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Rodney A. Fernandes , Venkati Bethi

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Graphical Abstract

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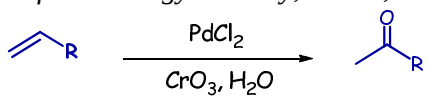
Rodney A. Fernandes* and Venkati Bethi
Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, Maharashtra, India



44 examples
Good FG compatibility
No aldehyde by-products
Simple operational procedure
Economical process

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Synthesis of methyl ketones from terminal olefins using $PdCl_2/CrO_3$ system mimicking the Wacker process

Rodney A. Fernandes[a,*] and Venkati Bethi[a]

[a], *Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, Maharashtra, India*

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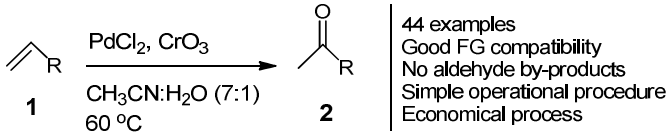
ABSTRACT

An efficient synthesis of methyl ketones from terminal olefins using $PdCl_2/CrO_3$ system mimicking the Wacker process is developed. The method shows good functional groups compatibility, no aldehyde by-products and is operationally simple. CrO_3 is the sole oxidant and replaces both Cu-salts and molecular oxygen, traditionally used in this process. The method holds potential for future applications in organic synthesis.

1. Introduction

The methyl ketone moiety is ubiquitously found in many natural products. There has been extensive development in the synthesis of this unit from terminal olefins by the Wacker type oxidation. The conventional Wacker process of oxidation of ethylene to acetaldehyde is catalyzed by an aq. solution of $PdCl_2$ combined with $CuCl_2$, under O_2 atmosphere.[1-4] Although commercially successful, the process suffers from certain limitations. Most significant being the generation of HCl [from $CuCl_2$ which is required to promote the re-oxidation of Pd(0) to Pd(II)] which corrodes the reactor and as well is responsible for the formation of chlorinated by-products. Tsuji and co-workers extended this elegant method to construct methyl ketones from terminal olefins using the $PdCl_2/CuCl_2$ catalytic system, known popularly as Wacker–Tsuji oxidation.[5-7] In order to overcome the drawbacks present in conventional Wacker process, several modifications and new advancements are documented.[5,8] Firstly, use of oxygen as a sole oxidant,[8u,v,aa,ae] then direct O_2 coupled Wacker oxidation associated with coordinating ability of solvents[8z,ad] such as DMF, DMA, NMP or ethylene carbonate were developed. Further, appropriate co-catalysts[8d,e,g,i,w,ae,ag] and/or solvents,[8q,r,s,t,ab] nitrogen based ligands,[8n,p,y] organic oxidants such as benzoquinone,[5,8f,h,j,ag] organic peroxides,[8a,c,x,ac] nitrites[8o,ag] and hydrogen peroxide[8b] were also investigated. Supporting the catalyst ingredients onto polymers[8k,l,m] was also explored. A recent development uses potassium bromate as a oxidant.[8af] Hence there is an on-going interest in search of alternatives for terminal oxidants.

In many palladium catalysed processes, inorganic oxidants [$Ag(OAc)_2$,[9] Tl(III)salts,[10] $CuCl_2$,[11] $Cu(OAc)_2$,[12] HNO_3,[13] HIO_4,[14] $K_2S_2O_8$,[15] and heteropolyoxometalates[16]] are known to promote the re-oxidation of Pd(0) into highly active Pd(II) thus enabling catalytic reactions. Inspired by the alternatives for terminal oxidation of Pd(0) to Pd(II), we believed that an inorganic oxidant can replace the use of both $CuCl_2$ and O_2 in the Wacker process. We envisioned examining the commonest oxidants used in normal alcohol oxidation, primarily based on chromium metal. We here in display a mild process using CrO_3 as the sole oxidant in $PdCl_2$ catalyzed oxidation of terminal olefins to methyl ketones in excellent yields (Scheme 1). No olefin isomerization or aldehyde formation was observed. The reaction does not require any pressurization of O_2 or any dry reagents. CrO_3 being a cheap oxidant and freely soluble in water makes this method advantageous and operationally simple.



Scheme 1. Oxidation of terminal olefins to methyl ketones. FG = functional group

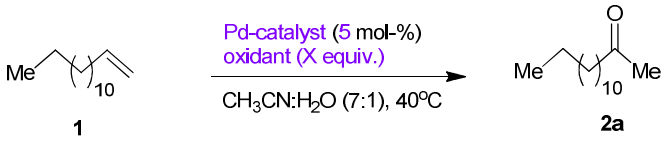
2. Results and Discussion

Initially, 1-tetradecene was treated with $PdCl_2$ (5 mol-%) and CrO_3 (1.0 equiv.) in a mixture of CH_3CN/H_2O (7:1) at 40 °C. The reaction was complete within 1.5 h giving tertadec-2-one as the sole product in quantitative yield. No trace of aldehyde was formed. The purification process was mere filtration of the reaction mixture through a pad of silica gel to remove water and chromium by-products delivering the product after filtrate concentration in virtually pure form.

The detailed optimization of reaction conditions for oxidation of 1-tetradecene as model substrate varying the palladium source, solvents, oxidants and temperature are shown below. From the optimization study in Table 1, the oxidation of 1-tetradecene with $PdCl_2$ (5 mol-%) and CrO_3 (1.0 equiv) gave the best results (entry 1). Other Pd-catalysts or oxidants gave inferior results. All the reactions were carried out in a closed flask. The reaction under N_2 atmosphere also worked well giving comparable results (entry 18, Table 1). The solvent screening indicated that the mixture of CH_3CN:H_2O in 7:1 ratio was the best combination (Table 2) for this oxidation.

From the optimization study based on catalyst and oxidant concentration it inferred that $PdCl_2$ (5 mol-%) and CrO_3 (0.5 equiv) were quite economical for this oxidation (Table 3). While preliminary investigations were carried out at 40 ºC, the temperature dependence study revealed that 60 ºC reaction was optimum with reduced reaction time (Table 4).

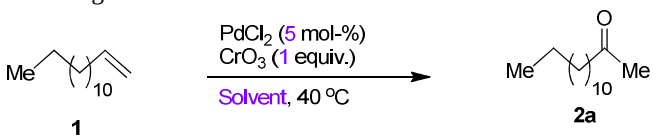
Table 1
Optimization varying different palladium catalysts and oxidants for oxidation of 1-tetradecene[a]



Entry	Pd-catalyst	Oxidant (equiv.)	*t* (h)	Yield (%)[b]
1	$PdCl_2$	CrO_3 (1.0)	1.5	Quant.
2	$PdCl_2$	PCC (1.0)	24	NR
3	$PdCl_2$	PCC (1.5)	24	NR
4	$PdCl_2$	PDC (1.0)	50	NR
5	$PdCl_2$	PDC (1.5)	50	NR
5	$PdCl_2$	$KMnO_4$ (1.0)	120	18
6	$PdCl_2$	$KMnO_4$(1.5)	120	21
7	$PdCl_2$	K_2CrO_4 (1.0)	24	40
8	$PdCl_2$	K_2CrO_4 (1.5)	20	45
9	$PdCl_2$	$K_2Cr_2O_7$ (1.0)	72	15
10	$PdCl_2$	$K_2Cr_2O_7$ (1.5)	60	18
11	$Pd(OAc)_2$	CrO_3 (1.0)	48	38
12	$Pd(OAc)_2$	CrO_3 (1.5)	46	54
13	$Pd(CF_3CO_2)_2$	CrO_3 (1.0)	24	61
14	$Pd(CF_3CO_2)_2$	CrO_3 (1.5)	16	77
15	$Pd(PPh_3)_4$	CrO_3 (1.0)	24	34
16	$Pd(PPh_3)_4$	CrO_3 (1.5)	24	37
17	--	CrO_3 (1.0)	3	NR
18	$PdCl_2$	CrO_3 (1.0)	1.7	97[c]

[a] All reactions were carried out on 0.4 mmol of olefin in closed flask. [b] Isolated yield. NR = no reaction. [c] Reaction under N_2.

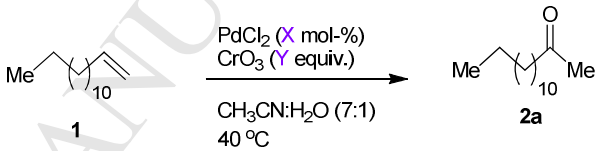
Table 2
Screening the different solvents for oxidation of 1-tetradecene[a]



Entry	Solvent	*t* (h)	Yield (%)[b]
1	THF:H_2O (7:1)	12	60
2	DMF:H_2O (7:1)	9	55
3	CH_3CN:H_2O (7:1)	1.5	Quant.
4	Toluene:H_2O (7:1)	16	70
5	CH_3CN:H_2O (1:1)	0.5	76
6	CH_3CN:H_2O (2:1)	1.0	88
7	CH_3CN:H_2O (5:1)	1.5	92

[a] All reactions were carried out on 0.4 mmol of olefin in closed flask. [b] Isolated yield.

Table 3
Optimization varying the mole ratio of $PdCl_2$ and equiv. of CrO_3 for oxidation of 1-tetradecene[a]

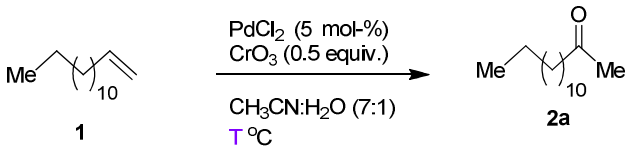


Entry	$PdCl_2$ (mol-%)	CrO_3 (equiv.)	*t*	Yield(%)[b]
1	5	0.25	120 h	57
2	5	0.5	10.5 h	94
3	5	1.0	1.5 h	Quant.
4	5	1.5	45 min	Quant.
5	5	2.0	40 min	Quant
6	10	0.5	5 h	97
7	10	1.0	1 h	Quant.
8	10	1.5	40 min	Quant.
9	2	1.5	2.5 h	97
10	2	1.0	2.5 h	96
11	2	0.5	12.5 h	87

[a] All reactions were carried out on 0.4 mmol of olefin in closed flask. [b] Isolated yield.

Table 4

Optimization varying the temperature for oxidation of 1-tetradecene[a]



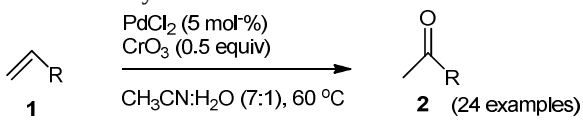
Entry	Temperature (°C)	*t* (h)	Yield %[b]
1	10	120	38
2	rt	90	65
3	40	10.5	94
4	50	8	96
5	60	6.5	96
6	80	6	91

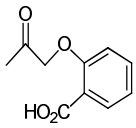
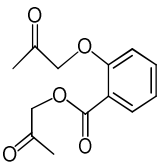
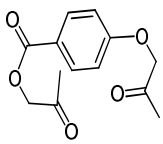
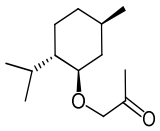
[a] All reactions were carried out on 0.4 mmol of olefin in closed flask. [b] Isolated yield.

Following the findings from the above optimization study, we chose a combination of $PdCl_2$ (5 mol-%), CrO_3 (0.5 equiv.), in CH_3CN:H_2O (7:1) at 60 °C as the optimum reaction condition. With this operationally simple procedure and optimized conditions, we evaluated the scope and limitations of this method. At the onset we explored the long chain inactivated olefins and aliphatic olefins with distal functional groups (Table 5). 1-Decene and 1- tetradecene gave the methyl ketones (**2a** and **2b**) in excellent yields in 6.5 h. The oxidation was compatible with diverse functional groups: halides, hydroxyl, benzoates, MOM, silyl, esters and acids were all tolerated giving the methyl ketone products in good to excellent yields (**2c-j**). No OH group oxidation or deprotection of acid labile groups was observed with CrO_3 involved. When the oxidation of terminal OH containing olefin **1d** was carried out over 7 h in absence of Pd-catalyst, it delivered the aldehyde through OH oxidation in <10% yield. The olefin bond was intact. This indicates the utilization of CrO_3 in Pd-oxidation and as well that it do not alone oxidize the OH group substantially. Terminal dienes gave methyl diketones in good yields (**2k** and **l**). Primary allyl alcohols with various protecting groups: phenyl, benzyl, 4-*t*butylphenyl, 2-bromo-5-methoxyphenyl, 2-naphthyl, 4-methylbenzoyl and nitrobenzoyl delivered methyl ketones (Table 5, **2m-t**) in good to excellent yields after 12-16 h of reaction time. Hydroxyl allylated salicylic acid gave the methyl ketone **2u** in 60% yield (Table 5, entry 21). Similarly bis-allylated salicylic acids (with ester and ether functionality) gave the diketones **2v** in 65% and **2w** in 69% yields (Table 5, entries 22 and 23). Menthyl allyl ether efficiently gave **2x** in 84% yield in a 8 h reaction (entry 24).

Table 5

Synthesis of methyl ketones from terminal olefins[a]

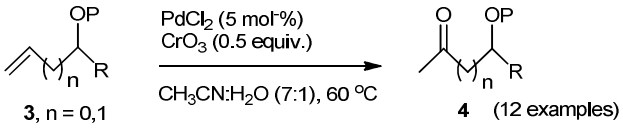


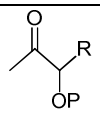
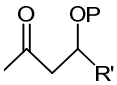
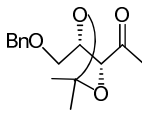
Entry	Product	t (h)	Yield (%)[c]
1	**2a**, R = nC_8H_{17}	6.5	95
2	**2b**, R = $nC_{12}H_{25}$	6.5	96
3	**2c**, X = Br, n = 7	7	91
4	**2d**, X = OH, n = 8	7	91
5	**2e**, X = OBz, n = 3	7	93
6	**2f**, X = OMOM, n = 8	8	78
7	**2g**, X = OTBDPS, n = 0	12	91
8	**2h**, X = CO_2Et, n = 0	7	85
9	**2i**, X = CO_2Me, n = 7	7	92
10	**2j**, X = CO_2H, n = 2	7	80
11[b]	**2k**, n = 6	14	75
12[b]	**2l**, n = 8	14	78
13	**2m**, R' = Ph	12	80
14	**2n**, R' = Bn	12	96
15	**2o**, R' = 4-*t*Bu-phenyl	14	81
16	**2p**, R' = 2-Br-5-OMe-phenyl	12	64
17	**2q**, R' = 2-naphthyl	16	96
18	**2r**, R' = 4-methylbenzoyl	12	72
19	**2s**, R' = 4-nitrobenzoyl	12	72
20	**2t**, R' = 3,5-dinitrobenzoyl	12	64
21	 **2u**	12	60
22[b]	 **2v**	18	65
23[b]	 **2w**	18	69
24	 **2x**	8	84

[a] Reaction conditions: Substrate (0.4 mmol), $PdCl_2$ (0.02 mmol), CrO_3 (0.2 mmol), CH_3CN (3.5 mL), H_2O (0.5 mL), at 60 °C in closed flask. [b] Diene substrate (0.4 mmol), $PdCl_2$ (0.04 mmol), CrO_3 (0.4 mmol), CH_3CN (3.5 mL), H_2O (0.5 mL), at 60 °C in closed flask. [c] Isolated yields.

Protected secondary allyl and homoallyl alcohols are considered to be classically difficult substrates due to possible coordination of neighbouring oxygen atom to the Lewis acidic palladium causing water attack through multiple pathways.[8ac,17] These compounds under the present protocol also reacted successfully, tolerating different protecting groups (Table 6). The acyloin products (**4a-d**, entries 1-4) were obtained in good yields. Homoallyl alcohols gave the protected *β*-hydroxy ketone products (**4e-k**, entries 5-11) in good yields in 8-18 h reaction time. Similarly, the acetonide protected compound (**4l**) was obtained in moderate yield with untouched acetonide moiety (entry 12).

Table 6
Oxidation of protected allyl and homoallyl alcohols[a]

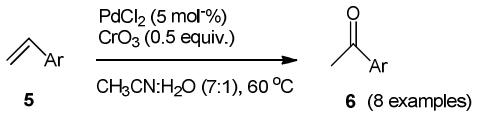


Entry	Product		t (h)	Yield (%)[b]
1		**4a**, P = Ac, R = nC_6H_{13}	24	61
2		**4b**, P = MOM, R = nC_6H_{13}	36	52
3		**4c**, P = Ac, R = Ph	36	73
4		**4d**, P = TBDPS, R = Ph	24	91
5		**4e**, P = TBDPS, R' = Ph	18	84
6		**4f**, P = Ac, R' = nC_5H_{11}	8	92
7		**4g**, P = Ac, R' = Ph	16	70
8		**4h**, P = Ac, R' = 4-OMe-phenyl	16	85
9		**4i**, P = Ac, R' = piperonyl	18	73
10		**4j**, P = Bz, R' = 1-naphthyl	16	74
11		**4k**, P = Bn, R' = 4-NO_2-phenyl	16	75
12		**4l**	28	52

[a] Reaction conditions: Substrate (0.4 mmol), $PdCl_2$ (0.02 mmol), CrO_3 (0.2 mmol), CH_3CN (3.5 mL), H_2O (0.5 mL), at 60 °C in closed flask. [b] Isolated yields.

Aryl methyl ketones are widely distributed in nature. Apart from direct acylation of aryl ring by Friedel-Craft procedure, there are limited one-step methods for their preparation. The Friedel-Craft method suffers from a serious limitation when electron deficient aryl rings are involved. Styrenes are excellent masked precursors for aryl methyl ketones synthesis through olefin oxidation protocol. Various aryl substituted styrenes reacted under the developed procedure to give aryl methyl ketones (**6a-h**) in good to excellent yields (Table 7).

Table 7
Oxidation of styrenes to aryl methyl ketones[a]



Entry	Product		t (h)	Yield %[b]
1		**6a**, Ar = Ph	8	82
2		**6b**, Ar = 4-Cl-phenyl	10	75
3		**6c**, Ar = 4-Me-phenyl	16	71
4		**6d**, Ar = 4-*t*Bu-phenyl	18	90
5		**6e**, Ar = 2-naphthyl	24	62[c]
6		**6f**, Ar = 4-Ph-phenyl	24	58[c]
7		**6g**, Ar = 3,4-dimethoxy phenyl	24	75[c]
8		**6h**, Ar = 2,5-dimethoxy phenyl	24	83

[a] Reaction conditions: Substrate (0.4 mmol), $PdCl_2$ (0.02 mmol), CrO_3 (0.2 mmol), CH_3CN (3.5 mL), H_2O (0.5 mL), at 60 °C in closed flask. [b] Isolated yields. [c] Trace amount of aldehyde was detected by ^{1}H NMR.

3. Conclusions

In summary, we have discovered a mild, efficient and general method to access methyl ketones from terminal olefins. Various long chain olefins, protected allyl and homoallyl alcohols and substituted styrenes have been explored (44 examples) for this Wacker-type oxidation. Wide spectrum of functional-group tolerance, mild reaction conditions and use of readily available CrO_3 as sole oxidant are key features of this methodology. Since it is a mild process with operational simplicity and exclusive ketone delivery, we expect this method to find broad application in synthetic chemistry.

4. Experimental Section

4.1. General considerations

Flasks were oven or flame dried and cooled in a desiccator. Solvents and reagents were purified by standard methods. Thin-layer chromatography was performed on EM 250 Kieselgel 60 F254 silica gel plates. The spots were visualized by staining with $KMnO_4$ or under UV lamp. ^{1}H and ^{13}C NMR were recorded with a Bruker, AVANCE III 500 or 400 spectrometer and the chemical shifts are based on TMS peak at δ = 0.00 pm for proton NMR and $CDCl_3$ peak at δ = 77.00 ppm (t) in carbon NMR. IR spectra were obtained on Perkin Elmer Spectrum One FT–IR spectrometer and samples were prepared by evaporation from $CHCl_3$ on CsBr plates. Optical rotations were measured with Jasco P–2000 digital polarimeter. High-resolution mass spectra (HRMS) were obtained using positive electrospray ionization by TOF method on a Bruker Maxis Impact spectrometer.

4.2. General procedure for oxidation of terminal olefins

To a stirred solution of olefin (0.4 mmol) in CH_3CN (3.5 mL) and H_2O (0.5 mL) were added $PdCl_2$ (3.6 mg, 0.02 mmol, 5 mol-%) and CrO_3 (20 mg, 0.6 mmol, 0.5 equiv.) at room temperature. The reaction mixture was warmed to 60 ^oC and stirred for specified time (see Table 5-7) in a closed falsk. The reaction mixture was then filtered through a small pad of silica gel and washed with EtOAc and the filtrate concentrated. The residue in some cases contained virtually pure compound and no further purification was necessary. In other cases the residue was purified by silica gel column chromatography using petroleum ether/EtOAc as an eluent to afford the methyl ketones.

*4.2.1. Decan-2-one (**2a**).* Isolated yield of **2a**, (59.4 mg, 95%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3020, 2950, 2928, 1715, 1465, 1401, 1361, 1163, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 2.41 (t, J = 7.5 Hz, 2H), 2.13 (s, 3H), 1.54–1.53 (m, 2H), 1.32–1.20 (m, 10H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.3, 43.7, 31.7, 29.4, 29.3, 29.1, 29.0, 23.8, 22.5, 14.0; HRMS (ESI-TOF) calcd for $[C_{10}H_{20}O+Na]^+$ 179.1406, found 179.1409.

*4.2.2. Tetradecan-2-one (**2b**).* Isolated yield of **2b**, (81.5 mg, 96%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3018, 2926, 2846, 1719, 1459, 1411, 1364, 1163, 1120, 966, 721, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 2.42 (t, J = 7.5 Hz, 2H), 2.14 (s, 3H), 1.58–1.55 (m, 4H), 1.36–1.19 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.3, 43.7, 31.8, 29.7, 29.6, 29.53, 29.5, 29.4, 29.3, 29.25, 29.1, 23.7, 22.6, 14.0; HRMS (ESI-TOF) calcd for $[C_{14}H_{28}O+Na]^+$ 235.2032, found 235.2030.

*4.2.3. 10-Bromodecan-2-one (**2c**).* Isolated yield of **2c**, (85.8 mg, 91%). Colorless oil; IR ($CHCl_3$): ν_{max} = 2931, 2856, 1717, 1459, 1439, 1359, 1259, 1224, 1166, 948, 721, 644 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 3.38 (t, J = 6.8 Hz, 2H), 2.41 (t, J = 7.4 Hz, 2H), 2.13 (s, 3H), 1.87–1.76 (m, 2H), 1.58–1.51 (m, 2H), 1.42–1.37 (m, 2H), 1.29–1.23 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.5, 43.9, 34.2, 32.9, 30.0, 29.3, 29.2, 28.7, 28.2, 23.9; HRMS (ESI-TOF) calcd for $[C_{10}H_{19}BrO+Na]^+$ 257.0511, found 257.0511.

*4.2.4. 11-Hydroxyundecan-2-one (**2d**).*[8ae] Isolated yield of **2d**, (67.8 mg, 91%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3415, 2929, 2855, 1712, 1465, 1363, 1169, 1055, 912 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 3.59 (t, J = 6.7 Hz, 2H), 2.38 (t, J = 7.4 Hz, 2H), 2.10 (s, 3H), 1.54–1.50 (m, 4H), 1.37–1.20 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.6, 62.8, 43.7, 32.6, 29.8, 29.3, 29.25, 29.21, 29.0, 25.6, 23.7; HRMS (ESI-TOF) calcd for $[C_{11}H_{22}O_2+Na]^+$ 209.1512, found 209.1510.

*4.2.5. 5-Oxohexyl benzoate (**2e**):* Isolated yield of **2e**, (81.8 mg, 93%). Colorless oil; IR ($CHCl_3$): ν_{max} = 2956, 2918, 2950, 1718, 1602, 1584, 1452, 1410, 1361, 1315, 1176, 1165, 1119, 1071, 1027, 963, 905, 807, 714, 688, 675 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 8.04–8.02 (m, 2H), 7.57–7.53 (m, 1H), 7.45–7.41(m, 2H), 4.32 (t, J = 6.1 Hz, 2H), 2.51 (t, J = 6.9 Hz, 2H), 2.15 (s, 3H), 1.81–1.71 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.4, 166.6, 132.9, 130.3, 129.5, 128.3, 64.5, 43.0, 29.9, 28.1, 20.2; HRMS (ESI-TOF) calcd for $[C_{13}H_{16}O_3+Na]^+$ 243.0992, found 243.0989.

*4.2.6. 11-(Methoxymethoxy)undecan-2-one (**2f**).* Isolated yield of **2f**, (71.9 mg, 78%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3014, 2929, 2856, 1716, 1465, 1410, 1361, 1145, 1111, 1043, 919, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 4.61 (s, 2H), 3.51 (t, J = 6.6 Hz, 2H), 3.35 (s, 3H), 2.41 (t, J = 7.5 Hz, 2H), 2.13 (s, 3H), 1.60–1.54 (m, 2H), 1.28–1.27 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.4, 96.3, 67.7, 55.0, 43.7, 29.8, 29.6, 29.3, 29.1, 26.1, 23.7; HRMS (ESI-TOF) calcd for $[C_{13}H_{26}O_3+Na]^+$ 253.1774, found 253.1778.

*4.2.7. 1-(tert-Butyldiphenylsilyloxy)propan-2-one (**2g**).* Isolated yield of **2g**, (113.8 mg, 91%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3071, 3050, 2933, 2893, 2859, 1736, 1717, 1589, 1473, 1428, 1391, 1354, 1231, 1189, 1113, 940, 824, 703, 615 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/TMS): δ = 7.65 (dd, J = 7.2, 0.7 Hz, 4H), 7.44–7.38 (m, 6H), 4.16 (s, 2H), 2.20 (s, 3H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.5, 135.5, 132.6, 130.0, 127.8, 69.9, 26.7, 26.3, 19.2; HRMS (ESI-TOF) calcd for $[C_{19}H_{24}SiO_2+Na]^+$ 335.1438, found 335.1437.

*4.2.8. Ethyl 3-oxobutanoate (**2h**).* Isolated yield of **2h**, (44.2 mg, 85%). Colorless oil; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 4.15 (q, J = 7.2 Hz, 2H), 3.40 (s, 2H), 2.23 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.6, 167.0, 61.3, 50.0, 30.0, 14.0.

*4.2.9. Methyl 10-oxo-undecanoate (**2i**).* Isolated yield of **2i**, (78.8 mg, 92%). Colorless oil; IR ($CHCl_3$): ν_{max} = 2931, 2857, 1740, 1717, 1459, 1437, 1362, 1197,1171, 1103, 1017, 882, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 3.65 (s, 3H), 2.40 (t, J = 7.4 Hz, 2H), 2.28 (t, J = 7.5 Hz, 2H), 2.12 (s, 3H), 1.61–1.52 (m, 4H), 1.34–1.22 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.3, 174.3, 51.4, 43.7, 34.0, 29.8, 29.1, 29.03, 29.0, 24.9, 23.7; HRMS (ESI-TOF) calcd for $[C_{12}H_{22}O_3+Na]^+$ 237.1461, found 237.1461.

*4.2.10. 5-Oxohexanoic acid (**2j**).* Isolated yield of **2j**, (41.6 mg, 80%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3501, 3020, 2920, 2851, 1715, 1416, 1373, 1161, 1070, 1049, 955, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 2.53 (t, J = 7.2 Hz, 2H), 2.39 (t, J = 7.2 Hz, 2H), 2.15 (s, 3H), 1.95–1.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.2, 179.0, 42.3, 32.9, 29.9, 18.5; HRMS (ESI-TOF) calcd for $[C_6H_{10}O_3+Na]^+$ 153.0522, found 153.0525.

*4.2.11. Decane-2,9-dione (**2k**).* Isolated yield of **2k**, (51.1 mg, 75%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3019, 2933, 2858, 1717, 1409, 1363, 1168, 1048, 967, 927, 667 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$/TMS): δ = 2.42 (t, J = 7.4 Hz, 4H) 2.13 (s, 6H), 1.62–1.51 (m, 4H), 1.40–1.26 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 209.2, 43.5, 29.8, 28.8, 23.5; HRMS (ESI-TOF) calcd for $[C_{10}H_{18}O_2+Na]^+$ 193.1199, found 193.1198.

*4.2.12. Dodecane-2,11-dione (**2l**).* Isolated yield of **2l**, (61.8 mg, 78%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3017, 2916, 1704, 1406, 1379, 1284, 1165, 1131, 1018, 949, 717, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 2.40 (t, J = 7.4 Hz, 4H), 2.12 (s, 6H), 1.63–1.51 (m, 4H), 1.28–1.23 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.2, 43.6, 29.7, 29.0, 28.9, 23.6; HRMS (ESI-TOF) calcd for $[C_{12}H_{22}O_2+Na]^+$ 221.1512, found 221.1512.

*4.2.13. 1-Phenoxypropan-2-one (**2m**).* Isolated yield of **2m**, (48 mg, 80%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3043, 3065, 2919, 2849, 1733, 1599, 1590, 1496, 1457, 1433, 1359, 1305, 1295, 1228, 1172, 1155, 1085, 1067, 967, 888, 817, 806, 782, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.33–7.28 (m, 2H), 7.02–6.98 (m, 1H), 6.90–6.87 (m, 2H), 4.54 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.9, 157.6, 129.6, 121.7, 114.4, 72.9, 26.6; HRMS (ESI-TOF) calcd for $[C_9H_{10}O_2+Na]^+$ 173.0573, found 173.0573.

*4.2.14. 1-(Benzyloxy)propan-2-one (**2n**).* Isolated yield of **2n**, (63.1 mg, 96%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3067, 3032, 2868, 1729, 1603, 1584, 1497, 1455, 1376, 1357, 1276, 1226, 1167, 1118, 1074, 1028, 1013, 939, 868, 699, 682 cm^{-1};^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.38–7.25 (m, 5H), 4.57 (s, 2H), 4.04 (s, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =

206.5, 137.0, 128.3, 127.8, 127.7, 75.0, 73.0, 26.2; HRMS (ESI-TOF) calcd for $[C_{10}H_{12}O_2+Na]^+$ 187.0730, found 187.0729.

*4.2.15. 1-[4-(tert-Butyl)phenoxy]propan-2-one (**2o**).* Isolated yield of **2o**, (66.9 mg, 81%.). Colorless oil; IR ($CHCl_3$): ν_{max} = 3041, 2963, 2906, 2869, 1724, 1610, 1583, 1514, 1480, 1464, 1435, 1364, 1297, 1255, 1234, 1185, 1066, 829, 809, 682 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.32 (d, J = 8.9 Hz, 2H), 6.82 (d, J = 8.9 Hz, 2H), 4.52 (s, 2H), 2.28 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.3, 155.4, 144.4, 126.4, 113.9, 73.2, 34.1, 31.4, 26.6; HRMS (ESI-TOF) calcd for $[C_{13}H_{18}O_2+Na]^+$ 229.1199, found 229.1199.

*4.2.16. 1-(2-Bromo-5-methoxyphenoxy)propan-2-one (**2p**).* Isolated yield of **2p**, (66.4 mg, 64%). White solid, m.p. 68–70 ^oC; IR ($CHCl_3$): ν_{max} = 2939, 1721, 1586, 1488, 1462, 1432, 1359, 1307, 1283, 1263, 1201, 1169, 1067, 1024, 910, 832, 649 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.45 (d, J = 8.7 Hz, 1H), 6.46 (dd, J = 8.7, 2.7 Hz, 1H), 6.35 (d, J = 2.7 Hz, 1H), 4.52 (s, 2H), 3.78 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.6, 160.1, 154.7, 133.5, 107.1, 102.7, 101.0, 73.6, 55.6, 27.0; HRMS (ESI-TOF) calcd for $[C_{10}H_{11}BrO_3+Na]^+$ 280.9784, found 280.9783.

*4.2.17. 1-(Napthalen-2-yloxy)propan-2-one (**2q**).* Isolated yield of **2q**, (76.8 mg, 96%). White solid, m.p. 63–65 °C; IR ($CHCl_3$): ν_{max} = 3028, 3056, 2924, 2850, 1732, 1631, 1600, 1509, 1470, 1432, 1390, 1358, 1272, 1259, 1222, 1173, 1122, 1071, 978, 950, 908, 875, 838, 819, 777, 638 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.79 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.2 Hz, 1H), 7.48–7.44 (m, 1H), 7.39–7.35 (m, 1H), 7.22 (dd, J = 9.0, 2.6 Hz, 1H), 7.03 (d, J = 2.5 Hz, 1H), 4.66 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.9, 155.6, 134.2, 129.9, 129.3, 127.7, 126.8, 126.6, 124.2, 118.5, 106.9, 73.0, 26.7; HRMS (ESI-TOF) calcd for $[C_{13}H_{12}O_2+Na]^+$ 223.0730, found 223.0729.

*4.2.18. 2-Oxopropyl 4-methylbenzoate (**2r**).* Isolated yield of **2r**, (55.4 mg, 72%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3036, 3006, 2927, 1735, 1719, 1611, 1577, 1509, 1420, 1374, 1279, 1177, 1112, 1022, 962, 841, 691, 639 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.97 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 4.85 (s, 2H), 2.40 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.1, 165.8, 144.2, 129.8, 129.1, 126.3, 68.6, 26.2, 21.6; HRMS (ESI-TOF) calcd for $[C_{11}H_{12}O_3+Na]^+$ 215.0679, found 215.0675.

*4.2.19. 2-Oxopropyl 4-nitrobenzoate (**2s**).* Isolated yield of **2s**, (64.3 mg, 72%). White solid, m.p. 101–103 °C; IR ($CHCl_3$): ν_{max} = 3115, 3081, 3060, 2977, 2934, 2855, 1742, 1721, 1607, 1524, 1421, 1367, 1320, 1274, 1184, 1120, 1106, 1011, 964, 883, 855, 720, 623 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 8.28 (d, J = 9.1 Hz, 2H), 8.23 (d, J = 9.1 Hz, 2H), 4.95 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.3, 163.9, 150.7, 134.5, 131.0, 123.6, 69.1, 26.0; HRMS (ESI-TOF) calcd for $[C_{10}H_9O_5N+Na]^+$ 246.0373, found 246.0379.

*4.2.20. 2-Oxopropyl 3,5-dinitrobenzoate (**2t**).*[8af] Isolated yield of **2t**, (68.6 mg, 64%). White solid, m.p. 138–140 °C; IR ($CHCl_3$): ν_{max} = 3093, 3020, 2923, 1735, 1630, 1599, 1547, 1462, 1418, 1345, 1285, 1157, 1075, 1035, 923, 905, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 9.27–9.25 (m, 1H), 9.24–9.20 (m, 2H), 5.05 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.2, 161.9, 148.7, 132.9, 129.7, 122.8, 69.6, 25.9; HRMS (ESI-TOF) calcd for $[C_{10}H_8O_7N_2+Na]^+$ 291.0224, found 291.0230.

*4.2.21. 2-(2-Oxopropoxy)benzoic acid (**2u**).* Isolated yield of **2u**, (46.6 mg, 60%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3212, 2919, 1781, 1717, 1600, 1485, 1458, 1418, 1341, 1295, 1252, 1184, 1165, 1095, 1058, 1036, 958, 862, 829, 798, 684, 646 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 8.13 (dd, J = 7.8, 1.4 Hz, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 4.89 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.5, 165.7, 156.4, 134.8, 133.9, 122.9, 118.7, 113.0, 73.6, 26.0; HRMS (ESI-TOF) calcd for $[C_{10}H_{10}O_4+Na]^+$ 217.0471, found 217.0472.

*4.2.22. 2-Oxopropyl 2-(2-oxopropoxy)benzoate (**2v**).* Isolated yield of **2v**, (65 mg, 65%). White solid, m.p. 62–64 °C; IR ($CHCl_3$): ν_{max} = 3020, 2928, 2846, 1728, 1603, 1586, 1491, 1457, 1420, 1364, 1306, 1253, 1180, 1168, 1134, 1097, 1060, 1012, 964, 884, 828, 703, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.96 (dd, J = 7.8, 1.8 Hz, 1H), 7.52–7.47 (m, 1H), 7.1 (td, J = 7.6, 0.8 Hz, 1H), 6.8 (d, J = 8.3 Hz, 1H), 4.87 (s, 2H), 4.58 (s, 2H), 2.35 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.7, 201.7, 164.7, 157.6, 134.2, 132.4, 121.5, 119.5, 113.5, 73.8, 68.6, 26.9, 26.1; HRMS (ESI-TOF) calcd for $[C_{13}H_{14}O_5+Na]^+$ 273.0733, found 273.0731.

*4.2.23. 2-Oxopropyl 4-(2-oxopropoxy)benzoate (**2w**).* Isolated yield of **2w**, (69 mg, 69%). White solid, m.p. 80–82 °C; IR ($CHCl_3$): ν_{max} = 3021, 2928, 1721, 1607, 1583, 1509, 1420, 1371, 1314, 1276, 1170, 1115, 1070, 1008, 966, 883, 848, 696, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 8.03 (d, J = 9.0 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 4.83 (s, 2H), 4.60 (s, 2H), 2.26 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.3, 202.0, 165.2, 161.6, 132.1, 122.5, 114.2, 72.7, 68.5, 26.5, 26.1; HRMS (ESI-TOF) calcd for $[C_{13}H_{14}O_5+Na]^+$ 273.0733, found 273.0734.

*4.2.24. 1-[(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyloxy]propan-2-one (**2x**).* Isolated yield of **2x**, (71.3 mg, 84%). Colorless oil; $[\alpha]_D^{25}$ = –73.3 (c = 1.0, $CHCl_3$); IR ($CHCl_3$): ν_{max} = 3020, 2958, 2928, 2872, 1720, 1457, 1370, 1116, 1015, 938, 842, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 4.14 (d, J = 16.8 Hz, 1H), 3.93 (d, J = 16.8 Hz, 1H), 3.11 (td, J = 10.6, 4.1 Hz, 1H), 2.28–2.24 (m, 1H), 2.18 (s, 3H), 2.06–2.01 (m, 1H), 1.68–1.62 (m, 2H), 1.36–1.28 (m, 2H), 1.01–0.84 (m, 8H), 0.78 (d, J = 7.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.0, 80.3, 74.3, 48.0, 39.9, 34.3, 31.4, 26.7, 25.6, 23.2, 22.2, 20.9, 16.1; HRMS (ESI-TOF) calcd for $[C_{13}H_{24}O_2+Na]^+$ 235.1669, found 235.1666.

*4.2.25. 2-Oxononan-3-yl acetate (**4a**).* Isolated yield of **4a**, (48.9 mg, 61%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3027, 2956, 2929, 2851, 1744, 1731, 1462, 1429, 1376, 1239, 1122, 1072, 1046, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 4.98 (dd, J = 8.2, 4.6 Hz, 1H), 2.16 (s, 3H), 2.15 (s, 3H), 1.76–1.71 (m, 2H), 1.54–1.25 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.5, 170.7, 78.7, 31.5, 30.2, 28.9, 26.1, 25.1, 22.5, 20.7, 14.0; HRMS (ESI-TOF) calcd for $[C_{11}H_{20}O_3+Na]^+$ 223.1305, found 223.1302.

*4.2.26. 3-(Methoxymethoxy)nonan-2-one (**4b**).* Isolated yield of **4b**, (42 mg, 52%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3019, 2956, 2928, 2857, 1719, 1466, 1355, 1153, 1122, 1104, 1037, 921, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 4.64 (s, 2H), 3.97 (t, J = 6.3 Hz, 1H), 3.38 (s, 3H), 2.17 (s, 3H), 1.66–1.62 (m, 2H), 1.41–1.32 (m, 8H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.1, 96.4, 82.8, 56.0, 32.0, 31.6, 29.0, 25.9, 25.1, 22.5, 14.0; HRMS (ESI-TOF) calcd for $[C_{11}H_{22}O_3+Na]^+$ 225.1461, found 225.1459.

