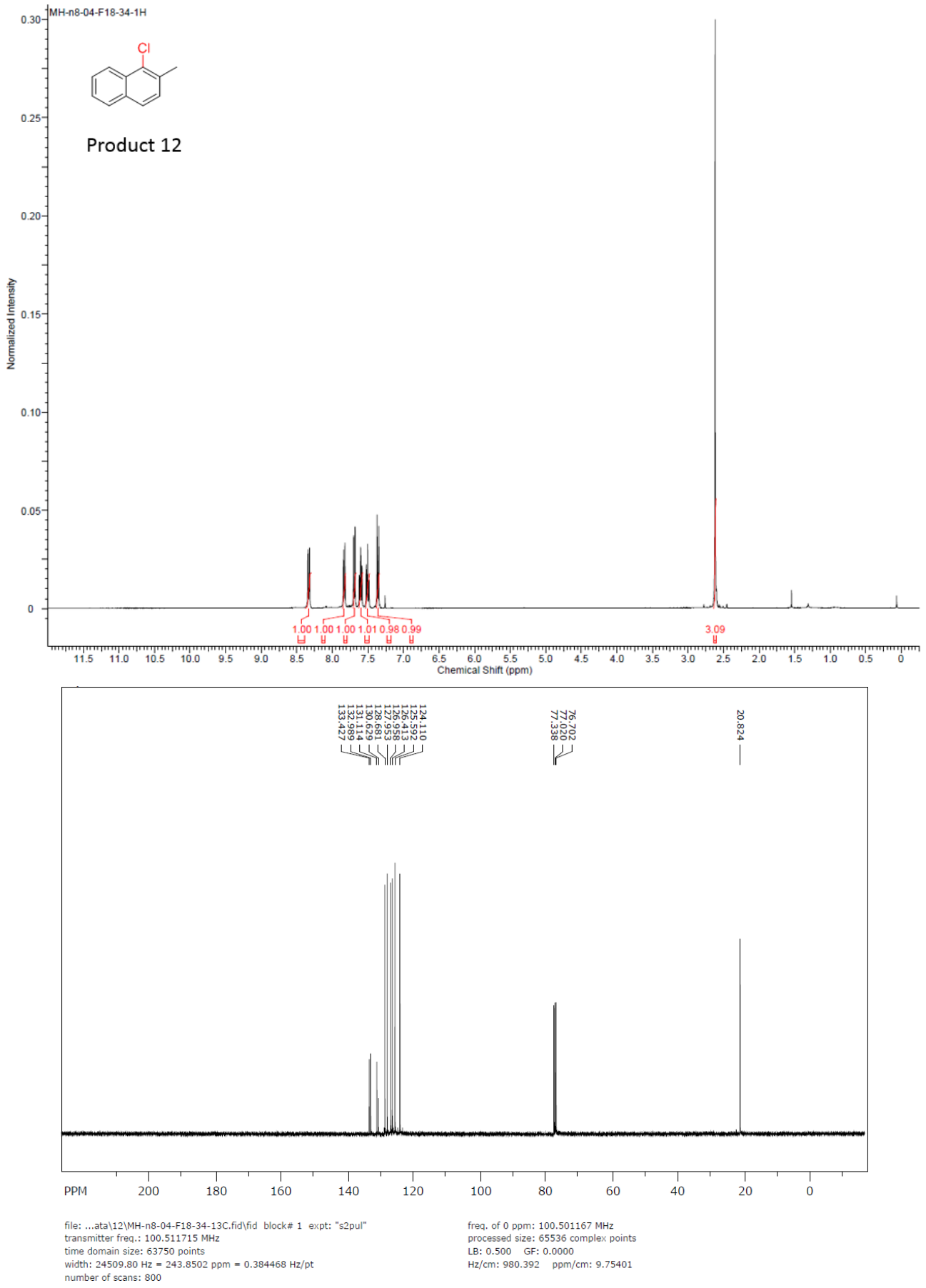


Figure S33. ^{1}H NMR and ^{13}C NMR of Product **12**.

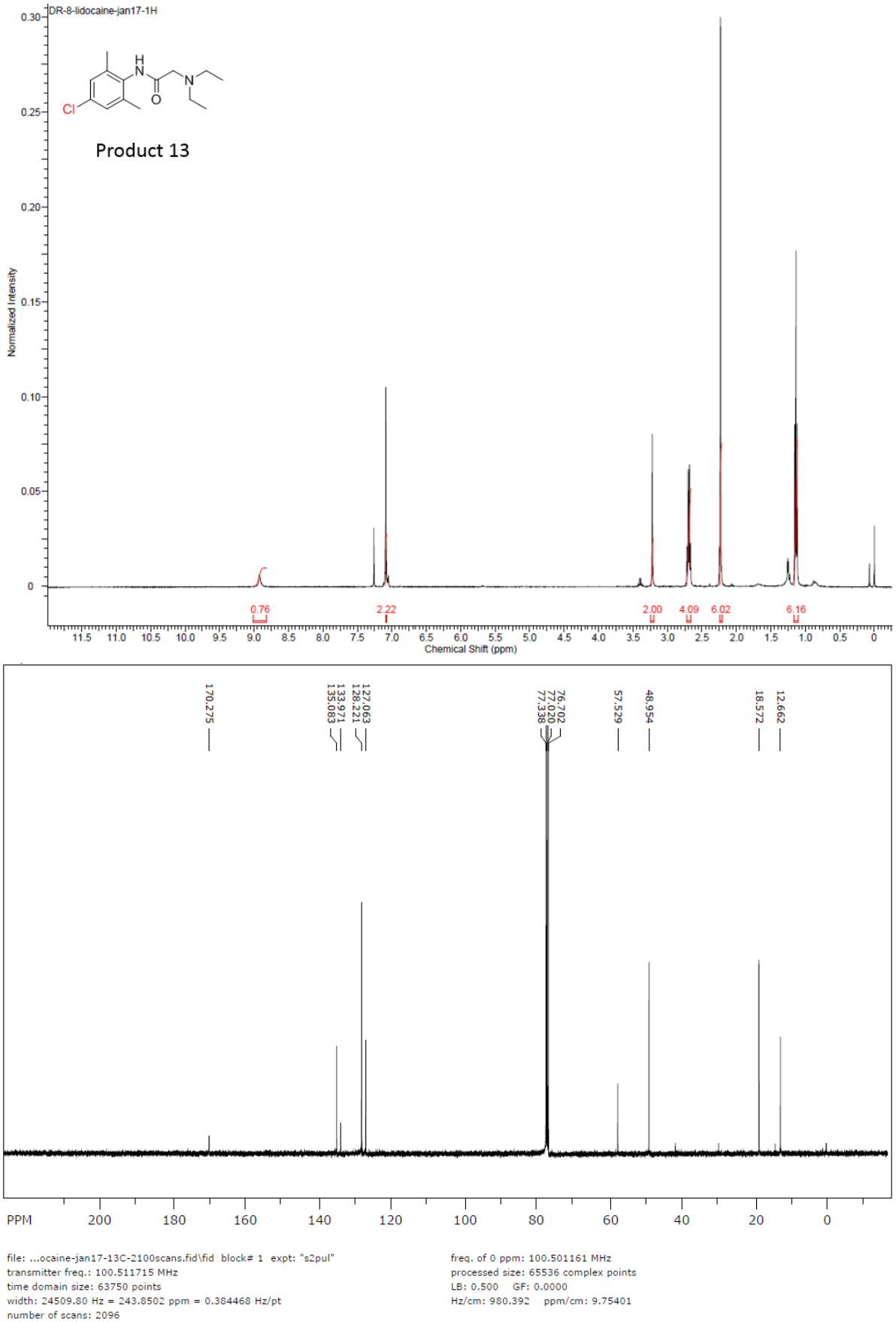


Figure S34. ^{1}H NMR and ^{13}C NMR of Product **13**.

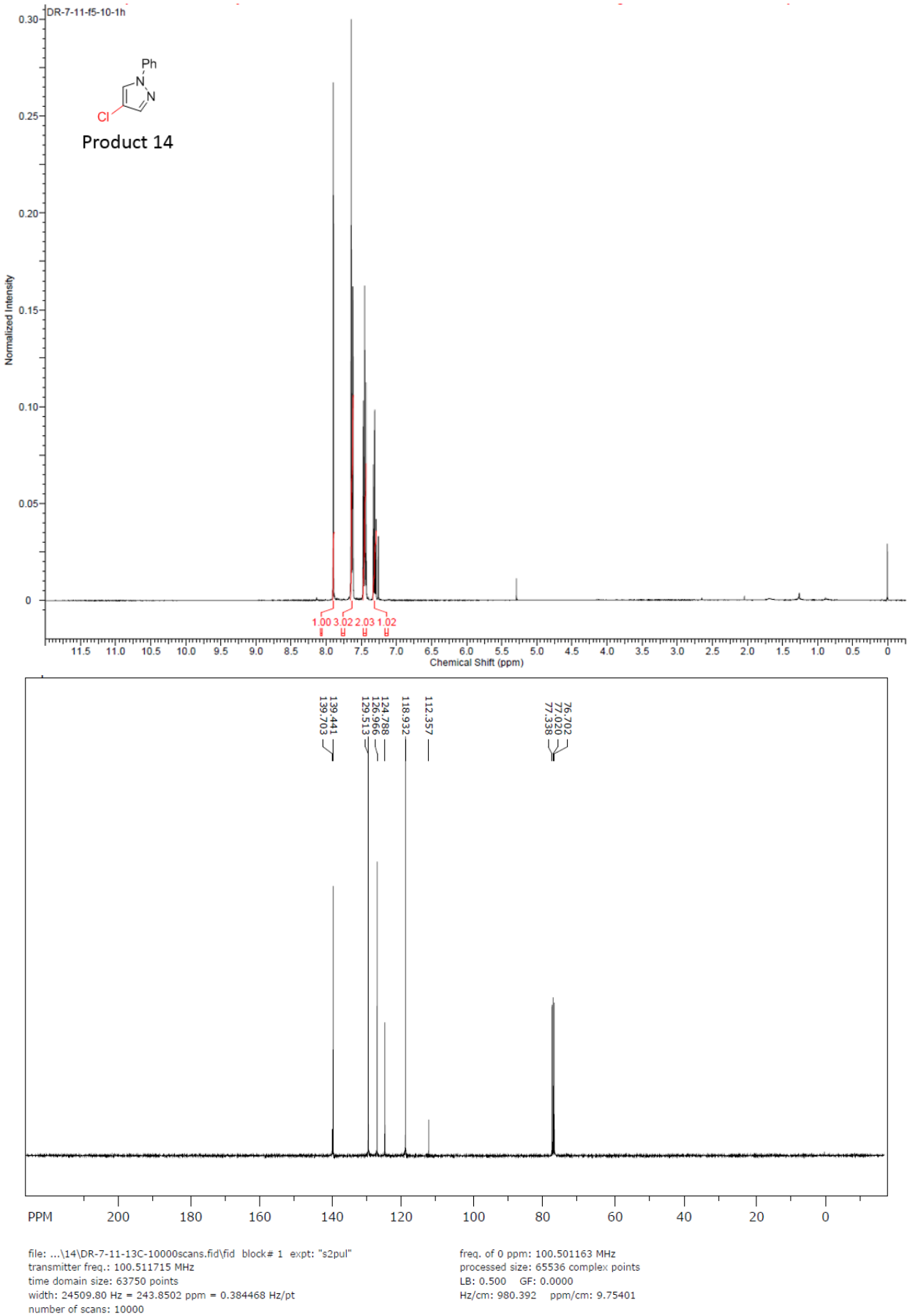


Figure S35. ^{1}H NMR and ^{13}C NMR of Product **14**.

