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Supporting Information

Photo-Induced Homologation of Carbonyl Compounds for Iterative Syntheses

*H. Wang, S. Wang, V. George, G. Llorente, B. König**

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Photo-Induced Homologation of Carbonyl Compounds for Iterative Syntheses

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Contents

1. General information

All NMR spectra were recorded at room temperature using a Bruker Avance 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C), or a Bruker Avance 400 (400 MHz for ^{1}H, 101 MHz for ^{13}C) NMR spectrometer.[1] All chemical shifts are reported in δ-scale as parts per million [ppm] (multiplicity, coupling constant *J*, number of protons) relative to the solvent residual peaks as the internal standard.[2] Coupling constants *J* are given in Hertz [Hz]. Abbreviations used for signal multiplicity: ^{1}H-NMR: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, and m = multiplet. High resolution mass spectra (HRMS) were obtained from the central analytic mass spectrometry facilities of the Faculty of Chemistry and Pharmacy, Regensburg University, and are reported according to the IUPAC recommendations 2013. All mass spectra were recorded on a Finnigan MAT 95, Thermo Quest Finnigan TSQ 7000, Finnigan MATSSQ 710 A or an Agilent Q-TOF 6540 UHD instrument. GC measurements were performed on a GC 7890 from Agilent Technologies. Data acquisition and evaluation were done with Agilent ChemStation Rev.C.01.04. [35]. Analytical TLC was performed on silica gel coated alumina plates (MN TLC sheets ALUGRAM® Xtra SIL G/UV254). Visualization was done by UV light (254 or 366 nm). If necessary, potassium permanganate was used for chemical staining. Purification by column chromatography was performed with silica gel 60 M (40-63 μm, 230-440 mesh, Merck) on a Biotage® Isolera TM Spektra One device. Photocatalytic reactions were performed with 385 nm LEDs (OSRAM Oslon SSL 80 royal-blue LEDs (λ = 385 nm (± 15 nm), 21 V, 700 mA). The sample was irradiated with a LED through the vial's plane bottom side and cooled from the side using custom-made aluminum cooling blocks connected to a thermostat (Figure S1). Gram-scale reactions were in a classic glass tube photochemical reactor setup irradiated from the outside (Figure S2). The glass tube with reaction mixture and LED cooling block were thermostated at 25 °C. UV–Vis and fluorescence measurements were performed with a Varian Cary 100 UV/Vis spectrophotometer and FluoroMax-4 spectrofluorometer, respectively. Commercially available starting materials and solvents were used without further purification.

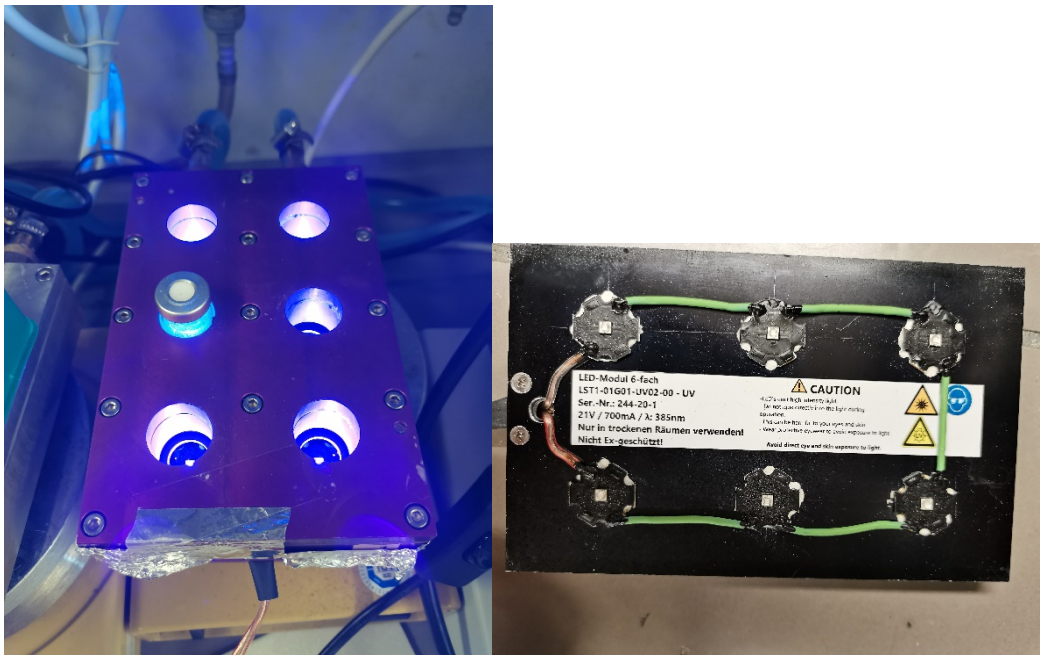


Figure S1. Photochemical set-up for regular-scale reactions

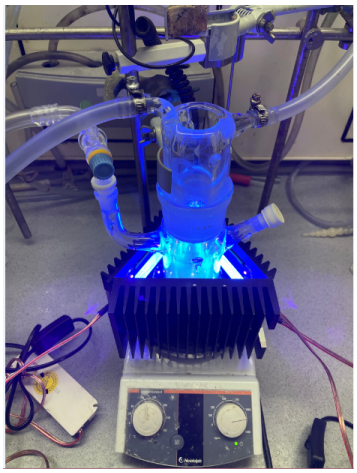
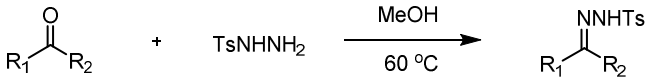


Figure S2. Photochemical set-up for large-scale reactions

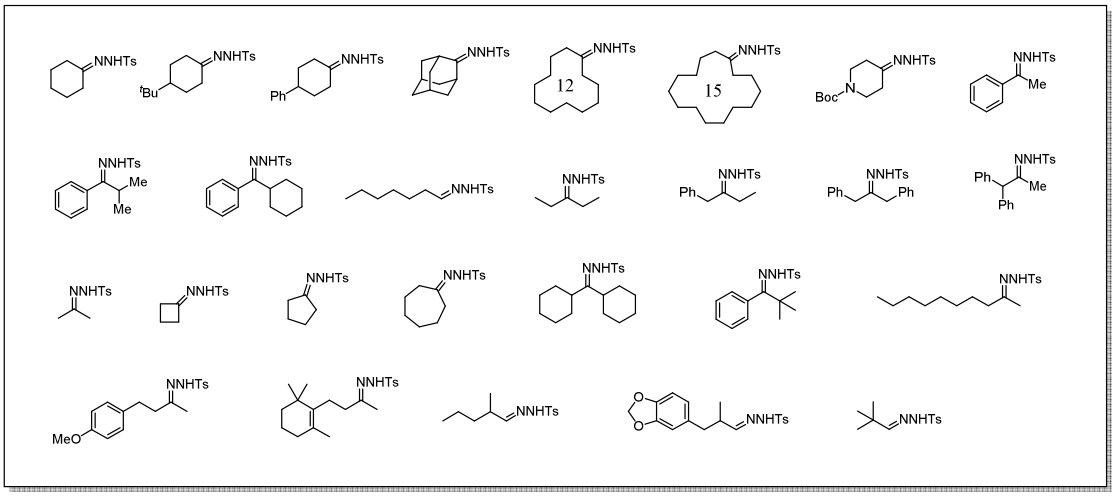
2. Starting materials

2.1 Synthesis of N-tosylhydrazones from ketones[1]

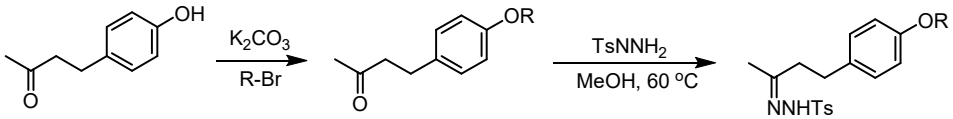


General procedure A-SM

To a stirred solution of tosylhydrazide (10 mmol) in MeOH (10 mL) at 60 °C, aldehyde or ketone (1 eq.) was added dropwise (or portionwise if solid). The reaction progress was monitored by TLC. After the completion of reaction, the reaction mixture was cooled and filtered to remove the solvent. The filtered solid was triturated with hexane/diethyl ether to get the pure N-sulfonylhydrazones.

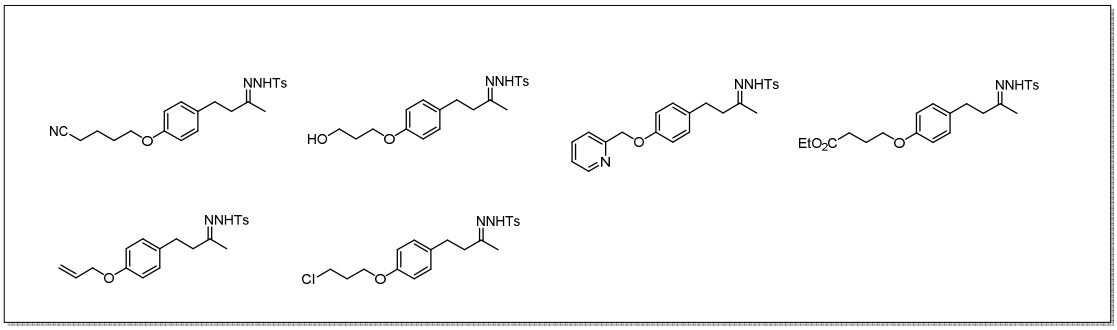


General procedure B-SM



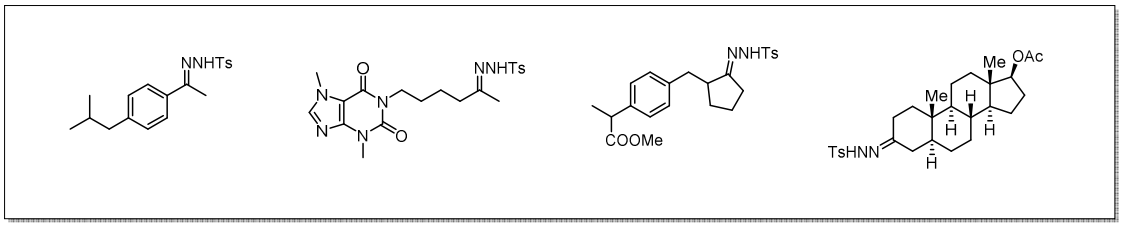
Step 1: Alkyl Bromides (3.15 mmol, 1.05 equiv.) and K_2CO_3 (4.5 mmol, 1.50 equiv.) were added to a solution of 4-(4-hydroxyphenyl)butan-2-one (3.0 mmol, 1.0 equiv.) in DMF (8.0 mL) in a 20-mL vial under air condition. After stirring at room temperature overnight, the reaction mixture was quenched with water (10 mL), before EtOAc (30 mL) was added. The organic phase was washed with water (3 × 20 mL) and brine (30 mL), and then dried over $MgSO_4$, filtered, and concentrated in vacuo. Then the crude product was used directly for next step without further purification.

Step 2: To a stirred solution of tosylhydrazide (3 mmol) in MeOH (10 mL) at 60 °C, ketone (1 eq.) from last step was added dropwise (or portionwise if solid). The solution was refluxed at 65 °C for around 30 min along with white solid crashes out, and the reaction was monitored by TLC until the complete consumption of both starting materials. The crude mixture was then purified by flash column chromatography (10% to 50%, EtOAc in petroleum ether) on silica gel.



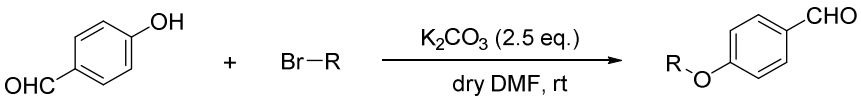
General procedure C-SM

Tosylhydrazide (0.2 mmol), aldehyde or ketone (0.2 mmol) were dissolved in MeOH (2 mL) at 60 °C. The reaction progress was monitored by TLC. After the completion of the reaction, the reaction mixture was concentrated in vacuo and directly used in the photochemical reaction.

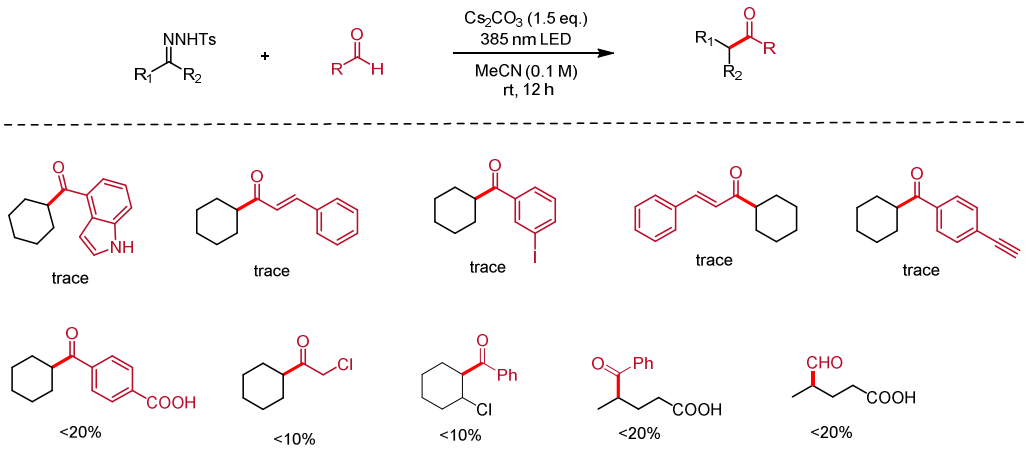


2.2 Synthesis of aldehydes

General procedure D-SM



Alkyl Bromides (3.15 mmol, 1.05 equiv.) and K_2CO_3 (4.5 mmol, 1.50 equiv.) were added to a solution of 4-hydroxybenzaldehyde (0.37 g, 3.0 mmol, 1.0 equiv.) in DMF (8.0 mL) in a 20-mL vial under air condition. After stirring at room temperature overnight, the reaction mixture was quenched with water (10 mL), before EtOAc (30 mL) was added. The organic phase was washed with water (3 × 20 mL) and brine (30 mL), and then dried over $MgSO_4$, filtered, and concentrated in vacuo. Then the crude product was purified by flash column chromatography (1% to 3%, EtOAc in petroleum ether) on silica gel to afford the product.

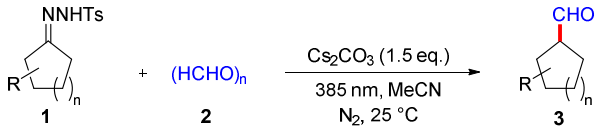


Scheme S1. List of unsuccessful substrates

3. Experimental procedures

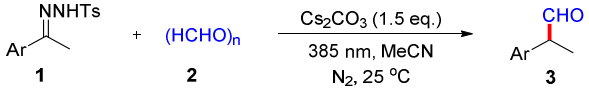
3.1 Synthesis of aldehydes from paraformaldehyde with N-tosylhydrazones

General procedure A



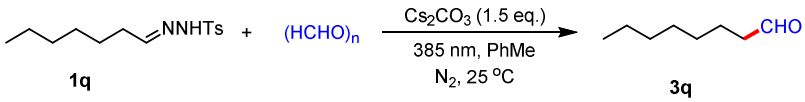
To a 5 mL snap vial with a magnetic stirring bar, tosylhydrazones (**1**, 0.2 mmol, 1.0 eq.), Cs_2CO_3 (0.3 mmol, 1.5 eq.), and paraformaldehyde (**2,** 0.24 mmol, 1.2 eq.) were added. The vial was evacuated and backfilled with N_2 three times. Then dry MeCN (2 mL) was added by syringe, and the mixture was irradiated with a 385 nm LED at 25 °C. After 20 h, the mixture was quenched with water and extracted with EtOAc or Et_2O (3 x 10 mL). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel flash chromatography (gradient eluent: petroleum ether in EtOAc =1% to 2%, or pentane in diethyl ether = 2% to 3%) to give the desired product.

General procedure B



To a 5 mL snap vial with a magnetic stirring bar, tosylhydrazones (**1**, 0.4 mmol, 2.0 eq.), Cs_2CO_3 (0.3 mmol, 1.5 eq.), and paraformaldehyde (**2,** 0.2 mmol, 1.0 eq.) were added. The vial was evacuated and back filled with N_2 for three times. Then dry MeCN (2 mL) was added by syringe, and the mixture was irradiated with a 385 nm LED at 25 °C. After 20 h, the mixture was quenched with water and extracted with Et_2O (10 mL *3). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel flash chromatography (gradient eluent: pentane in diethyl ether = 2% to 3%) to give the desired product.

General procedure C

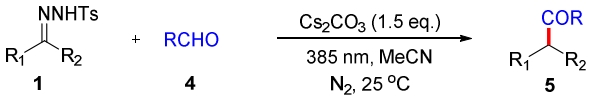


To a 5 mL snap vial with a magnetic stirring bar, tosylhydrazones (**1q**, 0.3 mmol, 1.5 eq.), Cs_2CO_3 (0.3 mmol, 1.5 eq.), and paraformaldehyde (**2,** 0.20 mmol, 1.0 eq.) were added. The vial was evacuated and back filled with N_2 for three times. Then dry toluene (2 mL) was added by syringe, and the mixture was irradiated with a 385 nm LED at 25 °C. After 20 h, the reaction mixture was diluted with EA (3 mL), dodecane was added as an internal standard, followed by water. After shaking for 1 min, the organic layer was separated, and the yield was determined by GC. *Note: we observed that tosylhydrazone **1q** decomposed considerably at ambient conditions after several days, and therefore this substrate should be freshly prepared before use.*

General procedure D

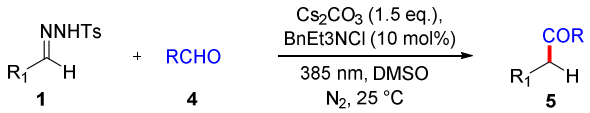
To a 5 mL snap vial with a magnetic stirring bar, tosylhydrazones (**1**, 0.2 mmol, 1.0 eq.), Cs_2CO_3 (0.3 mmol, 1.5 eq.), $BnEt_3NCl$ (20.0 µmol, 10 mol%) and paraformaldehyde (**2,** 0.2 mmol, 1.0 eq.) were added. The vial was evacuated and back filled with N_2 for three times. Then dry CH_2Cl_2 (2 mL) was added by syringe, and the mixture was irradiated with a 385 nm LED at 25 °C. After 20 h, the mixture was quenched with water and extracted with CH_2Cl_2 (10 mL *3). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel flash chromatography to give the desired product.

General procedure E



To a 5 mL snap vial with a magnetic stirring bar, tosylhydrazones (**1**, 0.2 mmol, 1.0 eq.), Cs_2CO_3 (0.3 mmol, 1.5 eq.), and aldehyde (**4,** 0.24 mmol, 1.2 eq.) were added. The vial was evacuated and back filled with N_2 for three times. Then dry MeCN (2 mL) was added by syringe, and the mixture was irradiated with a 385 nm LED at 25 °C. After 20 h, the mixture was quenched with water and extracted with Et_2O (10 mL *3). The combined organic phase was then washed with H2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel flash chromatography (gradient eluent: pentane in diethyl ether = 2% to 3%) to give the desired product.

General procedure F

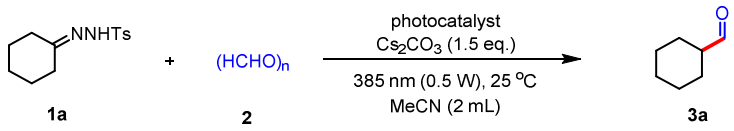


To a 5 mL snap vial with a magnetic stirring bar, tosylhydrazones (**1**, 240 µmol, 1.2 eq.), Cs_2CO_3 (300 µmol, 1.5 eq.), $BnEt_3NCl$ (20.0 µmol, 10 mol%), and aldehyde (**4,** 200 µmol, 1.0 eq., if solid) were added. The vial was evacuated and back filled with N_2 for three times. Then dry DMSO (200 µL) and aldehyde (**4,** 200 µmol, 1.0 eq., if liquid) were added by syringe, and the mixture was irradiated with a 385 nm LED at 25 °C. After 20 h, the mixture was quenched with water and extracted with EtOAc (10 mL *3). The combined organic phase was then washed with brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel column chromatography to give the desired product.

4. Optimization details for the reaction conditions

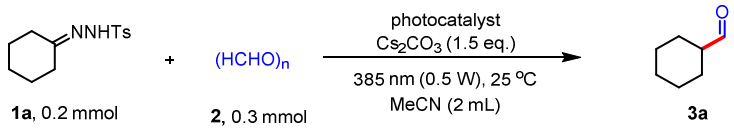
4.1 Optimization details for reaction of tosylhydrazone 1a with paraformaldehyde 2

General procedure:



To a 5 mL snap vial with magnetic stirring bar, tosylhydrazone (**1a**, 0.2 mmol, 1.0 eq.), Cs_2CO_3 (0.3 mmol, 1.5 eq.), and paraformaldehyde (**2**, 0.3 mmol, 1.5 eq.) were added. The vial was evacuated and back filled with N_2 for three times. Then dry MeCN (2 mL) was added by syringe, and the mixture was irradiated with a 385 nm LED at 25 °C. After 20 h, the mixture was quenched with water and EtOAc. Then yields were determined by GC analysis using mesitylene as internal standard.

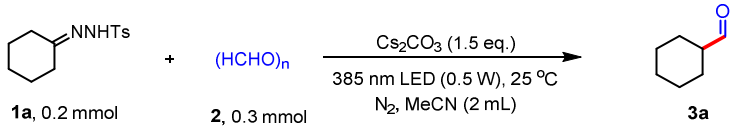
Table S1. Screening of photocatalysts[a]



Entry	Photocatalyst	Yield
1	TBADT (0.2 mol%)	40%
2[c]	Eosin Y (5 mol%), 455 nm LED	trace
3[c]	$[Ir(dFCF_3ppy)_2dtbpy]PF_6$ (1 mol%), 455 nm LED	trace
4[c]	$Ir(ppy)_2dtbpyPF_6$ (1 mol%), 455 nm LED	trace
5[c]	Mes-Acr^+ PF_6 (5 mol%), 455 nm LED	trace
6[c]	*fac*-$Ir(ppy)_3$ (1 mol%), 455 nm LED	22%
7	**-**	**70%**

[a] Reaction conditions: Unless otherwise noted, all reactions were carried out with **1a** (0.2 mmol), **2** (0.3 mmol), Cs_2CO_3 (0.3 mmol) and photocatalyst in 2 mL MeCN, irradiation with a 385 nm LED (0.5 W) at 25 °C for 20 hours. [b] Yields were determined by GC analysis using mesitylene as an internal standard. [c] Irradiation with a 455 nm LED (0.5 W).

Table S2. Screening of bases[a]

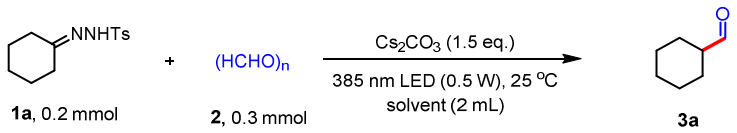


Entry	Base	Yield[b]
1	K_2CO_3	n.d.
2	Na_2CO_3	n.d.

3	$NaHCO_3$	n.d.
4	K_3PO_4	n.d.
5[c]	CsOAc	trace
6	DBU	trace
7	Cs_2CO_3 (1.0 eq.)	63%
8	Cs_2CO_3 (2.0 eq.)	68%
9	-	n.d.

[a] Reaction conditions: Unless otherwise noted, all reactions were carried out with **1a** (0.2 mmol), **2** (0.3 mmol), Cs_2CO_3 (0.3 mmol) and photocatalyst in 2 mL of MeCN, irradiation with a 385 nm LED at 25 °C for 20 hours, n.d. = not detected. [b] Yields were determined by GC analysis using mesitylene as an internal standard. [c] Cyclohexyl acetate was detected in a 48% yield.

Table S3. Screening of solvents[a]

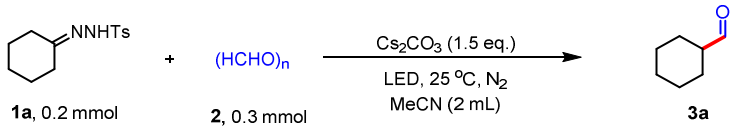


1a, 0.2 mmol **2**, 0.3 mmol **3a**

Entry	Solvent	Yield
1	DMF	20%
2	DMSO	5%
3	toluene	50%
4	dioxane	36%
5	THF	20%
6	$PhCF_3$	48%
7	PhCl	33%

[a] Reaction conditions: Unless otherwise noted, all reactions were carried out with **1a** (0.2 mmol), **2** (0.3 mmol), Cs_2CO_3 (0.3 mmol) and photocatalyst in 2 mL of solvent, irradiation with a 385 nm LED (0.5 W) at 25 °C for 20 hours. [b] Yields were determined by GC analysis using mesitylene as internal standard.

Table S4. Screening of light sources[a]



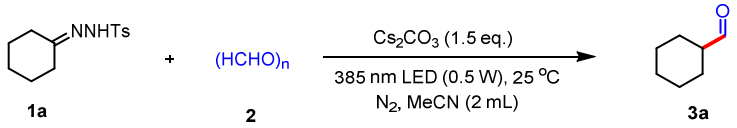
1a, 0.2 mmol **2**, 0.3 mmol **3a**

Entry	Light source	Yield
1	365 nm LED (0.5 W)	65%

2	400 nm LED (0.5 W)	trace
3	385 nm LED (3 W)	68%
4	455 nm LED (0.5 W)	n.d.
5	In the dark	n.d.
6[b]	In the dark and heating to 110 °C	n.d.

[a] Reaction conditions: Unless otherwise noted, all reactions were carried out with **1a** (0.2 mmol), **2** (0.3 mmol), Cs_2CO_3 (0.3 mmol) and photocatalyst in 2 mL MeCN, irradiation with a 385 nm LED at 25 °C for 20 hours. Yields were determined by GC analysis using mesitylene as the internal standard. [b] Cyclohexene was detected as the major product.

Table S5. Screening of ratio of **1a** with **2**[a]



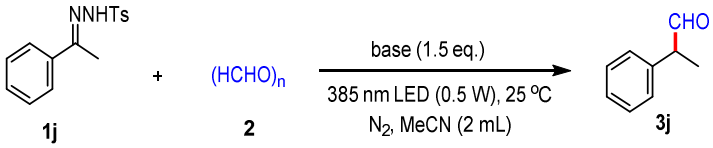
1a 2 3a

Entry	1a : 2	Yield[b]
1	**1:1.2**	**92%**
2	1:1	78%
3	1:2	90%
4[c]	1:1.2	68%

[a] Reaction conditions: Unless otherwise noted, all reactions were carried out with **1a** (0.2 mmol), **2** (0.3 mmol), Cs_2CO_3 (0.3 mmol) and photocatalyst in 2 mL of MeCN, irradiation with a 385 nm LED at 25 °C for 20 hours. [b]Yields were determined by GC analysis using mesitylene as internal standard. [c] Irradiation with a 385 nm LED (3 W).

4.2 Optimization details for reaction of tosylhydrazone 1j with paraformaldehyde 2

Table S6. Screening of reaction parameters[a]



1j 2 3j

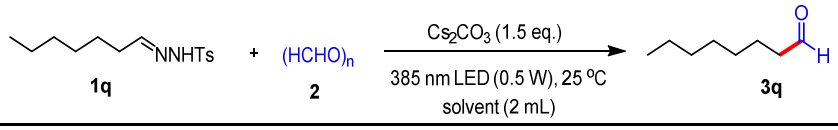
Entry	Solvent	Base	Yield
1	MeCN	Cs_2CO_3	5%
2	DMSO	Cs_2CO_3	trace
3	DMF	Cs_2CO_3	trace
4	DMAc	Cs_2CO_3	10%
5	dioxane	Cs_2CO_3	trace

6	toluene	Cs_2CO_3	3%
7	MeCN	K_2CO_3	n.d.
8	MeCN	Na_2CO_3	n.d.
9[c]	MeCN	CsOAc	trace
10[d]	MeCN	Cs_2CO_3	7%
11[e]	MeCN	Cs_2CO_3	43%
12[f]	MeCN	Cs_2CO_3	**86%**

[a] Reaction conditions: Unless otherwise noted, all reactions were carried out with **1j** (0.2 mmol), **2** (0.24 mmol), Cs_2CO_3 (0.3 mmol) and photocatalyst in 2 mL of solvent, irradiation with a 385 nm LED (0.5 W) at 25 °C for 20 hours. [b] Yields were determined by GC analysis using mesitylene as the internal standard. [c]1-phenylethyl acetate was formed in a 65% yield. [d] **1j** (0.24 mmol, 1.2 eq.), **2** (0.20 mmol, 1.0 eq.). [e]**1j** (0.3 mmol, 1.5 eq.), **2** (0.20 mmol, 1.0 eq.). [f] **1j** (0.4 mmol, 2.0 eq.), **2** (0.20 mmol, 1.0 eq.).

4.3 Optimization details for reaction of tosylhydrazone 1q with paraformaldehyde 2

Table S7. Screening of reaction conditons[a]

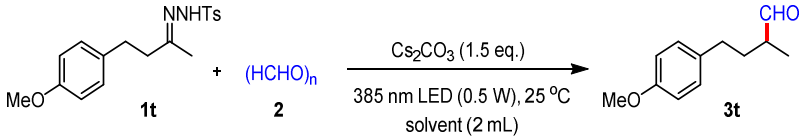


1q 2 3q

Entry	Solvent	Yield
1	DMSO	trace
2	DMAc	1%
3	MeCN	trace
4	toluene	13%
5[c]	toluene	29%
6[d]	toluene	**61%**
7[e]	toluene	43%
8[e]	toluene	47%
9[d]	$PhCF_3$	50%
10[d]	DCM	49%
11[d]	benzene	36%

[a] Reaction conditions: Unless otherwise noted, all reactions were carried out with **1q** (0.2 mmol), **2** (0.24 mmol), Cs_2CO_3 (0.3 mmol) and photocatalyst in 2 mL of solvent, irradiation with a 385 nm LED (0.5 W) at 25 °C for 20 hours. [b] Yields were determined by GC analysis using *n*-dodecane as internal standard. [c] **1q** (0.24 mmol, 1.2 eq.), **2** (0.20 mmol, 1.0 eq.). [d] **1q** (0.3 mmol, 1.5 eq.), **2** (0.20 mmol, 1.0 eq.). [e] **1q** (0.4 mmol, 2.0 eq.), **2** (0.20 mmol, 1.0 eq.).

Table S8. Screening of reaction conditions[a]

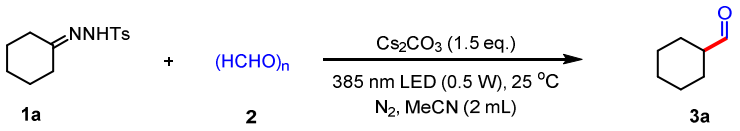


Entry	Solvent	Eq. of 2	Additives / changes	Yield
1	MeCN	1.2		50%
2	MTBE	1.2		33%
3	$(CH_2Cl)_2$	1.2		59%
4	$(CH_2Cl)_2$	1.0		67%
5	CH_2Cl_2	1.2		66%
6	CH_2Cl_2	1.0		70%
7	CH_2Cl_2	1.2	$BnEt_3NCl$ (10 mol%)	71%
8[b]	**CH_2Cl_2**	**1.0**	**$BnEt_3NCl$ (10 mol%)**	**78%**
9	CH_2Cl_2	1.2	$BnEt_3NCl$ (20 mol%)	66%
10	CH_2Cl_2	1.0	$BnEt_3NCl$ (20 mol%)	71%
11	$(CH_2Cl)_2$	1.0	Heating to 60 °C (dark)	n.d.

[a] Reaction conditions: Unless otherwise noted, all reactions were carried out with **1t** (0.2 mmol, 1.0 eq.), **2**, Cs_2CO_3 (0.3 mmol, 1.5 eq.) in 2 mL of solvent, irradiation with a 385 nm LED (0.5 W) at 25 °C for 20 hours. Yields of isolated products are given. [b] Epoxide **3t–1** was isolated in a 16% yield.

5. Mechanistic studies

Reaction profile and on/off Experiments



Procedure: Tosylhydrazone **1a** (0.2 mmol, 53.2 mg), Cs_2CO_3 (0.3 mmol, 98 mg), **2** (0.24 mmol, 7.2 mg), and internal standard (dodecane, 20 uL) were added into a 5 mL snap vial equipped with a stirring bar. The vial was evacuated and back filled with N_2 for three times, followed by the addition of MeCN (2 mL) *via* syringe. Then the reaction mixture was irradiated by a 385 nm LED (0.5 W) at 25 °C. An aliquot of the reaction mixture was then taken at the indicated times and analyzed by GC-FID.

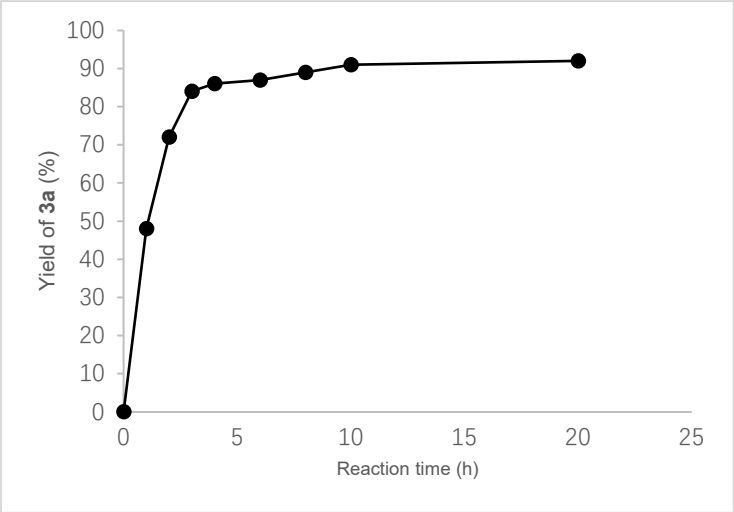


Figure S3. Reaction profile plot

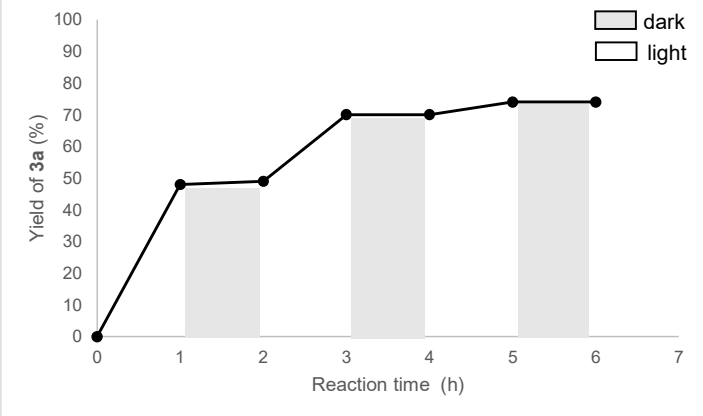
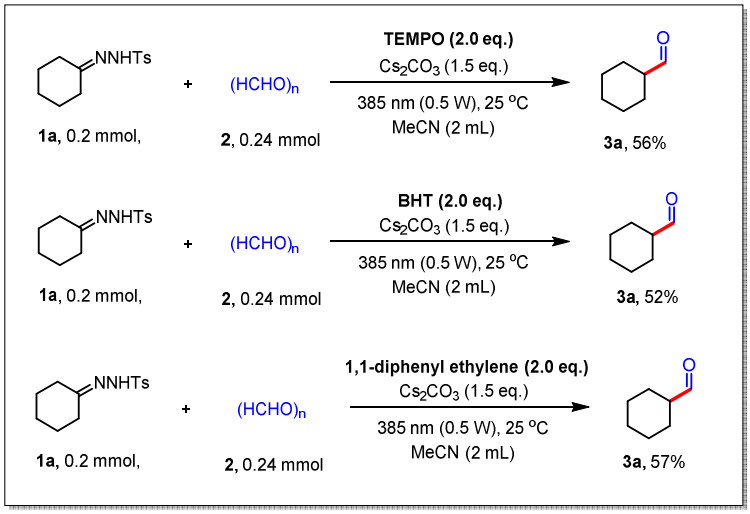


Figure S4. On/off experiments

Radical probing and deuterium labelling experiments



Scheme S2. Radical probing experiments

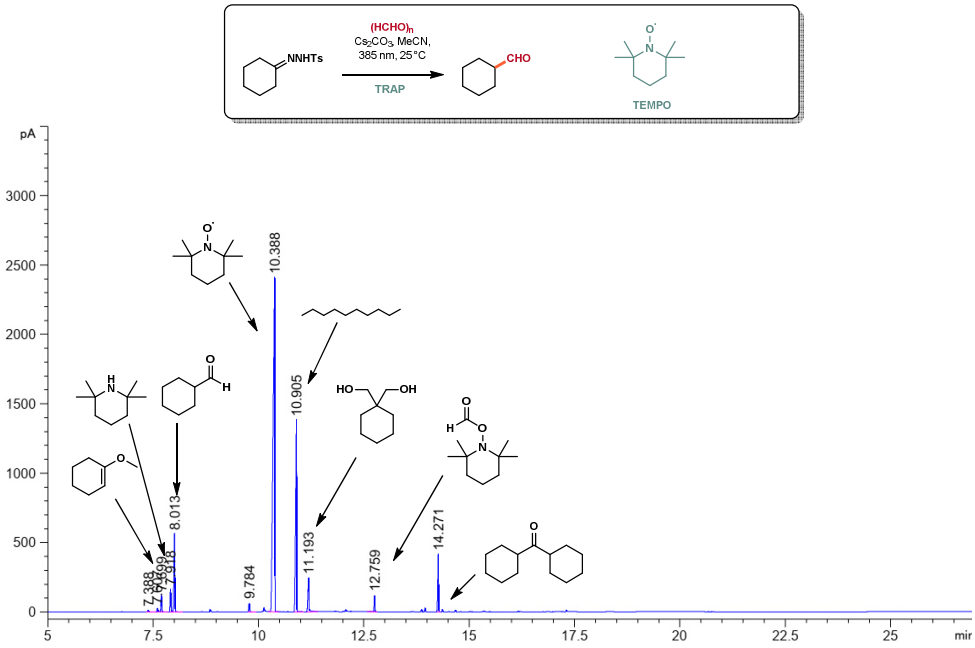


Figure S5. GCMS spectrum of the crude reaction mixture in the presence of TEMPO (2.0 eq.) after light irradiation (385 nm LED). Results: 93% of TEMPO is left unreacted. No radical trapping products can be observed, only small amounts of deoxygenated and formylated products originated from TEMPO were detected. The addition of TEMPO led to the formation of a considerable amount (~30%) of double insertion product dicyclohexyl ketone).

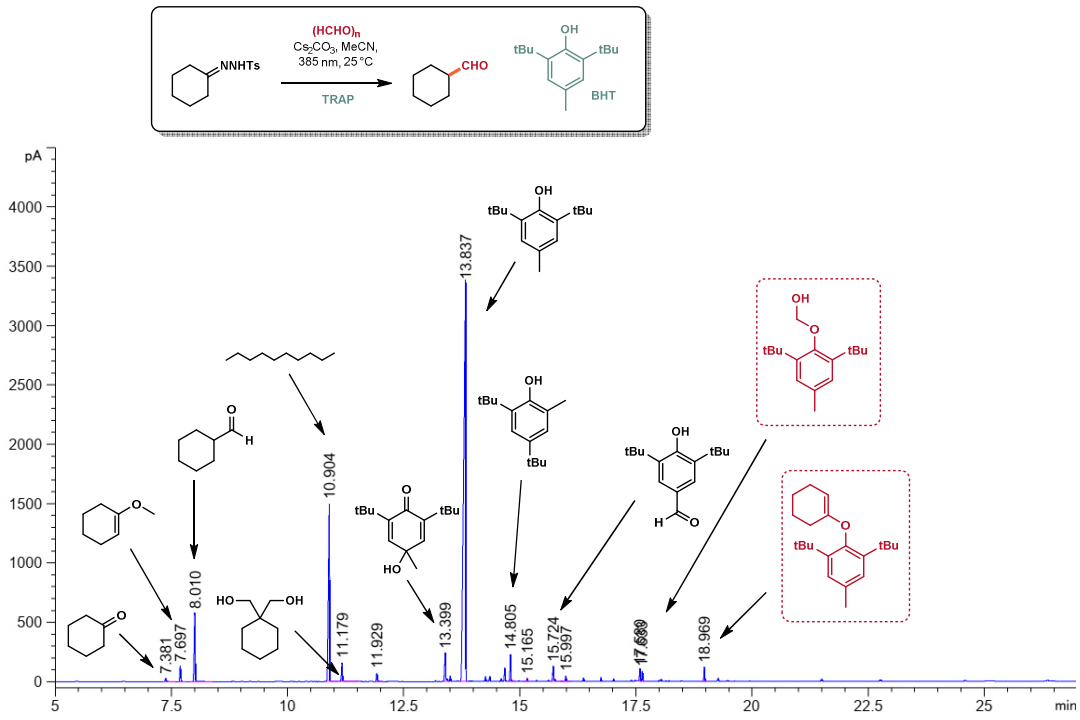


Figure S6. GCMS spectrum of the crude reaction mixture in the presence of BHT (2.0 eq.) after light irradiation (385 nm LED). Results: 75% of BHT (2.0 eq.) is left unreacted. Small amount of product originated from O-H insertion of BHT with diazo could be detected.

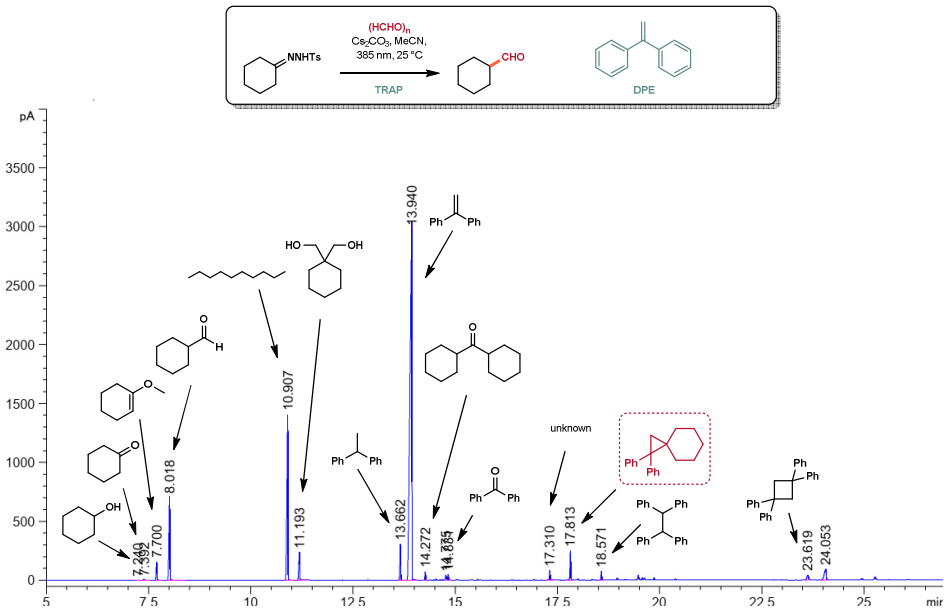
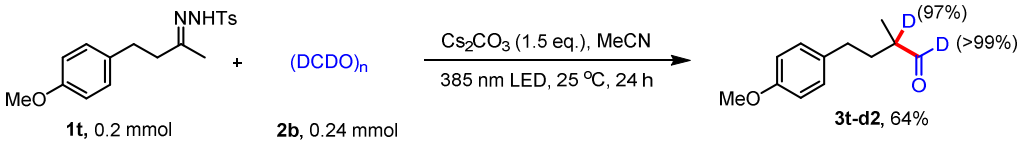
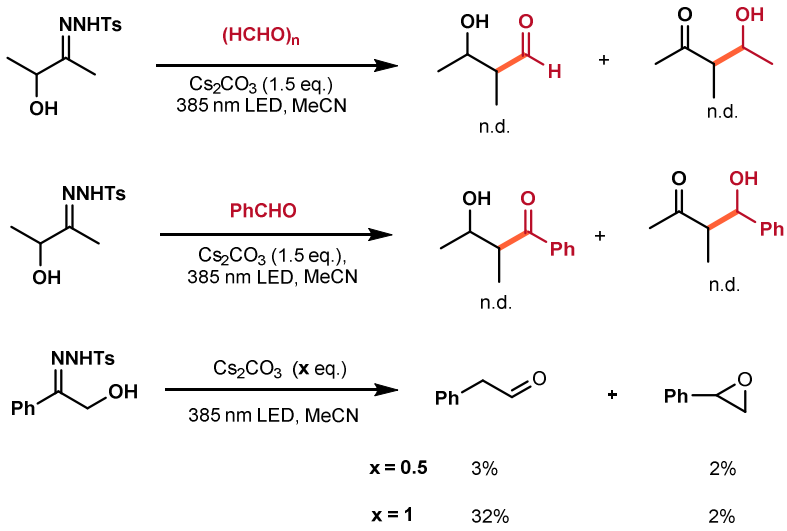


Figure S7. GCMS spectrum of the crude reaction mixture in the presence of 1,1-DPE (2.0 eq.) after light irradiation (385 nm LED). Results: 74% of 1,1-DPE (2.0 eq.) is left unreacted. A small amount of cyclopropanation product originating from carbene trapping by 1,1-DPE could be observed.



Scheme S3. Deuterium labelling experiments



Scheme S4. Semi-pinacol rearrangement experiments. 3-hydroxybutan-2-one-derived tosylhydrazone was synthesized and subjected to the reactions with paraformaldehyde or banzaldehyde, no desired products could be detected under standard conditions. When 2-hydroxy-phenylethanone derived tosylhydrazone was employed, we detected phenylacetaldehyde and styrene oxide in 3% and 2% yield respectively in the presence of Cs_2CO_3 (0.5 eq.). Increasing the amount of Cs_2CO_3 to (1.0 eq.) led to the formation of phenylacetaldehyde in 32% yield and styrene oxide in 2% yield.

Spectroscopic investigations

Optical absorption spectra of the reaction components and their combinations were measured in MeCN. *Note:* considering the poor solubility of paraformaldehyde in MeCN, 1-octanal was selected as the substrate in the UV-vis measurements. The reaction between acetone-derived tosylhydrazone **1aa** and 1-octanal afforded the desired ketone in a 90% yield under the optimized conditions.

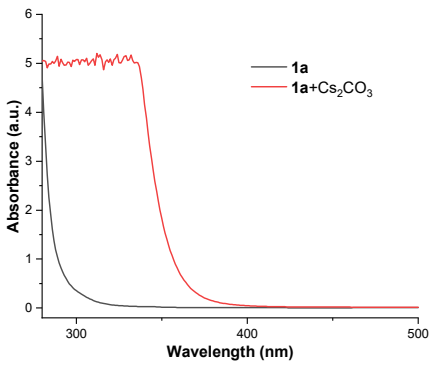


Figure S8. UV-vis spectrum of **1a** (0.1 M) in MeCN (black curve). UV-vis spectrum of **1a** (0.1 M)+Cs_2CO_3 (1.5 eq.) in MeCN (red curve).

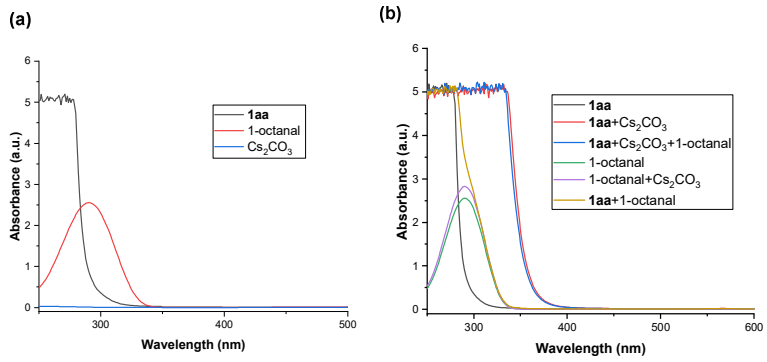
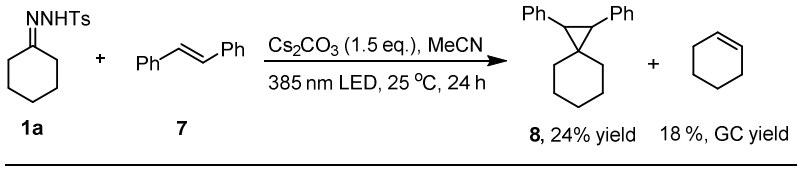
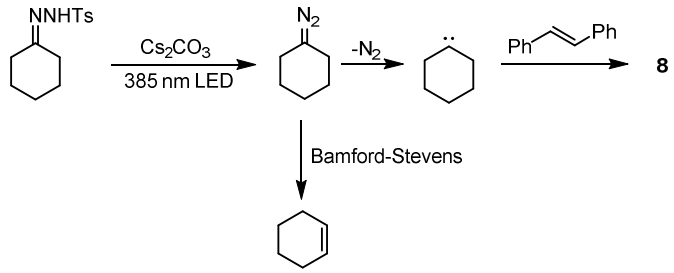


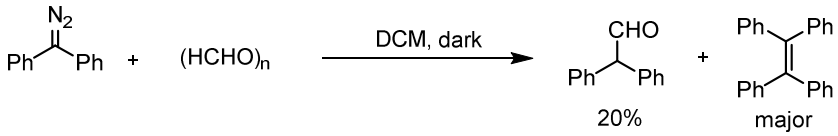
Figure S9. (a) UV-vis spectrum of acetone-derived N-tosylhydrazone **1aa** (0.1 M, black curve), 1-octanal (0.15 M, red curve), Cs_2CO_3 (sat., blue curve) in MeCN. (b) UV-vis spectrum of N-tosylhydrazone **1aa** (0.1 M, black curve), N-tosylhydrazone **1aa** (0.1 M)+Cs_2CO_3 (red curve), N-tosylhydrazone **1aa** (0.1 M)+1-octanal (0.15 M)+Cs_2CO_3 (blue curve),1-octanal (0.15 M, green curve), 1-octanal (0.15 M)+Cs_2CO_3 (purple curve), and N-tosylhydrazone **1aa** (0.1 M)+1-octanal (0.15 M) (brown curve) in MeCN.

Scheme S5. Trapping of diazo intermediates with *E*-stilbene





Scheme S5-1. Reaction of (diazomethylene)dibenzene with paraformaldehyde under dark conditions

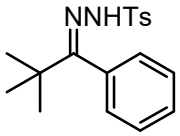


When E-stilbene was used as potential diazo trapping reagent in the reaction, the desired cyclopropanation process occurred to afford the desired product **8** in 24% yield and cyclohexene (18% yield). It is well-known that diazo species would undergo photolysis to produce carbene

intermediates under light irradiation. [2] Therefore, we propose that the diazo formed in our reaction could undergo photolysis to give carbene species and the Bamford-Stevens process to yield alkene in this case. We also showcase that the reaction between diazo and paraformaldehyde could proceed in the dark conditions (Scheme 5-1).

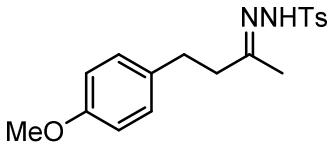
6. Characterization of compounds

(Z)-N'-(2,2-dimethyl-1-phenylpropylidene)-4-methylbenzenesulfonohydrazide



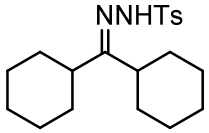
Following **General procedure A-SM** on 5 mmol scale, filtration afforded 1.57g (95%) of the title compound as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.44 – 7.35 (m, 3H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.87 (s, 1H), 6.84 – 6.76 (m, 2H), 2.44 (s, 3H), 1.05 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.46, 143.81, 135.30, 131.60, 129.28, 129.18, 127.82, 127.39,38.48, 27.96, 21.55. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{18}H_{31}N_2O_{22}S$ 331.1475, found 331.1479.

(Z)-N'-(4-(4-methoxyphenyl)butan-2-ylidene)-4-methylbenzenesulfonohydrazide



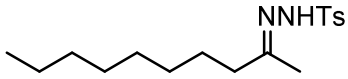
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.43 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 2.74 – 2.70 (m, 2H), 2.50 – 2.46 (m, 2H), 2.44 (s, 3H), 1.74 (s, 3H). **^{3}C NMR (101 MHz, Chloroform-*d*)** δ 157.84, 157.46, 157.44, 143.93, 135.41, 133.07, 129.44, 129.17, 128.07, 113.75, 55.19, 40.50, 31.11, 21.58, 16.05. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{18}H_{23}N_2O_3S$ 347.1424, found 347.1418.

N'-(dicyclohexylmethylene)-4-methylbenzenesulfonohydrazide



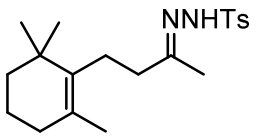
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.48 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.45-2.40 (m, 4H), 2.18-2.11 (m, 1H), 1.78 – 1.52 (m, 10H), 1.34 – 1.12 (m, 10H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 143.81, 135.24, 129.28, 128.15, 41.40, 31.72, 28.41, 26.36, 25.83, 25.76, 25.71, 21.60. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{20}H_{31}N_2O_2S$ 363.2101, found 363.2105.

(Z)-N'-(decan-2-ylidene)-4-methylbenzenesulfonohydrazide



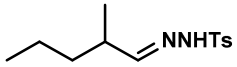
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.16 (s, 1H), 2.42 (s, 3H), 2.18 (t, *J* = 7.6 Hz, 2H), 1.74 (s, 3H), 1.42 (p, *J* = 7.6 Hz, 2H), 1.29 – 1.14 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 158.58, 143.85, 135.46, 129.41, 128.09, 38.68, 31.84, 29.33, 29.17, 28.95, 25.89, 22.65, 21.58, 15.44, 14.09. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{17}H_{29}N_2O_2S$ 325.1944, found 325.1939.

(Z)-4-methyl-N'-(4-(2,6,6-trimethylcyclohex-1-en-1-yl)butan-2 ylidene)benzenesulfonohydrazide



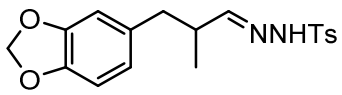
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 2.42 (s, 3H), 2.28 – 2.20 (m, 2H), 2.13-2.07 (m, 2H), 1.88 (t, *J* = 6.4 Hz, 2H), 1.78 (s, 3H), 1.57 – 1.52 (m, 5H), 1.43-1.34 (m, 2H), 0.93 (s, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 143.95, 136.05, 135.29, 129.98, 129.38, 128.23, 39.72, 39.29, 34.98, 32.72, 28.51, 28.48, 28.43, 24.98, 21.60, 19.76, 19.44, 15.84. **HRMS (ESI):** [M+H] $^{+}$ calcd for $C_{20}H_{31}N_2O_2S$ 363.2101, found 363.2009.

(Z)-4-methyl-N'-(2-methylpentylidene)benzenesulfonohydrazide



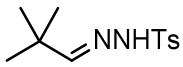
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.55 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 6.4 Hz, 1H), 2.42 (s, 3H), 2.37-2.30 (m, 1H), 1.34 – 1.20 (m, 2H), 1.16 – 1.07 (m, 2H), 0.97 (d, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 157.43, 144.04, 135.16, 129.50, 127.95, 36.37, 36.29, 21.56, 19.94, 17.53, 13.89. **HRMS (ESI):** [M+H] + calcd for $C_{13}H_{20}N_2O_2S$ 269.1318, found 269.1322.

(E)-N'-(3-(benzo[d][1,3]dioxol-5-yl)-2-methylpropylidene)-4-methylbenzenesulfonohydrazide



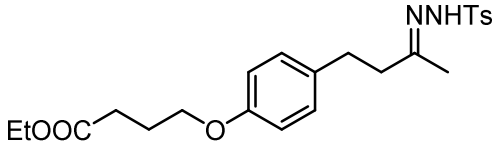
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.69 (s, 1H), 7.29 (dd, *J* = 8.8, 0.8 Hz, 2H), 7.09 (d, *J* = 4.2 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 1.6 Hz, 1H), 6.47 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.90 (dd, *J* = 2.4, 1.2 Hz, 2H), 2.70-2.65 (m, 1H), 2.63 – 2.55 (m, 1H), 2.49 – 2.45 (m, 1H), 2.43 (s, 3H), 0.98 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 155.94, 147.50, 145.86, 144.06, 135.19, 132.79, 129.52, 127.85, 121.89, 109.32, 108.05, 100.76, 40.05, 38.35, 21.57, 17.00. **HRMS (ESI):** [M+H] + calcd for $C_{18}H_{20}N_2O_4S$ 361.1217, found 361.1214.

(Z)-N'-(2,2-dimethylpropylidene)-4-methylbenzenesulfonohydrazide



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.23 (s, 1H), 7.06 (s, 1H), 2.43 (s, 3H), 1.01 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 160.23, 144.04, 129.41, 128.02, 35.13, 27.11, 21.59. **HRMS (ESI):** [M+H] + calcd for $C_{12}H_{18}N_2O_2S$ 255.1162, found 255.1164.

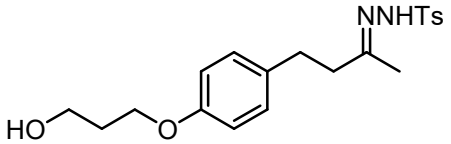
ethyl 4-(4-(3-methyl-4-oxobutyl)phenoxy)butanoate



Following **General procedure B-SM** on 3.15 mmol scale, purification by flash column chromatography (30% to 50%, EtOAc in petroleum ether) on silica gel afforded 1.04g (78%) of the

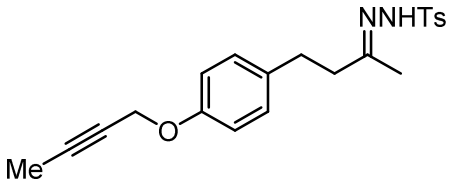
title compound as a white solid, Rf = 0.3 (silica gel, petroleum ether/ethyl acetate = 3:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.29 (m, 3H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 4.14 (dd, *J* = 14.0, 7.2 Hz, 2H), 4.00-3.94 (m, 2H), 2.70 (dd, *J* = 16.0, 8.0 Hz, 2H), 2.55 – 2.43 (m, 7H), 2.12 – 2.07 (m, 2H), 1.74 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.21, 157.52, 157.09, 143.89, 135.42, 133.18, 129.43, 129.15, 128.06, 114.36, 66.69, 60.39, 40.48, 31.12, 30.79, 24.64, 21.56, 16.08, 14.18.
HRMS (ESI): $[M+H]^+$ calcd for $C_{23}H_{31}N_2O_5S$ 447.1948, found 447.1951.

(Z)-N'-(4-(4-(3-hydroxypropoxy)phenyl)butan-2-ylidene)-4-methylbenzenesulfonohydrazide



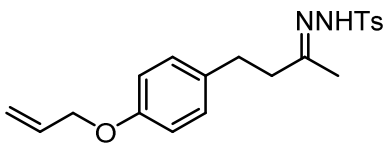
Following **General procedure B-SM** on 3.15 mmol scale, purification by flash column chromatography (30% to 50%, EtOAc in petroleum ether) on silica gel afforded 0.96g (82%) of the title compound as a white solid, Rf = 0.3 (silica gel, petroleum ether/ethyl acetate = 3:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 4.10 (t, *J* = 7.0 Hz, 2H), 3.87 (t, *J* = 7.0 Hz, 2H), 2.75-2.69 (m, 2H), 2.51-2.44 (m, 5H), 2.05 – 1.91 (m, 3H), 1.91 (s, 1H), 1.74 – 1.73 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.56 (d, *J* = 5.6 Hz), 156.99, 143.89, 135.40, 133.32, 129.42, 129.18, 128.04, 114.35, 65.78 (d, *J* = 3.1 Hz), 60.50 (d, *J* = 4.9 Hz), 40.43, 31.95, 31.10, 21.55, 16.11. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{20}H_{27}N_2O_4S$ 391.1686, found 391.1690.

(***Z)-N'-(4-(4-(but-2-yn-1-yloxy)phenyl)butan-2-ylidene)-4-methylbenzenesulfonohydrazide***



Following **General procedure B-SM** on 3.15 mmol scale, purification by flash column chromatography (15% to 20%, EtOAc in petroleum ether) on silica gel afforded 0.98g (85%) of the title compound as a white solid, Rf = 0.5 (silica gel, petroleum ether/ethyl acetate = 5:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 3H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 4.67 (s, 2H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.57-2.52 (m, 5H), 1.93 (s, 3H), 1.84 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.54, 156.01, 143.83, 135.36, 133.66, 129.37, 129.07, 127.95, 114.59, 83.50, 74.05, 56.30, 40.36, 31.03, 21.49, 16.11, 3.58.**HRMS (ESI):** $[M+H]^+$ calcd for $C_{21}H_{25}N_2O_3S$ 385.1580, found 385.1578.

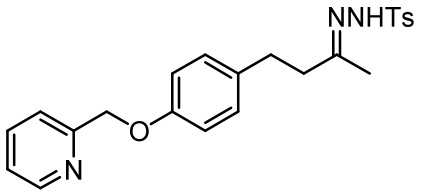
(Z)-N'-(4-(4-(allyloxy)phenyl)butan-2-ylidene)-4-methylbenzenesulfonohydrazide



Following **General procedure B-SM** on 3.15 mmol scale, purification by flash column

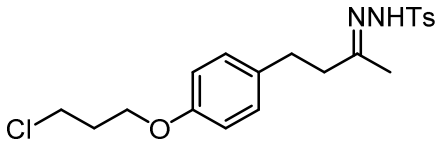
chromatography (10% to 15%, EtOAc in petroleum ether) on silica gel afforded 0.93 g (83% yield) of the title compound as a white solid, Rf = 0.5 (silica gel, petroleum ether/ethyl acetate = 5:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.10 – 6.00 (m, 1H), 5.43-5.37 (m, 1H), 5.29 – 5.26 (m, 1H), 4.51-4.48 (m, 2H), 2.74 – 2.70 (m, 2H), 2.50-2.43 (m, 6H), 1.75 (d, *J* = 2.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.54, 156.88, 143.92, 135.43, 133.39, 133.28, 129.44, 129.15, 128.07, 117.51, 114.63, 68.81, 40.45, 31.13, 21.58, 16.07.
HRMS (ESI): $[M+H]^+$ calcd for $C_{20}H_{25}N_2O_3S$ 373.1580, found 373.1577.

