Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Dirhodium(II)/P(*t*-Bu)$_3$ Catalyzed Tandem Reaction of α,β-Unsaturated Aldehyde with Arylboronic Acids

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Contents

1. General Experimental Details and Materials

All Reactions were performed under an atmosphere of nitrogen. All reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. Dichloromethane (DCE), 1,2-dimethoxyethane (DME), and toluene were distilled from CaH_2 prior to use. Cinnamaldehyde, (*E*)-but-2-enal, (*E*)-pent-2-enal, (*E*)-hex-2-enal, hexa-2,4-dienal (2*E*,4*E*/2*E*,4*Z* = 86/14) and hepta-2,4-dienal (2*E*,4*E*/2*E*,4*Z* = 91/9) were distilled under reduced pressure prior to use. (*E*)-3-(2-methoxyphenyl) acrylaldehyde, (*E*)-3-(2-chlorophenyl) acrylaldehyde, (*E*)-3-(2-nitrophenyl) acrylaldehyde, (*E*)-3-(4-methoxyphenyl) acrylaldehyde, (*E*)-3-(p-tolyl) acrylaldehyde, (*E*)-3-(4-bromophenyl) acrylaldehyde, (*E*)-3-(4-chlorophenyl) acrylaldehyde, (*E*)-3-(4-fluorophenyl) acrylaldehyde and (*E*)-3-(4-nitrophenyl) acrylaldehyde were purified by flash column chromatography prior to use. $Rh_2(OAc)_4$ and Tri-*tert*-butylphosphonium tetrifluoroborate were purchased from Admas-beta. $Rh_2(OAc)_2(P(t\text{-}Bu)_3)_2$, $Rh_2(OAc)_2(PCy_3)_2$ and $Rh_2(OAc)_2(PPh_3)_2$ were prepared according to the previous literature.[1,2]

Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize. ^1H NMR and ^{13}C NMR spectra were measured on 400 MHz Bruker spectrometer using $CDCl_3$ as the solvent at room temperature. The chemical shifts (δ) are reported in ppm

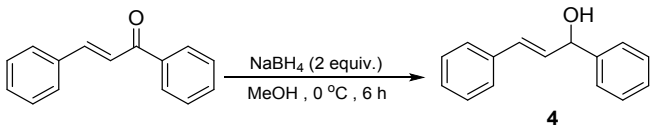
and coupling constants (*J*) in Hz. The following abbreviations were used to designate the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet.

X-Ray single-crystal diffraction data were collected on an Agilent Technologies Gemini plus single crystal diffraction and solved using SHELX program. UV/Vis spectra were measured on a Beijing Purkinje General Instrument TU-1901. The high-resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF Premier (ESI) instrument. Elemental analyses were performed with a Vario MICRO select instrument.

2. Experimental Procedures

2.1 Isotopic Labelling Experiments

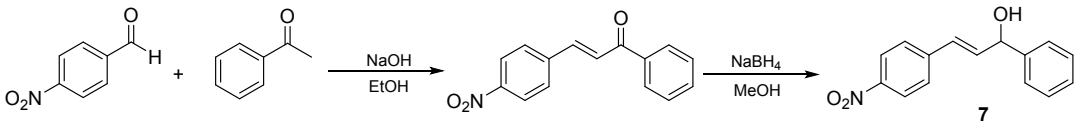
2.1.1 Preparation of Compound **4**[3]



4

To a cooled solution (0 °C) of (*E*)-1,3-diphenylprop-2-en-1-one (10.42 g, 50 mmol) in methanol (200 mL), the sodium borohydride (3.79 g, 100 mmol, 2 equiv) was added portion wise at 0 °C and stirred for about 6 h until (*E*)-1,3-diphenylprop-2-en-1-one was completely consumed. The reaction was quenched with water, and extracted with DCM. The combined extracts were washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo to afford **4** as white solid (9.58 g, 91%).

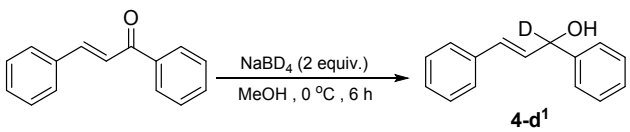
2.1.2 Preparation of Compound **7**[3,4,5]



7

1-Phenylethanone (792 mg, 6.6 mmol, 1.0 equiv), 4-nitrobenzaldehyde (1.0 g, 6.6 mmol, 1.0 equiv), and 3 mL ethanol were added in a round flask. An aqueous solution of 10% sodium hydroxide (3 mL) was added, the mixture was then stirred for 5 min. After completion of the reaction, the mixture was poured into ice and the resulting precipitate were filtered off. After recrystallization from ethanol, the pure (*E*)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one as yellow solid was obtained (1.4 g, 85%). To a cooled solution (0 °C) of (*E*)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (683.3 mg, 2.7 mmol) in methanol (7 mL), the sodium borohydride (204.3 mg, 5.4 mmol, 2 equiv.) was added portion wise and then stirred for 6 h until (*E*)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one was completely consumed. The reaction mixture was quenched with water, and extracted with DCM. The combined extracts were washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo to afford **7** as yellow solid (634.0 mg, 92%).

2.1.3 Preparation of Deuterated Substrate **4-d^1** [3,6]

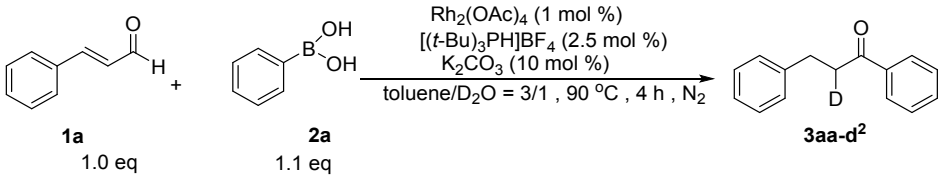


4-d^1

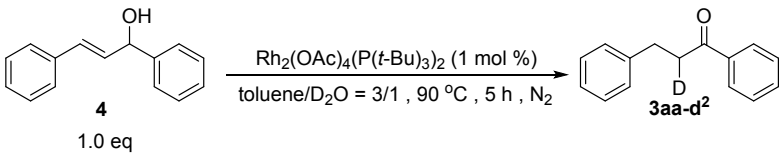
To a cooled solution (0 °C) of (*E*)-1,3-diphenylprop-2-en-1-one (520.9 mg, 2.5 mmol) in

methanol (10 mL), sodium borodeuteride (209.3 mg, 5.0 mmol, 2 equiv) was added portion wise at 0 °C and stirred for about 6 h until (*E*)-1,3-diphenylprop-2-en-1-one was completely consumed. The reaction was quenched with H_2O and extracted with DCM. The combined extracts were washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo to afford **4-d[1]** as white solid (496.8 mg, 94%).

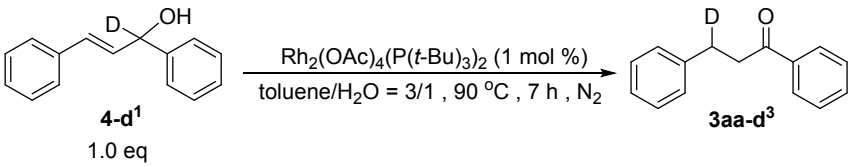
2.1.4 Deuterium Labeling Experiments[6]



The (*E*)-3-phenylprop-2-enal **(1a)** (0.50 mmol, 1.0 equiv), phenylboronic acid **(2a)** (0.55 mmol, 1.1 equiv), $Rh_2(OAc)_4$ (0.005 mmol, 1.0 mol %), $[(t\text{-}Bu)_3PH]BF_4$ (0.0125 mmol, 2.5 mol %), K_2CO_3 (0.05 mmol, 10.0 mol %) and toluene/D_2O (v/v = 3/1, 2 mL) were added in a sealed tube before freezing in a liquid nitrogen bath. The solution was then degassed using standard freeze-pump-thaw procedures. Afterward, the mixture was allowed to warm up to room temperature and then heated at 90 °C. After the reaction was complete (monitored by TLC), the reaction mixture was extracted with ethyl acetate (3 × 5 mL) and washed with water (2 × 10 mL). The ethyl acetate layer was separated and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash column chromatography (ethyl acetate/hexane) to give **3aa-d[2]** (96.7 mg, 92%).

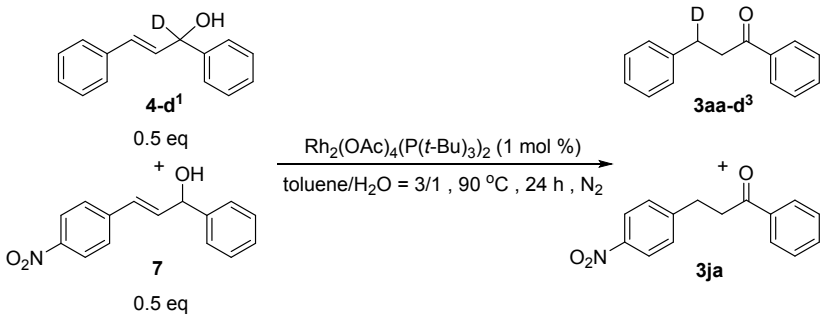


The (*E*)-1,3-diphenylprop-2-en-1-ol (**4**) (0.50 mmol, 1.0 equiv), $Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$ (0.005 mmol, 1.0 mol %) and toluene/D_2O (2 mL, 3/1 v/v) were added in a sealed tube. The solution was then degassed using standard freeze-pump-thaw procedures. Afterward, the mixture was allowed to warm up to room temperature and then heated at 90 °C. After the reaction was complete (monitored by TLC), the reaction mixture was extracted with ethyl acetate (3 × 5 mL) and washed with water (2 × 10 mL). The ethyl acetate layer was separated and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash column chromatography (ethyl acetate/hexane) to give **3aa-d²** (97.1 mg, 92%).



The substrate **4-d¹** (0.50 mmol, 1.0 equiv), $Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$ (0.005 mmol, 1.0 mol %), and toluene/H_2O (v/v =3/1, 2 mL) were added in a sealed tube. The solution was then degassed using standard freeze-pump-thaw procedures. Afterward, the mixture was allowed to warm up to room temperature and then heated at 90 °C. After the reaction was complete (monitored by TLC), the reaction mixture was extracted with ethyl acetate (3 × 5 mL) and washed with water (2 × 10 mL). The ethyl acetate layer was separated and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash

column chromatography (ethyl acetate/hexane) to give **3aa-d^3** (99.0 mg, 94%).



The substrate **4-d^1** (0.25 mmol, 1.0 equiv) and the substrate **7** (0.25 mmol, 1.0 equiv), $Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$ (0.005 mmol, 2.0 mol %), and toluene/H_2O (v/v =3/1, 2 mL) were added in a sealed tube. The solution was then degassed using standard freeze-pump-thaw procedures. Afterward, the mixture was allowed to warm up to room temperature and then heated at 90 °C. After the reaction was complete (monitored by TLC), the reaction mixture was extracted with ethyl acetate (3 × 5 mL) and washed with water (2 × 10 mL). The ethyl acetate layer was separated and dried over Na_2SO_4. After the evaporation of the solvent on a rotary evaporator, the residue was analyzed by ^{1}H NMR spectroscopy. The results of ^{1}H NMR indicated there was no transfer of deuterium between the two compounds.

2.2 Synthesis of $Rh_2(OAc)_4(PR_3)_2$

2.2.1 Synthesis of $Rh_2(OAc)_4(PCyPh_2)_2$

$Rh_2(OAc)_4$ (80 mg, 0.18 mol, 1.0 equiv) and $PCyPh_2$ (121 mg, 0.45 mol, 2.5 equiv) were placed in a Schlenk tube under a nitrogen atmosphere followed by the addition of DME (3 mL) and H_2O (3 mL). The reaction mixture was stirred at room temperature for 30 min. The orange complex was precipitated and separated by filtration. The solid was washed with DME/H_2O (v/v = 1/1) and dried under vacuum to give $Rh_2(OAc)_4(PCyPh_2)_2$ as an orange solid (158 mg, 90%). The single crystals of $Rh_2(OAc)_4(PCyPh_2)_2$ were grown by slow evaporation of the DCM.

$Rh_2(OAc)_4(PCyPh_2)_2$:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 8H), 7.35 (s, 12H), 2.86 (s, 2H), 2.16 (d, *J* = 11.5 Hz, 4H), 1.79-1.55 (m, 20H), 1.42-1.14 (m, 8H). Anal.Calcd for $Rh_2(OAc)_4(PCyPh_2)_2$ (M = 978.14 g/mol): C, 54.00; H, 5.56. Found: C, 53.79; H, 5.58.

2.2.2 Synthesis of $Rh_2(OAc)_4(PCy_2Ph)_2$

$Rh_2(OAc)_4$ (80 mg, 0.18 mol, 1.0equiv) and PCy_2Ph (123 mg, 0.45 mol, 2.5 equiv) were placed in a Schlenk tube under a nitrogen atmosphere followed by the addition of DME (3 mL) and H_2O (3 mL). The reaction mixture was stirred at room temperature for 30 min. The orange complex was precipitated and separated by filtration. The solid was washed with DME/H_2O (v/v = 1/1) and dried under vacuum to give $Rh_2(OAc)_4(PCy_2Ph)_2$ as an orange solid (157 mg, 88%). The single crystals of $Rh_2(OAc)_4(PCy_2Ph)_2$ were grown by

slow evaporation of the DCM.

$Rh_2(OAc)_4(PCy_2Ph)_2$:

^{1}H NMR (400 MHz, $CDCl_3$+ CD_3OD) δ 7.95 (d, *J* = 6.4 Hz, 4H), 7.42-7.35 (m, 6H),2.60 (s, 4H), 2.03-1.91 (m, 18H), 1.73-1.52 (m, 14H), 1.45-1.12 (m, 22H). Anal.Calcd for $Rh_2(OAc)_4(PCy_2Ph)_2$ (M = 990.23 g/mol): C, 53.34; H, 6.71. Found: C, 53.99; H, 6.89.

2.3 General Procedure for Dirhodium(II)-Catalyzed Arylation and Isomerization of α,β-unsaturated Aldehyde with Arylboronic Acid

2.3.1 General Procedure for Dirhodium(II)-Catalyzed Arylation and Isomerization of α,β-unsaturated Aromatic Aldehyde with Arylboronic Acid

The α,β-unsaturated aromatic aldehyde (0.50 mmol, 1.0 equiv), arylboronic acid (0.55 mmol, 1.1 equiv), $Rh_2(OAc)_4$ (0.005 mmol, 1.0 mol %), [(*t*-Bu)$_3$PH]BF_4 (0.0125 mmol, 2.5 mol %), K_2CO_3 (0.05 mmol, 10.0 mol %) and toluene/H_2O (2 mL, v/v = 3/1) or DME/H_2O (2 mL, v/v = 1/1) were added in a sealed tube before freezing in a liquid nitrogen bath. The solution was then degassed using standard freeze-pump-thaw procedures. Afterward, the mixture was allowed to warm up to room temperature and then heated at 90 °C. After the reaction was complete (as monitored by TLC), the reaction mixture was extracted with ethyl acetate (3 × 5 mL) and washed with water (2 × 10 mL). The ethyl acetate layer was

separated and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash column chromatography (ethyl acetate/hexane) to give the desired products.

2.3.2 General Procedure for Dirhodium(II)-Catalyzed Arylation and Isomerization of α,β-unsaturated Aliphatic Aldehyde with Arylboronic Acid

The α,β-unsaturated aliphatic aldehyde (1.00 mmol, 1.0 equiv), arylboronic acid (1.10 mmol, 1.1 equiv), $Rh_2(OAc)_4$ (0.010 mmol, 1.0 mol %), $[(t\text{-Bu})_3PH]BF_4$ (0.025 mmol, 2.5 mol %), K_2CO_3 (0.10 mmol, 10.0 mol %) and toluene/H_2O (4 mL, v/v = 3/1) or DME/H_2O (4 mL, v/v = 1/1) were added in a sealed tube before freezing in a liquid nitrogen bath. The solution was then degassed using standard freeze-pump-thaw procedures. Afterward, the mixture was allowed to warm up to room temperature and then heated at 90 °C. After the reaction was complete (as monitored by TLC), the reaction mixture was extracted with ethyl acetate (3 × 5 mL) and washed with water (2 × 10 mL). The ethyl acetate layer was separated and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash column chromatography (ethyl acetate/hexane) to give the desired products.

2.4 General Reaction for Investigation of the Profile of Tandem Reaction and the Isomerization of Allyl Alcohol 4

2.4.1 General Reaction for Investigation of the Profile of Tandem Reaction Catalyzed by $Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$ and $Rh_2(OAc)_4(PPh_3)_2$

The cinnamaldehyde **(1a)** (0.50 mmol, 1.0 equiv), phenylboronic acid **(2a)** (0.55 mmol, 1.1 equiv), $Rh_2(OAc)_4$ (0.005 mmol, 1.0 mol %), PR_3 (0.0125 mmol, 2.5 mol %), K_2CO_3 (0.05 mmol, 10.0 mol %) and toluene/H_2O (v/v = 3/1, 2 mL) were added in a sealed tube. Six parallel reactions were performed. The solution was then degassed using standard freeze-pump-thaw procedures. Afterward, the mixture was allowed to warm up to room temperature under N_2 and then heated at 90 °C for indicated time periods. The six reactions stopped at 10 min, 35 min, 60 min, 120 min, 180 min, and 240 min, respectively. The reaction mixture then was extracted with ethyl acetate (3 × 5 mL) and washed with water (2 × 10 mL). The ethyl acetate layer was separated and dried over Na_2SO_4. After evaporation of the solvent, the residue was analyzed by ^1H NMR spectroscopy for yield using 1,3,5-trimethyl-benzene (TMB) as the internal standard.

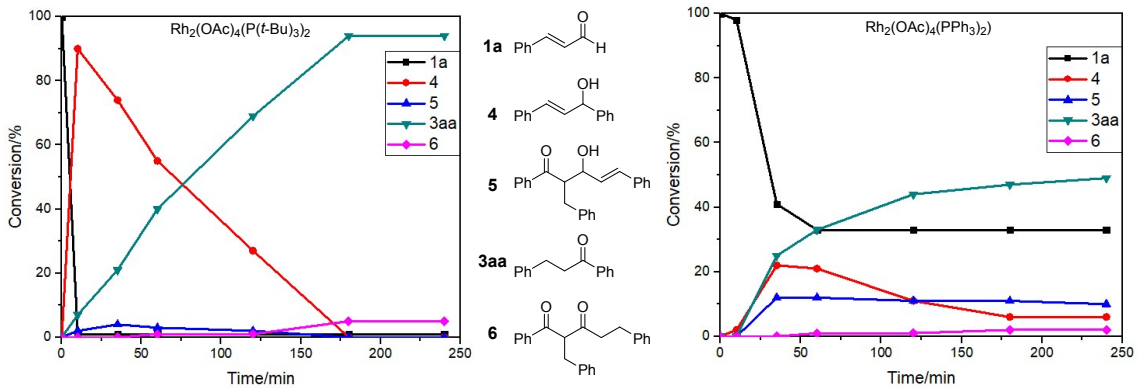


Figure S1. Reaction Profile of Tandem Reaction Catalyzed by $Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$ and $Rh_2(OAc)_4(PPh_3)_2$

2.4.2 General Reaction for investigation of the Profile of the Isomerization of Allyl Alcohol 4 Catalyzed by $Rh_2(OAc)(PR_3)_2$

The (*E*)-1,3-diphenylprop-2-en-1-ol (**4**) (0.50 mmol, 1.0 equiv), $Rh_2(OAc)_4{\cdot}(PR_3)_2$ (0.005 mmol, 1.0 mol %), and toluene/H_2O (2 mL, 3/1 v/v) were added in a sealed tube. Four parallel reactions were performed. The solution was then degassed using standard freeze-pump-thaw procedures. Afterward, the mixture was allowed to warm up to room temperature under N_2 and then heated at 90 °C for indicated time periods. The four reactions stopped at 60 min, 120 min, 180 min, and 240 min, respectively. The reaction mixture was then extracted with ethyl acetate (3 × 5 mL) and washed with water (2 × 10 mL). The ethyl acetate layer was separated and dried over Na_2SO_4. After evaporation of the solvent, the residue was analyzed by ^1H NMR spectroscopy for yield using 1,3,5-trimethyl-benzene (TMB) as the internal standard.

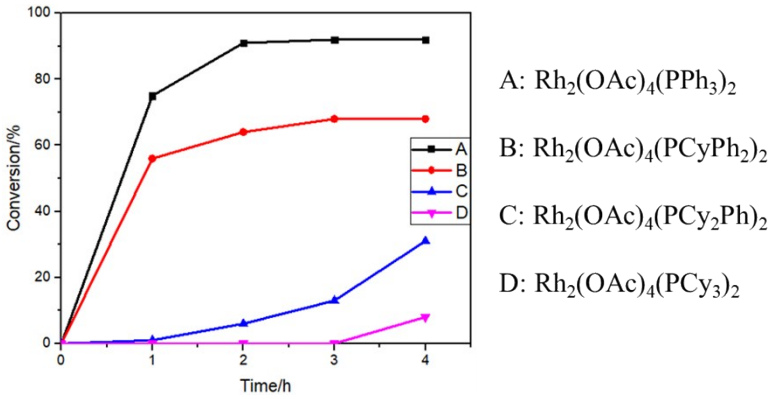
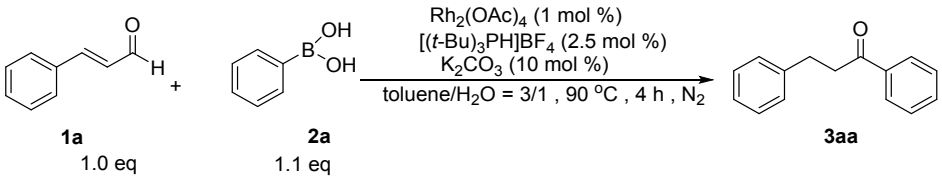


Figure S2. Reaction Profile of the Isomerization of Allyl Alcohol 4 Catalyzed by $Rh_2(OAc)(PR_3)_2$

2.5 Catalyst Recovery Experiment



The cinnamaldehyde **(1a)** (330.4 mg, 2.5 mmol, 1.0 equiv), phenylboronic acid **(2a)** (335.3 mg, 2.75 mmol, 1.1 equiv), $Rh_2(OAc)_4$ (11.1 mg, 0.025 mmol, 1.0 mol %), $[(t\text{-Bu})_3PH]BF_4$ (18.1 mg ,0.0625 mmol, 2.5 mol %), K_2CO_3 (34.6 mg, 0.25 mmol, 10.0 mol %) and toluene/H_2O (v/v = 3/1, 10 mL) were added in a sealed tube before freezing in a liquid nitrogen bath. The solution was then degassed using standard freeze-pump-thaw procedures. Afterward, the mixture was allowed to warm up to room temperature and then heated at 90 °C. After the reaction was complete (as monitored by TLC), the red-violet toluene layer and the light green water layer was separated. Then, 2.5 mL of DME was added to the mixture under the air. After that, the color of toluene layer immediately became green and the water layer still kept the light green. The 2.5 mL of H_2O was then added to the mixture, the resulting solution stirred at room temperature for 1 h under air. It was observed that the organic layer became yellow and the water layer became blue-green. The organic layer was separated and washed by 5.0 mL of H_2O. The combined

water layer was concentrated under vacuum to 4 mL and transferred to a Schlenk flask. To the concentrated water layer, the 25 mg of [(*t*-Bu)$_3$PH]BF$_4$, 24 mg of K_2CO_3 and 2 mL of DME were added subsequently. The resulting mixture was evacuated and purged three times with N_2 and the mixture was then stirred at room temperature. After 20 min, the red precipitate of $Rh_2(OAc)_4(P(t\text{-}Bu)_3)_2$ was produced. The precipitate was filtered, washed with DME/H_2O (v/v = 1/1) and dried under vacuum to give a red-violet solid. Recovery rate: 9.6 mg (45%).

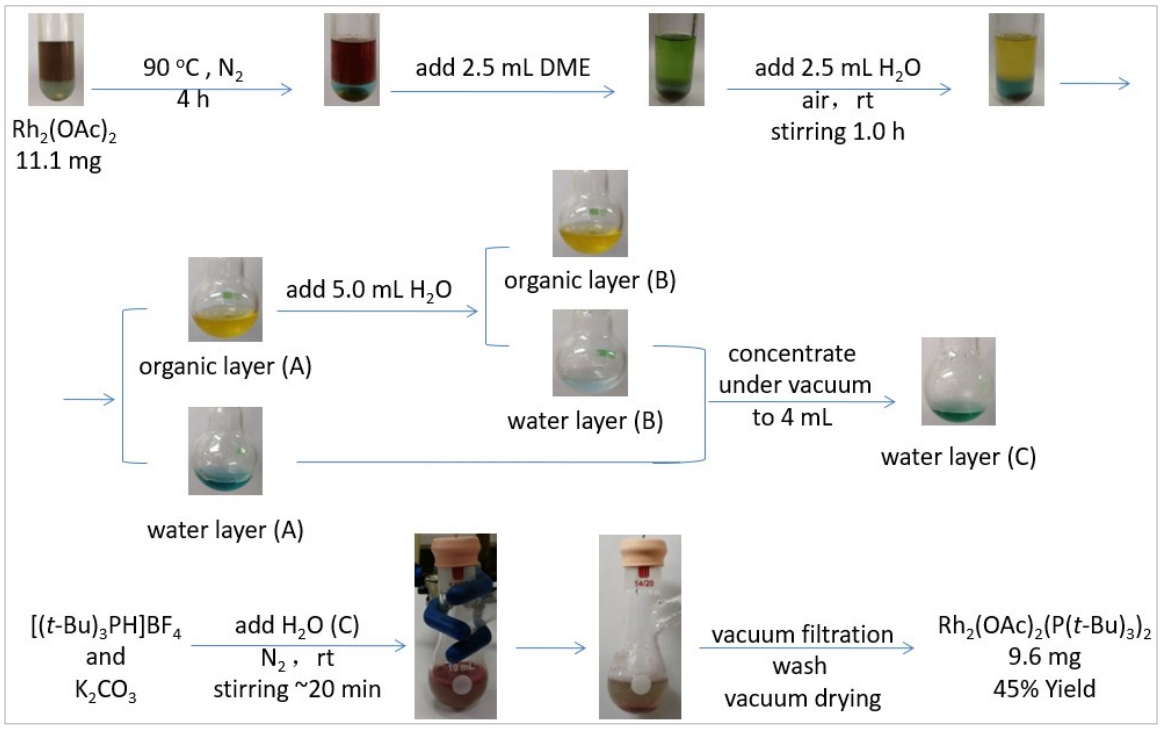
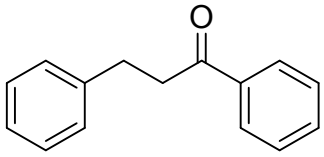


Figure S3. Experimental process of Catalyst recovery

3. Experimental Characterization Data for Products

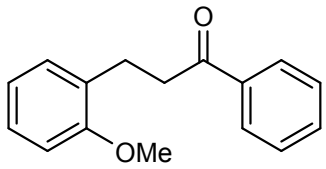
1,3-diphenylpropan-1-one (3aa)[7]:



Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1)

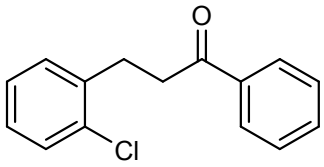
afforded 93 mg (88%); white solid. R_f = 0.70 (*n*-hexane/EtOAc = 10/1),^{1}H NMR (400 MHz, $CDCl_3$) δ7.96-7.94 (m, 2H), 7.56-7.52(m, 1H), 7.46-7.42 (m, 2H),7.31-7.18(m, 5H), 3.29 (t, *J* = 7.7 Hz, 2H), 3.08-3.05 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.4, 141.4, 137.0, 133.2, 128.7, 128.7, 128.6, 128.2, 126.3, 40.6, 30.3.

3-(2-methoxyphenyl)-1-phenylpropan-1-one (3ba)[8]:



Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 80/1) afforded 105 mg (87%); yellow oil. R_f = 0.65 (*n*-hexane/EtOAc = 10/1),^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.99 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.44(m, 2H), 7.24-7.21 (m, 2H), 6.93-6.87 (m, 2H), 3.84 (s, 3H), 3.30-3.27 (m, 2H), 3.09-3.05 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.1, 157.6, 137.0, 133.0, 130.2, 129.6, 128.6, 128.2, 127.6, 120.6, 110.3, 55.3, 39.0, 25.8.

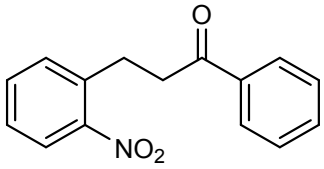
3-(2-chlorophenyl)-1-phenylpropan-1-one (3ca)[9]:



Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 104 mg (85%); white solid. R_f = 0.70 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400

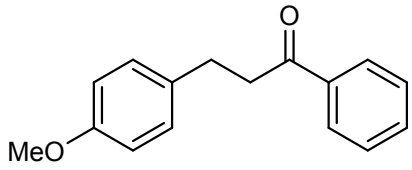
MHz, $CDCl_3$) δ 7.99-7.96 (m, 2H), 7.58-7.54 (m, 1H), 7.47-7.44 (m, 2H), 7.37-7.30 (m, 2H), 7.22-7.14 (m, 2H), 3.34-3.30 (m, 2H), 3.20-3.16 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.1, 139.0, 136.9, 134.1, 133.2, 130.9, 129.7, 128.7, 128.2, 127.9, 127.1, 38.6, 28.5.

3-(2-nitrophenyl)-1-phenylpropan-1-one (3da)[10]:



Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 70/1) afforded 107 mg (84%); light orange solid. R_f = 0.60 (*n*-hexane/EtOAc = 10/1), ^1H NMR (400 MHz, $CDCl_3$) δ 7.97-7.93(m, 3H), 7.57-7.51 (m, 2H), 7.48-7.43 (m, 3H), 7.39-7.35 (m, 1H), 3.42-3.38 (m, 2H), 3.35-3.31(m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.7, 149.4, 136.7, 136.7, 133.4, 132.8, 128.8, 128.2, 127.6, 125.0, 39.6, 27.9.

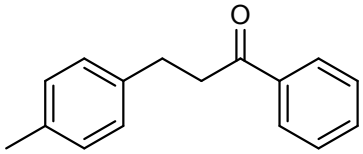
3-(4-methoxyphenyl)-1-phenylpropan-1-one (3ea)[7]:



Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 70/1) afforded 102 mg (85%); white solid. R_f = 0.55 (*n*-hexane/EtOAc = 10/1), ^1H NMR (400 MHz, $CDCl_3$) δ 7.98-7.95 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.43 (m, 2H), 7.20-7.16 (m,

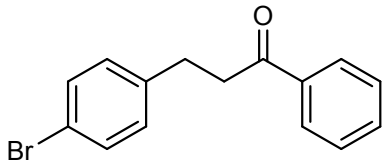
2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.28 (t, *J* = 7.7 Hz, 2H), 3.02 (t, *J* = 7.7 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ199.5, 158.1, 137.0, 133.4, 133.1, 129.5, 128.7, 128.12, 114.1, 55.4, 40.8, 29.4.

1-phenyl-3-(4-methylphenyl)propan-1-one (3fa)[8]:



Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 100 mg (89%); white solid. R_f = 0.70 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.97 (m, 2H), 7.59-7.58 (m, 1H), 7.49-7.45 (m, 2H), 7.18-7.12 (m, 4H), 3.32-3.28 (m, 2H), 3.07-3.03 (m, 2H), 2.34 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 199.4, 138.3, 137.0, 135.7, 133.1, 129.3, 128.7, 128.4, 128.1, 40.7, 29.8, 21.1.

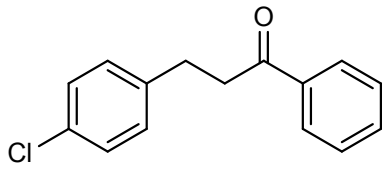
3-(4-bromophenyl)-1-phenylpropan-1-one (3ga)[11]:



Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 127 mg (88%); white solid. R_f = 0.68 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.94 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48-7.40 (m, 4H), 7.13 (d, *J* = 8.3 Hz, 2H), 3.28 (t, *J* = 7.5 Hz, 2H), 3.03 (t, *J* = 7.5 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100

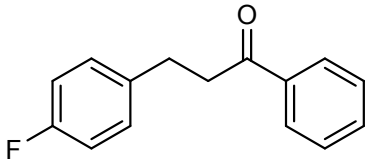
MHz, $CDCl_3$) δ 198.9, 140.4, 136.9, 133.3, 131.7, 130.4, 128.8, 128.1, 120.0, 40.2, 29.6.

3-(4-chlorophenyl)-1-phenylpropan-1-one (3ha)[7]:



Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 103 mg (84%); white solid. R_f = 0.68 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.93 (m, 2H), 7.58-7.54 (m, 1H), 7.47-7.43 (m, 2H), 7.27-7.24 (m, 2H), 7.20-7.16 (m, 2H), 3.28 (t, *J* = 7.5 Hz, 2H), 3.04 (t, *J* = 7.5 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.0, 139.9, 136.9, 133.3, 132.0, 130.0, 128.8, 128.7, 128.1, 40.3, 29.5.

3-(4-fluorophenyl)-1-phenylpropan-1-one (3ia) [7,12]:

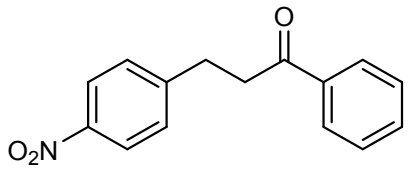


Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 70/1) afforded 94 mg (82%); light yellow solid. R_f = 0.65 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.23-7.19 (m, 2H), 7.01-6.95(m, 2H), 3.29 (t, *J* = 7.6 Hz, 2H), 3.05 (t, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ199.2, 161.5 (d, *J* = 243.9 Hz), 137.0 (d, *J* = 3.2

Hz), 136.9, 133.3, 129.9 (d, J =7.8 Hz), 128.8, 128.1, 115.4 (d, J = 21.2 Hz), 40.5, 29.4.

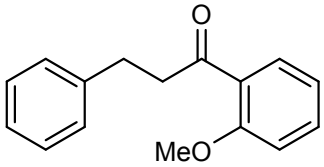
^{19}F NMR (376 MHz, $CDCl_3$) δ -117.27.

3-(4-nitrophenyl)-1-phenylpropan-1-one (3ja)[13]:



Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 30/1) afforded 102 mg (80%); yellow solid. R_f = 0.45 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.7 Hz, 2H), 7.96-7.94 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.48-7.41 (m, 4H), 3.36 (t, J = 7.4 Hz, 2H), 3.19 (t, J = 7.3 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.3, 149.3, 146.6, 136.6, 133.5, 129.5, 128.9, 128.1, 123.9, 39.5, 29.9.

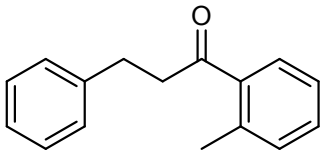
1-(2-methoxyphenyl)-3-phenylpropan-1-one (3ab)[14]:



Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 103 mg (86%); white solid. R_f = 0.70 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.67 (m, 1H), 7.47-7.42 (m, 1H), 7.30-7.17 (m, 5H),7.01-6.94 (m, 2H), 3.87 (s, 3H), 3.32-3.28 (m, 2H), 3.04-3.00 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.9, 158.7, 141.8, 133.5, 130.5, 128.6, 128.5, 128.4, 126.0, 120.8, 111.6, 55.6,

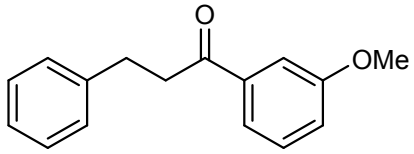
45.5, 30.6.

3-phenyl-1-(2-methylphenyl)propan-1-one (3ac)[7]:



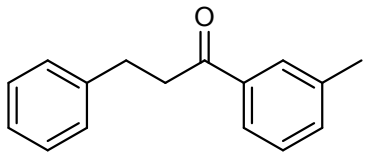
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 100 mg (89%); colorless liquid. R_f = 0.73 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ7.62-7.60 (m, 1H), 7.39-7.20 (m, 8H), 3.24 (t, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H), 2.49 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 203.5, 141.3, 138.2, 138.0, 132.1, 131.4, 128.6, 128.5, 128.5, 126.2, 125.8, 43.3, 30.4, 21.4.

1-(3-methoxyphenyl)-3-phenylpropan-1-one (3ad)[14]:



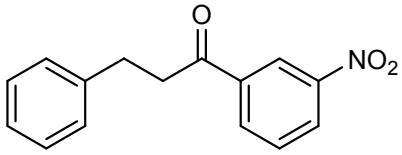
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 80/1) afforded 99 mg (82%); white solid. R_f = 0.65 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.52 (m, 1H), 7.49-7.48 (m, 1H), 7.37-7.18 (m, 6H), 7.11-7.08 (m, 1H), 3.84 (s, 3H), 3.29 (t, *J* = 7.6 Hz, 2H), 3.08-3.04 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.2, 160.0, 141.4, 138.4, 129.7, 128.7, 128.6, 126.3, 120.8, 119.7, 112.4, 55.6, 40.7, 30.3.

3-phenyl-1-(3-methylphenyl)propan-1-one (3ae) [14]:



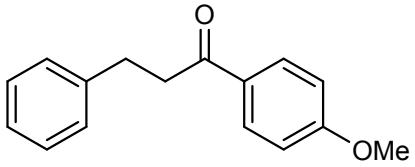
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 98 mg (87%); light yellow liquid. R_f = 0.71 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.73 (m, 2H), 7.36-7.17 (m, 7H), 3.29-3.25 (m, 2H), 3.05 (t, *J* = 7.7 Hz, 2H), 2.38 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.5, 141.4, 138.4, 137.0, 133.9, 128.7, 128.6, 128.6, 128.5, 126.2, 125.3, 40.6, 30.2, 21.4.

1-(3-nitrophenyl)-3-phenylpropan-1-one (3af)[15]:



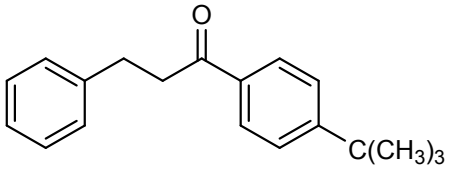
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 50/1) afforded 73 mg (65%); white solid. R_f = 0.50 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (t, *J* = 1.9 Hz, 1H), 8.41-8.38 (m, 1H), 8.28-8.26 (m, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.33-7.19 (m, 5H), 3.36 (t, *J* = 7.5 Hz, 2H), 3.10 (t, *J* = 7.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.1, 148.5, 140.7, 138.1, 133.7, 130.0, 128.8, 128.6, 127.5, 126.5, 123.1, 40.8, 29.9.

1-(4-methoxyphenyl)-3-phenylpropan-1-one (3ag)[7]:



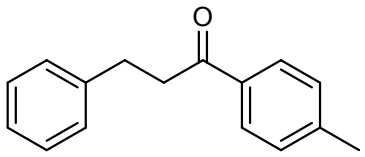
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 50/1) afforded 102 mg (85%); light yellow solid. R_f = 0.50 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.9 Hz, 2H), 7.32-7.18 (m, 5H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 3.25 (t, *J* = 7.6 Hz, 2H), 3.07 - 3.03 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.9, 163.5, 141.5, 130.3, 130.0, 128.5, 128.4, 126.1, 113.7, 55.5, 40.1, 30.3.

