

Supporting Information for

Highly active bidentate N-heterocyclic carbene/ruthenium complexes performing dehydrogenative coupling of alcohols and hydroxides in open air

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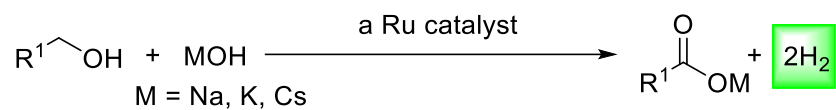
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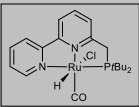
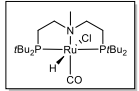
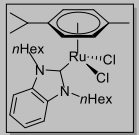
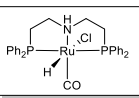
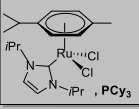
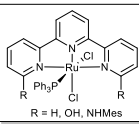
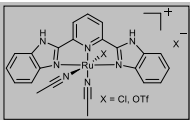
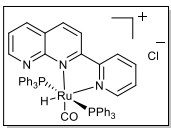
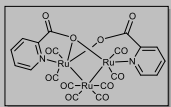
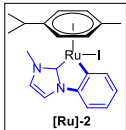
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1. Supplementary experiments

Table S1. Comparison of **[Ru]-2** with the previously reported Ru catalysts.



Ref	Year	Authors	Ru catalyst	Catalyst loading	Atmosphere	TON for the carboxylates	TOF for the carboxylates
1 ¹	2013	Milstein <i>et al.</i>		0.2 mol%	Inert	Not mentioned	Not mentioned
2 ²	2014	Prechtl <i>et al.</i>		0.2 mol%	Inert	Not mentioned	Not mentioned
3 ³	2015	M ěler <i>et al.</i>		1.0 mol%	Inert	Not mentioned	Not mentioned
4 ⁴	2016	Gauvin <i>et al.</i>		0.1 mol%	Inert or open air	4000	Not mentioned
5 ⁵	2016	Madsen <i>et al.</i>		1.0 mol%	Inert	Not mentioned	Not mentioned
6 ⁶	2017	Szymczak <i>et al.</i>		0.2 mol%	Inert	2500	Not mentioned
7 ⁷	2017	Peng <i>et al.</i>		0.2 mol%	Inert	10000	Not mentioned
8 ⁸	2017	Bera <i>et al.</i>		5.0 mol%	Inert	Not mentioned	Not mentioned
9 ⁹	2018	Mobin and Mathur <i>et al.</i>		1.0 mol%	Open air	Not mentioned	Not mentioned
10		This work		0.025 mol%	Open air	32800	3200

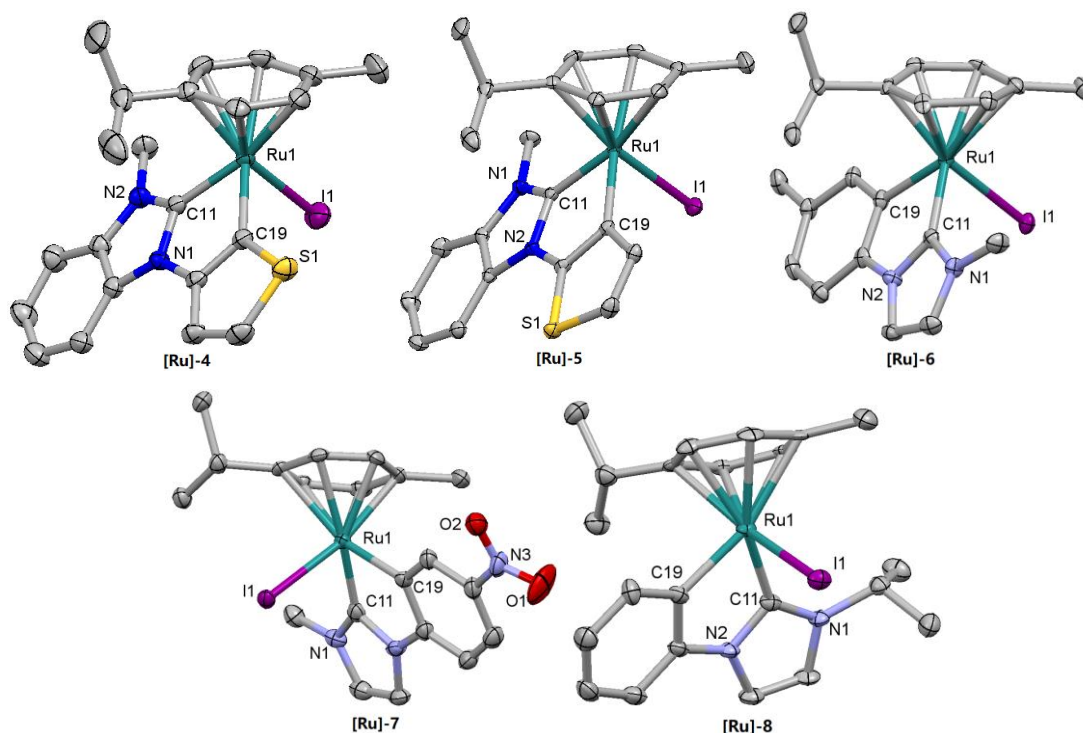


Figure S1. The molecular structures of complexes **[Ru]-4**~**[Ru]-8**, showing the atom labeling scheme of carbon atoms bound to the Ru center and the heteroatoms. The hydrogen atoms and the disorder of I (for **[Ru]-7**) were omitted for clarity. In addition, the ellipsoids of atoms were shown at probability levels of 30% for **[Ru]-4** and **[Ru]-6**, 50% for **[Ru]-5**, **[Ru]-7** and **[Ru]-8**.

For optimization of the reactions conditions, the reaction of benzyl alcohol (**1a**) and a hydroxide was selected as a model reaction (as listed in Table S2). At the outset, 0.1 mol% of **[Ru]-1** in THF at 120 °C was utilized, and various hydroxides were screened under an argon atmosphere (entries 1-4). It was found that KOH demonstrated the best result, providing the corresponding benzoic acid (**1a**) in 85% yield (entry 3). Afterwards, other solvents such as 1,4-dioxane, toluene and *m*-xylene were exploited instead of THF (entries 5-7). If the reaction was performed in refluxing 1, 4-dioxane, only 40% of **2a** was detected with 58% of unreacted **1a** (entry 5). Moreover, refluxing toluene led to a similar result with THF (entry 6 vs. entry 3). Replacing toluene with

m-xylene and performing the reaction at an elaborated temperature resulted in a slightly higher yield of **2a** with shorter reaction time (entry 7 vs. entry 6).

Table S2. Optimization of reaction conditions^a

Ph-CH₂-OH + hydroxide
(**1a**, 1.00 equiv.) (1.20 equiv.)

solvent, temperature, time, argon

3 N HCl

Ph-COOH
2a

Entry	hydroxide	Solvent /temperature	Time	Yields (%) ^b		TONs	TOFs
				2a	Unreacted 1a		
1	LiOH	THF/120 °C	16 h	25	72	250	16
2	NaOH	THF/120 °C	16 h	58	39	580	36
3	KOH	THF/120 °C	16 h	85	9	850	53
4	CsOH·H ₂ O	THF/120 °C	16 h	71	23	710	44
5	KOH	1,4-dioxane/reflux	16 h	40	58	400	25
6	KOH	toluene/ reflux	16 h	88	10	880	55
7	KOH	<i>m</i> -xylene/reflux	6 h	94	trace	940	157

^[a] **Conditions:** **1a** (1.00 equiv.), a hydroxide (1.20 equiv.) and **[Ru]-1** (0.1 mol%) under an open argon atmosphere; ^[b] NMR yields using 1,3,5-trimethoxybenzene as an internal standard (average of two consistent runs).

In order to comprehend the mechanistic insights of this reaction, we endeavored to perform further experiments. Generally, it has been postulated that the generation of Ru hydride species is crucial for this Ru-catalyzed dehydrogenative transformation.^{1, 5, 8} Therefore, Ru hydride formation was monitored by an NMR reaction (as shown in Fig. S2 of the supporting information). Initially, **[Ru]-2** (0.01 mmol, 5.2 mg), **1a** (0.05

mmol, 5 μ L) and toluene- d_8 (0.6 mL) were transferred to a screw-capped NMR tube, but no hydride formation was observed even if the mixture was heated at refluxing temperature. Afterwards, KOH (0.06 mmol, 3.3 mg) was added, and still, no hydride signal was detected at room temperature (as shown in Fig. S2a). Interestingly, a major singlet at -9.36 ppm and a minor singlet at -9.24 were found after heating the NMR tube at reflux for 5 min (Fig. S2b). As the heating period was elongated, the peak intensity at -9.24 ppm was intensified while that at -9.36 ppm gradually decreased until disappeared. (Fig. S2c-e). Afterwards, another singlet resonance at -7.81 ppm appeared and the peak intensity at -9.24 ppm was slowly decreased (Fig. S2e-g). These results implied that Ru-hydride species were probably involved in the catalytic cycle.

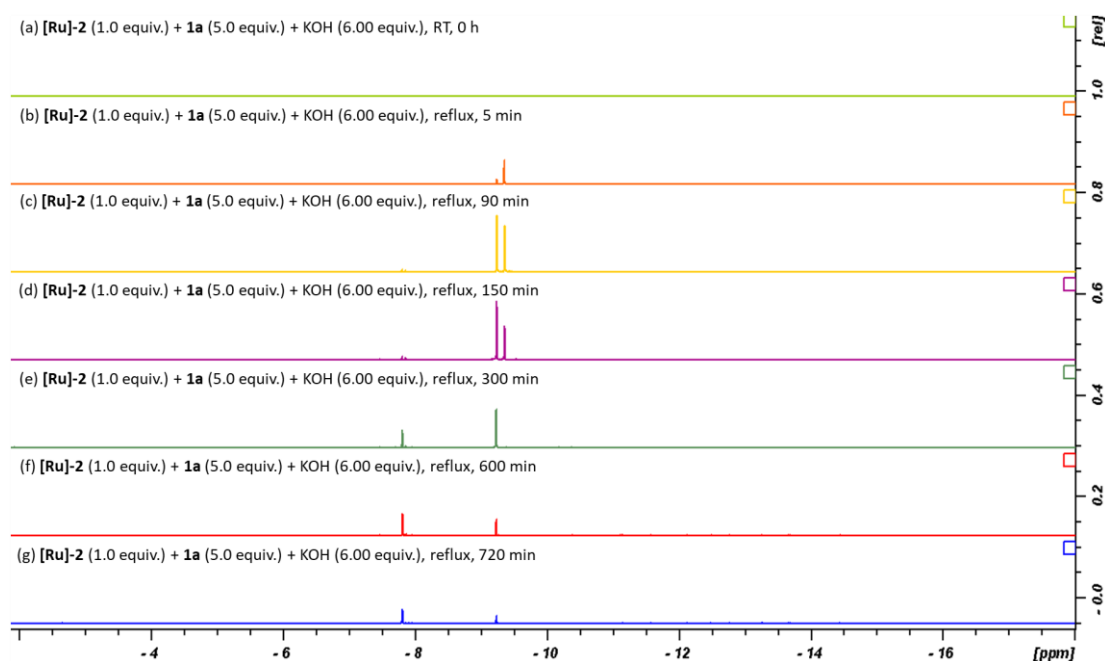


Figure S2. Detection of Ru hydride species via NMR reactions

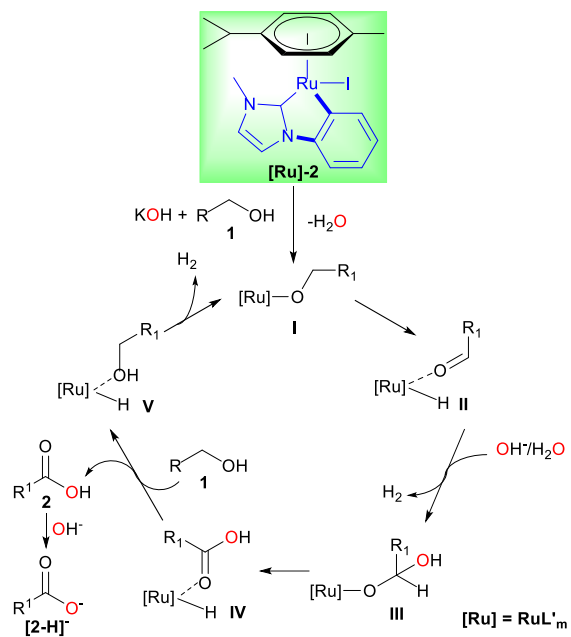


Figure S3. The proposed mechanism for the $[\text{Ru}]\text{-2}$ -catalyzed dehydrogenative coupling of an alcohol and KOH .

2. Experimental Section

2.1. General considerations

The reactions which have to be conducted under argon atmosphere were carried out using standard Schlenk techniques or in an argon-filled glove box unless otherwise mentioned, while the other reactions were conducted in open air. ¹H-NMR spectra were recorded on a Bruker Avance 500 spectrometer in CDCl₃, DMSO-*d*₆ or D₂O with/without TMS as the internal reference, and ¹³C-NMR spectra were recorded in CDCl₃, DMSO-*d*₆ or D₂O on a Bruker Avance 500 (126 MHz) spectrometer. Single crystal structures of **[Ru]-4~[Ru]-8** were obtained using a Bruker APEX-II CCD diffractometer. The following abbreviations were used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = doublet of doublets, dp = doublet of pentets, tt = triplet of triplets, qq = quartet of quartets, dtd = doublet of triplets of doublets, dddd = double of doublets of doublets of doublets,. Melting points were taken on a Buchi M-560 melting point apparatus and were uncorrected. HR-MS analysis was done with a Bruker Daltonics microTOF-QII instrument or a Thermo Fisher Q Exactive Mass Spectrometer. All the substrates and solvents were obtained from commercial suppliers and used as received without further purification. Bidentate NHC-Ru complexes including **[Ru]-1**¹⁰, **[Ru]-2**¹⁰ and **[Ru]-3**¹¹ were prepared according to literature procedures.

2.2. General procedure for the synthesis of L1~L5

2.2.1 General procedure for the synthesis of L1~L2

A mixture of CuI (70.1 mg, 0.368 mmol), L-proline (84.7 mg, 0.736 mmol) and K₂CO₃ (762.9 mg, 5.52 mmol) were added to a Schlenk tube. The weighing of these reagents happened inside a glove box under argon. Then benzimidazole (217.4 mg, 1.84 mmol), 3-bromothiophene (0.17 mL, 1.84 mmol) or 2-bromothiophene (0.18 mL, 1.84 mmol) and DMSO (3.0 mL) were added, and the mixture was stirred for 72 h at 120 °C before letting it cool down to room temperature. After cooling down, the mixture was then filtered using gravity filtration and the solution was transferred to a separation funnel with 30 mL of ethyl acetate. The organic solution dissolved in DCM was washed with water (3 × 30 mL), then dried over an excess amount of Na₂SO₄ to remove all the water and concentrated using the rotary evaporator. Since not all the benzimidazole was reacted, it had to be removed by silica-gel column chromatography. Petroleum ether was used as the starting eluent and was then swapped for a more polar solvent containing petroleum ether/ethyl acetate (from 5:1 to 3:1). After removing the solvent, a brown oil was obtained as pure product, which was directly used for the next step without characterization.

To a sealed pressure tube was loaded the above crude compound, 3.0 mL acetone and 0.5 mL methyl iodide. The tube was heated at 70 °C for 18 h, and the precipitate was collected through decantation, and washed several times with Et₂O. The solid was dried to afford 282.1 mg of pure 3-methyl-1-(thiophen-3-yl)-1H-benzo[d]imidazol-3-ium iodide (**L1**) or 232.5 mg of pure 3-methyl-1-(thiophen-2-yl)-1H-benzo[d]imidazole-3-ium iodide (**L2**). Both

compounds were quickly transferred to small glass vials and put inside the glovebox under an argon atmosphere.

2.2.2 General procedure for the synthesis of L3~L5

To a 25 mL Schlenk flask was added CuI (47.6 mg, 0.25 mmol) and KOH (285.5 mg, 5.00 mmol) inside an argon-filled glovebox. Then the flask was taken out of the glovebox and imidazole (255.3 mg, 3.75 mmol), 1-iodo-4-methylbenzene (0.32 mL, 2.50 mmol) [1-iodo-4-nitrobenzene (622.5 mg, 2.50 mmol) or iodobenzene (0.28 mL, 2.50 mmol)] and DMSO (4.0 mL) were added, and the mixture was stirred at 110 °C for 24 h. After the flask was cooled down to room temperature, the mixture was then filtered using gravity filtration and the solution was transferred to a separation funnel with 30 mL of ethyl acetate. The organic layer was washed with water (3 × 30 mL), brine (30 mL), dried over Na₂SO₄, and then concentrated using the rotary evaporator. Furthermore, silica-gel column chromatography was carried out to obtain the pure product. Petroleum ether was used as the starting eluent and was then swapped for a more polar solvent containing petroleum ether/ethyl acetate (from 5:1 to 2:1). After removing the solvent, 1-(*p*-tolyl)-1*H*-imidazole [1-(4-nitrophenyl)-1*H*-imidazole or 1-phenyl-1*H*-imidazole) was obtained as a pure product, which was directly used for the next step without characterization.

To a sealed tube was loaded the above purified 1-(*p*-tolyl)-1*H*-imidazole [1-(4-nitrophenyl)-1*H*-imidazole) or 1-phenyl-1*H*-imidazole], 0.5 mL of methyl iodide (or 0.4 mL 2-iodopropane) and acetone (3.0 mL). The tube was heated at 70 °C

for 12 h, and the precipitate was collected through decantation, and washed several times with Et₂O. The solid was dried to afford 600 mg of pure 3-methyl-1-(*p*-tolyl)-1*H*-imidazol-3-ium iodide (**L3**) [225 mg of pure 3-methyl-1-(4-nitrophenyl)-1*H*-imidazol-3-ium iodide (**L4**) or 360 mg of pure 3-isopropyl-1-phenyl-1*H*-imidazol-3-ium iodide (**L5**)].

2.3. General procedure for the synthesis of [Ru]-4~[Ru]-8

Inside an argon-filled glovebox, [Ru(*p*-cymene)Cl₂]₂ (60.0 mg, 0.098 mmol), **L1** (67.0 mg, 0.196 mmol) and THF (6.0 mL) were added to a seal tube. The tube was taken out of the glovebox, and the reaction mixture was heated for 12 h at 70 °C before it was cooled to room temperature. Afterwards, the solvent was removed and the crude mixture was purified by neutral alumina column chromatography using the eluent (petroleum ether: dichloromethane = 1:1~1:2) to give pure **[Ru]-4** (97.0 mg, 87% yield).

Synthesis of **[Ru]-5~[Ru]-8** followed that of **[Ru]-4**.

2.4. General procedure for the NHC/Ru-catalyzed dehydrogenative coupling of an alcohol and KOH.

To a 25 mL Schlenk tube was added **[Ru]-2** (0.8 mg, 0.0015625 mmol), benzyl alcohol (0.66 mL, 6.25 mmol), KOH (414.0 mg, 7.5 mmol) and *m*-xylene (1.5 mL), and a reflux condenser was placed on top of the Schlenk tube. Then the mixture was stirred at reflux in open air for 6 h, and the tube was then cooled to room temperature.

Afterwards, the procedures concerning the NMR yields and isolated yields of the required compounds could be described in the following sessions.

2.5. General procedure for the calculations of NMR yields

The resultant mixture after the reaction was acidified with 3N HCl solution (around 3.0 mL) until pH 2 for most cases, and the solution was then transferred to a separation funnel with a small amount of water and ethyl acetate. Afterwards, the aqueous layer was extracted with ethyl acetate (3×20 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated. Then 1,3,5-trimethoxybenzene (1.0 mmol, 168.0 mg) and CHCl_3 (3.0 mL) were added, and 0.1 mL of the above solution and 0.5 mL of CDCl_3 were added to an NMR tube. The NMR yields were obtained based on the exact amount of 1,3,5-trimethoxybenzene.

2.6. General procedure for the isolation of the products and their isolated yields

Generally, water (2 mL) was added to the reaction mixture and the reaction mixture extract with diethyl ether (3×20 mL) before acidification. The water layer was then acidified with 3N HCl (3 mL) until pH 2 for most cases, and extracted with ethyl acetate (3×20 mL). The combined organic layers were dried with Na_2SO_4 , concentrated and dried to obtain pure carboxylic acids **2**.

For the reactions of 4-chlorobenzyl alcohol (**1e**) or 4-bromobenzyl alcohol (**1f**) with KOH, column chromatography was conducted to separate 4-chlorobenzoic acid (**2e**) or 4-bromobenzoic acid (**2f**) and benzoic acid (**2a**) so as to obtain their respective

yields. **2a** was obtained with an eluent of petroleum ether/ethyl acetate (5:1), while **2e** or **2f** was isolated with an eluent of petroleum ether/ethyl acetate (2:1).

The reactions of 4-hydroxybenzyl alcohol (**1k**) or 4-aminobenzyl alcohol (**1l**) with KOH were relatively complicated, so column chromatography was also required to obtain pure acid products **2k** and **2l**. It is worth mentioning that the pH value was controlled to ca. 6 for **2l** before extraction.

For the reaction of pentane-1,4-diol (**1x**) with KOH, the pH value was controlled to 5 before extraction. Due to the good solubility of the acid product **2x** in water, extraction with EtOAc was done for 6 times and much excess amount of EtOAc was required for each extraction. Afterwards, silica gel column chromatography was required to purify compound **2x** with an eluent of petroleum ether/ethyl acetate (2:1).

For the reaction of hex-5-en-1-ol (**1w**) and KOH, a mixture of hex-5-enoic acid (**2w**), (E)-hex-4-enoic acid (**2w'**) and hexanoic acid (**2o**) were obtained, and their respective yields were provided according to the ratio of the three compounds from the ¹H NMR spectrum.

For the isolation of 3-pyridinepropionic acid (**2v**), 3 M HCl was added dropwise until the pH value was ca. 2. Then the solvent was evaporated, resulting in a yellow residue. Ethanol (50 mL) was added to the yellow residue and the mixture was refluxed for 0.5 h, and the resulting solution was filtered. The procedure was repeated for two more times and the filtrates were combined. The solution was concentrated under vacuum and the resulting solid was washed with diethyl ether (3 × 15 mL) and dried to offer the pure product 3-pyridinepropionic acid (**2v**). In addition, the isolation

of 6-aminocaproic acid (**2y**) and *N*-isopropylamino acetic acid (**2z**) followed the procedure of purifying **2v** with controlling the pH values to ca. 6 and 5, respectively.

2.7. X-ray crystallography

The single crystals of the Ru complexes were grown by slow evaporation of *n*-pentane into a solution of **[Ru]-4~[Ru]-8** in CDCl₃. Diffraction data of **[Ru]-5** was collected with MoK α ($\lambda = 0.71073 \text{ \AA}$) radiation, while that of the other Ru complexes were collected with CuK α ($\lambda = 1.54184 \text{ \AA}$) radiation. Besides, numerical absorption corrections were applied. The structure was solved by direct methods and refined on F2 with anisotropic thermal parameters for all non-hydrogen atoms. Protons were refined at the calculated positions using a riding model. The supplementary crystallographic data of **[Ru]-4** (with a deposition number of 1911712), **[Ru]-5** (with a deposition number of 1911713), **[Ru]-6** (with a deposition number of 1922986), **[Ru]-7** (with a deposition number of 1923220) and **[Ru]-8** (with a deposition number of 1922988) could be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC).

3. Characterization data for L1~L5, [Ru]-4~[Ru]-8, 2a-2z

1-(Furan-3-yl)-3-methyl-1H-benzo[d]imidazol-3-ium iodide (L1). White powder: m.p. 236.5-236.9 °C. Isolated yield: 45% in two steps. ¹H NMR (500 MHz, CDCl₃) δ 11.12 (s, 1H), 8.21 (dd, *J* = 2.9, 1.9 Hz, 1H), 7.85 – 7.78 (m, 2H), 7.76 – 7.69 (m, 2H), 7.65 – 7.61 (m, 2H), 4.43 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 141.98, 132.02, 131.08, 130.14, 128.79, 128.07, 127.82, 122.84, 122.00, 113.69, 112.99, 34.42. HR-MS (ESI positive): *m/z* calcd. for C₁₂H₁₁N₂S [M-I]⁺: 215.06375; Found: 215.06361.

3-Methyl-1-(thiophen-2-yl)-1H-benzo[d]imidazol-3-ium iodide (L2). White powder: m.p. 221.5-223.0 °C. Isolated yield: 37% in two steps. ¹H NMR (500 MHz, CDCl₃) δ 11.12 (s, 1H), 7.86 – 7.78 (m, 3H), 7.79 – 7.68 (m, 2H), 7.51 (dd, *J* = 5.5, 1.5 Hz, 1H), 7.21 (dd, *J* = 5.5, 3.8 Hz, 1H), 4.46 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 142.65, 131.92, 131.88, 131.57, 128.33, 128.05, 127.28, 126.66, 126.63, 113.63, 113.06, 34.63. HR-MS (ESI positive): *m/z* calcd. for C₁₂H₁₁N₂S [M-I]⁺: 215.06375; Found: 215.06368.

3-Methyl-1-(p-tolyl)-1H-imidazol-3-ium iodide (L3). White powder: m.p. 161.0-162.5 °C. Isolated yield: 75% in two steps. ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.72 (s, 1H), 8.26 (dd, *J* = 1.9, 1.8 Hz, 1H), 7.94 (dd, *J* = 1.8, 1.6 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 3.95 (s, 3H), 2.40 (s, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 140.07, 136.22, 132.87, 131.00, 124.85, 122.06, 121.42, 36.64, 21.04. HR-MS (ESI positive): *m/z* calcd. for C₁₁H₁₃N₂ [M-I]⁺: 173.10732; Found: 173.10731.

3-Methyl-1-(4-nitrophenyl)-1H-imidazol-3-ium iodide (L4). Yellow powder: m.p. 189.9-191.2 °C. Isolated yield: 31% in two steps. ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.96 (s, 1H), 8.53 (d, *J* = 9.1 Hz, 2H), 8.44 (dd, *J* = 1.9, 1.8 Hz, 1H), 8.09 (d, *J* = 9.1 Hz, 2H), 8.02 (dd, *J* = 1.9, 1.8 Hz, 1H), 3.98 (s, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 148.03, 139.75, 137.31, 126.10, 125.26, 123.38, 121.36, 36.86. HR-MS (ESI positive): *m/z* calcd. for C₁₀H₁₀N₃O₂ [M-I]⁺: 204.07730; Found: 204.07671.

3-Isopropyl-1-phenyl-1H-imidazol-3-ium iodide (L5). White powder: m.p. 130.4-131.7 °C. Isolated yield: 25% in two steps. ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.82 (s, 1H), 8.35 (d, *J* = 2.0 Hz, 1H), 8.18 (d, *J* = 1.9 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.68 (dd, *J* = 7.8, 7.6 Hz, 2H), 7.64 – 7.57 (m, 1H), 4.72 (qq, *J* = 6.8, 6.6 Hz, 1H), 1.58 (d, *J* = 6.7 Hz, 6H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 135.32, 134.65, 130.58, 130.19, 122.42, 122.00, 121.76, 53.45, 22.72. HR-MS (ESI positive): *m/z* calcd. for C₁₂H₁₅N₂ [M-I]⁺: 187.12297; Found: 187.12295.

[Ru]-4. Orange powder: m.p. 224.6-225.1 °C. Purified by neutral alumina column chromatography with an eluent of petroleum ether and dichloromethane (1:2). Isolated yield: 87%. ¹H NMR (500 MHz, CDCl₃) δ 5.74 (d, *J* = 6.1 Hz, 1H), 5.69 (d, *J* = 6.1 Hz, 1H), 5.61 (d, *J* = 5.9 Hz, 1H), 5.56 (d, *J* = 5.9 Hz, 1H), 4.27 (s, 3H), 2.63 – 2.46 (m, 1H), 2.35 (s, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 199.72, 151.04, 140.86, 135.31, 130.58, 126.34, 122.73, 121.91, 114.04, 110.50, 109.69, 104.93, 103.57, 91.21, 88.89, 88.01, 85.57, 35.38, 31.57, 23.27, 21.79, 20.84. HR-MS (ESI positive): *m/z* calcd. for C₂₂H₂₄IN₂RuS [M+H]⁺: 576.97429; found: 576.97632.

[Ru]-5. Orange powder: m.p. 203.3-204.8 °C. Purified by neutral alumina column chromatography with an eluent of petroleum ether and dichloromethane (1:2). Isolated yield: 71%. ¹H NMR (500 MHz, CDCl₃) δ 7.72 (dd, *J* = 6.8, 1.9 Hz, 1H), 7.42 (d, *J* = 4.9 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.31 (ddd, *J* = 7.2, 5.4, 1.6 Hz, 2H), 7.14 (d, *J* = 4.9 Hz, 1H), 5.69 (d, *J* = 5.7 Hz, 1H), 5.60 (t, *J* = 5.5 Hz, 2H), 5.48 (d, *J* = 5.5 Hz, 1H), 4.27 (s, 3H), 2.43 (qq, *J* = 7.0, 6.8 Hz, 1H), 2.34 (s, 3H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.84 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 201.17, 151.62, 136.40, 135.30, 133.16, 130.13, 122.85, 122.14, 116.75, 110.47, 109.68, 103.88, 103.09, 90.77, 89.09, 87.71, 84.59, 35.26, 31.69, 23.22, 21.81, 20.91. HR-MS (ESI positive): *m/z* calcd. for C₂₂H₂₃IN₂RuS [M]⁺: 575.96646; found: 575.96599.