(E)-4-methyl-N'-(4-(4-(pyridin-2-ylmethoxy)phenyl)butan-2-ylidene)benzenesulfonohydrazide



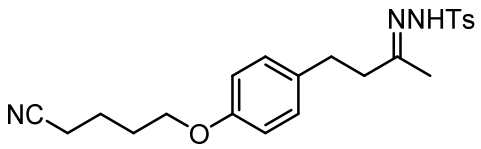
Following **General procedure B-SM** on 3.15 mmol scale, purification by flash column chromatography (25% to 50%, EtOAc in petroleum ether) on silica gel afforded 1.03 g (81% yield) of the title compound as a white solid, Rf = 0.5 (silica gel, petroleum ether/ethyl acetate = 5:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.49 (m, 2H), 7.78 – 7.65 (m, 4H), 7.26 – 7.20 (m, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.76-6.74 (d, *J* = 8.8 Hz, 2H), 4.96 (s, 2H), 2.68-2.62 (m, 2H), 2.42 – 2.35 (m, 5H), 1.68 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.42, 156.63, 149.29, 148.86, 143.85, 135.49, 135.26, 133.95, 132.65, 129.40, 129.33, 128.06, 123.49, 114.75, 67.57, 40.40, 31.11, 21.56, 16.16.
HRMS (ESI): $[M+H]^+$ calcd for $C_{23}H_{26}N_3O_3S$ 424.1689, found 424.1683.

(Z)-N'-(4-(4-(3-chloropropoxy)phenyl)butan-2-ylidene)-4-methylbenzenesulfonohydrazide



Following **General procedure B-SM** on 3.15 mmol scale, purification by flash column chromatography (25% to 50%, EtOAc in petroleum ether) on silica gel afforded 0.83 g (68% yield) of the title compound as a white solid, Rf = 0.3 (silica gel, petroleum ether/ethyl acetate = 4:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* =8.0 Hz, 2H), 7.71 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 4.07 (t, *J* = 6.0 Hz, 2H), 3.74 (t, *J* = 6.4 Hz, 2H), 2.73 – 2.68 (m, 2H), 2.49-2.44 (m, 5H), 2.27 – 2.19 (m, 2H), 1.75 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.40, 157.01, 143.94, 135.46, 133.41, 129.46, 129.24, 128.11, 114.45, 64.30, 41.53, 40.47, 32.30, 31.13, 21.59, 16.01. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{20}H_{26}ClN_2O_3S$ 409.1347, found 409.1356.

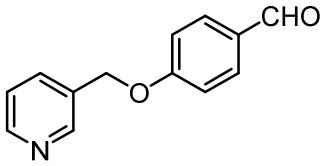
(Z)-N'-(4-(4-(4-cyanobutoxy)phenyl)butan-2-ylidene)-4-methylbenzenesulfonohydrazide



Following **General procedure B-SM** on 3.15 mmol scale, purification by flash column

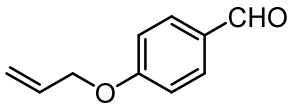
chromatography (15% to 25%, EtOAc in petroleum ether) on silica gel to afford 0.95 g (77% yield) of the title compound as a white solid, Rf = 0.3 (silica gel, petroleum ether/ethyl acetate = 3:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.47 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 2H), 4.01-3.95 (m, 2H), 2.74 – 2.70 (m, 2H), 2.49-2.44 (m, 7H), 1.96 – 1.89 (m, 4H), 1.74 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.53, 156.96, 143.91, 135.44, 133.39, 129.44, 129.25, 128.09, 119.49, 114.34, 66.63, 40.46, 31.13, 28.17, 22.44, 21.58, 16.97, 16.08.
HRMS (ESI): $[M+H]^+$ calcd for $C_{22}H_{28}N_3O_3S$ 414.1846, found 414.1854.

4-(pyridin-2-ylmethoxy)benzaldehyde



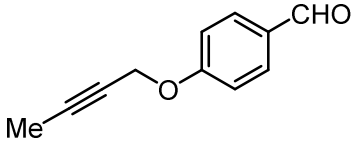
Following **General procedure D-SM** on 3 mmol scale starting from 3-Picolyl chloride hydrochlorid, purification by flash column chromatography (15% to 25%, EtOAc in petroleum ether) on silica gel afforded the title compound as a white solid 0.47 g (73% yield), Rf = 0.3 (silica gel, petroleum ether/ethyl acetate = 2:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.89 (s, 1H), 8.69-8.61 (m 2H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.36-7.33 (m, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 5.16 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 190.65, 163.19, 149.76, 148.95, 135.26, 132.00, 131.53, 130.45, 123.57, 115.03, 67.75. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{13}H_{12}NO_2$ 214.0863, found 214.0860.

4-(allyloxy)benzaldehyde



Following **General procedure D-SM** on 3 mmol scale starting from 3-bromoprop-1-ene (0.38 g, 3.15 mmol), purification by flash column chromatography (1% to 3%, EtOAc in petroleum ether) on silica gel afforded the title compound as a white solid 0.40 g (83% yield), Rf = 0.3 (silica gel, petroleum ether/ethyl acetate = 30:1).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.88 (s, 1H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.09-6.0 (m, 1H), 5.43 (d, *J* = 17.2 Hz, 1H), 5.33 (d, *J* = 10.4 Hz, 1H), 4.62 (d, *J* = 4.8 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 190.75, 163.57, 132.25, 131.92, 130.01, 118.31, 114.97, 68.97. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{10}H_{11}O_2$ 163.0754, found 163.0753.

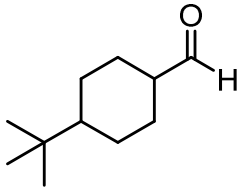
4-(but-2-yn-1-yloxy)benzaldehyde



Following **General procedure D-SM** on 3 mmol scale starting from 1-Bromo-2-butyne (0.42 g, 3.15 mmol, purification by flash column chromatography (1% to 3%, EtOAc in petroleum ether) on silica gel afforded the title compound as a white solid 0.45 g (86% yield), Rf = 0.3 (silica gel, petroleum ether/ethyl acetate = 30:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.89 (s, 1H), 7.84 (d, *J*

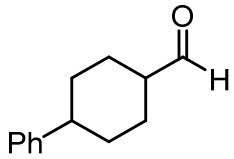
= 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.73 (d, *J* = 8.4 Hz, 2H), 1.86 (t, *J* = 2.4 Hz, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 190.79, 162.74, 131.85, 130.29, 115.14, 84.67, 73.07, 56.63, 3.64. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{11}H_{11}O_2$ 175.0754, found 175.0751.

4-(tert-Butyl)cyclohexane-1-carbaldehyde (3b)



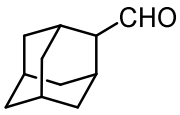
Following the general procedure A, the product was obtained as a colorless oil, 17.1 mg, 51% yield, (trans : cis = 3.8 : 1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.71 (s, 0.26 H), 9.60 (d, *J* = 1.8 Hz, 1H), 2.42-2.37 (m, 0.29 H), 2.31-2.24 (m, 0.59 H), 2.18-2.07 (m, 1H), 2.05-1.97 (m, 2H), 1.92-1.86 (m, 2H), 1.73-1.63 (m, 0.77H), 1.57-1.45(m, 1.6H), 1.29-1.15 (m, 2.4H), 1.09-0.90 (m, 6H), 0.85 (s, 9H), 0.79 (s, 2.5H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.97, 204.97, 50.51, 47.76, 47.55, 46.47, 32.46, 32.43, 31.75, 29.67, 27.45, 27.35, 26.46, 26.17, 25.44, 24.06. **HRMS** (EI), Calcd. for $C_{11}H_{20}O$ $[M]^+$ 168.1509, found, 168.1513.

4-Phenylcyclohexane-1-carbaldehyde (3c)



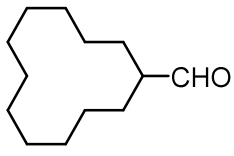
Following the general procedure A, the product was obtained as a white solid, 32.3 mg, 86% yield (trans : cis = 1:11.2). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.79 (s, 0.7H), 9.68 (d, J = 1.8, 0.1H), 7.32-7.25 (m, 2H), 7.24-7.14 (m, 3H), 2.91-2.70 (m, 0.2H), 2.58-2.48 (m, 1.8H), 2.38-2.31 (m, 1.73 H), 2.20-1.93 (m, 0.6 H), 1.85 – 1.67 (m, 4H), 1.57-1.41 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.50, 146.80, 134.96, 128.35, 126.73, 126.04, 46.24, 43.59, 32.91, 30.61, 26.3, 24.98. **HRMS** (EI), Calcd. for $C_{13}H_{16}O$ $[M]^+$ 188.1210, found, 188.1209.

Adamantane-2-carbaldehyde (3d)



Following the general procedure A, the product was obtained as a colorless oil, 24.0 mg, 73% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.73 (s, 1H), 2.42-2.38 (m, 3H), 1.98-1.91 (m, 2H), 1.89-1.83 (m, 2H), 1.80-1.61 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 206.01, 56.55, 37.79, 36.99, 33.48, 28.11, 27.87, 27.44. **HRMS** (EI) Calcd. for $C_{11}H_{16}O$ $[M]^+$: 164.1201. Found: 164.1209. **HRMS** (EI) Calcd. for $C_{11}H_{16}O$ $[M]^+$: 164.1201. Found: 164.1209.

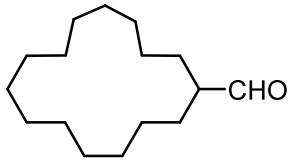
Cyclododecanecarbaldehyde (3e)



Following the general procedure A, the product was obtained as a colorless oil, 28.2 mg, 72% yield.

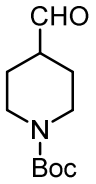
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.63 (d, *J* = 1.5 Hz, 1H), 2.44-2.35 (m, 1H), 1.70-1.59 (m, 2H), 1.57-1.44 (m, 2H), 1.42-1.29 (m, 18H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.41, 47.71, 23.72, 23.58, 23.52, 23.45, 23.33, 22.30. **HRMS** (EI), Calcd. for $C_{13}H_{24}O$ $[M]^+$ 196.1827, found, 196.1819.

Cyclopentadecanecarbaldehyde (3f)



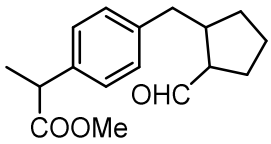
Following the general procedure A, the product was obtained as a colorless oil, 20.0mg, 42% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.61 (d, *J* = 1.8 Hz, 1H), 2.33-2.24 (m, 1H), 1.74-1.61 (m, 2H), 1.57-1.44 (m, 2H), 1.43-1.28 (m, 24H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.32, 50.20, 27.07, 26.70, 26.67, 26.60, 26.49, 26.38, 24.82. **HRMS** (EI) Calcd. for $C_{16}H_{30}O[M]^+$: 238.2291. Found: 238.2293.

tert-Butyl 4-formylpiperidine-1-carboxylate (3g)



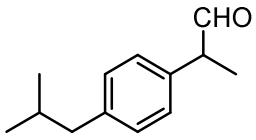
Following the general procedure A, the product was obtained as a yellowish oil, 14.5 mg, 34% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.65 (d, *J* = 1.2 Hz, 1H), 4.00-3.95 (m, 2H), 2.96-2.87 (m, 2H), 2.46 - 2.35 (m, 1H), 1.93-1.85 (m, 2H), 1.61-1.48 (m, 2H), 1.45 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 202.99, 154.65, 79.72, 47.99, 28.39, 25.13. **HRMS** (ESI) Calcd. for $C_{11}H_{20}NO_3^+$ $[M+H]^+$: 214.1438. Found: 214.1434.

Methyl 2-(4-((2-formylcyclopentyl)methyl)phenyl)propanoate (3i)



Following the general procedure A, the product was obtained as a yellowish oil, 27.9 mg, 51% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.44 (d, *J* = 2.4 Hz, 1H), 7.22-7.18 (m, 2H), 7.14-7.10 (m, 2H), 3.73-3.63 (m, 4H), 2.76-2.58 (m, 2H), 2.49-2.34 (m, 2H), 1.90-1.54 (m, 5H), 1.47 (d, *J* = 7.2 Hz, 3H), 1.39-1.32 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 203.59, 175.05, 139.35, 138.28, 129.14, 127.41, 57.20, 51.96, 44.93, 42.87, 40.41, 32.40, 26.19, 24.54, 18.52. **HRMS** (EI): Calcd. For $C_{17}H_{22}O_3$ $[M]^+$: 274.1563, Found: 274.1558. *Note: the stereochemistry of this product was not assigned due to NMR signal overlap.*

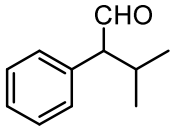
2-(4-Isobutylphenyl)propanal (3k)



Following the general procedure B, the product was obtained as a colorless oil, 23.9 mg, 63% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.68 (d, *J* = 1.5 Hz, 1H), 7.18-7.11 (m, 4H), 3.64-3.58 (m, 1H), 2.48 (d, *J* = 7.2 Hz, 2H), 1.92-1.82 (m, 1H), 1.44 (d, *J* = 7.2 Hz, 3H), 0.93 (s, 3H), 0.91 (s, 3H). **^{13}C NMR** (101

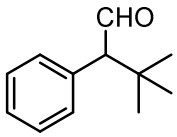
MHz, $CDCl_3$) δ 201.16, 140.97, 134.80, 129.75, 127.97, 52.58, 44.96, 30.14, 22.31, 14.51. **HRMS** (EI): Calcd. For $C_{13}H_{18}O$ $[M]^+$: 190.1358, Found: 190.1349.

3-Methyl-2-phenylbutanal (3l)



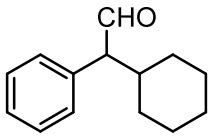
Following the general procedure A, the product was obtained as a colorless oil, 14.3 mg, 44% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.71 (d, *J* = 3.3 Hz, 1H), 7.40-7.27 (m, 3H), 7.21-7.17 (m, 2H), 3.18 (dd, *J* = 9.3, 3.3 Hz, 1H), 2.50-2.34 (m, 1H), 1.05 (d, *J* = 6.6 Hz, 3H), 0.77 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 201.13, 135.45, 129.29, 128.87, 127.44, 66.82, 28.75, 21.16, 20.01. **HRMS** (EI) Calcd. for $C_{11}H_{14}O$ $[M]^+$: 162.1045. Found: 162.1046. Spectroscopic results agree with preciously reported data.[5]

3,3-Dimethyl-2-phenylbutanal (3m)



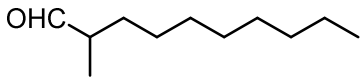
Following the general procedure A, the product was obtained as a colorless oil, 14.8 mg, 42% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.01 (d, *J* = 3.3 Hz, 1H), 7.39-7.27 (m, 3H), 7.24-7.20 (m, 2H), 3.29 (d, *J* = 3.3 Hz, 1H), 1.03 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 202.27, 135.20, 130.35, 128.29, 127.26, 68.34, 34.55, 28.18. **HRMS** (ESI) Calcd. for $[M+NH_4]^+$: 194.1539. Found: 194.1538. Spectroscopic results agree with previously reported data.[6]

2-Cyclohexyl-2-phenylacetaldehyde (3n)



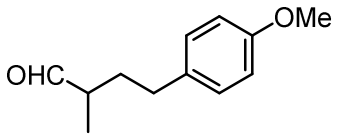
Following the general procedure A, the product was obtained as a colorless oil, 22.6 mg, 56% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.70 (d, *J* = 3.6 Hz, 1H), 7.39-7.26 (m, 3H), 7.20-7.16 (m, 2H), 3.25 (dd, *J* = 9.6, 3.6 Hz, 1H), 2.18-2.05 (m, 1H), 1.89-1.71 (m, 2H), 1.69-1.61 (m, 2H), 1.46-1.25 (m, 2H), 1.24-1.00 (m, 3H), 0.87-0.74 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 201.21, 135.19, 129.29, 128.85, 127.37, 65.82, 38.12, 31.77, 30.15, 26.20, 26.04, 26.00. **HRMS** (EI) Calcd. for $C_{14}H_{18}O$ $[M]^+$: 202.1352. Found: 202.1352. Spectroscopic results agree with preciously reported data.[6]

2-Methyldecanal (3s)



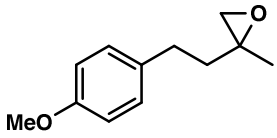
Following the general procedure D, the product was obtained as a colorless oil, 25.4 mg, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.60 (d, *J* = 2.0 Hz, 1H), 2.36-2.27 (m, 1H), 1.74-1.63 (m, 1H), 1.37 – 1.26 (m, 13H), 1.07 (d, *J* = 7.2 Hz, 3H), 0.88 – 0.85 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.32, 46.29, 31.82, 30.50, 29.60, 29.38, 29.20, 26.91, 22.62, 14.05, 13.28. **HRMS** (ESI): Calcd. For $[M+NH_4]^+$: 188.2009, Found: 188.2007.

4-(4-Methoxyphenyl)-2-methylbutanal (3t)



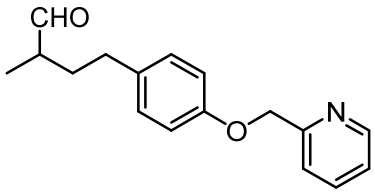
Following the general procedure D, the product was obtained as a colorless oil, 30.0 mg, 78% yield. Following the general procedure A with **1j** (8 mmol), the product was obtained as a colorless oil, 675.8 mg, 44% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.62 (d, *J* = 1.6 Hz, 1H), 7.12-7.08 (m, 2H), 6.85-6.82 (m, 2H), 3.79 (s, 3H), 2.68-2.55 (m, 2H), 2.42-2.32 (m, 1H), 1.68-1.59 (m, 1H), 1.14 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.89, 157.95, 133.37, 129.28, 113.88, 55.24, 45.57, 32.38, 32.12, 13.32. **HRMS** (EI): Calcd. For $C_{12}H_{16}O_2$ $[M]^+$: 192.1145, Found: 192.1150.

2-(4-Methoxyphenethyl)-2-methyloxirane (3t-1)



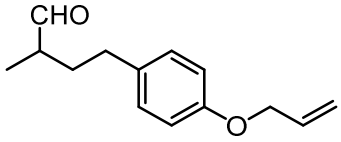
Following the general procedure E, the byproduct was obtained as a colorless oil, 6.2 mg, 16% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 2.68 – 2.62 (m, 2H), 2.62 – 2.56 (m. 2H), 1.90 (ddd, J = 13.8, 9.1, 6.9 Hz, 1H), 1.79 (ddd, J = 13.8, 9.1, 6.7 Hz, 1H), 1.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 133.7, 129.3, 129.2, 113.9, 113.9, 56.7, 55.3, 54.0, 38.8, 30.5, 21.0.

2-methyl-4-(4-(pyridin-2-ylmethoxy)phenyl)butanal (3u)



Following the general procedure D, the product was obtained as a colorless oil, 35 mg, 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.60 (d, *J* = 2.0 Hz, 1H), 8.67 – 8.56 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.32 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.10 (d, *J* = 8.4, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.05 (s, 2H), 2.65 – 2.57 (m, 2H), 2.38 – 2.32 (m, 1H), 2.07-1.97 (m, 1H), 1.67-1.58 (m, 1H), 1.13 (dd, *J* = 7.2, 2.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.78, 156.71, 149.21, 148.80, 135.30, 134.16, 132.68, 129.40, 123.49, 114.80, 67.53, 45.52, 32.27, 32.09, 13.30. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{17}H_{20}NO_2$ 270.1489, found 270.1489.

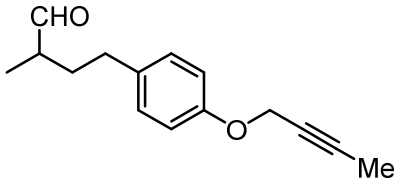
4-(4-(allyloxy)phenyl)-2-methylbutanal (3v)



Following the general procedure D, the product was obtained as a colorless oil, 24 mg, 55% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.61 (d, *J* = 1.6 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.10 (m, 1H), 5.44 – 5.26 (m, 2H), 4.53-4.50 (m, 2H), 2.68-2.54 (m, 2H), 2.41-2.32 (m, 1H),

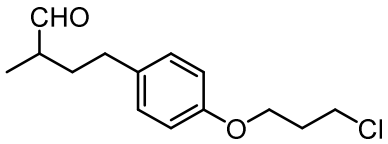
2.04-1.98 (m, 1H), 1.68 – 1.59 (m, 1H), 1.14 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 204.84, 156.97, 133.56, 133.41, 129.25, 117.52, 114.74, 68.84, 45.56, 32.33, 32.12, 13.31. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{14}H_{19}O_2$ 219.1380, found 219.1383.

4-(4-(but-2-yn-1-yloxy)phenyl)-2-methylbutanal (3w)



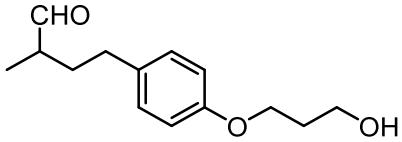
Following the general procedure D, the product was obtained as a colorless oil, 33 mg, 72% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.61 (d, *J* = 2.0 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 4.62 (d, *J* = 2.4 Hz, 2H), 2.68 – 2.54 (m, 2H), 2.41 – 2.32 (m, 1H), 2.07-1.98 (m, 1H), 1.86 (s, 3H), 1.68-1.58 (m, 1H), 1.14 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 204.81, 156.20, 133.96, 129.22, 114.80, 83.55, 74.11, 56.42, 45.53, 32.29, 32.11, 13.29, 3.65. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{15}H_{19}O_2$ 231.1380, found 231.1378.

4-(4-(3-chloropropoxy)phenyl)-2-methylbutanal (3x)



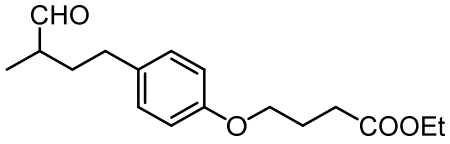
Following the general procedure D, the product was obtained as a colorless oil, 32 mg, 63% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.61 (d, *J* = 2.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 4.09 (t, *J* = 6.2 Hz, 2H), 3.74 (t, *J* = 6.4 Hz, 2H), 2.68-2.55 (m, 2H), 2.39 – 2.32 (m, 1H), 2.25-2.19 (m, 2H), 2.07-1.98 (m, 1H), 1.68-1.59 (m, 1H), 1.14 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 204.84, 157.06, 133.64, 129.31, 114.50, 64.26, 45.53, 41.53, 32.34, 32.28, 32.10, 13.30. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{14}H_{20}ClO_2$ 255.1146, found 255.1137.

4-(4-(3-hydroxypropoxy)phenyl)-2-methylbutanal (3y)



Following the general procedure D, the product was obtained as a colorless oil, 20 mg, 42% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.60 (d, *J* = 2.0 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.10 (t, *J* = 6.0 Hz, 2H), 3.85 (t, *J* = 6.0 Hz, 2H), 2.67 – 2.54 (m, 2H), 2.39-2.31 (m, 1H), 2.06 – 1.96 (m, 3H), 1.79 – 1.58 (m, 2H), 1.13 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 204.89, 157.11, 133.61, 129.30, 114.49, 65.82, 60.53, 45.54, 32.34, 32.10, 31.97, 13.30. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{14}H_{21}O_3$ 237.1485, found 237.1493.

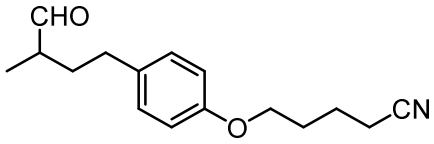
Ethyl 4-(4-(3-methyl-4-oxobutyl)phenoxy)butanoate (3z)



Following the general procedure D, the product was obtained as a colorless oil, 31 mg, 53% yield.

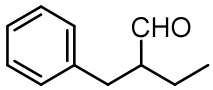
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.61 (d, *J* = 2.0 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 2.0 Hz, 2H), 4.17-4.11 (m, 2H), 3.98 (t, *J* = 6.2 Hz, 2H), 2.66 – 2.49 (m, 4H), 2.40-2.31 (m, 1H), 2.13 – 1.98 (m, 3H), 1.67 – 1.61 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.14 (d, *J* = 7.2 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 204.86, 173.25, 157.22, 133.47, 129.28, 114.50, 66.75, 60.40, 45.57, 32.38, 32.13, 30.83, 24.68, 14.21, 13.32. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{17}H_{25}O_4$ 293.1747, found 293.1752.

5-(4-(3-methyl-4-oxobutyl)phenoxy)pentanenitrile (3aa)



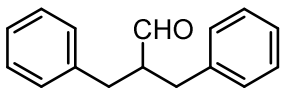
Following the general procedure D, the product was obtained as a colorless oil, 30 mg, 58% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.61 (d, *J* = 2.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.99-3.96 (m, 2H), 2.67 – 2.54 (m, 2H), 2.46 – 2.33 (m, 3H), 2.07 – 1.84 (m, 5H), 1.67-1.58 (m, 1H), 1.13 (d, *J* = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 204.79, 157.03, 133.64, 129.32, 119.47, 114.40, 66.61, 45.52, 32.32, 32.08, 28.16, 22.43, 16.94, 13.30. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{16}H_{22}NO_2$ 260.1465, found 260.1456.

2-Benzylbutanal (3ab)



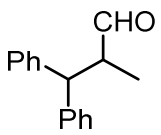
Following the general procedure D, the product was obtained as a colorless oil, 25.6 mg, 79% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.68 (d, *J* = 2.7 Hz, 1H), 7.32-7.15 (m, 5H), 3.04-2.97 (m, 1H), 2.76-2069 (m, 1H), 2.65-2.52 (m, 1H), 1.76-1.50 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 204.71, 138.91, 128.92, 128.48, 126.32, 54.79, 34.53, 21.52, 11.30. **HRMS** (EI) Calcd. for $C_{11}H_{14}O$ $[M]^+$: 162.1045. Found: 162.1047. Spectroscopic results agree with previously reported data.[3]

2-Benzyl-3-phenylpropanal (3ac)



Following the general procedure D, the product was obtained as a colorless oil, 23.4 mg, 53% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (d, *J* = 1.2 Hz, 1H), 7.32-7.27 (m, 4H), 7.24-7.14 (m, 6H), 3.03-2.85 (m, 3H), 2.81-2.73 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.03, 138.62, 129.83, 129.05, 128.63, 128.37, 126.55, 54.88, 34.94. **HRMS** (EI) Calcd. for $C_{16}H_{16}O$ $[M]^+$: 224.1196. Found: 224.1195. Spectroscopic results agree with previously reported data.[3]

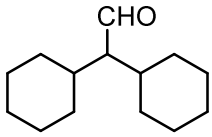
2-Methyl-3,3-diphenylpropanal (3ad)



Following the general procedure D, the product was obtained as a colorless oil, 39.0 mg, 87% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.59 (d, *J* = 3.0 Hz, 1H), 7.34-7.25 (m, 8H), 7.23-7.16 (m, 2H), 4.09 (d, *J* = 11.1 Hz, 1H), 3.38-3.26 (m, 1H), 1.05 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ

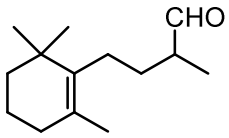
204.20, 142.17, 142.04, 128.80, 128.73, 128.11, 127.97, 126.79, 126.71, 53.35, 50.11, 13.61. **HRMS** (EI): Calcd. For $C_{16}H_{16}O$ $[M]^+$: 224.1196, Found: 224.1199. Spectroscopic results agree with previously reported data.[4]

2,2-Dicyclohexylacetaldehyde (3ae)



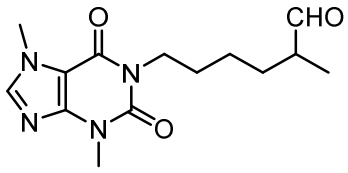
Following the general procedure D, the product was obtained as a colorless oil, 31.6 mg, 76% yield. Following the general procedure E starting from cyclohexananone (0.8 mmol), the product was obtained as a colorless oil, 36.8 mg, 41% yield over 2 steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.65 (d, J = 4.8 Hz, 1H), 1.87-1.63 (m, 13H), 1.32-1.12 (m, 6H), 1.06-0.91 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.77, 63.06, 35.44, 31.21, 30.00, 26.54, 26.45, 26.39. **HRMS** (ESI) Calcd. for $[M+NH_4]^+$: 226.2165. Found: 226.2164.

2-Methyl-4-(2,6,6-trimethylcyclohex-1-enyl)butanal (3ag)



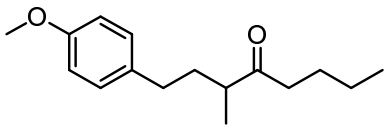
Following the general procedure D, the product was obtained as a colorless oil, 34.7 mg, 84% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.64 (d, J = 1.2 Hz, 1H), 2.41-2.29 (m, 0.8H), 2.07-1.95 (m, 2H), 1.92 – 1.87 (m, 2H), 1.82-1.69 (m, 1H), 1.60 - 1.52 (m, 5H), 1.49-1.37 (m, 3H), 1.13 (d, J = 6.9 Hz, 3H), 0.98 (s, 3H), 0.97 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.07, 136.60, 127.53, 47.16, 39.72, 34.87, 32.70, 30.99, 28.57, 26.05, 19.84, 19.44, 13.17. **HRMS** (EI): Calcd. For $C_{14}H_{24}O$ $[M]^+$: 208.1822, Found: 208.1827. Spectroscopic results agree with preciously reported data.[7]

6-(3,7-Dimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-1-yl)-2-methylhexanal (3ah)



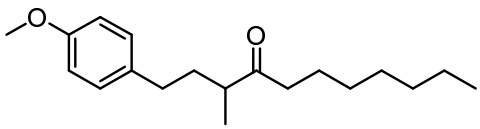
Following the general procedure D, the product was obtained as a yellowish oil, 27.6 mg, 48% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.57 (d, J = 2.1 Hz, 1H), 7.49 (d, J = 0.7 Hz, 1H), 3.98-3.93 (m, 5H), 3.52 (s, 3H), 2.37-2.25 (m, 1H), 1.79-1.58 (m, 3H), 1.46-1.32 (m, 3H), 1.05 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.05, 155.15, 151.35, 148.64, 141.38, 107.53, 46.09, 40.90, 33.49, 29.96, 29.58, 27.86, 24.17, 13.19. **HRMS** (EI): Calcd. For $C_{14}H_{24}O$ $[M]^+$: 208.1822, Found: 208.1827. **HRMS** (ESI): Calcd. For $[M+H]^+$: 293.1608, Found: 293.1610.

1-(4-Methoxyphenyl)-3-methyloctan-4-one (5c)



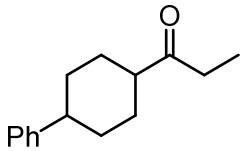
Following the general procedure E, the product was obtained as a colorless oil, 32.6 mg, 60% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 2.56-2.37 (m, 4H), 2.03-1.91 (m, 1H), 1.64-1.48 (m, 3H), 1.36-1.21 (m, 3H), 1.10 (d, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.64, 157.81, 133.82, 129.21, 113.78, 55.23, 45.58, 40.89, 34.71, 32.53, 25.78, 22.40, 16.48, 13.89. **HRMS** (EI): Calcd. For $C_{16}H_{24}O_2$ $[M]^+$: 248.1776, Found: 248.1773.

1-(4-Methoxyphenyl)-3-methylundecan-4-one (5d)



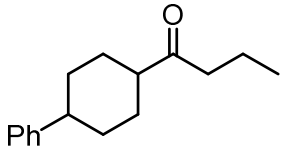
Following the general procedure E, the product was obtained as a colorless oil, 32.6 mg, 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09-7.07 (m, 2H), 6.84-6.81 (m, 2H), 3.79 (s, 3H), 2.57-2.47 (m, 3H), 2.45-2.33 (m, 2H), 2.01-1.92 (m, 1H), 1.63-1.51 (m, 3H), 1.34-1.21 (m, 8H), 1.10 (d, *J* = 7.0 Hz, 3H), 0.92-0.83 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.69, 157.82, 133.83, 129.22, 113.79, 55.23, 45.57, 41.19, 34.71, 32.53, 31.68, 29.26, 29.10, 23.68, 22.60, 16.48, 14.05. **HRMS** (EI): Calcd. For $C_{19}H_{30}O_2$ $[M]^+$: 290.2240, Found: 290.2249.

1-(4-Phenylcyclohexyl)propan-1-one (5e)



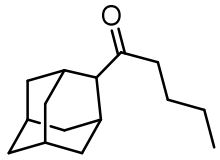
Following the general procedure E, the product was obtained as a colorless oil, 26 mg, yield = 60% (d.r.>20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.21-7.15 (m, 3H), 2.67-2.65 (m, 1H), 2.59 – 2.48 (m, 3H), 2.23 – 2.19 (m, 2H), 1.78-1.62 (m, 6H), 1.08 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.03, 147.00, 128.32, 126.94, 125.93, 46.01, 43.53, 33.47, 30.39, 26.96, 8.08. **HRMS** (EI): Calcd. For $C_{15}H_{20}O$ $[M]^+$: 215.1514, Found: 216.1518.

1-(4-Phenylcyclohexyl)butan-1-one (5f)



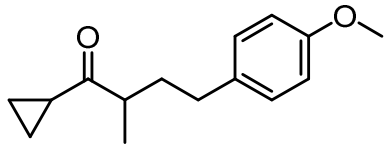
Following the general procedure E, the product was obtained as a colorless oil, 23 mg, 50% yield (d.r.>20:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.21 – 7.14 (m, 3H), 2.64-2.62 (m, 1H), 2.59 – 2.51 (m, 1H), 2.46 (t, *J* = 7.2 Hz, 2H), 2.26 – 2.18 (m, 2H), 1.77 – 1.57 (m, 8H), 0.93 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 213.56, 146.96, 128.26, 126.88, 125.87, 46.17, 43.49, 42.28, 30.32, 26.81, 17.34, 13.83. **HRMS** (EI): Calcd. For $C_{16}H_{22}O$ $[M]^+$: 230.1665, Found: 230.1669.

1-(Adamantan-2-yl)pentan-1-one (5g)



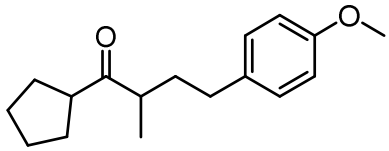
Following the general procedure E, the product was obtained as a colorless oil, 13.2 mg, 30% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.48-2.34 (m, 4H), 2.04-1.71 (m, 11H), 1.61-1.50 (m, 4H), 1.36-1.23 (m, 2H), 0.90 (t, *J* = 0.6 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 213.18, 57.02, 39.43, 38.45, 37.31, 33.31, 29.21, 27.67, 27.51, 26.02, 22.47, 13.94. **HRMS** (EI): Calcd. For $C_{15}H_{24}O$ $[M]^+$: 220.1822, Found: 220.1826.

1-Cyclopropyl-4-(4-methoxyphenyl)-2-methylbutan-1-one (5h)



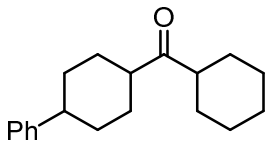
Following the general procedure E, the product was obtained as a colorless oil, 23.3 mg, 50% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 2.73-2.64 (m, 1H), 2.55 (t, *J* = 8.0 Hz, 2H), 2.09-1.99 (m, 1H), 1.97-1.91 (m, 1H), 1.69-1.60 (m, 1H), 1.17 (d, *J* = 6.8 Hz, 3H), 1.02-0.99(m, 2H), 0.87-0.84 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.18, 157.78, 133.92, 129.24, 113.76, 55.20, 46.44, 34.81, 32.51, 19.07, 16.28, 10.72, 10.70. **HRMS** (EI): Calcd. For $C_{15}H_{20}O_2$ $[M]^+$: 232.1458, Found: 232.1460.

1-Cyclopentyl-4-(4-methoxyphenyl)-2-methylbutan-1-one (5i)



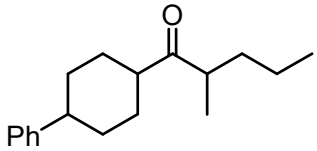
Following the general procedure E, the product was obtained as a colorless oil, 20.3 mg, 50% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 3.00-2.92 (m, 1H), 2.69-2.60 m, 1H), 2.55-2.47 (m, 2H), 2.02-1.93 (m, 1H), 1.78-1.66 (m, 6H), 1.61-1.54 (m, 3H), 1.11 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 217.09, 157.78, 133.93, 129.18, 113.76, 55.23, 49.97, 45.14, 34.79, 32.62, 29.49, 29.33, 26.08, 26.03, 16.67. **HRMS** (ESI): Calcd. For $C_{17}H_{25}O_2^+$ $[M+H]^+$: 261.1849, Found: 261.1850.

Cyclohexyl(4-phenylcyclohexyl)methanone (5j)



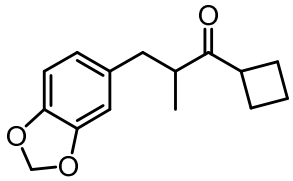
Following the general procedure E, the product was obtained as a colorless oil, 26.5 mg, 49% yield (d.r.>20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22-7.18 (m, 2H), 7.13-7.07 (m, 3H), 2.72-2.70 (m, 1H), 2.55-2.47 (m, 2H), 2.08-2.04 (m, 2H), 1.71-1.57 (m, 10H), 1.35-1.12 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 216.75, 128.25, 126.93, 125.83, 48.21, 44.27, 43.43, 30.30, 28.98, 26.86, 25.85, 25.76. **HRMS** (ESI): Calcd. For $C_{19}H_{30}NO^+$ $[M+NH_4]^+$: 288.2322, Found: 288.2322.

2-Methyl-1-(4-phenylcyclohexyl)pentan-1-one (5k)



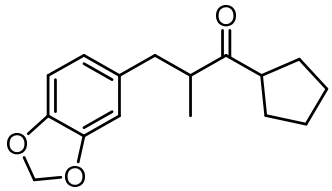
Following the general procedure E, the product was obtained as a colorless oil, 24.3 mg, 47% yield. (d.r.>20:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.31 – 7.14 (m, 5H), 2.83-2.75 (m, 2H), 2.61-2.52 (m, 1H), 2.16 – 2.09 (m, 2H), 1.81 – 1.60 (m, 7H), 1.33 – 1.19 (m, 3H), 1.06 (d, *J* = 6.9 Hz, 3H), 0.93 – 0.88 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 217.77, 146.99, 128.26, 126.94, 125.85, 45.10, 43.37, 43.29, 35.74, 30.32, 30.17, 26.91, 26.57, 20.67, 17.16, 14.20. **HRMS** (EI): Calcd. For $C_{18}H_{26}O$ $[M]^+$: 258.1978, Found: 258.1980.

3-(Benzo[d][1,3]dioxol-5-yl)-1-cyclobutyl-2-methylpropan-1-one (5l)



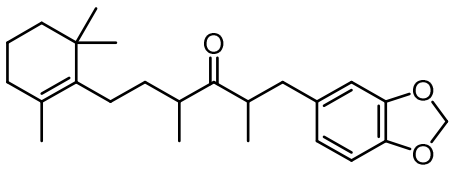
Following the general procedure E, the product was obtained as a colorless oil, 30 mg, 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.69 (d, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 1.6 Hz, 1H), 6.56 (dd, *J* = 8.0, 1.7 Hz, 1H), 5.90 (d, *J* = 0.8 Hz, 2H), 3.28-3.19 (m, 1H), 2.90-2.85 (m, 1H), 2.78-2.70 (m, 1H), 2.46-2.41 (m, 1H), 2.24-2.15 (m, 1H), 2.08-1.83 (m, 4H), 1.77-1.68 (m, 1H), 1.03 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.57, 147.46, 145.79, 133.68, 121.82, 109.25, 108.04, 100.73, 46.30, 44.62, 38.79, 24.16, 24.00, 17.61, 16.62. **HRMS** (EI): Calcd. For $C_{15}H_{18}O_3$ $[M]^+$: 246.1251, Found: 246.1246.

3-(Benzo[d][1,3]dioxol-5-yl)-1-cyclopentyl-2-methylpropan-1-one (5m)



Following the general procedure E, the product was obtained as a colorless oil, 34.9 mg, 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.69 (d, *J* = 7.6 Hz, 1H), 6.62-6.56(m, 2H), 5.90 (q, *J* = 1.6 Hz, 2H), 2.91-2.79 (m, 3H), 2.48-2.42 (m, 1H), 1.72-1.49 (m, 8H), 1.06 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 216.38, 147.45, 145.78, 133.75, 121.87, 109.31, 108.03, 100.73, 50.70, 47.78, 38.98, 28.77, 28.67, 25.96, 25.85, 16.85. **HRMS** (EI): Calcd. For $C_{16}H_{20}O_3$ $[M]^+$: 260.1407, Found: 260.1405.

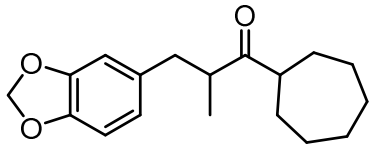
1-(Benzo[d][1,3]dioxol-5-yl)-2,4-dimethyl-6-(2,6,6-trimethylcyclohex-1-en-1-yl)hexan-3-one (5n)



Following the general procedure E, the product was obtained as a colorless oil, 40 mg, 54% yield (d.r. = 2.6:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.72-6.58 (m, 3H), 5.92-5.88 (m, 2H), 2.92-2.84 (m, 2H), 2.50 - 2.43 (2, 2H), 1.90-1.78 (m, 4H), 1.60-1.51 (m, 6H), 1.40-1.36 (m, 2H), 1.08-1.05 (m, 5H), 0.97-0.87 (m,

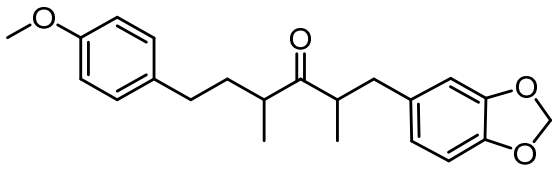
8H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 217.36, 217.16, 147.47, 145.84, 145.82, 136.77, 136.73, 133.80, 133.69, 127.29, 127.16, 121.98, 121.92, 109.41, 109.35, 108.10, 108.07, 100.77, 100.74, 47.64, 47.55, 46.76, 46.71, 39.76, 39.74, 39.00, 38.95, 34.87, 34.80, 33.00, 32.92, 32.68, 28.58, 28.51, 28.48, 28.44, 26.74, 26.62, 19.73, 19.70, 19.46, 17.05, 16.73, 16.06, 15.84. **HRMS** (EI): Calcd. For $C_{24}H_{34}O_3$ $[M]^+$:370.2503, Found: 370.2492.

3-(Benzo[d][1,3]dioxol-5-yl)-1-cycloheptyl-2-methylpropan-1-one (5o)



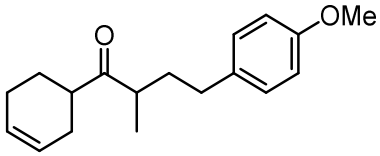
Following the general procedure E, the product was obtained as a colorless oil, 23 mg, 40% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.71-6.69 (d, *J* = 7.6 Hz,1H), 6.63-6.57 (m, 2H), 5.92-5.91 (m, 2H), 2.92-2.83 (m, 2H), 2.49-2.41 (m, 2H), 1.69-1.25 (m, 12H), 1.05 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 217.24, 147.48, 145.82, 133.82, 121.93, 109.38, 108.09, 100.77, 51.79, 47.22, 39.21, 29.59, 29.21, 28.27, 26.63, 26.51, 17.07. **HRMS** (EI): Calcd. For $C_{18}H_{24}O_3$ $[M]^+$: 288.1720, Found: 288.1713.

1-(Benzo[d][1,3]dioxol-5-yl)-6-(4-methoxyphenyl)-2,4-dimethylhexan-3-one (5p)



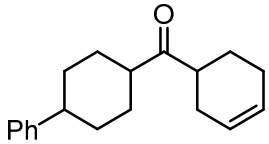
Following the general procedure E, the product was obtained as a colorless oil, 28.3 mg, 40% yield (d.r.=1.3:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.07 – 6.95 (m, 2H), 6.85 – 6.78 (m, 2H), 6.71 – 6.54 (m, 3H), 5.90 (s, 1H), 5.88 (q, *J* = 1.5 Hz, 1H), 3.80 (s, 1.3H), 3.78 (s, 1.7H), 2.91 – 2.82 (m, 2H), 2.54 – 2.40 (m, 3H), 2.34 (t, *J* = 8.1 Hz, 1H), 1.97 – 1.71 (m, 1H), 1.57 – 1.36 (m, 1H), 1.07-1.03 (m, 4.5H), 0.89 (d, *J* = 6.9 Hz, 1.5H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 217.28 (s), 217.01, 157.80, 157.75, 147.50, 147.46, 145.88, 145.83, 133.79, 133.73, 133.70, 129.16, 129.08, 122.01, 121.92, 113.76, 113.71, 109.43,109.34, 108.10, 108.06, 100.76, 55.21, 47.52, 47.27, 45.15, 45.11, 38.98, 38.91, 34.16, 32.52, 32.24, 17.07, 16.82, 16.17, 15.81. **HRMS** (ESI): Calcd. For $C_{22}H_{27}O_4^+$ $[M+H]^+$: 355.1904, Found: 355.1906.

1-(Cyclohex-3-en-1-yl)-4-(4-methoxyphenyl)-2-methylbutan-1-one (5q)



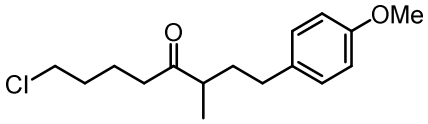
Following the general procedure E, the product was obtained as a colorless oil, 16.1 mg, 50% yield (d.r.=1:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.10-7.05 (m, 2H), 6.85-6.80 (m, 2H), 5.70-5.69 (m, 2H), 3.79 (s, 3H), 2.79-2.65 (m, 2H), 2.54-2.48 (m, 2H), 2.22-1.93 (m, 5H), 1.88- 1.83 (m, 1H), 1.63-1.52 (m, 2H), 1.12 (d, 1.8 Hz, 1.5H). 1.11 (d, 1.8 Hz, 1.5H). **^{13}C NMR** (75 MHz, CDCl3) δ 217.05, 157.78, 133.86, 133.79, 129.18, 126.52, 126.47, 125.54, 125.47, 113.77, 55.24, 45.54 ,45.34, 44.13, 44.04, 34.92, 34.64, 32.70, 32.64, 27.11, 27.06, 24.85, 24.82, 24.75, 16.87, 16.60. **HRMS** (EI): Calcd. For $C_{18}H_{24}O_2$ $[M]^+$: 272.1771, Found: 272.1764.

Cyclohex-3-en-1-yl(4-phenylcyclohexyl)methanone (5r)



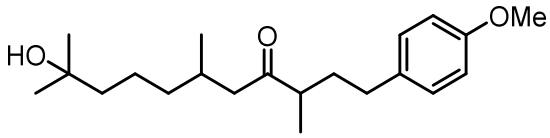
Following the general procedure E, the product was obtained as a colorless oil, 40.2 mg, 75% yield (d.r.>15:1). Following the general procedure A with **4e** (6 mmol), the product was obtained as a colorless oil, 1.126g, 70% yield (d.r.>15:1). **^{1}H NMR**. (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.22 – 7.15 (m, 3H), 5.74-5.67 (m, 2H), 2.90 – 2.83 (m, 2H), 2.61-2.53 (m, 1H), 2.22 – 2.08 (m, 6H), 2.02 – 1.84 (m, 2H), 1.77 – 1.63 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 216.48, 146.93, 128.26, 126.91, 126.51, 125.87, 125.64, 44.42, 43.91, 43.44, 30.31, 30.28, 27.57, 26.92, 26.82, 25.19, 24.86. **HRMS** (ESI): Calcd. For $C_{19}H_{28}NO^+$ $[M+NH_4]^+$: 286.2165, Found: 286.2171.

8-Chloro-1-(4-methoxyphenyl)-3-methyloctan-4-one (5s)



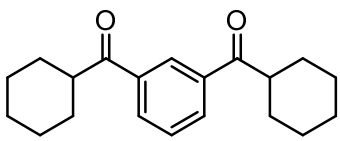
Following the general procedure E, the product was obtained as a colorless oil, 34.3 mg, 59% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.10-7.05 (m, 2H), 6.85-6.80 (m, 2H), 3.78 (s, 3H), 3.59-3.49 (m, 2H), 2.59-2.35 (m, 5H), 2.03-1.91 (m, 1H), 1.82-1.65 (m, 4H), 1.64-1.51 (m, 1H), 1.11 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 213.79, 157.82, 133.62, 129.21, 113.78, 55.21, 45.53, 44.67, 40.07, 34.62, 32.47, 31.98, 20.90, 16.45. **HRMS** (EI): Calcd. For $C_{16}H_{23}O_2Cl$ $[M]^+$: 282.1381, Found: 282.1386.

10-Hydroxy-1-(4-methoxyphenyl)-3,6,10-trimethylundecan-4-one (5t)



Following the general procedure E, the product was obtained as a colorless oil, 29.4 mg, 44% yield (d.r.=1:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.10-7.05 (m, 2H), 6.84-6.79 (m, 2H), 3.78 (s, 3H), 2.53-2.48 (m, 2H), 2.46-2.18 (m, 2H), 2.08-1.89 (m, 2H), 1.63-1.49 (m, 2H), 1.46-1.26 (m, 6H), 1.20 (d, *J* = 0.9 Hz, 6H), 1.08 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 3.0 Hz, 1.5 H), 0.86 (d, *J* = 3.0 Hz, 1.5 H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 214.34, 214.30, 157.74, 133.77, 133.75, 129.18, 113.81, 113.75, 70.92, 55.19, 48.70, 48.66, 45.88, 45.84, 43.87, 37.32, 37.29, 34.60, 34.46, 32.49, 32.45, 29.27, 29.12, 28.63, 23.82, 21.64, 19.89, 19.83, 16.32, 16.25. **HRMS** (ESI): Calcd. For $C_{21}H_{38}NO_3^+$ $[M+NH_4]^+$: 252.2846, Found: 252.2846.

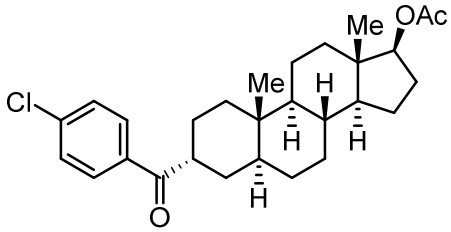
1,3-Phenylenebis(cyclohexylmethanone) (5u)



Following the general procedure E, starting from hydrazone (0.4 mmol) and isophthalaldehyde (0.2 mmol), the product was obtained as a white solid, 33.4 mg, 56% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.48 (t, *J* = 2.1 Hz, 1H), 8.11 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 3.35-3.25 (m, 2H), 1.92-1.82 (m, 8H), 1.77-1.71 (m, 2H), 1.57 – 1.24 (m, 10H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 203.25, 136.68,

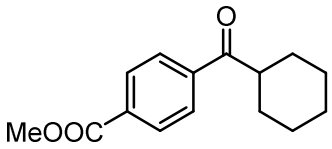
132.20, 128.99, 127.92, 45.69, 29.33, 25.89, 25.74. **HRMS** (EI): Calcd. For $C_{20}H_{26}O_2$ $[M]^+$:298.1927, Found: 298.1920.

(5S,8R,9S,10S,13S,14S,17S)-3-(4-Chlorobenzoyl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl acetate (5v)



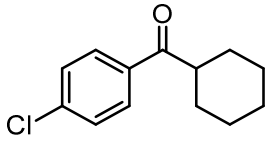
Following the general procedure E, the product was obtained as a white solid, 45.7 mg, 50% yield (d.r.>20:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.45 – 7.39 (m, 2H), 4.62-4.56 (m, 1H), 3.29 – 3.17 (m, 1H), 2.21 – 2.08 (m, 1H), 2.03 (s, 3H), 1.84 – 1.40 (m, 12H), 1.38 – 1.23 (m, 5H), 1.14 – 0.91 (m, 4H), 0.83 (s, 3H), 0.77 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 202.44, 171.24, 139.11, 134.59, 129.65, 128.87, 82.80, 54.43, 50.75, 46.30, 46.03, 42.57, 37.89, 36.89, 36.04, 35.21, 31.54, 28.53, 27.46, 24.76, 23.45, 21.17, 20.42, 12.29, 12.08. **HRMS** (ESI) Calcd. For $[M+H]^+$:457. 2504, Found 457.251.

Methyl 4-(cyclohexanecarbonyl)benzoate (5w)



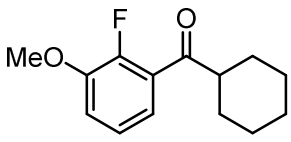
Following the general procedure E, the product was obtained as a white solid, 26.1 mg, 53% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.13-8.09 (m, 2H), 7.99-7.95 (m, 2H), 3.94 (s, 3H), 3.30-3.20 (m, 1H), 1.92-1.70 (m, 5H), 1.52-1.27 (m, 5H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 203.38, 166.28, 139.69, 133.49, 129.80, 128.12, 52.42, 45.96, 29.23, 25.86, 25.73. **HRMS** (EI): Calcd. For $C_{15}H_{18}O_3$ $[M]^+$:246.1256, Found: 246.1255. Spectroscopic results agree with preciously reported data.[8]

Cyclohexyl(4-chlorophenyl)methanone (5x)



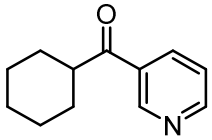
Following the general procedure E, the product was obtained as a white solid, 24.4 mg, 55% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90-7.86 (m, 2H), 7.44-7.41 (m, 2H), 3.23-3.16 (m, 1H), 1.90 -1.82 (m, 4H), 1.77-1.70 (m, 1H), 1.51-1.21 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.58, 139.10, 134.61, 129.68, 128.87, 45.62, 29.34, 25.88, 25.78. **HRMS** (EI): Calcd. For $C_{13}H_{15}OCl$ $[M]^+$:222.0806, Found: 222.0805. Spectroscopic results agree with preciously reported data.[8]

Cyclohexyl (2-fluoro-3-methoxyphenyl) methanone (5y)



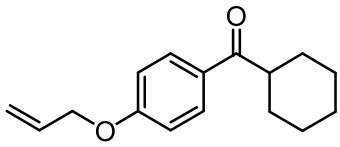
Following the general procedure E, the product was obtained as a white solid, 34.4 mg, 73% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37-7.32 (m, 1H), 7.23-7.17 (m, 2H), 4.02 (s, 3H), 3.26-3.16 (m, 1H), 2.09 -2.02 (m, 2H), 1.94-1.75 (m, 3H), 1.58-1.33 (m, 5H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 203.05 (d, *J* = 3.5 Hz), 151.10 (d, *J* = 253.0 Hz), 148.12 (d, *J* = 11.9 Hz), 127.04 (d, *J* = 11.5 Hz), 124.14 (d, *J* = 4.4 Hz), 121.23 (d, *J* = 2.4 Hz), 116.39 (d, *J* = 2.5 Hz), 56.52, 50.30 (d, *J* = 5.9 Hz), 28.79, 26.01, 25.82. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -135.60. **HRMS** (EI): Calcd. For $C_{14}H_{17}O_2F$ $[M]^+$: 236.1207, Found 236.1206.

cyclohexyl(pyridin-3-yl)methanone (5z)



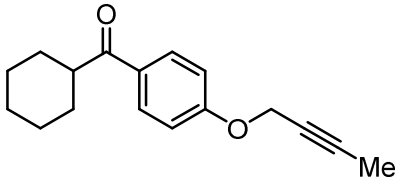
Following the general procedure E, the product was obtained as a colorless oil, 15 mg, 40% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.14 (s, 1H), 8.75 (d, *J* = 4.2 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.42 – 7.39 (m, 1H), 3.25-3.19 (m, 1H), 1.91 – 1.73 (m, 5H), 1.55-1.25 (m, 5H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.55, 153.15, 149.70, 135.68, 131.49, 123.66, 46.06, 29.13, 25.82, 25.68. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{12}H_{16}NO$ 190.1226, found 190.1230.

(4-(allyloxy)phenyl)(cyclohexyl)methanone (5aa)



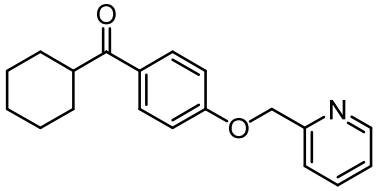
Following the general procedure E, the product was obtained as a colorless oil, 17.1 mg, 35% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.93 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.10-6.00 (m, 1H), 5.42 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.4 Hz, 1H), 4.60 (d, *J* = 5.2 Hz, 2H), 3.25-3.18 (m, 1H), 1.88 – 1.71 (m, 5H), 1.54 – 1.24 (m, 5H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.41, 162.19, 132.54, 130.45, 129.35, 118.13, 114.40, 68.84, 45.29, 29.53, 25.96, 25.89. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{16}H_{21}O_2$ 245.1536, found 245.1542.

(4-(but-2-yn-1-yloxy)phenyl)(cyclohexyl)methanone (5ab)



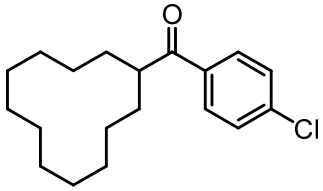
Following the general procedure E, the product was obtained as a colorless oil, 244.6 mg, 48% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.93 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 4.70 (s, 2H), 3.24-3.18 (m, 1H), 1.88 – 1.70 (m, 8H), 1.54 – 1.21 (m, 5H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 202.39, 161.35, 130.36, 129.65, 114.52, 84.35, 73.32, 56.46, 45.30, 29.50, 25.94, 25.87. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{17}H_{21}O_2$ 257.1536, found 257.1534.

cyclohexyl(4-(pyridin-2-ylmethoxy)phenyl)methanone (5ac)



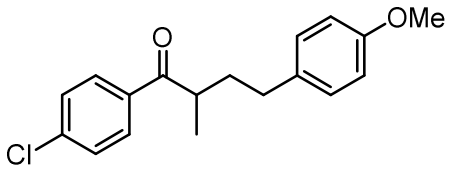
Following the general procedure E, the product was obtained as a colorless oil, 30 mg, 51% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.65 (d, *J* = 35.2 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.34 (s, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 5.13 (s, 2H), 3.24-3.17 (m, 1H), 1.87 – 1.70 (m, 5H), 1.53 – 1.22 (m, 5H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 201.38, 160.88, 134.35, 129.57, 128.86, 113.50, 66.67, 44.35, 28.51, 24.95, 24.88. **HRMS (ESI):** $[M+H]^+$ calcd for $C_{19}H_{22}NO_2$ 296.1645, found 296.1650.

(4-Chlorophenyl)(cyclododecyl)methanone (5ad)



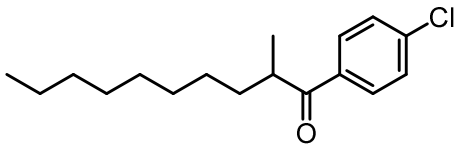
Following the general procedure E, the product was obtained as a white solid, 43.4 mg, 71% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.90-7.86 (m, 2H), 7.46-7.42 (m, 2H), 3.52-3.44 (m, 1H), 1.74-1.57 (m, 4H), 1.47-1.25 (m, 18H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 202.99, 139.07, 135.37, 129.60, 128.92, 42.19, 26.41, 23.94, 23.67, 23.37, 22.47. **HRMS** (EI): Calcd. For $C_{19}H_{27}OCl$ $[M]^+$:306.1744, Found: 306.1734.

1-(4-Chlorophenyl)-4-(4-methoxyphenyl)-2-methylbutan-1-one (5ae)



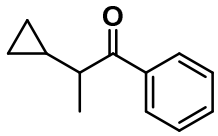
Following the general procedure E, the product was obtained as a white solid, 24.4 mg, 49% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.42 – 7.38 (m, 2H), 7.07 – 7.02 (m, 2H), 6.84 – 6.79 (m, 2H), 3.79 (s, 3H), 3.44-3.33 (m, 1H), 2.61-2.56 (m, 2H), 2.18-2.05 (m, 1H), 1.76 – 1.64 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 202.88, 157.87, 139.25, 134.75, 133.54, 129.67, 129.37, 128.87, 113.78, 55.24, 39.53, 35.30, 32.42, 17.10. **HRMS** (EI) Calcd. For $C_{18}H_{19}O_2Cl$ $[M]^+$:302.1074, Found: 302.1075.

1-(4-Chlorophenyl)-2-methyldecan-1-one (5af)



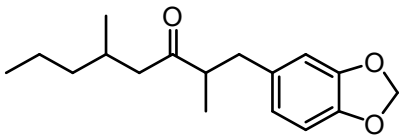
Following the general procedure E, the product was obtained as a white solid, 25.8 mg, 46% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.91-7.86 (m, 2H), 7.46-7.41 (m, 2H), 3.45-3.34 (m, 1H), 1.83-1.72 (m, 1H), 1.48-1.37 (m, 1H), 1.30-1.23 (m, 12H), 1.18 (d, *J* = 6.6 Hz, 3H), 0.89-0.84 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 203.32, 139.19, 135.02, 129.66, 128.90, 40.61, 33.67, 31.82, 29.69, 29.41, 29.22, 27.35, 22.63, 17.11, 14.08. **HRMS** (EI) Calcd. For $C_{17}H_{25}OCl$ $[M]^+$:280.1588, Found: 280.1591.

