

Supporting Information

Hydroxycarbonylation of Alkenes with Formic Acid Using Rhodium Iodide complex and Alkylammonium Iodide

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Experimental Section

Materials:

Unless stated otherwise, all chemicals were purchased as reagents of the best grade from Sigma-Aldrich Co., Tokyo Chemical Industry Co., or FUJIFILM Wako Pure Chemical Co., stored under a N₂ atmosphere, and used without further purification. RhI(CO)(PPh₃)₂ (**1**) was synthesized following a reported procedure.^[S1]

Instruments:

All operations were performed in a glovebox under an atmosphere of purified N₂. Catalytic reactions were performed in a 30 mL Hastelloy autoclave with a pressure gauge (TVS-N2, Taiatsu Techno Co.). A process reactor with aluminum block (DDS-1410, EYELA) was used for heating the reaction mixture in the autoclave. The reaction products were identified by GC-MS analysis (GCMS-QP2010SE, Shimadzu Co.; TC-FFAP capillary column, GL Sciences Inc.). The conversion rate of alkenes and the yield of products were determined by GC-FID analysis (GC-2025, Shimadzu Co.; TC-FFAP capillary column, GL Sciences Inc.). The conversion rate of HCOOH was determined by HPLC analysis (Prominence, Shimadzu Co.; PDA detector; Luna Omega Polar C18 column, Phenomenex Inc.) with 1% H₃PO₄ aqueous solution/acetonitrile (v:v = 9:1) as the mobile phase at 40 °C. The ¹H, ¹³C, and ³¹P NMR spectra were obtained using Bruker AVANCE-III high-resolution spectrometers (400 and 600 MHz for ¹H) at room temperature. FTIR spectra using the ATR method were obtained with a JASCO VIR-200 spectrometer installed in a glove box under an atmosphere of purified N₂. Elemental analyses were performed using a PerkinElmer 2400 II elemental analyzer. High resolution mass spectra (HRMS) were recorded on a Bruker MicroTOF ESI mass spectrometer.

General procedure for hydroxycarbonylation of alkenes:

RhI(CO)(PPh₃)₂ (**1**) (219 mg, 0.280 mmol), (Me)₄Ni (56.3 mg, 0.280 mmol), C₆H₁₀ (470 mg, 5.72 mmol), HCOOH (948 mg, 20.6 mmol), *p*-TsOH·H₂O (190 mg, 1.00 mmol), and toluene (6 mL) were introduced into an autoclave with a Hastelloy stir bar. Hydroxycarbonylation was carried out at 180 °C for 2.5 h in a batch manner. After 2.5 h, the autoclave was cooled to room temperature, and then carefully vented until reaching ambient pressure. The reaction products were then carefully collected from the autoclave using dichloromethane as the recovery solvent. A small amount of the collected mixture was diluted with dichloromethane, dodecane was added as an internal standard, and then this sample was analyzed by GC-MS and GC-FID. A small amount of the collected mixture was diluted with a mixed solution of 1% H₃PO₄ aqueous solution/acetonitrile (v:v = 9:1) and analyzed by HPLC. Isolation of the carboxylic acids was carried out based on the report of Leitner *et al.*^[S2] First, dichloromethane was added to the reaction mixture, and then the solvent was removed under vacuum. The residual solid was dissolved in dichloromethane (15 mL), and the resulting solution was extracted four times with saturated NaHCO₃ aqueous solution (4 x 10 mL). The aqueous phases were combined, and concentrated hydrochloric acid was added dropwise until pH 1 was reached. The aqueous phase was then re-extracted with dichloromethane (5 x 10 mL). The separated dichloromethane phase was dried over Na₂SO₄, and then, the solvent was removed under vacuum to give the carboxylic acids.

General procedure for the reaction of 1 with promoters:

RhI(CO)(PPh₃)₂ (**1**) (100 mg, 0.128 mmol), *p*-TsOH·H₂O (72.9 mg, 0.383 mmol), (Me)₄Ni (26.0 mg, 0.128 mmol), and toluene-*d*₈ (4.6 mL) were added to a 15 mL glass high-pressure tube (Ace Glass Incorporated) with a stirring bar and stirred at 50 °C for 1 h. After 1 h, the glass high-pressure tube was cooled to room temperature. The precipitate that formed was then separated from the reaction mixture by vacuum filtration, and the obtained solids were dissolved in CD₂Cl₂ and analyzed by NMR spectroscopy.

Synthesis of RhHI₂(CO)(PPh₃)₂ (2**) using hydriodic acid:**

RhHI₂(CO)(PPh₃)₂ (**2**) was synthesized by modifying the synthesis of RhHI₂(CO)(PEt₃)₂ reported by Cole-Hamilton et al.^[9] An aqueous solution of HI (56.4 wt%, 0.32 g, HI: 0.18 g, 1.41 mmol) was added to RhI(CO)(PPh₃)₂ (**1**) (1.00 g, 1.28 mmol) in acetone (90 mL) and the mixture was stirred at room temperature for 15 h. The volatiles were then removed by evaporation under reduced pressure. Recrystallization of the obtained orange-yellow solid from CH₂Cl₂/*n*-hexane at room temperature gave **2** as orange crystals (1.07 g, 81% yield). ¹H NMR (600 MHz, CD₂Cl₂): δ = 7.84-7.79 (m, 12H, Ph), 7.48-7.44 (m, 6H, Ph), 7.43-7.38 (m, 12H, Ph), -9.57 ppm (br, 1H; RhH), ¹³C{¹H} NMR (151 MHz, CD₂Cl₂): δ = 135.3 (vt, *J* = 6 Hz), 133.1 (vt, *J* = 26 Hz), 131.3; 128.5 ppm (vt, *J* = 6 Hz) (The signal of the CO ligand could not be detected due to complicated coupling and broadening.); ³¹P{¹H} NMR (243 MHz, CD₂Cl₂): δ = 16.6 ppm (br, ¹*J*_{PRh} = 84 Hz); IR (ATR): $\tilde{\nu}$ = 2079, 2062 cm⁻¹; elemental analysis calcd (%) for [RhHI₂(CO)(PPh₃)₂·0.5(CH₂Cl₂) = C_{37.5}H₃₂Cl₂OP₂Rh]: C 47.27, H 3.39; found: C 47.66, H 3.25.

X-ray structural analysis:

Diffraction intensity data were collected at 103 K on a Rigaku XtaLAB P200 with a Pilatus 200 K detector using multilayer mirror monochromated Mo K α radiation (λ = 0.71075 Å). The intensity data were corrected for Lorentz and polarization effects and for absorption (multiscan)^[S3] using CrysAlis PRO.^[S4] The structures were solved by direct methods (SHELXT)^[S5] and refined by least-squares calculations on *F*² for all reflections (SHELXL-2014/7)^[S6] by using Yadokari-XG 2009.^[S7] Hydrogen atoms were placed at calculated positions using AFIX instructions, and included in least-squares calculations without refinement of their parameters. The crystallographic data, summary of solutions, and refinement are listed in Table S9.

References:

- [S1] F. R. Hartley, S. G. Murray, and D. M. Potter, *J. Organomet. Chem.*, 1983, **254**, 119.
[S2] T. G. Ostapowicz, M. Schmitz, M. Krystof, J. Klankermayer, and W. Leitner, *Angew. Chem. Int. Ed.*, 2013, **52**, 12119.
[S3] R. H. Blessing, *Acta Crystallogr. Sect. A Found. Crystallogr.*, 1995, **51**, 33.
[S4] CrysAlisPRO, Oxford Diffraction; Agilent Technologies Ltd: Yarnton, Oxfordshire, England, 2014.
[S5] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Adv.*, 2015, **71**, 3.
[S6] G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 3.
[S7] C. Kabuto, S. Akine, T. Nemoto, and E. Kwon, *J. Cryst. Soc. Jpn.*, 2009, **51**, 218.