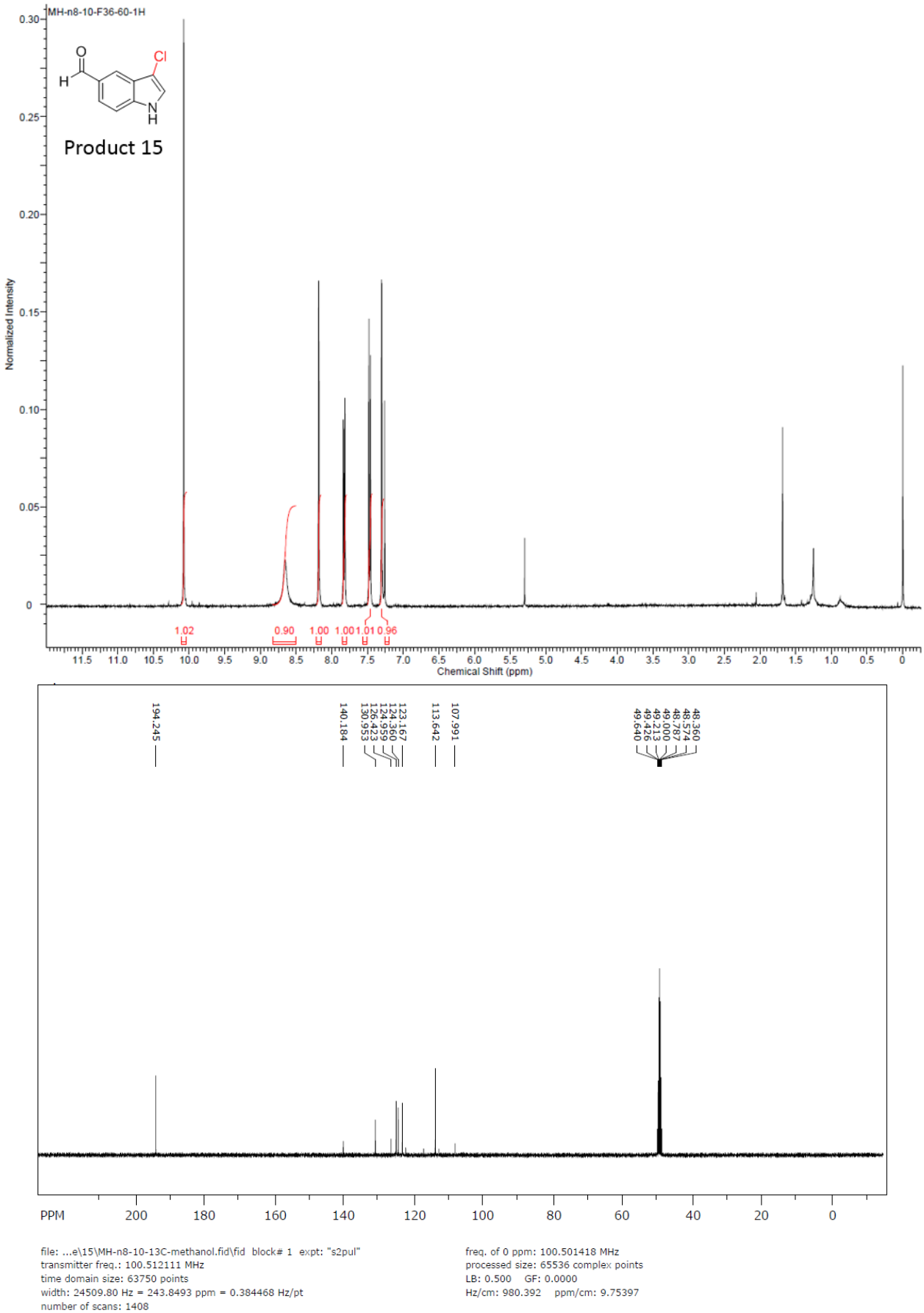


Figure S36. ^{1}H NMR and ^{13}C NMR of Product **15**.

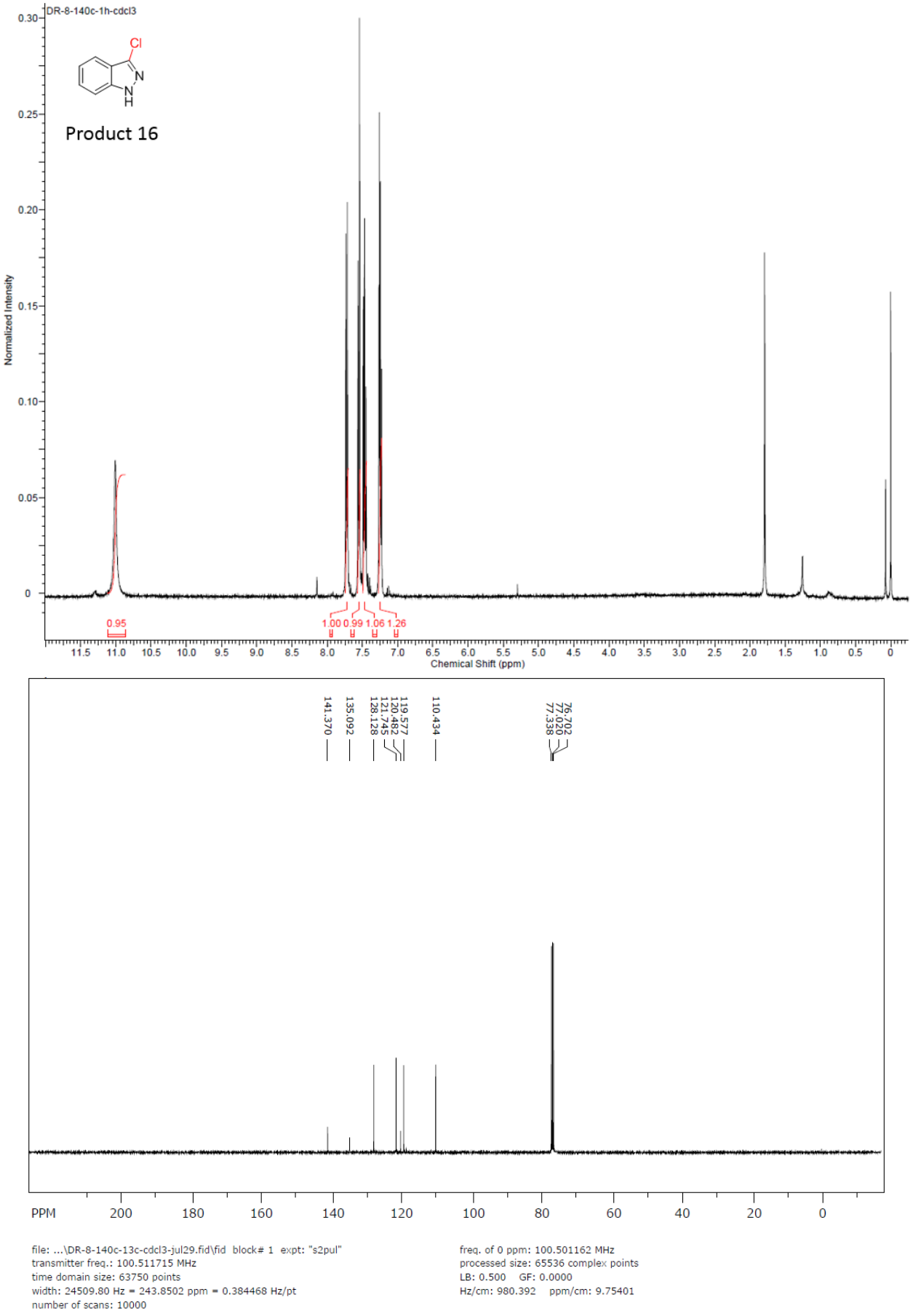


Figure S37. ^{1}H NMR and ^{13}C NMR of Product **16**.

