

Supporting Information

SBA-15 Supported 1-Me-AZADO as Recyclable Catalyst for Oxidation of Alcohol

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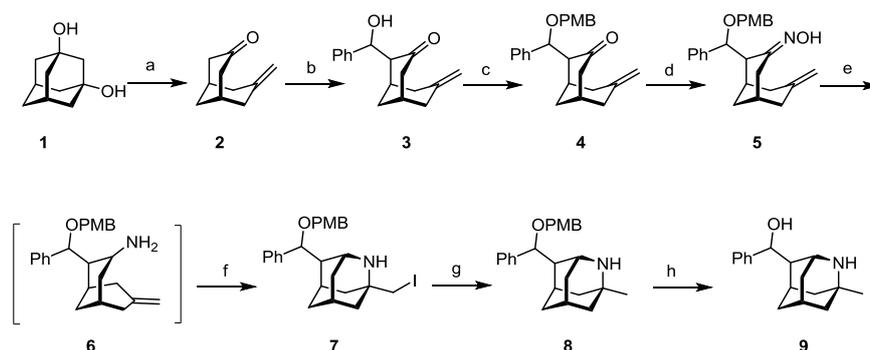
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1. General Methods and Materials

Anhydrous solvents were transferred via syringe to flame-dried glassware, which had been cooled under dry nitrogen. Tetrahydrofuran (THF) benzaldehyde and diisopropylamine were dried and distilled by standard procedures. Reagents were purchased from commercial suppliers and used without further purification unless otherwise stated. Reactions (a-h) were monitored by thin-layer chromatography (TLC). After the oxidation was completed, products were purified by 0.2 mm silica gel plates (HSGF254). All reactions were stirred under Heidolph MR Hei-Mix L and detected by SHIMADZU GC2010, low temperature reactor was used YUHUA DFY-5L/20. A system with a flame ionization detector (FID) and a SH-Rtx-Wax capillary column. GC-MS was performed on Thermo Trace ISQ instrument with TG 5MS capillary column. Column chromatography was performed on neutral silica gel (200-300 mesh), and flash column chromatography was performed on neutral silica gel (200-300 mesh) with ethyl acetate (EA)/petroleum ether (PE) or dichloromethane (DCM)/methanol (MeOH) as eluent. Products were characterized by ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz). CDCl_3 was used as the solvent with tetramethylsilane (TMS) as the internal standard. N_2 adsorption-desorption, BET and BJH were recorded on a Micromeritics ASAP 2010. Infrared spectra were recorded on a Thermo Scientific Nicolet 6700 instrument, equipped with nitrogen purge and aligned for signal clarity, was used to collect the data. TEM image were photographed by a 200 kV JEM-2100. TG/DTG were recorded on a NETZSCHTG20F3TGA209F3A-0139-L. Porton nuclear magnetic resonance (^1H -NMR) spectra were recorded using a Bruker AVANCEIII (500 MHz) and carbon-13 nuclear magnetic resonance (^{13}C -NMR) spectra were recorded using a Bruker AVANCEIII (125 MHz). High resolution mass spectra (HRMS) were recorded on an AB SCIEX 5600+ using electrospray ionization (ESI).

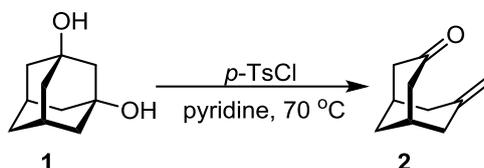
2. Experimental Section



Reagent and Conditions: (a) *p*-TsCl, pyridine, 70°C, 70.4%; (b) DIPA, *n*-BuLi, LiCl, PhCHO, THF, -78°C, 90%; (c) PMB acetimidate, CSA, DCM, rt, 92.9%; (d) NH₂OH·HCl, pyridine, 65°C, 82.7%; (e) MoO₃, NaBH₄, MeOH, 0°C; (f) I₂, MeCN, rt; (g) *n*-BuLi, THF, -78°C, 31.3% (two steps); (h) CeCl₃·7H₂O, NaI, MeCN, RT, 74.1%.

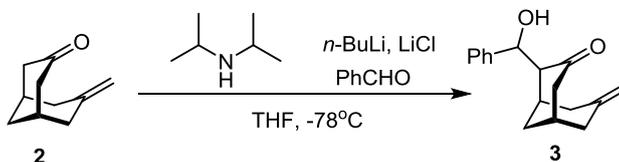
Abbreviation: PMB, *p*-Methoxybenzyl; CSA, Camphorsulfonic acid; DMAP, 4-Dimethylaminopyridine; EDCl, 3-(ethyliminomethylideneamino)-*N,N*-dimethylpropan-1-amine hydrochloride.

Synthesis of 7-methylene-bicyclo[3.3.1]nonan-3-one (2)^[1]:



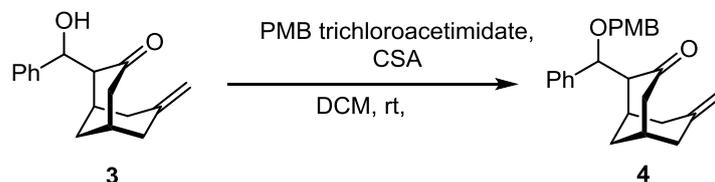
A flame-dried 1000-mL round-bottomed flask equipped with a stirring bar, added a solution of 1,3-Adamantanediol **1** (42.0 g, 250 mmol) in pyridine 500 mL, the *p*-TsCl (95.4 g, 500 mmol) slowly added dropwise to the solution, then the mixture was allowed to stir at 70°C (oil bath) for 6h. After cool to room temperature, the solvent was removed in *vacuo*, and the residue was poured into H₂O and extracted with ethyl acetate. The layers were separated and the aqueous phase extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in *vacuo*. The crude material was purified by column chromatography (Silica gel, petroleum ether: ethyl acetate = 20:1) to afford **2** (18.4 g, 150 mmol, 70%) as the white solid. The crude products can be further purified via recrystallized from *n*-hexane.

Synthesis of (hydroxy(phenyl)methyl)-7-methylenebicyclo[3.3.1]nonan-3-one (3)^[2]:



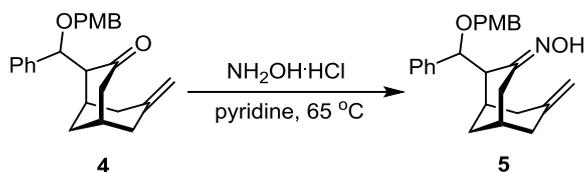
A flame-dried 500 mL, four-necked and round-bottom flask was equipped with a stirring bar, dropping funnel, LiCl 5.4 g (126.6 mmol) were introduced under nitrogen atmosphere, that were covered with dried THF (120 mL) at 0 °C. The dried diisopropylamine 7.1 g (70.2 mmol) was added by the syringe. A solution of 2.5 mol/L *n*-BuLi (28 mL, 70 mmol) was then added dropwise via a dropping funnel while stirring over a period of 30 min. The reaction solution was cooled to -78 °C (liquid nitrogen frozen ethyl acetate in Dewar flask), the color of the reaction liquid turns red. A solution of this ketone **2** (9.6 g, 63.6 mmol) in THF (40 mL) was then added dropwise *via* a dropping funnel while stirring over a period of 2 h and continue stirring for 1 hour. Benzaldehyde 12.8 mL (127.2 mmol) was slowly injected into the reaction solution with a syringe. The color of the solution changed from red to light yellow. Keep -78 °C and continue stirring for 4 h. then quenched with 6.0 g CH₃COOH and 1.6 g H₂O for 0.5h. Added aqueous NH₄Cl and recovered to room temperature, the aqueous phase was separated and extracted with ethyl acetate. The organic layers were combined, dried over Na₂SO₄, filtered and concentrated *in vacuo*. Chromatography (Silica gel, petroleum ether: ethyl acetate = 1:0 to 2:1) rapidly of the residue to afford **3** (8.3 g, 32.4 mmol, 51%) as the white solid.

Synthesis of 2-(((4-methoxybenzyl)oxy)(phenyl)methyl)-7-methylenebicyclo[3.3.1]nonan-3-one (4)^[3]:



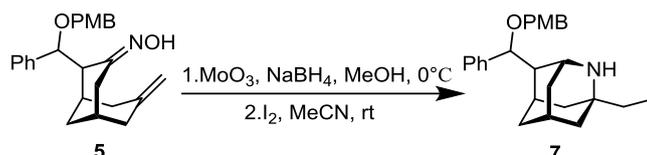
To a solution of this alcohol **3** (8.0 g, 31.2 mmol) in DCM (200 mL) was added CSA (0.73 g, 3.12 mmol) and *p*-Methoxybenzyl trichloroacetimidate^[3] (13.1 g, 46.8 mmol). The reaction mixture was stirred at r.t under air for 12 h. then quenched with aqueous NaHCO₃ and the aqueous phase extracted with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄, filtered and concentrated *in vacuo*. Chromatography (Silica gel, petroleum ether: ethyl acetate = 1:0 to 50:1) of the residue to afford (10.9 g, 29.0 mmol, 92.9%) of **4** as a pale-yellow liquid.

Synthesis of 2-(((4-methoxybenzyl)oxy)(phenyl)methyl)-7-methylenebicyclo[3.3.1]nonan-3-one oxime (5)^[4]:



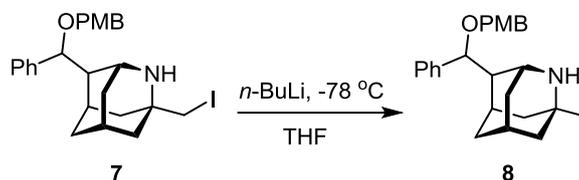
To a solution of ketone **4** (10.9 g, 29.0 mmol) in pyridine (200 mL) was added $\text{NH}_2\text{OH}\cdot\text{HCl}$ (6.0 g, 87 mmol). The reaction mixture was stirred at 65 °C (oil bath) for 5 h. The solvent was partly removed *in vacuo*, and the residue was poured into H_2O and extracted with EA. The layers were separated and the aqueous phase extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered and concentrated *in vacuo*. Chromatography (Silica gel, petroleum ether: ethyl acetate = 1:0 to 1:1) of the residue to afford (9.4 g, 24.0 mmol, 82.7%) of **5** as a pale-yellow liquid.

Synthesis of 1-(iodomethyl)-4-(((4-methoxybenzyl)oxy)(phenyl)methyl)-2-azaadamantane (**7**):



To a mixture of oxime **5** (4.7 g, 12.0 mmol) and MoO_3 (2.9 g, 20.1 mmol) in dry MeOH (120 mL) at 0 °C (jacketed three-neck flask connected low temperature reactor) nitrogen atmosphere was added NaBH_4 (1.36 g, 36 mmol) portionwise. The resulting dark brown reaction mixture was stirred at r.t for 6 h, then quenched with acetone and filtered through celite. The Celite was rinsed with MeOH, and the filtrate was concentrated *in vacuo*. The resulting residue was diluted with water (100 mL) and Et_2O (200 mL). The organic layer was separated, washed with a few brine, dried over Na_2SO_4 , filtered and concentrated *in vacuo* to afford 2.4 g of crude **7** as thick liquid, that was carried on without further purification. To a suspension of this amine (2.4 g, 6.4 mmol, crude) in MeCN (50 mL) at 0 °C was added I_2 (3.25 g, 12.8 mmol). The reaction mixture was stirred at rt for 3 h and then quenched with aqueous $\text{Na}_2\text{S}_2\text{O}_3$. The resulting yellow mixture was extracted with ethyl acetate, and the combined organic layers were dried over Na_2SO_4 , filtered and concentrated *in vacuo*. Chromatography (Silica gel, dichloromethane: methanol = 1:0 to 100:1) of the residue to afford (1.0 g, 2.0 mmol, 31%, 2 steps) of **7** as thick pale-yellow liquid.

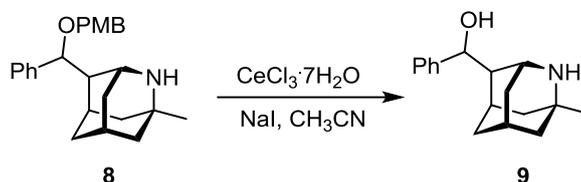
Synthesis of 4-(((4-methoxybenzyl)oxy)(phenyl)-1-methyl-2-azaadamantane (**8**):



To a solution of **7** (1.5 g, 3.0 mmol) in dry THF (20 mL) was added 2.5 mol/L *n*-BuLi (7.5 mL, 18.8 mmol) at -78 °C (liquid nitrogen frozen ethyl acetate in Dewar flask). The reaction mixture was stirred under nitrogen for 30 min, then quenched with aqueous NH_4Cl . The aqueous phase was extracted twice with ethyl acetate, and the combined organic layers were dried over Na_2SO_4 , filtered and concentrated *in vacuo*. Chromatography (Silica gel, dichloromethane: methanol:

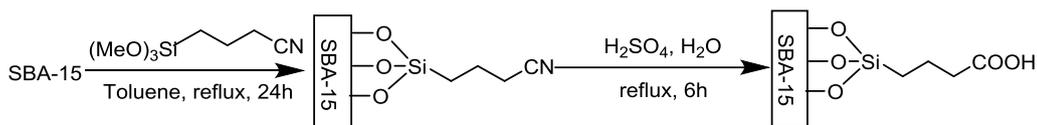
triethylamine = 1:0:0 to 0:1:0 to 0:100:1) of the residue to afford (0.49 g, 1.4 mmol, 43.3%) of **8** as a pale-yellow powder.

Synthesis of 1-methyl-2-azaadamantan-4-yl)(phenyl)methanol (**9**):



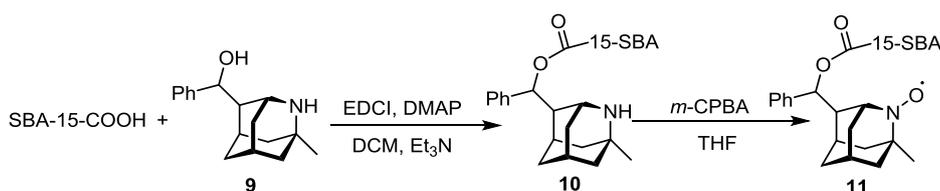
To a solution of **8** (1.0 g, 2.7 mmol) in MeCN (20 mL) was added $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (1.46 g, 4 mmol), NaI (0.40 g, 2.7 mmol). The reaction mixture was refluxed at 110 °C (oil bath) for 24 h, then filter, concentrated by further solvent distillation. Chromatography (Silica gel, dichloromethane: methanol = 1:0 to 50:1) of the residue to afford (0.52 g, 2.0 mmol, 74.1%) of **9** as a light-yellow powder.

Preparation of SBA-15 surface bound carboxylic acid (SBA-15-COOH):



The preparation of SBA-15 surface bound carboxylic acid was achieved according to the known procedure described by Clark.^[5,6] The SBA-15 (6 g) was allowed to react with 3-cyanopropyltriethoxysilan (5 mmol, 1.15 g, Fluka) in refluxing (oil bath) dry toluene (150 mL) under nitrogen atmosphere for 24 h. The solid was filtered off and was washed thoroughly with hot toluene and ethanol. It was dried in air at 90 °C overnight to furnish the corresponding surface bound cyanopropyl group at a loading $0.56 \text{ mmol} \cdot \text{g}^{-1}$ (Determined by elemental analysis). The SBA-15-CN was hydrolyzed by heating in 64.7% (wt) aqueous sulfuric acid at 150 °C (oil bath) for 6h. After cooling to room temperature, the resulting solid was filtered off and filter cake was washed with an excess of deionized water. Drying in an oven at 110 °C overnight furnished the corresponding SBA-15-COOH with approximately the loading $0.25 \text{ mmol} \cdot \text{g}^{-1}$.

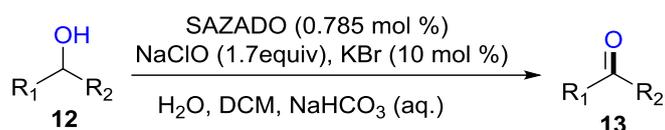
Synthesis of SBA-15-supported AZADO (**11**):



To a mixture of SBA-15-COOH (1.0 g), EDCI (0.66 mmol, 126 mg), DMAP (0.36 mmol, 44 mg) and

9 (84 mg, 0.33 mmol) in dry DCM (15 mL) at r.t was added Et₃N (0.66 mmol, 67mg). The reaction mixture was stirred under nitrogen for 24h. The resulting solid was filtered off and filter cake was washed with an excess of DCM. Drying in an oven at 70 °C overnight furnished the corresponding **10**. To a suspension of **10** (1g) in dry THF 20 mL at r.t was added *m*-CPBA (75%) (0.23 g, 0.66 mmol). The reaction mixture was stirred at r.t for 4.5 h and then quenched with sat. aq. NaHCO₃. The resulting solid was filtered off and filter cake was washed with an excess of DCM. Drying in an oven at 70 °C overnight furnished the corresponding **11** (SAZADO).

General procedure for oxidation of alcohols using SAZADO:



TO a 15-mL Schlenk tube equipped with a magnetic stirrer bar, were added alcohols **12** (0.2 mmol), SAZADO (20 mg, 0.785 mol%), dichloromethane (0.5 mL) and KBr (2.4 mg, 10 mol%)-saturated aqueous NaHCO₃ (0.5 mL), then the mixture was cooled to 0 °C (ice-water bath) with vigorous stirring. 7.5% (wt) NaClO (0.34 mmol) in saturated NaHCO₃ (0.21 mL) was slowly added. The reaction mixture was stirred for 10-20 min. Then, the progress of the reaction was monitored by means of GC and the reaction mixture quenched with sodium sulfite solution (1 mL). After the mixture was extracted with 2-3 times with methyl *tert*-butyl ether, the organic phases were combined, dried over anhydrous sodium sulfate, the reaction mixture was then concentrated. For isolation, the residue was purified by flash column chromatography on silica gel (solvents see Spectra Data of Products section for detail) to **13**.

1 mmol-Scale Synthesis for Products 13g

To a 50-ml, single-neck and round bottom flask equipped with a magnetic stirrer bar, were added *p*-tolylmethanol (122 mg, 1 mmol), SAZADO (100 mg, 0.393 mol%), dichloromethane (2.5 mL) and KBr (12 mg, 10 mol%)-saturated aqueous NaHCO₃ (2.5 mL), then the mixture was cooled to 0 °C (ice-water bath) with vigorous stirring. 7.5% (wt) NaClO (0.8 g) in saturated NaHCO₃ (1.7 mmol) was slowly added for 2 min. The reaction mixture was stirred for 10 min. Then, the progress of the reaction was monitored by means of GC and the catalyst is isolated by filtered, the liquid mixture quenched with sodium sulfite solution (5 ml). After the mixture was extracted with 2-3 times with methyl *tert*-butyl ether, the organic phases were combined, dried over anhydrous sodium sulfate, the reaction mixture was then concentrated. For isolation, the residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl ether = 1:0 to 10:1) to **13g** (114 mg, 95%).

Recycling procedure for oxidation of benzyl alcohol using SAZADO:

After the completion of first reaction of benzyl alcohol to afford benzaldehyde in quantitative yield, the catalyst was separated by centrifuge and finally used directly for a subsequent round of reaction. A new reaction was then performed with fresh reactants, under the same conditions.

Table S1. Recycling experiments.

Recycle	Conversion (%)	Selectivity (%)
1 st	99	>99
2 nd	99	>99
3 rd	99	>99
4 th	99	>99
5 th	99	>99
6 th	97	>99
7 th	86	>99
8 th	85	>99
9 th	85	>99
10 th	69	>99

The conversion rates obtained in the oxidation of benzyl alcohol to afford benzaldehyde in the presence of SAZADO catalyst after 10min.

Table S2. Elemental analysis of functionalized molecular sieve SAB-15

Compound	N %	mmol g ⁻¹
SBA-15-CN	0.80	0.557
SBA-15-COOH	0.45	0.250
SAZADO(fresh)	0.56	0.0785
Re-SAZADO(10th)	0.11	

Typical procedure for the control experiments of lower conversion:

A mixture of benzyl alcohol (0.4 mmol), KBr (4.8 mg, 10 mol%), and SAZADO (0.393 mol%, 10 mg) in CH₂Cl₂-saturated aqueous NaHCO₃ (1:1 v/v, 2.00 mL), the mixture was cooled to 0 °C (ice-water bath) with vigorous stirring. 7.5% (wt) NaClO (0.68 mmol) in saturated NaHCO₃ (0.42 mL) was slowly added. The reaction mixture was stirred for 2 min. Then, the progress of the reaction

was monitored by means of GC.

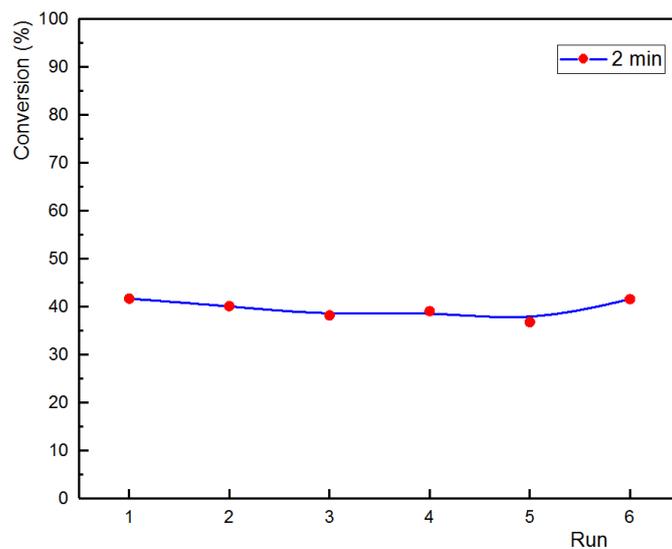
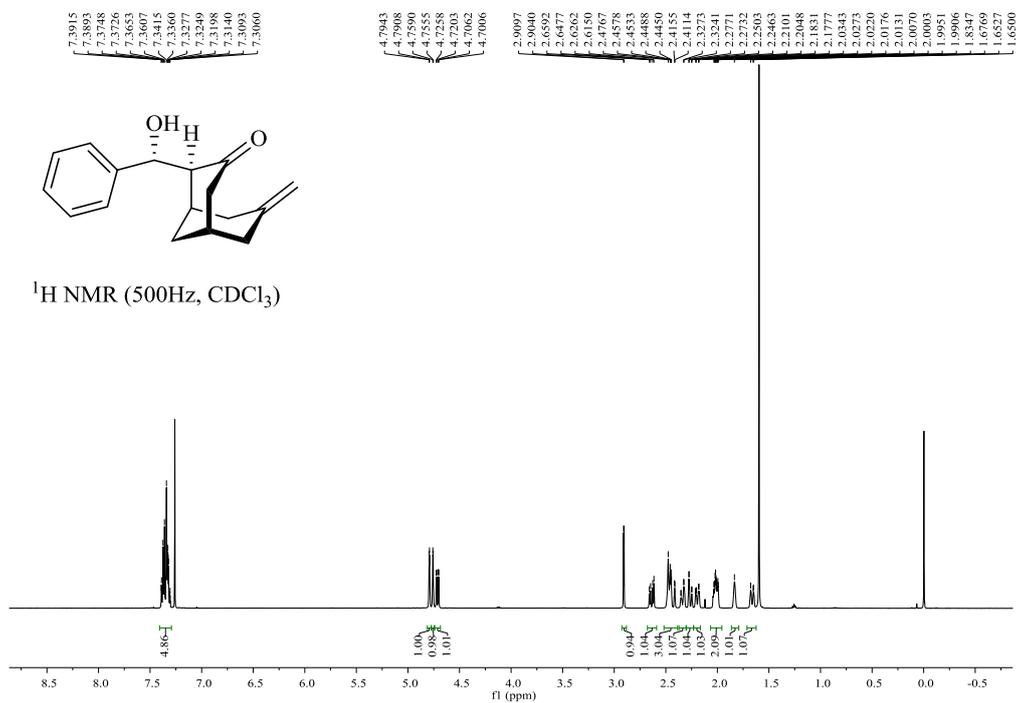


Figure S1. Control experiments for cycle stability of SAZADO

Structure study of compound 3

i) A comparison with the ^1H NMR spectra of compound 3 and chiral compounds 3I



^1H NMR Spectra of 3I

Table S3. Thermodynamic data

Structure	TCG	Single-point Energy	TCG + Single-point Energy
3I	0.296178	-810.2398988	-809.9437208
3II	0.297433	-810.23963	-809.9421977
3II'	0.294456	-810.2365952	-809.9421392
3I			
C	-0.462028000	-0.963152000	0.133986000
C	-1.057650000	-1.367425000	-1.222284000
C	-2.462416000	-0.768700000	-1.374796000
C	-3.379795000	-1.281229000	-0.247318000
C	-2.777753000	-0.966534000	1.098586000
C	-1.371830000	-1.482926000	1.266969000
C	-2.367037000	0.761351000	-1.354292000
C	-1.510174000	1.346003000	-0.243346000
C	-0.296089000	0.562156000	0.239749000
O	-1.689799000	2.489159000	0.136127000
C	0.924378000	1.158439000	-0.537913000
C	-3.394910000	-0.221479000	2.014871000
C	2.196466000	0.397580000	-0.240982000
C	2.880060000	0.631828000	0.953067000
C	4.022775000	-0.098883000	1.261365000
C	4.493898000	-1.070128000	0.379264000
C	3.820758000	-1.301832000	-0.816739000
C	2.678260000	-0.566702000	-1.125185000
H	0.522902000	-1.425385000	0.253109000
H	-0.412566000	-1.027979000	-2.043217000
H	-1.108071000	-2.461285000	-1.288119000
H	-2.890645000	-1.074825000	-2.336011000
H	-4.377937000	-0.838948000	-0.337949000
H	-3.488436000	-2.369808000	-0.355055000
H	-0.965653000	-1.193779000	2.242175000
H	-1.378699000	-2.581482000	1.224150000
H	-3.348274000	1.243700000	-1.303008000
H	-1.895607000	1.103989000	-2.287927000
H	-0.130561000	0.844789000	1.287836000
H	-2.921157000	0.020453000	2.962404000
H	-4.395028000	0.169946000	1.849415000
H	2.517510000	1.407704000	1.620263000
H	4.552207000	0.093204000	2.189727000
H	5.387385000	-1.637829000	0.620122000
H	4.188664000	-2.047964000	-1.514415000

H	2.159100000	-0.739023000	-2.065879000
H	0.722833000	1.082371000	-1.621153000
O	1.114431000	2.501813000	-0.164934000
H	0.243505000	2.894169000	0.023956000
3II			
C	-0.964902000	-0.506769000	1.264839000
C	-0.635038000	-1.693323000	0.344121000
C	-1.381264000	-1.544183000	-0.986126000
C	-2.902444000	-1.471353000	-0.747121000
C	-3.235694000	-0.390027000	0.248766000
C	-2.483217000	-0.513647000	1.549619000
C	-0.852303000	-0.300534000	-1.706245000
C	-0.726456000	0.948869000	-0.856665000
C	-0.569129000	0.854870000	0.658544000
O	-0.648870000	2.041175000	-1.394976000
C	0.854970000	1.351257000	1.058426000
O	1.028741000	2.698883000	0.699924000
C	-4.039728000	0.635244000	-0.031586000
C	1.962306000	0.466352000	0.514145000
C	2.496418000	-0.561942000	1.291326000
C	3.465756000	-1.417071000	0.771957000
C	3.919237000	-1.242714000	-0.532815000
C	3.410273000	-0.201438000	-1.307155000
C	2.443153000	0.652339000	-0.784326000
H	-0.432154000	-0.629148000	2.216985000
H	0.442619000	-1.759195000	0.159812000
H	-0.936813000	-2.623606000	0.841977000
H	-1.176157000	-2.415378000	-1.618460000
H	-3.430241000	-1.303285000	-1.692414000
H	-3.234550000	-2.441822000	-0.351458000
H	-2.749822000	0.301061000	2.231410000
H	-2.745864000	-1.460531000	2.041791000
H	-1.440876000	-0.038824000	-2.591808000
H	0.173314000	-0.500607000	-2.051639000
H	-1.238545000	1.629289000	1.057192000
H	0.892476000	1.303322000	2.155037000
H	0.501807000	2.864590000	-0.102685000
H	-4.237347000	1.417579000	0.696470000
H	-4.534285000	0.722236000	-0.995242000
H	2.148592000	-0.694516000	2.313938000
H	3.872333000	-2.212825000	1.388790000
H	4.676857000	-1.905044000	-0.939985000

H	3.775710000	-0.047547000	-2.318077000
H	2.062361000	1.478211000	-1.379456000
3H'			
C	-1.568794000	1.361189000	-0.197002000
C	-2.189251000	1.222544000	1.200021000
C	-2.604448000	-0.234519000	1.442754000
C	-3.660878000	-0.649600000	0.400272000
C	-3.142851000	-0.437966000	-1.001190000
C	-2.607837000	0.949084000	-1.259325000
C	-1.367375000	-1.144308000	1.375373000
C	-0.493700000	-0.934828000	0.143558000
C	-0.287751000	0.509305000	-0.316663000
O	0.083260000	-1.856138000	-0.385817000
C	0.884012000	1.114535000	0.494508000
O	0.947754000	2.485532000	0.141311000
C	-3.100780000	-1.411019000	-1.909454000
C	2.195320000	0.409252000	0.214785000
C	2.669694000	-0.587142000	1.066304000
C	3.867623000	-1.239816000	0.791202000
C	4.606031000	-0.893072000	-0.337047000
C	4.139656000	0.104670000	-1.190062000
C	2.939042000	0.751785000	-0.916105000
H	-1.288687000	2.402830000	-0.373329000
H	-1.483201000	1.554591000	1.971193000
H	-3.067664000	1.875931000	1.275459000
H	-3.048387000	-0.330287000	2.440524000
H	-3.953870000	-1.695116000	0.546719000
H	-4.556693000	-0.030890000	0.555640000
H	-2.173058000	1.011283000	-2.262989000
H	-3.437657000	1.669764000	-1.216242000
H	-1.630677000	-2.205730000	1.416167000
H	-0.727536000	-0.935489000	2.246871000
H	0.038964000	0.466211000	-1.362977000
H	0.661247000	1.015619000	1.570228000
H	1.766484000	2.842549000	0.515733000
H	-2.692510000	-1.243509000	-2.902359000
H	-3.464372000	-2.410855000	-1.688390000
H	2.094975000	-0.857209000	1.950006000
H	4.225740000	-2.016560000	1.459654000
H	5.542518000	-1.398773000	-0.550906000
H	4.711854000	0.377676000	-2.071540000
H	2.568141000	1.532252000	-1.574991000

3. Characterizations of Catalyst

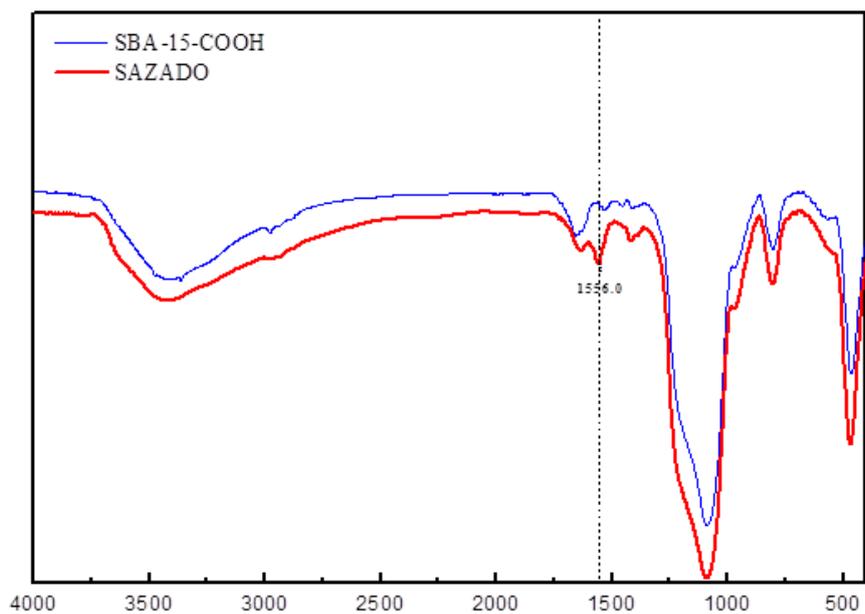


Figure S3. FTIR spectra of SBA-15-COOH and SAZADO

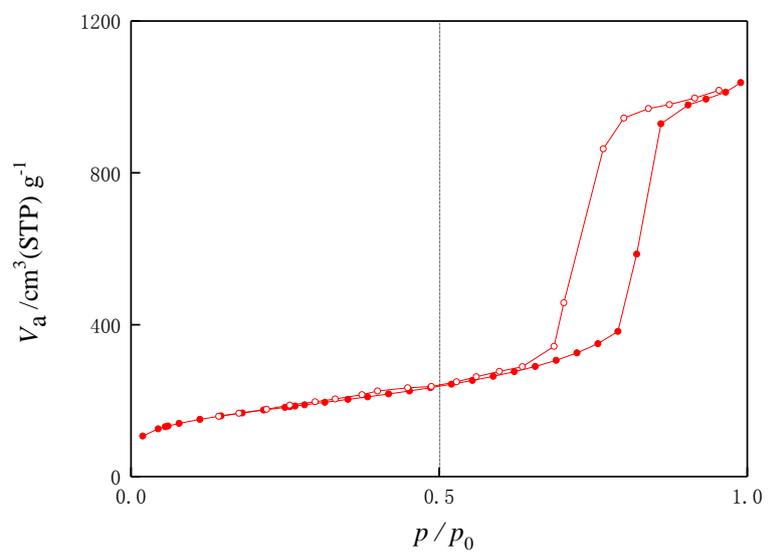


Figure S4. N₂ adsorption-desorption isotherm of SBA-15

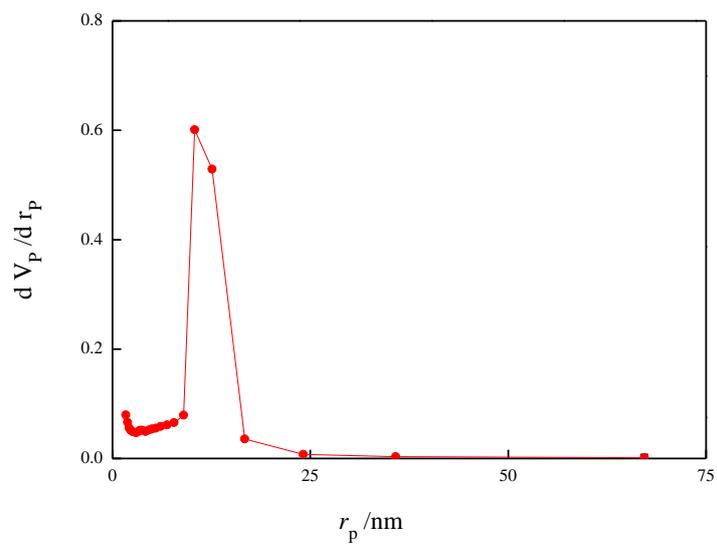


Figure S5. BJH average pore size diagram of SBA-15

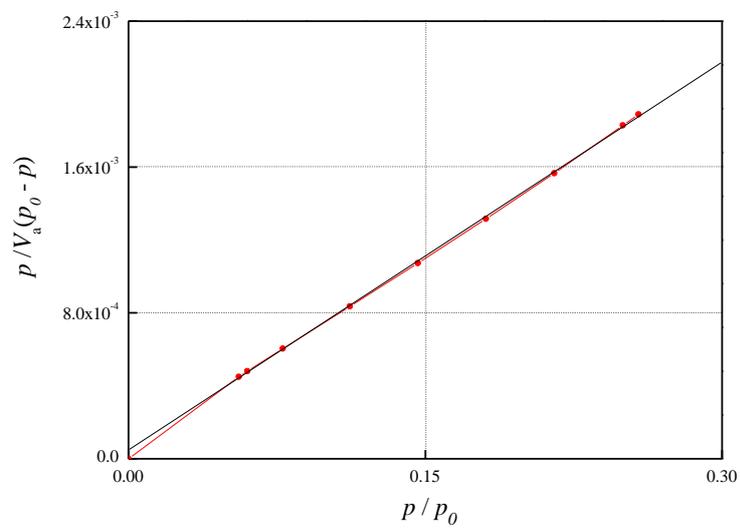


Figure S6. BET plot of SBA-15

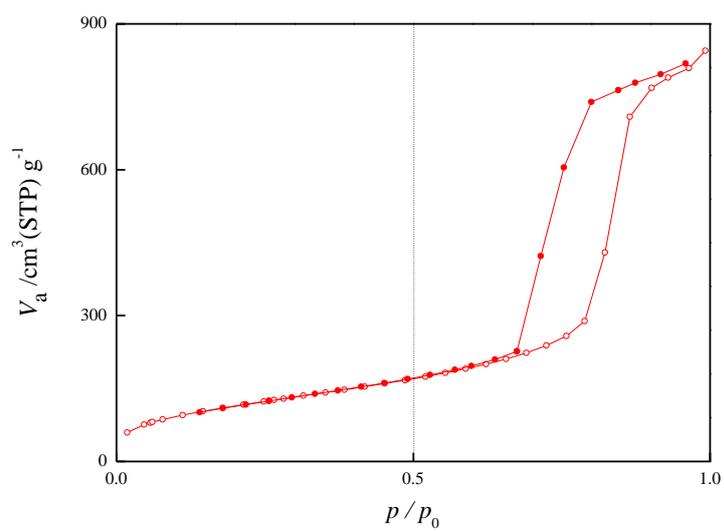


Figure S7. N₂ adsorption-desorption isotherm of SBA-15-COOH

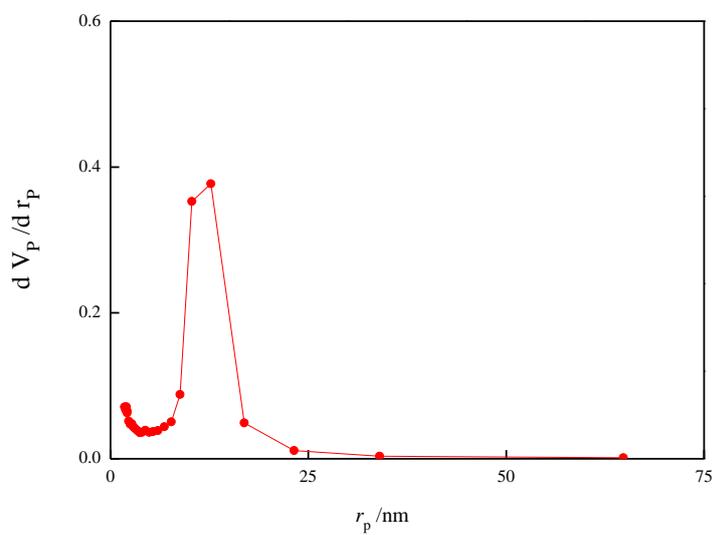


Figure S8. BJH average pore size diagram of SBA-15-COOH

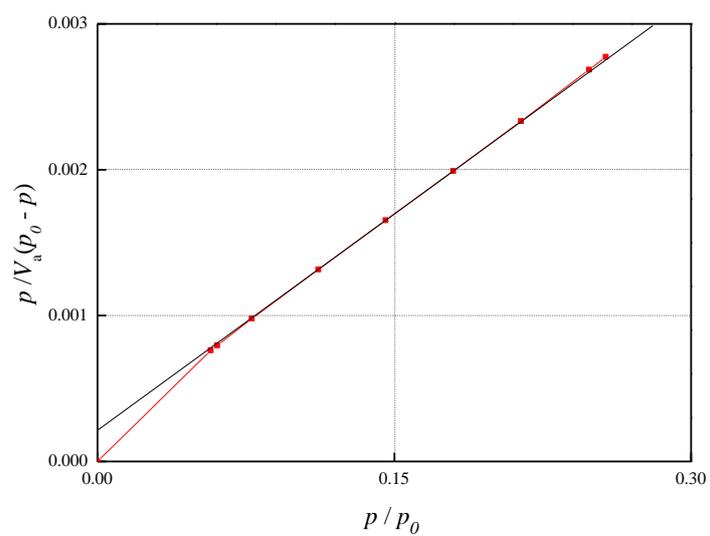


Figure S9. BET plot of SBA-15-COOH

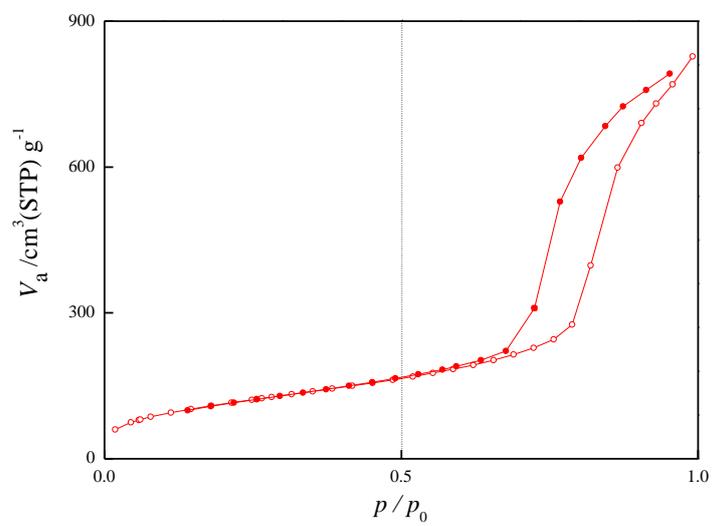


Figure S10. N_2 adsorption-desorption isotherm of SAZADO

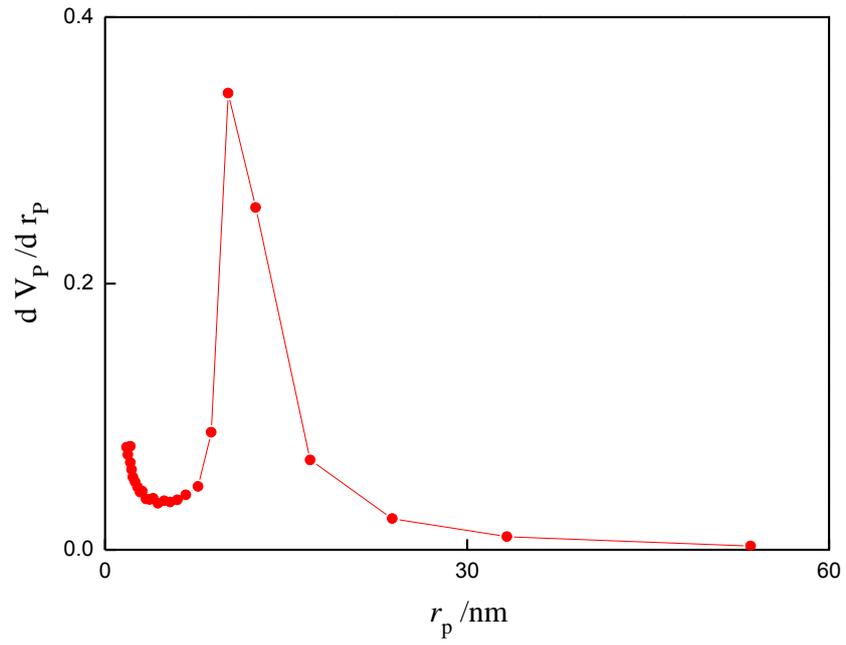


Figure S11. BJH average pore size diagram of SAZADO

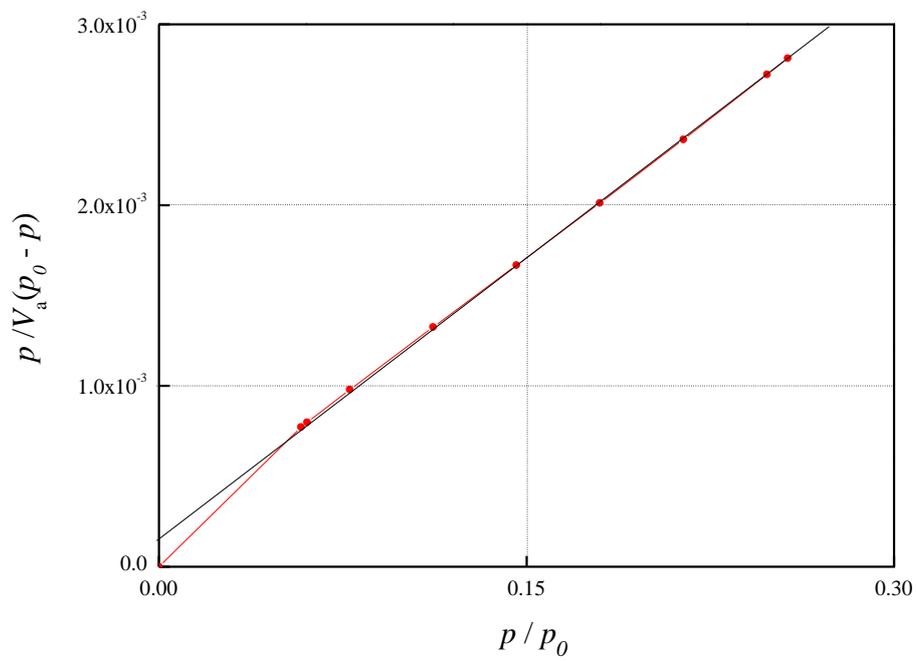


Figure S12. BET plot of SAZADO

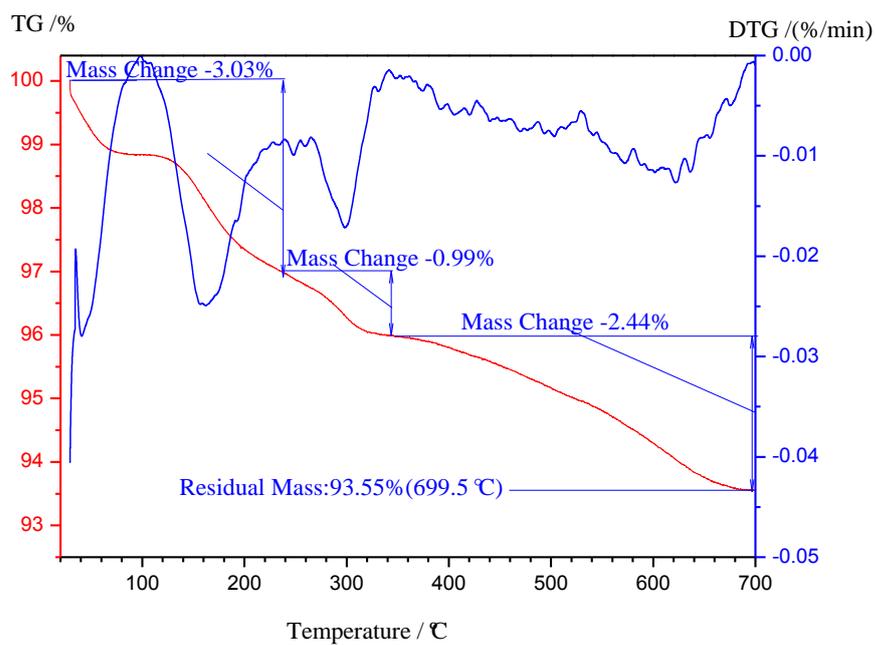


Figure S13. Thermogravimetric analysis curve of SBA-15-COOH

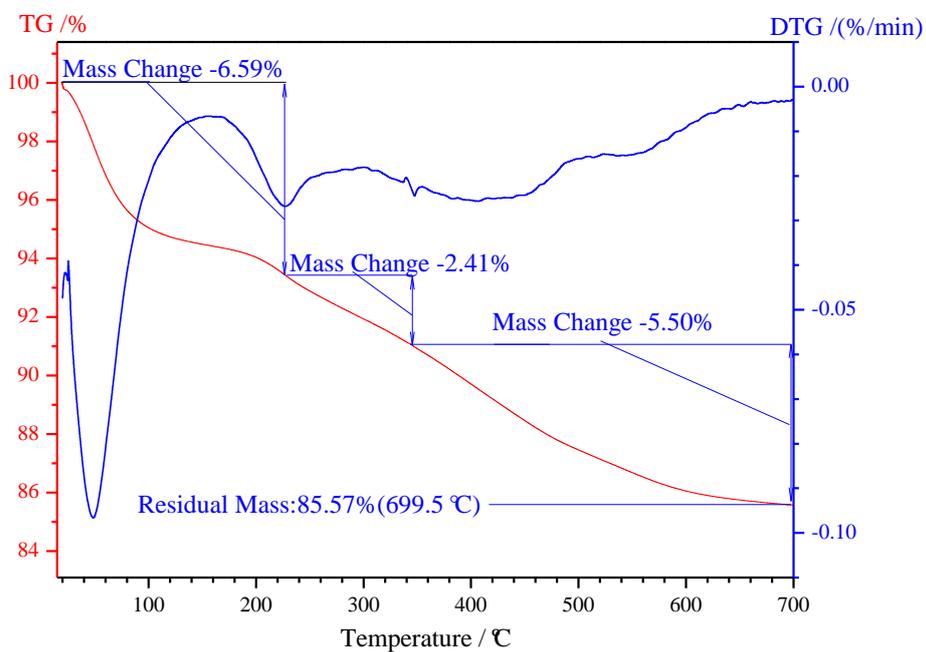


Figure S14. Thermogravimetric analysis curve of SAZADO

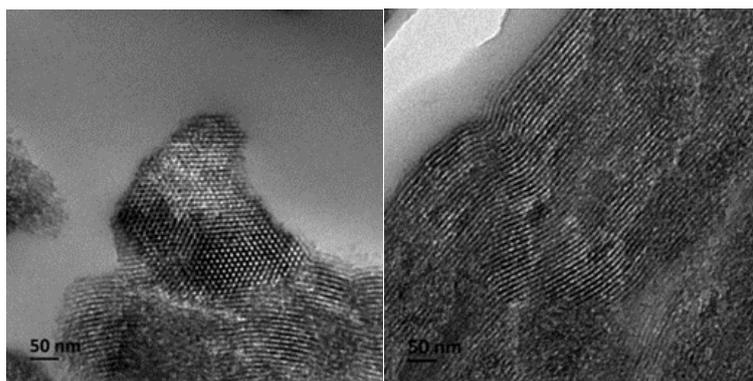


Figure S15. TEM images of SBA-15

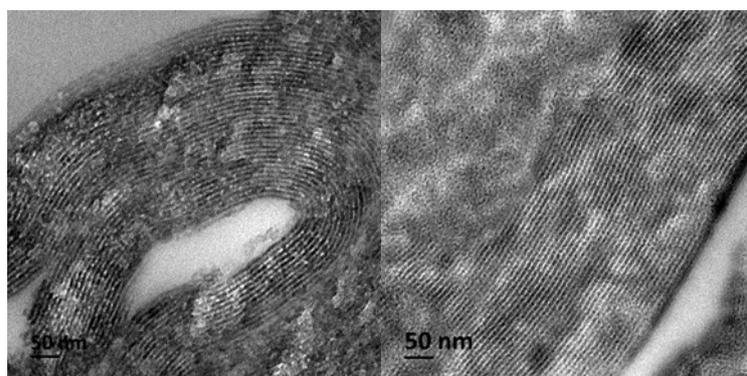


Figure S16. TEM image of SAZADO

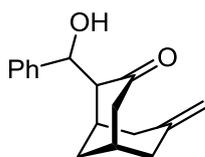
4. Spectra Data of Products



7-Methylene-bicyclo[3.3.1]nonan-3-one(2)^[4]: ¹HNMR (500 MHz, CDCl₃) δ 4.76 (t, *J*

= 1.8 Hz, 2H), 2.43 (d, *J* = 4.4 Hz, 2H), 2.40-2.31(m, 6H), 2.25 (d, *J* = 13.5 Hz, 2H), 1.97-1.85 (m, 2H).

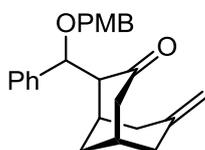
¹³C NMR (125 MHz, CDCl₃) δ 211.0, 141.7, 114.6, 47.3, 41.4, 32.0, 30.8.



(hydroxy(phenyl)methyl)-7-methylenebicyclo[3.3.1]nonan-3-one (3): ¹HNMR

(500 MHz, CDCl₃) δ 7.40-7.30 (m, 5H), 4.79 (d, *J* = 1.8 Hz, 1H), 4.75 (d, *J* = 1.8 Hz, 1H), 4.71 (dd, *J* = 9.9, 2.8Hz, 1H), 2.94 (d, *J* = 2.9 Hz, 1H), 2.70-2.58 (m, 1H), 2.51-2.38 (m, 3H), 2.37-2.30 (m, 1H), 2.26 (dd, *J* = 13.4, 2.0 Hz, 1H), 2.36-2.15 (m, 1H), 2.06-1.95 (m, 2H), 1.90-1.78 (m, 1H), 1.67-1.63

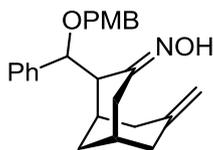
(m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 213.9, 141.7, 128.9, 128.5, 127.0, 114.9, 74.9, 74.8, 63.0, 62.9, 46.0, 42.5, 41.5, 32.7, 32.6, 31.2, 31.1, 28.6. HRMS (ESI) *m/z* calcd for C₁₇H₂₀O₂ [M+Na]⁺: 279.1356, found: 279.1363.



2-(((4-methoxybenzyl)oxy)(phenyl)methyl)-7-methylenebicyclo[3.3.1]

nonan-3-one (4): ¹HNMR (500 MHz, CDCl₃) δ 7.40-7.30 (m, 5H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.87- 6.82 (m, 2H), 4.77-4.68 (m, 2H), 4.47-4.42 (m, 2H), 4.01 (d, *J* = 12.1 Hz, 1H), 3.80 (s, 3H), 2.64 (d, *J* = 8.9 Hz, 1H), 2.30-2.18 (m, 6H), 2.07 (d, *J* = 13.6 Hz, 1H), 1.94-1.81 (m, 2H), 1.52 (d, *J* = 12.5 Hz, 1H). ¹³C

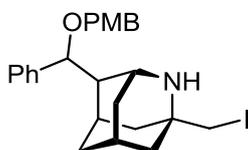
NMR (125 MHz, CDCl₃) δ 210.1, 159.2, 141.3, 139.7, 130.1, 129.5, 128.7, 128.3, 127.6, 114.7, 113.8, 80.3, 69.5, 62.1, 55.3, 46.2, 42.2, 41.2, 32.7, 31.2, 28.7. HRMS (ESI) *m/z* calcd for C₂₅H₂₉O₃ [M+H]⁺: 377.2111, found: 377.2113.



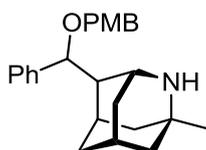
2-(((4-methoxybenzyl)oxy)(phenyl)methyl)-7-methylenebicyclo[3.3.1]

nonan-3-one oxime (5): ¹HNMR (500 MHz, CDCl₃) δ 7.42-7.30 (m, 5H), 7.19-7.17 (m, 2H), 6.91 - 6.83 (m, 2H), 4.74-4.72 (d, *J* = 6.9 Hz, 1H), 4.60-4.55 (m, 1H), 4.50-4.44 (m, 1H), 4.34 (d, *J* = 9.2 Hz, 1H), 4.10-4.03 (m, 1H), 3.79 (d, *J* = 2.0 Hz, 3H), 3.16 (d, *J* = 15.7 Hz, 1H), 2.74 (d, *J* = 9.2 Hz, 1H), 2.28 - 2.03 (m, 5H), 1.78 (d, *J* = 13.2 Hz, 1H), 1.72-1.68 (m, 2H), 1.41 (d, *J* = 12.9 Hz, 1H). ¹³C NMR (125

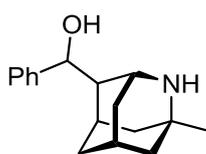
MHz, CDCl₃) δ 159.1, 157.2, 142.8, 140.6, 130.6, 129.4, 128.6, 128.0, 127.8, 113.8, 111.5, 80.0, 69.5, 55.3, 52.6, 41.6, 41.5, 31.9, 29.2, 28.8, 27.7. HRMS (ESI) m/z calcd for C₂₅H₃₀NO₃ [M+H]⁺: 392.2218, found: 392.2220.



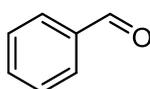
1-(iodomethyl)-4-(((4-methoxybenzyl)oxy)(phenyl)methyl)-2-azaadamantane (7): ¹H NMR (500 MHz, CDCl₃) δ 7.40-7.29 (m, 5H), 7.19-7.13 (m, 2H), 6.88-6.81 (m, 2H), 4.38-4.32 (m, 2H), 4.03 (d, J = 11.7 Hz, 1H), 3.84 (s, 1H), 3.78 (s, 3H), 3.34-3.25 (m, 2H), 2.20 (d, J = 10.4 Hz, 1H), 2.01 (s, 1H), 1.90-1.83 (m, 1H), 1.78 (d, J = 13.0 Hz, 2H), 1.74-1.68 (m, 1H), 1.67-1.60 (m, 2H), 1.54 (dd, J = 12.7, 3.5 Hz, 1H), 1.42-1.31 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 159.2, 140.2, 130.3, 129.6, 128.6, 128.1, 127.7, 113.8, 79.9, 69.6, 55.3, 51.0, 49.2, 49.1, 42.0, 40.8, 30.4, 29.1, 28.2, 27.0, 21.0. HRMS (ESI) m/z calcd for C₂₅H₃₁INO₂ [M+H]⁺: 504.1394, found: 504.1393.



4-(((4-methoxybenzyl)oxy)(phenyl)-1-methyl-2-azaadamantane (8): ¹H NMR (500 MHz, CDCl₃) δ 7.40-7.28 (m, 5H), 7.16 (d, J = 8.6 Hz, 2H), 6.88-6.81 (m, 2H), 4.37-4.33 (m, 2H), 4.06 (d, J = 11.6 Hz, 1H), 3.79 (s, 3H), 3.64 (s, 1H), 2.59 (s, 1H), 2.06 (d, J = 10.5 Hz, 1H), 1.99 (s, 1H), 1.84 (d, J = 12.5 Hz, 1H), 1.74-1.63 (m, 3H), 1.53-1.49 (m, 2H), 1.45-1.30 (m, 3H), 0.97 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 159.3, 141.2, 130.9, 129.6, 128.6, 127.9, 127.8, 113.9, 81.3, 69.9, 55.4, 51.0, 48.5, 48.3, 45.8, 44.1, 31.1, 30.7, 30.5, 29.0, 27.7. HRMS (ESI) m/z calcd for C₂₅H₃₂NO₂ [M+H]⁺: 378.2428, found: 378.2432.

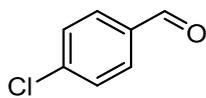


1-methyl-2-2-azaadamantan-4-yl(phenyl)methanol (9): ¹H NMR (500 MHz, CDCl₃) δ 7.43-7.27 (m, 5H), 4.82 (d, J = 10.7 Hz, 1H), 4.28 (s, 1H), 4.20 (s, 1H), 2.80 (d, J = 10.6 Hz, 1H), 2.52 (s, 2H), 2.41-2.26 (m, 2H), 2.25-2.14 (m, 2H), 2.08-1.98 (m, 2H), 1.93 (d, J = 13.2 Hz, 1H), 1.65-1.57 (m, 1H), 1.53 (dd, J = 13.8, 3.3 Hz, 1H), 1.48 (s, 3H), 1.39 (d, J = 13.0 Hz, 1H), 1.25 (t, J = 7.1 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 141.4, 129.1, 128.7, 127.1, 73.4, 56.5, 51.3, 46.0, 40.0, 38.7, 29.0, 27.3, 27.0, 25.6, 12.4. HRMS (ESI) m/z calcd for C₁₇H₂₄NO [M+H]⁺: 258.1853, found: 258.1847.



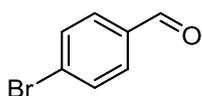
Benzaldehyde (13a)^[11] Chromatography (Silica gel, petroleum ether: ethyl ether = 1:0 to 10:1) of the residue to afford (18.9 mg, 0.182 mmol, yield: 91%) of **13a** as a colorless oil. ¹H

NMR (500 MHz, CDCl₃) δ 10.02 (s, 1H), 7.89-7.87 (m, 2H), 7.65-7.61 (m, 1H), 7.53 (d, J = 7.8 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 192.5, 136.6, 134.6, 129.9, 129.1.



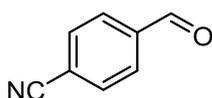
4-Chlorobenzaldehyde (13b)^[12] Chromatography (Silica gel, petroleum ether:

ethyl acetate = 1:0 to 10:1) of the residue to afford (27.5 mg, 0.194 mmol, yield: 97%) of **13b** as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 9.98 (s, 1H), 7.84-7.82 (m, 2H), 7.53-7.51 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 190.7, 140.9, 134.6, 130.8, 129.4.



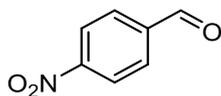
4-Bromobenzaldehyde (13c)^[12] Chromatography (Silica gel, petroleum ether:

ethyl acetate = 1:0 to 10:1) of the residue to afford (35.0 mg, 0.188 mmol, yield: 94%) of **13c** as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 9.97 (s, 1H), 7.75-7.73 (m, 2H), 7.69-7.67 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 191.0, 135.0, 132.4, 130.9, 129.7.



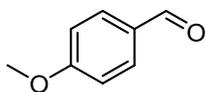
4-Cyanobenzaldehyde (13d)^[11] Chromatography (Silica gel, petroleum

ether: ethyl acetate = 1:0 to 10:1) of the residue to afford (25.2 mg, 19.2 mmol, yield: 96%) of **13d** as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 10.10 (s, 1H), 8.00 (d, J = 8.1 Hz, 2H), 7.85 (d, J = 8.2 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 190.5, 138.6, 132.8, 129.7, 117.6, 117.5.



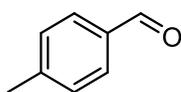
4-Nitrobenzaldehyde (13e)^[11] Chromatography (Silica gel, petroleum ether:

ethyl acetate = 1:0 to 10:1) of the residue to afford (29.2 mg, 0.196 mmol, yield: 98%) of **13e** as a yellow to brown solid. ¹H NMR (500 MHz, CDCl₃) δ 10.16 (s, 1H), 8.40 (d, J = 8.7 Hz, 2H), 8.07 (d, J = 8.7 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 190.7, 151.5, 140.4, 130.9, 124.7.



4-methoxybenzaldehyde (13f)^[12] Chromatography (Silica gel, petroleum

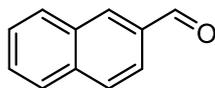
ether: ethyl acetate = 1:0 to 10:1) of the residue to afford (24.7 mg, 0.180 mmol, yield: 90%) of **13f** as a colorless to yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 9.87 (s, 1H), 7.83 (d, J = 8.75 Hz, 2H), 6.99 (d, J = 8.75 Hz, 2H), 3.88 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 190.7, 164.5, 131.8, 129.8, 114.2, 55.4.



4-methylbenzaldehyde (13g)^[12] Chromatography (Silica gel, petroleum ether:

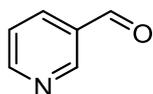
ethyl ether = 1:0 to 10:1) of the residue to afford (22.3 mg, 0.184 mmol, yield: 92%) of **13g** as a

colorless to yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 9.97 (s, 1H), 7.78 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 191.6, 145.1, 133.8, 129.4, 129.3, 21.5.



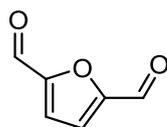
2-Naphthaldehyde (13h)^[12] Chromatography (Silica gel, petroleum ether:

ethyl acetate = 1:0 to 10:1) of the residue to afford (29.8 mg, 0.190 mmol, yield: 95%) of **13h** as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 10.16 (s, 1H), 8.34 (s, 1H), 8.05 (d, $J = 8.2$ Hz, 1H), 7.97-7.90 (m, 3H), 7.64 (t, $J = 7.2$ Hz, 1H), 7.58 (t, $J = 7.6$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 192.1, 136.3, 134.4, 134.0, 129.4, 129.0, 128.9, 128.0, 127.0, 122.6.



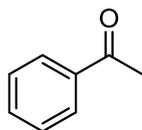
Pyridine-3-carbaldehyde (13i)^[13] Chromatography (Silica gel, petroleum ether:

ethyl ether = 1:0 to 10:1) of the residue to afford (18.8 mg, 0.174 mmol, yield: 87%) of **13i** as a brown-yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 10.11 (s, 1H), 9.07 (d, $J = 1.6$ Hz, 1H), 8.17-8.15 (m, 1H), 7.49-7.47 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 190.6, 154.7, 152.0, 135.6, 131.3, 123.9.



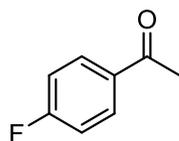
2,5-Diformylfuran (13j)^[14] Chromatography (Silica gel, petroleum ether: ethyl

acetate = 1:0 to 10:1) of the residue to afford (23.8 mg, 0.190 mmol, yield: 95%) of **13j** as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 9.86 (s, 2H), 7.33 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 179.1, 154.1, 119.1.



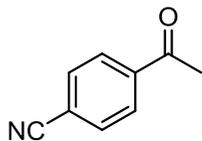
Acetophenone (13k)^[15] Chromatography (Silica gel, petroleum ether: ethyl ether

= 1:0 to 10:1) of the residue to afford (21.8 mg, 0.180 mmol, yield: 90%) of **13k** as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.97-7.95 (m, 2H), 7.58-7.55 (m, 1H), 7.48-7.45 (m, 2H), 2.61 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 198.1, 137.0, 133.0, 128.5, 128.2, 26.5.

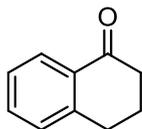


1-(4-Fluorophenyl)ethanone (13l)^[15] Chromatography (Silica gel, petroleum

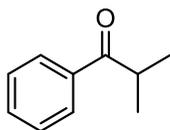
ether: ethyl acetate = 1:0 to 10:1) of the residue to afford (25.3 mg, 0.182 mmol, yield: 91%) of **13l** as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.99-7.97 (m, 2H), 7.14-7.11 (m, 2H), 2.59 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 196.9, 166.1 (d, $J = 254.7$ Hz), 134.0 (d, $J = 3.1$ Hz), 131.3 (d, $J = 9.4$ Hz), 116.0 (d, $J = 22.0$ Hz), 26.9.



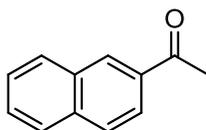
4-Acetylbenzotrile (13m)^[16] Chromatography (Silica gel, petroleum ether: ethyl acetate = 1:0 to 10:1) of the residue to afford (27.0 mg, 0.186 mmol, yield: 93%) of **13m** as a taupe solid. ¹H NMR (500 MHz, CDCl₃) δ 8.04-8.02 (m, 2H), 7.77-7.75 (m, 2H), 2.63(s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 196.9, 140.2, 132.9, 129.0, 118.3, 116.7, 27.1.



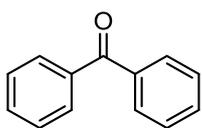
3,4-Dihydronaphthalen-1(2H)-one (13n)^[17] Chromatography (Silica gel, petroleum ether: ethyl ether = 1:0 to 10:1) of the residue to afford (27.2 mg, 0.186 mmol, yield: 93%) of **13n** as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 8.01 (m, 1H), 7.49-7.47 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 3.3 Hz, 1H), 2.98 (t, *J* = 6.5 Hz, 2H), 2.67 (t, *J* = 6.5 Hz), 2.18-2.13 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 198.3, 144.3, 133.2, 132.4, 128.6, 127.0, 126.5, 39.0, 29.6, 23.1.



2-Methyl-1-phenylpropan-1-one (13o)^[18] Chromatography (Silica gel, petroleum ether: ethyl ether = 1:0 to 10:1) of the residue to afford (25.2 mg, 0.170 mmol, yield: 85%) of **13o** as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.97-7.95 (m, 2H), 7.57-7.53 (m, 1H), 7.48-7.45 (m, 2H), 3.59-3.53 (m, 1H), 1.22 (d, *J* = 6.9 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 204.4, 136.1, 132.7, 128.5, 128.2, 35.2, 19.0.

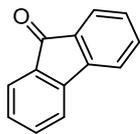


1-(Naphthalen-2-yl)ethanone (13p)^[15] Chromatography (Silica gel, petroleum ether: ethyl acetate = 1:0 to 10:1) of the residue to afford (31.6 mg, 0.186 mmol, yield: 93%) of **13p** as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 8.45 (s, 1H), 8.03-8.02 (m, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.87 (t, *J* = 8.1 Hz, 2H), 7.61-7.53 (m, 2H), 2.72 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 198.4, 135.9, 134.8, 132.9, 130.5, 129.9, 128.81, 128.76, 128.1, 127.1, 124.2, 27.0.

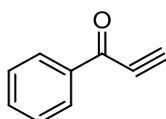


Benzophenone (13q)^[17] Chromatography (Silica gel, petroleum ether: ethyl acetate = 1:0 to 10:1) of the residue to afford (35.1 mg, 0.192 mmol, yield: 96%) of **13q** as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 7.4 Hz, 4H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.8 Hz,

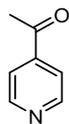
4H). ^{13}C NMR (125 MHz, CDCl_3) δ 196.6, 137.4, 132.3, 130.0, 128.1.



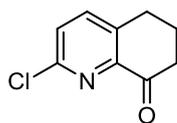
Fluoren-9-one (13r)^[19] Chromatography (Silica gel, petroleum ether: ethyl acetate = 1:0 to 10:1) of the residue to afford (35.6 mg, 0.198 mmol, yield: 99%) of **13r** as a yellow solid. ^1H NMR (500 MHz, CDCl_3) δ 7.65 (d, J = 7.4 Hz, 2H), 7.51-7.46 (m, 4H), 7.30-7.26 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 193.8, 144.3, 134.6, 134.0, 128.9, 124.2, 120.2.



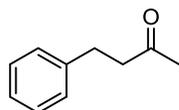
1-Phenylprop-2-yn-1-one (13s)^[20] Chromatography (Silica gel, petroleum ether: ethyl ether = 1:0 to 10:1) of the residue to afford (24.7 mg, 0.190 mmol, yield: 95%) of **13s** as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 8.16 (t, J = 7.3 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.9 Hz, 2H), 3.44 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 177.5, 136.3, 134.7, 129.8, 128.8, 80.9, 80.4.



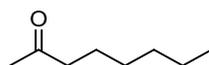
4-Acetylpyridine (13t)^[21] Chromatography (Silica gel, petroleum ether: ethyl ether = 1:0 to 10:1) of the residue to afford (21.5 mg, 0.178 mmol, yield: 89%) of **13t** as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 8.81-8.80 (m, 2H), 7.73-7.71 (m, 2H), 2.62 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 197.2, 150.9, 142.6, 121.1, 26.5.



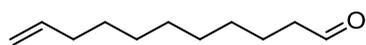
2-Chloro-6,7-dihydro-5H-quinolin-8-one (13u)^[22] Chromatography (Silica gel, petroleum ether: ethyl acetate = 1:0 to 10:1) of the residue to afford (34.8 mg, 0.192 mmol, yield: 96%) of **13u** as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.62 (d, J = 8.3 Hz, 1H), 7.39 (d, J = 8.1 Hz, 1H), 2.99 (t, J = 6.1 Hz, 2H), 2.76 (t, J = 6.3 Hz, 2H), 2.20-2.15 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 195.4, 151.2, 148.4, 141.0, 139.9, 128.5, 39.7, 28.9, 22.8.



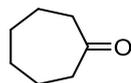
4-Phenylbutan-2-one (13v)^[23] Chromatography (Silica gel, petroleum ether: ethyl acetate = 1:0 to 10:1) of the residue to afford (28.1 mg, 0.190 mmol, yield: 95%) of **13v** as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.30-7.26 (m, 2H), 7.21-7.18 (t, J = 7.93 Hz, 3H), 2.93-2.91 (t, J = 7.46 Hz, 2H), 2.79-2.76 (t, J = 8.03 Hz, 2H), 2.14 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 208.3, 141.4, 128.9, 128.7, 126.5, 45.5, 30.4, 30.1.



Octan-2-one (13w)^[24] Chromatography (Silica gel, petroleum ether: ethyl ether = 1:0 to 10:1) of the residue to afford (20.7 mg, 0.162 mmol, yield: 81%) of **13w** as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 2.37 (t, *J* = 7.5 Hz, 2H), 2.08 (s, 3H), 1.55-1.49 (m, 2H), 1.27-1.21 (m, 6H), 0.83 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 209.3, 43.9, 31.7, 29.8, 28.9, 23.9, 22.5, 14.0.



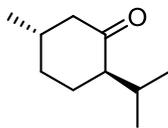
10-Undecenal (13x)^[25] Chromatography (Silica gel, petroleum ether: ethyl ether = 1:0 to 10:1) of the residue to afford (30.2 mg, 0.180 mmol, yield: 90%) of **13x** as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 9.69 (s, 1H), 5.78-5.70 (m, 1H), 4.94-4.85 (m, 2H), 2.37-2.34 (m, 2H), 2.00-1.95 (m, 2H), 1.56 (t, *J* = 6.2 Hz, 2H), 1.31 (t, *J* = 6.9 Hz, 3H), 1.23 (t, *J* = 3.3 Hz, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 202.5, 138.9, 114.0, 43.7, 33.6, 29.2, 29.1, 29.0, 28.9, 28.8, 21.9.



Cycloheptanone (13y)^[26] Chromatography (Silica gel, petroleum ether: ethyl ether = 1:0 to 10:1) of the residue to afford (18.8 mg, 0.168 mmol, yield: 84%) of **13y** as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 2.50-2.48 (m, 4H), 1.71-1.64 (m, 8H). ¹³C NMR (125 MHz, CDCl₃) δ 215.0, 43.5, 30.1, 24.0.

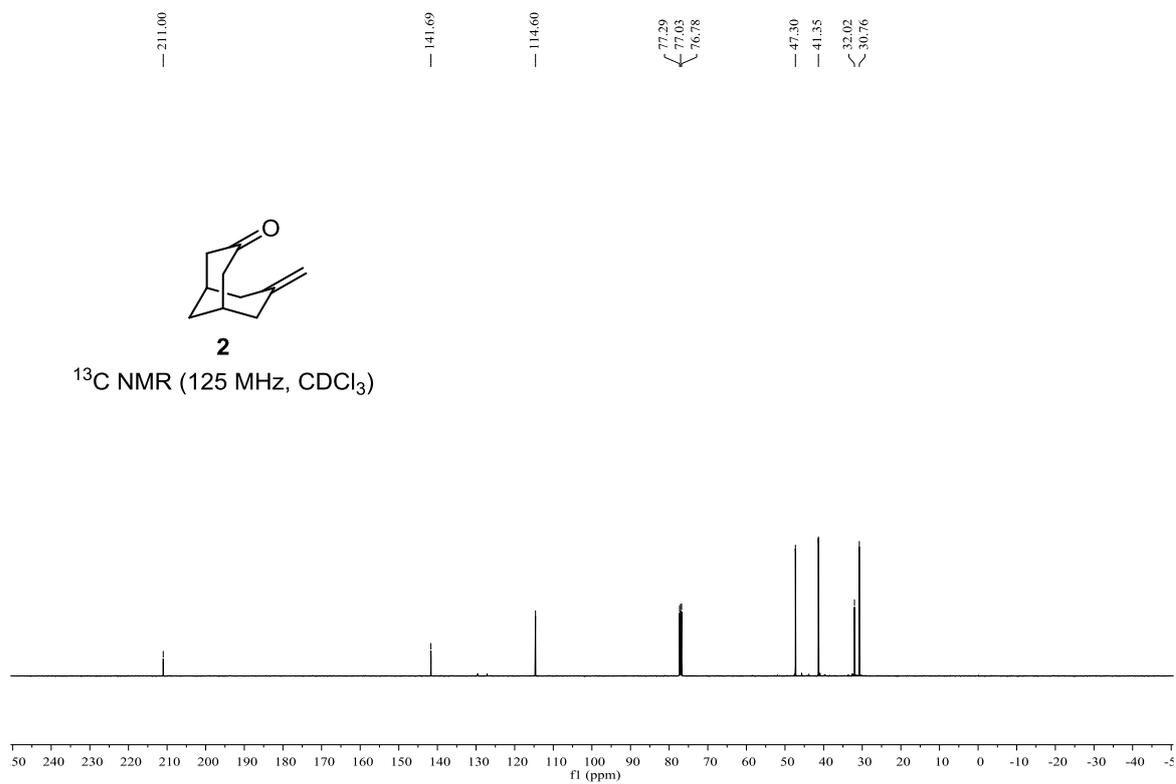
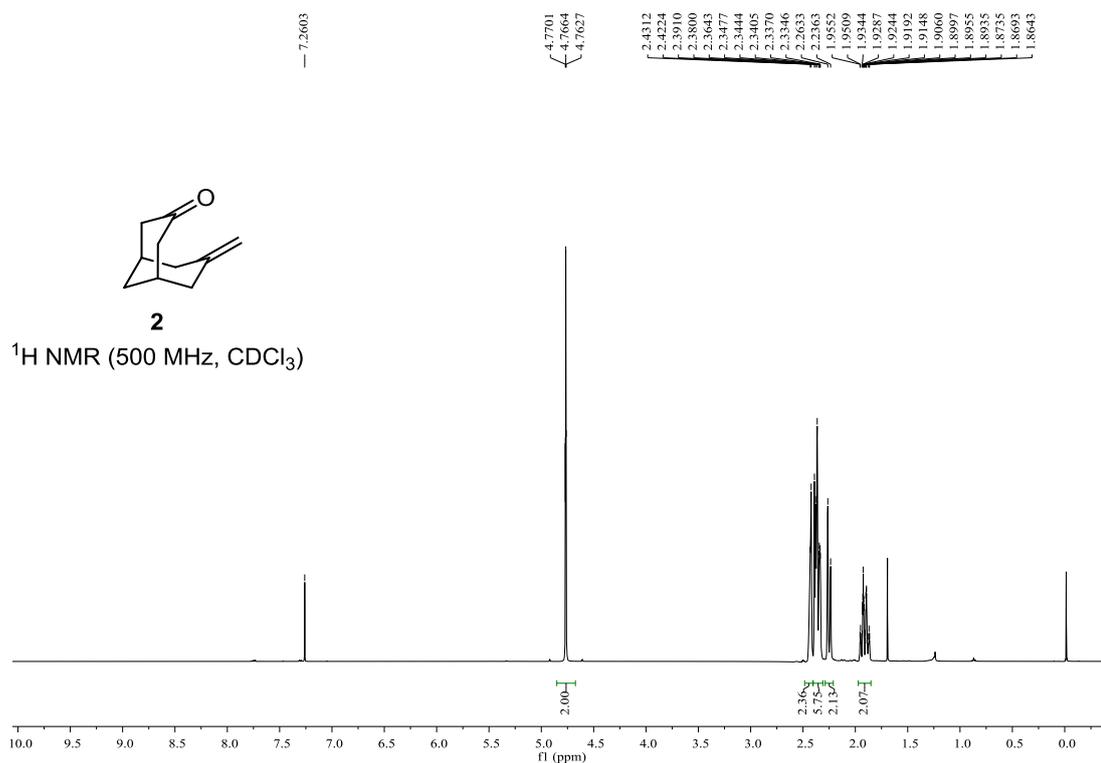


Adamantanone (13z)^[27] Chromatography (Silica gel, petroleum ether: ethyl acetate = 1:0 to 10:1) of the residue to afford (29.1 mg, 0.194 mmol, yield: 97%) of **13z** as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 2.52 (s, 2H), 2.06 (d, *J* = 11.11 Hz, 4H), 6.99 (d, *J* = 13.85 Hz, 6H), 1.91 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 218.4, 46.9, 39.2, 36.2, 27.3.

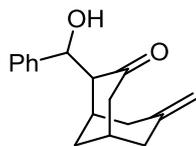


(2*R*, 5*S*)-2-isopropyl-5-methylcyclohexan-1-one (13aa)^[28] Chromatography (Silica gel, petroleum ether: ethyl acetate = 1:0 to 10:1) of the residue to afford (28.3 mg, 0.184 mmol, yield: 92%) of **13aa** as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 2.36-2.32 (m, 1H), 2.16-2.09 (m, 1H), 2.06-2.00 (m, 2H), 1.95 (t, *J* = 12.6 Hz, 1H), 1.91-1.82 (m, 2H), 1.41-1.24 (m, 2H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 212.3, 55.7, 50.7, 35.3, 33.8, 27.7, 25.8, 21.1, 18.6.

5. NMR Spectra

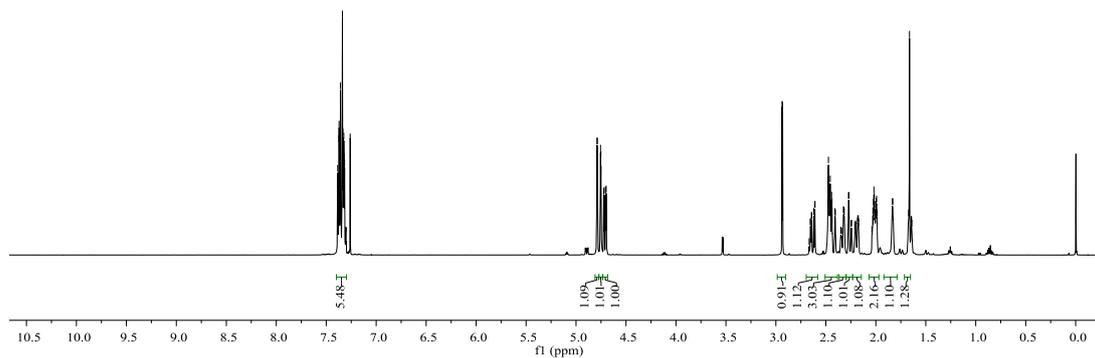


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7.3166
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4.6982
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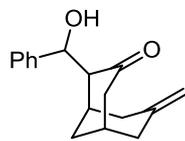


3

¹H NMR (500 MHz, CDCl₃)

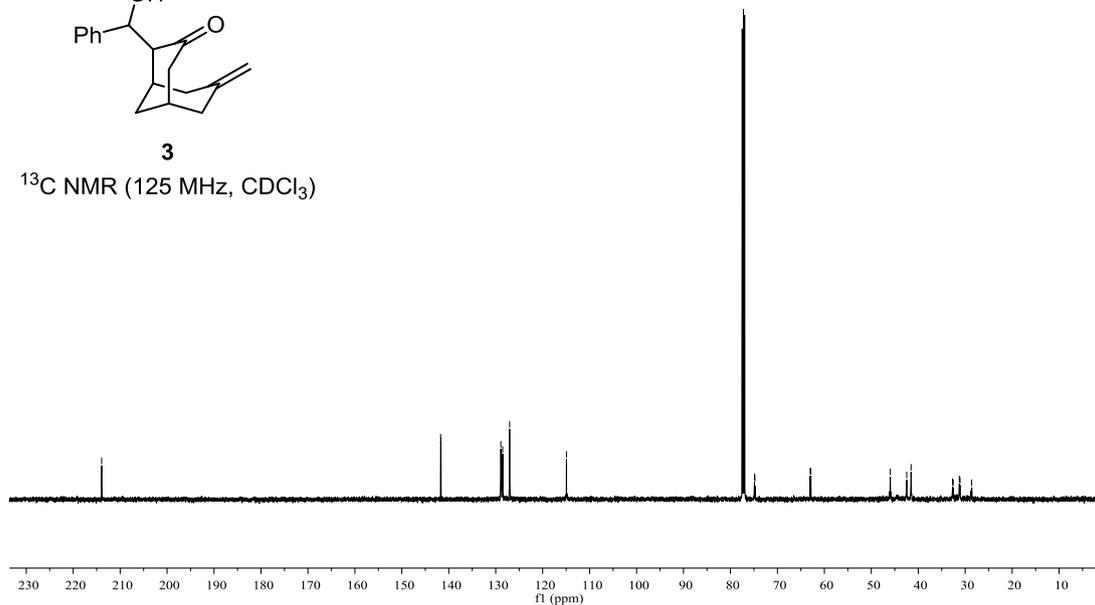


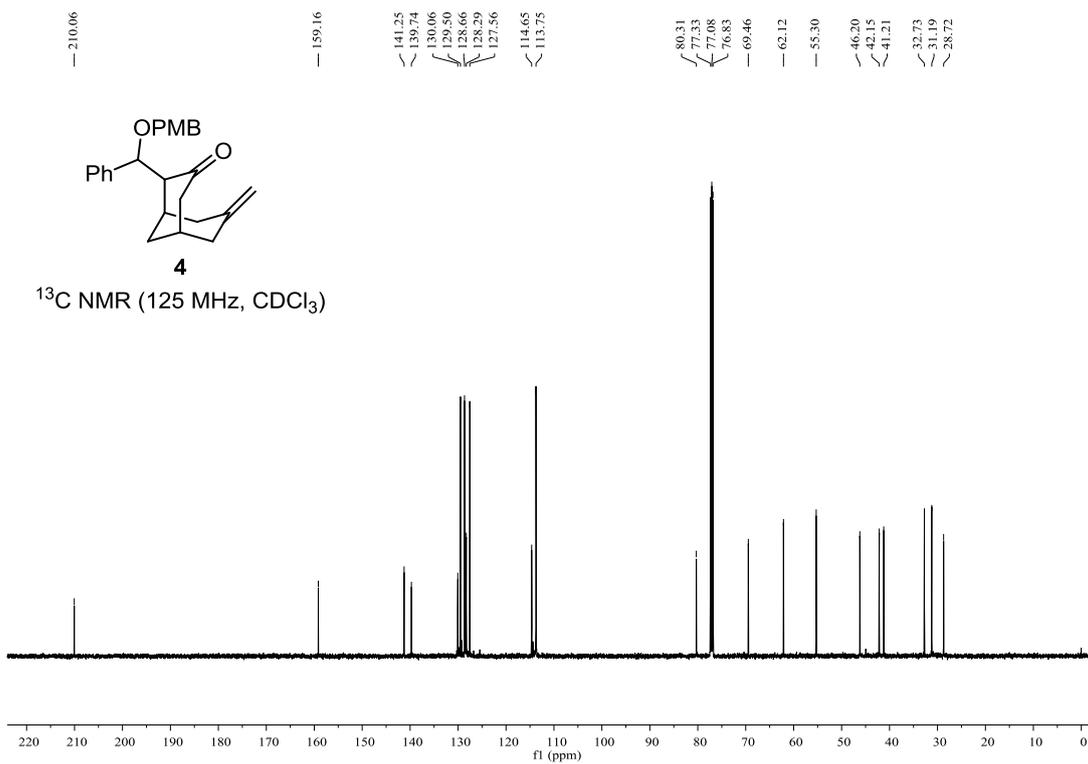
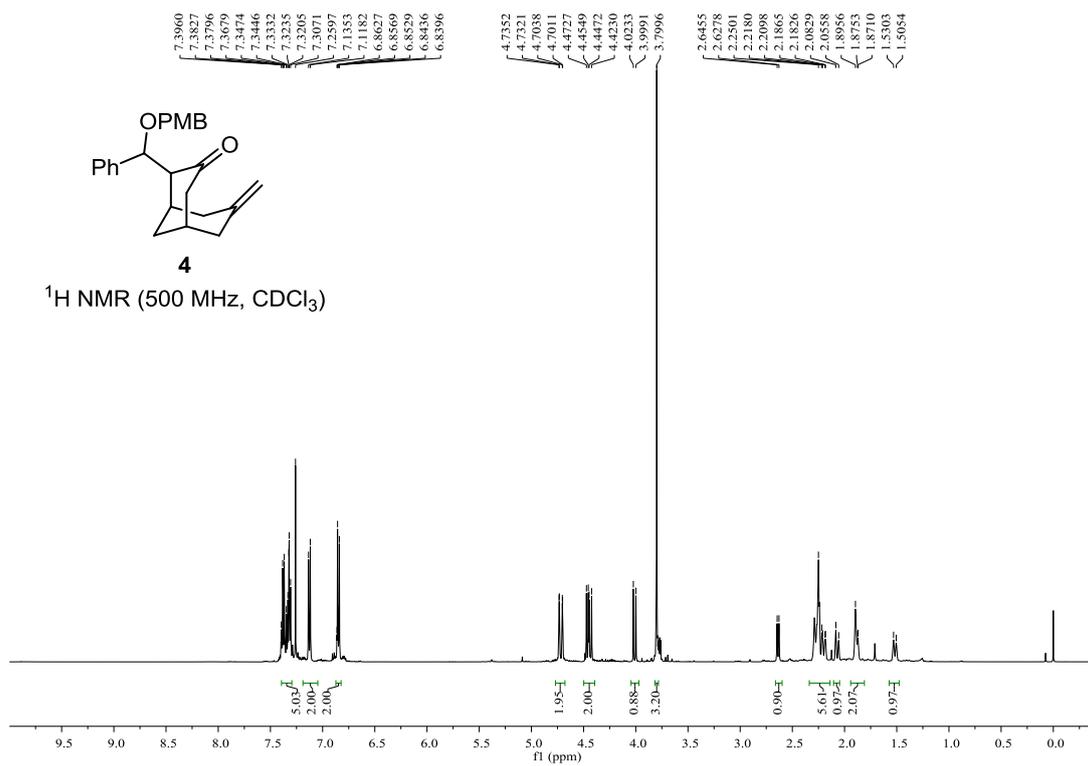
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127.04
114.93
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31.11
28.61

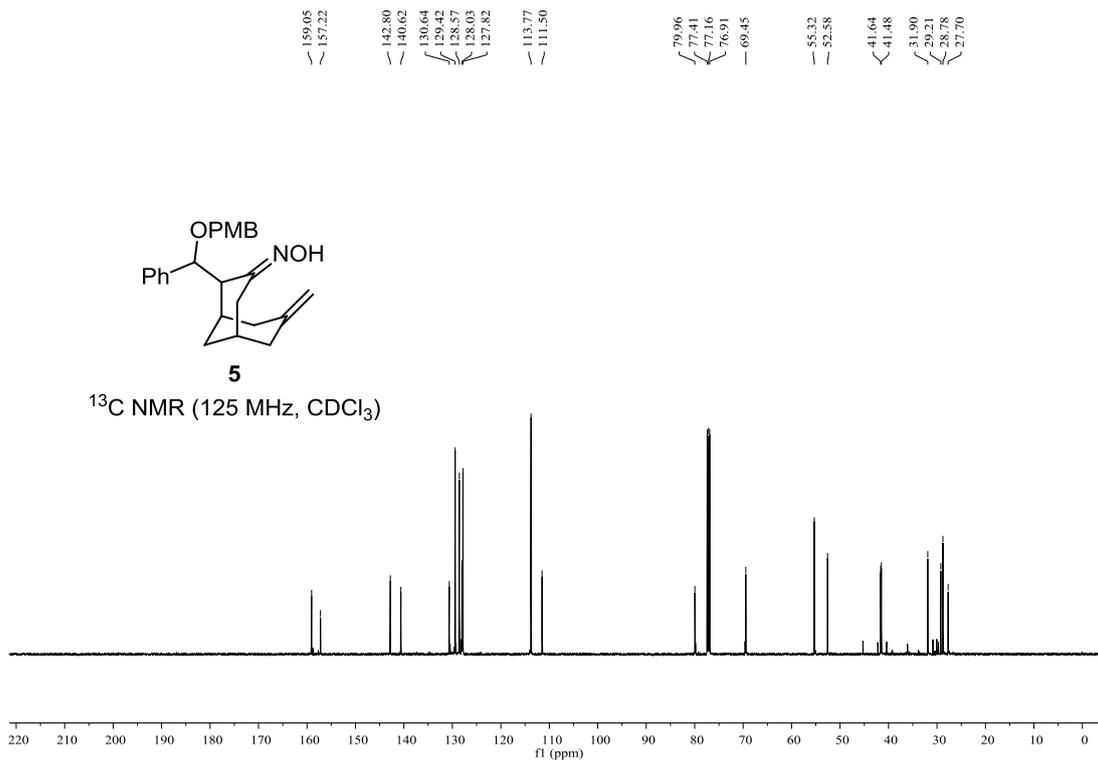
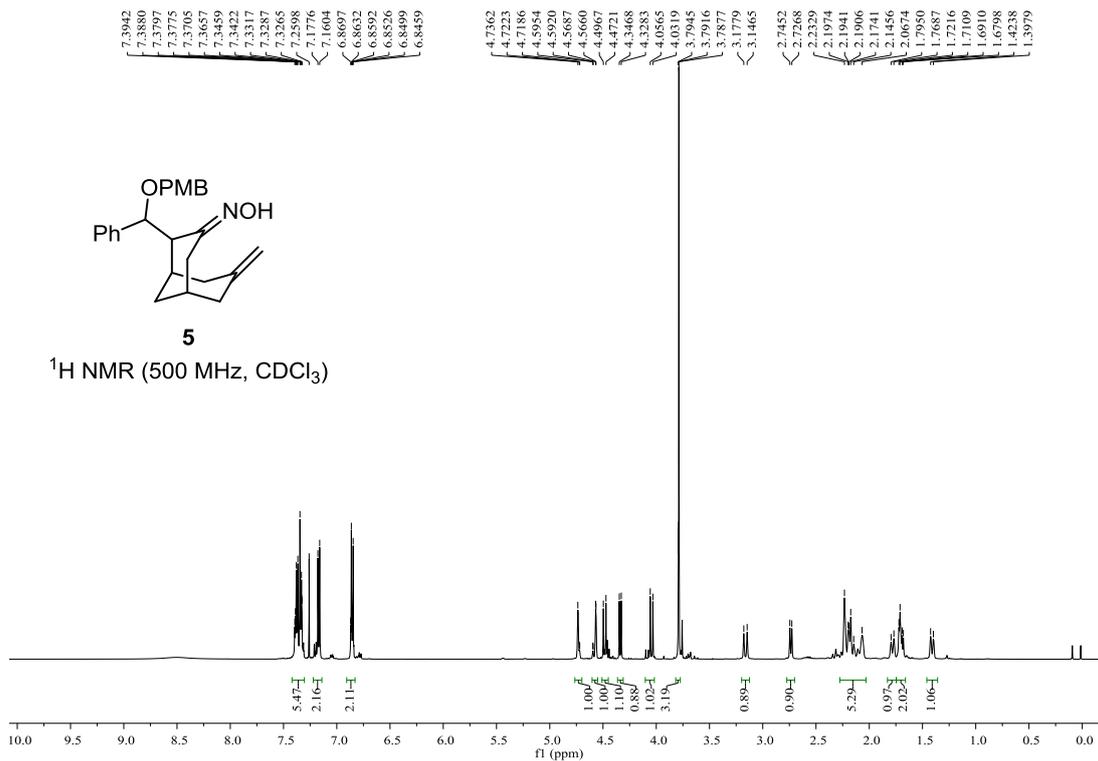


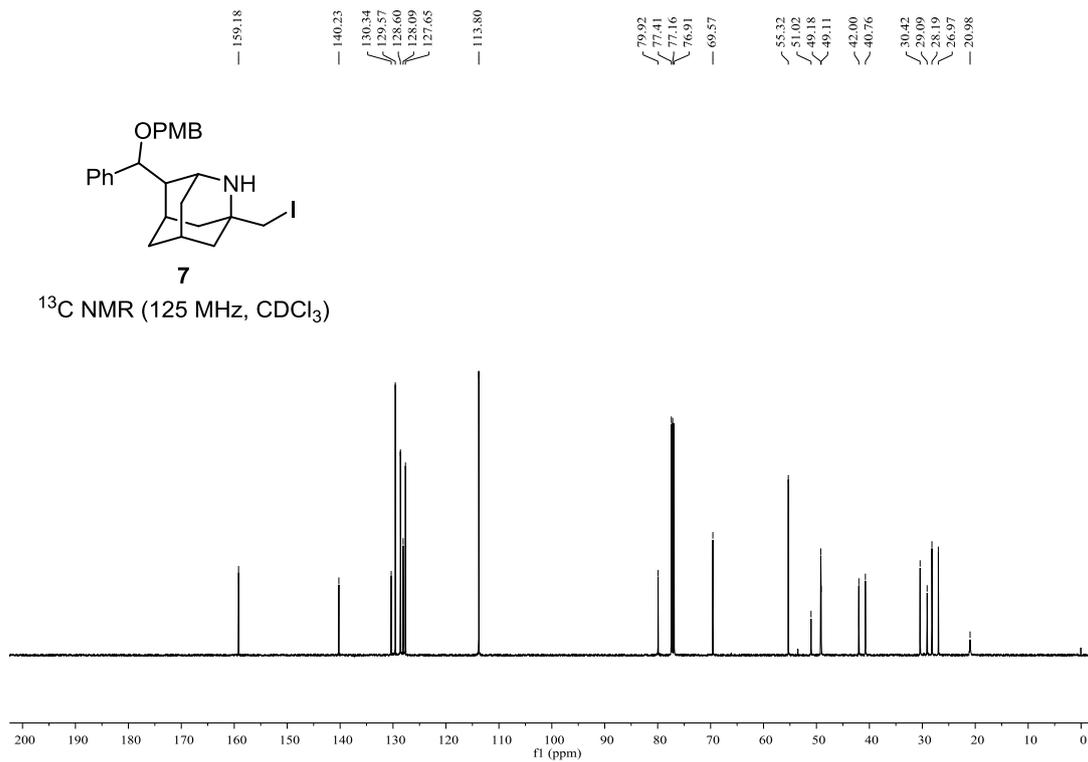
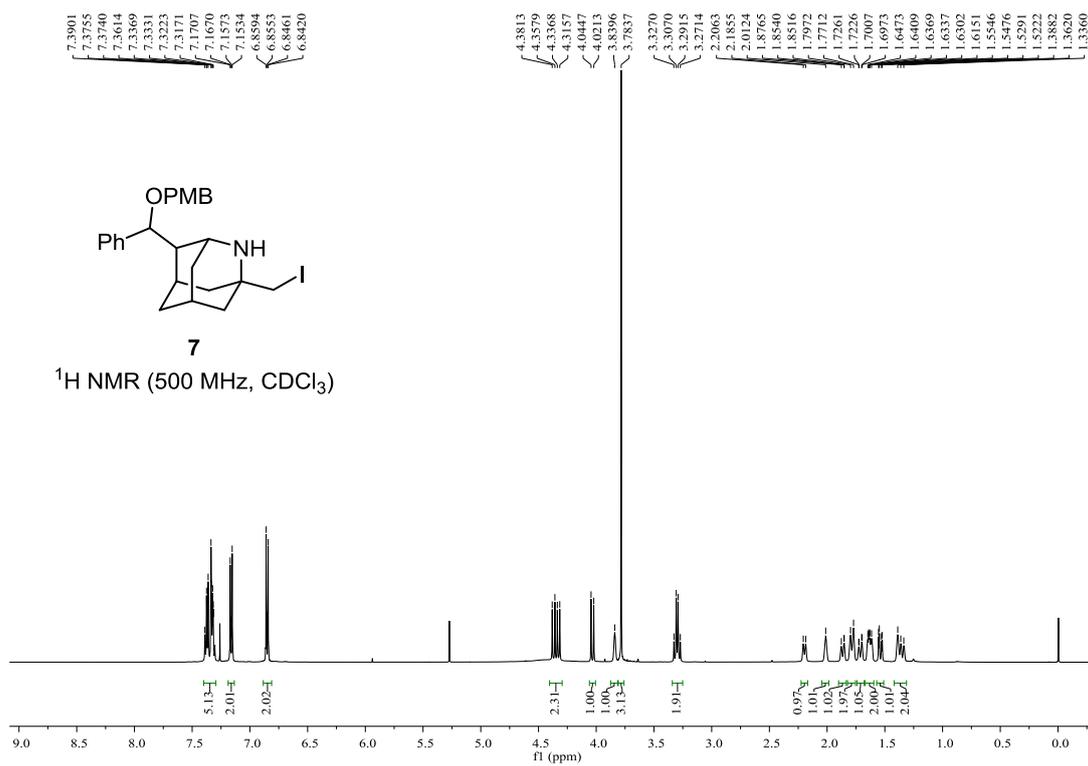
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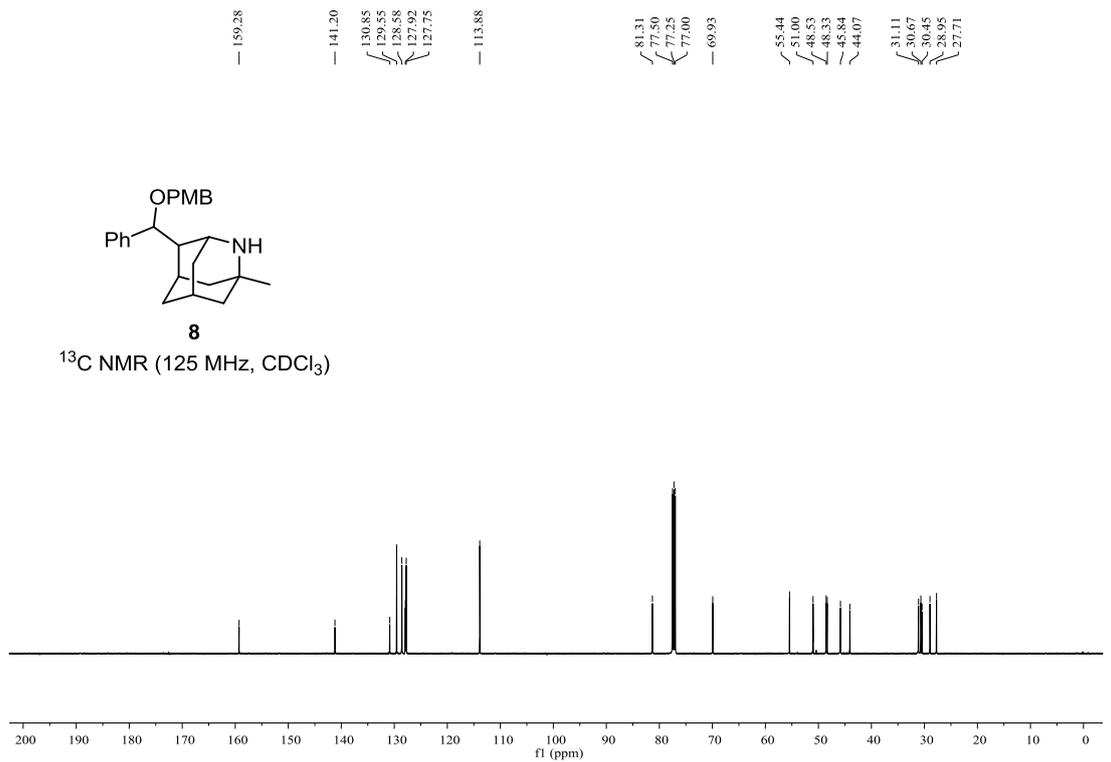
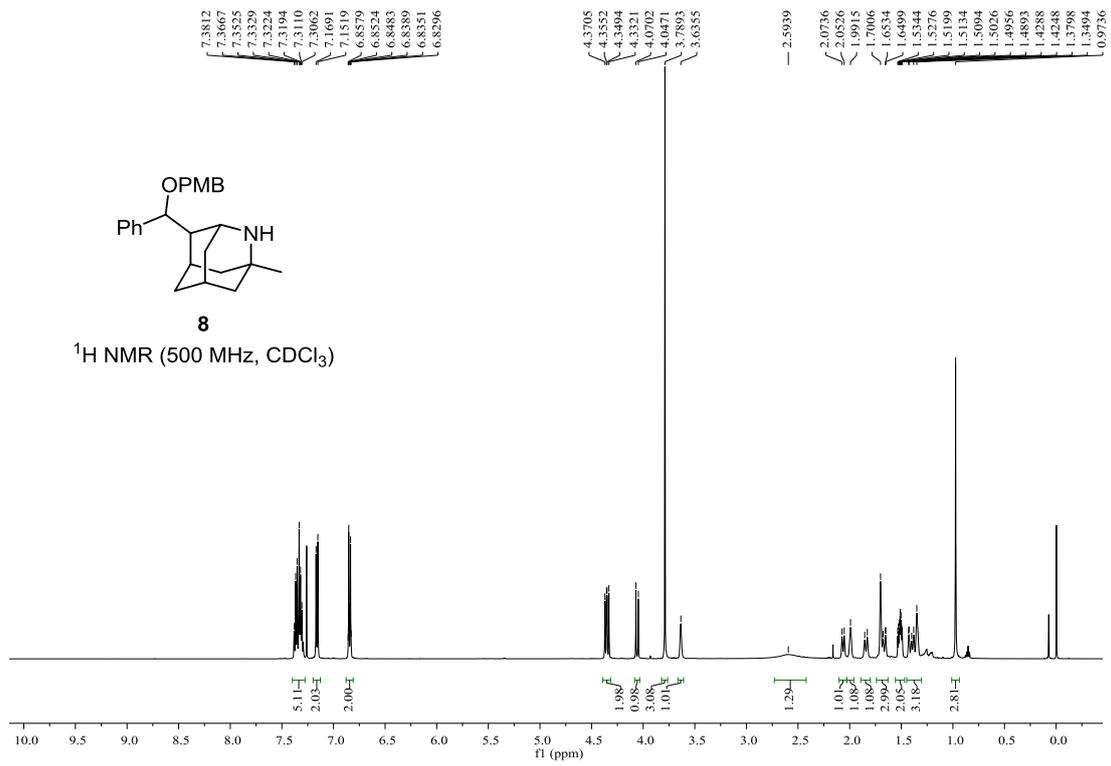
¹³C NMR (125 MHz, CDCl₃)

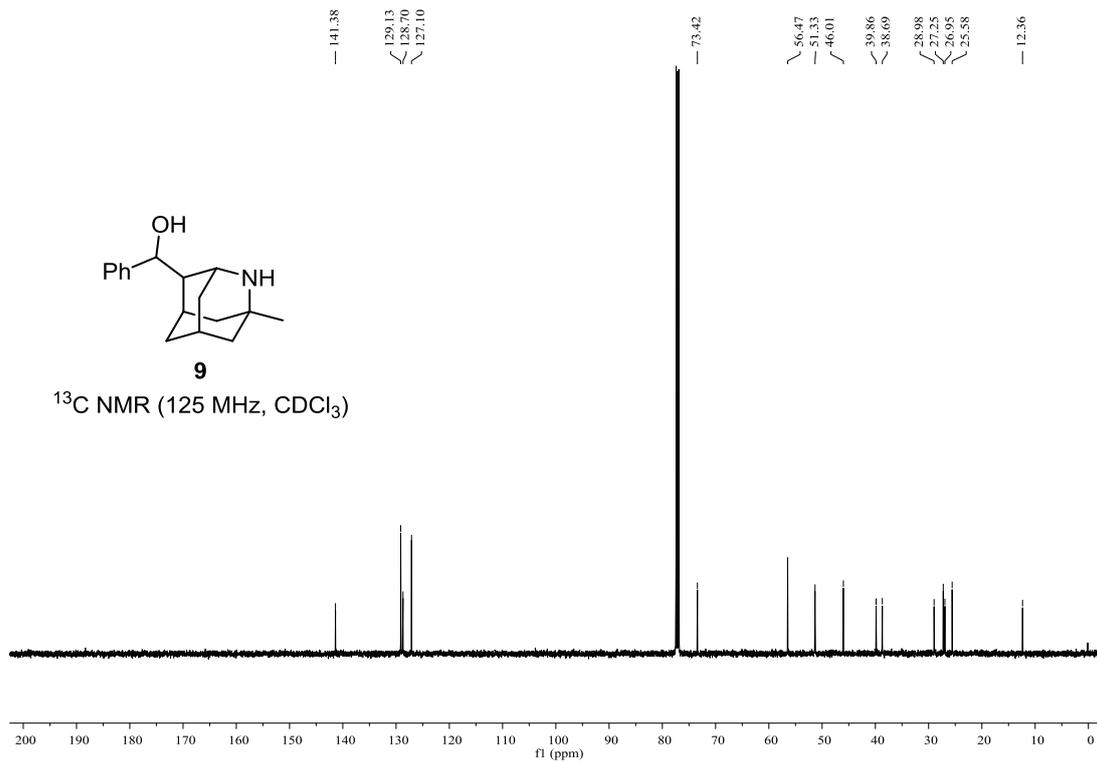
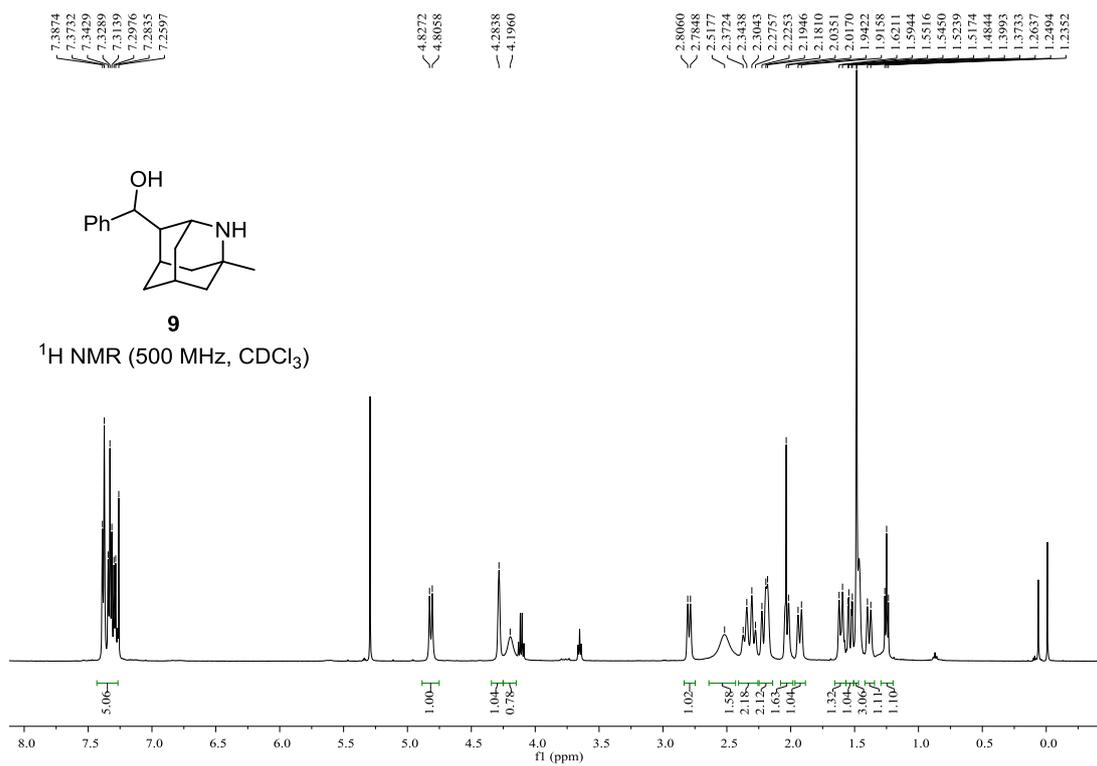


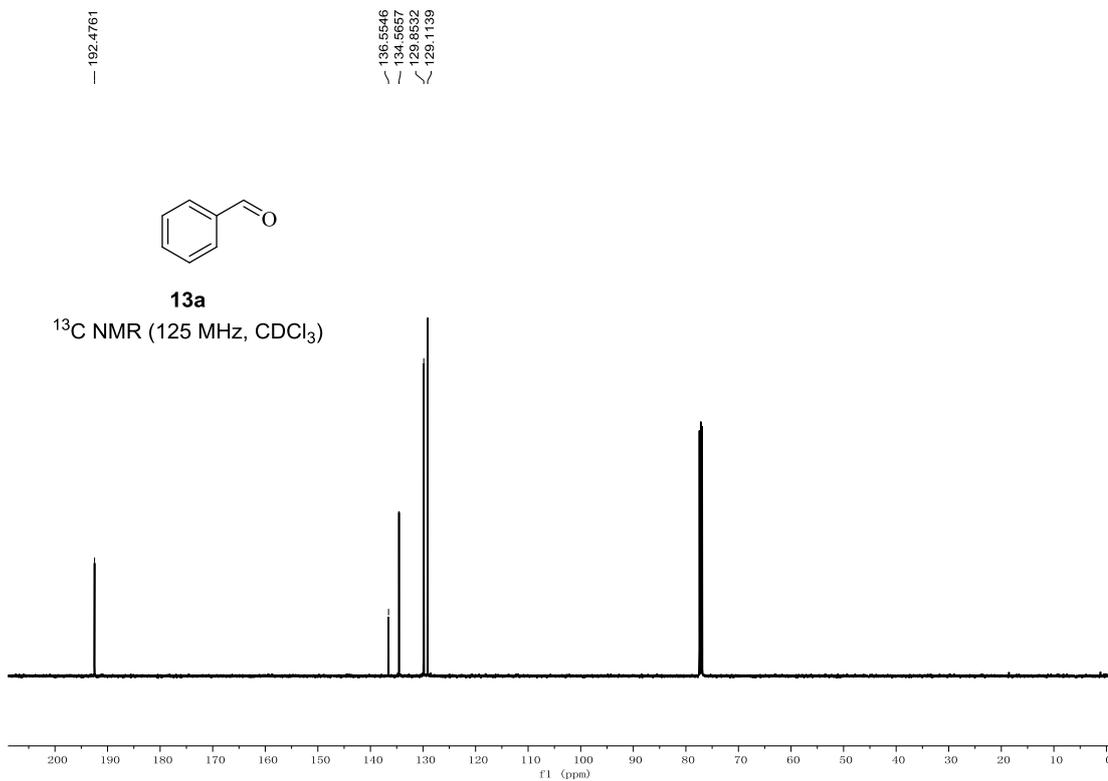
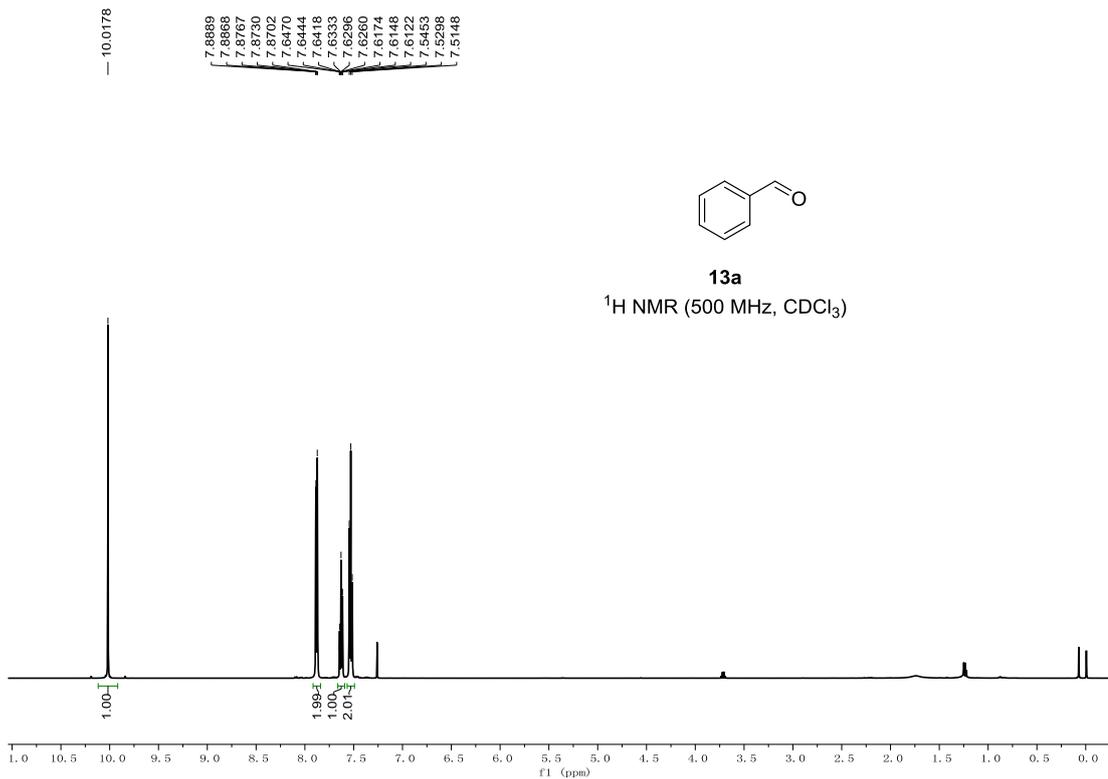


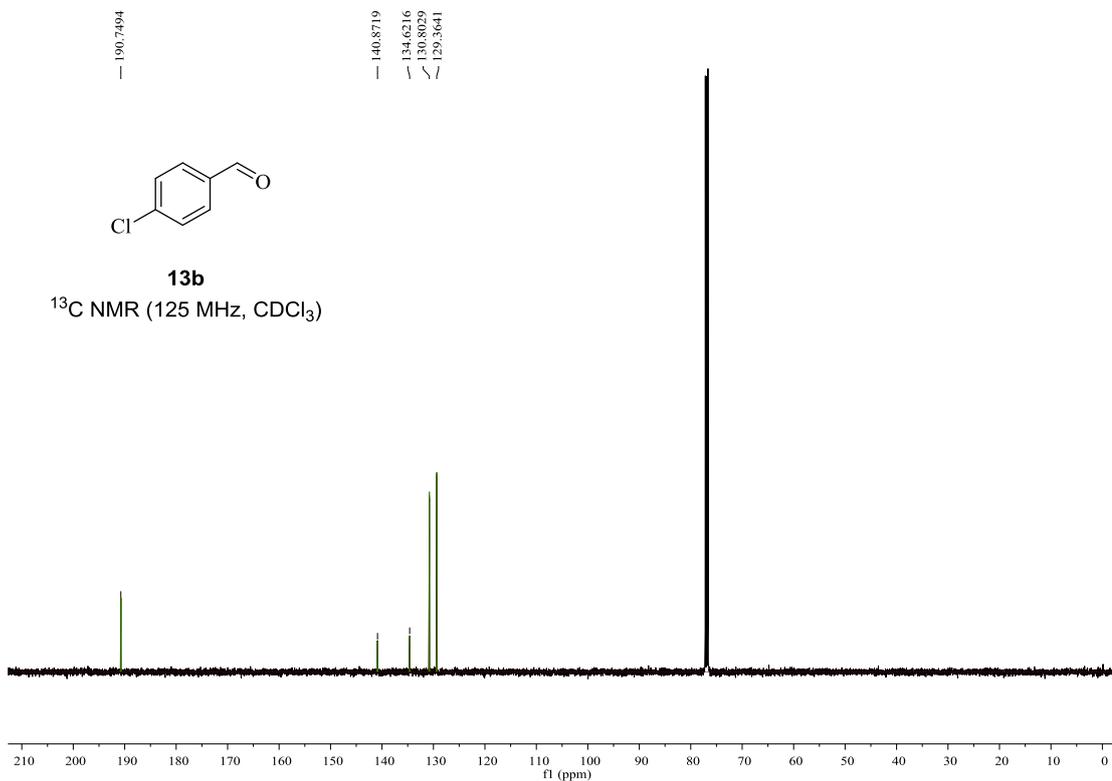
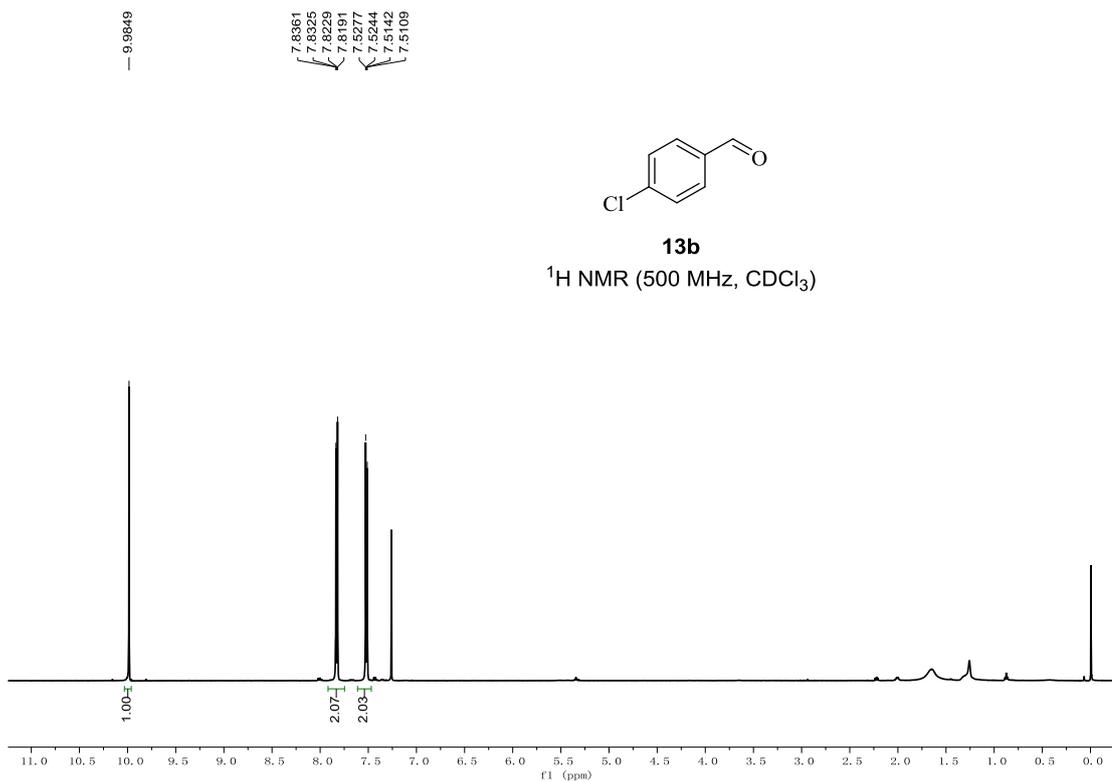


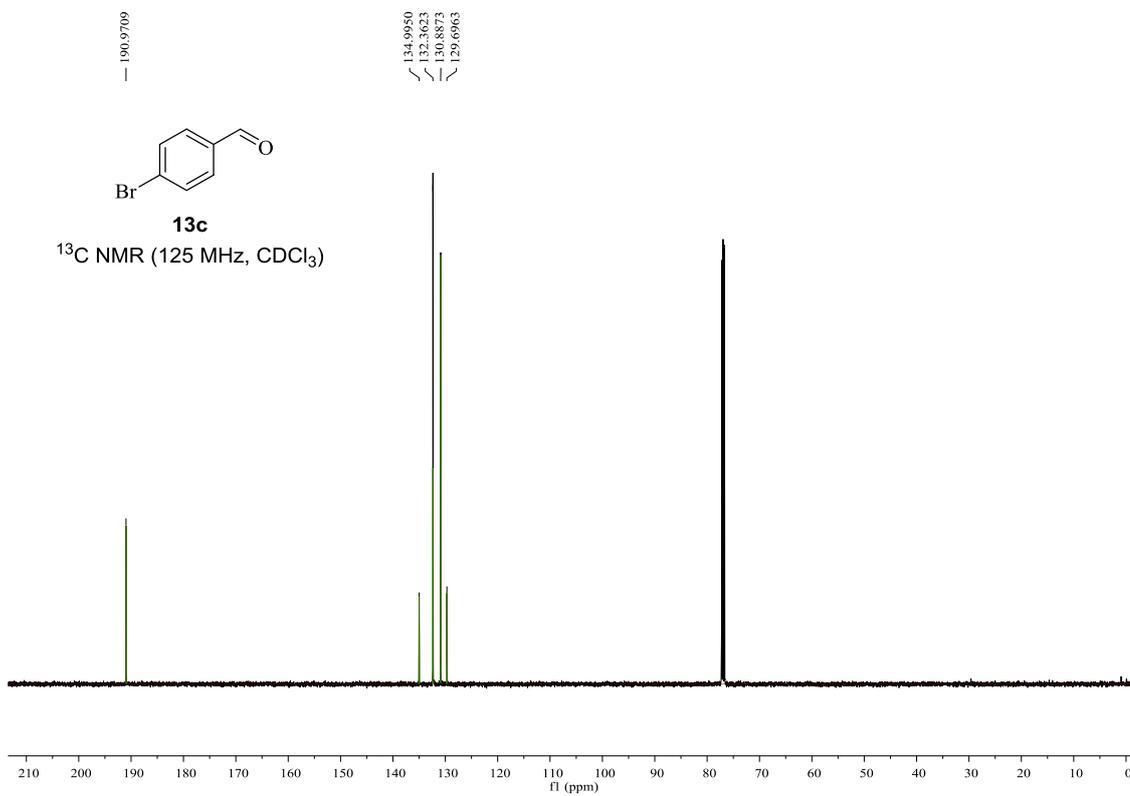
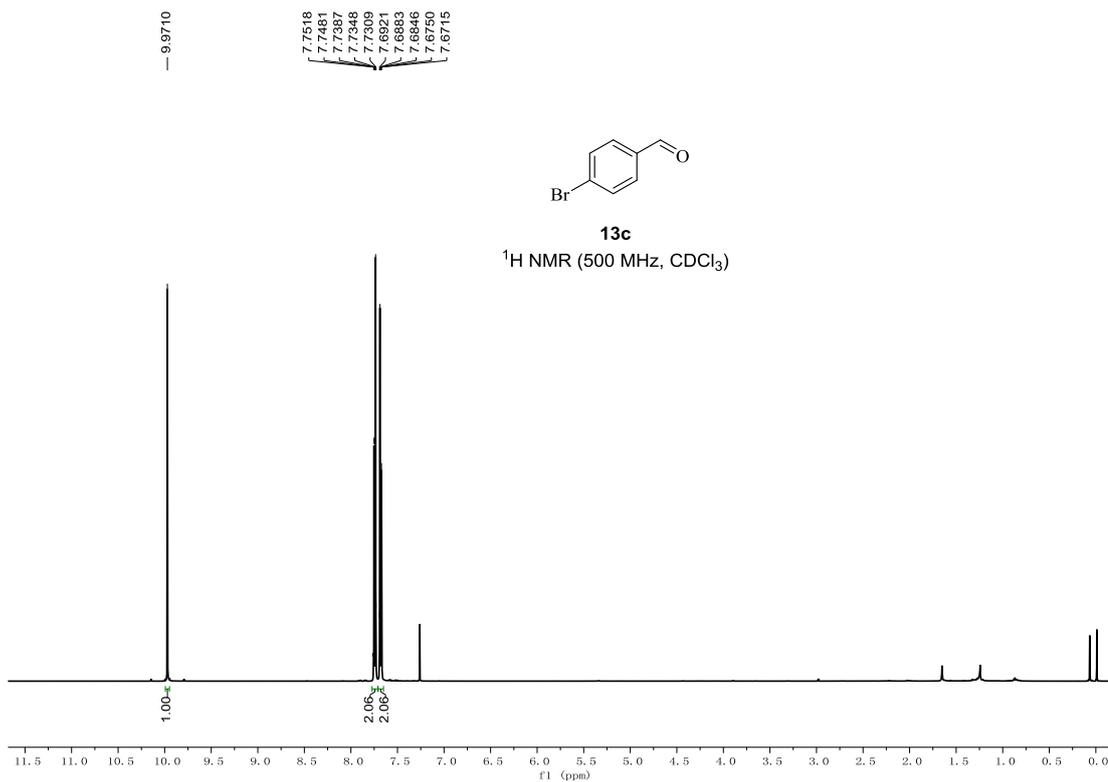




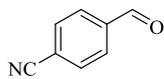






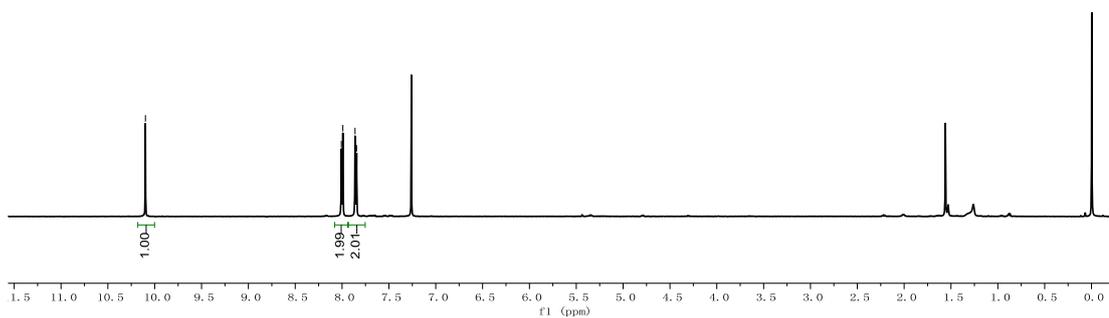


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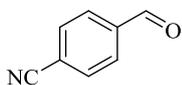


13d

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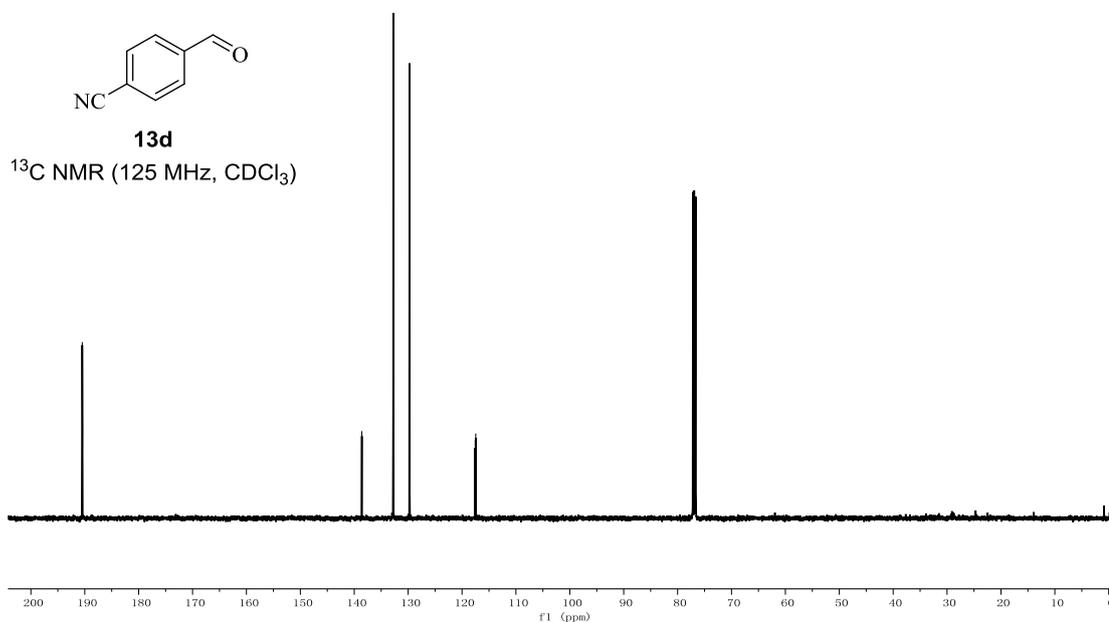


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117.4551



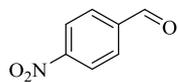
13d

¹³C NMR (125 MHz, CDCl₃)



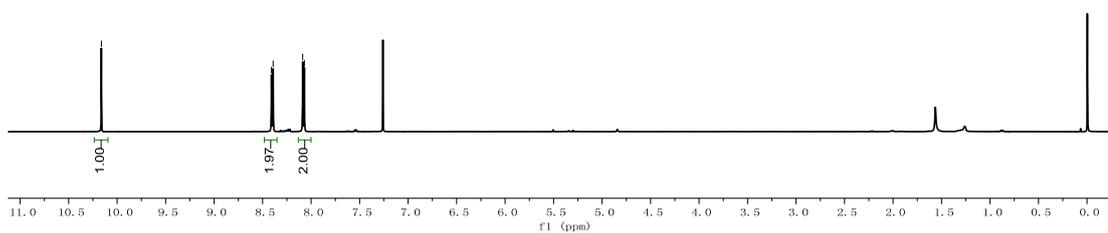
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8.0694



13e

¹H NMR (500 MHz, CDCl₃)



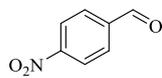
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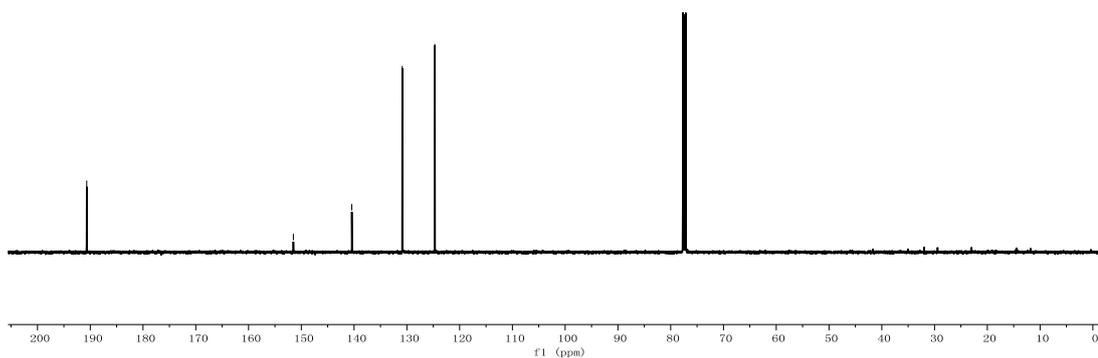
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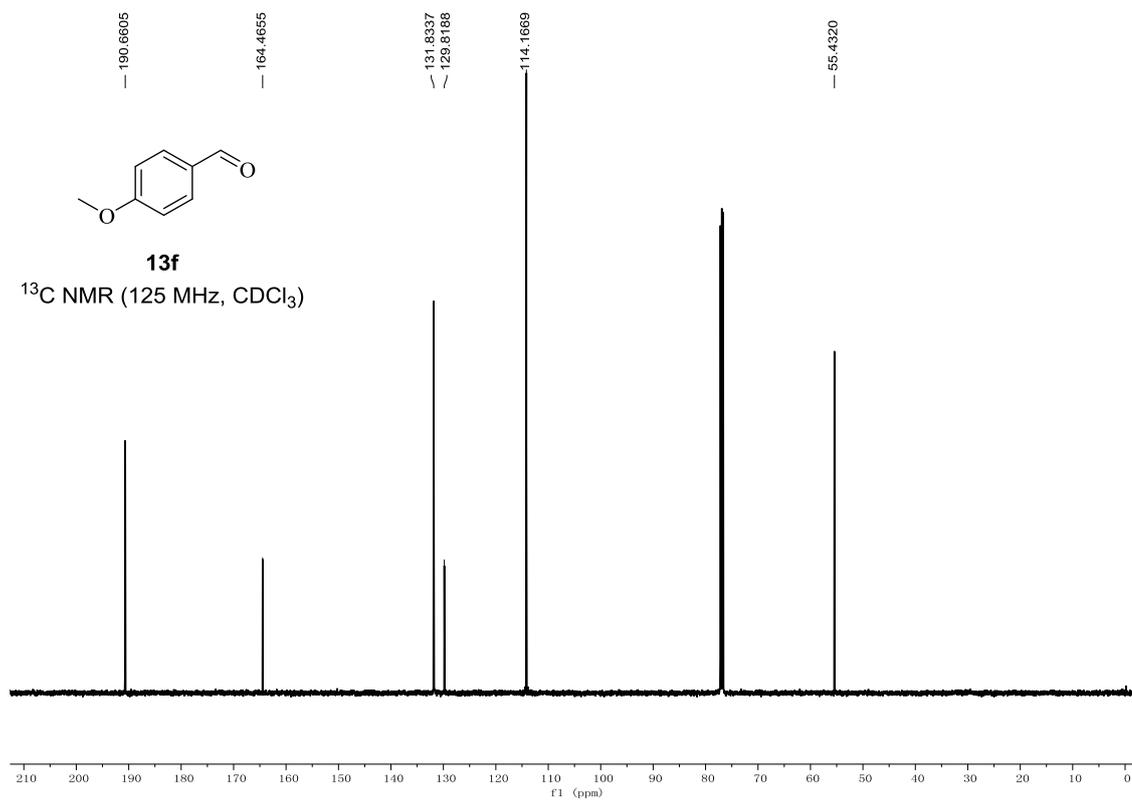
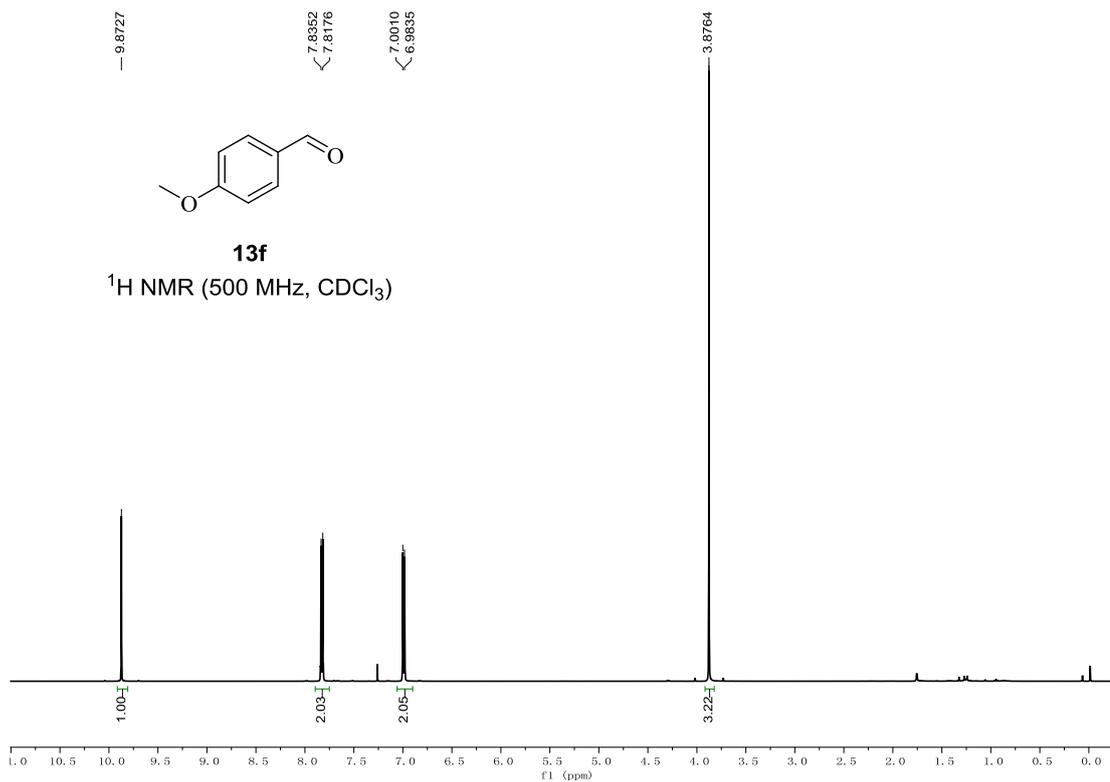
124.6923

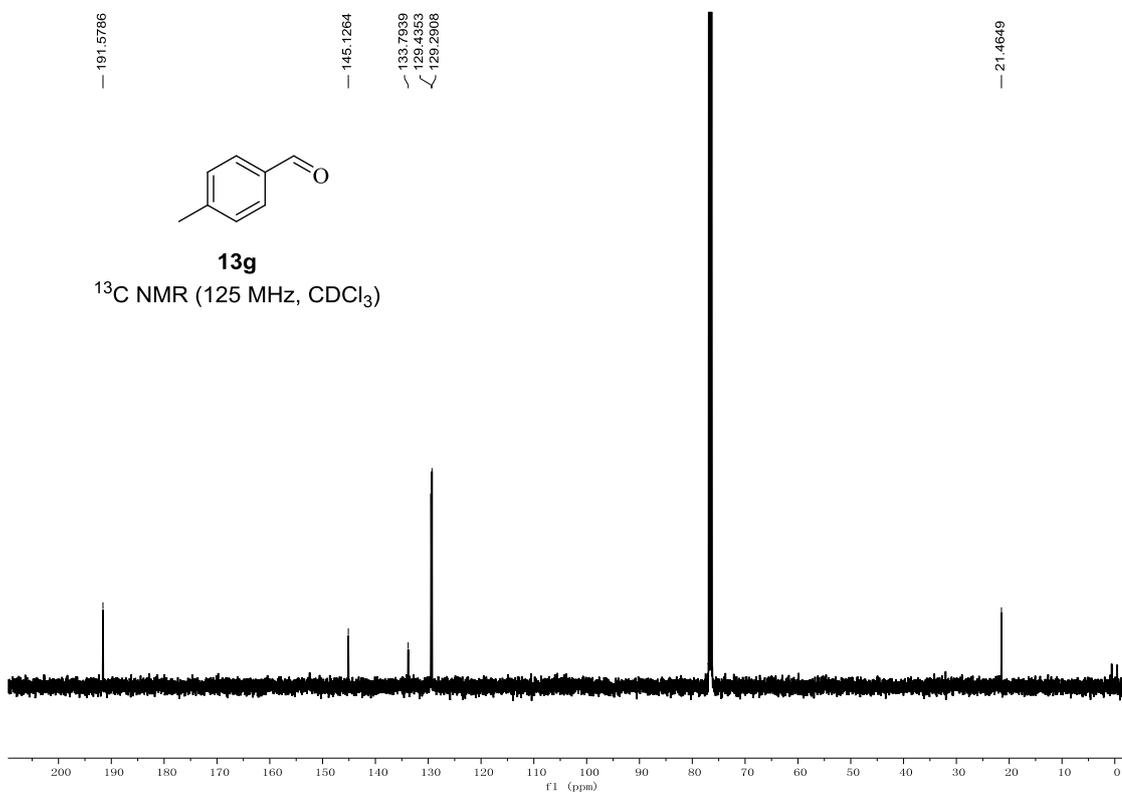
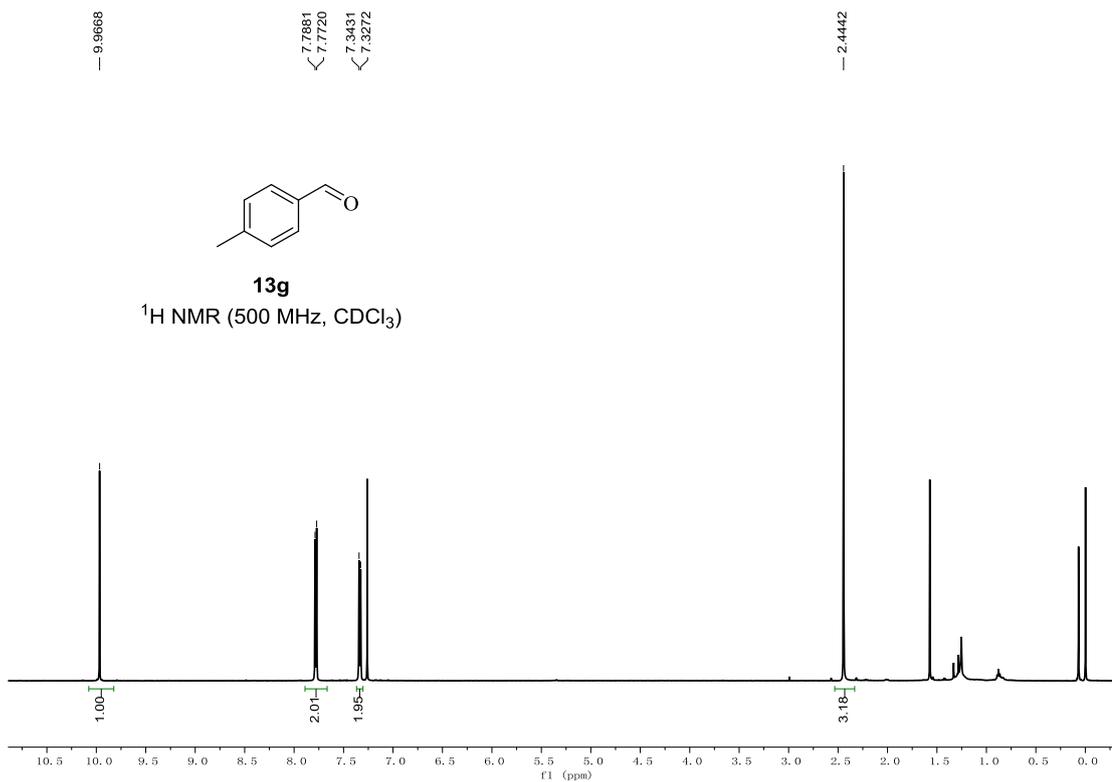


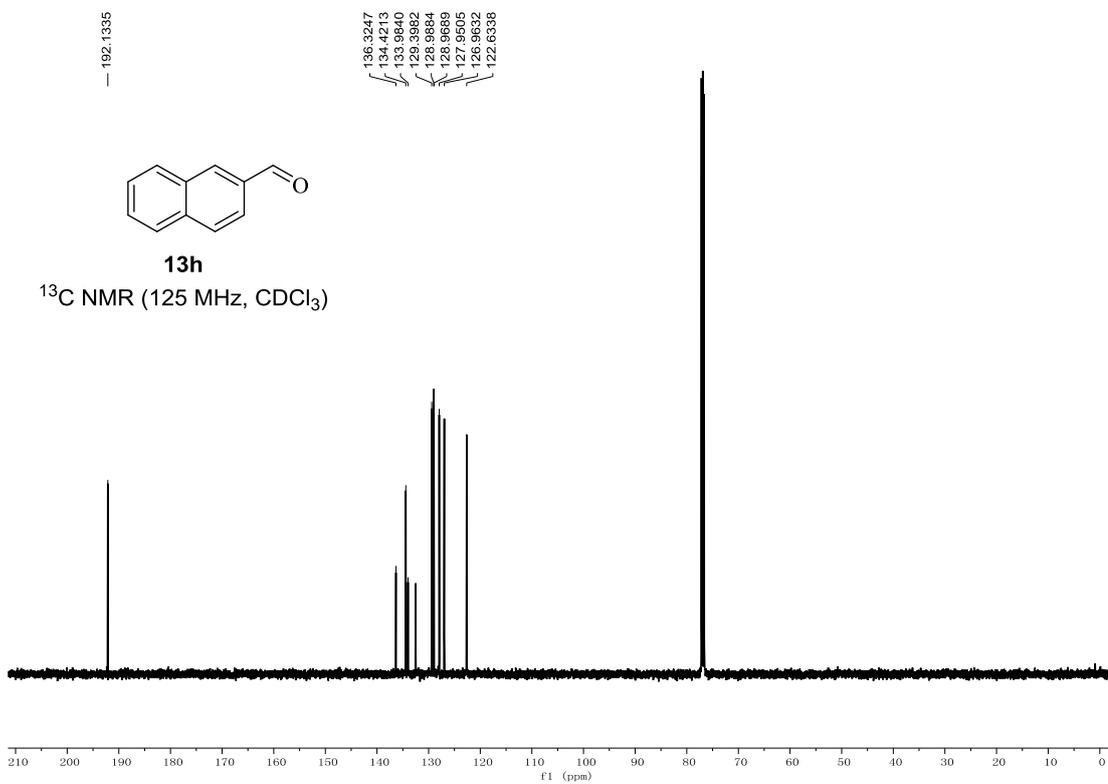
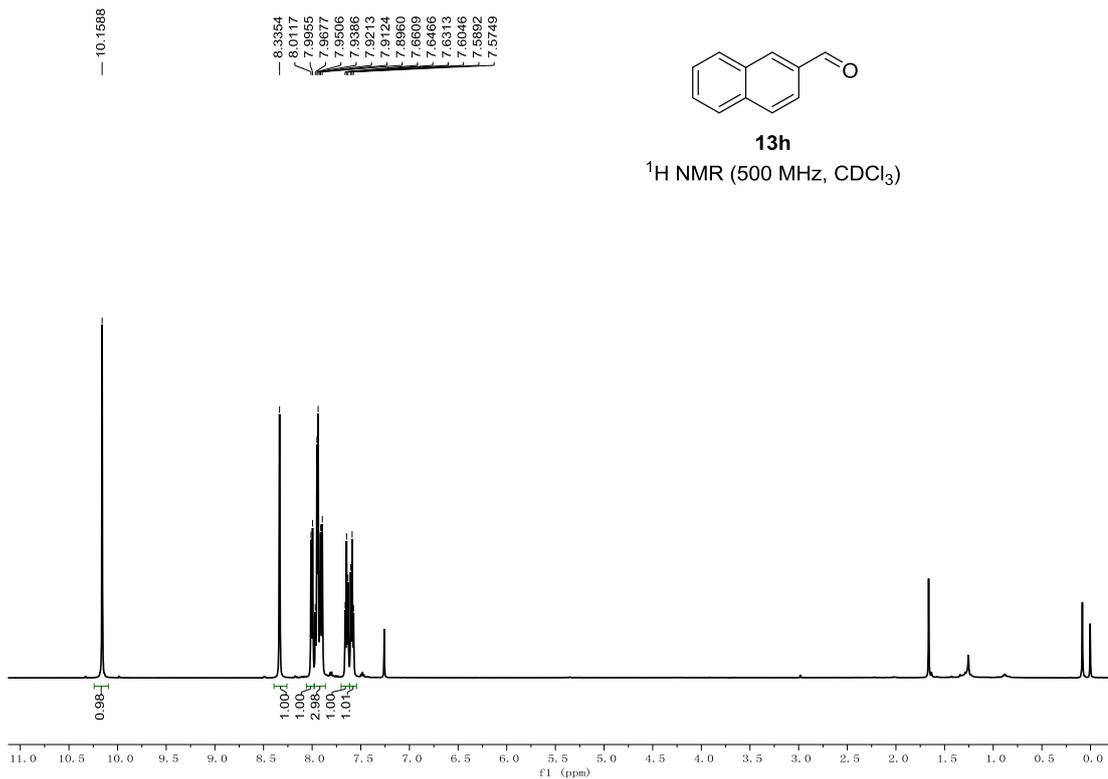
13e

¹³C NMR (125 MHz, CDCl₃)

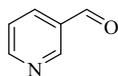






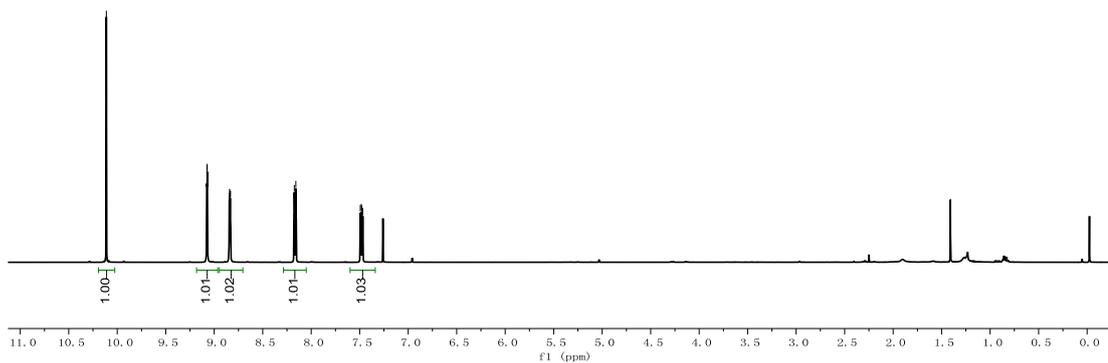


10.1122
 9.0751
 9.0720
 8.8453
 8.8419
 8.8357
 8.8322
 8.1744
 8.1724
 8.1704
 8.1625
 8.1586
 8.1547
 7.4936
 7.4840
 7.4780
 7.4683

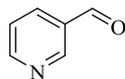


13i

$^1\text{H NMR}$ (500 MHz, CDCl_3)

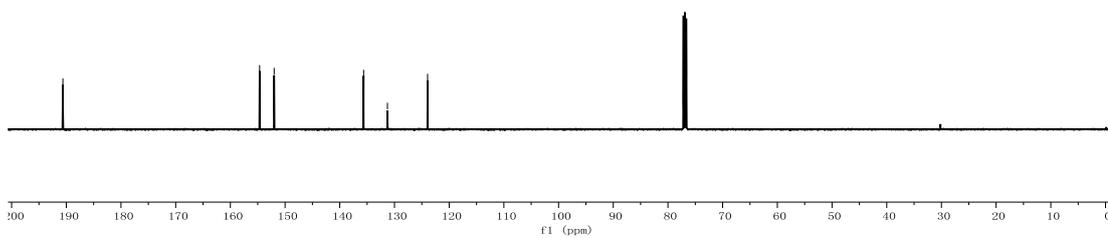


190.6232
 154.6574
 152.0017
 135.6432
 131.2867
 123.9442



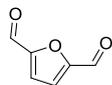
13i

$^{13}\text{C NMR}$ (125 MHz, CDCl_3)



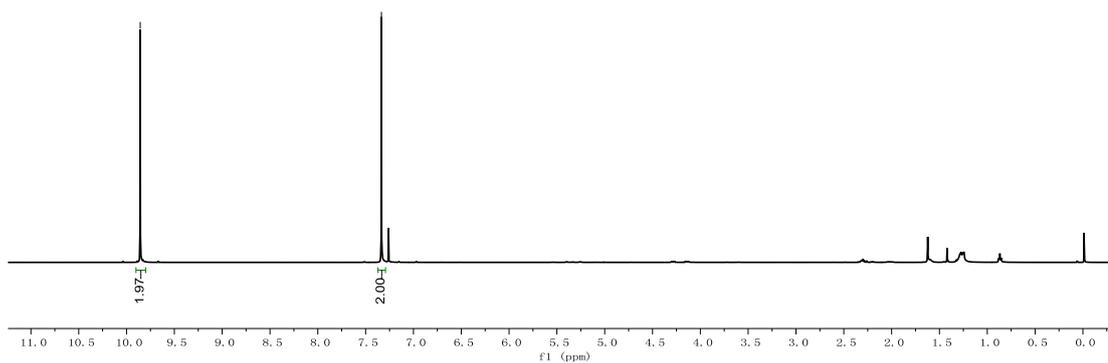
— 9.8567

— 7.3348



13j

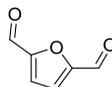
¹H NMR (500 MHz, CDCl₃)



— 179.0791

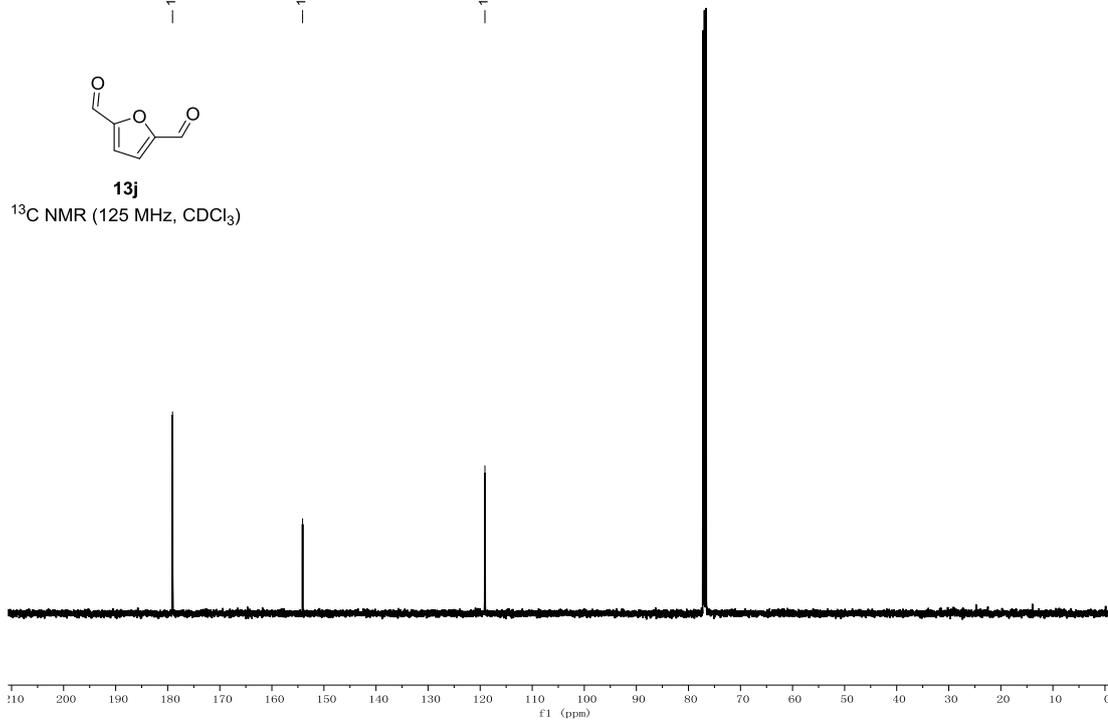
— 154.1010

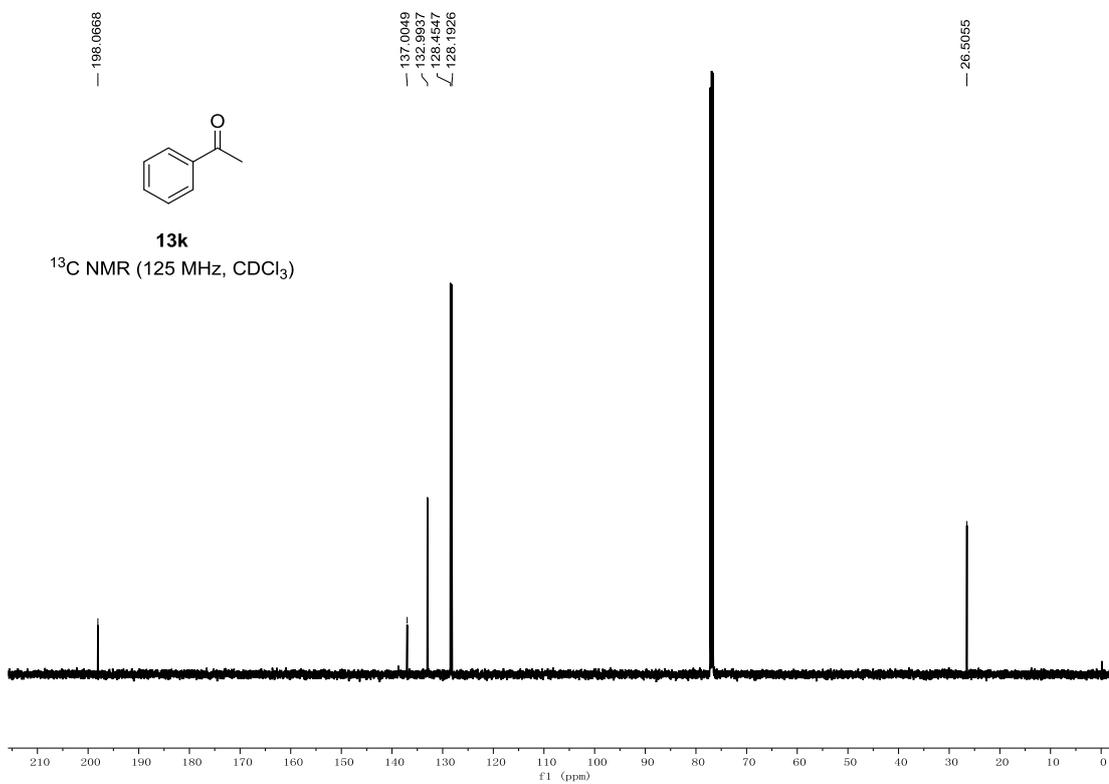
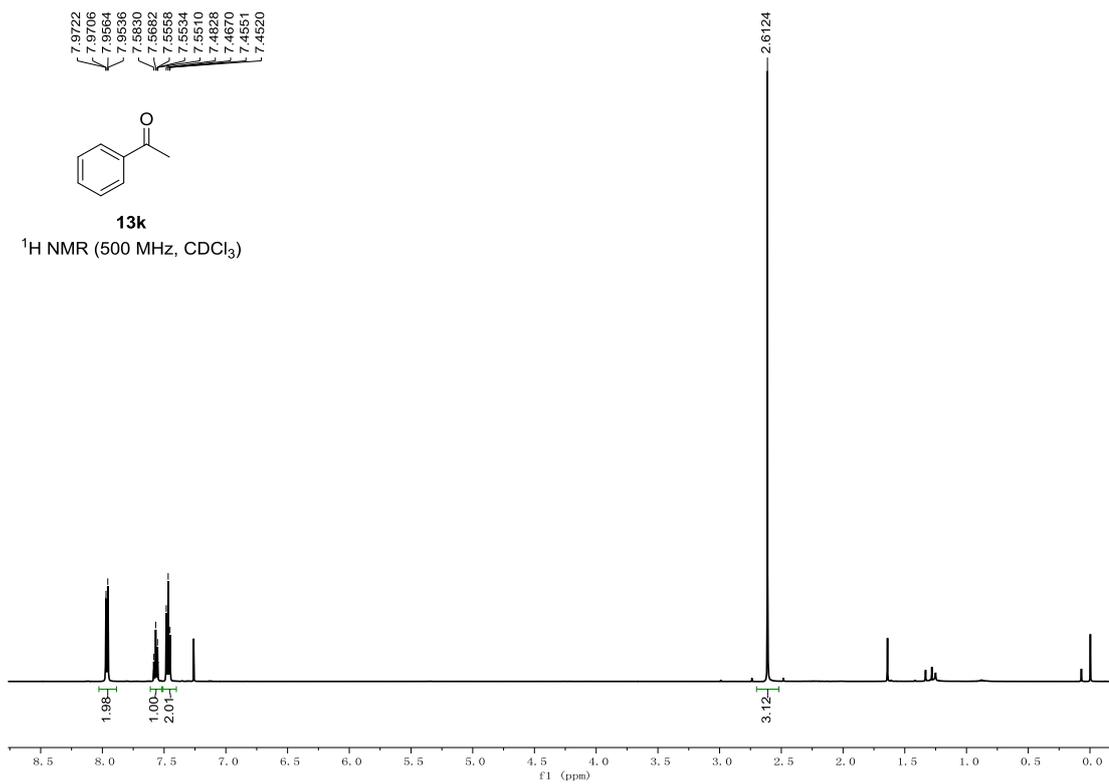
— 119.0858

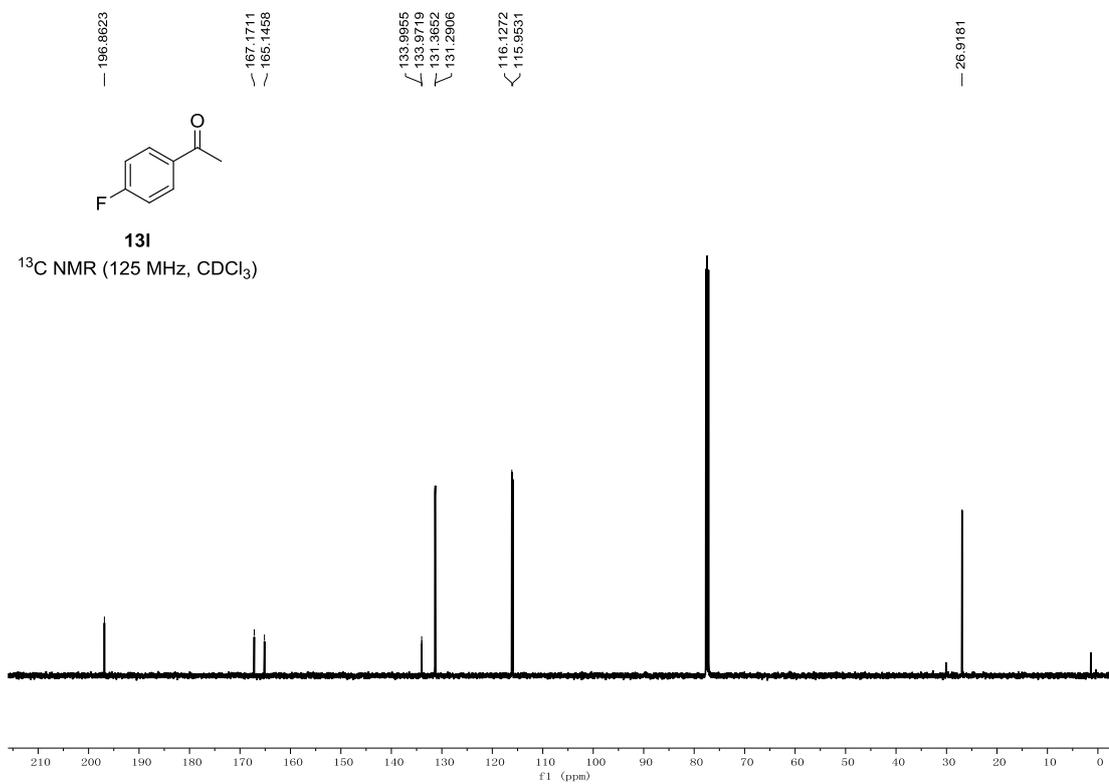
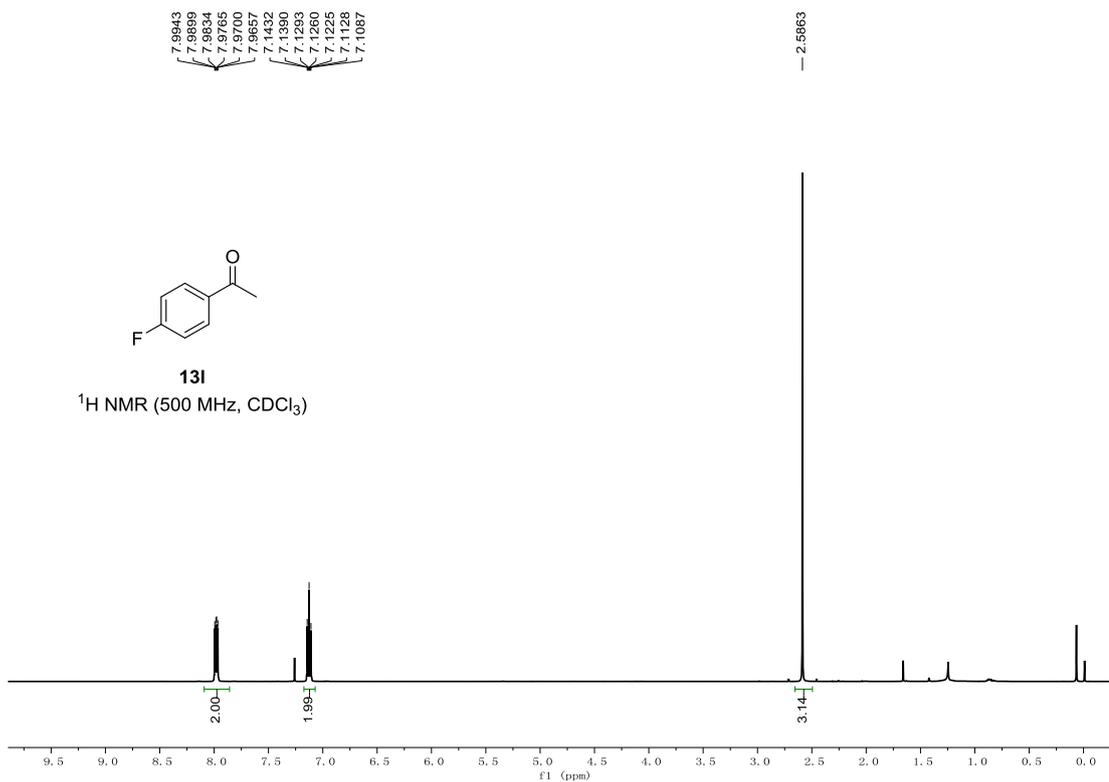


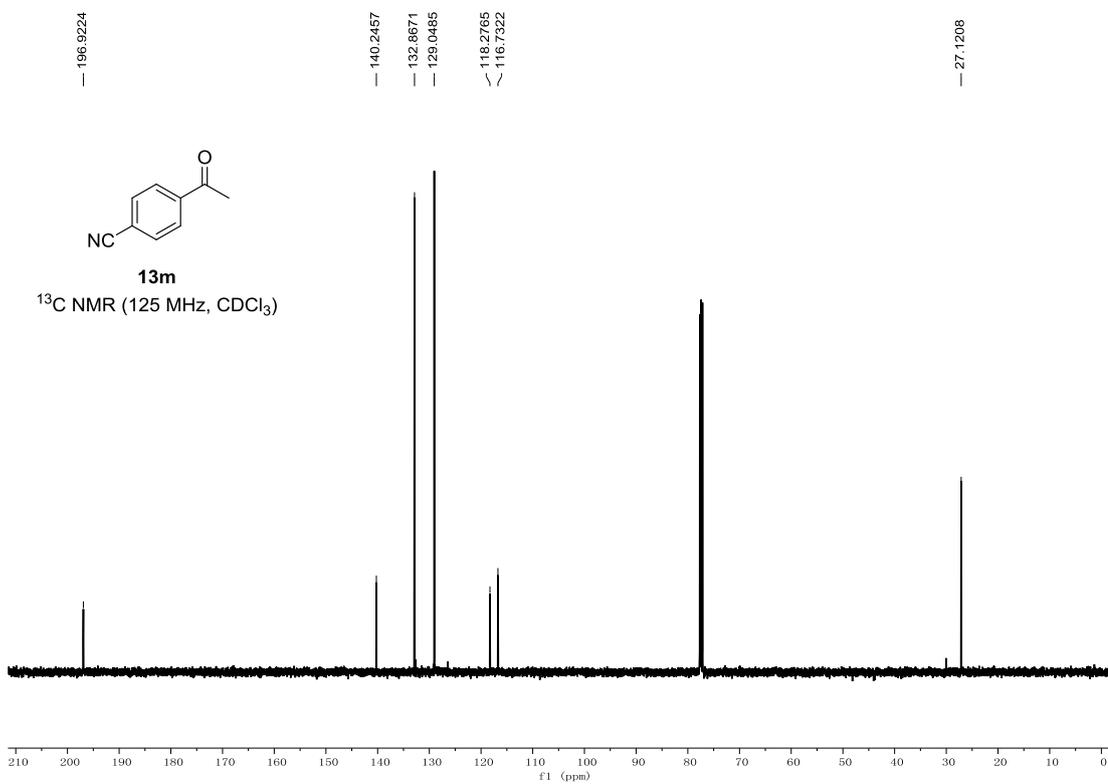
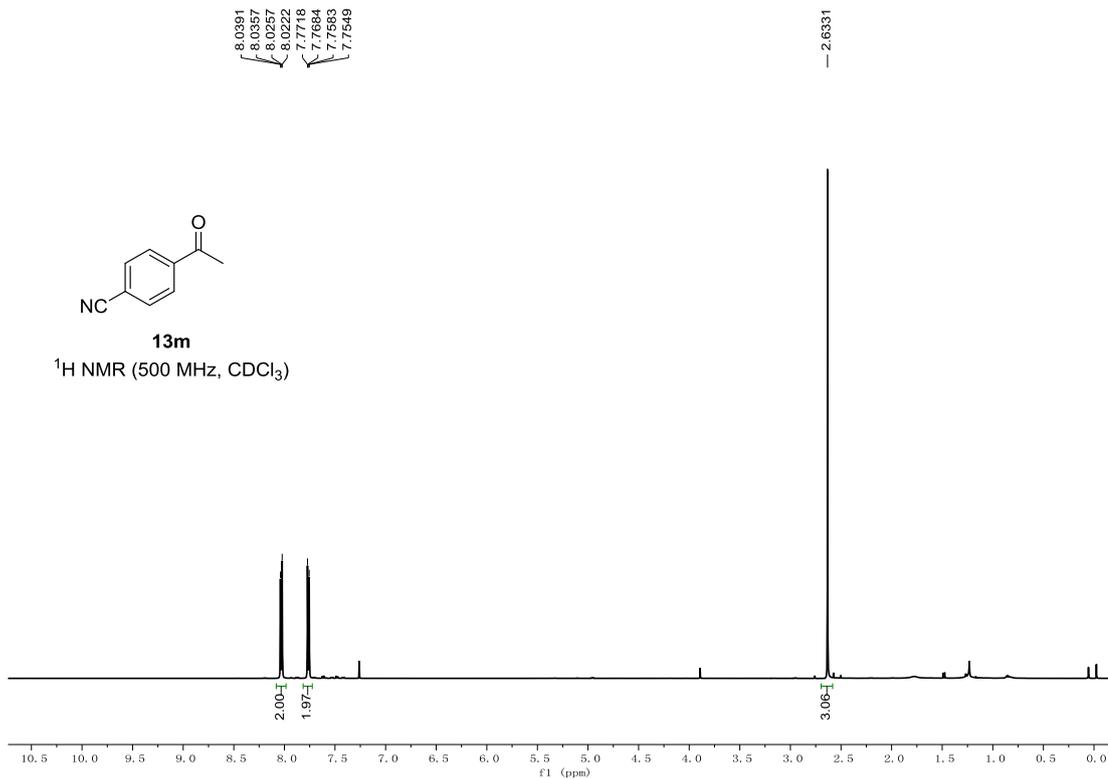
13j

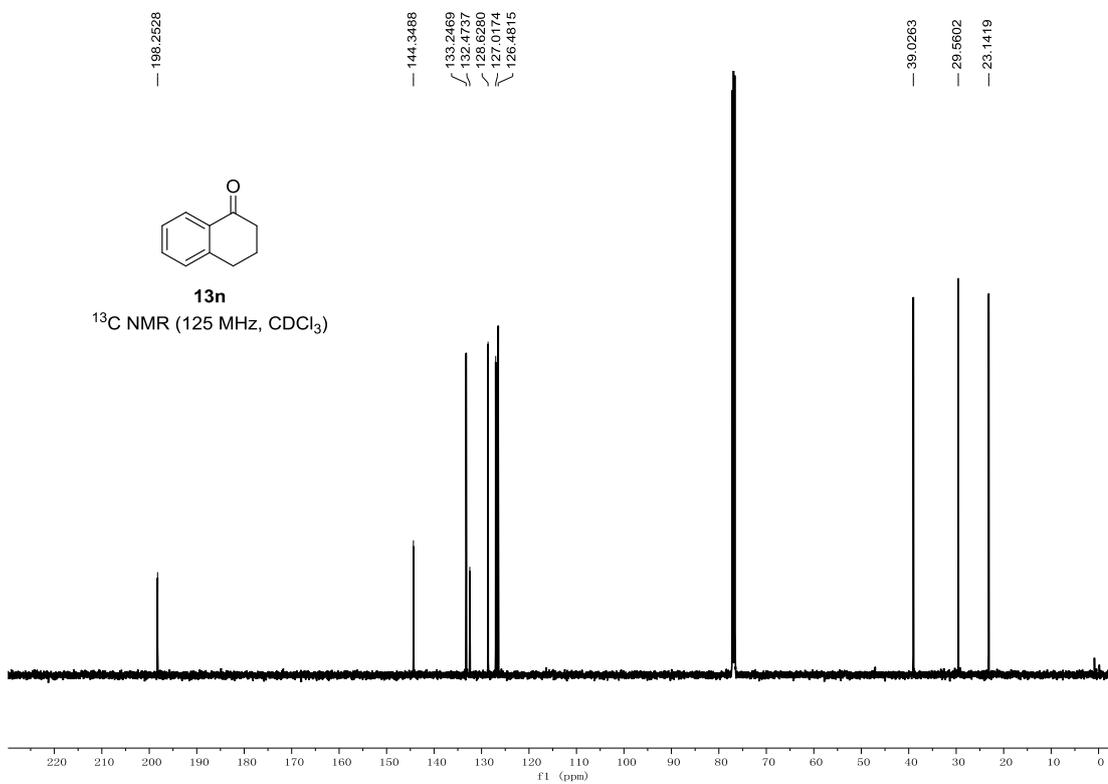
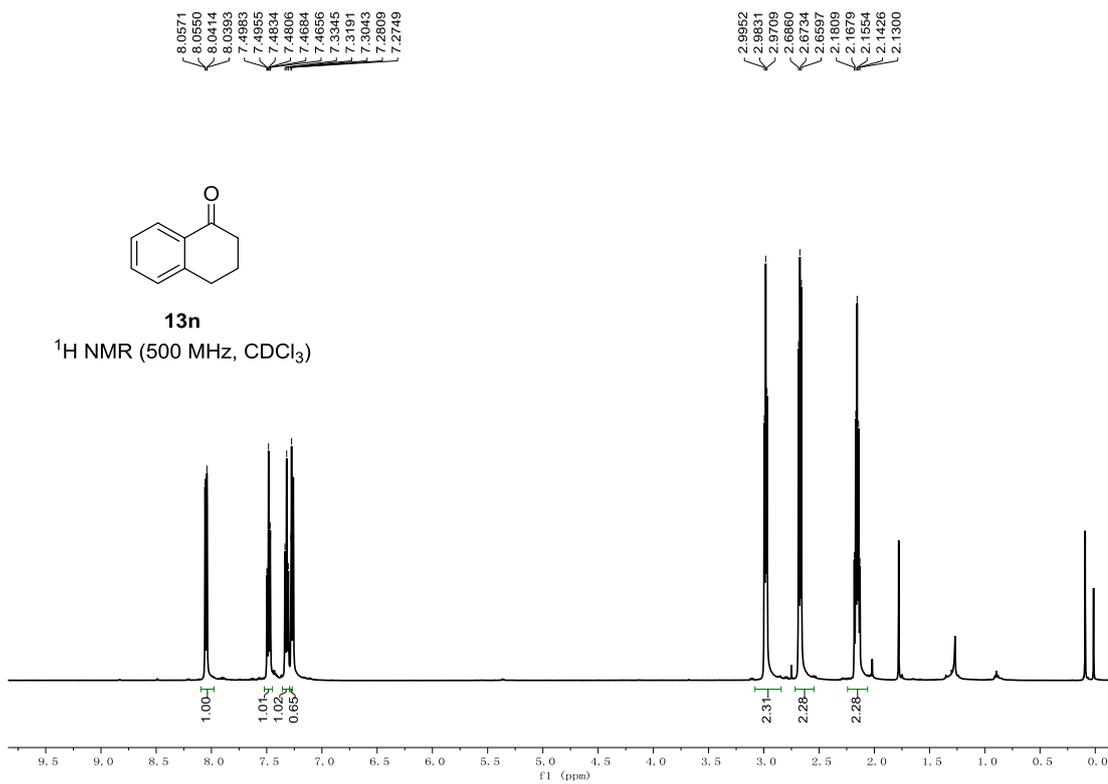
¹³C NMR (125 MHz, CDCl₃)

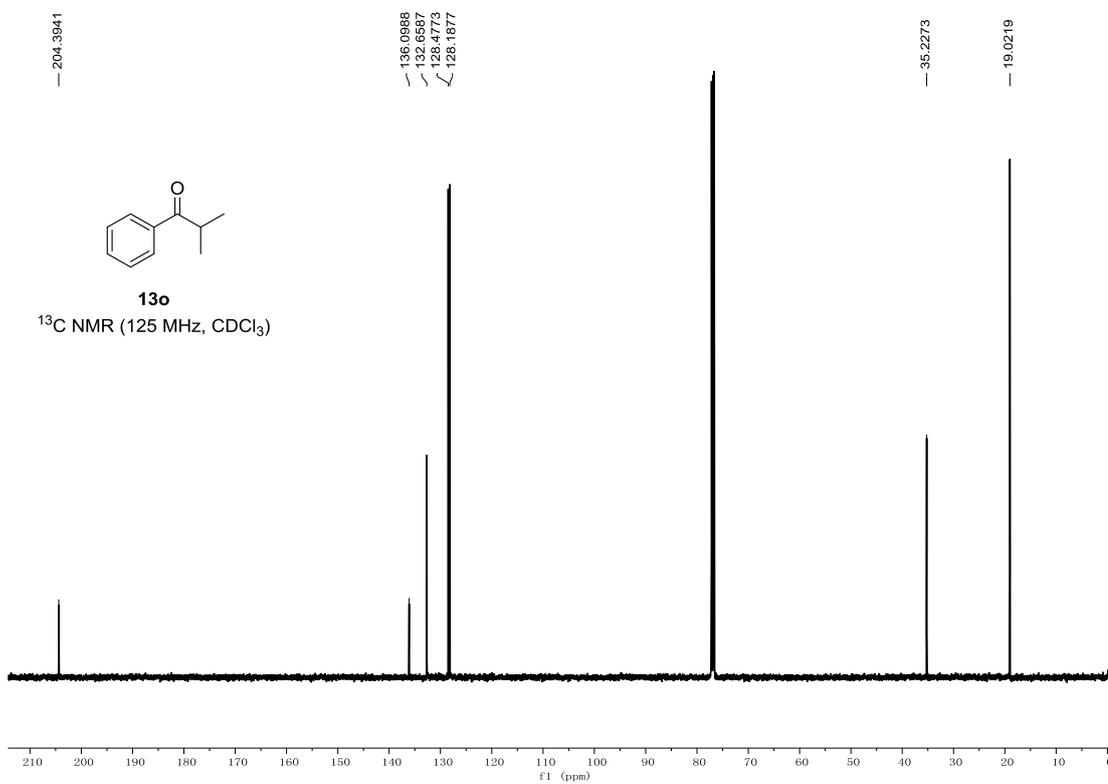
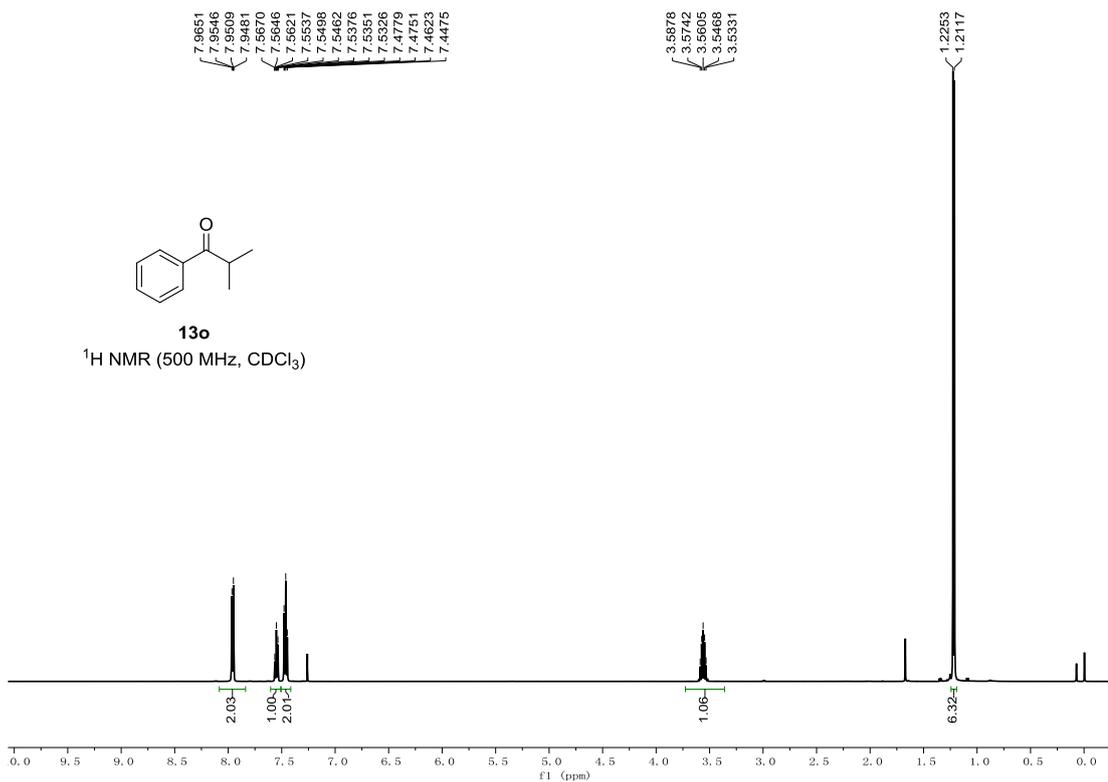


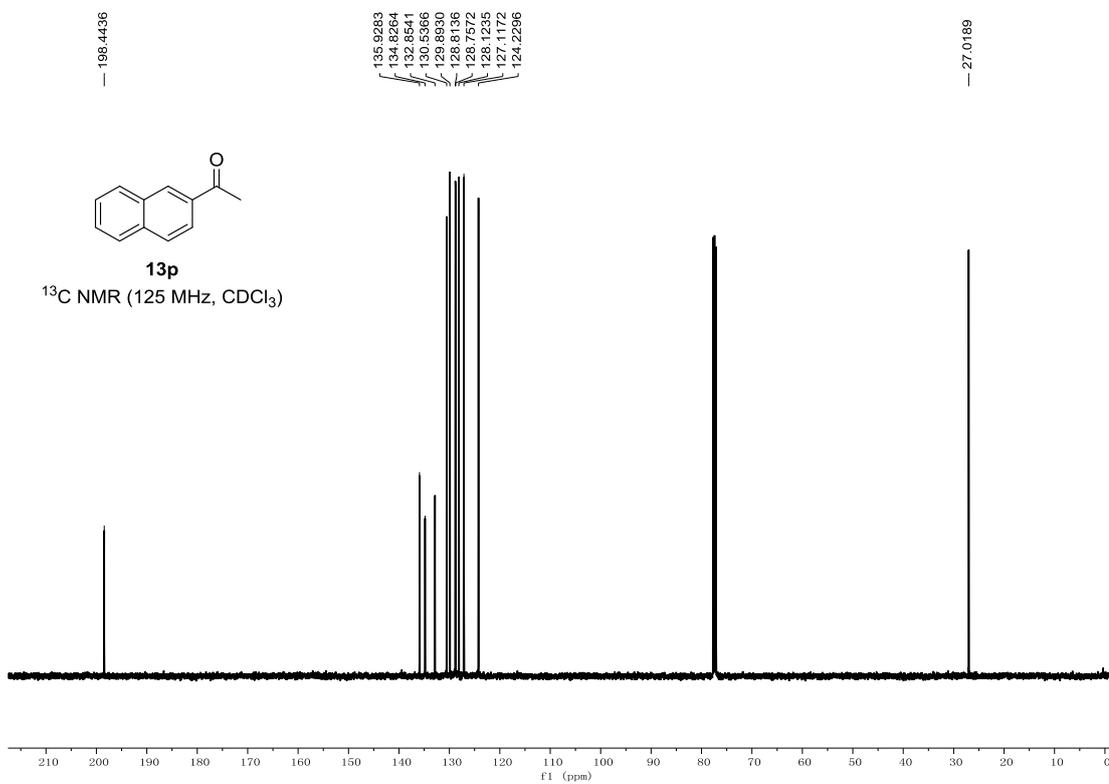
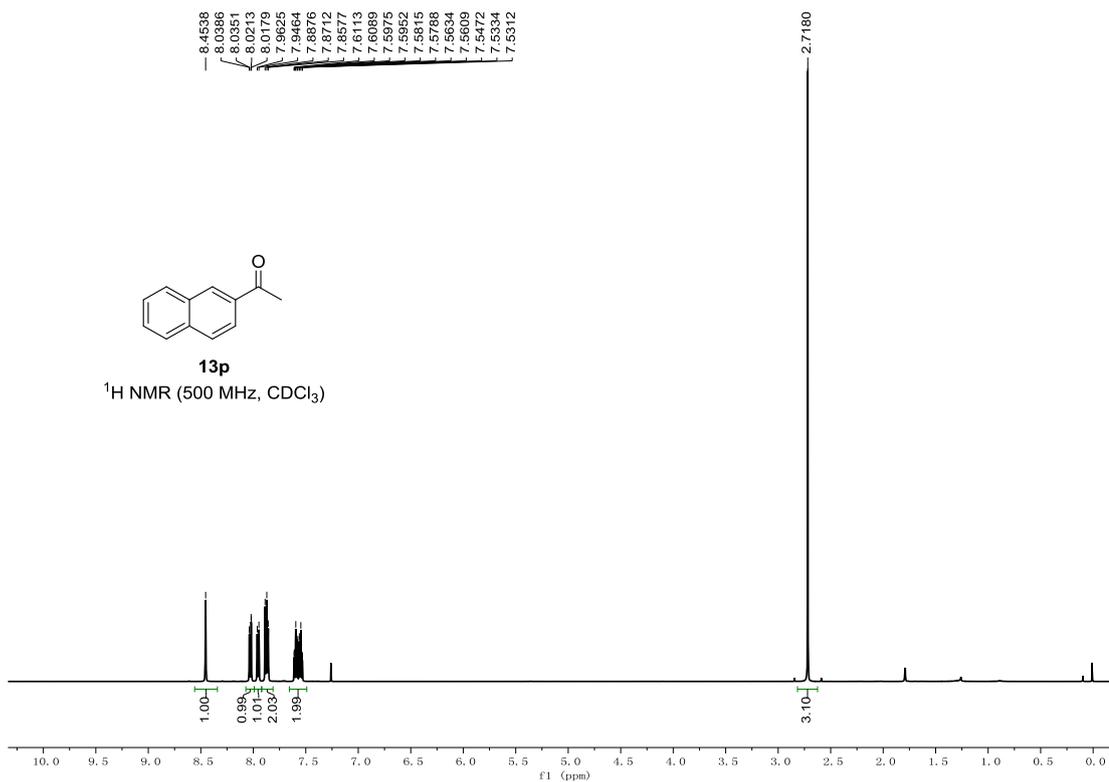


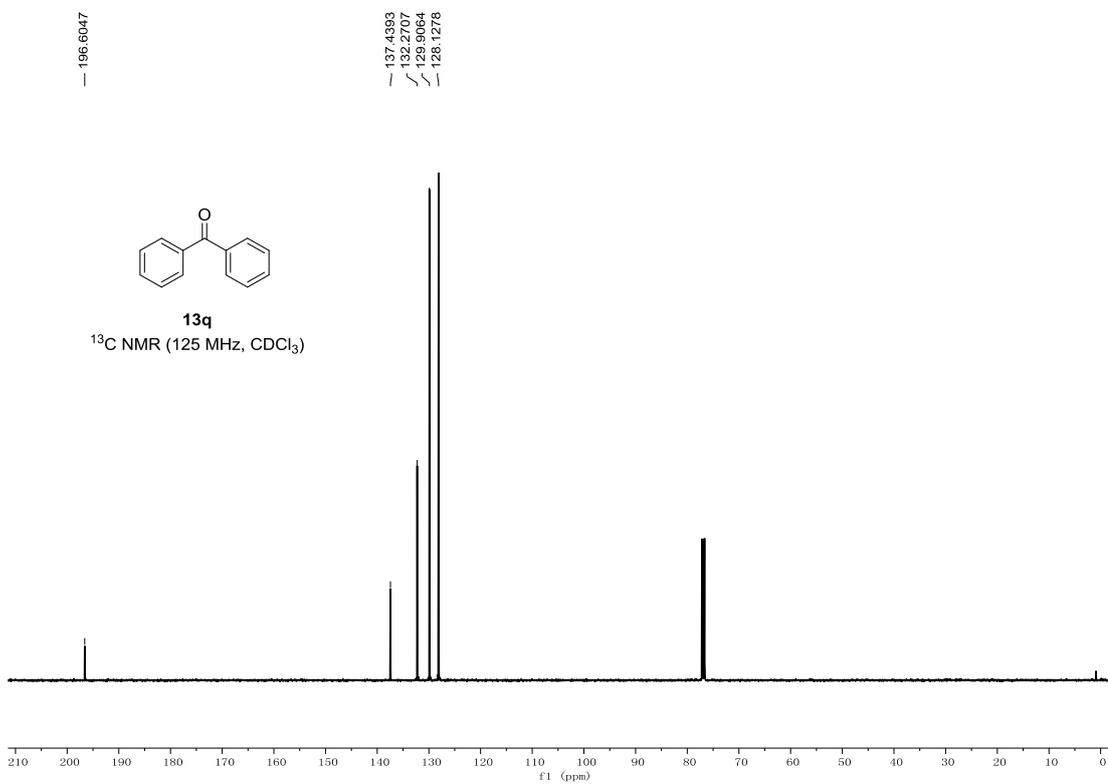
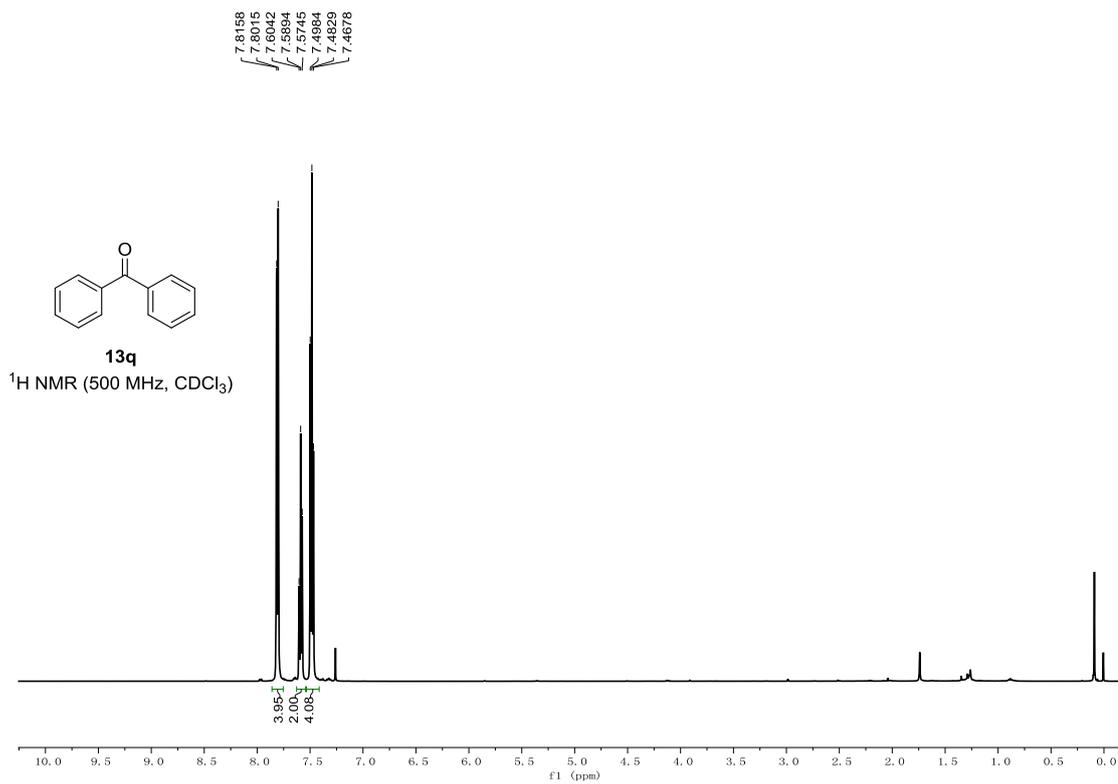


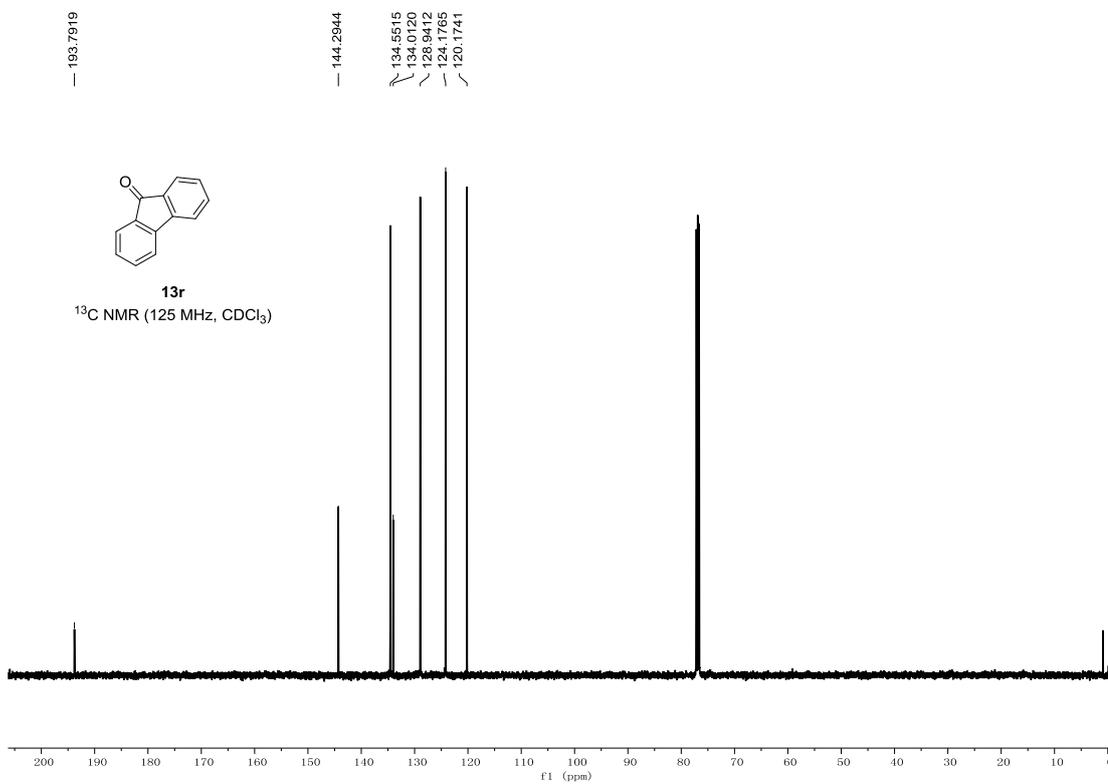
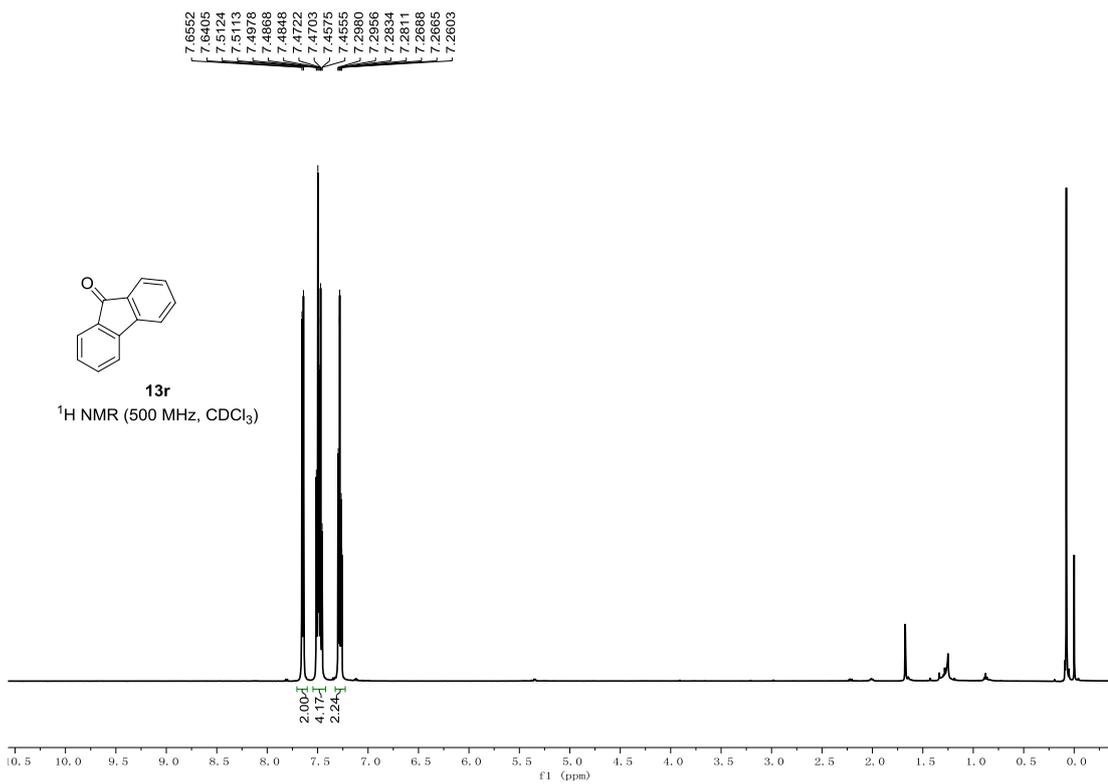


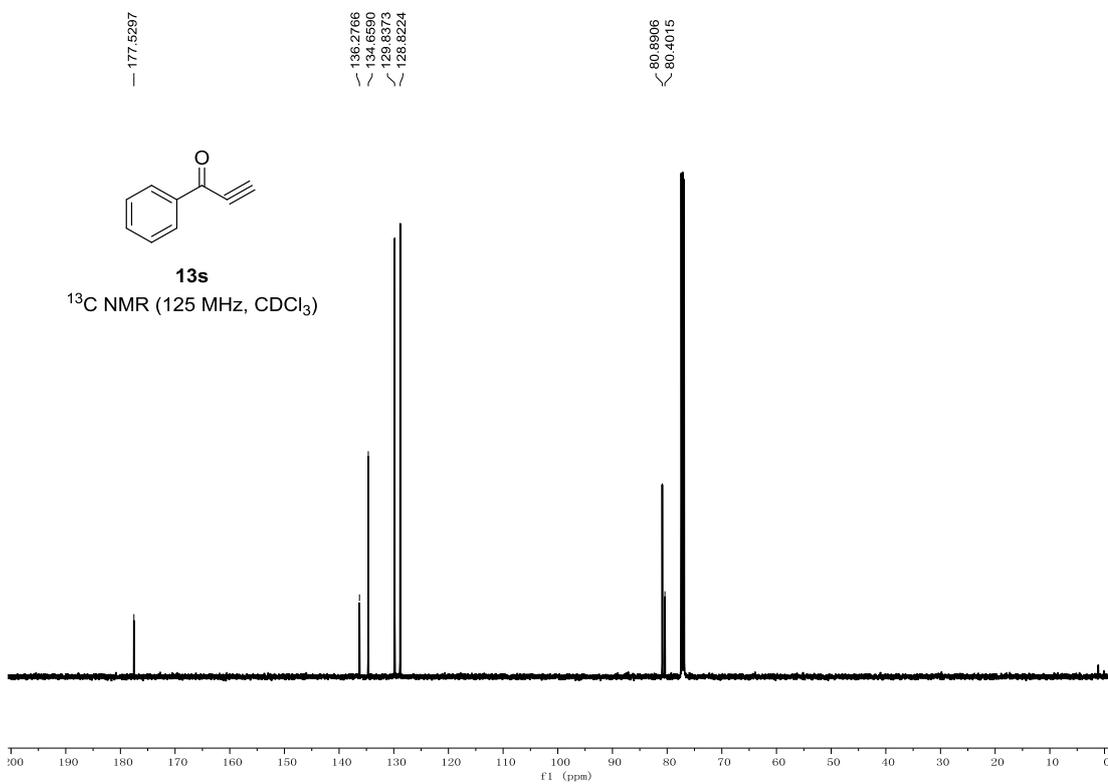
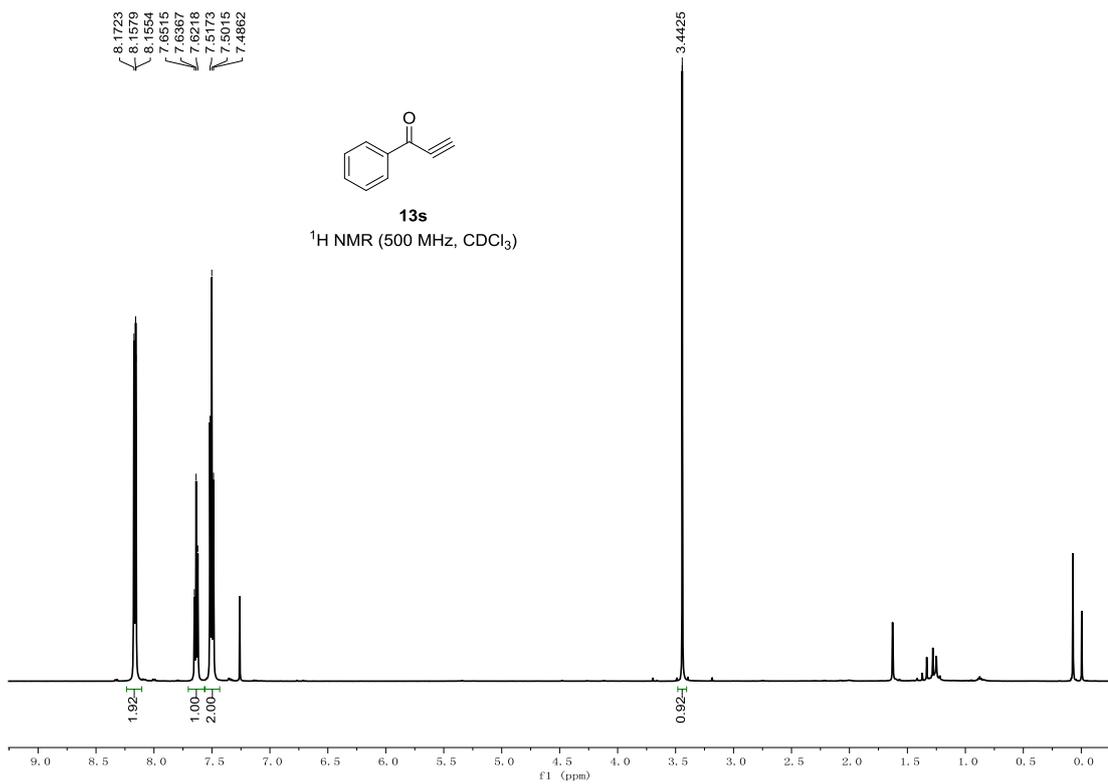


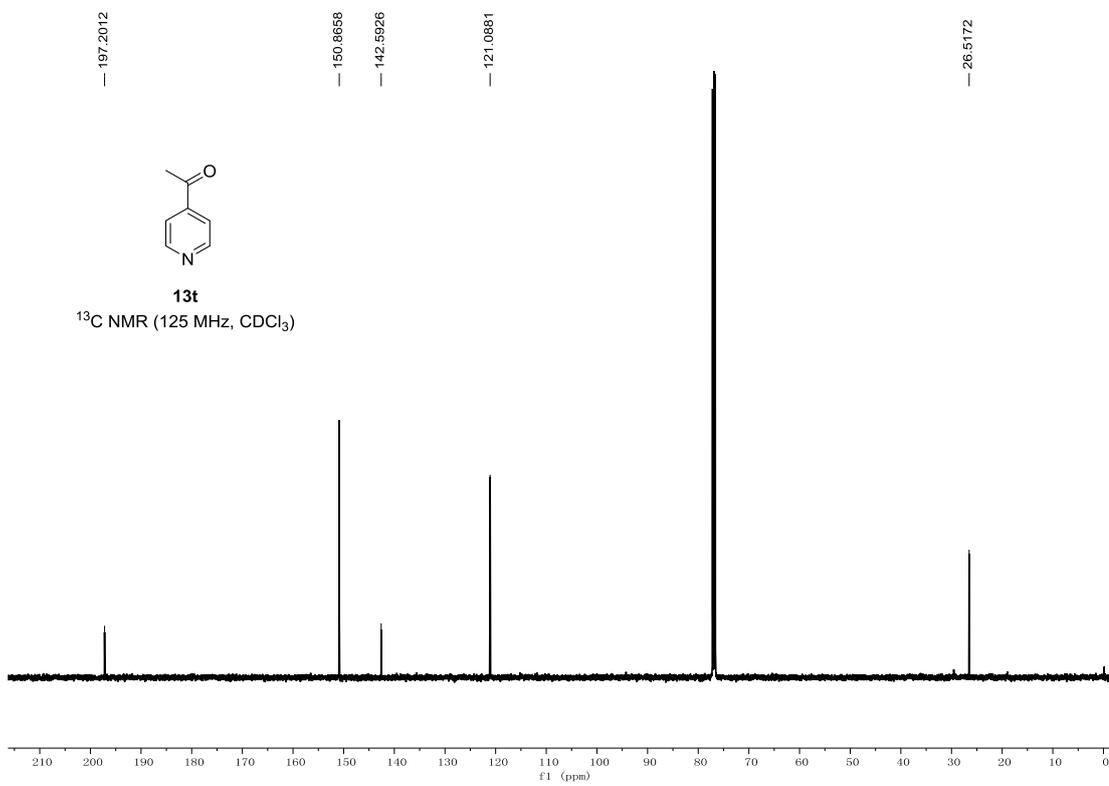
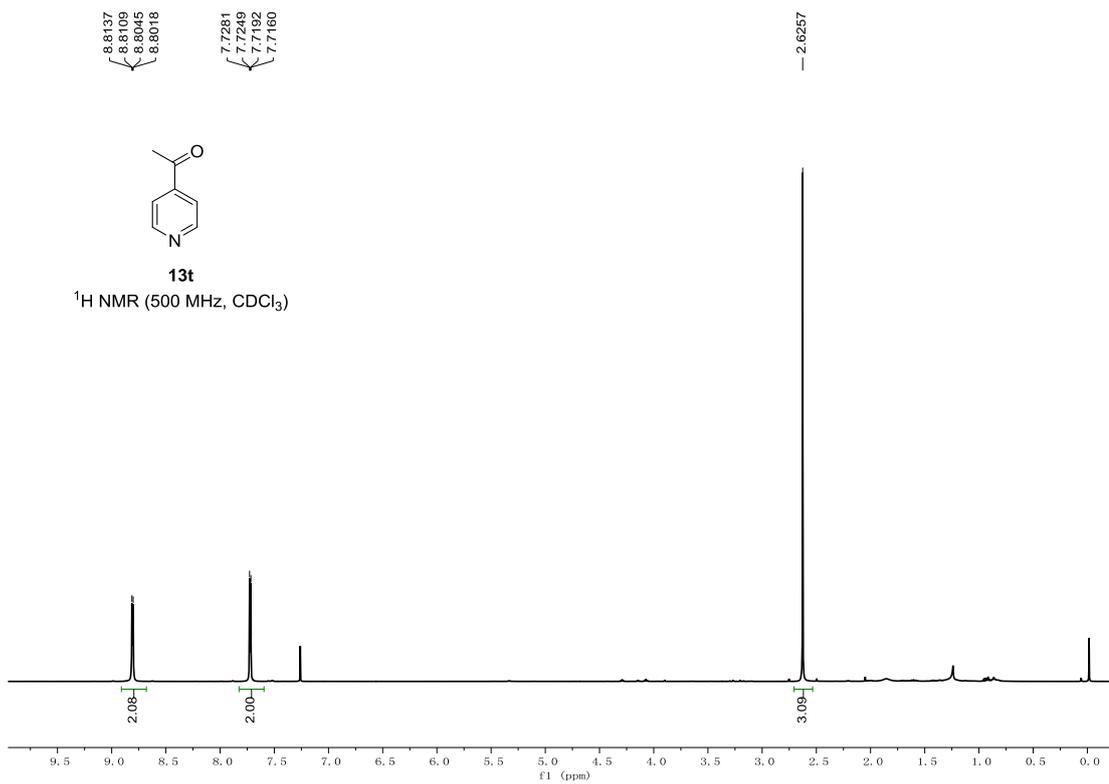


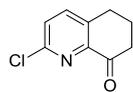






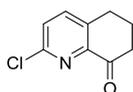
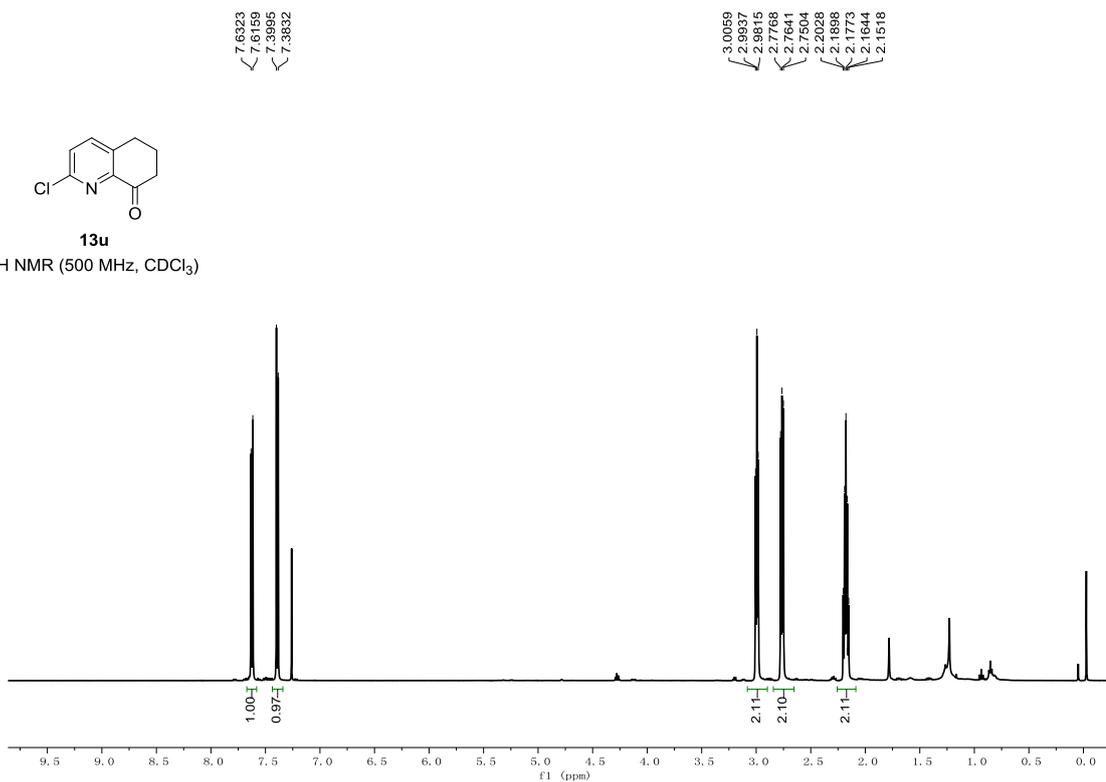






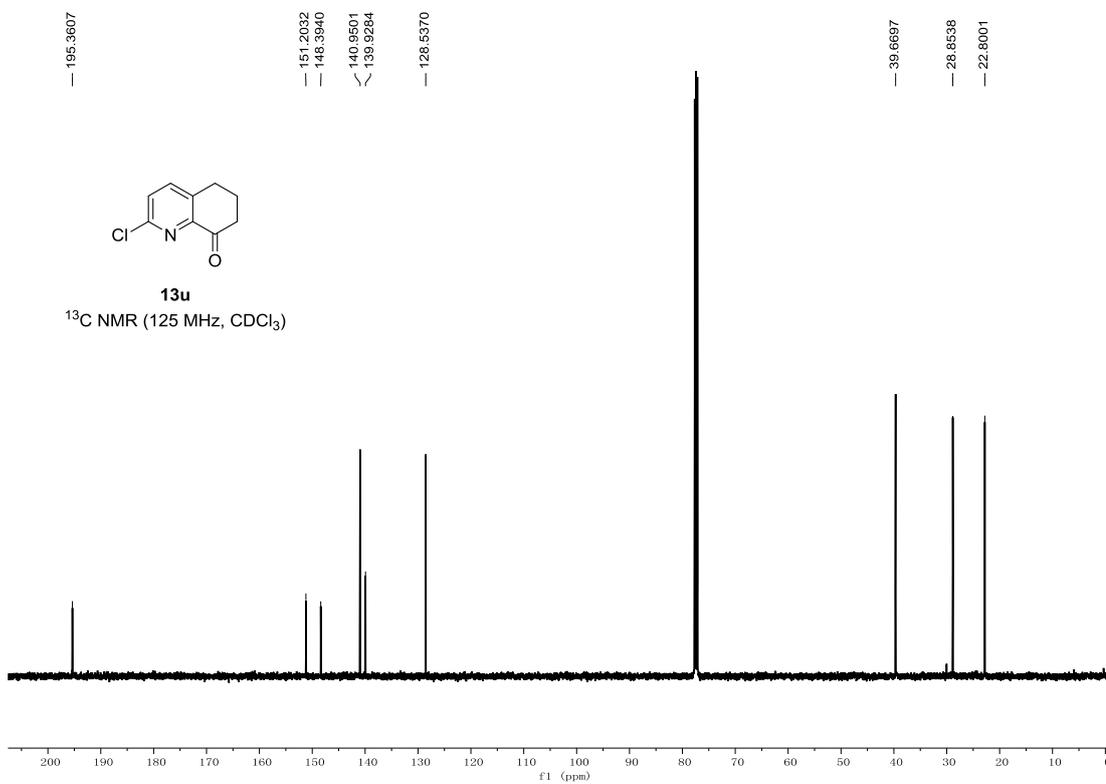
13u

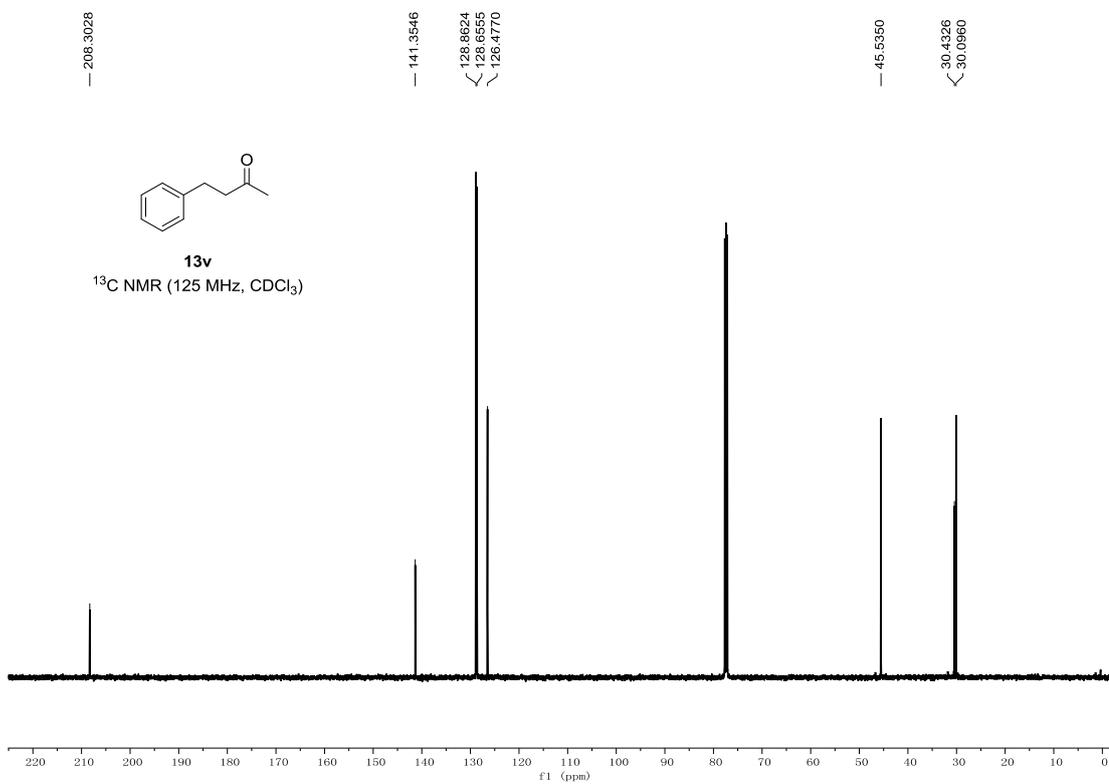
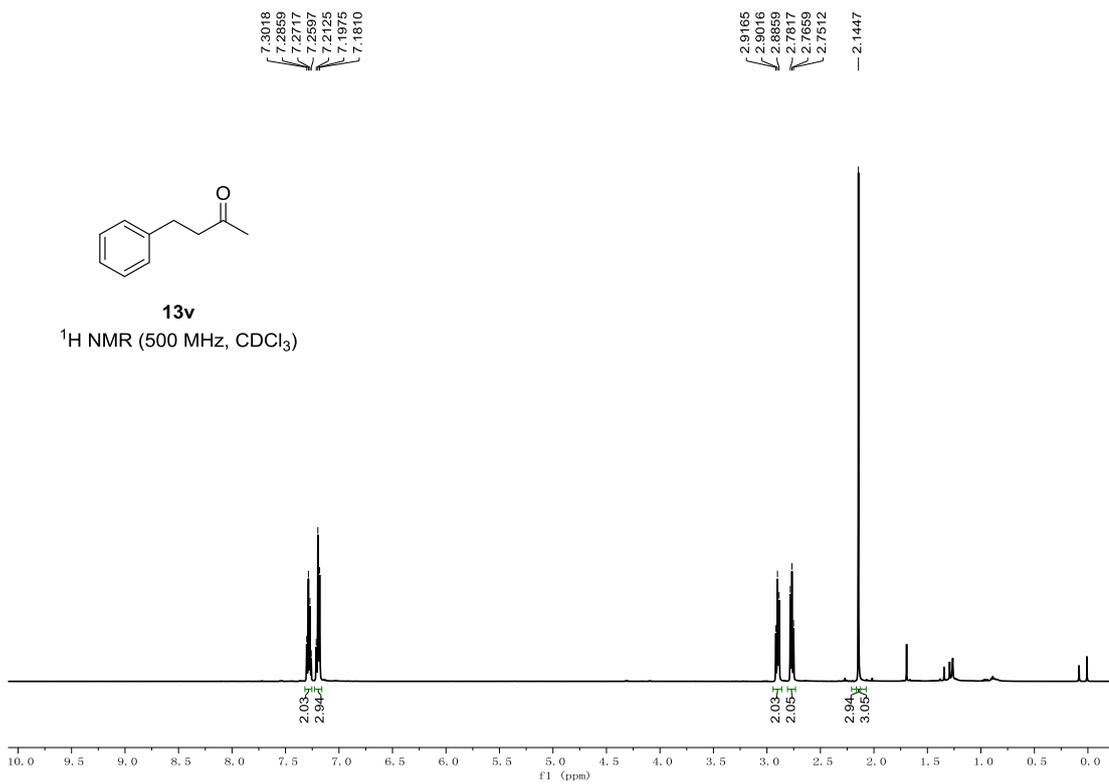
¹H NMR (500 MHz, CDCl₃)

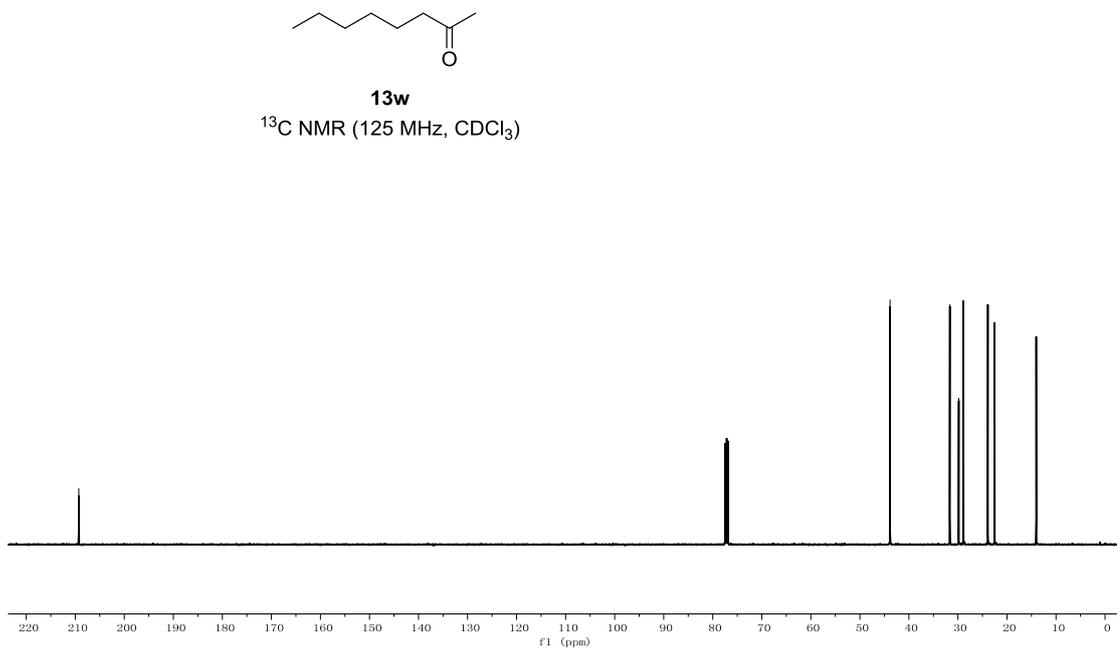
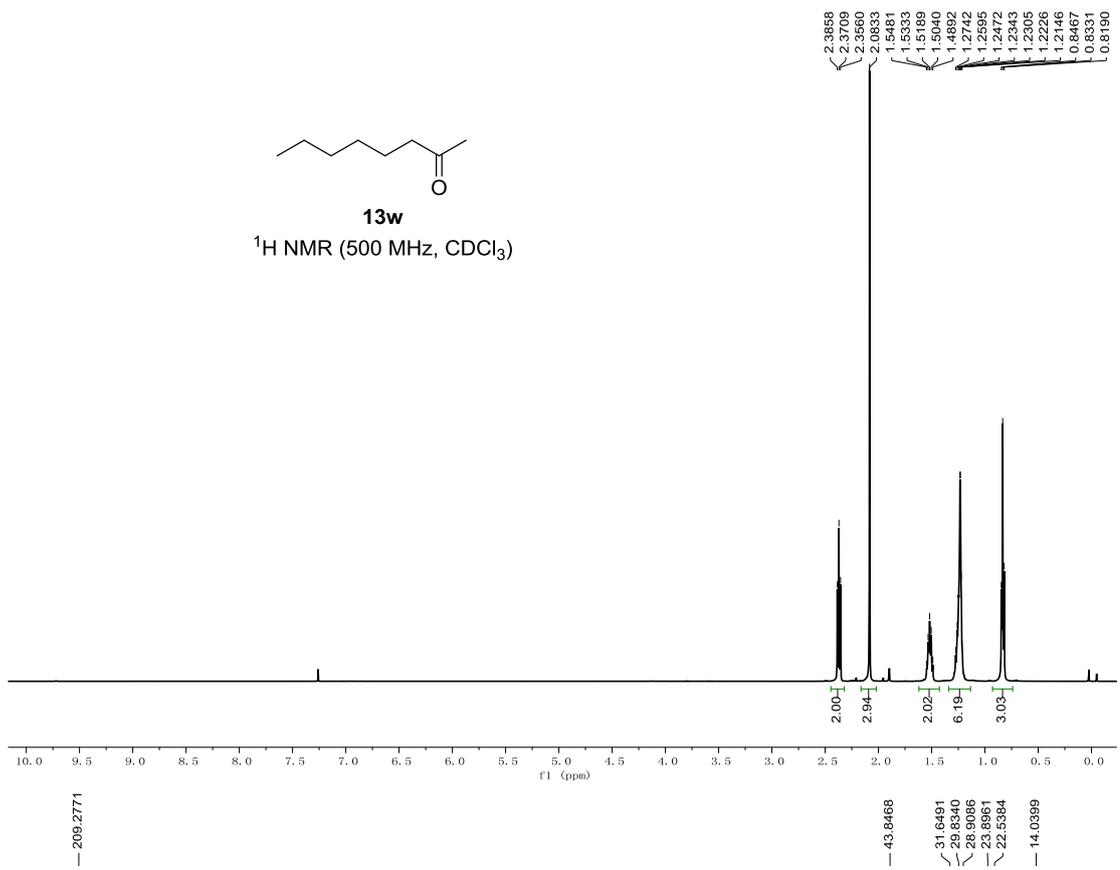


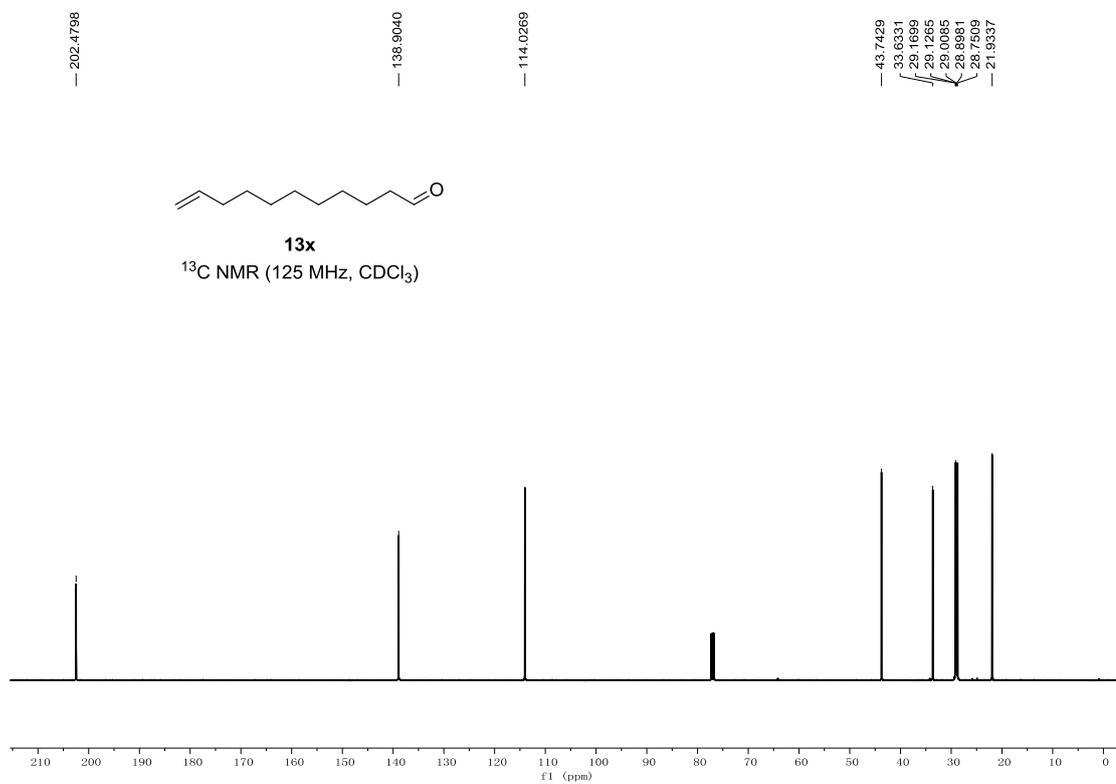
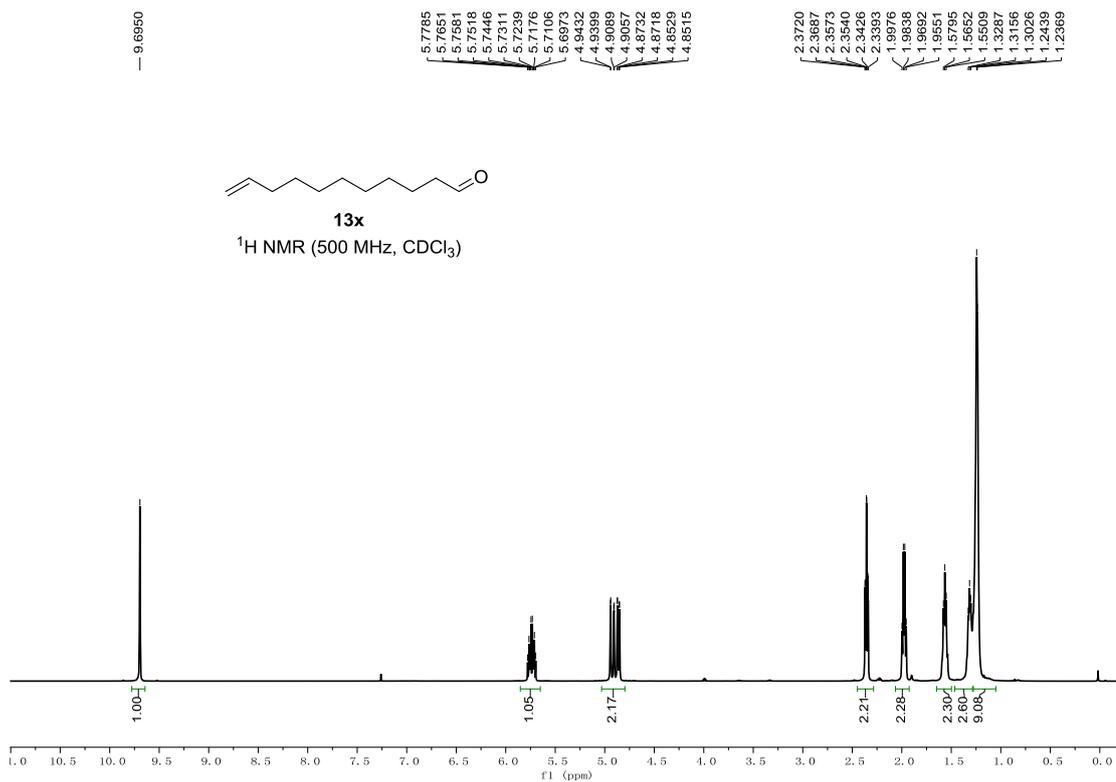
13u

¹³C NMR (125 MHz, CDCl₃)







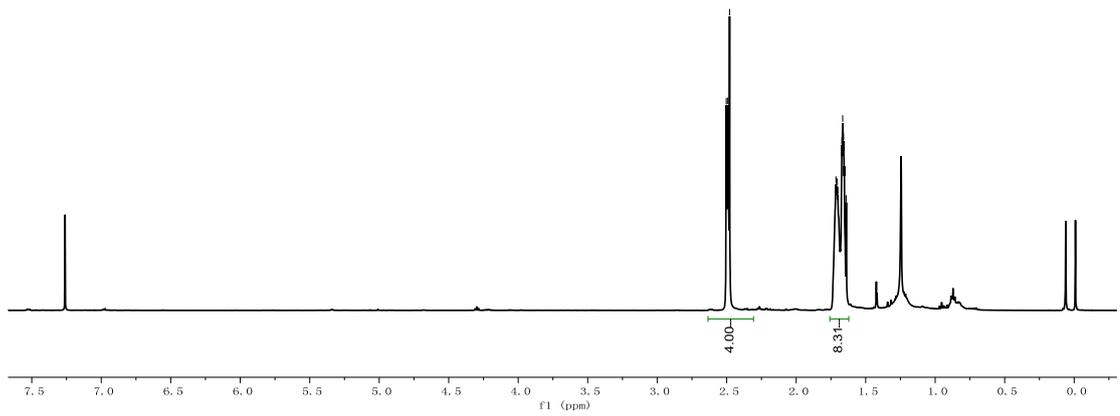




13y

¹H NMR (500 MHz, CDCl₃)

2.5031
2.4921
2.4867
2.4794
1.7140
1.7098
1.7061
1.7005
1.6714
1.6655
1.6592
1.6536
1.6395



215.8380



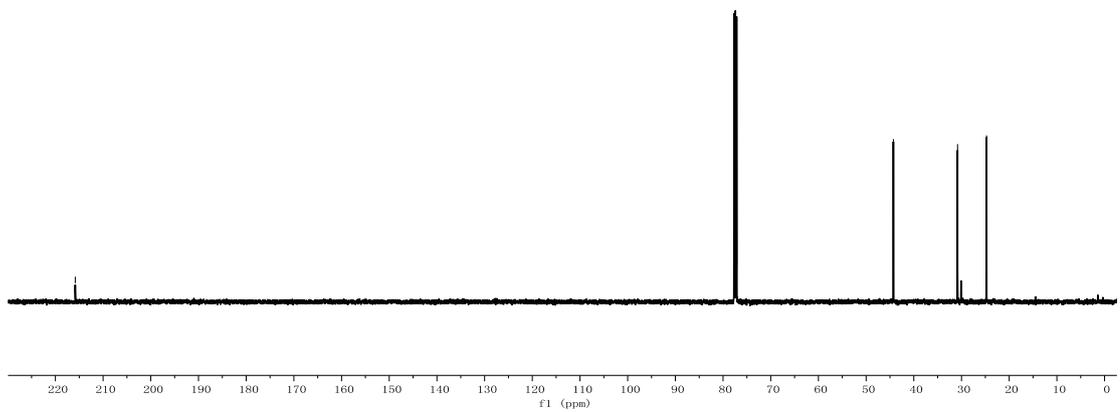
13y

¹³C NMR (125 MHz, CDCl₃)

44.2873

30.8315

24.7458

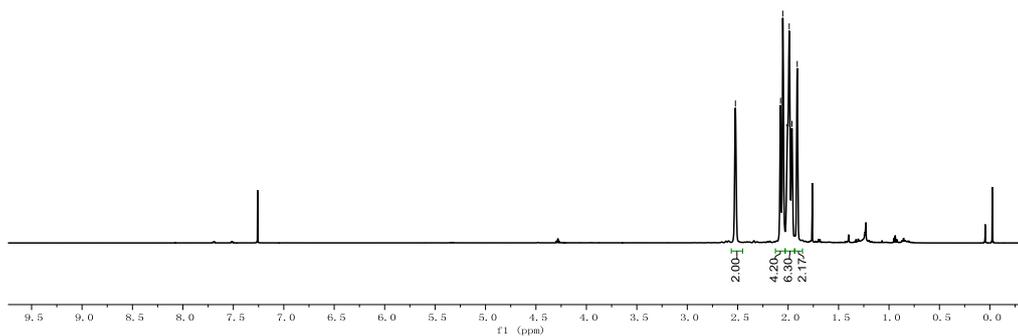




13z

¹H NMR (500 MHz, CDCl₃)

— 2.5227
2.0748
2.0631
1.9823
1.9099

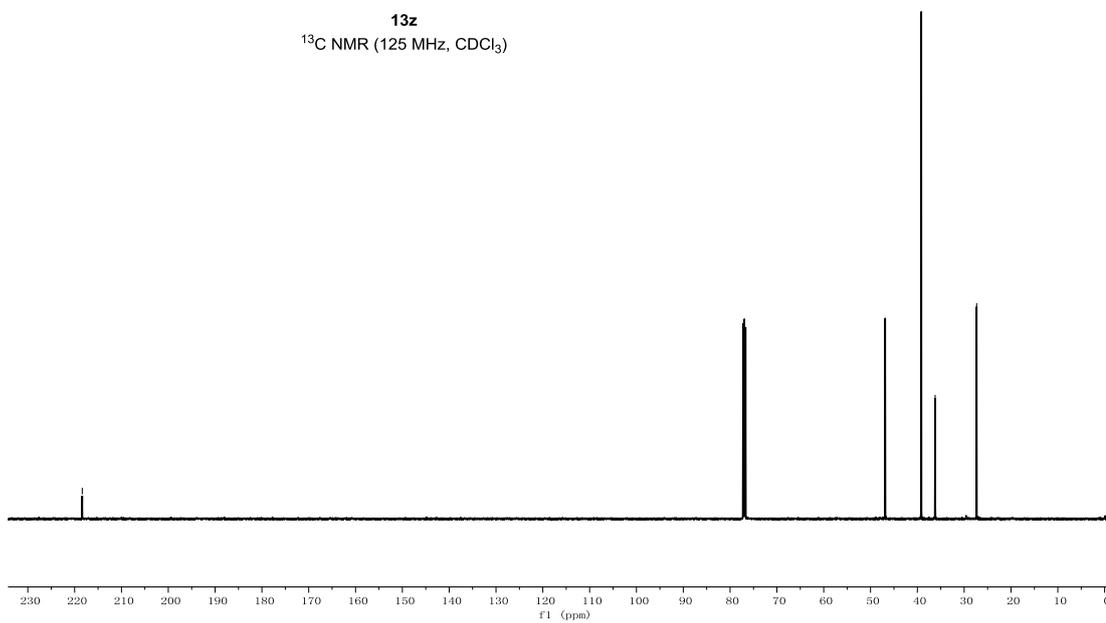


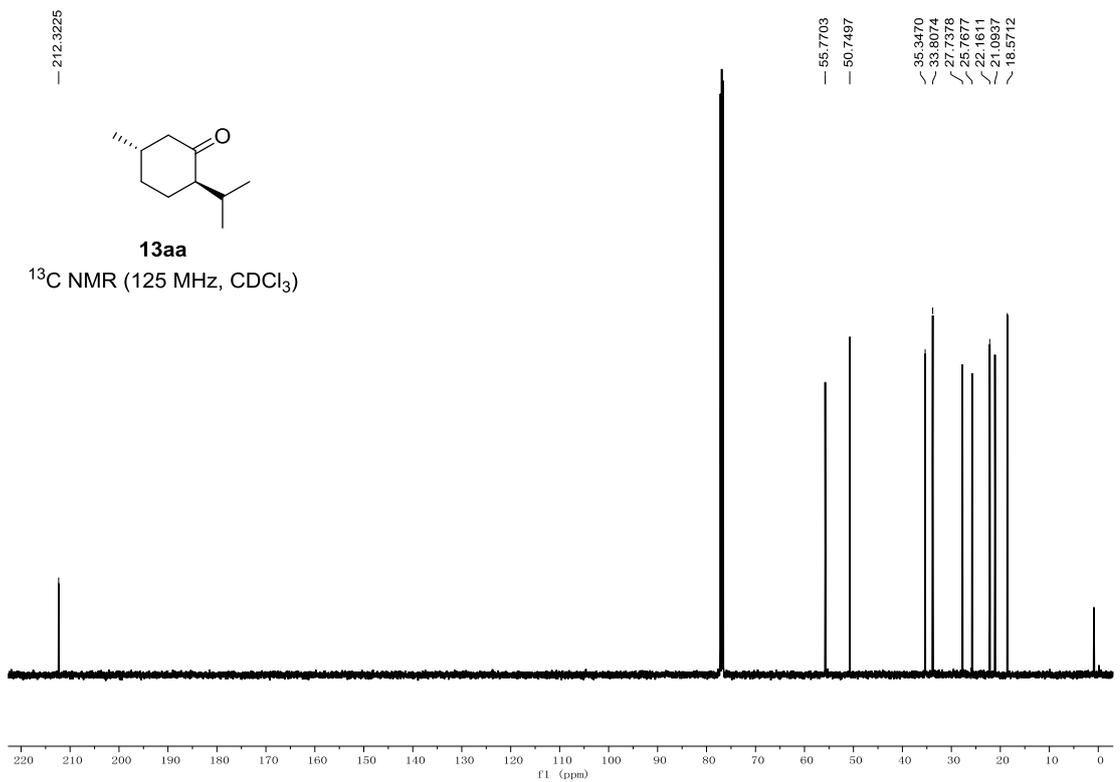
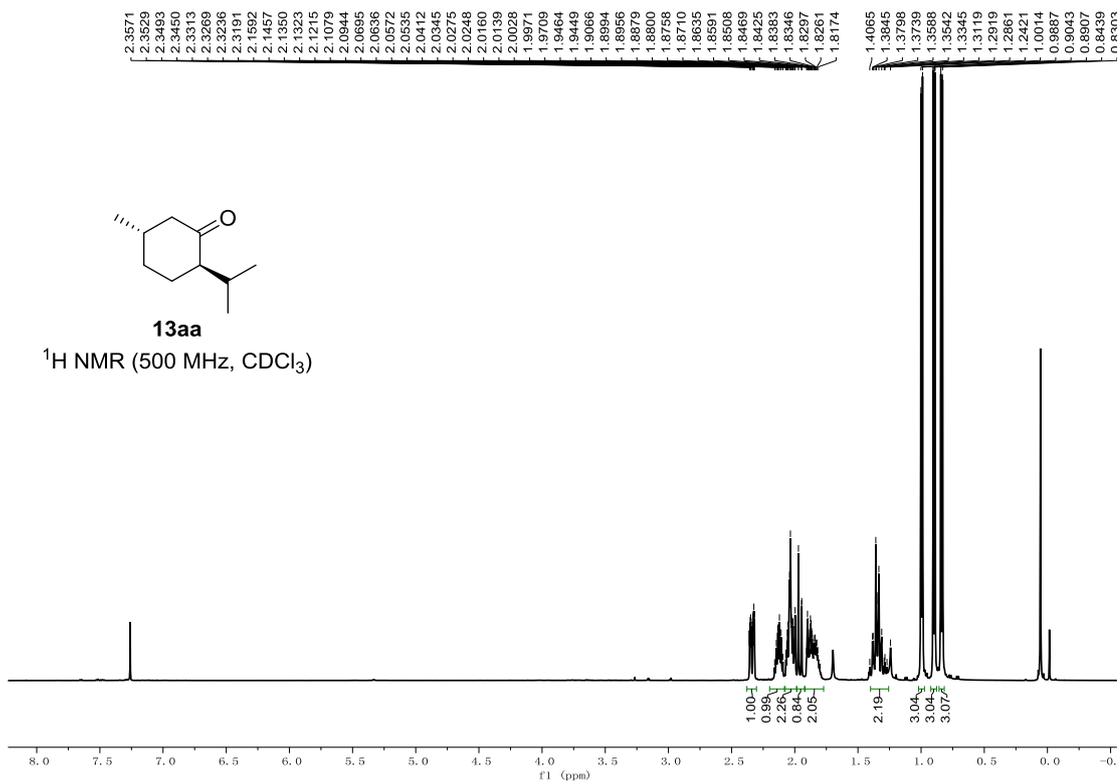
13z

¹³C NMR (125 MHz, CDCl₃)

— 218.3760

— 46.8737
— 38.1652
— 36.1934
— 27.3423





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