Supporting Information

Rhodium-terpyridine Catalyzed Redox-neutral Depolymerization of Lignin in Water

Yuxuan Liu,[a,b] Changzhi Li,*[b] Wang Miao,[a] Weijun Tang,[a] Dong Xue,[a] Jianliang Xiao,[c] Tao Zhang,[b] Chao Wang*[a]

[a] Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education and School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710119, China

[b] CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China

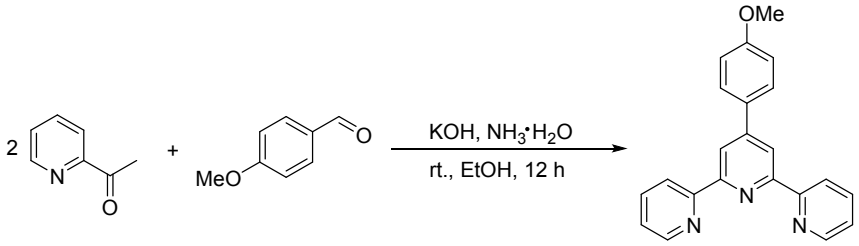
[c] Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD, UK

Table of contents

1. General information

Unless otherwise specified, the chemicals were obtained commercially and used without further purification. Solvents (ethyl acetate, petroleum ether) used for column chromatography were of technical grade and used after distillation. Water was ultrapure water. Poplar wood materials were obtained from Dalian Hongda Wood Co., Ltd, China. They were milled into powders in size of 40-60 meshes and dried under vacuum at 60 °C for 3 days before use. Analytical thin layer chromatography (TLC) was conducted with TLC plates (Silica gel 60 F254, Qingdao Haiyang) and visualization on TLC was achieved by UV light (254 nm). Flash column chromatography was performed on silica gel 200-300 mesh with freshly distilled solvents. Matrix assisted Laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) was carried out to check the oil molecular weight distribution in an AB Sciex TOF-5800 machine. A 15 g/L solution of DHB (2,5-dihydroxylbenzoic acid) in methanol was used as matrix. NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer with TMS as the internal standard. Multiplicities are given as: brs (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublets of doublet), dt (doublets of triplet), td (triplets of doublet) or m (multiplet). HRMS data were recorded on a Bruker maXis UHR-TOF mass spectrometer. Gas chromatography (GC) analysis was performed on a SHIMADZU GC-2014 gas chromatograph with a HP-5 MS column (quartz capillary column, 30 m x 0.25 mm x 0.25 μm). GC-MS analysis was carried out on Varian 450GC-320 MS with FID detector and HP-5 capillary column. GPC analysis was carried out on a Viscotek TDAmax with three detectors (refractive index, light scattering, and viscometry detectors), a Viscotek column (modified porous styrene-divinylbenzene copolymer, 300 mm length 7.8 mm inside diameter) and a guard column (40 mm length 7.8 mm inside diameter). Lignin model compounds **2a-2j** were synthesized according to the literature.[1-8] Poplar wood dioxasolv lignin was extracted according to the literature,[9-12] the yield of extracted lignin is *ca.* 20 mg/g. The compound **2a'** were prepared according to the literature.[13, 14]

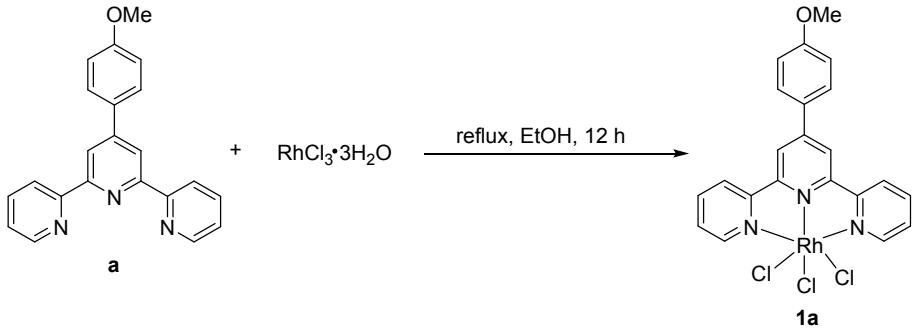
2. Typical procedure for the preparation of terpyridine ligands (a-e)



a

Ligands **a-e** was were synthesized according to the literature.[15] A typical procedure: 2-acetylpyridine (2.42 g, 20 mmol), 4-methoxybenzaldehyde (1.36 g, 10 mmol) and EtOH (50 mL) were added to a 200 mL round-bottom flask. Then, KOH pellets (1.54 g, 85%, 20 mmol) and NH_3•H_2O (29 mL, 29.3%, 25 mmol) were added to the solution. The solution was stirred at room temperature for 12 h. After the reaction, the solid was collected by filtration and washed with EtOH (3 × 20 mL). Recrystallization from $CHCl_3$/EtOH afforded white crystalline solid. (0.881 g, 26% yield). Other ligands were prepared following the same procedure as that of **a**. Ligands **f**, **g** and **h** were purchased from XPR INDUSTRIAL (CHINA) LIMITED.

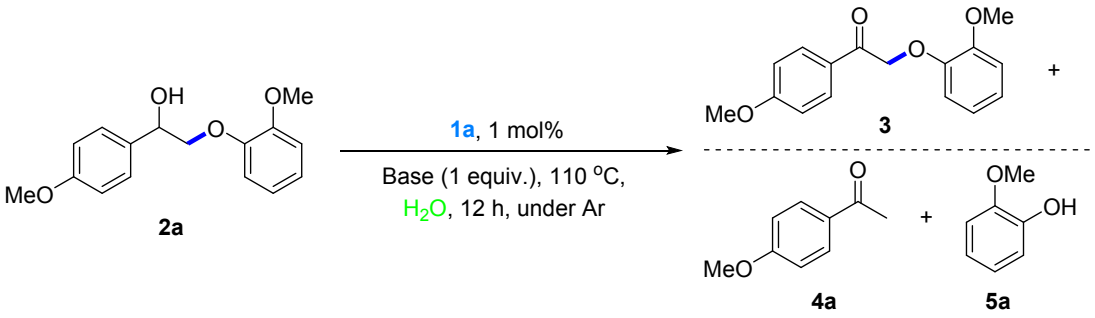
3. Typical procedure for the preparation of terpyridine Rh complexes (1a-1h)



Complex **1a-1h** were prepared according to the literature.[16] A typical procedure: $RhCl_3•3H_2O$ (0.132 g, 0.5 mmol), ligand **a** (0.170 g, 0.5 mmol) and ethanol (20 mL) were added to a 100 mL round-bottom flask, then the reaction mixture was refluxed for 12 h. The yellow solid was collected by filtration, washed with water, hot ethanol, and diethyl ether. The solid product **1a** was then dried at 50 °C overnight under vacuum (0.250 g, 91% yield). These complexes were characterized by NMR and HRMS. The ^{13}C NMR spectra of some complexes were not obtained due to their low solubilities.

4. Optimization of reaction conditions for the cleavage of 2a

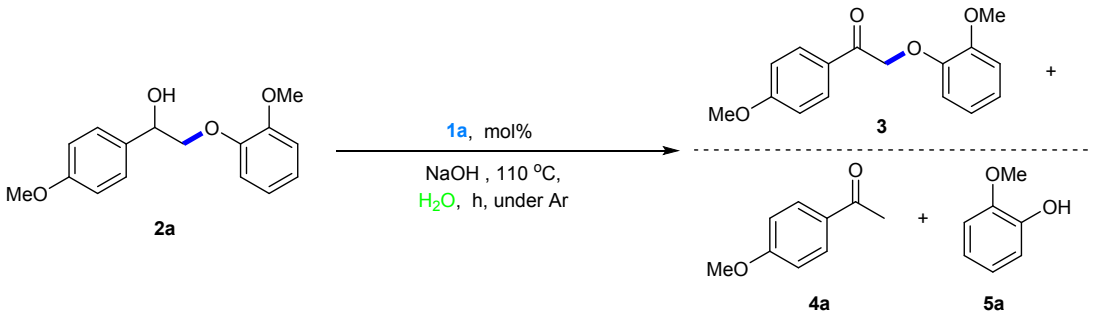
Table S1 The effect of different bases[a]



Entry	Base	Conversion (%)	Yield[b] (%)		
			3	**4a**	**5a**
1	NaOH	**86**	**7**	**73**	**77**
2	KOH	70	9	53	57
3	LiOH	80	9	64	68
4	Na_2CO_3	32	10	19	21
5	K_2CO_3	29	10	13	17
6	CH_3COONa	0	0	0	0

[a] Reaction conditions: **2a** (0.2 mmol), **1a** (0.002 mmol), base (0.2 mmol), H_2O (1 mL), 110 °C, 12 h, under Ar. After the reaction, hydrochloric acid (1 M) was used to acidify the solution to pH = ca. 1. [b] Yields were determined by GC-FID with diphenyl as internal standard.

Table S2 The effect of the amount of base, catalyst, reaction time, and temperature[a]



Entry	NaOH (equivalent)	**1a** (mol%)	Time (h)	Temp. (°C)	Conversion (%)	Yield[b] (%)		
						3	**4a**	**5a**
1	0.5	1	12	110	68	11	47	51
2	1	1	12	110	86	7	73	77
3	1.5	1	12	110	**100**	**10**	**84**	**87**
4	1.5	0.5	12	110	25	9	13	15
5	1.5	0.5	48	110	100	10	58	68
6	1.5	0.5	12	130	85	11	49	56
7	1.5	0.2	96	110	21	9	10	11
8	1.5	1	12	100	81	10	64	69
9	1.5	1	12	80	40	9	24	27
10	1.5	1	48	80	85	6	70	78
11	1.5	-	12	110	4	0	0	0
12	-	1	12	110	0	0	0	0

[a] Reaction conditions: **2a** (0.2 mmol), **1a** (mmol), NaOH, H_2O (1 mL), 110 °C, 12 h, under Ar. After the reaction, hydrochloric acid (1 M) was used to acidify the solution to pH = ca. 1. [b] Yields were determined by GC-FID with diphenyl as internal standard.

5. Typical procedure for the cleavage of lignin model compounds

2a (0.4 mmol), **1a** (2.19 mg, 1 mol%), NaOH (0.6 mmol) and degassed H_2O (1 mL) were added to a 35 mL pressure tube, then the tube was sealed under an atmosphere of argon. The mixture was stirred and heated at 110 °C (oil bath temperature) for 12 h. After cooling to room temperature, hydrochloric acid (1 M) was used to acidify the solution to pH = ca. 1, which was then extracted with ethyl acetate (3 x 10 mL). The organic layers were combined, washed with brine, dried over Na_2SO_4, filtered and evaporated in vacuo. The reaction was determined by GC-FID with diphenyl as the internal standard to give the GC yield. Alternatively, the crude products were purified by flash chromatography on silica gel, eluting with hexane/ethyl acetate (20:1) to get the desired products.

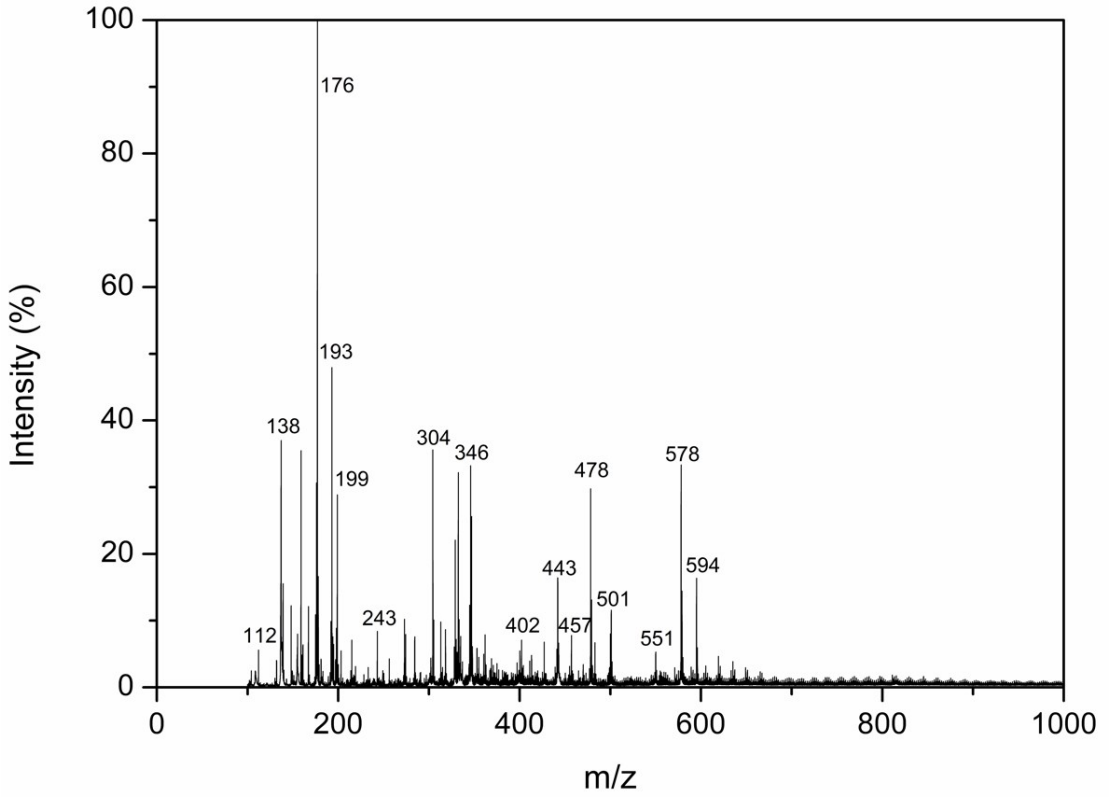
6. Depolymerization of the extracted poplar wood dioxasolv lignin

6.1 General procedure

A 35 mL pressure tube was charged with the extracted poplar wood lignin (100 mg), **1a** (2.74 mg), NaOH (30 mg) and degassed H_2O (1 mL), then the tube was sealed under an atmosphere of argon. The mixture was then heated at 110 °C (oil bath temperature) for 24 h. After cooling to room temperature, hydrochloric acid (1 M) was used to acidify the solution to pH = ca. 1, which was then extracted with ethyl acetate (3 x 10 mL). The organic layers were combined, washed with brine, dried over Na_2SO_4, filtered and evaporated in vacuo. The yield of the oil is 90 wt% based on the starting lignin. The monomer products in liquid oil were analyzed and quantified by GC-FID with mesitylene as internal standard (HP-5 column, 30 m × 0.32 mm × 0.25 μm). The total yield of the monomers is 9.7 wt% based on the starting lignin. The structures of the monomers are proposed based on the molecular weight of the GC-MS (Varian 450GC-320 MS with FID detector and HP-5 capillary column) analysis. (Scheme S2 and Scheme S4). The molecular weight distribution of the liquid oil was analyzed by MALDI-TOF with the mass range of m/z 50-1000.

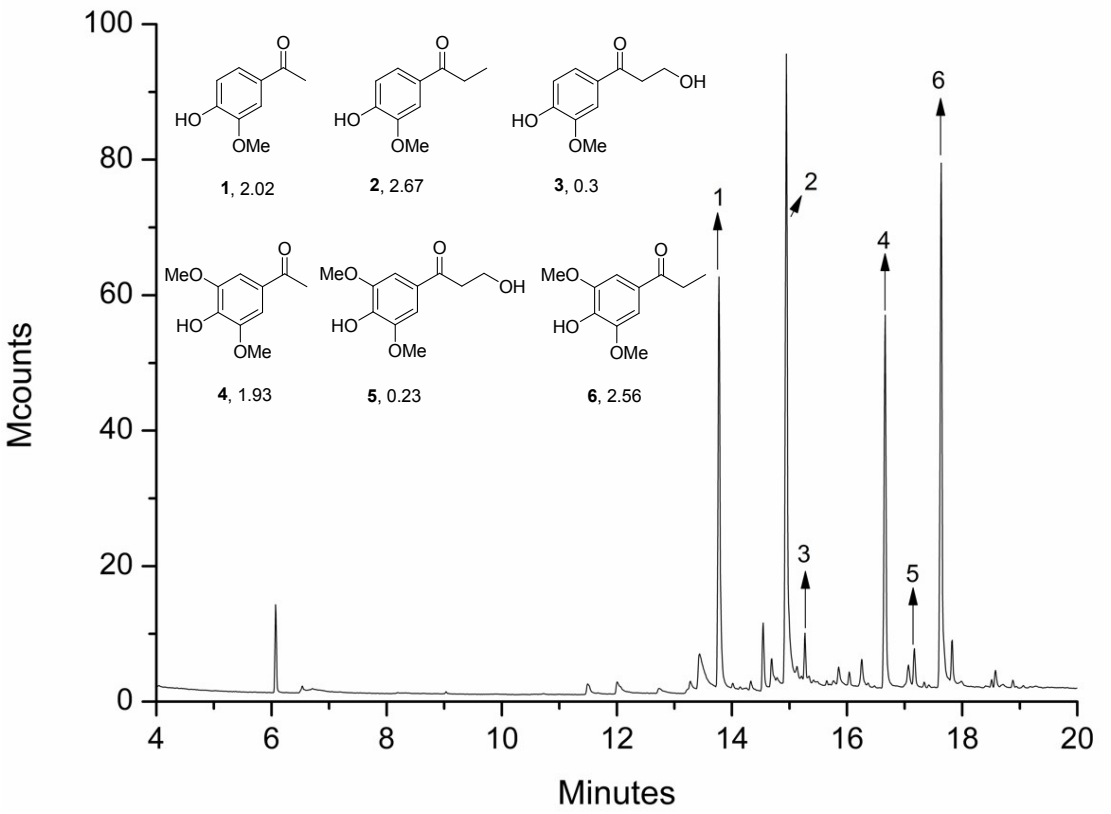
6.2 Characterization results of the oil from the extracted poplar wood dioxasolv lignin

6.2.1 MALDI-TOF spectroscopy



Scheme S1. MALDI-TOF spectrum of the oil from the depolymerization of the extracted poplar wood lignin.

6.2.2 GC-MS and GC-FID analysis of the oil from the extracted poplar wood lignin



Scheme S2. GC-MS spectrum of the oil from the depolymerization of the extracted poplar wood lignin.

Table S3. Yields of monomers in the oil from the depolymerization of the extracted poplar wood lignin[a]

Yield[b] (mg)	2.02	2.67	0.3	1.93	0.23	2.56

[a] Reaction conditions: Poplar wood dioxasolv lignin (100 mg), **1a** (2.74 mg), NaOH (30 mg), H_2O (1 mL), 110 °C, 24 h, under Ar. After the reaction, hydrochloric acid (1 M) was used to acidify the solution to pH = ca. 1. [b] Yields were determined by GC-FID with mesitylene as internal standard.

7. Depolymerization of the raw poplar wood powder

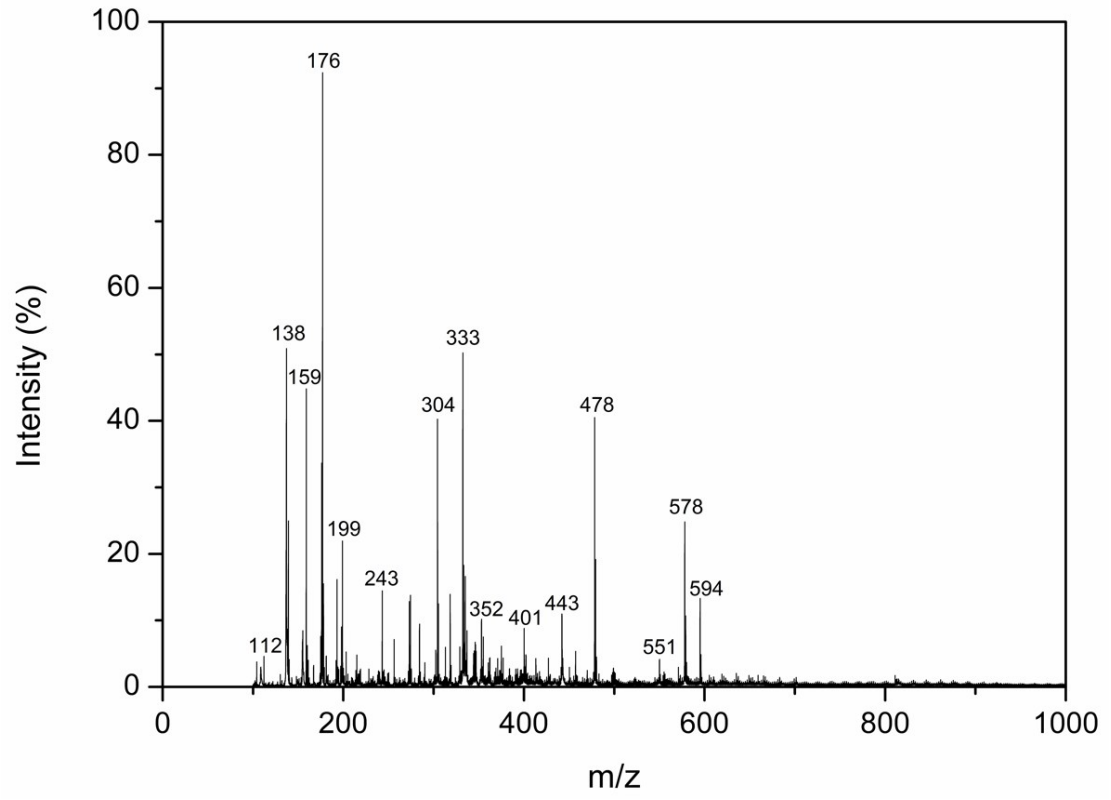
7.1 General procedure

A pressure tube was equipped with a magnetic stir bar and was charged with the raw poplar wood powder (1000 mg), **1a** (13.7 mg), NaOH (300 mg) and degassed H_2O (20 mL), then the tube was sealed under an atmosphere of argon, heated at 110 °C (oil bath temperature) for 24 h. After cooling to room temperature, hydrochloric acid (1 M) was used to acidify the solution to pH = ca. 1, the remaining solid was separated by vacuum filtration and heated at 50 °C overnight under vacuum. The filtrate was analyzed by HPLC-MS, which did not contain any sugar derivatives, such as glucose, xylose, 5-hydroxylfurfural, and polyols. The aqueous solution from the filtration was then extracted with ethyl acetate (3 x 20 mL). The organic layers were combined, washed with brine, dried over Na_2SO_4, filtered and evaporated in vacuo. The yield of the resulting oil is 15 wt% (150 mg) based on the starting raw poplar wood powder. The lignin component in the poplar

wood powder is 18.6 wt%,[17] thus most of the lignin in the poplar wood powder has been depolymerized. The molecular weight distribution of the oil was analyzed by MALDI-TOF with the mass range of m/z 50-1000. The monomer products in the oil were analyzed and quantified by GC-FID with mesitylene as an internal standard (HP-5 column, 30 m × 0.32 mm × 0.25 μm). The total yield of the monomers is 16.7 wt% based on the lignin oil and 2.5 wt% based on the starting raw poplar wood powder. Elemental analysis of the solid showed that it contains 36.65% carbon, 5.59% hydrogen and 56.2% oxygen, which fits with that of cellulose/hemicellulose.[18] The yield of the (hemi)cellulose is 65 wt% based on the starting raw poplar wood powder. Enzymatic hydrolysis of the solid yielded 72% of glucose and 20% of xylose respectively (based on the weight of solid). The enzymatic hydrolysis was carried out according the our previous procedure.[14]

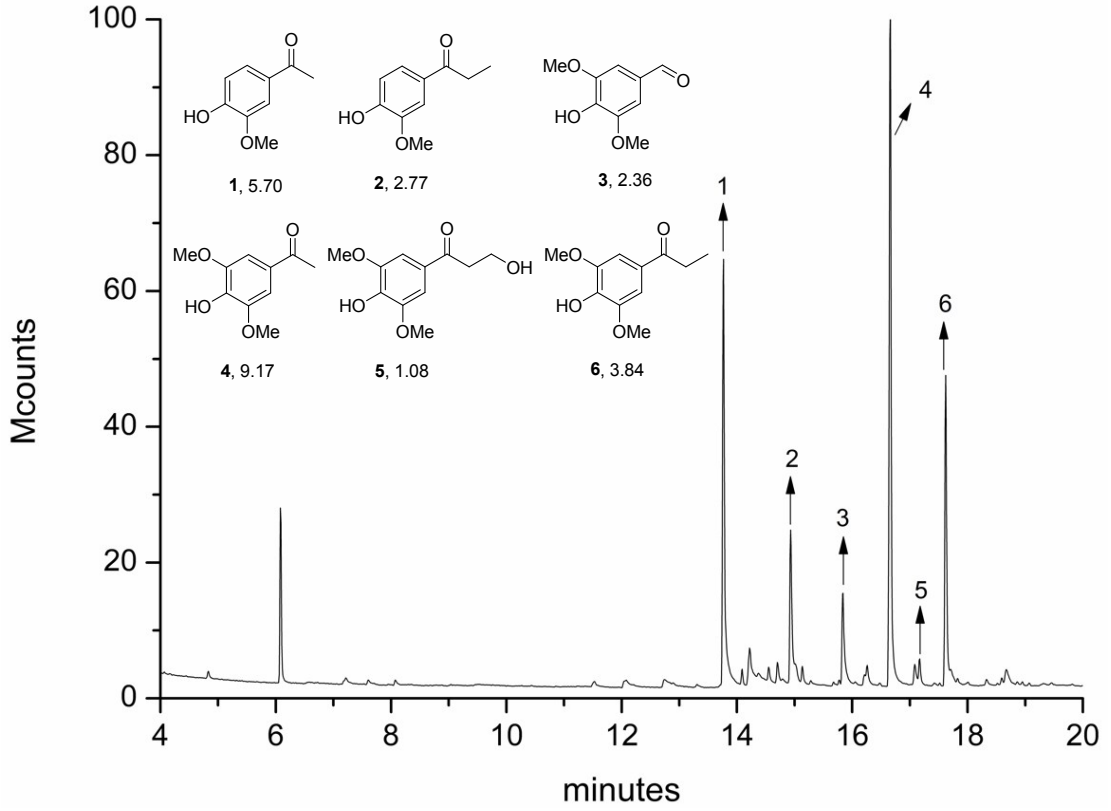
7.2 Characterization results of the liquid oil of raw poplar wood powder

7.2.1 MALDI-TOF spectroscopy



Scheme S3. MALDI-TOF spectrum of the oil from depolymerization of the raw poplar wood lignin.