[Ru]-6. Orange powder: m.p. 167.0-168.2 °C. Purified by neutral alumina column chromatography with an eluent of petroleum ether and dichloromethane (1:1). Isolated yield: 90%. ¹H NMR (500 MHz, CDCl₃) δ 7.87 (s, 1H), 7.32 (d, *J* = 2.1 Hz, 1H), 7.04 – 6.94 (m, 2H), 6.72 (dd, *J* = 7.7, 1.8 Hz, 1H), 5.52 (d, *J* = 5.9 Hz, 1H), 5.47

(d, $J = 6.0$ Hz, 1H), 5.45 (d, $J = 6.0$ Hz, 1H), 5.42 (d, $J = 5.9$ Hz, 1H), 4.06 (s, 3H), 2.40 – 2.29 (m, 1H), 2.37 (s, 3H), 2.33 (s, 3H), 0.94 (d, $J = 7.0$ Hz, 3H), 0.84 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 186.51, 160.62, 143.40, 143.21, 132.99, 122.64, 121.71, 114.04, 110.41, 102.69, 102.05, 91.08, 89.10, 87.82, 84.65, 38.20, 31.46, 23.05, 21.87, 21.45, 20.88. HR-MS (ESI positive): m/z calcd. for $\text{C}_{21}\text{H}_{25}\text{IN}_2\text{Ru}$ $[\text{M}]^+$: 534.01004; Found: 534.00946.

[Ru]-7. Brownish red powder: m.p. 228.9-230.2 °C. Purified by neutral alumina column chromatography with an eluent of petroleum ether and dichloromethane (1:2). Isolated yield: 92%. ^1H NMR (500 MHz, CDCl_3) δ 8.89 (d, $J = 2.4$ Hz, 1H), 7.85 (dd, $J = 8.5, 2.4$ Hz, 1H), 7.40 (d, $J = 2.1$ Hz, 1H), 7.14 (d, $J = 8.5$ Hz, 1H), 7.06 (d, $J = 2.0$ Hz, 1H), 5.64 (d, $J = 6.1$ Hz, 1H), 5.61 – 5.55 (m, 2H), 5.48 (d, $J = 6.1$ Hz, 1H), 4.08 (s, 3H), 2.38 (s, 3H), 2.38 – 2.32 (m, 1H), 0.95 (d, $J = 6.9$ Hz, 3H), 0.82 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 189.44, 163.50, 150.68, 143.55, 136.94, 123.11, 119.02, 114.72, 110.31, 104.37, 103.63, 92.00, 89.99, 88.91, 85.02, 38.44, 31.52, 23.06, 21.79, 20.94. HR-MS (ESI positive): m/z calcd. for $\text{C}_{20}\text{H}_{22}\text{IN}_3\text{O}_2\text{Ru}$ $[\text{M}]^+$: 564.97947; Found: 564.97901.

[Ru]-8. Light yellow powder: m.p. 197.1-198.6 °C. Purified by neutral alumina column chromatography with an eluent of petroleum ether and dichloromethane (1:1). Isolated yield: 89%. ^1H NMR (500 MHz, CDCl_3) δ 8.05 (dd, $J = 6.6, 2.1$ Hz, 1H), 7.42 (d, $J = 2.2$ Hz, 1H), 7.09 (dd, $J = 6.8, 2.1$ Hz, 1H), 7.06 (d, $J = 2.2$ Hz, 1H), 6.99 – 6.89 (m, 2H), 5.52 (d, $J = 5.9$ Hz, 1H), 5.49 (d, $J = 5.3$ Hz, 1H), 5.42 (d, $J = 5.9$ Hz, 1H), 5.33 (d, $J = 5.8$ Hz, 1H), 5.32 – 5.23 (m, 1H), 2.39 (qq, $J = 6.9$ Hz, 1H), 2.28 (s, 3H), 1.68 (d, $J = 6.9$ Hz, 3H), 1.58 (d, $J = 6.8$ Hz, 3H), 0.96 (d, $J = 6.9$ Hz, 3H), 0.84 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 185.40, 160.90, 145.09, 142.72, 123.99, 121.79, 116.24, 114.79, 110.73, 102.63, 102.33, 91.80, 89.67, 87.03, 84.23, 52.35, 31.38, 24.13, 23.92, 22.89, 21.90, 20.75. HR-MS (ESI positive): m/z calcd. for $\text{C}_{22}\text{H}_{27}\text{IN}_2\text{Ru}$ $[\text{M}]^+$: 548.02569; Found: 548.02529.

Benzoic acid (2a).¹² White solid: m.p. 124.2-125.7 °C. Isolated yield: 91%. ^1H NMR (500 MHz, CDCl_3) δ 11.91 (s, 1H), 8.16 (d, $J = 7.4$ Hz, 2H), 7.65 (dd, $J = 7.4, 7.3$ Hz, 1H), 7.51 (dd, $J = 7.8, 7.6$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.14,

133.81, 130.22, 129.31, 128.50. HR-MS (ESI): m/z calcd. for $C_7H_5O_2$ $[M-H]^-$: 121.02950; Found: 121.02951.

4-Methylbenzoic acid (2b).¹² White solid: m.p. 334.3-335.6 °C. Isolated yield: 90%. ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.80 (d, $J = 7.6$ Hz, 2H), 7.17 (d, $J = 7.6$ Hz, 2H), 2.33 (s, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 169.38, 140.34, 134.21, 129.63, 128.71, 21.46. HR-MS (ESI): m/z calcd. for $C_8H_7O_2$ $[M-H]^-$: 135.04515; Found: 135.04519.

4-Methoxybenzoic acid (2c).¹² White solid: m.p. 184.4-185.7 °C. Isolated yield: 92%. ¹H NMR (500 MHz, DMSO-*d*₆) δ 12.60 (s, 1H), 7.90 (d, $J = 8.8$ Hz, 2H), 7.02 (d, $J = 8.9$ Hz, 2H), 3.83 (s, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 167.43, 163.30, 131.79, 123.47, 114.27, 55.91. HR-MS (ESI): m/z calcd. for $C_8H_7O_3$ $[M-H]^-$: 151.04007; Found: 151.04010.

4-Biphenylcarboxylic acid (2d).¹² White solid: m.p. 222.7-224.1 °C. Isolated yield: 81%. ¹H NMR (500 MHz, DMSO-*d*₆) δ 12.96 (s, 1H), 8.03 (d, $J = 8.0$ Hz, 2H), 7.81 (d, $J = 8.0$ Hz, 2H), 7.74 (d, $J = 7.6$ Hz, 2H), 7.51 (dd, $J = 7.6, 7.4$ Hz, 2H), 7.43 (dd, $J = 7.4, 7.2$ Hz, 1H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 167.57, 144.78, 139.51, 130.41, 130.12, 129.53, 128.73, 127.42, 127.26. HR-MS (ESI): m/z calcd. for $C_{13}H_9O_2$ $[M-H]^-$: 197.06080; Found: 197.06085.

4-Chlorobenzoic acid (2e).¹² White solid: m.p. 236.6-238.1 °C. Isolated yield: 75% (with concurrent isolation of 10% of benzoic acid). ¹H NMR (500 MHz, DMSO-*d*₆) δ 13.17 (s, 1H), 7.95 (d, $J = 8.5$ Hz, 2H), 7.57 (d, $J = 8.6$ Hz, 2H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 166.90, 138.23, 131.59, 130.15, 129.20. HR-MS (ESI): m/z calcd. for $C_7H_4ClO_2$ $[M-H]^-$: 154.99053; Found: 154.99052.

4-Bromobenzoic acid (2f).¹² White solid: m.p. 260.1-261.0 °C. Isolated yield: 65% (with concurrent isolation of 12% of benzoic acid). ¹H NMR (500 MHz, DMSO-*d*₆) δ 13.17 (s, 1H), 7.87 (d, $J = 8.4$ Hz, 2H), 7.72 (dd, $J = 8.5, 1.8$ Hz, 2H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 167.04, 132.16, 131.74, 130.50, 127.31. HR-MS (ESI): m/z calcd. for $C_7H_4BrO_2$ $[M-H]^-$: 198.94002; Found: 198.94003.

4-(Trifluoromethoxy)benzoic acid (2g).¹³ White solid: m.p. 148.1-149.5 °C. Isolated yield: 75%. ¹H NMR (500 MHz, DMSO-*d*₆) δ 13.22 (s, 1H), 8.07 (d, $J = 8.7$ Hz, 2H),

7.48 (d, $J = 8.3$ Hz, 2H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 166.61, 151.91, 132.14, 130.33, 121.13, 120.38 (q, $J = 257.5$ Hz). HR-MS (ESI): m/z calcd. for $\text{C}_8\text{H}_4\text{F}_3\text{O}_3$ $[\text{M-H}]^-$: 205.01180; Found: 205.01182.

4-Trifluoromethylbenzoic acid (2h).¹² White solid: m.p. 223.6-224.9 °C. Isolated yield: 45%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 13.46 (s, 1H), 8.14 (d, $J = 8.0$ Hz, 2H), 7.88 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 166.62, 135.06, 132.95 (q, $J = 32.0$ Hz), 130.49, 125.93 (q, $J = 3.7$ Hz), 124.22 (q, $J = 272.4$ Hz). HR-MS (ESI): m/z calcd. for $\text{C}_8\text{H}_4\text{F}_3\text{O}_2$ $[\text{M-H}]^-$: 189.01689; Found: 189.01690.

3-Methylbenzoic acid (2i).¹² White solid: m.p. 112.5-113.9 °C. Isolated yield: 83%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 12.87 (s, 1H), 7.78 (s, 1H), 7.75 (d, $J = 7.7$ Hz, 1H), 7.40 (d, $J = 7.6$ Hz, 1H), 7.36 (dd, $J = 7.6, 7.4$ Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 167.87, 138.29, 133.82, 131.22, 130.18, 128.82, 126.90, 21.22. HR-MS (ESI): m/z calcd. for $\text{C}_8\text{H}_7\text{O}_2$ $[\text{M-H}]^-$: 135.04515; Found: 135.04517.

2-Methylbenzoic acid (2j).¹² White solid: m.p. 101.2-101.6 °C. Isolated yield: 73%. ^1H NMR (500 MHz, CDCl_3) δ 8.09 (d, $J = 7.4$ Hz, 1H), 7.48 (ddd, $J = 7.6, 7.4, 1.4$ Hz, 1H), 7.31 (dd, $J = 7.4, 7.2$ Hz, 2H), 2.69 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.57, 141.30, 132.88, 131.90, 131.54, 128.31, 125.84, 22.03. HR-MS (ESI): m/z calcd. for $\text{C}_8\text{H}_7\text{O}_2$ $[\text{M-H}]^-$: 135.04515; Found: 135.04518.

4-Hydroxybenzoic acid (2k). White solid: m.p. >400 °C. Isolated yield: 51%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 12.40 (s, 1H), 10.20 (s, 1H), 7.82 (d, $J = 8.7$ Hz, 2H), 6.84 (d, $J = 8.7$ Hz, 2H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 167.66, 162.05, 132.01, 121.85, 115.58. HR-MS (ESI): m/z calcd. for $\text{C}_7\text{H}_5\text{O}_3$ $[\text{M-H}]^-$: 137.02442; Found: 137.02441.

4-Aminobenzoic acid (2l). White solid: m.p. 188.7-189.6 °C. Isolated yield: 10%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 11.95 (s, 1H), 7.63 (d, $J = 8.7$ Hz, 2H), 6.56 (d, $J = 8.7$ Hz, 2H), 5.85 (s, 2H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 167.96, 153.58, 131.68, 117.38, 113.05. HR-MS (ESI): m/z calcd. for $\text{C}_7\text{H}_6\text{NO}_2$ $[\text{M-H}]^-$: 136.04040; Found: 136.04043.

2-Naphthoic Acid (2m).¹² White solid: m.p. 183.9-185.2 °C. Isolated yield: 73%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 13.07 (s, 1H), 8.61 (s, 1H), 8.12 (d, $J = 8.1$ Hz, 1H),

8.05 – 7.96 (m, 3H), 7.67 (dd, $J = 7.6, 7.4$ Hz, 1H), 7.61 (dd, $J = 7.6, 7.4$ Hz, 1H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 167.87, 135.40, 132.62, 130.95, 129.73, 128.77, 128.61, 128.56, 128.11, 127.26, 125.61. HR-MS (ESI): m/z calcd. for $\text{C}_{11}\text{H}_7\text{O}_2$ $[\text{M-H}]^-$: 171.04515; Found: 171.04520.

4-(Phenylthio)benzoic Acid (2n).¹² White solid: m.p. 175.6-176.0 °C. Isolated yield: 75%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 12.95 (s, 1H), 7.87 (d, $J = 8.5$ Hz, 2H), 7.55 – 7.42 (m, 5H), 7.25 (d, $J = 8.7$ Hz, 2H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 167.24, 143.20, 133.69, 132.12, 130.63, 130.45, 129.37, 128.95, 128.11. HR-MS (ESI): m/z calcd. for $\text{C}_{13}\text{H}_9\text{O}_2\text{S}$ $[\text{M-H}]^-$: 229.03287; Found: 229.03288.

Hexanoic acid (2o).¹² Pale yellow oil. Isolated yield: 93%. ^1H NMR (500 MHz, CDCl_3) δ 11.29 (s, 1H), 2.36 (t, $J = 7.5$ Hz, 2H), 1.71 – 1.58 (m, 2H), 1.40 – 1.29 (m, 4H), 0.96 – 0.85 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 180.59, 34.08, 31.19, 24.34, 22.26, 13.80. HR-MS (ESI): m/z calcd. for $\text{C}_6\text{H}_{11}\text{O}_2$ $[\text{M-H}]^-$: 115.07645; Found: 115.07644.

Octanoic acid (2p).¹² Yellow oil. Isolated yield: 82%. ^1H NMR (500 MHz, CDCl_3) δ 11.86 (s, 1H), 2.36 (t, $J = 7.6$ Hz, 2H), 1.65 (tt, $J = 7.6, 7.4$ Hz, 2H), 1.41 – 1.21 (m, 8H), 0.89 (t, $J = 6.7$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 180.69, 34.13, 31.62, 29.00, 28.89, 24.66, 22.58, 13.99. HR-MS (ESI): m/z calcd. for $\text{C}_8\text{H}_{15}\text{O}_2$ $[\text{M-H}]^-$: 143.10775; Found: 143.10777.

Cyclopentanecarboxylic acid (2q).¹² Yellow oil. Isolated yield: 88%. ^1H NMR (500 MHz, CDCl_3) δ 11.59 (s, 1H), 2.78 (tt, $J = 8.0, 7.8$ Hz, 1H), 1.99 – 1.89 (m, 2H), 1.89 – 1.80 (m, 2H), 1.79 – 1.68 (m, 2H), 1.66 – 1.55 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 183.57, 43.72, 29.94, 25.81. HR-MS (ESI): m/z calcd. for $\text{C}_6\text{H}_9\text{O}_2$ $[\text{M-H}]^-$: 113.06080; Found: 113.06080

Cyclohexanecarboxylic acid (2r).¹² Pale yellow oil. Isolated yield: 86%. ^1H NMR (500 MHz, CDCl_3) δ 12.00 (s, 1H), 2.39 – 2.28 (m, 1H), 1.98 – 1.88 (m, 1H), 1.81 – 1.72 (m, 2H), 1.68 – 1.61 (m, 1H), 1.54 – 1.39 (m, 2H), 1.37 – 1.16 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 182.86, 42.95, 28.74, 25.68, 25.31. HR-MS (ESI): m/z calcd. for $\text{C}_7\text{H}_{11}\text{O}_2$ $[\text{M-H}]^-$: 127.07645; Found: 127.07648.

3-Phenylpropionic acid (2s).¹⁴ White solid: m.p. 47.0-48.0 °C. Isolated yield: 81%. ¹H NMR (500 MHz, CDCl₃) δ 12.13 (s, 1H), 7.40 (dd, *J* = 8.5, 6.4 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 3H), 3.06 (t, *J* = 7.9 Hz, 2H), 2.78 (t, *J* = 7.8 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 179.77, 140.23, 128.66, 128.36, 126.48, 35.76, 30.64. HR-MS (ESI): *m/z* calcd. for C₉H₉O₂ [M-H]⁻: 149.06080; Found: 149.06078.

1-Adamantanecarboxylic acid (2t).¹⁴ White solid: m.p. 175.2-176.2 °C. Isolated yield: 65%. ¹H NMR (500 MHz, CDCl₃) δ 11.25 (s, 1H), 2.05 (s, 3H), 1.94 (s, 6H), 1.82 – 1.68 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 184.32, 40.51, 38.59, 36.44, 27.85. HR-MS (ESI): *m/z* calcd. for C₁₁H₁₅O₂ [M-H]⁻: 179.10775; Found: 179.10781.

2-Tetrahydrofuroic acid (2u).¹⁵ Pale yellow oil. Isolated yield: 73%. ¹H NMR (500 MHz, CDCl₃) δ 11.08 (s, 1H), 4.41 (dd, *J* = 8.6, 5.5 Hz, 1H), 3.93 (q, *J* = 7.0 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 1H), 2.28 – 2.14 (m, 1H), 2.06 – 1.93 (m, 1H), 1.93 – 1.77 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 177.56, 76.18, 69.41, 30.07, 25.12. HR-MS (ESI): *m/z* calcd. for C₅H₇O₃ [M-H]⁻: 115.04007; Found: 115.04005.

3-Pyridinepropionic acid (2v).¹² Yellow solid: m.p. 160.5-161.5 °C. Isolated yield: 85%. ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.87 (d, *J* = 1.9 Hz, 1H), 8.79 (d, *J* = 5.6 Hz, 1H), 8.54 (d, *J* = 8.0 Hz, 1H), 8.02 (dd, *J* = 8.0, 5.7 Hz, 1H), 3.03 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 173.59, 146.53, 141.55, 141.40, 139.59, 127.28, 34.23, 27.51. HR-MS (ESI): *m/z* calcd. for C₈H₁₀NO₂ [M+H]⁺: 152.07060; Found: 152.07059.

5-Hexenoic acid (2w).¹² Pale yellow oil. Isolated yield: 57% (with 18% of 4-hexenoic acid and 7% of hexanoic acid as byproducts). Isolated yield: 58%. ¹H NMR (500 MHz, CDCl₃) δ 11.82 (s, 1H), 5.96 – 5.67 (m, 1H), 5.14 – 4.93 (m, 2H), 2.44 – 2.33 (m, 2H), 2.17 – 2.01 (m, 2H), 1.88 – 1.66 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 180.33, 137.42, 115.47, 33.30, 32.88, 23.72. HR-MS (ESI): *m/z* calcd. for C₆H₉O₂ [M-H]⁻: 113.06080; Found: 113.06080.

4-Hydroxypentanoic acid (2x). Pale yellow oil. Isolated yield: 40%. ¹H NMR (500 MHz, CDCl₃) δ 3.96 – 3.84 (m, 1H), 2.53 (t, *J* = 7.2 Hz, 2H), 1.90 – 1.69 (m, 2H), 1.26 (d, *J* = 6.2 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 178.69, 67.43, 33.46, 30.41, 23.54. HR-MS (ESI): *m/z* calcd. for C₅H₉O₃ [M-H]⁻: 117.05572; Found: 117.05573.

6-Aminocaproic acid (2y).¹² White solid: m.p. 271.8-272.8 °C. Isolated yield: 81%. ¹H NMR (500 MHz, D₂O) δ 3.37 (t, *J* = 7.7 Hz, 2H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.03 (tt, *J* = 7.8, 7.6 Hz, 2H), 1.92 (tt, *J* = 7.8, 7.6 Hz, 2H), 1.72 (tt, *J* = 7.8, 7.6 Hz, 2H). ¹³C NMR (126 MHz, D₂O) δ 182.79, 40.10, 36.72, 26.89, 25.83, 25.21. HR-MS (ESI): *m/z* calcd. for C₅H₁₄NO₂ [M+H]⁺: 132.10191; Found: 132.10190.

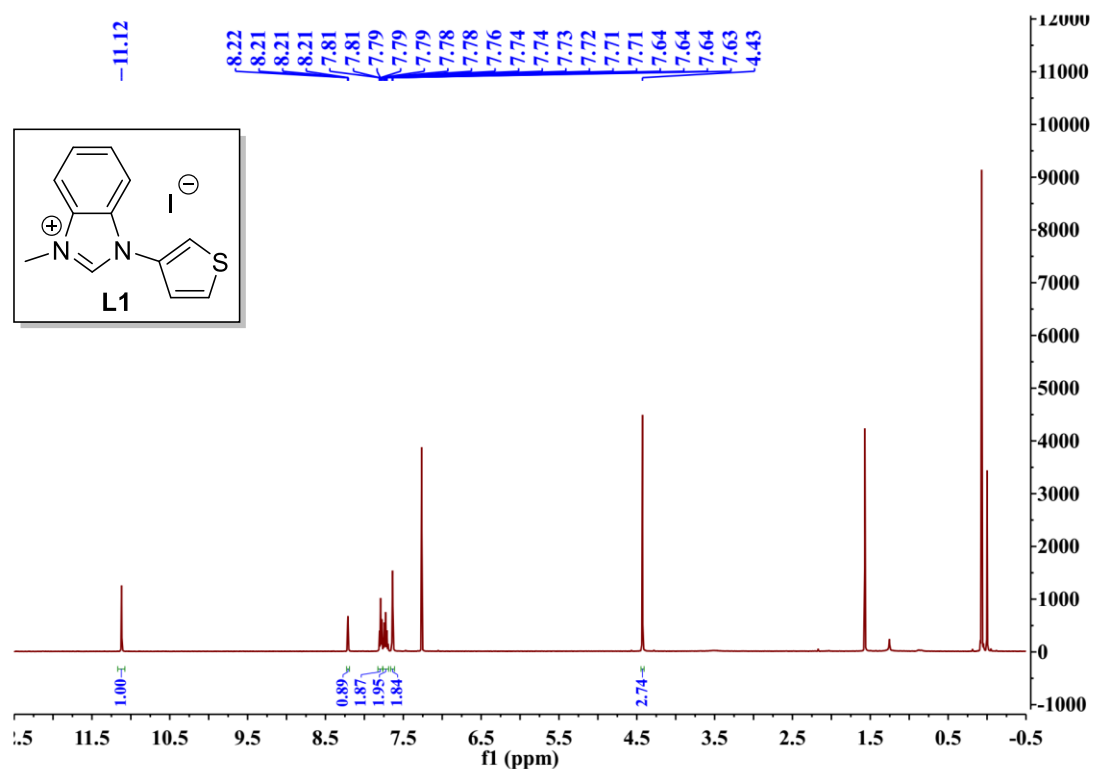
N-Isopropylamino acetic acid (2z).¹⁶ White solid: m.p. >400 °C. Isolated yield: 71%. ¹H NMR (500 MHz, D₂O) δ 3.91 (s, 2H), 3.45 (t, *J* = 6.8 Hz, 1H), 1.29 (d, *J* = 6.7 Hz, 6H). ¹³C NMR (126 MHz, D₂O) δ 169.31, 51.10, 44.89, 18.24, 18.17. HR-MS (ESI): *m/z* calcd. for C₅H₁₀NO₂ [M-H]⁻: 116.07170; Found: 116.07170.

References

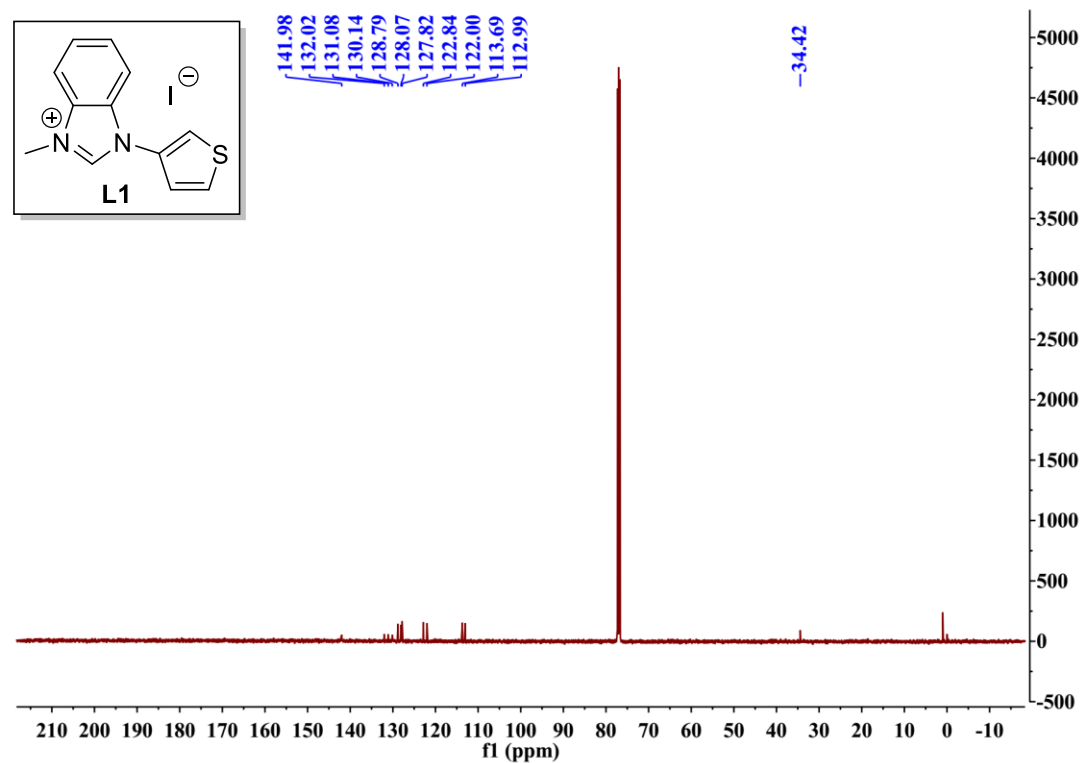
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4. Original ^1H and ^{13}C NMR spectra for L1~L5, [Ru]-4~[Ru]-8, 2a-2z:

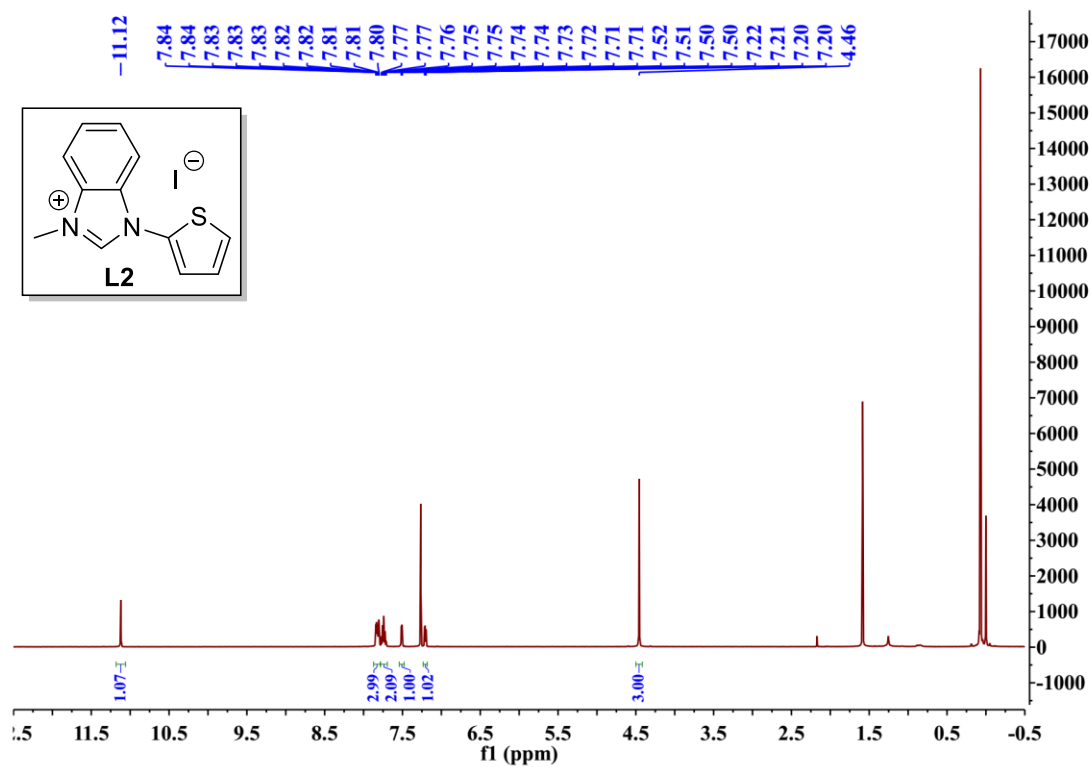
➤ ^1H NMR spectrum for L1



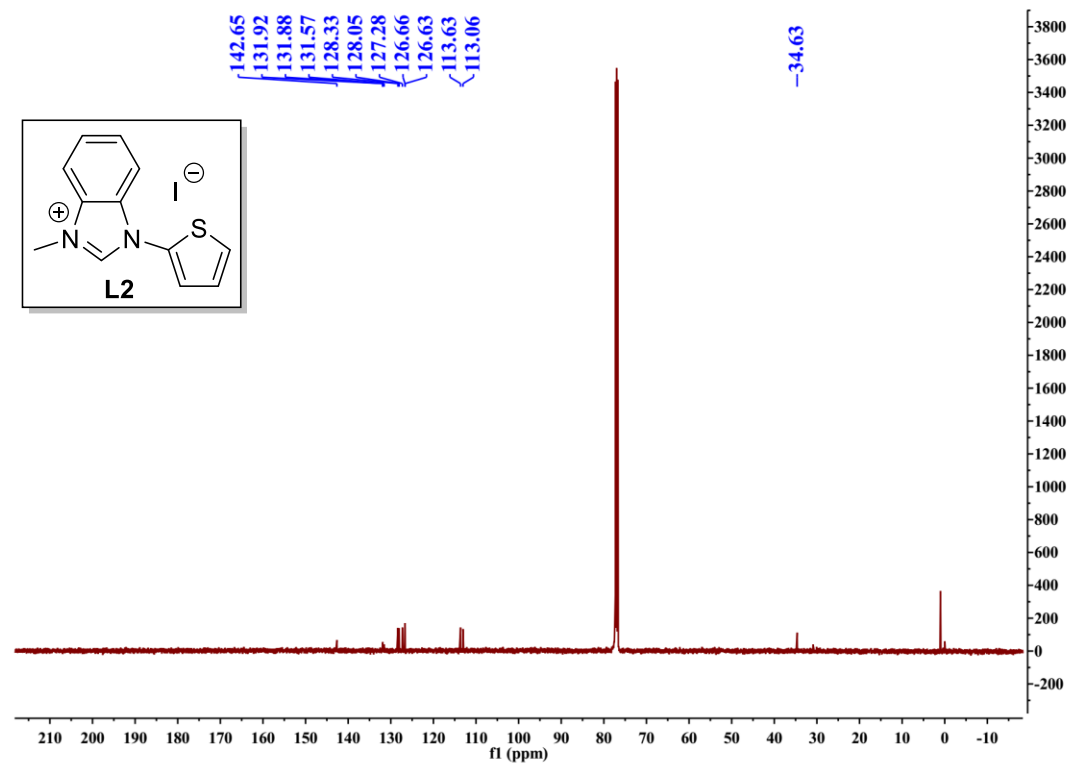
➤ ^{13}C NMR spectrum for L1



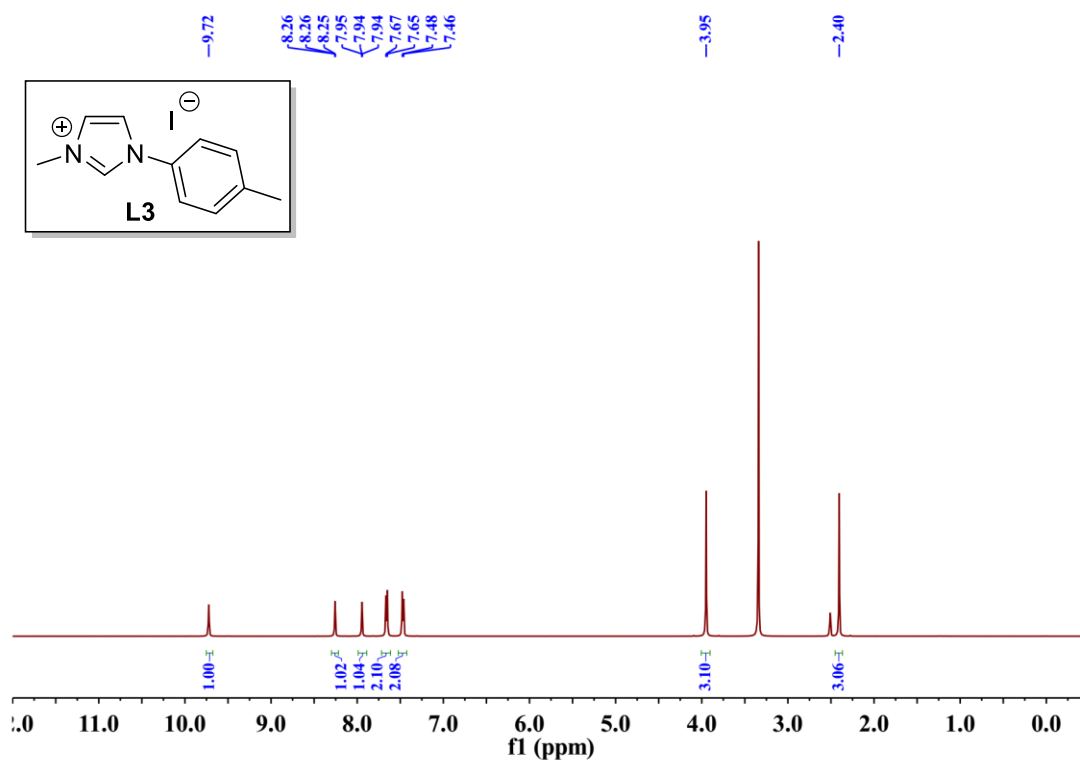
➤ ¹H NMR spectrum for L2



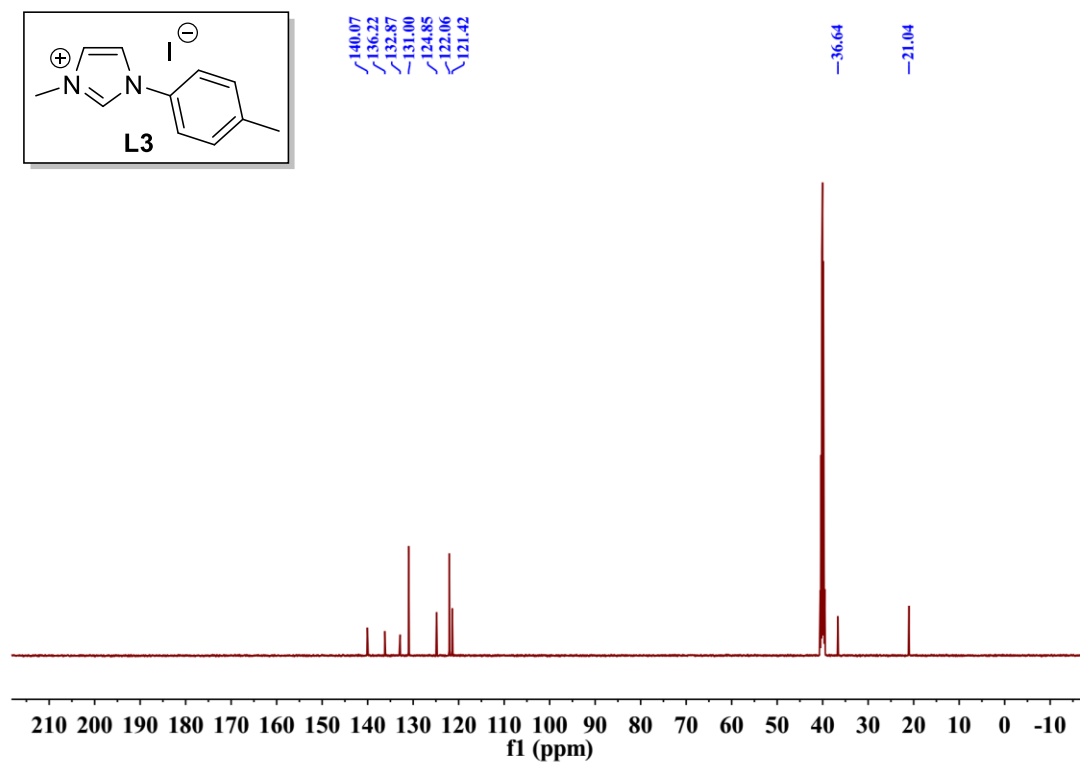
➤ ¹³C NMR spectrum for L2



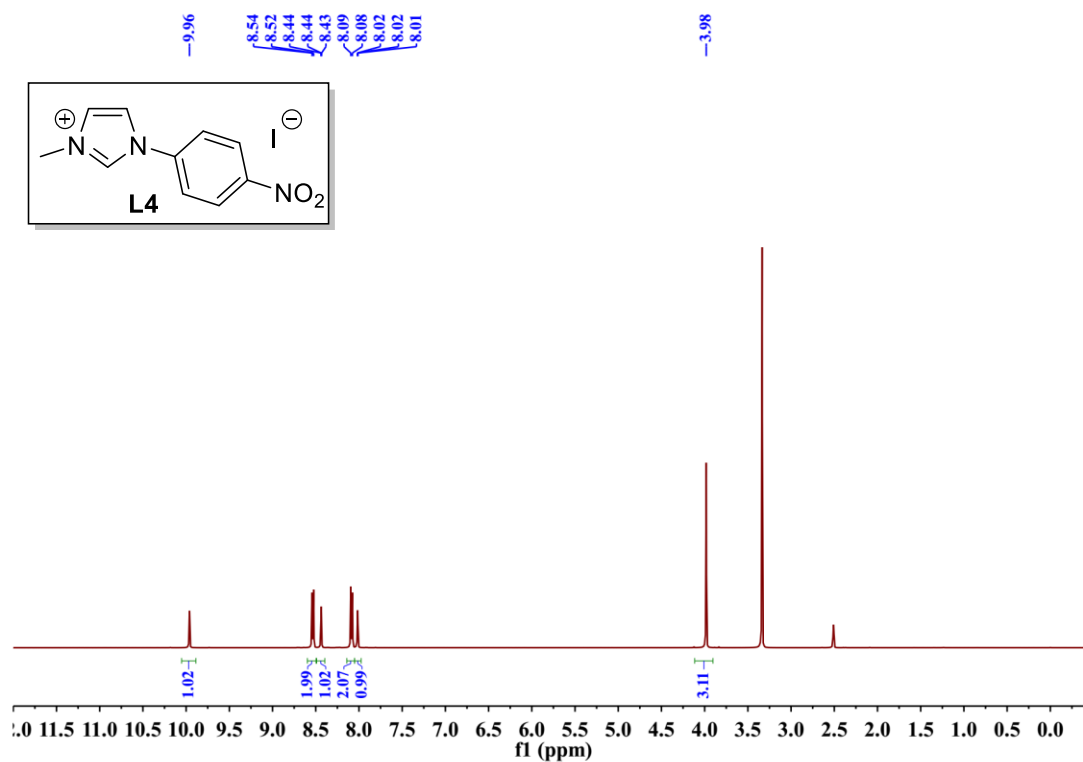
➤ ¹H NMR spectrum for L3



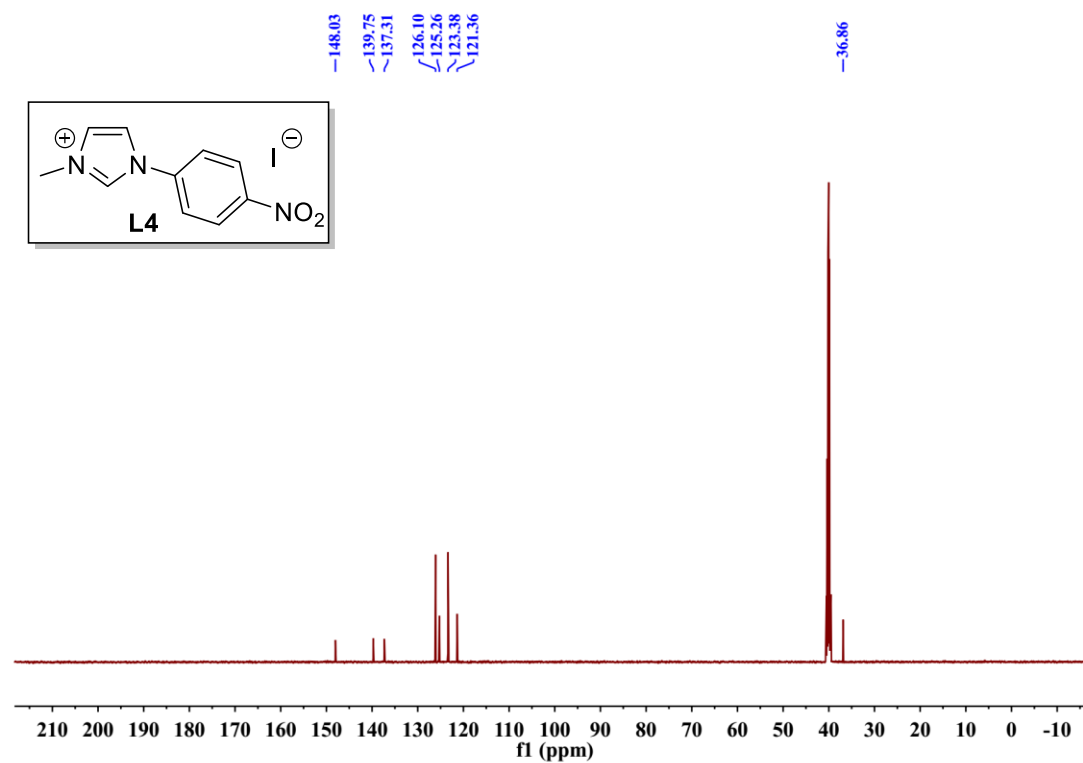
➤ ¹³C NMR spectrum for L3



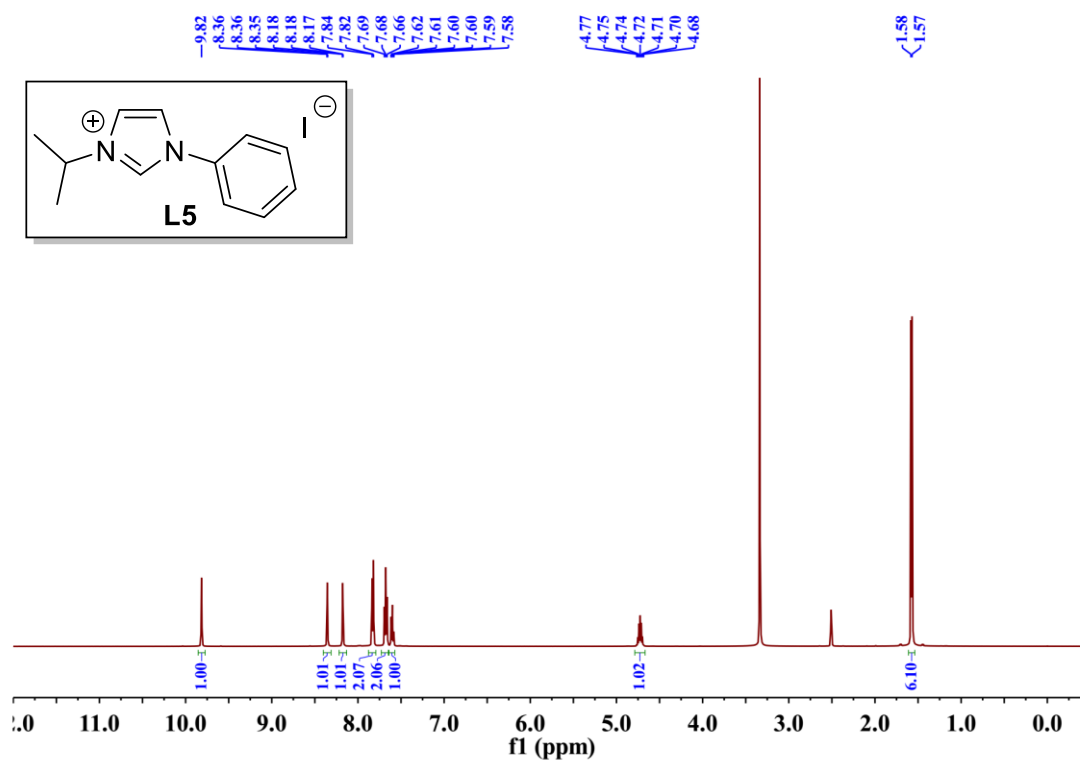
➤ ¹H NMR spectrum for L4



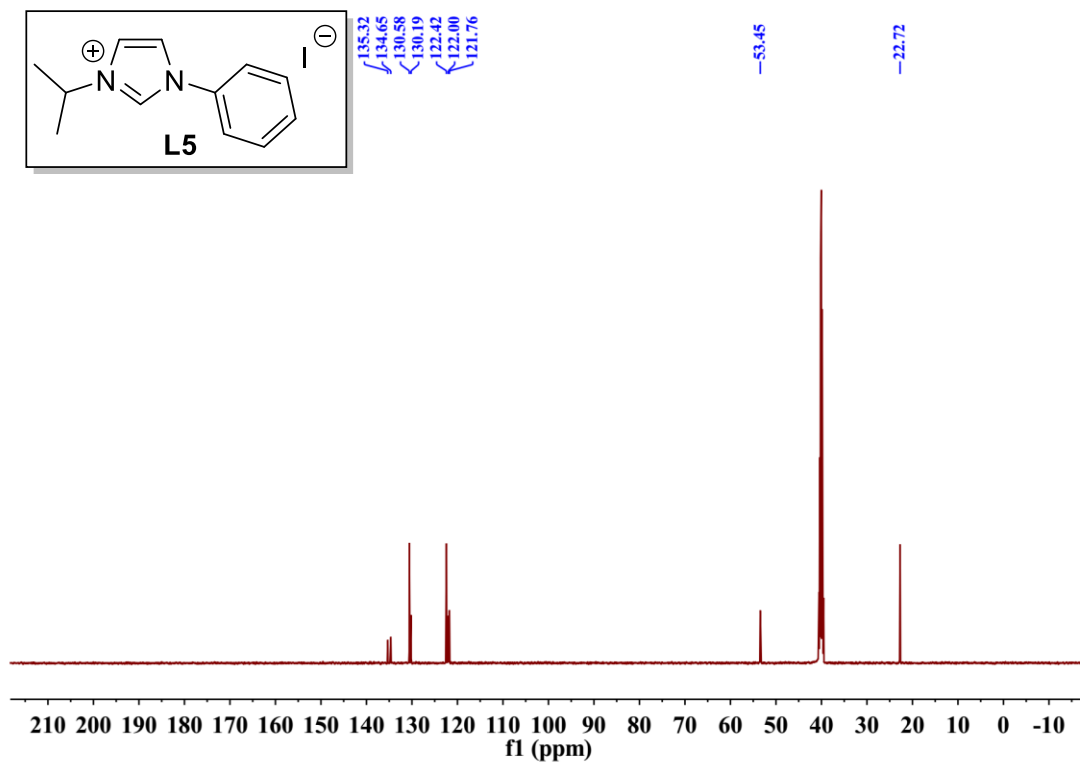
➤ ¹³C NMR spectrum for L4



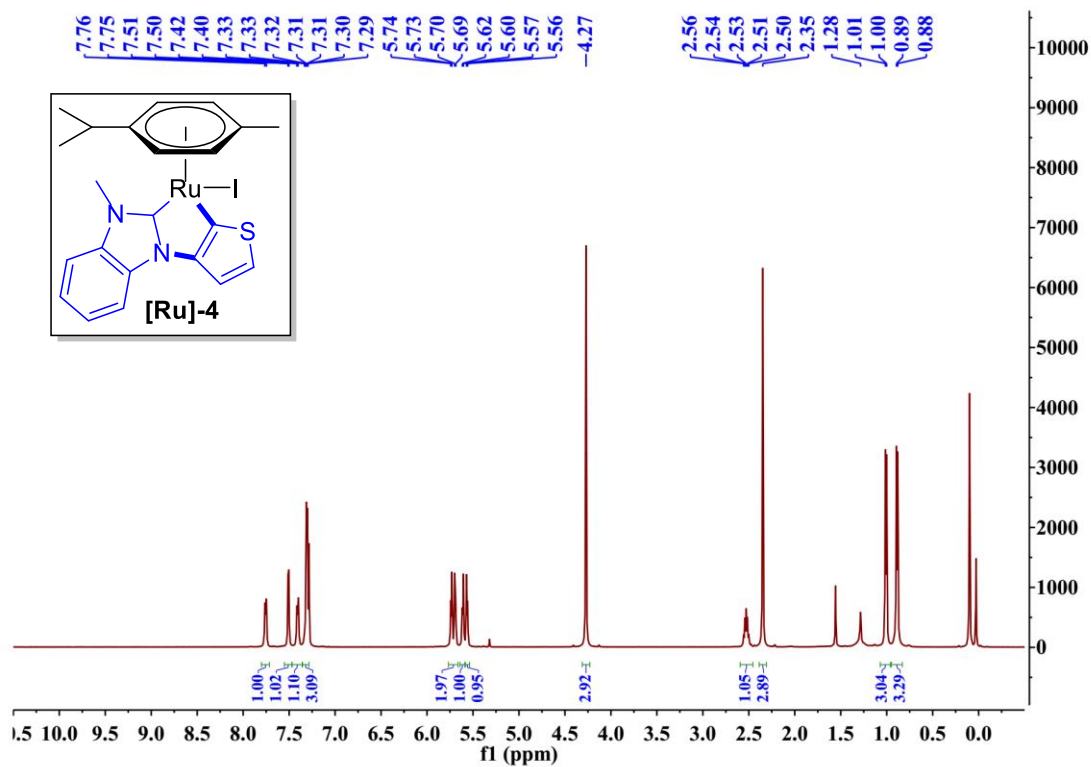
➤ ¹H NMR spectrum for **L5**



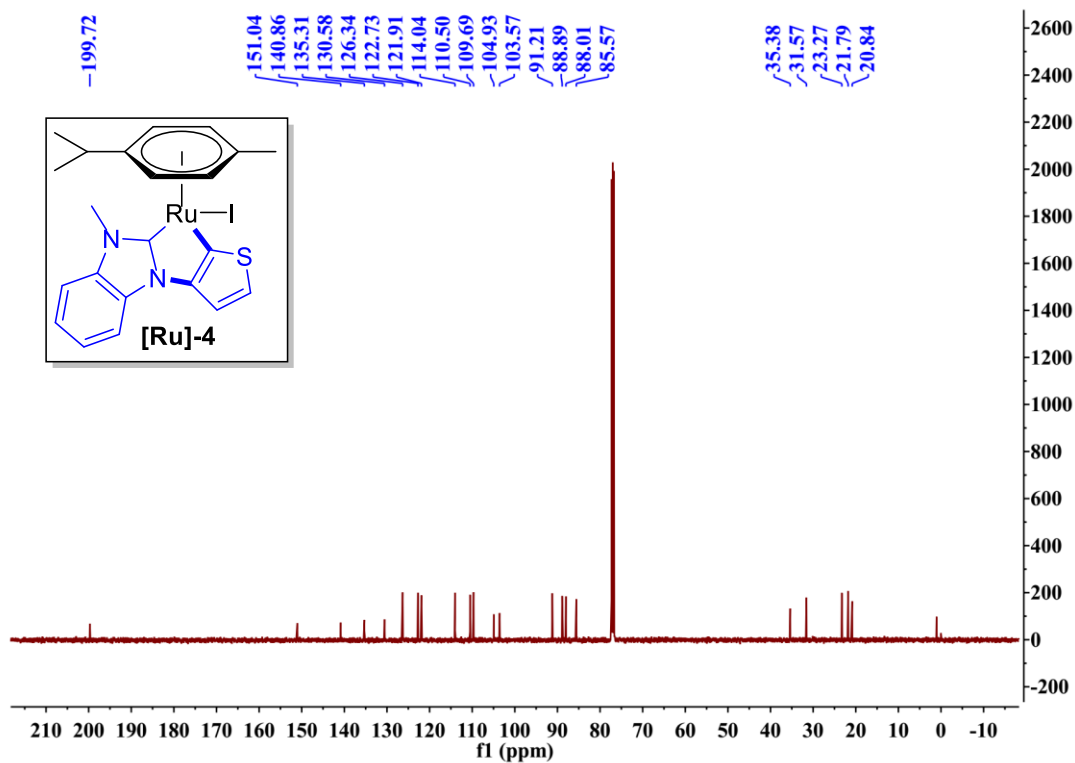
➤ ¹³C NMR spectrum for **L5**



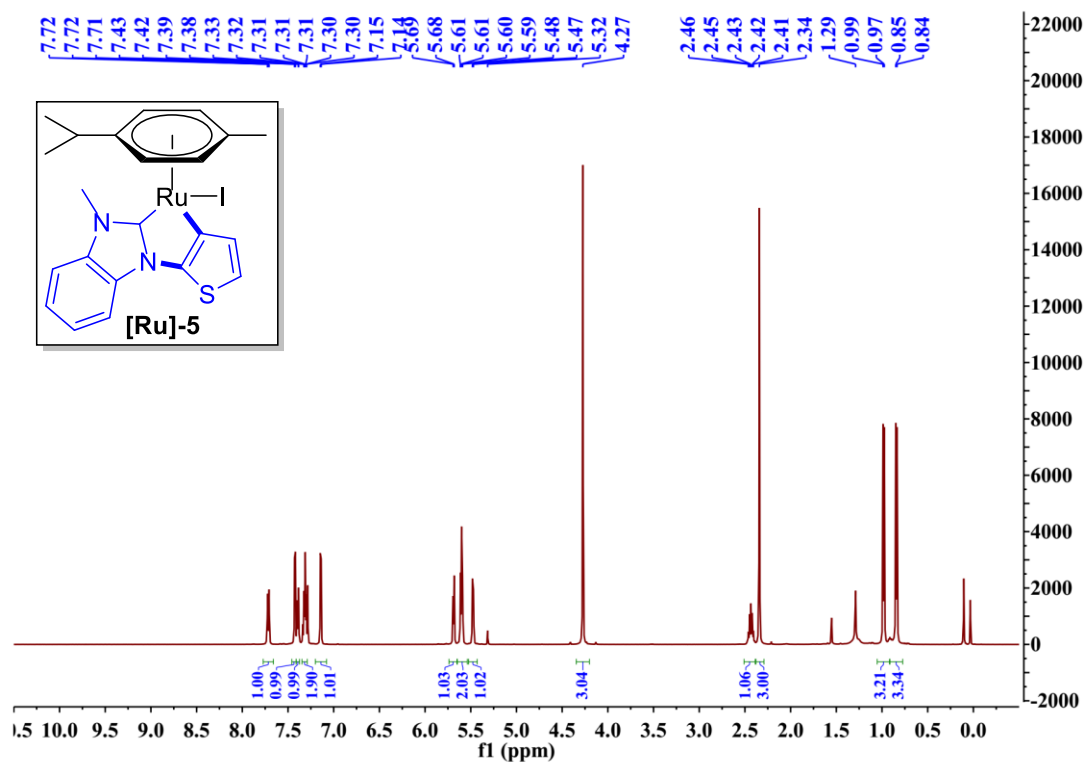
➤ ^1H NMR spectrum for [Ru]-4



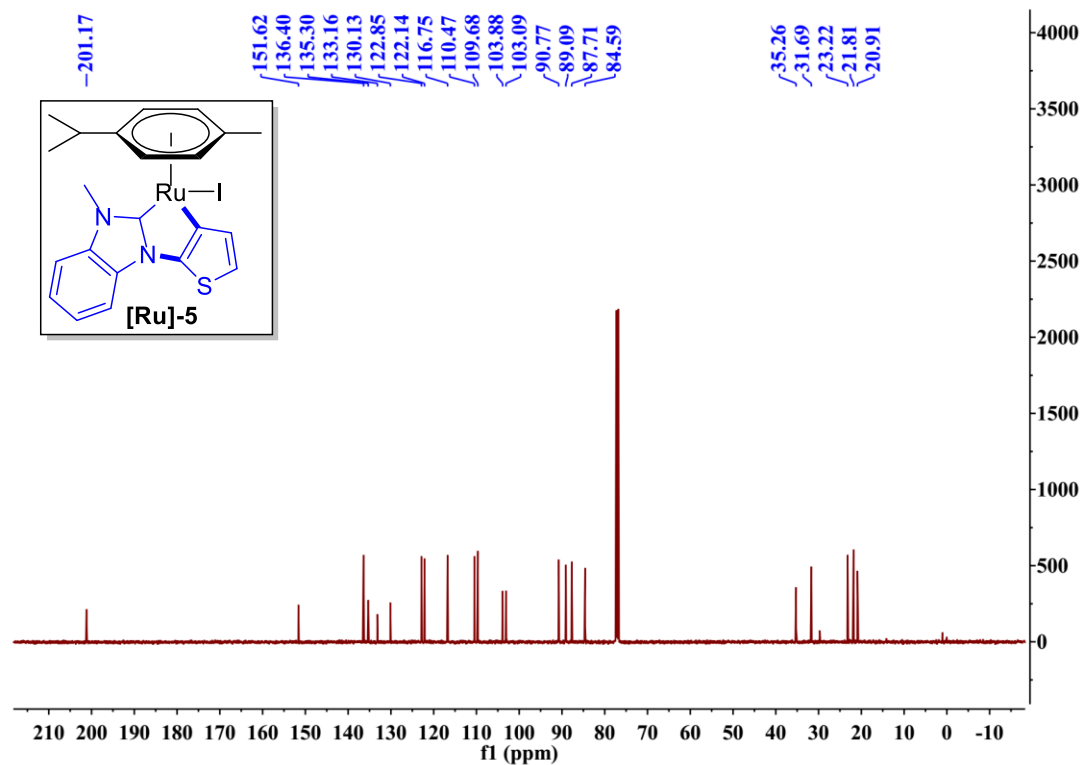
➤ ^{13}C NMR spectrum for [Ru]-4