*4.2.27. 2-Oxo-1-phenylpropyl acetate (**4c**).* Isolated yield of **4c**, (56.1 mg, 73%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3065, 3030, 2925, 2854, 1745, 1733, 1678, 1626, 1603, 1496, 1455, 1428, 1373, 1234, 1169, 1124, 1081, 1051, 961, 941, 914, 866, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.44–7.36 (m, 5H), 5.97 (s, 1H), 2.19 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 201.7, 170.3, 133.1, 129.4, 129.1, 128.1, 80.9, 26.1, 20.7; HRMS (ESI-TOF) calcd for $[C_{11}H_{12}O_3+Na]^+$ 215.0679, found 215.0676.

*4.2.28. 1-(tert-Butyldiphenylsilyloxy)-1-phenylpropan-2-one (**4d**).* Isolated yield of **4d,** (141.3 mg, 91%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3070, 2961, 2932, 2894, 2859, 1717, 1589, 1492, 1472, 1428, 1391, 1351, 1307, 1190, 1113, 1070, 1028, 910, 855, 823, 701, 648 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.66–7.64 (m, 2H), 7.47–7.42 (m, 3H), 7.40–7.32 (m, 5H), 7.31–7.27 (m, 5H), 5.08 (s, 1H), 2.02 (s, 3H), 1.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.7, 138.2, 135.7, 135.6, 132.8, 132.6, 130.0, 129.8, 128.5, 128.1, 127.8, 127.6, 126.2, 81.7, 26.9, 24.3, 19.3; HRMS (ESI-TOF) calcd for $[C_{25}H_{28}O_2Si+Na]^+$ 411.1751, found 411.1755.

*4.2.29. 4-(tert-Butyldiphenylsilyloxy)-4-phenylbutan-2-one (**4e**).* Isolated yield of **4e**, (135.5 mg, 84%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3070, 2999, 2931, 2894 2858, 1716, 1589, 1472, 1454, 1427, 1391, 1361, 1309, 1259, 1190, 1161, 1111, 1028, 1007, 956, 912, 855, 822, 701, 613 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.65–7.63 (m, 2H), 7.44–7.40 (m, 3H), 7.38–7.32 (m, 3H), 7.25–7.18 (m, 7H), 5.15 (t, J = 6.5 Hz, 1H), 2.92 (dd, J = 15.2, 6.5 Hz, 1H), 2.71 (dd, J = 15.2, 6.4 Hz, 1H), 1.90 (s, 3H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.4, 143.5, 135.8, 133.7, 133.2, 129.7, 129.5, 128.1, 127.5, 127.4, 127.3, 126.2, 72.3, 54.1, 31.1, 26.9, 19.2; HRMS (ESI-TOF) calcd for $[C_{26}H_{30}O_2Si+Na]^+$ 425.1907, found 425.1904.

*4.2.30. 2-Oxononan-4-yl acetate (**4f**).* Isolated yield of **4f**, (73.7 mg, 92%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3011, 2950, 2932, 2861, 1736, 1717, 1677, 1628, 1459, 1424, 1364, 1248, 1166, 1023, 981, 960, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 5.21–5.16 (m, 1H), 2.70 (dd, J = 16.2, 7.4 Hz, 1H), 2.57 (dd, J = 16.2, 5.3 Hz, 1H), 2.13 (s, 3H), 2.0 (s, 3H), 1.54–1.51 (m, 2H), 1.281.24 (m, 6H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.8, 170.5, 70.3, 47.9, 34.0, 31.4, 30.3, 24.7, 22.4, 21.0, 13.9; HRMS (ESI-TOF) calcd for $[C_{11}H_{20}O_3+Na]^+$ 223.1305, found 223.1307.

*4.2.31. 3-Oxo-1-phenylbutyl acetate (**4g**).* Isolated yield of **4g**, (57.8 mg, 70%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3064, 3032, 2927, 2853, 1736, 1721, 1608, 1495, 1454, 1373, 1239, 1163, 1043, 950, 917, 871, 701, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.36–7.28 (m, 5H), 6.18 (dd, J = 8.7, 4.9 Hz, 1H), 3.12 (dd, J = 16.6, 8.7 Hz, 1H), 2.82 (dd, J = 16.7, 4.9 Hz, 1H), 2.15 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.6, 169.7, 139.5, 128.5, 128.1, 126.3, 71.5, 49.7, 30.3, 20.9; HRMS (ESI-TOF) calcd for $[C_{12}H_{14}O_3+Na]^+$ 229.0835, found 229.0835.

*4.2.32. 1-(4-Methoxyphenyl)-3-oxobutyl acetate (**4h**).* Isolated yield of **4h**, (80.4 mg, 85%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3003, 2960, 2936, 2840, 1740, 1729, 1612, 1516, 1464, 1424, 1372, 1303, 1177, 1033, 948, 835, 657 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.29 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 6.13 (dd, J = 8.5, 5.3 Hz, 1H), 3.78 (s, 3H), 3.10 (dd, J = 16.5, 8.5 Hz, 1H), 2.81 (dd, J = 16.5, 5.3 Hz, 1H), 2.14 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.8, 169.9, 159.4, 131.6, 128.0, 113.9, 71.3, 55.2, 49.6, 30.4, 21.1; HRMS (ESI-TOF) calcd for $[C_{13}H_{16}O_4+Na]^+$ 259.0941, found 259.0948.

*4.2.33. 1-(Benzo[d][1,3]dioxol-5-yl)-3-oxobutyl acetate (**4i**).* Isolated yield of **4i**, (73.1 mg, 73%). Colorless oil; IR ($CHCl_3$): ν_{max} = 2919, 2852, 1773, 1736, 1660, 1625, 1600, 1503, 1489, 1448, 1359, 1239, 1178, 1103, 1037, 977, 929, 804, 788 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 6.84–6.75 (m, 3H), 6.09 (dd, J = 8.5, 5.1 Hz, 1H), 5.94, (s, 2H), 3.27 (dd, J = 16.6, 8.5 Hz, 1H), 2.80 (dd, J = 16.6, 5.2 Hz, 1H), 2.14 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.7, 169.8, 147.8, 147.5, 133.4, 120.3, 108.3, 106.9, 101.1, 71.4, 49.8, 30.4, 21.1; HRMS (ESI-TOF) calcd for $[C_{13}H_{14}O_5+Na]^+$ 273.0733, found 273.0735.

*4.2.34. 1-(Naphthalen-1-yl)-3-oxobutyl benzoate (**4j**).* Isolated yield of **4j**, (94.2 mg, 74%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3062, 3009, 2925, 2854, 1719, 1601, 1584, 1510, 1492, 1451, 1417, 1398, 1363, 1315, 1270, 1176, 1110, 1070, 1058, 1026, 975, 938, 862, 798, 713, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 8.25 (d, J = 8.4 Hz, 1H), 8.10–8.07 (m, 2H), 7.88 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.64–7.42 (m, 7H) 7.21 (dd, J = 9.0, 4.0 Hz, 1H), 3.40 (dd, J = 16.9, 8.6 Hz, 1H), 3.13 (dd, J = 16.9, 4.1 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.7, 165.4, 135.6, 133.9, 133.1, 130.1, 129.9, 129.7, 129.0, 128.8, 128.4, 126.6, 125.8, 125.3, 123.7, 123.0, 69.9, 49.7, 30.5; HRMS (ESI-TOF) calcd for $[C_{21}H_{18}O_3+Na]^+$ 341.1148, found 341.1148.

*4.2.35. 4-(Benzyloxy)-4-(4-nitrophenyl)butan-2-one (**4k**).* Isolated yield of **4k**, (89.8 mg, 75%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3066, 3032, 3008, 2865, 1716, 1606, 1521, 1497, 1415, 1347, 1162, 1096, 1075, 1028, 884, 857, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 8.15 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H), 7.27–7.21 (m, 5H), 4.93 (dd, J = 8.4, 4.6 Hz, 1H), 4.32 (d, J = 11.3 Hz, 1H), 4.27 (d, J = 11.3 Hz, 1H), 2.99 (dd, J = 16.5, 8.5 Hz, 1H), 2.57 (dd, J = 16.5, 4.6 Hz, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.4, 148.9, 147.6, 137.2, 128.4, 127.9, 127.8, 127.5, 123.9, 76.5, 71.5, 51.5, 30.9; HRMS (ESI-TOF) calcd for $[C_{17}H_{17}NO_4+Na]^+$ 322.1050, found 322.1049.

*4.2.36. (3R,4S)-5-Benzyloxy-3,4-isopropylidenedioxy-2-pentanone (**4l**).* Isolated yield of **4l**, (55 mg, 52%). Colorless oil; $[\alpha]_D^{25}$ = +23.4 (c = 0.16, $CHCl_3$); IR $CHCl_3$: ν_{max} = 2988, 2925, 2862, 1717, 1497, 1454, 1418, 1381, 1371, 1355, 1252, 1166, 1133, 1092, 1026, 911, 858, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.36–7.32 (m, 5H), 4.61 (s, 2H), 4.22–4.19 (m, 2H), 3.74 (dd, J = 10.6, 2.64 Hz, 1H), 3.64–3.60 (m, 1H), 2.27 (s, 3H), 1.47 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.4, 137.8, 128.4, 127.7, 111.1, 81.9, 77.3, 73.6, 70.2, 26.9, 26.5, 26.2; HRMS (ESI-TOF) calcd for $[C_{15}H_{20}O_4+Na]^+$ 287.1254, found 287.1252.

*4.2.37. Acetophenone **(6a).*** Isolated yield of **6a**, (39.4 mg, 82%). Colorless oil; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.97–7.92 (m, 2H), 7.57–7.51 (m, 1H), 7.48–7.41 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.1, 137.0, 133.0, 128.5, 128.2, 26.5.

*4.2.38. 4-Chloroacetophenone (**6b**).* Isolated yield of **6b**, (46.3 mg, 75%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3018, 2927, 2855, 1687, 1590, 1572, 1488, 1429, 1397, 1358, 1261, 1095, 1013, 958, 831, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS) δ = 7.89 (d, J = 8.6 Hz, 2H)**,** 7.43 (d, = 8.7 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.8, 139.5, 135.4, 129.7, 128.9, 26.5.

*4.2.39. 4-Methylacetophenone (**6c**).* Isolated yield of **6c**, (38.1 mg, 71%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3032, 3005, 2961, 2924, 2857, 1682, 1607, 1569, 1429, 1407, 1358, 1269, 1182, 1019, 954, 912, 815, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.86 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.58 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.9, 143.9, 134.7, 129.2, 128.4, 26.5, 21.6; HRMS (ESI-TOF) calcd for $[C_9H_{10}O+Na]^+$ 157.0624, found 157.0623.

*4.2.40. 4-tert-Butylacetophenone (**6d**).* Isolated yield of **6d**, (63.5 mg, 90%). Colorless oil; IR ($CHCl_3$): ν_{max} = 2965, 2907, 2871, 1719, 1685, 1607, 1407, 1363, 1271, 1114, 1015, 958, 838, 777,

701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.90 (d, J = 8.7 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H), 2.58 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.9, 156.8, 134.5, 128.3, 125.5, 35.1, 31.0, 26.5; HRMS (ESI-TOF) calcd for $[C_{12}H_{16}O+H]^+$ 177.1274, found 177.1276.

*4.2.41. 2-Acetylnaphthalene (**6e**).* Isolated yield of **6e**, (42.2 mg, 62%). Colorless oil; IR ($CHCl_3$): ν_{max} = 3060, 3018, 1678, 1628, 1597, 1508, 1468, 1426, 1362, 1282, 1193, 1129, 1019, 942, 896, 861, 823, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 8.47 (s, 1H), 8.04 (dd, J = 8.7, 1.7 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.92–7.85 (m, 2H), 7.66–7.53 (m, 2H), 2.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 198.1, 135.6, 134.5, 132.5, 130.2, 129.5, 128.5, 128.4, 127.8, 126.8, 123.9, 26.7; HRMS (ESI-TOF) calcd for $[C_{12}H_{10}O+Na]^+$ 193.0624, found 193.0623.

*4.2.42. 4-Phenylacetophenone (**6f**).* Isolated yield of **6f**, (45.5 mg, 58%). White solid, m.p. 115–117 °C; IR ($CHCl_3$): ν_{max} = 3019, 2923, 1679, 1599, 1404, 1359, 1267, 1119, 1078, 1044, 957, 927, 842, 694, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 8.04 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 7.0 Hz, 2H), 7.50–7.41 (m, 3H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.8, 145.8, 139.9, 135.8, 128.94, 128.9, 128.2, 127.3, 127.2, 26.6; HRMS (ESI-TOF) calcd for $[C_{14}H_{12}O+Na]^+$ 219.0780, found 219.0783.

*4.2.43. 3,4-Dimethoxyacetophenone (**6g**).* Isolated yield of **6g**, (54 mg, 75%); Colorless oil; IR ($CHCl_3$) ν_{max} = 3080, 3005, 2962, 2938, 2840, 1673, 1588, 1513, 1463, 1417, 1358, 1334, 1270, 1224, 1175, 1150, 1135, 1079, 1023, 976, 915, 878, 808, 732, 645 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.58 (dd, J = 8.4, 2.0 Hz, 2 H), 7.55 (d, J = 2.0 Hz, 1 H), 6.89 (d, J = 8.4 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.7, 153.1, 148.8, 130.3, 123.2, 109.9, 109.8, 55.9, 55.8, 26.1; HRMS (ESI-TOF) calcd for $[C_{10}H_{12}O_3+H]^+$ 181.0859, found 181.0862.

*4.2.44. 2,5-Dimethoxyacetophenone (**6h**).* Isolated yield of **6h**, (59.8 mg, 83%); Colorless oil; IR ($CHCl_3$) ν_{max} = 3002, 2944, 2836, 1674, 1610, 1586, 1495, 1465, 1411, 1357, 1316, 1281, 1179, 1044, 1024, 980, 882, 813, 701, 690, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.28 (d, J = 3.2 Hz, 1H), 7.02 (dd, J = 8.6, 3.6 Hz, 1H), 6.90 (d, J = 9.0 Hz, 1H), 3.87 (s, 3H), 3.78 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199. 4, 153.5, 153.3, 128.2, 120.3, 113.7, 113.1, 55.9, 55.7, 31.8; HRMS (ESI-TOF) calcd for $[C_{10}H_{12}O_3+Na]^+$ 203.0679, found 203.0682.

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Supplementary Material

Copies of ^1H and ^{13}CNMR for all compounds are available and can be found at http//:--

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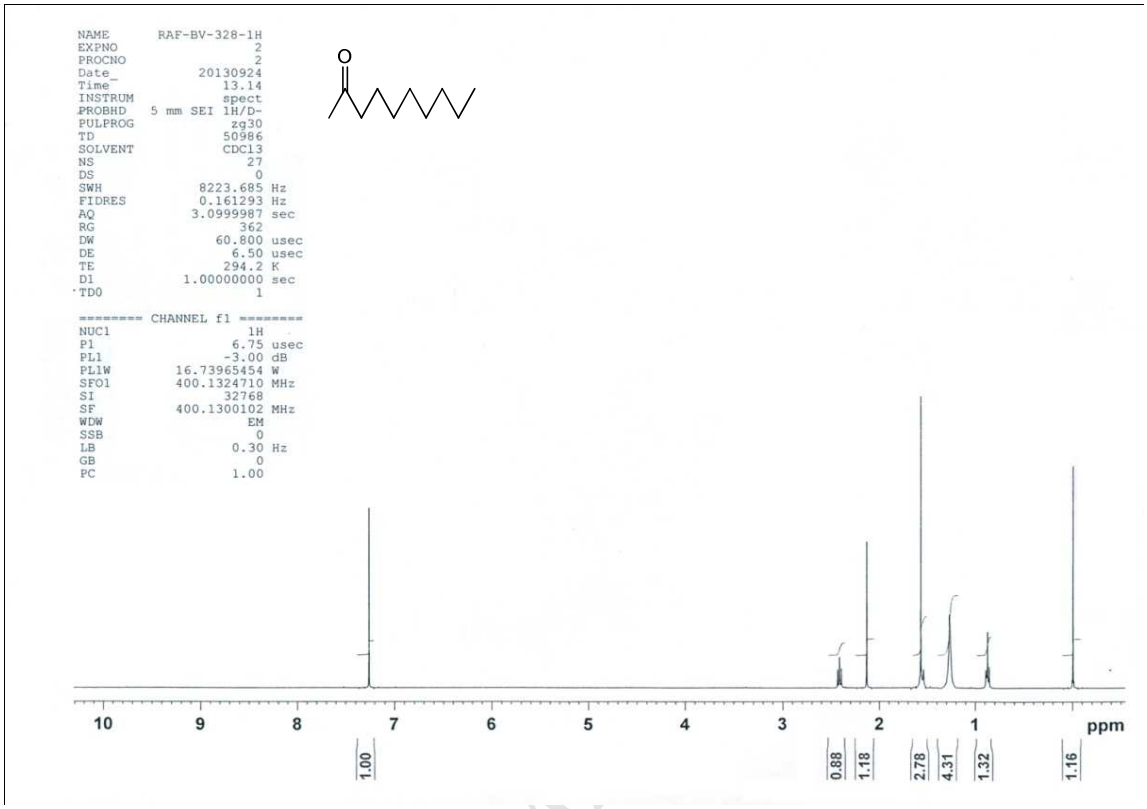
Supporting Information

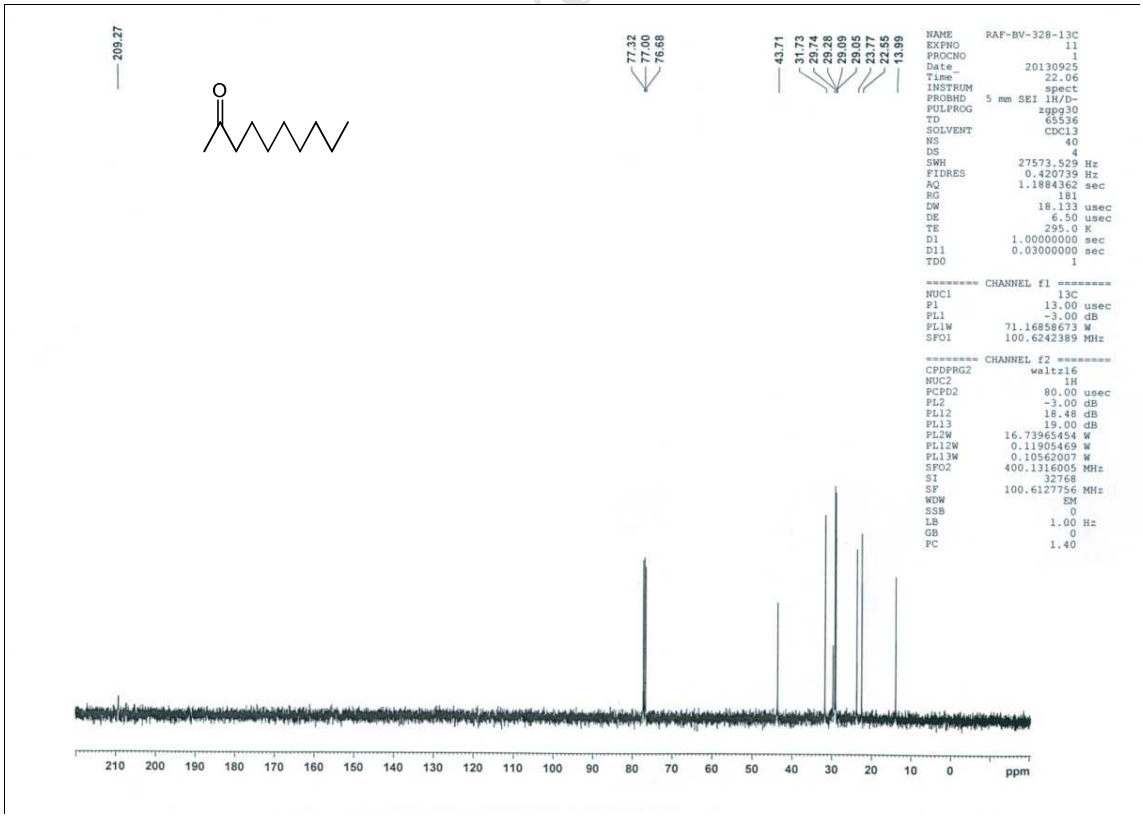
Synthesis of Methyl Ketones from Terminal Olefins using $PdCl_2/CrO_3$ System Mimicking the Wacker Process

Rodney A. Fernandes, Venkati Bethi*

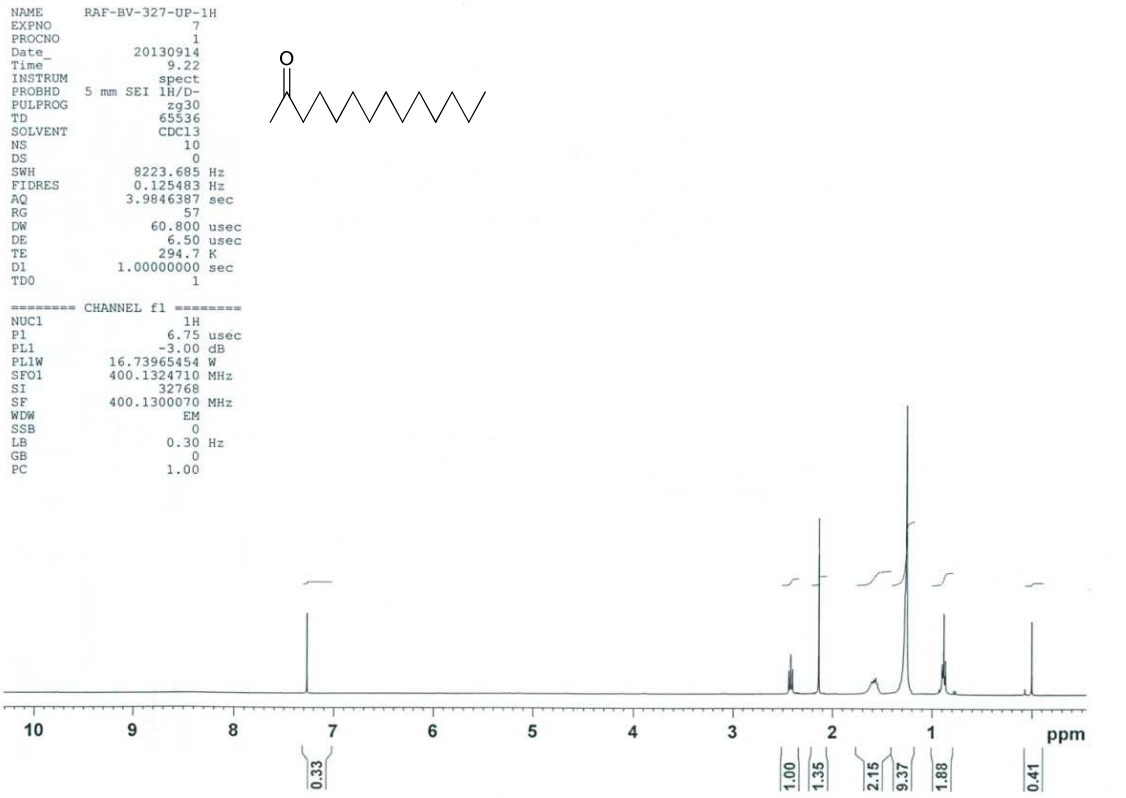
^{1}H and ^{13}C NMR for **2a-2x**, **4a-4l** and **6a-6h**

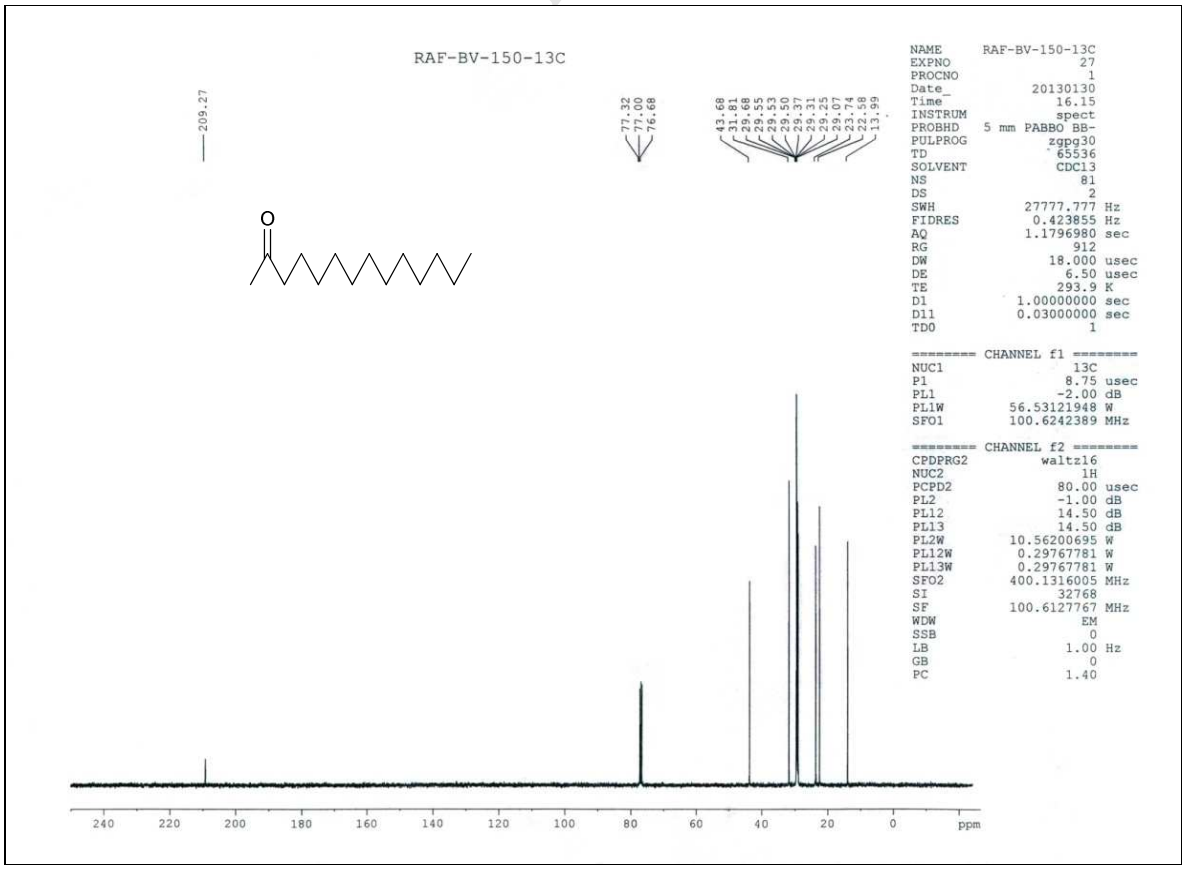
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2a



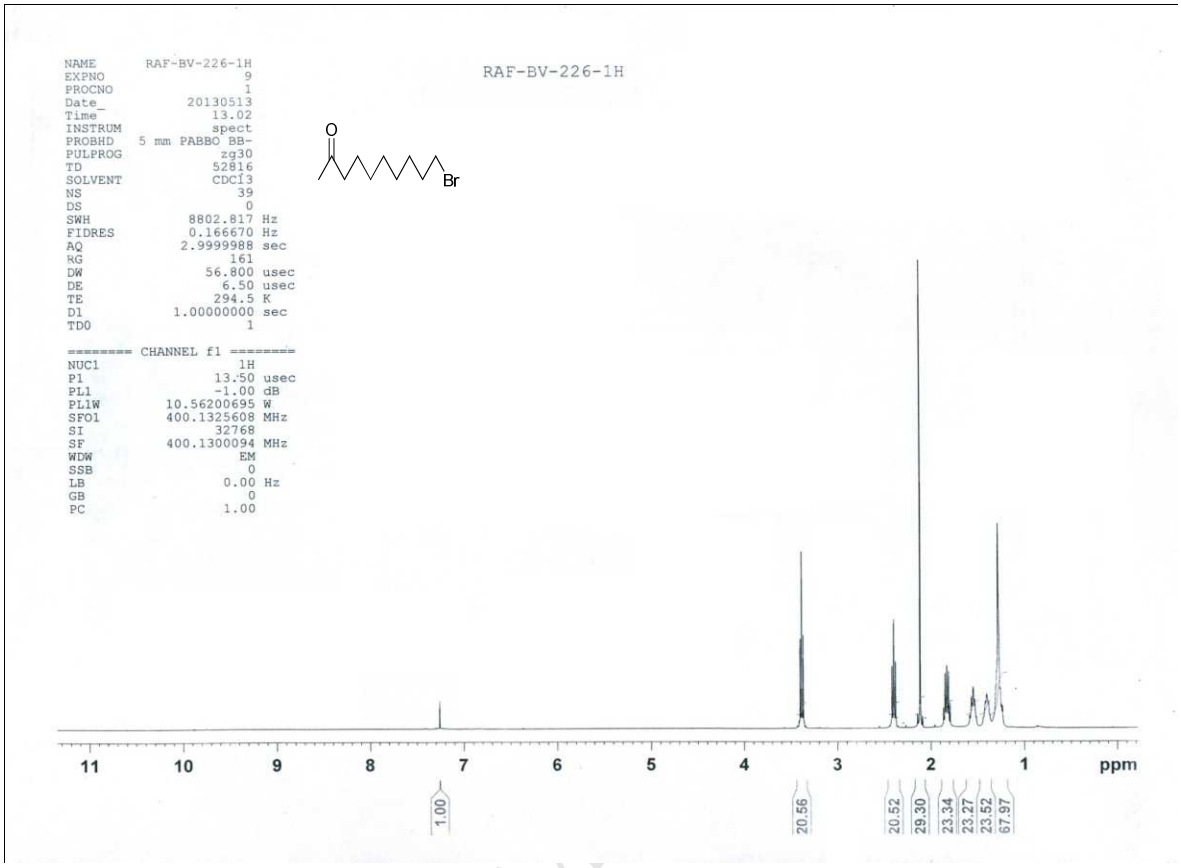


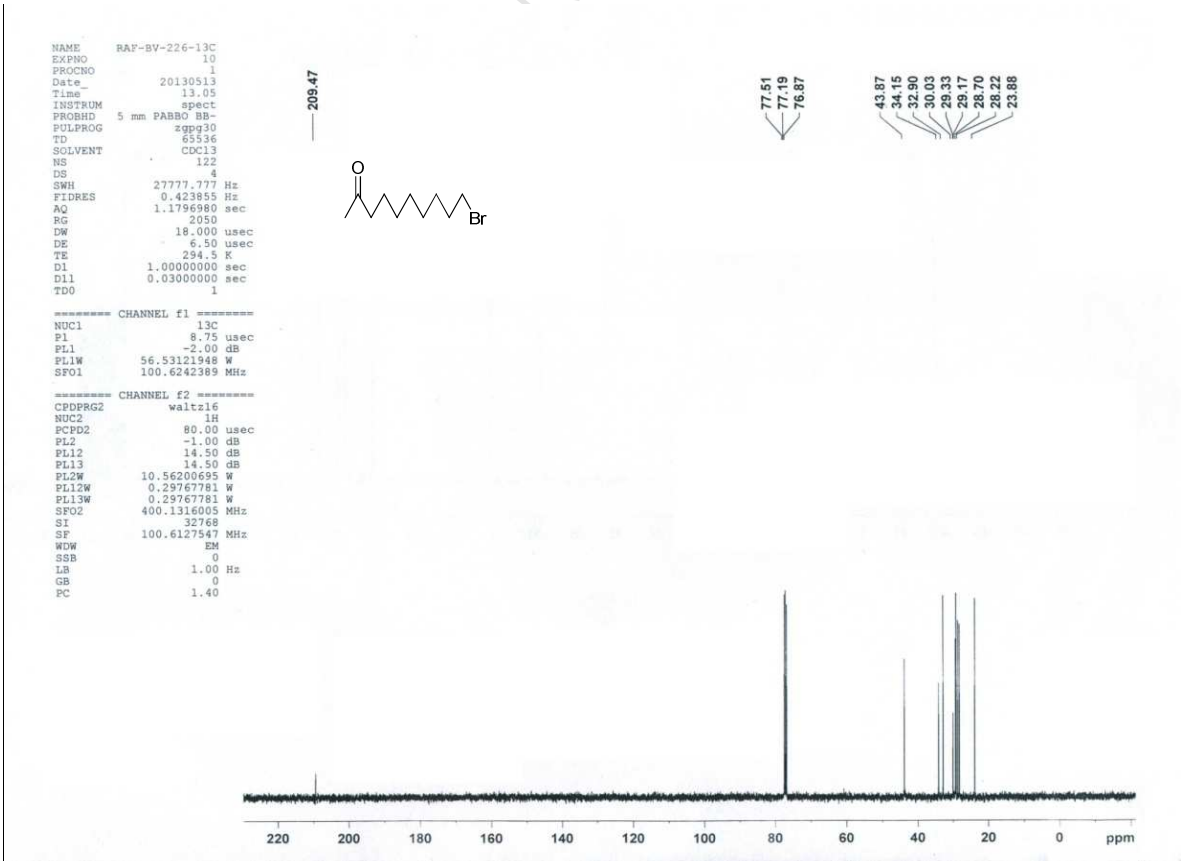
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2b



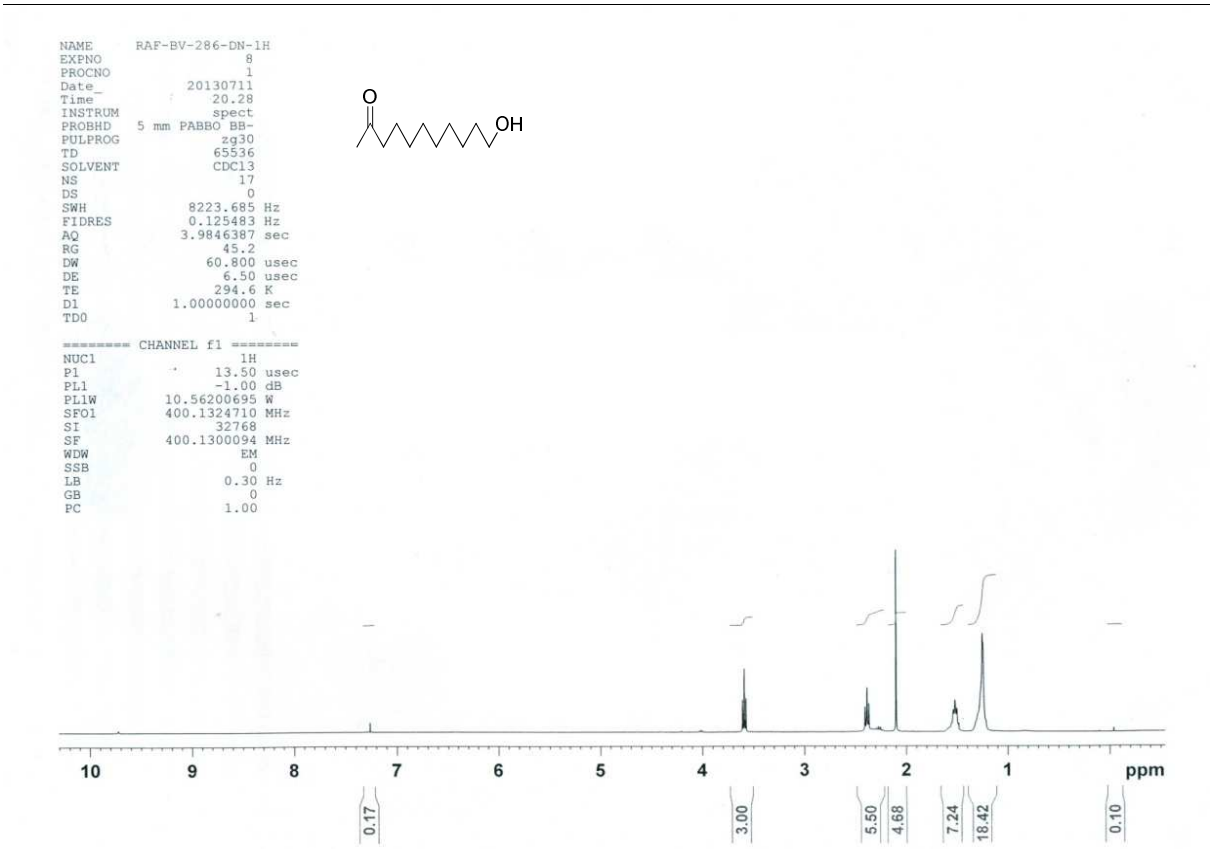


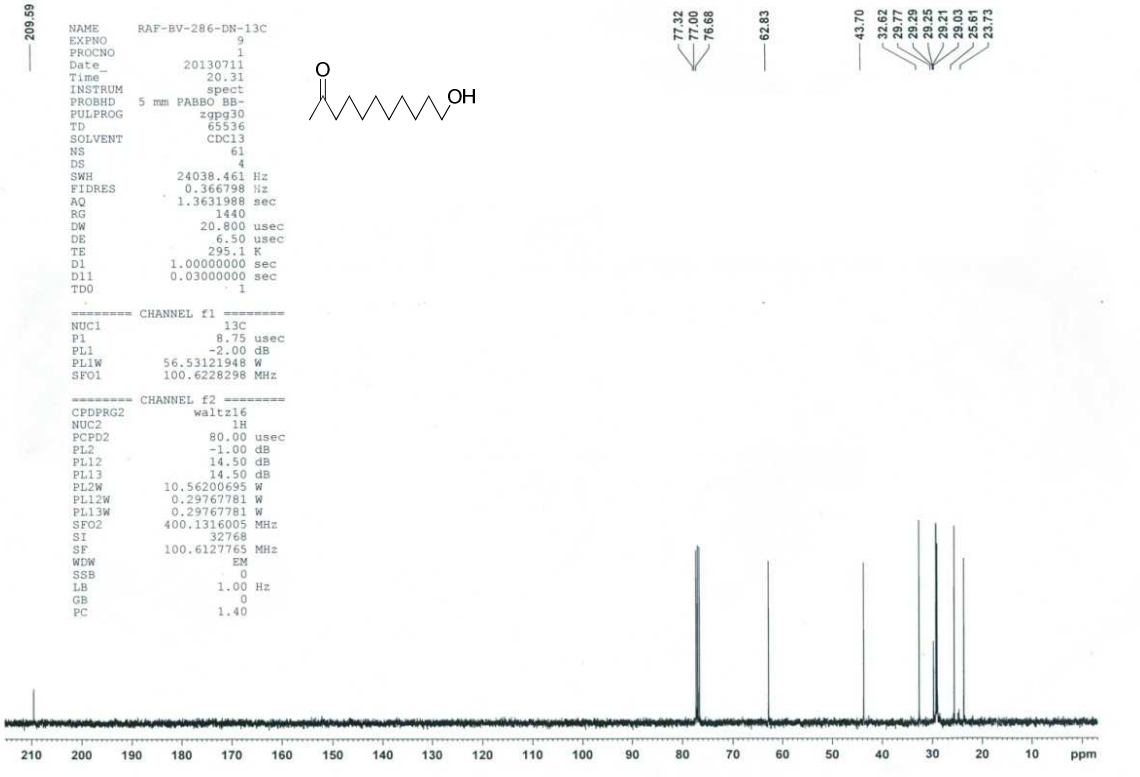
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2c



