Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for

An Unusual Chemoselective Oxidation Strategy by an Unprecedented Exploration of Electrophilic Center of DMSO:

A New Facet to Classical DMSO Oxidation

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Experimental Section

General

All the chemicals were purchased from Aldrich, Merck, Fluka, Loba etc. companies and purified prior to their use. Melting points were determined in open capillary method and are incorrect or cited from literature where applicable. NMR spectra were recorded on a JEOL-USA (JNM-ECX500) spectrometer in $CDCl_3$-d_1 taking TMS (Tetramethyl Silane) as the internal standard. The NMR chemical shift was reported in ppm relative to 7.26 ppm and 77.00 ppm of $CDCl_3$ solvent as the standards.^{1}H spectra were recorded in 500 MHz frequencies and ^{13}C NMR spectra were recorded in 125 MHz frequencies. Coupling constant '*J*' was calculated in Hz. FT-IR spectra were acquired on a Perkin-Elmer spectrum two spectrometer. Mass spectra were recorded on an advance Bruker Daltonics (impact HD) UHR-QqTOF (Ultra-High Resolution Qq-Time-Of-Flight) mass spectrometry.

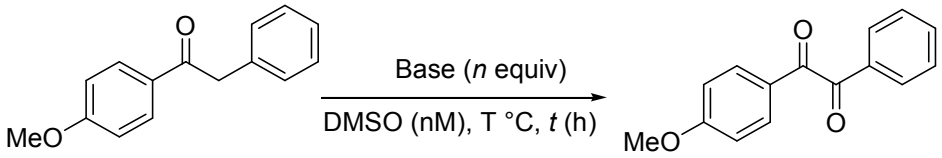
Representative procedures for substrates:

a) **Preperation of Benzhydrols:**The carboxaldehyde was dissolved in THF (0.2 M) and cooled to 0 ºC. Grignard reagent (ArMgBr, 1.2 equiv) was added drop wise to the above solution. After adding, the reaction mixture was stirred at 0 ºC for 1 hour after completion of the reaction (monitored by TLC). Saturated NH_4Cl solution was added to quench the reaction then the reaction mixture was warmed to room temperature. Extraction by EtOAc (3 times), dried over Na_2SO_4 and then concentrated. The crude product was purified by column chromatography to give pure benzhydrol.

b) **Preperation of α – keto aryl methylene compounds:** The carboxaldehyde was dissolved in diethylether (0.2 M) and cooled to 0 ºC. Grignard reagent (BnMgBr, 1.2 equiv) was added drop wise to the above solution. After adding, the reaction mixture was stirred at 0 ºC for 1 hour and TLC showed the starting material was completely consumed. Saturated NH_4Cl solution was added to quench the reaction then the mixtures was warmed to room temperature. Extraction by EtOAc (3 times), dried over Na_2SO_4 and then concentrated. The crude product was purified by column chromatography to give the pure alcohol.
The alcohol (1 equiv) was dissolved in EtOAc (0.1 M) and IBX (1.5 equiv) was added. The suspension was heated to reflux for 16 hours and TLC showed the starting material was completely consumed. The solution was cooled down to room temperature and filtrated through celite. The filtrate was concentrated to give the ketone which was further purified through column chromatography to give the desired compound.

Optimization of reaction parameters:

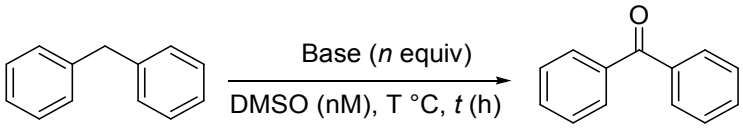
a) For oxidation of α – keto aryl methylene compounds:



entry	base	*n* equiv	nM	T °C	*t* (h)	Conversion (%)	Yield (%)
1.	K_2CO_3	1	0.05	150	2	100	64
2.	K_2CO_3	1	0.05	150	1	100	70
3.	K_2CO_3	1	0.05	150	0.5	100	76
4.	K_2CO_3	1	0.05	125	0.5	100	76
5.	K_2CO_3	1	0.05	100	0.5	100	78
6.	K_2CO_3	1	0.05	90	0.5	100	79
7.	K_2CO_3	1	0.05	80	0.5	100	79
8.	K_2CO_3	1	0.05	70	0.5	58	46
9.	K_2CO_3	0.5	0.05	80	0.75	100	79
10.	K_2CO_3	0.25	0.05	80	1.5	100	79
11.	K_2CO_3	0.25	0.1	80	1.5	92	61
12.	K_2CO_3	0.25	0.2	80	1.5	84	58
13.	K_2CO_3	0.25	0.4	80	1.5	29	22
14.	Li_2CO_3	0.25	0.05	80	1.5	0	0
15.	Na_2CO_3	0.25	0.05	80	1.5	34	30
16.	Cs_2CO_3	0.25	0.05	80	1.5	100	78
17.	$CaCO_3$	0.25	0.05	80	1.5	0	0
18.	$SrCO_3$	0.25	0.05	80	1.5	0	0
19.	$BaCO_3$	0.25	0.05	80	1.5	0	0
20.	$CaCO_3$	0.25	0.05	80	1.5	0	0

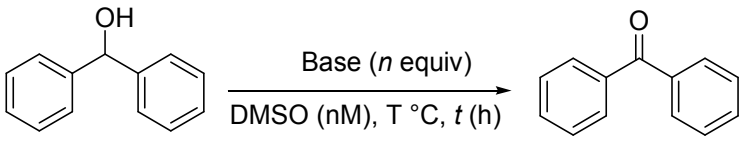
21.	KO^{t}Bu	0.25	0.05	80	1.5	85	30
22.	KOH	0.25	0.05	80	1.5	75	33
23.	KOAc	0.25	0.05	80	1.5	25	25
24.	**$KHCO_3$**	**0.25**	**0.05**	**80**	**1.5**	**100**	**96**

b) For oxidation of diaryl methylene compounds:



entry	base	*n* equiv	nM	T °C	*t* (h)	Conversion (%)	Yield (%)
1.	$KHCO_3$	1	0.05	150	24	48	46
2.	K_2CO_3	1	0.05	150	24	92	87
3.	KOH	1	0.05	150	24	89	55
4.	KO^{t}Bu	1	0.05	150	24	78	46
5.	KOAc	1	0.05	150	24	0	0
6.	Li_2CO_3	1	0.05	150	24	0	0
7.	Na_2CO_3	1	0.05	150	24	54	48
8.	Cs_2CO_3	1	0.05	150	4.5	100	95
9.	Cs_2CO_3	1	0.05	125	10	100	95
10.	Cs_2CO_3	1	0.05	100	24	57	54
11.	Cs_2CO_3	1	0.05	80	24	30	26
12.	Cs_2CO_3	0.5	0.05	125	12	100	95
13.	**Cs_2CO_3**	**0.25**	**0.05**	**125**	**16**	**100**	**94**

c) For oxidation of benzhydrols:



entry	base	*n* equiv	nM	T °C	*t* (h)	Conversion (%)	Yield (%)
1.	$KHCO_3$	1	0.05	150	24	55	55
2.	K_2CO_3	1	0.05	150	24	95	95
3.	KOH	1	0.05	150	24	92	55
4.	KO^{t}Bu	1	0.05	150	24	86	48
5.	KOAc	1	0.05	150	24	5	5
6.	Li_2CO_3	1	0.05	150	24	0	0
7.	Na_2CO_3	1	0.05	150	24	69.5	62.5
8.	Cs_2CO_3	1	0.05	150	4	100	100
9.	Cs_2CO_3	1	0.05	125	8	100	100
10.	Cs_2CO_3	1	0.05	100	24	66	66
11.	Cs_2CO_3	1	0.05	80	24	47	47
12.	Cs_2CO_3	0.5	0.05	125	12	100	100
13.	**Cs_2CO_3**	**0.25**	**0.05**	**125**	**15**	**100**	**100**

Typical procedure for the oxidation of α – keto aryl methylene compounds using $KHCO_3$:

A long neck round bottom flask was charged with 2-phenylacetophenone derivative (0.25 mmol), and potassium bicarbonate (25 mol %) in dry DMSO (0.05M). The reaction mixture was stirred at 80 °C for 0.5 – 3 h. After completion of reaction (monitored by TLC) the reaction mixture was cooled to room temperature and diluted it with ethyl acetate (5 times). To the diluted reaction mixture, equal volume of ice was added, stirred for 10 minutes and the organic layer was separated from aqueous layer. The aqueous layer was extracted twice with ethyl acetate to minimize the loss of product. The organic extract was dried over Na_2SO_4 and solvent was evaporated on a rotary evaporator. The crude extract was purified by silicagelcolumn chromatography using hexane-ethylacetate solvent system to get the pure 1, 2 diketone product. (**Note:** This reaction works equally well with up to 1% moist DMSO under open atmosphere conditions, in such case we have to use one equivalent base)

Typical procedure for the oxidation of diaryl methylene compounds using Cs_2CO_3:

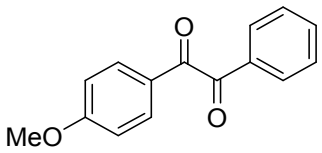
A long neck round bottom flask was charged with diarylmethylenecompound (0.25 mmol), and cesium carbonate (25 mol %) (*Note: reaction can also undergo with K_2CO_3 instead of cesium carbonate*) in dry DMSO (0.05M). Reaction was stirred in open-air atmosphere at 125 °C for 16 – 24 h. After completion of the reaction, the reaction mixture was cooled to room temperature and diluted it with ethyl acetate (5 times). To the diluted reaction mixture, equal volume of ice was added, stirred for 10 minutes and the organic layer was separated from aqueous layer. The aqueous layer was extracted twice with ethyl acetate to minimize the loss of product. The organic extract was dried over Na_2SO_4 and solvent was evaporated on a rotary evaporator. . The crude extract was purified by silicagel column chromatography using hexane-ethylacetate solvent system to get the pure oxidized product. (**Note:** This reaction works equally well with up to 1% moist DMSO under open atmosphere conditions, in such case we have to use one equivalent base. Reaction time also reduces considerably if we use equivalent base)

Typical procedure for the oxidation of benzhydrols using Cs_2CO_3:

A long neck round bottom flask was charged with benzhydrol (0.25 mmol), and cesium carbonate (25 mol %) (*Note: reaction can also undergo with K_2CO_3 instead of cesium carbonate*) in dry DMSO (0.05M). Reaction was stirred at 125 °C for 15 - 24 h. After completion of the reaction, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (5 times). To the diluted reaction mixture, equal volume of ice was added, stirred and separated the organic layer. The aqueous layer was extracted twice with ethyl acetate to minimize the loss of product. The organic extract was dried over Na_2SO_4 and solvent was evaporated on a rotary evaporator. . The crude extract was purified by silicagel column chromatography using hexane-ethylacetate solvent system to get the pure oxidized product. (**Note:** This reaction works equally well even up to 1% moist DMSO under open atmosphere conditions, in such case we have to use one equivalent base. Reaction time also reduces considerably if we use equivalent base)

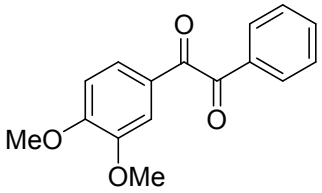
Compound Characterization:

1-(4-methoxyphenyl)-2-phenylethane-1,2-dione (2a)[1]



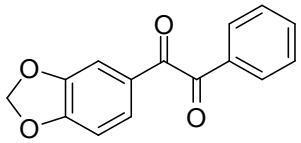
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.98-7.94 (*m*, 4H), 7.65 (*t*, 1H, *J*= 7.5 Hz),7.51 (*t*, 2H, *J*= 8.2 Hz), 6.98 (*d*, 2H, *J*= 8.9 Hz),3.89 (*s*, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 194.83, 193.17, 164.97, 134.73, 133.10, 132.39, 129.91, 128.95, 126.06, 114.35,55.65.

1-(3,4-dimethoxyphenyl)-2-phenylethane-1,2-dione (2b)[2]



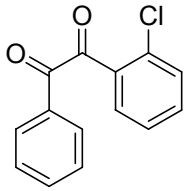
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.98 (*dd*, 2H,*J*= 1.3& 8.2 Hz), 7.66 (*t*, 1H, *J*= 7.6 Hz), 7.61 (*d*, 1H, *J*= 1.4 Hz), 7.53-7.47 (*m*, 3H), 6.89 (*d*, 1H, *J*= 1.4 Hz), 3.97 (*s*, 3H); 3.96 (*s*, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 194.71, 193.32, 154.93, 149.57, 134.74, 133.20, 129.90, 128.95, 126.40, 126.18,110.29,110.12,56.25,56.09.

1-(benzo[d][1,3]dioxol-6-yl)-2-phenylethane-1,2-dione (2c)[3]



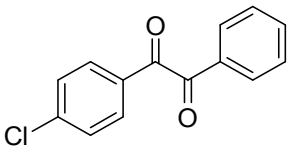
^{1}H NMR ($CDCl_3$, 500 MHz) δ7.95(*d*, 2H,*J*=6.7),7.65 (*t*, 1H, *J*=7.5Hz), 7.52-7.48 (*m*, 4H), 6.87 (*d*, 1H, *J*= 8.4 Hz), 6.09 (*s*, 2H),;^{13}C NMR ($CDCl_3$, 125 MHz) δ194.54, 192.80, 153.47, 148.62, 134.79, 133.04, 129.88, 128.95, 127.92, 127.81,108.39, 108.29, 102.22.

1-(2-chlorophenyl)-2-phenylethane-1,2-dione (2d)[1]



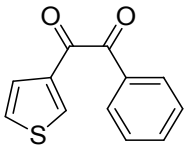
^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04-8.03 (*m*, 2H), 7.91 (*dd*, 1H, *J*= 1.4 & 7.5 Hz), 7.67 (*t*, 1H, *J*= 7.5 Hz), 7.56-7.52 (*m*, 3H), 7.44 (*t*, 2H, *J*= 8.2 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 193.68, 192.04, 134.59, 134.53, 133.98, 133.82, 132.38, 132.11, 130.50, 130.20, 128.88, 127.36.

1-(4-chlorophenyl)-2-phenylethane-1,2-dione (2e)[1]



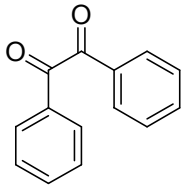
^{1}H NMR ($CDCl_3$, 500 MHz) δ7.98-7.92 (*m*, 4H,), 7.68 (*t*, 1H, *J* = 7.5 Hz),7.54-7.48 (*m*, 4H,); ^{13}C NMR ($CDCl_3$, 125 MHz) δ193.86, 193.05, 141.57, 135.06, 132.70, 131.27, 131.20, 129.92,129.41, 129.05.

1-phenyl-2-(thiophen-3-yl)ethane-1,2-dione (2f)[4]



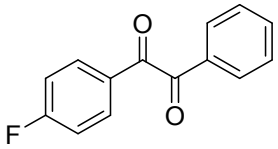
^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.22 (*dd*, 1H, *J*= 1.3& 2.7 Hz), 8.01 (*d*, 2H, *J*= 6.8 Hz), 7,68 – 7.65 (*m*, 2H), 7.52 (*t*, 2H, *J*= 7.9 Hz), 8.22 (*dd*, 1H, *J*= 2.7 &5.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ193.23, 187.26, 137.99, 137.04, 134.81, 132.64, 130.11, 128.93, 127.20, 127.09.

Benzil (2g)[5]



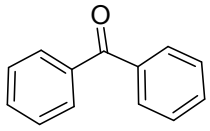
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.98 (*dd*, 4H, *J*= 1.3& 8.2 Hz), 7.67 (*t*, 2H, *J*= 6.8 Hz), 7.52 (t, 4H, J= 8.2 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 194.58, 134.90, 132.96, 129.90, 129.01.

1-(4-fluorophenyl)-2-phenylethane-1,2-dione (2h)[1]



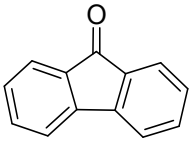
^{1}H NMR ($CDCl_3$, 500 MHz) δ8.04-8.01 (*m*, 2H), 7.97 (*dd*, 2H,*J* = 1.3 & 8.2 Hz),7.68 (*t*, 1H, *J*= 7.5 Hz),7.53 (*t*, 2H, *J*=8.2 Hz),7.19 (*t*, 2H, J = 8.6Hz);^{13}C NMR ($CDCl_3$, 125 MHz) δ194.08, 192.75, 166.78 (*J* = 256.3), 135.03, 132.74 (*J* = 9.5), 129.94,129.47, 129.06, 116.41 (*J* = 22.6).

Benzophenone (2l)[1]



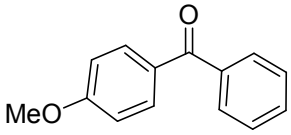
^{1}H NMR ($CDCl_3$, 500 MHz) δ7.83 – 7.80 (*m*, 4H), 7.59 (*t*, 2H, *J*= 7.5 Hz), 7.49 (*t*, 4H, *J*= 7.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ196.77, 137.54, 132.41, 130.04, 128.25.

9*H*-fluoren - 9 - one (2m)[6]



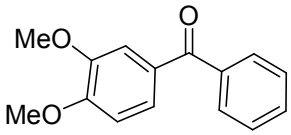
^{1}H NMR ($CDCl_3$, 500 MHz) δ7.62 (*d*, 2H, *J*= 7.5 Hz), 7.47 – 7.42 (*m*, 4H),7.27 – 7.24 (*m*, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ193.82, 144.28, 134.58, 133.98, 128.95, 124.16, 120.21.

(4-methoxyphenyl)(phenyl)methanone (4d)[7]



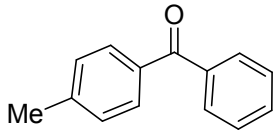
^{1}H NMR ($CDCl_3$, 500 MHz) δ7.83 (*dd*, 2H, *J*= 2.0 & 6.9 Hz), 7.76 (*d*, 2H, *J*= 6.9 Hz),7.57 (*t*, 1H, *J*= 7.5 Hz), 7.48 (*t*, 2H, *J*= 6.9 Hz), 6.97 (*dd*, 2H, *J*= 2.0 & 6.9 Hz), 3.89 (*s*, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ195.61, 163.20, 138.24, 132.56, 131.88, 130.11, 129.72, 128.16, 113.52, 55.48.

(3, 4 - dimethoxyphenyl) (phenyl) methanone (4e)[7]



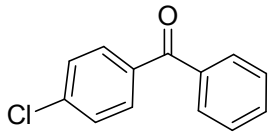
^{1}H NMR ($CDCl_3$, 500 MHz) δ7.77 – 7.75 (*m*, 2H),7.57 (*t*, 1H, *J*= 7.5 Hz), 7.50 – 7.47 (*m*, 3H),7.38 (*dd*, 1H, *J*= 1.3 & 8.2 Hz), 6.90 (*d*, 1H, *J*= 8.2 Hz), 3.96 (*s*, 3H), 3.95 (*s*, 3H);^{13}C NMR ($CDCl_3$, 125 MHz) δ195.57, 152.94, 148.93, 138.20, 131.84, 130.12, 129.67, 128.12, 125.48, 112.00, 109.64, 56.04, 55.99.

Phenyl (*p* - tolyl) methanone (4f)[8]



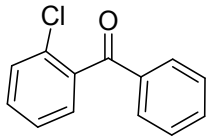
^{1}H NMR ($CDCl_3$, 500 MHz) δ7.79 – 7.77 (*m*, 2H), 7.20 (*d*, 2H, *J*= 8.2 Hz),7.57 (*t*, 1H, *J*= 7.5 Hz), 7.47 (*t*, 2H, *J*= 7.5 Hz), 7.27 (*d*, 2H, *J*= 8.2 Hz), 2.43 (*s*, 3H);^{13}C NMR ($CDCl_3$, 125 MHz) δ196.47, 143.20, 137.84, 134.76, 132.11, 130.25, 129.87, 128.91, 128.14, 21.60.

(4 - chlorophenyl) (phenyl) methanone (4g)[7]



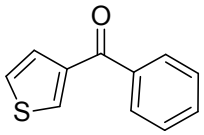
^{1}H NMR ($CDCl_3$, 500 MHz) δ7.78 – 7.75 (*m*, 4H),7.60 (*t*, 1H, *J*= 7.5 Hz), 7.51 – 7.45 (*m*, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ195.51, 138.87, 137.19, 135.81, 132.64, 131.44, 129.91, 128.61, 128.38.

(2 - chlorophenyl) (phenyl) methanone (4h)[8]



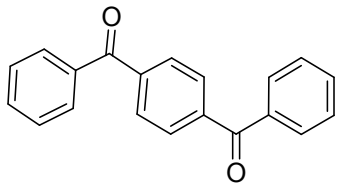
^{1}H NMR ($CDCl_3$ mixed with CCl_4, 500 MHz) δ7.80 – 7.78 (*m*, 2H), 7.58 (*t*, 1H, *J*= 7.5 Hz), 7.46 – 7.40 (*m*, 4H),7.37 – 7.35 (*m*, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ194.71, 138.78, 136.54, 133.56, 131.43, 131.00, 130.08, 129.15, 128.58, 126.61.

Phenyl (thiophen - 3 - yl) methanone (4i)[7]



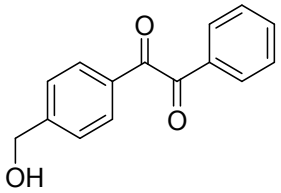
^{1}H NMR ($CDCl_3$, 500 MHz) δ7.94 (*d*, 1H, *J*= 3.5 Hz), 7.86 – 7.84 (*m*, 2H),7.61 – 7.58 (*m*, 2H), 7.51 – 7.48 (*m*, 2H), 7.40 – 7.38 (*m*, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ190.05, 141.22, 138.60, 133.95, 132.30, 129.36, 128.59, 128.37, 126.20.

4 –benzoyl benzophenone (4j)[9]



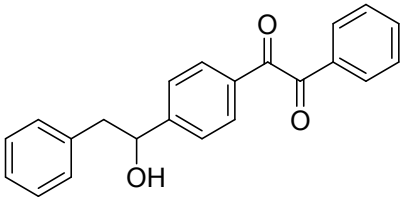
^{1}H NMR ($CDCl_3$, 500 MHz) δ7.90 (*s*, 4H), 7.85 – 7.84 (*m*, 4H),7.63 (*t*, 2H, *J*= 7.5 Hz), 7.52 (*t*, 4H, *J*= 7.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ196.03, 140.60, 136.89, 132.95, 130.10, 129.71, 128.46.

1-(4-(hydroxymethyl)phenyl)-2-phenylethane-1,2-dione (6a)[10]



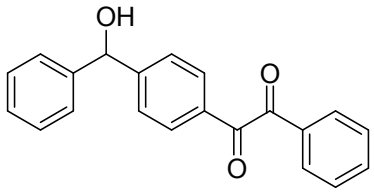
^{1}H NMR ($CDCl_3$, 500 MHz) δ7.98 (*d*, 4H, *J*= 8.2 Hz), 7.67 (*t*, 1H, *J*= 7.5 Hz),7.54 – 7.51 (*m*, 4H), 7.52 (*t*, 4H, *J*= 7.5 Hz), 4.81 (*s*, 2H), 1.86 (*brs*, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ194.54, 194.19, 148.23, 134.92, 132.93, 130.21, 129.92, 129.02, 126.87, 64.49.

1-(4-(1-hydroxy-2-phenylethyl)phenyl)-2-phenylethane-1,2-dione (6b)



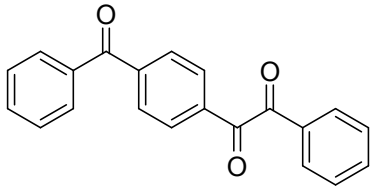
Pale yellow color powder (Mp 116-117 °C);^{1}H NMR ($CDCl_3$, 500 MHz) δ7.99 – 7.95 (*m*, 4H), 7.67 (*t*, 1H, *J*= 7.5 Hz),7.54 – 7.50 (*m*, 4H), 7.33 – 7.28 (*m*, 3H),7.19 (*d*, 2H, *J*= 6.8 Hz), 5.00 – 4.98 (*m*, 1H), 3.08 – 3.04 (*m*, 1H), 2.97 – 2.93 (*m*, 1H), 2.04 (*brs*, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ194.54, 194.18, 151.07, 137.01, 134.90, 132.94, 132.19, 130.10, 129.92, 129.48, 129.01, 128.70, 126.97, 126.43, 74.69, 46.01. IR (Neat) ν: 3748, 3530, 1667cm^{-1}. HRMS (EI): *m/z* = 353.1226 (M+Na$^+$), calculated for 353.1154, $C_{22}H_{18}NaO_3$.

1-(4-(hydroxy(phenyl)methyl)phenyl)-2-phenylethane-1,2-dione (6c)[11]



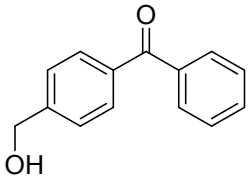
^{1}H NMR ($CDCl_3$, 500 MHz) δ7.97 – 7.94 (*m*, 4H), 7.66 (*t*, 1H, *J*= 7.5 Hz),7.56 (*d*, 2H, *J*= 8.2 Hz), 7.51 (*t*, 2H, *J*= 8.2 Hz), 7.37 – 7.29 (*m*, 5H), 5.90 (*s*, 1H), 2.33 (*brs*, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ194.52, 194.13, 150.81, 142.89, 134.89, 132.94, 132.06, 130.17, 129.92, 129.00, 128.83, 128.21, 126.84, 126.68, 75.88.