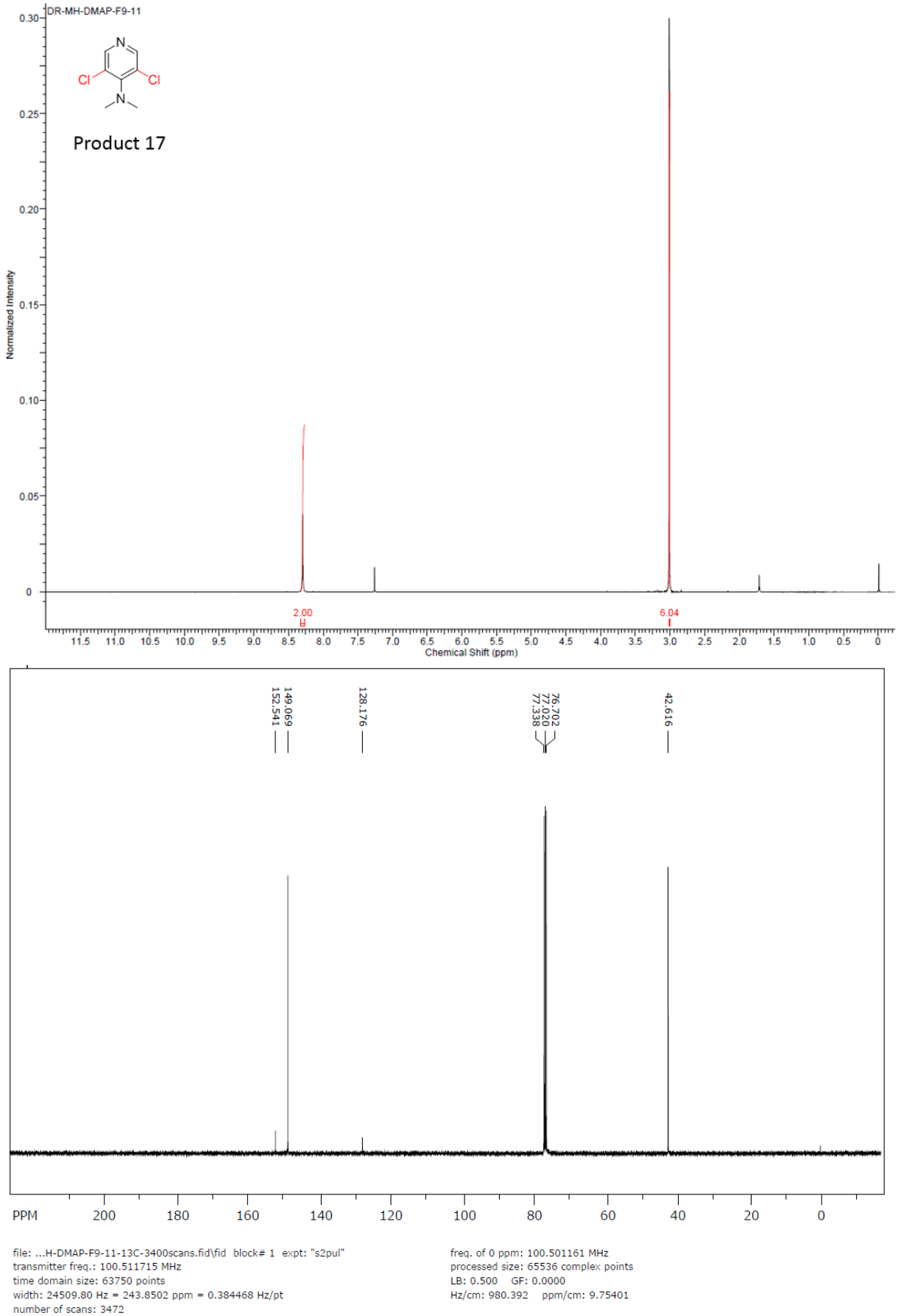


Figure S38. ^{1}H NMR and ^{13}C NMR of Product **17**.

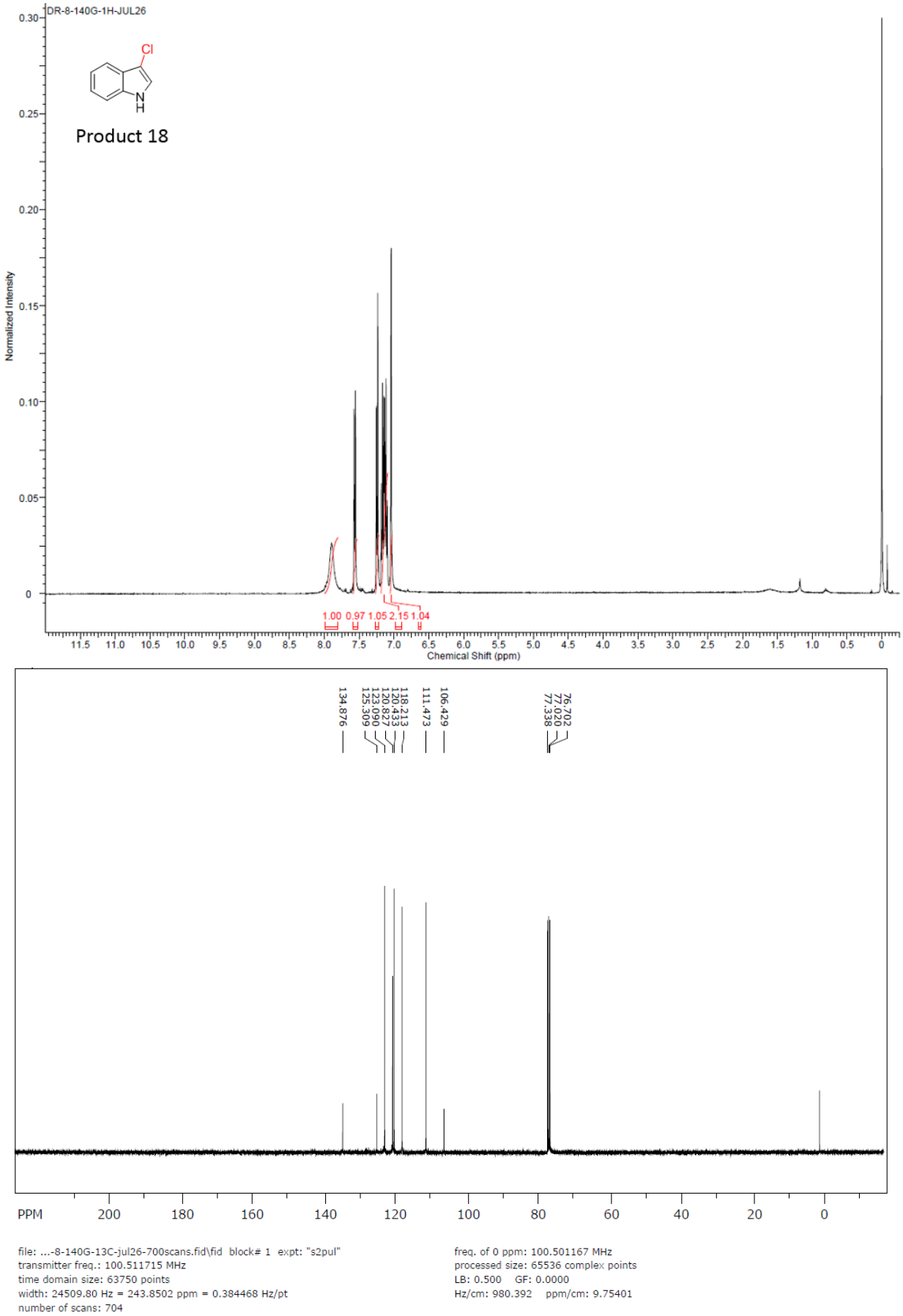


Figure S39. ^{1}H NMR and ^{13}C NMR of Product **18**.

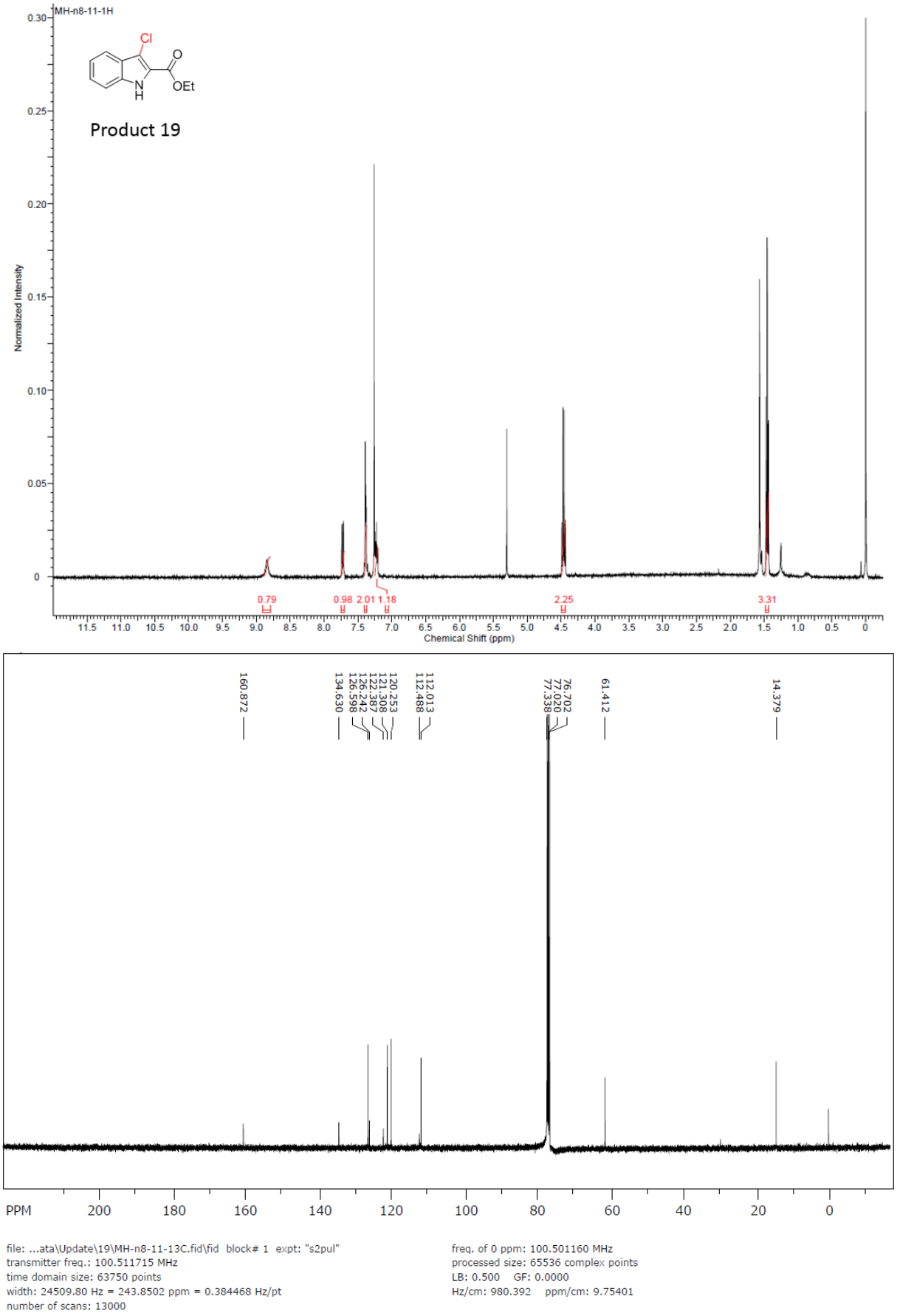


Figure S40. ^{1}H NMR and ^{13}C NMR of Product **19**.

