

Terpenylation of Ketones and Secondary Alcohol Under Hydrogen Borrowing Manganese Catalysis

3.1 History, Background and Objective

Carbon-Carbon bond formation is a crucial transformation in organic synthesis to install the carbon backbone of organic molecules.^{148,149} The construction of the C-C bonds induced by homogeneous catalysis is of paramount interest in both academia and industrial sectors.^{80,150} ‘Borrowing hydrogen’ or ‘hydrogen auto-transfer’ route mediated by transition metals is an attractive green and atom-efficient C-C bond forming reaction that is used to diversify the synthetic utility of readily-available commodity alcohols.^{33,68,77,151} In this process a catalyst first dehydrogenates an alcohol by expulsion of hydrogen to form a reactive carbonyl electrophile. This intermediate can undergo an assortment of subsequent transformations before the catalyst returns the “borrowed” hydrogen to liberate the product and the catalyst is regenerated.^{83,84,152} Based on this redox neutral reaction scheme, a great deal of alkylation reactions have been developed using alcohols as pro-electrophiles.^{51,76,81,82,93,153–162} Recent advances in the direct utilization of easily-accessible alcohols in various organic transformations resulted in growing interest towards unsaturated allylic alcohols as well.^{163–166} In this context, terpene alcohols are gaining significant momentum owing to the prevalence of these moieties in plants secondary metabolites and their bioactivities. A few of them are listed in Figure 3.1.^{167–169}

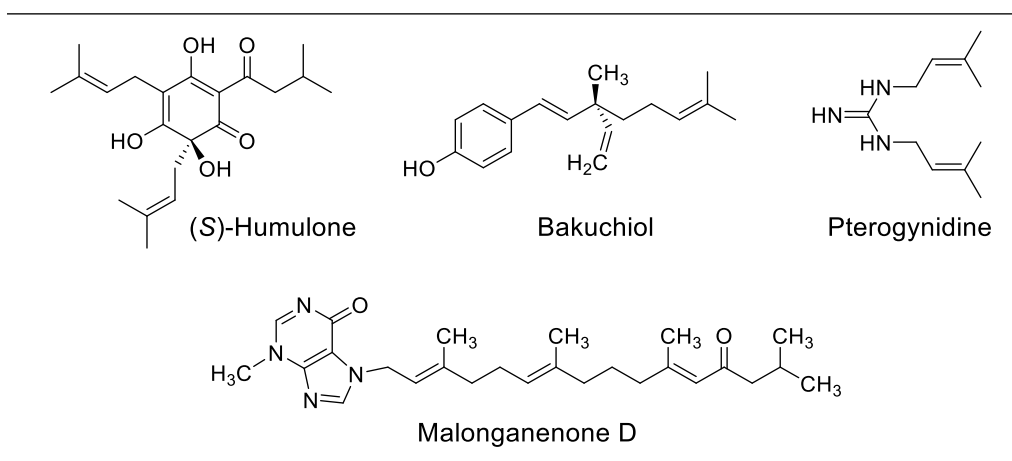


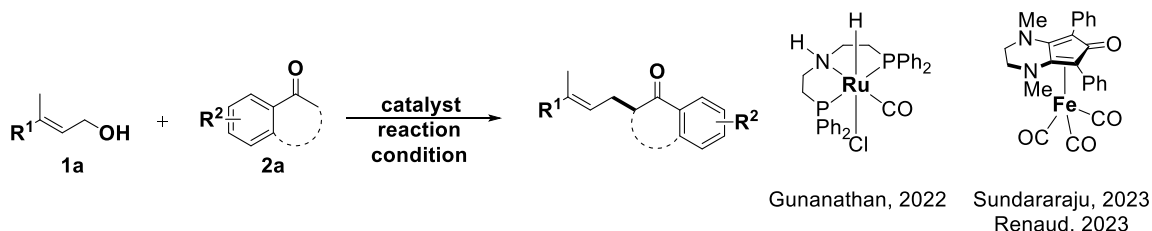
Figure 3.1. Examples of some naturally available terpenylated moieties.

Terpene alcohols such as prenol (3-methylbut-2-en-1-ol), and its derivatives (nerol, phytols, solanesol and farnesol etc) are greener, naturally occurring isoprenoids having immense importance in biological systems.^{170–172}

The traditional use of corresponding halides and strong (over)stoichiometric bases to prepare the desired terpenylated products suffers from hazardous precursors and copious waste generation.^{173,174} Over the years versatile catalytic methods have been developed using metal catalysts and terpenyl derivatives.^{175–181} In 2013 Bruneau reported Ru(II) catalyzed various C- and -N terpenylated alkaloid synthesis using saturated cyclic amines and terpenaldehydes generating water and CO₂ as only side products.^{175,176} Chen group developed protocols for prenylation and reverse prenylation of indoles¹⁷⁷ and oxindoles¹⁷⁸ using Rh and Pd metal catalysts and isoprene unit. Gunanathan and co-workers described the prenylation of ketones using

corresponding alcohols in the presence of the Ru-Macho complex utilizing borrowing hydrogen concept (Figure 3.2).¹⁸² In view of the high cost, low abundance, and toxicity issues of the heavy late transition metals, current research work is directed towards the usage of inexpensive, earth-abundant, bio-relevant base metals instead.^{7,13,88–94,183} In fact Sundararaju's group demonstrated a cyclopentadienone iron tricarbonyl complex catalyzed terpenylation of oxindoles (Figure 3.2).¹⁸⁴ Very recently Renaud reported visible light induced α -prenylation and alkynylation of ketone catalyzed by the same iron tricarbonyl complex at room temperature in the presence of allylic and propargylic alcohols as pro-electrophiles (Figure 3.2).¹⁸⁵ In this context, manganese complexes, being the third most earth-abundant element on the earth crust, have also drawn appreciable attention. Since the pioneering work by Milstein group¹⁸⁶ on dehydrogenative coupling reaction of alcohol and amines catalyzed by manganese, a slew of reports continue to appear on manganese dehydrogenative catalysis including alkylation reactions.^{34,52,53,71,104,108,109,111–115,118–120,187–197} We have recently reported a pincer N[^]N[^]N manganese complex catalyzed α -alkylation of methyl ketones using alcohols.¹⁹⁸ Prenylation of ketones was also attempted but we could hardly detect any desired product. Considering thriving application of PNP ligand-based manganese macho complex **Mn-2** (Figure 3.2) in dehydrogenative coupling reactions by various groups,^{191–197} we were prompted to explore its catalytic activity in terpenylation reactions. The complex **Mn-2** has been reported for isomerization of (homo)allylic alcohols to ketones by the group of Johannes d. Vries in 2019.¹⁹⁹ Very recently, Ling and Zhong have shown that this complex is capable to dehydrogenatively cross-couple allylic alcohol and nitriles giving delta-hydroxynitriles.²⁰⁰ To the best of our knowledge, manganese complexes were not exploited for terpenylation reactions thus far.

(a) previous reports on terpenylation of ketones



(b) our work

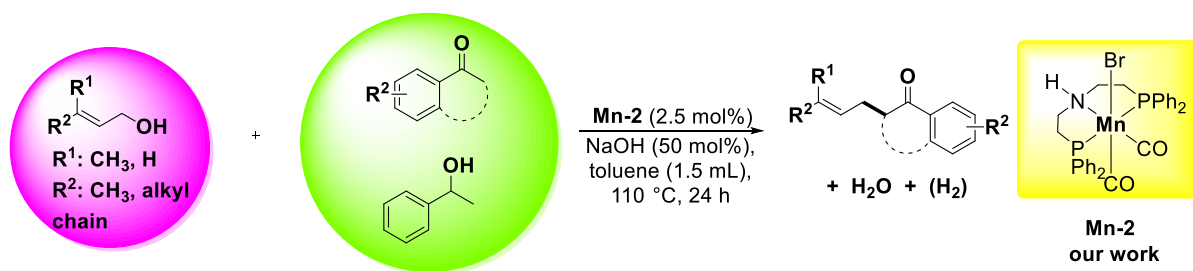


Figure 3.2. (a) Complexes known for terpenylation using hydrogen borrowing methodology. (b) Our work.

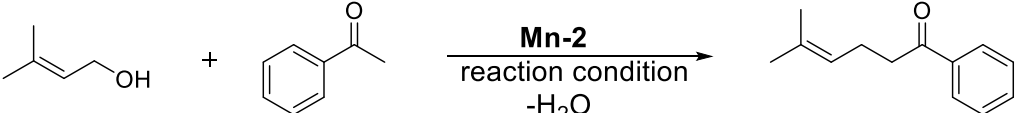
3.2 Result and Discussion

Here in this paper, we are presenting pincer PNP manganese complex **Mn-2** catalyzed terpenylation of ketones directly from prenyl and its derivatives. In addition, terpenylation of secondary alcohol 1-phenylethanol was also realized.

We chose the simplest hemiterpenoid, prenyl as the benchmark alkylating agent to couple with acetophenone for our optimization reaction studies. We set out to use 50 mol% KO^tBu and 2.5 mol% **Mn-2** in toluene and heated for 24 h at 130 °C. The desired prenylated product was obtained in 46% yield (Table 3.1, entry 1). Changing the base to NaOH increased the yield of the prenylated product to 70% (Table 3.1, entry 2). Further optimization studies revealed that the

reaction of acetophenone (0.5 mmol) with prenol (0.6 mmol), **Mn-2** (2.5 mol%) and NaOH (50 mol%) in 1.5 mL toluene, at 110 °C for 24 h provided the desired prenylated product **3a** in 82% isolated yield (Table 3.1, entry 10). We have also tested the reaction in the absence of catalyst using 50 mol% of base (Table 3.1, entry 16), a negligible amount of product (<10%) was detected. On the other hand, when catalyst was used without any base, no product formation was observed (Table 3.1, entry 17). Also, when the reaction was carried out in open air a trace amount of product was detected (Table 3.1, entry 18). A reaction was also carried out using complex (PN^HN)Mn(CO)₂Br (PN^HN = *N*-(2-(diphenylphosphanyl)benzyl)-1-(pyridin-2-yl)methanamine) giving traces of the desired product under optimized reaction conditions (Table 3.1, entry 19).

Table 3.1. Optimization table.^a

						
entry	base (mol %)	catalyst (mol %)	solvent (mL)	T (°C)	time (h)	yield (%)
1	KO ^t Bu (50)	Mn-2 (2.5)	Toluene (1.5)	130	24	46%
2	NaOH (50)	Mn-2 (2.5)	Toluene (1.5)	130	24	74%
3	Cs ₂ CO ₃ (50)	Mn-2 (2.5)	Toluene (1.5)	130	24	trace
4	KO ^t Bu (50)	Mn-2 (2.5)	THF (1.5)	130	24	37%
5	KO ^t Bu (50)	Mn-2 (2.5)	Dioxane (1.5)	130	24	34%
6	KO ^t Bu (50)	Mn-2 (2.5)	Benzene (1.5)	130	24	57%
7	NaOH (50)	Mn-2 (2.5)	Toluene (1.5)	130	48	80%
8	NaOH (50)	Mn-2 (2.5)	Toluene (1.5)	130	12	70%
9	NaOH (50)	Mn-2 (2.5)	Toluene (1.5)	150	24	72
10	NaOH (50)	Mn-2 (2.5)	Toluene (1.5)	110	24	>90% (82%)^b
11	NaOH (50)	Mn-2 (1)	Toluene (1.5)	110	24	52%
12	NaOH (50)	Mn-2 (5)	Toluene (1.5)	110	24	78%
13	NaOH (25)	Mn-2 (2.5)	Toluene (1.5)	110	24	36%
14	NaOH (100)	Mn-2 (2.5)	Toluene (1.5)	110	24	65%
15	NaOH (50)	Mn-2 (2.5)	Toluene (1.5)	110	12	45%
16	NaOH (50)	-	Toluene (1.5)	110	24	<10%
17	-	Mn-2 (2.5)	Toluene (1.5)	110	24	trace
18	NaOH (50)	Mn-2 (2.5)	Toluene (1.5)	110	12	10% ^c
19 ^d	NaOH (50)	Mn-3 (2.5)	Toluene (1.5)	110	24	trace

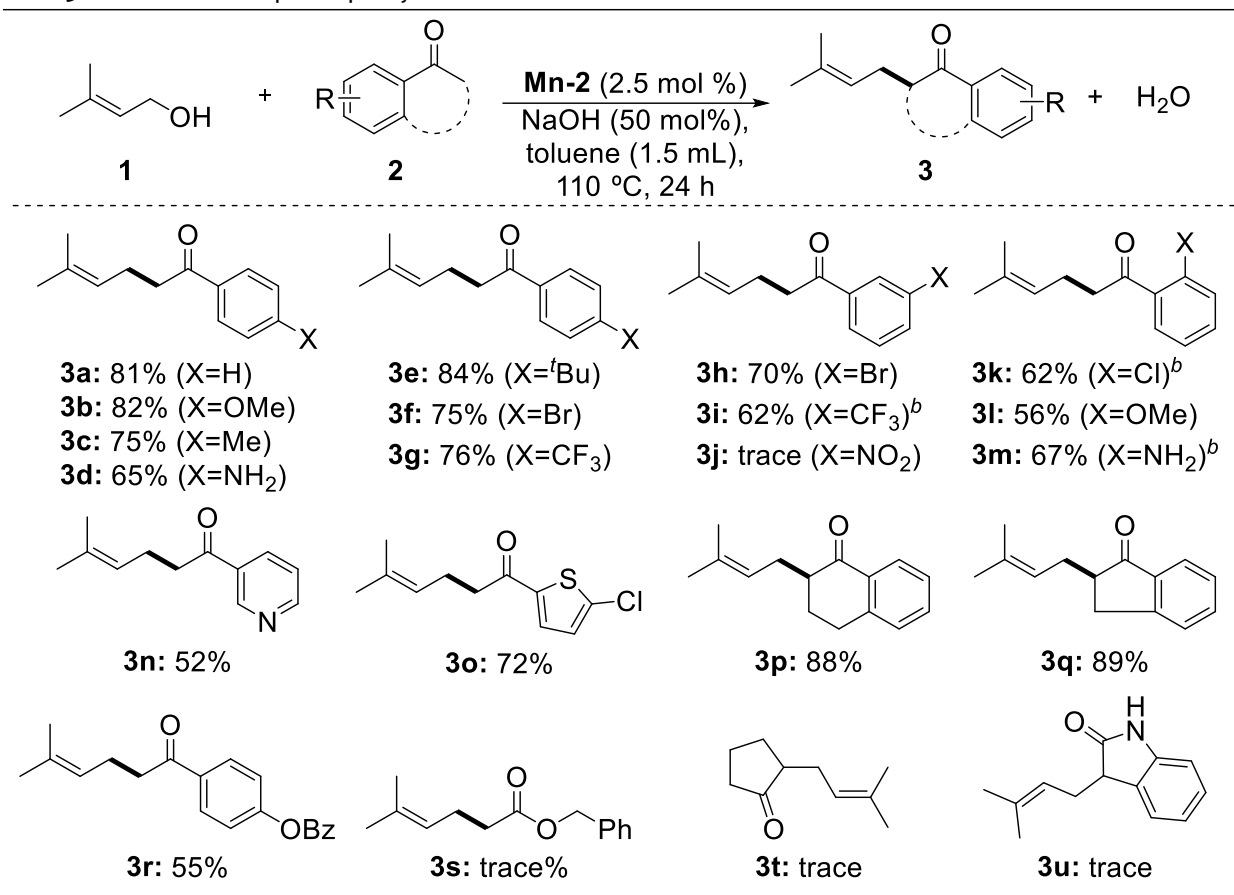
^aReaction conditions unless otherwise specified: 0.6 mmol of prenol and 0.5 mmol acetophenone, 50 mol% of NaOH and 2.5 mol% of cat. **Mn-2** and toluene (1.5 mL) were heated at 110 °C for 24 h. Yields were determined by ¹H NMR using 1,1,2,2-tetrachloroethane. ^bIsolated yield. ^cReaction was carried out in open air. ^d(PN^HN)Mn(CO)₂Br (**Mn-3**) complex was used as catalyst.

Now, that the optimised condition is known, we have investigated the substrate scope of various substituted acyclic and cyclic ketones with prenol to yield prenylated γ,δ -unsaturated ketones (Table 3.2). Prenylated compounds constitute one of the most crucial classes of terpenoids that exhibit a vast array of medicinal properties, including antibacterial, antibiotic, antimalarial, antioxidant, and anticancer properties.²⁰¹ Hydrophobic prenyl units in proteins or other biomolecules facilitates attachment to the cell membranes, like the lipid anchors.¹⁷⁰ Additionally, γ,δ -unsaturated ketones are essential component in a variety of functional molecules. Such ketones are prime intermediates in the synthesis of carbocycles and heterocycles.^{202,203}

Thus, under the optimized reaction conditions, acetophenone bearing electron donating groups (OMe, Me, NH₂, ^tBu) at *para* (**3b-e**), and *ortho* position (OMe, NH₂; **3l, m**) afforded decent yields of the corresponding prenylated products (Table 3.2, 56-84%). Acetophenone containing electron withdrawing substituents (Br, CF₃, Cl) at *para* (**3f, g**), *meta* (**3h, i**) and *ortho* position (**3k**) were also

successfully α -prenylated furnishing 62-76% yields of the corresponding products (Table 3.2), indicating electronics of the substituents impart negligible effect in determining the yield of the prenylated products. However, in case of 3-nitroacetophenone only traces of the corresponding prenylated product was observed (Table 3.2, **3j**). Next, the scope of the reaction was also explored with heteroaryl ketones like 3-acetylpyridine and 2-acetyl-4-Cl thiophene. Both the substrates were prenylated in good yields (52%, **3n** and 72%, **3o**) under the reaction conditions.