Details of results on catalytic reactions

The numbers of substrates, main products, and typical by-products are set as follows:

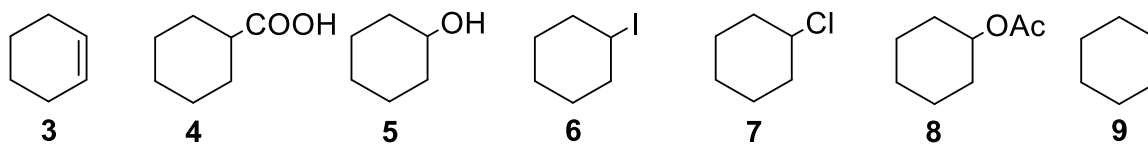
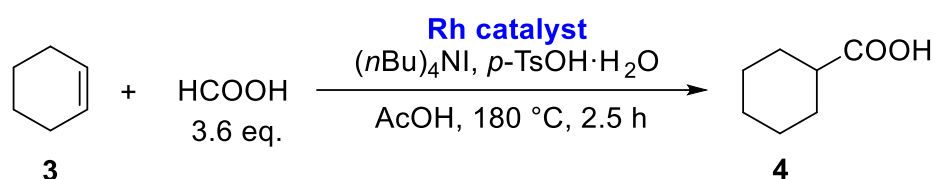


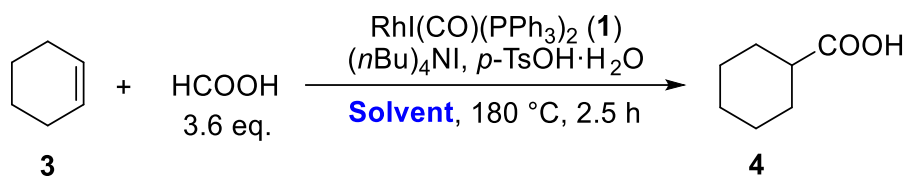
Table S1 Hydroxycarbonylation of cyclohexene **3** with HCOOH using Rh complex catalysts and (*n*Bu)₄NI promoter.^[a]



Entry	Rh catalyst	Mole ratio PPh ₃ /Rh ^[b]	Conv. [%]		Yield [%] ^[e]					
			3 ^[c]	HCOOH ^[d]	4	5	6	7	8	9
1	[RhCl(CO) ₂] ₂	0	62	77	13	3	1	2	22	1
2	[RhCl(CO) ₂] ₂ + PPh ₃	2	59	94	8	2	1	2	24	1
3	RhCl(CO)(PPh ₃) ₂	2	64	91	7	2	1	2	26	1
4	RhCl(PPh ₃) ₃	3	61	89	7	3	1	2	7	3
5	RhI(CO)(PPh ₃) ₂ (1)	2	90	89	83	0	1	-	2	1
6 ^[e]	RhCl(CO)(PPh ₃) ₂	2	82	88	61	1	1	1	6	1

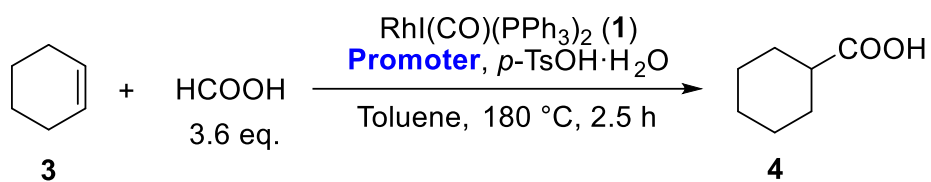
[a] Reaction conditions: Rh catalyst (0.280 mmol of Rh as mononuclear complex), **1** (470 mg, 5.72 mmol), HCOOH (948 mg, 20.6 mmol), (*n*Bu)₄NI (103 mg, 0.280 mmol), *p*-TsOH·H₂O (190 mg, 1.00 mmol), CH₃COOH (6 mL). [b] Total mol number of free PPh₃ and coordinated PPh₃ ligand in Rh complex. [c] Calculated from the GC results using dodecane as internal standard. [d] Calculated from the HPLC results [e] Using 2 equiv/Rh of (*n*Bu)₄NI (206 mg, 0.560 mmol).

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Table S2 Effect of solvent on hydroxycarbonylation of **3**.^[a]

Entry	Solvent	Conv. [%]		Yield [%] ^[b]			
		3 ^[b]	HCOOH ^[c]	4	5	6	9
1	Propionic acid	84	98	76	6	1	1
2	Dibutyl ether	19	44	1	6	0	4
3	Toluene	82	58	72	3	2	1
4	Hexane	54	61	38	4	2	2
5	Heptane	79	68	57	3	2	0
6	Undecane	72	82	53	2	2	1

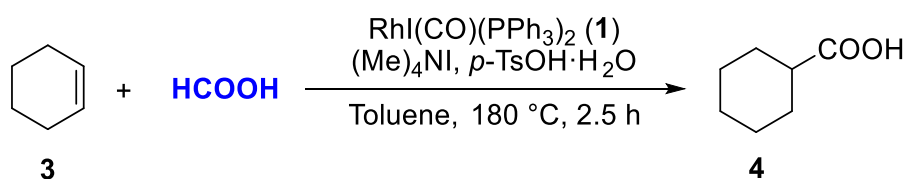
[a] Reaction conditions: **1** (219 mg, 0.280 mmol), **3** (470 mg, 5.72 mmol), HCOOH (948 mg, 20.6 mmol), (*n*Bu)₄NI (103 mg, 0.280 mmol), *p*-TsOH·H₂O (190 mg, 1.00 mmol), solvent (6 mL). [b] Calculated from the GC results using dodecane as internal standard. [c] Calculated from the HPLC results.

Table S3 Effect of promoter on hydroxycarbonylation of **3**.^[a]

Entry	Promoter	Mole ratio	Conv. [%]		Yield [%] ^[b]				
			Promoter/Rh	3 ^[b]	HCOOH ^[c]	4	5	6	7
1	-	-	29	81	1	7	1	-	4
2	(<i>n</i> Bu) ₄ NCl	1	33	69	2	11	0	1	4
3	(<i>n</i> Bu) ₄ NBr	1	56	67	30	9	2	-	1
4	[(Ph ₃ P)Me]I	1	87	98	76	2	1	-	1
5	(<i>n</i> Bu) ₄ NI	2	86	58	73	3	3	-	2
6	(Me) ₄ NI	1	89	50	81	2	2	-	1
7	(Et) ₄ NI	1	87	55	70	2	2	-	1
8	(<i>n</i> Pr) ₄ NI	1	86	56	71	2	1	-	1
9	(<i>n</i> Hex) ₄ NI	1	87	40	69	3	2	-	1

[a] Reaction conditions: **1** (219 mg, 0.280 mmol), **3** (470 mg, 5.72 mmol), HCOOH (948 mg, 20.6 mmol), *p*-TsOH·H₂O (190 mg, 1.00 mmol), toluene (6 mL) [b] Calculated from the GC results using dodecane as internal standard. [c] Calculated from the HPLC results.

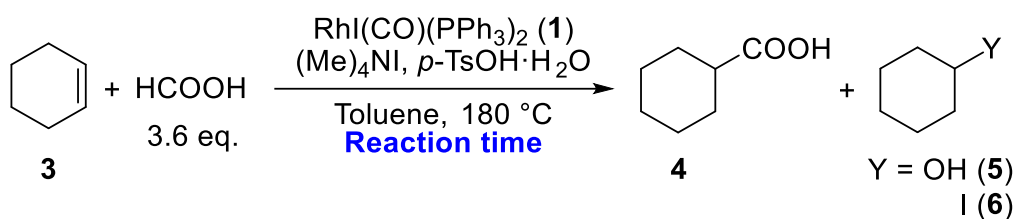
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Table S4 Effect of amount of HCOOH on hydroxycarbonylation of **3**.^[a]

Entry	Mole ratio HCOOH/ 3	Conv. [%]	Yield [%] ^[b]				
			3 ^[b]	HCOOH ^[d]	4	5	6
1	1	30	58	4	3	5	3
2	2	60	60	33	5	3	2
3	3	83	56	64	3	2	1
4	4	92	53	81	1	1	1
5	5	92	48	81	1	1	1
6 ^[c]	2	95	89	81	0	1	2

[a] Reaction conditions: **1** (219 mg, 0.280 mmol), **3** (470 mg, 5.72 mmol), (Me)₄Ni (56.3 mg, 0.280 mmol), *p*-TsOH·H₂O (190 mg, 1.00 mmol), toluene (6 mL). [b] Calculated from the GC results using dodecane as internal standard. [c] The reaction was carried out for 10h. [d] Calculated from the HPLC results.

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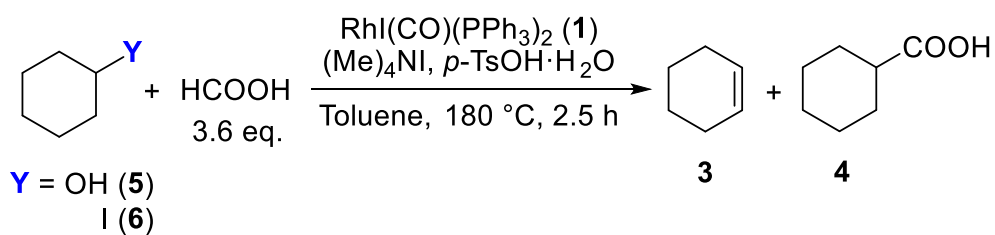
Table S5 Variation of composition relative to reaction time on hydroxy-carbonylation of **3**.^[a]

Entry	Reaction time [h]	Conv. [%]	Yield [%] ^[b]				
			3 ^[b]	HCOOH ^[c]	4	5	6
1	1.0	66	28	28	11	3	1
2	2.0	81	42	70	5	2	1
3	3.0	92	58	83	1	1	1
4	4.0	94	69	85	0	1	1
5	5.0	95	73	87	0	1	1
6	7.5	97	74	89	0	0	1
7	10	97	77	86	0	0	1

[a] Reaction conditions: **1** (219 mg, 0.280 mmol), **3** (470 mg, 5.72 mmol), HCOOH (948 mg, 20.6 mmol), (Me)₄NI (56.3 mg, 0.280 mmol), *p*-TsOH·H₂O (190 mg, 1.00 mmol), toluene (6 mL). [b] Calculated from the GC results using dodecane as internal standard. [c] Calculated from the HPLC results.