1-(4-(benzoyl)phenyl)-2-phenylethane-1,2-dione (6c')[12]



^{1}H NMR ($CDCl_3$, 500 MHz) δ8.10 (*d*, 2H, *J*= 8.2 Hz), 8.00 (*d*, 2H, *J*= 8.9 Hz),7.90 (*d*, 2H, *J*= 8.2 Hz), 7.81 (*d*, 2H, *J*= 8.2 Hz), 7.70 (*t*, 1H, *J*= 7.5 Hz),7.64 (*t*, 1H, *J*= 7.5 Hz),7.57 – 7.49 (*m*, 4H), 2.33 (*brs*, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ195.67, 193.87, 193.66, 142.79, 136.55, 135.29, 135.18, 133.23. 132.68, 130.18, 130.14, 129.99, 129.77, 129.14, 128.55

(4-(hydroxymethyl)phenyl)(phenyl)methanone (6d)[13]



^{1}H NMR ($CDCl_3$, 500 MHz) δ7.80 – 7.77 (*m*, 4H),7.59 (*t*, 1H, *J*= 7.5 Hz), 7.48 (*t*, 4H, *J*= 7.5 Hz), 4.80 (*s*, 4H), 2.17 (*brs*, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ196.54, 145.55, 137.57, 136.66, 132.43, 130.38, 129.99, 128.27, 126.37, 64.64.

Mechanistic Insights:

a) Detection of alkoxide ion II intermediate:

To trap the reactive intermediates, the reaction mixture of 1-(4-methoxyphenyl)-2-phenylethanone **1a** was subjected to ESI-MS mass experiment. Though we failed to trap the intermediates **I** & **III**,but the alkoxide ion intermediate **II** of **1a** was observed in – ve ESI-MS mode at *m/z* 241. To further conform this result, 1-(4-chlorophenyl)-2-phenylethanone **1e** was chosen as the substrate, since it could produce the M & M + 2 isotopic peaks of intermediate **II** in 3:1 intensity ratio respectively. The reaction mixture of **1e** was also subjected to ESI-MS mass experiment and delightfully, the peaks at *m/z* = 245 & 247 for the alkoxide ion intermediate **II** of **1e** was observed in 3:1 intensity ratio respectively.

*Negative ion mode ESI-MS analysis of reaction with 1**a***

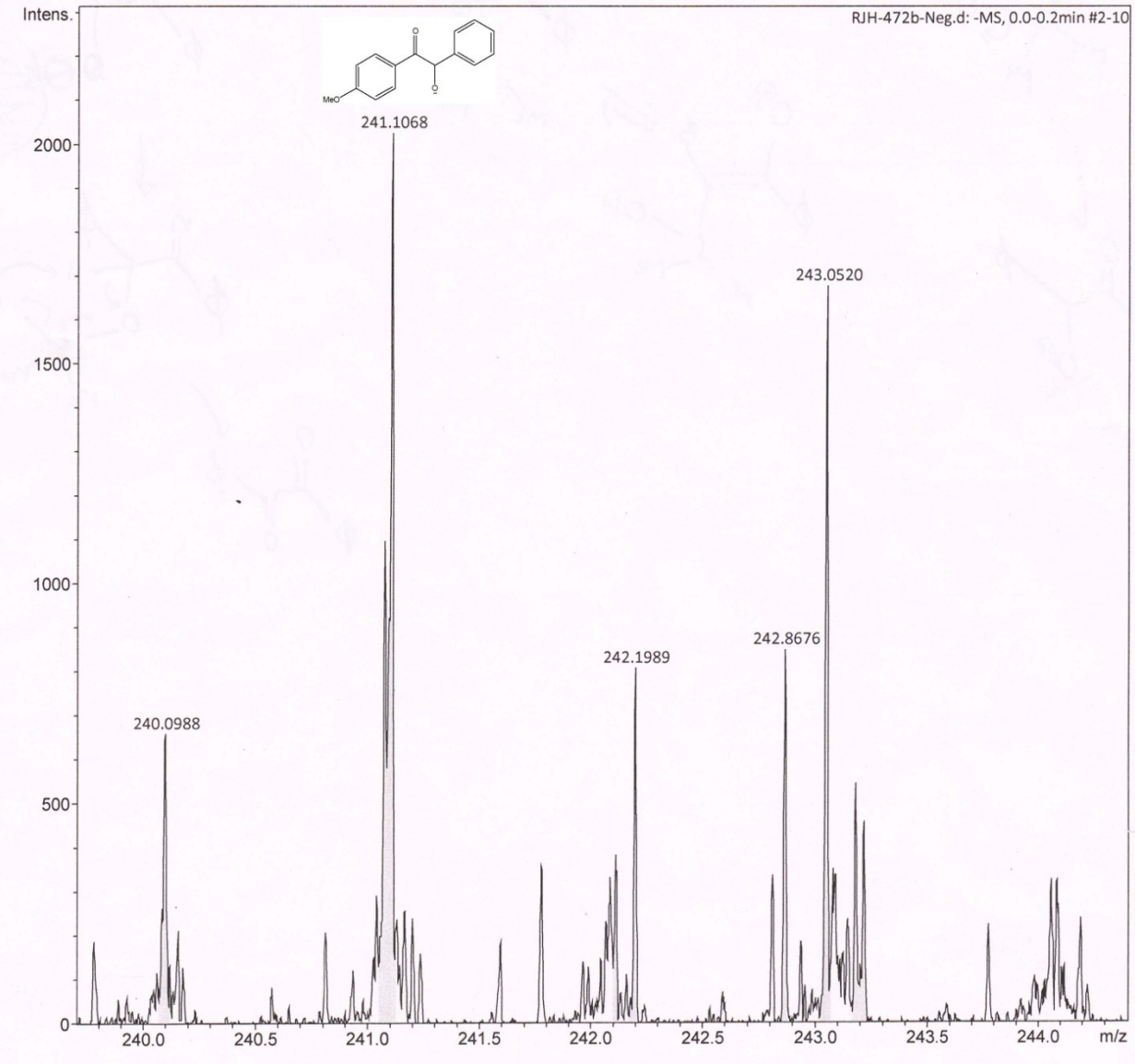
Display Report

Analysis Info

Analysis Name	D:\Data\User Data\Dr. Ravi\December-14\Rajesh\RJH-472b-Neg.d	Acquisition Date	12/19/2014 4:44:05 PM
Method	Tune_neg_Standard.m	Operator	IIT
Sample Name	ACN	Instrument	maXis impact 1819696.00160
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



RJH-472b-Neg.d

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*-ve ESI-MS analysis of reaction with **1e***

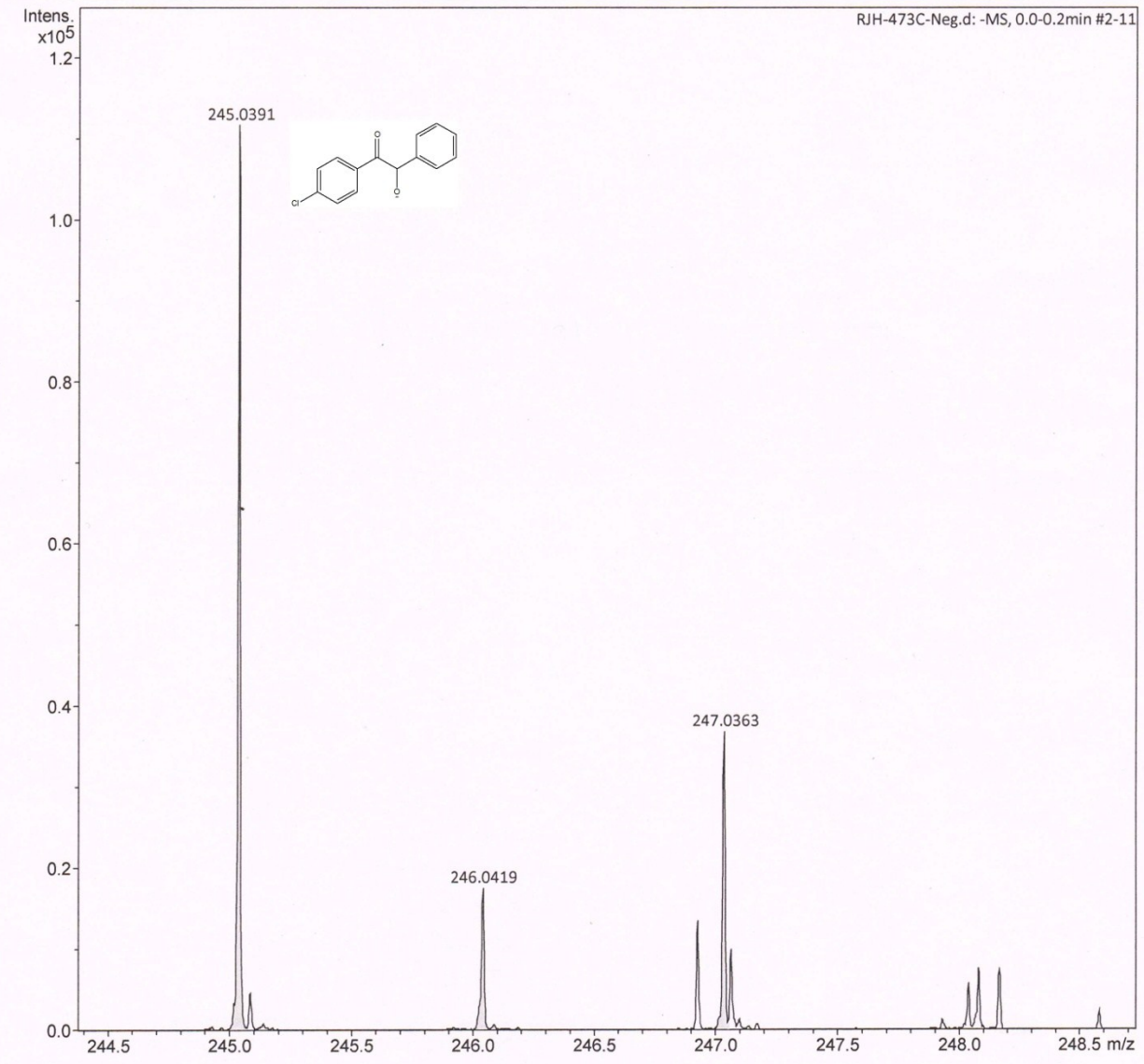
Display Report

Analysis Info

Analysis Name	D:\Data\User Data\Dr. Ravi\December-14\Rajesh\RJH-473C-Neg.d	Acquisition Date	12/20/2014 1:03:12 PM
Method	Tune_neg_Standard.m	Operator	IIT
Sample Name	ACN	Instrument	maXis impact 1819696.00160
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



RJH-473C-Neg.d

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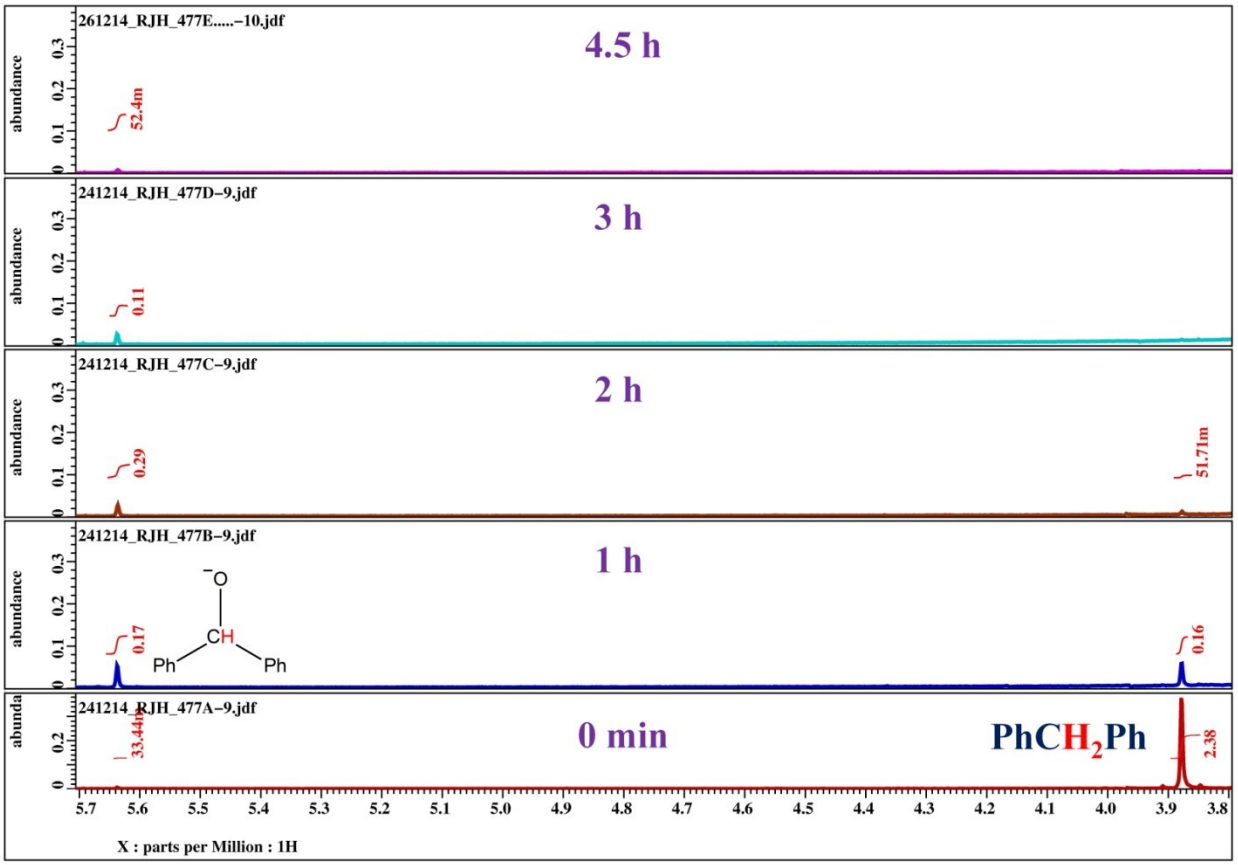
b) NMR study:

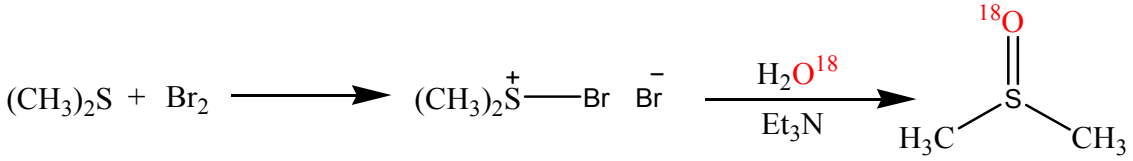
A time dependent NMR study was performed with the oxidation of diphenyl methane under the standard conditions with 1 equiv of Cs_2CO_3in DMSO-d_6 at 150 °C for 5 h. During the course of reaction, the peak at δ = 3.88 ppm for the methylene protons of the reactant slowly disappears and the diagnostic peak of the alkoxide ion intermediate **II** of diphenyl methane appears at δ = 5.64 ppm gradually increases its intensity up to a certain time interval, and completely disintegrates at the final stage. This particular experiment justifies the involvement of alkoxide ion intermediate **II**.

Overlay 1H-NMR spectra of oxidation reaction of diphenyl methane



c) ^{18}O Labeling experiment

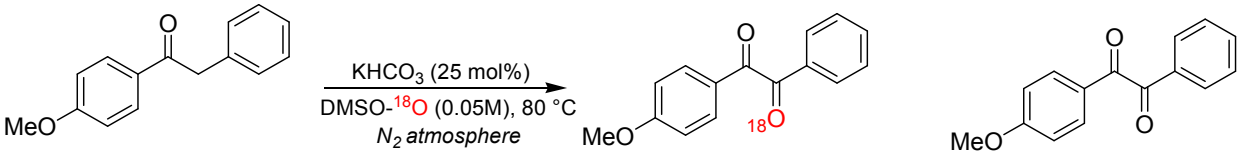
Method for preparation of ^{18}O labeled DMSO



I step: *Slight modification in purification step was applied to the reported procedure for dimethylsulfur dibromide synthesis.*[14]

Bromine (1.8 mL, 33 mmoles) was added dropwise over 40 min to a vigorously stirred, ice-cooled solution of dimethyl sulfide (2.43 mL, 33 mmoles) in carbon tetrachloride (30 mL). The resulting yellowish precipitate were removed by filtration and washed with cold chloroform to remove unreacted bromine. After removing the solvent on rotator evaporator under reduced pressure at room temperature, 71% (5.2 g) of yellow solid product was obtained. (***Avoid*** *heating dimethylsulfur dibromide, it may cause brominating side products of dimethyl sulfide*).

II step: Solid dimethylsulfur dibromide (5.0 g, 22.5 mmoles) was added portion wise over 15 min to a vigorously stirred solution of triethylamine (6.3 ml, 45 mmoles, freshly distilled from sodium hydroxide) and ^{18}O-labeled water (97 atom % ^{18}O) (0.20 ml, 11 mmoles) in 15 ml of tetrahydrofuran (freshly distilled from sodium metal). The temperature of the reaction was maintained below 50 °C by occasional cooling in ice. The precipitate of triethylamine hydrobromide was removed by centrifugation and washed twice with ether. The combined yellow supernatant and washings were dried on high vacuum pressure pump at room temperature (15 mm) to remove the solvent and the tan residue was distilled in a short path distillation to get 850 mg (97%) of ^{18}O-labeled DMSO.

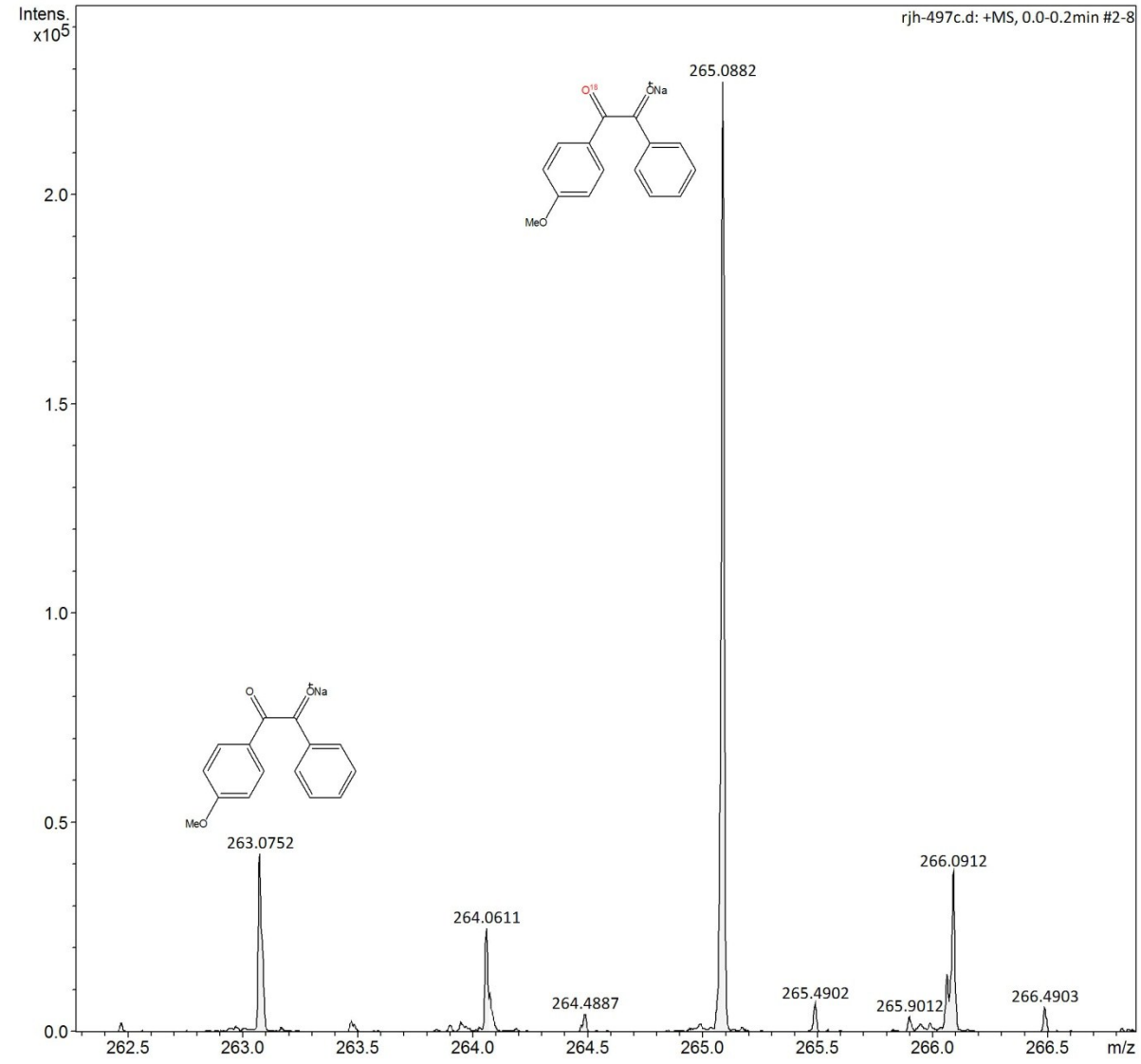


Without further purification the distilled ^{18}O-labeled DMSO was applied on the oxidation of substrate **1a** under the standard conditions. After 2 h, the reaction mixture was subjected to the ESI-MS analysis, a significant amount (69%) of ^{18}O incorporated oxidized product (M+Na, *m/z* = 265) along with the unlabeled product (M+Na,*m/z* = 263) was observed.

*ESI-MS analysis of reaction **1a** with ^{18}O-labeled DMSO*

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



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Bruker Compass DataAnalysis 4.1 printed: 1/13/2015 3:30:07 PM by: IIT Page 1 of 1

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Table 1, (2a)-^{1}H-NMR (500MHz, $CDCl_3$)

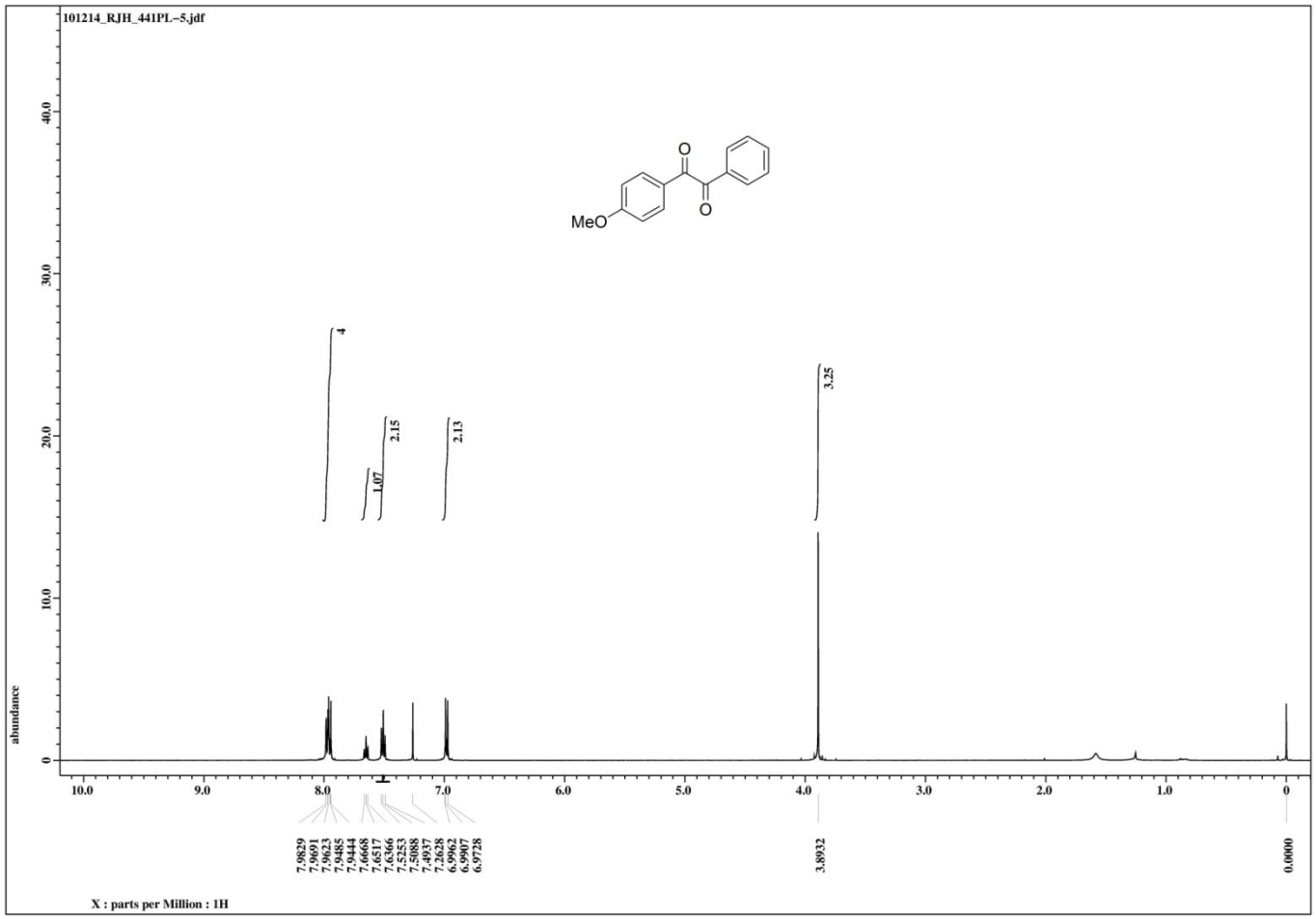


Table 1, (2a)-^{13}C-NMR (125 MHz, $CDCl_3$)