2-Cyclopropyl-1-phenylpropan-1-one (5ag)



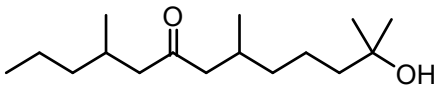
Following the general procedure E, the product was obtained as a colorless oil, 18.2 mg, 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.01 (M, 2H), 7.58 – 7.53 (M, 1H), 7.48 – 7.44 (m, 2H), 2.80 (dq, J = 7.0, 7.6 Hz, 1H), 1.28 (d, J = 7.0 Hz, 3H), 1.12 – 1.03 (m, 1H), 0.59 – 0.53 (m, 1H), 0.50 – 0.44 (m, 1H), 0.23 – 0.14 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.14, 136.95, 132.81, 128.55, 128.30, 45.11, 17.12, 14.58, 4.35, 3.41. This compound is commerically available (CAS number: 69096-84-0).

1-(Benzo[*d*][1,3]dioxol-5-yl)-2,5-dimethyloctan-3-one (5ah)



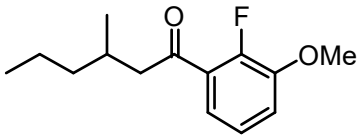
Following the general procedure F, the product was obtained as a colorless oil, 35.1 mg, 64% yield (d.r. = 1:1). Purification was achieved by silica column chromatography (PE/EtOAc = 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.70 (d, *J* = 7.9 Hz, 1H), 6.63 (d, *J* = 1.6 Hz, 1H), 6.58 (dd, *J* = 7.9, 1.6 Hz, 1H), 5.91 (s, 2H), 2.88 (dd, *J* = 13.5, 7.3 Hz, 1H), 2.75 (dqd, *J* = 14.1, 7.0, 2.5 Hz, 1H), 2.45 (ddd, J = 13.5, 7.3, 2.9 Hz, 1H), 2.30 (ddd, *J* = 31.7, 16.4, 5.8 Hz, 1H), 2.15 (ddd, *J* = 30.8, 16.4, 7.7 Hz, 1H), 2.01 – 1.89 (m, 1H), 1.32 – 1.07 (m, 4H), 1.05 (d, *J* = 6.9 Hz, 3H), 0.85 (td, *J* = 7.2, 2.2 Hz, 3H), 0.80 (dd, *J* = 6.6 1.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.2, 214.2, 147.7, 147.7, 146.0, 146.0, 133.8, 133.8, 122.1, 109.5, 109.5, 108.3, 100.9, 49.8, 49.8, 48.7, 48.7, 39.3, 39.3, 38.9, 38.8, 28.7, 28.6, 20.2, 20.2, 20.0, 16.6, 14.3, 14.3. **HRMS** (ESI) Calcd. For $[M+H]^+$: 277.1798, Found 277.1799.

12-Hydroxy-4,8,12-trimethyltridecan-6-one (5ai)



Following the general procedure F, the product was obtained as a colorless oil, 37.0 mg, 72% yield (d.r. = 1:1). Purification was achieved by silica column chromatography (PE/EtOAc = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.38 – 2.32 (m, 2H), 2.22 – 2.14 (m, 2H), 2.07 – 1.94 (m, 2H), 1.65 (br, 1H), 1.46 – 1.11 (m, 16H), 0.89 – 0.86 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.3, 211.2, 71.1, 51.1, 51.1, 51.0, 51.0, 44.1, 39.4, 39.3, 37.5, 37.5, 29.5, 29.4, 29.2, 29.2, 29.1, 29.0, 21.8, 21.8, 20.2, 20.2, 20.0, 20.0, 20.0, 14.3. **HRMS** (ESI) Calcd. For $[M+NH4]^+$: 274.2741, Found 274.274.

1-(2-Fluoro-3-methoxyphenyl)-3-methylhexan-1-one (5aj)

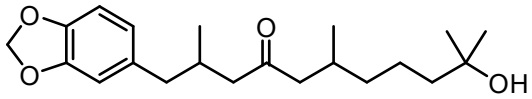


Following the general procedure F, the product was obtained as a colorless oil, 14.2 mg, 30% yield. Purification was achieved by silica column chromatography (PE/EtOAc = 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 1H), 7.15 – 7.08 (m, 2H), 3.91 (s, 3H), 2.96 (ddd, *J* =

16.1, 5.6, 2.9 Hz, 1H), 2.74 (ddd, *J* = 16.1, 8.0, 2.9 Hz, 1H), 2.18 – 2.06 (m, 1H), 1.39 – 1.17 (m, 4H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.2, 214.2, 147.7, 147.7, 146.0, 146.0, 133.8, 133.8, 122.1, 109.5, 109.5, 108.3, 100.9, 49.8, 49.8, 48.7, 48.7, 39.3, 39.3, 38.9, 38.8, 28.7, 28.6, 20.2, 20.2, 20.0, 16.6, 14.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -133.93. **HRMS** (EI+) Calcd. For $[M]^+$: 238.13636, Found 238.13622.

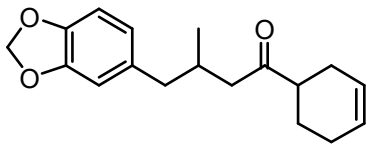
1-(Benzo[*d*][1,3]dioxol-5-yl)-10-hydroxy-2,6,10-trimethylundecan-4-one (5ak)



Following the general procedure F, the product was obtained as a colorless oil, 42.2 mg, 61% yield (d.r. = 1:1). Purification was achieved by silica column chromatography (PE/EtOAc = 5:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 1.5 Hz, 1H), 6.58 (d, *J* = 7.9, 1.5 Hz, 1H), 5.91 (s, 2H), 2.48 (dd, *J* = 13.8, 6.2 Hz, 1H), 2.41 – 2.28 (m, 3H), 2.28 – 2.11 (m, 3H), 2.03 – 1.93 (m, 1H), 1.71 (br, 1H), 1.45 – 1.09 (m, 12H), 0.90 – 0.84 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.8, 210.8, 147.6, 145.9, 134.4, 122.1, 109.6, 108.1, 100.9, 71.06, 51.0, 51.0, 50.0, 49.9, 44.0, 43.0, 43.0, 37.5, 37.4, 31.3, 31.3, 29.5, 29.3, 29.2, 29.1, 21.8, 21.8, 20.0, 20.0, 19.9, 19.9. **HRMS** (ESI) Calcd. For $[M+H]^+$:349.2373, Found 349.237.

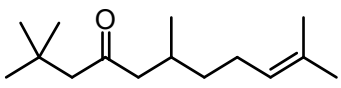
4-(Benzo[*d*][1,3]dioxol-5-yl)-1-(cyclohex-3-en-1-yl)-3-methylbutan-1-one (5al)



Following the general procedure F, the product was obtained as a colorless oil, 29.2 mg, 51% yield (d.r. = 1:1). Purification was achieved by silica column chromatography (PE/EtOAc = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (d, *J* = 7.9 Hz, 1H), 6.66 (d, *J* = 1.3 Hz, 1H), 6.59 (d, *J* = 7.9, 1.3 Hz, 1H), 5.91 (s, 2H), 5.73 – 5.61 (m, 2H), 2.59 – 2.46 (m, 2H), 2.46 – 2.25 (m, 4H), 2.25 – 1.99 (m, 4H), 1.95 – 1.83 (m, 1H), 1.60 – 1.45 (m, 1H), 0.88 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.4, 213.4, 147.6, 145.9, 134.5, 134.5, 126.8, 126.7, 125.6, 125.5, 122.1, 109.6, 108.1, 100.9, 47.4, 47.4, 47.1, 47.1, 43.0, 43.0, 31.2, 31.2, 27.0, 26.8, 24.9, 24.9, 24.8, 24.6, 19.9. **HRMS** (ESI) Calcd. For $[M+H]^+$: 287.1642, Found 287.1641.

2,2,6,10-Tetramethylundec-9-en-4-one (5am)

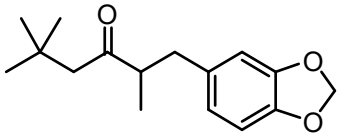


Following the general procedure F, the product was obtained as a colorless oil, 22.6 mg, 50% yield. Purification was achieved by silica column chromatography (PE/EtOAc = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 – 5.06 (m, 1H), 2.39 – 2.16 (m, 4H), 2.04 – 1.90 (m, 3H), 1.68 (s, 3H), 1.59 (s, 3H), 1.35 – 1.25 (m, 1H), 1.21 – 1.12 (m, 1H), 1.01 (s, 9H), 0.88 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.0, 131.6, 124.6, 55.6, 52.7, 37.1, 31.1, 29.9, 29.0, 25.9, 25.6, 19.9,

17.8. **HRMS** (ESI) Calcd. For $[M+H]^+$: 225.2213, Found 225.2213.

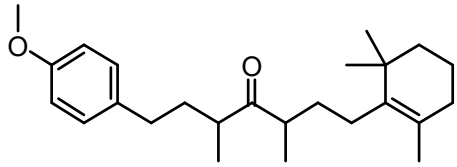
1-(Benzo[*d*][1,3]dioxol-5-yl)-2,5,5-trimethylhexan-3-one (5an)



Following the general procedure F, the product was obtained as a colorless oil, 25.4 mg, 48% yield. Purification was achieved by silica column chromatography (PE/EtOAc = 30:1).

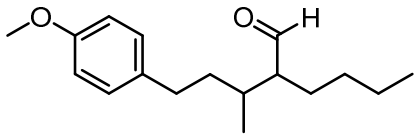
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (d, *J* = 7.8 Hz, 1H), 6.63 (d, *J* = 1.6 Hz, 1H), 6.58 (dd, *J* = 7.8, 1.6 Hz, 1H), 5.91 (s, 2H), 2.87 (dd, *J* = 13.5, 6.9 Hz, 1H), 2.72 (dq, *J* = 13.9, 7.0 Hz 1H), 2.42 (dd, *J* = 13.5, 7.5 Hz, 1H), 2.24 (dd, *J* = 34.9, 15.4 Hz, 2H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.96 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.1, 147.7, 146.0, 133.8, 122.1, 109.5, 108.3, 100.9, 54.5, 49.8, 38.8, 31.1, 29.8, 16.3. **HRMS** (ESI) Calcd. For $[M+H]^+$: 263.1642, Found 263.1641.

1-(4-Methoxyphenyl)-3,5-dimethyl-7-(2,6,6-trimethylcyclohex-1-en-1-yl)-heptan-4-one (5ao)



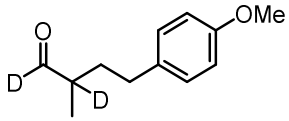
Following the general procedure G using dihydro-β-inone (0.4 mmol), the product was obtained as a colorless oil, 43.5 mg, 29% yield over 2 steps (d.r.=3.9:1). Following the general procedure F using 4-(4-methoxyphenyl)butan-2-one (0.4 mmol), the product was obtained as a colorless oil, 38.3 mg, 26% yield over 2 steps (d.r.=3.9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 - 7.05 (m, 2H), 6.85 – 6.79 (m, 2H), 3.78 (s, 2.4H), 3.78 (s, 0.6H), 2.70 – 2.60 (m, 1H), 2.59 – 2.46 (m, 2H), 2.09 – 1.81 (m, 5H), 1.63 – 1.52 (m, 8H), 1.43 – 1.26 (m, 4H), 1.15 – 1.03 (m, 5H), 1.02 – 0.94 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 217.75, 217.65, 157.91, 157.81, 136.77, 133.91, 129.20, 129.18, 129.11, 127.37, 127.34, 113.88, 113.80, 113.79, 55.24, 45.88, 45.83, 44.67, 44.63, 39.78, 34.91, 34.61, 34.56, 33.50, 33.43, 32.72, 32.65, 32.59, 28.61, 28.56, 28.53, 26.86, 26.82, 19.78, 19.75, 19.53, 19.49, 16.61, 16.55, 16.51, 16.43. **HRMS** (ESI) Calcd. For $[M+NH_4]^+$:388.3210, Found 388.3209.

2-(4-(4-Methoxyphenyl)butan-2-yl)hexanal (3ai)



Following the general procedure G using (4-methoxyphenyl)butan-2-one (0.4 mmol), the product was obtained as a colorless oil, 27.7 mg, 26% yield over 2 steps (d.r.=1.3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (d, J = 3.2 Hz, 0.4 H), 9.60 (d, J = 2.8 Hz, 0.5 H), 7.08 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 2.70-2.61 (m, 1H), 2.55-2.46 (m, 1H), 2.21-2.14 (m, 1H), 1.96-1.82 (m, 1H), 1.74-1.60 (m, 2H), 1.55-1.36 (m, 2H), 1.32- 1.25 (m, 4H), 1.02 (d, J = 6.8 Hz, 1.3 H), 0.95 (d, J = 6.8 Hz, 1.7 H), 0.88 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.01, 205.75, 157.78, 134.12, 134.07, 129.17, 113.81, 56.87, 56.79, 55.24, 36.52, 36.15, 33.15, 32.60, 32.44, 32.36, 30.10, 29.92, 25.95, 24.55, 22.83, 22.75, 16.83, 16.25, 13.89. **HRMS** (EI) Calcd. For $C_{17}H_{26}O_2[M]^+$:262.1933, Found 262.1926.

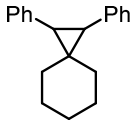
4-(4-Methoxyphenyl)-2-methylbutanal-1,2-d$_2$



To a 5 mL snap vial with a magnetic stirring bar, tosylhydrazone (**1t**, 0.2 mmol, 1.0 eq.), Cs_2CO_3 (0.3 mmol, 1.5 eq.), and paraformaldehyde-d2 (**2b,** 0.24 mmol, 1.2 eq.) were added. The vial was evacuated and back filled with N_2 for three times. Then dry MeCN (2 mL) was added by syringe, and the mixture was irradiated with a 385 nm LED at 25 °C. After 20 h, the mixture was quenched with water and extracted with Et_2O (10 mL *3). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel flash chromatography (gradient eluent: petroleum ether in EtOAc =2% to 3%), to give the desired product as a colorless oil, 24.8 mg, 64% yield, overall deuterium content >98%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12-7.08 (m, 2H), 6.85-6.82 (m, 2H), 3.79 (s, 3H), 2.67-2.55 (m, 2H), 2.40-2.32 (m, 0.03H), 2.06-1.98 (m, 1H), 1.661.59 (m, 1H), 1.13 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.61 (t, J = 26.0 Hz), 157.91, 133.34, 129.25, 113.84, 55.20, 32.16 (d, J = 19.9 Hz), 31.74, 13.19.

HRMS (EI): Calcd. For $C_{12}H_{14}O_2D_2$ $[M]^+$: 194.1276, Found: 194.1270.

1,2-Diphenylspiro[2.5]octane (8)



To a 5 mL snap vial with a magnetic stirring bar, tosylhydrazone (**1a**, 0.2 mmol, 1.0 eq.), and Cs_2CO_3 (0.3 mmol, 1.5 eq.) were added. The vial was evacuated and back filled with N_2 for three times. Then a solution of E-stilbene (0.4 mmol, 2.0 eq.) in MeCN (2 mL) was added by syringe, and the mixture was irradiated with a 385 nm LED at 25 °C. After 20 h, the mixture was quenched with water and extracted with Et_2O (10 mL *3). The combined organic phase was then washed with H_2O (10 mL) and brine, dried over sodium sulfate, concentrated under vacuum. The residue was purified by silica gel flash chromatography (gradient eluent: petroleum ether in EtOAc =2% to 3%), to give the desired product as a colorless oil, 23 mg, yield = 24%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 5H), 2.42 (s, 2H), 1.41 – 1.29 (m, 4H), 1.23 (dd, *J* = 6.7, 4.2 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.14, 128.99, 127.90, 125.75, 33.72, 33.52, 32.45, 26.22, 25.16. **HRMS** (EI) calcd for $C_{20}H_{22}$ $[M]^+$:262.1722 found: 262.1718 *Note: The product was contaminated with cis-stilbene, the yield has been calculated taking this into account.*

7. X-ray characterization data

X-ray crystal structure of **5v** (CCDC 2210656)

The XRD data of **5v** indicated that the 4-chloro-benzoyl group is anti to the methyl group in 4-position of the ketone.The detail of the obtained data is available as a crystallographic information file (CIF), which is available from CCDC (2210656). The crystal data are shown in Table S9.

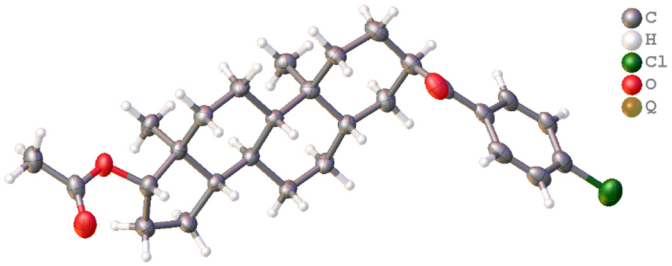
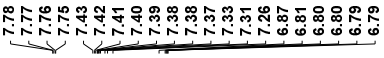


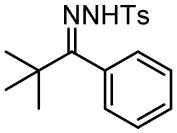
Table S9. Crystal data and structure refinement for **5v**

Crystal Data. $C_{28}H_{37}O_3Cl$, M_r = 457.02, orthorhombic, $P2_12_12_1$ (No. 19), a = 7.1817(2) Å, b = 10.2410(2) Å, c = 33.2457(6) Å, $a = b = g = 90^{\circ}$, V = 2445.15(9) Å^3, T = 123.00(10) K, Z = 4, Z' = 1, m(Cu K$_a$) = 1.586, 21249 reflections measured, 4307 unique (R_{int} = 0.0589) which were used in all calculations. The final wR_2 was 0.1117 (all data) and R_1 was 0.0397 (I≥2 s(I)).

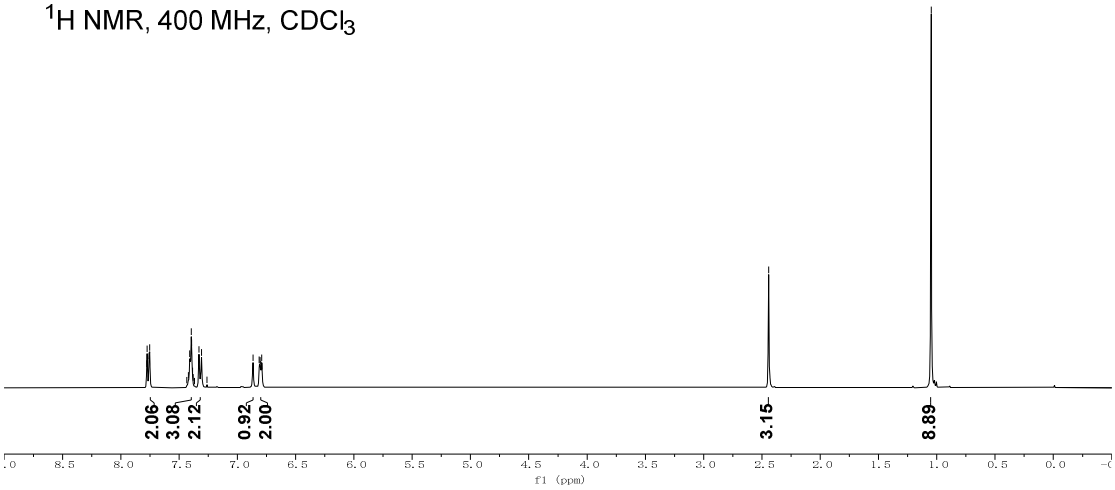
Compound	**V106**
Formula	$C_{28}H_{37}O_3Cl$
$D_{calc.}$/ g cm^{-3}	1.241
m/mm^{-1}	1.586
Formula Weight	457.02
Colour	clear colourless
Shape	block-shaped
Size/mm^3	0.14×0.11×0.09
T/K	123.00(10)
Crystal System	orthorhombic
Flack Parameter	-0.008(19)
Hooft Parameter	-0.017(8)
Space Group	$P2_12_12_1$
a/Å	7.1817(2)
b/Å	10.2410(2)
c/Å	33.2457(6)
a/°	90
b/°	90
g/°	90
V/Å^3	2445.15(9)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K_a
Q_{min}/°	4.518
Q_{max}/°	66.899
Measured Refl's.	21249
Indep't Refl's	4307
Refl's I≥2 s(I)	3978
R_{int}	0.0589
Parameters	292
Restraints	0
Largest Peak	0.165
Deepest Hole	-0.329
GooF	1.100
wR_2 (all data)	0.1117
wR_2	0.1088
R_1 (all data)	0.0435
R_1	0.0397

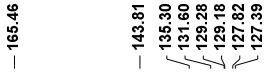
8. Copies of NMR spectra

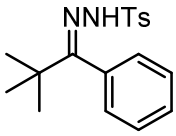




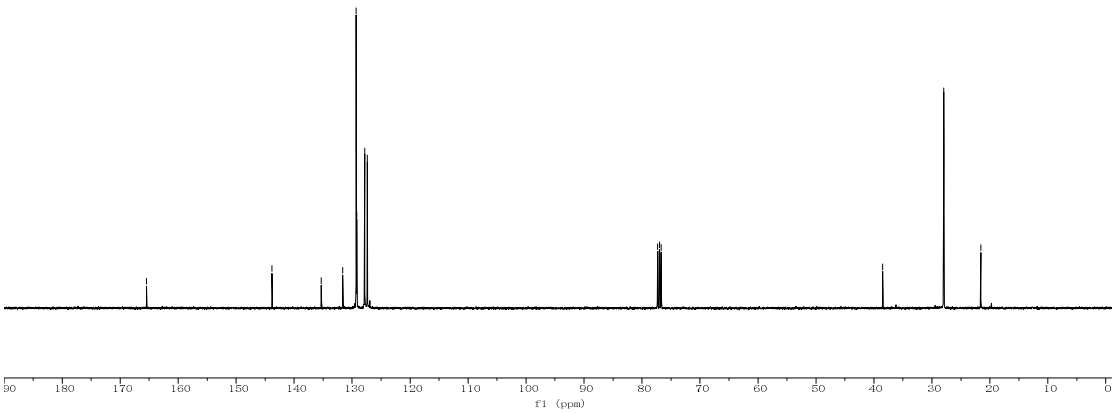
^{1}H NMR, 400 MHz, $CDCl_3$

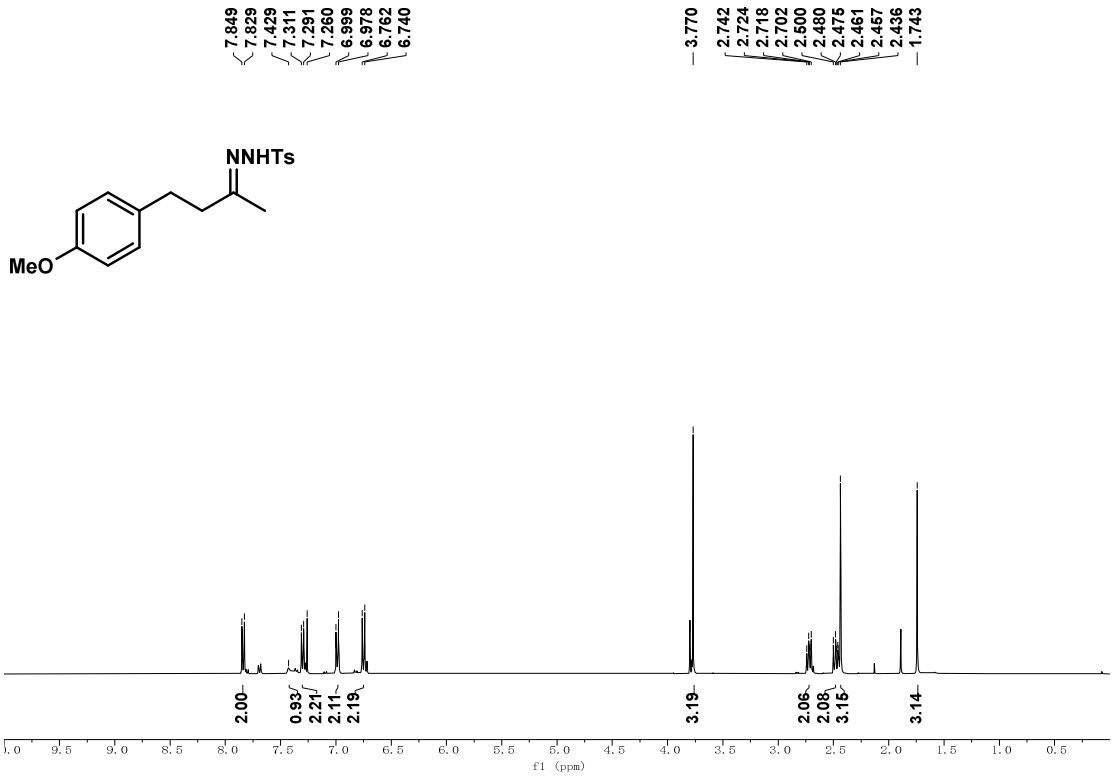






^{13}C NMR, 101 MHz, $CDCl_3$

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7.429
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7.260
6.999
6.978
6.762
6.740
3.770
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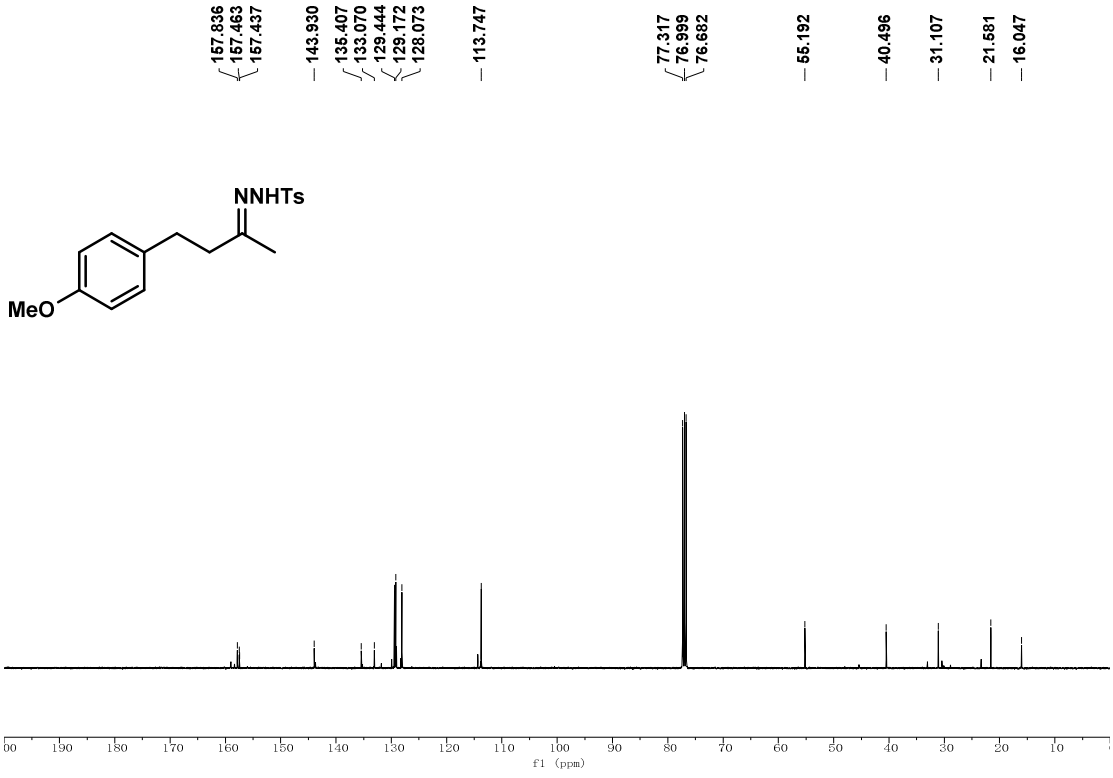
2.724
2.718
2.702
2.500
2.480
2.475
2.461
2.457
2.436
1.743
NNHTs
MeO
2.00
0.93
2.21
2.11
2.19
3.19
2.06
2.08
3.15
3.14
f1 (ppm)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135.407
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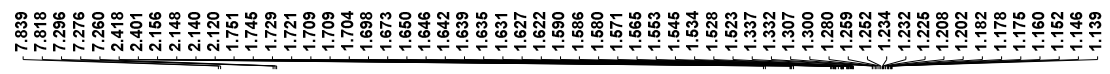
21.581
16.047
NNHTs
MeO
f1 (ppm)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2.140
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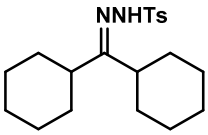
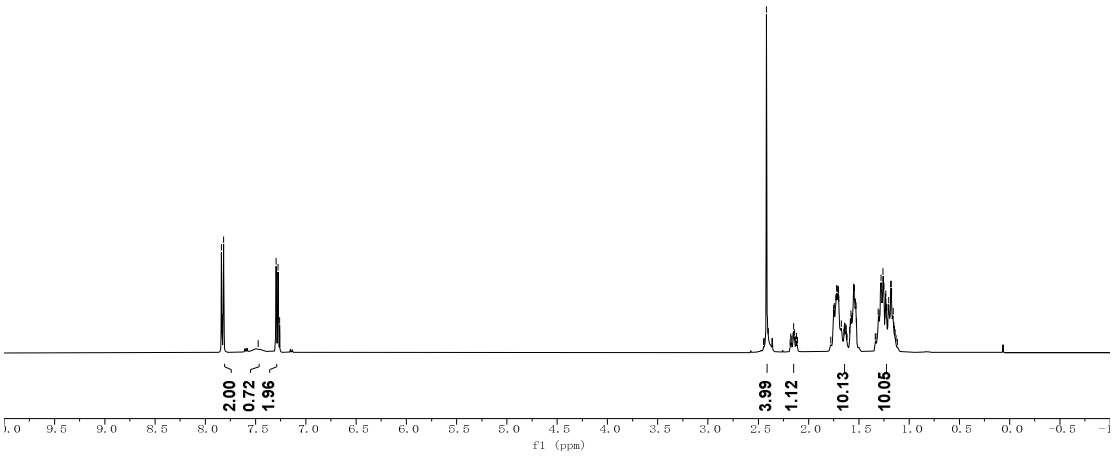
1.152
1.146
1.139


NNHTs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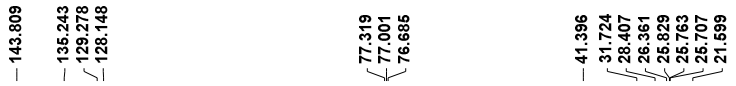
10.13
10.05
f1 (ppm)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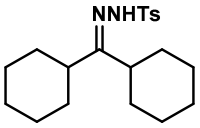
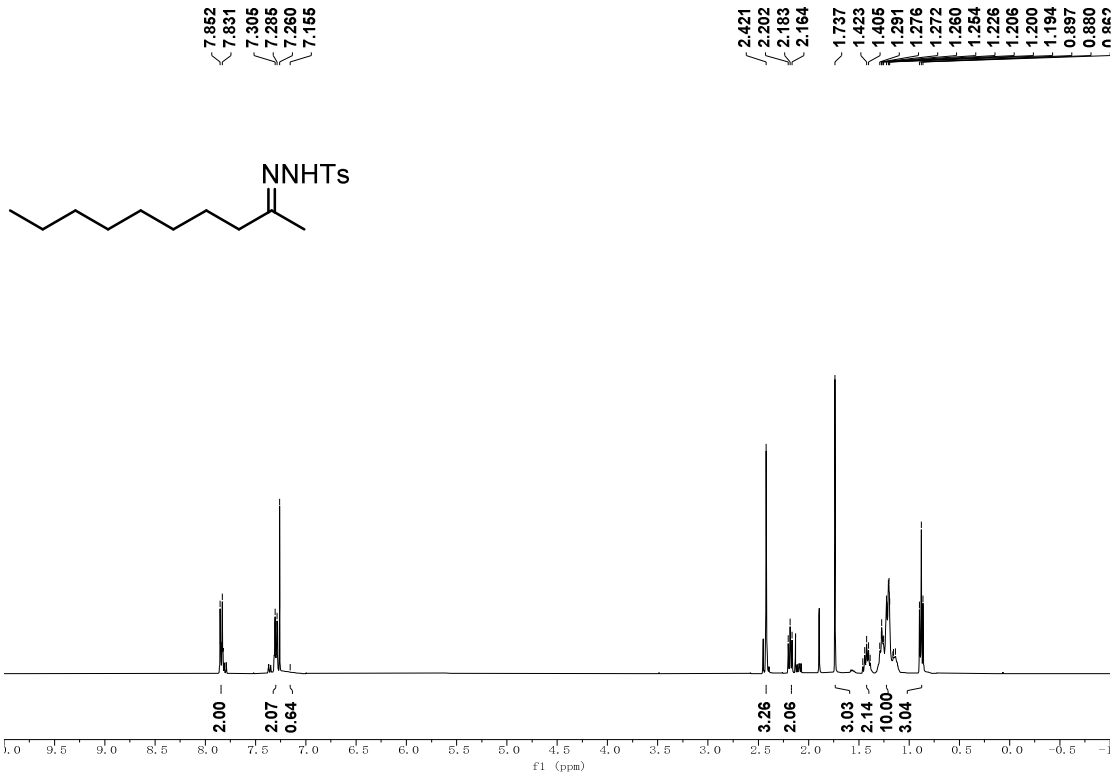
25.707
21.599


NNHTs

f1 (ppm)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2.202
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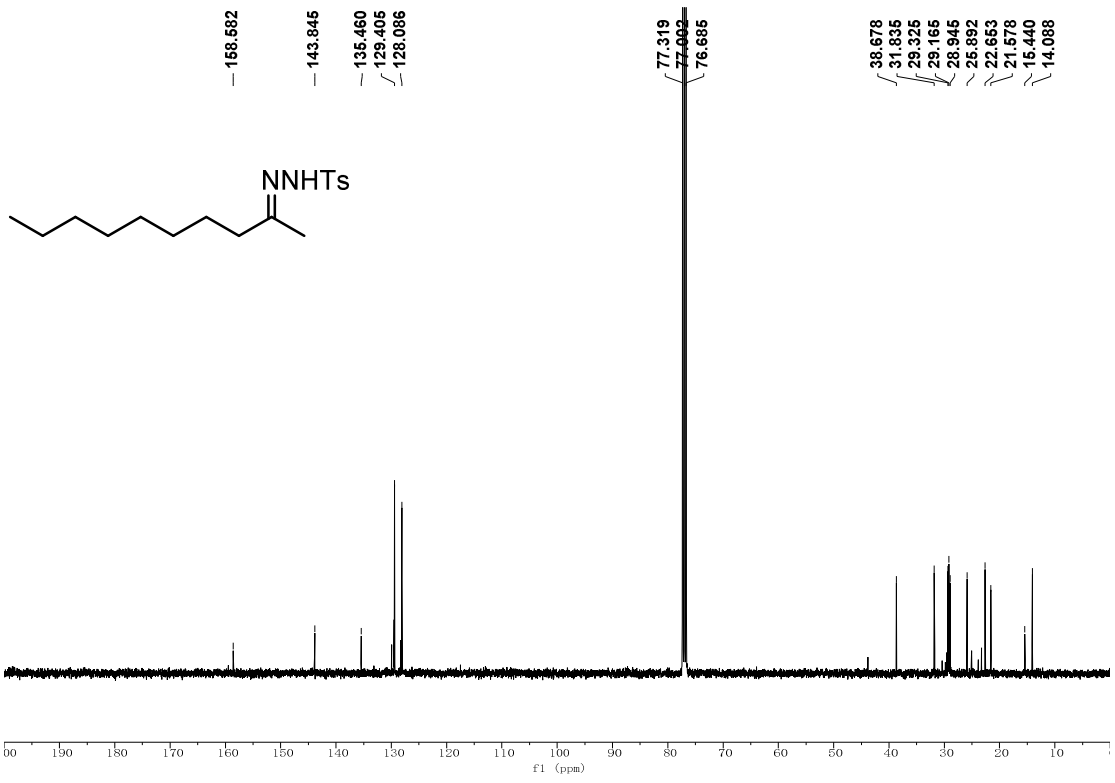
1.423
1.405
1.291
1.276
1.272
1.260
1.254
1.226
1.206
1.200
1.194
0.897
0.880
NNHTs
2.00
2.07
0.64
3.26
2.06
3.03
2.14
10.00
3.04
f1 (ppm)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135.460
129.405
128.086
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76.685
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29.165
28.945
25.892
22.653
21.578
16.440
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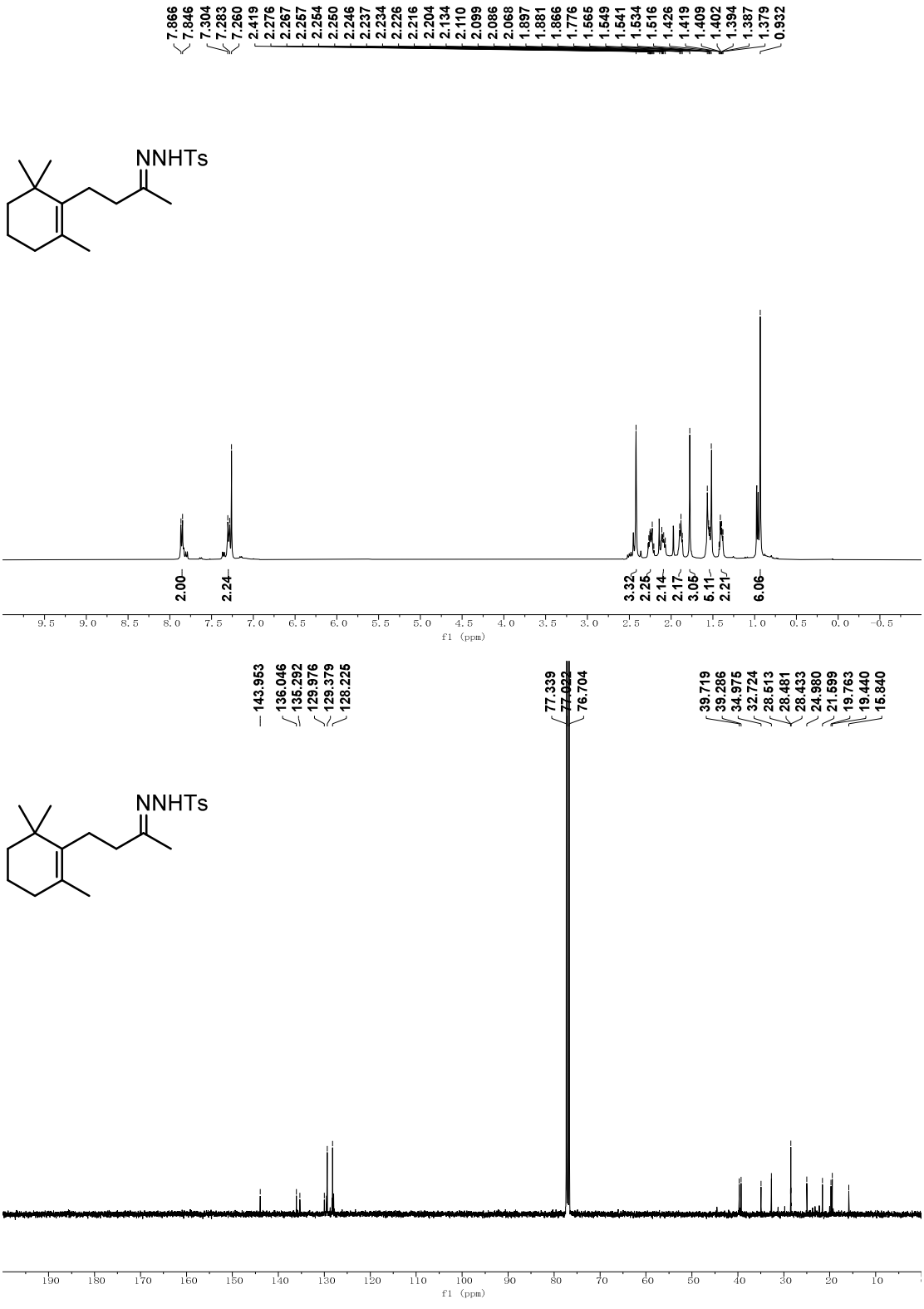
NNHTs
f1 (ppm)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7.304
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2.267
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2.234
2.226
2.216
2.204
2.134
2.110
2.099
2.086
2.068
1.897
1.881
1.866
1.776
1.565
1.549
1.541
1.534
1.516
1.426
1.419
1.409
1.402
1.394
1.387
1.379
0.932
NNHTs
2.00
2.24
3.32
2.25
2.14
2.17
3.05
5.11
2.21
6.06
f1 (ppm)
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136.046
135.292
129.976
129.379
128.225
77.339
77.022
76.704
39.719
39.286
34.975
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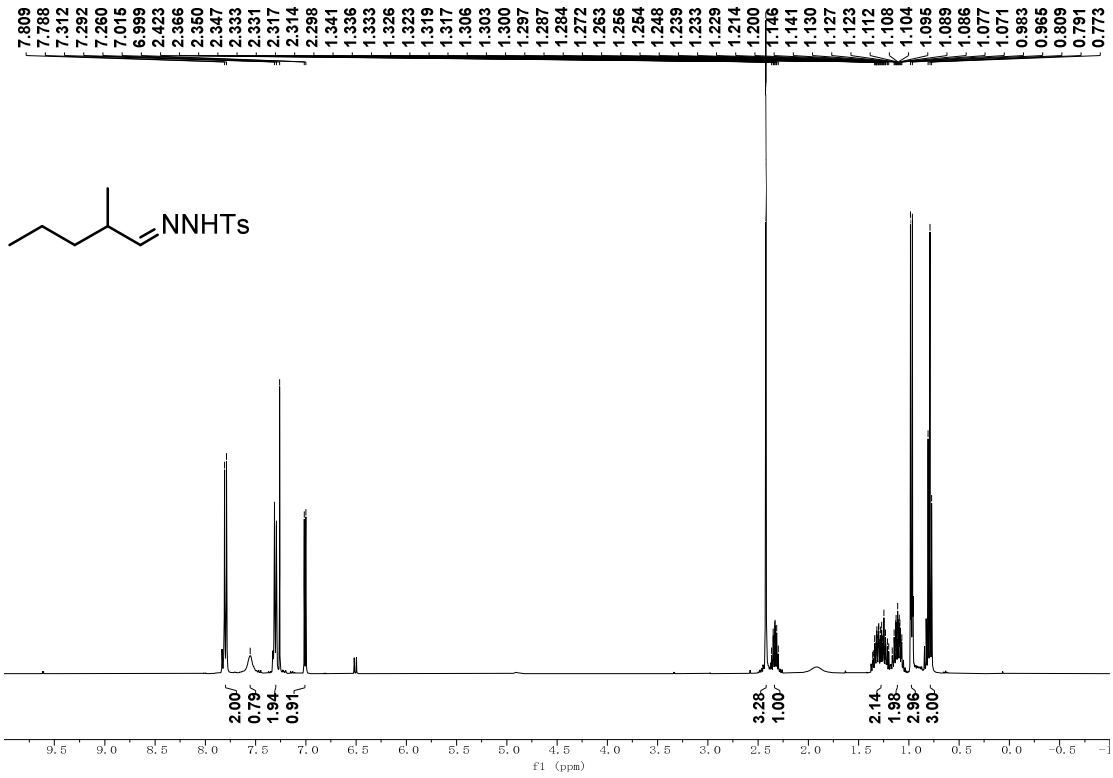
19.440
15.840
NNHTs
f1 (ppm)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7.260
7.015
6.999
2.423
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2.331
2.317
2.314
2.298
1.341
1.336
1.333
1.326
1.323
1.319
1.317
1.306
1.303
1.300
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1.287
1.284
1.272
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1.254
1.248
1.239
1.233
1.229
1.214
1.200
1.146
1.141
1.130
1.127
1.123
1.112
1.108
1.104
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1.089
1.086
1.077
1.071
0.983
0.965
0.809
0.791
0.773
NNHTs
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1.00
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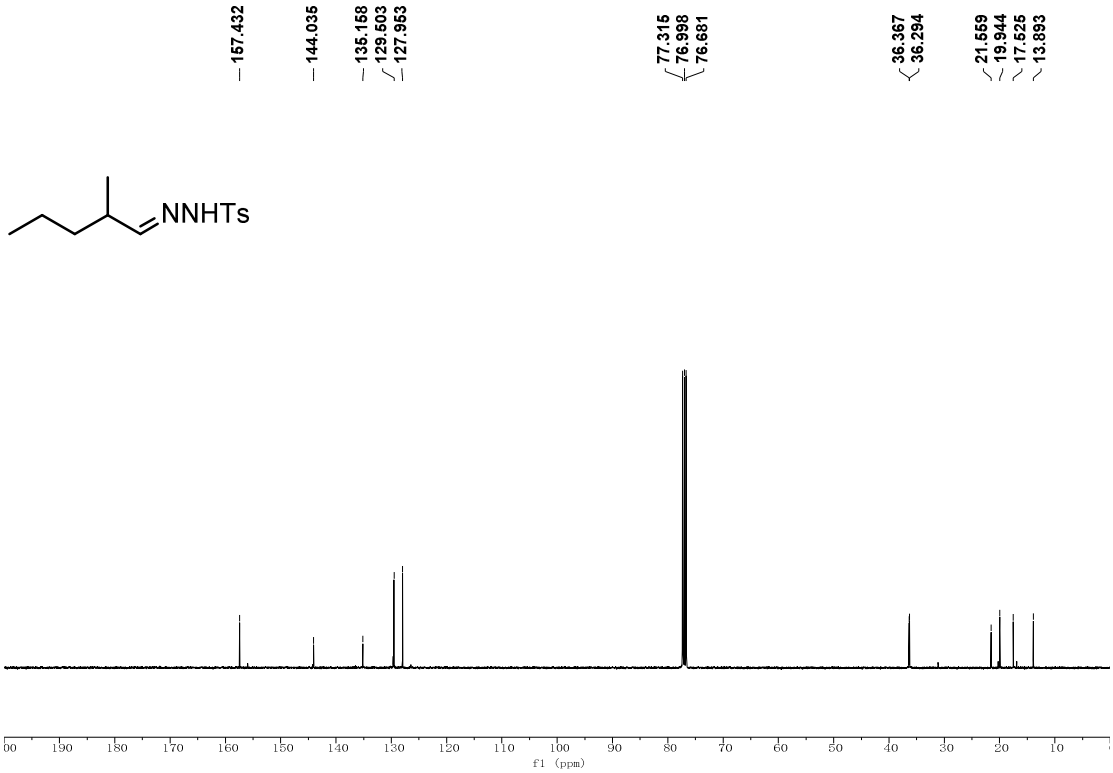
1.98
2.96
3.00
f1 (ppm)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129.503
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77.315
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76.681
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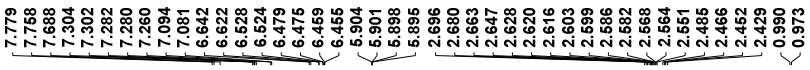
17.525
13.893
NNHTs
f1 (ppm)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7.280
7.260
7.094
7.081
6.642
6.622
6.528
6.524
6.479
6.475
6.459
6.455
5.904
5.901
5.898
5.895
2.696
2.680
2.663
2.647
2.628
2.620
2.616
2.603
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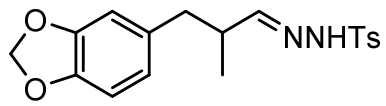
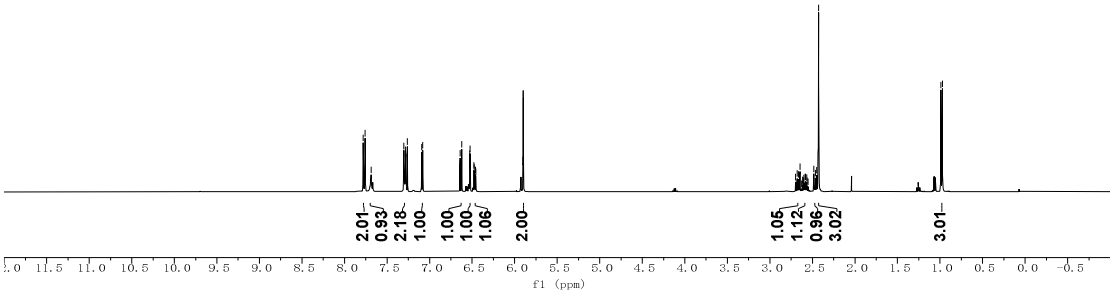
2.466
2.452
2.429
0.990
0.973


O
O
NNHTs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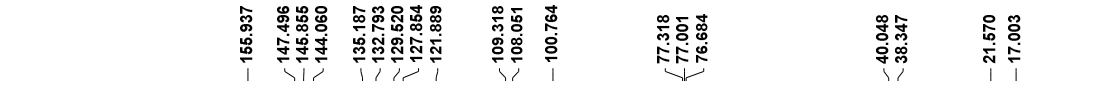
0.93
2.18
1.00
1.00
1.00
1.06
2.00
1.05
1.12
0.96
3.02
3.01
f1 (ppm)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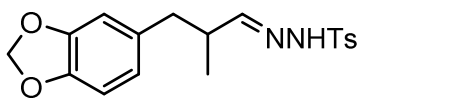
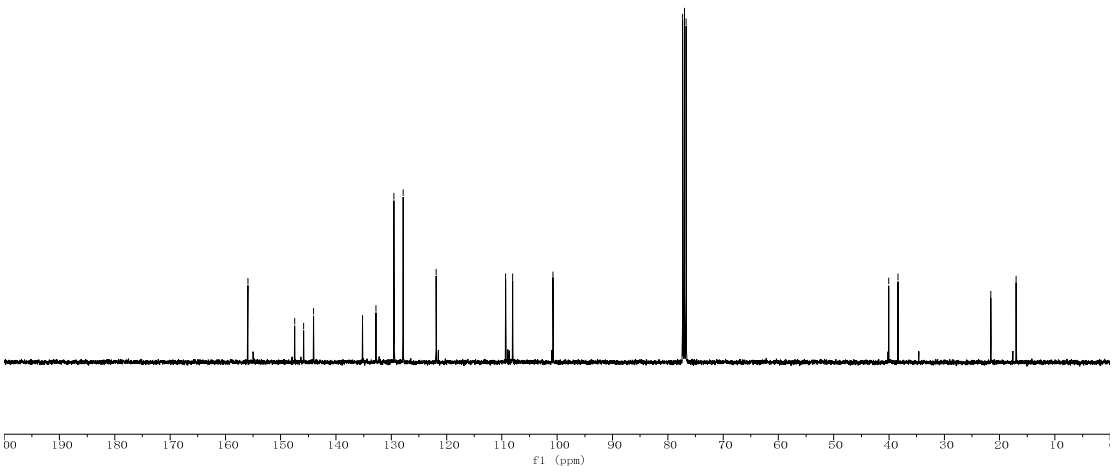
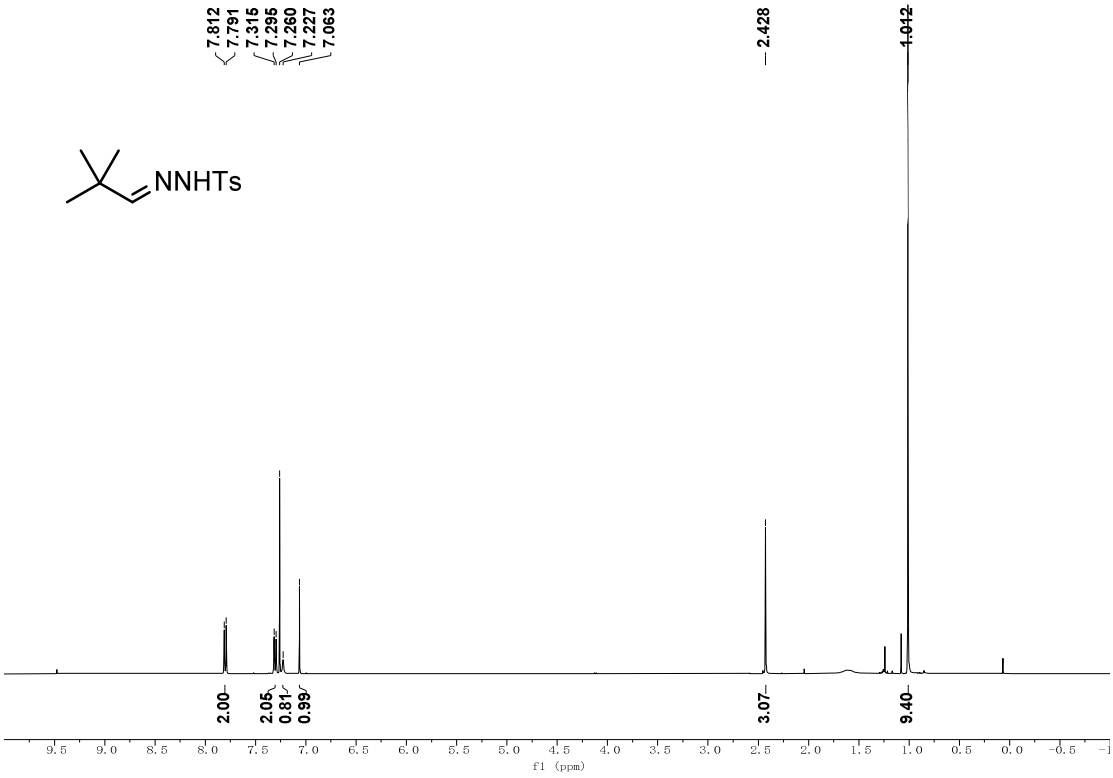
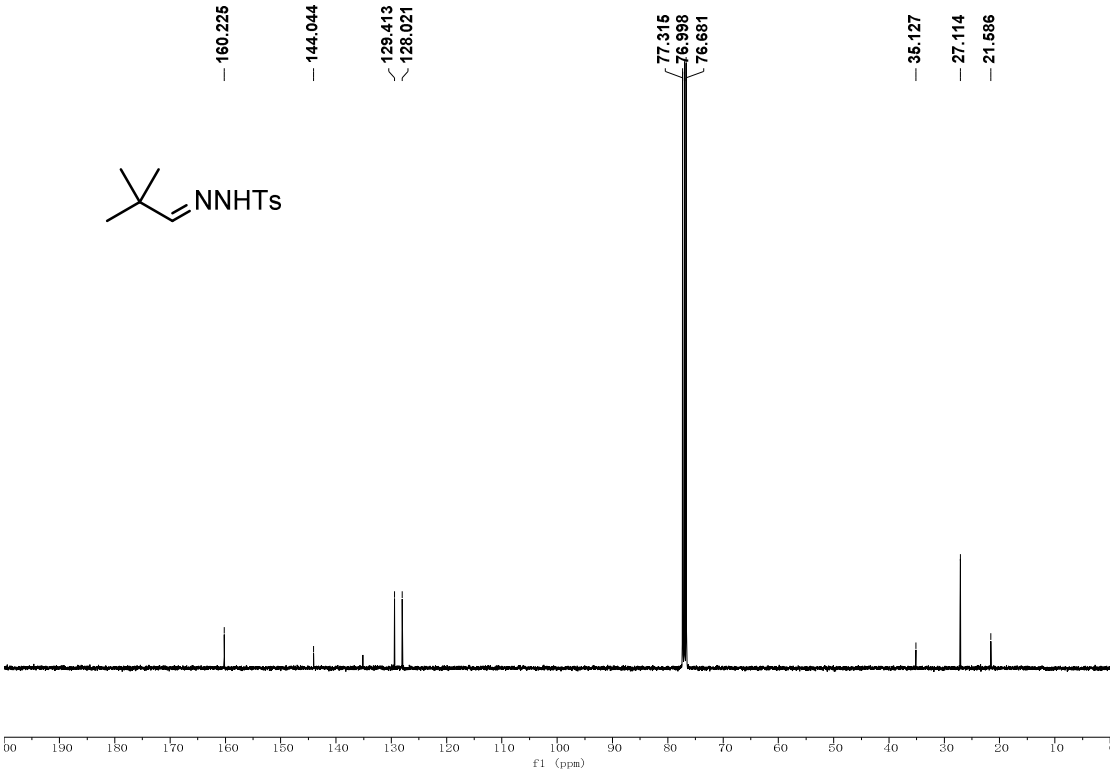

O
O
NNHTs


f1 (ppm)


7.812
7.791
7.315
7.295
7.260
7.227
7.063
2.428
1.012
NNHTs
2.00
2.05
0.81
0.99
3.07
9.40
f1 (ppm)


160.225
144.044
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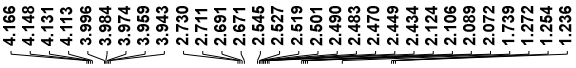
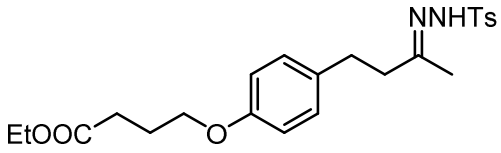
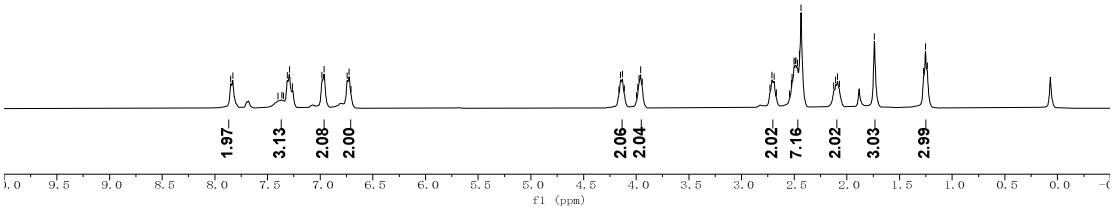
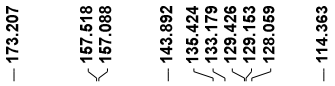
76.998
76.681
35.127
27.114
21.586
NNHTs
f1 (ppm)

