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Synthesis of 2-Acylphenol and Flavene Derivatives from the Ruthenium-Catalyzed Oxidative C-H Acylation of Phenols with Aldehydes

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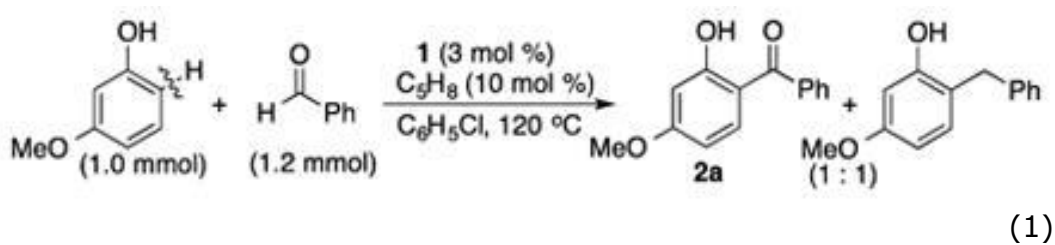
Abstract: The cationic ruthenium hydride complex $[(C_6H_6)(PCy_3)(CO)RuH]^+BF_4^-$ has been found to be an effective catalyst for the oxidative C–H coupling reaction of phenols with aldehydes to give 2-acylphenol compounds. The coupling of phenols with α,β -unsaturated aldehydes selectively gives the flavene derivatives. The catalytic method mediates direct oxidative C–H coupling of phenol and aldehyde substrates without using any metal oxidants or forming wasteful byproducts.

Keywords: acylation, phenol, aldehyde, ruthenium, flavene

2-Acylphenols are a common core structure present in many biologically active natural products and pharmaceutical agents.^[1] Traditionally, Friedel-Crafts type of acylation reactions have been used to form acylated phenol compounds,^[2] but these methods have been found to be problematic in controlling product regioselectivity, tolerating common functional groups as well as in forming wasteful byproducts. Pd-catalyzed arene carbonylative coupling methods have greatly advanced synthetic potency for forming acyl-substituted arene compounds.^[3] However, these catalytic methods typically require prefunctionalization of substrates, which lead to the formation of salt byproducts. More recently, transition metal catalyzed C–H coupling methods have emerged as step-efficient, environmentally compatible ways to form arylketone compounds.^[4–8] Chelate assisted oxidative C–H acylation methods have been shown to be particularly effective in promoting regioselective introduction of acyl groups to indoles, benzamides and other functionalized arene compounds.^[5] The intramolecular catalytic C–H coupling methods,^[6] catalytic oxidative bond cleavage reactions,^[7] multicomponent coupling reactions of arenes with CO/olefins,^[8] and arene hydroxylation methods^[9] have also been successfully applied to form 2-acylarene products. While these catalytic C–H coupling methods directly install acyl group to arene substrates, the methods are mostly limited to aromatic aldehydes and often require stoichiometric metal oxidants. A broadly applicable oxidative C–H acylation method on phenol substrates is desired to enhance its synthetic efficacy toward the synthesis of bioactive acyl-substituted phenol compounds.

We recently discovered that a well-defined cationic ruthenium hydride complex $[(C_6H_6)(PCy_3)(CO)RuH]^+BF_4^-$ (**1**) is a highly effective catalyst precursor for a number of dehydrative C–H coupling reactions of phenols with alcohols to form 2-alkylphenol and benzofuran products.^[10] In light of the recent reports on the coupling reactions of alcohols,^[11] one of the key mechanistic questions concerns with whether the alcohol substrate undergoes dehydrogenation to form aldehyde prior to the dehydrative coupling reactions. We have been probing this possibility by exploring the reactivity of phenols toward aldehydes. Here, we report a highly regioselective oxidative C–H coupling of phenols with aldehydes to form 2-acylphenol and flavene products. The catalytic method mediates direct C–H activation of both

phenol and aldehyde substrates without using any metal oxidants or resorting to prefunctionalization of phenol substrates.

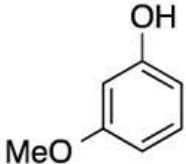
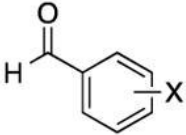
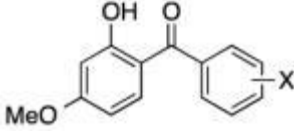
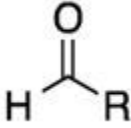
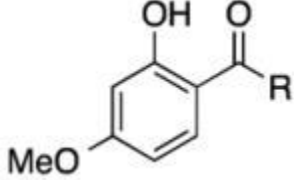
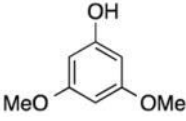
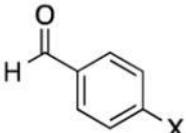
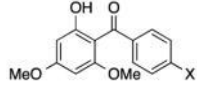
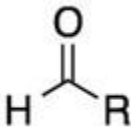
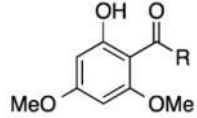


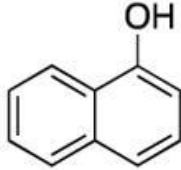
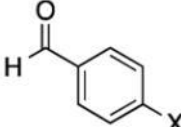
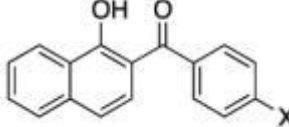
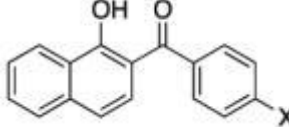
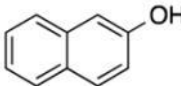
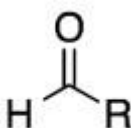
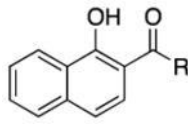
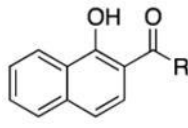
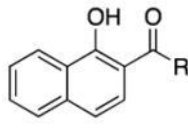
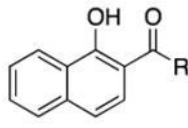
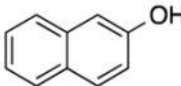
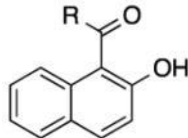
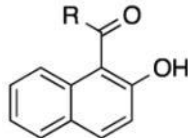
Initially, we have chosen the coupling reaction of 3-methoxyphenol with benzaldehyde to probe the selectivity between the acylation vs alkylation products. The treatment of 3-methoxyphenol with benzaldehyde and the catalyst **1** (3 mol %) under the previously reported dehydrative coupling reaction conditions led to the formation of a 1:1 mixture of the acylated phenol product **2a** along with the alkylated product, but with only ~20% of the combined yield (eq 1).^[10] Suspecting that the aldehyde substrate might have been reduced to benzyl alcohol in leading to the alkylation product, we screened additive effects to optimize for the acylation product **2a**. Among screened additives and selected ruthenium catalysts, the complex **1** with base additives, K_2CO_3 and PPh_3 , was found to be the most effective in promoting the acylation product **2a** (Table S1, Supporting Information (SI)).

We explored the scope of the coupling reaction by using the optimized catalytic system (Table 1). Both aliphatic and aryl-substituted aldehydes readily reacted with 3-methoxyphenol to form the 2-acylphenol products **2** (entries 1–9). For the coupling of 3,5-dimethoxyphenol, electron-deficient benzaldehydes gave significantly higher yields than the ones with electron-releasing group (entries 10–18). The coupling of 1-naphthol with both aliphatic and aryl-substituted aldehydes gave the 2-acylated products **2s–2x** (entries 19–24), while the analogous coupling of 2-naphthol selectively yielded 1-acylnaphthol products **2y** and **2z** (entries 25, 26). Although the crude mixture typically contained a small amount of the alkylation product as well as unidentified oligomeric side products (5–10% combined), analytically pure acylated products were readily isolated after column chromatography on silica gel. In most cases, two equivalents of aldehyde is required for the optimum yield of coupling

products, as the second equivalent of aldehyde is acting as an hydrogen acceptor.^[12] The catalytic method achieves regioselective acylation of phenol substrates without using any stoichiometric metal oxidants or reactive reagents.

Table 1. Oxidative C–H Acylation of Phenols with Aldehydes.^[a]

entry	phenol	aldehyde	product(s)	time yield (h) (%)	
					
1		X=H	2a	12	47
2		X=4-Me	2b	12	43
3		X=4-F	2c	12	53
4		X=2-Br	2d	12	58
					
5		R = Et	2e	12	56
6		R = <i>n</i> -Pr	2f	12	44
7		R = <i>i</i> -Bu	2g	12	58
8		R = Cy	2h	12	50
9		R = CH(Me)Ph	2i	12	67
					
10		X = H	2j	16	65
11		X = Me	2k	16	51
12		X = F	2l	16	73
13		X = Cl	2m	16	70
14		X = CF ₃	2n	16	74
					
15		R = Et	2o	8	74
16		R = <i>i</i> -Bu	2p	12	69
17		R = Cy	2q	12	71
18		R = CH(Me)Ph	2r	12	78

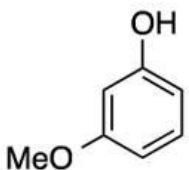
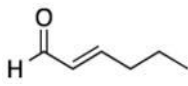
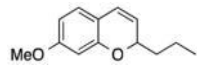
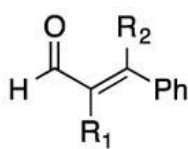
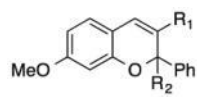
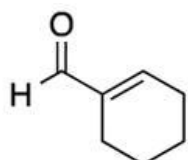
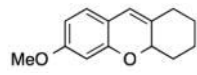
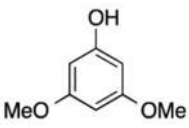
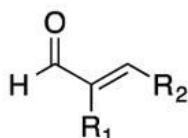
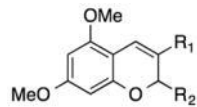
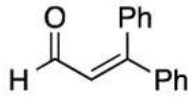
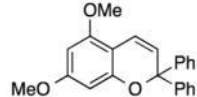
entry	phenol	aldehyde	product(s)	time yield (h) (%)
19		 X = H	 2s	8 48
20		X = F	 2t	8 35
21		 R = Et	 2u	8 47
22		R = Cy	 2v	8 40
23		R = 3-cyclohexenyl	 2w	12 33
24		R = CH(Me)Ph	 2x	12 61
25		R = Ph	 2y	20 35
26		R = Cy	 2z	20 38

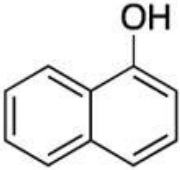
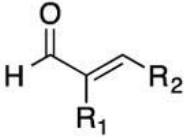

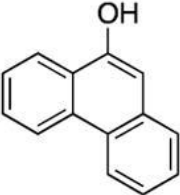
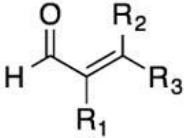
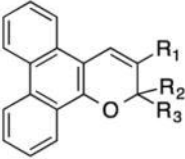
^[a]Reaction conditions: phenol (0.5 mmol), aldehyde (1.0 mmol), **1** (5 mol %), PPh₃ (20 mol %), K₂CO₃ (30 mol %), C₆H₅Cl (2–3 mL), 110 °C.

Flavonoids, a common group of polyphenol compounds in fruits and vegetables, have been shown to exhibit a wide range of pharmacological effects including anti-inflammatory, anti-aging and anticancer activities.^[13] To extend synthetic utility of the catalytic method, we next surveyed the coupling reaction of phenol substrates with α,β -unsaturated aldehydes to form flavonoid derivatives (Table 2). The coupling reaction of 3-methoxyphenol with both aliphatic and aryl-substituted enals smoothly occurred to give the substituted flavene derivatives (entries 1–6). A substantially higher product yield was obtained from the coupling of 3,5-dimethoxyphenol substrate with disubstituted enals (entries 7–12). The coupling with β -phenylcinnamaldehyde afforded the 2,2-disubstituted flavene product **3m** (entry 13). The analogous treatment of 1-naphthol and 9-phenanthrol with enals gave the corresponding polycyclic enol ether products **3n–3t** (entries 14–20). The formation of these flavene products **3** can be readily rationalized by *ortho*-C–H acylation followed by conjugate addition and dehydrative annulation sequences. The

structure of 2-acylphenol and flavene products **2** and **3** was completely established by standard spectroscopic methods. The solid-state structures of **2v** and **3t** were also determined by X-ray crystallography (Figures S3 and S4, SI). Recently, a number of intermolecular and intramolecular coupling and annulation catalytic methods have been reported to form flavene derivatives, but these typically require prefunctionalization of substrates and multiple reaction steps.^[14]

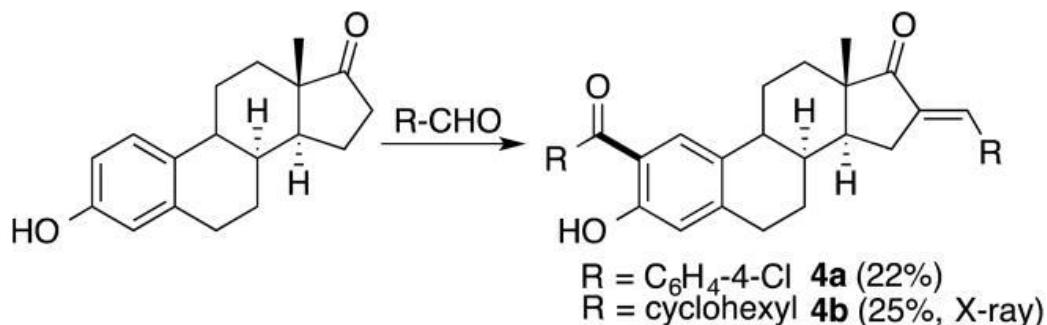
Table 2. Oxidative C–H Acylation and Dehydrative Annulation of Phenols with α,β -Unsaturated Aldehydes.^[a]

	phenol	aldehyde	product	temp (°C)	time (h)	yield (%)
1			 3a	110	24	37
						
2		R ₁ = H R ₂ = H	3b	130	16	23
3		R ₁ = Me R ₂ = H	3c	130	16	43
4		R ₁ = <i>n</i> -Hexyl R ₂ = H	3d	130	16	63
5		R ₁ = H R ₂ = Ph	3e	130	16	40
6			 3f	130	16	53
						
7		R ₁ = H R ₂ = <i>n</i> -Pr	3g	120	16	54
8		R ₁ = Me R ₂ = Et	3h	120	16	47
9		R ₁ = H R ₂ = Ph	3i	120	16	52
10		R ₁ = H R ₂ = 4-F-Ph	3j	120	16	55
11		R ₁ = Me R ₂ = Ph	3k	120	16	72
12		R ₁ = <i>n</i> -Hexyl R ₂ = Ph	3l	120	16	88
13				130	16	63

	phenol	aldehyde	product	temp (°C)	time (h)	yield (%)
						
14		R ₁ = H R ₂ = <i>n</i> -Pr	3n	100	20	40
15		R ₁ = H R ₂ = Ph	3o	130	12	46
16		R ₁ = Me R ₂ = Ph	3p	130	12	42
17		R ₁ = <i>n</i> -Hexyl R ₂ = Ph	3q	130	12	59
						
18		R ₁ = H R ₂ = H R ₃ = <i>n</i> -Pr	3r	120	16	71
19		R ₁ = Me R ₂ = H R ₃ = Ph	3s	120	16	60
20		R ₁ = H R ₂ = Ph R ₃ = Ph	3t	120	16	56

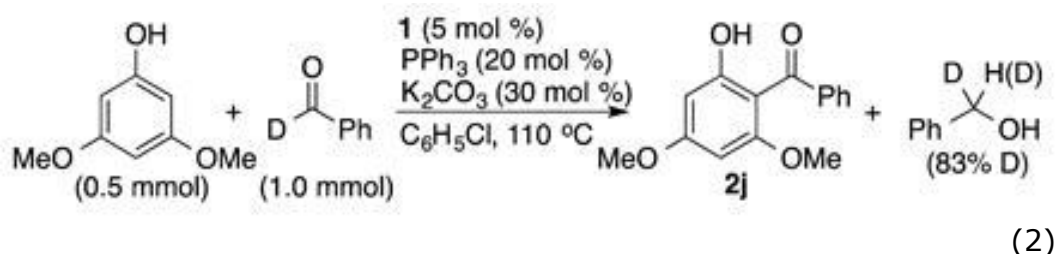
[^a]Reaction conditions: phenol (0.5 mmol), aldehyde (1.0 mmol), **1** (5 mol %), PPh₃ (20 mol %), C₆H₅Cl (2–3 mL).

The chemoselectivity of the coupling method has been explored by using bioactive phenol substrates ([Scheme 1](#)). For example, estrone reacted smoothly with both aliphatic and aryl-substituted aldehydes, 4-chlorobenzaldehyde and cyclohexanecarboxaldehyde, to give the 1:2 coupling products **4a** and **4b**, respectively. In this case, both arene C–H acylation and aldol-type couplings were occurred on the estrone substrate. Several attempts to form 1:1 coupling products were unsuccessful, as mixtures of both C–H acylation and aldol-type coupling products were resulted from using less than 1.5 equiv of aldehyde substrate. The structure of **4b**, as established by X-ray crystallography, clearly showed the (*E*)-enone configuration ([Figure S5, SI](#)).



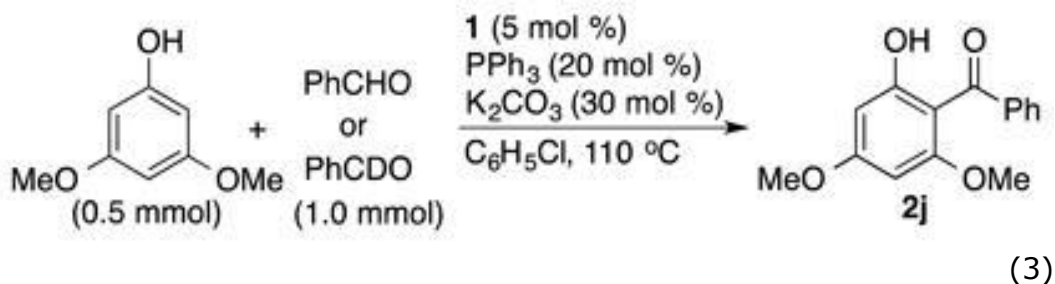
Scheme 1. Oxidative C-H Acylation and Aldol-Type Coupling of Estrone with Aldehydes.

We conducted the following preliminary experiments to gather mechanistic features. First, we examined the reaction of a phenol with a deuterium-labeled aldehyde to probe the possible H/D exchange pattern on both the phenol substrate and the products. The treatment of 3,5-dimethoxyphenol (0.5 mmol) with PhCDO (> 95% D, 1.0 mmol) in the presence of **1** (5 mol %), PPh₃ (20 mol %), and K₂CO₃ (30 mol %) in chlorobenzene (2 mL) was heated at 110 °C for 12 h, which led to 86 % conversion as analyzed by both GC-MS and NMR (eq 2). The ¹H and ²H NMR analysis showed exclusive deuterium incorporation on the benzyl position (83% D) of the isolated benzyl alcohol byproduct, but no deuterium incorporation was observed on either the starting material or the product **2j** (Figure S1, SI). The presence of mostly intact deuterium on α-CH₂ of benzyl alcohol byproduct suggests that the aldehyde substrate serves as both the hydrogen acceptor and the reagent for the coupling product.



To discern rate-limiting step of the coupling reaction, we next measured deuterium isotope effect of aldehyde substrate. Thus, the reaction rate of 3,5-dimethoxyphenol with PhCHO and PhCDO at 110 °C was measured separately (eq 3). The *k*_{obs} for each substrates was obtained from the first order plots of the formation of **2j**, which

led to a normal deuterium isotope effect of $k_H/k_D = 3.3 \pm 0.3$ (Figure S2, SI). The observation of a relatively high normal deuterium isotope effect is consistent with the rate-limiting aldehyde C–H activation step.



To probe electronic influence on the aldehyde substrate, we constructed a Hammett plot by comparing the rate of a series of 3,5-dimethoxyphenol with *para*-substituted benzaldehydes *p*-X-C₆H₄CHO (X = CH₃, H, F, Cl, CF₃). A linear correlation from the relative rate vs Hammett σ_p led to a positive ρ value of $+0.69 \pm 0.05$ (Figure 1). A strong promotional effect by the electron-withdrawing group suggests a substantial cationic character build-up on the carbonyl carbon in the transition state, which may be facilitated by the formation of Ru-acyl species. Similar Hammett ρ values have been observed in the catalytic coupling reactions of benzaldehyde and related arenes.^[15]

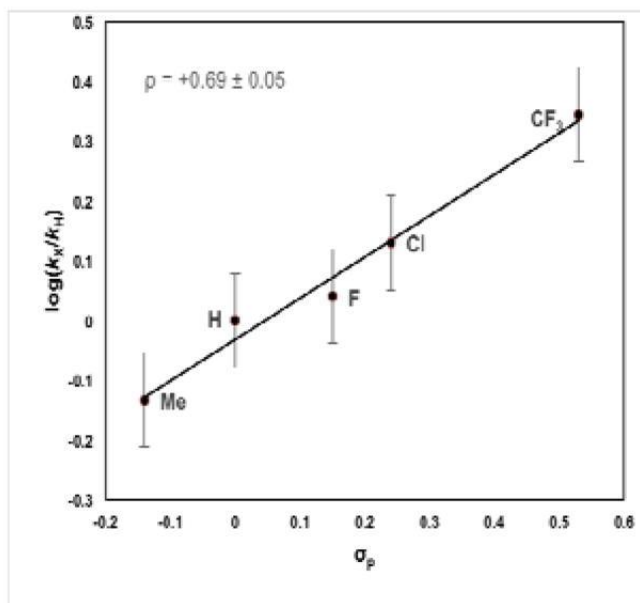
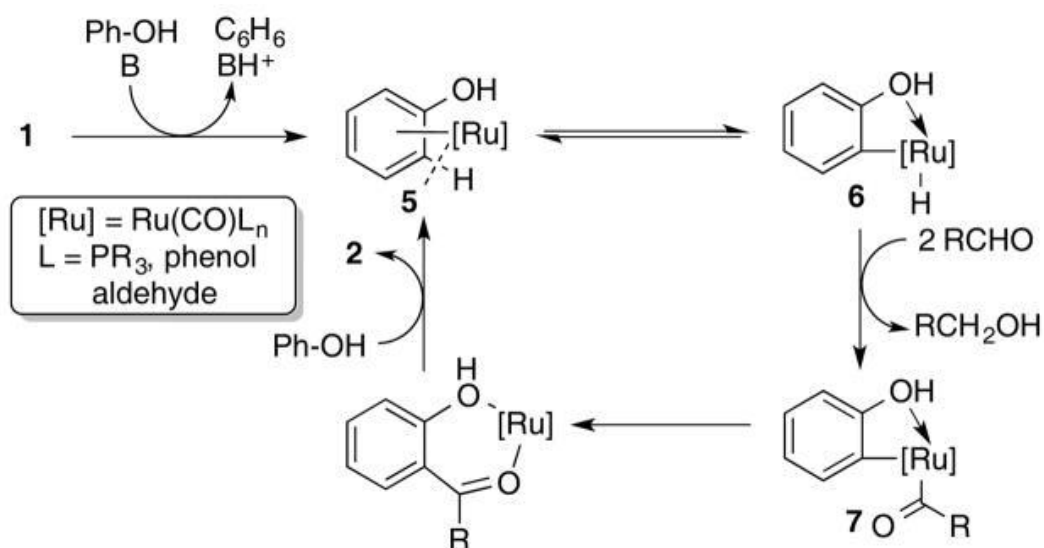


Figure 1. Hammett Plot from the Reaction of 3,5-Dimethoxyphenol with *p*-X-C₆H₄CHO (X = CH₃, H, F, Cl, CF₃).

On the basis of these results, we compile a plausible mechanistic repertoire for the oxidative C–H acylation reaction (Scheme 2). We propose that the initial displacement of benzene ligand with phenol substrate and deprotonation of Ru–H and would generate a catalytically active neutral Ru-arene species **5**. In support of this notion, we previously observed a facile arene exchange reaction of **1** at room temperature.^[16] The observed H/D exchange pattern on both the coupling product as well as the recovered benzyl alcohol byproduct suggests a facile *ortho*-C–H activation of the phenol substrate to form a metallated species **6**. Hydrogenation of the first equivalent of aldehyde, coupled with the C–H activation of second aldehyde substrate, can be envisioned to rationalize the formation of the Ru-acyl intermediate **7**. Both the deuterium isotope effect and Hammett studies signify that the aldehyde C–H activation is the turnover limiting step of the catalytic cycle. The subsequent reductive elimination of the coupling product **2** and the binding of another phenol substrate would complete the catalytic cycle.



Scheme 2. Mechanistic Hypothesis for the C–H Oxidative Acylation of Phenol with an Aldehyde.

In a concluding remark, we successfully devised an *ortho*-selective C–H acylation protocol for phenol substrates. The Ru catalytic system expedites the direct oxidative coupling of simple phenol and aldehyde substrates to give 2-acylphenol and flavene products without using any external oxidants or resorting to multistep synthetic

manipulations. Efforts to utilize the catalytic coupling method to synthesize bioactive flavene molecules are currently underway in our laboratory.

Experimental Section

General Procedure for the C-H Acylation of Phenol with Aldehyde

In a glove box, phenol (0.5 mmol), aldehyde (1.0 mmol), K₂CO₃ (30 mol %), PPh₃ (20 mol %) and complex **1** (14 mg, 5 mol %) were dissolved in chlorobenzene (2 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The tube was brought out of the glove box, and was stirred in an oil bath set at 110 °C for 8–16 h. The reaction tube was taken out of the oil bath, and was cooled to room temperature. After the tube was open to air, the solution was filtered through a short silica gel column by eluting with CH₂Cl₂ (10 mL), and the filtrate was analyzed by GC-MS. Analytically pure product was isolated by a simple column chromatography on silica gel (280–400 mesh, hexanes/EtOAc). The product was completely characterized by NMR and GC-MS spectroscopic methods.

Acknowledgments

Financial support from the US National Science Foundation (CHE-1358439) and National Institute of Health General Medical Sciences (R15 GM109273) is gratefully acknowledged. The authors thank Dr. Sergey Lindeman for the X-ray crystal structure determination of **2v**, **3t** and **4b**.

Footnotes

[Supporting information](#) for this article is given via a link at the end of the document.

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Supplementary Material

Table of Contents

1. General Information	S2
2. Experimental Procedure	S2
3. Catalyst Screening (Table S1)	S3
4. Deuterium Labeling Study (Figure S1)	S3
5. Deuterium Isotope Effect Study (Figure S2)	S4
6. Hammett Study	S5
7. X-Ray Crystallographic Determination of 2v , 3t and 4b (Figures S3-S5)	S6
8. Characterization Data of the Products	S8
9. ¹ H and ¹³ C NMR Spectra of the Products	S23
10. X-Ray Crystallographic Data of 2v , 3t and 4b (Tables S2-S24)	S71

1. General Information

All operations were carried out in a nitrogen-filled glove box or by using standard high vacuum and Schlenk techniques unless otherwise noted. Solvents were freshly distilled over appropriate drying reagents. Benzene, toluene, and hexanes were distilled from purple solutions of sodium and benzophenone, and dichloromethane was dried over calcium hydride prior to use. All organic substrates were received from commercial sources and were used without further purification. The ^1H , ^2H , ^{13}C , ^{19}F and ^{31}P NMR spectra were recorded on a Varian 300 or 400 MHz FT-NMR spectrometer, and the data are reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent; coupling constant(s) in Hz; integration. Mass spectra were recorded from Agilent 6850 GC-MS spectrometer with a HP-5 (5% phenylmethylpolysiloxane) column (30 m, 0.32 mm, 0.25 μm). High resolution mass spectra were obtained at the Mass Spectrometry/ICP Lab, Department of Chemistry and Biochemistry, University of Wisconsin Milwaukee, Milwaukee, WI and the Center of Mass Spectrometry, Washington University, St. Louis, MO. Elemental analyses were performed at the Midwest Microlab, Indianapolis, IN.

2. Experimental Procedure

General Procedure for the C-H Acylation of Phenol with Aldehyde. In a glove box, phenol (0.5 mmol), aldehyde (1.0 mmol), K_2CO_3 (30 mol %), PPh_3 (20 mol %) and complex **1** (14 mg, 5 mol %) were dissolved in chlorobenzene (2 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The tube was brought out of the glove box, and was stirred in an oil bath set at 110 °C for 8-16 h. The reaction tube was taken out of the oil bath, and was cooled to room temperature. After the tube was open to air, the solution was filtered through a short silica gel column by eluting with CH_2Cl_2 (10 mL), and the filtrate was analyzed by GC-MS. Analytically pure product was isolated by a simple column chromatography on silica gel (280-400 mesh, hexanes/EtOAc). The product was completely characterized by NMR and GC-MS spectroscopic methods.

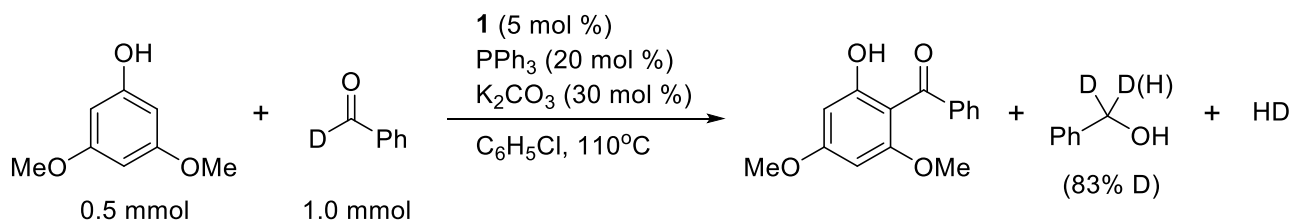
General Procedure for the C-H Acylation of Phenol with α,β -Unsaturated Aldehyde. In a glove box, phenol (0.5 mmol), α,β -unsaturated aldehyde (1.0 mmol), PPh_3 (20 mol %) and complex **1** (14 mg, 5 mol %) were dissolved in chlorobenzene (2 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The tube was brought out of the glove box, and was stirred in an oil bath set at 110-130 °C for 12-24 h. The reaction tube was taken out of the oil bath, and was cooled to room temperature. After the tube was open to air, the solution was filtered through a short silica gel column by eluting with CH_2Cl_2 (10 mL), and the filtrate was analyzed by GC-MS. Analytically pure product was isolated by a simple column chromatography on silica gel (280-400 mesh, hexanes/EtOAc). The product was completely characterized by NMR and GC-MS spectroscopic methods.

3. Catalyst Screening. In a glove box, 3-methoxyphenol (62 mg, 0.5 mmol), benzaldehyde (1.0 mmol), catalyst (5 mol %) and additive (20-30 mol %) were dissolved in chlorobenzene (2 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The tube was brought out of the glove box, and was stirred in an oil bath at 110 °C for 12 h. The reaction tube was cooled to room temperature, and the solvent was evaporated *in vacuo*. Hexamethylbenzene (16 mg, internal standard) was added to the reaction mixture, and the product yield was determined by ¹H NMR. The results are summarized in Table S1.

Table S1. Catalyst Screening for the Reaction of 3-Methoxyphenol with Benzaldehyde.^a

entry	catalyst	additive ^b	yield 2a (%) ^c
1	1	---	trace
2	1	cyclopentene	11
3	1	K ₂ CO ₃	34
4	1	PPh ₃	0
5	1	K₂CO₃, PPh₃	47
6	RuCl ₃ ·3H ₂ O	K ₂ CO ₃	0
7	RuCl ₃ ·3H ₂ O	K ₂ CO ₃ , PPh ₃	21
8	[RuH(CO)(PCy ₃) ₄ (O)(OH) ₂	K ₂ CO ₃ , PPh ₃	40
9	RuCl ₂ (PPh ₃) ₃	---	0
10	RuCl ₂ (PPh ₃) ₃	K ₂ CO ₃	28
11	[(<i>p</i> -cymene)RuCl ₂] ₂	K ₂ CO ₃	0
12	Ru ₃ (CO) ₁₂	K ₂ CO ₃	0
13	---	K ₂ CO ₃	0
14	---	PPh ₃	0

^a Reaction conditions: 3-methoxyphenol (0.5 mmol), benzaldehyde (1.0 mmol), additive, chlorobenzene (2 mL), catalyst (5 mol %), 110 °C, 12 h. ^b Amount of additives: cyclopentene (1.0 mmol), PPh₃ (20 mol %), K₂CO₃ (30 mol %). ^c The product yield of **2a** was determined by ¹H NMR using hexamethylbenzene as an internal standard.



4. Deuterium Labeling Study. In a glove box, 3,5-dimethoxyphenol (0.77 g, 5.0 mmol), benzaldehyde- α -*d*₁ (>95 % D, 1.0 mmol), K₂CO₃ (30 mol %), PPh₃ (20 mol %) and complex **1** (5 mol %) were dissolved in chlorobenzene (2 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock. The tube was brought out of the box, and immersed in an oil bath preset at 110 °C for 12 h. The reaction tube was taken out of the oil bath, and was cooled to room temperature. After the tube was open to air, the solution was filtered through a short silica gel column by eluting with CH₂Cl₂ (10 mL), and the filtrate was analyzed by GC-MS.

Analytically pure products and unreacted phenol substrate were isolated by a simple column chromatography on silica gel (280-400 mesh, hexanes/EtOAc = 100:1 to 1:1), and were completely characterized by ^1H and ^2H NMR and GC-MS spectroscopic methods. The result showed 83% deuterium incorporation on the $\alpha\text{-CH}_2$ of benzyl alcohol byproduct while no H/D exchange was observed on either the starting material or the product. The ^1H and ^2H NMR spectra of benzyl alcohol byproduct are shown in Figure S1.

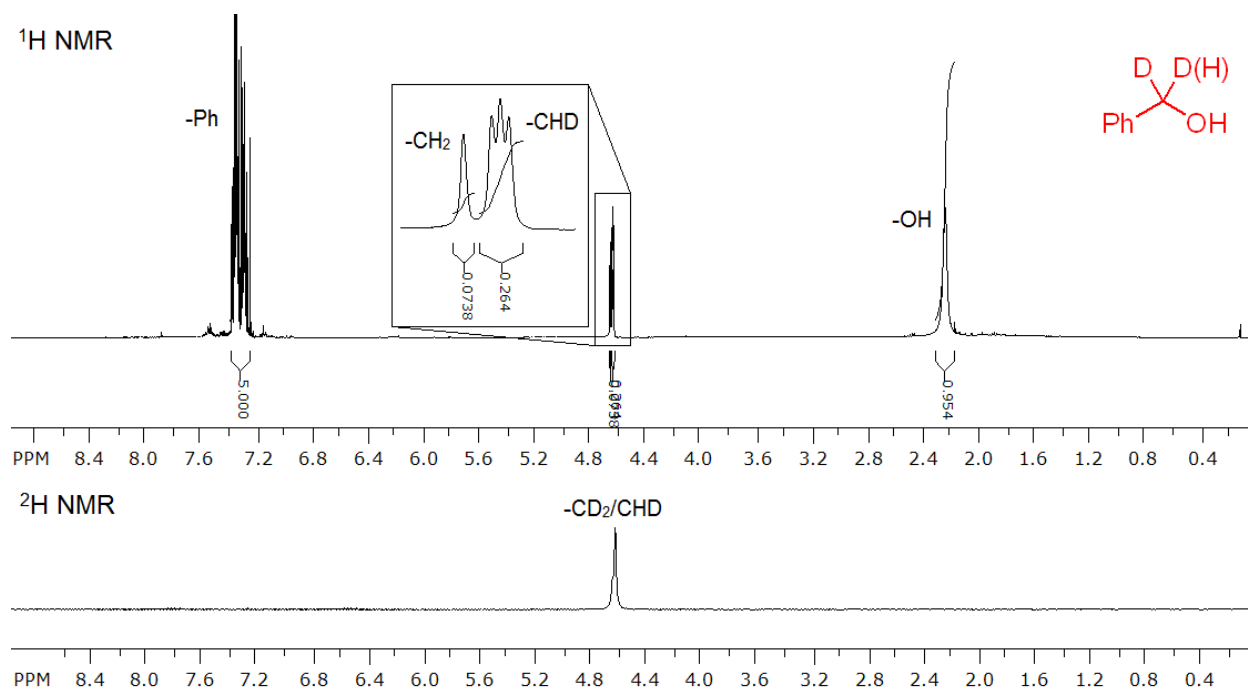


Figure S1. ^1H and ^2H NMR Spectra of Benzyl Alcohol Byproduct Isolated from the Reaction of 3,5-Dimethoxyphenol with Benzaldehyde- $\alpha\text{-d}_1$.

5. Deuterium Isotope Effect Study. In a glove box, 3,5-dimethoxyphenol (0.5 mmol), benzaldehyde- $\alpha\text{-d}_1$ (1.0 mmol), K_2CO_3 (30 mol %), PPh_3 (20 mol %) and complex **1** were dissolved in chlorobenzene (2 mL) in five separate 25 mL Schlenk tubes each equipped with a Teflon screw cap stopcock. The tubes were brought out of the box, and immersed in an oil bath preset at 110 $^\circ\text{C}$. The reaction rate was measured by monitoring the appearance of the product signals on ^1H NMR, which was normalized against the internal standard hexamethylbenzene in 20 min intervals for 100 min of the reaction time. The experiment was repeated by using benzaldehyde. The k_{obs} was determined from a first-order plot of $-\ln[(3,5\text{-dimethoxyphenol})_t/(3,5\text{-dimethoxyphenol})_0]$ vs time (Figure S2).

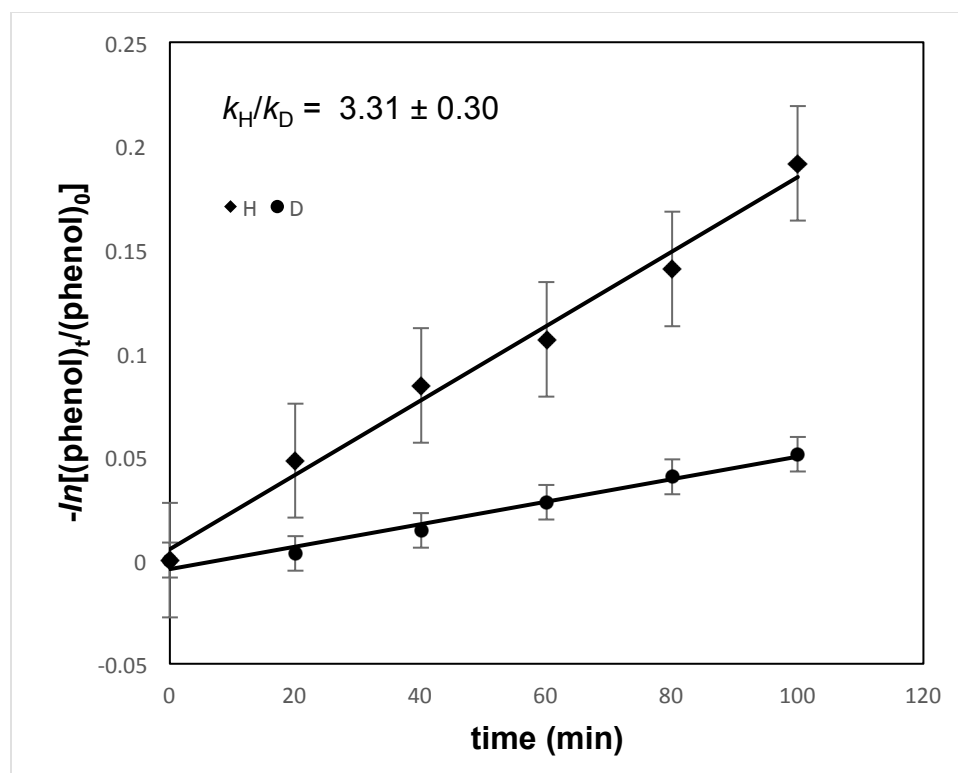
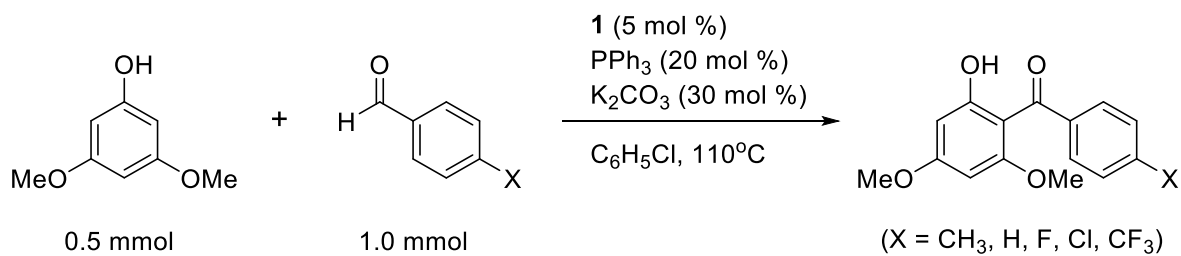


Figure S2. First Order Plots for the Reaction of 3,5-Dimethoxyphenol with Benzaldehyde and Benzaldehyde- α - d_1 .



6. Hammett Study. In a glove box, 3,5-dimethoxyphenol (0.5 mmol), p -X- C_6H_4CHO (1.0 mmol), K_2CO_3 (30 mol %), PPh_3 (20 mol %) and complex **1** were dissolved in chlorobenzene (2.0 mL) in five separate 25 mL Schlenk tubes each equipped with a Teflon screw cap stopcock. The tubes were brought out of the box, and immersed in an oil bath preset at $110^\circ C$. The reaction rate was measured by monitoring the appearance of the product signals on 1H NMR, which was normalized against the internal standard hexamethylbenzene peak in 20 min intervals for 100 min of the reaction time. The k_{obs} was determined from a first-order plot of $-\ln[(3,5\text{-dimethoxyphenol})_t/(3,5\text{-dimethoxyphenol})_0]$ vs time. The Hammett plot of $\log(k_X/k_H)$ vs σ_p is shown in the main text (Figure 1).

7. X-Ray Crystallographic Determination of 2v, 3t and 4b.

For **2v**: Colorless single crystals of **2v** were grown in CH₂Cl₂ at room temperature. A suitable crystal with the dimension of 0.28 × 0.14 × 0.11 mm³ was selected and mounted on an Oxford SuperNova diffractometer equipped with dual microfocus Cu/Mo X-ray sources, X-ray mirror optics, and Atlas CCD area detector. A total of 15224 reflection data were collected by using MoK α ($\lambda = 0.71073$) radiation while the crystal sample was cooled at 100.05 K during the data collection. Using Olex2, the molecular structure was solved with the ShelXS structure solution program by using Direct Methods, and the data were refined with the XL refinement package using Least Squares minimization. The molecular structure of **2v** is shown in Figure S3.

For **3t**: Colorless single crystals of **3t** were grown in CH₂Cl₂ at room temperature. A suitable crystal with the dimension of 0.42 × 0.35 × 0.18 mm³ was selected and mounted on an Oxford SuperNova diffractometer equipped with dual microfocus Cu/Mo X-ray sources, X-ray mirror optics, and Atlas CCD area detector. A total of 18380 reflection data were collected by using CuK α ($\lambda = 1.54184$) radiation while the crystal sample was cooled at 100.00 K during the data collection. Using Olex2, the molecular structure was solved with the ShelXS structure solution program by using Direct Methods, and the data were refined with the XL refinement package using Least Squares minimization. The molecular structure of **3t** is shown in Figure S4.

For **4b**: Colorless single crystals of **4b** were grown in CH₂Cl₂/hexanes at room temperature. A suitable crystal with the dimension of 0.18 × 0.14 × 0.02 mm³ was selected and mounted on an Oxford SuperNova diffractometer equipped with dual microfocus Cu/Mo X-ray sources, X-ray mirror optics, and Atlas CCD area detector. A total of 11892 reflection data were collected by using CuK α ($\lambda = 1.54184$) radiation while the crystal sample was cooled at 99.8 K during the data collection. Using Olex2, the molecular structure was solved with the ShelXS structure solution program by using Direct Methods, and the data were refined with the XL refinement package using Least Squares minimization. The molecular structure of **4b** is shown in Figure S5.

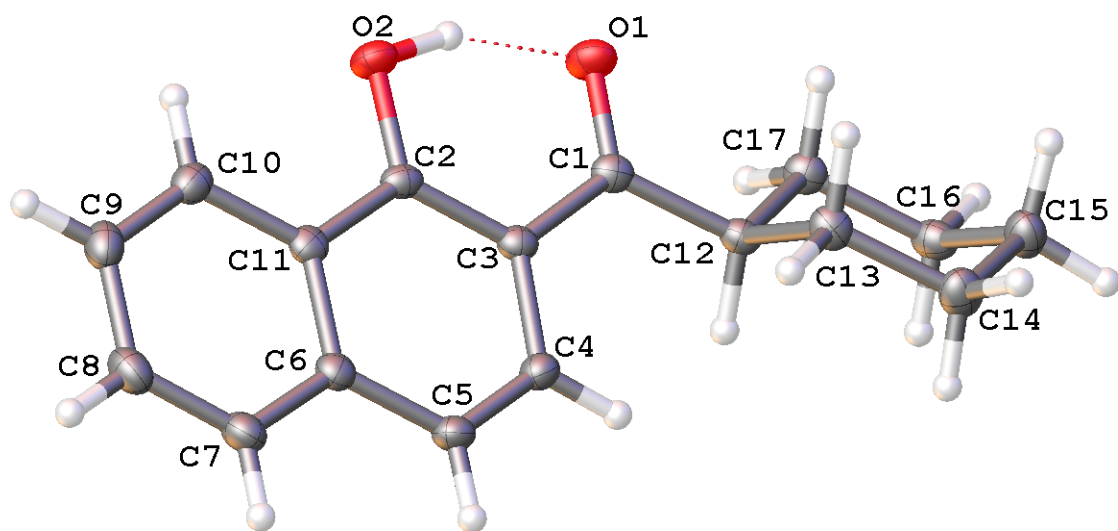


Figure S3. Molecular Structure of **2v**.

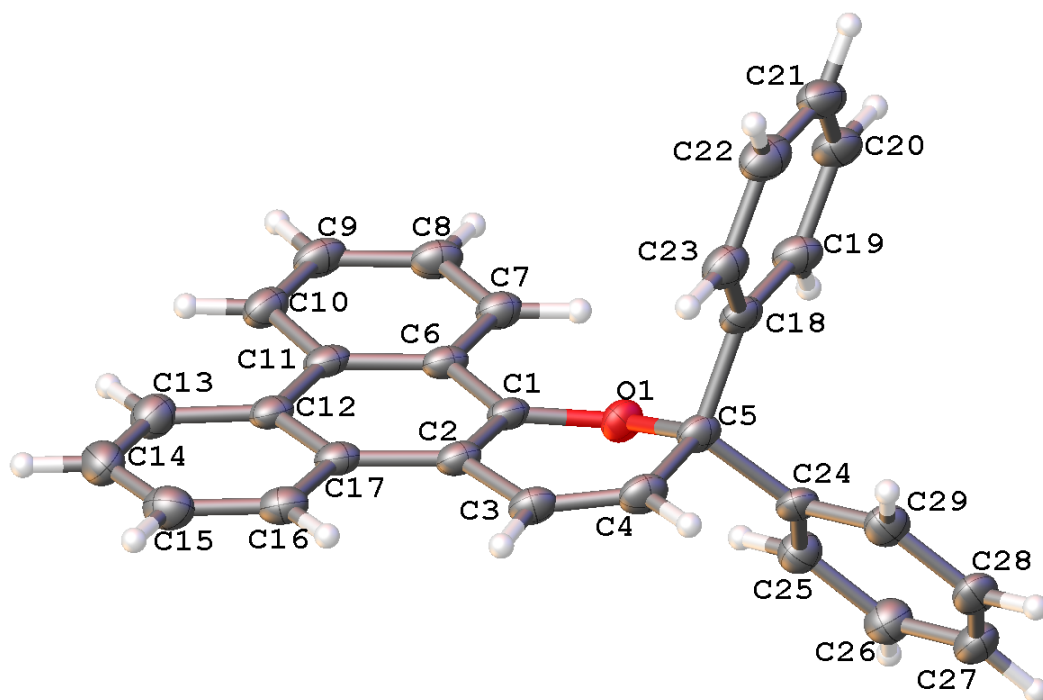


Figure S4. Molecular Structure of **3t**.

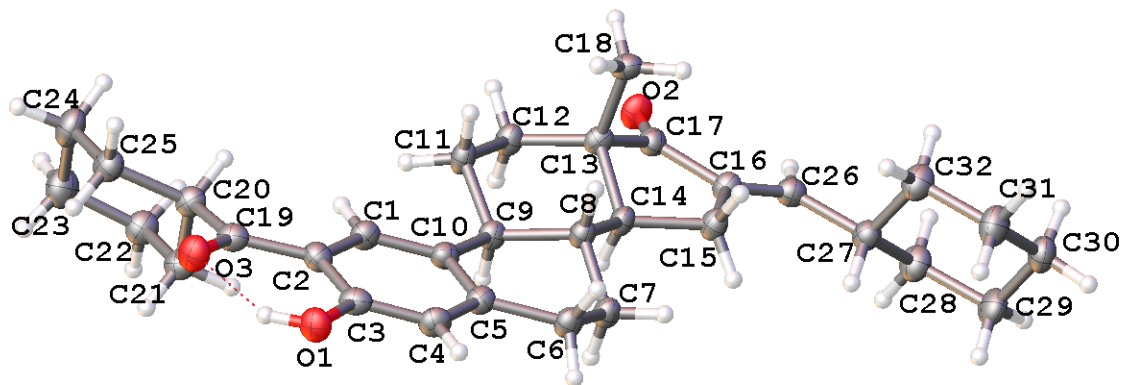


Figure S5. Molecular Structure of **4b**.

8. Characterization Data of the Products

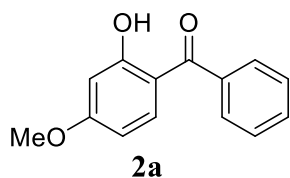


Table 1, compound 2a. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3-methoxyphenol (62 mg, 0.5 mmol), and benzaldehyde (106 mg, 1.0 mmol) was stirred at 110 °C for 12 h. The product **2a** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 54 mg, 47 %. Data for **2a**: ¹H NMR (400 MHz, CDCl₃) δ 12.70 (s, 1H), 7.65-7.62 (m, 2H), 7.59-7.54 (m, 1H), 7.52-7.47 (m, 2H), 7.50 (d, *J* = 9.0 Hz, 1H), 6.52 (d, *J* = 2.5 Hz, 1H), 6.41 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.86 (s, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 200.0, 166.3, 166.2, 138.2, 135.2, 131.4, 128.8, 128.3, 113.1, 107.4, 101.0, 55.6 ppm; GC-MS *m/z* = 228 (M⁺); Anal. Calcd for C₁₄H₁₂O₃: C, 73.67; H, 5.30. Found: C, 73.56; H, 5.25.

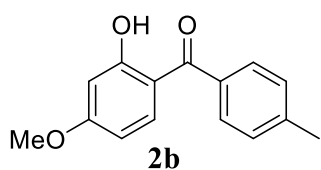


Table 1, compound 2b. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3-methoxyphenol (62 mg, 0.5 mmol), and *p*-tolualdehyde (120 mg, 1.0 mmol) was stirred at 110 °C for 12 h. The product **2b** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 52 mg, 43 %. Data for **2b**: ¹H NMR (400 MHz, CDCl₃) δ 12.73 (s, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.9 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.52 (d, *J* = 2.5 Hz, 1H), 6.41 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.86 (s, 3H), 2.44 (s, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 199.8, 166.2, 166.0, 142.1, 135.5, 135.2, 129.1, 128.9, 113.2, 107.2, 101.0, 55.6, 21.5 ppm; GC-MS *m/z* = 242 (M⁺); Anal. Calcd for C₁₅H₁₄O₃: C, 74.36; H, 5.82. Found: C, 74.29; H, 5.94.