1-(4-(*tert*-butyl)phenyl)-3-phenylpropan-1-one (3ah)[16]:



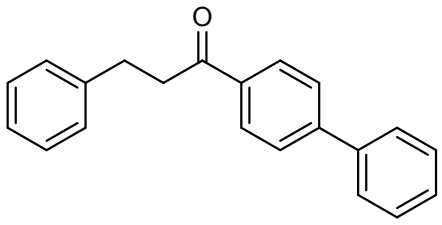
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 120/1) afforded 115 mg (86%); white solid. R_f = 0.80 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.31-7.18 (m, 5H), 3.28 (t, *J* = 7.7 Hz, 2H), 3.08-3.04 (m, 2H), 1.33 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.0, 156.9, 141.5, 134.4, 128.6, 128.5, 128.1, 126.2, 125.7, 40.5, 35.2, 31.2, 30.3.

3-phenyl-1-(4-methylphenyl)propan-1-one (3ai)[7]:



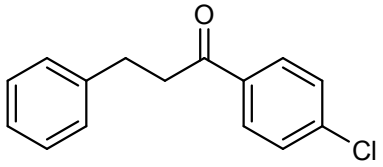
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 94 mg (84%); white solid. R_f = 0.70 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.32-7.18(m, 7H), 3.27 (t, *J* = 7.8 Hz, 2H), 3.08-3.04 (m, 2H), 2.40 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.0, 143.9, 141.5, 134.5, 129.4, 128.6, 128.5, 128.3, 126.2, 40.5, 30.3, 21.7.

1-([1,1'-biphenyl]-4-yl)-3-phenylpropan-1-one (3aj)[16]:



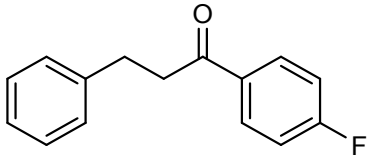
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 120 mg (84%); white solid. R_f = 0.70 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.63-7.60 (m, 2H), 7.48-7.44 (m, 2H), 7.41-7.37 (m, 1H), 7.32-7.19 (m, 5H), 3.35-3.31 (m, 2H), 3.11-3.07 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.0, 145.9, 141.4, 140.0, 135.6, 129.1, 128.8, 128.7, 128.6, 128.4, 127.4, 127.4, 126.3, 40.6, 30.3.

1-(4-chlorophenyl)-3-phenylpropan-1-one (3ak)[7]:



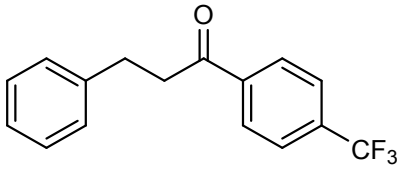
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 109 mg (89%); white solid. R_f = 0.70 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.24-7.11 (m, 5H), 3.19 (t, *J* = 7.5 Hz, 2H), 3.00-2.96 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.1, 141.2, 139.3, 135.3, 129.6, 129.0, 128.7, 128.5, 126.3, 40.5, 30.2.

1-(4-fluorophenyl)-3-phenylpropan-1-one (3al)[7,13]:



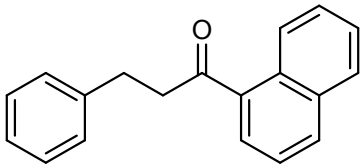
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 99 mg (87%); colorless liquid. R_f = 0.70 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.95 (m, 2H), 7.32-7.19 (m, 5H), 7.14-7.08 (m, 2H), 3.27 (t, *J* = 7.6 Hz, 2H), 3.08-3.04 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.7, 165.8 (d, J_{CF} = 254.6 Hz), 141.2, 133.4 (d, J_{CF} = 3.0 Hz), 130.8 (d, J_{CF} = 9.3 Hz), 128.7, 128.5, 126.3, 115.8 (d, J_{CF} = 21.8 Hz), 40.5, 30.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.30.

3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (3am)[7]:



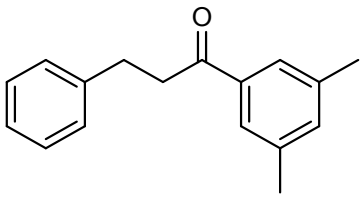
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 118 mg (85%); yellow solid. R_f = 0.70 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.32 - 7.20 (m, 5H), 3.32 (t, *J* = 7.6 Hz, 2H), 3.08 (t, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.3, 141.0, 139.6, 134.5 (q, *J* = 32.7 Hz), 128.7, 128.5, 128.5, 126.4, 125.8 (q, *J* = 3.7 Hz), 122.4, 40.9, 30.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.10.

1-(naphthalen-1-yl)-3-phenylpropan-1-one (3an)[17]:



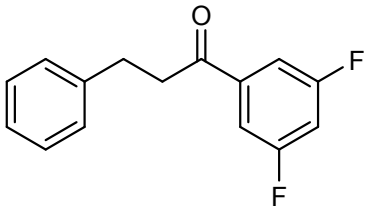
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 113 mg (87%); light yellow liquid. R_f = 0.68 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.87-7.85 (m, 1H), 7.81-7.79 (m,1H), 7.59-7.50 (m, 2H), 7.47-7.43 (m, 1H), 7.31-7.18 (m, 5H), 3.37 (t, *J* = 7.6 Hz, 2H), 3.13 (t, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 203.7, 141.2, 136.1, 134.1, 132.7, 130.2, 128.7, 128.6, 128.5, 128.0, 127.5, 126.6, 126.3, 125.9, 124.5, 43.9, 30.7.

1-(3,5-dimethylphenyl)-3-phenylpropan-1-one (3ao):



Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 104 mg (87%); light yellow liquid. R_f = 0.75 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 2H), 7.32-7.19 (m, 6H), 3.29-3.25 (m, 2H), 3.05 (t, *J* = 7.7 Hz, 2H), 2.36 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.7, 141.5, 138.3, 137.1, 134.8, 128.6, 128.6, 126.2, 126.0, 40.7, 30.3, 21.4. HRMS (ESI, m/z) calcd for $C_{17}H_{18}O$ $[M+H]^+$: 239.1430, found: 239.1442

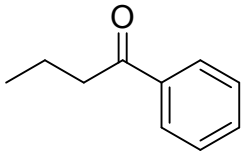
1-(3,5-difluorophenyl)-3-phenylpropan-1-one (3ap):



Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 83 mg (67%); light yellow liquid. R_f = 0.75 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.42 (m, 2H), 7.33-7.27 (m, 2H), 7.24-7.19 (m, 3H), 7.02-6.97 (m, 1H), 3.24 (t, *J* = 7.5 Hz, 2H), 3.05 (t, *J* = 7.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.7, 164.4 (d, *J* = 11.7 Hz), 161.9 (d, *J* = 11.7 Hz), 140.8, 139.8 (t, *J* = 7.4 Hz), 128.6 (d, *J* = 22.0 Hz), 126.5, 111.2, 111.2, 111.0, 110.0, 108.5 (t, *J* = 25.4 Hz) 40.7, 30.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.00. HRMS (ESI, m/z) calcd for $C_{15}H_{12}F_2O$ $[M+H]^+$:

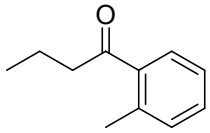
247.0929, found: 247.0942

1-phenylbutan-1-one (3ka)[18]:



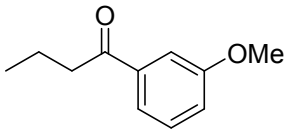
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 150/1) afforded 86 mg (58%); light yellow liquid. R_f = 0.75 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.94(m, 2H), 7.56-7.52 (m, 1H), 7.47-7.43 (m, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 1.81-1.72 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.5, 137.2, 133.0, 128.6, 128.1, 40.6, 17.9, 14.0.

1-(2-methylphenyl)butan-1-one (3kc):



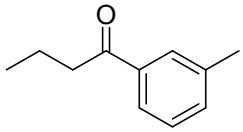
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 150/1) afforded 93 mg (57%); light yellow liquid. R_f = 0.75 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 1H), 7.37-7.33 (m, 1H), 7.27-7.23 (m, 2H), 2.87 (t, *J* = 7.3 Hz, 2H), 2.49 (s, 3H), 1.78-1.69 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 205.0, 138.5, 137.9, 132.0, 131.1, 128.4, 125.7, 43.7, 21.2, 18.0, 14.0. HRMS (ESI, m/z) calcd for $C_{11}H_{14}O$ $[M+H]^+$: 163.1117, found: 163.1132

1-(3-methoxyphenyl)butan-1-one (3kd)[19]:



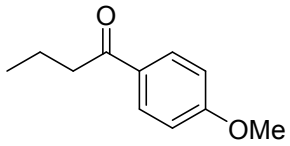
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 80/1) afforded 89 mg (50%); white solid. R_f = 0.65 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.52 (m, 1H), 7.49-7.48 (m, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.11-7.08 (m, 1H), 3.85 (s, 3H), 2.93 (t, *J* = 7.3 Hz, 2H), 1.81-1.72 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.4, 160.0, 138.6, 129.6, 120.8, 119.4, 112.5, 55.5, 40.8, 18.0, 14.0.

1-(3-methylphenyl)butan-1-one (3ke)[20]:



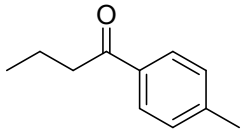
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 150/1) afforded 75 mg (46%); light yellow liquid. R_f = 0.75 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.74 (m, 2H), 7.37-7.32 (m, 2H), 2.93 (t, *J* = 7.3 Hz, 2H), 2.41 (s, 3H), 1.81-1.72 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.8, 138.4, 137.3, 133.7, 128.7, 128.5, 125.4, 40.7, 21.5, 17.9, 14.0.

1-(4-methoxyphenyl)butan-1-one (3kg)[20]:



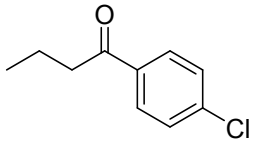
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 50/1) afforded 102 mg (57%); light yellow solid. R_f = 0.55 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 2.88 (t, *J* = 7.3 Hz, 2H), 1.79-1.70 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.2, 163.4, 130.4, 130.3, 113.7, 55.5, 40.3, 18.1, 14.0.

1-(4-methylphenyl)butan-1-one (3ki)[20]:



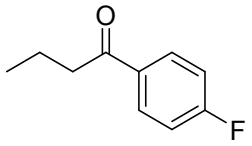
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 91 mg (56%); light yellow liquid. R_f = 0.72 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.40 (s, 3H), 1.81-1.71 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.2, 143.7, 134.7, 129.3, 128.3, 40.5, 21.7, 18.0, 14.0.

1-(4-chlorophenyl)butan-1-one (3kk)[20]:



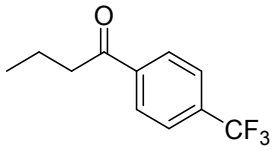
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 150/1) afforded 75 mg (41%); light yellow liquid. R_f = 0.75 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 2.91 (t, *J* = 7.3 Hz, 2H), 1.80-1.71 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.3, 139.4, 135.5, 129.6, 129.0, 40.6, 17.8, 14.0.

1-(4-fluorophenyl)butan-1-one (3kl):



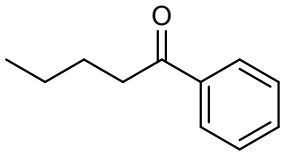
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 63 mg (38%); white solid. R_f = 0.70 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.96 (m, 2H), 7.14-7.09 (m, 2H), 2.91 (t, *J* = 7.3 Hz, 2H), 1.80-1.71 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.9, 165.7 (d, *J* = 254.3 Hz), 133.6 (d, *J* = 3.0 Hz), 130.8 (d, *J* = 9,2 Hz), 115.7 (d, *J* = 21.8 Hz), 40.5, 17.9, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.77. HRMS (ESI, m/z) calcd for $C_{10}H_{11}FO$ $[M+H]^+$: 167.0867, found: 167.0866

1-(4-(trifluoromethyl)phenyl)butan-1-one (3km)[21,22]:



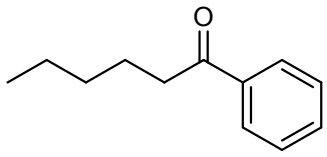
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 150/1) afforded 65 mg (30%); colorless liquid. R_f = 0.75 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 1.83-1.74 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.5, 139.8, 134.3(q, *J* = 32.7Hz), 128.5, 125.8(q, *J* = 3.7Hz), 122.4, 40.9, 17.7, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.09.

1-phenylpentan-1-one (3la)[23]:



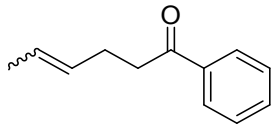
Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 100/1) afforded 88 mg (54%); colorless liquid. R_f = 0.70 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.94 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 1.76-1.68 (m, 2H), 1.46-1.36 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.6, 137.1, 132.9, 128.6, 128.1, 38.3, 26.5, 22.5, 14.0.

1-phenylhexan-1-one (3ma)[24]:



Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 150/1) afforded 108 mg (61%); light yellow liquid. R_f = 0.80 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.94 (m, 2H), 7.56-7.52 (m, 1H), 7.47-7.43 (m, 2H), 2.97-2.94 (m, 2H), 1.75-1.72 (m, 2H), 1.38-1.34 (m, 4H), 0.932-0.89 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.6, 137.1, 132.9, 128.6, 128.1, 38.6, 31.6, 24.1, 22.5, 14.0.

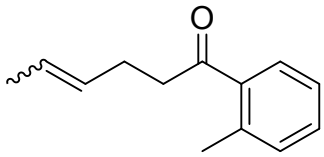
1-phenylhex-4-en-1-one (3na)[6]:



E/Z=78/22

Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 150/1) afforded 113 mg (65%); light yellow liquid. R_f = 0.75 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), 7.58-7.53 (m, 1H), 7.48-7.44 (m, 2H), 5.56-5.43 (m, 2H), 3.05-3.01 (m,2H), 2.52-2.46 (m, 0.45H), 2.45-2.39 (m,1.59H), 1.66-1.62 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.9, 137.1, 133.0, 129.9, 129.0, 128.6, 128.1, 126.0, 125.2, 38.6, 38.5, 27.3, 21.8, 18.0, 12.8.

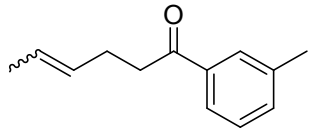
1-(2-methylphenyl)hex-4-en-1-one (3nc):



E/*Z* = 82/18

Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 150/1) afforded 132 mg (70%); light yellow liquid. R_f = 0.80 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.60 (m, 1H), 7.37-7.33 (m, 1H), 7.24 (t, *J* = 7.4 Hz, 2H), 5.53-5.42 (m, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.49-2.48 (m, 3H), 2.46-2.42 (m.0.37H), 2.41-2.36 (m, 1.63H), 1.64-1.61 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 204.2, 138.2, 138.0, 132.0, 131.2, 131.2, 129.7, 128.9, 128.5, 128.4, 126.0, 125.7, 125.2, 41.5, 41.4, 27.5, 22.0, 21.3, 18.0, 12.8. HRMS (ESI, m/z) calcd for $C_{13}H_{16}O$ [M+H]$^+$: 189.1274, found: 189.1279

1-(3-methylphenyl)hex-4-en-1-one (3ne):

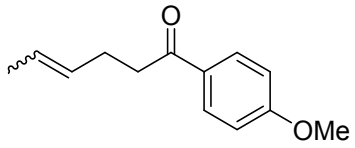


E/*Z*=79/21

Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 150/1) afforded 130 mg (69%); light yellow liquid. R_f = 0.80 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.74 (m, 2H), 7.37-7.32 (m, 2H), 5.56-5.42 (m, 2H), 3.03-2.99 (m, 2H), 2.51-2.45 (m, 0.44H), 2.44-2.39 (m, 4.68H), 2.41(s, 3H), 1.65-1.64 (m, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 200.1, 138.4, 137.1, 137.1,133.8,133.8, 129.9, 129.0, 128.7, 128.5, 126.0, 125.4, 125.2, 38.7, 38.6,27.3, 21.9, 21.5, 18.0, 12.9. HRMS (ESI, m/z) calcd for $C_{13}H_{16}O$ $[M+H]^+$: 189.1274, found: 189.1280

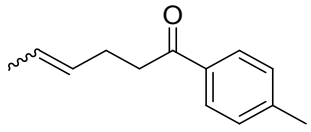
1-(4-methoxyphenyl)hex-4-en-1-one (3ng):



E/Z=84/16

Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 150/1) afforded 108 mg (53%); white solid. R_f = 0.75 (*n*-hexane/EtOAc = 10/1), ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 5.54-5.44 (m, 2H), 3.85 (s, 3H), 2.96 (t, *J* = 7.5 Hz, 2H), 2.49-2.43 (m, 0.32H), 2.40-2.37 (m, 1.68H), 1.64-1.63 (m, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 198.6, 163.5, 130.4, 130.2, 130.0, 129.2, 125.9, 125.1, 113.8, 55.6, 38.3, 38.2, 27.5, 22.1, 18.0, 12.9. HRMS (ESI, m/z) calcd for $C_{13}H_{16}O_2$ $[M+H]^+$: 205.1223, found: 205.1227

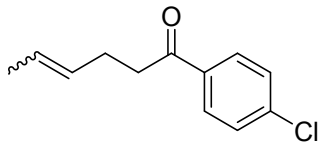
1-(4-methylphenyl)hex-4-en-1-one (3ni):



E/Z=79/21

Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 150/1) afforded 136 mg (72%); light yellow liquid. R_f = 0.75 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 5.55 - 5.45 (m, 2H), 2.99 (t, *J* = 7.4 Hz, 2H), 2.50-2.45 (m, 0.45H), 2.40 -2.38(m, 4.68H), 2.40 (s,3H), 1.65- 1.64 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.5, 143.7, 134.4, 130.0, 129.3, 129.1, 128.2, 125.9, 125.1, 38.5, 38.4, 27.3, 21.9, 21.7, 18.0, 12.9. HRMS (ESI, m/z) calcd for $C_{13}H_{16}O$ $[M+H]^+$: 189.1274, found: 189.1285

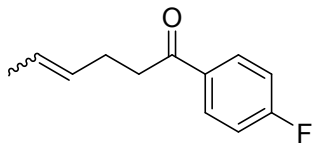
1-(4-chlorophenyl)hex-4-en-1-one (3nk)[25]:



E/Z=83/17

Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 150/1) afforded 131 mg (63%); white solid. R_f = 0.75 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, CDCl3) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 5.55- 5.43 (m, 2H), 3.01 - 2.97 (m, 2H), 2.50-2.45 (m, 0.34H), 2.43-2.38 (m, 1.66H), 1.65 - 1.63 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.7, 139.5, 135.4, 129.6, 129.6, 129.0, 128.7, 126.3, 125.5, 38.6, 38.5, 27.2, 21.8, 18.0, 12.9.

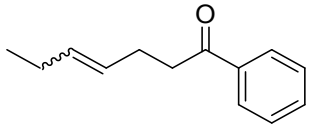
1-(4-fluorophenyl)hex-4-en-1-one (3nl):



E/*Z*=87/13

Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 150/1) afforded 117 mg (61%); white solid. R_f = 0.75 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.96 (m, 2H), 7.11 (t, *J* = 8.3 Hz, 2H), 5.55 - 5.38 (m, 2H), 2.99 (t, *J* = 7.4 Hz, 2H), 2.50-2.42 (m, 0.25H), 2.41-2.38 (m, 1.75H), 1.64-1.63 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.3, 167.8(d, *J* = 254.3 Hz), 133.5(d, *J* = 3.0 Hz), 130.80(d, *J* = 9.3Hz), 129.7, 128.8, 126.2, 125.4, 115.85(d, *J* = 21.8Hz), 38.6, 38.4, 27.3, 21.8, 18.0, 12.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.61. HRMS (ESI, m/z) calcd for $C_{12}H_{13}FO$ $[M+H]^+$: 193.1023, found:193.1026

1-phenylhept-4-en-1-one (3oa)[26]:

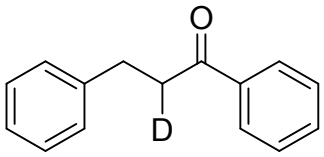


E/*Z*=88/12

Typical procedure was followed and flash chromatography (*n*-hexane/EtOAc = 150/1) afforded 117 mg (62%); light yellow liquid. R_f = 0.75 (*n*-hexane/EtOAc = 10/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), 7.55-7.53 (m, 1H), 7.48-7.44 (m, 2H), 5.57-5.40 (m, 2H), 3.05-3.02 (m, 2H), 2.51-2.47(m, 0.25H), 2.45-2.40 (m, 1.87H), 2.11-2.06(m,

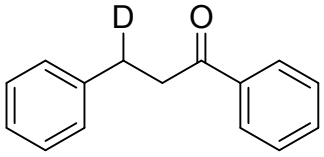
0.25H), 2.03-1.97 (m, 1.87H), 0.96 (t, J = 7.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 200.0, 137.2, 133.3, 133.1, 133.1,128.7, 128.2, 127.6, 127.4, 38.8, 38.8, 27.3, 25.7, 22.1, 20.7, 14.4, 13.9.

1,3-diphenyl-[2-^{2}H]-propan-1-one (3aa-d^{2})[6]:



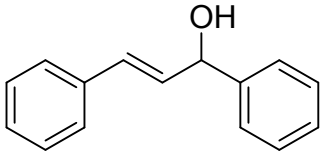
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.94 (m, 2H), 7.56-7.52 (m, 1H), 7.46-7.42 (m, 2H), 7.31-7.18 (m, 5H), 3.30-3.24 (m, 1H), 3.07 (t, J = 7.2 Hz, 2H).

1,3-diphenyl-[3-^{2}H]-propan-1-one (3aa-d^{3})[6]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.94 (m, 2H), 7.57-7.52 (m, 1H), 7.46-7.42 (m, 2H), 7.32-7.24 (m, 4H), 7.22-7.18 (m, 1H), 3.29 (d, J = 7.7 Hz, 2H), 3.05 (t, J = 7.6 Hz, 1H).

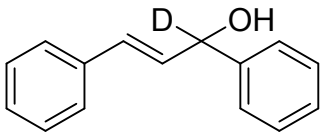
(*E*)-1,3-diphenylprop-2-en-1-ol (4)[27]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.39-7.33 (m, 4H), 7.31-7.27 (m, 3H),

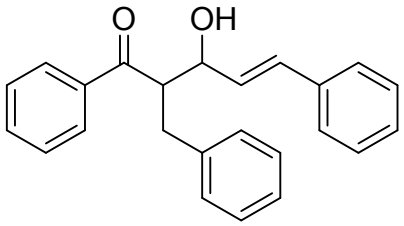
7.24-7.21 (m, 1H), 6.67 (d, *J* = 15.8 Hz, 1H), 6.37 (dd, *J* = 15.8, 6.5 Hz, 1H), 5.38-5.35 (m, 1H), 2.16 (s, *J* = 3.4 Hz, 1H).

(*E*)-1,3-diphenylprop-2-en-[1-^{2}H]-1-ol (4-d^1)[6]:



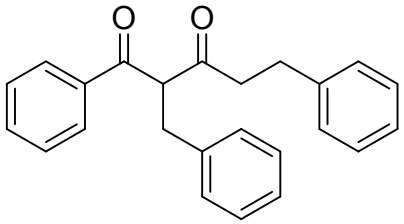
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.40 (m, 2H), 7.37-7.33 (m, 4H), 7.31-7.27 (m, 3H), 7.27-7.20 (m, 1H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.36 (d, *J* = 15.9 Hz, 1H), 2.23 (s, 1H).

(*E*)-2-benzyl-3-hydroxy-1,5-diphenylpent-4-en-1-one (5):



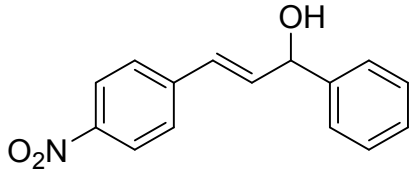
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.80 (m, 1H), 7.72-7.20 (m, 1H), 7.53-7.43 (m, 1H), 7.40-7.35 (m, 1H), 7.34-7.09 (m, 11H), 6.70-6.59 (m, 1H), 6.25-6.16 (m, 1H), 4.66 (s, 0.5H), 4.55-4.52 (m, 0.5H), 4.01-3.91(m, 1H), 3.30-3.28 (m, 0.5H), 3.18-3.16 (m, 1H), 3.11-3.10 (m, 1H), 2.88 (s, 0.5H). HRMS (ESI, m/z) calcd for $C_{24}H_{22}O_2$ $[M+Na]^+$: 365.1512, found: 365.1480

2-benzyl-1,5-diphenylpentane-1,3-dione (6)[28]**:**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.83 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.24-7.13 (m, 8H), 7.04 (d, *J* = 6.9 Hz, 2H), 4.76 (t, *J* = 7.1 Hz, 1H), 3.32 -3.22 (m, 2H), 2.83-2.75 (m, 3H), 2.69-2.59 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 204.5, 195.8, 140.7, 138.6, 136.6, 133.8, 129.0, 128.8, 128.6, 128.4, 126.8, 126.3, 64.4, 43.4, 34.9, 29.6.

(*E*)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-ol (7)[5]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.43-7.37 (m, 4H), 7.35-7.31 (m, 1H), 6.77 (d, *J* = 15.9 Hz, 1H), 6.58-6.53 (m, 1H), 5.43 (d, *J* = 5.6 Hz, 1H), 2.38 (s, 1H).

4. References

1. J. T. Tan, Y. Kuang, Y. Wang, Q. F. Huang, J. Zhu and Y. H. Wang, *Organometallics*, 2016, **35**, 3139−3147.

2. T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer and G. Wilkinson, *J. Chem. Soc.* 1965, 3632–3640.
3. P. S. Gao, F. Ye, X. Y. Dong, Y. Chen, Z. W. Gao, W. Q. Zhang and L. W. Xu, *RSC Adv*. 2015, **5**, 33818–33822.
4. J. Sivamani, V. Ashokkumar, V. Sadhasivam, K. Duraimurugan and A. Siva, *RSC Adv.* 2014, **4**, 60293−60299.
5. W. L. Xu, Y. G. Zhou, R. M. Wang, G. T. Wu and P. Chen, *Org. Biomol. Chem.* 2012, **10**, 367−371.
6. H. X. Zheng, Z. F. Xiao, C. Z. Yao, Q. Q. Li, X. S. Ning, Y. B. Kang and Y. Tang, *Org. Lett*. 2015, **17**, 6102–6105.
7. S. Elangovan, J. B. Sortais, M. Beller and C. Darcel, *Angew. Chem., Int. Ed.* 2015, **54**, 14483−14486.
8. T. Kuwahara, T. Fukuyama and I. Ryu, *Org. Lett.* 2012, **14**, 4703−4705.
9. Y. S. Feng, C. Y. Yang, Q. Huang and H. J. Xu, *Tetrahedron*. 2012, **68**, 5053−5059.
10. A. Sauza, J. A. Morales-Serna, M. Garcia-Molina, R. Gavino and J. Cardenas, *Synthesis*. 2012, **44**, 272−282.
11. R. Z. Wang, J. Ma and F. Li, *J. Org. Chem.* 2015, **80**, 10769 −10776.
12. X. N. Cao, X. M. Wan, F. L. Yang, K. Li, X. Q. Hao, T. Shao, X. J. Zhu and M. P. Song, *J. Org. Chem.* 2018, **83**, 3657−3668.
13. W. F. Li and X. F. Wu, *Eur. J.Org. Chem*. 2015, **2015**, 331–335.
14. P. Colbon, J. Ruan, M. Purdie and J. L. Xiao, *Org. Lett*. 2010, **12**, 3670−3673.
15. L. J. Gooßen and K. Ghosh, *Eur. J. Org. Chem*. 2002, **2002**, 3254−3267.
16. M. Zhang, R. Ruzi, J. Xi, N. Li, Z. K. Wu, W. P. Li, S. Y. Yu and C. J. Zhu, *Org. Lett*. 2017, **19**, 3430–3433.

17. Q. B. Jiang, T. L. Guo, Q. F. Wang, P. Wu and Z. K. Yu, *Adv. Synth. Catal.* 2013, **355**, 1874−1880.
18. X. W. Wang, C. Wang, Y. X. Liu and J. L. Xiao, *Green Chem.* 2016, **18**, 4605−4610.
19. S. Akai, A. J. Peat and S. L. Buchwald, *J. Am. Chem. Soc.* 1998, **120**, 9119–9125.
20. Y. Liu, B. Yao, C. L. Deng, R.Y. Tang, X. G. Zhang and J. H. Li, *Org. Lett.* 2011, **13**, 2184–2187.
21. A. Takemiya and J. F. Hartwig, *J. Am. Chem. Soc.* 2006, **128**, 14800−14801.
22. J. B. Metternich, D. G. Artiukhin, M. C. Holland, M. von Bremen-Kühne, J. Neugebauer and R. Gilmour, *J. Org. Chem.* 2017, **82**, 9955–9977.
23. X. Y. Wang, M. C. Liu, L. Xu, Q. Z. Wang, J. X. Chen, J. C. Ding and H. Y. Wu, *J.Org. Chem.* 2013, **78**, 5273–5281.
24. M. S. Kwon, N. Kim, S. H. Seo, I. S. Park, R. K. Cheedrala and J. Park, *Angew. Chem., Int. Ed.* 2005, **44**, 6913−6915.
25. G. Ouvry, B. Quiclet-Sire and S. Z. Zard, *Angew. Chem.*, *Int. Ed.* 2006, **45**, 5002–5006.
26. P. J. Wagner, K.C. Liu and Y. Noguchi, *J. Am. Chem. Soc.* 1981,**103**, 3837–3841.
27. M. H. Babu, G. R. Kumar, R. Kant and M. S. Reddy, *Chem. Commun.*, 2017, **53**, 3894–3897.
28. I. Seiichi, S. Osamu and S. Kikumasa, *Bull. Chem. Soc. Jpn.*,1989, **62**,1601–1605.

5. ^{1}H NMR and ^{13}C NMR Spectra of Compounds

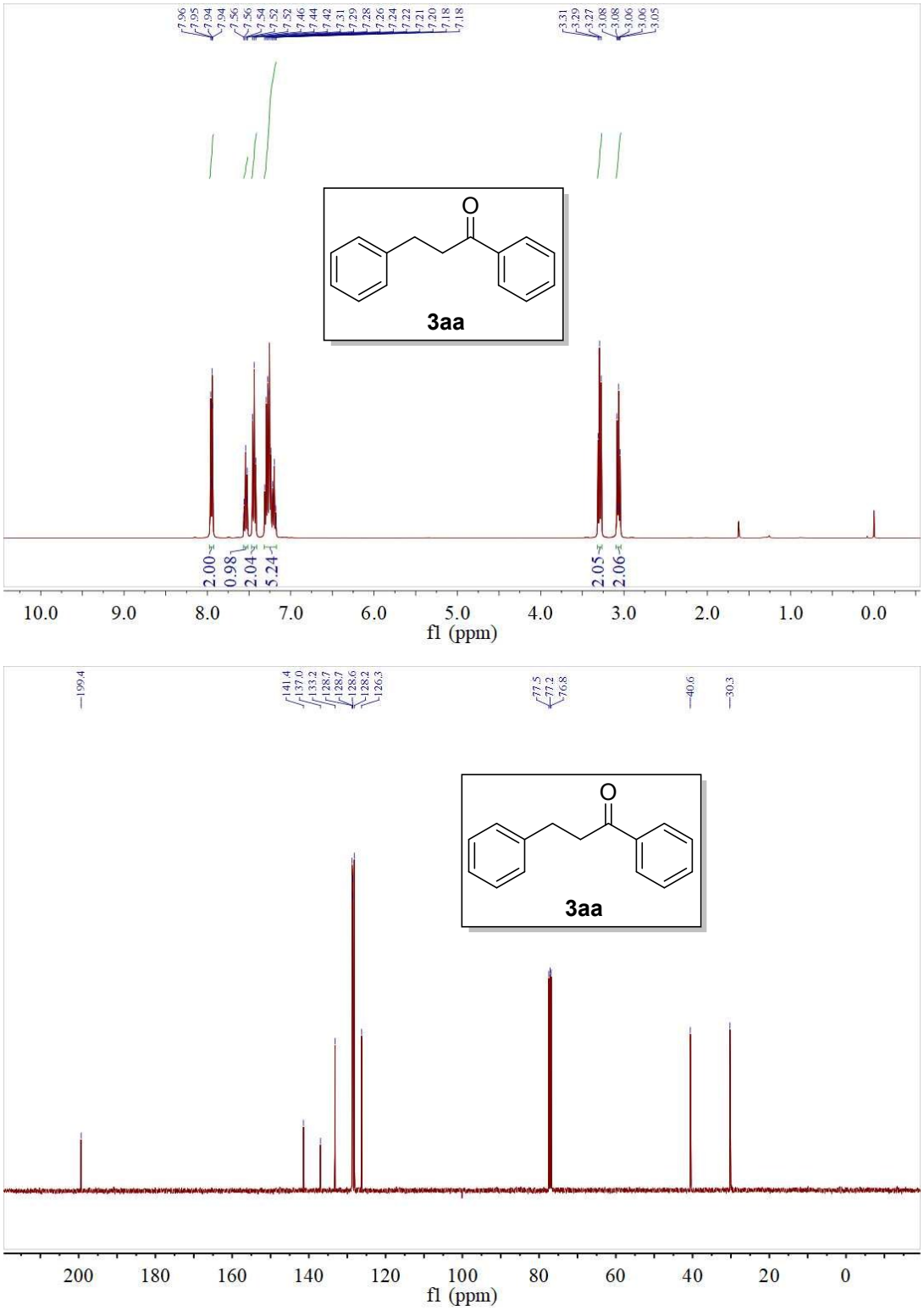


Figure S4. ^{1}H NMR of **3aa** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3aa** (100 MHz, $CDCl_3$)

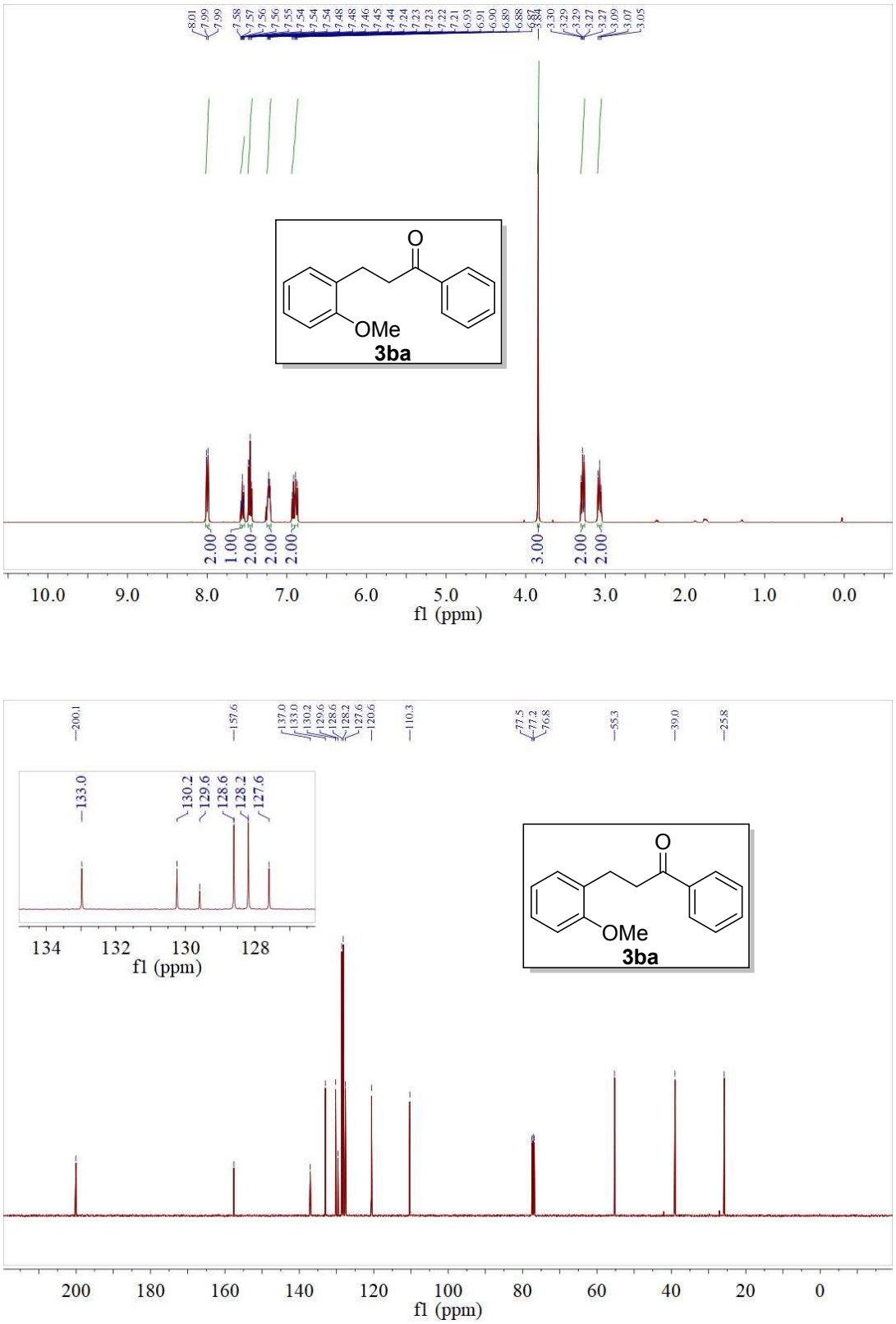


Figure S5. ^{1}H NMR of **3ba** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ba** (100 MHz, $CDCl_3$)

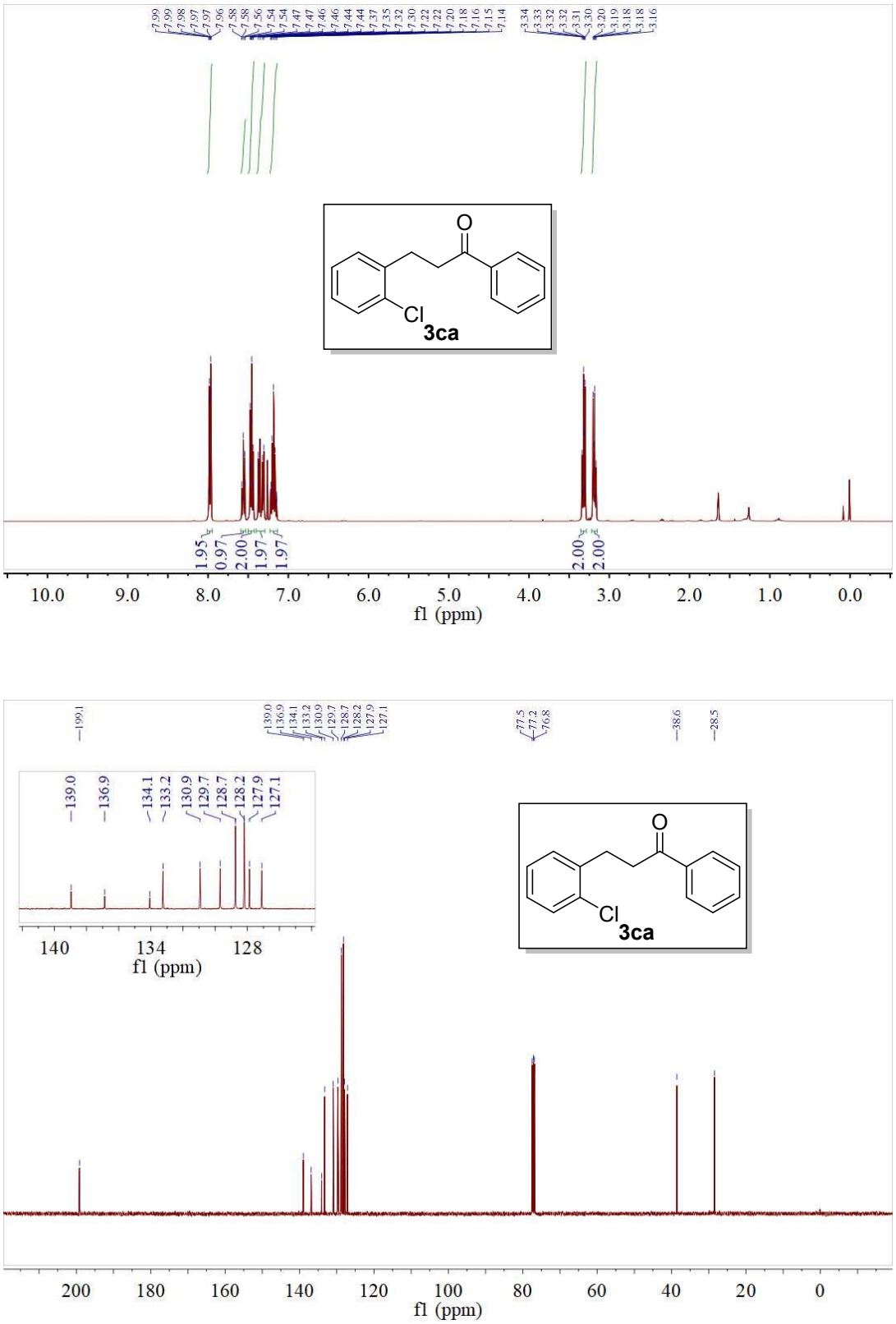


Figure S6. ^{1}H NMR of **3ca** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ca** (100 MHz, $CDCl_3$)