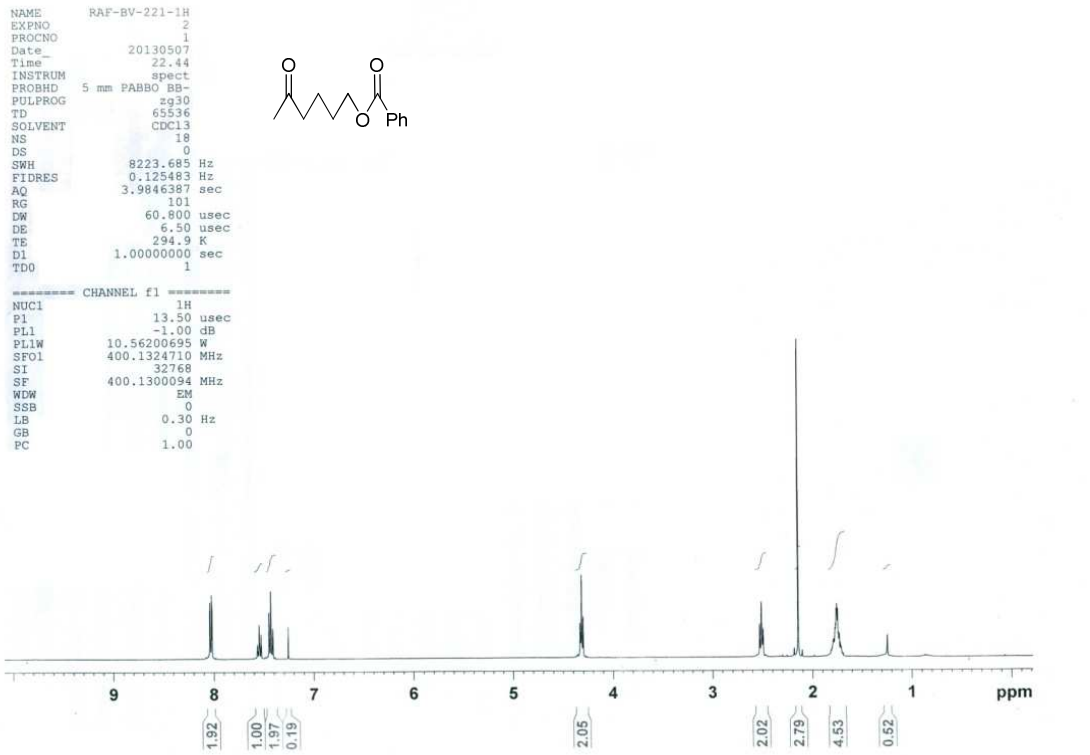


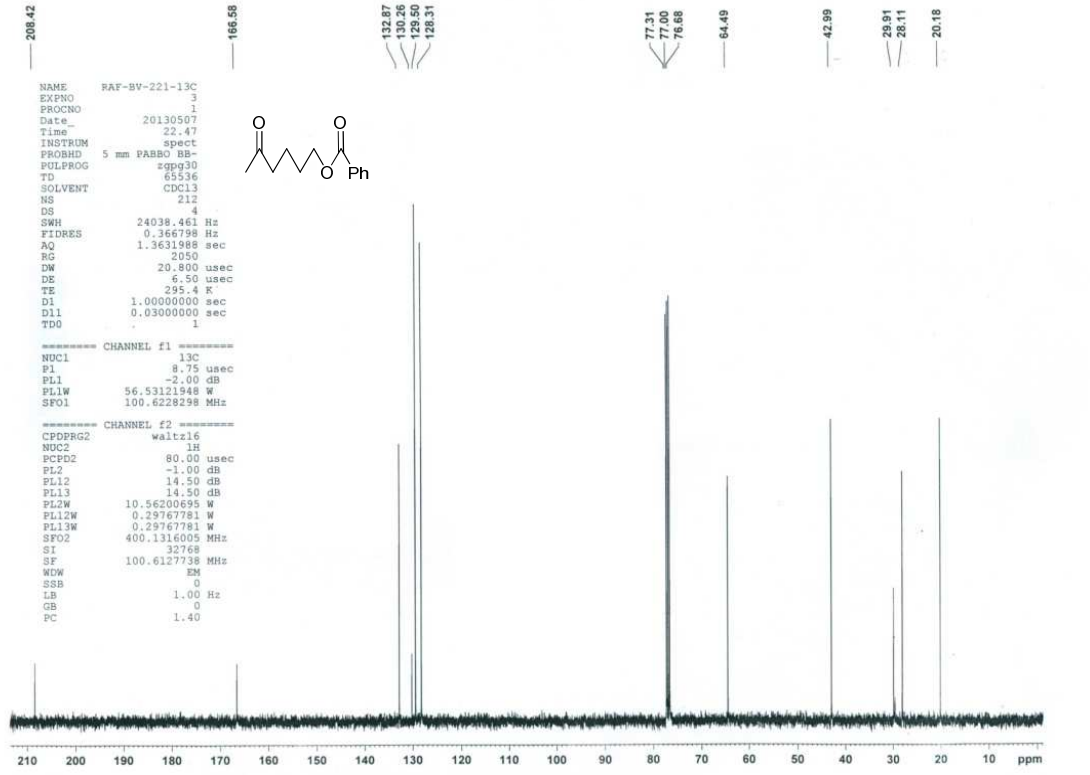
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2d



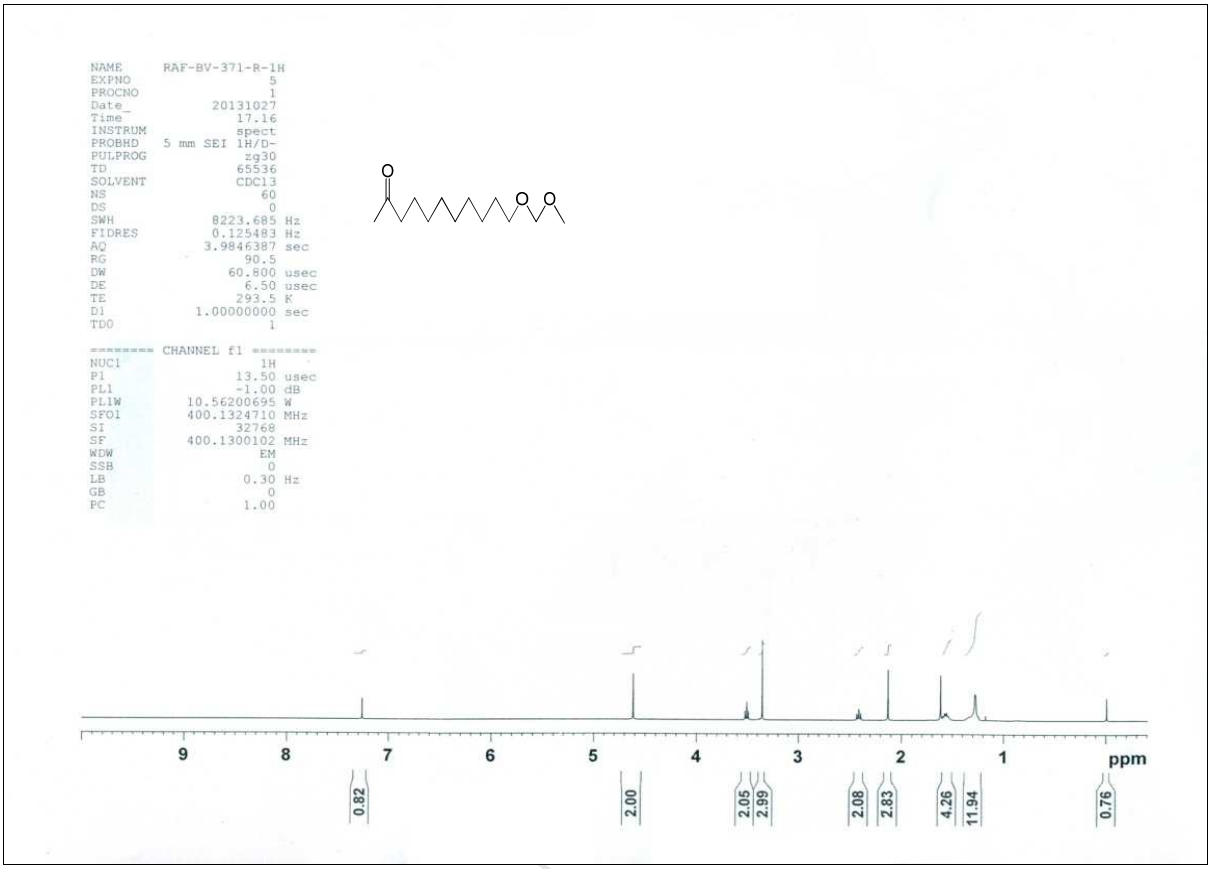


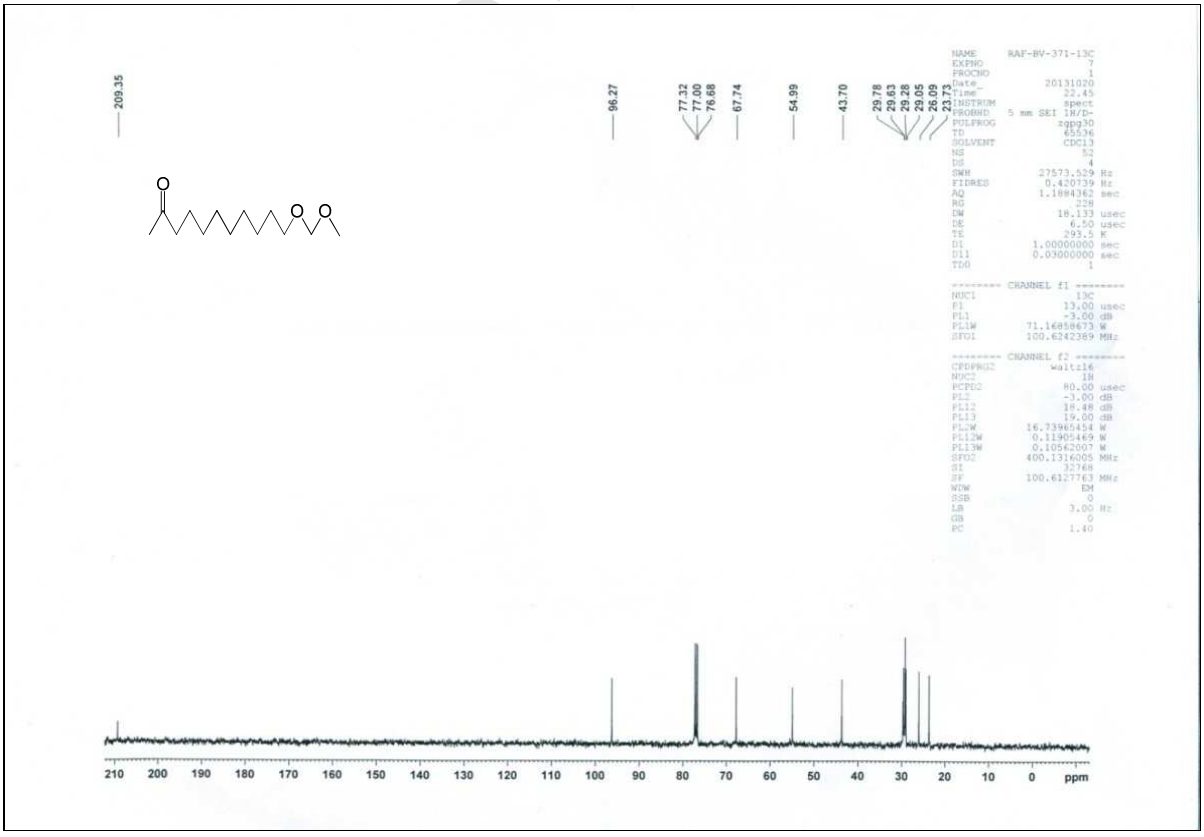
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2e



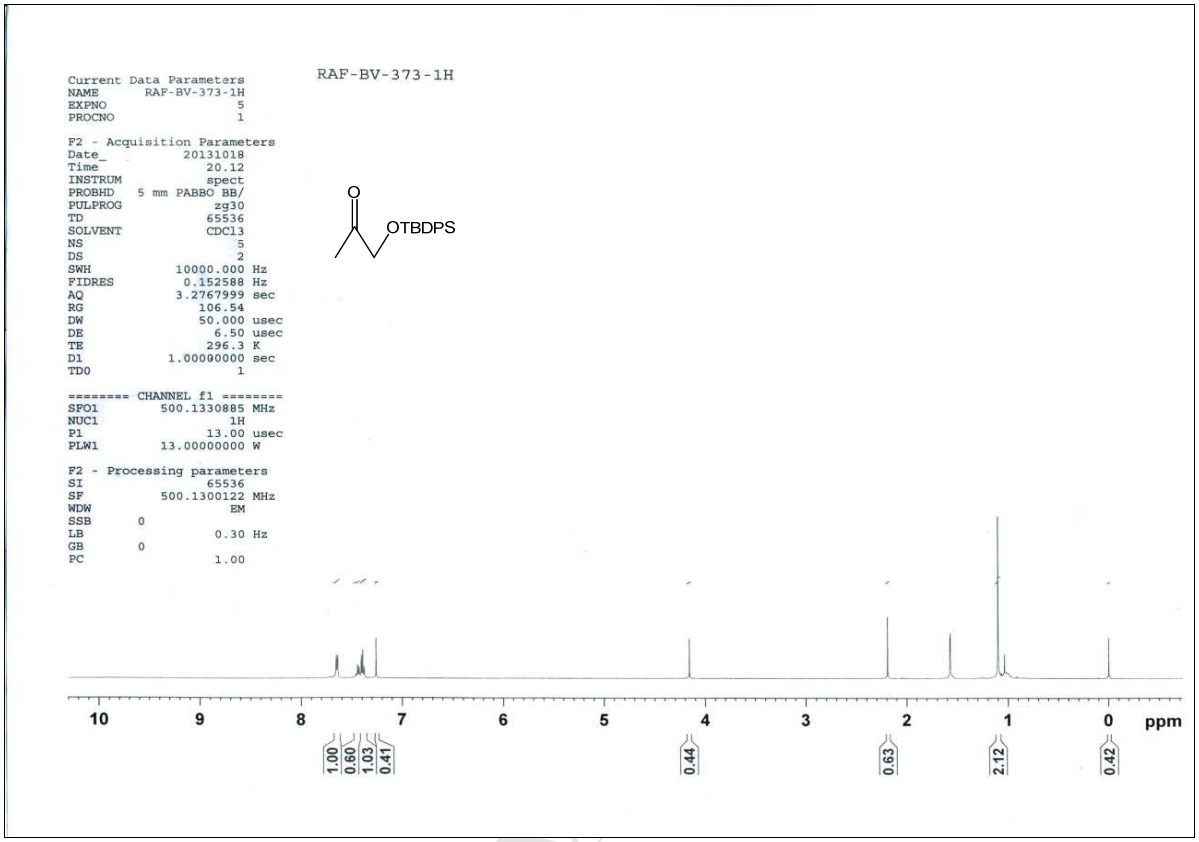


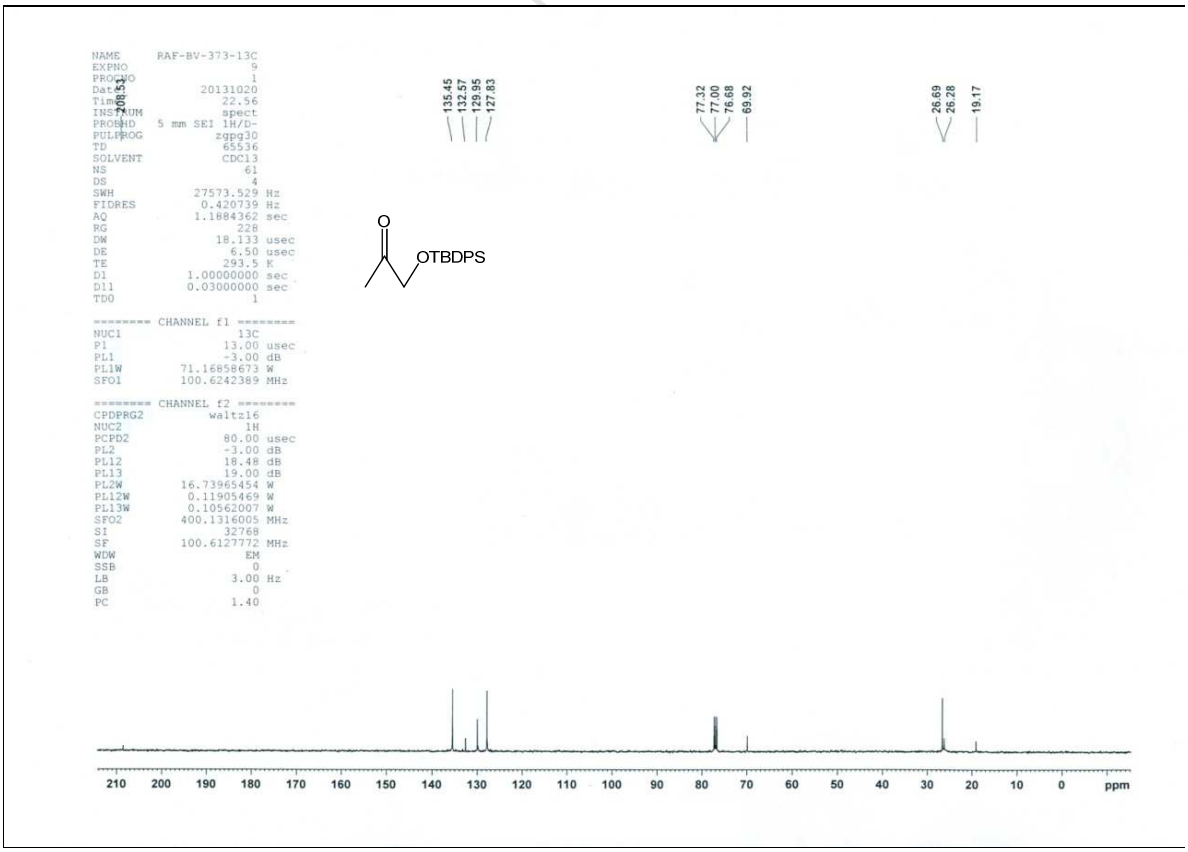
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2f



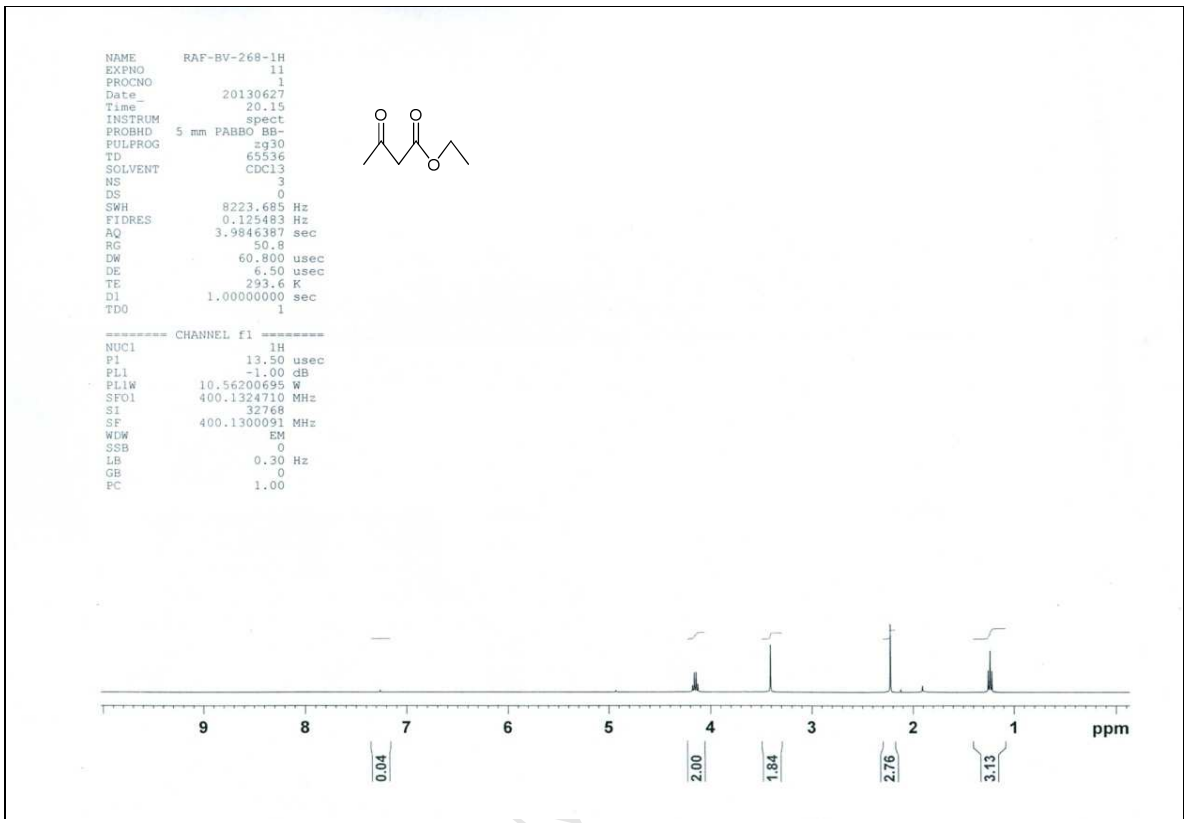


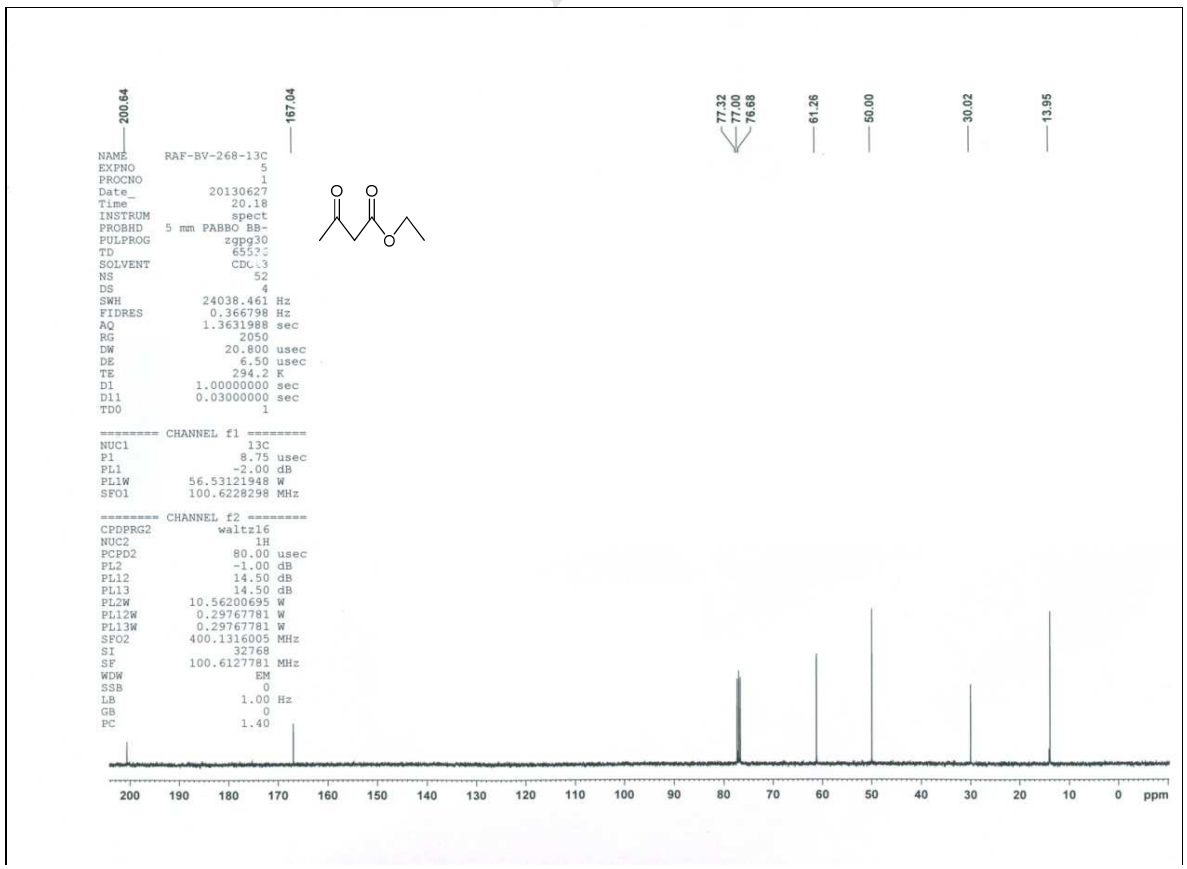
^{1}H NMR (500 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2g



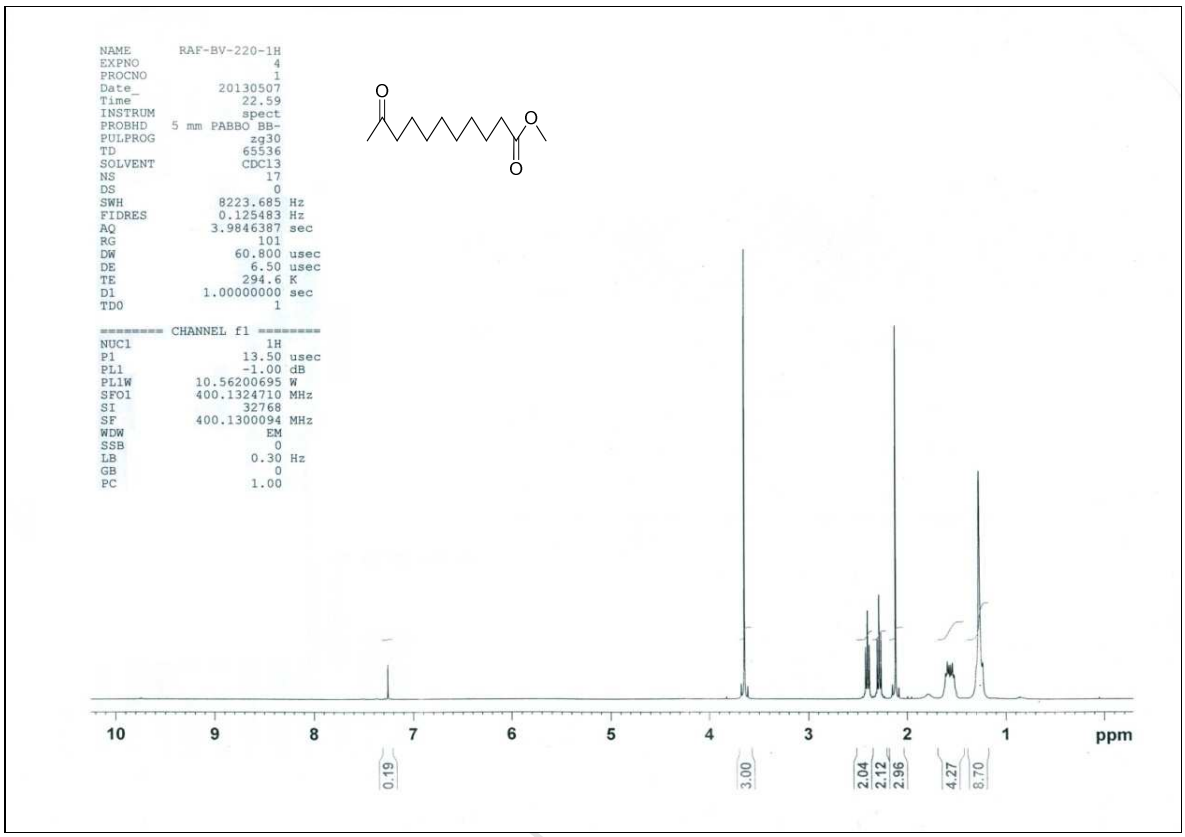


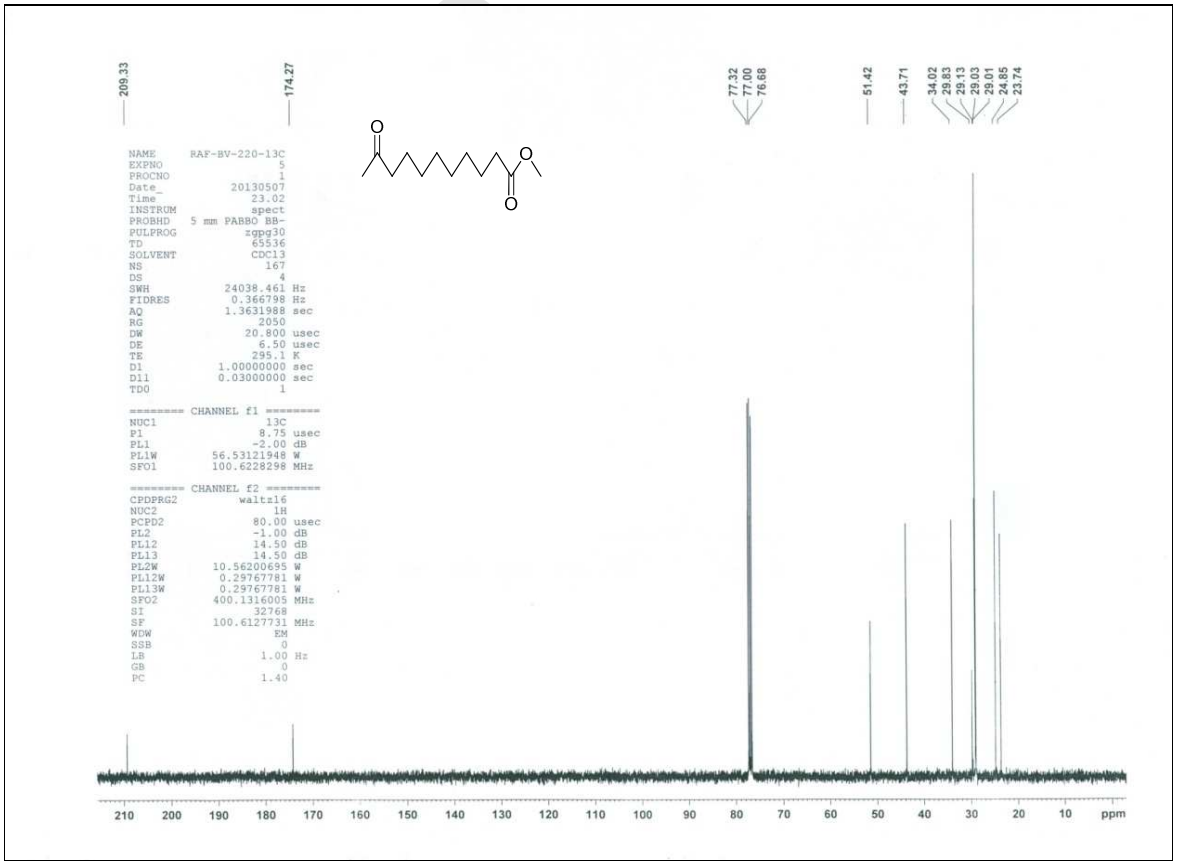
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2h



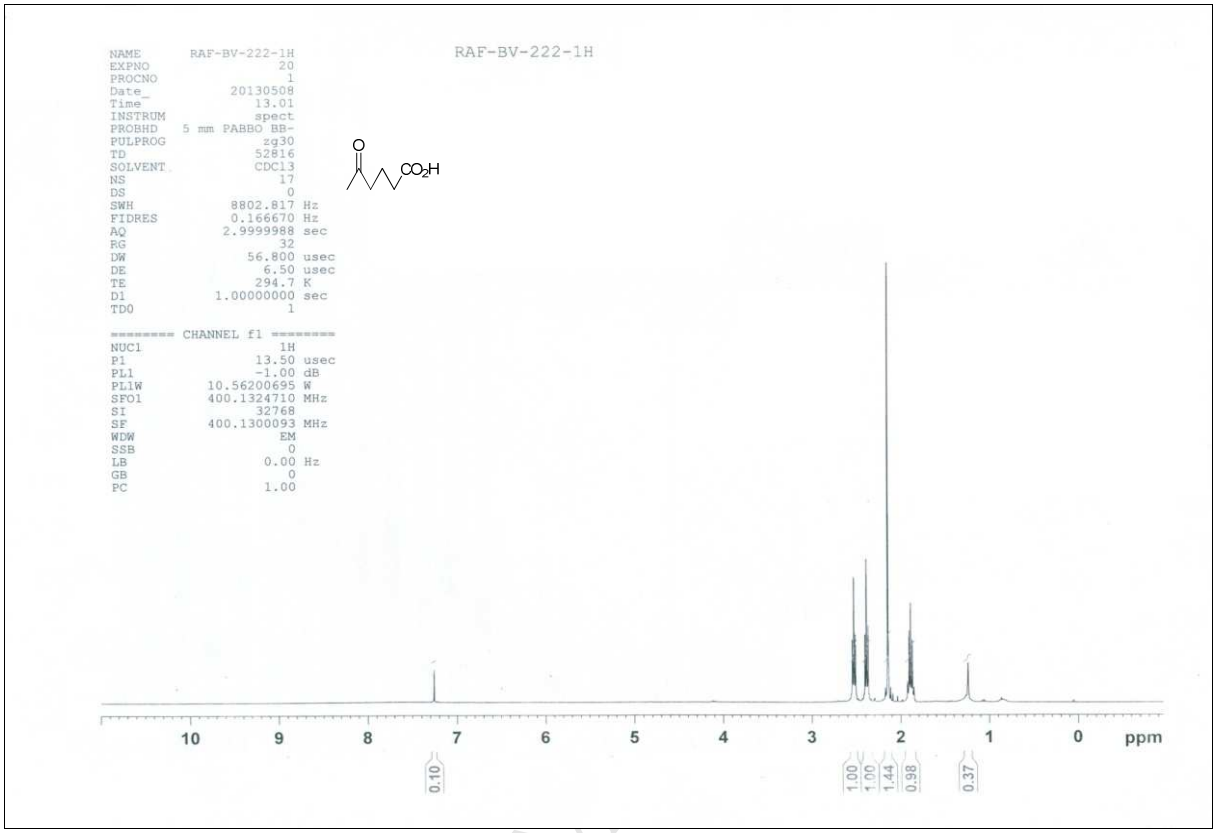


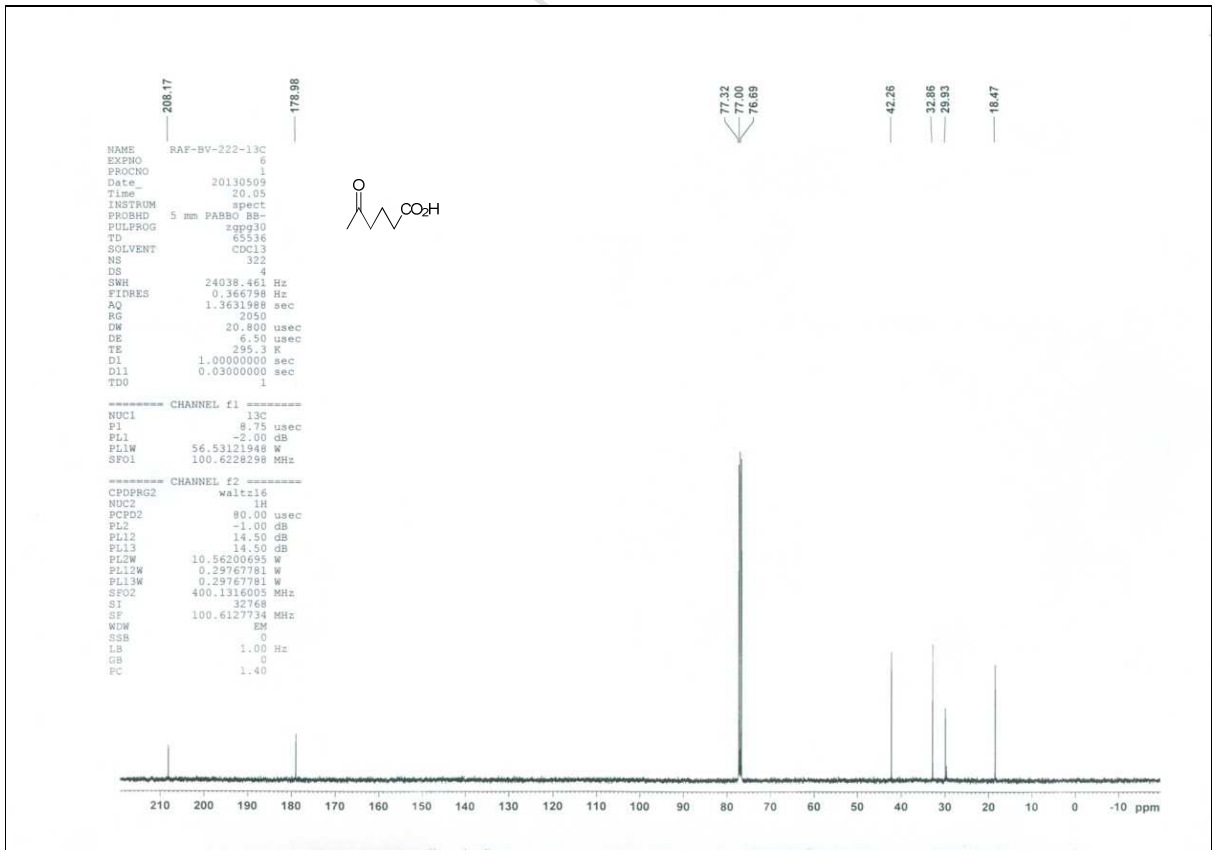
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2i



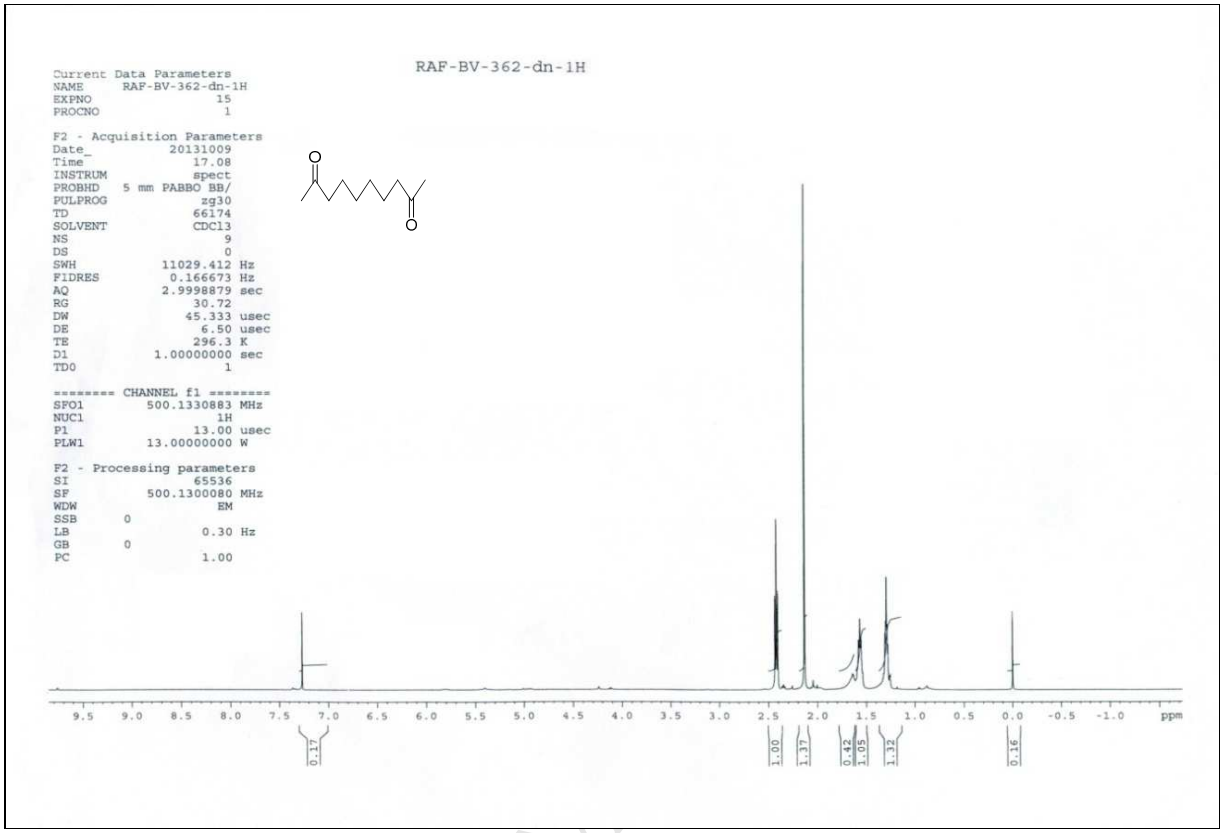


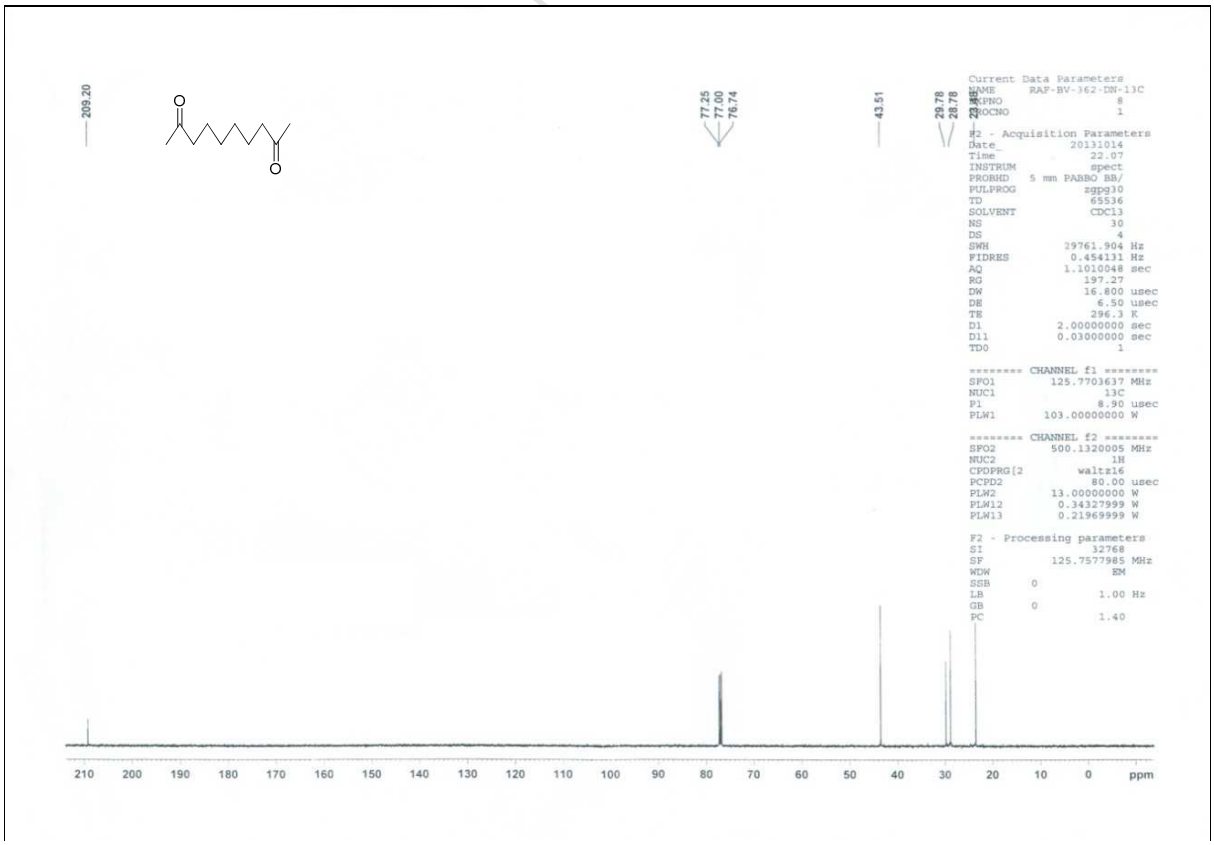
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2j