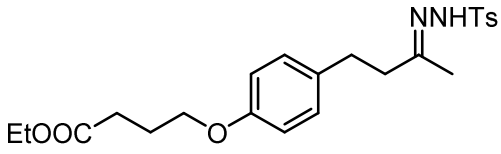




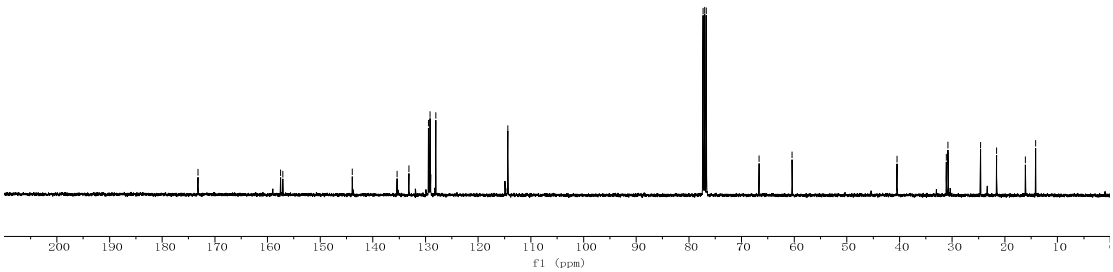
^{1}H NMR 400 MHz, $CDCl_3$

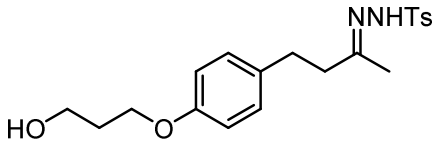




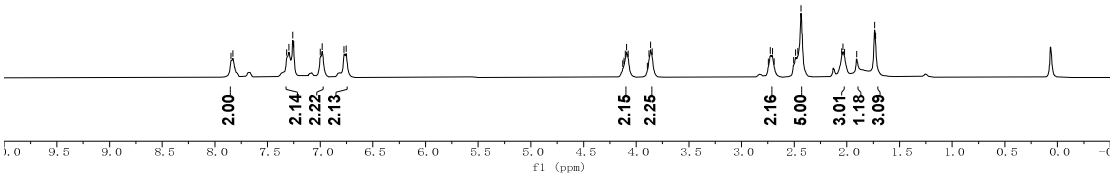


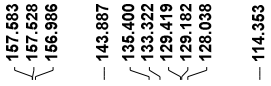
^{13}C NMR 101 MHz, $CDCl_3$

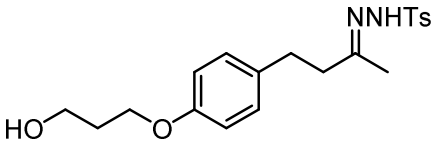




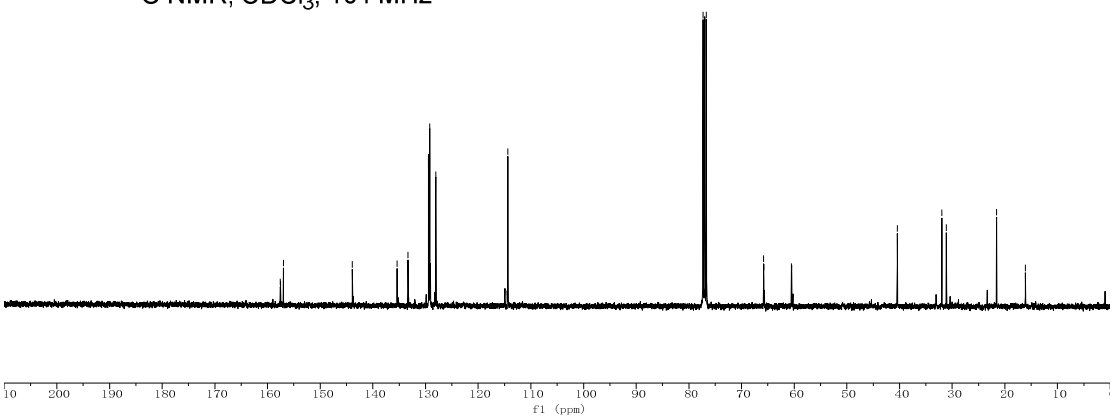
^{1}H NMR, $CDCl_3$, 400 MHz

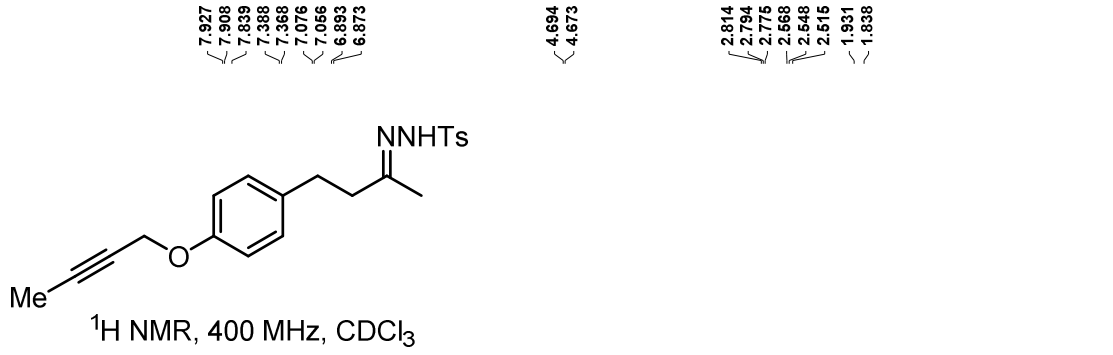




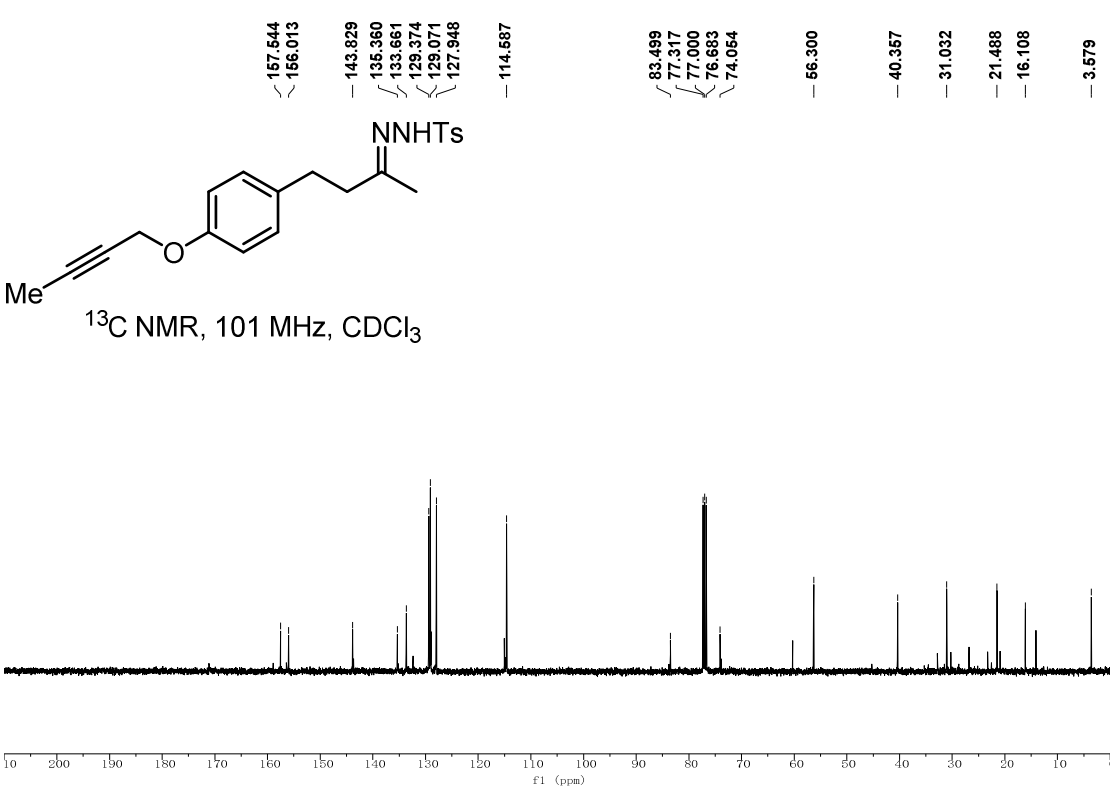


^{13}C NMR, $CDCl_3$, 101 MHz

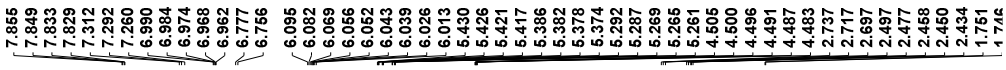


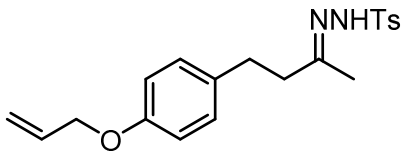


^{1}H NMR, 400 MHz, $CDCl_3$

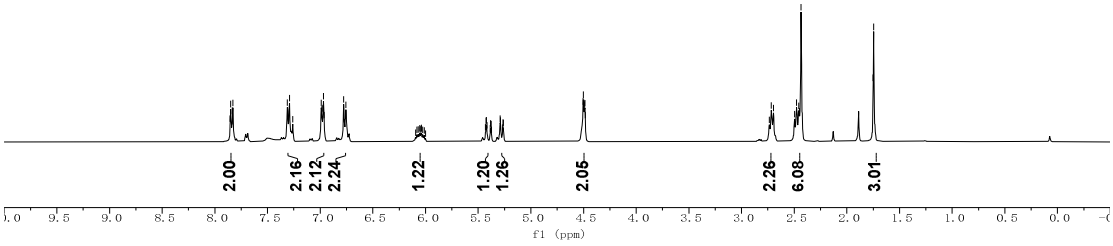


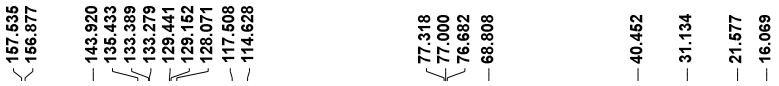
^{13}C NMR, 101 MHz, $CDCl_3$

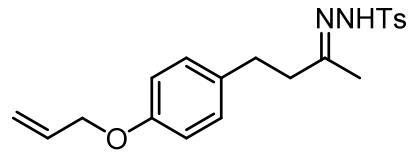




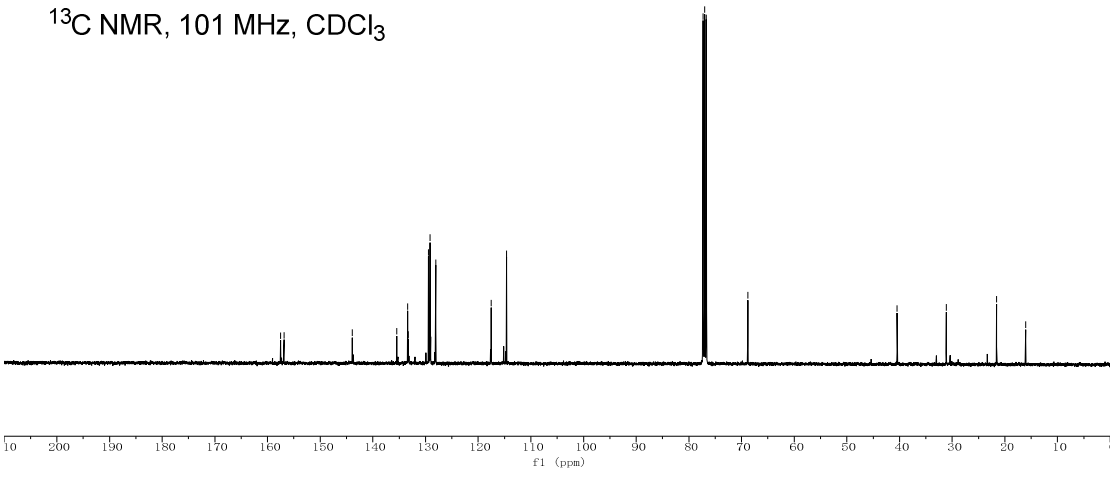
^{1}H NMR, 400 MHz, $CDCl_3$

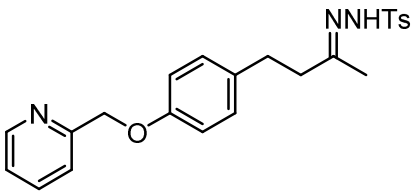




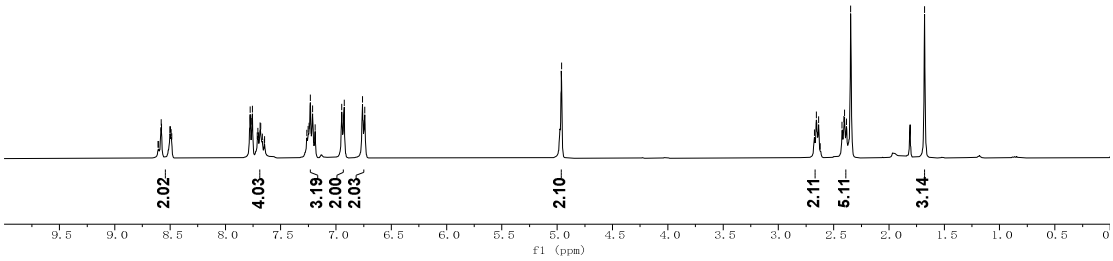


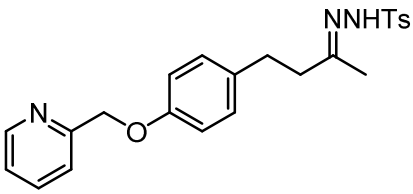
^{13}C NMR, 101 MHz, $CDCl_3$



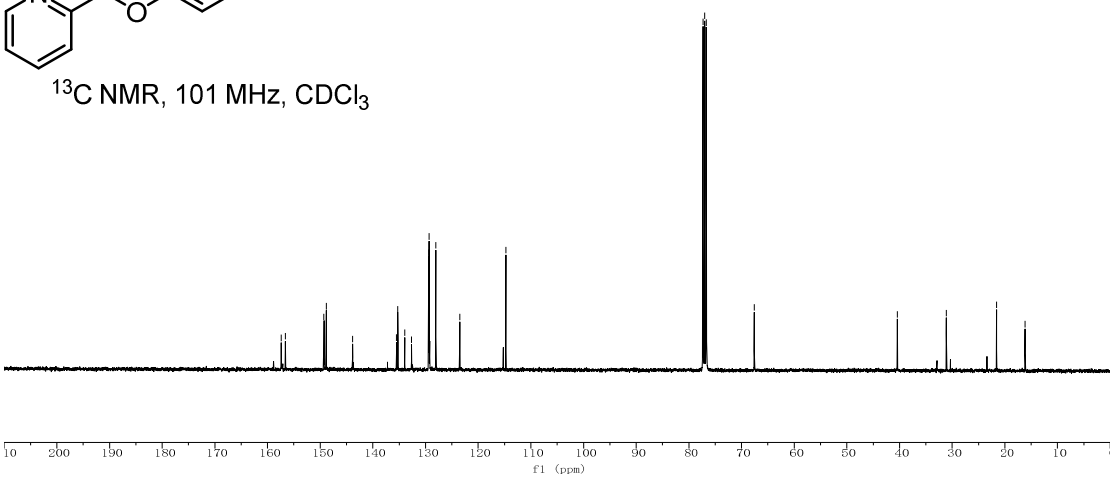


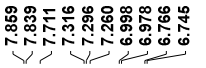
^{1}H NMR, 400 MHz, $CDCl_3$

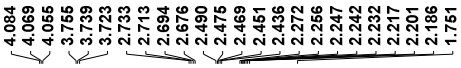


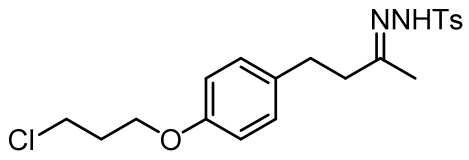


^{13}C NMR, 101 MHz, $CDCl_3$

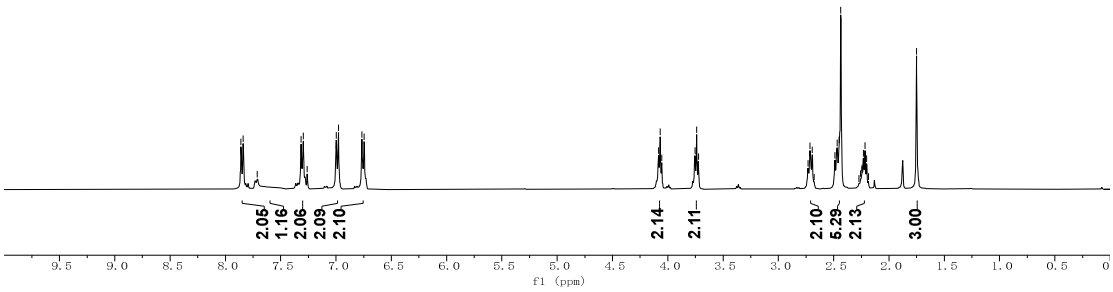


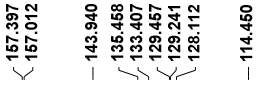


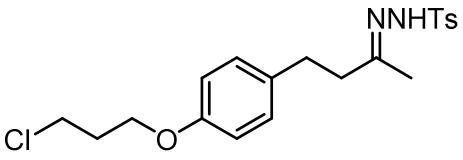




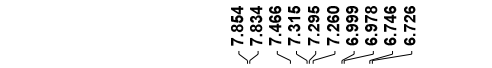
^{1}H NMR, 400 MHz, $CDCl_3$

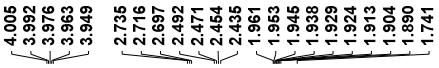


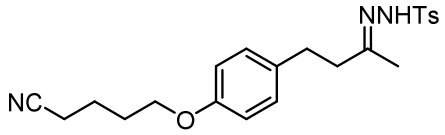




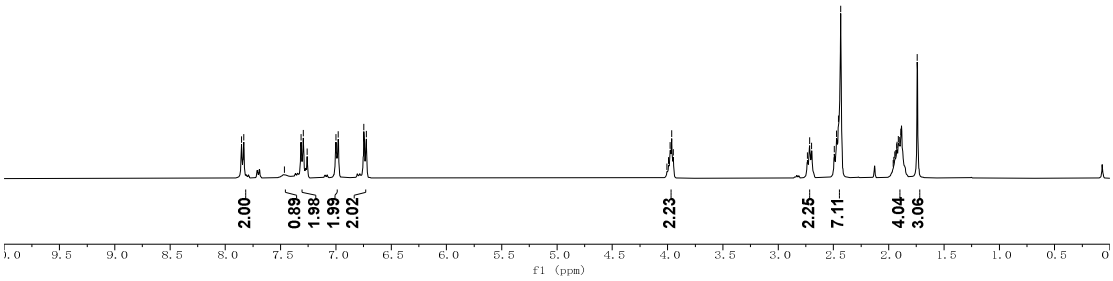
^{13}C NMR, 101 MHz, $CDCl_3$

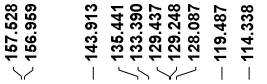


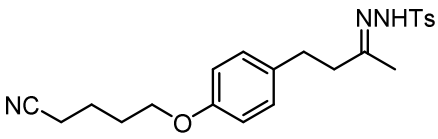




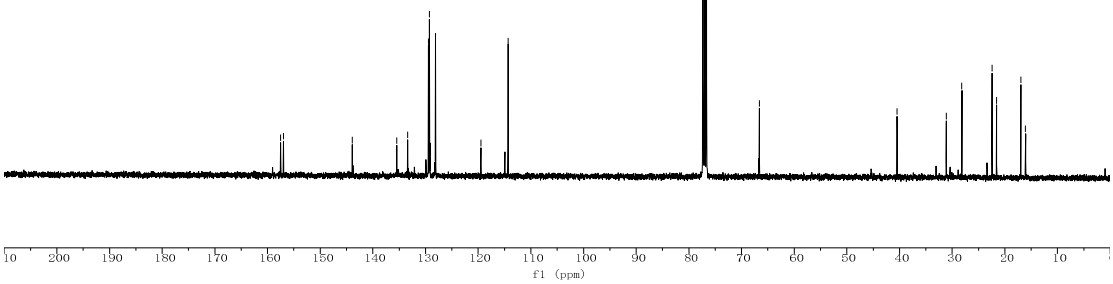
^{1}H NMR, 400 MHz, $CDCl_3$

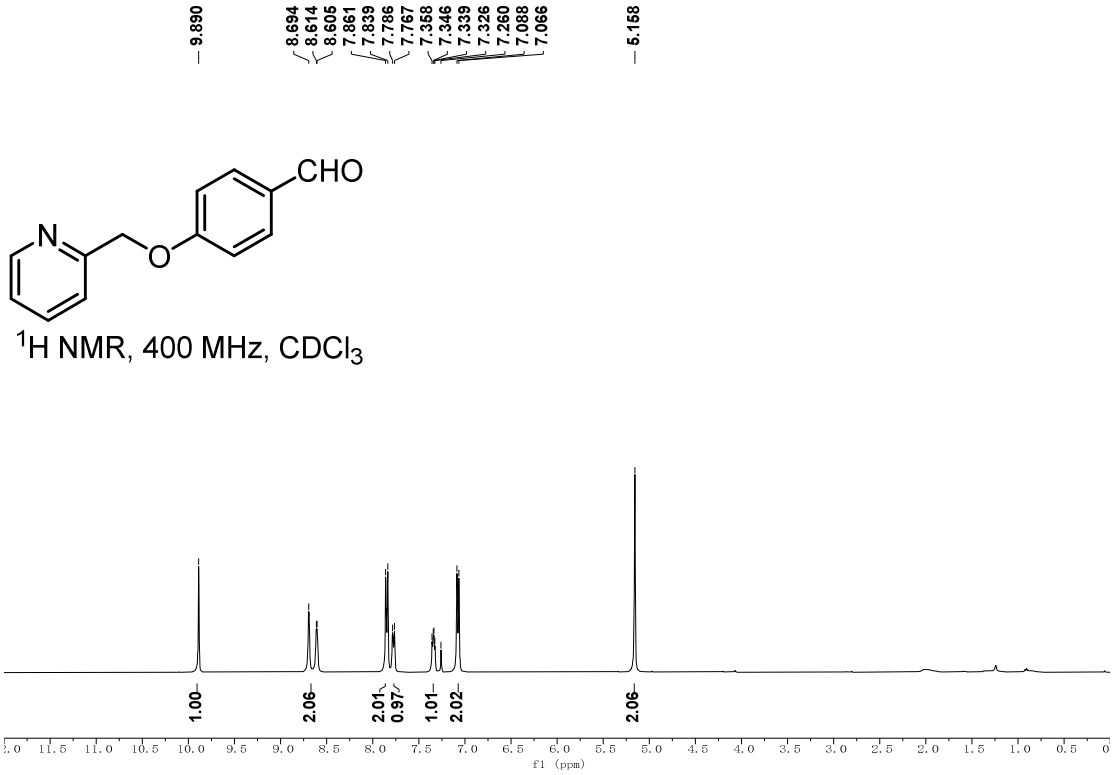


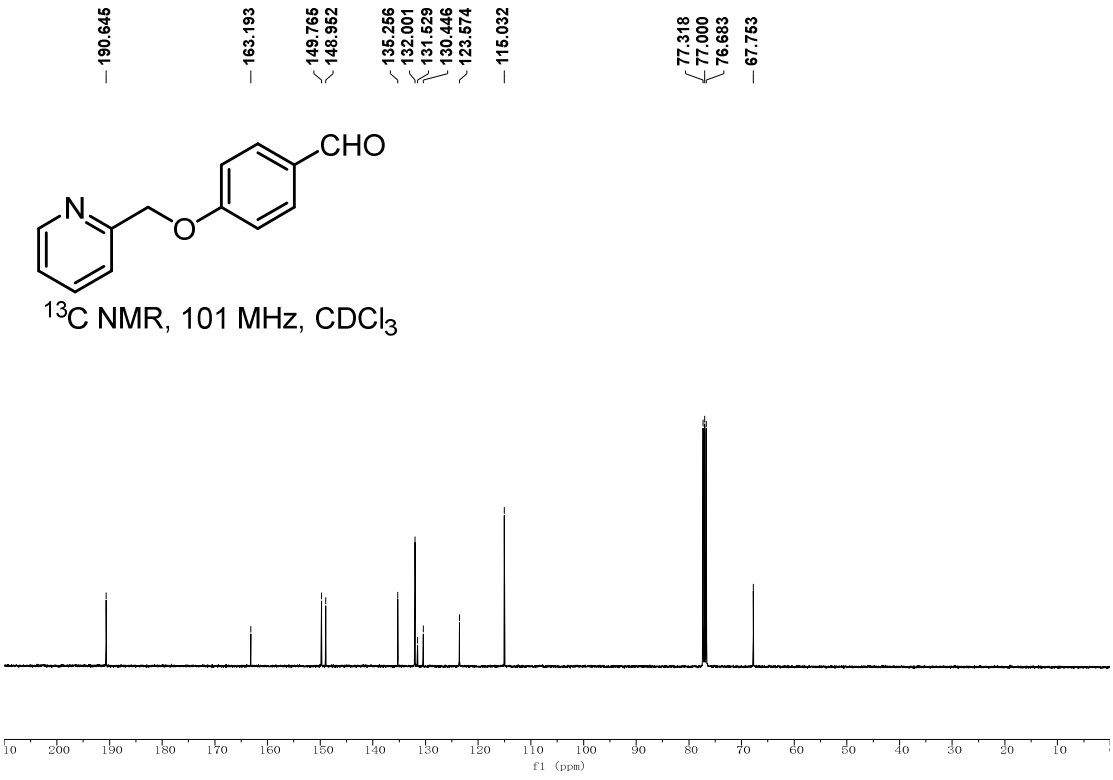


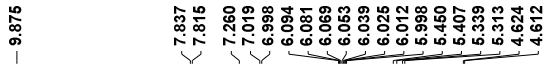


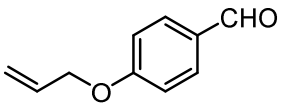
^{13}C NMR, 101 MHz, $CDCl_3$



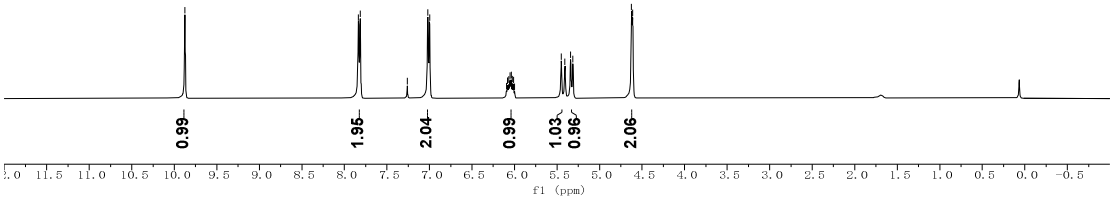

9.890
8.694
8.614
8.605
7.861
7.839
7.786
7.767
7.358
7.346
7.339
7.326
7.260
7.088
7.066
5.158
CHO
N
O
1H NMR, 400 MHz, CDCl3
1.00
2.06
2.01
0.97
1.01
2.02
2.06
f1 (ppm)

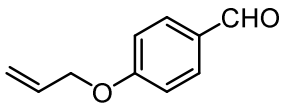

190.645
163.193
149.765
148.952
135.256
132.001
131.529
130.446
123.574
115.032
77.318
77.000
76.683
67.753
CHO
N
O
13C NMR, 101 MHz, CDCl3
f1 (ppm)



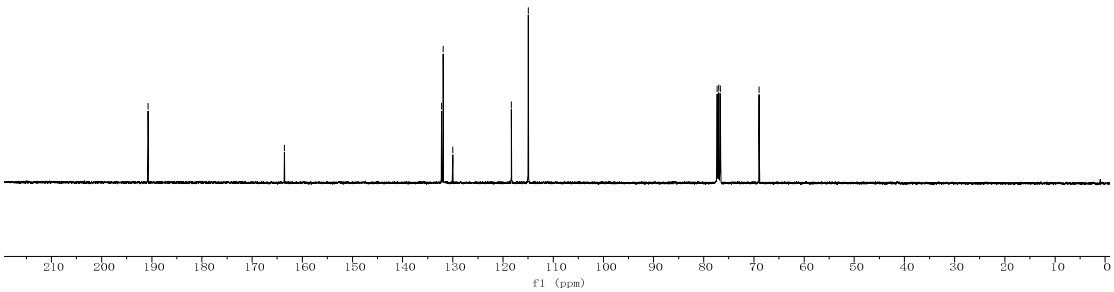


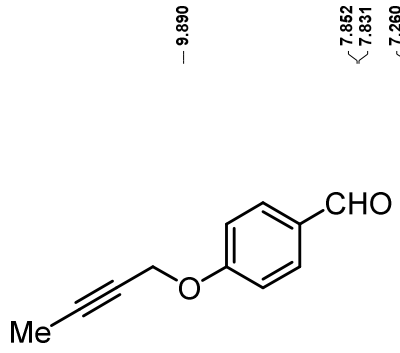
^{1}H NMR, 400 MHz, $CDCl_3$



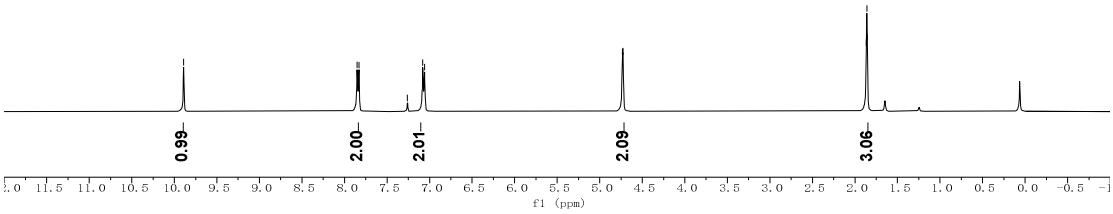


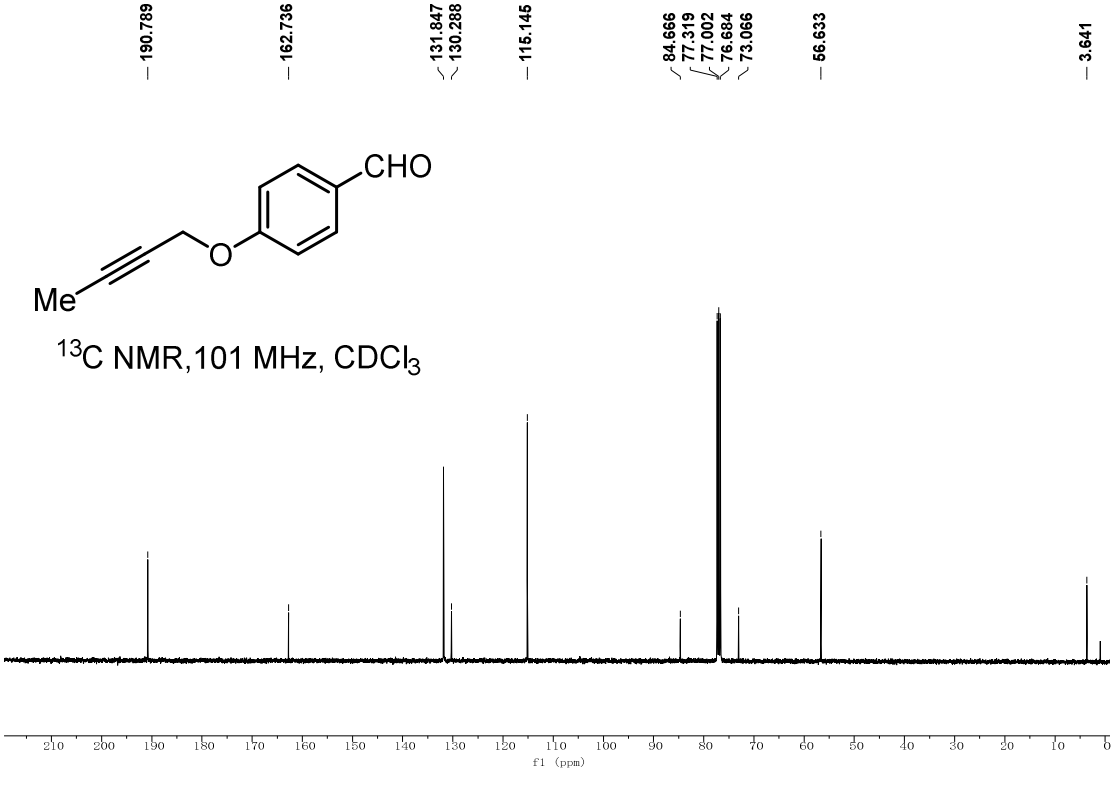
^{13}C NMR, 101 MHz, $CDCl_3$



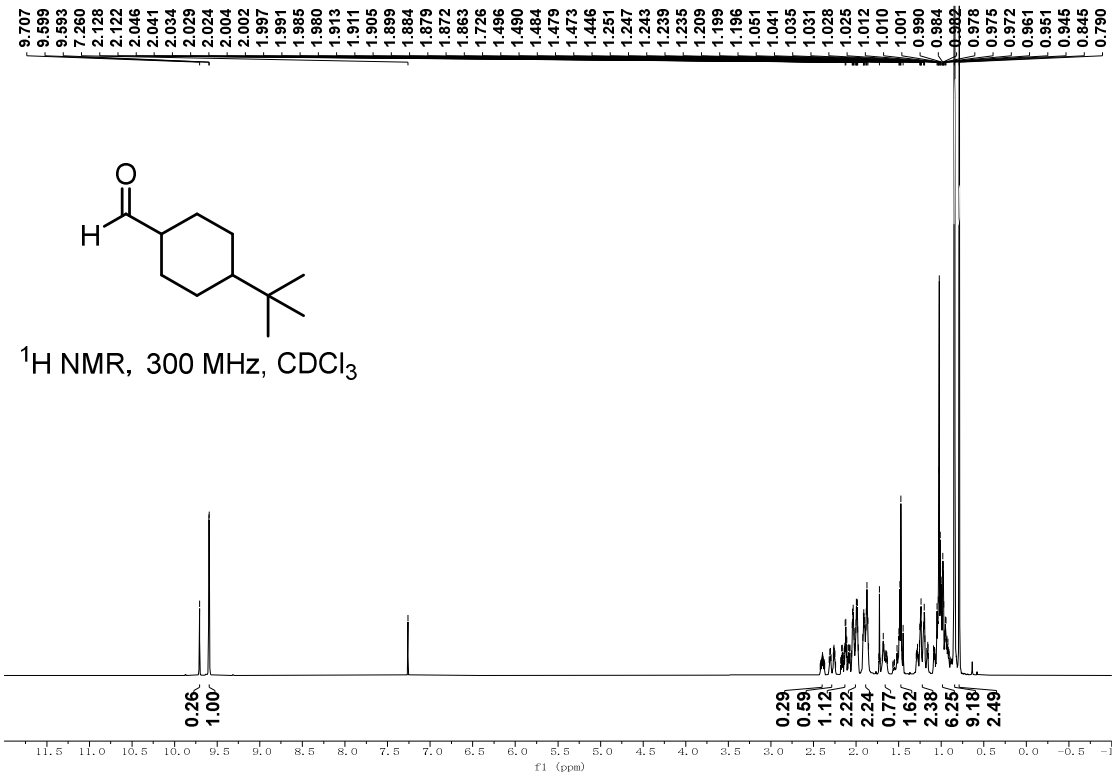


^{1}H NMR, 400 MHz, $CDCl_3$

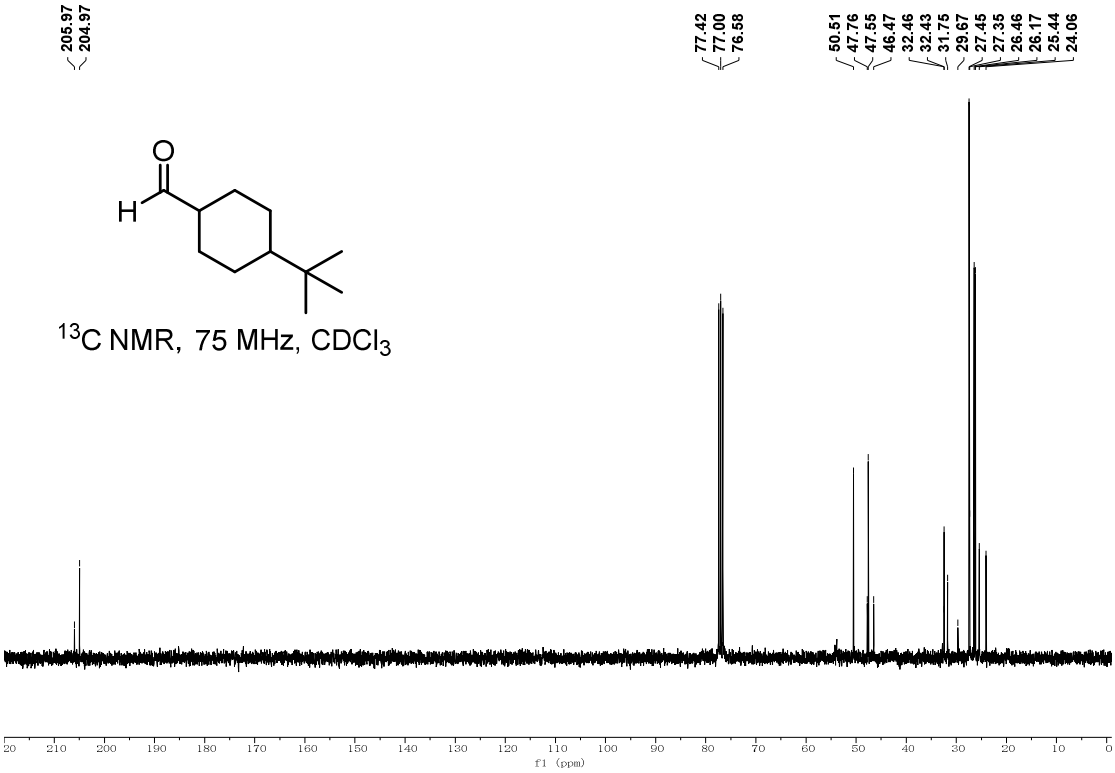




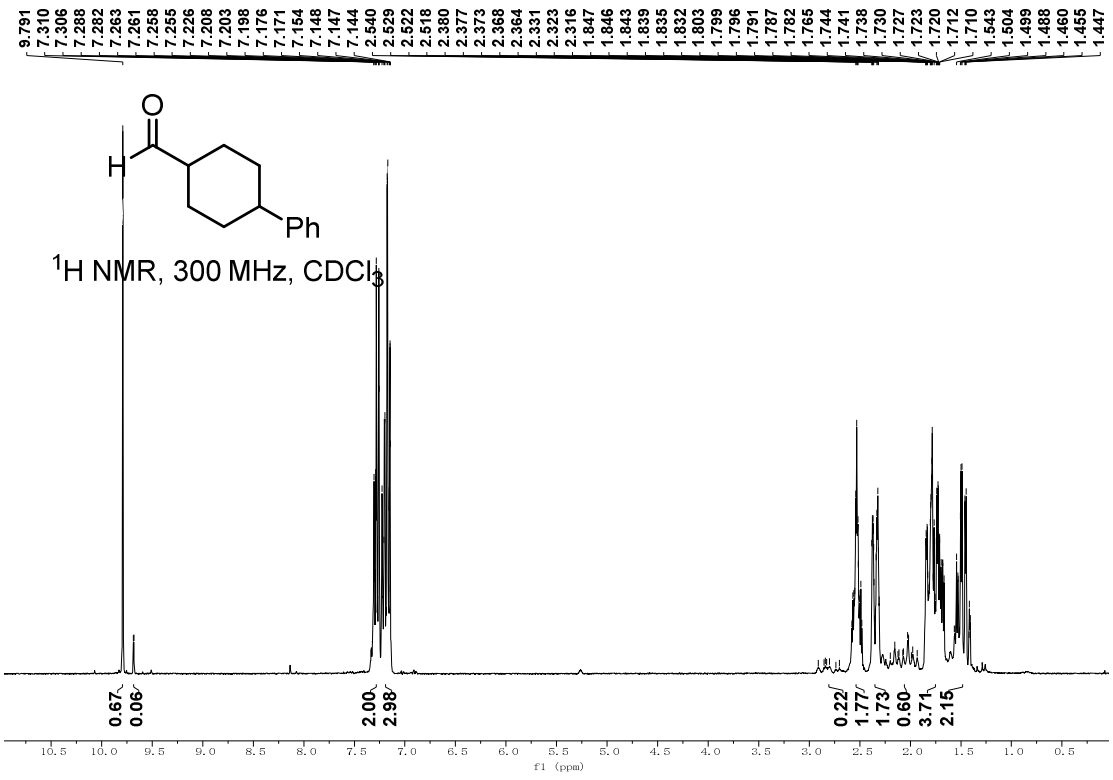
^{13}C NMR,101 MHz, $CDCl_3$



^{1}H NMR, 300 MHz, $CDCl_3$



^{13}C NMR, 75 MHz, $CDCl_3$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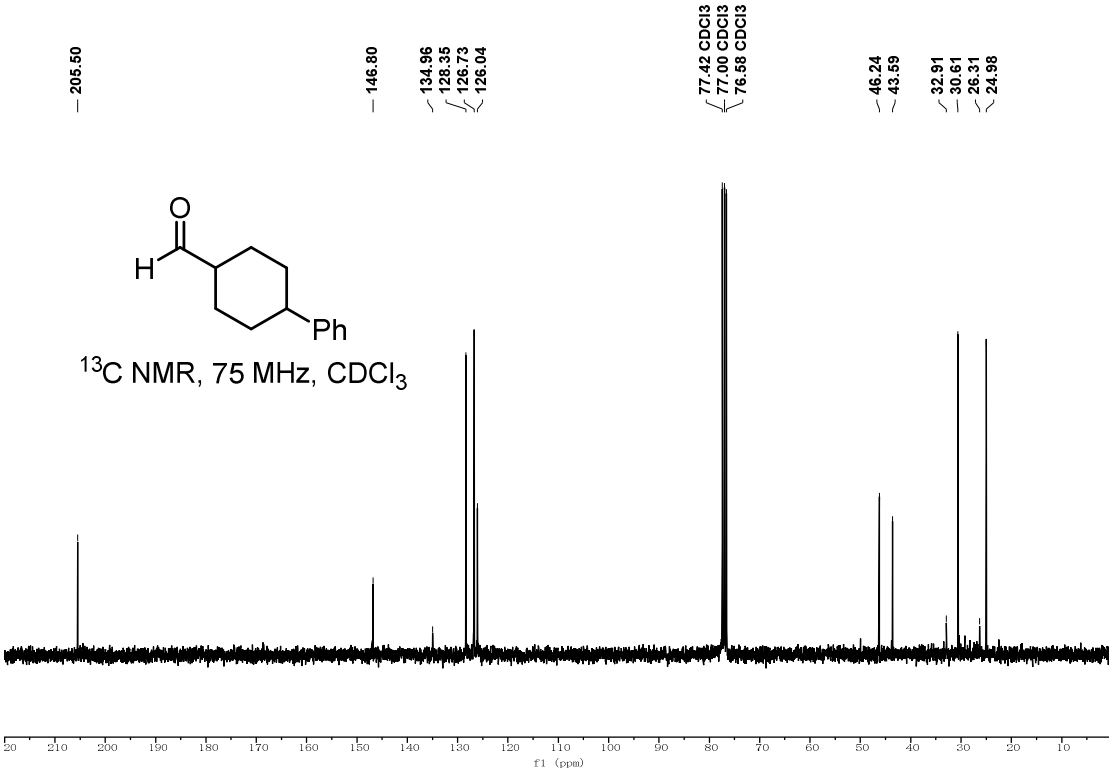
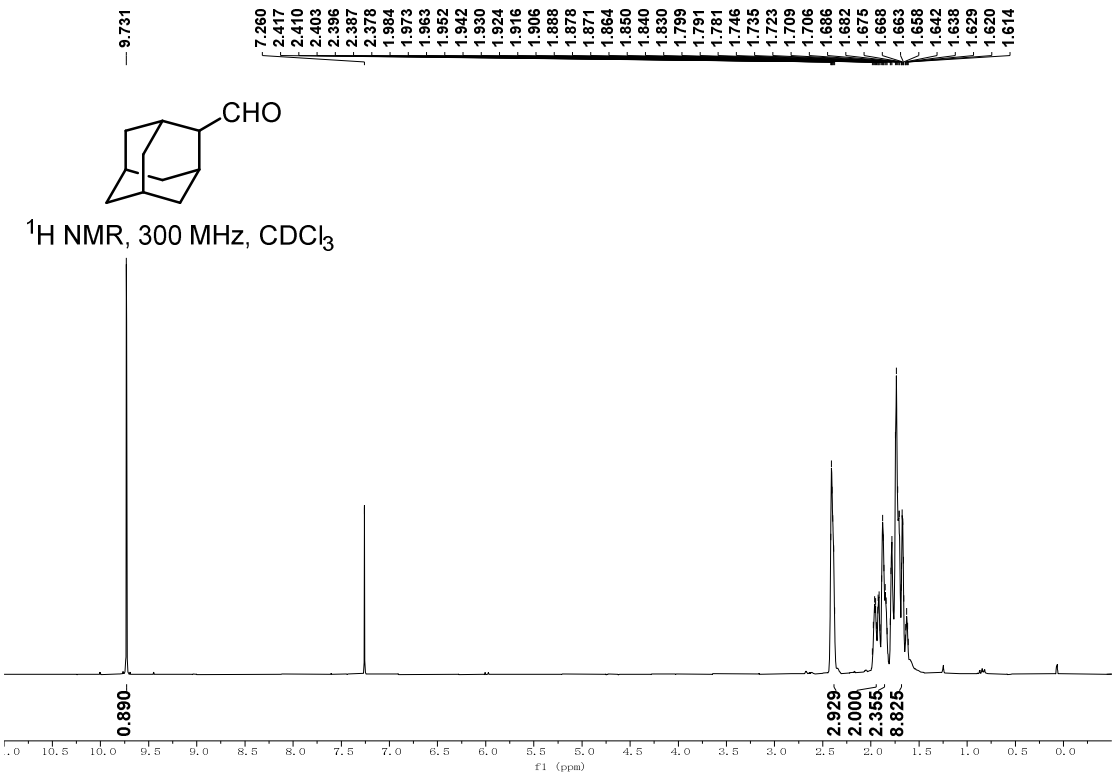
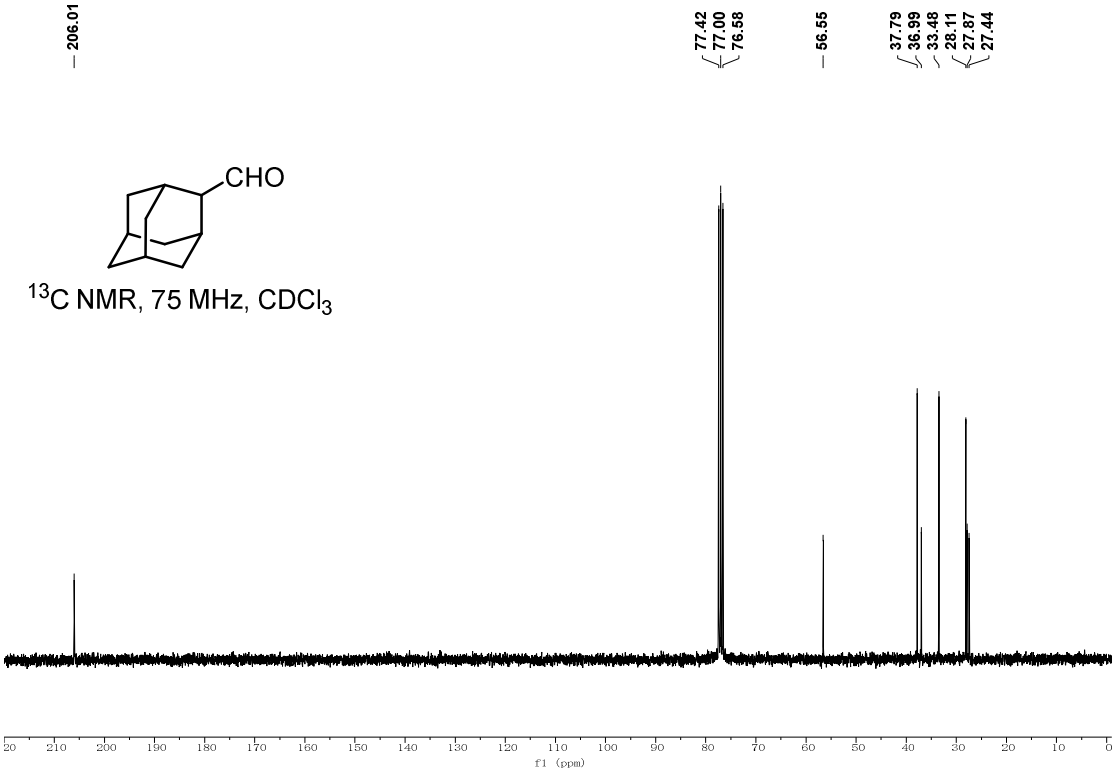
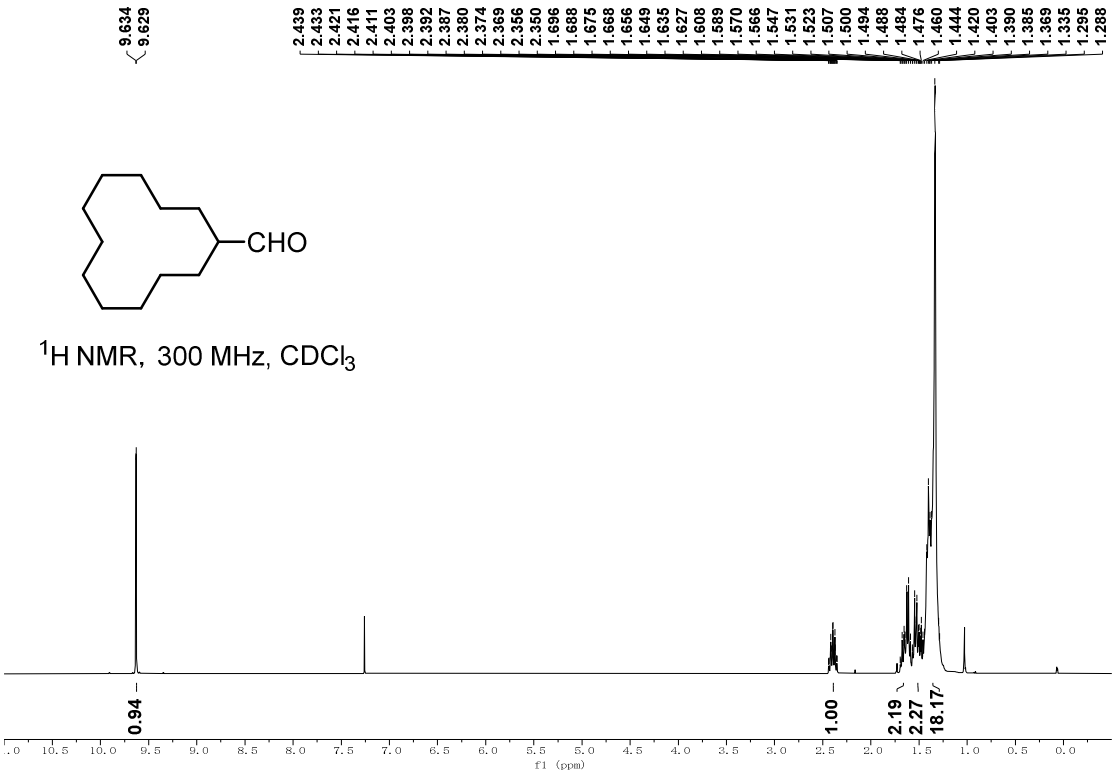
7.310
7.306
7.288
7.282
7.263
7.261
7.258
7.255
7.226
7.208
7.203
7.198
7.176
7.171
7.154
7.148
7.147
7.144
2.540
2.529
2.522
2.518
2.380
2.377
2.373
2.368
2.364
2.331
2.323
2.316
1.847
1.846
1.843
1.839
1.835
1.832
1.803
1.799
1.796
1.791
1.787
1.782
1.765
1.744
1.741
1.738
1.730
1.727
1.723
1.720
1.712
1.710
1.543
1.504
1.499
1.488
1.460
1.455
1.447
O
H
Ph
1H NMR, 300 MHz, CDCl3
0.67
0.06
2.00
2.98
0.22
1.77
1.73
0.60
3.71
2.15
f1 (ppm)

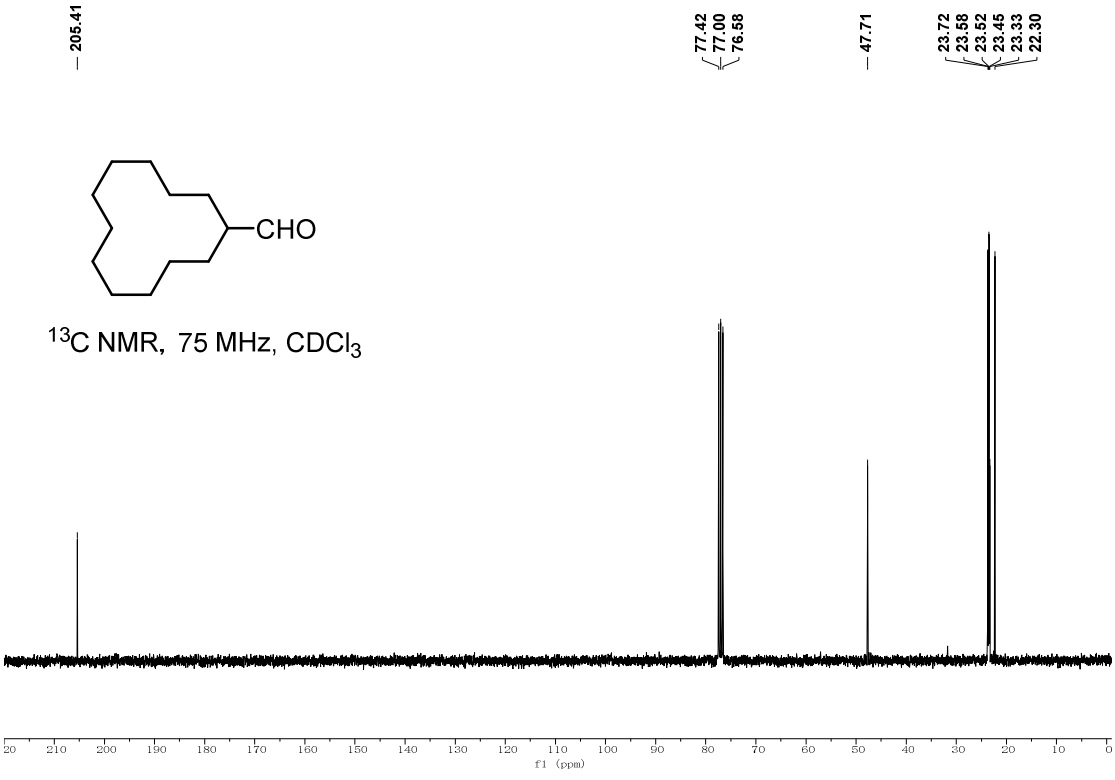

205.50
146.80
134.96
128.35
126.73
126.04
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
46.24
43.59
32.91
30.61
26.31
24.98
O
H
Ph
13C NMR, 75 MHz, CDCl3
f1 (ppm)


9.731
7.260
2.417
2.410
2.403
2.396
2.387
2.378
1.984
1.973
1.963
1.952
1.942
1.930
1.924
1.916
1.906
1.888
1.878
1.871
1.864
1.850
1.840
1.830
1.799
1.791
1.781
1.746
1.735
1.723
1.709
1.706
1.686
1.682
1.675
1.668
1.663
1.658
1.642
1.638
1.629
1.620
1.614
CHO
1H NMR, 300 MHz, CDCl3
0.890
2.929
2.000
2.355
8.825
f1 (ppm)

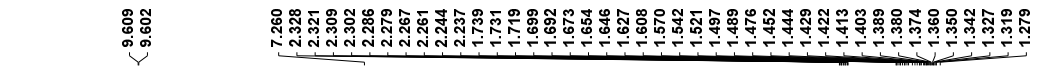

206.01
77.42
77.00
76.58
56.55
37.79
36.99
33.48
28.11
27.87
27.44
CHO
13C NMR, 75 MHz, CDCl3
f1 (ppm)