7.2.2 GC-MS and GC-FID analysis of the oil from the raw poplar wood lignin



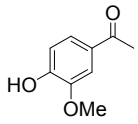
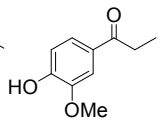
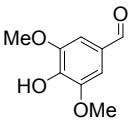
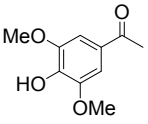
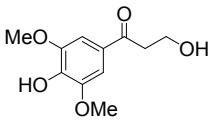
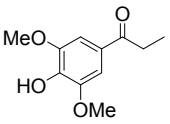
Scheme S4. GC-MS spectrum of the oil from the depolymerization of the raw poplar wood lignin.

Table S4. The catalytic activity of **1a** and **Rh-Rh** for depolymerization of raw poplar wood powder[a]

Entry	Catalyst (mg)	Time (h)	Oil (mg)	Residue (mg)
1	**1a** (13.7)	24	154	651
2	**Rh-Rh** (10)[b]	24	140	600

[a] Reaction conditions: raw poplar wood powder (1000 mg), **Catalyst**, NaOH (300 mg), H_2O (20 mL), 110 °C, 24 h, under Ar. After reaction, hydrochloric acid (1 M) was used to acidify the solution to pH = ca. 1. [b] Rh-Rh is our previous developed binuclear Rh complex (*ACS Catal.*, **2019**, *9*, 4441).

Table S5. Yields of monomers in the oil from the depolymerization of the raw poplar wood lignin[a]

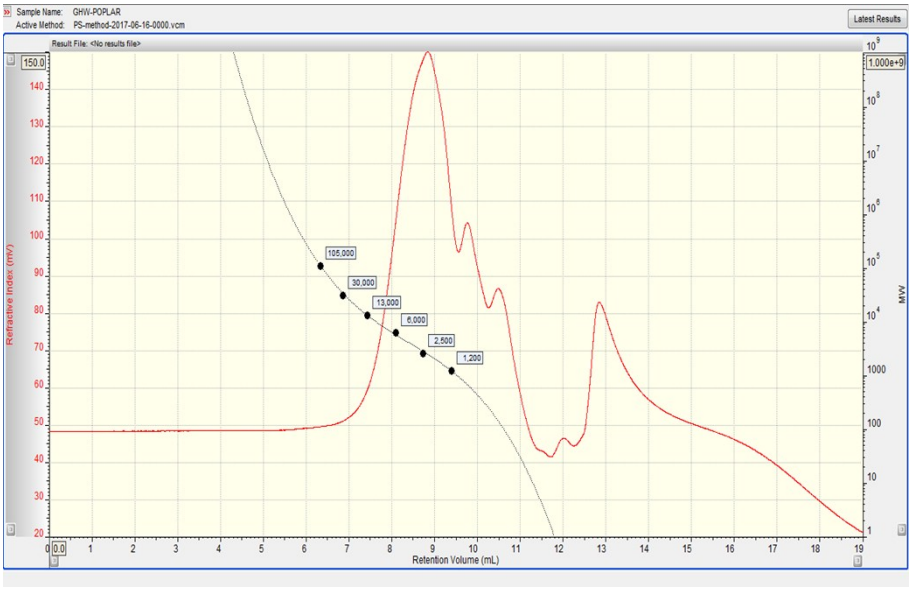
						
Yield[b] (mg)	5.70	2.77	2.36	9.17	1.08	3.84

[a] Reaction conditions: raw poplar wood powder (1000 mg), **1a** (13.7 mg), NaOH (300 mg), H_2O (20 mL), 110 °C, 24 h, under Ar. After the reaction, hydrochloric acid (1 M) was used to acidify the solution to pH = ca. 1. [b] Yields were determined by GC-FID with mesitylene as internal standard.

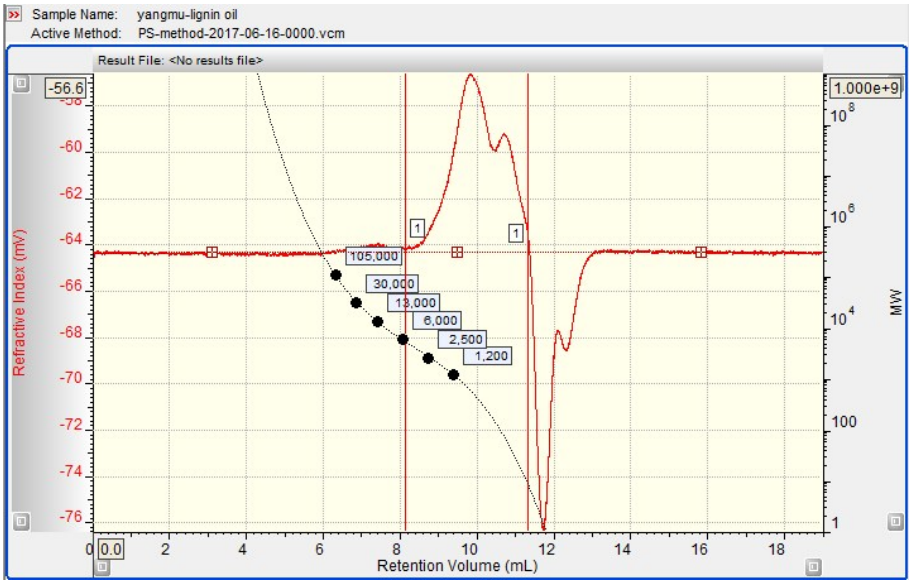
7.3 Gel-permeation Chromatography (GPC) of the extracted lignin and depolymerized liquid oil

Table S6. Weight-average (M_w), number-average (M_n) and polydispersity (M_w/M_n) of the extracted lignin and the oil products obtained from depolymerization by GPC analysis.

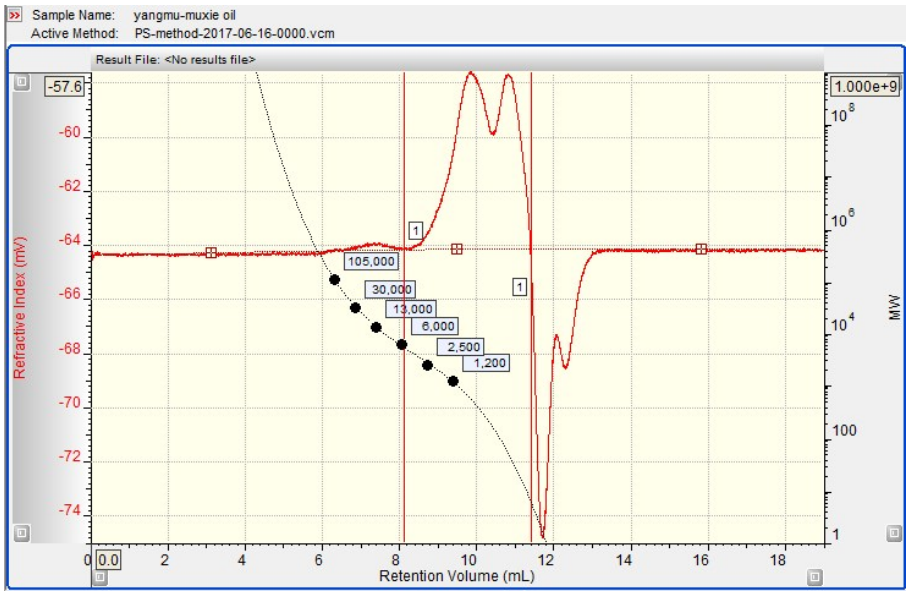
Sample	M_w	M_n	M_w/M_n
poplar wood dioxaslov lignin	3810	564	6.751
oil from poplar wood dioxaslov lignin	709	139	5.117
oil from poplar wood	794	129	6.143



i



j



k

Scheme S5. GPC molecular weight distribution of poplar wood dioxasolv lignin (**i**), oil from poplar wood dioxasolv lignin (**j**) and oil from poplar wood (**k**).

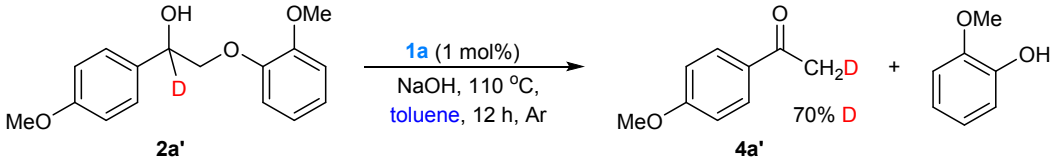
7.4 Linkage abundance calculated from HSQC NMR spectra

The linkage abundance for poplar wood dioxaslov lignin, oil products obtained from poplar wood dioxaslov lignin and oil products obtained from raw poplar wood powder are given in the table below.

Per 100 Units C_9	β-O-4 (%)	β-β (%)	β-5 (%)
poplar wood dioxaslov lignin	54.9	4.6	9.3
Oil from poplar wood dioxaslov lignin	0.1	0.1	5.3
Oil from poplar wood	1.3	0.06	4.0

8. Mechanistic studies

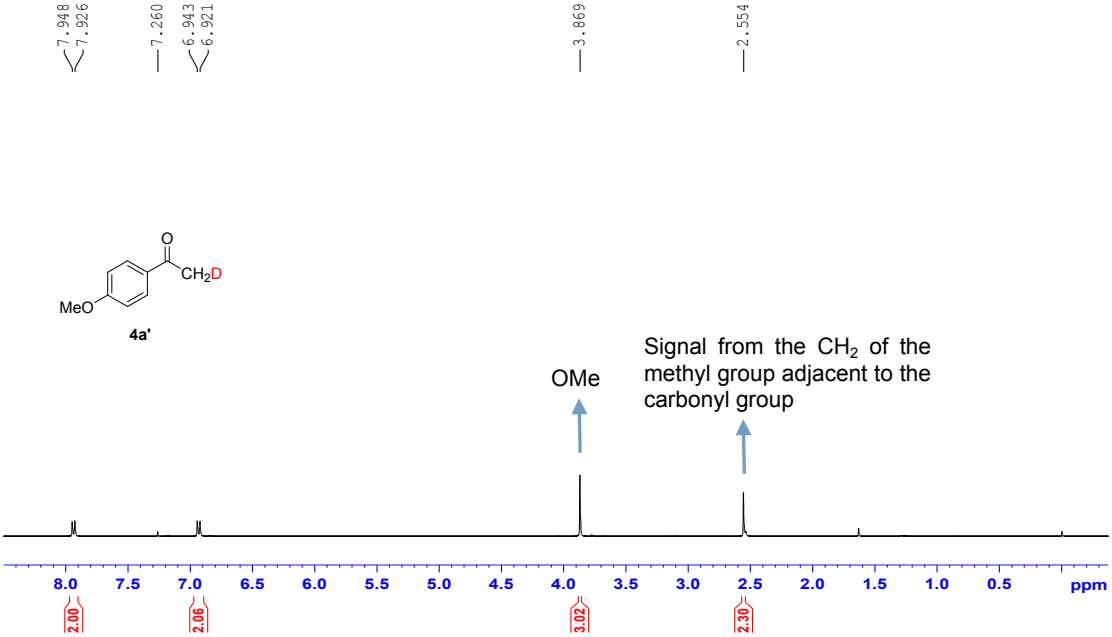
8.1 Deuterium labelling studies



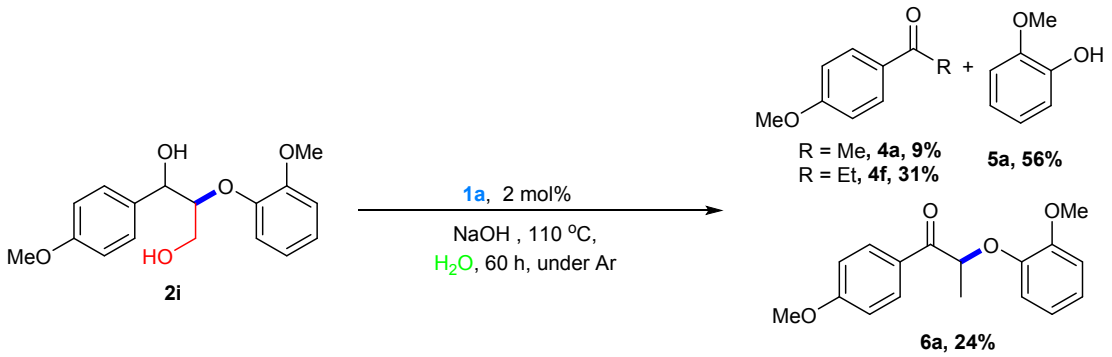
Scheme S6. Deuterium labelling studies.

In order to understand the mechanism, deuterium labelling studies were conducted to shed light on the pathway of hydrogen transfer, which was carried in the present of toluene instead of H_2O for the sake of avoiding the H/D exchange reaction of the ketone product under standard conditions. Procedure for the deuterium labelling studies: To a 35 mL pressure tube, a magnetic stir bar, **1a** (2.74 mg, 1 mol%), **2a'** (0.5

mmol), NaOH (0.75 mmol) and degassed toluene (1 mL) were added, then the tube was sealed under an atmosphere of argon. The mixture was heated at 110 °C (oil bath temperature) for 12 h. After cooling to room temperature, the solvent was evaporated in vacuo. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (20:1) as elution to give the product of **4a'**. 70% deuterium atom was transferred to the methyl near the group of carbonyl from the ^{1}H NMR analysis.



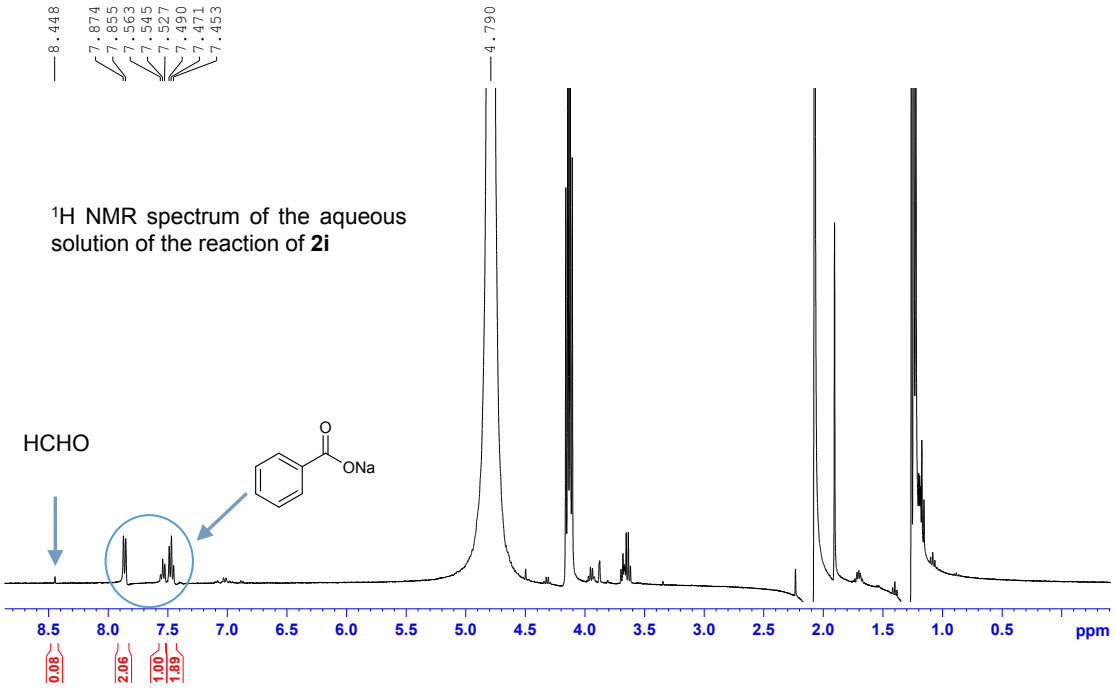
8.2 Procedure for the detection and quantification of formaldehyde for the cleavage of 2i



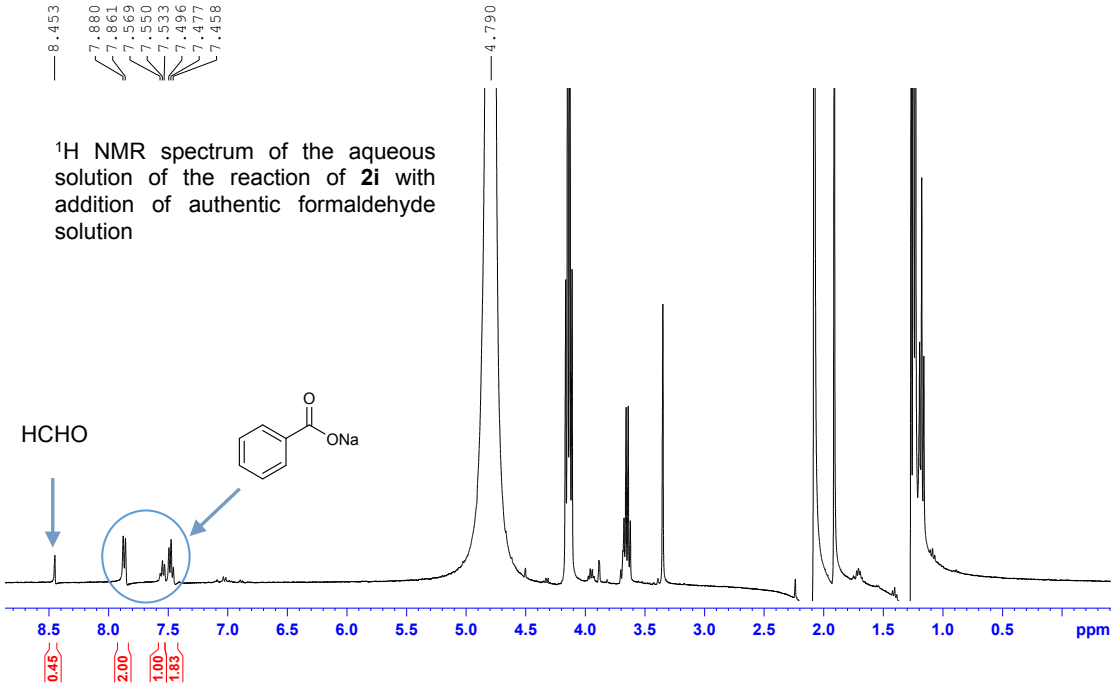
Scheme S7. Reaction conditions for the catalytic cleavage of **2i**.

In the proposed mechanism (Scheme 2), the formaldehyde was generated through Retro-Aldol reaction in the presence of NaOH. We have tried to detect and quantify the presence of formaldehyde after a catalytic reaction with substrate **2i** (Scheme S7). The signal of formaldehyde could be detected in the ^{1}H NMR spectrum of the aqueous solution of the reaction after extraction with organic solvent (Scheme S8). The peak at 8.45 ppm in the ^{1}H NMR was assigned to formaldehyde by addition of authentic formaldehyde solution (37 wt% formaldehyde solution, Scheme S8 and S9). The yield of formaldehyde is measured to be 0.5% with sodium benzoate (0.05 mmol) as internal standard (Scheme S9), which is lower than the yield of **4a** (9%, see Table 2 in the Main Article, the yield of formaldehyde and **4a** is supposed to be the same according to the proposed mechanism), possibly due to side reactions of formaldehyde under the conditions, e.g. forming a hemiacetal type compound via reacting with $^-$OH under the basic condition. Procedure for the detection and

quantification of formaldehyde: a magnetic stir bar, **1a** (4.39 mg, 2 mol%), **2i** (0.4 mmol), NaOH (0.6 mmol) and degassed H_2O (1 mL) were placed into a 35 mL pressure tube, then the tube was sealed under an atmosphere of argon. The mixture was heated at 110 °C (oil bath temperature) for 60 h. After the reaction, sodium benzoate (0.05 mmol) was added and the mixture was then extracted with ethyl acetate. Then, a sample was taken from the aqueous solution. The sample was diluted with D_2O and used for ^1H NMR analysis.



Scheme S8

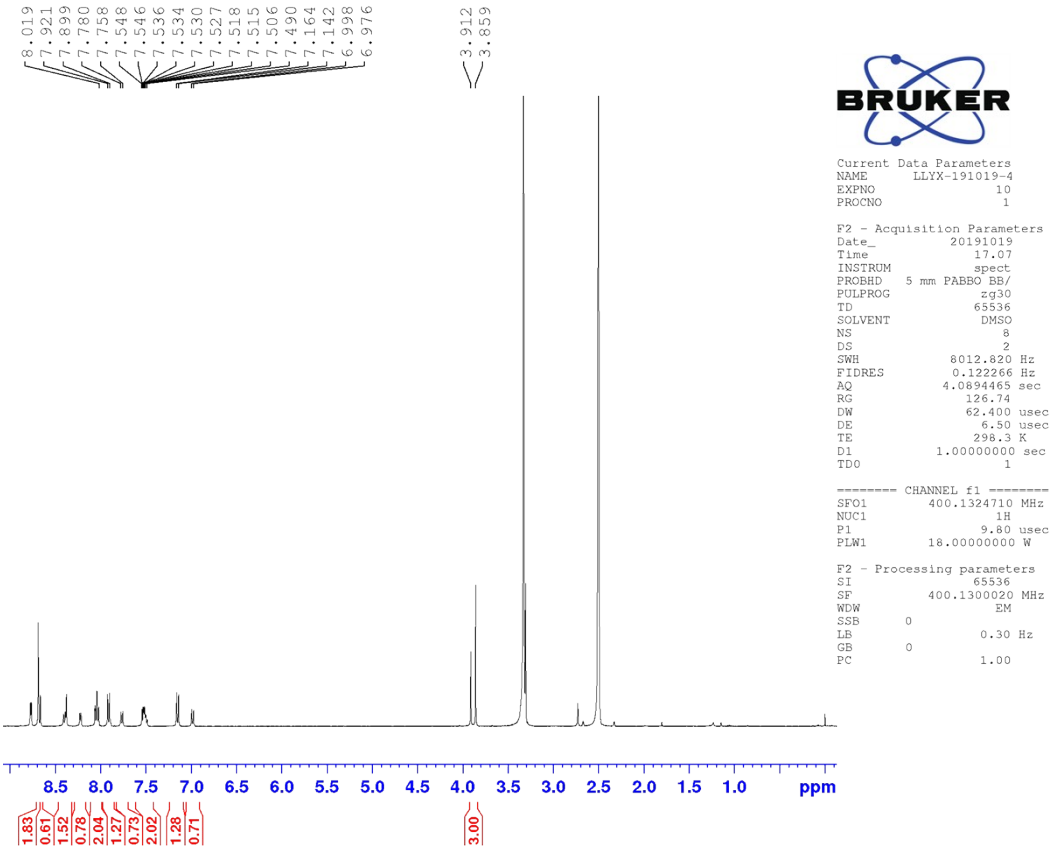


Scheme S9

8.3 Evidence for a mononuclear Rh catalyzed mechanism

We have carried out mechanistic studies to probe whether the reaction is catalyzed by a dimeric Rh complex. Based on the reaction conditions used and our experimental observations, we think the reaction is most likely catalyzed by a mononuclear Rh complex. The conclusion is supported by the following facts and results:

1. It is difficult to form a dimeric Rh complex with the ligand of the mononuclear Rh complex **1a**. The ligand of **1a** is more sterically hindered than the simple 2,2':6',2''-terpyridine, which makes it more difficult to form a dimeric structure due to steric hindrance. We tried to synthesize the dimeric complex with the ligand of **1a**, following the same procedure for our previous reported dimeric Rh complex (*ACS Catal.* **2019**, *9*, 4441-4447; *Green Chem.*, **2016**, *18*, 4605-4610). However, we were not able to isolate a dimeric Rh complex from this ligand. A mixture was formed according to the ^{1}H NMR spectrum of the obtained solid (Scheme S10). The result support that it is more difficult to form a dimeric Rh complex from the ligand of **1a** than the simple 2,2':6',2''-terpyridine ligand.

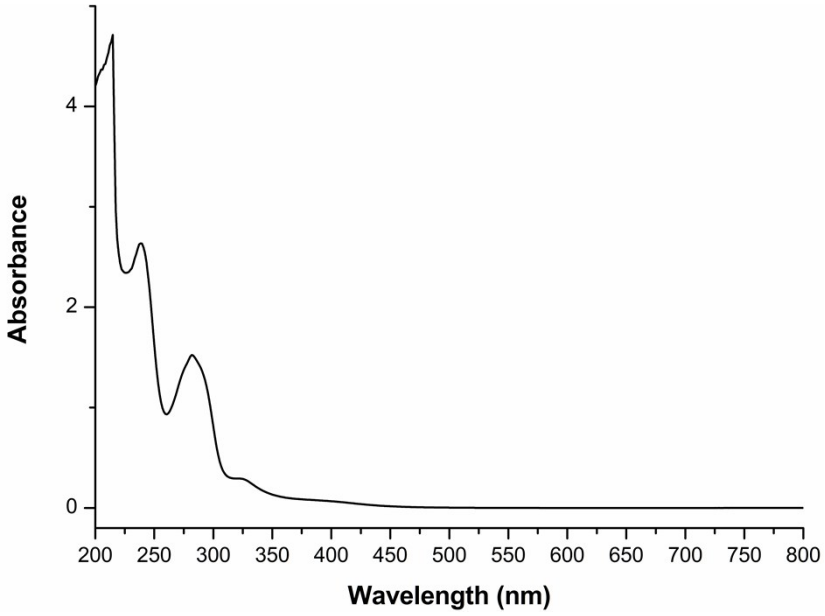


Scheme S10

2. It is difficult to form a dimeric Rh complex under the catalytic conditions. An acetate group (AcO^-) is essential for the formation of the dimeric structure, acting as a bridging ligand. Under the catalytic conditions (NaOH as base, H_2O as solvent), no such a bridging ligand is presented.

