Experimental Supporting Information

Amplification of Trichloroisocyanuric Acid (TCCA) Reactivity for Chlorination of Arenes and Heteroarenes via Catalytic Organic Dye Activation

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Materials and Instrumentation:

All reagents and solvents were purchased from commercial sources and used without further purification. Brilliant green was purchased from Alfa Aesar. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 400/100 (400 MHz) spectrometer in deuterated chloroform ($CDCl_3$) or acetonitrile (CD_3CN) with the solvent residual peak as internal reference unless otherwise stated ($CDCl_3$: ^{1}H = 7.26 ppm, ^{13}C = 77.02 ppm; CD_3CN: ^{1}H = 1.94 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 (mp) 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. HRMS (ESI+) accurate mass spectra were obtained at The University of Oklahoma with the assistance of Dr. Steven Foster. Additional ^{1}H NMR spectra were obtained with the assistance of Dr. Susan Nimmo at the University of Oklahoma on a Varian 400 MHz.

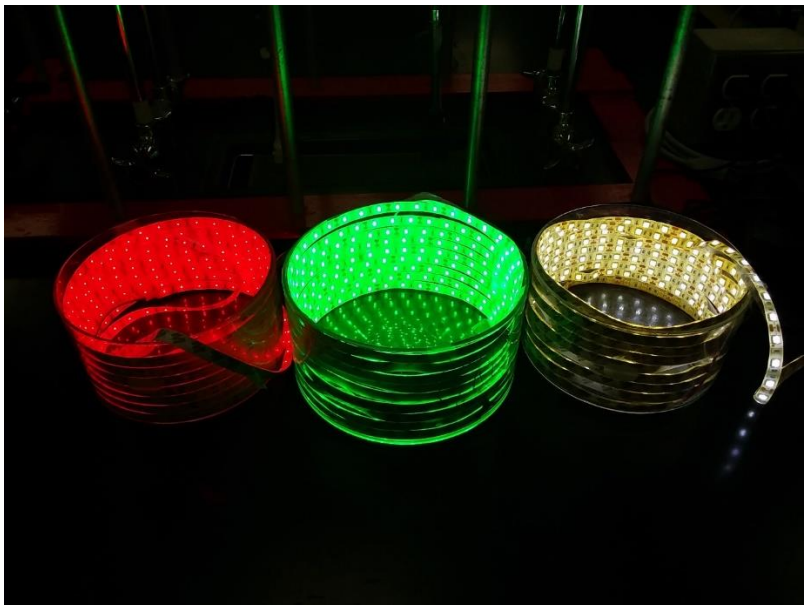
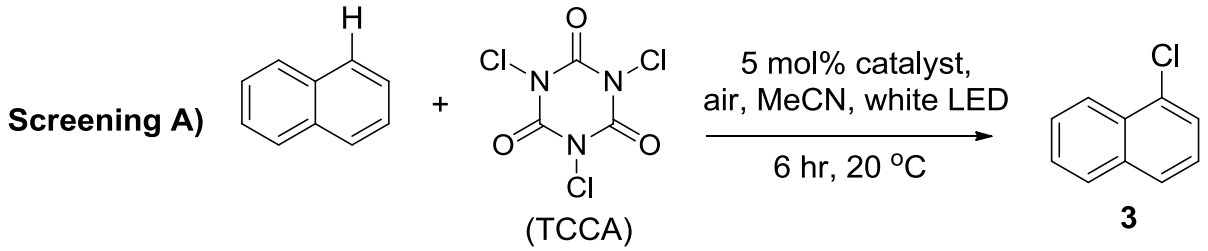
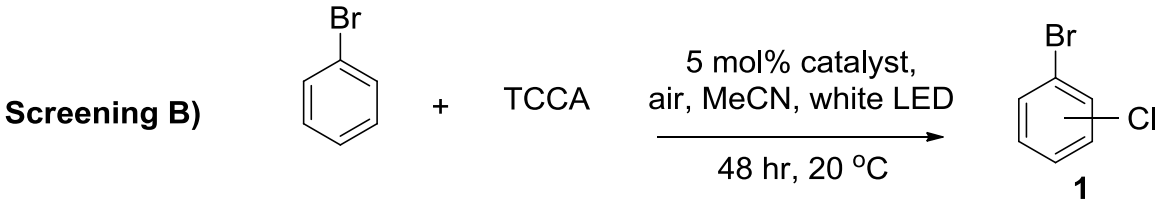


Figure S1. On the left – A red LED strip light bath reaction vessel; In the middle – A green LED strip light bath reaction vessel; On the right – A white LED strip (cool white) light bath reaction vessel.

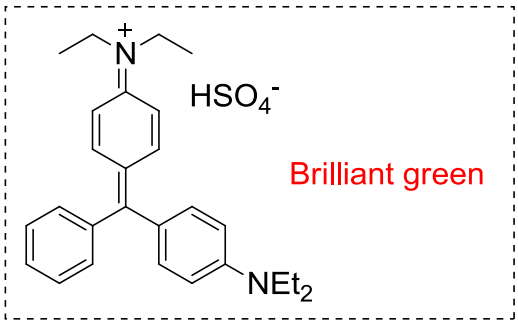
Photocatalytic reactions were set up in a light bath which was constructed in our laboratory by coiling LED strips around an evaporating dish according to our previous reports:[1-4]

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).



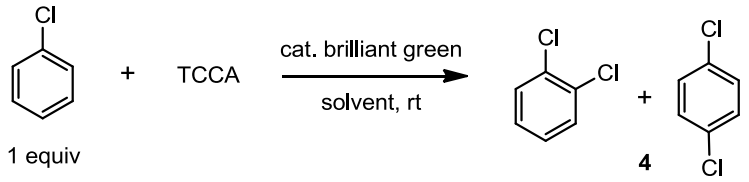


Entry	Catalyst	%Yld **3**[a,b]	% **1**[b,c]	Entry	Catalyst	%Yld **3**[a,b]	% **1**[b,c]
1	NONE	18	0	27	Methyl red	34	-
2	9-mesityl-10-methylacridinium	14	0	28	Methyl thymol blue	38	-
3	Acid alizarin violet	44	-	29	Methyl violet	33	-
4	Acid blue 20	27	-	30	Methylene blue	48	0
5	Acridine orange	49	0	31	Methylene green	54	0
6	Alizarin red S	29	-	32	Methylene violet 3RAX	50	0
7	Azure A	44	0	33	Nile blue A	52	0
8	Azure B	51	0	34	Orange II	48	0
9	Azure C	51	0	35	Rhodamine 6G	35	0
10	Azure II	62	0	36	Rhodamine B	38	0
11	Brilliant cresyl blue	36	0	37	Rose bengal	60	0
12	Brilliant green	54	16	38	Safranin O	39	0
13	Bromothymol blue	35	-	39	Thionin	29	0
14	Celestin Blue B	54	0	40	Victoria blue B	31	-
15	Crystal violet	34	-	41	$[Ru(bpy)_3]Cl_2$	47	0
16	DDQ	44	0				
17	Eosin Y	44	0				
18	Erythrosin B	57	0				
19	Ethyl violet	37	-				
20	Fast green	41	-				
21	Fluorescein	42	0				
22	Janus green B	45	-				
23	Light green SF yellowish	30	-				
24	Malachite green	38	-				
25	Methyl green	52	4				
26	Methyl orange	34	-				



b) Conditions: 0.25 mmol naphthalene, 0.083 mmol TCCA, 0.004 mmol catalyst, 3 mL MeCN, air, 20 °C, white LED, 6 hr; c) GC yields calculated using adamantane as internal standard. d) Conditions: 0.25 mmol bromobenzene, 0.25 mmol TCCA, 0.0125 mmol catalyst, 3 mL MeCN, air, 20 °C, white LED, 48 hr. Product **1** is a mixture of ortho and para isomers.

Table S1. Additional results from the screening of organic dye catalysts.



Entry	TCCA (equiv)	catalyst[a] (mol%)	solvent	time (h)	% yield 4[b]	lit. ref.
1	1	0	MeCN	168	0	5
2	0.34	0	1:1 98% H_2SO_4/HOAc	168	68	5
3	0.34	2	MeCN	48	2	
4	3	2	MeCN	48	8	
5	1	5	MeCN	48	12	
6	3	5	MeCN	48	29	
7	3	10	MeCN	48	35	
8	3	30	MeCN	48	9	
9	6	5	MeCN	48	21	

a) Reactions using brilliant green are conducted open to air in a white LED chamber. b) Yields for entries 3-9 were determined from GC integration using adamantane as internal standard.

Table S2. Optimization of stoichiometry of the TCCA/BG chlorination of chlorobenzene (entries 1 and 2 reported in literature[5]).

General procedure for TCCA/BG chlorination:

Stoichiometry A: To an oven-dried flask was added a magnetic stir bar, aromatic substrate (0.5 mmol, 1.5 equiv.), TCCA (76.6 mg, 0.33 mmol, 1 equiv.), and brilliant green (6.3 mg, 0.013 mmol) in CH_3CN (6 mL).

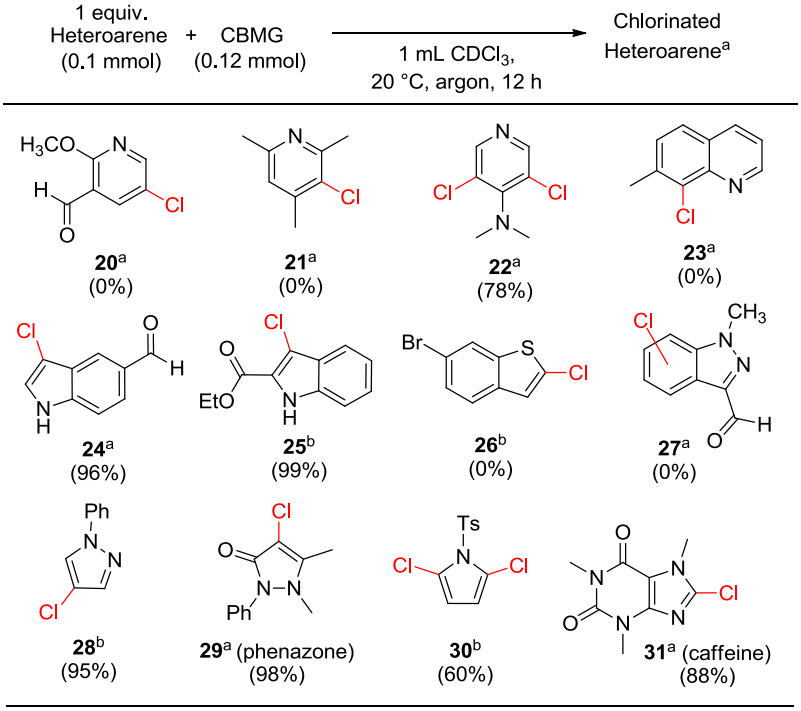
Stoichiometry B: To an oven-dried flask was added a magnetic stir bar, aromatic substrate (0.25 mmol, 1 equiv.), TCCA (174 mg, 0.75 mmol, 3 equiv.), and brilliant green (12 mg, 0.025 mmol) in CH_3CN (3 mL).

Stoichiometry C: To an oven-dried flask was added a magnetic stir bar, aromatic substrate (0.5 mmol, 2.8 equiv.), TCCA (41.8 mg, 0.18 mmol, 1 equiv.), and brilliant green (6.3 mg, 0.013 mmol) in CH_3CN (6 mL).

The reaction mixture was stirred open to air at room temperature (20 °C) in a white LED chamber for the time specified for each respective aromatic substrate. Reactions were monitored for completion by TLC (hexanes/ethyl acetate) and/or gas chromatography. For substrates that produced a mixture of mono- and di-chlorinated products using stoichiometry A, then stoichiometry B was employed to produce the dichlorinated product. Upon completion of the reaction, the crude mixture was evaporated under reduced pressure and the chlorinated product was isolated via column chromatography on silica gel. Uncatalyzed yields were determined using an identical procedure to the BG catalyzed version, but reactions were performed without addition of BG. Product yields were determined either via isolation of product or by calculation using nitrobenzene as internal standard (1 equiv. relative to aromatic substrate) in $CDCl_3$.

General procedure for CBMG chlorination of heteroaromatics:

Yields for products **25**, **28**, and **30** are reported.[6] Yields for all other products in Figure 3 and Table S3 were calculated using ^{1}H NMR integration with nitrobenzene as internal standard according to the following procedure: to an oven-dried reaction vessel was added heteroarene substrate (0.1 mmol), CBMG (Palau'chlor – purchased from Sigma-Aldrich) (25 mg, 0.12 mmol), nitrobenzene as internal standard (1 equiv., 10.3 μL, 0.1 mmol), and 1 mL $CDCl_3$. The reaction was purged with argon and stirred at room temperature for 12 hours. A ^{1}H NMR was performed directly on the crude reaction, and the product yield was calculated according to comparison with nitrobenzene signals.



a) Yield calculated from ^{1}H NMR integration using nitrobenzene internal standard.
b) Yield as reported in reference 6.

Table S3. Chlorination of heteroarenes using CBMG (Palau'chlor).

Procedure for light-dependent chlorination of 2-methoxy-3-pyridinecarboxaldehyde:

Using visible-light photochambers assembled in our laboratory (see Figure S1), the yield of product **20** was calculated using ^{1}H NMR integration with nitrobenzene as internal standard according to the following procedure: to an oven-dried reaction vessel was added 2-methoxy-3-pyridinecarboxaldehyde (11.8 μL, 0.1 mmol), TCCA (15.6 mg, 0.067 mmol), brilliant green (2 mg, 0.004 mmol), and nitrobenzene as internal standard (1 equiv., 10.3 μL, 0.1 mmol), in CH_3CN (1 mL) at ambient temperature in a visible-light photochamber that has been protected from any external background light (inside a light-proof chamber constructed in our laboratory) for 2.5 h. The crude was analyzed directly by ^{1}H NMR and a yield was calculated in comparison to internal standard signals. 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.

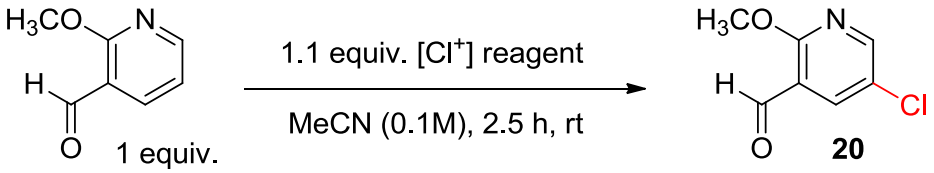
Procedure for TEMPO experiment:

To an oven-dried reaction vessel was added 2-methoxy-3-pyridinecarboxaldehyde (11.8 μL, 0.1 mmol), TCCA (15.6 mg, 0.067 mmol), brilliant green (2 mg, 0.004 mmol), TEMPO (15.6 mg, 0.1 mmol) and nitrobenzene as internal standard (1 equiv., 10.3 μL, 0.1 mmol), in CH_3CN (1 mL) at ambient temperature in a white LED photochamber for 2.5 h. The crude was analyzed directly by ^1H NMR and a yield was calculated in comparison to internal standard signals. The reaction was performed in triplicate and the three trials were averaged.

General procedure for chlorination of 2-methoxy-3-pyridinecarboxaldehyde using other [Cl^+] agents:

To an oven-dried reaction vessel was added 2-methoxy-3-pyridinecarboxaldehyde (11.8 μL, 0.1 mmol), chlorinating agent (0.11 mmol), and nitrobenzene as internal standard (1 equiv., 10.3 μL, 0.1 mmol), in CH_3CN (1 mL) at ambient temperature in a white LED photochamber for 2.5 h. The crude was analyzed directly by ^1H NMR and a yield was calculated in comparison to internal standard signals. Literature procedures and stoichiometries (based upon pyridine substrate = 0.1 mmol; 1 equiv.) were followed (though all reactions were run for 2.5 hours) for the following:

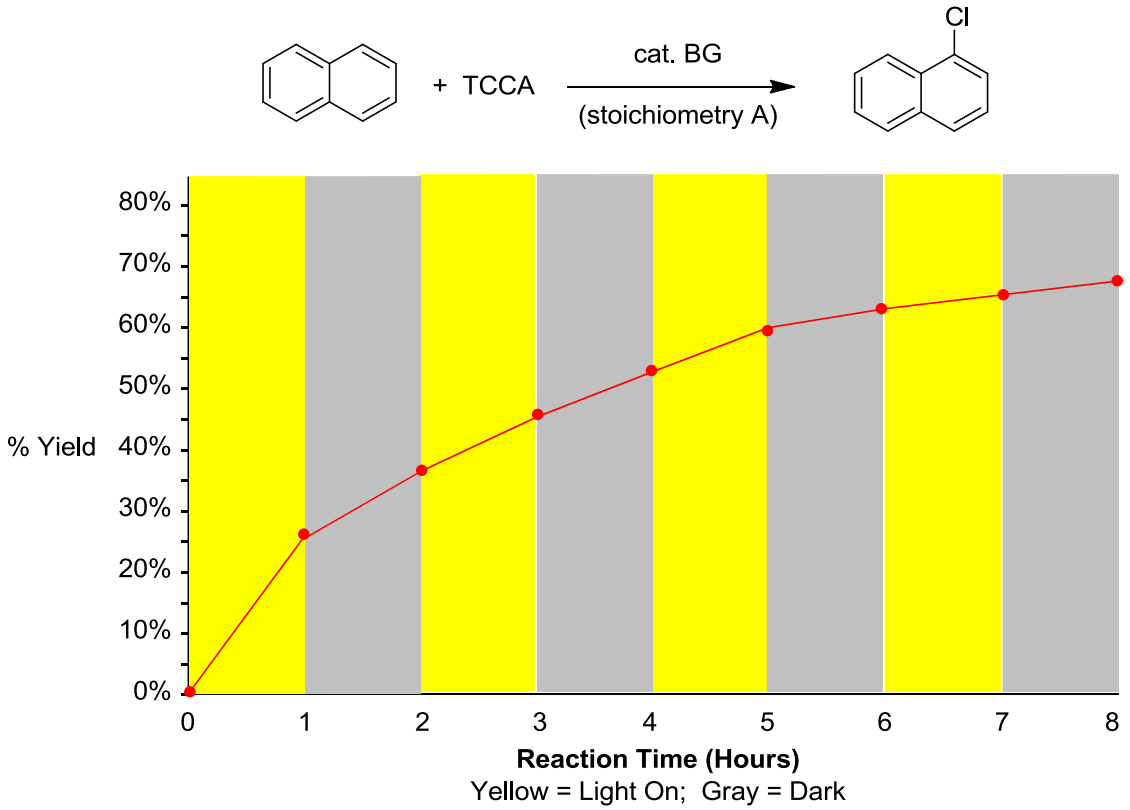
TCCA in H_2SO_4/AcOH[5]
NCS/Ph_3P=S[7]
CBMG[6]
KCl/oxone[8]
$Na_2S_2O_8$, NaCl, $[Ru(bpy)_3]Cl_2$ (reaction was performed in a blue LED chamber)[9]



Entry	[Cl^+] reagent	% conv.	% yield **20**[a]
1	TCCA, 4 mol% BG	70	67 (63)[b]
2	TCCA in H_2SO_4/AcOH	43	0
3	NCS	0	0[c]
4	NCS, 20 mol% Ph_3P=S	10	9
5	DCDMH	9	0
6	^{t}BuOCl	0	0
7	CBMG (Palau'chlor)	0	0[c]
8	KCl, oxone	91	0[d]
9[e]	$Na_2S_2O_8$, NaCl, $[Ru(bpy)_3]Cl_2$	20	14[d]

a) Yields are quantified via ^1H NMR integration using nitrobenzene as internal standard. b) Isolated yield in parantheses. c) Only starting material was observed. d) Conversion of aldehyde to carboxylic acid was observed. e) Solvent = 1:1 MeCN/H_2O; 3 equiv. NaCl, in a blue LED chamber.

Table S4. Comparison of methods of chlorination.



Scheme S1. Light/Dark Experiment.

Reaction was performed according to general procedure but alternating between light and dark conditions at 1 hour intervals. Yields were calculated by GC integration (see characterization of 1-chloronaphthalene on page S11).

Iodide Test to Detect Formation of Hydrogen Peroxide

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

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

On the left: Fresh KI test solution

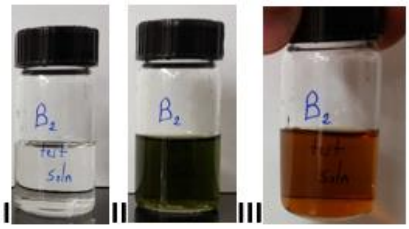
On the right: Test solution with 3 drops 3 wt% H_2O_2

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

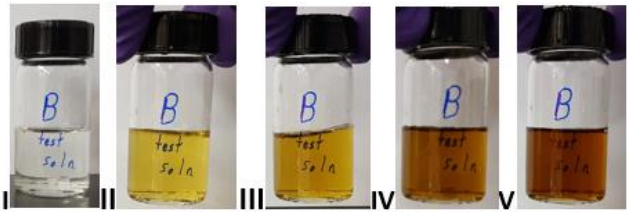
On the left: Crude reaction mixture at t = 0 h

On the right: 15 drops of crude rxn at t = 0 h added to KI test solution (dark green)

4-hour test: A test test was loaded following the general procedure using Stoichiometry A with 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 4 hours. At t = 4 h, fifteen drops of the crude reaction mixture was immediately transferred via pipette to a freshly prepared NaI/AcOH test solution in a 4-dram vial. The vial was capped and shaken, initially appearing green, then quickly (within 10 seconds) converting to an opaque red-brown color resembling the color of the control test, confirming the formation of I_2 via the presence of hydrogen peroxide.



I) Fresh test solution
II) Test solution immediately after adding 15 drops of 4-hr reaction mixture
III) Test solution ~1 minute after adding the 15 drops.



I) Fresh test solution
II) Test solution with 3 drops of 4-hour reaction mixture
III) Same test solution with 6 total drops reaction mixture
IV) Same test solution with 9 total drops reaction mixture
V) Same test solution with 15 total drops reaction mixture

Figure S2. Iodide Test for Detection of Hydrogen Peroxide Formation

Compound characterization:

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

1-bromo-4-chlorobenzene and 1-bromo-2-chlorobenzene (**1**)

The title compound was prepared using stoichiometry B (general procedure) and quantified using gas chromatography with adamantane as an internal standard. A standard curve of 1-bromo-4-chlorobenzene (Figure S2) was prepared in 4 separate reaction vessels by adding varying amounts of 1-bromo-4-chlorobenzene (between 0 and 0.25 mmol) to 3 mL of acetonitrile. 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 5 additional minutes. As seen in Figure S3, 1-1-bromo-4-chlorobenzene is observed at 12.75 minutes, 1-bromo-2-chlorobenzene is observed at 13.18 minutes, and each was confirmed by MS (EI) *m/z* 192(100), 190(78), 113(88), 75(90).

