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Regioselective Intermolecular Coupling Reaction of Arylketones and Alkenes Involving C-H Bond Activation Catalyzed by an *in Situ* Formed Cationic Ruthenium-Hydride Complex

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Regioselective Intermolecular Coupling Reaction of Arylketones and Alkenes Involving C-H Bond Activation Catalyzed by an In-Situ Formed Cationic Ruthenium-Hydride Complex

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Abstract: The cationic ruthenium-hydride complex, formed *in-situ* from the treatment of the tetranuclear ruthenium-hydride complex $\{[(PCy_3)(CO)RuH]_4(\mu_4\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OH)\}$ with $HBF_4{\cdot}OEt_2$, was found to be a highly effective catalyst for the intermolecular coupling reaction of arylketones and 1-alkenes to give the substituted indene and *ortho*-C–H insertion products. The formation of the indene products was resulted from the initial alkene isomerization followed by regioselective *ortho*-C–H insertion of 2-alkene and the dehydrative cyclization. The preliminary mechanistic studies revealed a

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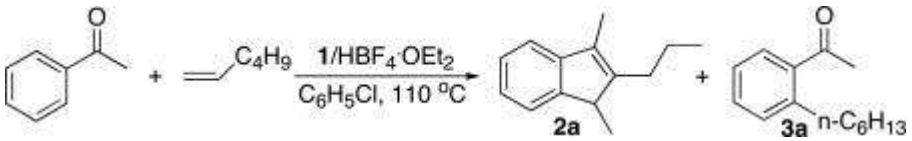
rapid and reversible *ortho*-C–H bond activation followed by the rate-limiting C–C bond formation step for the coupling reaction.

Electrophilic late transition metal complexes have been found to be highly effective in mediating unreactive C–H and C–C bond activation reactions, the activity and selectivity patterns of which are often complementary to their neutral counterparts.[1] In a series of seminal reports, electrophilic Pt, Hg and Pd catalysts have been successfully developed and utilized for Shilov's C–H oxidation and functionalization reactions of alkanes and other hydrocarbons.[2] Extensive research on electrophilic Pd and Pt complexes have also led to a detailed mechanistic understanding on the alkane oxidation reaction,[3] as well as to the applications in the synthesis of complex organic molecules.[4] Most notably, electrophilic Pd and Pt catalysts have been found to be effective for a number synthetically useful coupling reactions involving C–H bond activation.[5] Remarkable activity of cationic Ru and Ir complexes toward C–C bond activation reactions have also been demonstrated under stoichiometric conditions.[6]

Our own interest in electrophilic late metal catalysts stemmed from the recent discoveries that cationic ruthenium-hydride catalysts are highly effective in promoting both hydrogenation reactions,[7] as well as for selective coupling reactions involving C–H and N–H bond activation.[8] We have been searching for suitable ways to generate catalytically active electrophilic ruthenium-hydride complexes and to explore their activity for the C-H bond activation reactions. This report delineates *in-situ* generation of the cationic ruthenium-hydride catalyst from the protonation reaction of tetranuclear ruthenium complex $\{[(PCy_3)(CO)RuH]_4(\mu_4\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OH)\}$ (**1**),[9] and its unusual activity and selectivity pattern toward the coupling reaction of arylketones and alkenes involving C-H bond activation.



(1)

Initially, catalytic activity of electrophilic ruthenium complexes was surveyed for the coupling reaction of acetophenone and 1-hexene. 1-Hexene was chosen because it is normally not considered a suitable

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substrate for the chelate-assisted *ortho*-C–H insertion reaction pioneered by Murai and coworkers (eq 1).[10] Remarkably, the catalytic activity of **1** was "turned-on" upon the addition of $HBF_4{\cdot}OEt_2$ (2 equiv/Ru atom) to give a ~1:1 mixture of the substituted indene product **2a** and the *ortho*-C–H insertion product **3a** (Table 1).[11] Other selected ruthenium and rhenium catalysts were ineffective for the coupling reaction, giving only acid-catalyzed aldol condensation products. The structure of the coupling product **2a** revealed an unusual alkene insertion regioselectivity. The product **2a**, whose structure was completely established by 2-D NMR techniques, showed two methyl groups with 2-propyl group on the indenyl ring, even though 1-hexene was used as the substrate. While a conceptually similar dehydrative coupling reaction of imines and alkenes was reported by Takai and co-workers,[12] to the best of knowledge, the formation of substituted indenes from the coupling reaction of ketones and alkenes has not been achieved before.

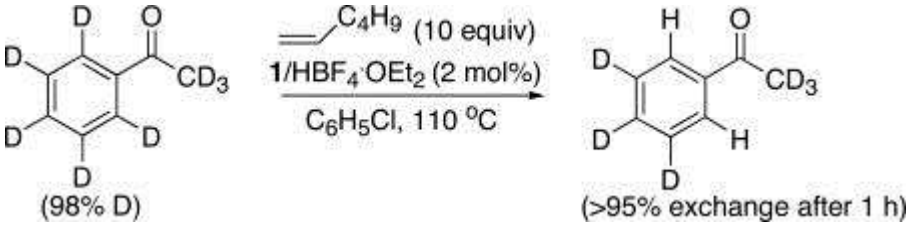
Table 1. Catalyst Survey for the Coupling Reaction of Acetophenone and 1-Hexene.[a]

entry	catalyst	additive	yield[b]	2a:3a
1	**1**	--	0	--
2	**1**	$HBF_4{\cdot}OEt_2$	44	43:57
3	$RuHCl(CO)(PCy_3)_2$	--	0	--
4	$RuHCl(CO)(PCy_3)_2$	$HBF_4{\cdot}OEt_2$	19	43:57
5	$RuH_2(CO)(PPh_3)_3$	--	7	0:100
6	$RuH_2(CO)(PPh_3)_3$	$HBF_4{\cdot}OEt_2$	0	--[c]
7	$RuCl_2(PPh_3)_3$	$HBF_4{\cdot}OEt_2$	5	100:0[c]
8	$RuCl_3{\cdot}3H_2O$	$HBF_4{\cdot}OEt_2$	0	--[c]
9	$[RuCl_2(COD)]_x$	$HBF_4{\cdot}OEt_2$	0	--[c]
10	$Ru_3(CO)_{12}$	NH_4PF_6	0	--
11[d]	$[RuH(CO)(PCy_3)_2(S)_2]^+BF_4^-$	--	0	--
12	$Re(CO)_3(THF)_2Br$	$HBF_4{\cdot}OEt_2$	0	--[c]
13	$BF_3{\cdot}OEt_2$	--	0	--[c]
14	$HBF_4{\cdot}OEt_2$	--	0	--[c]

[a]Reaction conditions: acetophenone (1.0 mmol), 1-hexene (10 mmol), catalyst (5 metal atom mol%), additive (2 equiv), C_6H_5Cl (1 mL), 110−120 °C, 15 h.
[b]GC yields based on acetophenone.
[c]10−15% of the aldol products was formed.
[d]S = CH_3CN.

The scope of the coupling reaction was explored by using **1**/$HBF_4{\cdot}OEt_2$ catalytic system (Table 2). Arylketone with an electron-withdrawing group was found to marginally favor the formation of the

indene product **2** (entry 2), while the ketone with sterically demanding group tended to increase the formation of the *ortho*-C–H insertion product **3** (entry 4, 5). The coupling reaction with both ethylene and 2-butene formed the same products **2j** and **3j** rapidly within 1 h (entry 10, 11), and this observation can be rationalized by the ethylene dimerization and 1-butene to 2-butene isomerization prior to the coupling reaction. In all cases, high regioselectivity in forming the substituted indene product **2**, and a mixture of the double bond isomers is formed for unsymmetric products such as **2h**, **2i** and **2l** (entry 8, 9 and 13). In contrast, the coupling reaction with styrene predominantly gave the *ortho*-alkenyl product **4k** (entry 12), which is likely resulted from the vinyl C–H bond activation. The reaction with a benzocyclic ketone such as α-tetralone gave the *ortho*-C–H insertion product **3o** exclusively (entry 16).



(2)

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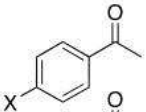
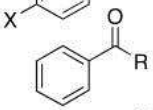
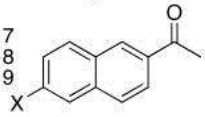
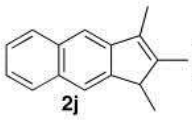
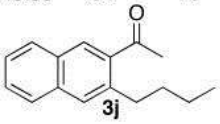
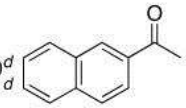
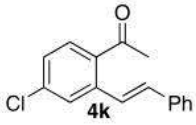
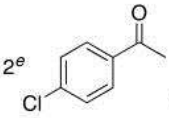
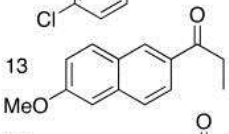
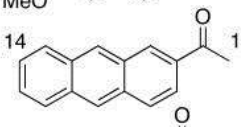
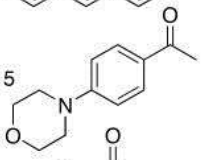
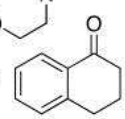
Table 2. Coupling Reaction of Arylketones and Alkenes.[a]

entry	ketone	alkene	product ratio (**2**:**3**)	convn (%)[b]	yd (%)[c]
1		1-hexene	X = H **2a**:**3a** = 41:59	57	47
2			X = Cl **2b**:**3b** = 56:44	67	61
3			X = OMe **2c**:**3c** = 33:67	47	40
4		1-hexene	R = Et **2d**:**3d** = 35:65	45	38
5			R = i-Pr **2e**:**3e** = 27:73	59	50
6			R = Ph **2f**:**3f** = 45:55	68	59
7		1-hexene	X = H **2g**:**3g** = 48:52	72	67
8			X = Me **2h**:**3h** = 50:50	73	65
9			X = OMe **2i**:**3i** = 45:55	84	75
	 **2j**				
	 **3j**				
10[d]		ethylene	**2j**:**3j** = 83:17	95	85
11[d]		2-butene	**2j**:**3j** = 71:29	99	90
	 **4k**				
12[e]		styrene	**2k**:**4k** = 10:90	47	35
13		1-hexene	**2l**:**3l** = 36:64	84	75
14		1-hexene	**2m**:**3m** = 35:65	88	82
15		1-hexene	**2n**:**3n** = 10:90	46	40
16		1-hexene	**2o**:**3o** = 0:100	76	72

[a] Reaction conditions: ketone (1.0 mmol), alkene (10 mmol), **1** (30 mg, 1.75 mol%, 7.0 Ru mol%), $HBF_4{\cdot}OEt_2$ (20 μL, 2 equiv per Ru), C_6H_5Cl (3 mL), 110 °C, 15 h. [b] Determined by GC based on ketone. [c] Combined isolated yield of **2** and **3**. [d] 4 atm of alkene was used. [e] 130 °C, 5 h.

The following experiments were performed to gain mechanistic insights on the coupling reaction. (1) The treatment acetophenone-d_8 with 1-hexene (10 equiv) led to a rapid and extensive H/D exchange on the ortho positions of acetophenone-d_8 within 1 h at 110 °C prior to the product formation (eq 2, Figure S2 in the Supporting Information). Also, a negligible isotope effect of k_H/k_D = 1.13±0.05 at 110 °C was obtained from the coupling reaction of acetophenone vs acetophenone-

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d_8 with 1-hexene. These results indicate a rapid and reversible *ortho*-C–H bond activation step. (2) Carbon isotope effect was measured from the coupling reaction of 2-acetonaphthone and 1-hexene by employing Singleton's isotope measurement technique at natural abundance.[13] The $^{12}C/^{13}C$ ratio of unreacted 2-acetonaphthone isolated at 71% conversion was compared with the virgin sample. The most pronounced carbon isotope effect was observed at the *ortho*-arene carbon atom of 2-acetonaphthone ($^{12}C/^{13}C$ at $C^{(3)}$ = 1.020 with $C^{(7)}$ as the internal standard, average of 3 runs) (Table S1, Supporting Information).

