Supporting Information

# $K_2S_2O_8$ Promoted Metal-Free Direct C-alkylation of Acetophenones with Alcohols

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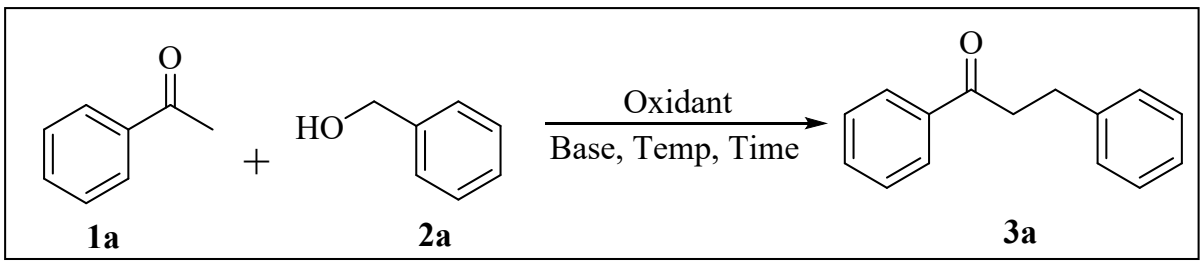
**1. General experimental conditions:**

Each component of laboratory glassware's were oven dried and then used for carrying out the general experimental procedures. $^{1}H$ proton NMR and $^{13}C$ proton NMR spectra were measured on a JEOL ECS-400 spectrometer which was functioning at 400 MHz for $^{1}H$ proton NMR and 100 MHz for $^{13}C$ proton NMR and utilization of $CDCl_3$ and DMSO-$d_6$ was done as solvent for preparing the samples. Both Tetramethylsilane (TMS) (0.00 ppm) and $CDCl_3$ were applied as the internal standards while recording the $^{1}H$ proton NMR (δ 7.246 ppm) and $^{13}C$ (δ 77.0 ppm)] proton NMR. Pattern of the chemical shifts in proton NMR were described in parts per million(ppm). While peak splitting patterns were defined as singlet (s), broad singlet (brs), doublet (d), double doublet (dd), triplet (t), and multiplet (m). All Coupling constant (J) values were stated in Hertz (Hz). High-Resolution Electron Impact Mass Spectra (HR-EIMS) were analyzed on Xevo G2-SQ-Tof (Waters, USA) which are compatible with ACQUITY UPLC® and nano ACQUITY UPLC® systems. Column chromatography was done using a normal (particle size: 100-200 Mesh) and flash (particle size: 230-400 Mesh) silica gel, which were obtained from QualigensTM (India), Spectrochem (India), and Rankem (India). TLC plates coated with silica gel (Kiesel 60-F254, Merck (India)) were used to track the progress of chemical reactions. The visualizing agents which were utilized for TLC were UV light. For drying and concentrating all the solvents, BUCHI's Rotavapor R-210 was used. All the supplied solvents were of analytical grade such as Toluene, EtOAc and they were used without any prior purification. The chemicals and reagents used for the chemical reactions were purchased from Sigma Aldrich chemicals company (USA), TCI (India) Pvt. Ltd., Merck (India), and/or Spectrochem (India) etc. were used without any purification prior to use.

**Optimization table[a] :**

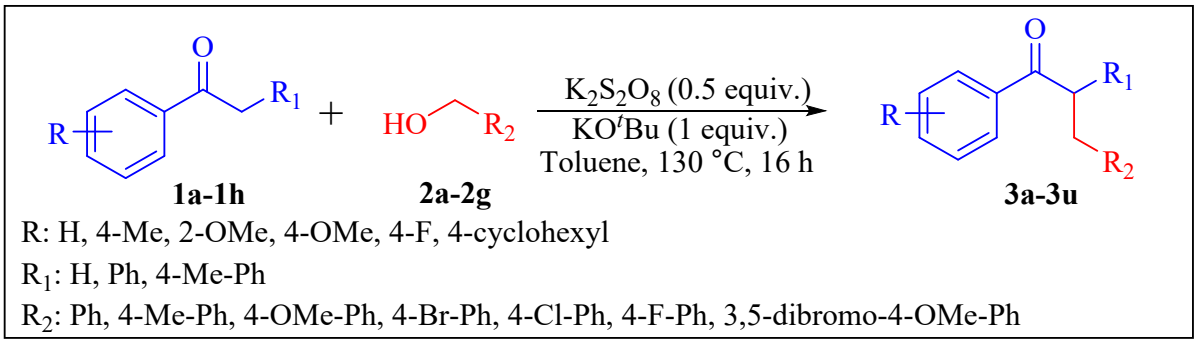


| Entry | Base (equiv.) | Oxidant (equiv.) | Temp | % Yield |
|---|---|---|---|---|
| 1 | $K_2CO_3$ | $K_2S_2O_8$ | 130 | 45 |
| 2 | NaO$^t$Bu | $K_2S_2O_8$ | 130 | 56 |
| 3 | KOH | $K_2S_2O_8$ | 130 | 76 |
| 4 | $Cs_2CO_3$ | $K_2S_2O_8$ | 130 | 45 |
| **5** | **KO$^t$Bu** | **$K_2S_2O_8$** | **130** | **87** |
| 6 | - | $K_2S_2O_8$ | 130 | 0 |
| 7 | KO$^t$Bu | - | 130 | 26 |
| 8 | KO$^t$Bu | $Na_2S_2O_8$ | 130 | 65 |
| 9 | KO$^t$Bu | PCC | 130 | 41 |
| 10 | KO$^t$Bu | Oxone | 130 | 35 |
| 11 | KO$^t$Bu | PIDA | 130 | 20 |
| 12 | KO$^t$Bu | $(NH4)_2S_2O_8$ | 130 | 57 |
| 13[b] | KO$^t$Bu | $K_2S_2O_8$ | 130 | 70 |
| 14[c] | KO$^t$Bu | $K_2S_2O_8$ | 130 | 75 |
| 15[d] | KO$^t$Bu | $K_2S_2O_8$ | 130 | 65 |
| 16[e] | KO$^t$Bu | $K_2S_2O_8$ | 130 | 81 |
| 17[f] | KO$^t$Bu | $K_2S_2O_8$ | 130 | 0 |

| | | | | |
|---|---|---|---|---|
| 18[g] | KO$^t$Bu | $K_2S_2O_8$ | 130 | 35 |
| 19[h] | KO$^t$Bu | $K_2S_2O_8$ | 130 | 28 |
| 20 | KO$^t$Bu | $K_2S_2O_8$ | 110 | 74 |
| 21 | KO$^t$Bu | $K_2S_2O_8$ | 80 | 56 |

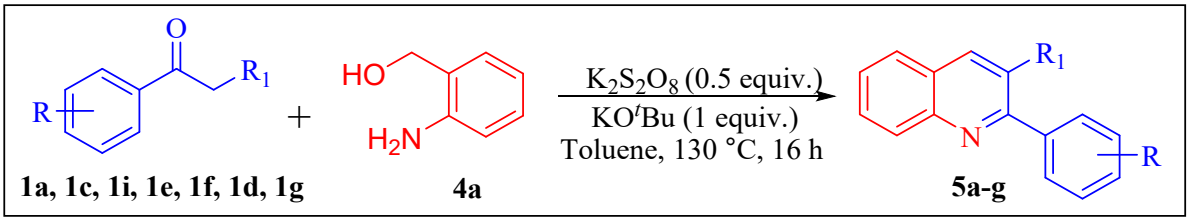
[a] General Reaction Condition: Acetophenone **1a** (0.5 mmol), benzyl alcohols **2a** (0.6 mmol), $K_2S_2O_8$ (50 mol%), KO$^t$Bu (0.5 mmol), toluene, 130 °C, 16 h. [b] 0.5 equivalent of base were used; [c] 1.5 equivalent of base were used; [d] 0.25 equivalent of oxidant were used; [e] 1 equivalent of oxidant were used; [f], [g], [h] different solvents DCE, $CH_3CN$, XYLENE respectively were used.

**2. General procedure for the C-alkylation of various acetophenones with different benzyl alcohols:** A mixture of different type of acetophenones **1a-1h** (0.5 mmol) with various benzyl alcohols **2a-2g** (0.6 mmol) in the presence of $K_2S_2O_8$ (0.25 mmol) and K$^t$OBu (0.5 mmol) dissolved in toluene was carried out in an oven dried reaction tube at a temperature of 130 °C for 16 h. After the completion of the reaction, the reaction mixture was cooled and the work-up was done with $H_2O$ (15 mL) and EtOAc (3 × 20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered, and concentrated under reduced pressure to get the crude residue which was further purified through column chromatography on silica gel (230-400 mesh) using hexane: ethyl acetate (99:1 ratio) as eluting solvent to afford the monoalkylated coupling products **3a-3u** in 55-90 % yield.