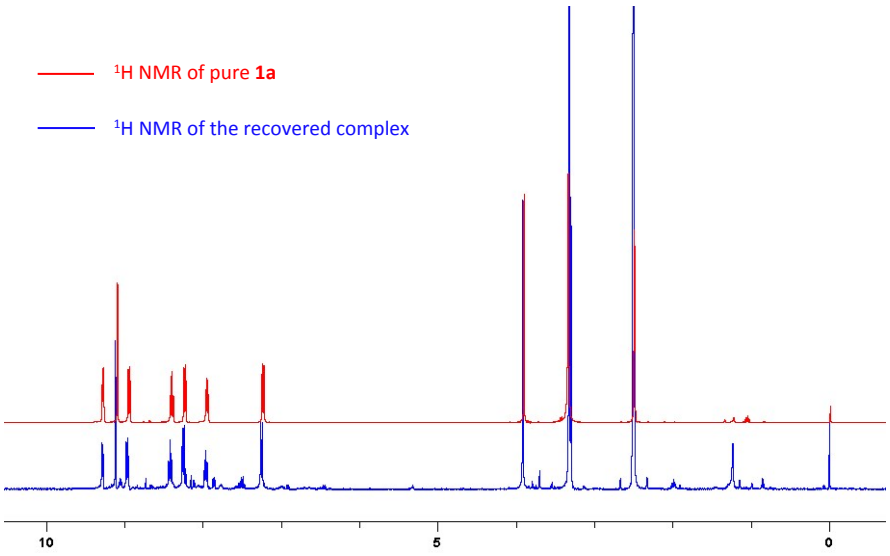
3. Electronic absorption studies suggest that the dimeric structure is not formed during the reaction. Nocera and coworkers reported that there will be typical absorption bands for a dimeric Rh complex in the electronic absorption spectrum, an intense band at around 300 nm for the allowed dσ ⟶ dσ* transition and a less intense band at around 400 nm for the ~~dπ~~ ⟶ dσ* transition (*Inorg. Chem.* **1996**, *35*, 811-817). We measured the electronic absorption spectrum of the aqueous solution after the reaction of cleaving **2a** with **1a**

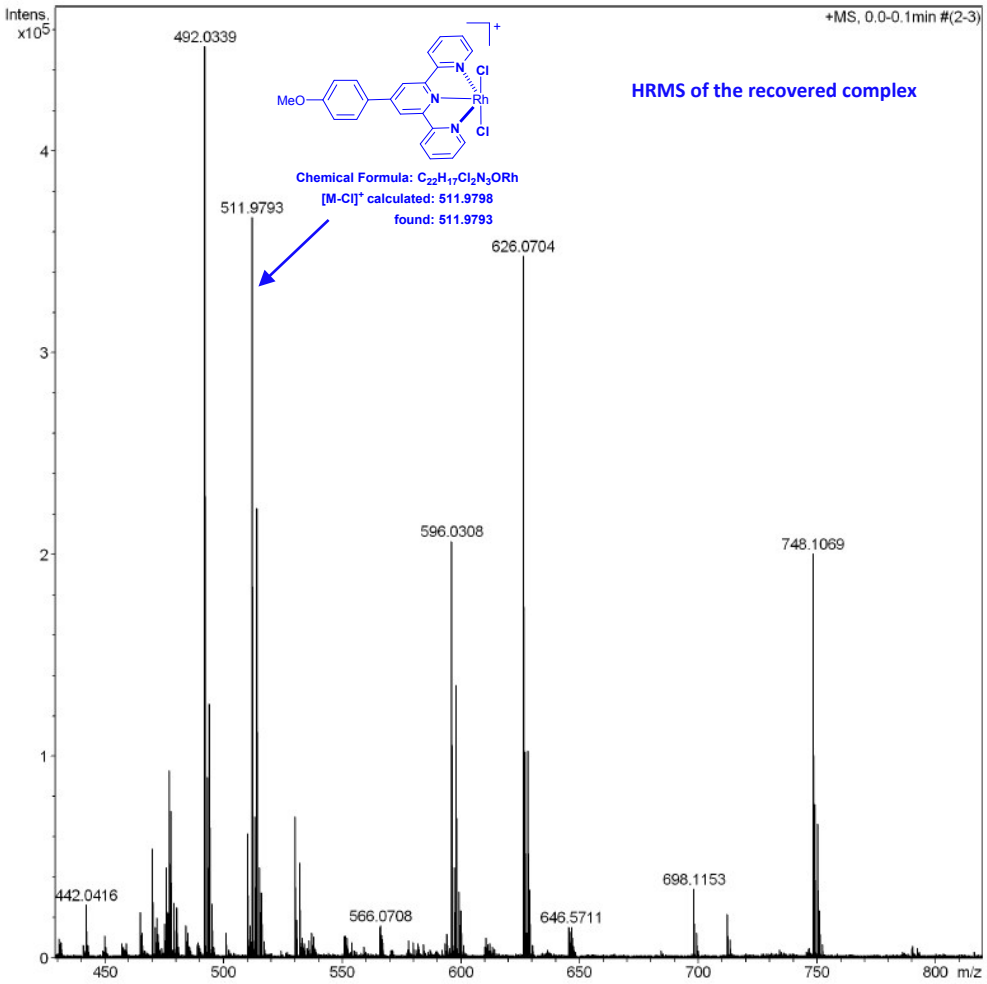
as catalyst (Scheme S11). From the spectrum, no characteristic absorption band corresponding to dimeric metal complexes was observed, which suggest that the Rh complex remained to be mononuclear during the catalytic reaction.



Scheme S11. Electronic absorption spectrum of the aqueous solution after a catalytic reaction. Conditions: **2a** (0.2 mmol), **1a** (2 mol%, 2.2 mg), NaOH (12 mg, 0.3 mmol), H_2O (1 mL). After the reaction, 0.8 mL of liquid was taken from the reaction mixture, which was passed through a membrane to remove any solid residue and diluted to 10 mL. The resulting solution was used for electronic absorption measurement.

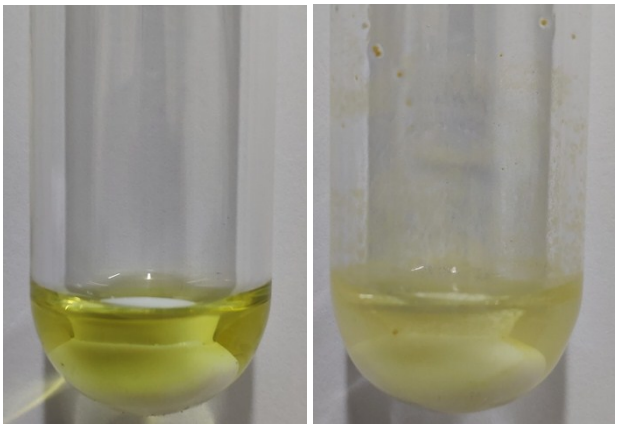
4. The mono-nuclear Rh catalyst **1a** could be isolated after the reaction from the reaction mixture. After a reaction of cleaving **2a** with **1a** as catalyst, upon treating the reaction mixture with hydrochloric acid (1 M), yellow precipitates were formed and isolated. The ^{1}H NMR and HRMS spectra of the yellow precipitates are identical to that of **1a** (Scheme S12).





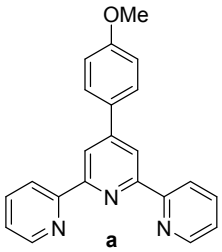
Scheme S12. ^{1}H NMR and HRMS spectra of the recovered complex. Reaction conditions: **2a** (0.3 mmol), **1a** (14 mol%, 23 mg), NaOH (0.45 mmol), H_2O (1 mL), 110 °C, 12 h, under Ar. After the reaction, hydrochloric acid (1 M) was used to acidify the solution to pH = ca. 1. The yellow precipitate was collected by filtration and used for ^{1}H NMR and HRMS measurements.

5. The solubility of the mononuclear Rh complex **1a** and our previously reported binuclear Rh complex is quite distinct. The binuclear complex is soluble in aqueous NaOH solution, while **1a** has very low solubility in it (Scheme S13). The **1a** catalyzed reaction could be proceed in a “on water” fashion, differing from the binuclear complex.



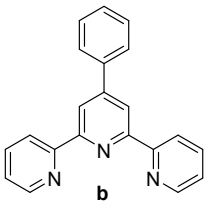
Scheme S13. Solubility of binuclear and mononuclear complexes. Left: binuclear complex used in our previous studies; right: the mononuclear complex **1a**.

9. Analytic data of the products



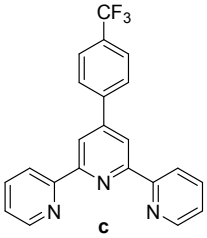
a

4'-(4-Methoxyphenyl)-2,2':6',2''-terpyridine:[15] white solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.73 (dd, *J* = 4.7, 0.7 Hz, 2H), 8.71 (s, 2H), 8.67 (d, *J* = 8.0 Hz, 2H), 7.89-7.85 (m, 4H), 7.35 (ddd, *J* = 5.8, 4.8, 1 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 160.6, 156.5, 155.9, 149.9, 149.2, 136.9, 130.9, 128.6, 123.9, 121.5, 118.4, 114.4, 55.5; HRMS (ESI) calculated for $C_{22}H_{17}N_3NaO$ $[M+Na]^+$ 362.1264, found 362.1269.



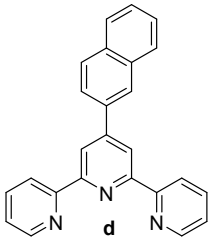
b

4'-Phenyl-2,2':6',2''-terpyridine:[15] light green solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.75 (s, 2H), 8.73 (d, *J* = 4.8 Hz, 2H), 8.68 (d, *J* = 8.0 Hz, 2H), 7.92-7.86 (m, 4H), 7.52 (t, *J* = 7.1 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.35 (dd, *J* = 6.4, 4.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 156.4, 156.0, 150.4, 149.2, 138.6, 136.9, 129.1, 129.0, 127.4, 123.9, 121.5, 119.0; HRMS (ESI) calculated for $C_{21}H_{15}N_3Na$ $[M+Na]^+$ 332.1158, found 332.1168.



c

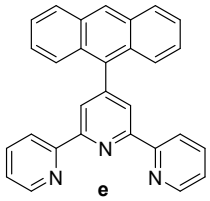
4'-(4-(Trifluoromethyl)phenyl)-2,2':6',2''-terpyridine: white solid; ^{1}H NMR (DMSO, 400 MHz) δ (ppm): 8.76 (d, *J* = 4.3 Hz, 2H), 8.73 (s, 2H), 8.66 (d, *J* = 7.9 Hz, 2H), 8.14 (d, *J* = 8.1 Hz, 2H), 8.04 (t, *J* = 7.7 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.53 (dd, *J* = 7.1, 5.2 Hz, 2H); ^{13}C NMR (DMSO, 100 MHz) δ (ppm): 155.8, 154.7, 149.3, 147.7, 141.4, 137.4, 129.5 (q, $^2J_{C\text{-}F}$ = 31.9 Hz), 127.8, 126.1 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 124.5, 124.1 (q, $^1J_{C\text{-}F}$ = 270.5 Hz), 120.9, 118.0; HRMS (ESI) calculated for $C_{22}H_{14}F_3N_3Na$ $[M+Na]^+$ 400.1032, found 400.1044.



d

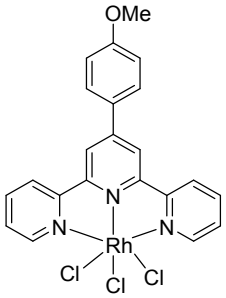
4'-(Naphthalen-2-yl)-2,2':6',2''-terpyridine: white solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.89 (s, 2H), 8.77 (d, *J* = 4.6 Hz, 2H), 8.71 (d, *J* = 7.9 Hz, 2H), 8.42 (s, 1H), 8.05-7.98 (m, 3H), 7.90(td, *J* = 7.6, 1.7 Hz, 3H), 7.56-7.53 (m, 2H), 7.39-7.36 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 156.3, 156.0, 150.2, 149.2, 137.0,

135.8, 133.6, 128.8, 128.7, 127.8, 126.8, 126.7, 126.6, 125.1, 123.9, 121.5, 119.1; HRMS (ESI) calculated for $C_{25}H_{17}N_3Na$ $[M+Na]^+$ 382.1315, found 382.1316.



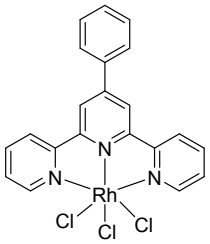
e

4'-(Anthracen-9-yl)-2,2':6',2''-terpyridine:[15] light green solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.79 (d, *J* = 8.0 Hz, 2H), 8.63 (d, *J* = 4.5 Hz, 2H), 8.61 (s, 2H), 8.55 (s, 1H), 8.07 (d, *J* = 8.5 Hz, 2H), 7.92 (td, *J* = 7.7, 1.4 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.47 (t, *J* = 7.1 Hz, 2H), 7.37-7.32 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 156.3, 155.8, 149.7, 149.4, 137.0, 134.5, 131.4, 129.7, 128.5, 127.5, 126.5, 126.0, 125.3, 124.0, 123.9, 121.5; HRMS (ESI) calculated for $C_{29}H_{19}N_3Na$ $[M+Na]^+$ 432.1471, found 432.1466.



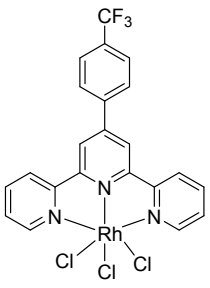
1a

Yellow solid; ^{1}H NMR (DMSO, 400 MHz) δ (ppm): 9.28 (d, *J* = 5.4 Hz, 2H), 9.10 (s, 2H), 8.95 (d, *J* = 8.0 Hz, 2H), 8.41 (t, *J* = 7.8 Hz, 2H), 8.24 (d, *J* = 8.8 Hz, 2H), 7.96 (t, *J* = 6.6 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (DMSO, 100 MHz) δ (ppm):161.8, 157.5, 155.1, 153.1, 151.2, 140.1, 129.7, 128.3, 127.3, 125.3, 121.0, 114.8, 55.6; HRMS (ESI) calculated for $C_{22}H_{17}Cl_2N_3ORh$ $[M-Cl]^+$ 511.9798, found 511.9797.



1b

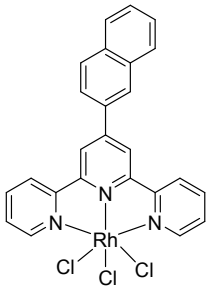
Yellow solid; ^{1}H NMR (DMSO, 400 MHz) δ (ppm): 9.29 (d, *J* = 5.1 Hz, 2H), 9.17 (s, 2H), 8.98 (d, *J* = 8.1 Hz, 2H), 8.43 (t, *J* = 7.6 Hz, 2H), 8.24 (d, *J* = 7.24 Hz, 2H), 7.97 (t, *J* = 6.6 Hz, 2H), 7.71 (t, *J* = 7.0 Hz, 2H), 7.66 (t, *J* = 7.2 Hz, 1H); HRMS (ESI) calculated for $C_{21}H_{15}Cl_2N_3Rh$ $[M-Cl]^+$ 481.9693, found 481.9689.



1c

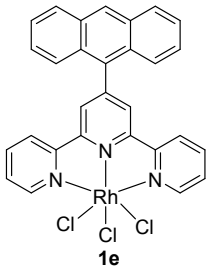
Gray solid; ^{1}H NMR (DMSO, 400 MHz) δ (ppm): 9.30 (d, *J* = 5.3 Hz, 2H), 9.23 (s, 2H), 8.96 (d, *J* = 7.9 Hz, 2H),

8.44 (t, *J* = 8.0 Hz, 4H), 8.09 (d, *J* = 8.2 Hz, 2H), 7.98 (t, *J* = 6.6 Hz, 2H); HRMS (ESI) calculated for $C_{22}H_{14}Cl_2F_3N_3Rh$ $[M\text{-}Cl]^+$ 549.9566, found 549.9552.



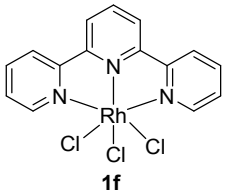
1d

Orange solid; ^1H NMR (DMSO, 400 MHz) δ (ppm): 9.31 (s, 1H), 9.30 (s, 3H), 9.01 (d, *J* = 7.9 Hz, 2H), 8.86 (s, 1H), 8.44 (td, *J* = 8.0, 0.9 Hz, 2H), 8.36 (dd, *J* = 8.5, 1.4 Hz, 1H), 8.25 (d, *J* = 8.7 Hz, 1H), 8.13-8.08 (m, 2H), 7.98 (t, *J* = 6.4 Hz, 2H), 7.70-7.68 (m, 2H); ^{13}C NMR (DMSO, 100 MHz) δ (ppm):157.4, 155.4, 153.2, 151.6, 140.2, 133.8, 132.9, 132.7, 129.1, 128.8, 128.4, 128.3, 128.0, 127.8, 127.2, 125.4, 124.9, 122.1; HRMS (ESI) calculated for $C_{25}H_{17}Cl_2N_3Rh$ $[M\text{-}Cl]^+$ 531.9849, found 531.9843.



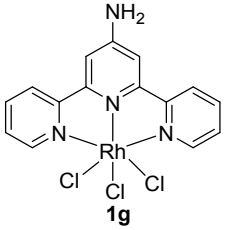
1e

Orange solid; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 9.74 (d, *J* = 5.4 Hz, 2H), 8.70 (s, 1H), 8.25 (s, 2H), 8.16 (d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 4.2 Hz, 2H), 8.09 (s, 2H), 7.75 (d, *J* = 4.1 Hz, 2H), 7.58 (t, *J* = 9.0 Hz, 4H), 7.51-7.48 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):157.4, 156.2, 155.0, 152.4, 139.5, 131.2, 130.1, 129.7, 129.5, 129.2, 128.5, 127.8, 126.0, 125.9, 124.9, 124.1; HRMS (ESI) calculated for $C_{29}H_{19}Cl_3N_3NaRh$ $[M+Na]^+$ 639.9592, found 639.9593.



1f

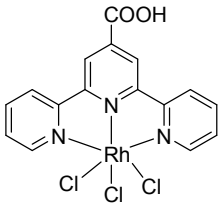
Yellow solid;[16, 19] ^1H NMR (DMSO, 400 MHz) δ (ppm): 9.28 (d, *J* = 3.6 Hz, 2H), 8.82 (d, *J* = 5.4 Hz, 2H), 8.78 (d, *J* = 5.2 Hz, 2H), 8.55 (t, *J* = 5.4 Hz, 2H), 8.39 (td, *J* = 5.2, 1.0 Hz, 2H), 7.96 (td, *J* = 3.7, 0.8 Hz, 2H); ^{13}C NMR (DMSO, 100 MHz) δ (ppm):157.2, 155.2, 153.2, 140.5, 140.3, 128.4, 125.1, 124.4; HRMS (ESI) calculated for $C_{15}H_{11}Cl_2N_2ORh$ $[M\text{-}Cl]^+$ 405.9380, found 405.9378.



1g

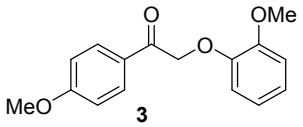
Yellow solid; ^1H NMR (DMSO, 400 MHz) δ (ppm): 9.24 (d, *J* = 5.4 Hz, 2H), 8.39 (d, *J* = 7.8 Hz, 2H), 8.29 (t, *J* = 7.8 Hz, 2H), 7.87 (t, *J* = 6.6 Hz, 2H), 7.65 (s, 2H), 7.44 (s, 2H); HRMS (ESI) calculated for $C_{15}H_{12}Cl_2N_4ORh$

[M-Cl]$^+$ 420.9489, found 420.9503.



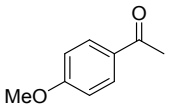
1h

Yellow solid; ^{1}H NMR (DMSO, 400 MHz) δ (ppm): 9.29 (d, *J* = 5.4 Hz, 2H), 9.19 (s, 2H), 9.00 (d, *J* = 8.0 Hz, 2H), 8.39 (t, *J* = 7.7 Hz, 2H), 7.98 (t, *J* = 6.6 Hz, 2H); HRMS (ESI) calculated for $C_{16}H_{11}Cl_2N_3O_2Rh$ [M-Cl]$^+$ 449.9278, found 449.9286.



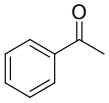
3

2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one:[14] yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.02 (d, *J* = 8.8 Hz, 2H), 6.96-6.92 (m, 4H), 6.85-6.84 (m, 2H), 5.28 (s, 2H), 3.88 (s, 3H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 193.1, 164.0, 149.8, 147.7, 130.5, 127.7, 122.3, 120.8, 114.8. 114.0, 112.2, 72.0, 55.9, 55.5.



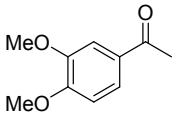
4a

1-(4-Methoxyphenyl)ethan-1-one:[8, 20, 21] white solid; m.p. = 36-38 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.94 (d, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 7.6 Hz, 2H), 3.88 (s, 3H), 2.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 196.9, 163.5, 130.7, 130.4, 113.7, 55.5, 26.4; MS (EI) for $C_9H_{10}O_2$ [M]$^+$: 150.



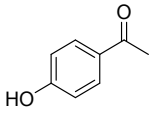
4b

Acetophenone:[21] white oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.97 (d, *J* = 8.0 Hz, 2H), 7.59-7.55 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 2.62 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 198.3, 137.2, 133.2, 128.7, 128.4, 26.8; MS (EI) for C_8H_8O [M]$^+$: 120.



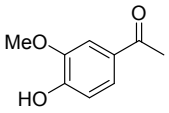
4c

1-(3,4-Dimethoxyphenyl)ethan-1-one:[14] white solid, m.p. = 48-52 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.58 (d, *J* = 8.4 Hz, 1H), 7.53 (s, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 2.58 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 196.9, 153.4, 149.1, 130.6, 123.4, 110.1, 109.9, 56.2, 56.1, 26.3; MS (EI) for $C_{10}H_{12}O_3$ [M]$^+$: 180.



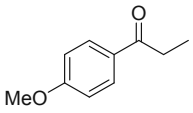
4d

1-(4-Hydroxyphenyl)ethan-1-one: white solid, m.p. = 132-135 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.91 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.18 (s, 1H), 2.57 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 198.9, 161.5, 131.4, 129.7, 115.7, 26.5; MS (EI) for $C_8H_8O_2$ [M]$^+$: 136.



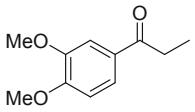
4e

1-(4-Hydroxy-3-methoxyphenyl)ethan-1-one: white solid, m.p. = 103-106 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.54 (s, 2H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.05 (s, 1H), 3.96 (s, 3H), 2.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 197.1, 150.6, 146.7, 130.2, 124.1, 113.9, 109.8, 56.1, 26.3; MS (EI) for $C_9H_{10}O_3$ [M]$^+$: 166.



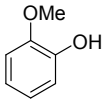
4f

1-(4-Methoxyphenyl)propan-1-one:[14, 22] white oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.95 (d, J = 7.6 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 3H), 2.96 (q, *J* = 14.0, 6.8 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 199.6, 163.4, 130.3, 130.1, 113.8, 55.6, 31.5, 8.6; MS (EI) for $C_{10}H_{12}O_2$ [M]$^+$: 164.



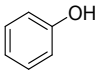
4g

1-(3,4-Dimethoxyphenyl)propan-1-one:[14] white solid, m.p. = 54-56 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.60 (d, *J* = 8.0, 2.0 Hz, 1H), 7.55 (s, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 6H), 2.97 (q, *J* = 14.4, 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 199.7, 153.1, 149.1, 130.2, 122.6, 110.1, 110.0, 56.1, 56.0, 31.4, 8.7; MS (EI) for $C_{11}H_{14}O_3$ [M]$^+$: 194.



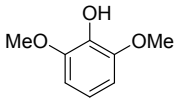
5a

2-Methoxyphenol:[8, 14] yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.95-6.93 (m, 1H), 6.89-6.87 (m, 3H), 5.63 (s, 1H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 146.7, 145.7, 121.5, 120.3, 114.6, 110.8, 55.9; MS (EI) for $C_7H_8O_2$ [M]$^+$: 124.



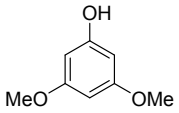
5b

Phenol: white solid, m.p. = 39-41 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.27-7.24 (m, 2H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 2H), 4.69 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 155.5, 129.8, 120.9, 115.4; MS (EI) for $C_7H_8O_2$ [M]$^+$: 94.



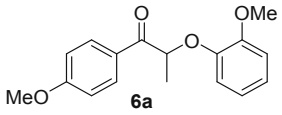
5c

2,6-Dimethoxyphenol: white solid, m.p. = 49-51 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.81 (t, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 2H), 5.52 (s, 1H), 3.89 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 147.3, 134.9, 119.2, 104.9, 56.3; MS (EI) for $C_8H_{10}O_3$ $[M]^+$: 154.



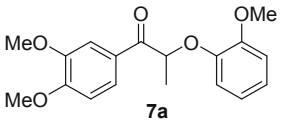
5d

3,5-Dimethoxyphenol: white solid, m.p. = 39-41 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.08 (s, 1H), 6.02 (s, 2H), 4.73 (s, 1H), 3.76 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 161.6, 157.3, 94.2, 93.2, 55.4; MS (EI) for $C_8H_{10}O_3$ $[M]^+$: 154.