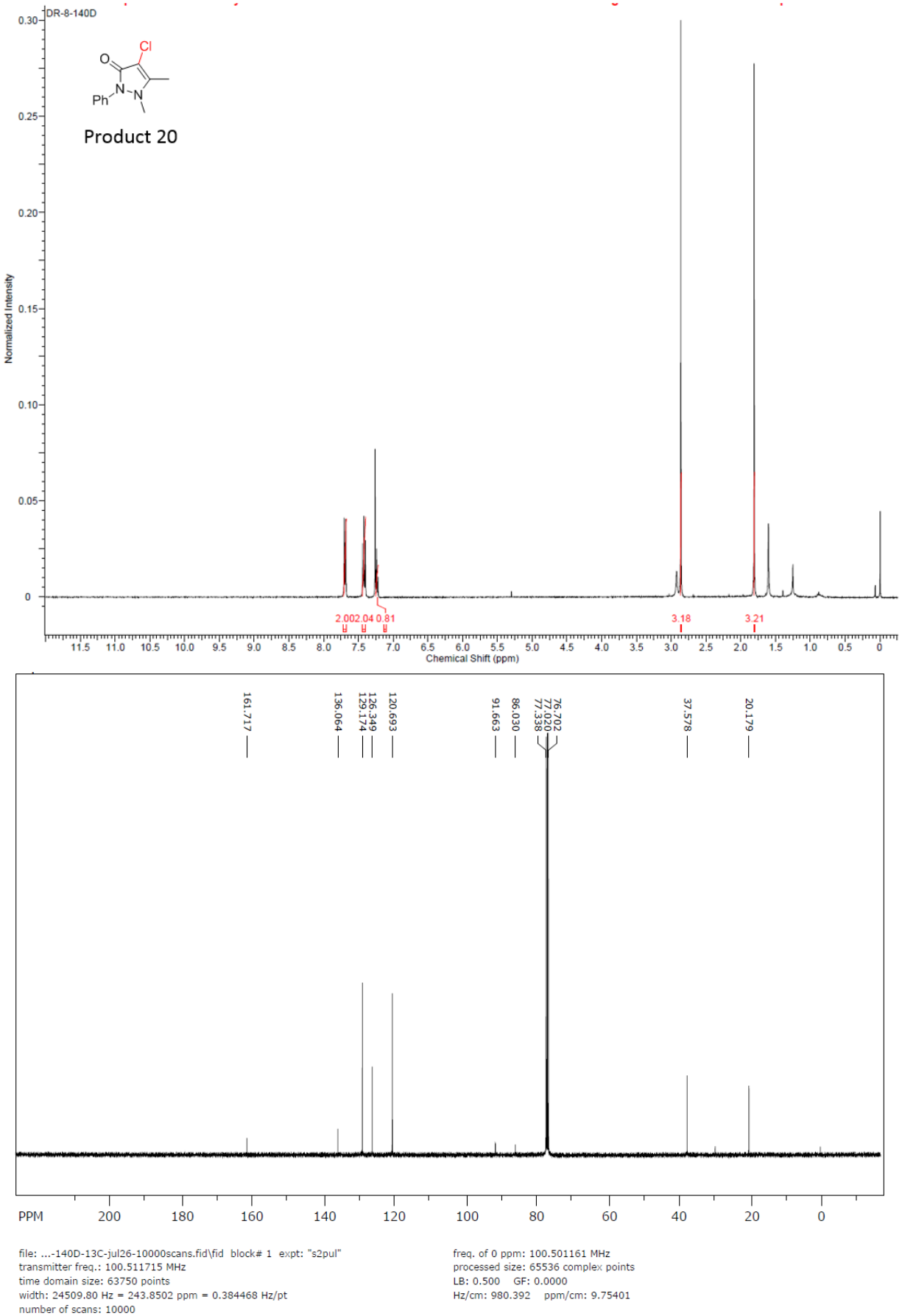


Figure S41. ^{1}H NMR and ^{13}C NMR of Product **20**.

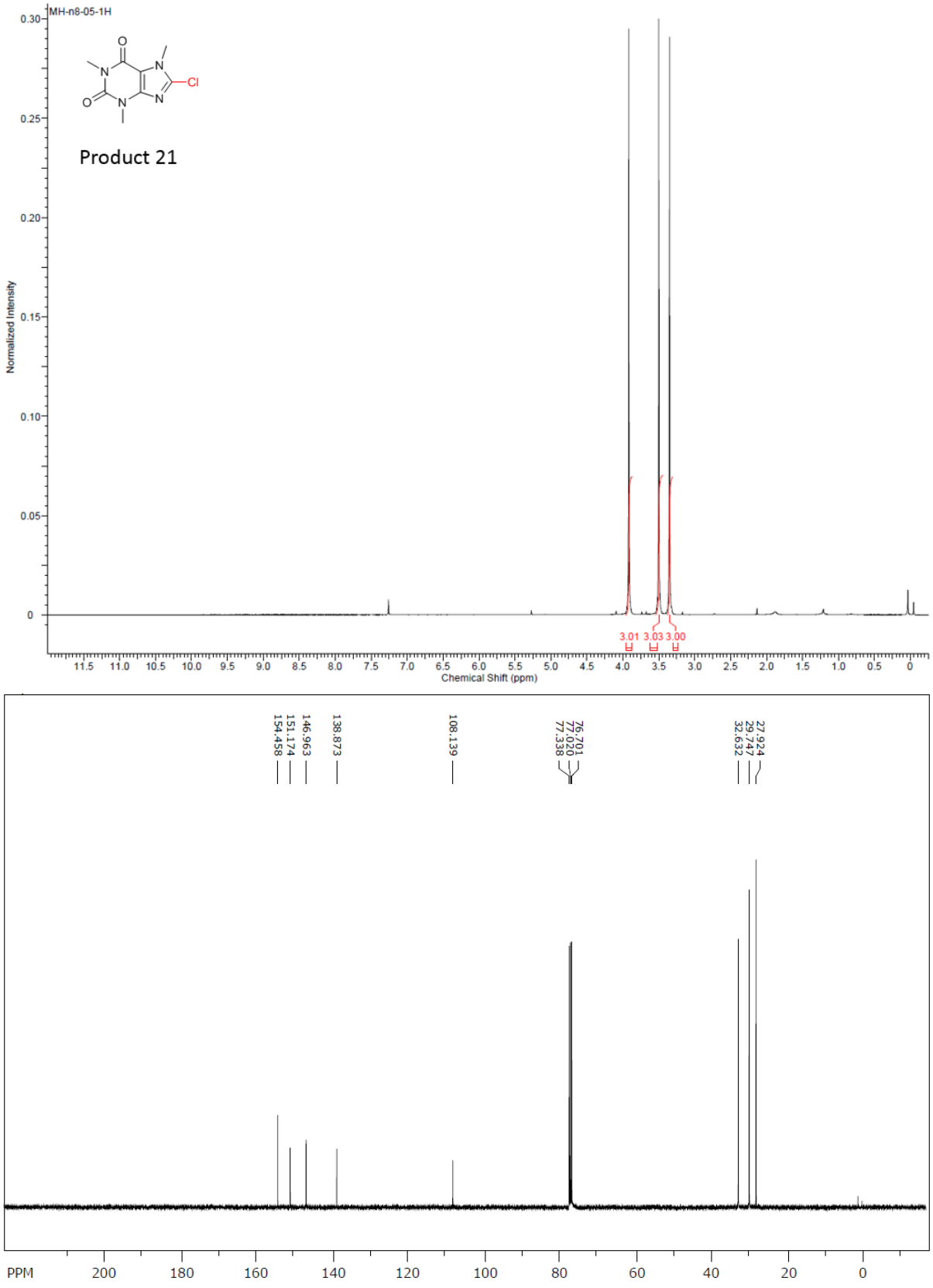


Figure S42. ^{1}H NMR and ^{13}C NMR of Product **21**.

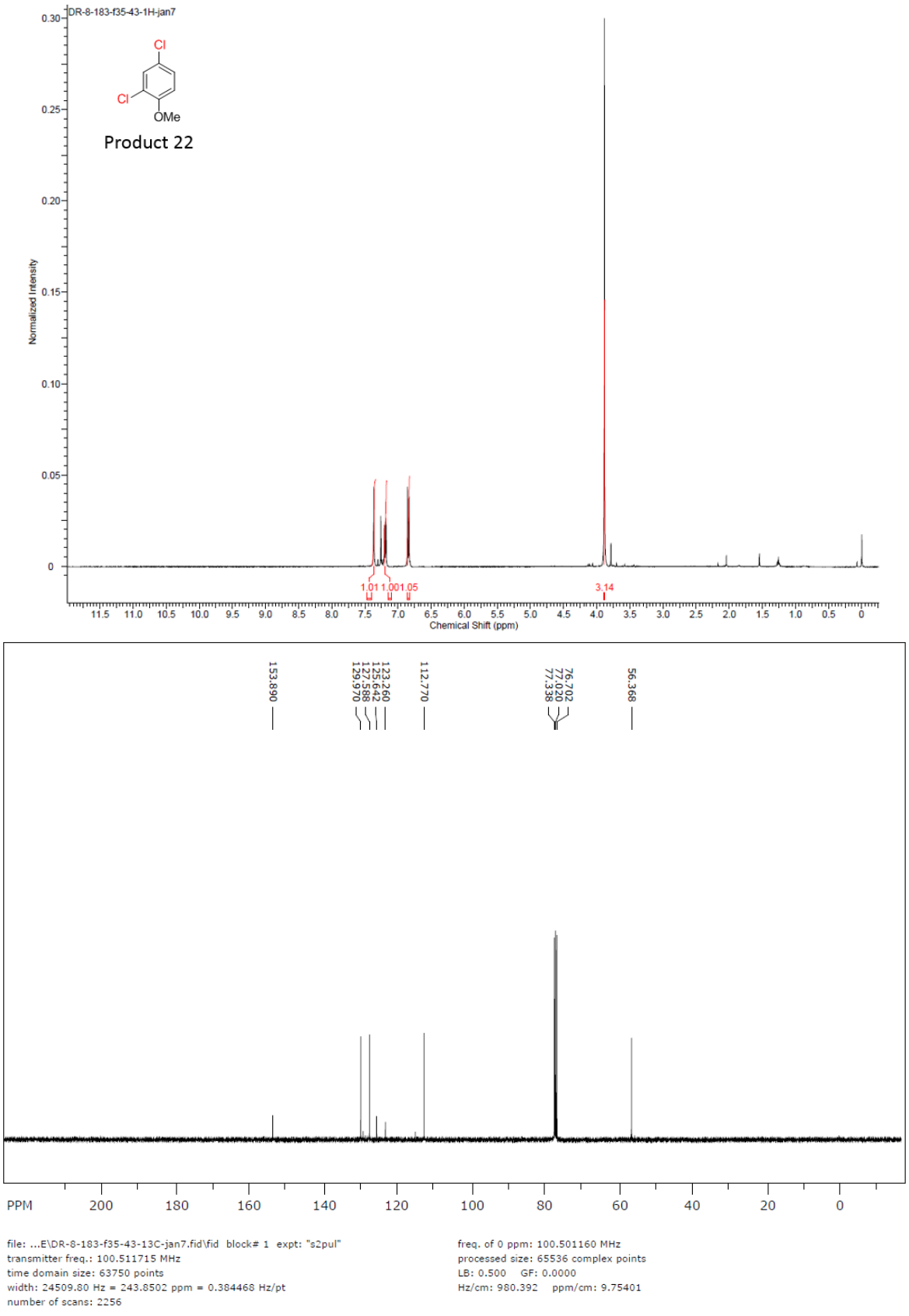


Figure S43. ^{1}H NMR and ^{13}C NMR of Product **22**.