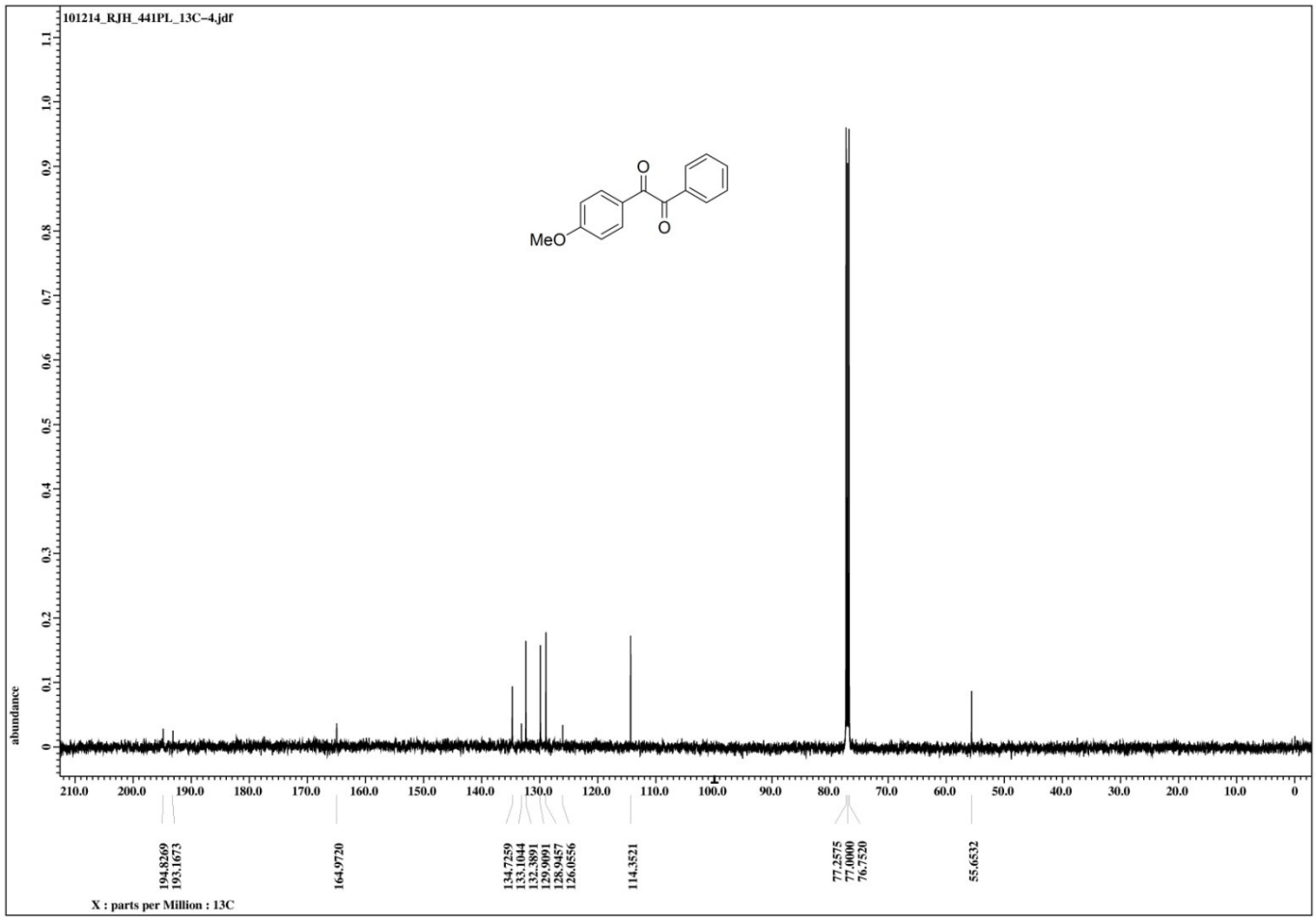


Table 1, (2b)-^{1}H-NMR (500MHz, $CDCl_3$)

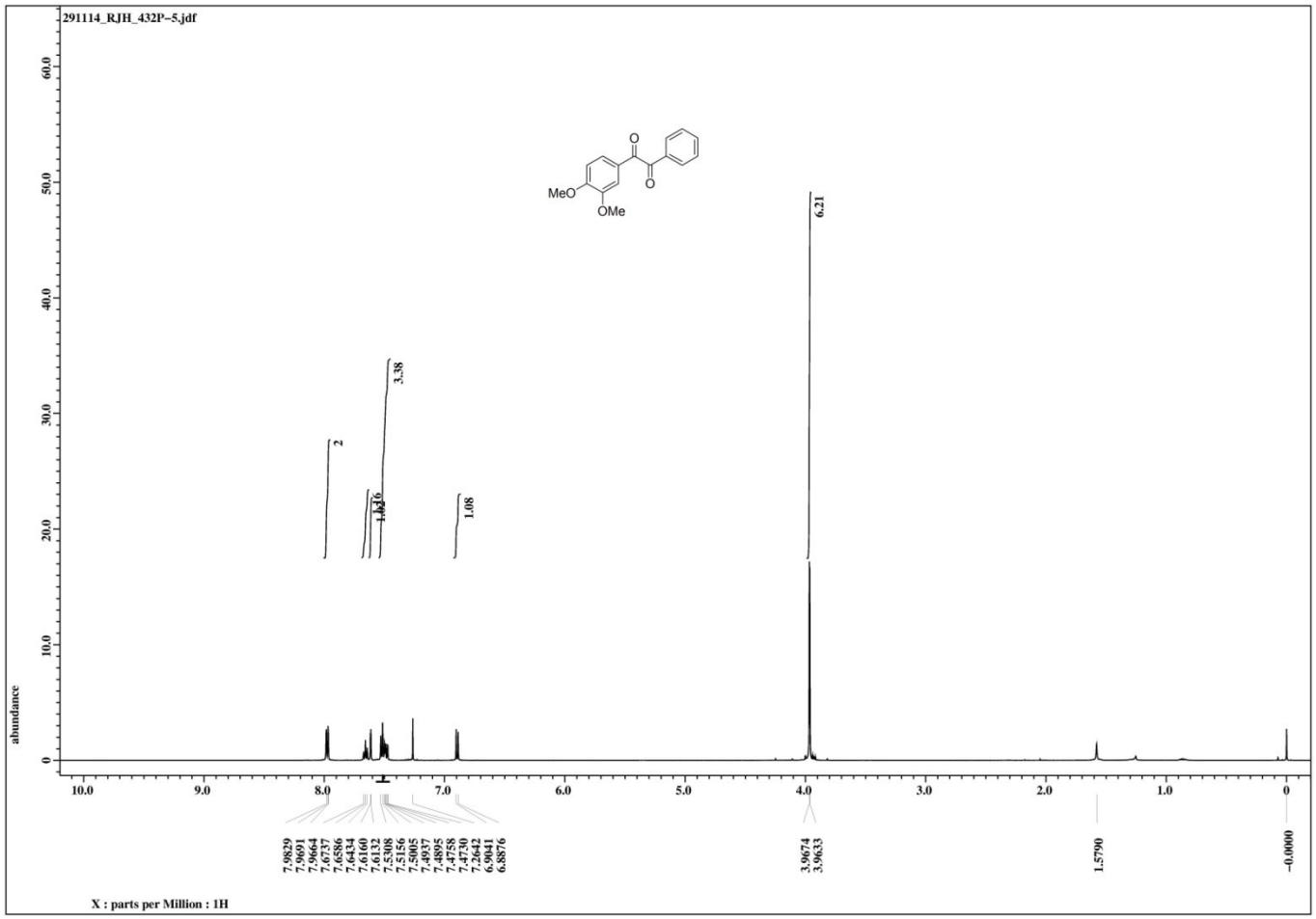


Table 1, (2b)-^{13}C-NMR (125 MHz, $CDCl_3$)

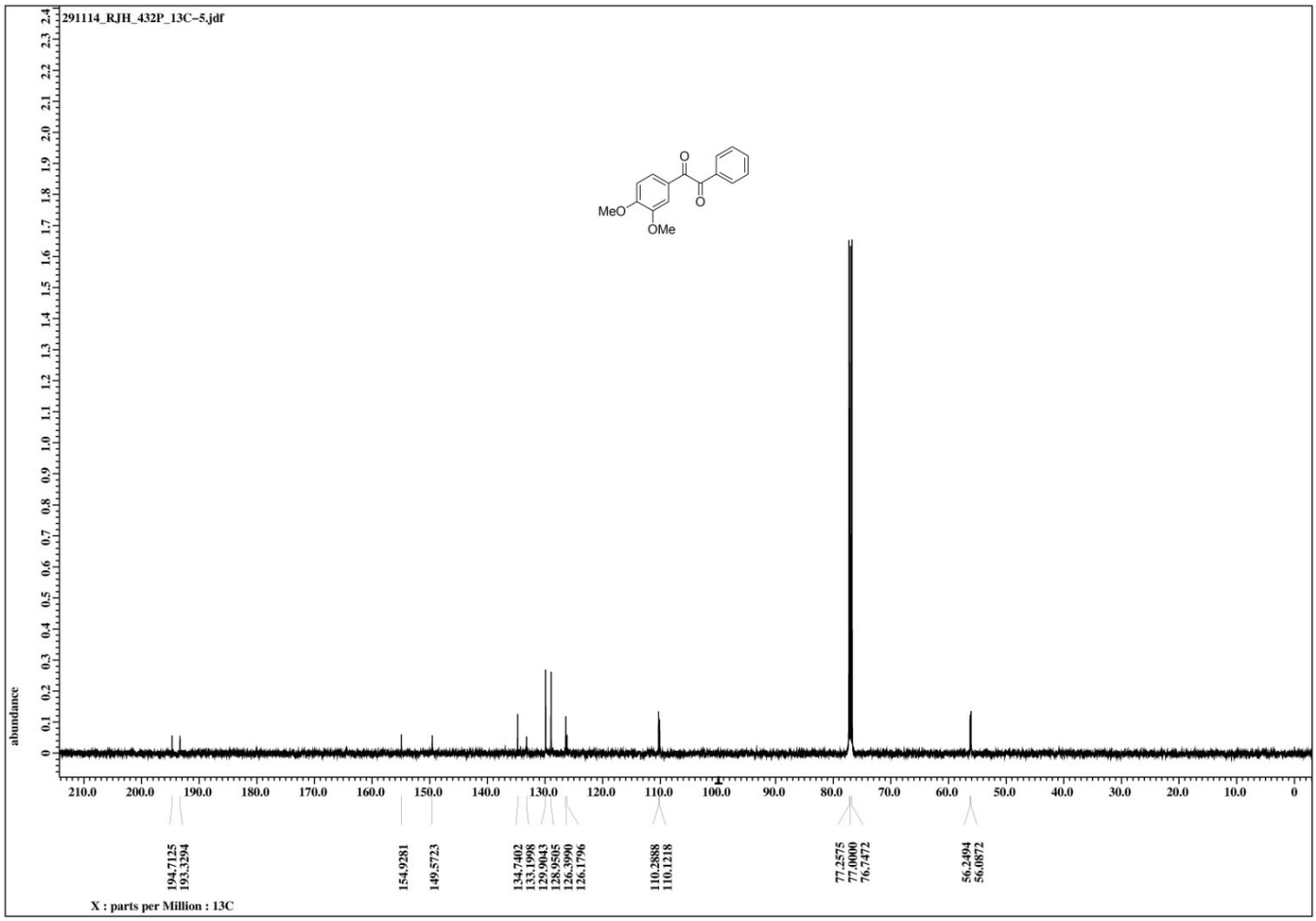


Table 1, (2c)-^{1}H-NMR (500MHz, $CDCl_3$)

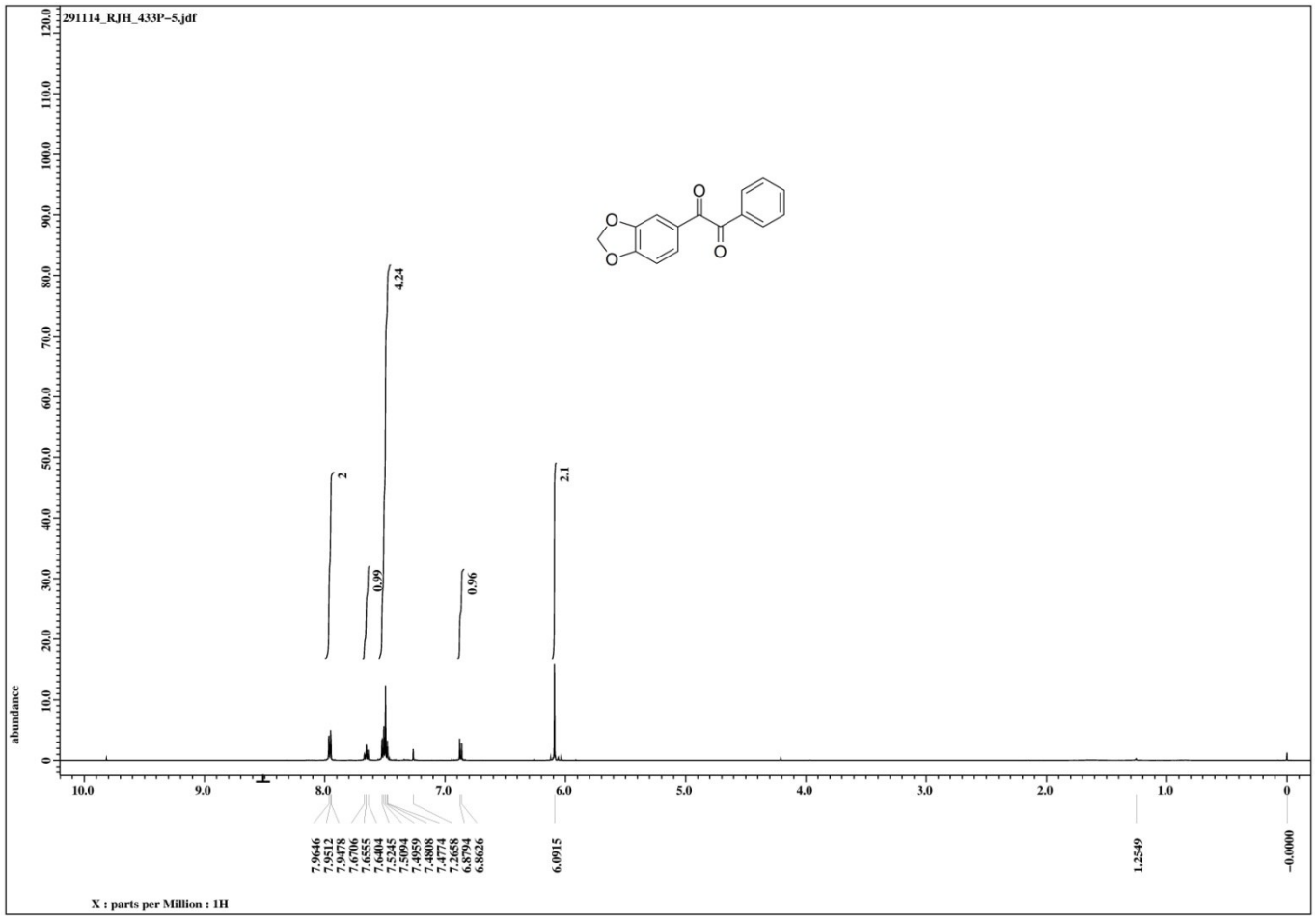


Table 1, (2c)-^{13}C-NMR (125 MHz, $CDCl_3$)

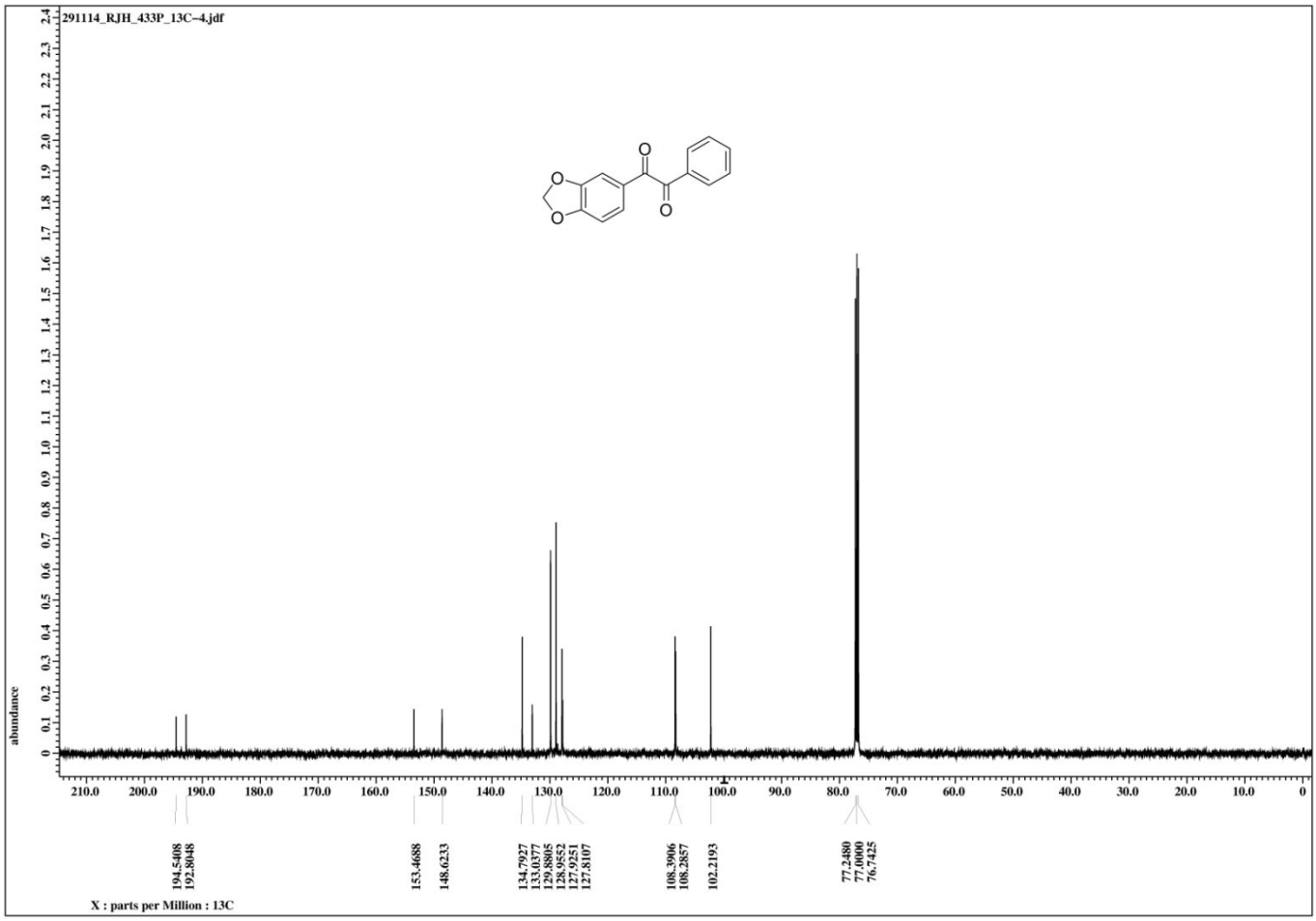


Table 1, (2d)-^{1}H-NMR (500MHz, $CDCl_3$)

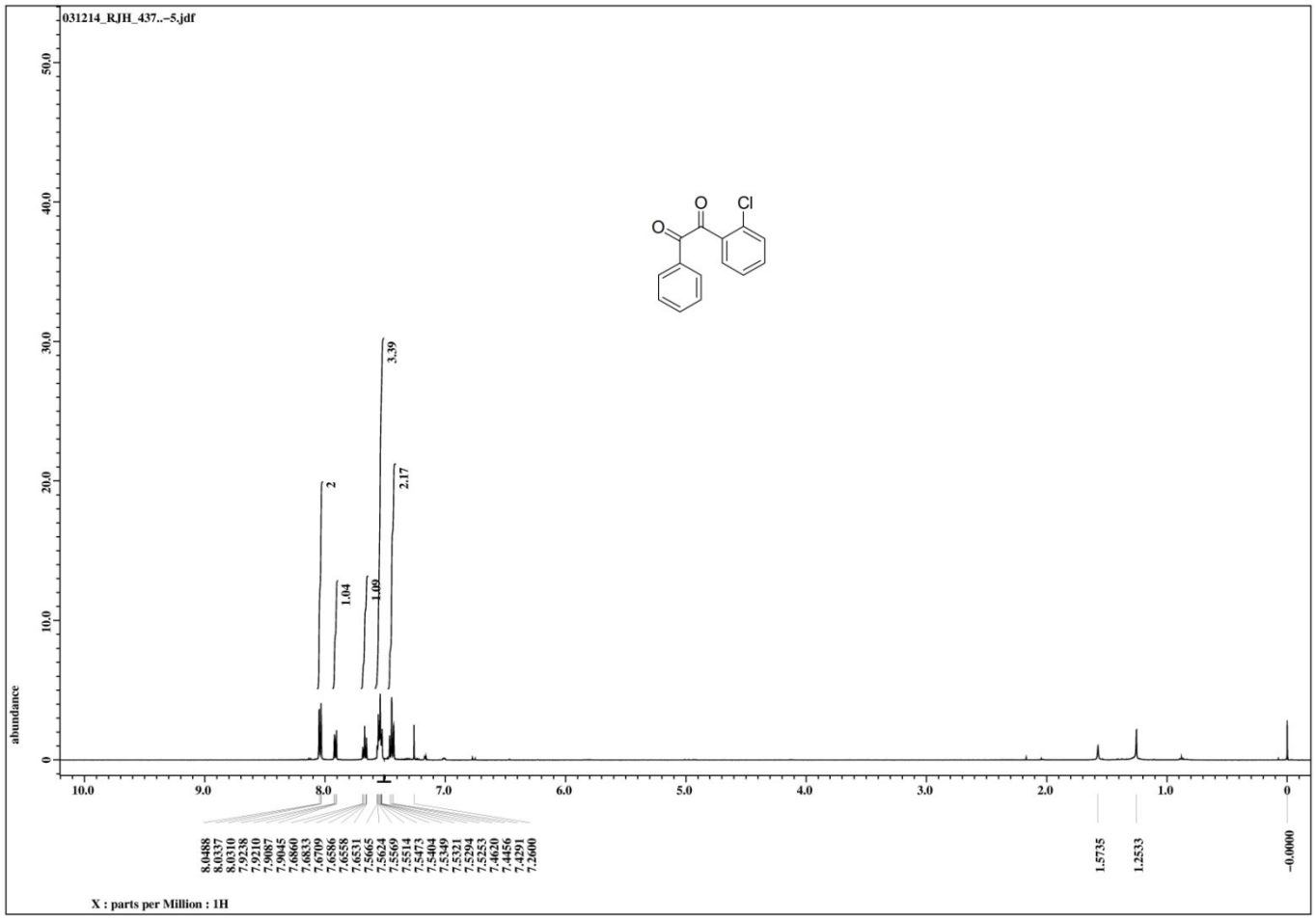


Table 1, (2d)-^{13}C-NMR (125 MHz, $CDCl_3$)

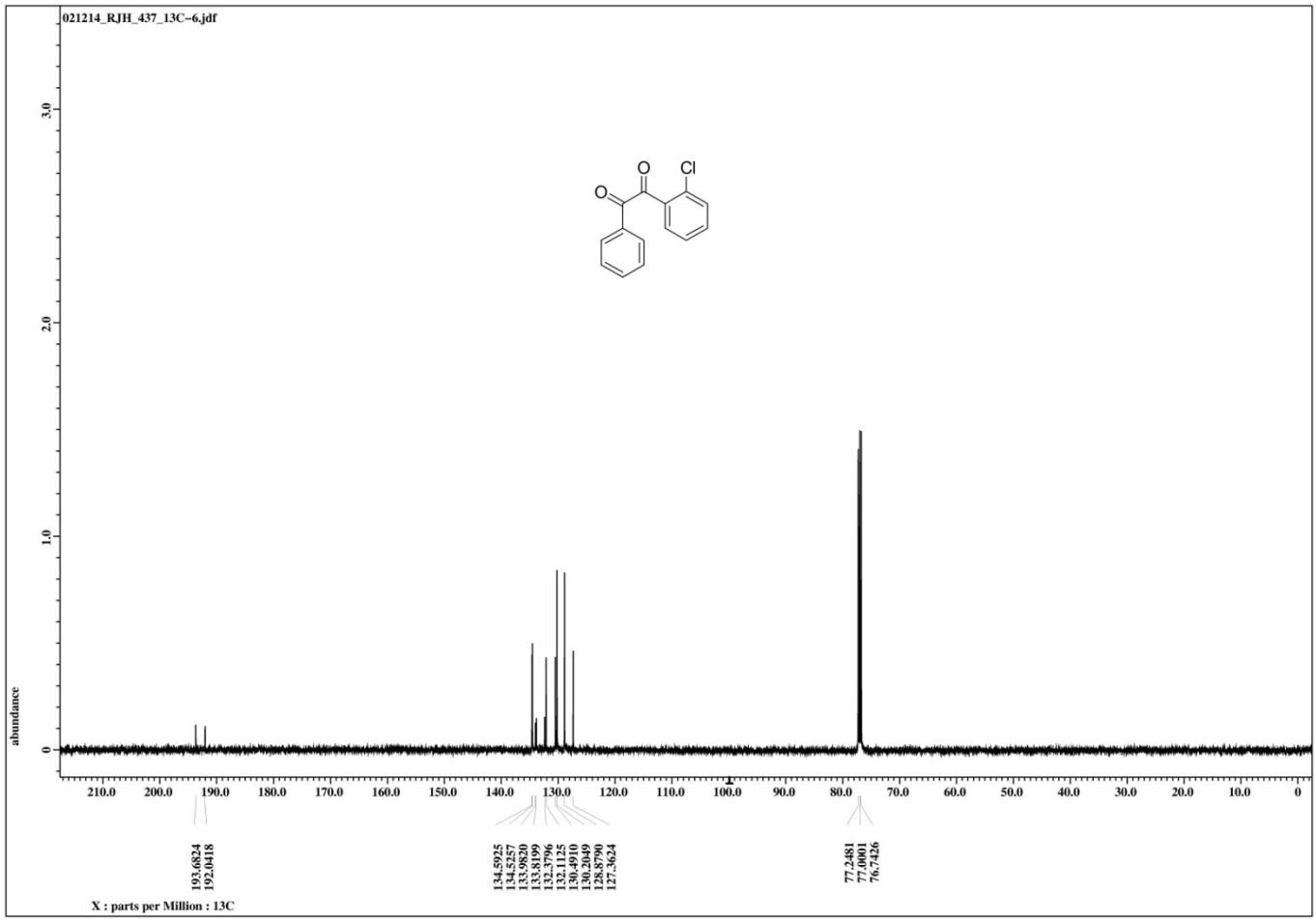


Table 1, (2e)-^{1}H-NMR (500MHz, $CDCl_3$)