6a

2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one:[14, 23] colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.12 (d, *J* = 8.7 Hz, 2H), 6.94-6.87 (m, 4H), 6.82-6.79 (m, 2H), 5.41 (q, *J* = 6.9 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 1.71(d, *J* = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 197.7, 163.9, 150.1, 147.1, 131.5, 127.4, 122.4, 120.9, 116.3, 113.9, 112.5, 78.3, 56.0, 55.6, 19.2; HRMS (ESI) calculated for $C_{17}H_{18}O_4Na$ $[M+Na]^+$ 309.1103, found 309.1100.



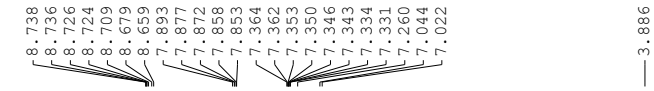
7a

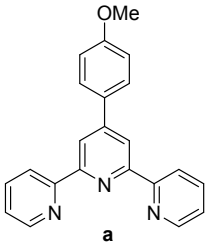
1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)propan-1-one: colorless solide; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.82 (d, *J* = 1.2 Hz, 1H), 7.68 (d, *J* = 1.6 Hz, 1H), 6.94-6.87 (m, 3H), 6.82-6.77 (m, 2H), 5.42 (q, *J* = 7.2 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.84 (s, 3H), 1.73(d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 197.8, 153.7, 149.1, 147.1, 127.5, 127.4,123.7, 120.9, 116.0, 112.4, 111.4, 110.2, 78.3, 56.2, 56.0, 55.9, 19.3; HRMS (ESI) calculated for $C_{18}H_{20}O_5Na$ $[M+Na]^+$ 339.1203, found 339.1201.

10. References

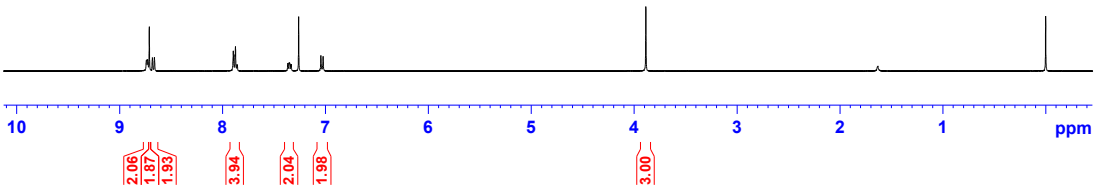
1. J. Buendia, J. Mottweiler and C. Bolm, *Chem. - Eur. J.*, 2011, **17**, 13877-13882.
2. J. Zhang, Y. Liu, S. Chiba and T.-P. Loh, *Chem. Commun.*, 2013, **49**, 11439-11441.
3. J. D. Moore, A. M. Harned, J. Henle, D. L. Flynn and P. R. Hanson, *Org. Lett.*, 2002, **4**, 1847-1849.
4. Y. Siddaraju and K. R. Prabhu, *Org. Biomol. Chem.*, 2015, **13**, 6749-6753.
5. H.-M. Yang and C.-C. Huang, *Catal. Lett.*, 2009, **128**, 235-242.
6. M. D. Kärkäs, I. Bosque, B. S. Matsuura and C. R. J. Stephenson, *Org. Lett.*, 2016, **18**, 5166-5169.
7. A. Rahimi, A. Azarpira, H. Kim, J. Ralph and S. S. Stahl, *J. Am. Chem. Soc.*, 2013, **135**, 6415-6418.
8. J. M. Nichols, L. M. Bishop, R. G. Bergman and J. A. Ellman, *J. Am. Chem. Soc.*, 2010, **132**, 12554-12555.
9. J. Ji, H. Guo, C. Li, Z. Qi, B. Zhang, T. Dai, M. Jiang, C. Ren, A. Wang and T. Zhang, *Chemcatchem*, 2018, **10**, 415-421.
10. N. Luo, M. Wang, H. Li, J. Zhang, T. Hou, H. Chen, X. Zhang, J. Lu and F. Wang, *ACS Catal.*, 2017, **7**, 4571-4580.
11. H. Guo, B. Zhang, C. Li, C. Peng, T. Dai, H. Xie, A. Wang and T. Zhang, *Chemsuschem*, 2016, **9**, 3220-3229.
12. C. S. Lancefield, O. S. Ojo, F. Tran and N. J. Westwood, *Angew. Chem., Int. Ed.*, 2015, **54**, 258-262.
13. J.-w. Zhang, G.-p. Lu and C. Cai, *Green Chem.*, 2017, **19**, 4538-4543.
14. Y. Liu, C. Li, W. Miao, W. Tang, D. Xue, C. Li, B. Zhang, J. Xiao, A. Wang, T. Zhang and C. Wang, *ACS Catal.*, 2019, **9**, 4441-4447.
15. J. Wang and G. S. Hanan, *Synlett*, 2005, **2005**, 1251-1254.
16. P. Paul, B. Tyagi, A. K. Bilakhiya, M. M. Bhadbhade, E. Suresh and G. Ramachandraiah, *Inorg. Chem.*, 1998, **37**, 5733-5742.
17. Z. Sun, G. Bottari, A. Afanasenko, M. C. A. Stuart, P. J. Deuss, B. Fridrich and K. Barta, *Nat. Catal.*, 2018, **1**, 82-92.
18. S. Vincent, R. Prado, O. Kuzmina, K. Potter, J. Bhardwaj, N. D. Wanasekara, R. L. Harniman, A. Koutsomitopoulou, S. J. Eichhorn, T. Welton and S. S. Rahatekar, *ACS Sustainable Chem. Eng.*, 2018, **6**, 5903-5910.
19. J. Cheng, M. Zhu, C. Wang, J. Li, X. Jiang, Y. Wei, W. Tang, D. Xue and J. Xiao, *Chem. Sci.*, 2016, **7**, 4428-4434.
20. X. Wang, C. Wang, Y. Liu and J. Xiao, *Green Chem.*, 2016, **18**, 4605-4610.
21. N. Luo, M. Wang, H. Li, J. Zhang, H. Liu and F. Wang, *ACS Catal.*, 2016, **6**, 7716-7721.
22. X. Wu, X. Fan, S. Xie, J. Lin, J. Cheng, Q. Zhang, L. Chen and Y. Wang, *Nat. Catal.*, 2018, **1**, 772-780.
23. F. Gao, J. D. Webb, H. Sorek, D. E. Wemmer and J. F. Hartwig, *ACS Catal.*, 2016, **6**, 7385-7392.

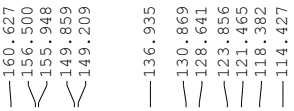
11. Traces of ^{1}H NMR and ^{13}C NMR spectra

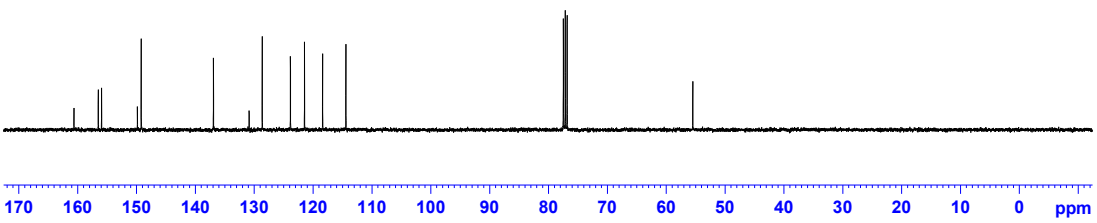


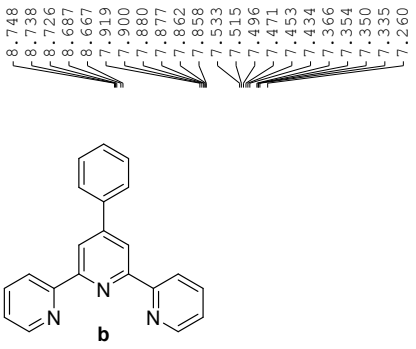


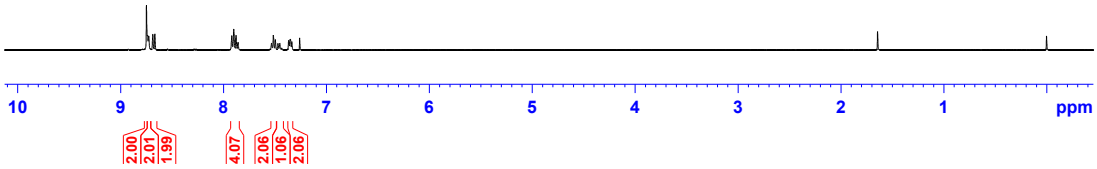
a

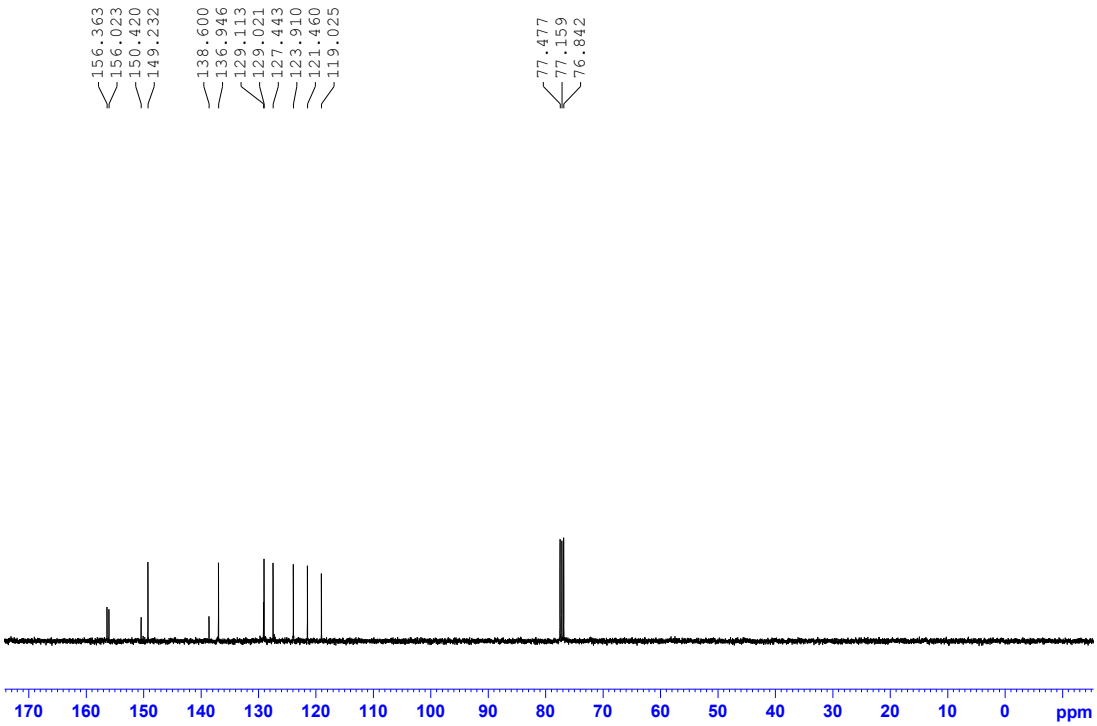


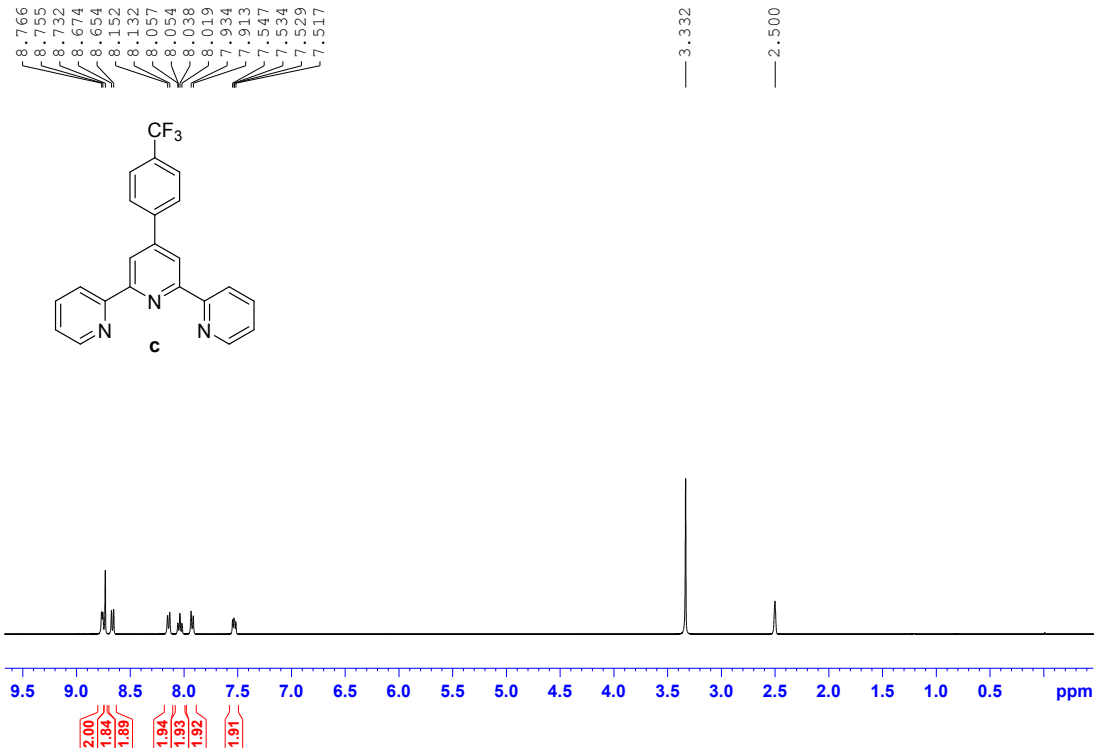


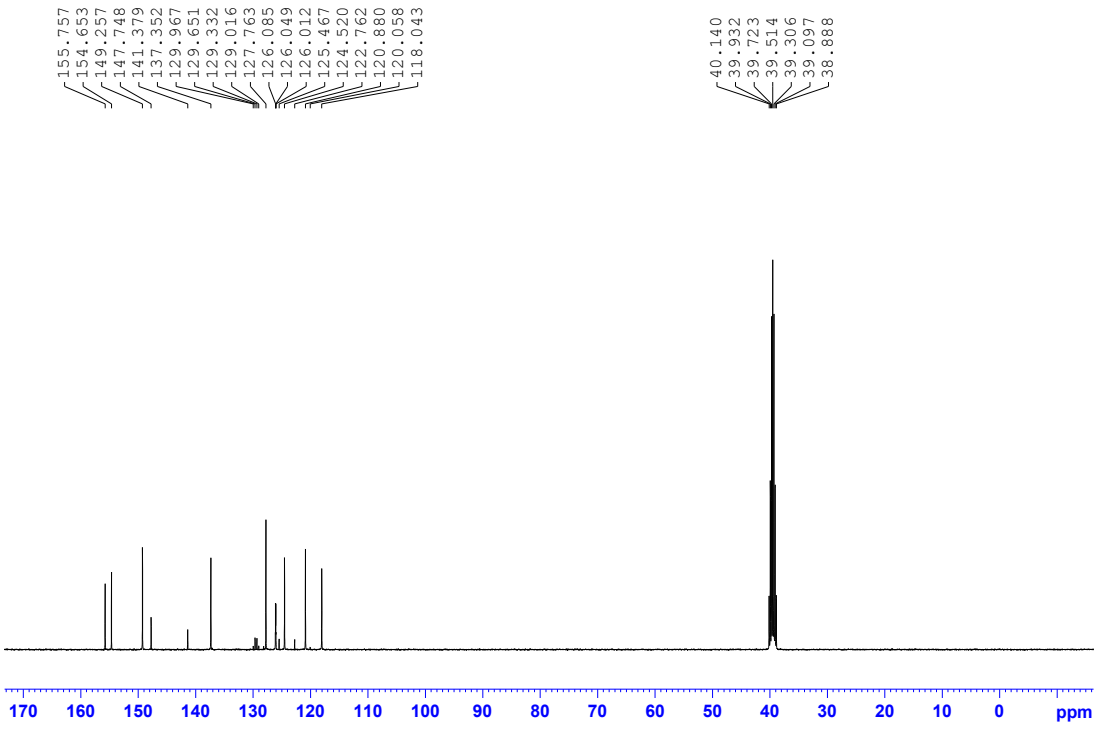


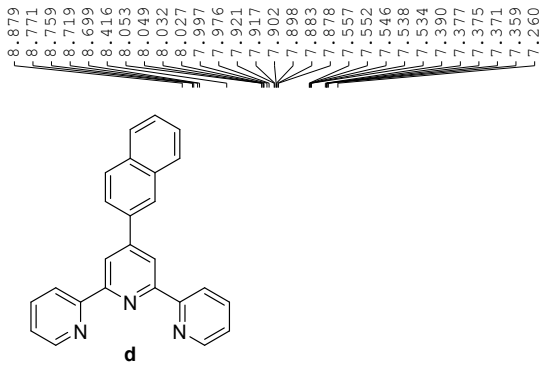

8.748
8.738
8.726
8.687
8.667
7.919
7.900
7.880
7.877
7.862
7.858
7.533
7.515
7.496
7.471
7.453
7.434
7.366
7.354
7.350
7.335
7.260
N
N
N
b

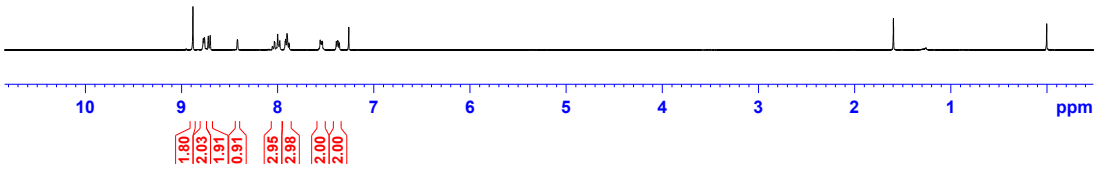

10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.01
1.99
4.07
2.06
1.06
2.06

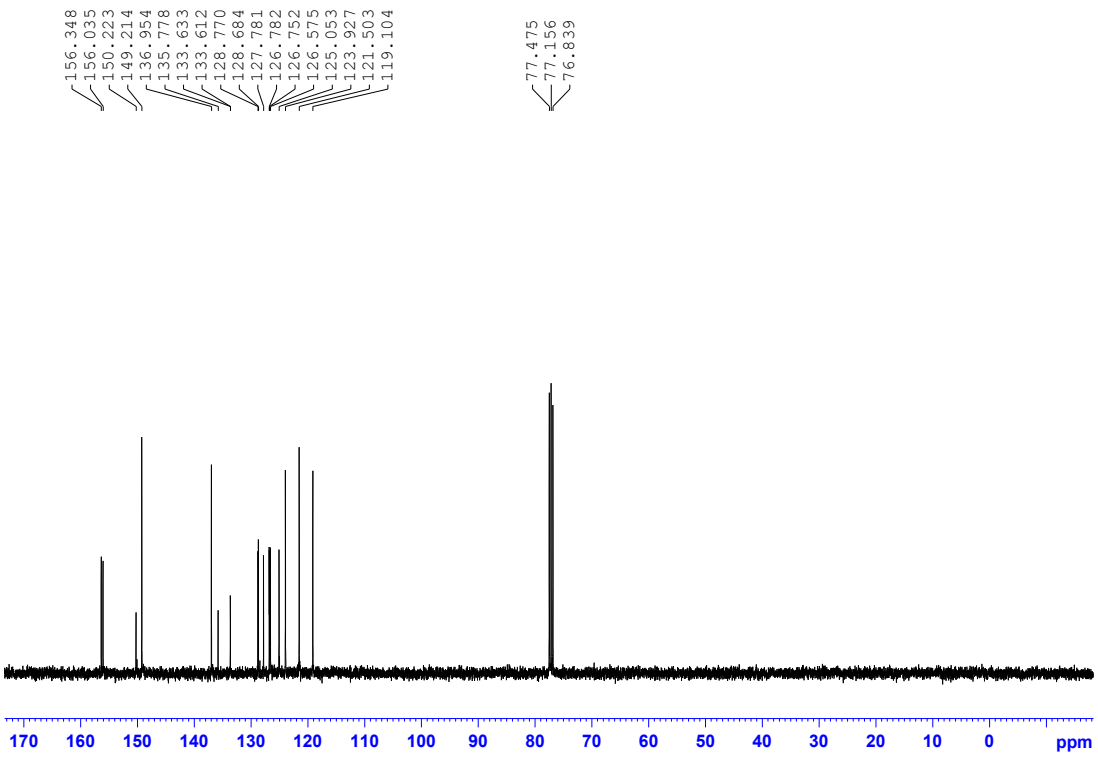

156.363
156.023
150.420
149.232
138.600
136.946
129.113
129.021
127.443
123.910
121.460
119.025
77.477
77.159
76.842
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

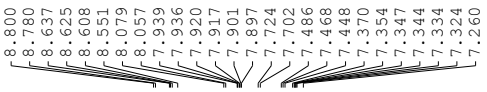

8.766
8.755
8.732
8.674
8.654
8.152
8.132
8.057
8.054
8.038
8.019
7.934
7.913
7.547
7.534
7.529
7.517
3.332
2.500
CF3
N
N
N
c
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.84
1.89
1.94
1.93
1.92
1.91

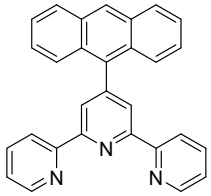

155.757
154.653
149.257
147.748
141.379
137.352
129.967
129.651
129.332
129.016
127.763
126.085
126.049
126.012
125.467
124.520
122.762
120.880
120.058
118.043
40.140
39.932
39.723
39.514
39.306
39.097
38.888
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.879
8.771
8.759
8.719
8.699
8.416
8.053
8.049
8.032
8.027
7.997
7.976
7.921
7.917
7.902
7.898
7.883
7.878
7.557
7.552
7.546
7.538
7.534
7.390
7.377
7.375
7.371
7.359
7.260
N
N
N
d

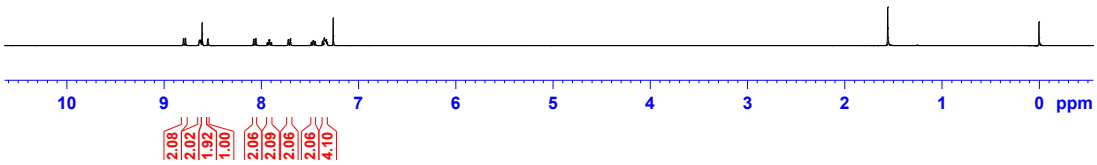

10
9
8
7
6
5
4
3
2
1
ppm
1.80
2.03
1.91
0.91
2.95
2.98
2.00
2.00

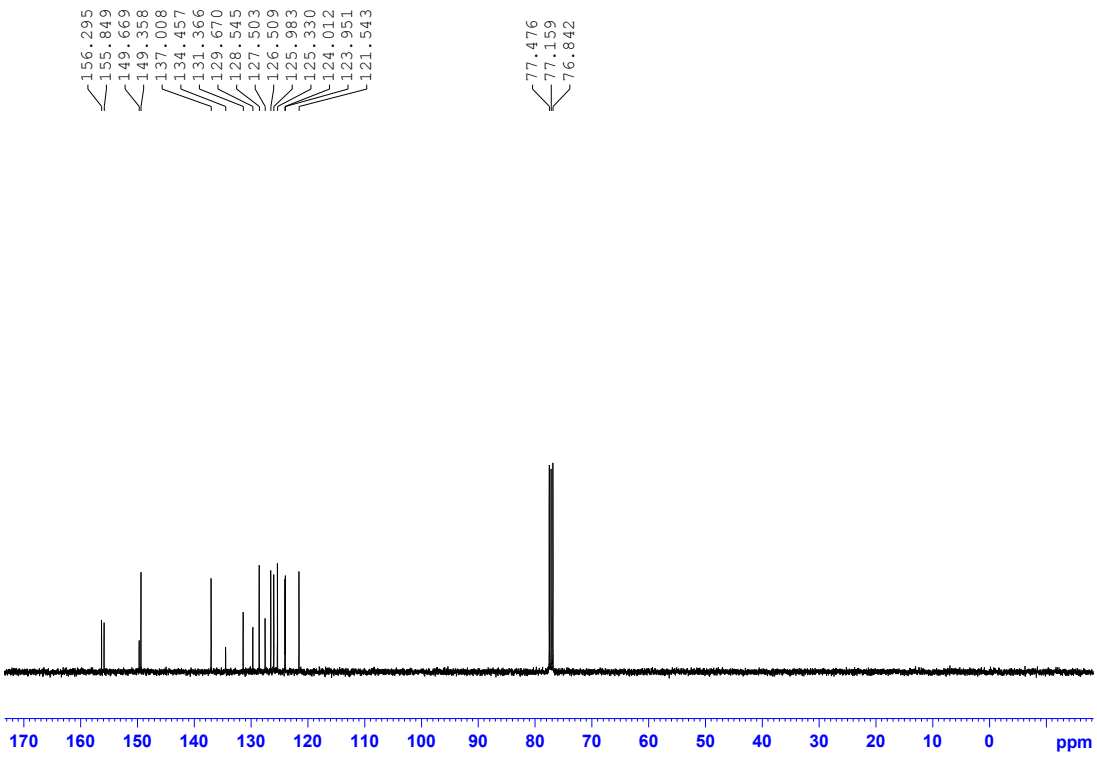

156.348
156.035
150.223
149.214
136.954
135.778
133.633
133.612
128.770
128.684
127.781
126.782
126.752
126.575
125.053
123.927
121.503
119.104
77.475
77.156
76.839
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