**Scheme 1.** $K_2S_2O_8$ Promoted C-alkylation of acetophenones.

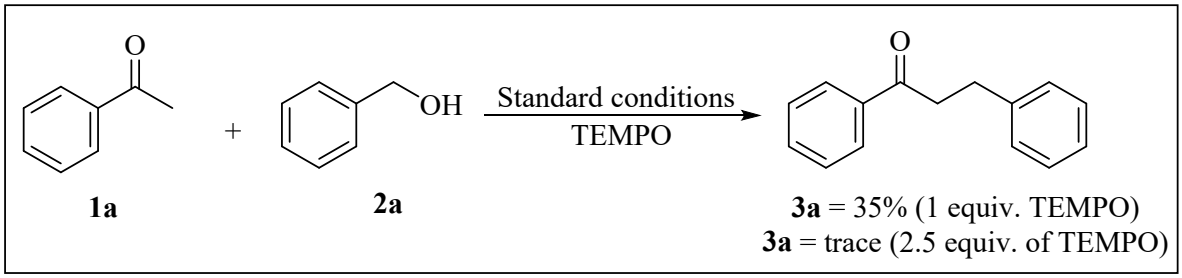
**3. General procedure for synthesis of substituted quinolines:**




**Scheme 2** Synthesis of various quinolines by $K_2S_2O_8$.

An oven dried 15 mL sealed tube was taken and performed with different acetophenones (0.5 mmol) with 2-amino benzyl alcohols **4a** (0.6 mmol) in the presence of $K_2S_2O_8$ (0.25 mmol) and KO$^t$Bu (0.5 mmol) dissolved in toluene at a temperature of 130 °C for 16 h. After the completion of the reaction, the reaction mixture was cooled and the work-up was done with $H_2O$ (15 mL) and ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered, and concentrated under reduced pressure to get the crude residue which was further purified through column chromatography on silica gel (230-400 mesh) using hexane: ethyl acetate (99:1 ratio) as eluting solvent to afford the monoalkylated coupling products **5a-5g** in 75-90 % yield.

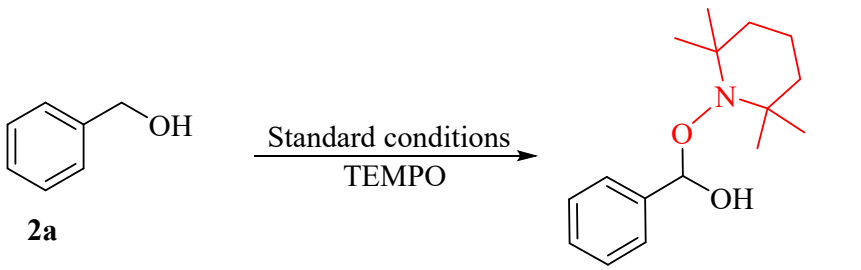
**4. Control experiments for mechanistic investigation:**




**Scheme 3** Control experiments.

An oven dried 15 mL sealed tube was taken and performed with acetophenone **1a** (0.5 mmol) with 4-methyl-benzyl alcohol **2a** (0.6 mmol) in the presence of TEMPO (0.5 mmol) utilizing standard reaction parameters. After the completion of the reaction, the reaction mixture was cooled and the work-up was done with $H_2O$ (15 mL) and ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered, and concentrated under reduced pressure to get the crude residue which was further purified through column chromatography on silica gel (230-400 mesh) using hexane: ethyl acetate (99:1 ratio) as eluting solvent to afford the monoalkylated coupling product **3a** in 35 % yield.

**5. Radical trapping experiment *via* TEMPO adducts formation:** After demonstrating the radical-mediated process is operating for alkylation, we examined substituted benzyl alcohol to trap the ketyl radical *via* production of TEMPO adduct.



**Scheme 4** TEMPO adduct formation

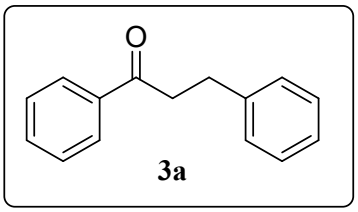
An oven dried 15 mL sealed tube was taken and reaction carried out with benzyl alcohol **2a** (0.6 mmol) in the presence of $K_2S_2O_8$ (0.25 mmol), KO$^t$Bu (0.5 mmol) and TEMPO (1 mmol) dissolved in toluene at a temperature of 130 °C for 16 h. After the completion of the reaction, the reaction mixture was cooled. The crude reaction mixture was then characterized by HRMS spectroscopy, and the corresponding mass of TEMPO-trapped ketyl radicals was determined.

**General procedure for crown ether experiment:**

An oven dried 15 mL sealed tube was taken and performed with acetophenone **1a** (0.5 mmol) with 4-methyl-benzyl alcohol **2b** (0.6 mmol) in the presence of 18-crown-6 utilizing standard reaction parameters. After the completion of the reaction, the reaction mixture was cooled and the work-up was done with $H_2O$ (15 mL) and ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered, and concentrated under reduced pressure to get the crude residue which was further purified through column chromatography on silica gel (230-400 mesh) using hexane: ethyl acetate (99:1 ratio) as eluting solvent to afford the monoalkylated coupling product **3b** in 85 % yield.

**$^1$H NMR and $^{13}$C Characterization data of selective monoalkylation of acetophenones and synthesized quinoline derivatives**

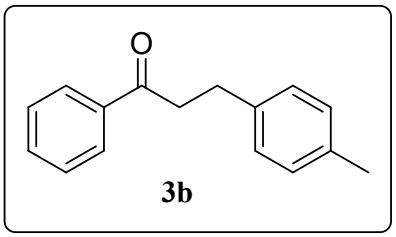
**1,3-diphenylpropan-1-one** (**3a**).




**3a**

Product **3a** was obtained by utilizing the general procedure (Scheme 2) taking acetophenone **1a** (0.5 mmol), benzyl alcohol **2a** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a white solid in 87% yield; $R_f$ (hexane/EtOAc = 90:10): 0.44; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.2 Hz, J = 0.8Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.31 – 7.20 (m, 5H), 3.31 – 3.27 (m, 2H), 3.08 – 3.04 (m, 2H); $^{13}$C NMR data matches with the already existing data ref (a).

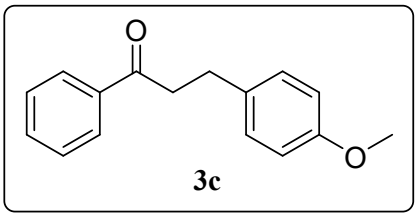
**1-phenyl-3-(p-tolyl)propan-1-one** (**3b**).




**3b**

Product **3b** was obtained by utilizing the general procedure (Scheme 2) taking acetophenone **1a** (0.5 mmol), 4-methyl-benzyl alcohol **2b** (0.6 mmol) and isolated by column chromatography (hexane: EtOAc = 99:01) as a colourless oil in 85% yield; $R_f$ (hexane/EtOAc = 90:10):0.41; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.86 (m, 2H), 7.48 – 7.44 (m, 1H), 7.38 – 7.34 (m, 2H), 7.08 – 7.02 (m, 4H), 3.21 – 3.18 (m, 2H), 2.97 – 2.93 (m, 2H), 2.24 (s, 3H); $^{13}$C NMR data matches with the already existing data ref (a).

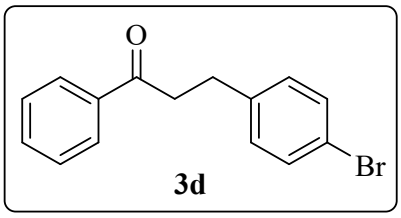
**3-(4-methoxyphenyl)-1-phenylpropan-1-one** (**3c**)




**3c**

Product **3c** was obtained by utilizing the general procedure (Scheme 2) taking acetophenone **1a** (0.5 mmol), 4-methoxy-benzyl alcohol **2c** (0.6 mmol) and isolated by column chromatography (hexane: EtOAc = 99: 01) as a yellow solid in 87% yield; $R_f$ (hexane/EtOAc = 90:10): 0.42; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.45 – 7.42 (m, 1H), 7.35 – 7.32 (m, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 3.67 (s, 3H), 3.17 – 3.14 (m, 2H), 2.93 – 2.89 (m, 2H); $^{13}$C NMR data matches with the already existing data ref (a).

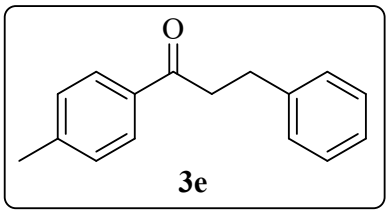
**3-(4-bromophenyl)-1-phenylpropan-1-one** (**3d**)




**3d**

Product **3d** was obtained by utilizing the general procedure (Scheme 2) taking acetophenone **1a** (0.5 mmol), 4-bromo-benzyl alcohol **2d** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a white solid in 75% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.45; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.41 – 7.34 (m, 5H), 7.11 – 7.07 (m, 2H), 3.24 – 3.21 (m, 2H), 2.97 (t, *J* = 7.6 Hz, 2H); $^{13}$C NMR data matches with the already existing data ref (a).

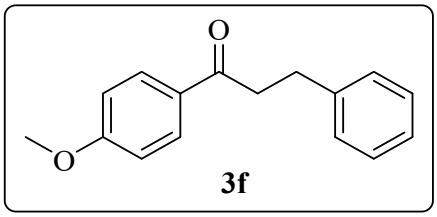
**3-phenyl-1-(p-tolyl)propan-1-one** (**3e**).




**3e**

Product **3e** was obtained by utilizing the general procedure (Scheme 2) taking 4-methyl-acetophenone **1b** (0.5 mmol), benzyl alcohol **2a** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a white solid in 81% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.42; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 6.90 – 6.78 (m, 7H), 2.88 – 2.84 (m, 2H), 2.66 – 2.62 (m, 2H), 1.98 (s, 3H); $^{13}$C NMR data matches with the already existing data ref (a).

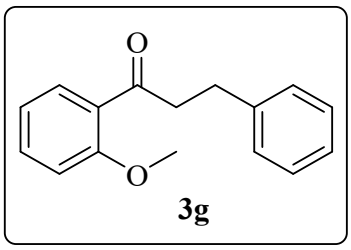
**1-(4-methoxyphenyl)-3-phenylpropan-1-one** (**3f**).




**3f**

Product **3f** was obtained by utilizing the general procedure (Scheme 2) taking 4-methoxy-acetophenone **1c** (0.5 mmol), benzyl alcohol **2a** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a white solid in 85% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.44; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 9.2 Hz, 2H), 7.21 – 7.09 (m, 5H), 6.82 (d, *J* = 9.2 Hz, 2H), 3.75 (s, 3H), 3.16 – 3.12 (m, 2H), 2.97 – 2.93 (m, 2H); $^{13}$C NMR data matches with the already existing data ref (a).