Table 3.2. Substrates scope for prenylation of ketones.^a



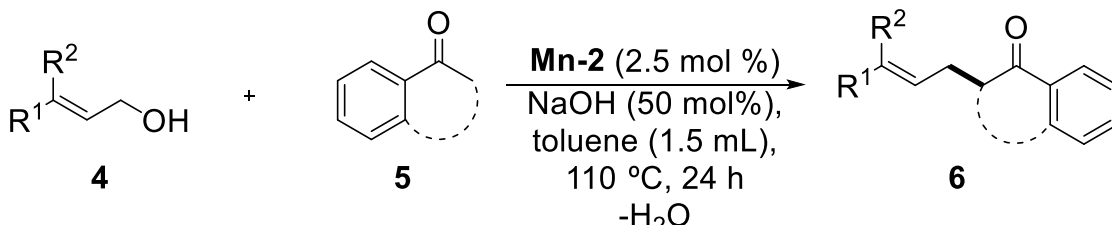
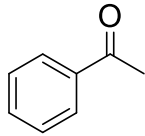
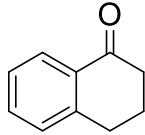
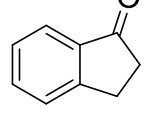
^aReaction conditions unless otherwise specified: 0.6 mmol of prenil and 0.5 mmol ketone, 50 mol% of NaOH and 2.5 mol% of cat. **Mn-2** and toluene (1.5 mL) were heated at 110 °C for 24 h and the yields are isolated. ^bNMR yield.

Considering the synthetic and biological importance of 1-tetralone and 1-indanone derivatives,^{204,205} we were also intrigued to examine the prenylation reactions with these substrates. To our delight, 1-tetralone and 1-indanone could be prenylated in 88% (**3p**) and 89% (**3q**) yields, respectively. 4-acetylphenyl benzoate gave the desired product (Table 3.2, **3r**) in moderate yield of 55%. However, we did not notice any product formation when prenylation reaction was carried out using benzyl acetate, cyclopentanone and oxindole as substrates (Table 3.2, **3s-3u**).

Next, we probed the catalytic performance of **Mn-1** in terpenylation reaction by using terpenoids like nerol, phytol, solanesol, E-farnesol with acetophenone, 1-tetralone and 1-indanone under identical optimized reaction conditions (Table 3.3). Monoterpenoid nerol gave corresponding terpenylated product with acetophenone in 37.5% yield (**6a**), whereas it coupled with 1-tetralone and 1-indanone to yield the corresponding products in 37% and 42% yields, respectively (Table 3.3, **6e**, **6i**). Acyclic hydrogenated diterpenoid phytol afforded alkylated products with acetophenone, 1-tetralone and with 1-indanone in yields of 38%, 38% and 40%, respectively (Table 3.3, **6b**, **6f**, **6j**). Nonaisoprenoid solanesol furnished terpenylated products by coupling with acetophenone (28%), 1-tetralone (31%) and with 1-indanone (29%). Sesquiterpene alcohol E-farnesol produces dehydrogenatively coupled product with 1-tetralone in low 25% yield and with 1-indanone in 38% yield (Table 3.3, **6g**, **6k**). Furthermore, cinnamyl alcohol produces

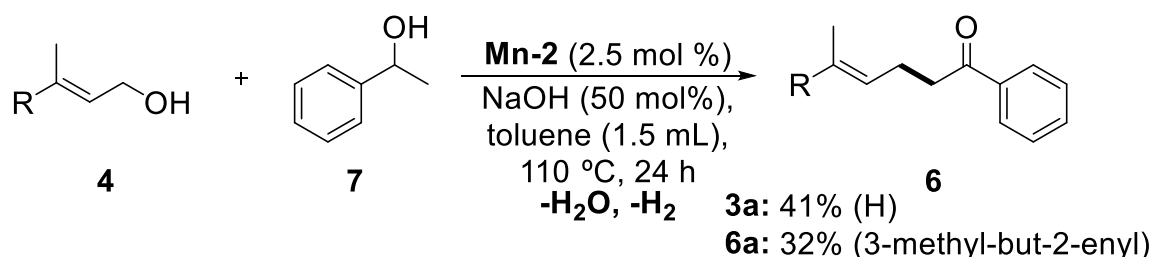
dehydrogenatively coupled product with acetophenone in low yield (26%, **6d**). Anticipating that the lower yield might be due to back reaction, the terpenylation reaction of acetophenone with nerol and phytol was carried out for 12 h otherwise analogous condition and the yields obtained for the corresponding products are 31% and 29.5% (Table 3.3). Additionally, the experiments were also conducted in open system under N₂ atmosphere, however in this case also no significant improvement of the yields was observed (39%, and 40%; Table 3.3).

Table 3.3. Substrates scope for the terpenylation of ketones.^a

		
4	5	Yield of 6 (%)
Nerol		6a: 37.5% (31%)^c (39%)^d
Phytol		6b: 38%^b (29.5%)^{b,c} (40%)^{b,d}
Solanesol		6c: 28%
Cinnamyl alcohol		6d: 26%^b
Nerol		6e: 37%
Phytol		6f: 38%
(E)-farnesol		6g: 25%^b
Solanesol		6h: 31%
Nerol		6i: 42%
Phytol		6j: 40%
(E)-farnesol		6k: 38%
Solanesol		6l: 29%

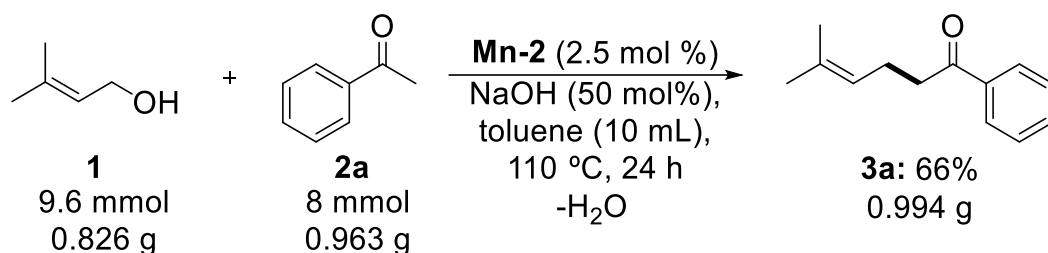
^aReaction conditions unless otherwise specified: 0.6 mmol of prenol derivatives and 0.5 mmol ketone, 50 mol% of NaOH and 2.5 mol% of cat. **Mn-2** and toluene (1.5 mL) were heated at 110 °C for 24 h and yields are isolated. ^bNMR yield. ^cReaction was carried out for 12 h. ^dReaction was carried out in open vessel under N₂.

Pleasingly, the scope of the manganese catalyzed terpenylation reaction can also be extended to secondary alcohol 1-phenylethanol. Dehydrogenative coupling of 1-phenylethanol with prenol and nerol afforded corresponding alkylated ketone products in moderate 41% and 32% yields, respectively (Scheme 3.1) liberating water and hydrogen as by-products. However, prenylation of cyclohexanol gave only traces of the desired product.



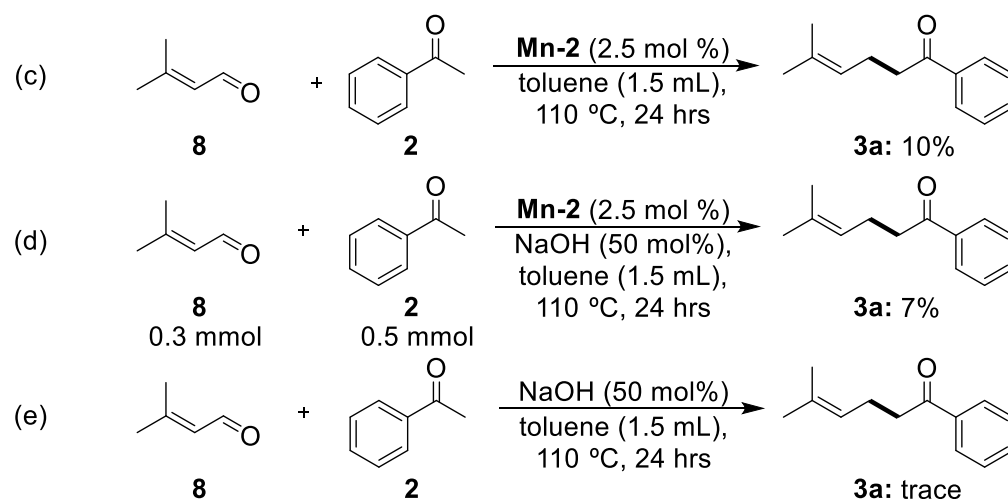
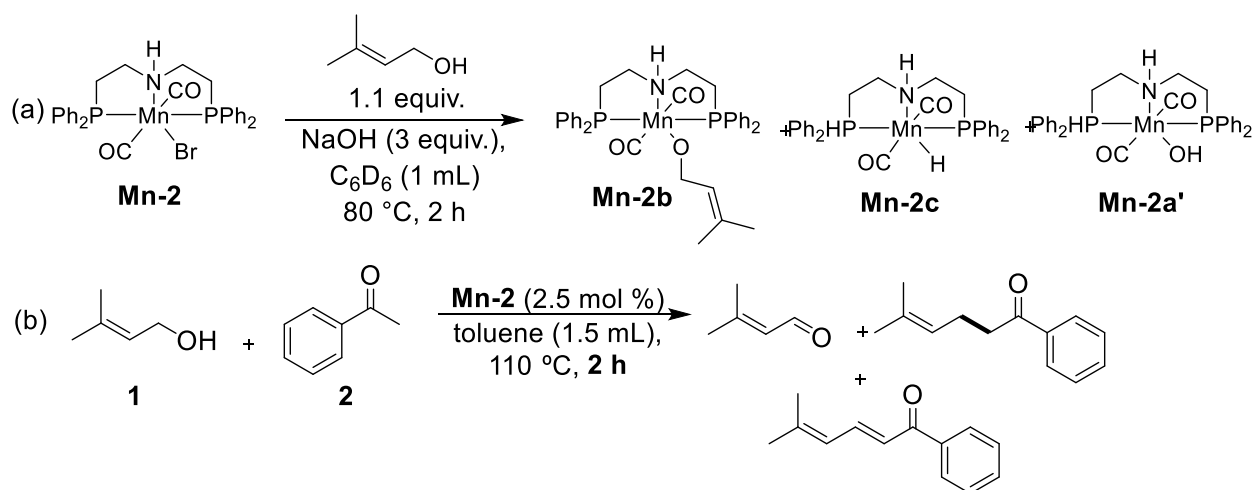
Scheme 3.1. Terpenylation of 1-phenylethanol.

To showcase the feasibility of this approach, a synthesis on a gram-scale was conducted, resulting in a 66% isolated yield of the prenylated product **3a** under optimized conditions (Scheme 3.2).



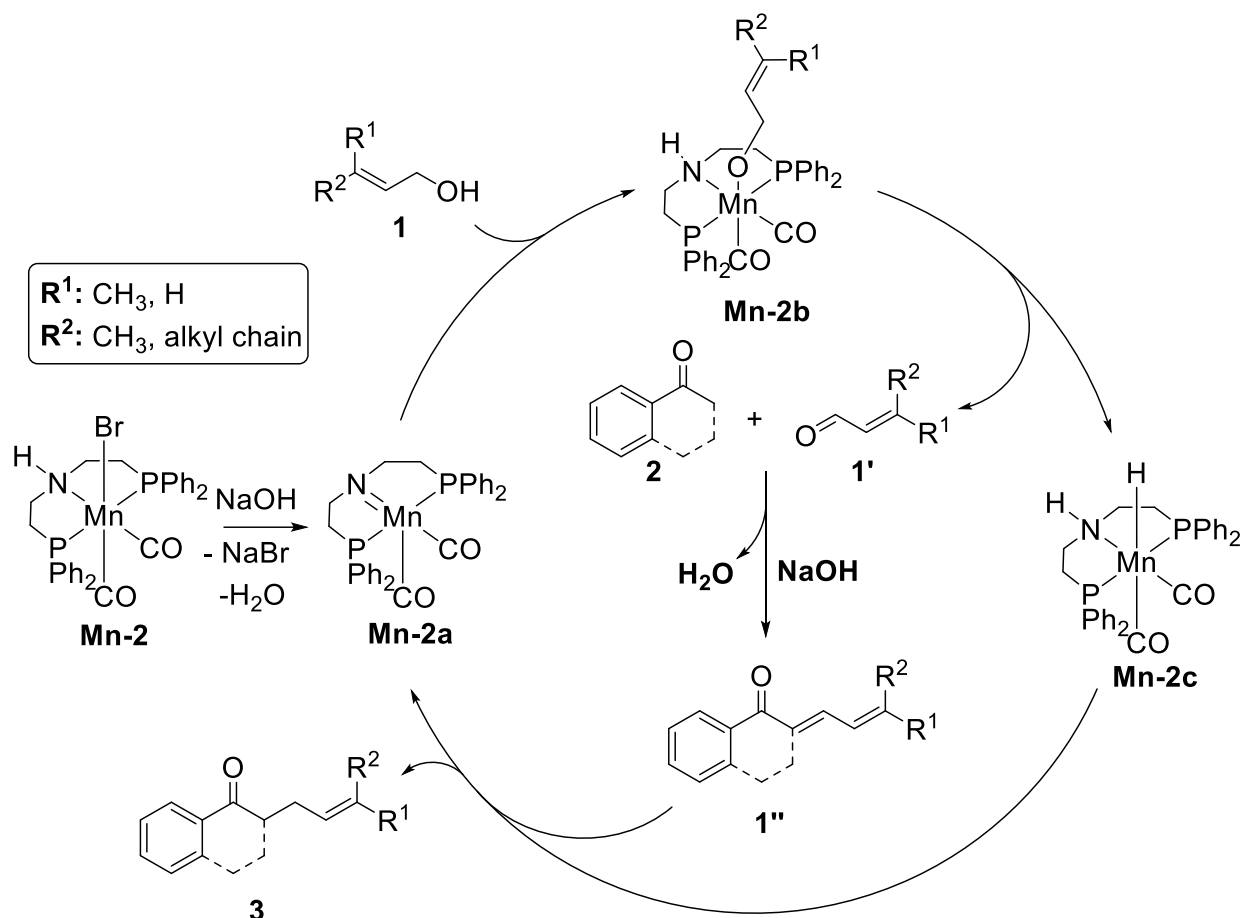
Scheme 3.2. Upscaling experiment for the **Mn-1** catalyzed terpenylation reaction.

Preliminary stoichiometric experiments were conducted to unravel the mechanistic pathways of the reaction scheme. Initially a solution of **Mn-2**, NaOH (3 equiv.) and prenil (1.1 equiv.) in benzene d_6 were heated at 80 °C for 2 h. Analysis of the reaction mixture by ^{31}P NMR and HRMS indicated presence of several complexes (see Figure S3.1-S3.3). An alkoxy compound **Mn-2b** (Scheme 3.3) was confirmed corresponding to a signal at 80 ppm in the ^{31}P NMR spectrum. A peak at 72 ppm in the ^{31}P NMR was also detected indicating formation of a Mn-hydroxo complex **Mn-2a'** (Scheme 3.3) as was also reported by other groups.^{206–208} Interestingly, formation of the hydride complex **Mn-2c** (Scheme 3.3) was also observed by the appearance of a triplet signal at -4.74 ppm ($^2J_{\text{PH}} = 51$ Hz) in the ^1H NMR spectrum (Figure S3.2). The signal at 90 ppm in the ^{31}P NMR was assigned to the hydride complex **Mn-2c**. The hydride signal in the ^1H NMR spectrum for the analogous MnPNP^{*i*Pr} complex was reported to appear at δ -5.53, (t, $^2J_{\text{P,H}} = 50.7$ Hz) by Beller group.¹⁴



Scheme 3.3. Detection of intermediates and control experiments.

Additionally, probing the catalytic reaction mixture after 2 h by ^1H NMR spectroscopy revealed the presence of an aldehyde product formed by prenol dehydrogenation. (Scheme 3.3, see Figure S3.4). Further analysis of the catalytic reaction mixture by HRMS confirmed the presence of aldehyde along with other expected catalytic intermediates and desired prenylated product (See Figure S3.5).