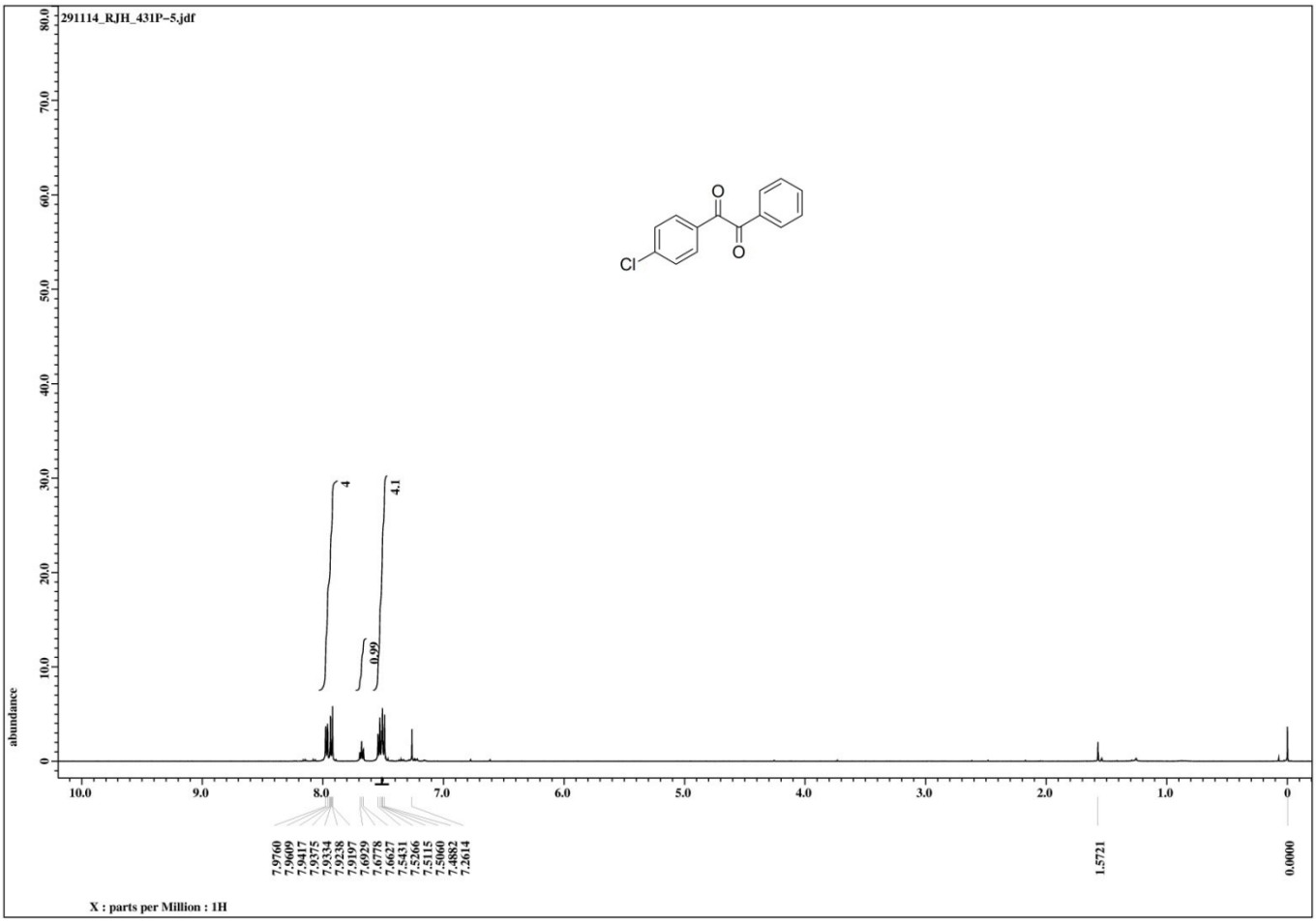


Table 1, (2e)-^{13}C-NMR (125 MHz, $CDCl_3$)

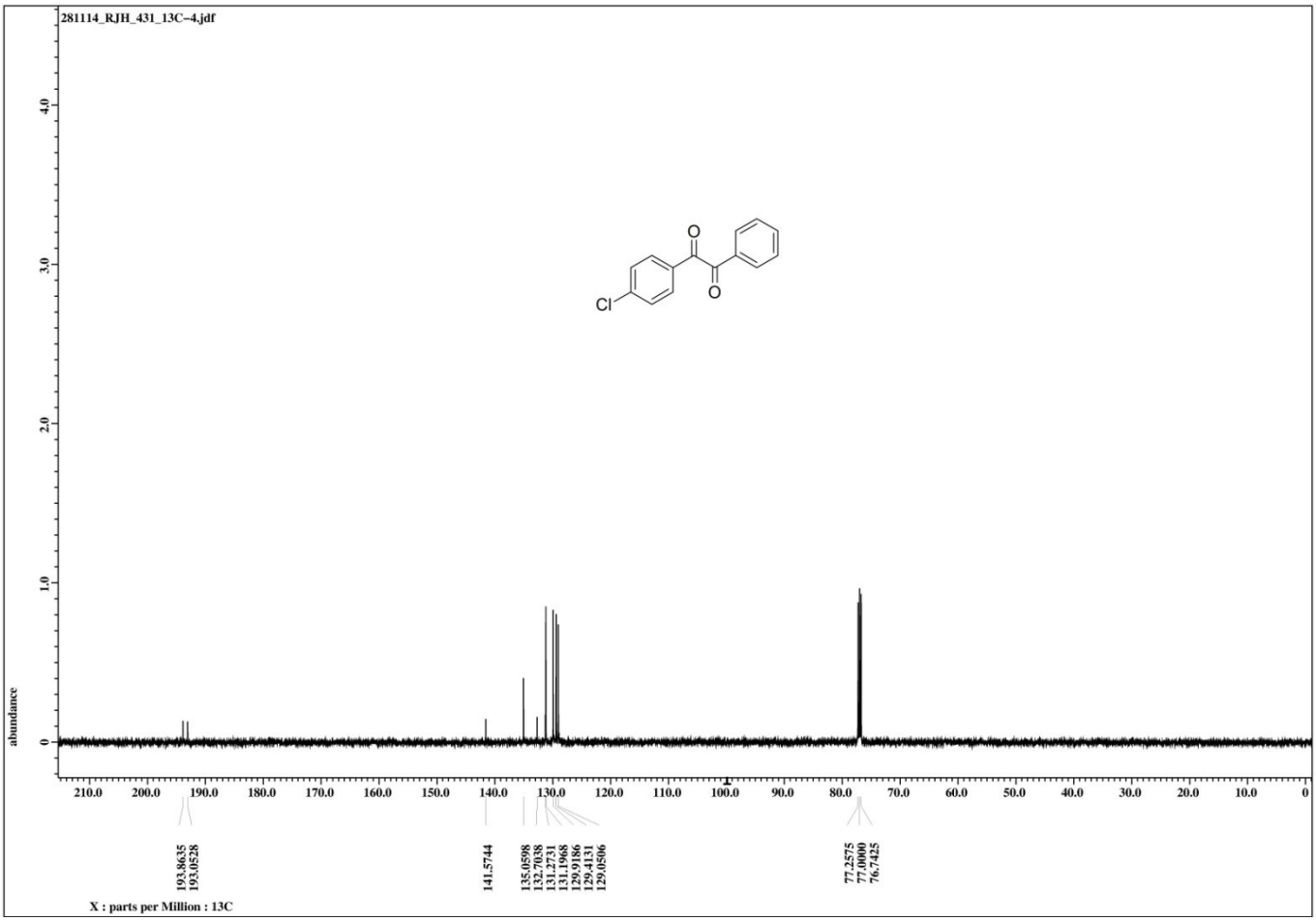


Table 1, (2f)-^{1}H-NMR (500MHz, $CDCl_3$)

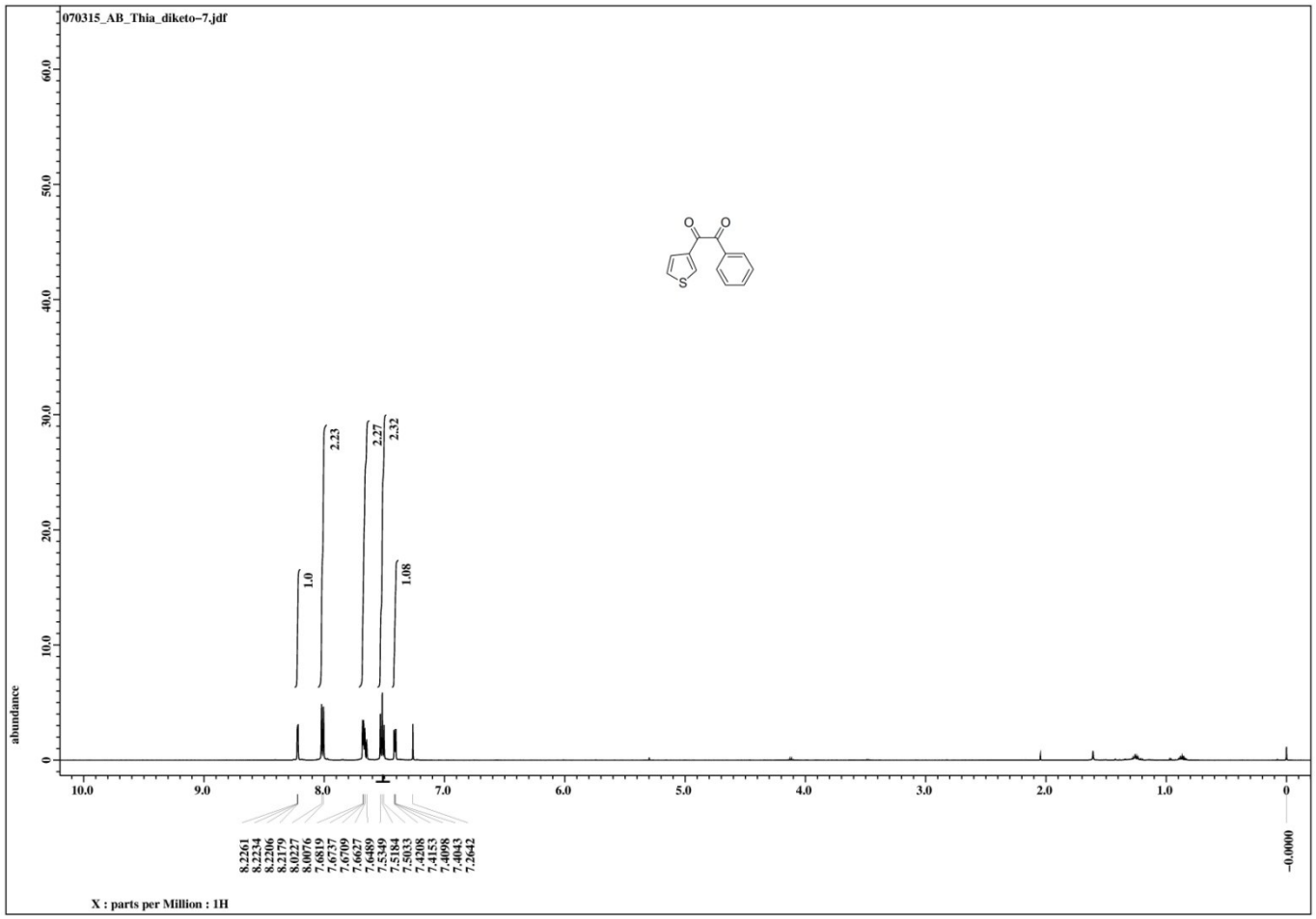


Table 1, (2f)-^{13}C-NMR (125 MHz, $CDCl_3$)

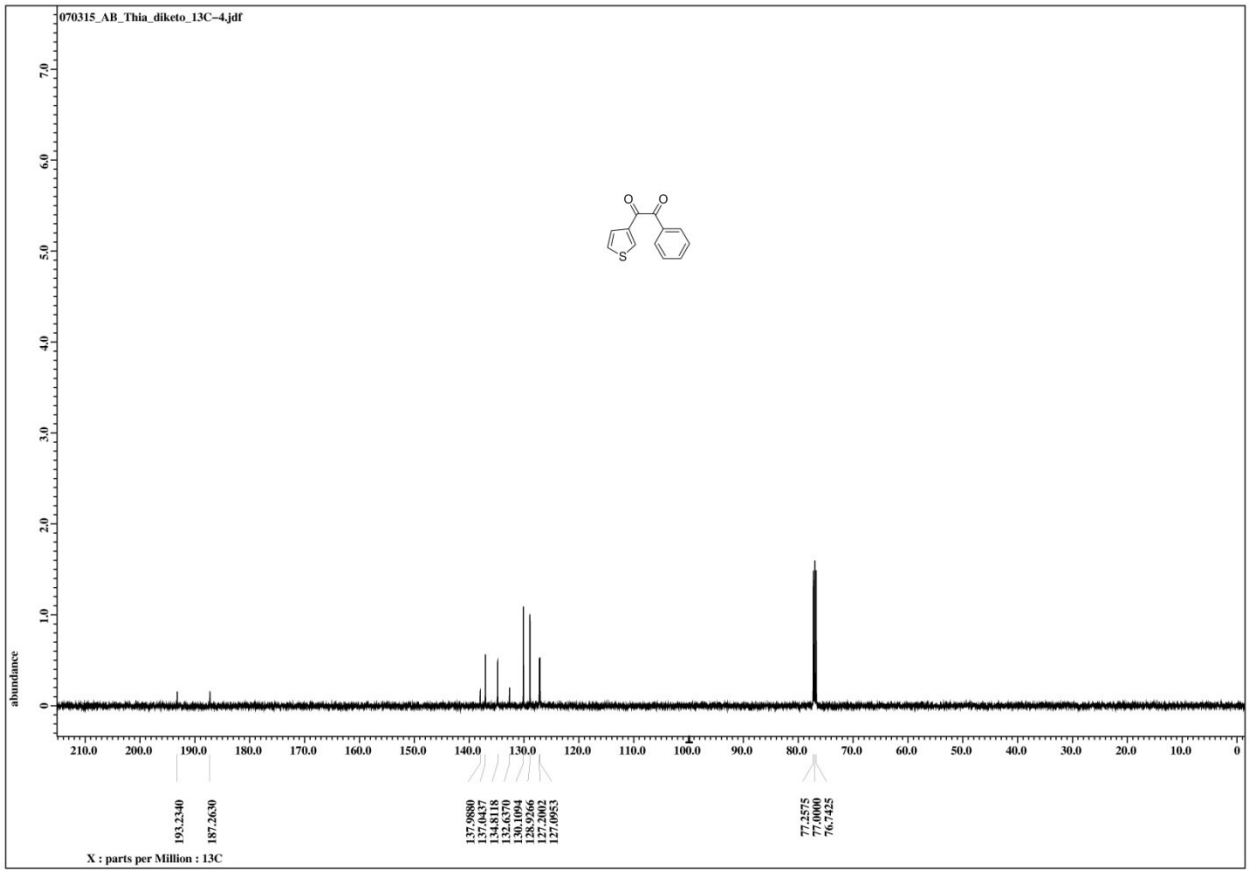


Table 1, (2g)-^{1}H-NMR (500MHz, $CDCl_3$)

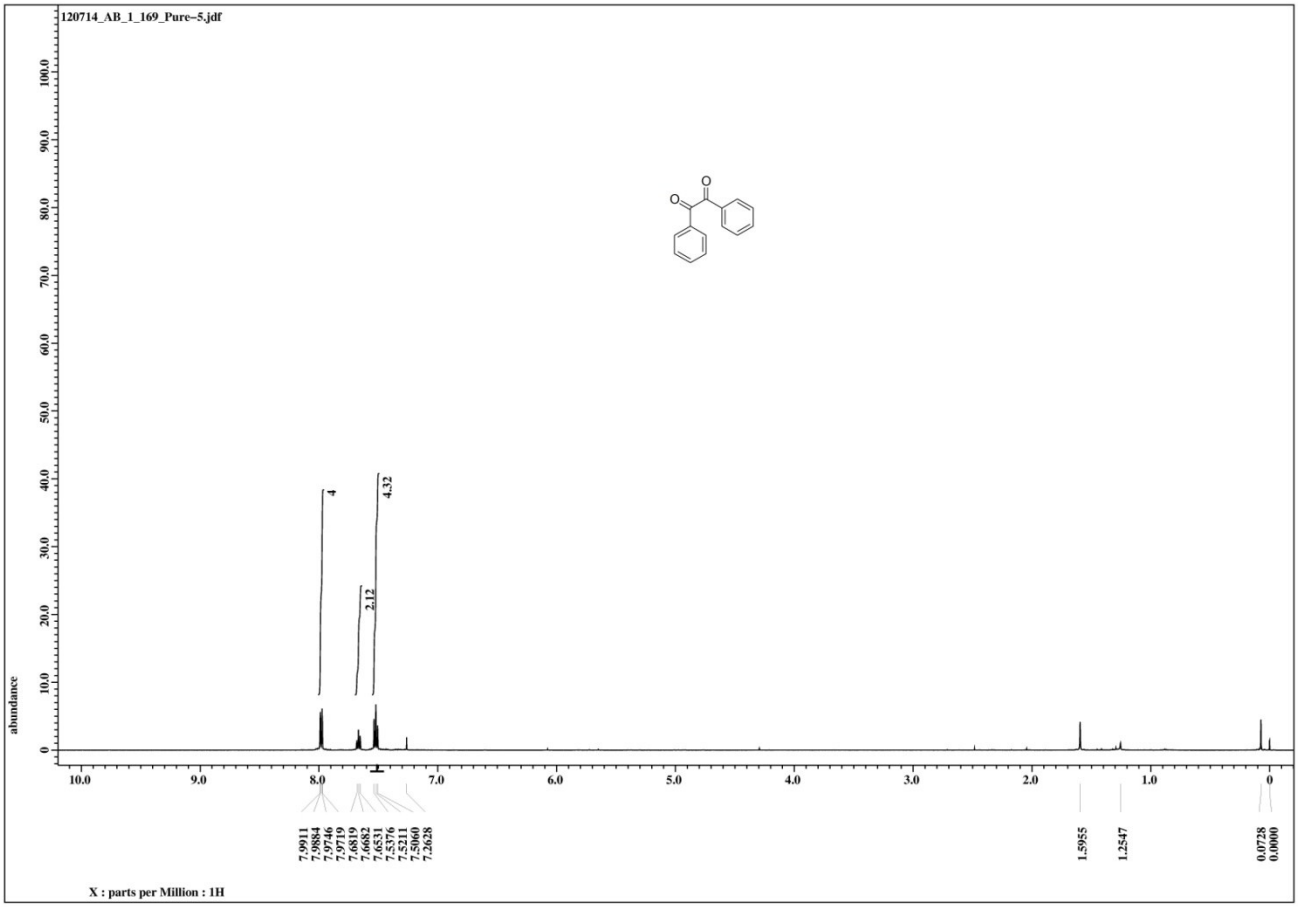


Table 1, (2g)-^{13}C-NMR (125 MHz, $CDCl_3$)

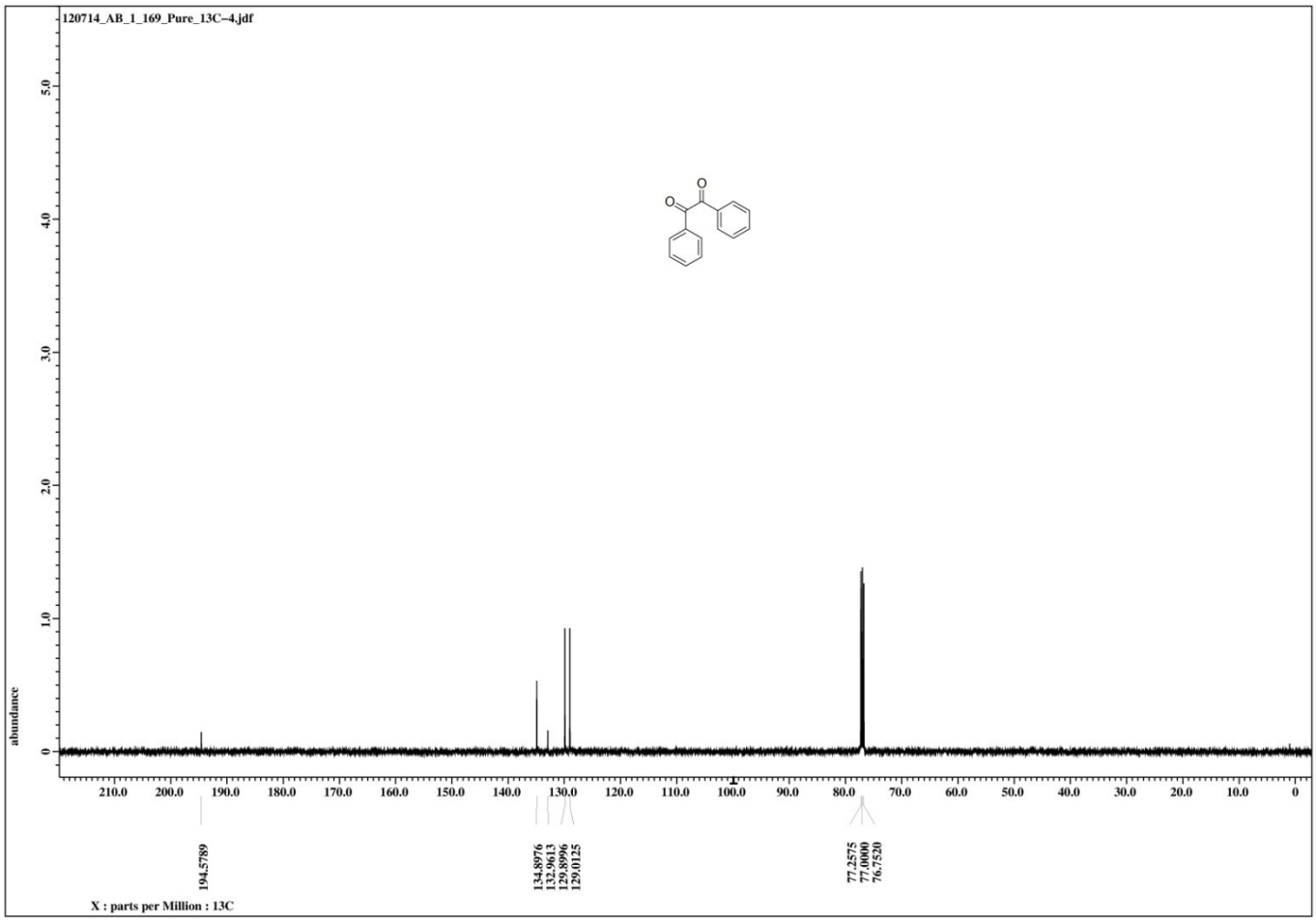


Table 1, (2h)-^{1}H-NMR (500MHz, $CDCl_3$)