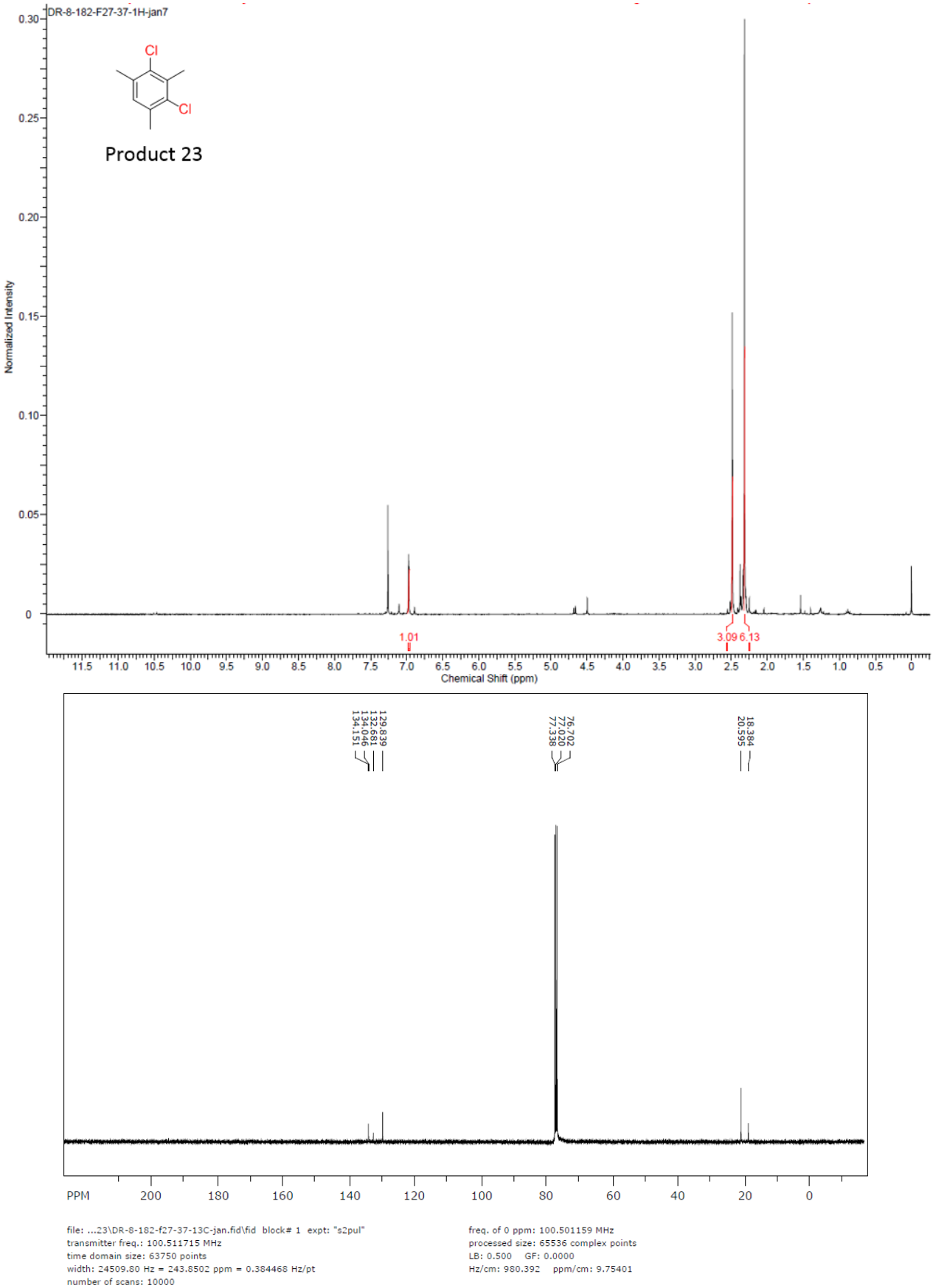
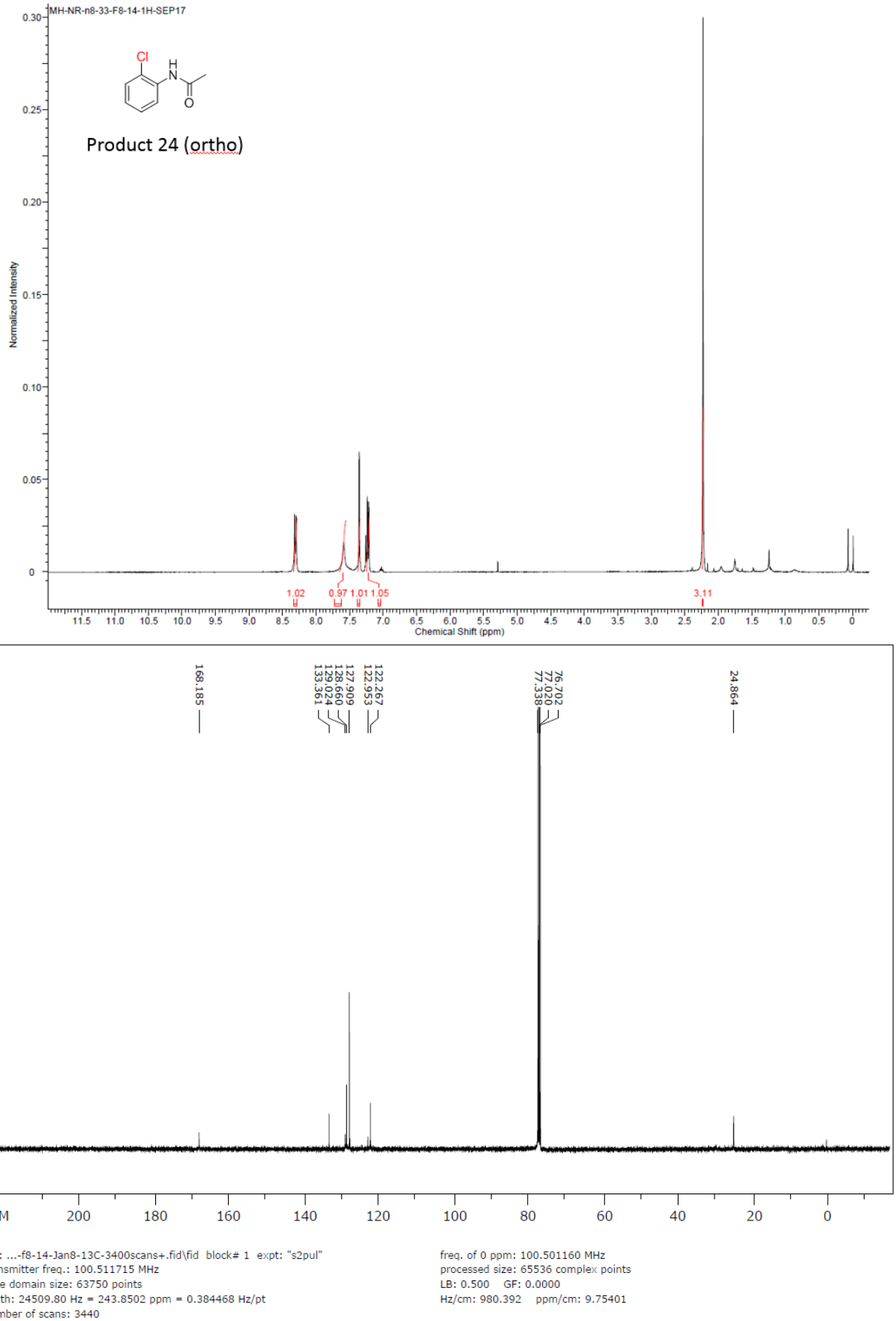


Figure S44. ^{1}H NMR and ^{13}C NMR of Product **23**.



file: ...-f8-14-Jan8-13C-3400scans+.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 100.511715 MHz
time domain size: 63750 points
width: 24509.80 Hz = 243.8502 ppm = 0.384468 Hz/pt
number of scans: 3440

freq. of 0 ppm: 100.501160 MHz
processed size: 65536 complex points
LB: 0.500 GF: 0.0000
Hz/cm: 980.392 ppm/cm: 9.75401

Figure S45. ^{1}H NMR and ^{13}C NMR of Product **24** (ortho).

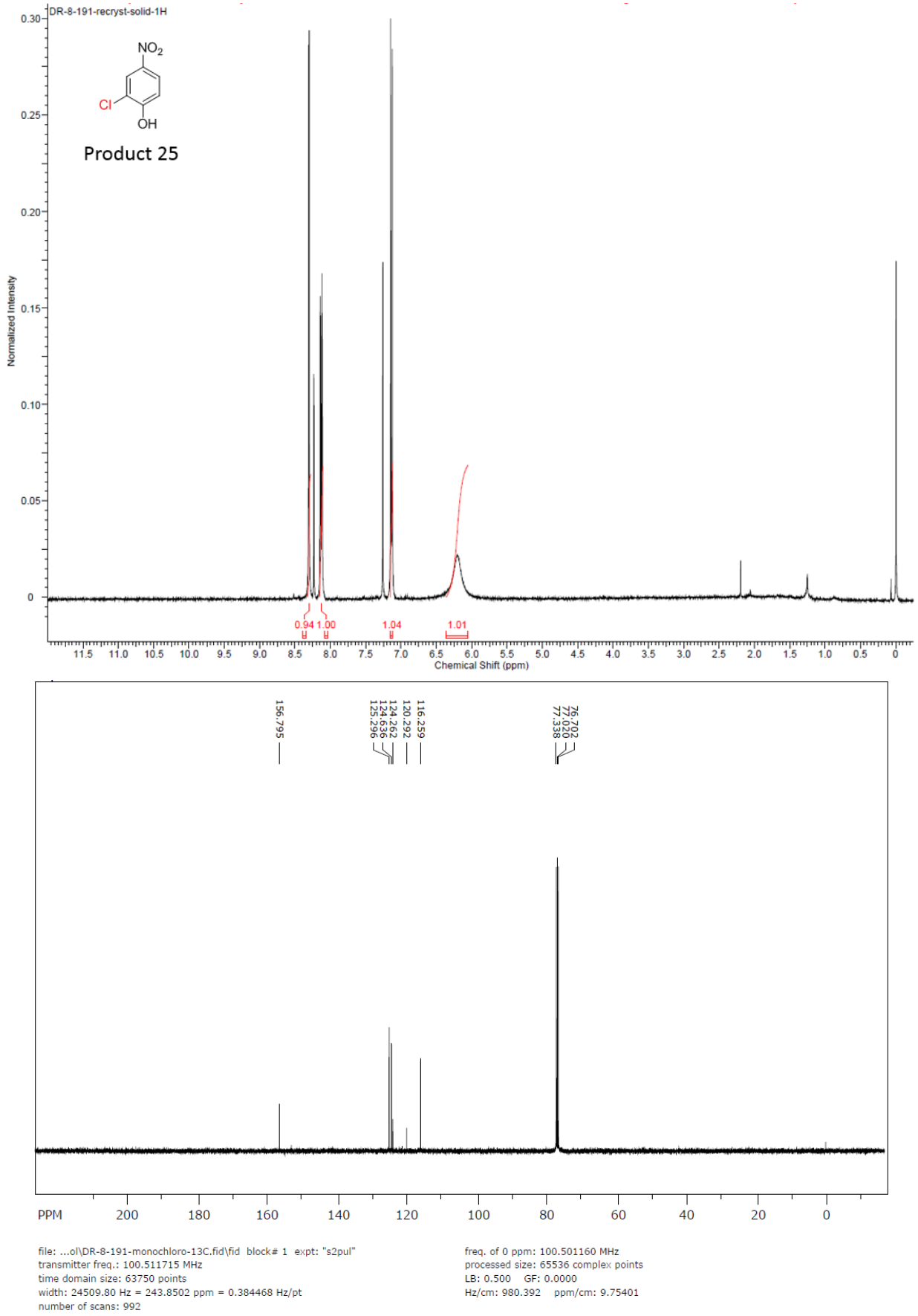


Figure S46. ^{1}H NMR and ^{13}C NMR of Product **25**.