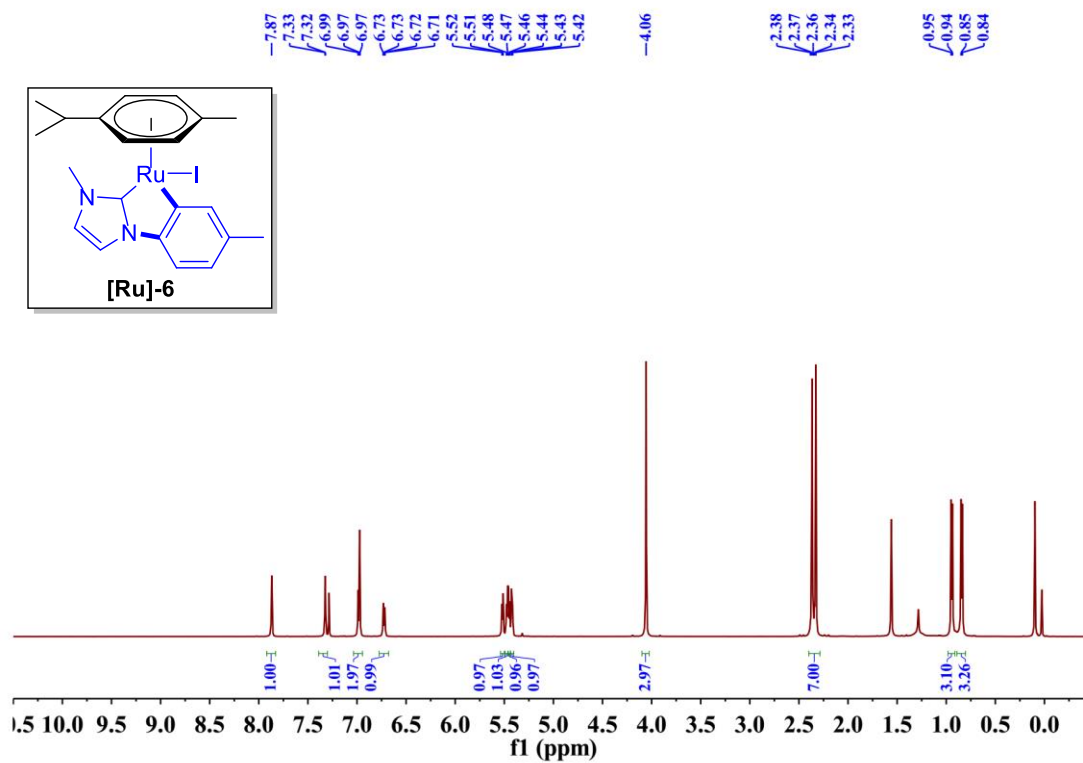
➤ ¹H NMR spectrum for [Ru]-5



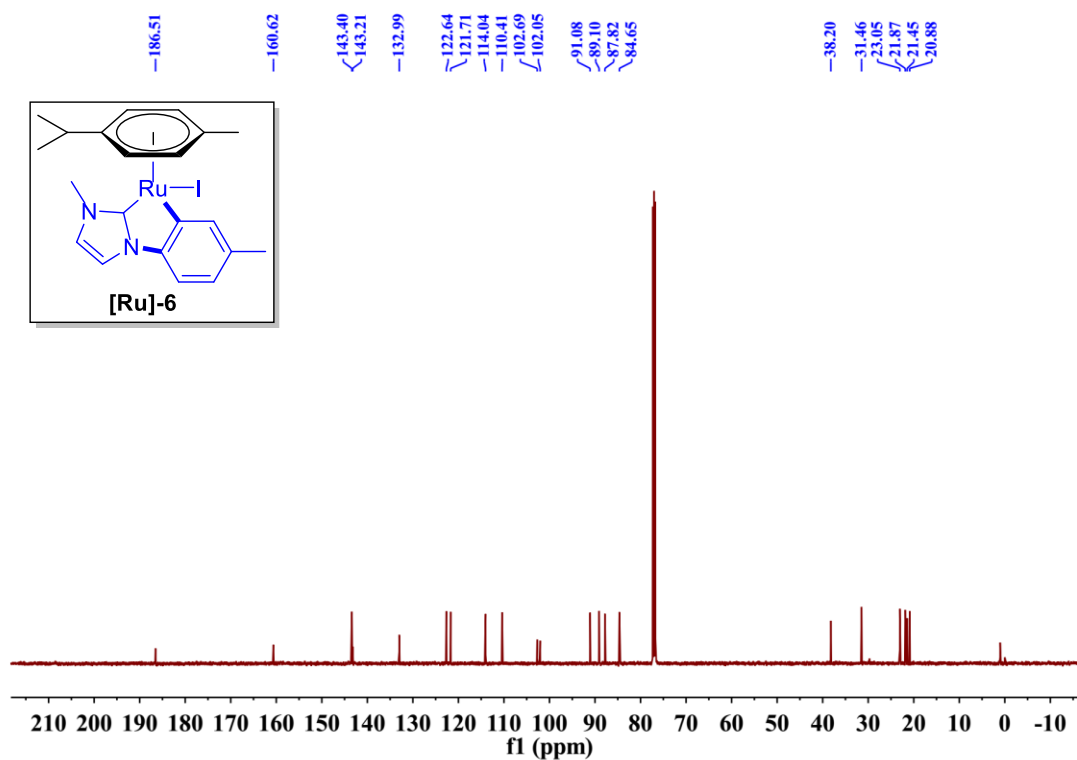
➤ ¹³C NMR spectrum for [Ru]-5



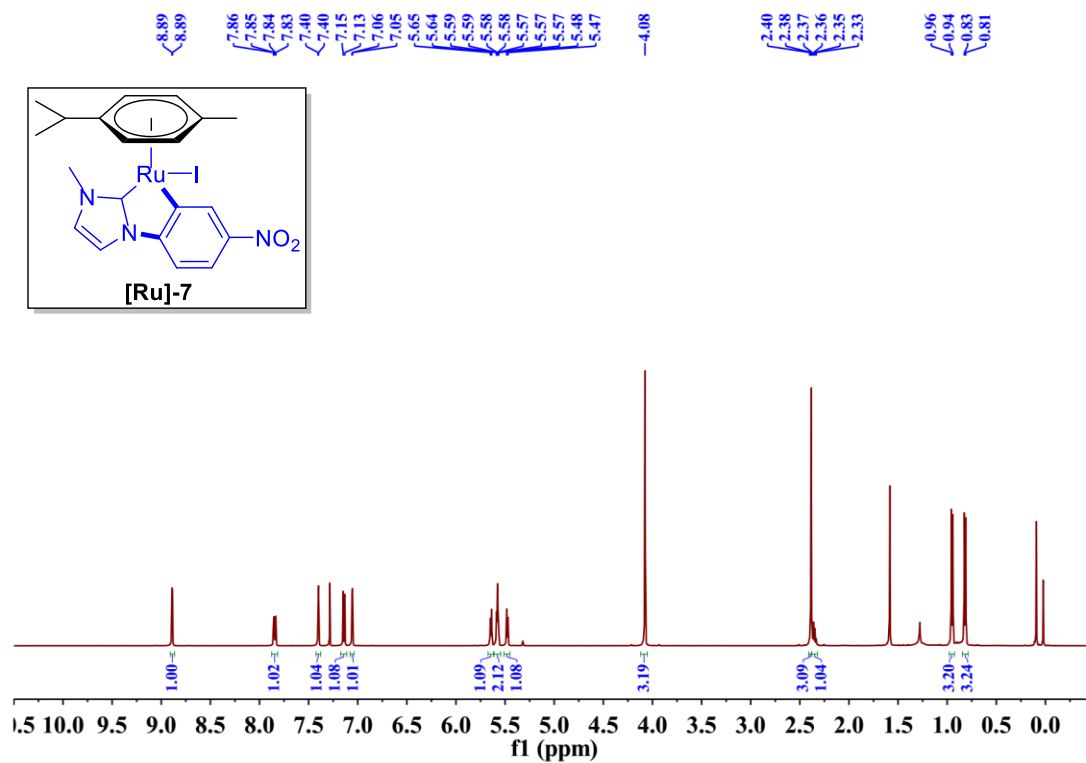
➤ ^1H NMR spectrum for [Ru]-6



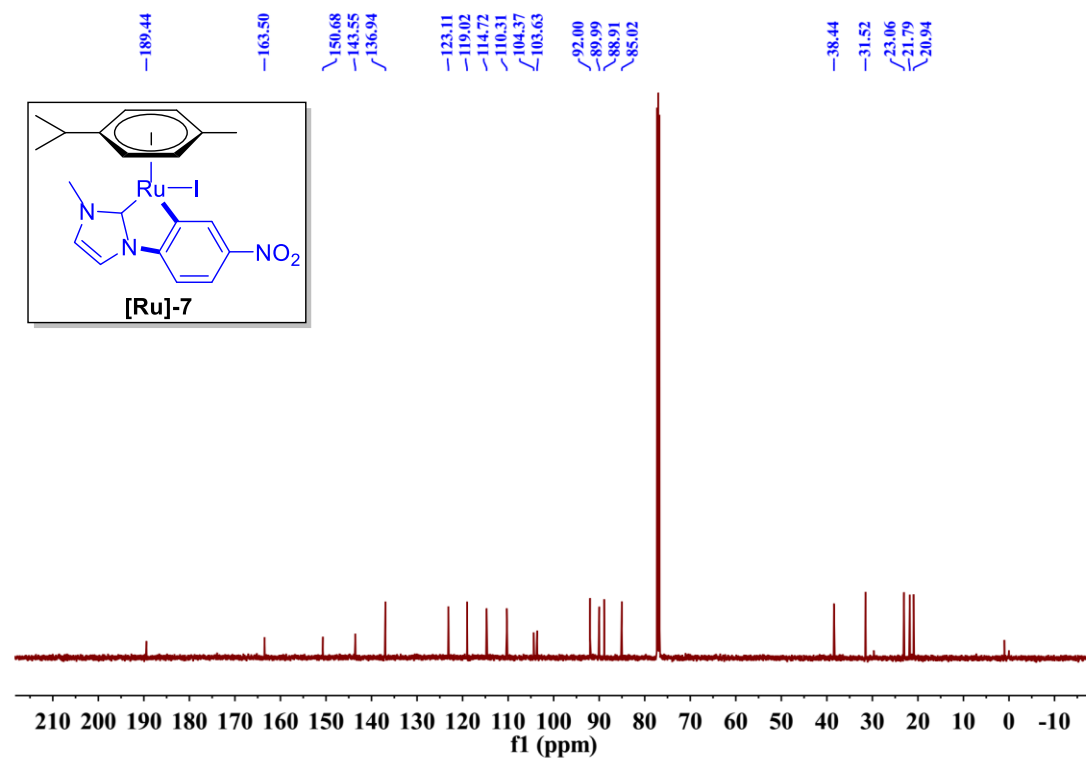
➤ ^{13}C NMR spectrum for [Ru]-6



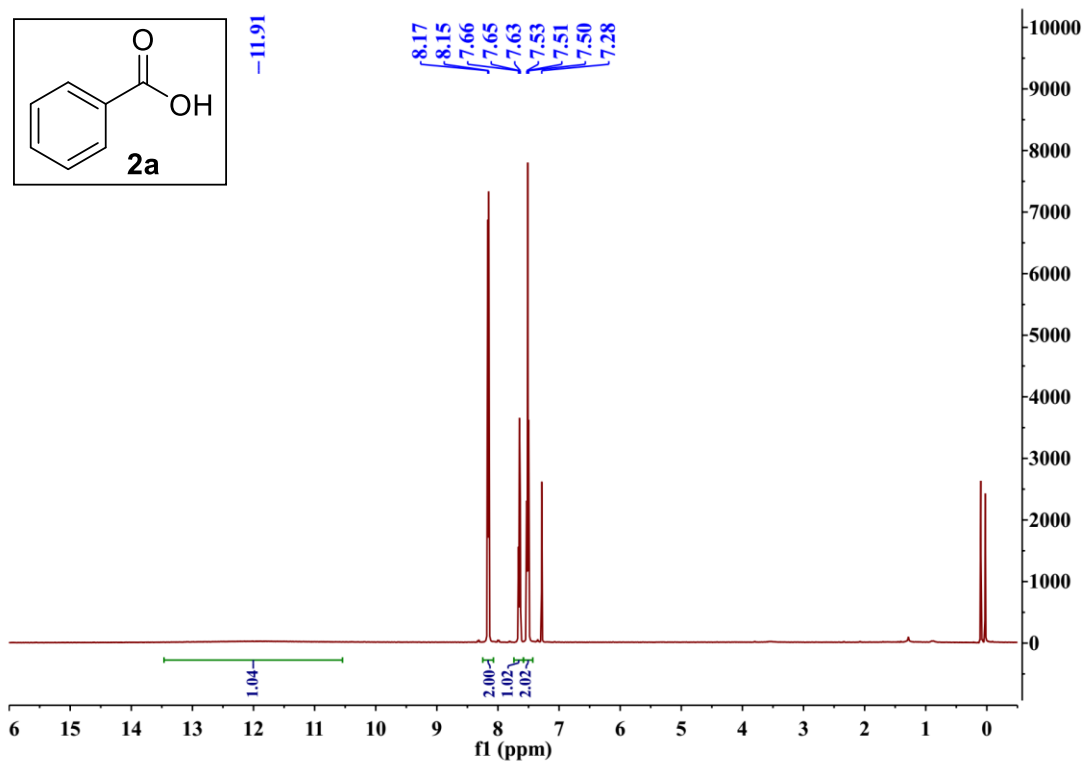
➤ ¹H NMR spectrum for [Ru]-7



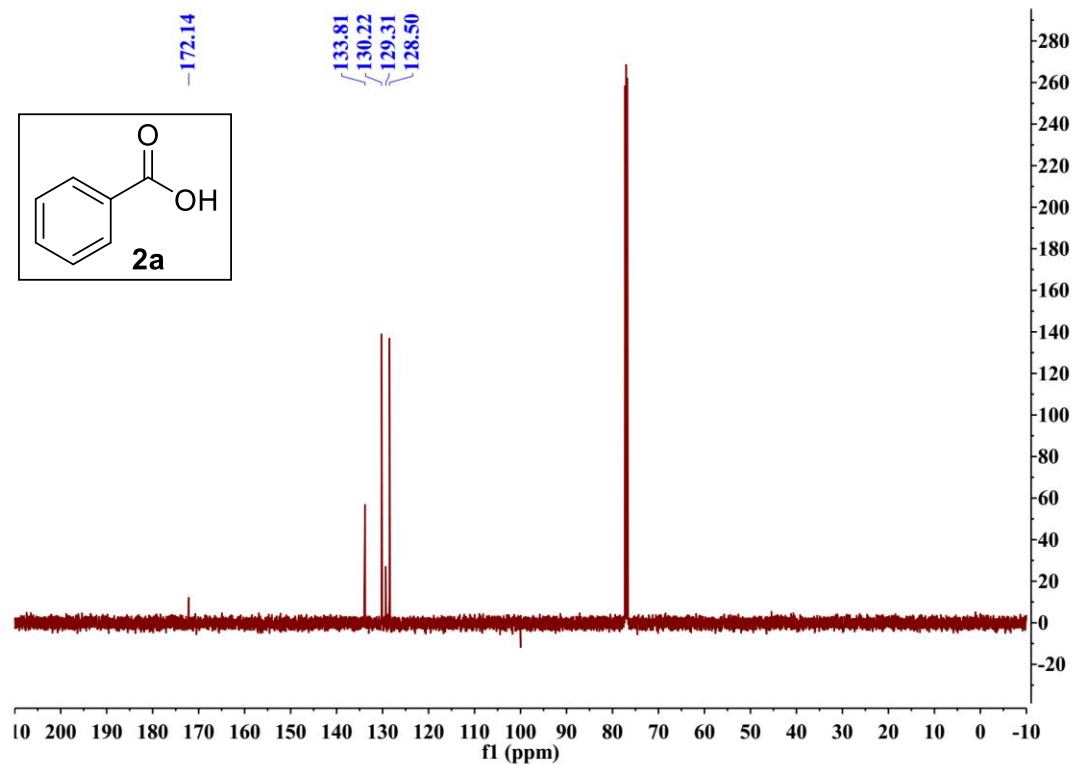
➤ ¹³C NMR spectrum for [Ru]-7



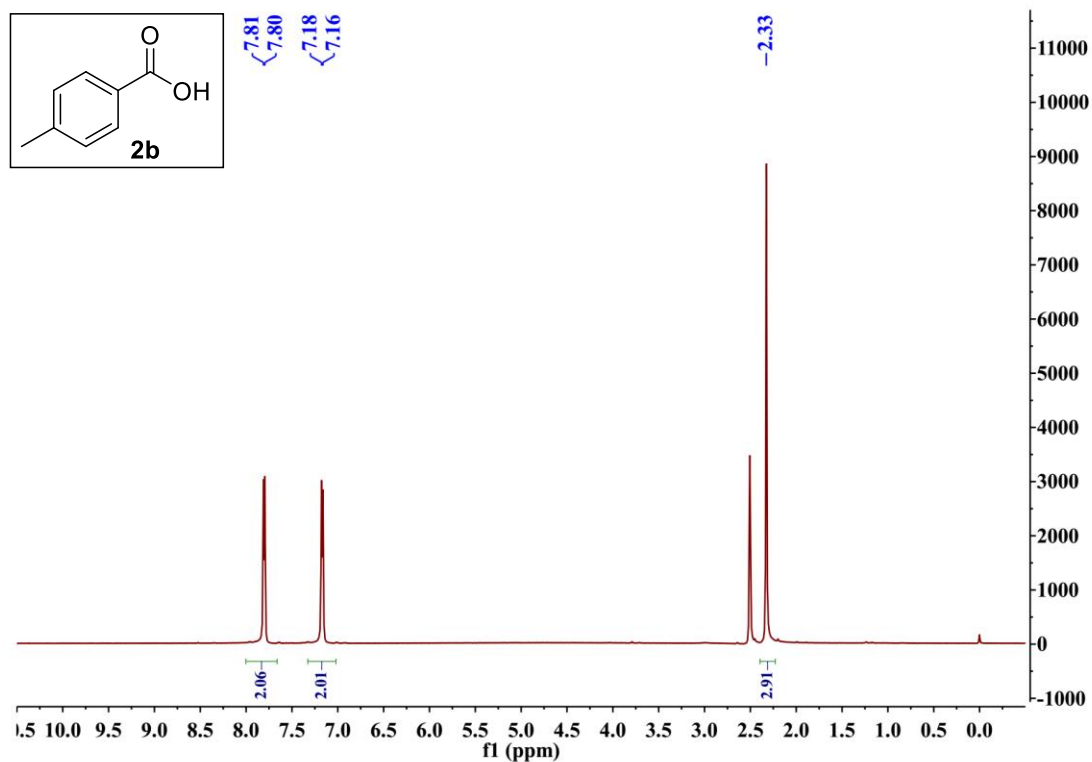
➤ ¹H NMR spectrum for **2a**



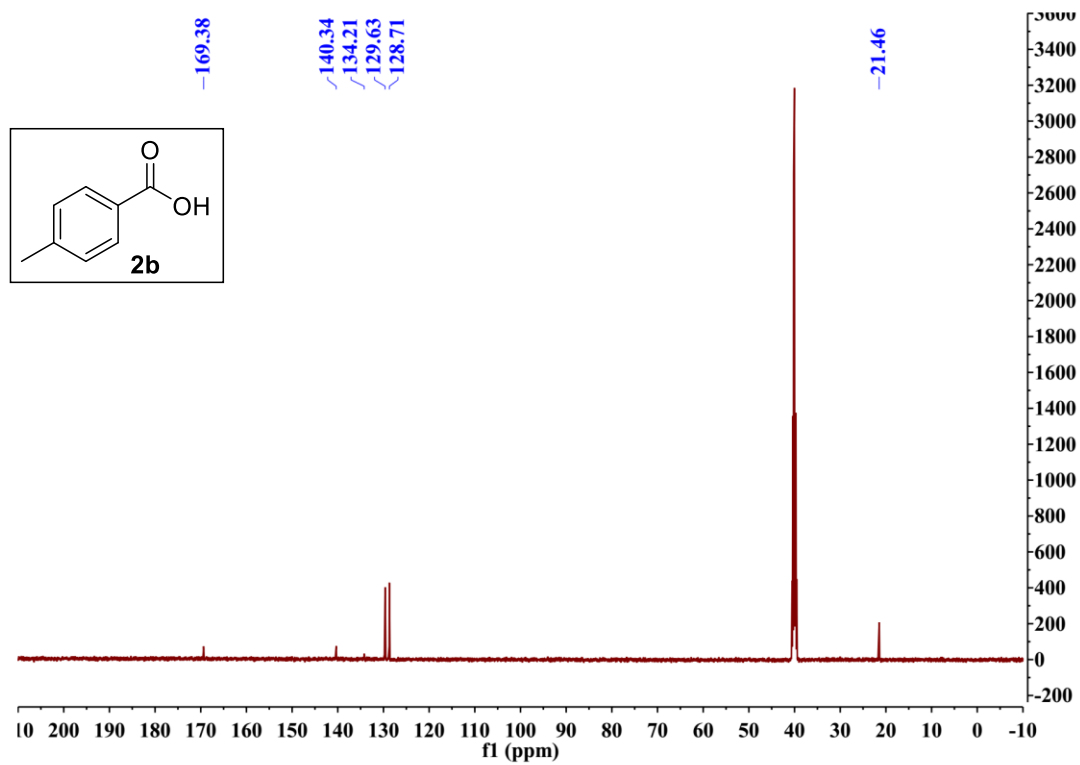
➤ ¹³C NMR spectrum for **2a**



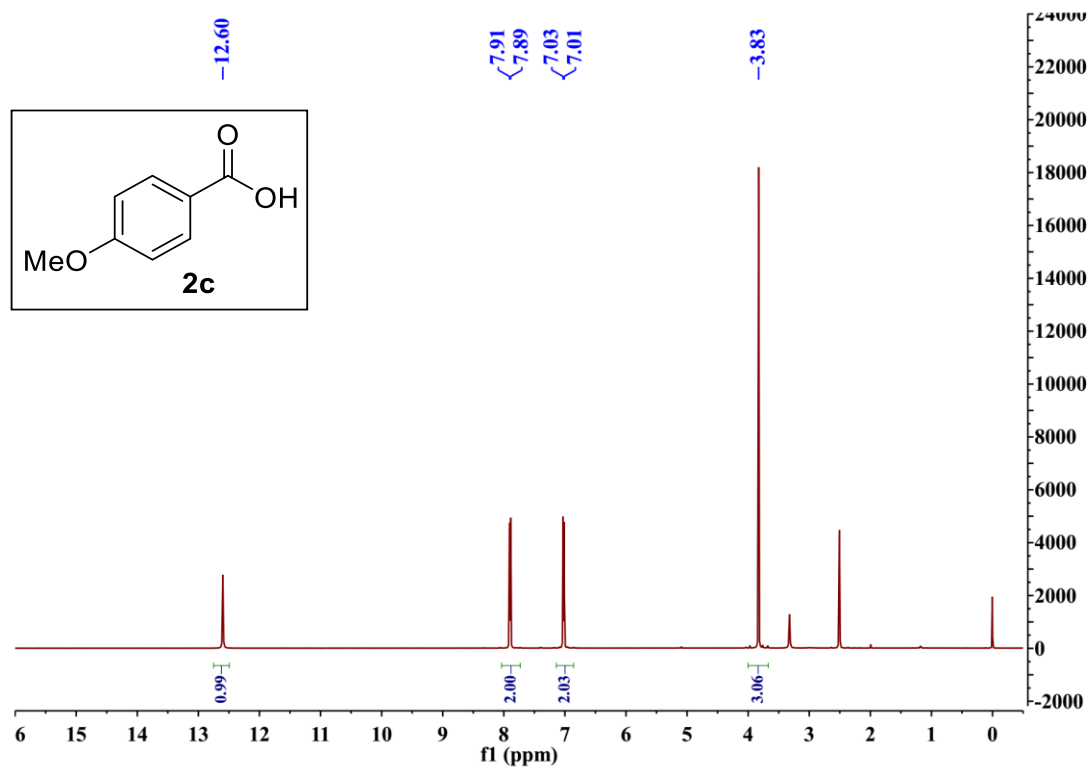
➤ ¹H NMR spectrum for **2b**



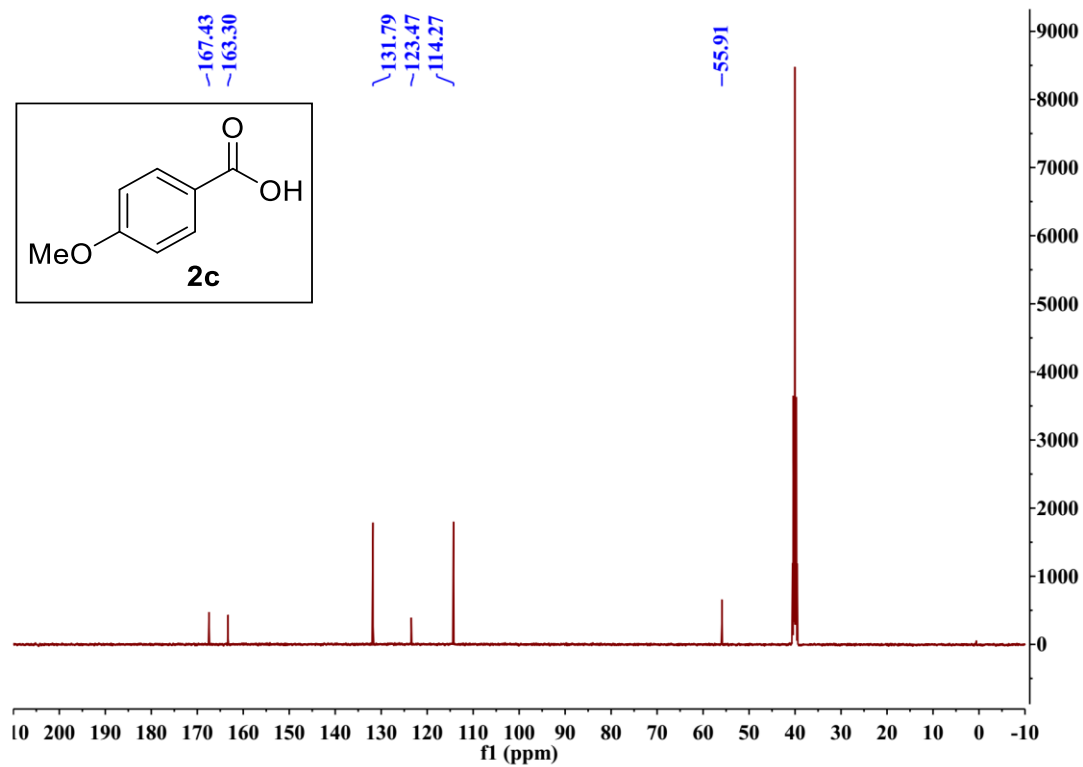
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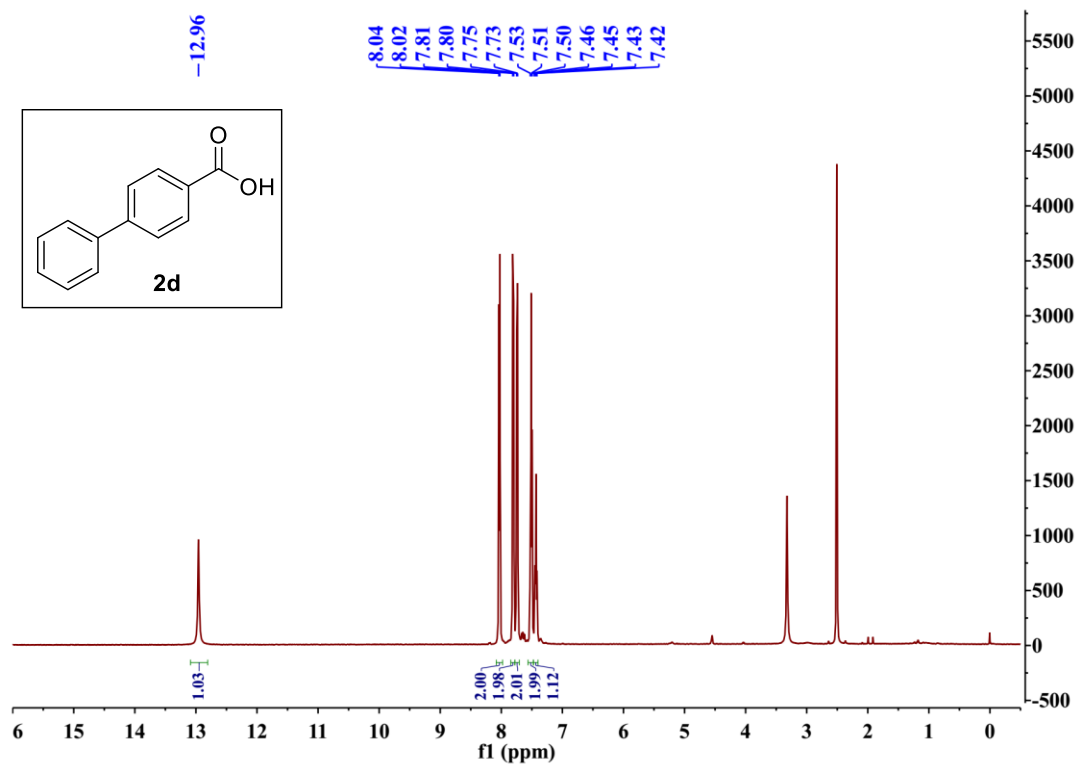
➤ ¹H NMR spectrum for **2c**