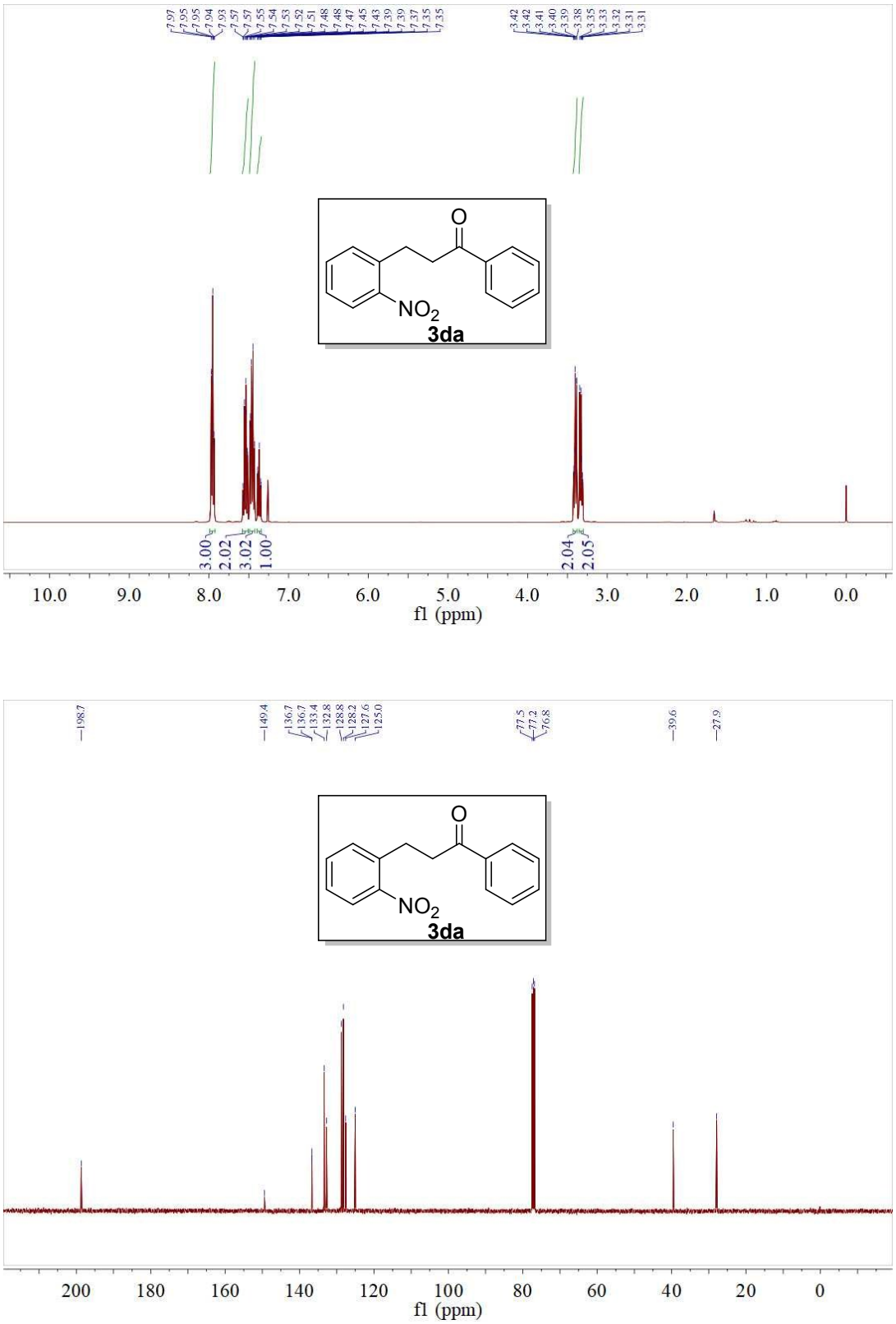


Figure S7. ^{1}H NMR of **3da** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3da** (100 MHz, $CDCl_3$)

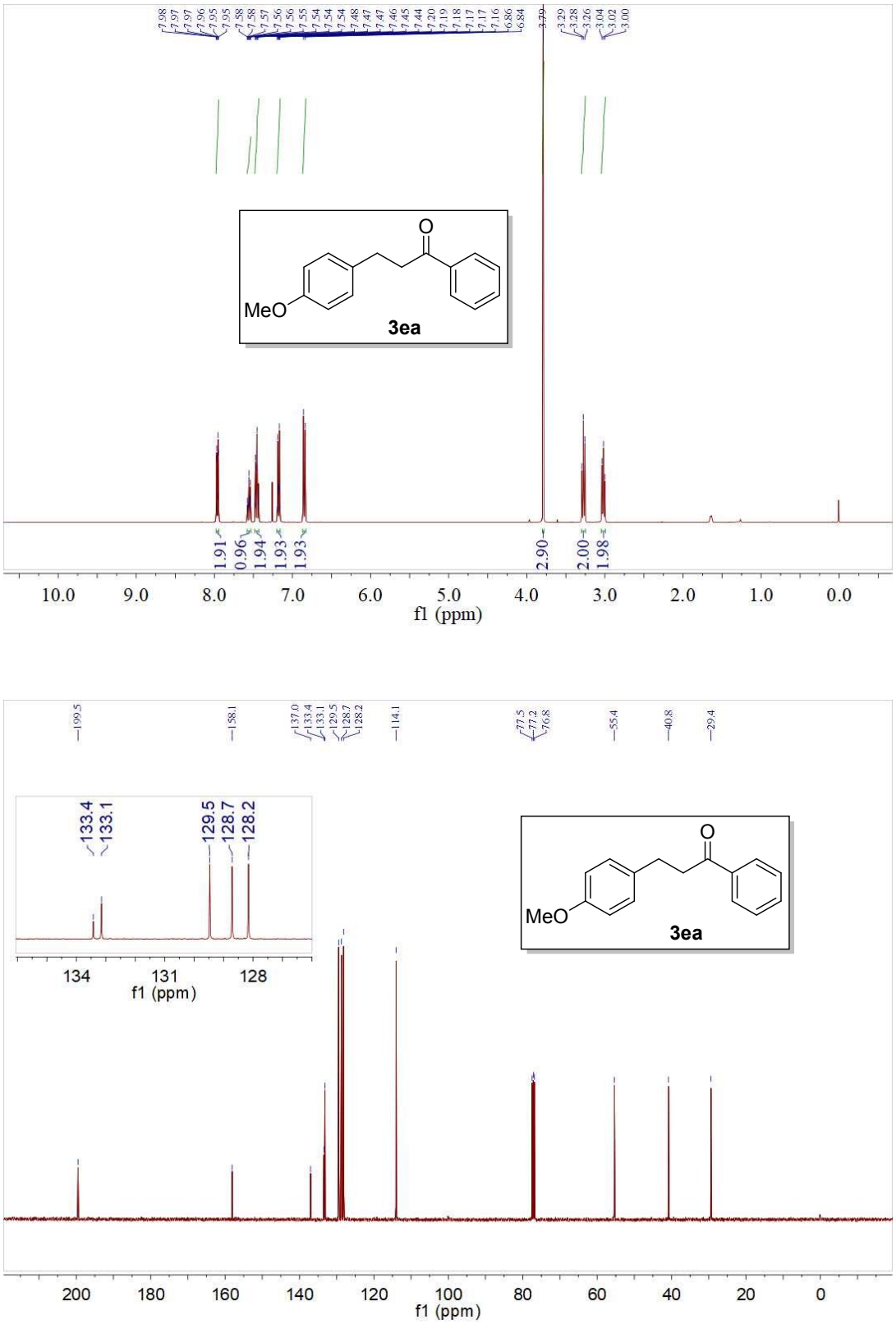


Figure S8. ^{1}H NMR of **3ea** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ea** (100 MHz, $CDCl_3$)

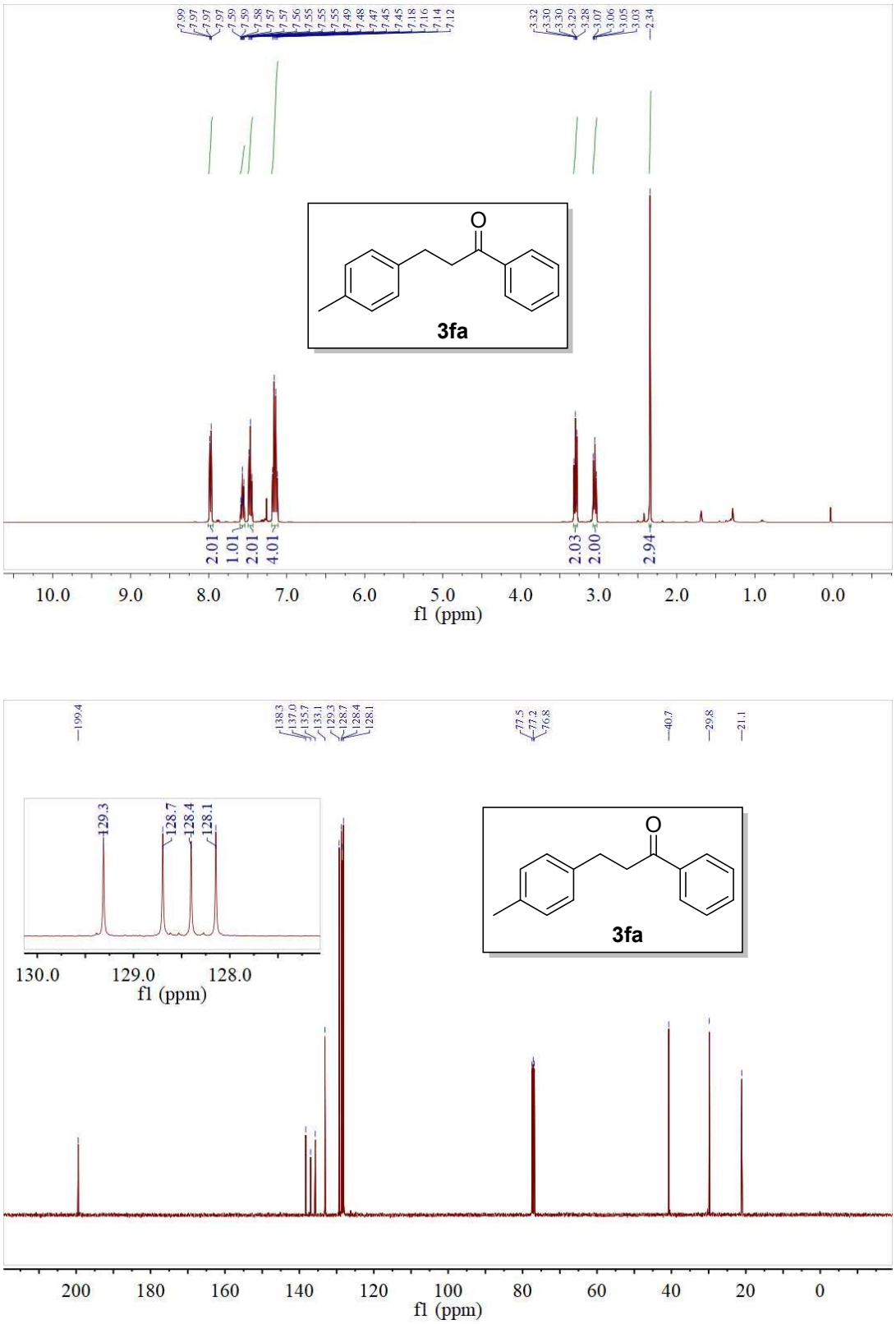


Figure S9. ^{1}H NMR of **3fa** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3fa** (100 MHz, $CDCl_3$)

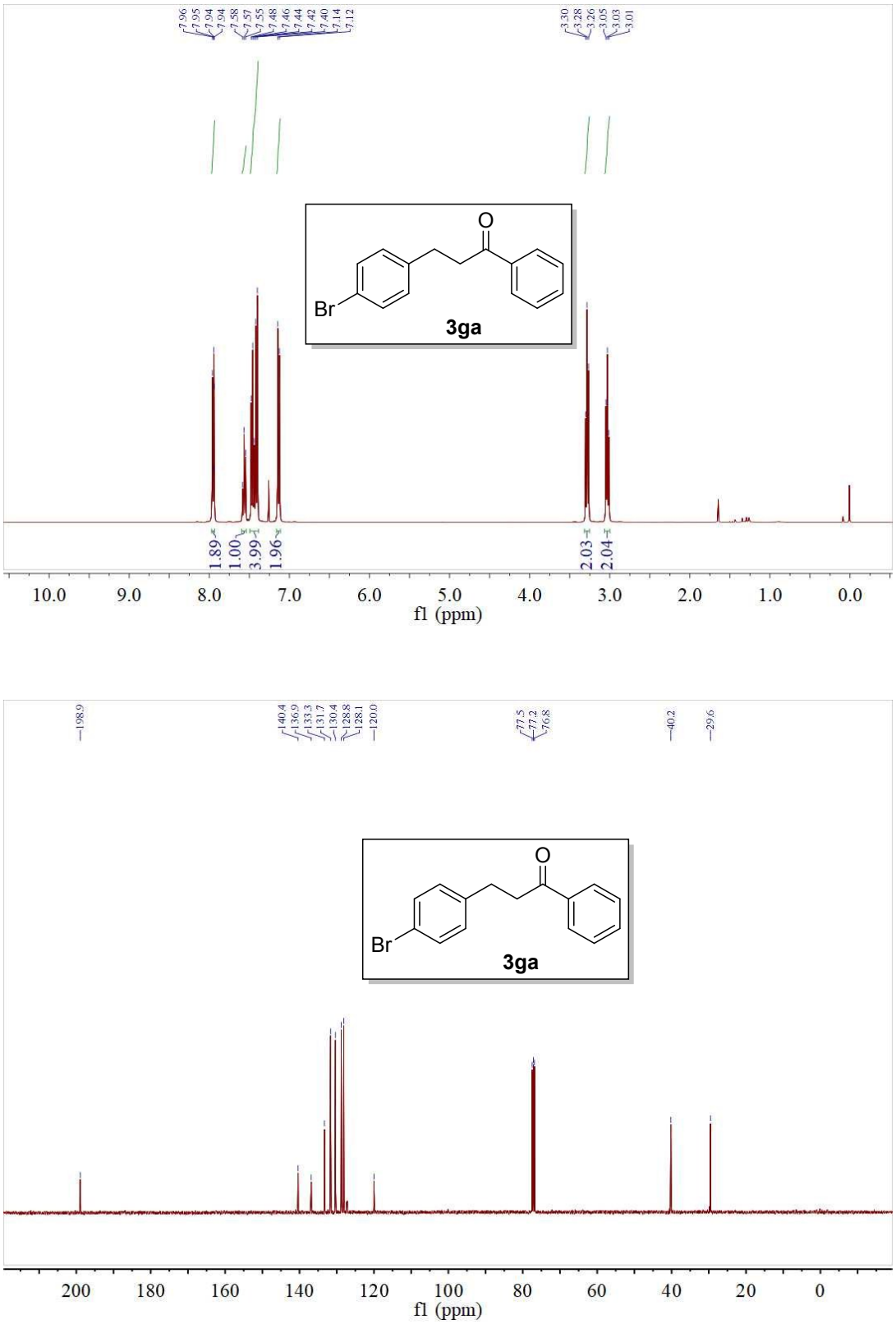


Figure S10. ^{1}H NMR of **3ga** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ga** (100 MHz, $CDCl_3$)

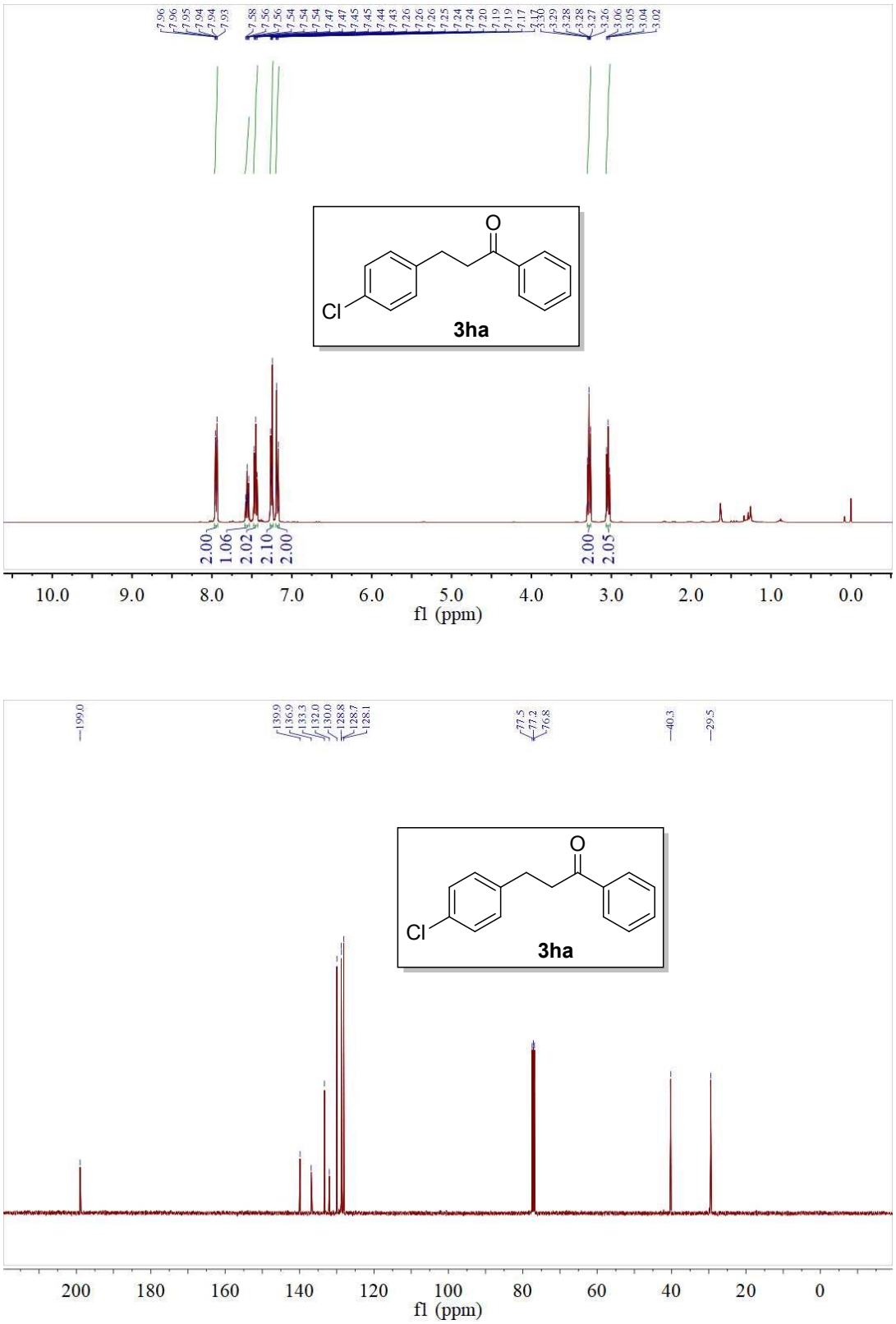
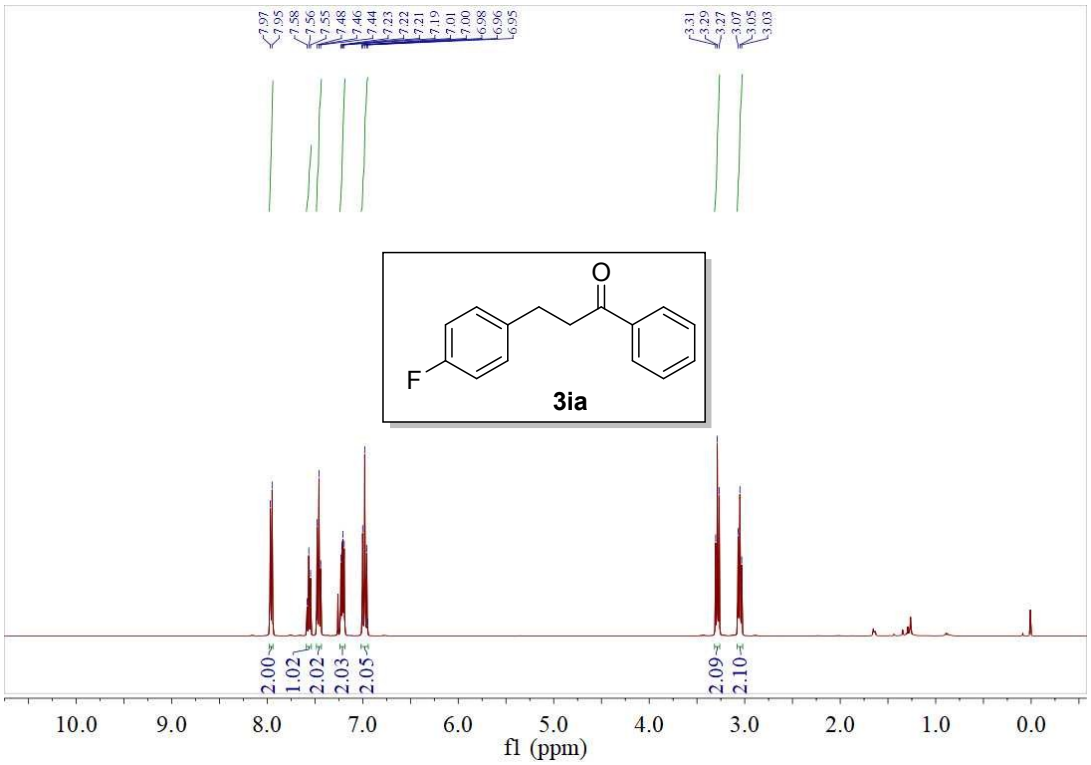
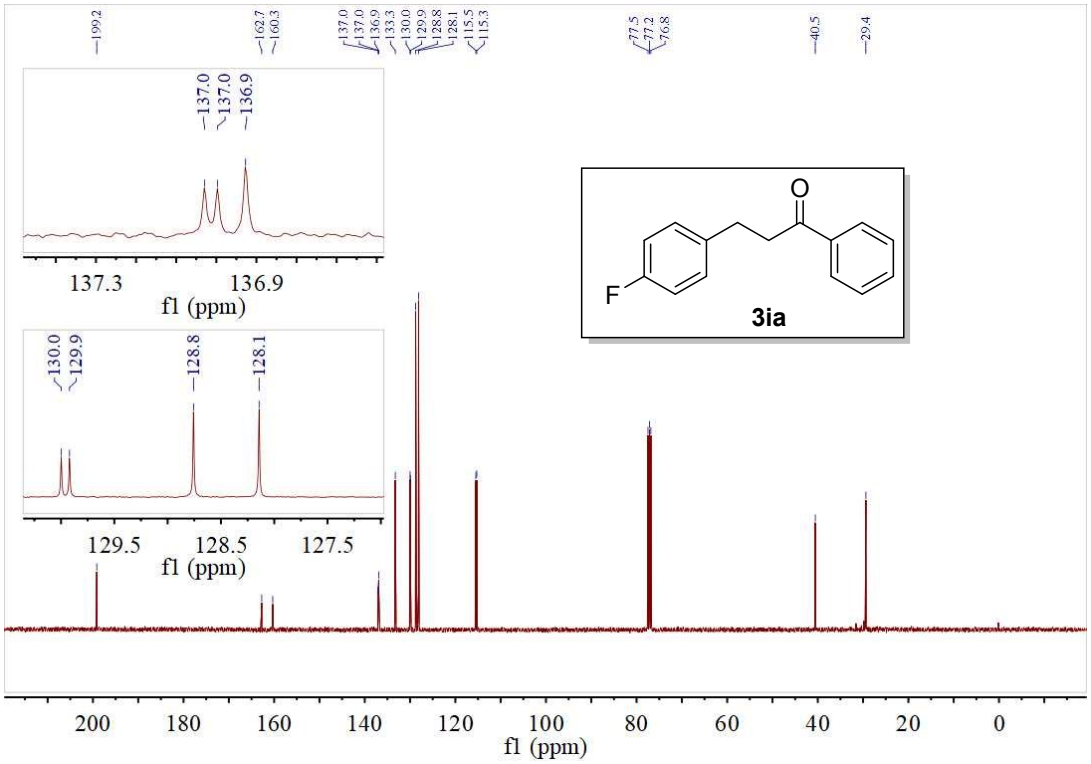


Figure S11. ^{1}H NMR of **3ha** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ha** (100 MHz, $CDCl_3$)


7.97
7.95
7.58
7.56
7.55
7.48
7.46
7.44
7.23
7.22
7.21
7.19
7.01
7.00
6.98
6.96
6.95
3.31
3.29
3.27
3.07
3.05
3.03
O
F
3ia
2.00
1.02
2.02
2.03
2.05
2.09
2.10
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


199.2
162.7
160.3
137.0
137.0
136.9
133.3
130.0
129.9
128.8
128.1
115.5
115.3
77.5
77.2
76.8
40.5
29.4
137.3
136.9
f1 (ppm)
129.5
128.5
127.5
f1 (ppm)
O
F
3ia
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

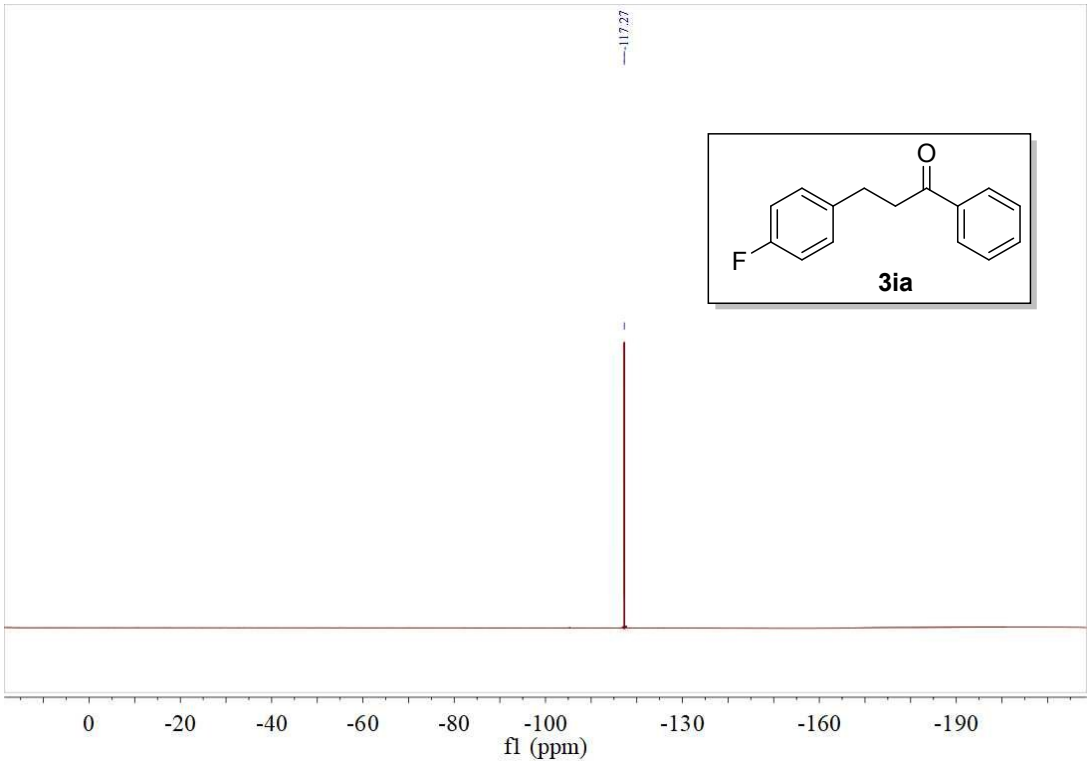
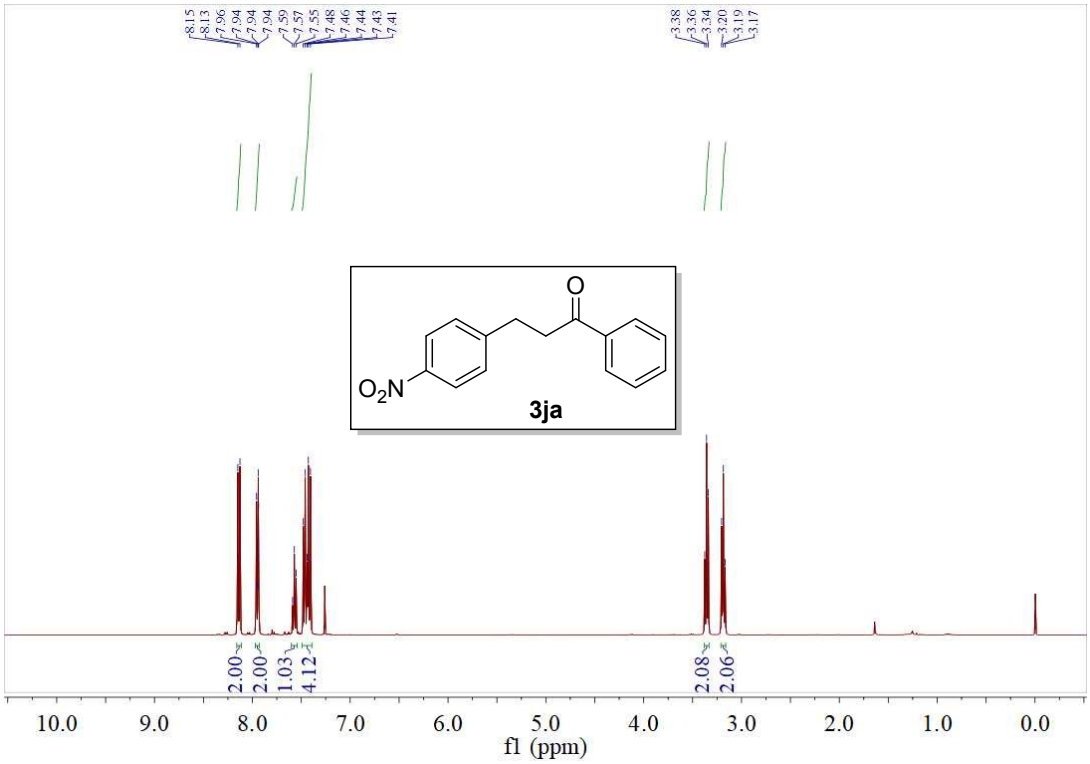


Figure S12. ^{1}H NMR of **3ia** (400 MHz, $CDCl_3$), ^{13}C NMR of **3ia** (100 MHz, $CDCl_3$) and ^{19}F NMR of **3ia** (376 MHz, $CDCl_3$)



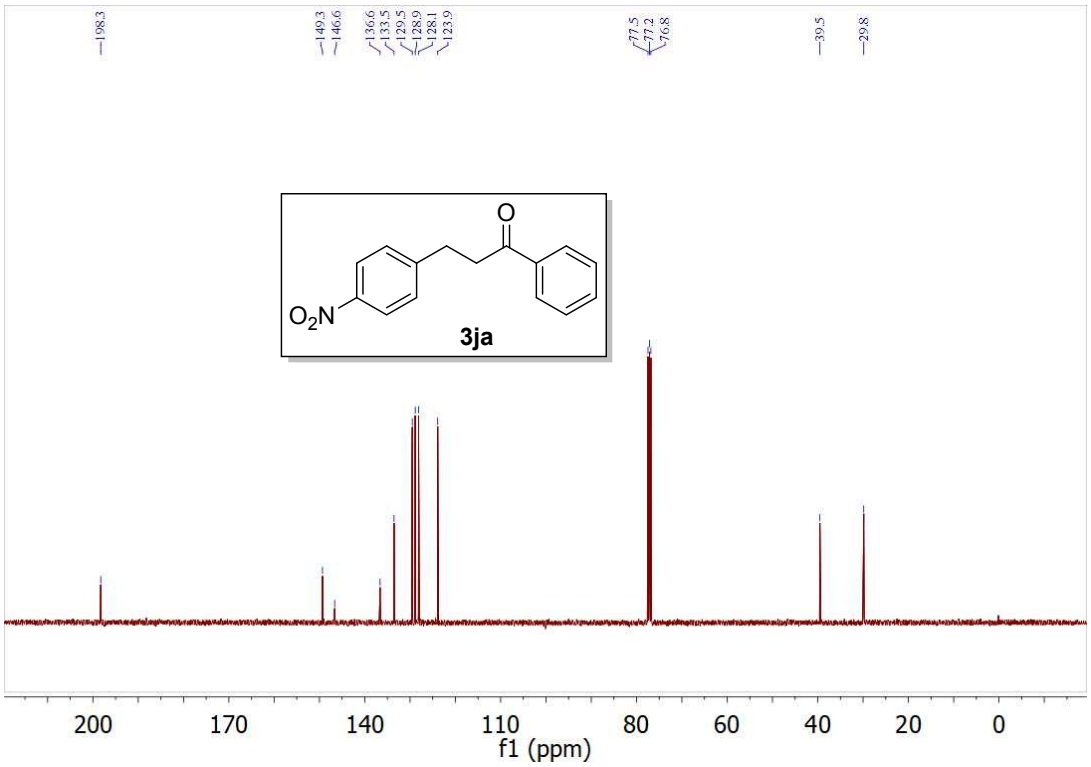
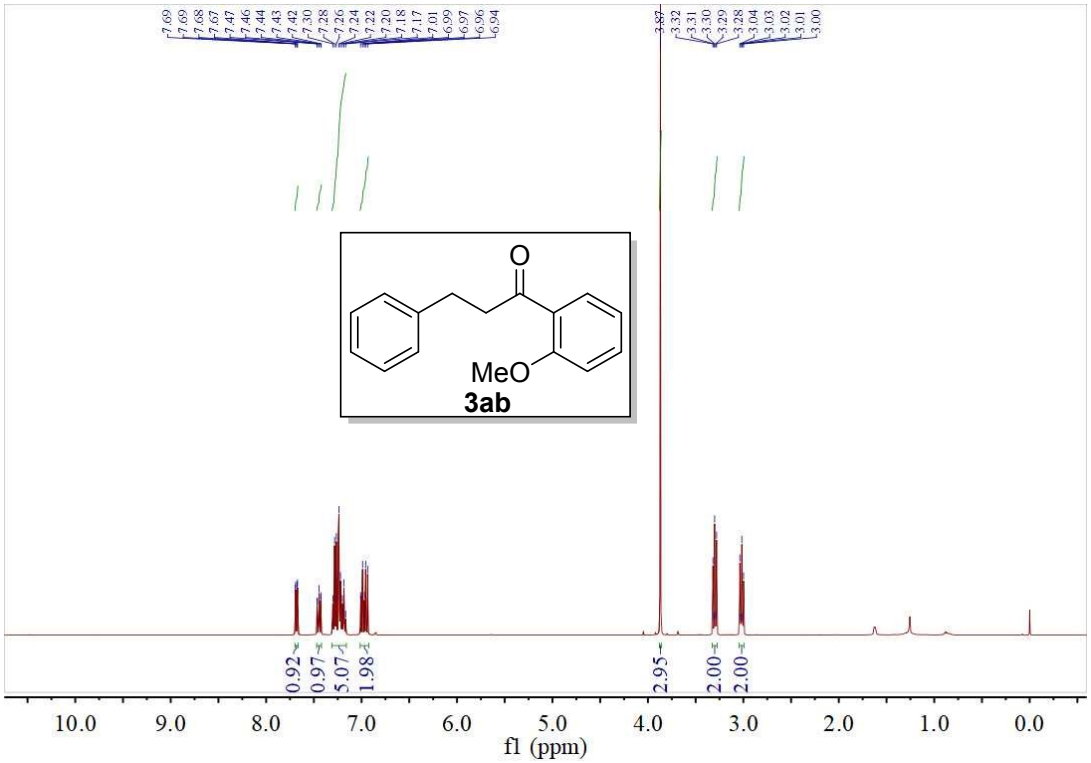


Figure S13. ^{1}H NMR of **3ja** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ja** (100 MHz, $CDCl_3$)