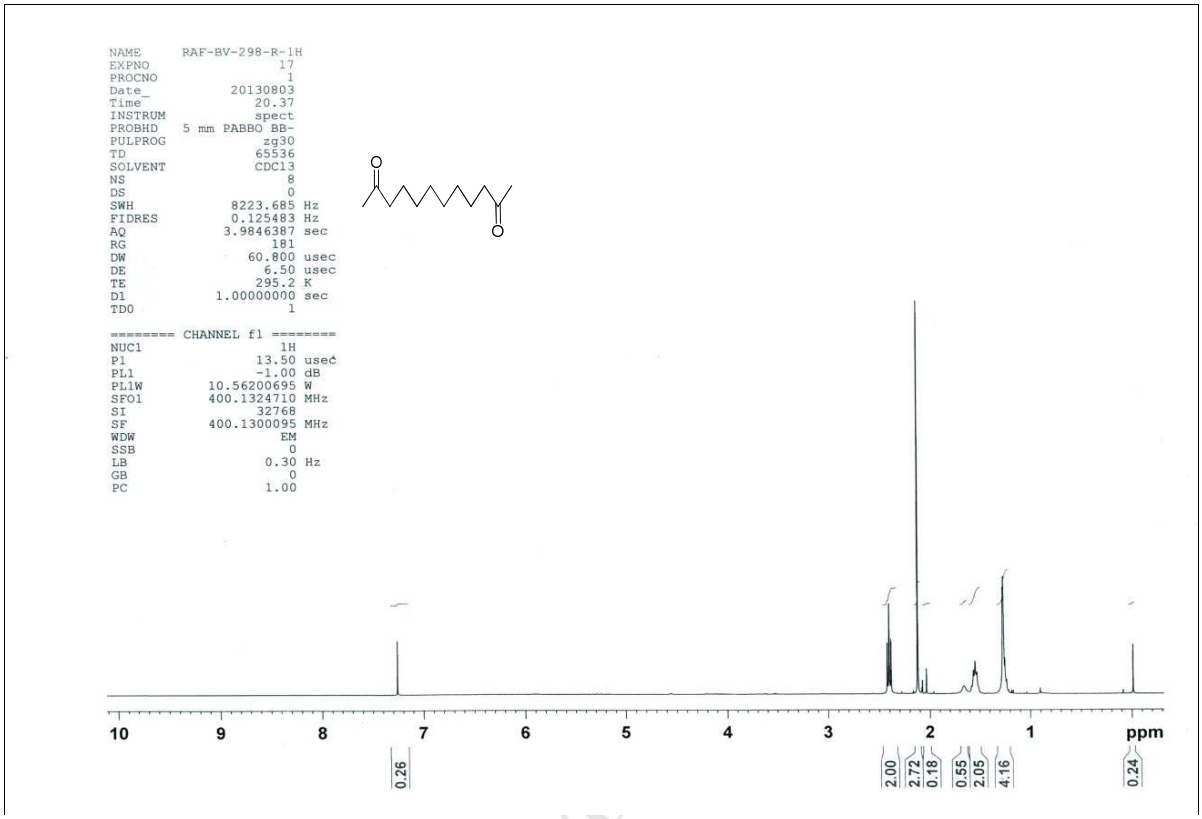


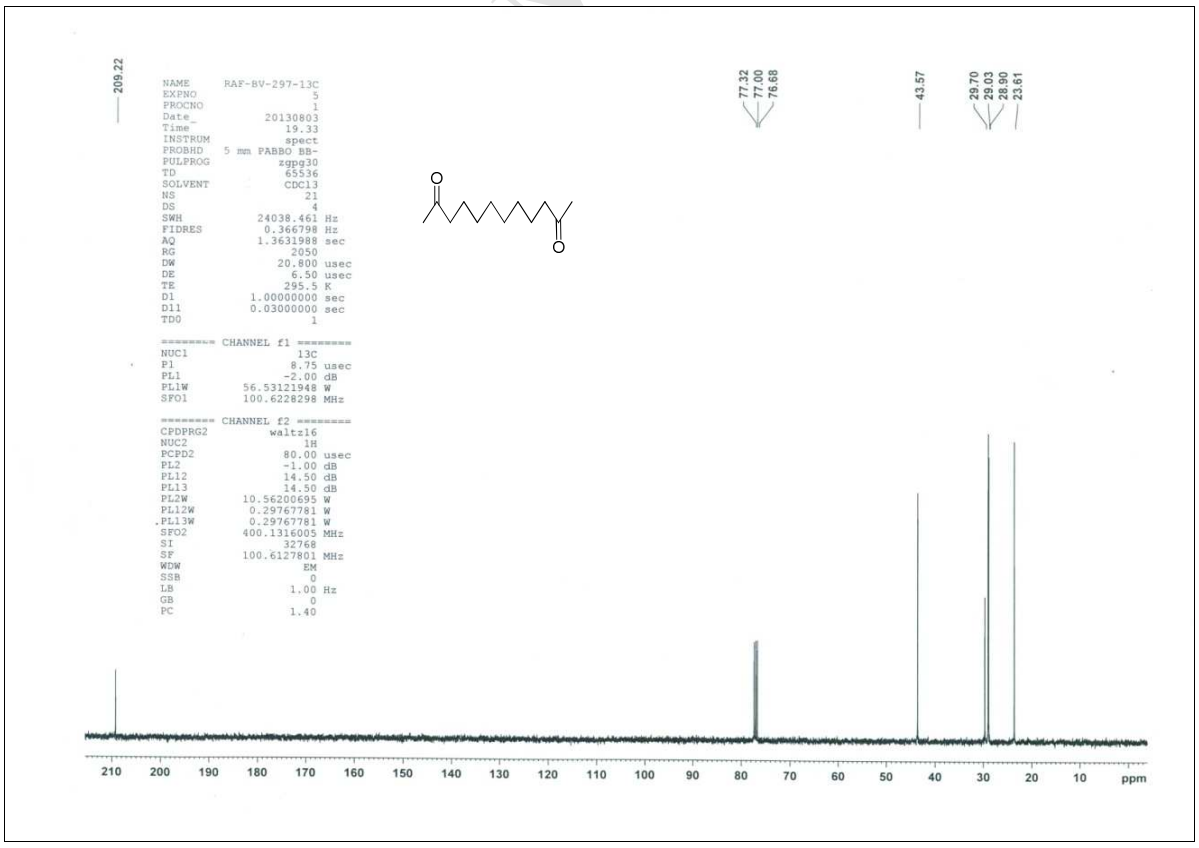
^{1}H NMR (500 MHz, $CDCl_3$/TMS) and ^{13}C NMR (125 MHz, $CDCl_3$) of compound 2k



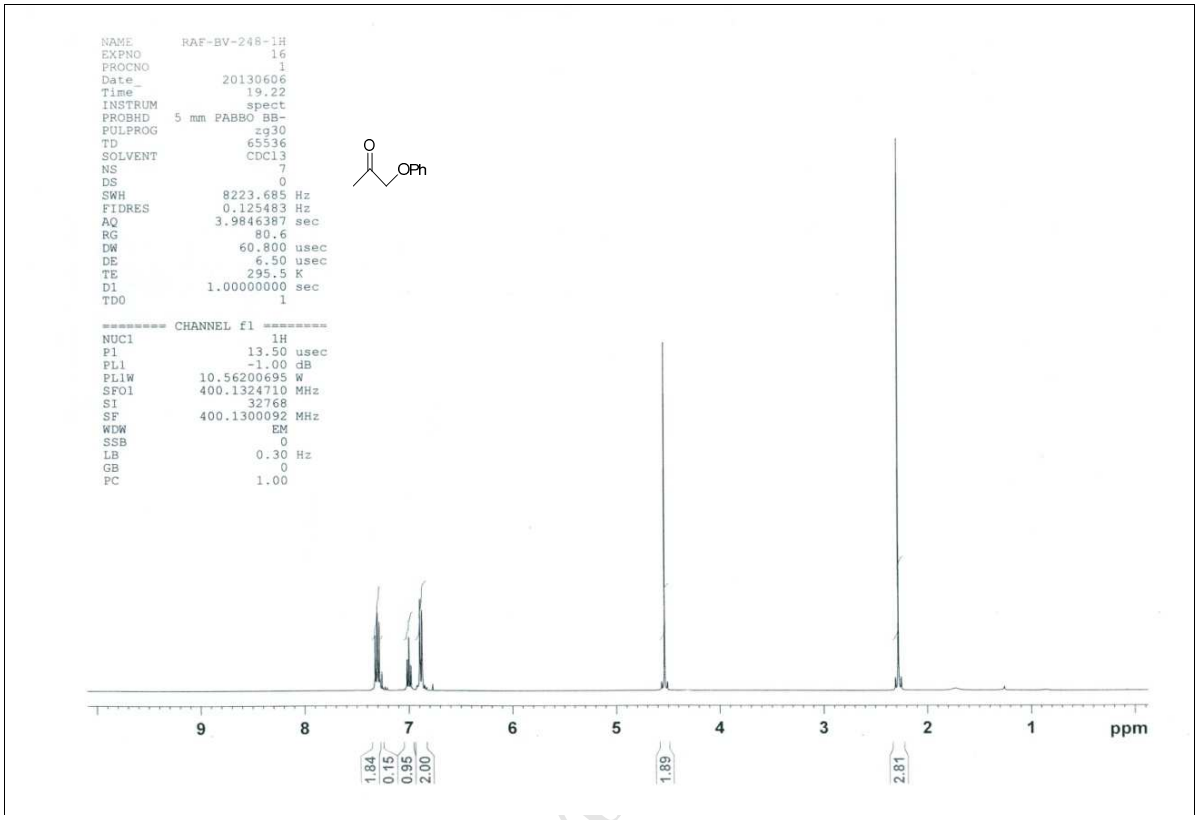


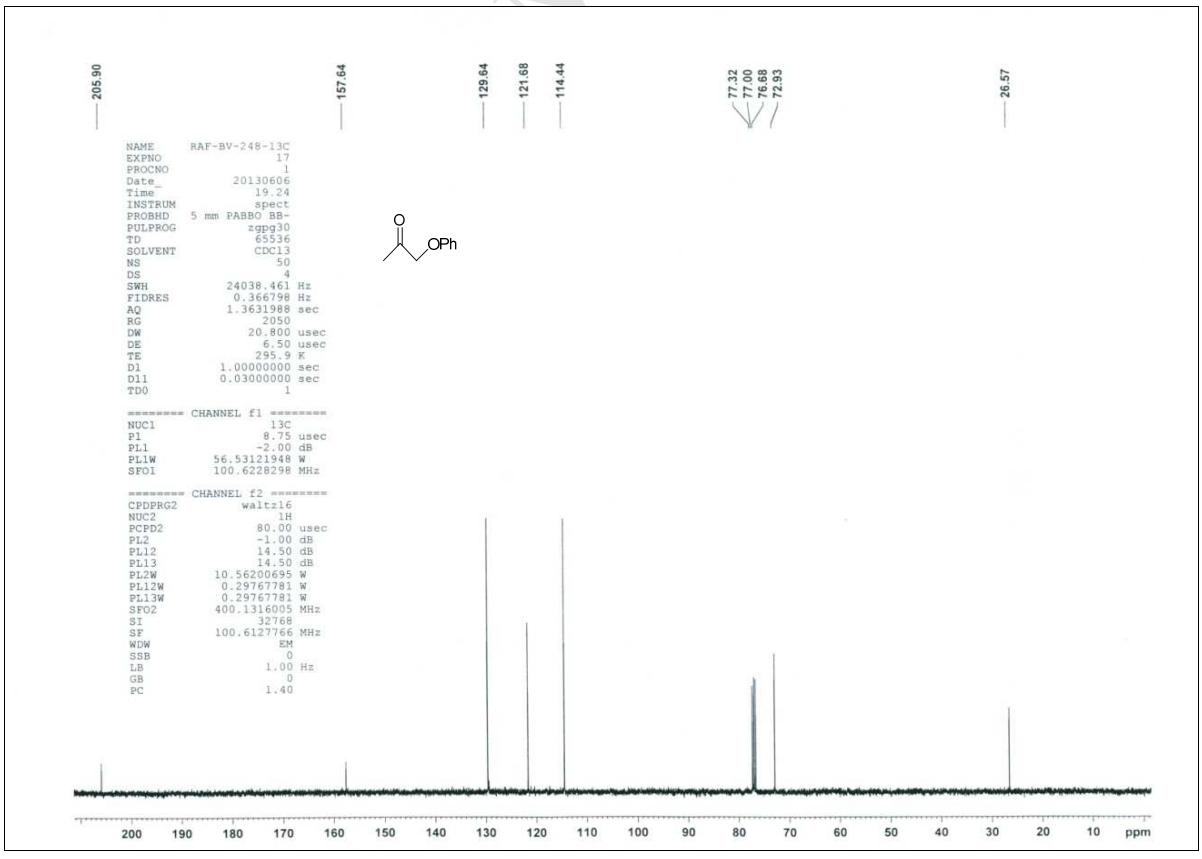
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2l



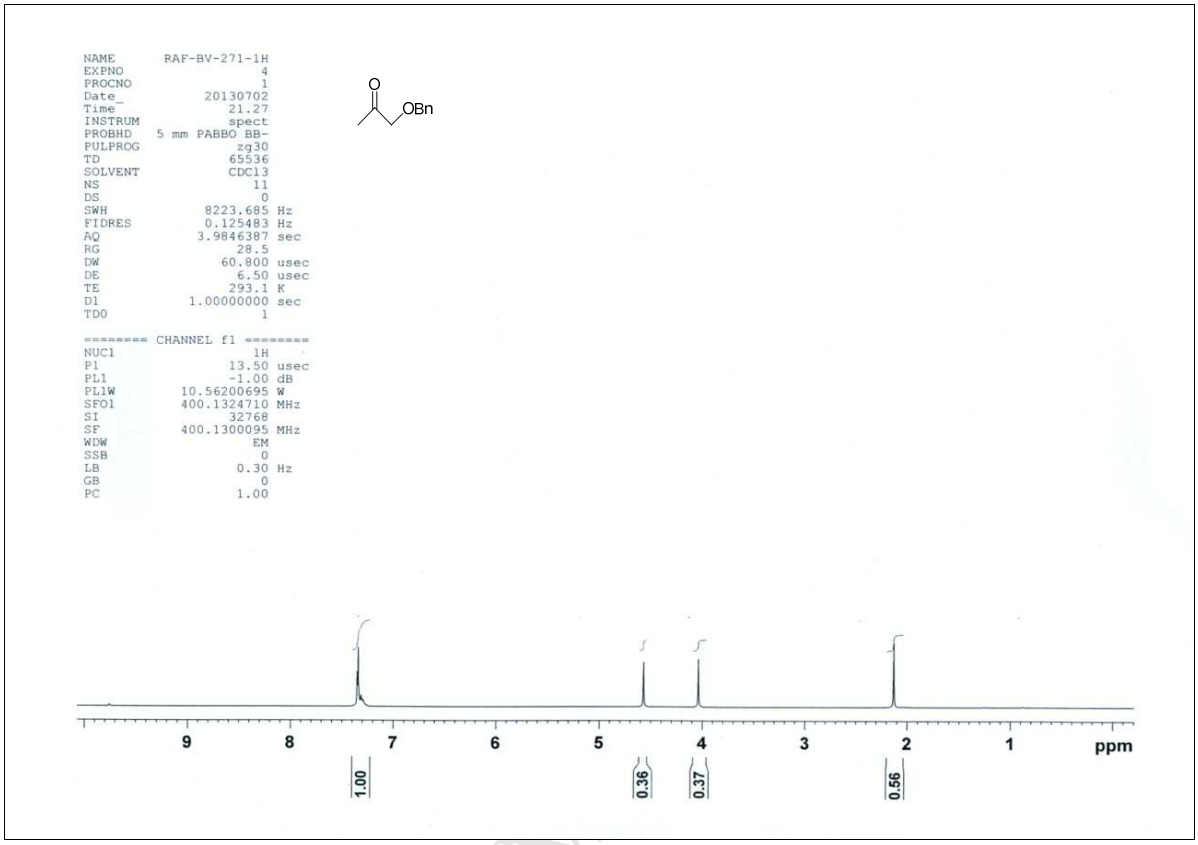


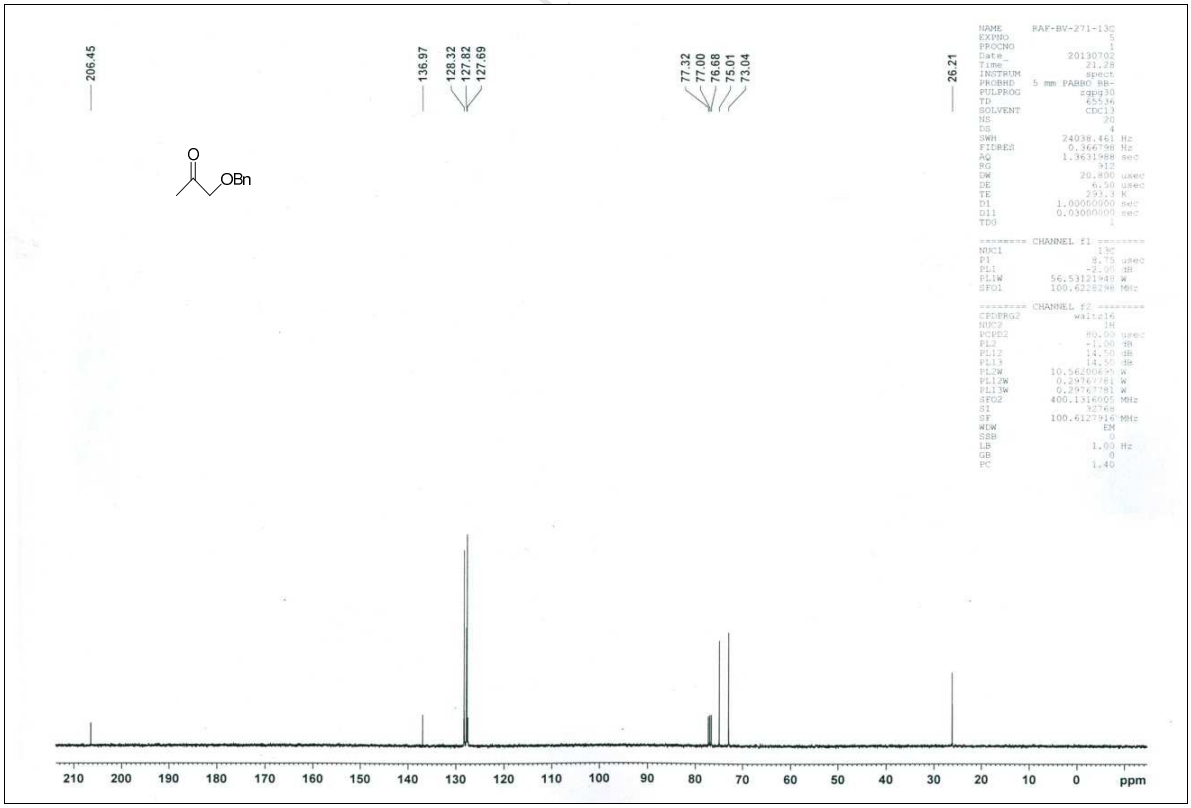
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2m



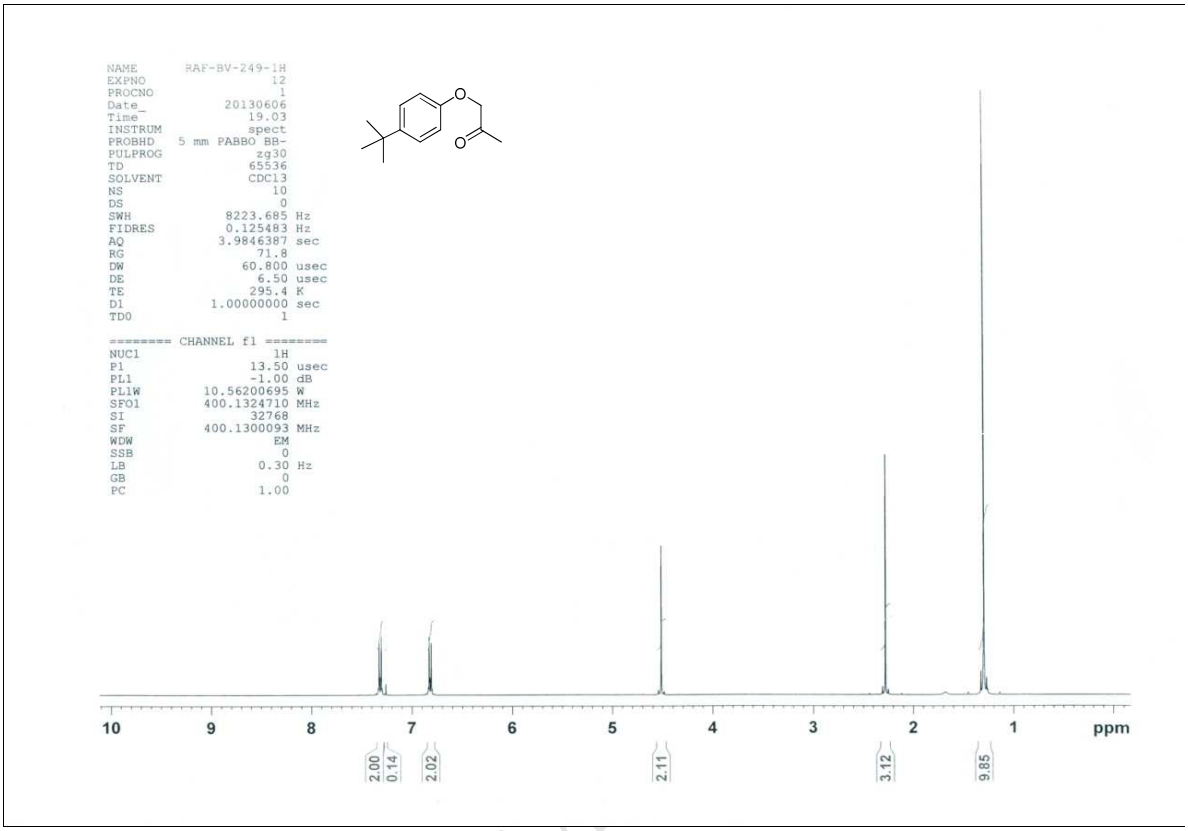


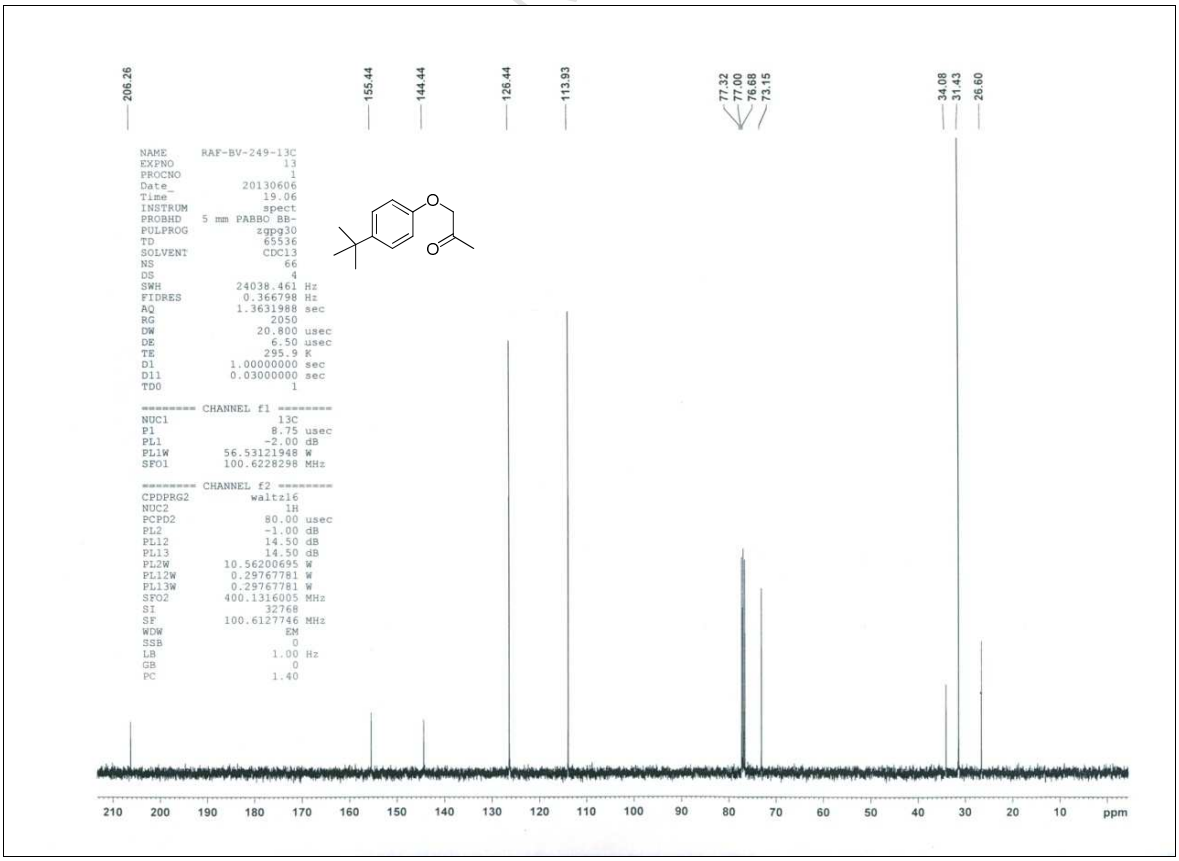
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2n



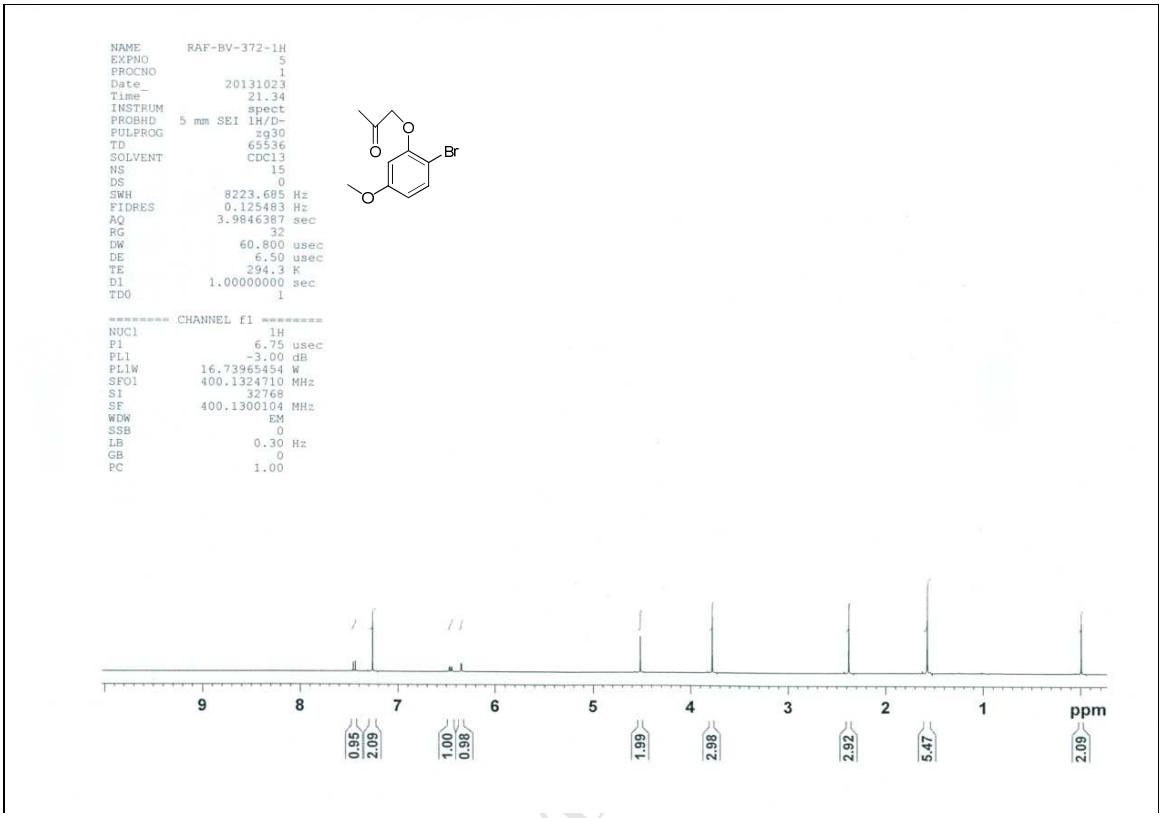


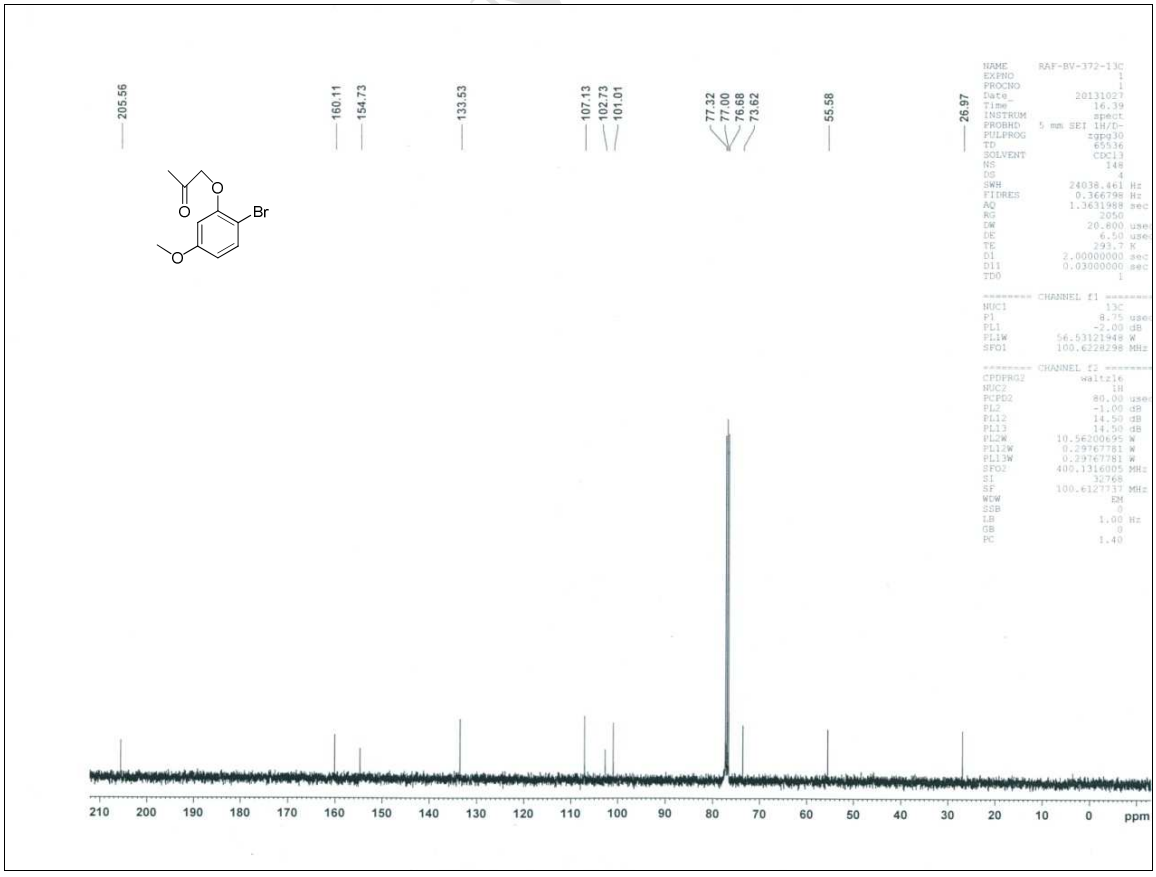
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2o



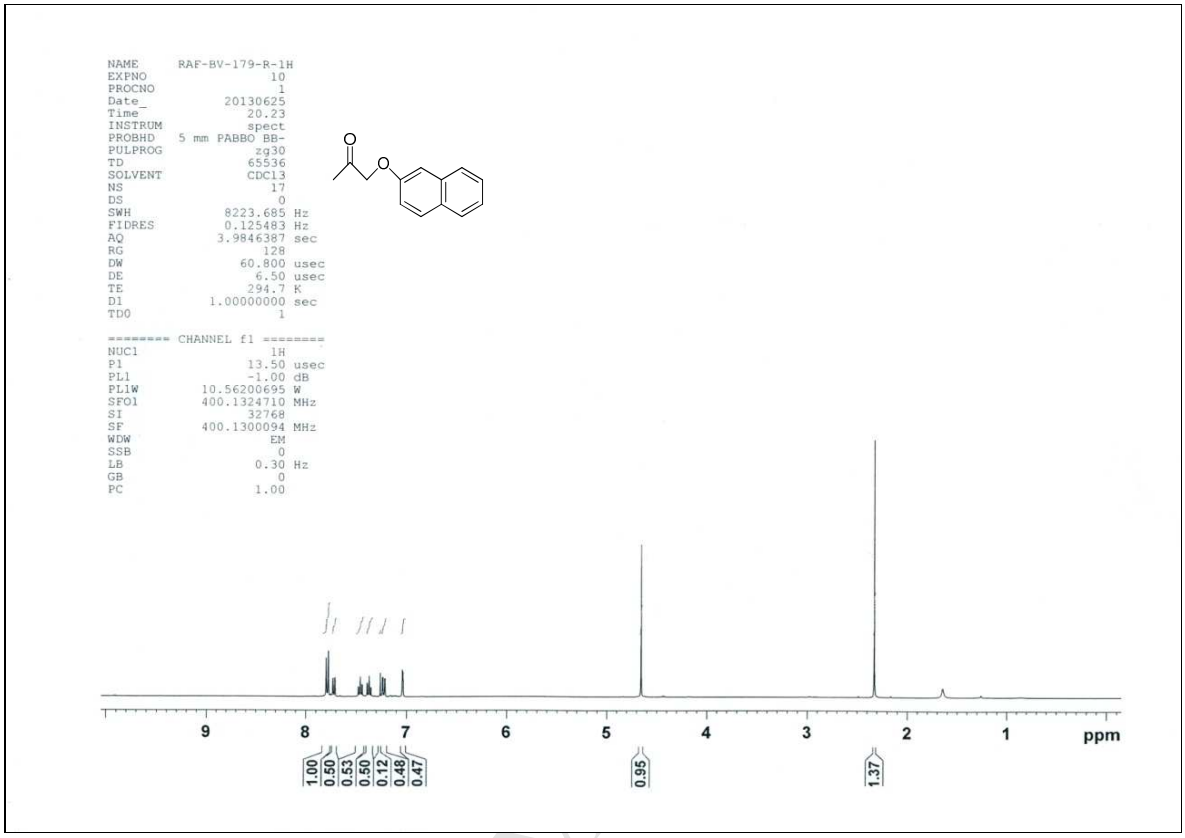


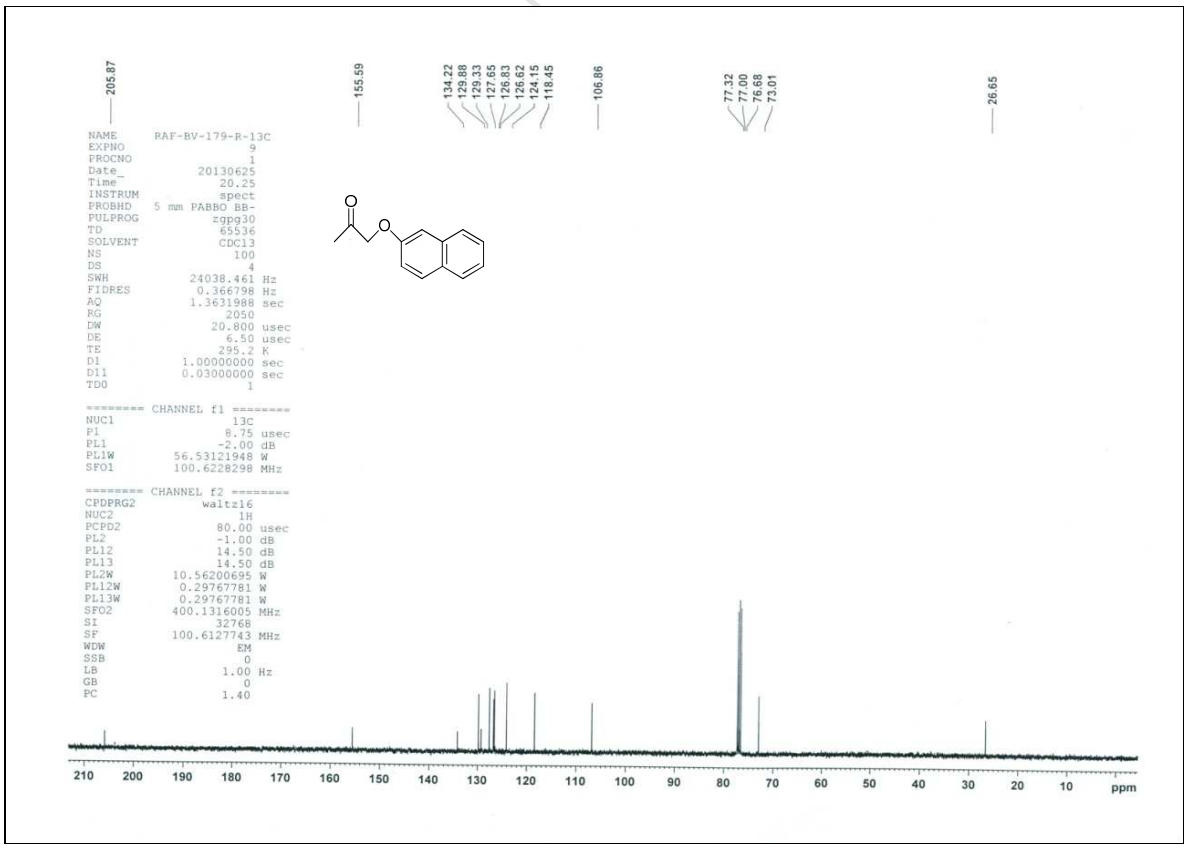
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2p