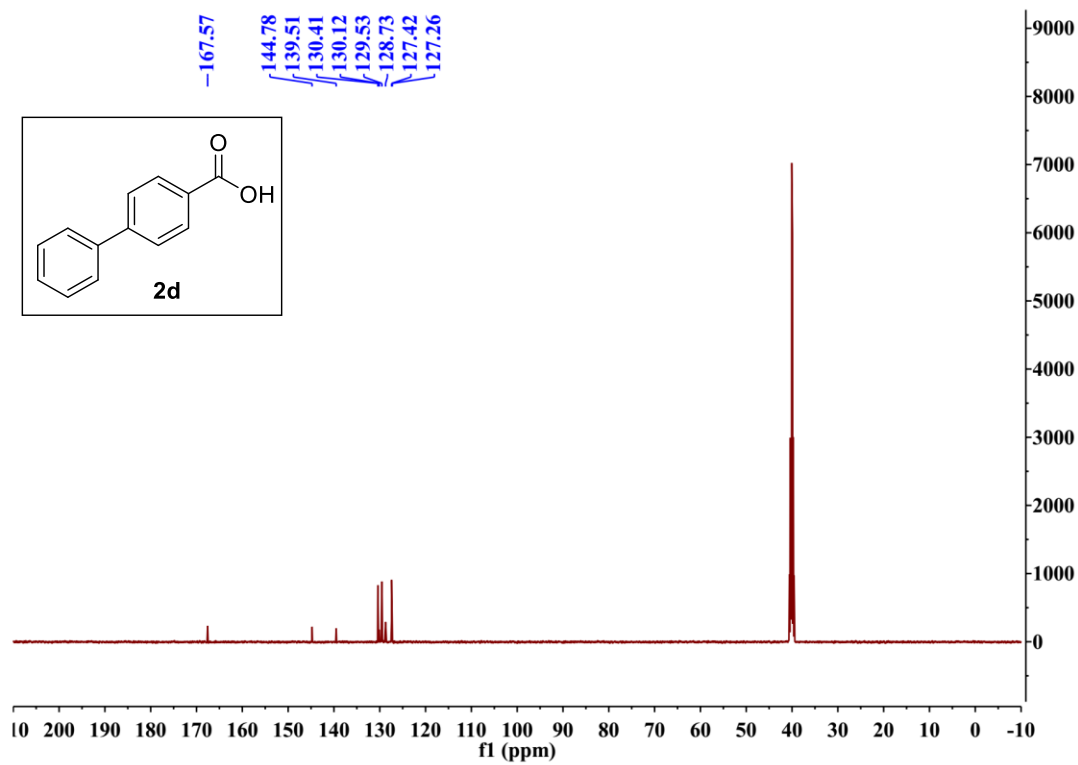
➤ ¹³C NMR spectrum for **2c**



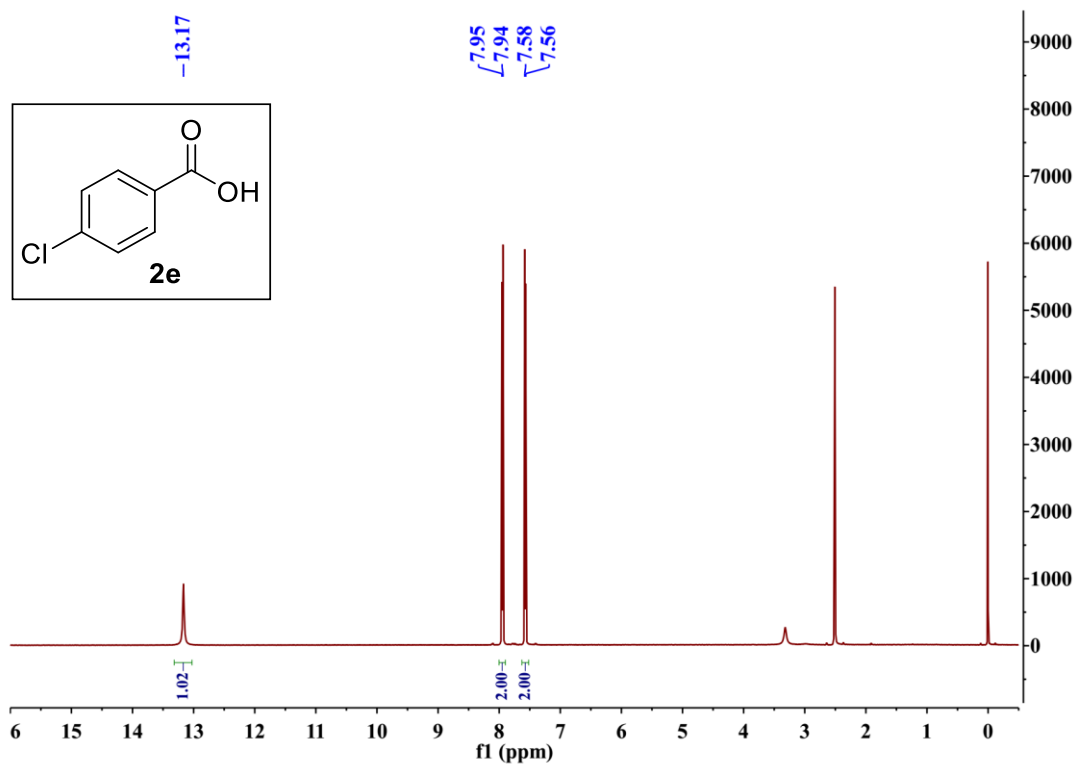
➤ ¹H NMR spectrum for **2d**



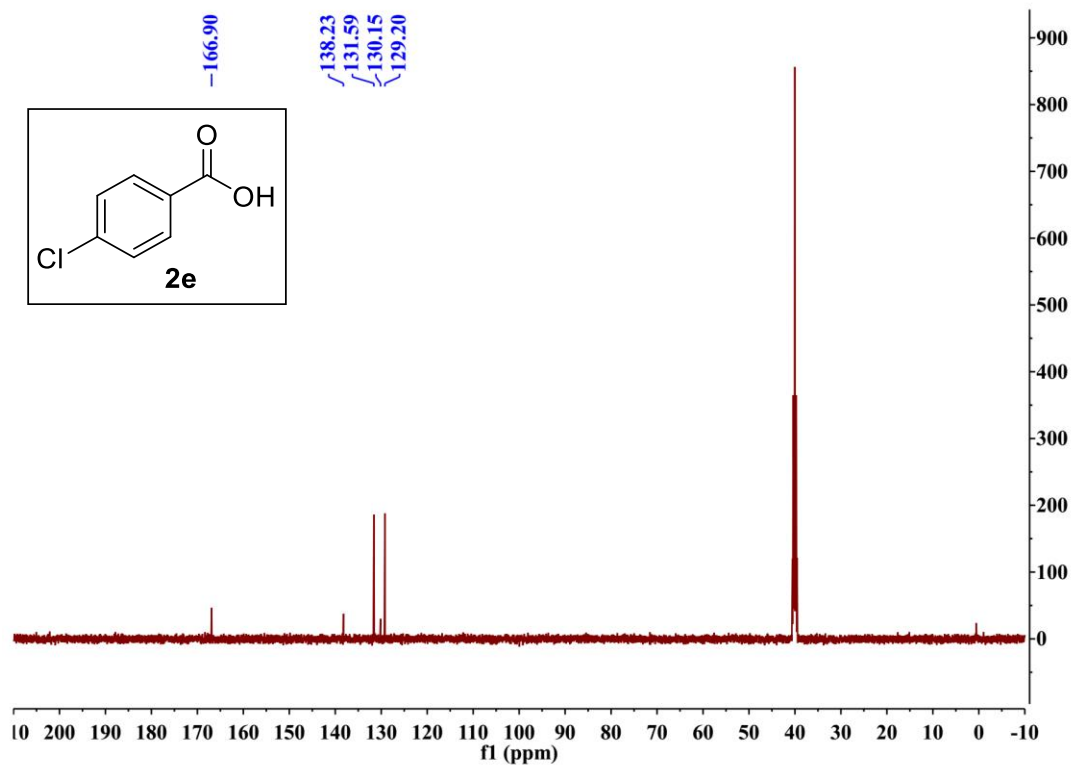
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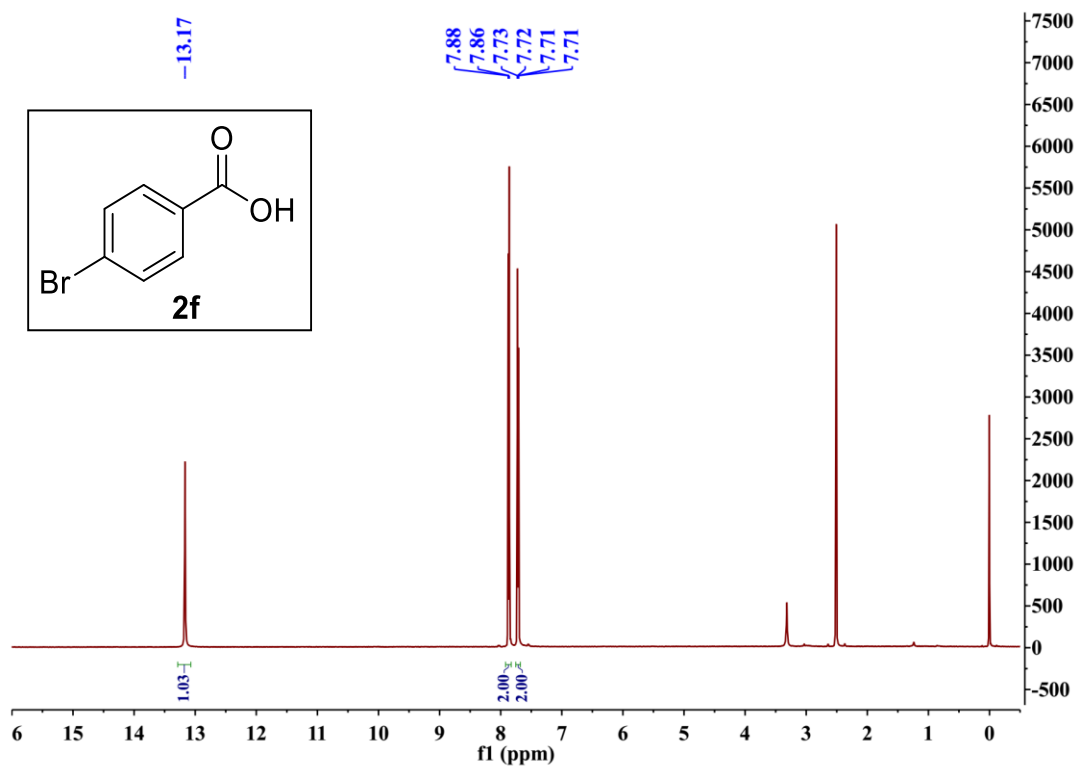
➤ ^1H NMR spectrum for **2e**



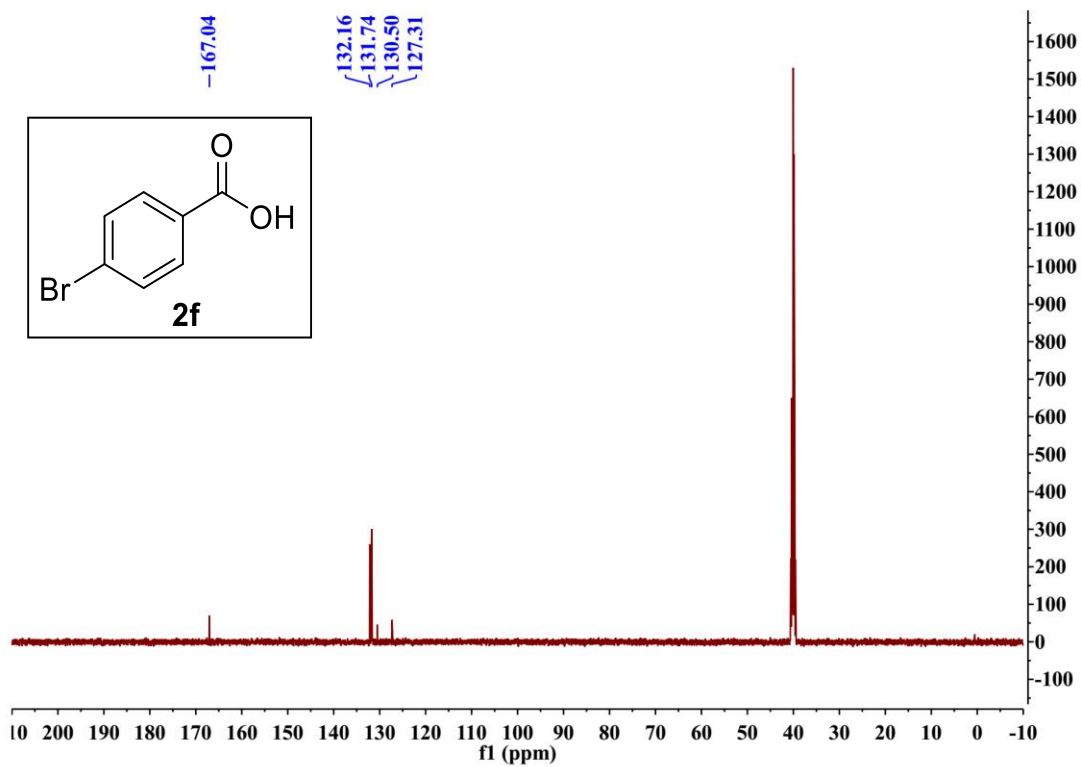
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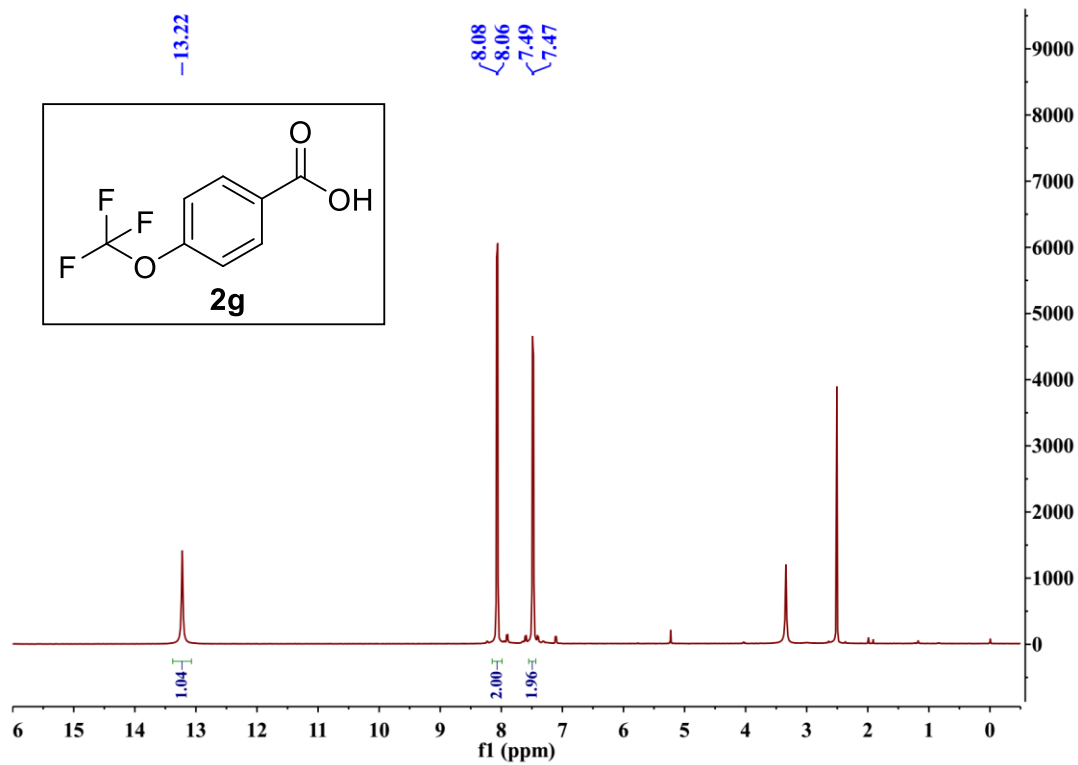
➤ ¹H NMR spectrum for **2f**



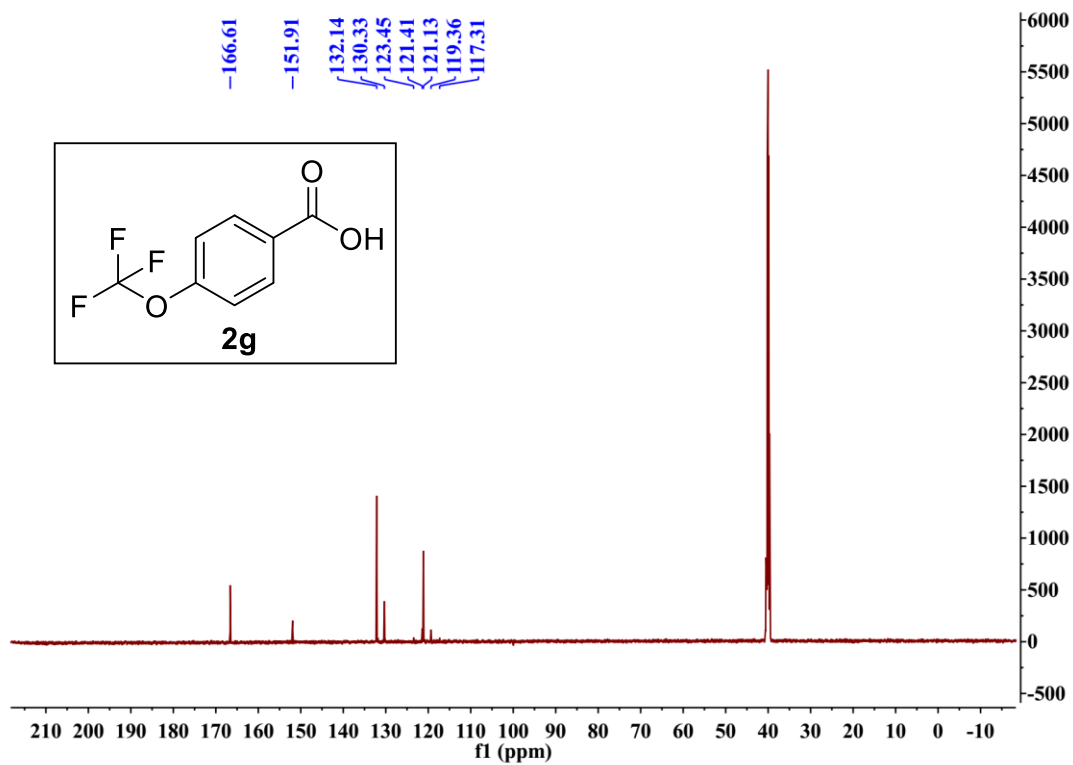
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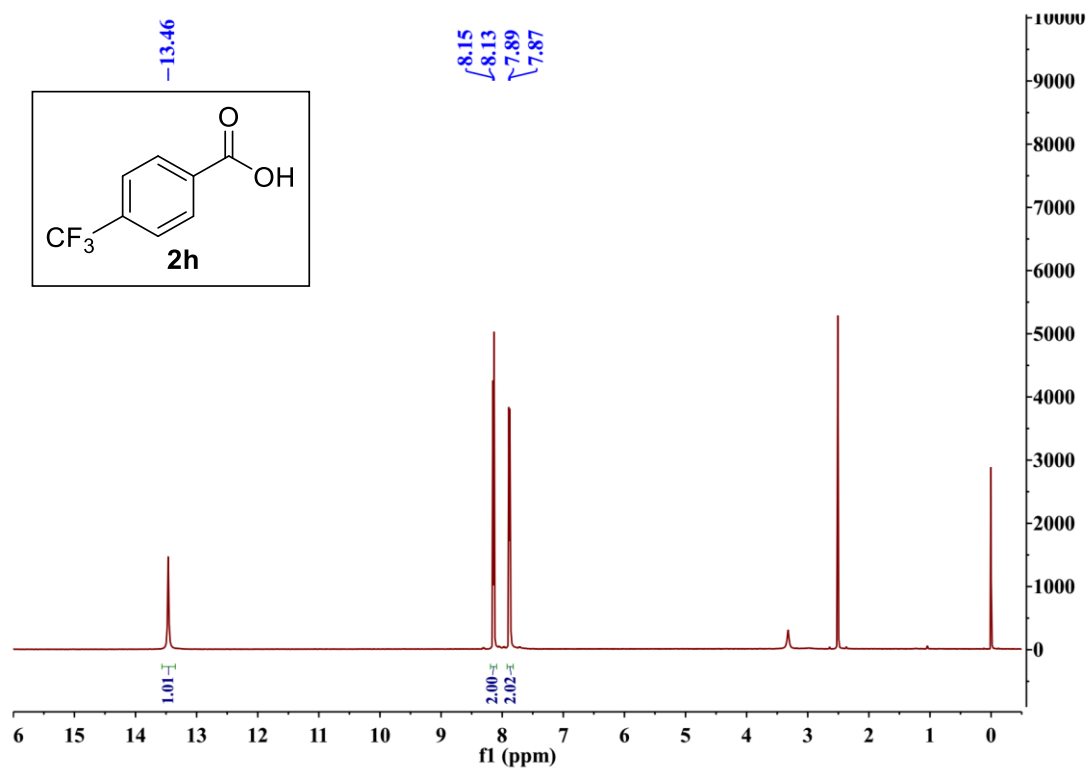
➤ ¹H NMR spectrum for **2g**