**1-(2-methoxyphenyl)-3-phenylpropan-1-one** (**3g**).

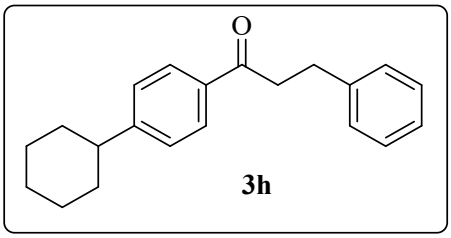



**3g**

Product **3g** was obtained by utilizing the general procedure (Scheme 2) taking 2-methoxy-acetophenone **1d** (0.5 mmol), benzyl alcohol **2a** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a white solid in 81% yield; $R_f$ (hexane/EtOAc = 90 : 10):0.42; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.2 Hz, 2H), 7.30 – 7.19 (m, 5H),

6.89 (d, *J* = 9.2 Hz, 2H), 3.83 (s, 3H), 3.24 – 3.21 (m, 2H), 3.06 – 3.02 (m, 2H); $^{13}$C NMR data matches with the already existing data ref (g).

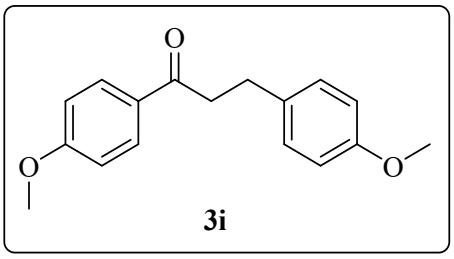
**1-(4-cyclohexylphenyl)-3-phenylpropan-1-one** (**3h**).




**3h**

Product **3h** was obtained by utilizing the general procedure (Scheme 2) taking 4-cyclohexyl-acetophenone **1e** (0.5 mmol), benzyl alcohol **2a** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a light yellow oil in 73% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.41; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.17 (m, 7H), 3.21 – 3.17 (m, 2H), 2.99 – 2.96 (m, 2H), 2.49 – 2.46 (m, 1H), 1.78 – 1.76 (m, 4H), 1.68 (d, *J* = 12.4 Hz, 1H), 1.34 – 1.32 (m, 5H); $^{13}$C NMR data matches with the already existing data ref (f).

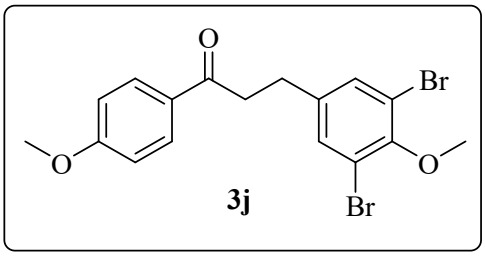
**1,3-bis(4-methoxyphenyl)propan-1-one** (**3i**).




**3i**

Product **3i** was obtained by utilizing the general procedure (Scheme 2) taking 4-4-methoxy-acetophenone **1c** (0.5 mmol), 4-OMe-benzyl alcohol **2c** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a white solid in 86% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.40; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.2 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H), 3.75 (s, 3H), 3.20 – 3.16 (m, 2H), 2.98 – 2.94 (m, 2H); $^{13}$C NMR data matches with the already existing data ref (d).

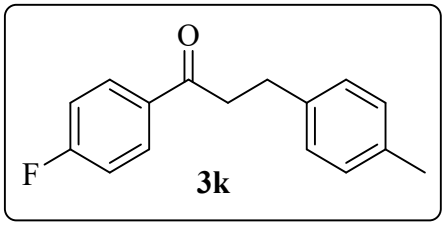
**3-(3,5-dibromo-4-methoxyphenyl)-1-(4-methoxyphenyl)propan-1-one** (**3j**).




**3j**

Product **3j** was obtained by utilizing the general procedure (Scheme 2) taking 4-methoxy-acetophenone **1c** (0.5 mmol), 3,5-dibromo-4-methoxy-benzyl alcohol **2e** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a white solid in 71% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.44; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.53 – 6.51 (m, 2H), 3.60 – 3.58 (m, 6H), 2.98 – 2.94 (m, 2H), 2.74 (t, *J* = 7.6 Hz, 2H). $^{13}$C NMR (101 MHz, ) δ 198.01 (s), 163.46 (s), 148.89 (s), 147.36 (s), 134.10 (s), 130.33 (s), 130.01 (s), 120.18 (s), 113.74 (s), 111.84 (s), 111.32 (s), 55.95 (s), 55.85 (s), 40.37 (s), 30.03 (s). HRMS (m/z): Calculated: 426.9539, Obtained: 426.9537.

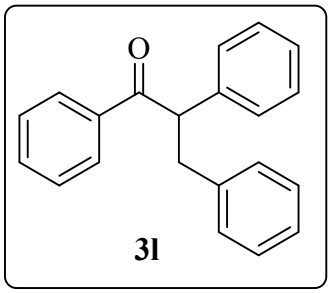
**1-(4-fluorophenyl)-3-(p-tolyl)propan-1-one** (**3k**).




**3k**

Product **3k** was obtained by utilizing the general procedure (Scheme 2) taking 4-fluoro-acetophenone **1f** (0.5 mmol), 4-methyl-benzyl alcohol **2b** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a light yellow solid in 75% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.43; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.89 (m, 2H), 7.08 – 7.02 (m, 6H), 3.20 – 3.16 (m, 2H), 2.97 – 2.93 (m, 2H), 2.25 (s, 3H); $^{13}$C NMR data matches with the already existing data ref (d).

**1,2,3-triphenylpropan-1-one** (**3l**).

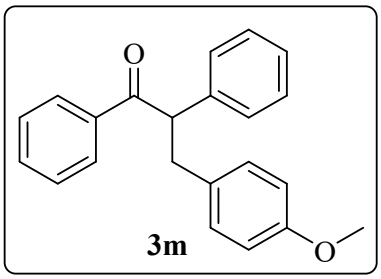



**3l**

Product **3l** was obtained by utilizing the general procedure (Scheme 2) taking benzyl phenyl ketone **1g** (0.5 mmol), benzyl alcohol **2a** (0.6 mmol) and isolated by column chromatography

(hexane : EtOAc = 99 : 01) as a white solid in 80% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.41;$^1$H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.24 – 7.20 (m, 2H), 7.17 – 6.97 (m, 10H), 4.72 (t, *J* = 7.2 Hz, 1H), 3.50 – 3.45 (m, 1H), 2.97 (dd, *J* = 13.6, 6.8 Hz, 1H); $^{13}$C NMR data matches with the already existing data ref (b).

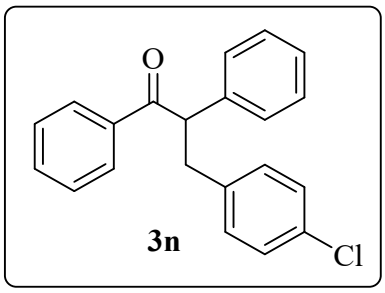
**3-(4-methoxyphenyl)-1,2-diphenylpropan-1-one** (**3m**).



**3m**

Product **3m** was obtained by utilizing the general procedure (Scheme 2) taking benzyl phenyl ketone **1g** (0.5 mmol), 4-methoxy-benzyl alcohol **2c** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a white solid in 81% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.43; $^1$H NMR (400 MHz, $CDCl_3$) 7.90 – 7.88 (m, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.32 (t, *J* =7.6 Hz, 2H), 7.27-7.18 (m, 5H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 4.77 (t, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 3.53 – 3.48 (m, 1H), 3.03 – 2.98 (m, 1H); $^{13}$C NMR data matches with the already existing data ref (b).

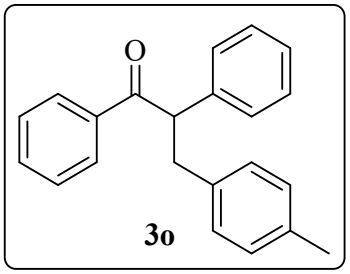
**3-(4-chlorophenyl)-1,2-diphenylpropan-1-one** (**3n**).



**3n**

Product **3n** was obtained by utilizing the general procedure (Scheme 2) taking benzyl phenyl ketone **1g** (0.5 mmol), 4-chloro-benzyl alcohol **2f** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a white solid in 76% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.45;$^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 6.8 Hz, 2H), 7.39 – 7.35 (m, 1H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.06 (m, 7H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.67 (t, *J* = 7.2 Hz, 1H), 3.45 – 3.40 (m, 1H), 2.96 (dd, *J* = 14.0, 7.2 Hz, 1H); $^{13}$C NMR data matches with the already existing data ref (b).

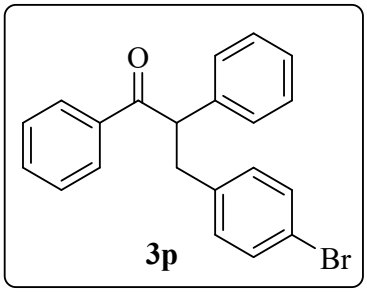
**1,2-diphenyl-3-(p-tolyl)propan-1-one** (**3o**).




**3o**

Product **3o** was obtained by utilizing the general procedure (Scheme 2) taking benzyl phenyl ketone **1g** (0.5 mmol), 4-Me-benzyl alcohol **2b** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a light yellow solid in 78% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.40; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.45 – 7.42 (m, 1H), 7.35 – 7.31 (m, 2H), 7.25 – 7.16 (m, 5H), 6.98 (dd, *J* = 12.8, 8.4 Hz, 4H), 4.80 – 4.77 (m, 1H), 3.52 (dd, *J* = 13.6, 7.6 Hz, 1H), 3.01 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.25 (s, 3H); $^{13}$C NMR data matches with the already existing data ref (b).