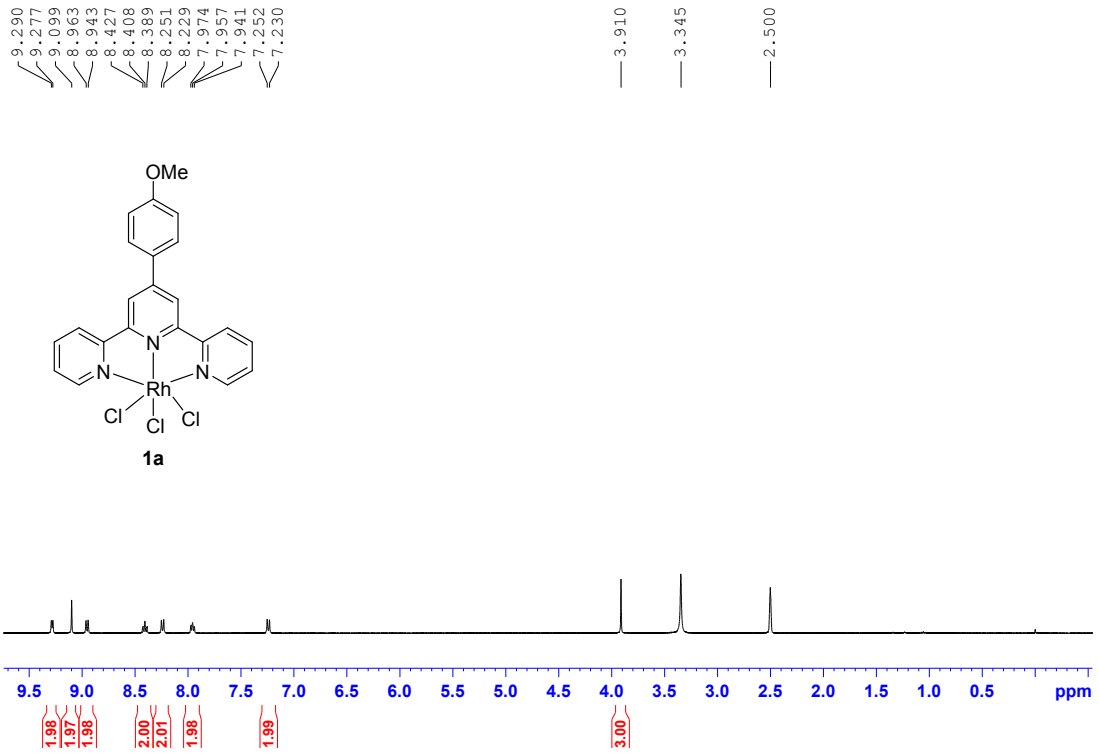

8.800
8.780
8.637
8.625
8.608
8.551
8.079
8.057
7.939
7.936
7.920
7.917
7.901
7.897
7.724
7.702
7.486
7.468
7.448
7.370
7.354
7.347
7.344
7.334
7.324
7.260

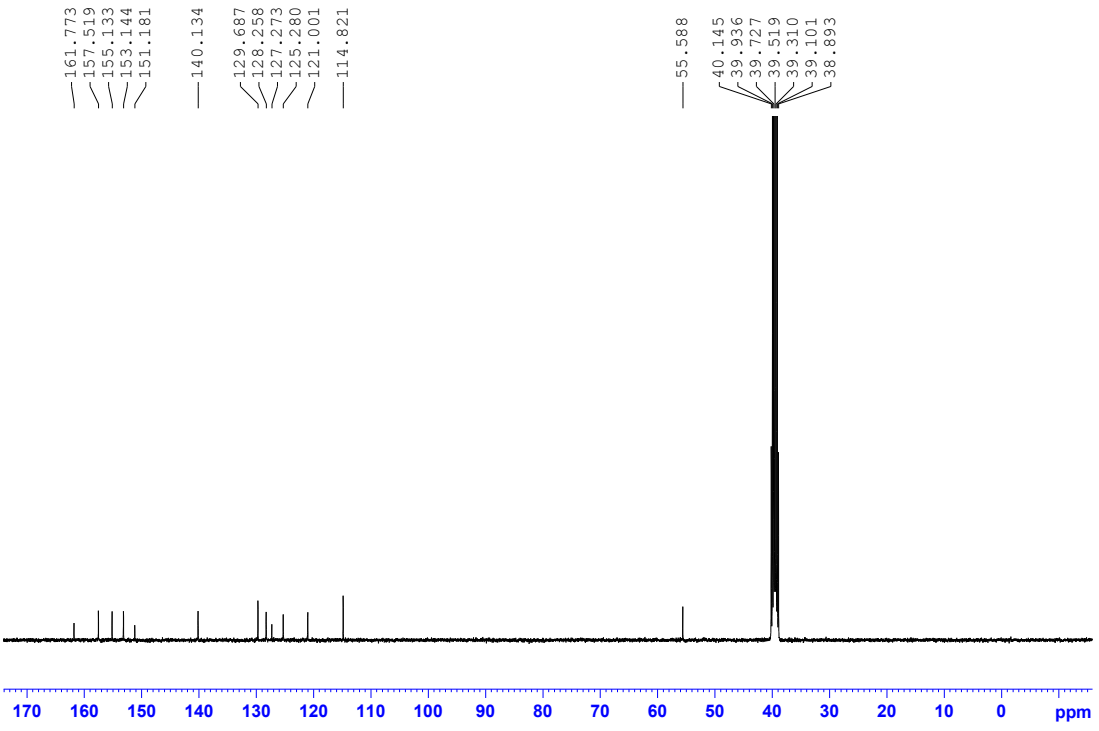

N
N
N

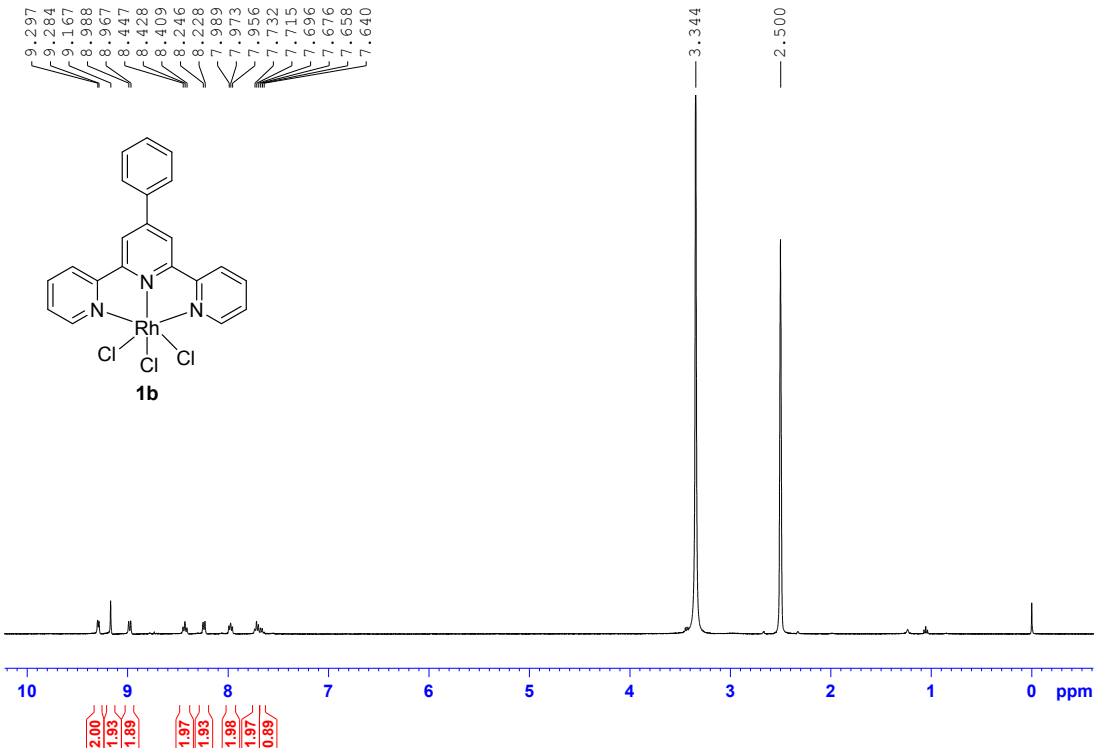
e

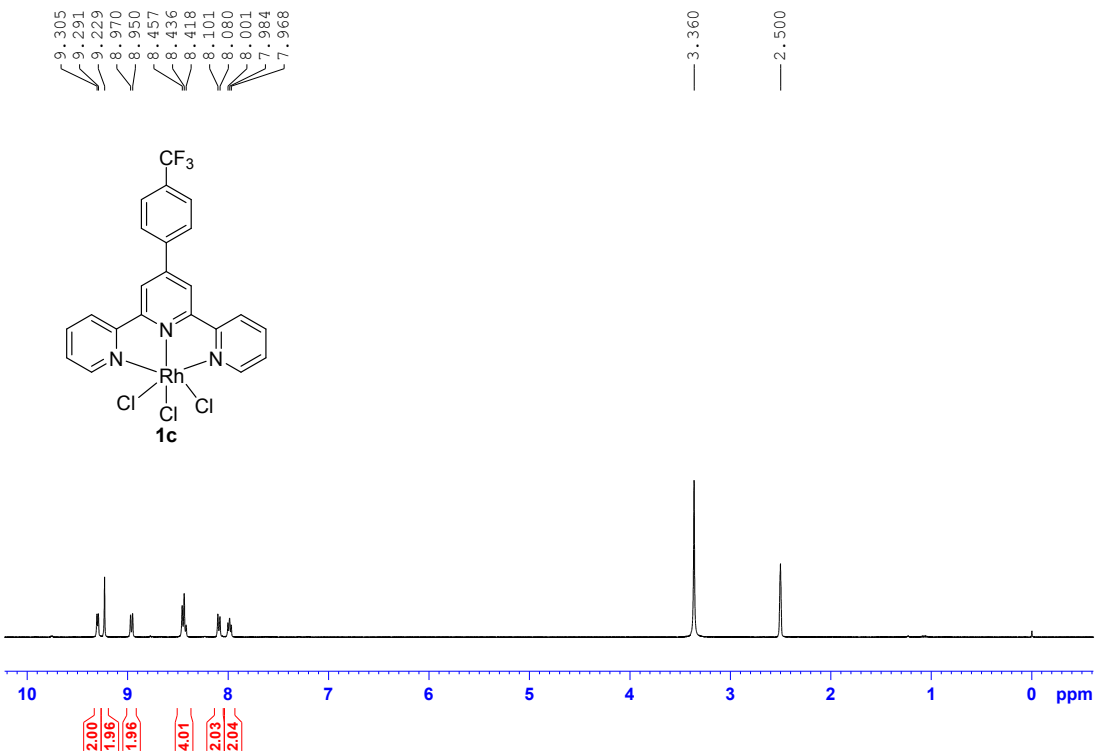

10
9
8
7
6
5
4
3
2
1
0
ppm
2.08
2.02
1.92
1.00
2.06
2.09
2.06
2.06
4.10

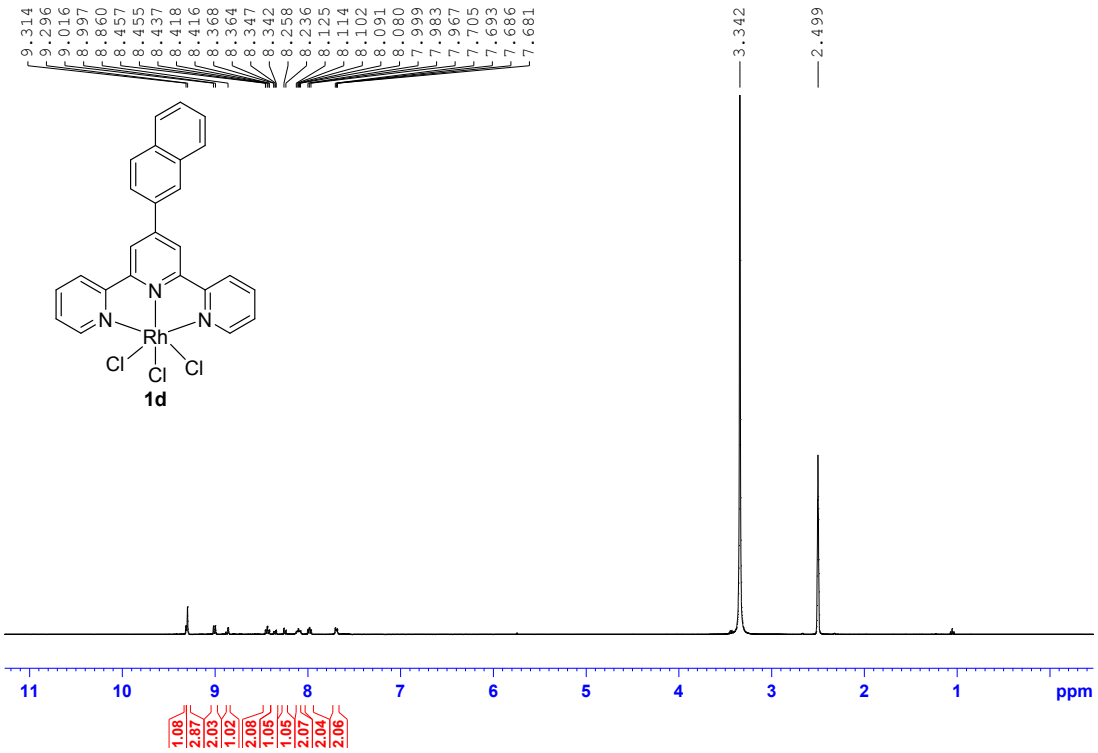

156.295
155.849
149.669
149.358
137.008
134.457
131.366
129.670
128.545
127.503
126.509
125.983
125.330
124.012
123.951
121.543
77.476
77.159
76.842
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

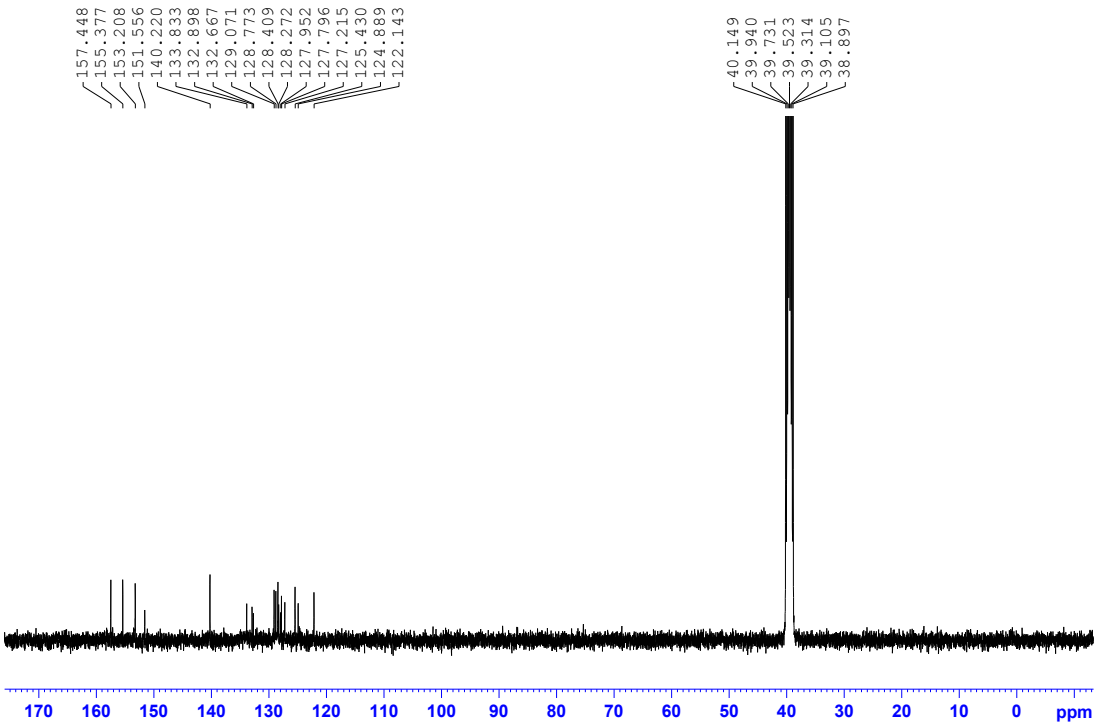

9.290
9.277
9.099
8.963
8.943
8.427
8.408
8.389
8.251
8.229
7.974
7.957
7.941
7.252
7.230
3.910
3.345
2.500
OMe
N
N
N
Rh
Cl
Cl
Cl
1a
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.98
1.97
1.98
2.00
2.01
1.98
1.99
3.00

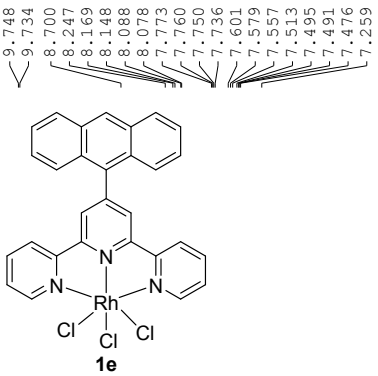

161.773
157.519
155.133
153.144
151.181
140.134
129.687
128.258
127.273
125.280
121.001
114.821
55.588
40.145
39.936
39.727
39.519
39.310
39.101
38.893
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


9.297
9.284
9.167
8.988
8.967
8.447
8.428
8.409
8.246
8.228
7.989
7.973
7.956
7.732
7.715
7.696
7.676
7.658
7.640
3.344
2.500
N
N
N
Rh
Cl
Cl
Cl
1b
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.93
1.89
1.97
1.93
1.98
1.97
0.89

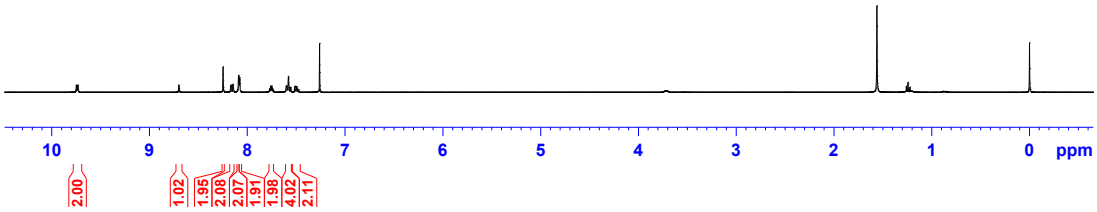

9.305
9.291
9.229
8.970
8.950
8.457
8.436
8.418
8.101
8.080
8.001
7.984
7.968
3.360
2.500
CF3
N
N
N
Rh
Cl
Cl
Cl
1c
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.96
1.96
4.01
2.03
2.04

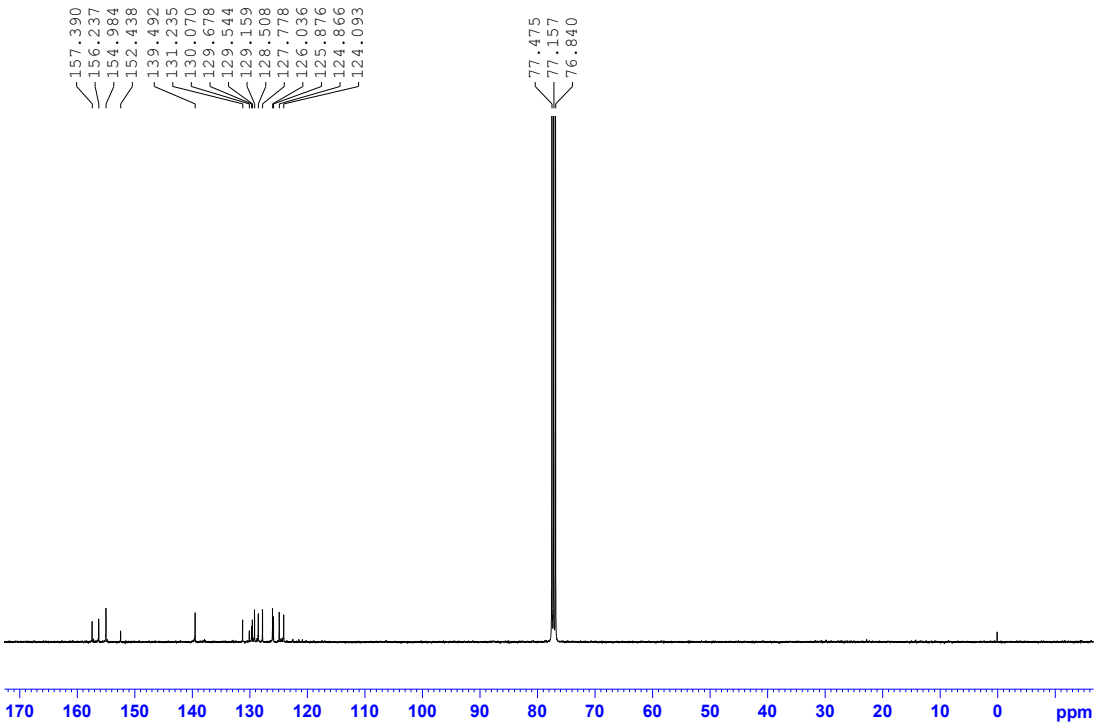

9.314
9.296
9.016
8.997
8.860
8.457
8.455
8.437
8.418
8.416
8.368
8.364
8.347
8.342
8.258
8.236
8.125
8.114
8.102
8.091
8.080
7.999
7.983
7.967
7.705
7.693
7.686
7.681
3.342
2.499
N
N
N
Rh
Cl
Cl
Cl
1d
11
10
9
8
7
6
5
4
3
2
1
ppm
1.08
2.87
2.03
1.02
2.08
1.05
1.05
2.07
2.04
2.06

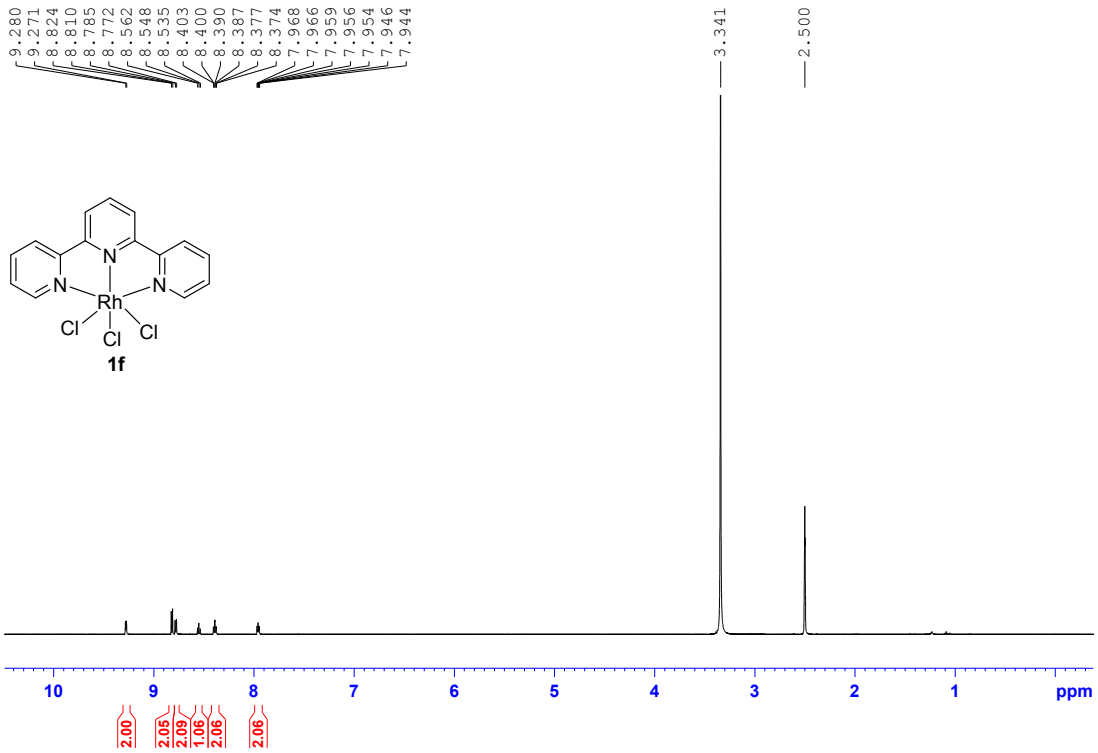

157.448
155.377
153.208
151.556
140.220
133.833
132.898
132.667
129.071
128.773
128.409
128.272
127.952
127.796
127.215
125.430
124.889
122.143
40.149
39.940
39.731
39.523
39.314
39.105
38.897
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

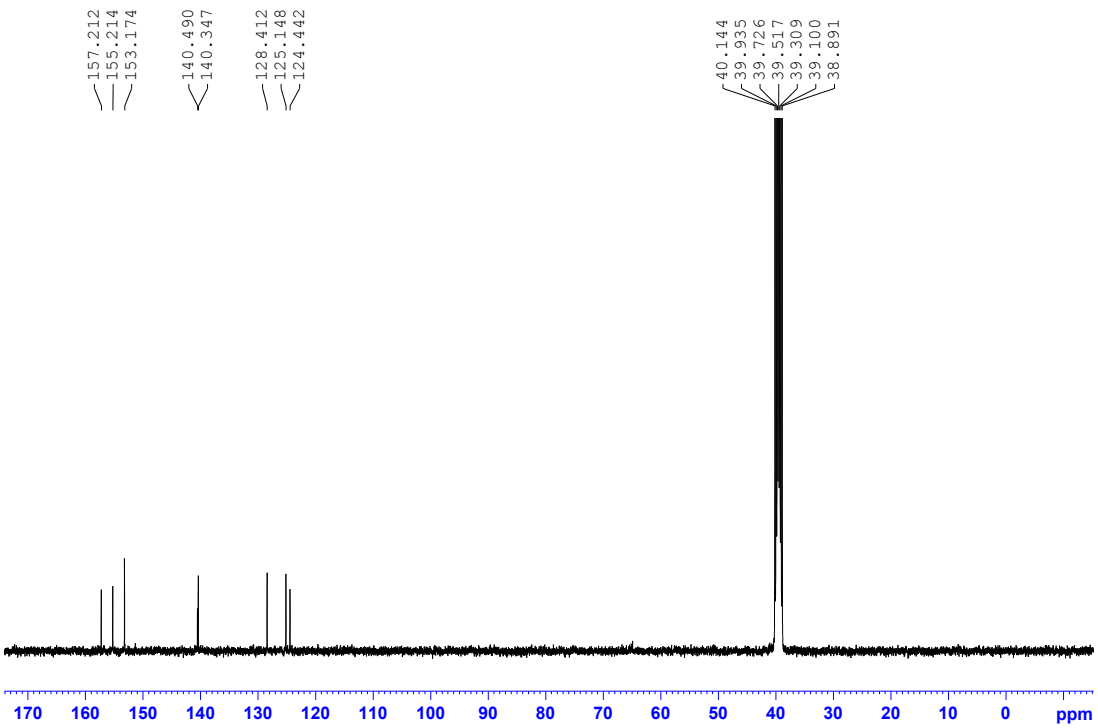

9.748
9.734
8.700
8.247
8.169
8.148
8.088
8.078
7.773
7.760
7.750
7.736
7.601
7.579
7.557
7.513
7.495
7.491
7.476
7.259
N
N
N
Rh
Cl
Cl
Cl