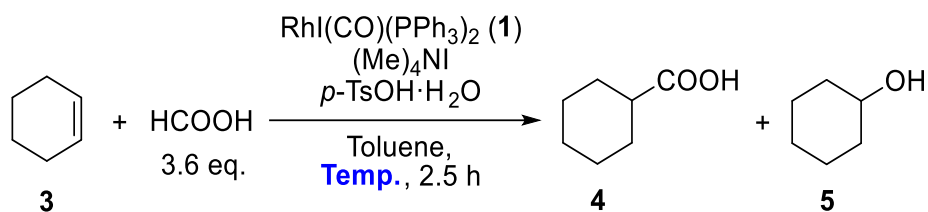
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Table S6 Hydroxycarbonylation of substituted alkanes (major by-products). ^[a]



Entry	Y	Conv. [%]		Yield [%] ^[b]				
		5 ^[b] or 6 ^[b]	HCOOH ^[c]	3	4	5	6	7
1	OH (5)	99	62	24	40	-	3	1
2	I (6)	18	94	7	1	0	-	1

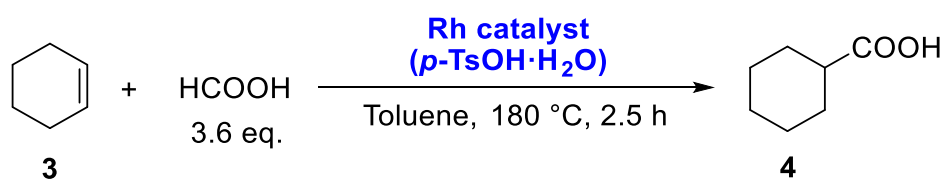
[a] Reaction conditions: **1** (219 mg, 0.280 mmol), substituted alkane (470 mg, 5.72 mmol), HCOOH (948 mg, 20.6 mmol), (Me)₄NI (56.3 mg, 0.280 mmol), *p*-TsOH·H₂O (190 mg, 1.00 mmol), toluene (6 mL). [b] Calculated from the GC results using dodecane as internal standard. [c] Calculated from the HPLC results.

Table S7 Effect of reaction temperature on hydroxycarbonylation of **3**.^[a]

Entry	Temp. [°C]	Conv. [%]		Yield [%] ^[b]			
		3 ^[b]	HCOOH ^[c]	4	5	6	9
1	120	59	3	0	26	4	1
2	140	65	6	4	28	5	1
3	160	78	10	36	15	4	1
4	180	89	50	81	2	2	1
5	200	95	86	78	0	1	1

[a] Reaction conditions: **1** (219 mg, 0.280 mmol), **3** (470 mg, 5.72 mmol), HCOOH (948 mg, 20.6 mmol), $(\text{Me})_4\text{NI}$ (56.3 mg, 0.280 mmol), $p\text{-TsOH}\cdot\text{H}_2\text{O}$ (190 mg, 1.00 mmol), toluene (6 mL), 2.5 h. [b] Calculated from the GC results using dodecane as internal standard. [c] Calculated from the HPLC results.

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Table S8 Hydroxycarbonylation of **3** using Rh catalyst without (Me)₄Ni. [a]

Entry	Catalyst	<i>p</i> -TsOH·H ₂ O [mmol]	Conv. [%]		Yield [%] ^[b]			
			3 ^[b]	HCOOH ^[d]	4	5	6	9
1	RhH ₂ (CO)(PPh ₃) ₂ (2)	-	52	46	9	0	0	4
2	RhH ₂ (CO)(PPh ₃) ₂ (2)	1.00	92	79	71	0	0	1
3	RhI(CO)(PPh ₃) ₂ (1)	-	31	60	0	0	0	7
4 ^[c]	RhH ₂ (CO)(PPh ₃) ₂ (2)	-	89	83	74	0	0	1

[a] Reaction conditions: Rh catalyst (0.280 mmol), **3** (470 mg, 5.72 mmol), HCOOH (948 mg, 20.6 mmol), toluene (6 mL) [b] Calculated from the GC results using dodecane as internal standard. [c] Using AcOH as solvent instead of toluene. [d] Calculated from the HPLC results.

NMR analysis for the product obtained from the reaction of $\text{RhI}(\text{CO})(\text{PPh}_3)_2$ (**1**) with the promoters.

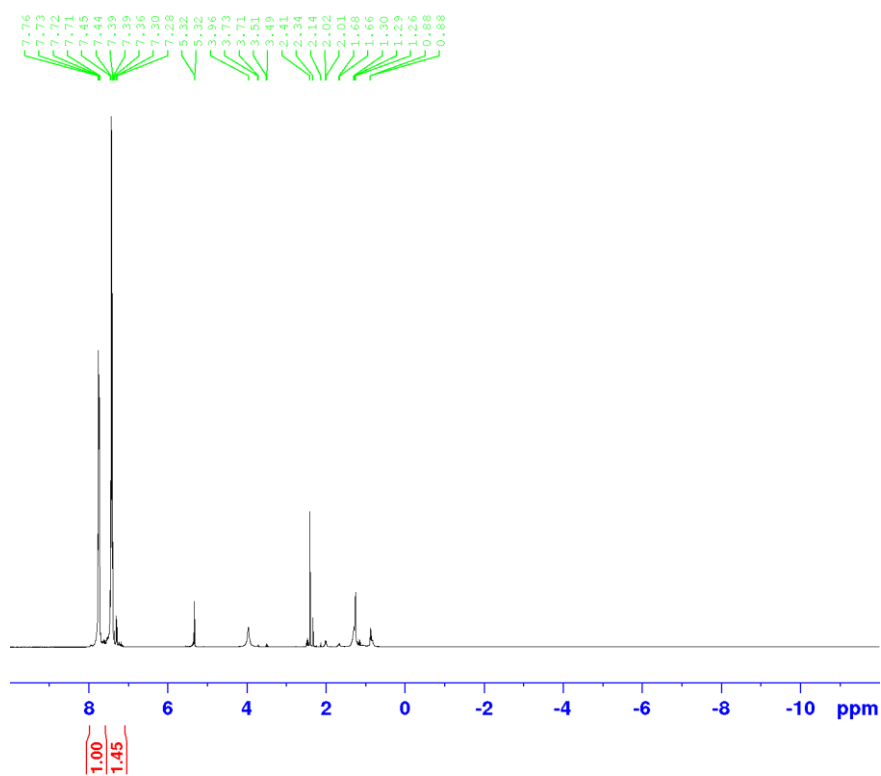


Fig. S1 ^1H NMR spectra (400 MHz, CD_2Cl_2) of the products of the reaction of **1** with 3 equiv of $p\text{-TsOH}\cdot\text{H}_2\text{O}$.

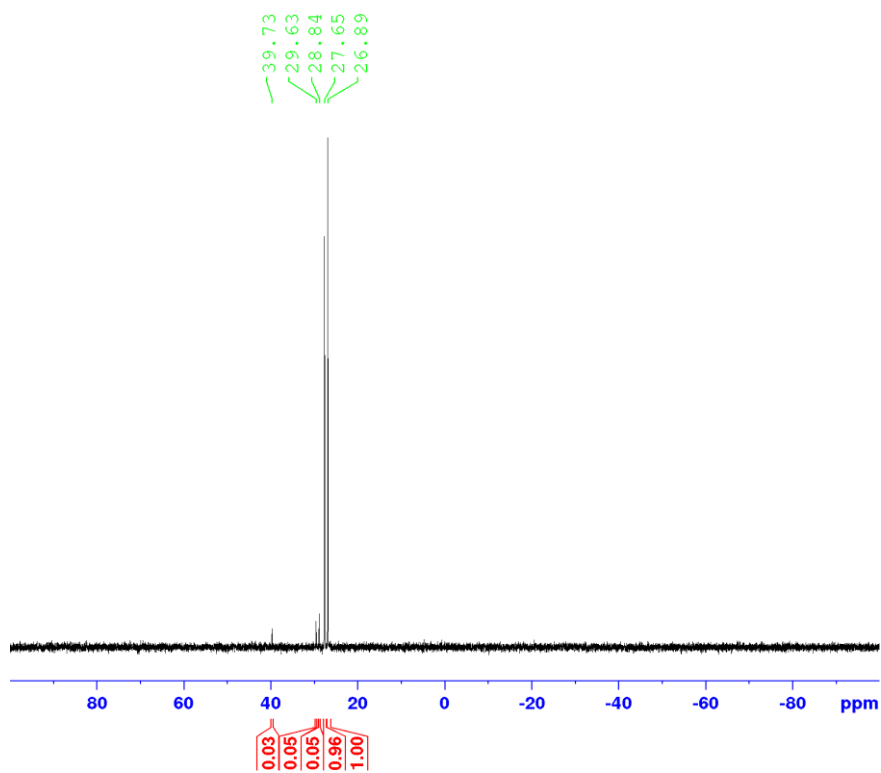


Fig. S2 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (162 MHz, CD_2Cl_2) of the products of the reaction of **1** with 3 equiv of $p\text{-TsOH}\cdot\text{H}_2\text{O}$.