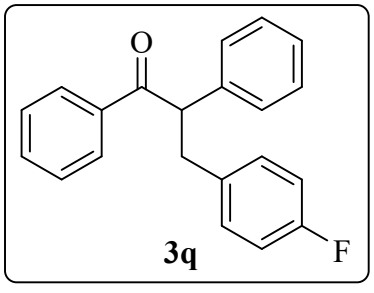
**3-(4-bromophenyl)-1,2-diphenylpropan-1-one** (**3p**).




**3p**

Product **3p** was obtained by utilizing the general procedure (Scheme 2) taking benzyl phenyl ketone **1g** (0.5 mmol), 4-bromo-benzyl alcohol **2d** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a white solid in 75% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.42; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.89 (m, 2H), 7.47 – 7.43 (m, 1H), 7.36 – 7.18 (m, 9H), 6.94 (d, *J* = 8.4 Hz, 2H), 4.77 – 4.74 (m, 1H), 3.52 – 3.47 (m, 1H), 3.05 – 3.00 (m, 1H); $^{13}$C NMR data matches with the already existing data ref (c).

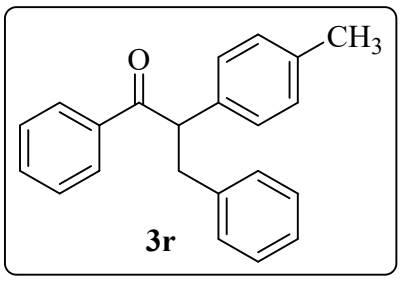
**3-(4-fluorophenyl)-1,2-diphenylpropan-1-one** (**3q**).




**3q**

Product **3q** was obtained by utilizing the general procedure (Scheme 3) taking benzyl phenyl ketone **1g** (0.5 mmol), 4-fluoro benzyl alcohol **2g** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a brown solid in 55% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.43; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.50 – 7.47 (m, 2H), 7.25 (d, *J* = 7.6 Hz, 4H), 6.76 (t, *J* = 8.8 Hz, 4H), 4.64 (t, *J* = 7.2 Hz, 1H), 3.43 – 3.38 (m, 1H), 2.93 (dd, *J* = 14.0, 7.2 Hz, 1H); $^{13}$C NMR data matches with the already existing data ref (c).

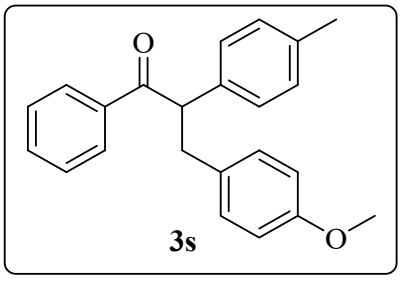
**1,3-diphenyl-2-(p-tolyl)propan-1-one** (**3r**).




**3r**

Product **3r** was obtained by utilizing the general procedure (Scheme 2) taking 4-methylbenzyl phenyl ketone **1h** (0.5 mmol), benzyl alcohol **2a** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a white solid in 81% yield; $R_f$ (hexane/EtOAc = 90 : 10):0.42;$^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.36 – 7.32 (m,1H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.13 – 6.97 (m, 9H), 4.72 – 4.68 (m, 1H), 3.47 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.96 (dd, *J* = 14.0, 6.8 Hz, 1H), 2.18 (s, 3H); $^{13}$C NMR (101 MHz, ) δ 199.27 (s), 139.87 (s), 136.71 (s), 136.69 (s), 136.00 (s), 132.71 (s), 129.55 (s), 129.08 (s), 128.61 (s), 128.38 (s), 128.14 (s), 128.07 (s), 126.00 (s), 55.42 (s), 40.03 (s), 20.97 (s). HRMS (m/z): Calculated: 301.1587, Obtained: 301.1585.

**3-(4-methoxyphenyl)-1-phenyl-2-(p-tolyl)propan-1-one** (**3s**).

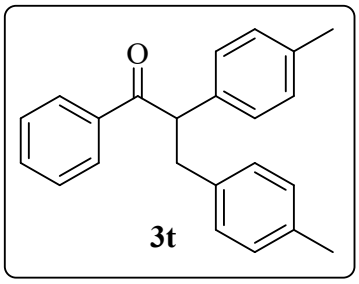



**3s**

Product **3s** was obtained by utilizing the general procedure (Scheme 2) taking 4-methylbenzyl phenyl ketone **1h** (0.5 mmol), 4-methoxy-benzyl alcohol **2c** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a white solid in 80% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.41; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.36

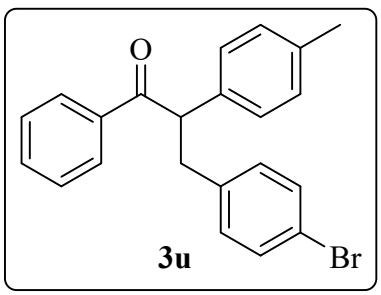
– 7.32 (m, 1H), 7.26 – 7.22 (m, 2H), 7.06 – 6.92 (m, 6H), 6.65 (d, *J* = 8.8 Hz, 2H), 4.67 (t, *J* = 7.2 Hz, 1H), 3.64 (s, 3H), 3.44 (dd, *J* = 14.0, 7.6 Hz, 1H) , 2.90 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.18 (s, 3H); $^{13}$C NMR (101 MHz, ) δ 199.53 (s), 157.91 (s), 136.84 (s), 136.73 (s), 136.14 (s), 132.77 (s), 132.02 (s), 130.10 (s), 129.61 (s), 128.67 (s), 128.45 (s), 128.16 (s), 113.63 (s), 55.75 (s), 55.17 (s), 39.26 (s), 21.05 (s). HRMS (m/z): Calculated: 331.1693, Obtained: 331.1693.

**1-phenyl-2,3-di-p-tolylpropan-1-one** (**3t**).




Product **3t** was obtained by utilizing the general procedure (Scheme 2) taking 4-methylbenzyl phenyl ketone **1h** (0.5 mmol), 4-methyl-benzyl alcohol **2b** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a white solid in 78% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.39; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.81 (m, 2H), 7.38 – 7.34 (m, 1H), 7.28 – 7.24 (m, 2H), 7.07 – 6.98 (m, 4H), 6.92 (d, *J* = 1.6 Hz, 4H), 4.69 (t, *J* = 7.2 Hz, 1H), 3.44 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.92 (dd, *J* = 14.0, 6.8 Hz, 1H), 2.19 (d, *J* = 3.6 Hz, 6H); $^{13}$C NMR (101 MHz, ) δ 199.43 (s), 136.84 (s), 136.80 (s), 136.72 (s), 136.18 (s), 135.49 (s), 132.75 (s), 129.61 (s), 128.99 (s), 128.91 (s), 128.69 (s), 128.44 (s), 128.14 (s), 55.52 (s), 39.67 (s), 21.05 (s), 21.01 (s). HRMS (m/z): Calculated: 315.1743, Obtained: 315.1745.

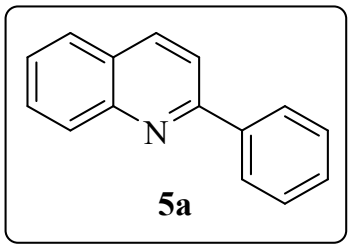
**3-(4-bromophenyl)-1-phenyl-2-(p-tolyl)propan-1-one** (**3u**).




Product **3u** was obtained by utilizing the general procedure (Scheme 2) taking 4-methylbenzyl phenyl ketone **1h** (0.5 mmol), 4-bromo-benzyl alcohol **2d** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a white solid in 75%

yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.42; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.46 – 7.42 (m, 1H), 7.36 – 7.29 (m, 4H), 7.08 (dd, *J* = 15.2, 8.4 Hz, 4H), 6.95 (d, *J* = 8.4 Hz, 2H), 4.72 (t, *J* = 7.2 Hz, 1H), 3.50 – 3.45 (m, 1H), 3.02 – 2.97 (m, 1H), 2.27 (s, 3H); $^{13}$C NMR (101 MHz, ) δ 199.03 (s), 138.94 (s), 137.02 (s), 136.60 (s), 135.70 (s), 132.97 (s), 131.31 (s), 130.99 (s), 129.77 (s), 128.73 (s), 128.55 (s), 128.15 (s), 120.01 (s), 55.41 (s), 39.51 (s), 21.09 (s). HRMS (m/z): Calculated: 379.0692, Obtained: 379.0680.

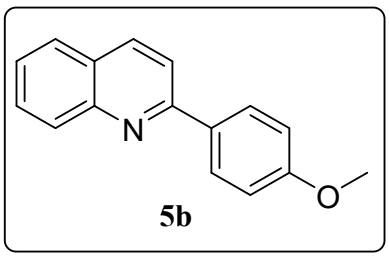
**2-phenylquinoline** (**5a**).




**5a**

Product **5a** was obtained by utilizing the general procedure (Scheme 3) taking acetophenone **1a** (0.5 mmol), 2-amino benzyl alcohol **4a** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a white solid in 89% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.41; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 4H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.46 – 7.41 (m, 3H), 7.39 – 7.35 (m, 1H); $^{13}$C NMR data matches with the already existing data ref (d).

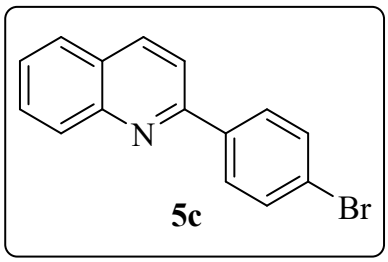
**2-(4-methoxyphenyl)quinoline** (**5b**).