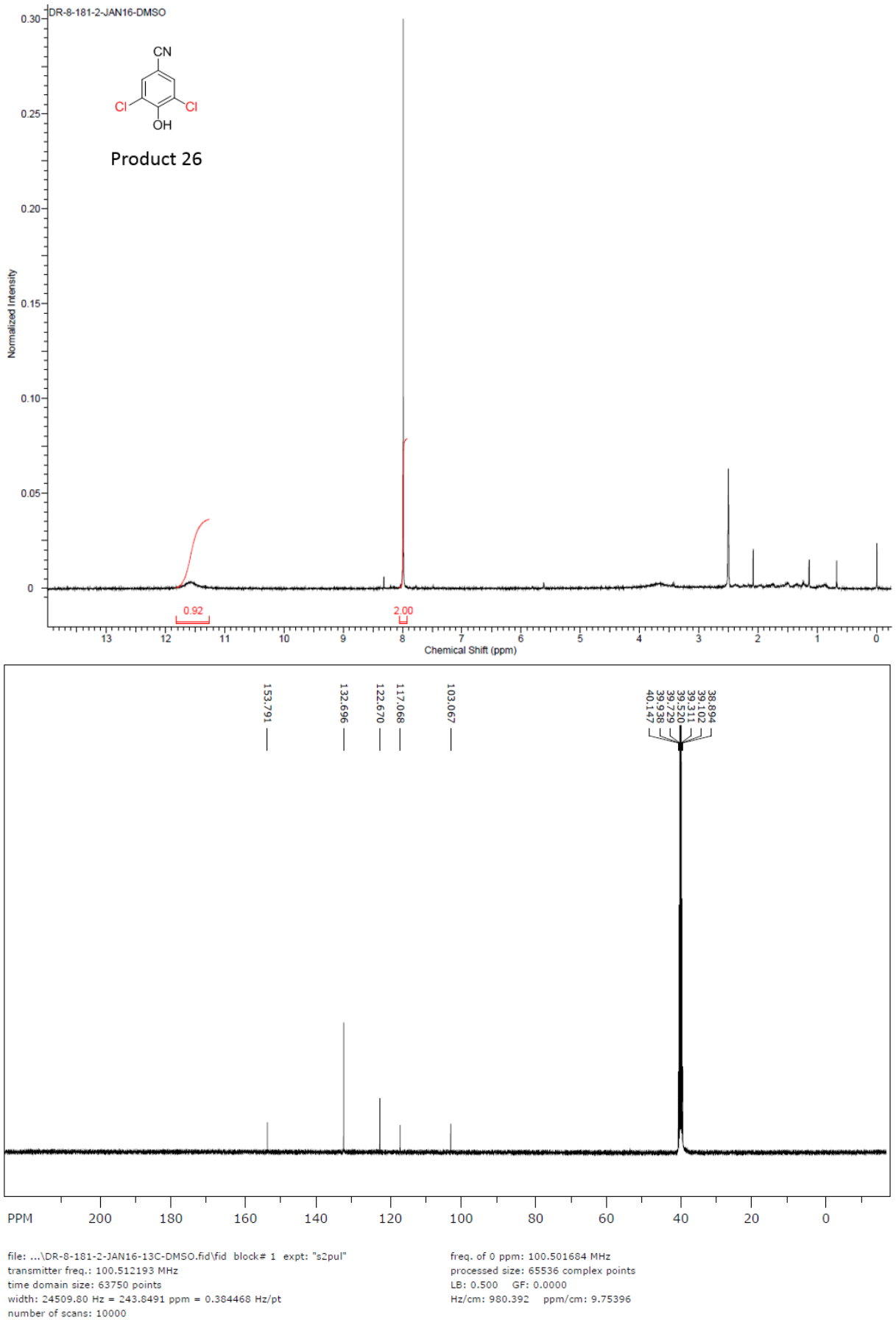


Figure S47. ^{1}H NMR and ^{13}C NMR of Product **26**.

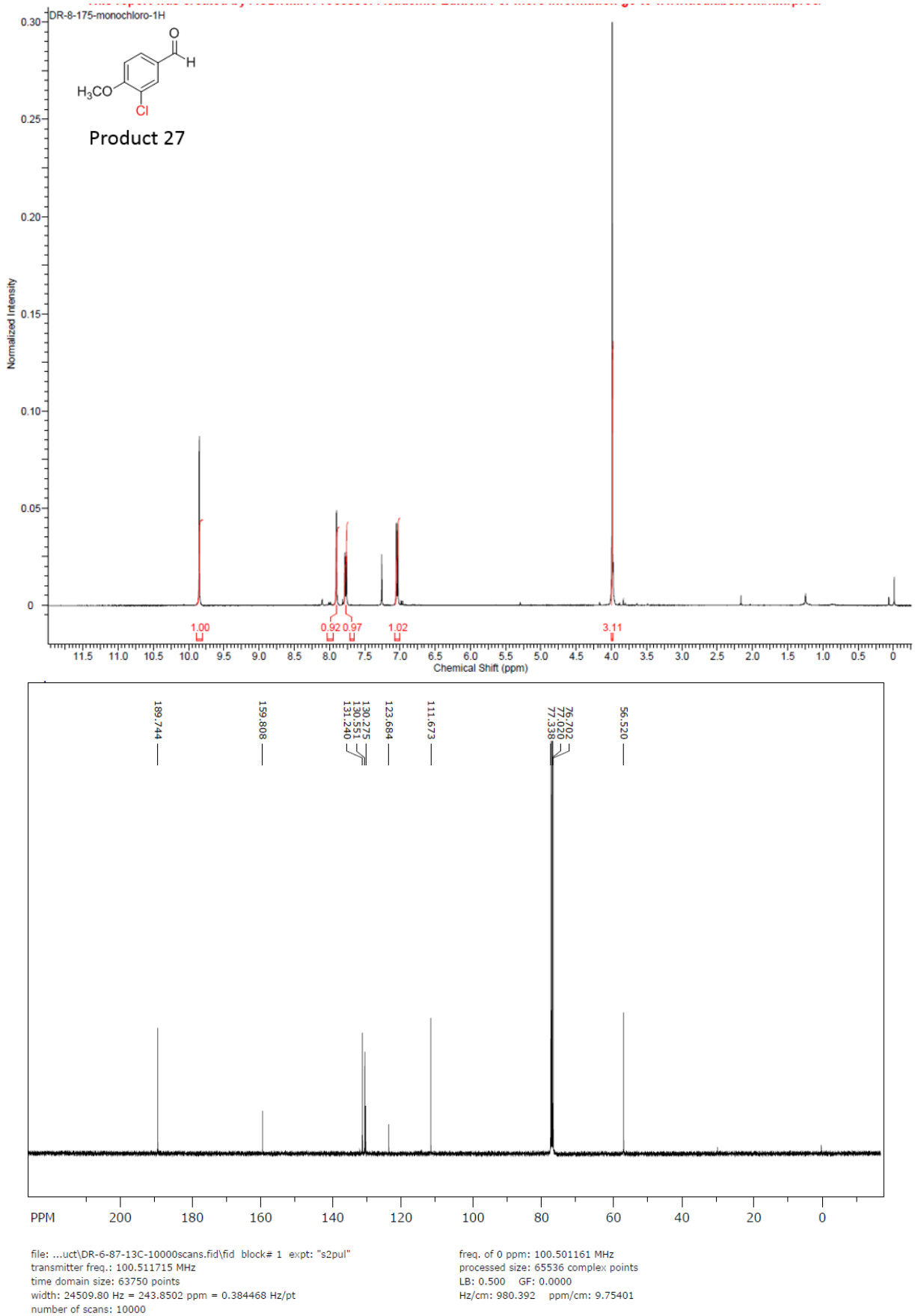


Figure S48. ^{1}H NMR and ^{13}C NMR of Product **27**.