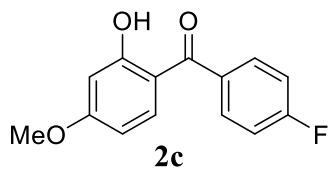


Table 1, compound 2c. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3-methoxyphenol (62 mg, 0.5 mmol), and 4-fluorobenzaldehyde (124 mg, 1.0 mmol) was stirred at 110 °C for 12 h. The product **2c** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 65 mg, 53 %. Data for **2c**: ¹H NMR (400 MHz, CDCl₃) δ 12.58 (s, 1H), 7.69-7.64 (m, 2H), 7.47 (d, *J* = 9.0 Hz, 1H), 7.20-7.14 (m, 2H), 6.52 (d, *J* = 2.5 Hz, 1H), 6.42 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.86 (s, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 198.4, 166.3, 166.2, 164.7 (d, *J*_{CF} = 252.7 Hz), 134.9, 134.4 (d, *J*_{CF} = 3.4 Hz), 131.4 (d, *J*_{CF} = 9.0 Hz), 115.5 (d, *J*_{CF} = 21.7 Hz), 112.9, 107.5, 101.1, 55.6 ppm; GC-MS *m/z* = 246 (M⁺); Anal. Calcd for C₁₄H₁₁FO₃: C, 68.29; H, 4.50. Found: C, 68.23; H, 4.47.

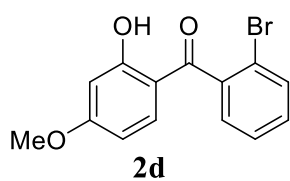


Table 1, compound 2d. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3-methoxyphenol (62 mg, 0.5 mmol), and 2-bromobenzaldehyde (185 mg, 1.0 mmol) was stirred at 110 °C for 12 h. The product **2d** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 89 mg, 58 %. Data for **2d**: ¹H NMR (400

MHz, CDCl₃) δ 12.45 (s, 1H), 7.64 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.41 (td, $J = 7.4, 1.2$ Hz, 1H), 7.34 (td, $J = 7.9, 1.8$ Hz, 1H), 7.30 (dd, $J = 7.4, 1.8$ Hz, 1H), 7.10 (d, $J = 9.0$ Hz, 1H), 6.50 (d, $J = 2.5$ Hz, 1H), 6.36 (dd, $J = 9.0, 2.5$ Hz, 1H), 3.84 (s, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 199.0, 166.8, 166.1, 139.5, 135.1, 133.0, 131.0, 128.4, 127.2, 119.1, 113.2, 108.0, 100.8, 55.6 ppm; GC-MS $m/z = 306$ (M⁺); Anal. Calcd for C₁₄H₁₁BrO₃: C, 54.75; H, 3.61. Found: C, 54.68; H, 3.70.

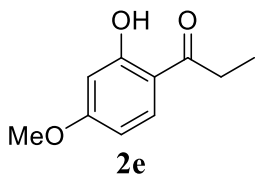


Table 1, compound 2e. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3-methoxyphenol (62 mg, 0.5 mmol), and propionaldehyde (58 mg, 1.0 mmol) was stirred at 110 °C for 12 h. The product **2e** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 50 mg, 56 %. Data for **2e**: ¹H NMR (400 MHz, CDCl₃) δ 12.83 (s, 1H), 7.64 (d, $J = 10.5$ Hz, 1H), 6.42 (dd, $J = 10.5, 2.5$ Hz, 1H), 6.40 (d, $J = 2.5$ Hz, 1H), 3.81 (s, 3H), 2.93 (q, $J = 7.3$ Hz, 2H), 1.21 (t, $J = 7.3$ Hz, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 205.3, 165.7, 165.1, 131.3, 113.2, 107.4, 100.8, 55.4, 31.0, 8.4 ppm; GC-MS $m/z = 180$ (M⁺); Anal. Calcd for C₁₀H₁₂O₃: C, 66.65; H, 6.71. Found: C, 66.57; H, 6.68.

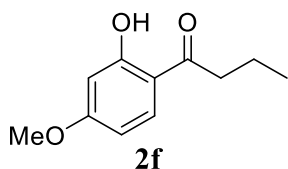


Table 1, compound 2f. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3-methoxyphenol (62 mg, 0.5 mmol), and butyraldehyde (72 mg, 1.0 mmol) was stirred at 110 °C for 12 h. The product **2f** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 43 mg, 44 %. Data for **2f**: ¹H NMR (400 MHz, CDCl₃) δ 12.91 (s, 1H), 7.66 (d, $J = 9.2$ Hz, 1H), 6.44 (dd, $J = 9.2, 2.5$ Hz, 1H), 6.42 (d, $J = 2.5$ Hz, 1H), 3.84 (s, 3H), 2.88 (t, $J = 7.4$ Hz, 2H), 1.76 (sextet, $J = 7.4$ Hz, 2H), 1.01 (t, $J = 7.4$ Hz, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 205.0, 165.9, 165.4, 131.6, 113.5, 107.5, 100.9, 55.5, 39.8, 18.2, 13.9 ppm; GC-MS $m/z = 194$ (M⁺); Anal. Calcd for C₁₁H₁₄O₃: C, 68.02; H, 7.27. Found: C, 67.81; H, 7.19.

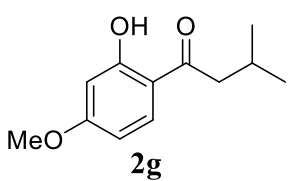


Table 1, compound 2g. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3-methoxyphenol (62 mg, 0.5 mmol), and isovaleraldehyde (86 mg, 1.0 mmol) was stirred at 110 °C for 12 h. The product **2g** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 60 mg, 58 %. Data for **2g**: ¹H NMR (400 MHz, CDCl₃) δ 12.99 (s, 1H), 7.63 (d, $J = 9.3$ Hz, 1H), 6.41 (dd, $J = 9.3, 2.5$ Hz, 1H), 6.40 (d, $J = 2.5$ Hz, 1H), 3.81 (s, 3H), 2.74 (d, $J = 6.9$ Hz, 2H), 2.25 (m, 1H), 0.99 (d, $J = 6.7$ Hz, 6H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 204.8, 165.8, 165.5, 131.7, 113.7, 107.4, 100.8, 55.5, 46.7, 25.8, 22.7 ppm; GC-MS $m/z = 208$ (M⁺); Anal. Calcd for C₁₂H₁₆O₃: C, 69.21; H, 7.74. Found: C, 69.08; H, 7.59.

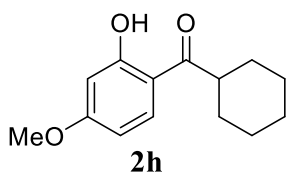


Table 1, compound 2h. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3-methoxyphenol (62 mg, 0.5 mmol), and cyclohexanecarboxaldehyde (112 mg, 1.0 mmol) was stirred at 110 °C for 12 h. The product **2h** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 58 mg, 50 %. Data for **2h**: ¹H NMR (400 MHz, CDCl₃) δ 13.10 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 6.44 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.42 (d, *J* = 2.4 Hz, 1H), 3.83 (s, 3H), 3.19 (tt, *J* = 11.6, 2.9 Hz, 1H), 1.90-1.17 (m, 10H) ppm; ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 208.3, 166.0, 165.8, 131.3, 112.3, 107.5, 101.1, 55.5, 45.0, 29.6, 25.8, 25.8 ppm; GC-MS *m/z* = 234 (M⁺); Anal. Calcd for C₁₄H₁₈O₃: C, 71.77; H, 7.74. Found: C, 71.53; H, 7.58.

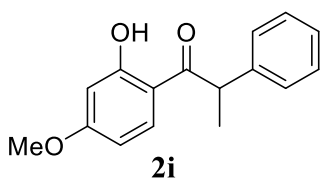


Table 1, compound 2i. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3-methoxyphenol (62 mg, 0.5 mmol), and 2-phenylpropionaldehyde (134 mg, 1.0 mmol) was stirred at 110 °C for 12 h. The product **2i** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 86 mg, 67 %.

Data for **2i**: ¹H NMR (400 MHz, CDCl₃) δ 12.99 (s, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.35-7.21 (m, 5H), 6.42 (d, *J* = 2.5 Hz, 1H), 6.37 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.66 (q, *J* = 6.9 Hz, 1H), 3.78 (s, 3H), 1.56 (d, *J* = 6.9 Hz, 3H) ppm; ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 204.6, 166.1, 166.1, 141.5, 132.0, 129.0, 127.5, 127.1, 107.6, 101.0, 101.0, 55.5, 46.9, 19.2 ppm; GC-MS *m/z* = 256 (M⁺); Anal. Calcd for C₁₆H₁₆O₃: C, 74.98; H, 6.29. Found: C, 74.82; H, 6.16.

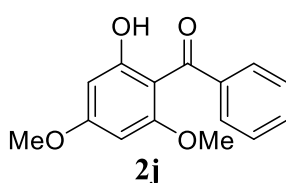


Table 1, compound 2j. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3,5-dimethoxyphenol (77 mg, 0.5 mmol), and benzaldehyde (106 mg, 1.0 mmol) was stirred at 110 °C for 16 h. The product **2j** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 84 mg, 65 %.

Data for **2j**: ¹H NMR (400 MHz, CDCl₃) δ 12.27 (s, 1H), 7.54-7.51 (m, 2H), 7.48-7.44 (m, 1H), 7.41-7.36 (m, 2H), 6.17 (d, *J* = 2.3 Hz, 1H), 5.92 (d, *J* = 2.3 Hz, 1H), 3.85 (s, 3H), 3.45 (s, 3H) ppm; ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 199.1, 166.4, 166.0, 161.9, 141.7, 130.8, 127.8, 127.5, 105.6, 93.6, 91.3, 55.6, 55.1 ppm; GC-MS *m/z* = 258 (M⁺); Anal. Calcd for C₁₅H₁₄O₄: C, 69.76; H, 5.46. Found: C, 69.44; H, 5.44.

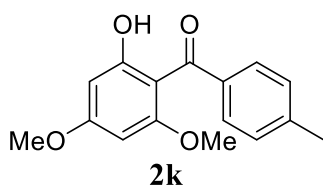


Table 1, compound 2k. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3,5-dimethoxyphenol (77 mg, 0.5 mmol), and *p*-tolualdehyde (120 mg, 1.0 mmol) was stirred at 110 °C for 16 h. The product **2k** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 69 mg, 51 %.

Data for **2k**: ¹H NMR (400 MHz, CDCl₃) δ 12.11 (s, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.18 (m, *J* = 8.1 Hz, 2H), 6.16 (d, *J* = 2.3 Hz, 1H), 5.94

(d, $J = 2.3$ Hz, 1H), 3.85 (s, 3H), 3.48 (s, 3H), 2.40 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 198.7, 166.1, 165.6, 161.8, 141.6, 138.7, 128.3, 128.2, 105.7, 93.6, 91.3, 55.6, 55.1, 21.6 ppm; GC-MS $m/z = 272$ (M^+); Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_4$: C, 70.58; H, 5.92. Found: C, 70.57; H, 5.95.

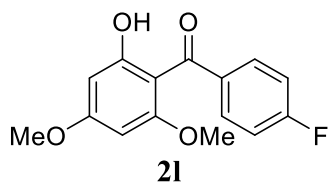


Table 1, compound 2l. A $\text{C}_6\text{H}_5\text{Cl}$ (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3,5-dimethoxyphenol (77 mg, 0.5 mmol), and 4-fluorobenzaldehyde (124 mg, 1.0 mmol) was stirred at 110 °C for 16 h. The product **2l** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 101 mg, 73 %. Data for **2l**: ^1H NMR (400 MHz, CDCl_3) δ 12.09 (s, 1H), 7.58-7.53 (m, 2H), 7.09-7.03 (m, 2H), 6.16 (d, $J = 2.3$ Hz, 1H), 5.93 (d, $J = 2.3$ Hz, 1H), 3.85 (s, 3H), 3.48 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 197.4, 166.4, 165.8, 164.4 (d, $J_{\text{CF}} = 251.8$ Hz), 161.7, 137.7 (d, $J_{\text{CF}} = 3.5$ Hz), 130.4 (d, $J_{\text{CF}} = 9.0$ Hz), 114.5 (d, $J_{\text{CF}} = 21.9$ Hz), 105.4, 93.7, 91.3, 55.7, 55.1 ppm; GC-MS $m/z = 276$ (M^+); Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{FO}_4$: C, 65.21; H, 4.74. Found: C, 65.17; H, 4.76.

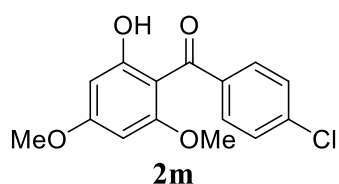


Table 1, compound 2m. A $\text{C}_6\text{H}_5\text{Cl}$ (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3,5-dimethoxyphenol (77 mg, 0.5 mmol), and 4-chlorobenzaldehyde (140 mg, 1.0 mmol) was stirred at 110 °C for 16 h. The product **2m** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 102 mg, 70 %. Data for **2m**: ^1H NMR (400 MHz, CDCl_3) δ 12.17 (s, 1H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H), 6.16 (d, $J = 2.3$ Hz, 1H), 5.92 (d, $J = 2.3$ Hz, 1H), 3.85 (s, 3H), 3.48 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 197.6, 166.6, 166.0, 161.7, 140.0, 136.9, 129.3, 127.8, 105.3, 93.7, 91.3, 55.6, 55.1 ppm; GC-MS $m/z = 292$ (M^+); Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{ClO}_4$: C, 61.55; H, 4.48. Found: C, 61.20; H, 4.34.

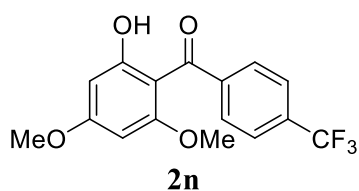


Table 1, compound 2n. A $\text{C}_6\text{H}_5\text{Cl}$ (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3,5-dimethoxyphenol (77 mg, 0.5 mmol), and 4-(trifluoromethyl)benzaldehyde (174 mg, 1.0 mmol) was stirred at 110 °C for 16 h. The product **2n** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 121 mg, 74 %. Data for **2n**: ^1H NMR (400 MHz, CDCl_3) δ 12.41 (s, 1H), 7.65 (d, $J = 8.1$ Hz, 2H), 7.58 (d, $J = 8.1$ Hz, 2H), 6.16 (d, $J = 2.3$ Hz, 1H), 5.91 (d, $J = 2.3$ Hz, 1H), 3.85 (s, 3H), 3.42 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 197.8, 167.1, 166.6, 161.9, 145.3 (q, $J_{\text{CF}} = 1.2$ Hz), 131.9 (q, $J_{\text{CF}} = 32.4$ Hz), 127.6, 124.5 (q, $J_{\text{CF}} = 3.8$ Hz), 123.8 (q, $J_{\text{CF}} = 272.6$ Hz), 105.2, 93.7, 91.3, 55.7, 55.0 ppm; GC-MS $m/z = 326$ (M^+); Anal. Calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{O}_4$: C, 58.90; H, 4.02. Found: C, 58.81; H, 3.94.

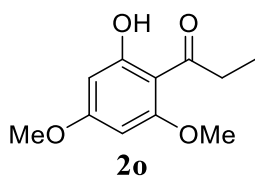


Table 1, compound 2o. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3,5-dimethoxyphenol (77 mg, 0.5 mmol), and propionaldehyde (58 mg, 1.0 mmol) was stirred at 110 °C for 8 h. The product **2o** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 78 mg, 74 %. Data for **2o**: ¹H NMR (400 MHz, CDCl₃) δ 14.10 (s, 1H), 6.04 (d, *J* = 2.3 Hz, 1H), 5.90 (d, *J* = 2.3 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.00 (q, *J* = 7.2 Hz, 2H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 206.3, 167.4, 165.7, 162.7, 105.6, 93.5, 90.6, 55.4, 55.4, 37.3, 8.5 ppm; GC-MS *m/z* = 210 (M⁺); Anal. Calcd for C₁₁H₁₄O₄: C, 62.85; H, 6.71. Found: C, 62.45; H, 6.66.

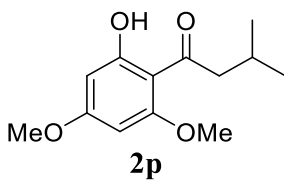


Table 1, compound 2p. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3,5-dimethoxyphenol (77 mg, 0.5 mmol), and isovaleraldehyde (86 mg, 1.0 mmol) was stirred at 110 °C for 12 h. The product **2p** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 82 mg, 69 %. Data for **2p**: ¹H NMR (400 MHz, CDCl₃) δ 14.15 (s, 1H), 6.04 (d, *J* = 2.4 Hz, 1H), 5.89 (d, *J* = 2.4 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.83 (d, *J* = 6.7 Hz, 2H), 2.18 (nonet, *J* = 6.7 Hz, 1H), 0.95 (d, *J* = 6.7 Hz, 6H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 205.5, 167.7, 165.7, 162.5, 105.8, 93.6, 90.7, 55.4, 55.4, 53.0, 25.2, 22.8 ppm; GC-MS *m/z* = 238 (M⁺); Anal. Calcd for C₁₃H₁₈O₄: C, 65.53; H, 7.61. Found: C, 65.59; H, 7.62.

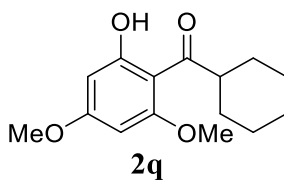


Table 1, compound 2q. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3,5-dimethoxyphenol (77 mg, 0.5 mmol), and cyclohexanecarboxaldehyde (112 mg, 1.0 mmol) was stirred at 110 °C for 12 h. The product **2q** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 94 mg, 71 %. Data for **2q**: ¹H NMR (400 MHz, CDCl₃) δ 14.14 (s, 1H), 6.04 (d, *J* = 2.4 Hz, 1H), 5.90 (d, *J* = 2.4 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.43 (tt, *J* = 11.0, 2.9 Hz, 1H), 1.89-1.78 (m, 4H), 1.73-1.67 (m, 1H), 1.45-1.19 (m, 5H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 209.2, 167.9, 165.6, 162.3, 105.1, 93.7, 90.8, 55.6, 55.4, 50.0, 29.4, 26.2, 26.1 ppm; GC-MS *m/z* = 264 (M⁺); Anal. Calcd for C₁₅H₂₀O₄: C, 68.16; H, 7.63. Found: C, 67.86; H, 7.46.

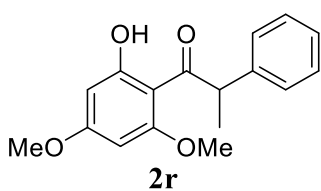


Table 1, compound 2r. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 3,5-dimethoxyphenol (77 mg, 0.5 mmol), and 2-phenylpropionaldehyde (134 mg, 1.0 mmol) was stirred at 110 °C for 12 h. The product **2r** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 10:1). Yield: 112 mg, 78 %. Data for **2r**: ¹H NMR (400 MHz, CDCl₃) δ 14.07 (s, 1H), 7.32-7.24 (m, 4H), 7.22-7.18 (m, 1H), 6.06 (d, *J* = 2.4 Hz, 1H), 5.84 (d, *J* = 2.4

Hz, 1H), 5.00 (q, $J = 6.9$ Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 1.49 (d, $J = 6.9$ Hz, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 205.8, 168.0, 165.9, 162.1, 142.4, 128.3, 127.7, 126.3, 105.4, 93.6, 90.8, 55.4, 55.1, 50.8, 19.7 ppm; GC-MS $m/z = 286$ (M^+); Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_4$: C, 71.31; H, 6.34. Found: C, 71.26; H, 6.34.

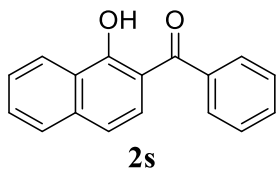


Table 1, compound 2s. A $\text{C}_6\text{H}_5\text{Cl}$ (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 1-naphthol (72 mg, 0.5 mmol), and benzaldehyde (106 mg, 1.0 mmol) was stirred at 110°C for 8 h. The product **2s** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 40:1). Yield: 60 mg, 48 %. Data for **2s**: ^1H NMR (400 MHz, CDCl_3) δ 13.96 (s, 1H), 8.55-8.52 (m, 1H), 7.80-7.76 (m, 1H), 7.74-7.71 (m, 2H), 7.69-7.64 (m, 1H), 7.63-7.51 (m, 5H), 7.23 (d, $J = 8.8$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 201.4, 163.9, 138.2, 137.3, 131.6, 130.4, 129.1, 128.3, 127.4, 127.3, 126.0, 125.3, 124.5, 117.8, 112.5 ppm; GC-MS $m/z = 248$ (M^+); Anal. Calcd for $\text{C}_{17}\text{H}_{12}\text{O}_2$: C, 82.24; H, 4.87. Found: C, 82.01; H, 4.89.

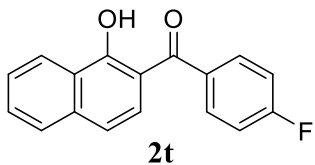


Table 1, compound 2t. A $\text{C}_6\text{H}_5\text{Cl}$ (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 1-naphthol (72 mg, 0.5 mmol), and 4-fluorobenzaldehyde (124 mg, 1.0 mmol) was stirred at 110°C for 8 h. The product **2t** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 40:1). Yield: 47 mg, 35 %. Data for **2t**: ^1H NMR (400 MHz, CDCl_3) δ 13.84 (s, 1H), 8.54-8.51 (m, 1H), 7.79-7.74 (m, 3H), 7.69-7.64 (m, 1H), 7.59-7.55 (m, 1H), 7.52 (d, $J = 8.9$ Hz, 1H), 7.26-7.19 (m, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 199.8, 164.8 (d, $J_{\text{CF}} = 253.4$ Hz), 163.9, 137.3, 134.3 (d, $J_{\text{CF}} = 3.3$ Hz), 131.7 (d, $J_{\text{CF}} = 9.0$ Hz), 130.4, 127.4, 127.0, 126.1, 125.2, 124.5, 118.0, 115.5 (d, $J_{\text{CF}} = 22.0$ Hz), 112.4 ppm; GC-MS $m/z = 266$ (M^+); Anal. Calcd for $\text{C}_{17}\text{H}_{11}\text{FO}_2$: C, 76.68; H, 4.16. Found: C, 76.46; H, 4.36.

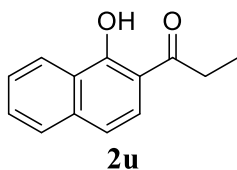


Table 1, compound 2u. A $\text{C}_6\text{H}_5\text{Cl}$ (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 1-naphthol (72 mg, 0.5 mmol), and propionaldehyde (58 mg, 1.0 mmol) was stirred at 110°C for 8 h. The product **2u** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 40:1). Yield: 47 mg, 47 %. Data for **2u**: ^1H NMR (400 MHz, CDCl_3) δ 14.09 (s, 1H), 8.46 (dd, $J = 8.3, 1.3$ Hz, 1H), 7.75 (d, $J = 8.1$ Hz, 1H), 7.67 (d, $J = 8.9$ Hz, 1H), 7.62 (ddd, $J = 8.1, 6.9, 1.3$ Hz, 1H), 7.52 (ddd, $J = 8.3, 6.9, 1.2$ Hz, 1H), 7.26 (d, $J = 8.9$ Hz, 1H) 3.10 (q, $J = 7.3$ Hz, 2H), 1.29 (t, $J = 7.3$ Hz, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 206.9, 162.3, 137.2, 129.9, 127.3, 125.8, 125.3, 124.4, 124.2, 118.2, 112.7, 31.9, 8.2 ppm; GC-MS $m/z = 200$ (M^+); Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2$: C, 77.98; H, 6.04. Found: C, 78.16; H, 6.05.

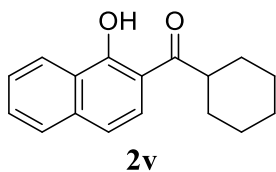


Table 1, compound 2v. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 1-naphthol (72 mg, 0.5 mmol), and cyclohexanecarboxaldehyde (112 mg, 1.0 mmol) was stirred at 110 °C for 8 h. The product **2v** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 40:1). Yield: 51 mg, 40 %. Data for **2v**: ¹H NMR (400 MHz, CDCl₃) δ 14.40 (s, 1H), 8.47 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.62 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.52 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.26 (d, *J* = 8.9 Hz, 1H), 3.35 (tt, *J* = 11.4, 3.1 Hz, 1H), 1.99-1.86 (m, 4H), 1.82-1.75 (m, 1H), 1.65-1.54 (m, 2H), 1.50-1.38 (m, 2H), 1.36-1.25 (m, 1H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 209.8, 163.3, 137.2, 129.9, 127.3, 125.8, 125.6, 124.4, 124.2, 118.0, 111.8, 45.3, 29.4, 25.9, 25.8 ppm; GC-MS *m/z* = 254 (M⁺); Anal. Calcd for C₁₇H₁₈O₂: C, 80.28; H, 7.13. Found: C, 80.22; H, 7.15.

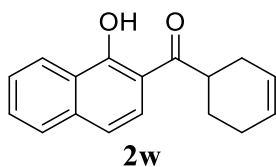


Table 1, compound 2w. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 1-naphthol (72 mg, 0.5 mmol), and 3-cyclohexene-1-carboxaldehyde (110 mg, 1.0 mmol) was stirred at 110 °C for 12 h. The product **2w** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 40:1). Yield: 42 mg, 33 %. Data for **2w**: ¹H NMR (400 MHz, CDCl₃) δ 14.32 (s, 1H), 8.48 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.63 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.53 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.27 (d, *J* = 8.9 Hz, 1H), 5.82-5.78 (m, 2H), 3.68-3.59 (m, 1H), 2.50-2.40 (m, 1H), 2.32-2.17 (m, 3H), 2.09-2.02 (m, 1H), 1.89-1.78 (m, 1H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 209.3, 163.4, 137.2, 130.0, 127.3, 126.6, 125.9, 125.6, 125.5, 124.4, 124.1, 118.2, 111.9, 41.2, 27.9, 25.8, 24.9 ppm; GC-MS *m/z* = 252 (M⁺); Anal. Calcd for C₁₇H₁₆O₂: C, 80.93; H, 6.39. Found: C, 80.95; H, 6.47.

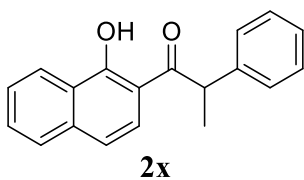


Table 1, compound 2x. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 1-naphthol (72 mg, 0.5 mmol), and 2-phenylpropionaldehyde (134 mg, 1.0 mmol) was stirred at 110 °C for 12 h. The product **2x** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 40:1). Yield: 84 mg, 61 %. Data for **2x**: ¹H NMR (400 MHz, CDCl₃) δ 14.20 (s, 1H), 8.46-8.43 (m, 1H), 7.71-7.67 (m, 2H), 7.61-7.57 (m, 1H), 7.52-7.47 (m, 1H), 7.36-7.29 (m, 4H), 7.25-7.20 (m, 1H), 7.16 (d, *J* = 9.0 Hz, 1H), 4.80 (q, *J* = 6.9 Hz, 1H), 1.60 (t, *J* = 6.9 Hz, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 206.2, 163.4, 141.3, 137.1, 130.1, 129.0, 127.6, 127.3, 127.1, 125.9, 125.4, 124.5, 124.4, 118.2, 112.3, 47.5, 19.2 ppm; GC-MS *m/z* = 276 (M⁺); Anal. Calcd for C₁₉H₁₆O₂: C, 82.58; H, 5.84. Found: C, 82.27; H, 5.81.

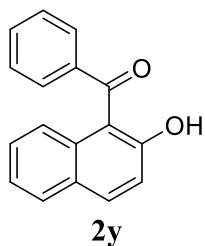


Table 1, compound 2y. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 2-naphthol (72 mg, 0.5 mmol), and benzaldehyde (106 mg, 1.0 mmol) was stirred at 110 °C for 20 h. The product **2y** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 20:1). Yield: 43 mg, 35 %. Data for **2y**: ¹H NMR (400 MHz, CDCl₃) δ 11.24 (s, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.65-7.62 (m, 2H), 7.56 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.43-7.39 (m, 2H), 7.33-7.26 (m, 2H), 7.25 (d, *J* = 9.0 Hz, 1H), 7.16 (dd, *J* = 7.0, 1.5 Hz, 1H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 200.4, 161.4, 140.3, 136.3, 132.6, 132.3, 129.4, 128.5, 128.5, 128.4, 126.7, 126.3, 123.7, 119.1, 114.3 ppm; GC-MS *m/z* = 248 (M⁺); Anal. Calcd for C₁₇H₁₂O₂: C, 82.24; H, 4.87. Found: C, 81.97; H, 4.67.

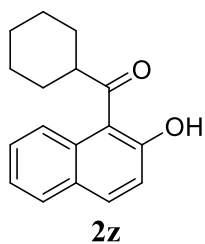


Table 1, compound 2z. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), 2-naphthol (72 mg, 0.5 mmol), and cyclohexanecarboxaldehyde (112 mg, 1.0 mmol) was stirred at 110 °C for 20 h. The product **2z** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 20:1). Yield: 48 mg, 38 %. Data for **2z**: ¹H NMR (400 MHz, CDCl₃) δ 11.95 (s, 1H), 7.91-7.88 (m, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.80-7.77 (m, 1H), 7.58-7.53 (m, 1H), 7.42-7.37 (m, 1H), 7.14 (d, *J* = 9.0 Hz, 1H), 3.49 (tt, *J* = 11.5, 3.2 Hz, 1H), 1.99-1.91 (m, 2H), 1.88-1.81 (m, 2H), 1.77-1.62 (m, 3H), 1.40-1.24 (m, 3H) ppm; ¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ 212.0, 161.1, 136.1, 131.6, 129.2, 128.6, 127.8, 124.2, 123.8, 119.4, 115.5, 50.2, 29.9, 25.7, 25.6 ppm; GC-MS *m/z* = 254 (M⁺); Anal. Calcd for C₁₇H₁₈O₂: C, 80.28; H, 7.13. Found: C, 79.97; H, 6.99.

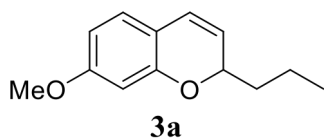


Table 2, compound 3a. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 3-methoxyphenol (62 mg, 0.5 mmol), and *trans*-2-hexen-1-al (98 mg, 1.0 mmol) was stirred at 110 °C for 24 h. The product **3a** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 20:1). Yield: 38 mg, 37 %. Data for **3a**: ¹H NMR (400 MHz, CDCl₃) δ 6.86 (d, *J* = 8.2 Hz, 1H), 6.40 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.37 (d, *J* = 2.5 Hz, 1H), 6.34 (dd, *J* = 9.9, 1.6 Hz, 1H), 5.54 (dd, *J* = 9.9, 3.3 Hz, 1H), 4.85-4.80 (m, 1H), 3.77 (s, 3H), 1.83-1.74 (m, 1H), 1.67-1.42 (m, 3H), 0.95 (t, *J* = 7.3, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 160.5, 154.8, 127.0, 123.5, 123.0, 115.3, 106.6, 101.8, 75.1, 55.3, 37.5, 18.1, 14.0 ppm; GC-MS *m/z* = 204 (M⁺); Anal. Calcd for C₁₃H₁₆O₂: C, 76.44; H, 7.90. Found: C, 76.52; H, 7.89.

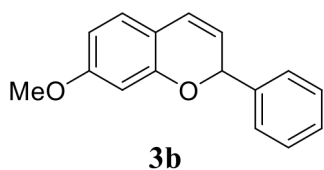


Table 2, compound 3b. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 3-methoxyphenol (62 mg, 0.5 mmol), and *trans*-cinnamaldehyde (132 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **3b** was isolated by a column chromatography on silica gel

(hexane/EtOAc = 100:1 to 20:1). Yield: 27 mg, 23 %. Data for **3b**: ^1H NMR (400 MHz, CDCl_3) δ 7.48-7.45 (m, 2H), 7.41-7.31 (m, 3H), 6.94 (d, $J = 8.2$, 1H), 6.50 (dd, $J = 9.8$, 1.8 Hz, 1H), 6.44 (dd, $J = 8.2$, 2.5 Hz, 1H), 6.40 (d, $J = 2.5$ Hz, 1H), 5.90 (dd, $J = 3.4$, 1.8 Hz, 1H), 5.67 (dd, $J = 9.8$, 3.4 Hz, 1H), 3.76 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 160.8, 154.3, 140.9, 128.6, 128.3, 127.2, 127.0, 123.6, 121.8, 114.6, 107.0, 101.8, 77.3, 55.3 ppm; GC-MS $m/z = 238$ (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.^{S1}

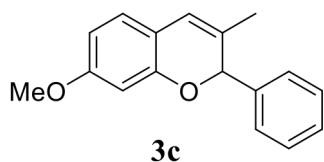


Table 2, compound 3c. A $\text{C}_6\text{H}_5\text{Cl}$ (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 3-methoxyphenol (62 mg, 0.5 mmol), and α -methylcinnamaldehyde (146 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **3c** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 20:1). Yield: 54 mg, 43 %. Data for **3c**: ^1H NMR (400 MHz, CDCl_3) δ 7.41-7.31 (m, 5H), 6.89 (d, $J = 8.3$, 1H), 6.42 (dd, $J = 8.3$, 2.5 Hz, 1H), 6.33 (d, $J = 2.5$ Hz, 1H), 6.31 (s, 1H), 5.64 (s, 1H), 3.73 (s, 3H), 1.69 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 160.1, 152.6, 139.3, 129.4, 128.6, 128.5, 127.5, 126.1, 119.4, 115.2, 106.6, 101.6, 81.2, 55.2, 19.8 ppm; GC-MS $m/z = 252$ (M^+); HRMS (APCI) Calcd for $\text{C}_{17}\text{H}_{17}\text{O}_2$ ($[\text{M}+\text{H}]^+$): 253.1223. Found: 253.1229.

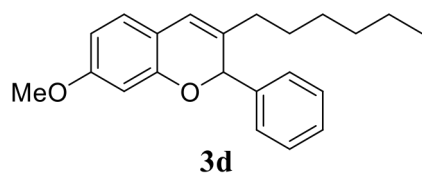


Table 2, compound 3d. A $\text{C}_6\text{H}_5\text{Cl}$ (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 3-methoxyphenol (62 mg, 0.5 mmol), and α -hexylcinnamaldehyde (216 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **3d** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 40:1). Yield: 102 mg, 63 %. Data for **3d**: ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.36 (m, 2H), 7.34-7.29 (m, 3H), 6.90 (d, $J = 8.3$ Hz, 1H), 6.41 (dd, $J = 8.3$, 2.5 Hz, 1H), 6.32 (s, 1H), 6.30 (d, $J = 2.5$ Hz, 1H), 5.66 (s, 1H), 3.72 (s, 3H), 1.97-1.91 (m, 2H), 1.54-1.40 (m, 2H), 1.33-1.19 (m, 6H), 0.87 (t, $J = 6.9$ Hz, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 160.1, 152.7, 139.4, 133.7, 128.6, 128.5, 127.7, 126.3, 118.3, 115.5, 106.7, 101.7, 80.2, 55.2, 33.0, 31.6, 28.9, 27.0, 22.5, 14.1 ppm; GC-MS $m/z = 322$ (M^+); HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_2$ (M^+): 322.1927. Found: 322.1903.

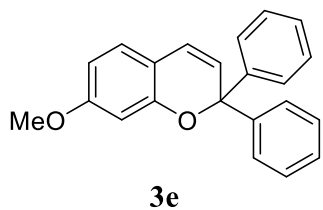


Table 2, compound 3e. A $\text{C}_6\text{H}_5\text{Cl}$ (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 3-methoxyphenol (62 mg, 0.5 mmol), and β -phenylcinnamaldehyde (208 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **3e** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 40:1). Yield: 63 mg, 40 %. Data for **3e**: ^1H NMR (400 MHz, CDCl_3) δ 7.46-7.43 (m, 4H), 7.35-7.24 (m, 6H), 6.92 (d, $J = 8.3$ Hz, 1H), 6.58 (d, $J = 9.8$ Hz, 1H), 6.53 (d, $J = 2.5$ Hz, 1H), 6.41 (dd, $J = 8.3$, 2.5 Hz, 1H), 6.03 (d, $J = 9.8$ Hz, 1H), 3.77 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 160.9, 153.7, 145.0, 128.1, 127.4, 127.2, 127.0, 125.9, 123.0, 114.4, 107.1, 102.1, 82.8, 55.3 ppm; GC-MS $m/z = 314$ (M^+); HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{18}\text{O}_2$ (M^+): 314.1301. Found: 314.1289.

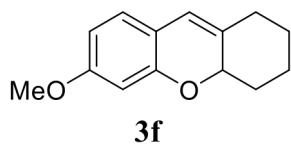


Table 2, compound 3f. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 3-methoxyphenol (62 mg, 0.5 mmol), and 1-cyclohexene-1-carboxaldehyde (112 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **3f** was isolated by a column chromatography on silica

gel (hexane/EtOAc = 100:1 to 40:1). Yield: 57 mg, 53 %. Data for **3f**: ¹H NMR (400 MHz, CDCl₃) δ 6.74 (d, *J* = 8.2 Hz, 1H), 6.33 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.29 (d, *J* = 2.5 Hz, 1H), 5.97-5.95 (m, 1H), 4.94-4.88 (m, 1H), 3.74 (s, 3H), 2.43-2.36 (m, 1H), 2.23-2.16 (m, 1H), 2.08-1.98 (m, 1H), 1.92-1.85 (m, 1H), 1.80-1.68 (m, 2H), 1.51-1.39 (m, 1H), 1.38-1.27 (m, 1H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 159.8, 154.0, 134.7, 126.0, 115.8, 114.8, 106.0, 100.9, 77.4, 55.3, 35.1, 32.9, 26.7, 24.4 ppm; GC-MS *m/z* = 216 (M⁺); HRMS (APCI) Calcd for C₁₄H₁₇O₂ ([M+H]⁺): 217.1223. Found: 217.1229.

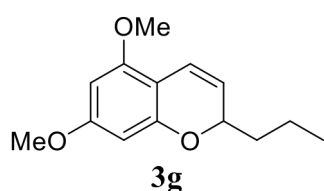


Table 2, compound 3g. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 3,5-dimethoxyphenol (77 mg, 0.5 mmol), and *trans*-2-hexen-1-al (98 mg, 1.0 mmol) was stirred at 120 °C for 16 h. The product **3g** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 40:1). Yield: 63 mg, 54 %. Data for **3g**: ¹H NMR (400

MHz, CDCl₃) δ 6.64 (dd, *J* = 9.9, 1.6 Hz, 1H), 6.04 (d, *J* = 2.3 Hz, 1H), 6.01 (d, *J* = 2.3 Hz, 1H), 5.49 (dd, *J* = 9.9, 3.4 Hz, 1H), 4.80-4.75 (m, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 1.84-1.74 (m, 1H), 1.68-1.42 (m, 3H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 160.9, 156.1, 155.3, 120.9, 118.4, 104.9, 93.7, 91.5, 74.9, 55.5, 55.3, 37.2, 18.1, 13.9 ppm; GC-MS *m/z* = 234 (M⁺); HRMS (ESI) Calcd for C₁₄H₁₈O₃ (M⁺): 234.1250. Found: 234.1239; Anal. Calcd for C₁₄H₁₈O₃: C, 71.77; H, 7.74. Found: C, 71.78; H, 7.89.

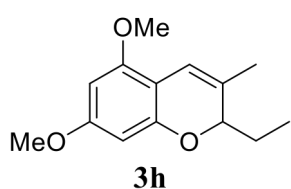


Table 2, compound 3h. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 3,5-dimethoxyphenol (77 mg, 0.5 mmol), and 2-methyl-2-pentenal (98 mg, 1.0 mmol) was stirred at 120 °C for 16 h.

The product **3h** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 40:1). Yield: 55 mg, 47 %. Data for **3h**: ¹H NMR (400 MHz, CDCl₃) δ 6.39-6.37 (m, 1H), 6.06 (d, *J* = 2.3 Hz, 1H), 6.01 (d, *J* = 2.3 Hz, 1H), 4.51 (dd, *J* = 8.7, 3.5 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 1.82-1.81 (m, 3H), 1.78-1.56 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 160.1, 155.3, 153.1, 129.5, 113.2, 105.3, 93.8, 91.4, 80.1, 55.5, 55.3, 25.4, 19.7, 9.7 ppm; GC-MS *m/z* = 234 (M⁺); HRMS (APCI) Calcd for C₁₄H₁₉O₃ ([M+H]⁺): 235.1329. Found: 235.1339.

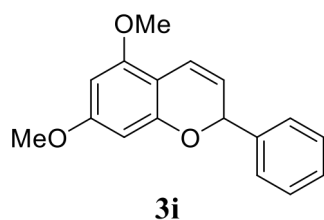


Table 2, compound 3i. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 3,5-dimethoxyphenol (77 mg, 0.5 mmol), and *trans*-cinnamaldehyde (132 mg, 1.0 mmol) was stirred at 120 °C for 16 h. The product **3i** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 40:1). Yield: 70 mg, 52 %. Data for **3i**: ¹H NMR (400

MHz, CDCl₃) δ 7.51-7.47 (m, 2H), 7.42-7.32 (m, 3H), 6.84 (dd, $J = 9.9, 1.9$ Hz, 1H), 6.09 (d, $J = 2.1$ Hz, 1H), 6.06 (d, $J = 2.1$ Hz, 1H), 5.86 (dd, $J = 3.5, 1.9$ Hz, 1H), 5.64 (dd, $J = 9.9, 3.5$ Hz, 1H), 3.82 (s, 3H), 3.76 (s, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 161.2, 156.2, 154.8, 140.8, 128.5, 128.2, 127.1, 119.7, 118.7, 104.3, 93.7, 91.7, 77.1, 55.5, 55.3 ppm; GC-MS $m/z = 268$ (M⁺). ¹H and ¹³C NMR spectral data are in good agreement with the literature data.^{S2}

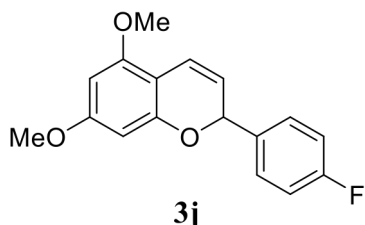


Table 2, compound 3j. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 3,5-dimethoxyphenol (77 mg, 0.5 mmol), and 4-fluorocinnamaldehyde (150 mg, 1.0 mmol) was stirred at 120 °C for 16 h. The product **3j** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 40:1). Yield: 79 mg, 55 %. Data for **3j**:

¹H NMR (400 MHz, CDCl₃) δ 7.47-7.42 (m, 2H), 7.08-7.02 (m, 2H), 6.84 (dd, $J = 9.9, 1.8$ Hz, 1H), 6.04 (s, 2H), 5.82 (dd, $J = 3.5, 1.8$ Hz, 1H), 5.59 (dd, $J = 9.9, 3.5$ Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 162.6 (d, $J_{CF} = 246.8$ Hz), 161.3, 156.2, 154.6, 136.6 (d, $J_{CF} = 3.2$ Hz), 129.0 (d, $J_{CF} = 8.3$ Hz), 119.3, 119.0, 115.4 (d, $J_{CF} = 21.5$ Hz), 104.3, 93.7, 91.8, 76.3, 55.5, 55.3 ppm; GC-MS $m/z = 286$ (M⁺); Anal. Calcd for C₁₇H₁₅FO₃: C, 71.32; H, 5.28. Found: C, 71.18; H, 5.05.

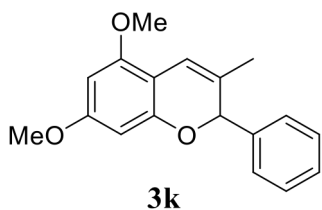


Table 2, compound 3k. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 3,5-dimethoxyphenol (77 mg, 0.5 mmol), and α -methylcinnamaldehyde (146 mg, 1.0 mmol) was stirred at 120 °C for 16 h. The product **3k** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 40:1). Yield: 102 mg, 72 %. Data for **3k**:

¹H NMR (400 MHz, CDCl₃) δ 7.42-7.39 (m, 2H), 7.36-7.30 (m, 3H), 6.64-6.62 (m, 1H), 6.03 (d, $J = 2.3$ Hz, 1H), 5.99 (d, $J = 2.3$ Hz, 1H), 5.62 (br s, 1H), 3.82 (s, 3H), 3.71 (s, 3H), 1.72-1.71 (m, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 160.3, 155.3, 153.1, 139.3, 128.6, 128.5, 127.6, 127.4, 114.1, 104.6, 93.6, 91.6, 81.0, 55.5, 55.2, 19.9 ppm; GC-MS $m/z = 282$ (M⁺); HRMS (APCI) Calcd for C₁₈H₁₉O₃ ([M+H]⁺): 283.1329. Found: 283.1334.

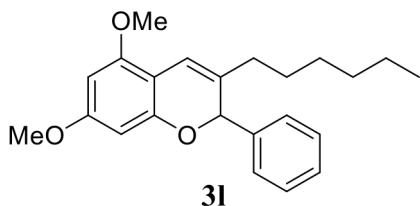
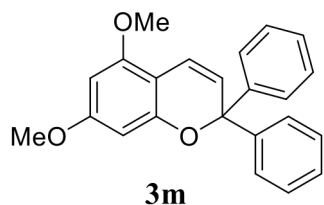


Table 2, compound 3l. A C₆H₅Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 3,5-dimethoxyphenol (77 mg, 0.5 mmol), and α -hexylcinnamaldehyde (216 mg, 1.0 mmol) was stirred at 120 °C for 16 h. The product **3l** was isolated by a column

chromatography on silica gel (hexane/EtOAc = 100:1 to 40:1). Yield: 155 mg, 88 %. Data for **3l**: ¹H NMR (400 MHz, CDCl₃) δ 7.41-7.37 (m, 2H), 7.34-7.28 (m, 3H), 6.63-6.61 (m, 1H), 6.02 (d, $J = 2.3$ Hz, 1H), 5.96 (d, $J = 2.3$ Hz, 1H), 5.63 (br s, 1H), 3.82 (s, 3H), 3.70 (s, 3H), 2.04-1.89 (m, 2H), 1.54-1.39 (m, 2H), 1.33-1.18 (m, 6H), 0.86 (t, $J = 7.0$, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 160.3, 155.5, 153.1, 139.4, 131.8, 128.5, 128.4,

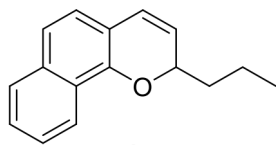
127.8, 113.0, 104.9, 93.7, 91.6, 80.0, 55.5, 55.3, 33.3, 31.6, 29.0, 27.2, 22.5, 14.1 ppm; GC-MS $m/z = 352$ (M^+); HRMS (ESI) Calcd for $C_{23}H_{28}O_3$ (M^+): 352.2033. Found: 352.2014.



3m

Table 2, compound 3m. A C_6H_5Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 3,5-dimethoxyphenol (77 mg, 0.5 mmol), and β -phenylcinnamaldehyde (208 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **3m** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 40:1). Yield: 108 mg, 63 %. Data for **3m**:

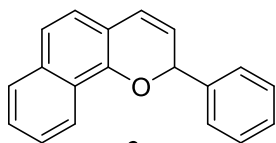
1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.43 (m, 4H), 7.35-7.23 (m, 6H), 6.89 (dd, $J = 9.9, 0.6$ Hz, 1H), 6.19 (dd, $J = 2.2, 0.6$ Hz, 1H), 6.00 (d, $J = 2.2$ Hz, 1H), 5.96 (d, $J = 9.9$ Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.3, 156.2, 154.1, 145.0, 128.0, 127.3, 126.9, 123.9, 118.0, 104.2, 94.0, 91.7, 82.6, 55.4, 55.3 ppm; GC-MS $m/z = 344$ (M^+); HRMS (APCI) Calcd for $C_{23}H_{21}O_3$ ($[M+H]^+$): 345.1485. Found: 345.1491.



3n

Table 2, compound 3n. A C_6H_5Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 1-naphthol (72 mg, 0.5 mmol), and *trans*-2-hexene-1-al (98 mg, 1.0 mmol) was stirred at 100 °C for 20 h. The product **3n** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1). Yield:

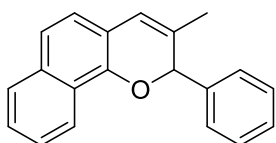
45 mg, 40 %. Data for **3n**: 1H NMR (400 MHz, $CDCl_3$) δ 8.22-8.15 (m, 1H), 7.77-7.73 (m, 1H), 7.48-7.41 (m, 2H), 7.36 (d, $J = 8.3$ Hz, 1H), 7.15 (d, $J = 8.3$ Hz, 1H), 6.52 (dd, $J = 9.7, 1.6$ Hz, 1H), 5.73 (dd, $J = 9.7, 3.5$ Hz, 1H), 5.10-5.05 (m, 1H), 2.00-1.90 (m, 1H), 1.74-1.53 (m, 3H), 1.00 (t, $J = 7.2$ Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.7, 134.4, 127.6, 126.1, 125.3, 124.7, 124.6, 124.6, 124.3, 121.8, 120.0, 116.3, 75.4, 37.3, 18.1, 13.9 ppm; GC-MS $m/z = 224$ (M^+); HRMS (ESI) Calcd for $C_{16}H_{16}O$ (M^+): 224.1196. Found: 224.1202. Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.86; H, 7.49.



3o

Table 2, compound 3o. A C_6H_5Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 1-naphthol (72 mg, 0.5 mmol), and *trans*-cinnamaldehyde (132 mg, 1.0 mmol) was stirred at 130 °C for 12 h. The product **3o** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1). Yield: 59

mg, 46 %. Data for **3o**: 1H NMR (400 MHz, $CDCl_3$) δ 8.22-8.19 (m, 1H), 7.77-7.73 (m, 1H), 7.56-7.53 (m, 2H), 7.45-7.33 (m, 6H), 7.19 (d, $J = 8.3$ Hz, 1H), 6.67 (dd, $J = 9.7, 1.7$ Hz, 1H), 6.15 (dd, $J = 3.6, 1.7$ Hz, 1H), 5.90 (dd, $J = 9.7, 3.6$ Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.4, 141.0, 134.5, 128.6, 128.2, 127.5, 126.7, 126.3, 125.4, 124.6, 124.5, 124.5, 123.2, 121.9, 120.3, 115.6, 77.1 ppm; GC-MS $m/z = 258$ (M^+); HRMS (ESI) Calcd for $C_{19}H_{14}O$ (M^+): 258.1039. Found: 258.1038.



3p

Table 2, compound 3p. A C_6H_5Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 1-naphthol (72 mg, 0.5 mmol), and α -methylcinnamaldehyde (146 mg, 1.0 mmol) was stirred at 130 °C for 12 h. The product

3p was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1). Yield: 57 mg, 42 %. Data for **3p**: ^1H NMR (400 MHz, CDCl_3) δ 8.13-8.09 (m, 1H), 7.74-7.70 (m, 1H), 7.50-7.46 (m, 2H), 7.40-7.30 (m, 6H), 7.18 (d, $J = 8.3$ Hz, 1H), 6.50 (s, 1H), 5.92 (s, 1H), 1.83 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 146.5, 139.4, 134.0, 131.2, 128.6, 128.5, 127.4, 127.4, 125.7, 125.2, 124.4, 124.2, 121.7, 120.3, 120.2, 116.2, 81.2, 20.0 ppm; GC-MS $m/z = 272$ (M^+); HRMS (APCI) calcd for $\text{C}_{20}\text{H}_{17}\text{O}$ ($[\text{M}+\text{H}]^+$): 273.1274. Found: 273.1279.

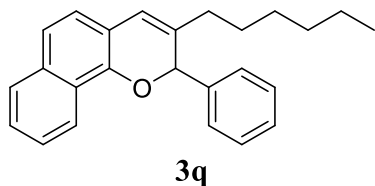


Table 2, compound 3q. A $\text{C}_6\text{H}_5\text{Cl}$ (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 1-naphthol (72 mg, 0.5 mmol), and α -hexylcinnamaldehyde (216 mg, 1.0 mmol) was stirred at 130 °C for 12 h.