**5b**

Product **5b** was obtained by utilizing the general procedure (Scheme 3) taking 4-methoxy-acetophenone **1c** (0.5 mmol), 2-amino benzyl alcohol **4a** (0.6 mmol) and isolated by column chromatography (hexane: EtOAc = 99 : 01) as a white solid in 90% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.43; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.12 (m, 4H), 7.83 – 7.78 (m, 2H), 7.72 – 7.68 (m, 1H), 7.50 – 7.47 (m, 1H), 7.05 – 7.03 (m, 2H), 3.88 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 160.84 (s), 156.96 (s), 148.32 (s), 136.68 (s), 132.30 (s), 129.615 (s), 129.546 (s), 128.93 (s), 127.47 (s), 126.94 (s), 125.95 (s), 118.61 (s), 114.26 (s), 55.43 (s). Mass spectroscopy (HRMS) data matches with the already existing data ref (a).

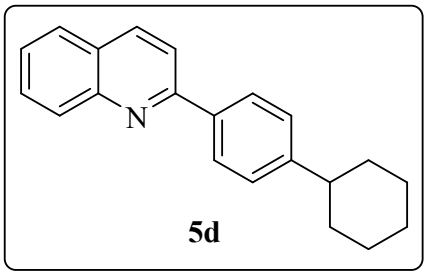
**2-(4-bromophenyl)quinoline** (**5c**).




**5c**

Product **5c** was obtained by utilizing the general procedure (Scheme 3) taking 4-bromo-acetophenone **1i** (0.5 mmol), 2-amino benzyl alcohol **4a** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a brown solid in 82% yield; $R_f$ (hexane/EtOAc = 90 : 10):0.39; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.19 (m, 2H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.76 – 7.71 (m, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.52 (m, 1H); $^{13}$C NMR data matches with the already existing data ref (d).

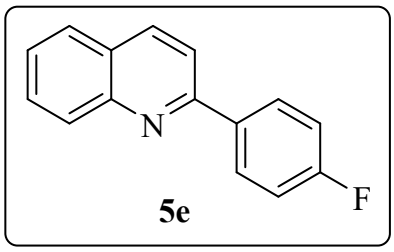
**2-(4-cyclohexylphenyl)quinoline** (**5d**).




**5d**

Product **5d** was obtained by utilizing the general procedure (Scheme 3) taking 4-cyclohexylacetophenone **1e** (0.5 mmol), 2-amino benzyl alcohol **4a** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a light yellow solid in 75% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.41; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.21 (m, 2H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.87 – 7.81 (m, 2H), 7.75 – 7.71 (m, 1H), 7.54 – 7.50 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.61 – 2.54 (m, 1H), 1.93 – 1.85 (m, 3H), 1.76 (d, *J* = 12.4 Hz, 1H), 1.52 – 1.25 (m, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 156.20 (s), 150.38 (s), 138.40 (s), 130.42 (s), 129.17 (s), 127.73 (s), 127.07 (s), 126.95 (s), 126.48 (s), 125.47 (s), 118.85 (s), 43.92 (s), 33.65 (s), 26.21 (s), 25.51 (s). HRMS (m/z): Calculated: 288.1747, Obtained: 288.1745.

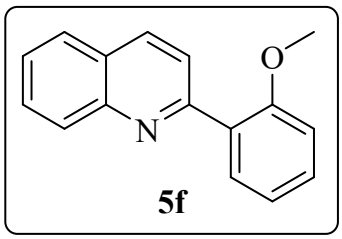
**2-(4-fluorophenyl)quinoline** (**5e**).




**5e**

Product **5e** was obtained by utilizing the general procedure (Scheme 3) taking 4-fluoro-acetophenone **1f** (0.5 mmol), 2-amino benzyl alcohol 4a (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a light yellow solid in 81% yield; $R_f$ (hexane/EtOAc = 90 : 10): 0.44; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 2H), 8.12 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.71 – 7.67 (m, 1H), 7.51 – 7.47 (m, 1H), 7.19 – 7.13 (m, 2H); $^{13}$C NMR data matches with the already existing data ref (d).

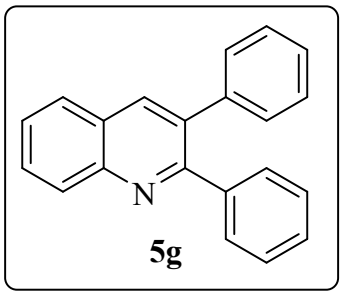
**2-(2-methoxyphenyl)quinoline** (**5f**).




**5f**

Product **5f** was obtained by utilizing the general procedure (Scheme 3) taking 2-OMe-acetophenone **1d** (0.5 mmol), 2-amino benzyl alcohol **4a** (0.6 mmol) and isolated by column chromatography (hexane : EtOAc = 99 : 01) as a brown oil in 85% yield; $R_f$ (hexane/EtOAc = 90 : 10):0.41; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.76 – 7.74 (m, 2H), 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.39 – 7.35 (m, 1H), 7.30 – 7.26 (m, 1H), 7.02 – 6.98 (m, 1H), 6.88 (dd, *J* = 8.0, 0.8 Hz, 1H), 3.69 (s, 3H); $^{13}$C NMR data matches with the already existing data ref (e).

**2,3-diphenylquinoline** (**5g**).




**5g**

Product **5g** was obtained by utilizing the general procedure (Scheme 3) taking benzyl phenyl ketone **1g** (0.5 mmol), 2-amino benzyl alcohol **4a** (0.6 mmol) and isolated by column

chromatography (hexane : EtOAc = 99 : 01) as a yellow oil in 88% yield; $R_f$ (hexane/EtOAc = 90 : 10):0.40; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 1H), 8.18 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.58 – 7.54 (m, 1H), 7.47 – 7.45 (m, 2H), 7.30 – 7.23 (m, 8H); $^{13}$C NMR data matches with the already existing data ref (a).

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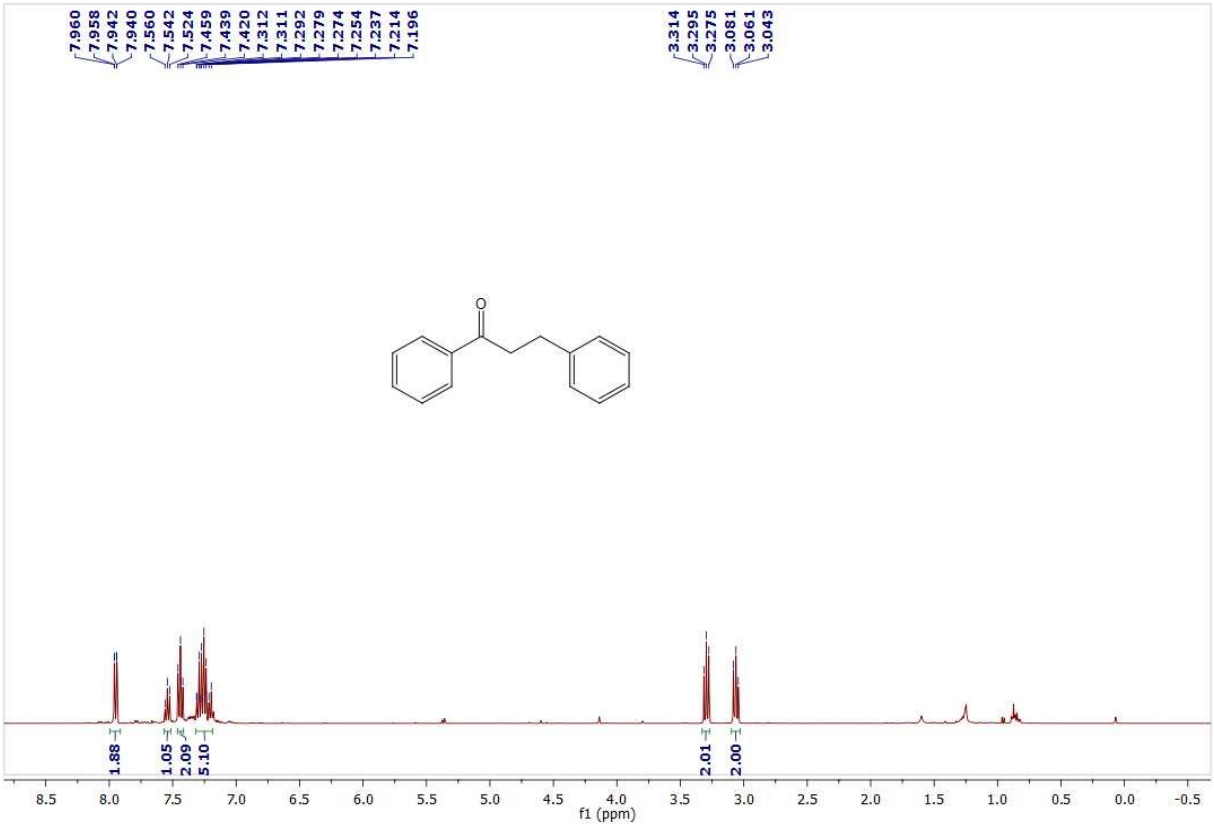
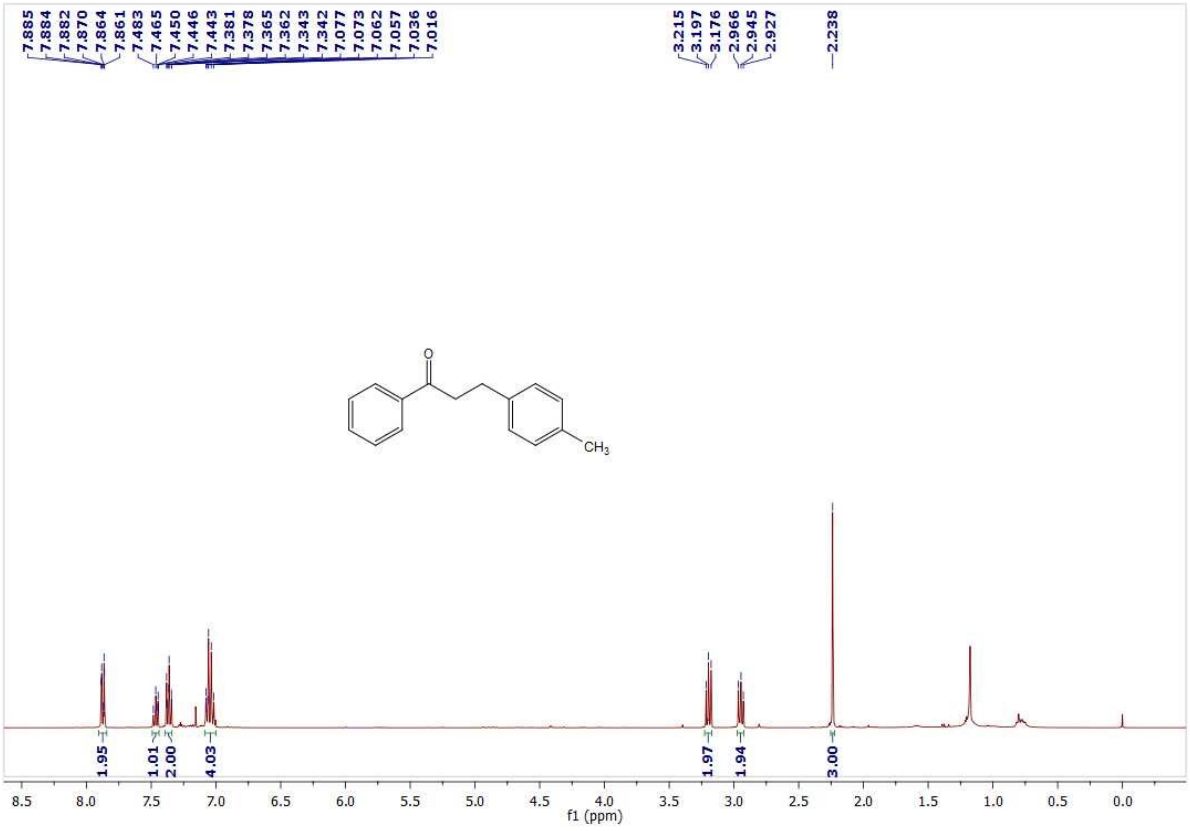
g) Xuchao Wang, Feipeng Liu, Zijuan Yan, Qing Qiang, Wei Huang, and Zi-Qiang Rong , *ACS Catalysis*, **2021**, *11* (12), 7319-7326, DOI: 10.1021/acscatal.1c00951.