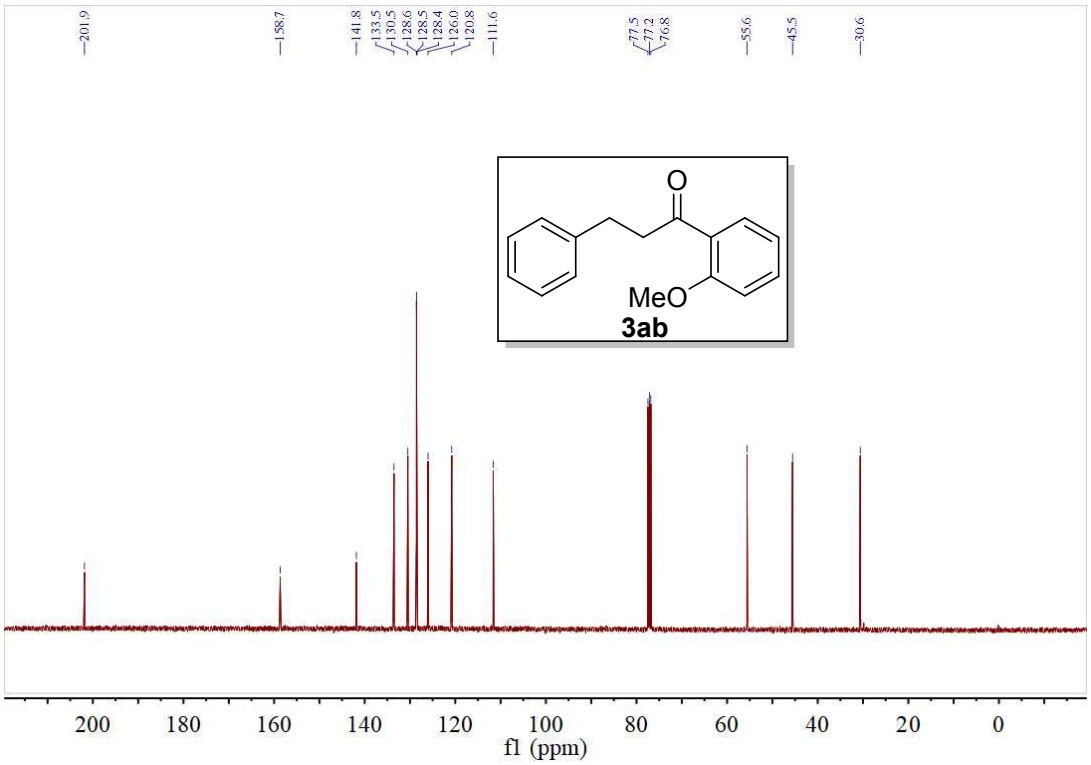
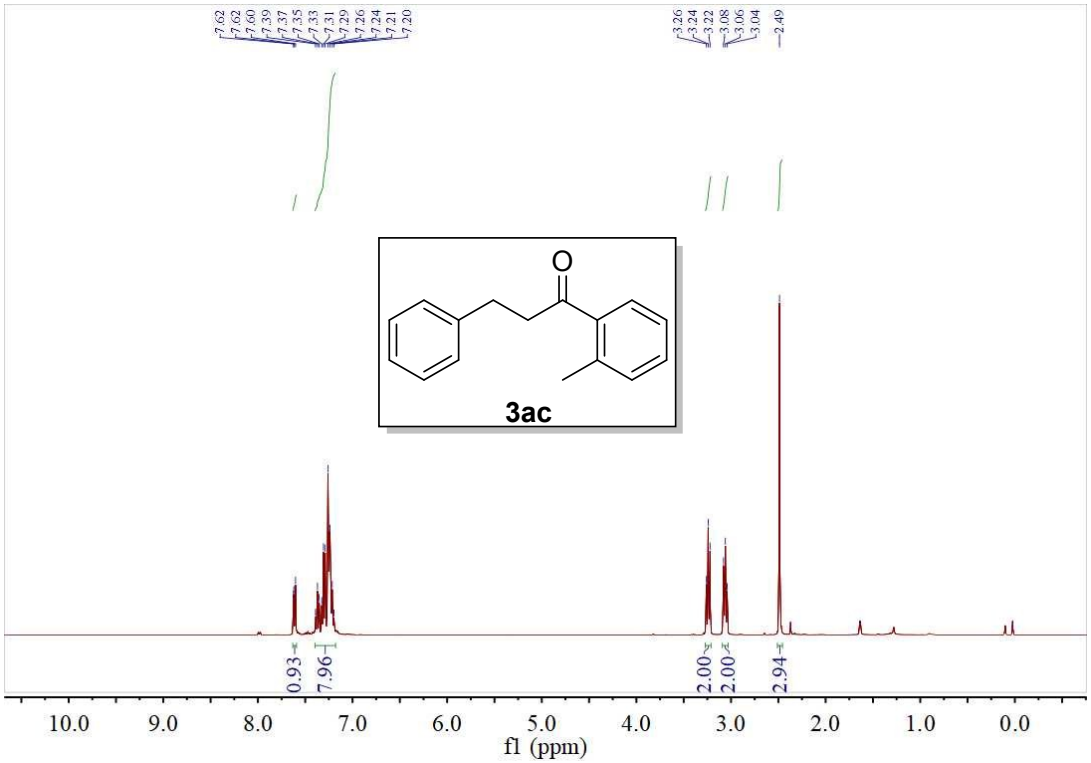


Figure S14. ^{1}H NMR of **3ab** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ab** (100 MHz, $CDCl_3$)



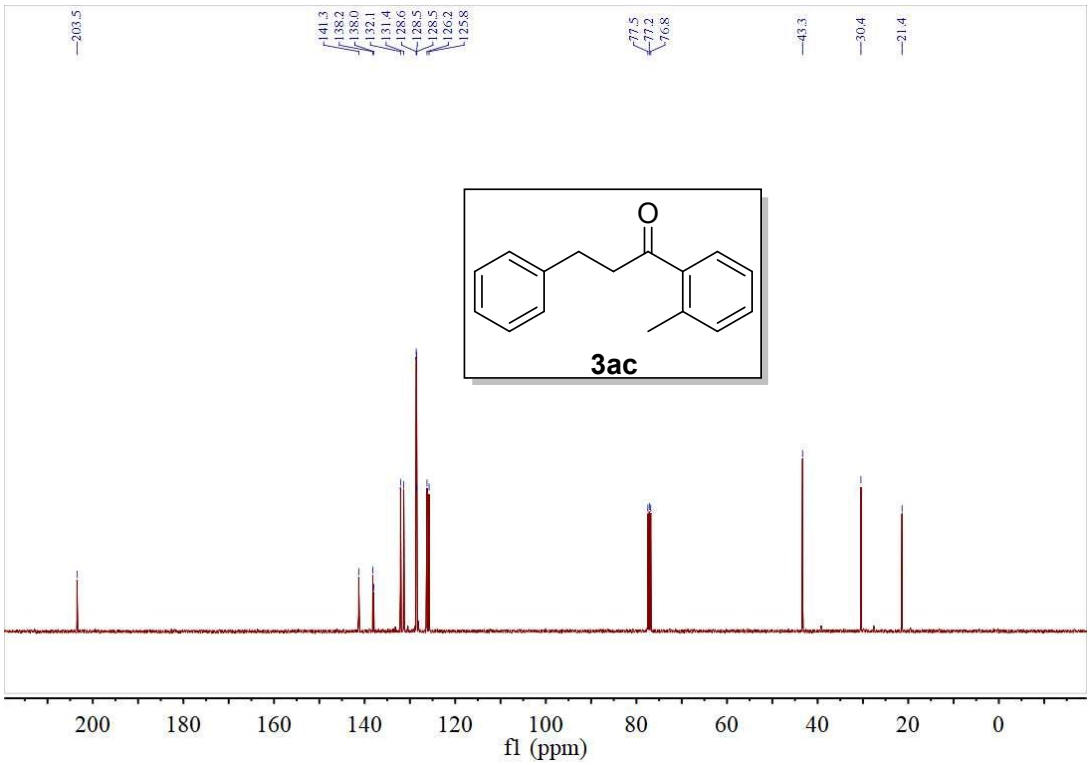
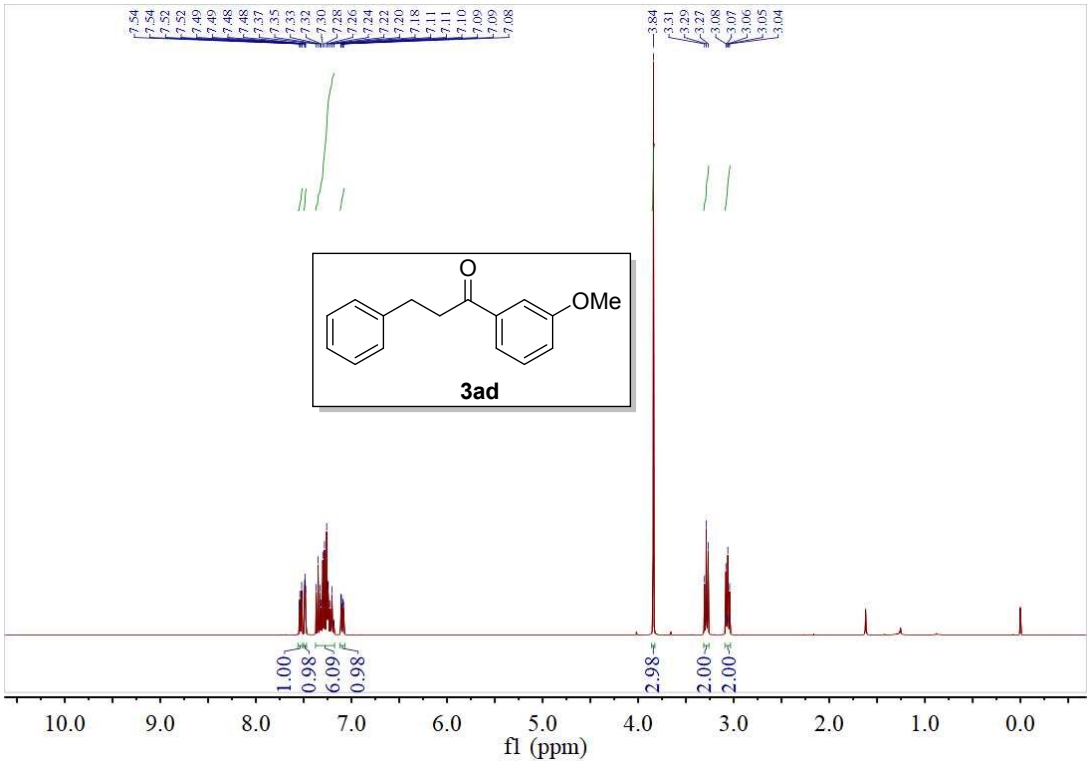


Figure S15. ^{1}H NMR of **3ac** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ac** (100 MHz, $CDCl_3$)



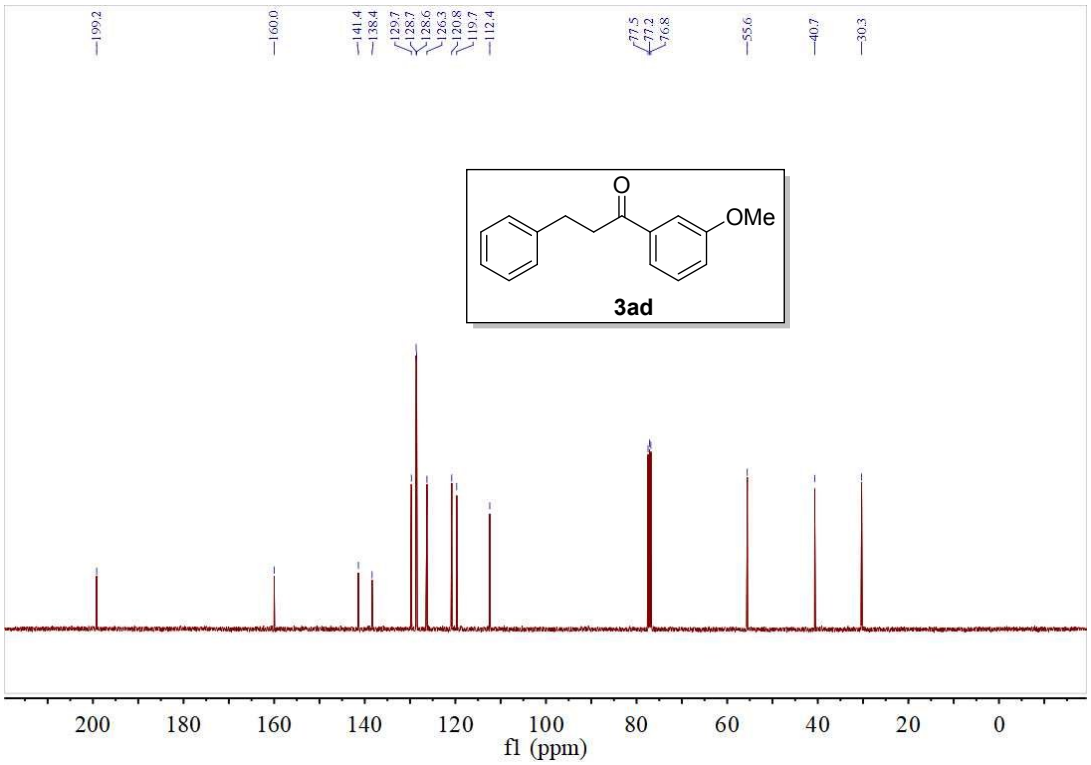
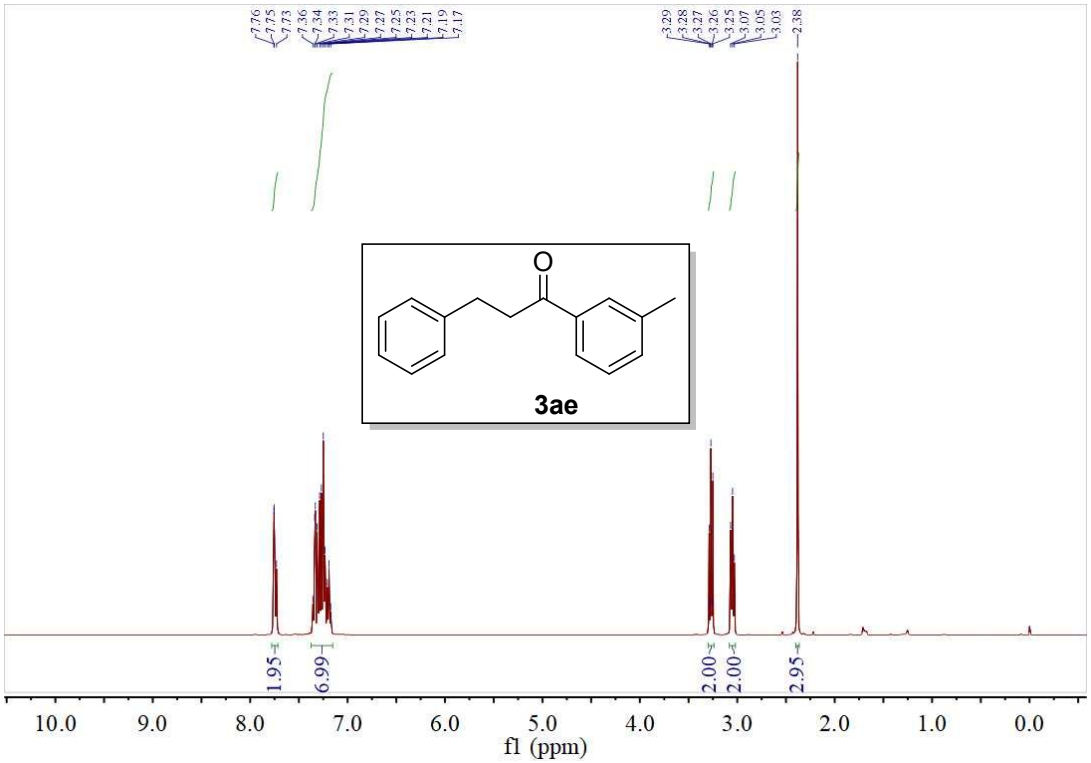


Figure S16. ^{1}H NMR of **3ad** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ad** (100 MHz, $CDCl_3$)



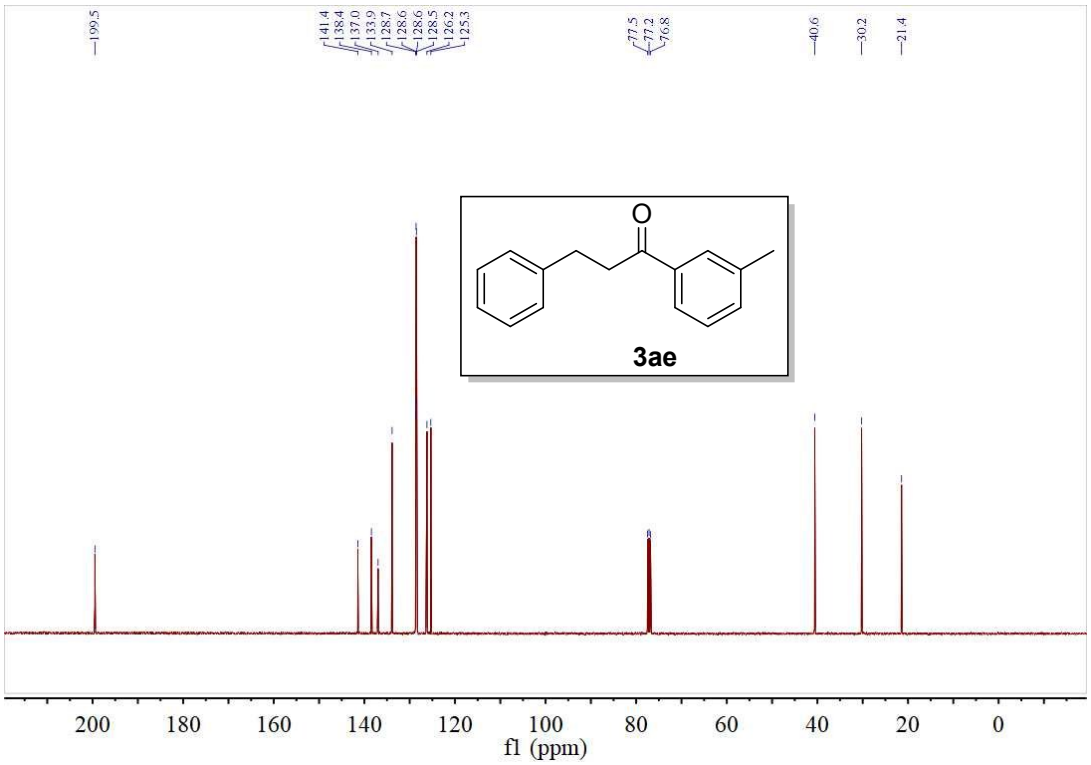
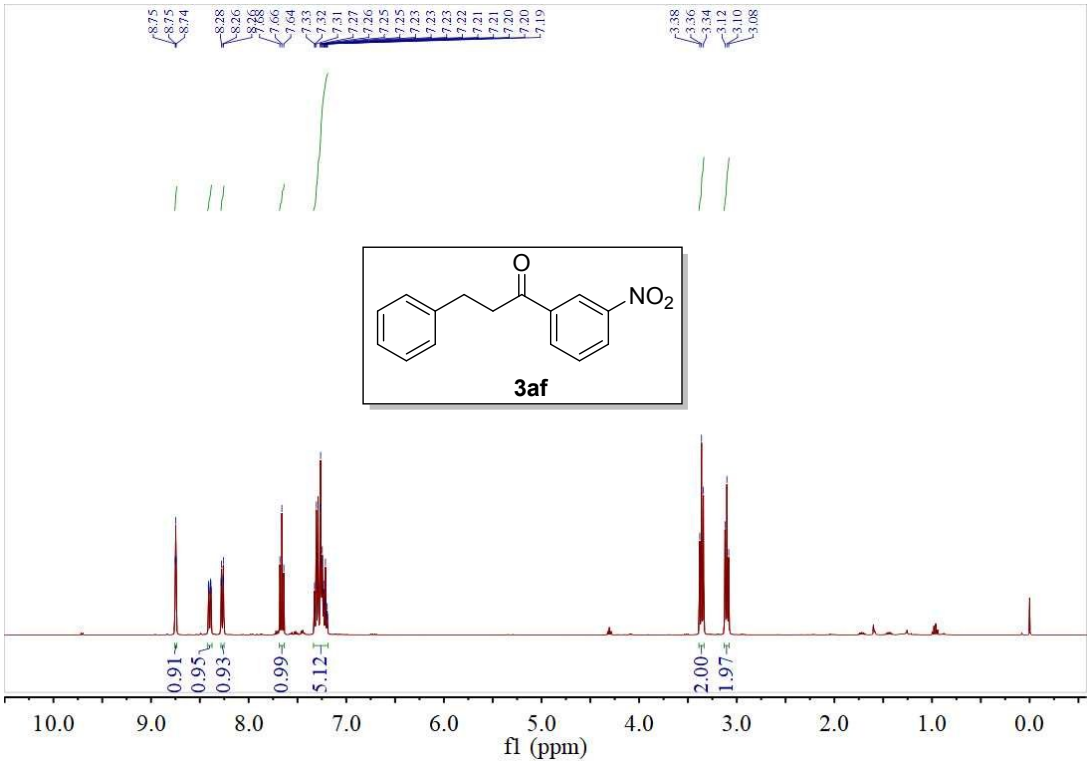


Figure S17. ^{1}H NMR of **3ae** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ae** (100 MHz, $CDCl_3$)



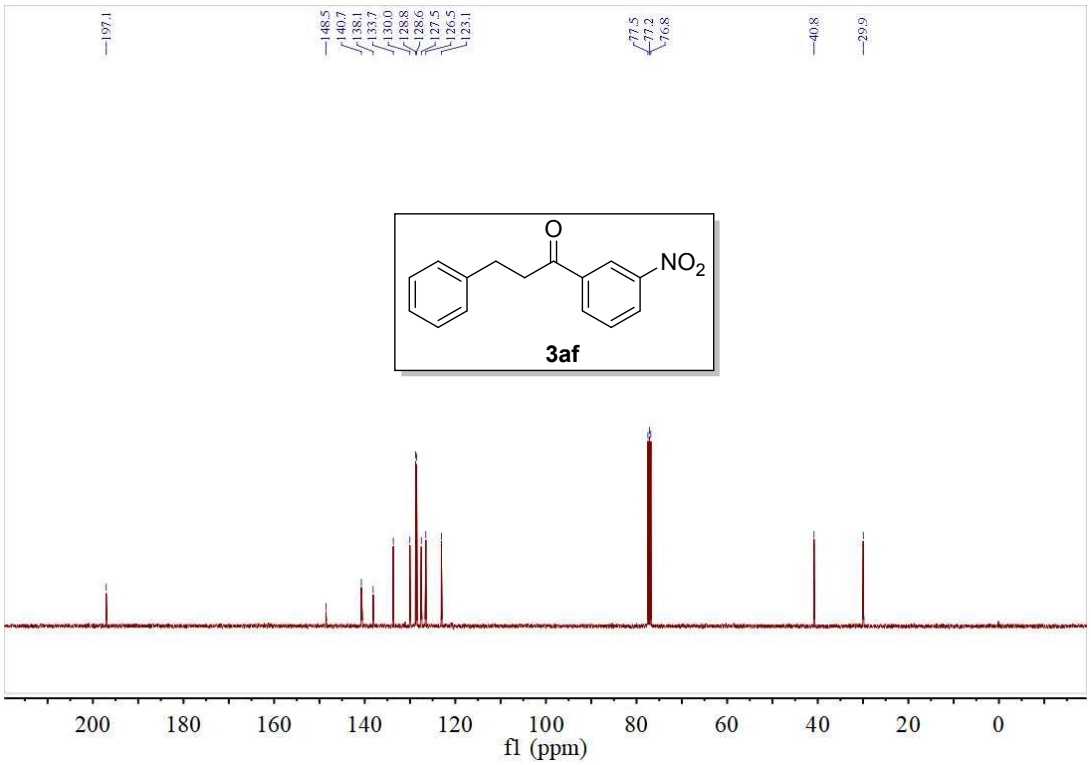
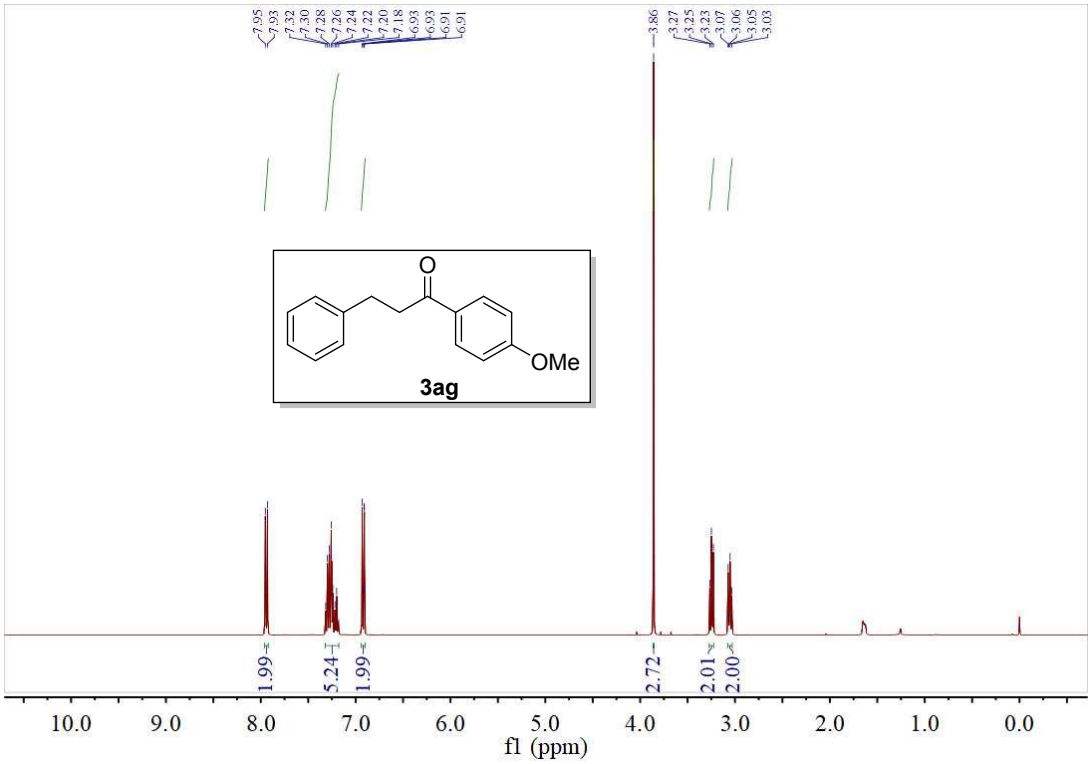


Figure S18. ^{1}H NMR of **3af** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3af** (100 MHz, $CDCl_3$)



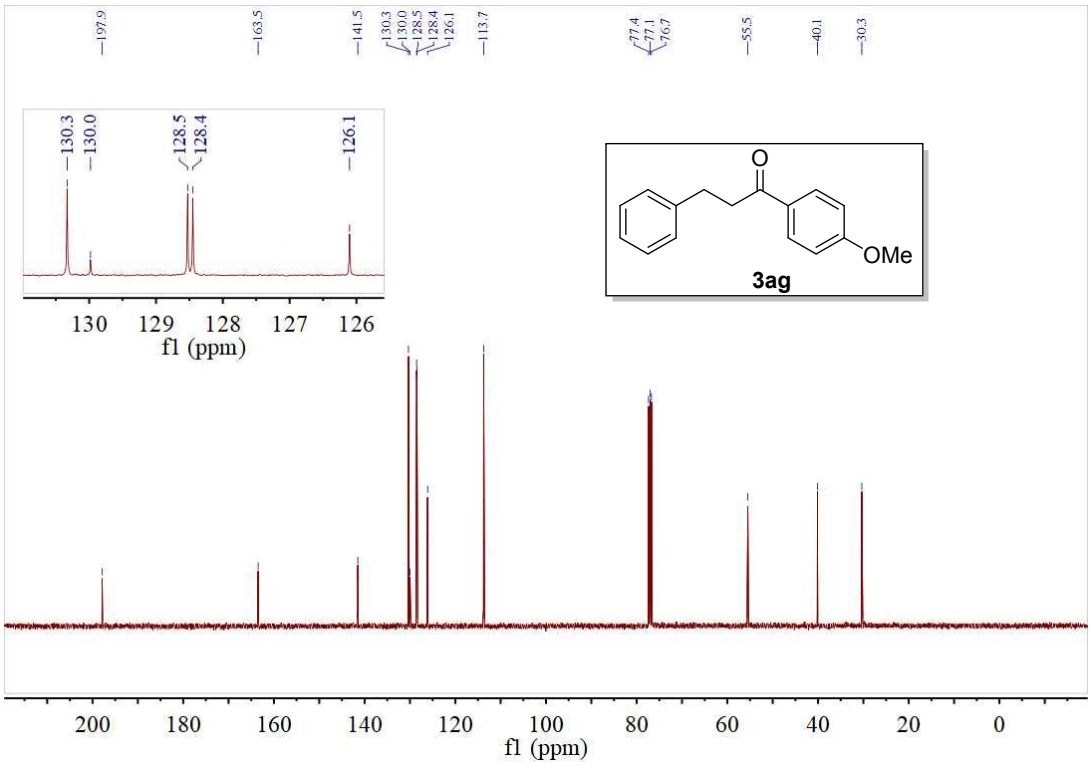
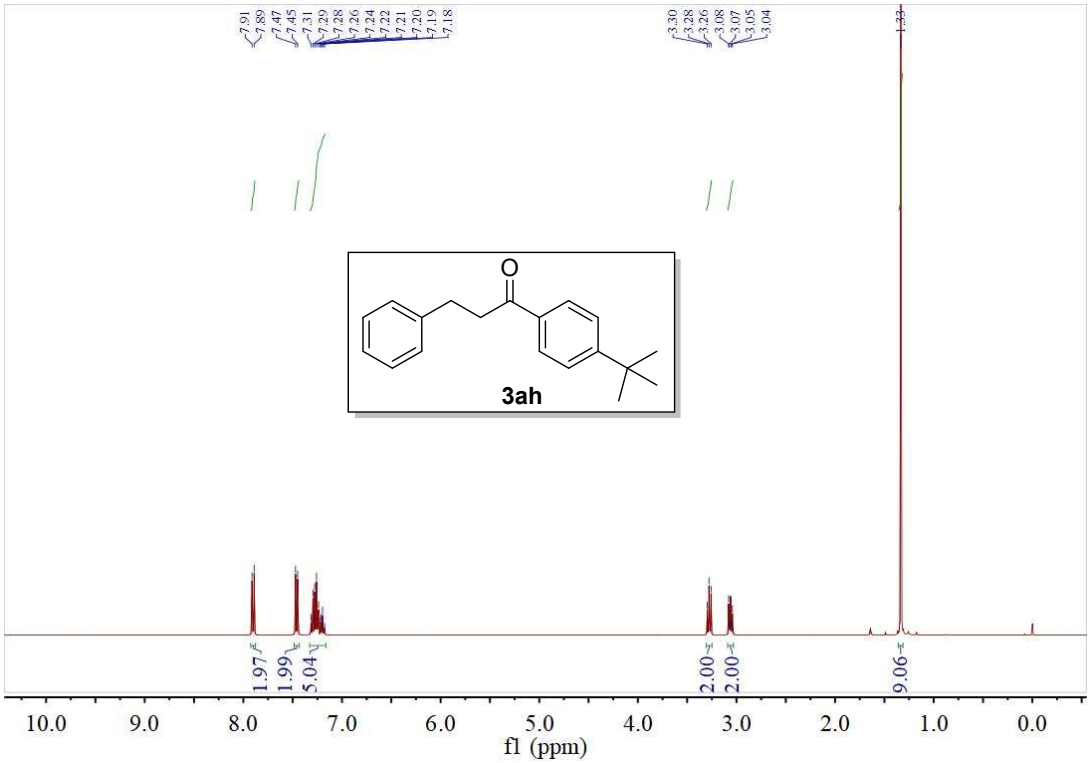


Figure S19. ^{1}H NMR of **3ag** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ag** (100 MHz, $CDCl_3$)



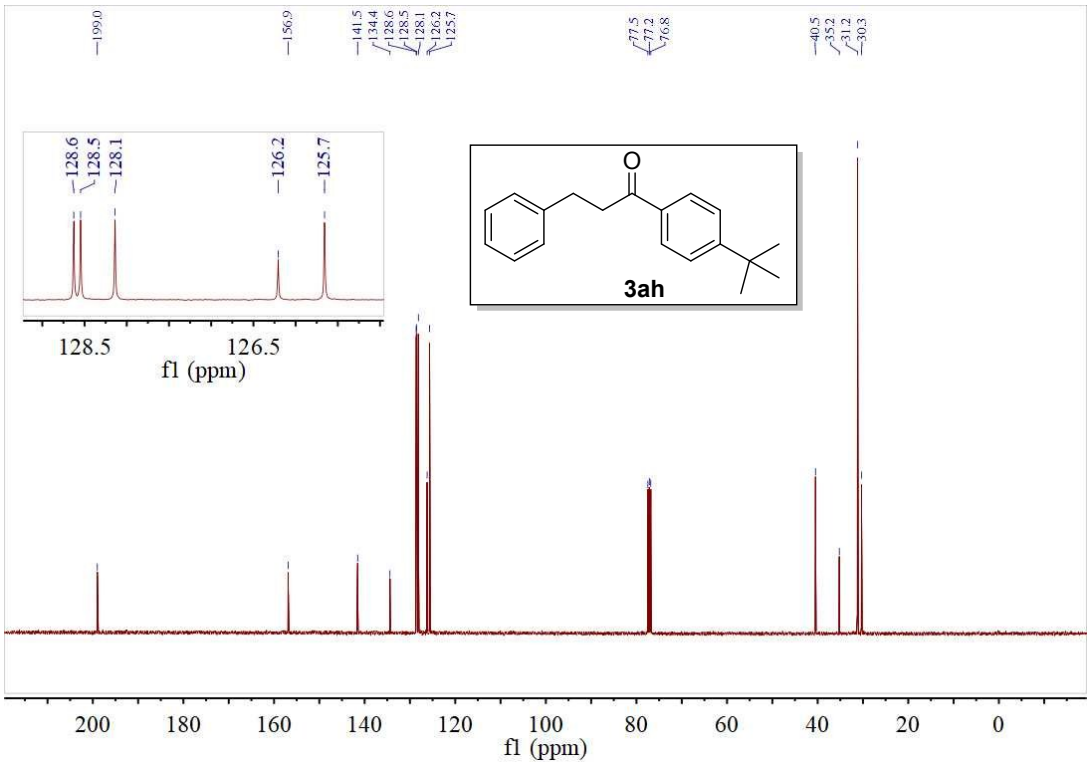
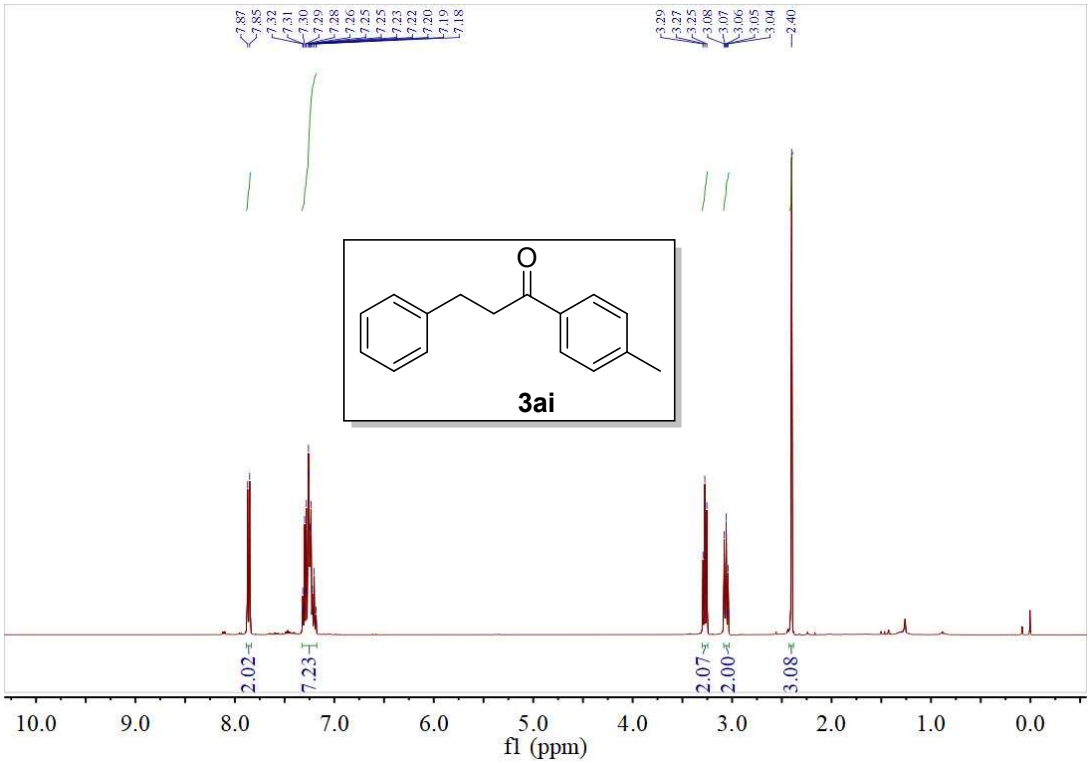


Figure S20. ^{1}H NMR of **3ah** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ah** (100 MHz, $CDCl_3$)



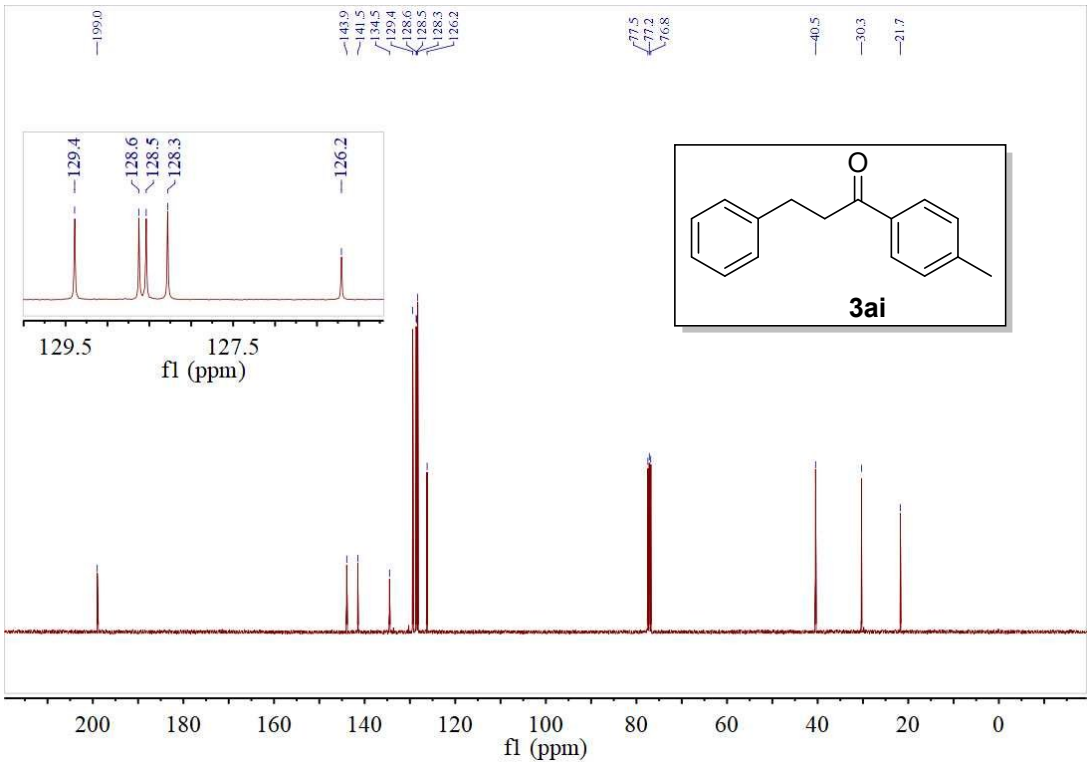
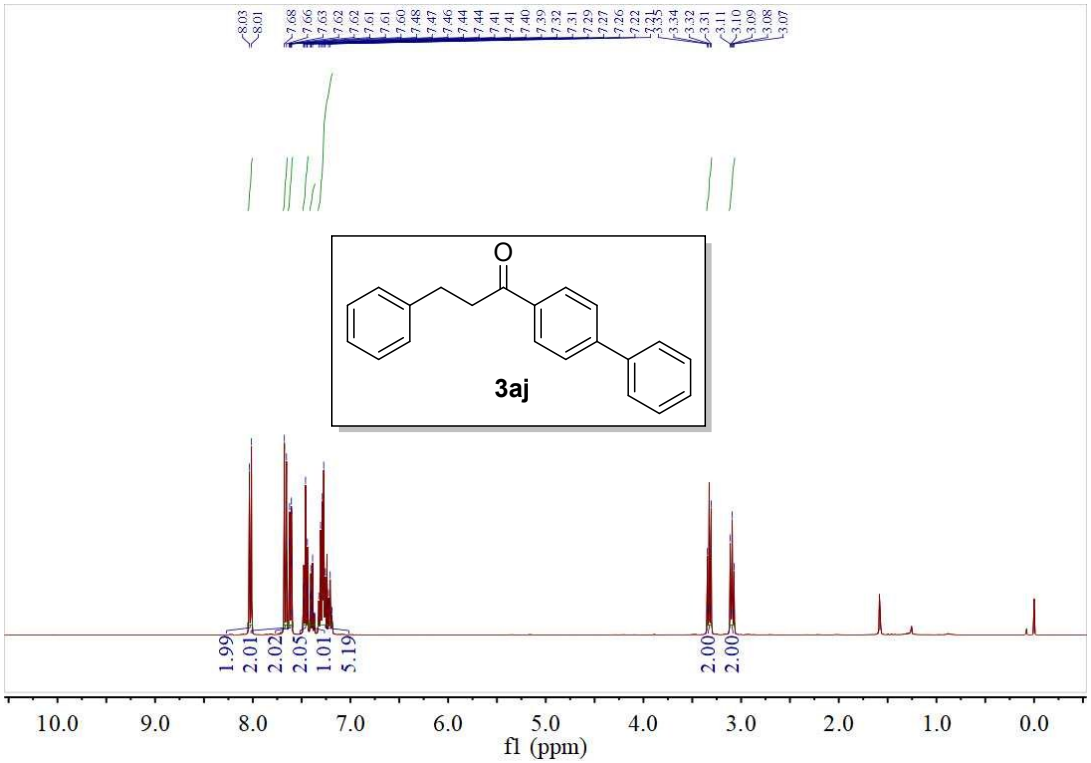