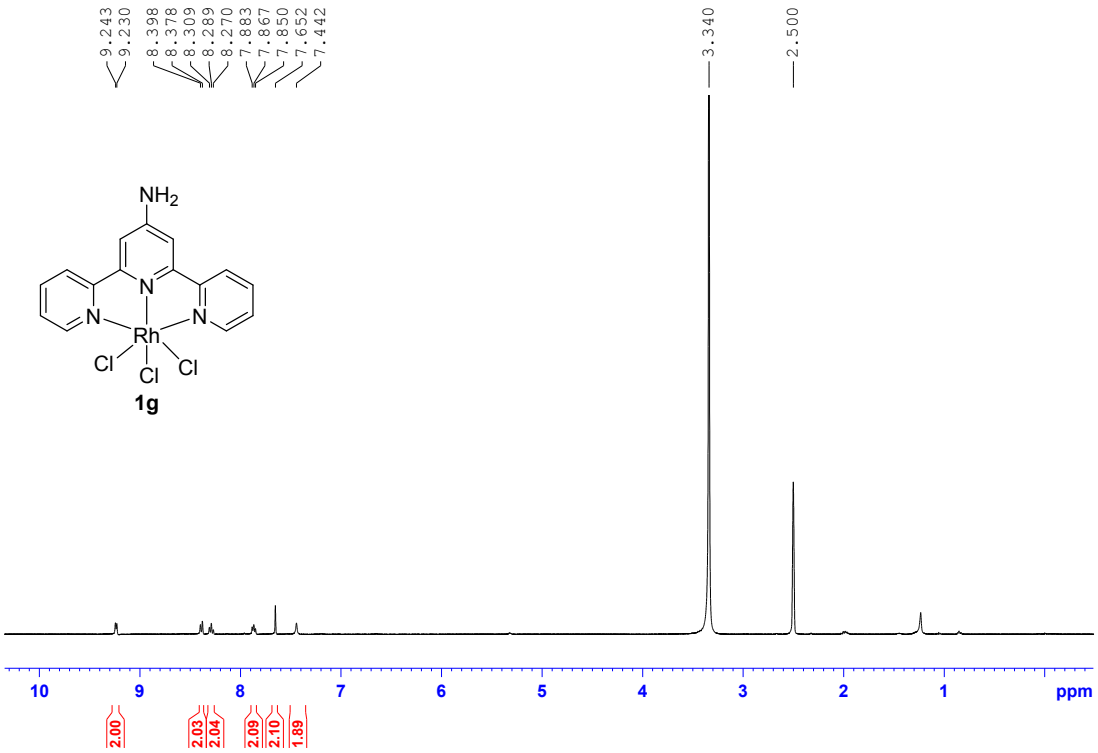
1e

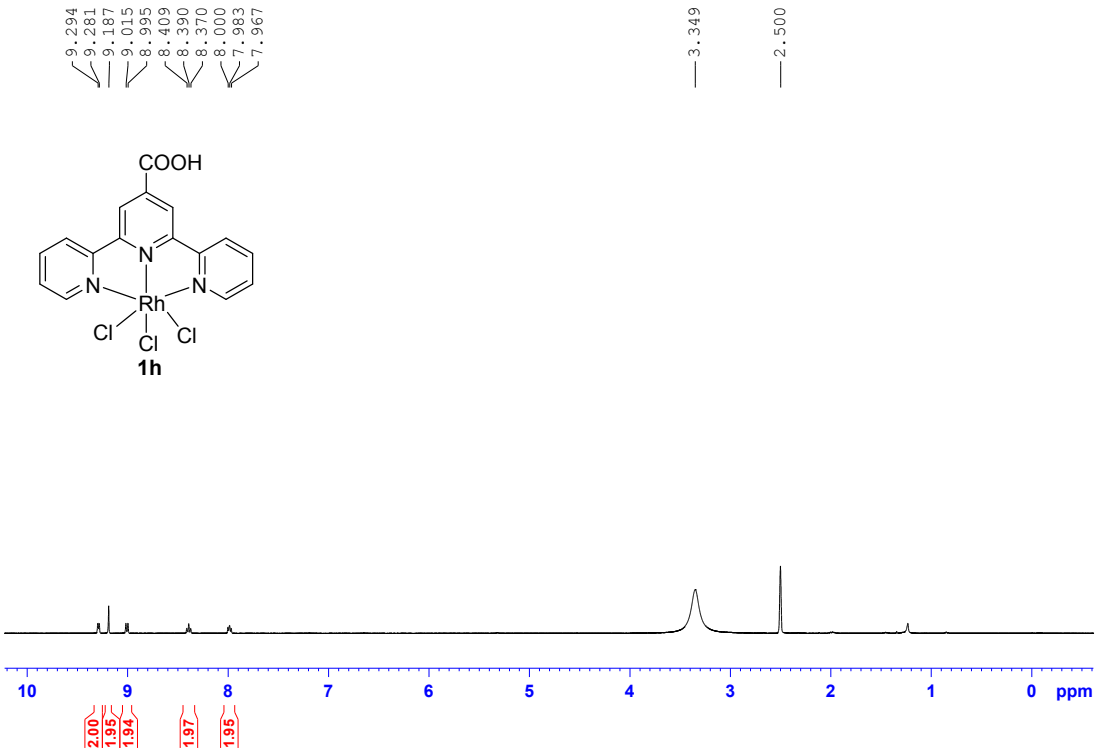

10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.02
1.95
2.08
2.07
1.91
1.98
4.02
2.11


157.390
156.237
154.984
152.438
139.492
131.235
130.070
129.678
129.544
129.159
128.508
127.778
126.036
125.876
124.866
124.093
77.475
77.157
76.840
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

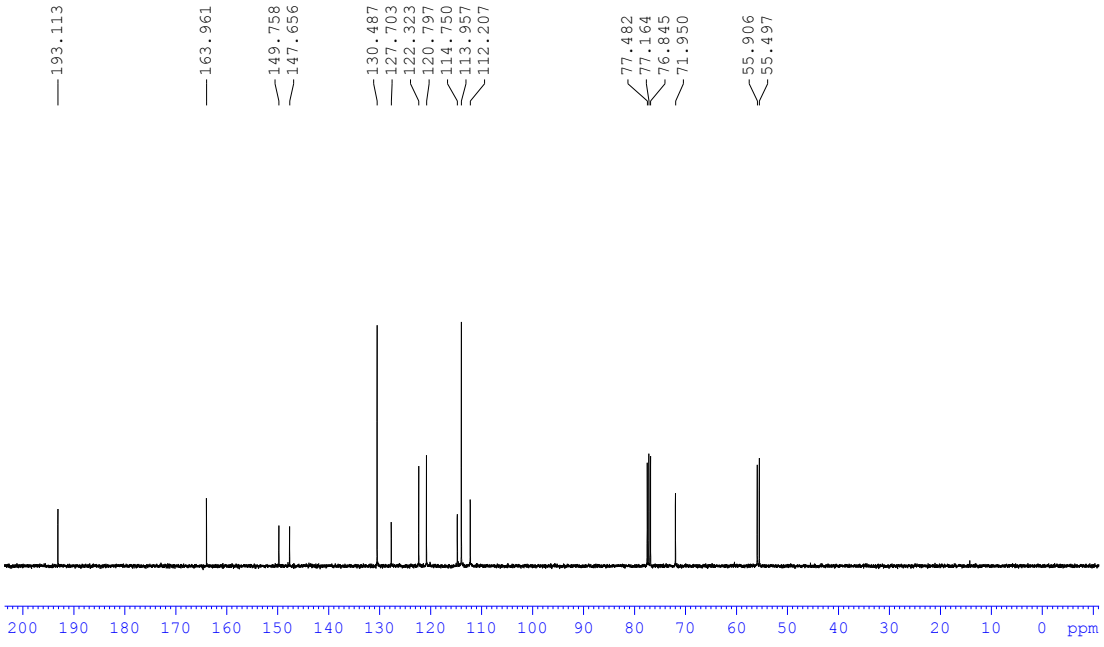

9.280
9.271
8.824
8.810
8.785
8.772
8.562
8.548
8.535
8.403
8.400
8.390
8.387
8.377
8.374
7.968
7.966
7.959
7.956
7.954
7.946
7.944
3.341
2.500
N
N
N
Rh
Cl
Cl
Cl
1f
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.05
2.09
1.06
2.06
2.06

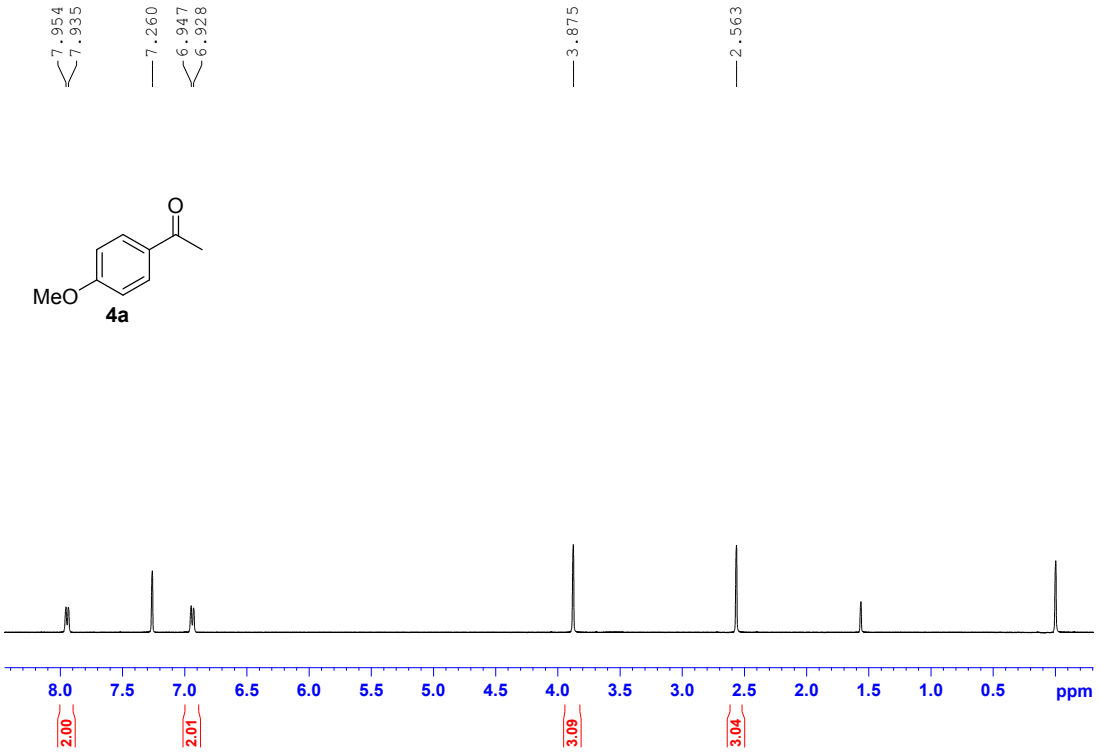

157.212
155.214
153.174
140.490
140.347
128.412
125.148
124.442
40.144
39.935
39.726
39.517
39.309
39.100
38.891
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

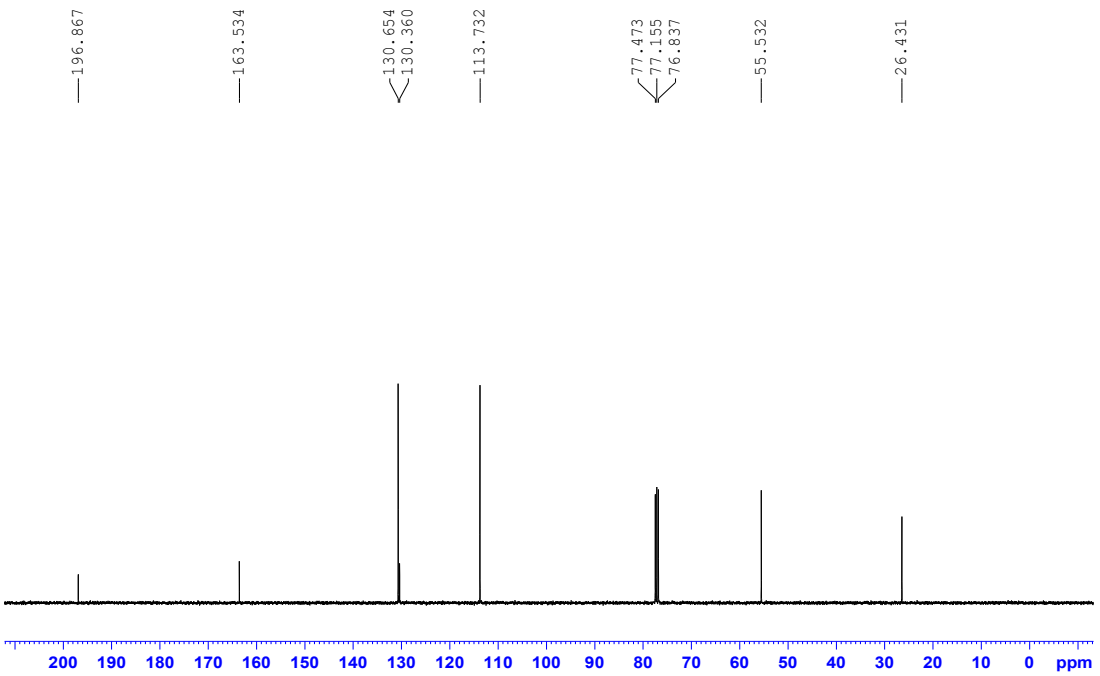

9.243
9.230
8.398
8.378
8.309
8.289
8.270
7.883
7.867
7.850
7.652
7.442
3.340
2.500
NH2
N
N
N
Rh
Cl
Cl
Cl
1g
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.03
2.04
2.09
2.10
1.89

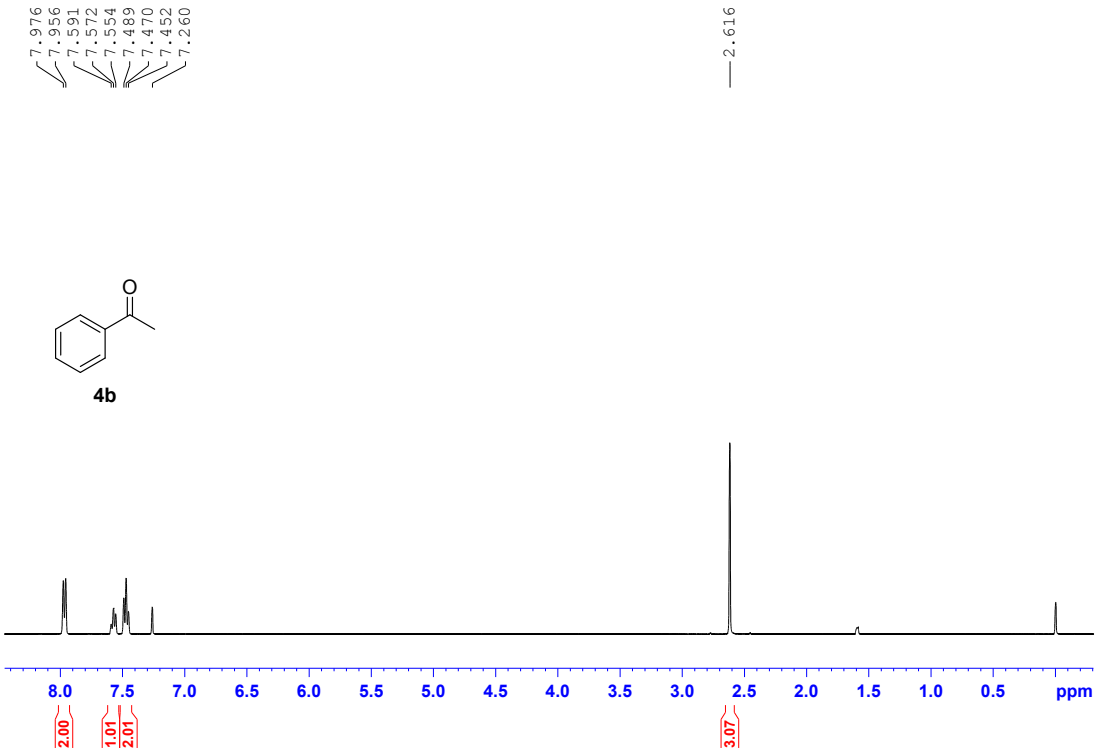

9.294
9.281
9.187
9.015
8.995
8.409
8.390
8.370
8.000
7.983
7.967
3.349
2.500
COOH
N
N
N
Rh
Cl
Cl
Cl
1h
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.95
1.94
1.97
1.95

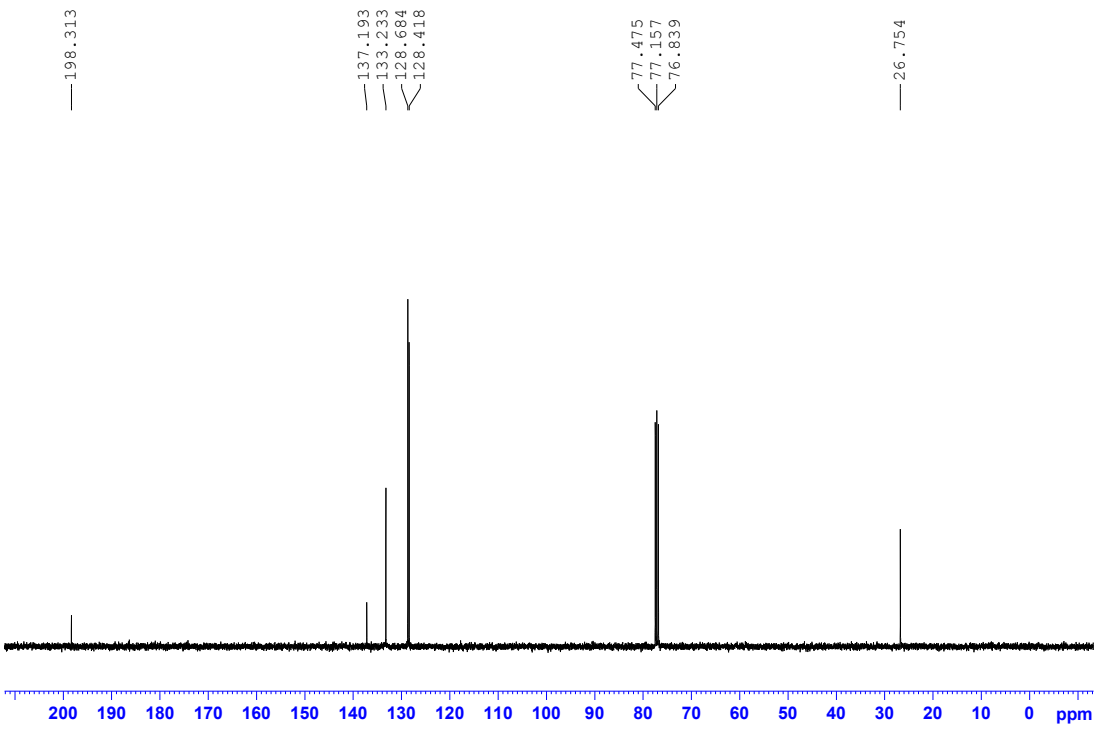

8.028
8.006
7.260
6.965
6.959
6.948
6.942
6.939
6.918
6.853
6.849
6.840
6.838
5.279
3.883
3.875
O
OMe
O
MeO
3
8
7
6
5
4
3
2
1
0
ppm
2.00
3.75
1.96
2.08
3.16
2.97

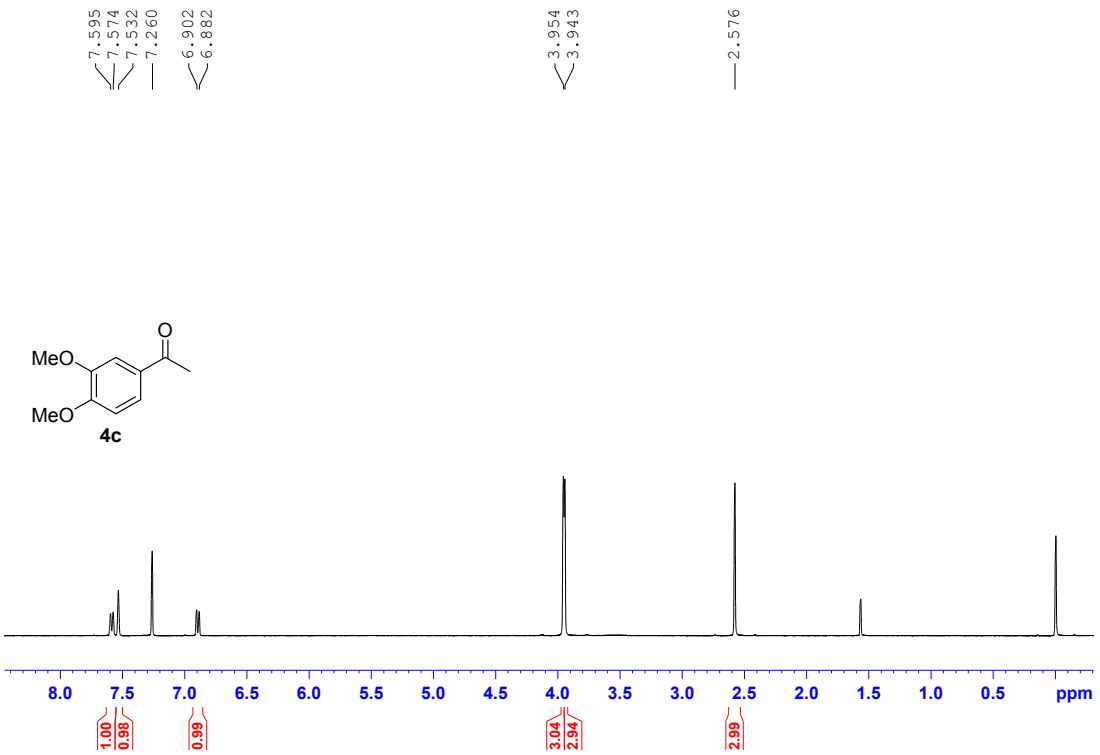

193.113
163.961
149.758
147.656
130.487
127.703
122.323
120.797
114.750
113.957
112.207
77.482
77.164
76.845
71.950
55.906
55.497
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

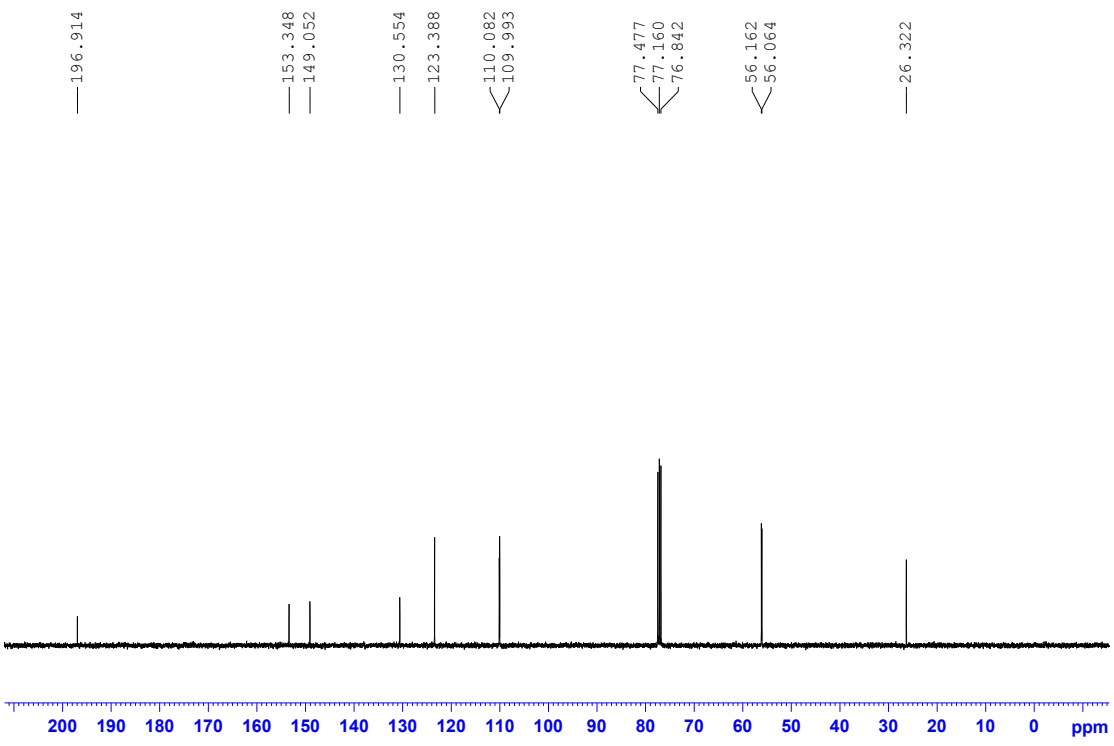

7.954
7.935
7.260
6.947
6.928
3.875
2.563
O
MeO
4a
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.01
3.09
3.04

