Supporting Information

Palladium-catalyzed direct carbonylation of thiophenes and furans under CO/CO_2-binary conditions leading to carboxylic acids

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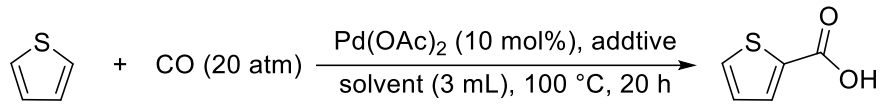
Table S1. Reaction Conditions for Pd-mediated Carbonylation of Thiophene **1j**

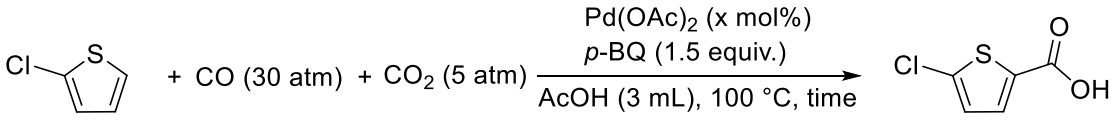


1j (3 mmol) **2j**

Entry	Solvent	Additive	Yield **2i** (%)[a]
1	Glacial AcOH	-	N. D.
2	Glacial AcOH	NaOAc (1 equiv.)	N. D.
3	Glacial AcOH	H_2O (100 μL)	N. D.
4	Glacial AcOH	PivOH (30 mol%)	N. D.
5	Glacial AcOH	K_2CO_3 (30 mol%)	N. D.
6	Glacial AcOH (CO_2 bubbling)	-	8
7	Glacial AcOH (N_2 + O_2 (79 : 21) bubbling)	-	N. D.

[a]Yields were determined by ^{1}H NMR spectroscopy based on **1j**.

Table S2. Optimization of Reaction Conditions for Pd-catalyzed Carbonylation of **1h**

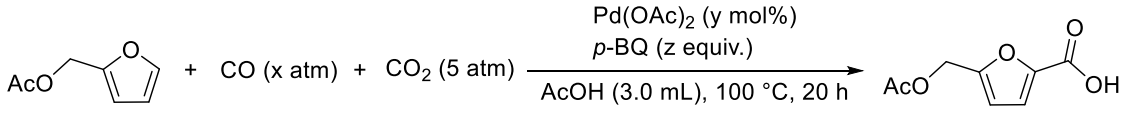


1h (3 mmol) **2h**

Entry	Pd cat. (mol%)	Time (h)	Yield **2e** (%)[a]
1	1	20	45
2	1	72	66
3	**5**	**20**	**87**

[a]Yields were determined by ^{1}H NMR spectroscopy.

Table S3. Optimization of Reaction Conditions for Pd-Catalyzed Carbonylation of Furfuryl Acetate **3a**[a]



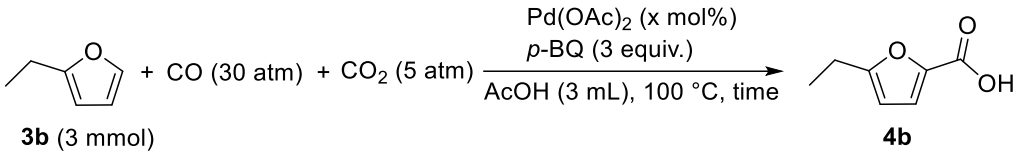
3a (3 mmol) **4a**

Entry	CO (atm)	CO_2 (atm)	$Pd(OAc)_2$ (mol%)	*p*-BQ (equiv.)	Yield **4a** (%)
1	10	1	10	3.0	41
2	20	1	10	3.0	60
3	50	1	10	3.0	90
4	30	5	1	1.5	55
5	30	5	5	1.5	76

6	30	5	10	1.5	78
7	50	5	5	1.5	40
8	**30**	**5**	**5**	**3.0**	**92**
9	30	-	5	3.0	70

[a]Yields were determined by ^{1}H NMR spectroscopy.

Table S4. Optimization of Reaction Conditions for Pd-catalyzed Carbonylation of 2-Ethylfuran **3b**[a]



Entry	Pd cat. (mol%)	Time (h)	Yield **4b** (%)
1	5	20	29
2	15	20	54
3	**15**	**48**	**(78)**
4[b]	15	48	39

[a]Yields were determined by ^{1}H NMR spectroscopy (isolated yield). [b]The reaction was conducted under CO (30 atm).

General Remarks

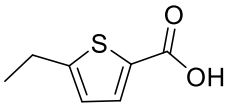
Unless otherwise stated, all starting materials and catalysts were purchased from commercial sources and used without further purification. All solvents were distilled and degassed with nitrogen before use. Thiophene derivatives (**1e**,[S1] **1f**[S2]) and furan derivatives (**3f**,[S3] **3g**[S4]) were prepared according to the previously reported procedures. ^{1}H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) FT NMR system, a JEOL JNM-ECX400 (400 MHz) FT NMR system, or a Bruker BioSpin Ascend 400 spectrometer (400 MHz) with Me_4Si as an internal standard. $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL JNM-ECX400 (100 MHz) FT NMR, a JEOL JNM-ECS400 (100 MHz) FT NMR system, or a Bruker BioSpin Ascend 400 spectrometer (100 MHz). The ^{1}H NMR yields of the crude mixture were determined using 1,3,5-trioxane as the internal standard. IR spectra were recorded on a Jasco FT/IR-410, and reported in wavenumbers (cm^{-1}).

Experimental Procedure for Pd-Catalyzed Carbonylation of Thiophenes (Table 2).

Thiophene **1** (3 mmol), $Pd(OAc)_2$ (1–5 mol%), *p*-benzoquinone (1.5 equiv. 486.4 mg), and AcOH (3.0 mL, bubbled with CO_2 for 30 min) were sequentially added to a 50 mL stainless steel autoclave with a magnetic stirring bar under a N_2 atmosphere. The vessel was purged five times with CO_2 and then charged with CO_2 (5 atm) and CO (30 atm), respectively. The reaction was conducted with magnetic stirring at 100 °C for 20–72 h. The resulting mixture was filtered through silica-gel with CH_2Cl_2, and

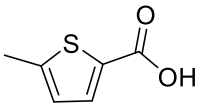
concentrated under reduced pressure. The residue was basified by sat. $NaHCO_3$ aq. (pH = 9), and the solvent was removed under reduced pressure. Then, the residue was washed with Et_2O (30 mL), and acidified with 10% HCl aq. (pH = 1). The solution was concentrated under reduced pressure. The residue was dissolved in acetone (10 mL), and filtered. Finally, the filtrate was concentrated to give the corresponding carboxylic acids **2**.

5-Ethylthiophene-2-carboxylic acid **(2a)** (CAS no. 23229-72-3)[S5]



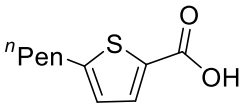
Brown solid, 403.0 mg, 86%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.08 (br, 1H), 7.73 (d, *J* = 3.7 Hz, 1H), 6.84 (d, *J* = 3.2 Hz, 1H), 2.89 (q, *J* = 7.5 Hz, 2H), 1.34 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.1, 157.7, 135.5, 129.8, 125.1, 24.1, 15.7.

5-Methylthiophene-2-carboxylic acid **(2b)** (CAS no. 1918-79-2)[S6]



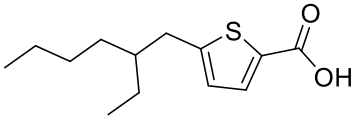
Brown solid, 358.5 mg, 84%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.98 (br, 1H), 7.71 (d, *J* = 3.6 Hz, 1H), 6.80 (d, *J* = 3.2 Hz, 1H), 2.54 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.0, 150.1, 135.7, 130.2, 126.9, 16.0.

5-Pentylthiophene-2-carboxylic acid **(2c) (**CAS no. 63068-75-7)[S7]



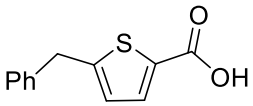
Brown solid, 475.8 mg, 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (br, 1H), 7.72 (d, *J* = 3.7 Hz, 1H), 6.82 (d, *J* = 3.7 Hz, 1H), 2.85 (t, *J* = 7.6 Hz, 2H), 1.71 (m, 2H), 1.35 (m, 4H), 0.90 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.7, 156.1, 135.3, 129.8, 125.6, 31.2, 31.1, 30.6, 22.3, 13.9.

5-(2-Ethylhexyl)thiophene-2-carboxylic acid **(2d)** (CAS no. 1810058-94-6)[S8]



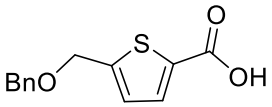
Brown solid, 653.5 mg, 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.07 (br, 1H), 7.73 (d, *J* = 3.6 Hz, 1H), 6.80 (d, *J* = 3.6 Hz, 1H), 2.79 (d, *J* = 6.8 Hz, 2H), 1.64-1.61 (m, 1H), 1.38-1.28 (m, 8H), 0.91-0.88 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.8, 155.0, 135.4, 130.0, 126.6, 41.6, 34.6, 32.4, 28.9, 25.6, 23.0, 14.2, 10.9.

***5-Benzylthiophene-2-carboxylic acid* (2e)** (CAS no. 13132-16-6)[S9]



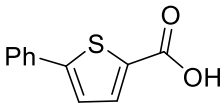
Gray solid, 655.8 mg, 100%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.30 (br, 1H), 7.70 (m, 1H), 7.30–7.29 (m, 2H), 7.23 (m, 3H), 6.80 (m, 1H), 4.13 (s, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 167.9, 154.3, 139.0, 135.5, 130.9, 128.8, 128.7, 127.0, 126.5, 36.7.

***5-((Benzyloxy)methyl)thiophene-2-carboxylic acid* (2f)** (CAS no. 1481274-88-7)



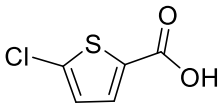
Dark brown solid, 618.0 mg, 83%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.36 (br, 1H), 7.77 (d, *J* = 3.6 Hz, 1H), 7.37-7.36 (m, 4H), 7.33-7.29 (m, 1H), 7.00 (d, *J* = 3.6 Hz, 1H), 4.71 (s, 2H), 4.59 (s, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 167.8, 150.9, 137.4, 135.1, 132.4, 128.7, 128.1, 128.0, 126.6, 72.4, 66.7.

***5-Phenylthiophene-2-carboxylic acid* (2g)** (CAS no. 19163-24-7)[S10]



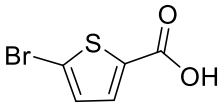
Light brown solid, 540.3 mg, 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 4.1 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.45-7.38 (m, 3H), 7.33 (d, *J* = 3.6 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 167.6, 153.1, 136.1, 133.3, 131.2, 129.25, 129.16, 126.4, 124.0.

***5-Chlorothiophene-2-carboxylic acid* (2h)** (CAS no. 24065-33-6)[S11]



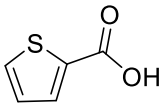
Brown solid, 336.7 mg, 69%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.52 (br, 1H), 7.69 (d, *J* = 4.1 Hz, 1H), 6.97 (d, *J* = 4.1 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 167.9, 140.4, 135.9, 132.0, 128.8.

***5-Bromothiophene-2-carboxylic acid* (2i)** (CAS no. 7311-63-9)[S12]



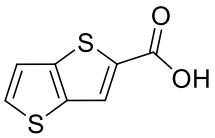
Dark gray solid, 433.5 mg, 70%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (br, 1H), 7.63 (d, *J* = 4.0 Hz, 1H), 7.10 (d, *J* = 4.0 Hz); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 166.5, 136.3, 133.9, 131.3, 122.3.

***2-Thiophenylcarboxylic acid* (2j)** (CAS no. 527-72-0)[S13]



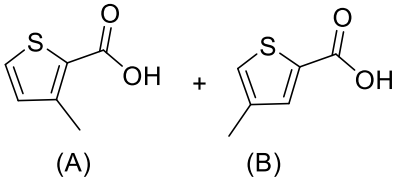
Brown solid, 211.6 mg, 55%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.66 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.15 (dd, *J* = 5.0, 4.1 Hz, 1H); ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ 167.7, 135.1, 134.1, 132.9, 128.2.

***Thieno[3,2-b]thiophene-2-carboxylic acid* (2k)** (CAS no. 1723-27-9)[S14]



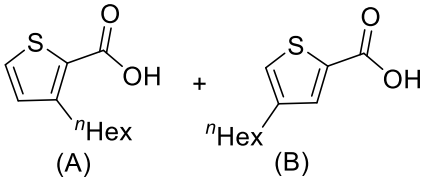
Light brown solid, 311.3 mg, 56%; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.12 (s, 1H), 7.93 (d, *J* = 5.3 Hz, 1H), 7.52 (d, *J* = 5.3 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 163.9, 143.7, 139.1, 136.1, 133.5, 126.6, 120.8.

***3-Methylthiophene-2-carboxylic acid* (A) and *4-methylthiophene-2-carboxylic acid* (B) (2l)**



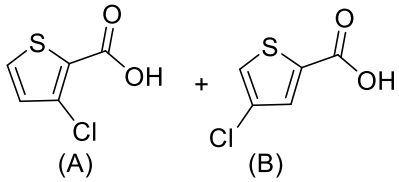
Brown solid, 322.0 mg, 75%; [compound A] (CAS no. 23806-24-8)[S15]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.1 (br, 1H), 7.48 (d, *J* = 5.0 Hz, 1H), 6.95 (d, *J* = 5.0 Hz, 1H), 2.58 (s, 3H); [compound B] (CAS no. 14282-78-1)[S15]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.1 (br, 1H), 7.69 (d, *J* = 1.3 Hz, 1H), 7.24-7.23 (m, 1H), 2.30 (s, 3H).

***3-Hexylthiophene-2-carboxylic acid* (A) and *4-hexylthiophene-2-carboxylic acid* (B) (2m)**



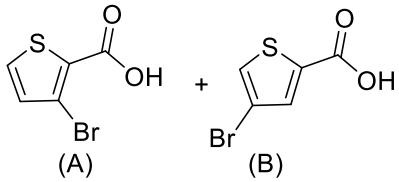
Reddish brown solid, 551.9 mg, 87%; [compound A] (CAS no. 214409-28-6)[S16]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.6 (br, 1H), 7.47 (d, *J* = 5.0 Hz, 1H), 6.98 (d, *J* = 5.0 Hz, 1H), 3.02 (t, *J* = 7.8 Hz, 2H), 1.67–1.59 (m, 2H), 1.39–1.26 (m, 4H), 0.91–0.87 (m, 3H); [compound B] (CAS no. 1261539-24-5)[S8]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.6 (br, 1H), 7.72 (d, *J* = 1.4 Hz, 1H), 7.23 (d, *J* = 1.4 Hz. 1H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.67–1.59 (m, 2H), 1.39–1.26 (m, 4H), 0.91–0.87 (m, 3H).

***3-Chlorothiophene-2-carboxylic acid* (A) and *4-chlorothiophene-2-carboxylic acid* (B) (2n)**



Light Brown solid, 343.9 mg, 71%; [compound A] (CAS no. 59337-89-2)[S17]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 5.0 Hz, 1H), 7.07 (d, *J* = 5.4 Hz, 1H); [compound B] (CAS no. 59614-95-8)[S18]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.73 (m, 1H), 7.43-7.43 (m, 1H)

***3-Bromothiophene-2-carboxylic acid* (A) and *4-bromothiophene-2-carboxylic acid* (B) (2o)**



Light gray solid, 482.3 mg, 78%; [compound A] (CAS no. 7311-64-0)[S19]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 5.2 Hz, 1H), 7.15 (d, *J* = 5.2 Hz, 1H); [compound B] (CAS no. 16694-18-1)[S20] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 1.5 Hz, 1H), 7.54 (d, *J* = 1.5 Hz, 1H).

Experimental Procedure for Gram-scale Synthesis of 2a via Pd-catalyzed Direct Carbonylation (Table 2).

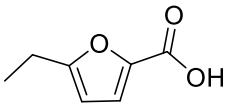
2-Ethylthiophene **1a** (10 mmol, 1.12 g), $Pd(OAc)_2$ (1 mol%, 22.5 mg), *p*-benzoquinone (1.5 equiv. 1.62 g), and AcOH (10 mL, bubbled with CO_2 for 30 min) were sequentially added to a 50 mL stainless steel autoclave with a magnetic stirring bar under a N_2 atmosphere. The vessel was purged three times with CO_2 and then charged with CO_2 (5 atm) and CO (30 atm), respectively. The reaction was conducted with magnetic stirring at 100 °C for 20 h. After the reaction was completed, the resulting mixture was filtered through silica-gel with CH_2Cl_2 and concentrated under reduced pressure. The residue was basified by sat. $NaHCO_3$ aq. (pH = 9), and the solution was removed in vacuo. The residue was washed with Et_2O (50 mL), then acidified with 10% HCl aq. (pH = 1). The solution was concentrated under reduced pressure. The residue was dissolved in acetone (20 mL), and filtered. Finally, the filtrate was concentrated to give pure **2a** in 83% isolated yield (brown solid, 1.3 g).

Experimental Procedure for Pd-Catalyzed Carbonylation of Furans (Table 3).

Furan **3** (3 mmol), $Pd(OAc)_2$ (5–15 mol%), *p*-benzoquinone (3 equiv. 972.8 mg), and AcOH (3.0 mL, bubbled with CO_2 for 30 min) were sequentially added to a 50 mL stainless steel autoclave with a magnetic stirring bar under a N_2 atmosphere. The vessel was purged three times with CO_2 and then charged with CO_2 (5 atm) and CO (30 atm), respectively. The reaction was conducted with magnetic stirring at 100 °C for 20–48 h. After the reaction was completed, the resulting mixture was filtered

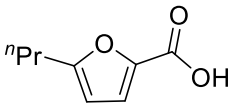
through silica-gel with CH_2Cl_2 and concentrated under reduced pressure. The residue was basified by sat. $NaHCO_3$ aq. (pH = 9), and the solution was removed in vacuo. The residue was washed with Et_2O (30 mL), then acidified with 10% HCl aq. (pH = 1). The solution was concentrated under reduced pressure. The residue was disollved in acetone (10 mL), and filtered. Finally, the filtrate was concentrated to give the corresponding carboxylic acids **4**.

***5-Ethylfuran-2-carboxylic acid* (4b)** (CAS no. 56311-37-6)[S21]



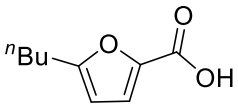
Dark brown solid, 326.3 mg, 78%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.1 (br, 1H), 7.26 (d, *J* =3.6 Hz, 1H), 6.18 (d, *J* = 3.4 Hz, 1H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) : δ 164.1, 163.7, 142.0, 121.6, 107.4, 21.8, 11.8.

***5-Propylfuran-2-carboxylic acid* (4c)** (CAS no. 14497-25-7)[S22]



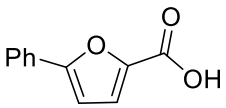
Brown solid, 384.7 mg, 83%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (br, 1H), 7.25 (d, *J* = 3.4 Hz, 1H), 6.18 (d, *J* = 3.4 Hz, 1H), 2.69 (t, *J* = 7.5 Hz, 2H), 1.78–1.68 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) : δ 163.6, 162.8, 142.1, 121.6, 108.2, 30.3, 21.1, 13.7.

***5-Butylfuran-2-carboxylic acid* (4d)** (CAS no. 67238-23-7)[S23]



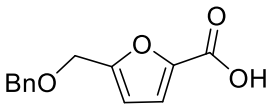
Brown solid, 400.1 mg, 79%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (br, 1H), 7.25 (d, *J* = 3.4 Hz, 1H), 6.17 (d, *J* = 3.4 Hz, 1H), 2.71 (t, *J* = 7.7 Hz, 2H), 1.68 (m, 2H), 1.38 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) : δ 163.7, 163.0, 142.0, 121.6, 108.1, 29.7, 28.1, 22.2, 13.7.

***5-Phenylfuran-2-carboxylic acid* (4f)** (CAS no. 52938-97-3)[S24]



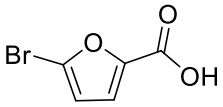
Brown solid, 203.4 mg, 36%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (br, 1H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.45–7.35 (m, 4H), 6.78 (d, *J* = 2.7 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) : δ 163.7, 158.8, 142.8, 129.31, 129.25, 128.9, 125.1, 122.3, 107.3.

***5-((Benzyloxy)methyl)furan-2-carboxylic acid* (4g)** (CAS no. 42890-01-7)[S25]



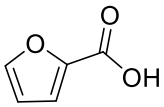
Light brown solid, 574.4 mg, 82%; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.38–7.28 (m, 5H), 7.18 (d, J = 3.3 Hz, 1H), 6.63 (d, J = 3.3 Hz, 1H), 4.59 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) : δ 163.4, 157.6, 143.9, 137.3, 128.9, 128.7, 128.3, 121.7, 112.4, 73.9, 65.7.

