Supporting Information

Endogenous *X*-C=O species enable catalyst-free formylation prerequisite for CO_2 reductive upgrading

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Experimental details

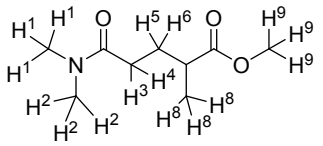
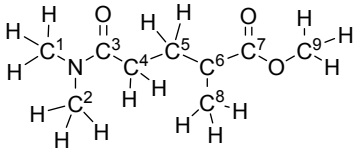
Materials

Anhydrous propylene carbonate (PPC, 99.7%), *γ*-valerolactone (GVL, 98%), *N*-methyl formamide (NMF, 99%), formamide (FMA, ≥99.5%), dimethyl sulfoxide-d_6 (DMSO-d_6, 99.9 atom % D), *N,N*-dimethylformamide-d_7 (DMF-d_7, 99.5 atom % D), *N,N*-dimethylacetamide-d_9 (DMA-d_9, 99 atom % D), acetonitrile-d_3 (CAN-d_3, 99.8 atom % D), phenylsilane ($PhSiH_3$, 97%), 1,1,1,3,5,5,5-heptamethyltrisiloxane (≥98%), triethoxysilane (97%), diphenylsilane (Ph_2SiH_2, 97%), 1,1,3,3-tetramethyldisiloxane (98%), polymethylhydrosiloxane (PMHS), 4-bromobenzene-1,2-diamine (97%), *o*-phenylenediamine (98%), 2-aminophenol (98%), 4-fluoro-1,2-phenylenediamine (≥98%), 4,5-dimethylbenzene-1,2-diamine (>98%), 4,5-dichloro-1,2-benzenediamine (98%), 4-nitro-*o*-phenylenediamine (97%), 2-aminobenzenethiol (96%), sodium bicarbonate-^{13}C (Na_2CO_3-^{13}C), 2-benzenediamine (95%), and benzimidazole (>98%) were purchased from Aladdin Industrial Inc. (Shanghai). *N,N*-Dimethyl formamide (DMF, 99.8%), *N*-methyl pyrrolidone (NMP, >99%), dimethyl sulfoxide (DMSO, 99.8%), anhydrous *N,N*-dimethylacetamide (DMA, 99.8%), formic acid (HCOOH, 99%), acetone-d_6 (DMK-d_6, 99.9 atom % D), methanol-d_4 (MeOH-d_4, 99.8 atom % D), tetrahydrofuran-d_8 (THF-d_8, 99.5 atom % D), chloroform-d_1 (TCM-d_1, 99.8 atom % D), triethylsilane (Et_3SiH, 99%), acetone (DMK, ≥99.0%), and concentrated hydrochloric acid (HCl, 33%) were provided by Innochem Inc. (Beijing). Dichloromethane (DCM, ≥99.5%), 2-methyltetrahydrofuran (MTHF, ≥99.5%), acetonitrile (MeCN, ≥99.0%), and methanol (MeOH, ≥99.5%) were obtained from J&K Scientific Ltd. (Beijing). Chloroform (TCM, ≥99.0%) was purchased from Acros Inc. (Shanghai). Diphenylsilane-d_2 (Ph_2SiD_2, 97 atom% D) was bought from Sigma-Aldrich Co. LLC.

$^{13}CO_2$ was prepared by addition of 15 mL HCl (1.8 M) into 15 mL Na_2CO_3-^{13}C (1.0 M) aqueous solution at 50 °C stirring for 30 min, and collected with a balloon.

Methyl 5-(dimethylamino)-2-methyl-5-oxopentanoate (DMO) was (Rhodiasolv® PolarClean) was available from Solvay Novecare (Cranbury, US).[S1] In the present

study, DMO was prepared using a reported method,[S2] and its ^{1}H and ^{13}C NMR data in DMSO-d_6 are provided below:

Type	Structure	NMR data (ppm)
^{1}H NMR		$H^{1\text{-}2}$ 2.92 (s), $H^{3\text{-}4}$ 2.27 (t), $H^{5\text{-}6}$ 1.75 (dq), H^{7} 2.49, H^{8} 1.09 (d), H^{9} 3.57 (s)
^{13}C NMR		C^{1} 36.4, C^{2} 34.6, C^{3} 171.2, C^{4} 38.1, C^{5} 28.7, C^{6} 29.8, C^{7} 176.2, C^{8} 16.7, C^{9} 21.3

Reaction procedures

Synthesis of HCOOH

The reaction was carried out in a quartz glass tube (10 mL) coupled with a magnetic stirrer and a sealed cap that was inserted by a hollow steel needle. After loading the samples, the tube was transferred into a stainless steel autoclave and sealed. In a typical procedure, 1 mmol $PhSiH_3$ and 2 mL solvent were added into the tube, which was then put into the stainless steel reactor. After sealing up and evacuating, CO_2 was charged into the reactor up to the desired pressure (1-4 MPa) or with a balloon. Afterward, the reactor was heated at a specified temperature (30-80 ℃) for a certain reaction time. Upon completion, the reactor was flushed with tap water until cooling down to ambient temperature. Finally, HCOOH could be liberated by following two post-treatment methods, including: (1) after release of CO_2, 2 mL hydrochloric acid aqueous solution (0.3 M) or 3% acetic acid aqueous solution was added, followed by heating at 30 ℃ for 0.5 h; (2) without release of CO_2, in situ injection of 1 mL H_2O, followed by heating at 100 °C for 15 min. Along with liquid HCOOH, phenylsilanetriol was obtained as white precipitate.

Synthesis of N-containing benzoheterocyclic compounds

For the synthesis of benzimidazoles, benzothiazole or benzoxazole, similar reaction procedures to the HCOOH synthesis were adopted except the addition of 0.5 mmol of relevant *o*-phenylenediamines, 2-aminobenzenethiol or 2-aminophenol. It is worth noting that no additional post-treatment was required for the synthesis of these N-containing benzoheterocyclic compounds.

Product analysis

For determining the concentration of HCOOH after reaction, the resulting mixture was transferred to a volumetric flask (25 mL) with addition of water to gain a constant volume, which was then analysed quantitatively by HPLC (Agilent 1260) based on the standard curves [HCOOH yield = (mole of HCOOH) / (mole of used total H^-) × 100%]. Representative HPLC chromatogram of standard HCOOH aqueous solution (Figure S5) and HCOOH standard curve (Figure S6) are supplied.

Regarding the commercially available *N*-containing benzoheterocyclics, their concentrations were determined by GC (Agilent 7890B) and GC-MS (Agilent 6890N GC/5973 MS) after dilution with 5 mL methanol using 10 mg naphthalene as the internal standard (the product yield was calculated relative to the used total H^-).

For both cases, ^1H NMR (diluted with DMSO-d_6) was used to quantitatively analyse unpurified products in the reaction mixtures using 1,3,5-trimethoxybenzene as the internal standard. For the structural identification of products, HRMS (ESI) analysis was measured on a Q Exactive LC-MS/MS (Thermo Scientific) instrument. ^1H and ^{13}C NMR analysis were recorded in DMSO-d_6 on Bruker NMR spectrometers at 400 MHz and 101 MHz respectively, JOEL ECX-500M spectrometers at 500 MHz and 125 MHz using tetramethylsilane (TMS) as the internal standard. All the experiments were repeated thrice, and the average results are presented.

Isotopic labeling experiments

^1H and ^{13}C NMR spectra of the reaction mixtures were used in the experiments at the given reaction conditions using normal Ph_2SiH_2 or deuterium counterpart

(Ph_2SiD_2) with $^{13}CO_2$ or $^{12}CO_2$. Analyses were performed after dilution with the deuterated solvent DMSO-d_6 on a JEOL-ECX 500 NMR spectrometer.

Computational methods

All structure optimization and energy calculations were performed using density functional theory (DFT) employing the B3LYP functional implemented in the Gaussian 09 program package. Pople's all-electron basis set 6-311G (d,p) was used for all atoms.[S3-S5]

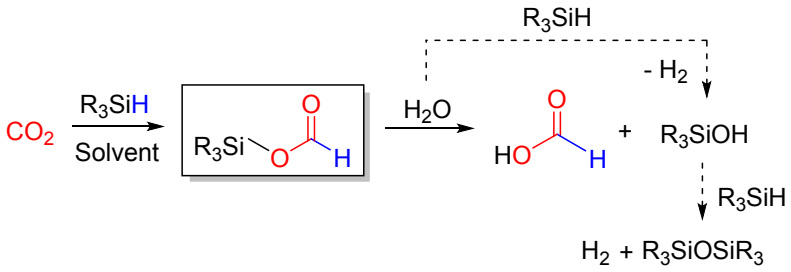
Calculation of pressurized CO_2-H_2O system pH values

As demonstrated in previous literature,[S6] the expected pH of the binary CO_2-H_2O system can be expressed as a function of temperature (T) and pressure (P):

$$\mathrm{pH} = 8.00 \times 10^{-6} \times T^2 + 0.00209 \times T - 0.216 \times \ln(P_{CO2}) + 3.92$$

The pH values shown in Figure 3A were obtained by plugging the specific temperature and pressure into the equation.

Table S1. Effect of various solvents on the synthesis of HCOOH from CO_2 and $PhSiH_3$



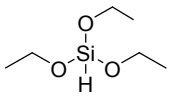
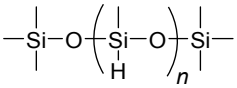
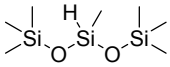
Solvent	Abbreviation	Acidity (α) [a]	Basicity (β) [a]	Polarity (π*) [a]	HCOOH yield (%)	(β - α) / π*	(β - α)
$CHCl_3$	TCM	0.44	0	0.58	0.2	-0.76	-0.44
CH_2Cl_2	DCM	0.13	0.1	0.82	0.2	-0.04	-0.03
CH_3CN	ACN	0.19	0.4	0.66	0.4	0.32	0.21
CH_3OH	MeOH	0.93	0.66	0.58	0.4	-0.47	-0.27
H_2O	Water	1.17	0.14	1.09	0	-0.95	-1.03
Acetone	DMK	0.08	0.48	0.71	0.3	0.56	0.40
2-Methyltetrahydrofuran	MTHF	0	0.45	0.53	1	0.85	0.45
Propylene carbonate	PPC	0	0.4	0.83	2	0.48	0.40
γ-Valerolactone	GVL	0	0.6	0.83	3	0.72	0.60
N-Methyl-2-pyrrolidone	NMP	0	0.72	0.92	59	0.78	0.72
N,N-Dimethylformamide	DMF	0	0.69	0.88	72	0.78	0.69
N-Methyl formamide	NMF	0.62	0.8	0.9	43	0.20	0.18
Formamide	FMA	0.71	0.48	0.97	0	-0.24	-0.23
N,N-Dimethylacetamide	DMA	0	0.76	0.85	91	0.89	0.76
N,N-Dimethylacetamide [b]	DMA	0	0.76	0.85	73	0.89	0.76

Reaction conditions: 1 mmol $PhSiH_3$, 2 mL solvent, 3 MPa CO_2, 50 ℃, 4 h

[a] The Kamlet–Taft parameters (α, β, and π*) were obtained from the references.[S7-S9]

[b] 5 wt% water was added.

Table S2. Synthesis of HCOOH using different hydrosilanes in DMA

Entry	Substrate	Hydrosilane	Yield/ %
1		Phenylsilane	91
2		Triethoxysilane	6
3		Polymethylhydrosiloxane (PMHS)	6
4		Heptamethyltrisiloxane	0
5		Diphenylsilane	25

Reaction conditions: 1 mmol hydrosilane, 3 MPa CO_2, 2 mL DMA, 50 ℃, 4 h.

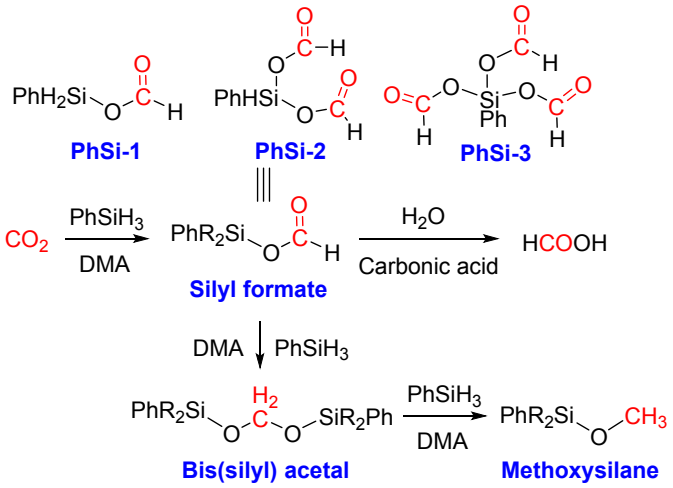
Table S3. Experiments conducted for sensitivity assessment of HCOOH synthesis from CO_2

Experiment	Variation	Yield 1 (%)	Yield 2 (%)	Average yield (%)	Deviation (%)
High T	70 °C	53.4	56.8	55.1	-30.7
Low T	30 °C	55.8	52.6	54.2	-40.4
High P	4 MPa	92.4	91.4	91.9	1.0
Low P	2 MPa	78.1	82.5	80.3	-11.8
Long t	6 h	85.8	88.6	87.2	-4.2
Short t	2 h	82.5	85.1	83.8	-7.9
High C	1.25 mmol	87.2	89	88.1	-3.2
Low C	0.75 mmol	85.4	83	84.2	-7.5

Optimal reaction conditions (Best yield: 91%): 1 mmol $PhSiH_3$, 3 MPa CO_2, 50 °C, 4 h

Average yield (%) = (Yield 1+Yield 2) / 2

Deviation (%) = (Average yield - Best yield) / Best yield × 100%



Scheme S1. Illustration of representative CO_2-derived products in the reaction system