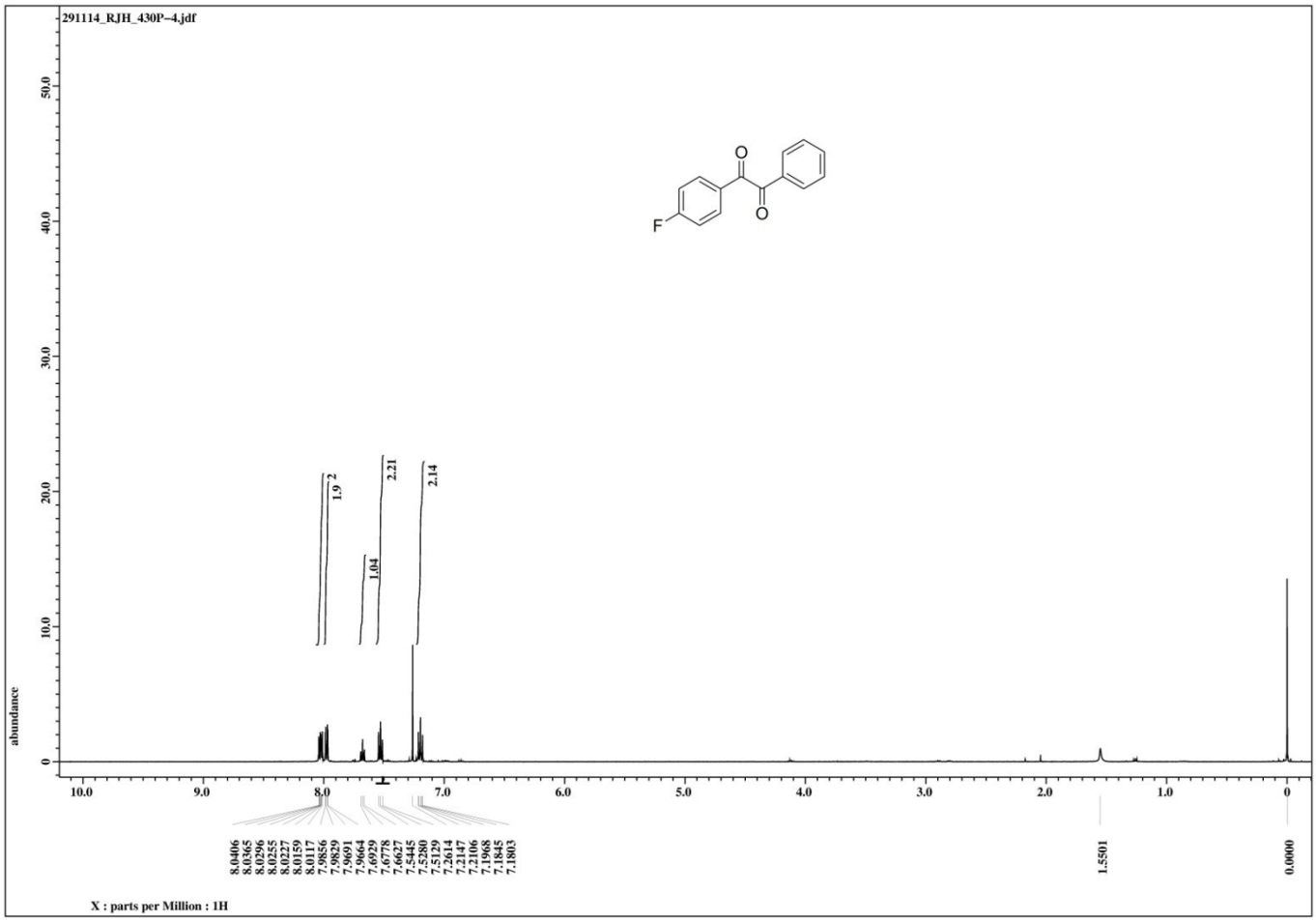


Table 1, (2h)-^{13}C-NMR (125 MHz, $CDCl_3$)

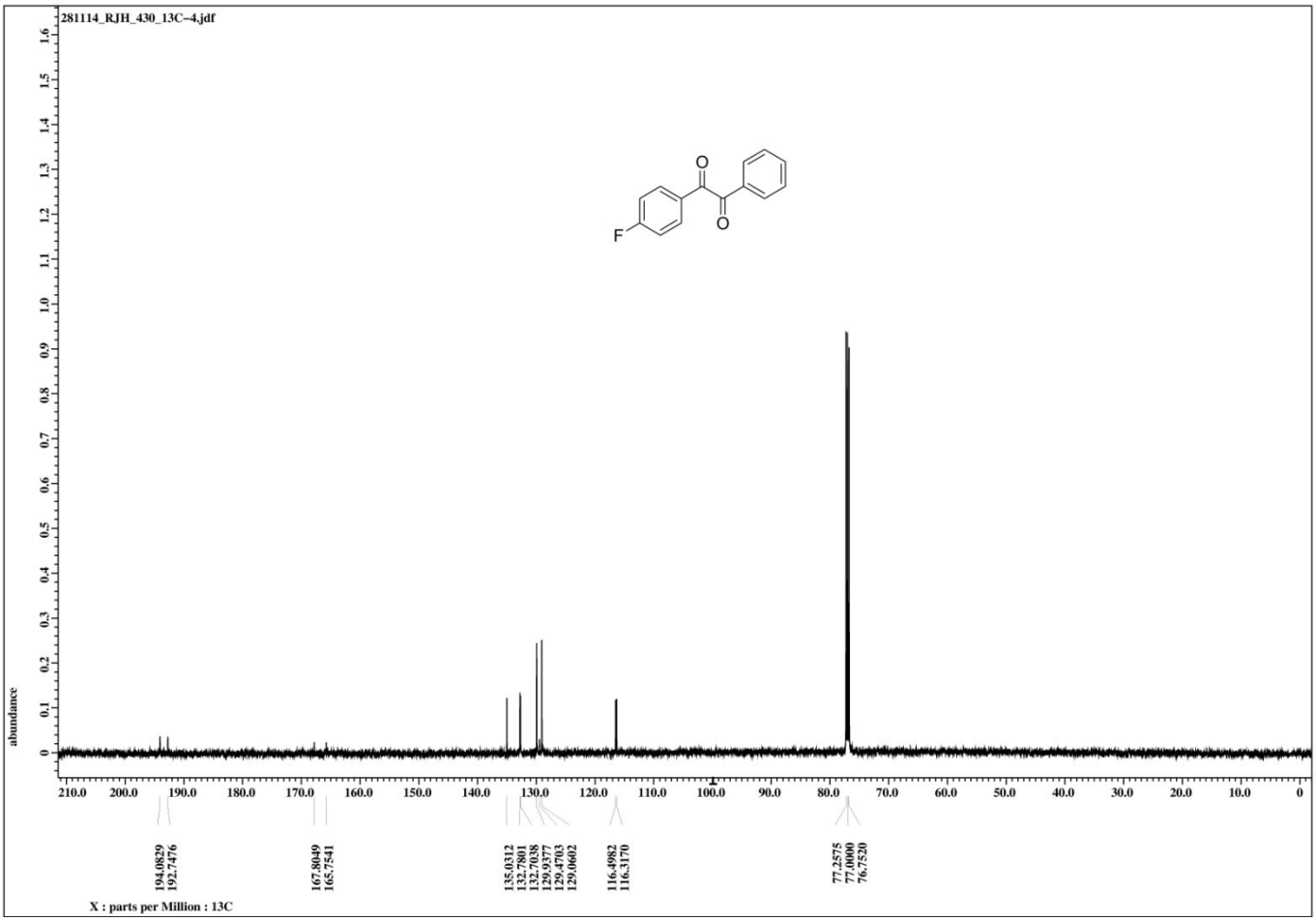


Table 1, (2l)-^{1}H-NMR (500MHz, $CDCl_3$)

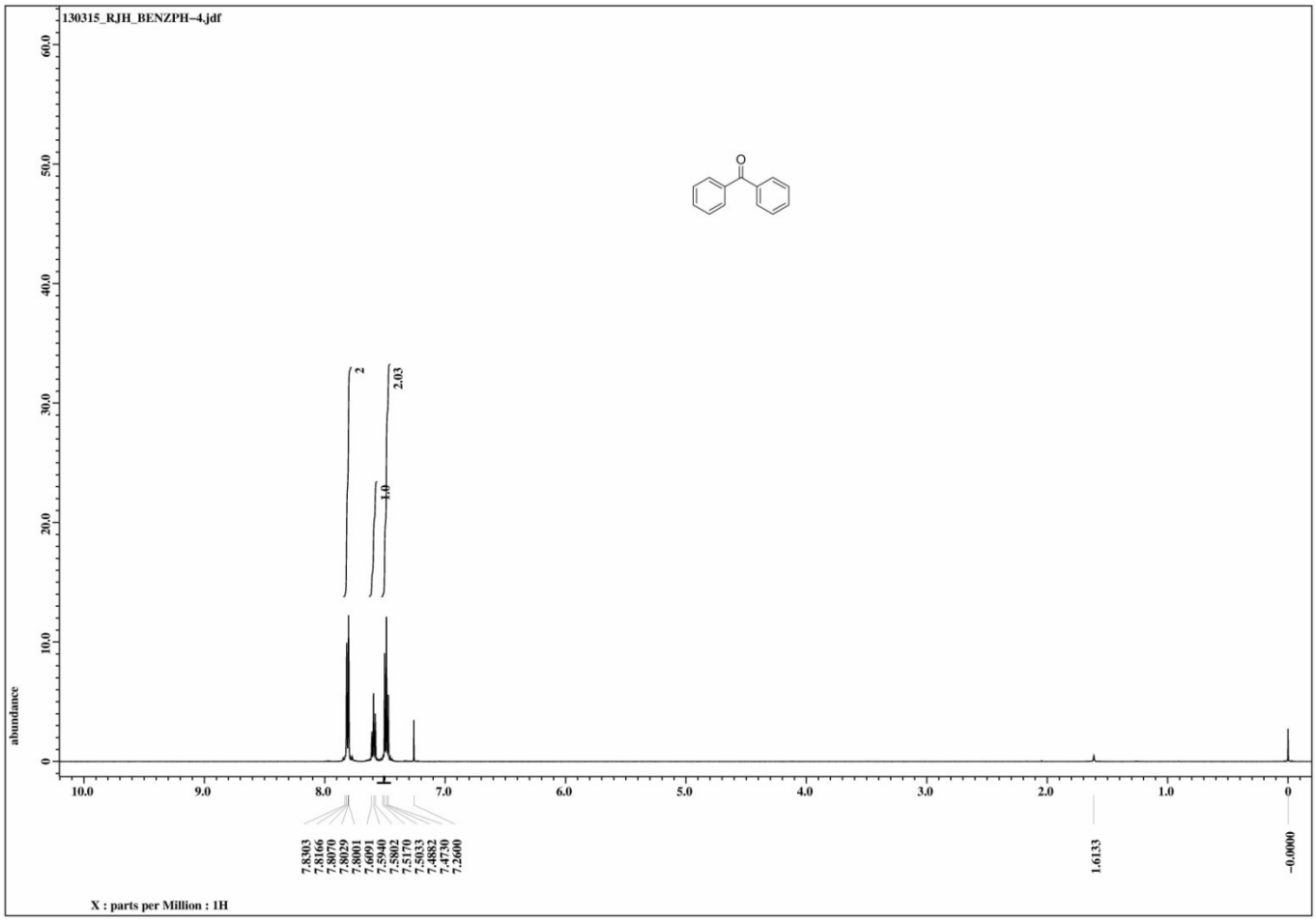


Table 1, (2l)-^{13}C-NMR (125 MHz, $CDCl_3$)

Table 1, (2m)-^{1}H-NMR (500MHz, $CDCl_3$)

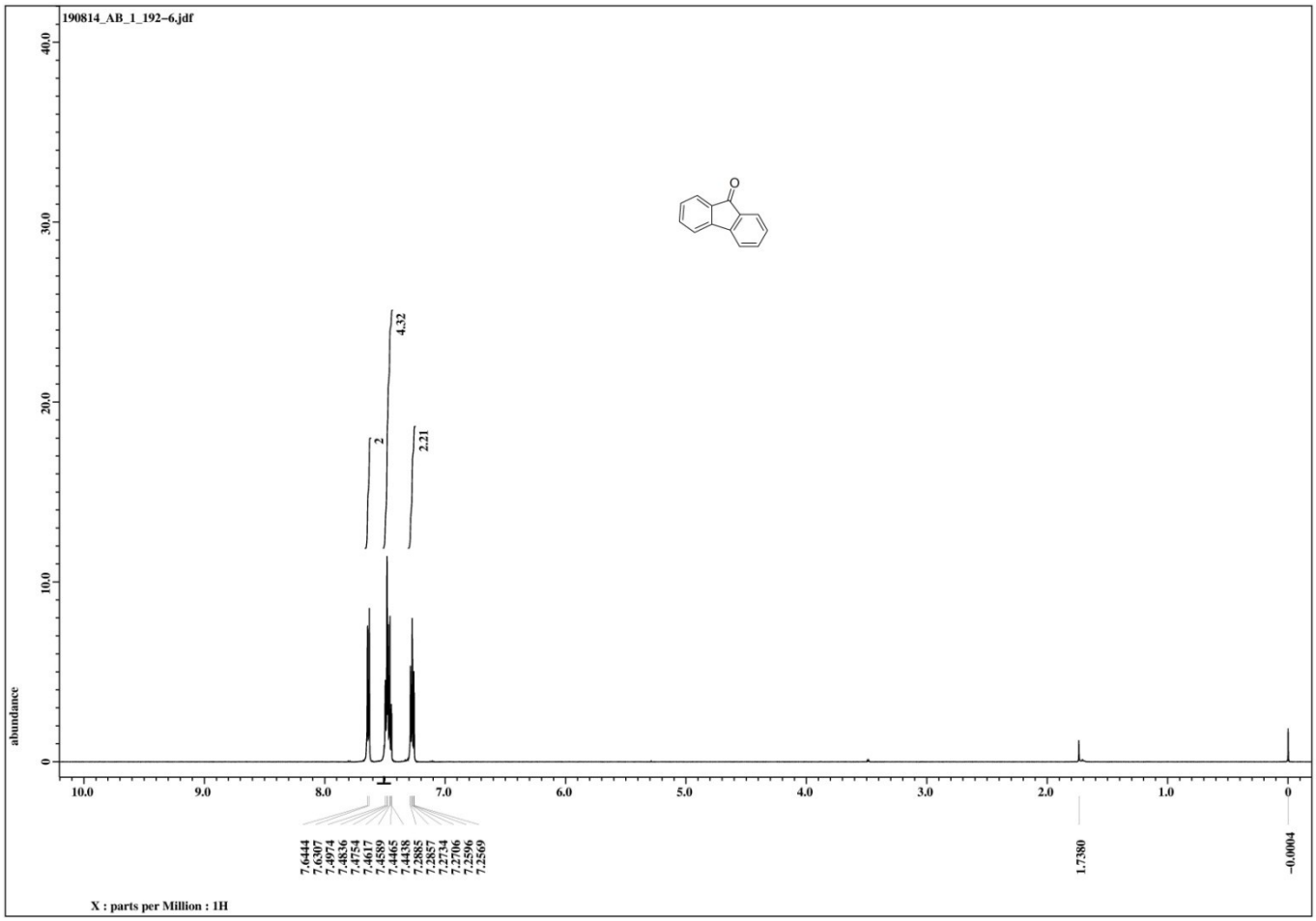


Table 1, (2m)-^{13}C-NMR (125 MHz, $CDCl_3$)

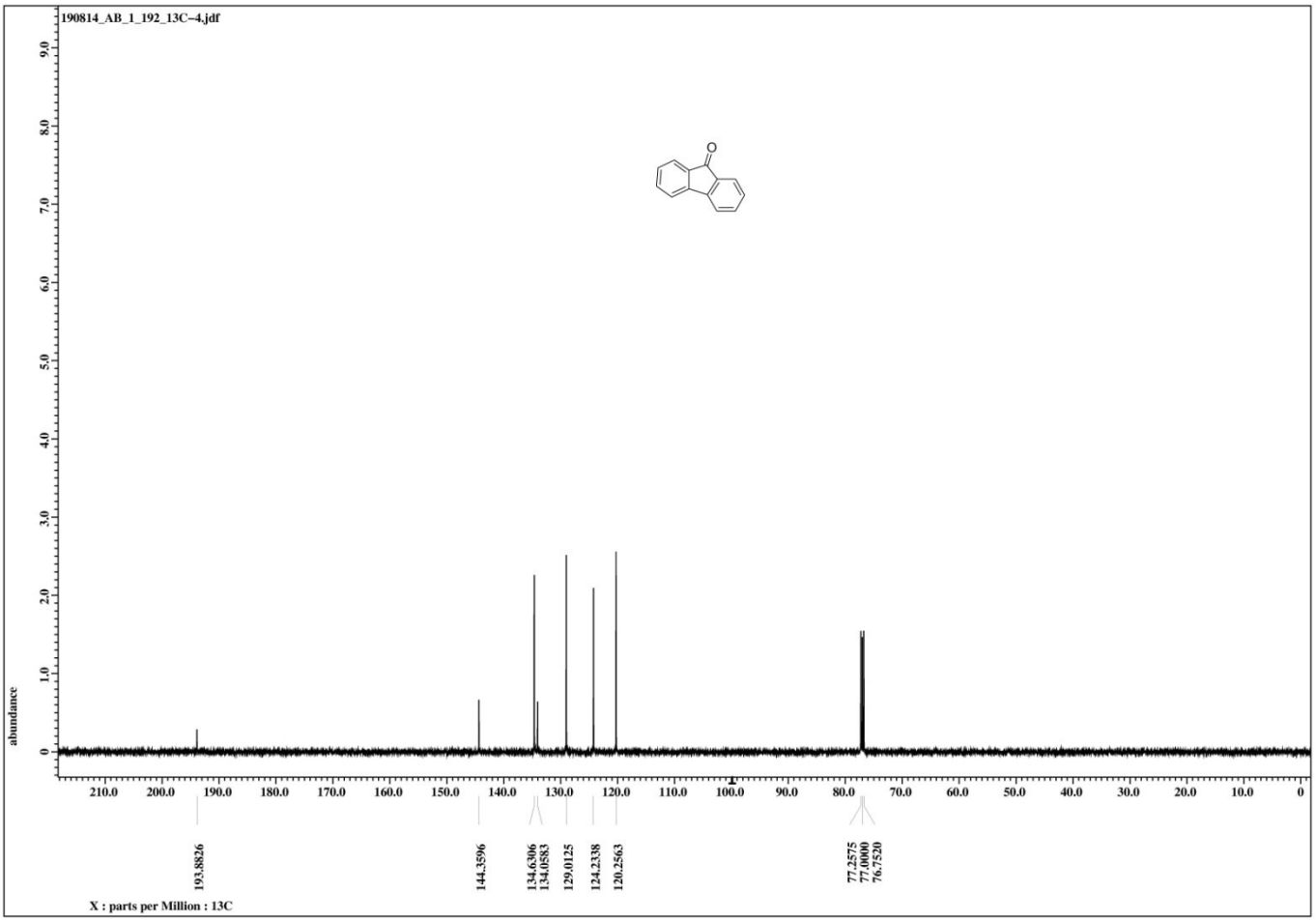


Table 2, (4d)-^{1}H-NMR (500MHz, $CDCl_3$)

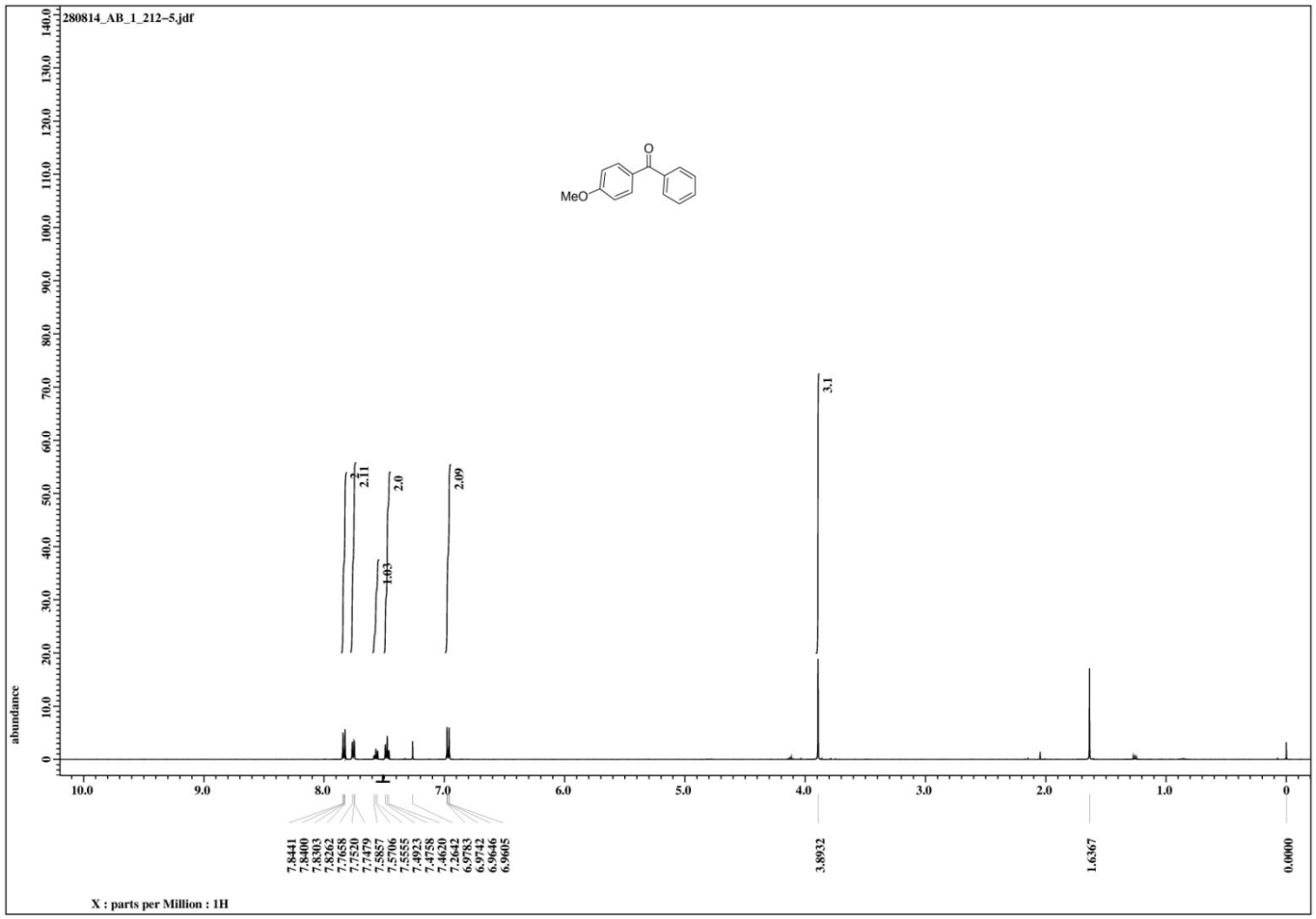


Table 2, (4d)-^{13}C-NMR (125 MHz, $CDCl_3$)

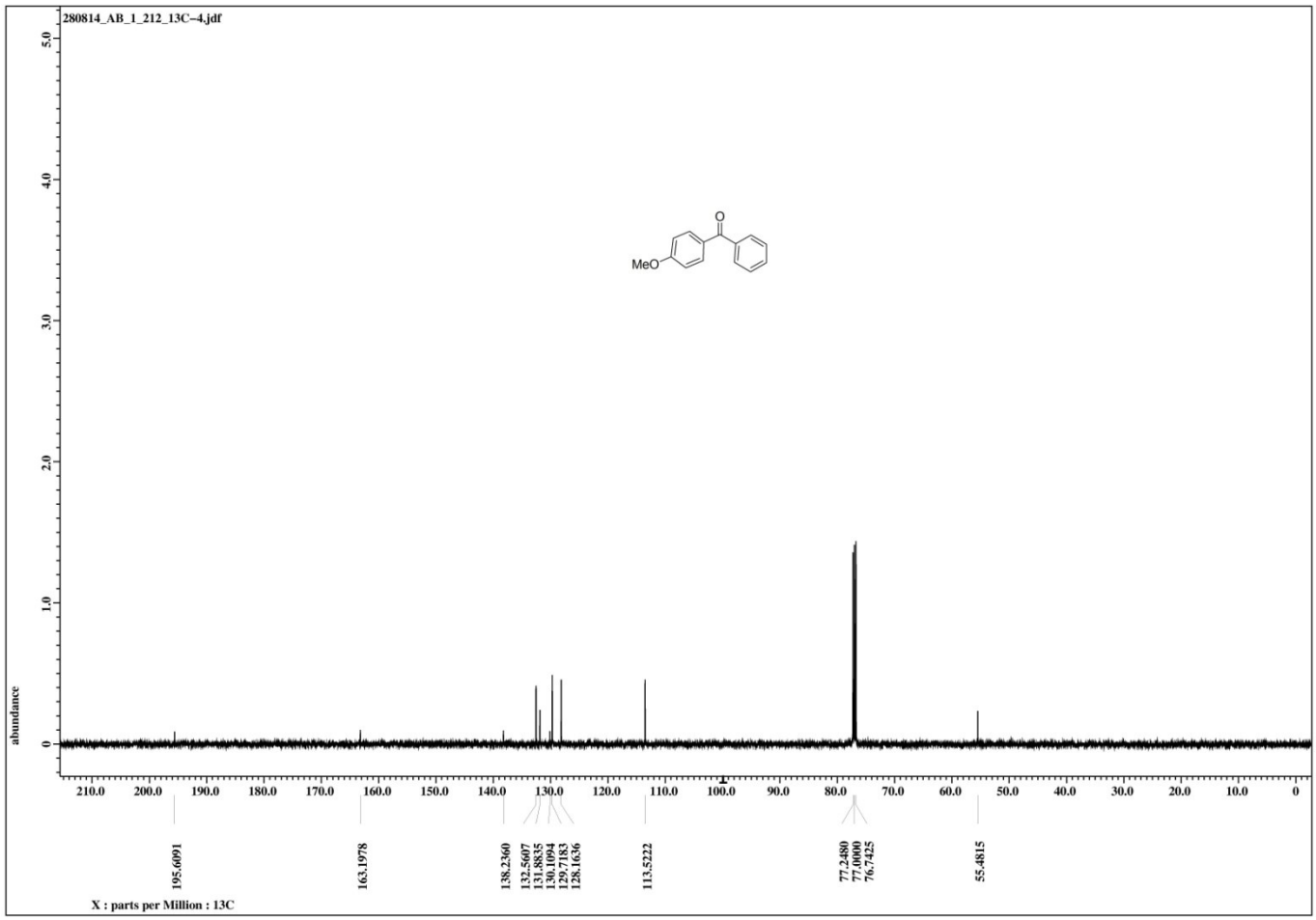


Table 2, (4e)-^{1}H-NMR (500MHz, $CDCl_3$)