The product **3q** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1). Yield: 101 mg, 59 %. Data for **3q**: ^1H NMR (400 MHz, CDCl_3) δ 8.19-8.15 (m, 1H), 7.78-7.74 (m, 1H), 7.55-7.52 (m, 2H), 7.44-7.32 (m, 6H), 7.25 (d, $J = 8.3$ Hz, 1H), 6.57 (s, 1H), 6.00 (s, 1H), 2.19-2.09 (m, 2H), 1.71-1.55 (m, 2H), 1.46-1.32 (m, 6H), 0.98 (t, $J = 7.0$ Hz, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 146.5, 139.4, 135.4, 134.0, 128.5, 128.5, 127.6, 127.4, 125.7, 125.2, 124.5, 124.3, 121.7, 120.2, 119.2, 116.4, 80.1, 33.3, 31.7, 29.0, 27.0, 22.6, 14.1 ppm; GC-MS $m/z = 342$ (M^+); HRMS (ESI) Calcd for $\text{C}_{25}\text{H}_{26}\text{O}$ (M^+): 342.1978. Found: 342.1979.

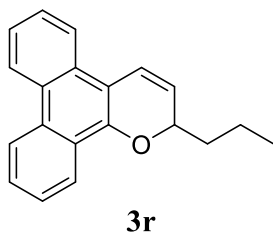


Table 2, compound 3r. A $\text{C}_6\text{H}_5\text{Cl}$ (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 9-phenanthrol (72 mg, 0.5 mmol), and *trans*-2-hexen-1-al (98 mg, 1.0 mmol) was stirred at 120 °C for 16 h. The product **3r** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1). Yield: 97 mg, 71 %.

Data for **3r**: ^1H NMR (400 MHz, CDCl_3) δ 8.70-8.66 (m, 2H), 8.47-8.43 (m, 1H), 8.09-8.05 (m, 1H), 7.72-7.63 (m, 2H), 7.61-7.56 (m, 1H), 7.42-7.40 (m, 1H), 7.18 (dd, $J = 9.9, 1.6$ Hz, 1H), 5.90 (dd, $J = 9.9, 3.7$ Hz, 1H), 5.12-5.07 (m, 1H), 2.11-2.02 (m, 1H), 1.82-1.60 (m, 3H), 1.07 (t, $J = 7.2$ Hz, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 147.3, 131.0, 129.2, 127.0, 126.9, 126.5, 126.3, 125.5, 124.1, 123.9, 122.9, 122.5, 122.4, 121.8, 120.4, 111.5, 75.0, 36.6, 18.2, 13.9 ppm; HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{18}\text{O}$ (M^+): 274.1352. Found: 274.1366; Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{O}$: C, 87.56; H, 6.61. Found: C, 87.56; H, 6.69.

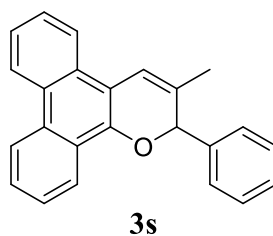


Table 2, compound 3s. A $\text{C}_6\text{H}_5\text{Cl}$ (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 9-phenanthrol (72 mg, 0.5 mmol), and α -methylcinnamaldehyde (146 mg, 1.0 mmol) was stirred at 120 °C for 16 h. The product **3s** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1). Yield: 97 mg, 60 %.

Data for **3s**: ^1H NMR (400 MHz, CDCl_3) δ 8.69-8.62 (m, 2H), 8.37-8.34 (m, 1H), 8.19-8.16 (m, 1H), 7.70-7.54 (m, 6H), 7.37-7.31 (m, 3H), 7.18 (s, 1H), 5.97 (s, 1H), 2.00 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 144.8, 138.9, 130.9, 130.6, 129.0, 128.5, 128.4, 127.5, 126.8,

126.6, 126.5, 126.4, 125.4, 124.0, 123.0, 122.3, 121.7, 116.2, 111.0, 80.5, 20.5 ppm; GC-MS $m/z = 322$ (M^+); HRMS (APCI) Calcd for $C_{24}H_{19}O$ ($[M+H]^+$): 323.1430. Found: 323.1444.

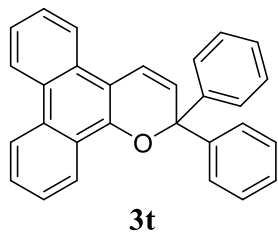
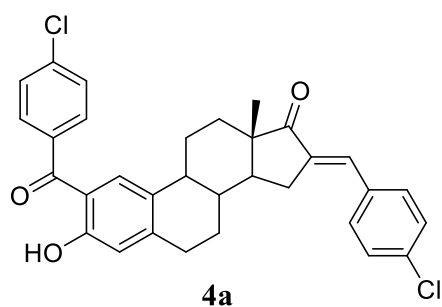
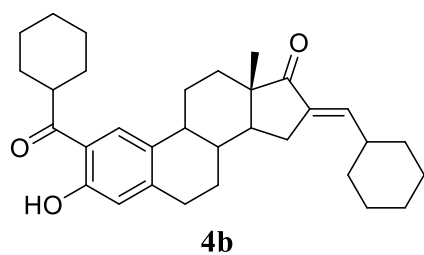


Table 2, compound 3t. A C_6H_5Cl (2.5 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), 9-phenanthrol (72 mg, 0.5 mmol), and β -phenylcinnamaldehyde (208 mg, 1.0 mmol) was stirred at 120 °C for 16 h. The product **3t** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1). Yield: 108 mg, 56 %. Data for **3t**: 1H NMR (400 MHz, $CDCl_3$) δ 8.64-8.54 (m, 2H), 8.07-8.03 (m, 1H), 7.69-7.64 (m, 2H), 7.61-7.56 (m, 5H), 7.54-7.49 (m, 1H), 7.41-7.30 (m, 5H), 7.27-7.23 (m, 2H) 6.35 (d, $J = 9.9$ Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.2, 144.9, 131.3, 129.0, 128.1, 127.5, 127.2, 127.0, 126.9, 126.8, 126.7, 126.5, 125.5, 124.3, 123.0, 122.7, 122.5, 121.9, 120.1, 110.9, 82.8 ppm; GC-MS $m/z = 384$ (M^+); Anal. Calcd for $C_{29}H_{20}O$: C, 90.60; H, 5.24. Found: C, 90.44; H, 5.34.



Scheme 1, compound 4a. A C_6H_5Cl (3.0 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), estrone (135 mg, 0.5 mmol) and 4-chlorobenzaldehyde (280 mg, 2.0 mmol) was stirred at 150 °C for 24 h. The product **4a** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 5:1). Yield: 57 mg, 22 %. Data for **4a**: 1H NMR (400 MHz, $CDCl_3$) δ 11.74 (s, 1H), 7.63 (d, $J = 8.7$ Hz, 2H), 7.51 (d, $J = 8.7$ Hz, 2H), 7.48 (d, $J = 8.5$ Hz, 2H), 7.45 (s, 1H), 7.41 (s, 1H), 7.39 (d, $J = 8.5$ Hz, 2H), 6.83 (s, 1H), 3.01-2.91 (m, 3H), 2.52 (ddd, $J = 15.5, 12.6, 2.9$ Hz, 1H), 2.30-2.01 (m, 3H), 1.78-1.23 (m, 6H), 0.99 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 208.9, 199.7, 161.0, 147.0, 138.3, 136.4, 136.1, 135.2, 133.9, 132.0, 131.4, 130.8, 130.5, 129.9, 129.0, 128.7, 117.9, 117.0, 48.4, 47.6, 43.6, 37.6, 31.4, 29.8, 29.0, 26.3, 25.7, 14.5 ppm; HRMS (ESI) Calcd for $C_{32}H_{29}Cl_2O_3$ ($[M+H]^+$): 531.1488. Found: 531.1485.

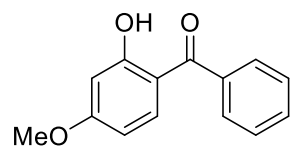


Scheme 1, compound 4b. A C_6H_5Cl (3.0 mL) solution of complex **1** (14 mg, 5 mol %), triphenylphosphine (26 mg, 20 mol %), potassium carbonate (21 mg, 30 mol %), estrone (135 mg, 0.5 mmol) and cyclohexanecarboxaldehyde (224 mg, 2.0 mmol) was stirred at 150 °C for 24 h. The product **4b** was isolated by a column chromatography on silica gel (hexane/EtOAc = 100:1 to 5:1). Yield: 59 mg, 25 %. Data for **4b**: 1H NMR (400 MHz, $CDCl_3$) δ 12.38 (s, 1H), 7.65 (s, 1H), 6.70 (s, 1H), 6.49 (ddd, $J = 9.6, 2.6, 1.8$ Hz, 1H), 3.30-3.22 (m, 1H), 2.96-2.84 (m, 2H), 2.67 (ddd, $J = 15.2, 6.4, 1.7$ Hz, 1H), 2.43-2.37 (m, 1H), 2.30-1.99 (m, 5H), 1.91-1.81 (m, 4H), 1.80-1.14 (m, 21H), 0.92 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 209.6, 209.2, 160.8, 146.4, 142.5, 134.6, 130.7, 126.2, 117.9, 116.2, 48.1, 47.9, 45.0, 43.6, 38.9, 37.6, 31.7, 31.4, 29.7, 29.6, 26.3, 26.0, 25.9, 25.8, 25.7, 25.5, 25.5, 14.4 ppm; HRMS (ESI) Calcd for $C_{32}H_{43}O_3$ ($[M+H]^+$): 475.3207. Found: 475.3209.

References

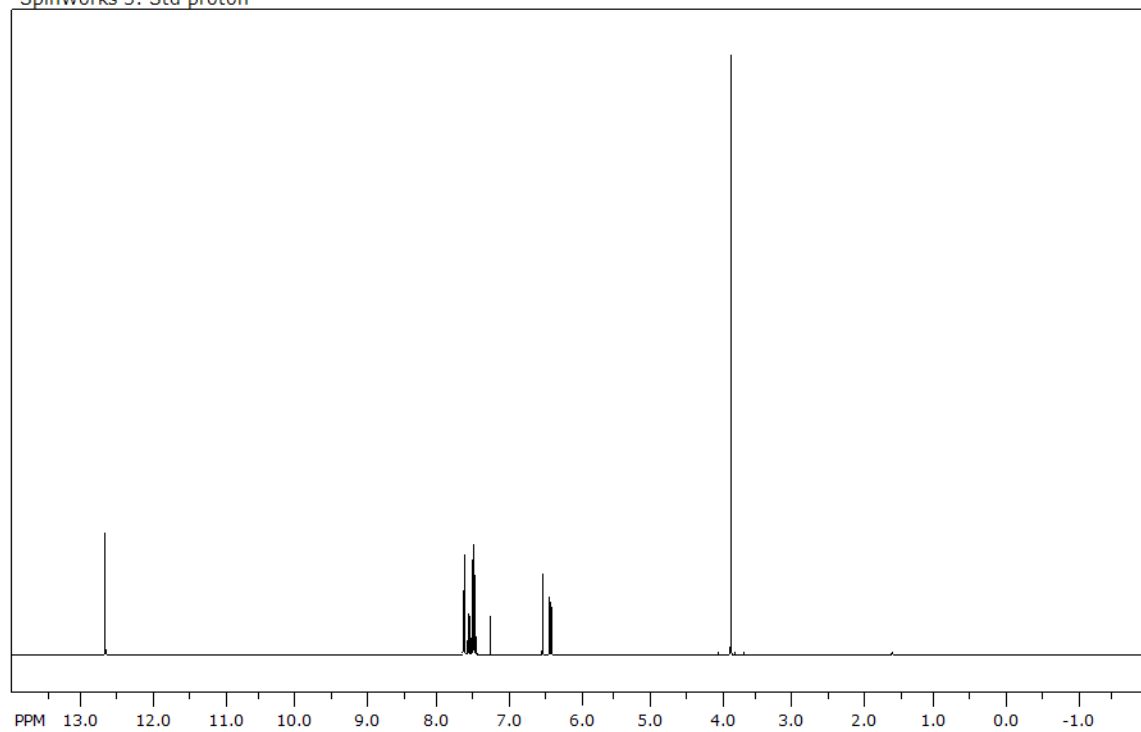
- S1. C. Pouget, C. Fagnere, J.-P. Basly, H. Leveque, A.-J. Chulia, *Tetrahedron* **2000**, 56, 6047.
- S2. B. Nay, J.-F. Peyrat, J. Vercauteren, *Eur. J. Org. Chem.* **1999**, 9, 2231.

9. ^1H and ^{13}C NMR Spectra of the Products

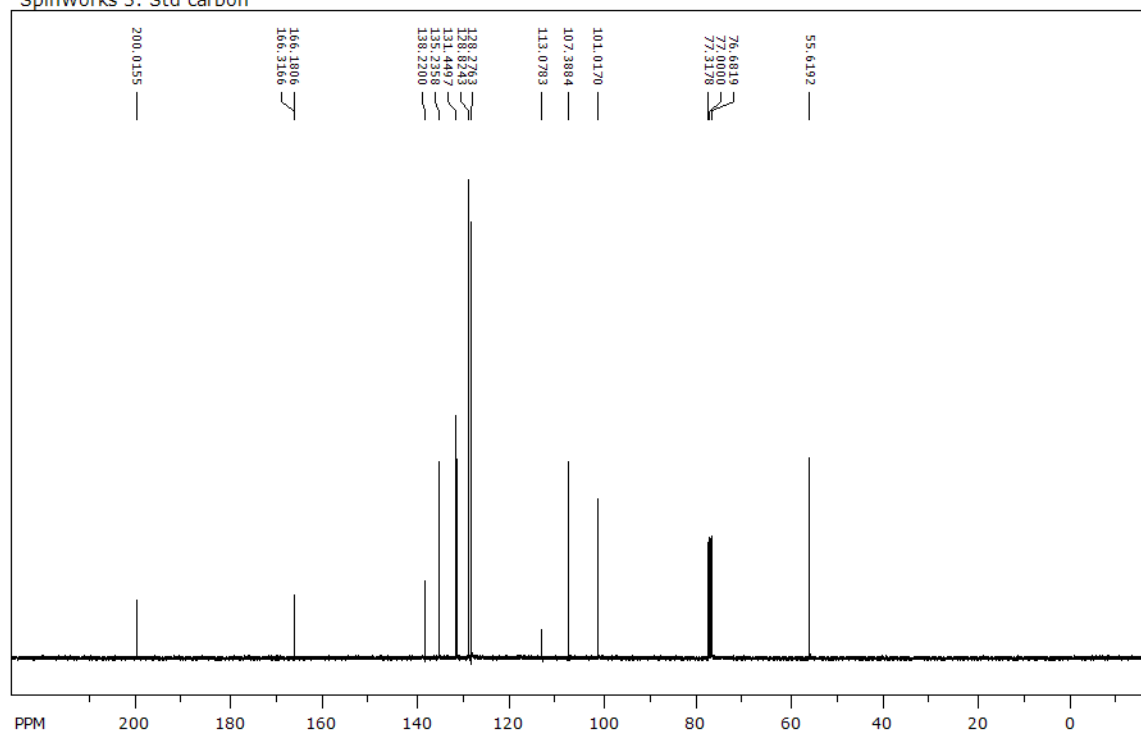


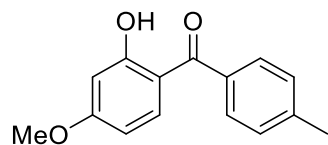
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SpinWorks 3: Std proton



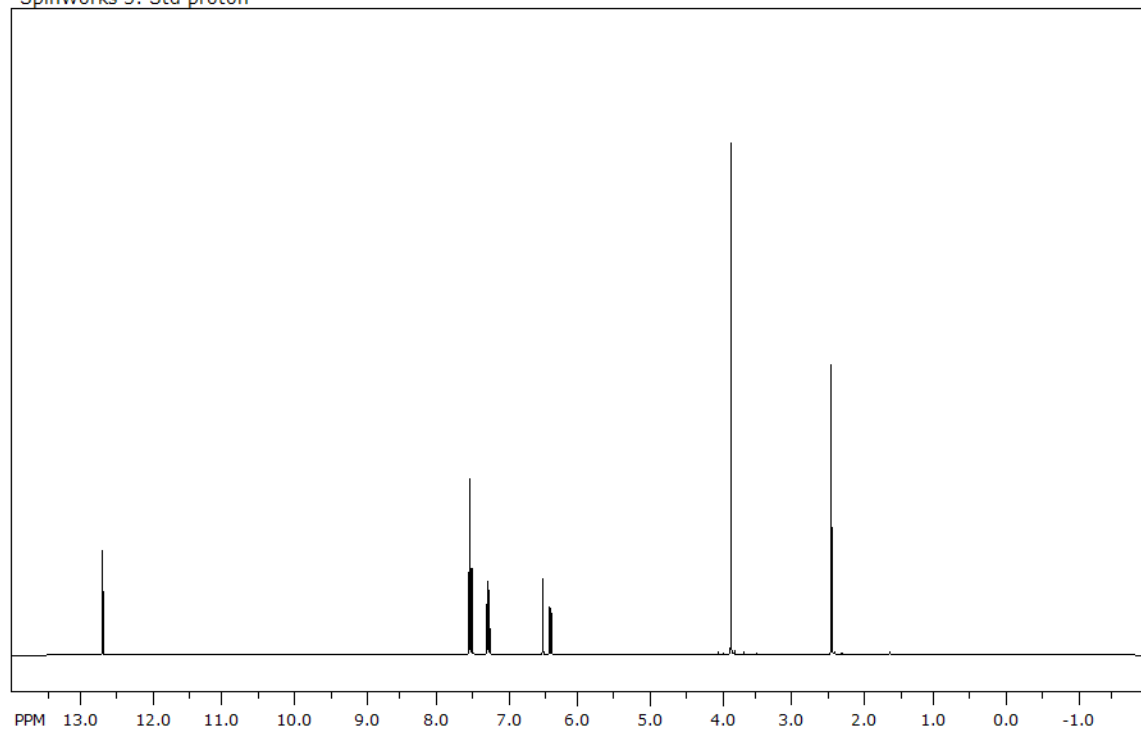
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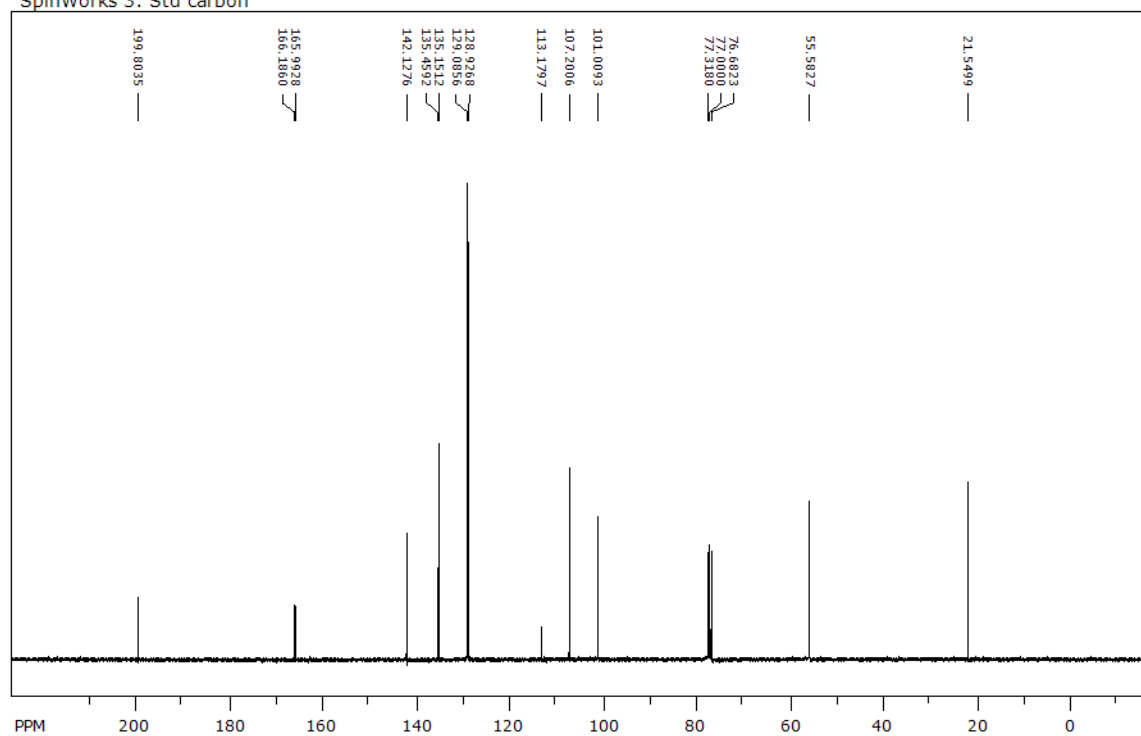


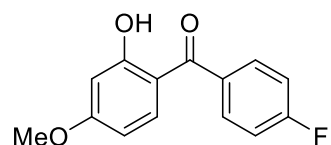
2b

SpinWorks 3: Std proton



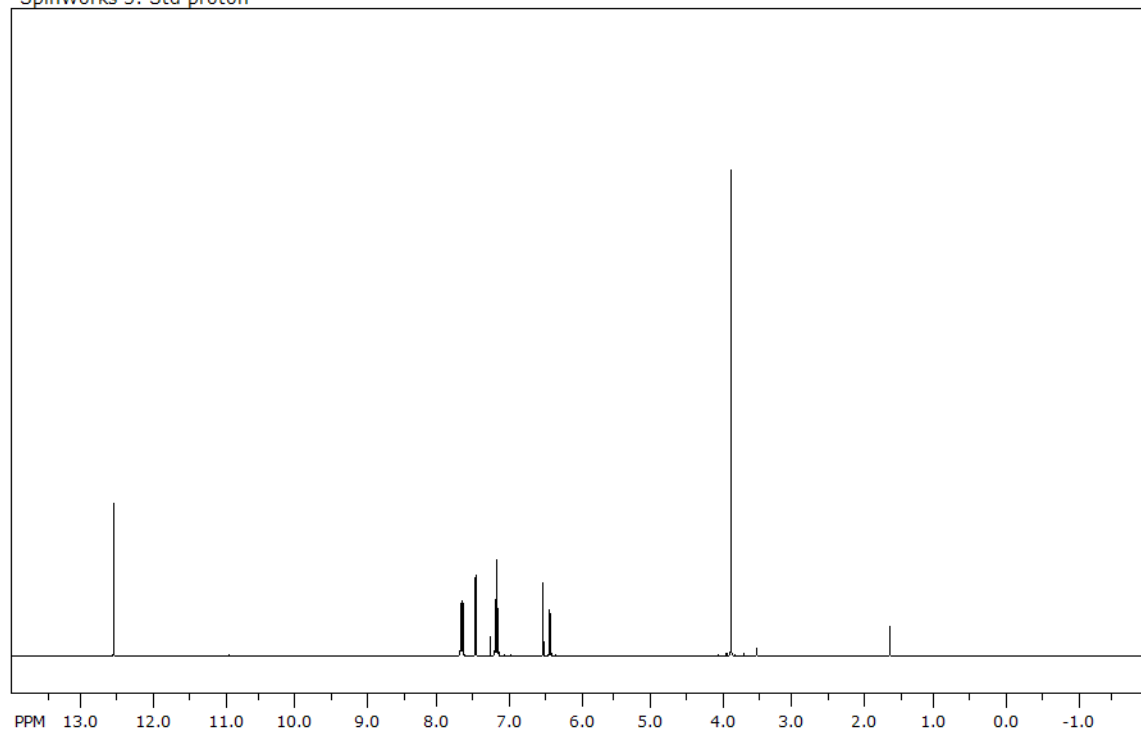
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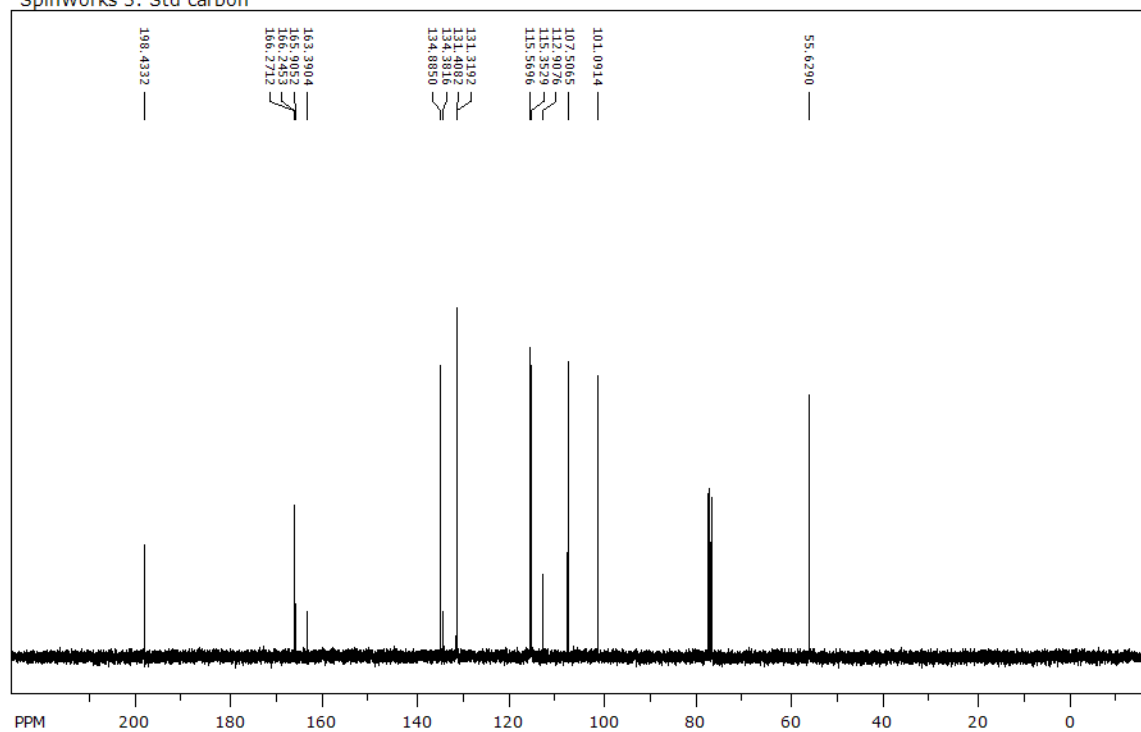


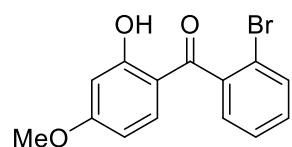
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SpinWorks 3: Std proton



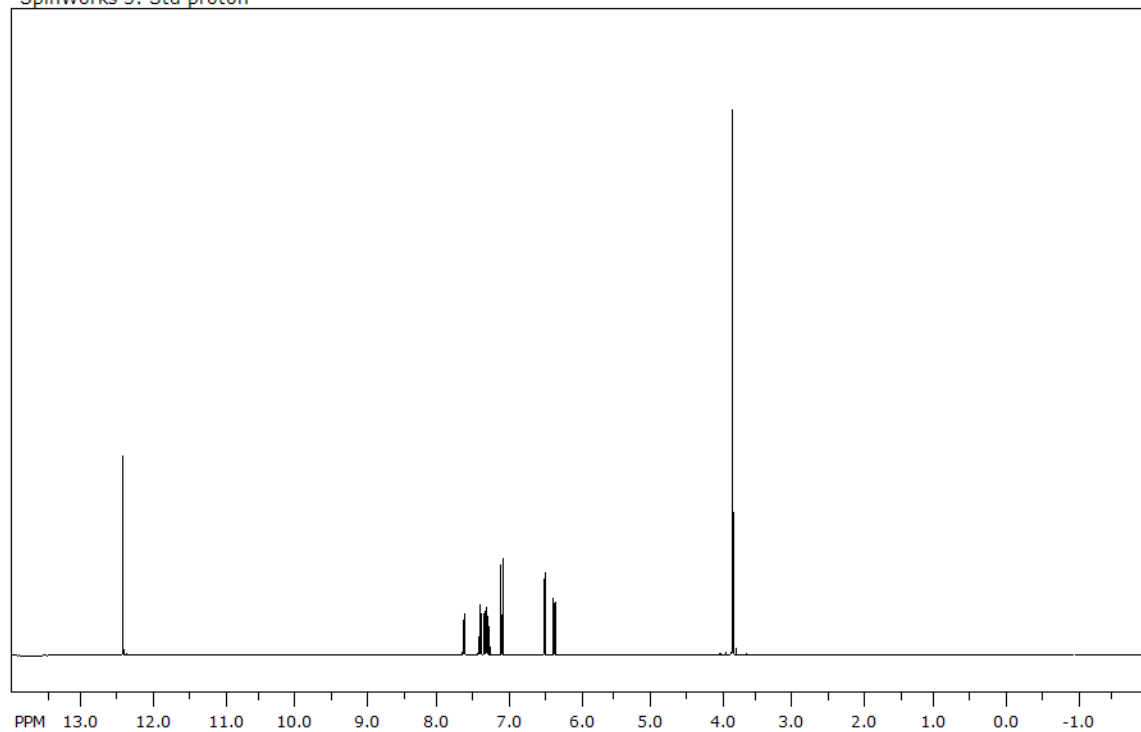
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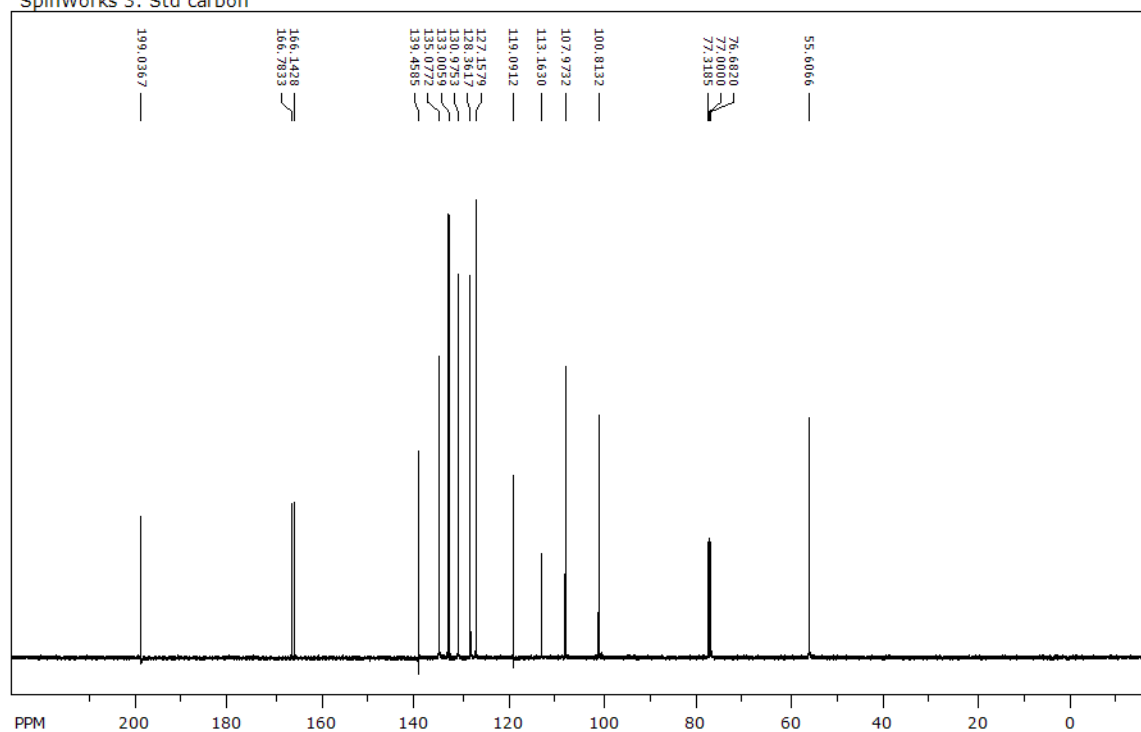


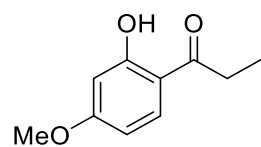
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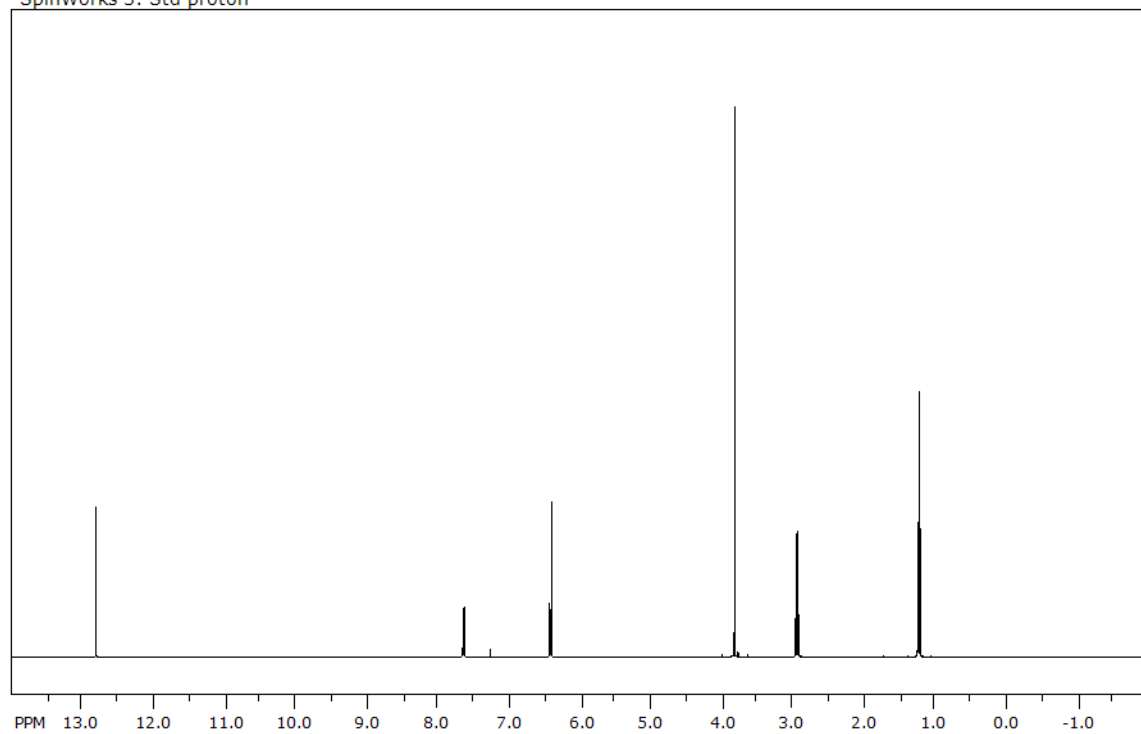
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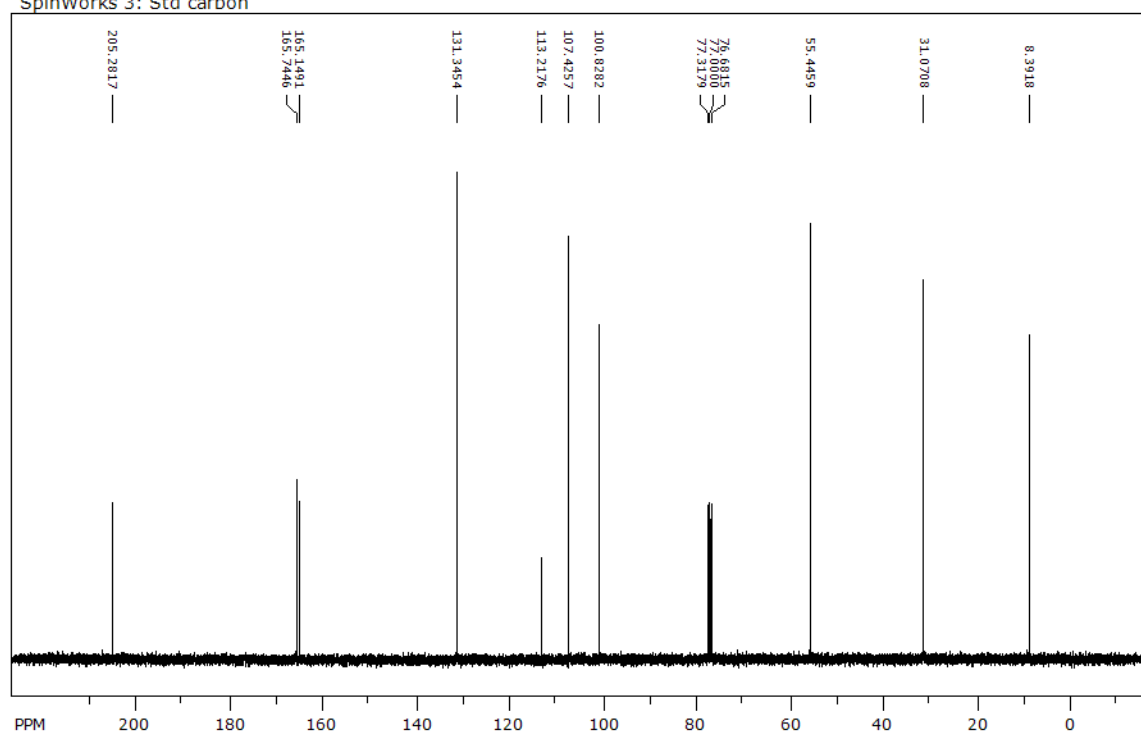


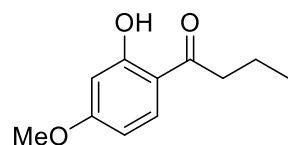
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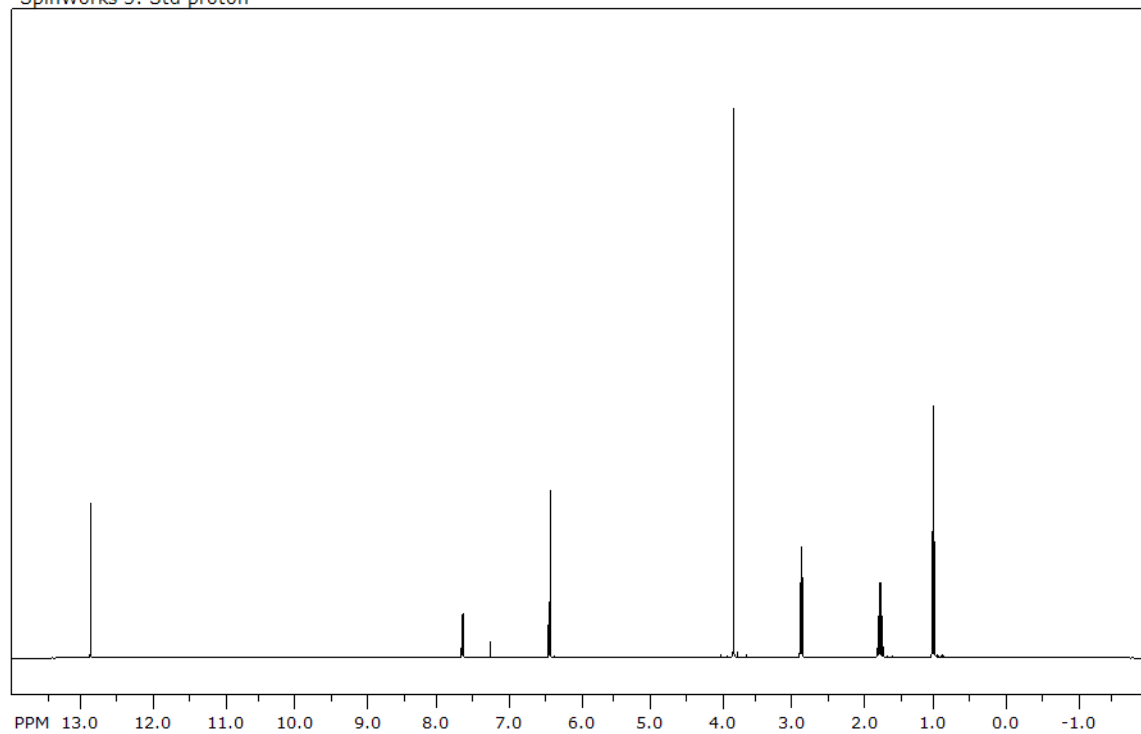
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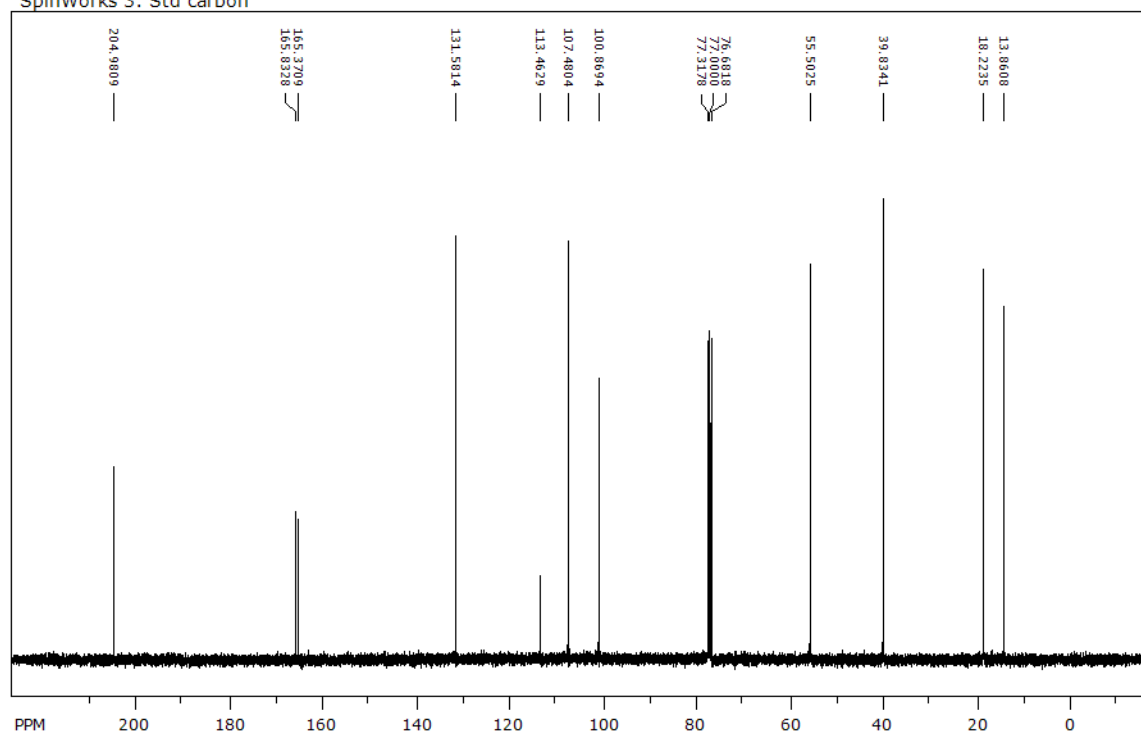


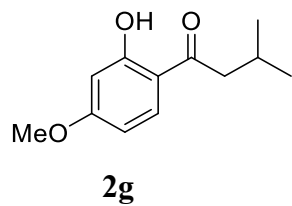
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SpinWorks 3: Std proton

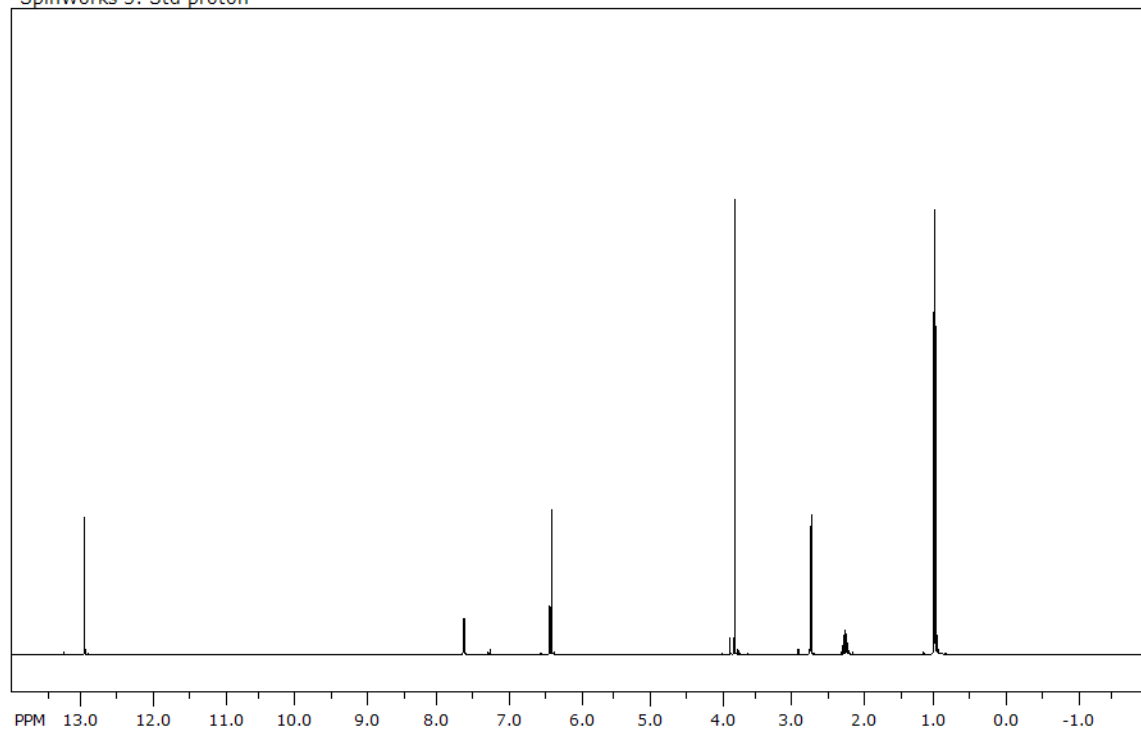


SpinWorks 3: Std carbon

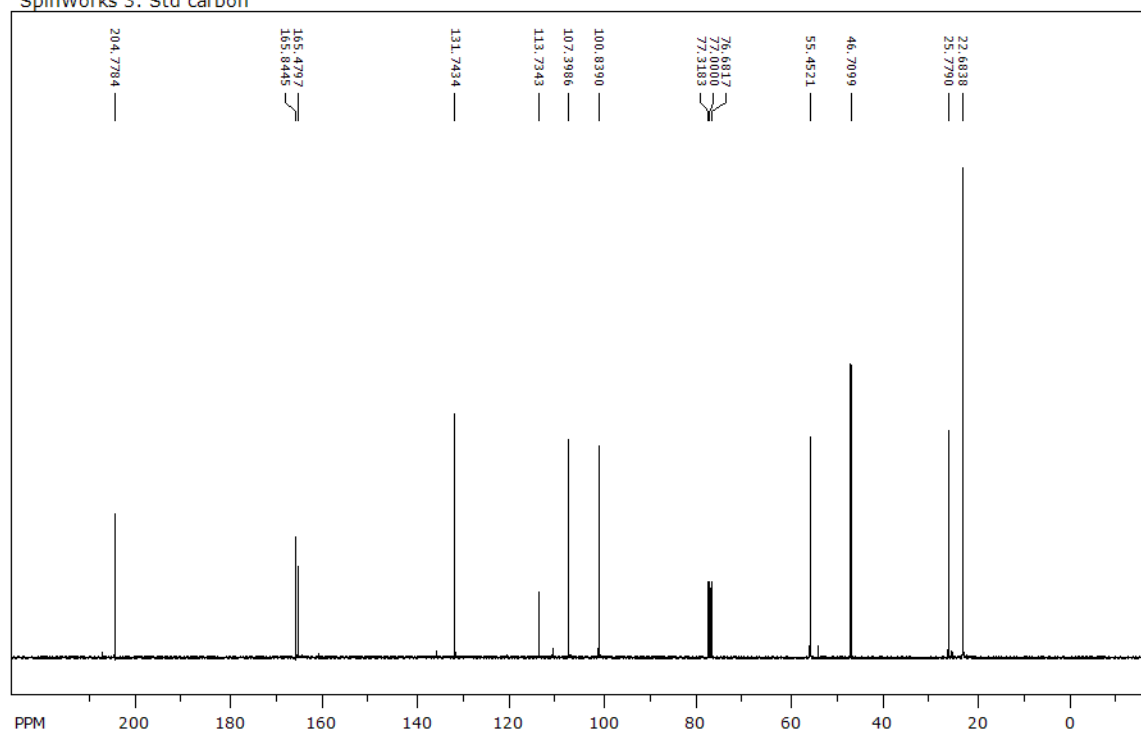


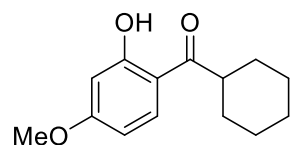


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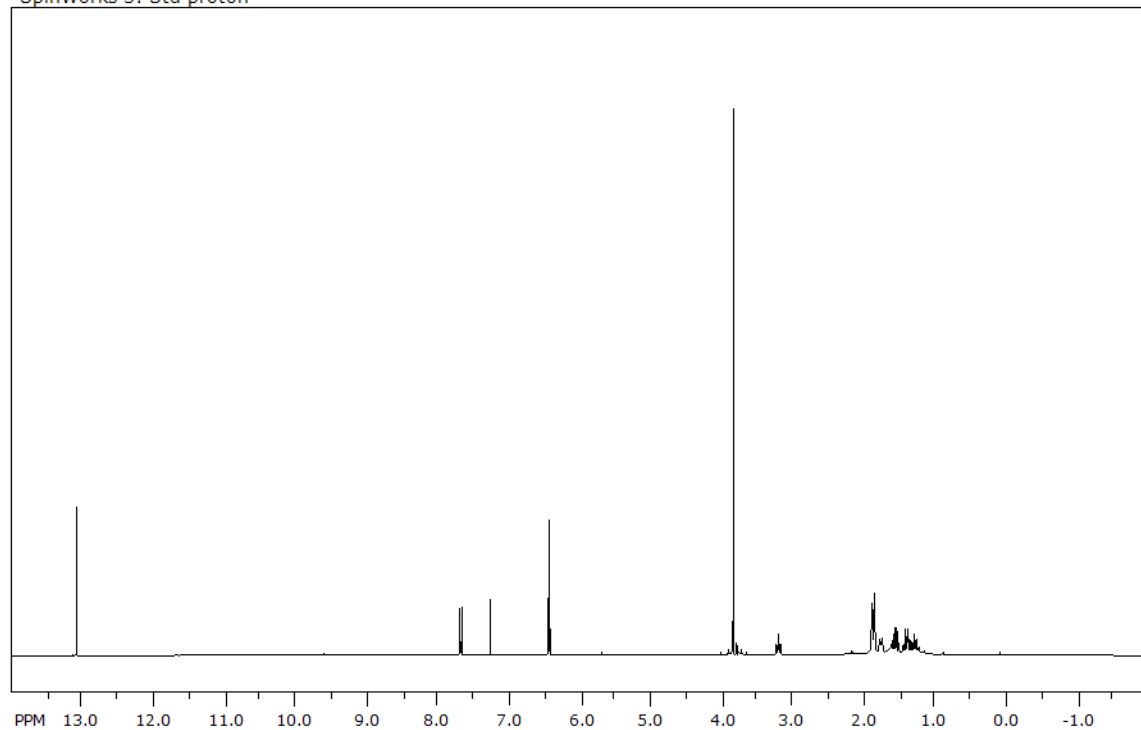
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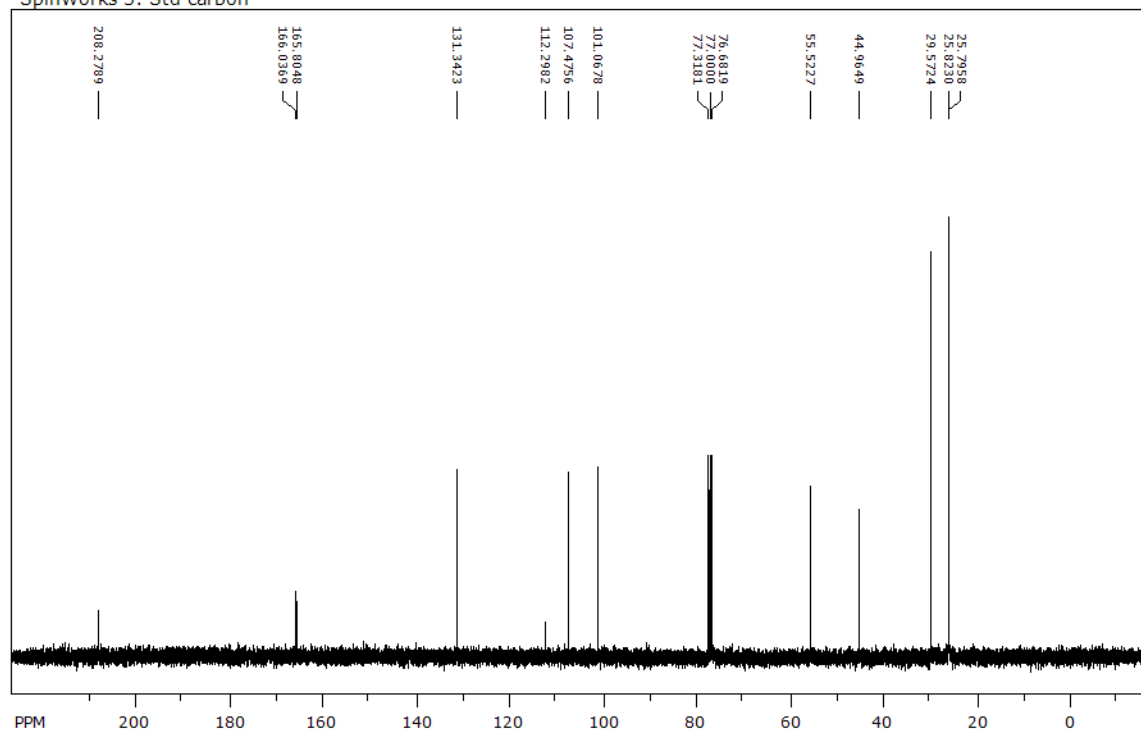