(3) A catalytically relevant ruthenium-hydride species was detected from the reaction mixture of **1** and $HBF_4{\cdot}OEt_2$. Thus, the treatment of **1** (20 mg, 12 μmol) with $HBF_4{\cdot}OEt_2$ (6.5 μL, 2 equiv per Ru) in C_6D_6 at 20 °C led to a clean formation of the ruthenium-hydride complex, whose spectroscopic features are characterized by the Ru–H signal at δ −10.79 (d, J_{PH} = 25.8 Hz) by ^1H NMR and a single phosphine peak at δ 73.8 by $^{31}P\{^1H\}$ NMR. We tentatively formulate the structure of the cationic Ru–H species as $[(L)_3(PCy_3)(CO)RuH]^+$ on the basis of these spectroscopic data. Furthermore, the *in-situ* formed complex was found to be an active catalyst for the coupling reaction.

While details of the reaction mechanism remain unclear, these preliminary results suggest a mechanism involving a rapid and reversible *ortho*-C–H bond activation followed by the rate-limiting olefin insertion step for the coupling reaction (Scheme 1). We propose that the cationic *ortho*-metalated complex **5**, formed from the *ortho*-C–H bond activation of an arylketone and the reductive elimination of an alkane, is the key species for the coupling reaction.[14] The regioselective insertion of 2-alkene to **5** and the subsequent cyclization and dehydration sequence can be envisioned for the formation of **2**. The observation of significant carbon isotope effect on the *ortho*-arene carbon of an arylketone substrate supports the notion that the C-C bond-forming step involving the migratory insertion of 2-alkene to the *ortho*-metalated species **5** is the rate-limiting step of the coupling reaction.

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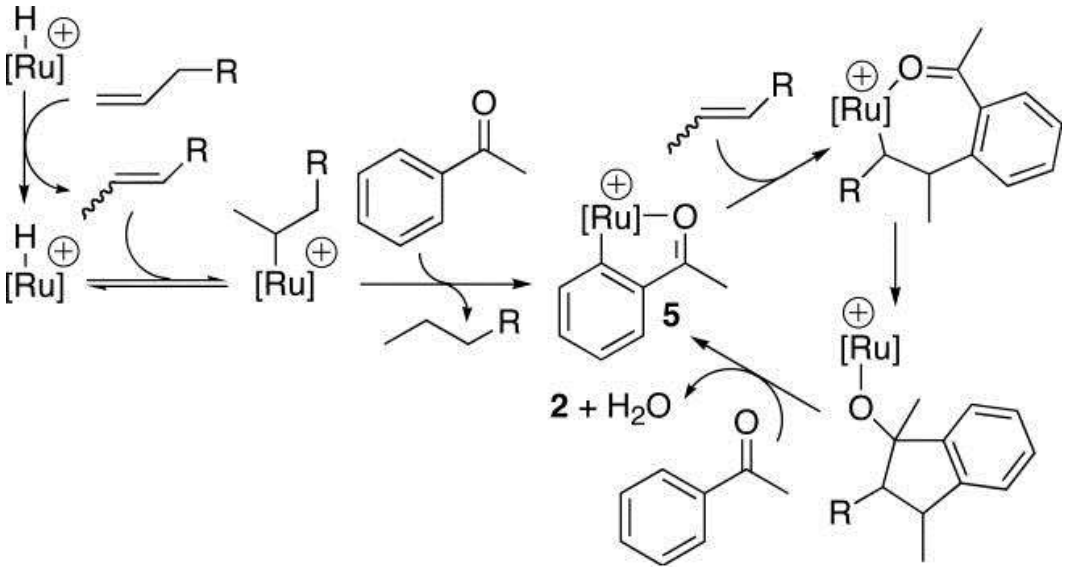

Scheme 1. Proposed Mechanism for the Formation of **2**.

Electrophilic nature of the ruthenium-hydride catalyst appears to be an important factor in mediating the coupling reaction, in that the cationic ruthenium catalyst would promote the dehydrative cyclization steps by facilitating strong dative bonding interaction with the ketone oxygen atom. Heteroatomchelated *ortho*-metalated late transition complexes have been widely considered to be the key intermediate species in both Murai-type of C-H/olefin insertion and oxidative C-H arylation reactions.[15] The cationic nature of the ruthenium-hydride catalyst would also be proficient in mediating the isomerization of terminal alkenes, and in this regard, the activity of electrophilic ruthenium catalysts towards alkenes isomerization and other coupling reactions has been well-documented in the literature.[16] Detailed kinetic and mechanistic investigations are currently underway to further discern the electrophilic nature of the ruthenium-hydride catalyst on the coupling reaction.

Acknowledgment

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Footnotes

Supporting Information **Available:** Experimental procedures and spectroscopic data of organic products (25 pages, print/PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] See the Supporting Information for experimental details.

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[14] The formation of hexane was detected by GC-MS in the crude reaction mixture of acetophenone, 1-hexene and 1/HBF_4·OEt_2 (1.75 mol % Ru).

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Supplementary Material

Supporting Information

Regioselective Intermolecular Coupling Reaction of Arylketones and Alkenes Involving C-H Bond Activation Catalyzed by an In-Situ Formed Cationic Ruthenium-Hydride Complex

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General Information. All operations were carried out in an inert-atmosphere glove box or by using standard high vacuum and Schlenk techniques unless otherwise noted. Tetrahydrofuran, benzene, hexanes and Et_2O were distilled from purple solutions of sodium and benzophenone immediately prior to use. The NMR solvents were dried from activated molecular sieves (4 Å). All organic substrates were received from commercial sources and used without further purification. The ^{1}H, ^{2}H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian 300 or 400 MHz FT-NMR spectrometer. Mass spectra were recorded from a Agilent 6850 GC/MS spectrometer. The conversion of organic products was measured from a Hewlett-Packard HP 6890 GC spectrometer. Elemental analysis was performed at the Midwest Microlab, Indianapolis, IN.

Representative Procedure of the Catalytic Reaction. In a glove box, complex **1** (30 mg, 17.7 μmol) was dissolved in chlorobenzene (3 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The tube was brought out of the box, and $HBF_4{\cdot}OEt_2$ (20 μL, 0.14 mmol) was added to the reaction tube under a stream of nitrogen gas. The tube was brought into the glove box, and both ketone (1.0 mmol) and alkene (10 mmol) substrates were added to the tube. The tube was brought out of the box, and was stirred for 15 h in an oil bath which was preset at 110 °C. After the tube was cooled to room temperature, the solution was filtered through a short silica plug (hexanes/EtOAc = 2:1) in air, and the solution was analyzed by GC. Analytically pure organic product was isolated after a simple column chromatography on silica gel (hexanes/EtOAc).

Detection of the Cationic Ruthenium-Hydride Complex. In a J-Young NMR tube equipped with a screw cap, complex **1** (20 mg, 12 μmol) was dissolved in C_6D_6 (0.5 mL) at room temperature. $HBF_4{\cdot}OEt_2$ (6.5 μL, 47 μmol) was added to the NMR tube via syringe under nitrogen atmosphere. The color of solution was changed from dark red to pale yellow after the tube was shaken a few times. Selected spectroscopic data of the new ruthenium-hydride complex: ^{1}H NMR (C_6D_6, 400.0 MHz) δ -10.79 (d, J_{PH} = 25.8 Hz, Ru-H); $^{31}P\{^{1}H\}$ NMR (C_6D_6,

161.8 MHz) δ 73.8 (PCy_3); IR (C_6D_6) ν_{CO} = 1992 cm^{-1}.

Deuterium Isotope Effect Study. In a glove box, complex **1** (30 mg, 17.7 μmol) was dissolved in chlorobenzene (3 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The tube was brought out of the box, and $HBF_4{\cdot}OEt_2$ (20 μL, 0.14 mmol) was added to the reaction tube under nitrogen atmosphere. The tube was again brought into the glove box, and acetophenone (0.120 g, 1.0 mmol) or acetophenone-d_8 (0.128 g, 1.0 mmol) and 1-hexene (0.84 g, 10 mmol) were added to the tube. After the solution was stirred at room temperature for 10 min, an equal amount of the solution (0.6 mL) was divided and placed in 6 different Schlenk tubes. The tubes were brought out of the box, and were stirred in an oil bath which was preset at 110 °C. Each reaction tube was taken out from the oil bath in 10 min intervals, and was immediately cooled in a dry ice/acetone bath. After filtering through a small silica gel column (hexanes/EtOAc = 2:1), the solution was analyzed by GC. The k_{obs} was determined from a first-order plot of *ln*[**2a**] vs time as measured by the appearance of the product **2a** by GC (Figure S1).

Deuterium Labeling Study. Complex **1** (10 mg, 5.9 μmol) was dissolved in chlorobenzene (0.5 mL) in a J-Young NMR tube. $HBF_4{\cdot}OEt_2$ (6.5 μL, 47 μmol) was added to the NMR tube under nitrogen atmosphere. The tube was brought into the glove box, and acetophenone-d_8 (43 mg, 0.34 mmol) and 1-hexene (0.28 g, 3.4 mmol) were added to the NMR tube. The tube was brought out of the box, and ^2H NMR was initially recorded at room temperature. The NMR tube was immersed in an oil bath which was preset at 110 °C for 1 h. The tube was cooled and the ^2H NMR was recorded at room temperature (Figure S2).

Figure S1. First-Order Plots of the Reaction of Acetophenone and Acetophenone-d_8 with 1-Hexene.

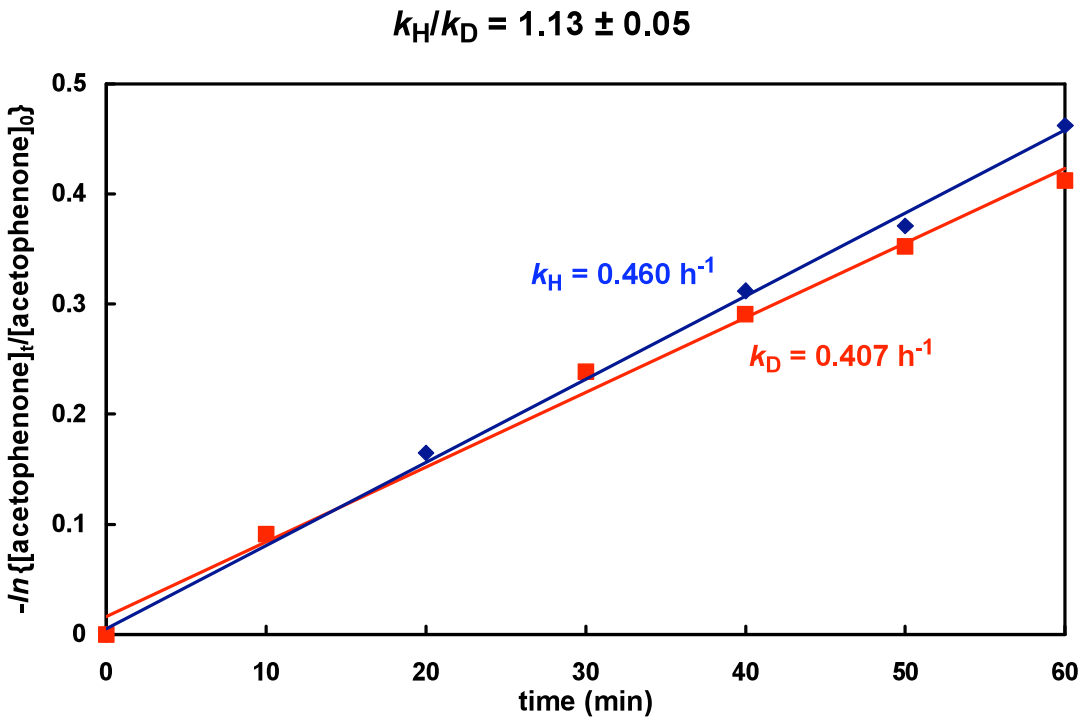
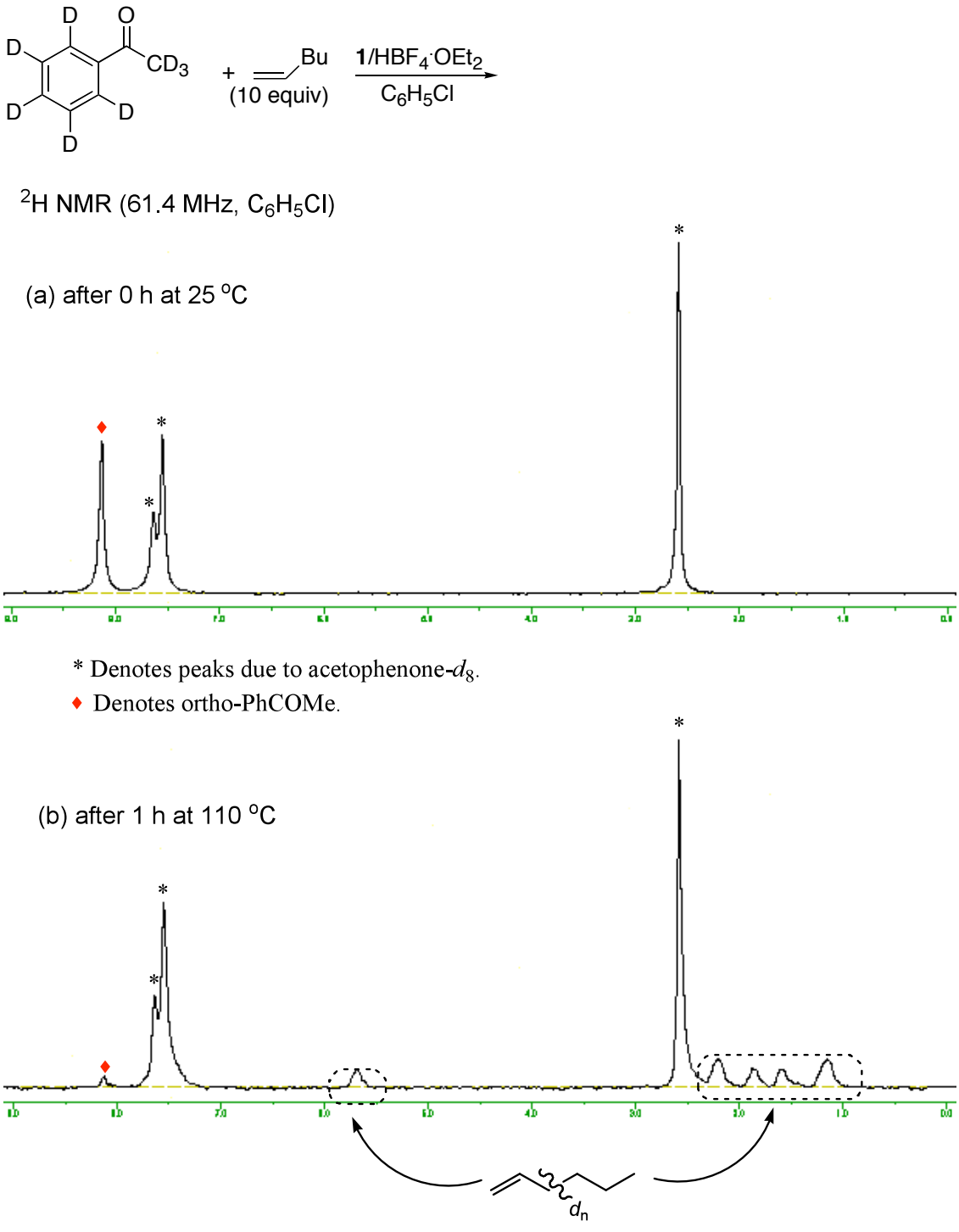


Figure S2. ^{2}H NMR Spectra from the Reaction of Acetophenone-d_8 and 1-Hexene in Chlorobenzene.



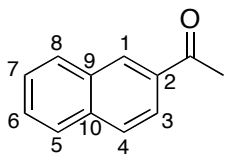
Carbon Isotope Effect Study. In a glove box, complex **1** (150 mg, 89 μmol) was dissolved in chlorobenzene (10 mL) in two separate 25 mL Schlenk tubes equipped with a Teflon stopcock and a magnetic stirring bar. The tubes were brought out of the box, and $HBF_4 \cdot OEt_2$ (100 μL, 0.70 mmol) was added via syringe to each reaction tubes under nitrogen atmosphere. The tubes were brought into the glove box, and 2-acetonaphthone (0.60 g, 3.5 mmol) and 1-hexene (3.0 g, 36 mmol) were added to each tubes. The tubes were brought out of the box, and were stirred in an oil bath which was preset at 110 °C for 10 and 14 h, respectively. The tubes were immediately cooled. After filtering through a small silica gel column (hexanes/EtOAc = 2:1) in air, the product conversion was determined by GC (71% and 78% conversion). Unreacted 2-acetonaphthone was recovered by a column chromatography on silica gel (hexanes/EtOAc) for the $^{13}C\{^1H\}$ NMR analysis.

The ^{13}C NMR analysis of the recovered and virgin samples of 2-acetonaphthone was performed by following Singleton's ^{13}C NMR method (ref #12 in the main text). The NMR sample of virgin and recovered 2-acetonaphthone was prepared identically by dissolving 2-acetonaphthone (100 mg) in $CDCl_3$ (0.5 mL) in a 5 mm high precision NMR tube. The $^{13}C\{^1H\}$ NMR spectra were recorded with H-decoupling and 45 degree pulses. A 60 s delay between pulses was imposed to minimize T_1 variations (d1 = 60 s, at = 5.0 s, np = 245098, nt = 512). The data are summarized in Table S1.

Table S1. Average ^{13}C Integration of the Recovered and Virgin Samples of 2-Acetonaphthone.

C #	virgin	recovered (71% conv.)	recovered/virgin	change (%)
1	1.011(3)	1.005(4)	0.994(4)	-0.59(4)
2	1.032(3)	1.023(4)	0.991(4)	-0.87(4)
3	0.994(4)	1.014(5)	1.020(5)	+2.01(5)
4	1.036(4)	1.027(5)	0.991(5)	-0.87(5)
5	1.040(2)	1.038(4)	0.998(3)	-0.19(3)
6	1.036(4)	1.027(5)	0.991(5)	-0.87(5)
7(ref)	1.000	1.000	1.000	0.00
8	0.992(3)	0.999(2)	1.007(3)	+0.71(3)
9	1.034(4)	1.029(4)	0.995(4)	-0.48(4)
10	1.032(4)	1.025(5)	0.993(5)	-0.68(5)

C #	virgin	recovered (78% conv.)	recovered/virgin	change (%)
1	1.011(3)	1.008(4)	0.997(4)	0.30(4)
2	1.032(3)	1.040(5)	1.008(5)	0.78(5)
3	0.994(4)	1.032(6)	1.038(6)	3.82(6)
4	1.036(4)	1.031(4)	0.995(4)	-0.48(4)
5	1.040(2)	1.020(5)	0.981(5)	-1.92(5)
6	1.036(4)	1.030(4)	0.994(4)	-0.58(4)
7(ref)	1.000	1.000	1.000	0.00
8	0.992(3)	1.008(6)	1.016(6)	1.61(6)
9	1.034(4)	1.036(4)	1.002(4)	0.19(4)
10	1.032(4)	1.041(4)	1.009(4)	0.87(4)



Characterization Data of Organic Products

For **2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.15 (m, 5H, Ar), 3.36 (q, J = 7.8 Hz, C*H*CH_3), 2.52 (m, =CCH_2), 2.20 (s, =CCH_3), 1.50 (m, C*H*$_2$$CH_3$), 1.34 (d, J = 7.8 Hz, CHC*H*$_3$), 1.01 (t, J = 7.5 Hz, CH_2C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.6 (=*C*CH_2), 147.8, 146.3 (Ar), 131.5 (=*C*CH_3), 126.4, 124.0 and 118.3 (Ar), 44.8 (*C*HCH_3), 28.6 (=C*C*H_2), 23.3 (*C*H_2CH_3), 16.6 (CH*C*H_3), 14.4 (CH_2*C*H_3), 10.5 (=C*C*H_3); GC-MS *m/z* = 186 (M^+).

For **2b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H, Ar), 7.27 and 7.15 (d, J = 8.8 Hz, 2H, Ar), 3.31 (m, C*H*CH_3), 2.50 (m, =CCH_2), 2.06 (s, =CC*H*$_3$), 1.50 (m, C*H*$_2$$CH_3$), 1.29 (d, J = 7.5 Hz, CHC*H*$_3$), 1.01 (t, J = 7.5 Hz, CH_2C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.8 (=*C*CH_2), 148.2, 146.7 and 144.8 (Ar), 131.0 (=*C*CH_3), 126.5, 123.2 and 118.6 (Ar), 44.5 (*C*HCH_3), 28.7 (=C*C*H_2), 23.1 (*C*H_2CH_3), 15.9 (CH*C*H_3), 14.3 (CH_2*C*H_3), 10.4 (=C*C*H_3); GC-MS *m/z* = 220 (M^+).

For **2c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 and 7.19 (d, J = 8.2 Hz, 2H, Ar), 6.88 (s, 1H, Ar), 3.85 (s, OCH_3), 3.39 (q, J = 7.8 Hz, C*H*CH_3), 2.50 (m, =CCH_2), 2.12 (s, =CC*H*$_3$), 1.42 (m, C*H*$_2$$CH_3$), 1.26 (d, J = 7.5 Hz, CHC*H*$_3$), 0.97 (t, J = 7.5 Hz, CH_2C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.0, 142.5, 138.6, 122.7, 110.1 and 105.3 (Ar), 150.8 (=*C*CH_2), 132.3 (=*C*CH_3), 55.7 (OCH_3), 43.1 (*C*HCH_3), 30.3 (=C*C*H_2), 23.2 (*C*H_2CH_3), 16.8 (CH*C*H_3), 14.3 (CH_2*C*H_3), 10.5 (=C*C*H_3); GC-MS *m/z* = 216 (M^+).

For **2d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.20 (m, 5H, Ar), 3.42 (m, C*H*CH_2), 2.60 (m, =CCH_2), 2.10 (s, =CC*H*$_3$), 1.70 (m, CHC*H*$_2$), 1.40 (m, C*H*$_2$$CH_3$), 1.01 (t, J = 7.5 Hz, CH_2CH_2C*H*$_3$), 0.62 (t, J = 7.5 Hz, CH_2C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.7 (=*C*CH_2), 145.6 and 143.8 (Ar), 132.9 (=*C*CH_3), 126.3, 122.6, 119.1 and 118.2 (Ar), 50.5

(Ar*C*H), 32.0, 28.8 and 25.0 (CH_2), 23.3 (=C*C*H_3), 14.4 (CH_2CH_2*C*H_3), 8.9 ($CHCH_2$*C*H_3); GC-MS *m/z* = 200 (M^+).

For **2e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.10 (m, 5H, Ar), 3.38 (m, C*H*CH$(CH_3)_2$), 2.35 (m, C*H*$(CH_3)_2$), 2.05 (s, =CC*H*$_3$), 1.70 (m, CHC*H*$_2$), 1.40 (m, C*H*$_2$CH$_3$), 0.98 (t, *J* = 7.5 Hz, $CH_2CH_2CH_3$), 0.63 (t, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.9 (=*C*CH_2), 144.6 and 130.8 (Ar), 130.5 (=*C*CH_3), 126.3, 124.6, 123.1 and 119.0 (Ar), 55.6 (Ar*C*H), 30.4 and 17.9 (CH_2), 29.1 (*C*H$(CH_3)_2$), 22.9 (=C*C*H_3), 21.9 (CH(*C*H$_3$)$_2$), 14.3 (CH_2CH_2*C*H_3), 8.9 ($CHCH_2$*C*H_3); GC-MS *m/z* = 214 (M^+).

For **2f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.18 (m, 9H, Ar), 3.70 (m, C*H*CH_3), 2.78 (m, =CCH_2), 1.82 (m, C*H*$_2$CH$_3$), 1.58 (d, *J* = 7.8 Hz, CHC*H*$_3$), 1.02 (t, *J* = 7.5 Hz, $CH_2CH_2CH_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.8 (=*C*CH_2), 129.4 (=*C*Ph), 140.7, 128.7, 128.5, 128.3, 127.7, 126.7, 124.6, 123.4, 118.4 (Ar), 57.2 (Ar*C*H), 29.0 and 23.1 (CH_2), 14.4 (CH_2*C*H_3), 10.6 (CH*C*H_3); GC-MS *m/z* = 248 (M^+).

For **2g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (m, 2H, Ar), 7.97 and 7.87 (s, 2H, Ar), 7.71 (m, 2H, Ar), 3.73 (q, *J* = 7.5 Hz, C*H*CH_3), 2.80 and 2.62 (m, =CC*H*$_2$), 2.42 (s, =CC*H*$_3$), 1.79 (m, C*H*$_2$CH$_3$), 1.61 (d, *J* = 7.5 Hz, CHC*H*$_3$), 1.28 (t, *J* = 7.5 Hz, CH_2C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.4 (=*C*CH_2), 147.0, 145.5, 133.6 and 132.0 (Ar), 131.6 (=*C*CH_3), 128.0, 127.9, 125.1, 124.5, 120.7 and 115.5 (Ar), 44.1 (*C*HCH_3), 28.8 (=C*C*H_2), 22.7 (*C*H_2CH_3), 16.8 (CH*C*H_3), 14.4 (CH_2*C*H_3), 10.5 (=C*C*H_3); GC-MS *m/z* = 236 (M^+); Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.64; H, 8.46.

For **2h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 10.9, 8.4 Hz, 1H, Ar), 7.72 (t, *J* = 10.7 Hz, 2H, Ar), 7.59 (d, *J* = 11.3 Hz, 1H, Ar), 7.33 (dt, *J* = 8.1, 1.4 Hz, 1H, Ar), 3.53 (q, *J* = 7.4 Hz, C*H*CH_3), 2.61 (s, ArC*H*$_3$), 2.60 and 2.42 (m, 2H, =CC*H*$_2$), 2.21 (s, =CC*H*$_3$), 1.72 and 1.60 (m,

2H, CH_2CH$_3$), 1.42 (d, J = 7.4 Hz, CHCH_3), 1.07 (t, J = 7.4 Hz, CH$_2$CH_3); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 149.4 (=*C*CH$_2$), 148.9, 147.2, 146.2, 145.6, 144.8, 134.5, 134.0, 133.8 and 132.2 (Ar), 131.7 (=*C*CH$_3$), 131.6, 130.2, 127.8, 127.3, 127.1, 126.7, 120.5, 120.2, 115.3 and 115.0 (Ar), 44.2 and 44.1 (*C*HCH$_3$), 28.9 (=C*C*H$_2$), 22.7 (*C*H$_2$CH$_3$), 21.9 (Ar*C*H$_3$), 16.9 (CH*C*H$_3$), 14.4 (CH$_2$*C*H$_3$), 10.5 (=C*C*H$_3$); GC-MS *m/z* = 250 (M$^+$); Anal. Calcd for C$_{19}$H$_{22}$: C, 91.14; H, 8.86. Found: C, 91.28; H, 8.91.

For **2i**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.77 (m, 1H, Ar), 7.70 and 7.56 (s, 2H, Ar), 7.24 (d, J = 12.8 Hz, 1H, Ar), 7.15 (m, 1H, Ar), 3.97 (s, OCH$_3$), 3.50 (m, C*H*CH$_3$), 2.58 and 2.40 (m, =CCH_2), 2.18 (s, =CCH_3), 1.70 and 1.56 (m, CH_2CH$_3$), 1.38 (m, CHCH_3), 1.05 (m, CH$_2$CH_3); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 157.3 and 156.8 (Ar), 149.8 (=*C*CH$_2$), 148.1, 147.8, 146.1, 144.9, 143.7, 134.6 and 132.9 (Ar), 131.6 (=*C*CH$_3$), 129.4, 128.8, 127.3, 120.5, 119.9, 117.4, 116.8, 115.4, 114.7, 106.6, 106.5 (Ar), 55.4 (OCH$_3$), 44.1, 44.0 (*C*HCH$_3$), 28.9 and 28.8 (=C*C*H$_2$), 22.8 (*C*H$_2$CH$_3$), 16.9 (CH*C*H$_3$), 14.4 (CH$_2$*C*H$_3$), 10.5 (=C*C*H$_3$); GC-MS *m/z* = 266 (M$^+$); Anal. Calcd for C$_{19}$H$_{22}$O: C, 85.67; H, 8.32. Found: C, 85.58; H, 8.39.

For **2j**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (m, 2H, Ar), 7.73 and 7.55 (s, 2H, Ar), 7.42 (m, 2H, Ar), 3.38 (q, J = 7.5 Hz, C*H*CH$_3$), 2.13 and 2.05 (s, =CCH_3), 1.37 (d, J = 7.5 Hz, CHCH_3); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 147.0 and 131.3 (=*C*CH$_3$), 145.6, 145.3, 133.5, 131.9, 128.0, 127.9, 125.1, 124.5, 120.6 and 115.3 (Ar), 46.4 (*C*HCH$_3$), 16.8 (CH*C*H$_3$), 12.6 and 10.5 (=C*C*H$_3$); GC-MS *m/z* = 208 (M$^+$).

For **2l**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.74 (d, J = 8.9 Hz, 1H, Ar), 7.68 and 7.51 (s, 2H, Ar), 7.22 (d, J = 2.2 Hz, 1H, Ar), 7.10 (dd, J = 8.9, 2.6 Hz, 1H, Ar), 3.95 (s, OCH$_3$), 2.54, 1.82 and 1.50 (m, CH$_2$), 1.00 and 0.60 (t, J = 7.3 Hz, CH$_3$); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 157.2 (Ar), 147.7 (=*C*CH$_2$), 142.8, 134.5, 132.9 and 129.4 (Ar), 127.1 (=*C*CH$_3$), 120.7, 116.8, 114.5 and 106.5 (Ar), 55.4 (OCH$_3$), 49.5 (*C*HCH$_2$), 29.0, 23.4 and 22.8 (CH$_2$), 14.4, 10.5 and 8.9

(CH_3); GC-MS *m/z* = 280 (M^+); Anal. Calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.74; H, 8.68.

For **2m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 and 8.38 (s, 2H, Ar), 8.00 (d, *J* = 9.3 Hz, 2H, Ar), 7.85 and 7.69 (s, 1H, Ar), 7.45 (m, 2H, Ar), 3.58 (q, *J* = 7.4 Hz, C*H*CH_3), 2.56 and 2.41 (m, =CC*H*$_2$), 2.17 (s, =CC*H*$_3$), 1.70 and 1.56 (m, C*H*$_2$$CH_3$), 1.40 (d, *J* = 7.4 Hz, CHC*H*$_3$), 1.02 (t, *J* = 7.4 Hz, CH_2C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.3 (=*C*CH_2), 146.9, 145.8, 132.3, 131.9, 131.6 and 131.2 (Ar), 131.1 (=*C*CH_3), 128.2, 128.1, 126.0, 125.7, 125.0, 124.7, 120.5 and 114.8 (Ar), 43.9 (*C*HCH_3), 29.0 (=C*C*H$_2$), 22.5 (*C*H$_2$$CH_3$), 17.2 (CH*C*H$_3$), 14.5 ($CH_2$*C*H$_3$), 10.5 (=C*C*H$_3$); GC-MS *m/z* = 286 ($M^+$).

For **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.8 Hz, 1H, Ar), 7.36 (dt, *J* = 7.5, 1.3 Hz, 1H, Ar), 7.24 (d, *J* = 7.4 Hz, 2H, Ar), 2.84 (pseudo t, *J* = 7.9 Hz, ArC*H*$_2$), 2.56 (s, COC*H*$_3$), 1.55 (m, ArCH$_2$C*H*$_2$), 1.4-1.2 (m, C*H*$_2$), 0.88 (t, *J* = 6.7 Hz, CH_2C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 202.2 (C=O), 142.9, 138.0, 131.3, 131.1, 129.0 and 125.6 (Ar), 34.0, 31.9, 31.7, 29.4 and 22.7 (CH_2), 29.9 (CO*C*H$_3$), 14.1 (CH_2*C*H$_3$); GC-MS *m/z* = 204 (M^+).

For **3b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 1H, Ar), 7.21 (m, 2H, Ar), 2.80 (pseudo t, *J* = 7.9 Hz, 2H, ArC*H*$_2$), 2.53 (s, 3H, COC*H*$_3$), 1.51 (m, ArCH$_2$C*H*$_2$), 1.4-1.2 (m, C*H*$_2$), 0.87 (t, *J* = 6.8 Hz, CH_2C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.9 (C=O), 145.5, 137.4, 136.2, 131.2, 130.7 and 125.9 (Ar), 34.0, 31.8, 31.7, 29.5 and 22.8 (CH_2), 30.0 (CO*C*H$_3$), 14.2 (CH_2*C*H$_3$); GC-MS *m/z* = 238 (M^+).

For **3c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 9.1 Hz, 1H, Ar), 6.73 (m, 2H, Ar), 3.84 (s, OCH_3), 2.89 (pseudo t, *J* = 7.9 Hz, ArC*H*$_2$), 2.53 (s, $COCH_3$), 1.55 (m, ArCH$_2$C*H*$_2$), 1.4-1.2 (m, 6H, C*H*$_2$), 0.88 (t, *J* = 6.7 Hz, CH_2C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.0 (C=O),

162.0, 147.1, 132.7, 130.1, 116.9 and 110.6 (Ar), 55.5 (OCH_3), 35.0, 31.9, 31.8, 29.7 and 22.9 (CH_2), 29.7 ($COCH_3$), 14.3 (CH_2CH_3); GC-MS *m/z* = 234 (M^+).

For **3d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 1H, Ar), 7.34 (t, *J* = 7.7 Hz, 1H, Ar), 7.23 (d, *J* = 7.1 Hz, 1H, Ar), 7.19 (d, *J* = 7.1 Hz, 1H, Ar), 2.88 (q, *J* = 7.3 Hz, $COCH_2$), 2.78 (pseudo t, *J* = 7.9 Hz, 2H, $ArCH_2$), 1.55 (m, $ArCH_2CH_2$), 1.4-1.2 (m, 6H, CH_2), 1.20 (t, *J* = 7.3 Hz, $COCH_2CH_3$), 0.88 (t, *J* = 6.7 Hz, CH_2CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 205.6 (C=O), 142.3, 138.6, 130.9, 130.7, 127.9 and 125.5 (Ar), 35.2 ($COCH_2$), 33.9, 31.9, 31.7, 29.4 and 22.6 (CH_2), 14.1 (CH_2CH_3), 8.4 ($COCH_2CH_3$); GC-MS *m/z* = 218 (M^+).

For **3e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.7 Hz, 1H, Ar), 7.33 (t, *J* = 7.3 Hz, 1H, Ar), 7.24 (d, *J* = 7.7 Hz, 1H, Ar), 7.20 (d, *J* = 7.3 Hz, 1H, Ar), 3.31 (heptet, *J* = 6.9 Hz, $CH(CH_3)_2$), 2.71 (pseudo t, *J* = 7.9 Hz, $ArCH_2$), 1.55 (m, $ArCH_2CH_2$), 1.4-1.2 (m, 6H, CH_2), 1.15 (d, *J* = 6.9 Hz, 6H, $CH(CH_3)_2$), 0.87 (t, *J* = 6.7 Hz, CH_2CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 209.5 (C=O), 142.2, 138.7, 130.7, 130.4, 127.3 and 125.4 (Ar), 39.1 ($COCH$), 33.7, 32.0, 31.7, 29.4 and 22.6 (CH_2), 18.6 ($CH(CH_3)_2$), 14.1 (CH_2CH_3); GC-MS *m/z* = 232 (M^+).

For **3f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (m, 2H, Ar), 7.60-7.20 (m, 7H, Ar), 2.67 (pseudo t, *J* = 7.9 Hz, 2H, $ArCH_2$), 1.55-1.15 (m, 8H, CH_2), 0.83 (t, *J* = 6.8 Hz, CH_2CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.8 (C=O), 141.9, 138.7, 138.0, 133.2, 130.2, 128.5 and 125.2 (Ar), 33.4, 31.8, 31.6, 29.2 and 22.6 (CH_2), 14.1 (CH_2CH_3); GC-MS *m/z* = 266 (M^+); Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 86.04; H, 8.69.

For **3g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H, Ar), 7.84 (d, *J* = 8.1 Hz, 1H, Ar), 7.76 (d, *J* = 8.1 Hz, 1H, Ar), 7.67 (s, 1H, Ar), 7.53 (t, *J* = 6.9 Hz, 1H, Ar), 7.46 (t, *J* = 6.9 Hz, 1H, Ar), 3.05 (pseudo t, *J* = 7.8 Hz, $ArCH_2$), 2.70 (s, 3H, $COCH_3$), 1.65 (m, $ArCH_2CH_2$), 1.5-1.3 (m, 6H, CH_2), 0.94 (t, *J* = 7.1 Hz, CH_2CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.9 (C=O), 139.3,

136.7, 134.7, 131.0, 130.3, 129.3, 128.5, 128.1, 127.2 and 126.0 (Ar), 34.3, 31.9, 31.8, 29.5 and 22.8 (CH_2), 29.9 ($CO\mathit{C}H_3$), 14.2 ($CH_2\mathit{C}H_3$); GC-MS *m/z* = 254 (M^+); Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 85.49; H, 8.74.

For **3h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H, Ar), 7.74 (d, *J* = 8.4 Hz, 1H, Ar), 7.57 and 7.54 (s, 2H, Ar), 7.30 (dd, *J* = 8.3, 1.6 Hz, 1H, Ar), 3.05 (pseudo t, *J* = 7.7 Hz, $ArCH_2$), 2.70 (s, $COCH_3$), 2.52 (s, $ArCH_3$), 1.65 (m, $ArCH_2C\mathit{H}_2$), 1.5-1.3 (m, 6H, $C\mathit{H}_2$), 0.94 (t, *J* = 7.1 Hz, $CH_2C\mathit{H}_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.7 (C=O), 139.6, 138.2, 135.7, 135.1, 130.4, 129.2, 128.7, 128.4, 128.3 and 126.2 (Ar), 34.4, 31.9, 31.8, 29.6 and 22.8 (CH_2), 29.8 ($CO\mathit{C}H_3$), 22.0 ($Ar\mathit{C}H_3$), 14.3 ($CH_2\mathit{C}H_3$); GC-MS *m/z* = 268 (M^+); Anal. Calcd for $C_{19}H_{24}O$: C, 85.03; H, 9.01. Found: C, 85.13; H, 9.11.

For **3i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H, Ar), 7.71 (d, *J* = 9.0 Hz, 1H, Ar), 7.53 (s, 1H, Ar), 7.11 (dd, *J* = 9.0, 2.5 Hz, 1H, Ar), 7.04 (d, *J* = 2.5 Hz, 1H, Ar), 3.90 (s, 3H, OCH_3), 3.03 (pseudo t, *J* = 7.7 Hz, 2H, $ArC\mathit{H}_2$), 2.67 (s, $COCH_3$), 1.60 (m, $ArCH_2C\mathit{H}_2$), 1.5-1.3 (m, 6H, $C\mathit{H}_2$), 0.91 (t, *J* = 6.9 Hz, $CH_2C\mathit{H}_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.2 (C=O), 159.5, 140.4, 136.3, 133.9, 130.8, 130.1, 128.2, 126.3, 118.9 and 104.9 (Ar), 55.3 (OCH_3), 34.5, 31.8 and 22.8 (CH_2), 29.5($CO\mathit{C}H_3$), 14.2 ($CH_2\mathit{C}H_3$); GC-MS *m/z* = 284 (M^+); Anal. Calcd for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.64; H, 8.66.

For **3j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H, Ar), 7.86 and 7.78 (d, *J* = 8.1 Hz, 2H, Ar), 7.67 (s, 1H, Ar), 7.54 and 7.48 (t, *J* = 6.9 Hz, 2H, Ar), 3.05 (pseudo t, *J* = 7.8 Hz, $ArC\mathit{H}_2$), 2.71 (s, $COCH_3$), 1.64 and 1.45 (m, 4H, $ArCH_2C\mathit{H}_2$), 0.98 (t, *J* = 7.3 Hz, $CH_2C\mathit{H}_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 202.1 (C=O), 139.4, 136.8, 134.8, 131.1, 130.4, 129.4, 128.6, 128.2, 127.2 and 126.1 (Ar), 34.1, 34.0 and 22.9 (CH_2), 30.0 ($CO\mathit{C}H_3$), 14.2 ($CH_2\mathit{C}H_3$); GC-MS *m/z* = 226 (M^+).

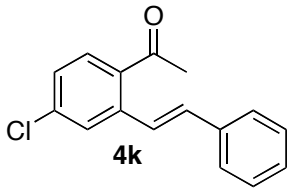
For **3l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H, Ar), 7.71 (d, *J* = 8.9 Hz, 1H, Ar), 7.55 (s, 1H, Ar), 7.11 (dd, *J* = 8.9, 2.5 Hz, 1H, Ar), 7.05 (d, *J* = 2.5 Hz, 1H, Ar), 3.03 (q, *J* = 7.3 Hz, $COCH_2$), 2.99 (pseudo t, *J* = 7.8 Hz, ArCH_2), 1.60, 1.40 and 1.30 (m, 8H, CH_2), 1.25 (t, *J* = 7.3 Hz, $COCH_2CH_3$), 0.91 (t, *J* = 7.0 Hz, 3H, CH_2CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 204.9 (C=O), 159.4, 140.2, 136.2, 134.7, 130.1, 129.4, 128.2, 126.4, 119.0 and 105.1 (Ar), 55.4 (OCH_3), 34.9 ($COCH_2$), 34.4, 32.0, 31.9, 29.6 and 22.8 (CH_2), 14.2 and 8.8 (CH_3); GC-MS *m/z* = 298 (M^+); Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 81.13; H, 9.00.

For **3m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 and 8.27 (s, 2H, Ar), 8.23 (s, 1H, Ar), 7.95 (m, 2H, Ar), 7.71 (s, 1H, Ar), 7.48 (m, 2H, Ar), 3.07 (pseudo t, *J* = 7.8 Hz, ArCH_2), 2.72 (s, $COCH_3$), 1.68 (m, $ArCH_2CH_2$), 1.5-1.3 (m, 6H, CH_2), 0.95 (t, *J* = 7.0 Hz, CH_2CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.7 (C=O), 138.3, 136.6, 133.2, 132.2, 131.7, 131.5, 129.3, 128.8, 128.5, 128.2, 127.7, 126.4, 125.5 and 125.3 (Ar), 34.5, 31.9, 31.7, 29.6 and 22.8 (CH_2), 29.7 ($COCH_3$), 14.3 (CH_2CH_3); GC-MS *m/z* = 304 (M^+); Anal. Calcd for $C_{22}H_{24}O$: C, 86.80; H, 7.95. Found: C, 86.73; H, 8.06.

For **3n**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 9.4 Hz, 1H, Ar), 6.67 (m, 2H, Ar), 3.83 (pseudo t, *J* = 5.0 Hz, 4H, OCH_2), 3.26 (pseudo t, *J* = 5.0 Hz, 4H, NCH_2), 2.90 (pseudo t, *J* = 7.6 Hz, ArCH_2), 2.51 (s, $COCH_3$), 1.55-1.25 (m, 8H, CH_2), 0.87 (t, *J* = 6.6 Hz, CH_2CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.0 (C=O), 153.1, 146.7, 132.8, 127.6, 116.7 and 110.8 (Ar), 66.7 (OCH_2), 47.7 (NCH_2), 35.5, 31.9, 31.8, 29.7 and 22.8 (CH_2), 29.2 ($COCH_3$), 14.2 (CH_3); GC-MS *m/z* = 289 (M^+); Anal. Calcd for $C_{18}H_{27}NO_2$: C, 74.70; H, 9.40. Found: C, 74.90; H, 9.47.

For **3o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.6 Hz, 1H, Ar), 7.09 and 7.08 (d, *J* = 7.6 Hz, 2H, Ar), 3.02 (pseudo t, *J* = 7.7 Hz, 2H, $ArCH_2$), 2.94 (t, *J* = 6.1 Hz, $COCH_2$), 2.64 (t, *J* = 6.6 Hz, $=CCH_2$), 2.07 (quintet, *J* = 6.4 Hz, 2H, $COCH_2CH_2$), 1.55-1.25 (m, 8H, CH_2), 0.89 (t, *J* = 7.0 Hz, CH_2CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.1 (C=O), 146.5, 146.0, 132.3, 131.0,

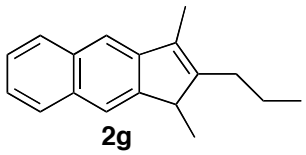
130.0 and 126.9 (Ar), 41.3, 35.6 and 22.9 (cyclic CH_2), 31.9, 31.7, 31.3, 29.8 and 23.1 (CH_2), 14.3 (CH_3); GC-MS *m/z* = 230 (M^+); Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.40; H, 9.72.