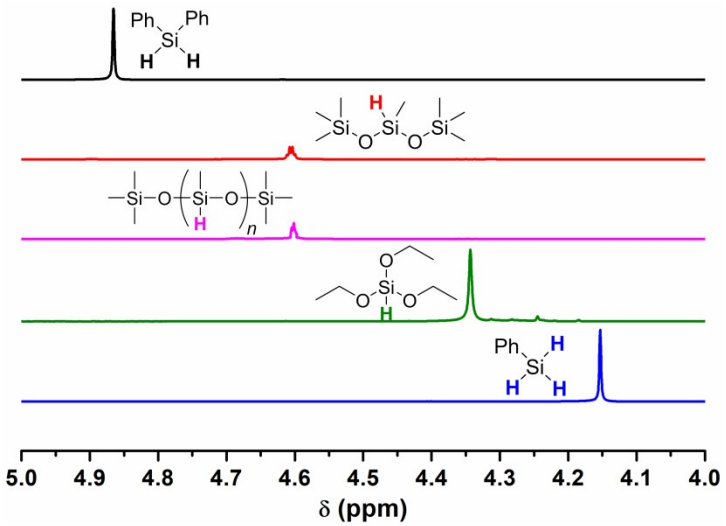


Figure S1. ^{1}H NMR spectra of different hydrosilanes in DMA-d_9

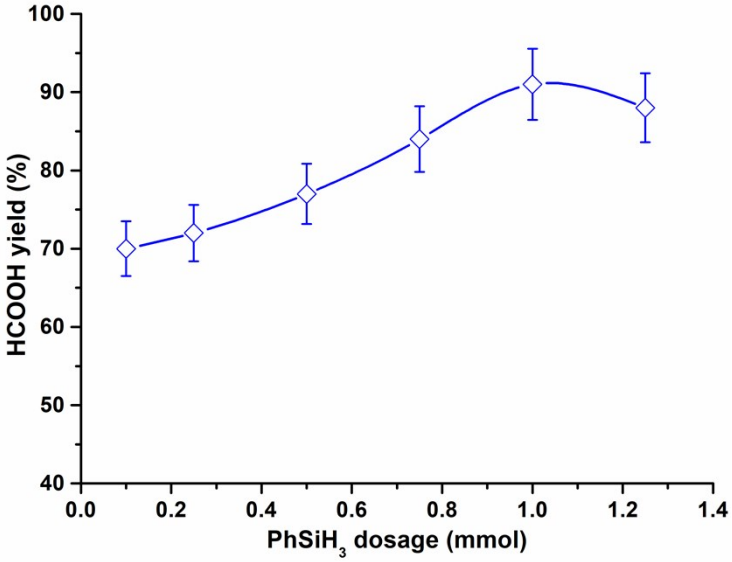


Figure S2. Effect of $PhSiH_3$ dosage on the synthesis of HCOOH from CO_2 in DMA
Reaction conditions: 1 mmol $PhSiH_3$, 3 MPa CO_2, 2 mL solvent, 50 °C, 4 h

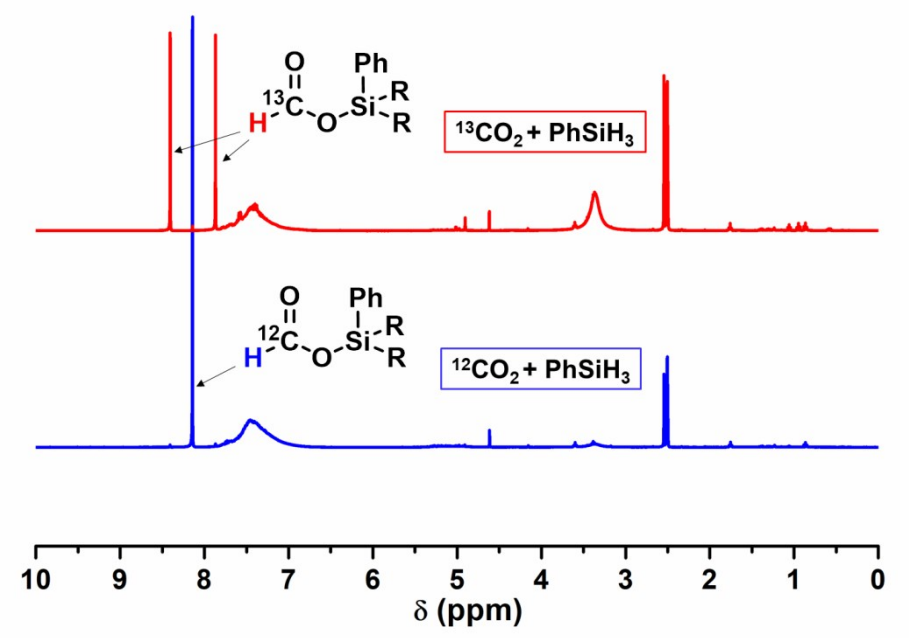


Figure S3. ^{1}H NMR spectra of the reaction mixtures after reductive insertion of $PhSiH_3$ with $^{13}CO_2$ or $^{12}CO_2$
Reaction conditions: 0.25 mmol $PhSiH_3$, CO_2 balloon, 1 mL DMSO-d_6, 50 ℃, 8 h

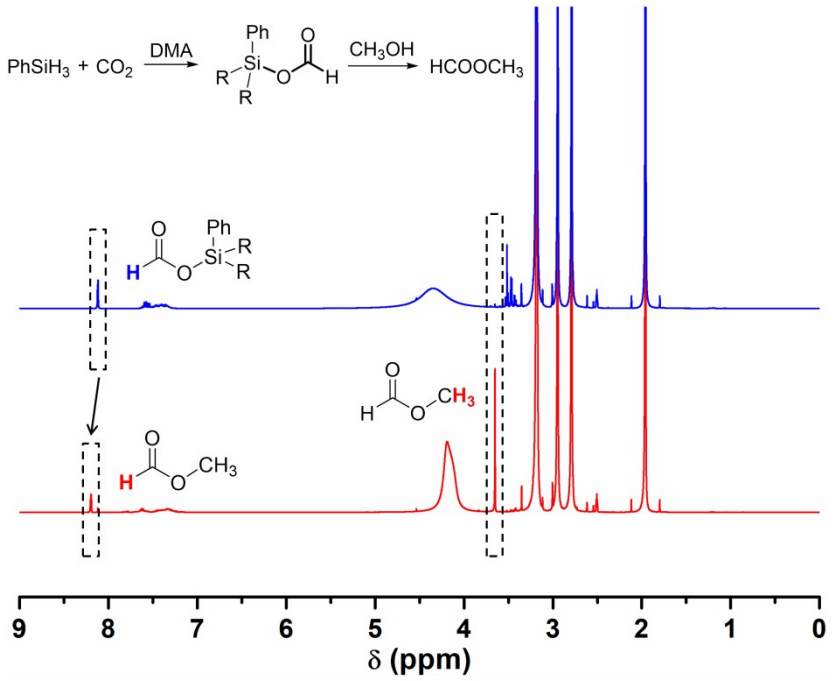


Figure S4. ^{1}H NMR spectra of the mixtures obtained after reaction of $PhSiH_3$ with CO_2 in DMA (A), and subsequent treatment with MeOH (B).
Reaction conditions: (A) 1 mmol $PhSiH_3$, 3 MPa CO_2, 2 mL DMA, 50 °C, 4 h; (B) 2 mL MeOH (0.3 M HCl), 30 °C, 0.5 h. Diluted with DMSO-d_6 for NMR analysis.

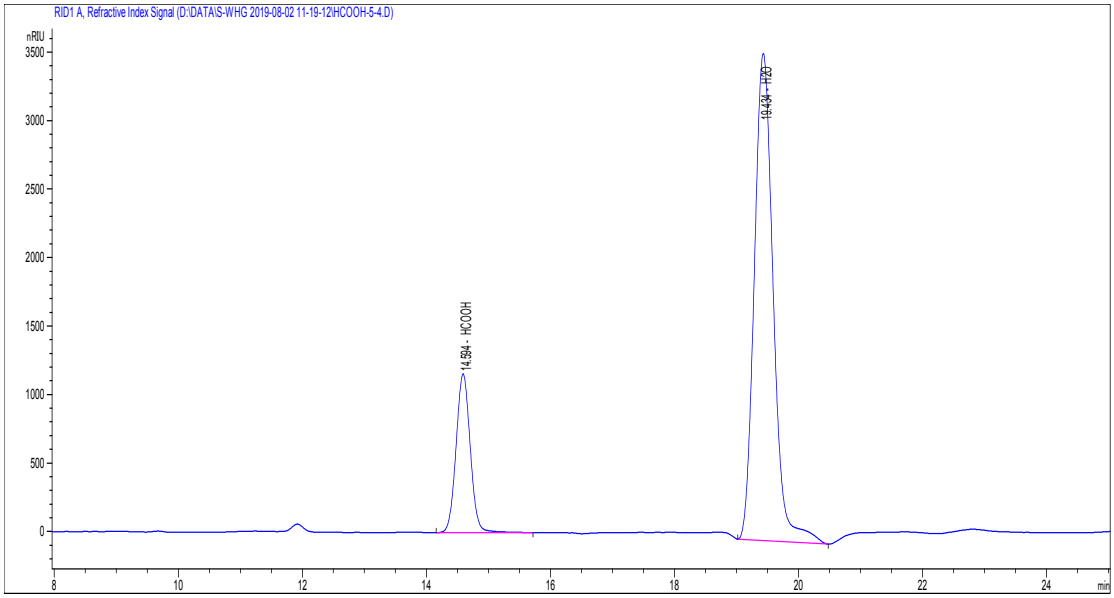


Figure S5. HPLC spectrum of standard HCOOH aqueous solution (Retention time: 14.594 min for HCOOH, and 19.434 min for H_2O)

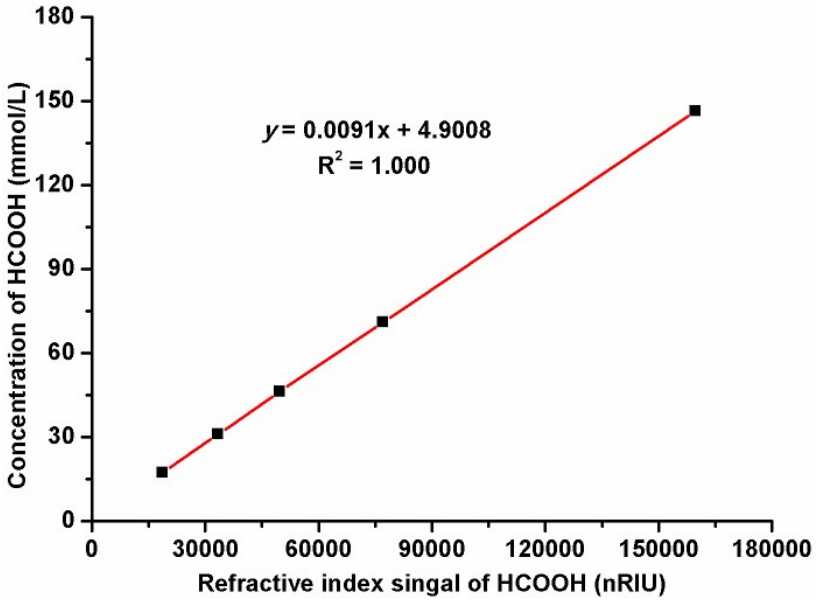
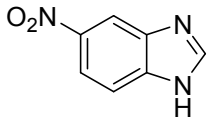
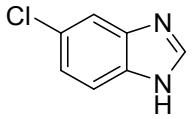


Figure S6. The standard curve of HCOOH

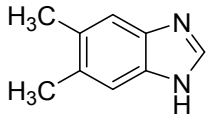
NMR data of the isolated products



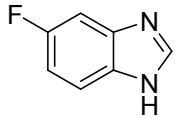
^{1}H NMR (400 MHz, DMSO) δ ppm: 8.56 (s, 1H), 8.51 (d, *J* = 2.2 Hz, 1H), 8.12 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.77 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ ppm: 147.25 (s), 143.06 (s), 118.09 (s), 115.38 (s), 113.24 (s). HRMS: Calculated for $C_7H_6N_3O_2$, [M+H] 164.0455, Found: 164.0457.



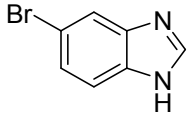
^{1}H NMR (400 MHz, DMSO) δ ppm: 8.29 (s, 1H), 7.66 (d, *J* = 1.9 Hz, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.22 (dd, *J* = 8.6, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ ppm: 143.93 (s), 126.65 (s), 122.53 (s). HRMS: Calculated for $C_7H_5ClN_2$, [M+H] 153.0214, Found: 153.0217.



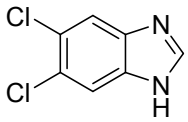
^{1}H NMR (400 MHz, DMSO) δ ppm: 12.22 (s, 1H), 8.06 (s, 1H), 7.35 (s, 2H), 2.30 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ ppm: 141.44 (s), 20.44 (s). HRMS: Calculated for $C_9H_{11}N_2$, [M+H] 147.0917, Found: 147.0919.



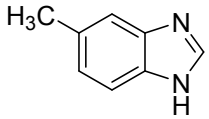
^{1}H NMR (400 MHz, DMSO) δ ppm: 12.59 (s, 1H), 8.26 (s, 1H), 7.59 (dd, *J* = 8.7, 4.9 Hz, 1H), 7.40 (dd, *J* = 9.5, 2.4 Hz, 1H), 7.20 – 6.84 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ ppm: 160.09 (s), 157.76 (s), 143.83 (s), 110.40 (d, *J* = 25.6 Hz). HRMS: Calculated for $C_7H_6FN_2$, [M+H] 137.0510, Found: 137.0509.



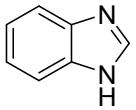
^{1}H NMR (400 MHz, DMSO) δ ppm: 8.28 (s, 1H), 7.80 (d, *J* = 1.7 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.33 (dd, *J* = 8.5, 1.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ ppm: 143.78 (s), 125.14 (s), 118.66 (s), 117.33 (s), 114.50 (s). HRMS: Calculated for $C_7H_6BrN_2$, [M+H] 196.9709, Found: 196.9714.



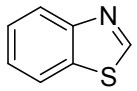
^{1}H NMR (400 MHz, DMSO) δ ppm: 8.35 (s, 1H), 7.87 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ ppm: 145.23 (s), 124.75 (s), 117.18 (s). HRMS: Calculated for $C_7H_5Cl_2N_2$, [M+H] 186.9824, Found: 186.9829.



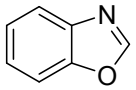
^{1}H NMR (400 MHz, DMSO) δ ppm: 12.34 (s, 1H), 8.13 (s, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.37 (s, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ ppm: 142.05 (s), 131.27 (s), 123.61 (s), 21.71 (s). HRMS: Calculated for $C_8H_9N_2$, [M+H] 133.0760, Found: 133.0760.



^{1}H NMR (400 MHz, DMSO) δ ppm: 8.23 (s, 1H), 7.60 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.19 (dd, *J* = 6.0, 3.2 Hz, 2H). HRMS: Calculated for $C_7H_7N_2$, [M+H] 119.0604, Found: 119.0604.