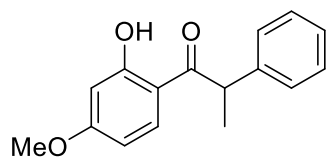
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SpinWorks 3: Std proton



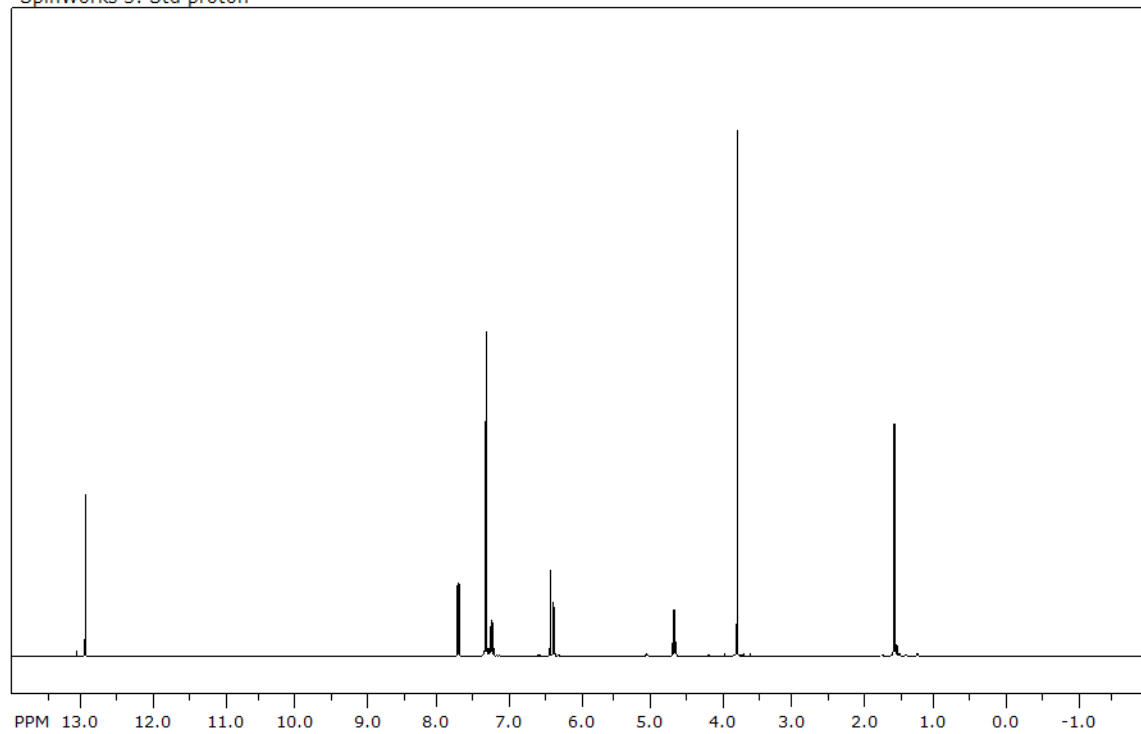
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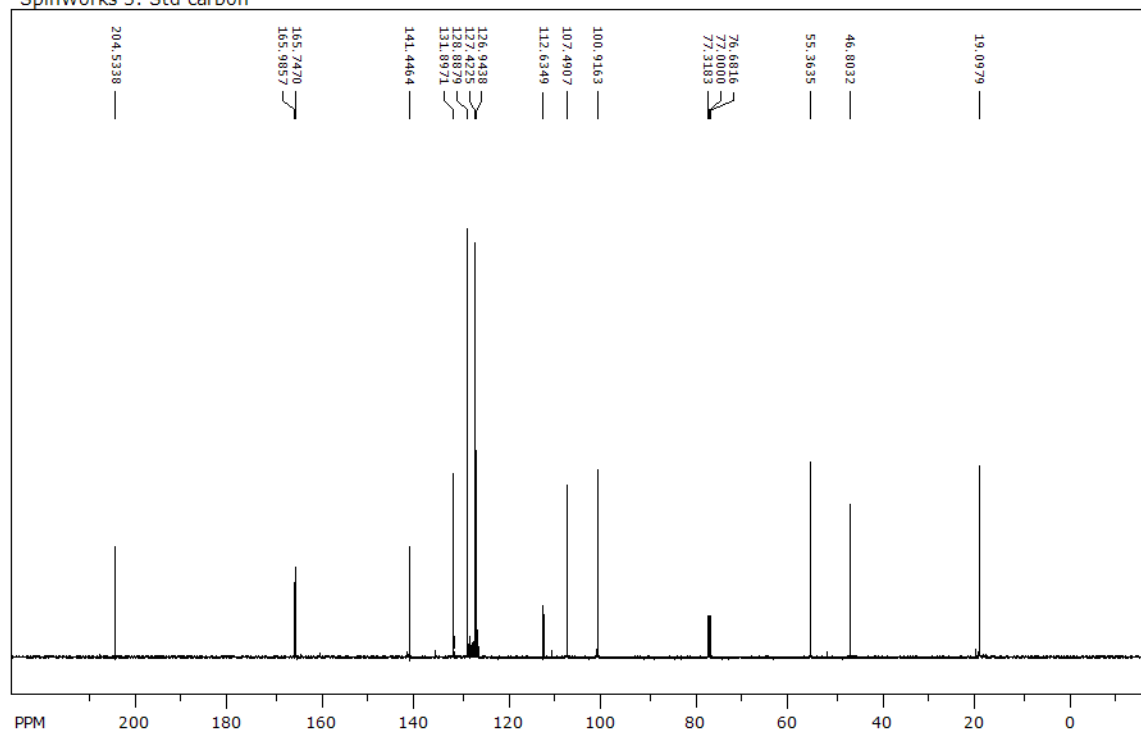


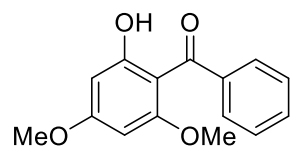
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SpinWorks 3: Std proton



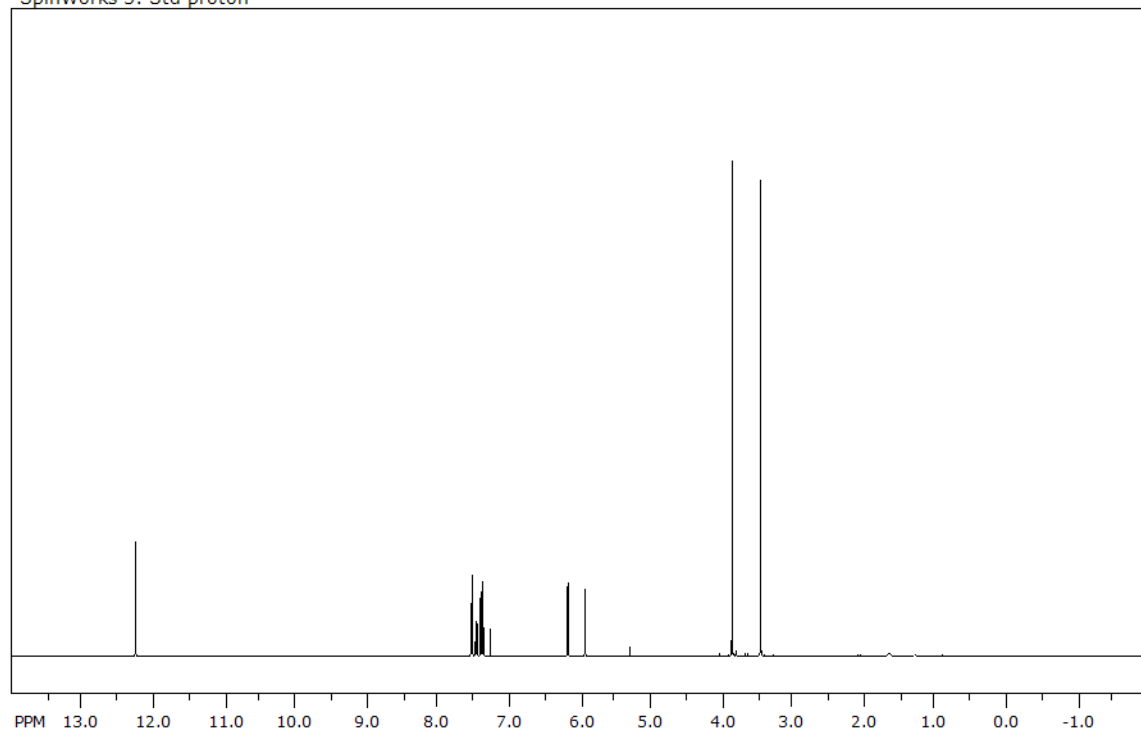
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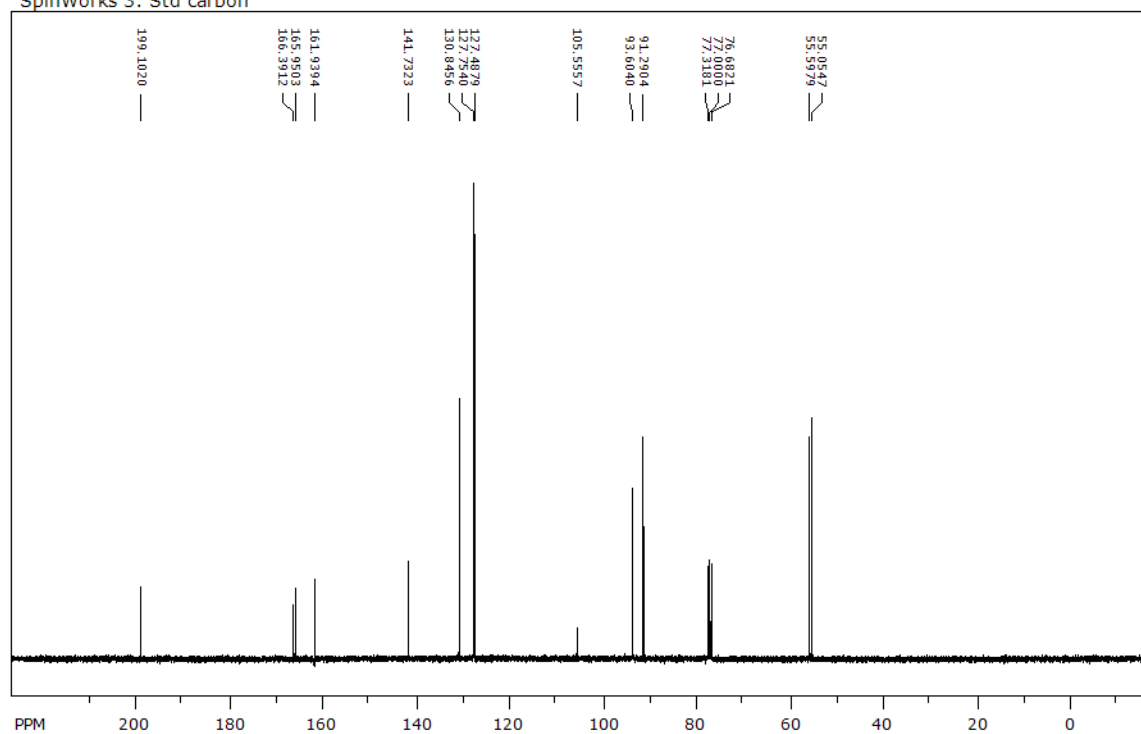


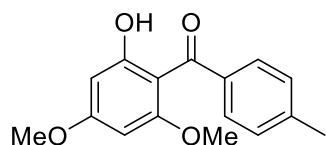
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SpinWorks 3: Std proton



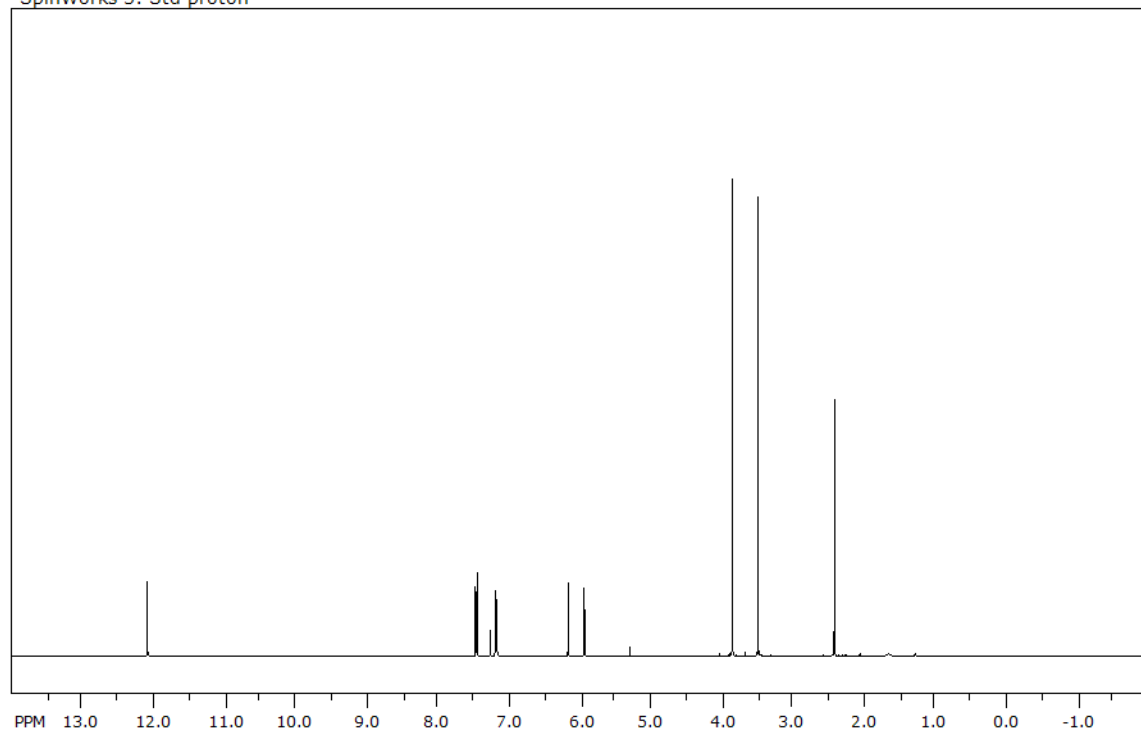
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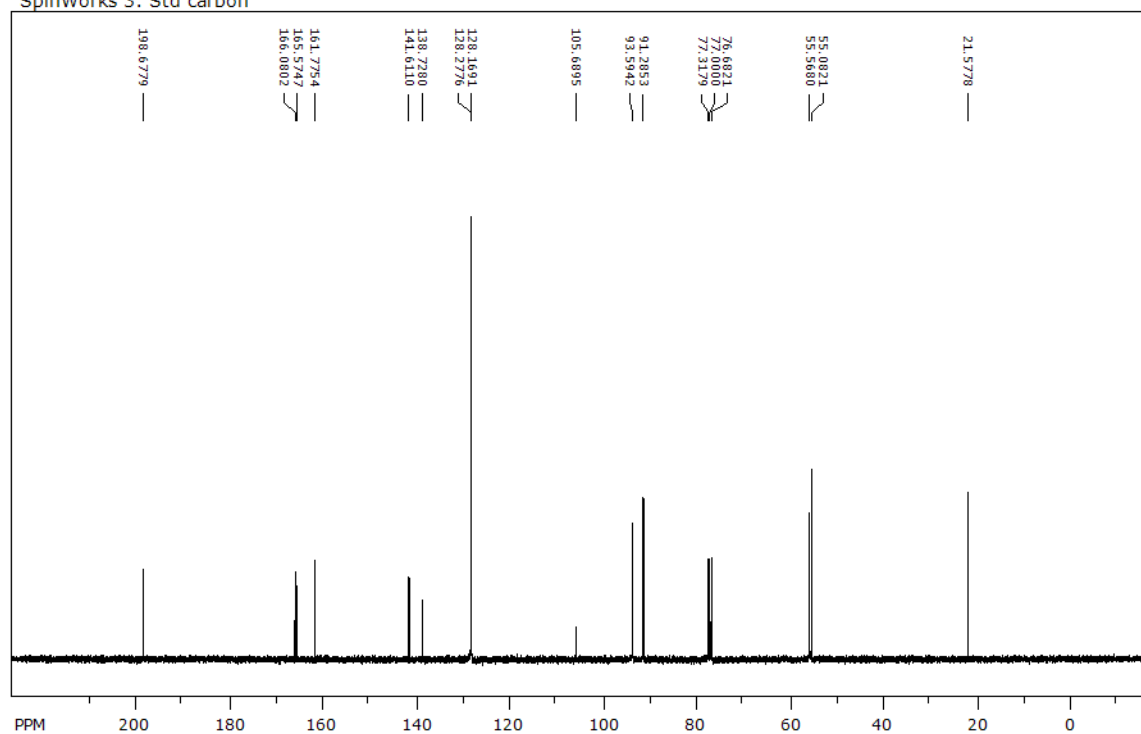


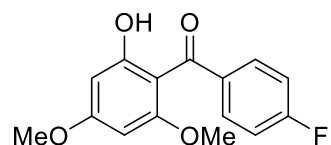
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SpinWorks 3: Std proton



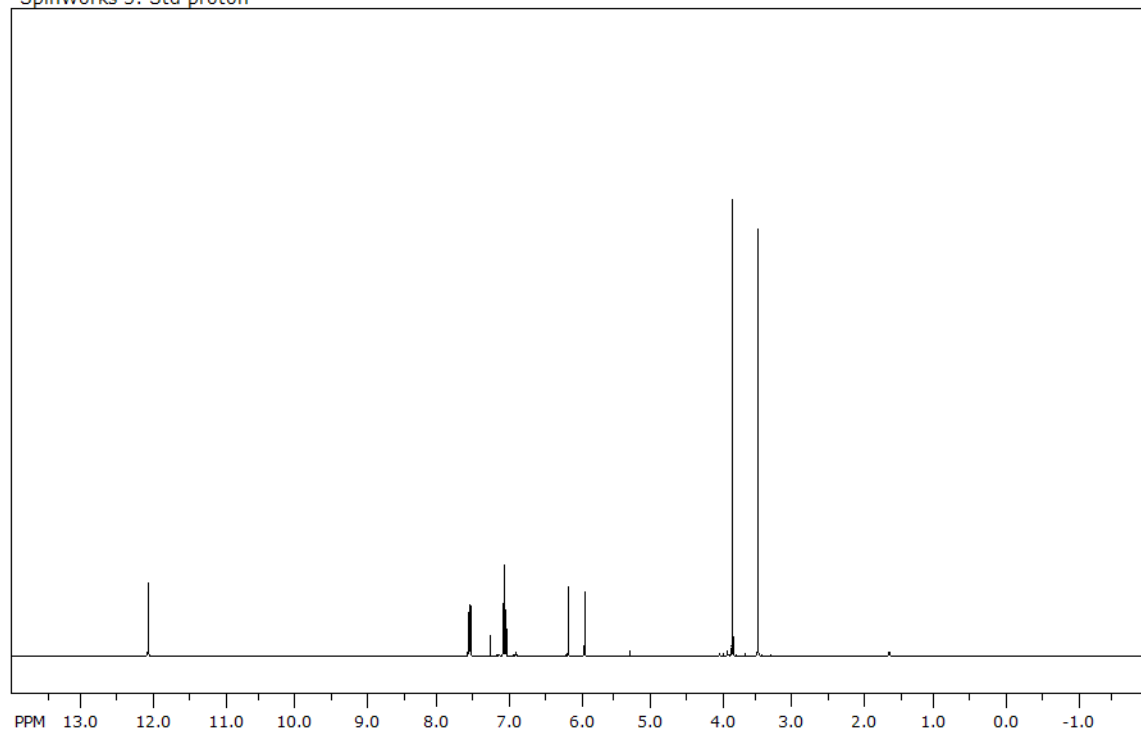
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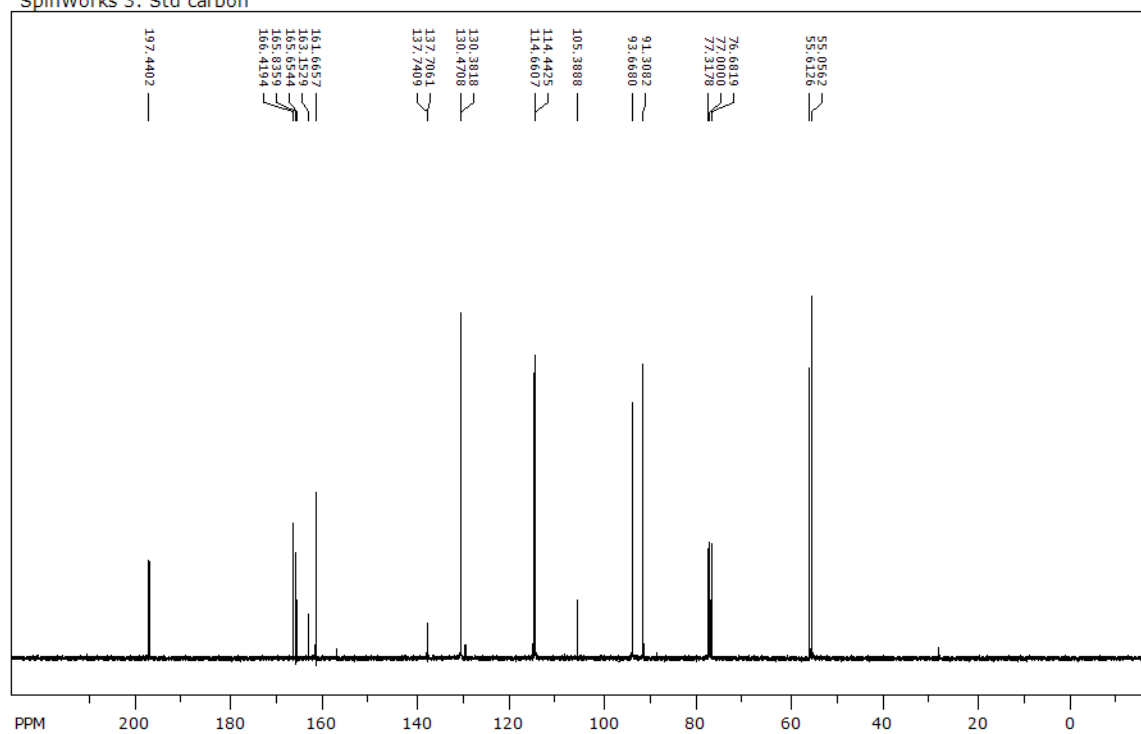


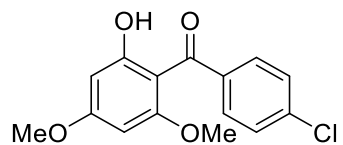
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SpinWorks 3: Std proton



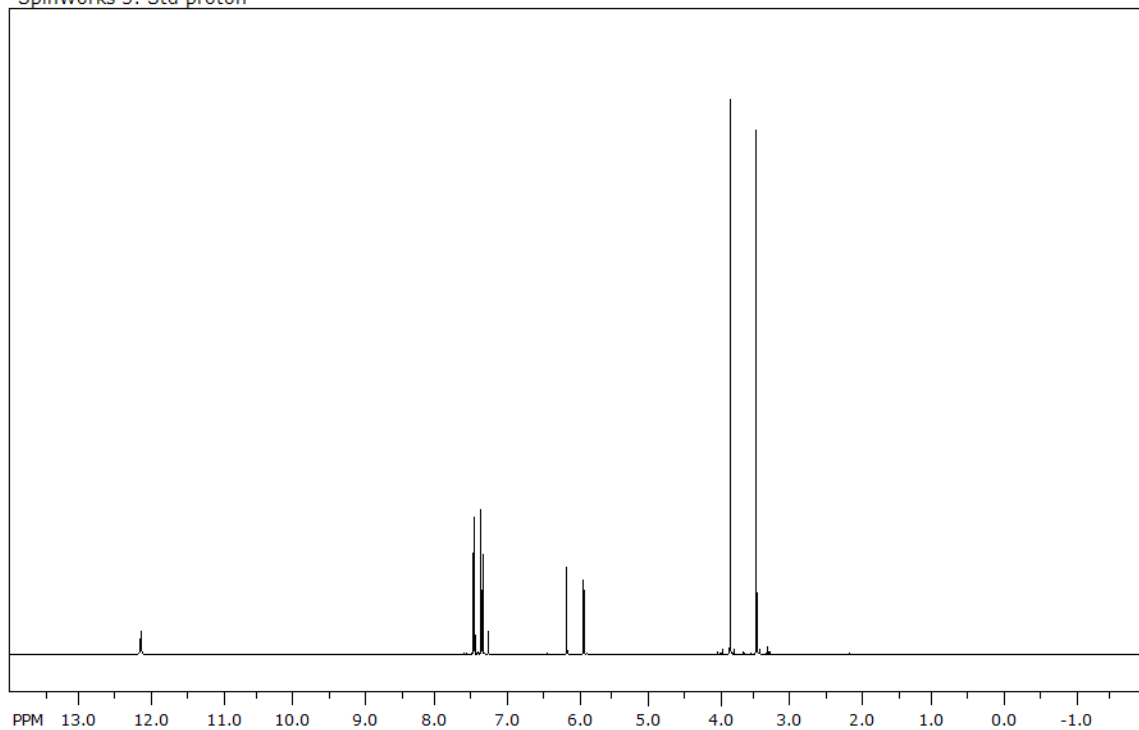
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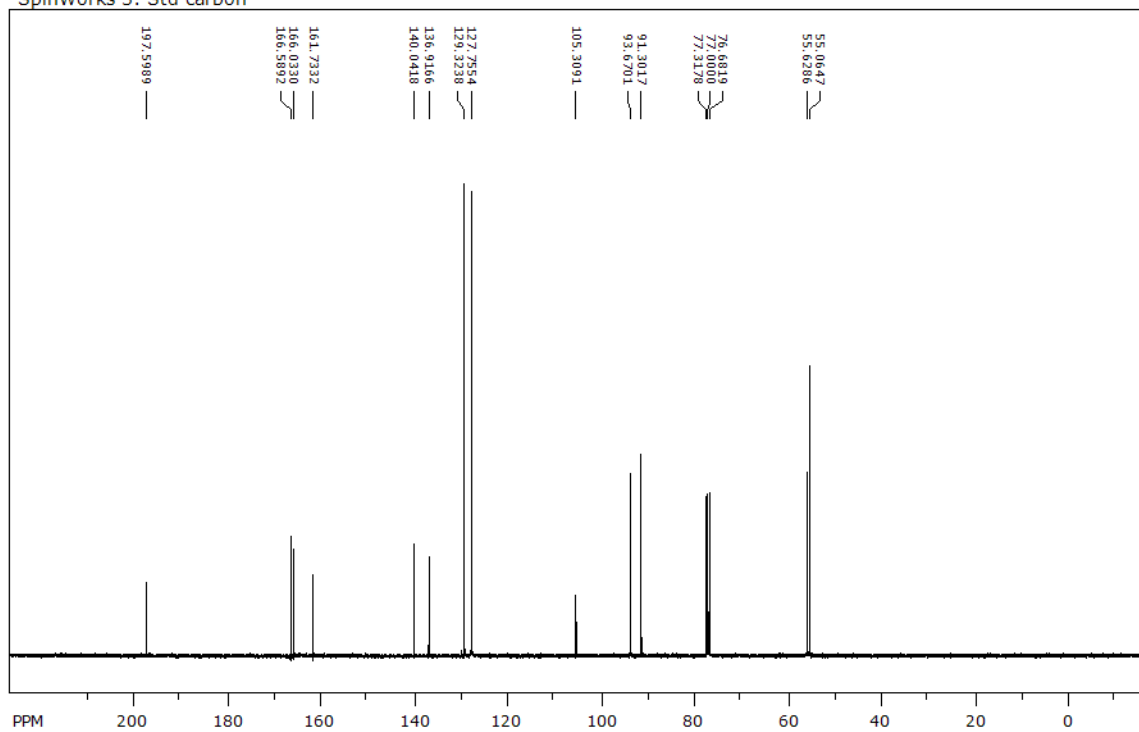


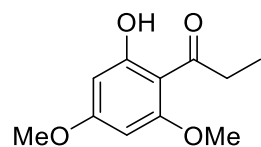
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SpinWorks 3: Std proton



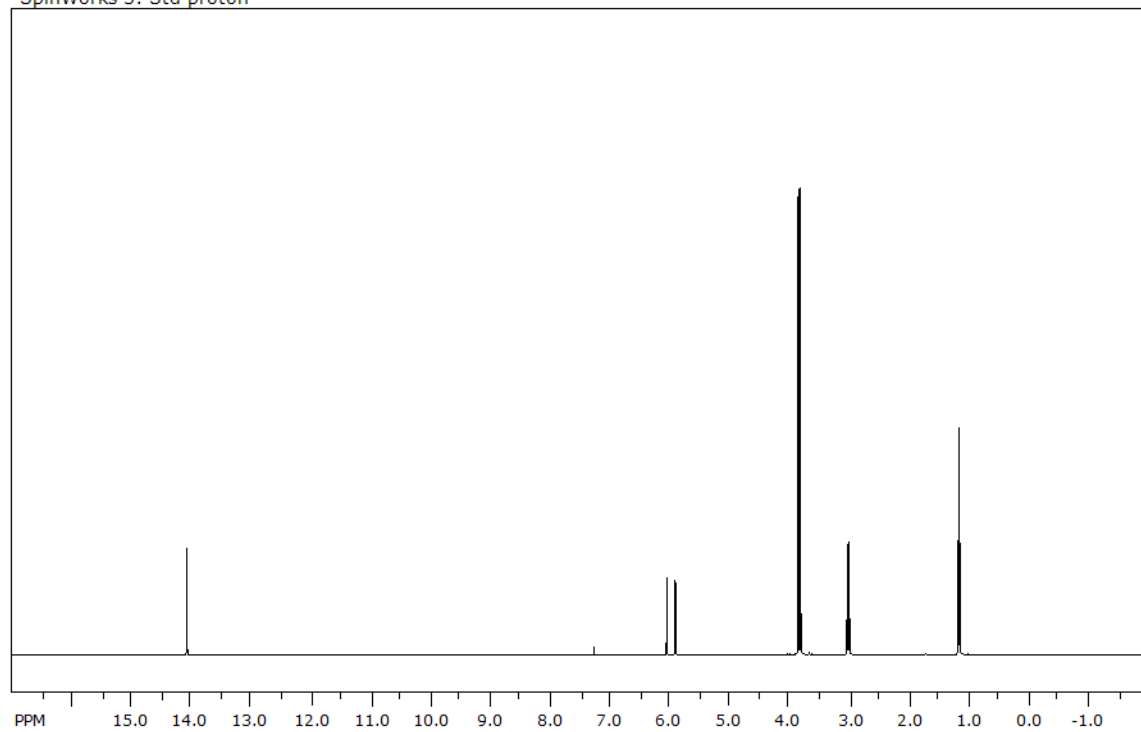
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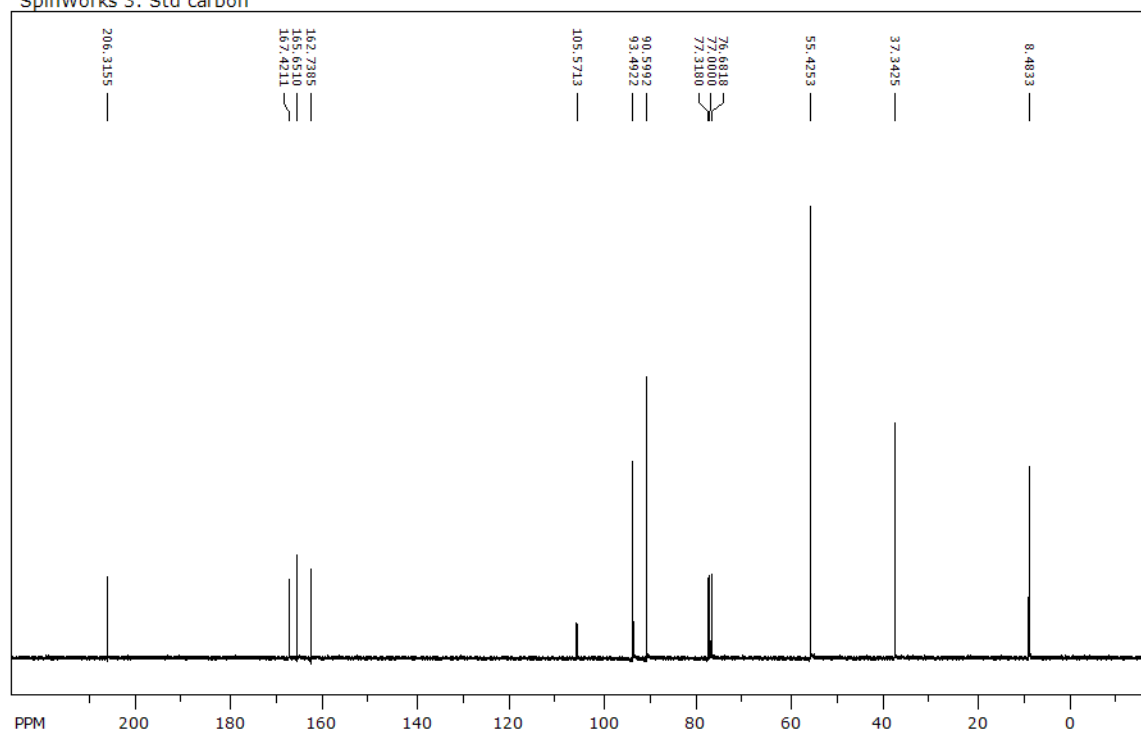


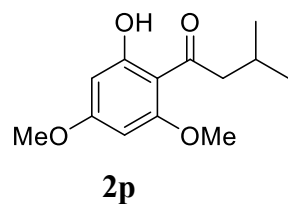
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SpinWorks 3: Std proton

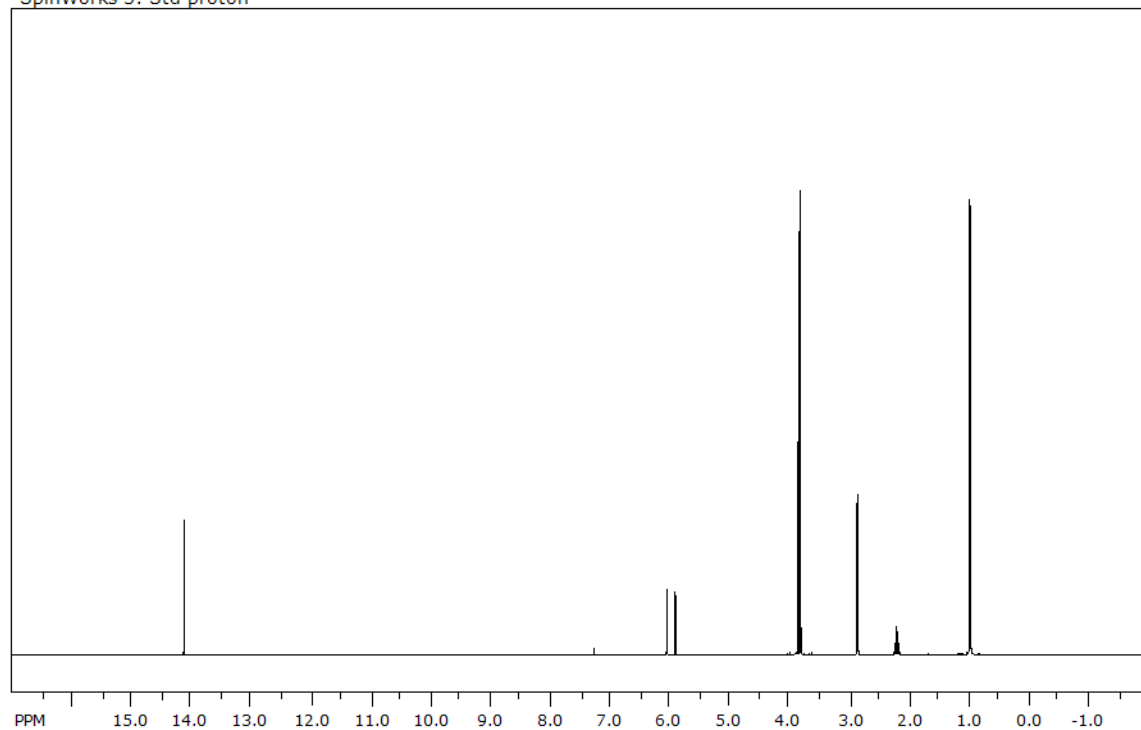


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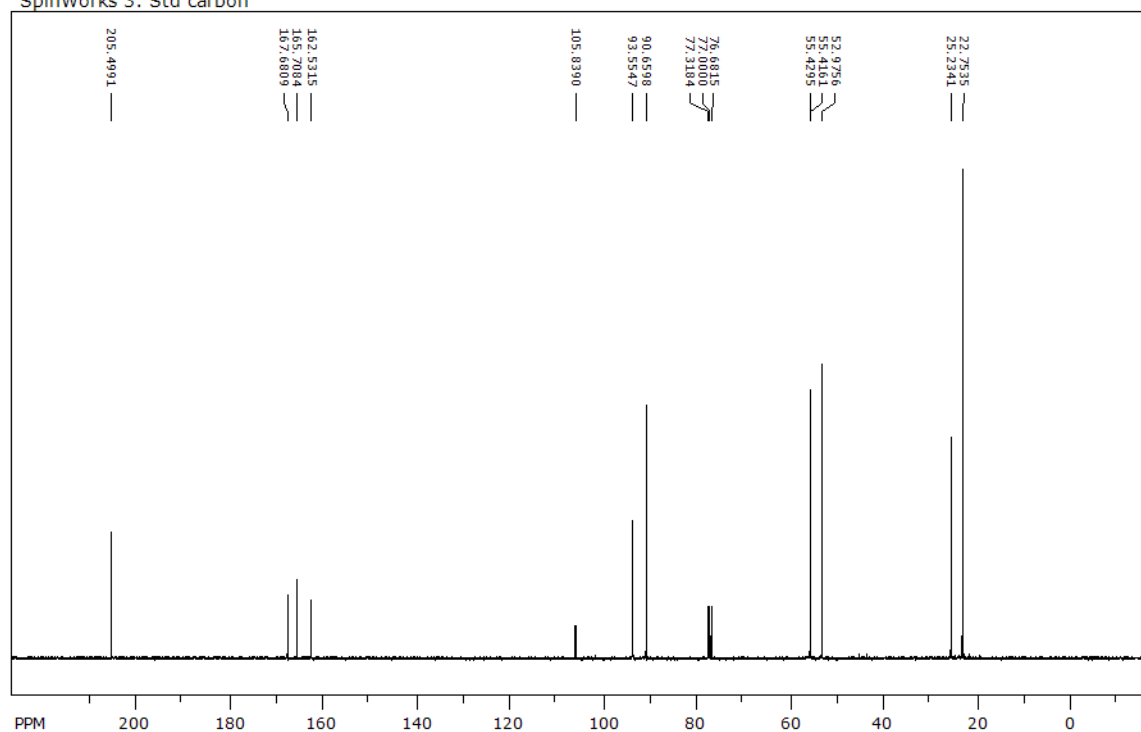


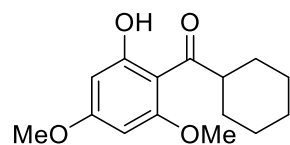


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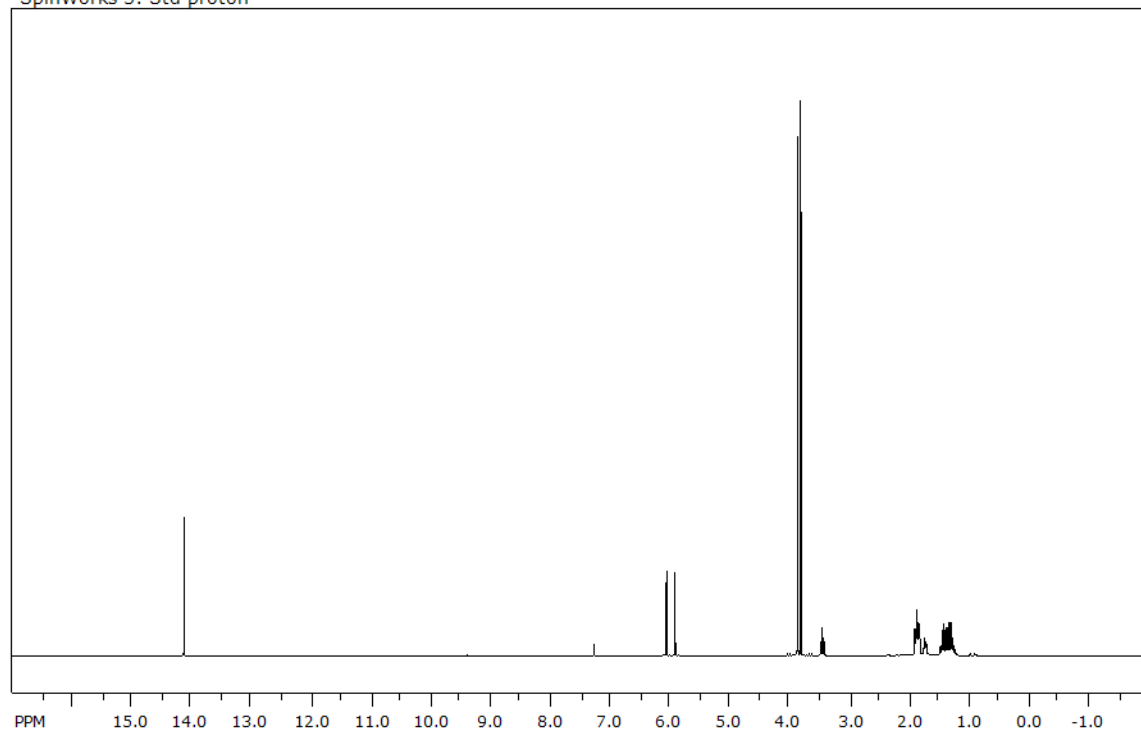
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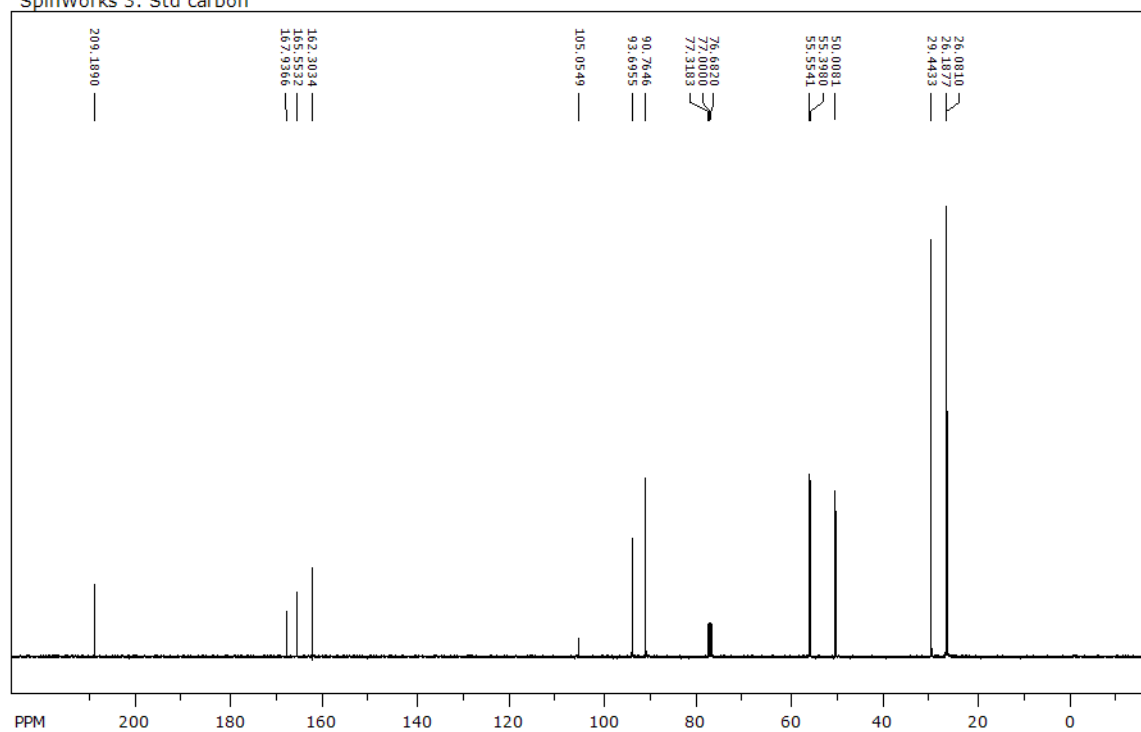


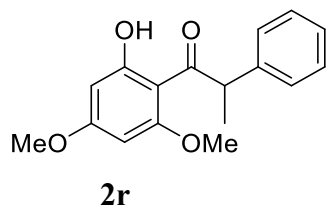
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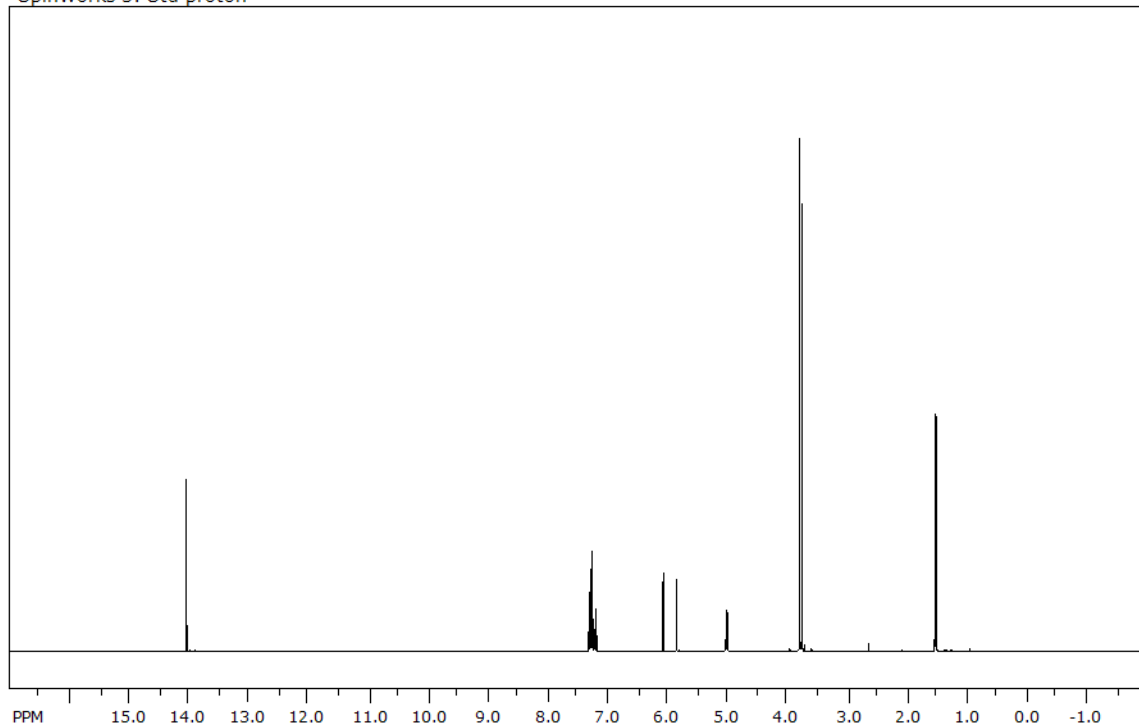


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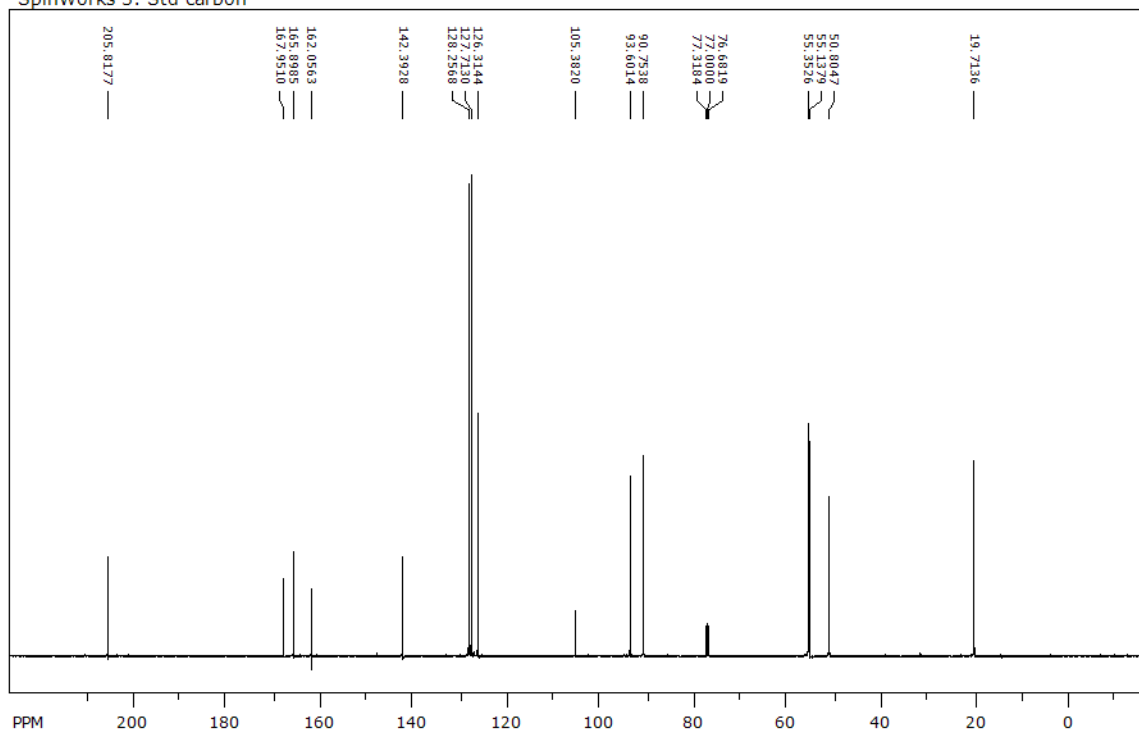