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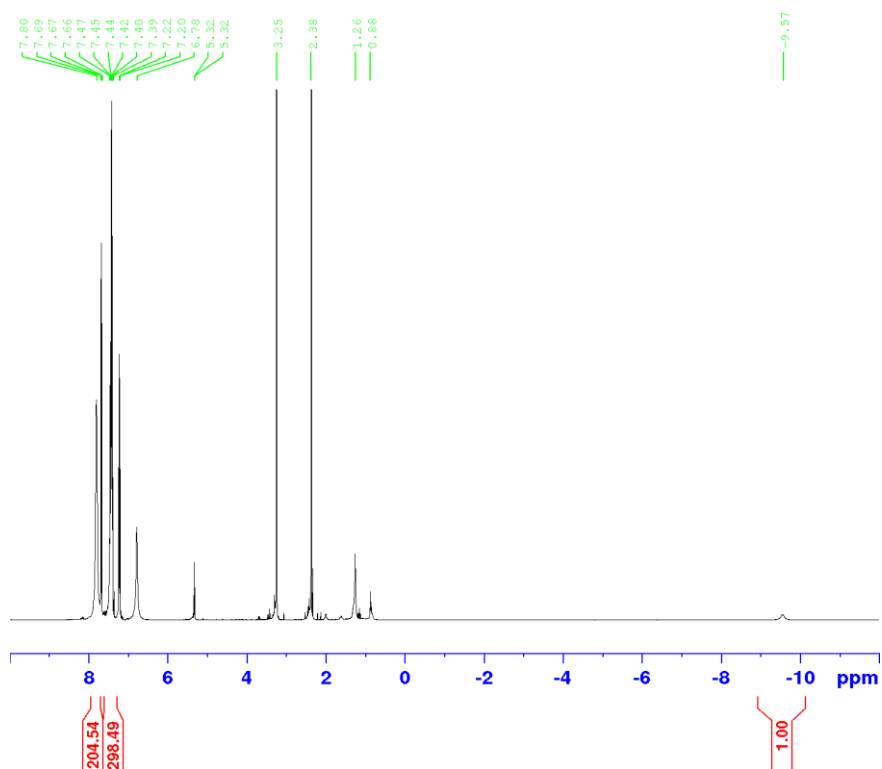


Fig. S3 ^1H NMR spectra (400 MHz, CD_2Cl_2) of the products of the reaction of **1** with 3 equiv of $p\text{-TsOH}\cdot\text{H}_2\text{O}$ and 1 equiv of $(\text{Me})_4\text{Ni}$.

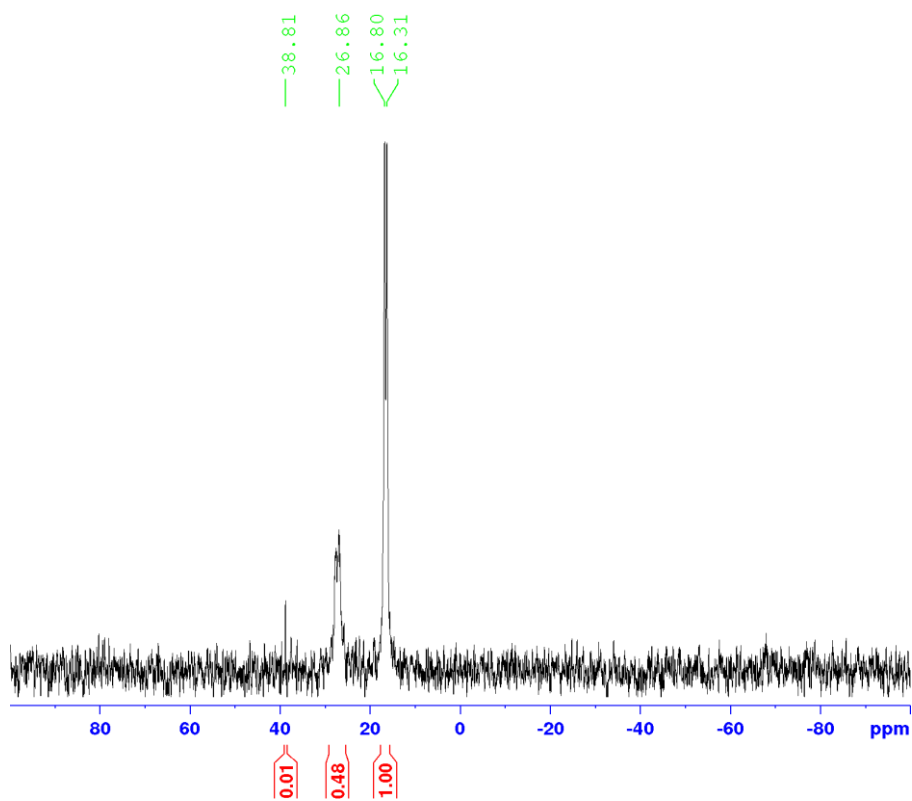


Fig. S4 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (162 MHz, CD_2Cl_2) of the products of the reaction of **1** with 3 equiv of $p\text{-TsOH}\cdot\text{H}_2\text{O}$ and 1 equiv of $(\text{Me})_4\text{Ni}$.

Characterization of $\text{RhH}_2(\text{CO})(\text{PPh}_3)_2$ (**2**) synthesised from the reaction of $\text{Rh}(\text{CO})(\text{PPh}_3)_2$ (**1**) with HI.

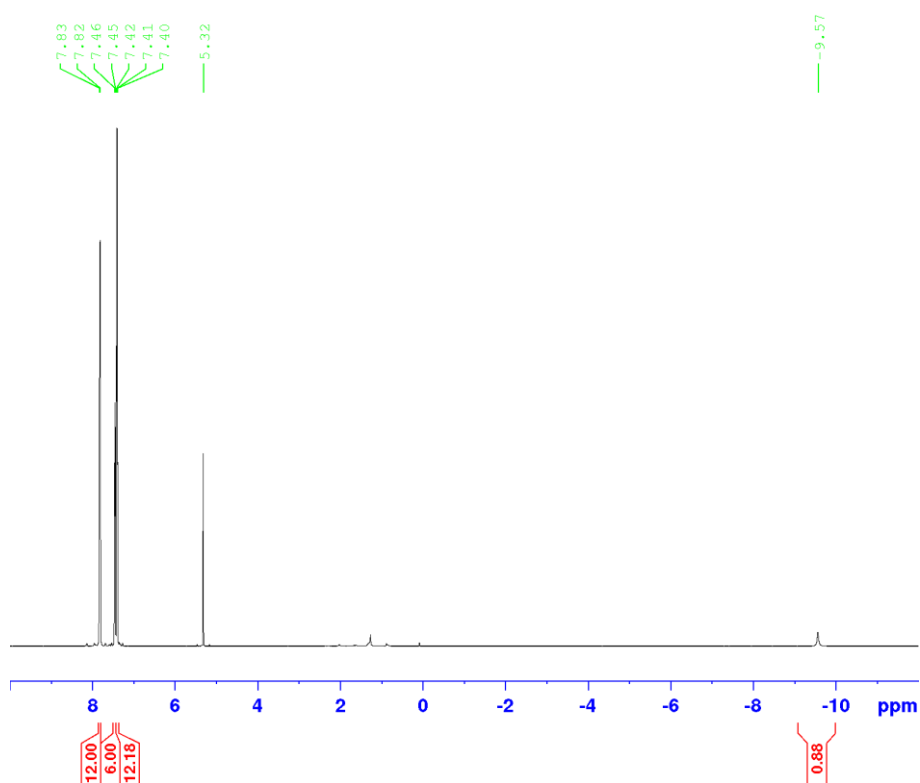


Fig. S5 ^1H NMR spectra (600 MHz, CD_2Cl_2) of **2**.