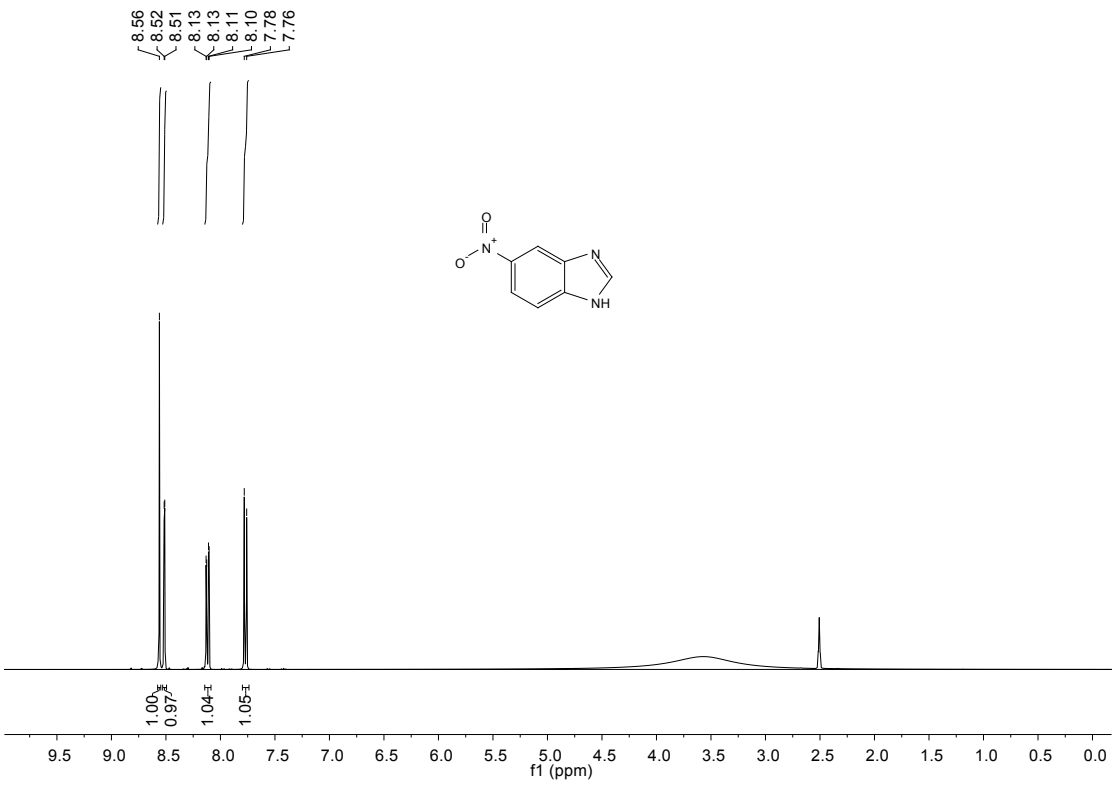


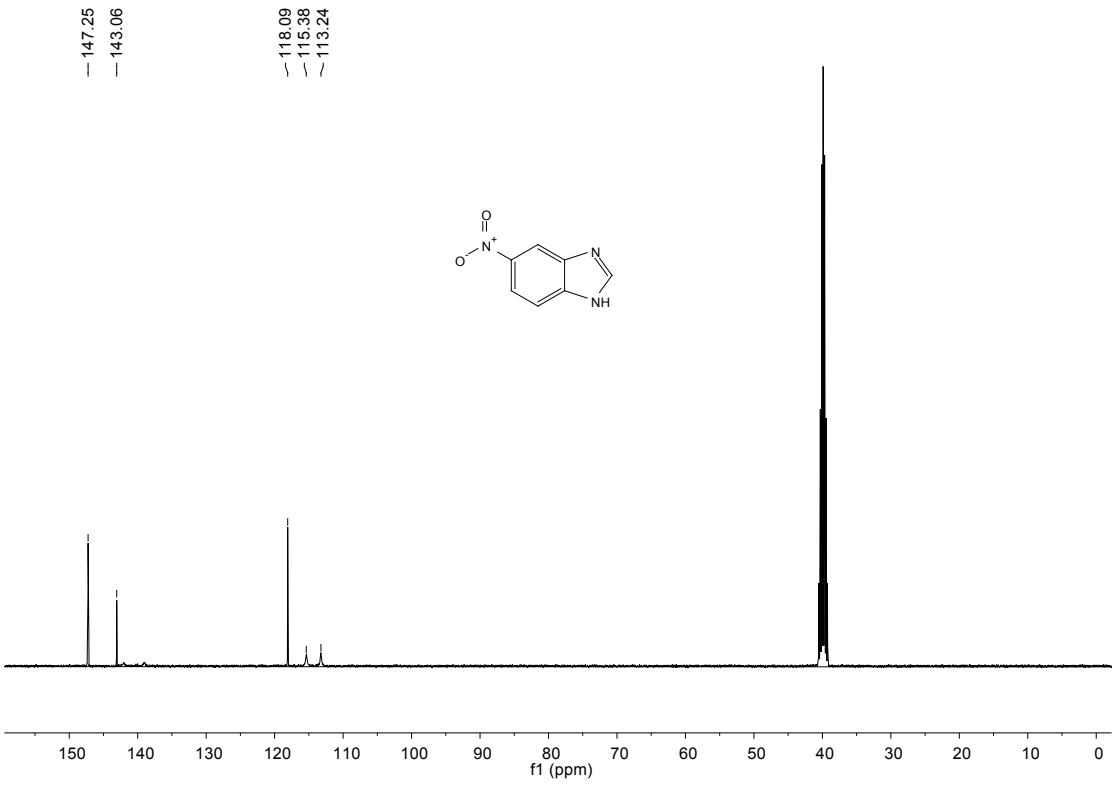
^{1}H NMR (400 MHz, DMSO) δ ppm: 8.56 (s, 1H), 8.52 (d, *J* = 2.2 Hz, 1H), 8.13 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.78 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ ppm: 155.78 (s), 153.76 (s), 134.32 (s), 126.51 (s), 125.83 (s), 123.66 (s), 122.65 (s). HRMS: Calculated for C_7H_6NS, [M+H] 136.0215, Found: 136.0221.

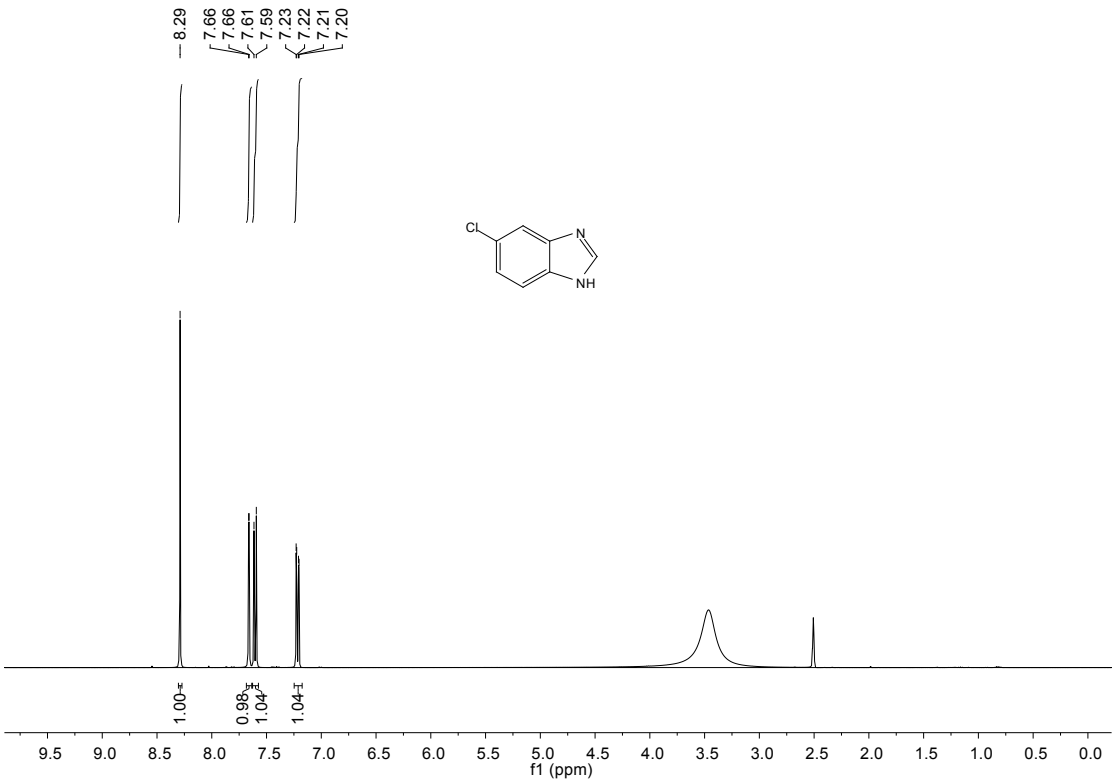


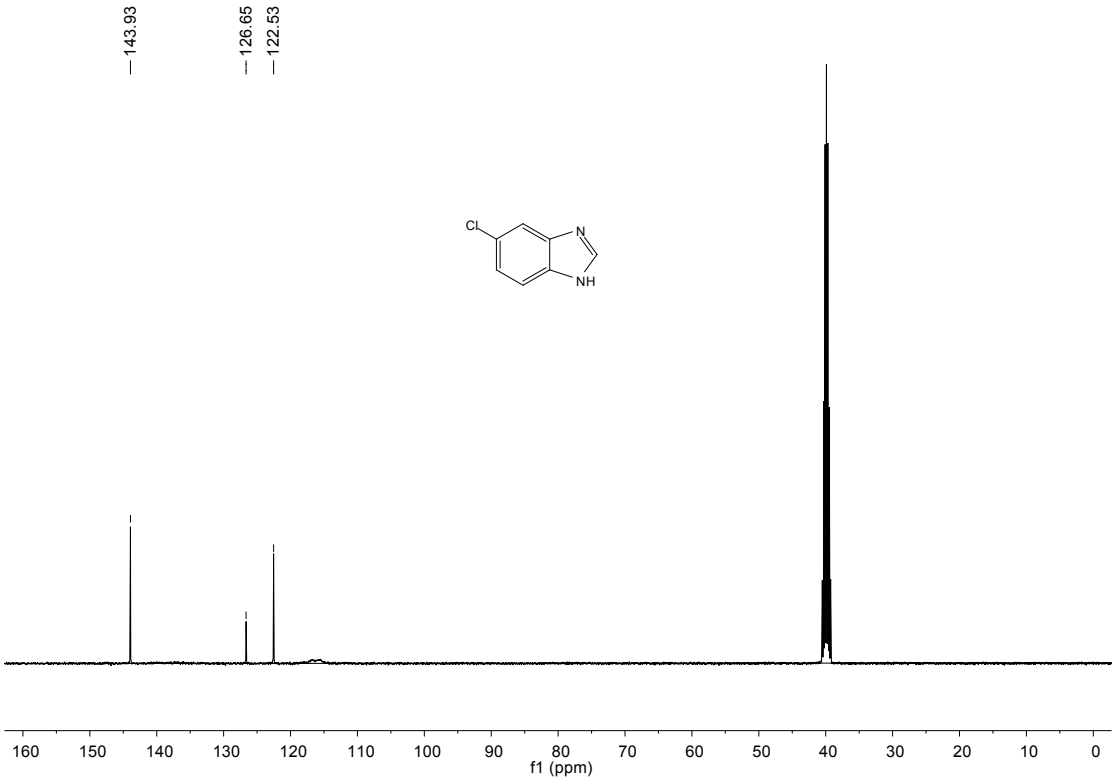
^{1}H NMR (400 MHz, DMSO) δ ppm: 8.73 (s, 1H), 7.79 (d, *J* = 7.1 Hz, 1H), 7.66 (dd, *J* = 12.2, 6.3 Hz, 1H), 7.35 (dd, *J* = 13.4, 6.6 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ ppm: 154.40 (s), 149.89 (s), 140.23 (s), 125.82 (s), 124.83 (s), 120.51 (s), 111.36 (s).

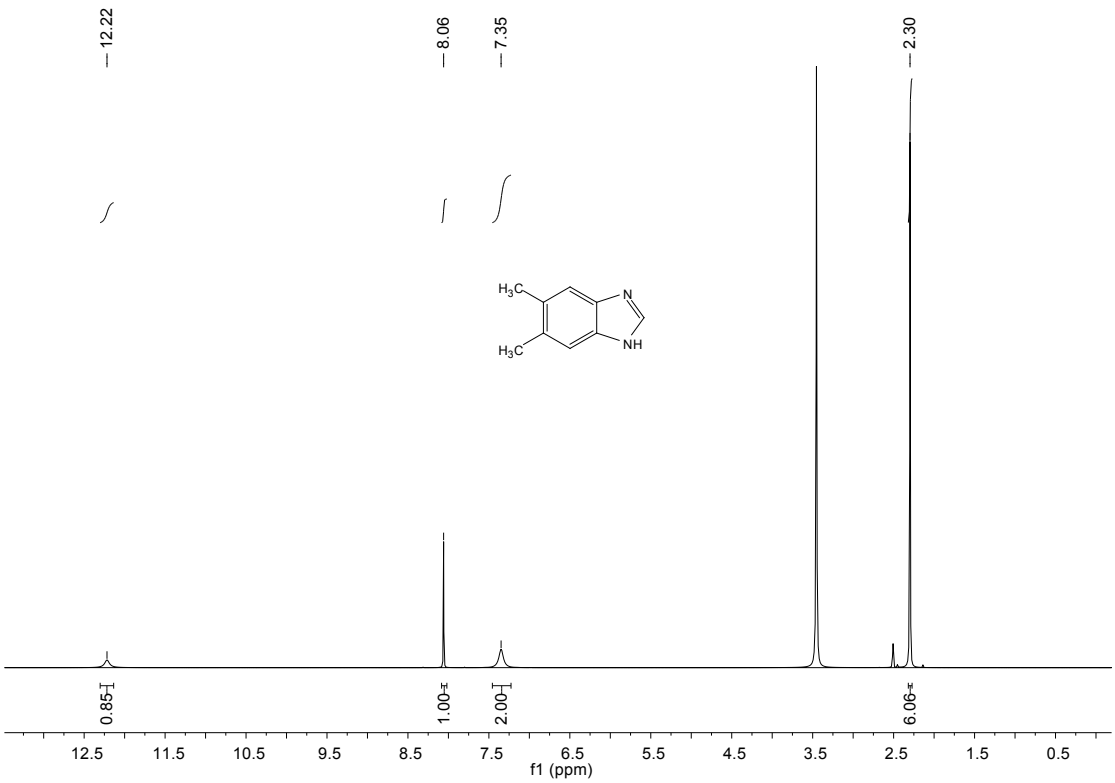
NMR spectra of the isolated products

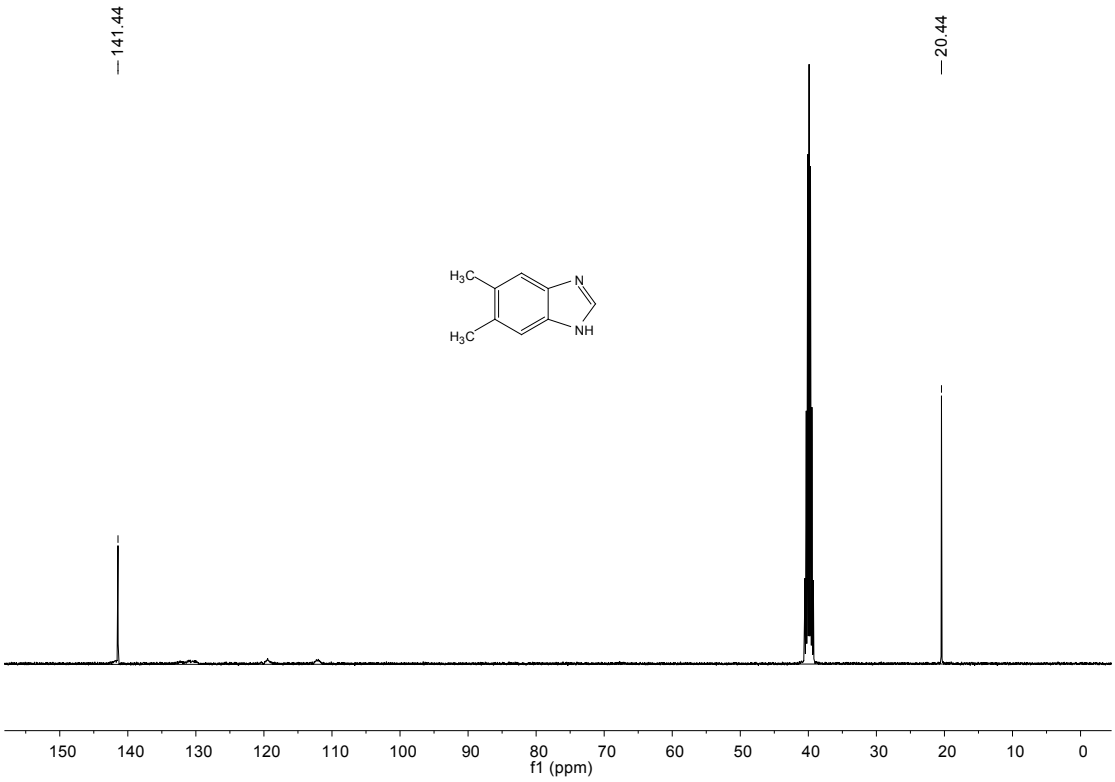


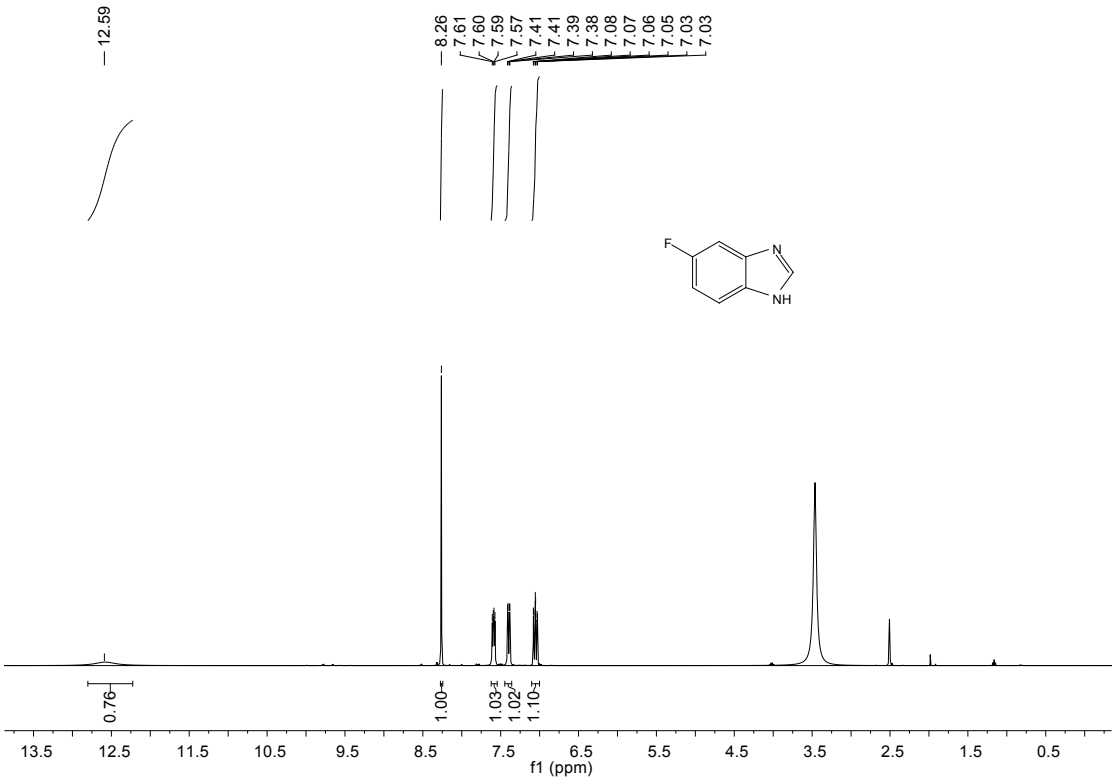


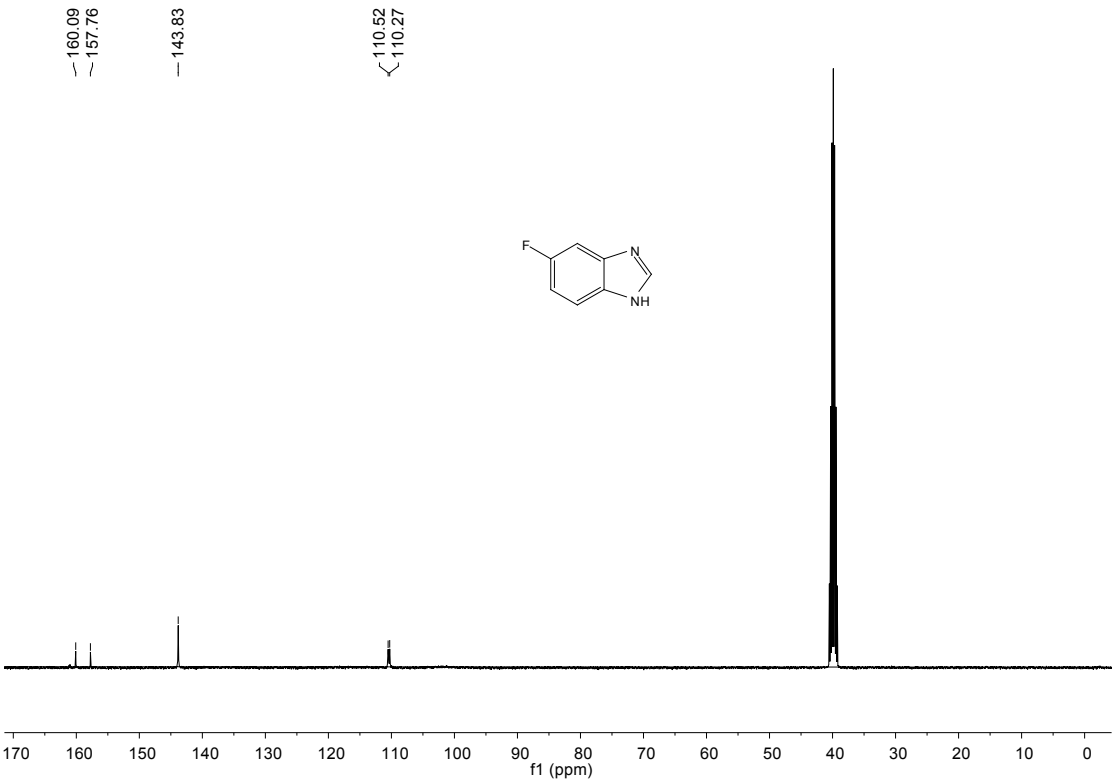

8.29
7.66
7.66
7.61
7.59
7.23
7.22
7.21
7.20
Cl
N
NH
1.00
0.98
1.04
1.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

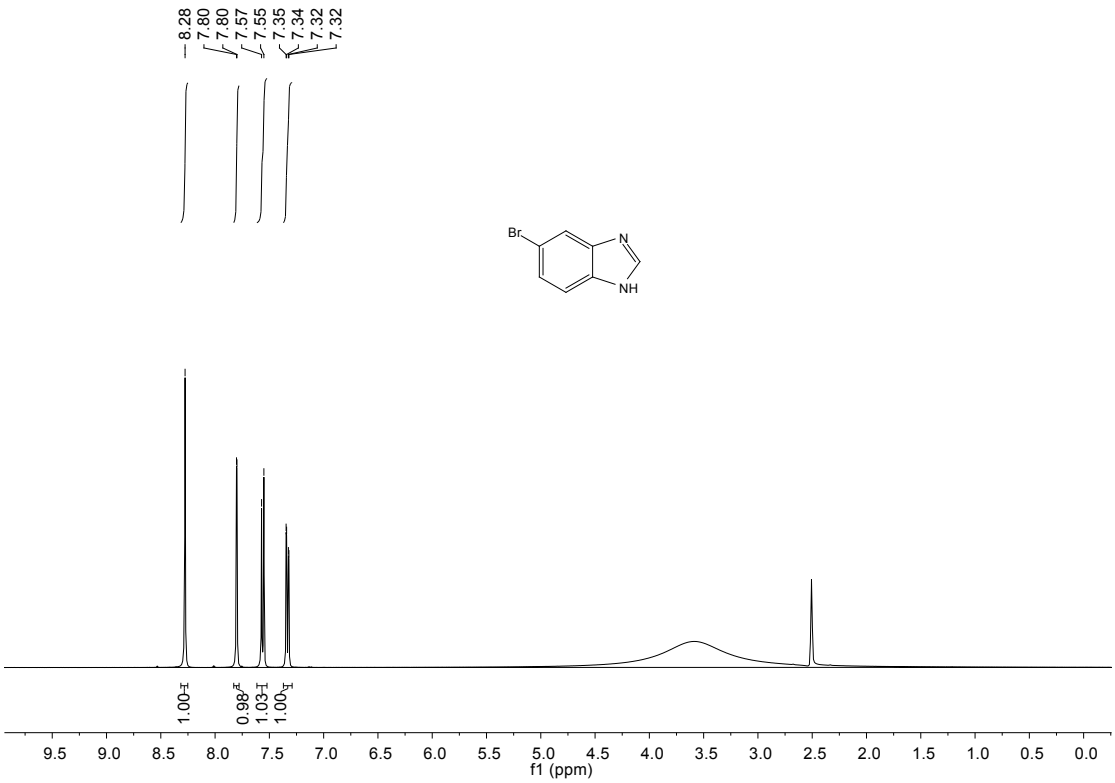

143.93
126.65
122.53
Cl
N
NH
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

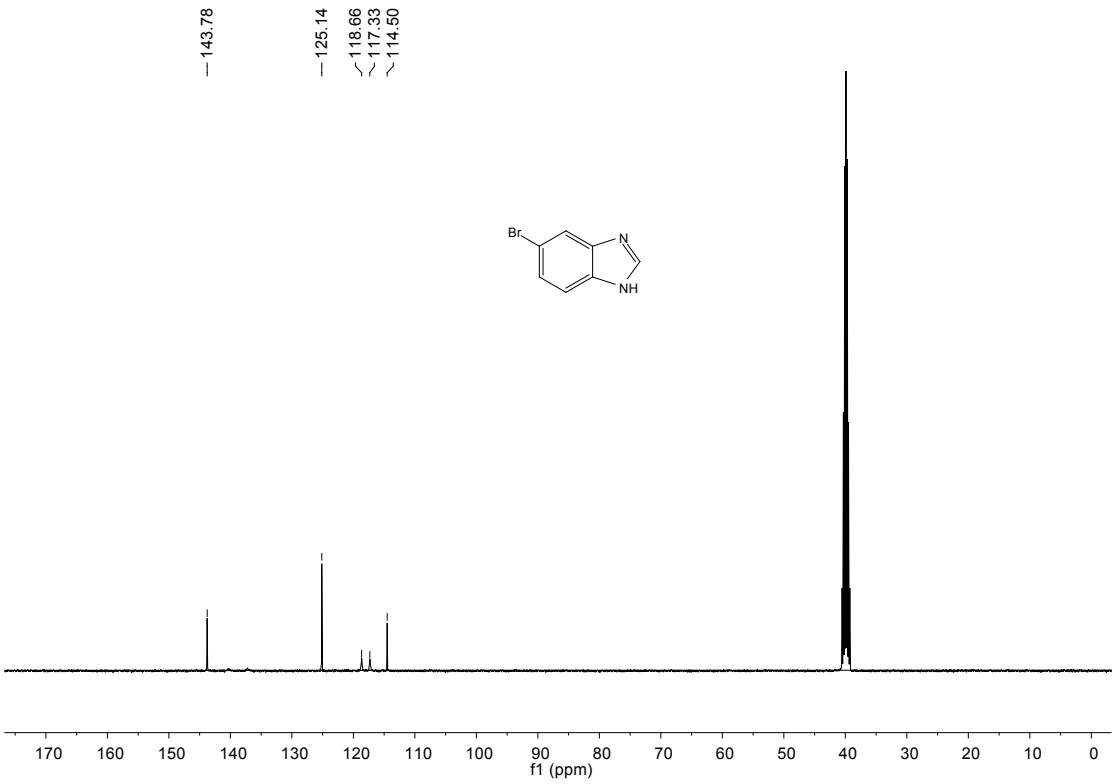

12.22
8.06
7.35
2.30
H3C
H3C
N
NH
0.85
1.00
2.00
6.06
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