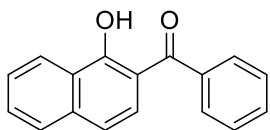


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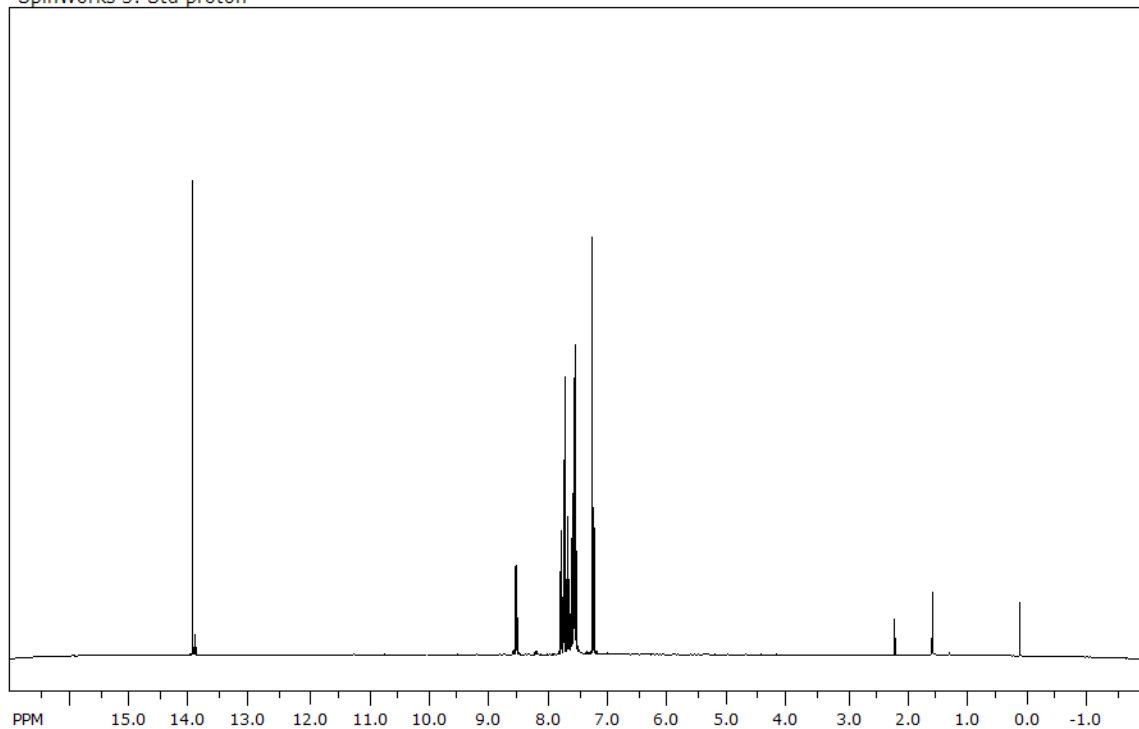
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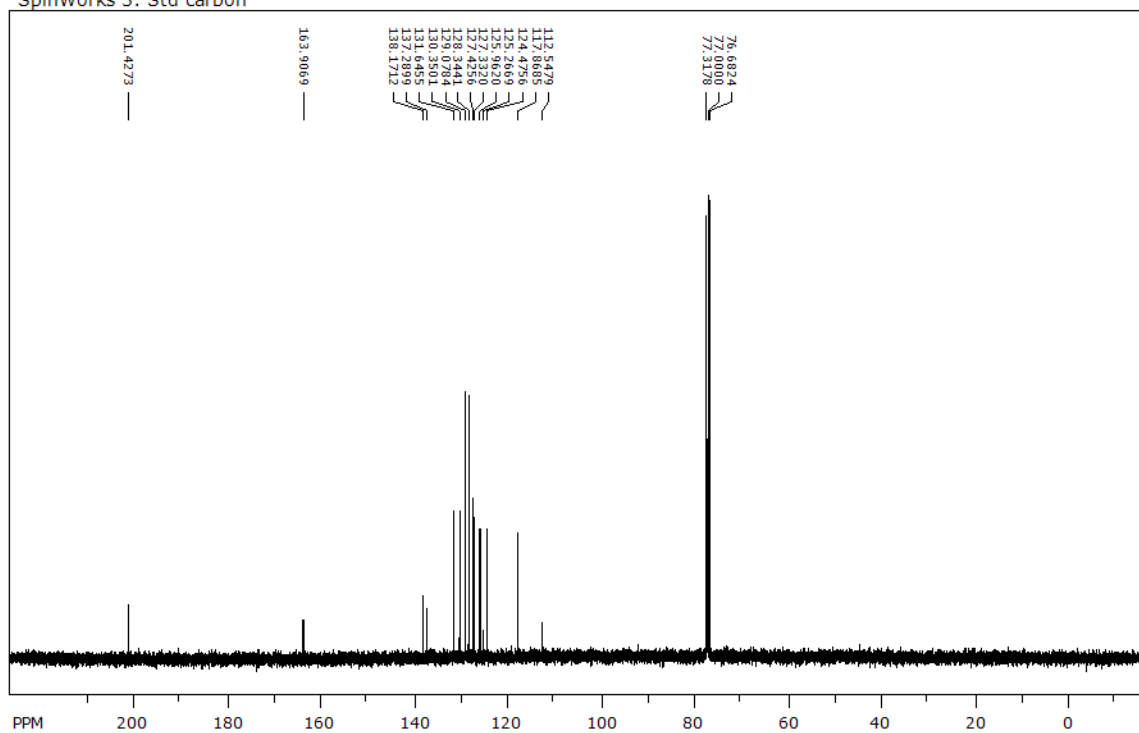


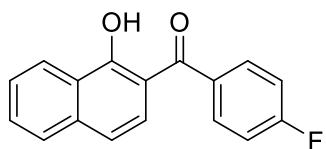
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SpinWorks 3: Std proton



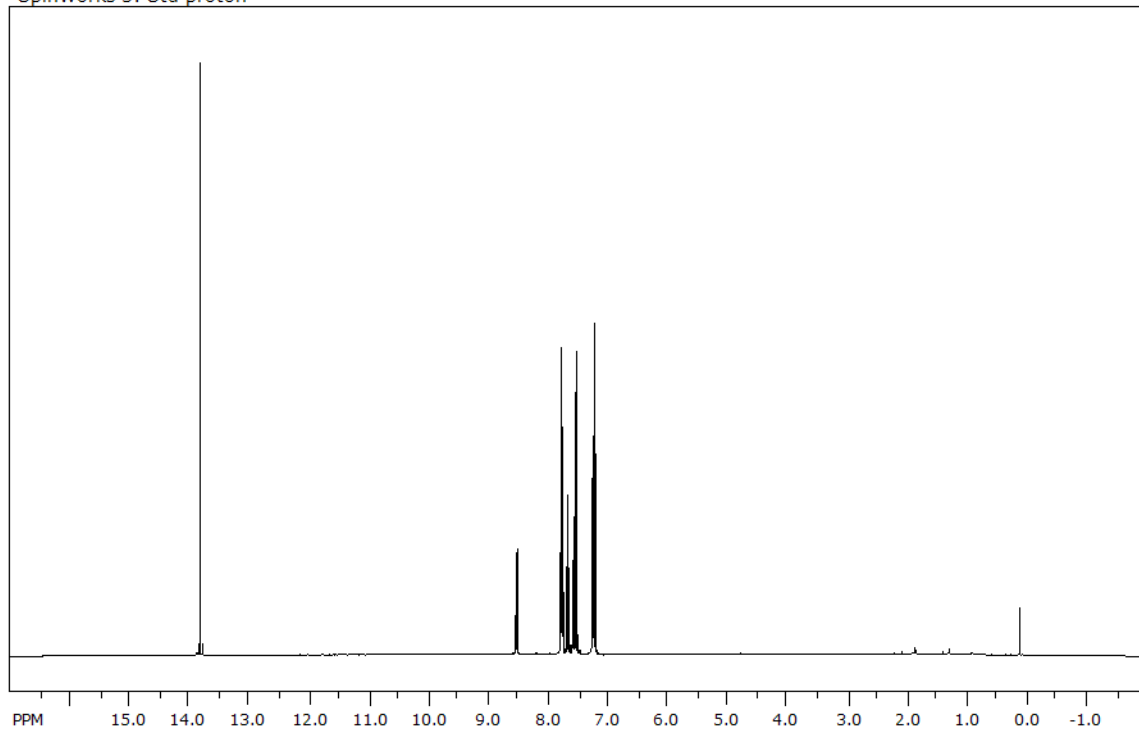
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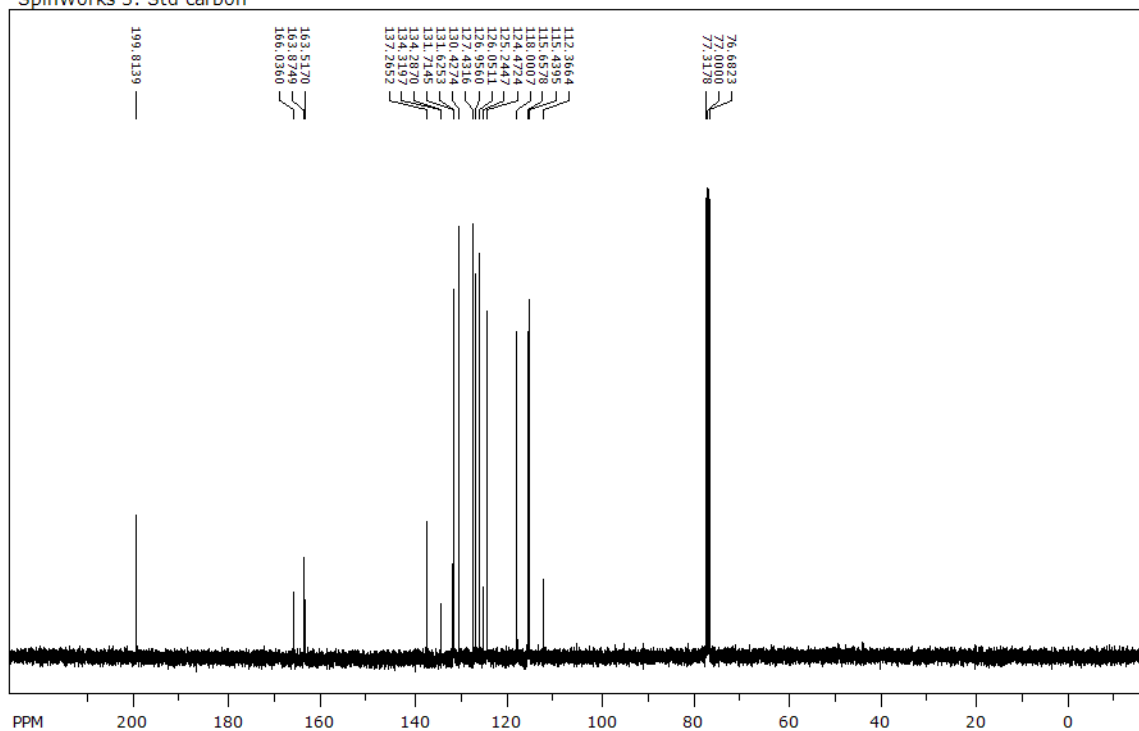


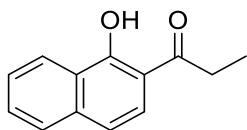
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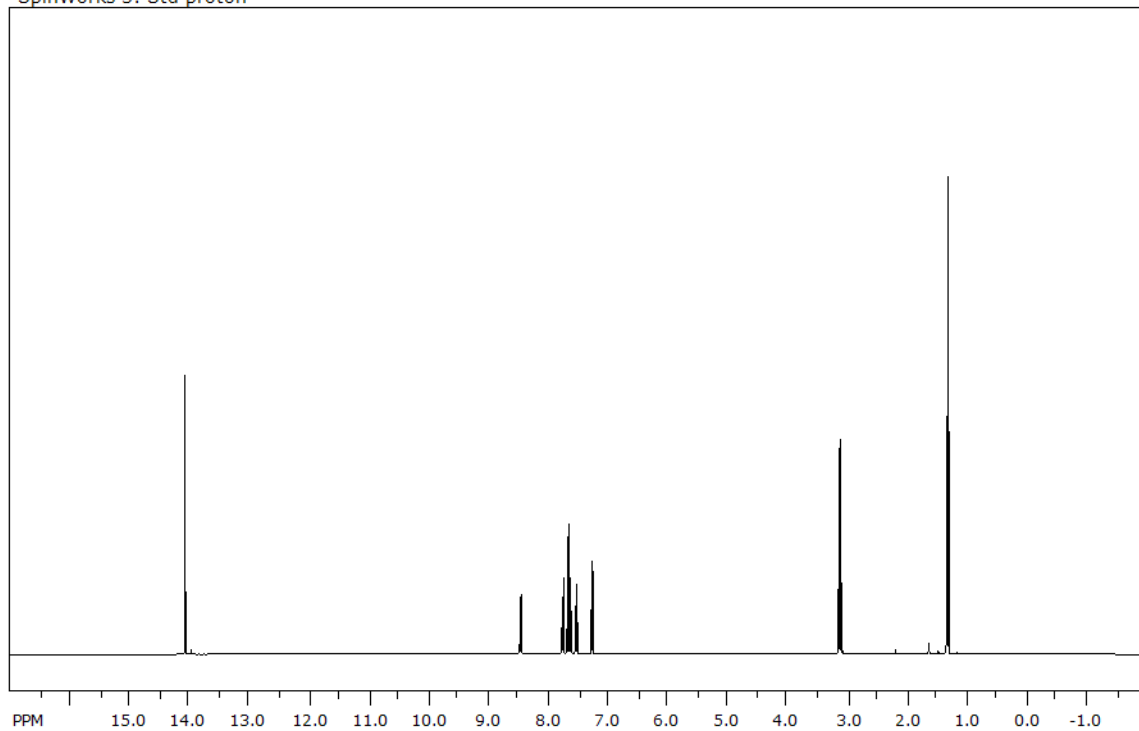
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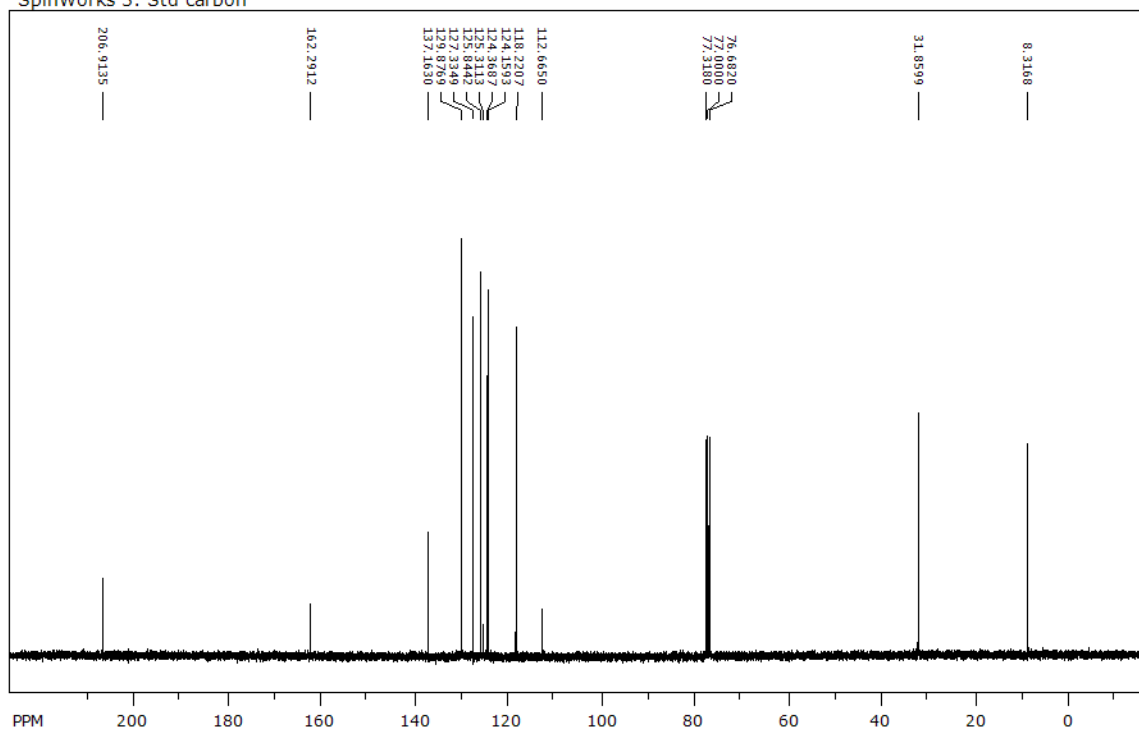


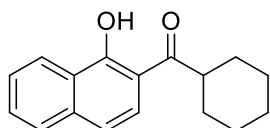
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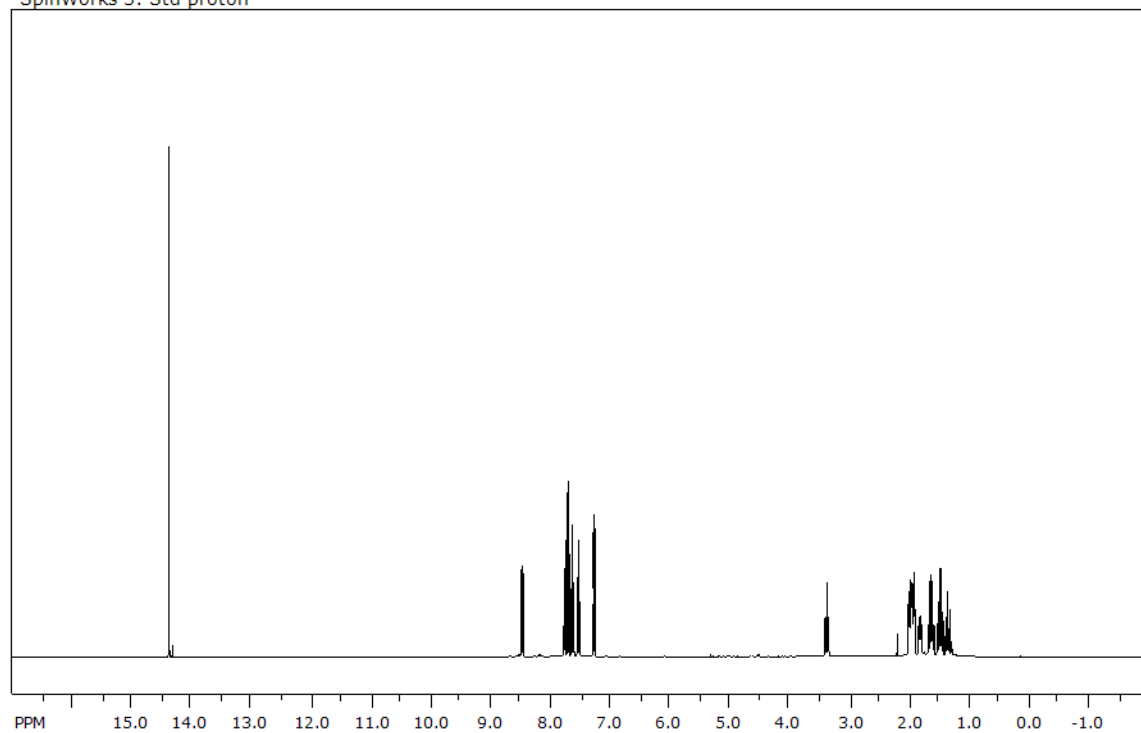
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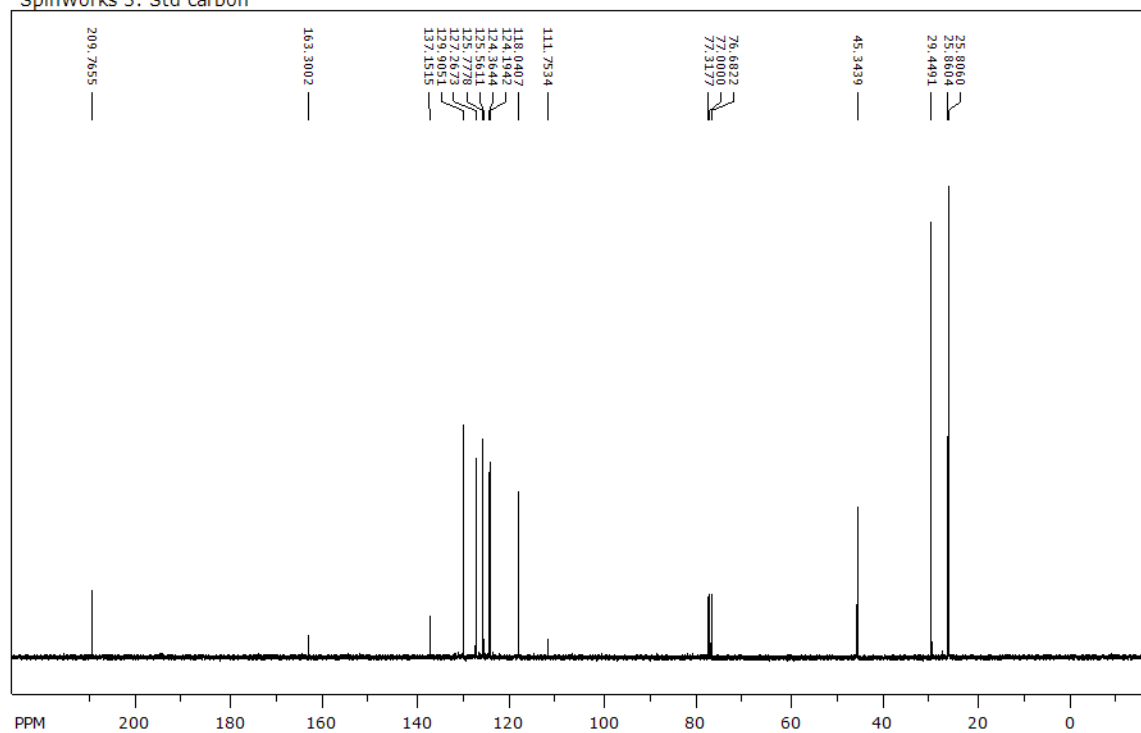


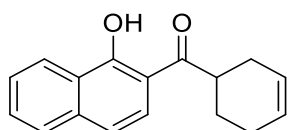
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SpinWorks 3: Std proton



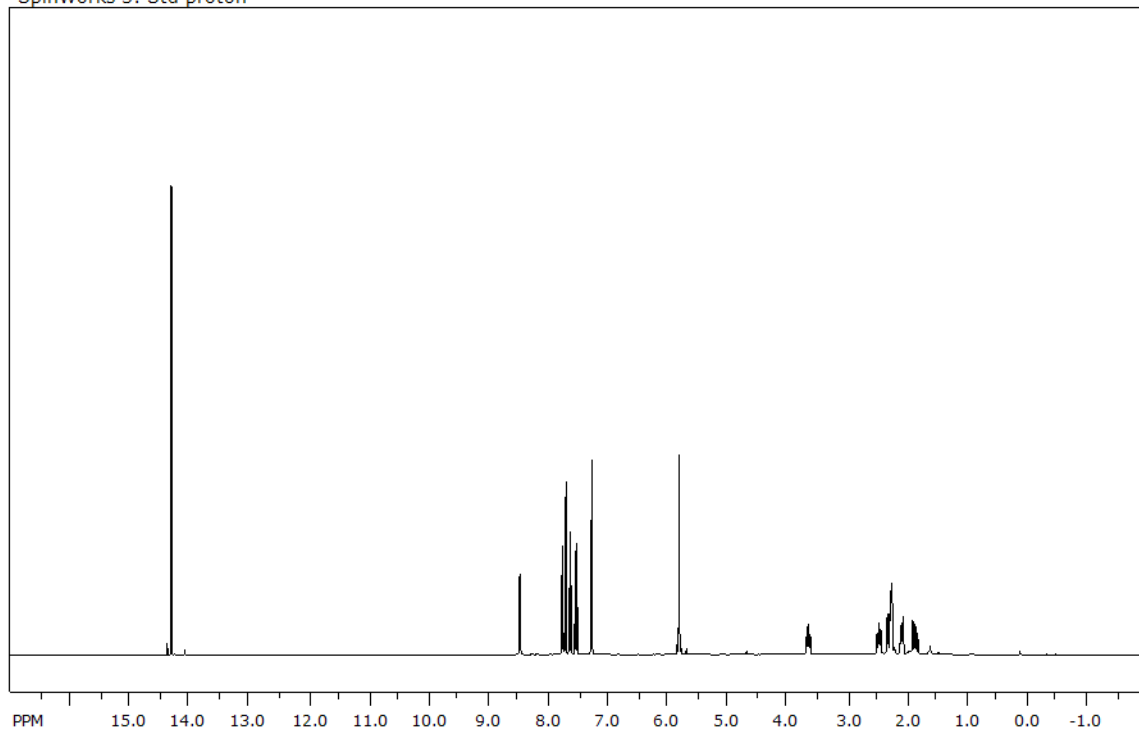
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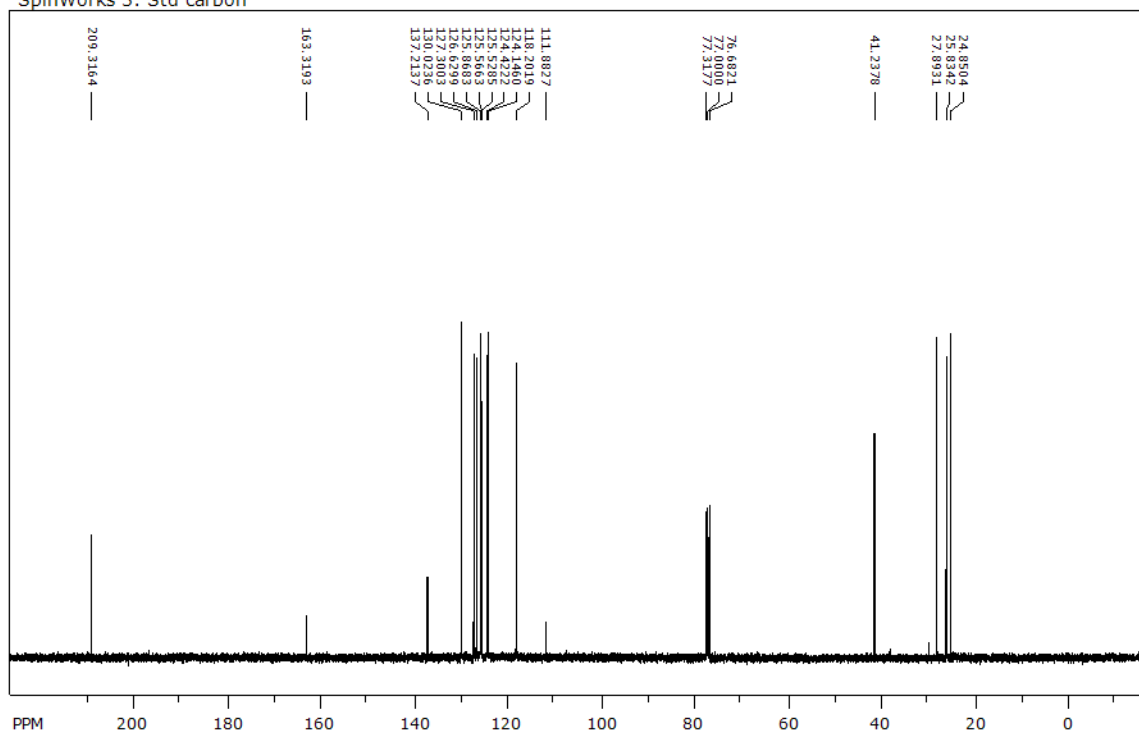


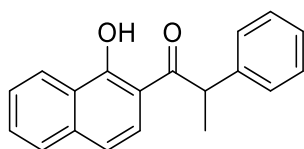
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SpinWorks 3: Std proton



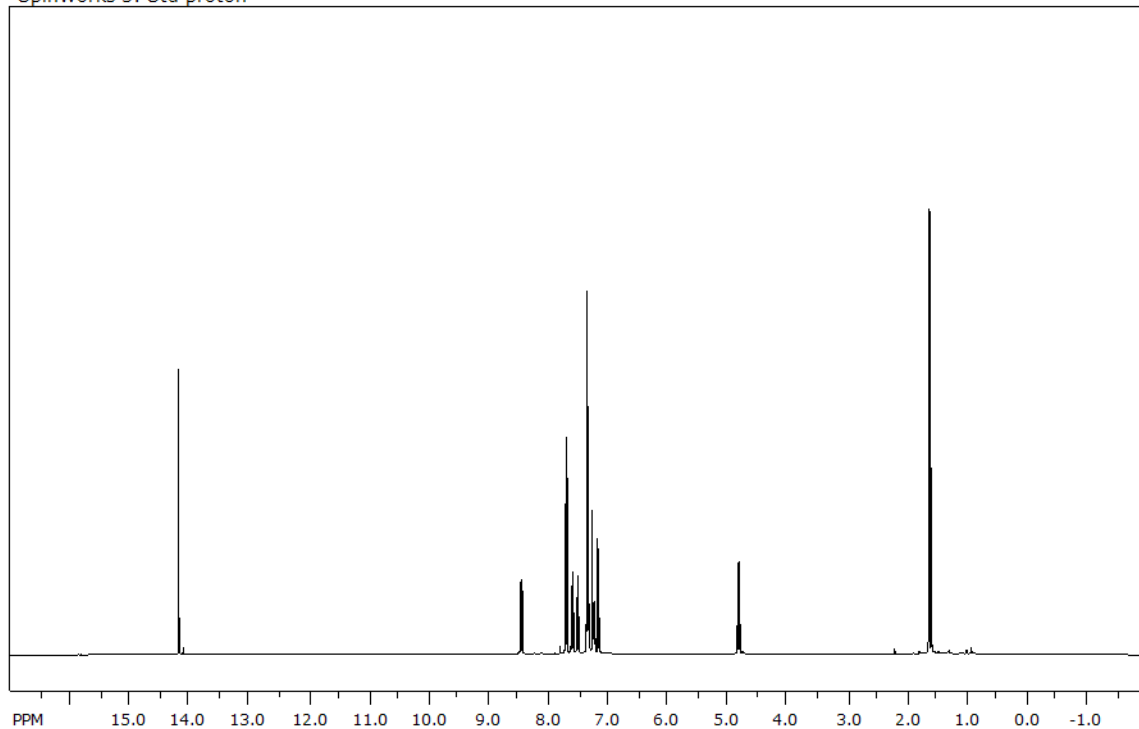
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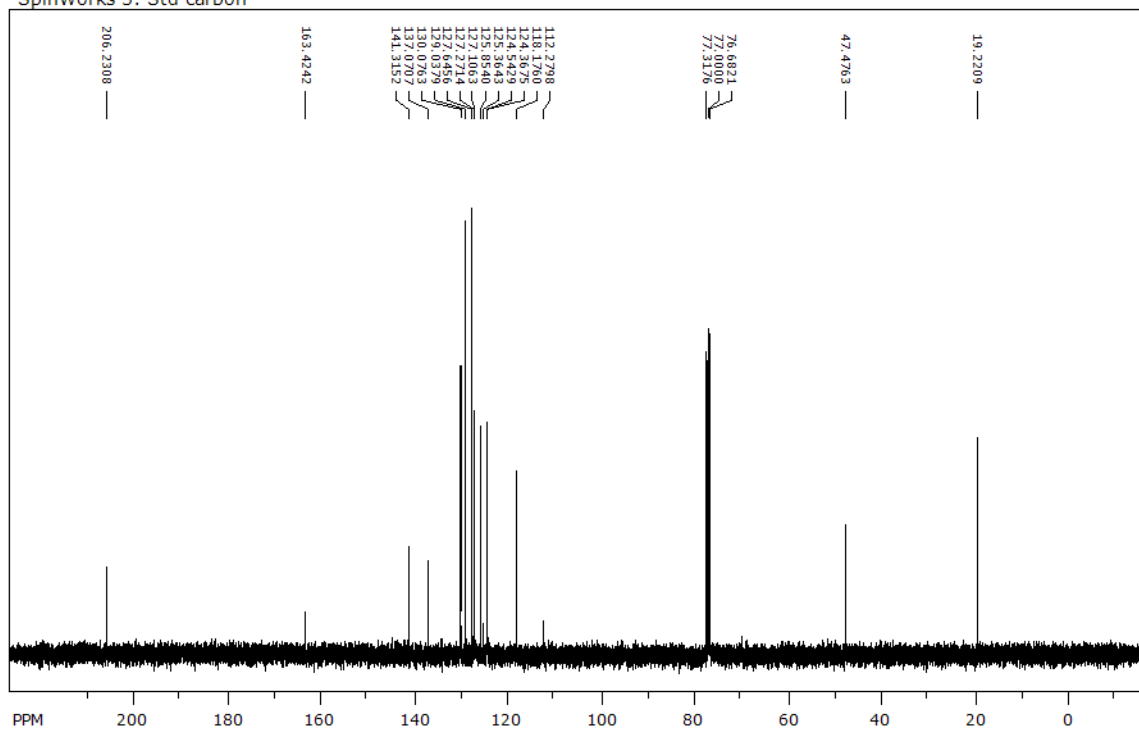


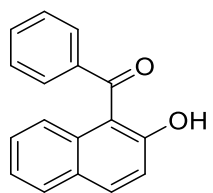
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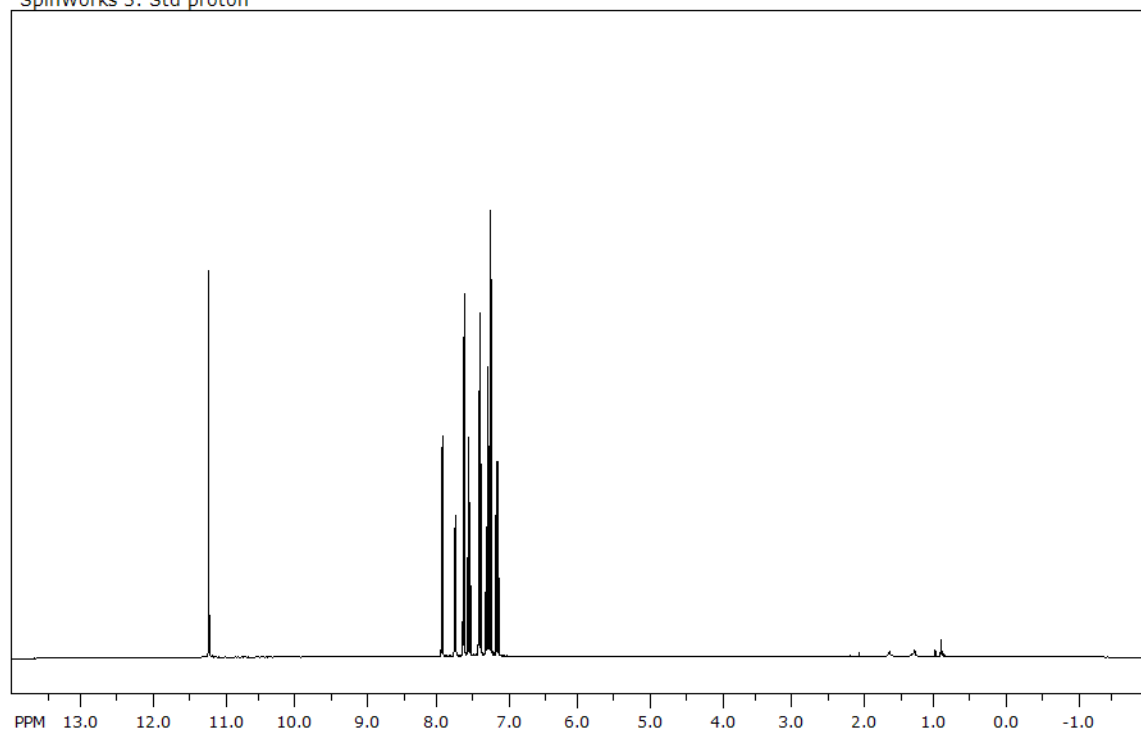
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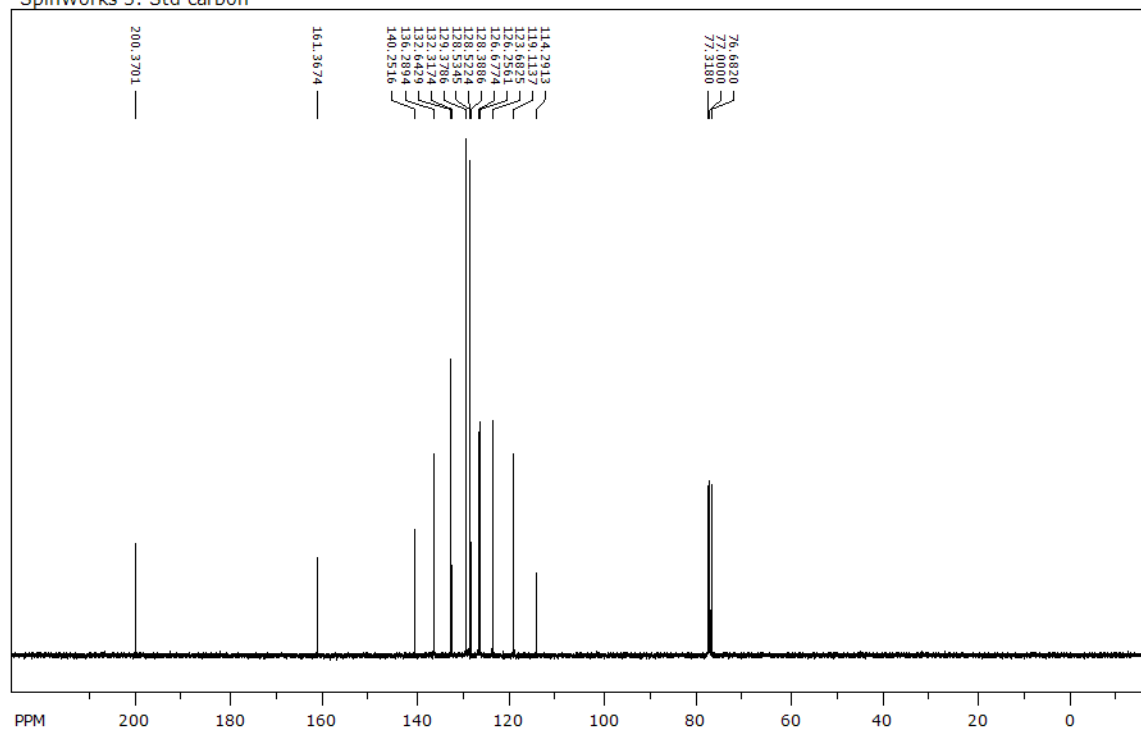


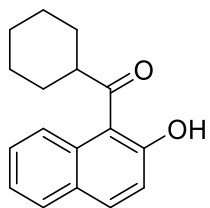
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SpinWorks 3: Std proton



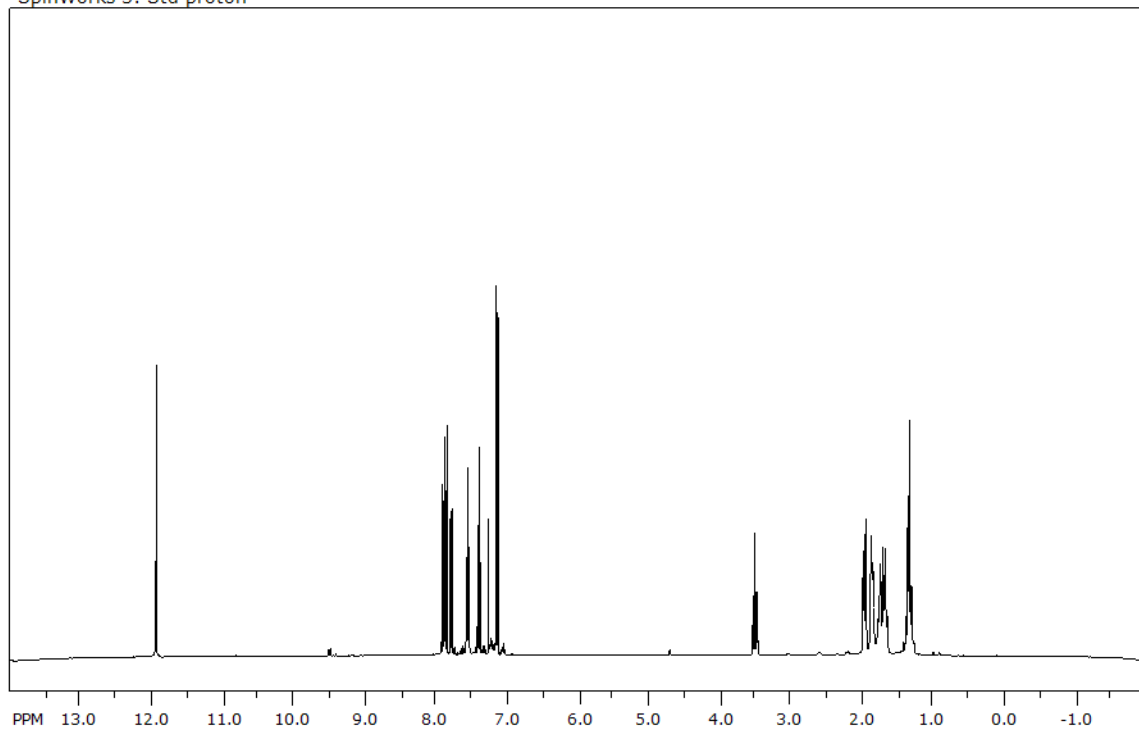
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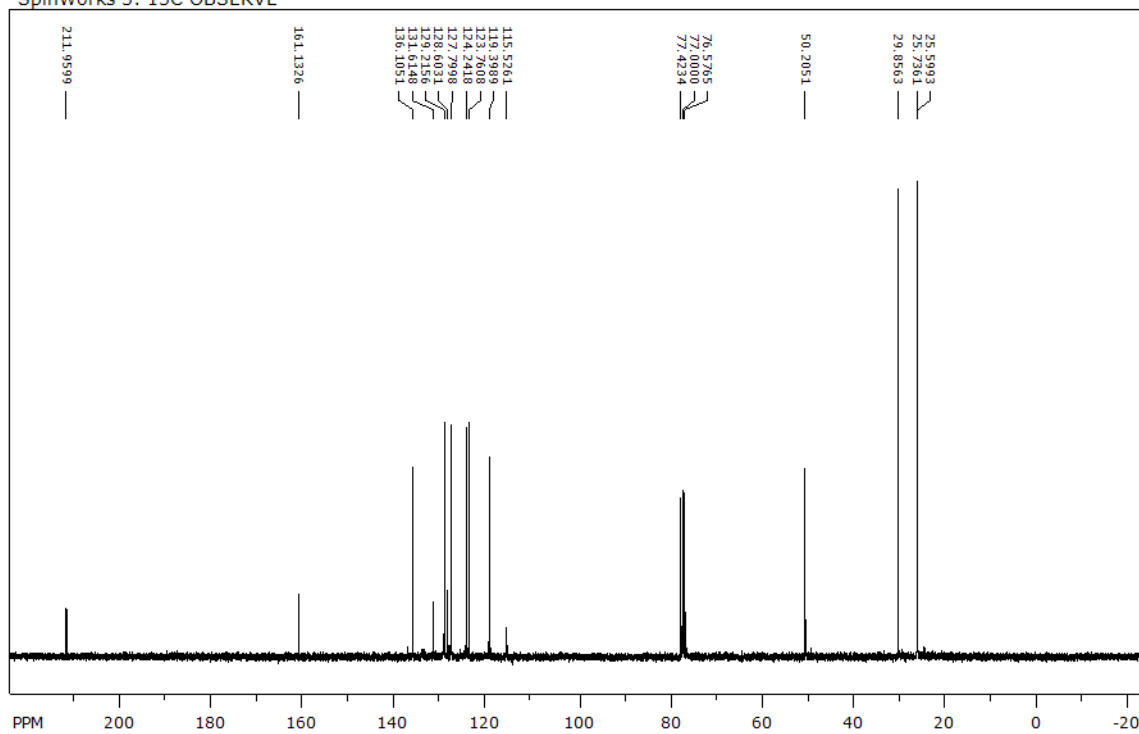


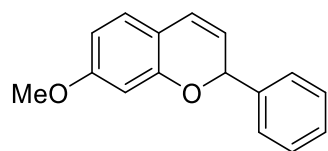
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SpinWorks 3: Std proton