^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2q





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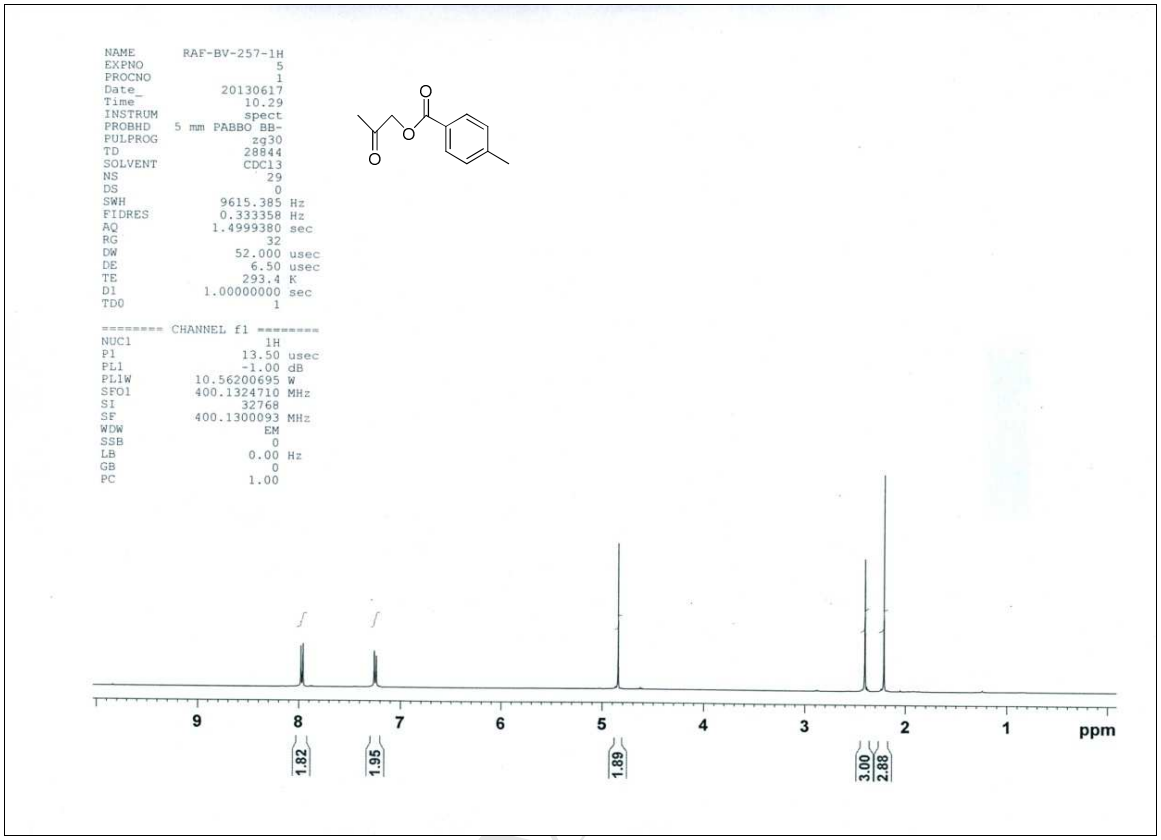

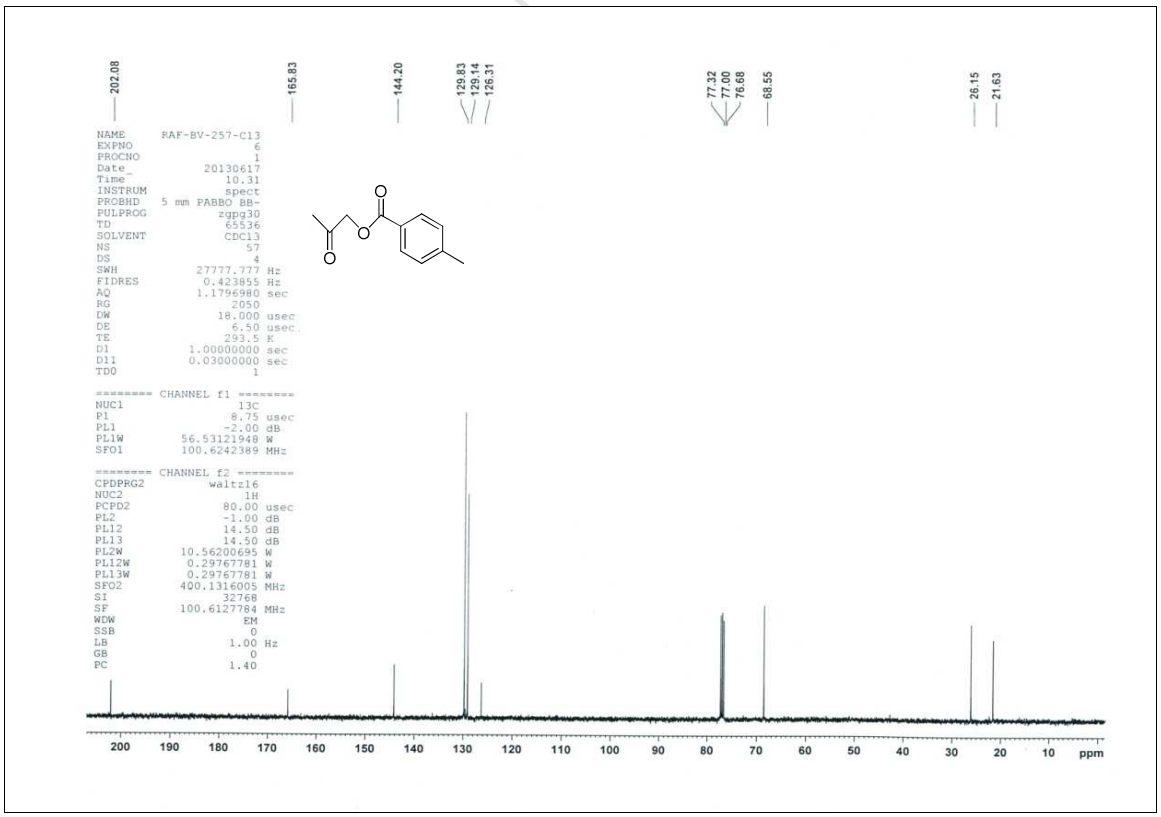

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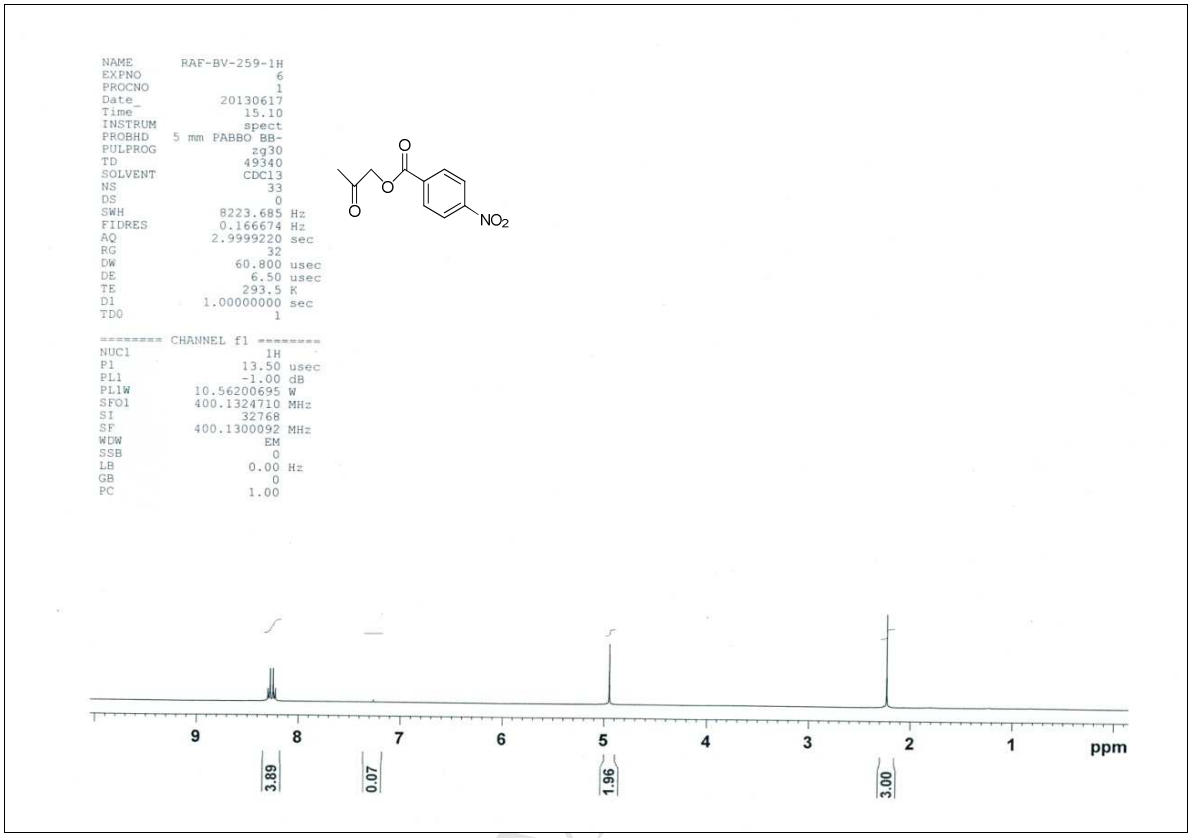

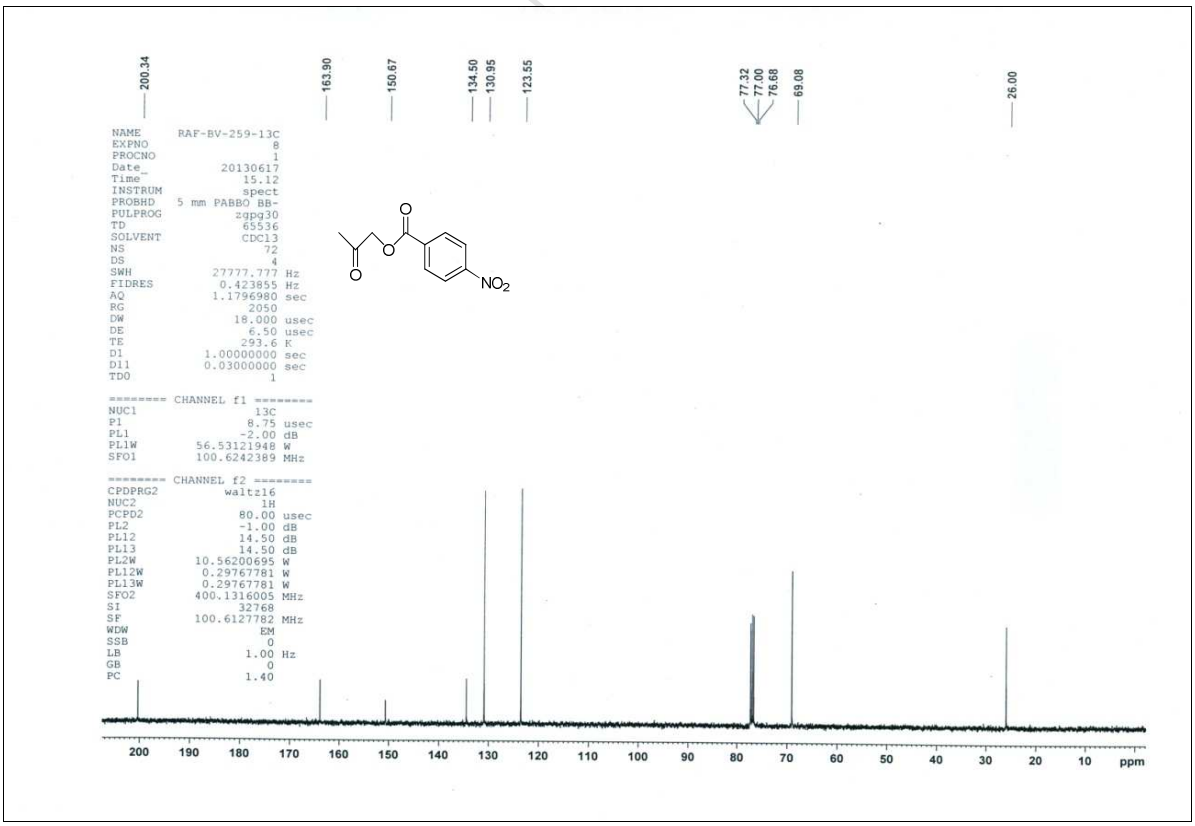

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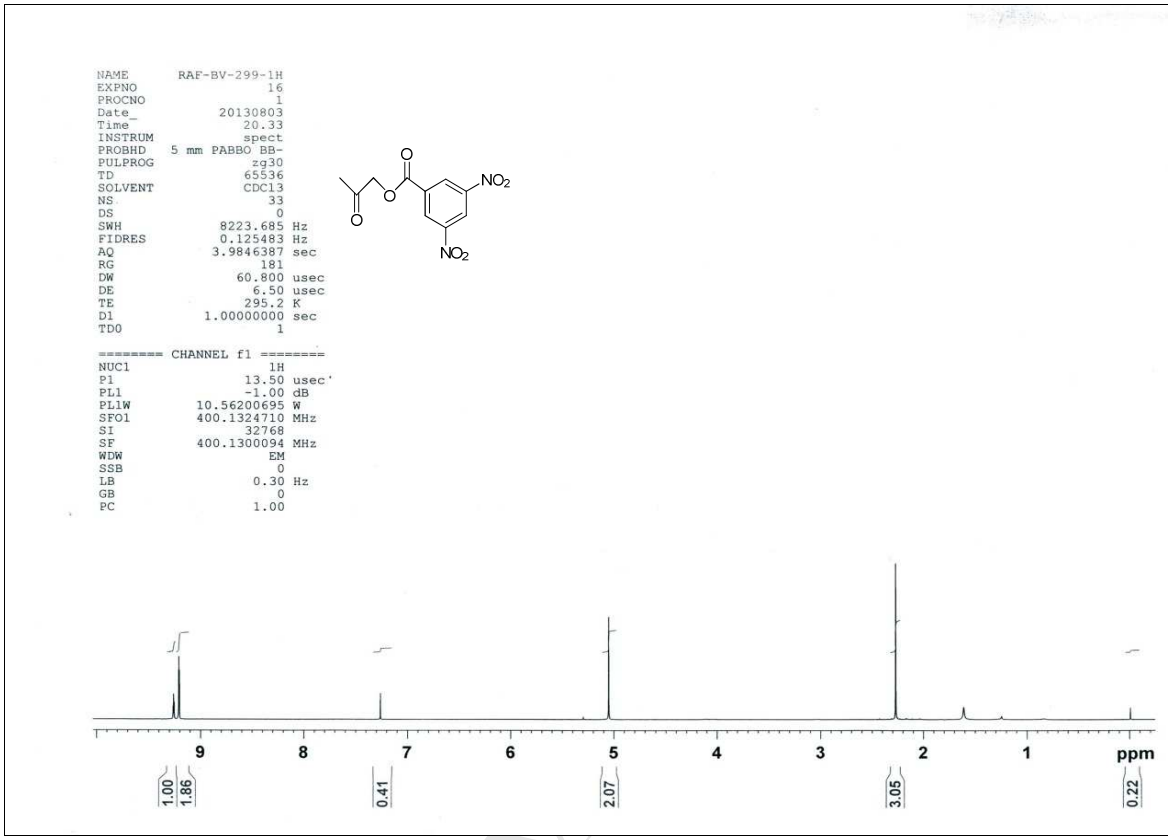

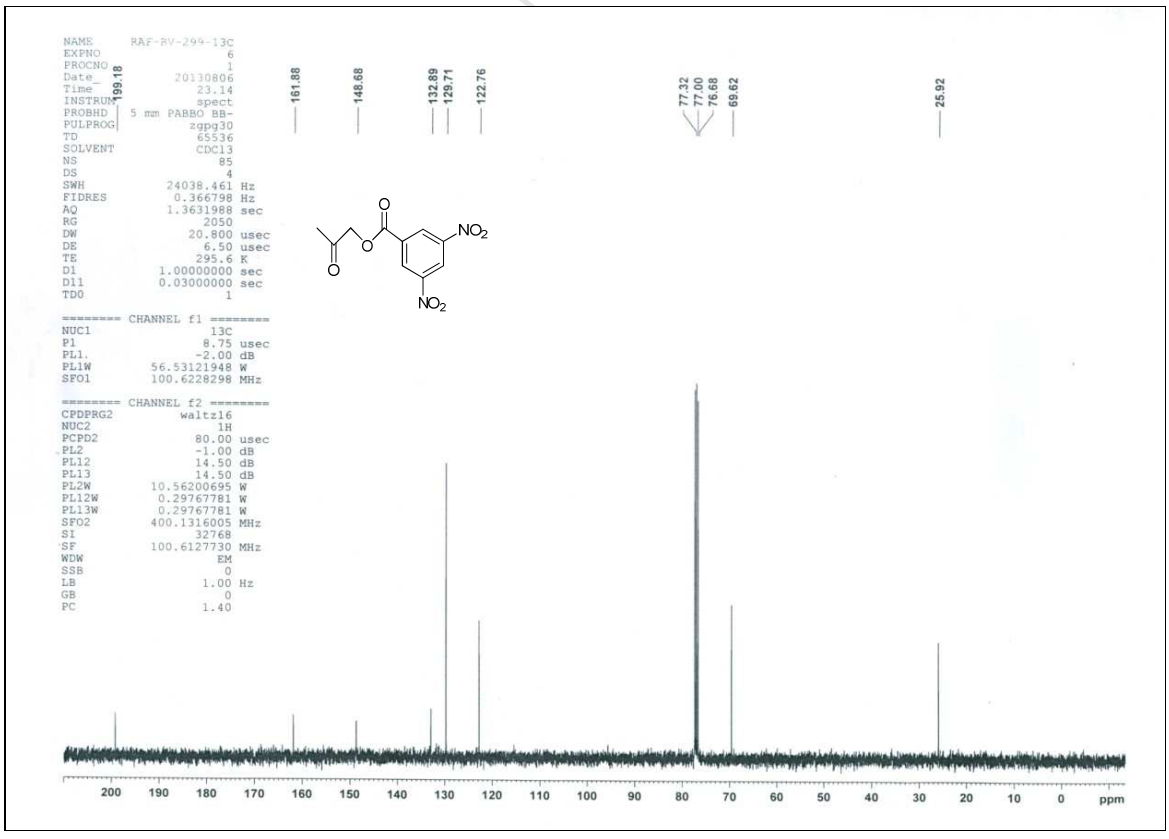

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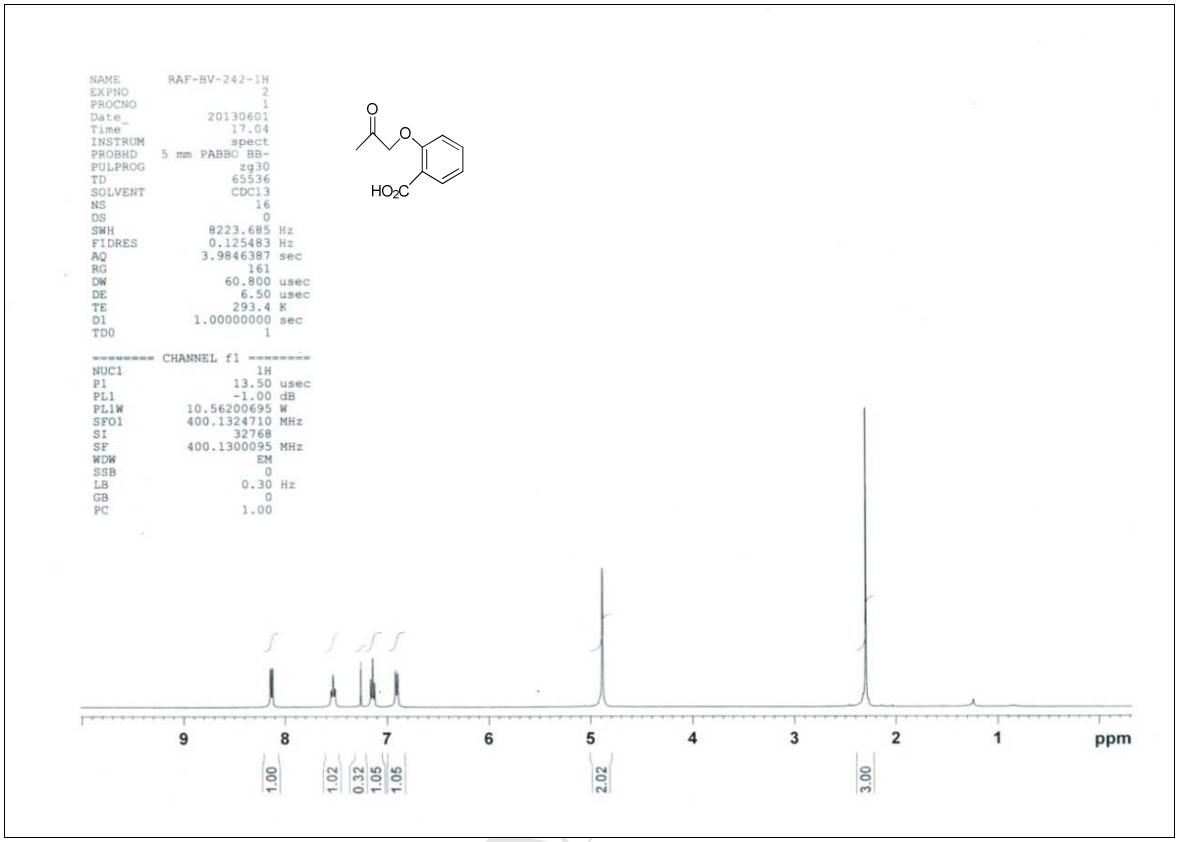

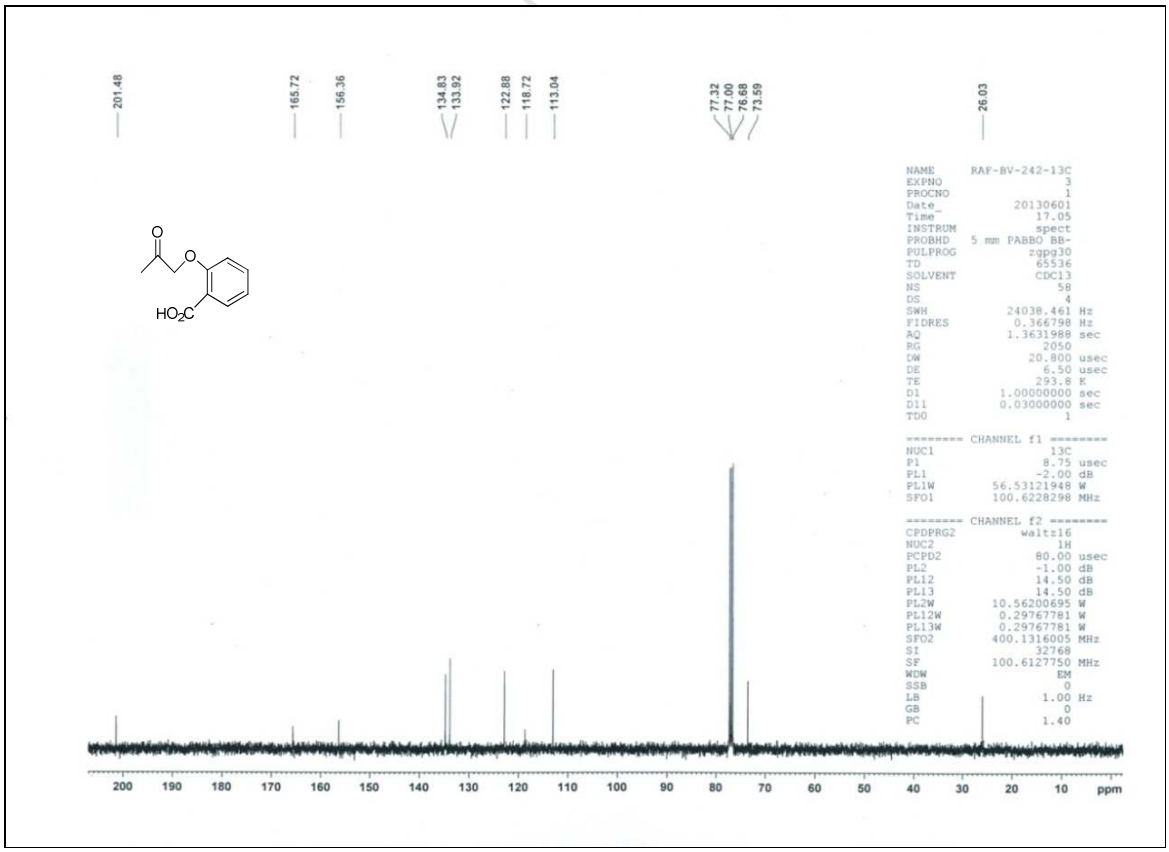

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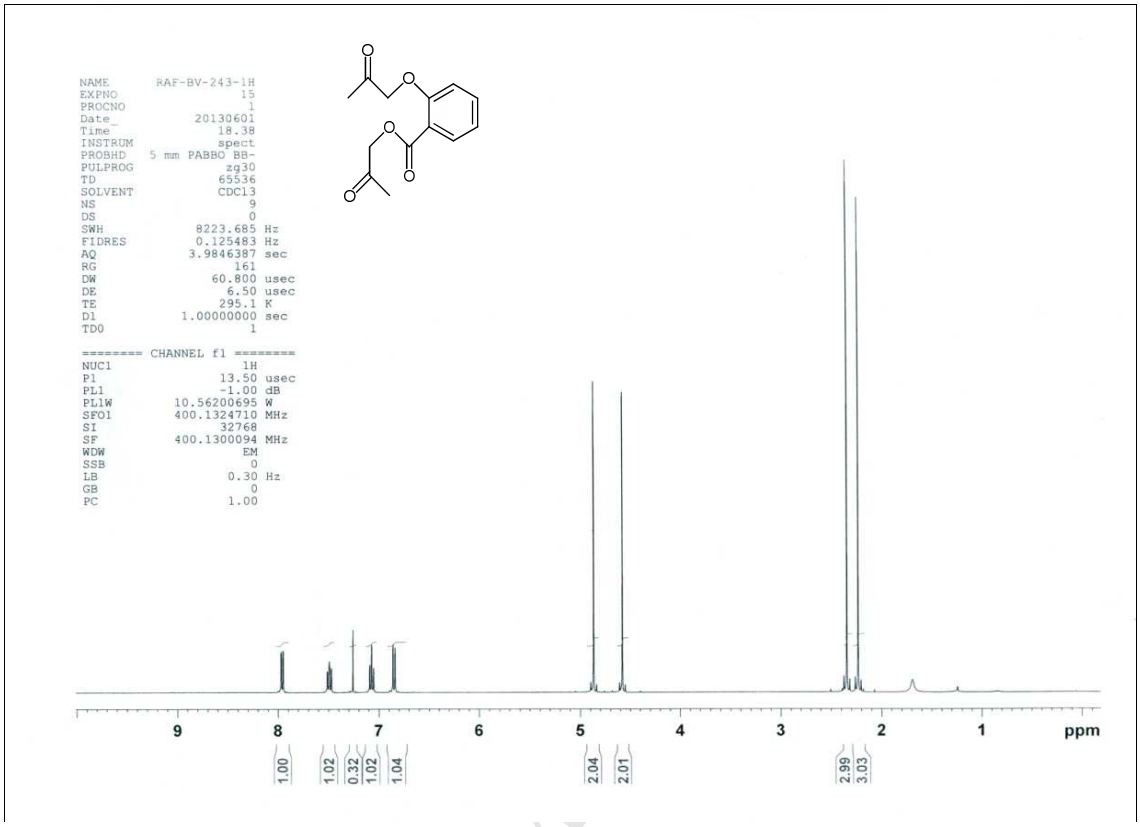
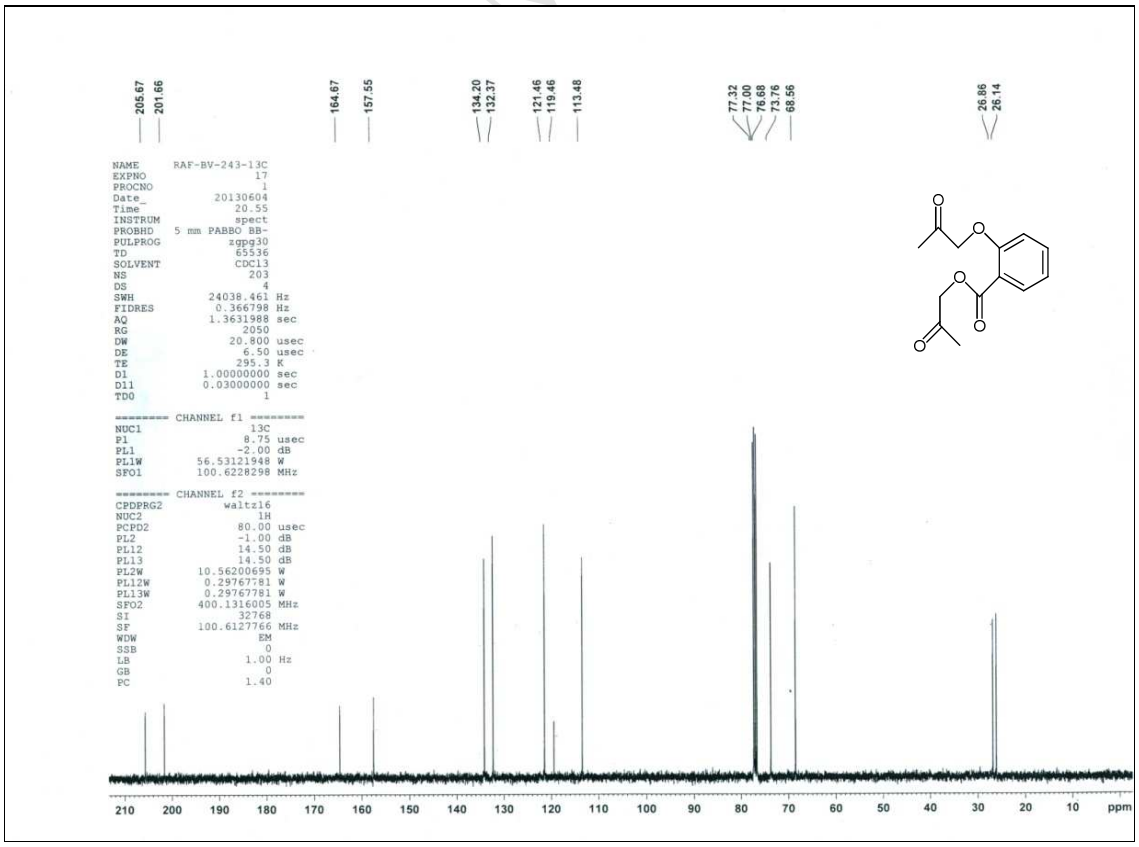
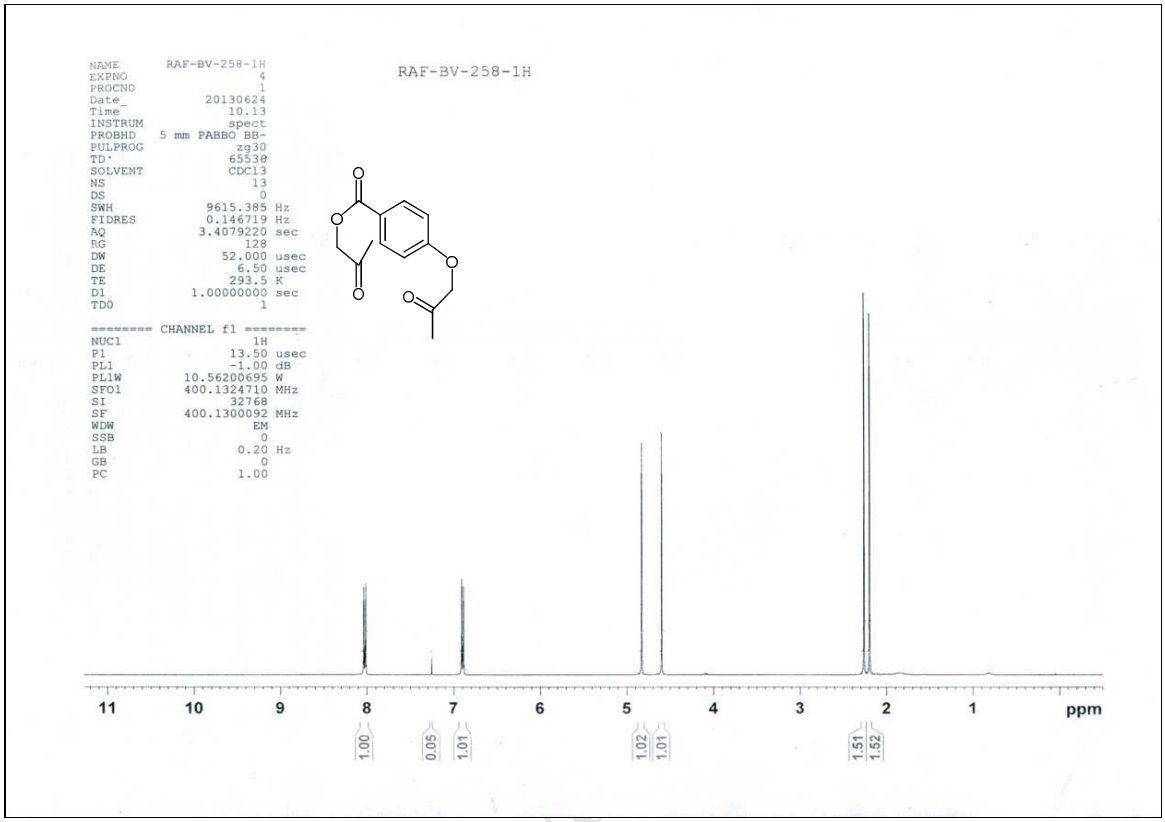
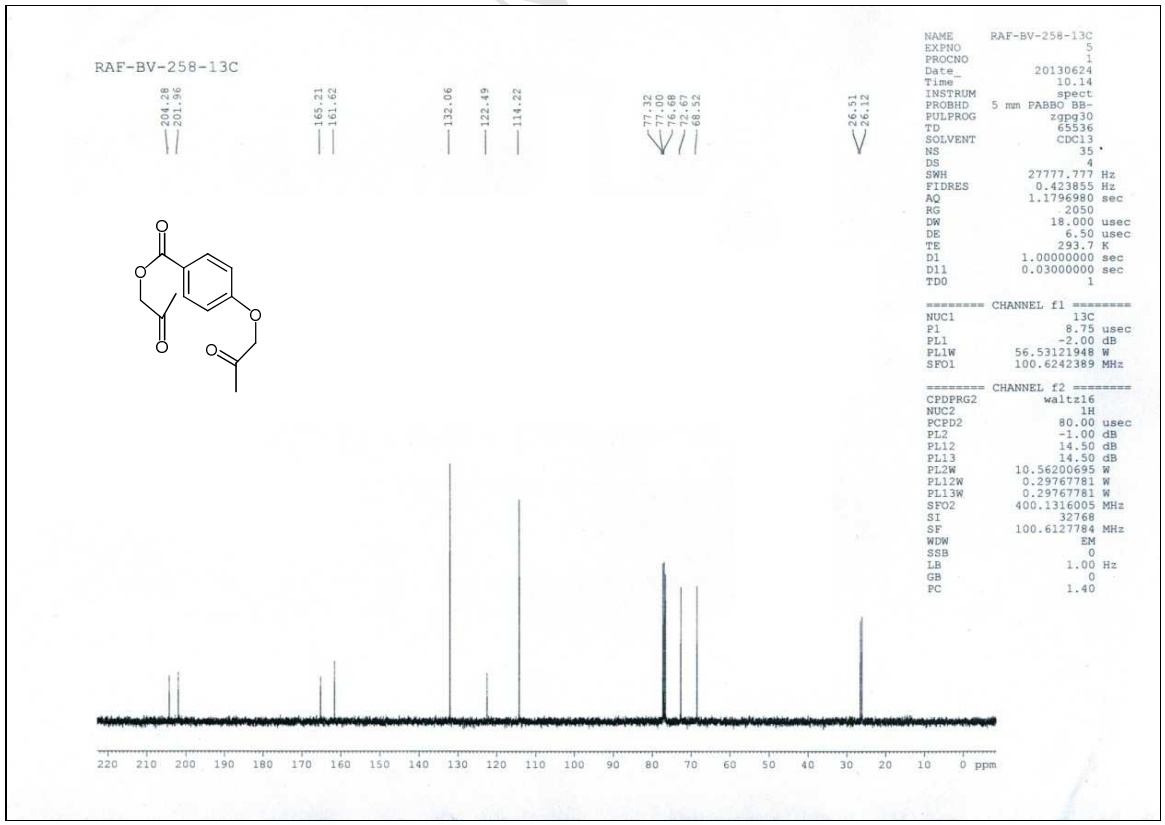