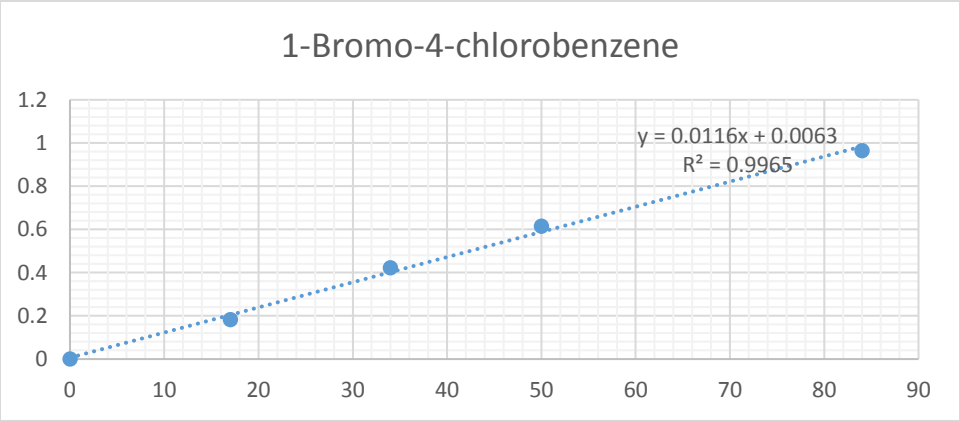


Figure S2. Standard curve of 1-bromo-4-chlorobenzene versus internal standard (adamantane)

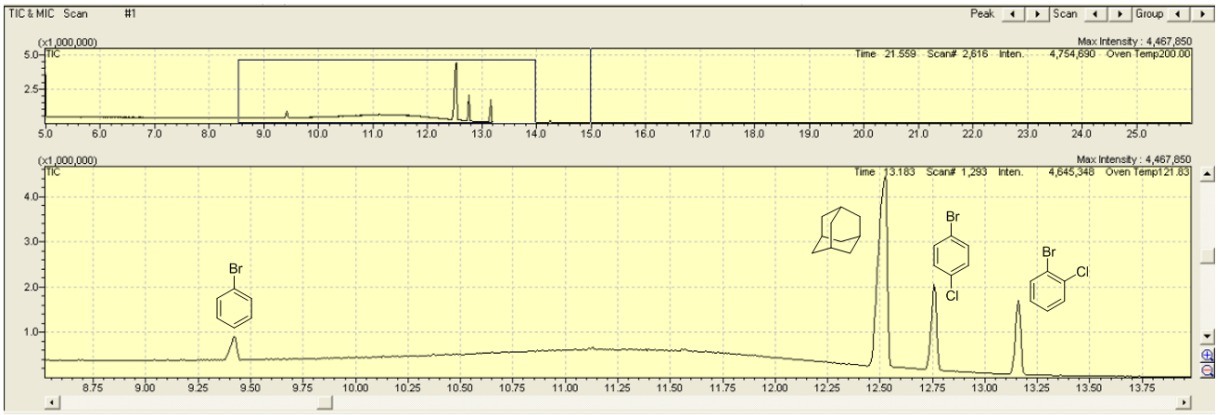


Figure S3. Expanded view of a typical GCMS chromatogram.

1-Chloronaphthalene (**3**)

The title compound was prepared using stoichiometry A (general procedure) and quantified using gas chromatography with adamantane as an internal standard. A standard curve of 1-chloronaphthalene (Figure S4) 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. 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. As seen in Figure S5, 1-chloronaphthalene is observed at 16.8 minutes, and confirmed by MS (EI) *m/z* 164 (30), 162 (100), 127 (48), 74, (36), 63 (56).

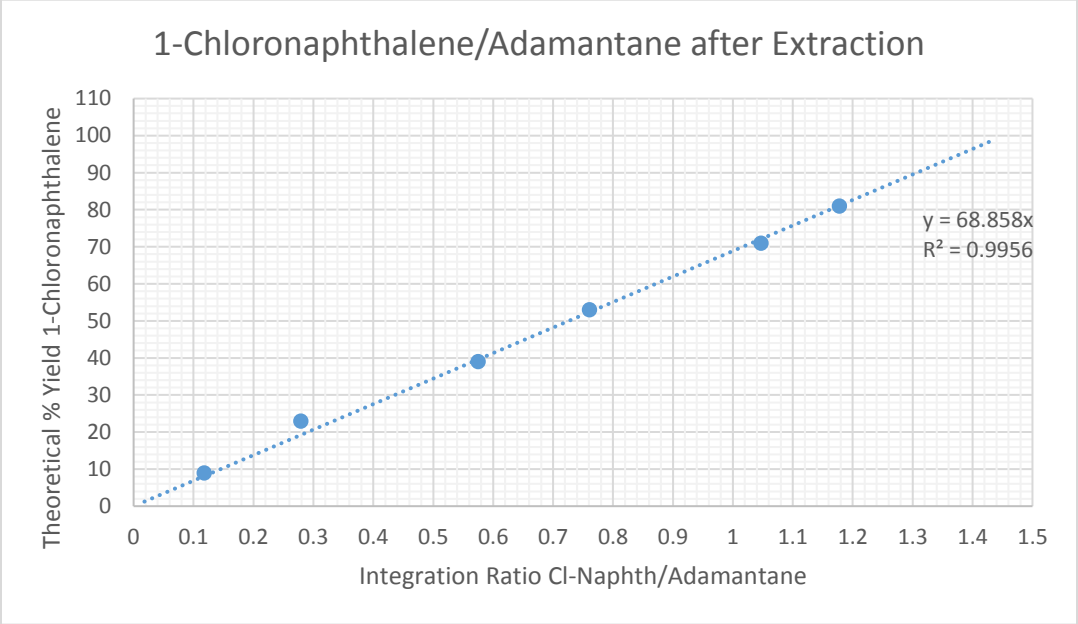


Figure S4. Standard curve of 1-chloronaphthalene versus internal standard (adamantane)

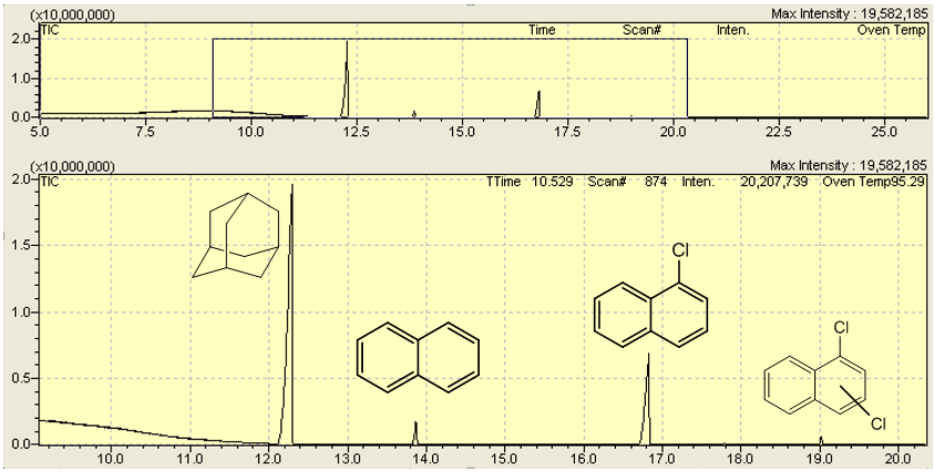


Figure S5. Expanded view of a typical GCMS chromatogram.

1,4-Dichlorobenzene and 1,2-dichlorobenzene (**4**)

The title compound was prepared using stoichiometry B (general procedure) and quantified using gas chromatography with adamantane as an internal standard. Separate standard curves of both 1,4-dichlorobenzene and 1,2-dichlorobenzene (Figures S6 and S7) were prepared from 5-6 separate reaction vessels by adding varying amounts of the dichlorinated product (between 0 and 0.25 mmol) to 3 mL of acetonitrile. 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 5 additional minutes. As seen in Figure S8, 1,4-dichlorobenzene is observed at 10.75 minutes, 1,2-dichlorobenzene at 11.2 minutes, and each was confirmed by MS (EI) *m/z* 148(48), 146(79), 111(41), 75(82), 50(100).

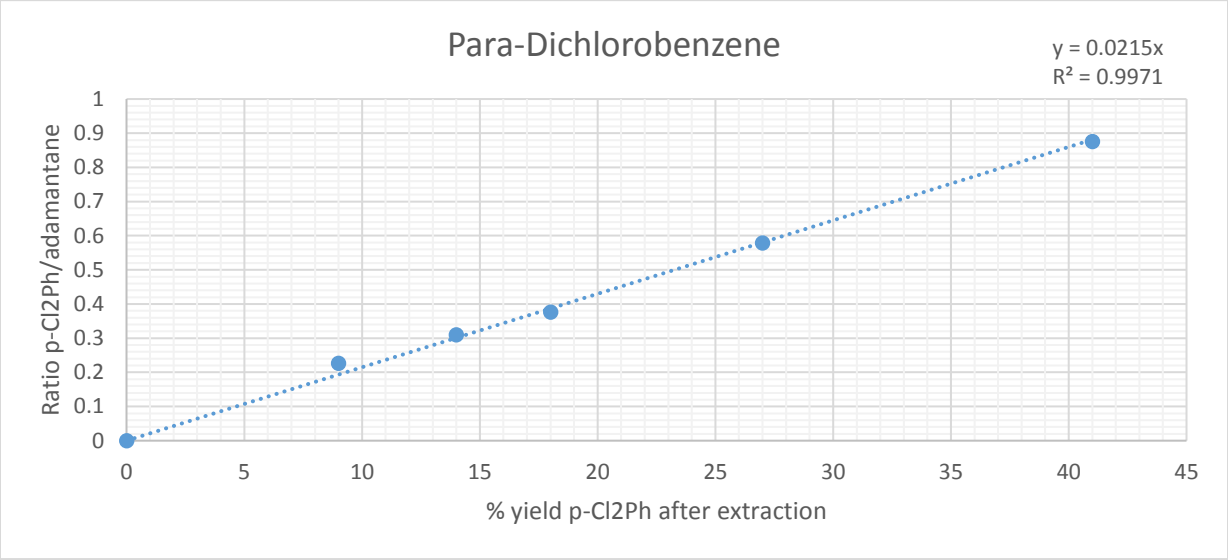


Figure S6. Standard curve of 1,4-dichlorobenzene versus internal standard (adamantane)

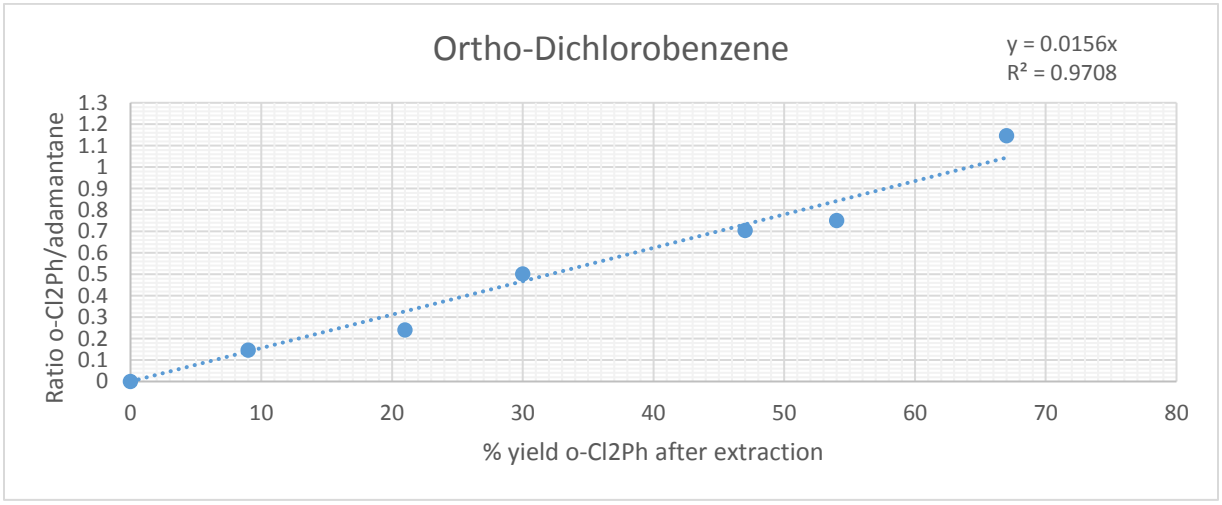


Figure S7. Standard curve of 1,2-dichlorobenzene versus internal standard (adamantane)

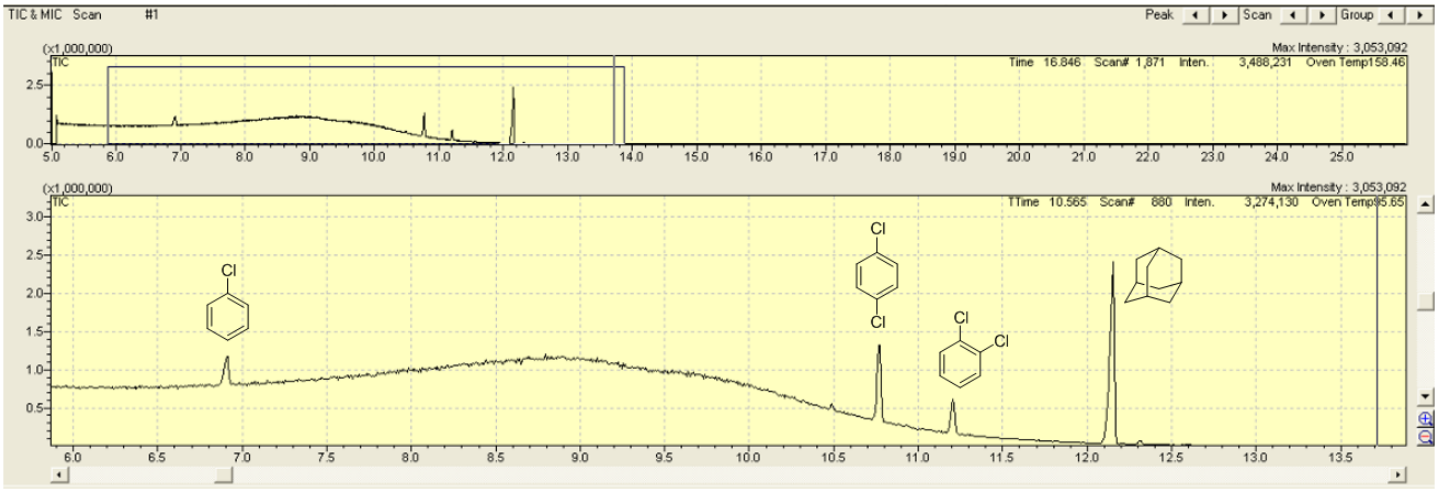
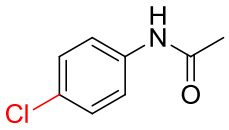


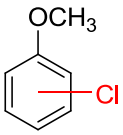
Figure S8. Expanded view of a typical GCMS chromatogram.

N-(4-chlorophenyl)acetamide (**5**)[10]



The title compound was prepared according to the general procedure (Stoichiometry A) from acetanilide (67.4 mg, 0.5 mmol), TCCA (77.1 mg, 0.33 mmol), and brilliant green (9.2 mg, 0.019 mmol) in CH_3CN (6 mL) at ambient temperature for 2 h. Yellow solid (63.5 mg, 74%); purification (hexanes:EtOAc = 80:20), R_f = 0.10. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.8 Hz, 2H), 7.37 (bs, 1H), 7.27 (d, *J* = 8.8 Hz, 2H), 2.17 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4, 136.4, 129.3, 129.0, 121.1, 24.6 ppm. IR (neat): ν = 3299, 3206, 3064, 2835, 1695, 1661, 1607, 1535, 1486, 1314, 1091 cm^{-1}. MS (EI): 171(4), 169(13), 168(4), 129(30), 127(100).

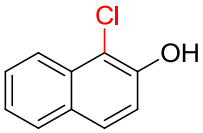
4-chloroanisole and 2-chloroanisole (**6**)[11-12]



The title compound was prepared according to the general procedure (Stoichiometry A) from anisole (54.0 µL, 0.5 mmol), TCCA (77.2 mg, 0.33 mmol), and brilliant green (6.4 mg, 0.013 mmol) in CH_3CN (6 mL) at ambient temperature for 20 minutes. Upon completion, the reaction was quenched with 6 mL sodium carbonate and extracted with ethyl acetate (3 x 10 mL). The organic portion was dried with magnesium sulfate, filtered, and

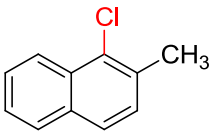
evaporated under pressure. Oil (66.0 mg, 92%; 8:1 p/o ratio): purification (extraction). An 8:1 para/ortho ratio was produced, and the following characterization applies to the major (para) isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 3.78 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 129.3, 125.5, 115.2, 55.5 ppm. IR (neat): ν = 2922, 2872, 2779, 1714, 1491, 1406, 1243, 822, 547 cm^{-1}. MS (EI): 144(31), 142(100), 127, (69), 99(89).

1-chloro-2-naphthol (**7**)[13]



The title compound was prepared according to the general procedure (Stoichiometry A) from 2-naphthol (68.3 mg, 0.5 mmol), TCCA (79.7 mg, 0.33 mmol), and brilliant green (6.8 mg, 0.014 mmol) in CH_3CN (6 mL) at ambient temperature for 10 minutes. Green solid (84.6 mg, 97%): m.p. 66-68 °C; purification (hexanes:EtOAc, 80:20), R_f = 0.42. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.6 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 1H), 5.90 (bs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.3, 131.0, 129.4, 128.4, 128.2, 127.5, 124.1, 122.7, 117.2, 113.3 ppm. IR (neat): ν = 3352, 1626, 1601, 1505, 1433, 1349, 1000, 807 cm^{-1}. MS (EI): 180(16), 179(4), 178(48), 130(100), 114(41), 102(98), 76(56), 51(77), 50(82).

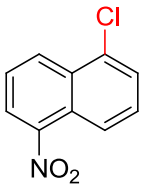
1-chloro-2-methylnaphthalene (**8**)[14]



The title compound was prepared according to the general procedure (Stoichiometry A) from 2-methylnaphthalene (71.0 mg, 0.5 mmol), TCCA (75.8 mg, 0.32 mmol), and brilliant green (7.3 mg, 0.015 mmol) in CH_3CN (6 mL) at ambient temperature for 70 minutes. Clear oil (71.7 mg, 81%); purification (hexanes), R_f = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (dd, J_1 = 8.6 Hz, J_2 = 1.2 Hz, 1H), 7.82 (dd, J_1 = 8.4 Hz, J_2 = 1.0 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.59 (ddd, J_1 = 8.4 Hz, J_2 = 6.8 Hz, J_3 = 1.2 Hz, 1H), 7.49 (ddd, J_1 = 8.2 Hz, J_2 =

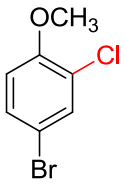
7.0 Hz, J_3 = 1.2 Hz, 1H), 7.36 (d, J = 8.6 Hz, 1H), 2.61 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.4, 133.0, 131.1, 130.7, 128.7, 128.0, 127.0, 126.4, 125.6, 124.1, 20.8 ppm. IR (neat): ν = 3053, 2921, 1504, 1332, 1260, 1225, 1032, 978, 900, 804, 766, 739 cm^{-1}. MS (EI): 178(16), 176(52), 141(100), 139(32), 115(26), 70(68).

1-chloro-5-nitronaphthalene (**9**)[15]



The title compound was prepared according to the general procedure (Stoichiometry B) from 1-nitronaphthalene (42.9 mg, 0.25 mmol), TCCA (174.6 mg, 0.75 mmol), and brilliant green (14.1 mg, 0.03 mmol) in CH_3CN (3 mL) at ambient temperature for 24 h. Yellow solid (32.9 mg, 63%): m.p. 87-90 °C; purification (hexanes:EtOAc, 90:10), R_f = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (dd, J_1 = 8.2 Hz, J_2 = 1.2 Hz, 1H), 7.88 (dd, J_1 = 8.2 Hz, J_2 = 1.2 Hz, 1H), 7.71 (ddd, J_1 = 7.6 Hz, J_2 = 3.7 Hz, J_3 = 1.2 Hz, 2H), 7.57-7.51 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.4, 135.9, 132.3, 131.0, 128.2, 127.9, 127.5, 125.2, 123.2, 121.5 ppm. IR (neat): ν = 2922, 2851, 1721, 1707, 1520, 1359, 1200, 817, 745 cm^{-1}. MS (EI): 209(8), 207(23), 172(100), 161(38), 149(35), 126(98), 114(29), 75(44), 63(56).

4-bromo-2-chloroanisole (**10**)[16]



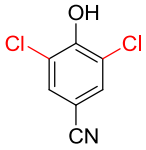
The title compound was prepared according to the general procedure (Stoichiometry A) from 4-bromoanisole (46.2 mg, 0.25 mmol), TCCA (37.6 mg, 0.162 mmol), and brilliant green (3.5 mg, 0.007 mmol) in CH_3CN (3 mL) at ambient temperature for 6 h. The reaction was quenched with 3 mL saturated sodium carbonate, then extracted with 3 x 10 mL EtOAc. The organic portions were combined and dried with $MgSO_4$, filtered, and evaporated under vacuum. Green solid (51.7 mg, 94%); purification (extraction: EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 2.4 Hz, 1H), 7.34 (dd, J_1 = 8.6 Hz, J_2 = 2.4 Hz, 1H), 6.80 (d, J = 8.6 Hz, 1H), 3.89 (s,

3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.0, 132.2, 130.3, 123.2, 113.0, 112.1, 55.9 ppm. IR (neat): ν = 3089, 3067, 3024, 2976, 2939, 2838, 1578, 1482, 1460, 1292, 1251, 1064, 1019, 805, 705 cm^{-1}. MS (EI): 222(63), 220(62), 207(69), 205(60), 179(39), 177(39), 75(32), 63(100), 62(39).

GRAM SCALE:

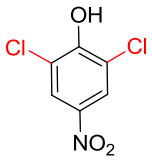
The title compound was prepared using stoichiometry A from 4-bromoanisole (0.905 g, 4.84 mmol), TCCA (0.750 g, 3.23 mmol), and brilliant green (60.3 mg, 0.125 mmol) in CH_3CN (60 mL) at ambient temperature for 6 h. The reaction was quenched with 60 mL saturated sodium carbonate, then extracted with 3 x 60 mL EtOAc. The organic portions were combined and dried with $MgSO_4$, filtered, and evaporated under vacuum. Green solid (1.040 g, 97%); purification (extraction: EtOAc).

3,5-Dichloro-4-hydroxybenzonitrile (**11**)[17]



The title compound was prepared according to the general procedure (Stoichiometry B) from 4-hydroxybenzonitrile (29 mg, 0.243 mmol), TCCA (175 mg, 0.752 mmol), and brilliant green (14.2 mg, 0.03 mmol) in CH_3CN (3 mL) at ambient temperature for 20 minutes. Dark orange oil (36.3 mg, 79%); purification (hexanes:EtOAc = 80:20), R_f = 0.50. ^{1}H NMR (400 MHz, DMSO): δ = 7.99 (s, 2H) ppm. ^{13}C NMR (100 MHz, DMSO): δ = 153.8, 132.7, 122.7, 117.1, 103.1 ppm. IR (neat): ν = 3284 (br), 3069, 2928, 2856, 2224, 1716, 1482, 1298, 1241, 1152, 816 cm^{-1}. MS (EI): 189(58), 187(100), 111(50), 88(96), 76(38), 62(46).