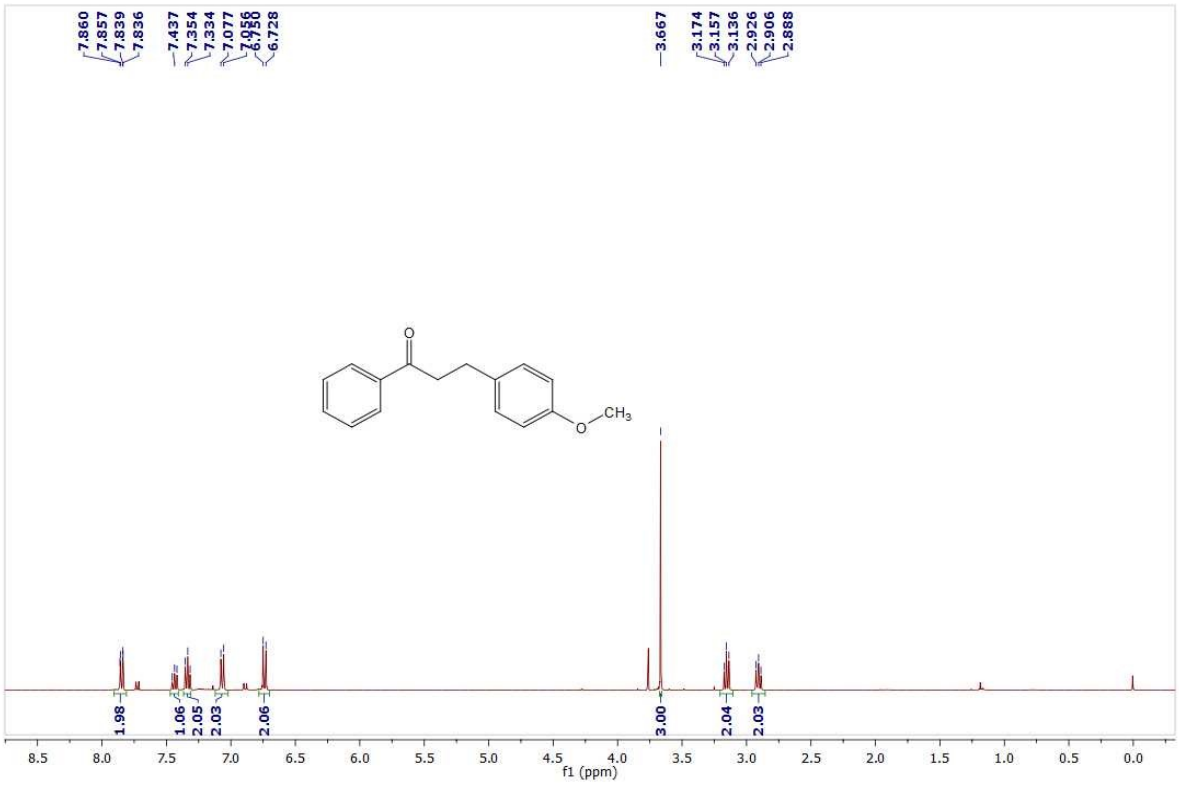

**$^1$H NMR and $^{13}$C Characterization data of selective monoalkylation of acetophenones and synthesized quinoline derivatives**