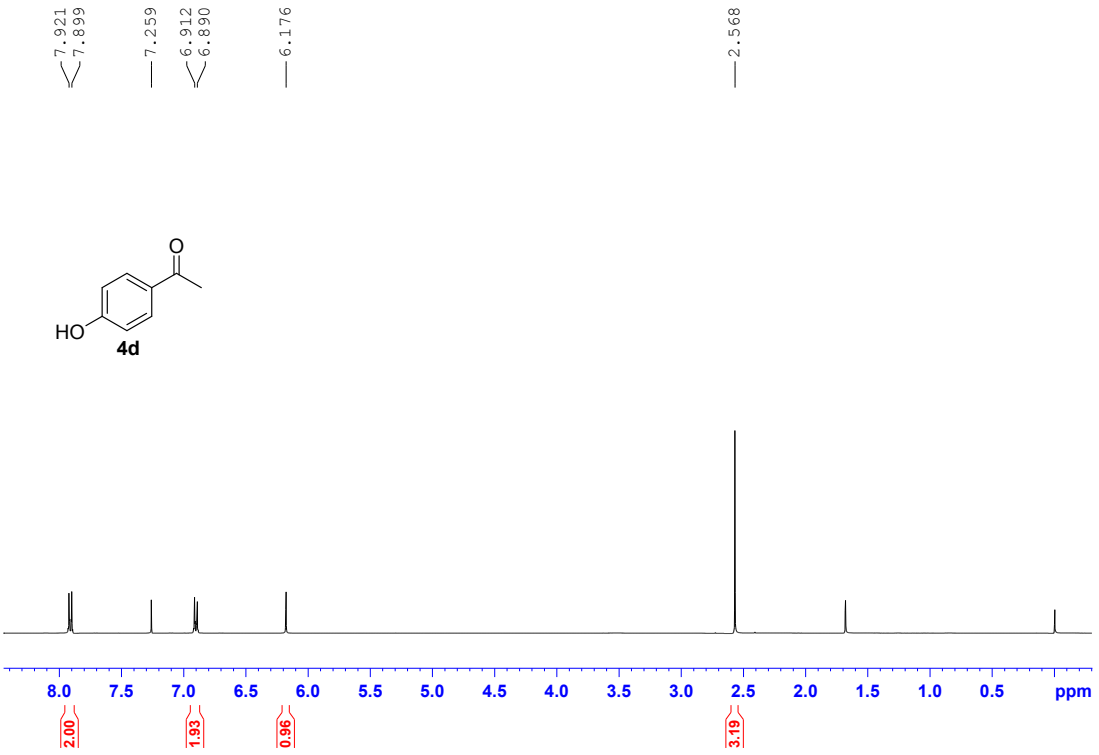

196.867
163.534
130.654
130.360
113.732
77.473
77.155
76.837
55.532
26.431
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

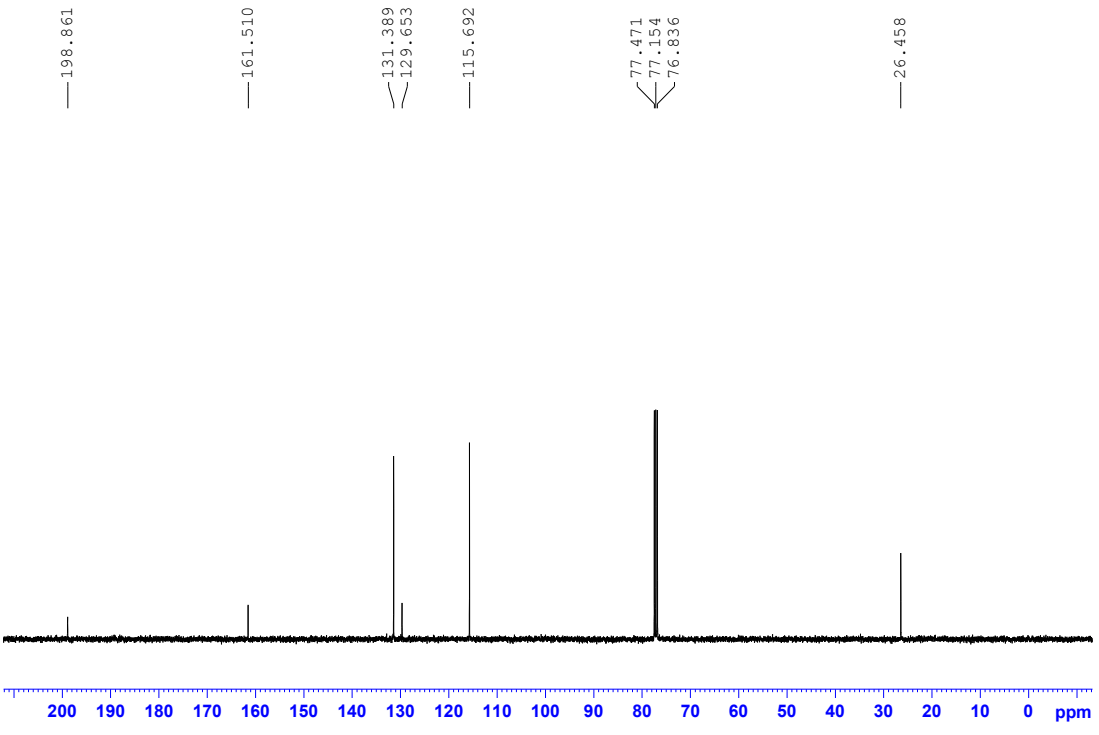

7.976
7.956
7.591
7.572
7.554
7.489
7.470
7.452
7.260
2.616
O
4b
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.01
2.01
3.07

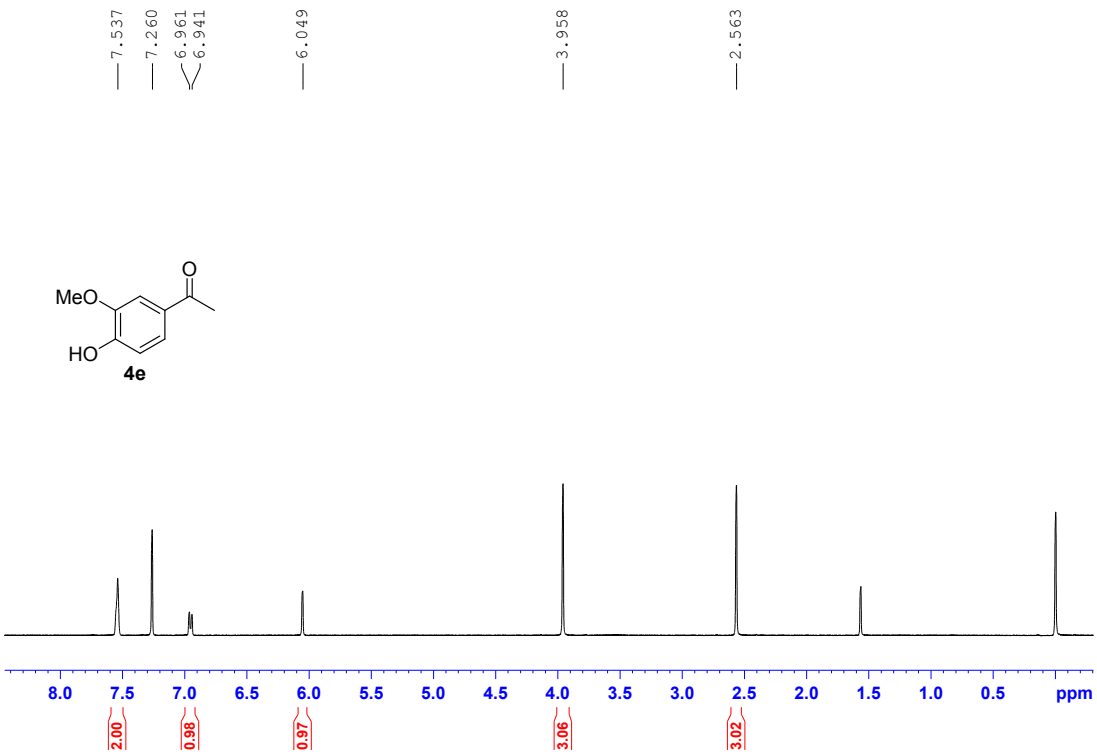

198.313
137.193
133.233
128.684
128.418
77.475
77.157
76.839
26.754
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

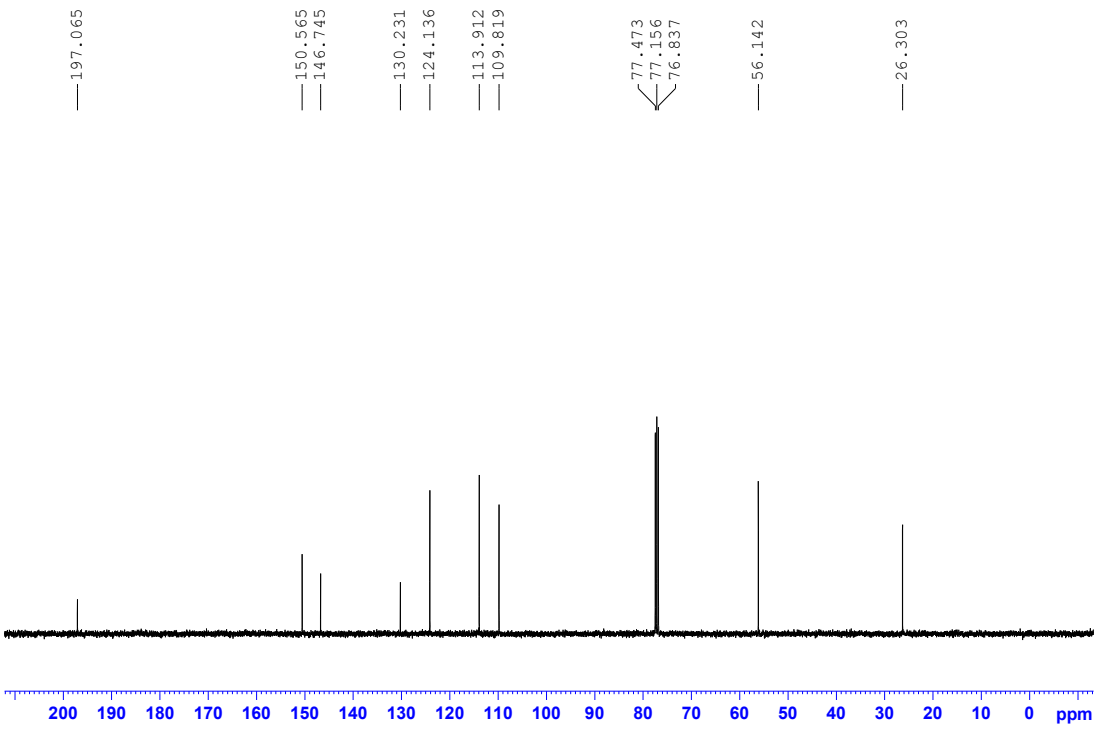

7.595
7.574
7.532
7.260
6.902
6.882
3.954
3.943
2.576
MeO
MeO
O
4c
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.98
0.99
3.04
2.94
2.99

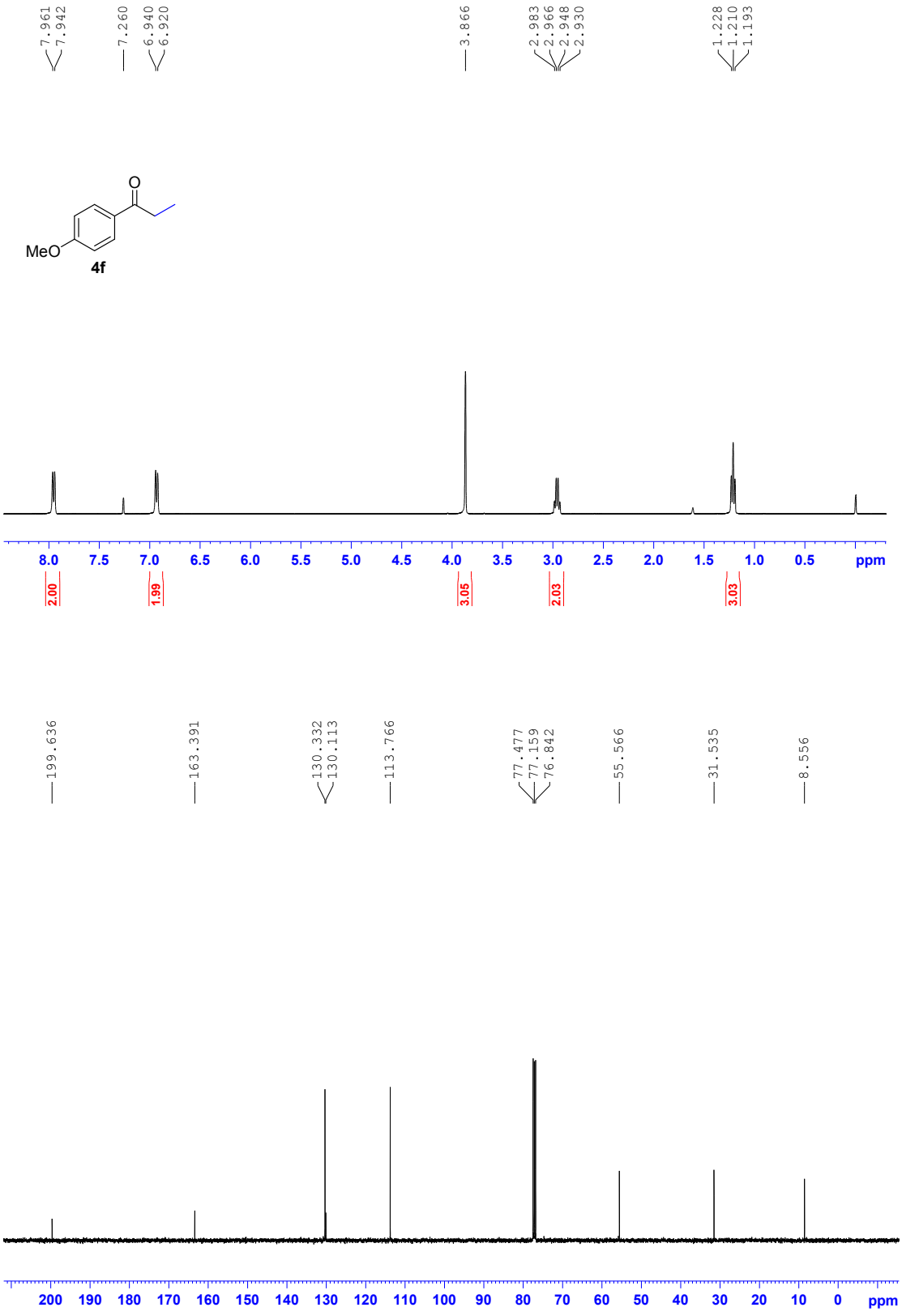

196.914
153.348
149.052
130.554
123.388
110.082
109.993
77.477
77.160
76.842
56.162
56.064
26.322
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

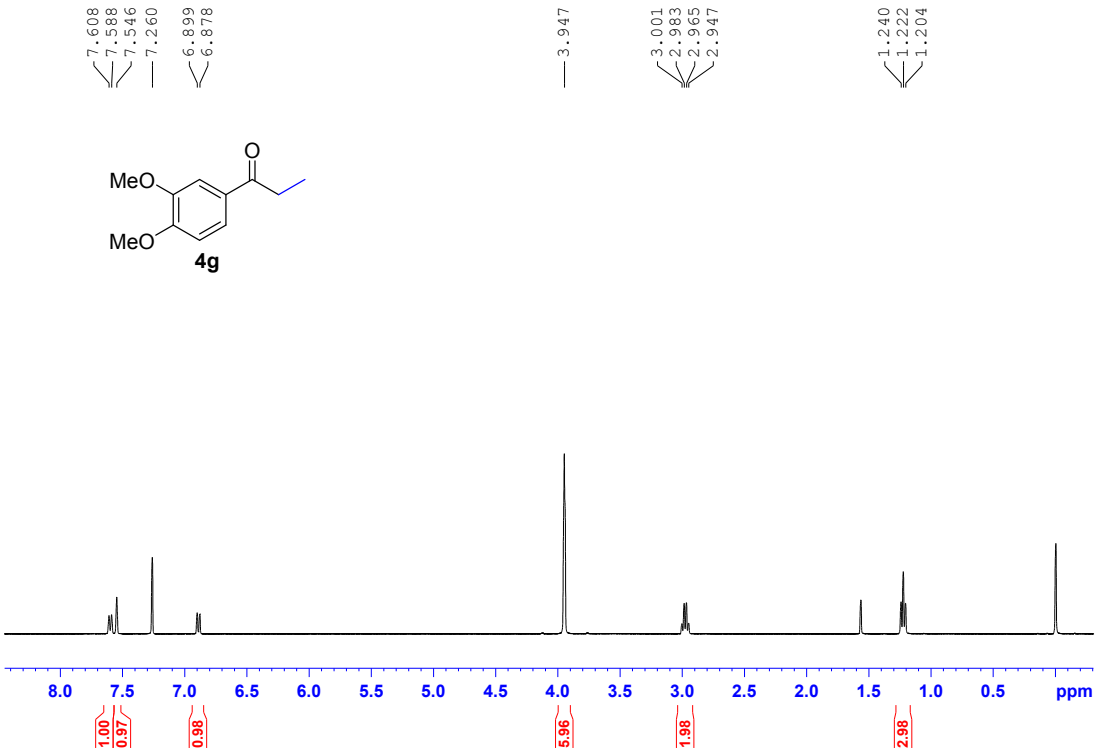

7.921
7.899
7.259
6.912
6.890
6.176
2.568
O
HO
4d
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.93
0.96
3.19

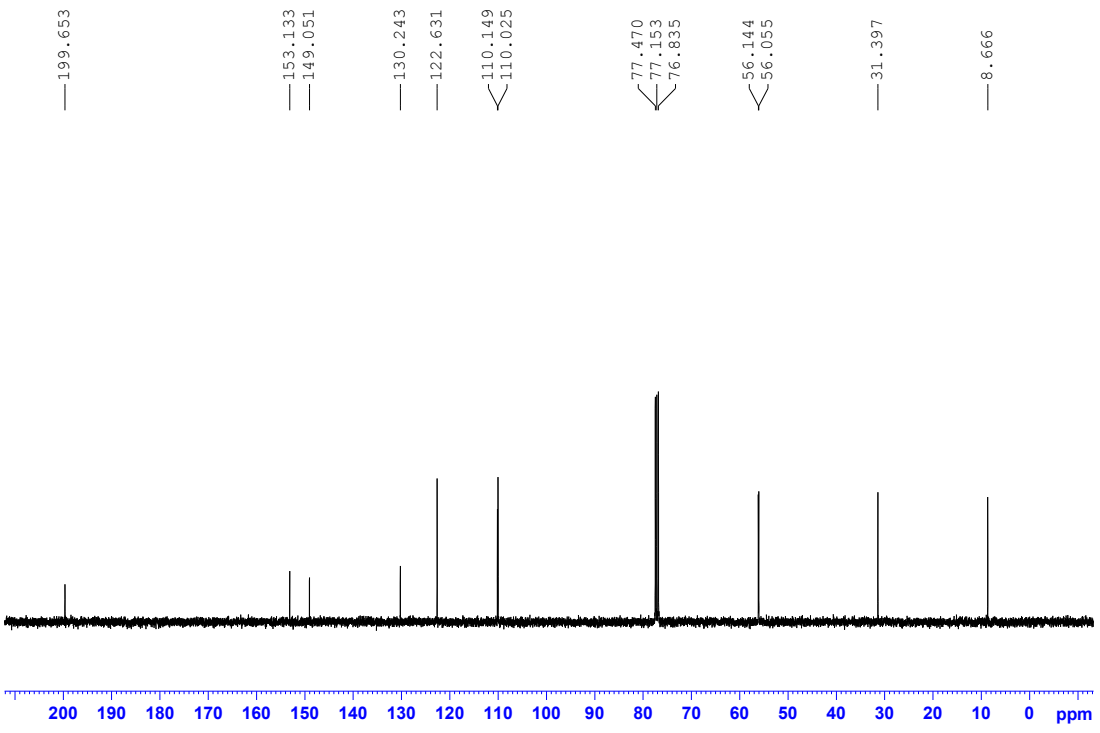

198.861
161.510
131.389
129.653
115.692
77.471
77.154
76.836
26.458
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

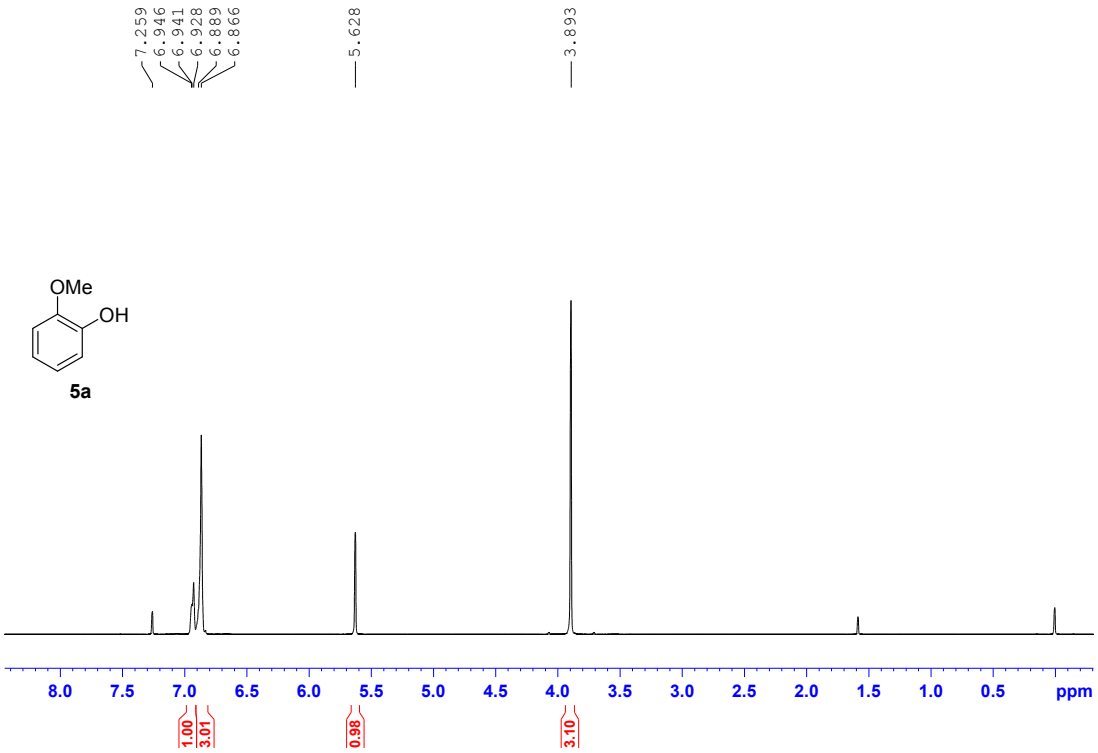

7.537
7.260
6.961
6.941
6.049
3.958
2.563
MeO
HO
O
4e
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
0.98
0.97
3.06
3.02

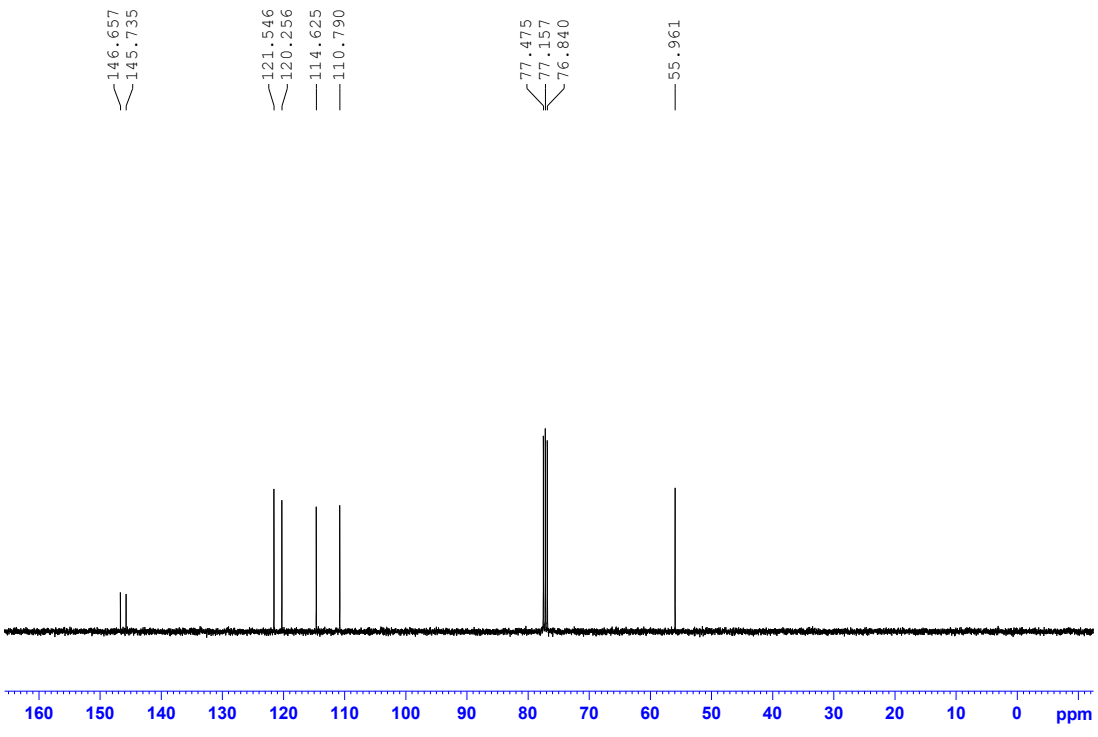

197.065
150.565
146.745
130.231
124.136
113.912
109.819
77.473
77.156
76.837
56.142
26.303
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