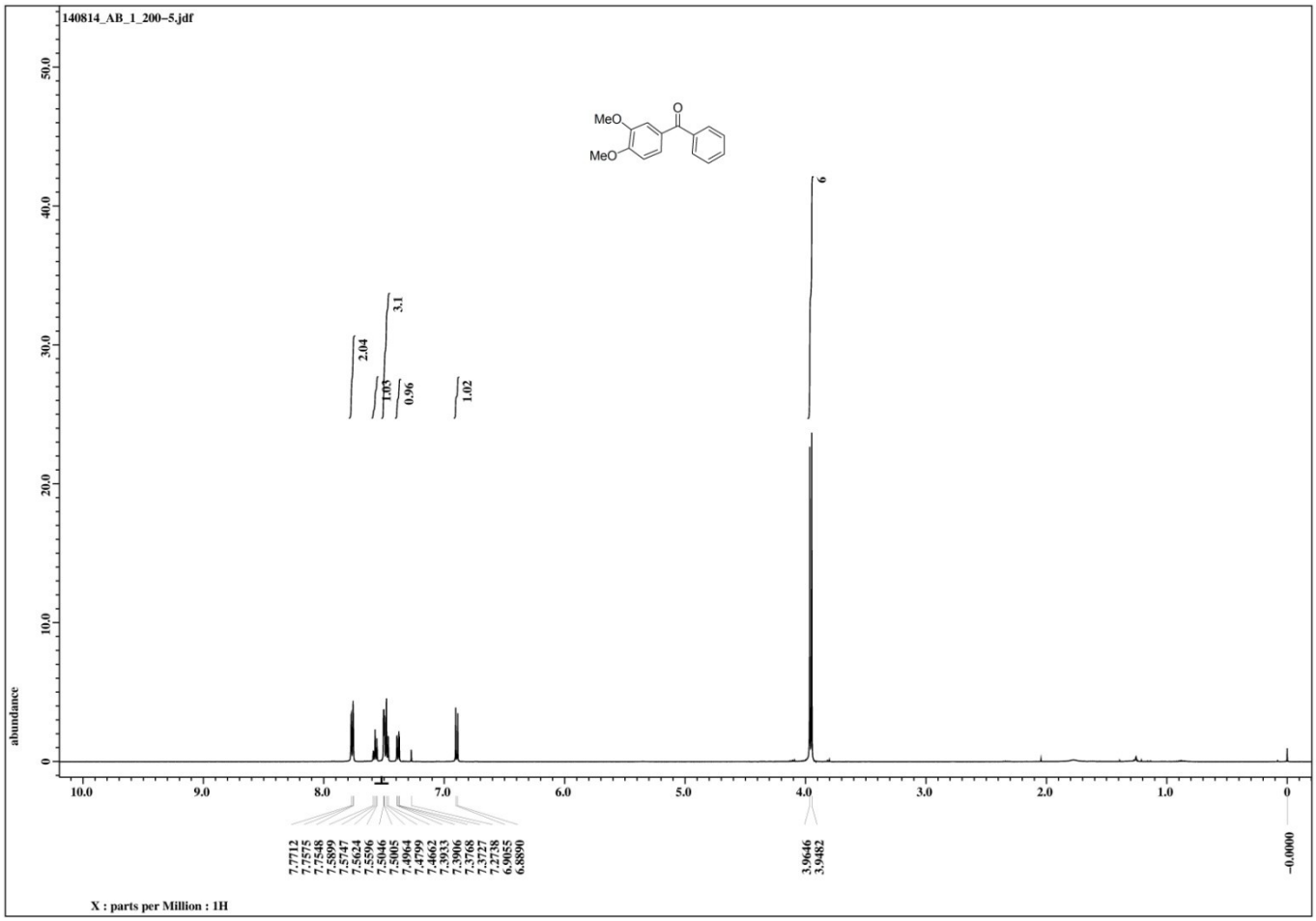


Table 2, (4e)-^{13}C-NMR (125 MHz, $CDCl_3$)

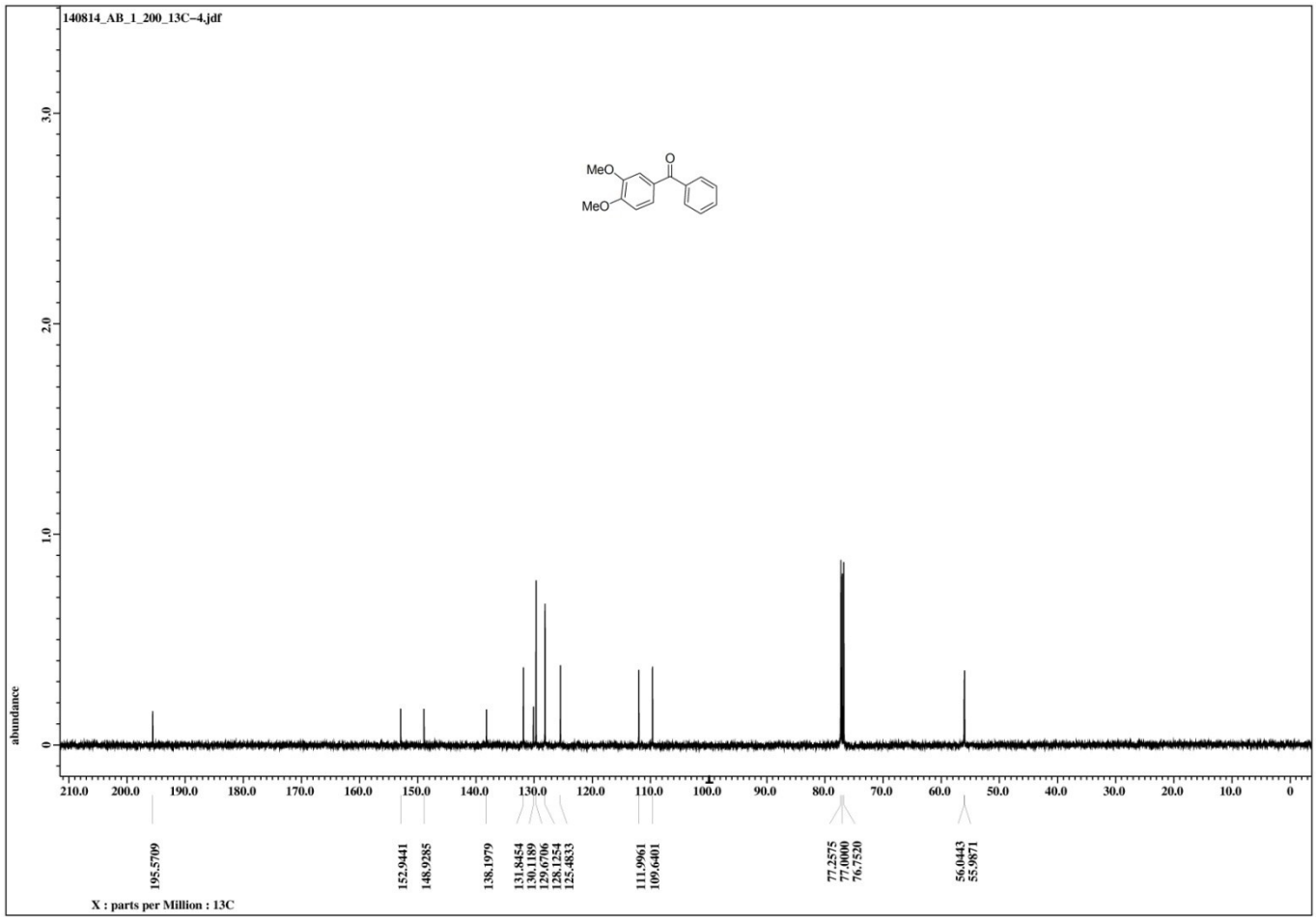


Table 2, (4f)-^{1}H-NMR (500MHz, $CDCl_3$)

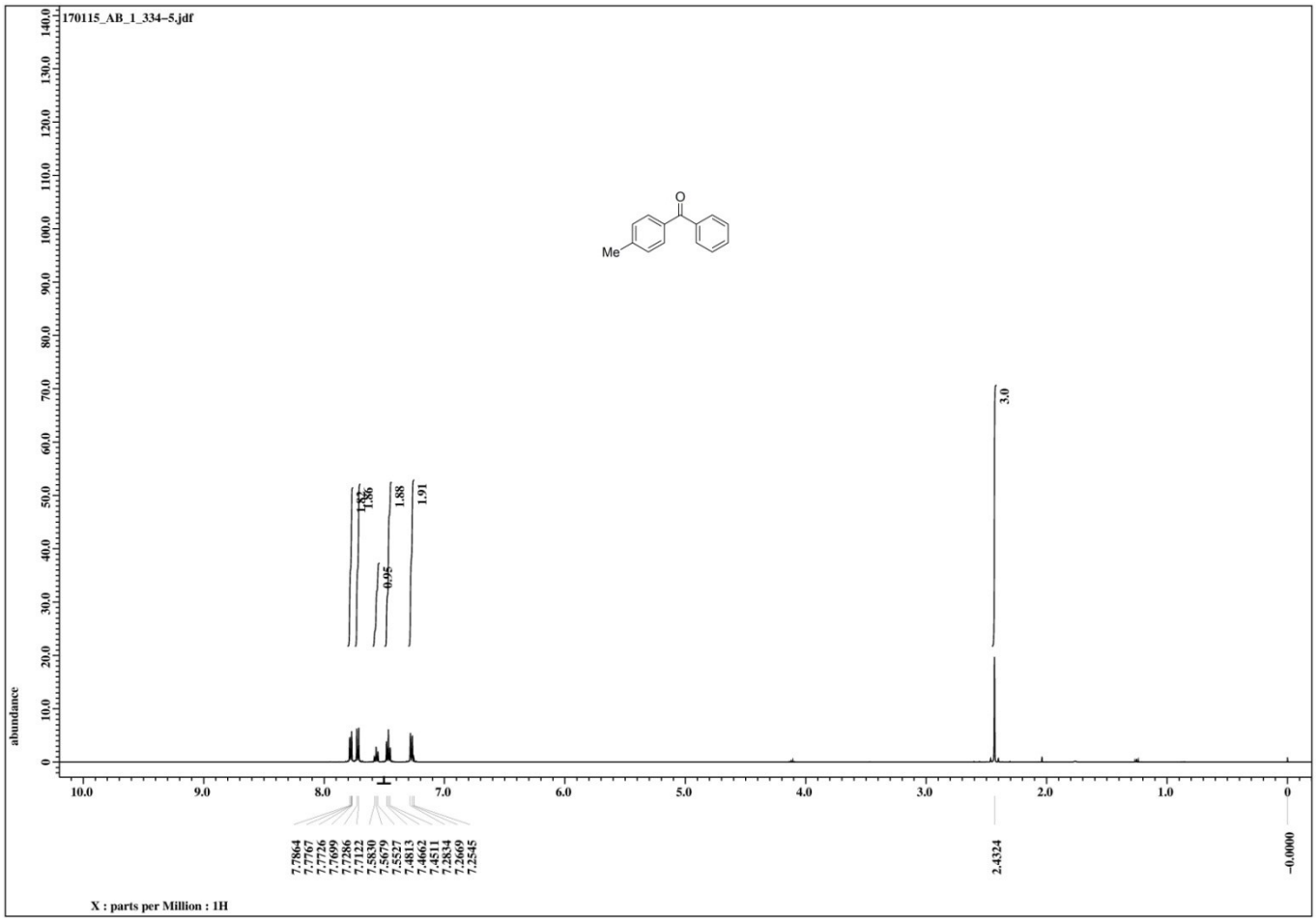


Table 2, (4f)-^{13}C-NMR (125 MHz, $CDCl_3$)

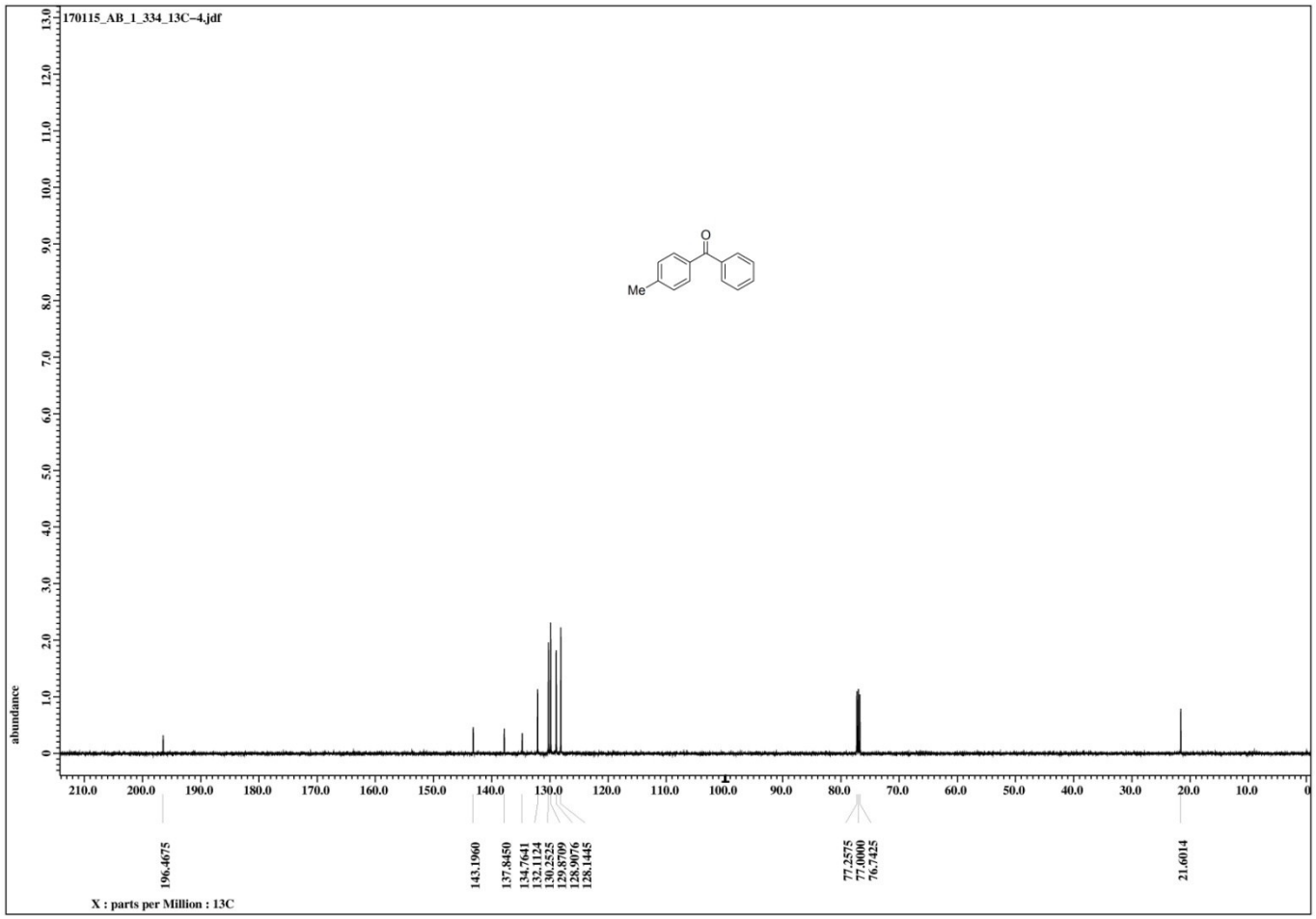


Table 2, (4g)-^{1}H-NMR (500MHz, $CDCl_3$)

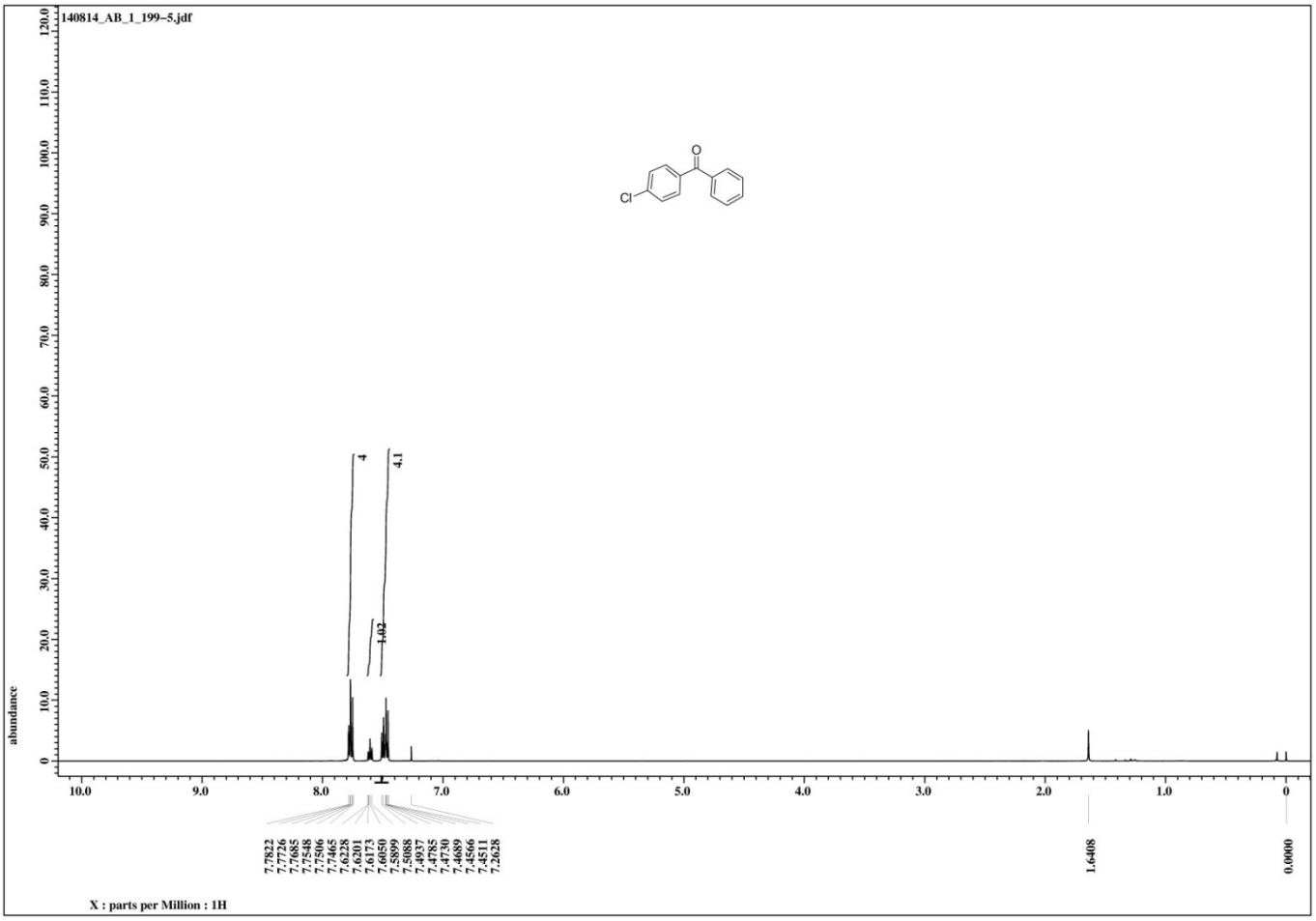


Table 2, (4g)-^{13}C-NMR (125 MHz, $CDCl_3$)

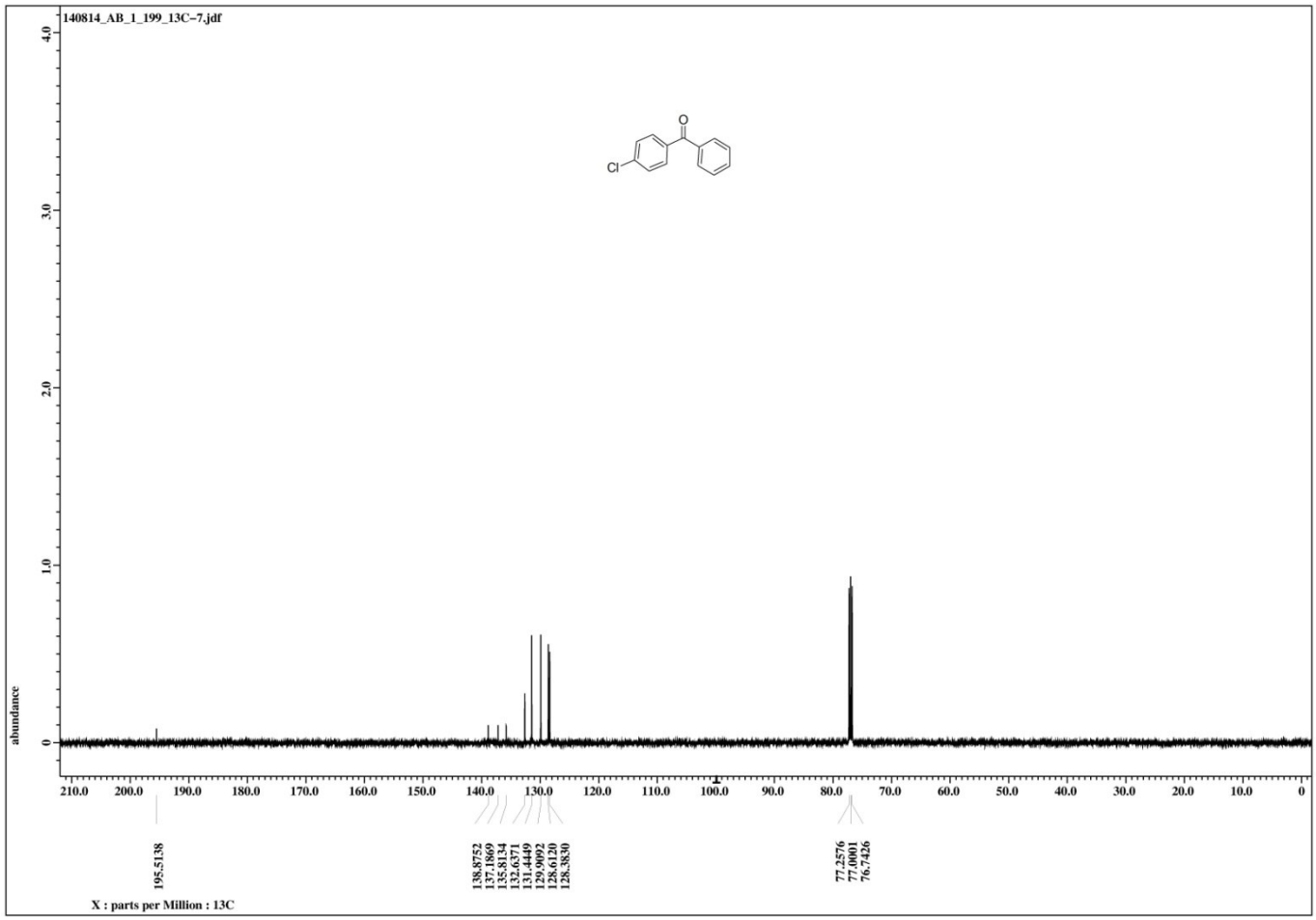


Table 2, (4h)-^{1}H-NMR (500 MHz, $CDCl_3$)

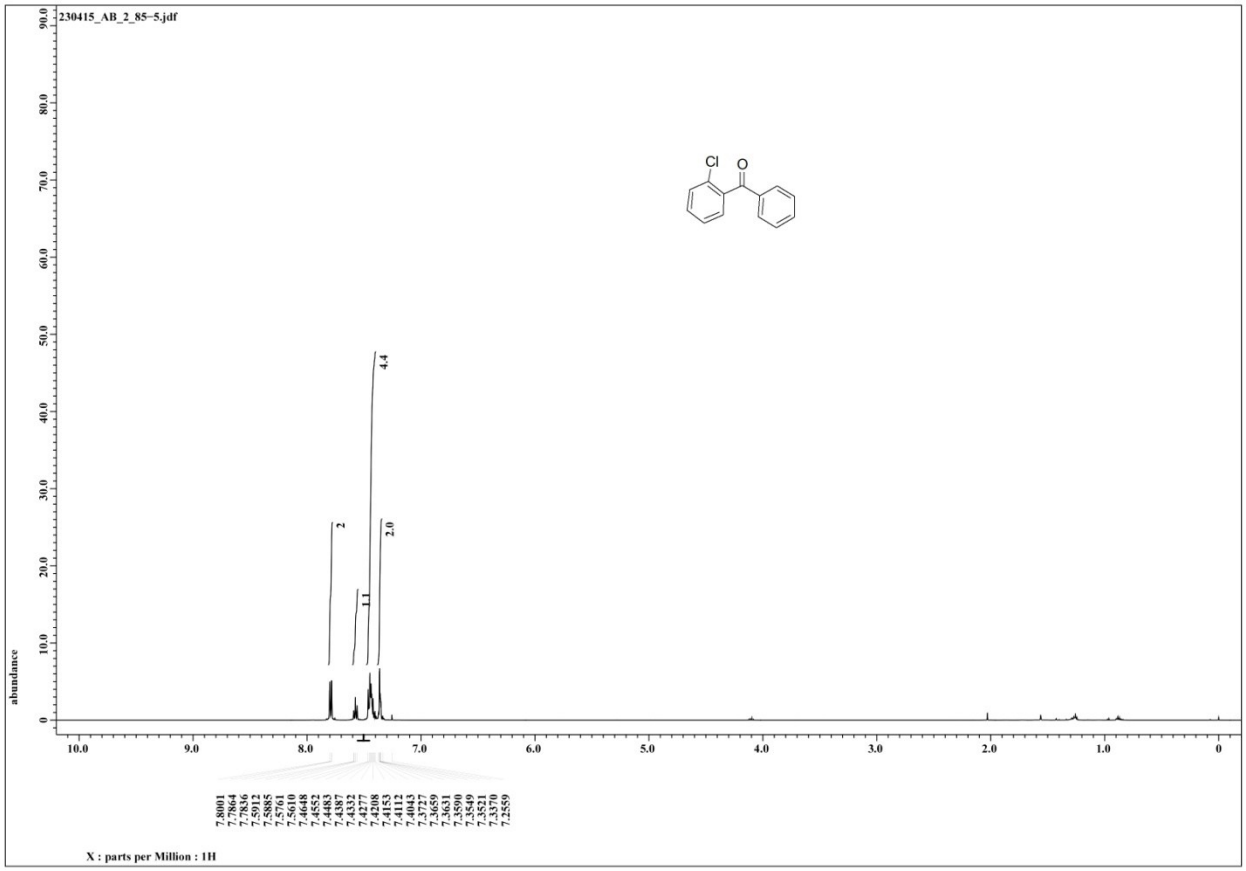


Table 2, (4h)-^{13}C-NMR (125 MHz, $CDCl_3$)