4k

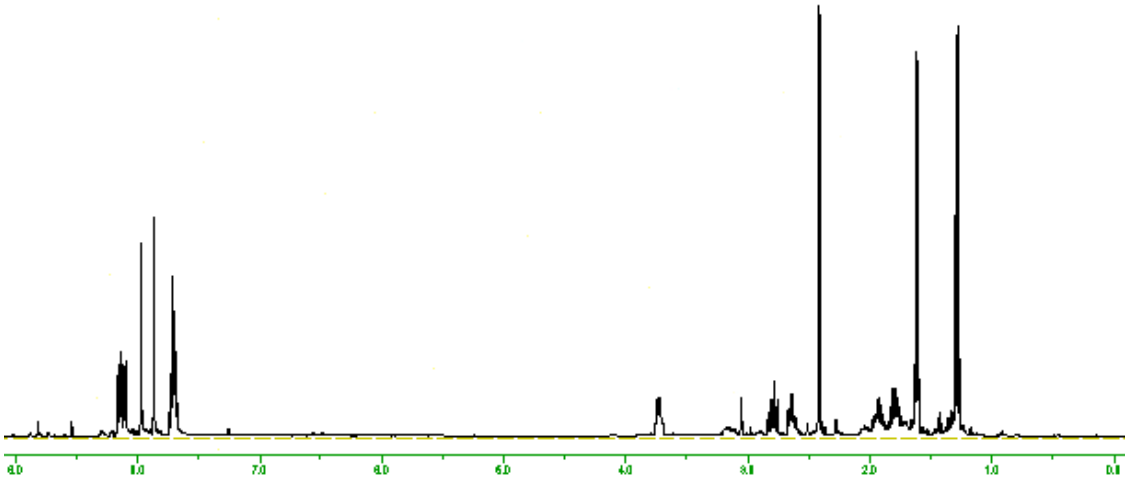
For **4k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (m, 1H, Ar), 7.65 (d, *J* = 16.5 Hz, CH=CH), 7.53-7.30 (m, 4H, Ar), 6.69 (d, *J* = 16.5 Hz, CH=CH), 2.60 (s, $COCH_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.0 (C=O), 139.7, 138.1, 137.0, 135.5, 133.0, 128.9, 127.5, 127.3, 127.2 and 126.4 (Ar), 130.9 and 128.5 (CH), 30.0 ($COCH_3$); GC-MS *m/z* = 256 (M^+).

The ^{1}H and ^{13}C NMR Spectra of Selected Organic Products

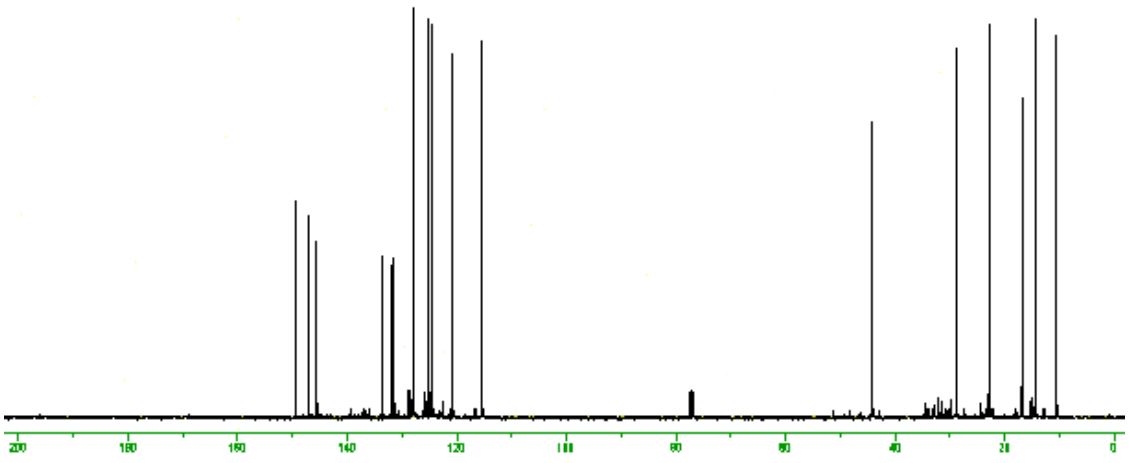


2g

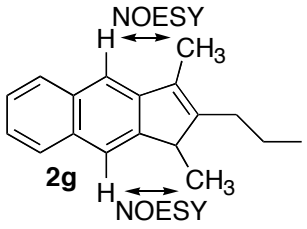
^{1}H NMR (400 MHz, $CDCl_3$)

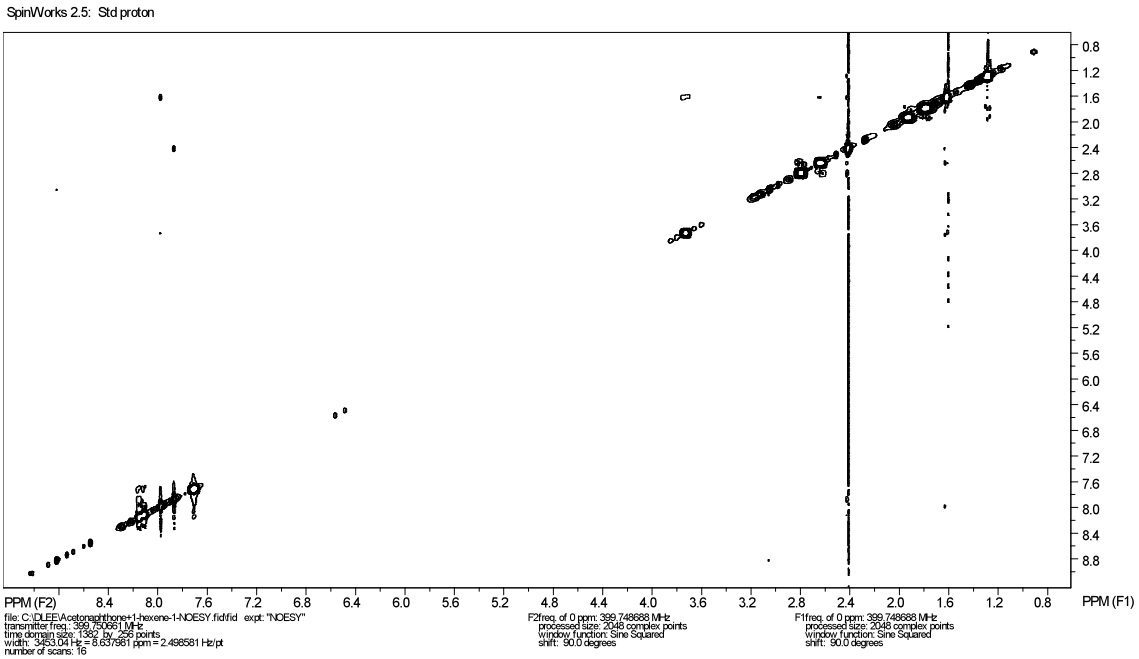


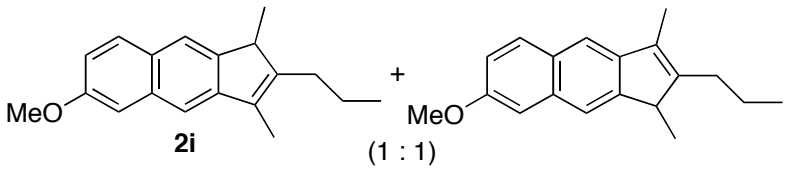
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