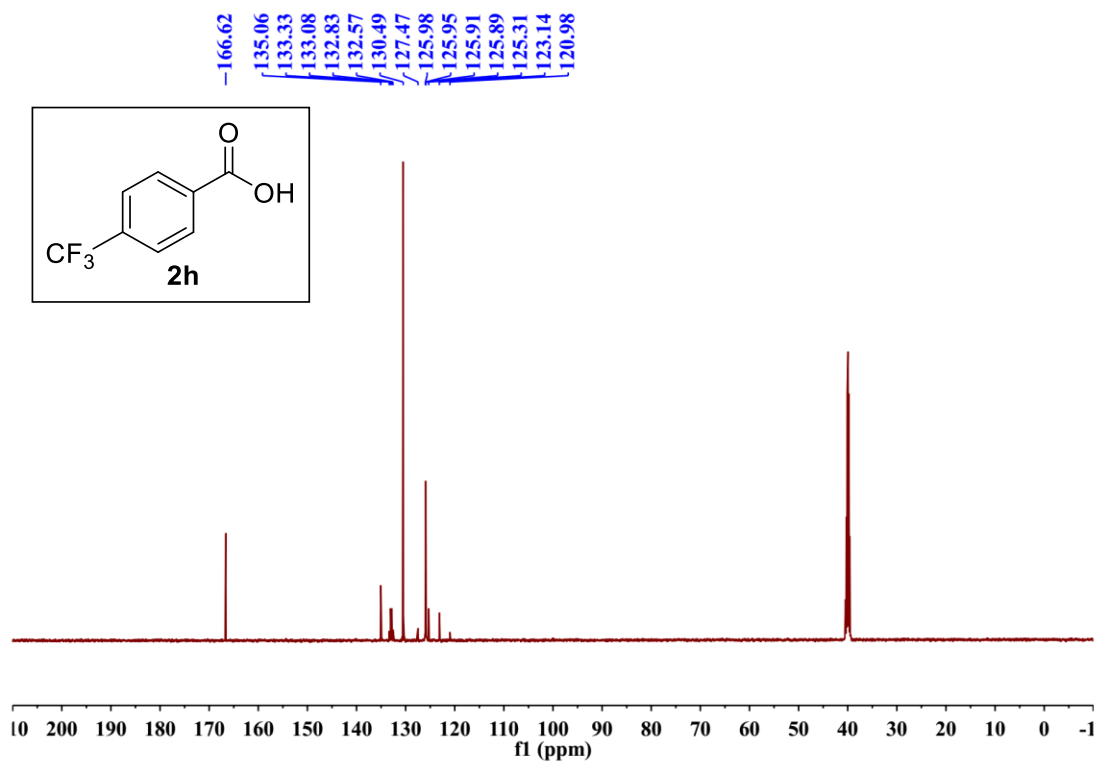
➤ ¹³C NMR spectrum for **2g**



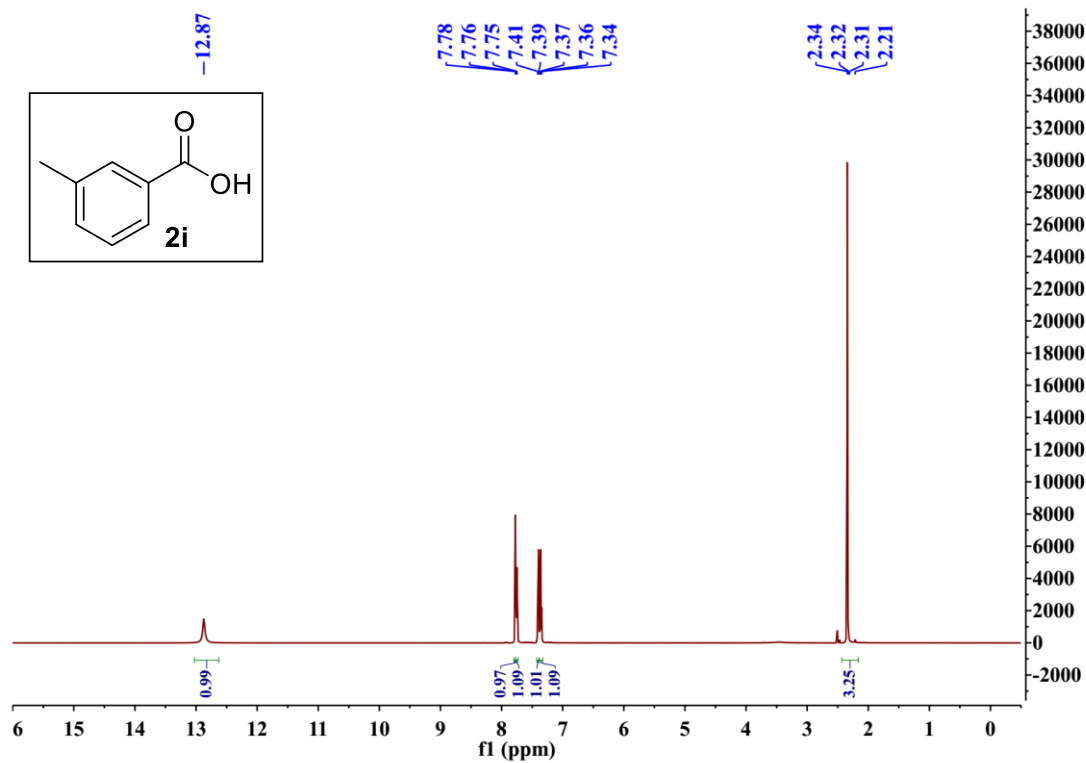
➤ ¹H NMR spectrum for **2h**



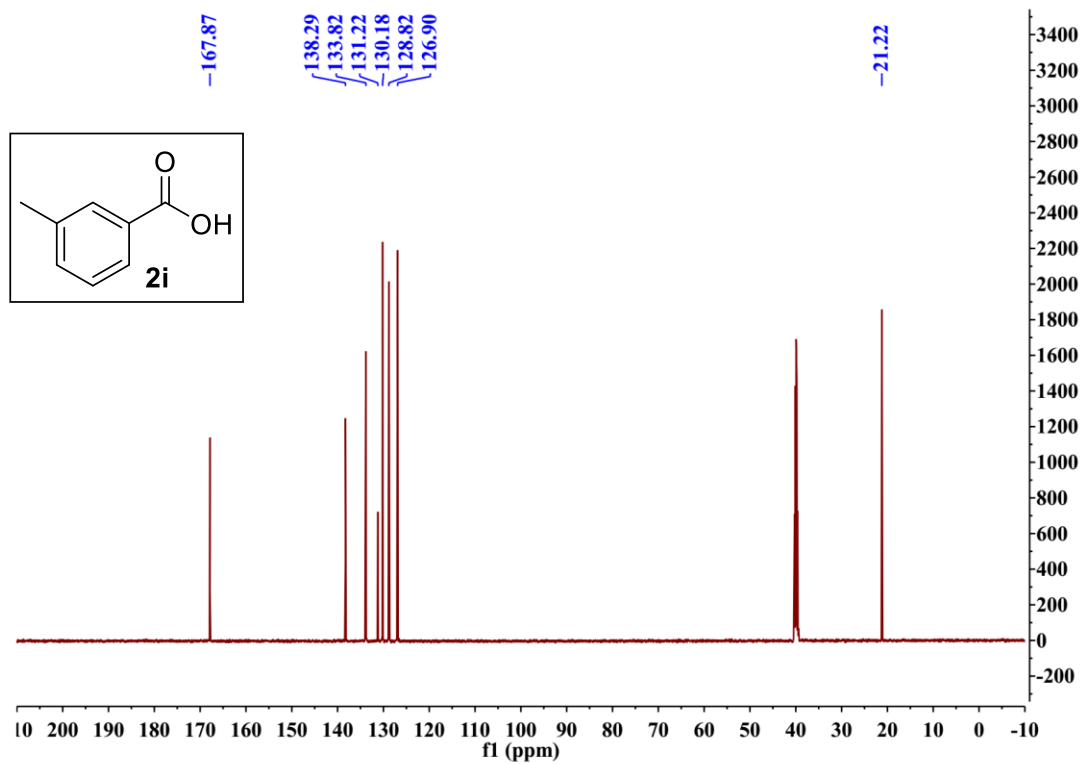
➤ ¹³C NMR spectrum for **2h**



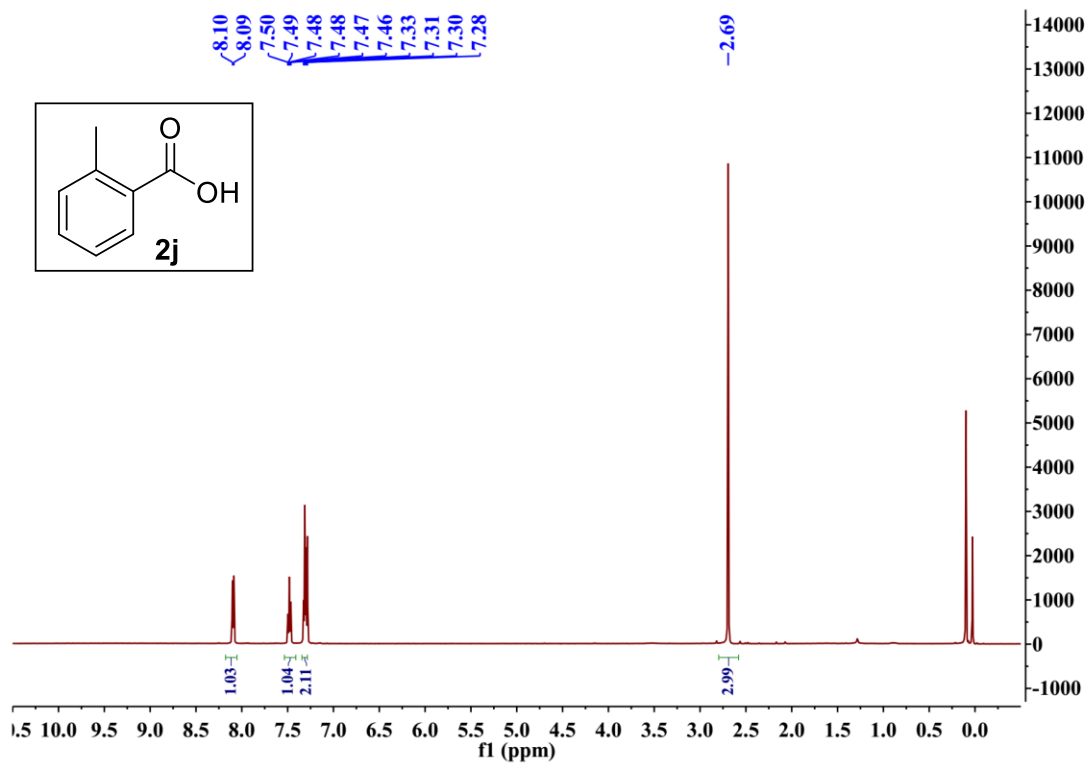
➤ ¹H NMR spectrum for **2i**



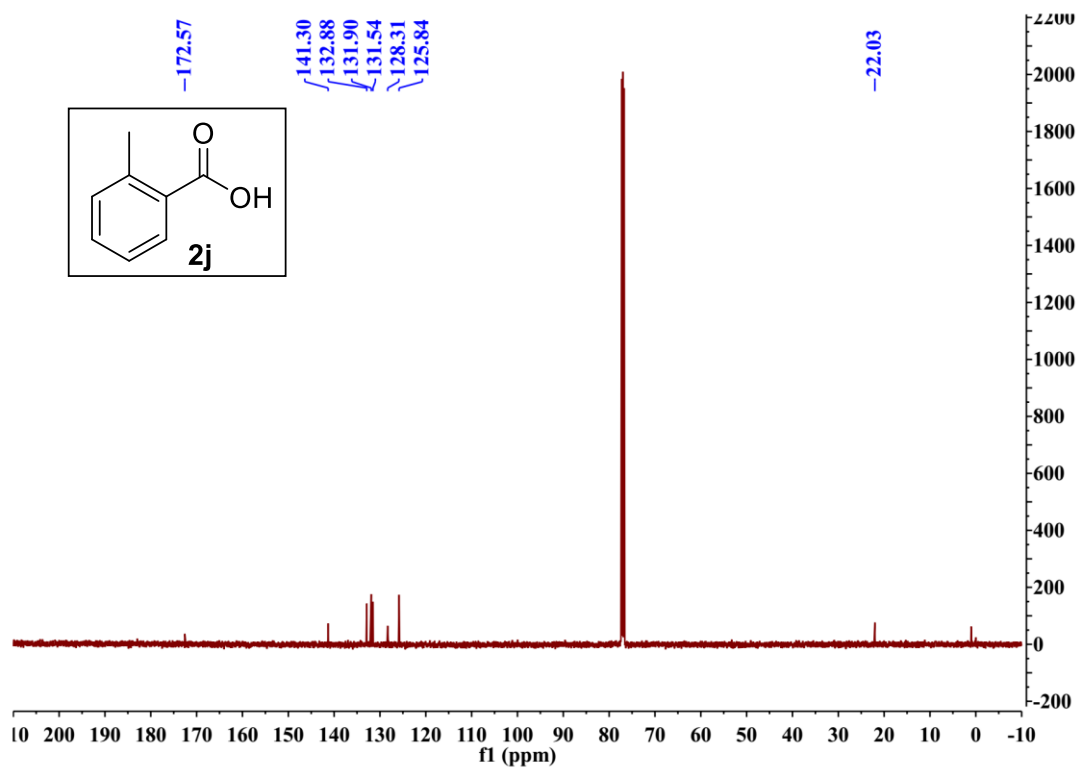
➤ ¹³C NMR spectrum for **2i**



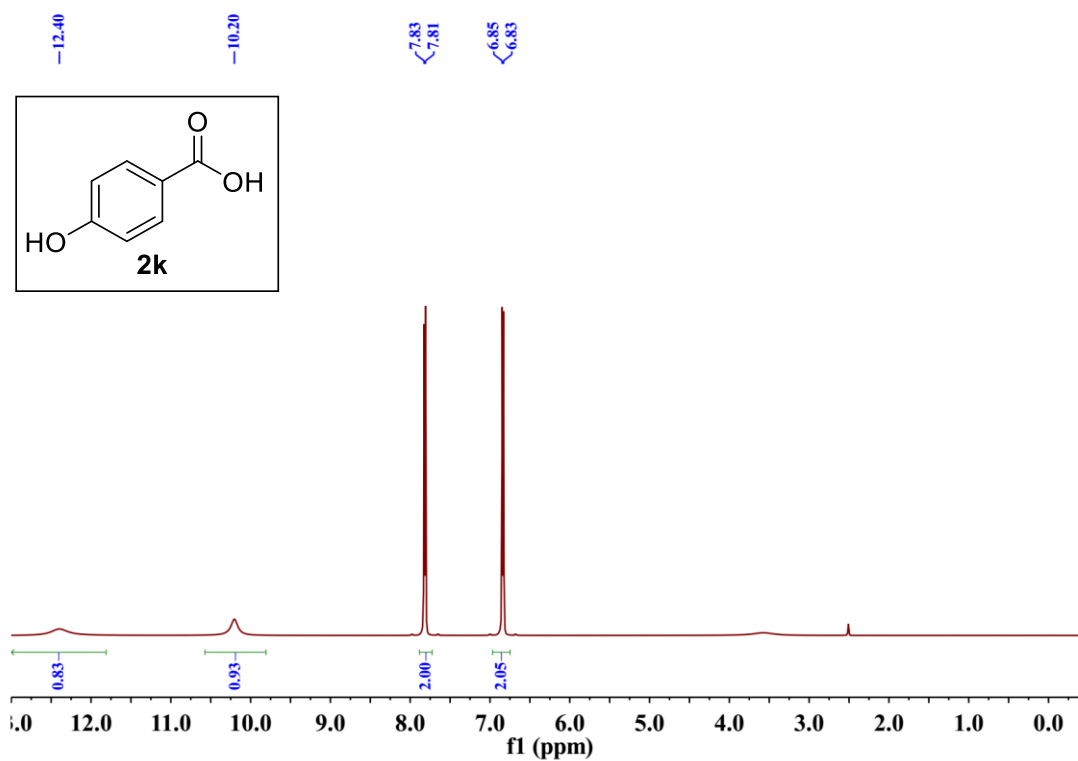
➤ ¹H NMR spectrum for **2j**



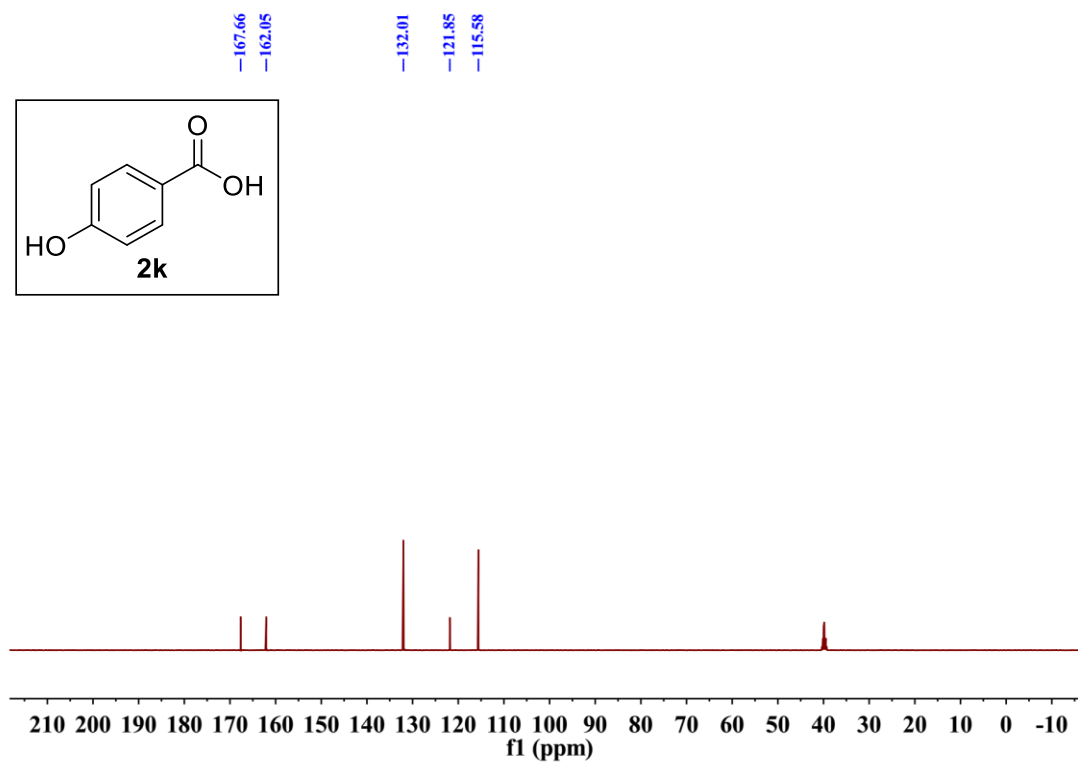
➤ ¹³C NMR spectrum for **2j**



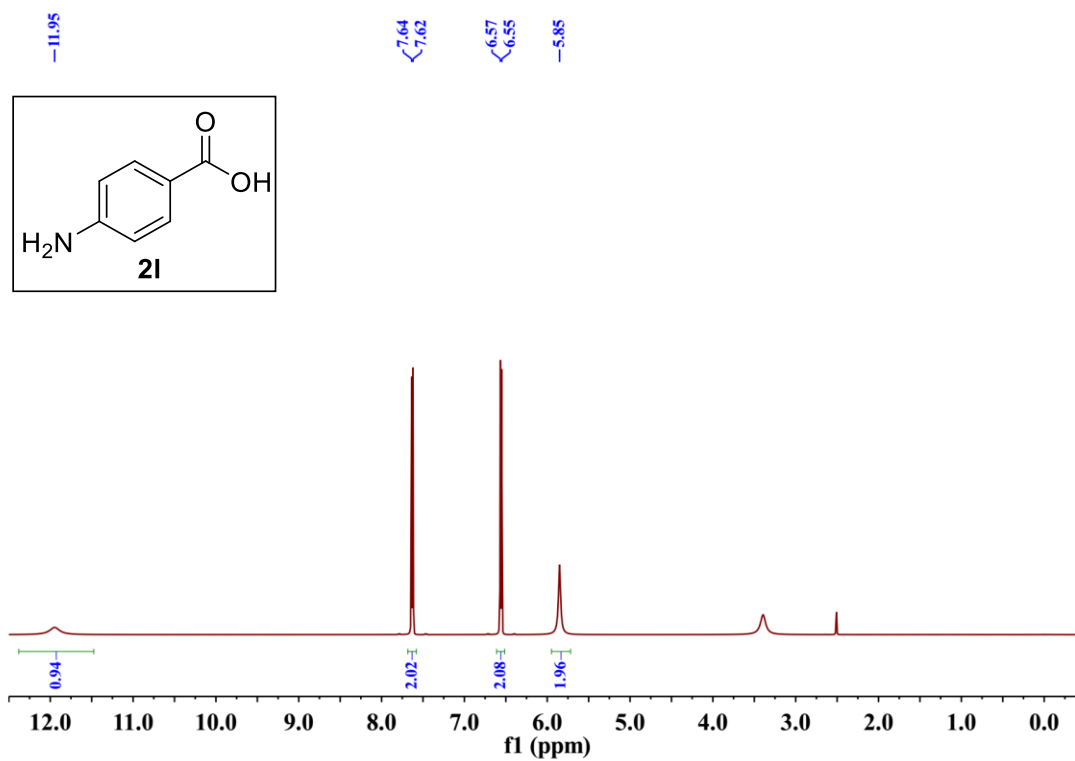
➤ ¹H NMR spectrum for **2k**



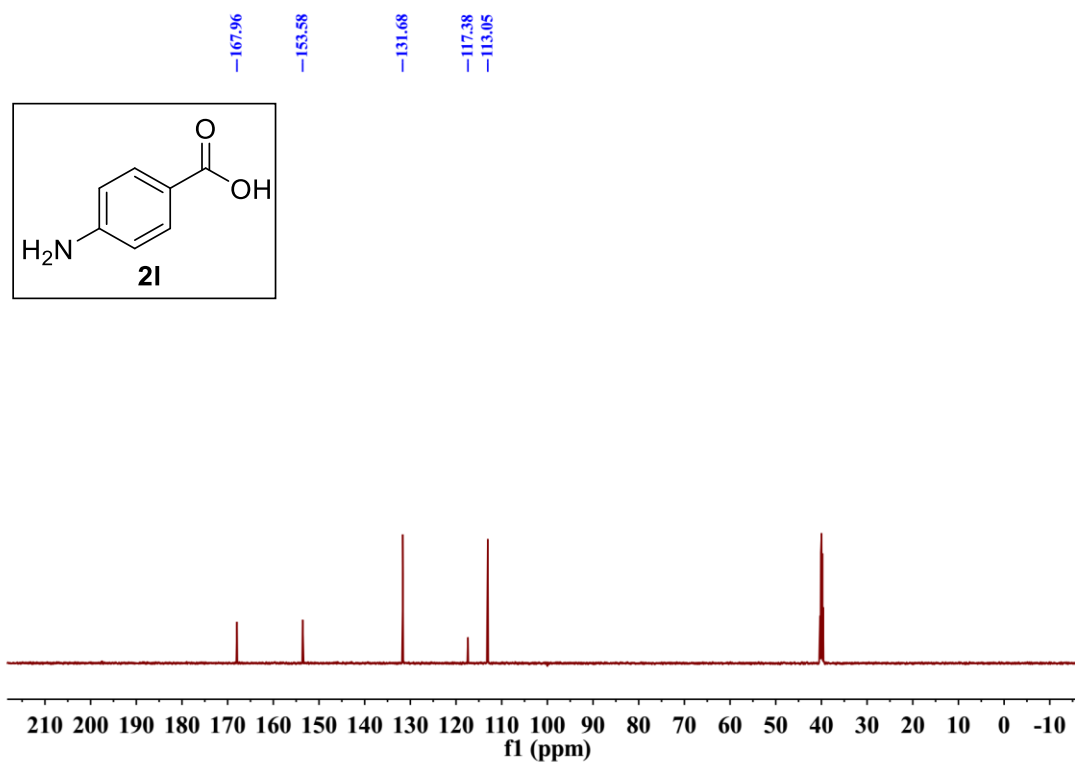
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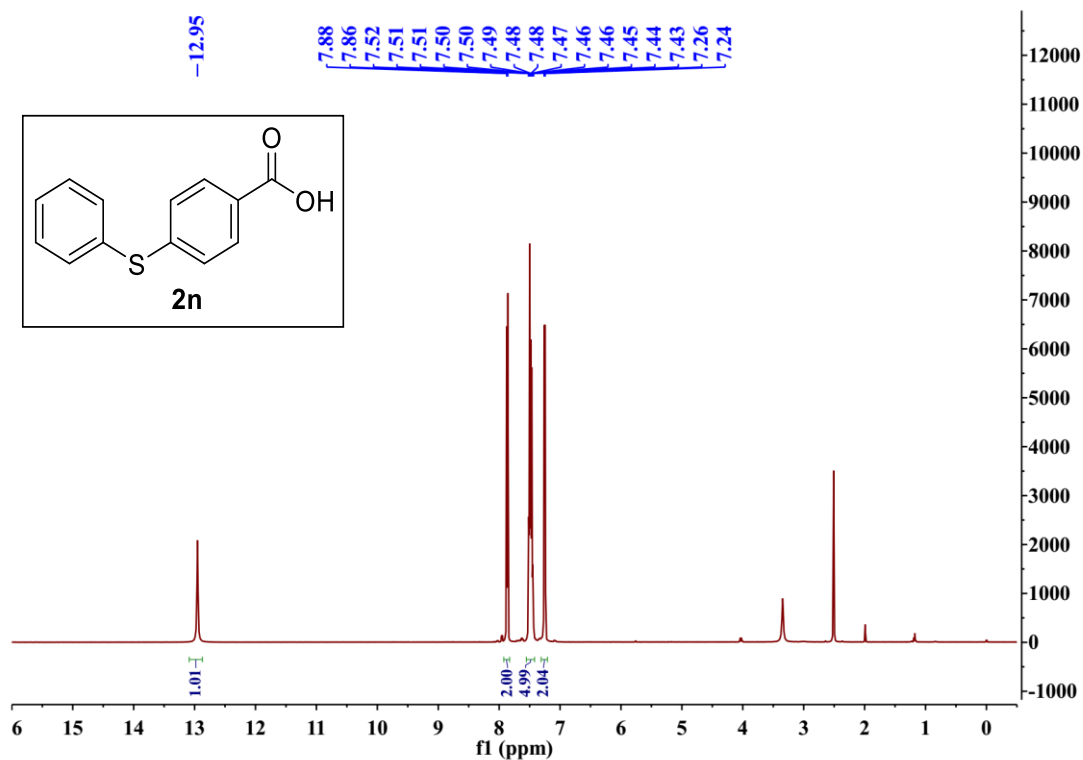
➤ ^1H NMR spectrum for **21**



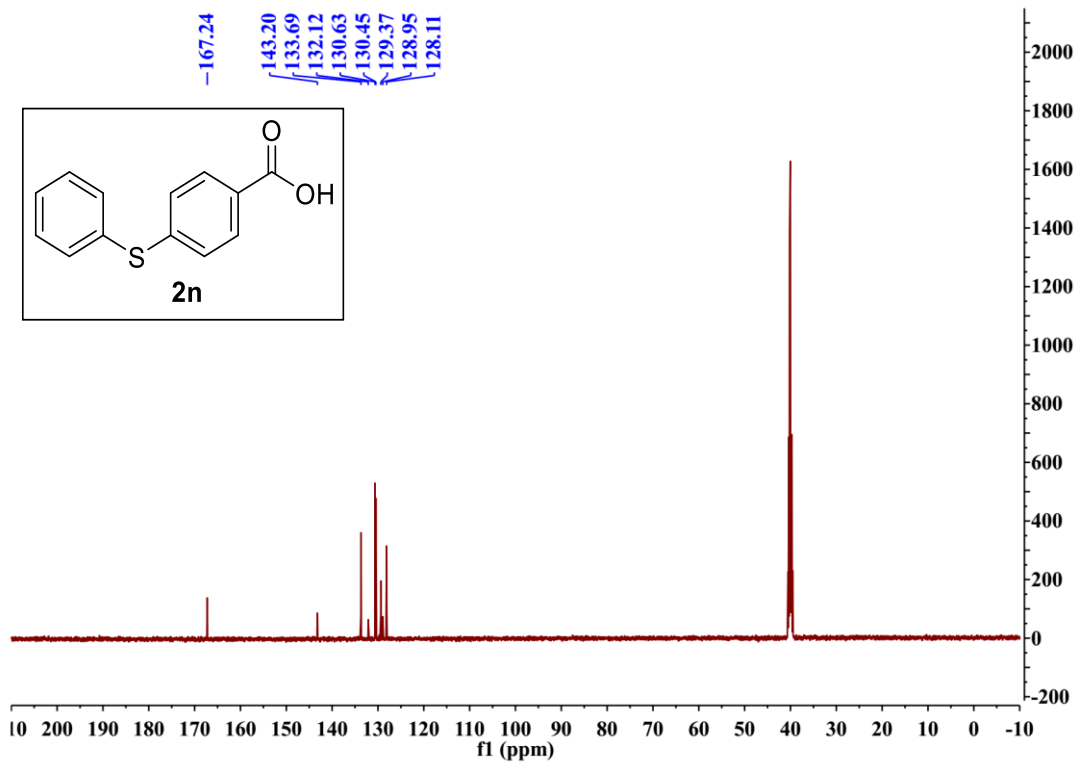
➤ ^{13}C NMR spectrum for **21**



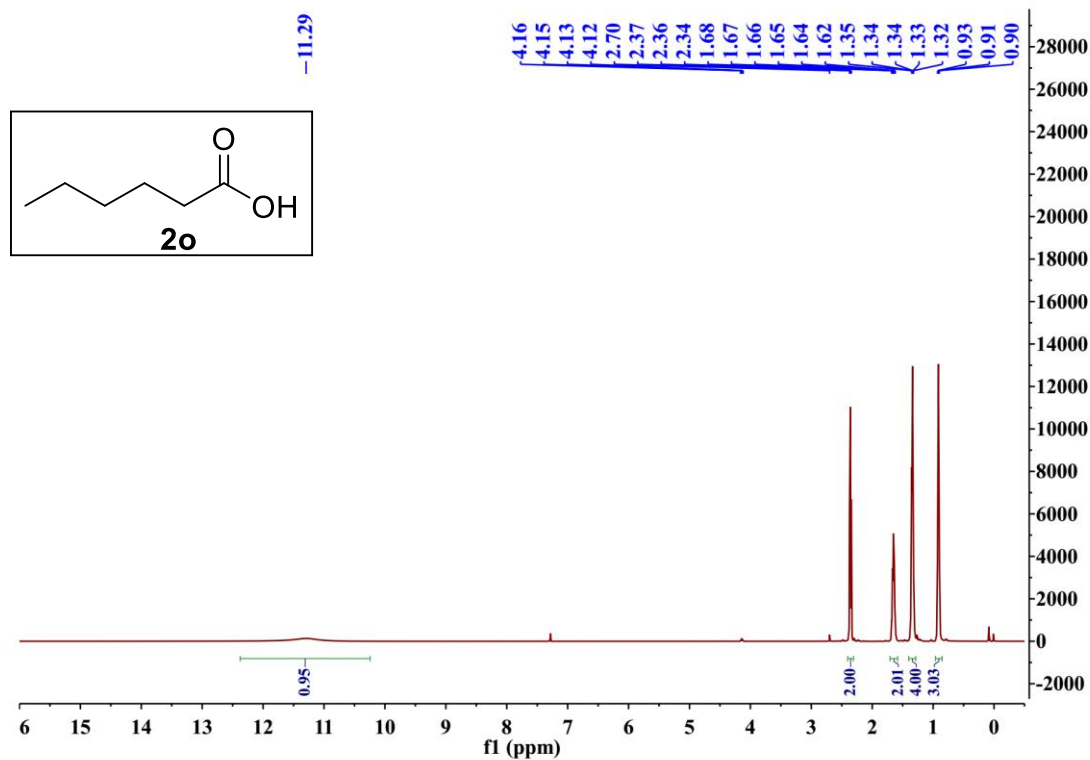
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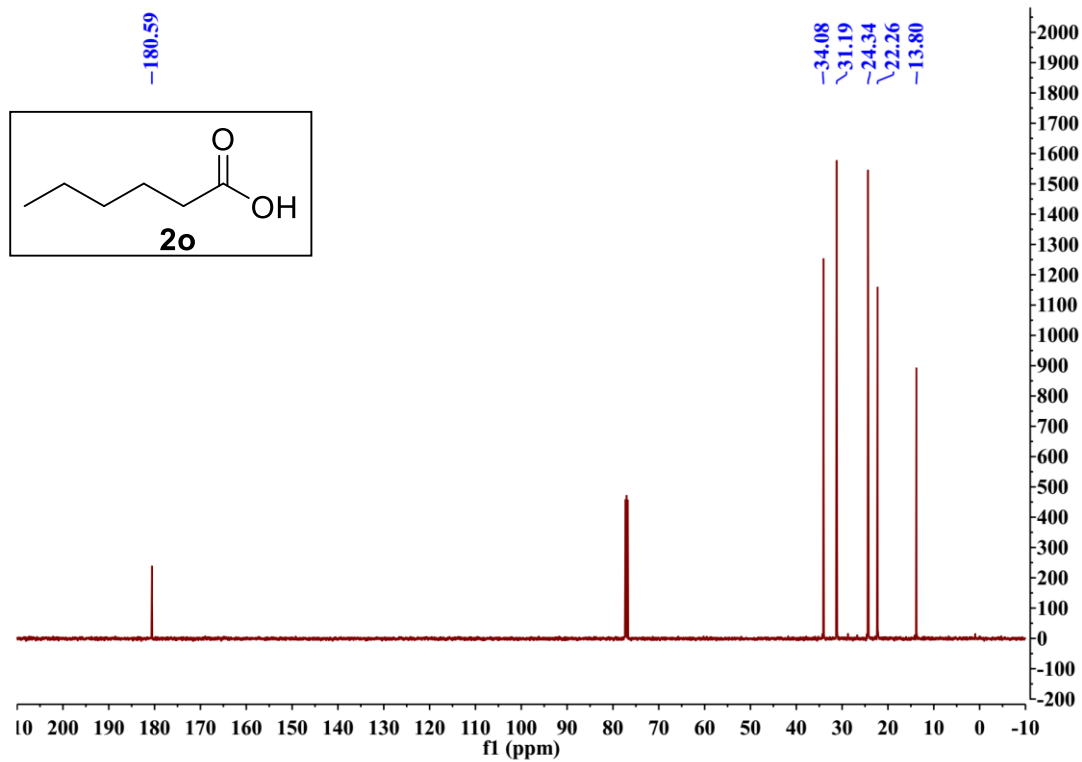
➤ ¹³C NMR spectrum for **2n**