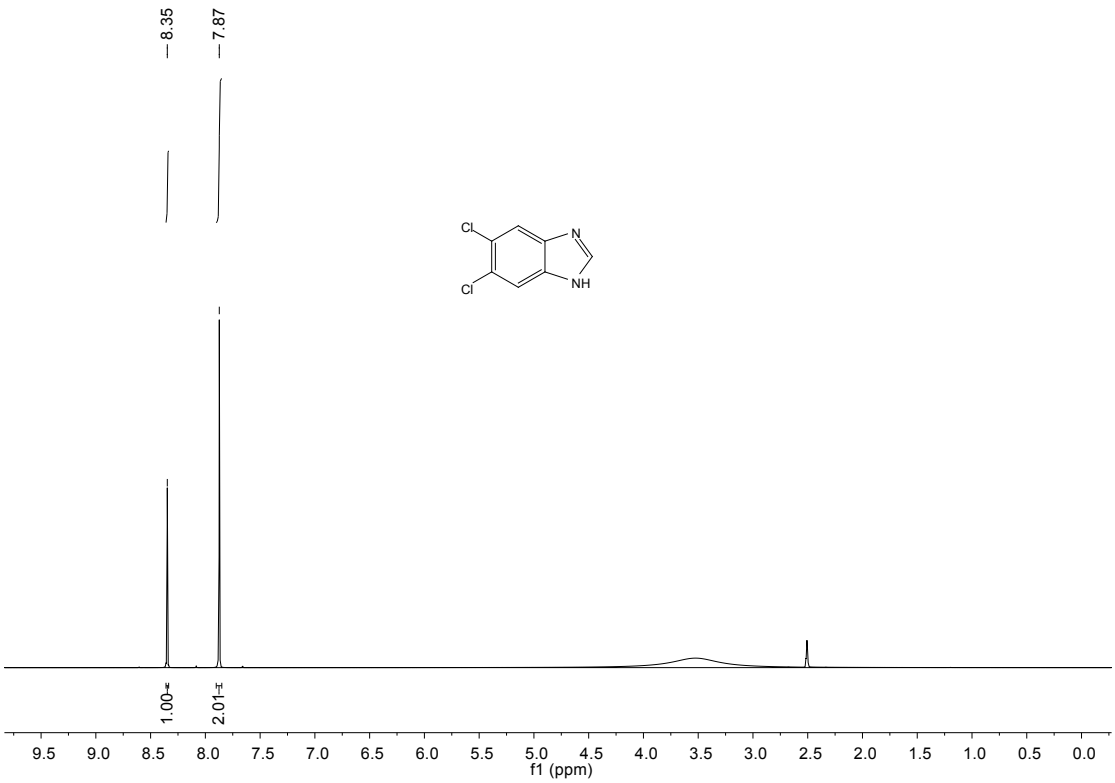

141.44
20.44
H3C
H3C
N
NH
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

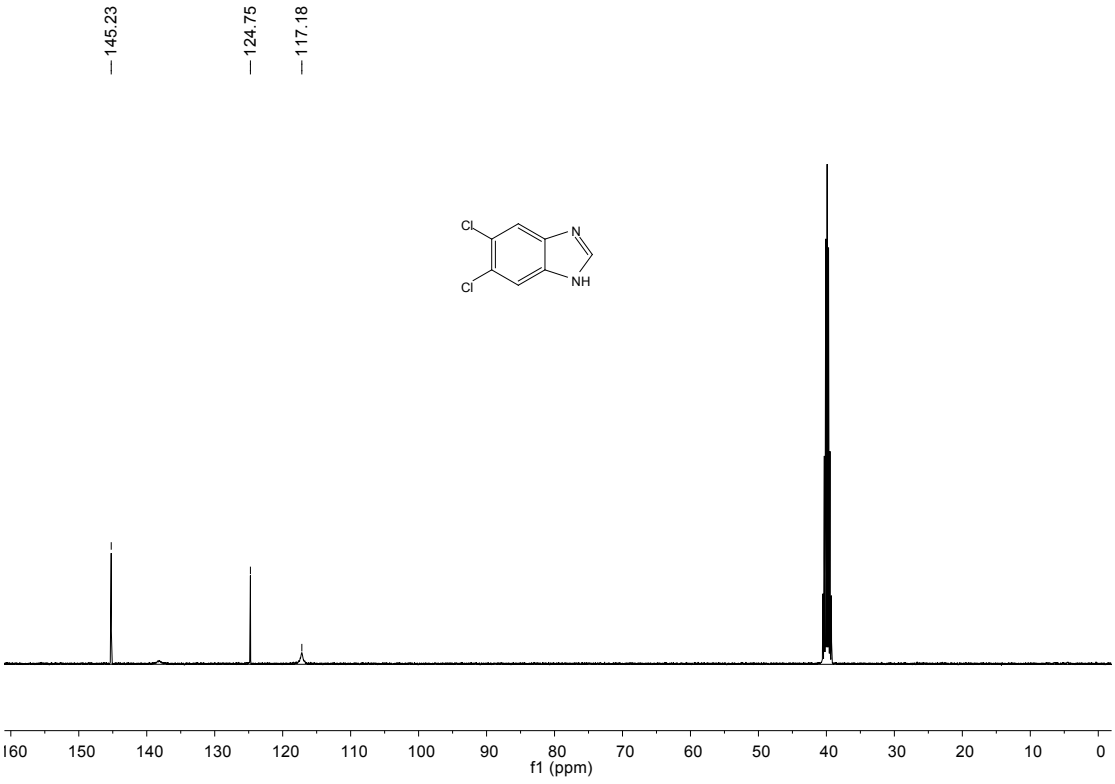

12.59
8.26
7.61
7.60
7.59
7.57
7.41
7.41
7.39
7.38
7.08
7.07
7.06
7.05
7.03
7.03
F
N
NH
0.76
1.00
1.03
1.02
1.10
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

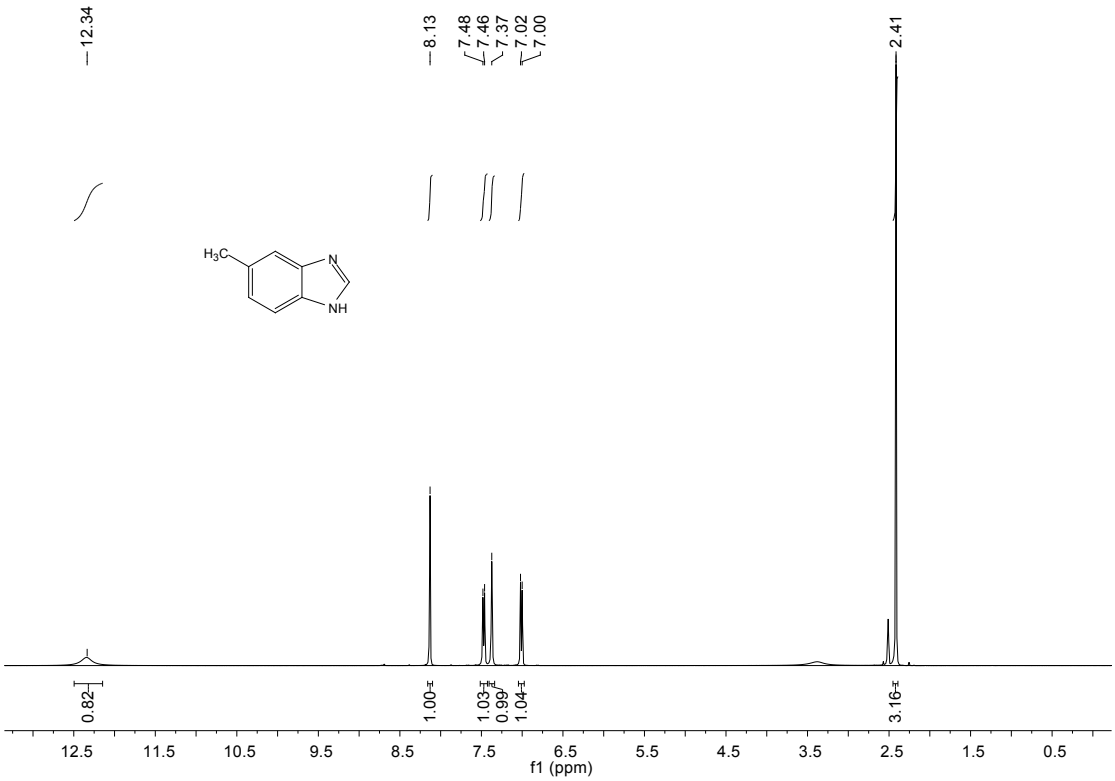

160.09
157.76
143.83
110.52
110.27
F
N
NH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

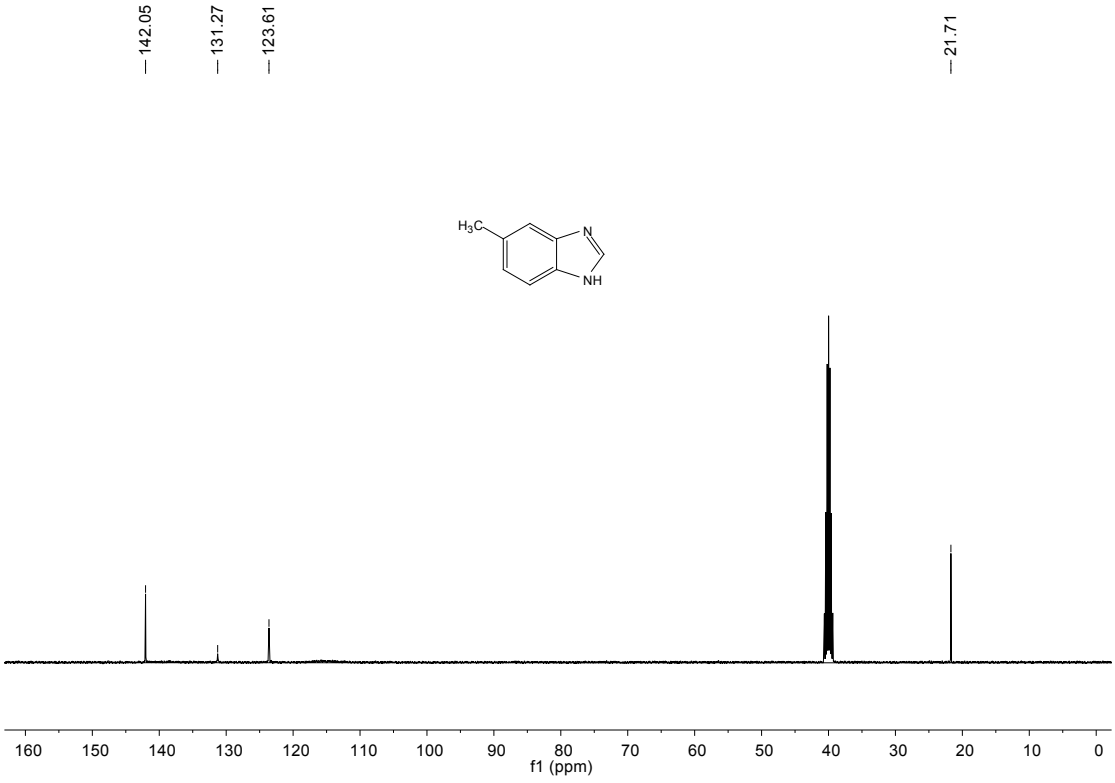

8.28
7.80
7.80
7.57
7.55
7.35
7.34
7.32
7.32
Br
N
NH
1.00
0.98
1.03
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

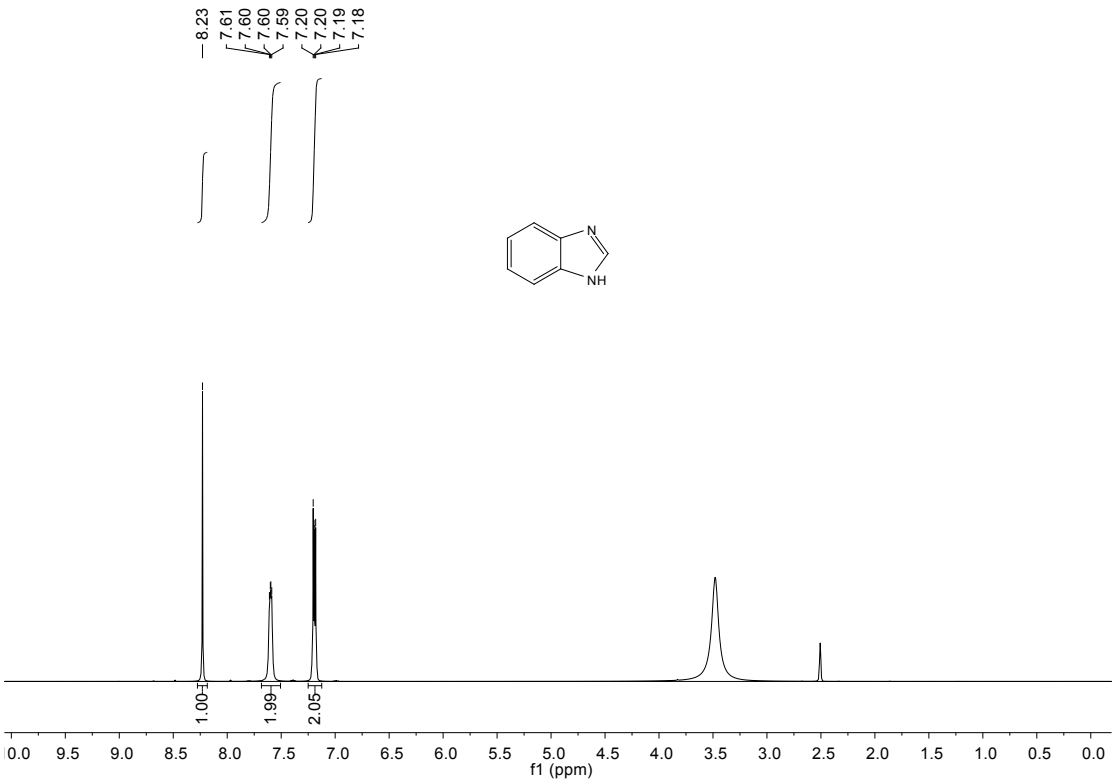

143.78
125.14
118.66
117.33
114.50
Br
N
NH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