Scheme 3.4. Proposed mechanism for **Mn-2** catalyzed terpenylation reactions.

Moreover, a reaction was also conducted between acetophenone and 3-methyl-2-butenal (**8**) under the standard reaction conditions. ^1H NMR analysis of the reaction mixture revealed a very low yield of prenylated product **3a** (10%, Scheme 3.3). Further conducting the experiment using 3-methyl-2-butenal (**5**) at lower concentrations (0.3 mmol, Scheme 3.3) revealed formation of product **3a** in 7% yield. This implicates that catalyst reactivity is retarded when aldehyde is available at high concentrations. Hence the involvement of the corresponding aldehyde intermediate via dehydrogenation of prenol is essential. The reaction of acetophenone and a base (NaOH, 50 mol%) with 3-methyl-2-butenal without using **Mn-1** led to the trace amount of desired product (Scheme 3.3). The aforementioned experiments suggest that the 3-methyl-2-butenal is produced in situ through the dehydrogenation of prenol by **Mn-1** and then it reacts simultaneously with ketone in the presence of base.

Based on our experimental observation and previous mechanistic reports of Mn-macho complexes^{52,113,114,118,209} in hydrogen borrowing reactions, we propose a plausible mechanism as depicted in Scheme 3.4.

Treatment of the manganese complex **Mn-2** with base initiate the dehydrobromination generating a highly active amido intermediate **Mn-2a**. This intermediate then interacts with terpenoid derivatives through a metal-ligand cooperative mechanism^{32,133} involving substrate O-

H and metal-nitrogen bond via metal-ligand interactions. This process leads to the formation of alkoxy complex **Mn-2b**. Further β -hydride elimination released corresponding aldehyde and a manganese hydride complex **Mn-2c**. The newly formed aldehyde undergoes a condensation reaction with the ketones facilitated by the base. This reaction produces a conjugated α,β -unsaturated carbonyl compound. Subsequently, the enone functionality undergoes selective C-C double bond hydrogenation of the electron-deficient conjugated alkene by the manganese hydride intermediate **Mn-2c**. This hydrogenation step releases the terpenylated product and regenerates the active catalyst (**Mn-2a**), closing the catalytic cycle.

3.3 Summary

In conclusion, our work successfully established C-C bond formation through terpenylation of a diverse range of ketones in moderate to good yields. This includes acetophenone derivatives, homocyclic and heterocyclic ketones, using a variety of terpenoid derivatives such as prenol, nerol, phytol, solanesol, and E-farnesol. The reaction is catalyzed by the manganese pincer complex **Mn-2** with catalytic amount of sodium hydroxide as base. Moreover, we have also disclosed the catalytic applicability of **Mn-2** in terpenylation of secondary alcohol 1-phenylethanol. These methods are atom-economical, producing water (and H₂) as byproduct(s), which aligns with the borrowing hydrogen strategy. A plausible mechanism based on our stoichiometric studies is proposed following alcohol activation and dehydrogenation aided by metal-ligand cooperation. At this stage the catalytic efficiency of our Mn system for terpenylation of ketones is not at par with the existing state of the art Ru-or Fe based systems developed by others.^{12,16} However, we believe that our study highlights on the earth-abundant Mn-based catalyst development, mechanistic intermediate detection, and more importantly potential of the system for terpenylation of secondary alcohols.

3.4 Experimental procedure and supporting data

General information: All experiments were conducted under inert atmosphere by using standard Schlenk techniques or a nitrogen glove box, unless stated otherwise. Tetrahydrofuran (THF), toluene, dichloromethane (CH₂Cl₂), chloroform, hexane, 1,4-dioxane and methanol (MeOH) were heated under reflux over suitable drying agent (sodium/benzophenone for THF, hexane and toluene; calcium hydride for CH₂Cl₂, 3Å molecular sieves for MeOH), distilled and stored under nitrogen atmosphere. Deuterated (toluene, chloroform, benzene) solvents were stored in 3 Å molecular sieves under nitrogen atmosphere. Unless otherwise stated, commercial reagents were used without purification, only 3-Methylbut-2-en-1-ol (prenol) and acetophenone were purified via vacuum distillation. Pentacarbonyl manganese bromide (Mn(CO)₅Br) was purchased from Sigma- Aldrich, Bis(2-(diphenylphosphino)ethyl)amine hydrochloride was purchased from BLD pharma, calcium hydride (CaH₂) and all other materials were purchased from Avra, BLDpharma, TCI and Sigma- Aldrich, stored under nitrogen and used as received. All the reaction for substrate scope was monitored by TLC and isolated by column chromatography (silica gel 60-120). Then product was condensed with the help of rotta vapour. Then, isolated product was characterized by using ¹H NMR, ¹³C NMR from Bruker 500 MHz and 400 MHz spectrometer. All spectra were recorded at room temperature, unless otherwise noted. FT-IR spectra were recorded by Perkin-Elmer FT-IR spectrometer. Mass spectra were recorded on Agilent spectrometer with quadrupole mass analyser.

General Procedure for PN^HP-Mn(CO)₂Br catalyst synthesis (**Mn-2**):

Catalyst was synthesised as reported in literature,¹⁹¹ A flame dried Schlenk tube was charged with ligand bis(2-(diphenylphosphanyl)ethyl)amine hydrochloride (478 mg, 1.0 mmol, 1 equiv.), toluene (8 mL), water (2 mL) and NaOH (120 mg, 3.0 mmol, 3.0 equiv.). The reaction mixture was stirred at room temperature for 30 min. The two phases were separated, and the organic layer was washed with water (3 × 5 mL). The organic layer was concentrated under reduced pressure. Subsequently, toluene (12 mL) and Mn(CO)₅Br (275 mg, 1.0 mmol, 1 equiv.) precursor were added to the Schlenk tube. The reaction mixture was heated up to 110 °C and the atmosphere was exchanged three times by evacuating and backfilled with nitrogen. After the mixture was

stirred for 20 h at reflux temperature, it was cooled to room temperature and concentrated in vacuo. The crude precipitate was washed with pentane and extracted with dichloromethane/diethylether to remove insoluble inorganic side products. The solution was concentrated under reduced pressure and dried to afford the complex **Mn-2** as a yellow powder in 85%. The product was confirmed by analysing the complex by ^{31}P NMR, which matched with the literature reported data.

General procedure for synthesis of $(\text{PN}^H\text{N})\text{Mn}(\text{CO})_2\text{Br}$ catalyst:

Catalyst was synthesised as reported in literature,²¹⁰ Under N_2 atmosphere, A 100 mL young Schlenk tube was charge with PN^HN ligand [$\text{PN}^H\text{N} = N$ -(2-(diphenylphosphanyl)benzyl)-1-(pyridin-2-yl)methanamine] (95.67 mg, 0.25 mmol, 1 equiv.), $\text{Mn}(\text{CO})_5\text{Br}$ (68.63 mg, 0.25 mmol, 1 equiv.) and dry THF (5 mL) and stirred for overnight at 80 °C. The reaction mixture cooled and concentrated in *vacuo*. The residue was thoroughly washed with *n*-pentane and dried under *vacuo*, affording light yellow powder (126 mg, 85%). The product was confirmed by analysing the complex by ^{31}P NMR, which matched with the literature reported data.

General procedure for the optimization of prenylation of ketone with prenol (Table 3.1):

A flame-dried Schlenk tube (10 mL) under the nitrogen atmosphere was added with **Mn-2** (7.9 mg, 0.0125 mmol, 2.5 mol%), and base (0.25 mmol, 50 mol%, 20 equiv. with respect to catalyst loading) dissolved in 1.5 mL solvent reported in the Table 3.1. Next, 0.5 mmol (58.5 μL) of acetophenone and 0.6 mmol of prenol (61 μL , 1.2 equiv. with respect to acetophenone) were mixed into the solution and stirred for 5 minutes. Then, the Schlenk flask was closed tightly and kept at reported temperature and time. At the end, the Schlenk flask was cooled to room temperature and 0.5 mmol 1,1,2,2-tetrachloroethane was added as internal standard. From the mixture, an aliquot was taken for determination of conversion and yield by NMR analysis.

General procedure for the stoichiometric reaction of Mn-2 with prenol and NaOH:

In a glovebox, to a solution of **Mn-2** (24 mg, 0.04 mmol, 1.0 equiv.) in benzene- d_6 (1 mL), NaOH (4.8 mg, 0.1220 mmol, 3 equiv.) and prenol (6 μL , 0.06 mmol, 1.5 equiv.) were added in a Schlenk tube and stirred for 2 h at 80 °C. The NMR spectrum was recorded afterwards. A multiplet at -4.74 ppm in ^1H NMR revealed the formation of Mn-hydride and a signal at 9.6 ppm shows the formation of aldehyde (Figure S3.2). In the ^{31}P NMR, signals at 72.28, 80.15 and 90.21 ppm revealed the formation of metal hydroxide (**Mn-2a'**), metal alkoxy intermediate (**Mn-2b**) and metal hydride (**Mn-2c**) of the complex (Figure S3.1) which was confirmed by HRMS (Figure S3.3). ^{31}P NMR: -20.45, 67.74, 72.28, 80.15, 90.21.

General procedure for the stoichiometric reaction for intermediate trapping in reaction mixture:

A flame-dried Schlenk tube (25 mL) under the nitrogen atmosphere was charged with **Mn-2** (5 mg, 0.0125 mmol, 2.5 mol%), and sodium hydroxide (10.0 mg, 0.25 mmol, 50 mol%) dissolved in 1.5 mL toluene. Subsequently, prenol (61 μL , 0.6 mmol, 1.2 equiv. with respect to acetophenone) and acetophenone (58.33 μL , 0.5 mmol, 40 equiv. with respect to **Mn-2**) were added and stirred for 5 minutes. Then, the Schlenk flask was closed tightly and kept at 90 °C for 2 h. After that reaction was stopped and the Schlenk flask was cooled to room temperature and an aliquot was taken for analysis of intermediates by NMR (Figure S4) and HRMS (Figure S3.5) analysis.

General procedure for Mn-2 catalyzed terpenylation of ketones (Table 3.2 and 3.3):

A flame-dried Schlenk tube (25 mL) under the nitrogen atmosphere was charged with **Mn-2** (5.6 mg, 0.0125 mmol, 2.5 mol%), and sodium hydroxide (10.0 mg, 0.25 mmol, 50 mol%, 20 equiv. with respect to **Mn-2**) dissolved in 1.5 mL toluene. Subsequently, 0.5 mmol of ketone and prenol derivative (0.6 mmol, 1.2 equiv. with respect to ketone) were added and stirred for 5 minutes. Then, the Schlenk flask was closed tightly and kept at 110 °C for 24 h. After the completion of reaction, the Schlenk flask was cooled to room temperature and an aliquot was taken for determination of reaction conversion by NMR analysis. Purification was accomplished by

column chromatography (EtOAc:Hexane; 2:98) and isolated compounds were characterised by NMR technique.

General procedure for Mn-2 catalyzed terpenylation of secondary alcohols (Scheme 3.1):

To a solution of **Mn-2** (5.6 mg, 0.0125 mmol, 2.5 mol%) dissolved in 1.5 mL toluene was added sodium hydroxide (10.0 mg, 0.25 mmol, 50 mol%, 20 equiv. with respect to **Mn-2**) in a flame-dried Schlenk tube (25 mL) under the nitrogen atmosphere. Then 1-phenylethanol (60.36 μ L, 0.5 mmol, 1 equiv.) and prenol derivative (0.6 mmol, 1.2 equiv. with respect to alcohol) were added and stirred for 5 minutes. The Schlenk flask was closed tightly and kept at 110 °C in a pre-heated oil bath for 24 h. After the completion of reaction, the Schlenk flask was cooled to room temperature and an aliquot was taken for determination of reaction conversion by NMR analysis. Purification was done by column chromatography (EtOAc:Hexane; 2:98) and isolated compounds were analysed by NMR.

Experimental procedure for gram-scale reaction:

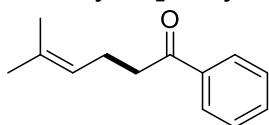
A flame-dried Schlenk tube (100 mL) was equipped with a stir bar, **Mn-2** (96 mg, 0.2 mmol, 2.5 mol %), NaOH (448 mg, 4 mmol, 50 mol %, 20 equiv. with respect to **Mn-2**), acetophenone (0.963 gm, 8 mmol), prenol (0.826 gm, 9.6 mmol, 1.2 equiv. with respect to acetophenone), and toluene (10 mL) were added under nitrogen atmosphere in a glove box. The flask was taken out of the glove box and the solution was heated at 110 °C with for 24 h. Upon completion, the reaction mixture was cooled to room temperature. Further, the solvent was evaporated the reaction was quenched using water (5 mL) and extracted by dichloromethane (10 $\times$ 5 mL). The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated. The resulted residue was purified by column chromatography over silica gel (60–120 mesh) using hexane/ethyl acetate mixture as eluent. Yield was calculated for isolated pure product.

General procedure for control experiment of acetophenone with 3-methyl-2-butanal:

A Schlenk tube (25 mL) was equipped with a stirring bar, **Mn-2** (6 mg, 0.0125 mmol, 2.5 mol %), NaOH (10 mg, 0.25 mmol, 50 mol %, 20 equiv. with respect to **Mn-2**), acetophenone (58.33 μ L, 0.5 mmol), 3-methyl-2-butanal (50.47 mg, 0.6 mmol, 1.2 equiv. with respect to acetophenone) and toluene (1.5 mL) were added under nitrogen atmosphere in a glove box. The flask was taken out of the glove box and the solution was heated at 100 °C with stirring for 24 h. The reaction was monitored using NMR using 1,1,2,2-tetrachloroethane as internal standard.

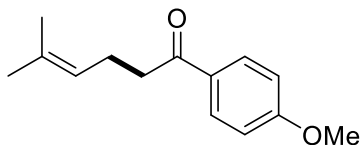
NMR Spectra and HRMS Data^{182,185}

5-methyl-1-phenylhex-4-en-1-one (3a)



Yellow liquid (152 mg, 81%) ¹H NMR (500 MHz, Chloroform-*d*) δ 8.1 – 7.9 (m, 2H), 7.7 – 7.5 (m, 1H), 7.5 (dd, *J* = 8.4, 7.1 Hz, 2H), 5.2 (t, *J* = 7.2, 5.7, 1.5 Hz, 1H), 3.0 (t, *J* = 7.5 Hz, 2H), 2.5 – 2.4 (m, 2H), 1.7 (d, *J* = 1.5 Hz, 3H), 1.7 (s, 3H). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*) δ 200.1, 137.1, 132.9, 132.8, 128.6 (2C), 128.1 (2C), 123.0, 38.8, 25.7, 23.0, 17.7. HRMS for C₁₃H₁₇O [M + H]⁺ calcd. 189.1279, found 189.1262.

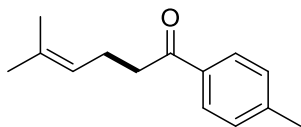
1-(4-methoxyphenyl)-5-methylhex-4-en-1-one (3b)



Yellow solid (179 mg, 82%) ¹H NMR (500 MHz, Chloroform-*d*) δ 8.0 (d, *J* = 8.9 Hz, 2H), 6.9 (d, *J* = 8.9 Hz, 2H), 5.2 (ddq, *J* = 8.6, 5.7, 1.4 Hz, 1H), 3.9 (s, 3H), 3.0 – 2.9 (m, 2H), 2.5 – 2.4 (m, 2H), 1.7 (d, *J* = 1.4 Hz, 3H), 1.6 (d, *J* = 1.4 Hz, 3H). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*) δ 198.6, 163.3, 132.6,

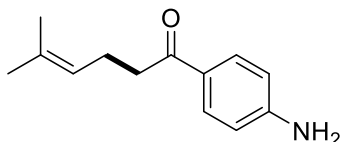
130.3 (2C), 130.1, 123.1, 113.7 (2C), 55.4, 38.4, 25.7, 23.1, 17.7. HRMS for $C_{14}H_{19}O_2$ $[M + H]^+$ calcd. 219.1385, found 219.1362.

5-methyl-1-(p-tolyl)hex-4-en-1-one (3c)



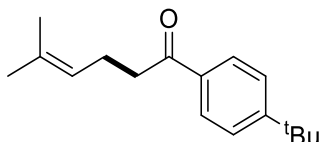
Light yellow liquid (152 mg, 75%) ^1H NMR (400 MHz, Chloroform-*d*) δ 7.9 (d, J = 8.3 Hz, 2H), 7.4 – 7.2 (m, 2H), 5.3 – 5.1 (m, 1H), 3.0 (dd, J = 8.1, 7.0 Hz, 2H), 2.4 (s, 3H), 1.7 (d, J = 1.4 Hz, 3H), 1.7 (d, J = 1.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 199.8, 143.6, 134.6, 132.7, 129.2, 128.2, 123.1, 38.7, 25.7, 23.0, 21.6, 17.7. HRMS for $C_{14}H_{19}O$ $[M + H]^+$ calcd. 203.1436, found 203.1422.