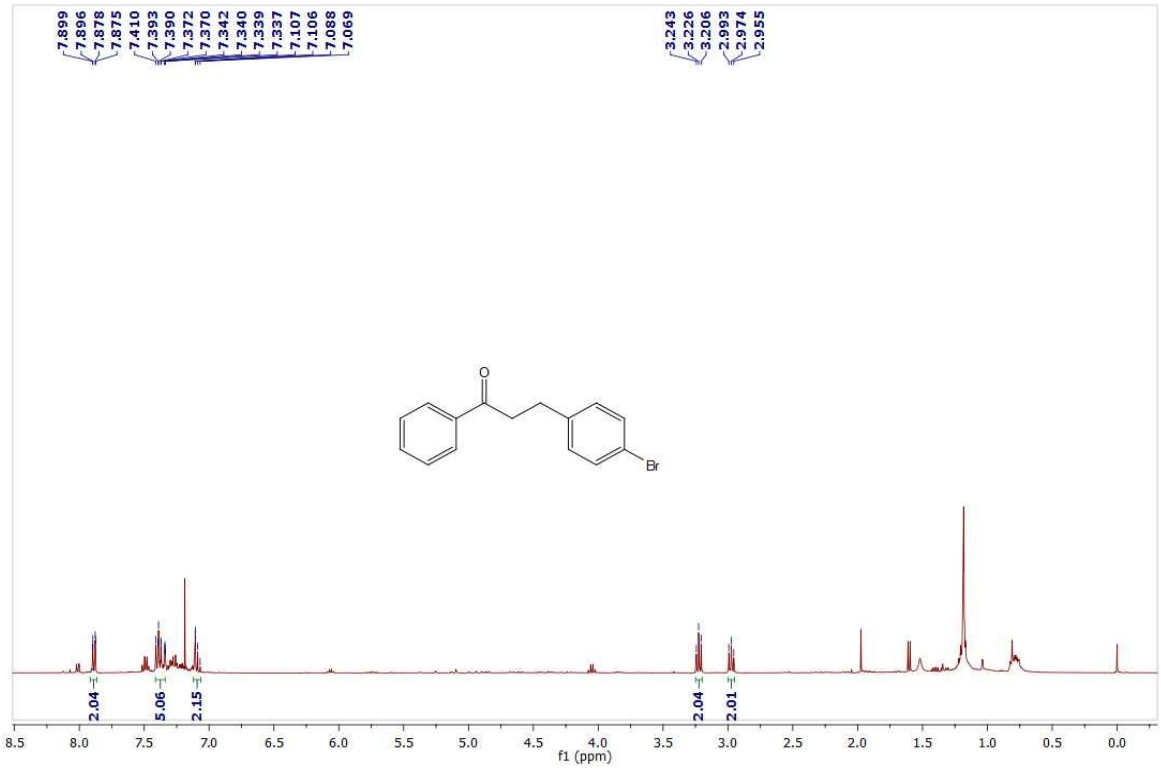

$^1$H NMR (400 MHz, Chloroform-*d*) Spectra of **3a**



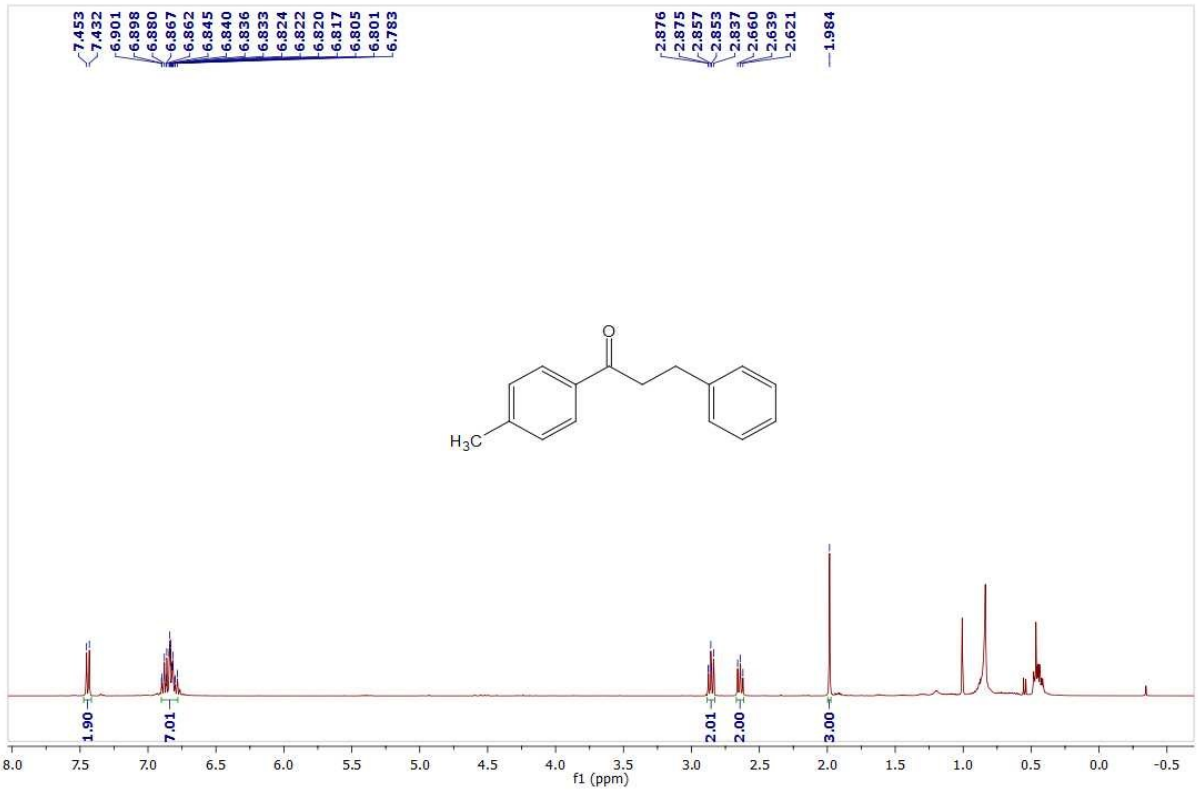

$^1$H NMR (400 MHz, Chloroform-*d*) Spectra of **3b**



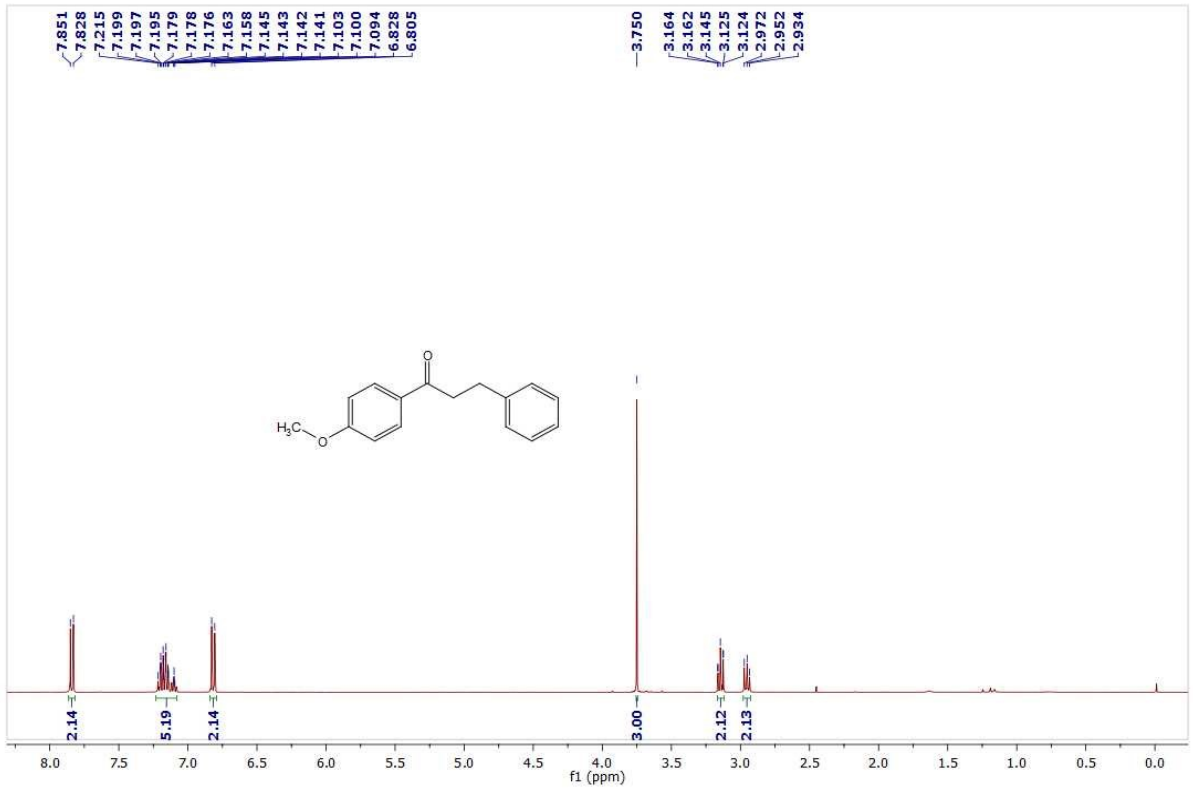

$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **3c**



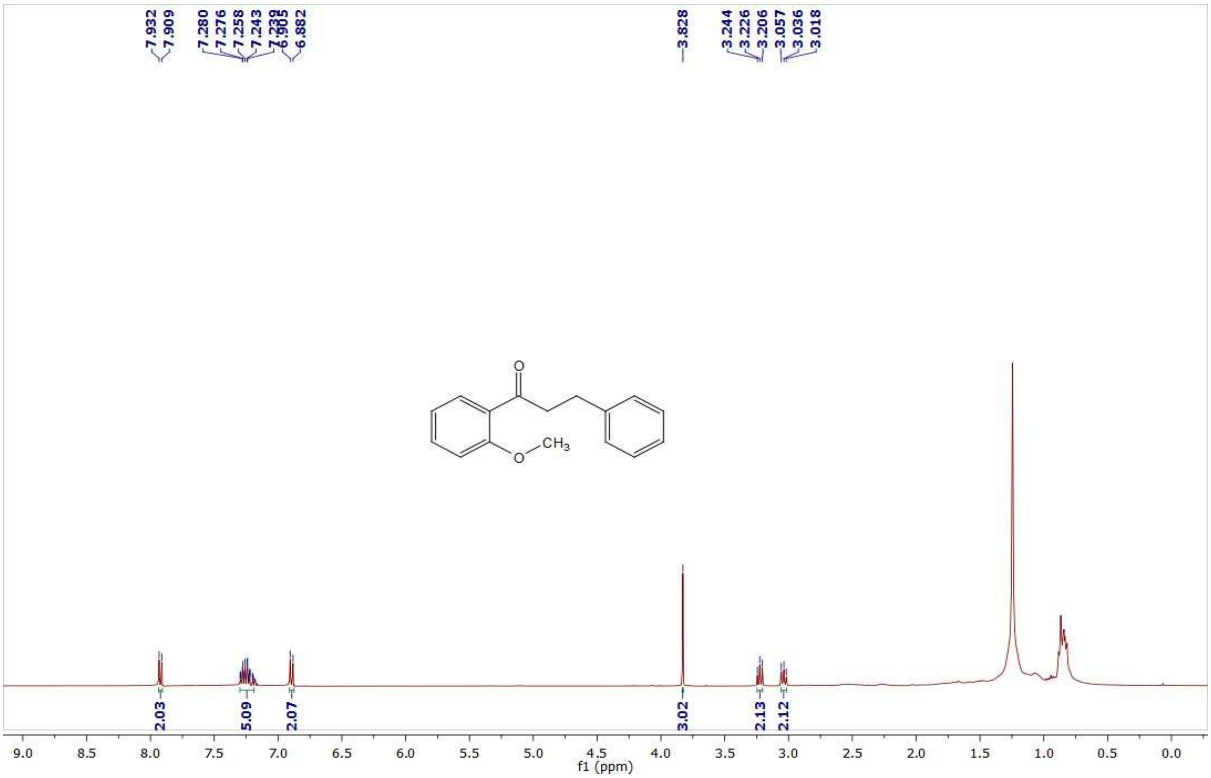

$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **3d**