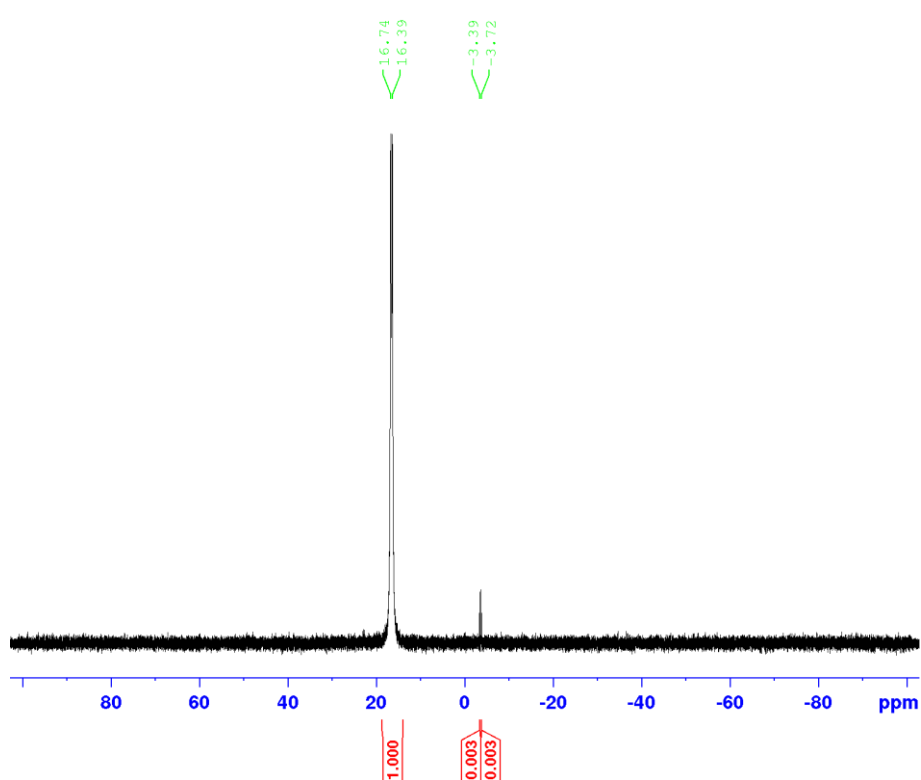


Fig. S6 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (243 MHz, CD_2Cl_2) of **2**.

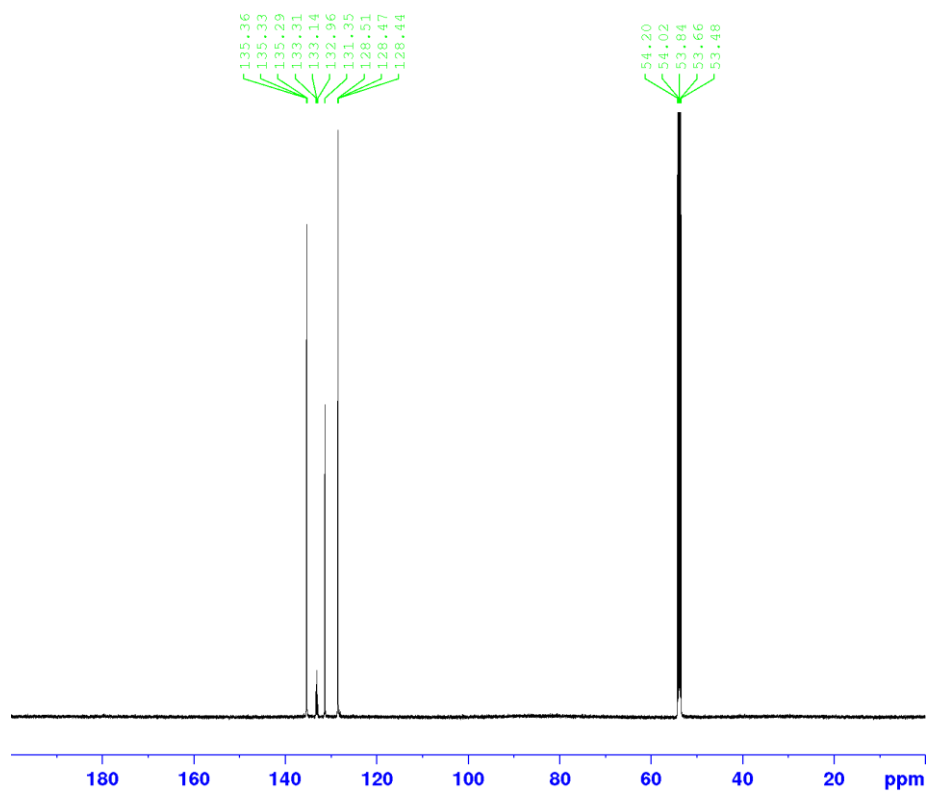


Fig. S7 $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (151 MHz, CD_2Cl_2) of **2**.

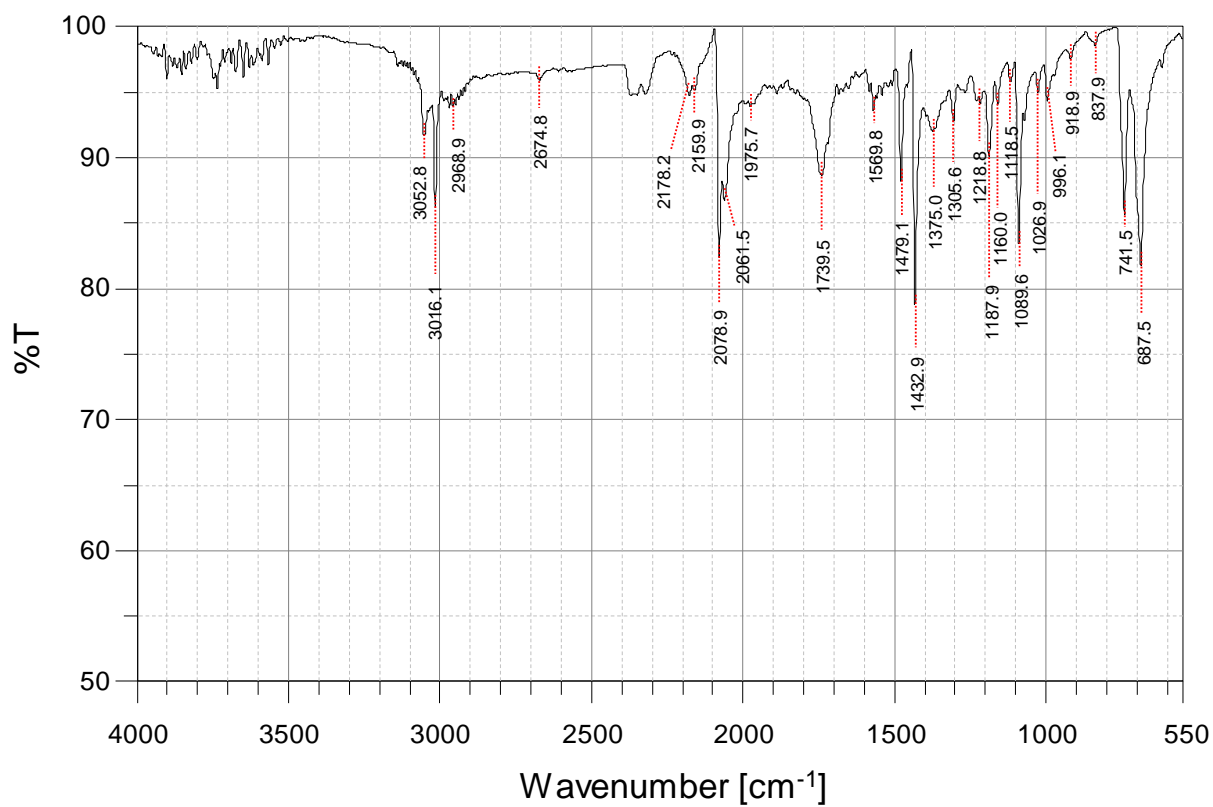


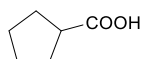
Fig. S8 FTIR spectra (ATR) of **2**.

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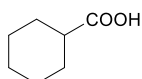
Table S9 Crystal data and details of crystal structure determination for **2**.

Empirical formula	C ₃₉ H ₃₃ I ₂ OCl ₂ RhP ₂
Formula weight	995.19
<i>T</i> (K)	93(2)
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	10.1542(2)
<i>b</i> (Å)	13.7673(3)
<i>c</i> (Å)	14.3456(3)
α (°)	72.6361(19)
β (°)	88.2388(16)
γ (°)	74.6748(18)
<i>V</i> (Å ³)	1843.48(7)
<i>Z</i>	2
<i>d</i> _{calc} (g/cm ³)	1.793
μ (Mo K α) (mm ⁻¹)	2.399
<i>F</i> (000)	968.0
Crystal size	0.210 × 0.200 × 0.180
2 θ range (°)	4.992 to 49.998
Reflections collected	29529
Independent reflections (<i>R</i> _{int})	6457 (0.0243)
Absorption correction	Multi-scan
Max. / min. transmission	1.00000 / 0.63902
Data / restraints / parameters	6457 / 0 / 419
GOF on <i>F</i> ²	1.305
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0247, 0.0678
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0256, 0.0680
Largest peak and hole (e Å ³)	0.70 and -0.61

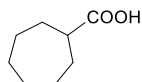
NMR and HRMS data of synthesized carboxylic acids.



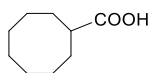
Cyclopentanecarboxylic acid: ^1H NMR (CD_2Cl_2 , 400 MHz): 9.79 (brs, 1H, COOH), 2.76 (quint, $J = 7.9$ Hz, 1H, CHCOOH), 2.03-1.49 (m, 9H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): 183.6, 44.0, 30.3, 26.2. HRMS (ESI): calcd for $\text{C}_6\text{H}_{10}\text{O}_2\text{Na}$ ($[\text{M}+\text{Na}]^+$) 137.0573; found 137.0572.