1-(4-aminophenyl)-5-methylhex-4-en-1-one (3d)



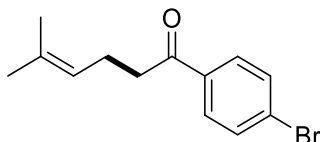
Brown liquid (132 mg, 65%) ^1H NMR (500 MHz, Chloroform-*d*) δ 7.8 (d, J = 8.6 Hz, 2H), 6.7 – 6.6 (m, 2H), 5.2 (t, J = 7.2 Hz, 1H), 4.1 (s, 2H), 2.9 (dd, J = 8.3, 6.9 Hz, 2H), 2.4 – 2.4 (m, 2H), 1.7 (d, J = 1.4 Hz, 3H), 1.6 (d, J = 1.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*) δ 198.4, 150.9, 132.5, 130.5 (2C), 123.3, 113.8 (2C), 38.1, 25.7, 23.4, 17.7. HRMS for $C_{13}H_{18}NO$ $[M + H]^+$ calcd. 204.1388, found 204.1372.

1-(4-(tert-butyl)-phenyl)-5-methylhex-4-en-1-one (3e)



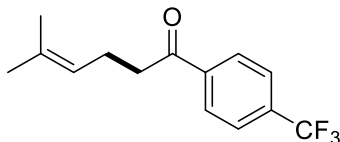
Yellow liquid (132 mg, 65%) ^1H NMR (500 MHz, Chloroform-*d*) δ 7.9 (d, J = 8.4 Hz, 2H), 7.5 – 7.5 (d, 2H), 5.2 (t, J = 7.0, 1.5 Hz, 1H), 3.0 (t, J = 7.5 Hz, 2H), 2.5 – 2.4 (m, 2H), 1.7 (s, J = 1.6 Hz, 3H), 1.7 (s, 3H), 1.4 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*) δ 199.7, 156.6, 134.5, 132.6, 128.1 (2C), 125.5 (2C), 123.1, 38.7, 35.1, 31.1, 25.7, 23.0, 17.7. HRMS for $C_{17}H_{25}O$ $[M + H]^+$ calcd. 245.1905, found 245.1889.

1-(4-bromophenyl)-5-methylhex-4-en-1-one (3f)



Yellow solid (200 mg, 75%) ^1H NMR (500 MHz, Chloroform-*d*) δ 7.8 (d, J = 8.4 Hz, 2H), 7.6 (d, J = 8.6 Hz, 2H), 5.2 (tt, J = 7.3, 1.6 Hz, 1H), 3.0 (t, J = 7.5 Hz, 2H), 2.4 – 2.4 (m, 2H), 1.7 – 1.7 (m, 3H), 1.6 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*) δ 199.0, 135.7, 133.0, 131.9 (2C), 129.6 (2C), 128.1, 122.7, 38.7, 25.7, 22.8, 17.7. HRMS for $C_{13}H_{16}BrO$ $[M + H]^+$ calcd. 267.0385, found 267.0353.

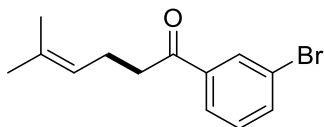
5-methyl-1-(4-(trifluoromethyl)phenyl)hex-4-en-1-one (3g)



Yellow solid (195 mg, 76%) ^1H NMR (400 MHz, Chloroform-*d*) δ 8.1 (dt, J = 7.9, 0.8 Hz, 2H), 7.8 – 7.7 (m, 2H), 5.2 (tt, J = 7.3, 1.4 Hz, 1H), 3.0 (dd, J = 7.9, 7.0 Hz, 2H), 2.5 – 2.4 (m, 2H), 1.7 (q, J = 1.3 Hz, 3H), 1.7 (d, J = 1.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 199.0, 139.6, 133.2, 128.4,

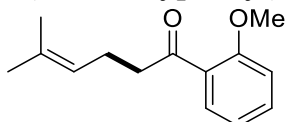
125.6 (d, $J = 3.7$ Hz), 122.5, 39.1, 25.7, 22.7, 17.7. HRMS for $C_{14}H_{16}F_3O$ $[M + H]^+$ calcd. 257.1153, found 257.1124.

1-(3-bromophenyl)-5-methylhex-4-en-1-one (3h)



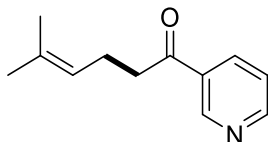
Yellow liquid (187 mg, 70%) ^1H NMR (500 MHz, Chloroform- d) δ 8.1 (t, $J = 1.9$ Hz, 1H), 7.9 (dd, $J = 7.8, 1.3$ Hz, 1H), 7.7 (dt, $J = 7.9, 1.4$ Hz, 1H), 7.4 (t, $J = 7.9$ Hz, 1H), 5.3 – 5.1 (m, 1H), 3.0 (t, $J = 7.4$ Hz, 2H), 2.4 (s, 2H), 1.7 (s, $J = 1.6$ Hz, 3H), 1.7 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform- d) δ 198.7, 138.7, 135.8, 131.2, 130.2 (2C), 126.6, 123.0, 122.6, 38.9, 25.7, 22.8, 17.7. HRMS for $C_{13}H_{16}BrO$ $[M + H]^+$ calcd. 267.0385, found 267.0353.

1-(2-methoxyphenyl)-5-methylhex-4-en-1-one (3l)



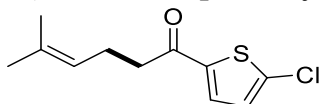
Yellow liquid (122 mg, 56%) ^1H NMR (500 MHz, Chloroform- d) δ 7.6 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.4 (ddd, $J = 8.7, 7.3, 1.9$ Hz, 1H), 6.9 (t, $J = 7.5$ Hz, 1H), 6.9 (d, $J = 8.3$ Hz, 1H), 5.1 (ddt, $J = 8.7, 7.2, 1.4$ Hz, 1H), 3.8 (s, 3H), 2.9 (t, $J = 7.6$ Hz, 2H), 2.3 – 2.2 (m, 2H), 1.6 (d, $J = 1.6$ Hz, 3H), 1.5 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform- d) δ 202.7, 158.4, 133.2, 130.2, 128.7, 123.4, 120.6, 119.3, 111.5, 55.5, 43.9, 25.7, 23.2. HRMS for $C_{14}H_{19}O_2$ $[M + H]^+$ calcd. 219.1385, found 219.1364.

5-methyl-1-(pyridin-3-yl)hex-4-en-1-one (3n)



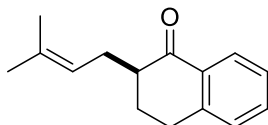
Dark yellow liquid (98 mg, 52%) ^1H NMR (400 MHz, Chloroform- d) δ 9.2 (d, $J = 2.2$ Hz, 1H), 8.8 (dd, $J = 5.0, 1.7$ Hz, 1H), 8.2 (dt, $J = 8.0, 1.9$ Hz, 1H), 7.4 (dd, $J = 8.0, 4.7$ Hz, 1H), 5.2 (ddt, $J = 8.7, 5.8, 1.5$ Hz, 1H), 3.0 (dd, $J = 7.8, 7.0$ Hz, 2H), 2.5 – 2.4 (m, 2H), 1.7 (q, $J = 1.3$ Hz, 3H), 1.6 (d, $J = 1.4$ Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform- d) δ 198.8, 153.4, 149.6, 135.3, 133.2, 132.2, 123.6, 122.4, 39.0, 25.7, 22.6, 17.7. HRMS for $C_{12}H_{16}NO$ $[M + H]^+$ calcd. 190.1232, found 190.1211.

1-(5-chlorothiophen-2-yl)-5-methylhex-4-en-1-one (3o)



Yellow liquid (165 mg, 72%) ^1H NMR (500 MHz, Chloroform- d) δ 7.5 (d, $J = 4.1$ Hz, 1H), 7.0 (d, $J = 4.0$ Hz, 1H), 5.2 (td, $J = 7.1, 3.8$ Hz, 1H), 2.9 (t, $J = 7.5$ Hz, 2H), 2.5 – 2.4 (m, 2H), 1.7 (s, 3H), 1.6 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform- d) δ 192.7, 143.6, 139.8, 133.8, 131.8 (2C), 128.1, 123.0, 39.2, 26.2, 23.8, 18.2. HRMS for $C_{11}H_{14}ClOS$ $[M + H]^+$ calcd. 229.0454, found 229.0430.

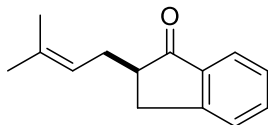
2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (3p)



Light yellow liquid (189 mg, 88%) ^1H NMR (500 MHz, Chloroform- d) δ 8.1 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.5 (td, $J = 7.4, 1.5$ Hz, 1H), 7.4 – 7.3 (m, 1H), 7.3 – 7.2 (m, 1H), 5.2 (ddt, $J = 9.5, 6.7, 1.4$ Hz, 1H), 3.0 (dd, $J = 7.8, 4.6$ Hz, 2H), 2.7 – 2.6 (m, 1H), 2.5 (ddt, $J = 11.6, 8.8, 4.5$ Hz, 1H), 2.3 – 2.2 (m, 2H), 1.9 – 1.8 (m, 1H), 1.7 (d, $J = 1.4$ Hz, 3H), 1.7 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform- d)

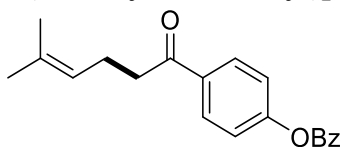
δ 200.0, 144.1, 133.5, 133.1, 132.6, 128.7, 127.4, 126.5, 121.8, 48.1, 28.7, 28.1, 28.0, 25.9, 17.9. HRMS for $C_{15}H_{19}O$ $[M + H]^+$ calcd. 215.1436, found 215.1423.

2-(3-methylbut-2-en-1-yl)-2,3-dihydro-1H-inden-1-one (3q)



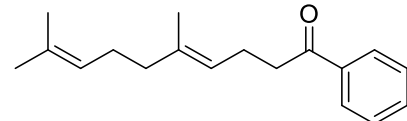
Light yellow liquid (178 mg, 89%) ^1H NMR (500 MHz, Chloroform-*d*) δ 7.8 (d, J = 7.6 Hz, 1H), 7.6 (t, J = 7.4 Hz, 1H), 7.5 (d, J = 7.6 Hz, 1H), 7.4 (t, J = 7.4 Hz, 1H), 5.1 (tt, J = 7.2, 1.5 Hz, 1H), 3.3 (dd, J = 17.2, 7.9 Hz, 1H), 2.8 (dd, J = 17.2, 4.0 Hz, 1H), 2.7 (tt, J = 8.5, 4.2 Hz, 1H), 2.6 (dt, J = 11.8, 5.9 Hz, 1H), 2.3 (dt, J = 15.6, 8.3 Hz, 1H), 1.7 (d, J = 1.8 Hz, 3H), 1.7 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*) δ 208.6, 153.9, 136.9, 134.6, 133.9, 127.3, 126.6, 123.9, 121.0, 47.6, 32.2, 29.6, 25.8, 18.0. HRMS for $C_{14}H_{17}O$ $[M + H]^+$ calcd. 201.1279, found 201.1261.

4-(5-methylhex-4-enoyl)phenyl benzoate (3r)



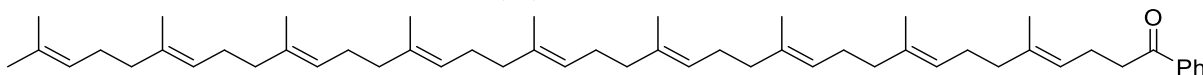
Light yellow solid (170 mg, 55%) ^1H NMR (500 MHz, Chloroform-*d*) δ 8.0 (d, J = 8.5 Hz, 2H), 7.5 – 7.4 (m, 4H), 7.4 (d, J = 7.2 Hz, 1H), 7.0 (d, J = 8.4 Hz, 2H), 5.3 – 5.2 (m, 1H), 5.1 (s, 2H), 3.0 (t, J = 7.5 Hz, 2H), 2.5 (q, J = 6.2, 4.9 Hz, 2H), 1.7 (s, 3H), 1.7 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*) δ 198.6, 162.5, 136.3 (2C), 132.6 (2C), 130.4 (3C), 128.7 (2C), 127.5, 123.2 (2C), 114.6, 70.1, 38.4, 25.8, 23.2, 17.8. HRMS for $C_{20}H_{23}O_2$ $[M + H]^+$ calcd. 295.1698, found 295.1673.

(E)-5,9-dimethyl-1-phenyldeca-4,8-dien-1-one (6a)



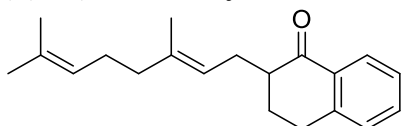
Yellow liquid (96 mg, 37.5%) ^1H NMR (400 MHz, Chloroform-*d*) δ 8.0 – 7.9 (m, 2H), 7.6 – 7.5 (m, 1H), 7.5 – 7.4 (m, 2H), 5.2 (ddq, J = 8.6, 5.6, 1.3 Hz, 1H), 5.1 (dddt, J = 6.9, 5.5, 2.8, 1.4 Hz, 1H), 3.0 (dd, J = 8.0, 7.0 Hz, 2H), 2.5 – 2.4 (m, 2H), 2.2 – 2.0 (m, 4H), 1.7 – 1.7 (m, 3H), 1.7 (d, J = 1.3 Hz, 3H), 1.6 (d, J = 1.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 200.1, 137.1, 136.4, 132.9, 131.4, 128.6, 128.3 – 127.8 (m), 124.3, 122.8, 39.7, 38.8, 26.7, 25.7, 22.9, 17.7, 16.0. HRMS for $C_{18}H_{25}O$ $[M + H]^+$ calcd. 257.1905, found 257.1892.

(4E,8E,12E,16E,20E,24E,28E,32E)-5,9,13,17,21,25,29,33,37-nonamethyl-1-phenyloctatriaconta-4,8,12,16,20,24,28,32,36-nonaen-1-one (6c)



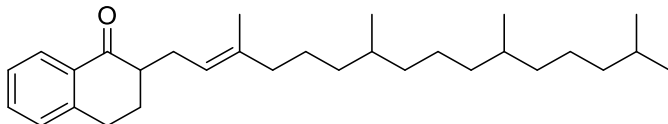
Yellow liquid (205 mg, 28%) ^1H NMR (400 MHz, Chloroform-*d*) δ 8.1 – 7.9 (m, 2H), 7.6 – 7.5 (m, 1H), 7.5 – 7.4 (m, 2H), 5.3 – 5.0 (m, 9H), 3.1 – 2.9 (m, 1H), 2.5 (q, J = 7.4 Hz, 1H), 2.1 (t, J = 7.1 Hz, 18H), 2.0 (dd, J = 10.1, 5.8 Hz, 18H), 1.7 – 1.6 (m, 28H). $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 200.0, 137.1, 136.4, 134.9 (d, J = 5.1 Hz), 132.9, 131.2, 128.6, 128.1, 124.4, 124.3, 122.8, 39.8 (d, J = 2.1 Hz), 38.9 (d, J = 24.3 Hz), 29.7, 26.7, 25.7, 17.7, 16.0 (d, J = 2.5 Hz). HRMS for $C_{55}H_{81}O$ $[M + H]^+$ calcd. 733.6287, found 733.6265.

(E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-3,4-dihydronaphthalen-1(2H)-one (6e)



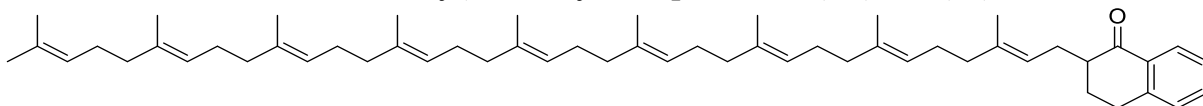
Light yellow liquid (104 mg, 37%) $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.1 (dd, J = 7.9, 1.5 Hz, 1H), 7.5 (td, J = 7.4, 1.5 Hz, 1H), 7.3 (td, J = 7.6, 1.3 Hz, 1H), 7.3 – 7.2 (m, 1H), 5.3 – 5.2 (m, 1H), 5.1 (ddp, J = 7.0, 5.7, 1.6 Hz, 1H), 3.0 (dd, J = 7.7, 4.6 Hz, 2H), 2.8 – 2.6 (m, 1H), 2.5 (ddt, J = 11.5, 8.8, 4.4 Hz, 1H), 2.3 – 2.2 (m, 2H), 2.2 – 2.0 (m, 4H), 2.0 – 1.8 (m, 1H), 1.7 (d, J = 1.4 Hz, 3H), 1.7 (d, J = 1.2 Hz, 3H), 1.6 (d, J = 1.4 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 200.0, 144.2, 137.1, 133.1, 132.6, 131.4, 128.7, 127.4, 126.6, 124.3, 121.8, 48.1, 39.9, 28.7, 28.0, 27.9, 26.6, 25.7, 17.7, 16.2. HRMS for $\text{C}_{20}\text{H}_{27}\text{O}$ $[\text{M} + \text{H}]^+$ calcd. 283.2062, found 283.2049.