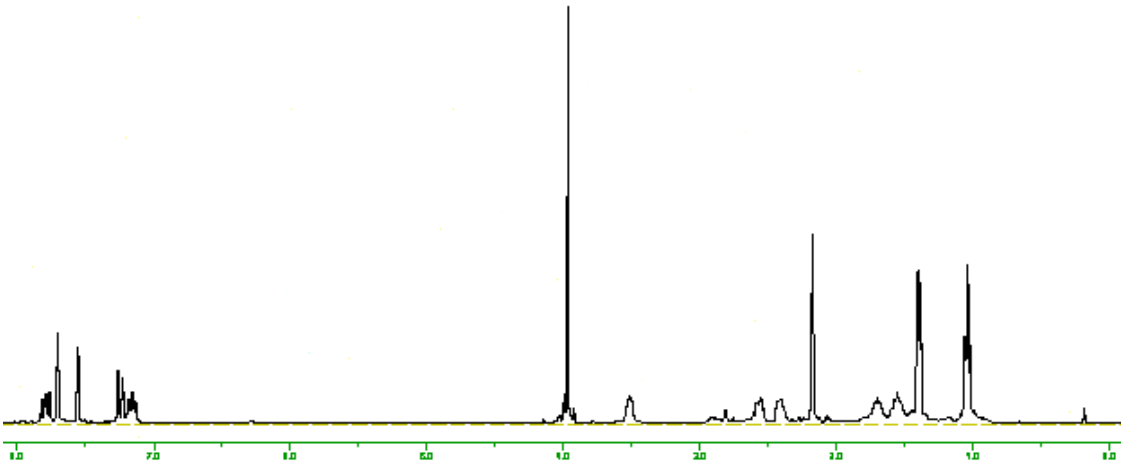
NOESY spectrum of **2g**



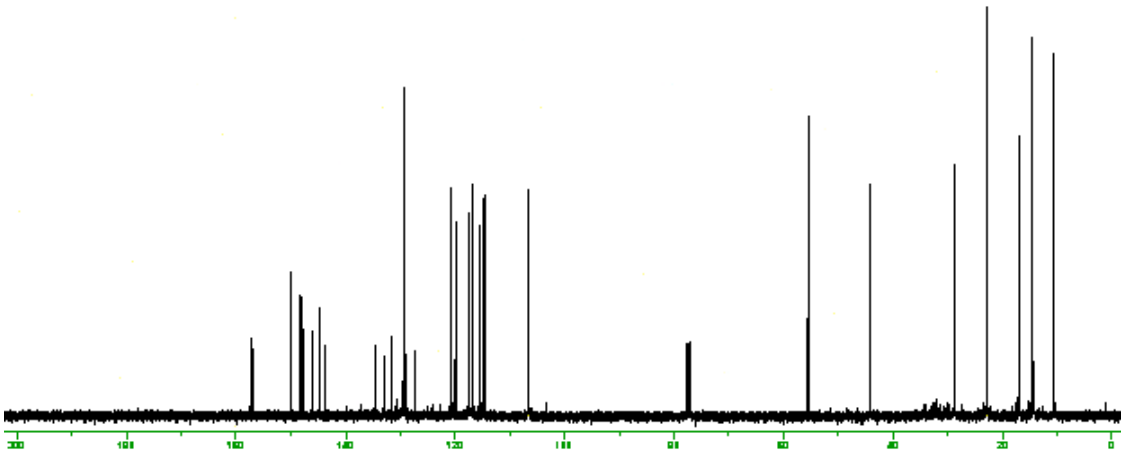


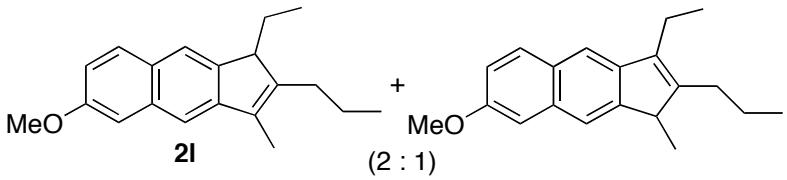


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

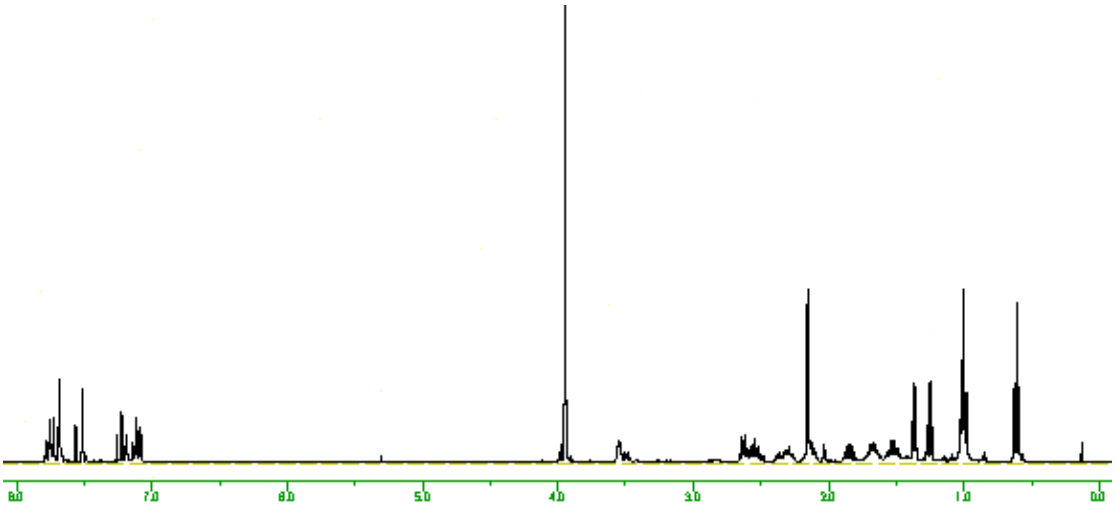




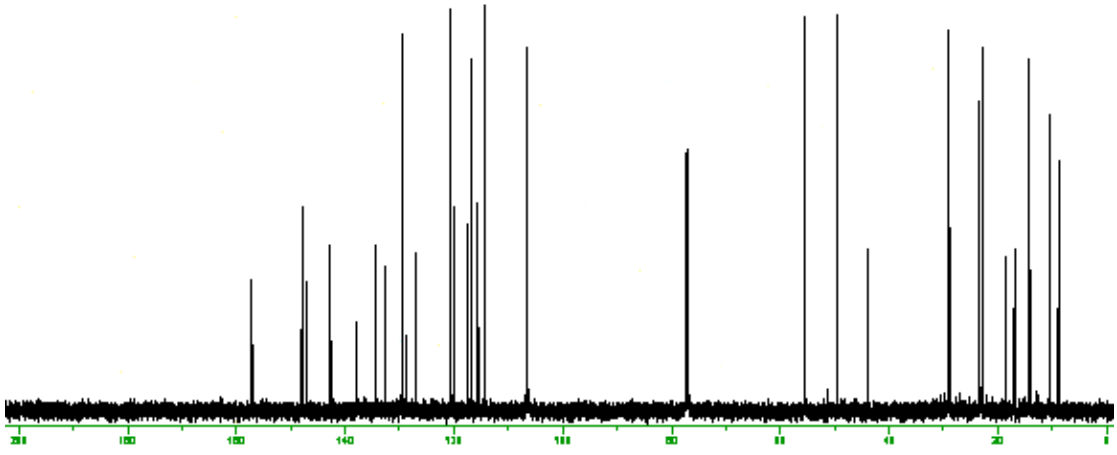
2l

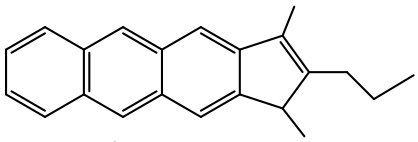
(2 : 1)

^{1}H NMR (400 MHz, $CDCl_3$)



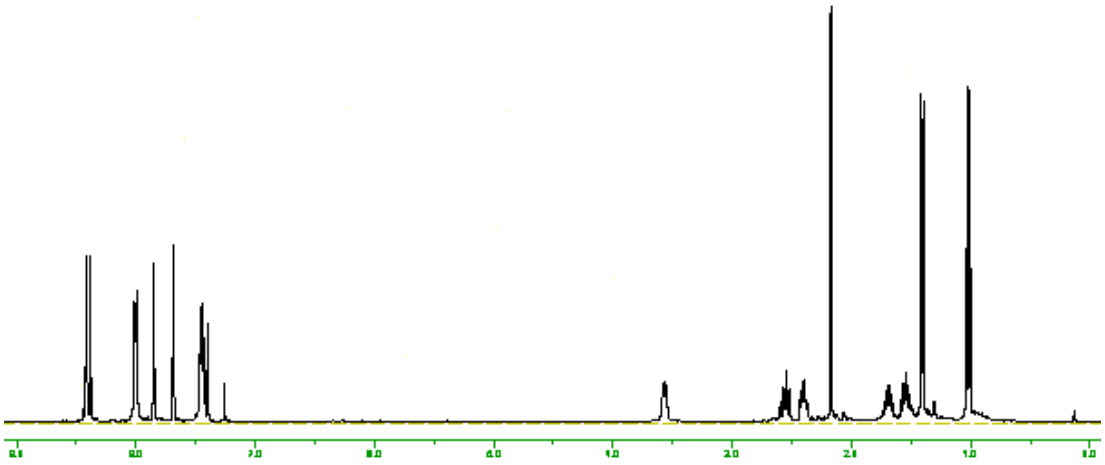
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



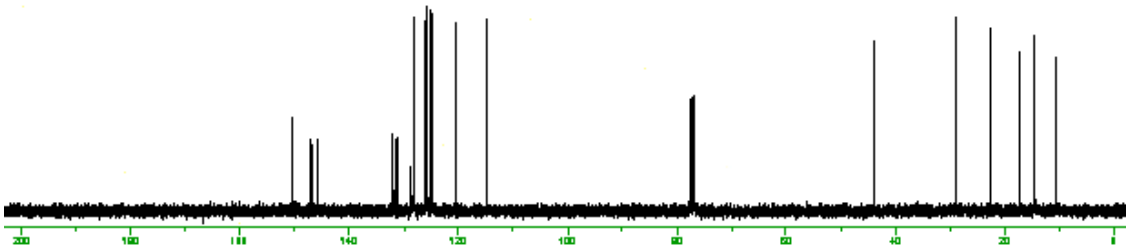


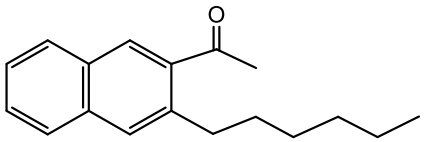
2m

^{1}H NMR (400 MHz, $CDCl_3$)



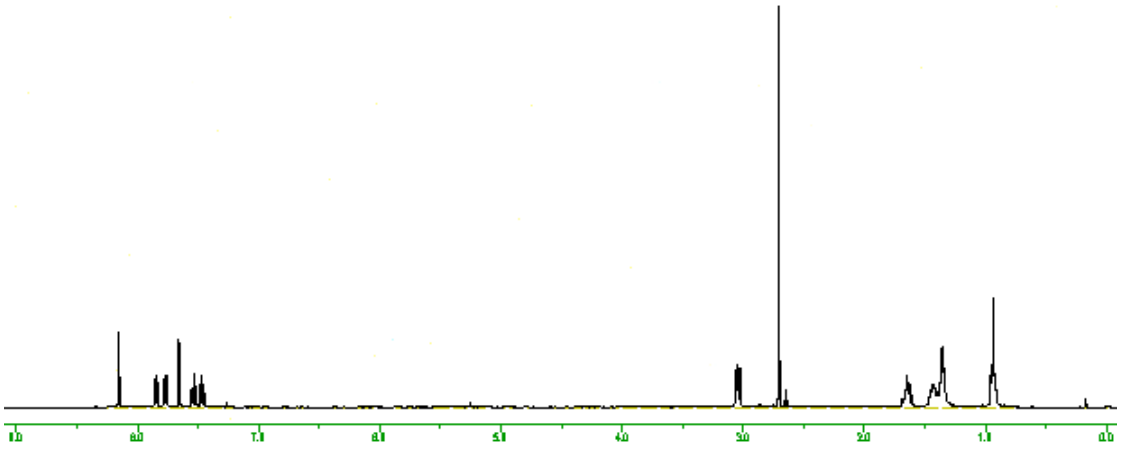
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



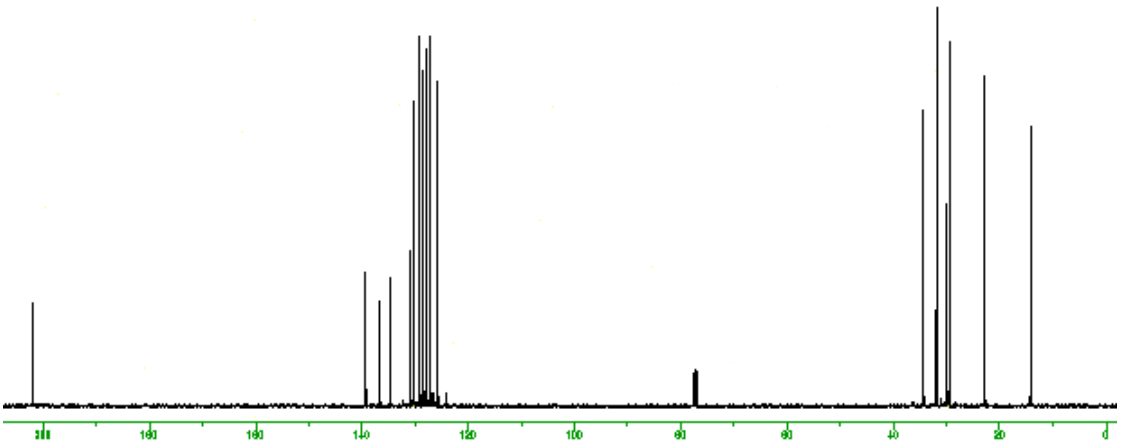


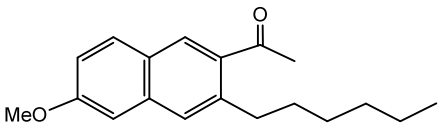
3g

^{1}H NMR (400 MHz, $CDCl_3$)



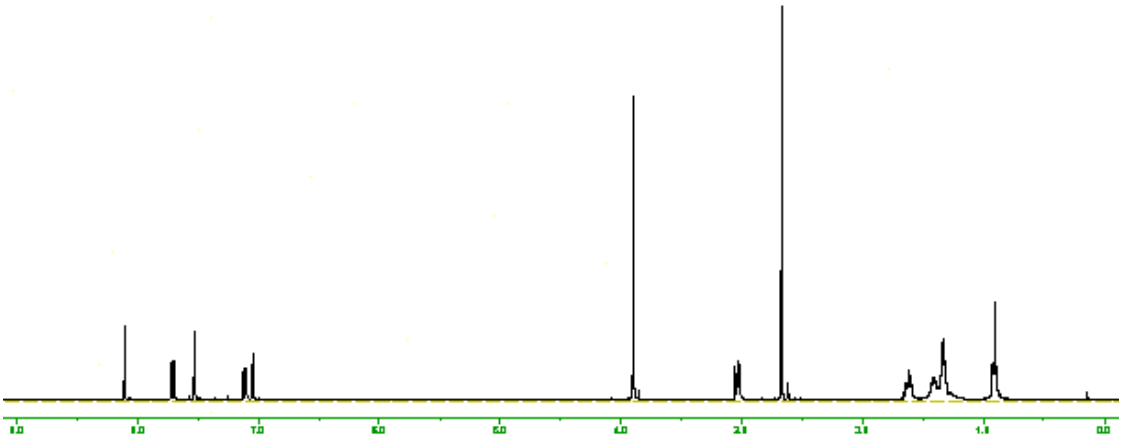
^{13}C{^{1}H }NMR (100 MHz, $CDCl_3$)