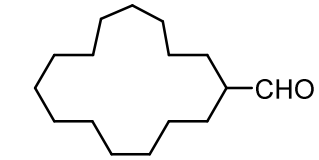


^{1}H NMR, 300 MHz, $CDCl_3$

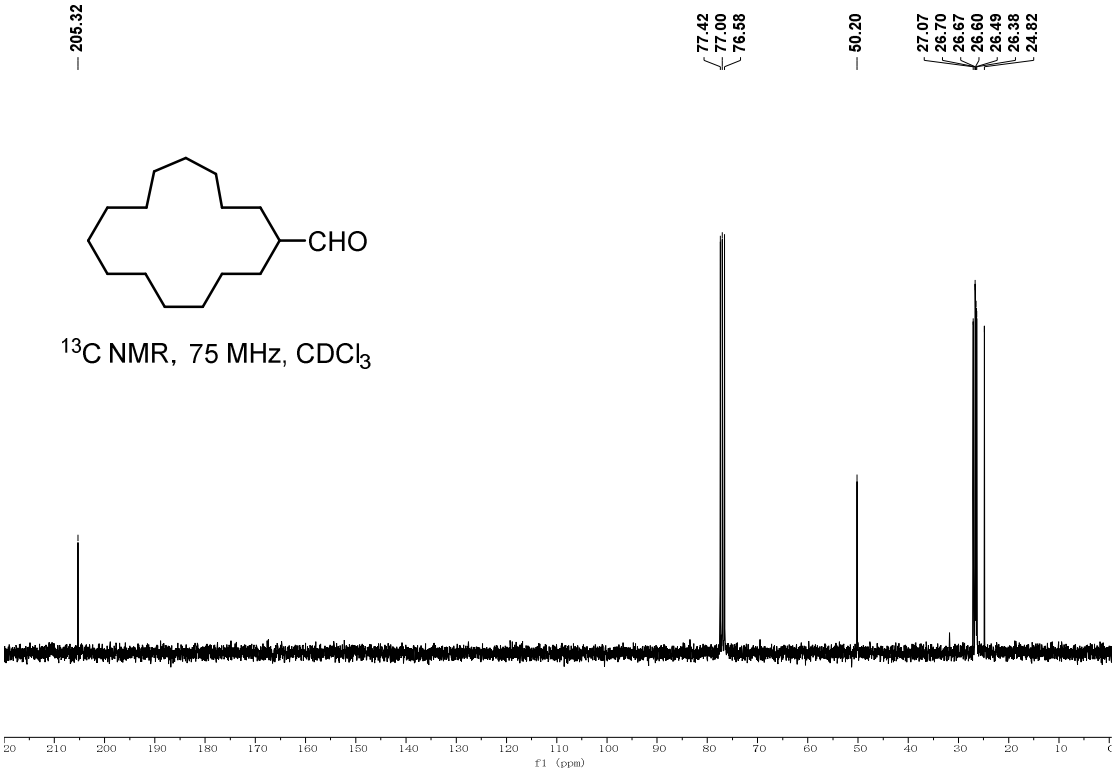


^{13}C NMR, 75 MHz, $CDCl_3$

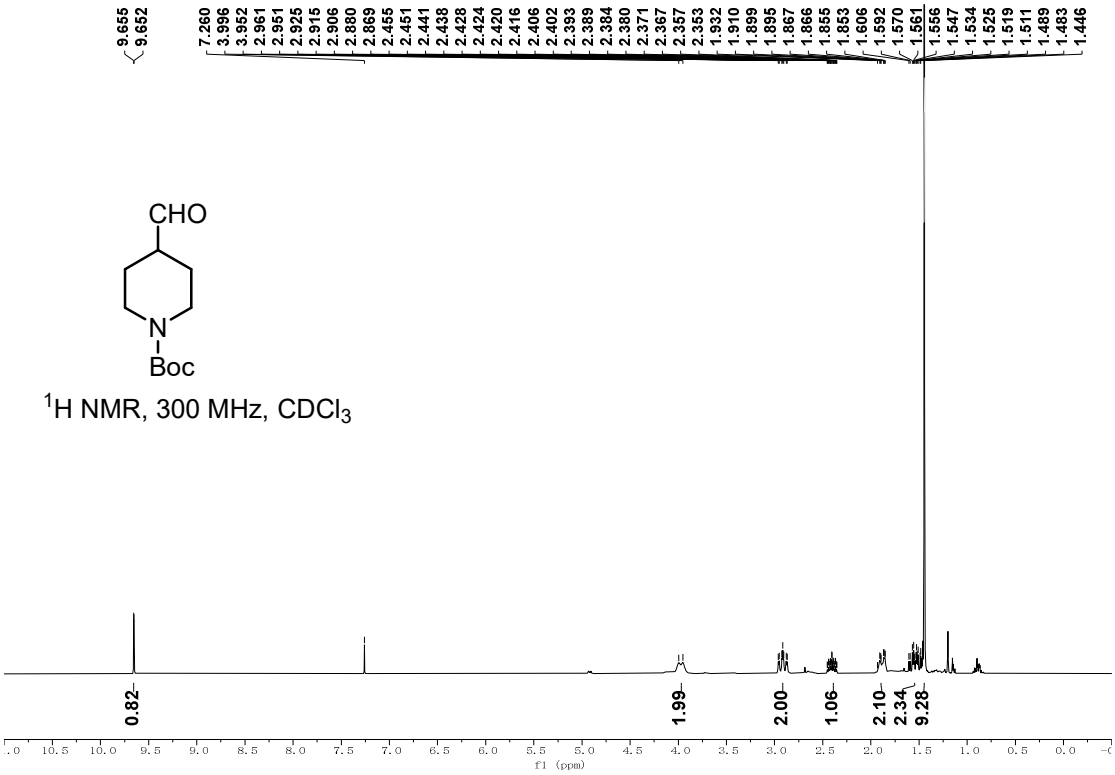




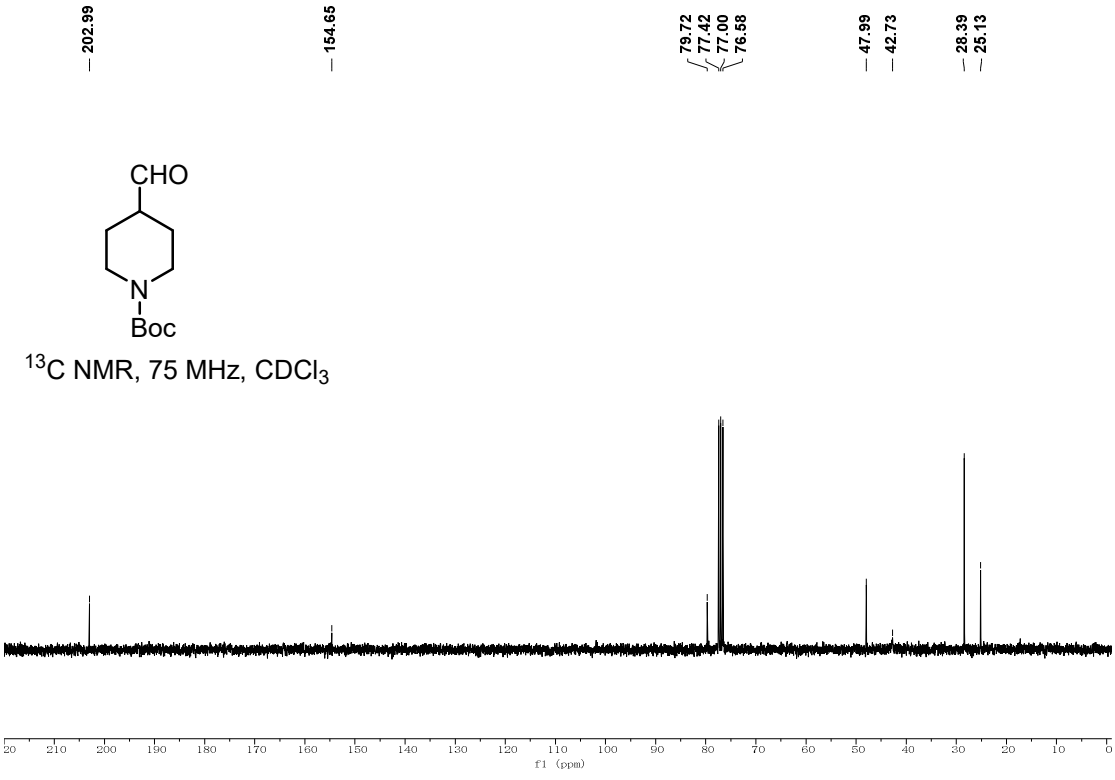
^{1}H NMR, 300 MHz, $CDCl_3$



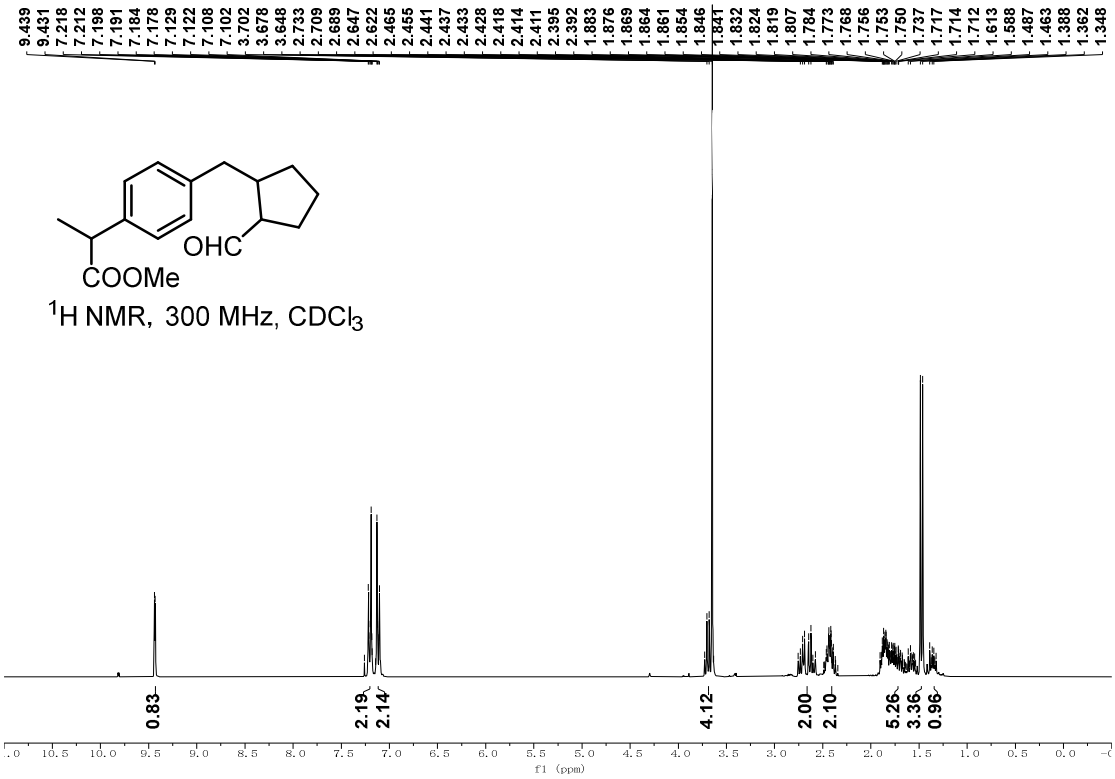
^{13}C NMR, 75 MHz, $CDCl_3$



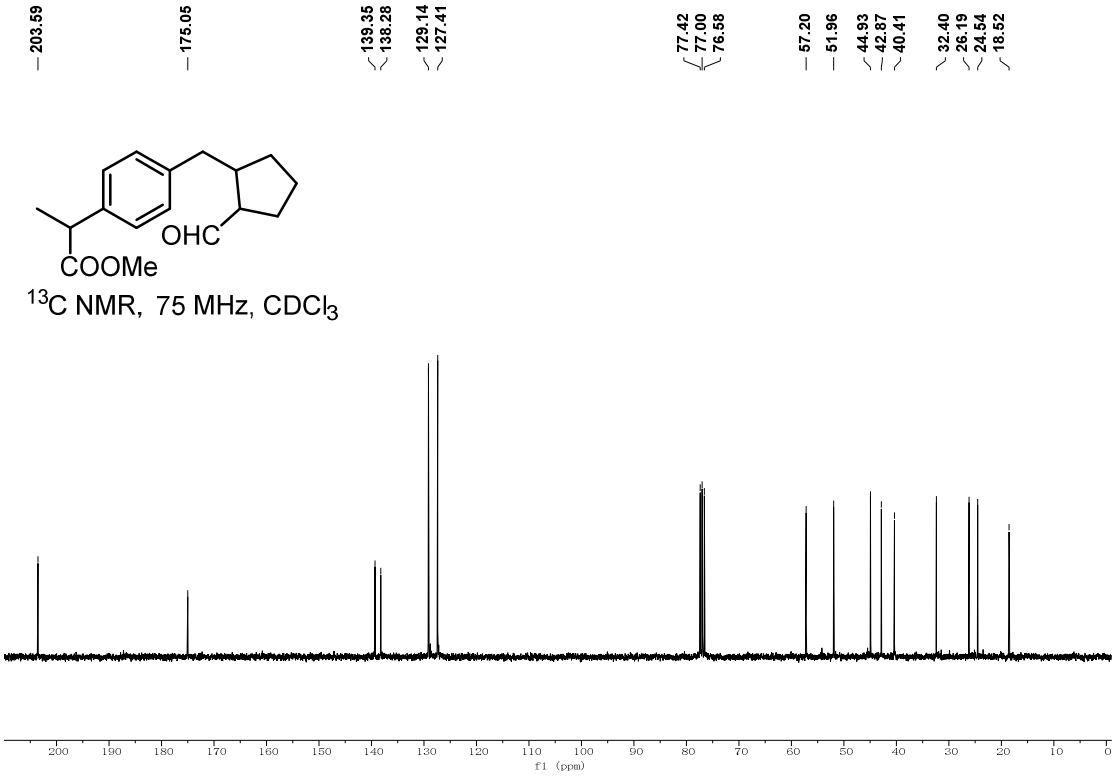
^{1}H NMR, 300 MHz, $CDCl_3$



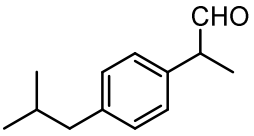
^{13}C NMR, 75 MHz, $CDCl_3$



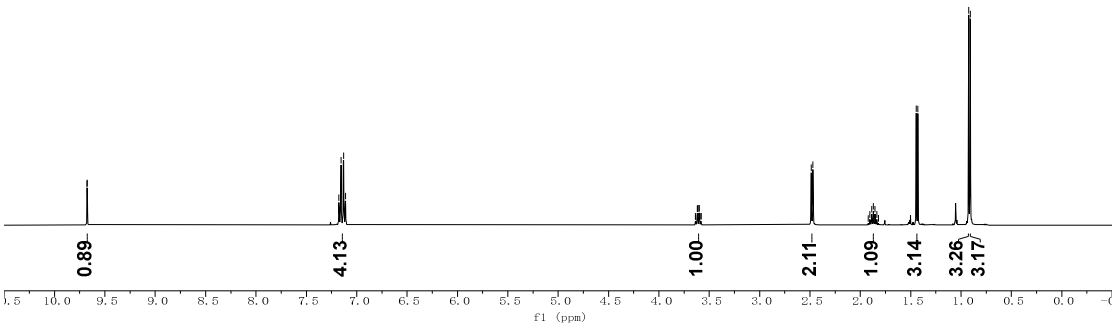
^{1}H NMR, 300 MHz, $CDCl_3$

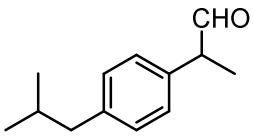


^{13}C NMR, 75 MHz, $CDCl_3$

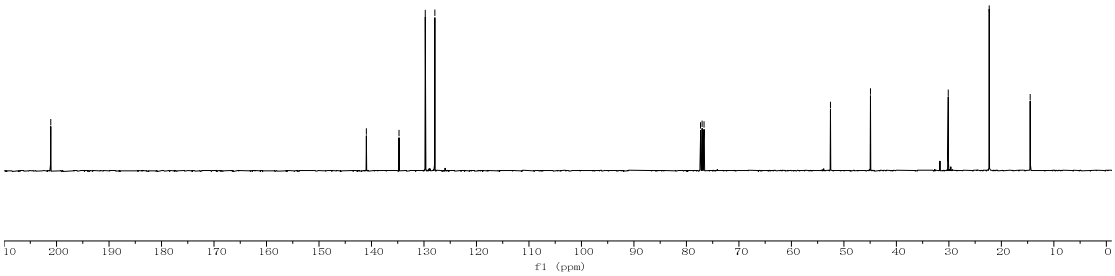


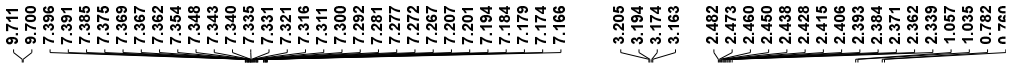
^{1}H NMR, 400 MHz, $CDCl_3$

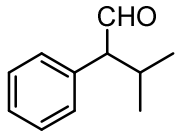




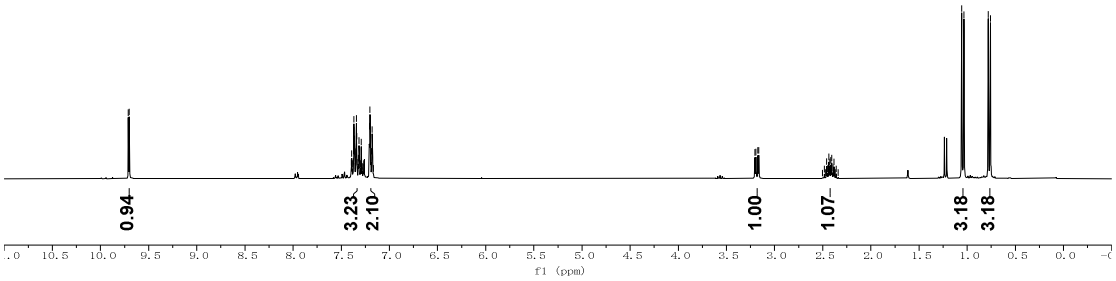
^{13}C NMR, 101 MHz, $CDCl_3$

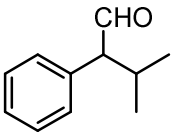




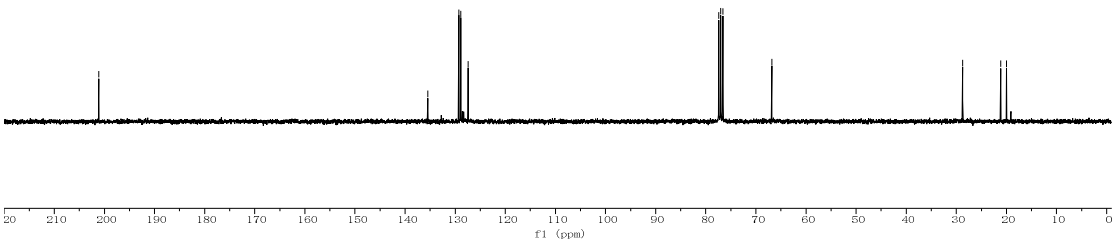


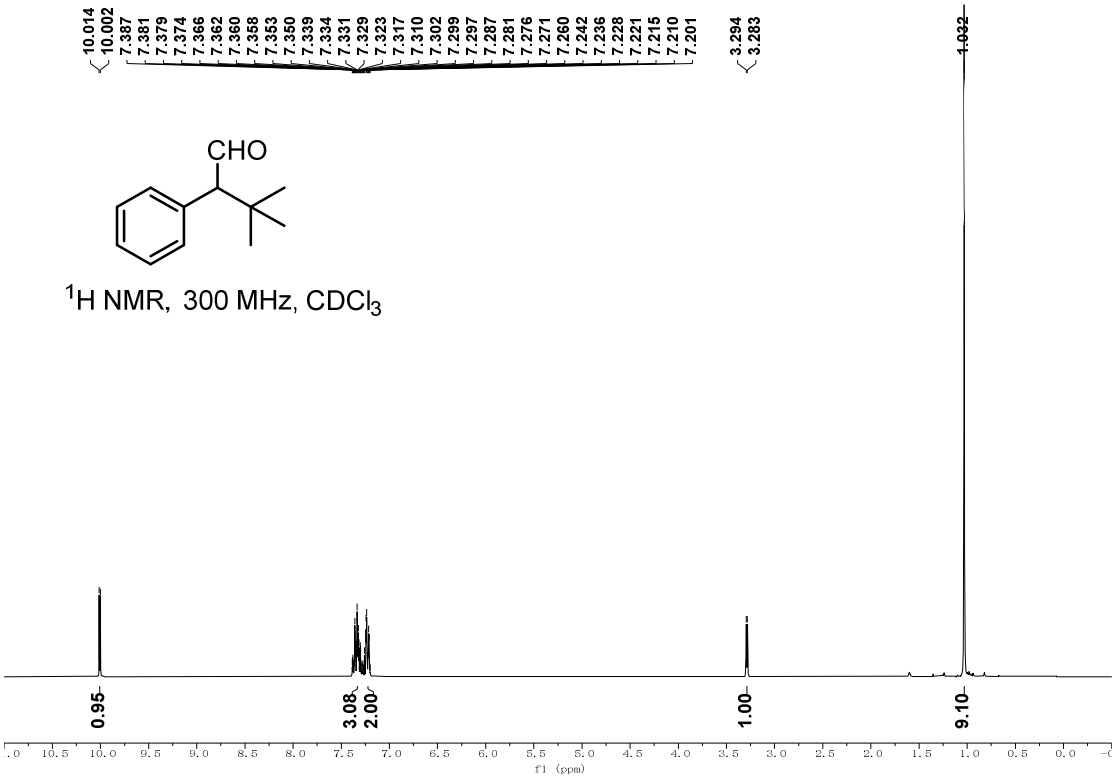
^{1}H NMR, 300 MHz, $CDCl_3$



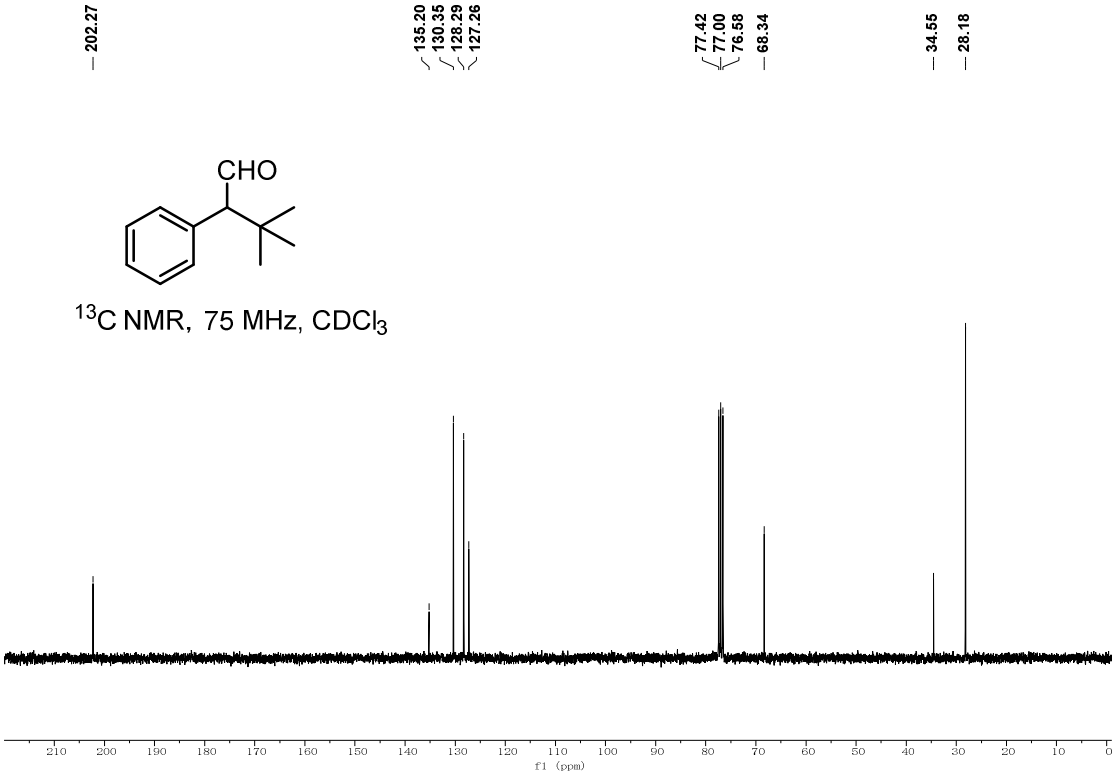


^{13}C NMR, 75 MHz, $CDCl_3$

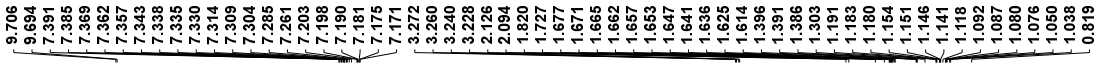


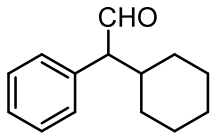


^{1}H NMR, 300 MHz, $CDCl_3$

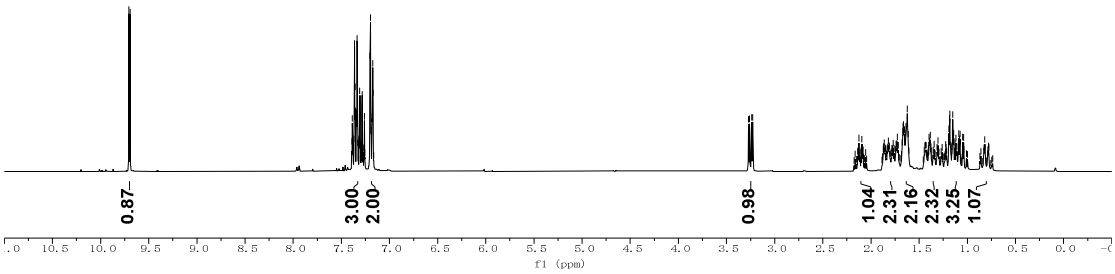


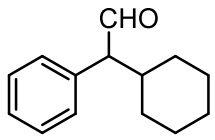
^{13}C NMR, 75 MHz, $CDCl_3$



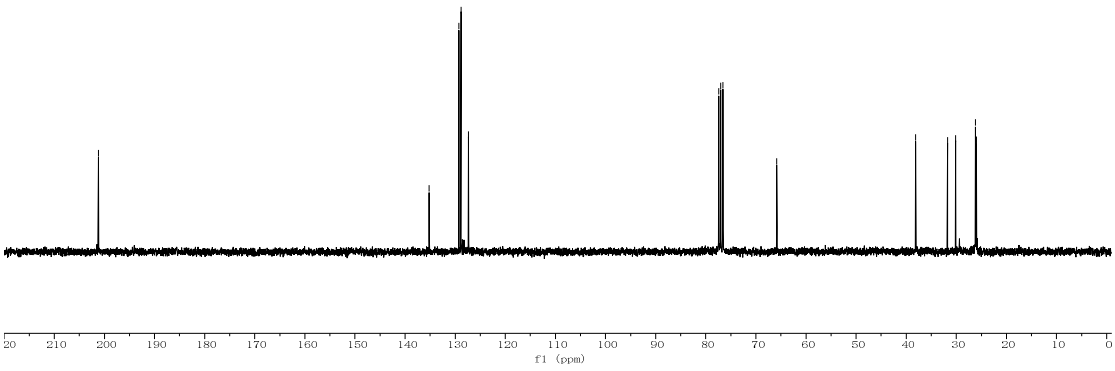


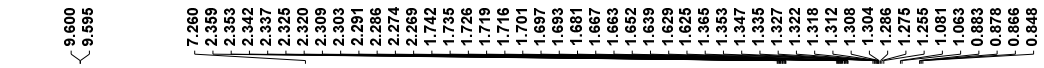
^{1}H NMR, 300 MHz, $CDCl_3$

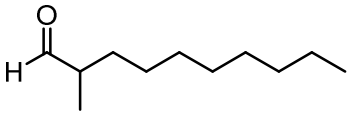




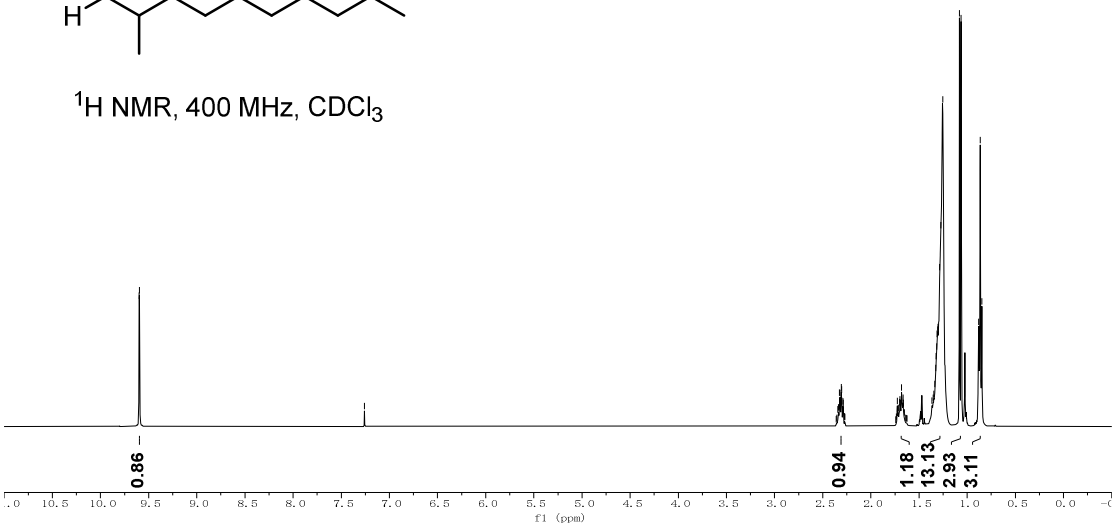
^{13}C NMR, 75 MHz, $CDCl_3$

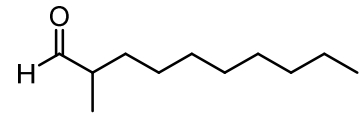




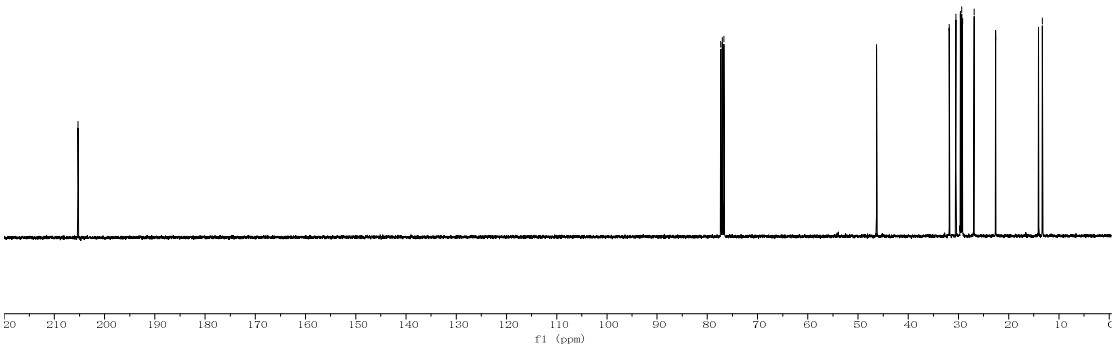


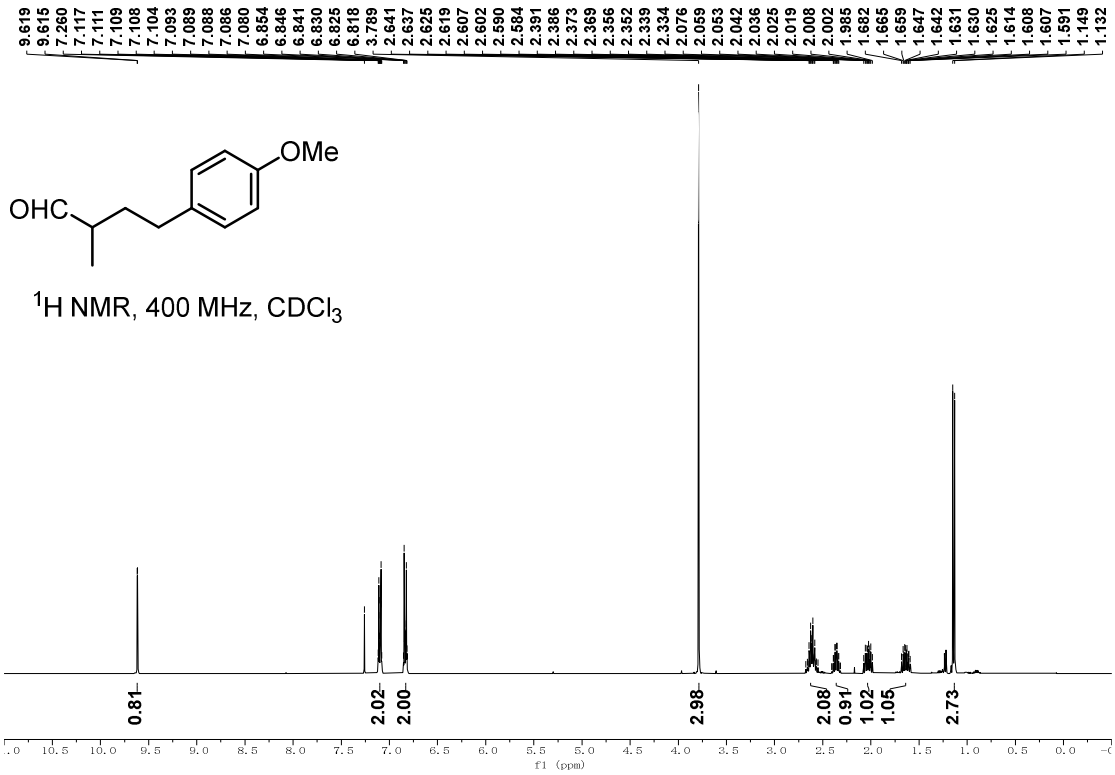
^{1}H NMR, 400 MHz, $CDCl_3$



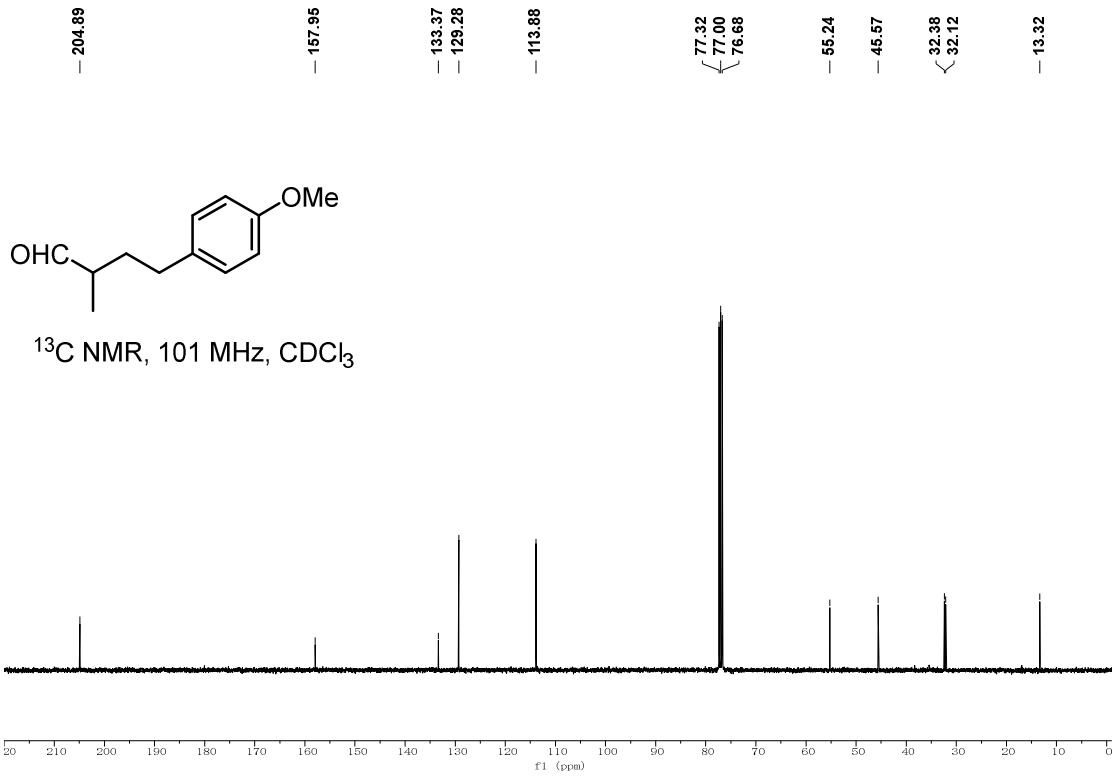


^{13}C NMR, 101 MHz, $CDCl_3$

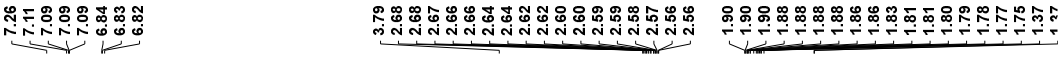


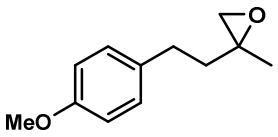


^{1}H NMR, 400 MHz, $CDCl_3$

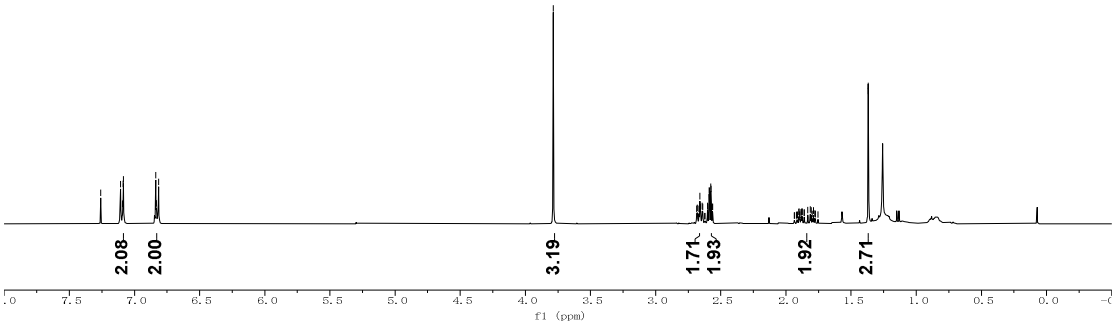


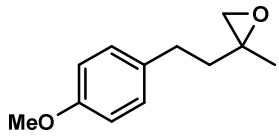
^{13}C NMR, 101 MHz, $CDCl_3$



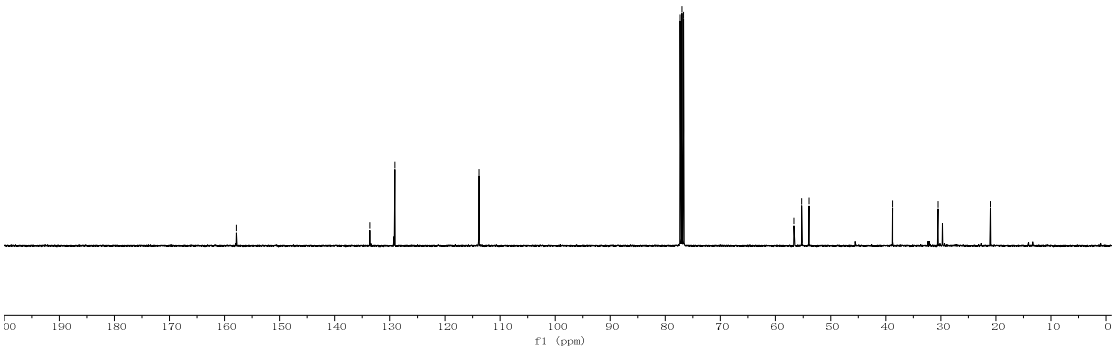


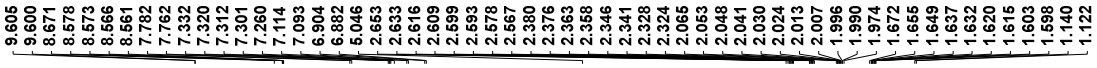
^{1}H NMR, 400 MHz, $CDCl_3$

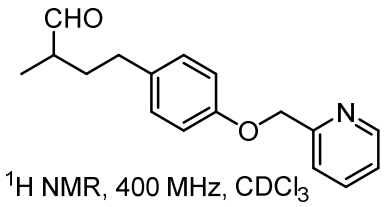




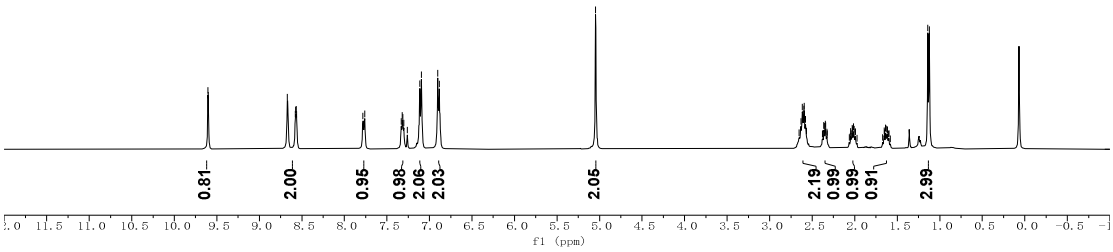
^{13}C NMR, 101 MHz, $CDCl_3$

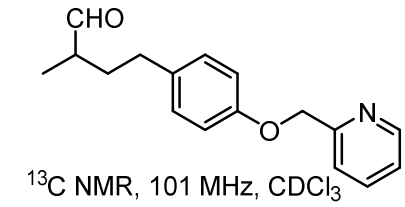




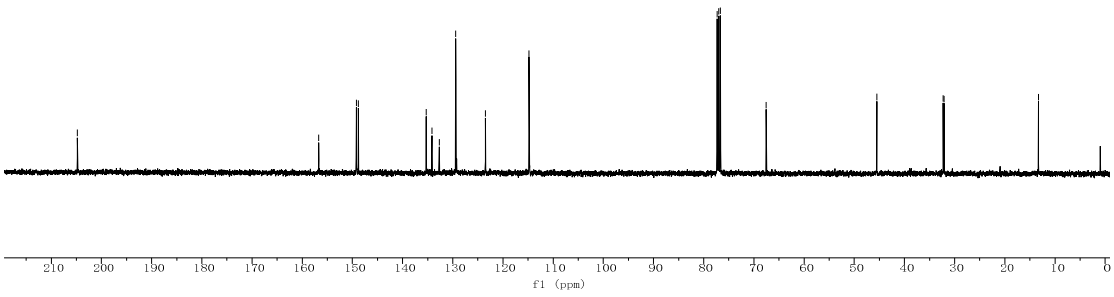


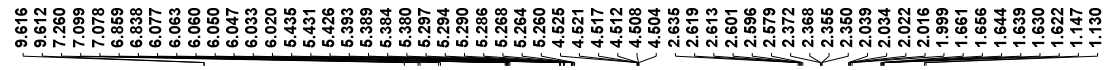
^{1}H NMR, 400 MHz, $CDCl_3$

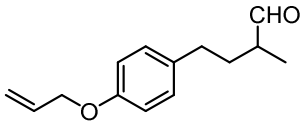




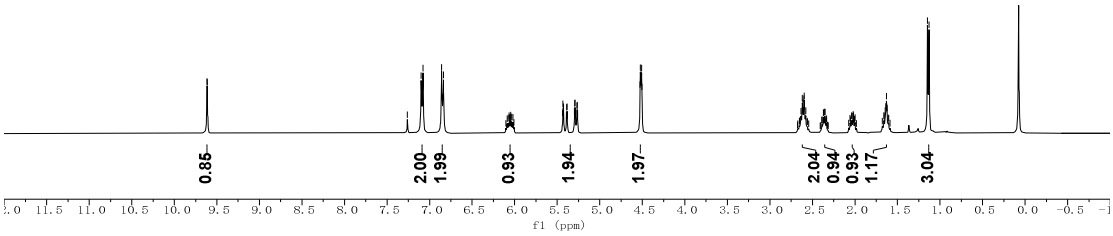
^{13}C NMR, 101 MHz, $CDCl_3$

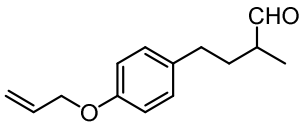




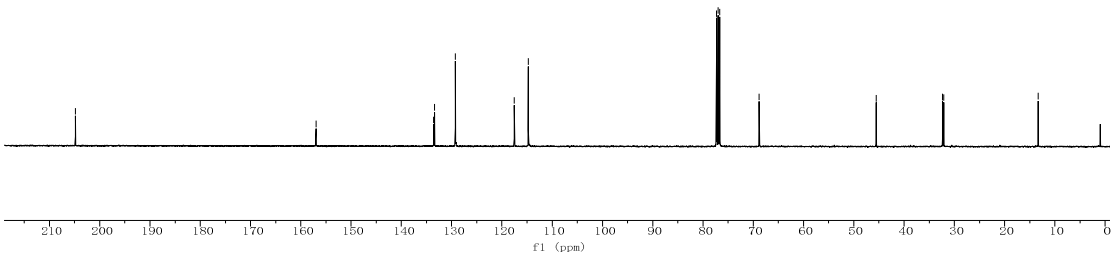


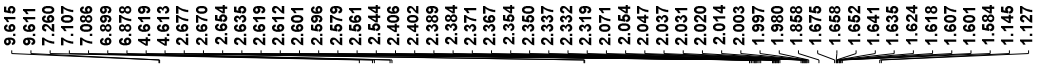
^{1}H NMR, 400 MHz, $CDCl_3$

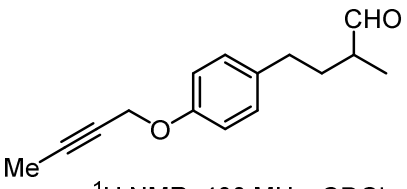




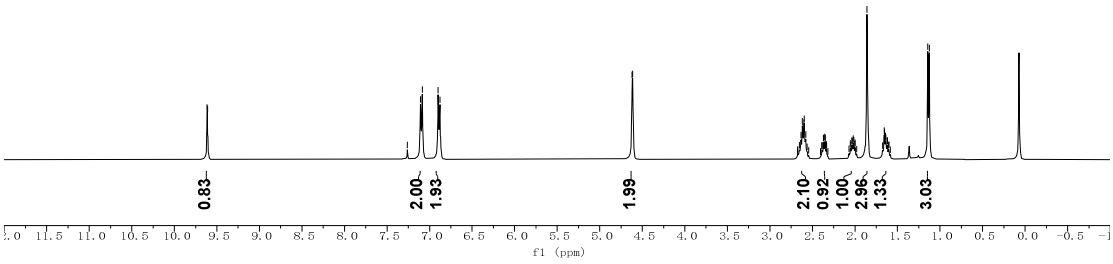
^{13}C NMR, 101 MHz, $CDCl_3$

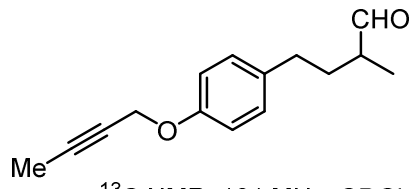




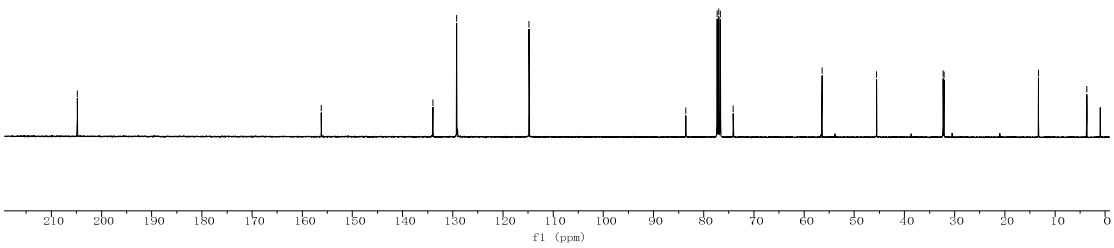


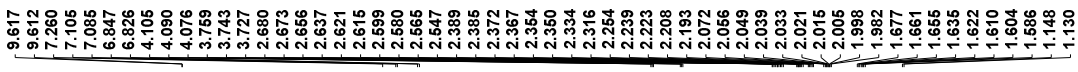
^{1}H NMR, 400 MHz, $CDCl_3$

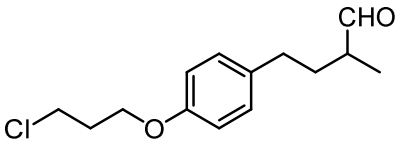




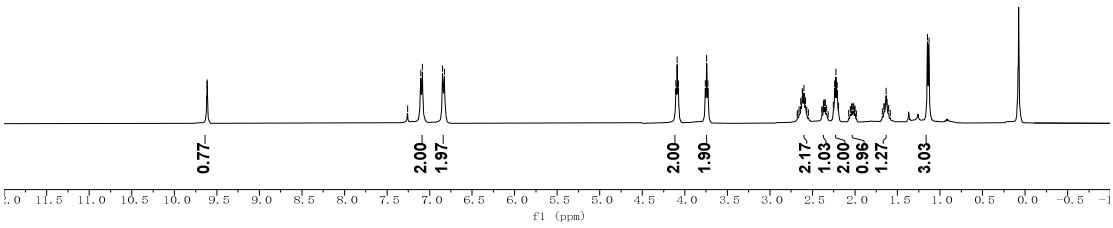
^{13}C NMR, 101 MHz, $CDCl_3$

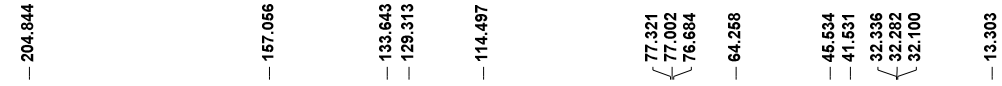


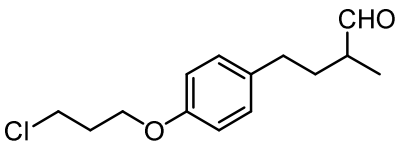




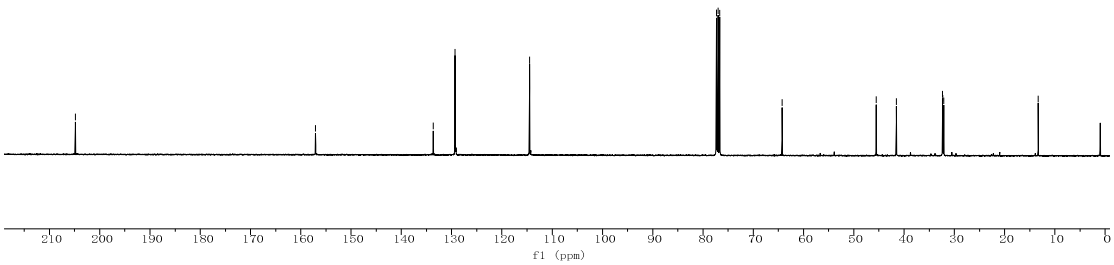
^{1}H NMR, 400 MHz, $CDCl_3$







^{13}C NMR, 101 MHz, $CDCl_3$



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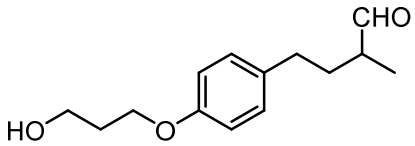
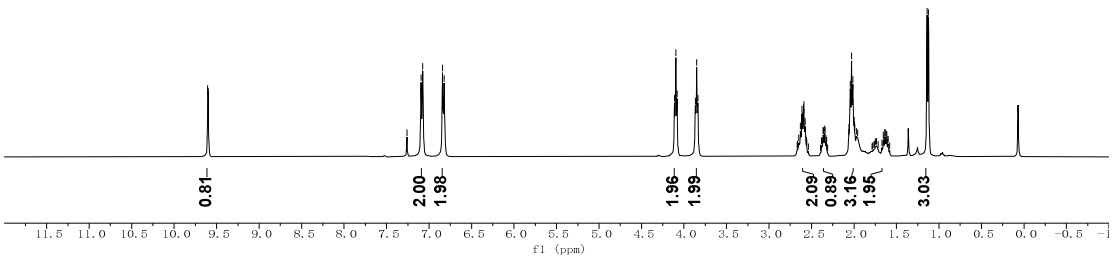


^{1}H NMR, 400 MHz, $CDCl_3$



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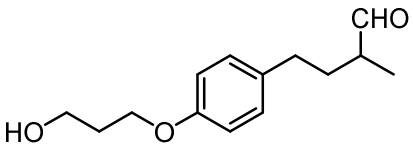
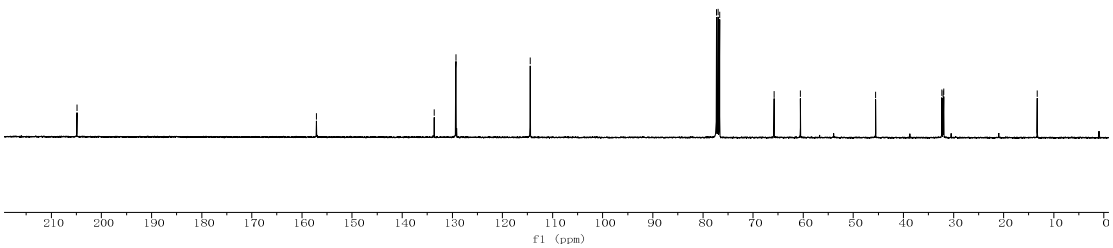
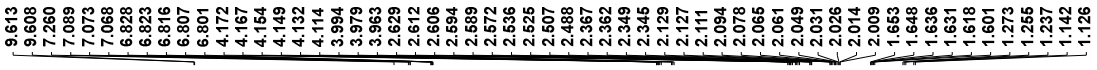
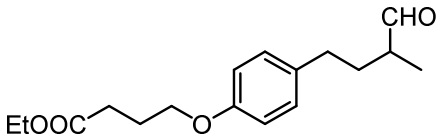