(E)-2-(3,7,11,15-tetramethylhexadec-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (6f)



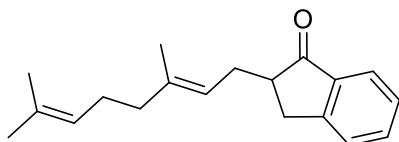
Yellow liquid (161 mg, 38%) $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.1 (dd, J = 7.8, 1.5 Hz, 1H), 7.6 – 7.4 (m, 1H), 7.3 (td, J = 7.6, 1.3 Hz, 1H), 7.3 – 7.2 (m, 1H), 5.2 (ddt, J = 6.7, 5.1, 1.3 Hz, 1H), 3.0 (dd, J = 7.8, 4.6 Hz, 2H), 2.5 (ddt, J = 11.4, 8.7, 4.4 Hz, 1H), 2.4 – 2.1 (m, 2H), 2.1 – 2.0 (m, 1H), 1.7 (dd, J = 2.3, 1.2 Hz, 1H), 1.7 (dd, J = 4.0, 1.2 Hz, 2H), 1.6 (dt, J = 13.3, 6.6 Hz, 1H), 1.5 – 1.0 (m, 21H), 0.9 (t, J = 6.9 Hz, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 199.9, 144.1, 137.6, 133.1, 132.6, 128.7, 127.5, 126.6, 121.5, 48.1, 40.2, 39.4, 37.5, 37.3, 36.7, 32.8, 28.7, 28.0, 25.4, 24.9, 24.5, 22.8, 22.7, 19.8, 16.1. HRMS for $\text{C}_{30}\text{H}_{49}\text{O}$ $[\text{M} + \text{H}]^+$ calcd. 425.3782, found 425.3757.

2-((2E,6E,10E,14E,18E,22E,26E,30E)-3,7,11,15,19,23,27,31,35-nonamethylhexatriaconta-2,6,10,14,18,22,26,30,34-nonaen-1-yl)-3,4-dihydronaphthalen-1(2H)-one (6h)



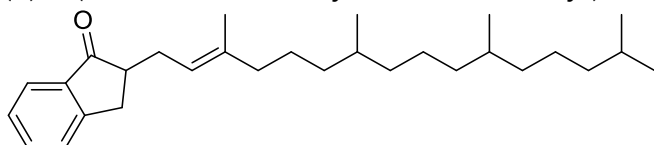
Yellow liquid (235 mg, 35%) $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.1 (dd, J = 7.9, 1.5 Hz, 1H), 7.5 (td, J = 7.4, 1.5 Hz, 1H), 7.3 (td, J = 7.6, 1.2 Hz, 1H), 7.3 (d, J = 7.6 Hz, 1H), 5.2 – 5.1 (m, 9H), 3.0 (dd, J = 7.5, 4.6 Hz, 2H), 2.8 – 2.6 (m, 1H), 2.5 (ddt, J = 11.4, 8.7, 4.4 Hz, 1H), 2.4 – 2.3 (m, 1H), 2.1 (d, J = 8.2 Hz, 20H), 2.0 (dd, J = 9.5, 5.5 Hz, 16H), 1.6 (d, J = 1.4 Hz, 28H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 200.0, 144.1, 137.2, 134.9 (d, J = 1.9 Hz), 133.1, 132.6, 131.3, 128.7, 127.5, 126.6, 124.4, 124.3 (d, J = 1.6 Hz), 121.8, 48.1, 39.8 (d, J = 2.0 Hz), 29.7, 28.7, 26.7, 25.7, 17.7, 16.1. HRMS for $\text{C}_{55}\text{H}_{83}\text{O}$ $[\text{M} + \text{H}]^+$ calcd. 759.6444, found 744.6422.

(E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-2,3-dihydro-1H-inden-1-one (6i)



Yellow liquid (113 mg, 42%) $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.7 (d, J = 7.6 Hz, 1H), 7.6 (td, J = 7.5, 1.4 Hz, 1H), 7.4 (d, J = 7.7 Hz, 1H), 7.3 (t, J = 7.4 Hz, 1H), 5.1 (td, J = 7.2, 1.5 Hz, 1H), 5.0 (tt, J = 6.7, 1.5 Hz, 1H), 3.3 (dd, J = 17.2, 7.8 Hz, 1H), 2.8 (dd, J = 17.2, 4.0 Hz, 1H), 2.8 – 2.6 (m, 2H), 2.3 (dt, J = 14.4, 8.2 Hz, 1H), 2.0 (dd, J = 12.8, 6.7 Hz, 3H), 1.7 – 1.6 (m, 6H), 1.6 (d, J = 1.4 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 208.6, 153.9, 137.4, 136.9, 134.6, 131.3, 127.3, 126.6, 124.1, 123.8, 121.0, 47.6, 39.8, 32.1, 29.5, 26.5, 25.7, 17.7, 16.2. HRMS for $\text{C}_{19}\text{H}_{25}\text{O}$ $[\text{M} + \text{H}]^+$ calcd. 269.1905, found 269.1892.

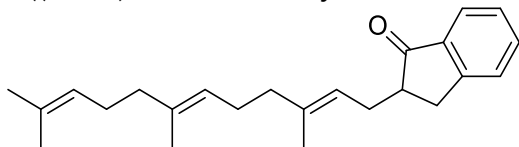
(E)-2-(3,7,11,15-tetramethylhexadec-2-en-1-yl)-2,3-dihydro-1H-inden-1-one (6j)



Light yellow liquid (164 mg, 40%) $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.8 (dt, J = 7.7, 1.0 Hz, 1H), 7.6 (td, J = 7.4, 1.3 Hz, 1H), 7.5 (dt, J = 7.7, 1.0 Hz, 1H), 7.4 (td, J = 7.4, 0.9 Hz, 1H), 5.1 (ddt, J

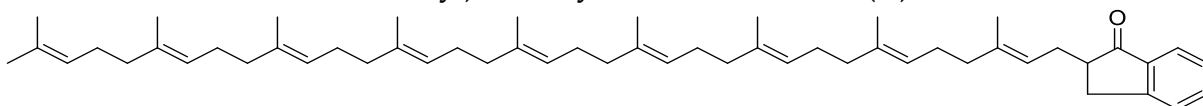
= 7.2, 5.9, 1.3 Hz, 1H), 3.3 (dd, $J = 17.2, 7.8$ Hz, 1H), 2.9 (d, $J = 3.9$ Hz, 1H), 2.8 (d, $J = 3.9$ Hz, 1H), 2.8 – 2.7 (m, 1H), 2.7 – 2.6 (m, 1H), 2.6 – 2.6 (m, 1H), 2.3 (dt, $J = 14.5, 8.2$ Hz, 1H), 2.0 (td, $J = 7.4, 4.0$ Hz, 2H), 1.6 (d, $J = 1.4$ Hz, 3H), 1.5 (dt, $J = 13.2, 6.6$ Hz, 1H), 1.4 – 1.0 (m, 11H), 1.0 – 0.8 (m, 16H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) δ 208.7, 154.0, 138.0, 136.9, 134.6, 127.3, 126.6, 123.9, 120.7, 47.6, 40.1, 39.4, 37.5, 36.6, 32.8, 32.2, 29.6, 28.0, 25.3, 24.8, 24.5, 22.7, 22.7, 19.8 (d, $J = 3.5$ Hz), 16.2. HRMS for $\text{C}_{29}\text{H}_{47}\text{O}$ $[\text{M} + \text{H}]^+$ calcd. 411.3627, found 411.3609.

2-((2E,6E)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl)-2,3-dihydro-1H-inden-1-one (6k)



Yellow liquid (128 mg, 38%) ^1H NMR (400 MHz, Chloroform- d) δ 8.1 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.5 (td, $J = 7.4, 1.6$ Hz, 1H), 7.3 (td, $J = 7.6, 1.4$ Hz, 1H), 7.2 (d, $J = 7.7$ Hz, 1H), 5.3 – 5.0 (m, 3H), 3.0 (dd, $J = 7.8, 4.6$ Hz, 2H), 2.8 – 2.6 (m, 1H), 2.6 – 2.4 (m, 1H), 2.3 – 2.2 (m, 1H), 2.1 (ddt, $J = 13.4, 6.9, 3.8$ Hz, 6H), 1.7 (dq, $J = 4.2, 1.4$ Hz, 6H), 1.7 (t, $J = 1.8$ Hz, 2H), 1.6 – 1.6 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) δ 199.9, 144.1, 137.1, 135.0, 133.1, 132.6, 131.5, 131.2, 128.7, 127.4, 126.5, 125.0, 124.4, 124.1, 124.1, 123.9, 122.5, 121.9, 121.8, 48.1, 40.2, 39.9, 39.8, 36.9, 32.0 (d, $J = 2.1$ Hz), 28.7, 28.0, 26.8, 26.5, 26.4, 25.7, 23.6, 23.4, 17.7, 17.7, 16.2, 16.1. HRMS for $\text{C}_{24}\text{H}_{33}\text{O}$ $[\text{M} + \text{H}]^+$ calcd. 337.2531, found 337.2527.

2-((2E,6E,10E,14E,18E,22E,26E,30E)-3,7,11,15,19,23,27,31,35-nonamethylhexatriaconta-2,6,10,14,18,22,26,30,34-nonaen-1-yl)-2,3-dihydro-1H-inden-1-one (6l)



Yellow liquid (216 mg, 29%) ^1H NMR (400 MHz, Chloroform- d) δ 7.8 (d, $J = 7.7$ Hz, 1H), 7.6 (td, $J = 7.4, 1.3$ Hz, 1H), 7.5 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.4 (t, $J = 7.3$ Hz, 1H), 5.1 (ddd, $J = 7.5, 5.7, 1.5$ Hz, 9H), 3.3 (dd, $J = 17.2, 7.8$ Hz, 1H), 2.8 – 2.7 (m, 1H), 2.7 (ddd, $J = 14.3, 6.8, 4.4$ Hz, 1H), 2.1 (t, $J = 6.9$ Hz, 18H), 2.1 – 1.9 (m, 18H), 1.6 (d, $J = 1.5$ Hz, 28H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d) δ 208.6, 153.9, 137.6, 136.9, 135.1, 134.9, 134.6, 131.2, 127.3, 126.6, 124.3 (d, $J = 2.3$ Hz), 121.0, 47.6, 39.8 (d, $J = 2.1$ Hz), 32.2, 29.5, 26.7, 25.7, 17.7, 16.1. HRMS for $\text{C}_{55}\text{H}_{81}\text{O}$ $[\text{M} + \text{H}]^+$ calcd. 745.6287, found 745.6265.

The yields of compounds 3i, 3k, 3m, 6b, 6d, 6g were determined by NMR from the crude mixture using internal standards. Attempts to isolate the pure compounds by TLC and Column Chromatography under various conditions led to mixtures of compounds including desired products due to very similar retention times of the corresponding mixtures. However, the HRMS data of the crude compounds also confirmed the formation of the products as reported below.

5-methyl-1-(3-(trifluoromethyl)phenyl)hex-4-en-1-one (3i)

HRMS for $C_{14}H_{16}F_3O$ $[M + H]^+$ calcd. 257.1153, found 257.1141.

1-(2-chlorophenyl)-5-methylhex-4-en-1-one (3k)

HRMS for $C_{13}H_{16}ClO$ $[M + H]^+$ calcd. 223.0890, found 223.0868.

1-(2-aminophenyl)-5-methylhex-4-en-1-one (3m)

HRMS for $C_{14}H_{19}O_2$ $[M + H]^+$ calcd. 219.1385, found 219.1372.

(E)-5,9,13,17-tetramethyl-1-phenyloctadec-4-en-1-one (6b)

HRMS for $C_{28}H_{47}O$ $[M + H]^+$ calcd. 399.3627, found 399.3601.

(E)-1,5-diphenylpent-4-en-1-one (6d)

HRMS for $C_{17}H_{17}O$ $[M + H]^+$ calcd. 237.1279, found 237.1262.

2-((2E,6E)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl)-3,4-dihydronaphthalen-1(2H)-one (6g)

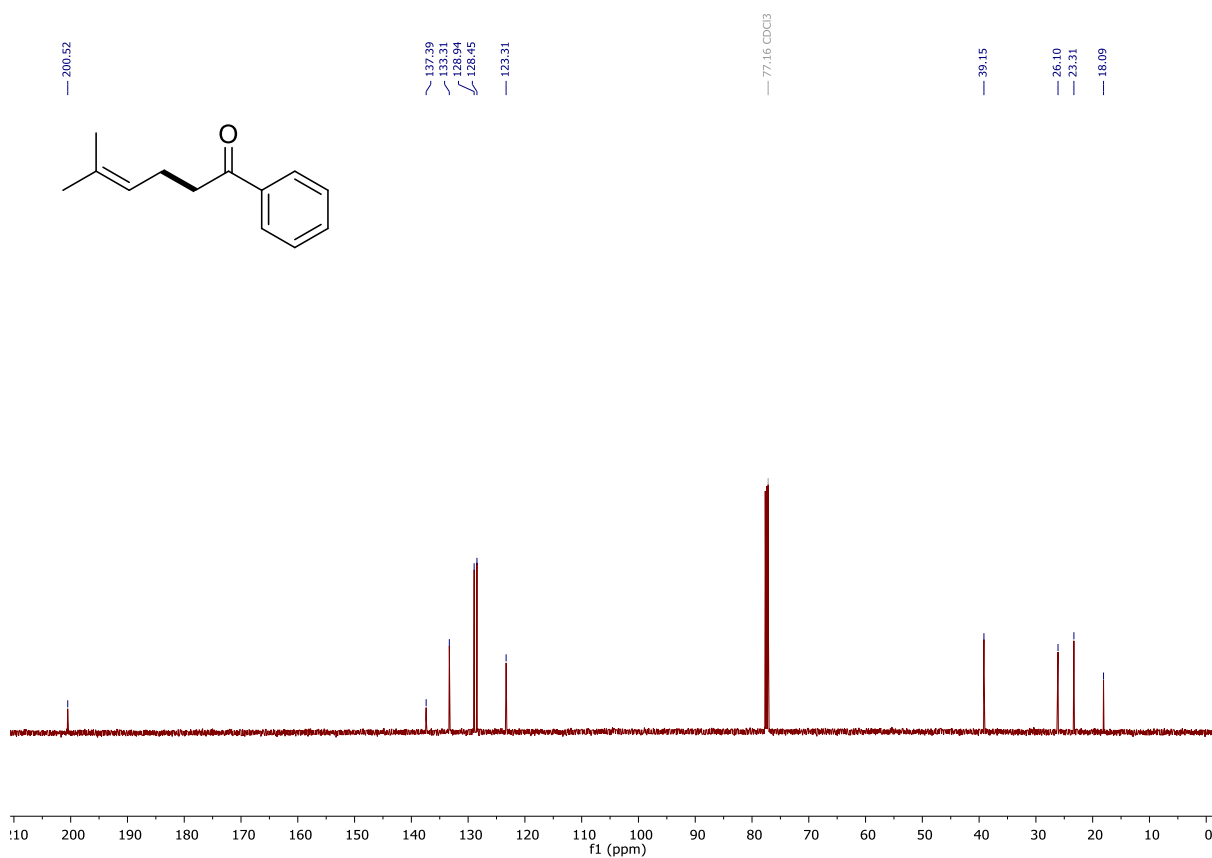
HRMS for $C_{25}H_{35}O$ $[M + H]^+$ calcd. 351.2688, found 351.2663.