Figure S21. ^{1}H NMR of **3ai** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ai** (100 MHz, $CDCl_3$)



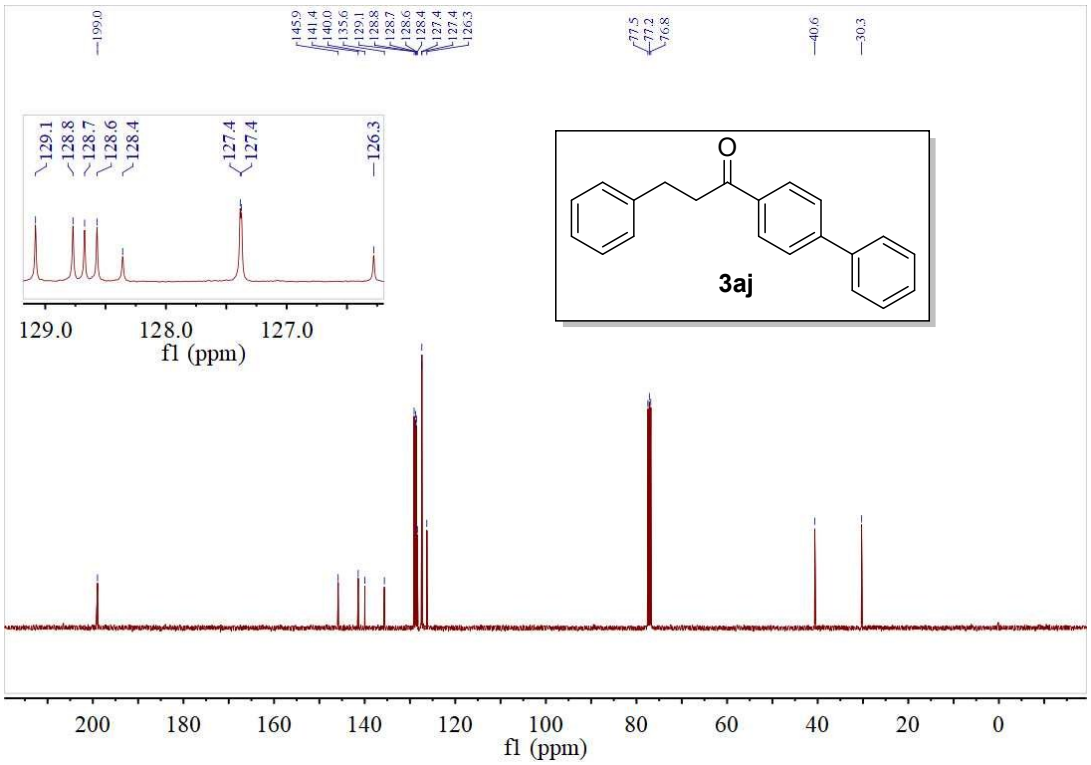
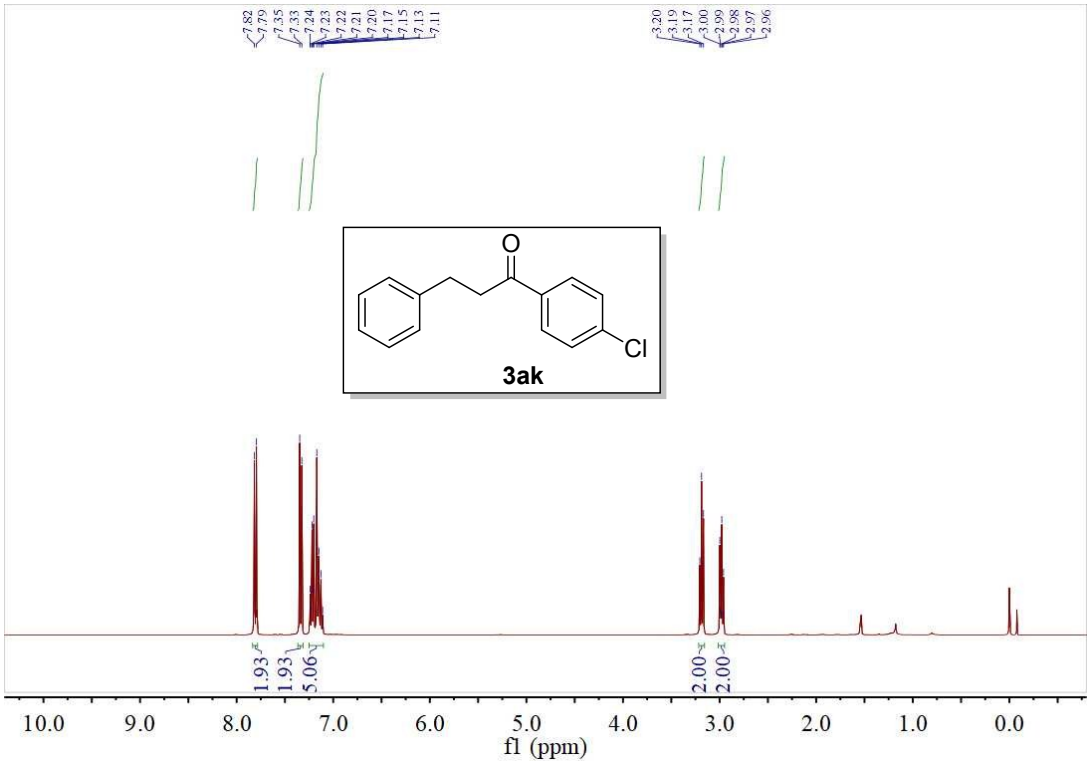


Figure S22. ^{1}H NMR of **3aj** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3aj** (100 MHz, $CDCl_3$)



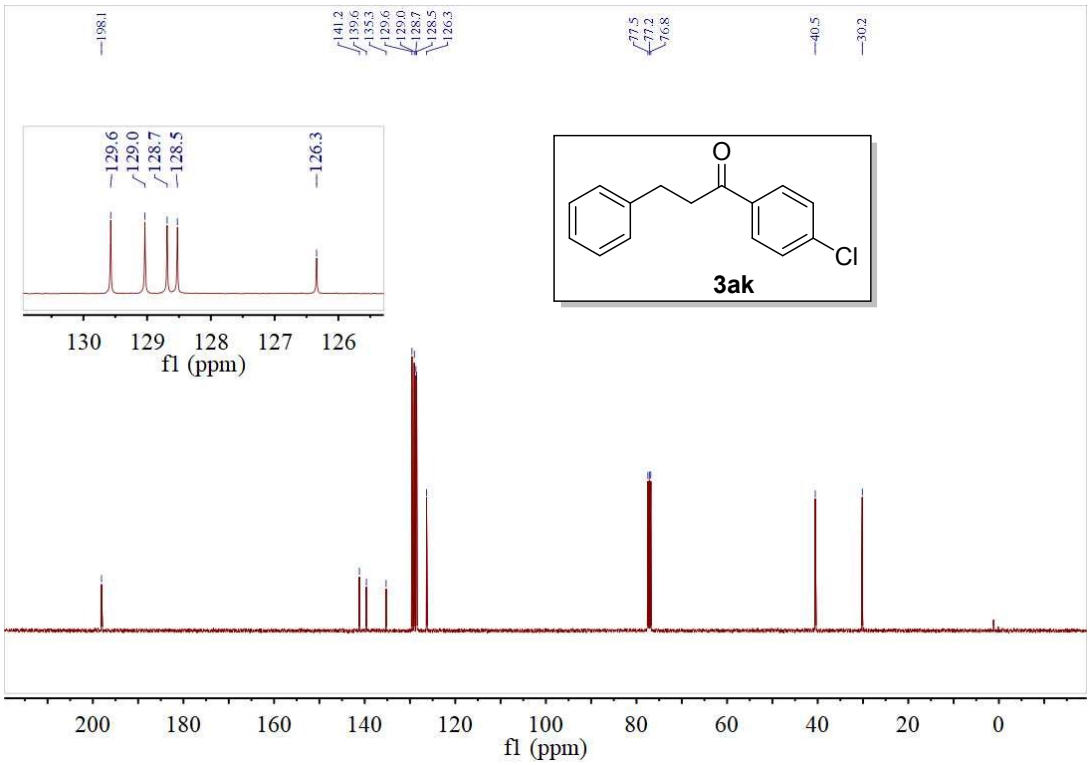
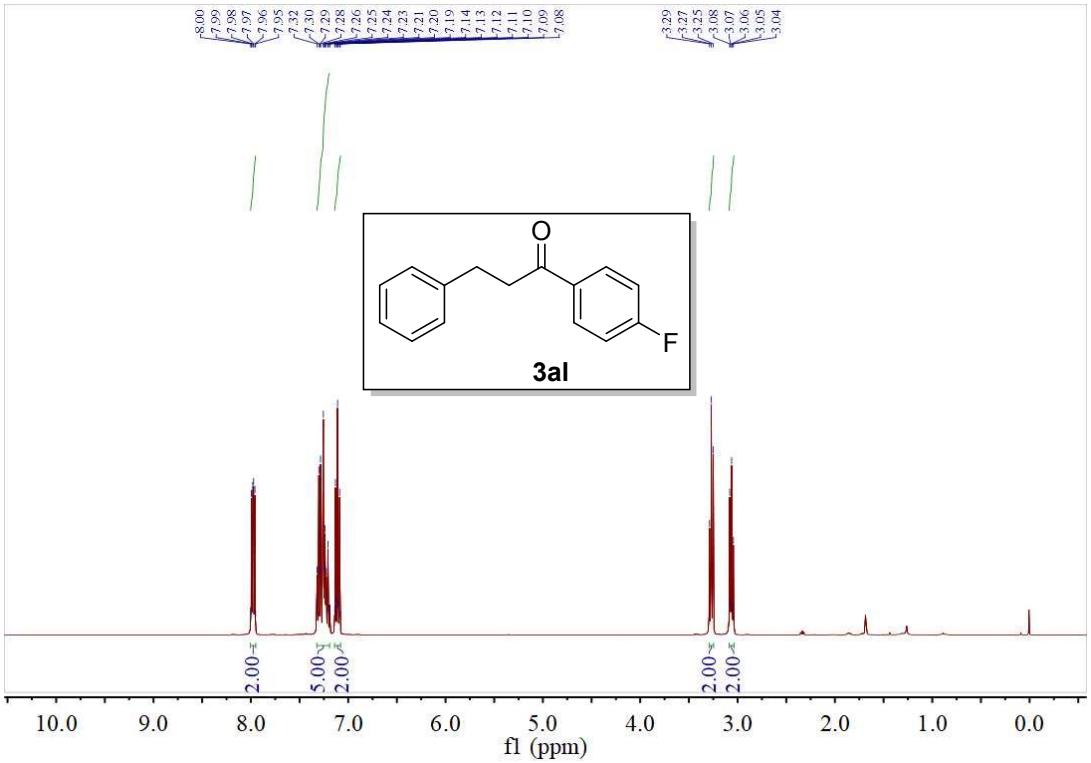
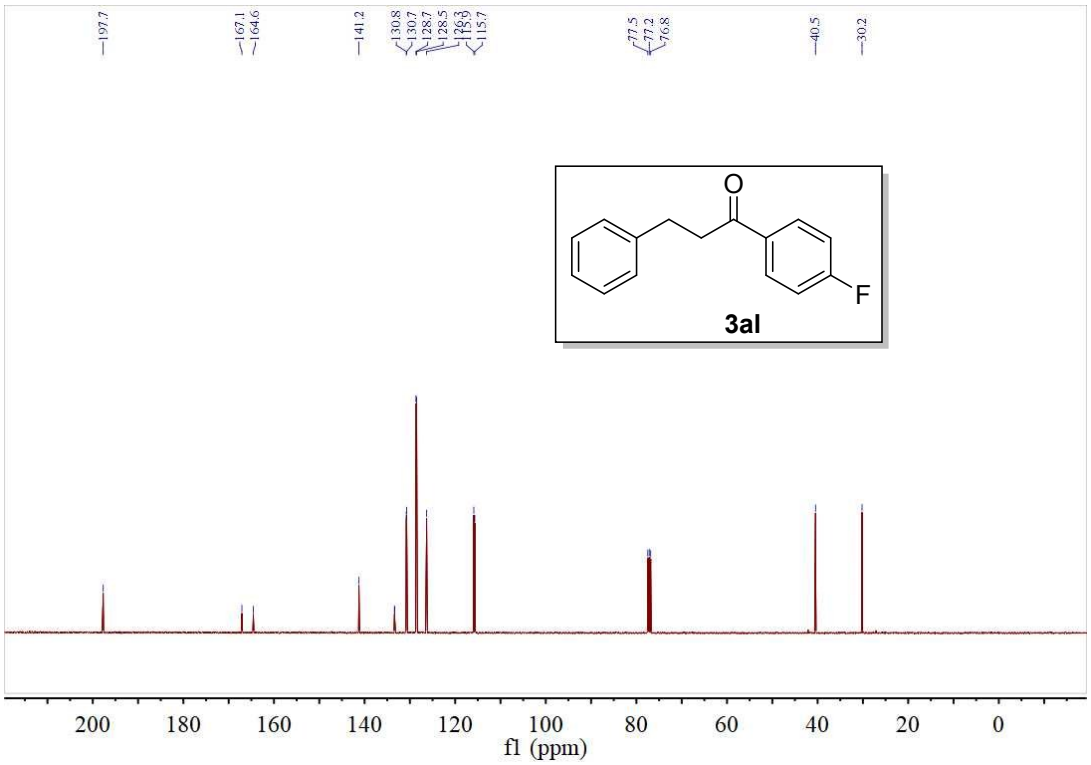


Figure S23. ^{1}H NMR of **3ak** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ak** (100 MHz, $CDCl_3$)





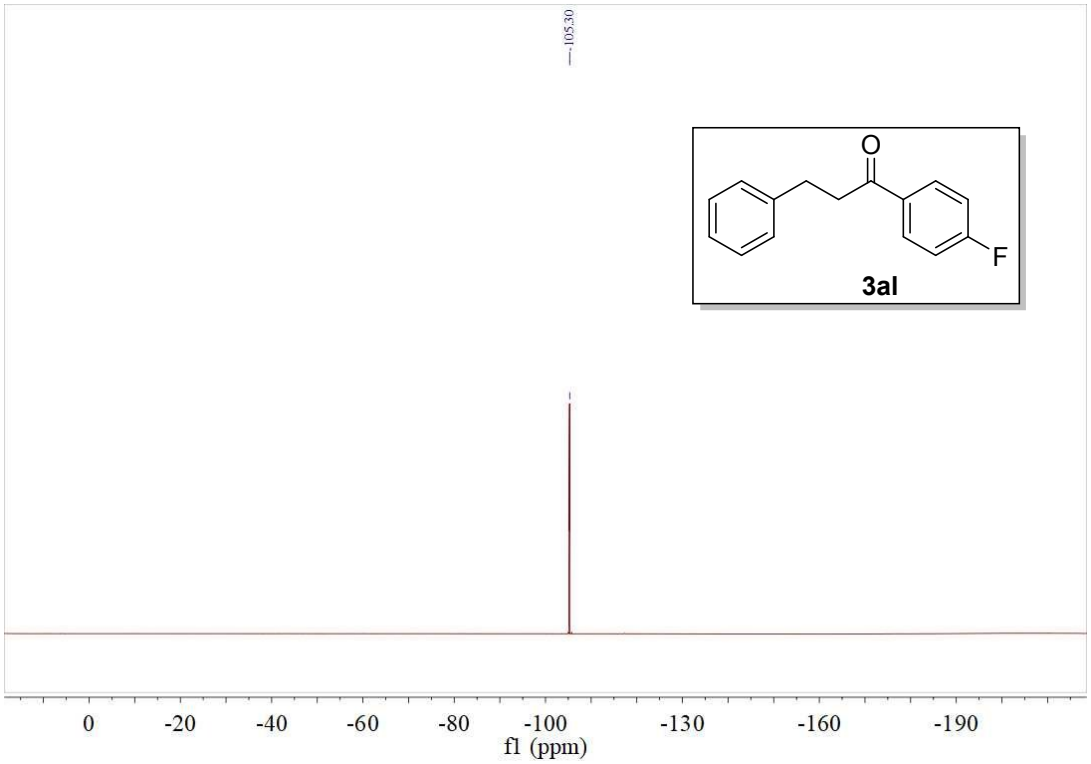
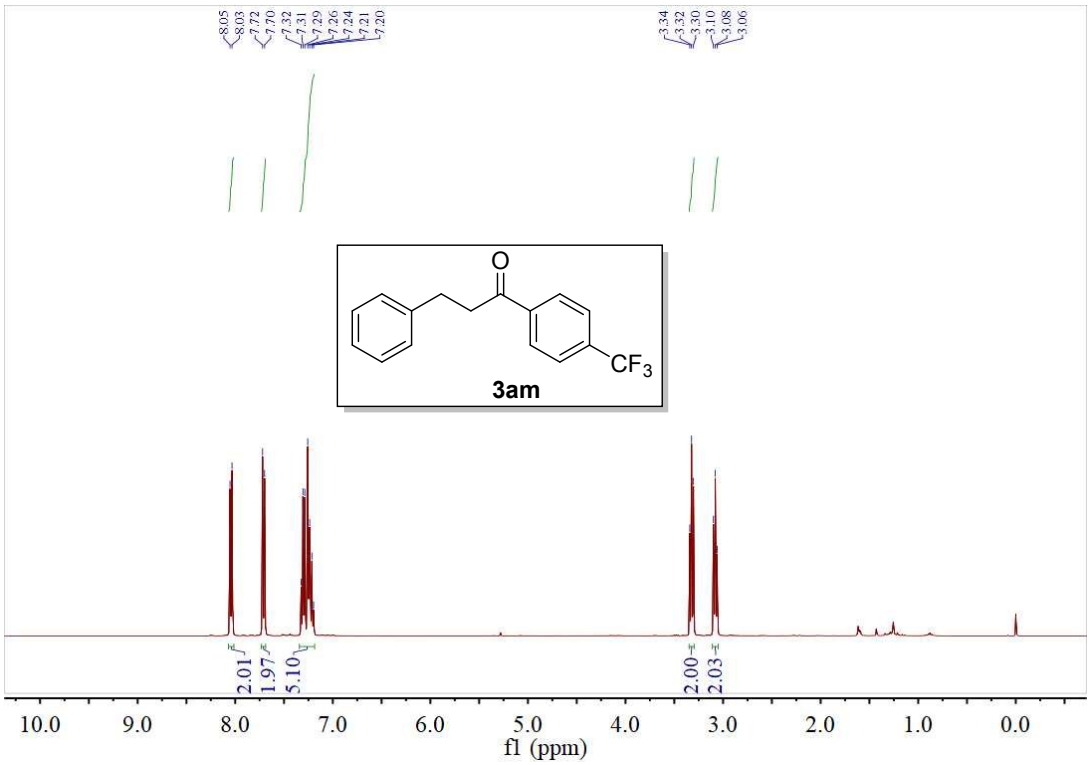
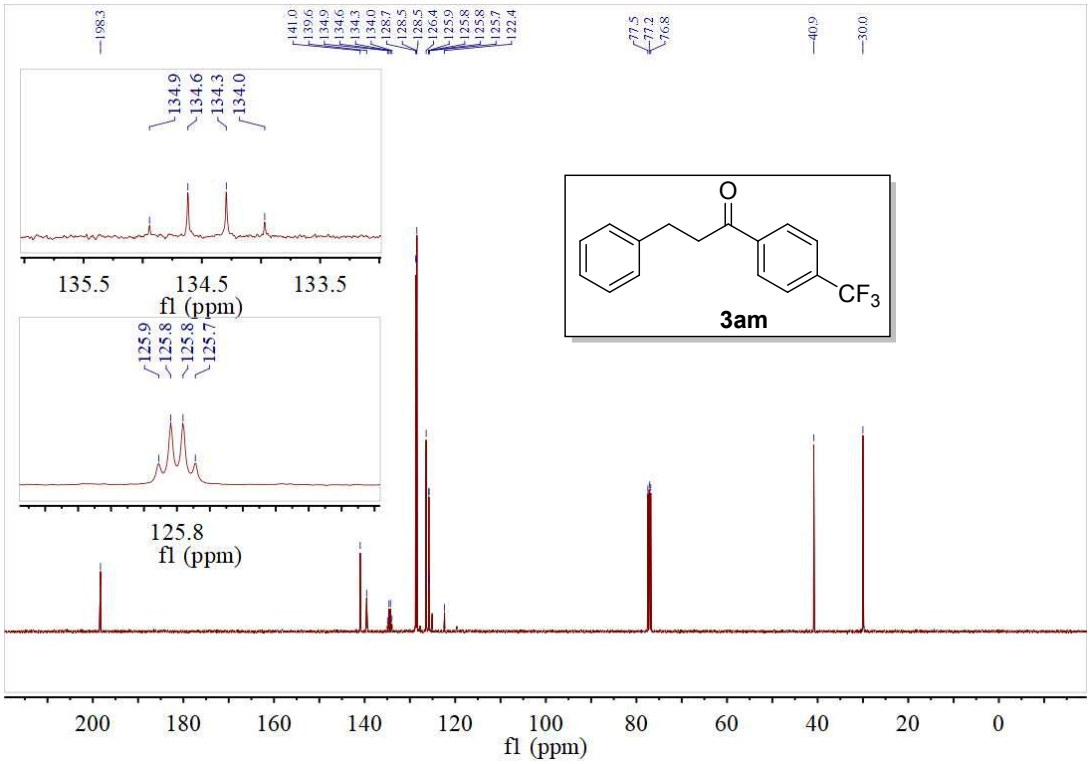


Figure S24. ^{1}H NMR of **3al** (400 MHz, $CDCl_3$), ^{13}C NMR of **3al** (100 MHz, $CDCl_3$) and ^{19}F NMR of **3al** (376 MHz, $CDCl_3$)


8.05
8.03
7.72
7.70
7.32
7.31
7.29
7.26
7.24
7.21
7.20
3.34
3.32
3.30
3.10
3.08
3.06
O
CF3
3am
2.01
1.97
5.10
2.00
2.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


198.3
141.0
139.6
134.9
134.6
134.3
134.0
128.7
128.5
126.4
125.9
125.8
125.8
125.7
122.4
77.5
77.2
76.8
40.9
30.0
134.9
134.6
134.3
134.0
135.5
134.5
133.5
f1 (ppm)
125.9
125.8
125.8
125.7
125.8
f1 (ppm)
O
CF3
3am
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

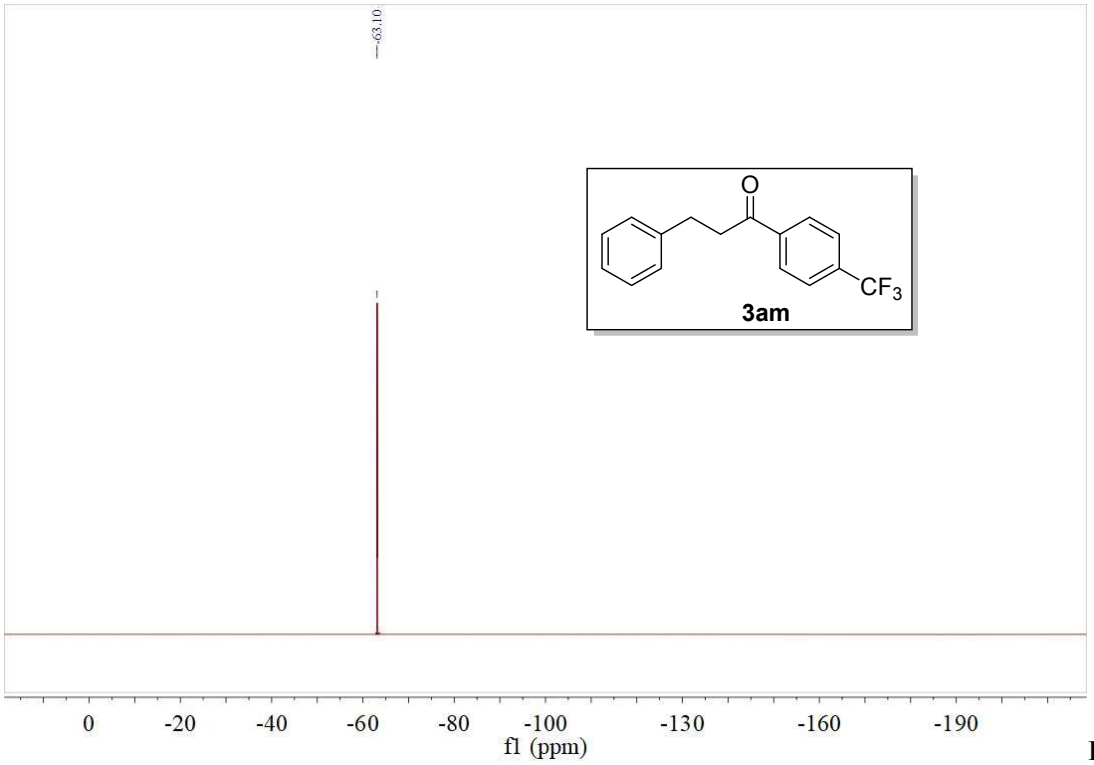
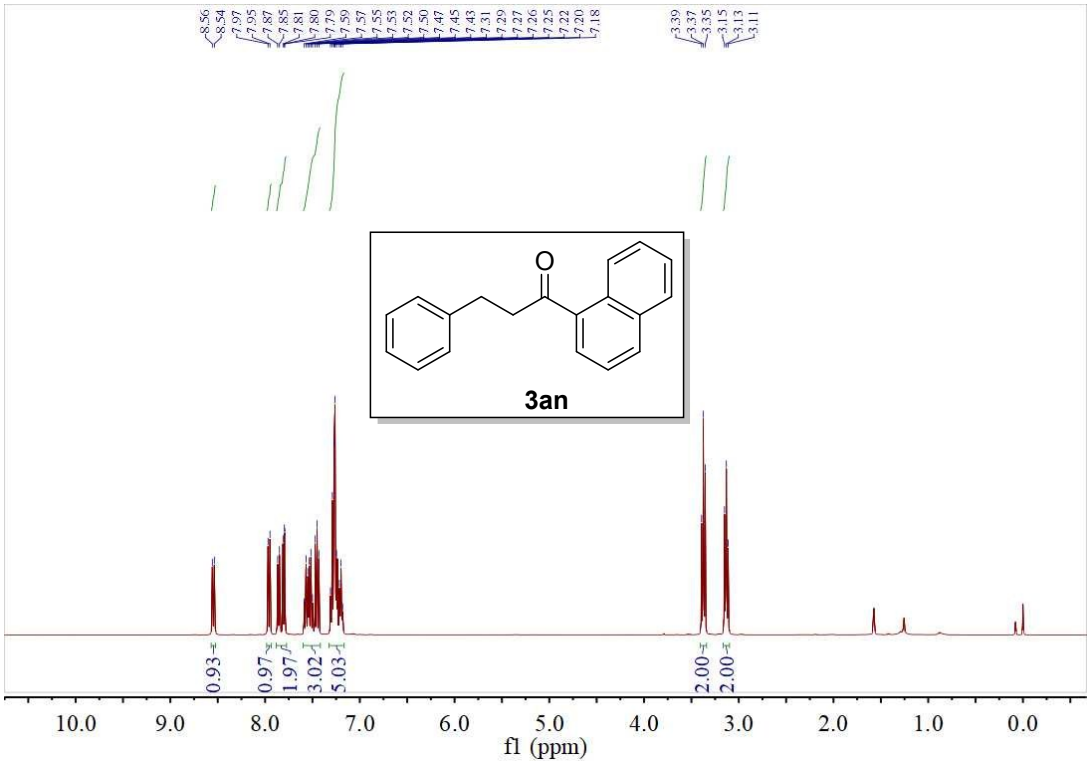


Figure S25. ^{1}H NMR of **3am** (400 MHz, $CDCl_3$), ^{13}C NMR of **3am** (100 MHz, $CDCl_3$) and ^{19}F NMR of **3am** (376 MHz, $CDCl_3$).



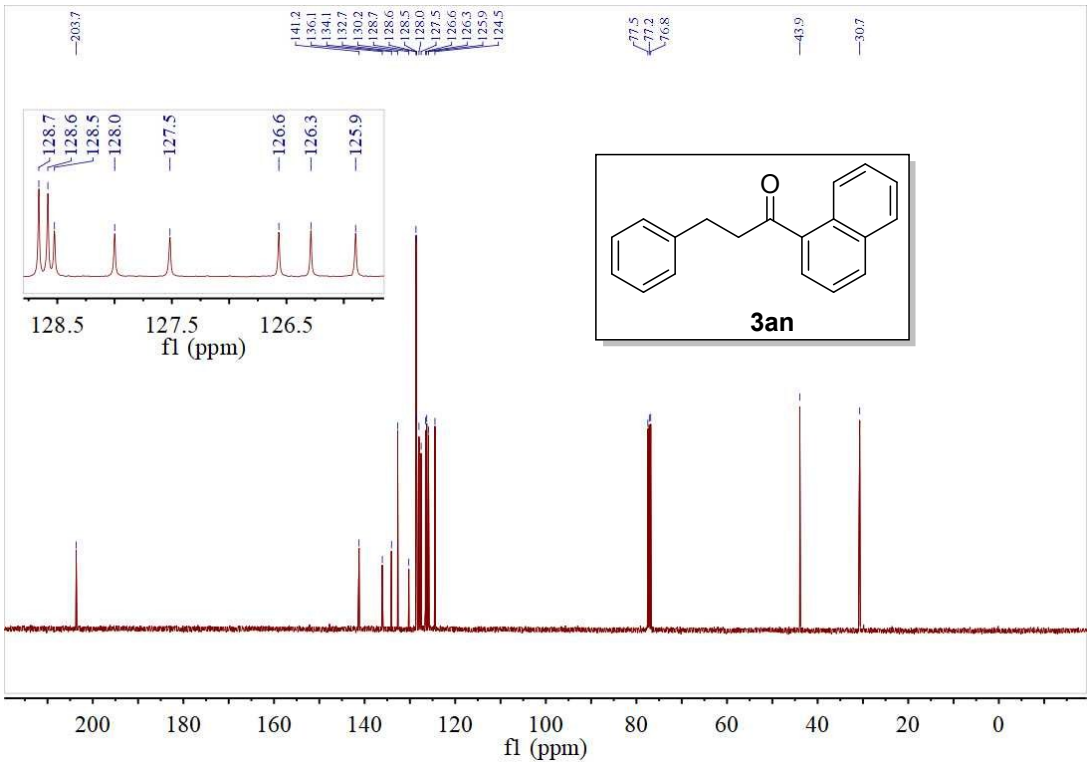
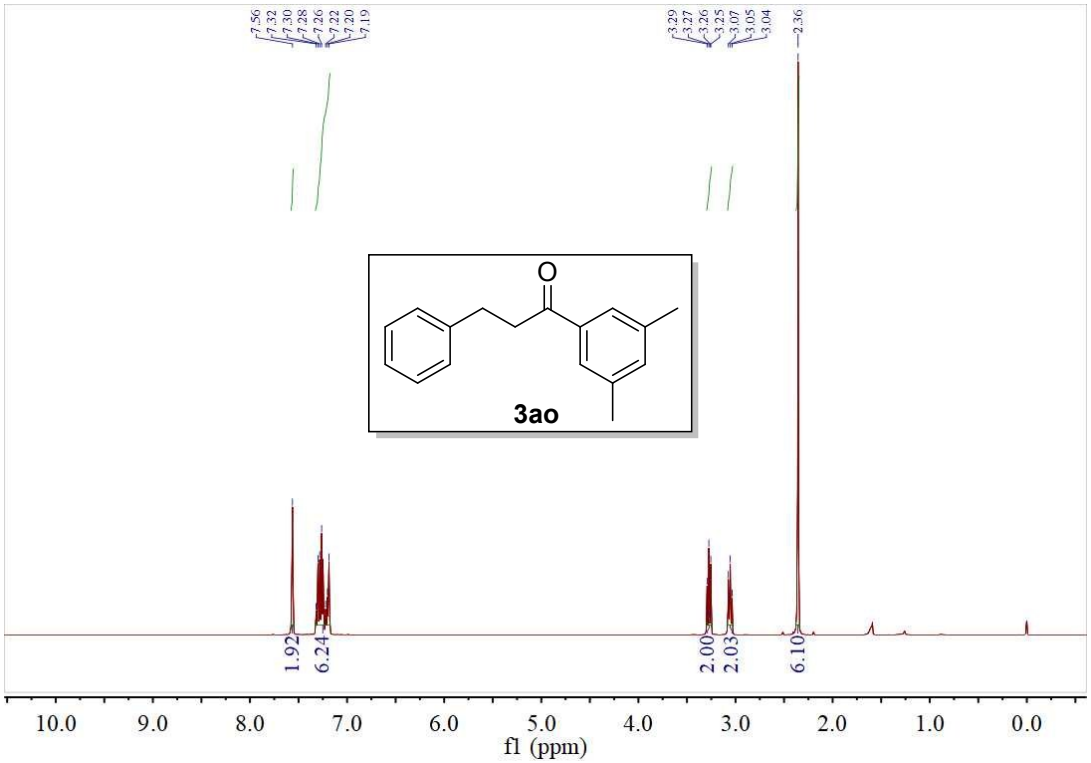


Figure S26. ^{1}H NMR of **3an** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3an** (100 MHz, $CDCl_3$)



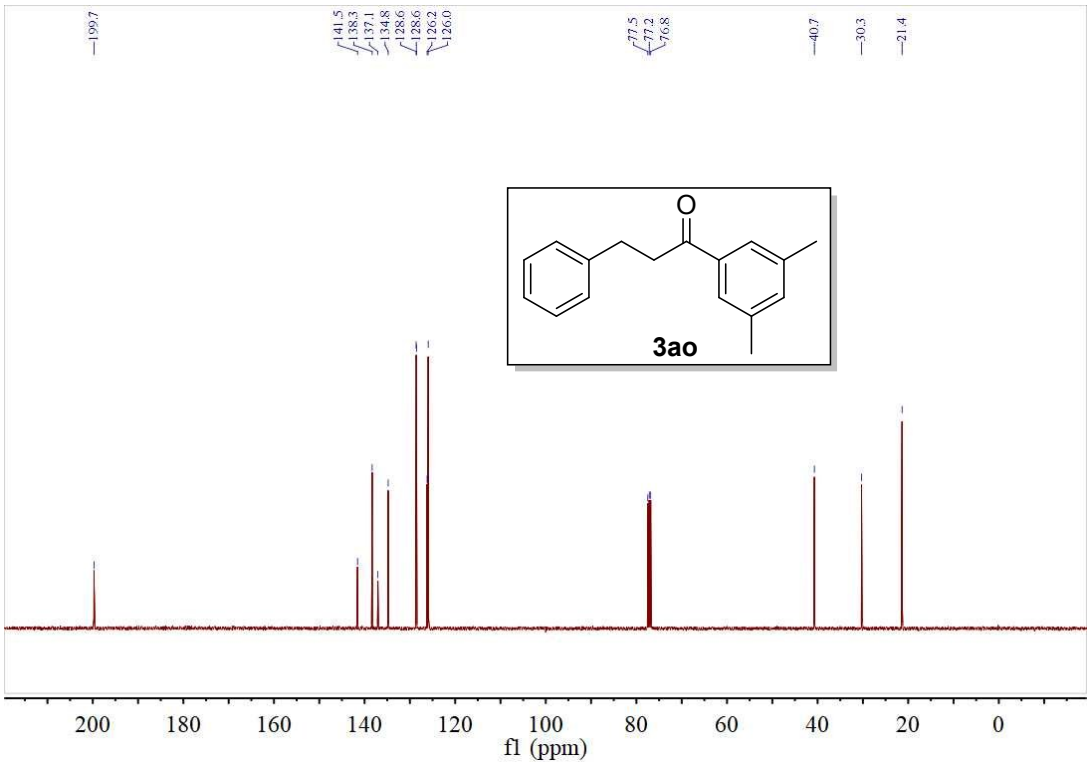
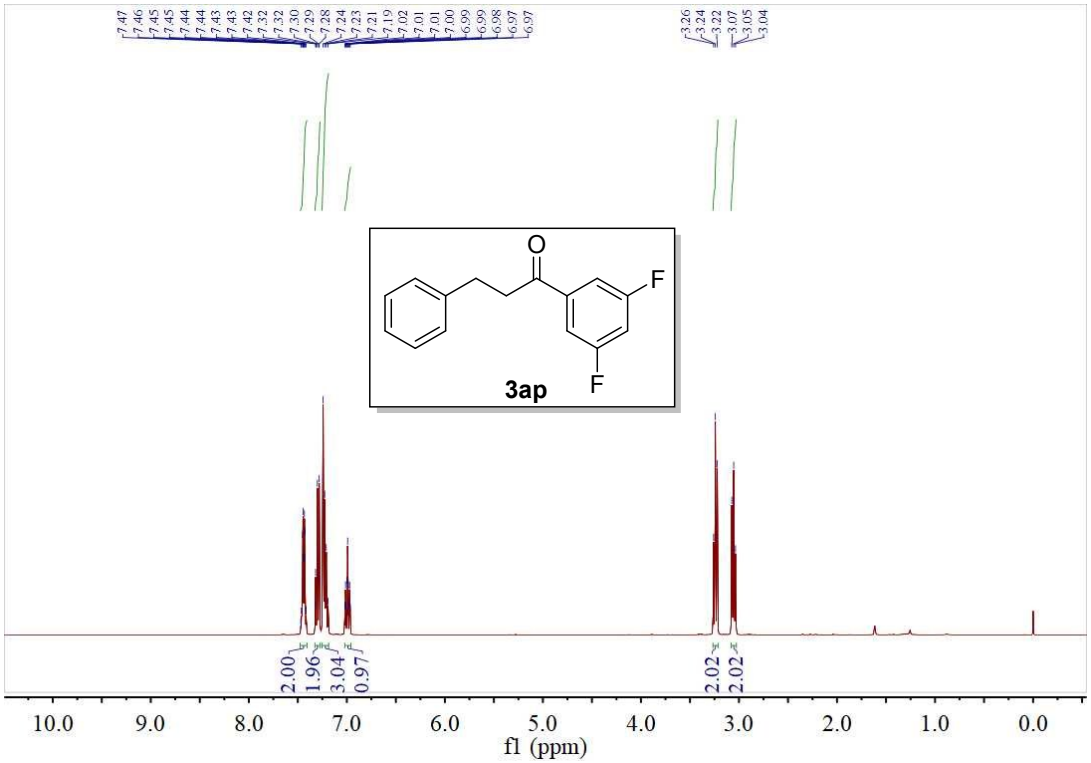


Figure S27. ^{1}H NMR of **3ao** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ao** (100 MHz, $CDCl_3$)