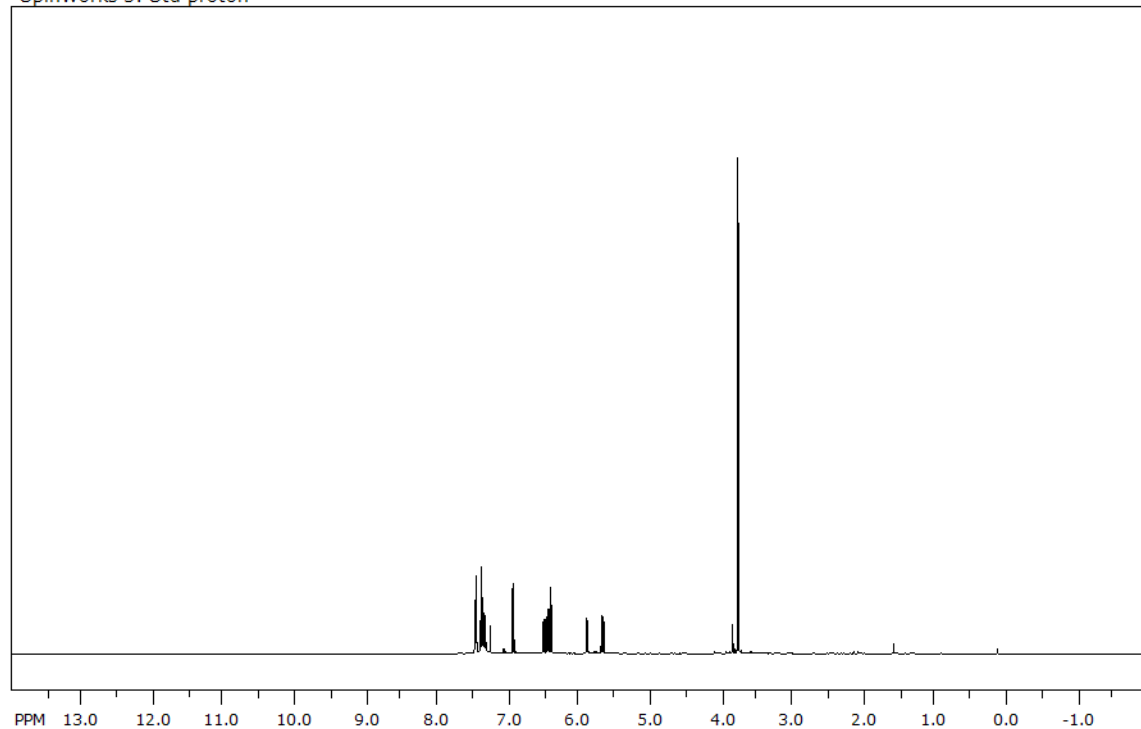
SpinWorks 3: 13C OBSERVE



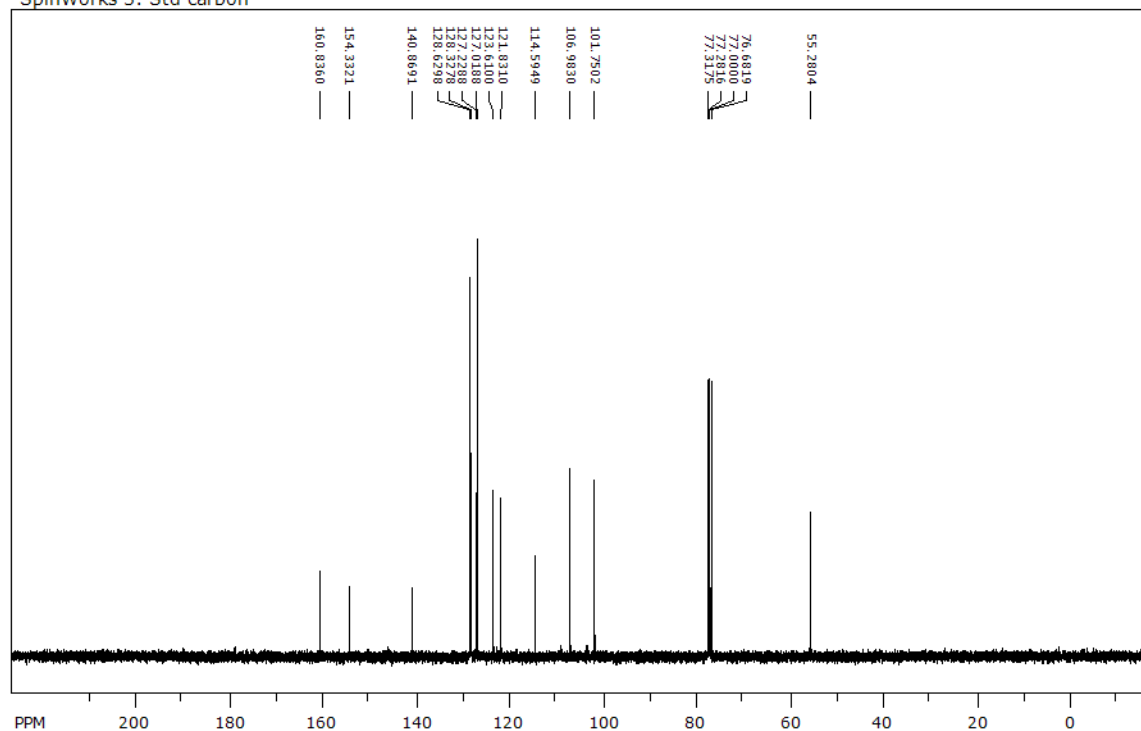


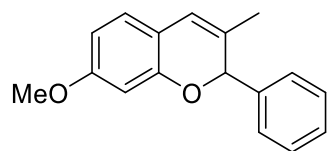
3b

SpinWorks 3: Std proton



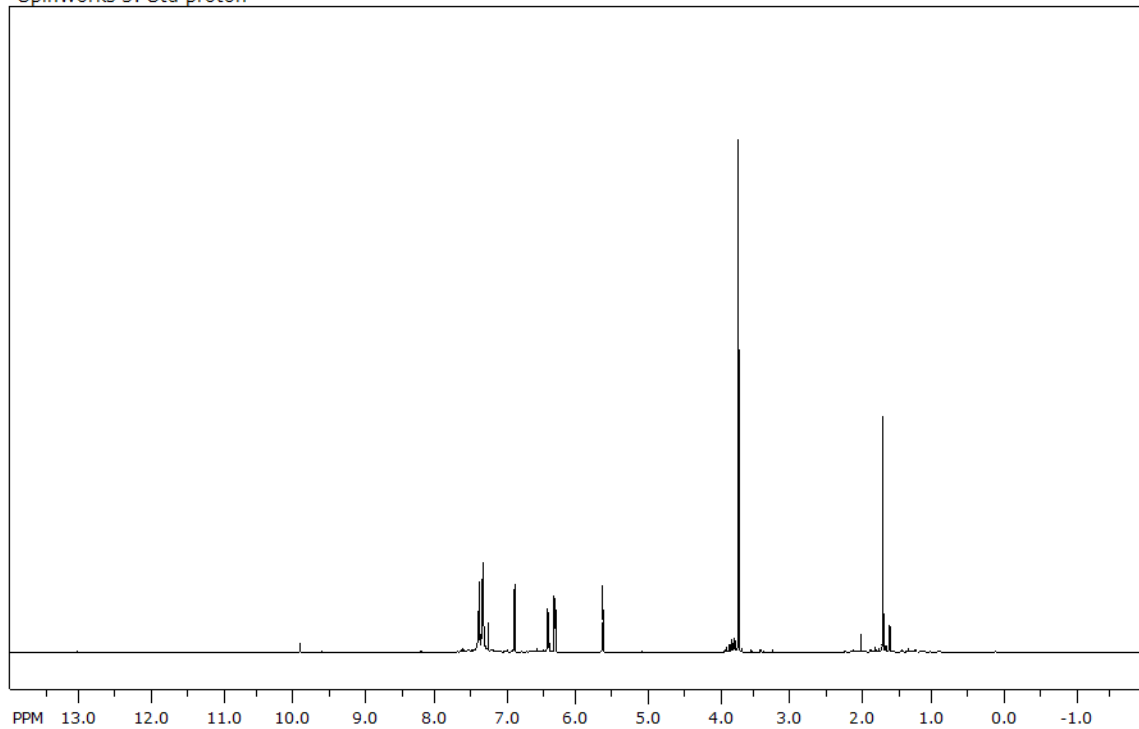
SpinWorks 3: Std carbon



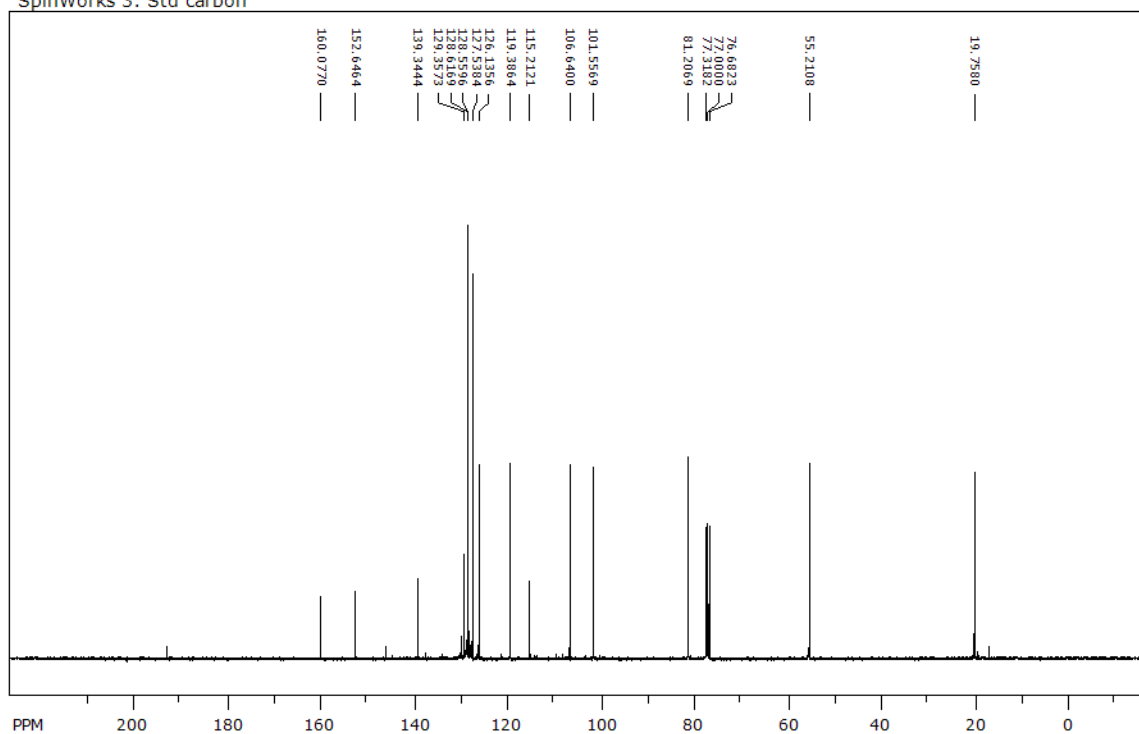


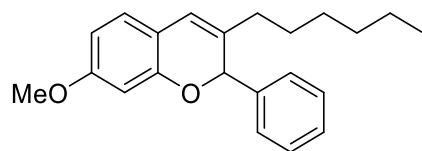
3c

SpinWorks 3: Std proton



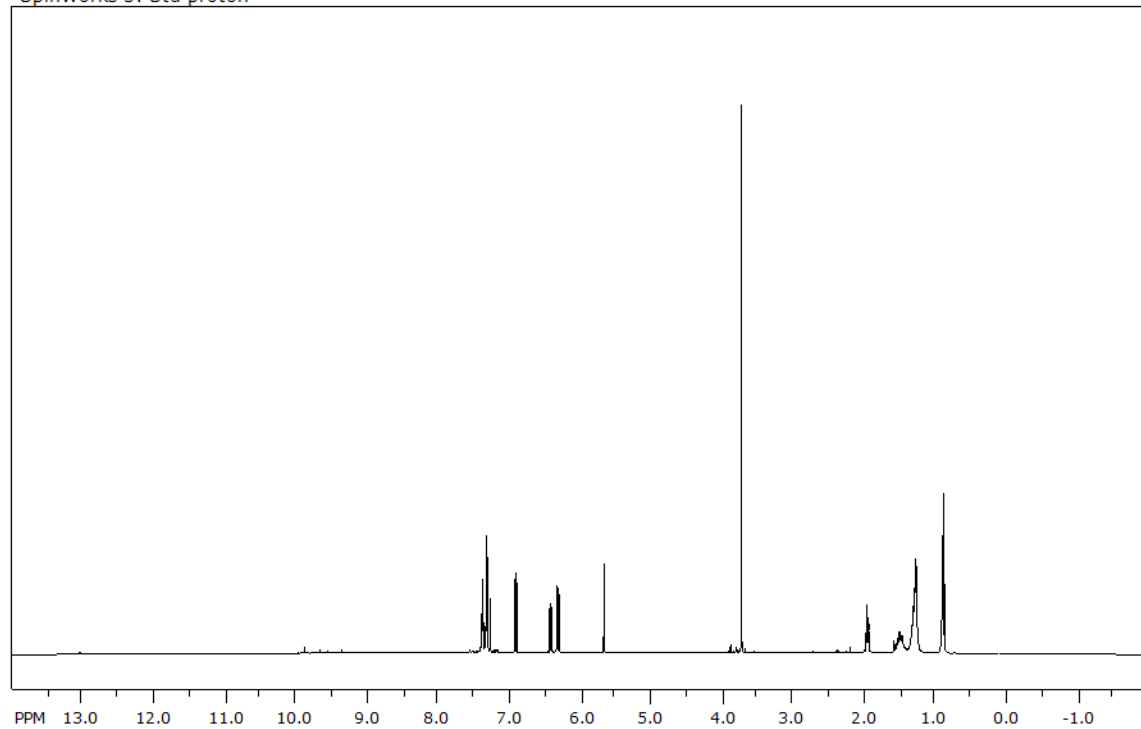
SpinWorks 3: Std carbon



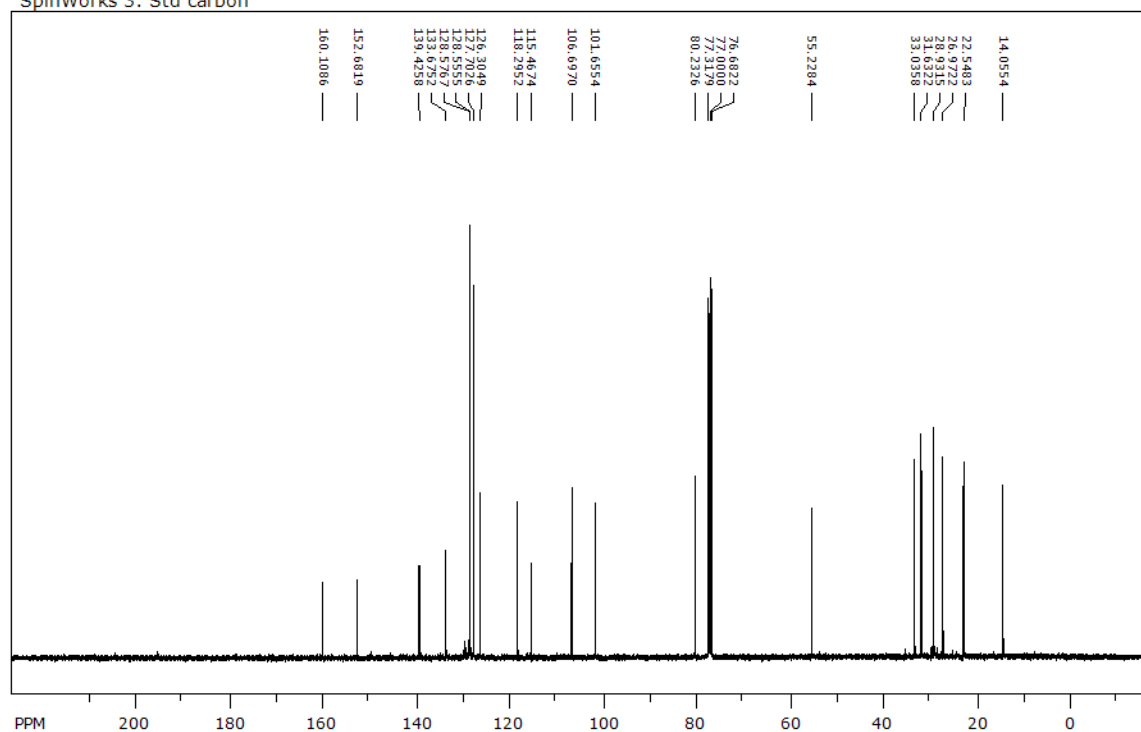


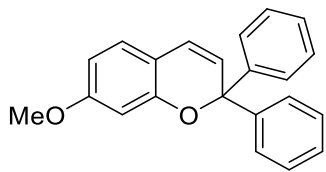
3d

SpinWorks 3: Std proton



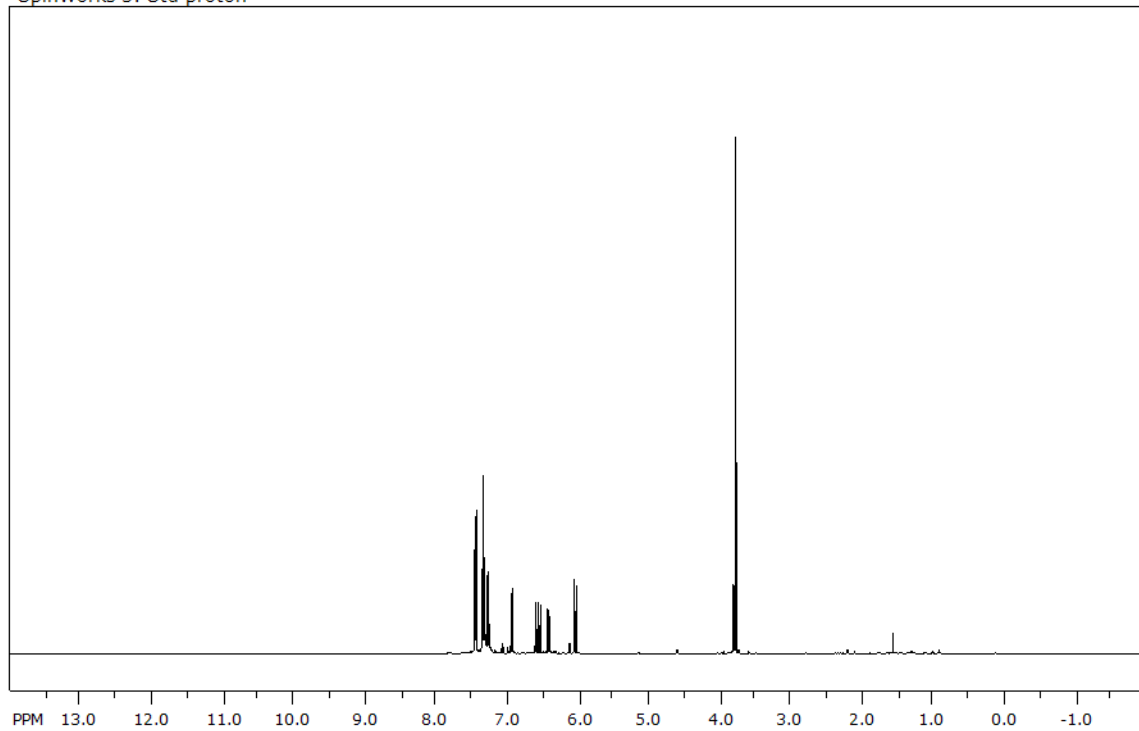
SpinWorks 3: Std carbon



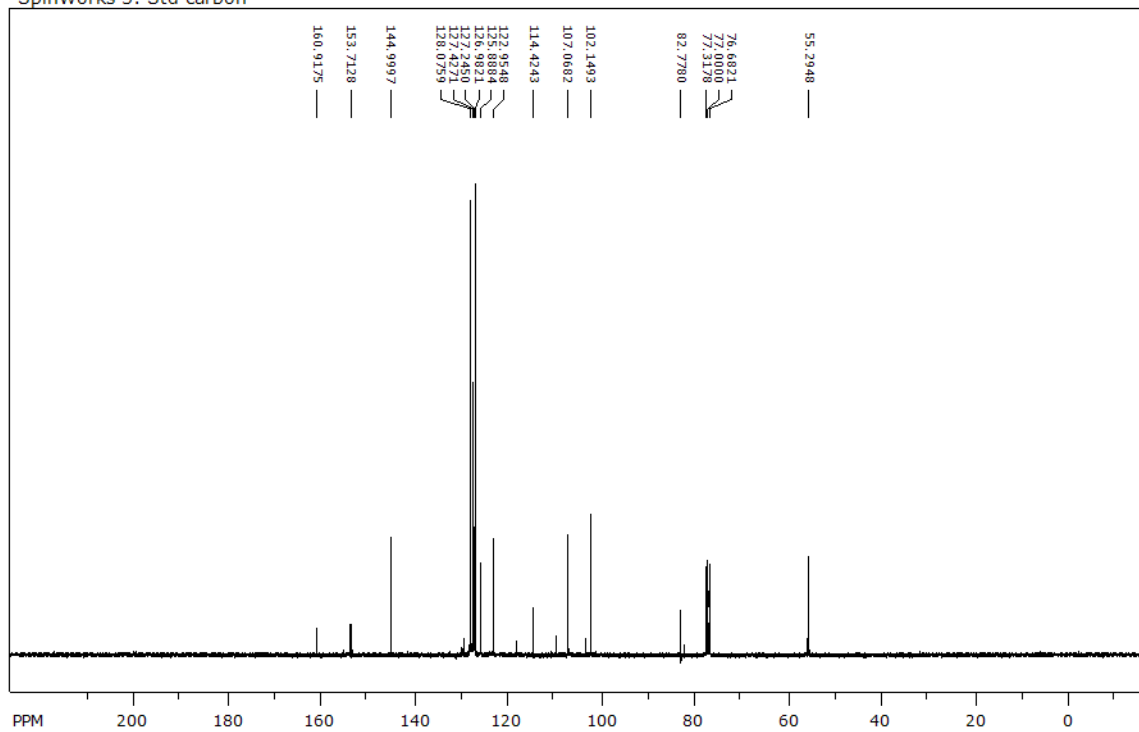


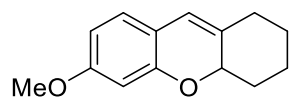
3e

SpinWorks 3: Std proton



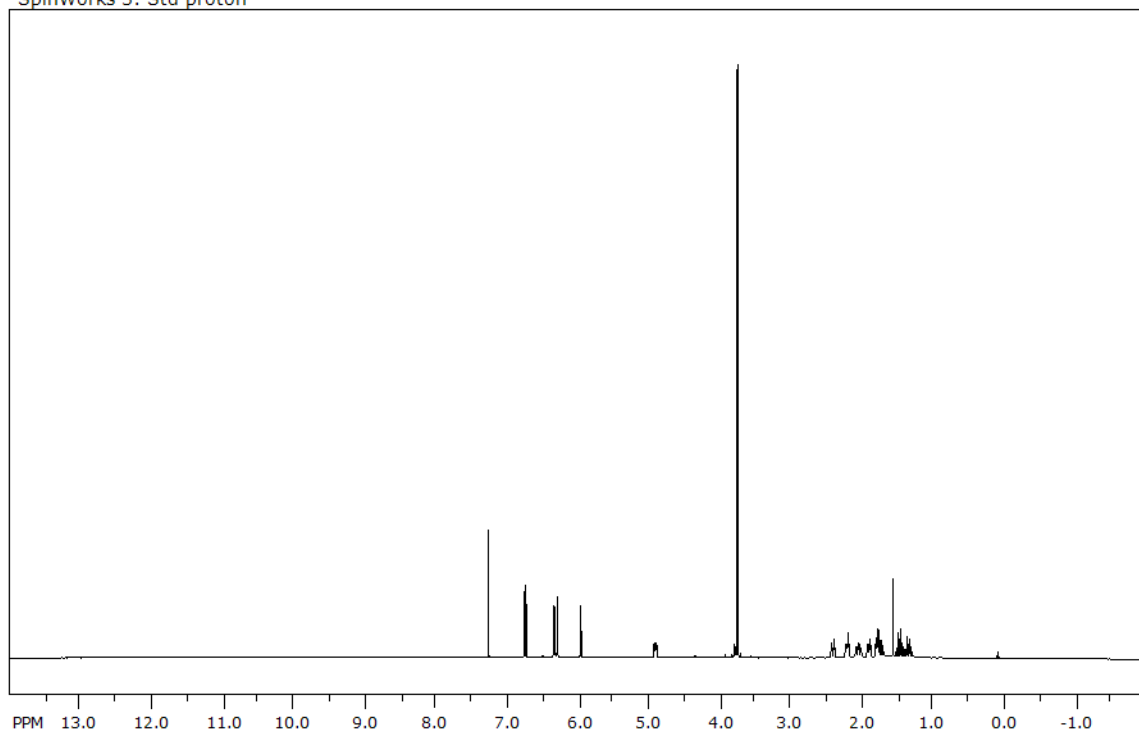
SpinWorks 3: Std carbon



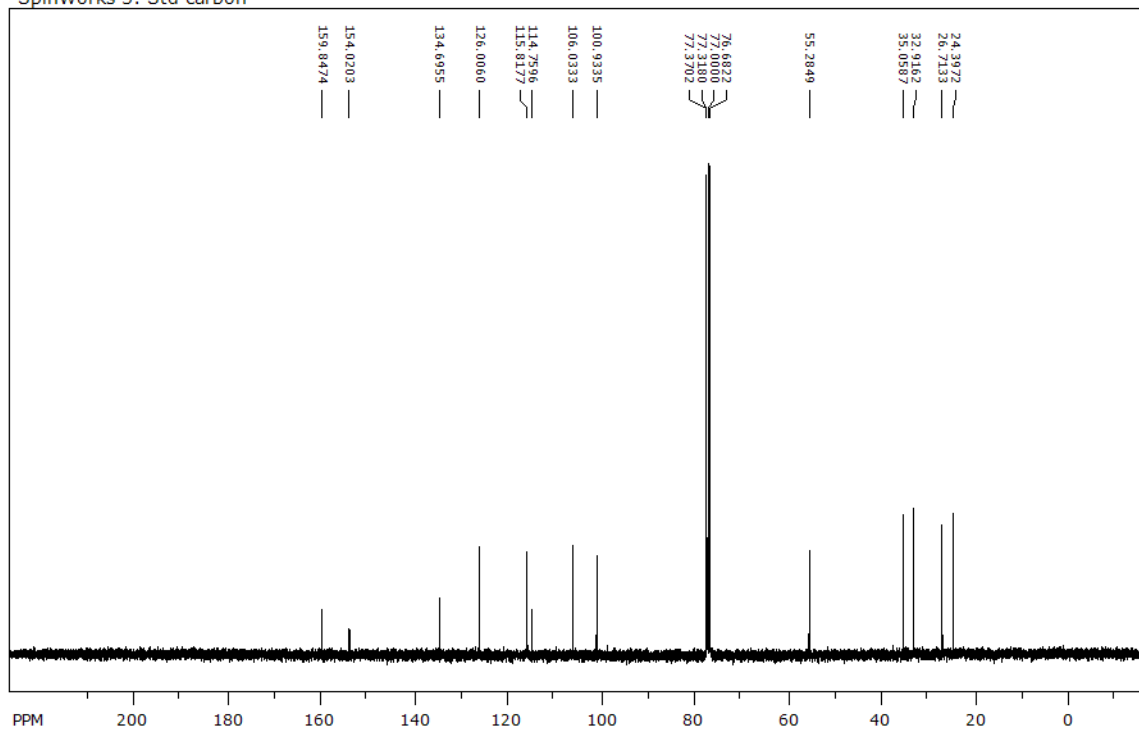


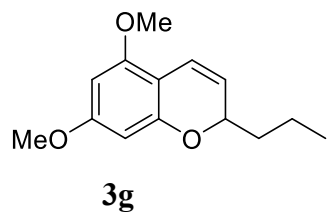
3f

SpinWorks 3: Std proton

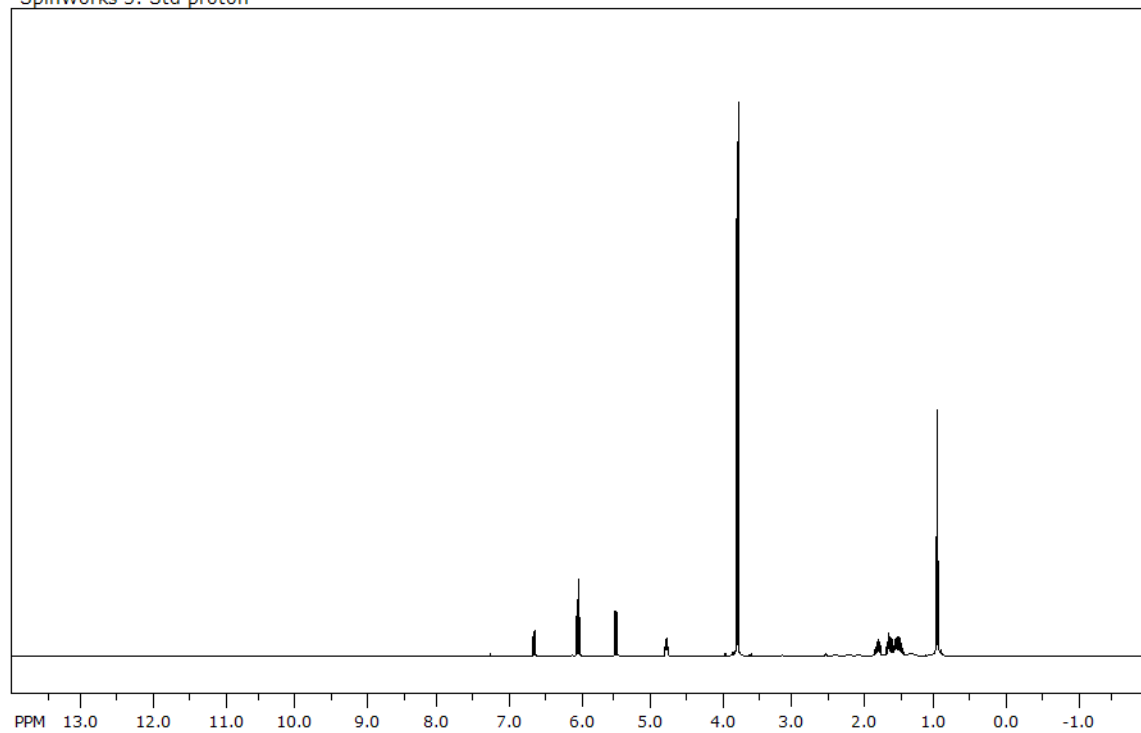


SpinWorks 3: Std carbon

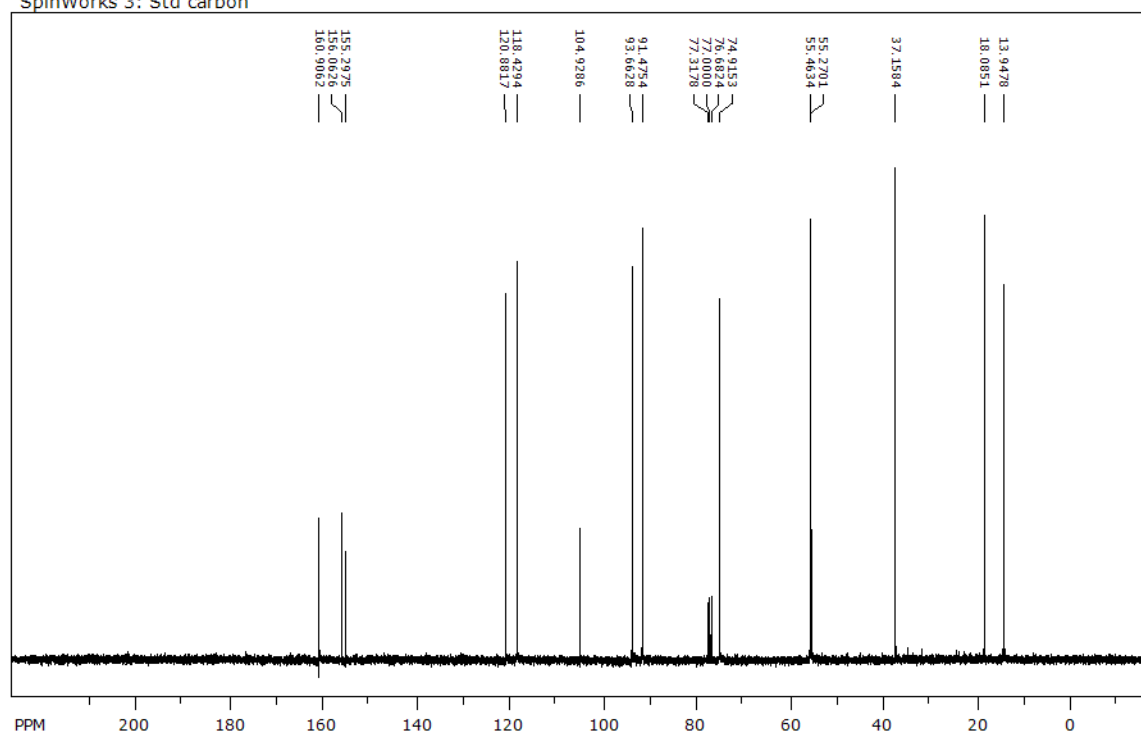


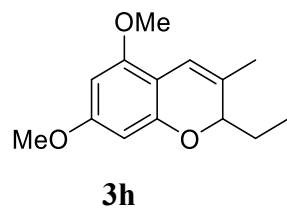


SpinWorks 3: Std proton

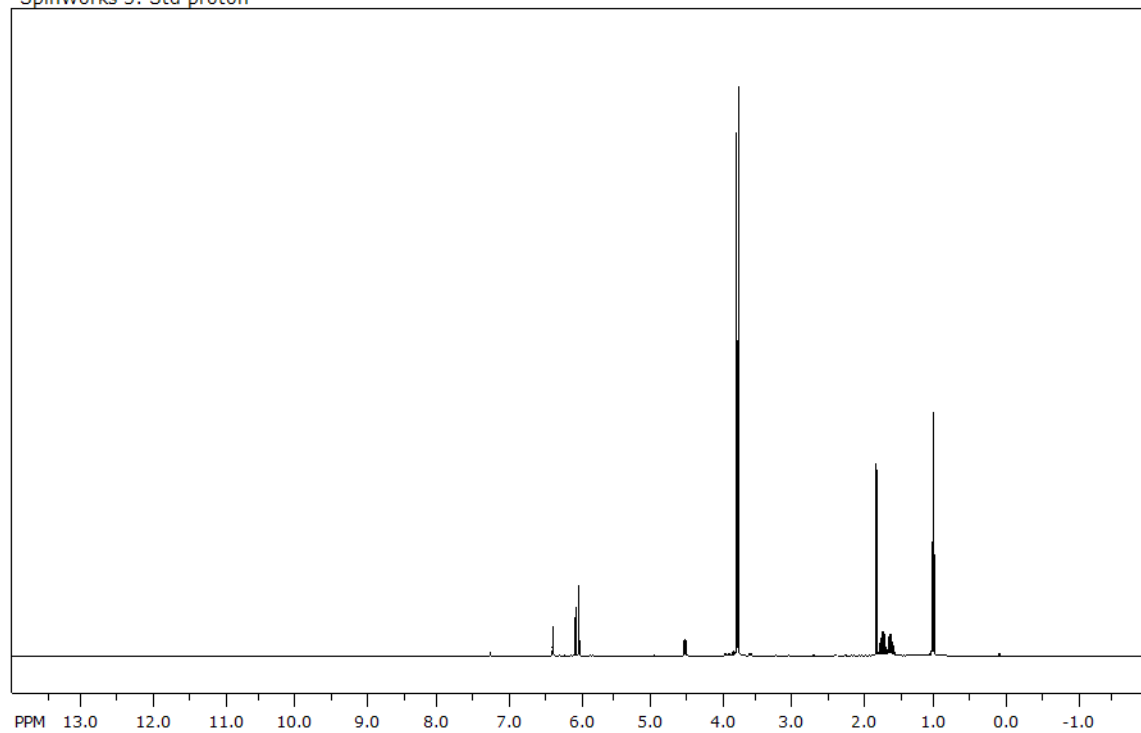


SpinWorks 3: Std carbon

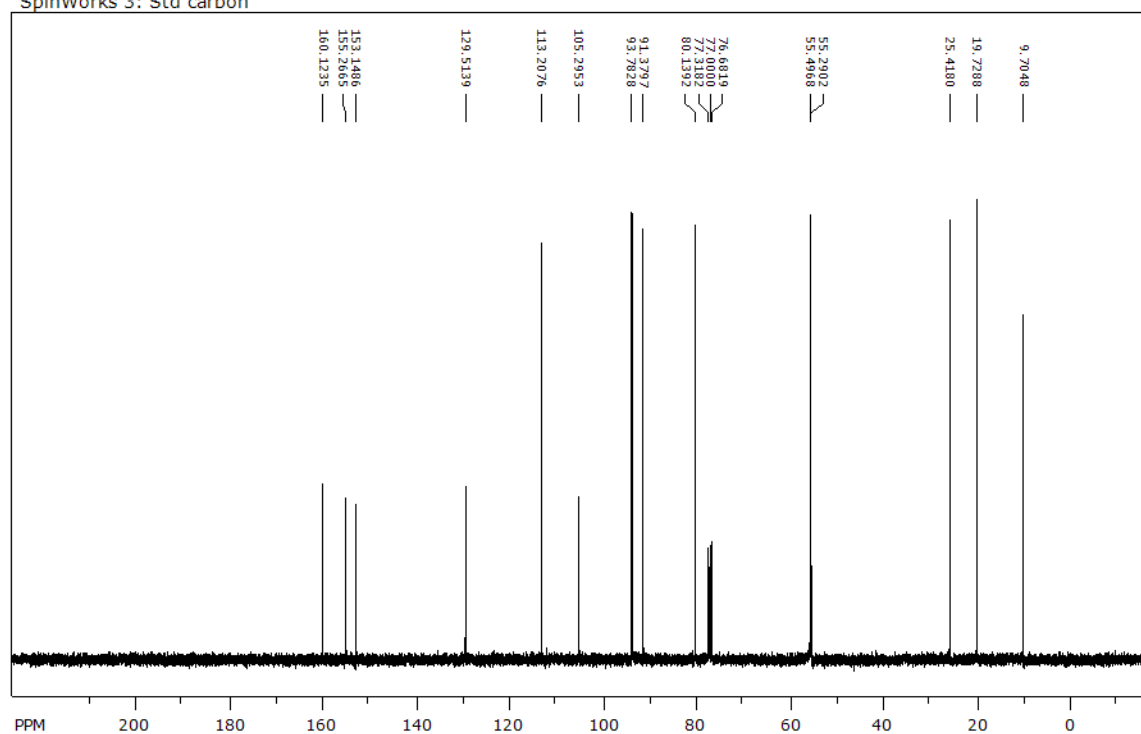


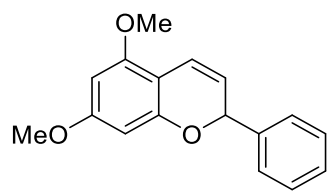


SpinWorks 3: Std proton



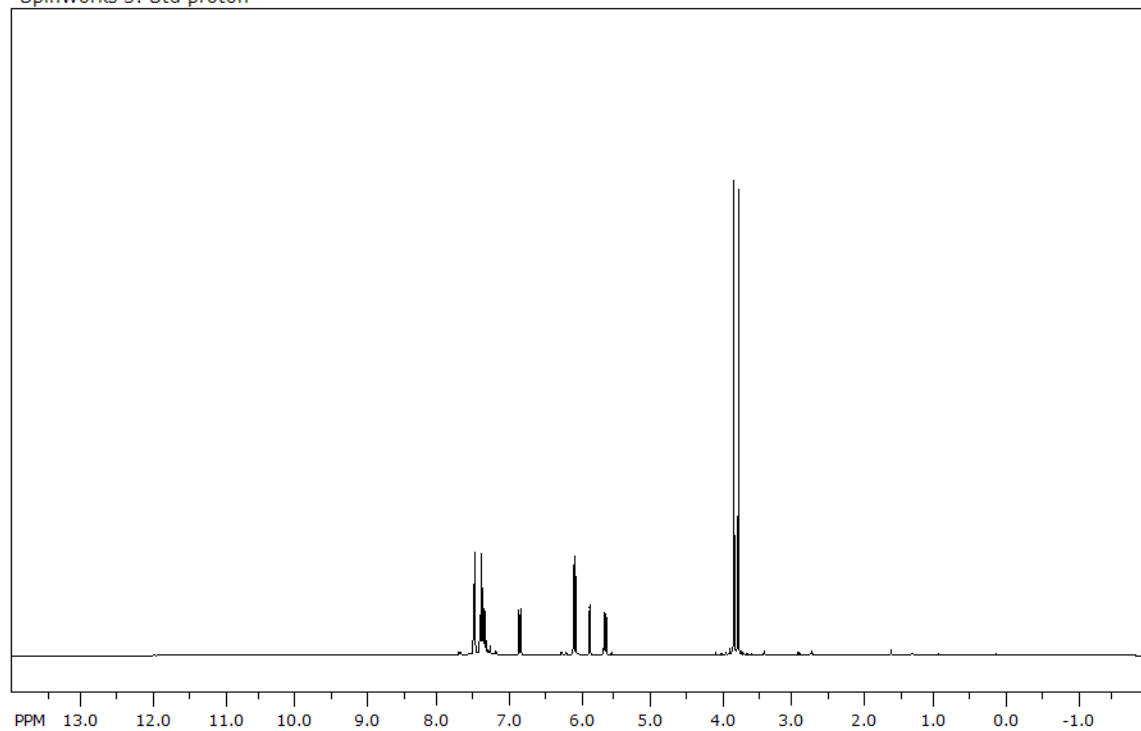
SpinWorks 3: Std carbon



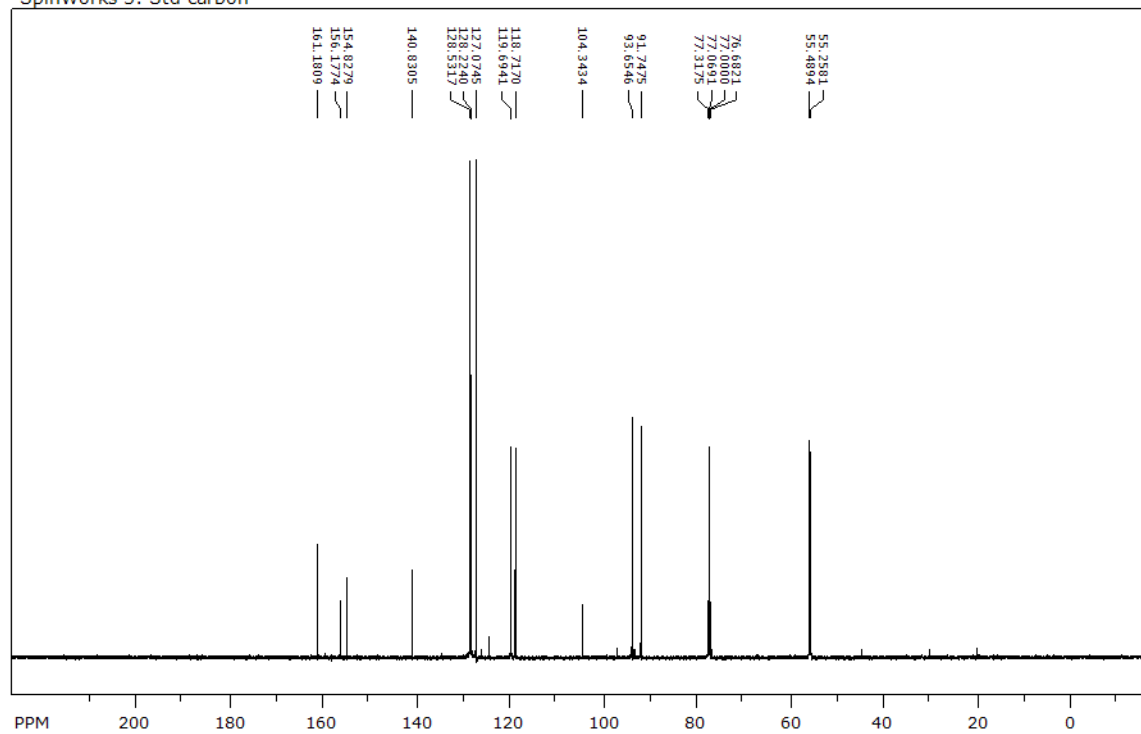


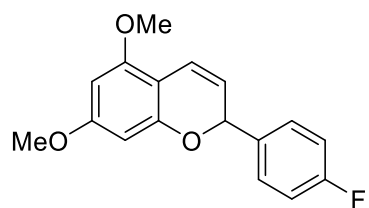
3i

SpinWorks 3: Std proton



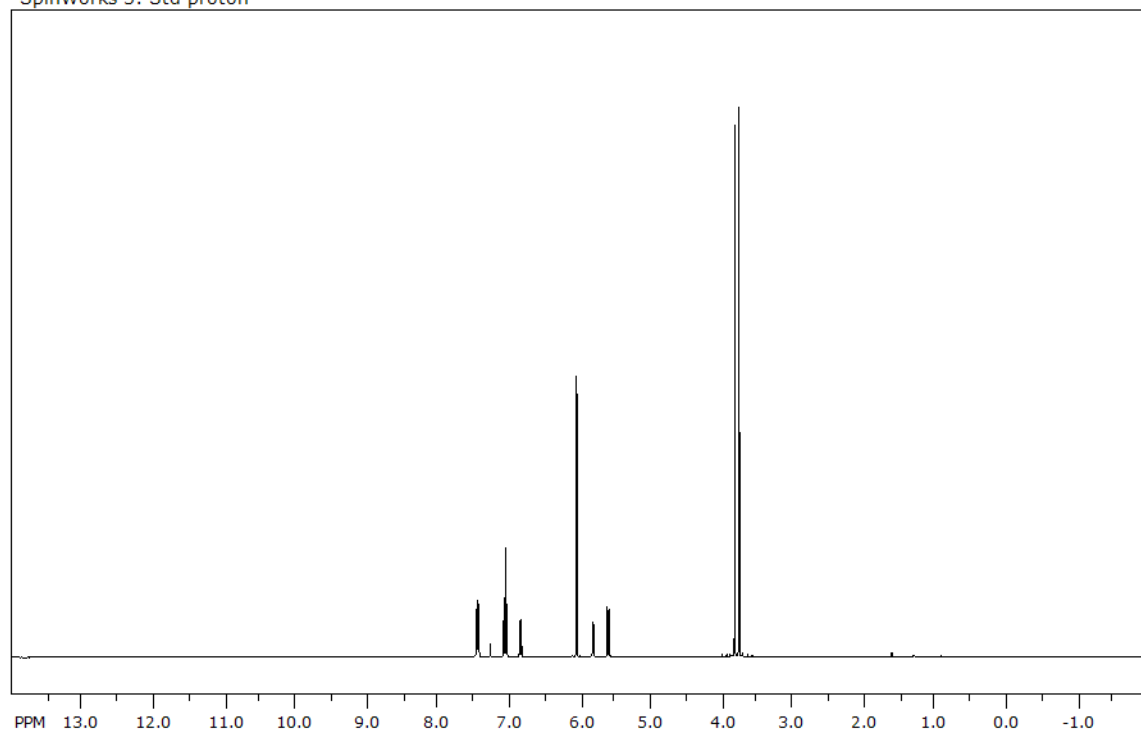
SpinWorks 3: Std carbon



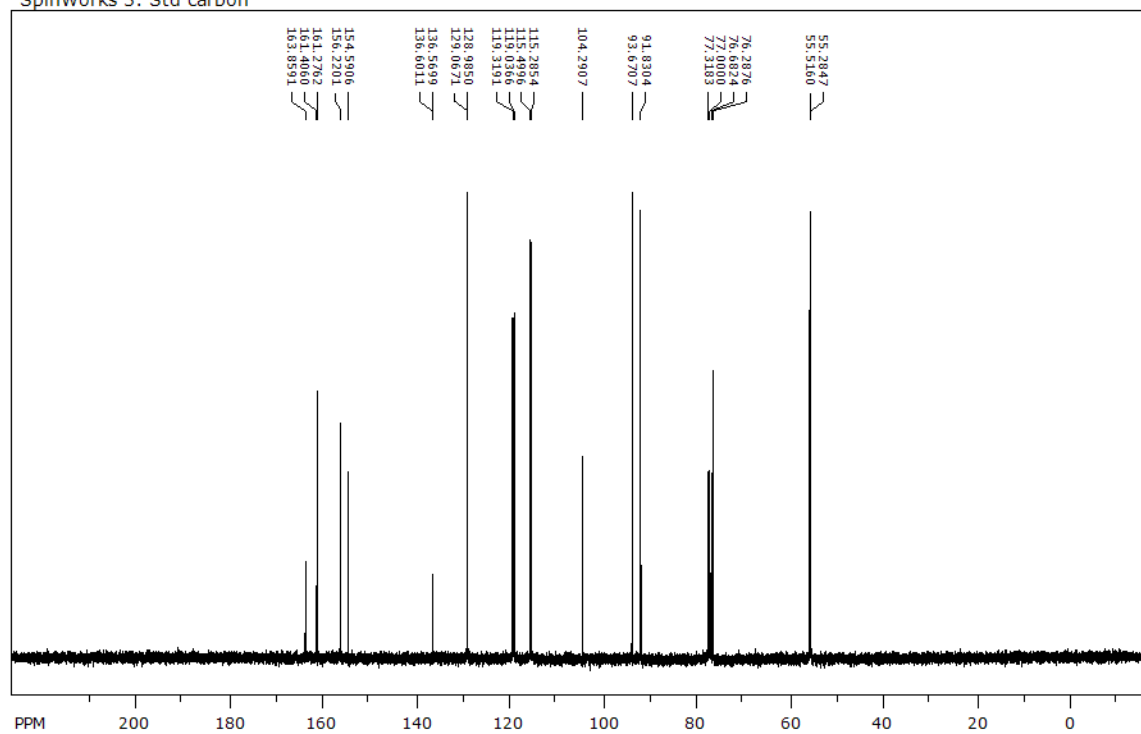


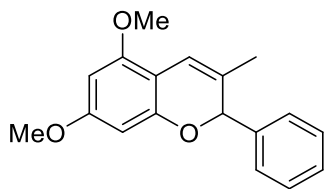
3j

SpinWorks 3: Std proton



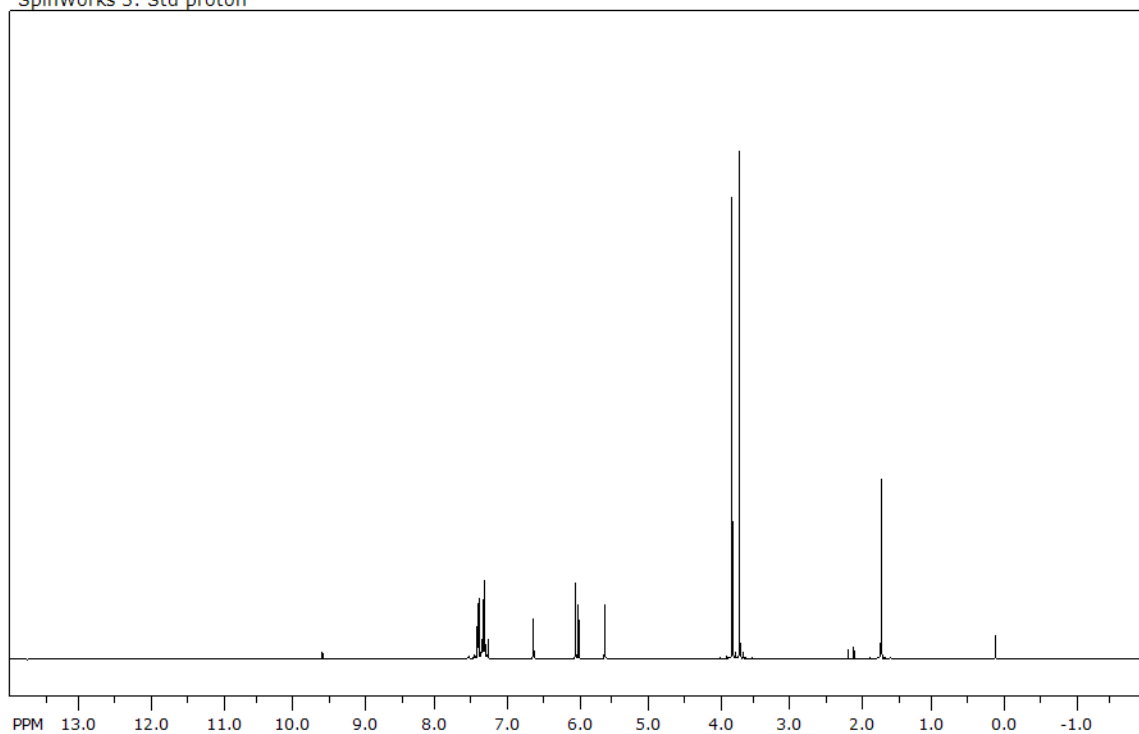
SpinWorks 3: Std carbon



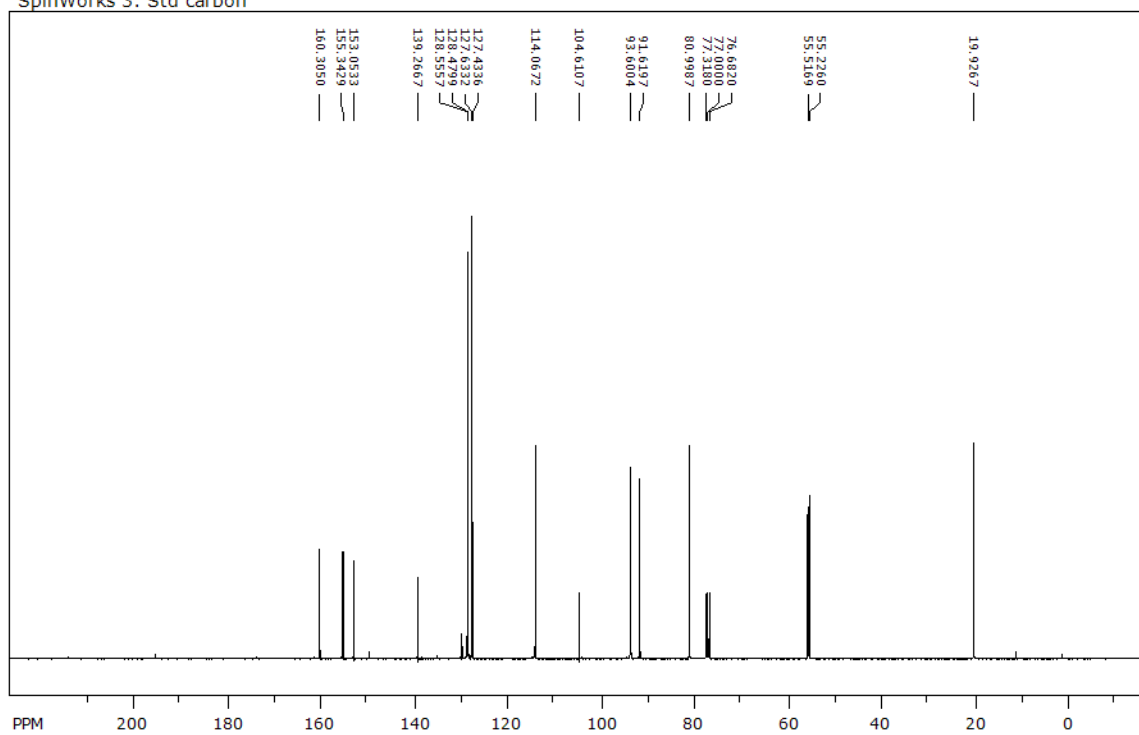


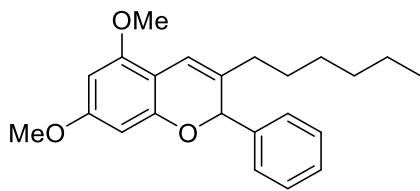
3k

SpinWorks 3: Std proton



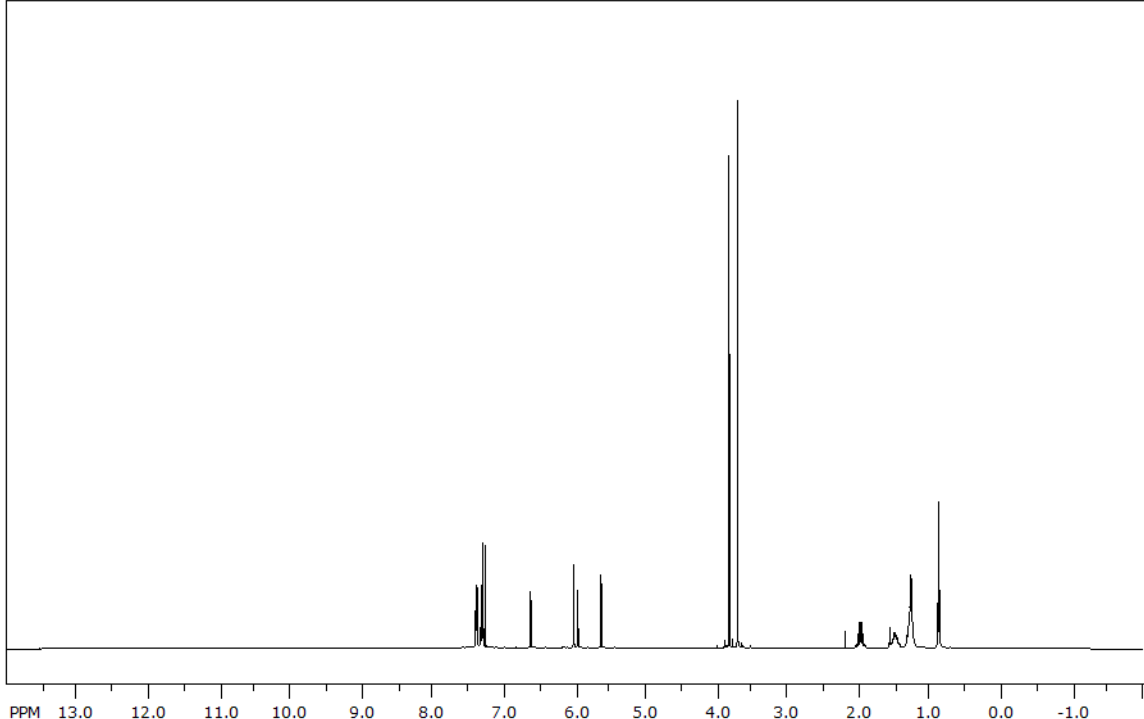