Selected ^1H and ^{13}C NMR data of isolated products

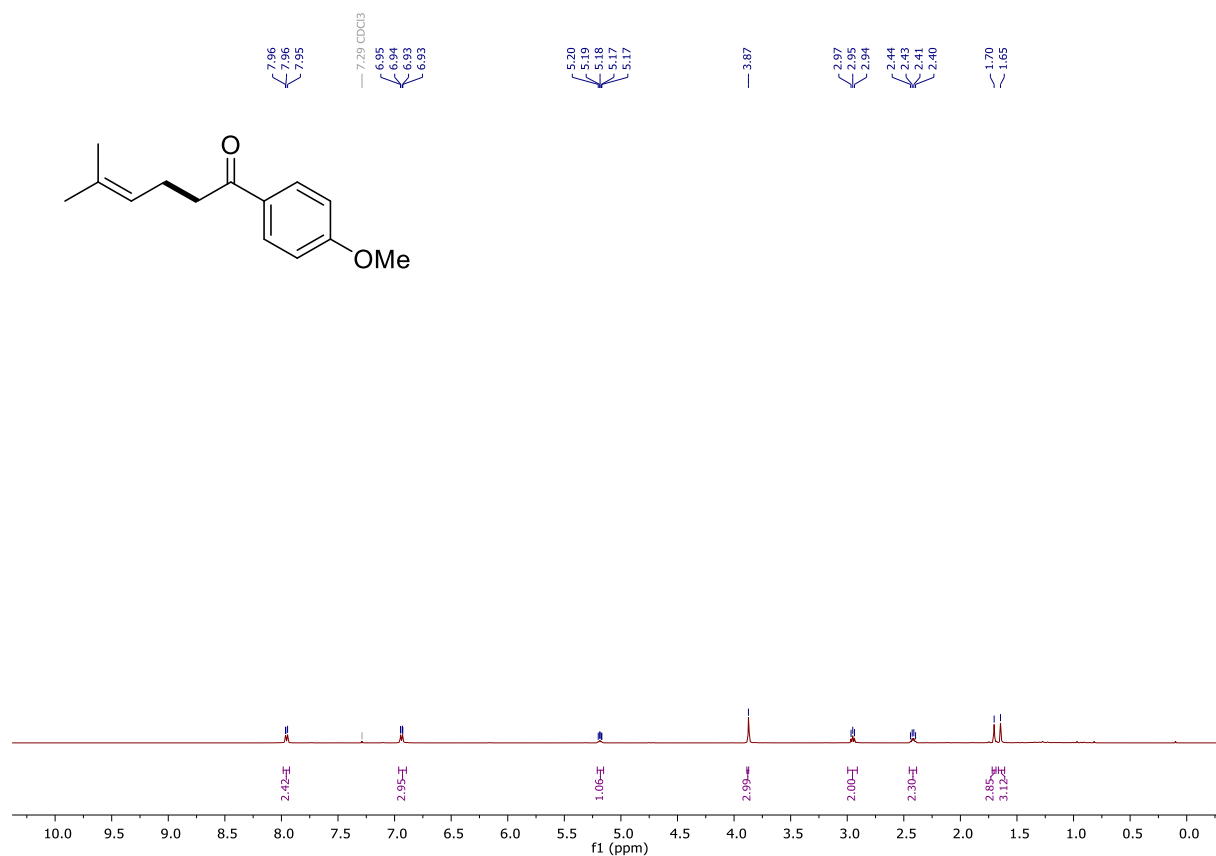
^1H NMR of **3a** (500 MHz, CDCl_3):



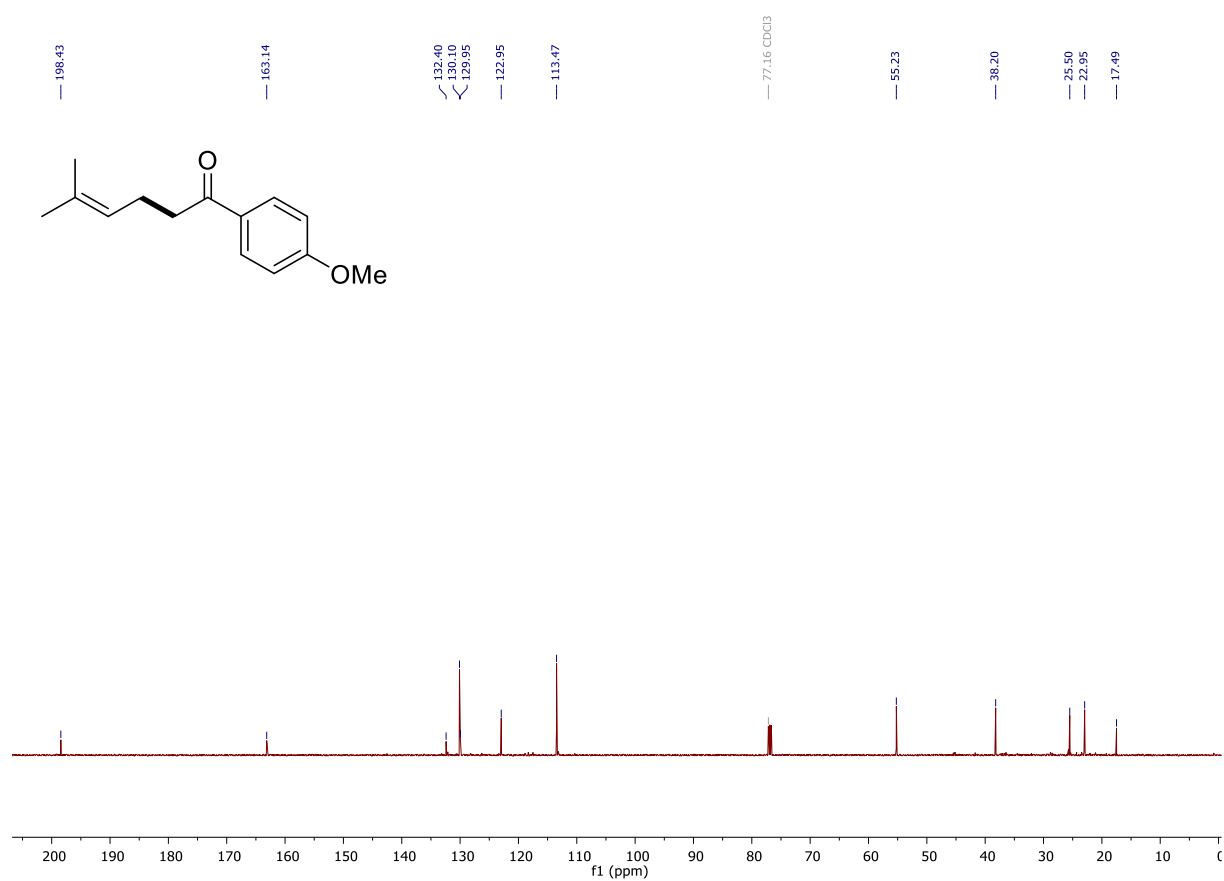
$^{13}\text{C}\{^1\text{H}\}$ NMR of **3a** (126 MHz, CDCl_3):



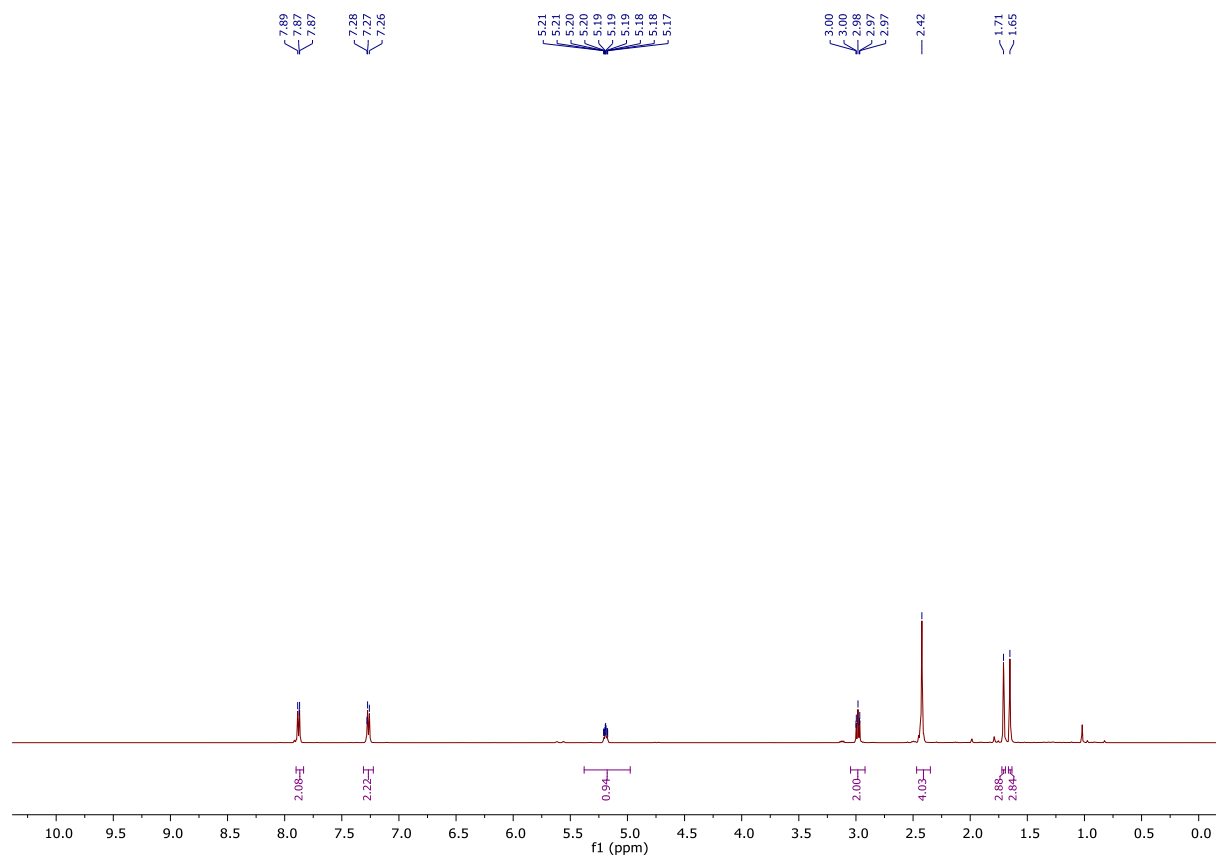
¹H NMR of 3b (500 MHz, CDCl₃):



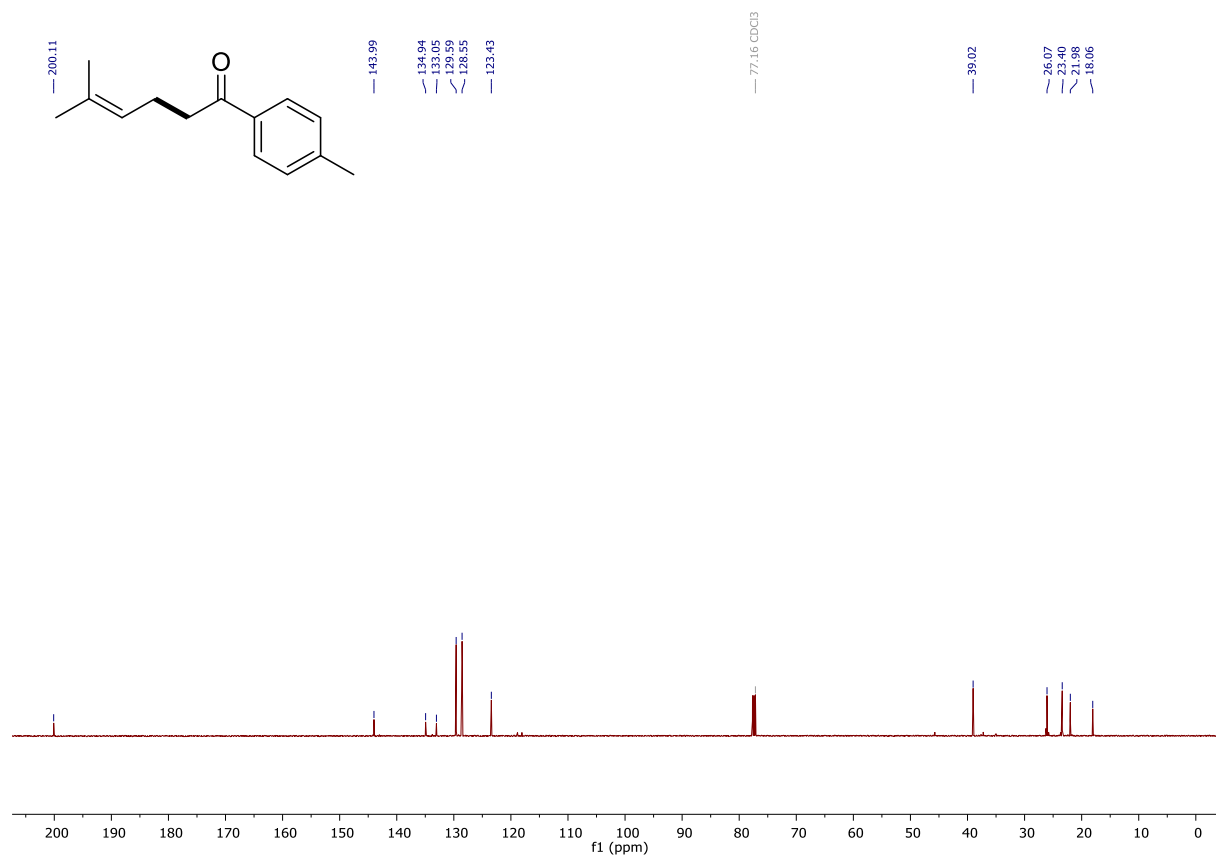
¹³C{¹H} NMR of 3b (126 MHz, CDCl₃):



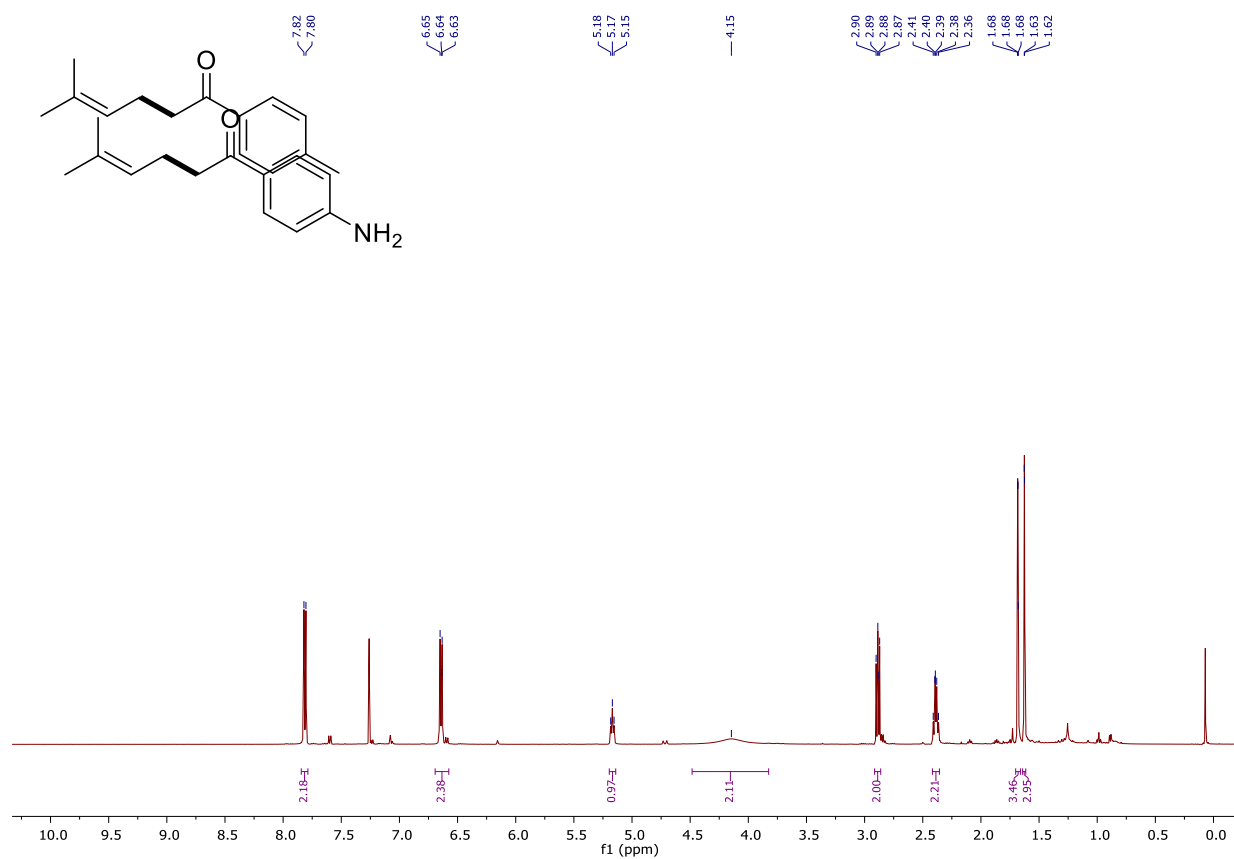
¹H NMR of 3c (400 MHz, CDCl₃):