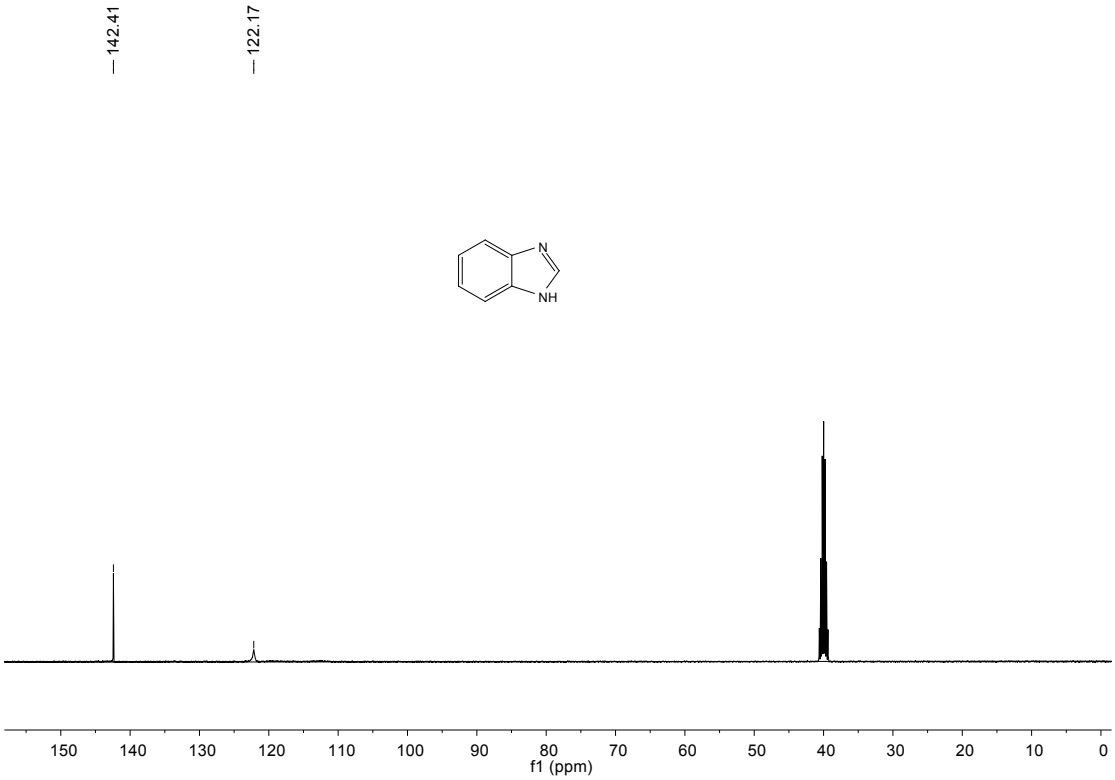

8.35
7.87
Cl
Cl
N
NH
1.00
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

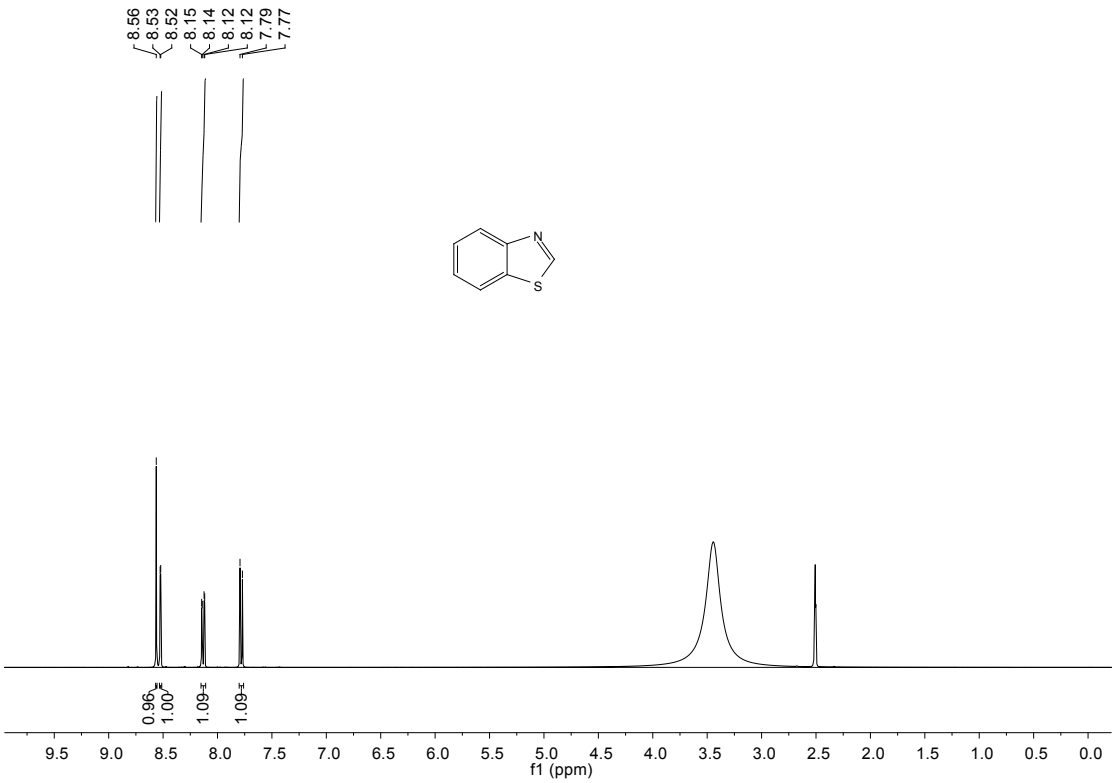

145.23
124.75
117.18
Cl
Cl
N
NH
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

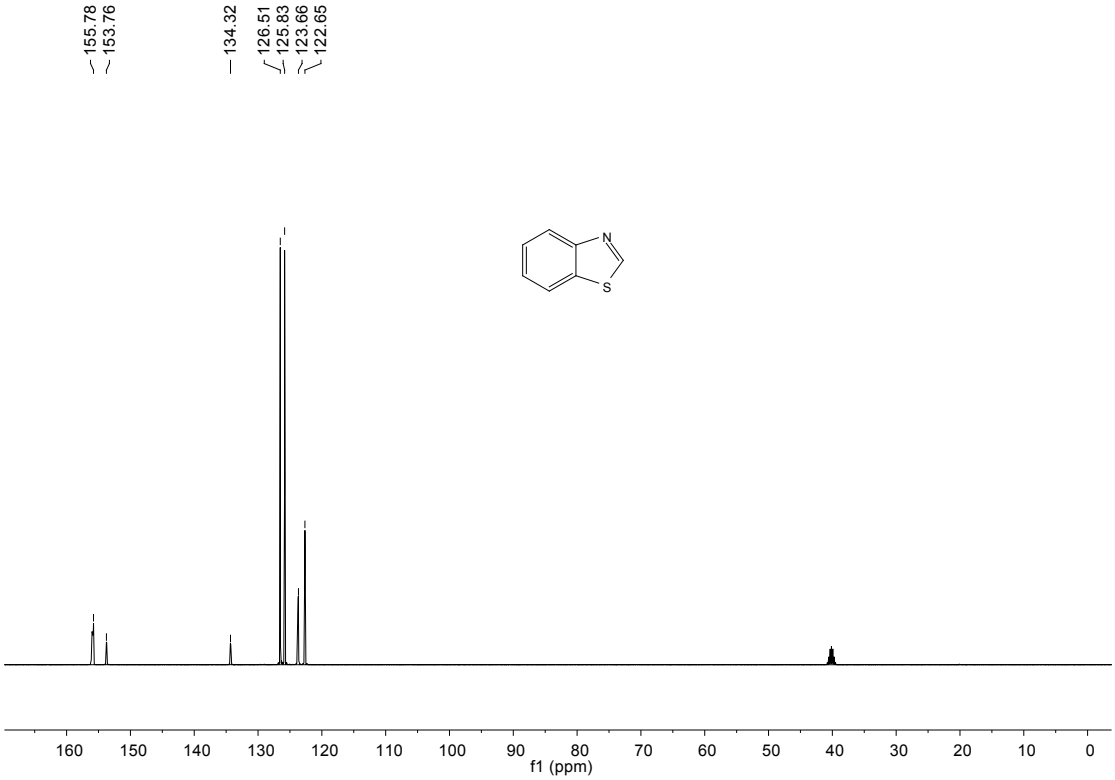

12.34
8.13
7.48
7.46
7.37
7.02
7.00
2.41
H3C
N
NH
0.82
1.00
1.03
0.99
1.04
3.16
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

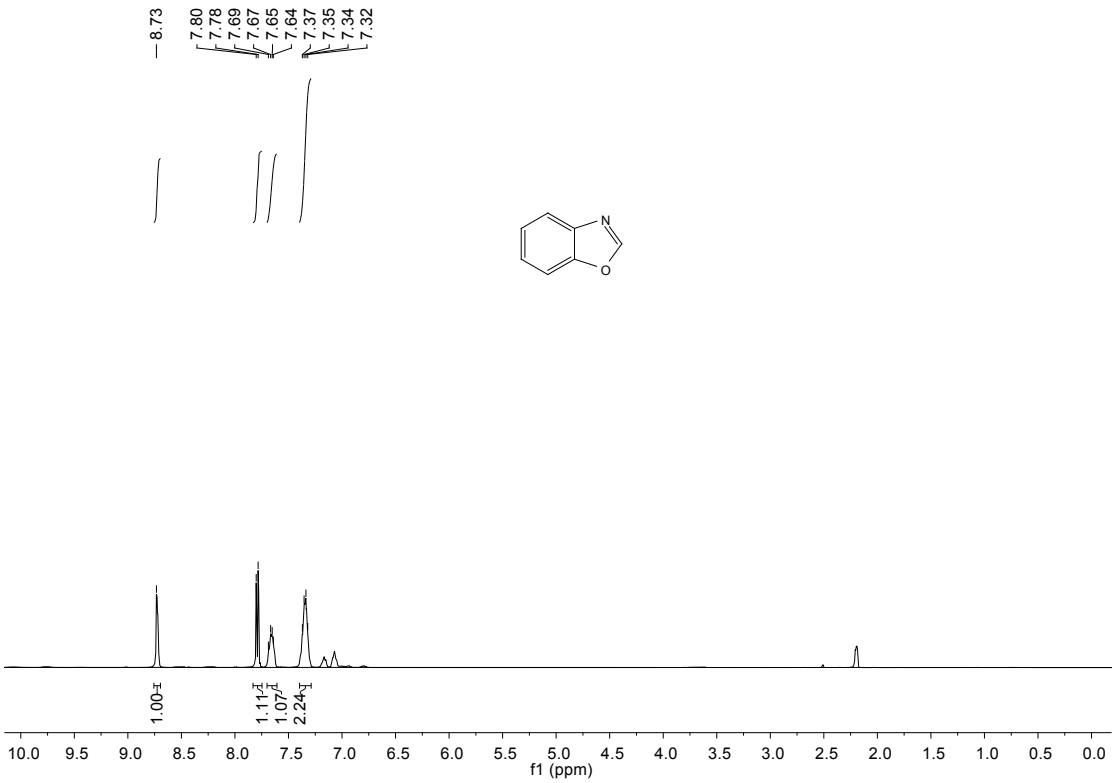

142.05
131.27
123.61
21.71
H3C
N
NH
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

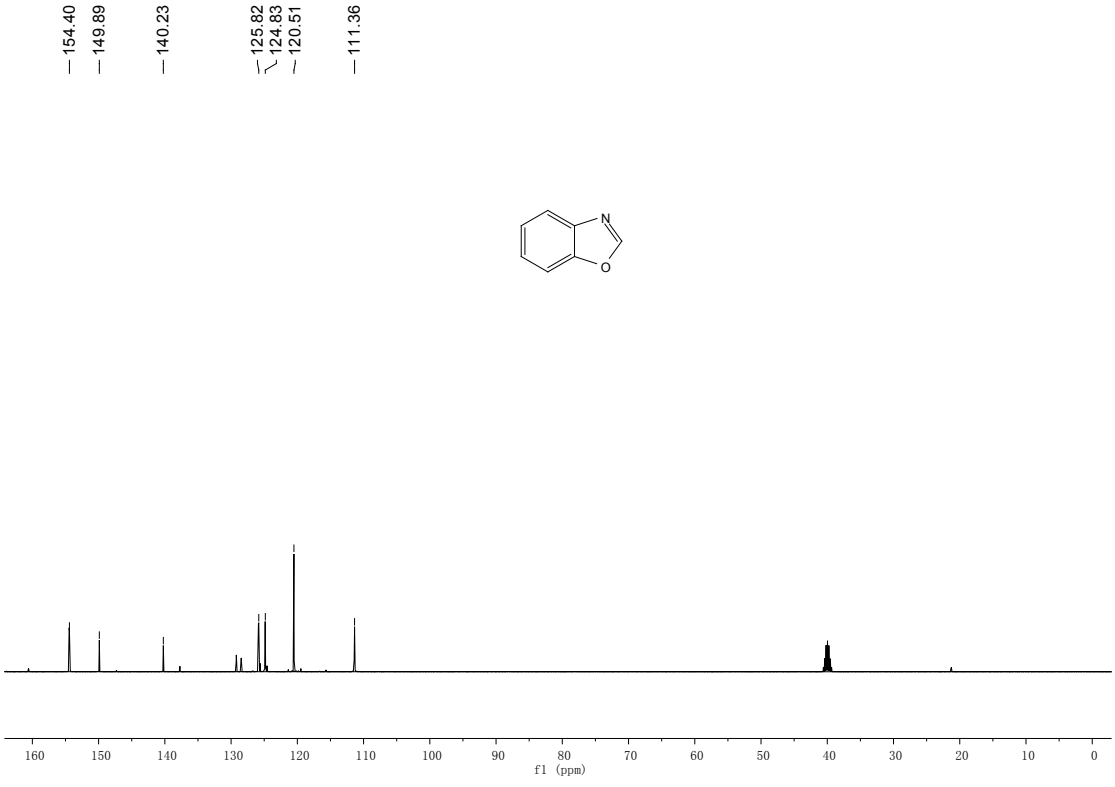

8.23
7.61
7.60
7.60
7.59
7.20
7.20
7.19
7.18
N
NH
1.00
1.99
2.05
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.41
122.17
N
NH
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.56
8.53
8.52
8.15
8.14
8.12
8.12
7.79
7.77
N
S
0.96
1.00
1.09
1.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

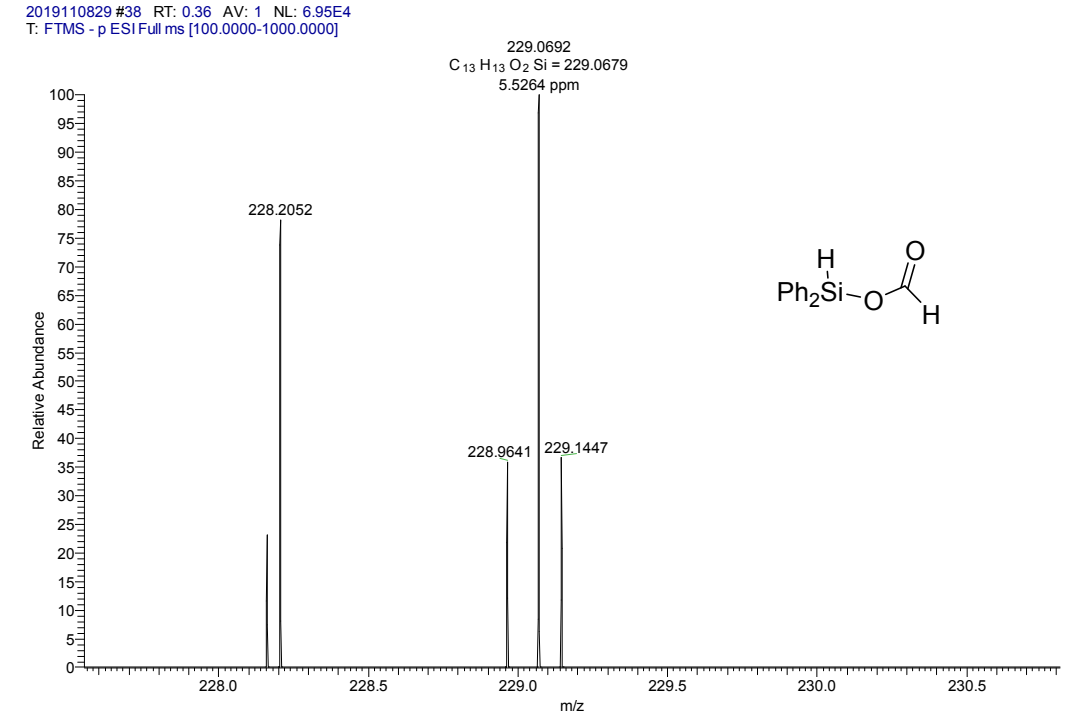

155.78
153.76
134.32
126.51
125.83
123.66
122.65
N
S
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.73
7.80
7.78
7.69
7.67
7.65
7.64
7.37
7.35
7.34
7.32
N
O
1.00
1.11
1.07
2.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