SpinWorks 3: Std carbon



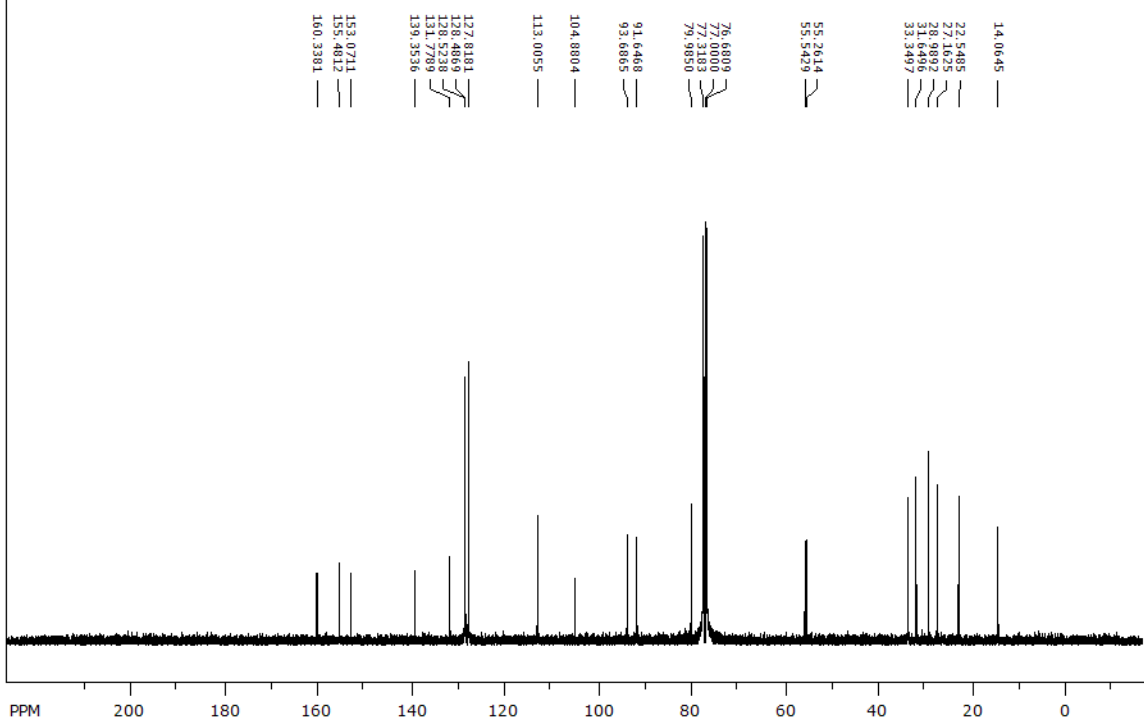


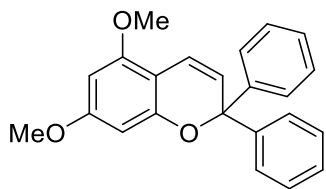
31

SpinWorks 3: Std proton



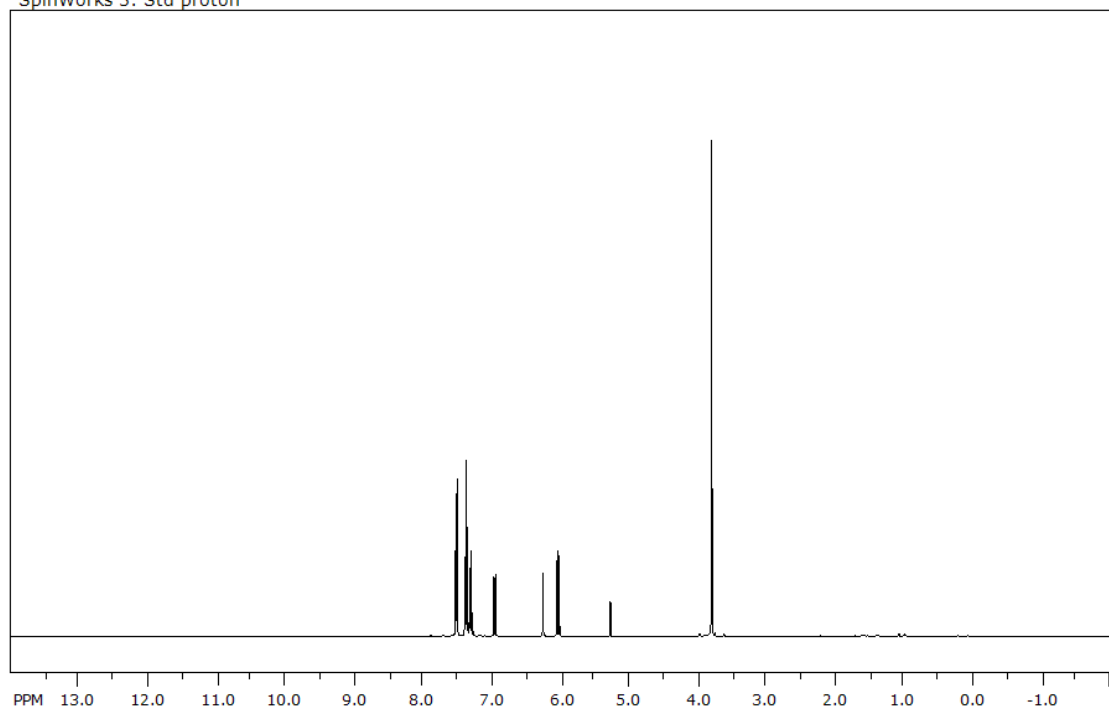
SpinWorks 3: Std carbon



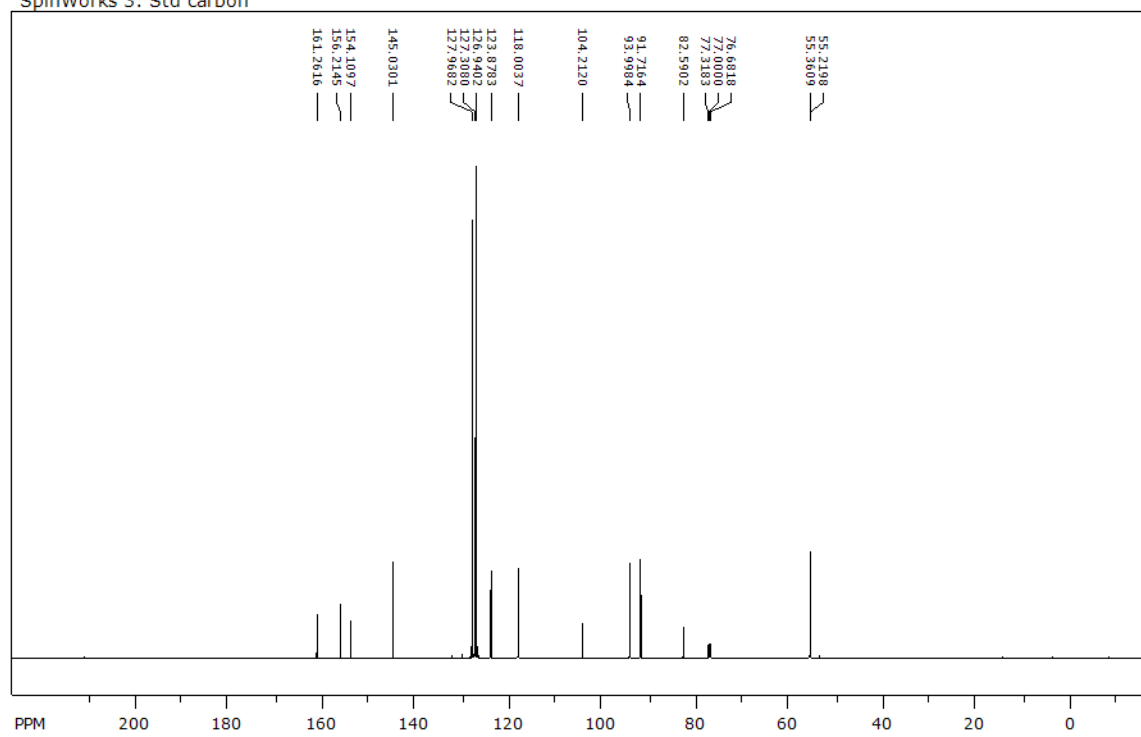


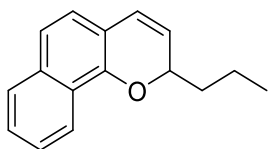
3m

SpinWorks 3: Std proton



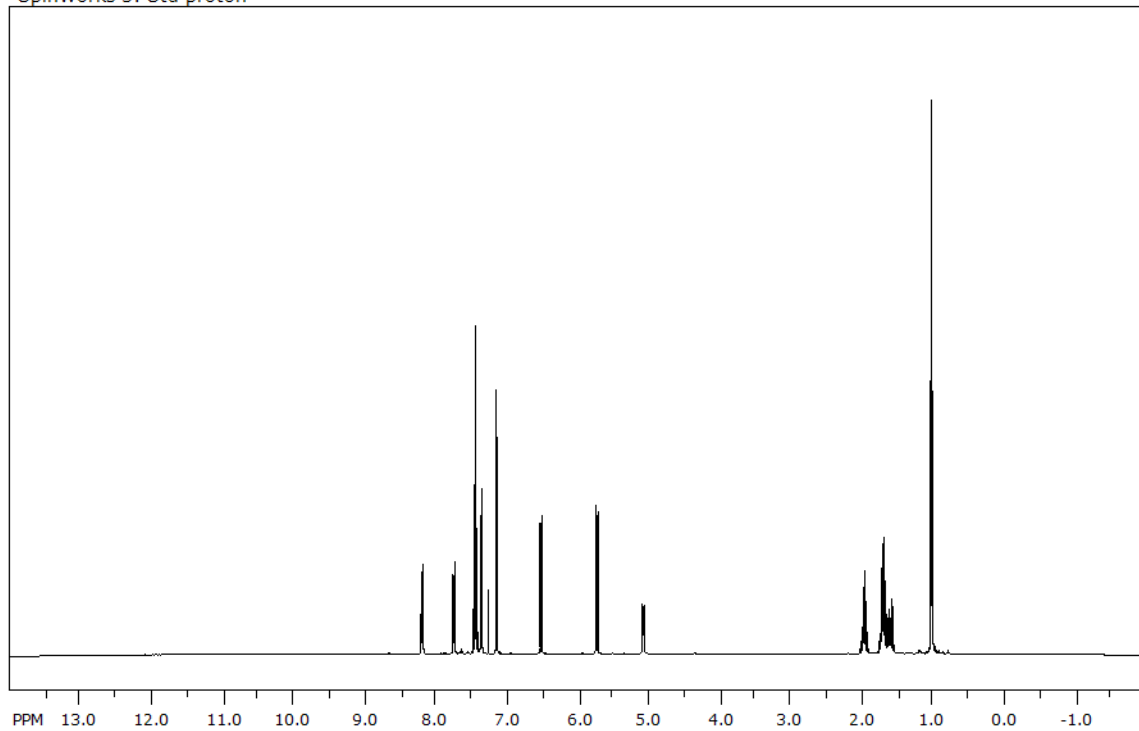
SpinWorks 3: Std carbon



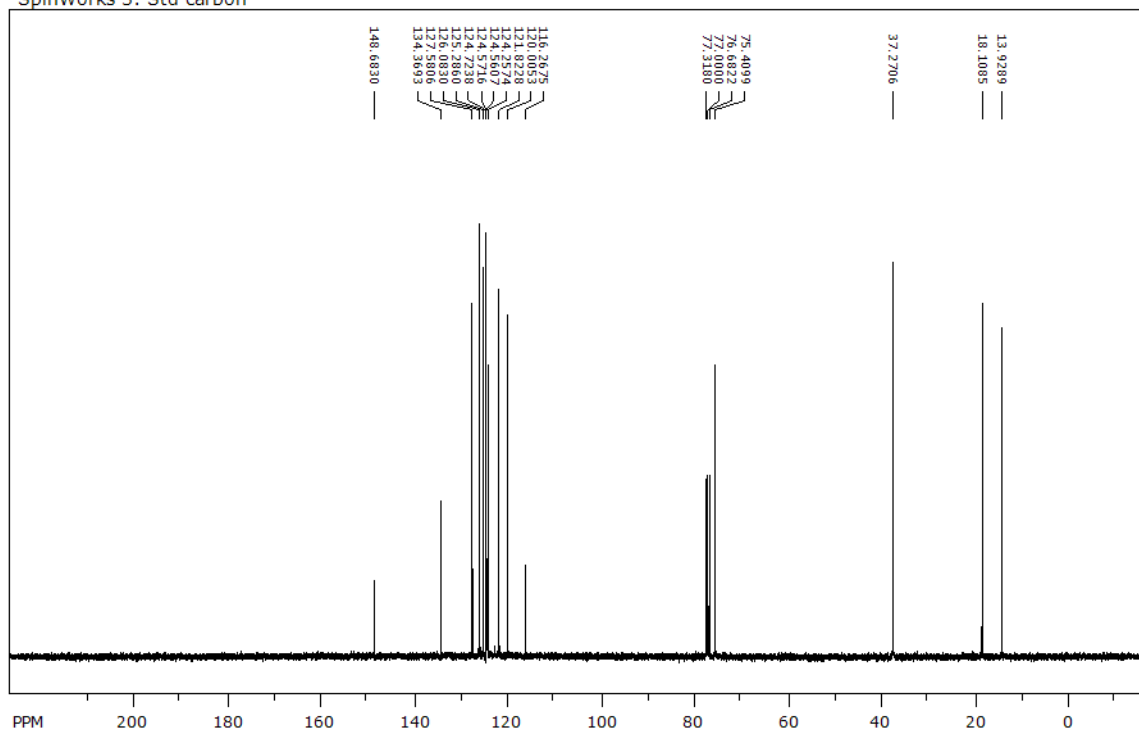


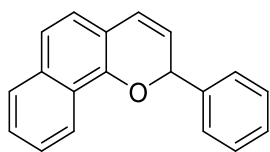
3n

SpinWorks 3: Std proton



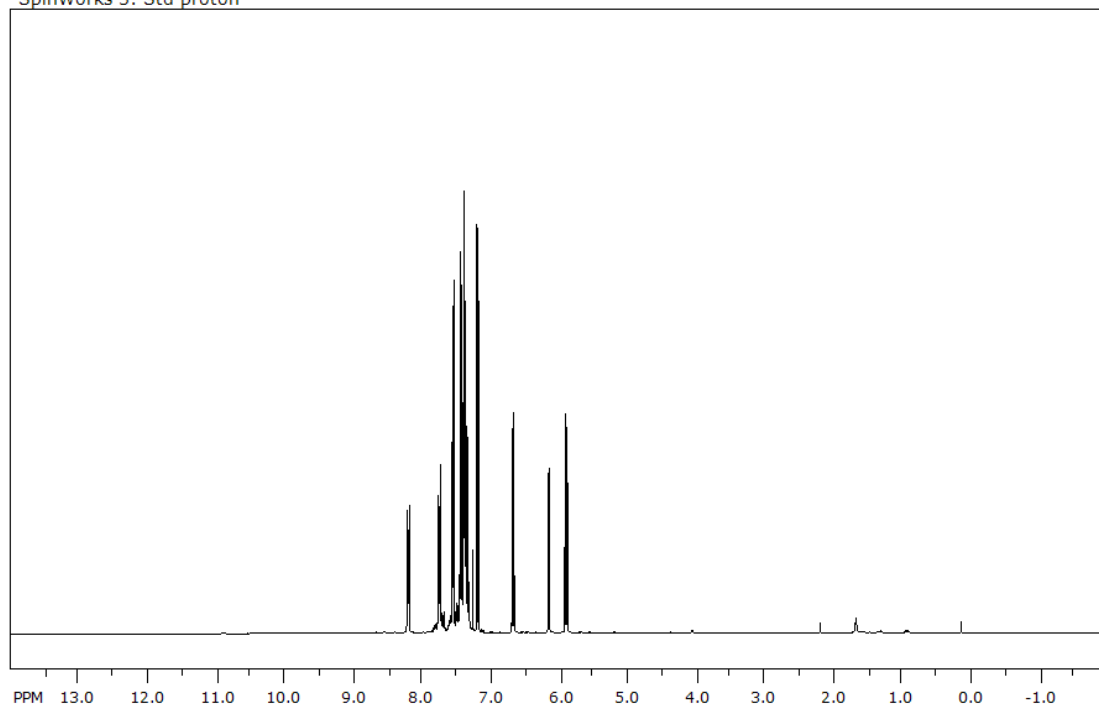
SpinWorks 3: Std carbon



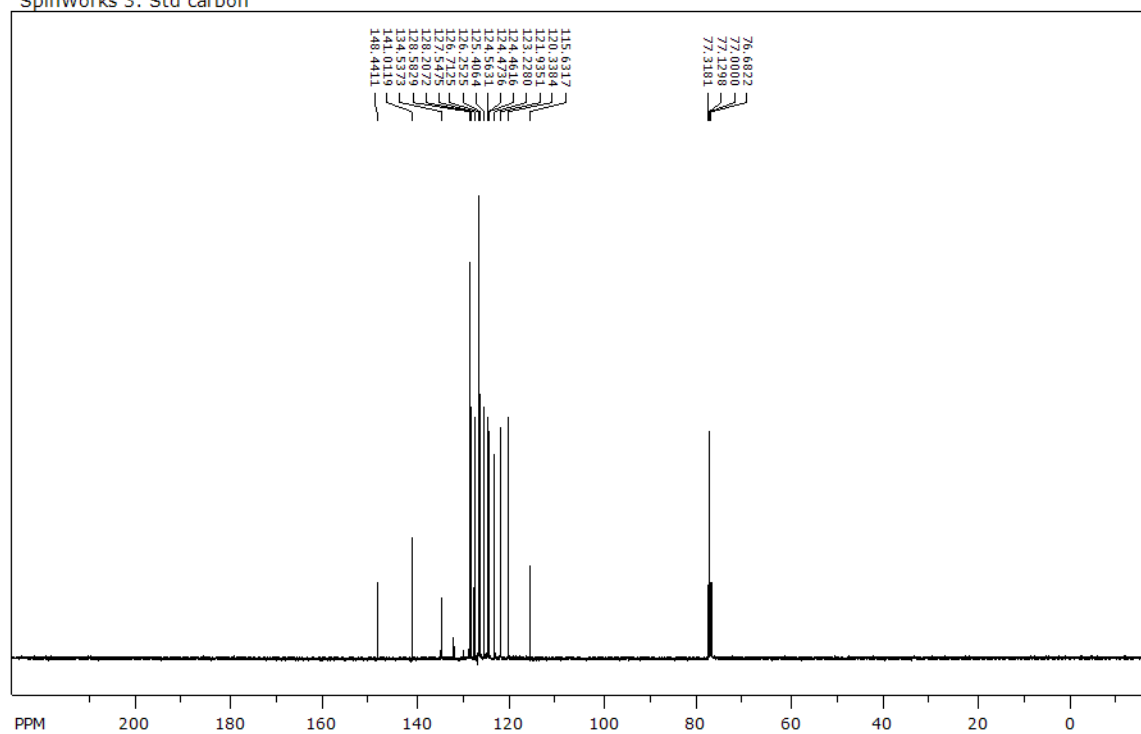


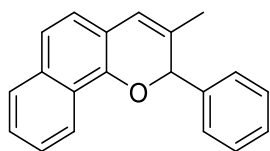
30

SpinWorks 3: Std proton



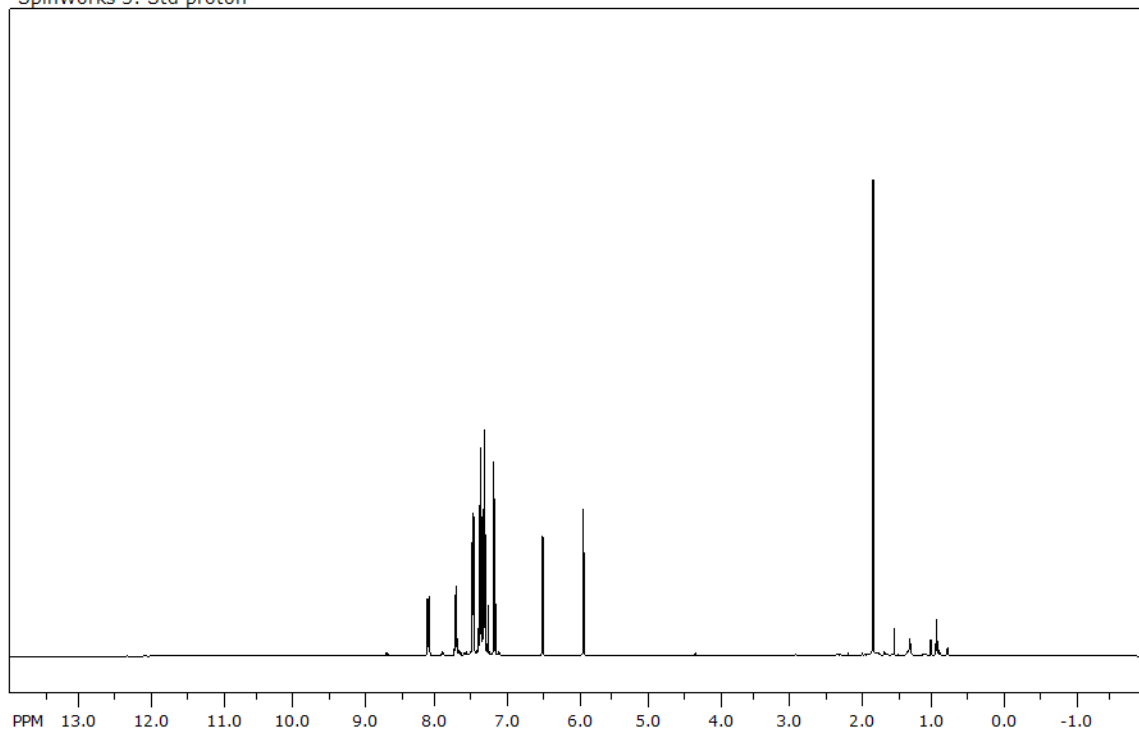
SpinWorks 3: Std carbon



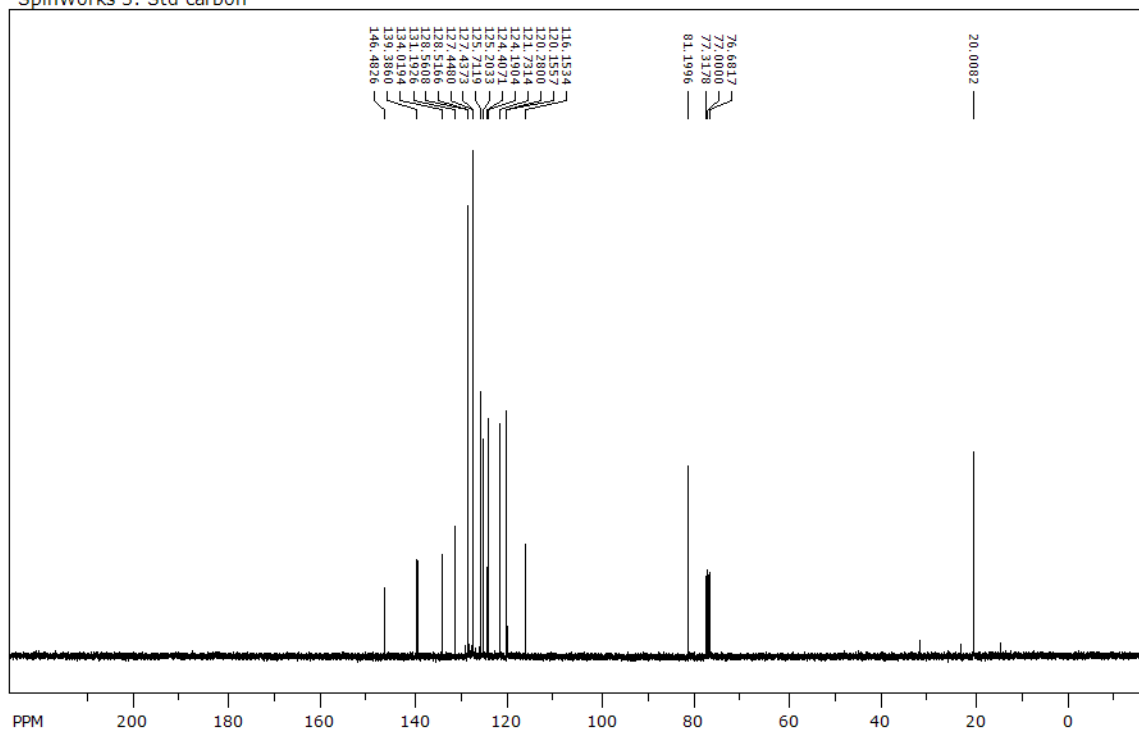


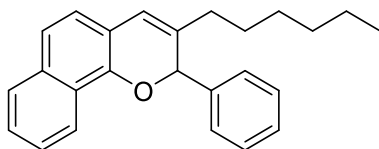
3p

SpinWorks 3: Std proton



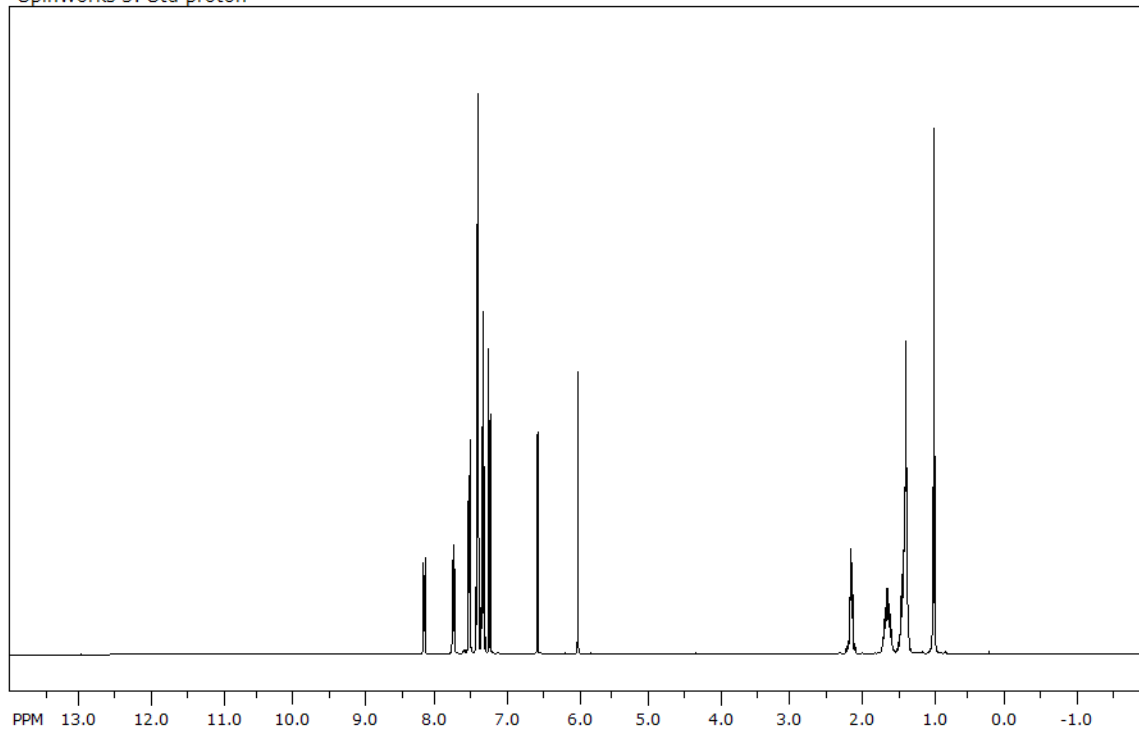
SpinWorks 3: Std carbon



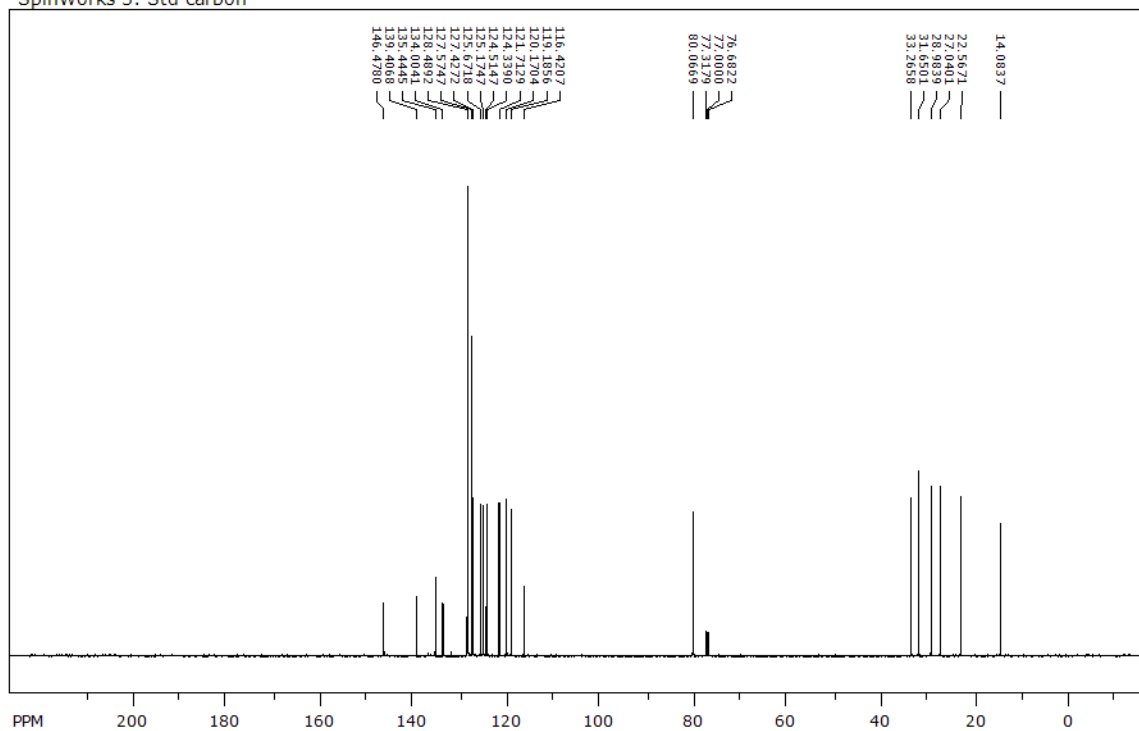


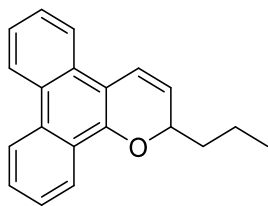
3q

SpinWorks 3: Std proton



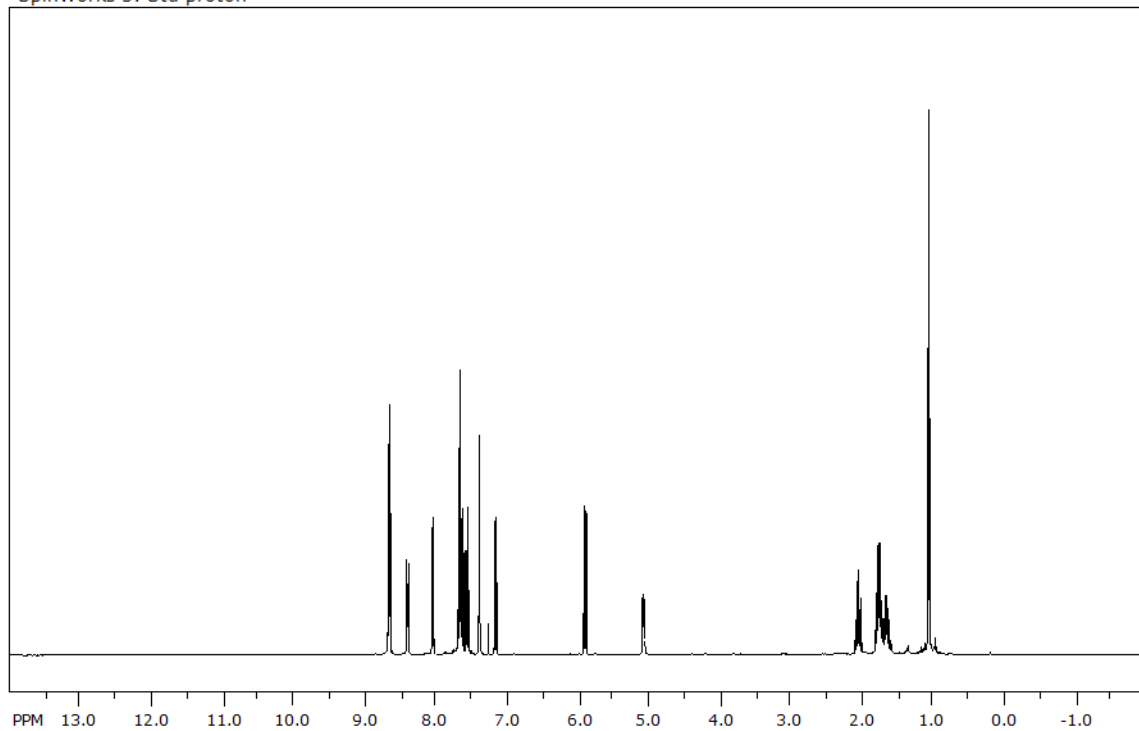
SpinWorks 3: Std carbon



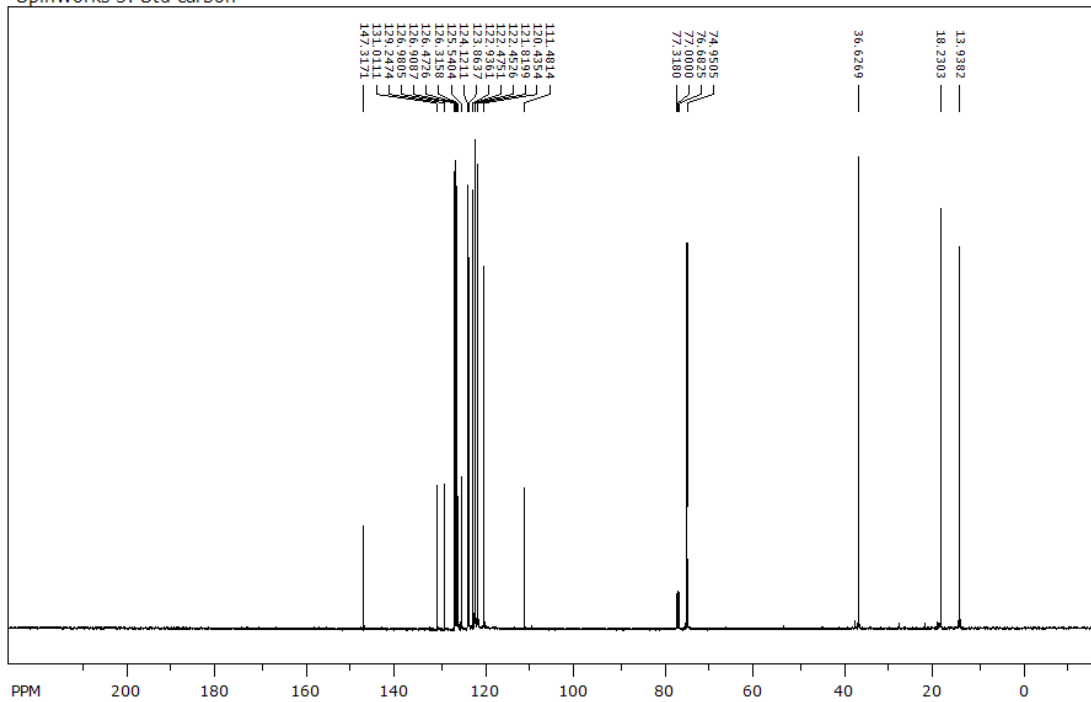


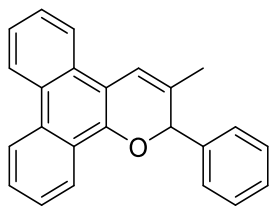
3r

SpinWorks 3: Std proton



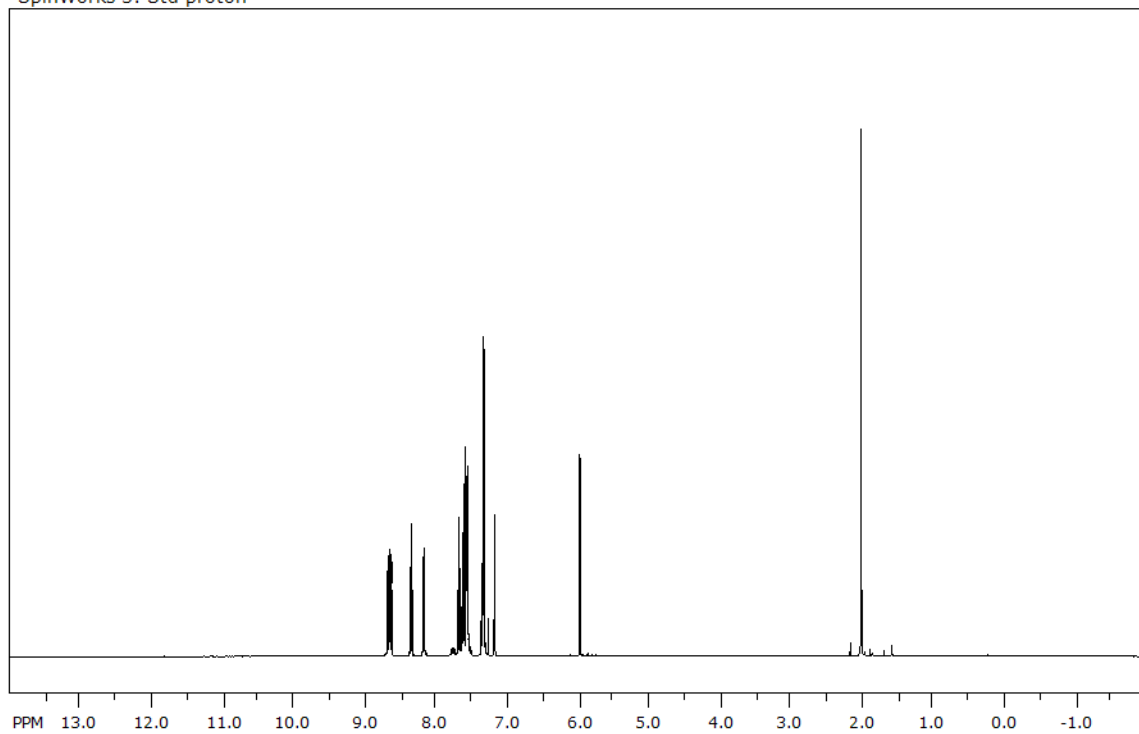
SpinWorks 3: Std carbon



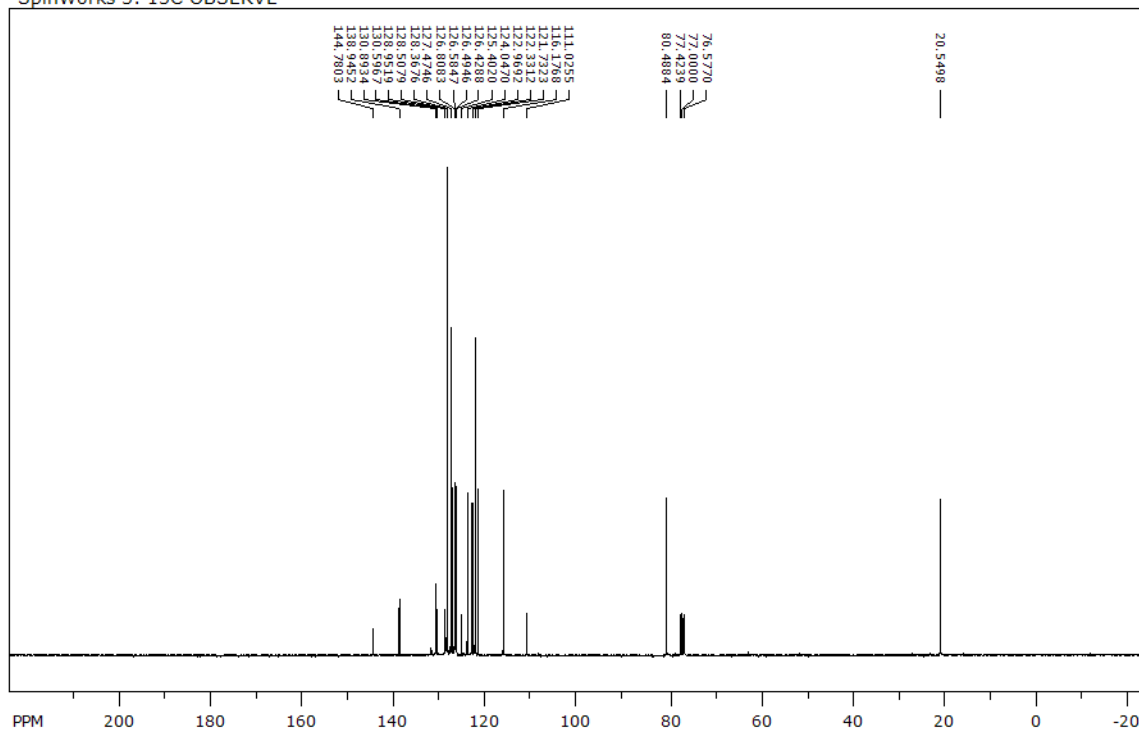


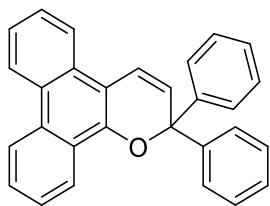
3s

SpinWorks 3: Std proton



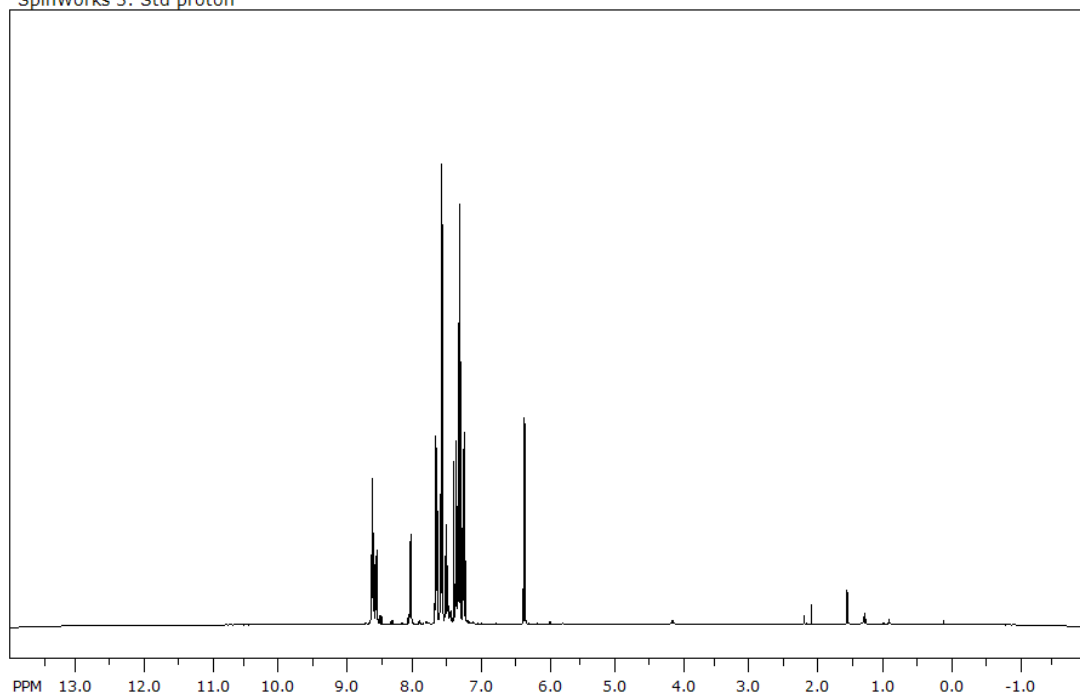
SpinWorks 3: 13C OBSERVE



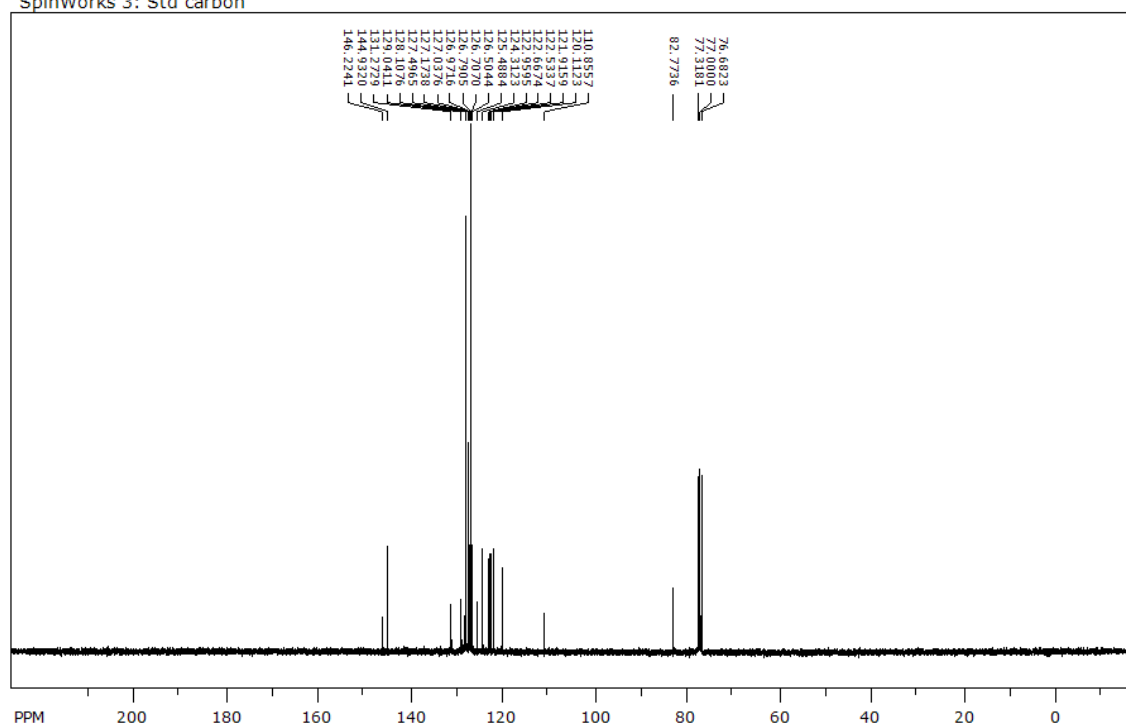


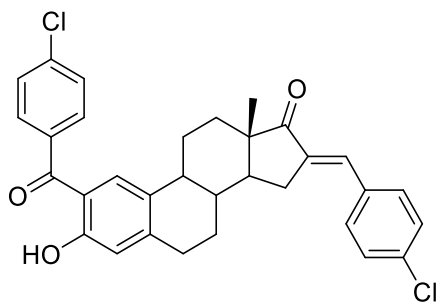
3t

SpinWorks 3: Std proton



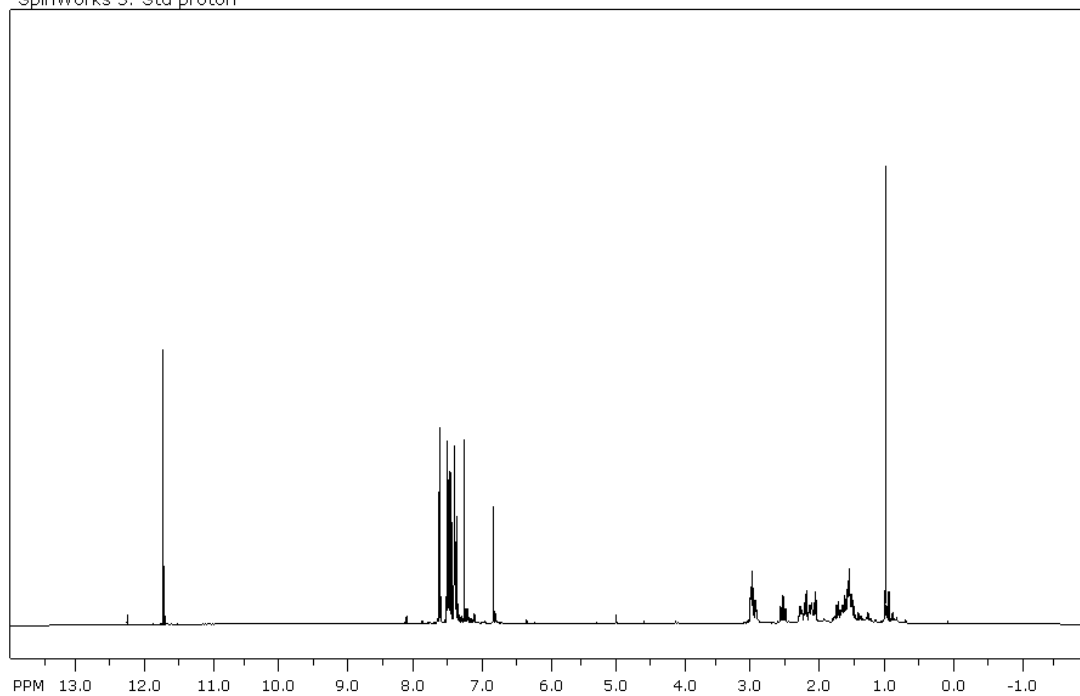
SpinWorks 3: Std carbon



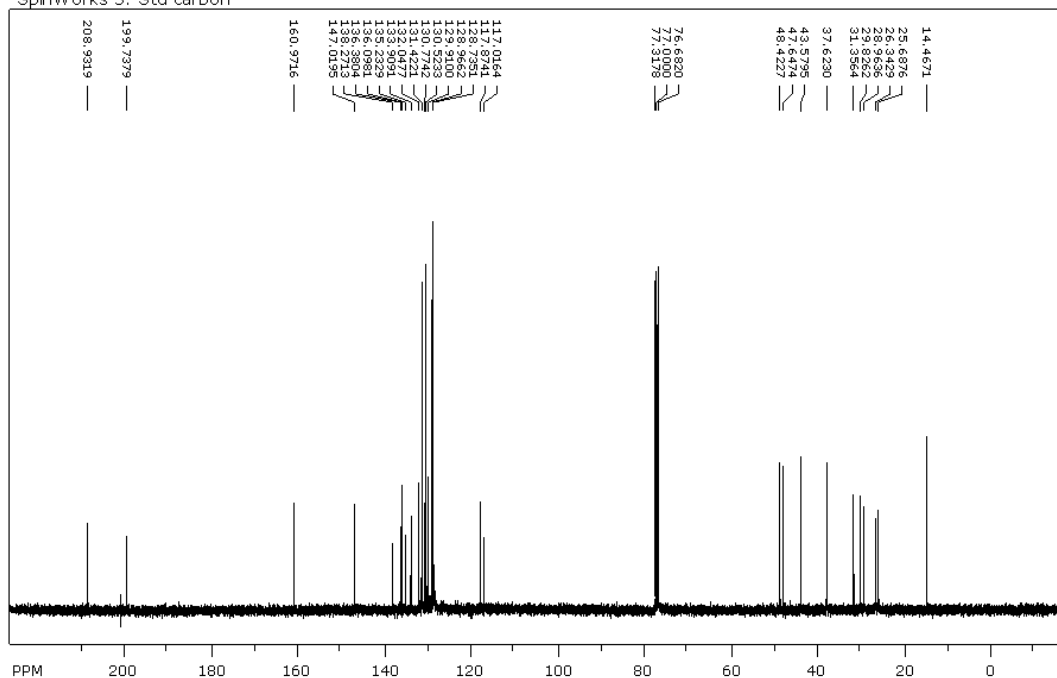


4a

SpinWorks 3: Std proton



SpinWorks 3: Std carbon



10. X-Ray Crystallographic Data of 2v, 3t and 4b.

Table S2. Crystal data and structure refinement for **2v**.