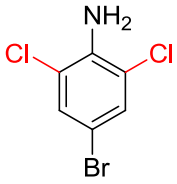
2,6-Dichloro-4-nitrophenol (**12**)[18]



The title compound was prepared according to the general procedure (Stoichiometry B) from 4-nitrophenol (34.5 mg, 0.25 mmol), TCCA (176.1 mg, 0.75 mmol), and brilliant green (13.8 mg, 0.029 mmol) in CH_3CN (3 mL) at

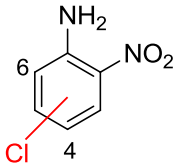
ambient temperature for 15 minutes. Red solid (29.7 mg, 58%); purification (DCM:EtOAc = 3:1), R_f = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.24 (s, 2H), 6.44 (bs, 1H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$) δ 153.3, 124.3, 121.6 (the peak at 140.8 R_2**C**-NO_2 was undetectable using our NMR parameters) ppm. MS (EI): 207(100), 209(78), 211(12), 177(63), 133(54), 125(52).

2,6-dichloro-4-bromoaniline (**13**)



The title compound was prepared according to the general procedure (Stoichiometry A) from 4-bromoaniline (86.7 mg, 0.5 mmol), TCCA (79.6 mg, 0.33 mmol), and brilliant green (7.1 mg, 0.014 mmol) in CH_3CN (6 mL) at ambient temperature for 10 minutes. Red solid (116.3 mg, 97%): m.p. 77-79 °C; purification (hexanes:EtOAc = 95:5), R_f = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (s, 2H), 4.45 (bs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.4, 130.2, 120.0, 107.9 ppm. IR (neat): ν = 3423, 3299, 3082, 1726, 1612, 1559, 1466, 1389, 1073, 856 cm^{-1}. MS (EI): 243(47), 241(100), 239(56), 160(26), 124(44), 63(65), 62(71), 61(65). MS data matches that available from AIST: Integrated Spectral Database System of Organic Compounds. (Data were obtained from the National Institute of Advanced Industrial Science and Technology (Japan)).

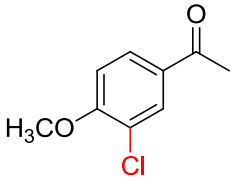
4-chloro-2-nitroaniline and 6-chloro-2-nitroaniline (**14**)[19-20]



The title compound was prepared according to the general procedure (Stoichiometry A) from 2-nitroaniline (69.0 mg, 0.5 mmol), TCCA (79.6 mg, 0.33 mmol), and brilliant green (7.0 mg, 0.014 mmol) in CH_3CN (6 mL) at ambient temperature for 1.5 h. Yellow solid (81.1 mg, 94% combined; 9:1 ratio of 4-Cl to 6-Cl isomers): purification (hexanes:EtOAc = 80:20), 4-Cl isomer R_f = 0.40; 6-Cl isomer R_f = 0.70. ^{1}H NMR of 4-Cl isomer[19]

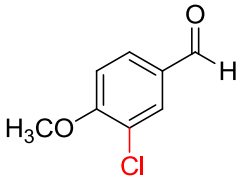
(400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 2.4 Hz, 1H), 7.30 (dd), J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 1H), 6.11 (bs, 2H) ppm. ^{1}H NMR of 6-Cl isomer[20] (400 MHz, $CDCl_3$): δ = 8.10 (m, 1H), 7.53 (m, 1H), 6.67 (dd, J_1 = 8.6 Hz, J_2 = 7.6 Hz, 1H), 6.55 (bs, 2H) ppm. ^{13}C NMR of 4-Cl isomer[19] (100 MHz, $CDCl_3$): δ = 143.2, 135.9, 132.0, 125.3, 121.5, 120.0 ppm. IR (neat) of 4-Cl isomer (major isomer): ν = 3472, 3350, 3091, 2924, 1618, 1500, 1434, 1352, 1317, 1247, 1101 cm^{-1}. MS (EI) of 4-Cl isomer: 174(16), 172(56), 126(32), 90(100), 63(74).

1-(3-chloro-4-methoxyphenyl)ethan-1-one (**15**)[9]



The title compound was prepared according to the general procedure (Stoichiometry A) from 4-methoxyacetophenone (75.0 mg, 0.5 mmol), TCCA (76.7 mg, 0.33 mmol), and brilliant green (6.2 mg, 0.013 mmol) in CH_3CN (6 mL) at ambient temperature for 4 h. White solid (81 mg, 88%); purification (hexanes:DCM 50:50), R_f = 0.15. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 2.3 Hz, 1H), 7.84 (dd, J_1 = 8.6 Hz, J_2 = 2.3 Hz, 1H), 6.94 (d, *J* = 8.6 Hz, 1H), 3.95 (s, 3H), 2.53 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.7, 158.7, 130.8, 130.6, 128.7, 122.8, 111.2, 56.4, 26.3 ppm. IR (neat): ν = 2992, 2961, 2851, 1671, 1595, 1498, 1408, 1261, 1232, 1054, 1015 cm^{-1}. MS (EI): 186(7), 184(25), 169(100), 126(16), 77(38), 63(39).

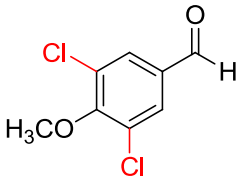
3-chloro-4-methoxybenzaldehyde (**16**)[17]



The title compound was prepared according to the general procedure (Stoichiometry A) from 4-anisaldehyde (68.0 mg, 0.5 mmol), TCCA (76.4 mg, 0.33 mmol), and brilliant green (6.5 mg, 0.013 mmol) in CH_3CN (6 mL) at ambient temperature for 7 h. Light pink solid (74.2 mg, 87%); purification (hexanes:DCM 50:50), R_f = 0.15. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.84 (s, 1H), 7.89 (d, *J* = 2.0 Hz, 1H), 7.76 (dd, J_1 = 8.6 Hz, J_2 = 2.0 Hz, 1H),

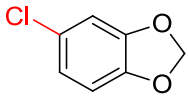
7.04 (d, *J* = 8.6 Hz, 1H), 3.98 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.7, 159.8, 131.2, 130.5, 130.3, 123.7, 111.7, 56.5 ppm. IR (neat): ν = 2955, 2849, 1693, 1591, 1568, 1497, 1313, 1268, 1255, 1197, 1057, 1012 cm^{-1}. MS (EI): 172(18), 171(20), 170(59), 169(100), 126(14), 99(22), 77(30), 75(28), 63(52).

3,5-dichloro-4-methoxybenzaldehyde (**17**)[21]



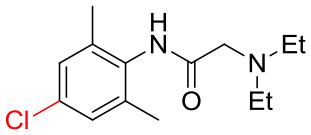
The title compound was prepared according to the general procedure (Stoichiometry B) from 4-anisaldehyde (34.0 mg, 0.25 mmol), TCCA (173.8 mg, 0.75 mmol), and brilliant green (12.0 mg, 0.025 mmol) in CH_3CN (3 mL) at ambient temperature for 20 h. Red-orange solid (33.3 mg, 65%); m.p. 59-61 °C; purification (hexanes:DCM 50:50), R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.84 (s, 1H), 7.79 (s, 2H), 3.96 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.6, 157.2, 133.1, 130.6, 130.0, 61.0 ppm. IR (neat): ν = 3062, 3044, 2941, 2855, 1692, 1556, 1477, 1371, 1265, 1078, 981 cm^{-1}. MS (EI): 206(43), 205(67), 203(100), 135(22), 133(37), 97(30), 75(43), 74(35), 73(34), 62(35).

3,4-methylenedioxychlorobenzene (**18**)[22]



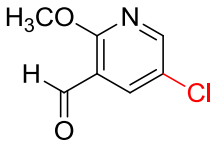
The title compound was prepared according to the general procedure (Stoichiometry C) from 1,3-benzodioxole (51 µL, 0.5 mmol), TCCA (42.6 mg, 0.18 mmol), and brilliant green (6.5 mg, 0.013 mmol) in CH_3CN (6 mL) at ambient temperature for 15 minutes. Clear oil (57.8 mg, 75%); purification (hexanes:EtOAc = 95:5 to 85:15), R_f = 0.70. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.82-6.78 (m, 2H), 6.72 (d, *J* = 7.8 Hz, 1H), 5.97 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.3, 146.4, 126.3, 121.3, 109.6, 108.9, 101.7 ppm. IR (neat): ν = 2897, 1607, 1501, 1475, 1229, 1035 cm^{-1}. MS (EI): 158(22), 157(36), 156(73), 155(100), 98(13), 79(19), 62(34), 63(100), 44(35), 37(23).

N-(4-chloro-2,6-dimethylphenyl)-2-(diethylamino)-acetamide (**19**)



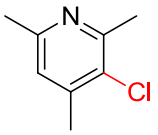
The title compound was prepared according to the general procedure (Stoichiometry C) from lidocaine (116.0 mg, 0.5 mmol), TCCA (43.3 mg, 0.18 mmol), and brilliant green (6.2 mg, 0.013 mmol) in CH_3CN (6 mL) at ambient temperature for 10 minutes. Light green oil (124.6 mg, 94%); purification (hexanes:EtOAc = 50:50 w/ 2% Et_3N), R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.93 (bs, 1H), 7.08 (s, 2H), 3.21 (s, 2H), 2.69 (q, *J* = 7.3 Hz, 4H), 2.23 (s, 6H), 1.13 (t, *J* = 7.3 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 135.0, 133.8, 128.1, 127.0, 57.4, 48.9, 18.5, 12.6 ppm. IR (neat): ν = 3285, 2969, 2929, 1675, 1593, 1492, 750 cm^{-1}. MS (EI): 244(2), 177(1), 160(1), 147(17), 132(7), 119(12), 118(12), 105(7), 86(69), 58(29), 44(100). HRMS (ESI): calculated for $C_{14}H_{21}N_2O_1Cl_1$ $[M + Na]^+$ requires *m/z* 291.12401, found *m/z* 291.14100.

5-chloro-2-methoxy-3-pyridinecarboxaldehyde (**20**)[23]



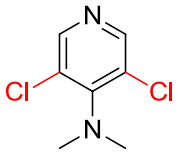
The title compound was prepared according to the general procedure (Stoichiometry A) from 2-methoxy-3-pyridinecarboxaldehyde (68.5 mg, 0.5 mmol), TCCA (76.6 mg, 0.33 mmol), and brilliant green (6.4 mg, 0.013 mmol) in CH_3CN (6 mL) at ambient temperature for 2.5 h. Pale yellow solid (54.0 mg, 63%); purification (hexanes:EtOAc = 70:30), R_f = 0.73. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.32 (s, 1H), 8.32 (d, *J* = 2.7 Hz, 1H), 8.06 (d, *J* = 2.7 Hz, 1H), 4.07 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.0, 162.8, 151.1, 136.9, 125.1, 119.1, 54.4 ppm. IR (neat): ν = 2956, 2925, 2853, 1683, 1569, 1467, 1381, 1239 cm^{-1}. MS (EI): 171(44), 142(96), 114(36), 113(74), 78(100).

3-chloro-2,4,6-trimethylpyridine (**21**)



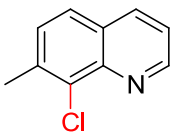
The title compound was prepared according to the general procedure (Stoichiometry A) from 2,4,6-collidine (33 µL, 0.25 mmol), TCCA (43.1 mg, 0.19 mmol), and brilliant green (3.5 mg, 0.007 mmol) in CH_3CN (3 mL) at ambient temperature for 27 h. Yellow oil (27.8 mg, 72%); purification (hexanes:EtOAc = 30:70), R_f = 0.62. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.89 (s, 1H), 2.59 (s, 3H), 2.46 (s, 3H), 2.33 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9 (x2), 145.2, 128.9, 123.3, 23.7, 23.0, 20.0 ppm. IR (neat): ν = 2955, 2923, 2854, 1592, 1450, 1388, 1376, 1198, 1063, 1050, 1028 cm^{-1}. MS (EI): 157(30), 156(12), 155(100), 154(9), 120(21), 79(29), 77(41), 51(44), 39(60). HRMS (ESI): calculated for $C_8H_{11}N_1Cl_1$ $[M + H]^+$ requires *m/z* 156.05800, found *m/z* 156.05790.

3,5-dichloro-4-(N,N-dimethylamino)pyridine (**22**)[24]



The title compound was prepared according to the general procedure (Stoichiometry A) from 4-(*N*,*N*-dimethylamino)pyridine (59.8 mg, 0.49 mmol), TCCA (78.9 mg, 0.34 mmol), and brilliant green (6.9 mg, 0.014 mmol) in CH_3CN (6 mL) at ambient temperature for 5 minutes. Yellow oil (76.6 mg, 82%); purification (hexanes:EtOAc = 50:50), R_f = 0.75. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 2H), 3.01 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.6, 149.1, 128.2, 42.6 ppm. IR (neat): ν = 2925, 2886, 2803, 1558, 1501, 1423, 956, 809 cm^{-1}. MS (EI): 191(43), 190(36), 189(64), 175(35), 169(100), 112(44).

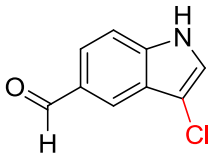
8-Chloro-7-methylquinoline (**23**)



The title compound was prepared according to the general procedure (Stoichiometry A) from 7-methylquinoline (71.5 mg, 0.5 mmol), TCCA (76.2 mg, 0.33 mmol), and brilliant green (6.4 mg, 0.013 mmol) in CH_3CN (6 mL) at ambient temperature for 5.5 h. Pink solid (53.3 mg, 60%); m.p. 44-46 °C; purification (hexanes:EtOAc =

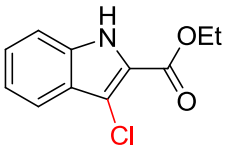
80:20), R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.01 (dd, J_1 = 4.1 Hz, J_2 = 1.8 Hz, 1H), 8.13 (dd, J_1 = 8.2 Hz, J_2 = 1.8 Hz, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.43-7.38 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.8, 144.7, 137.7, 136.3, 132.2, 129.4, 127.8, 125.8, 121.0, 21.1 ppm. IR (neat): ν = 3036, 2998, 2974, 2921, 2852, 1617, 1595, 1499, 1455, 1437, 1346, 1314, 1051, 1030, 979, 826, 785, 720, 640 cm^{-1}. MS (EI): 179(20), 177(63), 142(100), 141(24), 140(12), 115(18), 114(18), 113(11), 75(30), 71(33). HRMS (ESI): calculated for $C_{10}H_9N_1Cl_1$ $[M + H]^+$ requires *m/z* 178.04235, found *m/z* 178.04220.

3-chloro-1H-indole-5-carboxaldehyde (**24**)[25]



The title compound was prepared according to the general procedure (Stoichiometry C) from 5-formylindole (36.6 mg, 0.25 mmol), TCCA (21.7 mg, 0.09 mmol), and brilliant green (3.7 mg, 0.008 mmol) in CH_3CN (3 mL) at ambient temperature for 50 minutes. Light pink solid (28.2 mg, 63%); purification (hexanes:EtOAc = 60:40), R_f = 0.41. ^{1}H NMR (400 MHz, CD_3OD): δ = 9.99 (s, 1H), 8.13 (d, J = 1.6 Hz, 1H), 7.76 (dd, J_1 = 8.6 Hz, J_2 = 1.6 Hz, 1H), 7.52 (m, 1H), 7.42 (s, 1H), 3.35 (s, 1H) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 194.2, 140.2, 131.0, 126.5, 125.0, 124.3, 123.2, 113.7, 108.0 ppm. IR (neat): ν = 3347, 2961, 2926, 2829, 1672, 1609, 1576, 1510, 1422, 1290, 1164 cm^{-1}. MS (EI): 179(26), 178(34), 159(65), 132(34), 131(48), 104(50), 103(100), 75(98), 74(63).

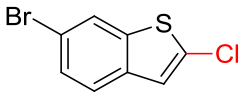
Ethyl 3-chloroindole-2-carboxylate (**25**)[24]



The title compound was prepared according to the general procedure (Stoichiometry A) from ethylindole-2-carboxylate (93.7 mg, 0.5 mmol), TCCA (76.8 mg, 0.33 mmol), and brilliant green (7.0 mg, 0.014 mmol) in CH_3CN (6 mL) at ambient temperature for 5 minutes. Yellow solid (69.8 mg, 63%): m.p. 146-150 °C; purification (hexanes:EtOAc = 90:10), R_f = 0.08. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (bs, 1H), 7.73 (m, 1H), 7.40-7.37 (m,

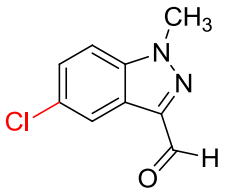
2H), 7.25-7.20 (m, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 1.45 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9, 134.7, 126.6, 126.3, 122.4, 121.3, 120.3, 112.5, 112.0, 61.4, 14.4 ppm. IR (neat): ν = 3291, 2982, 2922, 1680, 1521 cm^{-1}. MS (EI): 179(10), 178(5), 177(28), 148(5), 147(10), 146(100), 114(9), 90(41).

6-bromo-2-chlorobenzothiophene (**26**)



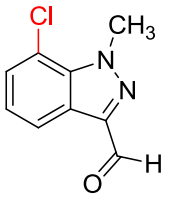
The title compound was prepared according to the general procedure (Stoichiometry A) from 6-bromo-1-benzothiophene (53.3 mg, 0.25 mmol), TCCA (40.0 mg, 0.168 mmol), and brilliant green (3.4 mg, 0.007 mmol) in CH_3CN (3 mL) at ambient temperature for 1.5 h. White solid (24.8 mg, 40%); decomposition point 79-81 °C; purification (hexanes), R_f = 0.57. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 1.6 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.57 (dd, J_1 = 8.6 Hz, J_2 = 1.6 Hz, 1H), 7.29 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.8, 135.0, 128.4, 125.4, 123.1, 121.3, 119.6 ppm. IR (neat): ν = 3060, 2922, 1699, 1591, 1480, 1428, 1248, 1248, 1083, 1039 cm^{-1}. MS (EI): 248(100), 246(84), 167(53), 132(46), 123(55), 83(36), 69(34), 66(92). HRMS (ESI): calculated for $C_8H_5S_1Br_1Cl_1$ $[M + H]^+$ requires *m/z* 246.89839, found *m/z* 246.89740.

5-chloro-1-methyl-indazole-3-carboxaldehyde and 7-chloro-1-methyl-indazole-3-carboxaldehyde (**27**)



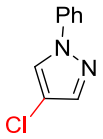
The title compound was prepared according to the general procedure (Stoichiometry A) from 1-methyl-indazole-3-carboxaldehyde (19.9 mg, 0.125 mmol), TCCA (19.0 mg, 0.08 mmol), and brilliant green (1.6 mg, 0.003 mmol) in CH_3CN (1.5 mL) at ambient temperature for 4.5 h. Pale yellow solid (11.8 mg, 49%); m.p. 113-115 °C; purification (hexanes:EtOAc = 80:20), R_f = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.19 (s, 1H), 8.30 (d, *J* = 2.0 Hz, 1H), 7.46-7.39 (m, 2H), 4.19 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.3, 142.2, 139.8, 130.2, 128.3, 122.8, 121.6, 110.5, 36.8 ppm. IR (neat): ν = 3210, 3076, 2828, 1673, 1476, 1341, 1293, 1233, 1140, 1079,

1041, 1021, 836, 789 cm^{-1}. HRMS (ESI): calculated for $C_9H_8N_2O_1Cl_1$ $[M + H]^+$ requires *m/z* 195.032516, found *m/z* 195.03120.



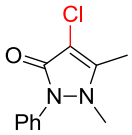
The title compound was prepared according to the general procedure (Stoichiometry A) from 1-methyl-indazole-3-carboxaldehyde (19.9 mg, 0.125 mmol), TCCA (19.0 mg, 0.08 mmol), and brilliant green (1.6 mg, 0.003 mmol) in CH_3CN (1.5 mL) at ambient temperature for 4.5 h. Pale yellow solid (9.7 mg, 40%); m.p. 136-139 °C; purification (hexanes:EtOAc = 80:20), R_f = 0.74. ^1H NMR (400 MHz, $CDCl_3$): δ = 10.19 (s, 1H), 8.23 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 7.44 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 7.25 (t, J = 8.0 Hz, 1H), 4.52 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.4, 142.5, 137.6, 128.5, 124.9, 124.7, 121.0, 116.5, 40.4 ppm. IR (neat): ν = 2956, 2920, 2842, 2815, 1682, 1499, 1461, 1288, 1220, 1178, 1074, 1026, 796, 779, 743, 519 cm^{-1}.

4-chloro-1-phenylpyrazole (**28**)[24]



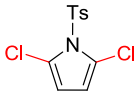
The title compound was prepared according to the general procedure (Stoichiometry A) from 1-phenylpyrazole (66 µL, 0.5 mmol), TCCA (76.4 mg, 0.33 mmol), and brilliant green (6.6 mg, 0.014 mmol) in CH_3CN (6 mL) at ambient temperature for 10 minutes. Yellow solid (65.6 mg, 74%): m.p. 58-61 °C; purification (hexanes:EtOAc = 85:15), R_f = 0.50. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (s, 1H), 7.65-7.61 (m, 3H), 7.49-7.43 (m, 2H), 7.34-7.29 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.5, 129.5, 127.0, 124.8, 119.0, 118.9, 112.4 ppm. IR (neat): ν = 3116, 3051, 1766, 1597, 1498 cm^{-1}. MS (EI): 180(31), 178(96), 116(26), 89(38), 77(92), 51(100).

4-chloro-1,2-dihydro-1,5-dimethyl-2-phenyl- 3H-Pyrazol-3-one (**29**)[26]



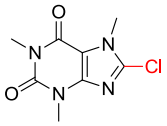
The title compound was prepared according to the general procedure (Stoichiometry C) from phenazone (94.3 mg, 0.5 mmol), TCCA (42.4 mg, 0.18 mmol), and brilliant green (6.4 mg, 0.013 mmol) in CH_3CN (6 mL) at ambient temperature for 10 minutes. Light green solid (68.3 mg, 61%): m.p. 118-120 °C; purification (hexanes:EtOAc = 80:20), R_f = 0.75. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.43 (m, 2H), 7.40-7.37 (m, 2H), 7.32-7.27 (m, 1H), 3.06 (s, 3H), 2.29 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5, 152.0, 134.7, 129.3, 127.0, 124.1, 103.5, 36.5, 11.2 ppm. IR (neat): ν = 3024, 2924, 1662, 1592, 1492, 1458, 1347, 1243, 1126, 760, 585 cm^{-1}. MS (EI): 224(4), 222(5), 189(4), 132(7), 130(8), 119(13), 105(38), 91(38), 77(100), 56(59), 51(62).