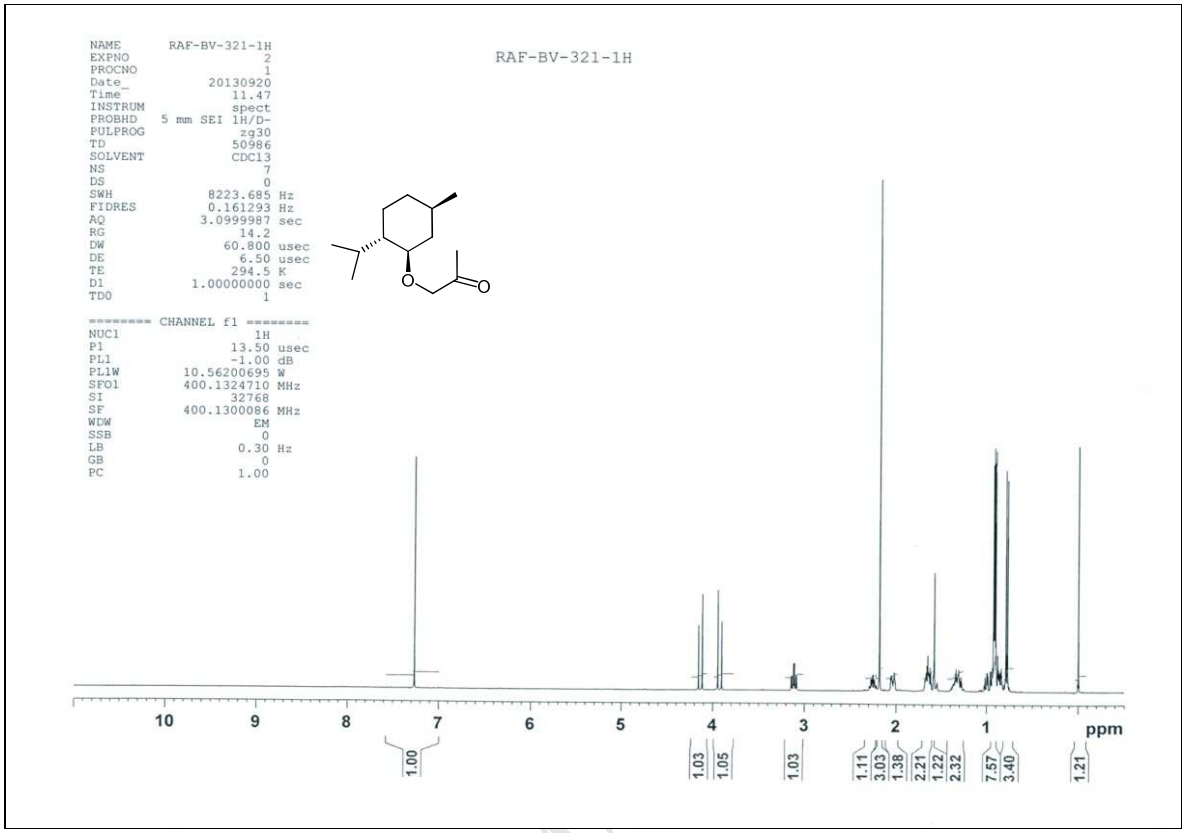


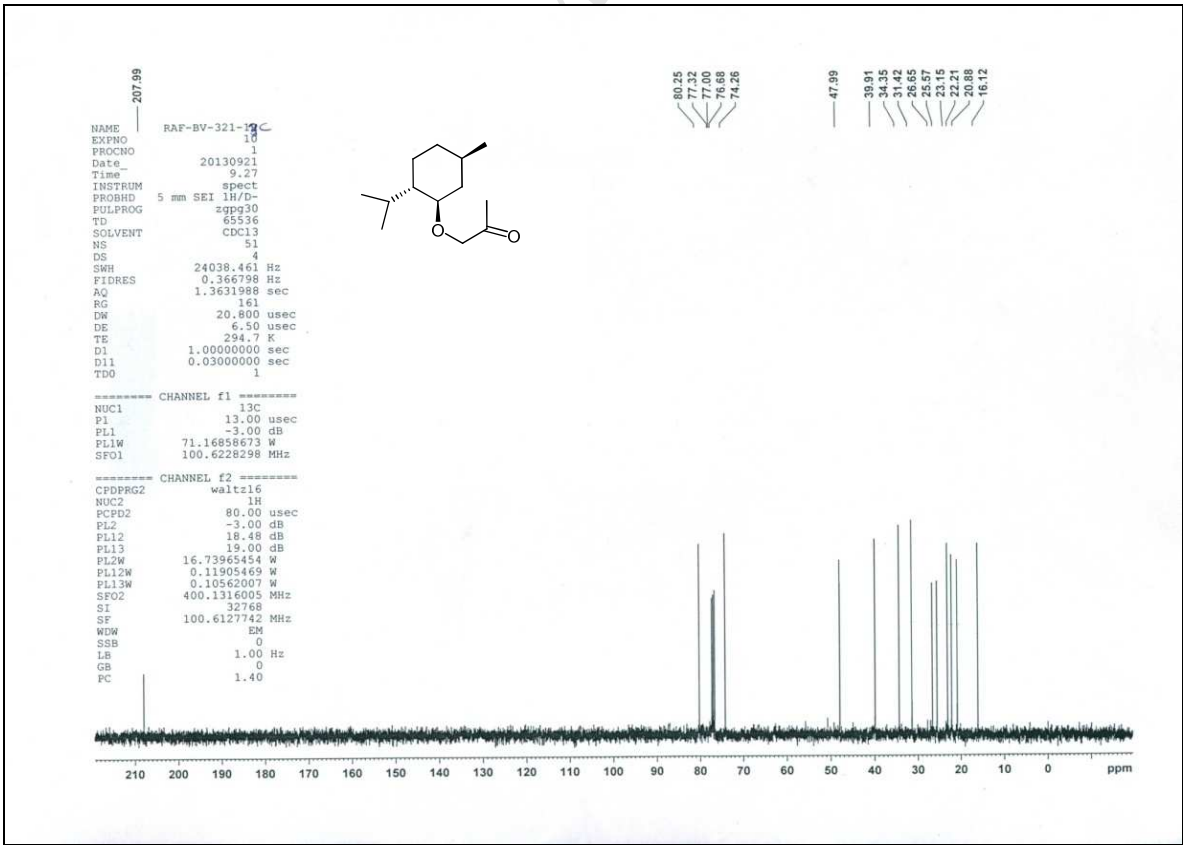
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2w



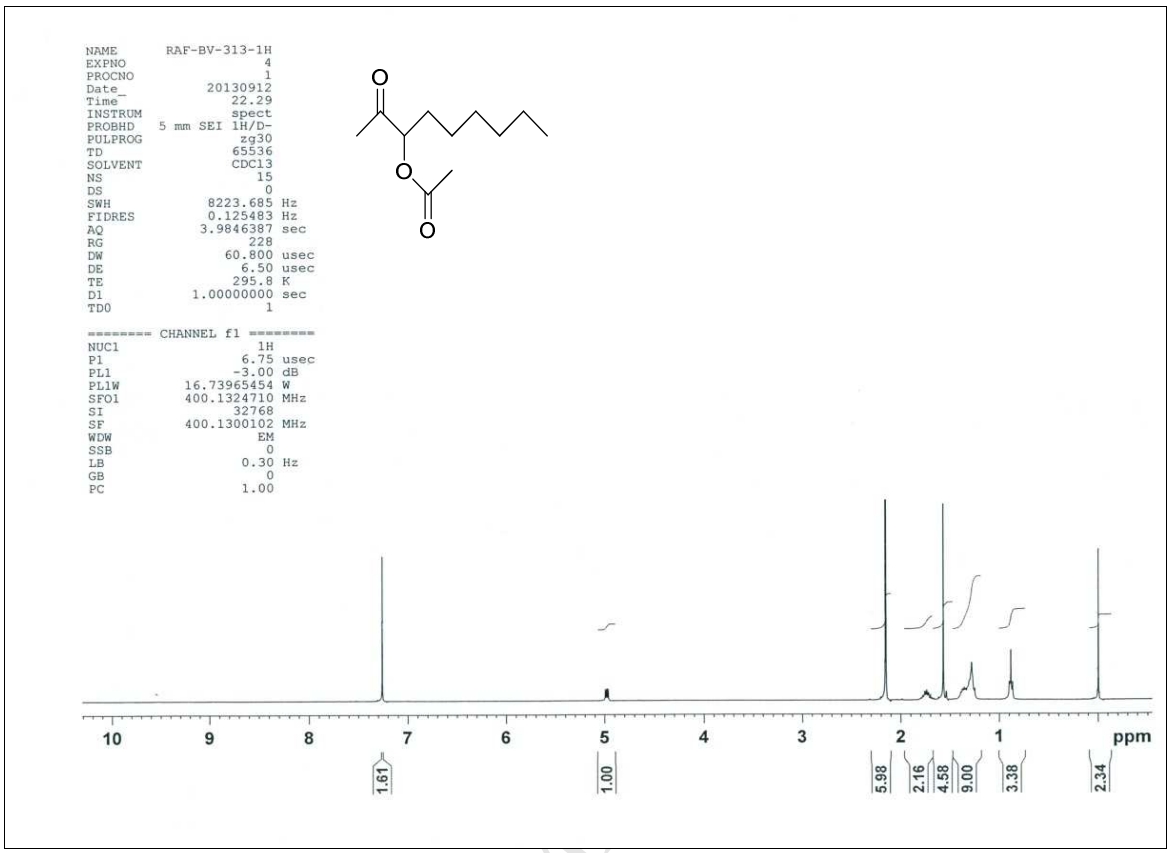


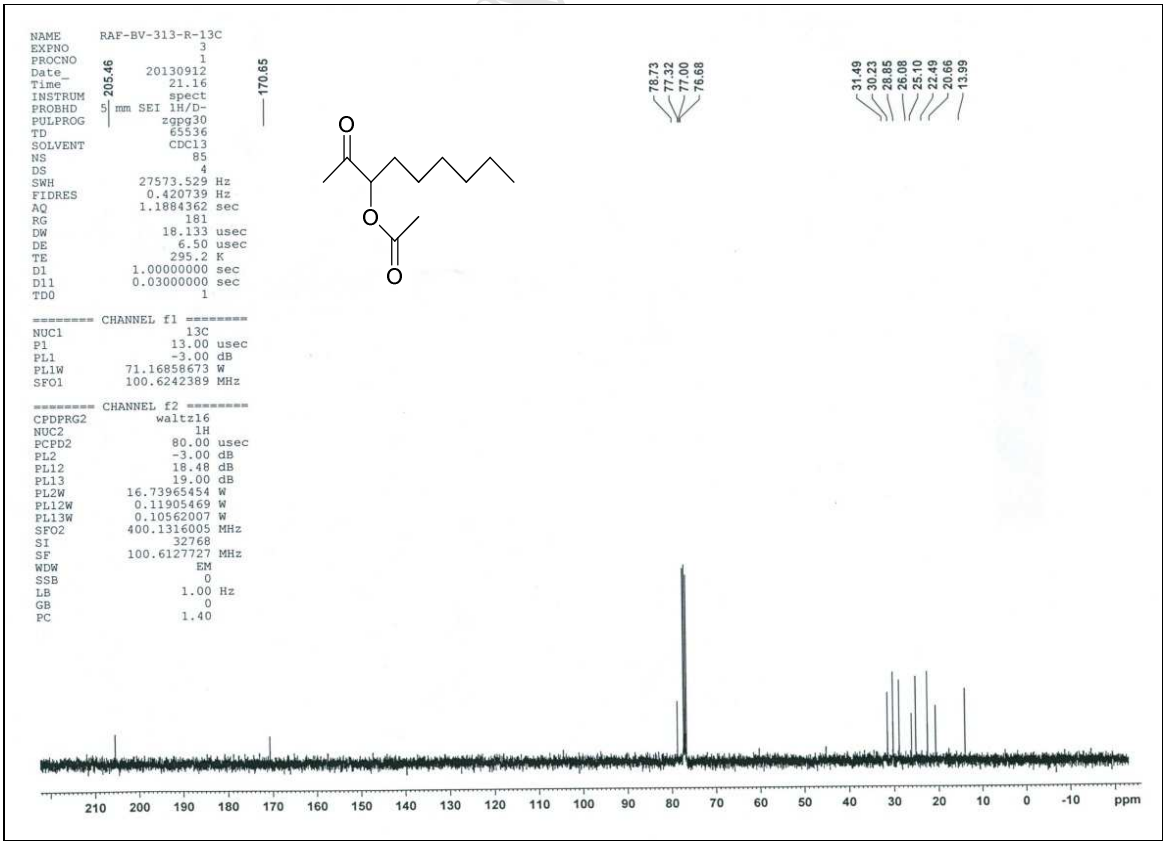
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 2x



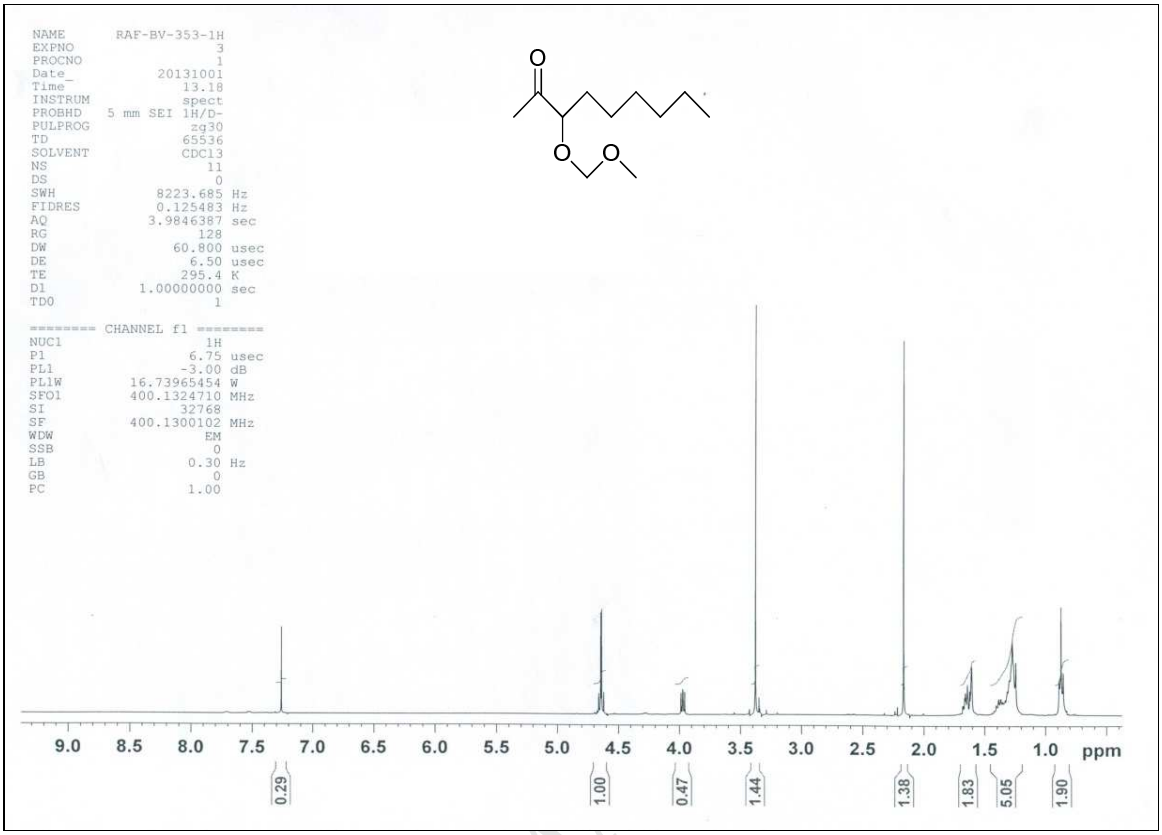


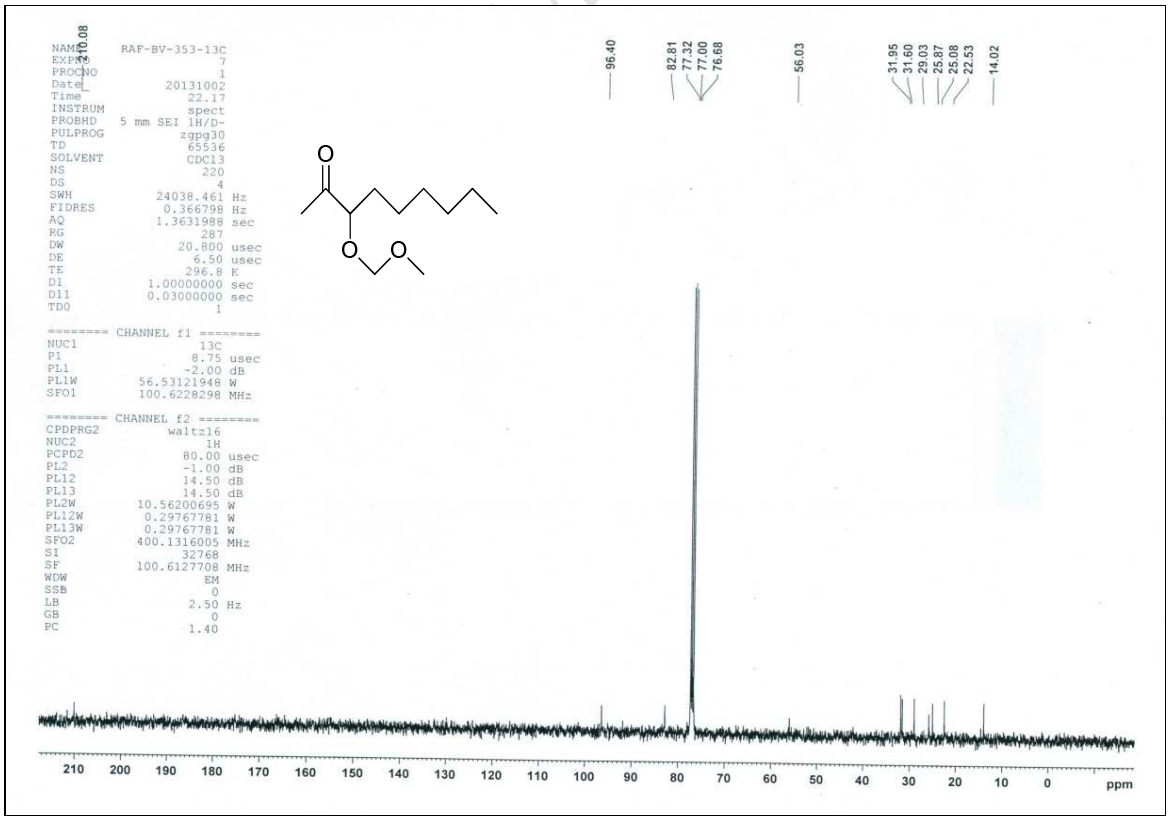
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 4a



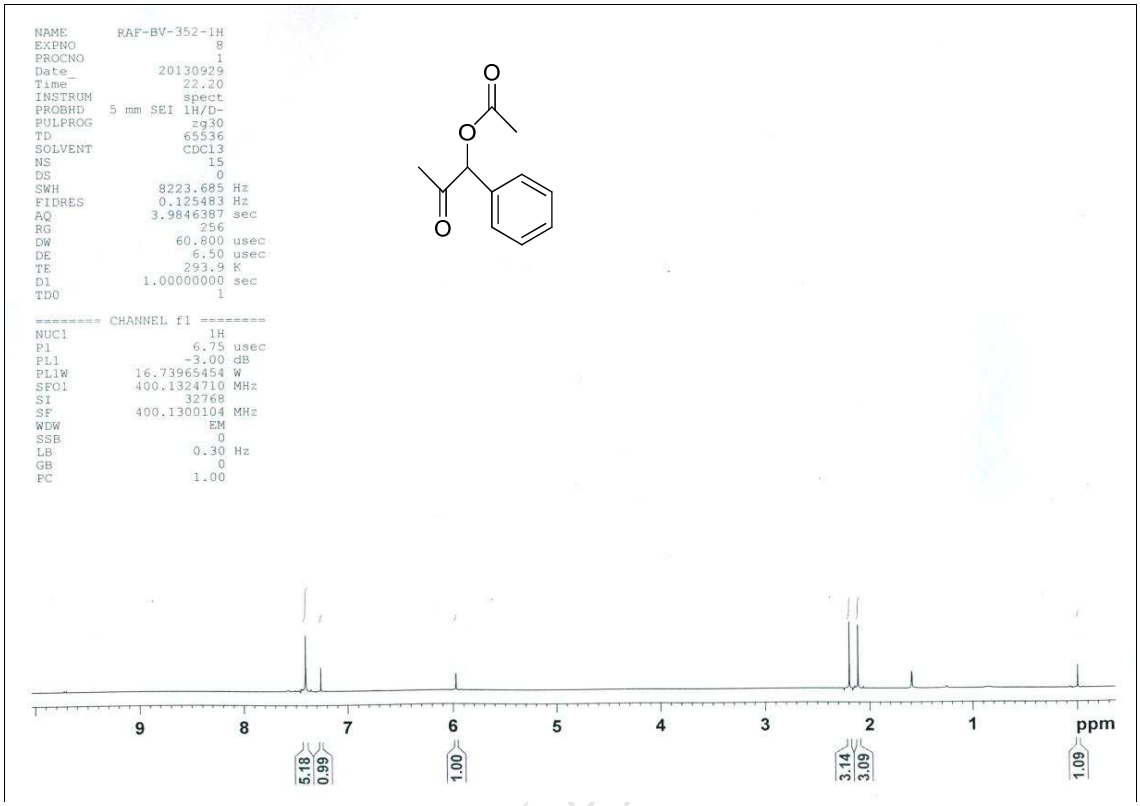


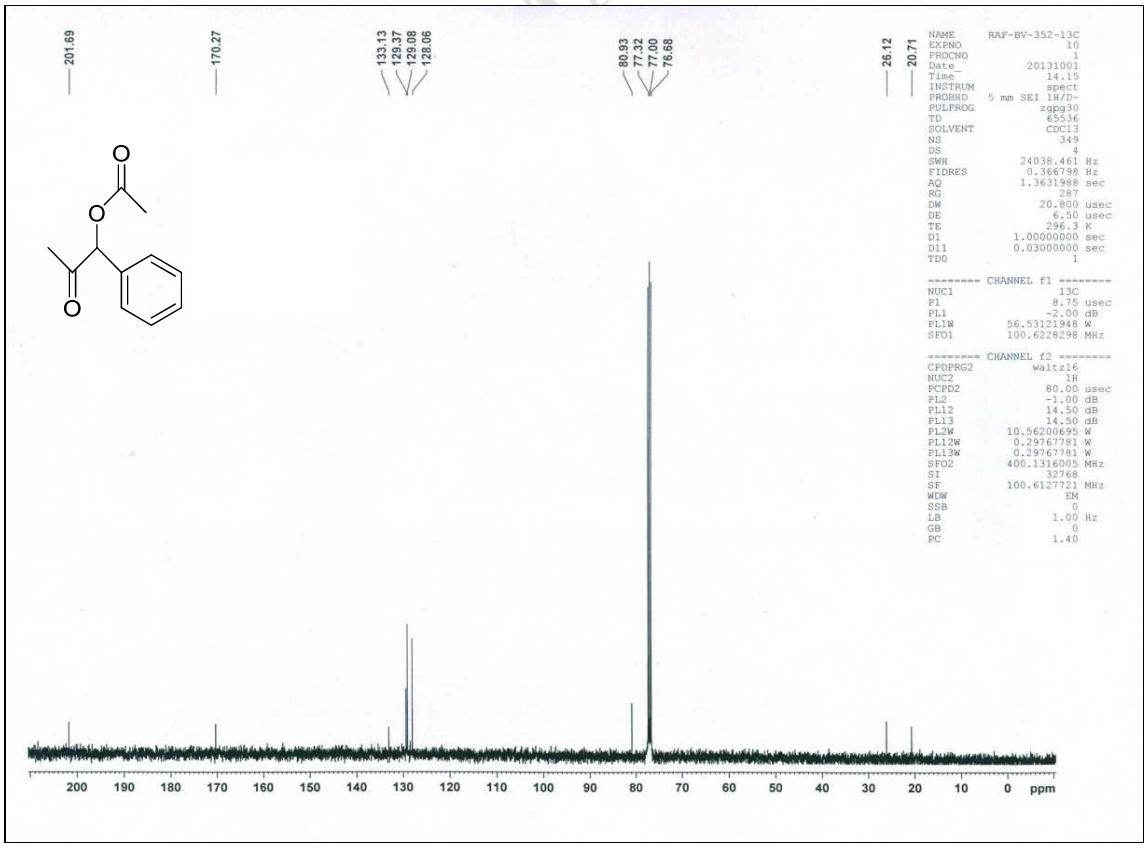
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 4b



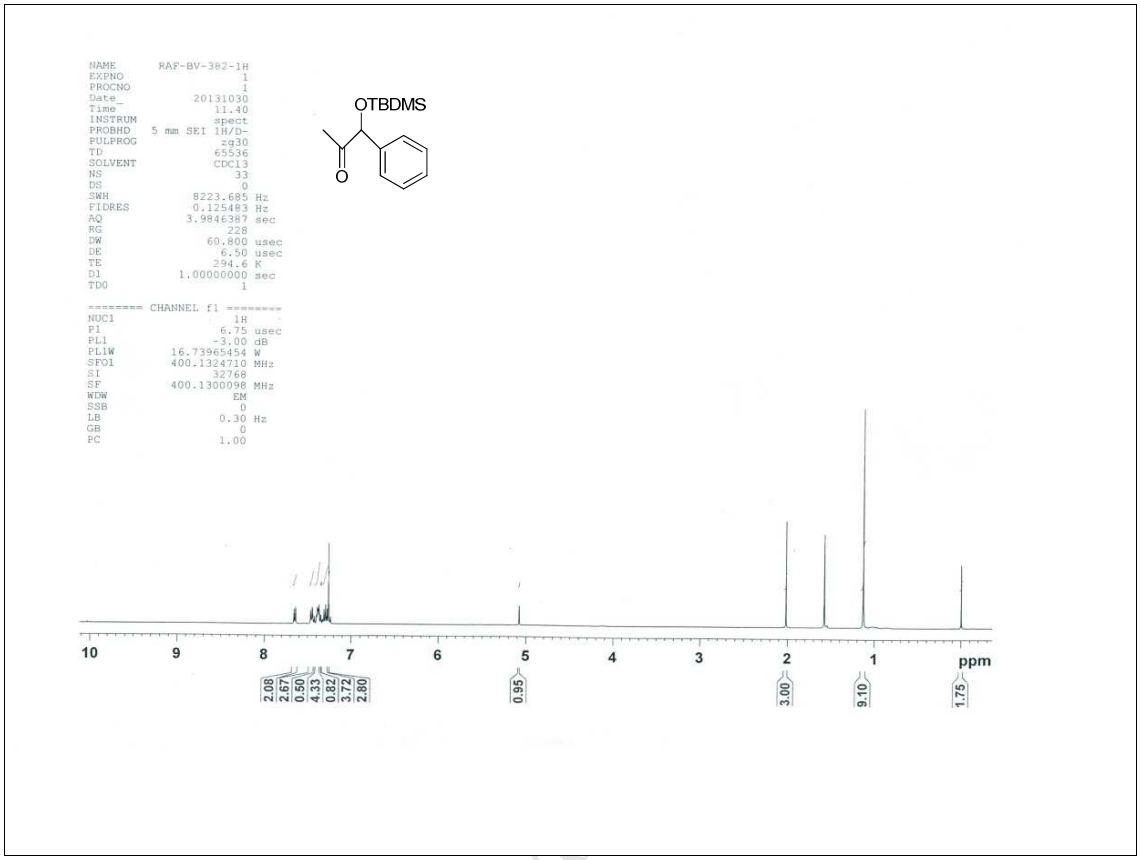


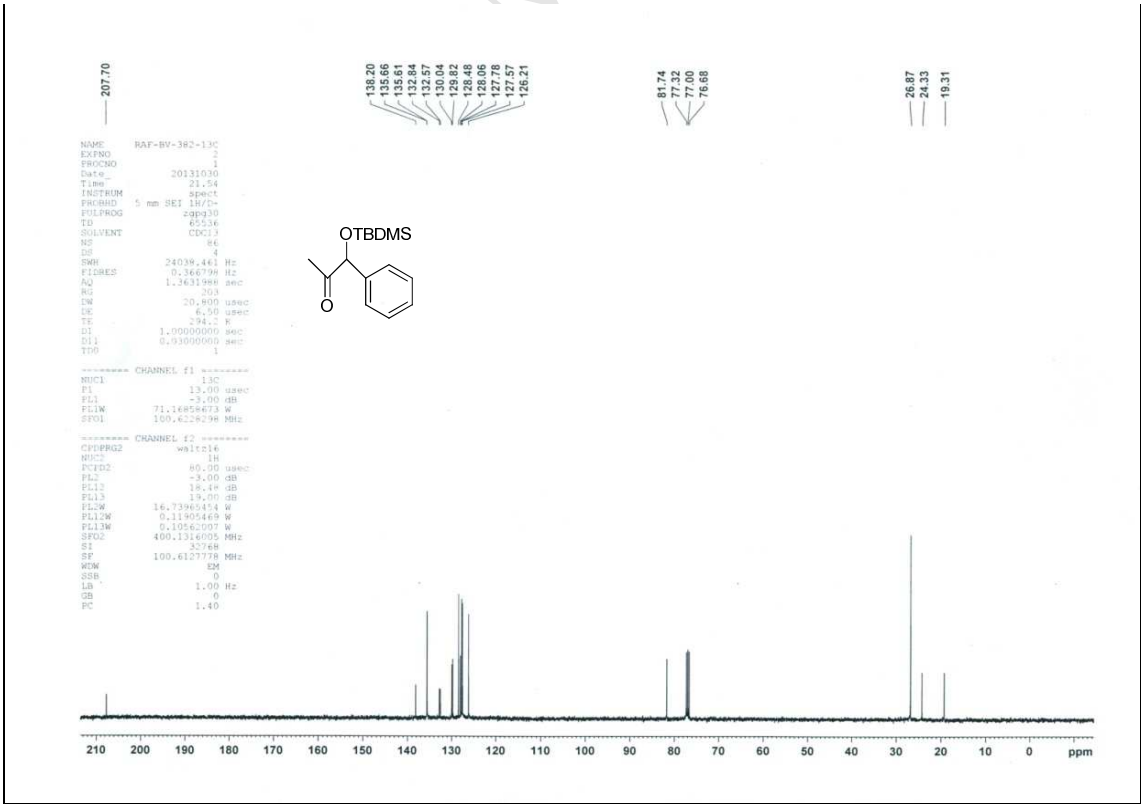
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 4c



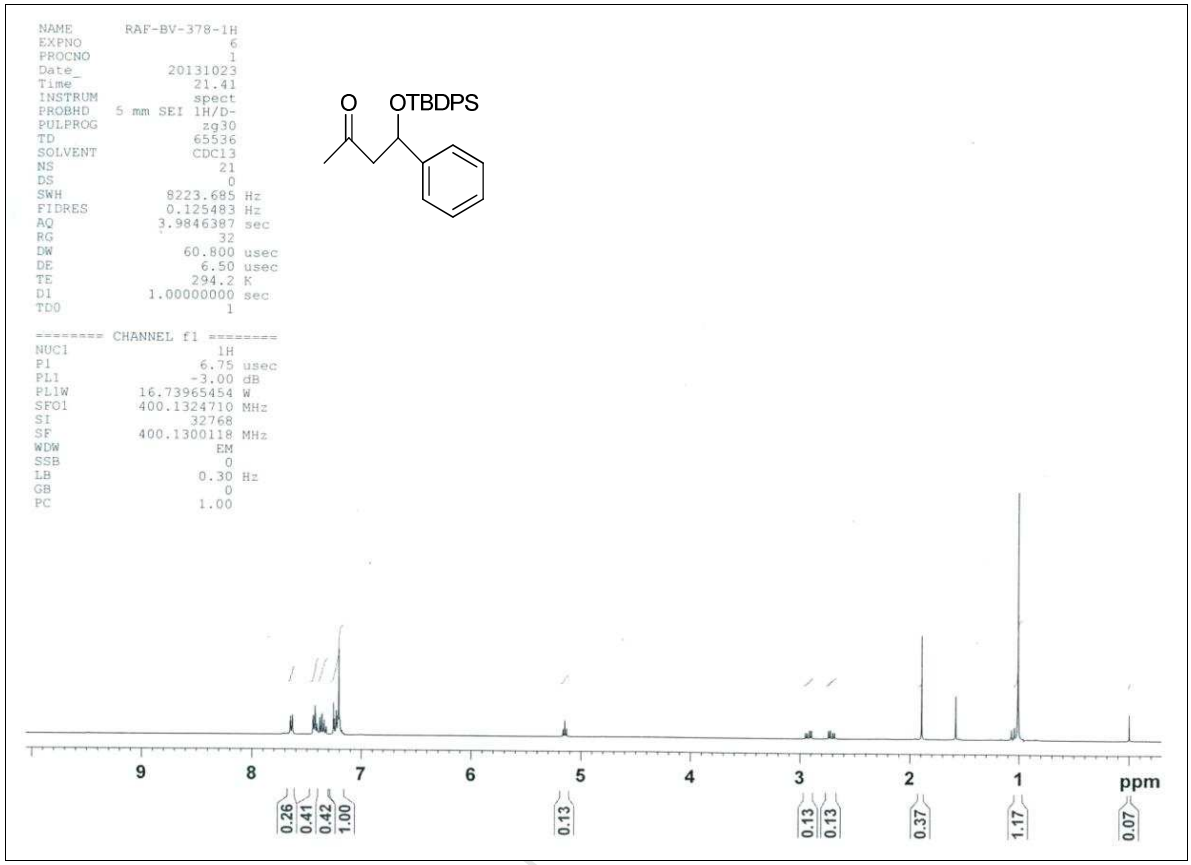


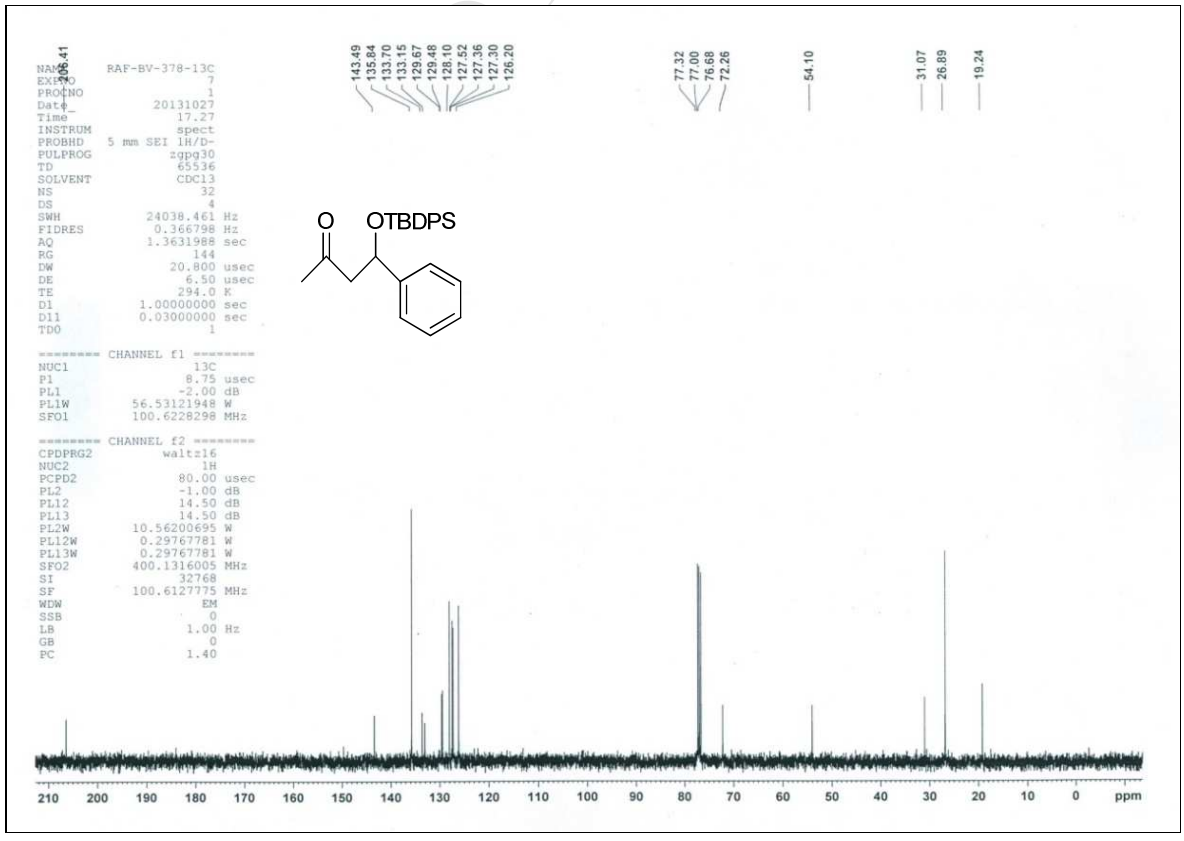
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 4d



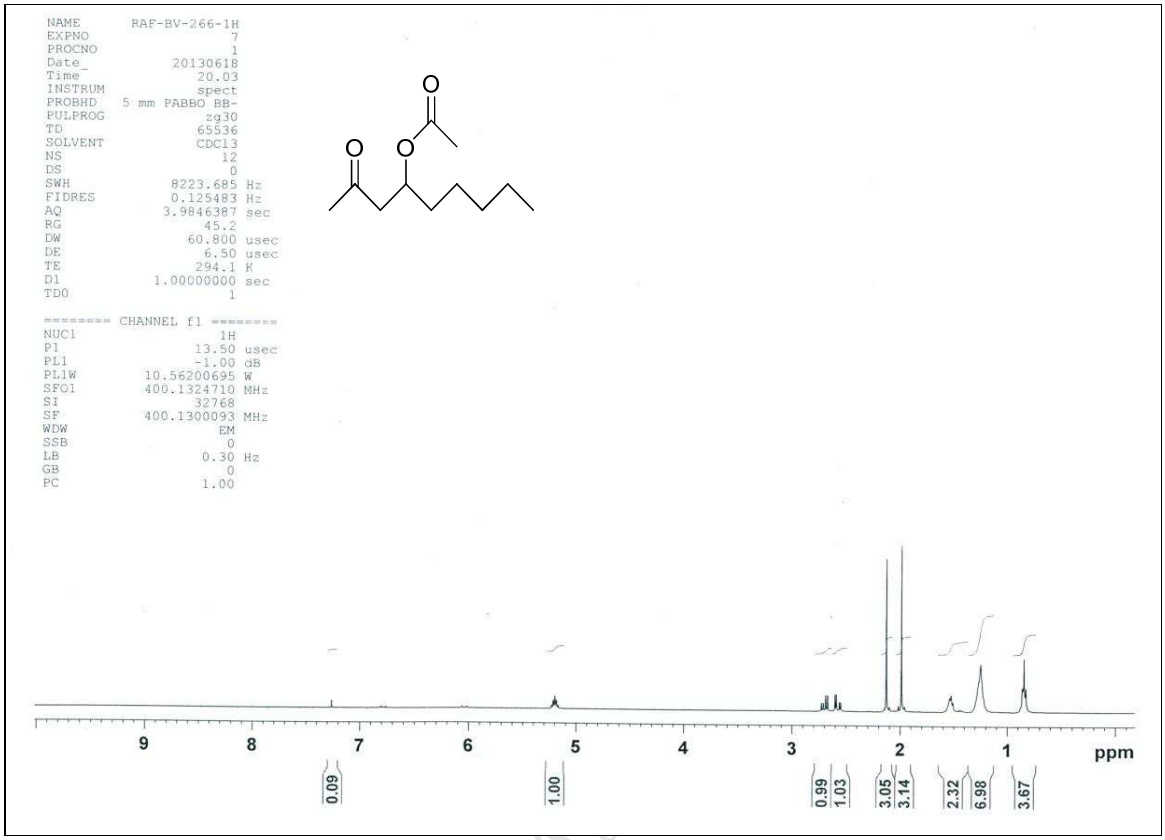


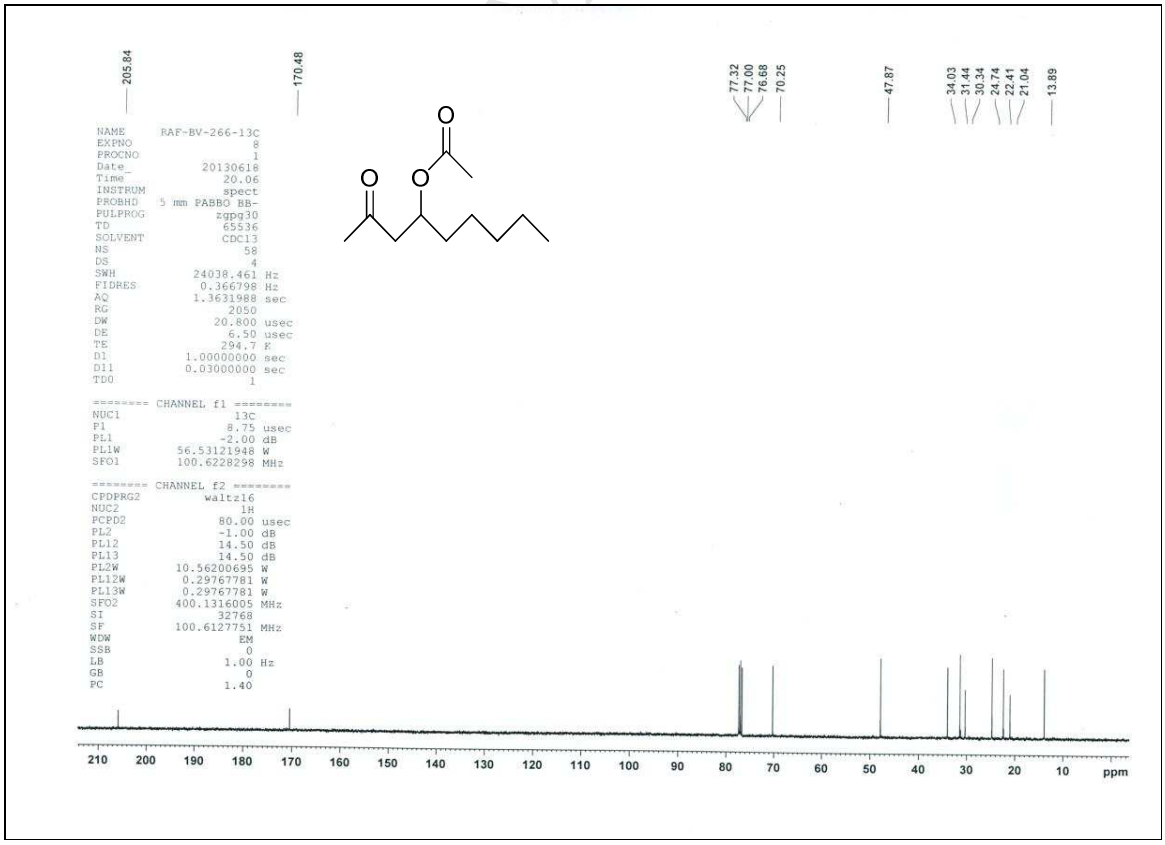
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 4e



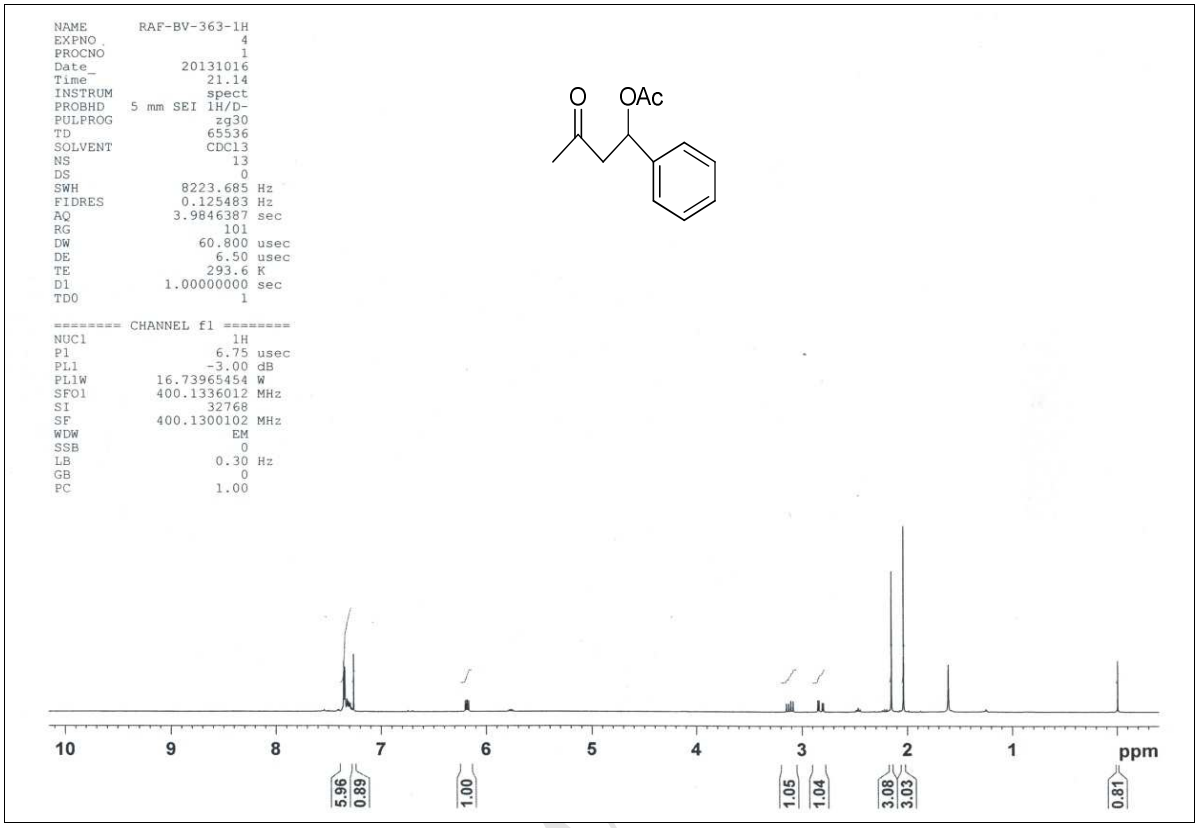


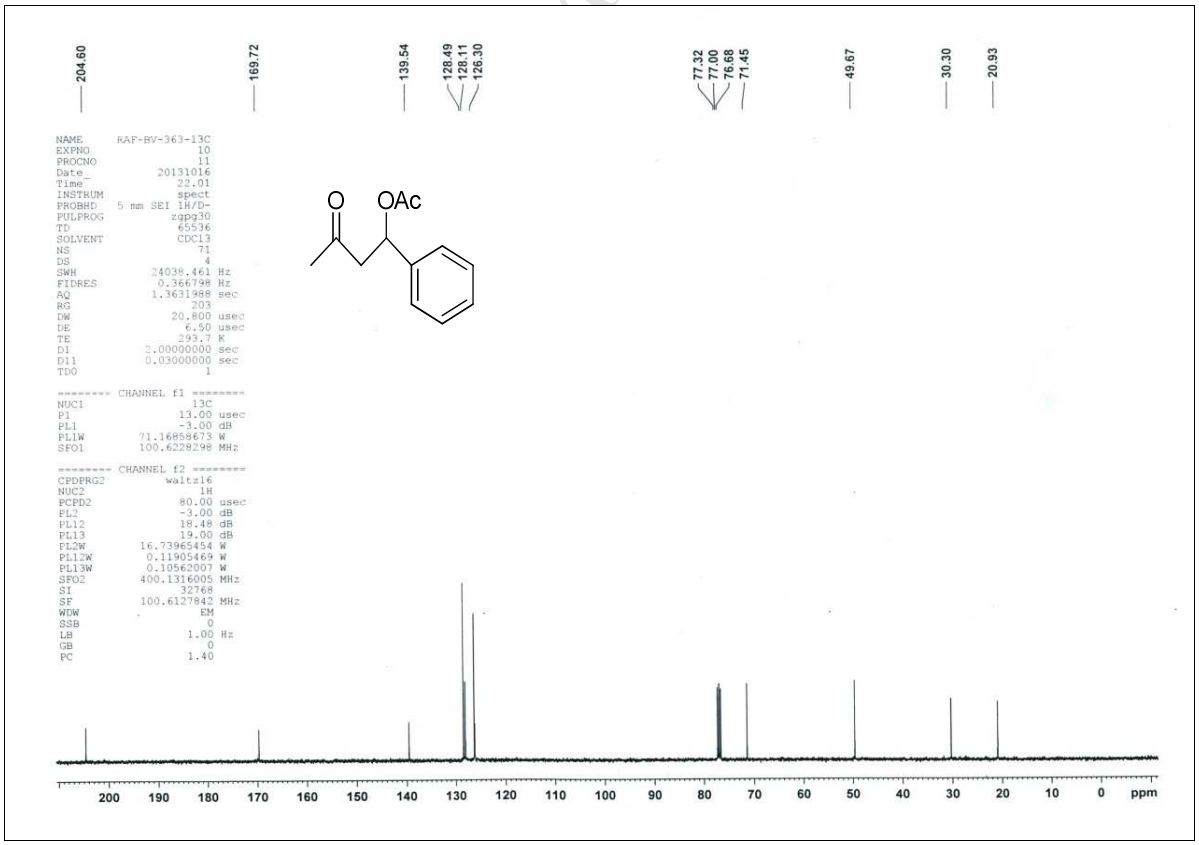
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 4f



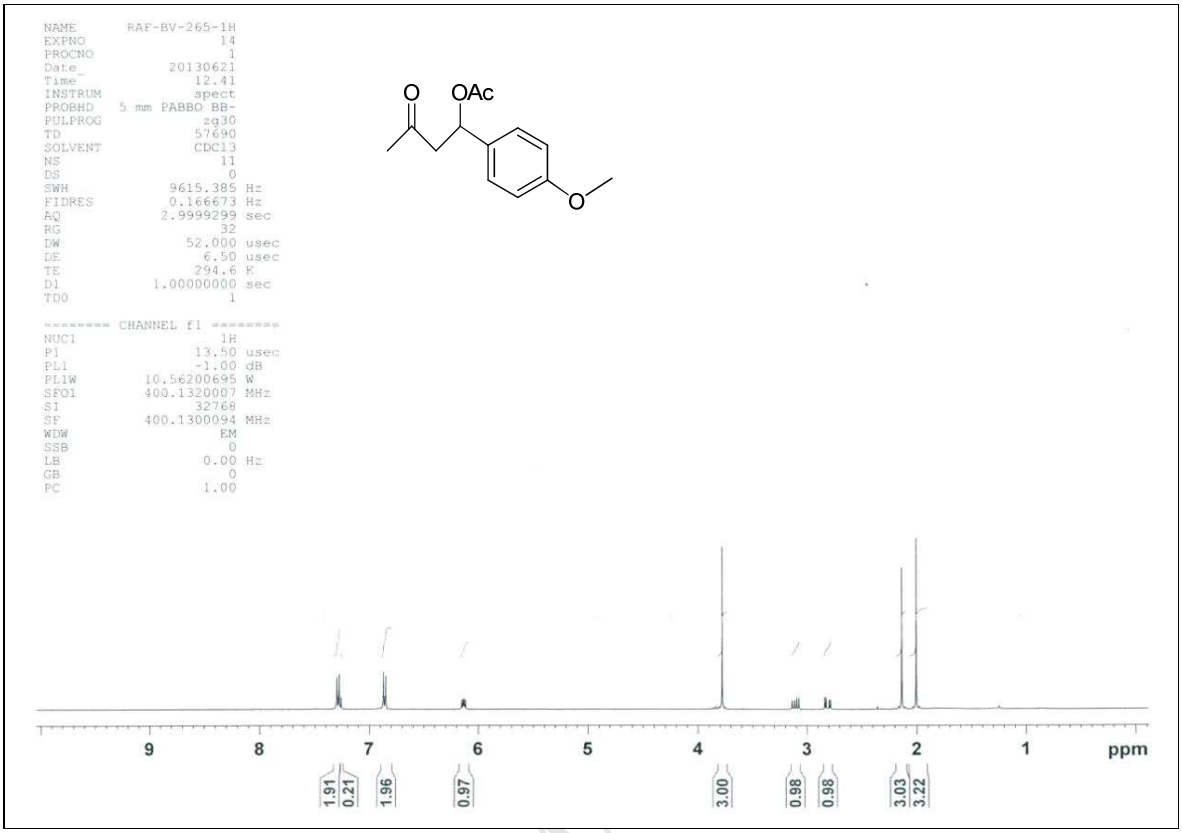


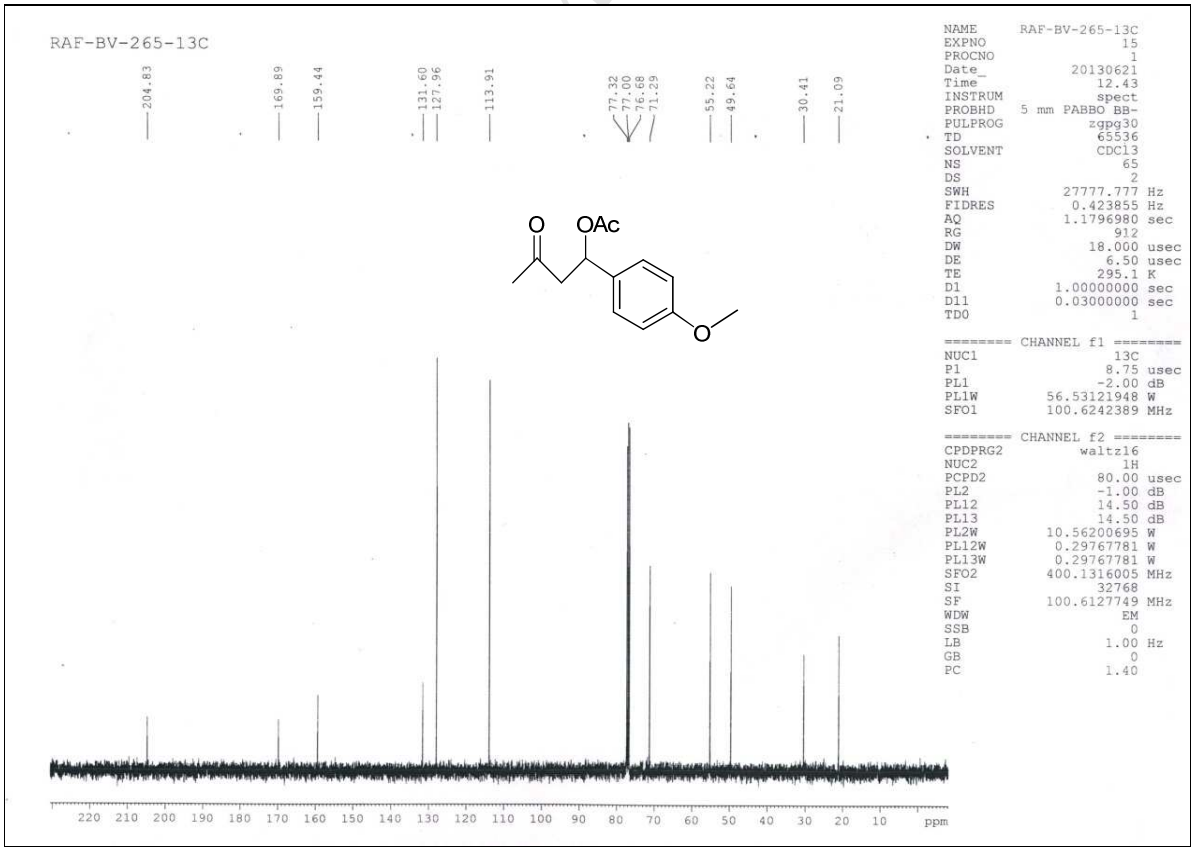
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 4g



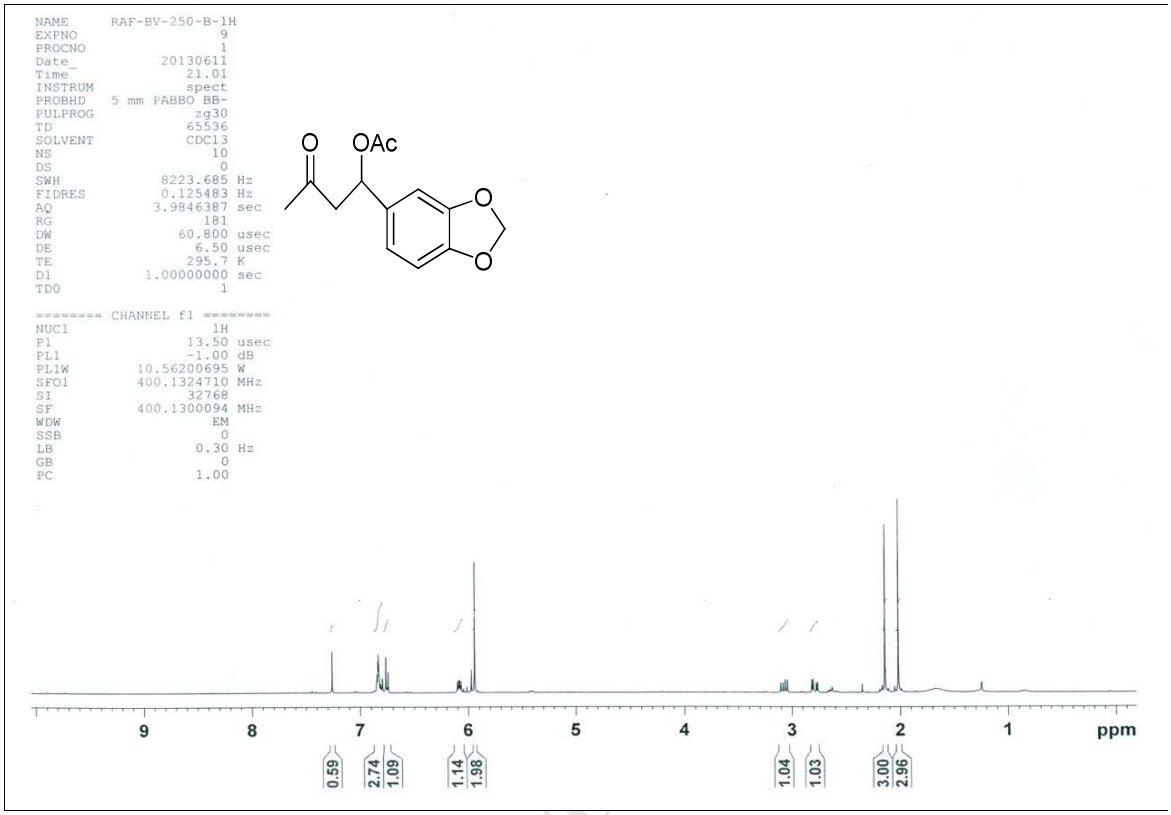


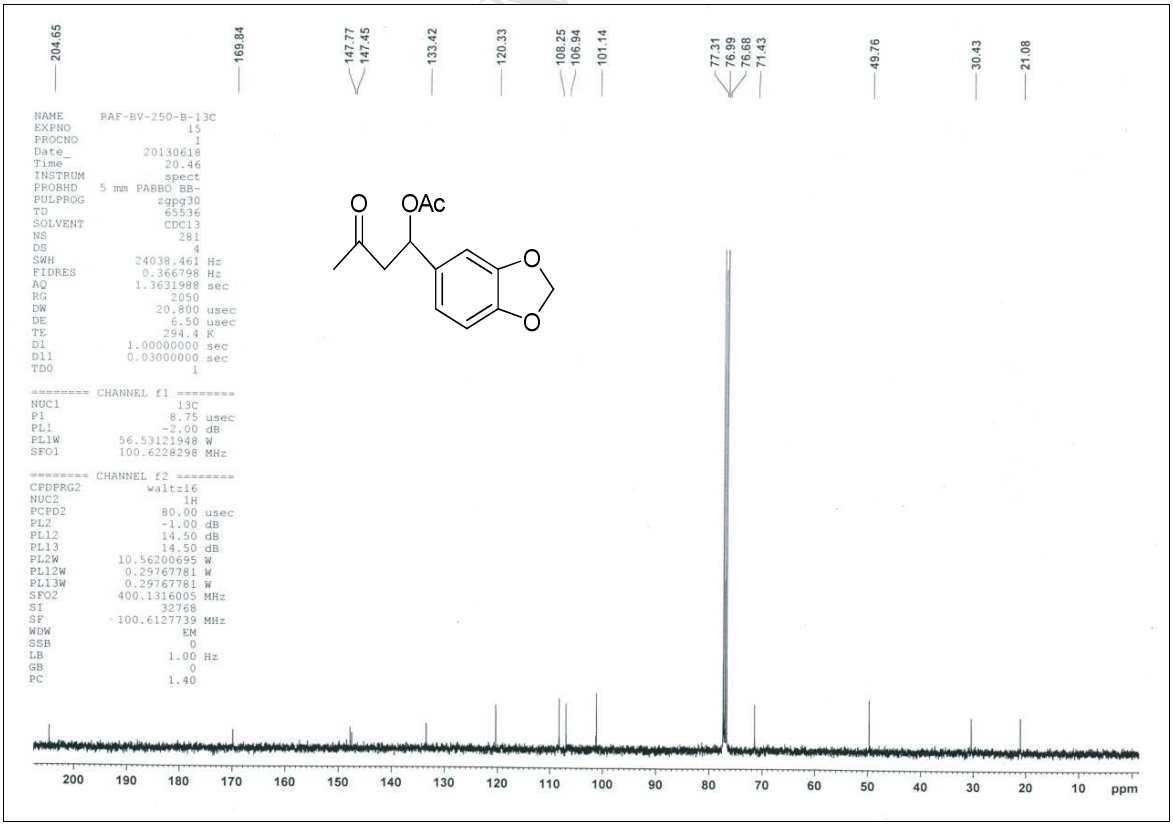
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 4h



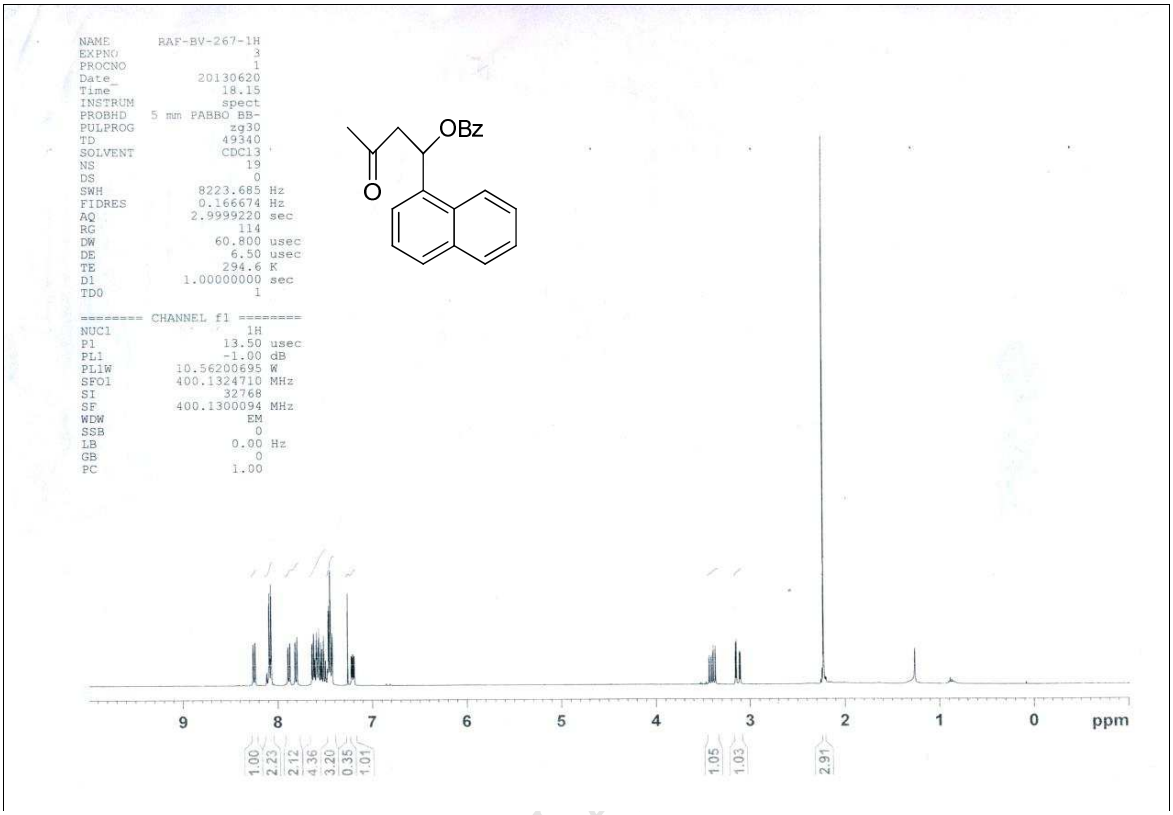


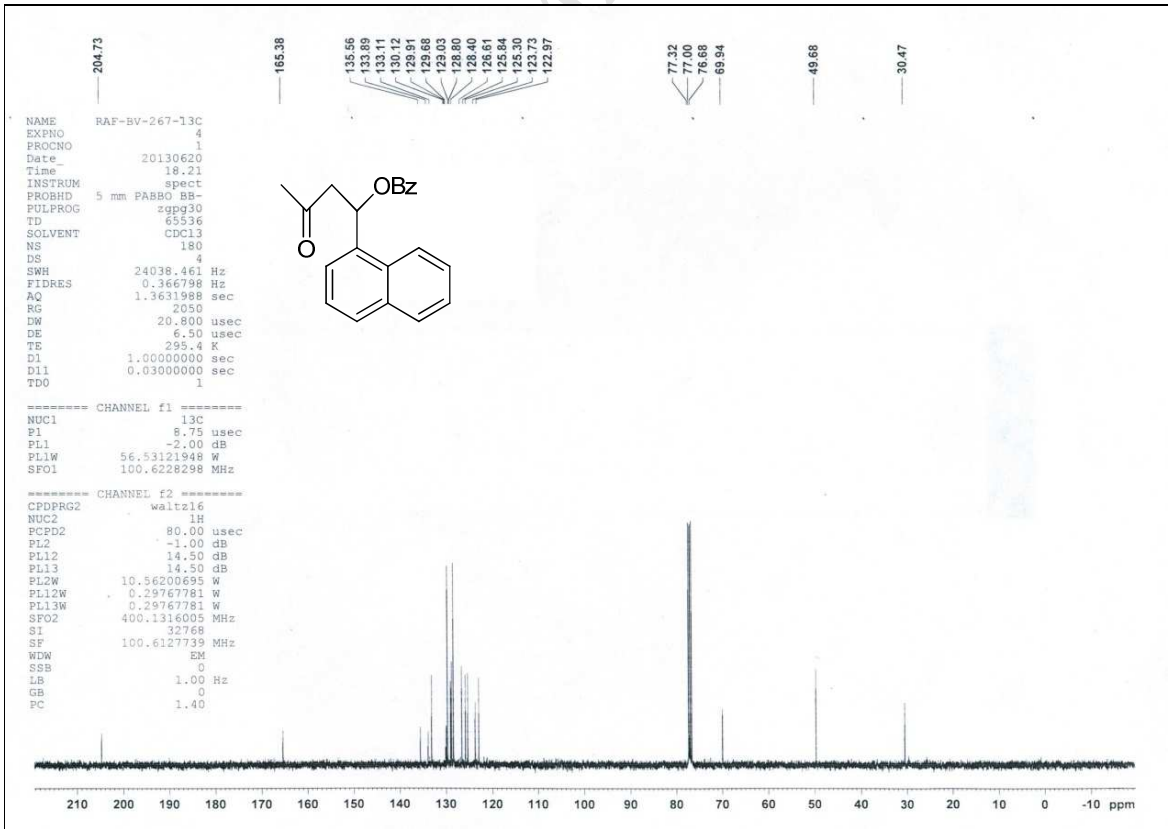
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 4i



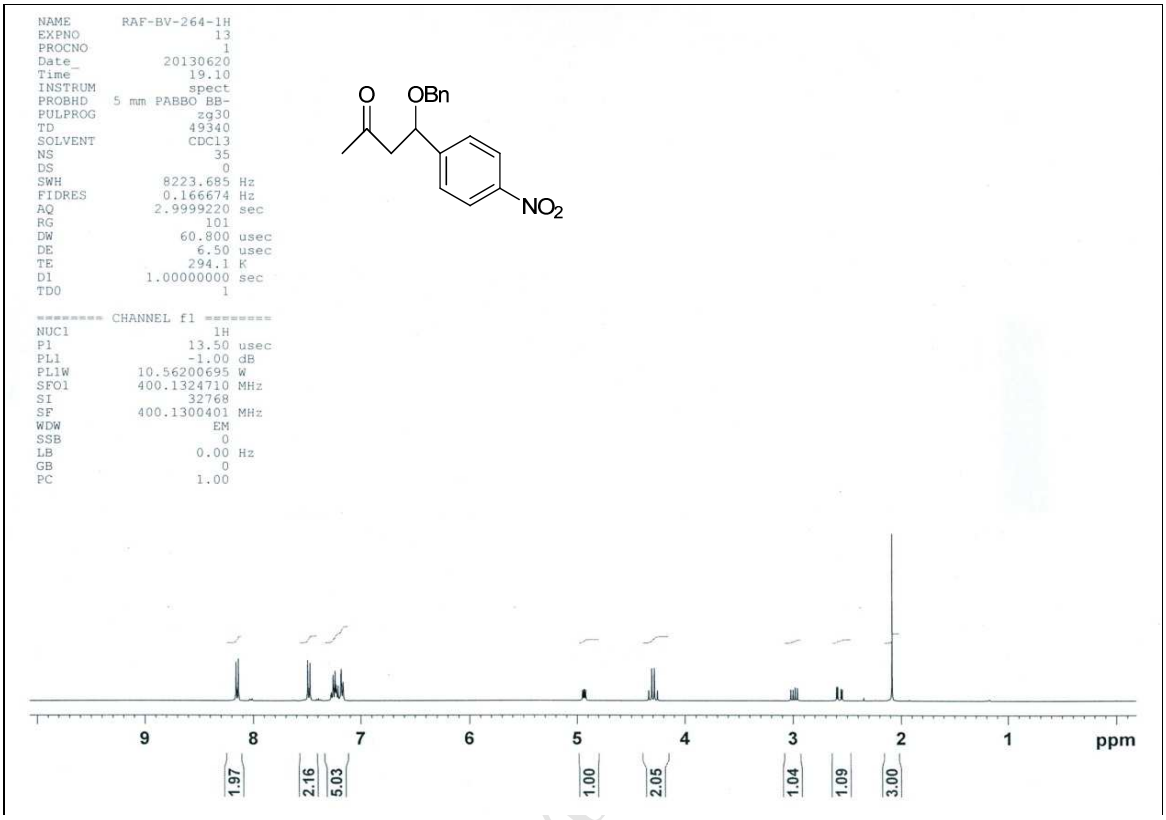


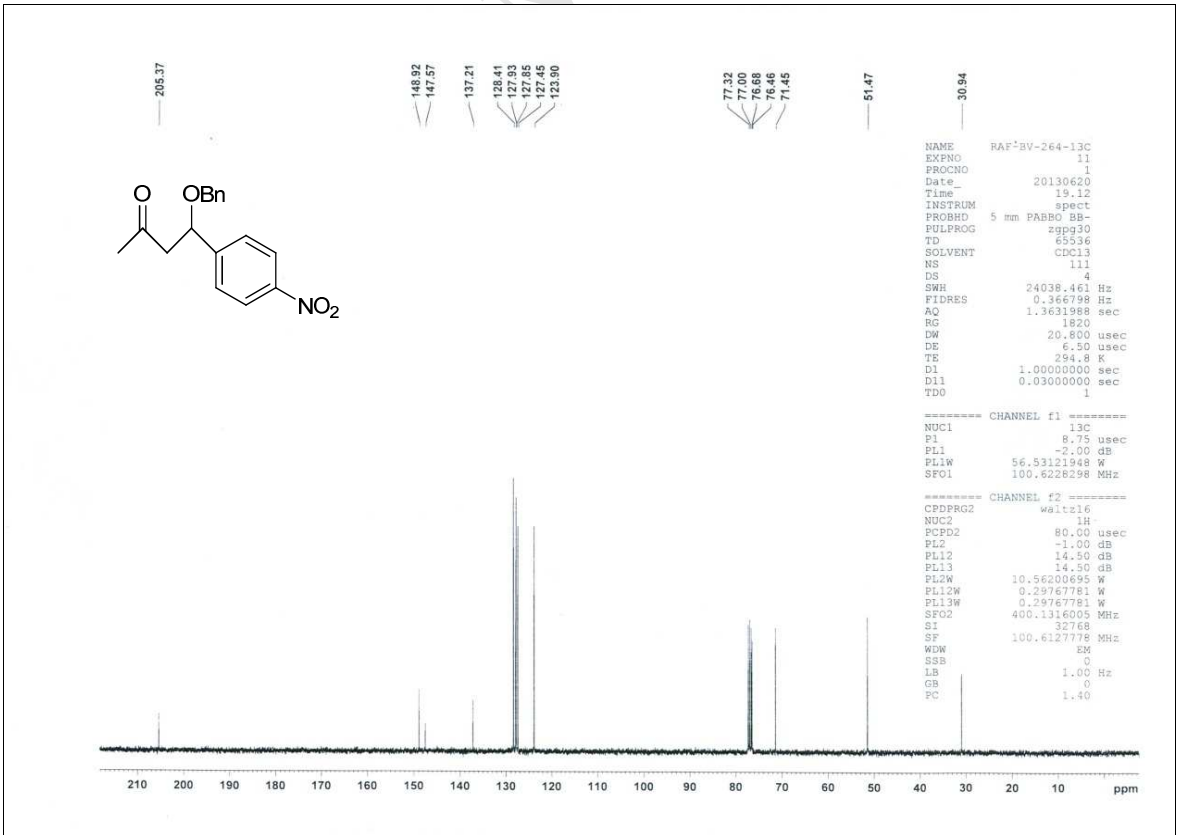
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 4j



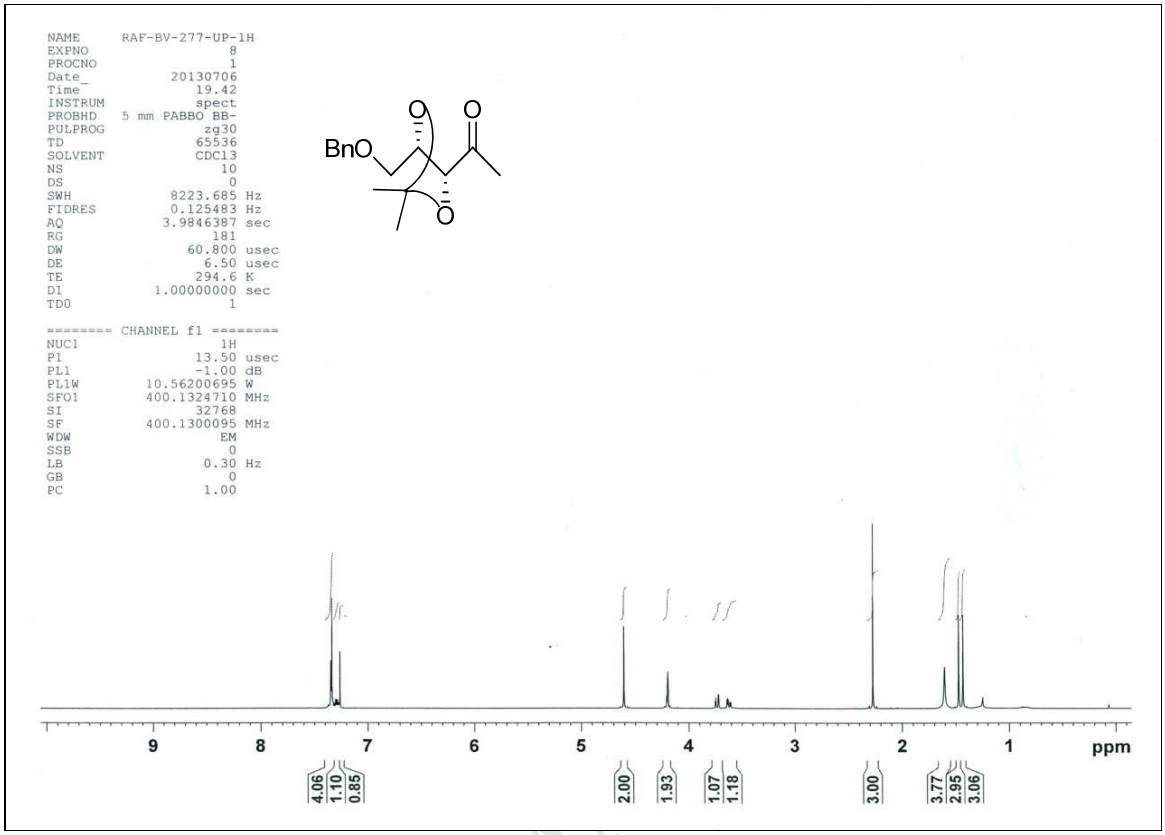


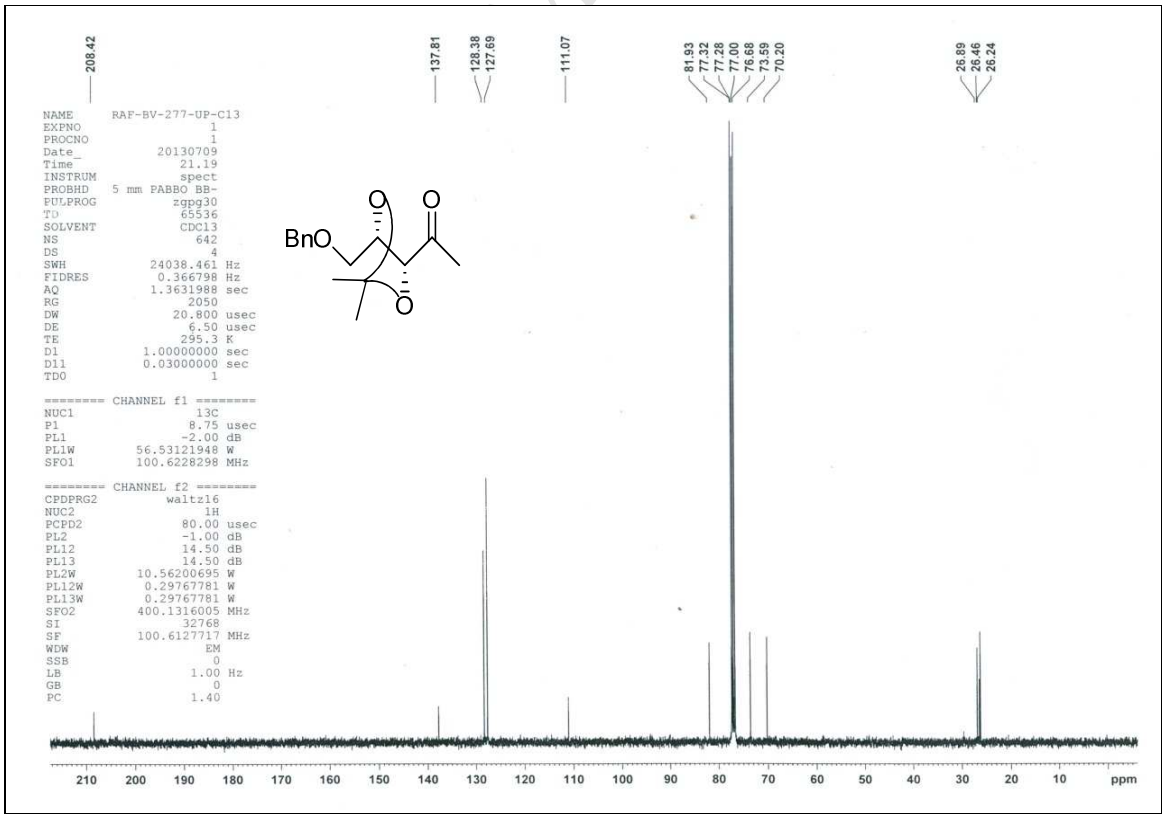
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 4k



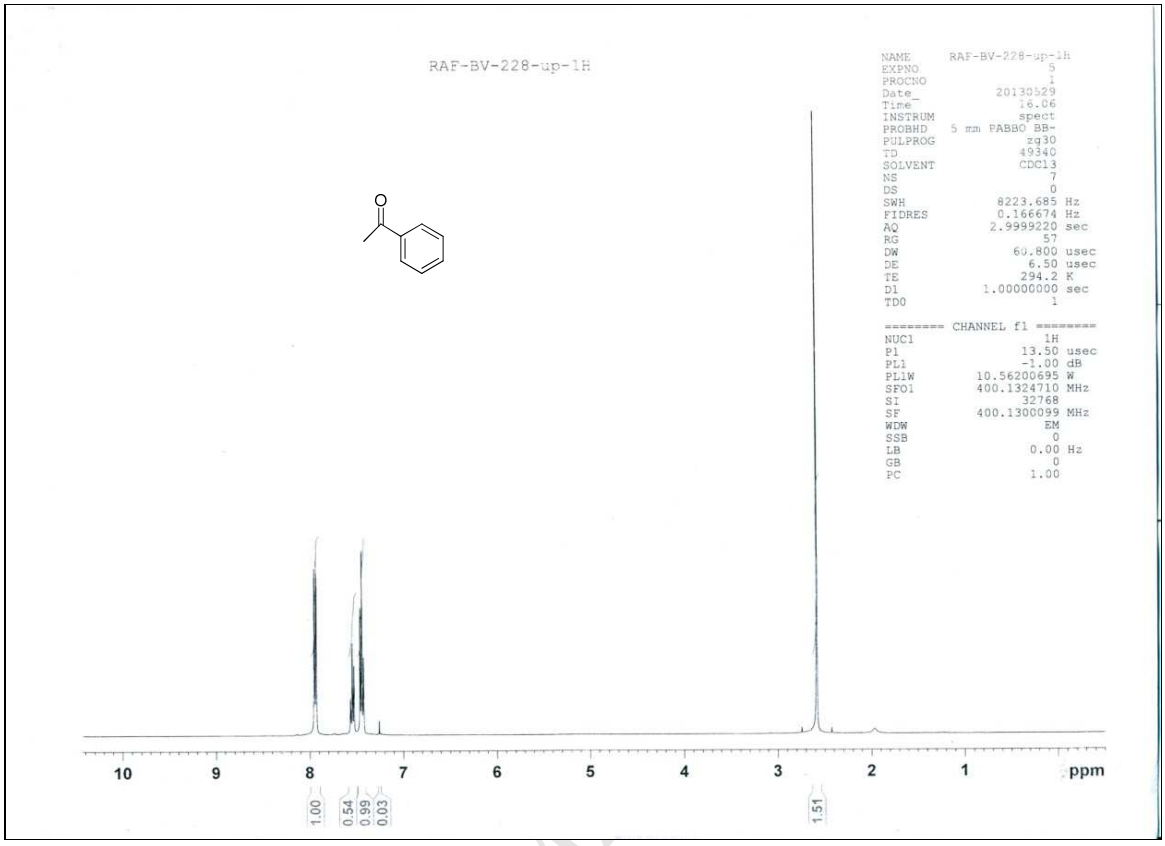


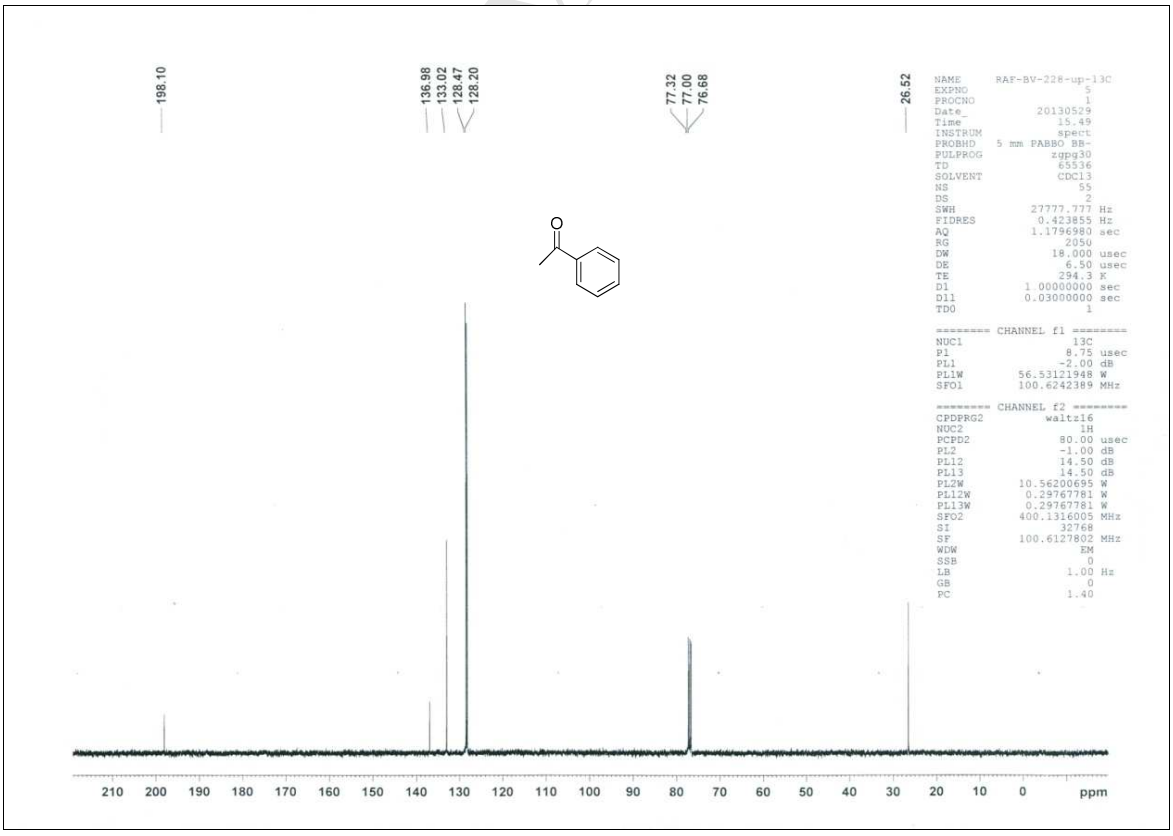
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 4l



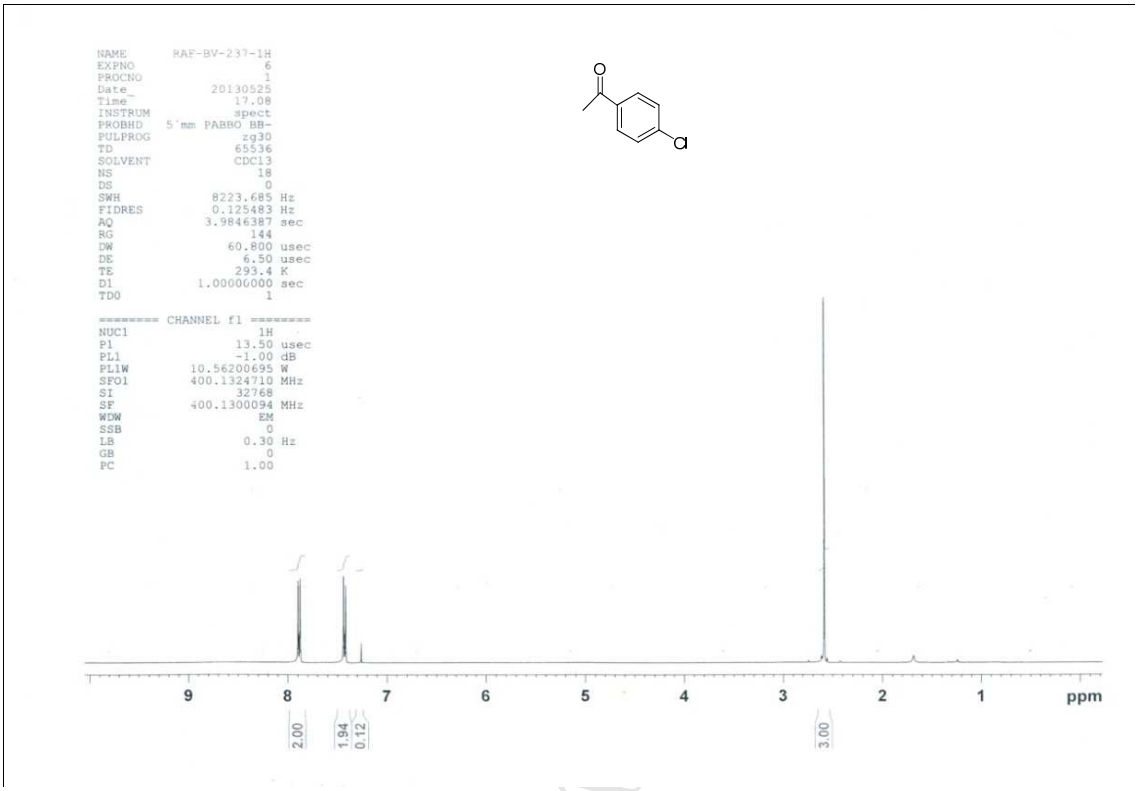


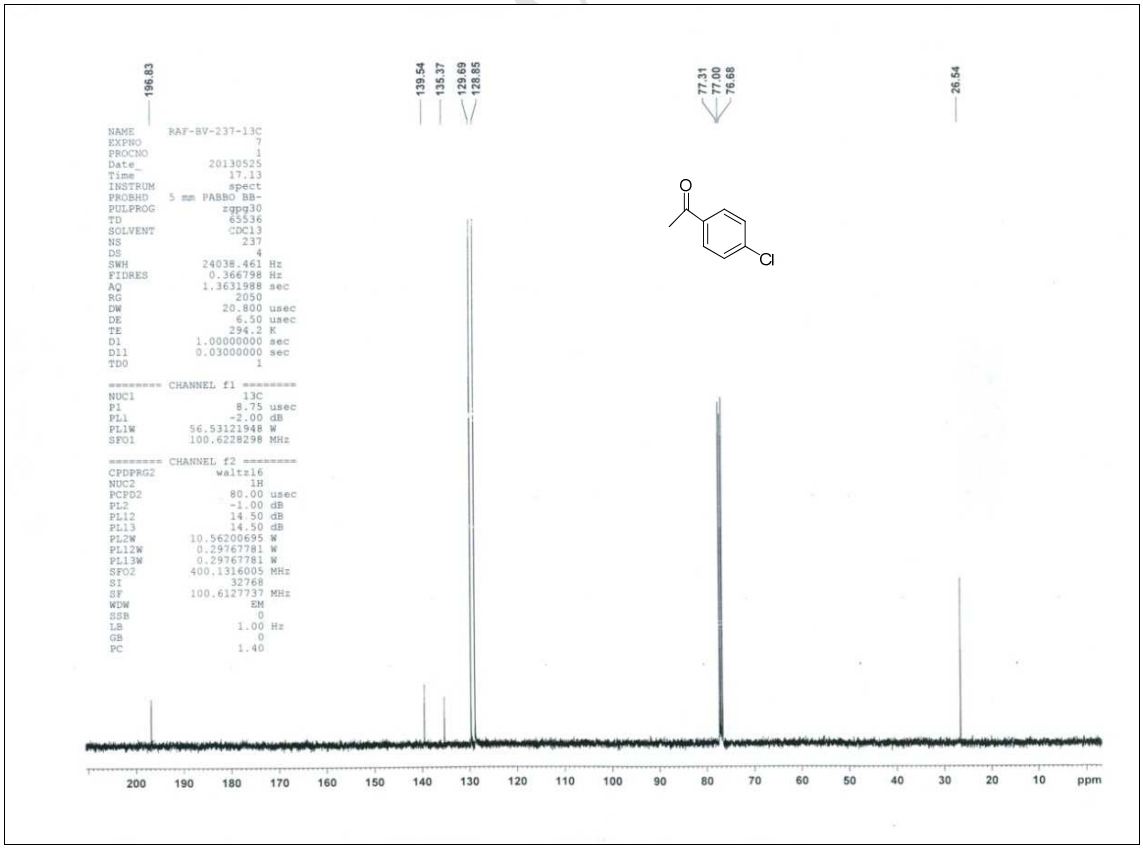
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 6a



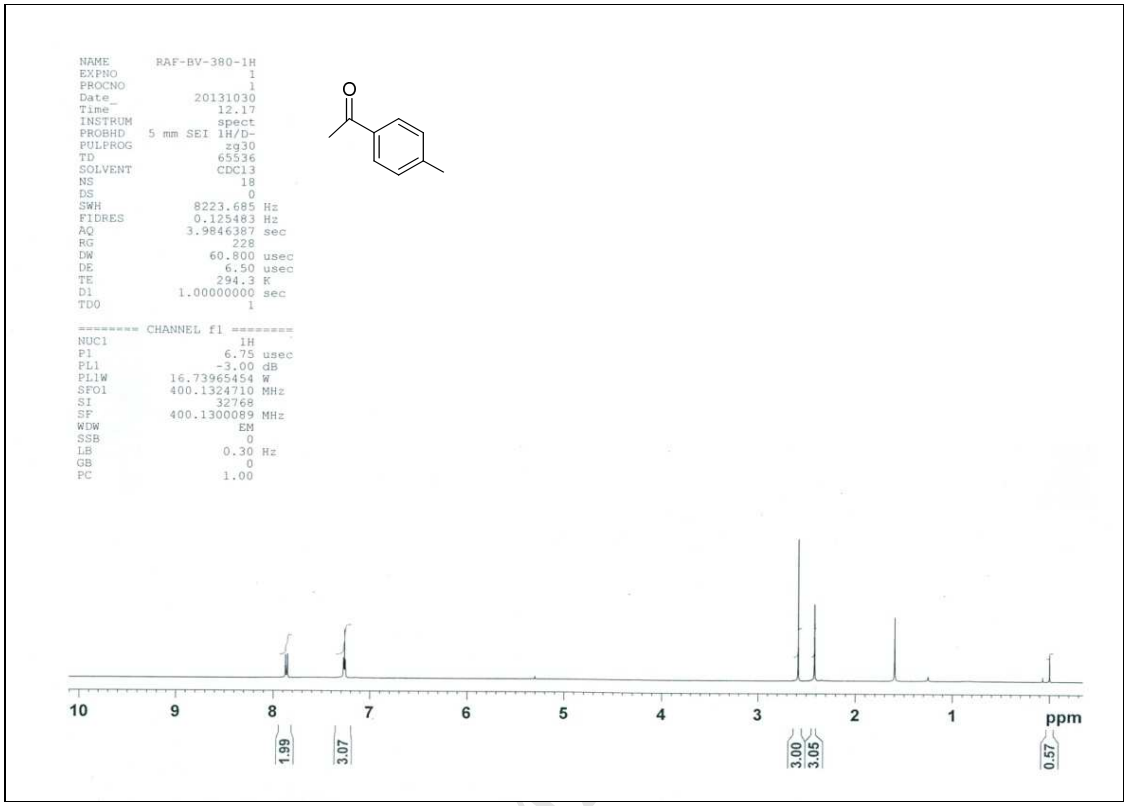


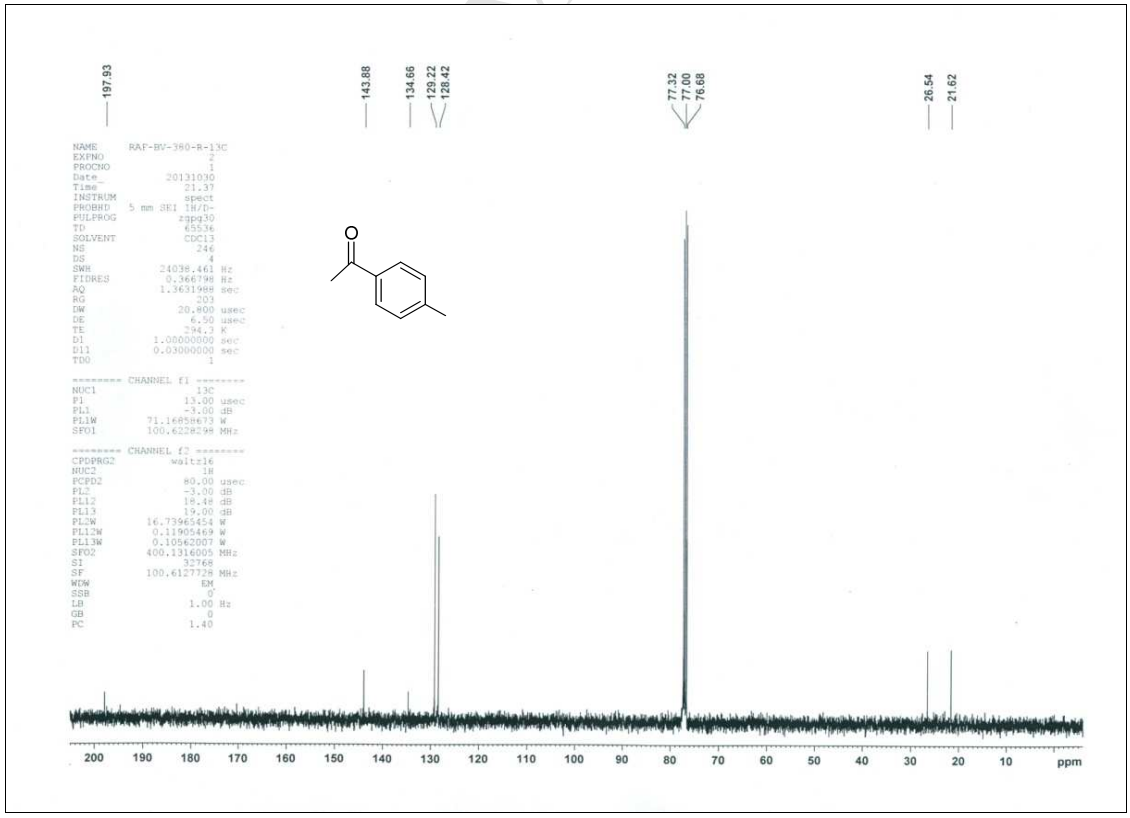
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 6b



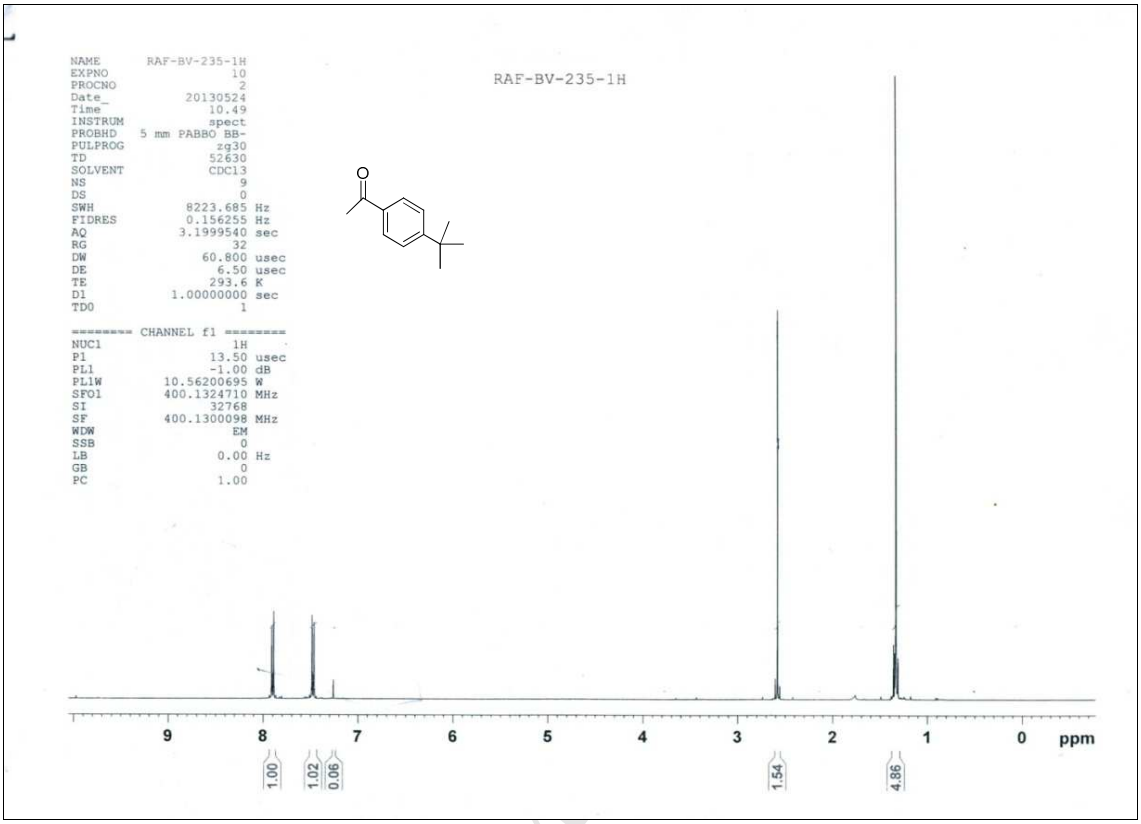


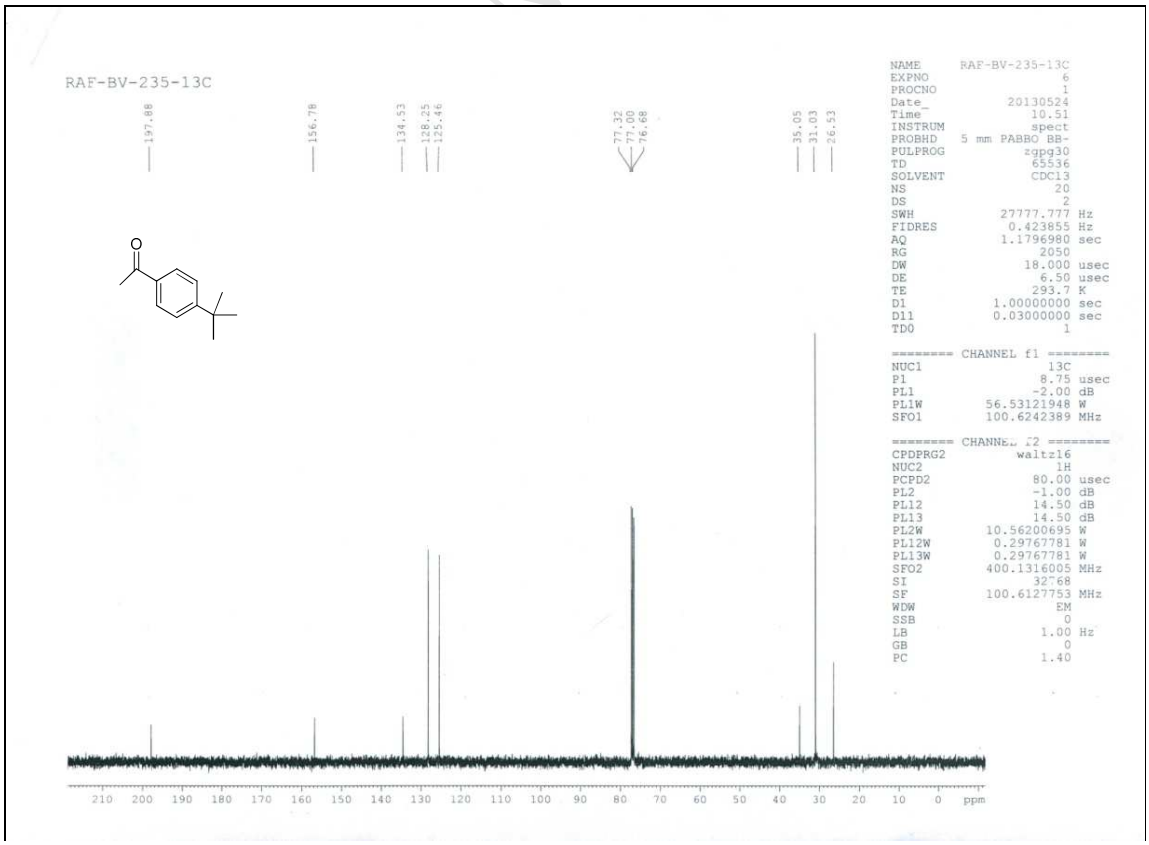
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 6c



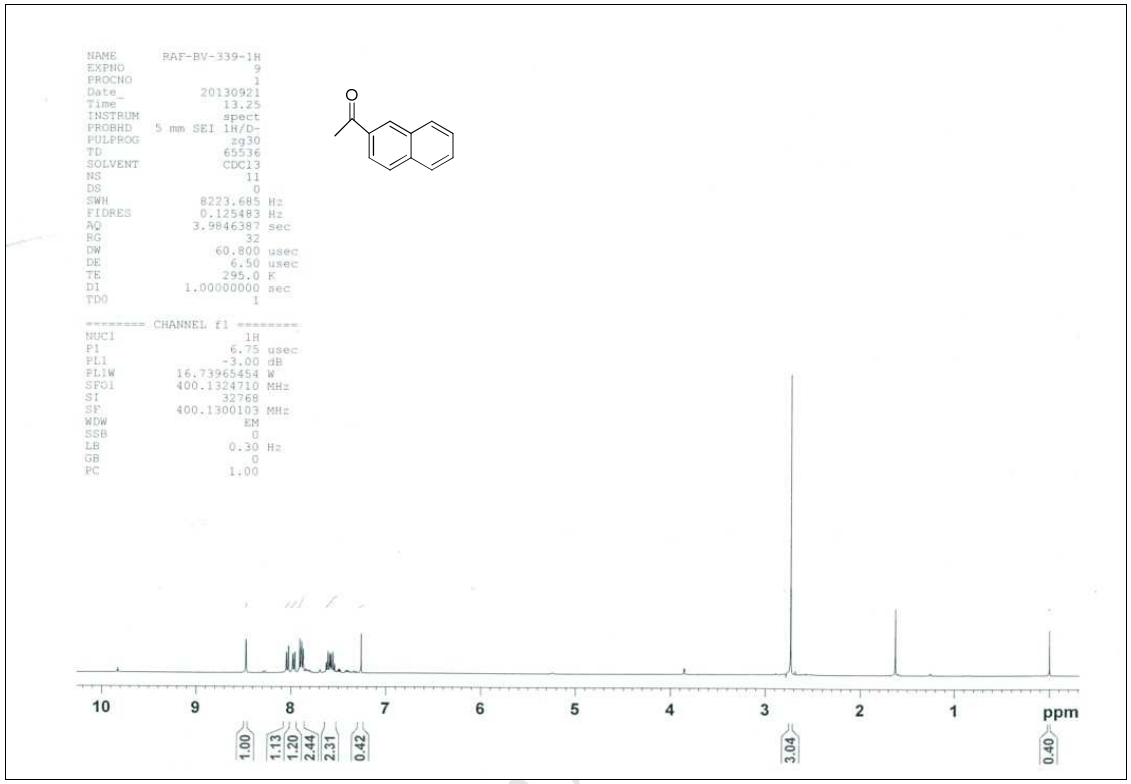


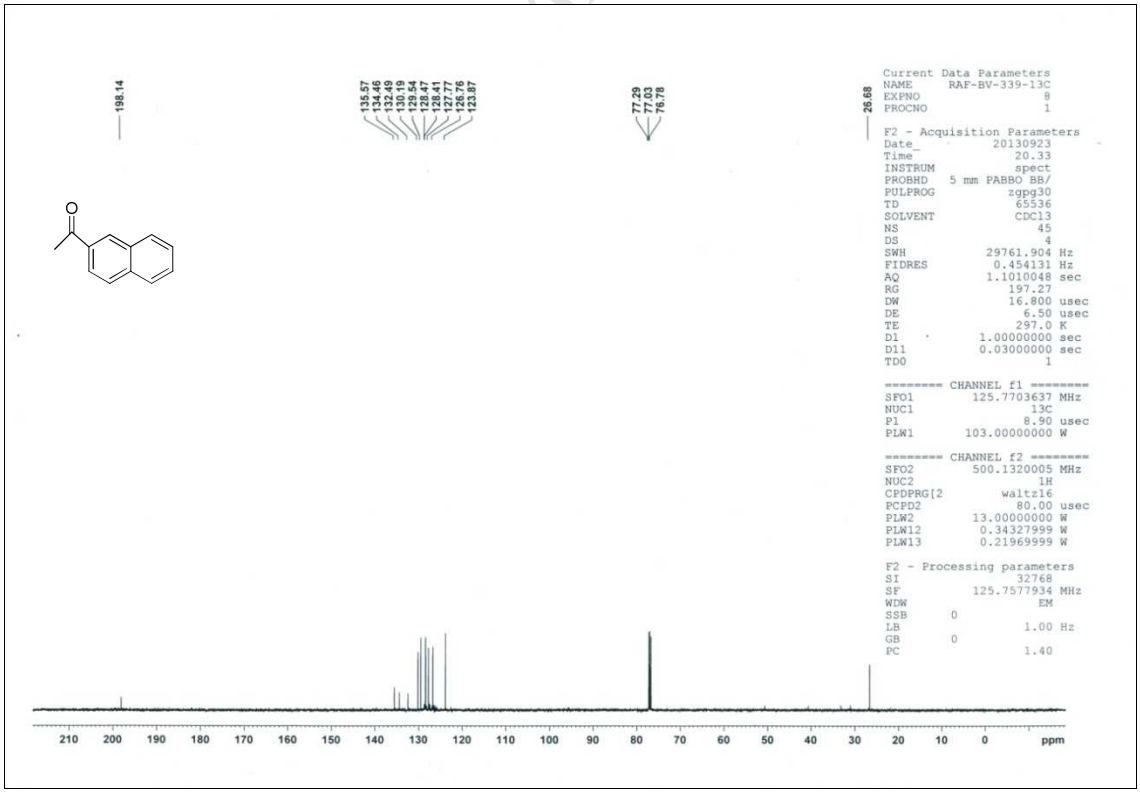
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 6d



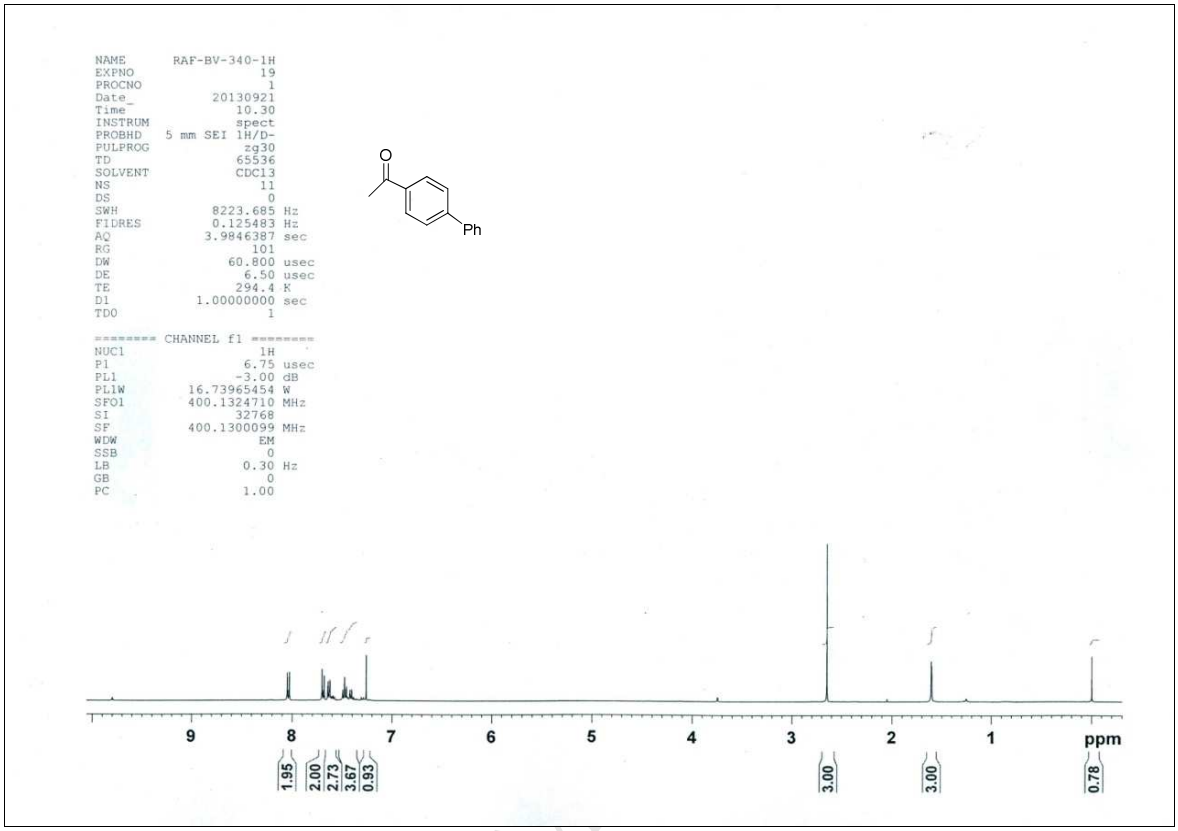


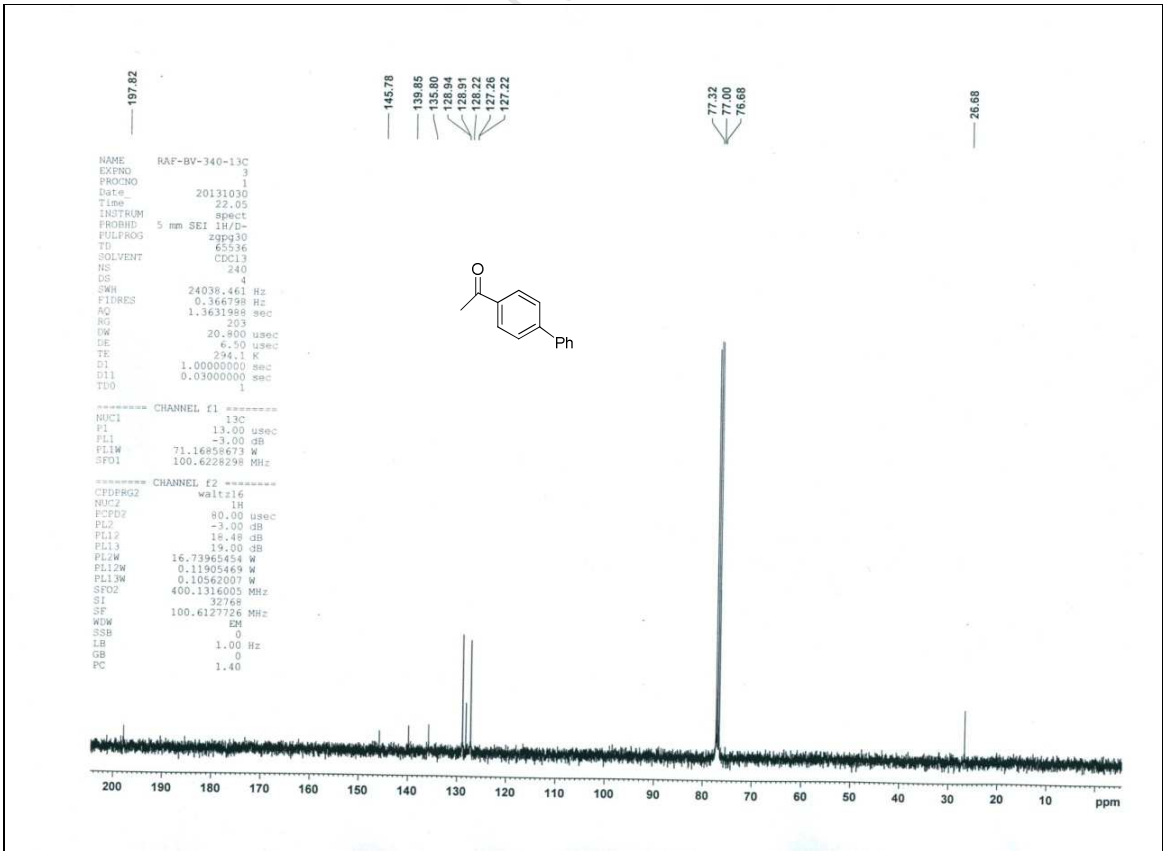
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (125 MHz, $CDCl_3$) of compound 6e



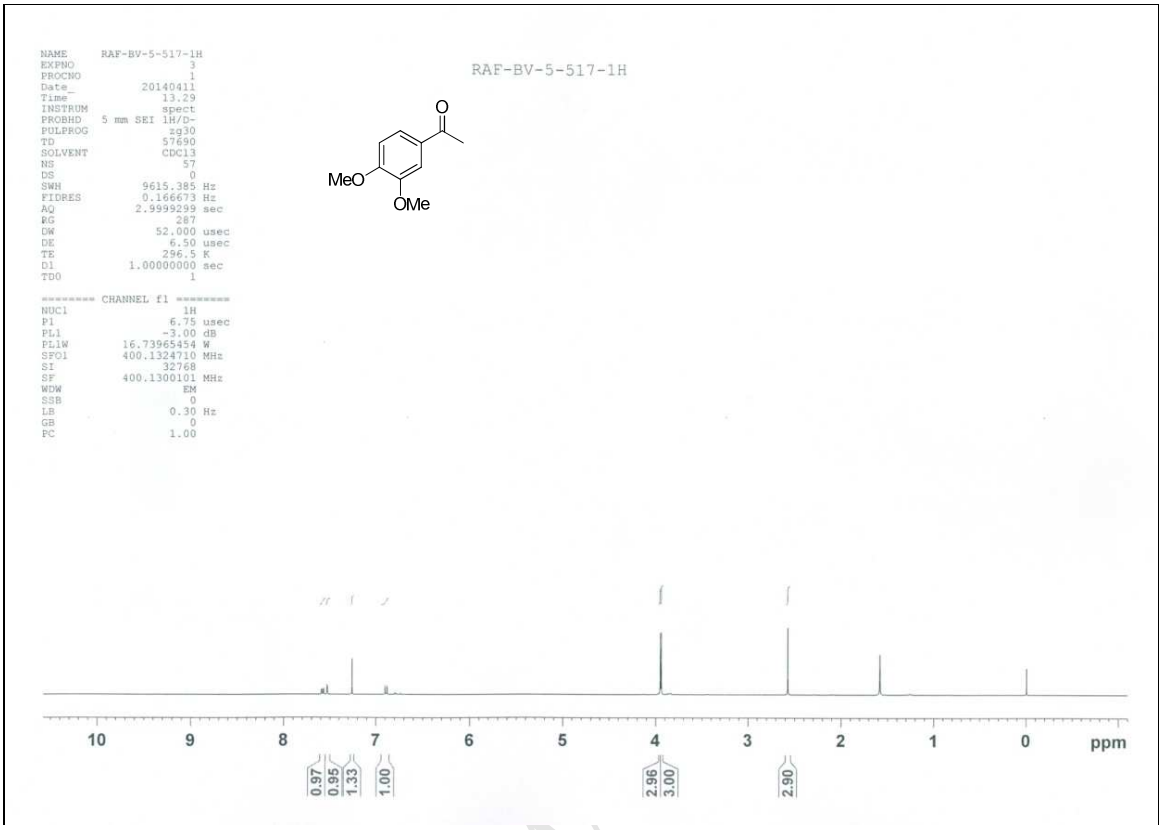


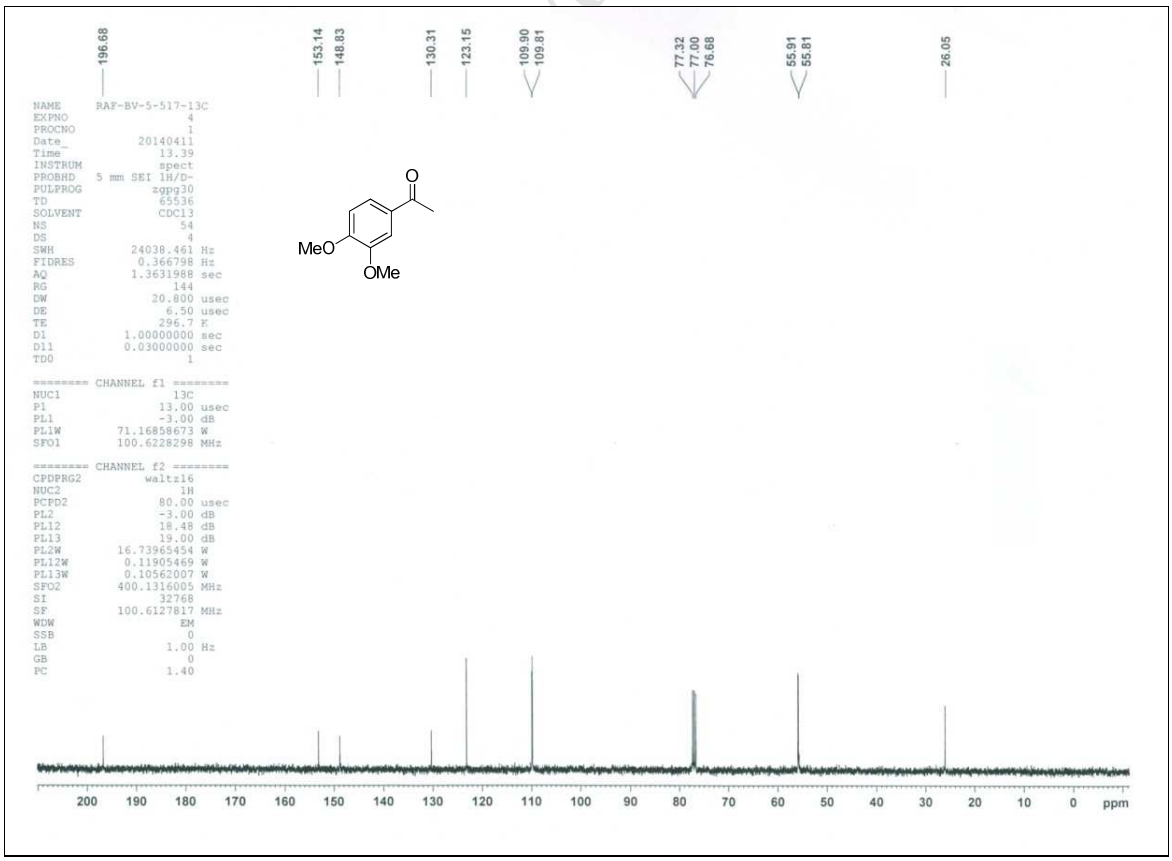
^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 6f





^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 6g





^{1}H NMR (400 MHz, $CDCl_3$/TMS) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound 6h