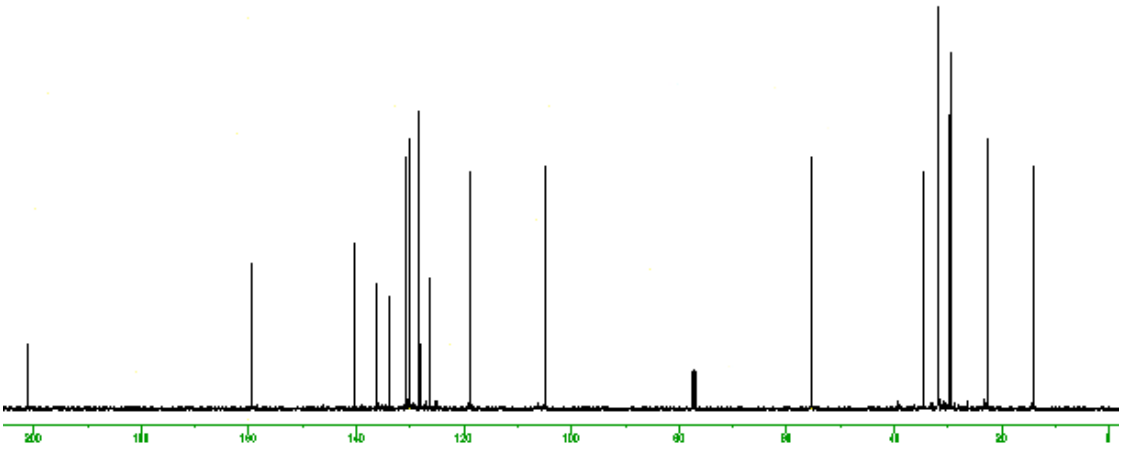


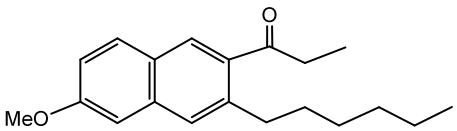
3i

^{1}H NMR (400 MHz, $CDCl_3$)



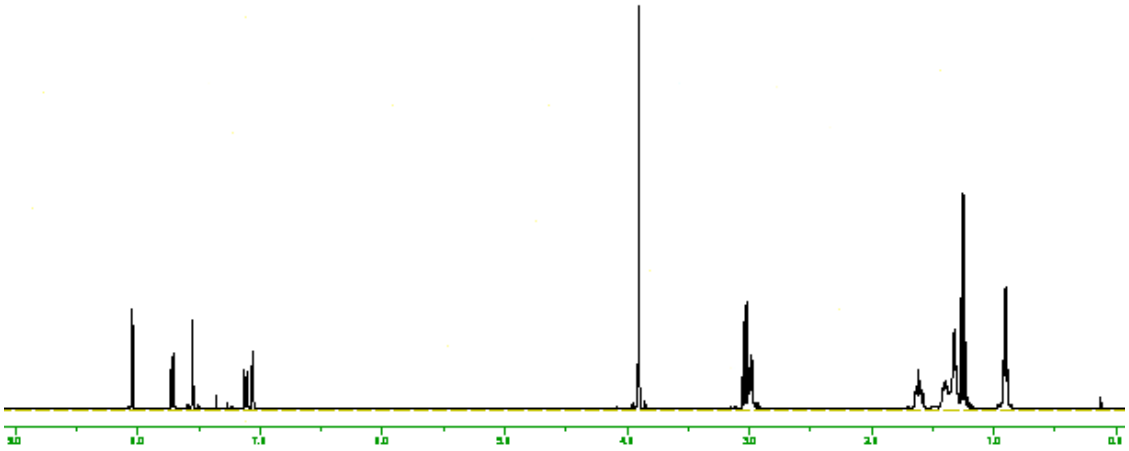
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



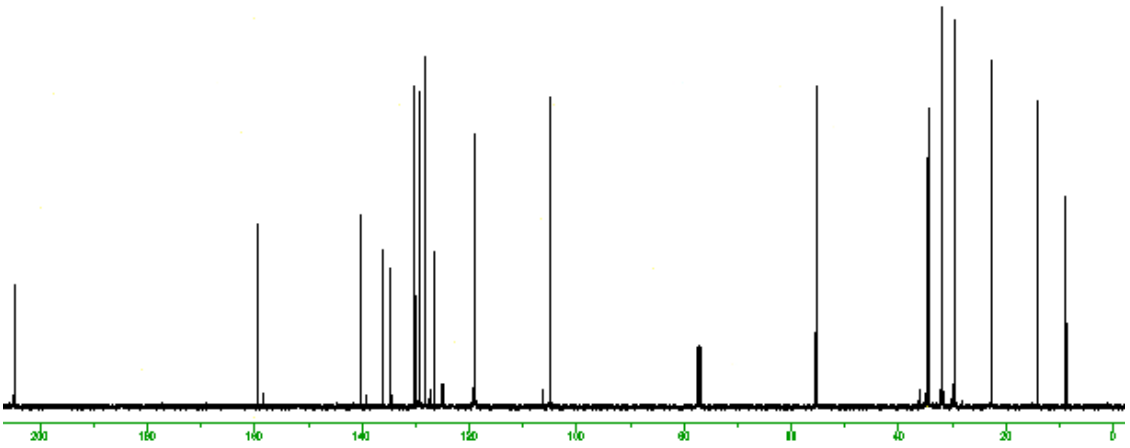


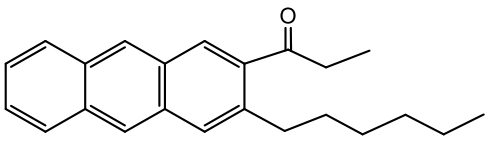
3l

^{1}H NMR (400 MHz, $CDCl_3$)



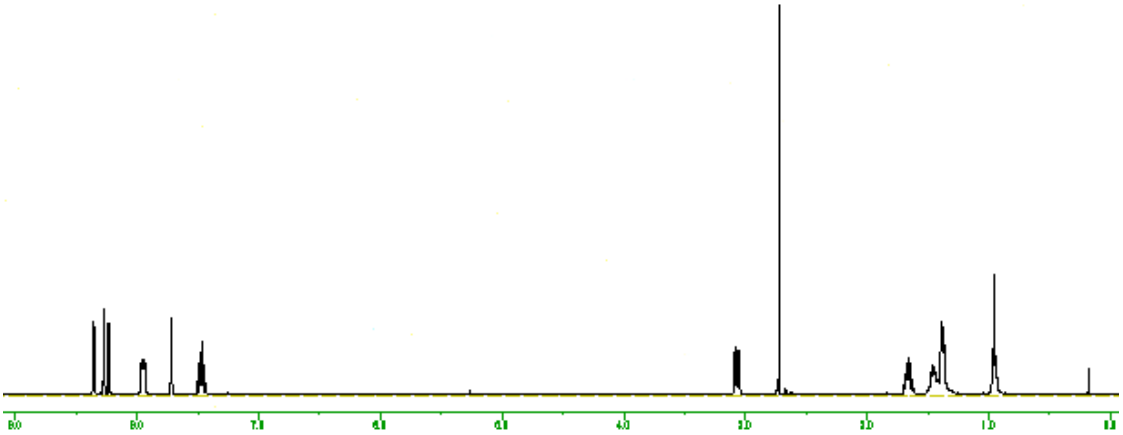
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



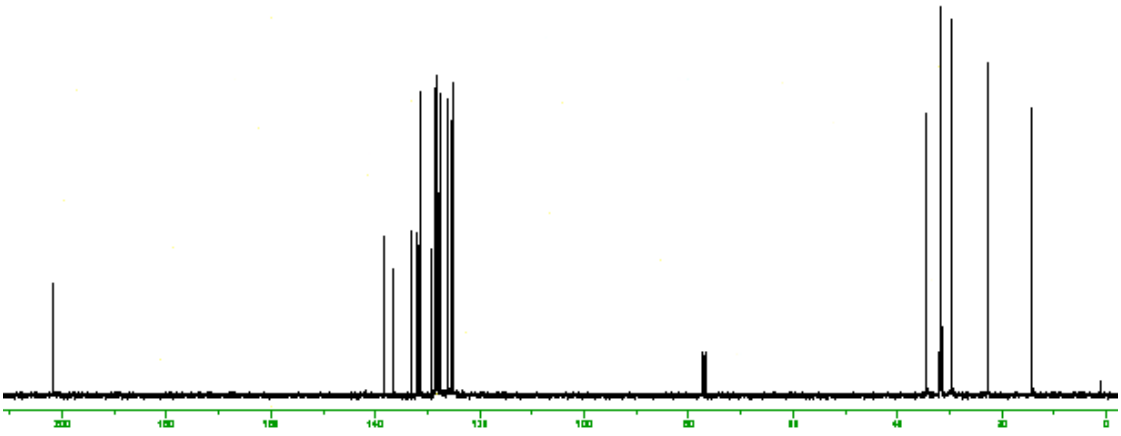


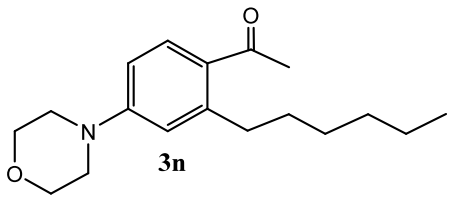
3m

^{1}H NMR (400 MHz, $CDCl_3$)



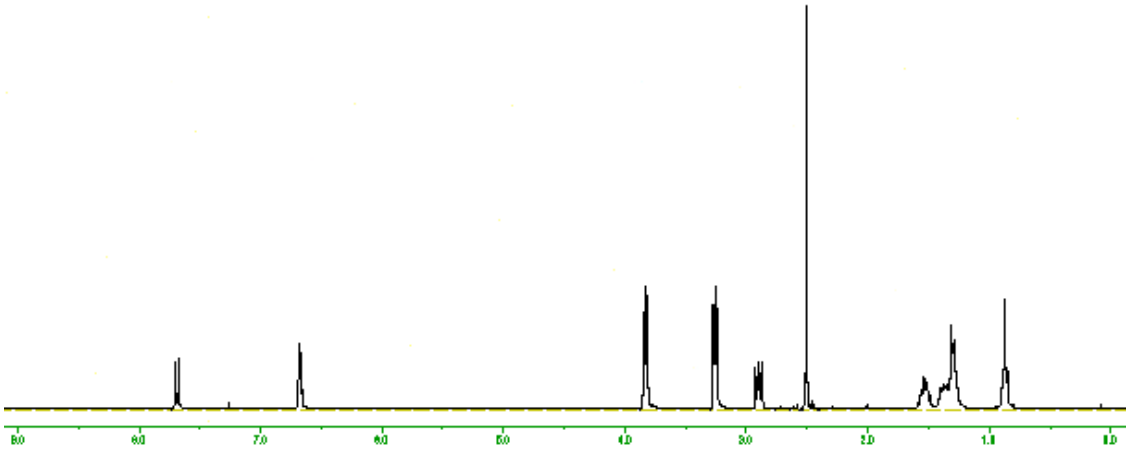
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)





3n

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)