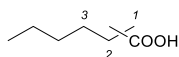
Cyclohexanecarboxylic acid: ^1H NMR (CD_2Cl_2 , 400 MHz): 11.57 (brs, 1H, COOH), 2.32 (tt, $J = 11.1$ and 3.6 Hz, 1H, CHCOOH), 1.98-1.87 (m, 2H, CH_2), 1.81-1.70 (m, 2H, CH_2), 1.68-1.60 (m, 1H, CH_2), 1.51-1.37 (m, 2H, CH_2), 1.36-1.16 (m, 3H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): 183.4, 43.4, 29.2, 26.1, 25.8. HRMS (ESI): calcd for $\text{C}_7\text{H}_{12}\text{O}_2\text{Na}$ ($[\text{M}+\text{Na}]^+$) 151.0730; found 151.0731.



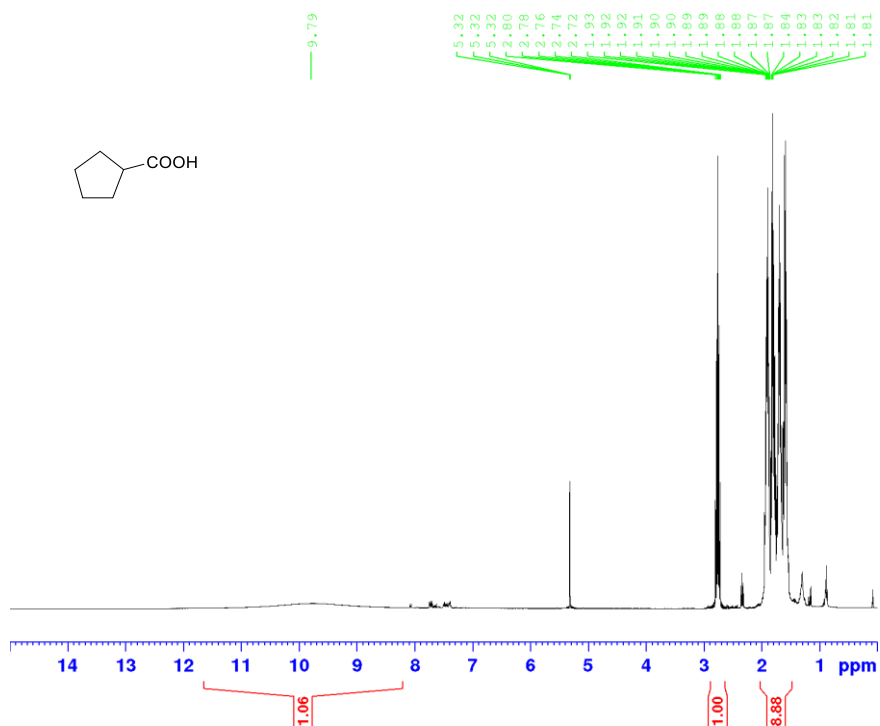
Cycloheptanecarboxylic acid: ^1H NMR (CD_2Cl_2 , 400 MHz): 11.00 (brs, 1H, COOH), 2.42 (tt, $J = 8.3$ and 4.5 Hz, 1H, CHCOOH), 1.94-1.79 (m, 2H, CH_2), 1.72-1.31 (m, 10H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): 184.2, 45.2, 31.0, 28.7, 26.7. HRMS (ESI): calcd for $\text{C}_8\text{H}_{14}\text{O}_2\text{Na}$ ($[\text{M}+\text{Na}]^+$) 165.0886; found 165.0885.



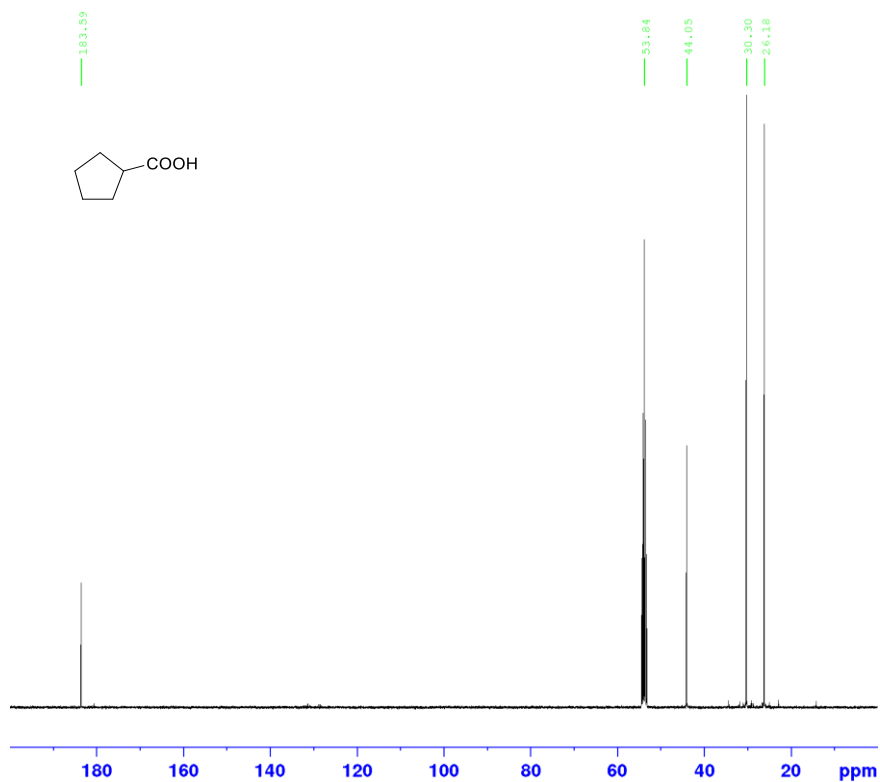
Cyclooctanecarboxylic acid: ^1H NMR (CD_2Cl_2 , 400 MHz): 11.67 (brs, 1H, COOH), 2.55 (tt, $J = 9.1$ and 3.9 Hz, 1H, CHCOOH), 2.02-1.87 (m, 2H, CH_2), 1.80-1.42 (m, 12H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): 184.6, 43.9, 28.9, 27.2, 26.5, 25.6. HRMS (ESI): calcd for $\text{C}_9\text{H}_{16}\text{O}_2\text{Na}$ ($[\text{M}+\text{Na}]^+$) 179.1043; found 179.1042. Note: The product, cyclooctanecarboxylic acid, contains small amounts of isomeric carboxylic acids as by-products, which were detected by GC-MS.



Heptanoic acid (isomeric mixtures with 2-methylhexanoic acid and 2-ethylpentanoic acid): ^1H NMR (CD_2Cl_2 , 400 MHz): 10.3 (brs, 1H, COOH), 2.34 (t, $J = 7.8$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{COOH}$), 1.61 (q, $J = 7.8$ Hz, 2H, CH_2), 1.37-1.24 (m, 6H, CH_2), 0.89 (t, $J = 7.8$ Hz, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz): 180.7, 34.4, 31.8, 29.1, 25.0, 22.9, 14.2. HRMS (ESI): calcd for $\text{C}_7\text{H}_{14}\text{O}_2\text{Na}$ ($[\text{M}+\text{Na}]^+$) 153.0886; found 153.0884. Note: Since the minor products, 2-methylhexanoic acid and 2-ethylpentanoic acid, have low content and overlapping signals, only the assignment of the main product, heptanoic acid, is shown.