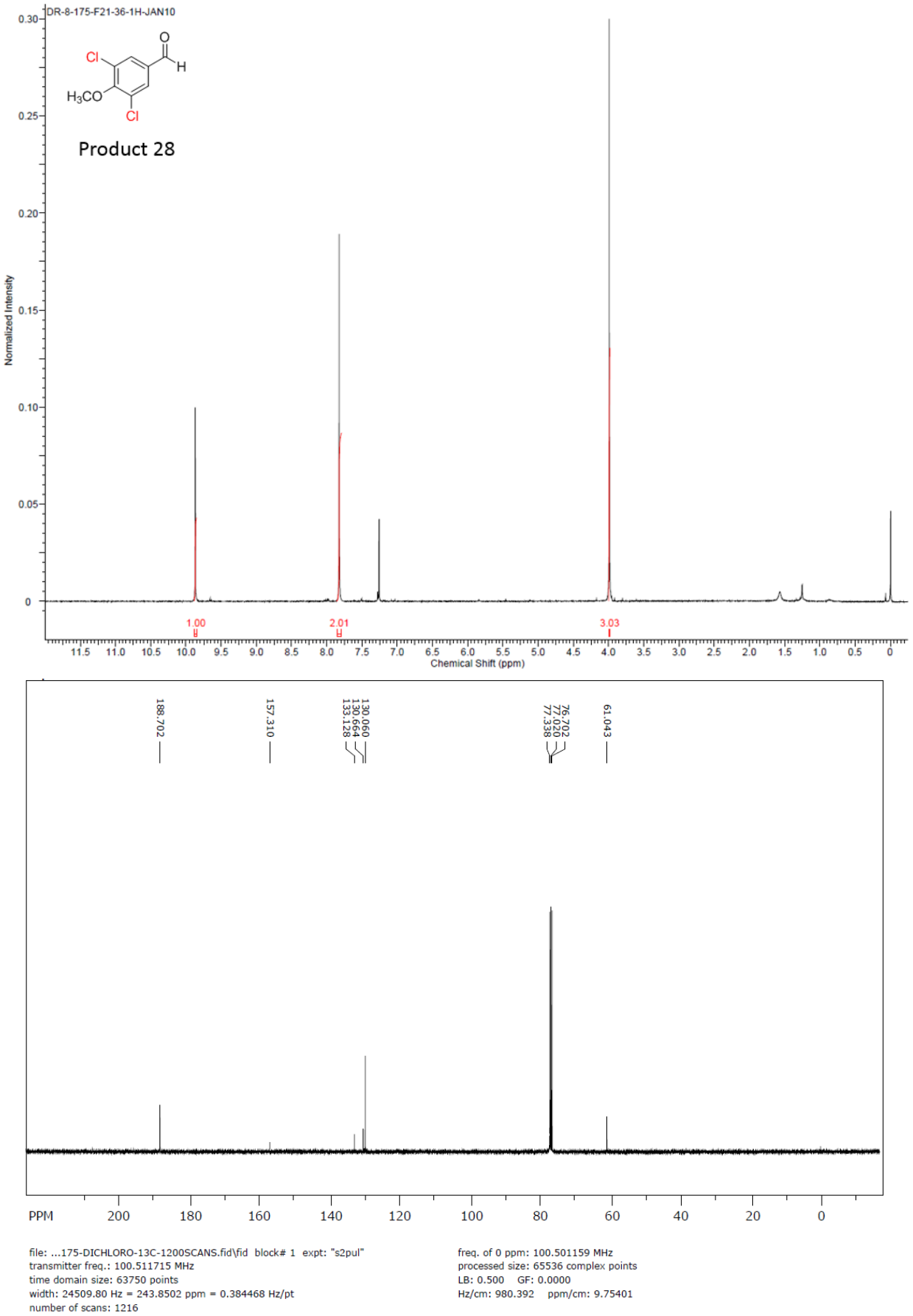


Figure S49. ^{1}H NMR and ^{13}C NMR of Product **28**.

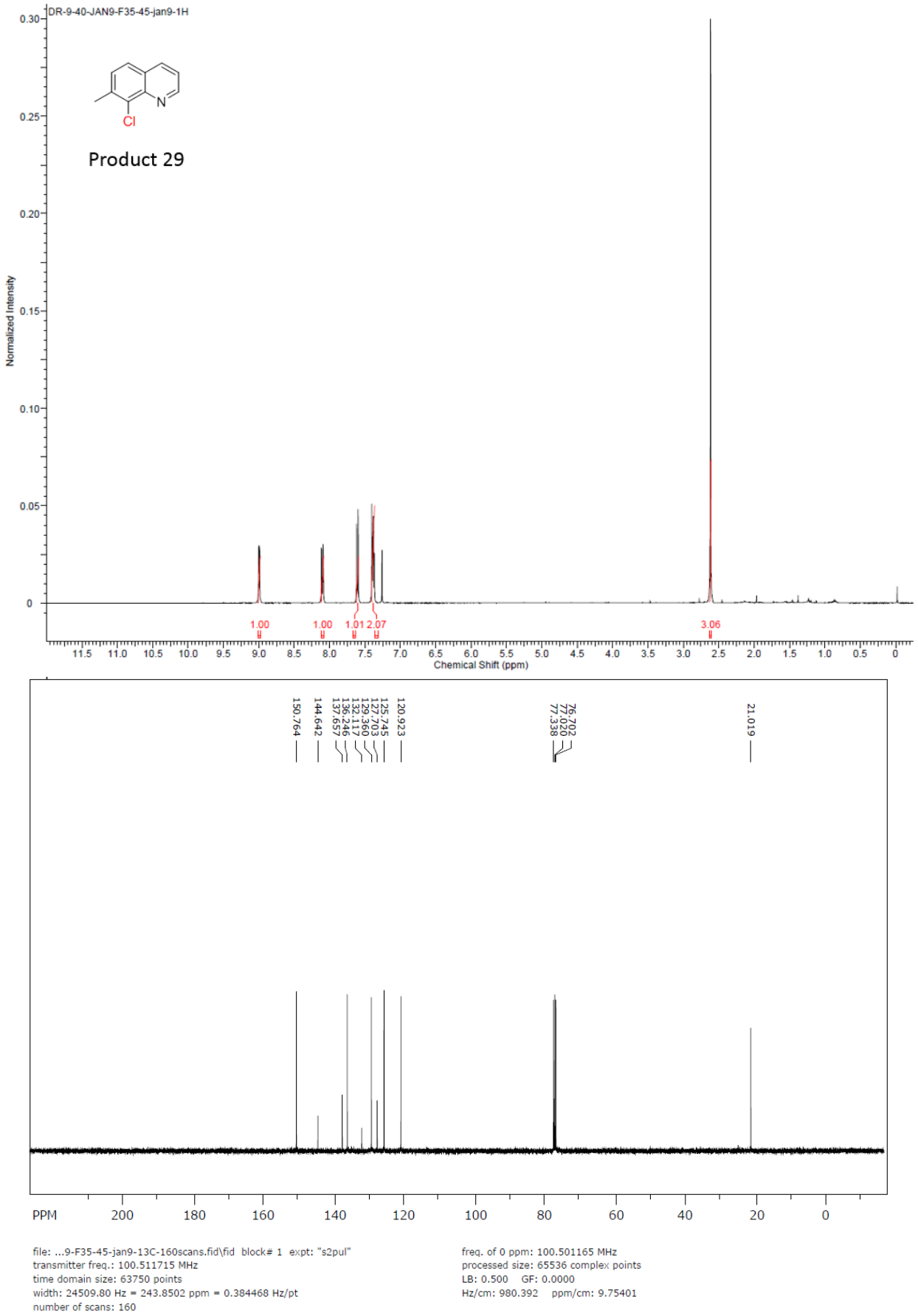


Figure S50. ^{1}H NMR and ^{13}C NMR of Product **29**.

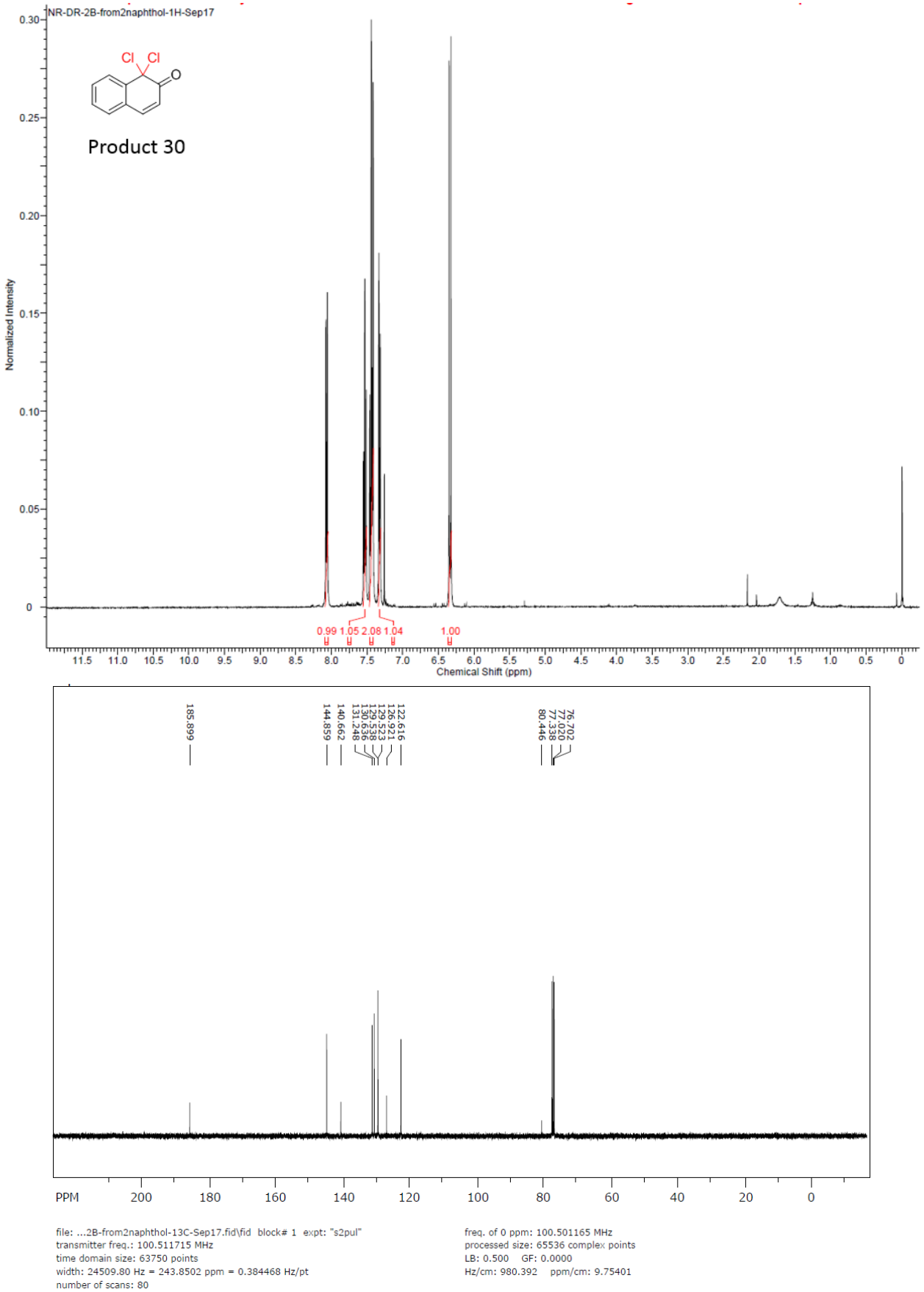


Figure S51. ^{1}H NMR and ^{13}C NMR of Product **30**.