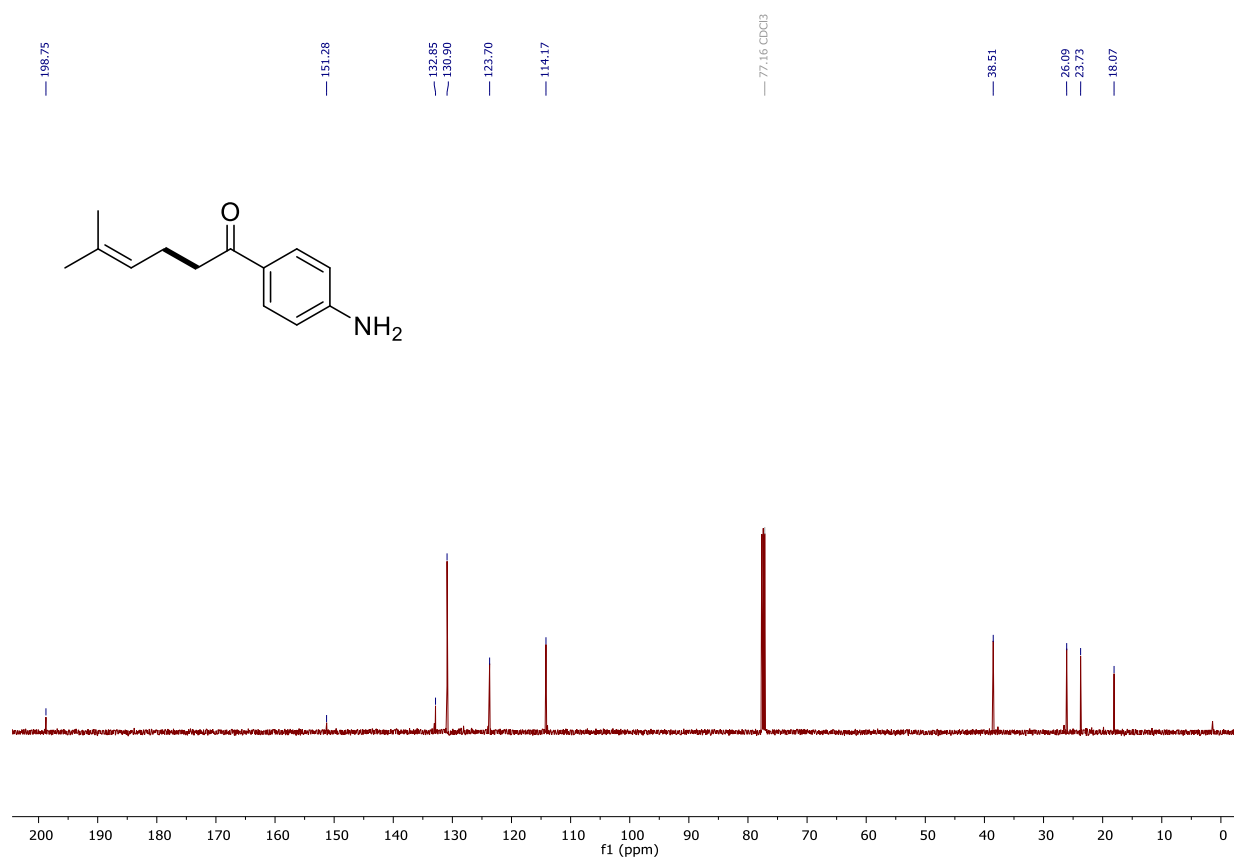
¹³C{¹H} NMR of 3c (101 MHz, CDCl₃):



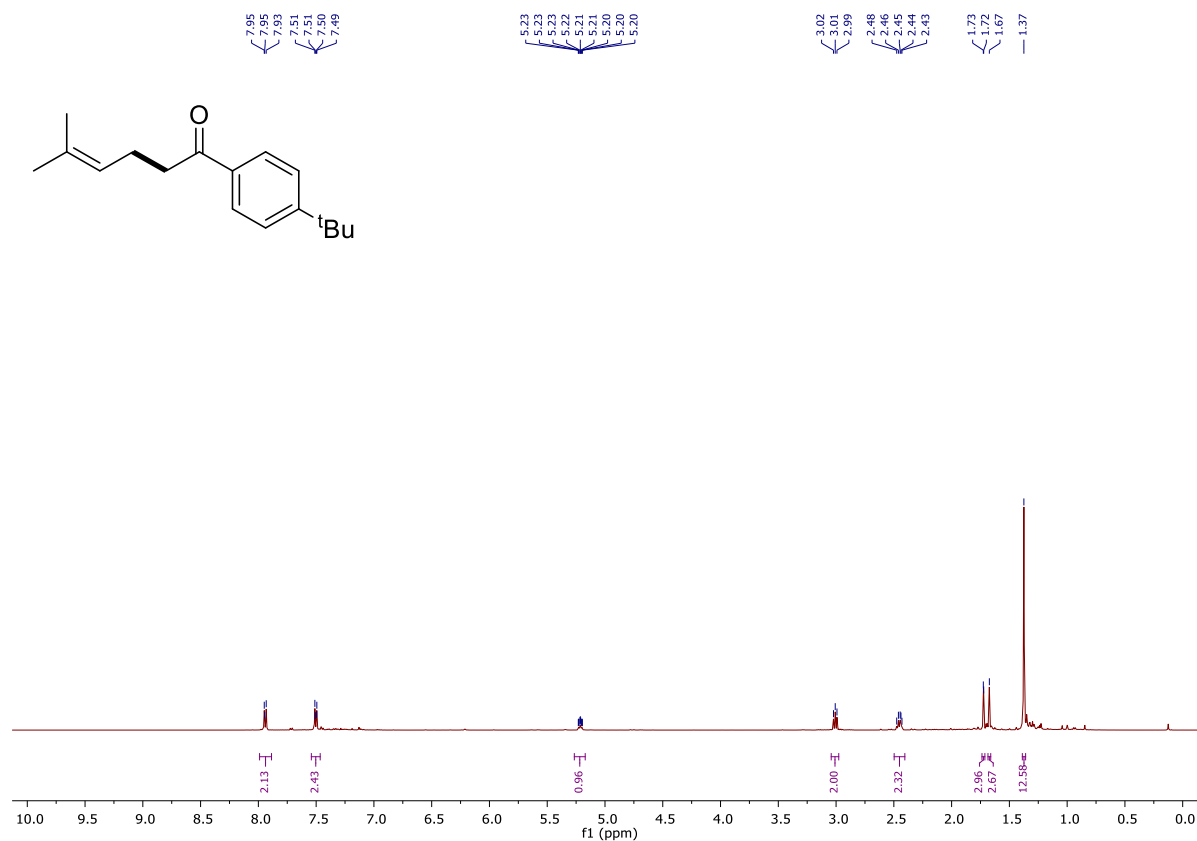
¹H NMR of 3d (500 MHz, CDCl₃):



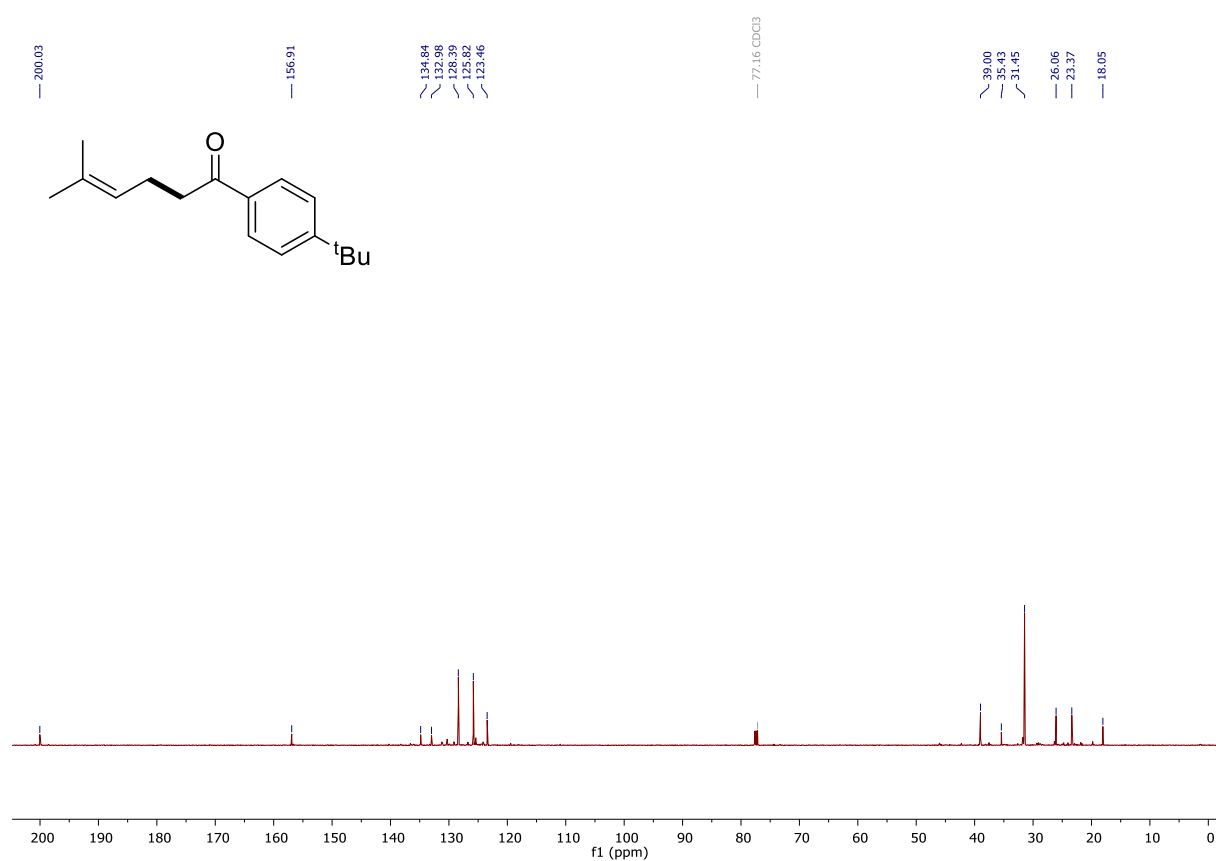
¹³C{¹H} NMR of 3d (126 MHz, CDCl₃):



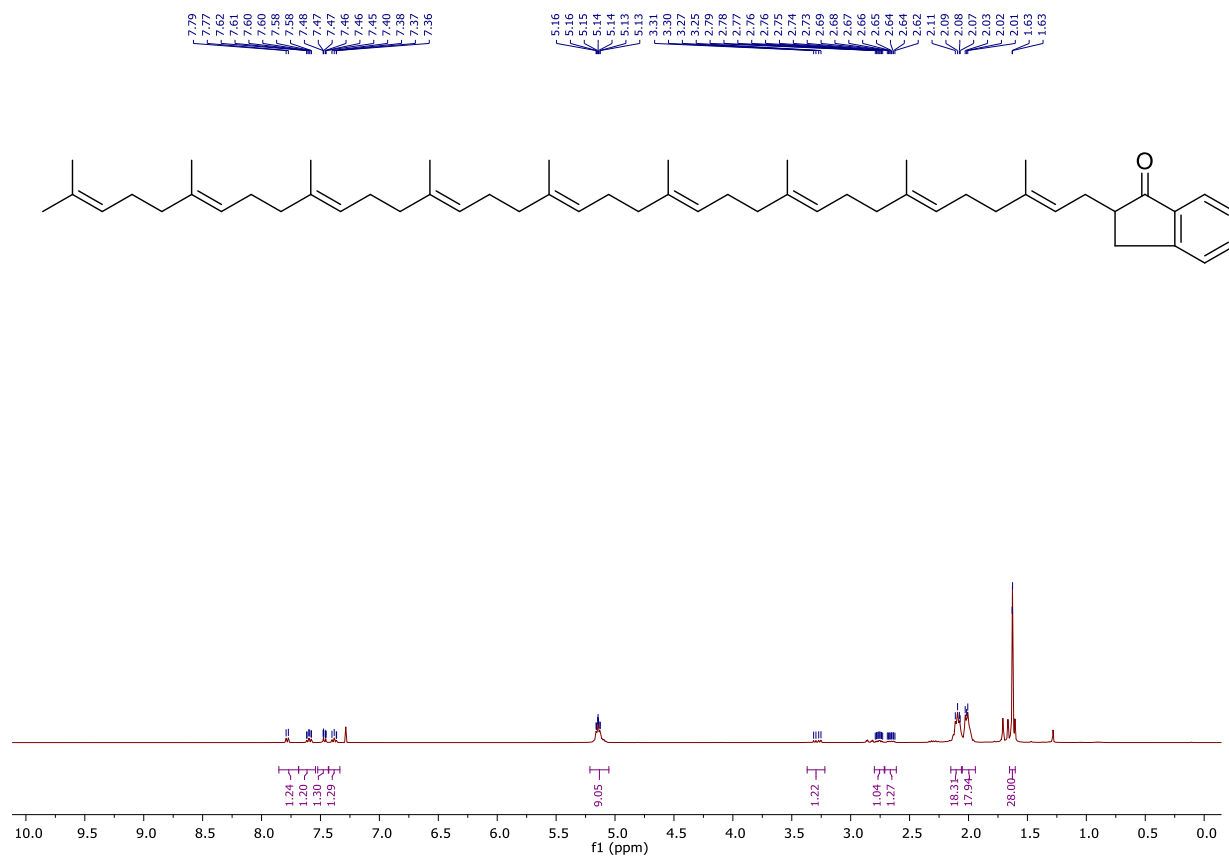
¹H NMR of **3e** (500 MHz, CDCl₃):



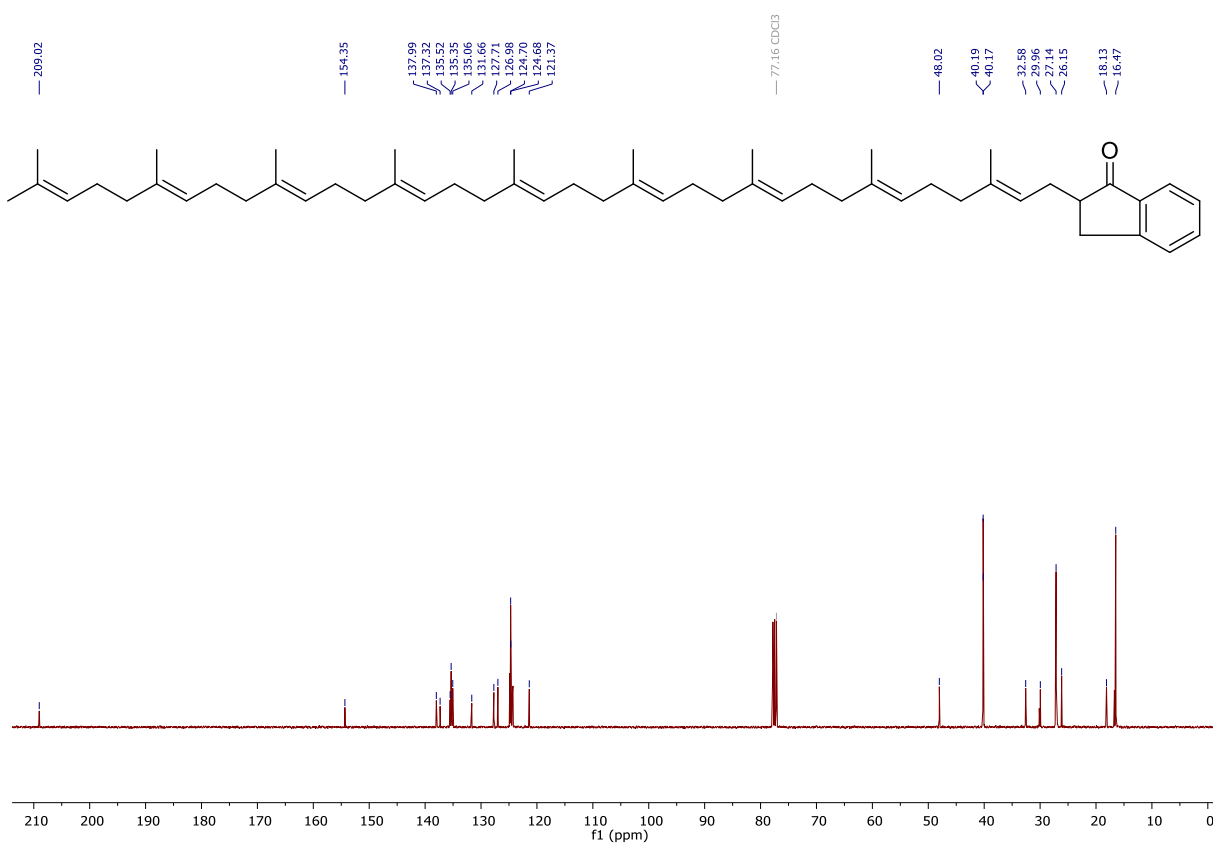
¹³C{¹H} NMR of **3e** (126 MHz, CDCl₃):



¹H NMR of 6l (400 MHz, CDCl₃):



¹³C{¹H} NMR of 6l (101 MHz, CDCl₃):