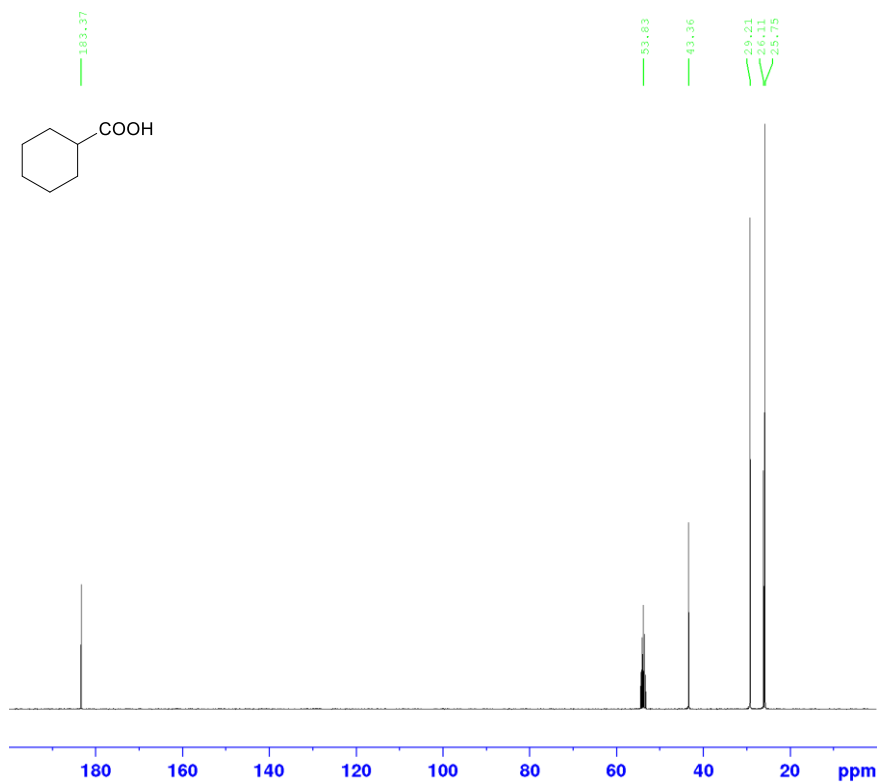
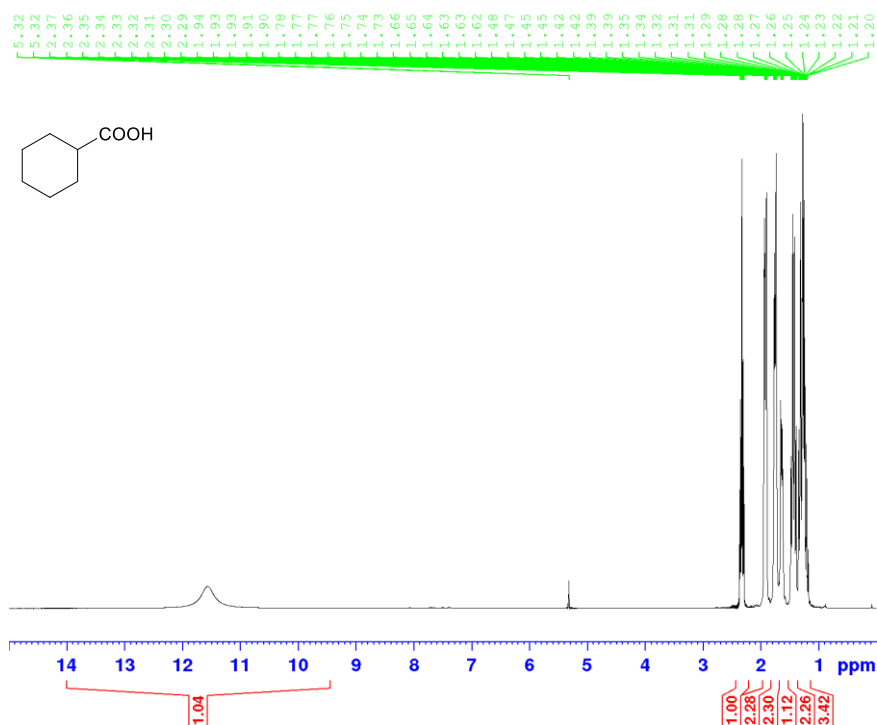


^1H NMR spectrum of cyclopentanecarboxylic acid (CD_2Cl_2 , 400 MHz).

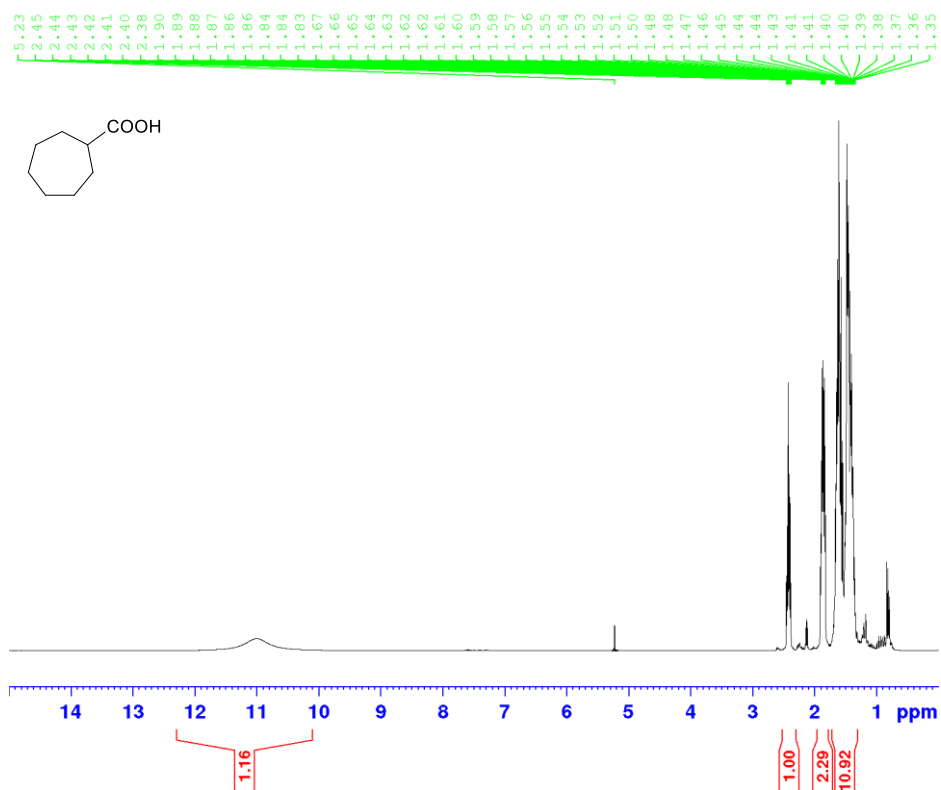


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of cyclopentanecarboxylic acid (CD_2Cl_2 , 100 MHz).

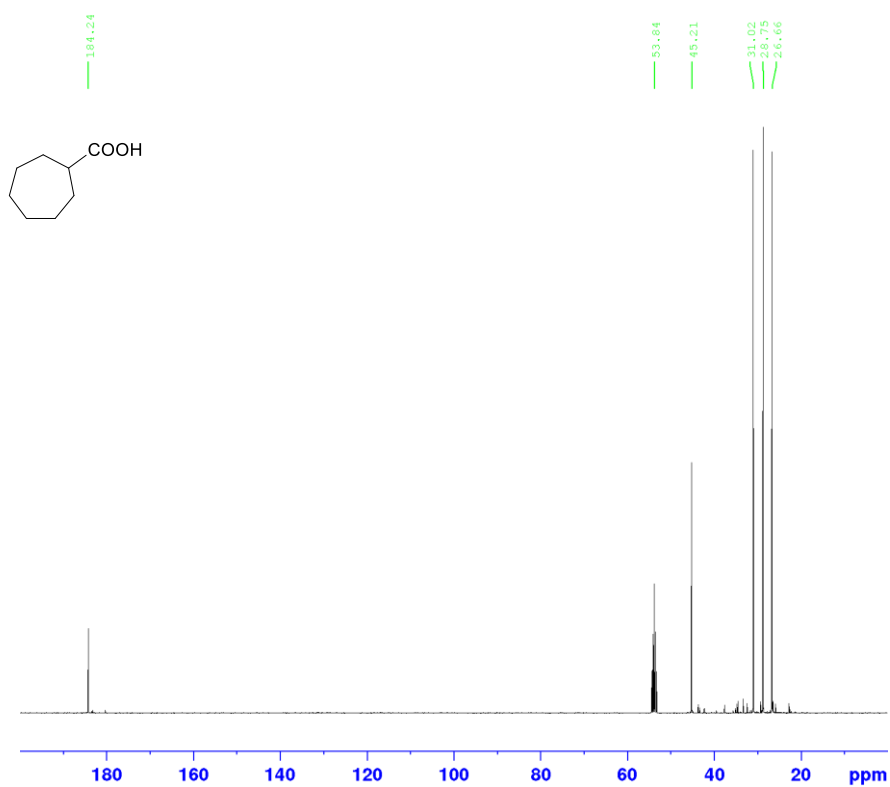
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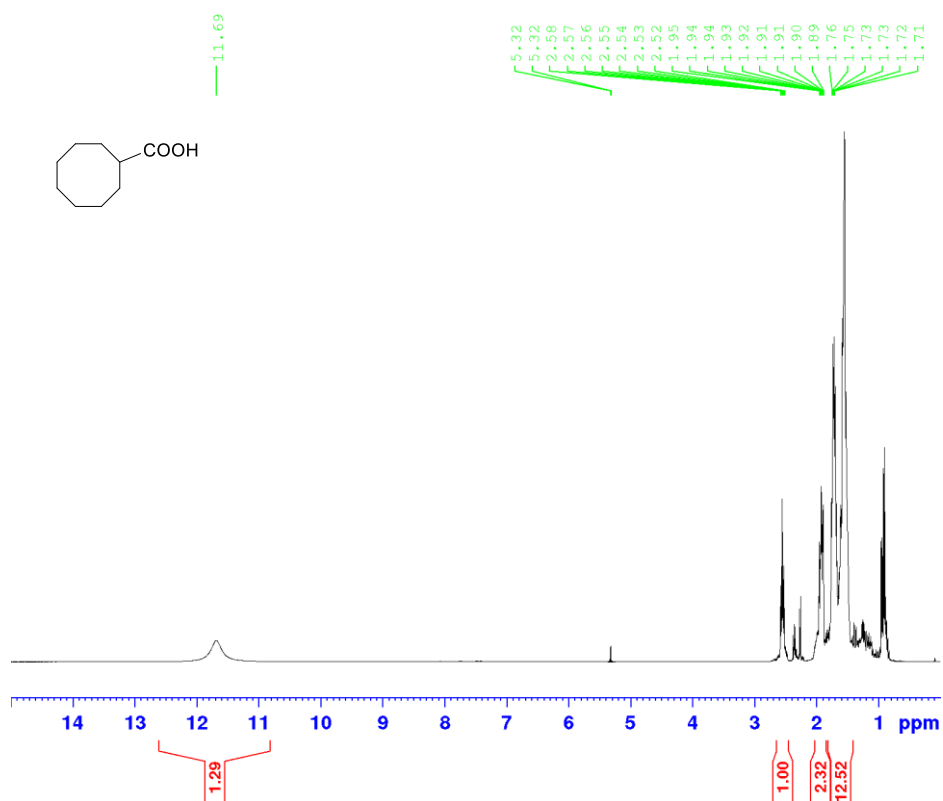