2,5-dichloro-1-(p-toluenesulfonyl)-pyrrole (**30**)[24]



The title compound was prepared according to the general procedure (Stoichiometry A) from 1-(p-toluenesulfonyl)-pyrrole (110.7 mg, 0.5 mmol), TCCA (84.6 mg, 0.36 mmol), and brilliant green (6.3 mg, 0.013 mmol) in CH_3CN (6 mL) at ambient temperature for 30 minutes. Yellow solid (125.2 mg, 86%): m.p. 95-97 °C; purification (hexanes:EtOAc = 95:5), R_f = 0.20. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 6.10 (s, 2H), 2.45 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.9, 135.4, 130.0, 127.6, 117.6, 112.6, 21.7 ppm. IR (neat): ν = 3146, 2924, 1921, 1595, 1552, 1458, 1384 cm^{-1}. MS (EI): 258(2), 255(6), 187(2), 155(234), 91(100), 65(36), 44(62).

8-chloro-1,3,7-trimethylpurinedione (**31**)[7]



The title compound was prepared according to the general procedure (Stoichiometry A) from caffeine (100.1 mg, 0.5 mmol), TCCA (78.0 mg, 0.33 mmol), and brilliant green (6.7 mg, 0.014 mmol) in CH_3CN (6 mL) at ambient temperature for 35 minutes. White powdery solid (92.2 mg, 78%): m.p. 178-180 °C; purification (DCM:EtOAc = 5:3), R_f = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.95 (s, 3H), 3.54 (s, 3H), 3.39 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6, 151.3, 147.1, 139.0, 108.3, 32.7, 29.8, 28.0 ppm. IR (neat): ν = 2955, 2920, 1752, 1703, 1657, 1538, 1452, 755, 742 cm^{-1}. MS (EI): 230(19), 228(72), 145(16), 143(47), 82(29), 67(100), 55(78), 42(29), 40(30).

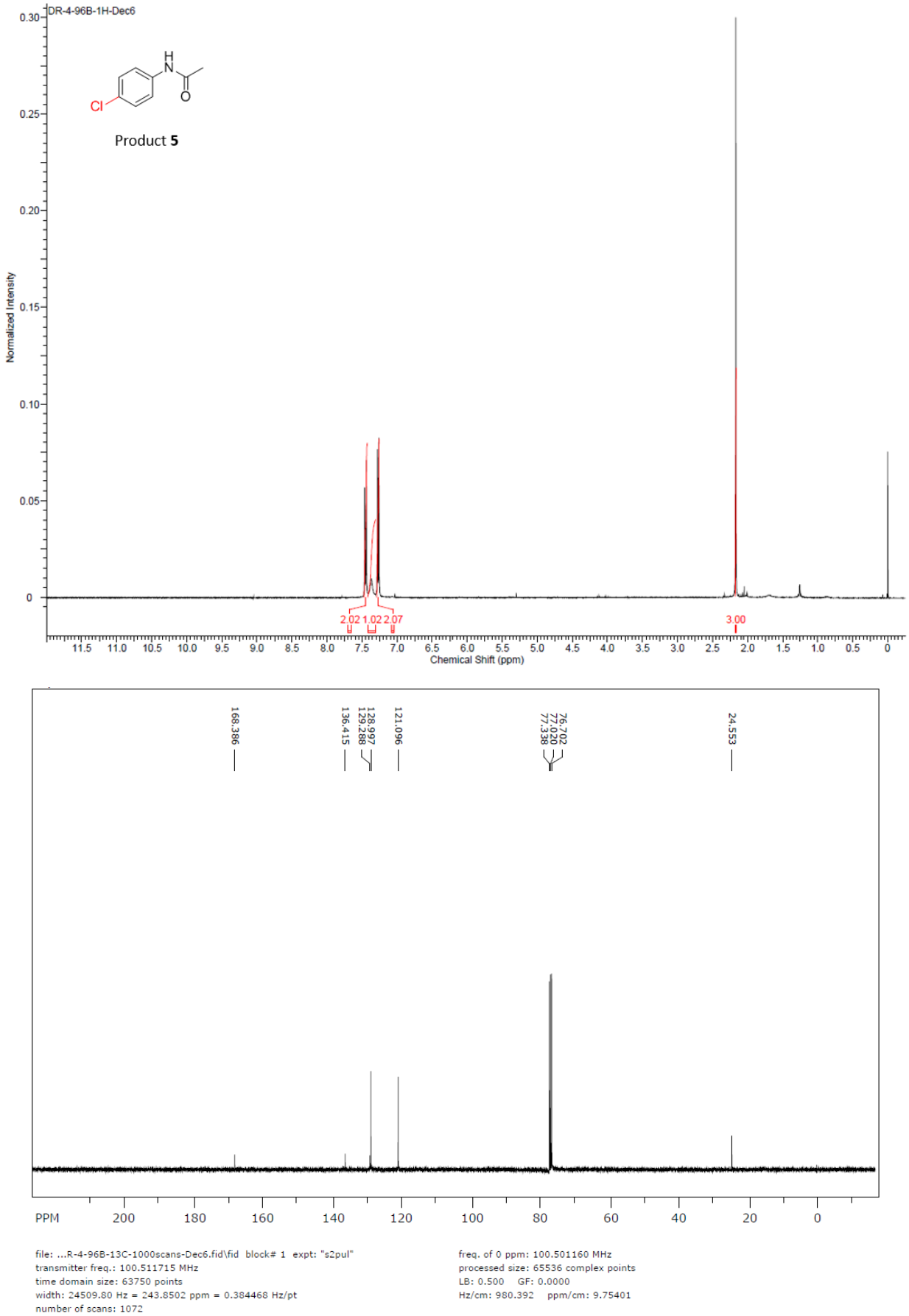


Figure S9. ^{1}H and ^{13}C NMR of Product **5**.

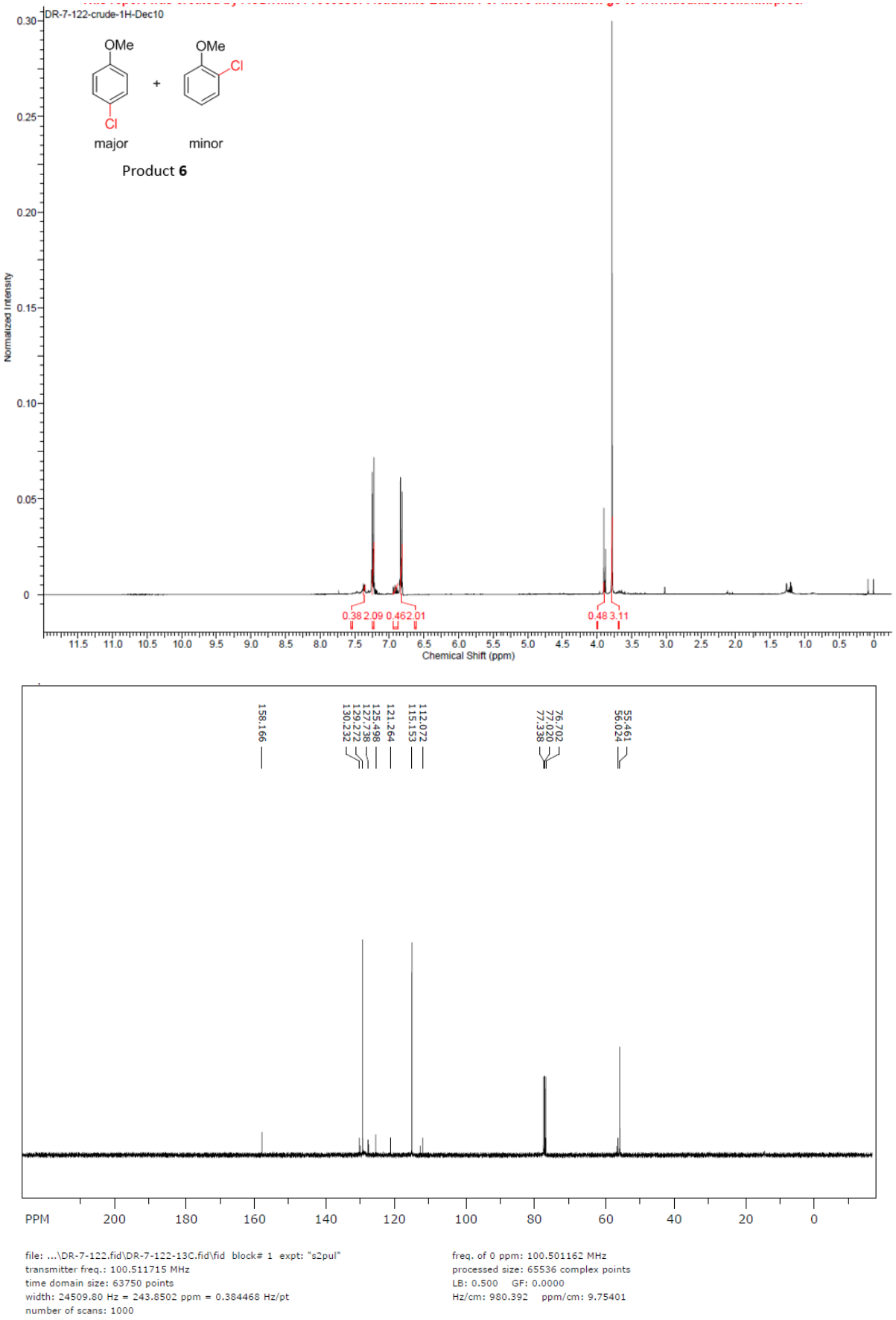


Figure S10. ^{1}H and ^{13}C NMR of Product **6**.

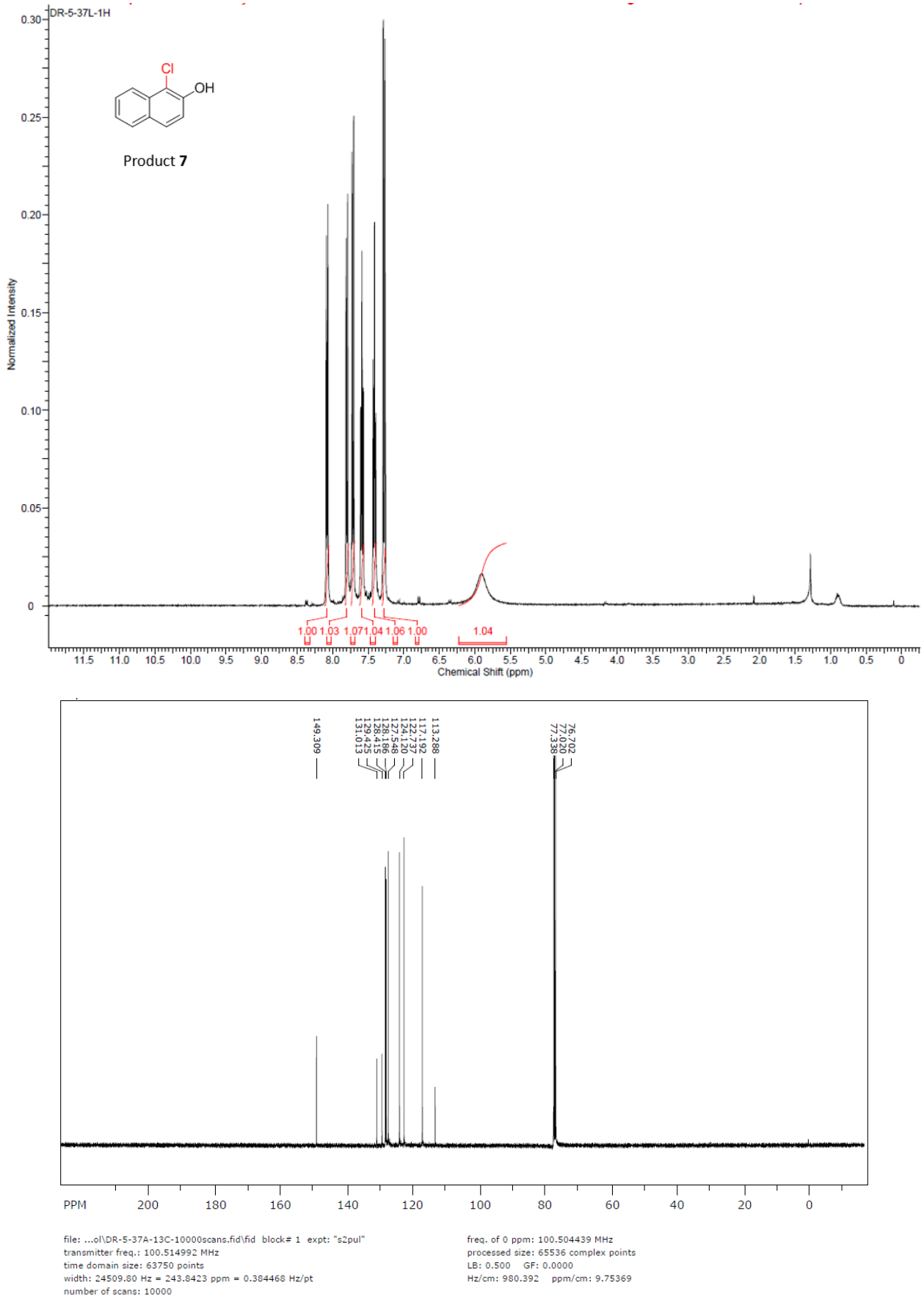


Figure S11. ^{1}H and ^{13}C NMR of Product **7**.

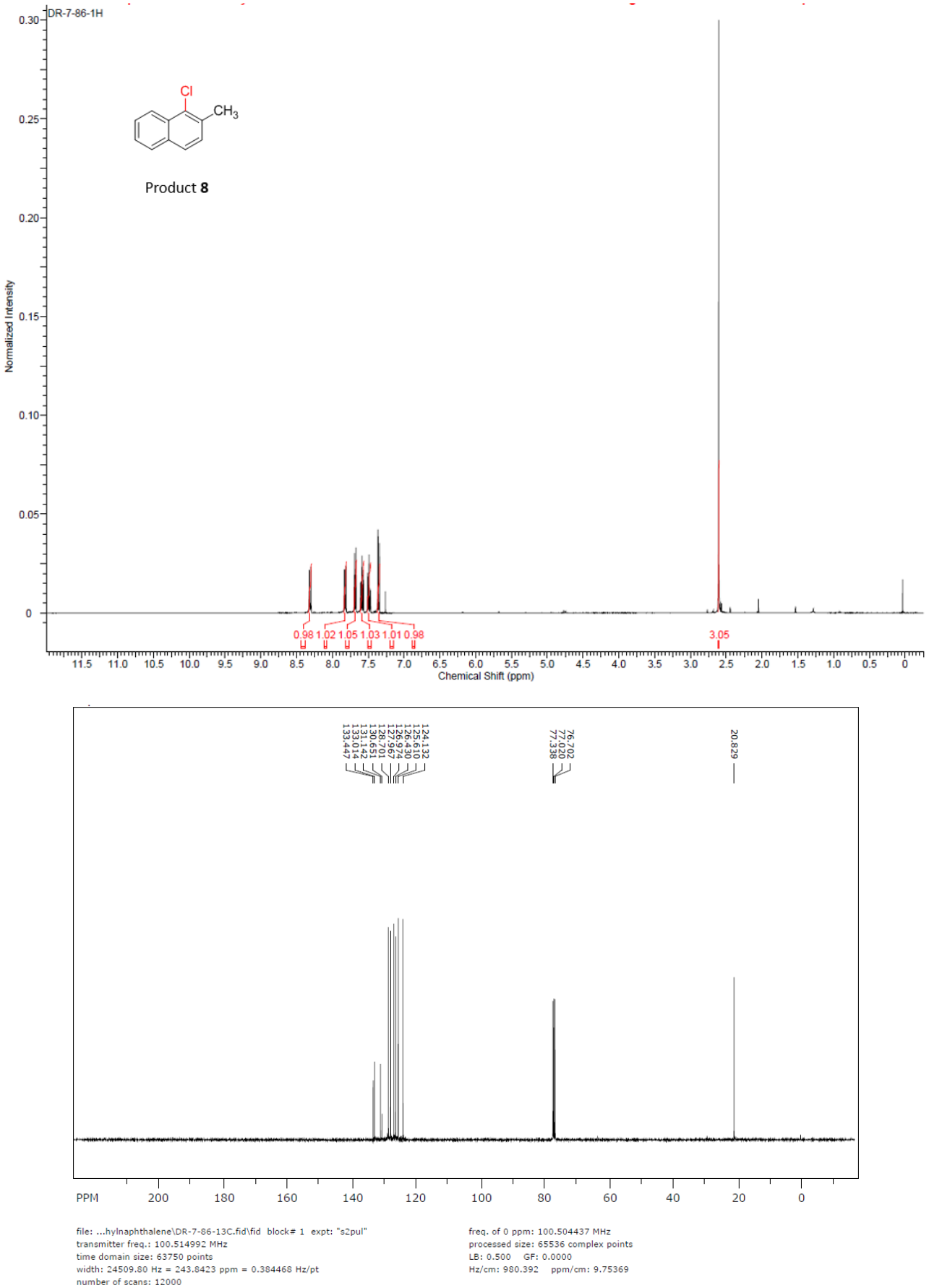


Figure S12. ^{1}H and ^{13}C NMR of Product **8**.

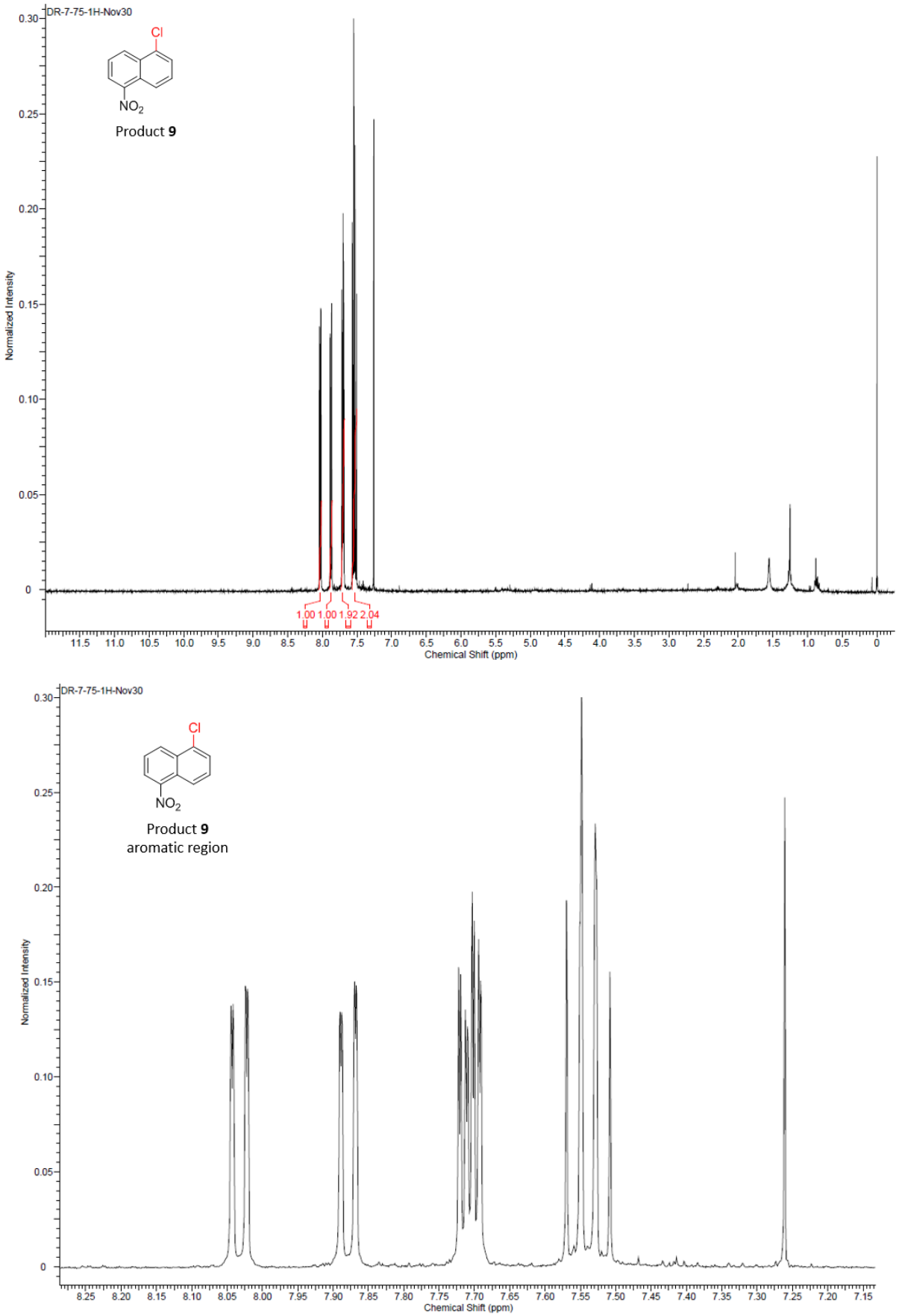


Figure S13. ^{1}H of Product **9**.

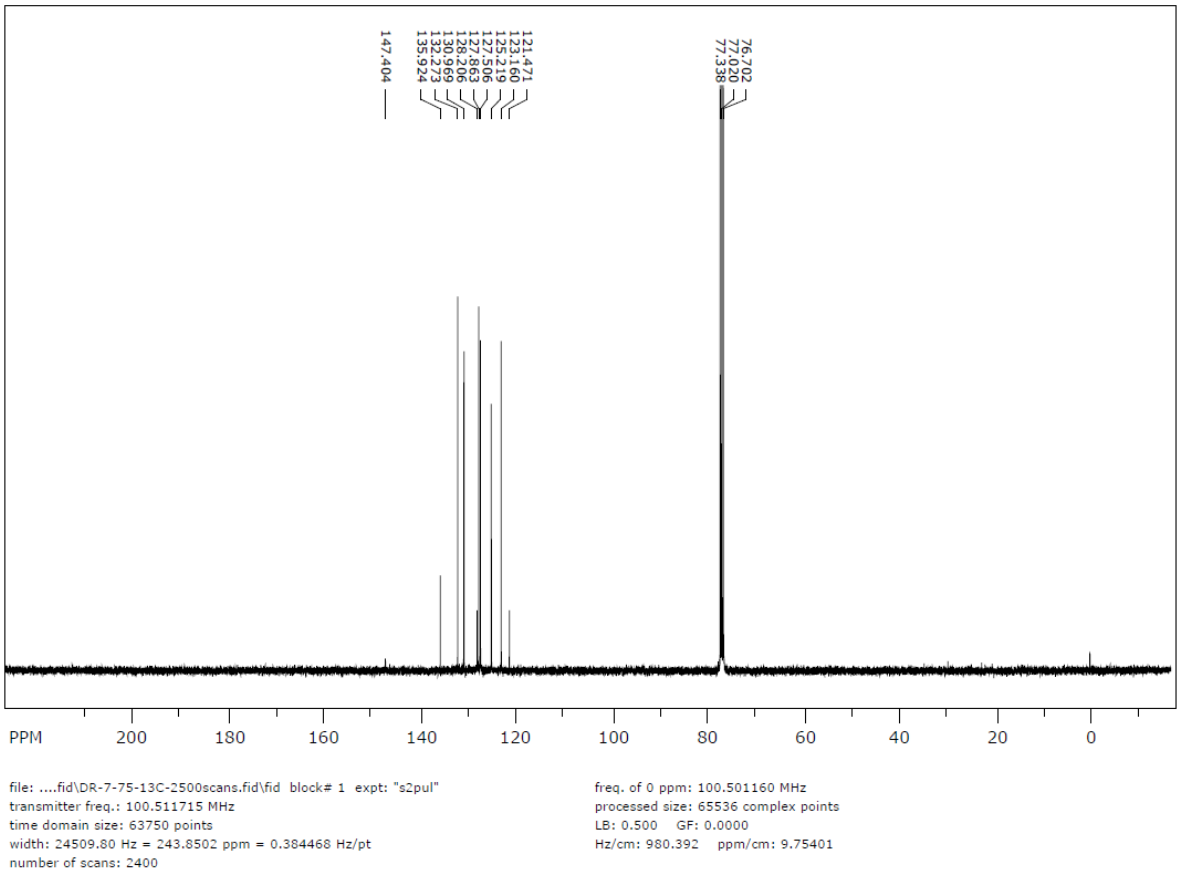


Figure S14. ^{13}C NMR of Product **9**.

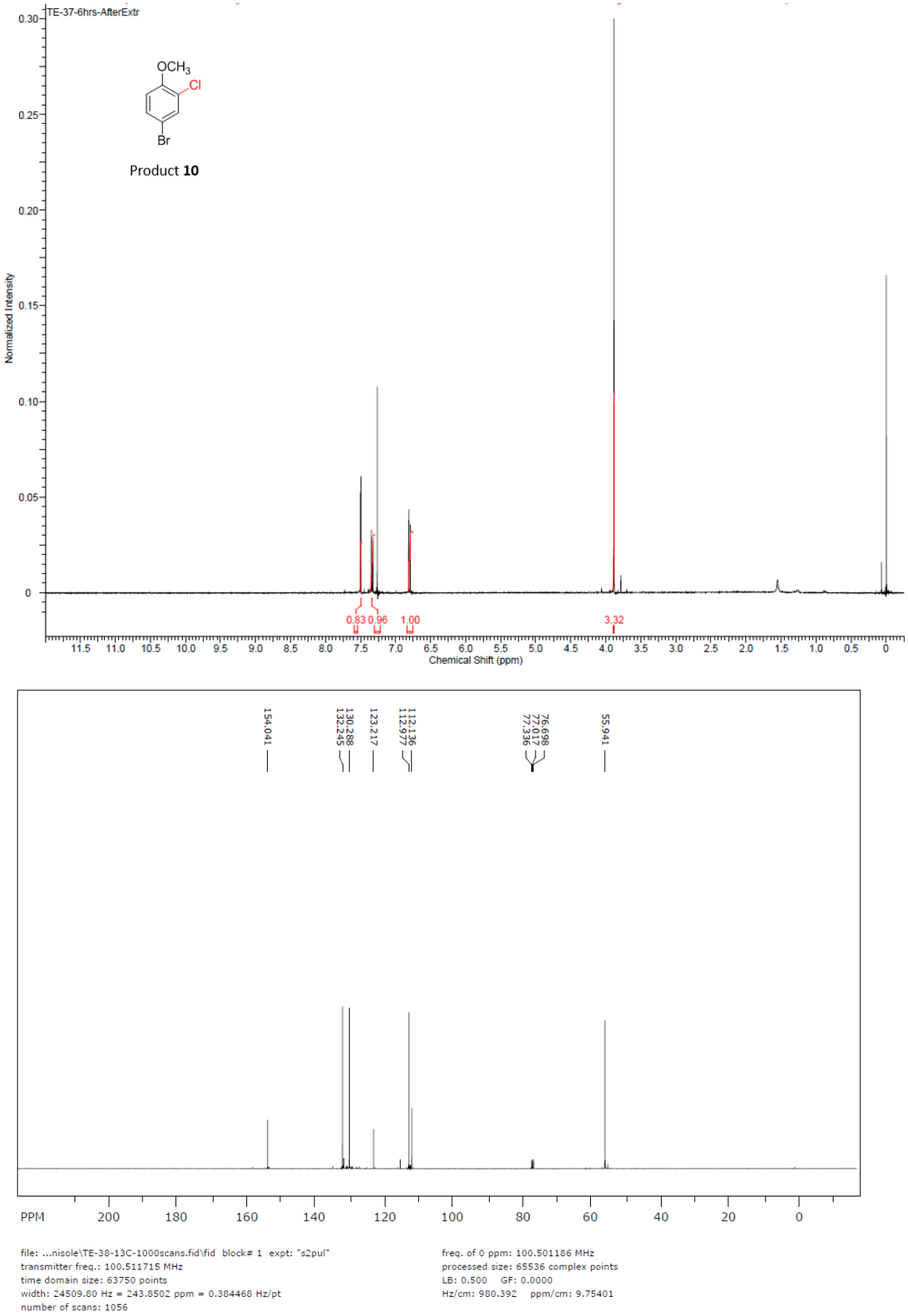


Figure S15. ^{1}H and ^{13}C NMR of Product **10**.

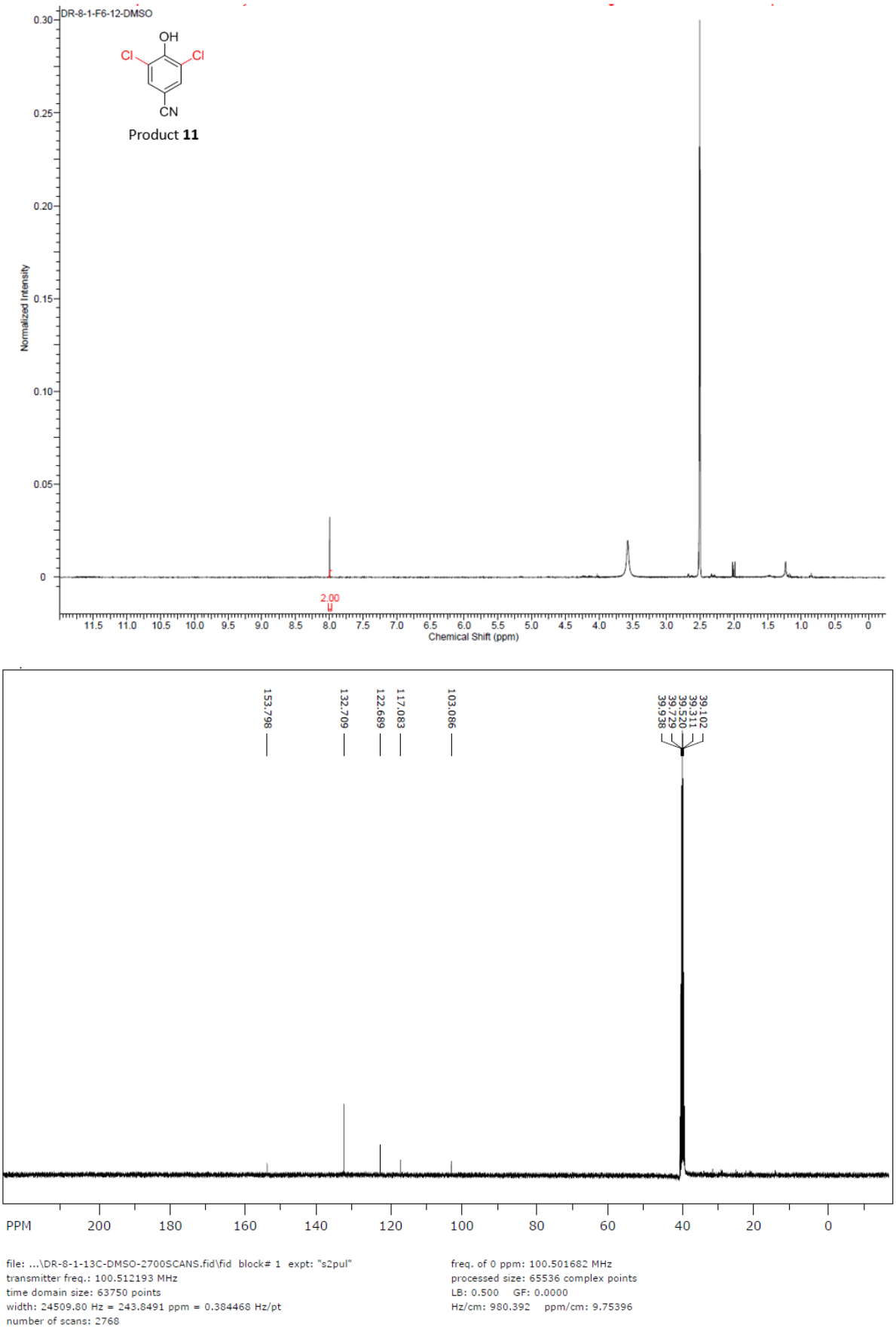


Figure S16. ^{1}H and ^{13}C NMR of Product **11**.

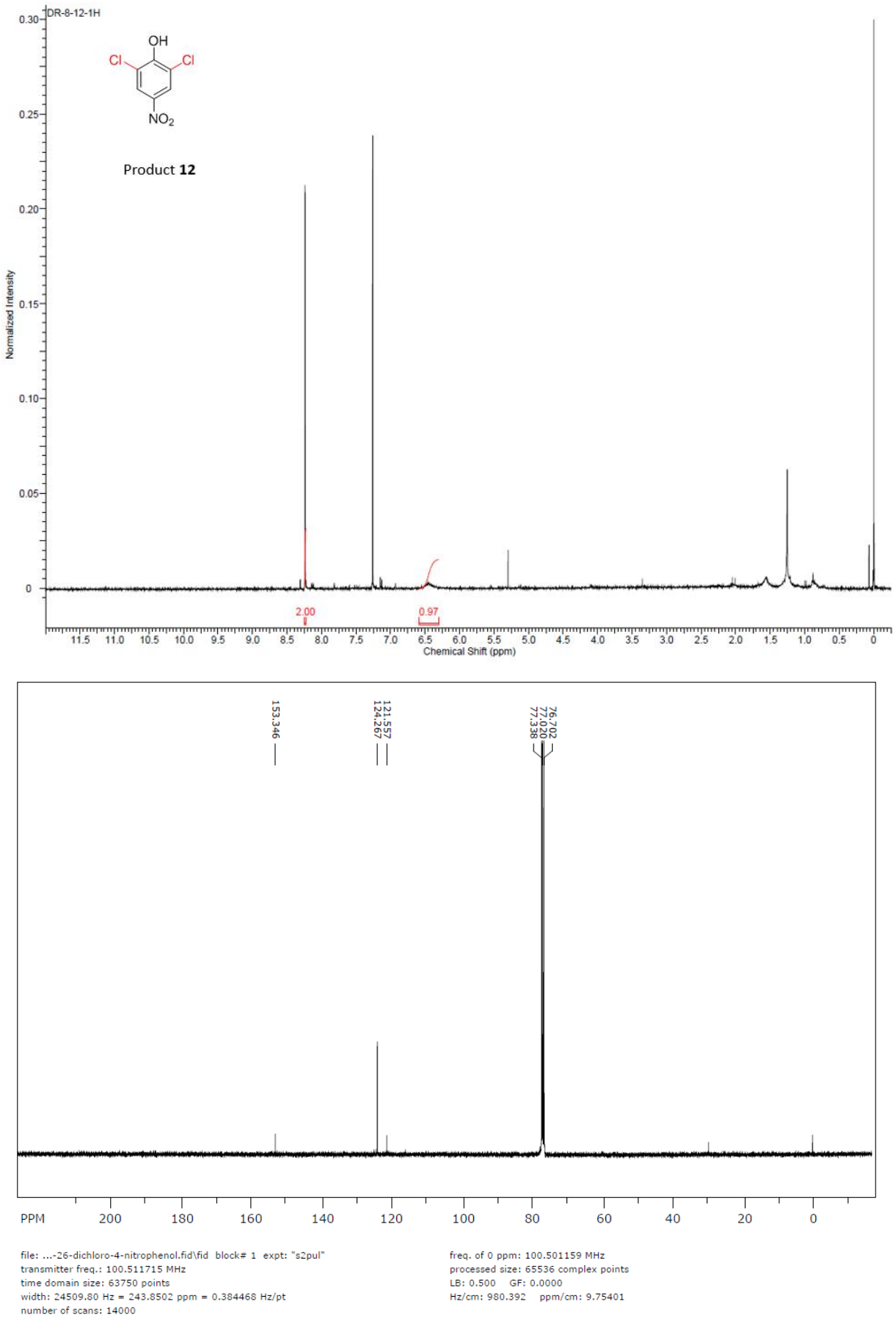


Figure S17. ^{1}H and ^{13}C NMR of Product **12**.

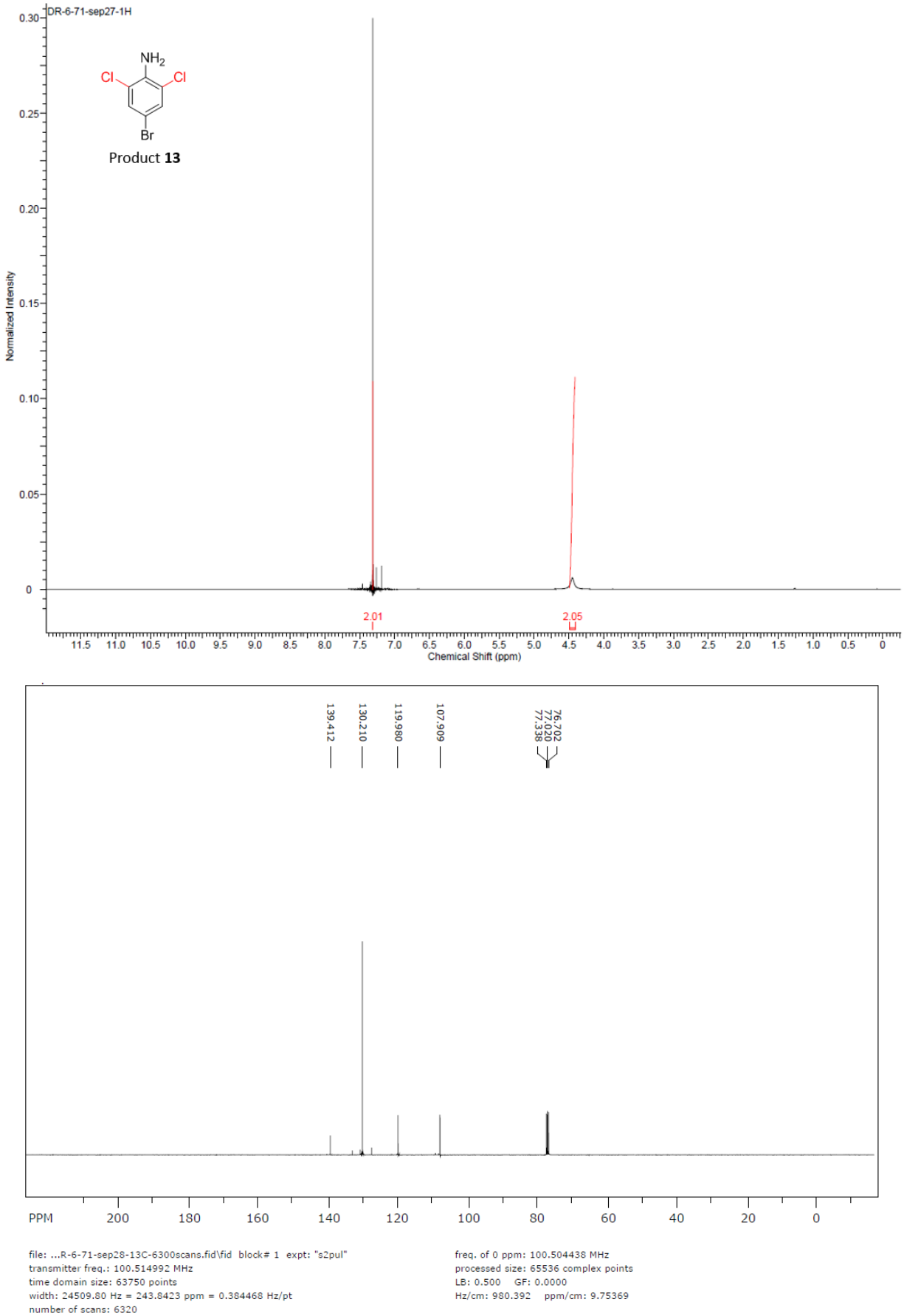


Figure S18. ^{1}H and ^{13}C NMR of Product **13**.

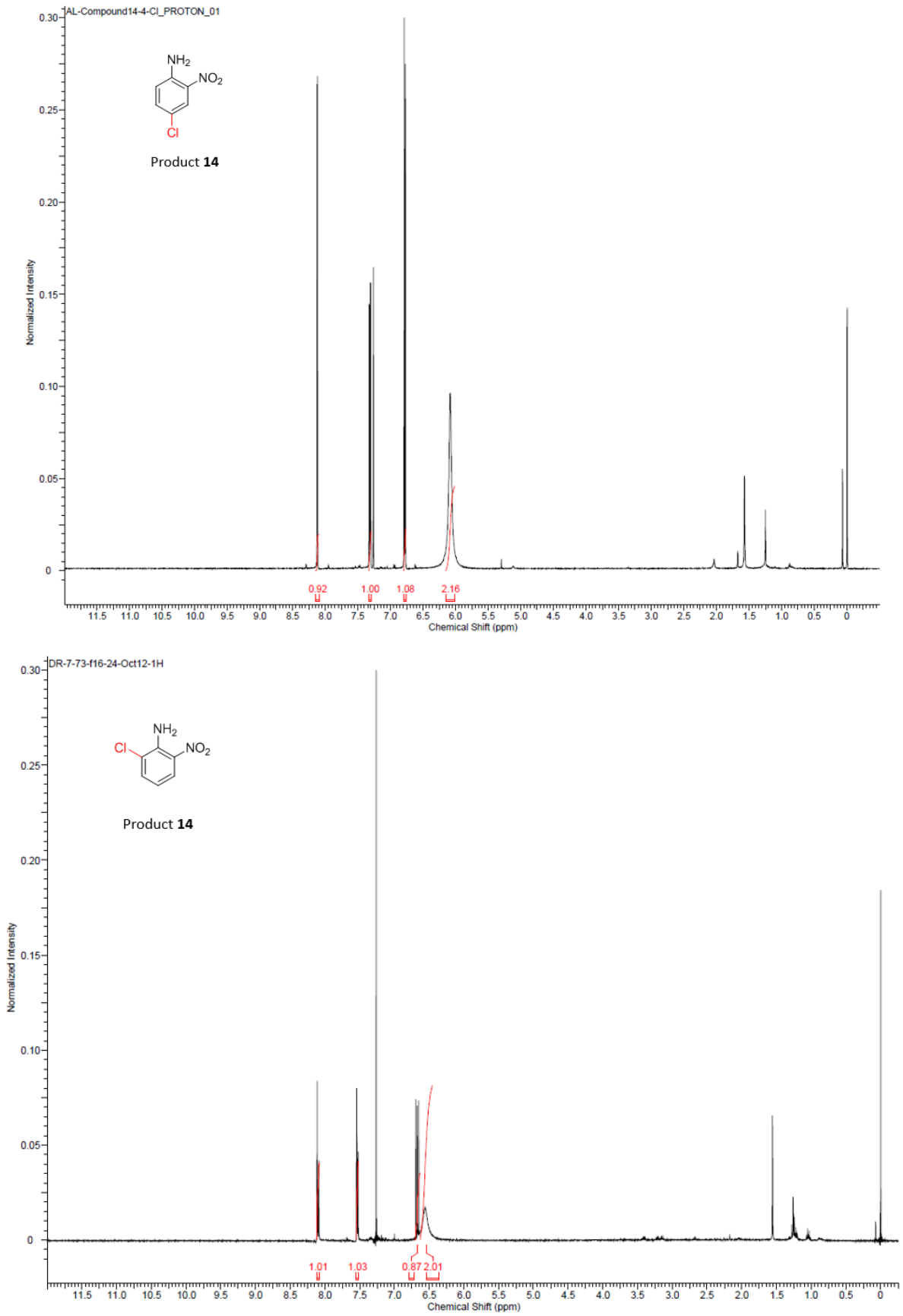


Figure S19. ^{1}H of both (4-Cl and 6-Cl) Product **14** isomers.

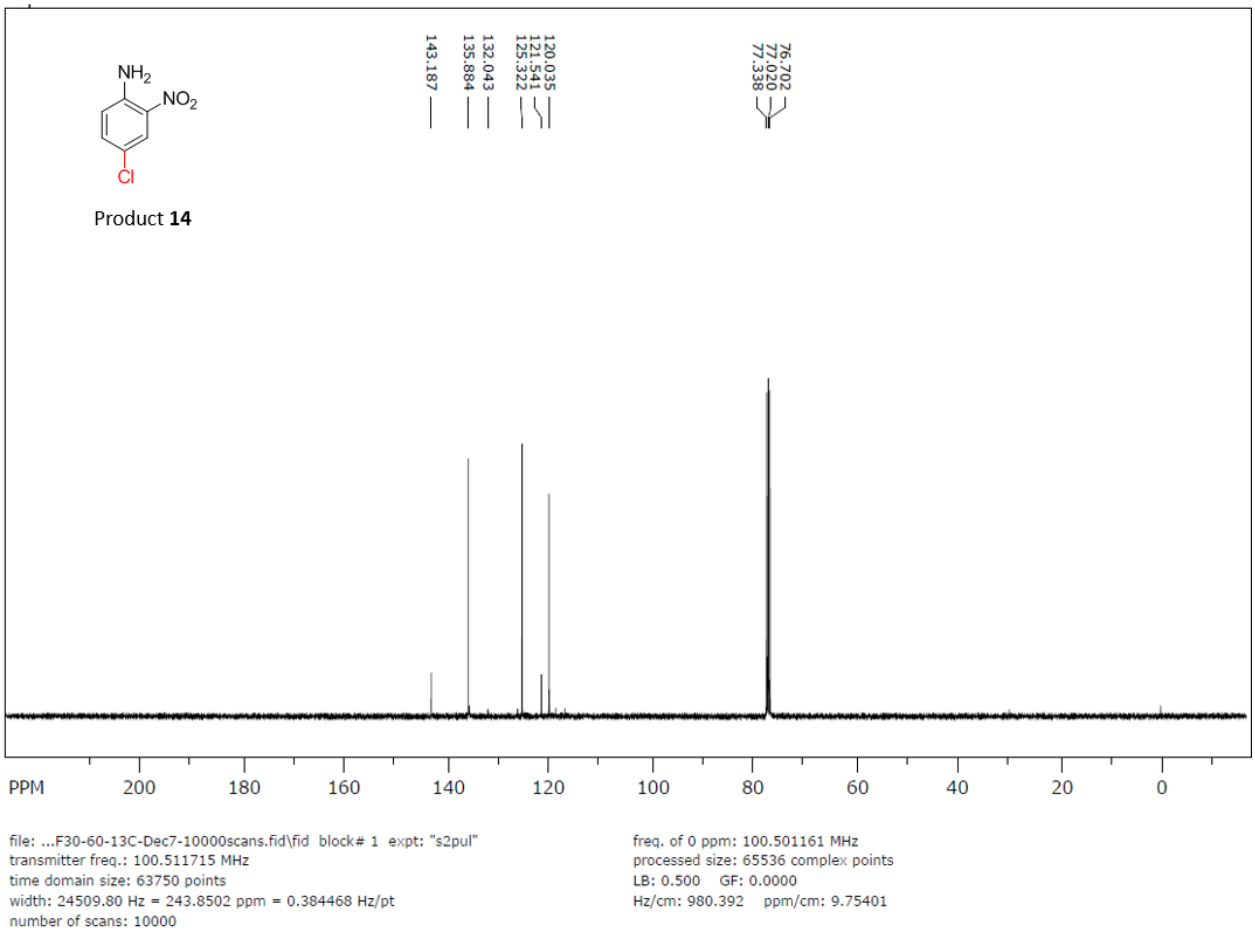


Figure S20. ^{13}C of 4-Cl Product **14** (major) isomer.