Identification code	yi2q
Empirical formula	C ₁₇ H ₁₈ O ₂
Formula weight	254.31
Temperature/K	100.05(10)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	7.08927(18)
b/Å	10.1152(2)
c/Å	18.6070(5)
α/°	90.00
β/°	96.927(2)
γ/°	90.00
Volume/Å ³	1324.56(6)
Z	4
ρ _{calc} /mg/mm ³	1.275
m/mm ⁻¹	0.082
F(000)	544.0
Crystal size/mm ³	0.28 × 0.14 × 0.11
Radiation	MoKα (λ = 0.71073)
2θ range for data collection	5.78 to 58.8°
Index ranges	-9 ≤ h ≤ 9, -13 ≤ k ≤ 13, -25 ≤ l ≤ 24
Reflections collected	15224
Independent reflections	3372 [R _{int} = 0.0343, R _{sigma} = 0.0279]
Data/restraints/parameters	3372/0/176
Goodness-of-fit on F ²	1.076
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0467, wR ₂ = 0.1265
Final R indexes [all data]	R ₁ = 0.0592, wR ₂ = 0.1374
Largest diff. peak/hole / e Å ⁻³	0.38/-0.23

Table S3. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2v**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$
O1	6030.4(13)	-1312.7(9)	2093.5(5)	25.0(2)
O2	7941.5(13)	-342.6(9)	1169.1(5)	22.7(2)
C1	4645.8(18)	-603.2(12)	1881.6(7)	18.2(3)
C2	6429.2(17)	430.6(12)	965.8(7)	17.2(3)
C3	4756.1(17)	348.1(12)	1292.1(7)	17.0(3)
C4	3234.4(18)	1225.2(13)	1050.4(7)	19.2(3)
C5	3378.3(18)	2136.9(13)	525.0(7)	20.6(3)
C6	5076.4(17)	2240.0(13)	188.8(7)	18.9(3)
C7	5288.2(19)	3185.8(14)	-356.6(7)	23.9(3)
C8	6936(2)	3254.6(15)	-674.5(7)	26.0(3)
C9	8446.7(19)	2382.4(14)	-461.0(7)	25.3(3)
C10	8295.0(18)	1465.4(13)	72.1(7)	21.0(3)
C11	6610.2(17)	1371.8(12)	404.7(6)	17.7(3)
C12	2874.4(17)	-676.1(12)	2261.0(7)	17.2(3)
C13	2909.1(19)	479.1(13)	2803.1(7)	21.1(3)
C14	1128(2)	462.6(13)	3191.7(8)	25.9(3)
C15	903(2)	-855.0(14)	3573.4(7)	25.5(3)
C16	913.0(18)	-1999.6(13)	3039.7(7)	22.4(3)
C17	2711.0(18)	-1986.0(12)	2659.2(7)	19.7(3)

Table S4. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2v**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^2U_{11}+2hka*b*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	22.3(5)	21.2(5)	31.0(5)	6.1(4)	1.8(4)	4.4(4)
O2	18.4(5)	21.3(5)	28.1(5)	2.2(4)	1.7(4)	4.6(4)
C1	19.8(6)	15.0(6)	19.1(6)	-1.9(4)	-0.5(5)	-0.2(5)
C2	16.1(6)	15.9(6)	18.7(6)	-3.1(4)	-1.9(4)	1.2(4)
C3	16.4(6)	16.4(6)	17.3(6)	-1.2(4)	-1.3(4)	-0.2(4)
C4	16.1(6)	22.2(6)	19.2(6)	-0.8(5)	1.4(4)	1.1(5)

C5	17.6(6)	23.0(6)	20.5(6)	1.3(5)	-0.9(5)	2.9(5)
C6	18.9(6)	21.3(6)	15.8(6)	-1.5(5)	-0.9(5)	-0.9(5)
C7	23.5(6)	27.5(7)	19.7(6)	3.3(5)	-1.0(5)	0.3(5)
C8	28.5(7)	30.1(7)	19.0(6)	3.8(5)	0.6(5)	-4.6(6)
C9	22.9(6)	32.7(7)	20.7(7)	-2.6(5)	4.9(5)	-5.2(5)
C10	18.3(6)	23.7(7)	20.9(6)	-4.9(5)	1.3(5)	-0.7(5)
C11	18.0(6)	18.4(6)	16.0(6)	-3.9(4)	-0.5(4)	-2.1(5)
C12	18.2(6)	15.8(6)	16.9(6)	0.8(4)	-0.5(4)	-0.5(4)
C13	25.4(6)	17.0(6)	20.7(6)	-0.8(5)	2.0(5)	-1.1(5)
C14	31.9(7)	21.2(7)	25.5(7)	0.0(5)	7.0(6)	5.5(5)
C15	29.3(7)	25.3(7)	22.8(7)	3.8(5)	6.8(5)	3.1(5)
C16	21.7(6)	21.5(6)	23.3(7)	5.4(5)	-0.2(5)	-1.3(5)
C17	21.9(6)	15.3(6)	21.5(6)	0.9(5)	1.5(5)	-0.7(5)

Table S5. Bond Lengths for **2v**.

Atom Atom Length/Å			Atom Atom Length/Å		
O1	C1	1.2412(15)	C7	C8	1.3734(19)
O2	C2	1.3439(15)	C8	C9	1.407(2)
C1	C3	1.4683(17)	C9	C10	1.3719(19)
C1	C12	1.5149(17)	C10	C11	1.4131(17)
C2	C3	1.3986(17)	C12	C13	1.5418(17)
C2	C11	1.4301(17)	C12	C17	1.5292(17)
C3	C4	1.4269(17)	C13	C14	1.5290(18)
C4	C5	1.3568(18)	C14	C15	1.5276(19)
C5	C6	1.4258(17)	C15	C16	1.5258(19)
C6	C7	1.4158(18)	C16	C17	1.5311(18)
C6	C11	1.4176(17)			

Table S6. Bond Angles for **2v**.

Atom Atom Atom Angle/°				Atom Atom Atom Angle/°			
O1	C1	C3	120.33(11)	C7	C8	C9	120.31(13)

O1	C1	C12	119.47(11)	C10	C9	C8	120.31(12)
C3	C1	C12	120.13(10)	C9	C10	C11	120.40(12)
O2	C2	C3	122.18(11)	C6	C11	C2	119.08(11)
O2	C2	C11	117.01(11)	C10	C11	C2	121.28(11)
C3	C2	C11	120.80(11)	C10	C11	C6	119.63(11)
C2	C3	C1	119.19(11)	C1	C12	C13	108.62(10)
C2	C3	C4	118.34(11)	C1	C12	C17	112.55(10)
C4	C3	C1	122.45(11)	C17	C12	C13	109.63(10)
C5	C4	C3	122.00(12)	C14	C13	C12	110.62(11)
C4	C5	C6	120.44(12)	C15	C14	C13	111.59(11)
C7	C6	C5	122.14(12)	C16	C15	C14	110.52(11)
C7	C6	C11	118.54(11)	C15	C16	C17	111.33(11)
C11	C6	C5	119.32(11)	C12	C17	C16	110.35(10)
C8	C7	C6	120.81(13)				

Table S7. Hydrogen Bonds for **2v**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2	H2	O1	0.95(2)	1.63(2)	2.5138(13)	154(2)

Table S8. Torsion Angles for **2v**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C1	C3	C2	0.92(18)	C5	C6	C11	C2	-1.27(17)
O1	C1	C3	C4	-177.22(12)	C5	C6	C11	C10	179.79(11)
O1	C1	C12	C13	98.62(13)	C6	C7	C8	C9	-0.1(2)
O1	C1	C12	C17	-22.96(16)	C7	C6	C11	C2	178.69(11)
O2	C2	C3	C1	0.65(18)	C7	C6	C11	C10	-0.26(18)
O2	C2	C3	C4	178.87(11)	C7	C8	C9	C10	-0.7(2)
O2	C2	C11	C6	-177.89(11)	C8	C9	C10	C11	1.0(2)
O2	C2	C11	C10	1.04(17)	C9	C10	C11	C2	-179.45(11)
C1	C3	C4	C5	177.31(12)	C9	C10	C11	C6	-0.53(19)
C1	C12	C13	C14	179.02(10)	C11	C2	C3	C1	-178.14(11)

C1 C12 C17 C16	179.30(10)	C11 C2 C3 C4	0.07(18)
C2 C3 C4 C5	-0.85(19)	C11 C6 C7 C8	0.56(19)
C3 C1 C12 C13	-78.29(14)	C12 C1 C3 C2	177.82(10)
C3 C1 C12 C17	160.13(11)	C12 C1 C3 C4	-0.33(18)
C3 C2 C11 C6	0.97(18)	C12 C13 C14 C15	56.44(15)
C3 C2 C11 C10	179.89(11)	C13 C12 C17 C16	58.30(13)
C3 C4 C5 C6	0.5(2)	C13 C14 C15 C16	-55.17(15)
C4 C5 C6 C7	-179.42(12)	C14 C15 C16 C17	55.85(14)
C4 C5 C6 C11	0.54(19)	C15 C16 C17 C12	-58.06(14)
C5 C6 C7 C8	-179.49(12)	C17 C12 C13 C14	-57.63(13)

Table S9. Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for **2v**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H2	7540(30)	-870(20)	1547(13)	65(7)
H4	2086	1169	1264	23
H5	2341	2710	380	25
H7	4278	3780	-504	29
H8	7057	3894	-1040	31
H9	9577	2429	-687	30
H10	9329	890	219	25
H12	1737	-575	1892	21
H13A	4052	407	3163	25
H13B	2979	1328	2542	25
H14A	1206	1186	3552	31
H14B	-4	621	2836	31
H15A	1956	-968	3969	31
H15B	-307	-857	3789	31
H16A	-218	-1936	2673	27
H16B	839	-2846	3302	27
H17A	3841	-2108	3021	24
H17B	2667	-2726	2309	24

Table S10. Crystal data and structure refinement for **3t**.

Identification code	yi2s4
Empirical formula	C ₂₉ H ₂₀ O
Formula weight	384.45
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.6412(4)
b/Å	11.9623(5)
c/Å	14.3355(6)
α/°	94.336(3)
β/°	103.650(3)
γ/°	90.068(3)
Volume/Å ³	1933.99(12)
Z	4
ρ _{calc} /mg/mm ³	1.320
m/mm ⁻¹	0.605
F(000)	808.0
Crystal size/mm ³	0.42 × 0.35 × 0.18
Radiation	CuKα (λ = 1.54184)
2θ range for data collection	6.36 to 147.4°
Index ranges	-14 ≤ h ≤ 10, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17
Reflections collected	18380
Independent reflections	7504 [R _{int} = 0.0657, R _{sigma} = 0.0456]
Data/restraints/parameters	7504/0/541
Goodness-of-fit on F ²	1.044
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0743, wR ₂ = 0.2135
Final R indexes [all data]	R ₁ = 0.0827, wR ₂ = 0.2229
Largest diff. peak/hole / e Å ⁻³	0.45/-0.35

Table S11. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3t**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{II} tensor.

Atom	<i>x</i>	<i>Y</i>	<i>z</i>	U(eq)
O1A	6716.5(14)	5728.8(14)	3051.3(11)	27.9(4)
C1A	6758.4(19)	5612.4(19)	4005.2(16)	24.9(5)
C2A	7633.1(19)	5031.2(19)	4572.5(17)	26.3(5)
C3A	8453(2)	4430(2)	4095.2(18)	30.1(5)
C4A	8268(2)	4341(2)	3147.1(18)	31.1(5)
C5A	7232(2)	4877(2)	2502.8(17)	27.9(5)
C6A	5870.5(19)	6197.0(19)	4376.9(17)	25.7(5)
C7A	4930(2)	6725(2)	3766.4(17)	28.9(5)
C8A	4070(2)	7257(2)	4142.9(19)	31.7(5)
C9A	4119(2)	7279(2)	5122.3(19)	33.7(5)
C10A	5024(2)	6767(2)	5726.4(18)	31.5(5)
C11A	5923(2)	6212.8(19)	5375.6(17)	27.4(5)
C12A	6874(2)	5641.9(19)	6001.6(17)	27.3(5)
C13A	6989(2)	5656(2)	7001.0(18)	33.7(5)
C14A	7894(2)	5111(2)	7582.6(19)	37.4(6)
C15A	8716(2)	4519(2)	7177.1(19)	36.6(6)
C16A	8628(2)	4483(2)	6206.6(18)	32.4(5)
C17A	7717(2)	5046.2(19)	5592.9(17)	27.0(5)
C18A	6231(2)	4053(2)	1999.2(17)	29.0(5)
C19A	6236(2)	2928(2)	2184.1(18)	32.0(5)
C20A	5282(2)	2218(2)	1721.0(19)	35.4(6)
C21A	4330(2)	2633(2)	1085.1(19)	35.9(6)
C22A	4317(2)	3765(2)	889.3(19)	35.3(6)
C23A	5265(2)	4459(2)	1344.7(19)	32.3(5)
C24A	7700.5(19)	5485(2)	1757.6(17)	28.6(5)
C25A	8156(2)	4834(2)	1087.2(18)	32.2(5)
C26A	8680(2)	5333(3)	444.4(18)	37.3(6)

C27A	8751(2)	6491(3)	462.8(19)	42.7(7)
C28A	8275(2)	7137(3)	1108.0(19)	40.1(6)
C29A	7739(2)	6647(2)	1758.1(18)	33.6(5)
O1	1726.2(14)	8979.5(14)	3104.0(12)	28.2(4)
C1	1784.1(19)	9244.3(19)	4059.7(16)	25.3(5)
C2	2666(2)	9916.2(19)	4634.2(17)	26.4(5)
C3	3497(2)	10431(2)	4163.6(18)	29.2(5)
C4	3316(2)	10352(2)	3211.8(18)	30.6(5)
C5	2268(2)	9723(2)	2563.2(17)	27.2(5)
C6	900.7(19)	8715.7(19)	4433.5(17)	26.2(5)
C7	-47(2)	8079(2)	3815.6(18)	29.8(5)
C8	-898(2)	7600(2)	4188.4(19)	32.1(5)
C9	-842(2)	7738(2)	5172(2)	34.1(5)
C10	69(2)	8354(2)	5783.3(19)	32.4(5)
C11	964(2)	8856(2)	5429.1(18)	28.5(5)
C12	1921(2)	9529.6(19)	6063.0(17)	27.2(5)
C13	2048(2)	9676(2)	7065.9(18)	34.2(5)
C14	2947(2)	10331(2)	7651.5(19)	37.6(6)
C15	3761(2)	10872(2)	7243.9(19)	37.1(6)
C16	3663(2)	10745(2)	6273.9(19)	32.7(5)
C17	2752(2)	10068.9(19)	5655.3(17)	27.4(5)
C18	1291(2)	10480(2)	2058.9(17)	29.0(5)
C19	308(2)	9965(2)	1418.1(19)	33.7(5)
C20	-607(2)	10601(2)	944(2)	38.7(6)
C21	-557(2)	11766(3)	1098(2)	40.6(6)
C22	411(3)	12282(2)	1733(2)	40.4(6)
C23	1343(2)	11643(2)	2213.5(19)	34.1(5)
C24	2701.4(19)	8975(2)	1806.2(17)	28.2(5)
C25	2639(2)	7813(2)	1759.6(18)	31.7(5)
C26	3105(2)	7176(2)	1092.6(19)	36.5(6)
C27	3631(2)	7686(2)	456.6(19)	37.3(6)

C28	3678(2)	8848(2)	487.7(18)	35.8(6)
C29	3218(2)	9486(2)	1153.7(18)	32.1(5)

Table S12. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3t**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^2U_{11}+2hka*b*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1A	24.2(8)	32.6(9)	29.8(8)	4.0(6)	11.5(6)	6.3(6)
C1A	20.4(10)	26.3(11)	30.1(11)	2.3(8)	10.3(8)	-2.1(8)
C2A	19.4(10)	26.9(11)	34.7(12)	4.9(9)	10.0(9)	-0.2(8)
C3A	19.9(11)	32.9(12)	39.9(13)	7.3(10)	10.1(9)	4.3(9)
C4A	21.9(11)	34.6(12)	39.7(13)	3.9(10)	12.8(10)	6.8(9)
C5A	23.9(11)	31.4(12)	31.6(12)	2.0(9)	13.0(9)	6.9(9)
C6A	19.9(10)	25.9(11)	33.9(12)	3.5(9)	11.4(9)	-2.1(8)
C7A	24.5(11)	31.3(12)	33.2(12)	4.6(9)	10.6(9)	0.5(9)
C8A	20.5(11)	33.3(12)	43.1(14)	6.8(10)	9.9(10)	4.1(9)
C9A	25.0(12)	34.3(13)	46.9(14)	3.8(10)	18.8(10)	1.9(10)
C10A	30.5(12)	34.0(12)	34.2(12)	3.7(9)	15.3(10)	0.3(10)
C11A	23.8(11)	27.2(11)	33.8(12)	3.8(9)	11.3(9)	-0.3(9)
C12A	25.6(11)	26.4(11)	31.8(12)	3.9(9)	9.9(9)	-2.6(9)
C13A	35.2(13)	34.7(13)	33.9(13)	4.5(10)	13(1)	-2.4(10)
C14A	39.4(14)	42.3(14)	30.6(12)	7.3(10)	7.1(10)	-7.0(11)
C15A	30.3(13)	39.6(14)	37.9(13)	12.9(10)	1.2(10)	-1.8(10)
C16A	24.9(12)	33.7(12)	39.2(13)	8.3(10)	7.3(10)	1.0(9)
C17A	20.8(10)	26.1(11)	35.5(12)	5.7(9)	8.6(9)	-1.7(8)
C18A	19.9(11)	37.6(13)	33.7(12)	4.2(9)	14.5(9)	5.2(9)
C19A	30.3(12)	34.8(13)	35.2(12)	4.8(10)	15.7(10)	4.5(10)
C20A	36.2(13)	34.3(13)	40.4(13)	3(1)	18.5(11)	-1.6(10)
C21A	27.6(12)	38.6(14)	44.6(14)	-1.3(11)	16.3(10)	-3.4(10)
C22A	21.0(11)	45.0(14)	42.7(14)	3.8(11)	12.8(10)	5(1)
C23A	24.9(12)	33.3(12)	41.8(13)	5(1)	13.4(10)	4.6(9)
C24A	16.1(10)	40.0(13)	31.0(12)	3.5(9)	8.0(9)	1.7(9)

C25A	20.0(11)	44.0(14)	34.0(12)	3.1(10)	9.0(9)	2.4(10)
C26A	18.6(11)	62.7(17)	32.9(13)	3.3(11)	10.6(9)	4.3(11)
C27A	25.6(12)	73(2)	32.4(13)	12.7(12)	9.3(10)	-7.5(12)
C28A	35.6(14)	50.2(16)	35.1(13)	8.3(11)	7.9(11)	-9.3(12)
C29A	26.3(12)	43.5(14)	32.9(12)	4(1)	10.2(10)	-1.1(10)
O1	24.6(8)	33.2(9)	30.0(8)	4.8(6)	12.0(6)	-1.9(6)
C1	19.1(10)	29.0(11)	30.7(11)	6.8(9)	10.2(8)	6.4(8)
C2	20.8(10)	27.0(11)	34.0(12)	4.6(9)	11.2(9)	4.5(8)
C3	20.1(11)	31.5(12)	37.5(12)	2.2(9)	10.2(9)	0.6(9)
C4	22.4(11)	33.0(12)	40.5(13)	5.9(10)	14.7(10)	-0.4(9)
C5	22.4(11)	30.3(11)	32.7(12)	7.0(9)	13.0(9)	1.5(9)
C6	19.3(10)	26.3(11)	35.5(12)	6.5(9)	10.3(9)	4.9(8)
C7	22.9(11)	32.9(12)	35.6(12)	5.5(9)	10.4(9)	4.1(9)
C8	20.9(11)	33.1(12)	44.5(14)	5.9(10)	11.4(10)	0.4(9)
C9	25.4(12)	35.1(13)	47.7(14)	8(1)	19(1)	3.3(10)
C10	30.5(12)	35.1(13)	37.1(13)	8(1)	17.4(10)	7(1)
C11	22.3(11)	28.7(11)	38.3(13)	6.8(9)	13.2(9)	8.7(9)
C12	23.0(11)	27.4(11)	34.0(12)	5.8(9)	11.2(9)	8.2(9)
C13	34.6(13)	35.9(13)	35.4(13)	5.2(10)	14(1)	4.8(10)
C14	38.1(14)	42.9(14)	31.5(12)	1.2(10)	8.5(10)	9.8(11)
C15	29.5(13)	39.8(14)	40.2(14)	1.0(11)	5.1(10)	2.7(10)
C16	24.7(12)	33.4(12)	40.4(13)	1.9(10)	8.9(10)	5.5(9)
C17	21.0(11)	27.9(11)	34.9(12)	5.3(9)	9.2(9)	6.1(9)
C18	23.9(11)	35.8(12)	32.4(12)	7.4(9)	15.2(9)	5.9(9)
C19	24.5(12)	37.1(13)	42.0(14)	4.8(10)	12.2(10)	4.3(10)
C20	25.1(12)	52.1(16)	41.9(14)	7.2(12)	12.8(10)	7.4(11)
C21	31.1(13)	54.3(17)	42.2(14)	16.5(12)	16.2(11)	15.0(12)
C22	42.9(15)	37.4(14)	49.1(15)	13.9(11)	23.7(12)	10.4(11)
C23	31.6(13)	37.3(13)	38.0(13)	4.6(10)	17(1)	1.9(10)
C24	17.3(10)	39.1(13)	30.3(11)	4.6(9)	8.9(9)	5.3(9)
C25	28.6(12)	36.6(13)	32.4(12)	6(1)	11.0(9)	2.6(10)

C26	35.0(13)	38.3(14)	37.8(13)	2.5(10)	11.6(11)	4.7(11)
C27	28.7(13)	51.6(16)	34.0(13)	0.4(11)	13(1)	8.0(11)
C28	23.3(12)	53.3(16)	35.0(13)	8.5(11)	13.7(10)	3(1)
C29	23.5(11)	40.8(13)	34.7(12)	7.5(10)	10.5(9)	-0.9(10)

Table S13. Bond Lengths for **3t**.

Atom Atom Length/Å			Atom Atom Length/Å		
O1A	C1A	1.374(3)	O1	C1	1.368(3)
O1A	C5A	1.456(3)	O1	C5	1.457(3)
C1A	C2A	1.370(3)	C1	C2	1.370(3)
C1A	C6A	1.431(3)	C1	C6	1.433(3)
C2A	C3A	1.460(3)	C2	C3	1.462(3)
C2A	C17A	1.442(3)	C2	C17	1.441(3)
C3A	C4A	1.321(4)	C3	C4	1.327(3)
C4A	C5A	1.511(3)	C4	C5	1.508(3)
C5A	C18A	1.530(3)	C5	C18	1.533(3)
C5A	C24A	1.536(3)	C5	C24	1.531(3)
C6A	C7A	1.413(3)	C6	C7	1.420(3)
C6A	C11A	1.417(3)	C6	C11	1.409(3)
C7A	C8A	1.379(3)	C7	C8	1.375(3)
C8A	C9A	1.390(4)	C8	C9	1.393(4)
C9A	C10A	1.373(4)	C9	C10	1.378(4)
C10A	C11A	1.409(3)	C10	C11	1.413(3)
C11A	C12A	1.458(3)	C11	C12	1.458(3)
C12A	C13A	1.406(3)	C12	C13	1.408(3)
C12A	C17A	1.422(3)	C12	C17	1.419(3)
C13A	C14A	1.378(4)	C13	C14	1.377(4)
C14A	C15A	1.399(4)	C14	C15	1.406(4)
C15A	C16A	1.368(4)	C15	C16	1.365(4)
C16A	C17A	1.416(3)	C16	C17	1.418(3)
C18A	C19A	1.391(4)	C18	C19	1.396(4)

C18A C23A 1.398(3)	C18 C23 1.392(4)
C19A C20A 1.400(4)	C19 C20 1.384(4)
C20A C21A 1.378(4)	C20 C21 1.393(4)
C21A C22A 1.403(4)	C21 C22 1.382(4)
C22A C23A 1.381(4)	C22 C23 1.401(4)
C24A C25A 1.393(3)	C24 C25 1.387(4)
C24A C29A 1.390(4)	C24 C29 1.400(3)
C25A C26A 1.388(4)	C25 C26 1.387(4)
C26A C27A 1.385(4)	C26 C27 1.388(4)
C27A C28A 1.377(4)	C27 C28 1.388(4)
C28A C29A 1.399(4)	C28 C29 1.383(4)

Table S14. Bond Angles for **3t**.

Atom Atom Atom Angle/°	Atom Atom Atom Angle/°
C1A O1A C5A 119.70(17)	C1 O1 C5 120.22(18)
O1A C1A C6A 115.3(2)	O1 C1 C2 122.4(2)
C2A C1A O1A 122.1(2)	O1 C1 C6 115.4(2)
C2A C1A C6A 122.4(2)	C2 C1 C6 122.1(2)
C1A C2A C3A 116.9(2)	C1 C2 C3 117.0(2)
C1A C2A C17A 119.8(2)	C1 C2 C17 119.7(2)
C17A C2A C3A 123.3(2)	C17 C2 C3 123.3(2)
C4A C3A C2A 121.0(2)	C4 C3 C2 120.9(2)
C3A C4A C5A 122.5(2)	C3 C4 C5 122.5(2)
O1A C5A C4A 110.73(19)	O1 C5 C4 110.84(18)
O1A C5A C18A 106.78(17)	O1 C5 C18 106.87(17)
O1A C5A C24A 106.62(18)	O1 C5 C24 106.63(18)
C4A C5A C18A 114.1(2)	C4 C5 C18 114.1(2)
C4A C5A C24A 107.92(18)	C4 C5 C24 108.72(18)
C18A C5A C24A 110.41(19)	C24 C5 C18 109.44(19)
C7A C6A C1A 121.4(2)	C7 C6 C1 121.1(2)
C7A C6A C11A 119.7(2)	C11 C6 C1 119.1(2)

C11A C6A C1A	118.9(2)	C11 C6 C7	119.8(2)
C8A C7A C6A	120.1(2)	C8 C7 C6	120.1(2)
C7A C8A C9A	120.5(2)	C7 C8 C9	120.4(2)
C10A C9A C8A	120.3(2)	C10 C9 C8	120.4(2)
C9A C10A C11A	121.3(2)	C9 C10 C11	120.9(2)
C6A C11A C12A	119.7(2)	C6 C11 C10	118.4(2)
C10A C11A C6A	118.2(2)	C6 C11 C12	119.9(2)
C10A C11A C12A	122.1(2)	C10 C11 C12	121.7(2)
C13A C12A C11A	122.2(2)	C13 C12 C11	122.5(2)
C13A C12A C17A	118.6(2)	C13 C12 C17	118.6(2)
C17A C12A C11A	119.2(2)	C17 C12 C11	119.0(2)
C14A C13A C12A	121.4(2)	C14 C13 C12	121.7(2)
C13A C14A C15A	119.8(2)	C13 C14 C15	119.6(2)
C16A C15A C14A	120.3(2)	C16 C15 C14	120.1(2)
C15A C16A C17A	121.2(2)	C15 C16 C17	121.5(2)
C12A C17A C2A	119.8(2)	C12 C17 C2	120.1(2)
C16A C17A C2A	121.5(2)	C16 C17 C2	121.3(2)
C16A C17A C12A	118.7(2)	C16 C17 C12	118.6(2)
C19A C18A C5A	122.6(2)	C19 C18 C5	117.7(2)
C19A C18A C23A	119.0(2)	C23 C18 C5	123.0(2)
C23A C18A C5A	118.4(2)	C23 C18 C19	119.2(2)
C18A C19A C20A	120.2(2)	C20 C19 C18	120.5(2)
C21A C20A C19A	120.1(2)	C19 C20 C21	120.3(3)
C20A C21A C22A	120.2(2)	C22 C21 C20	119.5(2)
C23A C22A C21A	119.3(2)	C21 C22 C23	120.5(3)
C22A C23A C18A	121.1(2)	C18 C23 C22	119.9(3)
C25A C24A C5A	117.7(2)	C25 C24 C5	122.8(2)
C29A C24A C5A	122.8(2)	C25 C24 C29	118.7(2)
C29A C24A C25A	119.4(2)	C29 C24 C5	118.5(2)
C26A C25A C24A	120.7(3)	C24 C25 C26	120.3(2)
C27A C26A C25A	120.0(2)	C25 C26 C27	120.9(3)

C28A C27A C26A	119.4(2)	C26 C27 C28	119.1(2)
C27A C28A C29A	121.2(3)	C29 C28 C27	120.2(2)
C24A C29A C28A	119.2(2)	C28 C29 C24	120.8(2)

Table S15. Torsion Angles for **3t**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1A	C1A	C2A	C3A	-6.6(3)	O1	C1	C2	C3	5.5(3)
O1A	C1A	C2A	C17A	172.65(19)	O1	C1	C2	C17	-173.5(2)
O1A	C1A	C6A	C7A	8.2(3)	O1	C1	C6	C7	-7.6(3)
O1A	C1A	C6A	C11A	-173.78(19)	O1	C1	C6	C11	173.96(19)
O1A	C5A	C18A	C19A	-117.6(2)	O1	C5	C18	C19	-59.4(3)
O1A	C5A	C18A	C23A	61.0(3)	O1	C5	C18	C23	120.5(2)
O1A	C5A	C24A	C25A	-174.98(19)	O1	C5	C24	C25	-4.9(3)
O1A	C5A	C24A	C29A	8.2(3)	O1	C5	C24	C29	177.25(19)
C1A	O1A	C5A	C4A	-30.6(3)	C1	O1	C5	C4	29.2(3)
C1A	O1A	C5A	C18A	94.2(2)	C1	O1	C5	C18	-95.6(2)
C1A	O1A	C5A	C24A	-147.77(19)	C1	O1	C5	C24	147.40(19)
C1A	C2A	C3A	C4A	-8.1(3)	C1	C2	C3	C4	7.6(3)
C1A	C2A	C17A	C12A	1.5(3)	C1	C2	C17	C12	-0.3(3)
C1A	C2A	C17A	C16A	-178.2(2)	C1	C2	C17	C16	179.1(2)
C1A	C6A	C7A	C8A	178.3(2)	C1	C6	C7	C8	-178.6(2)
C1A	C6A	C11A	C10A	-178.3(2)	C1	C6	C11	C10	178.4(2)
C1A	C6A	C11A	C12A	0.2(3)	C1	C6	C11	C12	-0.2(3)
C2A	C1A	C6A	C7A	-175.5(2)	C2	C1	C6	C7	176.1(2)
C2A	C1A	C6A	C11A	2.5(3)	C2	C1	C6	C11	-2.4(3)
C2A	C3A	C4A	C5A	2.0(4)	C2	C3	C4	C5	-0.9(4)
C3A	C2A	C17A	C12A	-179.3(2)	C3	C2	C17	C12	-179.1(2)
C3A	C2A	C17A	C16A	1.0(3)	C3	C2	C17	C16	0.3(3)
C3A	C4A	C5A	O1A	16.5(3)	C3	C4	C5	O1	-16.6(3)
C3A	C4A	C5A	C18A	-104.0(3)	C3	C4	C5	C18	104.1(3)
C3A	C4A	C5A	C24A	132.9(2)	C3	C4	C5	C24	-133.5(2)

C4A C5A C18A C19A 5.1(3)	C4 C5 C18 C19 177.7(2)
C4A C5A C18A C23A -176.3(2)	C4 C5 C18 C23 -2.3(3)
C4A C5A C24A C25A 66.0(3)	C4 C5 C24 C25 114.7(2)
C4A C5A C24A C29A -110.7(2)	C4 C5 C24 C29 -63.2(3)
C5A O1A C1A C2A 27.5(3)	C5 O1 C1 C2 -25.3(3)
C5A O1A C1A C6A -156.25(19)	C5 O1 C1 C6 158.34(19)
C5A C18A C19A C20A 178.3(2)	C5 C18 C19 C20 179.7(2)
C5A C18A C23A C22A -178.0(2)	C5 C18 C23 C22 -179.4(2)
C5A C24A C25A C26A -174.8(2)	C5 C24 C25 C26 -176.4(2)
C5A C24A C29A C28A 174.4(2)	C5 C24 C29 C28 176.7(2)
C6A C1A C2A C3A 177.4(2)	C6 C1 C2 C3 -178.5(2)
C6A C1A C2A C17A -3.4(3)	C6 C1 C2 C17 2.6(3)
C6A C7A C8A C9A 0.0(4)	C6 C7 C8 C9 0.3(4)
C6A C11A C12A C13A 178.2(2)	C6 C11 C12 C13 -178.3(2)
C6A C11A C12A C17A -2.0(3)	C6 C11 C12 C17 2.4(3)
C7A C6A C11A C10A -0.3(3)	C7 C6 C11 C10 -0.1(3)
C7A C6A C11A C12A 178.3(2)	C7 C6 C11 C12 -178.7(2)
C7A C8A C9A C10A -0.2(4)	C7 C8 C9 C10 -0.2(4)
C8A C9A C10A C11A 0.2(4)	C8 C9 C10 C11 0.0(4)
C9A C10A C11A C6A 0.0(3)	C9 C10 C11 C6 0.2(3)
C9A C10A C11A C12A -178.5(2)	C9 C10 C11 C12 178.7(2)
C10A C11A C12A C13A -3.2(4)	C10 C11 C12 C13 3.2(3)
C10A C11A C12A C17A 176.5(2)	C10 C11 C12 C17 -176.1(2)
C11A C6A C7A C8A 0.3(3)	C11 C6 C7 C8 -0.2(3)
C11A C12A C13A C14A 180.0(2)	C11 C12 C13 C14 -178.9(2)
C11A C12A C17A C2A 1.1(3)	C11 C12 C17 C2 -2.2(3)
C11A C12A C17A C16A -179.2(2)	C11 C12 C17 C16 178.4(2)
C12A C13A C14A C15A -0.7(4)	C12 C13 C14 C15 0.1(4)
C13A C12A C17A C2A -179.1(2)	C13 C12 C17 C2 178.5(2)
C13A C12A C17A C16A 0.6(3)	C13 C12 C17 C16 -0.9(3)
C13A C14A C15A C16A 0.3(4)	C13 C14 C15 C16 -0.2(4)

C14A C15A C16A C17A 0.6(4)	C14 C15 C16 C17 -0.3(4)
C15A C16A C17A C2A 178.7(2)	C15 C16 C17 C2 -178.6(2)
C15A C16A C17A C12A -1.0(4)	C15 C16 C17 C12 0.8(3)
C17A C2A C3A C4A 172.7(2)	C17 C2 C3 C4 -173.5(2)
C17A C12A C13A C14A 0.2(4)	C17 C12 C13 C14 0.5(4)
C18A C5A C24A C25A -59.4(3)	C18 C5 C24 C25 -120.2(2)
C18A C5A C24A C29A 123.9(2)	C18 C5 C24 C29 62.0(3)
C18A C19A C20A C21A -0.5(4)	C18 C19 C20 C21 0.2(4)
C19A C18A C23A C22A 0.6(3)	C19 C18 C23 C22 0.5(3)
C19A C20A C21A C22A 0.8(4)	C19 C20 C21 C22 -0.4(4)
C20A C21A C22A C23A -0.4(4)	C20 C21 C22 C23 0.6(4)
C21A C22A C23A C18A -0.3(4)	C21 C22 C23 C18 -0.7(4)
C23A C18A C19A C20A -0.2(3)	C23 C18 C19 C20 -0.2(3)
C24A C5A C18A C19A 126.9(2)	C24 C5 C18 C19 55.7(3)
C24A C5A C18A C23A -54.6(3)	C24 C5 C18 C23 -124.4(2)
C24A C25A C26A C27A -0.2(4)	C24 C25 C26 C27 -0.5(4)
C25A C24A C29A C28A -2.3(4)	C25 C24 C29 C28 -1.3(4)
C25A C26A C27A C28A -1.4(4)	C25 C26 C27 C28 -0.6(4)
C26A C27A C28A C29A 1.2(4)	C26 C27 C28 C29 0.8(4)
C27A C28A C29A C24A 0.7(4)	C27 C28 C29 C24 0.1(4)
C29A C24A C25A C26A 2.1(4)	C29 C24 C25 C26 1.5(4)

Table S16. Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3t**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H3A	9130	4099	4472	36
H4A	8806	3924	2860	37
H7A	4889	6714	3096	35
H8A	3440	7611	3730	38
H9A	3524	7650	5375	40
H10A	5044	6787	6394	38
H13A	6429	6049	7281	40

H14A	7959	5138	8257	45
H15A	9338	4141	7577	44
H16A	9188	4072	5940	39
H19A	6889	2641	2626	38
H20A	5291	1449	1845	42
H21A	3680	2151	778	43
H22A	3664	4051	448	42
H23A	5259	5225	1211	39
H25A	8107	4039	1070	39
H26A	8991	4880	-8	45
H27A	9125	6836	34	51
H28A	8310	7931	1112	48
H29A	7406	7102	2195	40
H3	4175	10827	4544	35
H4	3866	10705	2928	37
H7	-93	7984	3144	36
H8	-1528	7172	3773	39
H9	-1436	7406	5422	41
H10	97	8442	6452	39
H13	1500	9313	7346	41
H14	3016	10416	8327	45
H15	4381	11327	7644	45
H16	4217	11118	6007	39
H19	267	9171	1307	40
H20	-1272	10242	510	46
H21	-1183	12202	769	49
H22	445	13075	1845	49
H23	2010	12004	2644	41
H25	2275	7452	2187	38
H26	3062	6381	1071	44
H27	3956	7245	6	45

H28	4027	9206	50	43
H29	3252	10281	1169	39

Table S17. Crystal data and structure refinement for **4b**.

Identification code	yi2z4
Empirical formula	C ₃₂ H ₄₂ O ₃
Formula weight	474.66
Temperature/K	99.8(5)
Crystal system	triclinic
Space group	P1
a/Å	6.6192(2)
b/Å	6.9546(2)
c/Å	14.6658(7)
α/°	99.503(3)
β/°	96.444(3)
γ/°	95.740(3)
Volume/Å ³	656.79(4)
Z	1
ρ _{calc} /cm ³	1.200
μ/mm ⁻¹	0.581
F(000)	258.0
Crystal size/mm ³	0.18 × 0.14 × 0.02
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	13 to 146.86
Index ranges	-8 ≤ h ≤ 8, -8 ≤ k ≤ 8, -17 ≤ l ≤ 18
Reflections collected	11892
Independent reflections	4532 [R _{int} = 0.0521, R _{sigma} = 0.0369]
Data/restraints/parameters	4532/3/321
Goodness-of-fit on F ²	1.127
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0644, wR ₂ = 0.1789
Final R indexes [all data]	R ₁ = 0.0667, wR ₂ = 0.1804
Largest diff. peak/hole / e Å ⁻³	0.29/-0.30
Flack parameter	-0.1(4)

Table S18. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **4b**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
O1	10444(4)	4464(4)	1911(2)	30.0(6)
O2	-2247(4)	2354(4)	5846(2)	29.2(6)
O3	9363(4)	857(4)	1131(2)	32.5(7)
C1	5863(5)	2382(5)	2767(3)	25.6(8)
C2	7502(6)	2451(6)	2237(3)	26.2(8)
C3	8816(5)	4245(6)	2382(3)	25.7(8)
C4	8415(6)	5827(6)	3010(3)	27.3(8)
C5	6779(5)	5722(5)	3525(3)	24.1(8)
C6	6503(6)	7508(5)	4231(3)	27.6(8)
C7	4426(6)	7387(6)	4578(3)	27.0(8)
C8	3822(6)	5367(5)	4806(3)	23.8(8)
C9	3563(5)	3841(5)	3908(3)	23.6(8)
C10	5454(6)	3953(5)	3399(3)	24.5(8)
C11	2912(6)	1756(5)	4084(3)	26.4(8)
C12	945(6)	1651(5)	4562(3)	26.0(8)
C13	1175(5)	3192(5)	5441(3)	23.2(8)
C14	1769(5)	5229(5)	5191(3)	23.7(8)
C15	1403(6)	6701(6)	6046(3)	26.2(8)
C16	-522(5)	5699(5)	6329(3)	23.9(8)
C17	-777(6)	3570(6)	5873(3)	25.3(8)
C18	2688(6)	2702(6)	6232(3)	27.0(8)
C19	7837(6)	783(6)	1544(3)	26.5(8)
C20	6244(6)	-1001(6)	1290(3)	26.2(8)
C21	4315(6)	-536(6)	714(3)	28.3(8)
C22	2656(6)	-2288(6)	506(3)	31.4(9)
C23	3456(7)	-4116(7)	10(4)	39.4(10)
C24	5401(7)	-4570(6)	549(4)	36.7(10)
C25	7043(6)	-2799(6)	748(3)	30.4(9)
C26	-1796(6)	6510(6)	6870(3)	26.7(8)
C27	-1520(6)	8612(6)	7347(3)	27.0(8)
C28	-3515(6)	9387(6)	7564(3)	33.7(9)
C29	-3178(7)	11551(6)	8061(3)	35.1(10)
C30	-1638(7)	11814(6)	8933(3)	35.2(10)
C31	376(7)	11052(7)	8727(4)	37.3(10)
C32	13(6)	8893(6)	8241(3)	35.2(10)

Table S19. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **4b**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^2U_{11}+2hka*b*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
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O1	23.1(14)	34.6(15)	33.0(17)	5.6(13)	10.6(12)	0.4(11)
O2	22.5(13)	25.0(13)	38.7(17)	2.1(12)	9.6(12)	-4.9(10)
O3	25.9(14)	34.8(15)	37.6(18)	3.8(13)	13.4(13)	1.2(12)
C1	21.9(18)	24.8(18)	30(2)	5.1(16)	3.6(16)	0.0(14)
C2	23.1(18)	31(2)	24(2)	5.5(16)	3.6(15)	2.9(15)
C3	18.2(17)	31(2)	31(2)	11.3(17)	4.5(15)	3.5(14)
C4	22.6(18)	26.1(19)	34(2)	8.1(17)	5.5(16)	-1.1(14)
C5	19.0(17)	24.8(18)	28(2)	4.5(16)	1.7(15)	2.6(14)
C6	28(2)	23.0(18)	32(2)	3.3(16)	8.4(17)	0.5(15)
C7	28(2)	23.4(18)	30(2)	3.1(16)	9.0(16)	1.9(14)
C8	23.2(18)	21.1(17)	27(2)	2.9(15)	6.5(15)	1.6(13)
C9	20.1(17)	23.0(18)	27(2)	2.7(15)	3.9(15)	-0.2(13)
C10	24.7(18)	23.9(18)	25(2)	6.0(16)	2.2(16)	1.7(14)
C11	25.1(19)	21.3(18)	32(2)	-1.2(16)	11.0(16)	-0.8(14)
C12	22.0(17)	24.1(18)	31(2)	1.7(16)	8.6(15)	-0.1(14)
C13	17.2(16)	22.2(16)	30(2)	5.5(15)	4.7(14)	-0.2(13)
C14	22.6(17)	19.3(17)	28(2)	0.4(15)	5.5(15)	2.1(13)
C15	23.2(18)	24.5(18)	32(2)	2.4(16)	10.6(15)	2.7(14)
C16	17.2(16)	24.6(17)	30(2)	3.9(15)	5.2(14)	1.5(14)
C17	25.1(19)	26.5(18)	24(2)	4.0(16)	3.7(15)	4.8(15)
C18	25.3(18)	25.7(18)	32(2)	10.7(16)	5.1(16)	4.8(14)
C19	20.7(18)	31(2)	30(2)	9.4(16)	5.0(15)	4.7(14)
C20	20.4(17)	28.3(19)	31(2)	6.2(16)	7.5(15)	3.1(14)
C21	23.1(18)	32(2)	32(2)	7.6(17)	6.9(16)	5.7(15)
C22	23.0(19)	33(2)	37(2)	4.4(17)	4.3(17)	0.9(15)
C23	34(2)	38(2)	42(3)	-2(2)	2(2)	-0.1(18)
C24	36(2)	29(2)	45(3)	-1.9(19)	13(2)	4.1(17)
C25	26.9(19)	31(2)	34(2)	4.9(17)	9.5(17)	5.7(16)
C26	25.0(18)	27.4(19)	28(2)	6.4(16)	3.5(16)	1.0(15)
C27	26(2)	26.4(19)	30(2)	4.8(16)	8.0(16)	4.9(15)
C28	26(2)	36(2)	39(3)	1.6(19)	6.3(17)	8.0(16)
C29	33(2)	33(2)	39(3)	-1.0(19)	8.4(19)	12.3(17)
C30	39(2)	31(2)	35(2)	-2.0(18)	10.8(19)	5.0(18)
C31	30(2)	36(2)	41(3)	-6.0(19)	3.7(18)	2.8(17)
C32	28(2)	34(2)	41(3)	0.5(19)	2.0(18)	5.9(17)

Table S20. Bond Lengths for **4b**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C3	1.353(4)	C13	C17	1.528(5)
O2	C17	1.216(5)	C13	C18	1.550(5)
O3	C19	1.236(5)	C14	C15	1.541(5)
C1	C2	1.405(5)	C15	C16	1.522(5)
C1	C10	1.381(5)	C16	C17	1.505(5)
C2	C3	1.419(5)	C16	C26	1.326(5)

C2	C19	1.463(6)	C19	C20	1.512(5)
C3	C4	1.381(6)	C20	C21	1.543(5)
C4	C5	1.390(5)	C20	C25	1.541(5)
C5	C6	1.520(6)	C21	C22	1.523(5)
C5	C10	1.411(5)	C22	C23	1.530(6)
C6	C7	1.518(5)	C23	C24	1.522(6)
C7	C8	1.522(5)	C24	C25	1.525(6)
C8	C9	1.529(5)	C26	C27	1.497(5)
C8	C14	1.529(5)	C27	C28	1.522(5)
C9	C10	1.530(5)	C27	C32	1.538(6)
C9	C11	1.541(5)	C28	C29	1.542(6)
C11	C12	1.547(5)	C29	C30	1.517(7)
C12	C13	1.517(6)	C30	C31	1.526(6)
C13	C14	1.546(5)	C31	C32	1.535(6)

Table S21. Bond Angles for **4b**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	C1	C2	123.9(3)	C8	C14	C13	112.4(3)
C1	C2	C3	117.0(3)	C8	C14	C15	120.8(3)
C1	C2	C19	122.4(3)	C15	C14	C13	104.4(3)
C3	C2	C19	120.5(3)	C16	C15	C14	102.1(3)
O1	C3	C2	121.8(4)	C17	C16	C15	108.0(3)
O1	C3	C4	118.8(3)	C26	C16	C15	127.5(4)
C4	C3	C2	119.5(3)	C26	C16	C17	124.5(3)
C3	C4	C5	122.4(3)	O2	C17	C13	125.5(4)
C4	C5	C6	118.9(3)	O2	C17	C16	127.2(3)
C4	C5	C10	119.4(3)	C16	C17	C13	107.3(3)
C10	C5	C6	121.6(3)	O3	C19	C2	120.6(4)
C7	C6	C5	113.6(3)	O3	C19	C20	119.5(4)
C6	C7	C8	111.3(3)	C2	C19	C20	119.8(3)
C7	C8	C9	108.9(3)	C19	C20	C21	110.9(3)
C7	C8	C14	112.3(3)	C19	C20	C25	113.1(3)
C14	C8	C9	106.5(3)	C25	C20	C21	109.2(3)
C8	C9	C10	112.0(3)	C22	C21	C20	111.1(3)
C8	C9	C11	111.8(3)	C21	C22	C23	110.9(3)
C10	C9	C11	112.8(3)	C24	C23	C22	112.0(4)
C1	C10	C5	117.7(3)	C23	C24	C25	111.0(4)
C1	C10	C9	121.7(3)	C24	C25	C20	110.5(3)
C5	C10	C9	120.4(3)	C16	C26	C27	124.8(3)
C9	C11	C12	112.1(3)	C26	C27	C28	113.6(3)
C13	C12	C11	110.9(3)	C26	C27	C32	110.1(3)
C12	C13	C14	108.7(3)	C28	C27	C32	110.4(3)
C12	C13	C17	116.8(3)	C27	C28	C29	112.3(3)
C12	C13	C18	112.1(3)	C30	C29	C28	110.5(4)

C14	C13	C18	113.2(3)	C29	C30	C31	112.1(4)
C17	C13	C14	99.9(3)	C30	C31	C32	111.0(4)
C17	C13	C18	105.6(3)	C31	C32	C27	111.1(3)

Table S22. Hydrogen Bonds for **4b**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1	H1	O3	0.89(5)	1.78(5)	2.574(4)	148(5)

Table S23. Torsion Angles for **4b**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C3	C4	C5	-179.7(4)	C12	C13	C14	C8	-61.9(4)
O3	C19	C20	C21	-105.1(4)	C12	C13	C14	C15	165.5(3)
O3	C19	C20	C25	17.9(5)	C12	C13	C17	O2	31.6(6)
C1	C2	C3	O1	179.7(4)	C12	C13	C17	C16	-148.4(3)
C1	C2	C3	C4	-1.2(5)	C13	C14	C15	C16	-37.6(4)
C1	C2	C19	O3	-175.7(4)	C14	C8	C9	C10	174.7(3)
C1	C2	C19	C20	7.9(6)	C14	C8	C9	C11	-57.6(4)
C2	C1	C10	C5	-0.6(6)	C14	C13	C17	O2	148.6(4)
C2	C1	C10	C9	175.7(4)	C14	C13	C17	C16	-31.5(4)
C2	C3	C4	C5	1.2(6)	C14	C15	C16	C17	17.5(4)
C2	C19	C20	C21	71.3(4)	C14	C15	C16	C26	-161.9(4)
C2	C19	C20	C25	-165.7(3)	C15	C16	C17	O2	-171.0(4)
C3	C2	C19	O3	6.0(6)	C15	C16	C17	C13	9.1(4)
C3	C2	C19	C20	-170.4(3)	C15	C16	C26	C27	-2.5(7)
C3	C4	C5	C6	177.5(4)	C16	C26	C27	C28	155.1(4)
C3	C4	C5	C10	-0.8(6)	C16	C26	C27	C32	-80.5(5)
C4	C5	C6	C7	166.5(3)	C17	C13	C14	C8	175.2(3)
C4	C5	C10	C1	0.5(5)	C17	C13	C14	C15	42.6(4)
C4	C5	C10	C9	-175.9(4)	C17	C16	C26	C27	178.2(4)
C5	C6	C7	C8	44.3(5)	C18	C13	C14	C8	63.4(4)
C6	C5	C10	C1	-177.7(4)	C18	C13	C14	C15	-69.3(4)
C6	C5	C10	C9	5.9(6)	C18	C13	C17	O2	-93.7(5)
C6	C7	C8	C9	-64.3(4)	C18	C13	C17	C16	86.2(3)
C6	C7	C8	C14	178.0(3)	C19	C2	C3	O1	-1.9(6)
C7	C8	C9	C10	53.3(4)	C19	C2	C3	C4	177.1(4)
C7	C8	C9	C11	-179.0(3)	C19	C20	C21	C22	-176.5(3)
C7	C8	C14	C13	-178.8(3)	C19	C20	C25	C24	177.5(4)
C7	C8	C14	C15	-54.9(5)	C20	C21	C22	C23	-56.1(5)
C8	C9	C10	C1	158.5(3)	C21	C20	C25	C24	-58.6(4)
C8	C9	C10	C5	-25.3(5)	C21	C22	C23	C24	54.2(5)
C8	C9	C11	C12	55.2(4)	C22	C23	C24	C25	-54.8(5)
C8	C14	C15	C16	-165.2(3)	C23	C24	C25	C20	57.2(5)

C9 C8 C14C13	62.0(4)	C25C20C21C22	58.3(4)
C9 C8 C14C15	-174.1(3)	C26C16C17O2	8.5(6)
C9 C11C12C13	-53.3(4)	C26C16C17C13	-171.5(4)
C10C1 C2 C3	1.0(6)	C26C27C28C29	179.6(4)
C10C1 C2 C19	-177.3(4)	C26C27C32C31	178.2(4)
C10C5 C6 C7	-15.3(5)	C27C28C29C30	-55.0(5)
C10C9 C11C12	-177.6(3)	C28C27C32C31	-55.6(4)
C11C9 C10C1	31.4(5)	C28C29C30C31	54.6(5)
C11C9 C10C5	-152.4(3)	C29C30C31C32	-55.8(5)
C11C12C13C14	55.1(4)	C30C31C32C27	55.8(5)
C11C12C13C17	167.1(3)	C32C27C28C29	55.5(5)
C11C12C13C18	-70.9(4)		

Table S24. Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **4b**.

Atom	x	y	z	U(eq)
H1	10260(80)	3400(80)	1470(40)	34(13)
H1A	4983	1184	2685	31
H4	9289	7029	3094	33
H6A	7584	7660	4770	33
H6B	6687	8693	3942	33
H7A	3381	7664	4095	32
H7B	4471	8398	5144	32
H8	4914	5049	5266	29
H9	2411	4181	3486	28
H11A	4037	1342	4482	32
H11B	2673	831	3481	32
H12A	-231	1862	4125	31
H12B	664	330	4721	31
H14	711	5369	4670	28
H15A	2569	6883	6551	31
H15B	1175	7992	5879	31
H18A	2157	1465	6406	40
H18B	2841	3760	6776	40
H18C	4023	2572	6015	40
H20	5835	-1358	1882	31
H21A	3785	608	1063	34
H21B	4679	-188	120	34
H22A	1465	-1978	109	38
H22B	2192	-2554	1097	38
H23A	2387	-5255	-69	47
H23B	3737	-3912	-618	47
H24A	5924	-5697	183	44
H24B	5085	-4941	1146	44
H25A	7441	-2491	153	36

H25B	8273	-3113	1118	36
H26	-2970	5698	6962	32
H27	-914	9417	6917	32
H28A	-4182	8573	7965	40
H28B	-4450	9267	6976	40
H29A	-2673	12395	7632	42
H29B	-4496	11963	8231	42
H30A	-2228	11104	9392	42
H30B	-1367	13225	9213	42
H31A	1303	11178	9318	45
H31B	1047	11857	8324	45
H32A	-520	8069	8671	42
H32B	1330	8457	8082	42