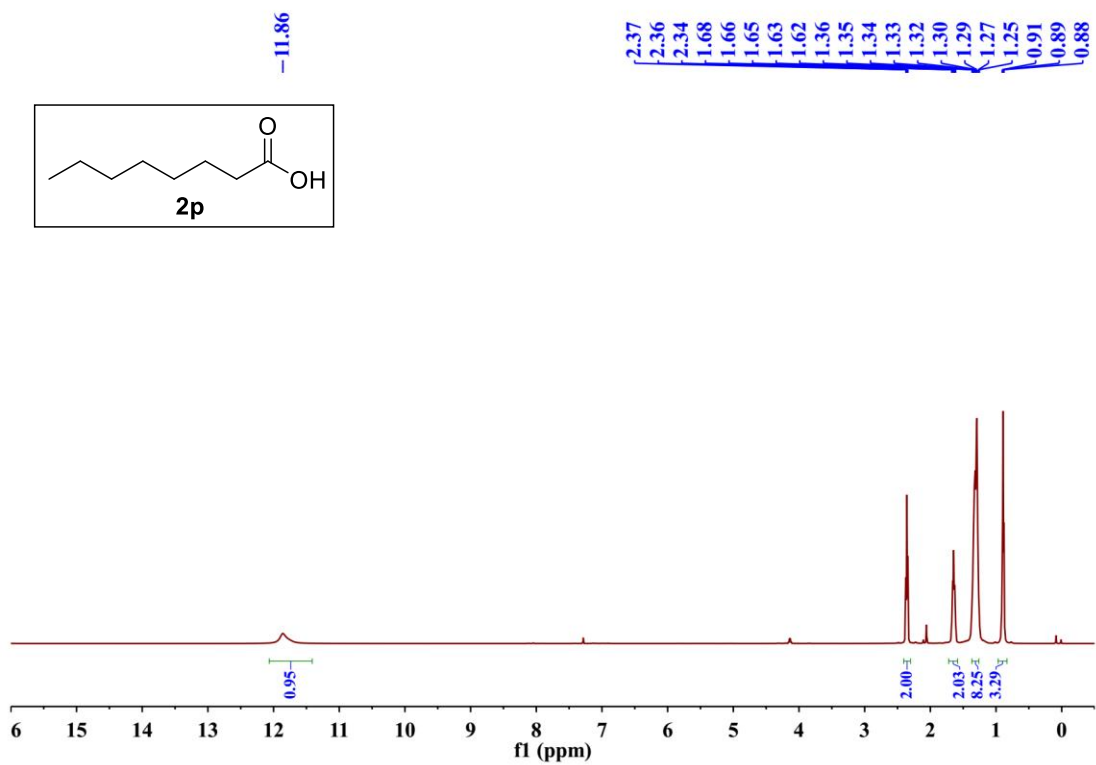
➤ ¹H NMR spectrum for **2o**



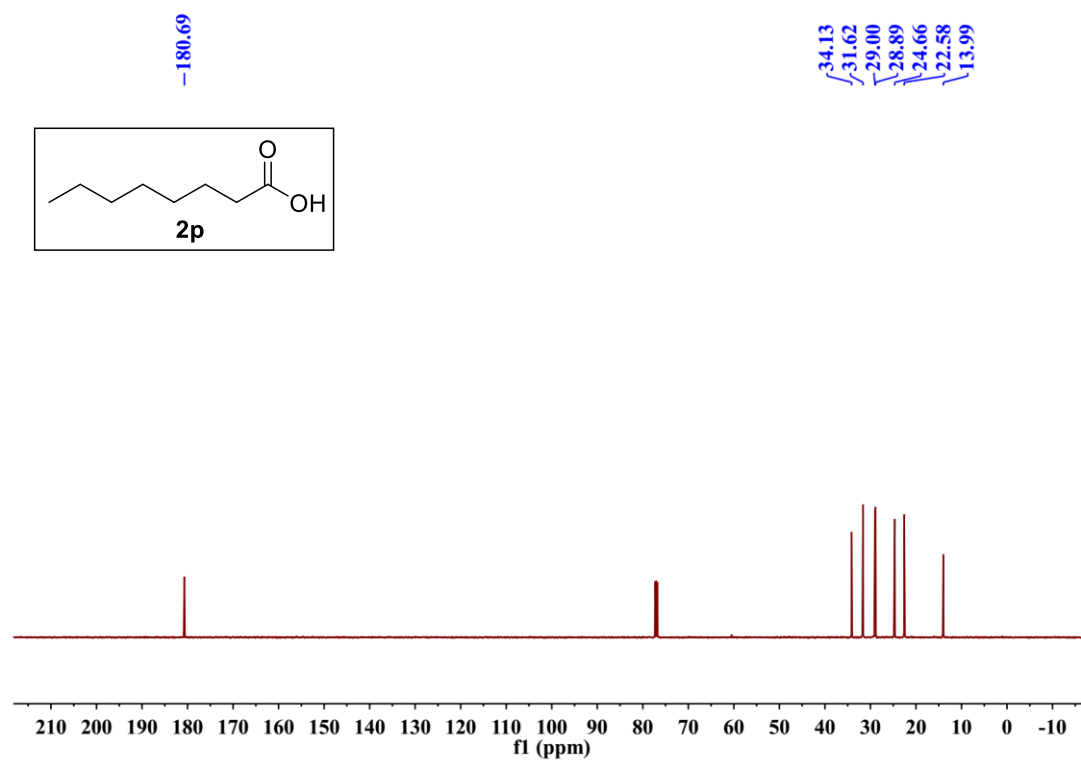
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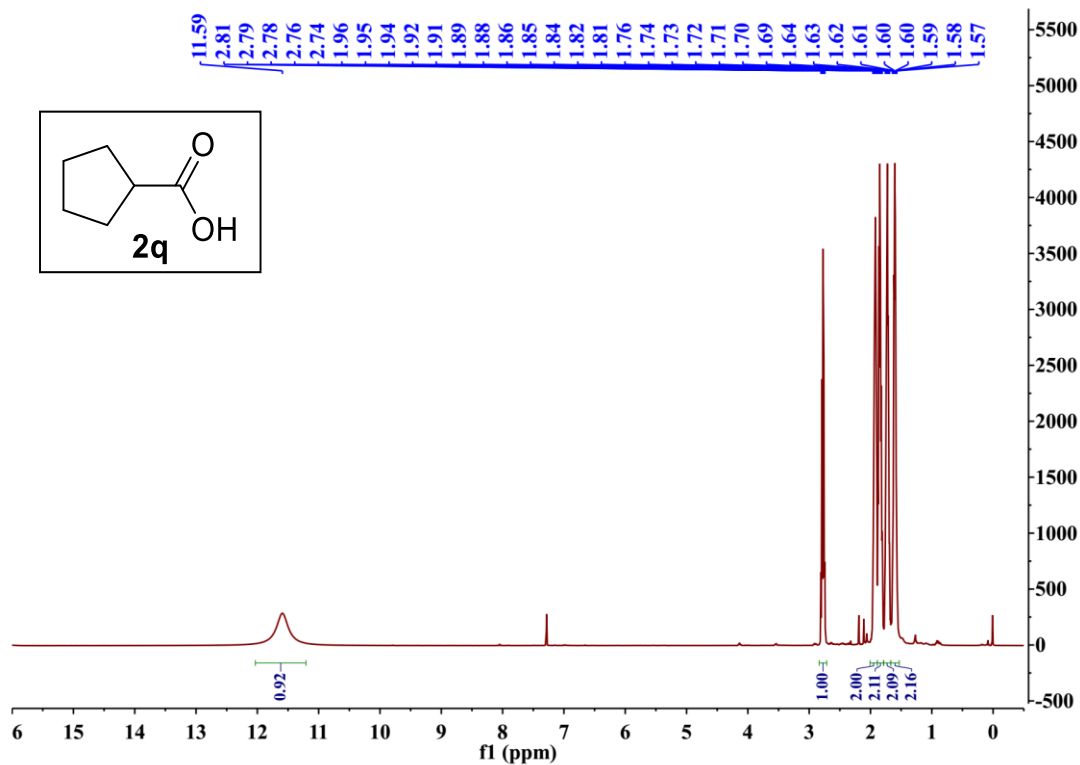
➤ ^1H NMR spectrum for **2p**



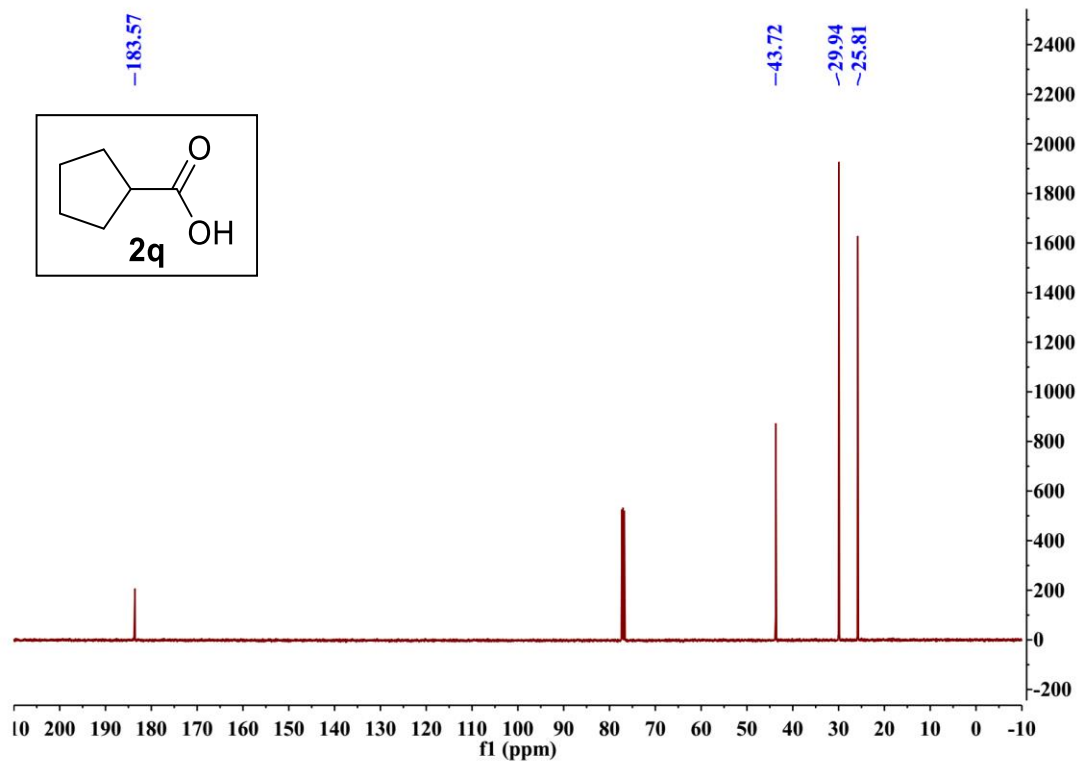
➤ ^{13}C NMR spectrum for **2p**



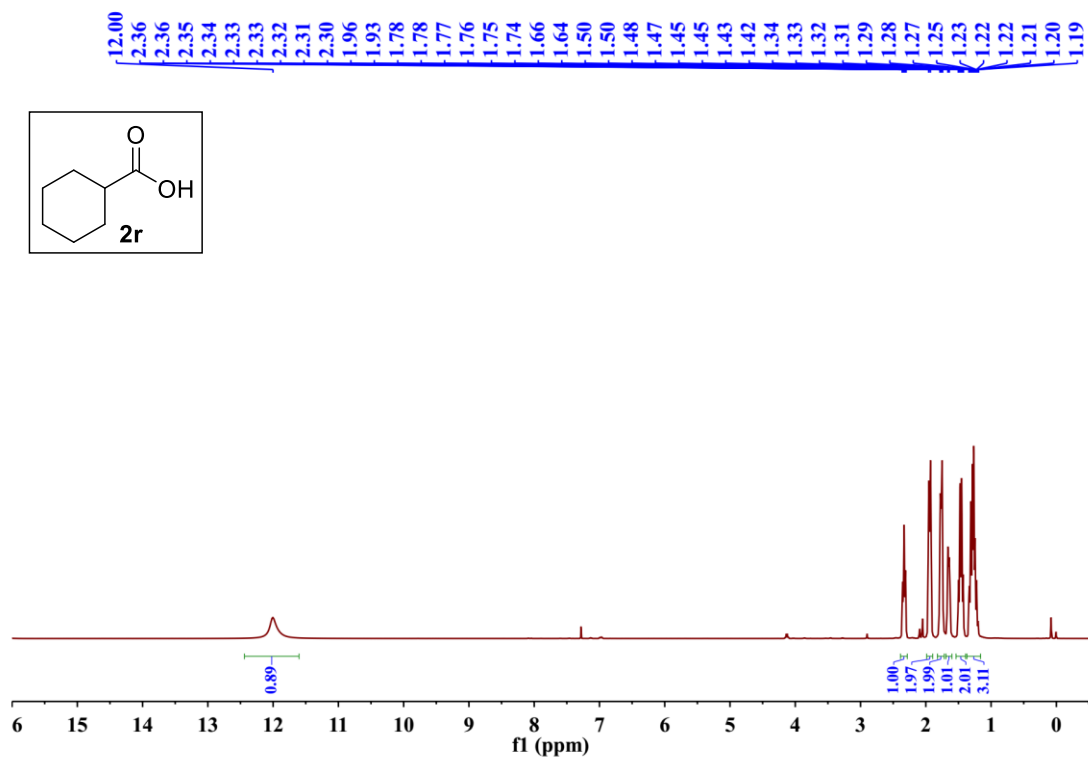
➤ ¹H NMR spectrum for **2q**



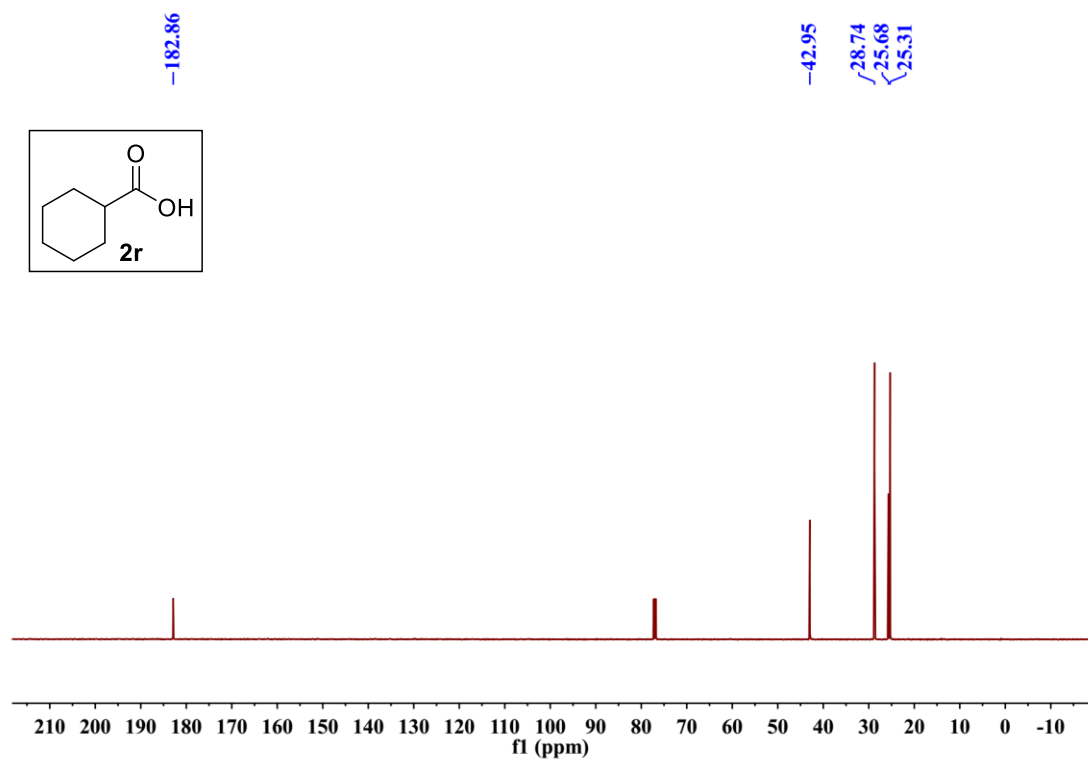
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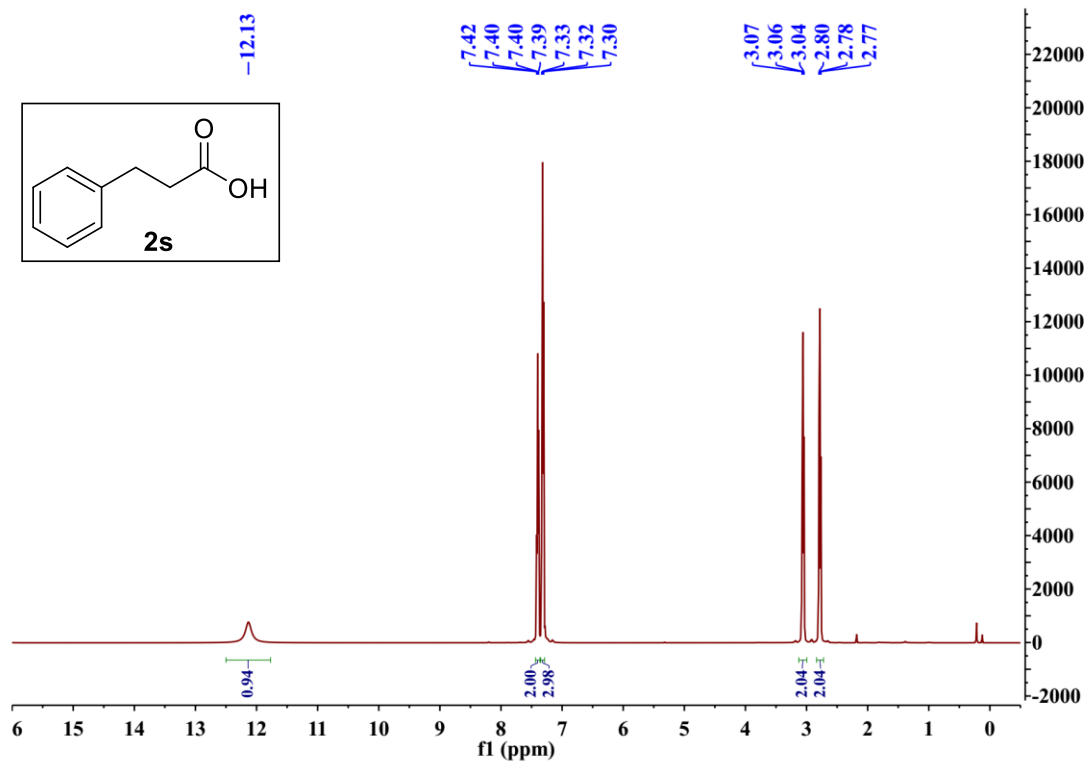
➤ ¹H NMR spectrum for **2r**



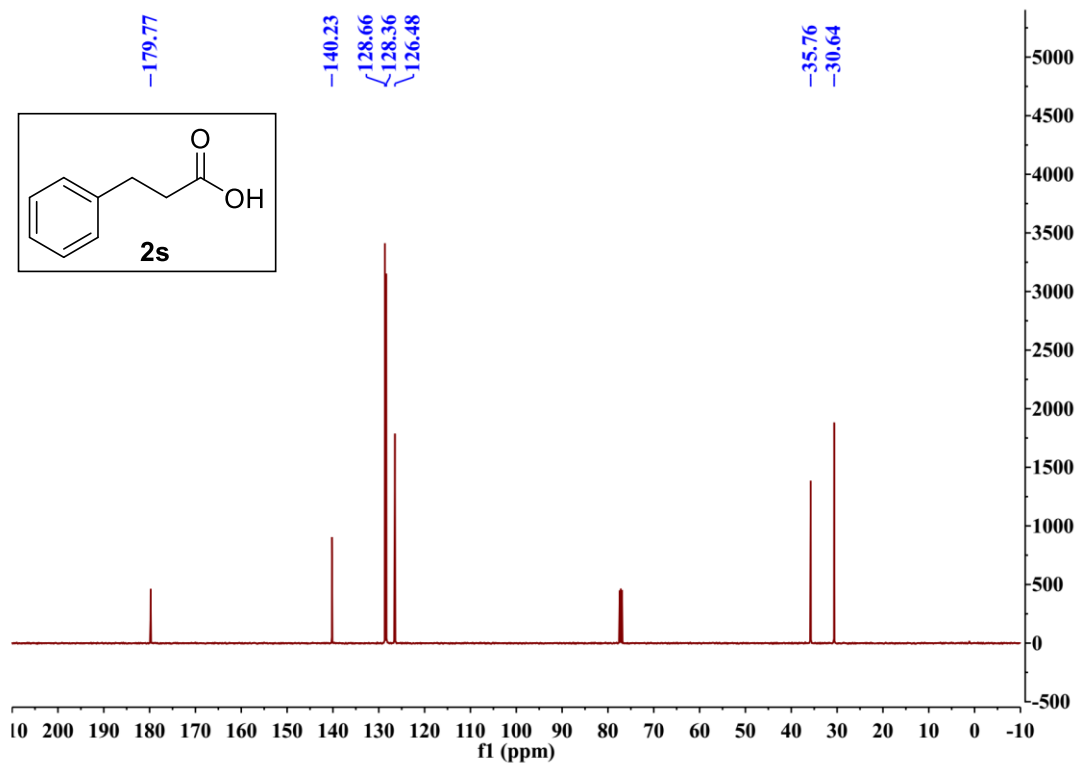
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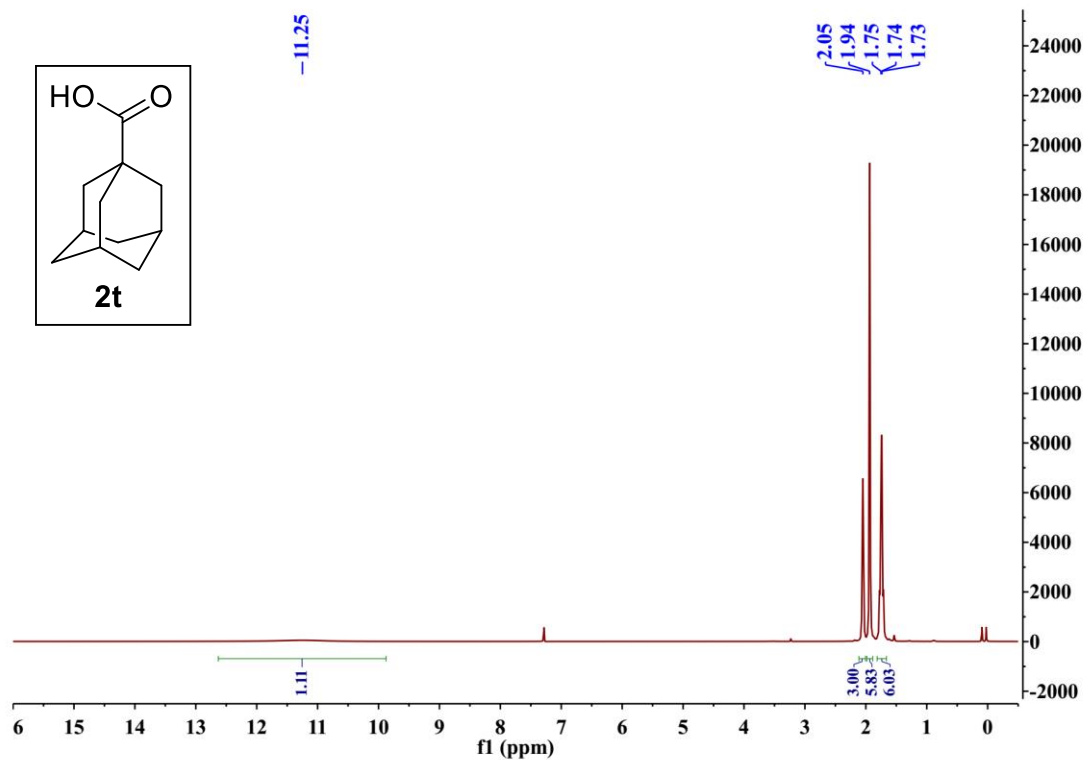
➤ ¹H NMR spectrum for **2s**



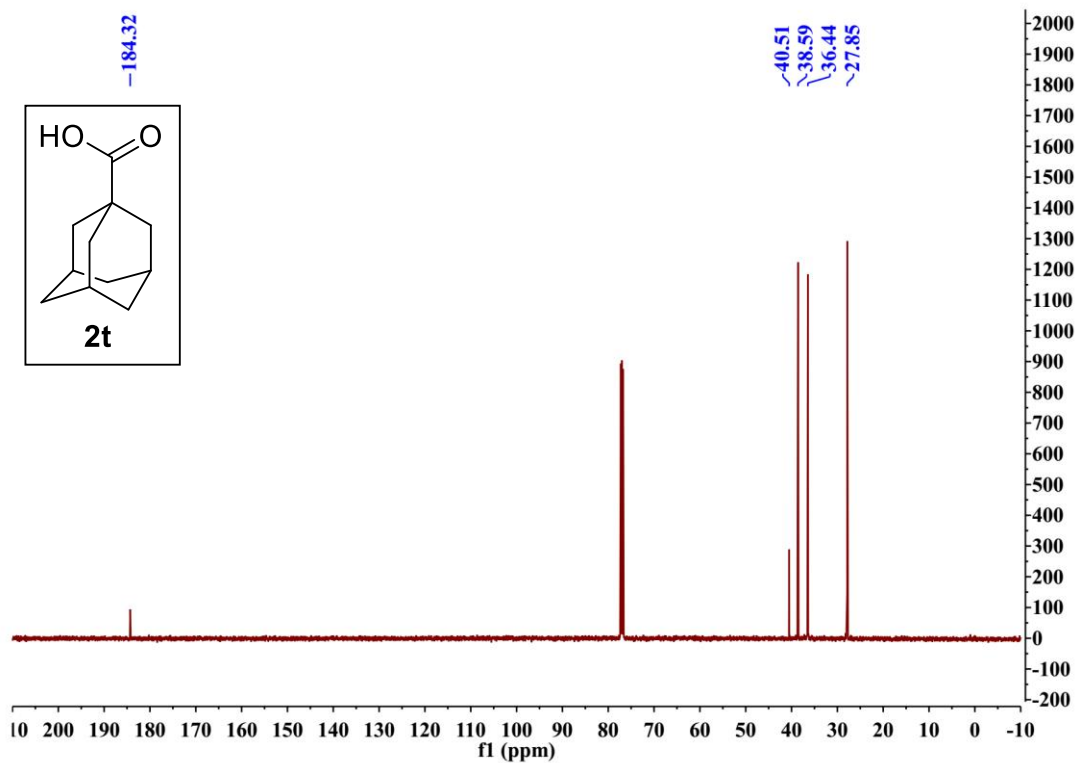
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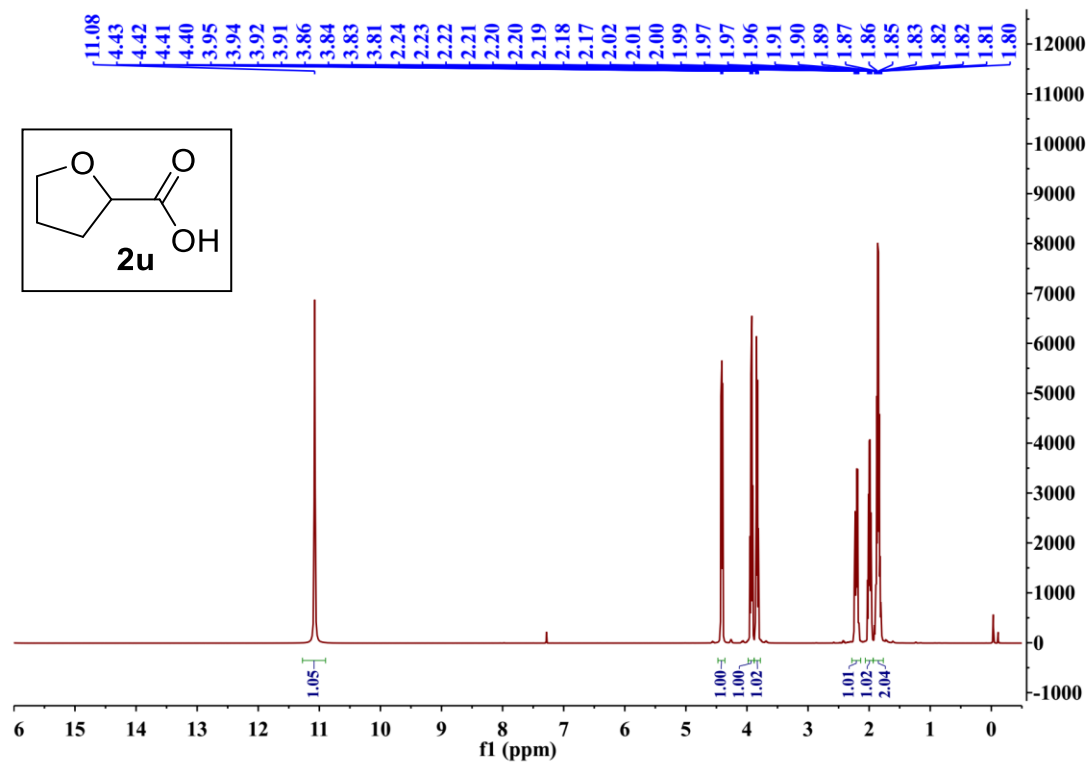
➤ ¹H NMR spectrum for **2t**



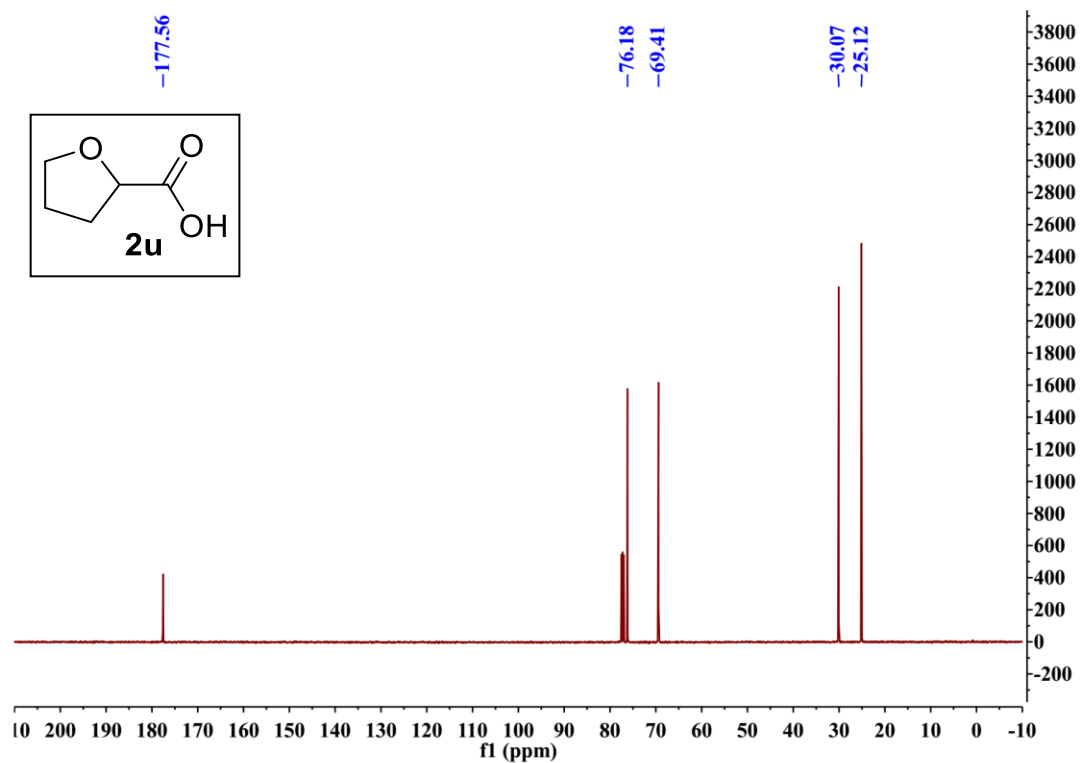
➤ ¹³C NMR spectrum for **2t**



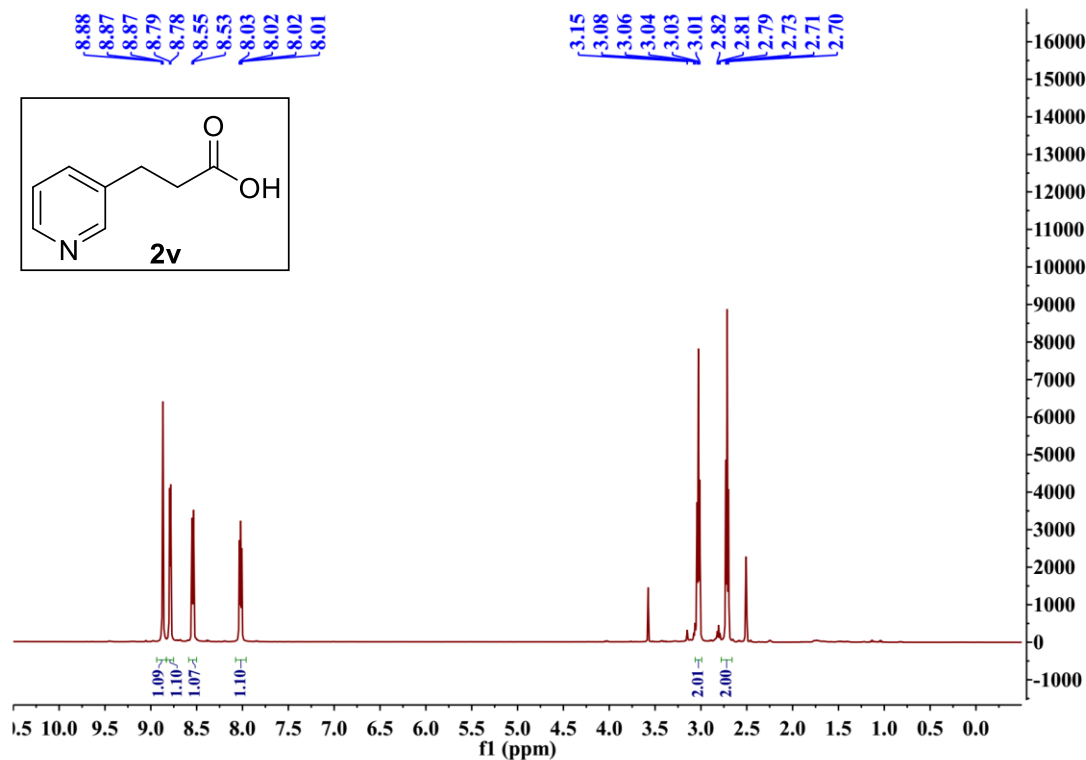
➤ ¹H NMR spectrum for **2u**



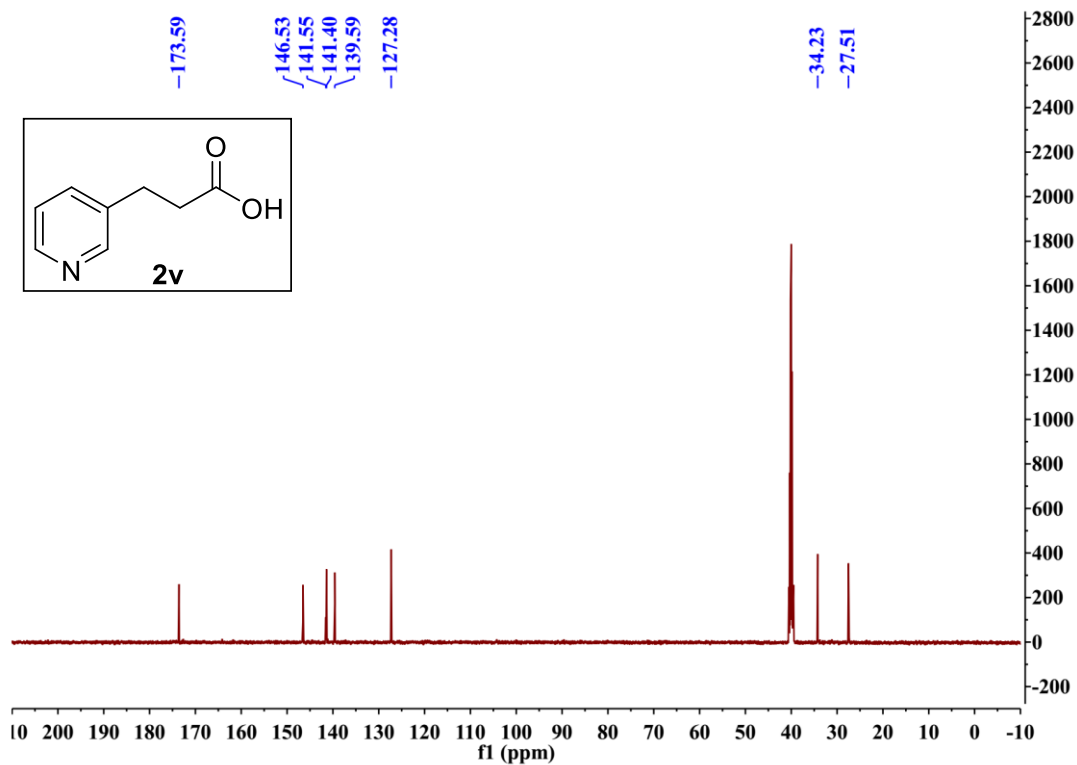
➤ ¹³C NMR spectrum for **2u**



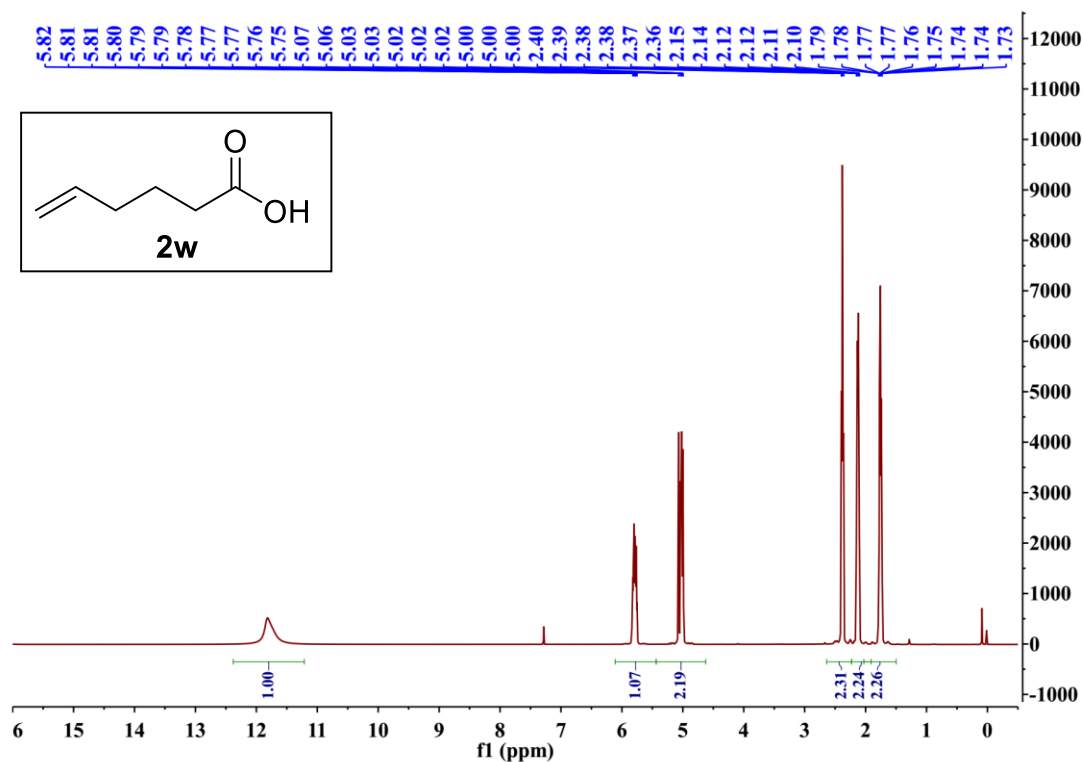
➤ ¹H NMR spectrum for **2v**



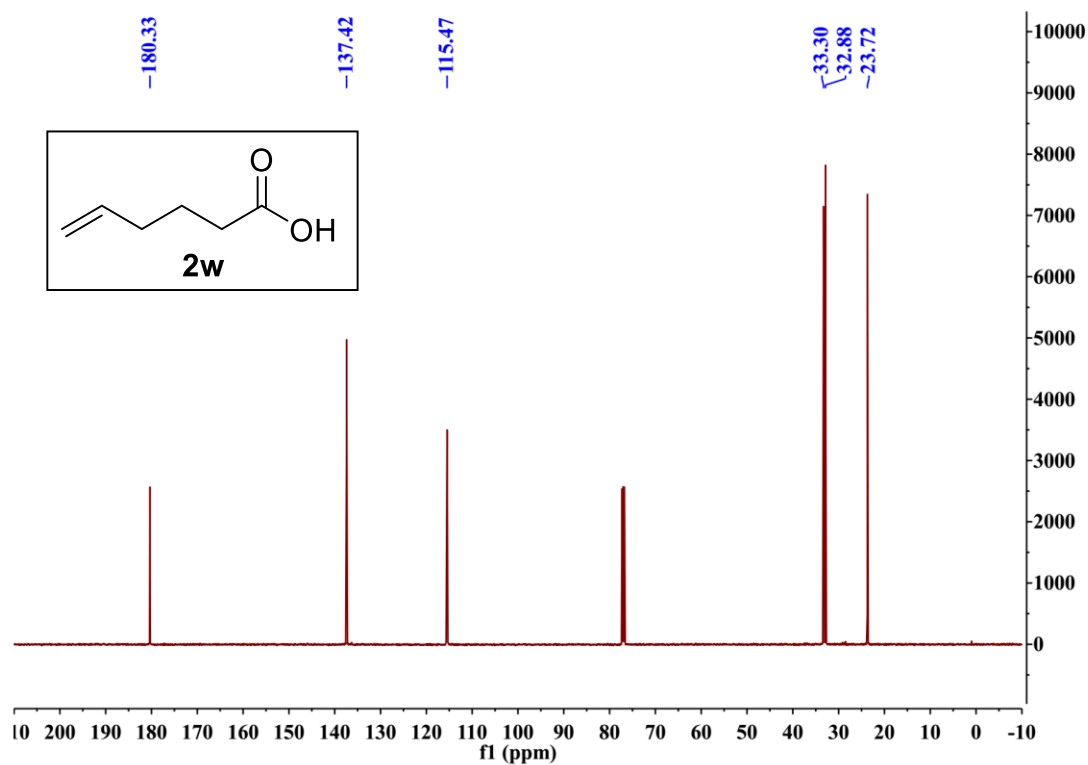
➤ ¹³C NMR spectrum for **2v**



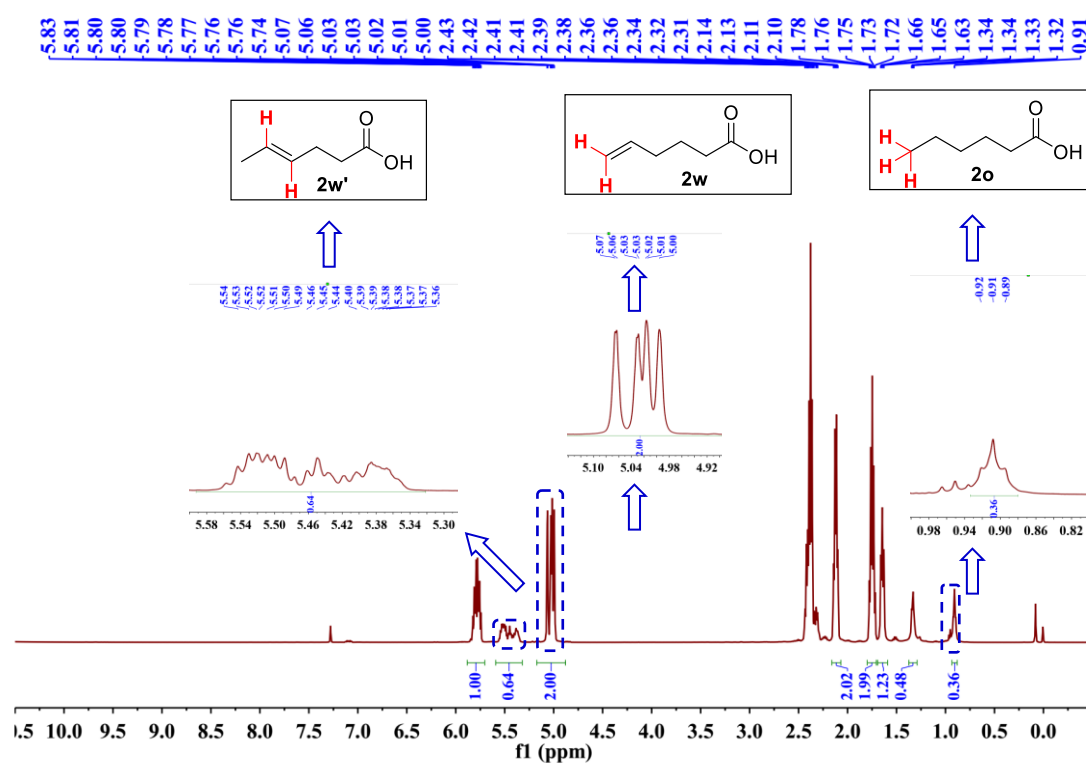
➤ The pure ^1H NMR spectrum of **2w**



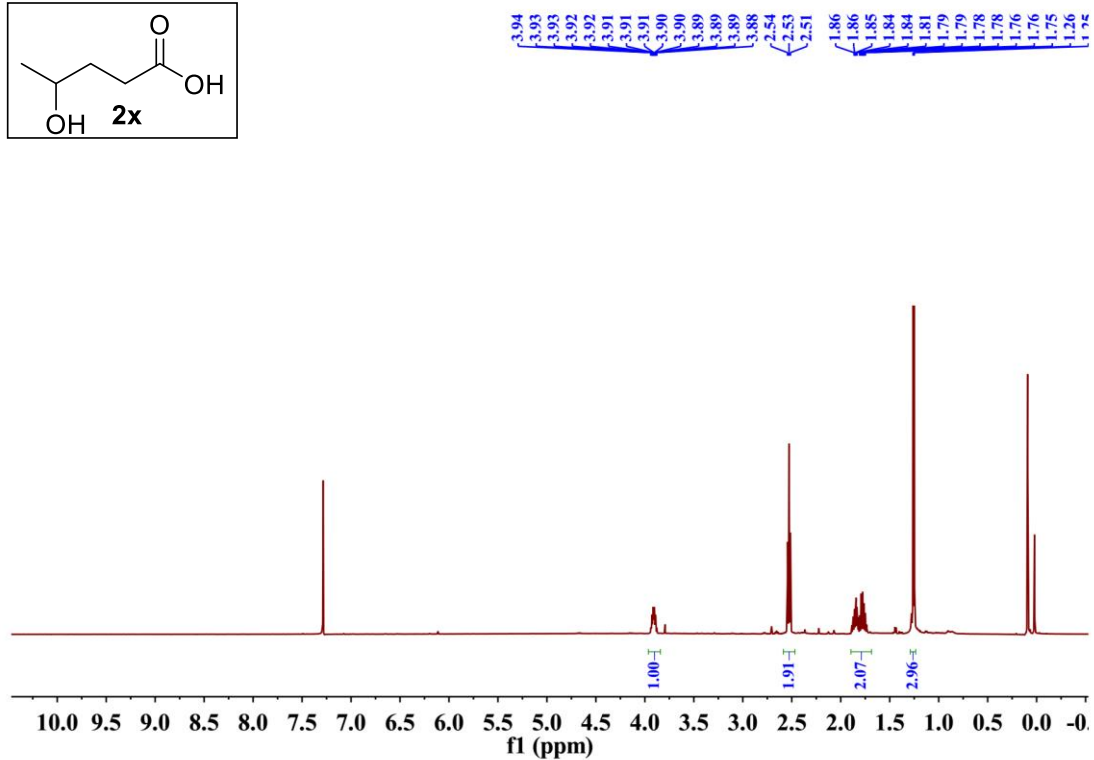
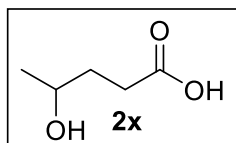
➤ The pure ^{13}C NMR spectrum for **2w**



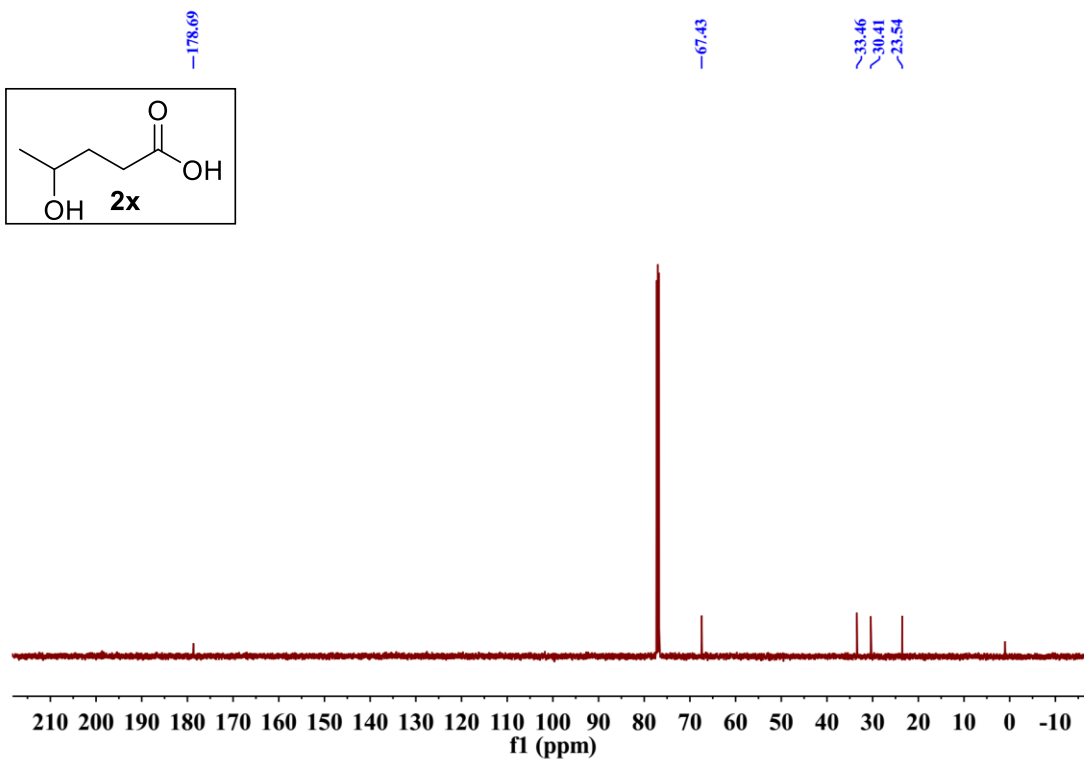
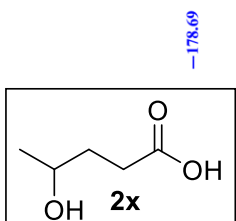
- The reaction of **1w** and KOH afforded a mixture of **2w**, **2w'** and **2o**, as shown in the following ¹H NMR spectrum. The ratio of the three compounds were calculated based on the characteristic peaks in these compounds (the two protons from the terminal alkene group of **2w**, the two protons from the internal alkene group of **2w'** and the three protons from the methyl group of **2o**). Therefore, the ratio of the two compounds is 2/2: 0.64/2 : 0.36/3 = 1 : 0.32: 0.12.



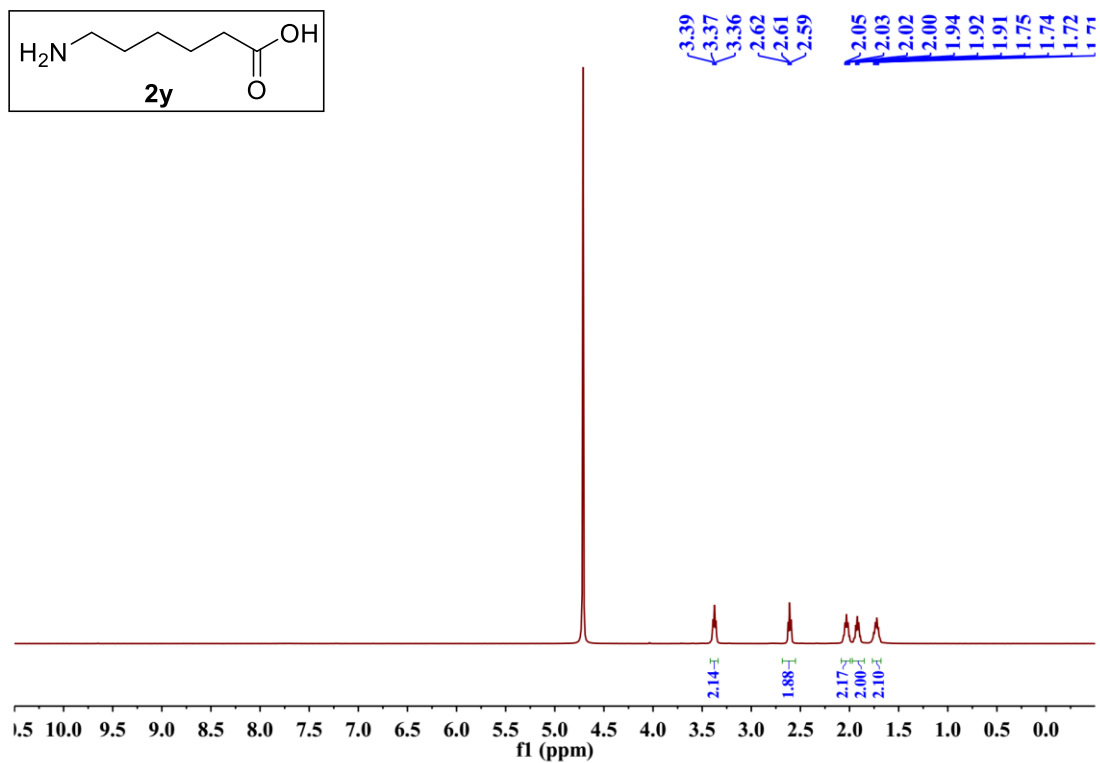
➤ ¹H NMR spectrum for **2x**



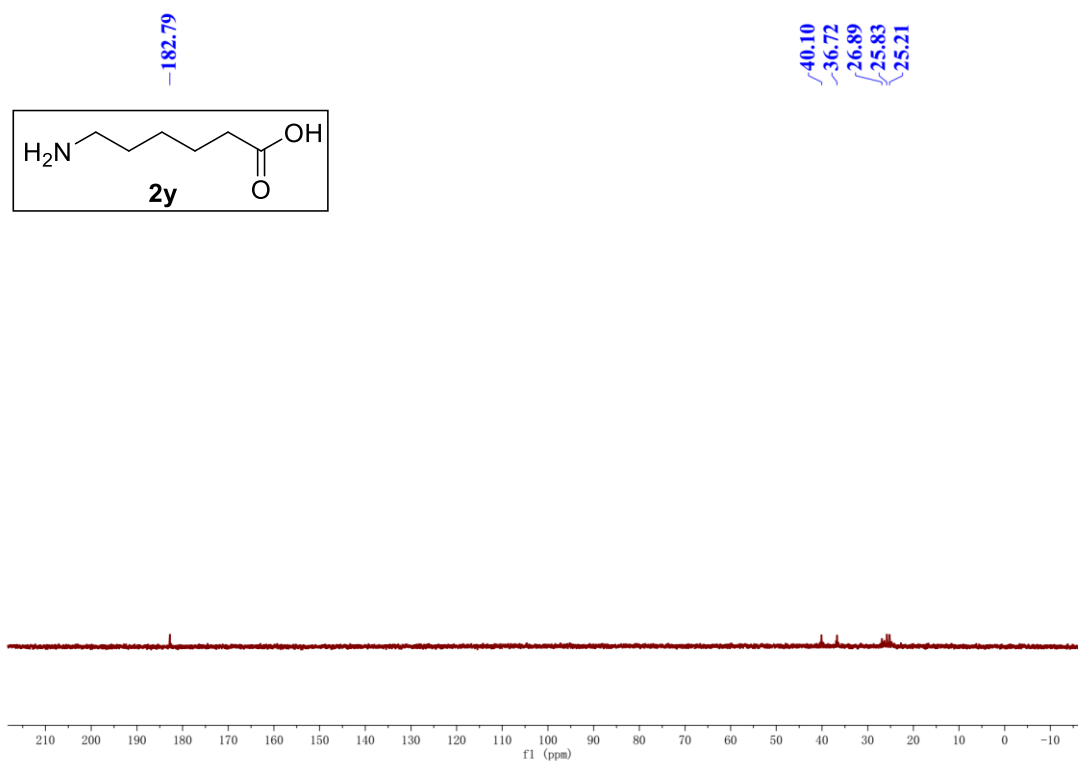
➤ ¹³C NMR spectrum for **2x**



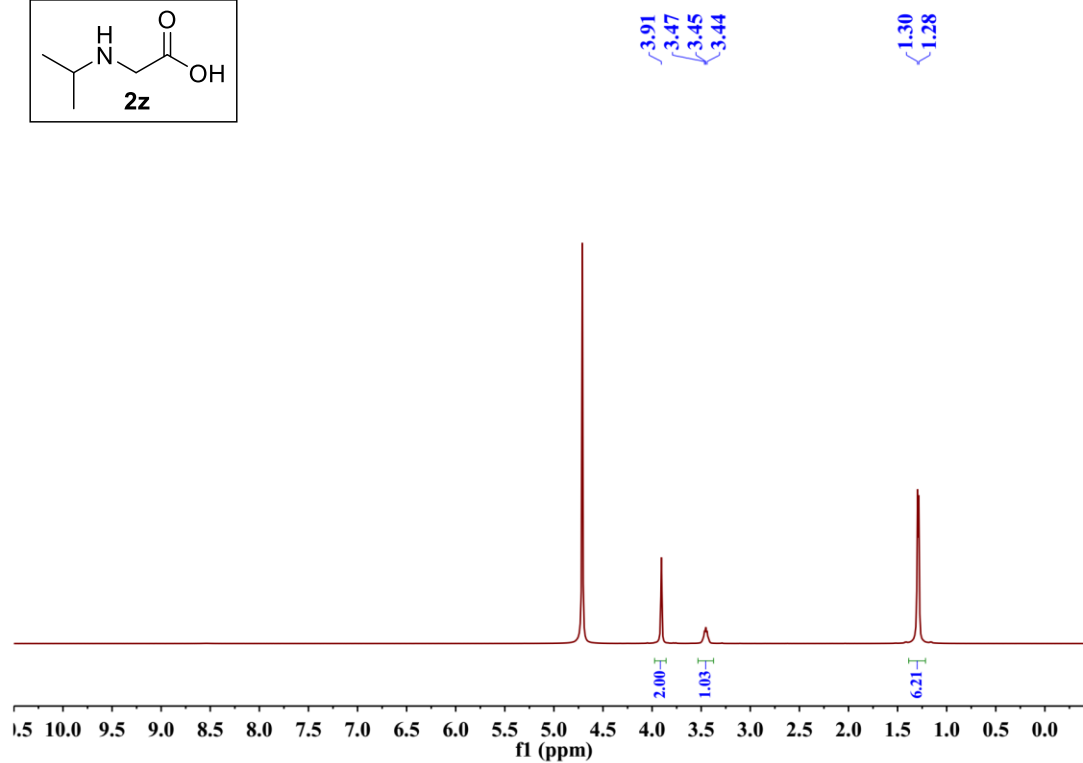
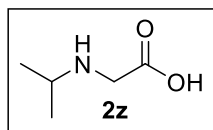
➤ ¹H NMR spectrum for **2y**



➤ ¹³C NMR spectrum for **2y**



➤ ¹H NMR spectrum for **2z**



➤ ¹³C NMR spectrum for **2z**