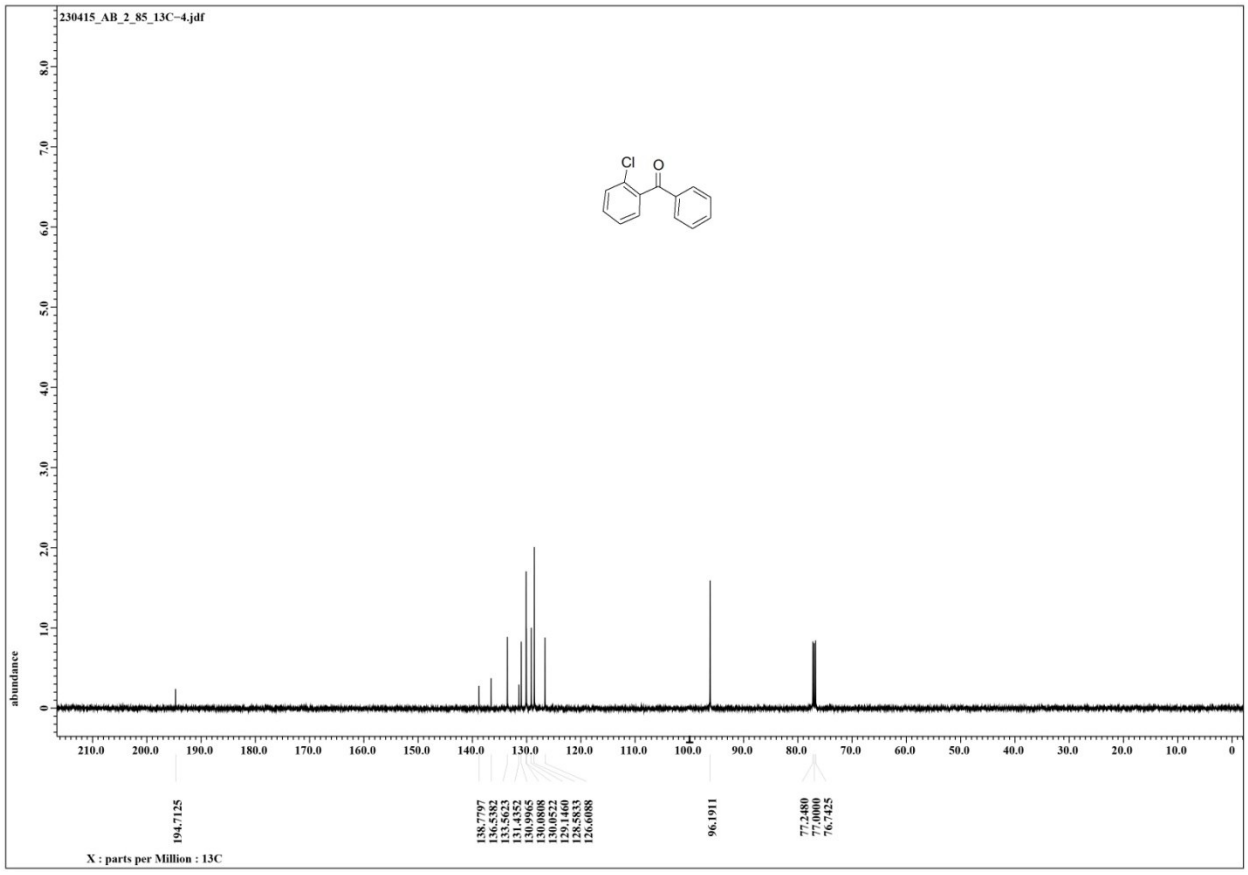


Table 2, (4i)-^{1}H-NMR (500MHz, $CDCl_3$)

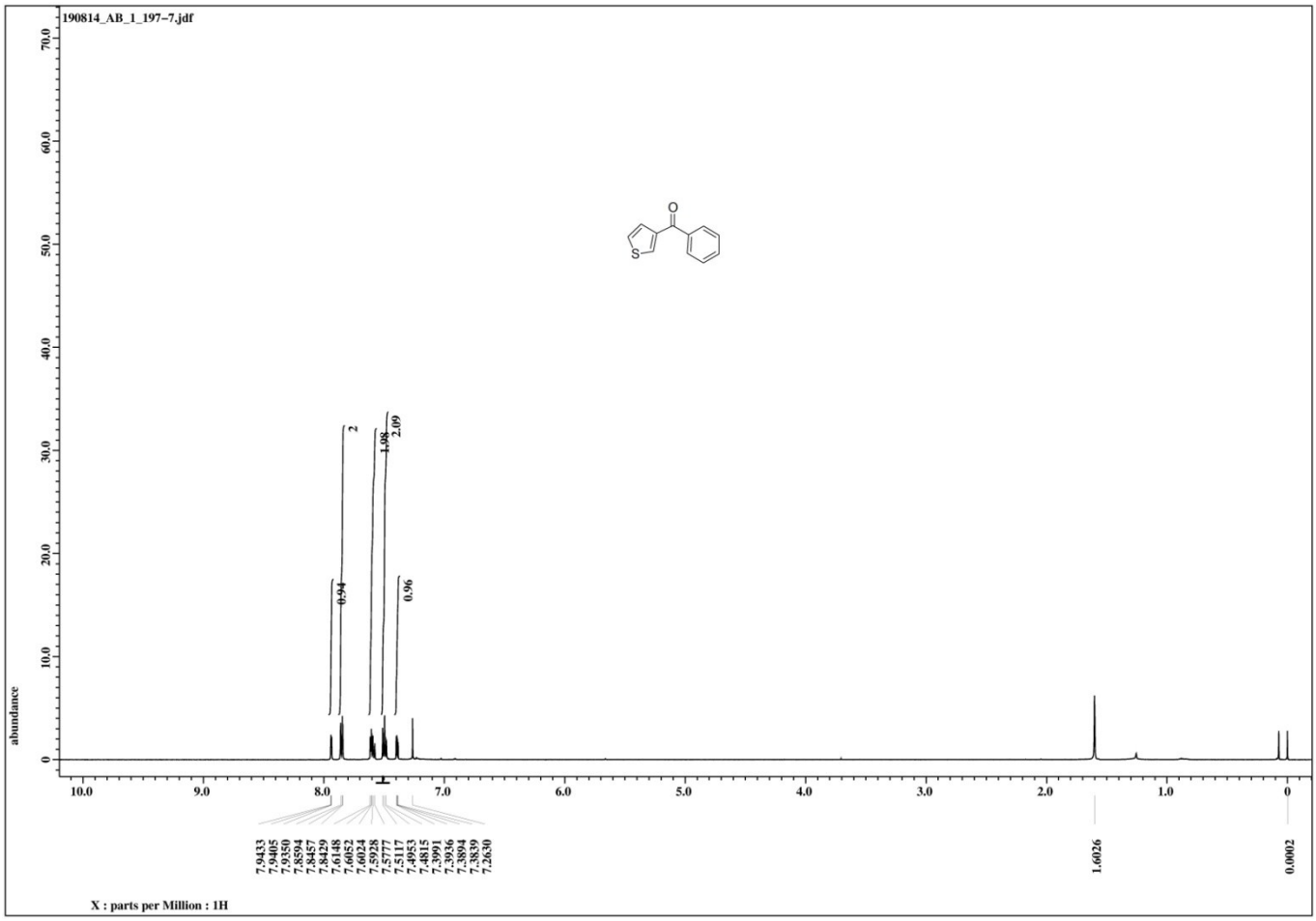


Table 2, (4i)-^{13}C-NMR (125 MHz, $CDCl_3$)

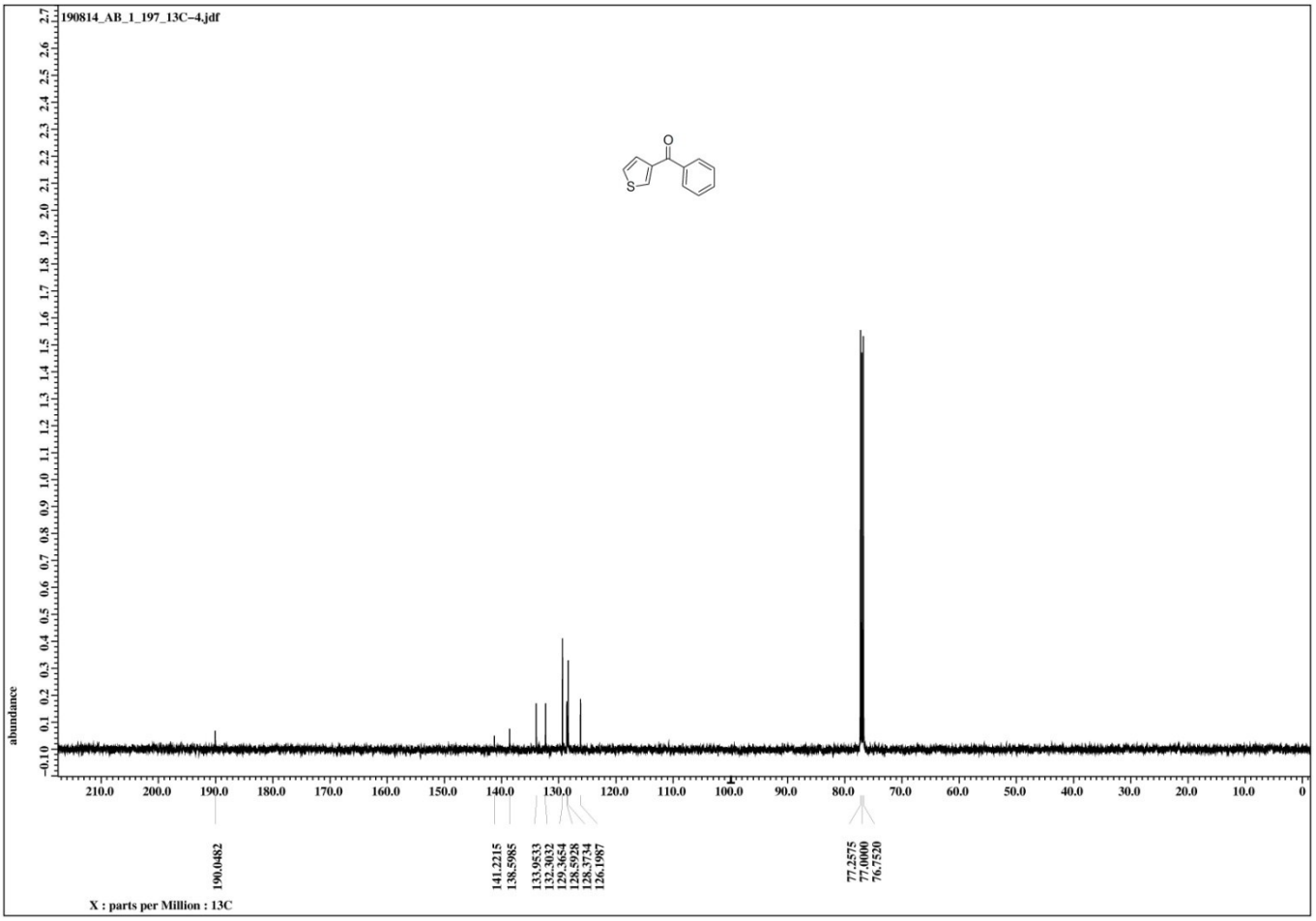


Table 2, (4j)-^{1}H-NMR (500MHz, $CDCl_3$)

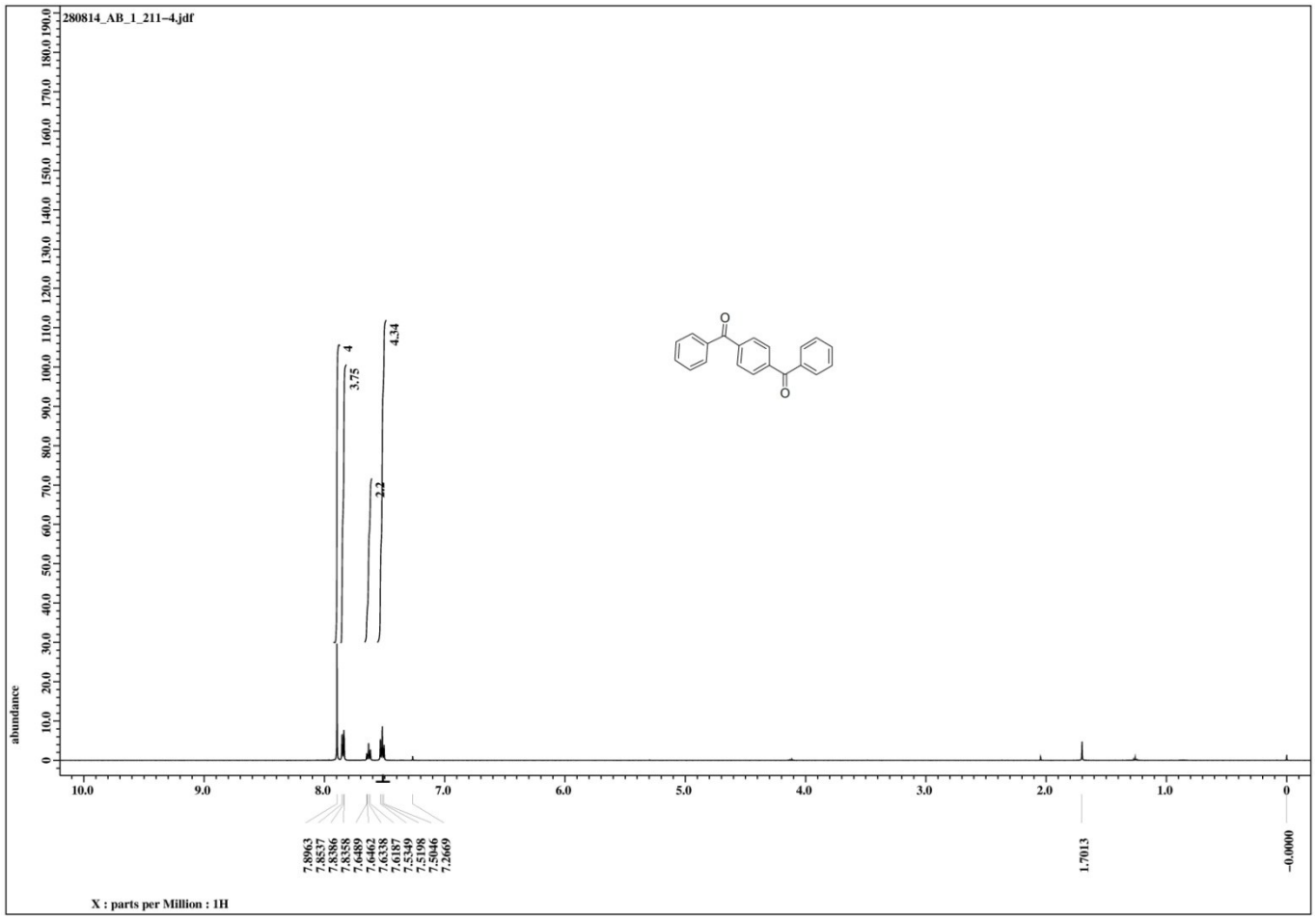
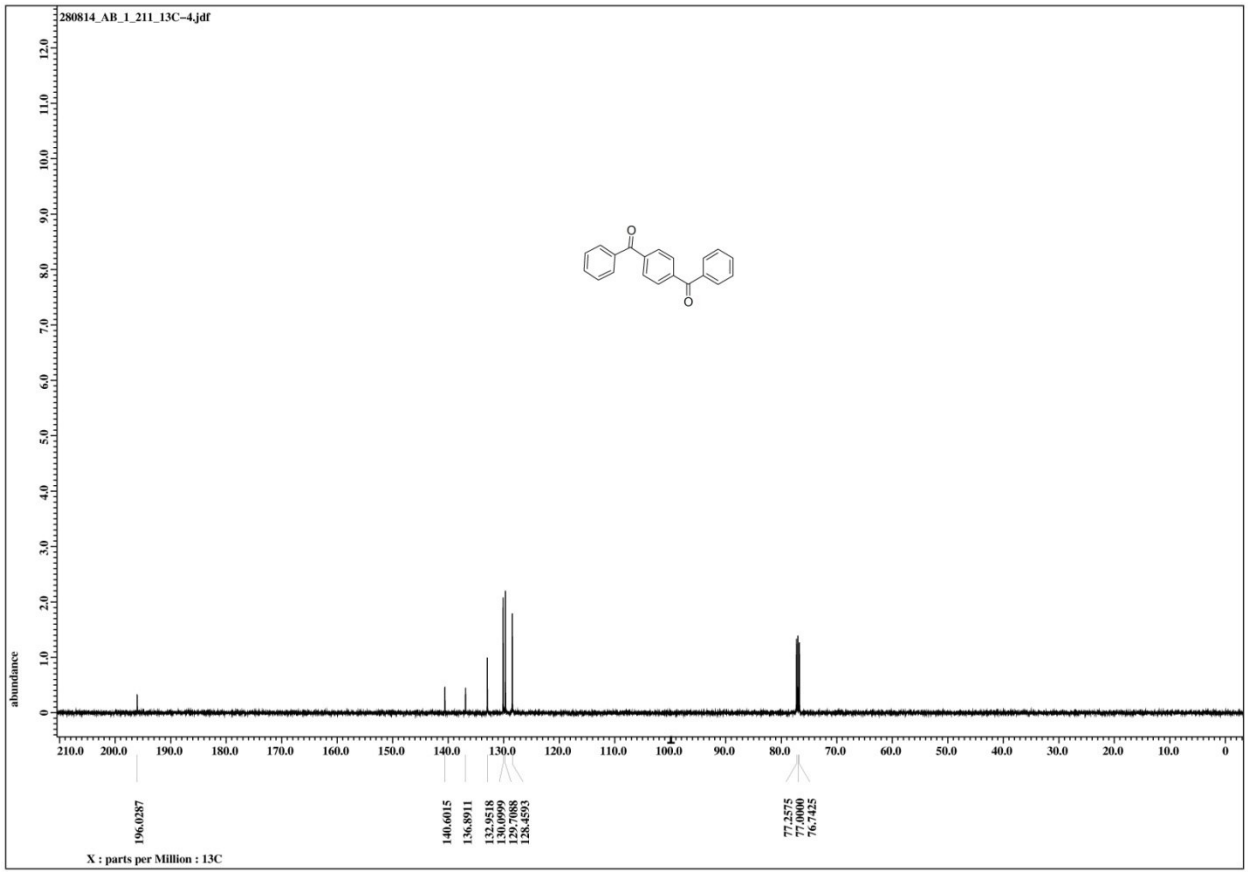
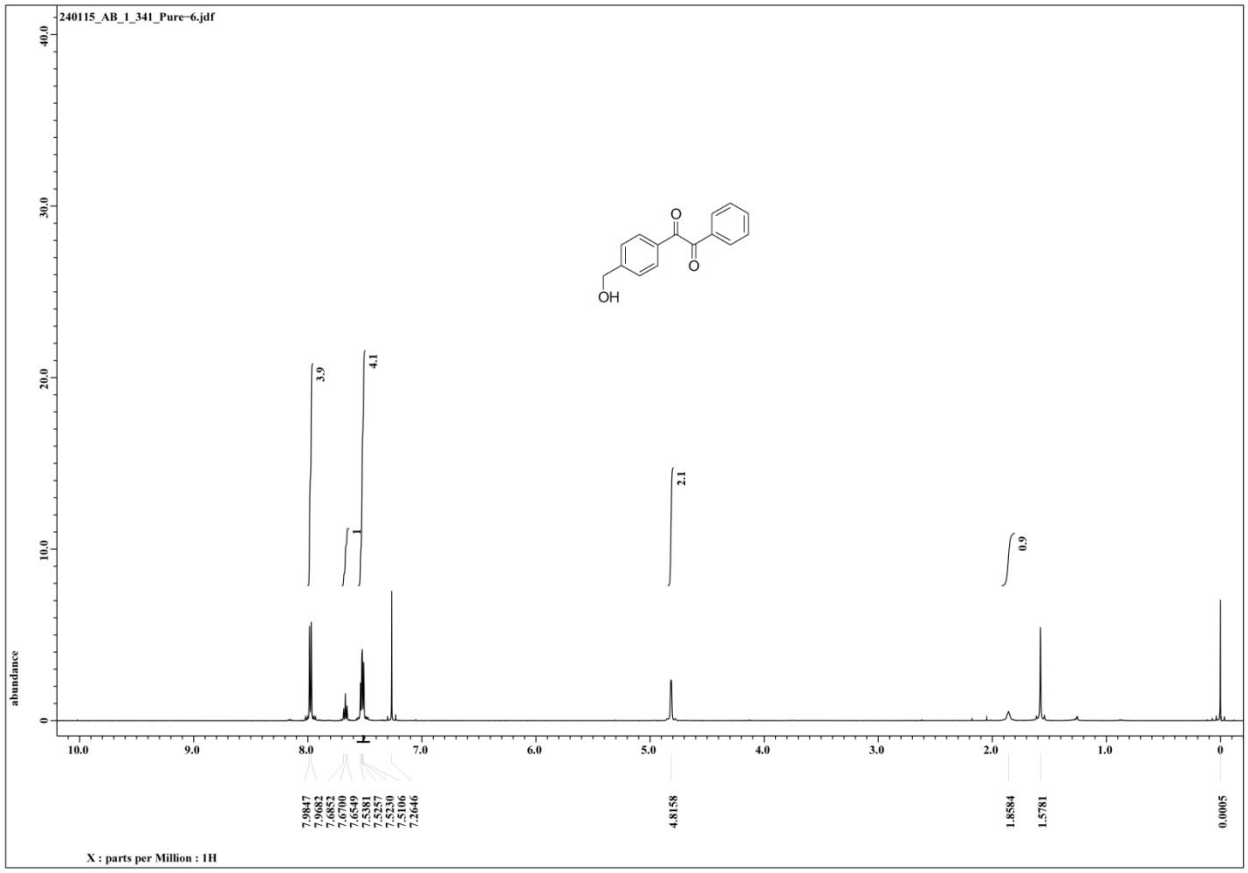


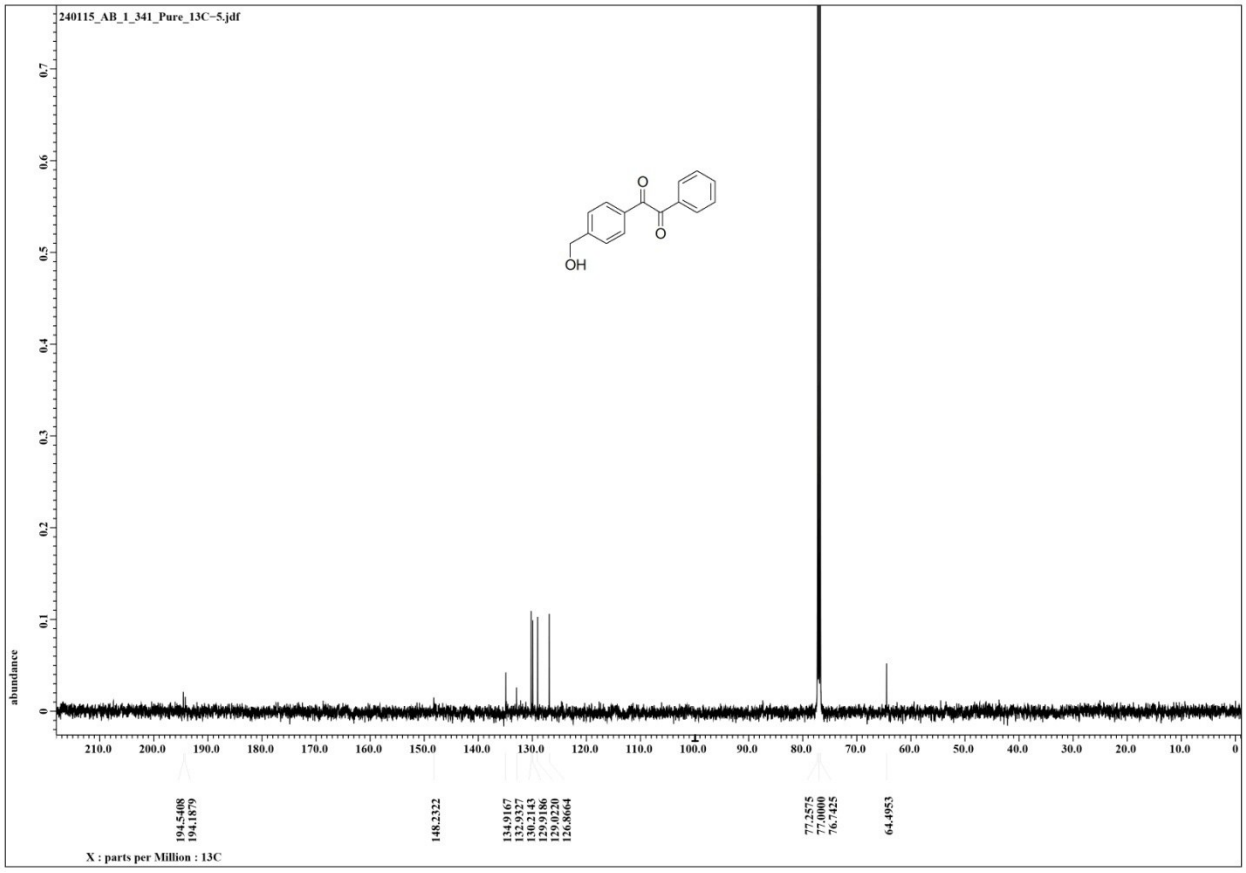
Table 2, (4j)-^{13}C-NMR (125 MHz, $CDCl_3$)