***5-Bromofuran-2-carboxylic acid* (4h)** (CAS no. 585-70-6)[S26]



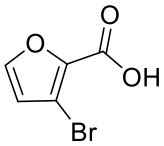
Dark brown solid, 497.2 mg, 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (s, overlapped with $CDCl_3$, 1H), 6.51 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 158.7, 147.2, 127.2, 120.6, 114.9.

***Furan-2-carboxylic acid* (4i)** (CAS no. 88-14-2)[S27]



Light brown solid, 200.3 mg, 60%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (br, 1H), 7.65 (m, 1H), 7.34 (d, J = 3.5 Hz, 1H), 6.57–6.56 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.5, 147.5, 143.8, 120.2, 112.3.

***3-Bromofuran-2-carboxylic acid* (4j)** (CAS no. 14903-90-3)[S28]



Brown solid, 546.1 mg, 95%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.2 (br, 1H), 7.59 (m, 1H), 6.67 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.8, 146.9, 140.4, 117.5, 111.1.

Experimental Procedure for the Structual Charactrization of Palladium Carbonyl Complexes by IR Measurment

[Fig. 1, eq. 1]

$Pd(OAc)_2$ (0.3 mmol) and AcOH (3.0 mL, bubbled with Ar for 30 min) were sequentially added to a 50 mL stainless steel autoclave with a magnetic stirring bar under a N_2 atmosphere. The vessel was purged five times with CO and then charged with CO (1 atm). The reaction was conducted with

magnetic stirring at 50 °C for 15 min. The resulting mixture was filtered by suction and the residue was washed with dry Et_2O (15 mL), and the suction was continued for 10 min. The resulting solid was then dried between filter papers and the IR measurment of the resulting powder was conducted by KBr method without any further purification.

[Fig. 1, eq. 2]

$Pd(OAc)_2$ (0.3 mmol) and AcOH (3.0 mL, bubbled with Ar for 30 min) were sequentially added to a 50 mL stainless steel autoclave with a magnetic stirring bar under a N_2 atmosphere. The vessel was purged five times with CO and then charged with CO (30 atm). The reaction was conducted with magnetic stirring at 50 °C for 15 min. After removing excess CO from the reaction vessel, the vessel was purged five times with CO_2 and then charged with CO_2 (5 atm). The reaction was conducted with magnetic stirring at 100 °C for 15 min. The resulting mixture was filtered by suction and the residue was washed with dry Et_2O (15 mL), and the suction was continued for 10 min. The resulting solid was then dried between filter papers and the IR measurment of the resulting powder was conducted by KBr method without any further purification.

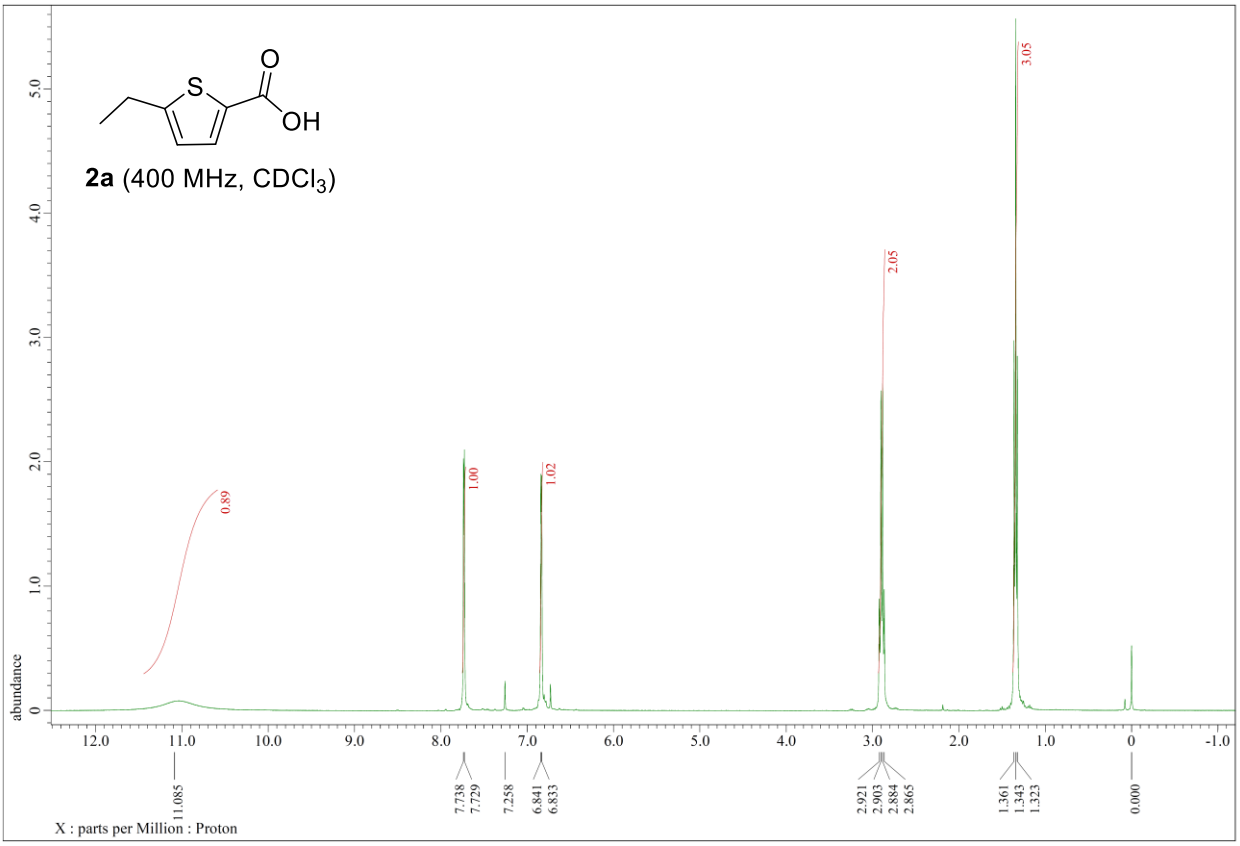
[Fig 2, eq. 6]

$Pd(OAc)_2$ (0.3 mmol) and AcOH (3.0 mL, bubbled with Ar for 30 min) were sequentially added to a 50 mL stainless steel autoclave with a magnetic stirring bar under a N_2 atmosphere. The vessel was purged five times with CO and then charged with CO (10 atm). The reaction was conducted with magnetic stirring at 100 °C for 15 min. The resulting mixture was filtered by suction and the residue was washed with dry Et_2O (15 mL), and the suction was continued for 10 min. The resulting solid was then dried between filter papers and the IR measurment of the resulting powder was conducted by KBr method without any further purification.

[Fig. 2, eq. 7]

$Pd(OAc)_2$ (0.3 mmol) and AcOH (3.0 mL, bubbled with Ar for 30 min) were sequentially added to a 50 mL stainless steel autoclave with a magnetic stirring bar under a N_2 atmosphere. The vessel was purged five times with CO_2 and then charged with CO_2 (5 atm) and CO (10 atm), respectively. The reaction was conducted with magnetic stirring at 100 °C for 15 min. The resulting mixture was filtered by suction and the residue was washed with dry Et_2O (15 mL), and the suction was continued for 10 min. The resulting solid was then dried between filter papers and the IR measurment of the resulting powder was conducted by KBr method without any further purification.

Figure S1 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2a**



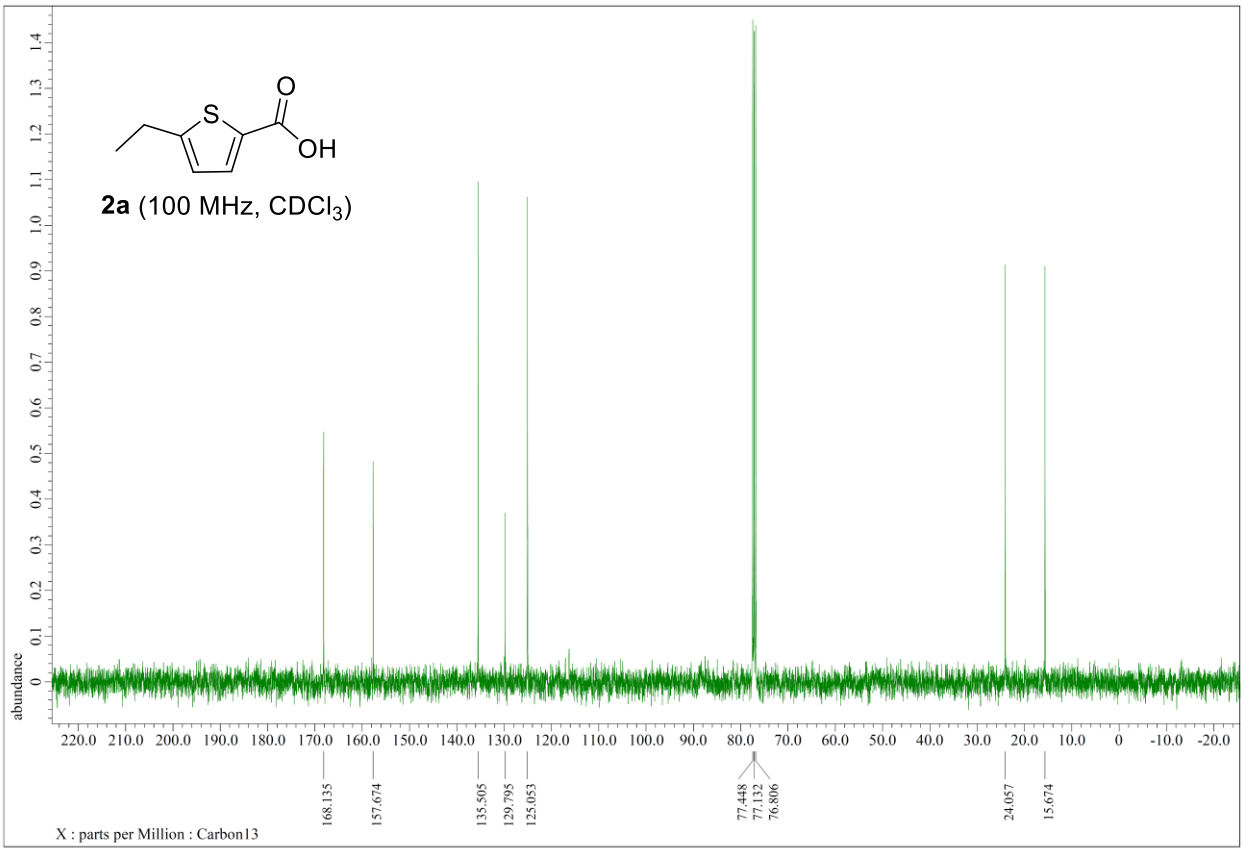
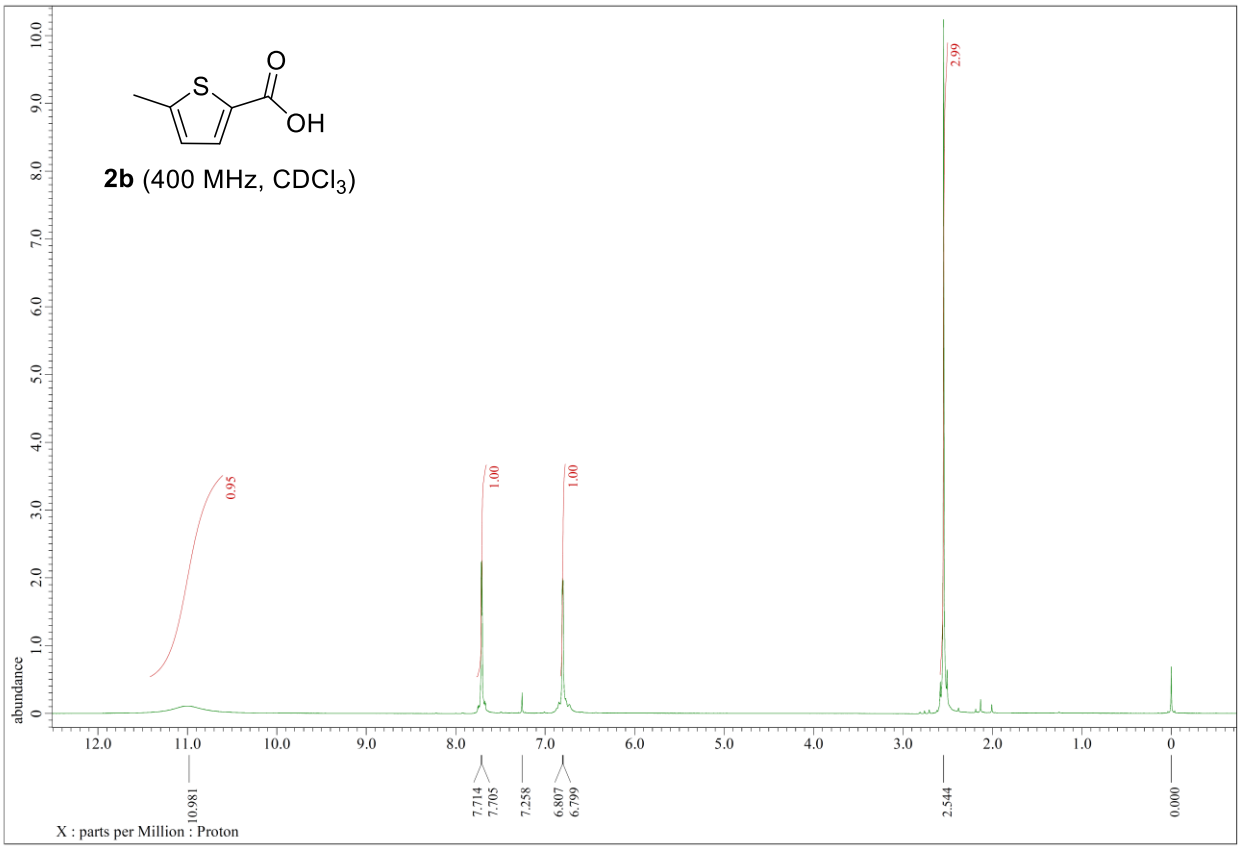


Figure S2 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2b**



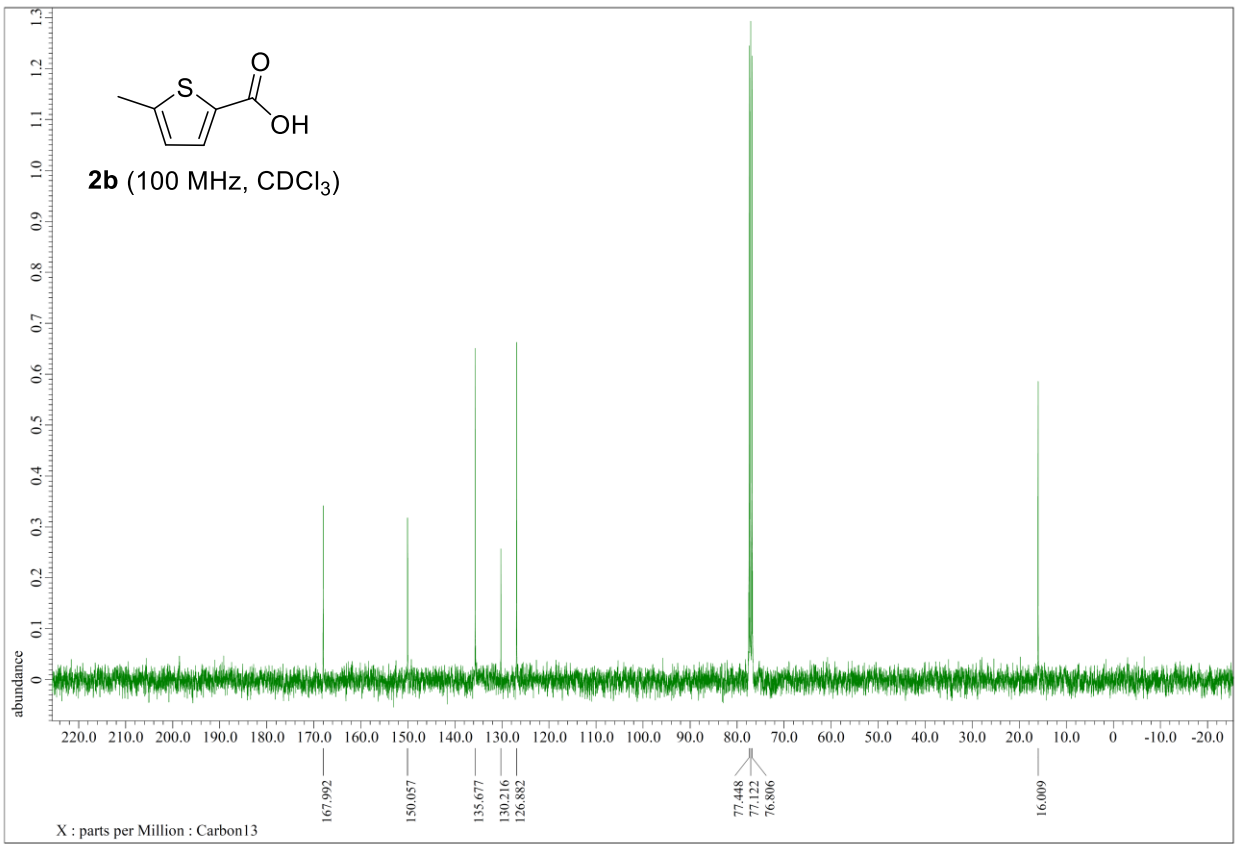


Figure S3 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2c**

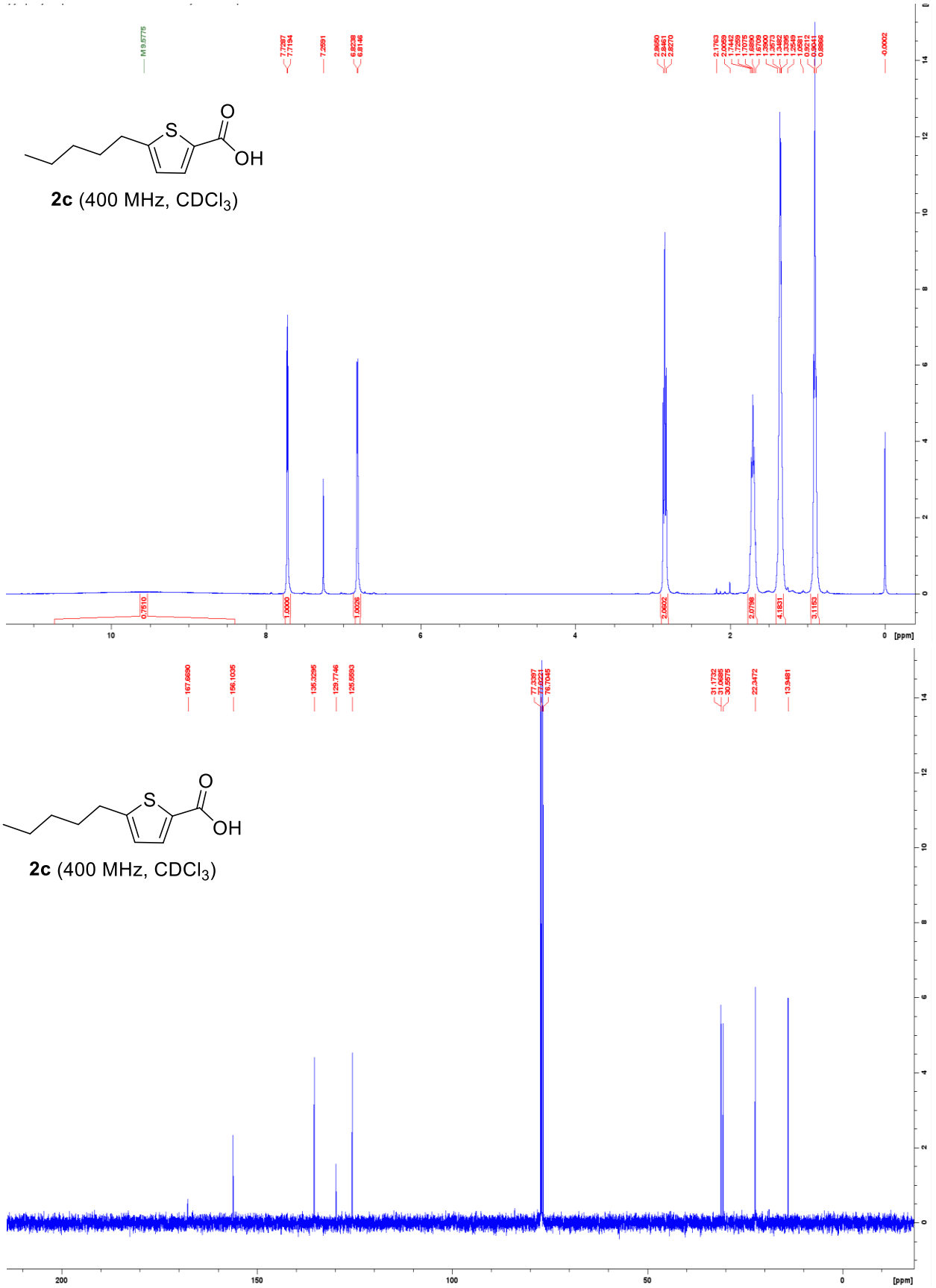
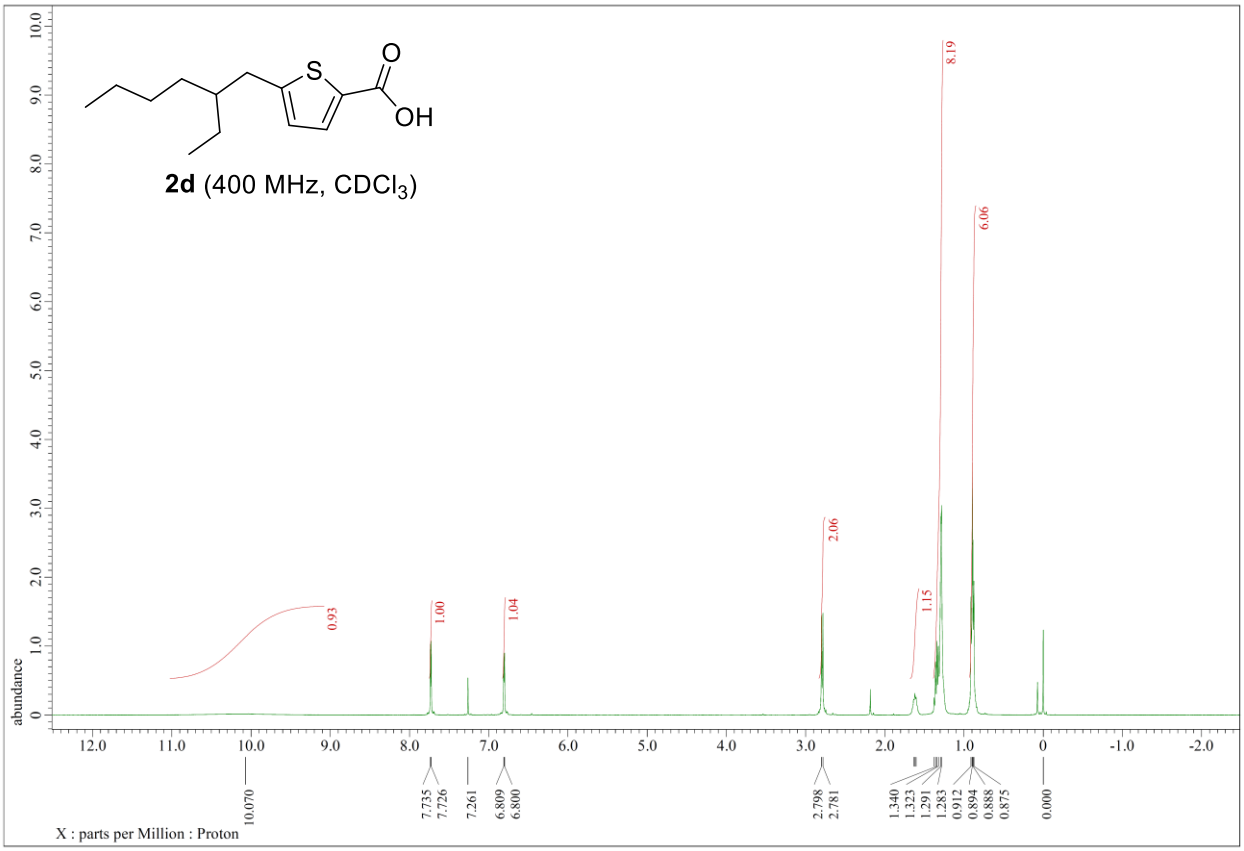