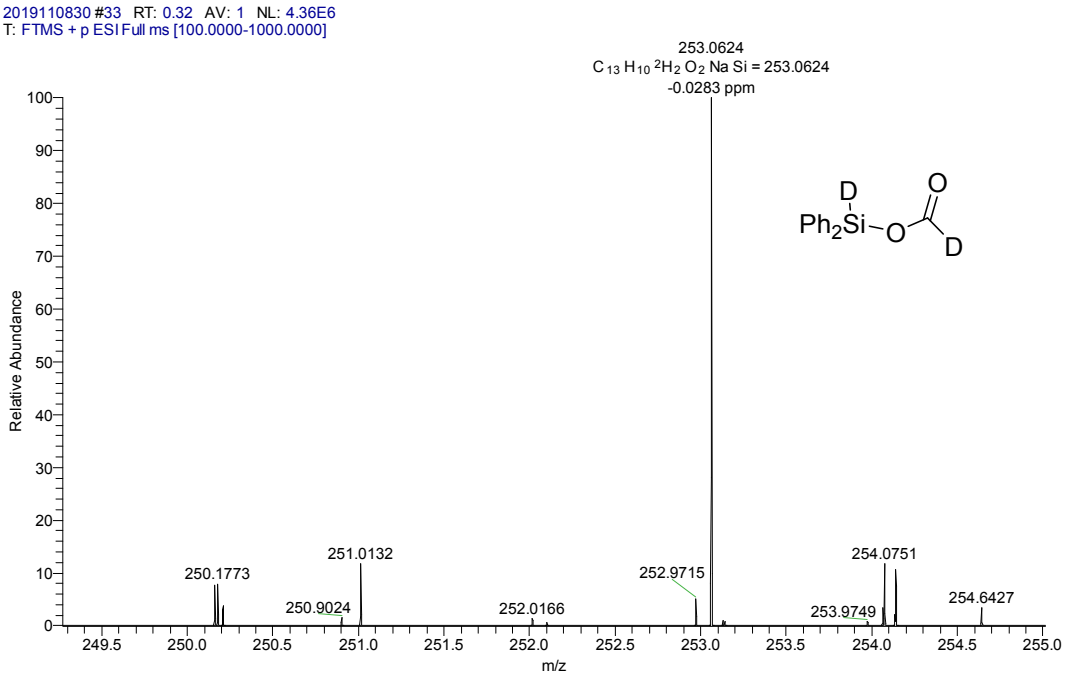

154.40
149.89
140.23
125.82
124.83
120.51
111.36
N
O
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

HR-MS spectra of some representative products formed in the reaction mixture

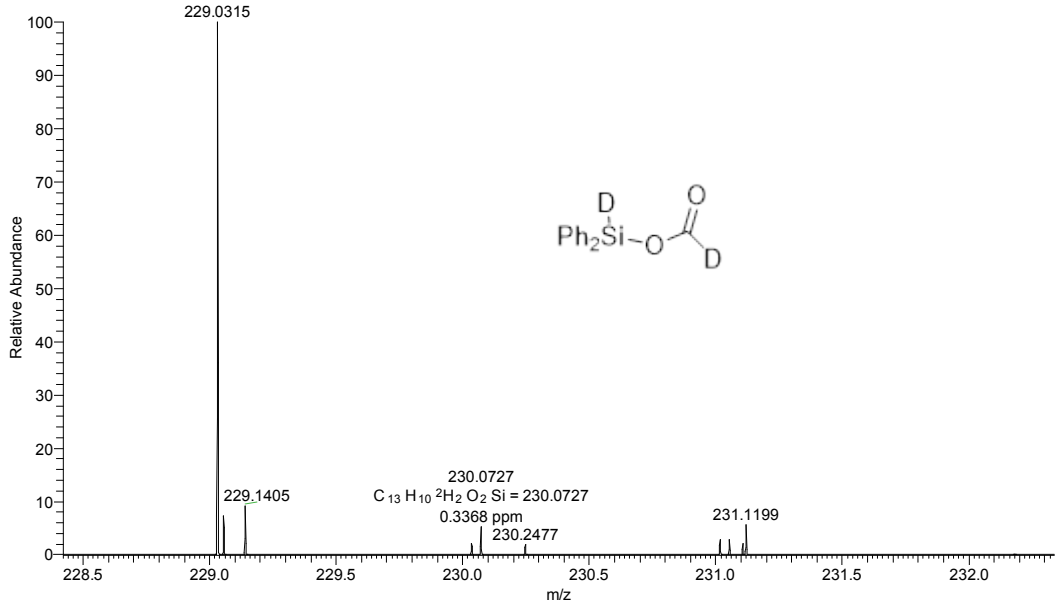
m/z 228 [M+H] $C_{13}H_{12}O_2Si$



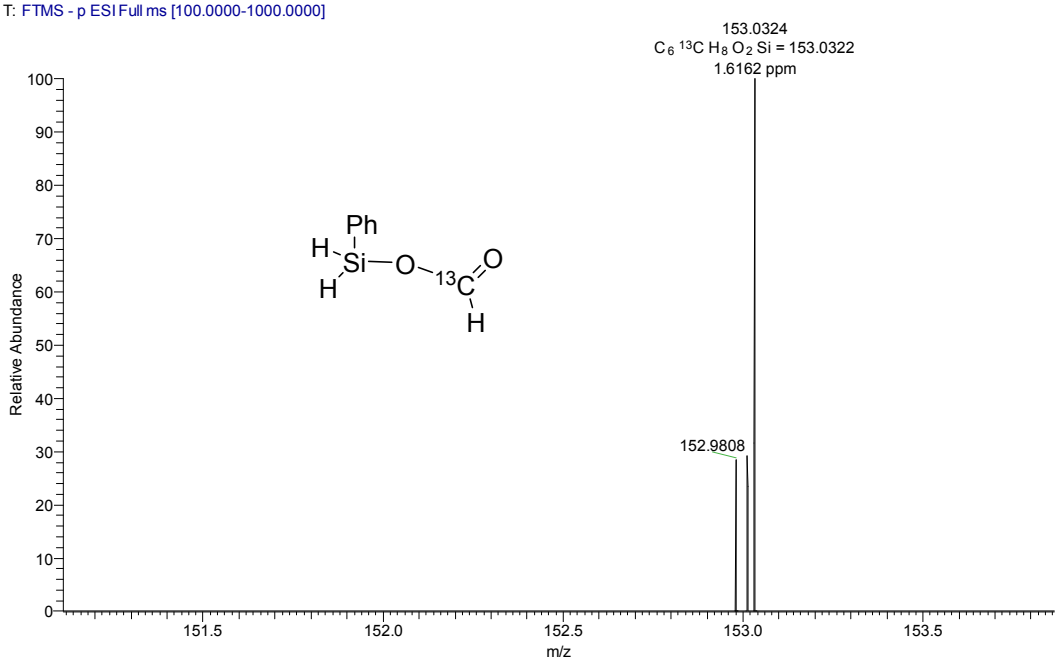
m/z 253 [M+Na] $C_{13}H_{10}D_2O_2NaSi$



m/z 230 [M$^+$] $C_{13}H_{10}D_2O_2Si$

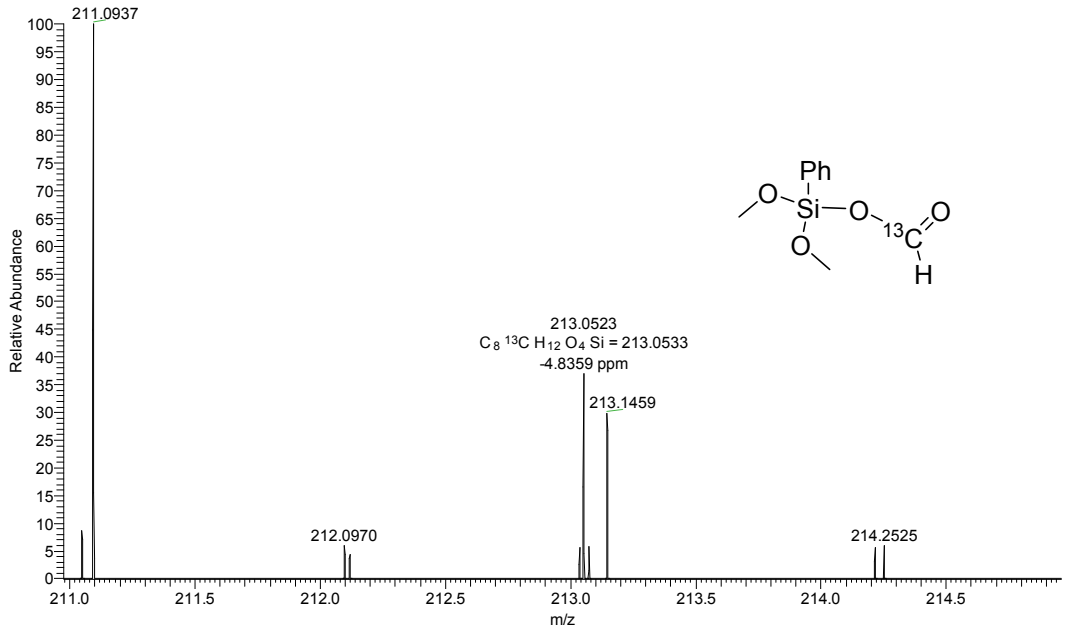


m/z 153 [M$^+$] $C_6{}^{13}CH_8O_2Si$



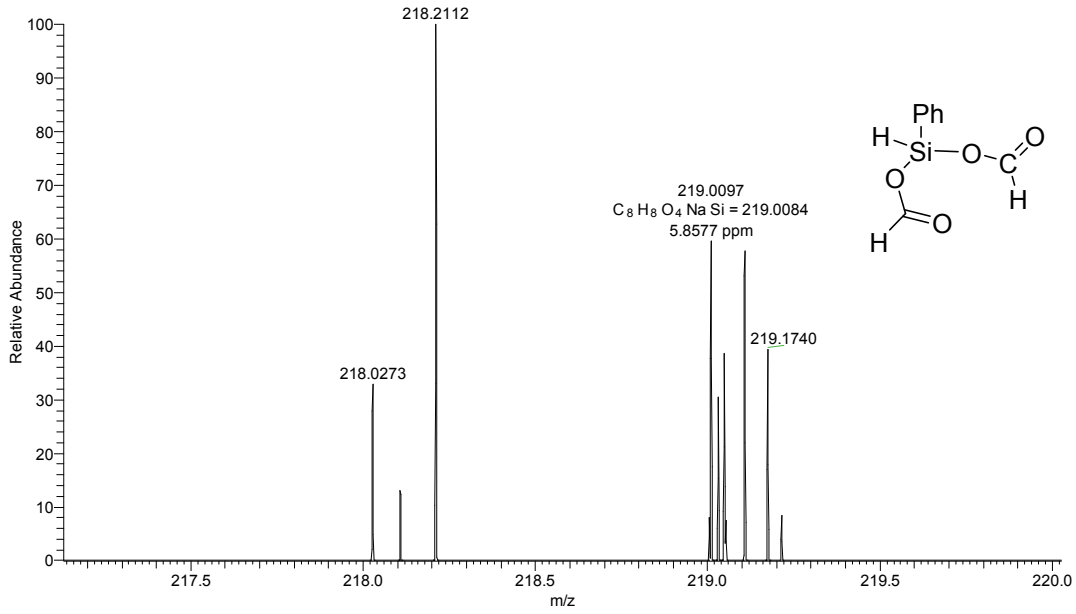
m/z 213 [M+] $C_8{}^{13}CH_{12}O_4Si$

2019110827 #67 RT: 0.64 AV: 1 NL: 7.50E5
T: FTMS + p ESI Full ms [100.0000-1000.0000]



m/z 196 [M+Na] $C_8H_8O_4NaSi$

2019110828 #49 RT: 0.47 AV: 1 NL: 4.60E5
T: FTMS + p ESI Full ms [100.0000-1000.0000]



Structural coordinates of reaction intermediates and transition states:

DMA

TS-1-DMA

C	-1.85157400	-0.32617500	-0.33578000
C	-2.46880700	-1.37441600	0.34966800
C	-3.80714600	-1.30328600	0.72247400
C	-4.55215900	-0.17293800	0.41443400
C	-3.95437100	0.88374500	-0.26409500
C	-2.61849800	0.80490300	-0.63317700
H	-1.89524500	-2.26188500	0.60346700
H	-4.26599700	-2.12850800	1.25632200
H	-5.59503900	-0.11114700	0.70551400
H	-4.52993800	1.77148400	-0.50248900
H	-2.16653400	1.64576800	-1.15241500
Si	-0.06824600	-0.53803600	-0.93565900
H	0.25568300	-1.85004700	-0.30857200
H	0.11900200	1.14590500	-0.80810600
H	-0.12695600	-0.61061700	-2.41448900
C	0.43275900	1.61331700	0.38657700
O	0.62926000	0.68561600	1.16364800
O	0.45698500	2.80127500	0.31726600
O	1.90224300	-0.31534400	-1.17217600
C	3.63841033	-2.00568541	-0.56103593
H	4.47663958	-2.06708884	0.13513648
H	2.86004926	-2.72875916	-0.32371173
H	3.99275141	-2.13254588	-1.58260789
C	3.07325637	-0.58938550	-0.43615363
N	3.58962395	0.53700433	0.35473857
C	4.60511364	1.25877518	-0.42547135
H	4.76306232	2.22634331	0.00320583
H	5.52274369	0.70861564	-0.41207086
H	4.26870054	1.36673699	-1.43545674
C	4.19410684	0.02880843	1.59459234
H	4.40389554	0.84754037	2.25076816
H	3.51472207	-0.64595328	2.07212032
H	5.10370050	-0.48507296	1.36336674

TS-2-DMA

C	2.05720900	0.11729600	-0.26708900
C	2.67365600	-0.26092100	-1.46159600
C	4.05837200	-0.27735900	-1.58633100

C	4.85320400	0.08790000	-0.50746500
C	4.25681100	0.46853800	0.68962200
C	2.87270300	0.48289900	0.80653800
H	2.06391100	-0.54608300	-2.31586900
H	4.51615900	-0.57319600	-2.52418200
H	5.93391700	0.07638500	-0.59914800
H	4.87356000	0.75512100	1.53488200
H	2.41628400	0.77970100	1.74437700
Si	0.16840800	0.11787000	-0.20730800
H	0.14724500	-1.50783200	-0.33372900
C	0.06012100	-1.95384000	1.12713000
O	0.28335800	-0.93704300	1.74177000
O	-0.20257900	-3.09573100	1.10016900
O	-1.68773100	-0.22883100	0.25004300
C	-3.43768013	1.61798406	-0.75440865
H	-4.38354725	1.58990544	-1.29744732
H	-3.57756267	1.93652149	0.27841828
H	-2.71383379	2.24566064	-1.26951098
O	0.04287900	1.62777600	0.67890200
C	-0.87923800	2.54907900	0.62574500
H	-0.64263300	3.38588600	1.29999700
O	-1.87824800	2.54859600	-0.05949700
H	-0.21522700	0.44360300	-1.61615600
C	-2.73721824	-0.03257560	-0.74577845
N	-3.51188626	-1.25338578	-1.01113098
C	-3.34494032	-1.64342010	-2.41857628
H	-2.51173325	-2.30877030	-2.50787963
H	-4.23195446	-2.13478490	-2.76014111
H	-3.16961480	-0.77060746	-3.01217468
C	-4.93398167	-1.00034163	-0.73815973
H	-5.14861956	-1.23638574	0.28316967
H	-5.15401155	0.03093039	-0.91972208
H	-5.53444416	-1.61138104	-1.37923355