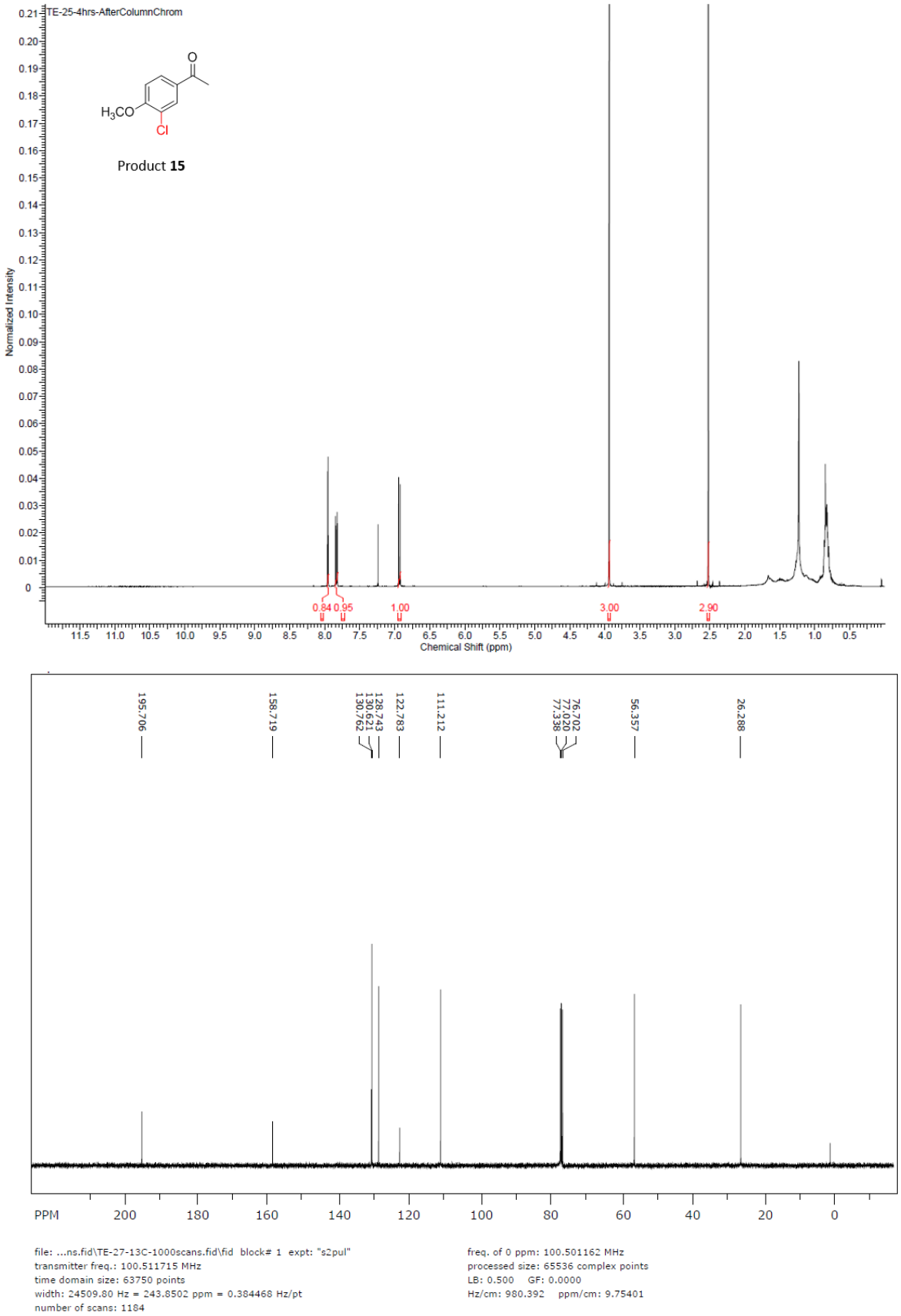


Figure S21. ^{1}H and ^{13}C NMR of Product **15**.

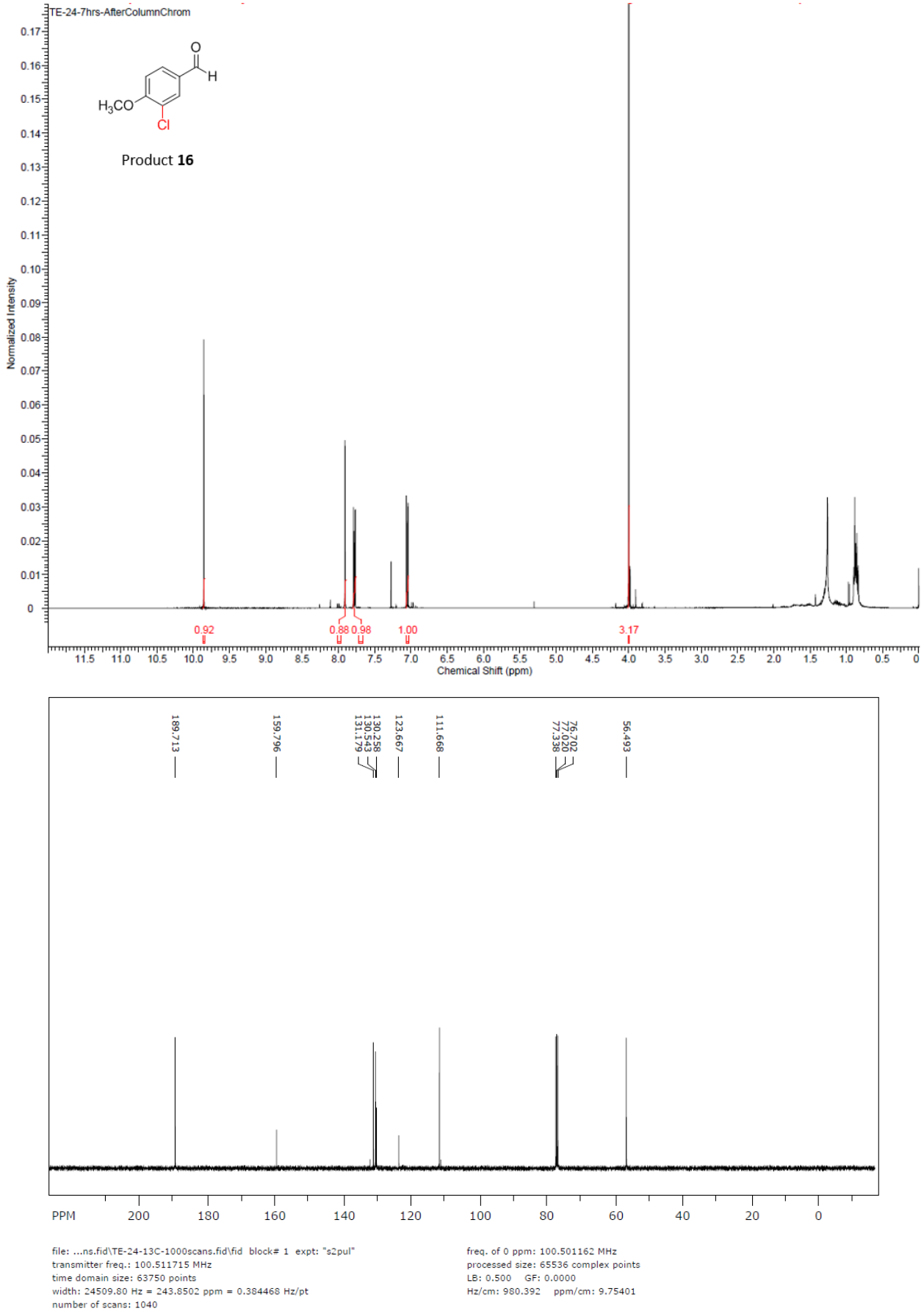


Figure S22. ^{1}H and ^{13}C NMR of Product **16**.

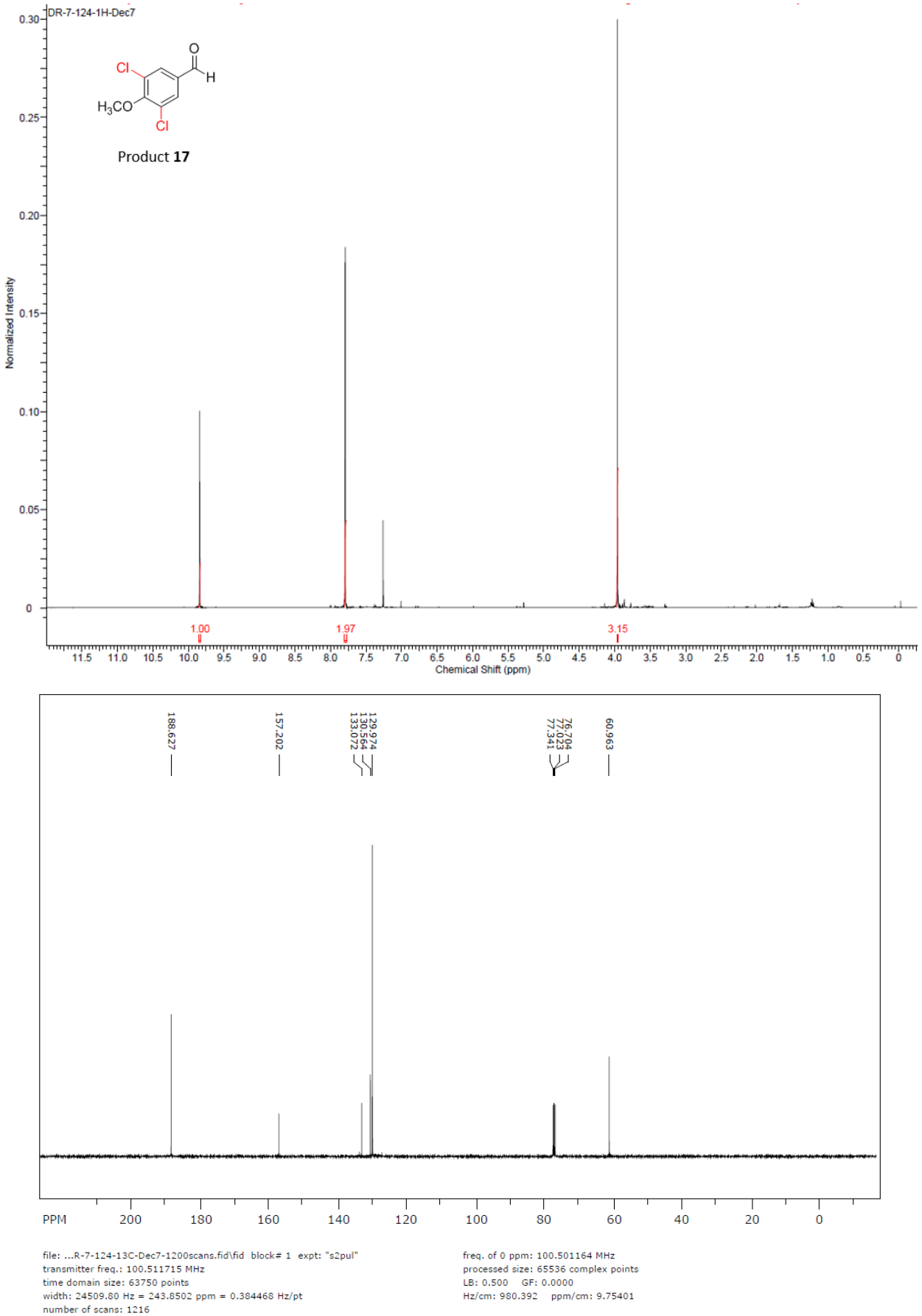


Figure S23. ^{1}H and ^{13}C NMR of Product **17**.

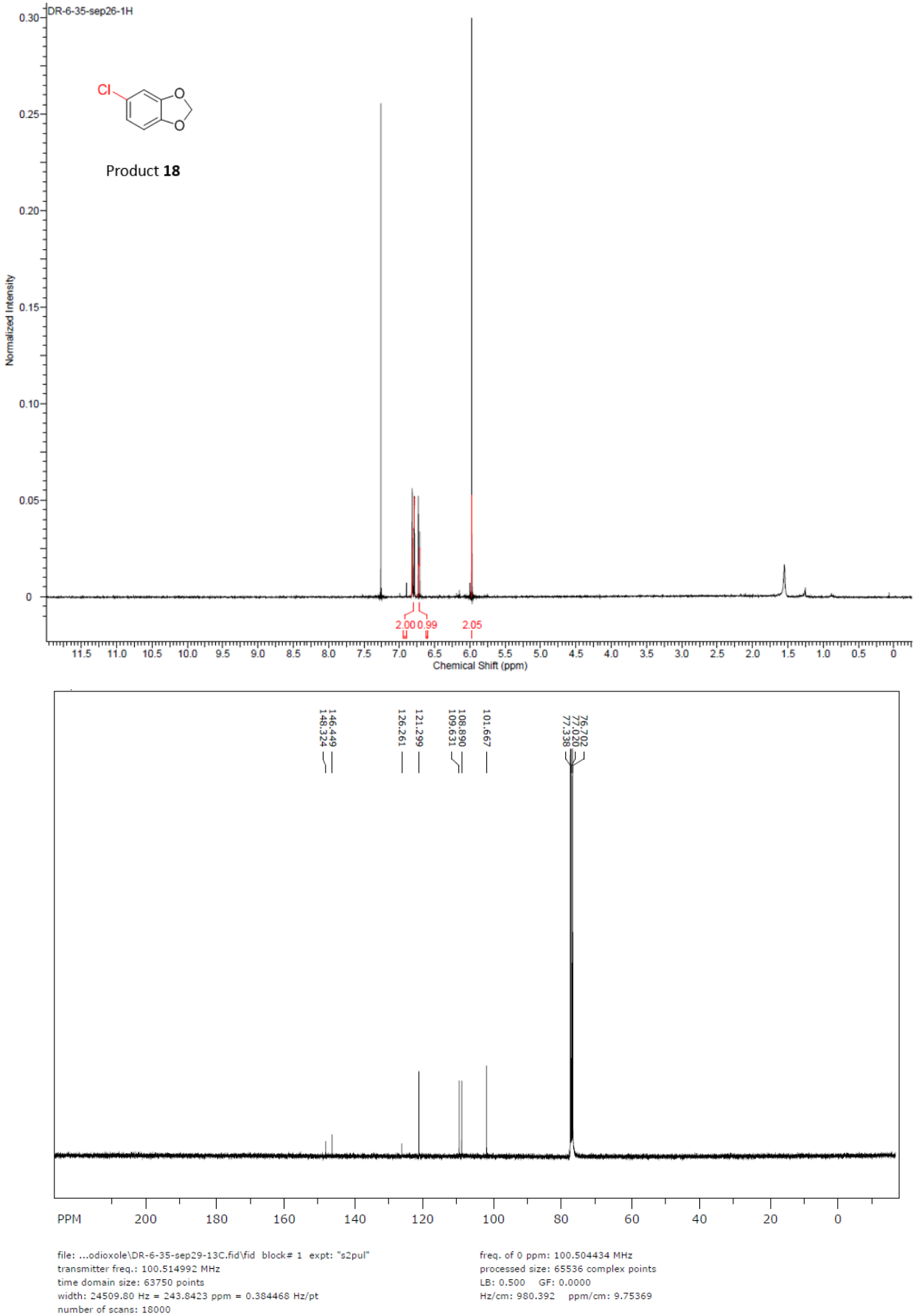


Figure S24. ^{1}H and ^{13}C NMR of Product **18**.

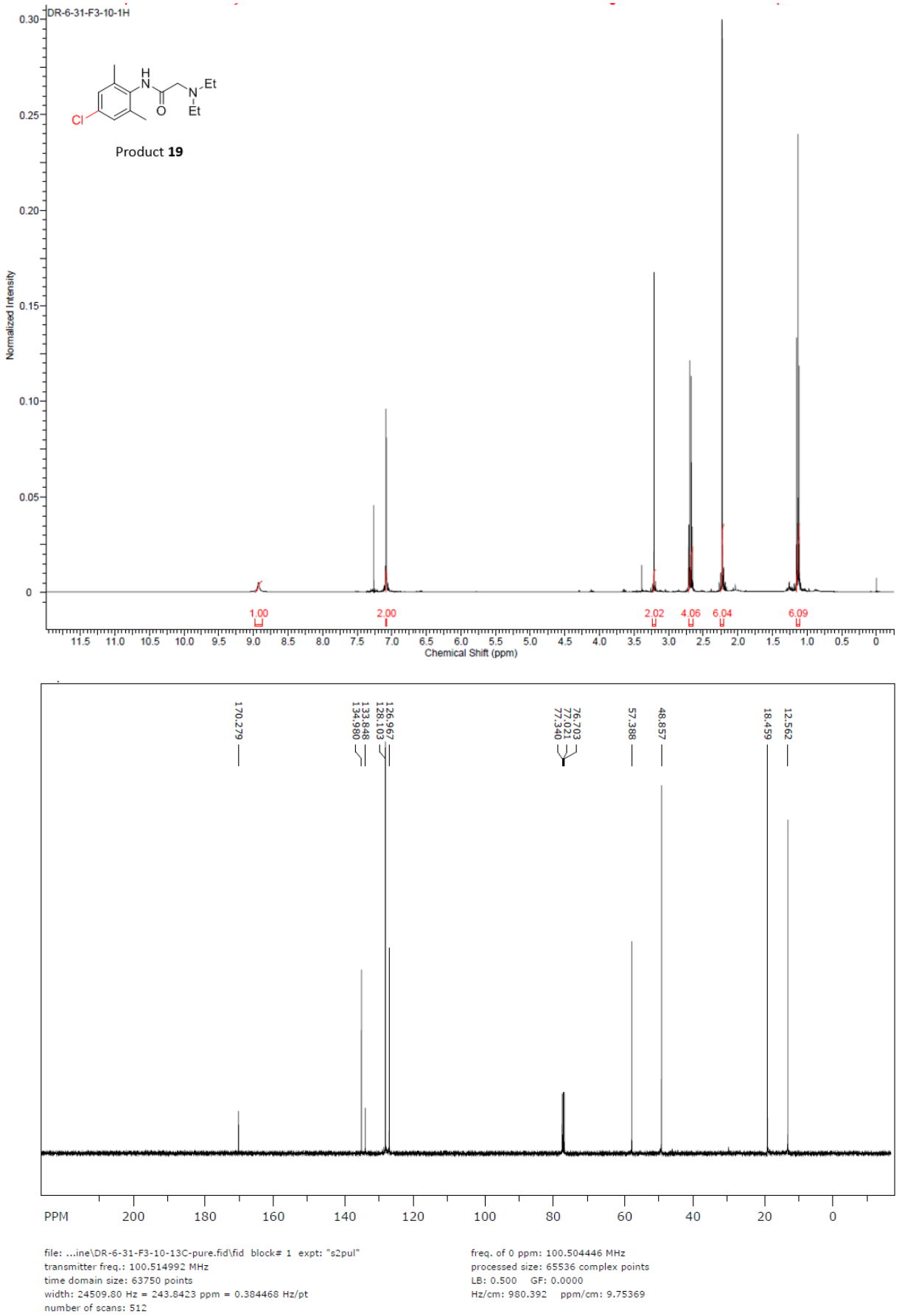


Figure S25. ^{1}H and ^{13}C NMR of Product **19**.

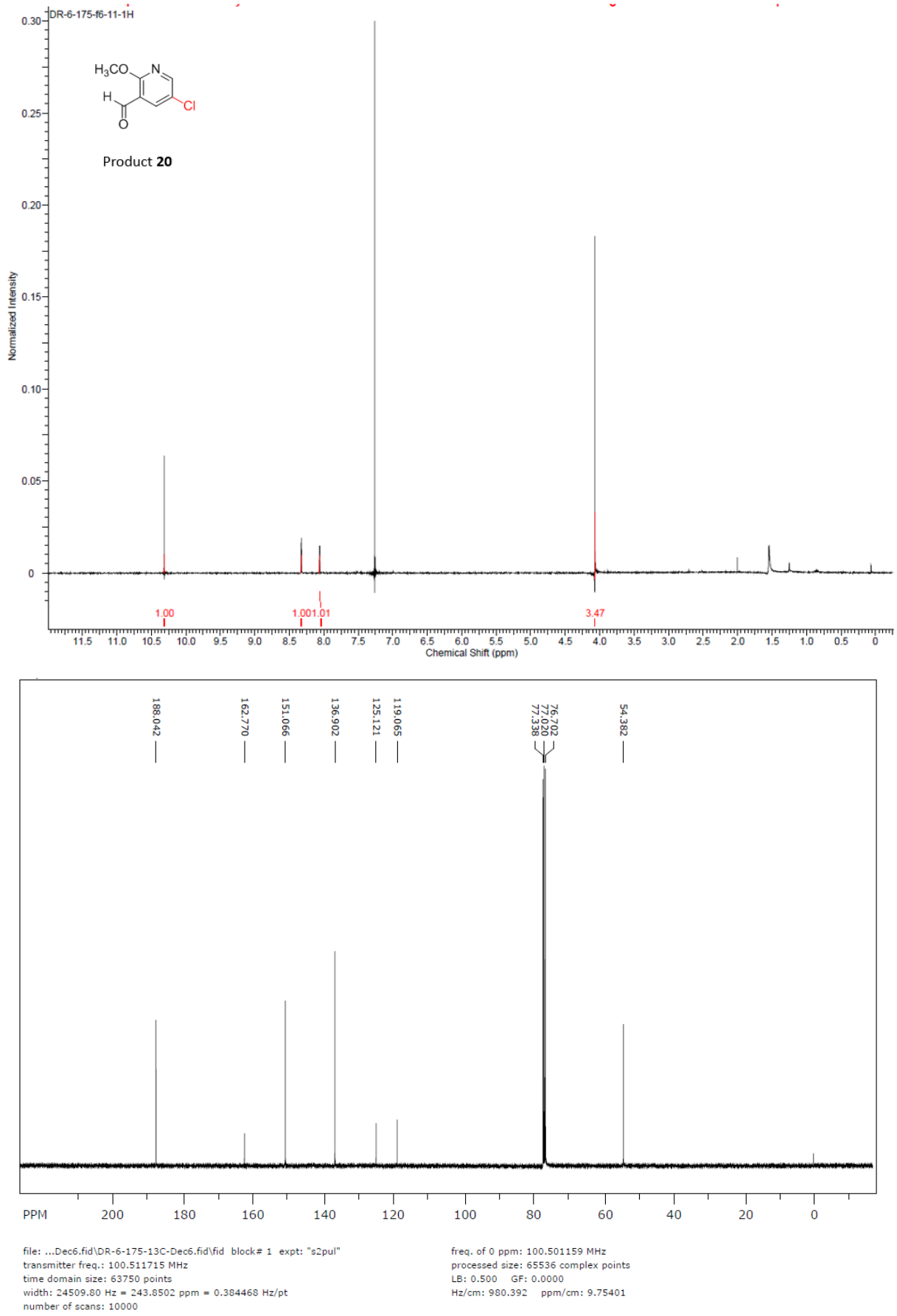


Figure S26. ^{1}H and ^{13}C NMR of Product **20**.