Figure S4 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2d**



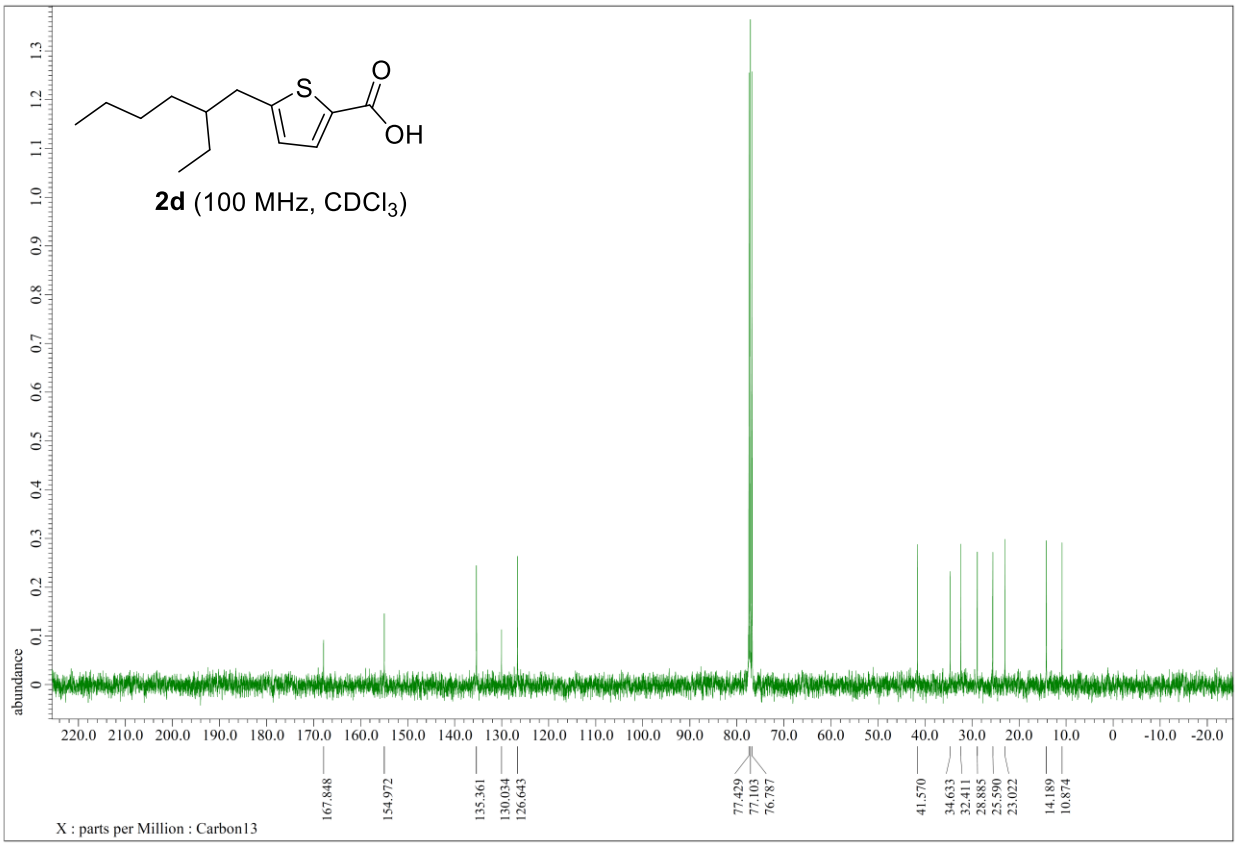
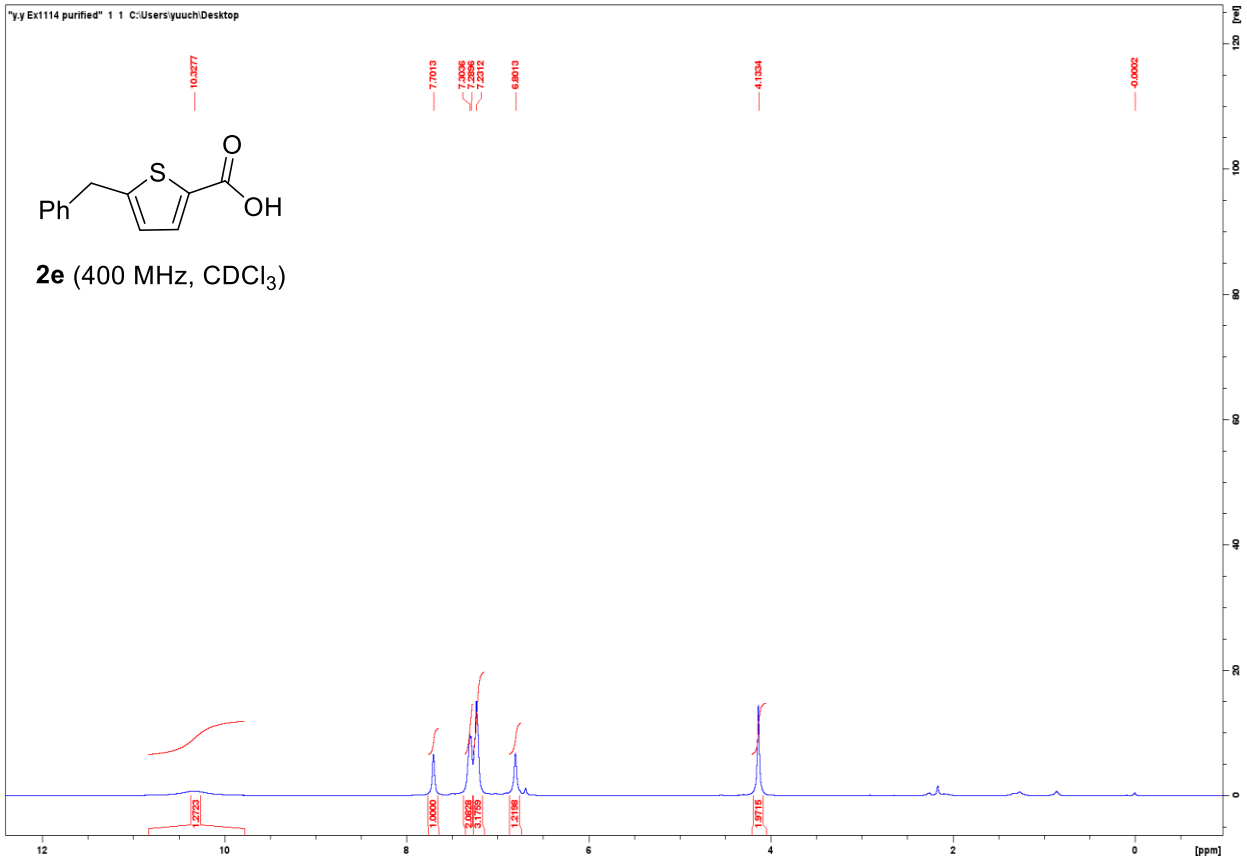


Figure S5 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2e**



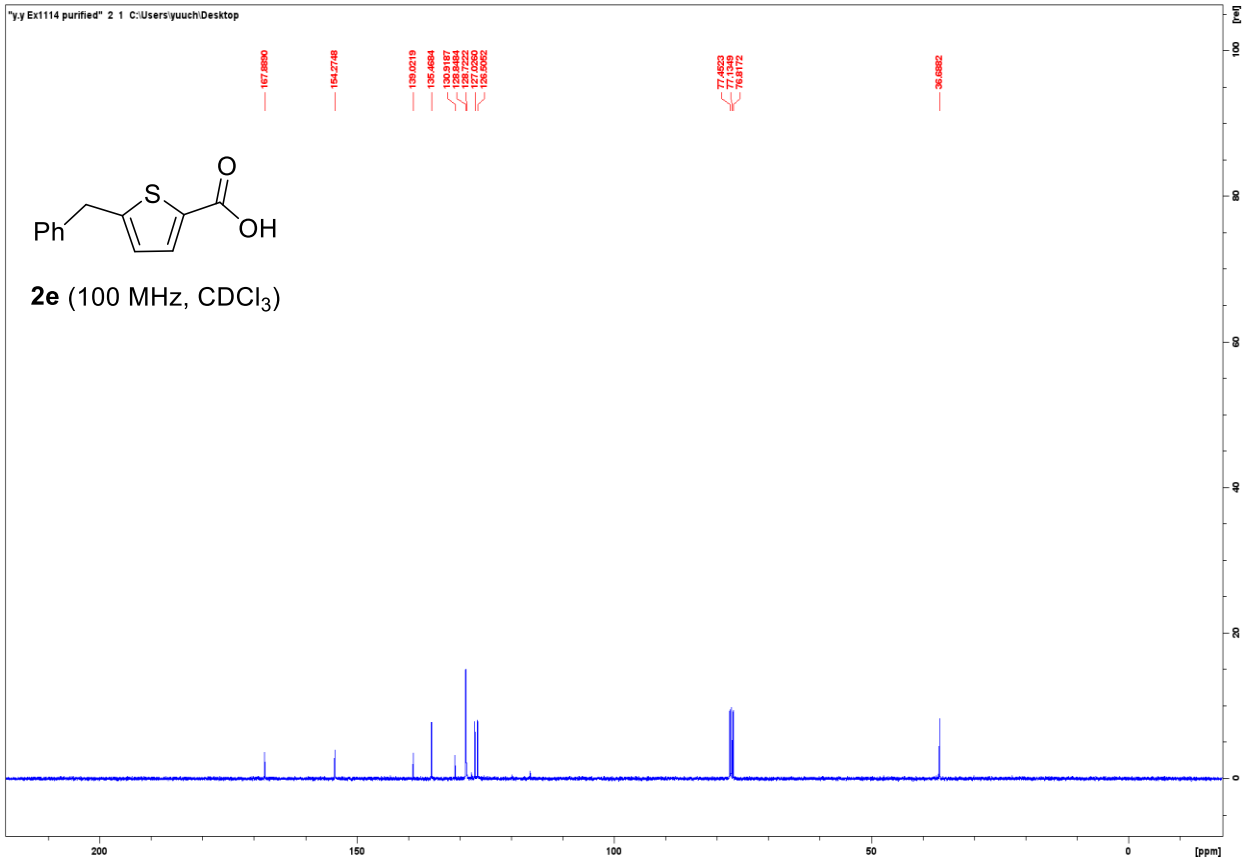
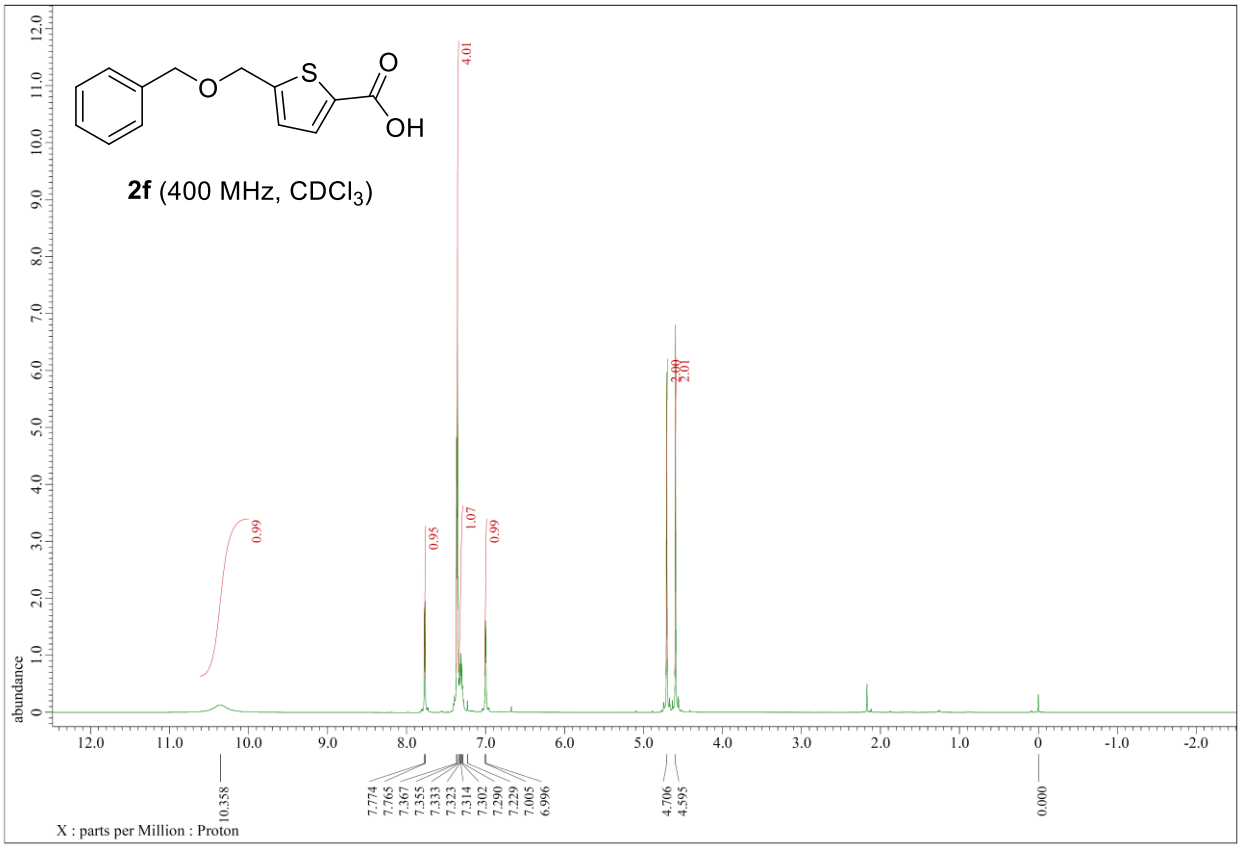


Figure S6 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2f**



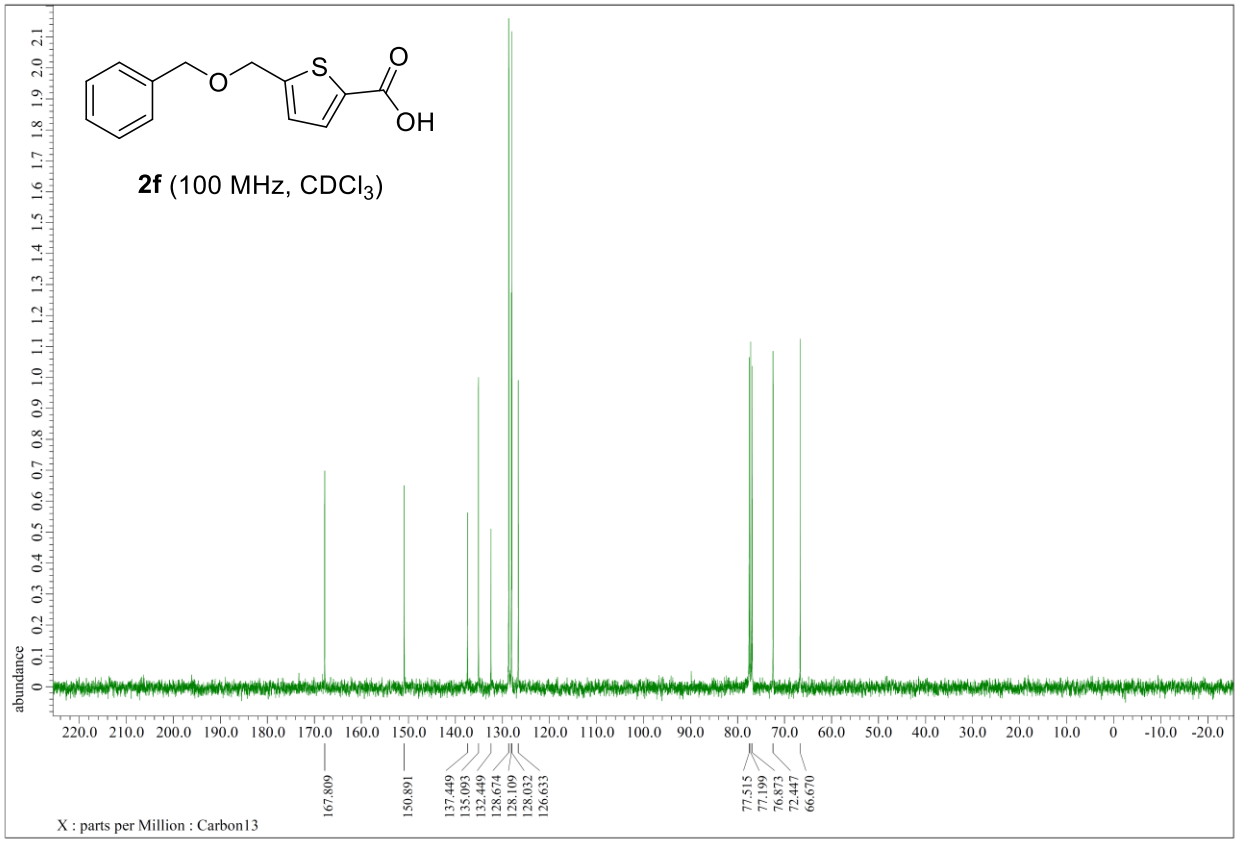
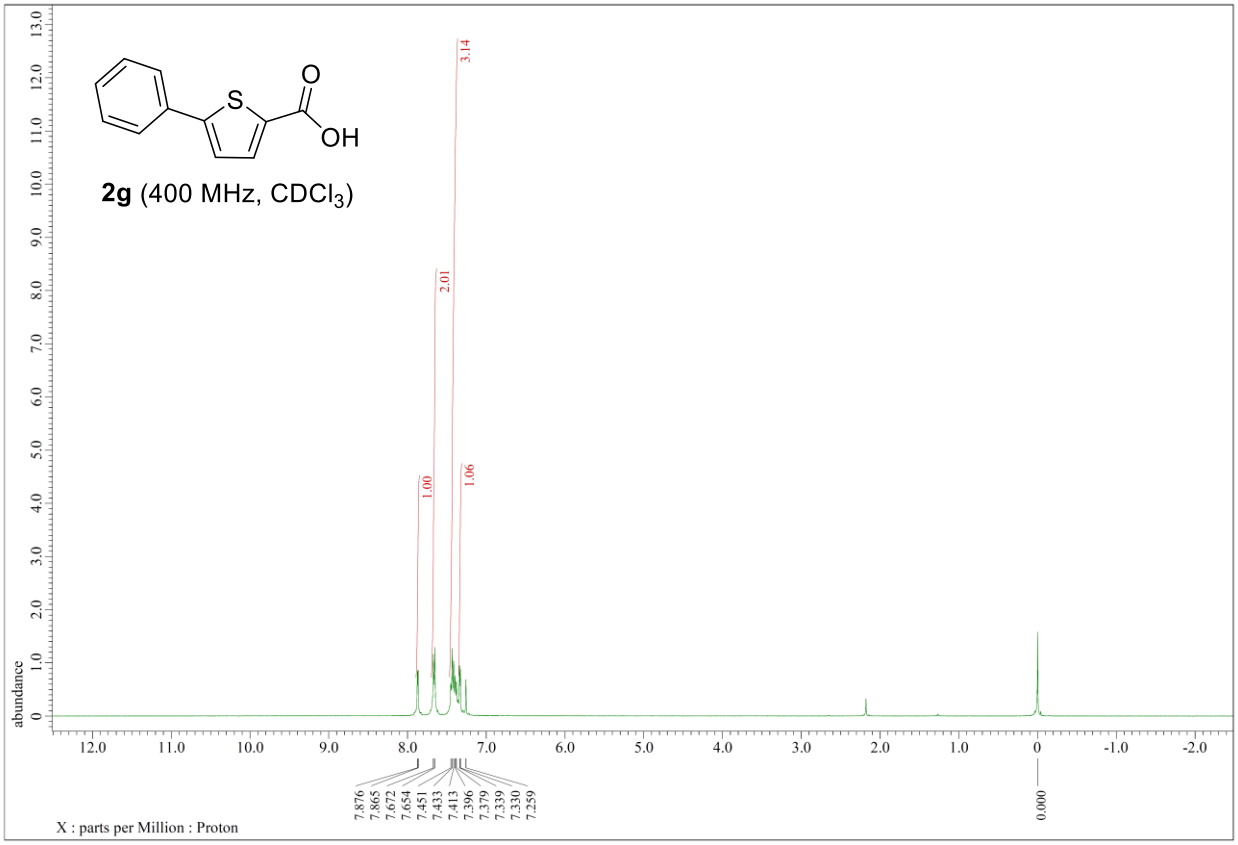


Figure S7 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2g**



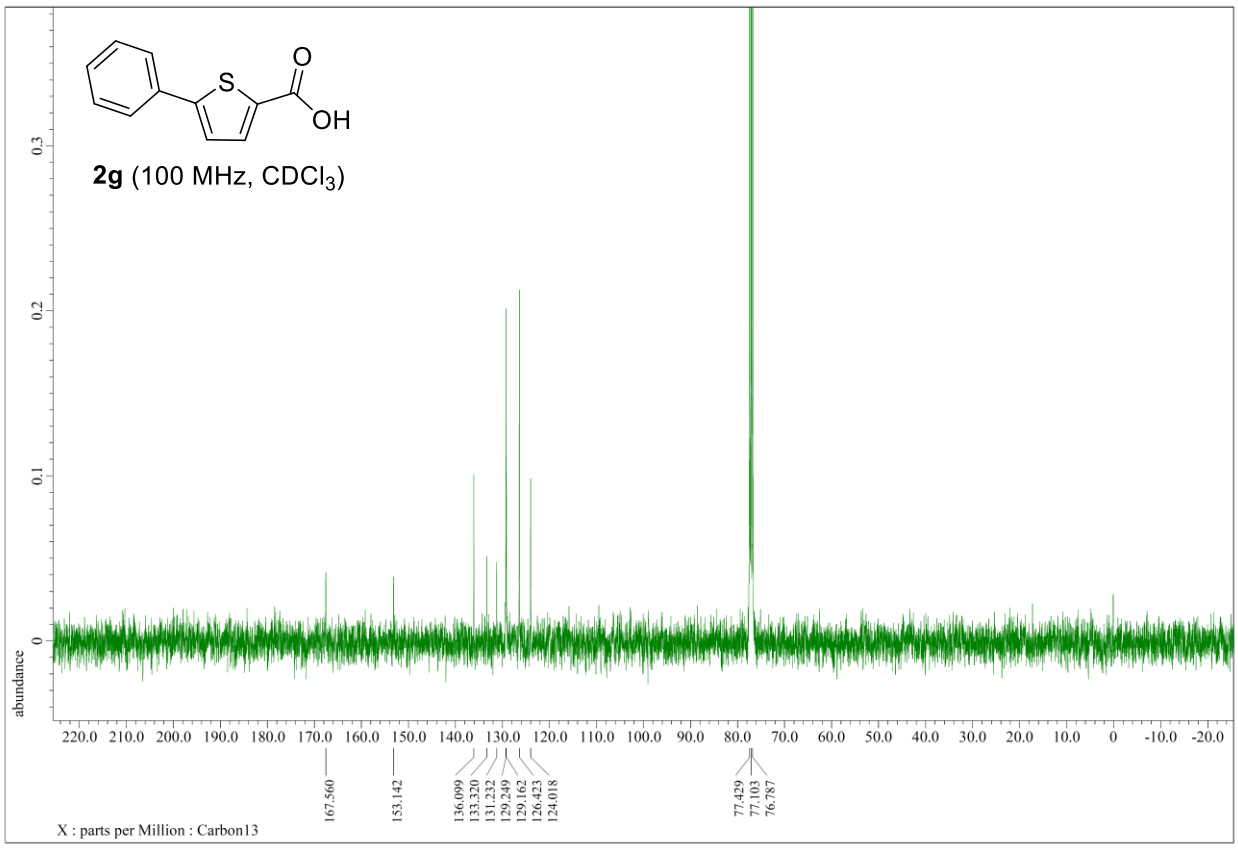
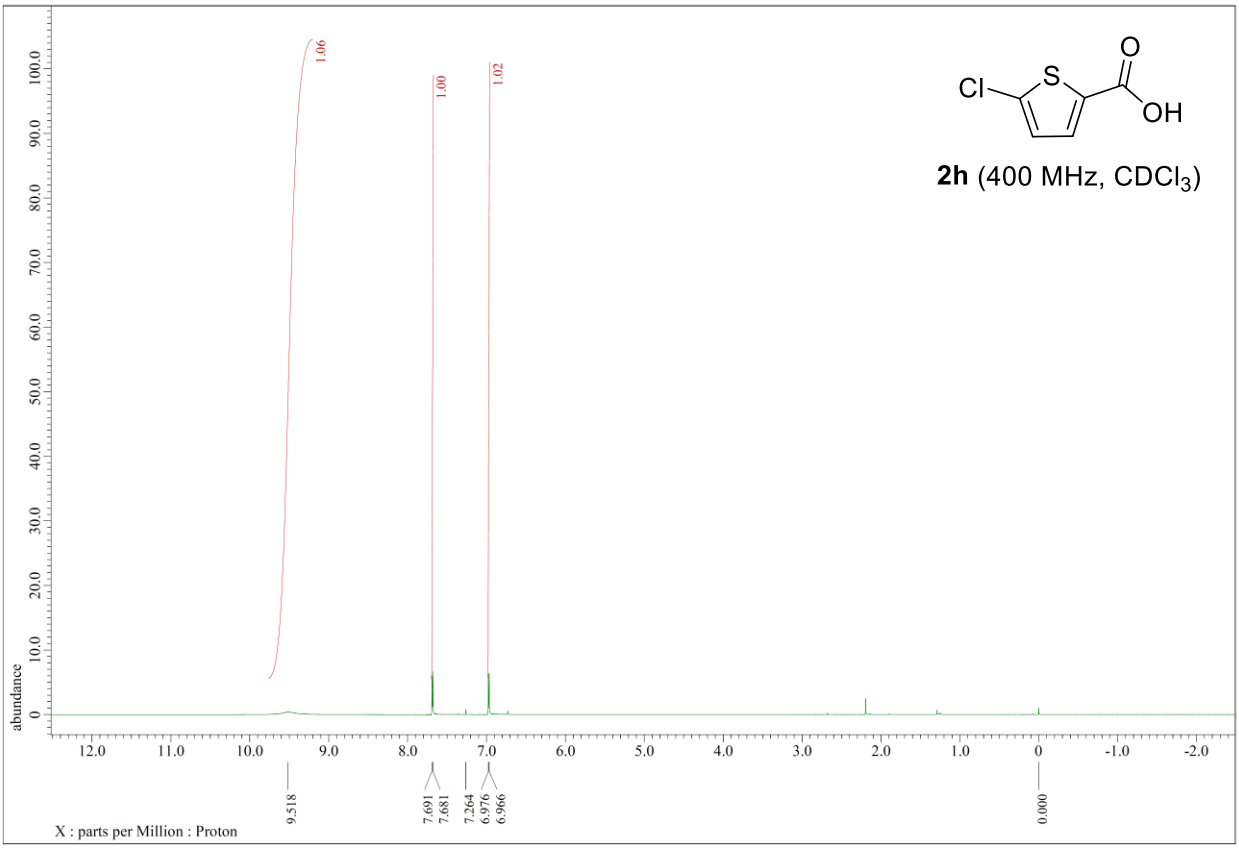


Figure S8 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2h**



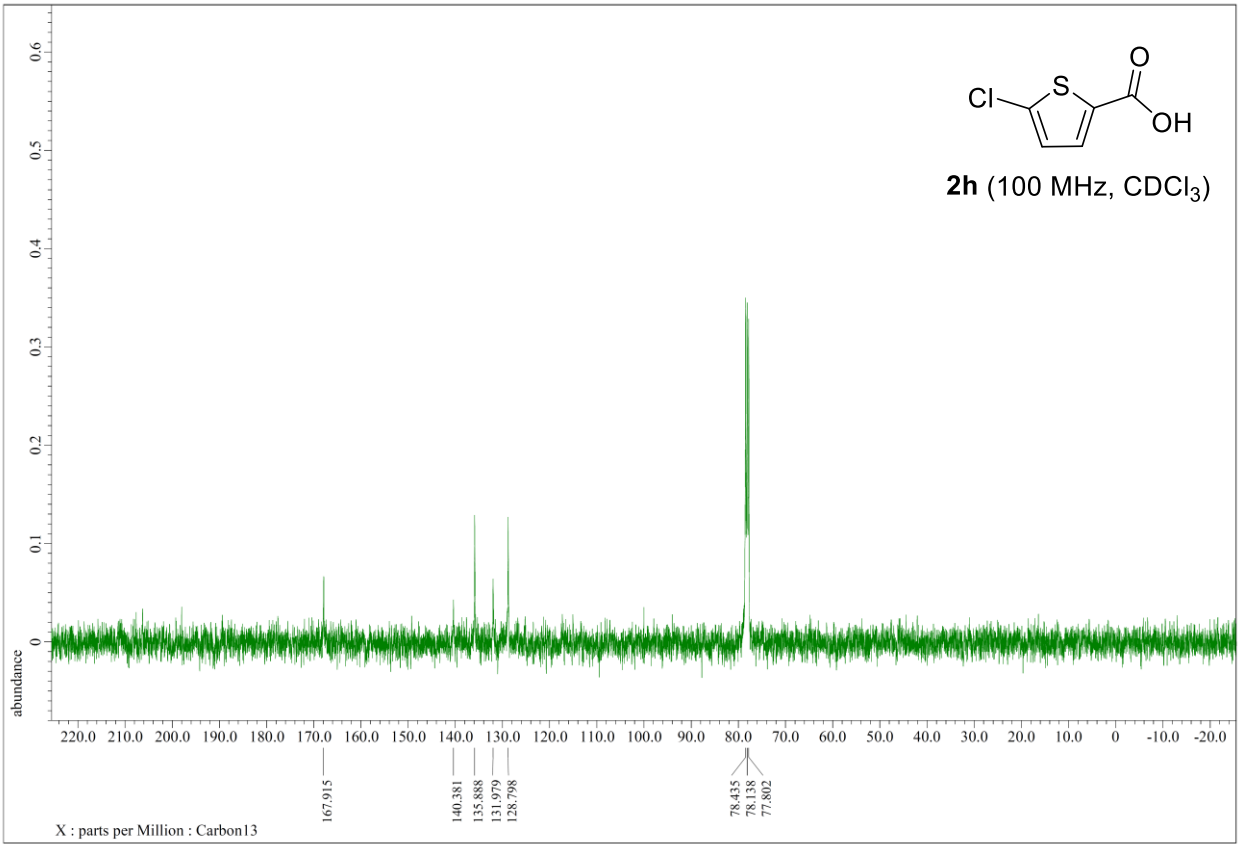
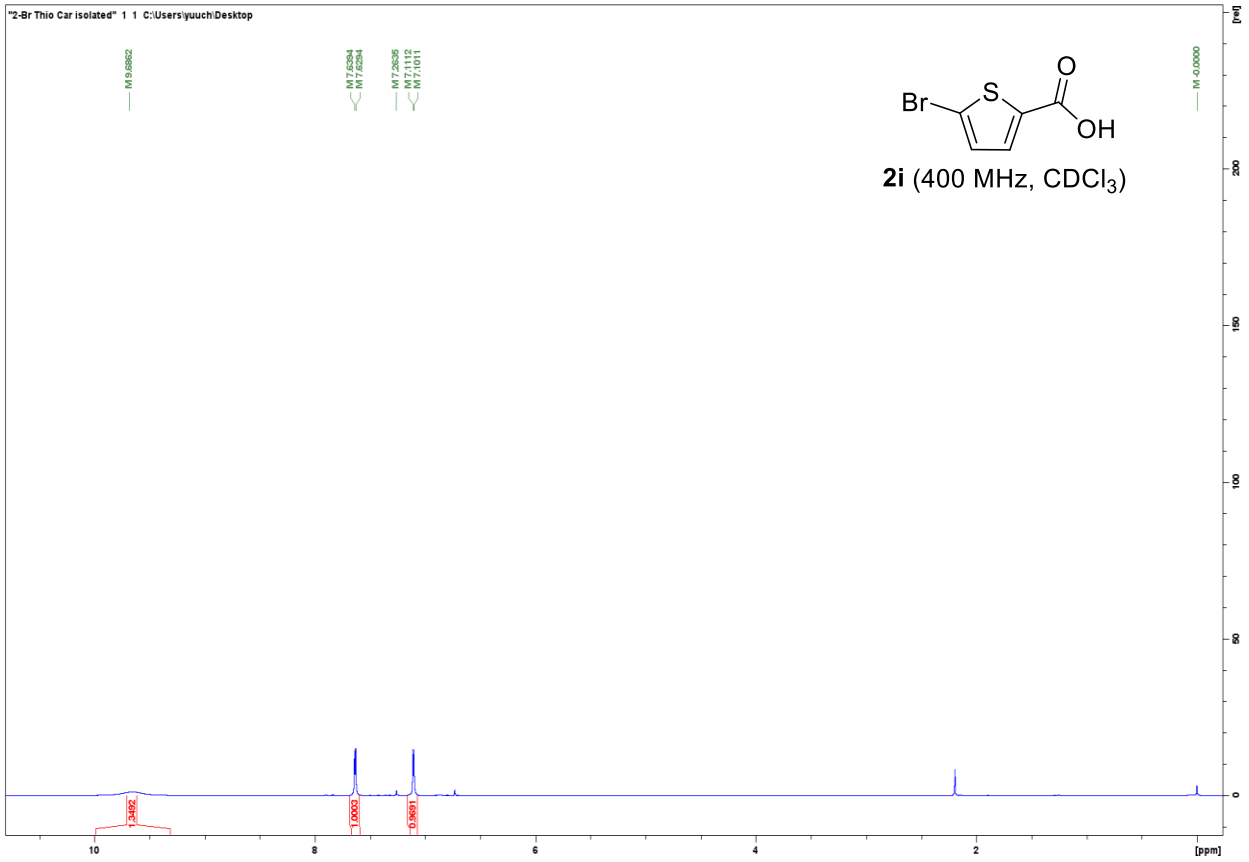


Figure S9 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2i**



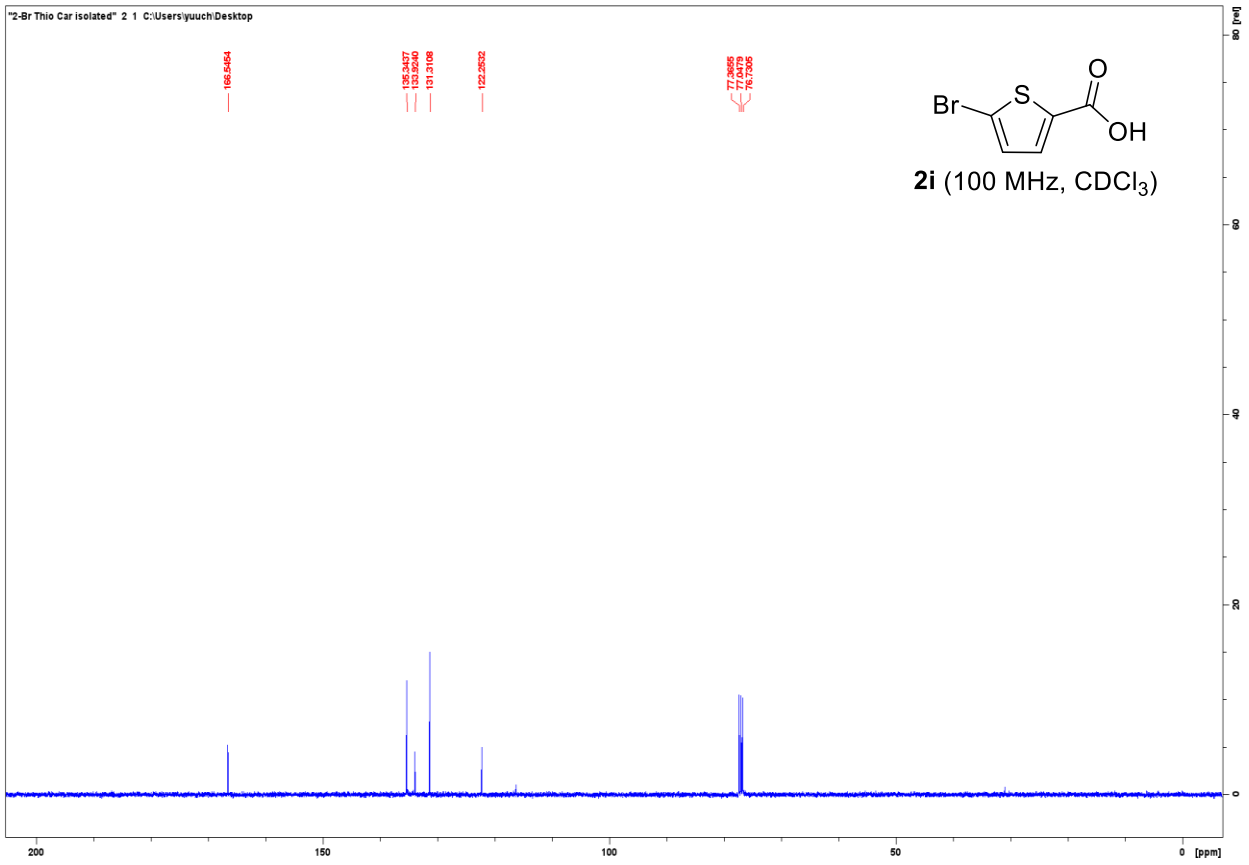
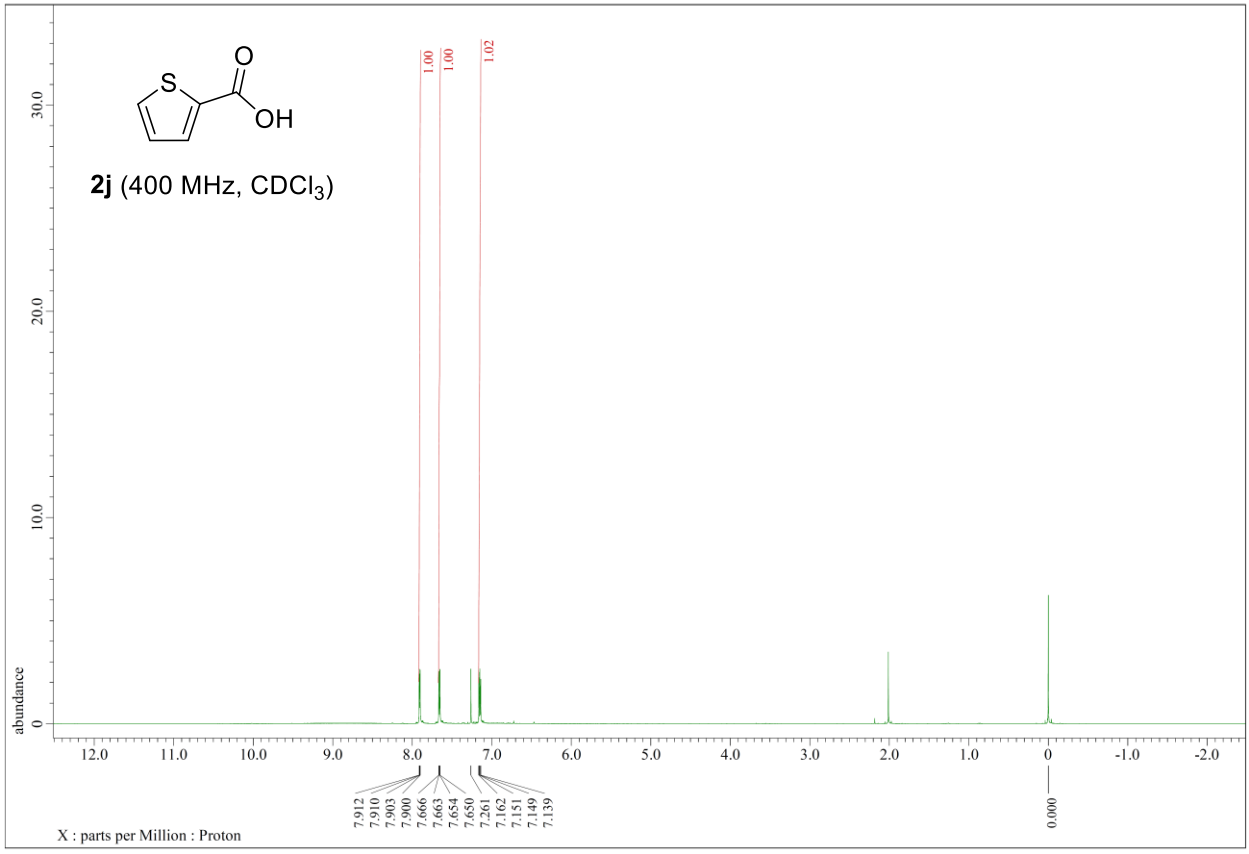


Figure S10 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2j**



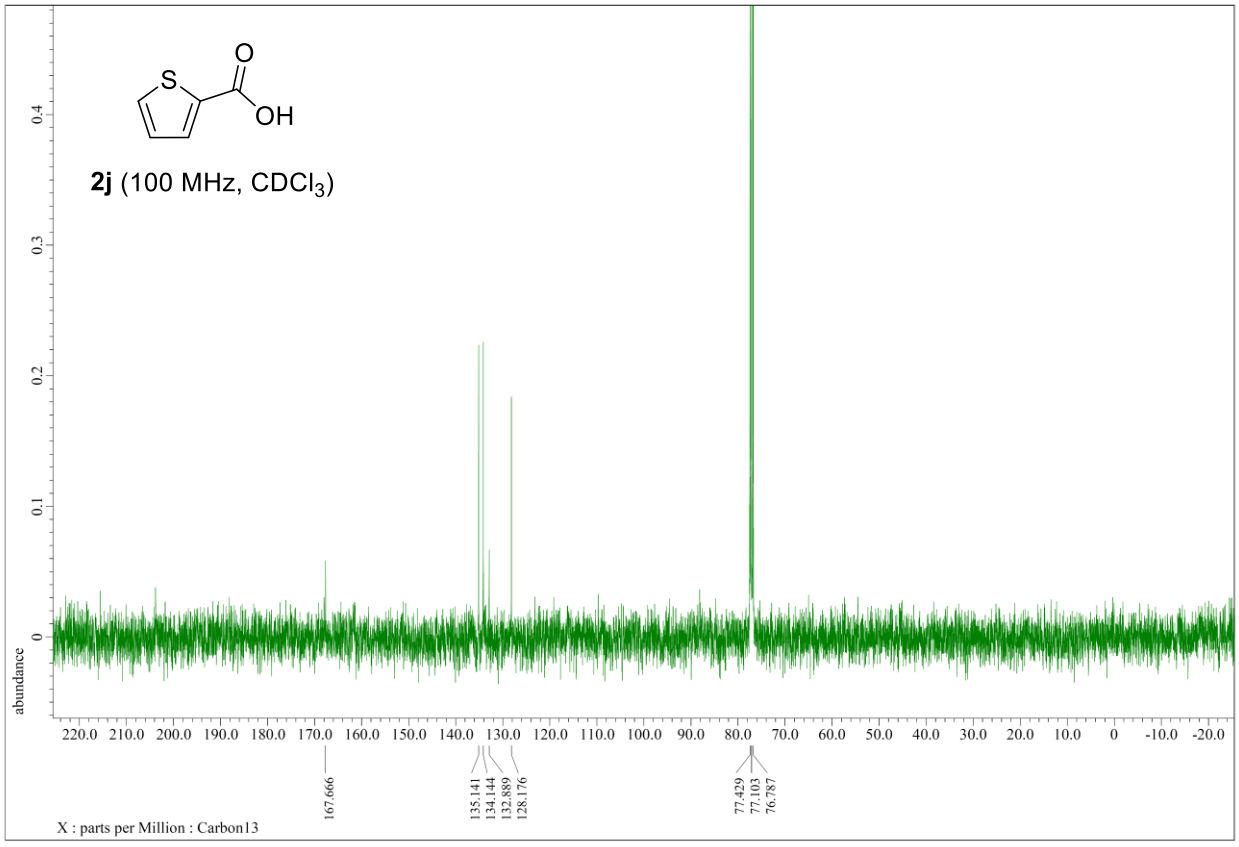
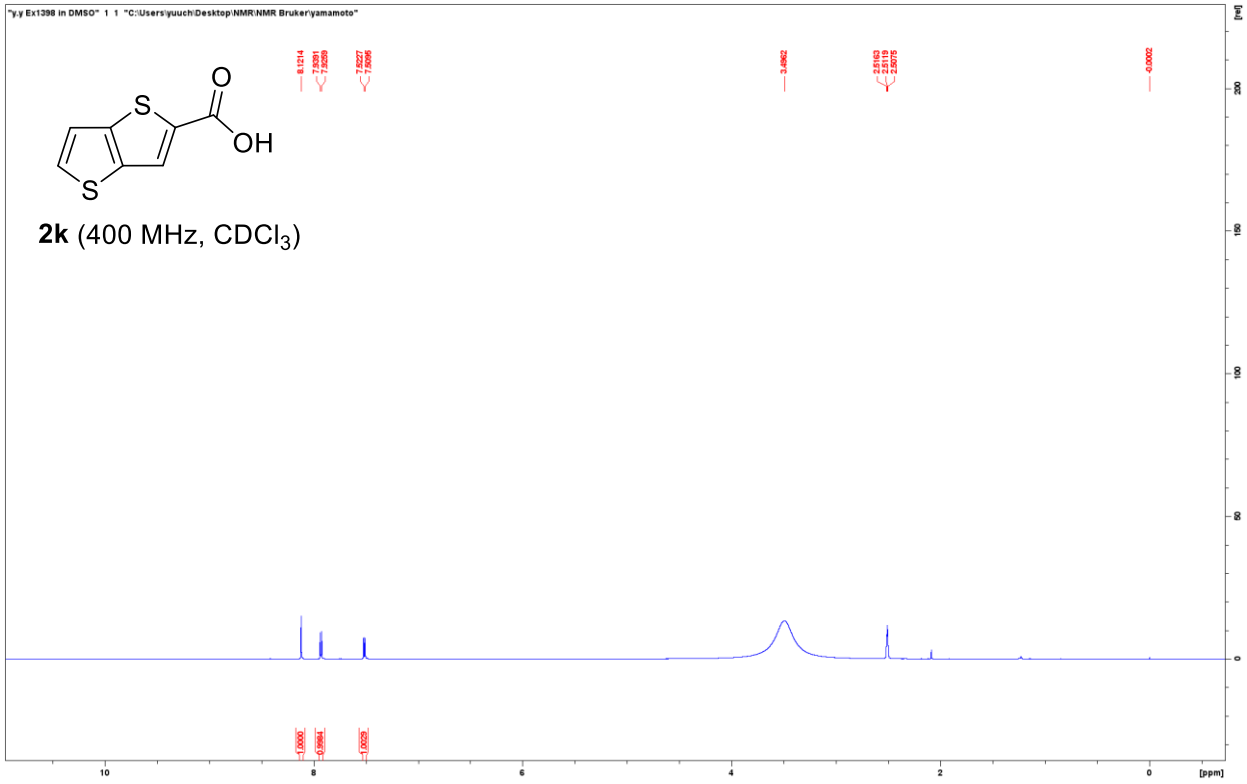


Figure S11 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2k**



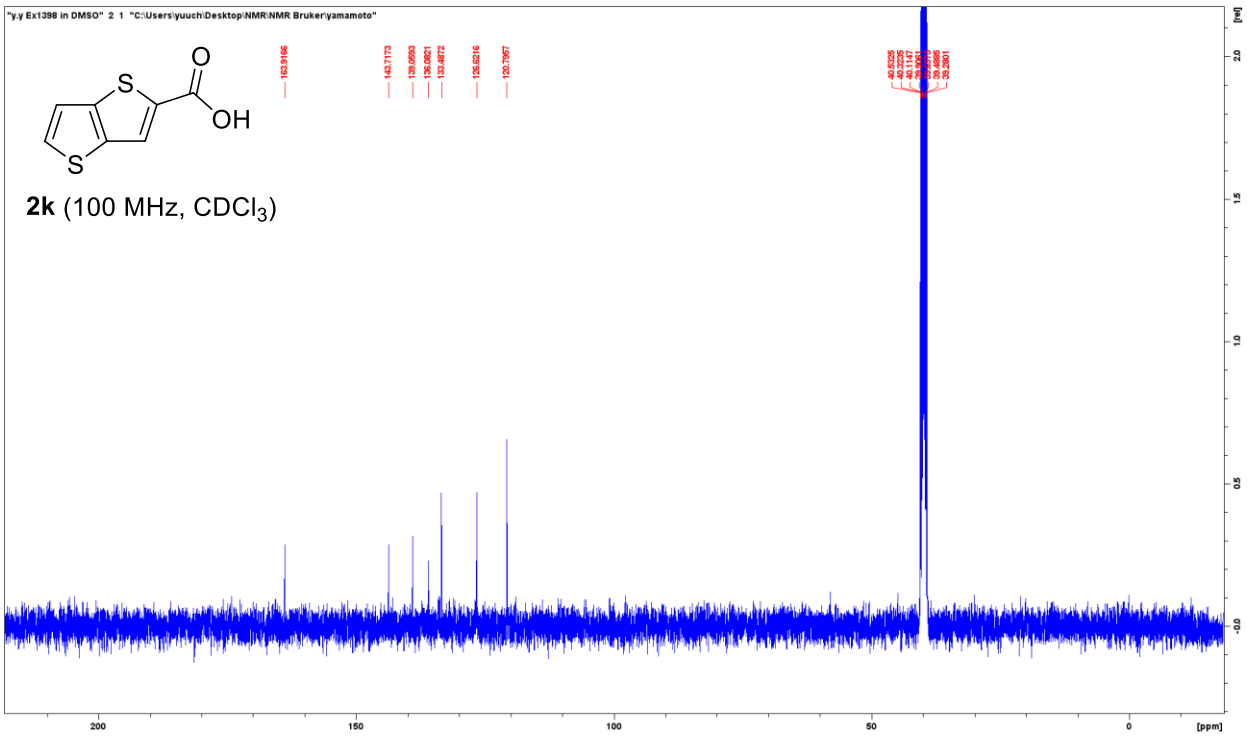


Figure S12 The copy of ^{1}H NMR spectrum of **2l**

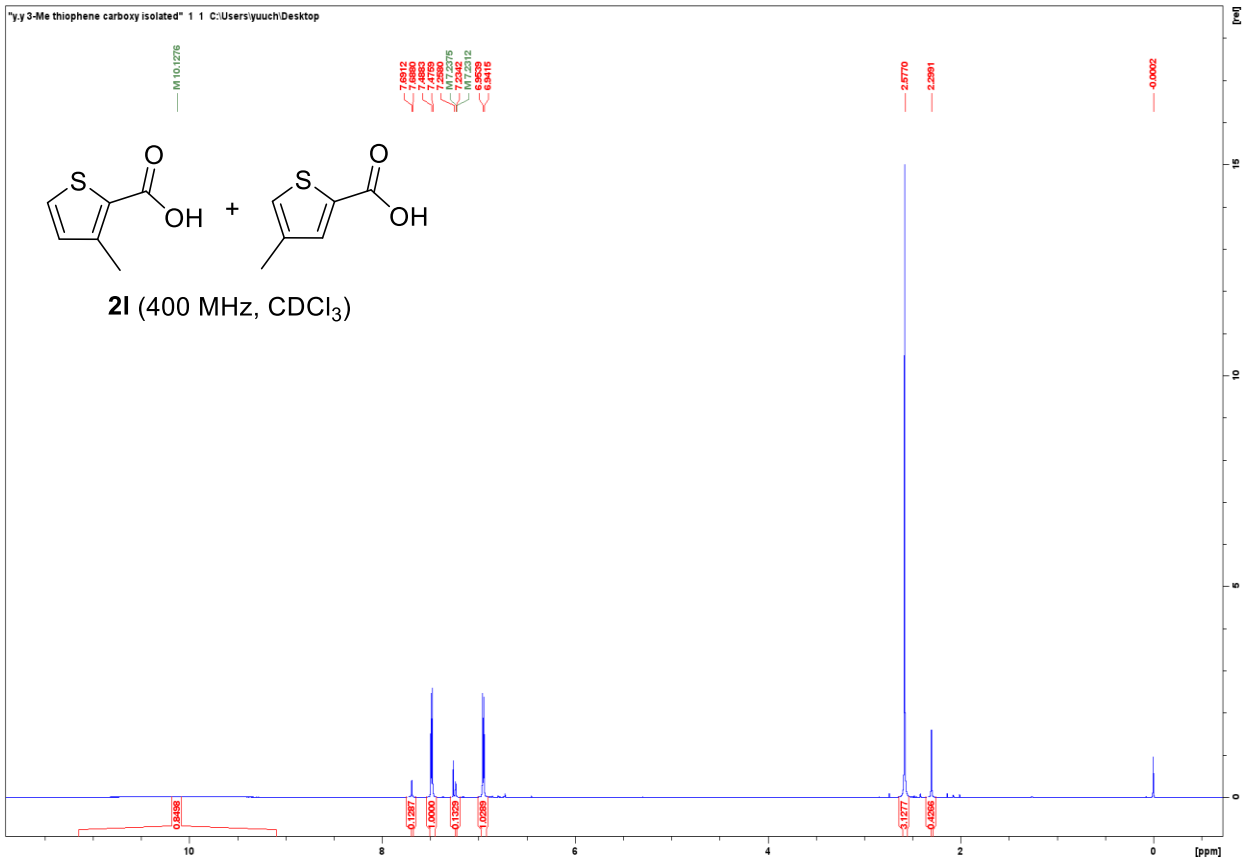


Figure S13 The copy of ^{1}H NMR spectrum of **2m**

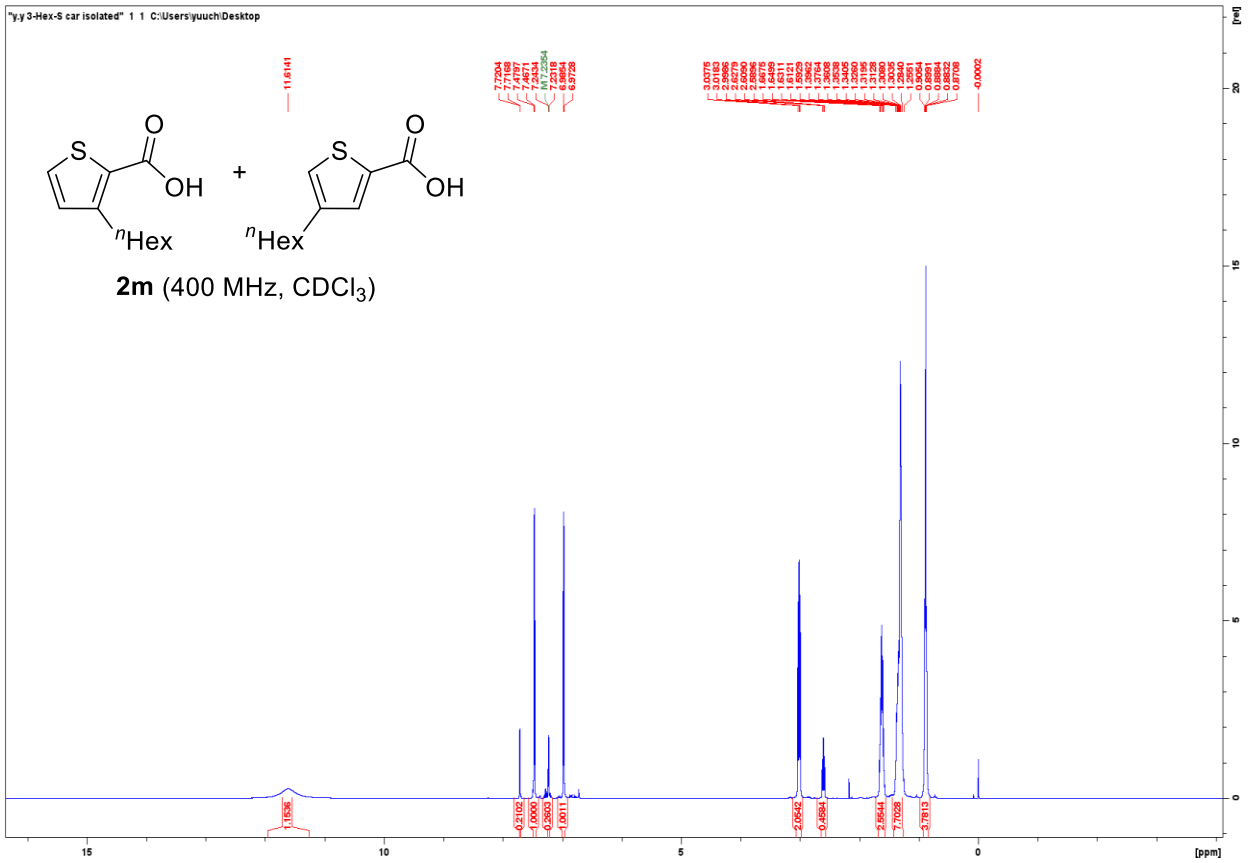


Figure S14 The copy of ^{1}H NMR spectrum of **2n**

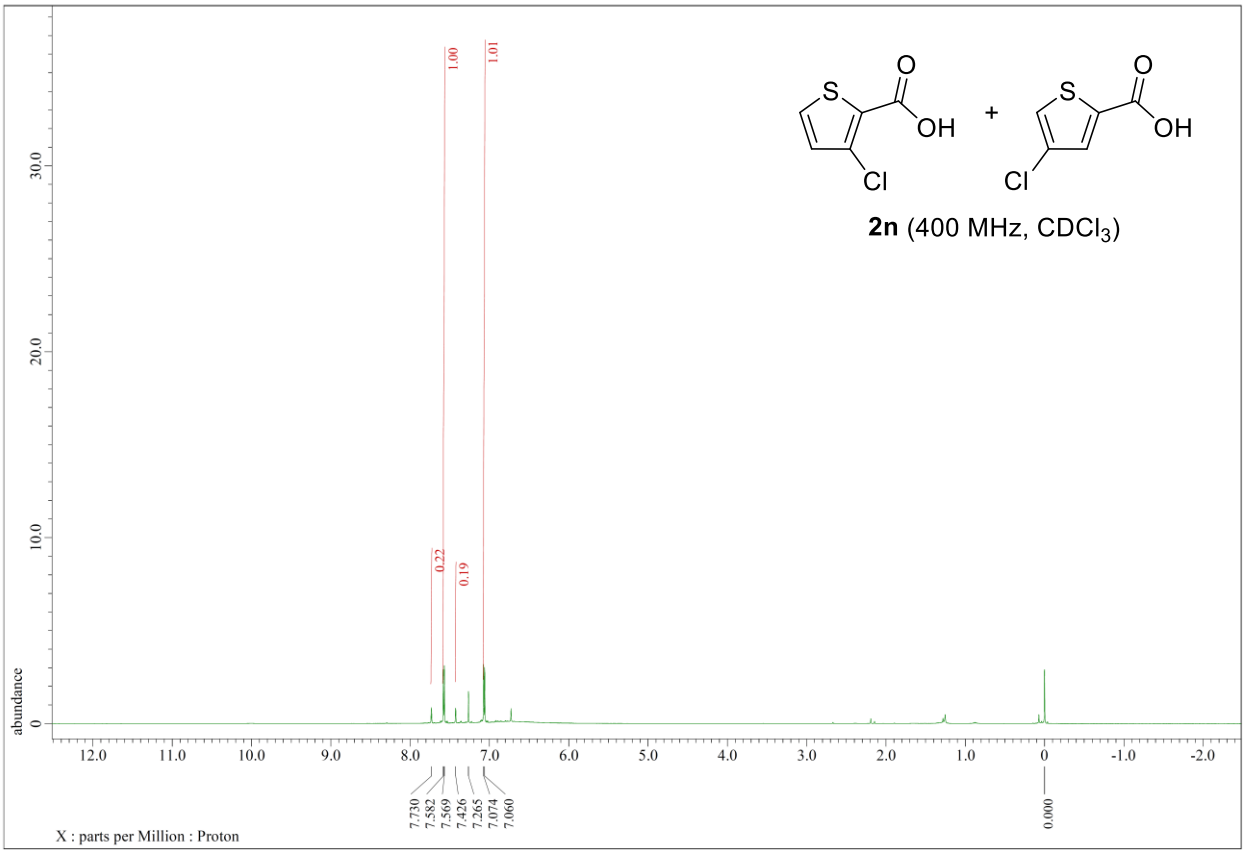


Figure S15 The copy of ^{1}H NMR spectrum of **2o**

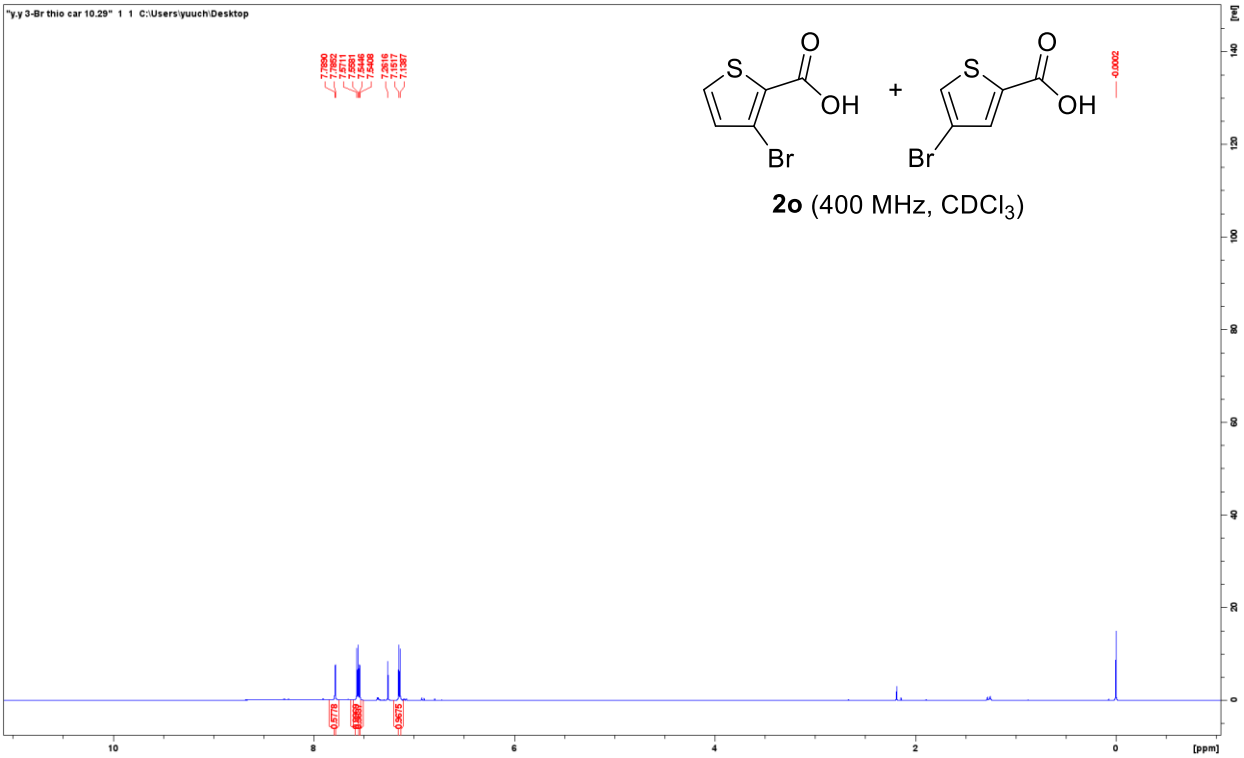
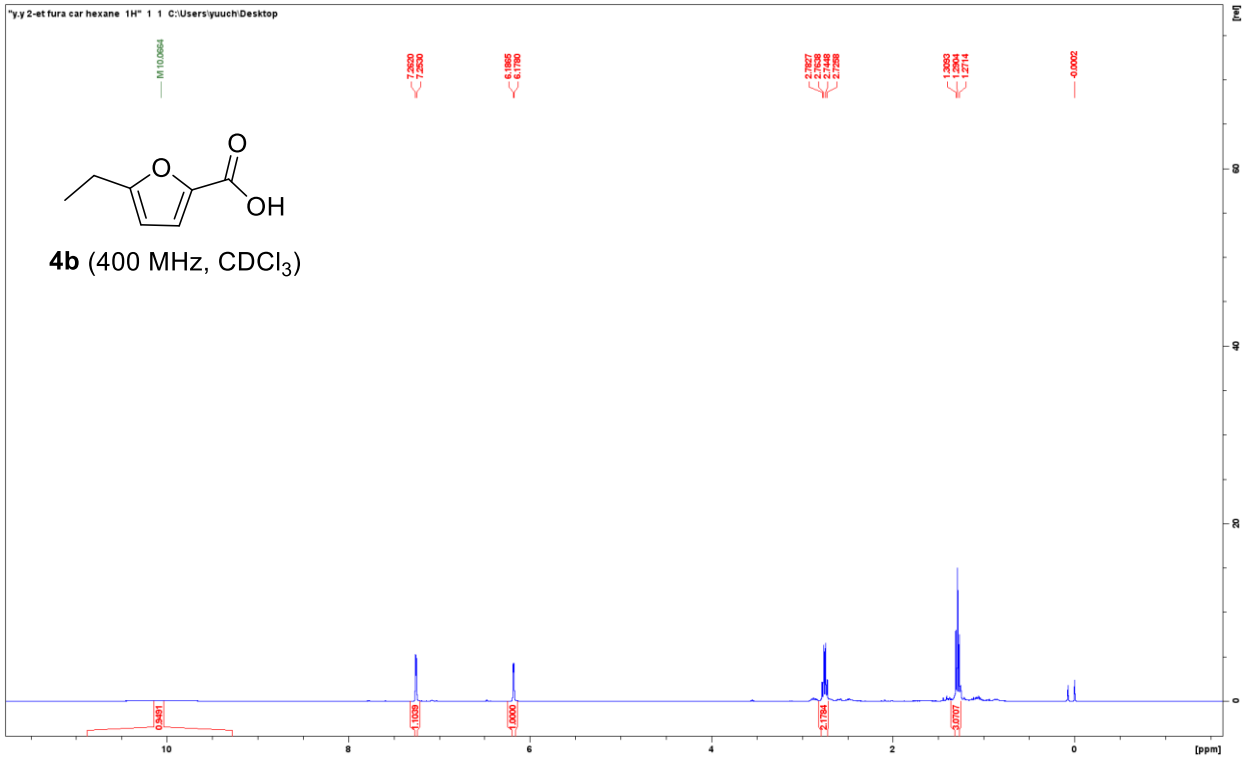


Figure S16 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4b**



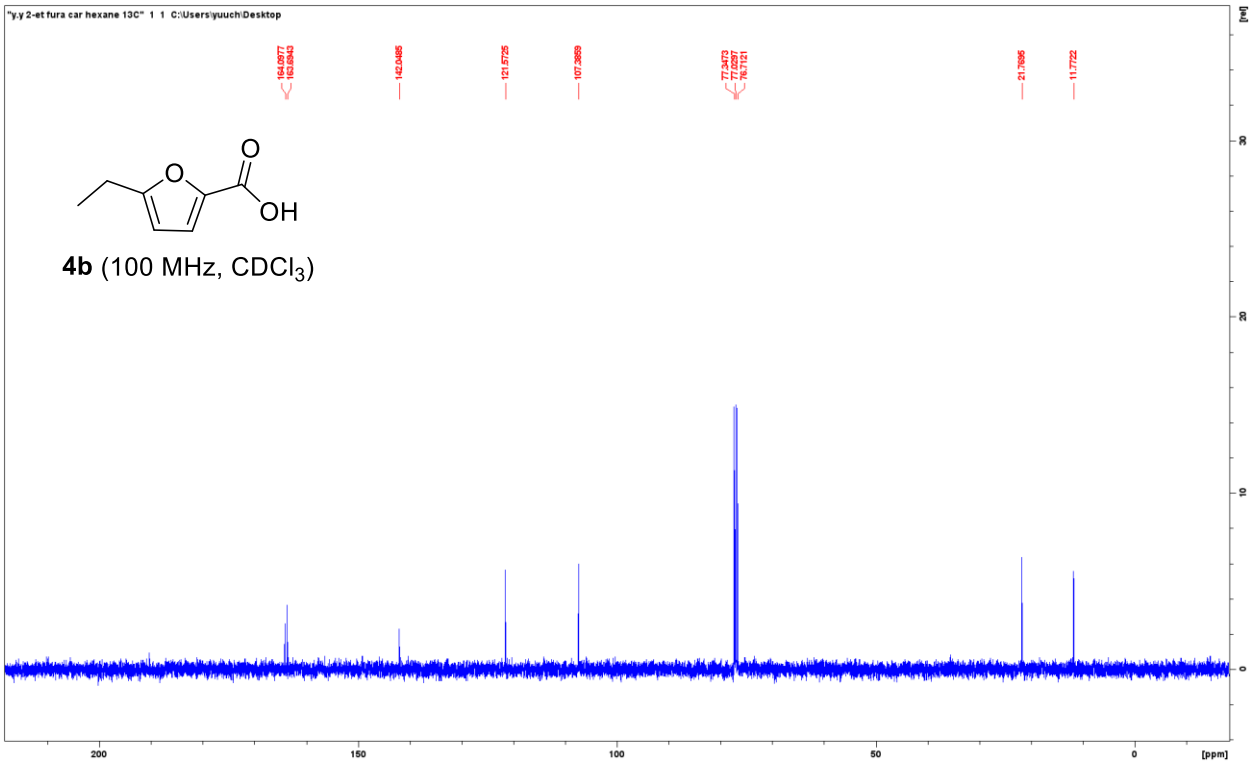
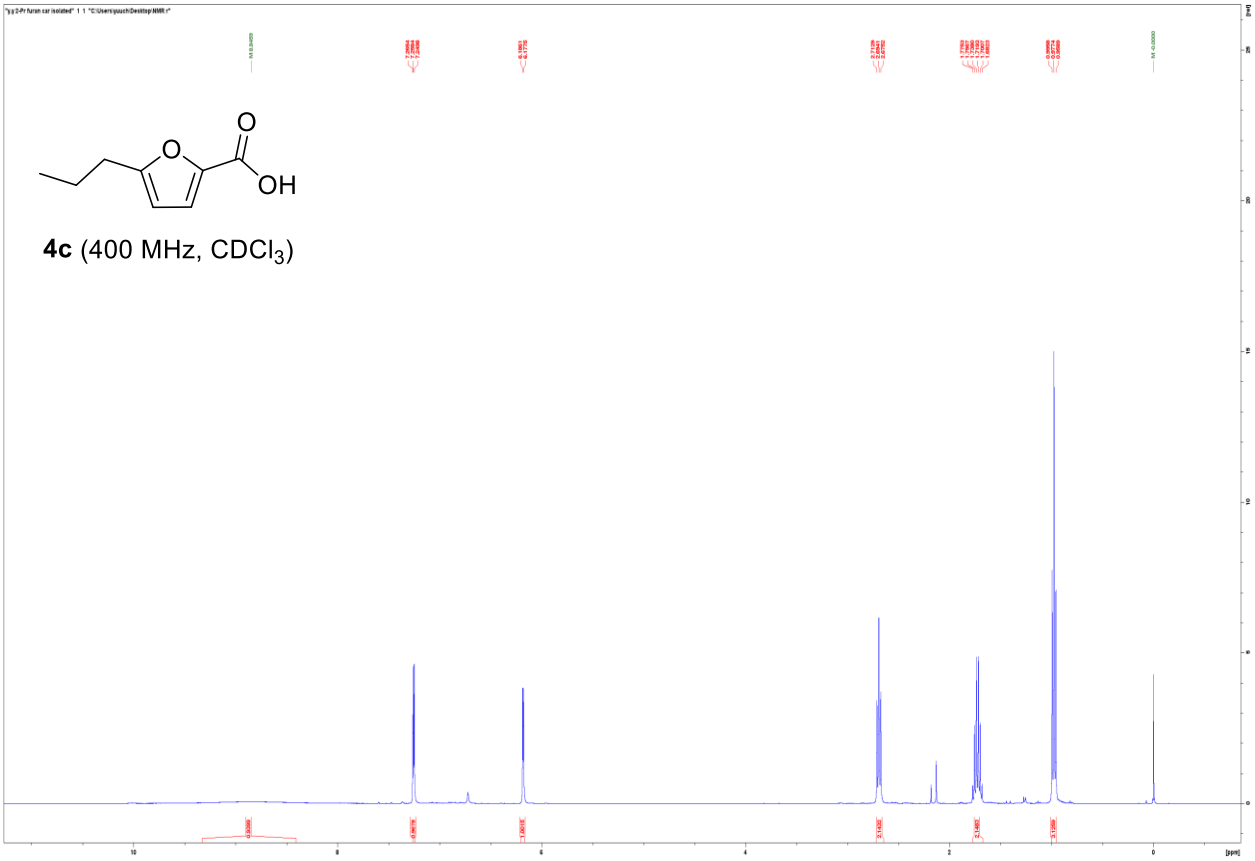


Figure S17 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4c**



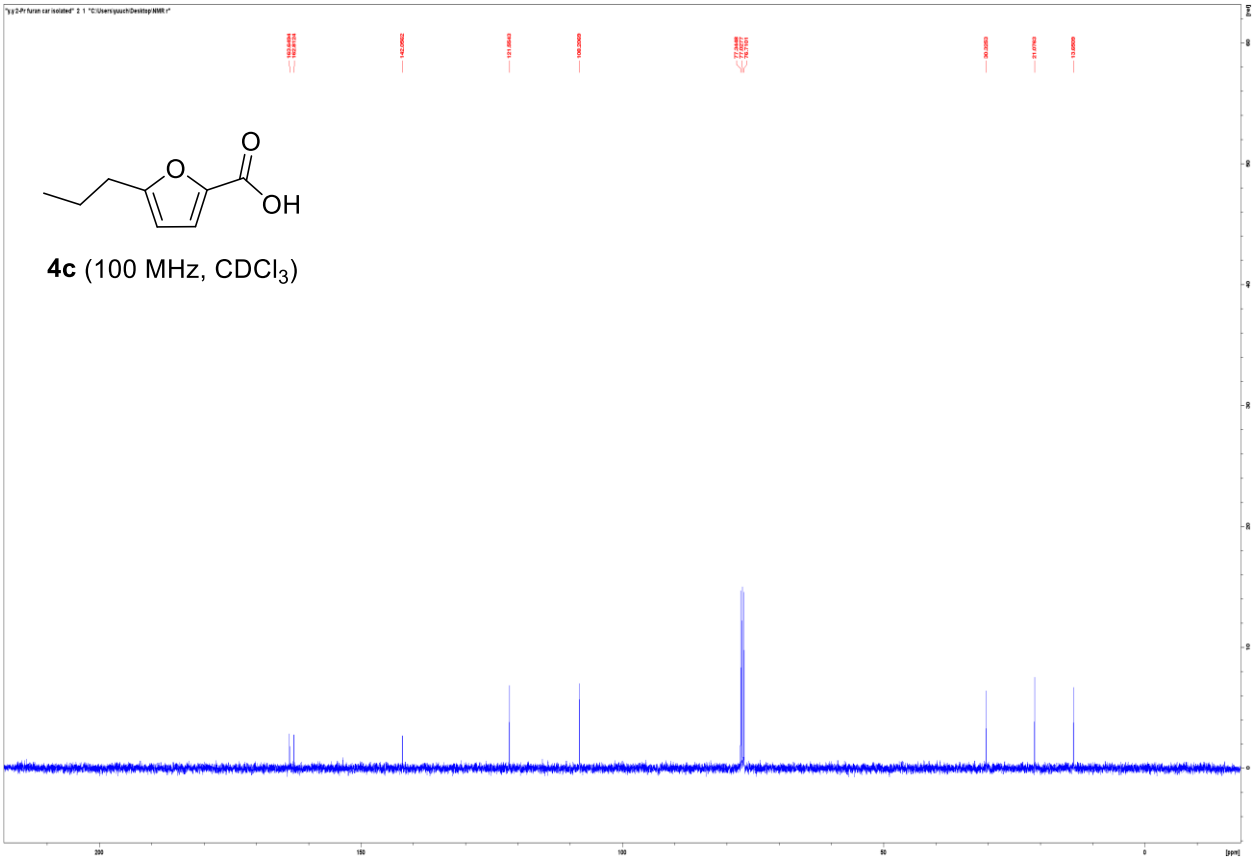
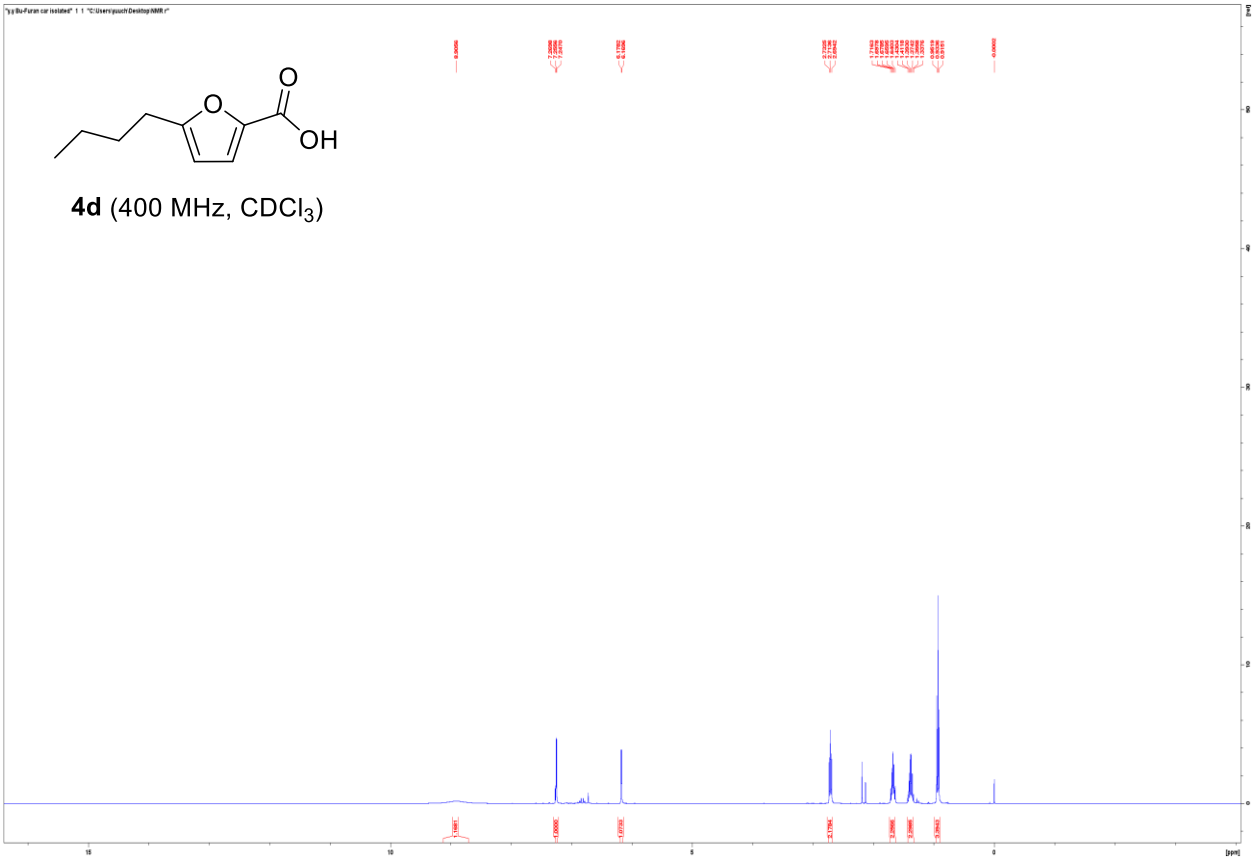


Figure S18 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4d**



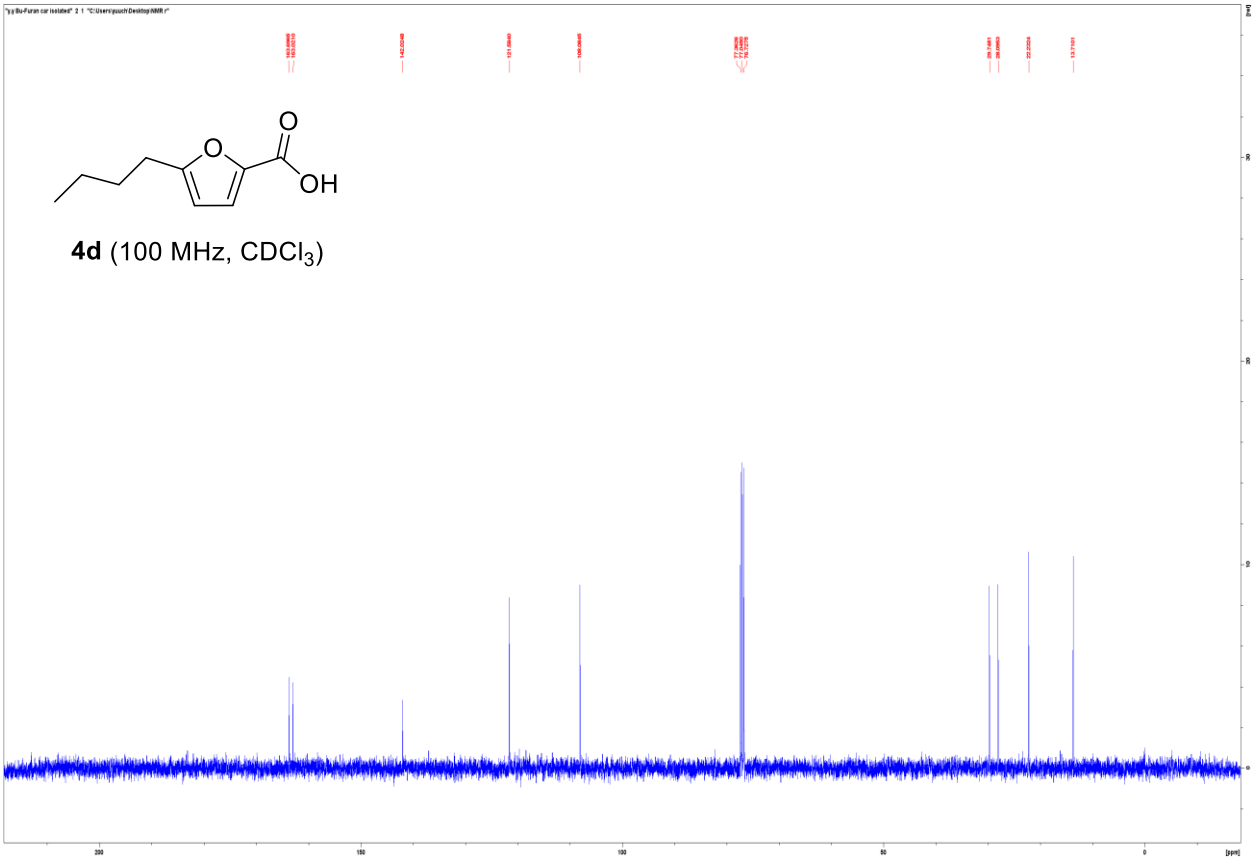
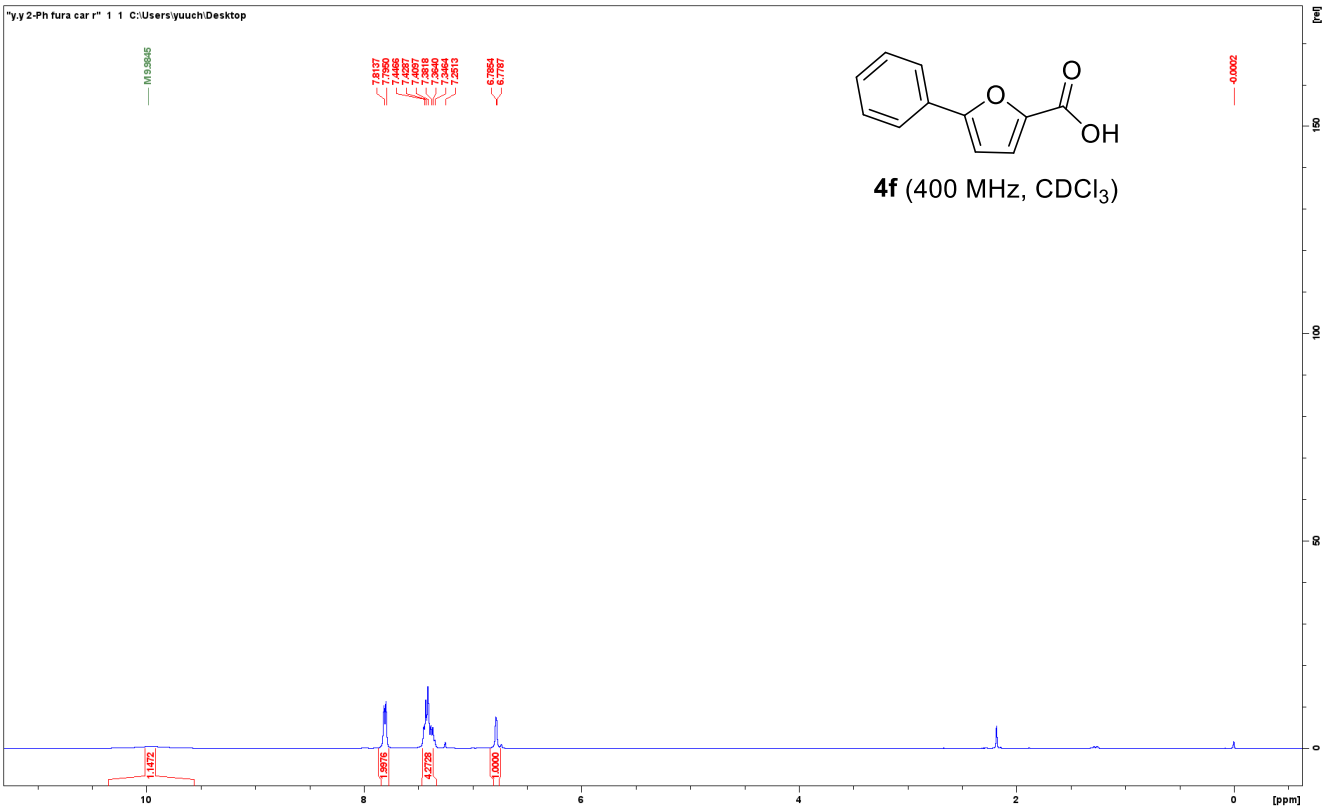


Figure S19 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4f**



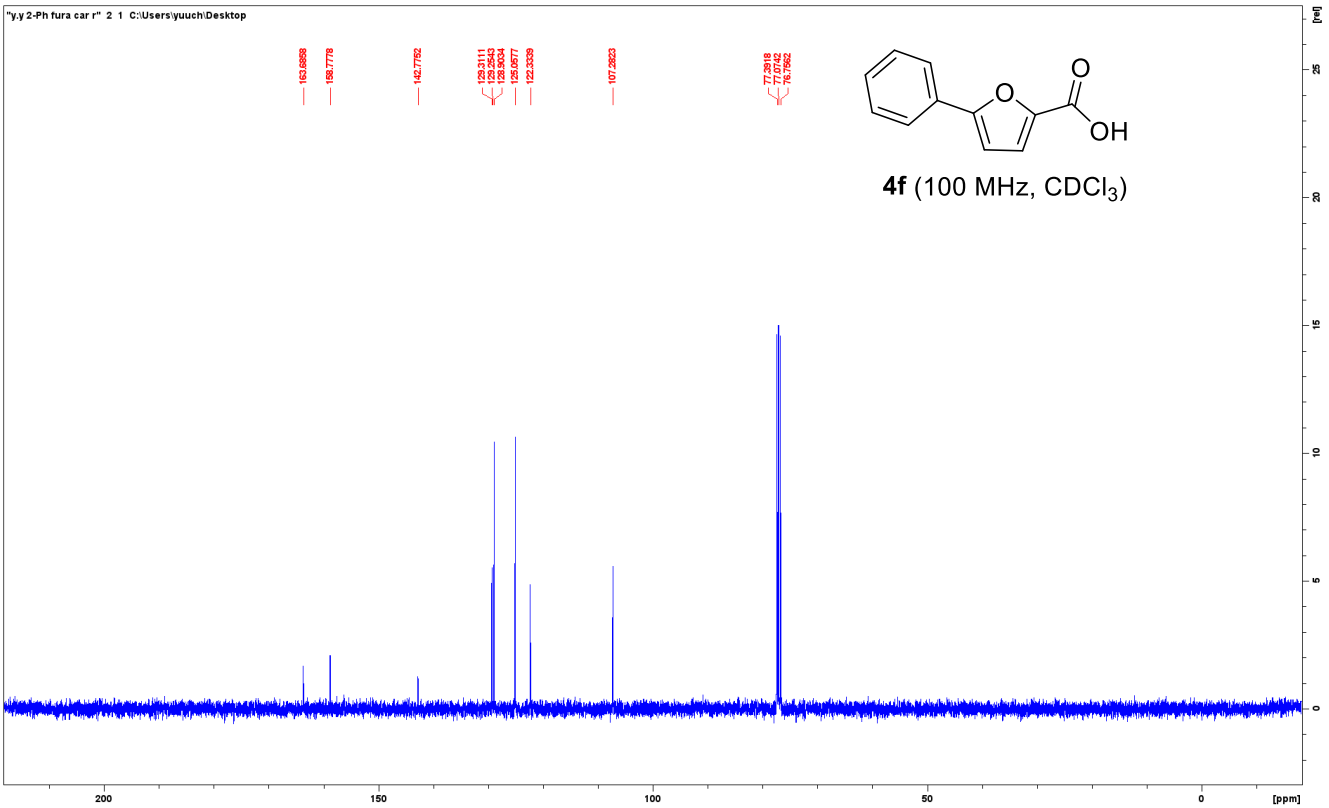
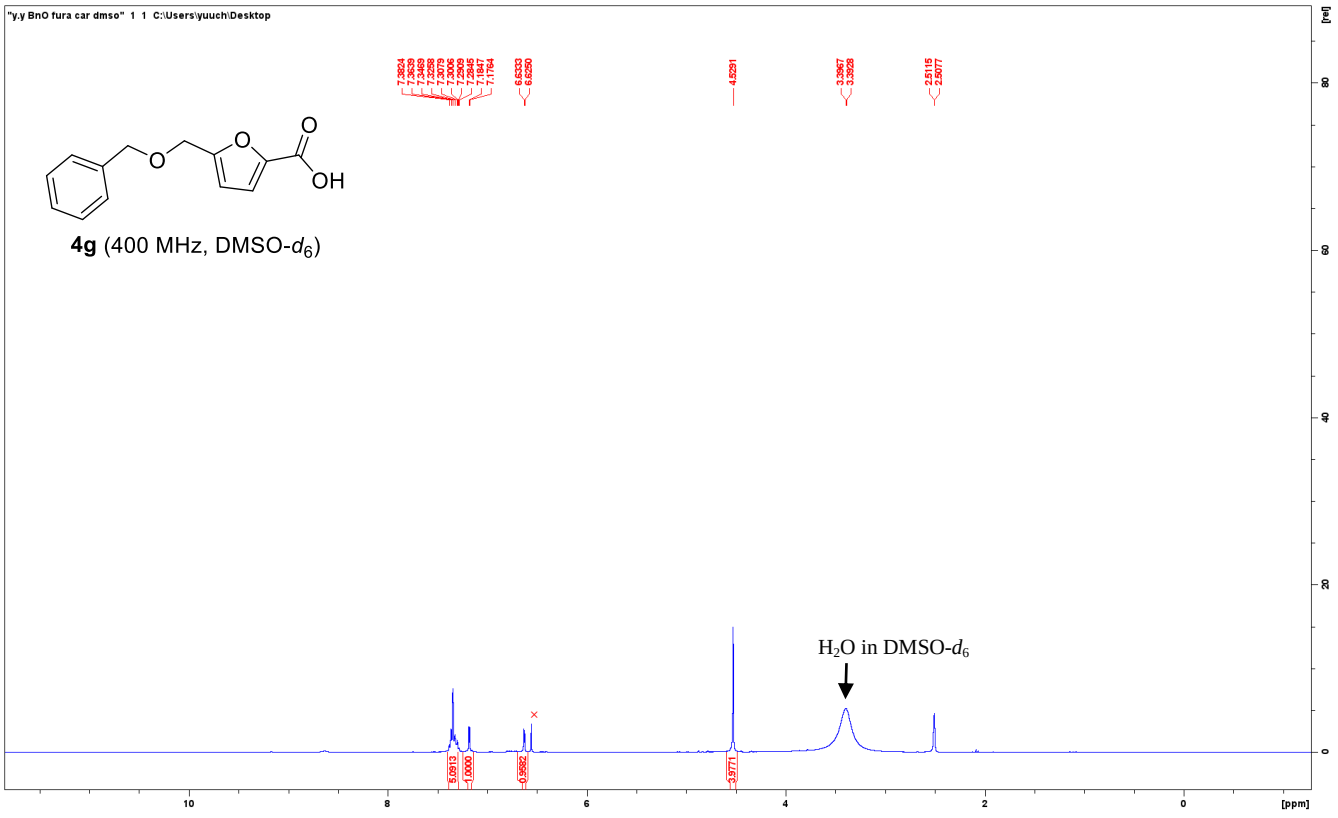


Figure S20 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4g**



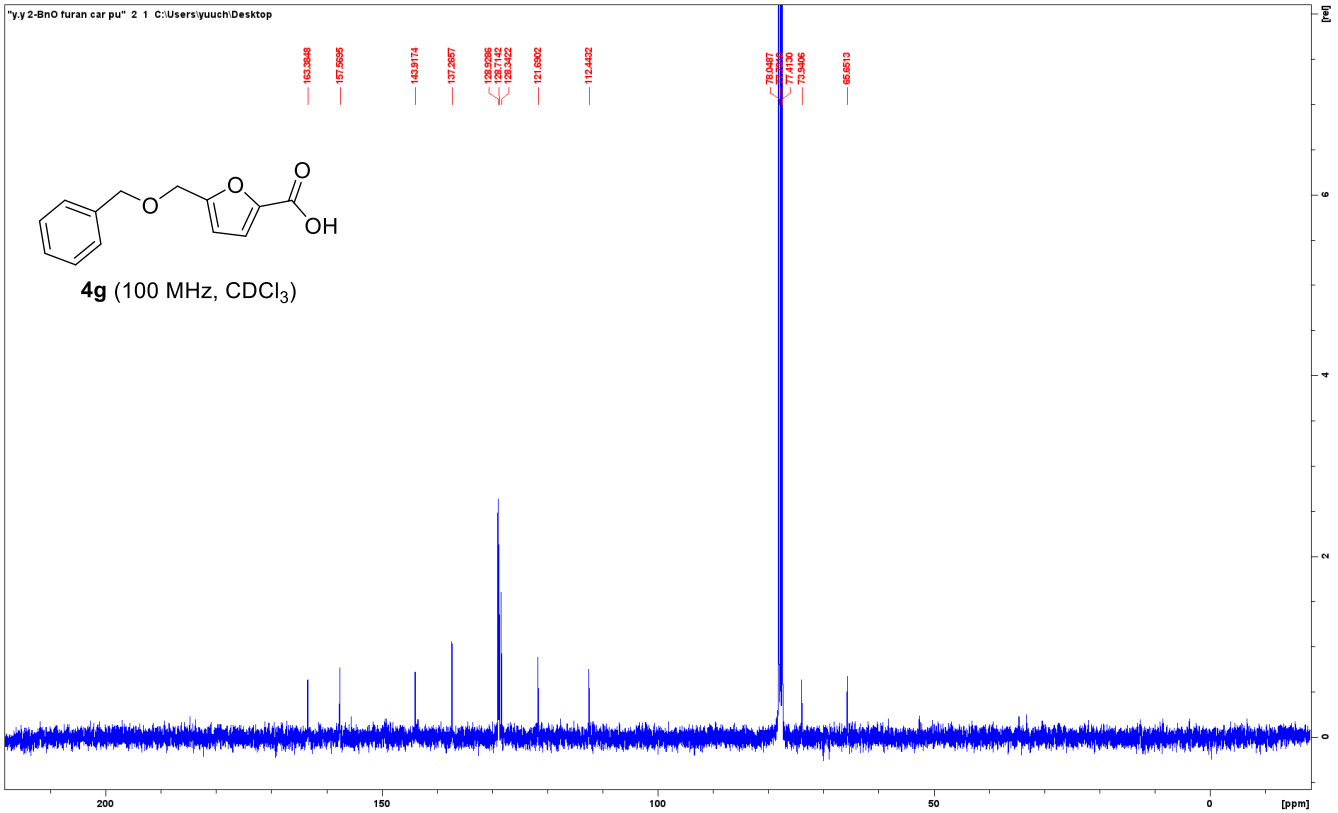
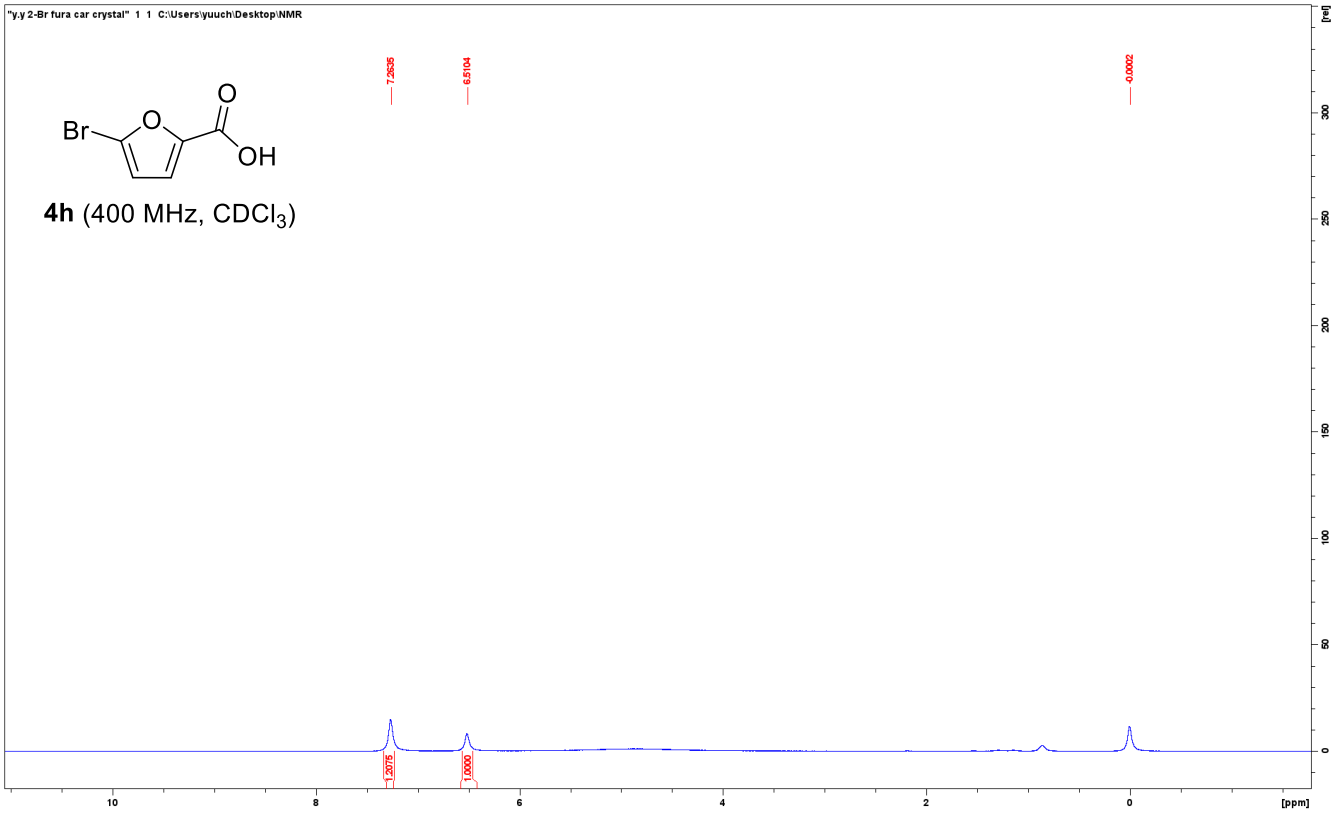