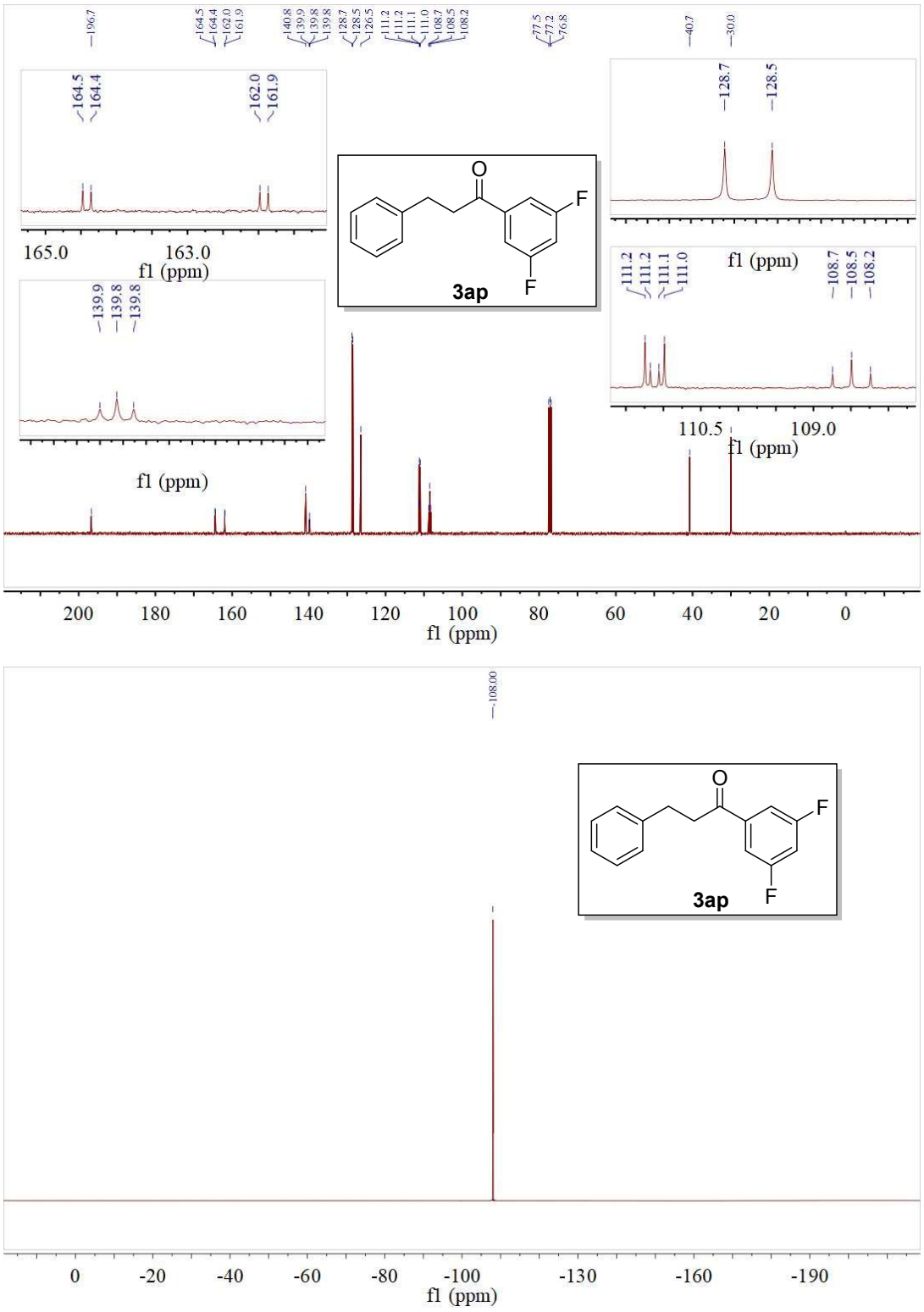


Figure S28. ^{1}H NMR of **3ap** (400 MHz, $CDCl_3$), ^{13}C NMR of **3ap** (100 MHz, $CDCl_3$) and ^{19}F NMR of **3ap** (376 MHz, $CDCl_3$)

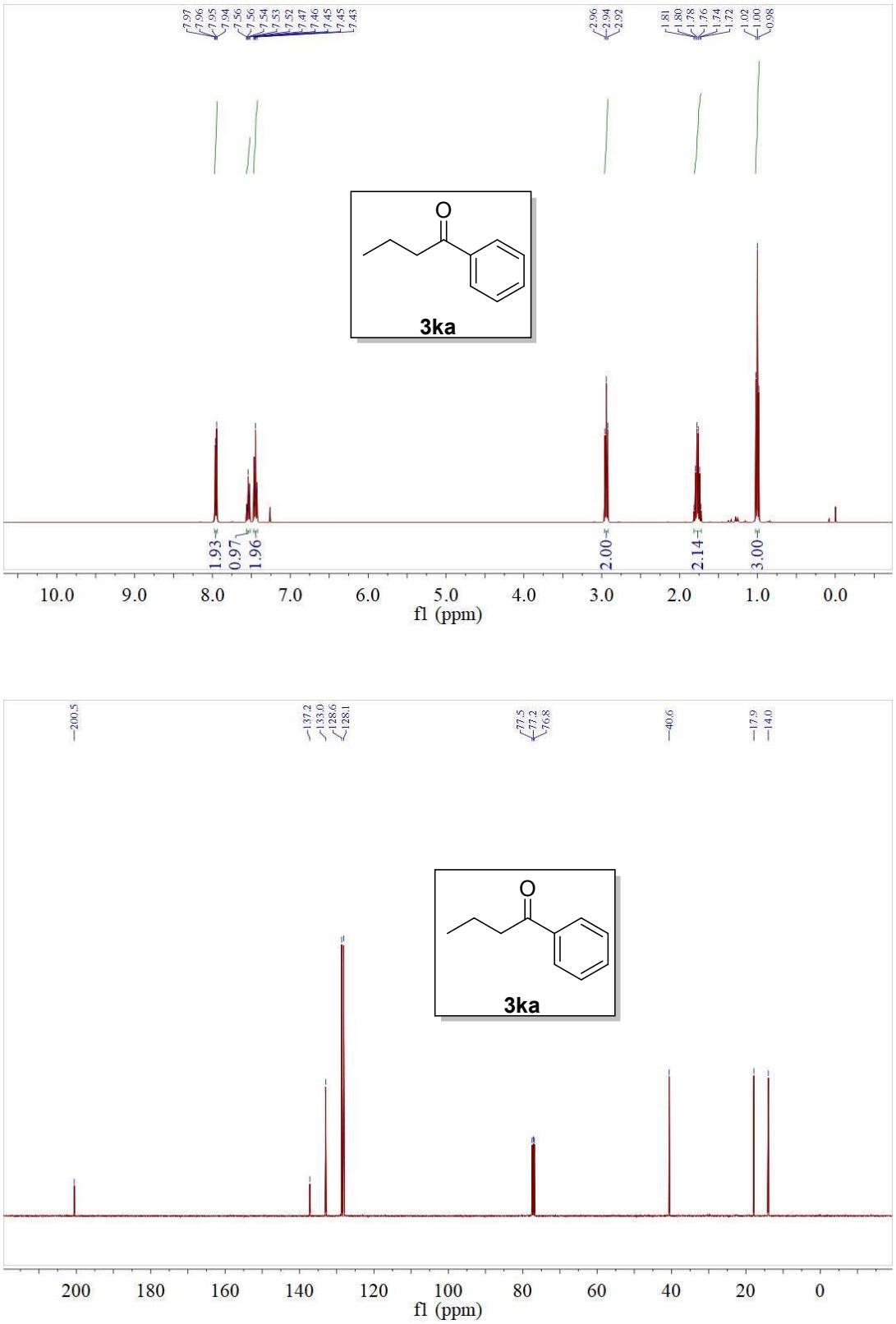


Figure S29. ^{1}H NMR of **3ka** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ka** (100 MHz, $CDCl_3$)

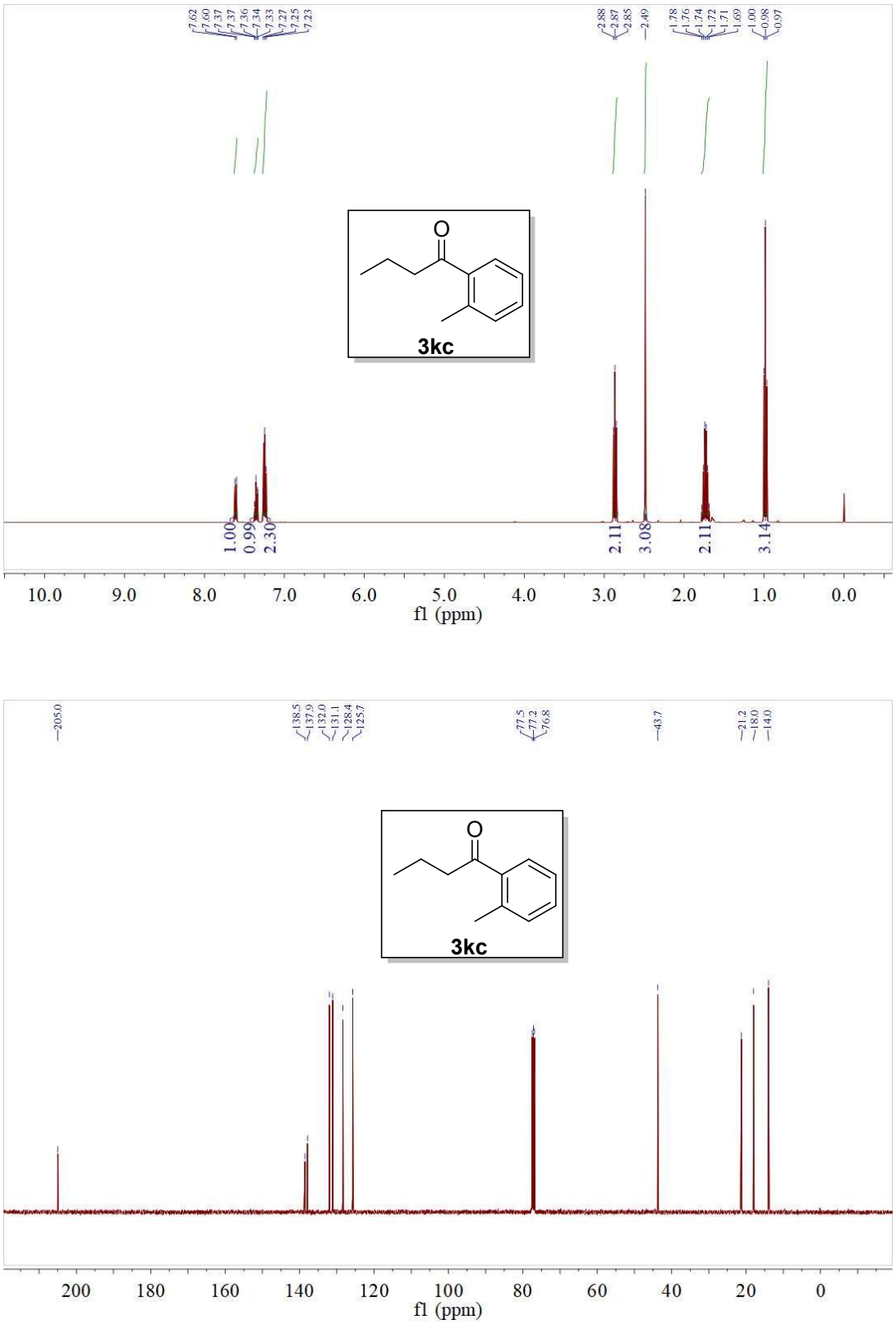


Figure S30. ^{1}H NMR of **3kc** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3kc** (100 MHz, $CDCl_3$)

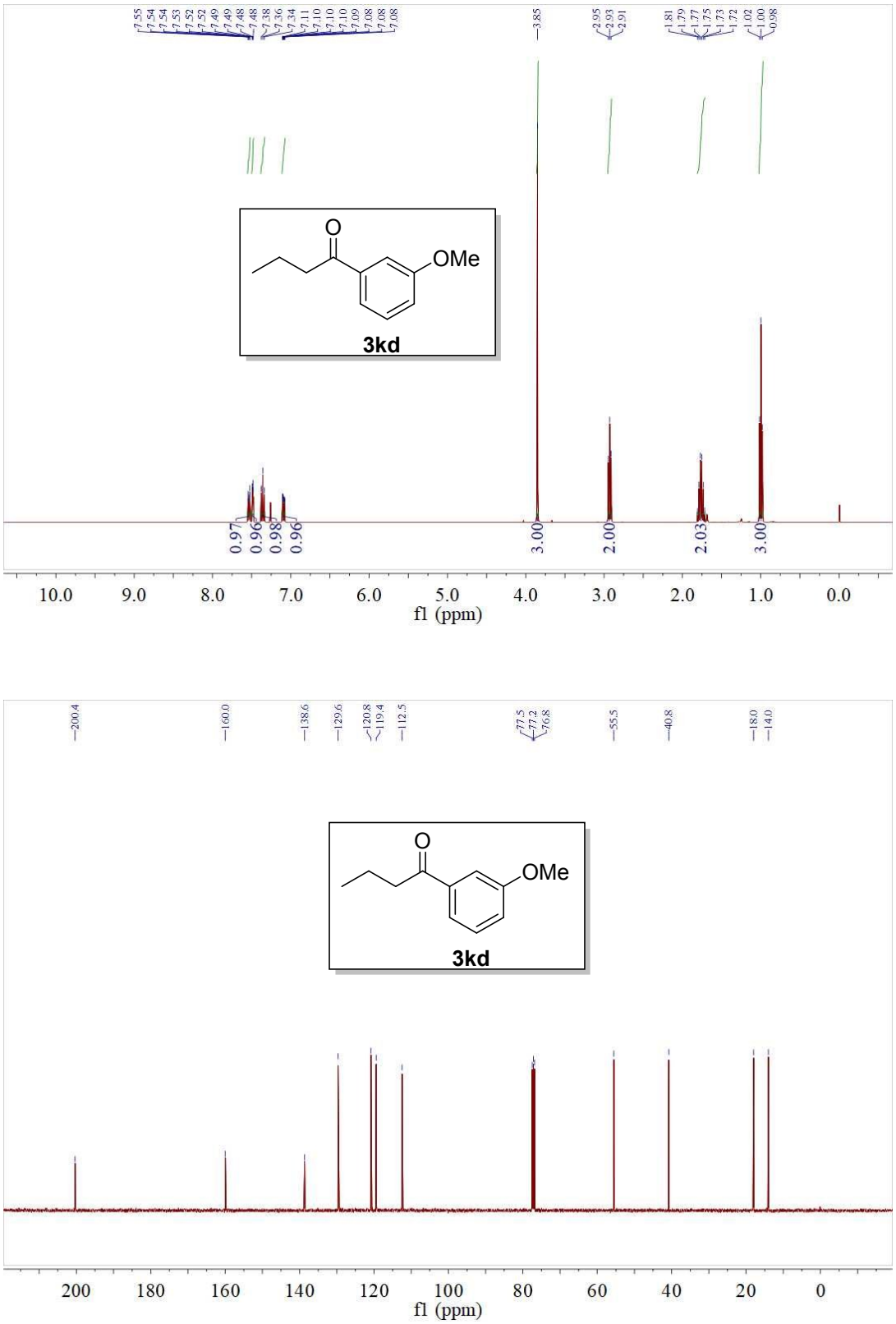


Figure S31. ^{1}H NMR of **3kd** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3kd** (100 MHz, $CDCl_3$)

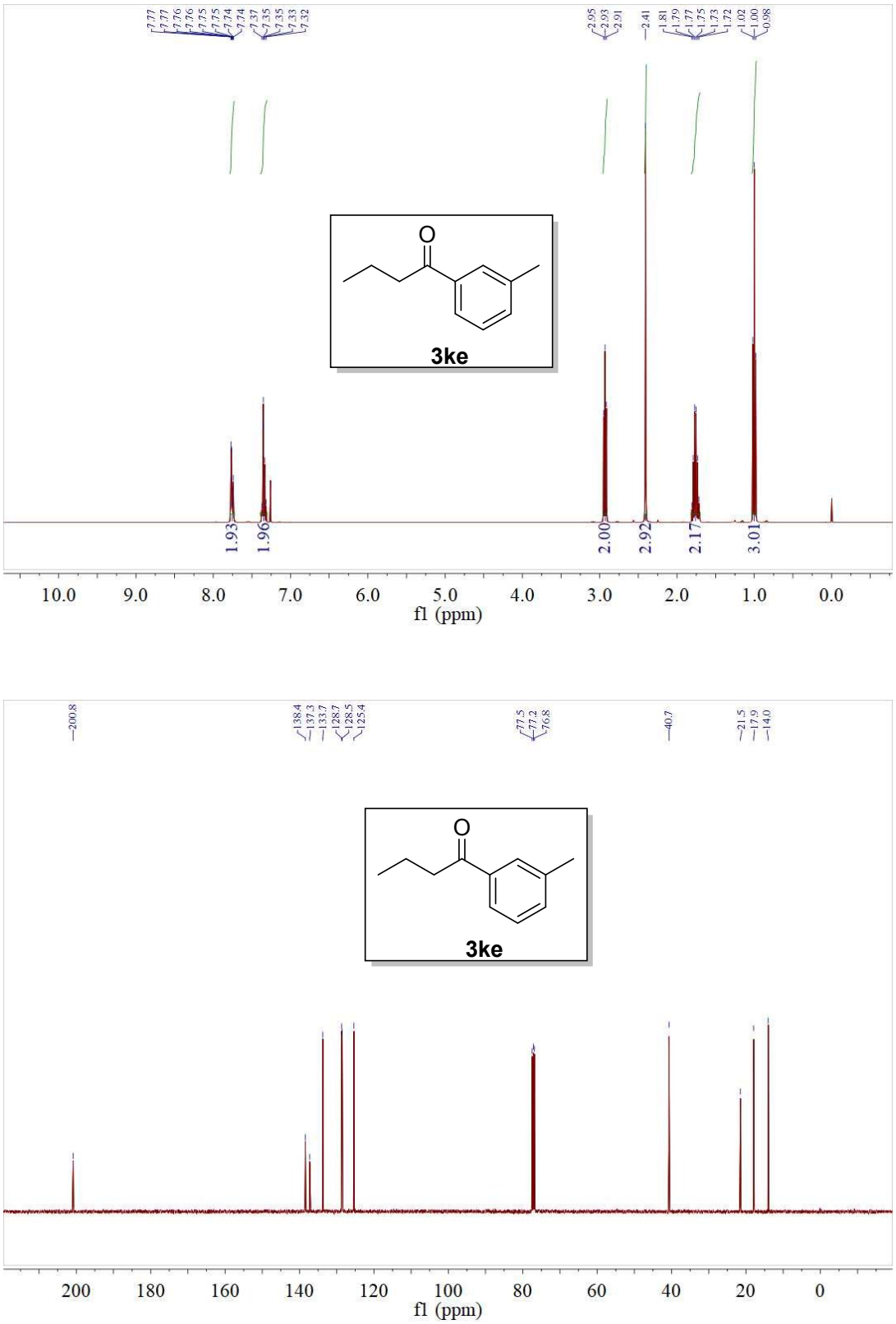


Figure S32. ^{1}H NMR of **3ke** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ke** (100 MHz, $CDCl_3$)

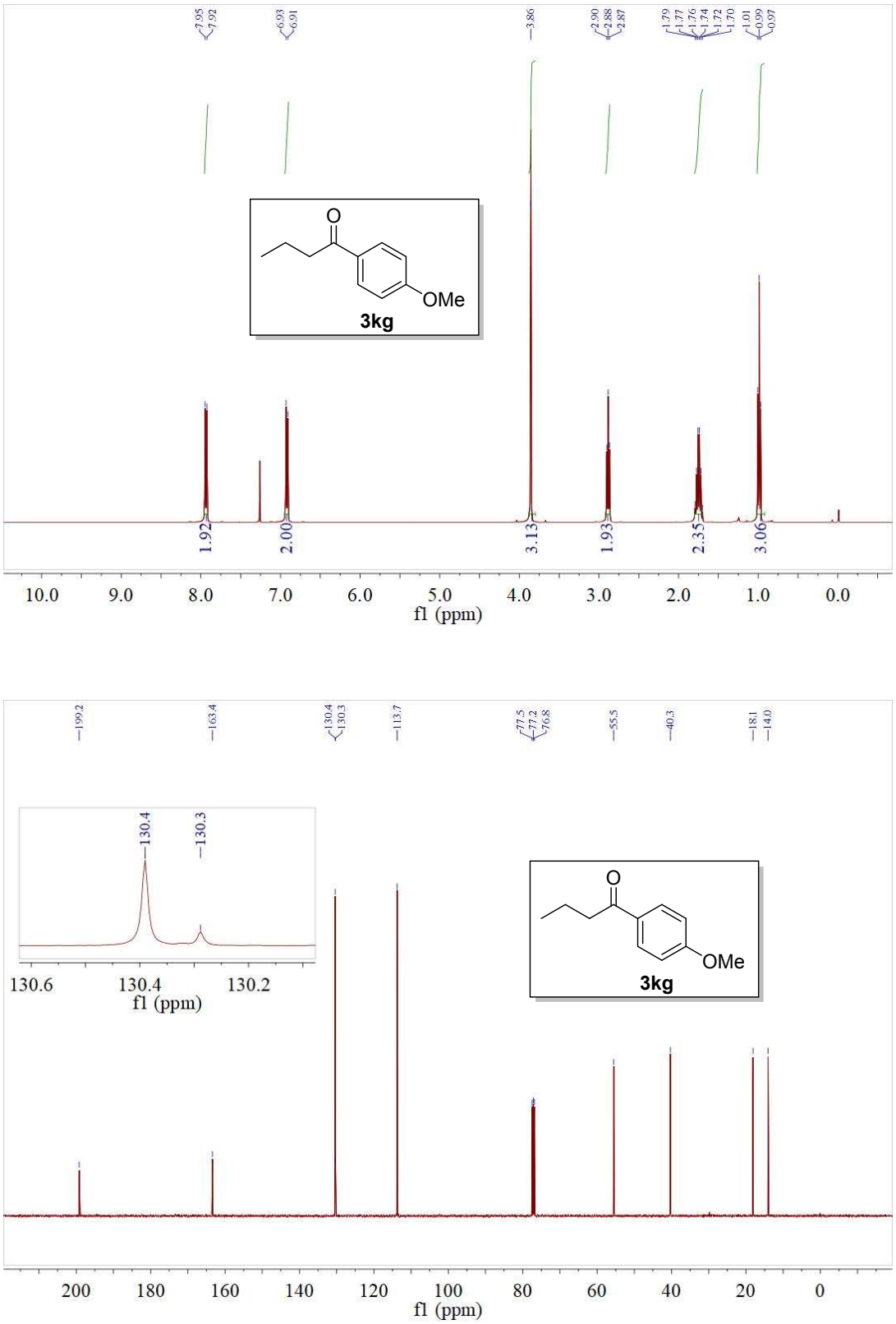


Figure S33. ^{1}H NMR of **3kg** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3kg** (100 MHz, $CDCl_3$)

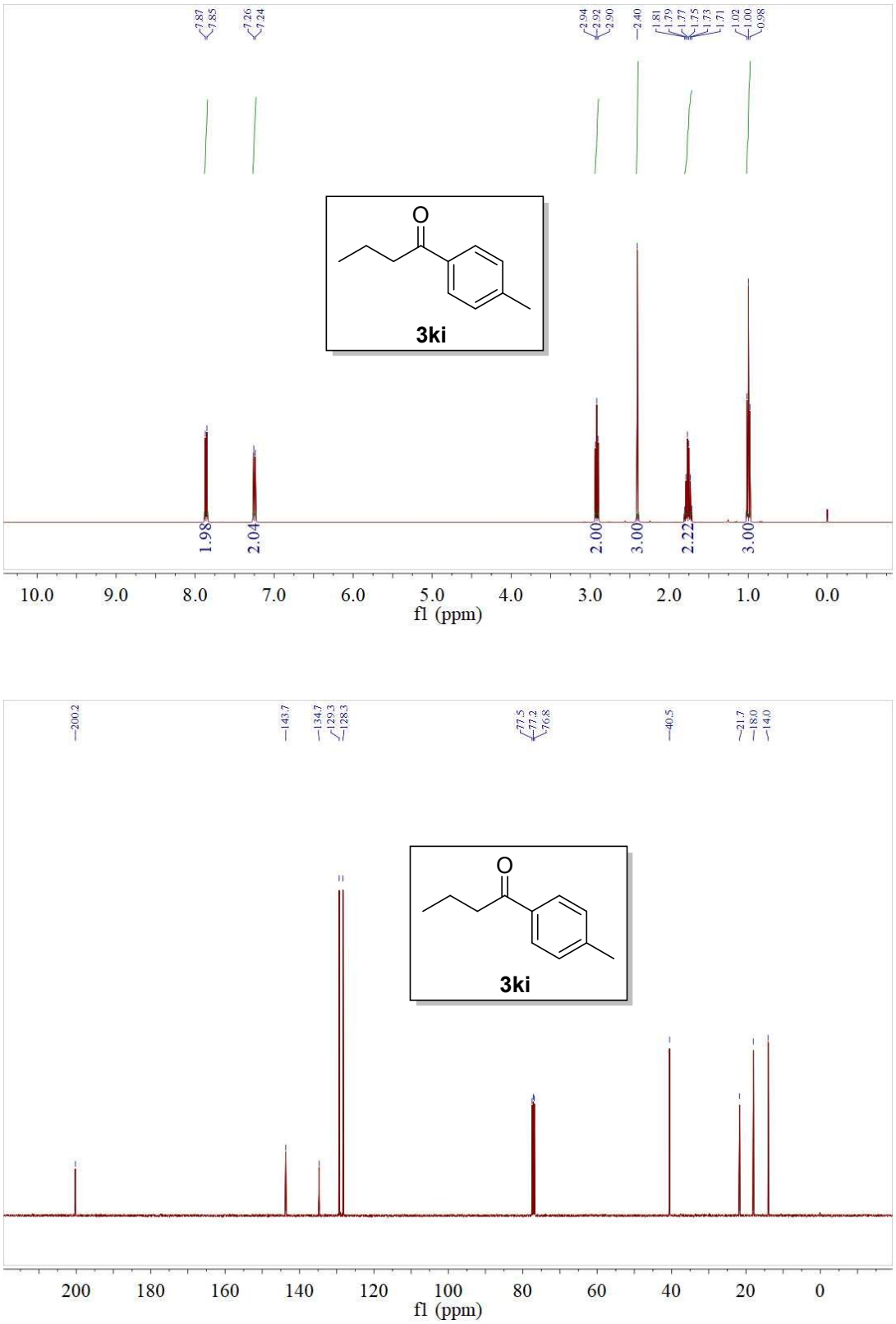


Figure S34. ^{1}H NMR of **3ki** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ki** (100 MHz, $CDCl_3$)

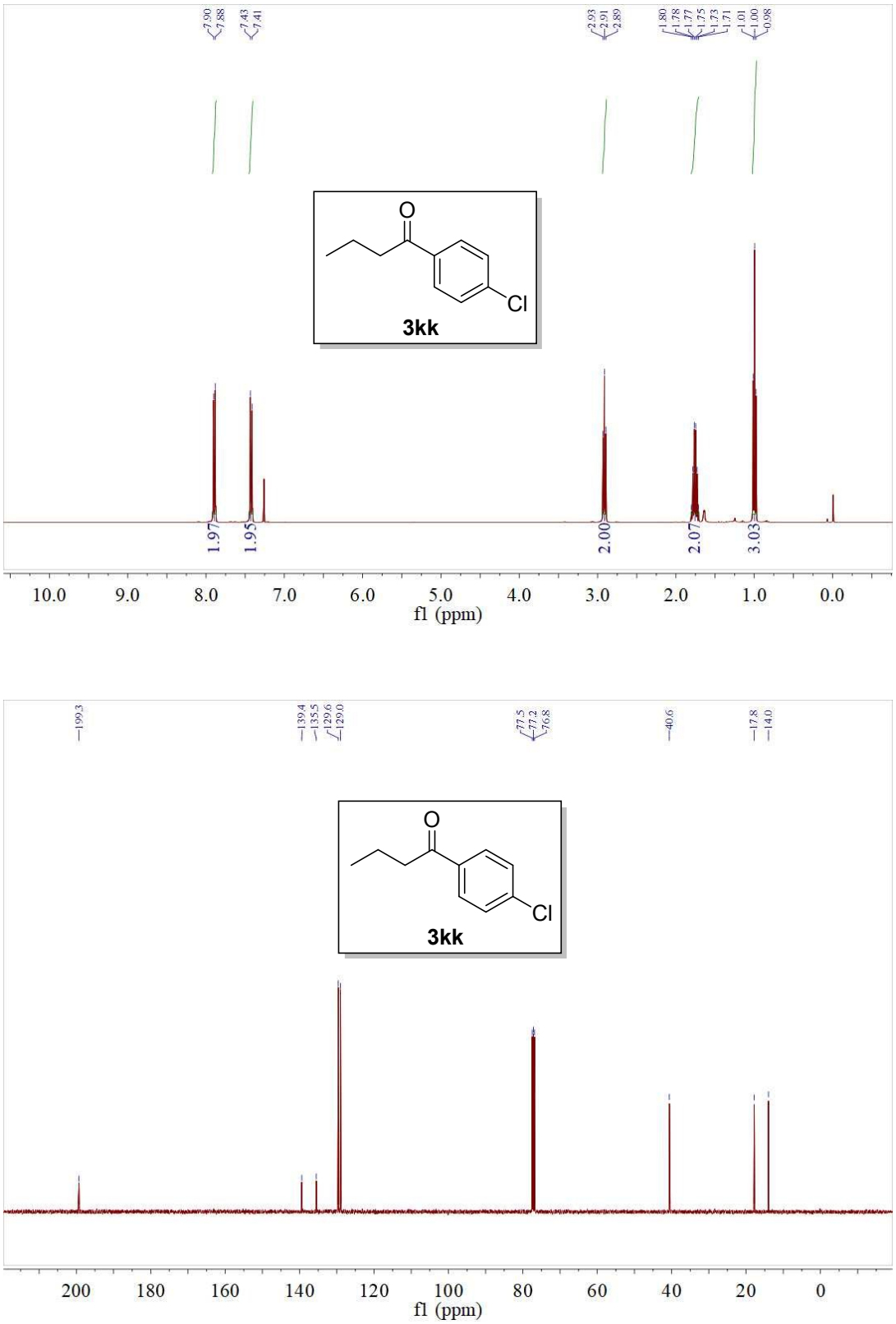
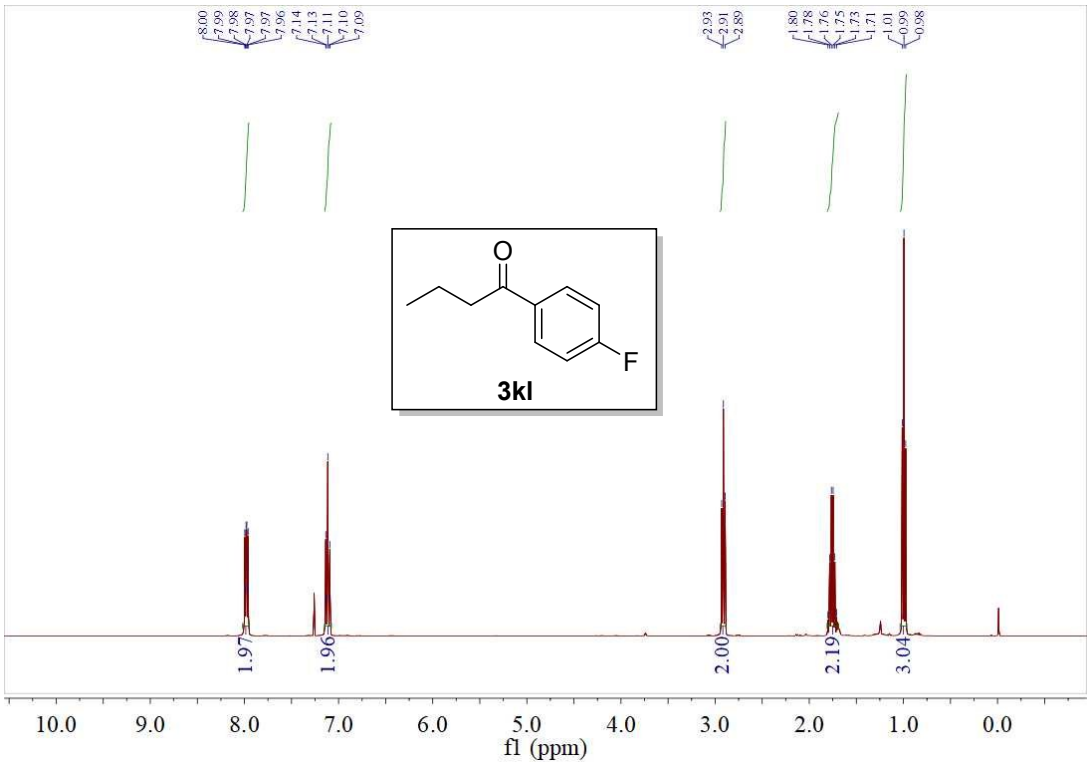
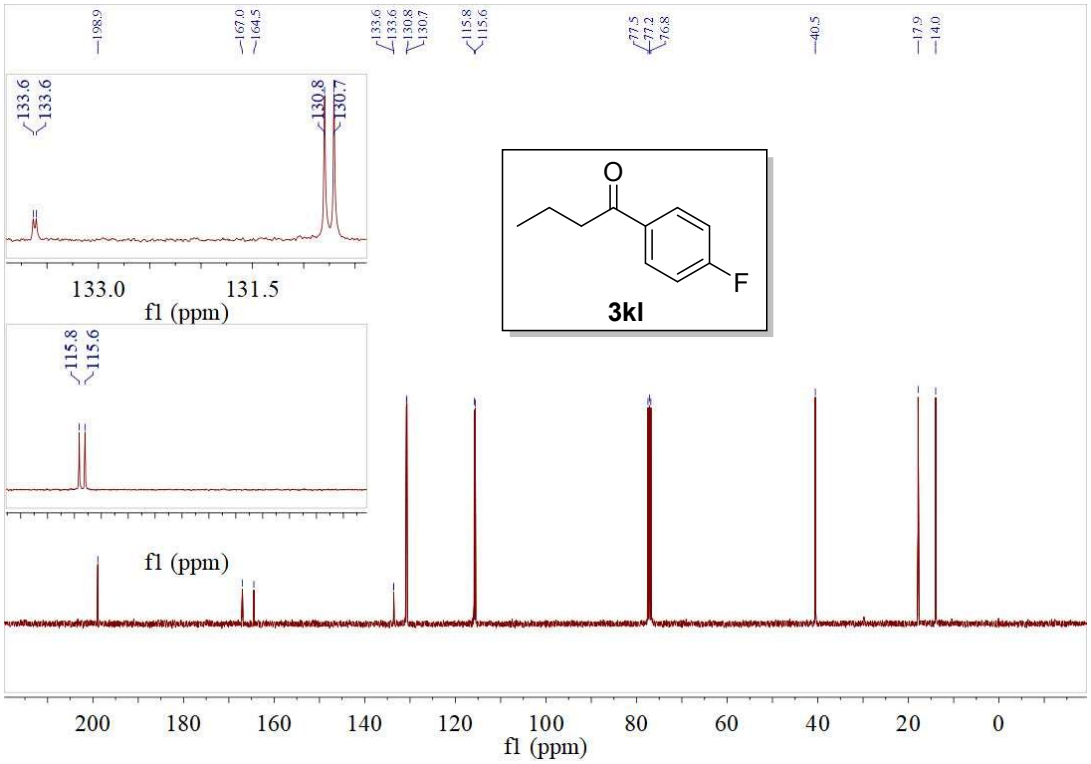


Figure S35. ^{1}H NMR of **3kk** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3kk** (100 MHz, $CDCl_3$)


8.00
7.99
7.98
7.97
7.97
7.96
7.14
7.13
7.11
7.10
7.09
2.93
2.91
2.89
1.80
1.78
1.76
1.75
1.73
1.71
1.01
0.99
0.98
O
F
3kl
1.97
1.96
2.00
2.19
3.04
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


198.9
167.0
164.5
133.6
133.6
130.8
130.7
115.8
115.6
77.5
77.2
76.8
40.5
17.9
14.0
133.6
133.6
130.8
130.7
133.0
131.5
f1 (ppm)
115.8
115.6
O
F
3kl
f1 (ppm)
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

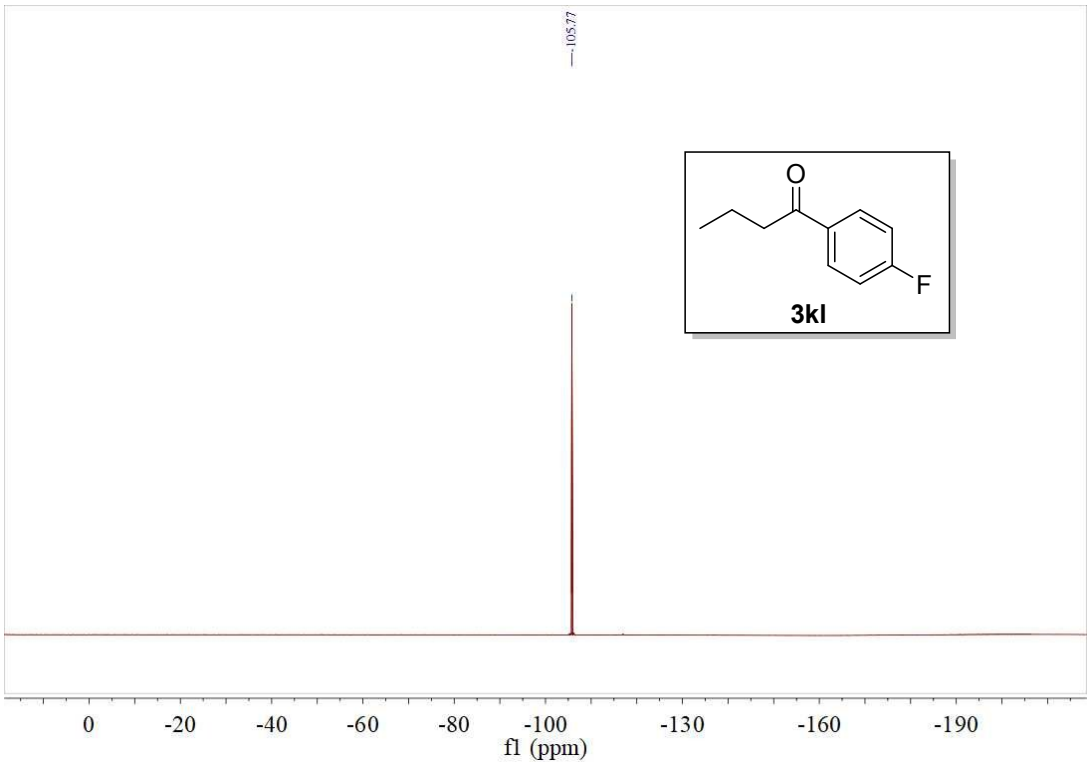
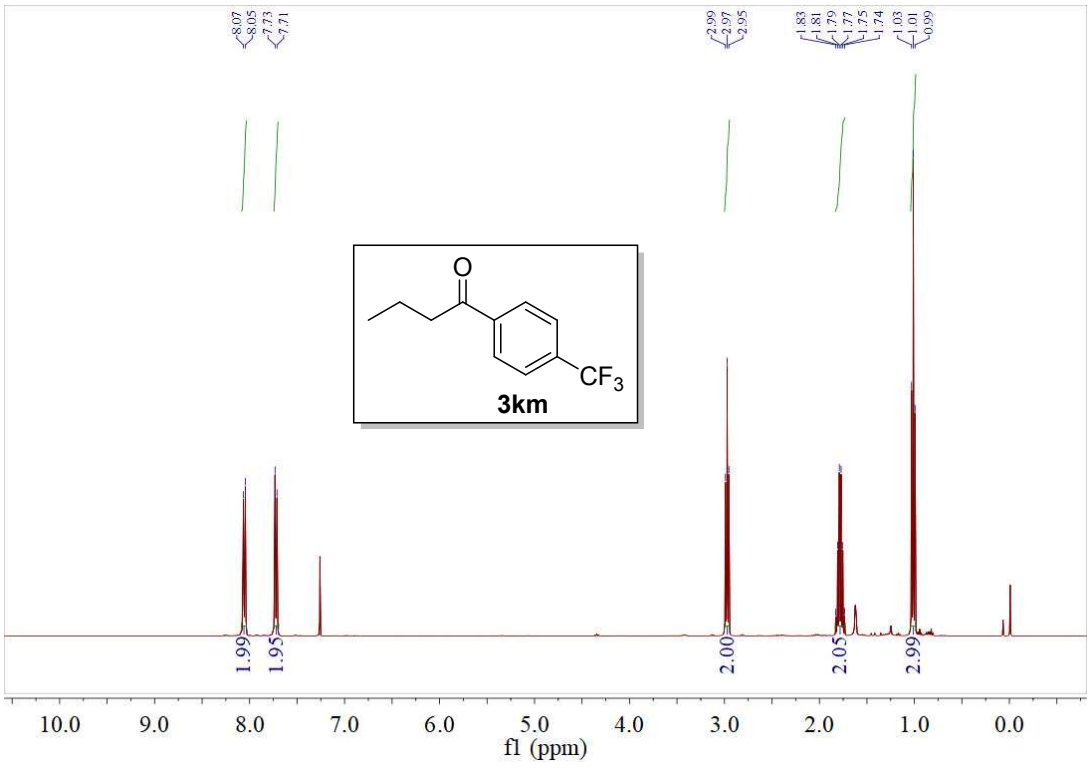


Figure S36. ^{1}H NMR of **3kl** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3kl** (100 MHz, $CDCl_3$) and ^{19}F NMR of **3kl** (376 MHz, $CDCl_3$)



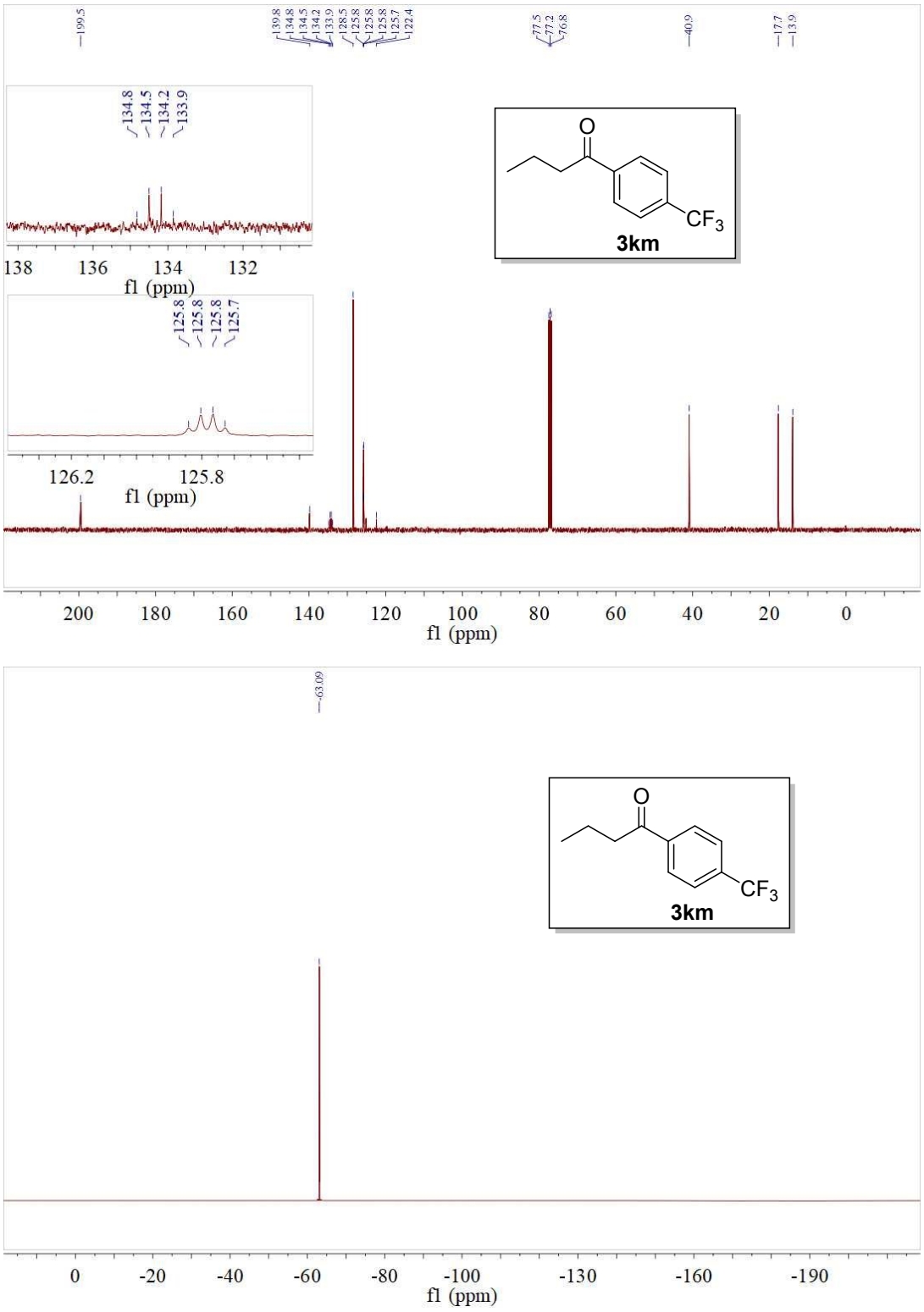


Figure S37. ^{1}H NMR of **3km** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3km** (100 MHz, $CDCl_3$) and ^{19}F NMR of **3km** (376 MHz, $CDCl_3$)

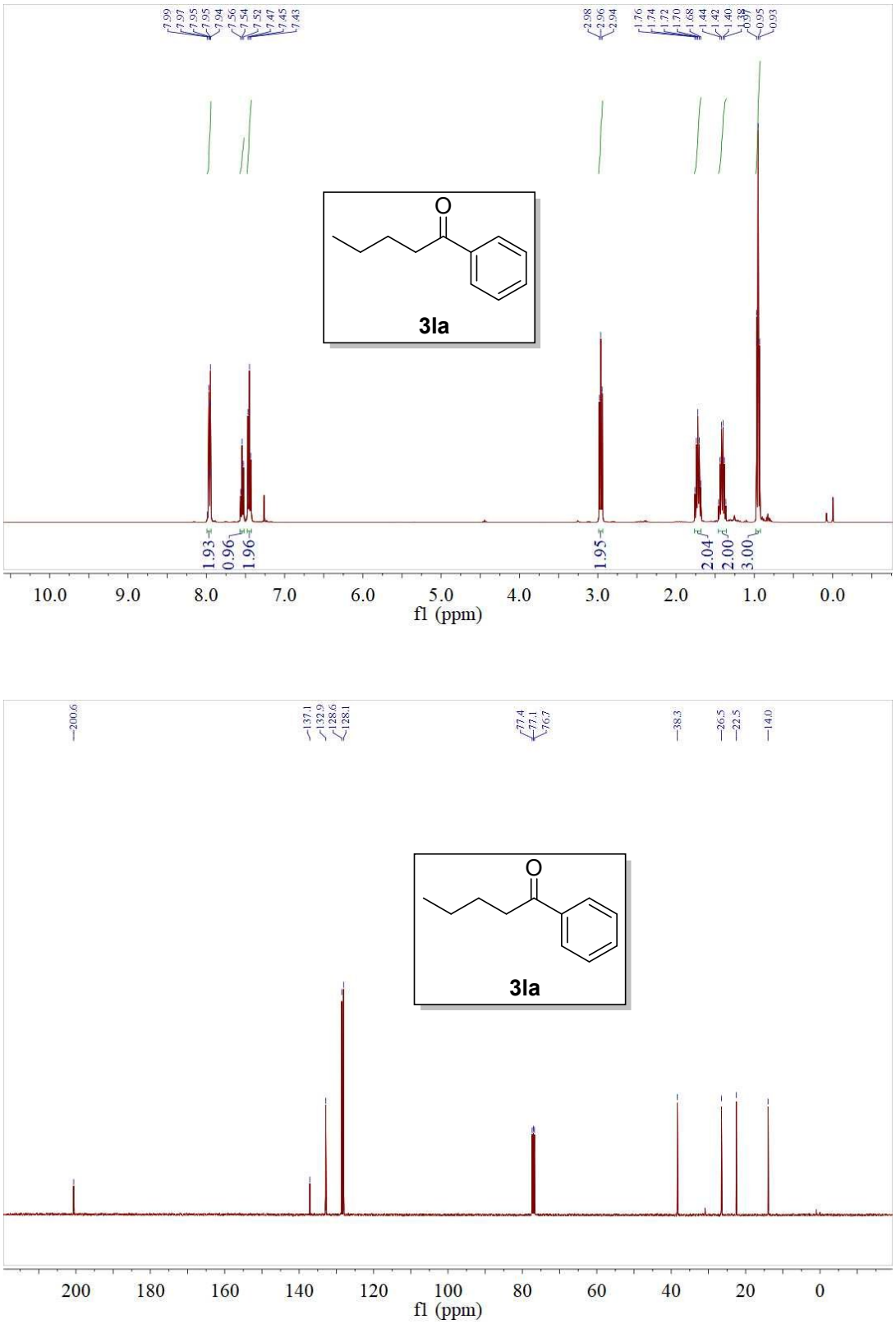


Figure S38. ^{1}H NMR of **3la** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3la** (100 MHz, $CDCl_3$)

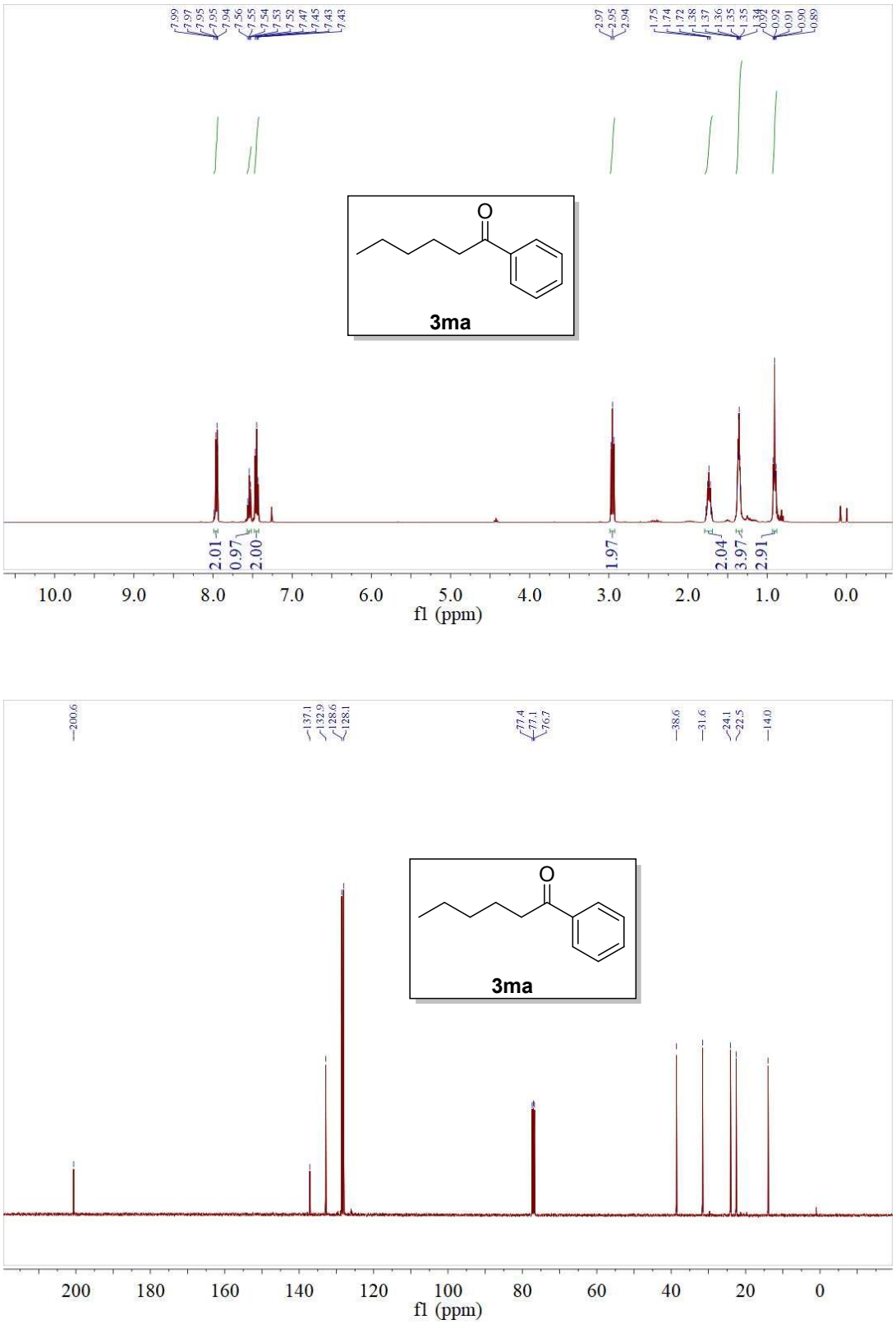


Figure S39. ^{1}H NMR of **3ma** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ma** (100 MHz, $CDCl_3$)

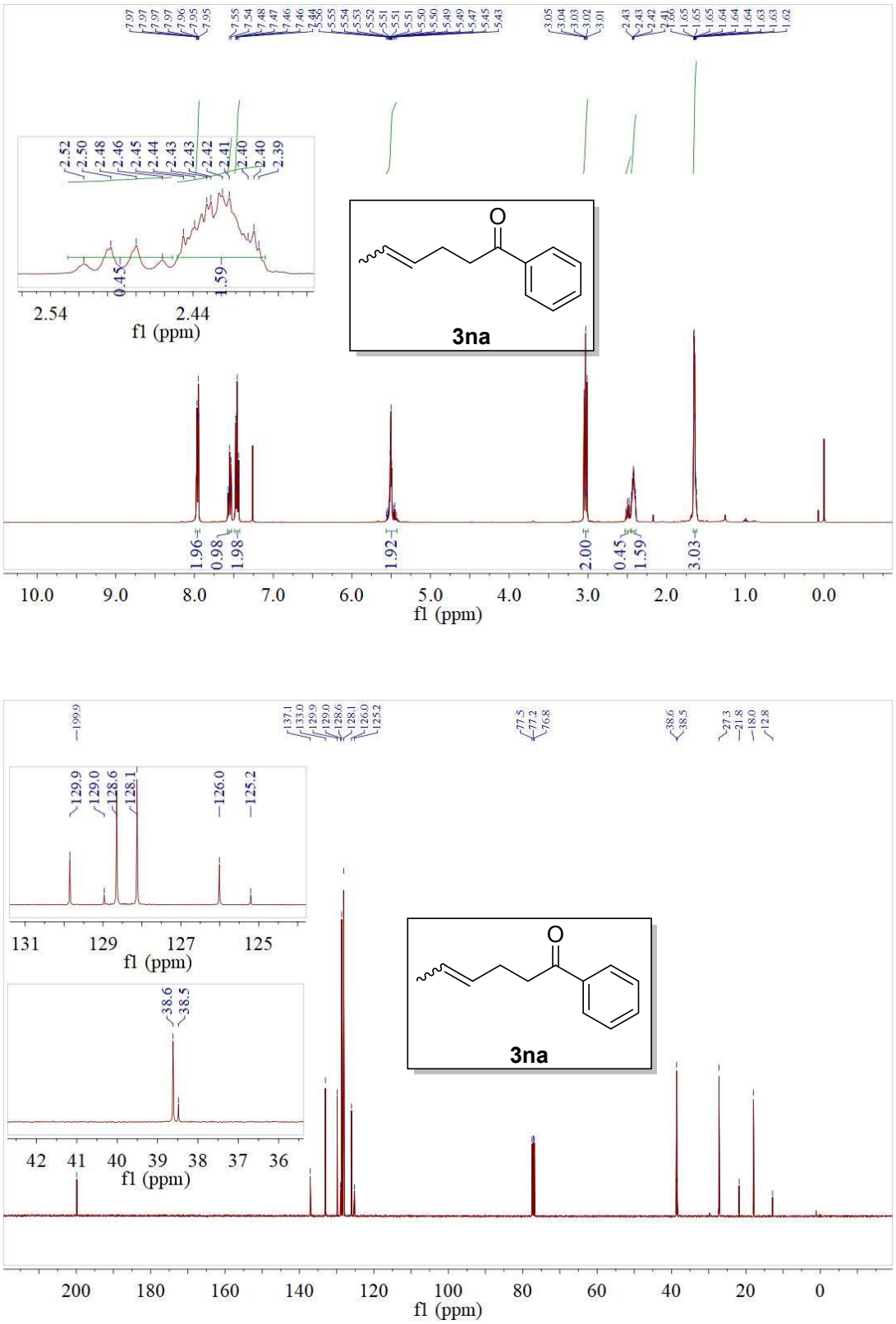


Figure S40. ^{1}H NMR of **3na** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3na** (100 MHz, $CDCl_3$)

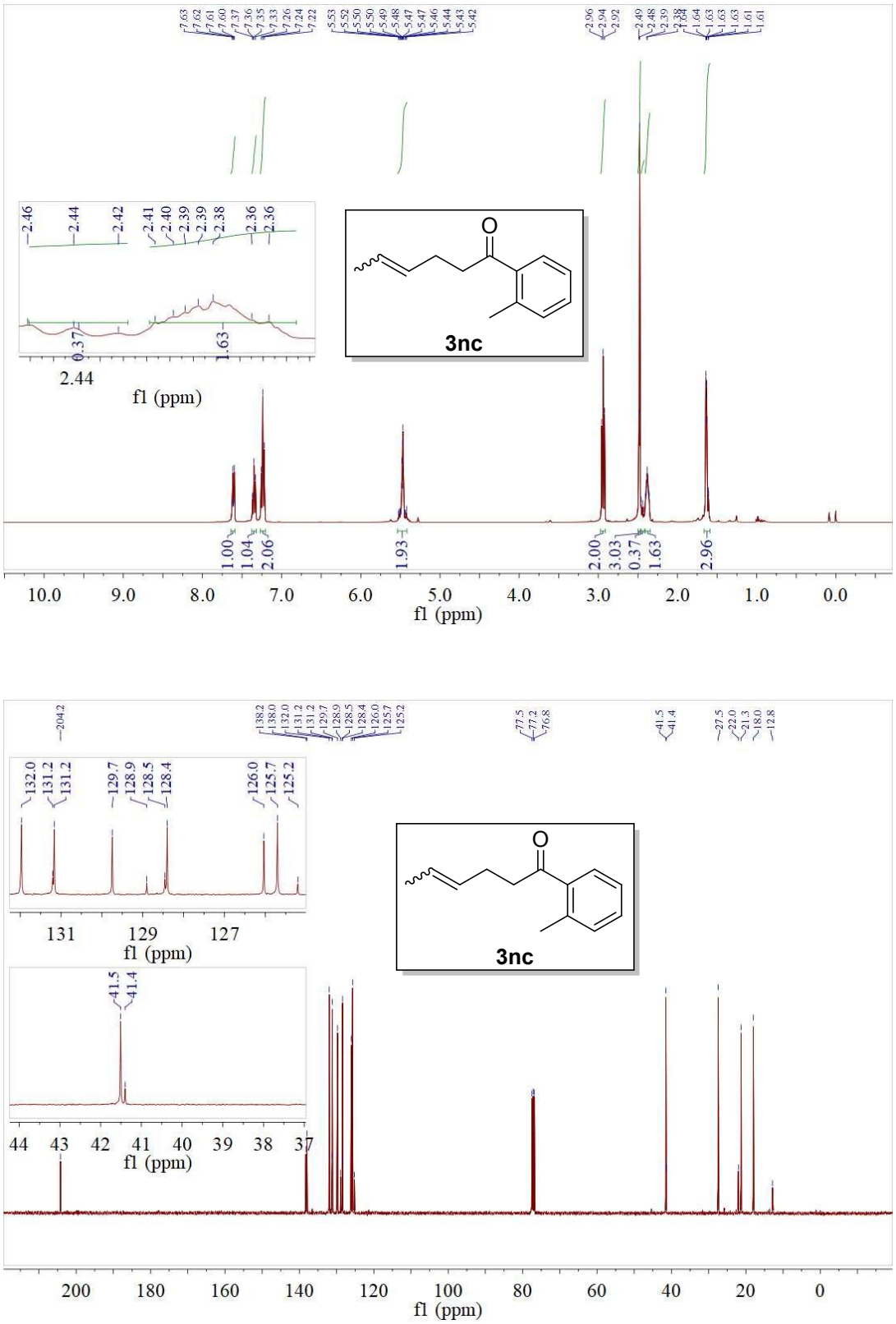


Figure S41. ^{1}H NMR of **3nc** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3nc** (100 MHz, $CDCl_3$)

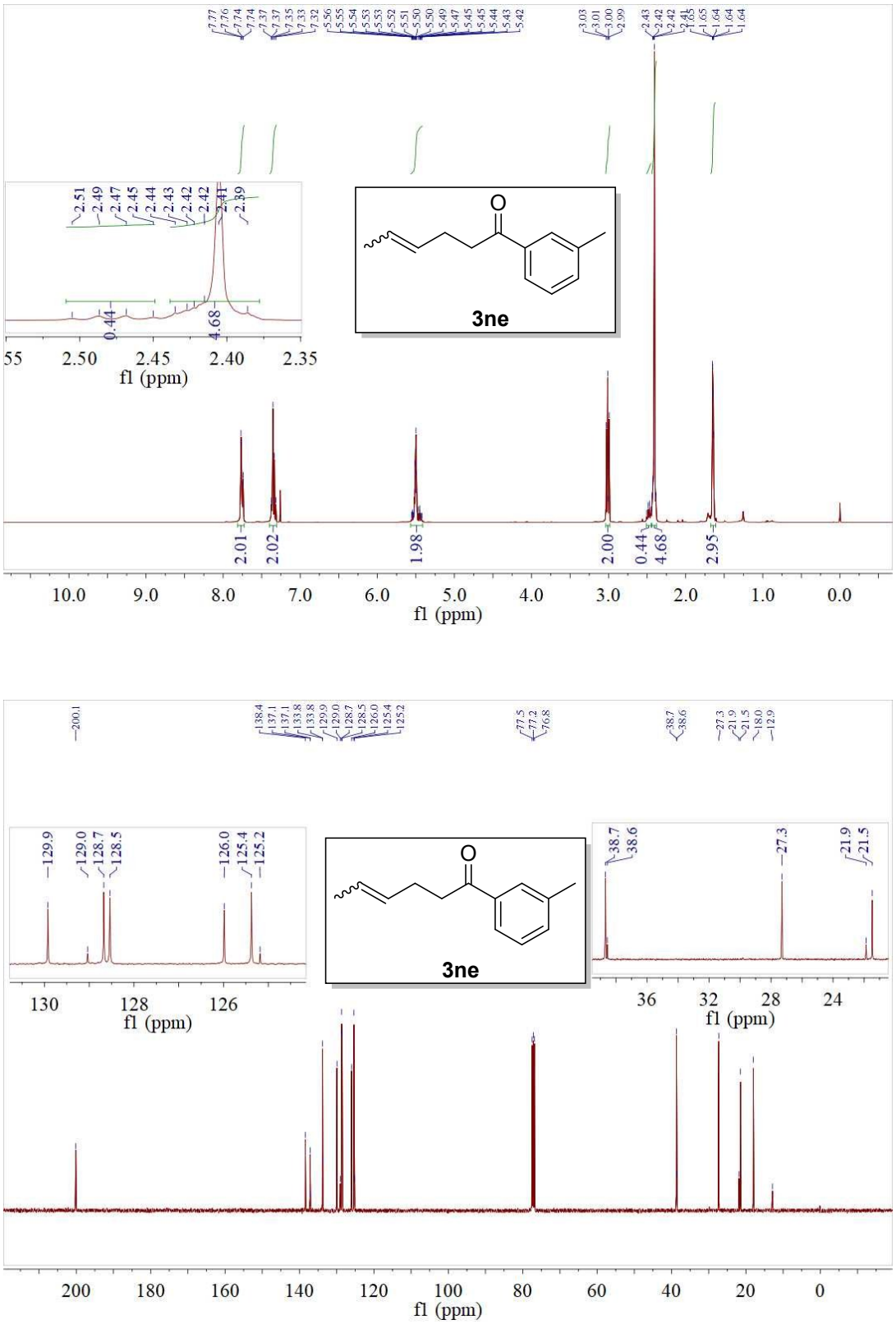


Figure S42. ^{1}H NMR of **3ne** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ne** (100 MHz, $CDCl_3$)

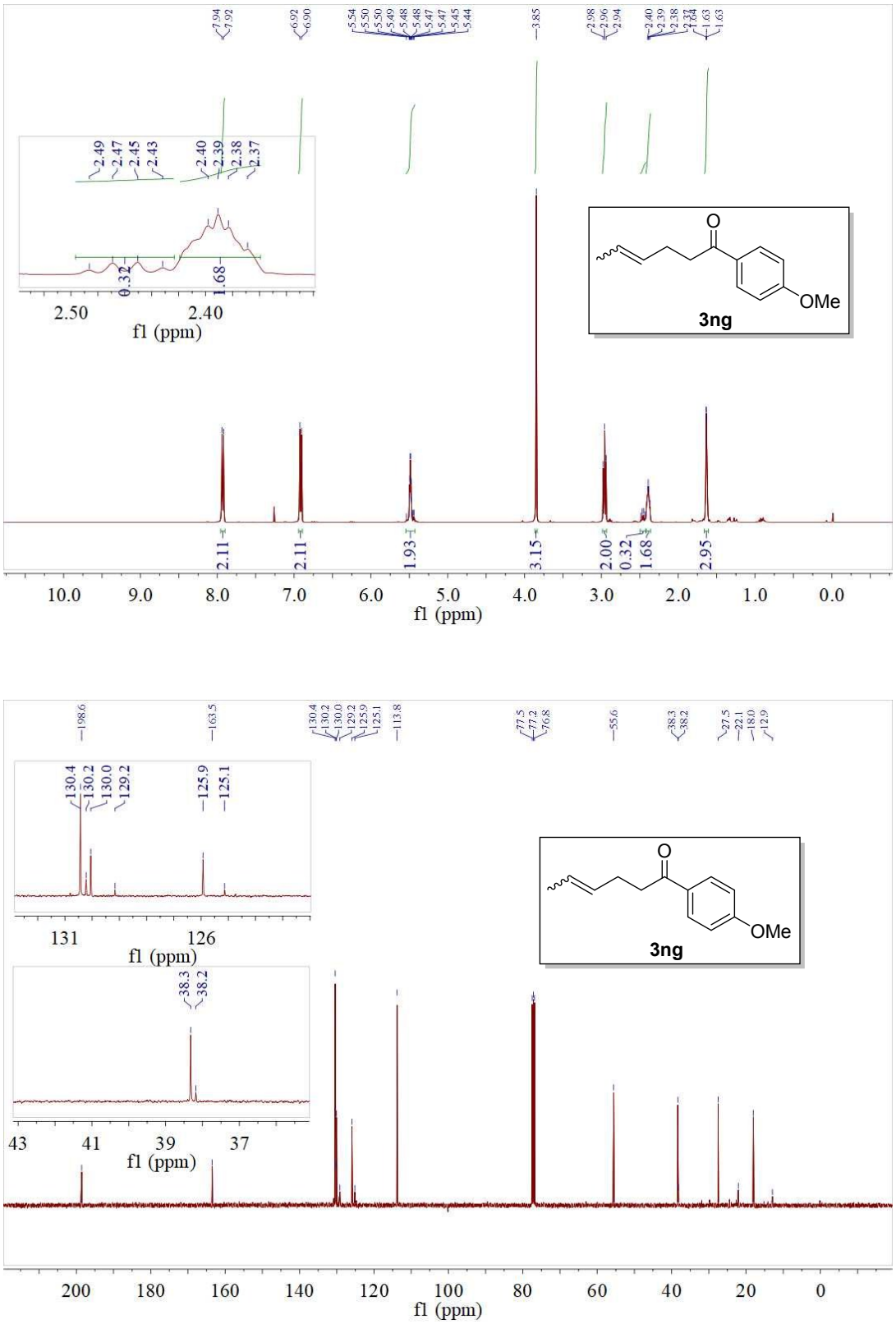


Figure S43. ^{1}H NMR of **3ng** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ng** (100 MHz, $CDCl_3$)

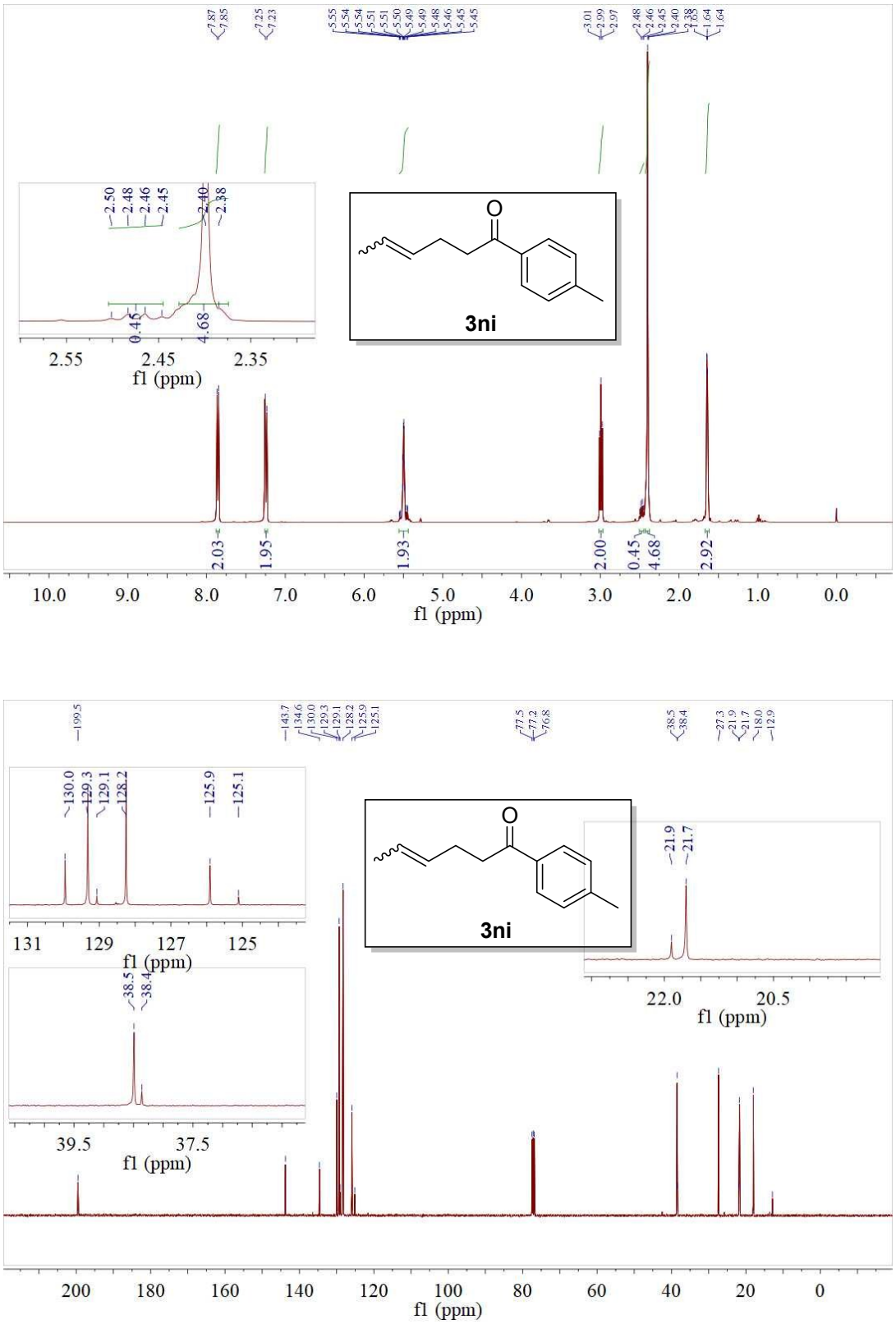


Figure S44. ^{1}H NMR of **3ni** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3ni** (100 MHz, $CDCl_3$)

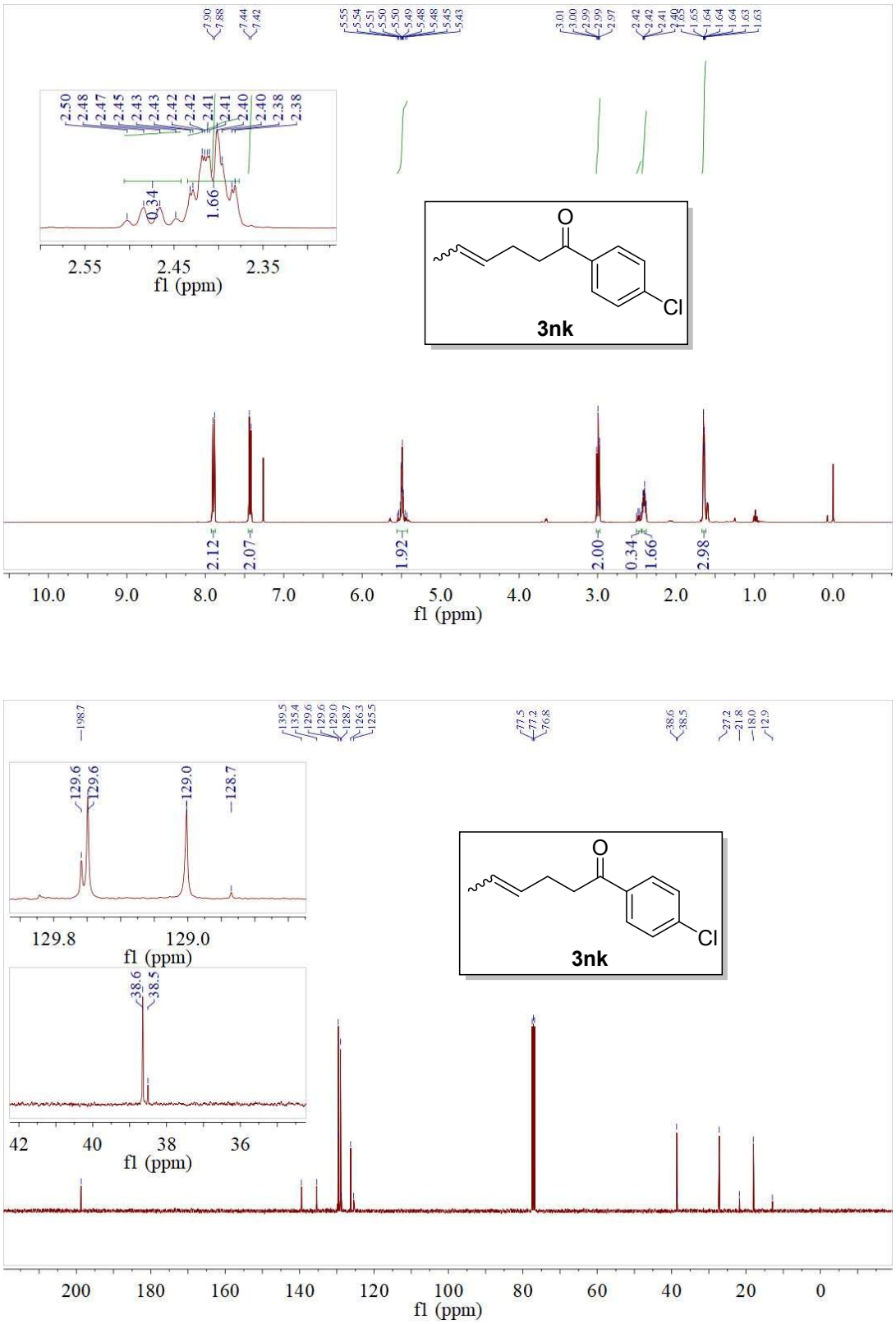
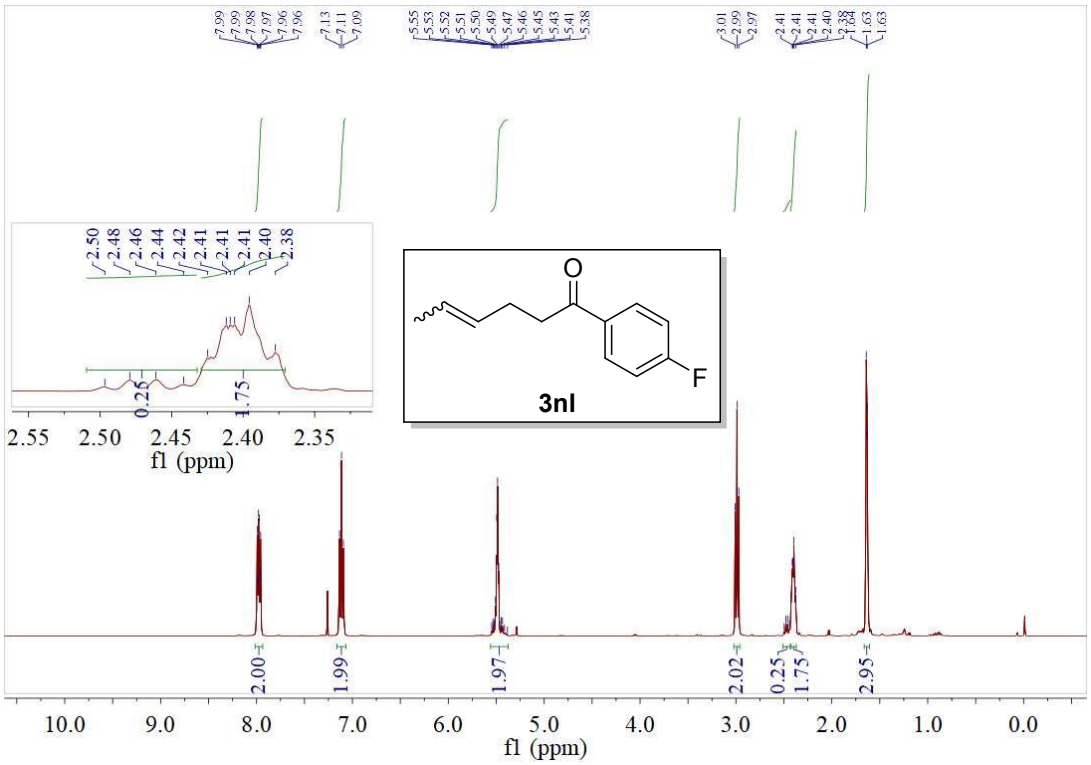
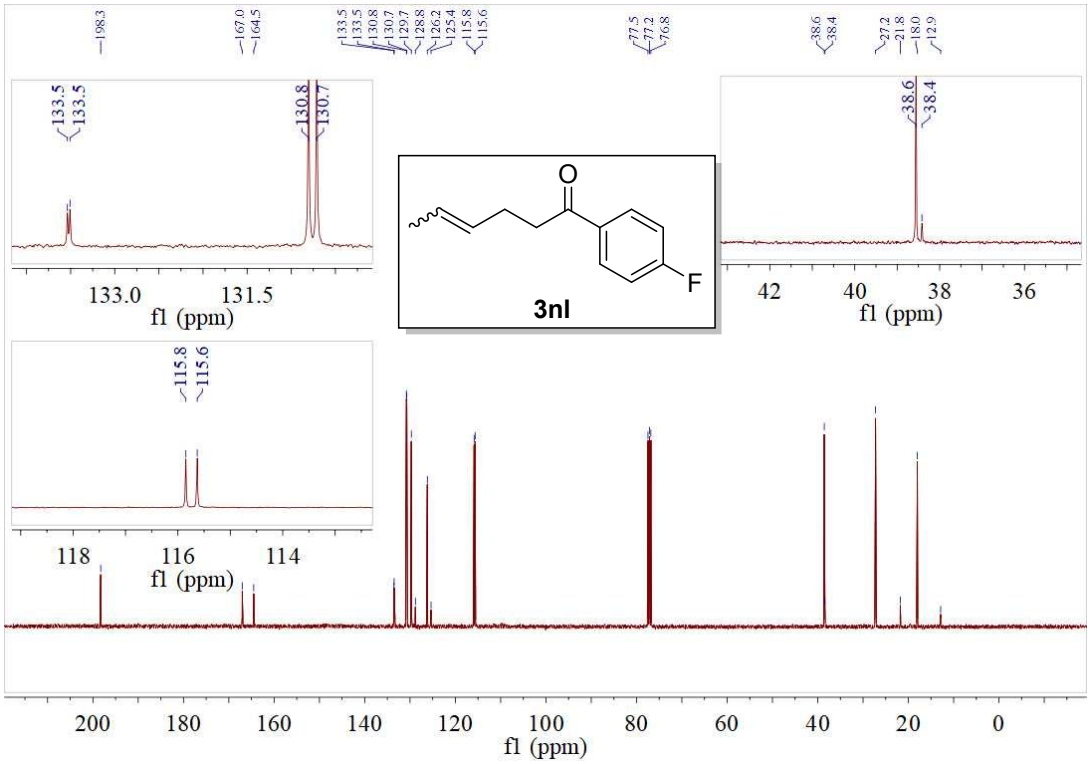