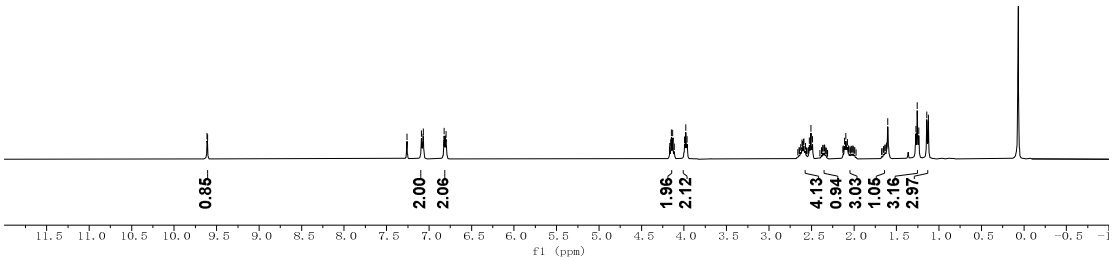
^{13}C NMR, 101 MHz, $CDCl_3$

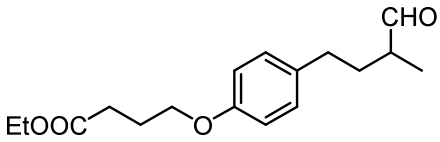




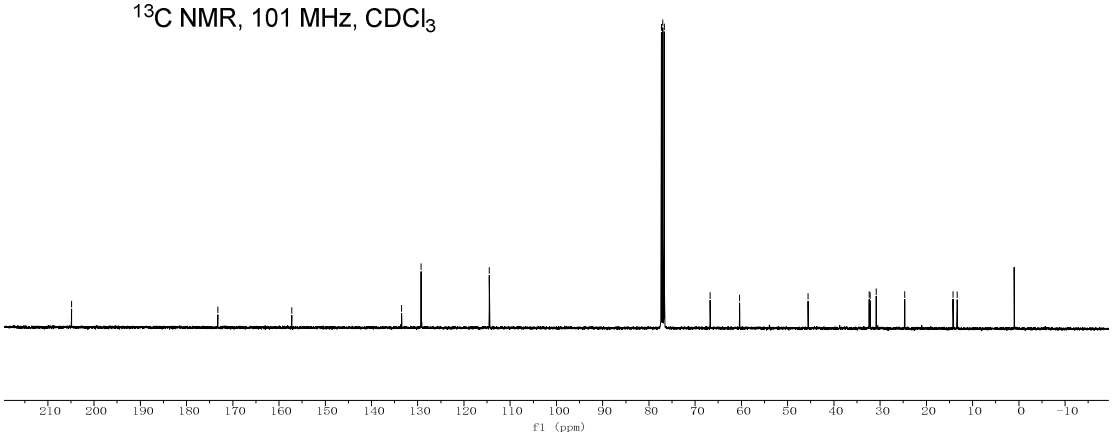


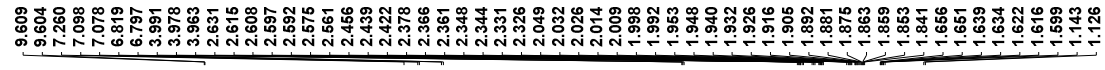
^{1}H NMR, 400 MHz, $CDCl_3$

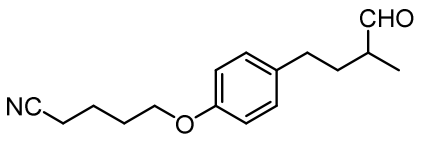




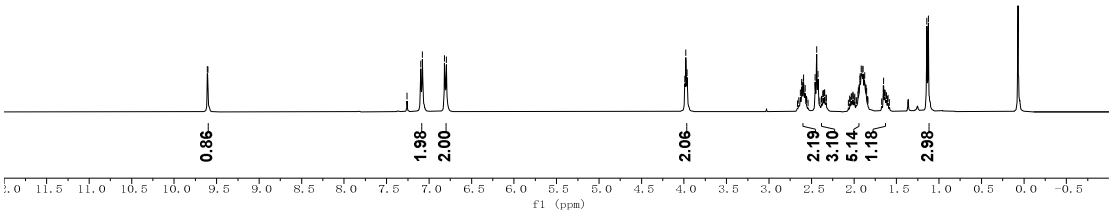
^{13}C NMR, 101 MHz, $CDCl_3$

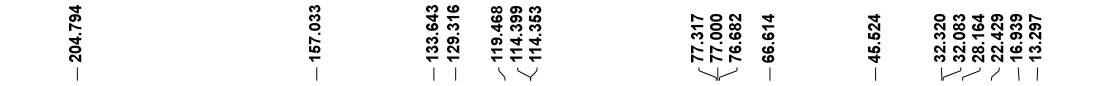


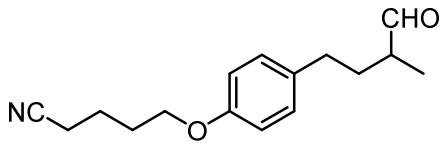




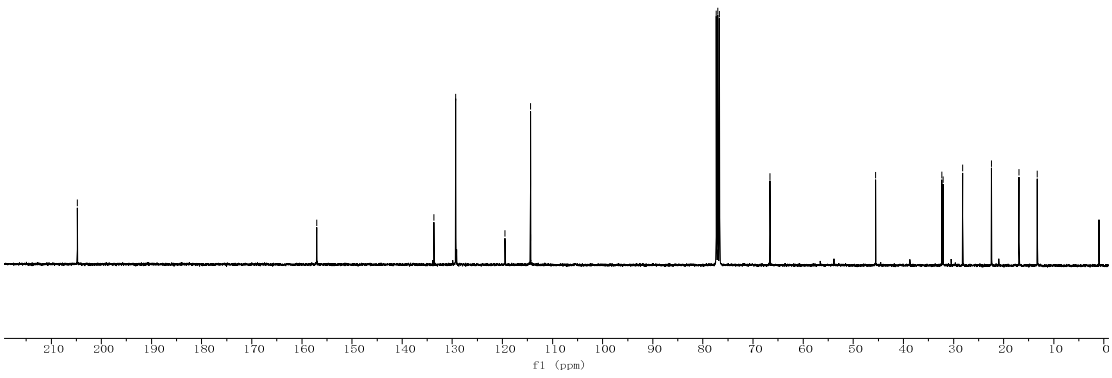
^{1}H NMR, 400MHz, $CDCl_3$

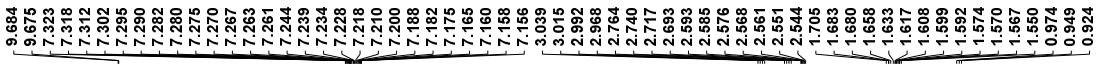


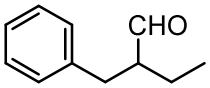




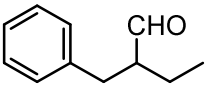
^{13}C, 101 MHz, NMR, $CDCl_3$



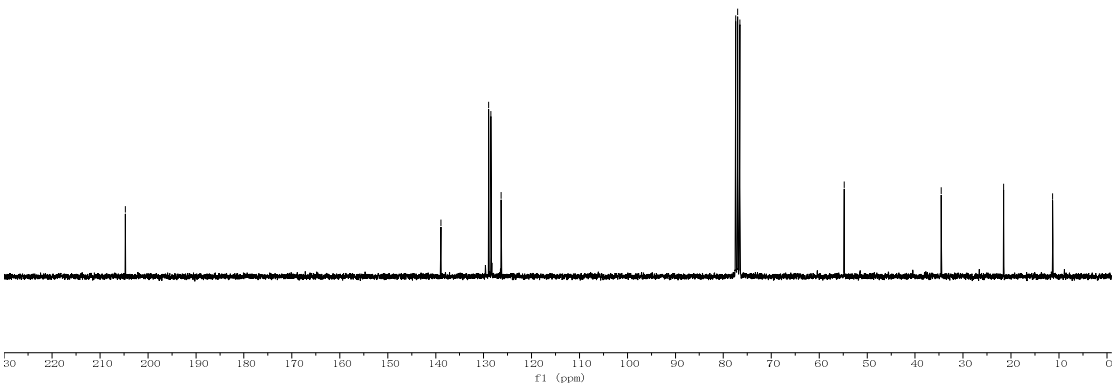


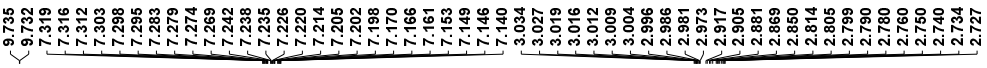


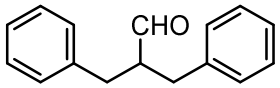
^{1}H NMR, 300 MHz, $CDCl_3$



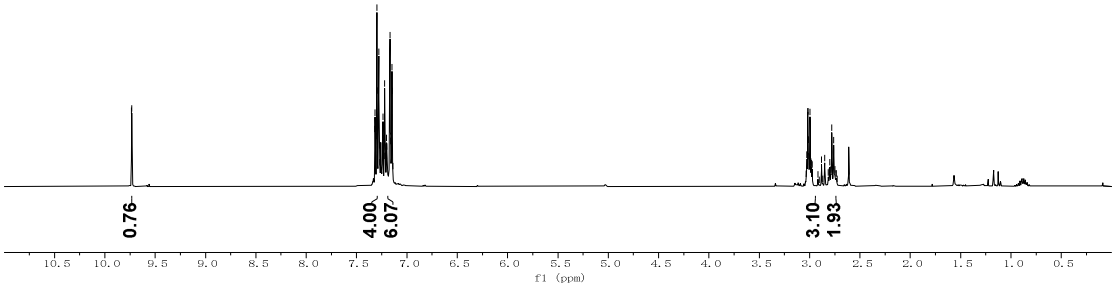
^{13}C NMR, 75 MHz, $CDCl_3$

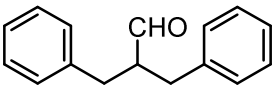




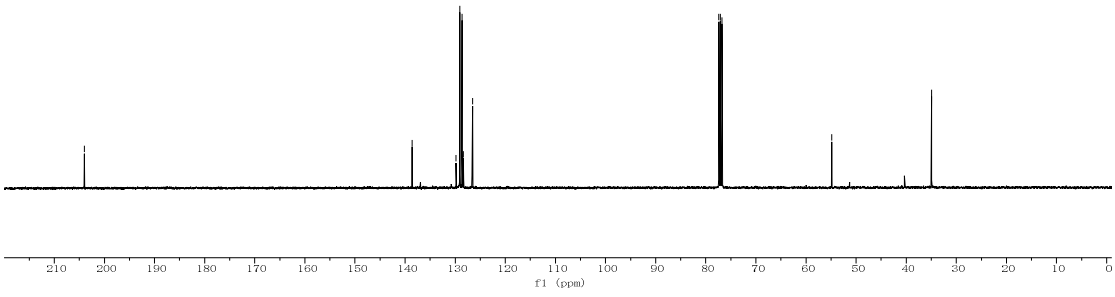


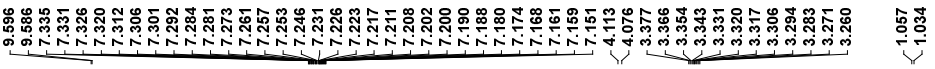
^{1}H NMR, 400 MHz, $CDCl_3$

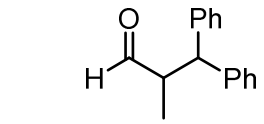




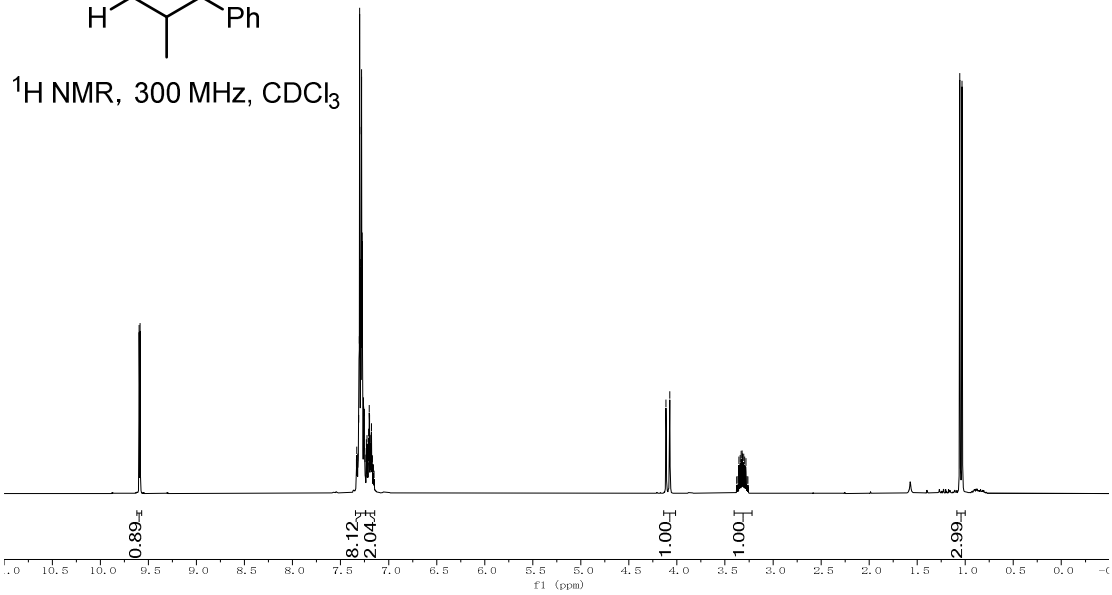
^{13}C NMR, 101 MHz, $CDCl_3$

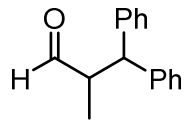




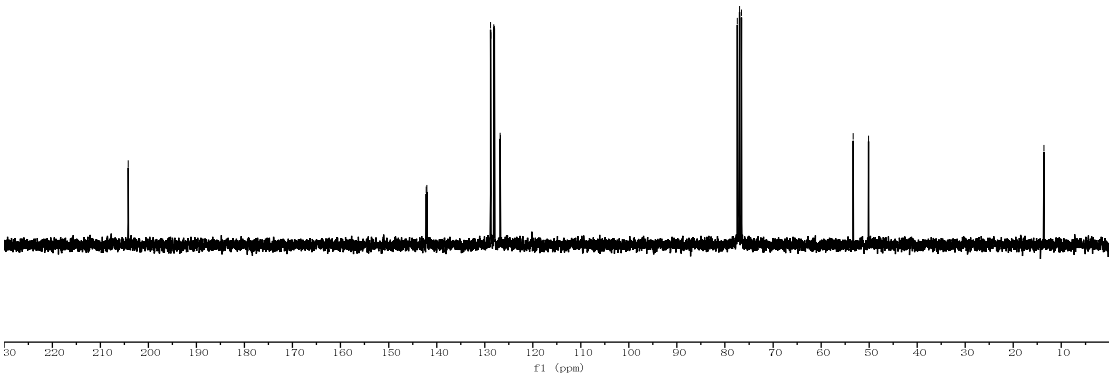


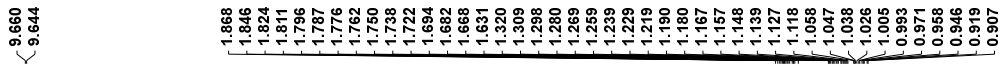
^{1}H NMR, 300 MHz, $CDCl_3$

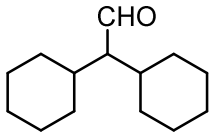




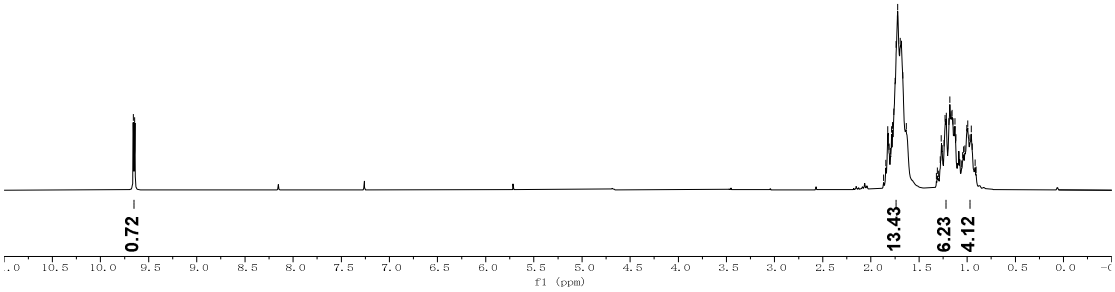
^{13}C NMR, 75 MHz, $CDCl_3$

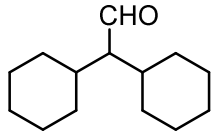




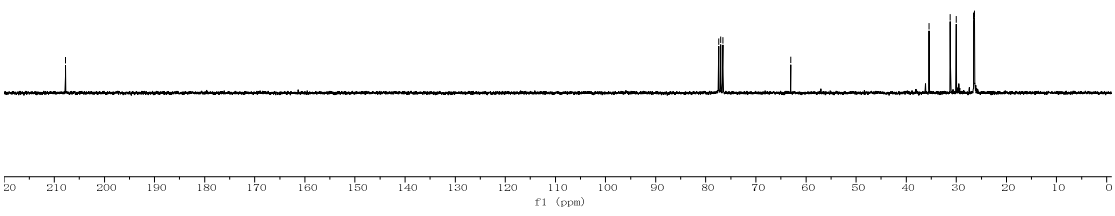


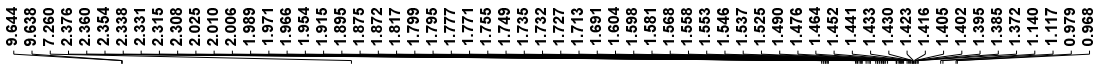
^{1}H NMR, 300 MHz, $CDCl_3$

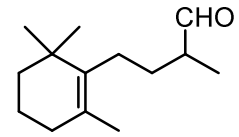




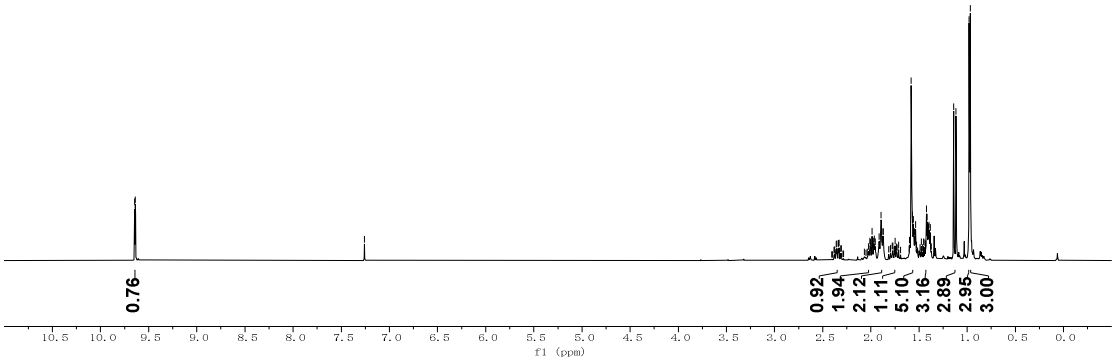
^{13}C NMR, 75 MHz, $CDCl_3$

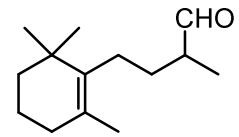




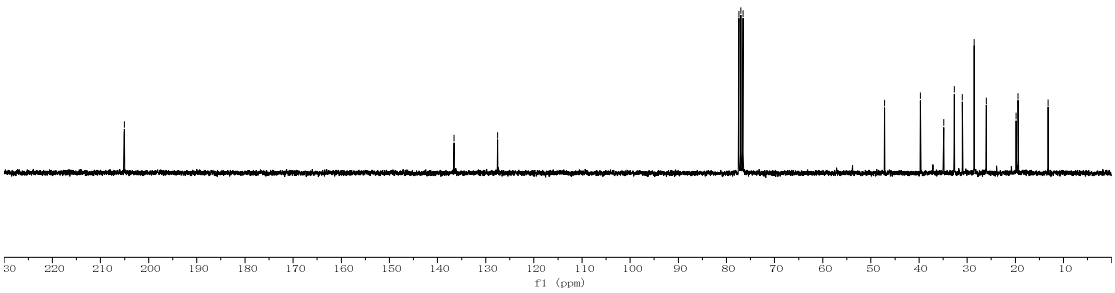


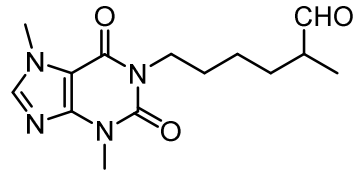
^{1}H NMR, 300 MHz, $CDCl_3$



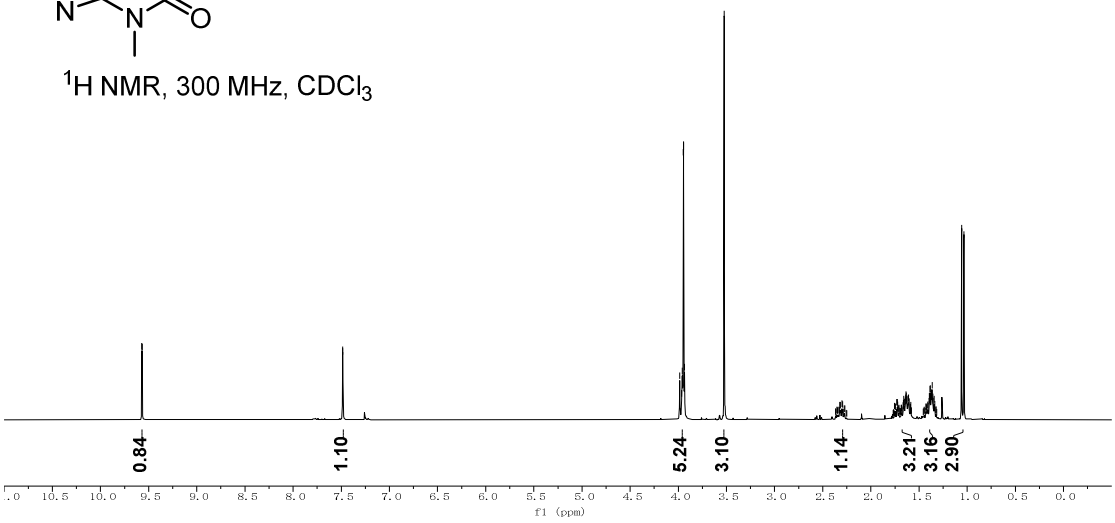


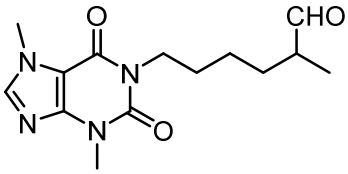
^{13}C NMR, 75 MHz, $CDCl_3$



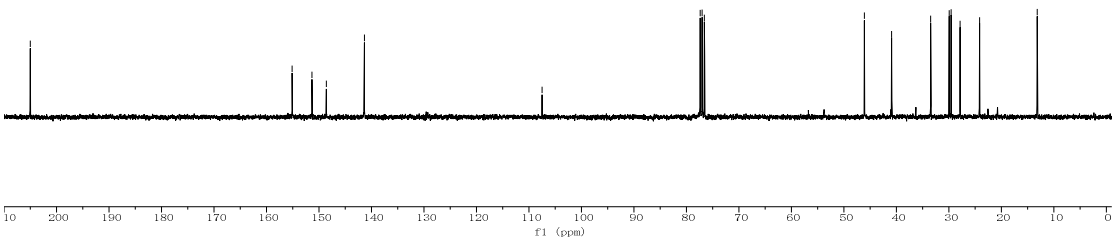


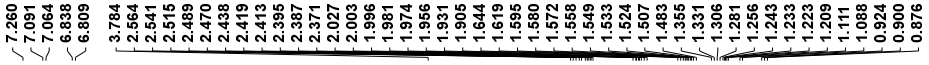
^{1}H NMR, 300 MHz, $CDCl_3$

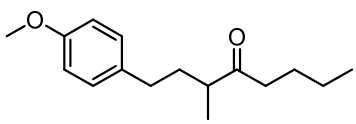




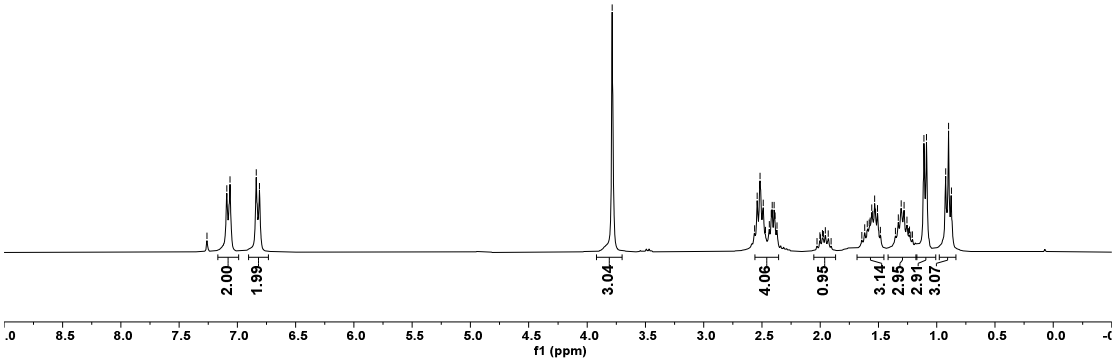
^{13}C NMR, 75 MHz, $CDCl_3$

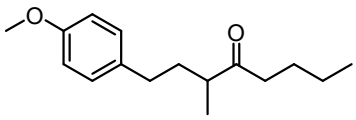




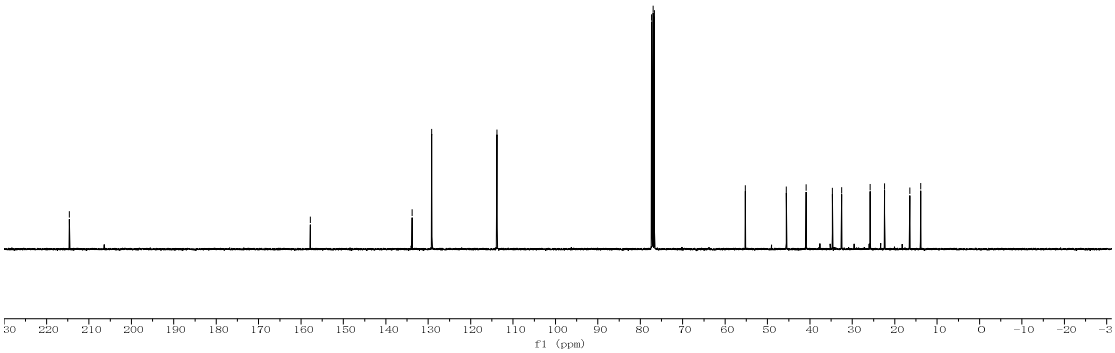


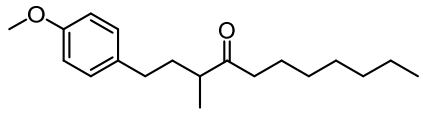
^{1}H NMR, 300 MHz, $CDCl_3$



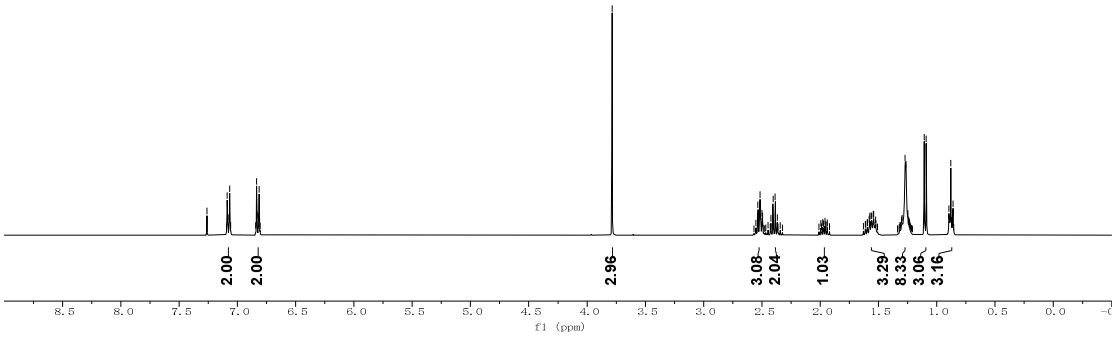


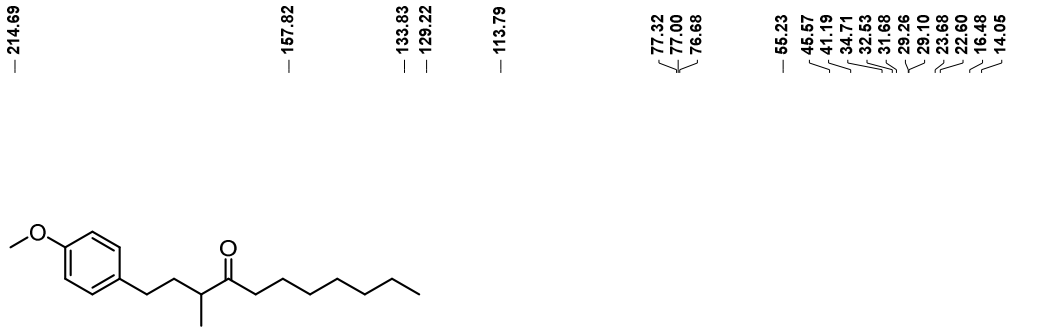
^{13}C NMR, 75 MHz, $CDCl_3$



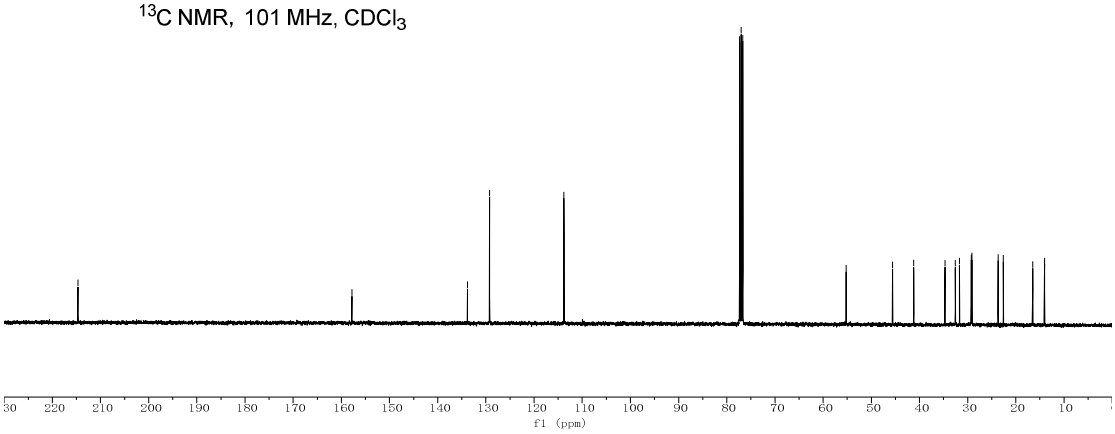


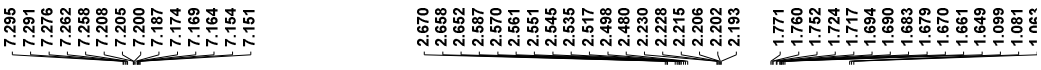
^{1}H NMR, 400 MHz, $CDCl_3$

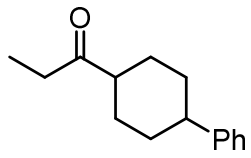




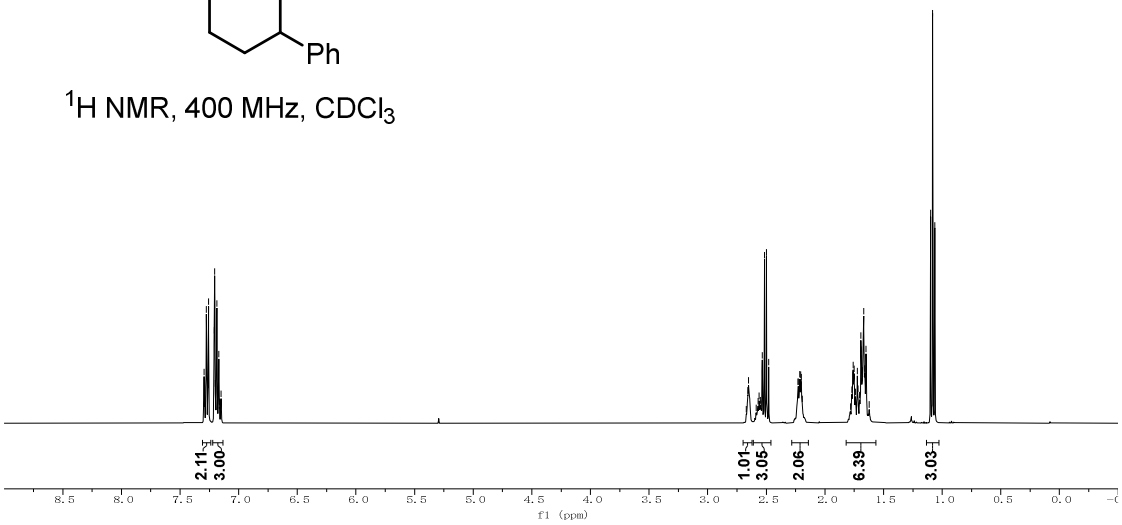
^{13}C NMR, 101 MHz, $CDCl_3$

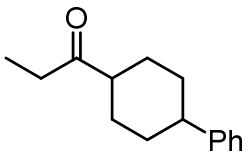




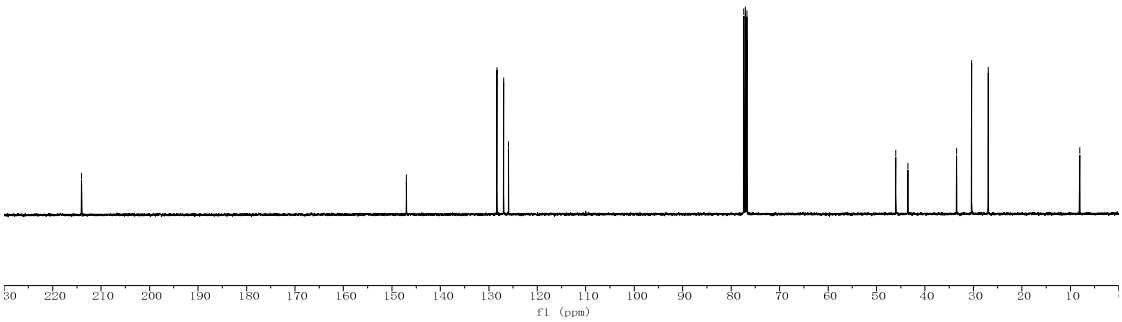


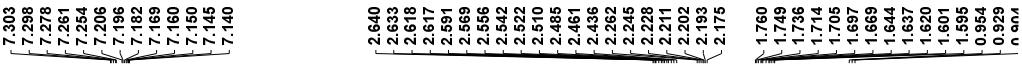
^{1}H NMR, 400 MHz, $CDCl_3$

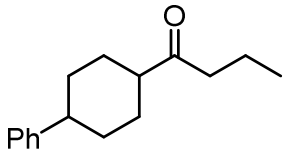




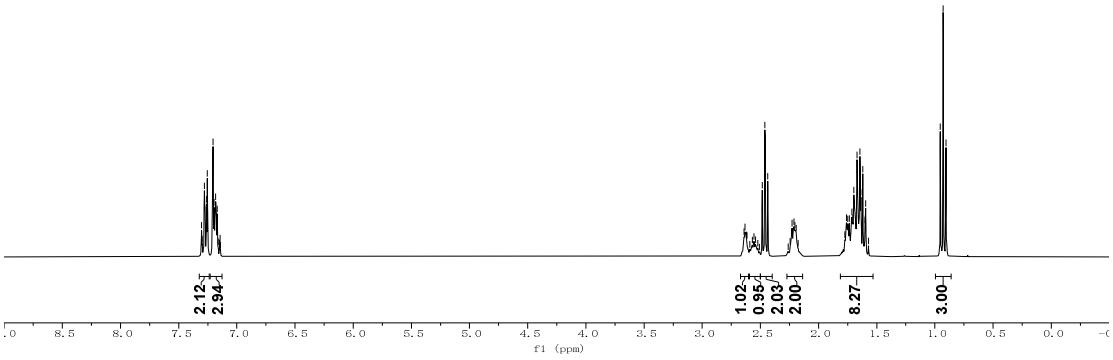
^{13}C NMR, 101 MHz, $CDCl_3$

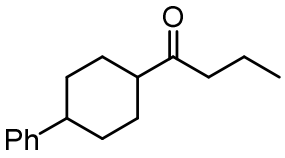




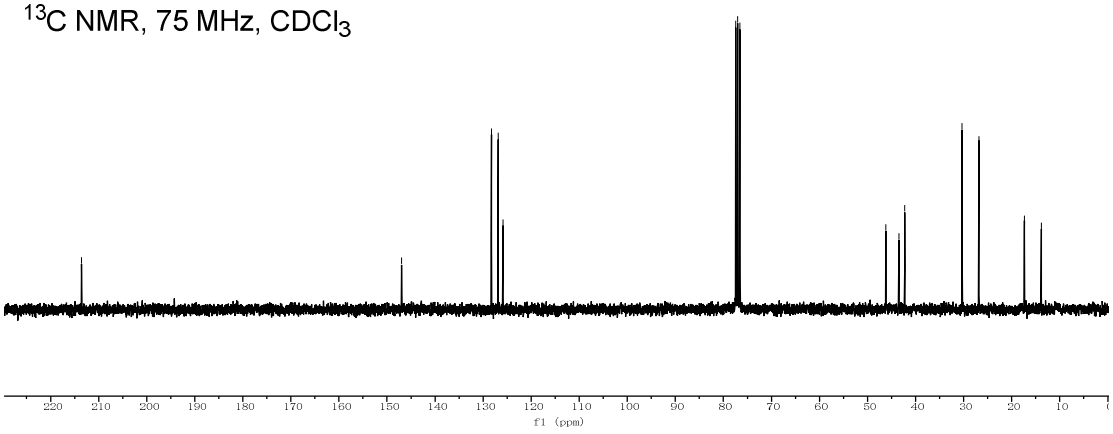


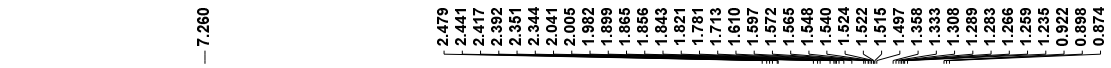
^{1}H NMR, 300 MHz, $CDCl_3$

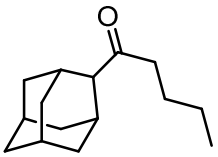




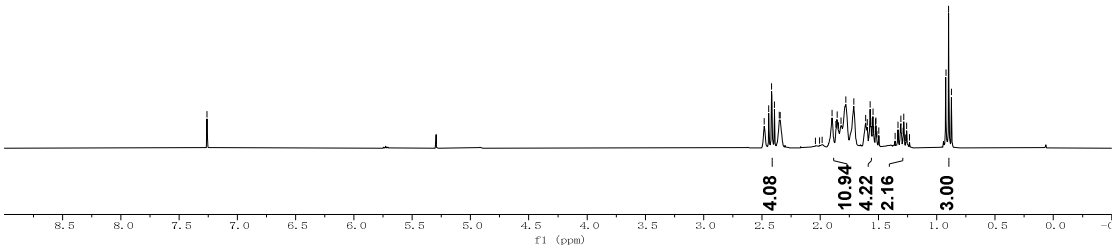
^{13}C NMR, 75 MHz, $CDCl_3$

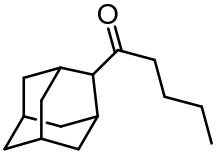




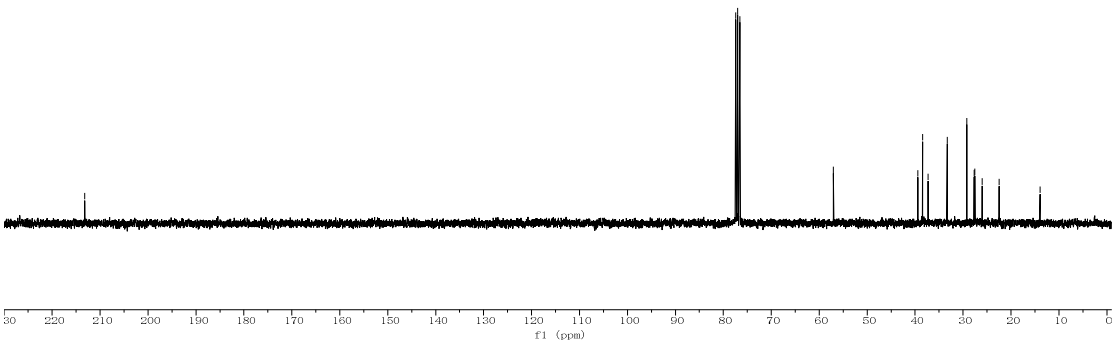


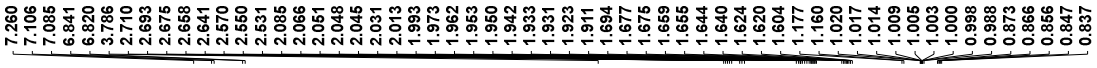
^{1}H NMR, 300 MHz, $CDCl_3$

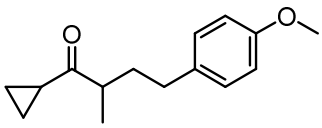




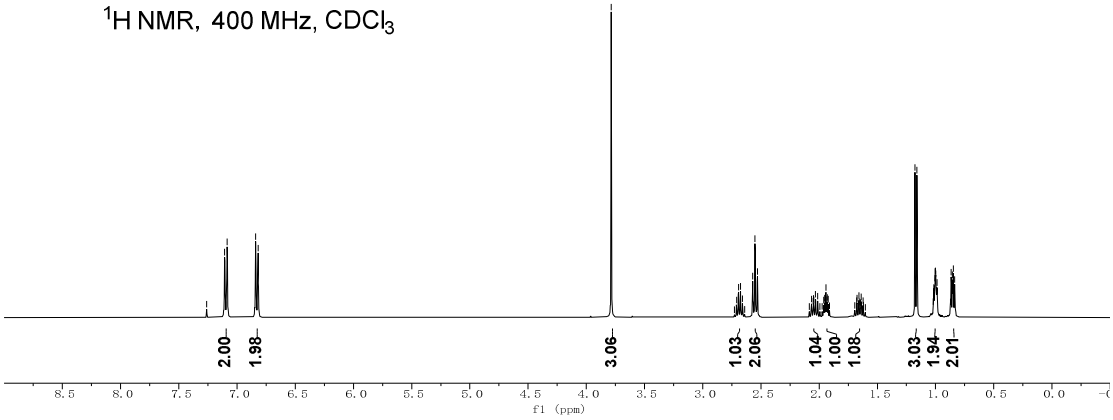
^{13}C NMR, 75 MHz, $CDCl_3$

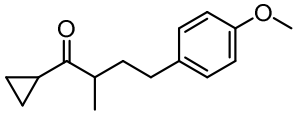




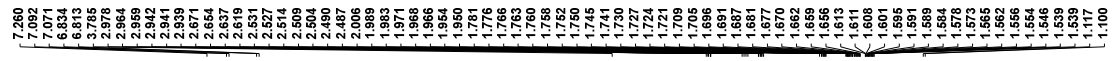


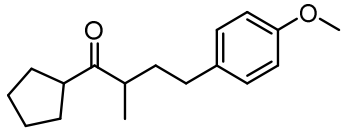
^{1}H NMR, 400 MHz, $CDCl_3$



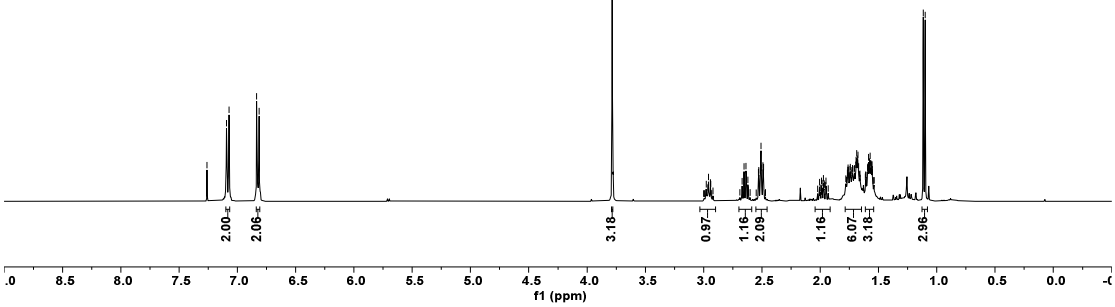


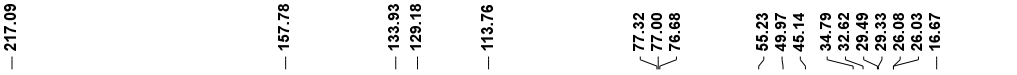
^{13}C NMR, 101 MHz, $CDCl_3$

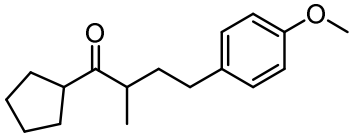




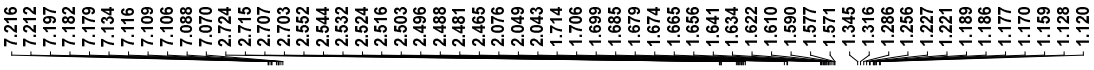
^{1}H NMR, 400 MHz, $CDCl_3$

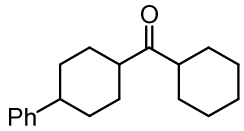




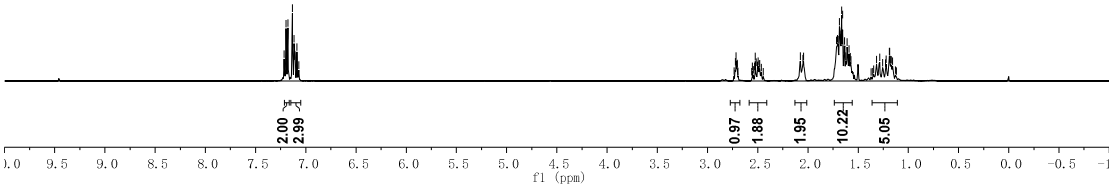


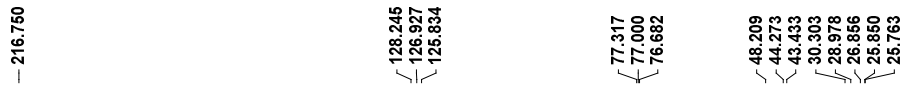
^{13}C NMR, 101 MHz, $CDCl_3$

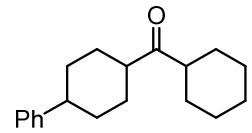




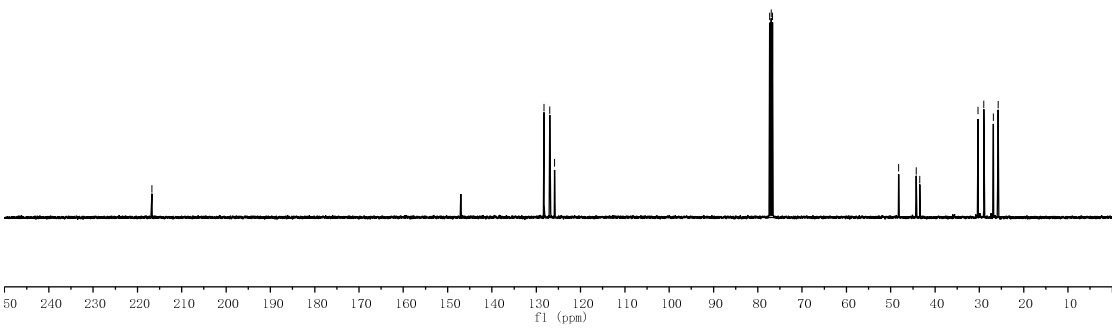
^{1}H NMR, 400 MHz, $CDCl_3$

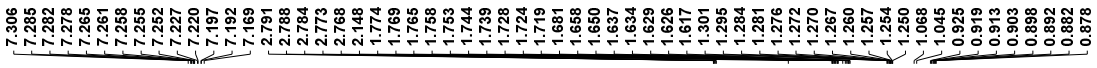


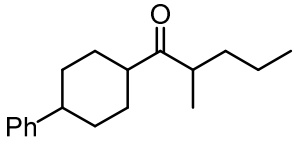




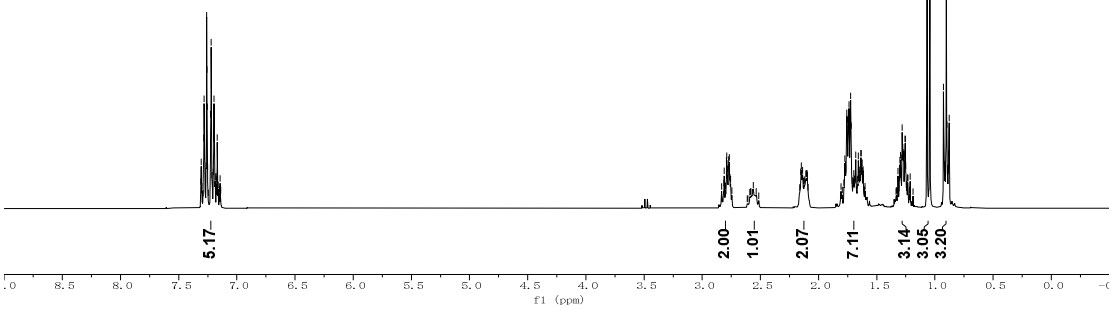
^{13}C NMR, 101 MHz, $CDCl_3$

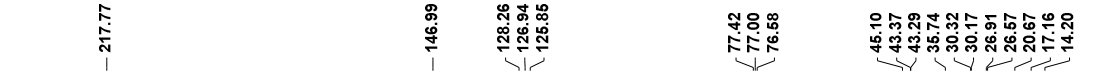


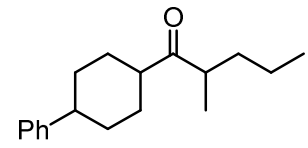




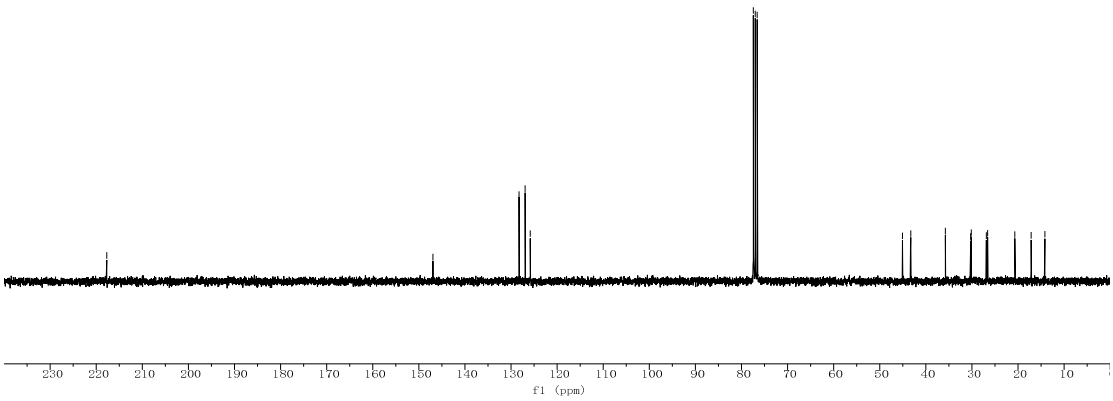
^{1}H NMR, 300 MHz, $CDCl_3$

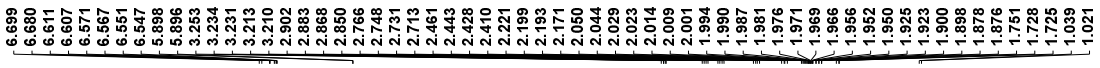


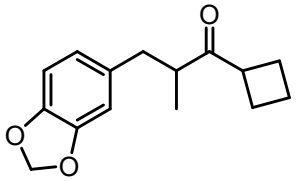




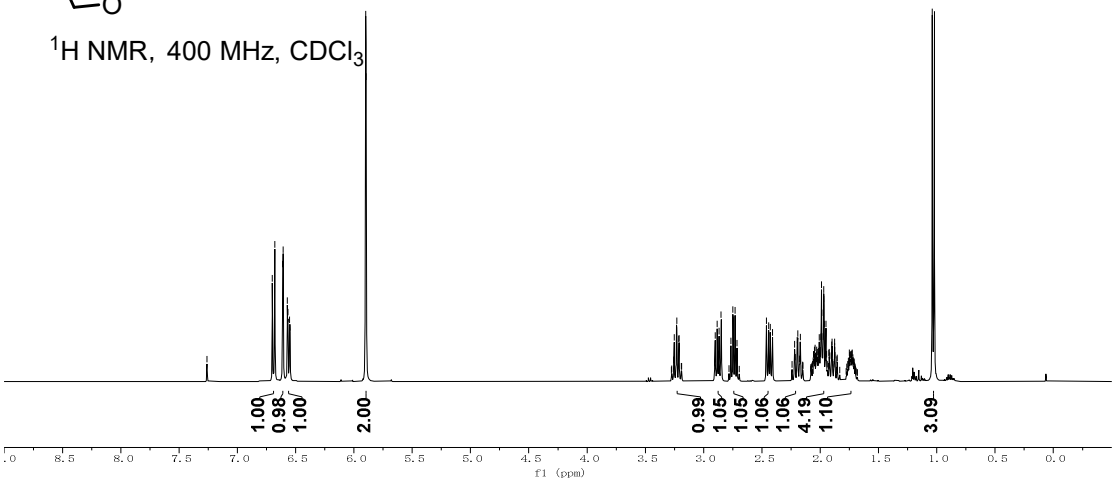
^{1}H NMR, 75 MHz, $CDCl_3$

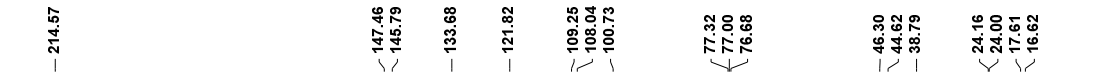


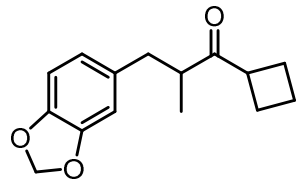




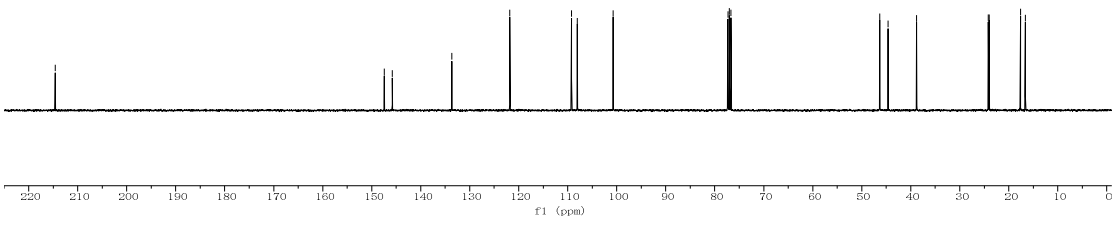
^{1}H NMR, 400 MHz, $CDCl_3$

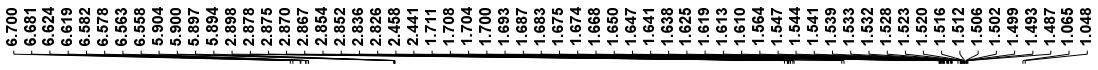


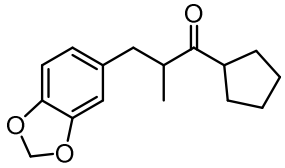




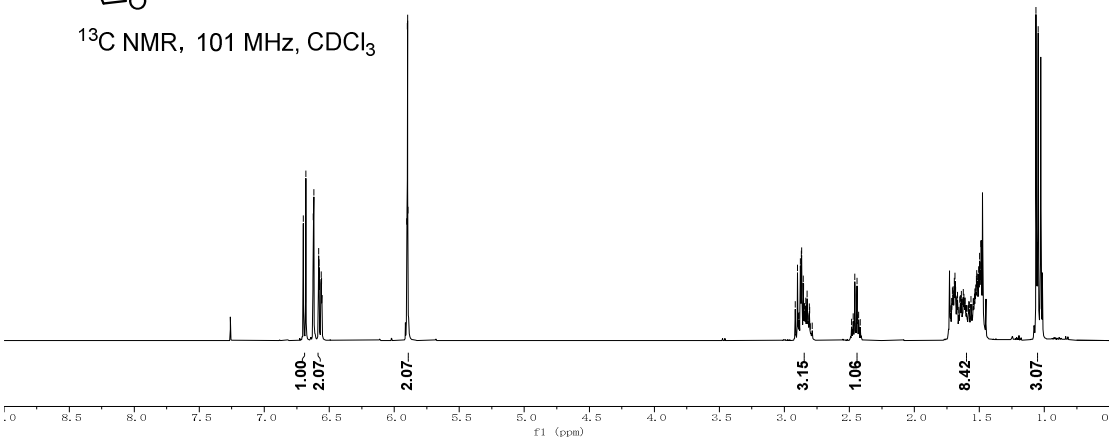
^{13}H NMR, 101 MHz, $CDCl_3$

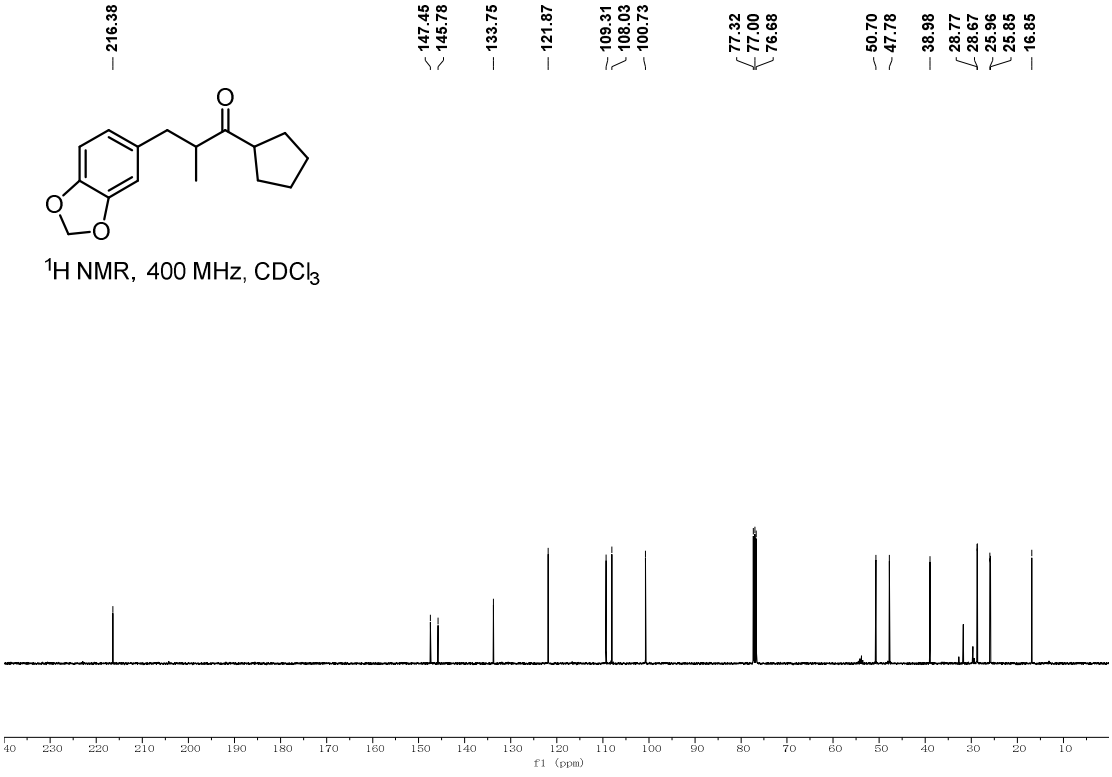




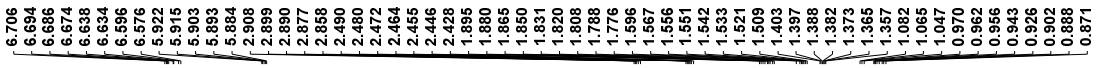


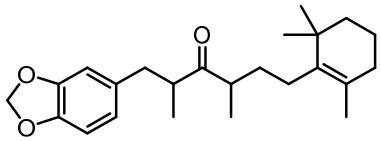
^{13}C NMR, 101 MHz, $CDCl_3$



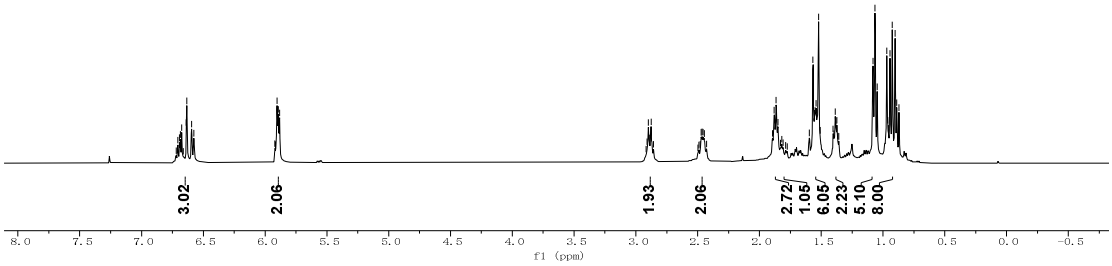


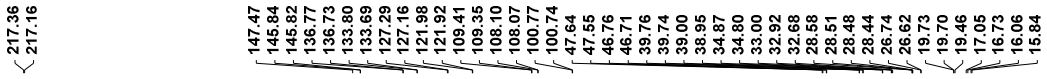
^{1}H NMR, 400 MHz, $CDCl_3$

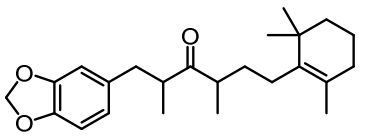




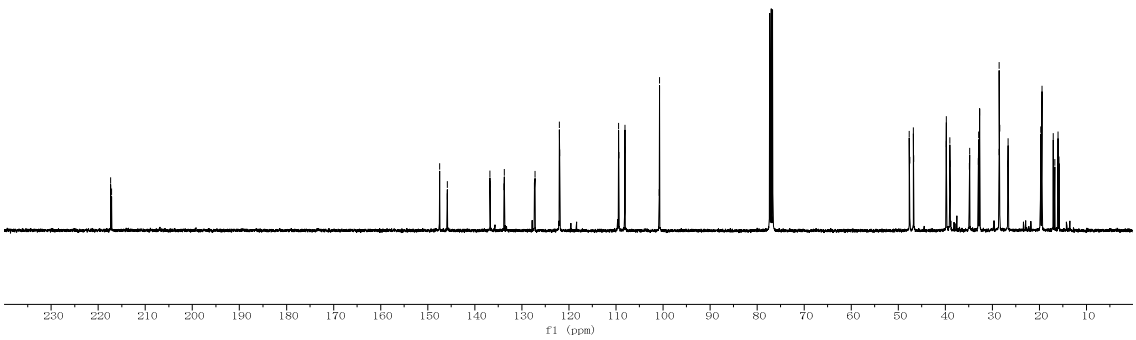
^{1}H NMR, 400 MHz, $CDCl_3$

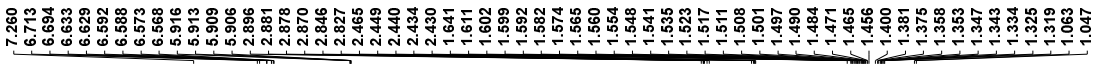


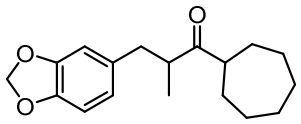




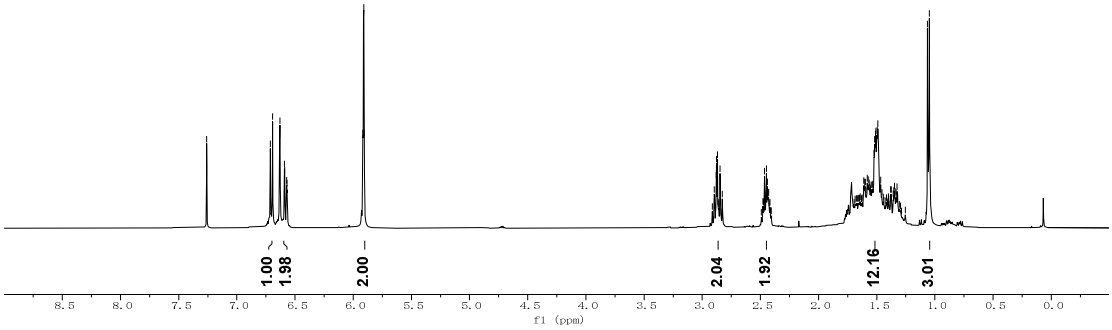
^{13}C NMR, 101 MHz, $CDCl_3$

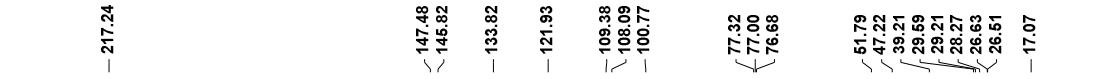


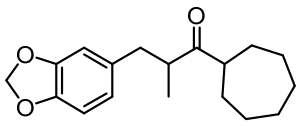




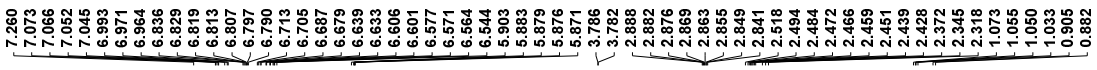
^{1}H NMR, 400 MHz, $CDCl_3$

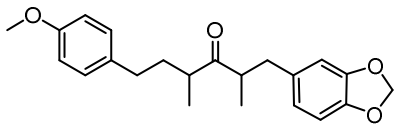




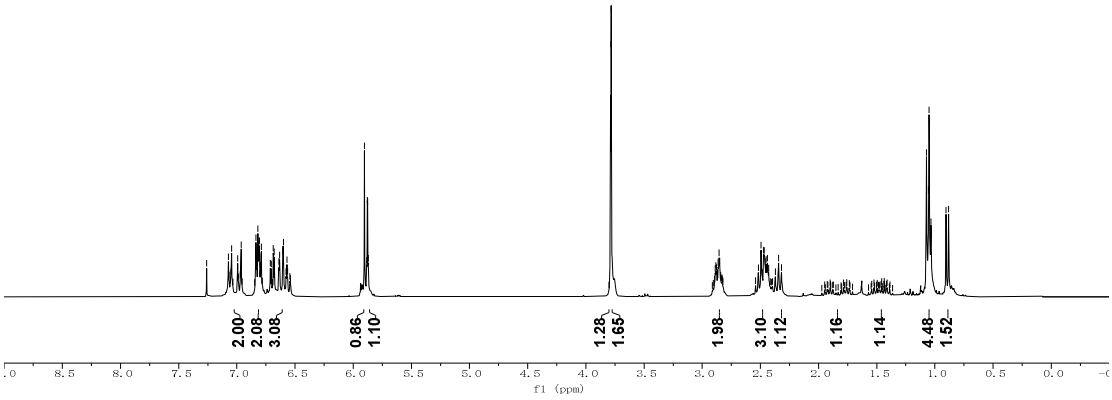


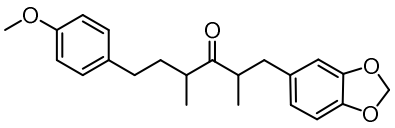
^{13}C NMR, 101 MHz, $CDCl_3$



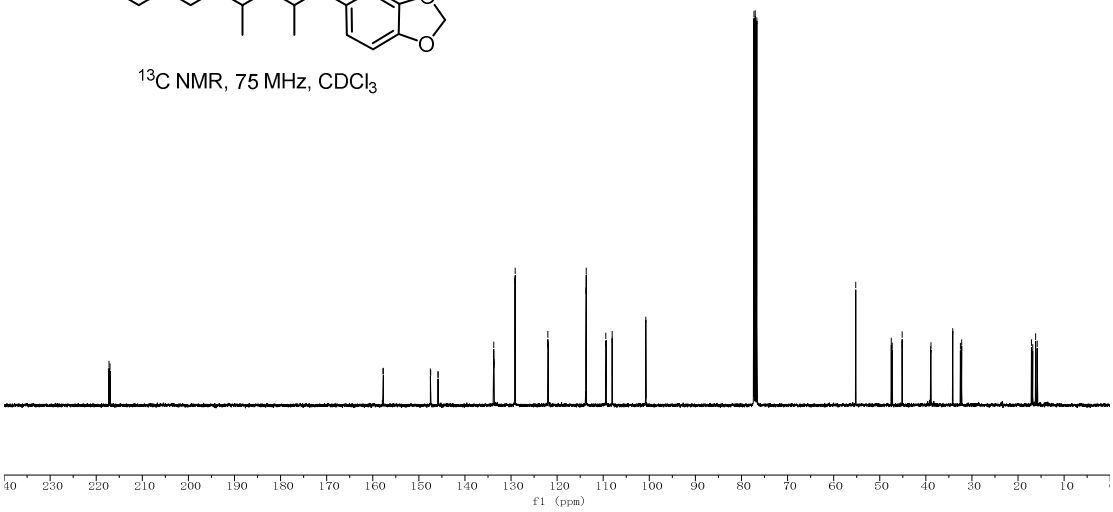


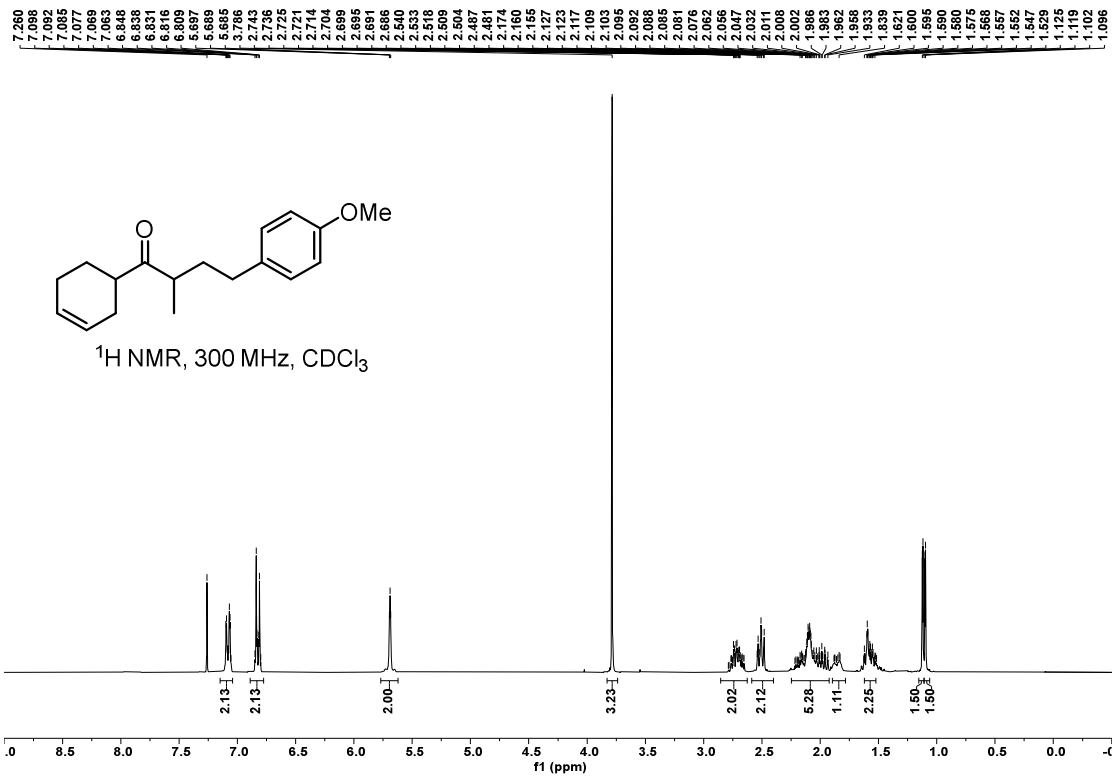
^{1}H NMR, 300 MHz, $CDCl_3$

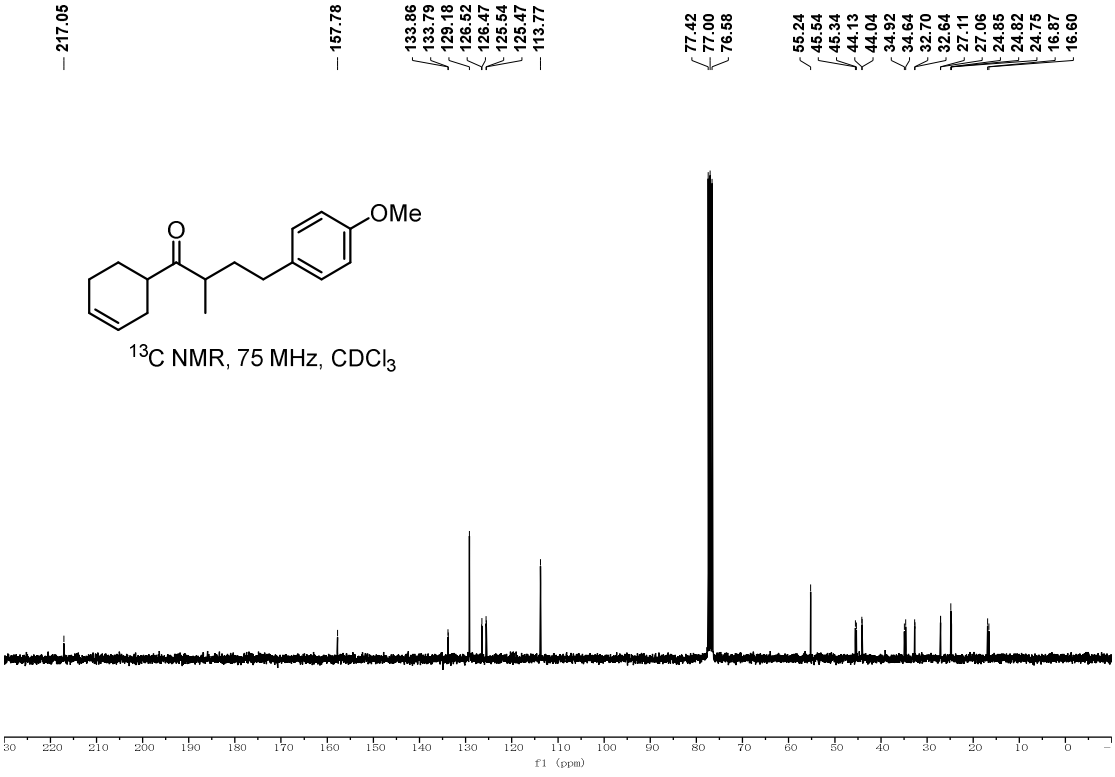


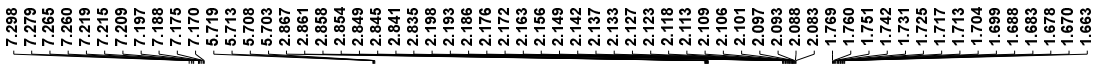


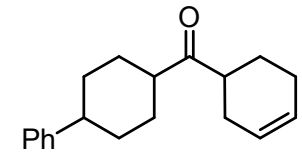
^{13}C NMR, 75 MHz, $CDCl_3$



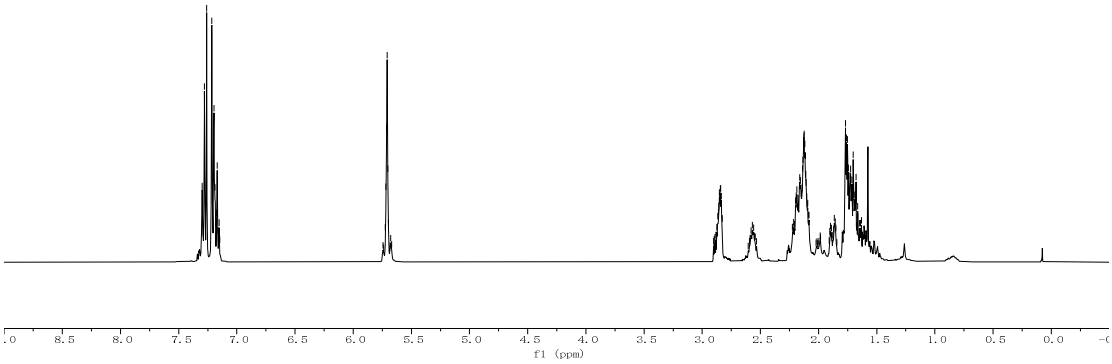

OMe
O
1H NMR, 300 MHz, CDCl3
f1 (ppm)

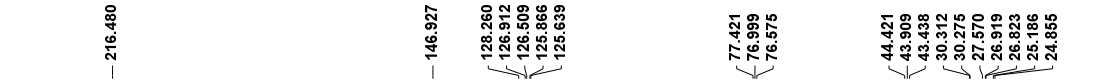

OMe
O
13C NMR, 75 MHz, CDCl3
f1 (ppm)