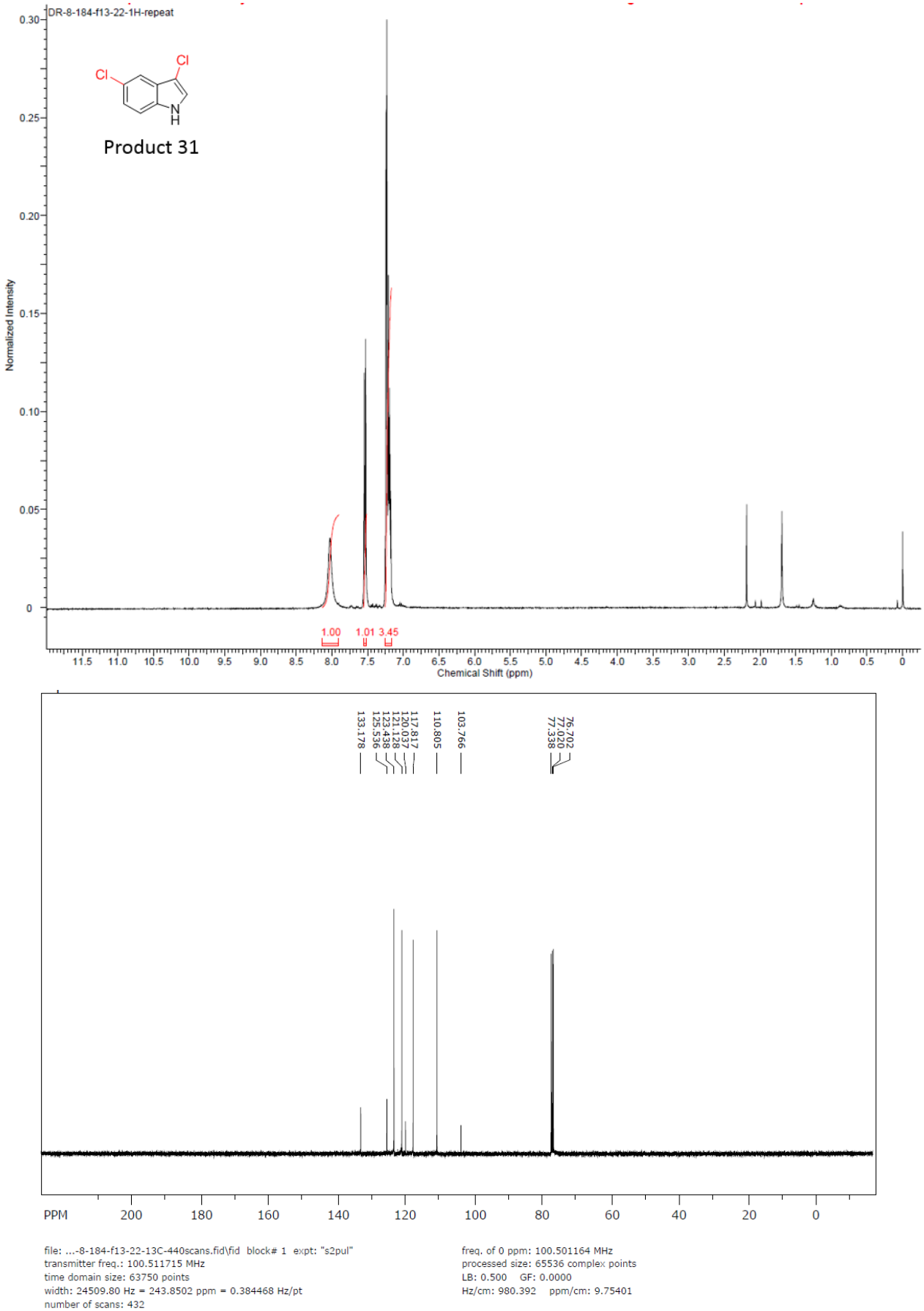


Figure S52. ^{1}H NMR and ^{13}C NMR of Product **31**.

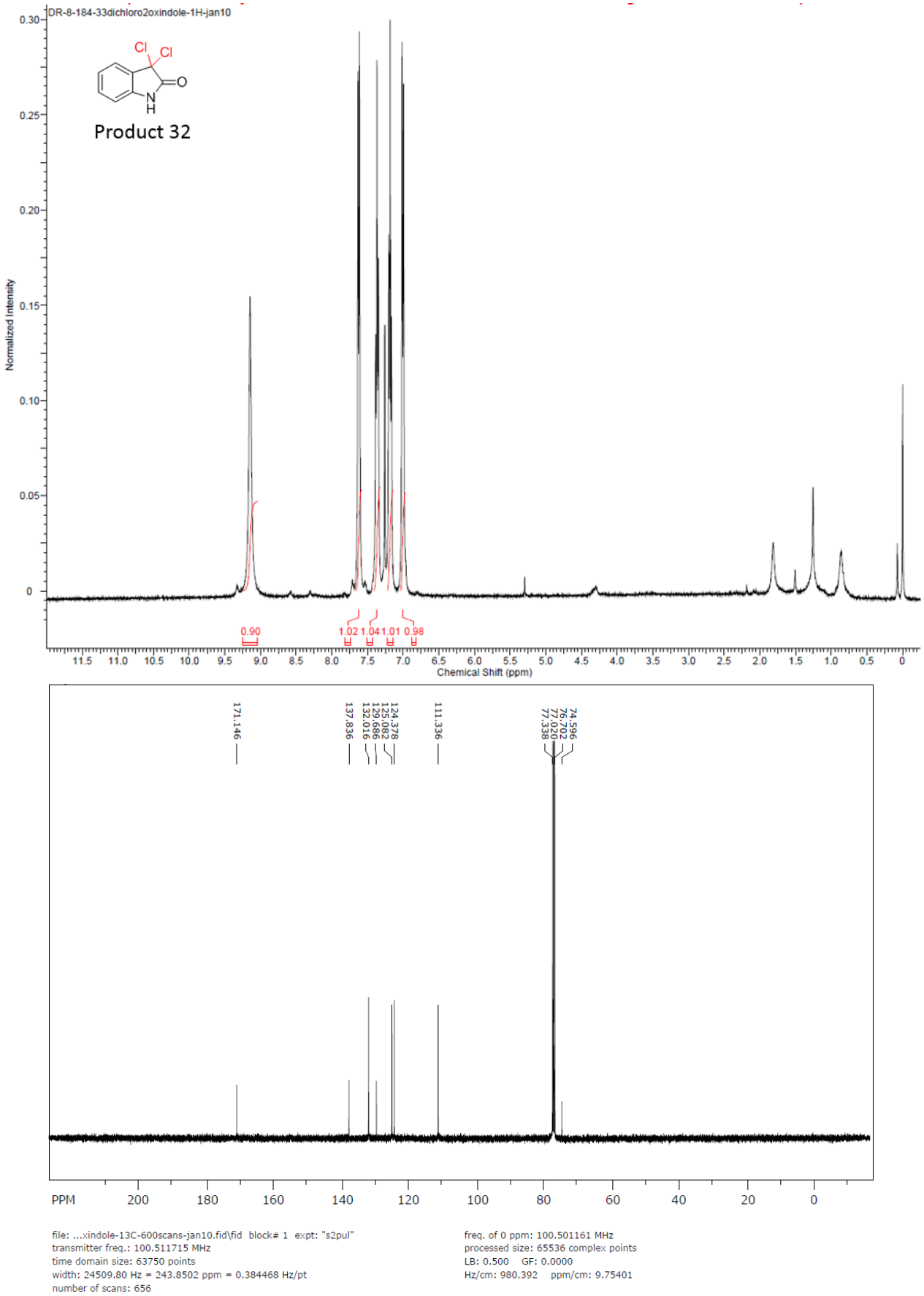


Figure S53. ^{1}H NMR and ^{13}C NMR of Product **32**.

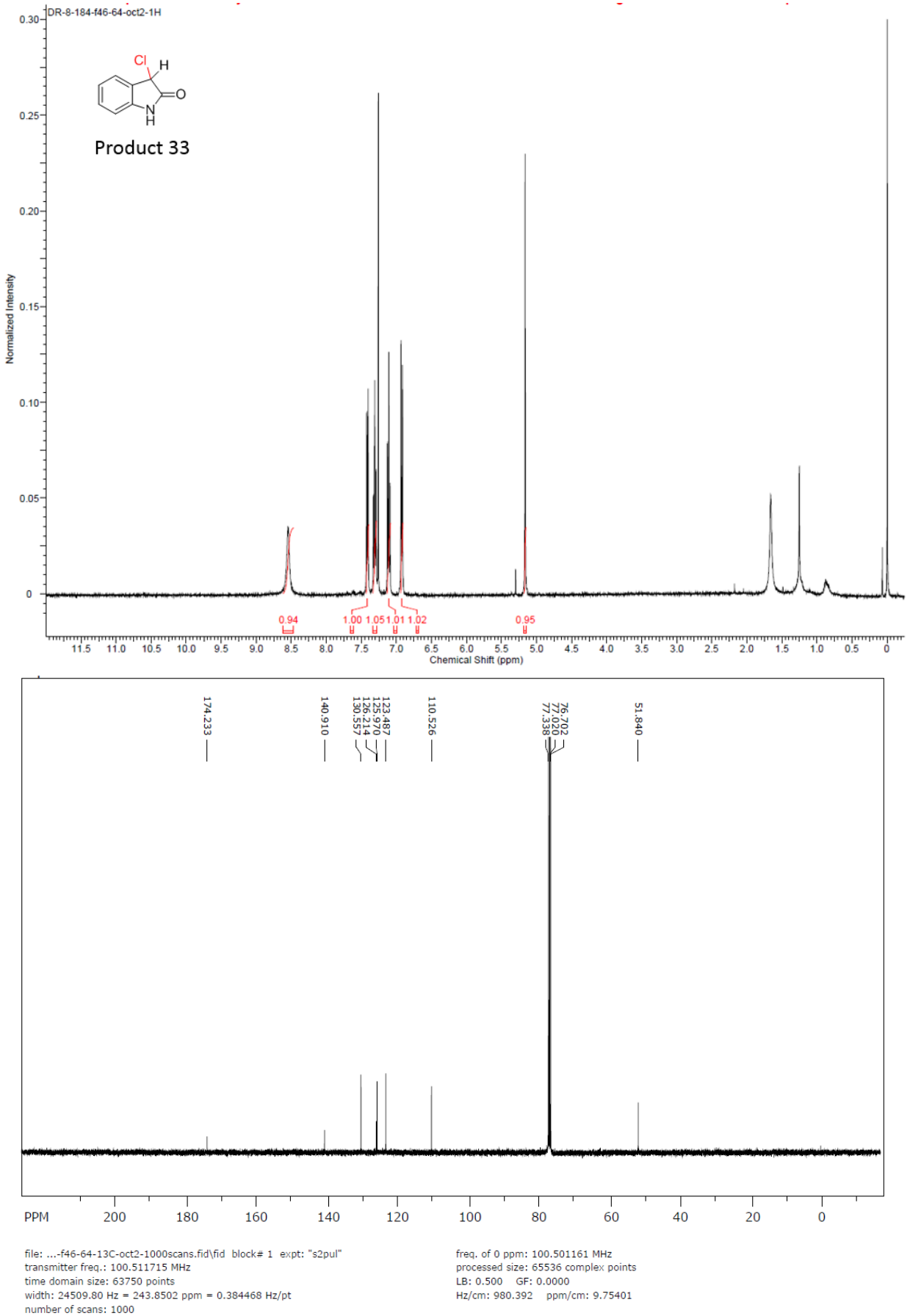


Figure S54. ^{1}H NMR and ^{13}C NMR of Product **33**.