Figure S45. ^{1}H NMR of **3nk** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3nk** (100 MHz, $CDCl_3$)


3nl
fl (ppm)


3nl
fl (ppm)

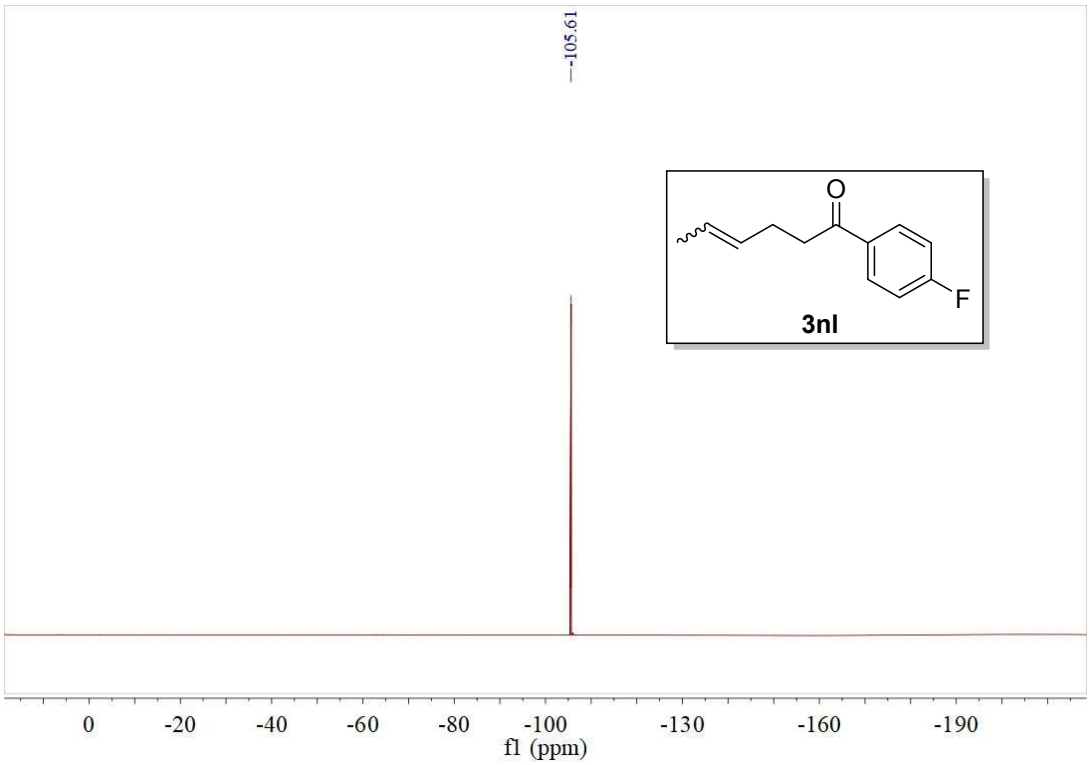
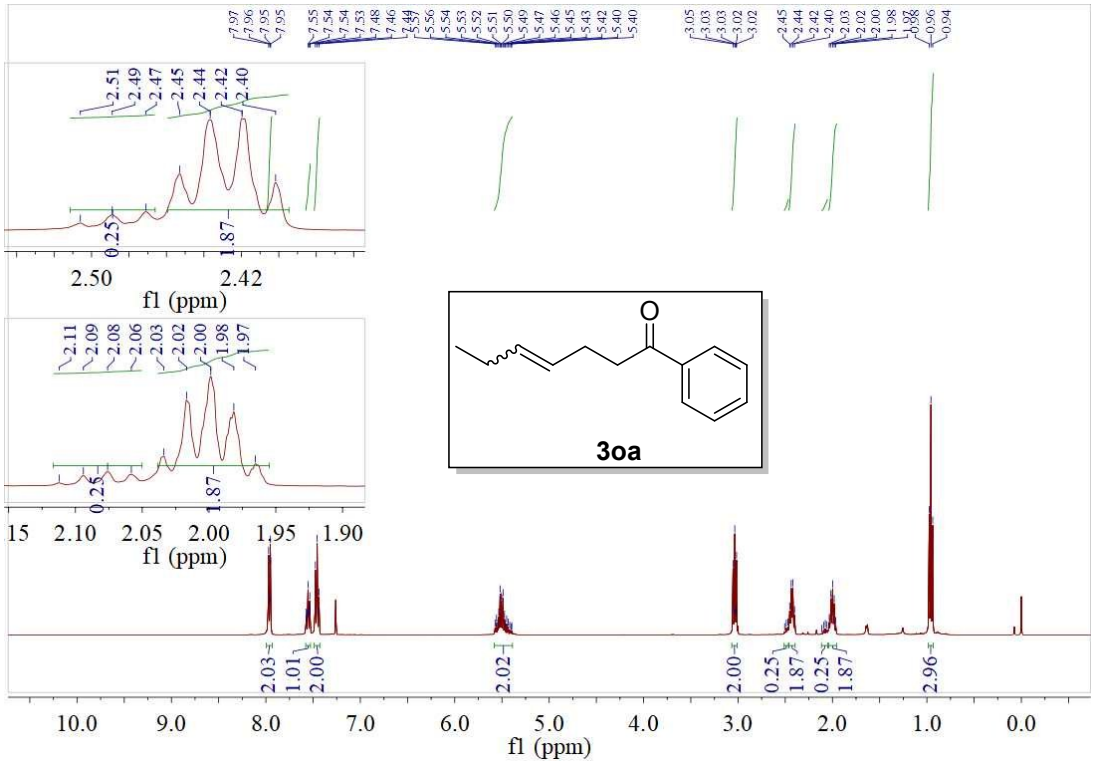


Figure S46. ^{1}H NMR of **3nl** (400 MHz, $CDCl_3$), ^{13}C NMR of **3nl** (100 MHz, $CDCl_3$) and ^{19}F NMR of **3nl** (376 MHz, $CDCl_3$)



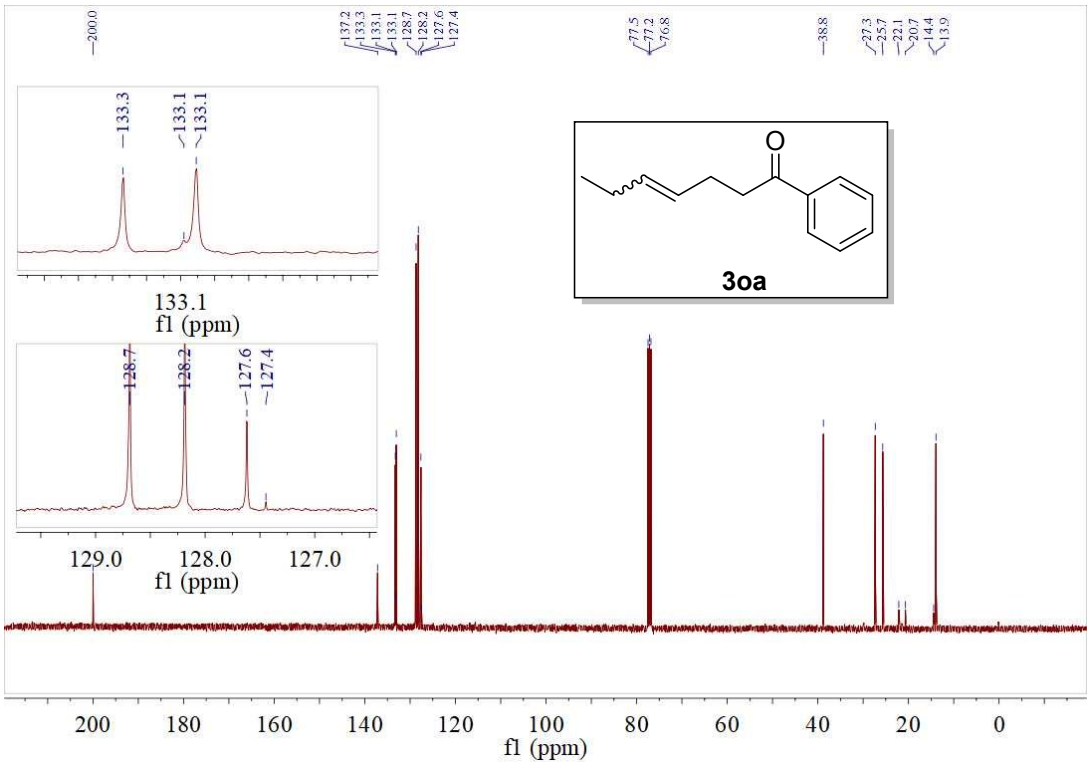


Figure S47. ^{1}H NMR of **3oa** (400 MHz, $CDCl_3$) and ^{13}C NMR of **3oa** (100 MHz, $CDCl_3$)

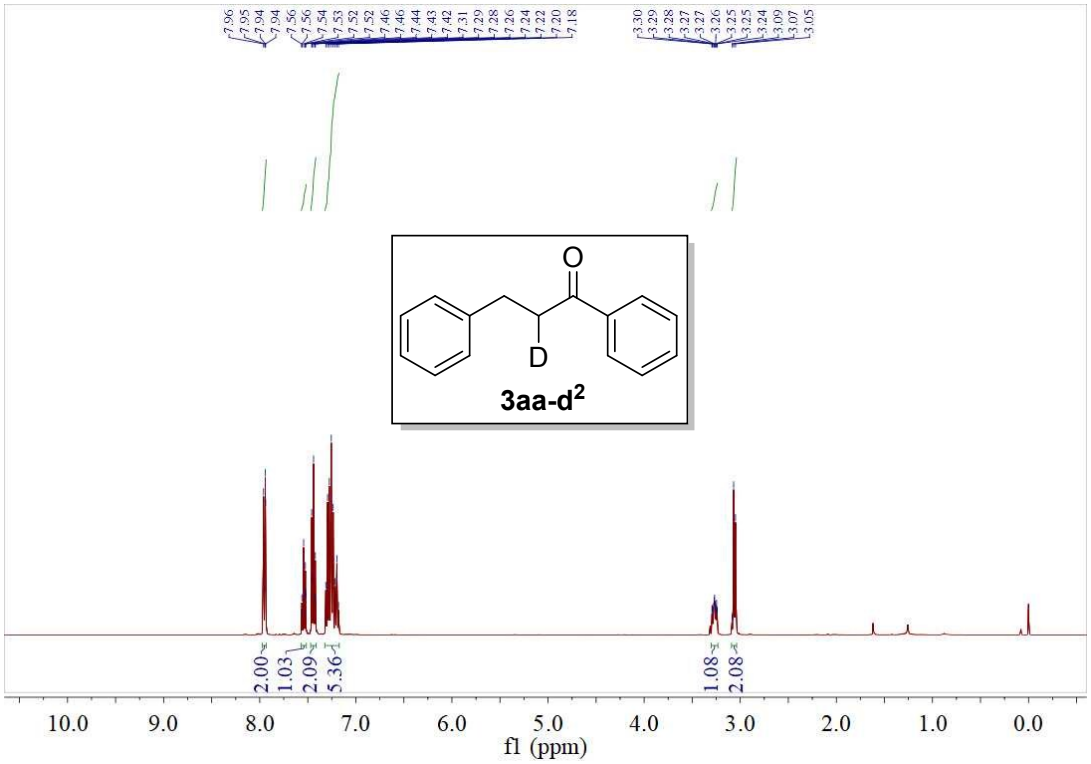


Figure S48. ^{1}H NMR of **3aa-d^2** (400 MHz, $CDCl_3$)

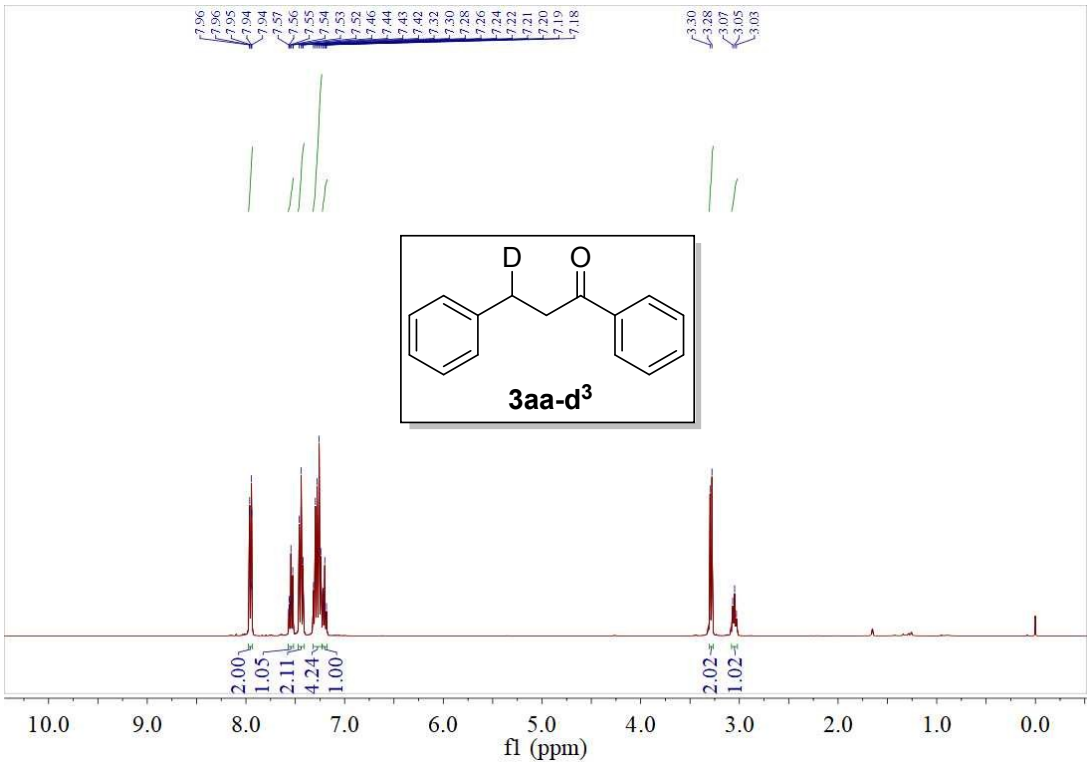


Figure S49. ^{1}H NMR of **3aa-d^3** (400 MHz, $CDCl_3$)

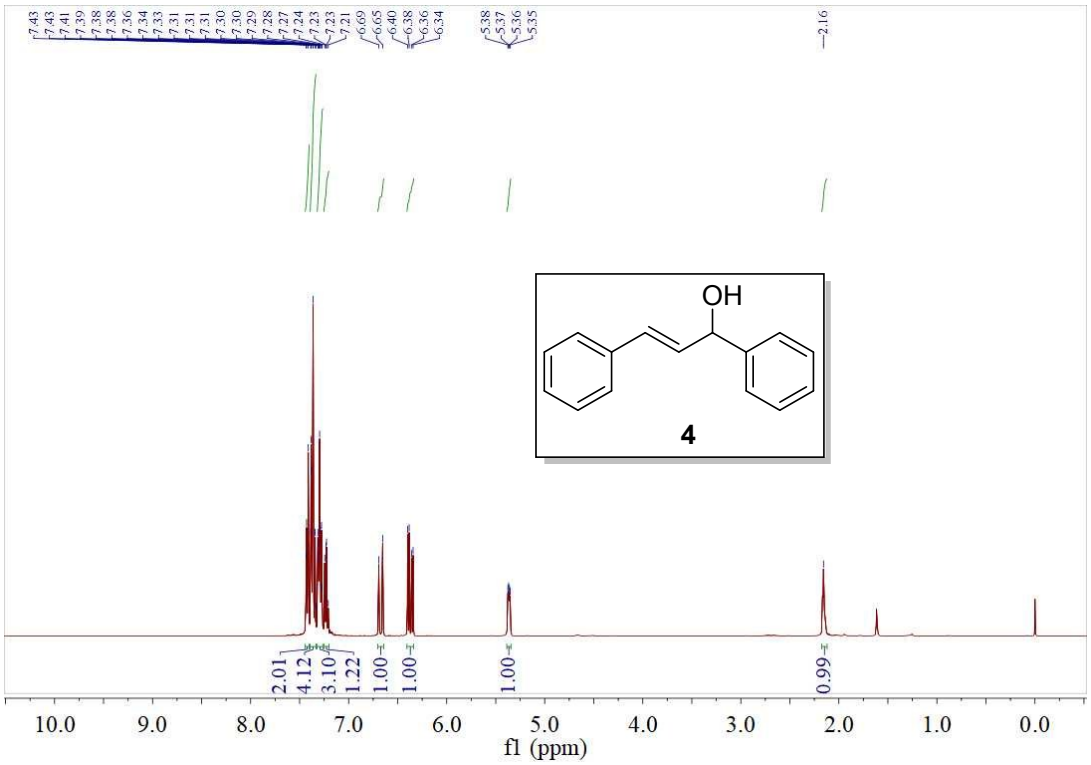


Figure S50. ^{1}H NMR of **4** (400 MHz, $CDCl_3$)

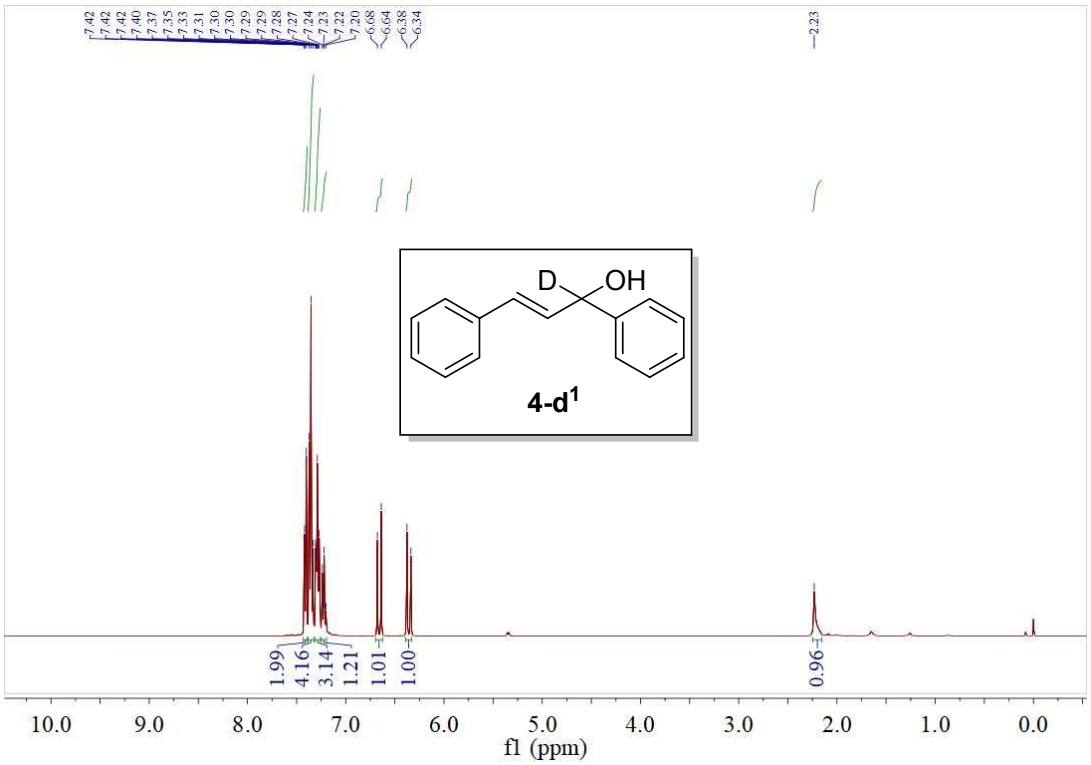


Figure S51. ^{1}H NMR of **4-d^1** (400 MHz, $CDCl_3$)

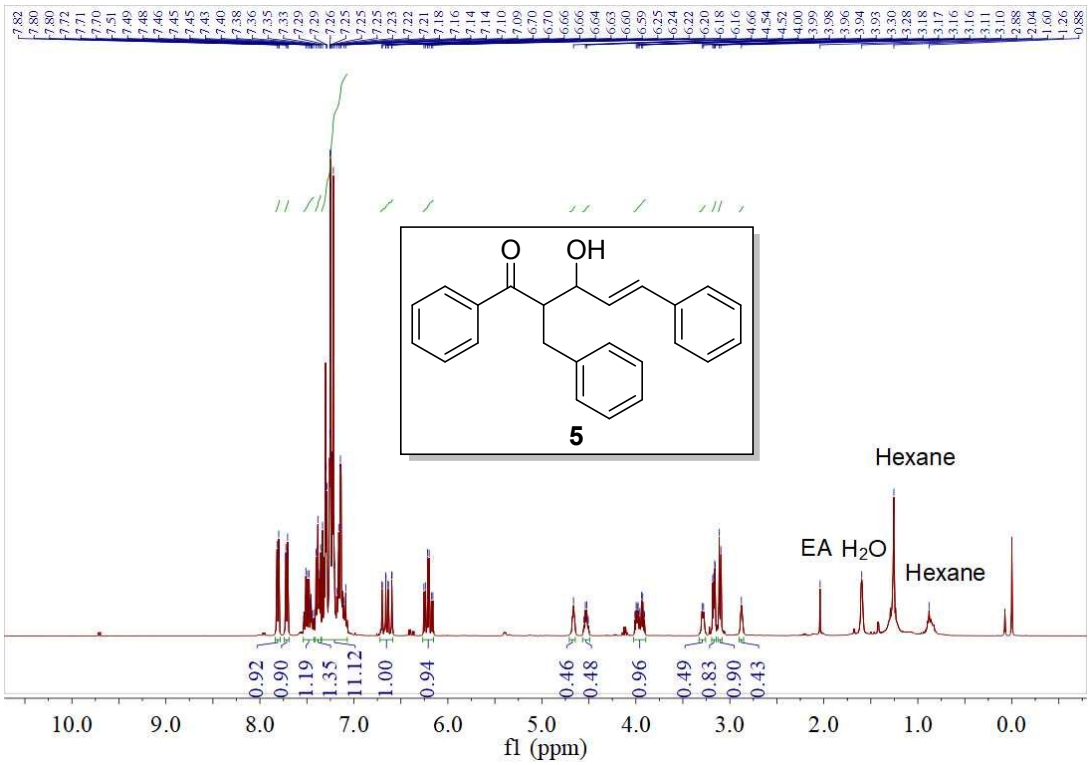


Figure S52. ^{1}H NMR of **5** (400 MHz, $CDCl_3$)

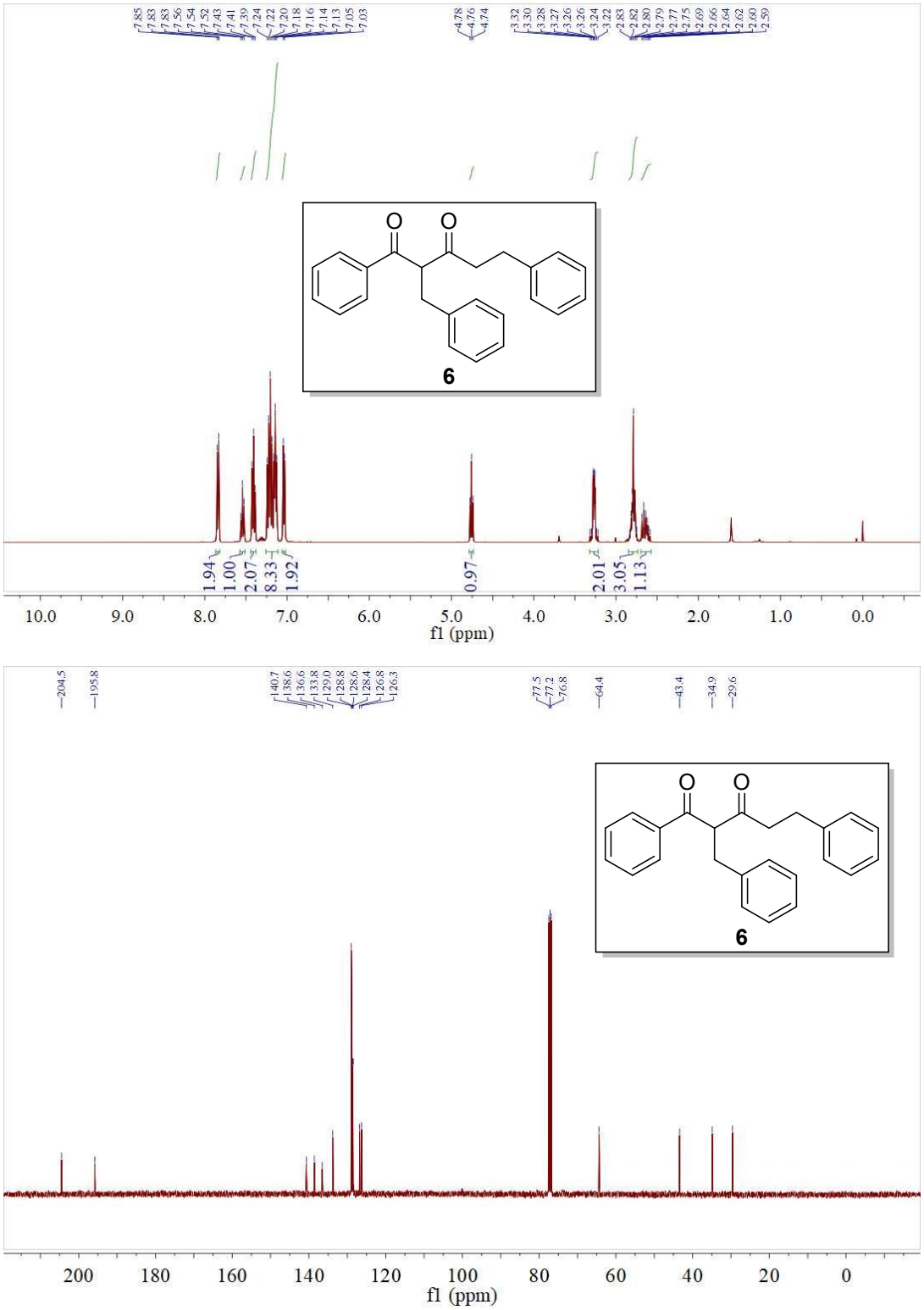


Figure S53. ^{1}H NMR of **6** (400 MHz, $CDCl_3$) and ^{13}C NMR of **6** (100 MHz, $CDCl_3$)

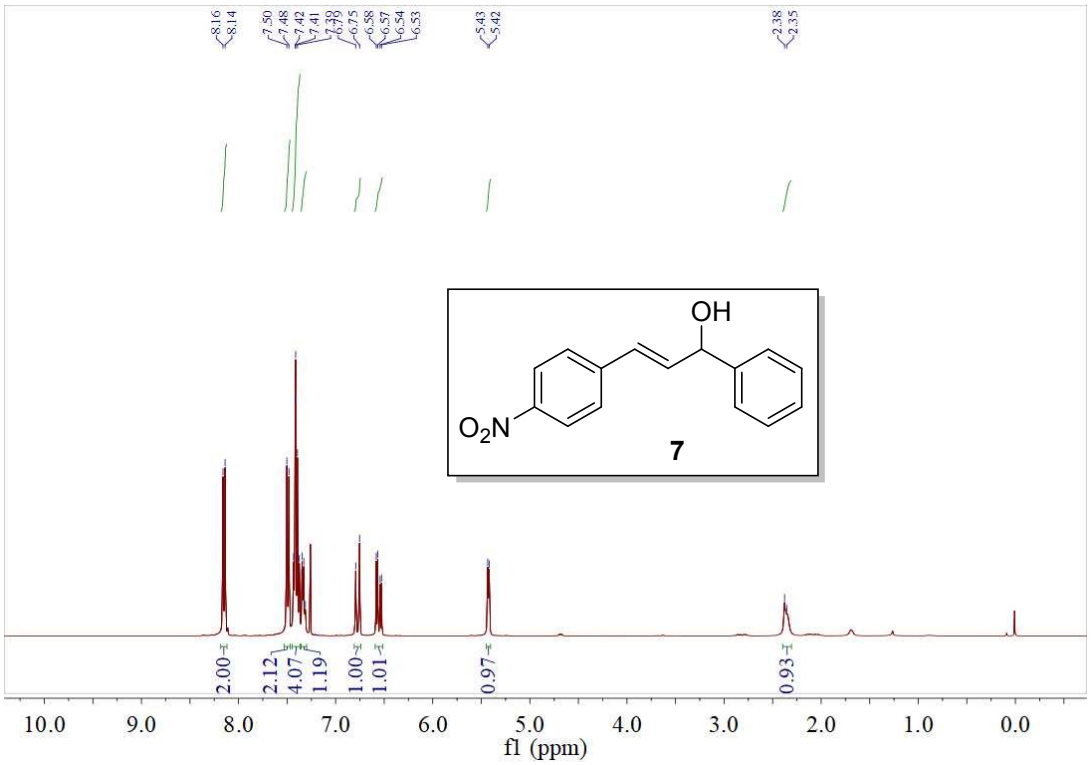


Figure S54. ^{1}H NMR of **7** (400 MHz, $CDCl_3$)

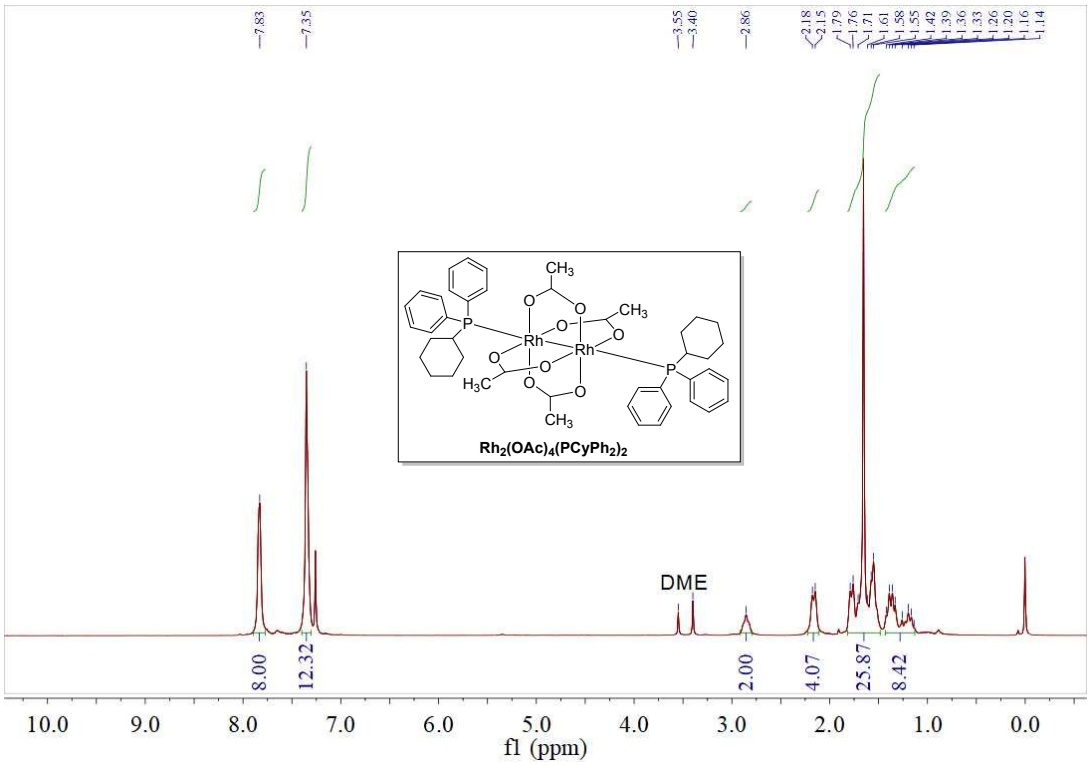


Figure S55. ^{1}H NMR of **$Rh_2(OAc)_4(PCyPh_2)_2$** (400 MHz, $CDCl_3$)

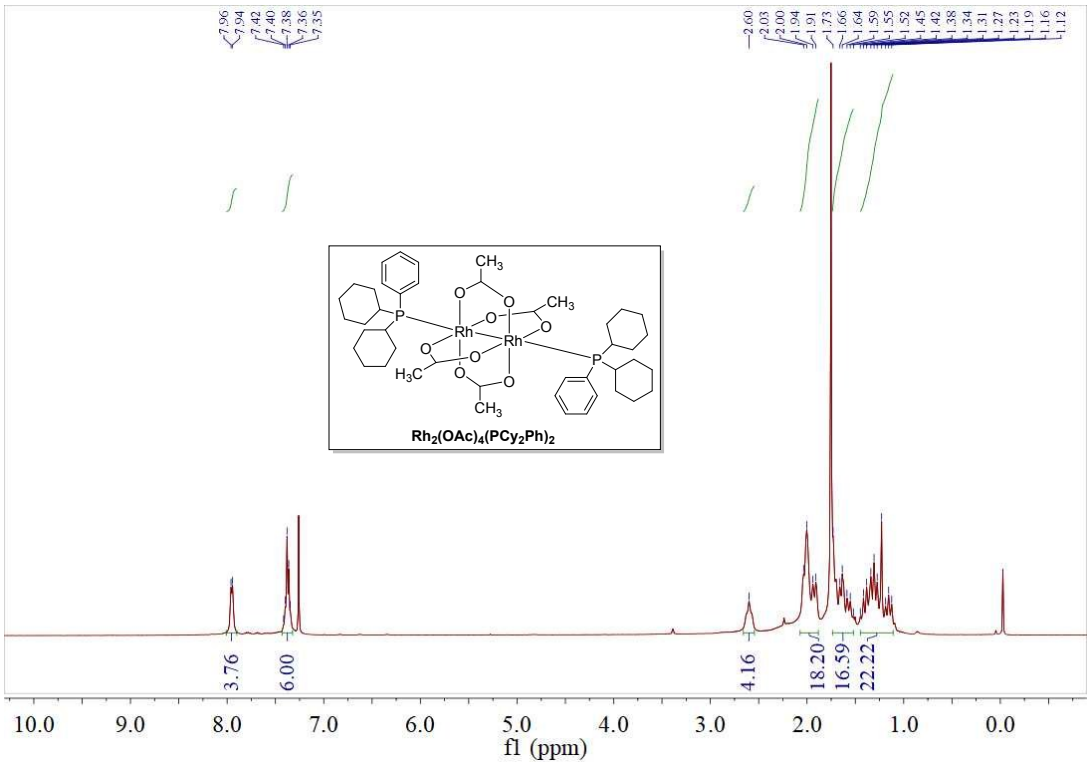
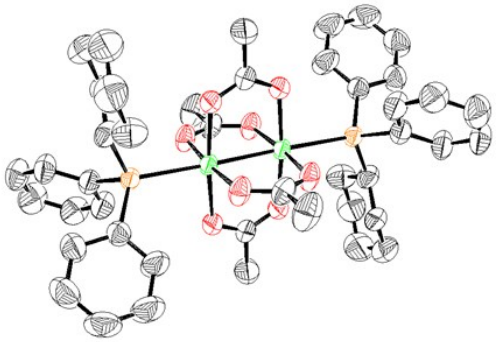


Figure S56. ^{1}H NMR of **$Rh_2(OAc)_4(PCy_2Ph)_2$** (400 MHz, $CDCl_3$)

6. X-Ray Crystallographic Analysis of $Rh_2(OAc)_4(PCyPh_2)_2$ and $Rh_2(OAc)_4(PCy_2Ph)_2$

6.1 Crystal Data and Structure Refinement for $Rh_2(OAc)_4(PCyPh_2)_2$

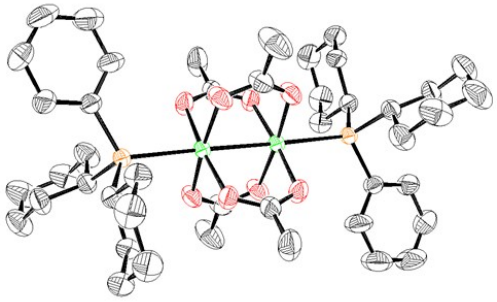


Identification code	CCDC1843000
Empirical formula	$C_{44}H_{54}O_8P_2Rh_2$
Formula weight	978.63

Temperature/K	294.24(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.7113(4)
b/Å	9.9865(5)
c/Å	14.7594(8)
α/°	78.689(4)
β/°	73.106(5)
γ/°	64.253(5)
Volume/Å^3	1102.96(11)
Z	1
ρ_{calc}g/cm^3	1.473
μ/mm^{-1}	7.143
F(000)	502.0
Crystal size/mm^3	0.5 × 0.5 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.866 to 144.928
Index ranges	$-10 \leq h \leq 7$, $-12 \leq k \leq 8$, $-18 \leq l \leq 18$
Reflections collected	8322
Independent reflections	4120 [R_{int} = 0.0325, R_{sigma} = 0.0374]
Data/restraints/parameters	4120/0/255
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0538, wR_2 = 0.1420
Final R indexes [all data]	R_1 = 0.0626, wR_2 = 0.1563

Largest diff. peak/hole / e Å^{-3}	1.30/-0.98

6.2 Crystal Data and Structure Refinement for $Rh_2(OAc)_4(PCy_2Ph)_2$



Identification code	CCDC1842999
Empirical formula	$C_{44}H_{66}O_8P_2Rh_2$
Formula weight	990.72
Temperature/K	294.24(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.9977(4)
b/Å	10.0861(6)
c/Å	14.7007(6)
α/°	86.402(4)
β/°	72.916(4)
γ/°	65.810(5)
Volume/Å^3	1160.72(11)
Z	1
ρ_{calc}g/cm^3	1.417
μ/mm^{-1}	6.788
F(000)	514.0

Crystal size/mm^3	0.5 × 0.3 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.634 to 145.352
Index ranges	-11 ≤ h ≤ 10, -12 ≤ k ≤ 12, -11 ≤ l ≤ 18
Reflections collected	12821
Independent reflections	4516 [R_{int} = 0.0385, R_{sigma} = 0.0349]
Data/restraints/parameters	4516/0/255
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0422, wR_2 = 0.1138
Final R indexes [all data]	R_1 = 0.0466, wR_2 = 0.1200
Largest diff. peak/hole / e Å^{-3}	0.63/-1.14