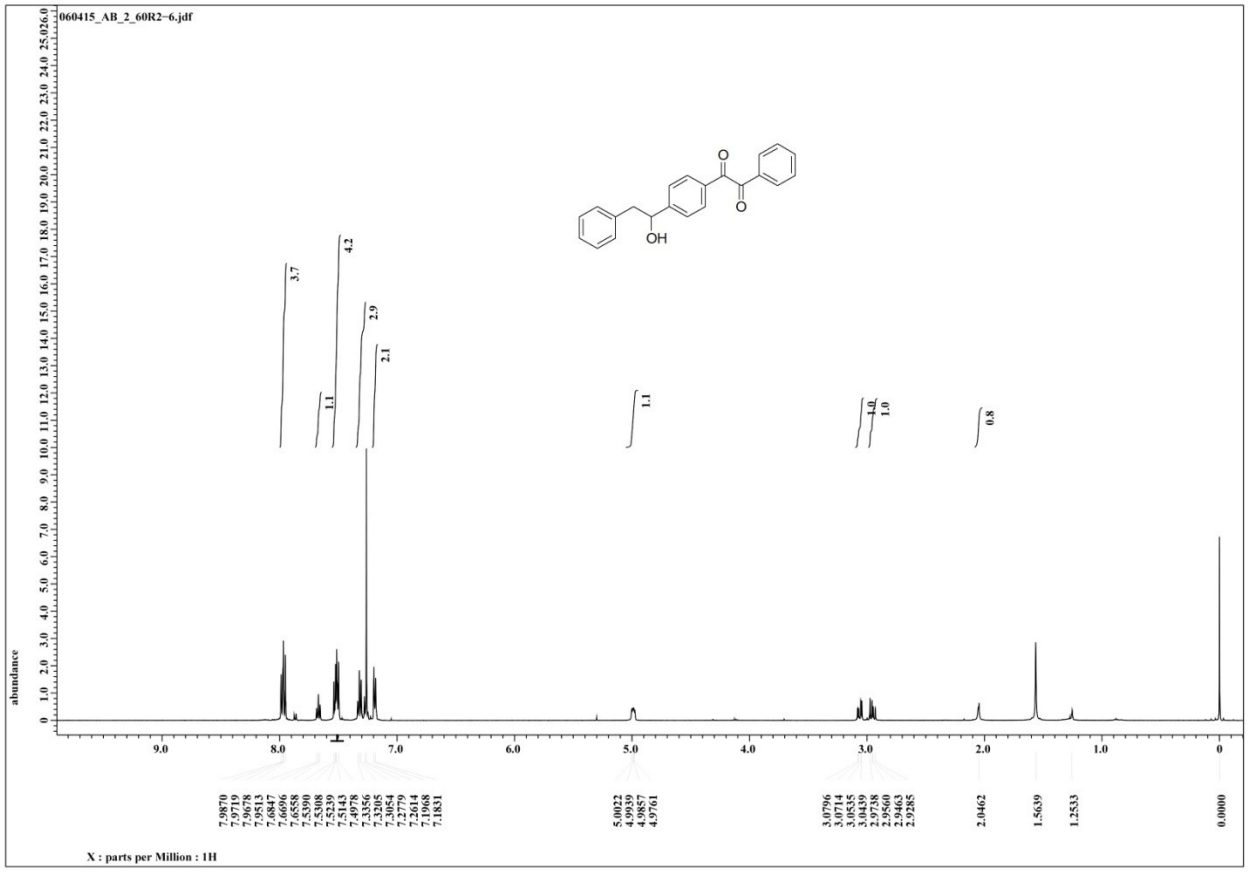
6a-^{1}H-NMR (500MHz, $CDCl_3$)



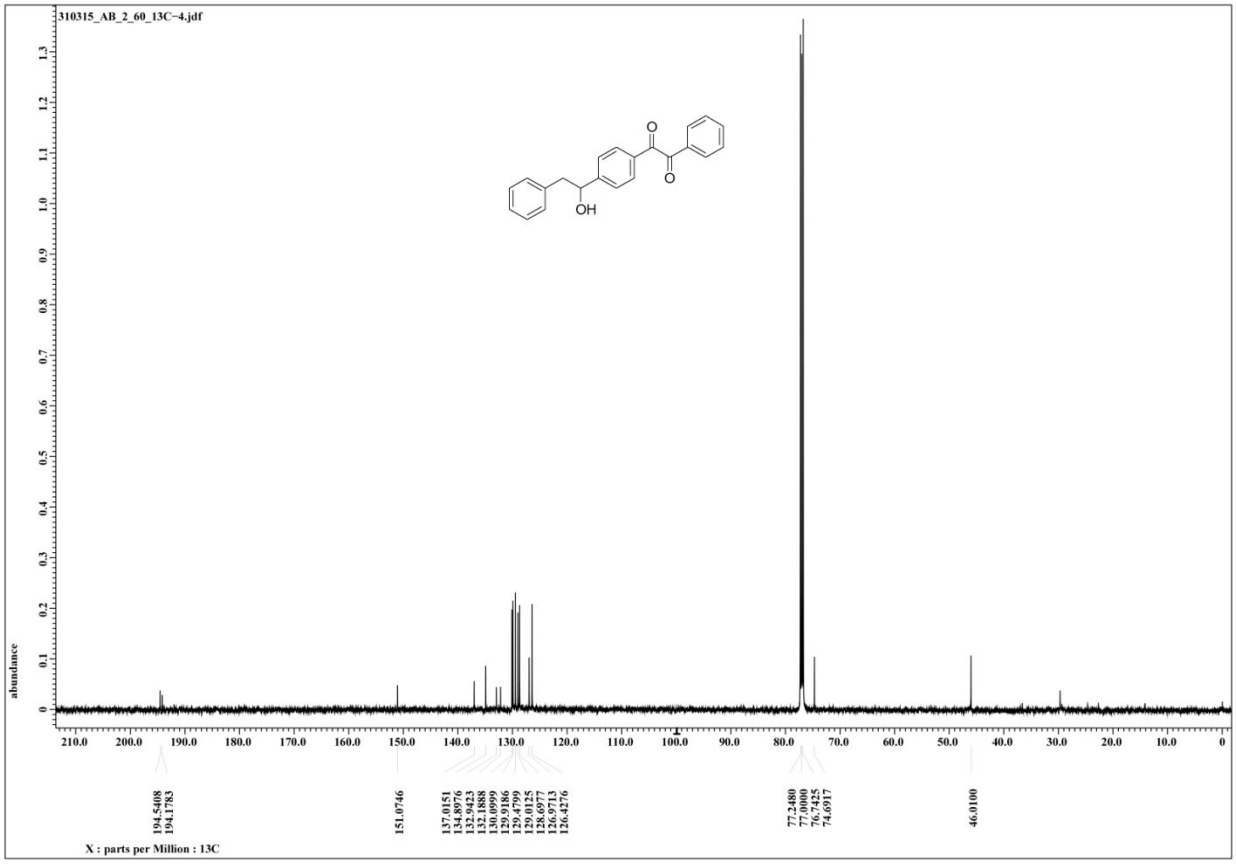
6a-^{13}C-NMR (125 MHz, $CDCl_3$)



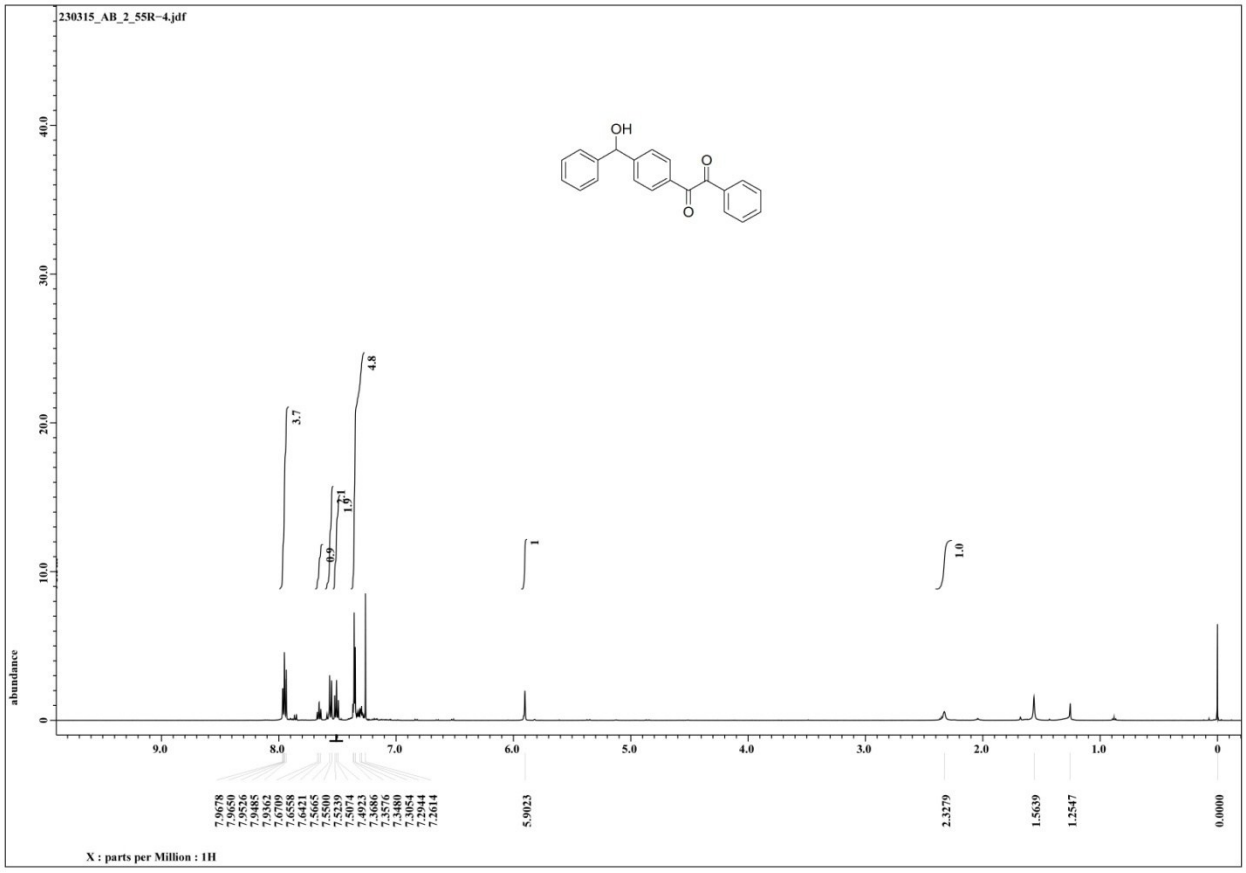
6b-^{1}H-NMR (500MHz, $CDCl_3$)



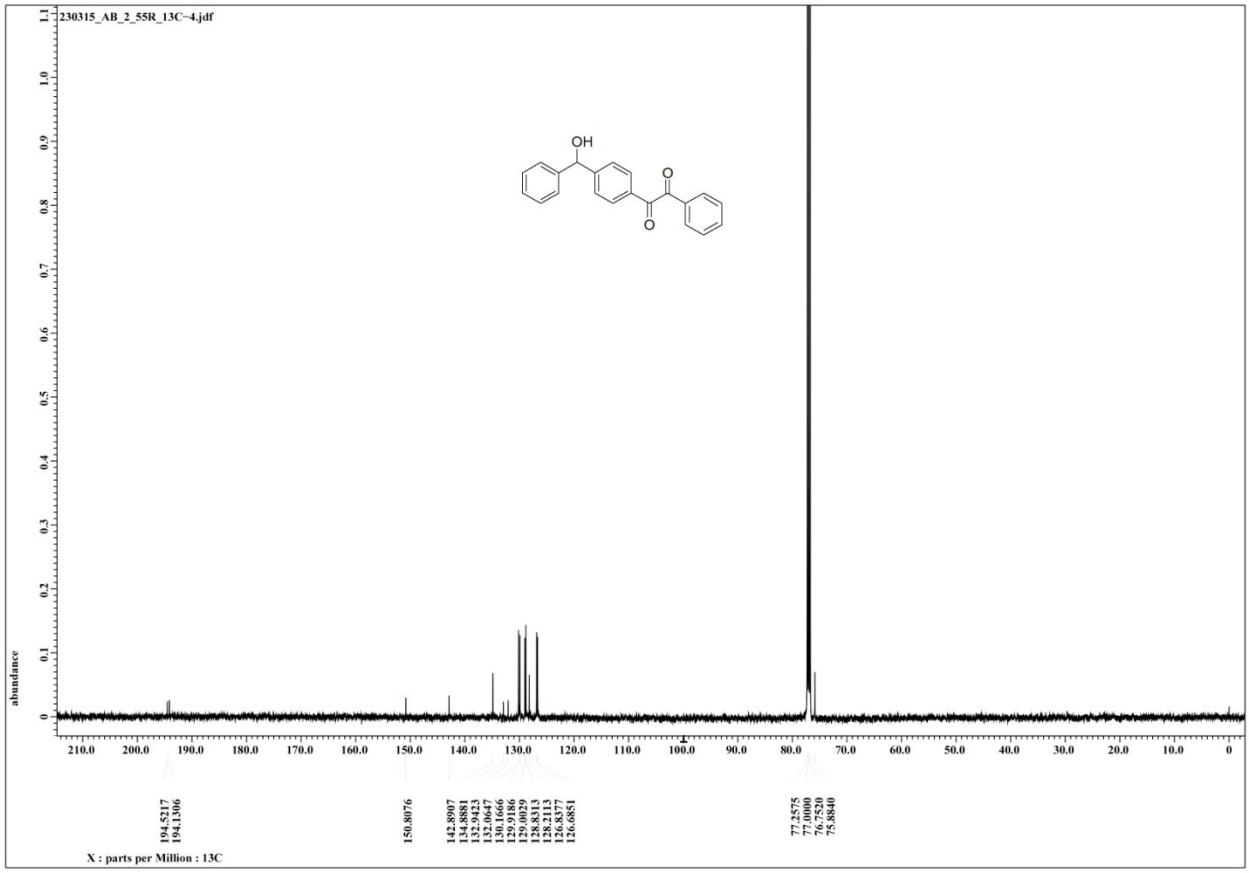
6b-^{13}C-NMR (125 MHz, $CDCl_3$)



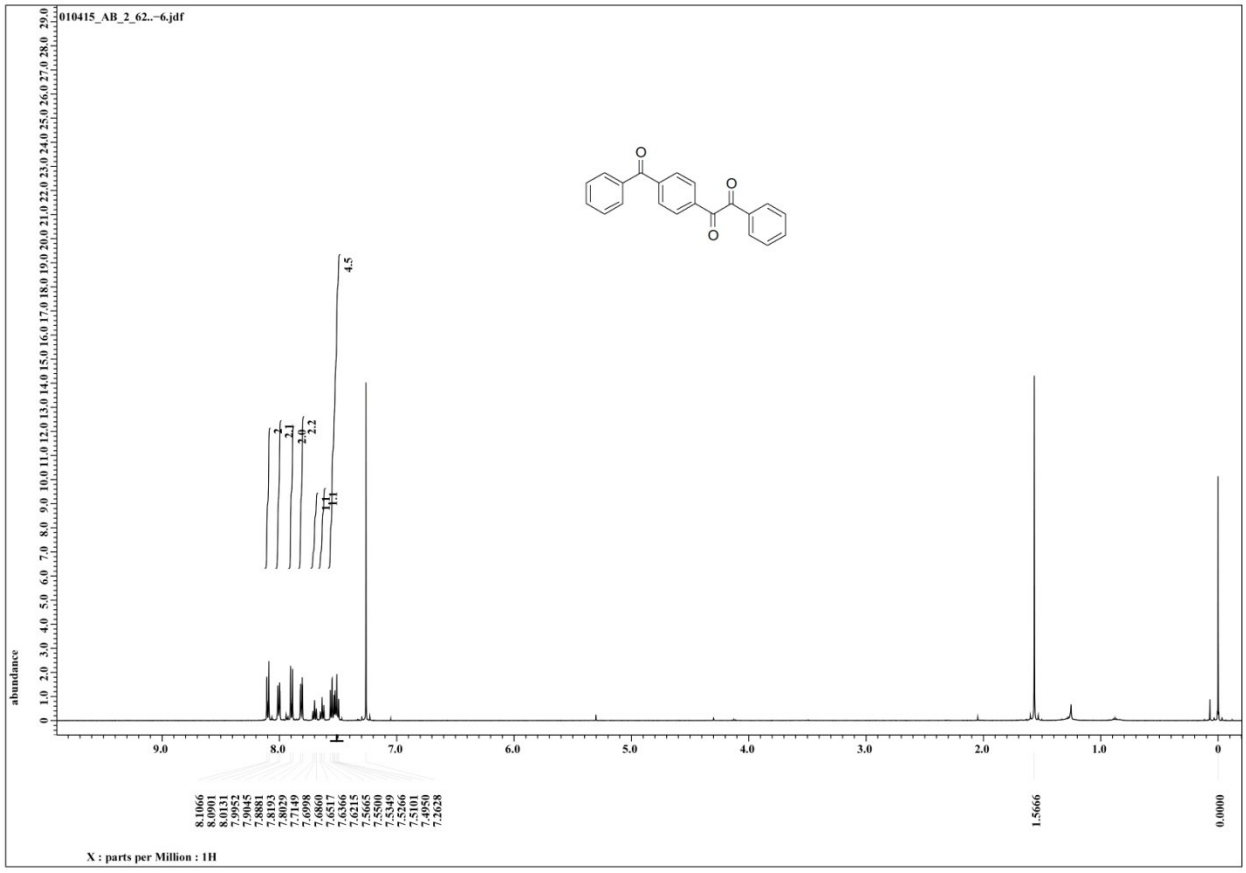
6c-^{1}H-NMR (500MHz, $CDCl_3$)



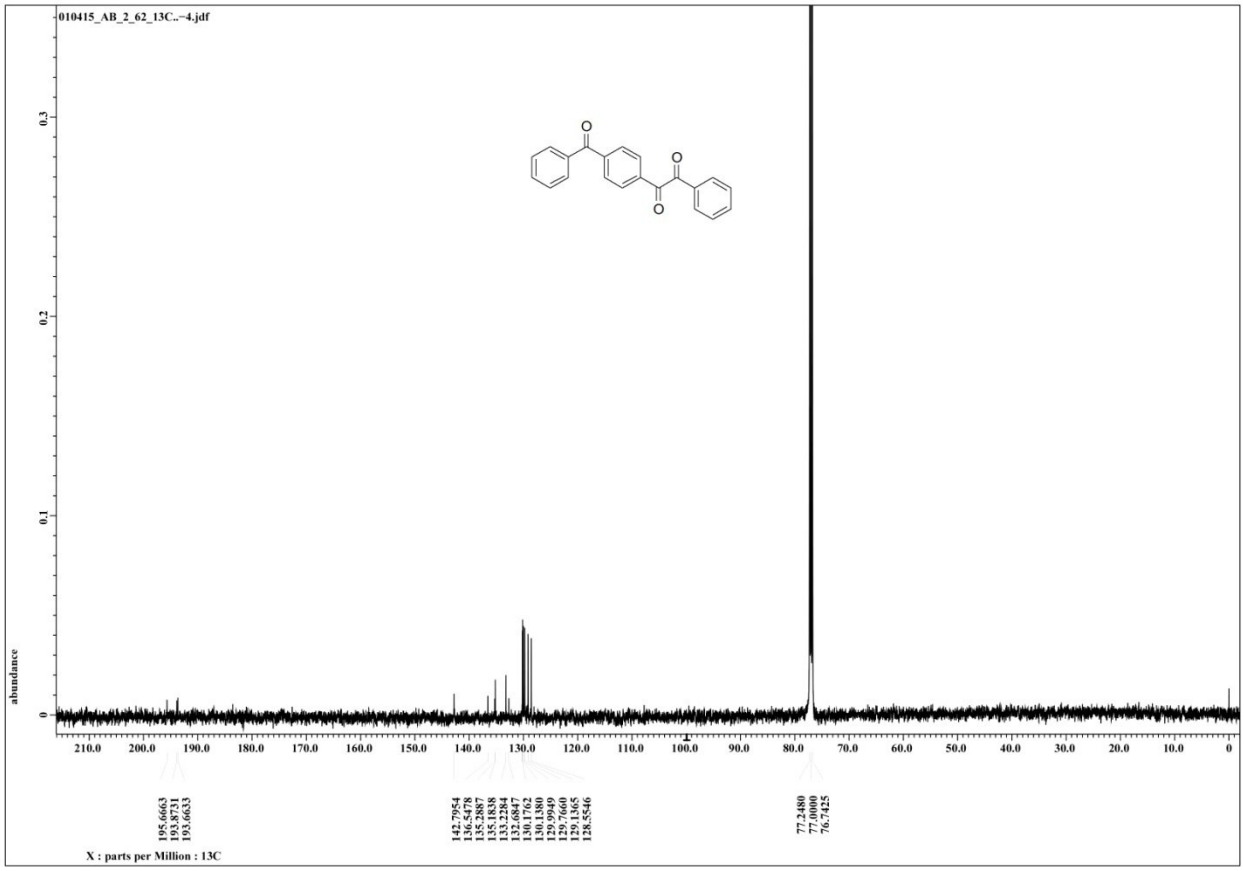
6c-^{13}C-NMR (125 MHz, $CDCl_3$)



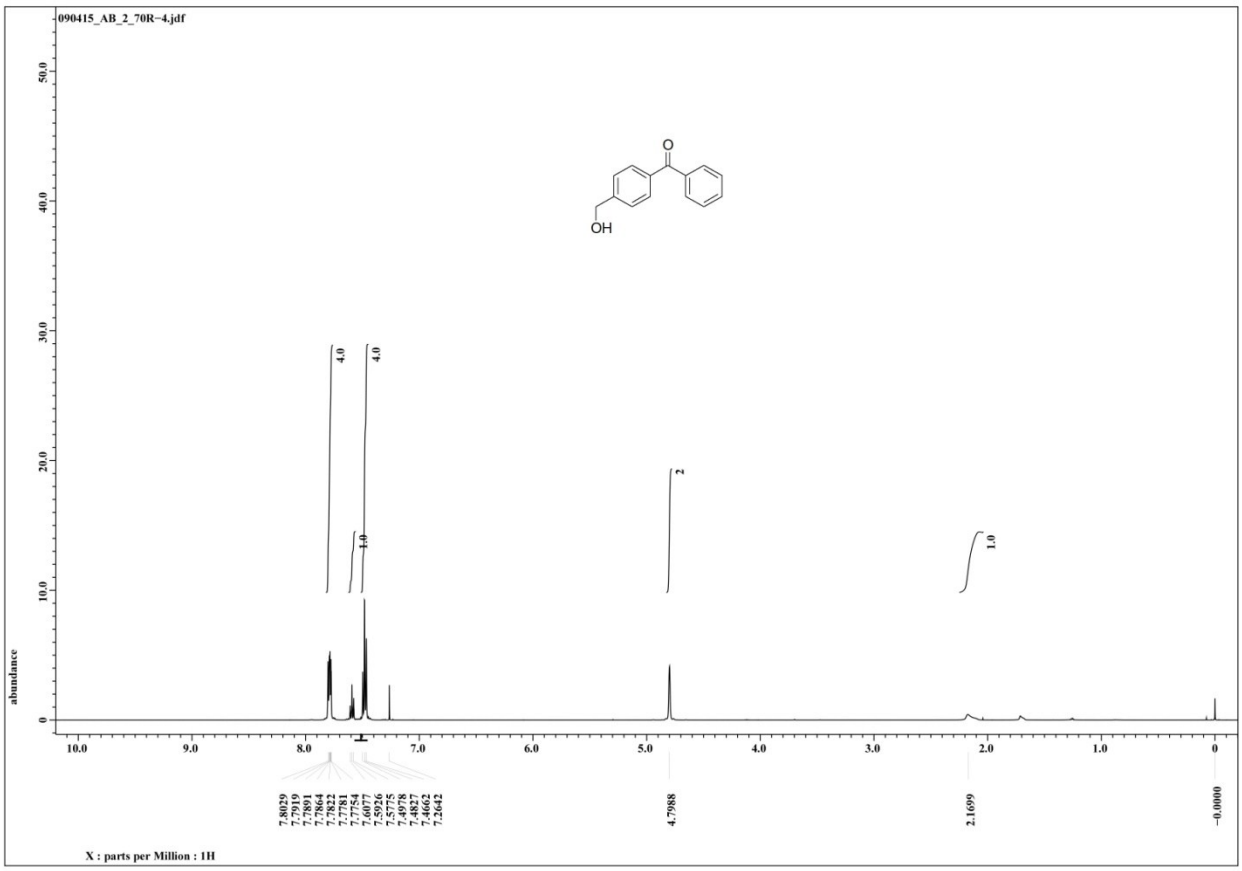
6c'-^{1}H-NMR (500MHz, $CDCl_3$)



6c'-^{13}C-NMR (125 MHz, $CDCl_3$)



6d-^{1}H-NMR (500MHz, $CDCl_3$)



6d-^{13}C-NMR (125 MHz, $CDCl_3$)