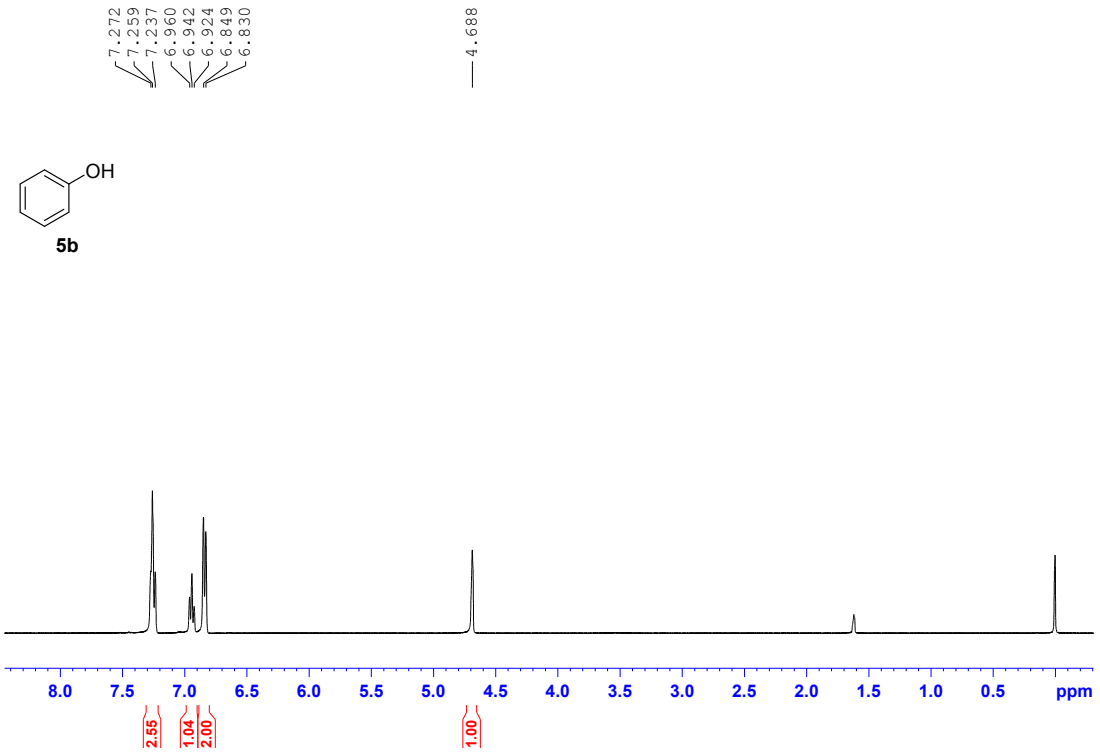

7.961
7.942
7.260
6.940
6.920
3.866
2.983
2.966
2.948
2.930
1.228
1.210
1.193
O
MeO
4f
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.99
3.05
2.03
3.03
199.636
163.391
130.332
130.113
113.766
77.477
77.159
76.842
55.566
31.535
8.556
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

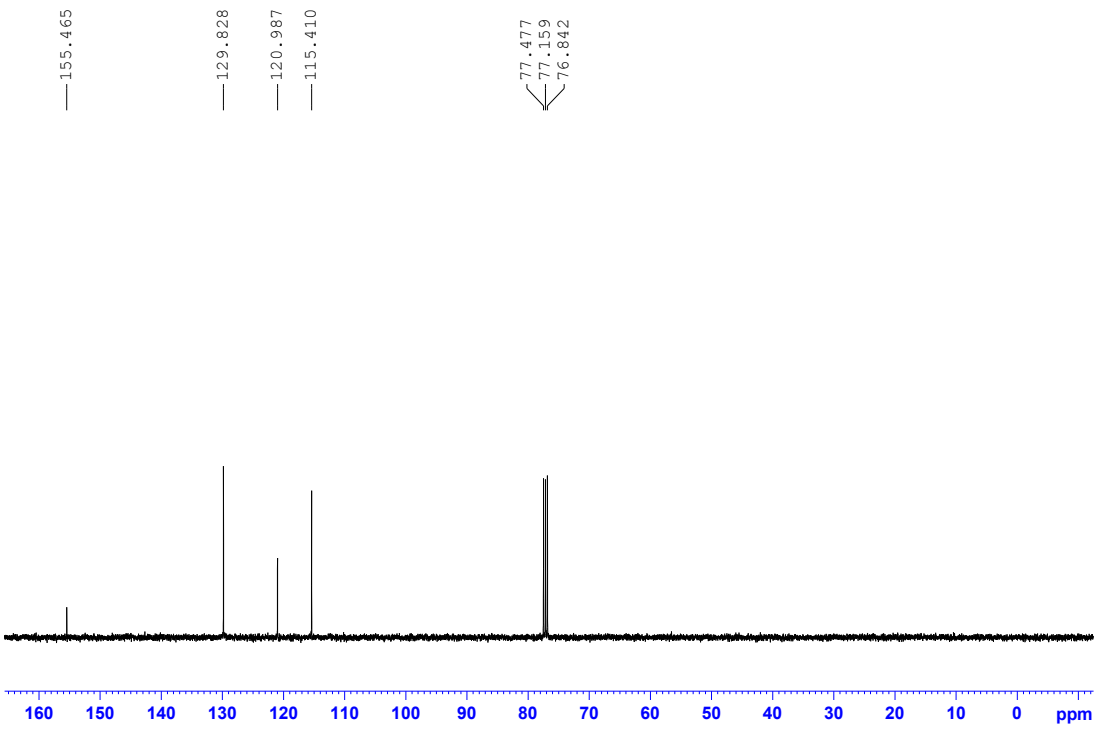

7.608
7.588
7.546
7.260
6.899
6.878
3.947
3.001
2.983
2.965
2.947
1.240
1.222
1.204
O
MeO
MeO
4g
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.97
0.98
5.96
1.98
2.98

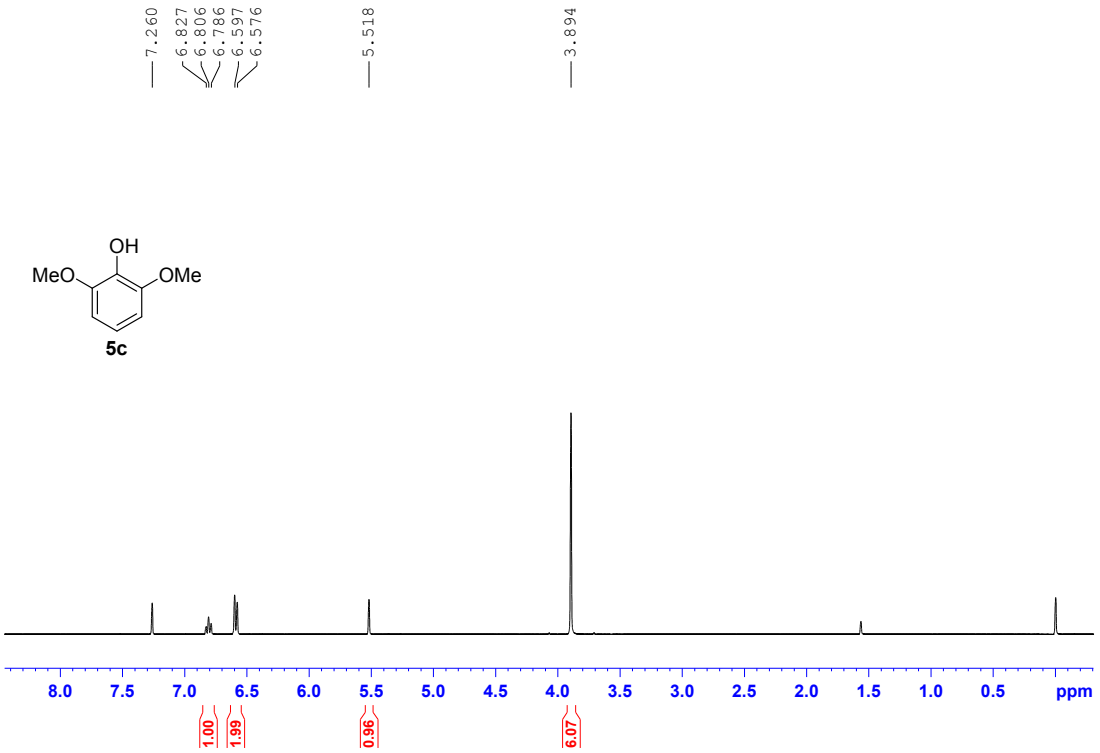

199.653
153.133
149.051
130.243
122.631
110.149
110.025
77.470
77.153
76.835
56.144
56.055
31.397
8.666
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

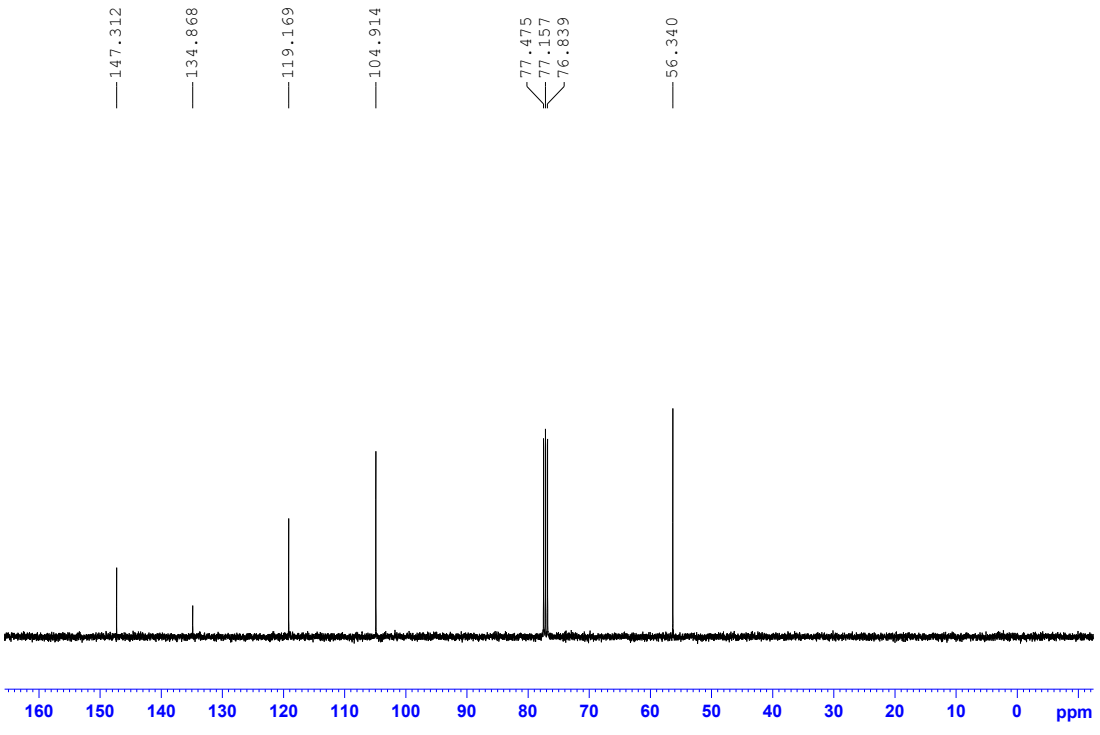

7.259
6.946
6.941
6.928
6.889
6.866
5.628
3.893
OMe
OH
5a
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
3.01
0.98
3.10

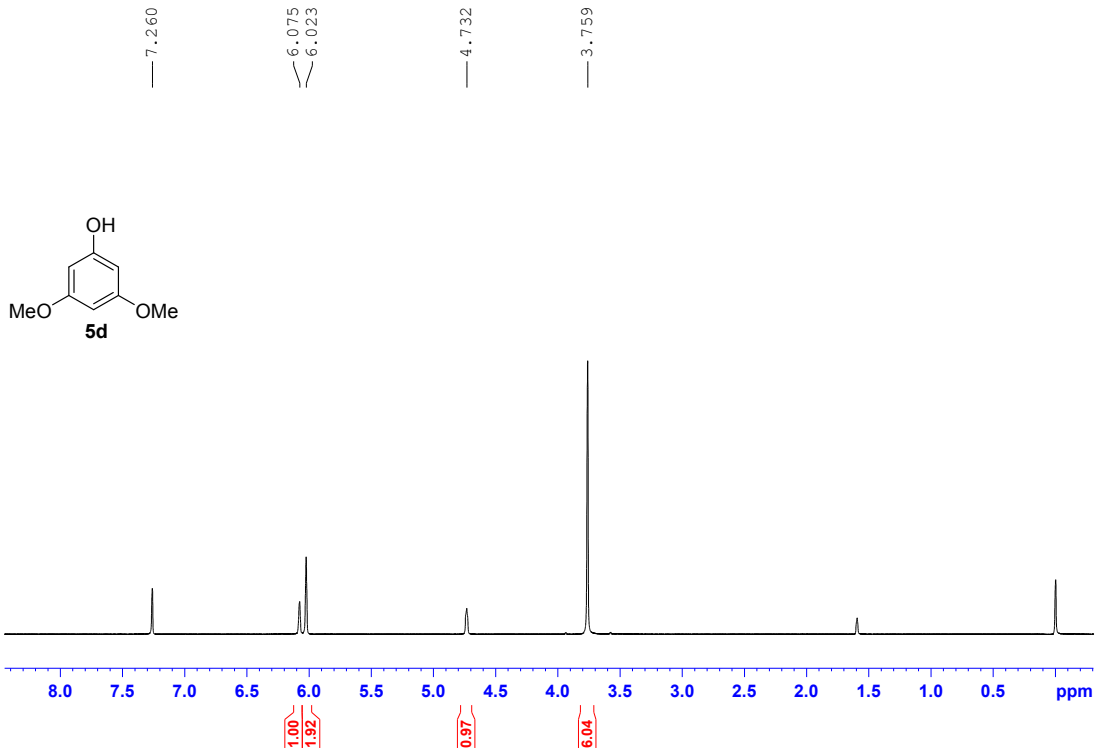

146.657
145.735
121.546
120.256
114.625
110.790
77.475
77.157
76.840
55.961
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

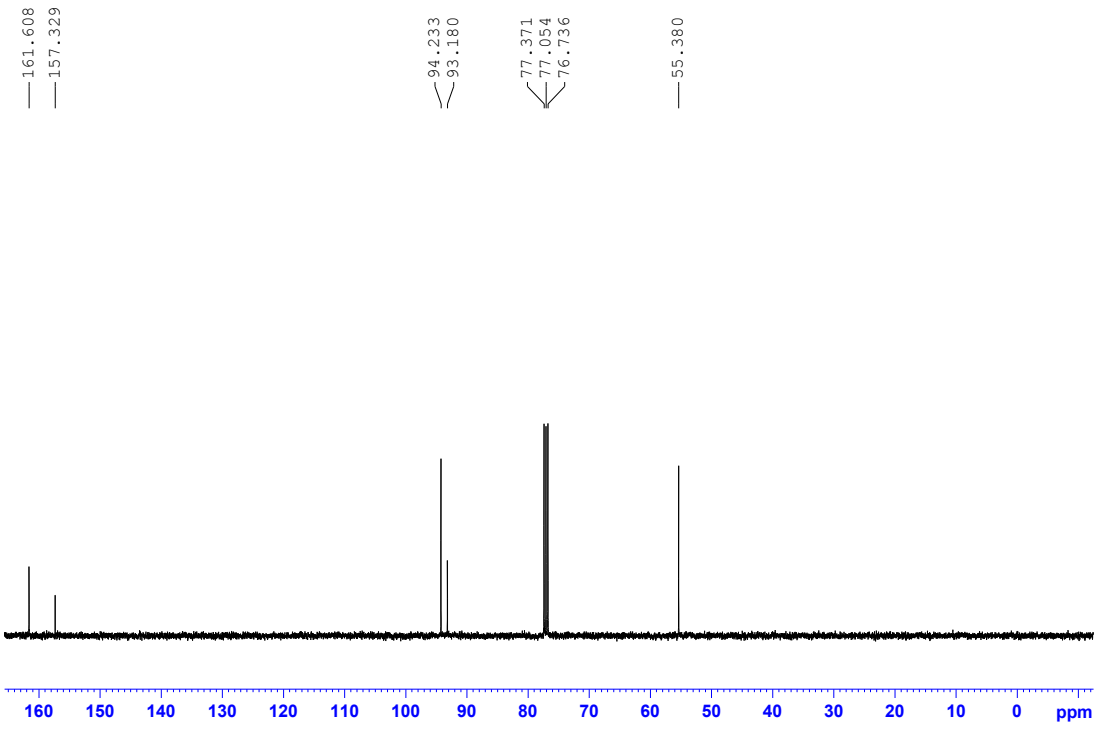

7.272
7.259
7.237
6.960
6.942
6.924
6.849
6.830
4.688
OH
5b
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.55
1.04
2.00
1.00

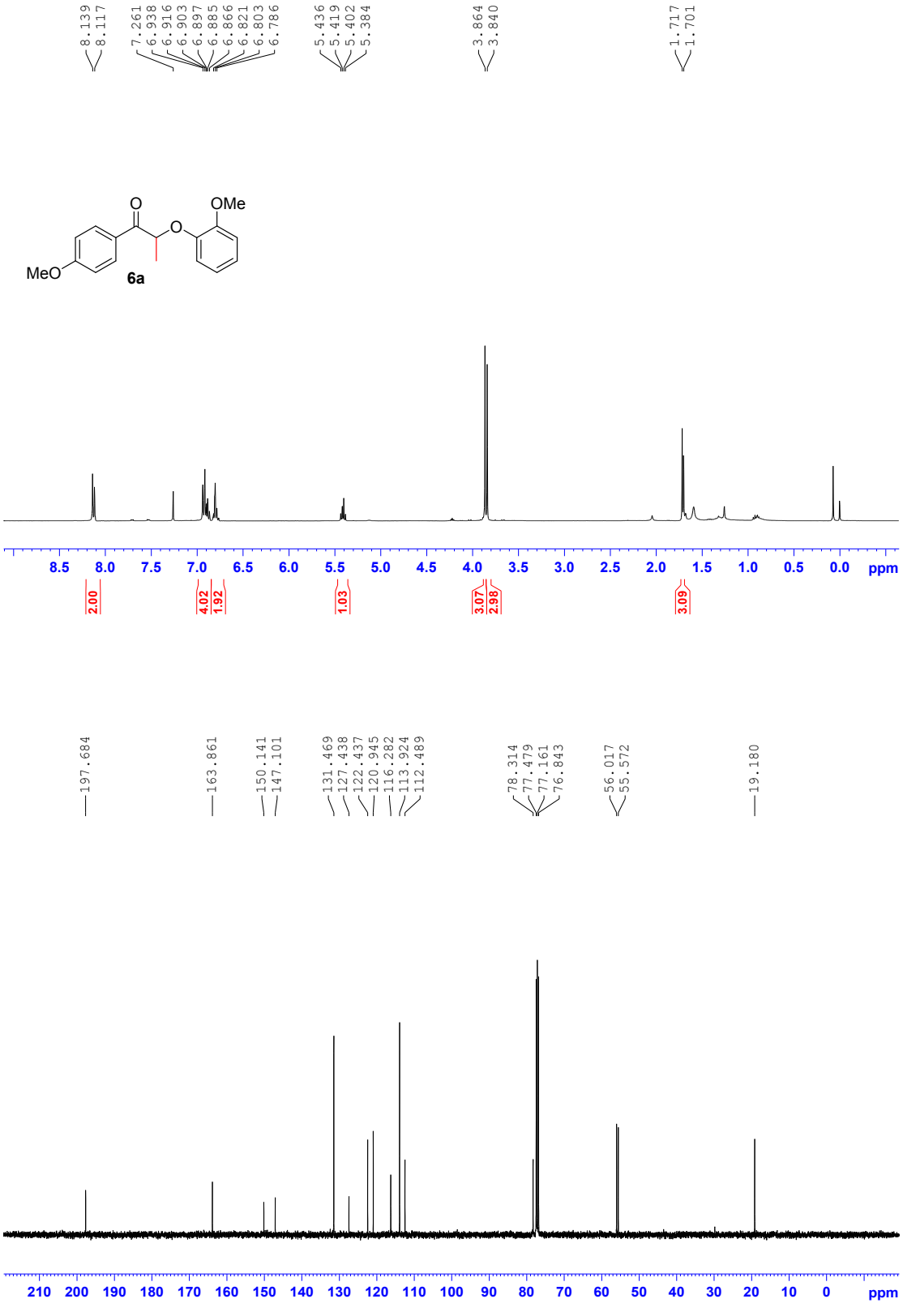

155.465
129.828
120.987
115.410
77.477
77.159
76.842
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

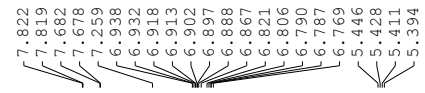

7.260
6.827
6.806
6.786
6.597
6.576
5.518
3.894
OH
MeO
OMe
5c
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.99
0.96
6.07

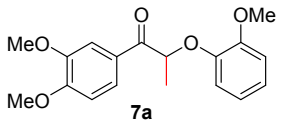

147.312
134.868
119.169
104.914
77.475
77.157
76.839
56.340
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.260
6.075
6.023
4.732
3.759
OH
MeO
OMe
5d
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.92
0.97
6.04

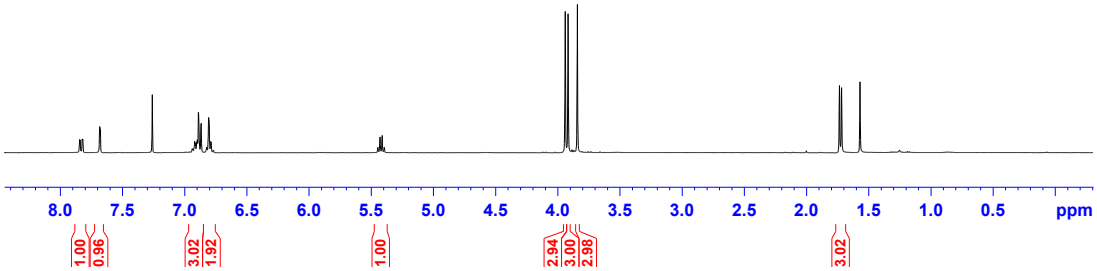

161.608
157.329
94.233
93.180
77.371
77.054
76.736
55.380
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

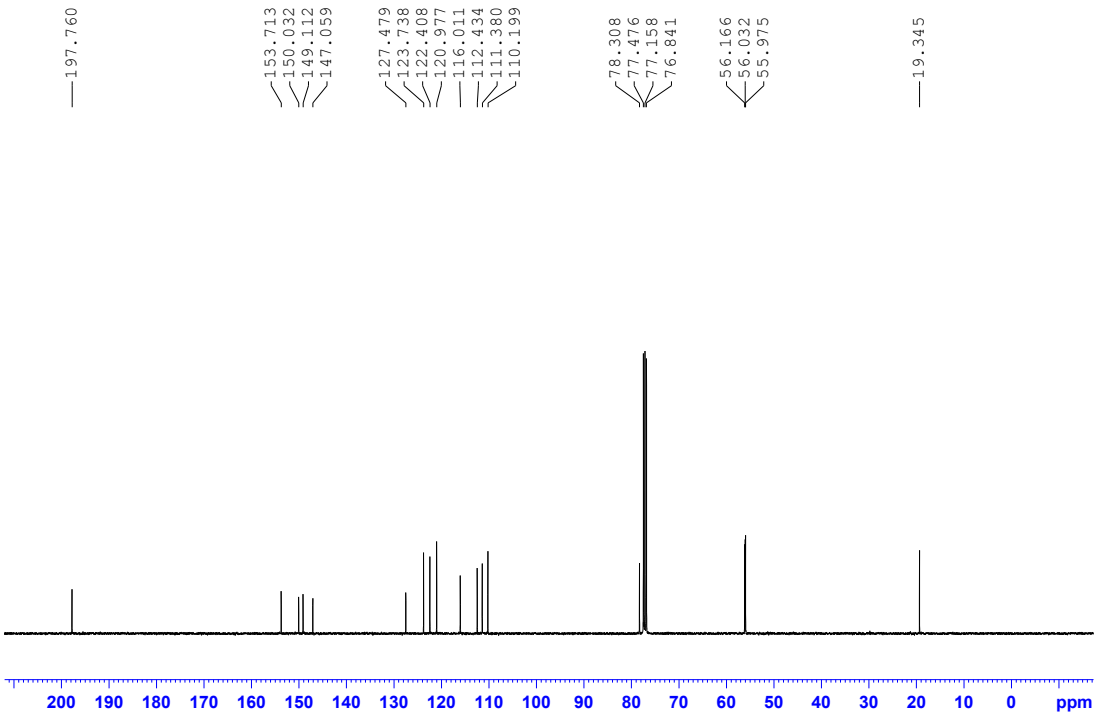

8.139
8.117
7.261
6.938
6.916
6.903
6.897
6.885
6.866
6.821
6.803
6.786
5.436
5.419
5.402
5.384
3.864
3.840
1.717
1.701
O
OMe
O
MeO
6a
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
4.02
1.92
1.03
3.07
2.98
3.09
197.684
163.861
150.141
147.101
131.469
127.438
122.437
120.945
116.282
113.924
112.489
78.314
77.479
77.161
76.843
56.017
55.572
19.180
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.822
7.819
7.682
7.678
7.259
6.938
6.932
6.918
6.913
6.902
6.897
6.888
6.867
6.821
6.806
6.790
6.787
6.769
5.446
5.428
5.411
5.394
3.939
3.916
3.842
1.735
1.717


O
OMe
MeO
O
MeO

7a


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.96
3.02
1.92
1.00
2.94
3.00
2.98
3.02


197.760
153.713
150.032
149.112
147.059
127.479
123.738
122.408
120.977
116.011
112.434
111.380
110.199
78.308
77.476
77.158
76.841
56.166
56.032
55.975
19.345
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm