N-Hydroxyphthalimide/Benzoquinone-Catalyzed Chlorination of Hydrocarbon C−H Bond with N-Chlorosuccinimide

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[‖] Quantum chemical calculations

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1. General Method

Commercial reagents were purchased from TCI or ALADDIN and unless otherwise stated, all solvents were dried and distilled before use according to the standard methods. Analytical thin layer chromatography (TLC) was performed on precoated silica gel. Visualization on TLC was achieved with UV light (254 nm) as the visualization method. ^{1}H NMR spectra were recorded on a bruker ASCEND spectrometer (^{1}H, 600 MHz; $^{13}C\{^{1}H\}$, 151 MHz) or a JEOL JNM-ECA600 spectrometer. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ shift), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double of doublet, ddd = double of dd, dt = double of triplet, td = triple of doublet), integration, coupling constant (Hz), and assignment. ^{13}C NMR spectra were recorded on bruker ASCEND spectrometer ($^{13}C\{^{1}H\}$, 151 MHz). Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-d or a heptet at 39.5 ppm of dimethyl sulfoxide-d_6. GC analysis was performed using Aglient GC-7890B equipped with a DB-FFAP capillary column, 30 m×0.32 mm; FID detector: 280 ^{o}C; injection: 220 ^{o}C; oven temperature: 85 ^{o}C for 15 min, raised to 190 ^{o}C at a rate of 30 ^{o}C/min, and held for 15 min. GC-MS analysis was performed using Shimadzu GCMS-QP2020 with HP-5MS column, 30 m×0.32 mm; FID detector: 250 ^{o}C; injection: 250 ^{o}C; oven temperature: 40 ^{o}C for 2 min, raised to 100 ^{o}C at a rate of 10 ^{o}C/min, then to 240 ^{o}C at a rate of 20 ^{o}C/min, and held for 8 min. All reagents were

commercially available and weighed out under Argon conditions. All chemicals were used without further purification.

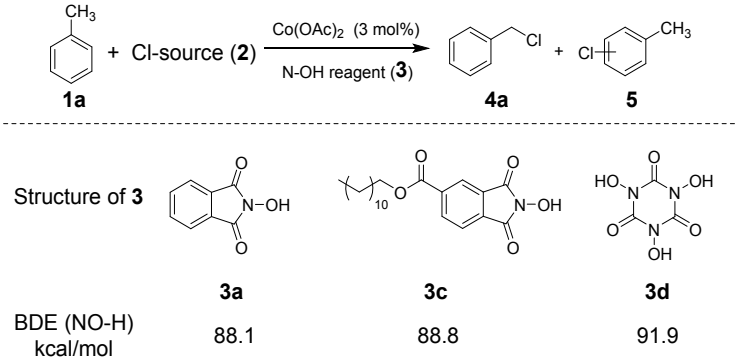
Chlorination of toluene

A typical chlorination procedure: NCS (0.5 mmol, 1 equiv.), toluene (2.5 mmol, 5 equiv.), CH_3CN (2 mL), DDQ (0.0025 mmol, 0.005 equiv.), NHPI (0.05mmol, 0.1equiv.) were added to an oven-dried tube. The reaction tube was equipped with a magnetic stir bar and sealed with a Teflon-lined cap for 3 hours or 16 hours at 80 ^oC.

After the reaction was finished, the reaction mixture was diluted and detected by GC containing biphenyl as an internal standard. Or concentrate the reaction mixture in vacuo to remove the solvent. Notably, the vacuum degree of concentration and the time should be controlled, avoiding the product loss. The crude reaction mixture was detected by ^1H NMR with CH_2Br_2 as an internal standard. Otherwise the residue was purified by column chromatography to give the product. The products were detected by ^1H NMR analysis.

2. Efforts on optimization of transition metal catalyzed chlorination reaction

Table S1. Condition screening for chlorination of toluene in transition metal catalyzed system.[a]



entry	1a (mmol)	2a (mmol)	3 (mol%)	t (h)	variations	conv. (%)	yield (%)
1	0.5	0.5	**3a** (10)	6	-	68	31
2	0.5	0.5	**3a** (10)	6	50 °C	30	n.d.
3	0.5	0.5	**3a** (10)	6	100 °C	100	6
4	0.5	0.5	**3a** (10)	6	160 °C	65	29
5	0.5	0.5	**3a** (10)	6	$Co(acac)_2$ (3 mol%)	73	27
6	0.5	0.5	**3a** (10)	6	$CoCl_2$ (3 mol%)	87	18
7	0.5	0.5	**3c** (10)	6	-	65	21
8	0.5	0.5	**3d** (10)	6	-	75	34
9	0.5	0.5	**3a** (10)	6	CH_3COOH (2 mL)	100	n.d.
10	0.5	0.5	**3a** (10)	6	1,2-DCE (2 mL)	49	7
11	0.5	0.5	**3a** (10)	6	CF_3COOH (2 mL)	100	n.d.
12	0.5	0.5	**3a** (10)	6	DMSO (2 mL)	43	n.d.
13	0.5	0.5	**3a** (10)	6	PhCN (2 mL)	83	17

14	0.5	0.5	**3a** (10)	6	CCl_4 (2 mL)	76	21
15	0.5	0.5	**3a** (10)	6	O_2 (10 atm)	89	5
16	0.5	0.5	**3a** (10)	6	pyridine (20 mol%)	65	12
17	0.5	0.5	**3a** (10)	6	TsOH (5 mol%)	71	31
18[b]	1	0.5	**3a** (10)	16		-	41
19[b]	1	0.5	**3d** (3)	16		-	48

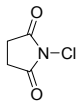
[a] Conditions: CH_3CN (2 mL), O_2 (1atm), 140 ^oC, conversions and yields are determined by GC using diphenyl as internal standard and are on the basis of toluene; [b] yields are determined by GC using diphenyl as internal standard and are on the basis of NCS.

3. N-Cl BDE calculation of chlorine reagents

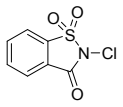
Four different chlorine reagents (**2a**-**2d**) were compared and their N-Cl bond dissociation energy (BDE_{NCl}, **eq. 1**) values were calculated (Table S2).[1-4] **2a** has the highest BDE_{N-Cl}, followed by **2b**. The corresponding N-Cl BDEs of **2c** and **2d** are lower by more than10 kcal/mol.

$$\text{R-N--Cl} \rightarrow \text{R-N}^{\bullet} + \text{Cl}^{\bullet} \quad \textbf{(eq. 1)}$$

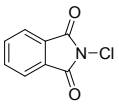
Table S2. Comparison of N-Cl BDE of the chlorine reagents based on B3LYP/6-31+G(d) and M06/6-31+G(d) level of theories.



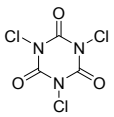
2a



2b



2c



2d

	B3LYP/6-31+G(d) (kcal/mol)	**M06/6-31+G(d) (kcal/mol)**
2a	64.8	73.3
2b	62.6	70.5
2c	54.2	63.0
2d	50.0	58.8

The calculations were performed by the B3LYP[5-7] and M06[8] density functionals in combination with the 6-31+G(d) basis set as implemented in the Gaussian 09 program package.[9]

Normal mode analysis was carried out on each optimized structure in order to verify that they have the right number of imaginary frequencies.

Cartesian coordinates of 2b-2d at the B3LYP/6-31+G(d) level of theory

2b

C	-0.99927	0.84365	-0.02339
C	-1.02052	-0.55119	-0.00164
C	-2.19889	-1.28507	0.02073
C	-3.39898	-0.56389	0.03151
C	-3.39764	0.83752	0.01561
C	-2.19782	1.55474	-0.01407
H	-2.19214	-2.37043	0.03189
H	-4.34236	-1.10178	0.05387
H	-4.34243	1.37327	0.02489
H	-2.18030	2.63998	-0.03107
C	0.36356	1.45002	-0.05432
O	0.64188	2.62688	0.02538
O	0.90634	-2.01631	-1.18940
N	1.28857	0.40812	-0.22576
Cl	2.96095	0.66319	0.01990
S	0.63746	-1.22141	0.00355
O	1.02668	-1.71611	1.32140

2b·

C	-0.79063	0.70448	0.00009
C	-0.30744	-0.60384	0.00016
C	-1.14392	-1.71232	0.00008
C	-2.52153	-1.46726	0.00002
C	-3.02613	-0.15602	0.00001
C	-2.16654	0.94408	0.00003
H	-0.74955	-2.72360	0.00008
H	-3.21150	-2.30636	-0.00003
H	-4.10085	0.00110	-0.00005
H	-2.54227	1.96261	-0.00001
C	0.29613	1.72476	-0.00001
O	0.14571	2.93620	-0.00014
O	2.02623	-1.02628	-1.27287
N	1.60190	1.16024	-0.00002
S	1.48517	-0.54568	-0.00003
O	2.02661	-1.02589	1.27281

2c

C	-0.82529	-0.69948	0.00015
C	-0.82530	0.69949	0.00008
C	-2.00813	1.42539	0.00013
C	-3.20977	0.70060	0.00032
C	-3.20977	-0.70060	0.00043
C	-2.00812	-1.42539	0.00035
H	-1.99784	2.51109	0.00008
H	-4.15598	1.23453	0.00039
H	-4.15597	-1.23453	0.00057
H	-1.99783	-2.51108	0.00040
C	0.58538	1.18811	-0.00002
C	0.58539	-1.18811	-0.00009
O	1.01653	-2.31758	-0.00004
O	1.01655	2.31757	-0.00020
N	1.35940	-0.00001	-0.00015
Cl	3.06005	0.00000	-0.00039

2c·

C	-0.14419	-0.69974	0.00000
C	-0.14420	0.69975	-0.00008
C	-1.33076	1.42875	0.00005
C	-2.52697	0.70426	0.00024
C	-2.52696	-0.70427	0.00032
C	-1.33075	-1.42875	0.00020
H	-1.32157	2.51456	0.00000
H	-3.47577	1.23384	0.00035
H	-3.47576	-1.23386	0.00047
H	-1.32155	-2.51456	0.00025
C	1.27929	1.14730	-0.00028
C	1.27930	-1.14728	-0.00017
O	1.70851	-2.28724	0.00005
O	1.70851	2.28725	-0.00019
N	2.13284	-0.00001	-0.00022

2d

C	-0.15439	1.45231	0.00019
C	-1.18044	-0.85968	0.00012
C	1.33464	-0.59223	-0.00013
N	0.14261	-1.34199	0.00029
N	-1.23361	0.54756	0.00007
N	1.09081	0.79474	0.00030
O	2.43406	-1.08005	-0.00052
O	-2.15270	-1.56776	0.00003
O	-0.28146	2.64837	0.00016
Cl	2.47692	1.80364	-0.00001
Cl	0.32392	-3.04703	0.00006

Cl	-2.80065	1.24286	-0.00023

2d·

C	1.20761	1.25617	-0.04420
C	-1.20762	1.25617	-0.04419
C	0.00001	-0.94187	-0.07845
N	-1.17366	-0.15311	-0.07450
N	0.00000	1.85179	-0.41985
N	1.17367	-0.15310	-0.07453
O	0.00001	-2.14347	-0.06820
O	-2.19499	1.90640	0.21155
O	2.19496	1.90640	0.21162
Cl	2.66452	-0.98813	0.06303
Cl	-2.66451	-0.98814	0.06305

Cartesian coordinates of 2b-2d at the M06/6-31+G(d) level of theory

2b

C	-0.99540	0.83975	-0.02245
C	-1.00831	-0.54972	-0.00440
C	-2.17725	-1.28872	0.01442
C	-3.37626	-0.57545	0.02716
C	-3.38214	0.82074	0.01632
C	-2.19116	1.54343	-0.01094
H	-2.16044	-2.37668	0.02193
H	-4.31937	-1.11780	0.04728
H	-4.33208	1.35128	0.02784
H	-2.17581	2.63131	-0.02486
C	0.35795	1.44941	-0.05309
O	0.63554	2.62050	0.02152
O	0.91362	-1.99011	-1.17977
N	1.27798	0.40641	-0.21200
Cl	2.93641	0.64804	0.01640
S	0.63734	-1.20581	0.00489
O	1.02093	-1.69206	1.31483

2b·

C	-0.78316	0.70166	0.00018
C	-0.30004	-0.60013	0.00024
C	-1.13061	-1.70673	0.00003
C	-2.50277	-1.46209	-0.00004
C	-3.00706	-0.15584	0.00002
C	-2.15322	0.94192	0.00010
H	-0.73042	-2.71841	-0.00003
H	-3.19407	-2.30257	-0.00018
H	-4.08416	-0.00185	-0.00005
H	-2.52725	1.96379	0.00008
C	0.29469	1.71940	0.00001
O	0.14210	2.92326	-0.00020
O	2.00610	-1.01890	-1.26593
N	1.59600	1.15043	0.00006
S	1.47617	-0.54422	-0.00002
O	2.00658	-1.01879	1.26575

2c

C	-0.81943	-0.69646	0.00015
C	-0.81943	0.69646	0.00007
C	-1.99609	1.42146	0.00014
C	-3.19275	0.69795	0.00032
C	-3.19275	-0.69795	0.00042
C	-1.99608	-1.42145	0.00034
H	-1.98074	2.50964	0.00009
H	-4.14142	1.23159	0.00040
H	-4.14142	-1.23159	0.00056
H	-1.98073	-2.50964	0.00039
C	0.58332	1.18501	-0.00005
C	0.58333	-1.18501	-0.00007
O	1.01261	-2.30893	-0.00003
O	1.01263	2.30891	-0.00021
N	1.35394	-0.00001	-0.00015
Cl	3.03906	0.00000	-0.00037

2c·

C	-0.14114	-0.69633	0.00001
C	-0.14114	0.69634	-0.00007
C	-1.32161	1.42532	0.00005
C	-2.51200	0.70195	0.00024
C	-2.51199	-0.70196	0.00031
C	-1.32161	-1.42532	0.00020
H	-1.30714	2.51350	0.00000
H	-3.46334	1.23102	0.00034
H	-3.46333	-1.23104	0.00047
H	-1.30713	-2.51350	0.00026
C	1.27274	1.14485	-0.00027
C	1.27275	-1.14483	-0.00016
O	1.69304	-2.28061	0.00003
O	1.69305	2.28061	-0.00020
N	2.12517	-0.00001	-0.00023

2d

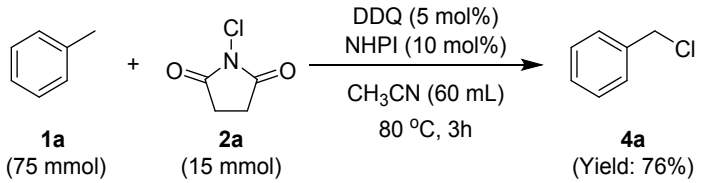
C	1.45137	0.13180	-0.00011
C	-0.83998	1.19095	-0.00034
C	-0.61150	-1.32257	0.00035
N	-1.33806	-0.12167	0.00008
N	0.56385	1.21962	-0.00060
N	0.77427	-1.09782	0.00030
O	-1.11354	-2.40876	0.00059
O	-1.52984	2.16861	-0.00026
O	2.64303	0.23983	-0.00023
Cl	1.75333	-2.48648	-0.00021
Cl	-3.03044	-0.27491	-0.00012

Cl	1.27729	2.76143	0.00042

2d·

C	1.20584	1.25258	-0.04615
C	-1.20586	1.25260	-0.04621
C	0.00000	-0.94293	-0.08594
N	-1.16907	-0.15427	-0.08600
N	0.00001	1.82133	-0.45685
N	1.16906	-0.15428	-0.08595
O	-0.00001	-2.13825	-0.06576
O	-2.17805	1.90056	0.22996
O	2.17809	1.90054	0.22984
Cl	2.64530	-0.97841	0.06822
Cl	-2.64531	-0.97840	0.06820

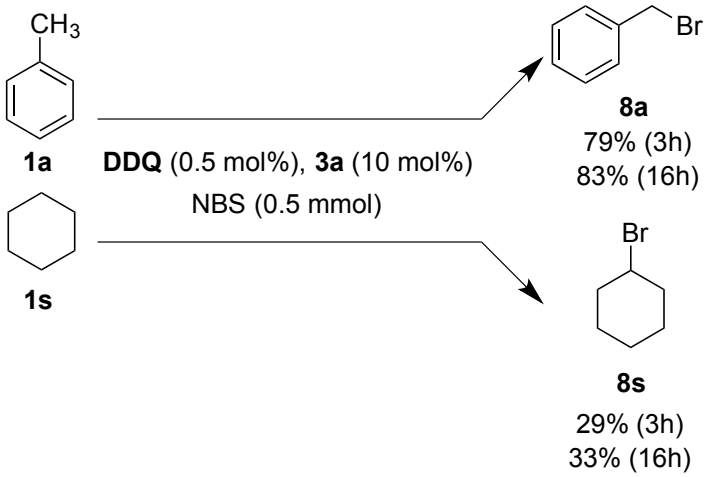
4. Toluene side-chain chlorination on gram-scale



Scheme S1. Toluene side-chain chlorination on gram-scale.[a]

[a] Conditions: toluene (**1a**, 75 mmol), NCS (**2a**, 15 mmol), NHPI (**3a**, 10 mol%), DDQ (5 mol%), CH_3CN (60 mL), 80 °C, 3h; GC yield with diphenyl as internal standard and is on the basis of NCS (**2a**).

5. Oxidative bromination of 1a and 1s with NBS.[a]



Scheme S2. Oxdaive bromination of **1a** and **1s** with NBS.[a]

[a] Conditions: **1** (2.5 mmol, 5.0 equiv.), NBS (0.5 mmol), NHPI (**3a**, 10 mol%), DDQ (0.5 mol%), CH_3CN (2 mL), 80 °C, 3h; yield determined by GC using diphenyl as internal standard and is on the basis of NBS.

6. DFT calculation of mechanism

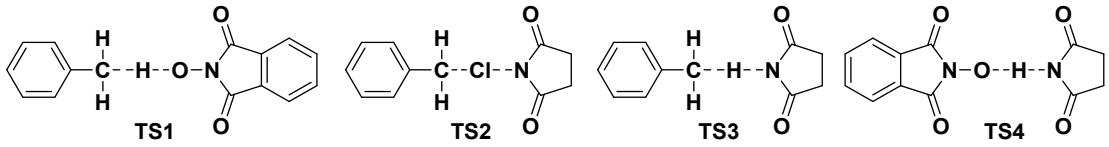
I + 1a → 3a + II (**eq. 2**)

II + 2a → 4a + III (**eq. 3**)

III + 1a → 7a + II (**eq. 4**)

III + 3a → 7a + I (**eq. 5**)

Table S3. Comparison of relative Gibbs free energies (ΔG_r, kcal/mol) and barrier heights ($\Delta G^{\ddagger}$, kcal/mol) of the reaction steps. The calculations were performed to mimic the optimized experimental conditions (80 °C, CH_3CN).



		B3LYP/6-31+G(d)	M06/6-31+G(d)	M06-2X/6-31+G(d)
ΔG_r	eq. 2	13.7	8.8	12.2
	eq. 3	-1.7	1.0	-0.3
	eq. 4	-28.4	-32.4	-30.2
	eq. 5	-42.1	-41.2	-42.4
$\Delta G^{\ddagger}$	TS1	29.8	- **	- **
	TS2	17.0	19.7	21.7
	TS3	13.5*	9.4	13.1
	TS4	12.5*	- **	- **

* - Single-point calculations on gas phase optimized structures

** - Attempts to locate the corresponding transition states were not successful

Computational Methods

All calculations were carried out by using the Gaussian 09 program package. The calculations were performed by the B3LYP,[5-7] M06[8] and M06-2X[8] density functionals in combination with the 6-31+G(d) basis set as implemented in the Gaussian 09

program package.[9] Normal mode analysis was carried out on each optimized structure in order to verify that they have the right number of imaginary frequencies. To mimic the optimized experimental conditions the calculations were performed using the CPCM solvent model[10, 11] with acetonitrile (CH_3CN) as solvent at 80 ^oC and 1 atm.

Cartesian coordinates of all computed structures at the B3LYP/6-31+G(d) (solvent: CH_3CN) level of theory

1a			
C	0.19873	-1.20276	0.00000
C	0.91709	0.00547	0.00000
C	0.19187	1.20629	0.00000
C	-1.20842	1.20517	0.00000
C	-1.90966	-0.00384	0.00000
C	-1.19865	-1.21031	0.00000
H	0.74108	-2.14651	0.00000
H	0.72767	2.15334	0.00000
H	-1.74810	2.14921	0.00000
H	-2.99670	-0.00823	0.00000
H	-1.73322	-2.15729	0.00000
C	2.42981	0.00291	0.00000
H	2.82733	-0.51504	-0.88195
H	2.83002	1.02193	-0.00002
H	2.82733	-0.51500	0.88197

2a			
C	1.89116	-0.77039	0.00000
C	1.89116	0.77039	0.00006
C	0.43187	1.18697	-0.00006
C	0.43187	-1.18697	-0.00009
H	2.37515	-1.19895	-0.88276
H	2.37508	-1.19901	0.88277
H	2.37520	1.19902	-0.88265
H	2.37504	1.19894	0.88288
O	-0.04245	-2.30336	0.00003
O	-0.04245	2.30336	0.00000
N	-0.31922	0.00000	-0.00004
Cl	-2.02724	0.00000	0.00002

3a			
C	0.50398	0.70124	0.00395
C	0.50398	-0.70123	0.00395
C	1.68766	-1.42552	0.00384
C	2.89016	-0.70044	-0.00081
C	2.89016	0.70044	-0.00088
C	1.68766	1.42553	0.00371
H	1.68489	-2.51110	0.00513
H	3.83578	-1.23439	-0.00497
H	3.83578	1.23439	-0.00506
H	1.68489	2.51110	0.00502
C	-0.90699	-1.17816	0.00791
C	-0.90699	1.17817	0.00834
N	-1.67282	-0.00001	0.09707
O	-1.35842	-2.30632	-0.04155
O	-1.35845	2.30630	-0.04161
O	-3.03107	0.00002	-0.11986
H	-3.44587	-0.00012	0.76458

4a			
C	-1.99588	-1.21093	-0.15970
C	-0.65937	-1.20996	0.24760
C	0.02156	0.00017	0.45244
C	-0.65962	1.21012	0.24730
C	-1.99612	1.21072	-0.15999
C	-2.66656	-0.00020	-0.36574
H	-2.51367	-2.15419	-0.31205
H	-0.14164	-2.15273	0.40879
H	-0.14208	2.15304	0.40826
H	-2.51411	2.15384	-0.31256
H	-3.70672	-0.00034	-0.68065
C	1.45297	0.00038	0.89240
H	1.71627	0.89354	1.45791
H	1.71633	-0.89232	1.45861
Cl	2.62375	-0.00016	-0.55025

I			
C	-0.45218	0.70415	0.00029
C	-0.45218	-0.70415	0.00032
C	-1.64034	-1.42645	0.00011
C	-2.83937	-0.70195	-0.00001
C	-2.83937	0.70195	0.00001
C	-1.64034	1.42645	0.00015
H	-1.63709	-2.51163	0.00012
H	-3.78560	-1.23426	-0.00013
H	-3.78560	1.23426	-0.00011
H	-1.63709	2.51163	0.00012

C	0.93597	-1.20174	0.00062
C	0.93597	1.20174	0.00035
N	1.75723	0.00000	-0.00020
O	1.39497	-2.32015	-0.00015
O	1.39497	2.32015	-0.00008
O	3.02202	0.00000	-0.00097

II

C	0.00000	1.13594	1.21448
C	0.00000	-0.25291	1.22087
C	0.00000	-0.99712	0.00000
C	0.00000	-0.25291	-1.22087
C	0.00000	1.13594	-1.21448
C	0.00000	1.84351	0.00000
H	0.00000	1.67898	2.15640
H	0.00000	-0.79384	2.16442
H	0.00000	-0.79384	-2.16442
H	0.00000	1.67898	-2.15640
H	0.00000	2.93000	0.00000
C	0.00000	-2.40655	0.00000
H	0.00000	-2.96788	-0.92956
H	0.00000	-2.96788	0.92956

III

C	0.76277	1.24904	-0.02672
C	-0.76283	1.24908	0.02676
C	-1.11205	-0.23991	0.03834
C	1.11203	-0.24004	-0.03827
H	1.16360	1.71029	-0.93514
H	1.24343	1.72425	0.83288
H	-1.24344	1.72432	-0.83286
H	-1.16363	1.71045	0.93512
O	2.24441	-0.71907	0.02379
O	-2.24431	-0.71918	-0.02416
N	-0.00005	-1.06748	0.00033

7a

C	0.76946	-1.26012	0.00343
C	1.16844	0.20911	0.00033
C	-1.16844	0.20911	-0.00031
H	1.20682	-1.74750	-0.87338
H	1.19728	-1.73905	0.88975
O	-2.29374	0.68093	0.00160
O	2.29374	0.68093	-0.00161
N	0.00000	0.95934	0.00000
H	0.00000	1.97498	-0.00001
C	-0.76946	-1.26012	-0.00344
H	-1.20682	-1.74751	0.87337
H	-1.19728	-1.73904	-0.88976

TS1

C	2.96487	-0.70141	-0.08041
C	2.96481	0.70144	-0.08044
C	4.11822	1.42534	0.18707
C	5.28992	0.70063	0.45894
C	5.28998	-0.70039	0.45896
C	4.11833	-1.42521	0.18712
H	4.11561	2.51093	0.18630
H	6.21104	1.23470	0.67268
H	6.21114	-1.23437	0.67273
H	4.11581	-2.51080	0.18639
C	1.59172	1.17801	-0.39883
C	1.59182	-1.17811	-0.39879
N	0.83339	-0.00008	-0.57825
O	1.15564	2.31006	-0.49855
O	1.15583	-2.31019	-0.49847
O	-0.45635	-0.00014	-0.93490
C	-3.99910	1.21714	0.40176
C	-3.32175	-0.00005	0.66950
C	-3.99922	-1.21714	0.40169
C	-5.29767	-1.21465	-0.09746
C	-5.95285	0.00012	-0.35013
C	-5.29755	1.21481	-0.09739
H	-3.49181	2.15869	0.59736
H	-3.49203	-2.15877	0.59722
H	-5.80546	-2.15568	-0.29064
H	-6.96689	0.00018	-0.74032
H	-5.80524	2.15590	-0.29050
C	-1.95748	-0.00013	1.16300
H	-1.16776	-0.00015	0.07128
H	-1.61159	0.91567	1.64651
H	-1.61168	-0.91598	1.64648

TS2

C	4.09990	1.34984	-0.34525
C	4.49914	-0.13006	-0.47765
C	3.21136	-0.91277	-0.21298
C	2.60755	1.32898	-0.00695

H	4.63283	1.87363	0.45446
H	4.24116	1.92171	-1.26775
H	5.25402	-0.44228	0.25079
H	4.87071	-0.39241	-1.47314
O	1.89514	2.30179	0.19411
O	3.08768	-2.12908	-0.21427
N	2.20985	0.00685	0.02617
C	-1.68723	-1.37047	1.14975
H	-1.51200	-1.17543	2.20295
H	-1.49043	-2.38488	0.81729
C	-2.68716	-0.60795	0.46801
C	-3.20806	0.58247	1.04363
C	-3.17897	-1.02804	-0.79743
C	-4.19038	1.31009	0.38564
H	-2.83215	0.91369	2.00794
C	-4.16113	-0.29467	-1.44905
H	-2.78069	-1.93374	-1.24673
C	-4.66876	0.87541	-0.86129
H	-4.59011	2.21448	0.83478
H	-4.53809	-0.62568	-2.41228
H	-5.43679	1.44760	-1.37404
Cl	0.29602	-0.55667	0.45913

TS3

C	-3.61956	-1.30295	0.02981
C	-4.18098	0.05961	-0.35655
C	-2.92454	0.98543	-0.37480
C	-2.10795	-1.03636	0.10006
H	-3.96965	-1.67177	0.99918
H	-3.81389	-2.08607	-0.71031
H	-4.89525	0.47364	0.36106
H	-4.63885	0.09520	-1.34967
O	-1.25638	-1.85631	0.44218
O	-2.99647	2.18971	-0.58421
N	-1.77357	0.25813	-0.21084
C	1.00225	1.11441	1.39554
H	0.79788	0.55333	2.31640
H	1.19298	2.16106	1.65387
C	2.13686	0.50997	0.62620
C	2.16842	-0.88194	0.38057
C	3.17871	1.30438	0.10831
C	3.20530	-1.45226	-0.35266
H	1.35827	-1.50168	0.75530
C	4.21899	0.73429	-0.62202
H	3.16529	2.37752	0.28479
C	4.23750	-0.64867	-0.85562
H	3.21277	-2.52382	-0.53494
H	5.01710	1.36170	-1.01072
H	5.04936	-1.09424	-1.42473
H	0.07177	1.06556	0.79886

TS4

C	2.70259	-0.39377	0.01005
C	1.86289	0.68293	0.31877
C	2.34550	1.98229	0.38861
C	3.71266	2.17879	0.14055
C	4.55255	1.10148	-0.17085
C	4.05405	-0.20859	-0.24247
C	0.48011	0.16313	0.52618
C	1.89373	-1.65023	0.00822
N	0.57462	-1.20929	0.27746
O	-0.54092	0.76868	0.80753
O	2.23392	-2.79507	-0.17732
O	-0.42833	-2.08757	0.59370
N	-2.99468	-0.77471	-0.16219
C	-3.69681	0.13540	0.64964
C	-2.45799	-0.04599	-1.23929
C	-3.67426	1.55062	0.07196
O	-4.28512	-0.22426	1.65951
C	-2.98306	1.38231	-1.28953
O	-1.63672	-0.56332	-1.98756
H	1.68818	2.81174	0.63195
H	4.12742	3.18168	0.19205
H	5.60705	1.28401	-0.35849
H	4.69691	-1.04986	-0.48364
H	-1.05083	-2.08034	-0.16399
H	-4.69085	1.95151	0.02428
H	-3.09569	2.18338	0.75364
H	-3.68060	1.47487	-2.13139
H	-2.15541	2.07313	-1.46928

Cartesian coordinates of all computed structures at the M06/6-31+G(d) (solvent: CH_3CN) level of theory

1a			
C	0.19152	1.20313	-0.00466
C	0.91331	0.00655	-0.00571
C	0.20001	-1.19819	-0.00466
C	-1.19205	-1.20695	0.00100
C	-1.90069	-0.00492	0.00441
C	-1.20318	1.20082	0.00109
H	0.73193	2.15087	-0.00914
H	0.74933	-2.14122	-0.00911
H	-1.72769	-2.15562	0.00090
H	-2.98960	-0.01000	0.00749
H	-1.74566	2.14556	0.00112
C	2.41379	0.00286	0.00454
H	2.82069	1.00766	-0.16198
H	2.80507	-0.35750	0.96617
H	2.81961	-0.65957	-0.77148

2a			
C	1.87566	0.75995	0.08126
C	1.87566	-0.75996	-0.08125
C	0.42978	-1.17769	-0.11711
C	0.42978	1.17769	0.11711
H	2.35450	1.09525	1.00828
H	2.36956	1.28496	-0.74402
H	2.36956	-1.28496	0.74402
H	2.35450	-1.09525	-1.00827
O	-0.04290	2.28360	0.22399
O	-0.04291	-2.28360	-0.22399
N	-0.32059	0.00000	0.00000
Cl	-2.01150	0.00000	-0.00001

3a			
C	0.49997	0.69818	0.00236
C	0.49996	-0.69817	0.00235
C	1.67750	-1.42161	0.00401
C	2.87499	-0.69780	0.00243
C	2.87499	0.69781	0.00237
C	1.67750	1.42162	0.00390
H	1.67054	-2.50966	0.00513
H	3.82305	-1.23144	0.00087
H	3.82306	1.23144	0.00080
H	1.67055	2.50967	0.00504
C	-0.90282	-1.17540	0.00461
C	-0.90282	1.17541	0.00501
N	-1.66595	-0.00001	0.09356
O	-1.35037	-2.29837	-0.04644
O	-1.35039	2.29835	-0.04651
O	-3.01171	0.00002	-0.10787
H	-3.42136	-0.00011	0.77748

4a			
C	-1.97373	-1.20731	-0.15908
C	-0.64445	-1.20620	0.25423
C	0.02888	0.00015	0.46469
C	-0.64465	1.20634	0.25398
C	-1.97394	1.20713	-0.15933
C	-2.64015	-0.00016	-0.36690
H	-2.49143	-2.15205	-0.31646
H	-0.12081	-2.14895	0.41770
H	-0.12118	2.14921	0.41725
H	-2.49180	2.15175	-0.31690
H	-3.68052	-0.00028	-0.68772
C	1.45490	0.00032	0.89250
H	1.72284	0.89410	1.46200
H	1.72289	-0.89309	1.46257
Cl	2.57758	-0.00013	-0.55994

I			
C	-0.44925	0.70100	0.00022
C	-0.44925	-0.70100	0.00024
C	-1.63115	-1.42249	0.00011
C	-2.82531	-0.69928	0.00002
C	-2.82531	0.69928	0.00003
C	-1.63115	1.42249	0.00012
H	-1.62360	-2.51011	0.00011
H	-3.77386	-1.23140	-0.00005
H	-3.77386	1.23140	-0.00004
H	-1.62360	2.51011	0.00010

C	0.93151	-1.19886	0.00043
C	0.93151	1.19886	0.00026
N	1.74848	0.00000	-0.00017
O	1.38898	-2.31171	-0.00012
O	1.38898	2.31171	-0.00007
O	3.00278	0.00000	-0.00074

II

C	0.00000	1.13127	1.21094
C	0.00000	-0.25251	1.21704
C	0.00000	-0.99221	0.00000
C	0.00000	-0.25251	-1.21704
C	0.00000	1.13127	-1.21094
C	0.00000	1.83613	0.00000
H	0.00000	1.67579	2.15432
H	0.00000	-0.79867	2.16096
H	0.00000	-0.79867	-2.16096
H	0.00000	1.67579	-2.15432
H	0.00000	2.92465	0.00000
C	0.00000	-2.39527	0.00000
H	0.00000	-2.95796	-0.93223
H	0.00000	-2.95796	0.93223

III

C	0.74547	1.22421	-0.09193
C	-0.77211	1.21201	0.11753
C	-1.13966	-0.25817	0.18195
C	1.13965	-0.23992	-0.13419
H	1.06136	1.69285	-1.03086
H	1.29150	1.71801	0.71998
H	-1.33789	1.67433	-0.69916
H	-1.08558	1.69817	1.04852
O	2.18256	-0.72575	-0.50575
O	-2.23634	-0.76208	0.11002
N	0.05639	-0.96679	0.38783

7a

C	-0.75934	1.24837	0.07918
C	-1.15735	-0.20744	0.11991
C	1.15735	-0.20744	-0.11991
H	-1.28512	1.73458	-0.75055
H	-1.10237	1.73216	1.00091
O	2.27345	-0.67163	-0.23497
O	-2.27345	-0.67163	0.23497
N	0.00000	-0.95846	0.00000
H	0.00000	-1.97469	0.00000
C	0.75934	1.24837	-0.07918
H	1.28512	1.73458	0.75055
H	1.10237	1.73216	-1.00091

TS2

C	4.22719	0.83330	-0.59769
C	4.26940	-0.69227	-0.63549
C	2.88340	-1.14019	-0.20864
C	2.81835	1.18230	-0.15269
H	4.93597	1.27445	0.11273
H	4.41105	1.30109	-1.57184
H	5.00296	-1.12832	0.05256
H	4.47595	-1.10105	-1.63138
O	2.37019	2.29826	0.02985
O	2.49978	-2.28742	-0.08093
N	2.13428	-0.00360	0.00123
C	-1.64579	-0.14647	1.76034
H	-1.47765	0.72672	2.38897
H	-1.49198	-1.10819	2.24826
C	-2.63569	-0.06188	0.73113
C	-3.10209	1.19567	0.28662
C	-3.13621	-1.23514	0.12351
C	-4.05231	1.27260	-0.71682
H	-2.70425	2.10061	0.74550
C	-4.08747	-1.15121	-0.87865
H	-2.76618	-2.20362	0.45931
C	-4.54657	0.10108	-1.30072
H	-4.41520	2.24173	-1.05258
H	-4.47805	-2.05715	-1.33727
H	-5.29309	0.16577	-2.09009
Cl	0.23220	-0.07178	0.68298

TS3

C	1.72130	-1.75827	0.23654
C	2.90165	-1.13628	-0.49278
C	2.81881	0.34107	-0.13306
C	1.09189	-0.57703	0.95122
H	0.98018	-2.22064	-0.42799
H	2.00641	-2.51842	0.97425
H	2.84911	-1.23638	-1.58395
H	3.87649	-1.53010	-0.18073
O	0.02998	-0.61909	1.58014

O	3.54685	1.21095	-0.59709
N	1.81874	0.56959	0.79065
C	-0.43516	2.09912	-0.32277
H	-0.06271	2.33708	-1.32690
H	-0.75065	3.00212	0.21128
C	-1.42993	1.03324	-0.31393
C	-1.36374	-0.01403	-1.27203
C	-2.46674	1.00369	0.65678
C	-2.29875	-1.02563	-1.27235
H	-0.55777	0.00062	-2.00685
C	-3.40556	-0.00646	0.64897
H	-2.51059	1.79855	1.39990
C	-3.32540	-1.02591	-0.31191
H	-2.24561	-1.82344	-2.00955
H	-4.20572	-0.01863	1.38527
H	-4.06226	-1.82665	-0.31185
H	0.48722	1.71283	0.23003

Cartesian coordinates of all computed structures at the M06-2X/6-31+G(d) (solvent: CH_3CN) level of theory

1a

C	-0.19718	-1.20076	-0.00848
C	-0.91284	0.00250	-0.01098
C	-0.19400	1.20269	-0.00850
C	1.20154	1.20377	0.00199
C	1.90269	-0.00185	0.00792
C	1.19726	-1.20615	0.00194
H	-0.74059	-2.14337	-0.01676
H	-0.73403	2.14708	-0.01689
H	1.74051	2.14726	0.00203
H	2.98886	-0.00374	0.01330
H	1.73367	-2.15112	0.00189
C	-2.42140	0.00101	0.00870
H	-2.82438	-0.82541	-0.58428
H	-2.79675	-0.11579	1.03188
H	-2.82371	0.93782	-0.38671

2a

C	0.01731	-0.76708	-1.88368
C	-0.01731	0.76708	-1.88368
C	-0.00337	1.18075	-0.42708
C	0.00337	-1.18075	-0.42708
H	-0.84436	-1.21877	-2.38040
H	0.92193	-1.17310	-2.34319
H	-0.92193	1.17310	-2.34319
H	0.84436	1.21877	-2.38040
O	0.00000	-2.28912	0.04799
O	0.00000	2.28912	0.04799
N	0.00000	0.00000	0.32347
Cl	0.00000	0.00000	2.00848

3a

C	-0.50568	-0.69773	0.00476
C	-0.50568	0.69773	0.00477
C	-1.68323	1.42370	0.00425
C	-2.88156	0.69869	0.00068
C	-2.88156	-0.69869	0.00072
C	-1.68322	-1.42370	0.00433
H	-1.67708	2.50913	0.00496
H	-3.82746	1.23101	-0.00267
H	-3.82746	-1.23102	-0.00262
H	-1.67707	-2.50913	0.00502
C	0.90863	1.17304	0.00639
C	0.90863	-1.17303	0.00608
N	1.66922	-0.00001	0.09623
O	1.35741	2.29256	-0.04707
O	1.35739	-2.29256	-0.04709
O	3.01507	0.00001	-0.11111
H	3.42754	-0.00009	0.77186

4a

C	-1.95109	-1.22852	-0.12818
C	-0.62027	-1.18952	0.28272
C	0.02931	0.03605	0.45997
C	-0.66966	1.22325	0.22372
C	-2.00179	1.18619	-0.18594
C	-2.64396	-0.03969	-0.36342
H	-2.44780	-2.18504	-0.26124
H	-0.07970	-2.11531	0.46693
H	-0.16878	2.17872	0.36196
H	-2.53809	2.11365	-0.36393
H	-3.68215	-0.06878	-0.68101
C	1.46565	0.07472	0.88368
H	1.72164	1.00781	1.38434
H	1.73046	-0.77105	1.51753
Cl	2.57737	-0.03146	-0.55646

I

C	0.45532	-0.69979	0.00003
C	0.45532	0.69979	0.00001
C	1.63690	1.42416	0.00009
C	2.83231	0.69986	0.00012
C	2.83231	-0.69986	0.00010
C	1.63690	-1.42416	0.00004
H	1.63006	2.50929	0.00008
H	3.77850	1.23127	0.00016
H	3.77850	-1.23127	0.00013
H	1.63006	-2.50929	0.00005
C	-0.93795	1.19624	-0.00013
C	-0.93795	-1.19624	0.00006
N	-1.75198	0.00000	-0.00007
O	-1.39557	2.30516	-0.00003

O	-1.39557	-2.30516	-0.00008
O	-3.00789	0.00000	-0.00012

II

C	0.00000	1.21028	-1.13346
C	0.00000	1.21570	0.25303
C	0.00000	0.00000	0.98991
C	0.00000	-1.21570	0.25303
C	0.00000	-1.21028	-1.13346
C	0.00000	0.00000	-1.83814
H	0.00000	2.15160	-1.67562
H	0.00000	2.15773	0.79581
H	0.00000	-2.15773	0.79581
H	0.00000	-2.15160	-1.67562
H	0.00000	0.00000	-2.92363
C	0.00000	0.00000	2.40276
H	0.00000	-0.92936	2.96056
H	0.00000	0.92936	2.96056

III

C	0.76270	1.23717	-0.02819
C	-0.76502	1.23694	0.03834
C	-1.13552	-0.23476	0.01109
C	1.13518	-0.23405	0.00466
H	1.15430	1.67495	-0.95052
H	1.24130	1.74699	0.81152
H	-1.24587	1.74507	-0.80066
H	-1.15452	1.67566	0.96151
O	2.25387	-0.70696	-0.03263
O	-2.25170	-0.70883	-0.06325
N	0.00049	-1.07832	0.08425

7a

C	-0.76238	1.25588	0.07842
C	-1.15645	-0.20988	0.12160
C	1.15645	-0.20988	-0.12160
H	-1.28282	1.73194	-0.75628
H	-1.10255	1.73493	0.99986
O	2.27021	-0.67486	-0.23997
O	-2.27021	-0.67486	0.23997
N	0.00000	-0.96089	0.00000
H	0.00000	-1.97619	0.00000
C	0.76238	1.25588	-0.07843
H	1.28282	1.73194	0.75628
H	1.10255	1.73493	-0.99986

TS2

C	4.46094	-0.04030	-0.21042
C	3.93183	-1.47868	-0.17000
C	2.41617	-1.33920	-0.06341
C	3.21756	0.84076	-0.13896
H	5.10555	0.20807	0.63648
H	5.00360	0.19770	-1.12862
H	4.28641	-2.04873	0.69240
H	4.16444	-2.05082	-1.07166
O	3.18703	2.05450	-0.11336
O	1.60800	-2.23962	0.03932
N	2.12159	0.00645	-0.11431
C	-1.53903	1.59167	0.84082
H	-1.41623	2.54727	0.33834
H	-1.33231	1.59981	1.90696
C	-2.57953	0.71153	0.36801
C	-3.16027	0.90531	-0.90345
C	-3.00812	-0.37233	1.16349
C	-4.15573	0.05014	-1.35452
H	-2.82461	1.73422	-1.52132
C	-4.00101	-1.22613	0.70613
H	-2.55281	-0.52834	2.13810
C	-4.57579	-1.01642	-0.55253
H	-4.60705	0.20736	-2.32903
H	-4.33081	-2.05599	1.32308
H	-5.35185	-1.68669	-0.90964
Cl	0.27072	0.67964	0.18862

TS3

C	-1.05916	0.69464	-1.66641
C	-1.74891	-0.66490	-1.51778
C	-2.01358	-0.77518	-0.02153
C	-1.24931	1.36241	-0.31344
H	0.02285	0.59685	-1.82115
H	-1.46084	1.32443	-2.46283
H	-1.14241	-1.51631	-1.83506
H	-2.70675	-0.70998	-2.04539
O	-0.85568	2.46020	0.02002
O	-2.25428	-1.78233	0.60768
N	-1.95692	0.50760	0.54871
C	0.11746	-0.00934	2.27746
H	-0.09558	-0.94381	2.80295

H	0.40343	0.78226	2.97478
C	1.06987	-0.17066	1.14516
C	1.14205	-1.38052	0.43511
C	1.86017	0.90804	0.71819
C	1.97964	-1.50641	-0.67073
H	0.53952	-2.22647	0.75870
C	2.70159	0.78180	-0.38499
H	1.80641	1.85119	1.25631
C	2.76082	-0.42474	-1.08460
H	2.02618	-2.44898	-1.20851
H	3.30897	1.62515	-0.69999
H	3.41512	-0.52327	-1.94584
H	-0.90266	0.32190	1.86480

7. Time-course plot of the chlorination reaction

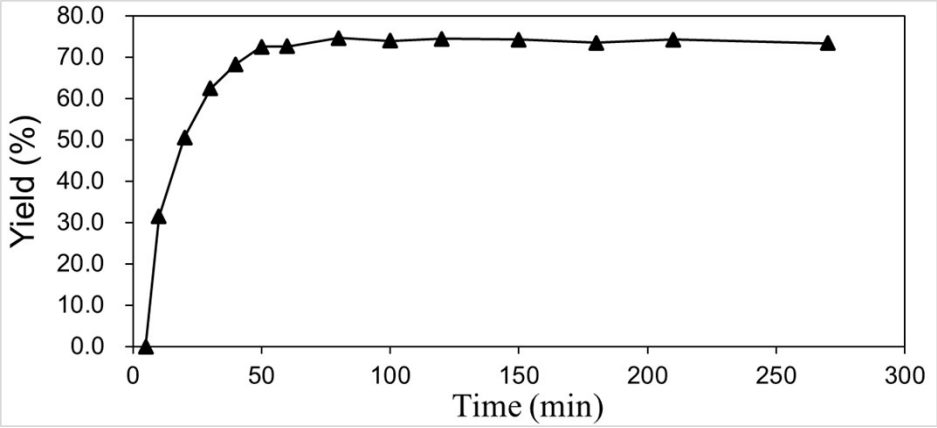
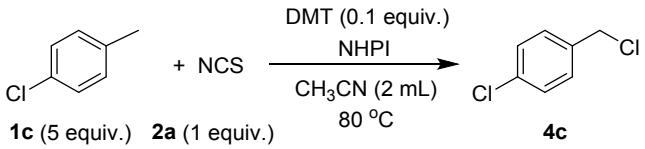


Figure S1. Time-course plot of the chlorination reaction.[a]

[a] Conditions: toluene (**1a**, 6.91g, 75 mmol), NCS (**2a**, 2g, 15 mmol), NHPI (**3a**, 10 mol%), DDQ (0.5 mol%), CH_3CN (60 ml), 80 °C; yield is determined by GC using diphenyl as internal standard; the calculation of yield is on the basis of NCS (**2a**).

8. Chain length experiment

Table S4. Radical chain length initiated by NHPI.[a]



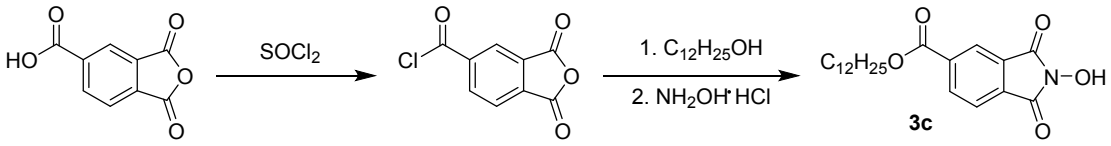
1c (5 equiv.) **2a** (1 equiv.) **4c**

NHPI / equiv	20 min		40min	
	Y_{4c} / %	Chain Length 1[a]	Y_{4c} / %	Chain Length 2[a]
0.03	33.7 (±1.6)	11.2 (±0.5)	44.6 (±0.05)	14.9 (±0.02)
0.07	40.1 (±0.2)	5.7 (±0.03)	45.9 (±0.6)	6.6 (±0.1)
0.1	41.9 (±0.1)	4.2 (±0.01)	47.1 (±0.3)	4.7 (±0.03)
0.2	41.8 (±0.5)	2.1 (±0.02)	48.7 (±1.9)	2.4 (±0.1)
0.3	44.1 (±0.5)	1.5 (±0.02)	49.3 (±0.05)	1.6 (±0.002)
Average Chain Length[b]		4.9 (±0.1)		6.0 (±0.001)

[a] yield determined by GC with diphenyl as internal standard, on the basis of NCS; [b] chain length refers to yield divide NHPI in mol%; [c] average chain length refers to sum of chain length divide sum of experiments.

9. Preparation and characterization of NO-H agents

The procedures for the synthesis of 3c



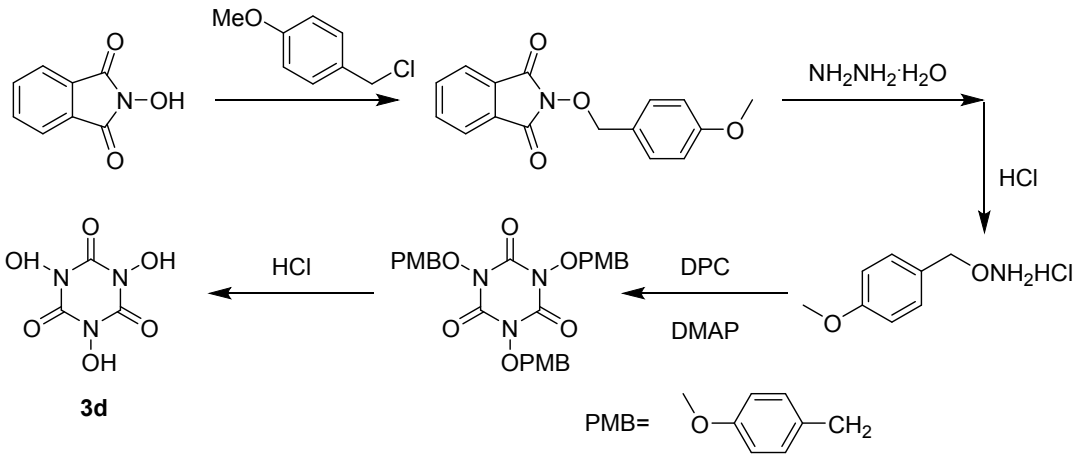
Scheme S3. Preparation of **3c**.

3c was prepared according to the literature procedure in Scheme S3.[12, 13] Trimellitic acid anhydride (7.68 g, 0.04 mol) was boiled in thionyl chloride (10 mL) for 12 h. The anhydride acid chloride was isolated by vacuum distillation of the solvent. Remove the thionyl chloride with 20ml petroleum ether three times giving rise to white solid. Pyridine (10 mmol, 0.75 mL) was added in a few portions to a stirred mixture of trimellitic anhydride chloride (10 mmol, 2.16 g) in toluene (10 mL) at 0ºC. Next, a solution of dodecyl alcohol (10 mmol, 2.25 mL) in toluene (5 mL) was added dropwise over 30 min. The mixture was stirred for 4 h at room temperature, then for 10 h at 85ºC and for 7 h at 100ºC. Toluene was evaporated, and product in form of white paste was obtained. Dried pyridine (12.5 mL) and hydroxylamine hydrochloride (11 mmol, 0.76 g) were added and the reaction mixture was stirred at 90ºC for 15 h. The product was poured to 30 mL of water and acidified by hydrochloric acid to pH 1. The precipitate was filtered, and washed with ice water. The product was recrystallised from methanol.

^{1}H NMR (600 MHz, DMSO-D^6, 298 K): δ = 11.01 (s, 1H,N-OH), 8.35 (dd, $^3J_{HH}$ = 7.8

Hz, $^{4}J_{HH}$ = 1.8 Hz, 1H, Ar-H), 8.17 (s, 1H, Ar-H), 7.97 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H, Ar-H), 4.32 (t, $^{3}J_{HH}$ = 6.6 Hz, 2H, CO-OCH_2), 1.73 (m, 2H, OCH_2-C**H**$_2$), 1.22 - 1.32 (m, 18H, CH_2), 0.84 (t, 3H, $^{3}J_{HH}$ = 6.6 Hz, CH_3); **^{13}C{^{1}H} NMR** (151 MHz, DMSO-D^6, 298 K): δ = 164.2, 163.2 (Ar-**C**O-N), 135.2, 135.1, 132.5, 129.4, 123.5, 122.3 (Ar), 65.6 (COO), 31.3 (OCH_2), 29.0, 28.94, 28.88, 28.7, 28.6, 28.0, 25.4 (CH_2), 22.1 (**C**H_2CH_3), 14.0 (CH_3).

The procedures for the synthesis of 3d



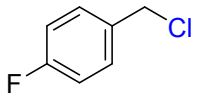
Scheme S4. Preparation of the THICA (**3d**) catalyst.

3d was prepared according to the literature procedure in Scheme S4.[14]

^{1}H NMR (600 MHz, DMSO-D^6, 298 K): δ = 11.04 (s, 3H, NO-H). **^{13}C{^{1}H} NMR** (151 MHz, DMSO-D^6, 298 K): δ = 146.7 (C=O).

10. Characterization of Chlorinated products

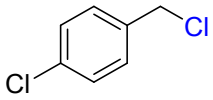
1-(chloromethyl)-4-fluorobenzene (4b)



4b

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.37 (m, 2H, Ar-H), 7.05 (t, $^{3}J_{HH}$ = 8.4 Hz, 2H, Ar-H), 4.57 (s, 2H, CH_2). **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K): δ =163.6, 133.5, 130.5, 115.9 (Ar), 45.5 (CH_2). NMR data correspond to the reported values.[15]

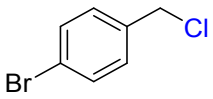
Chloro-4-(chloromethyl)benzene (4c).



4c

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.35−7.31 (m, 4H, Ar-H), 4.55 (s, 2H, CH_2). **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K): δ = 136.1, 134.4, 130.0, 129.0 (Ar), 45.5 (CH_2). NMR data correspond to the reported values.[16]

Bromo-4-(chloromethyl)benzene (4d).

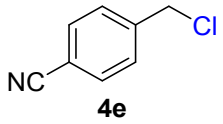


4d

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.49 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, Ar-H), 7.27 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, Ar-H), 4.54 (s, 2H, CH_2). **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K): δ =

136.6, 132.0, 130.4, 122.6 (Ar), 45.5 (CH_2). NMR data correspond to the reported values.[17]

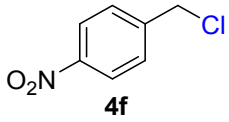
4-(chloromethyl)benzonitrile (4e).



4e

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.64 (d, 2H, $^3J_{HH}$ = 8.4 Hz, Ar-H), 7.50 (d, 2H, $^3J_{HH}$ = 8.4 Hz, Ar-H), 4.59 (s, 2H, CH_2). **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K): δ = 142.5 (CN), 132.5, 129.2, 118.5, 112.2 (Ar), 45.0 (CH_2). NMR data correspond to the reported values.[15]

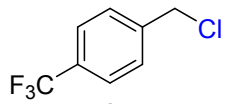
1-(chloromethyl)-4-nitrobenzene (4f).



4f

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 8.21 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar-H), 7.57 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar-H), 4.64 (s, 2H, CH_2). **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K): δ = 147.8, 144.4, 129.4, 124.0 (Ar), 44.6 (CH_2). NMR data correspond to the reported values.[18]

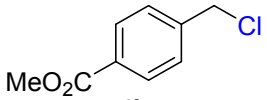
1-(chloromethyl)-4-(trifluoromethyl)benzene (4g).



4g

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.64 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar-H), 7.52 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar-H), 4.62 (s, 2H, CH_2). **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K): δ = 141.4 (CF_3), 130.6, 129.0, 125.8, 123.2 (Ar), 45.2 (CH_2). NMR data correspond to the reported values.[19]

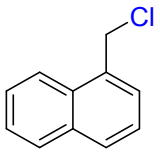
Methyl 4-(chloromethyl)benzoate (**4h**).



4h

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 8.02 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar-H), 7.45 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar-H), 4.60 (s, 2H, CH_2), 3.91 (s, 3H, CH_3). **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K): δ = 166.7 (C=O), 142.3, 130.2, 130.1, 128.6 (Ar), 52.3 (CH_3), 45.5 (CH_2). NMR data correspond to the reported values.[20]

1-(chloromethyl)naphthalene (4i).

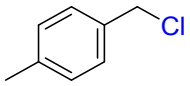


4i

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 8.18 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ar-H), 7.91−7.86 (m, 2H, Ar-H), 7.64−7.61 (m, 1H, Ar-H), 7.57−7.54 (m, 2H, Ar-H), 7.46−7.43 (m, 1 H, Ar-H), 5.07 (s, 2 H, CH_2). **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K): δ = 134.1, 133.1,

131.2, 129.9, 129.0, 127.8, 126.8, 126.3, 125.4, 123.8 (Ar), 44.7 (CH_2). NMR data correspond to the reported values.[21]

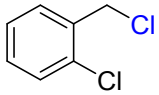
1-(chloromethyl)-4-methylbenzene (4k).



4k

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.3 (d, 2H, $^3J_{HH}$ = 8.4 Hz), 7.19 (d, 2H, $^3J_{HH}$ = 7.8 Hz), 4.57 (s, 2H), 2.37 (s, 3 H). **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K): δ = 138.4, 134.7, 129.5, 128.7, 46.4 (Ar), 21.3 (CH_2). NMR data correspond to the reported values.[15]

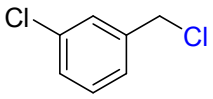
1-chloro-2-(chloromethyl)benzene (4m).



4m

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.48−7.47 (m, 1H, Ar-H), 7.42−7.40 (m, 1H, Ar-H), 7.29−7.26 (m, 2H, Ar-H), 4.72 (s, 2H, CH_2). **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K): δ = 135.1, 134.2, 131.0, 130.0, 129.9, 127.3 (Ar), 43.7 (CH_2). NMR data correspond to the reported values.[21]

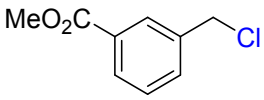
1-chloro-3-(chloromethyl)benzene (4n).



4n

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.40 (bs, 1H, Ar-H), 7.31−7.27 (m, 3H, Ar-H), 4.54 (s, 2H, CH_2). **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K): δ = 139.4, 134.6, 130.1, 128.8, 128.7, 126.8 (Ar), 45.3 (CH_2). NMR data correspond to the reported values.[17]

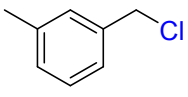
methyl 3-(chloromethyl)benzoate (4o).



4o

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 8.05 (s, 1H, Ar-H), 7.98 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, Ar-H), 7.57 (d, $^{3}J_{HH}$ =7.8 Hz, 1H, Ar-H), 7.43 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, Ar-H), 4.61 (s, 2H, CH_2), 3.92 (s, 3H, CH_3). **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K): δ = 166.6 (C=O), 137.9, 133.2, 130.8, 129.7, 129.6, 128.9 (Ar), 52.3 (CH_3), 45.6 (CH_2). NMR data correspond to the reported values.[22]

1-(chloromethyl)-3-methylbenzene (4p).

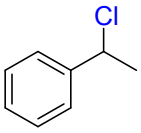


4p

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.28−7.15 (m, 4H, Ar-H), 4.57 (s, 2H, CH_2), 2.38 (s, 3H, CH_3). **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K): δ = 138.6, 137.5, 129.4, 129.3, 128.8, 125.8 (Ar), 46.5 (CH_2), 21.4 (CH_3). NMR data correspond to the reported

values.[21]

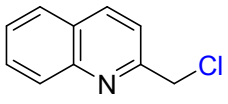
(1-chloroethyl)benzene (4r).



4r

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.44−7.30 (m, 5H, Ar), 5.12 (q, 1H, $^{3}J_{HH}$ = 6.6 Hz, CH), 1.87 (d, 3H, $^{3}J_{HH}$ = 6.6 Hz, CH_3). **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K): δ = 143.0, 128.8, 128.4, 126.6 (Ar), 58.9 (CH), 26.6 (CH_3). NMR data correspond to the reported values.[23]

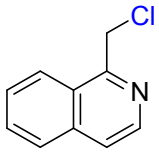
2-(chloromethyl)quinolone (4x).



4x

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 8.18 (d, 1H, $^{3}J_{HH}$ = 8.4 Hz, Ar-H), 8.07 (d, 1H, $^{3}J_{HH}$ = 8.4 Hz, Ar-H), 7.81 (d, 1H, $^{3}J_{HH}$ = 7.8 Hz, Ar-H), 7.73 (t, 1H, $^{3}J_{HH}$ = 7.8 Hz, Ar-H), 7.60−7.54 (m, 2H, Ar), 4.84 (s, 2H, CH_2). **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K): δ = 156.8, 147.5, 137.4, 130.1, 129.4, 127.7, 127.6, 127.1, 120.6 (Ar), 47.5 (CH_2). NMR data correspond to the reported values.[15]

1-(chloromethyl)isoquinoline (4y).



4y

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 8.48 (d, 1H, $^{3}J_{HH}$ = 5.4 Hz, Ar-H), 8.25 (d, 1H, $^{3}J_{HH}$ = 8.4 Hz, Ar-H), 7.86 (d, 1H, $^{3}J_{HH}$ = 7.8 Hz, Ar-H), 7.74−7.65 (m, 3H, Ar), 5.15 (s, 2H, CH_2). **^{13}C NMR** (151 MHz, $CDCl_3$, 298 K): δ = 155.8, 142.1, 136.8, 130.5, 128.0, 127.7, 126.6, 125.2, 121.9 (Ar), 45.1 (CH_2). NMR data correspond to the reported values.[15]

11. References

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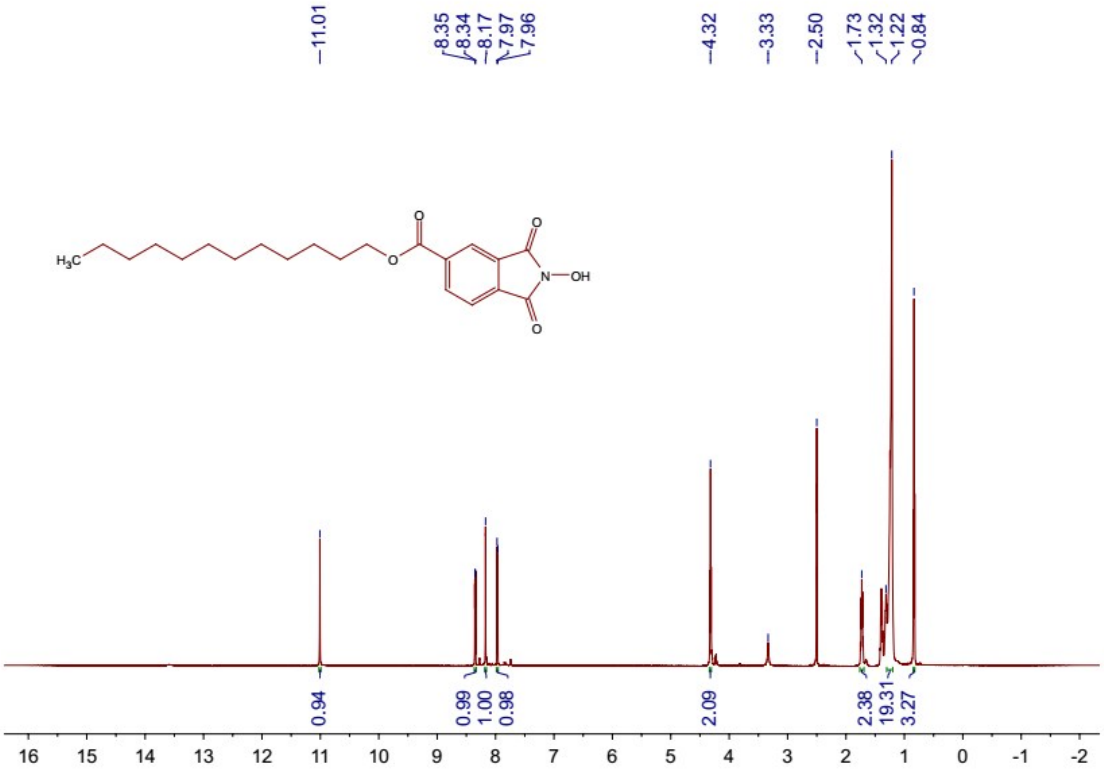
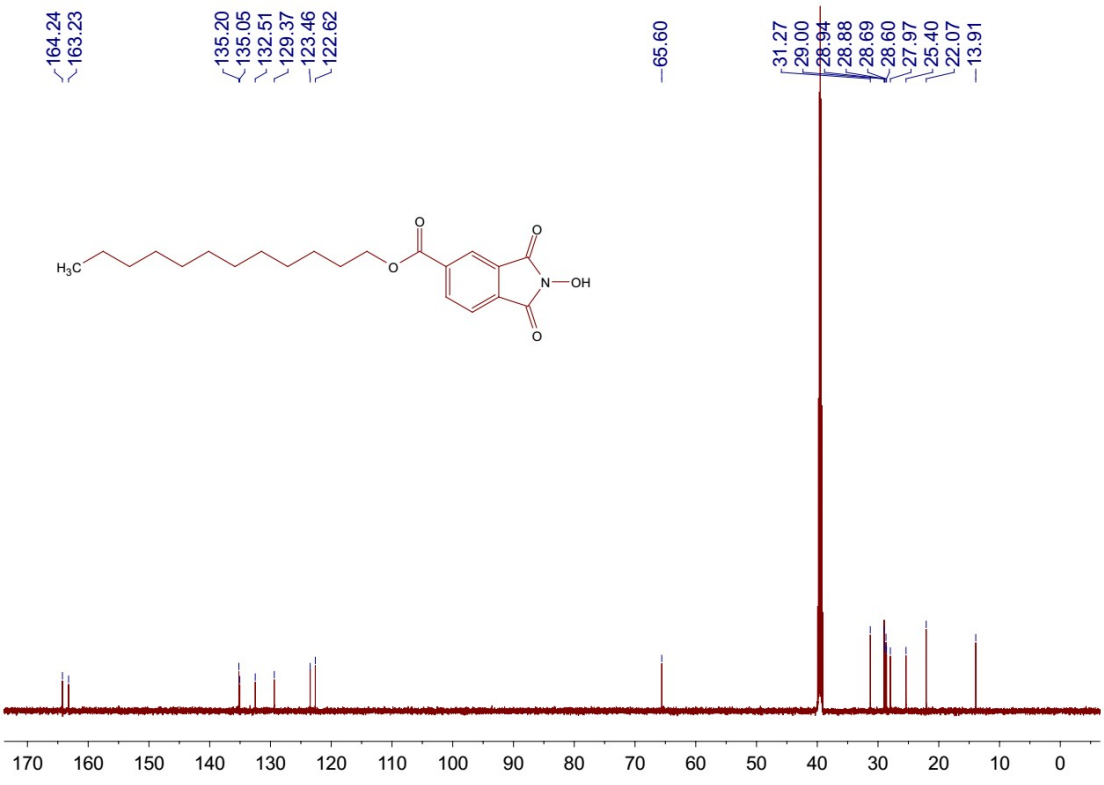
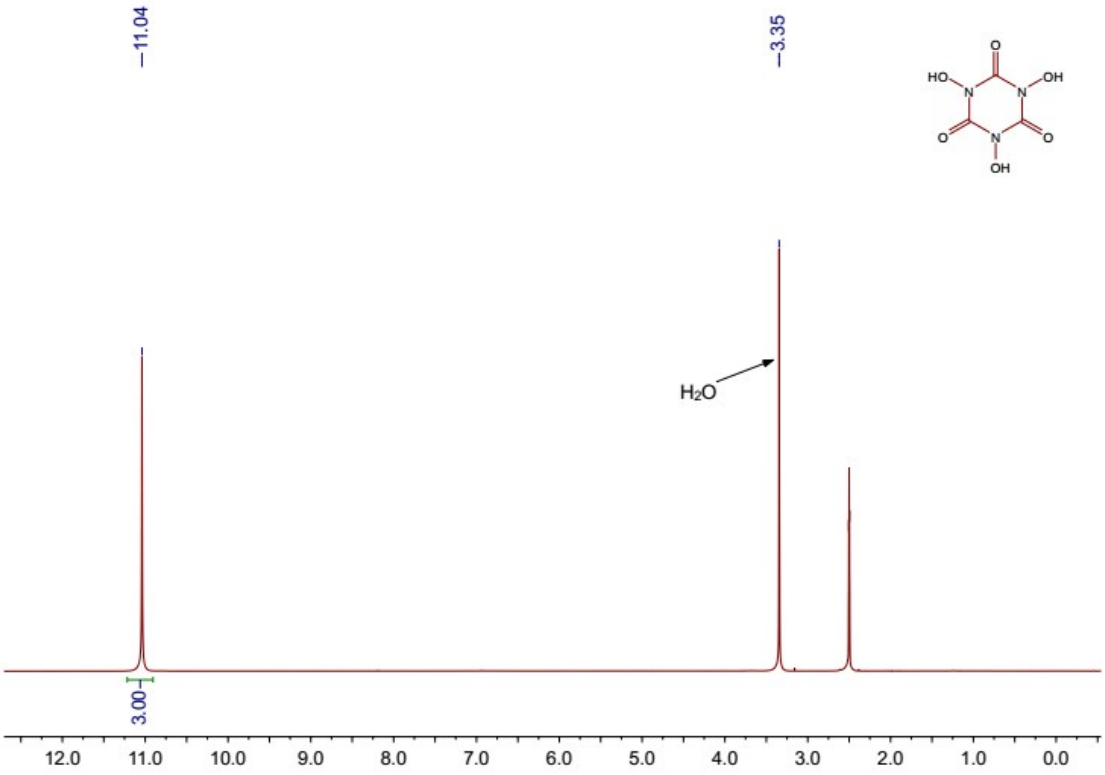
GC and NMR spectral



^{1}H NMR (600 MHz, DMSO-D^{6}, 298 K) of **3c**



^{13}C{^{1}H} NMR (151 MHz, DMSO-D^{6}, 298 K) of **3c**



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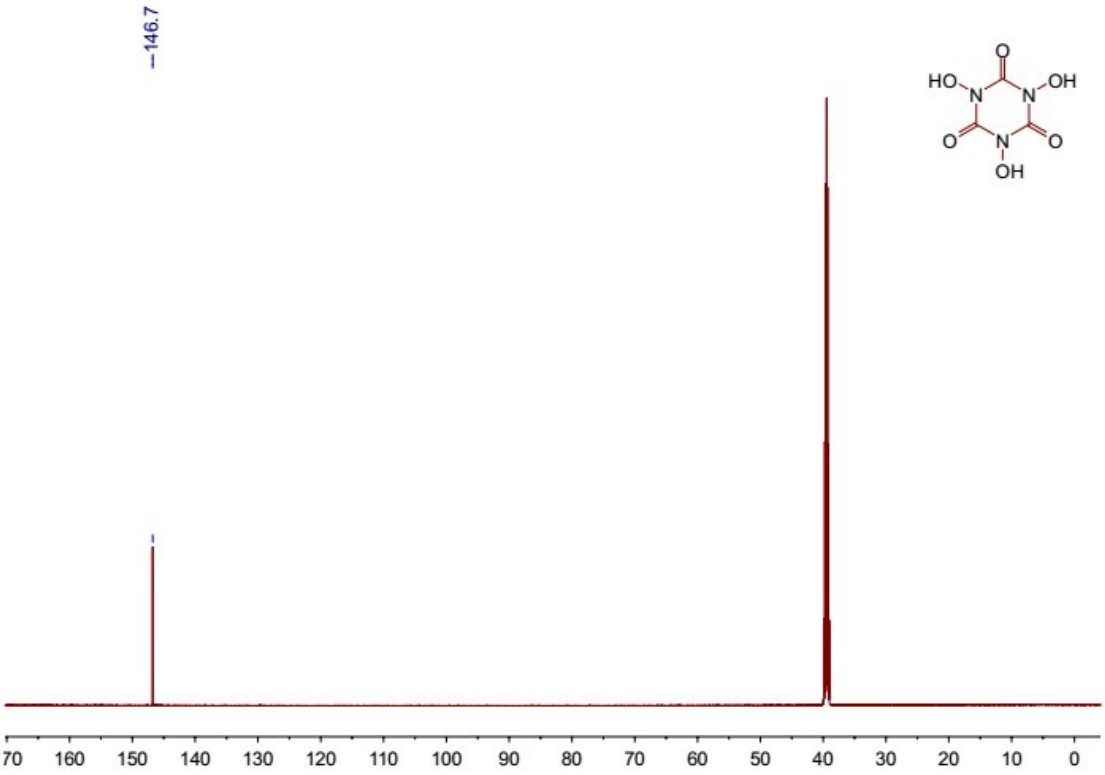
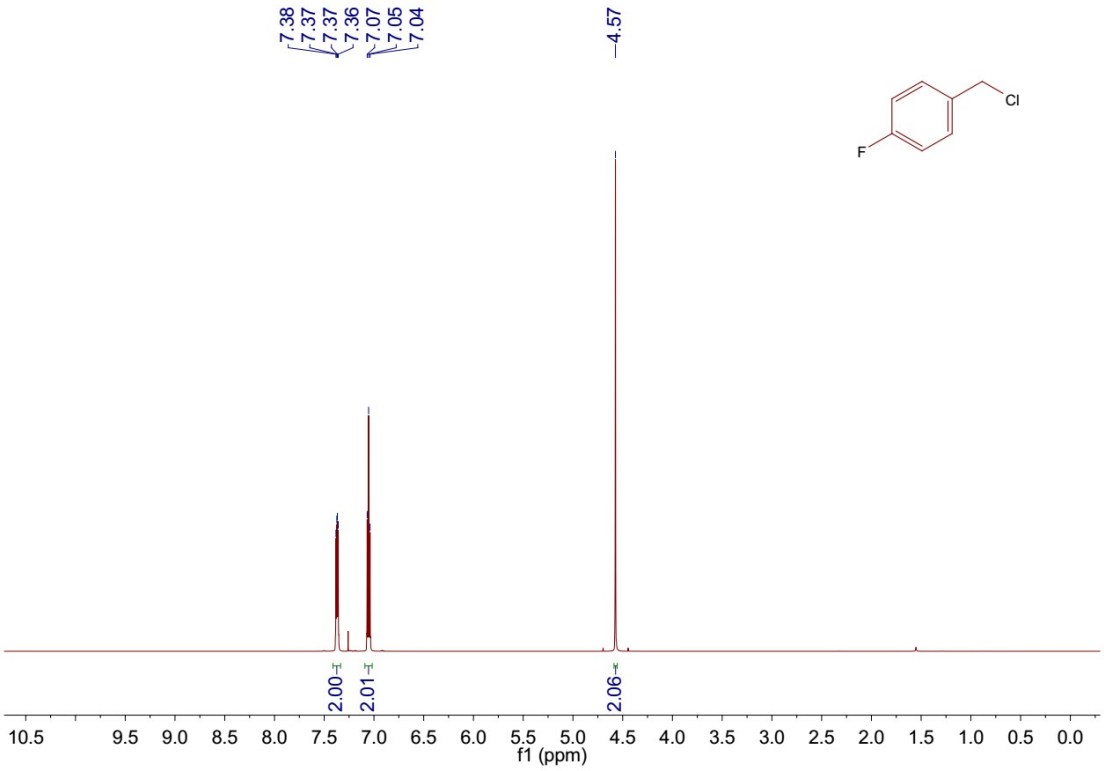
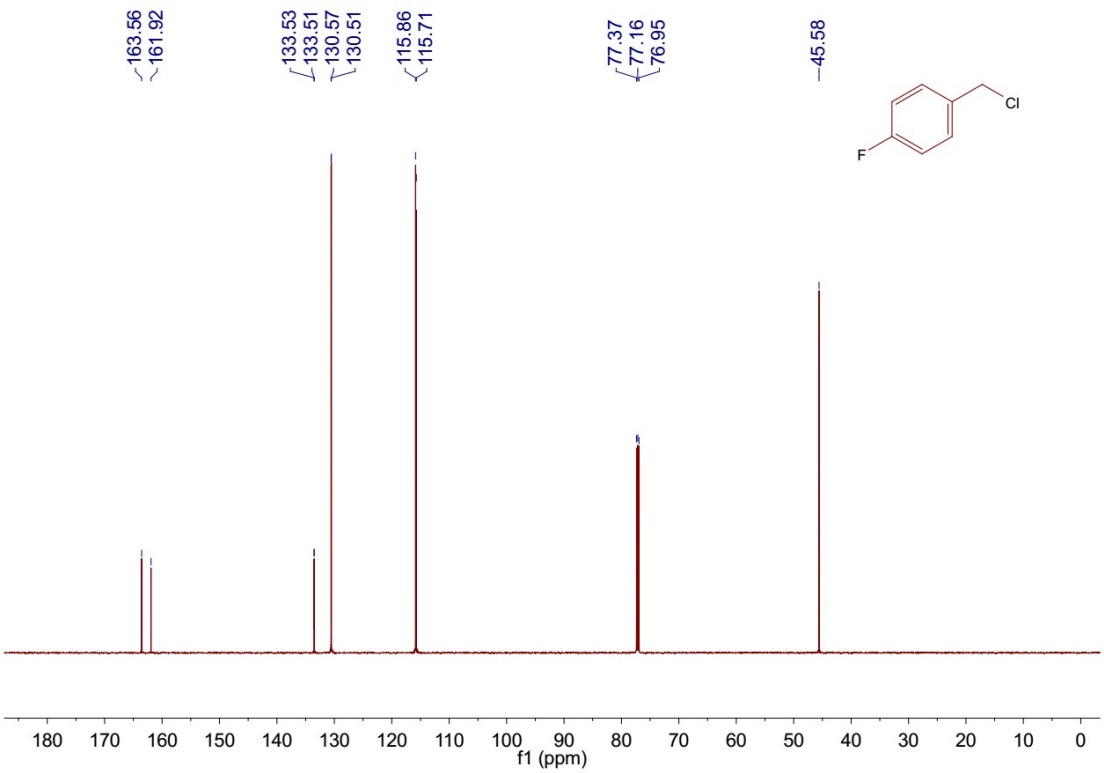


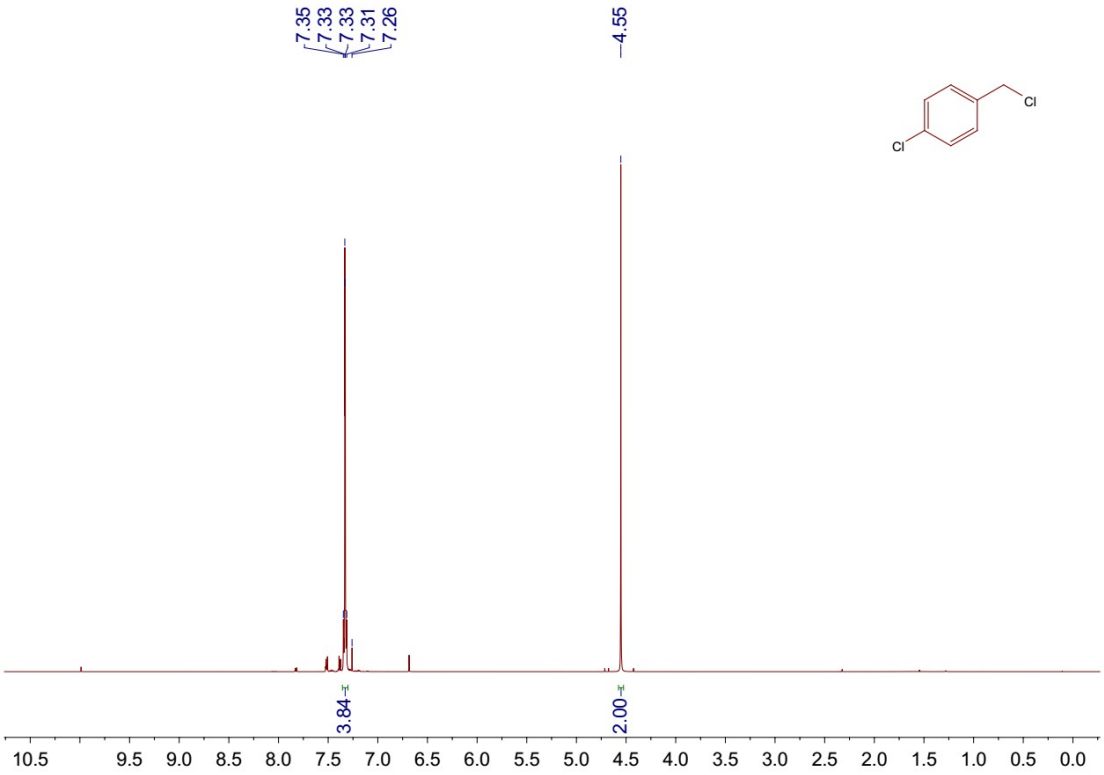
^{13}C{^{1}H} NMR (151 MHz, DMSO-D^{6}, 298 K) of **3d**



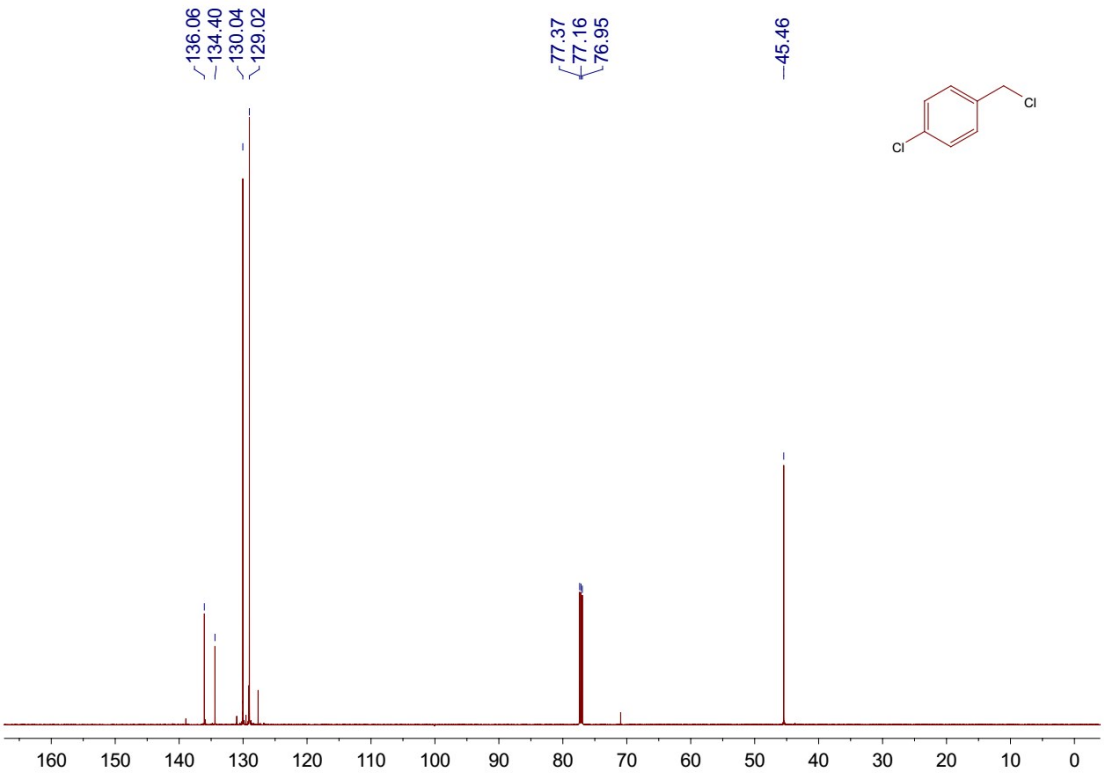
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4b**



^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4b**



^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4c**



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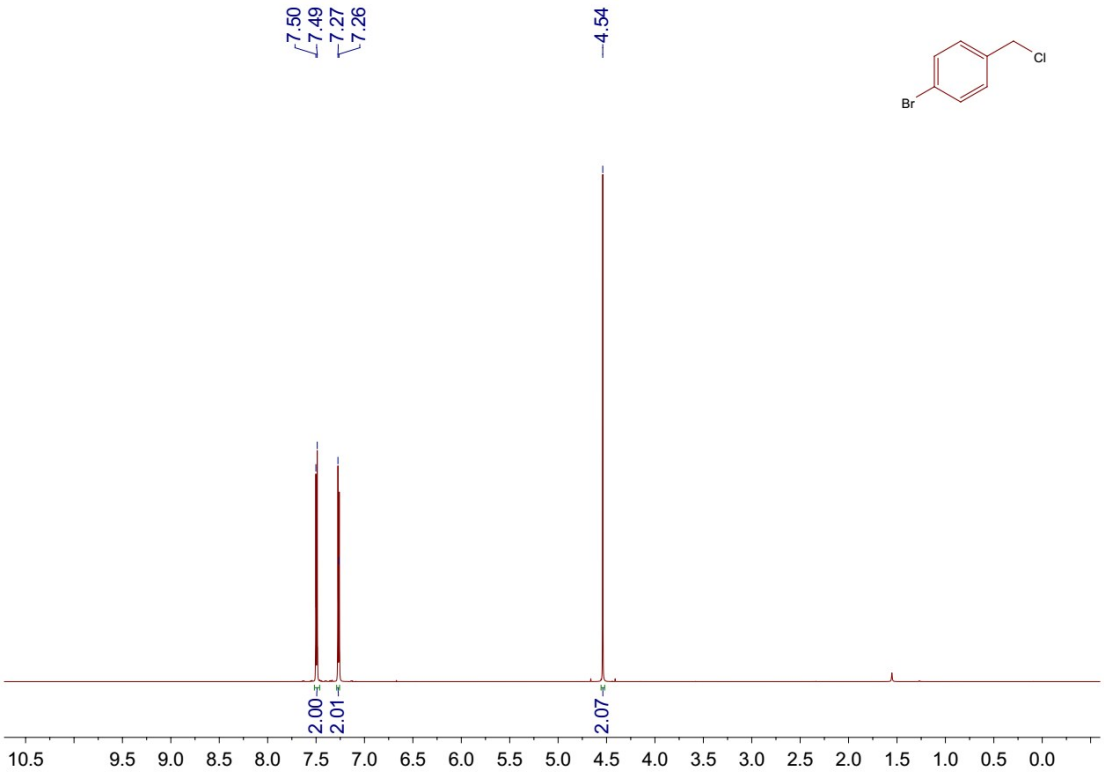

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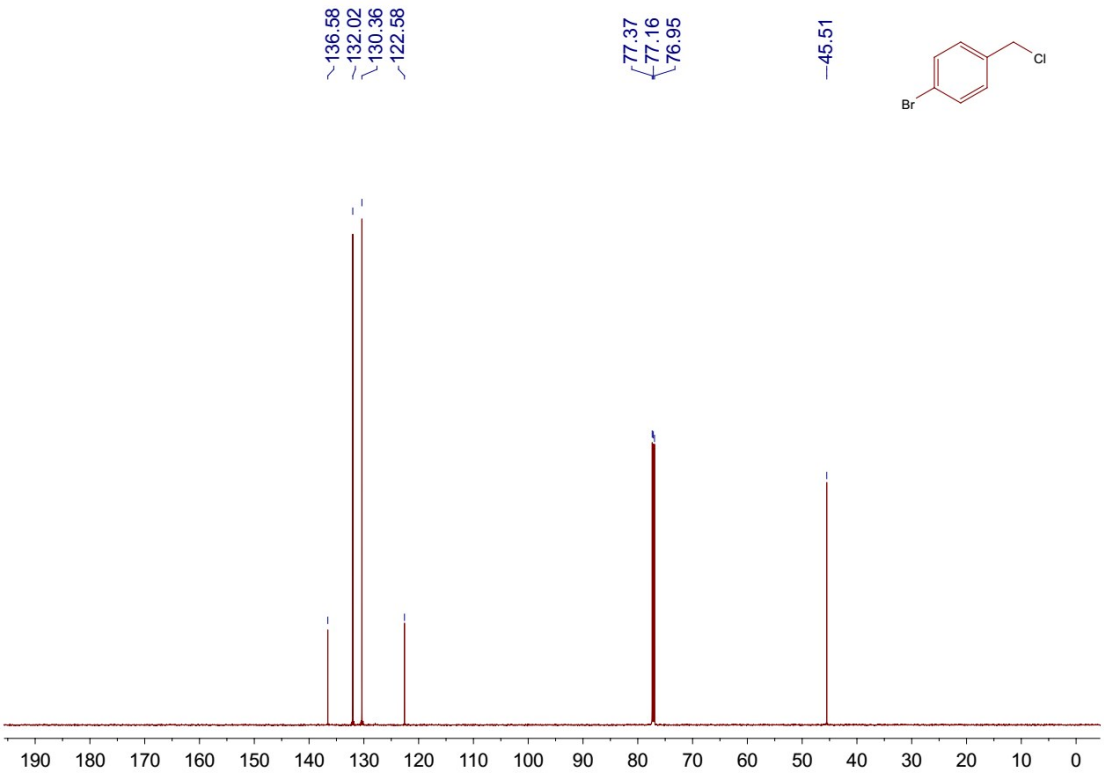

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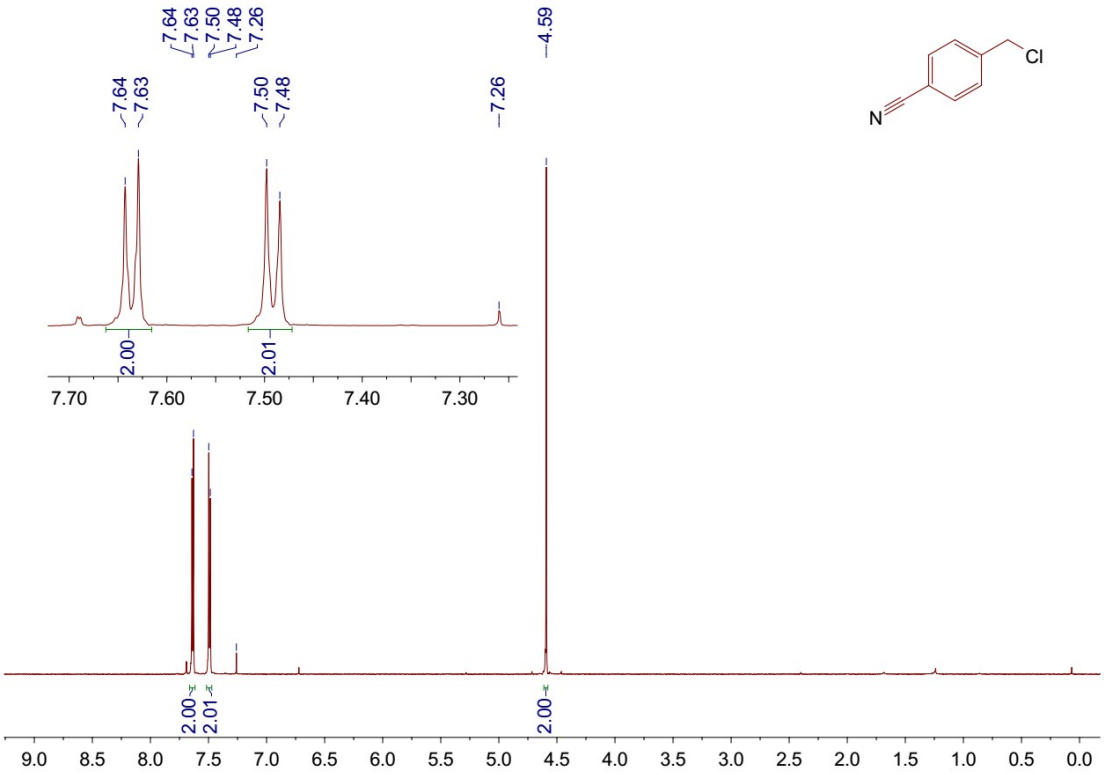

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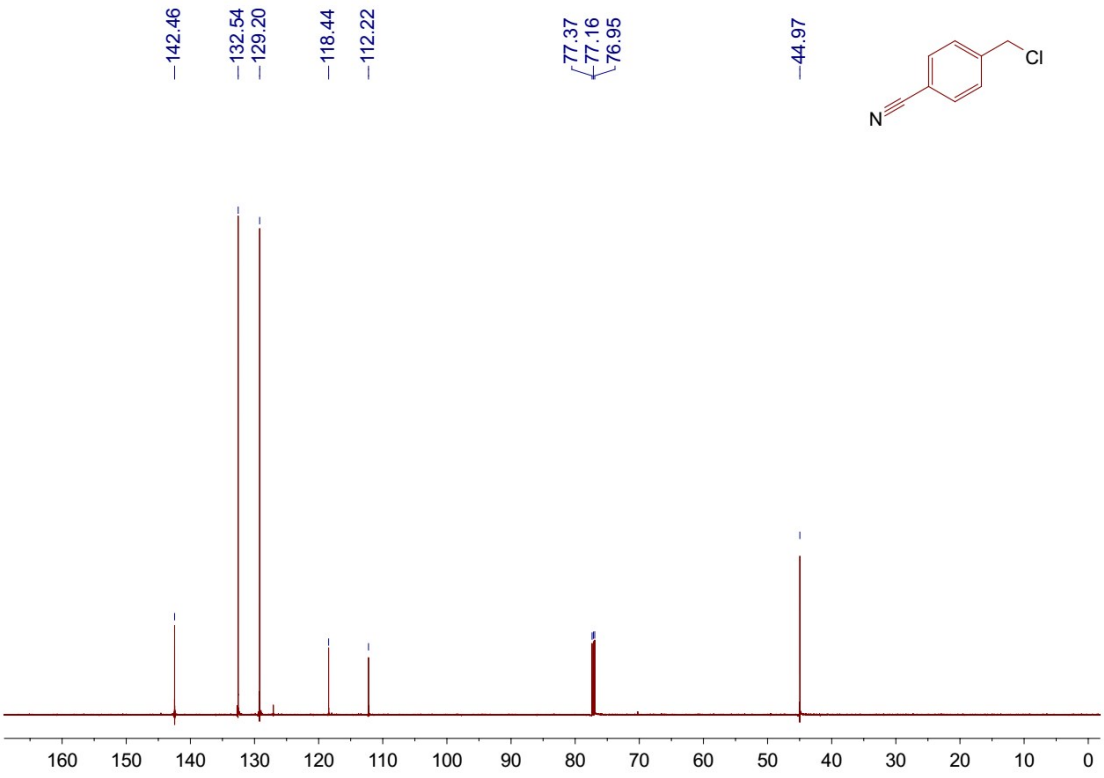

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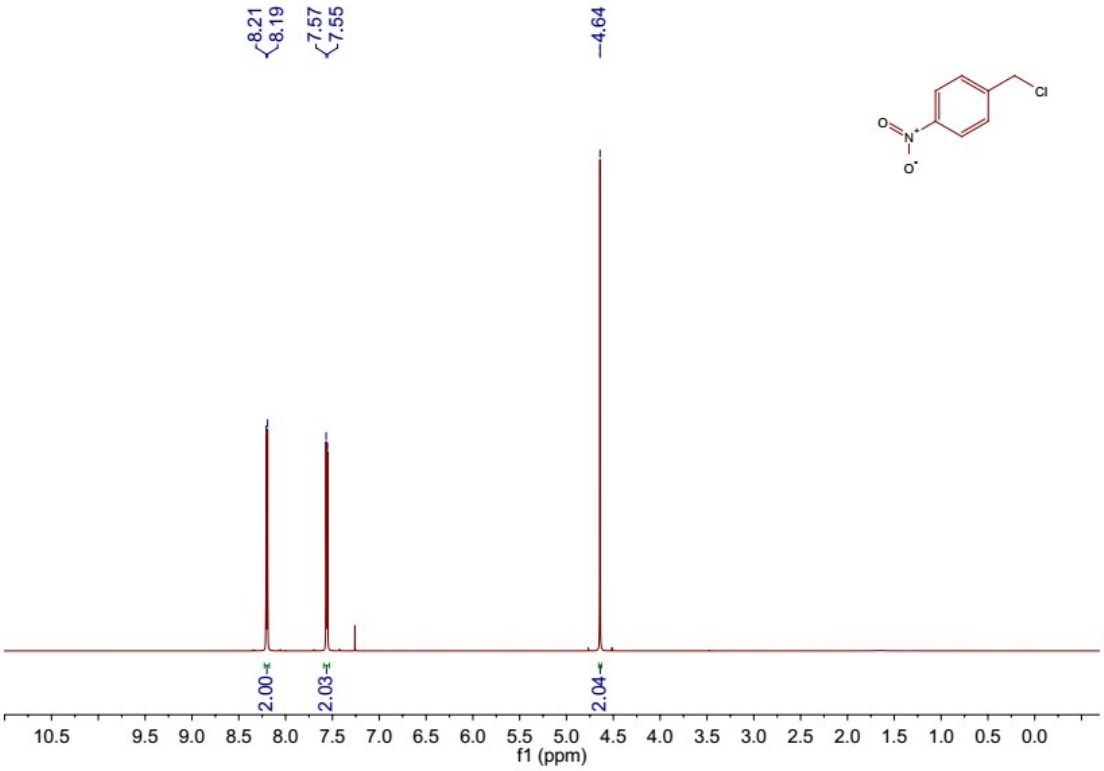

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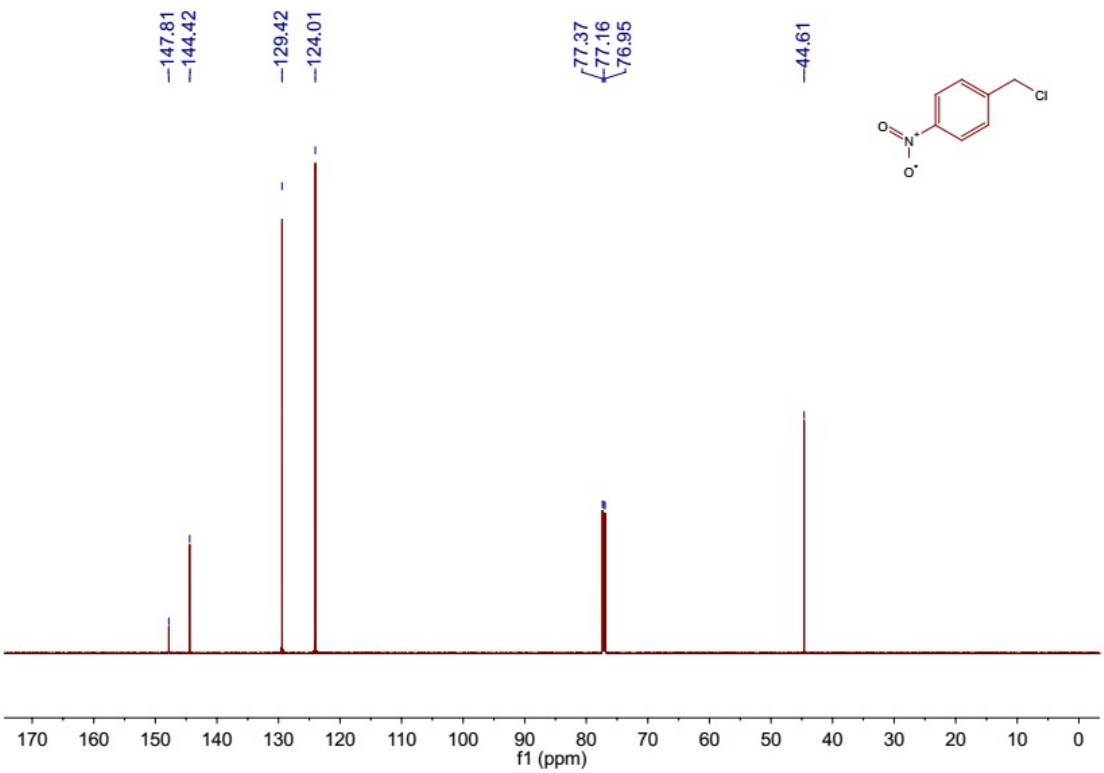

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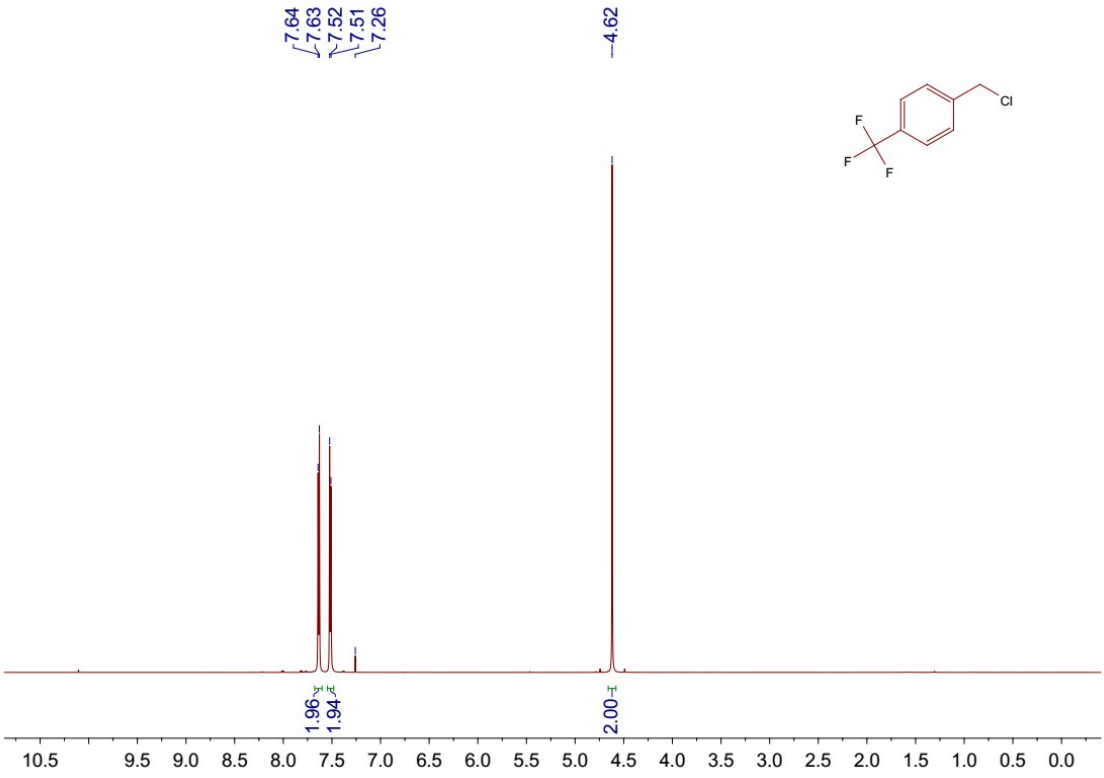
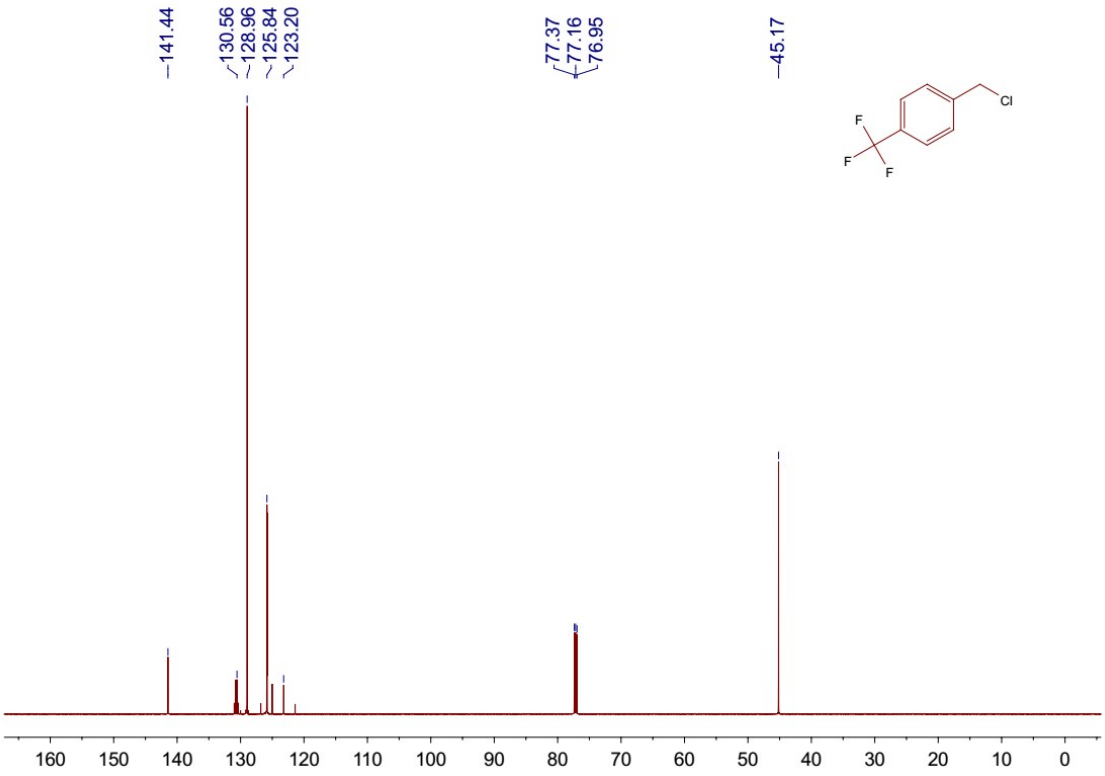


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4g**



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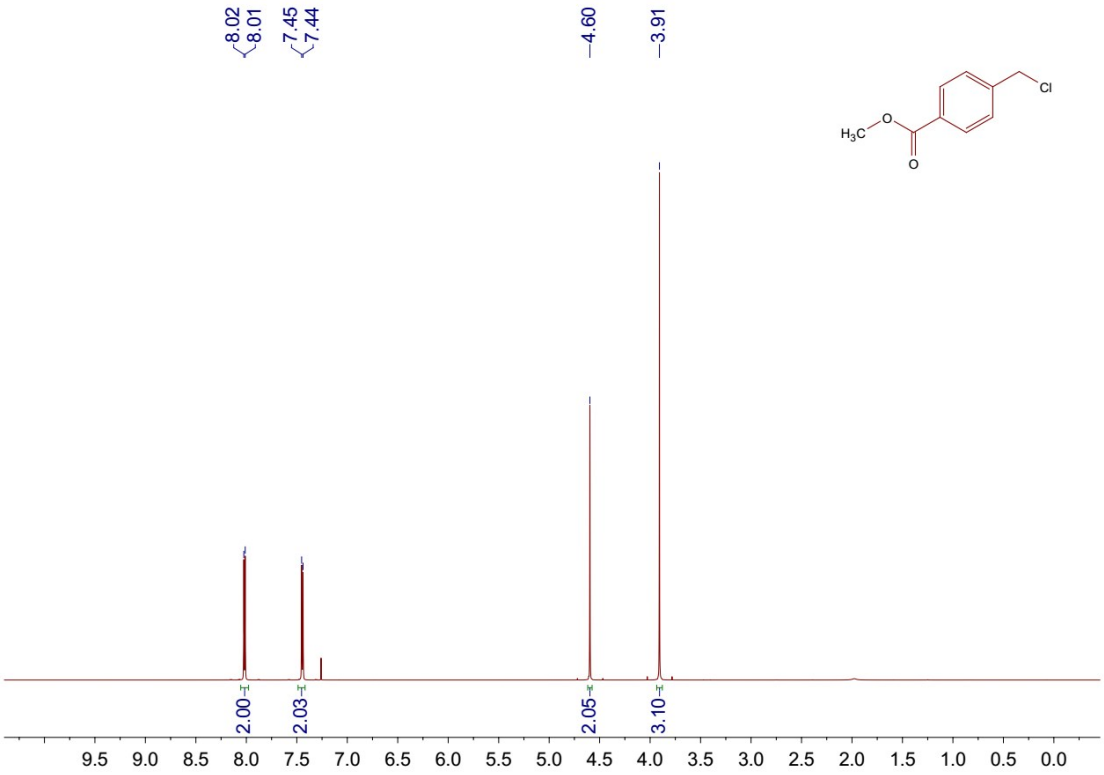

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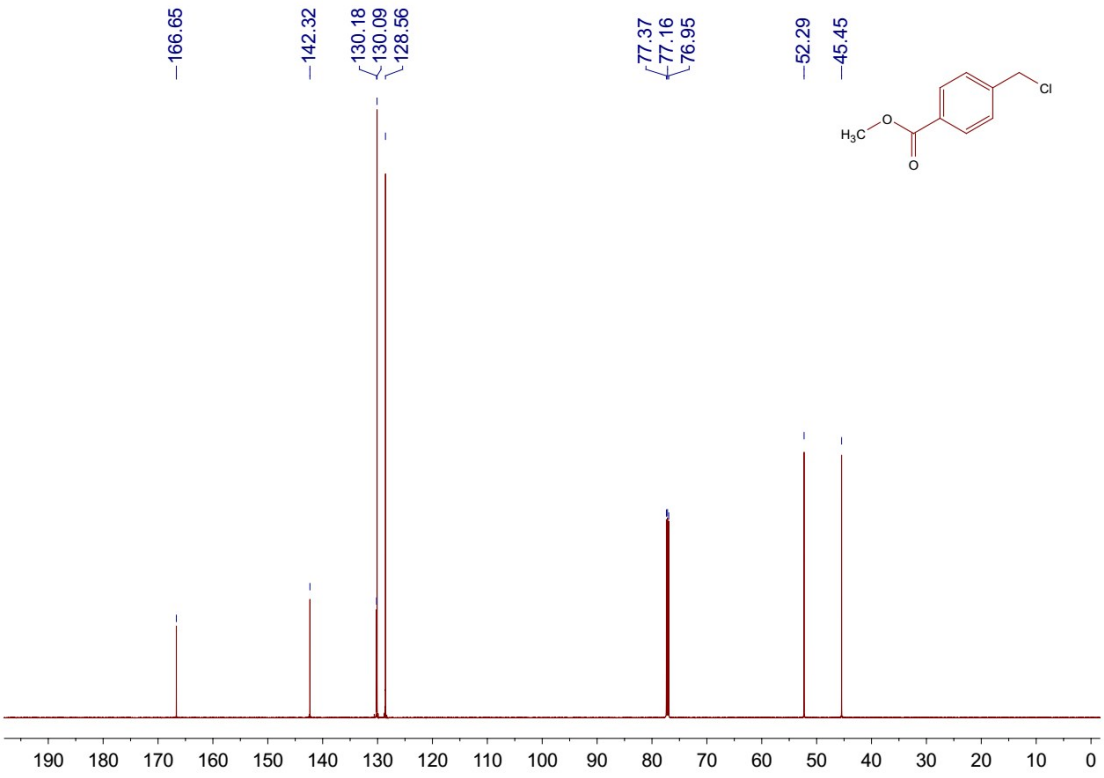

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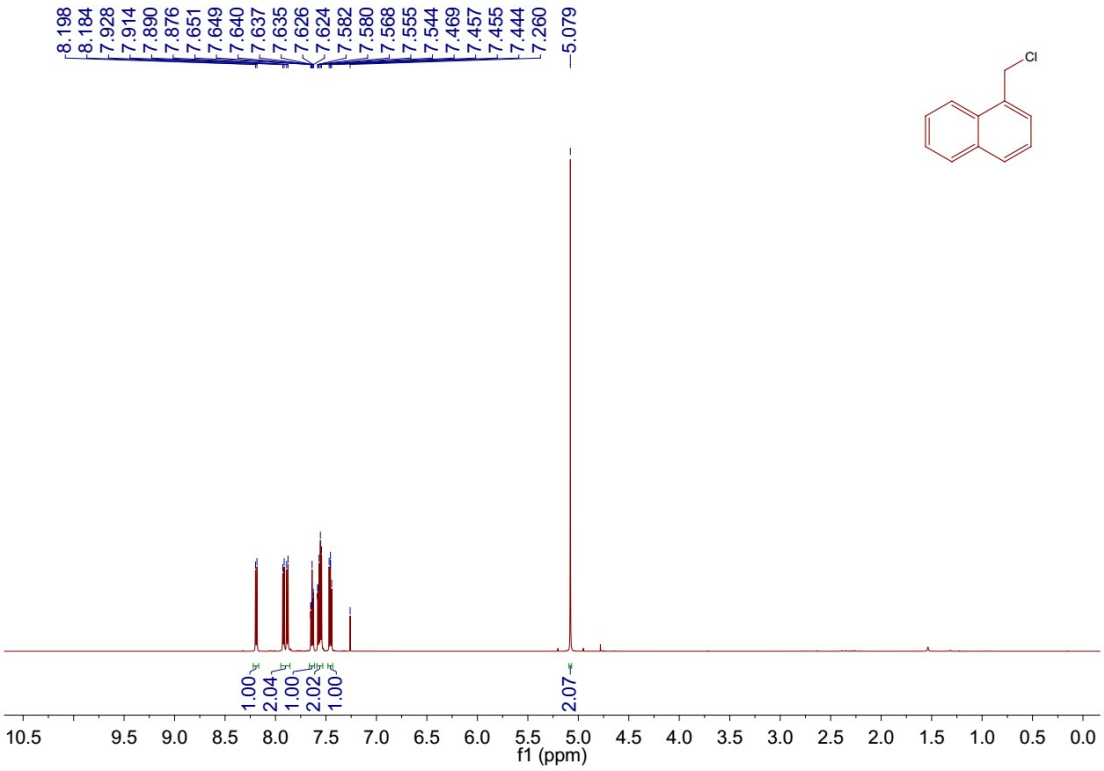

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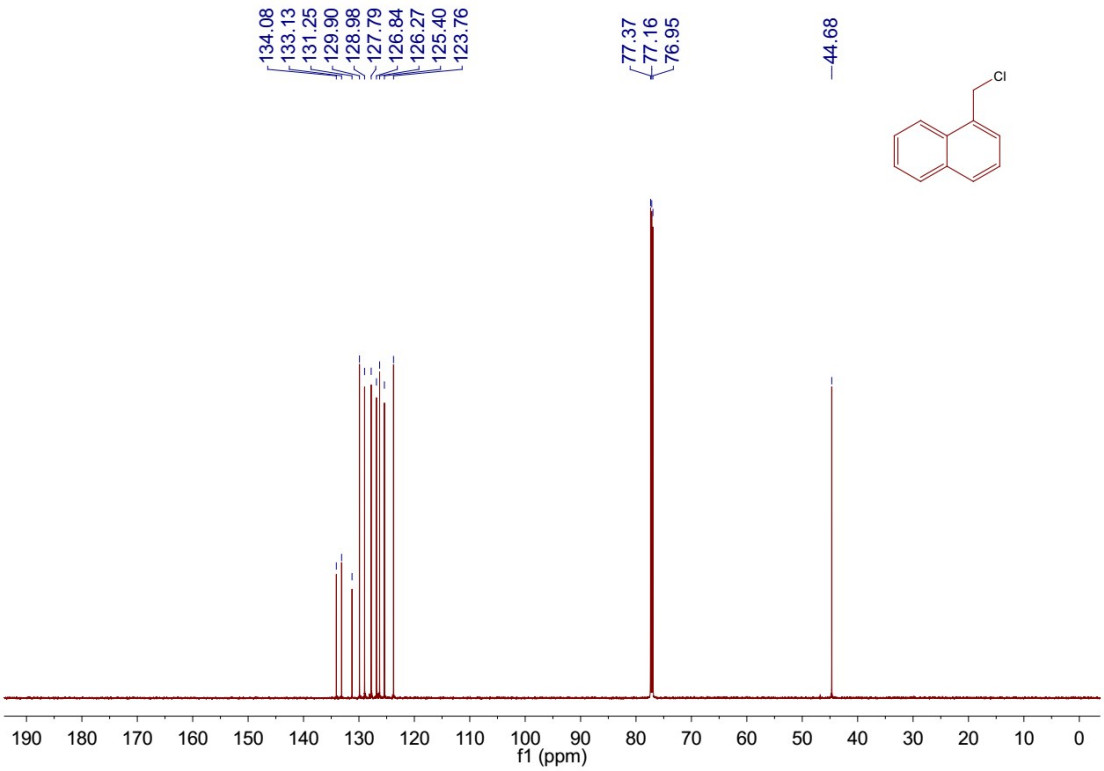

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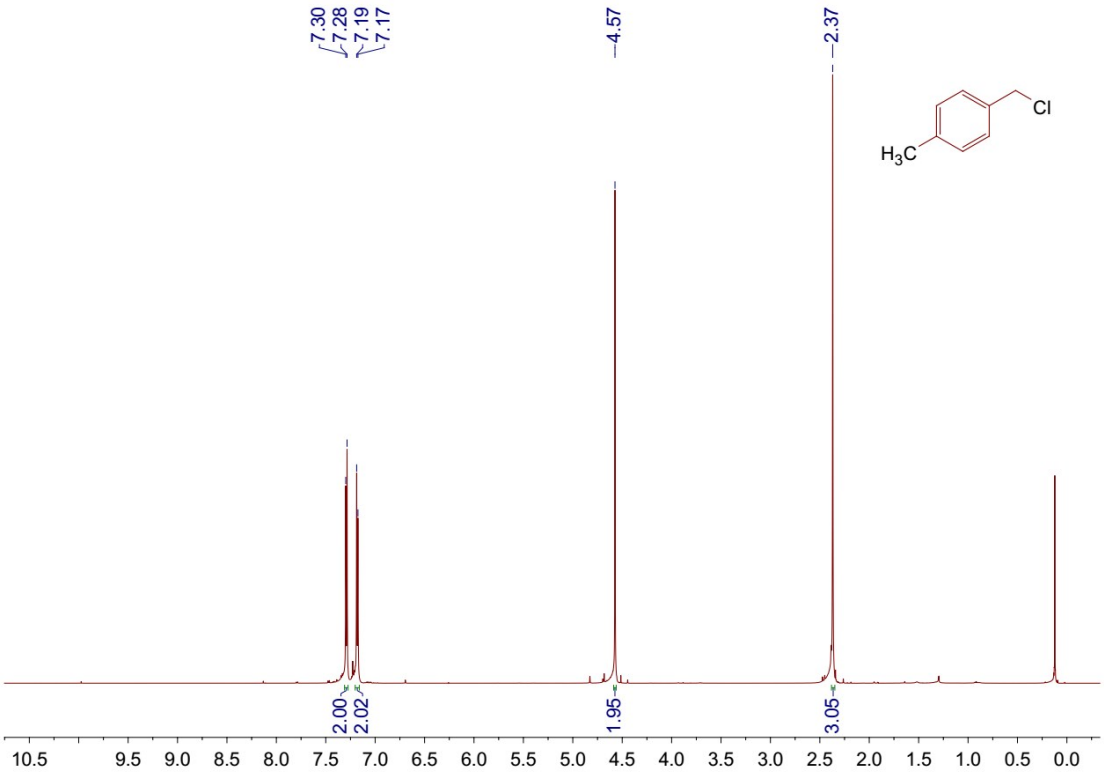

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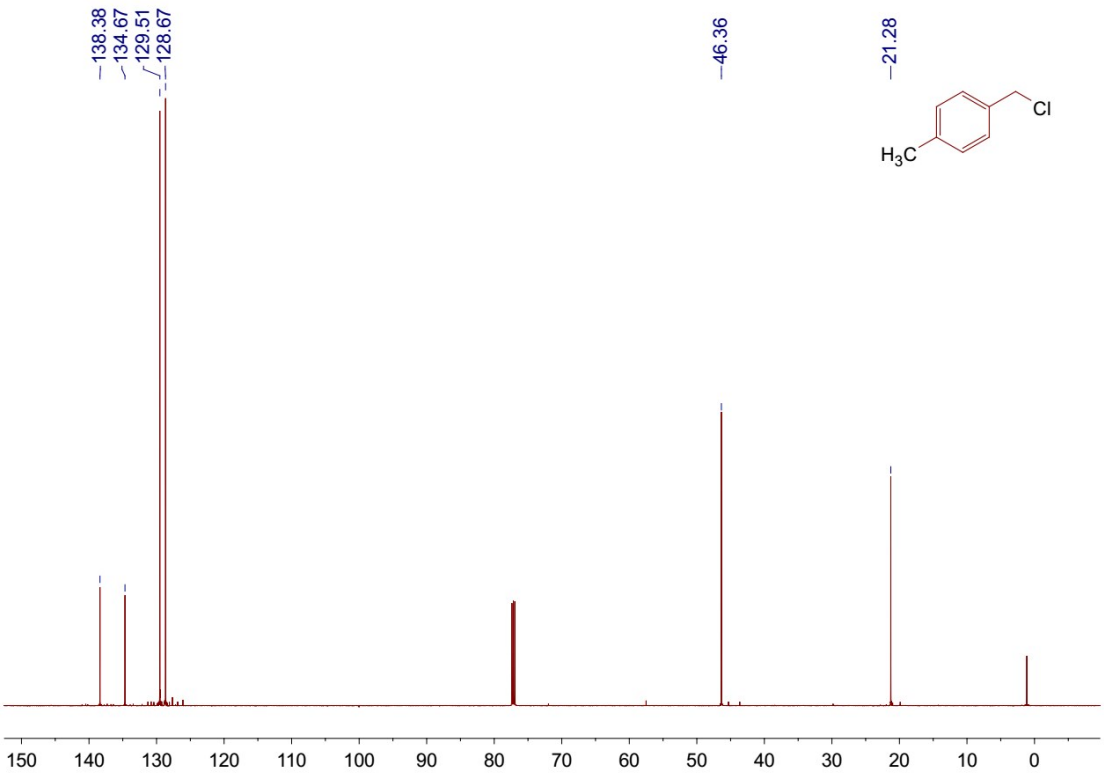
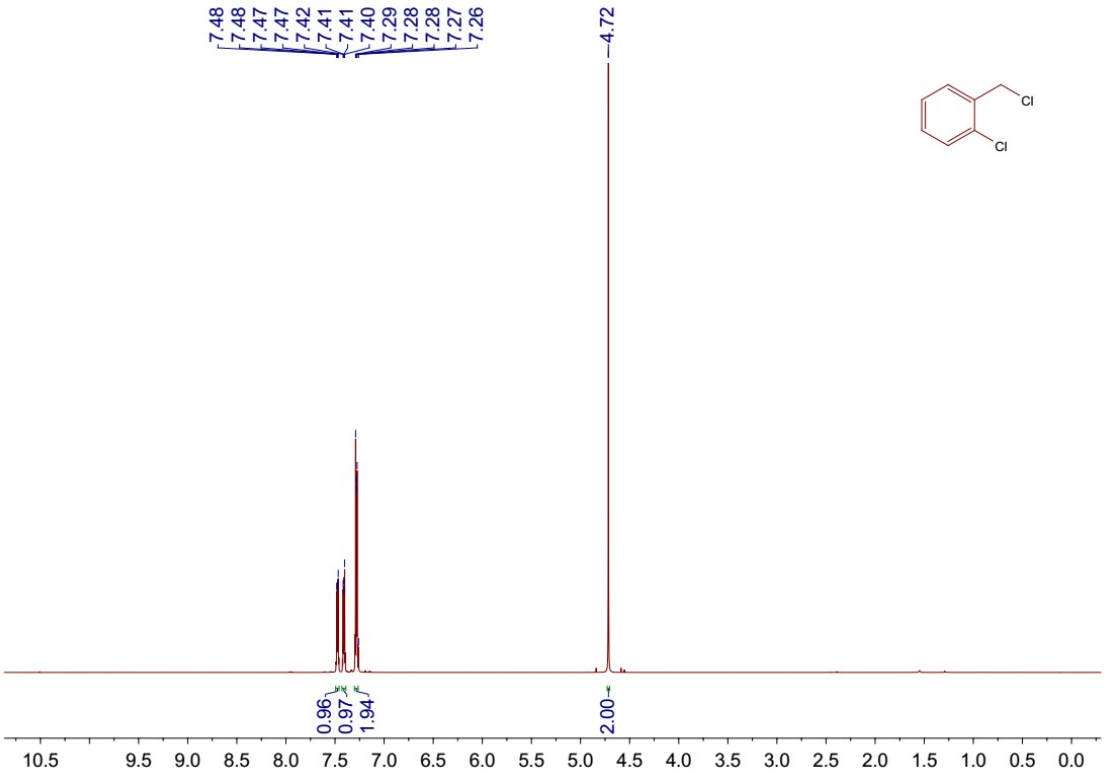
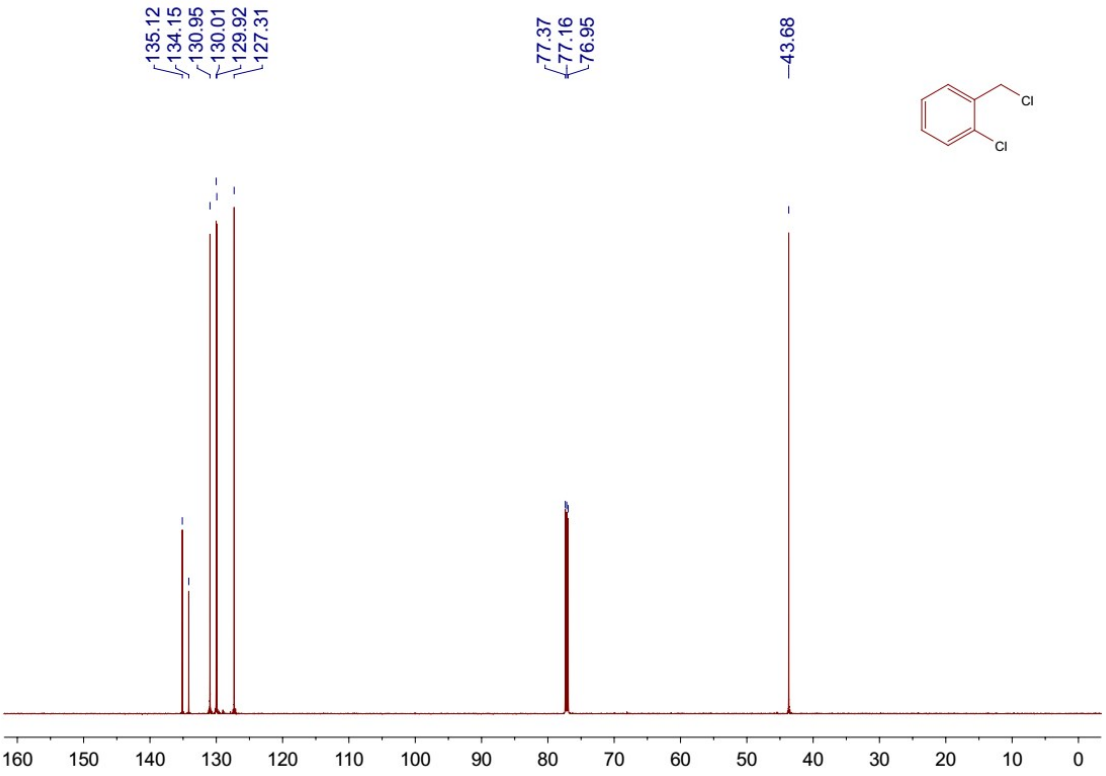


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4k**



^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4m**



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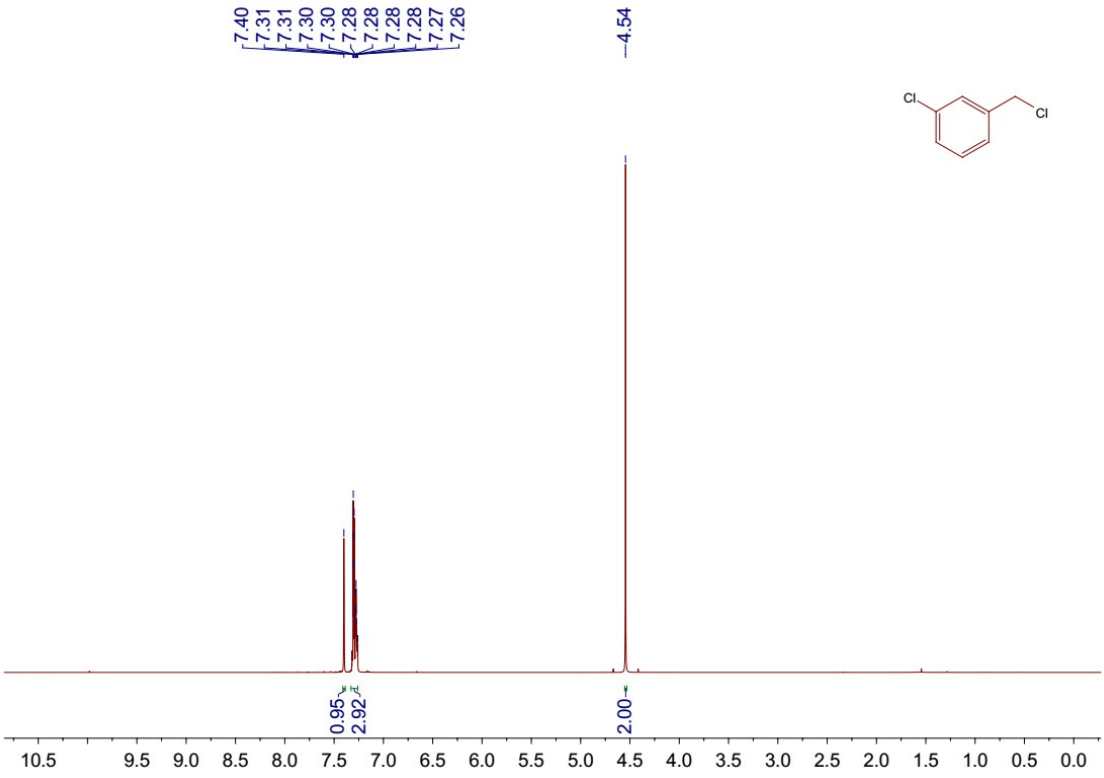

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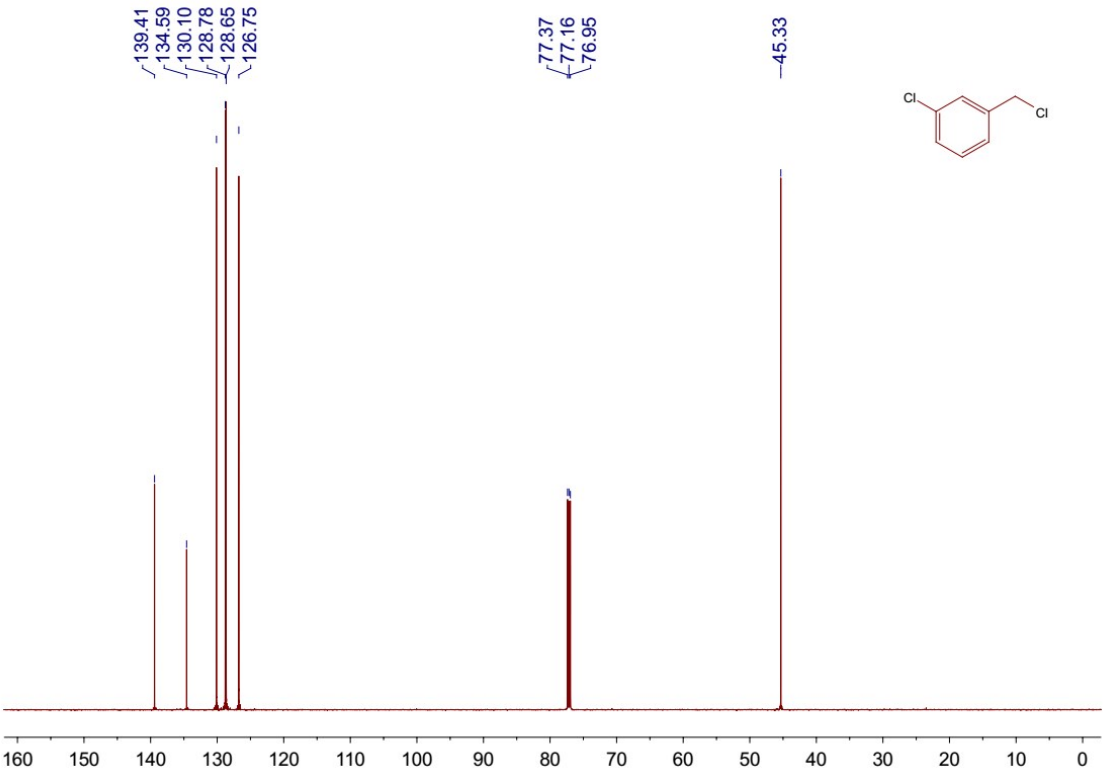

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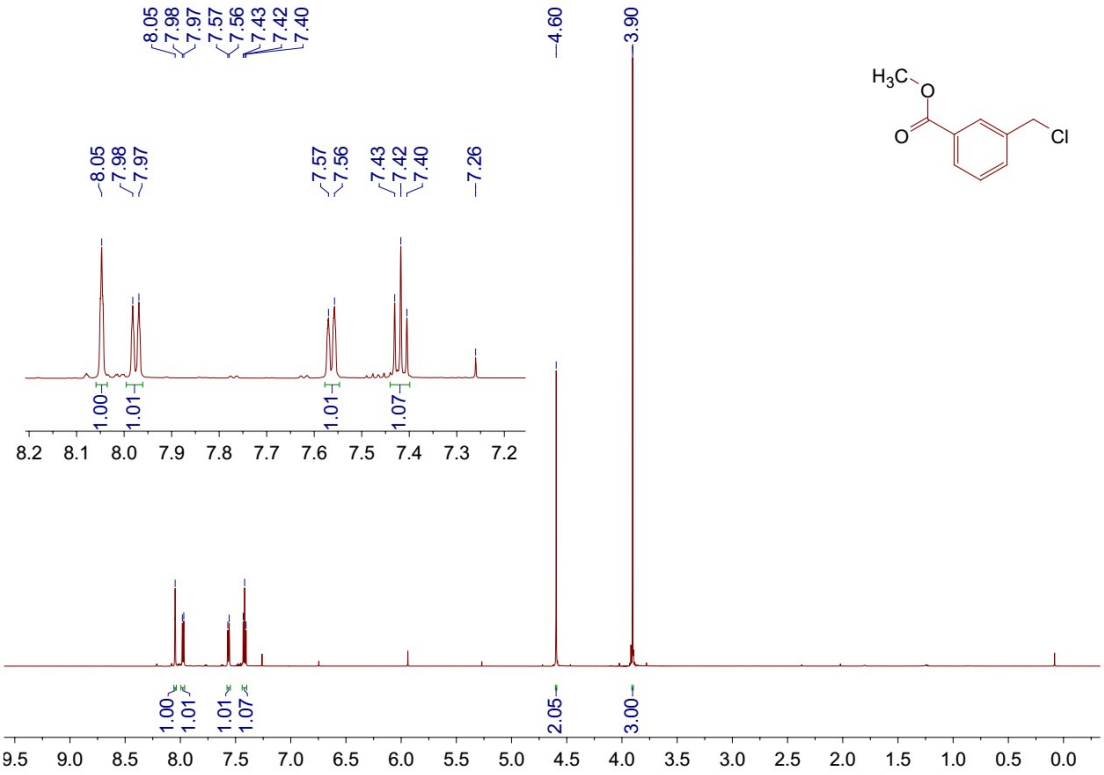

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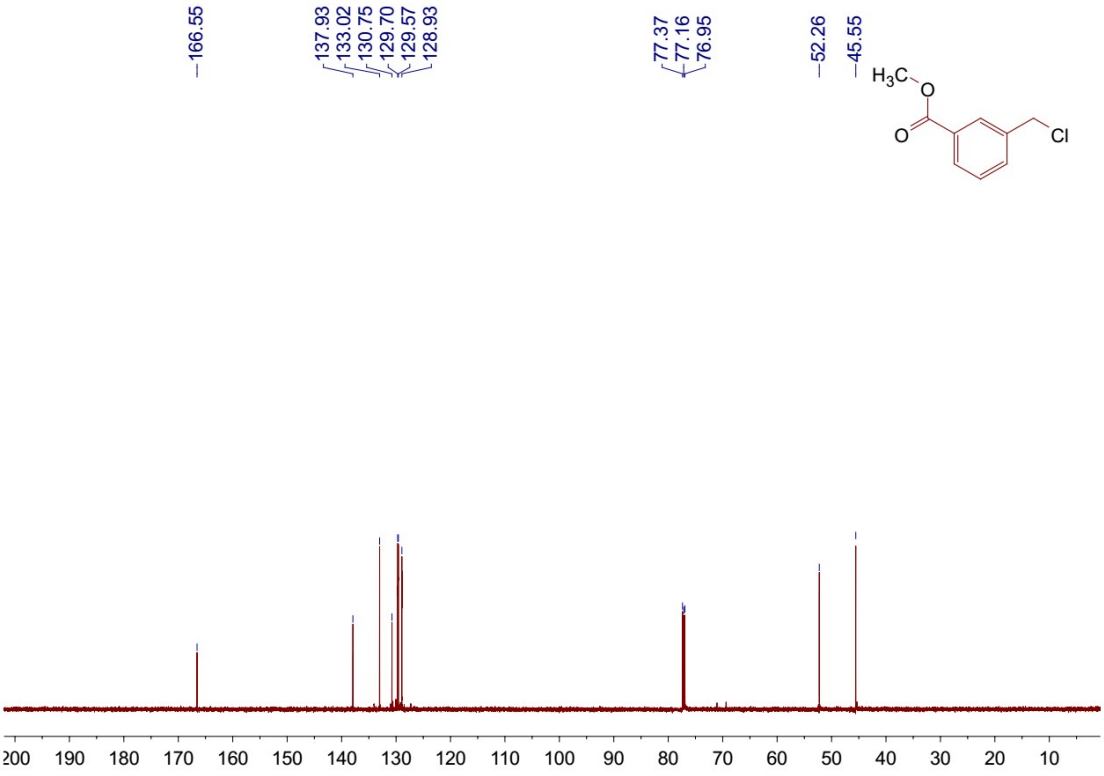

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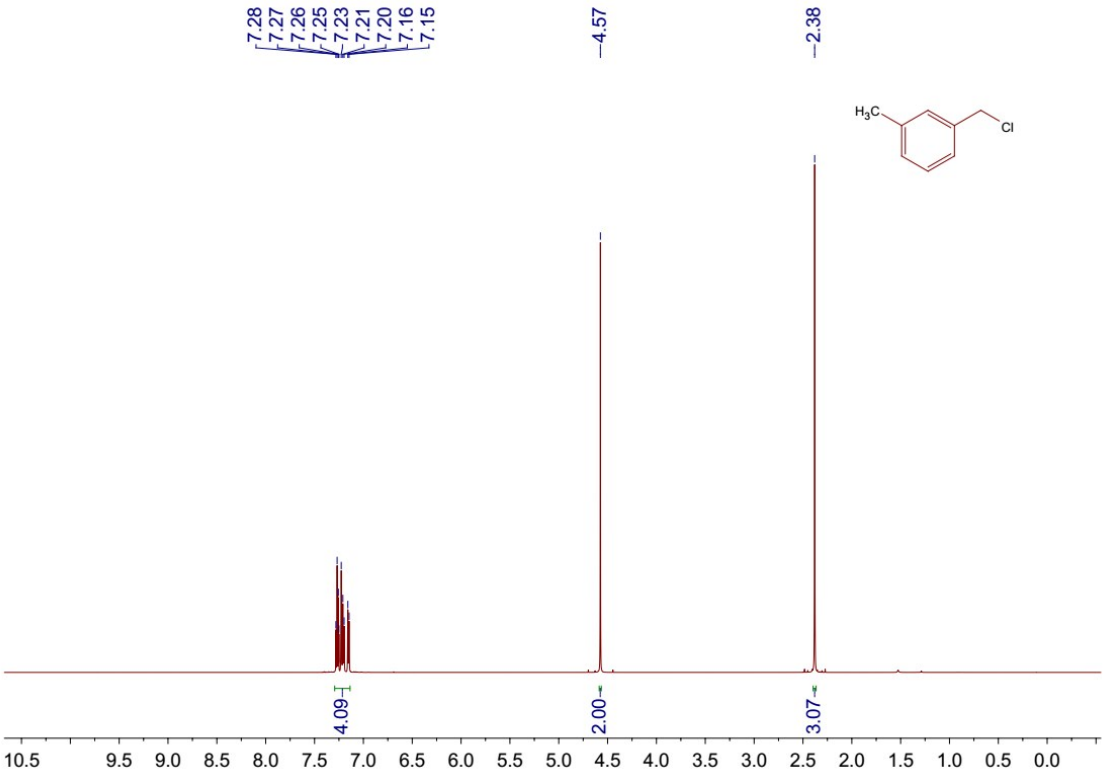

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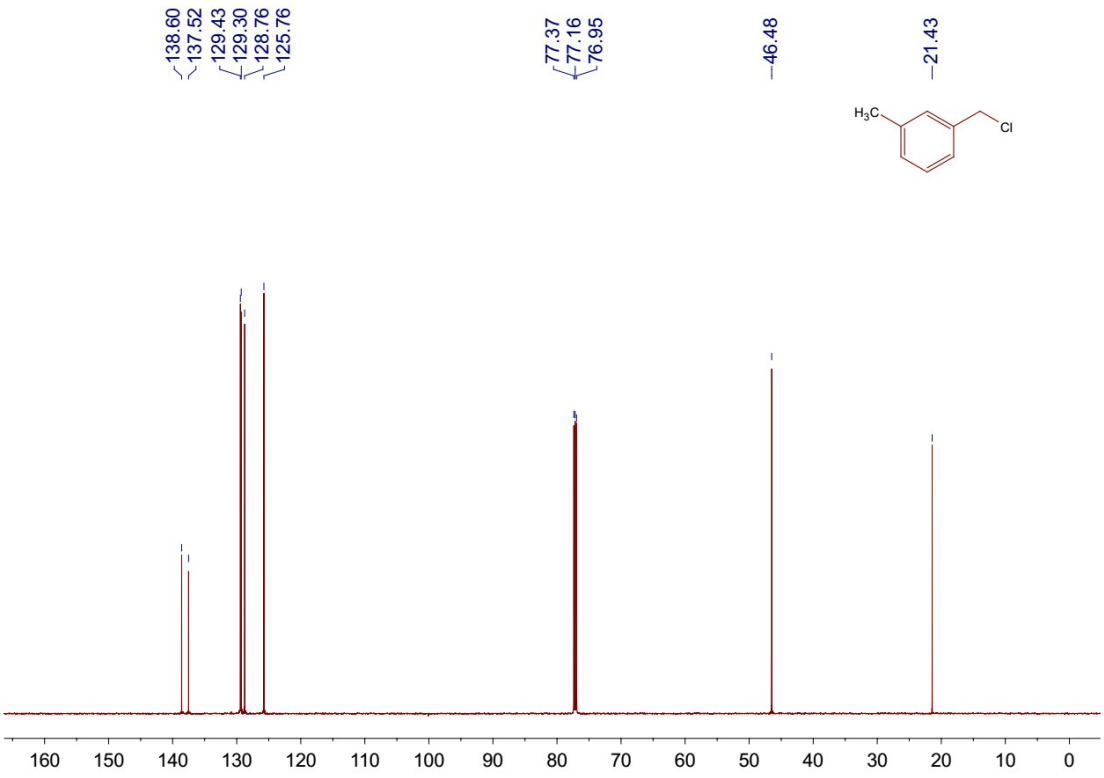

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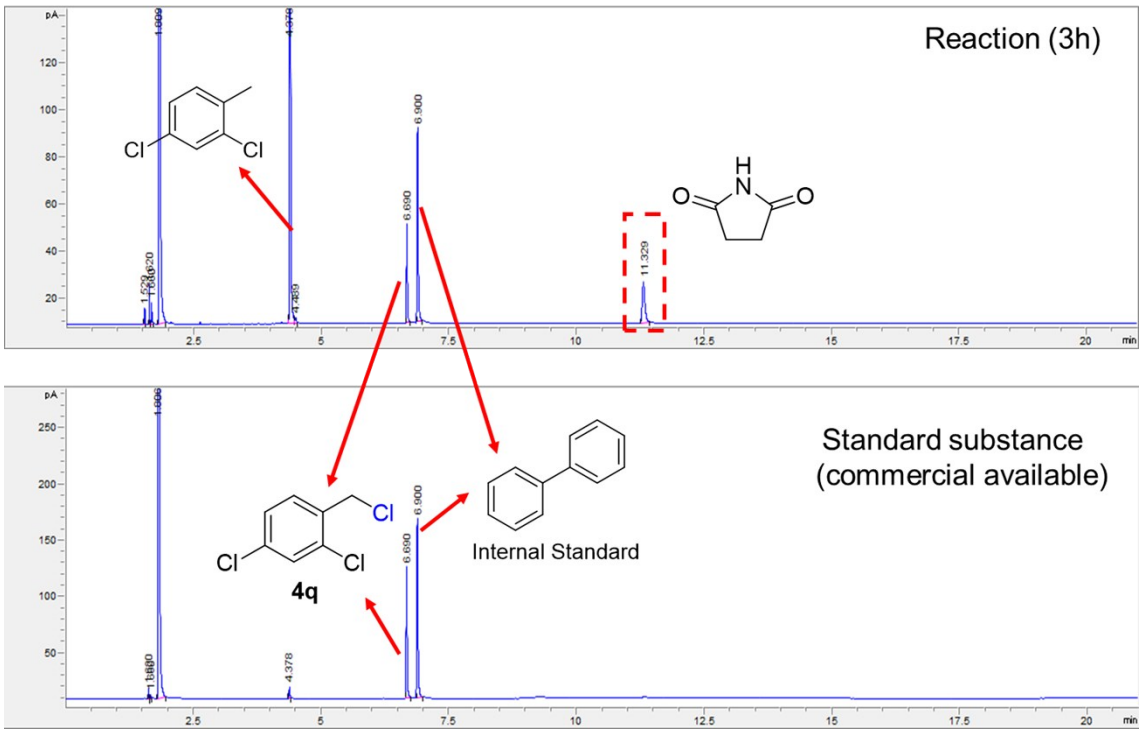
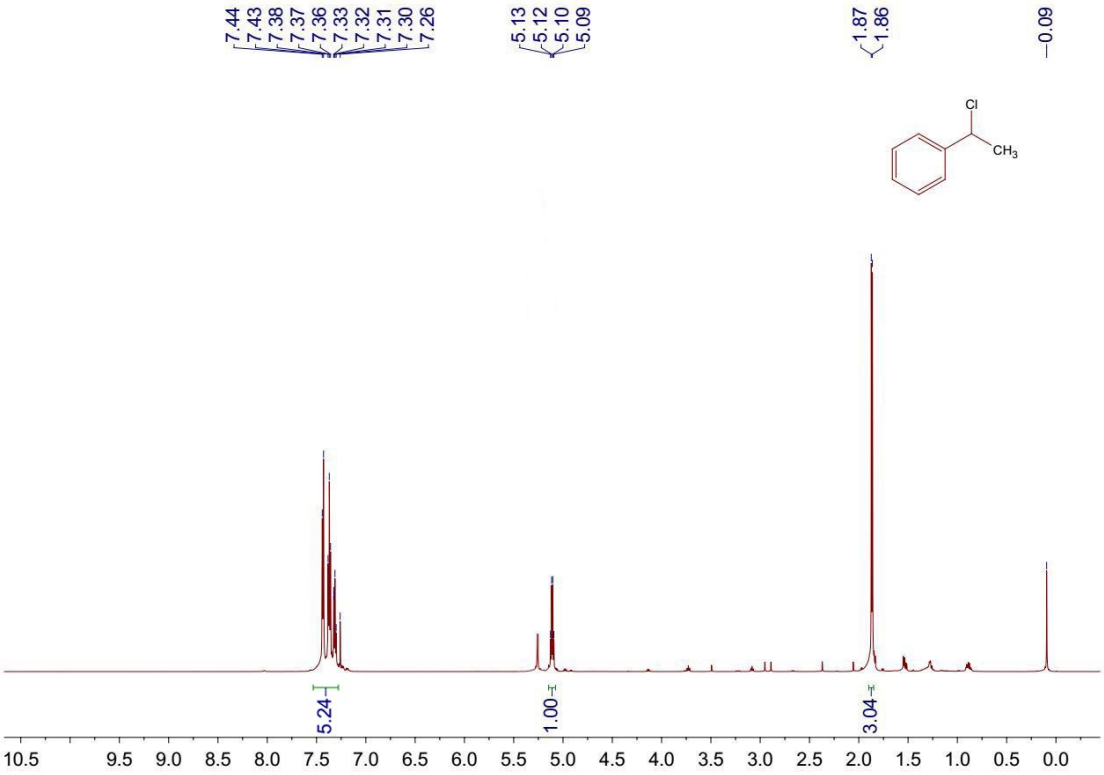


GC spectral of **4q** crude reaction mixture and standard substance



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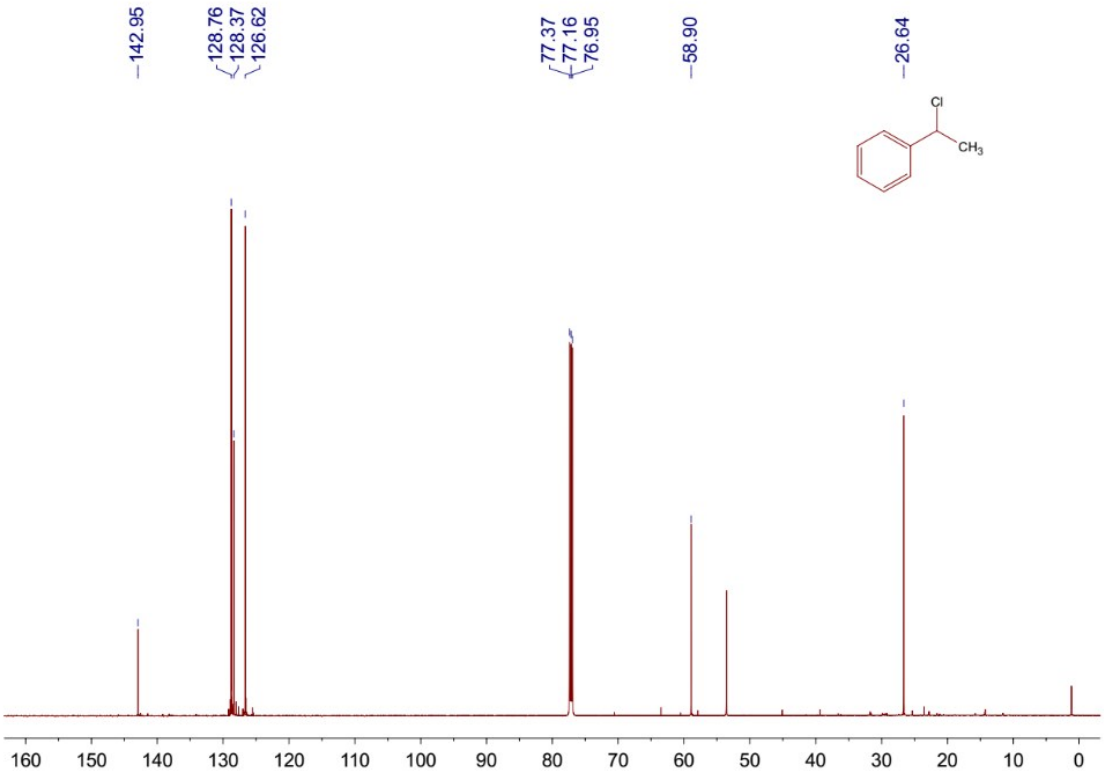
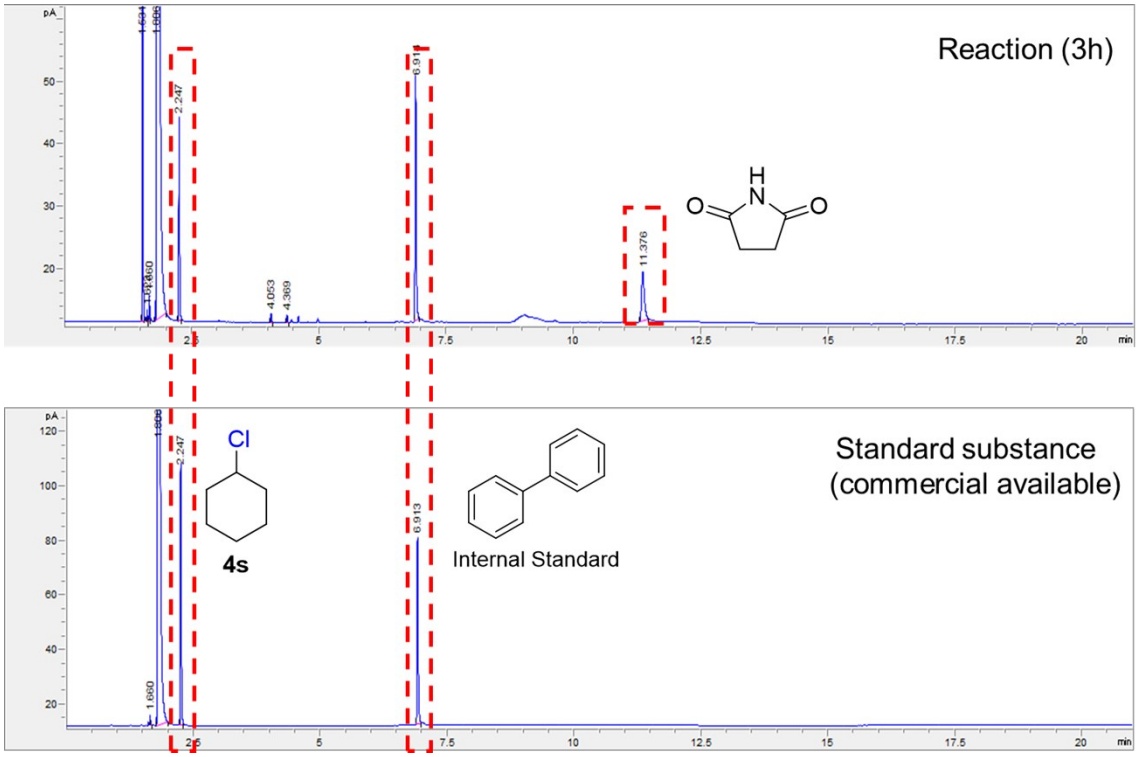
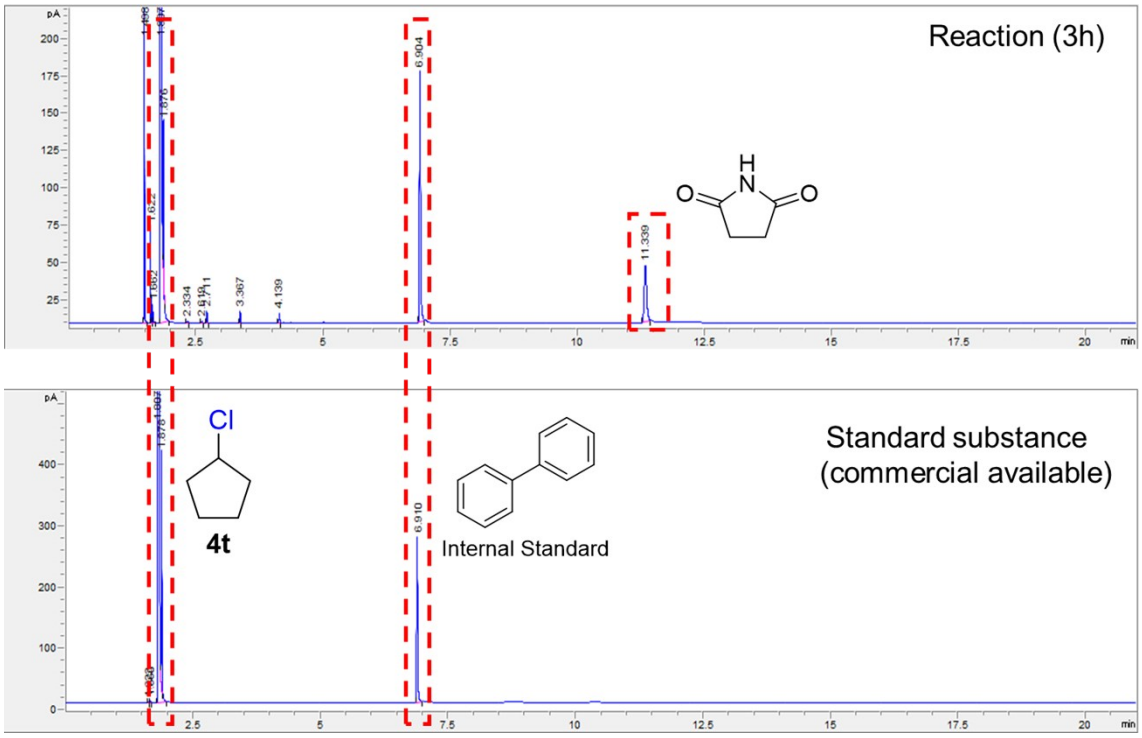