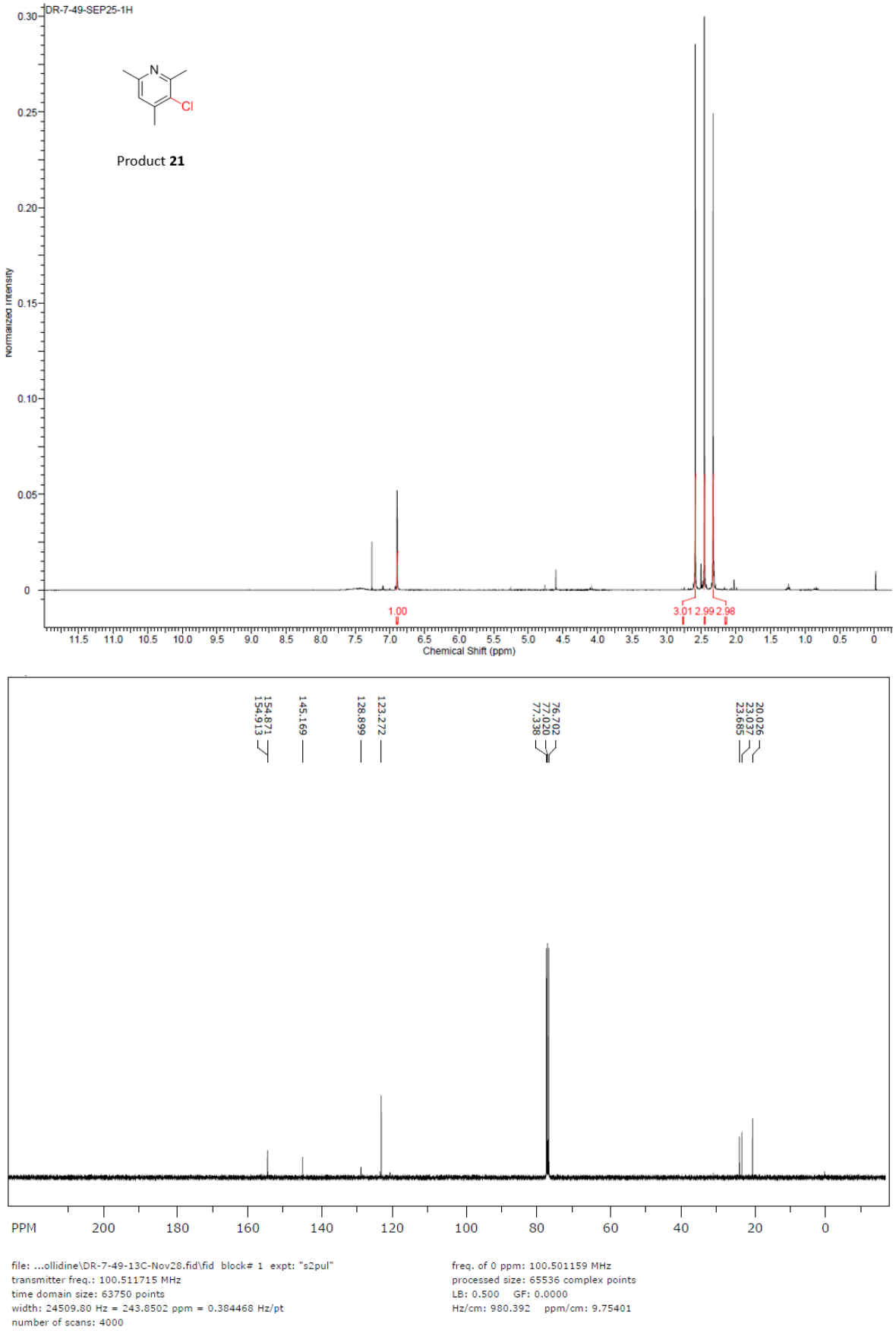


Figure S27. ^{1}H and ^{13}C NMR of Product **21**.

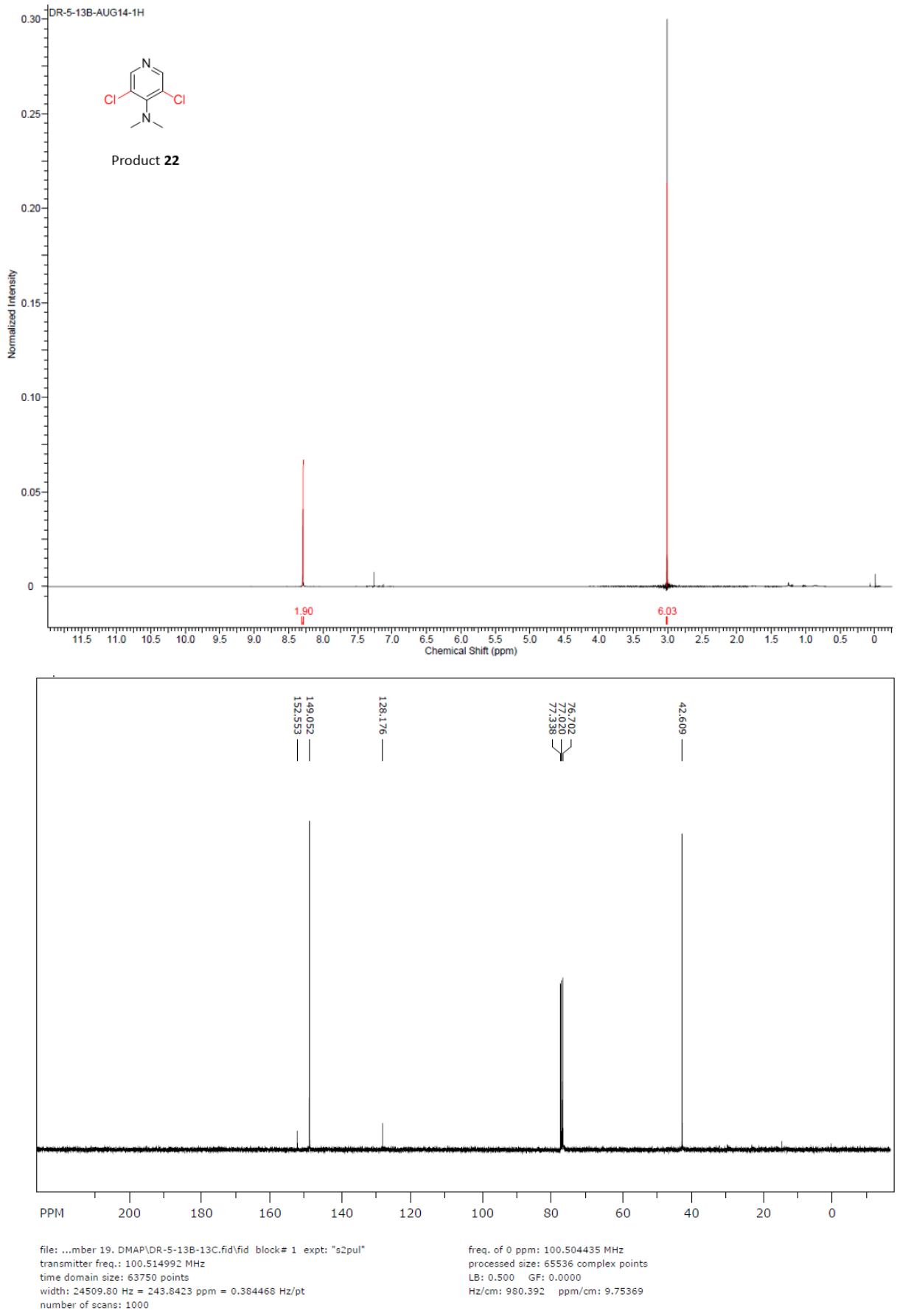


Figure S28. ^{1}H and ^{13}C NMR of Product **22**.

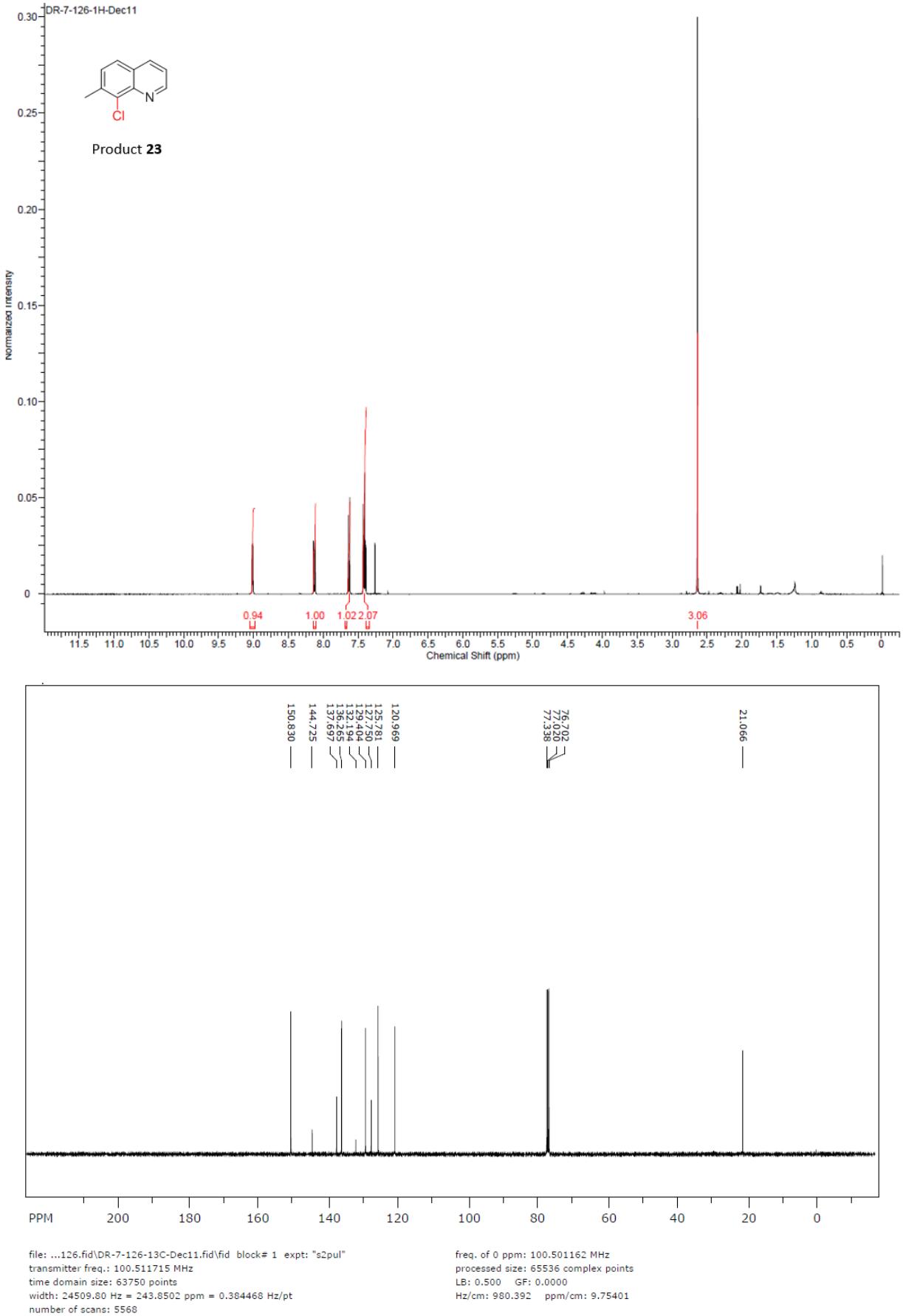


Figure S29. ^{1}H and ^{13}C NMR of Product **23**.

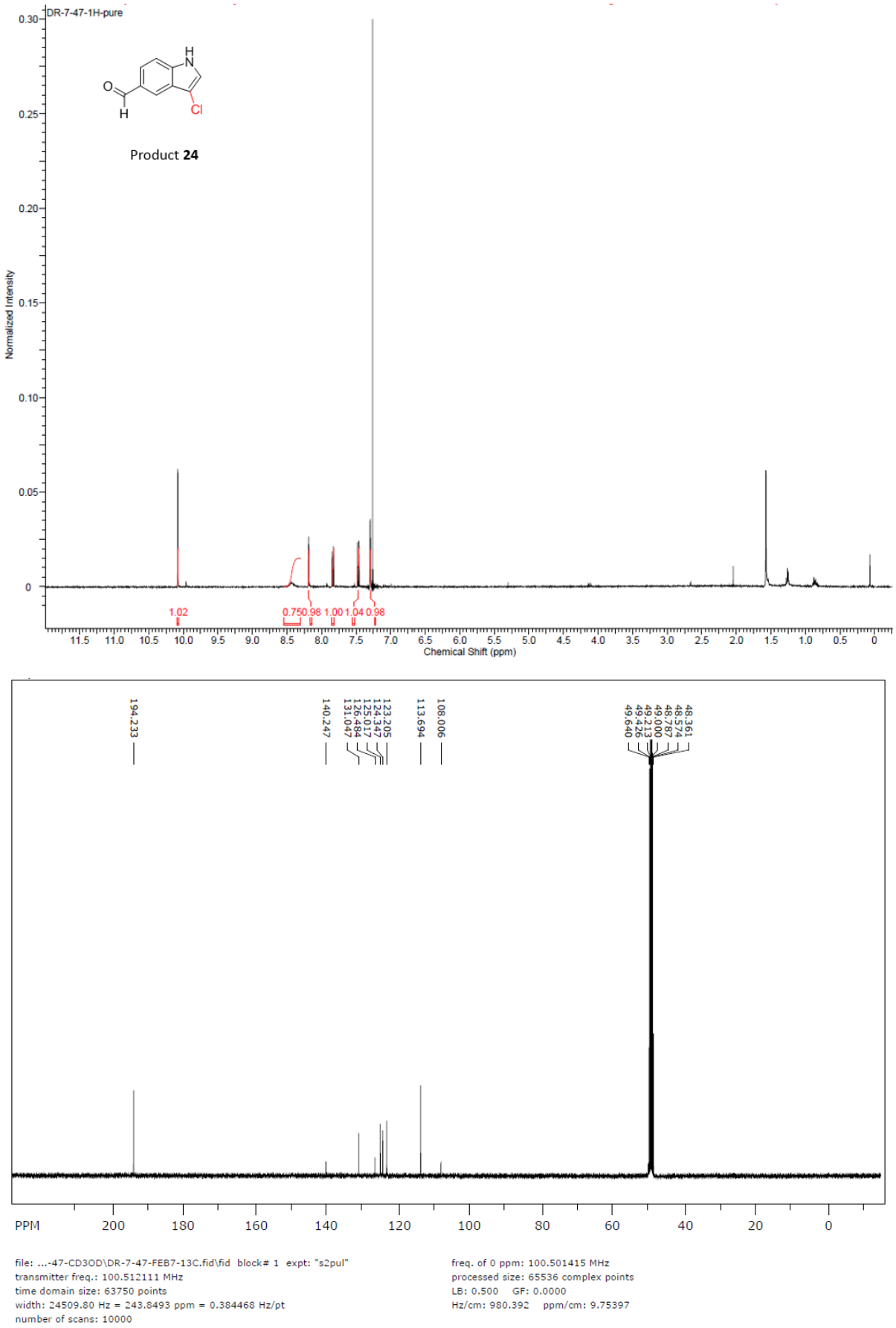


Figure S30. ^{1}H and ^{13}C NMR of Product **24**.

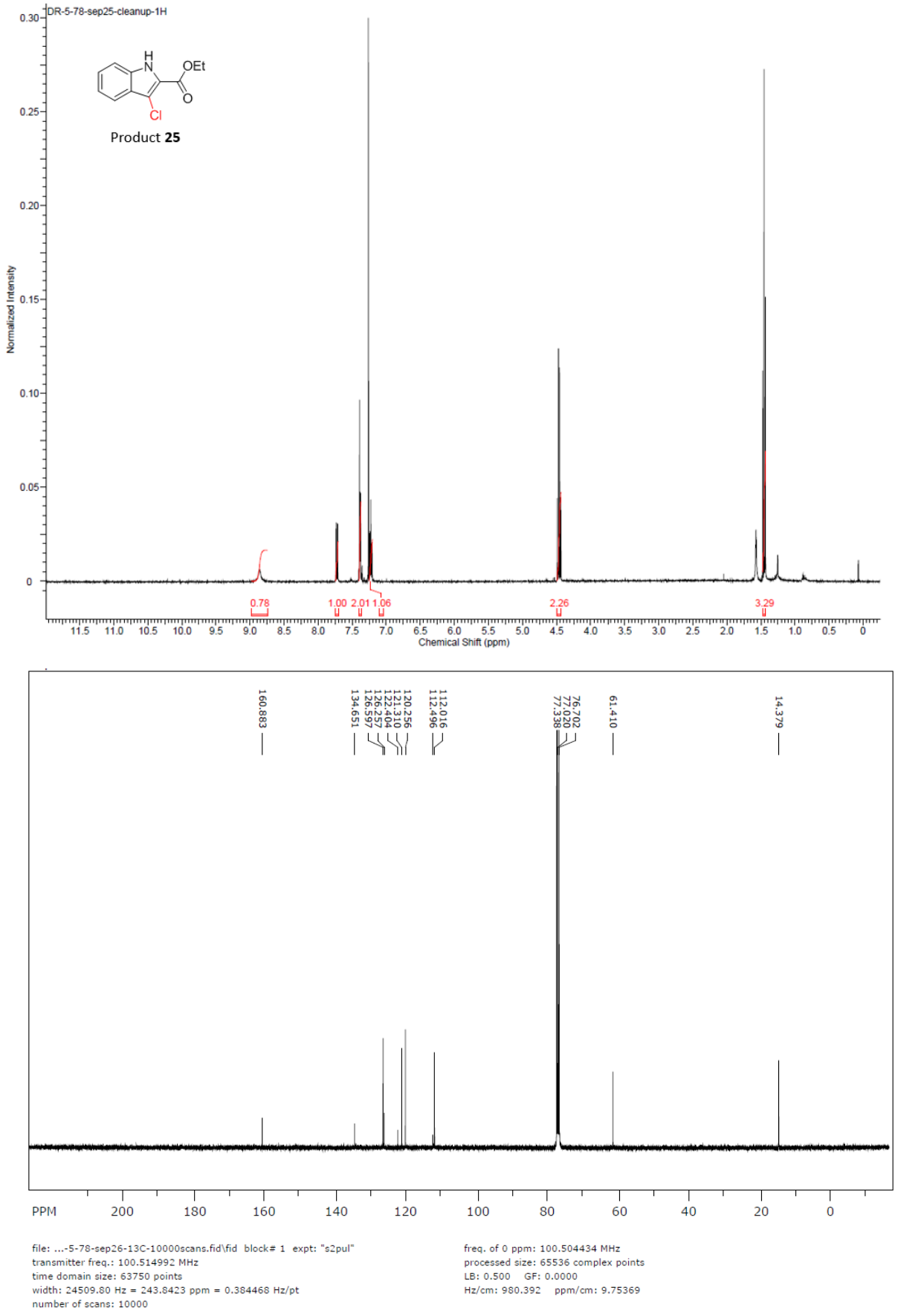


Figure S31. ^{1}H and ^{13}C NMR of Product **25**.

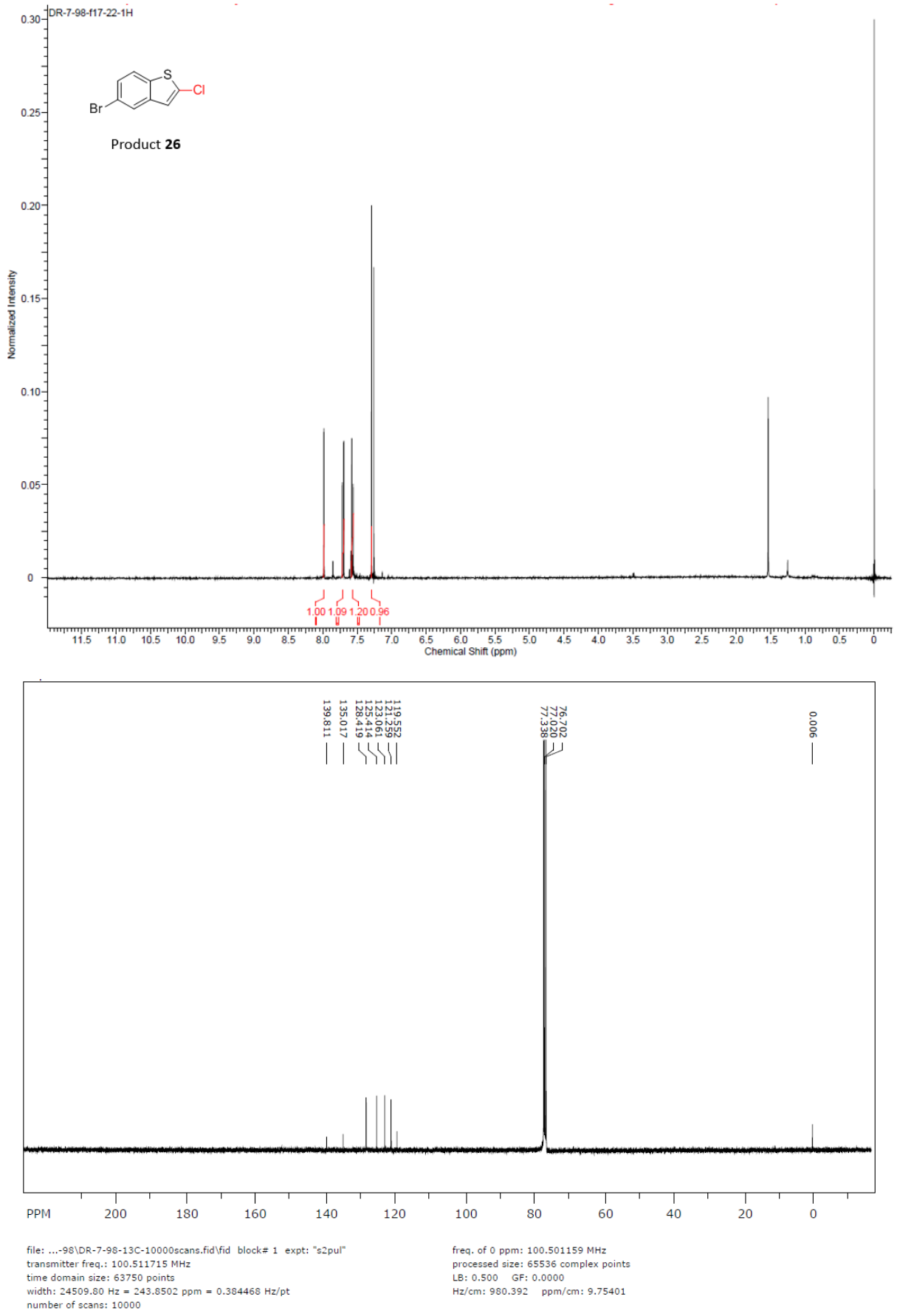


Figure S32. ^{1}H and ^{13}C NMR of Product **26**.