Figure S21 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4h**



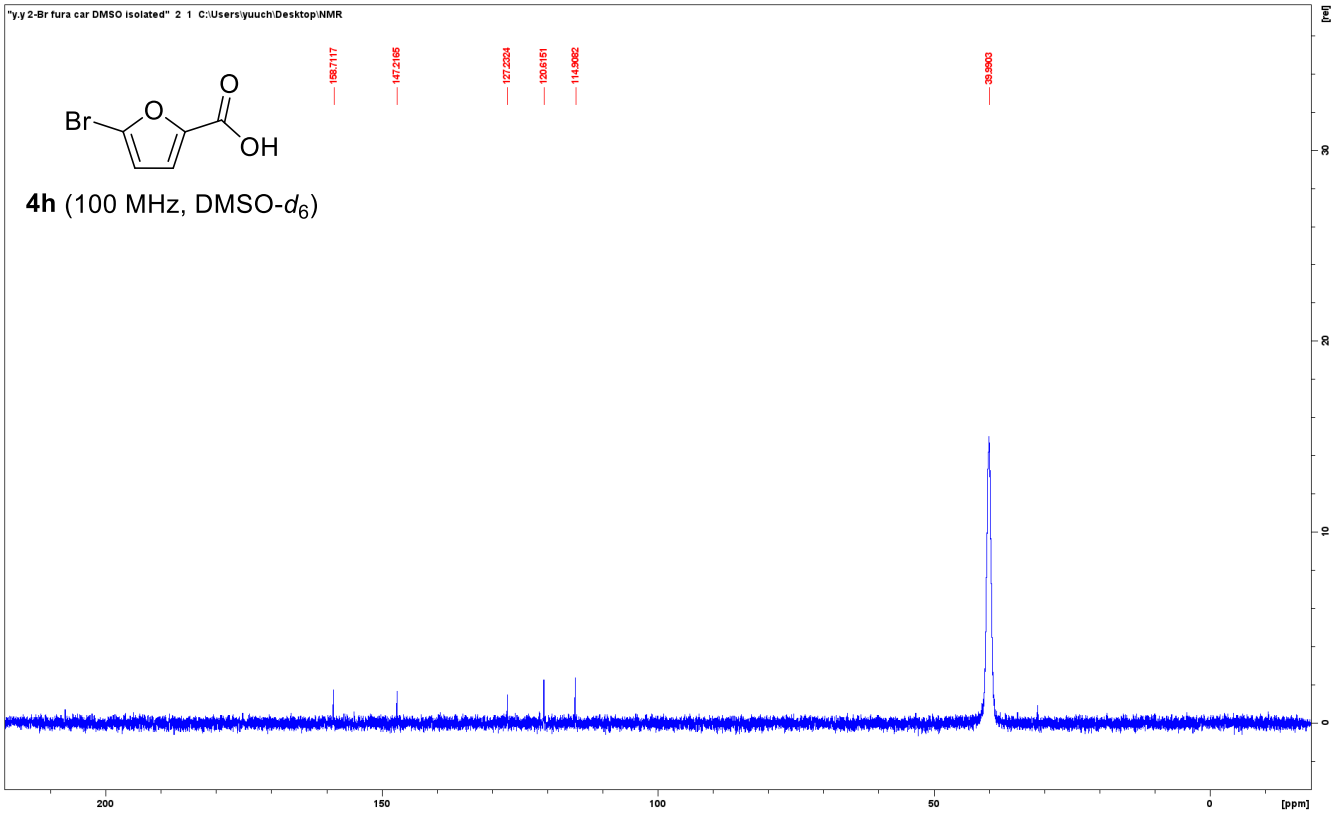
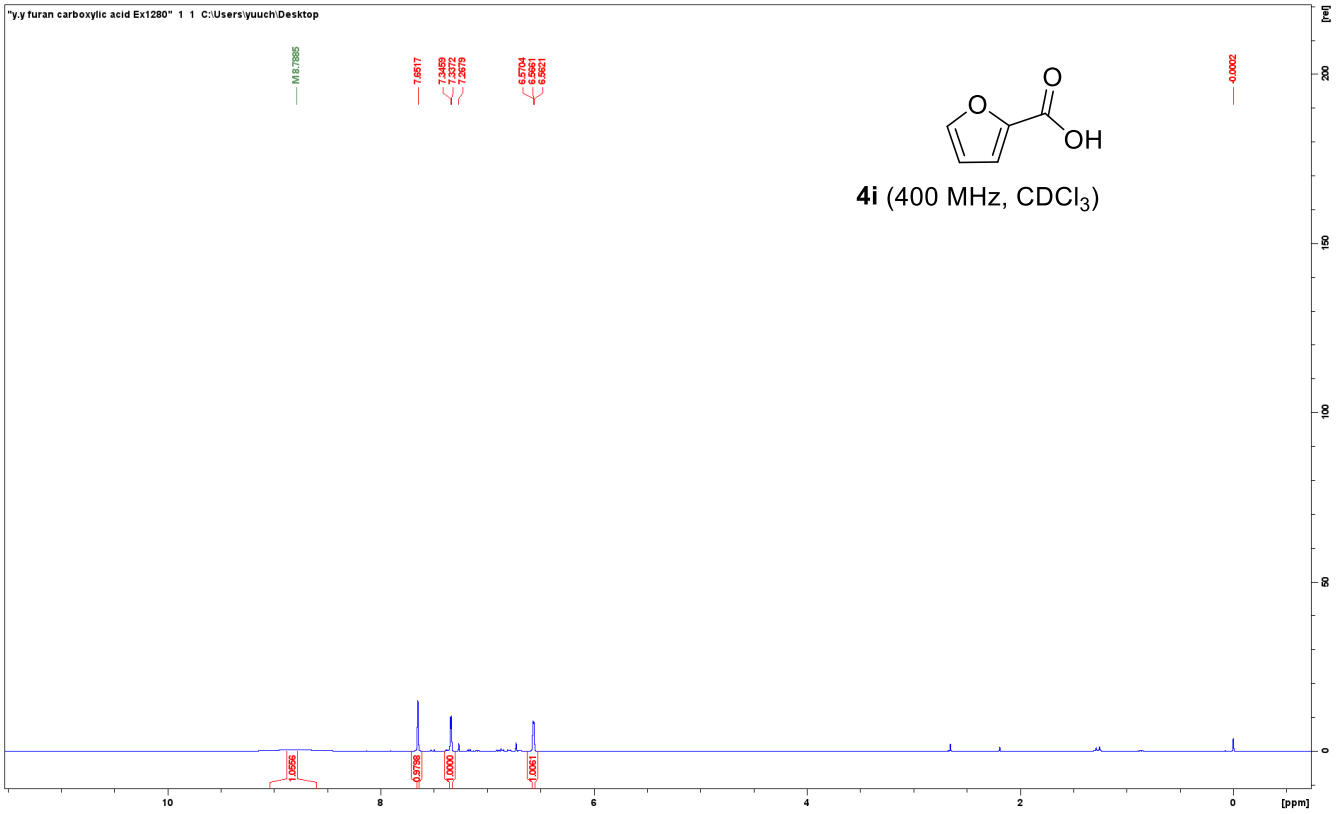


Figure S22 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4i**



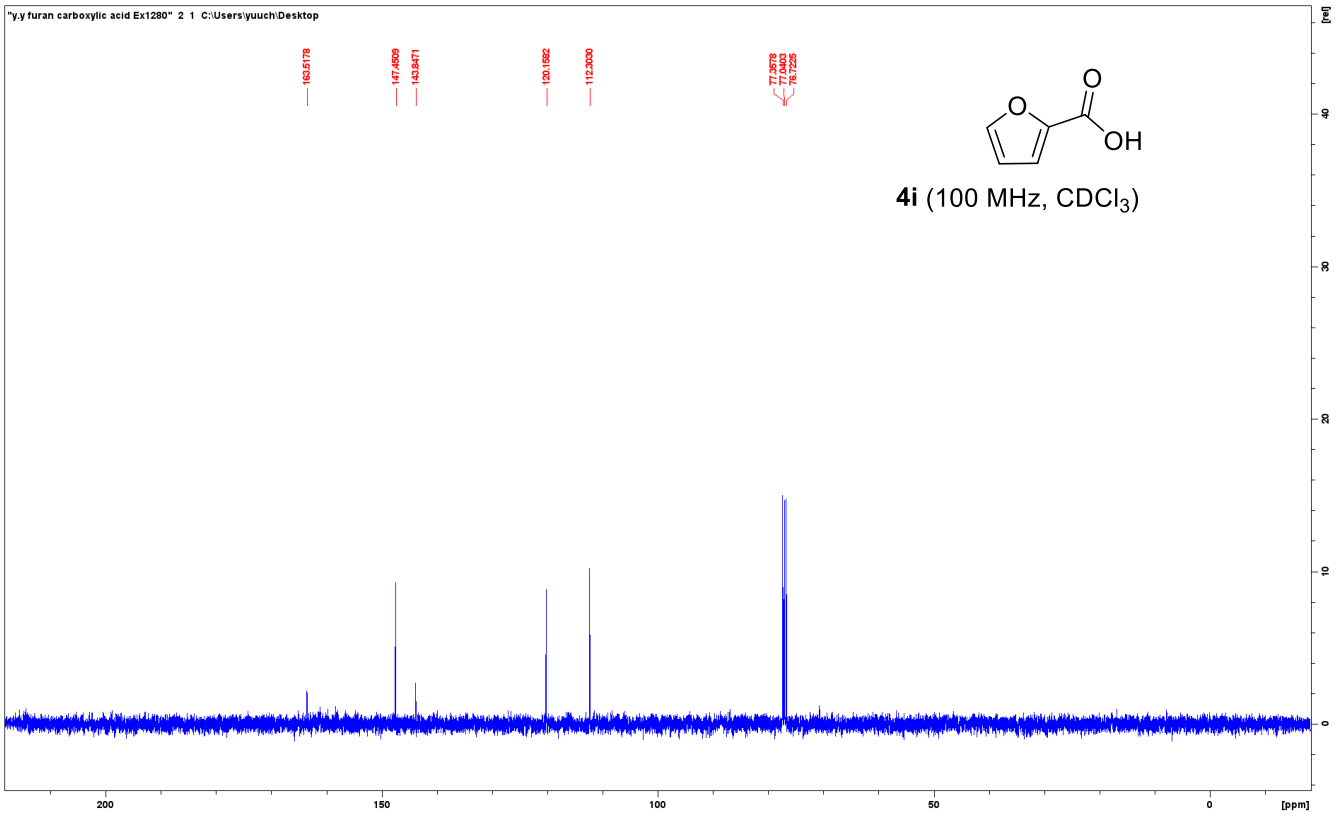
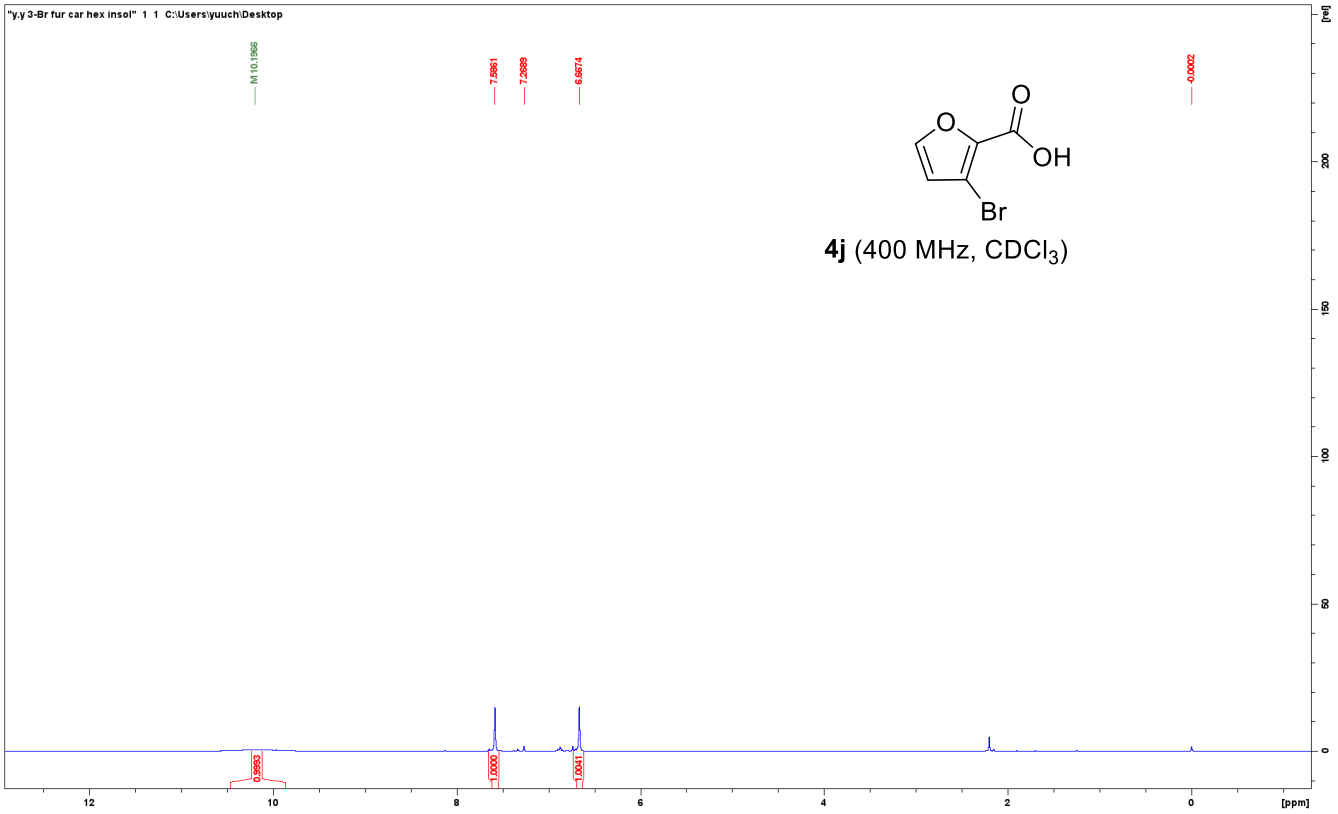


Figure S23 Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4j**



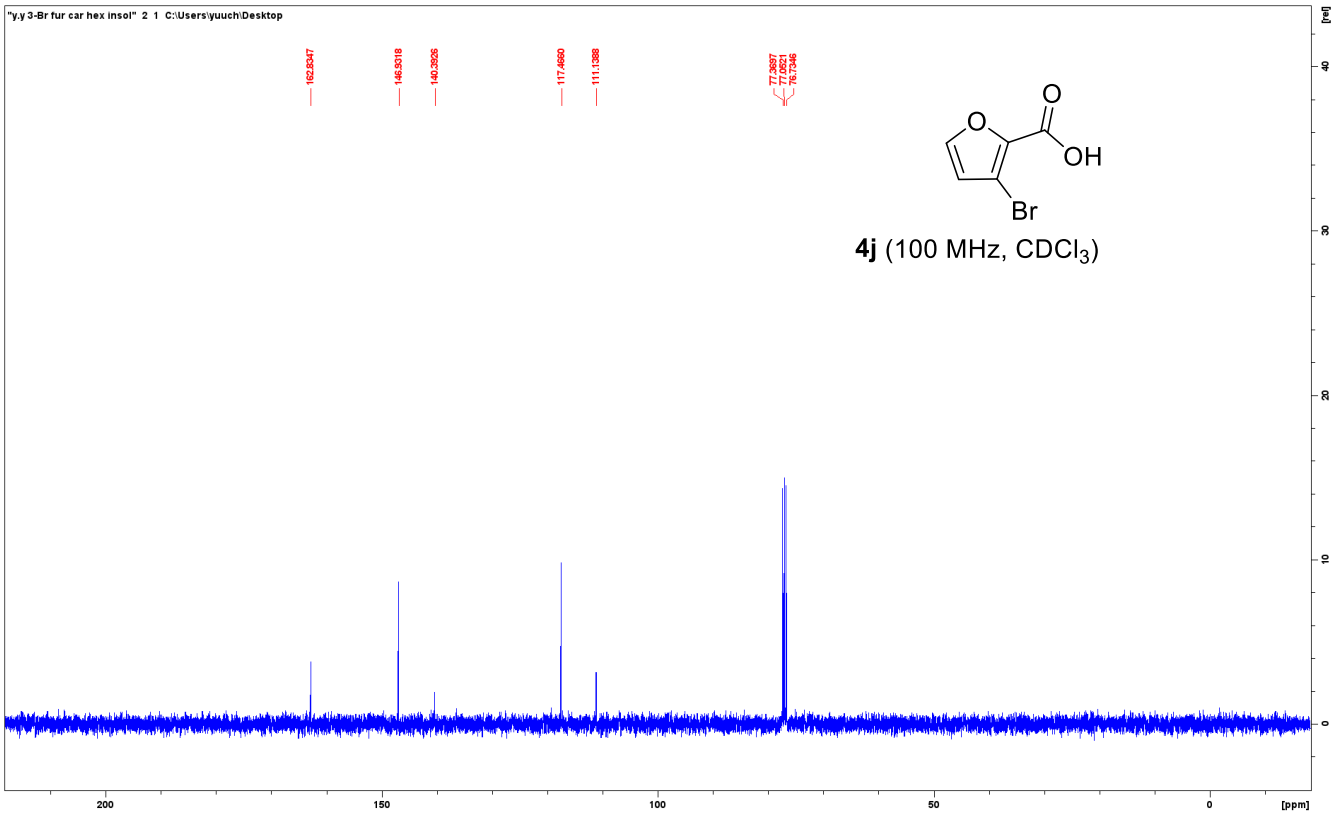
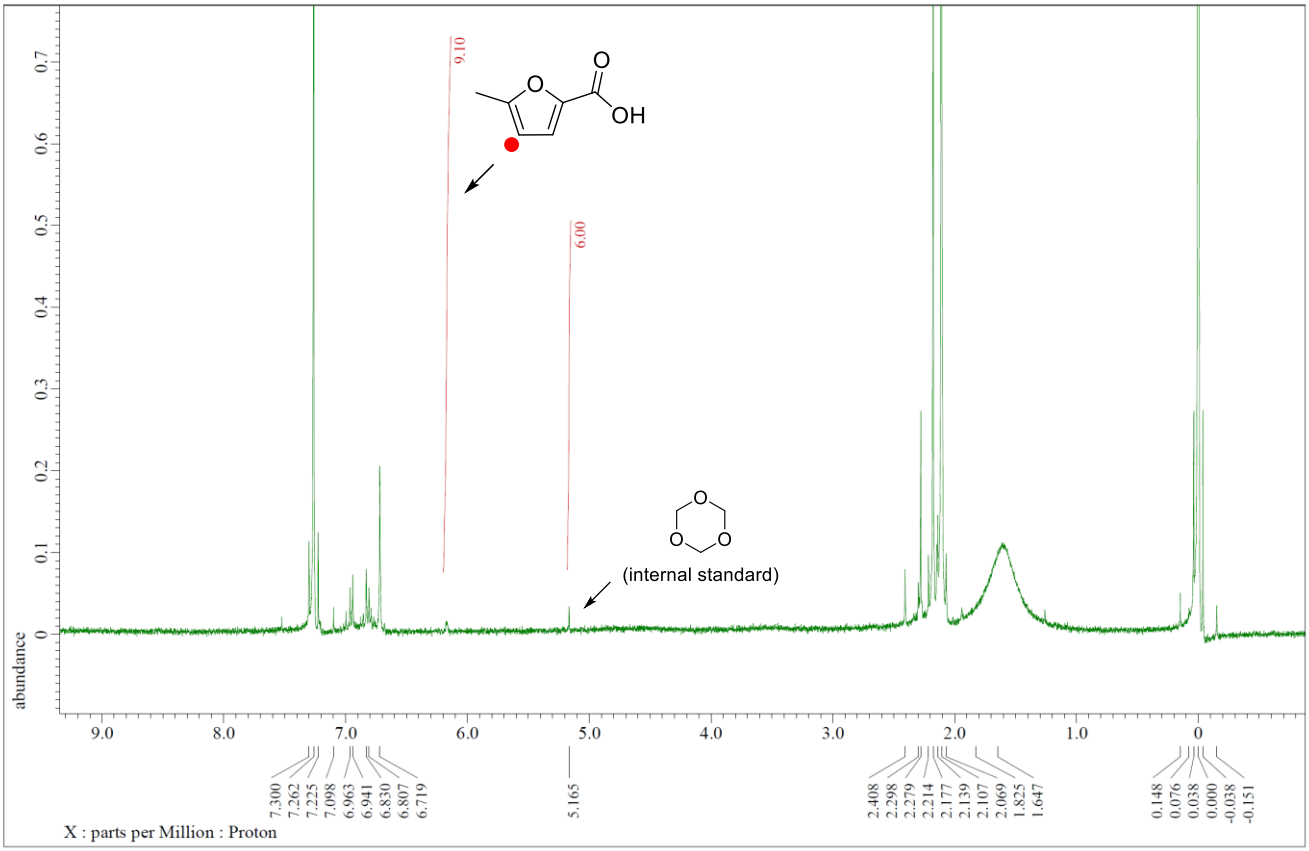


Figure S24 The ^{1}H NMR spectrum of **4e** (crude mixture in $CDCl_3$)



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