^1H NMR spectrum of cycloheptanecarboxylic acid (CD_2Cl_2 , 400 MHz).

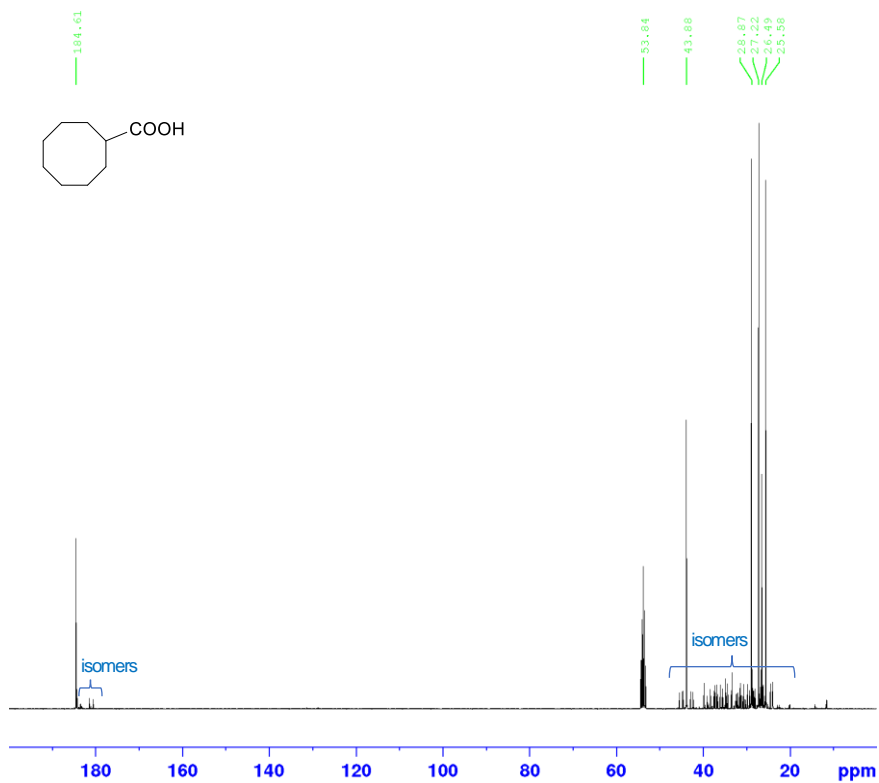


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of cycloheptanecarboxylic acid (CD_2Cl_2 , 100 MHz).

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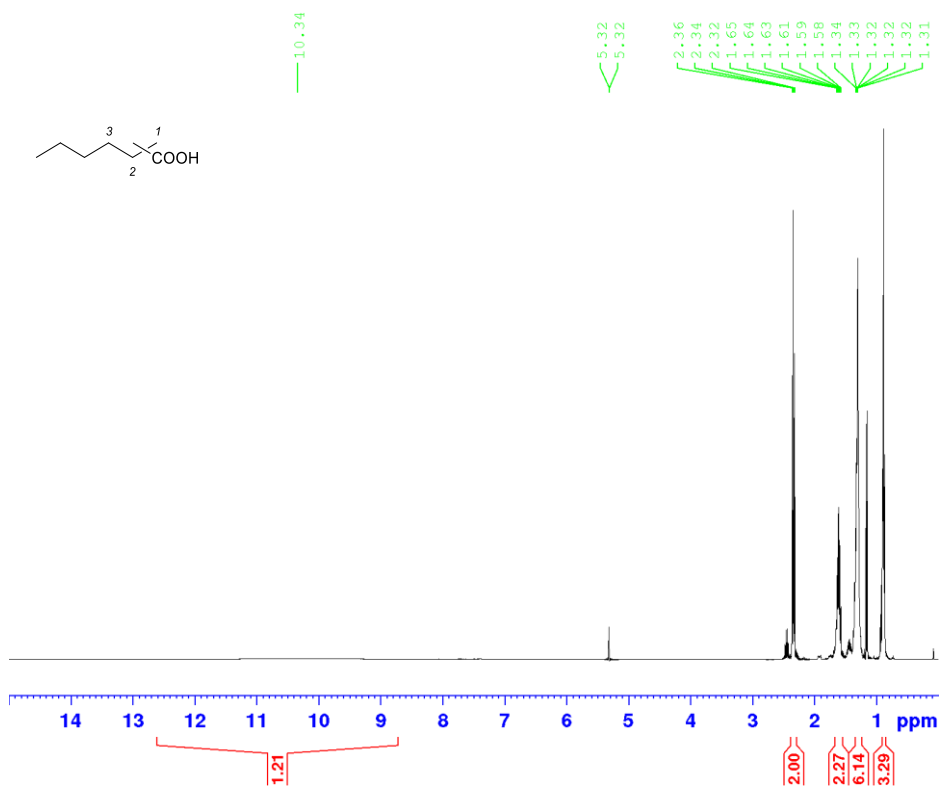


¹H NMR spectrum of cyclooctanecarboxylic acid (CD₂Cl₂, 400 MHz).

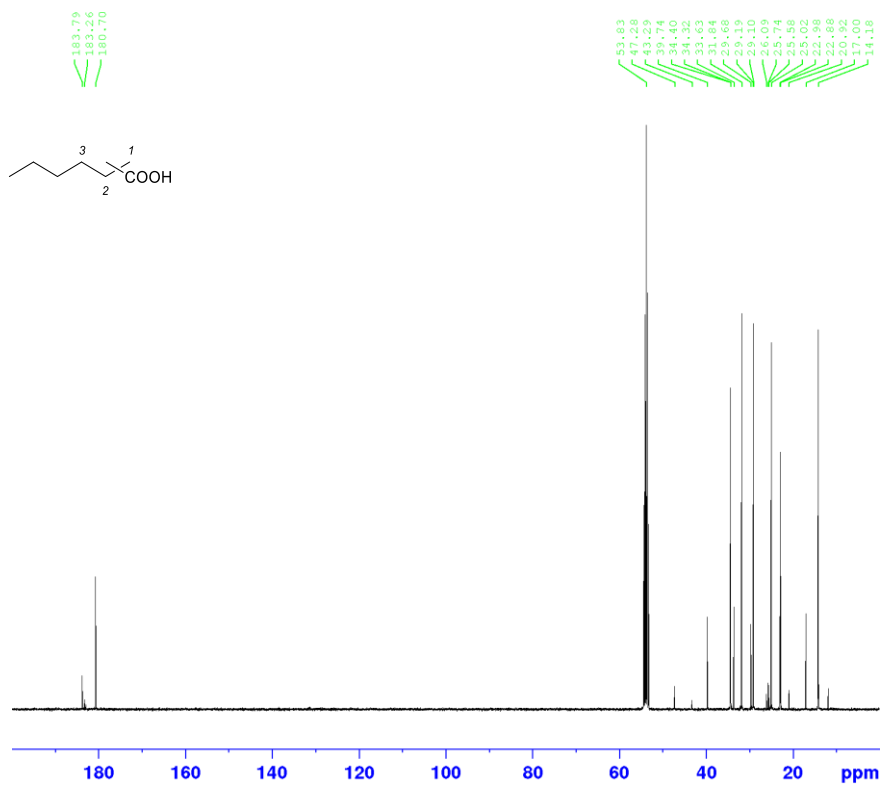


¹³C{¹H} NMR spectrum of cyclooctanecarboxylic acid (CD₂Cl₂, 100 MHz).

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¹H NMR spectrum of heptanoic acid and its isomeric mixtures (CD₂Cl₂, 400 MHz).



¹³C{¹H} NMR spectrum of heptanoic acid and its isomeric mixtures (CD₂Cl₂, 100 MHz).

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GC-MS data of cyclooctanecarboxylic acid and its isomers