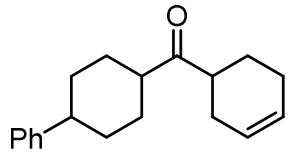




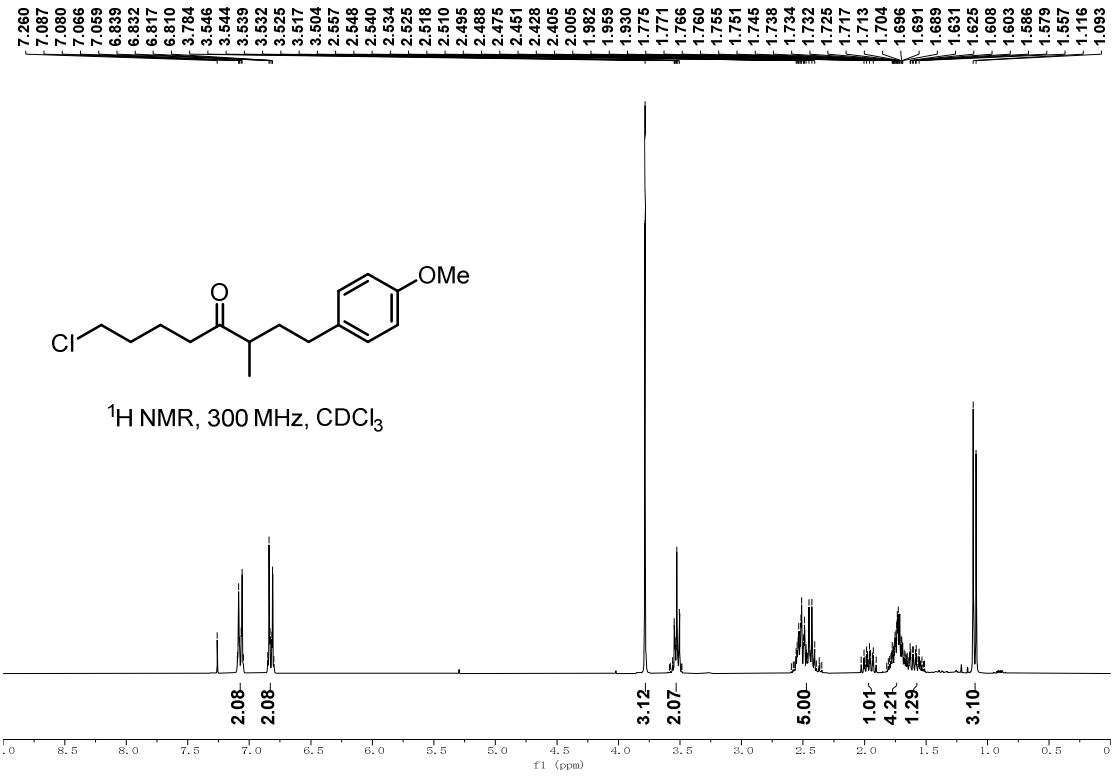
^{1}H NMR, 400 MHz, $CDCl_3$







^{13}C NMR, 101 MHz, $CDCl_3$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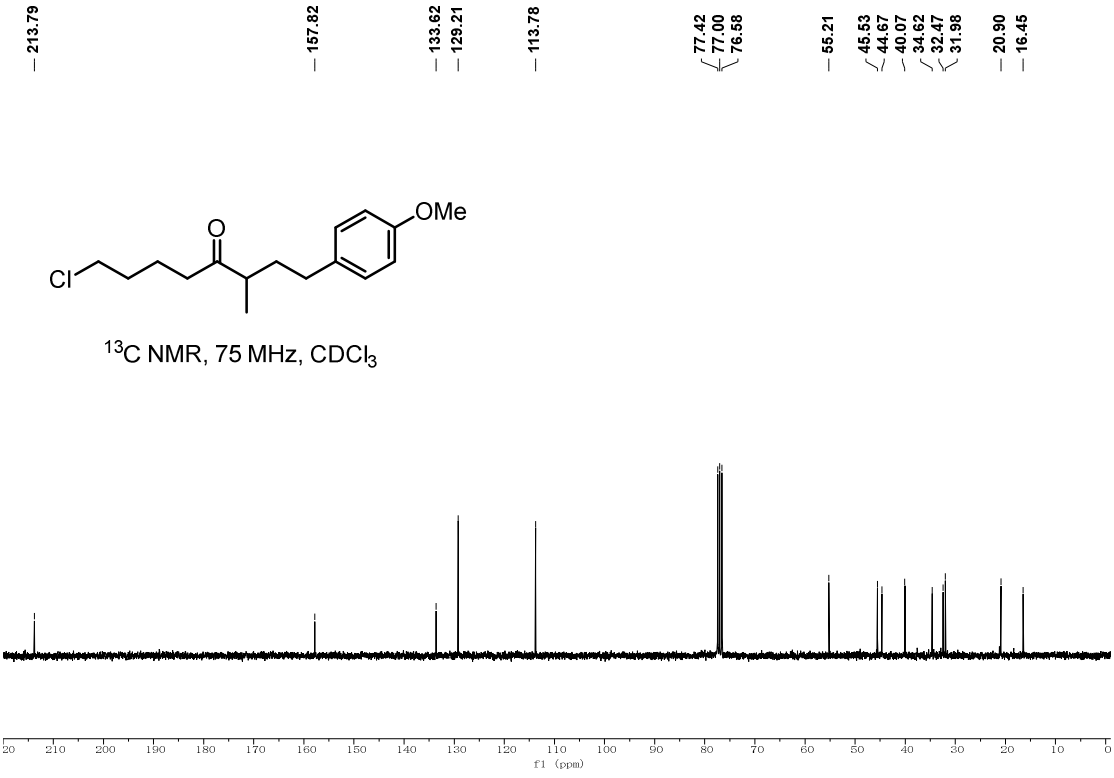
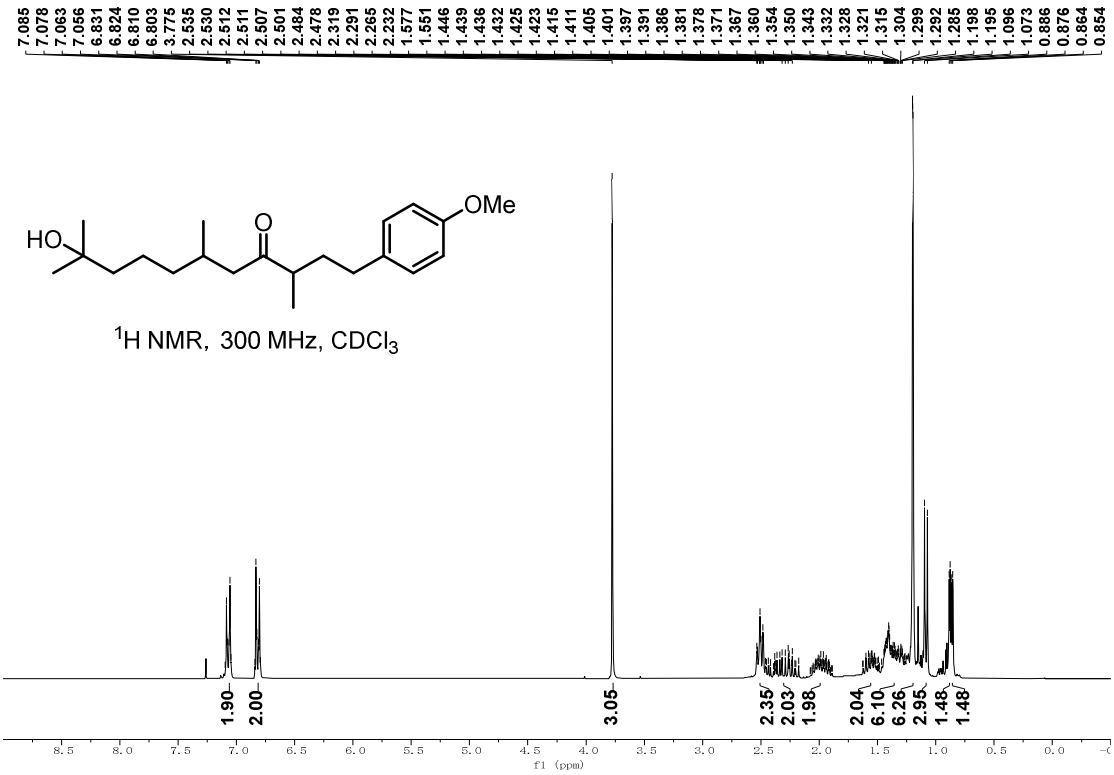
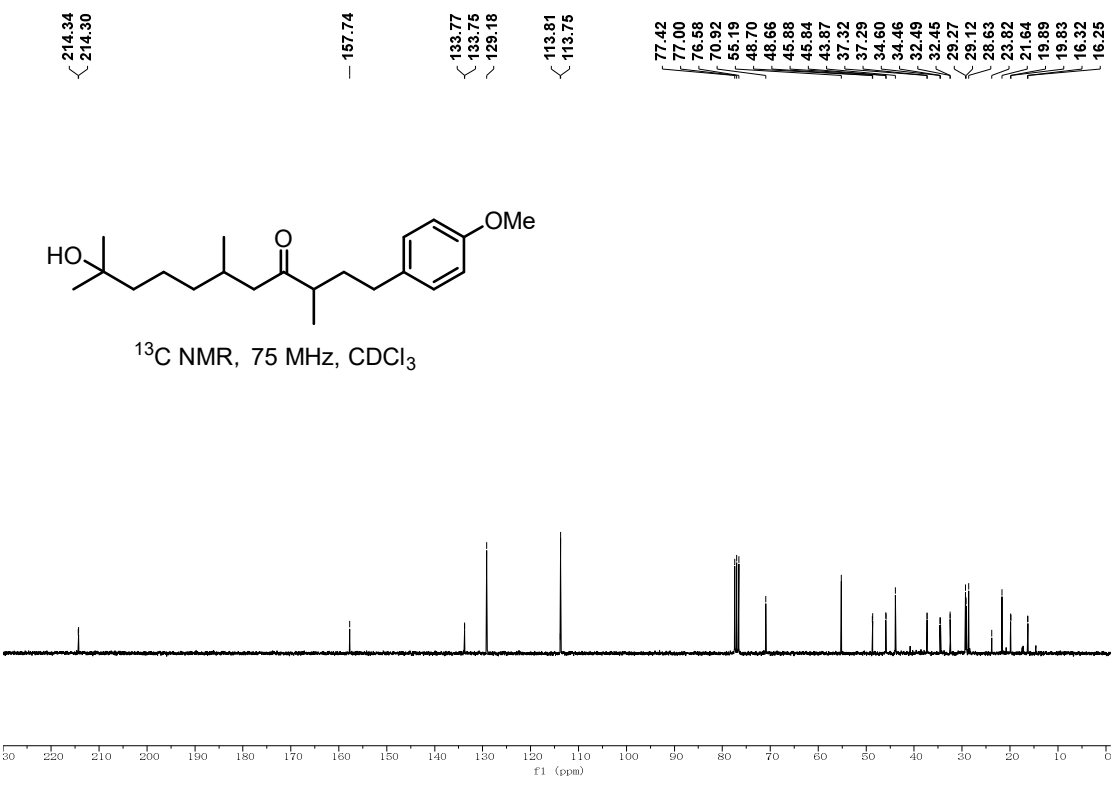
7.087
7.080
7.066
7.059
6.839
6.832
6.817
6.810
3.784
3.546
3.544
3.539
3.532
3.525
3.517
3.504
2.557
2.548
2.540
2.534
2.525
2.518
2.510
2.495
2.488
2.475
2.451
2.428
2.405
2.005
1.982
1.959
1.930
1.775
1.771
1.766
1.760
1.755
1.751
1.745
1.738
1.734
1.732
1.725
1.717
1.713
1.704
1.696
1.691
1.689
1.631
1.625
1.608
1.603
1.586
1.579
1.557
1.116
1.093
O
OMe
Cl
1H NMR, 300 MHz, CDCl3
2.08
2.08
3.12
2.07
5.00
1.01
4.21
1.29
3.10
f1 (ppm)

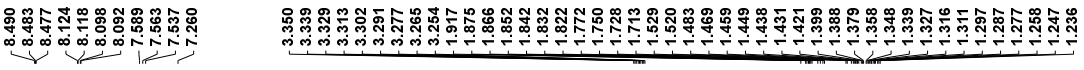

213.79
157.82
133.62
129.21
113.78
77.42
77.00
76.58
55.21
45.53
44.67
40.07
34.62
32.47
31.98
20.90
16.45
O
OMe
Cl
13C NMR, 75 MHz, CDCl3
f1 (ppm)

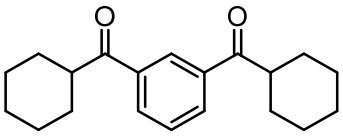


^{1}H NMR, 300 MHz, $CDCl_3$

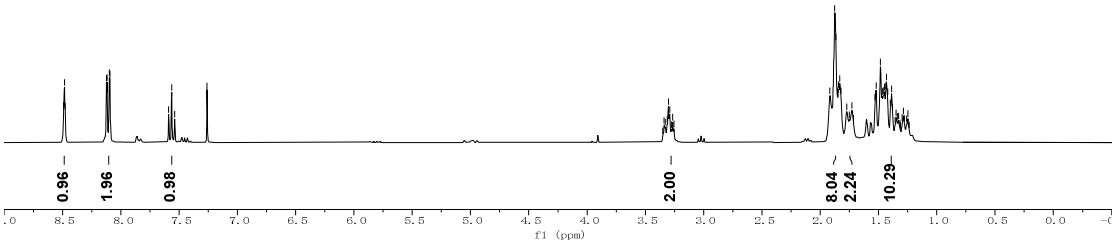


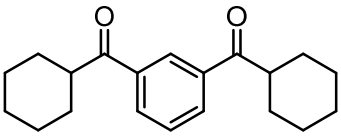
^{13}C NMR, 75 MHz, $CDCl_3$



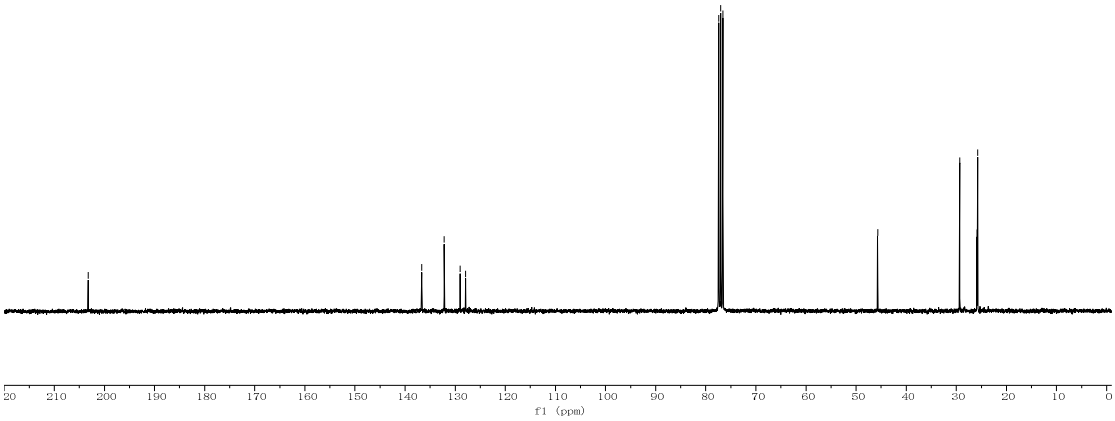


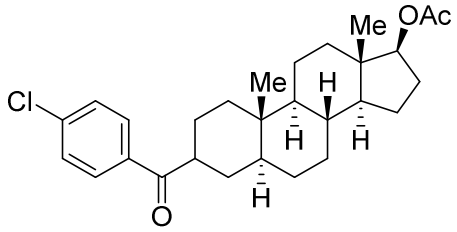
^{1}H NMR 300 MHz, $CDCl_3$



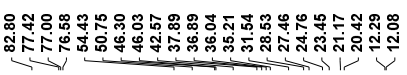


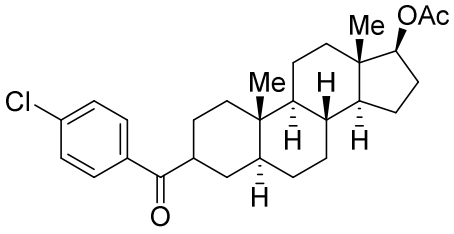
^{13}C NMR 75 MHz, $CDCl_3$



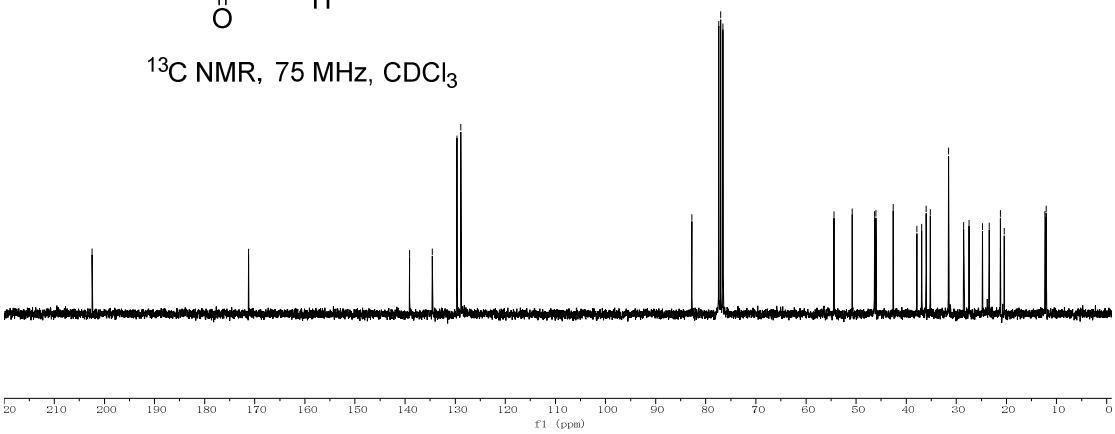


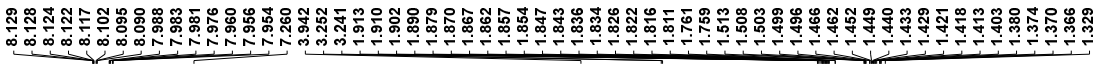
^{1}H NMR, 300 MHz, $CDCl_3$

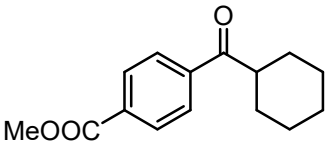




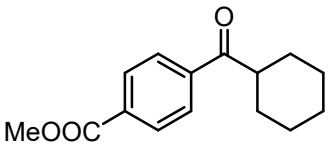
^{13}C NMR, 75 MHz, $CDCl_3$



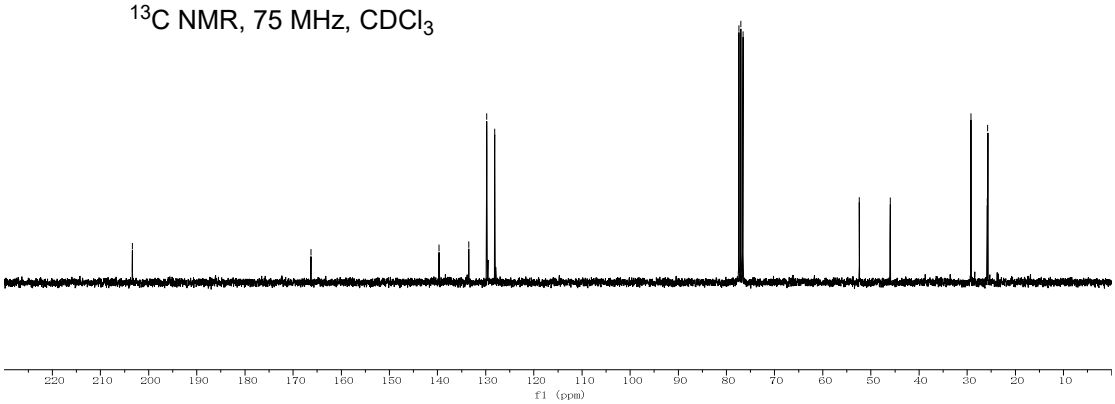


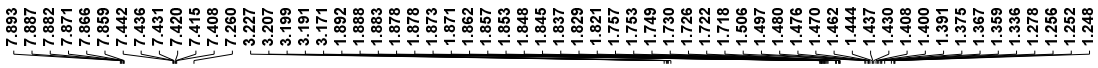


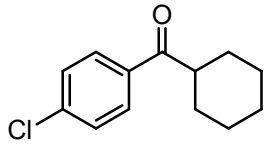
^{1}H NMR, 300 MHz, $CDCl_3$



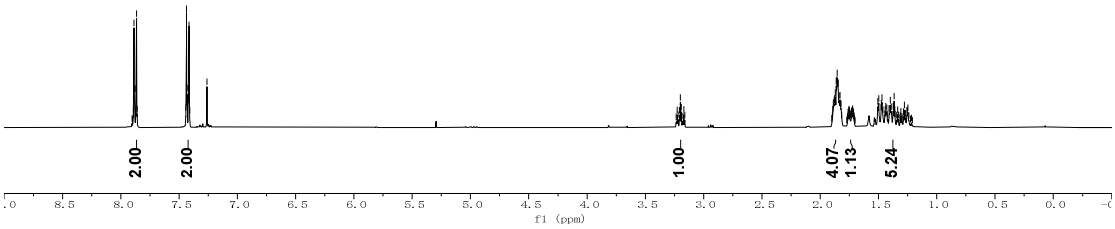
^{13}C NMR, 75 MHz, $CDCl_3$

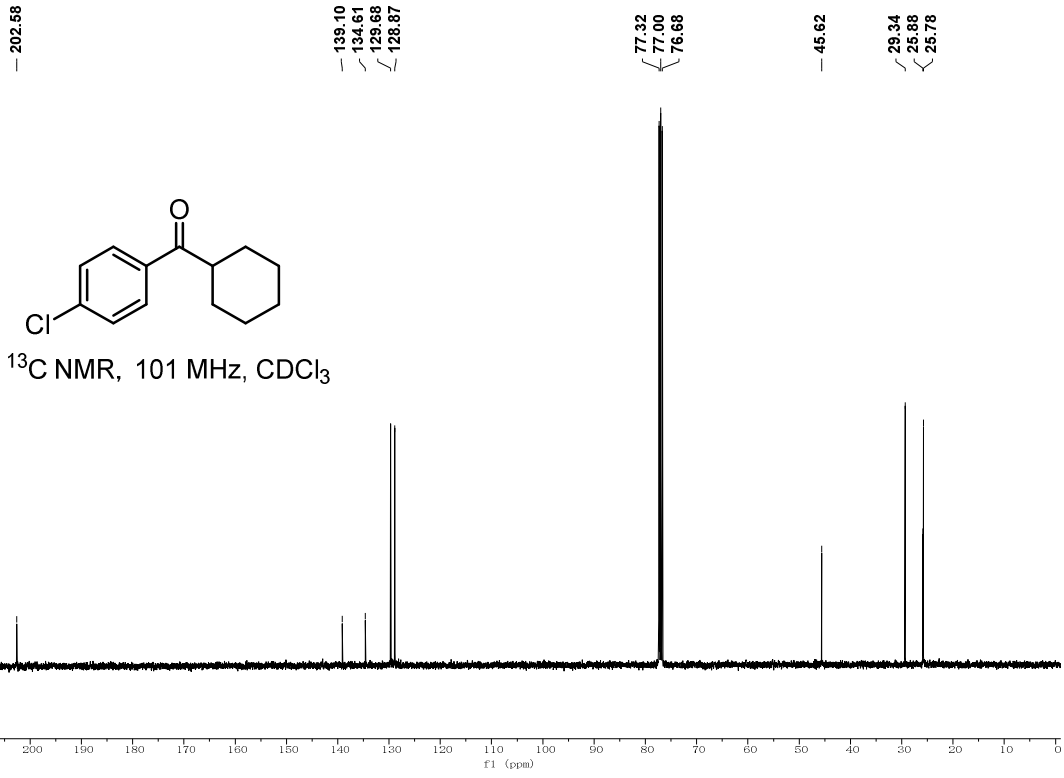




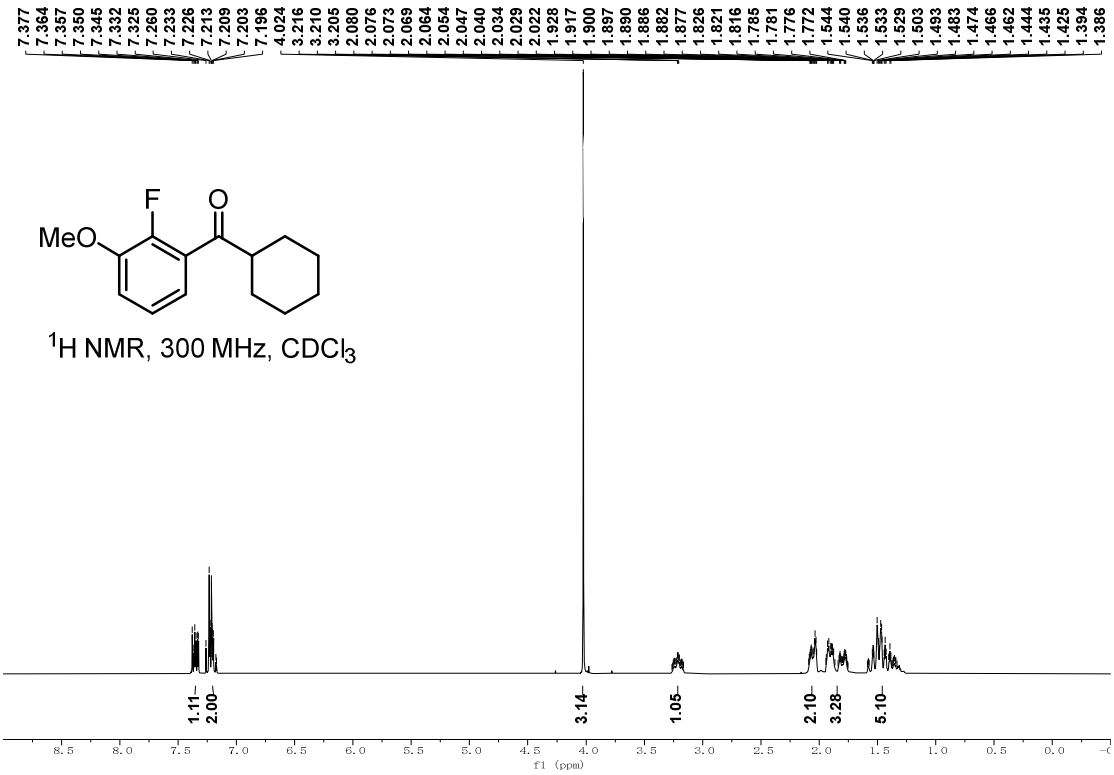


^{1}H NMR, 400 MHz, $CDCl_3$





^{13}C NMR, 101 MHz, $CDCl_3$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7.357
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7.260
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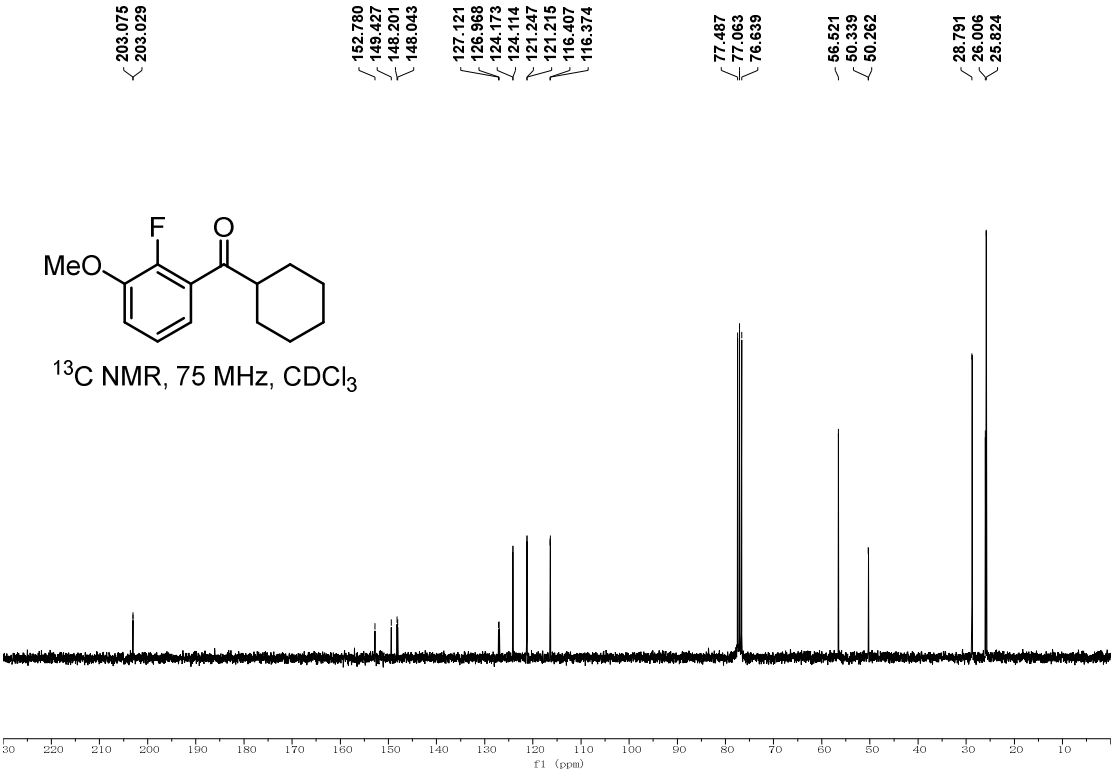
7.213
7.209
7.203
7.196
4.024
3.216
3.210
3.205
2.080
2.076
2.073
2.069
2.064
2.054
2.047
2.040
2.034
2.029
2.022
1.928
1.917
1.900
1.897
1.890
1.886
1.882
1.877
1.826
1.821
1.816
1.785
1.781
1.776
1.772
1.544
1.540
1.536
1.533
1.529
1.503
1.493
1.483
1.474
1.466
1.462
1.444
1.435
1.425
1.394
1.386
F
O
MeO
1H NMR, 300 MHz, CDCl3
1.11
2.00
3.14
1.05
2.10
3.28
5.10
f1 (ppm)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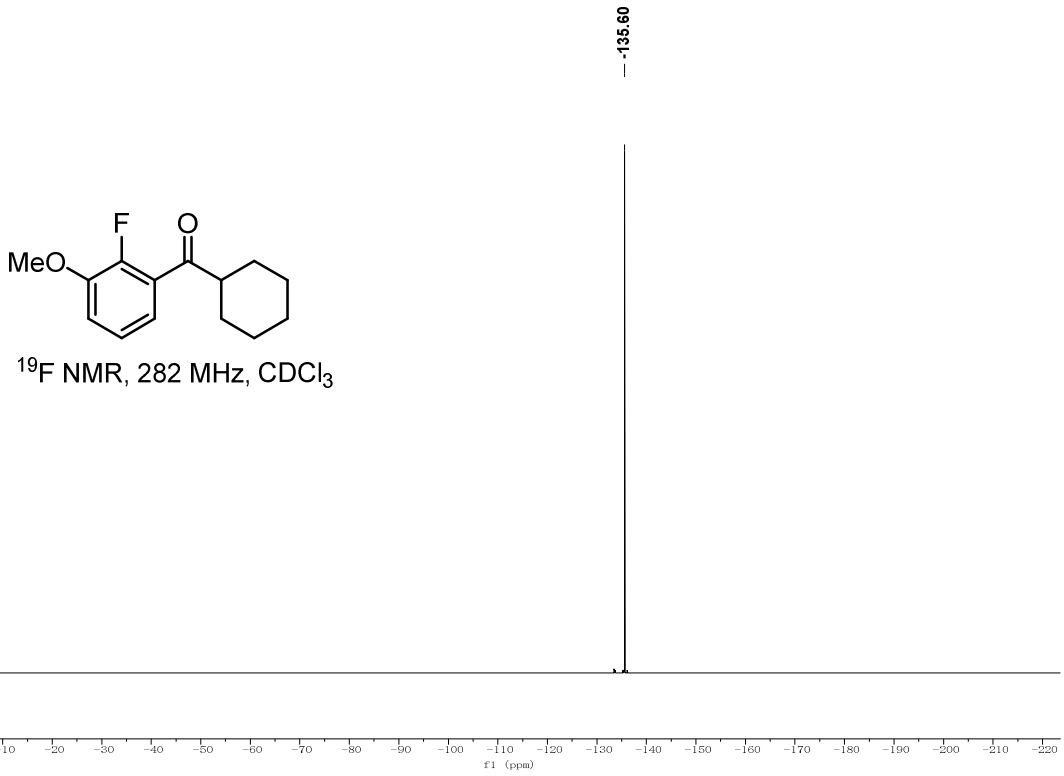
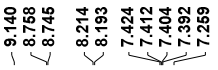
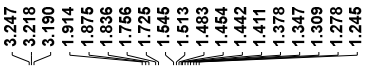
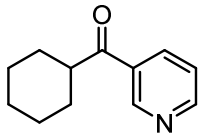
116.374
77.487
77.063
76.639
56.521
50.339
50.262
28.791
26.006
25.824
F
O
MeO
13C NMR, 75 MHz, CDCl3
f1 (ppm)