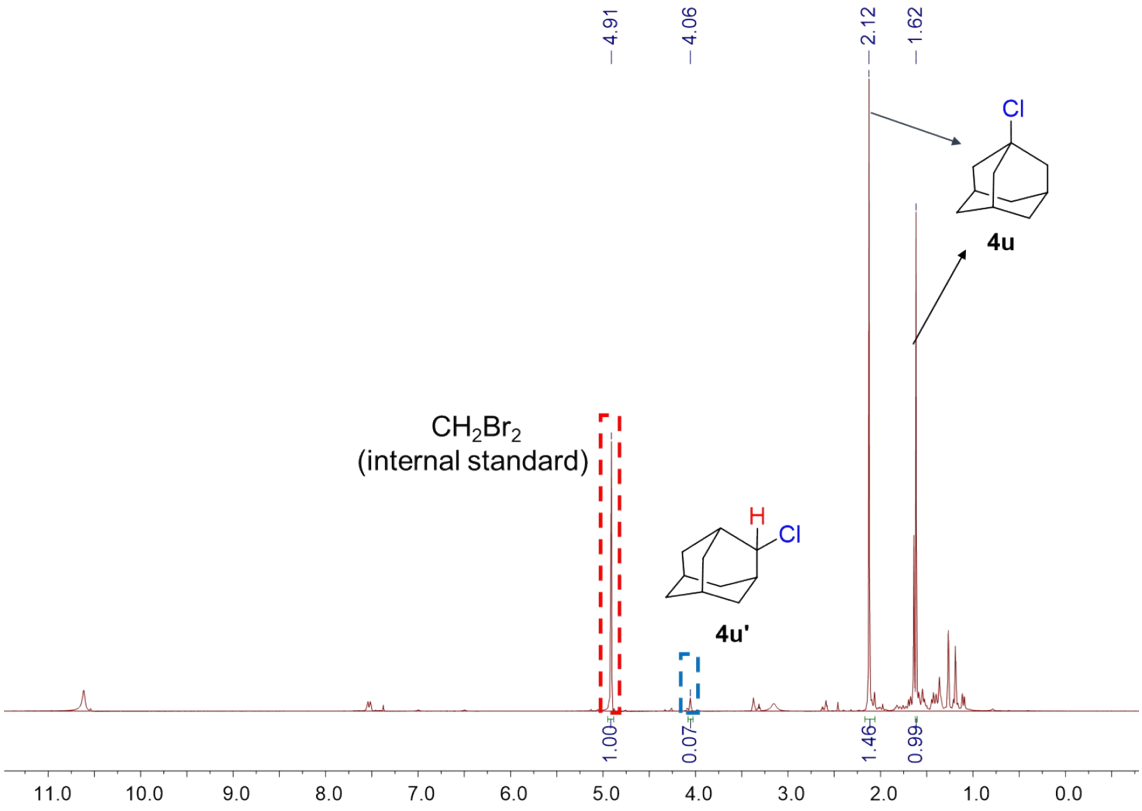
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4r**



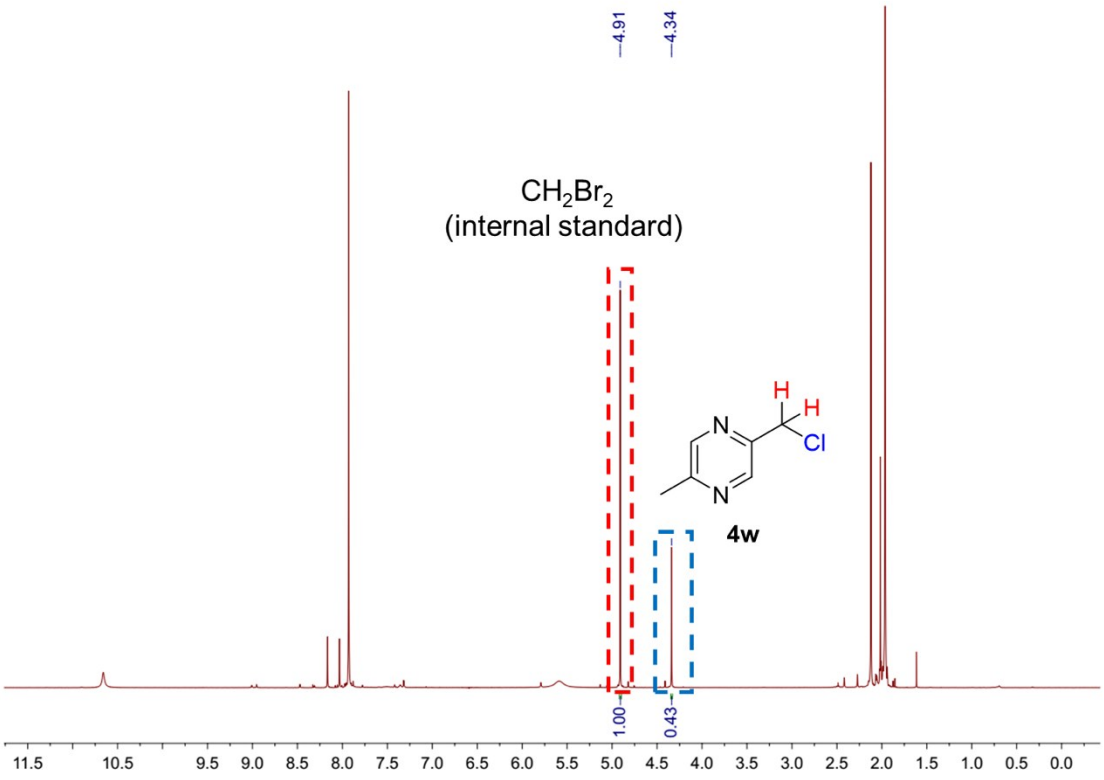
GC spectral of **4s** crude reaction mixture and standard substance



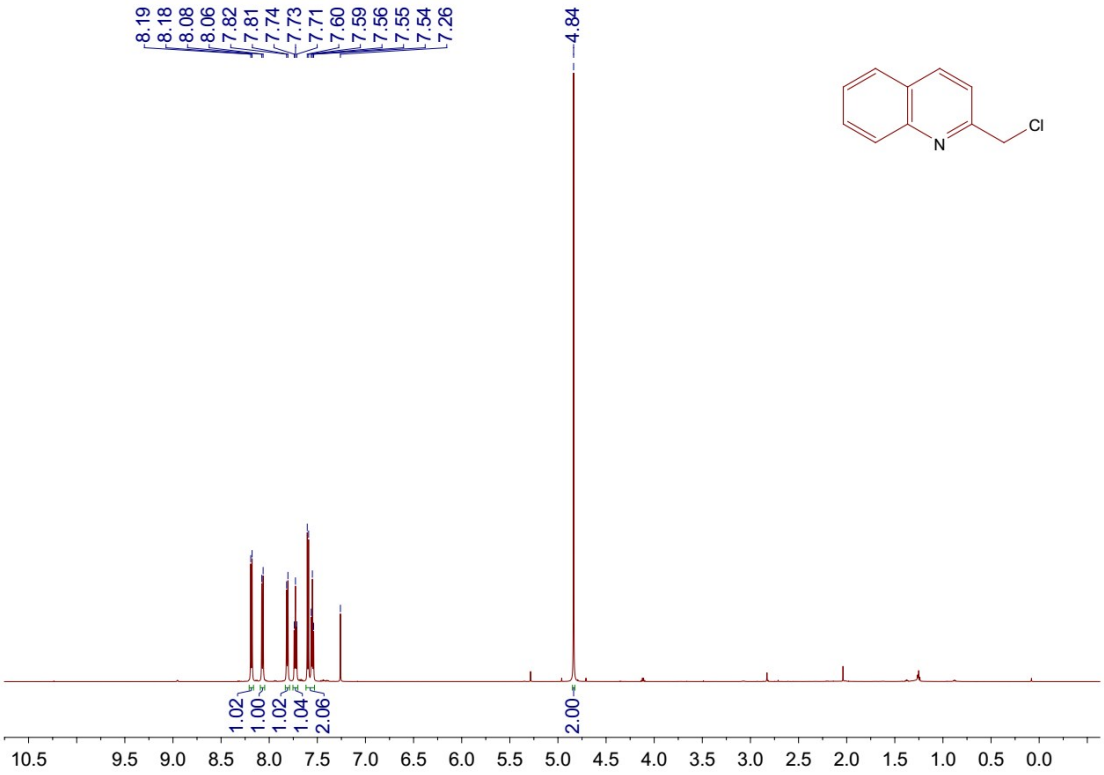
GC spectral of **4t** crude reaction mixture and standard substance



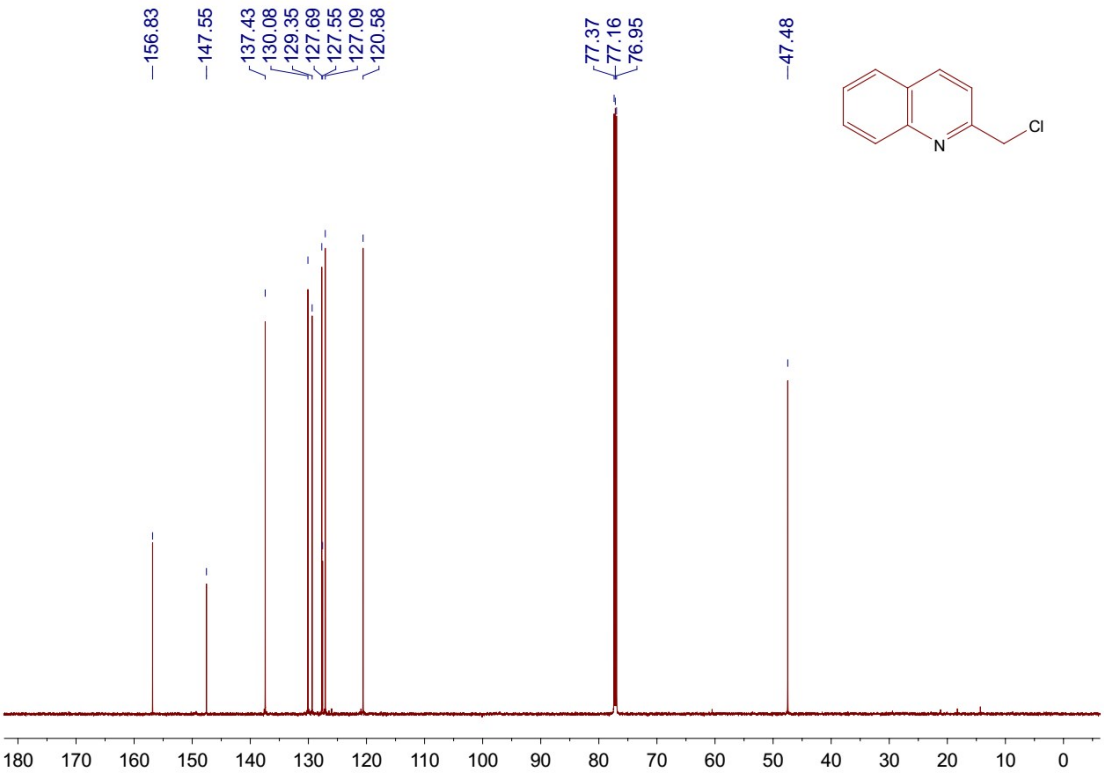
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4u** and **4u'** crude reaction mixture



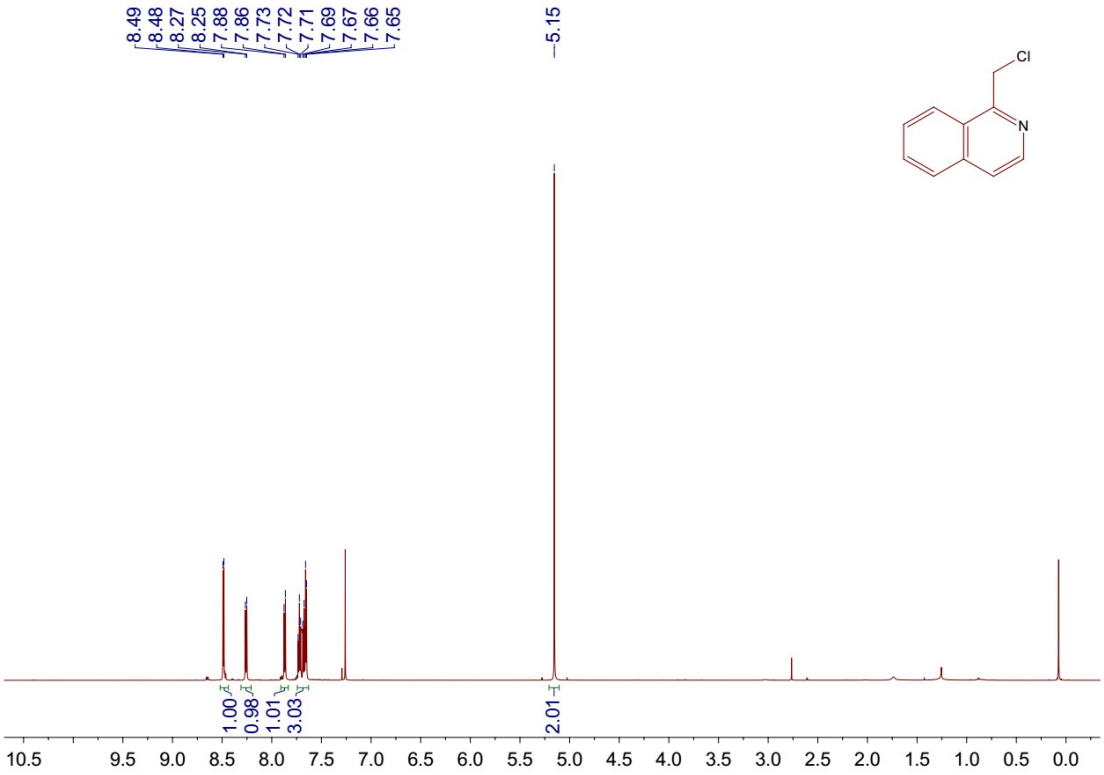
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4w** crude reaction mixture



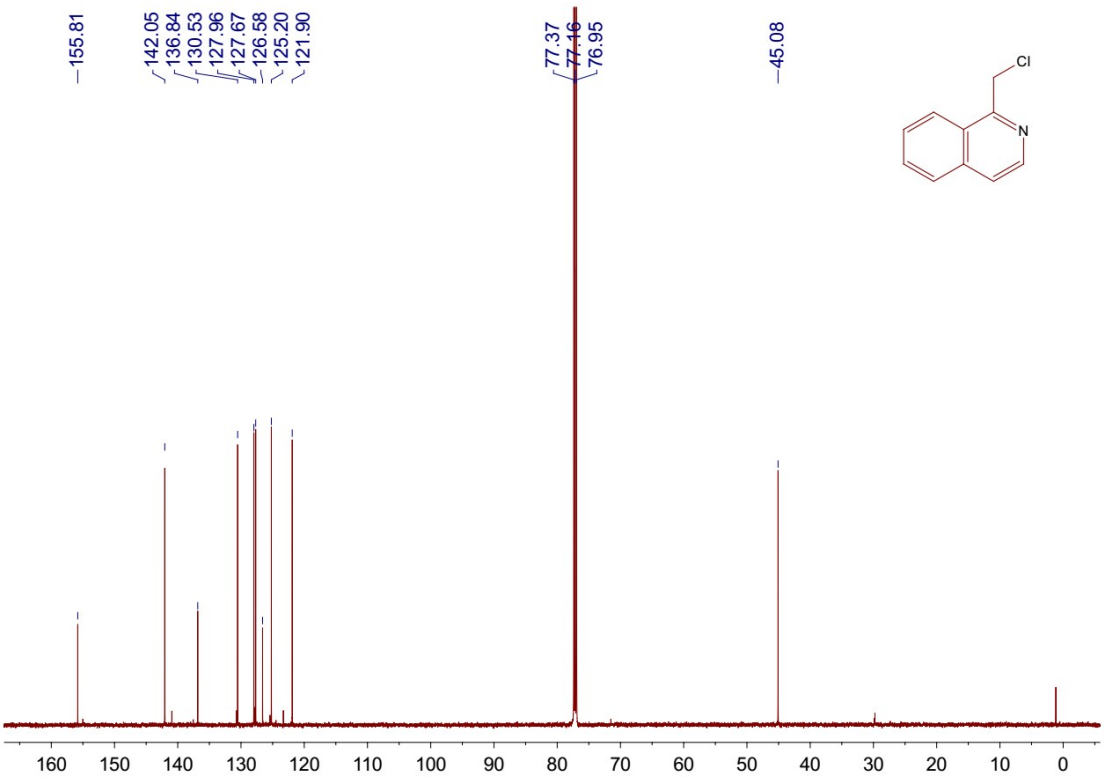
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4x**



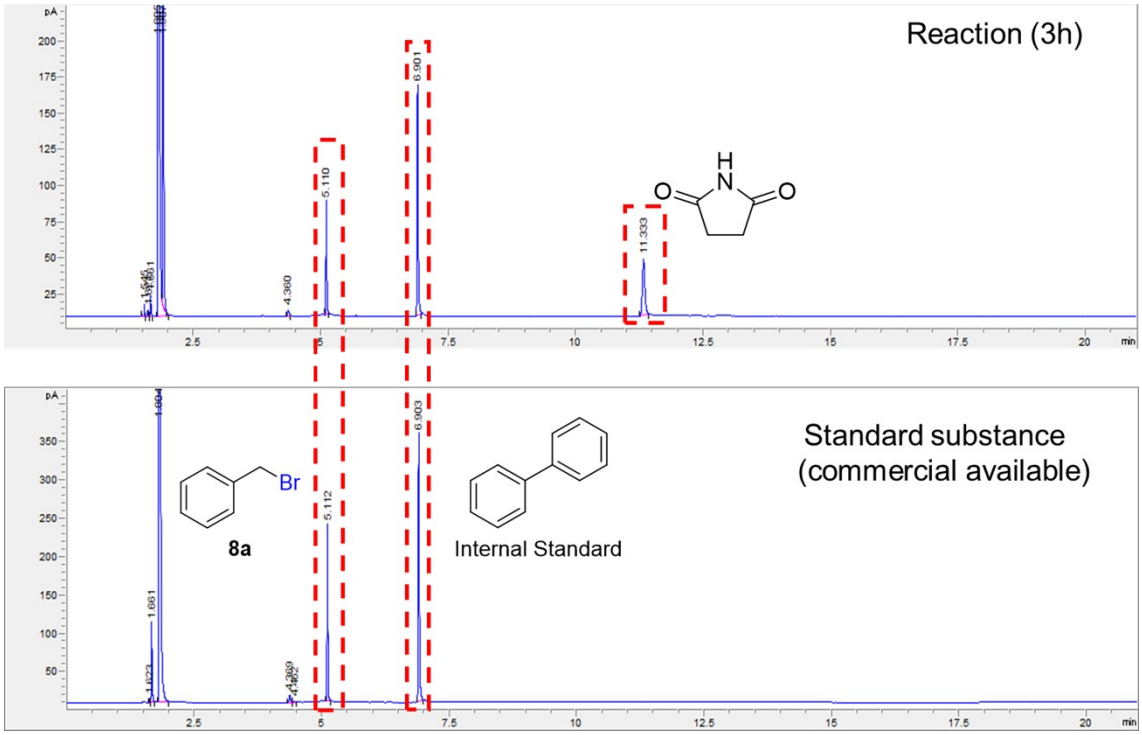
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4x**



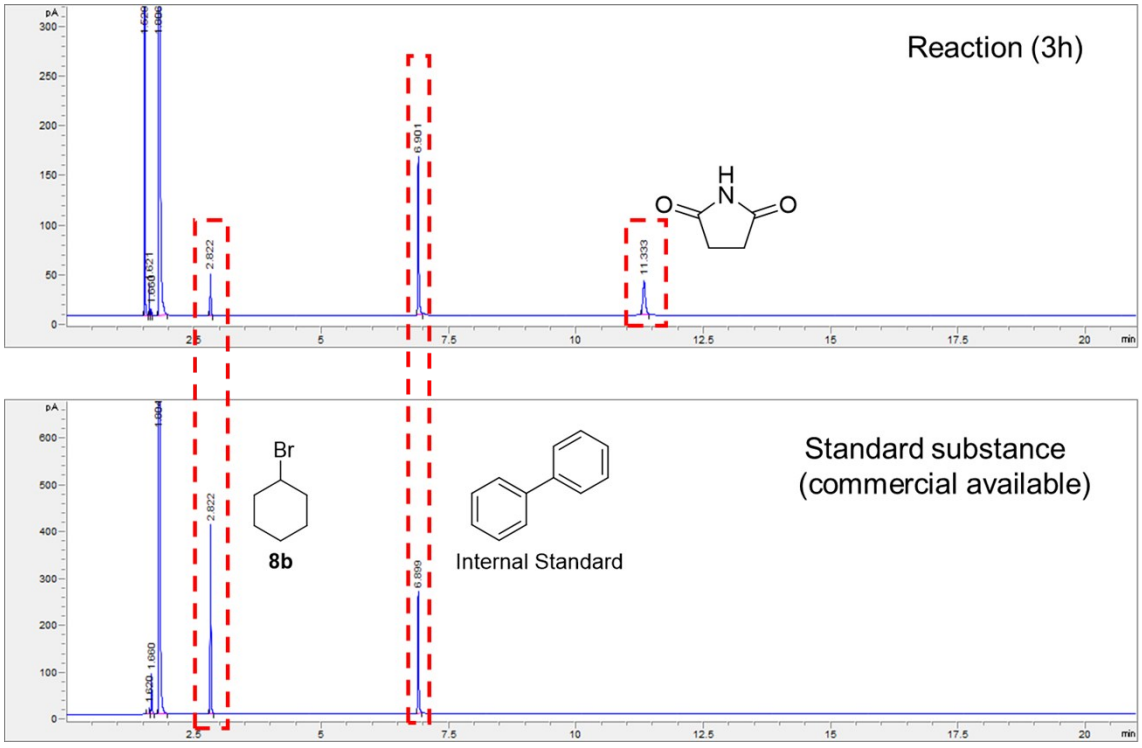
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4y**



^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4y**



GC spectral of **8a** crude reaction mixture and standard substance



GC spectral of **8b** crude reaction mixture and standard substance