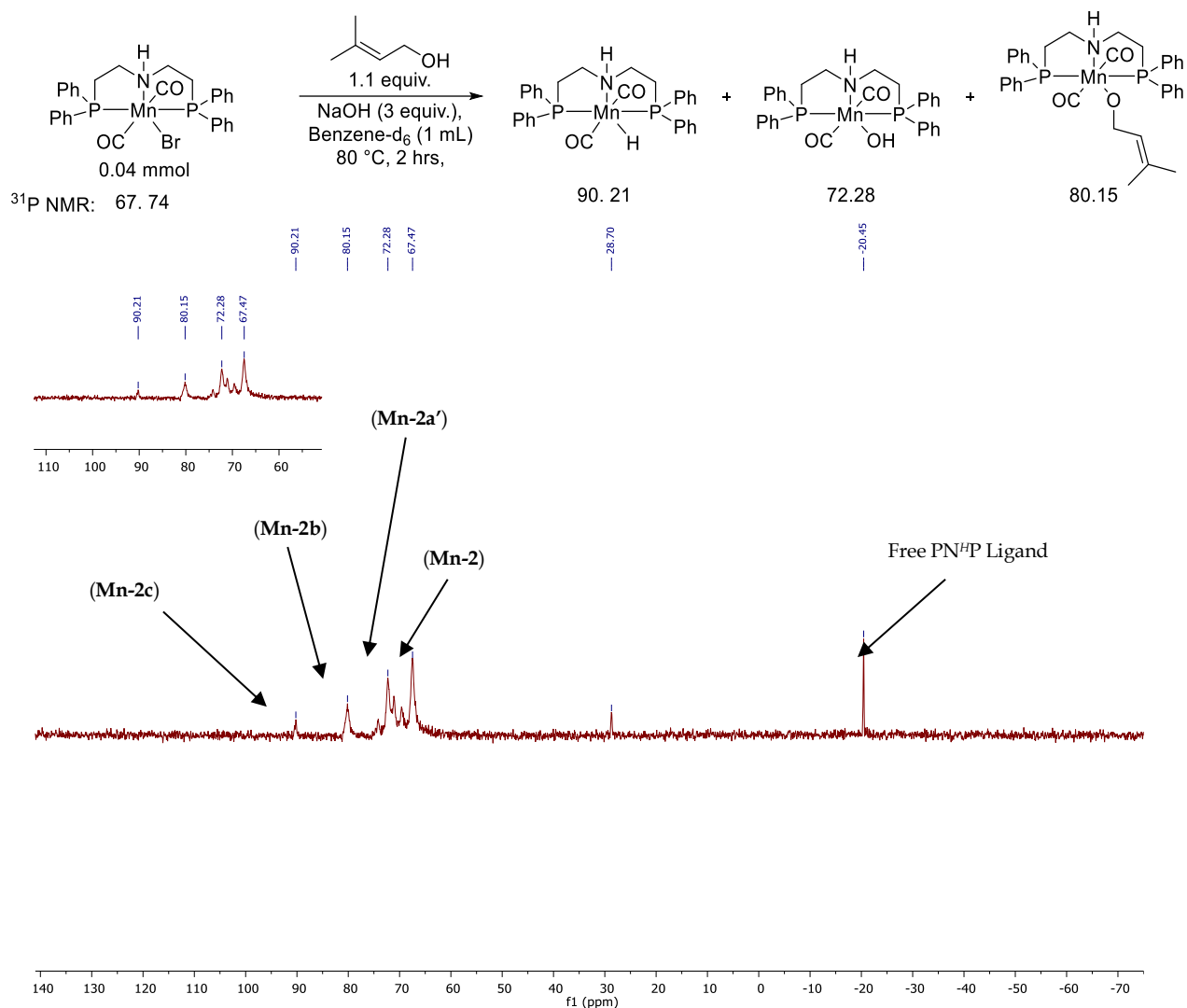


Figure S3.1. ³¹P NMR of the stoichiometric reaction of **Mn-2** with prenol and NaOH.

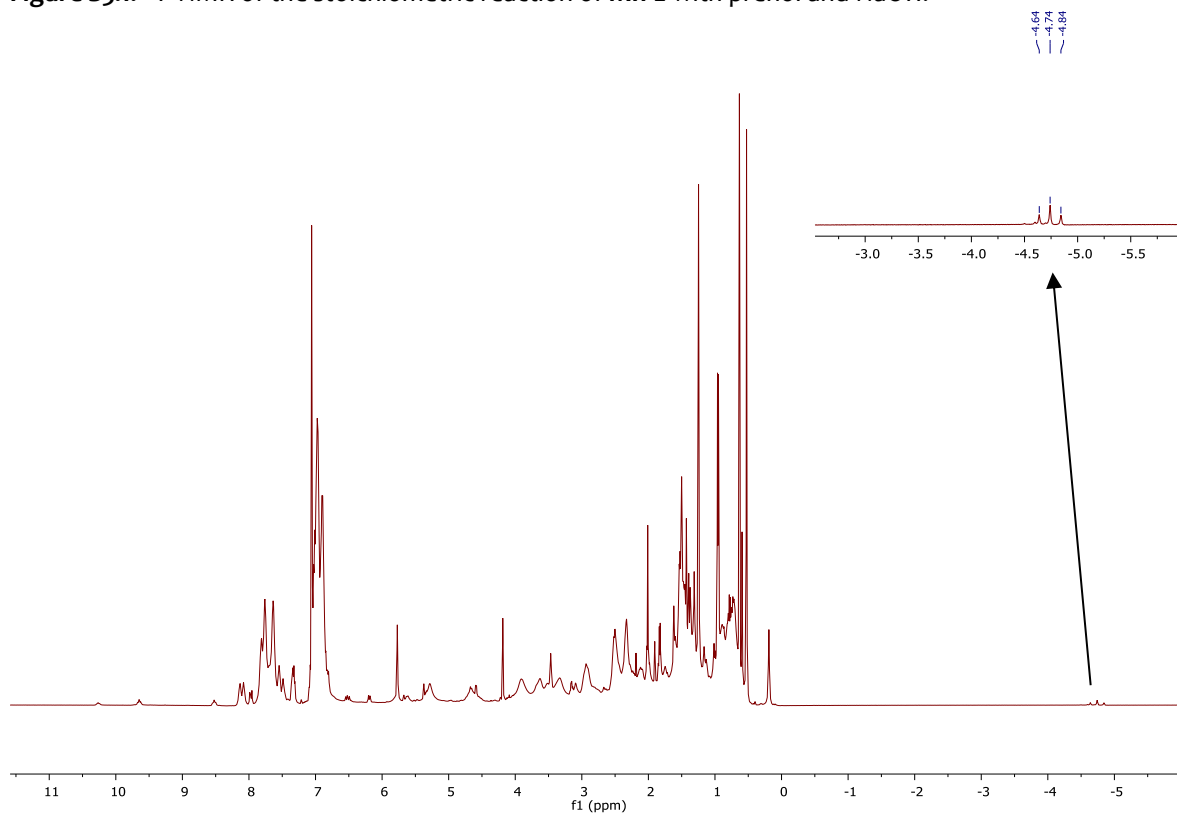


Figure S3.2. ¹H NMR of the stoichiometric reaction of **Mn-2** with prenol and NaOH.

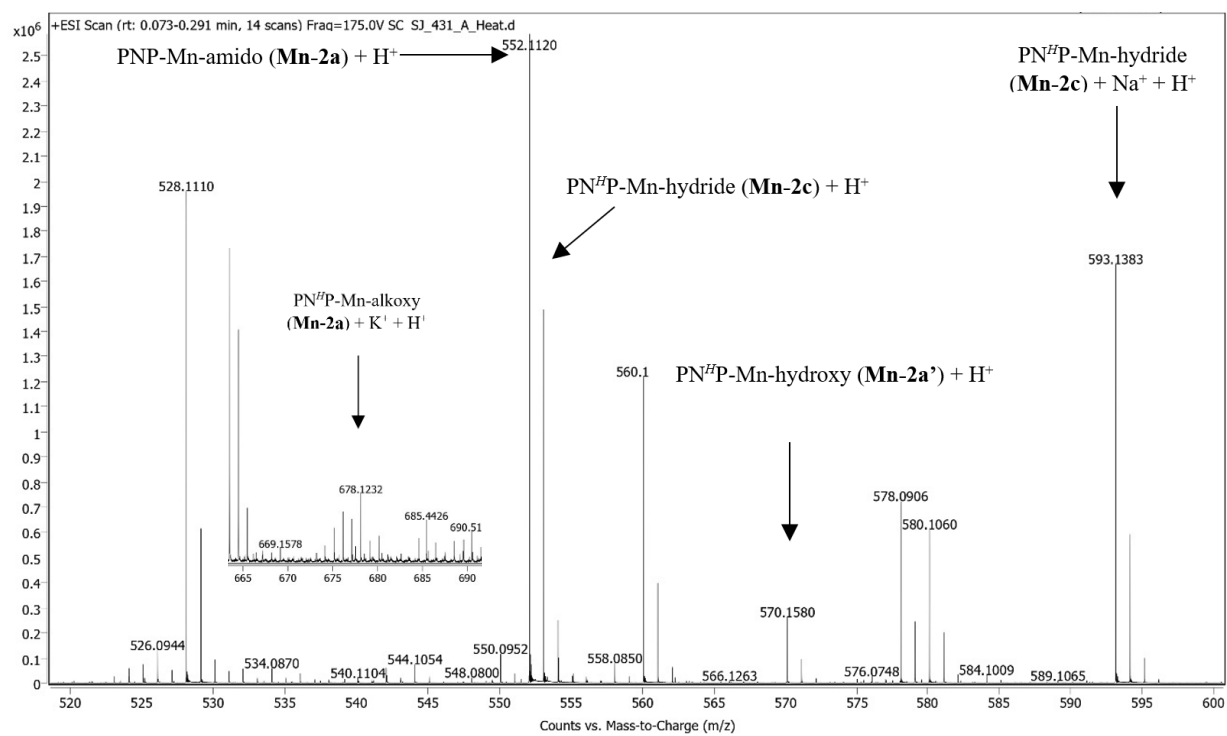


Figure S3.3. HRMS data of the stoichiometric reaction mixture of **Mn-2** with prenol and NaOH.

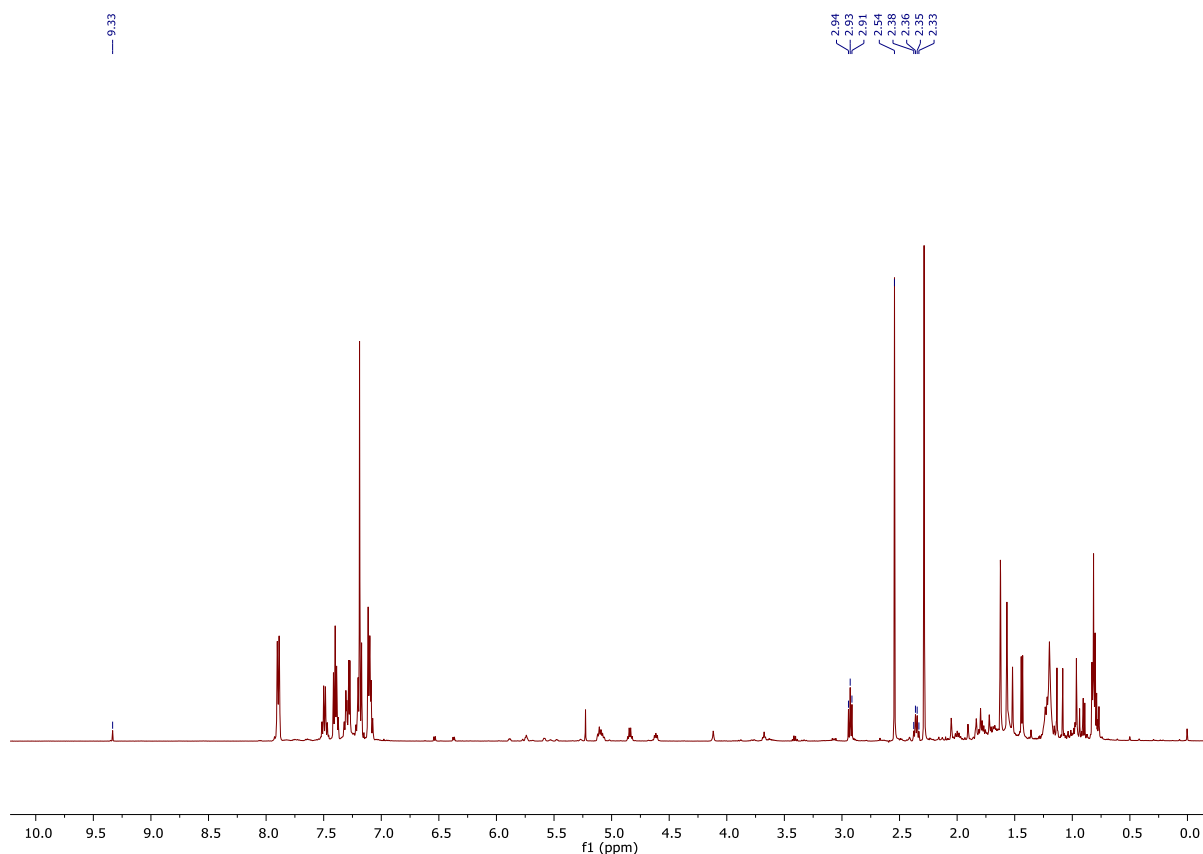


Figure S3.4. ¹H NMR of the catalytic reaction mixture after 2 h.

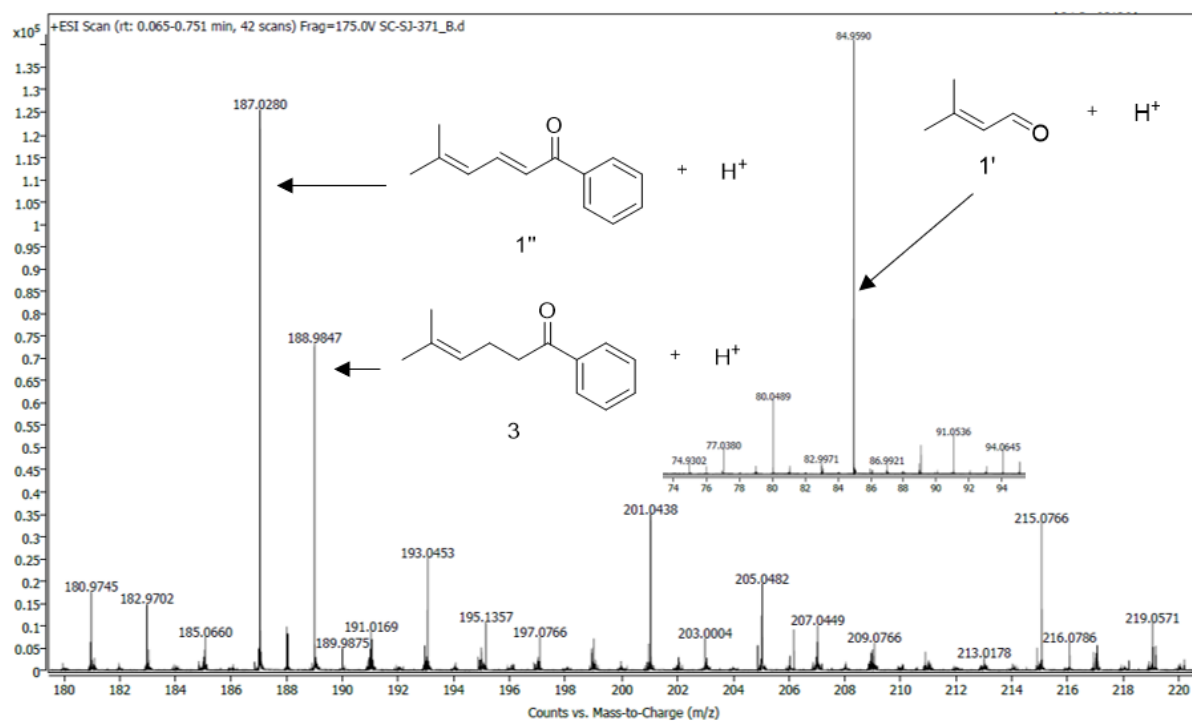


Figure S3.5. HRMS of the catalytic reaction mixture after 2 h.

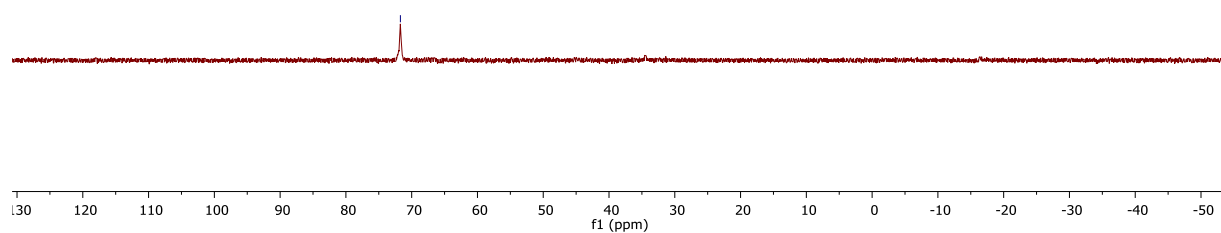
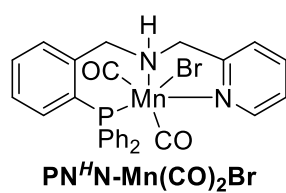


Figure S3.6. ³¹P NMR of (PN^HN)Mn(CO)₂Br (**Mn-3**) catalyst.