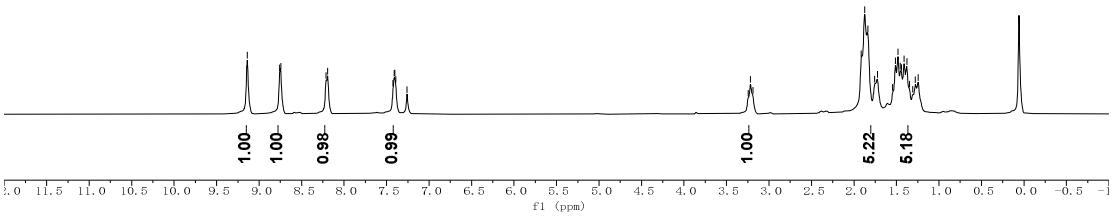
^{19}F NMR, 282 MHz, $CDCl_3$

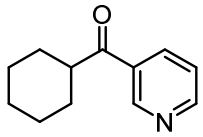




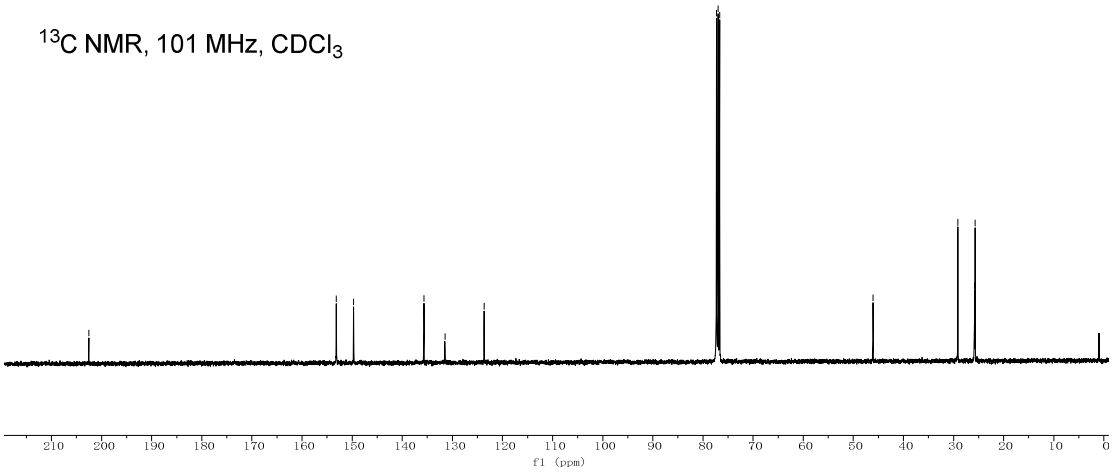


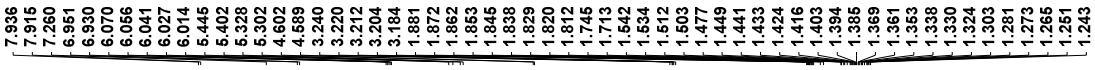
^{1}H NMR, 400 MHz, $CDCl_3$

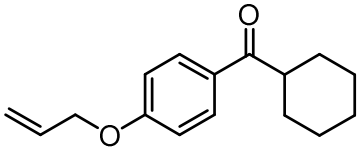




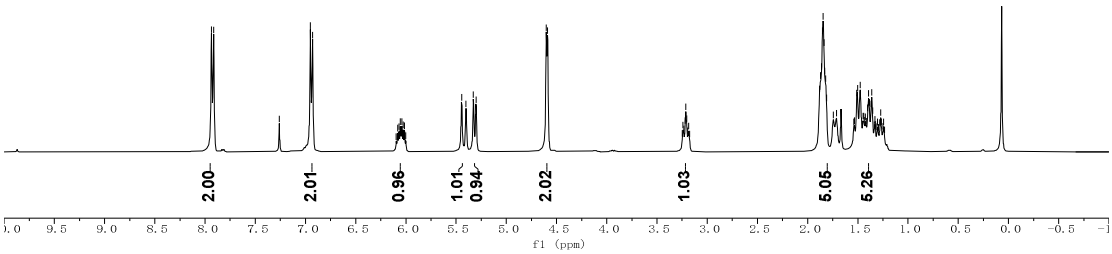
^{13}C NMR, 101 MHz, $CDCl_3$

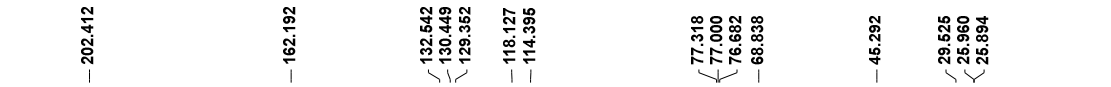


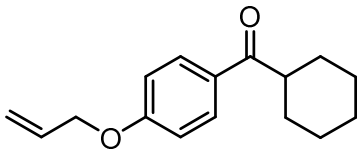




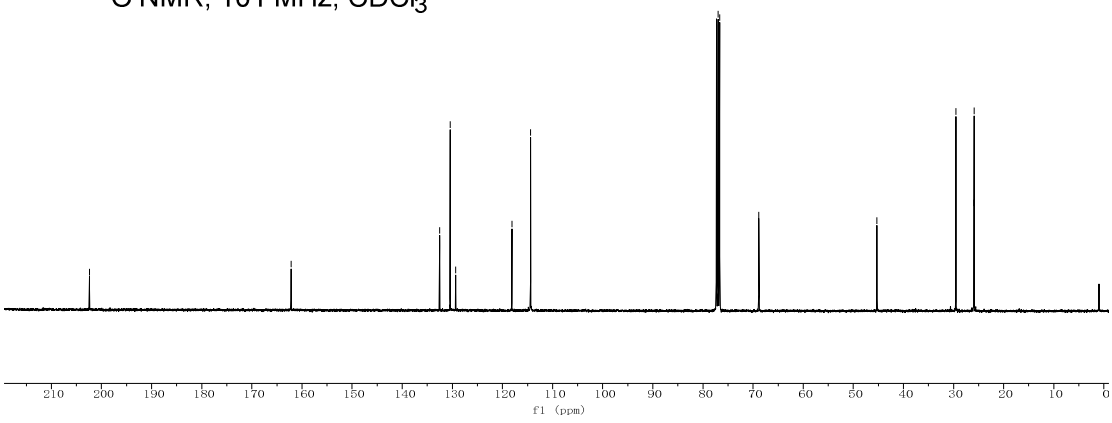
^{1}H NMR, 400 MHz, $CDCl_3$

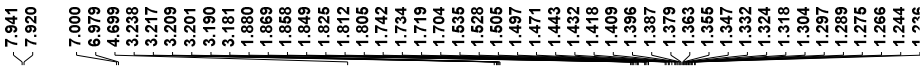


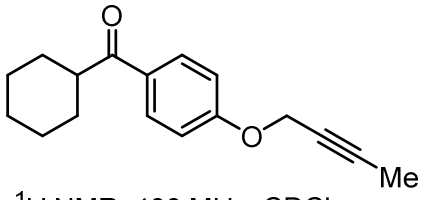




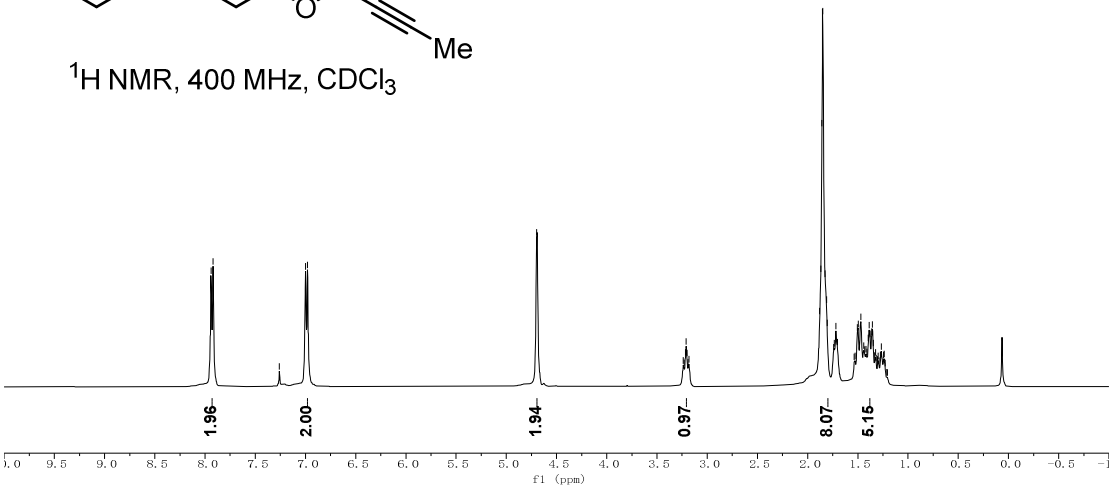
^{13}C NMR, 101 MHz, $CDCl_3$

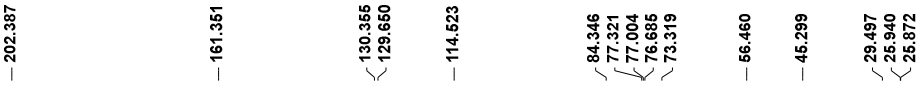


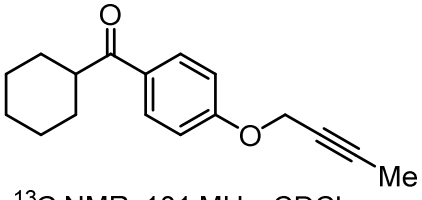




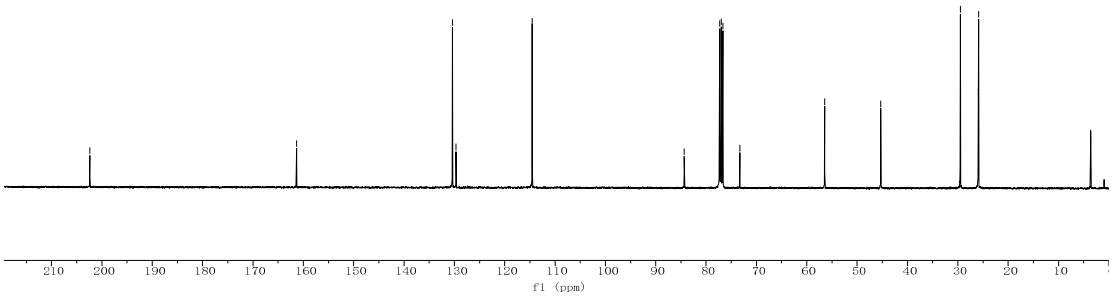
^{1}H NMR, 400 MHz, $CDCl_3$

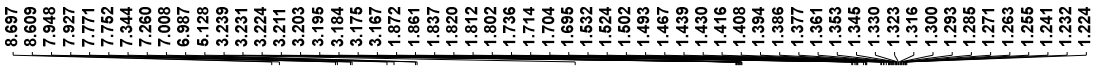


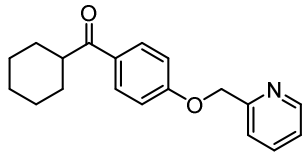




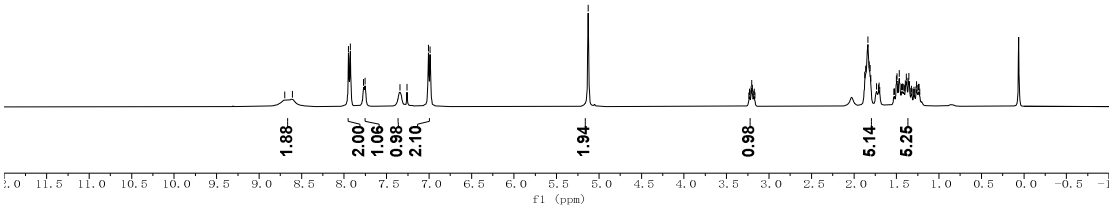
^{13}C NMR, 101 MHz, $CDCl_3$

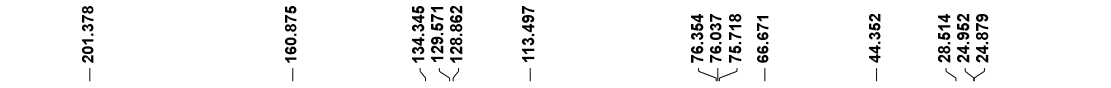


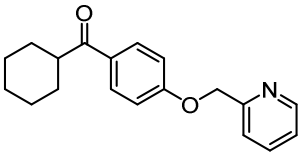




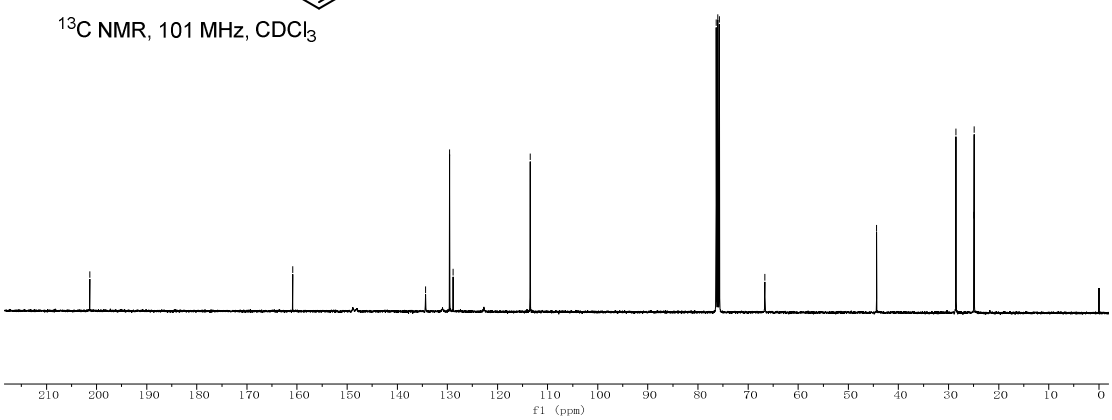
^{1}H NMR, 400 MHz, $CDCl_3$

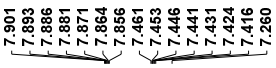


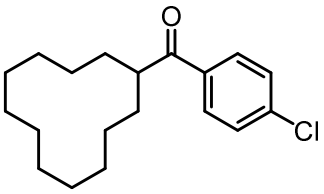




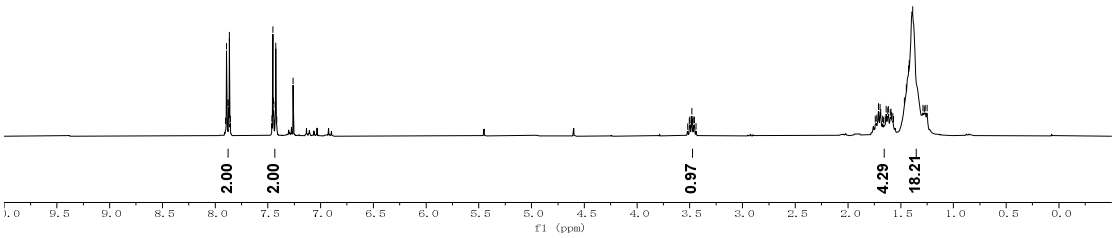
^{13}C NMR, 101 MHz, $CDCl_3$

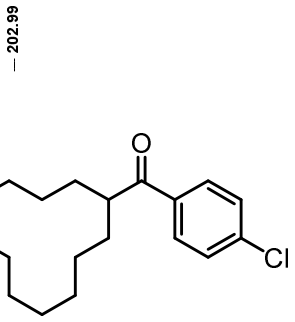




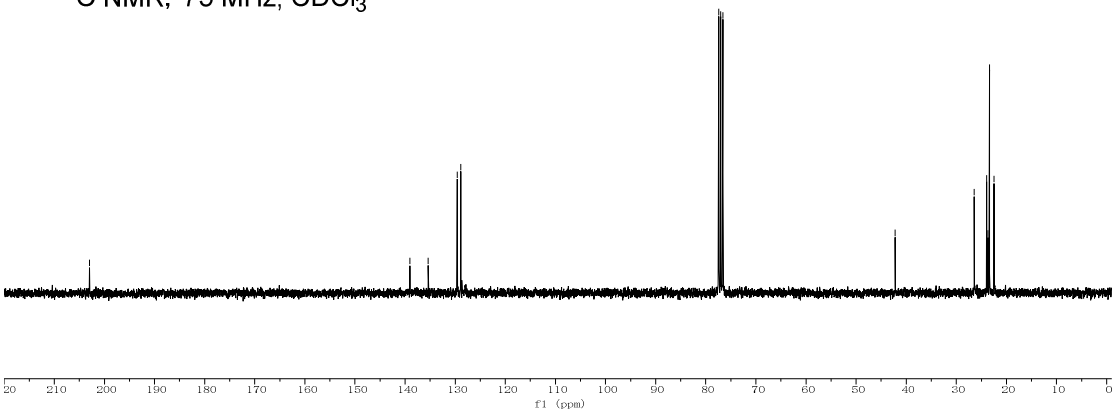


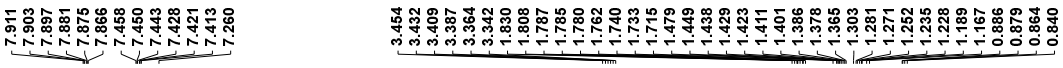
^{1}H NMR, 300 MHz, $CDCl_3$

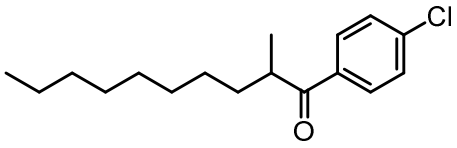




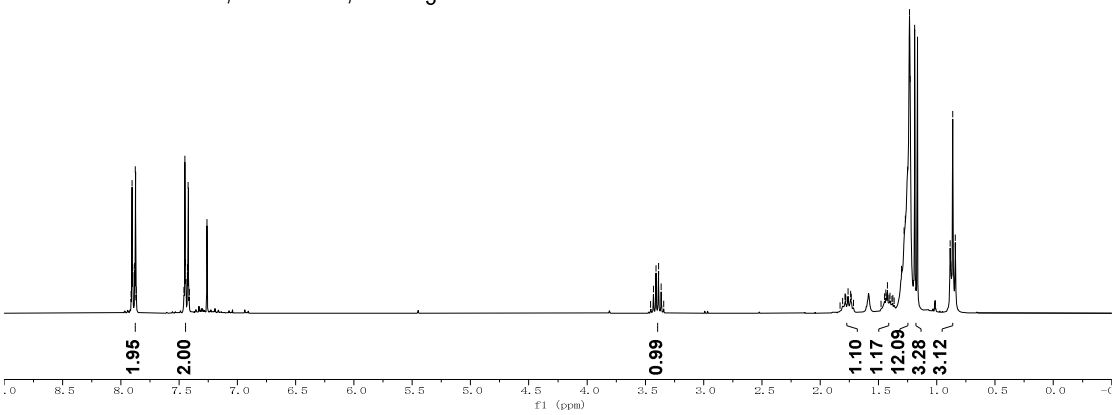
^{13}C NMR, 75 MHz, $CDCl_3$

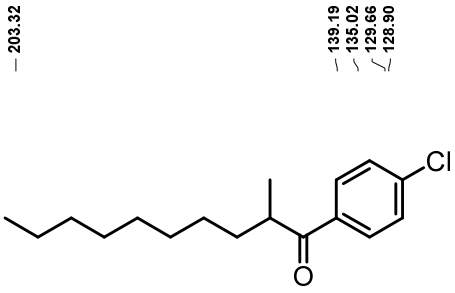




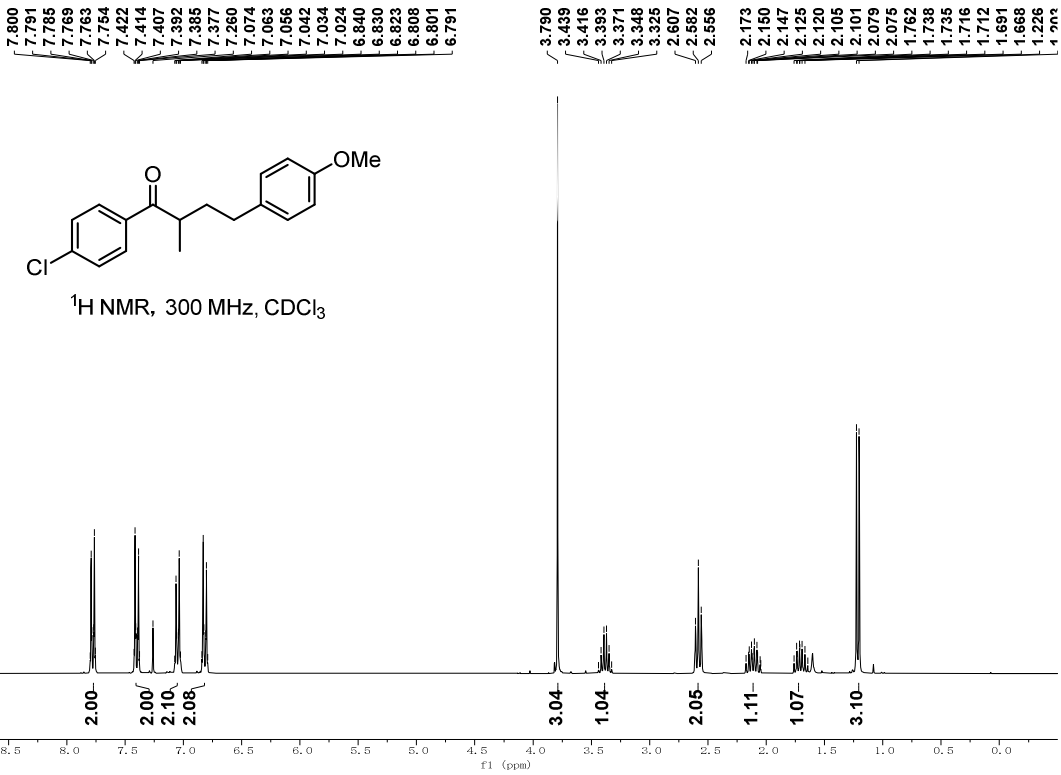


^{1}H NMR, 300 MHz, $CDCl_3$

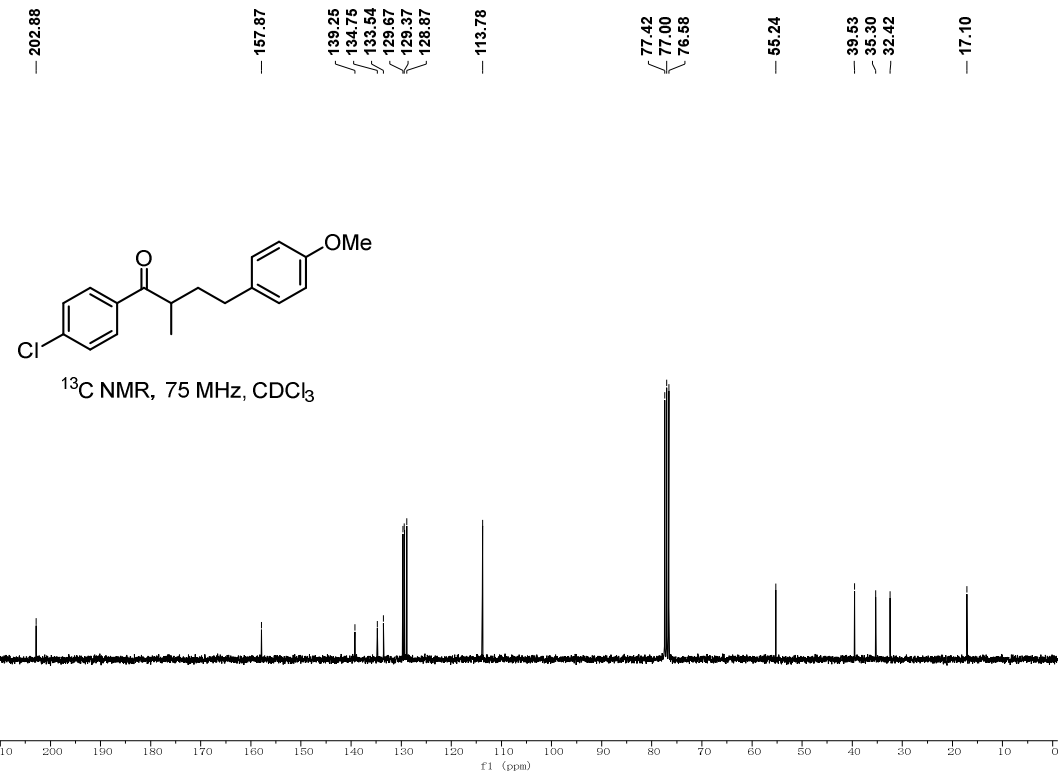




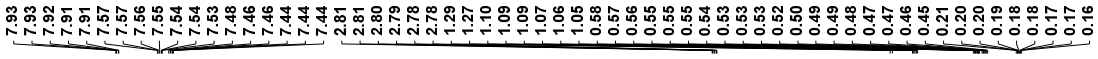
^{13}C NMR, 75 MHz, $CDCl_3$

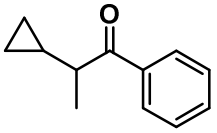


^{1}H NMR, 300 MHz, $CDCl_3$

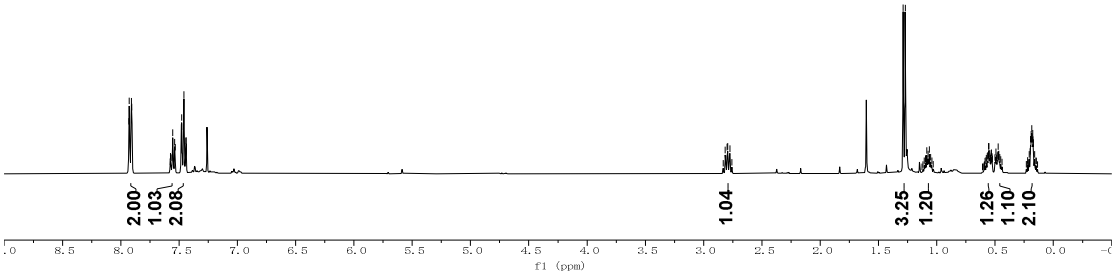


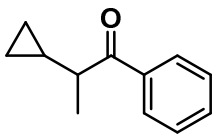
^{13}C NMR, 75 MHz, $CDCl_3$



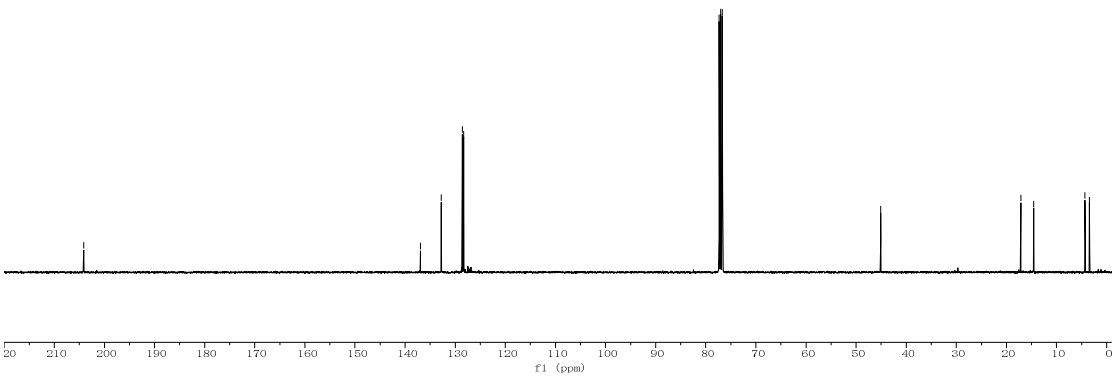


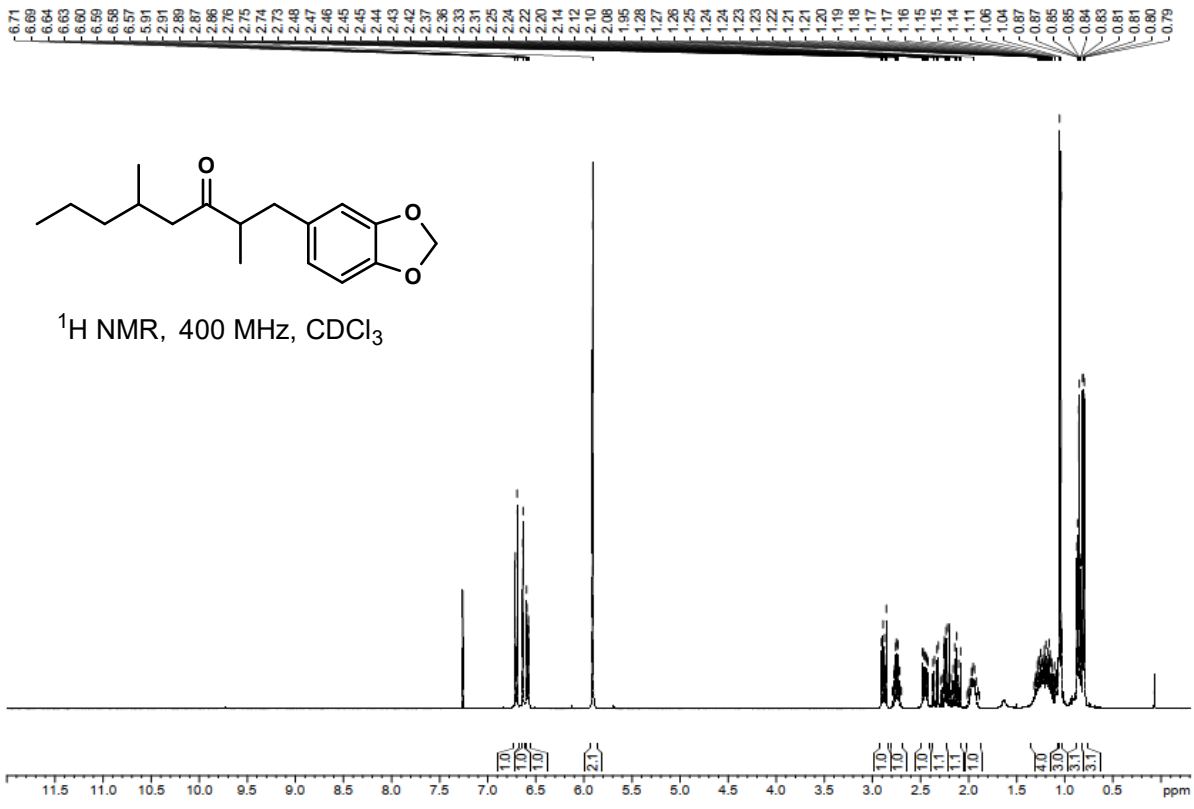
^{1}H NMR, 400 MHz, $CDCl_3$



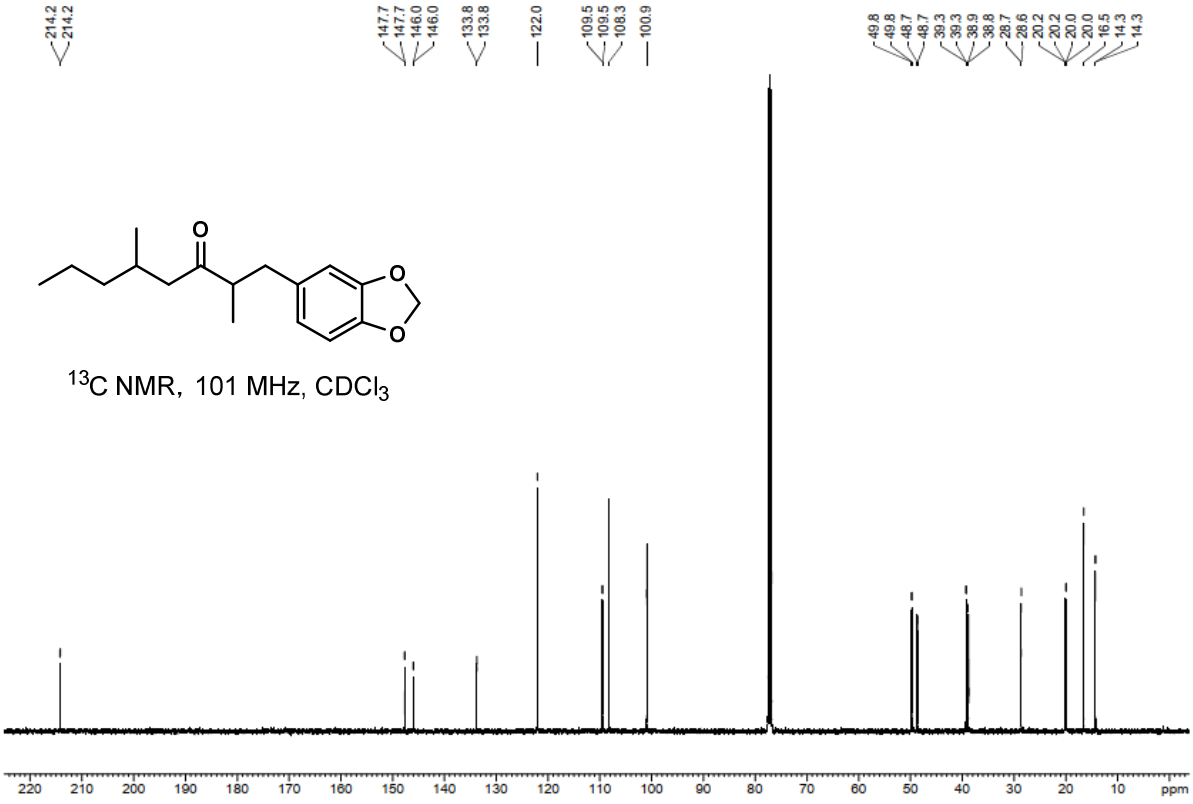


^{13}C NMR, 101 MHz, $CDCl_3$

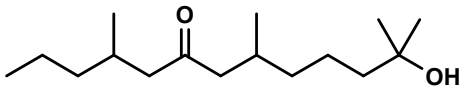




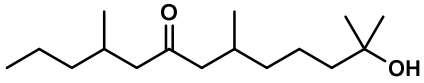
^{1}H NMR, 400 MHz, $CDCl_3$



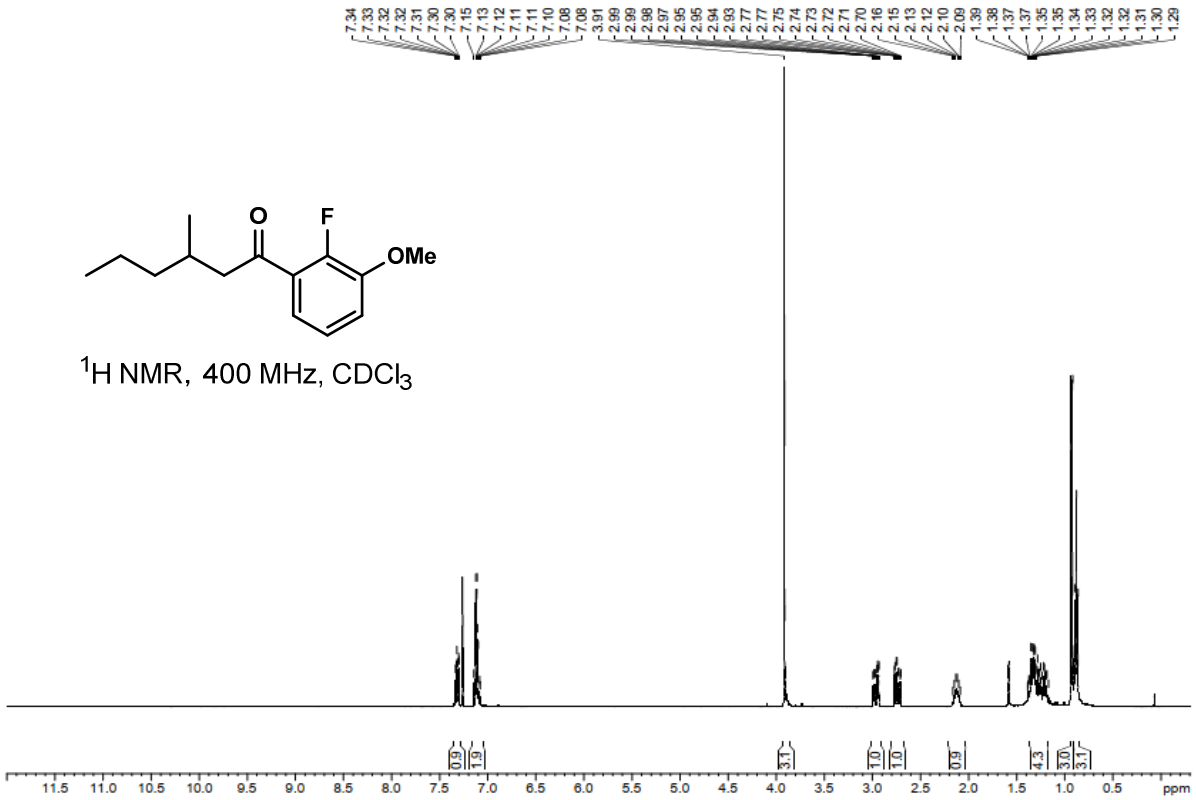
^{13}C NMR, 101 MHz, $CDCl_3$



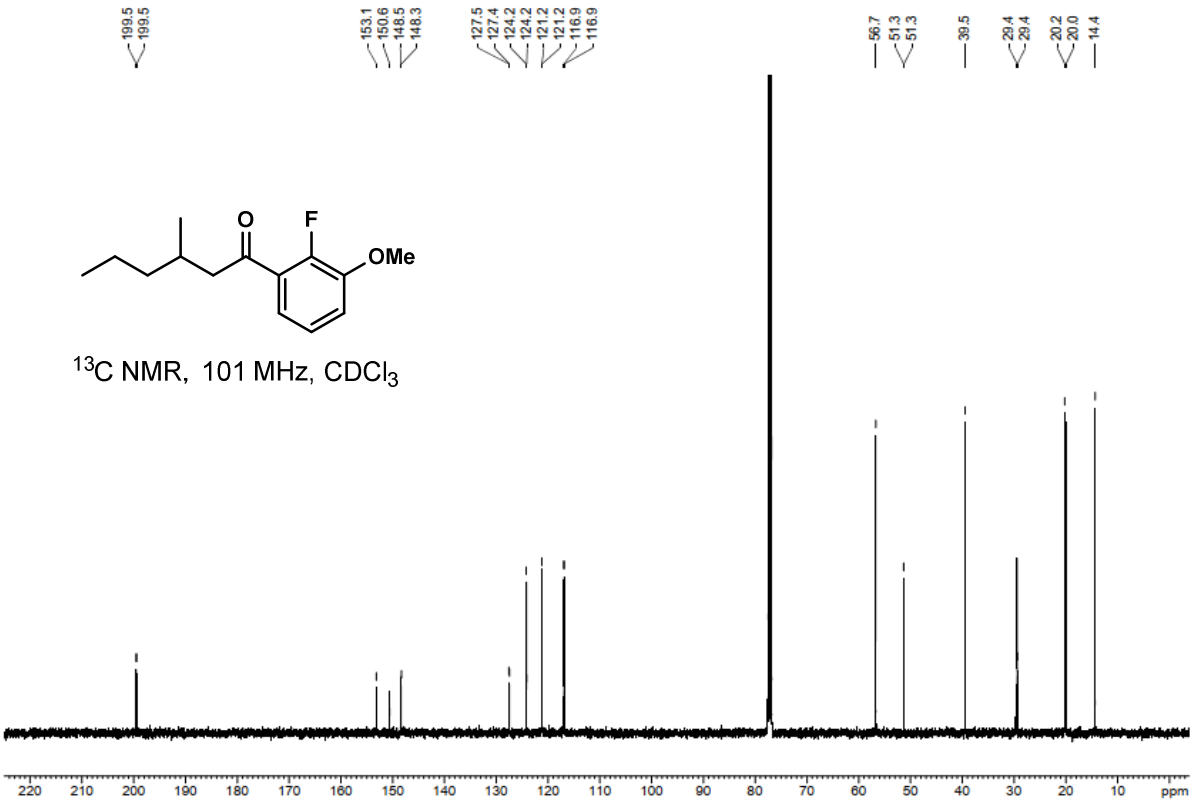
^{1}H NMR, 400 MHz, $CDCl_3$



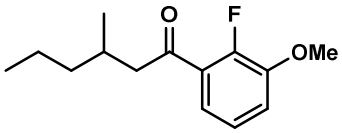
^{13}C NMR, 101 MHz, $CDCl_3$



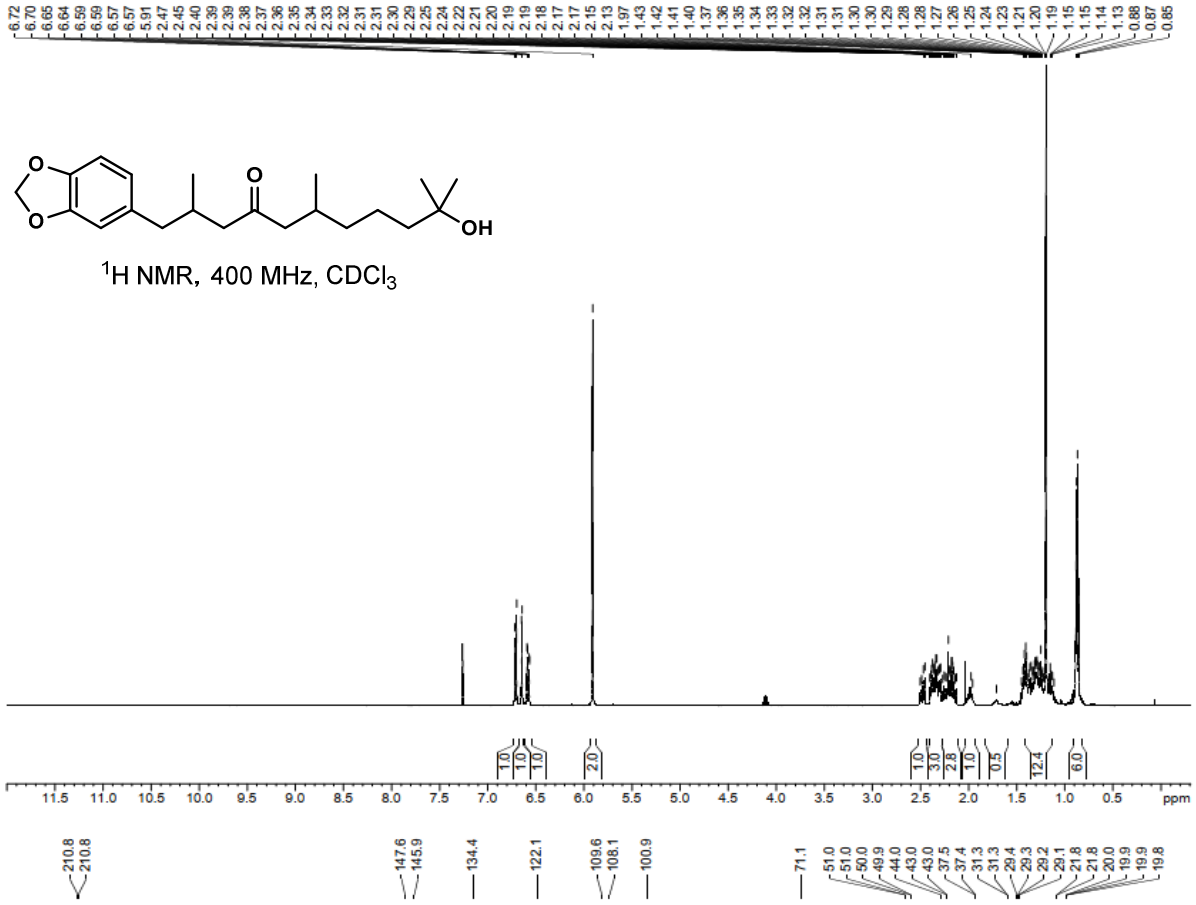
^{1}H NMR, 400 MHz, $CDCl_3$



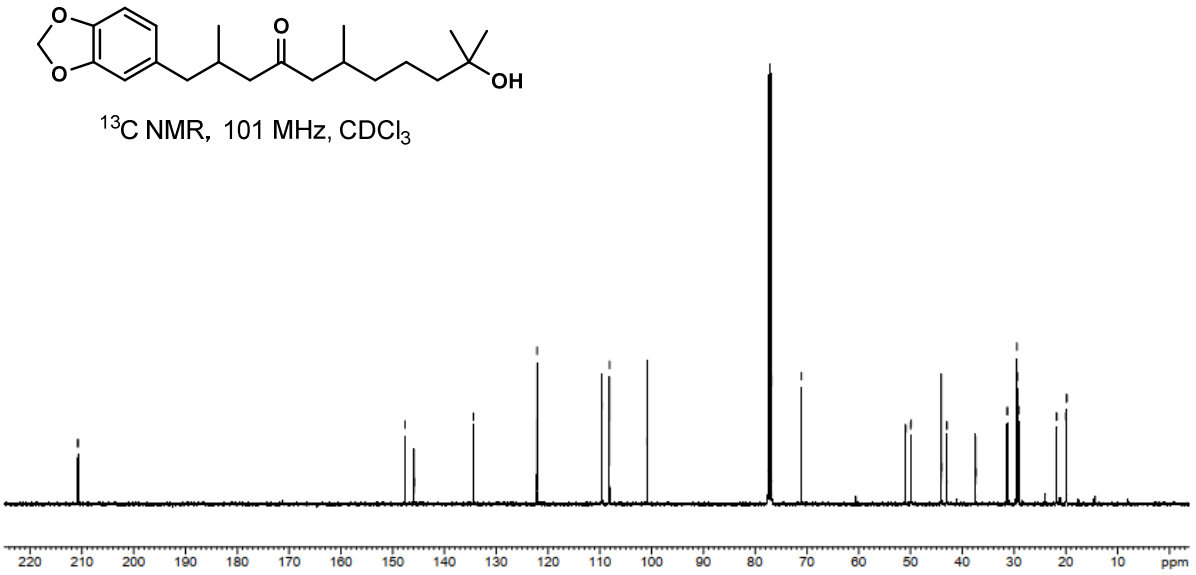
^{13}C NMR, 101 MHz, $CDCl_3$



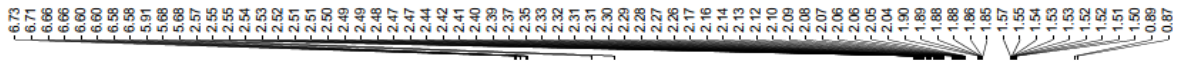
^{19}F NMR, 377 MHz, $CDCl_3$

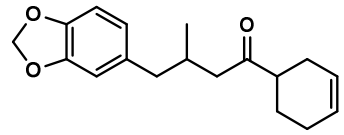


^{1}H NMR, 400 MHz, $CDCl_3$

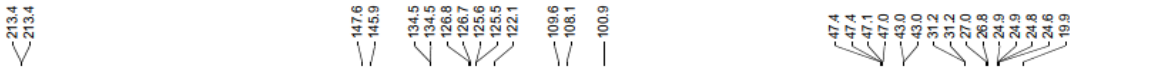


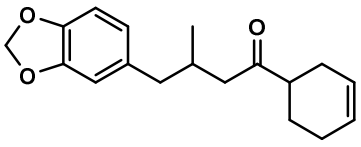
^{13}C NMR, 101 MHz, $CDCl_3$



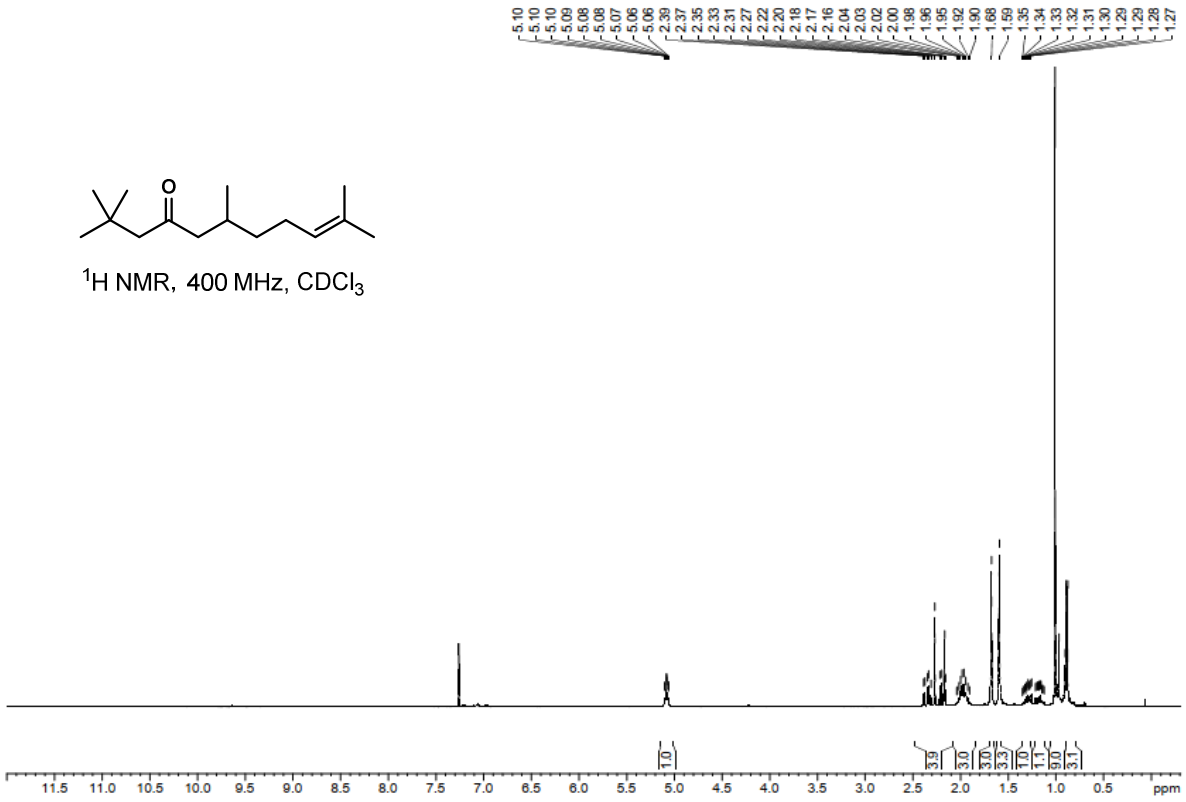


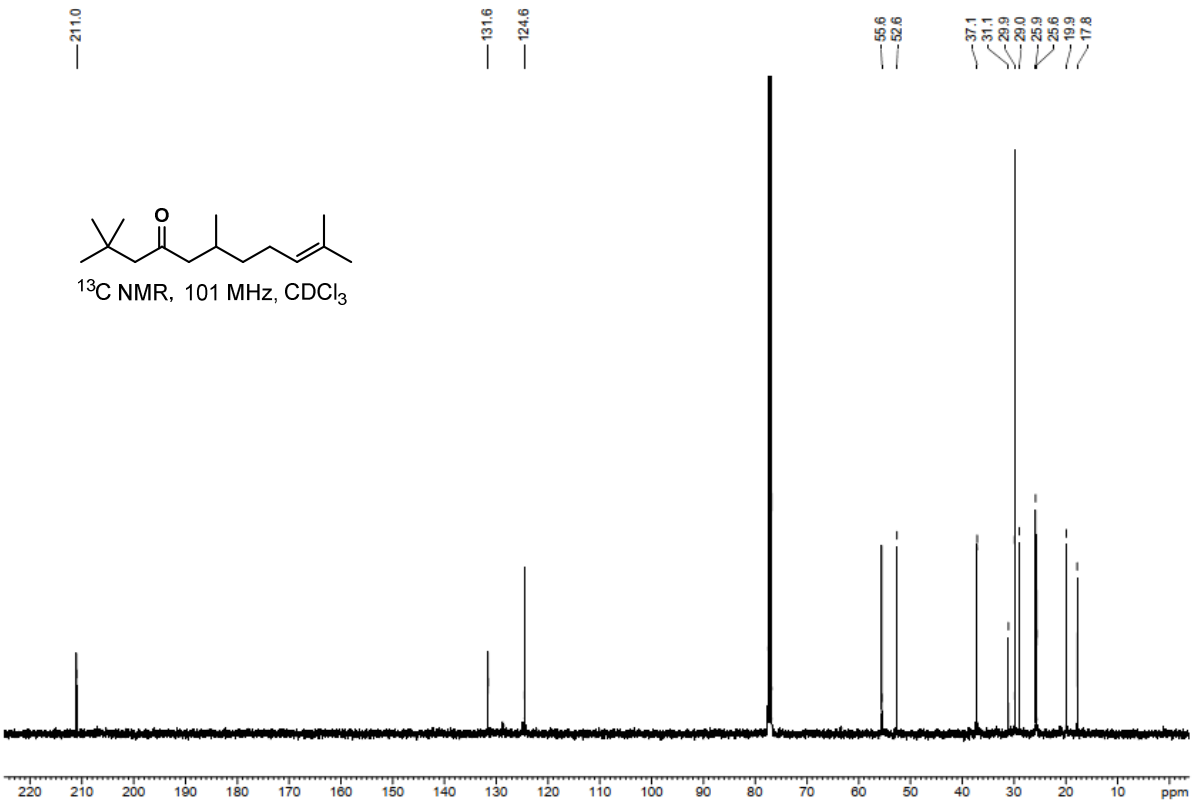
^{1}H NMR, 400 MHz, $CDCl_3$

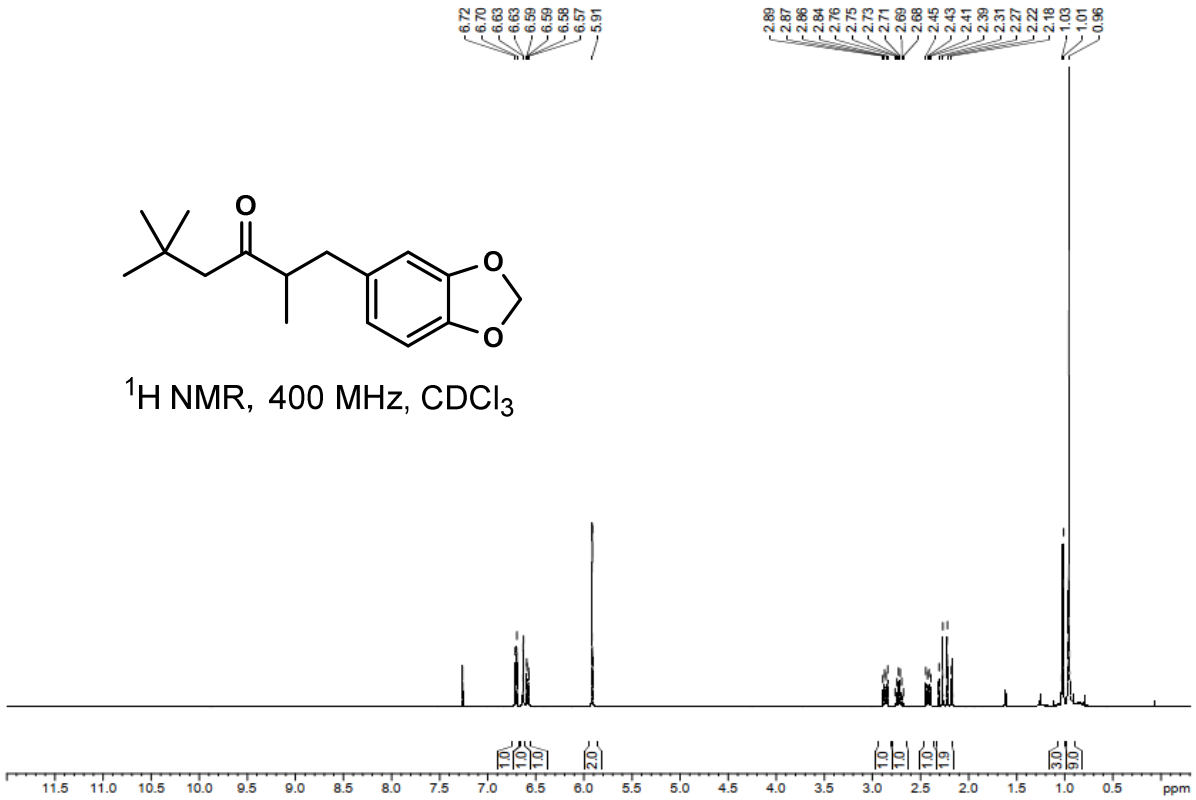




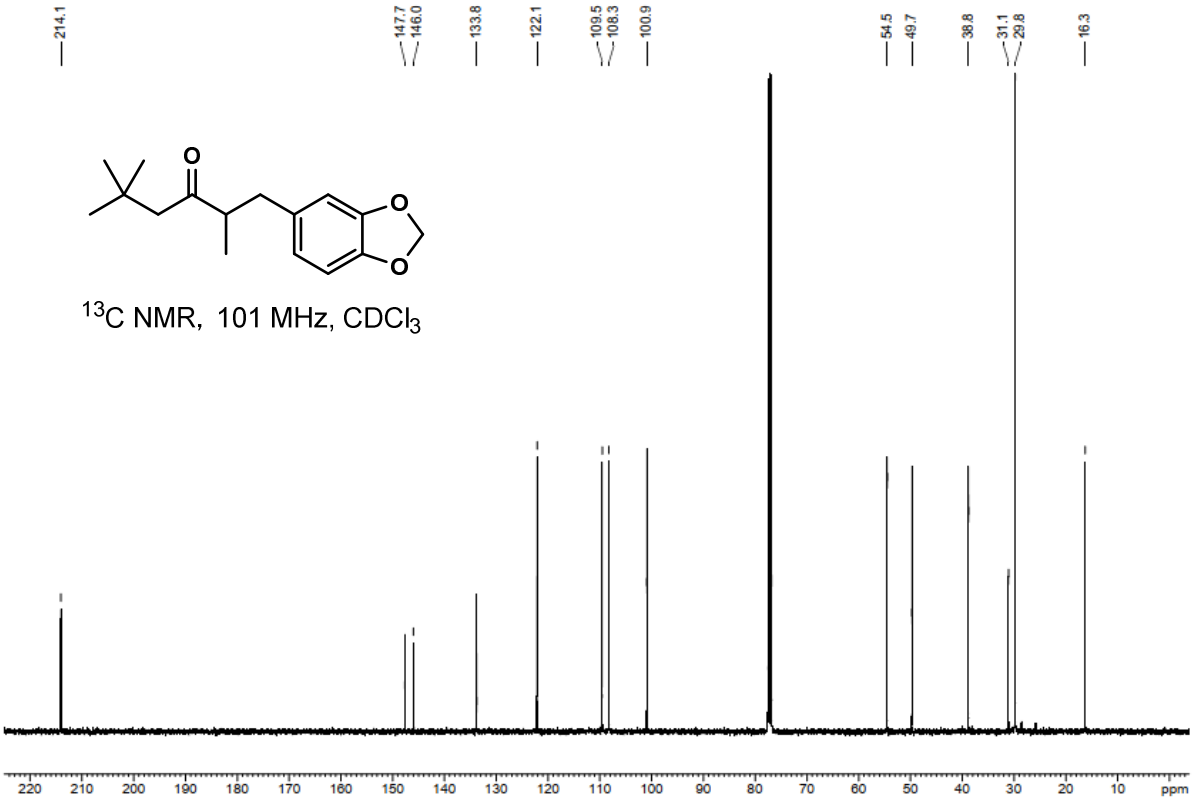
^{13}C NMR, 101 MHz, $CDCl_3$


O
1H NMR, 400 MHz, CDCl3
5.10
5.10
5.10
5.09
5.08
5.08
5.07
5.06
5.06
2.39
2.37
2.35
2.33
2.31
2.27
2.22
2.20
2.18
2.17
2.16
2.04
2.03
2.02
2.00
1.98
1.96
1.95
1.92
1.90
1.68
1.59
1.35
1.34
1.33
1.32
1.31
1.30
1.29
1.29
1.28
1.27
1.0
3.9
3.0
3.0
3.3
1.0
1.1
9.0
3.1
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

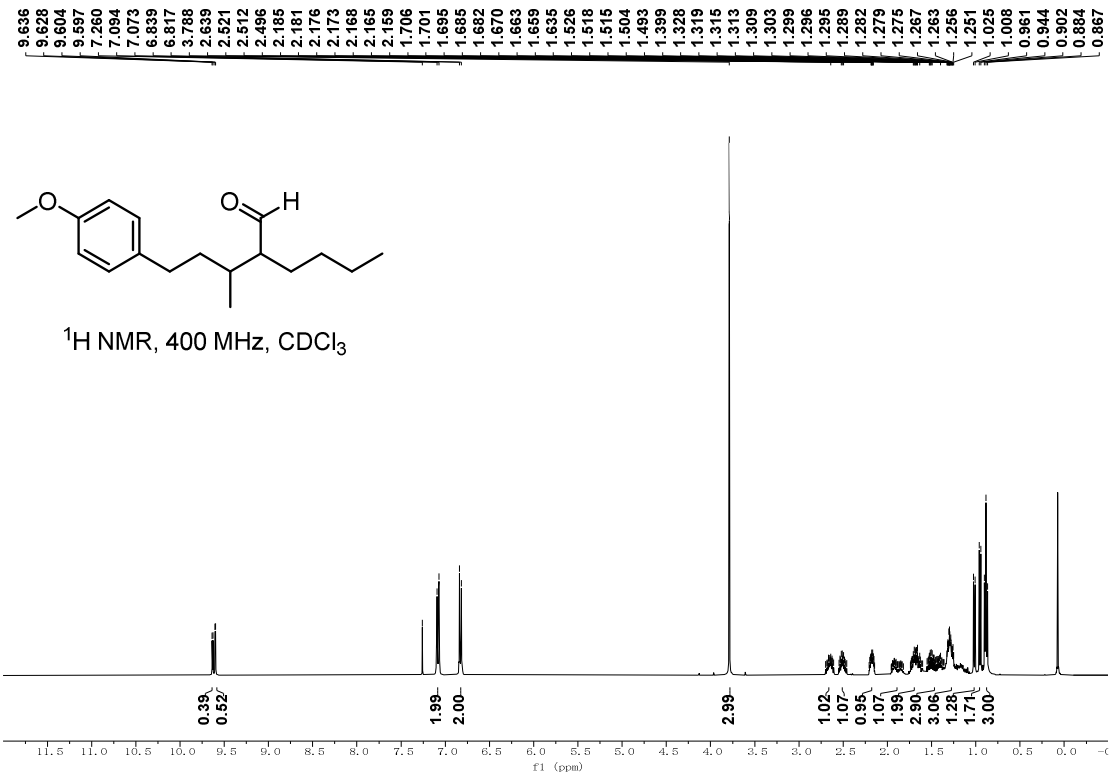

211.0
131.6
124.6
55.6
52.6
37.1
31.1
29.9
29.0
25.9
25.6
19.9
17.8
O
13C NMR, 101 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

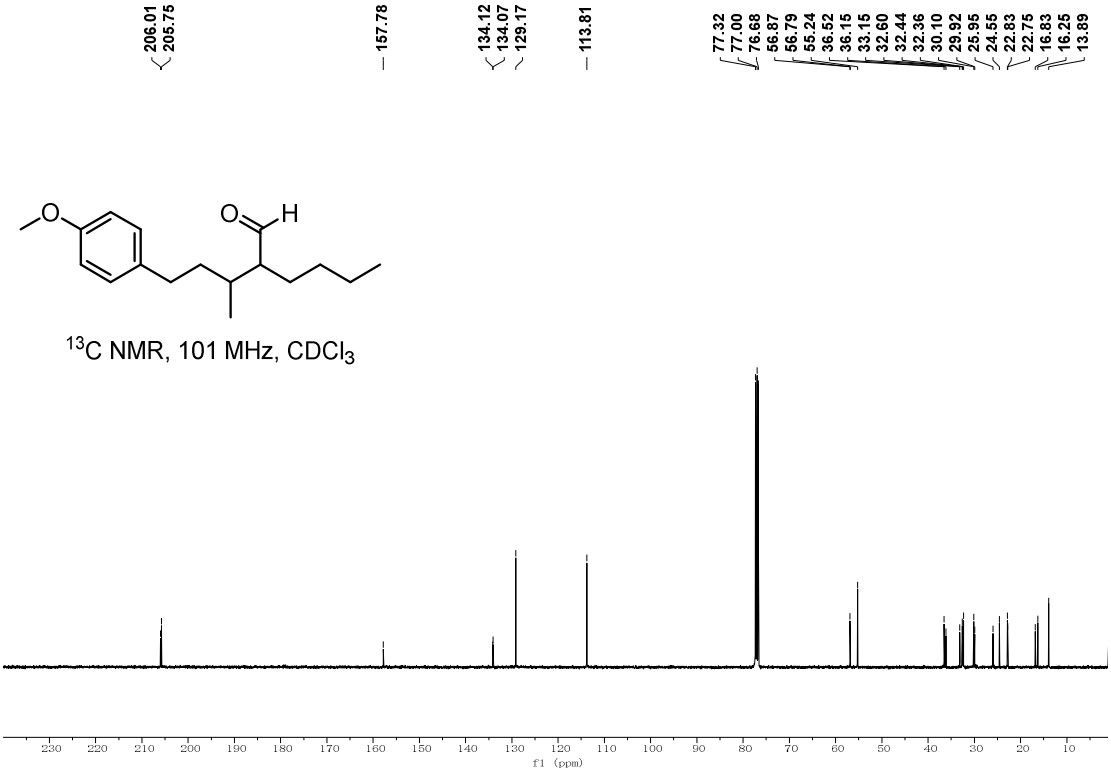


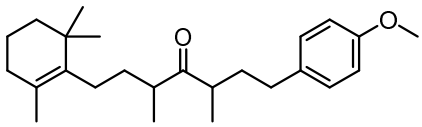
^{1}H NMR, 400 MHz, $CDCl_3$



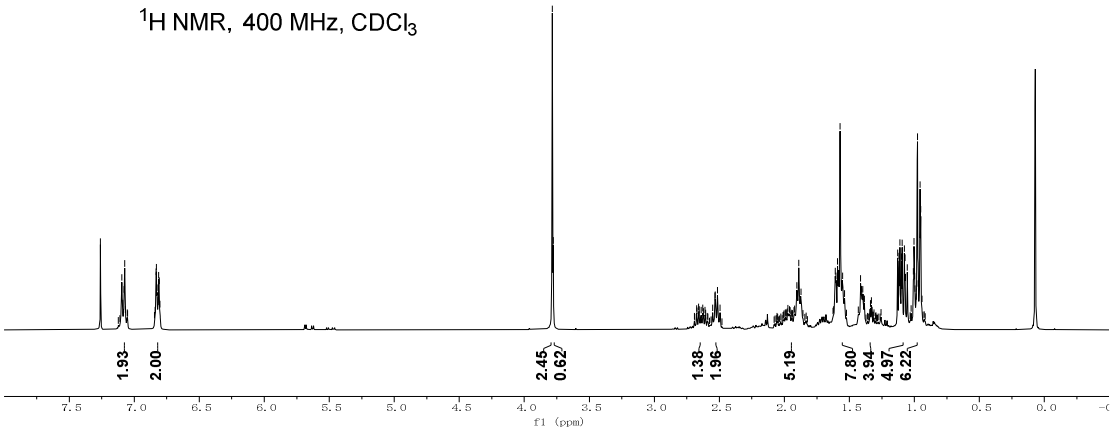
^{13}C NMR, 101 MHz, $CDCl_3$

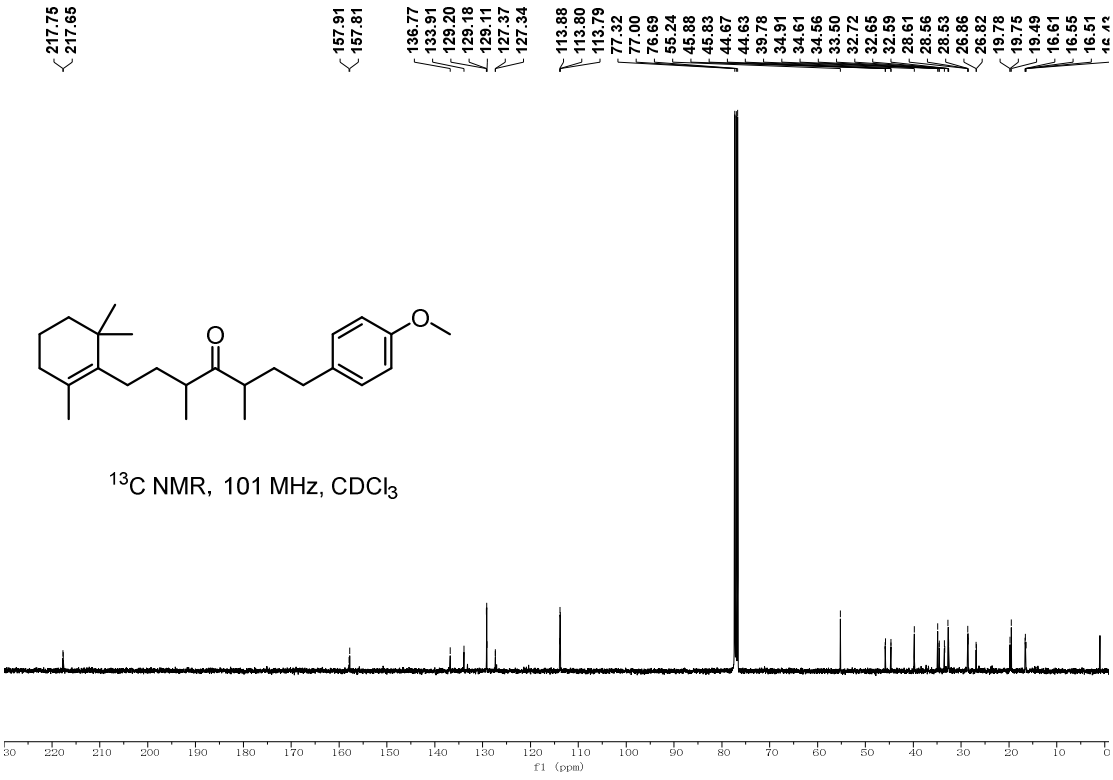

9.636
9.628
9.604
9.597
7.260
7.094
7.073
6.839
6.817
3.788
2.639
2.521
2.512
2.496
2.185
2.181
2.176
2.173
2.168
2.165
2.159
1.706
1.701
1.695
1.685
1.682
1.670
1.663
1.659
1.635
1.526
1.518
1.515
1.504
1.493
1.399
1.328
1.319
1.315
1.313
1.309
1.303
1.299
1.296
1.295
1.289
1.282
1.279
1.275
1.267
1.263
1.256
1.251
1.025
1.008
0.961
0.944
0.902
0.884
0.867
O
O
H
^{1}H NMR, 400 MHz, CDCl$_3$
0.39
0.52
1.99
2.00
2.99
1.02
1.07
0.95
1.07
1.99
2.90
3.06
1.28
1.71
3.00
f1 (ppm)


206.01
205.75
157.78
134.12
134.07
129.17
113.81
77.32
77.00
76.68
56.87
56.79
55.24
36.52
36.15
33.15
32.60
32.44
32.36
30.10
29.92
25.95
24.55
22.83
22.75
16.83
16.25
13.89
O
O
H
^{13}C NMR, 101 MHz, CDCl$_3$
f1 (ppm)

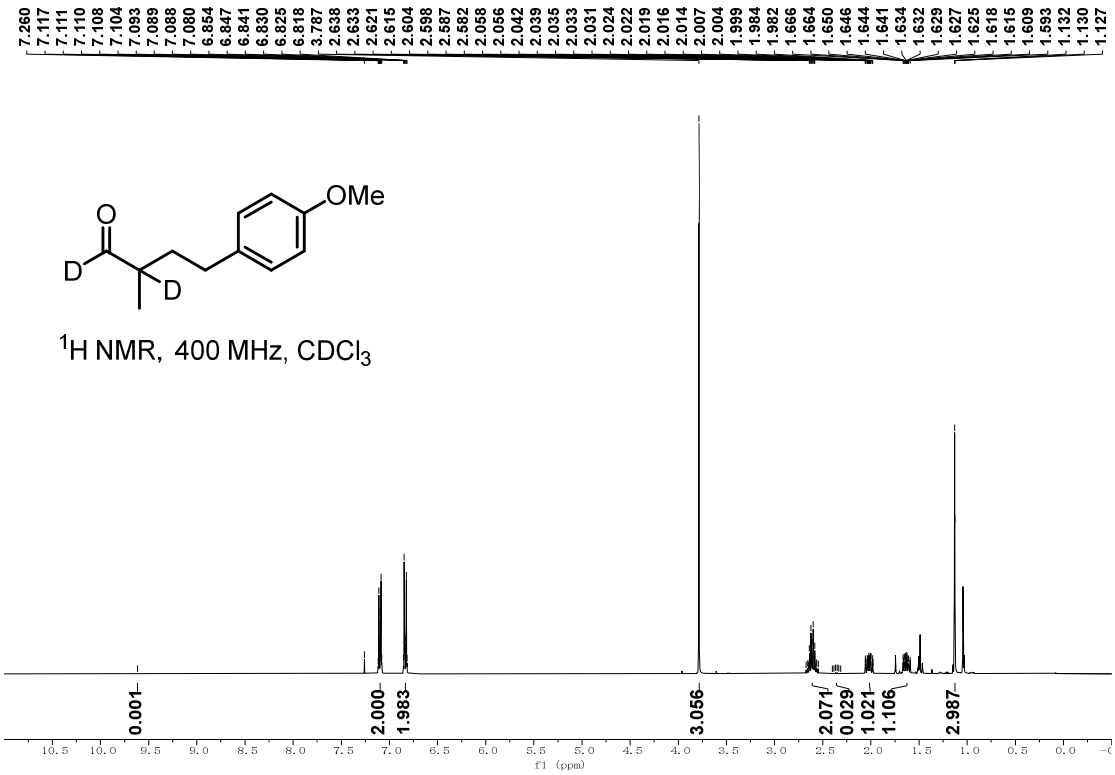


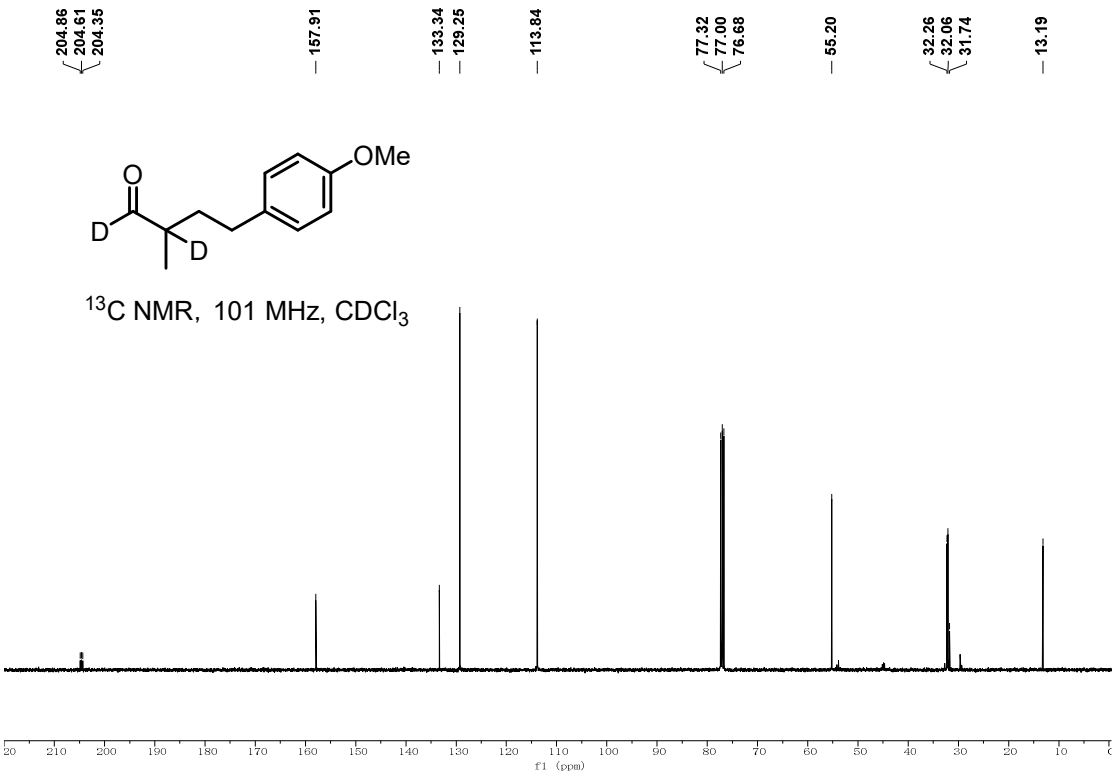
^{1}H NMR, 400 MHz, $CDCl_3$

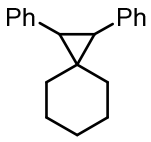




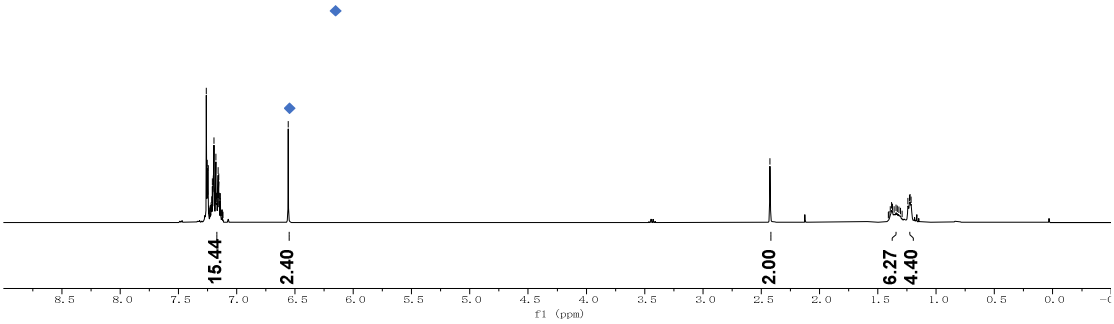
^{13}C NMR, 101 MHz, $CDCl_3$

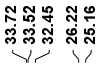

7.260
7.117
7.111
7.110
7.108
7.104
7.093
7.089
7.088
7.080
6.854
6.847
6.841
6.830
6.825
6.818
3.787
2.638
2.633
2.621
2.615
2.604
2.598
2.587
2.582
2.058
2.056
2.042
2.039
2.035
2.033
2.031
2.024
2.022
2.019
2.016
2.014
2.007
2.004
1.999
1.984
1.982
1.666
1.664
1.650
1.646
1.644
1.641
1.634
1.632
1.629
1.627
1.625
1.618
1.615
1.609
1.593
1.132
1.130
1.127
OMe
O
D
D
1H NMR, 400 MHz, CDCl3
0.001
2.000
1.983
3.056
2.071
0.029
1.021
1.106
2.987
f1 (ppm)

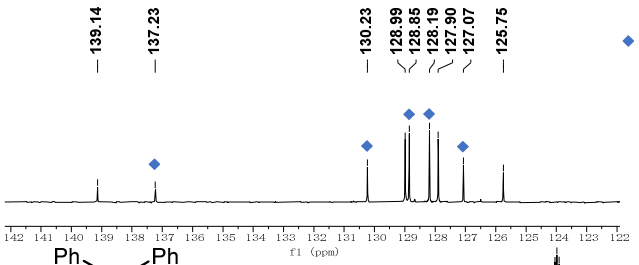

204.86
204.61
204.35
157.91
133.34
129.25
113.84
77.32
77.00
76.68
55.20
32.26
32.06
31.74
13.19
OMe
O
D
D
13C NMR, 101 MHz, CDCl3
f1 (ppm)

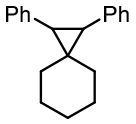


^{1}H NMR, 400 MHz, $CDCl_3$



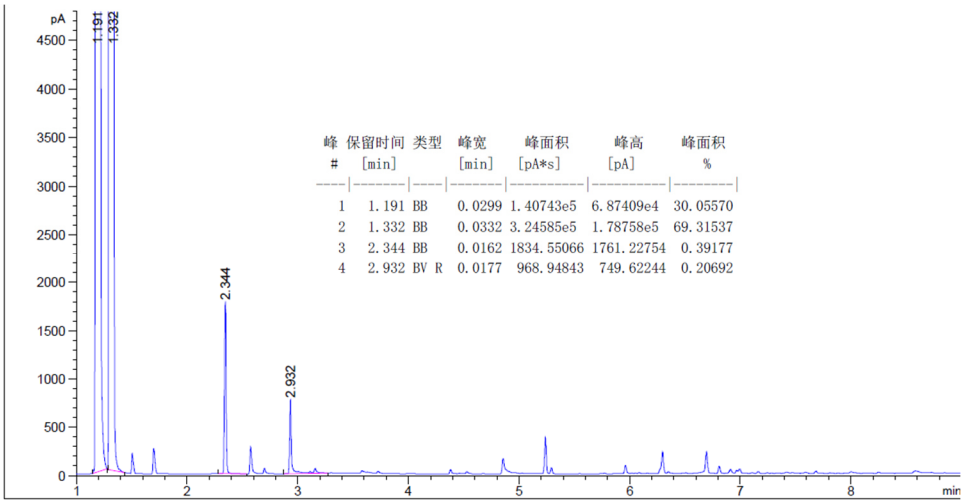






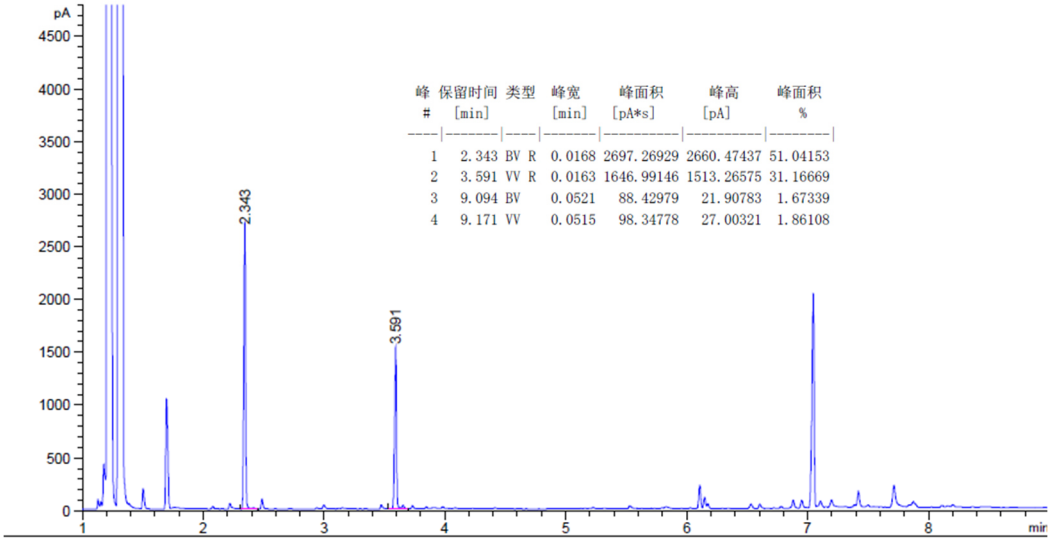
^{13}C NMR, 101 MHz, $CDCl_3$

9. GC spectra



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	1.191	BB	0.0299	1.40743e5	6.87409e4	30.05570
2	1.332	BB	0.0332	3.24585e5	1.78758e5	69.31537
3	2.344	BB	0.0162	1834.55066	1761.22754	0.39177
4	2.932	BV R	0.0177	968.94843	749.62244	0.20692

Figure S10. GC Spectrum of **3o**. RT = 2.932 min (area = 968.9); **3o**, 2.344 min (area = 1834.5): anisole (internal std.).



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	2.343	BV R	0.0168	2697.26929	2660.47437	51.04153
2	3.591	VV R	0.0163	1646.99146	1513.26575	31.16669
3	9.094	BV	0.0521	88.42979	21.90783	1.67339
4	9.171	VV	0.0515	98.34778	27.00321	1.86108

Figure S11. GC Spectrum of **3p**. RT = 3.591 min (area = 1646.99); **3p**, 2.343 min (area = 2697.3): anisole (internal std.).

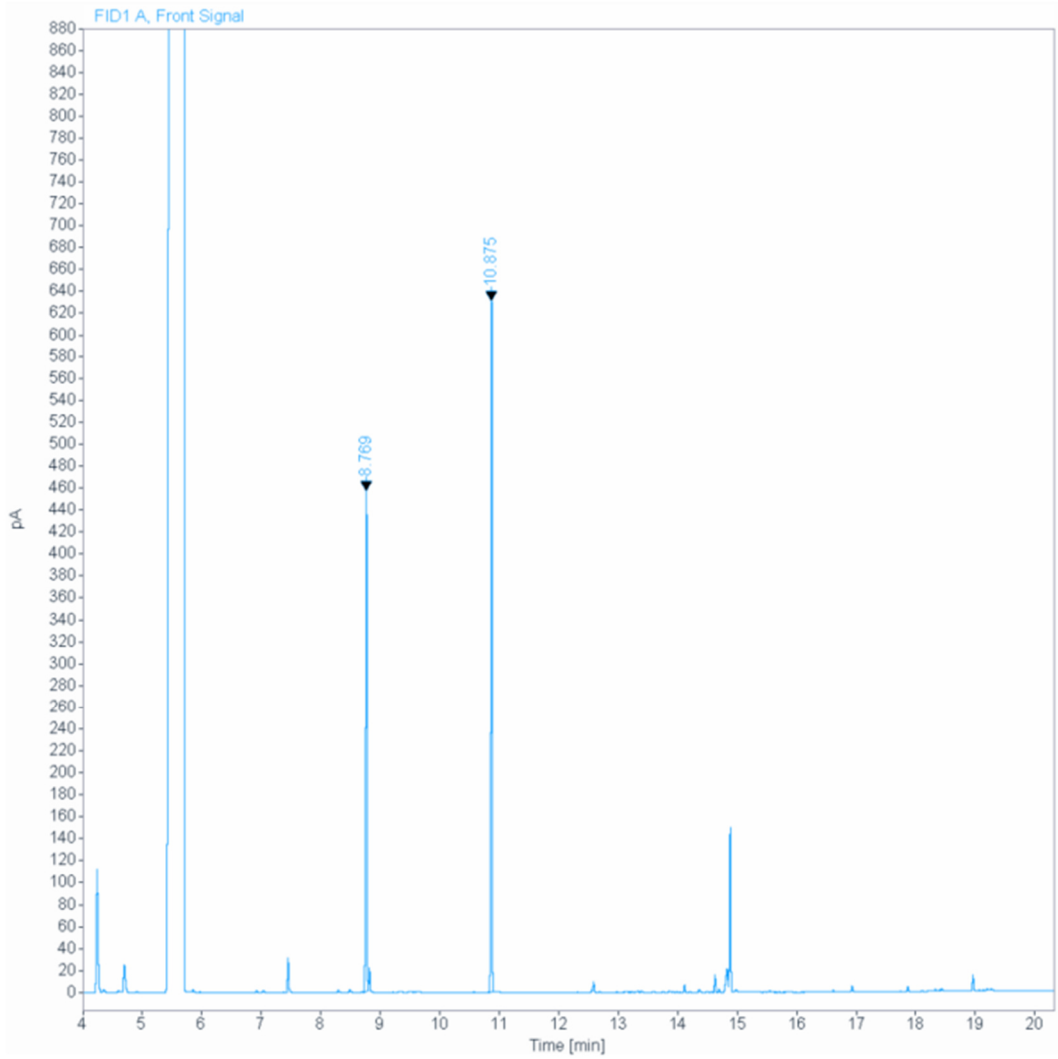


Figure S12. GC Spectrum of **3q**. *t* = 8.769 min: **3q**; 10.875 min: *n*-dodecane (internal std.).

Signal: FID1 A, Front Signal

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.769	MM	0.0247	678.8668	457.7612	43.8198	
10.875	BB	0.0209	870.3565	632.1578	56.1802	
		Sum	1549.2233			

Figure S13. Integration of the GC Spectrum of **3q**. RT = 8.769 min; **3q**, 10.875 min: *n*-dodecane (internal std.). *n*(std) = 87.25 µmol.

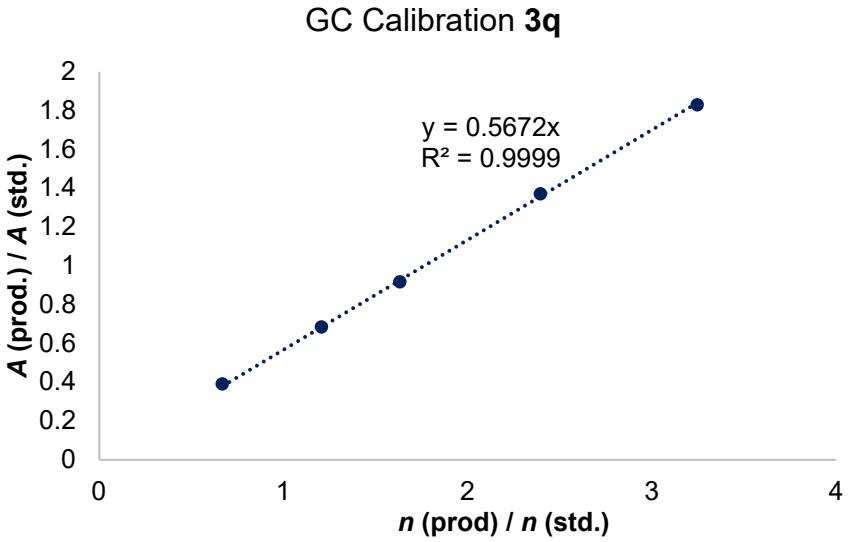


Figure S14. GC Calibration curve of **3q** with dodecane as internal standard.

10. References

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