TS-2-DMA2

C	2.16873300	0.20760100	-0.24807800
C	2.82309000	0.31909800	-1.47684100
C	4.20700900	0.43248600	-1.55034200
C	4.96252800	0.43820600	-0.38503400
C	4.32828300	0.32924500	0.84763200
C	2.94548400	0.21512600	0.91330900
H	2.24496400	0.32152300	-2.39793300
H	4.69417800	0.51950400	-2.51553700
H	6.04211000	0.52873900	-0.43685400

H	4.91365400	0.33379400	1.76099300
H	2.46025600	0.12891800	1.87941800
Si	0.28463600	0.08202400	-0.25766100
H	0.32383300	-1.41086200	-0.89164800
C	0.32199100	-2.29156200	0.36532800
O	0.38397300	-1.47855300	1.26104500
O	0.25288800	-3.39667800	-0.00876400
O	-1.61735600	-0.45320000	-0.06147000
O	0.01917600	1.19966900	1.06246300
C	-0.90517800	2.10798900	1.25111000
H	-0.72317400	2.66103200	2.18505700
O	-1.84655600	2.35551500	0.53461300
H	-0.09131700	0.83184200	-1.49647000
C	-2.50920000	0.14595300	-0.69614000
N	-3.79469400	-0.07521300	-0.50415900
C	-4.25900900	-0.98109600	0.53414000
H	-4.77906000	-0.41432500	1.31103500
H	-4.94585000	-1.71295500	0.10312700
H	-3.40394900	-1.49150600	0.96963100
C	-4.79728400	0.69512600	-1.21736300
H	-4.84758716	1.70367488	-0.80913349
H	-4.54327862	0.75022057	-2.27861603
H	-5.77742034	0.22485558	-1.10609540
C	-2.14718094	1.17402347	-1.78407994
H	-1.66806954	0.67545874	-2.60064928
H	-3.03808717	1.65357566	-2.13224050
H	-1.48385344	1.90734444	-1.37525602

TS-3-DMA

C	2.01429300	-0.09650100	0.08548700
C	2.74562400	0.03952300	-1.09977700
C	4.12743700	0.18614200	-1.08976100
C	4.81417000	0.19526700	0.11719700
C	4.10958200	0.05718300	1.30637000
C	2.72669900	-0.08416600	1.28916400
H	2.23140400	0.03037500	-2.05718000
H	4.66574500	0.29213800	-2.02514500
H	5.89256000	0.30858200	0.13114600
H	4.63824300	0.05849300	2.25349000
H	2.19078400	-0.18935800	2.22409600
Si	0.12061400	-0.19688300	-0.00544400
H	0.23708700	-0.67053700	-1.54202600
C	0.20959500	-2.20581300	-1.35639900
O	0.19682600	-2.31269900	-0.14800100

O	0.20693600	-2.67080000	-2.42618300
O	-1.66248600	-0.55283500	-0.37480600
C	-2.41687289	2.21150133	0.18906940
H	-1.72760510	2.52408247	-0.59482609
H	-3.34954470	2.77690805	0.14955641
H	-1.96494498	2.29717425	1.17607302
O	-0.09986400	-0.32560700	1.71668500
C	-1.03032200	-0.66964700	2.57513900
H	-0.59103200	-0.87284300	3.56330400
O	-2.21802300	-0.74904800	2.38229000
O	-0.29753300	1.46975900	-0.28137600
C	0.39394900	2.60447600	-0.18483200
H	1.41466700	2.47889800	0.20800600
O	-0.07229900	3.65965900	-0.50299500
C	-2.80663600	0.47003500	-0.02558400
N	-4.16815023	-0.06739057	0.10988839
C	-4.54185495	-0.10265602	1.53115583
H	-5.36974497	0.55418371	1.69866608
H	-4.81738001	-1.10023638	1.80285304
H	-3.71045609	0.21241522	2.12647594
C	-5.10923447	0.79172046	-0.62304317
H	-6.08046035	0.34273172	-0.61762021
H	-5.15725045	1.75126054	-0.15200464
H	-4.77499920	0.90650817	-1.63299890

TS-3-DMA2

C	-2.13143600	0.08537000	0.09562100
C	-2.86840000	0.33788000	-1.06668300
C	-4.25430400	0.24254600	-1.08191400
C	-4.93690400	-0.10373700	0.07731700
C	-4.22503900	-0.35347800	1.24372500
C	-2.83767100	-0.26276100	1.25083200
H	-2.35392400	0.61440500	-1.98340100
H	-4.79966900	0.43979400	-1.99821600
H	-6.01876800	-0.17812500	0.07169500
H	-4.75151200	-0.61904800	2.15411700
H	-2.29488500	-0.45905500	2.16734100
Si	-0.24175000	0.16553000	0.01065200
H	-0.32937900	1.23758200	-1.19447400
C	-0.31449400	2.54567900	-0.39082800
O	-0.29350800	2.14179100	0.75425800
O	-0.31841100	3.41810800	-1.16565500
O	1.58607200	0.65488100	-0.11293600
O	0.03430600	-0.41563600	1.62558000

C	1.01508300	-1.06336500	2.21561400
H	0.78475300	-1.22644900	3.27919200
O	2.03911100	-1.45583000	1.71581700
O	0.13621200	-1.20830000	-0.95895700
C	-0.52571900	-2.34928200	-1.16548700
H	-1.54020900	-2.36195400	-0.73649500
O	-0.04857300	-3.26452100	-1.76698300
C	2.51776400	-0.12178800	-0.45095300
N	3.77961700	0.22421600	-0.35033000
C	4.18289400	1.48051900	0.26171700
H	4.85087900	2.01887900	-0.41379200
H	3.29974200	2.08122600	0.46164500
H	4.70514400	1.27711700	1.20003000
C	4.83012700	-0.71998700	-0.69282500
H	5.80581898	-0.23490473	-0.61785171
H	4.79638595	-1.57279190	-0.01059558
H	4.68544598	-1.07839336	-1.71080016
C	2.19709131	-1.50240541	-1.05316939
H	1.62551737	-2.07347278	-0.35168147
H	1.63344665	-1.37643232	-1.95391102
H	3.10950498	-2.01657090	-1.27233859

DMF

TS-1-DMF

C	-1.85157400	-0.32617500	-0.33578000
C	-2.46880700	-1.37441600	0.34966800
C	-3.80714600	-1.30328600	0.72247400
C	-4.55215900	-0.17293800	0.41443400
C	-3.95437100	0.88374500	-0.26409500
C	-2.61849800	0.80490300	-0.63317700
H	-1.89524500	-2.26188500	0.60346700
H	-4.26599700	-2.12850800	1.25632200
H	-5.59503900	-0.11114700	0.70551400
H	-4.52993800	1.77148400	-0.50248900
H	-2.16653400	1.64576800	-1.15241500
Si	-0.06824600	-0.53803600	-0.93565900
H	0.25568300	-1.85004700	-0.30857200
H	0.11900200	1.14590500	-0.80810600
H	-0.12695600	-0.61061700	-2.41448900
C	0.43275900	1.61331700	0.38657700
O	0.62926000	0.68561600	1.16364800
O	0.45698500	2.80127500	0.31726600

O	1.90224300	-0.31534400	-1.17217600
C	3.06495131	-0.58744195	-0.44137364
N	4.05170997	0.49847496	-0.35197669
C	4.84980024	0.53814561	-1.58582359
H	5.33047366	1.49045748	-1.66922123
H	5.59021076	-0.23376197	-1.55665236
H	4.20963887	0.38661722	-2.42970306
C	4.93748565	0.26229032	0.79716136
H	5.52039736	1.13980669	0.98445515
H	4.34826857	0.03446463	1.66076931
H	5.58853905	-0.55931705	0.58270668
H	3.16041155	-1.55723439	0.00054259

TS-2-DMF

C	2.05720900	0.11729600	-0.26708900
C	2.67365600	-0.26092100	-1.46159600
C	4.05837200	-0.27735900	-1.58633100
C	4.85320400	0.08790000	-0.50746500
C	4.25681100	0.46853800	0.68962200
C	2.87270300	0.48289900	0.80653800
H	2.06391100	-0.54608300	-2.31586900
H	4.51615900	-0.57319600	-2.52418200
H	5.93391700	0.07638500	-0.59914800
H	4.87356000	0.75512100	1.53488200
H	2.41628400	0.77970100	1.74437700
Si	0.16840800	0.11787000	-0.20730800
H	0.14724500	-1.50783200	-0.33372900
C	0.06012100	-1.95384000	1.12713000
O	0.28335800	-0.93704300	1.74177000
O	-0.20257900	-3.09573100	1.10016900
O	-1.68773100	-0.22883100	0.25004300
O	0.04287900	1.62777600	0.67890200
C	-0.87923800	2.54907900	0.62574500
H	-0.64263300	3.38588600	1.29999700
O	-1.87824800	2.54859600	-0.05949700
H	-0.21522700	0.44360300	-1.61615600
C	-2.80559000	-0.01979000	-0.81065400
H	-2.93034612	1.00867134	-1.07824170
N	-3.35977746	-1.34467267	-1.12444082
C	-4.79347416	-1.36537935	-0.80042689
H	-5.29086523	-0.58193400	-1.33307640
H	-5.20961763	-2.30947983	-1.08397390
H	-4.92351430	-1.21979643	0.25161644
C	-3.17675340	-1.62593664	-2.55562661

H	-3.59662447	-2.58236279	-2.78769838
H	-3.66817119	-0.87104692	-3.13316455
H	-2.13224296	-1.62912968	-2.78776394

TS-3-DMF

C	2.01429300	-0.09650100	0.08548700
C	2.74562400	0.03952300	-1.09977700
C	4.12743700	0.18614200	-1.08976100
C	4.81417000	0.19526700	0.11719700
C	4.10958200	0.05718300	1.30637000
C	2.72669900	-0.08416600	1.28916400
H	2.23140400	0.03037500	-2.05718000
H	4.66574500	0.29213800	-2.02514500
H	5.89256000	0.30858200	0.13114600
H	4.63824300	0.05849300	2.25349000
H	2.19078400	-0.18935800	2.22409600
Si	0.12061400	-0.19688300	-0.00544400
H	0.23708700	-0.67053700	-1.54202600
C	0.20959500	-2.20581300	-1.35639900
O	0.19682600	-2.31269900	-0.14800100
O	0.20693600	-2.67080000	-2.42618300
O	-1.66248600	-0.55283500	-0.37480600
O	-0.09986400	-0.32560700	1.71668500
C	-1.03032200	-0.66964700	2.57513900
H	-0.59103200	-0.87284300	3.56330400
O	-2.21802300	-0.74904800	2.38229000
O	-0.29753300	1.46975900	-0.28137600
C	0.39394900	2.60447600	-0.18483200
H	1.41466700	2.47889800	0.20800600
O	-0.07229900	3.65965900	-0.50299500
C	-2.68019087	0.35699306	-0.06417808
N	-4.01075073	-0.25661943	0.05410192
H	-2.38966232	1.38022700	0.05194888
C	-4.61644892	-0.37427537	-1.28013448
H	-5.67750643	-0.47214632	-1.18277829
H	-4.39003990	0.50061634	-1.85302492
H	-4.22268256	-1.23693686	-1.77577872
C	-4.86370500	0.58348578	0.90709210
H	-5.62351069	1.04262469	0.30977578
H	-5.32059115	-0.02230588	1.66152666
H	-4.26787074	1.34164347	1.37085763

TS-3-DMF2

C	2.01429300	-0.09650100	0.08548700

C	2.74562400	0.03952300	-1.09977700
C	4.12743700	0.18614200	-1.08976100
C	4.81417000	0.19526700	0.11719700
C	4.10958200	0.05718300	1.30637000
C	2.72669900	-0.08416600	1.28916400
H	2.23140400	0.03037500	-2.05718000
H	4.66574500	0.29213800	-2.02514500
H	5.89256000	0.30858200	0.13114600
H	4.63824300	0.05849300	2.25349000
H	2.19078400	-0.18935800	2.22409600
Si	0.12061400	-0.19688300	-0.00544400
H	0.23708700	-0.67053700	-1.54202600
C	0.20959500	-2.20581300	-1.35639900
O	0.19682600	-2.31269900	-0.14800100
O	0.20693600	-2.67080000	-2.42618300
O	-1.66248600	-0.55283500	-0.37480600
O	-0.09986400	-0.32560700	1.71668500
C	-1.03032200	-0.66964700	2.57513900
H	-0.59103200	-0.87284300	3.56330400
O	-2.21802300	-0.74904800	2.38229000
O	-0.29753300	1.46975900	-0.28137600
C	0.39394900	2.60447600	-0.18483200
H	1.41466700	2.47889800	0.20800600
O	-0.07229900	3.65965900	-0.50299500
C	-2.69118418	-1.55729940	-0.46367297
N	-2.42639661	-3.00321781	-0.47404028
H	-3.68303568	-1.16885346	-0.56486769
C	-2.87001019	-3.57343692	-1.75425790
H	-3.01820307	-4.62727448	-1.64305872
H	-3.78954399	-3.11321508	-2.05015224
H	-2.12518573	-3.39487844	-2.50142147
C	-3.15925134	-3.64348388	0.62772344
H	-3.95201225	-4.24127788	0.22888451
H	-2.49112778	-4.26437616	1.18719075
H	-3.56805228	-2.89084137	1.26905881

References:

S1. N. T. Hassankiadeh, Z. Cui, J. Kim, D. W. Shin, S. Y. Lee, A. Sanguineti, V. Arcella, Y. M. Lee, E. Drioli, Microporous poly(vinylidene fluoride) hollow fiber membranes fabricated with PolarClean as water-soluble green diluent and additives. *J. Memb. Sci.*, 2015, **479**, 204-212.

S2. L. Cseri, G. Szekely, Towards cleaner PolarClean: efficient synthesis and extended applications of the polar aprotic solvent methyl 5-(dimethylamino)-2-methyl-5-oxopentanoate. *Green Chem.*, 2019, **21**, 4178-4188.

S3. R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650-654.

S4. P. J. Stephens, F. J. Devlin, C. F. N. Chabalowski, M. J. Frisch, *J. Chem. Phys.*, 1994, **98**, 11623-11627.

S5. A. D. McLean, G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639-5648.

S6. G. P. van Walsum, Severity function describing the hydrolysis of xylan using carbonic acid. *Appl. Biochem. Biotechnol.*, 2001, **91-93**, 317-329.

S7. M. A. Rauf, A. A. Soliman, M. Khattab, Solvent effect on the spectral properties of Neutral Red. *Chem. Cent. J.*, 2008, **2**, 19.

S8. P. G. Jessop, D. A. Jessop, D. Fu, L. Phan, Solvatochromic parameters for solvents of interest in green chemistry. *Green Chem.*, 2012, **14**, 1245-1259.

S9. V. I. Smirnov, V. G. Badelin, Enthalpies of solution of L-phenylalanine in aqueous solution of amides at 298.15 K. *Thermochim. Acta*, 2013, **551**, 145-148.