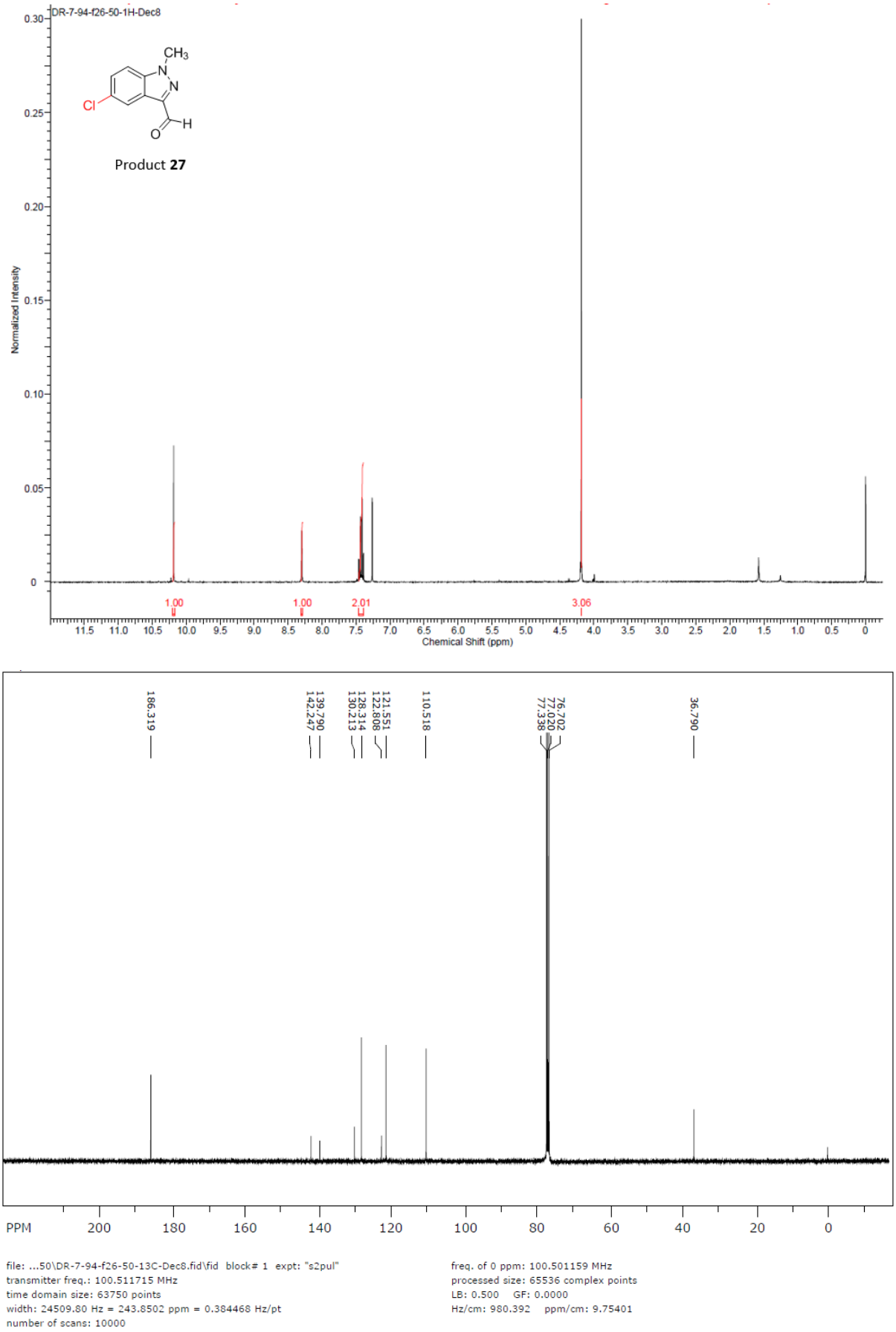


Figure S33. ^{1}H and ^{13}C NMR of Product **27** (5-Cl isomer).

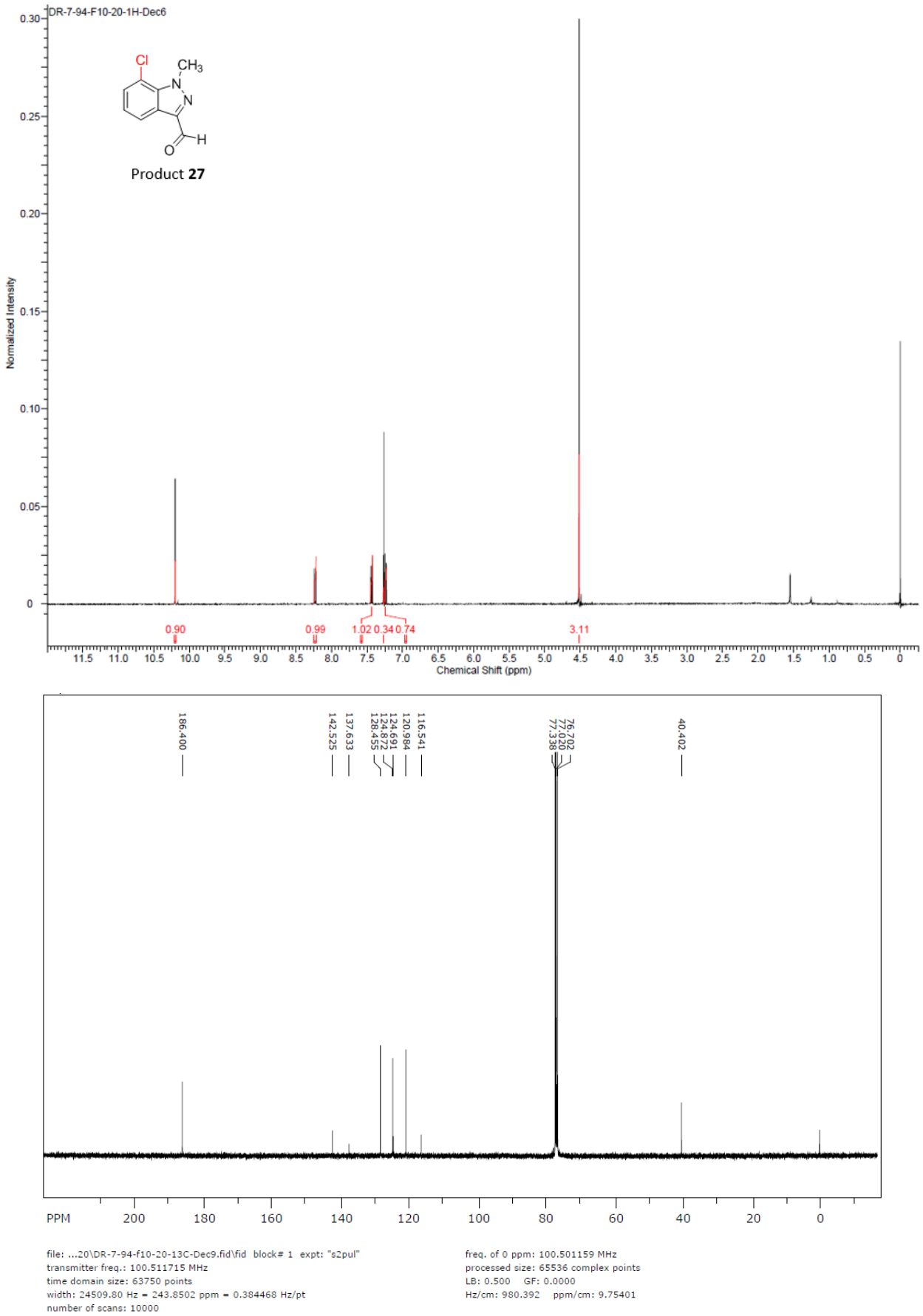


Figure S34. ^{1}H and ^{13}C NMR of Product **27** (7-Cl isomer).

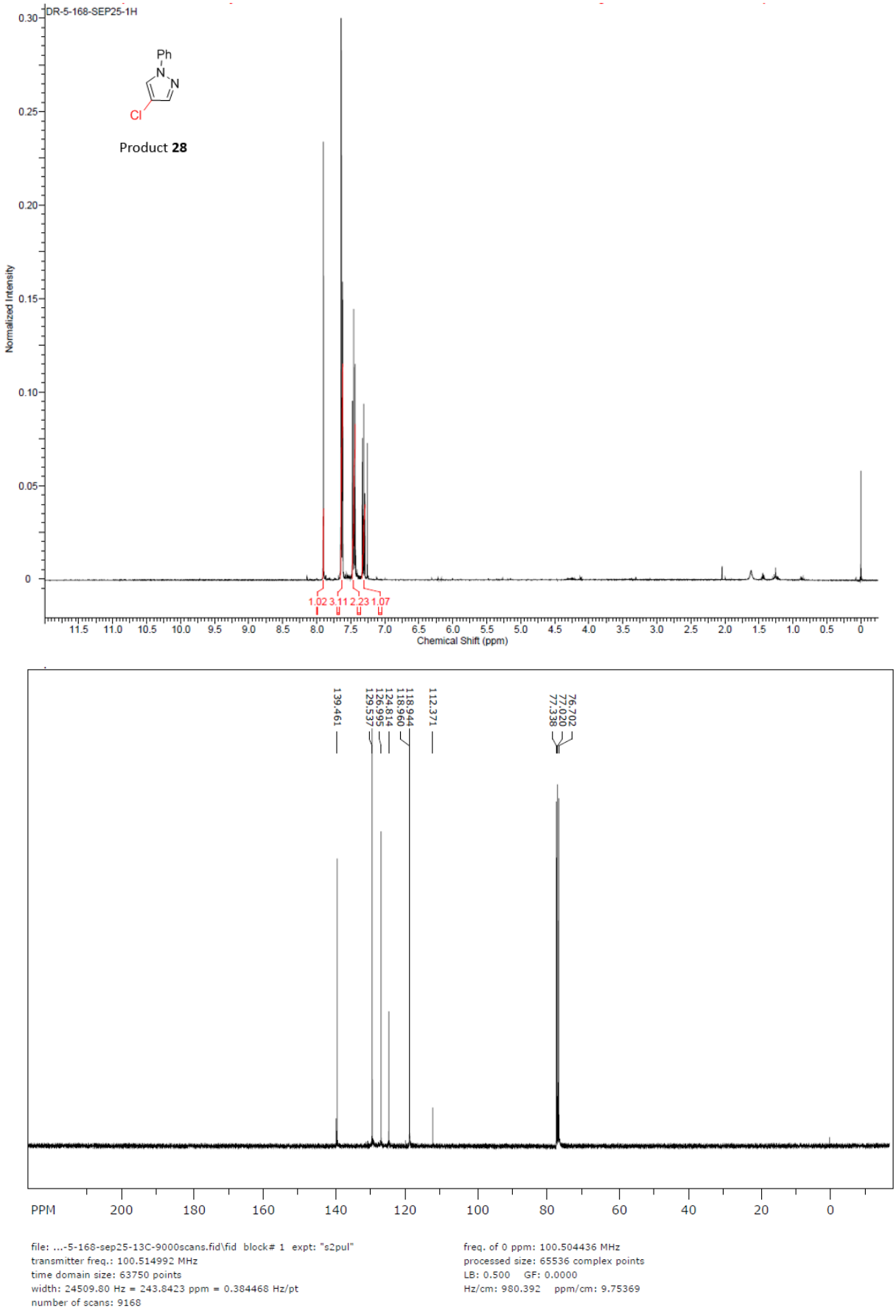


Figure S35. ^{1}H and ^{13}C NMR of Product **28**.

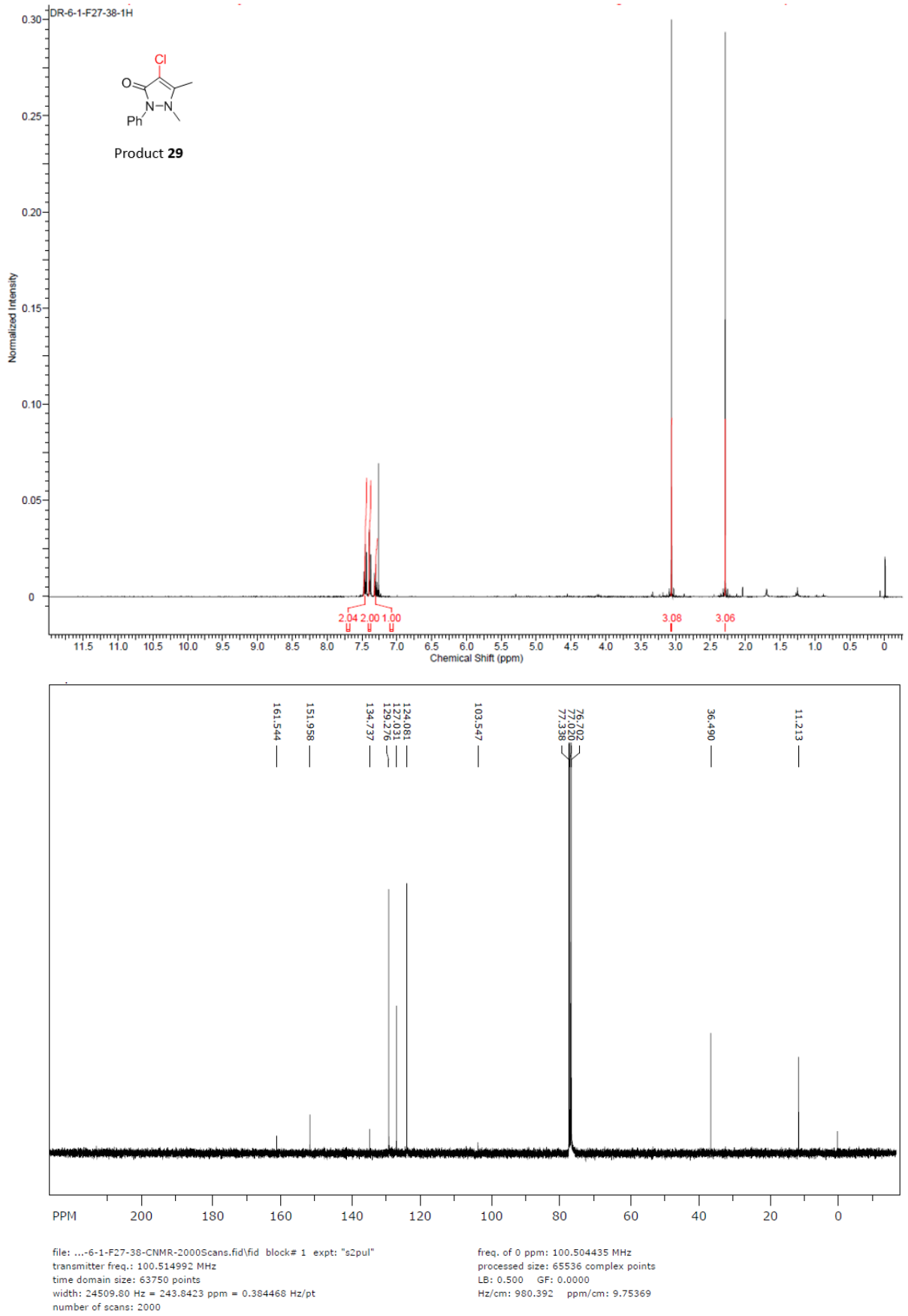


Figure S36. ^{1}H and ^{13}C NMR of Product **29**.

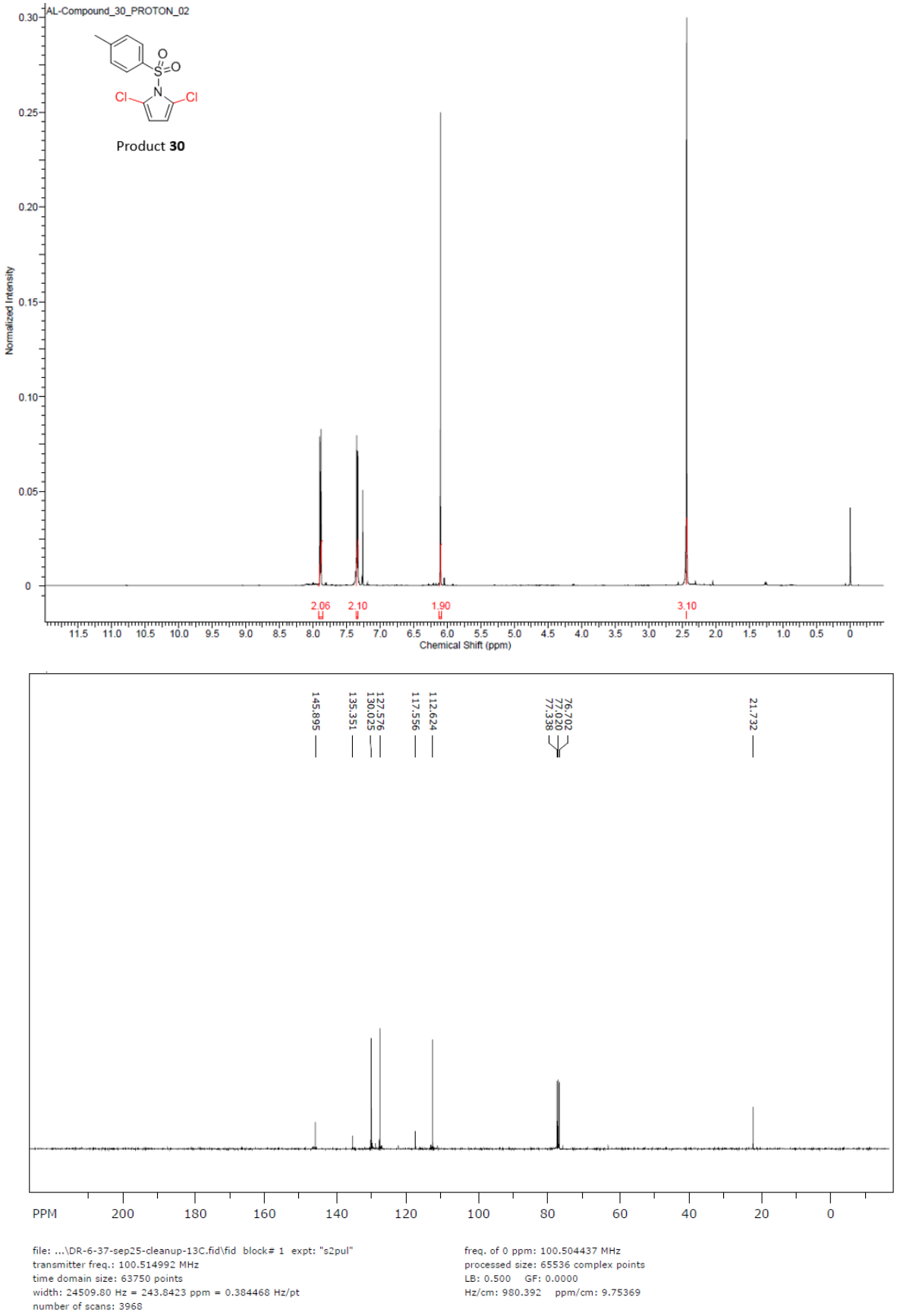


Figure S37. ^{1}H and ^{13}C NMR of Product **30**.

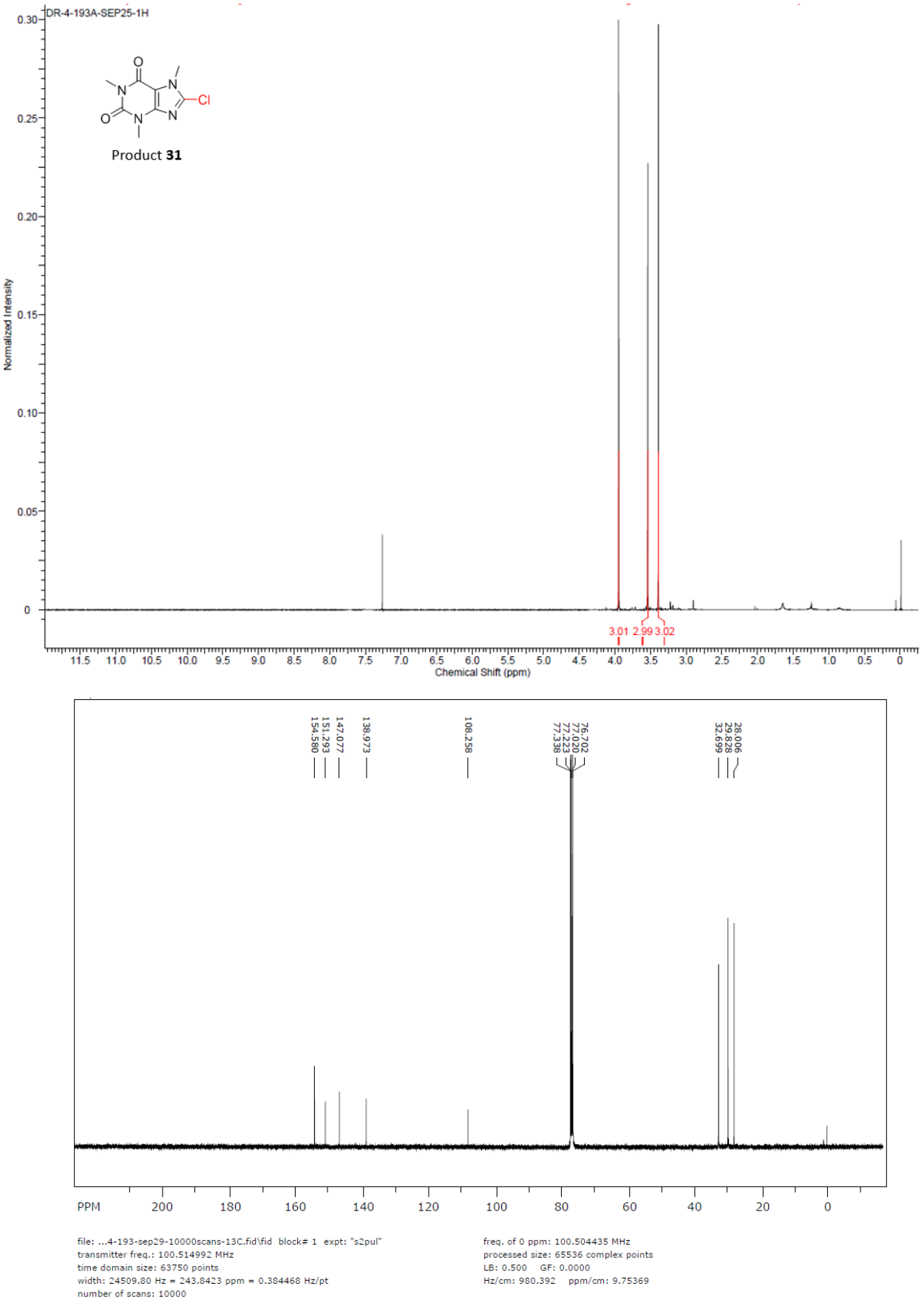


Figure S38. ^{1}H and ^{13}C NMR of Product **31**.

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