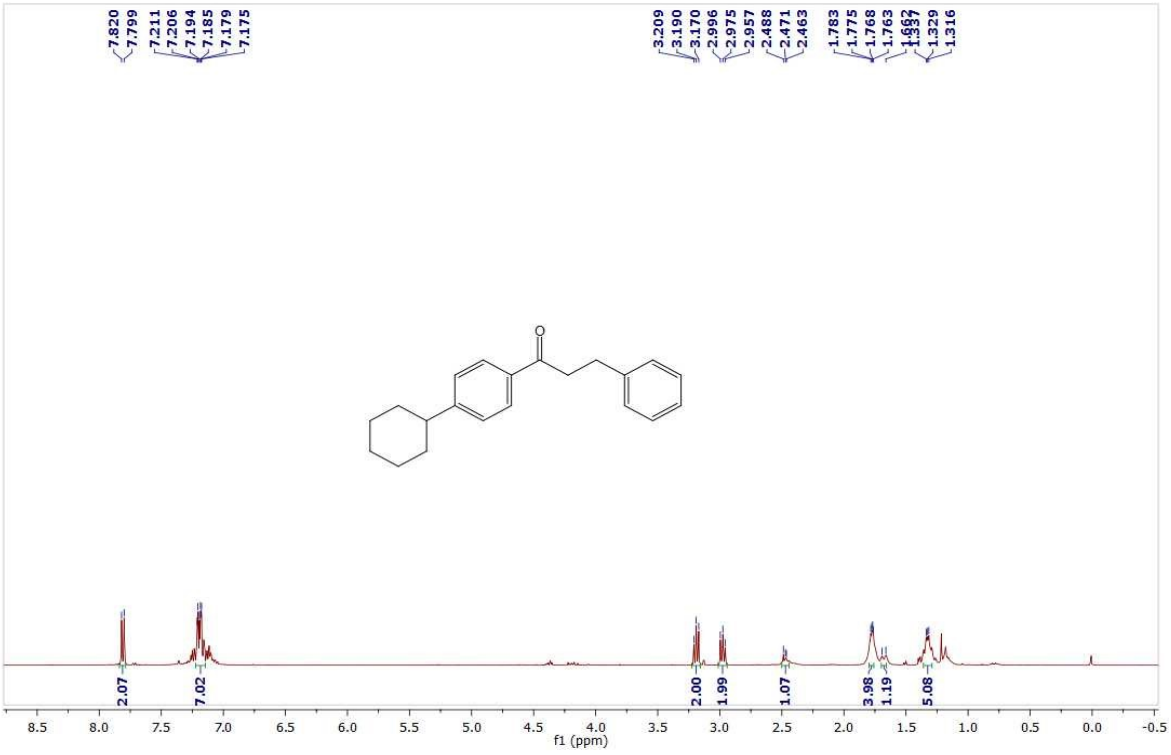

$^1$H NMR (400 MHz, Chloroform-*d*) Spectra of **3e**



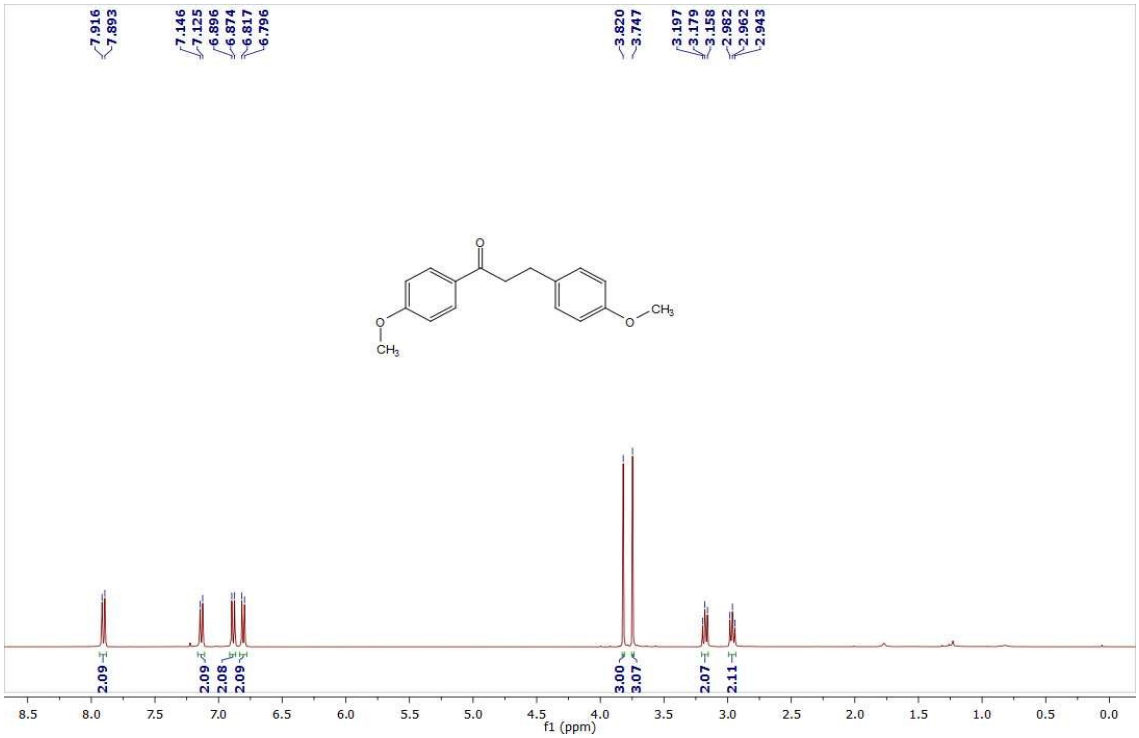

$^1$H NMR (400 MHz, Chloroform-*d*) Spectra of **3f**



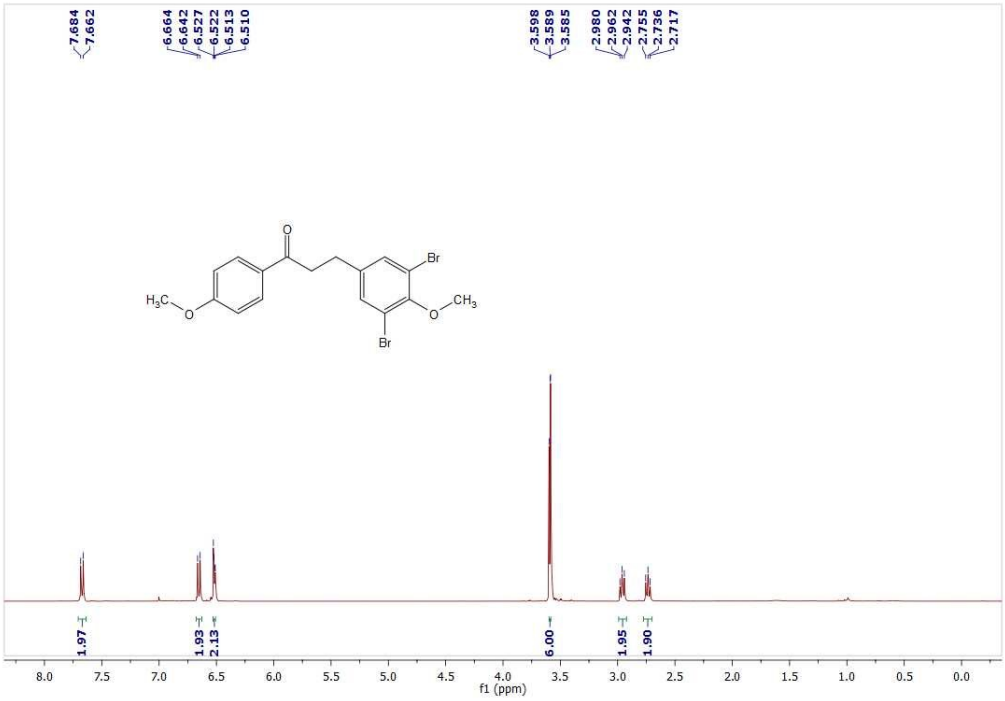

$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **3g**



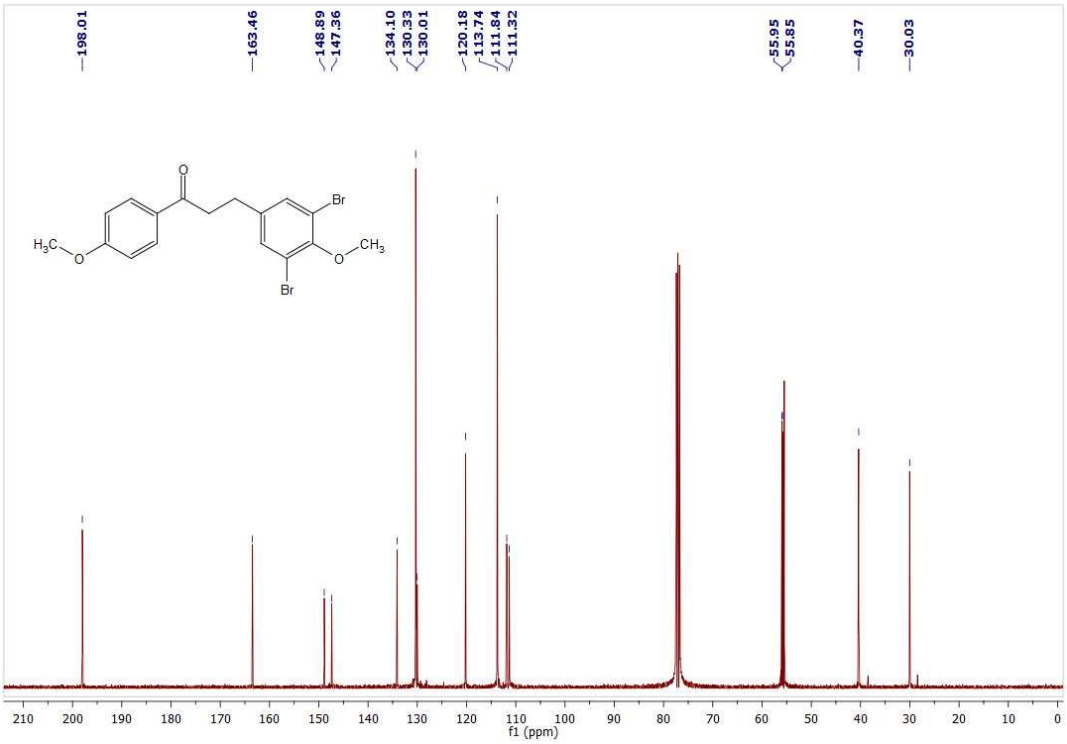

$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **3h**



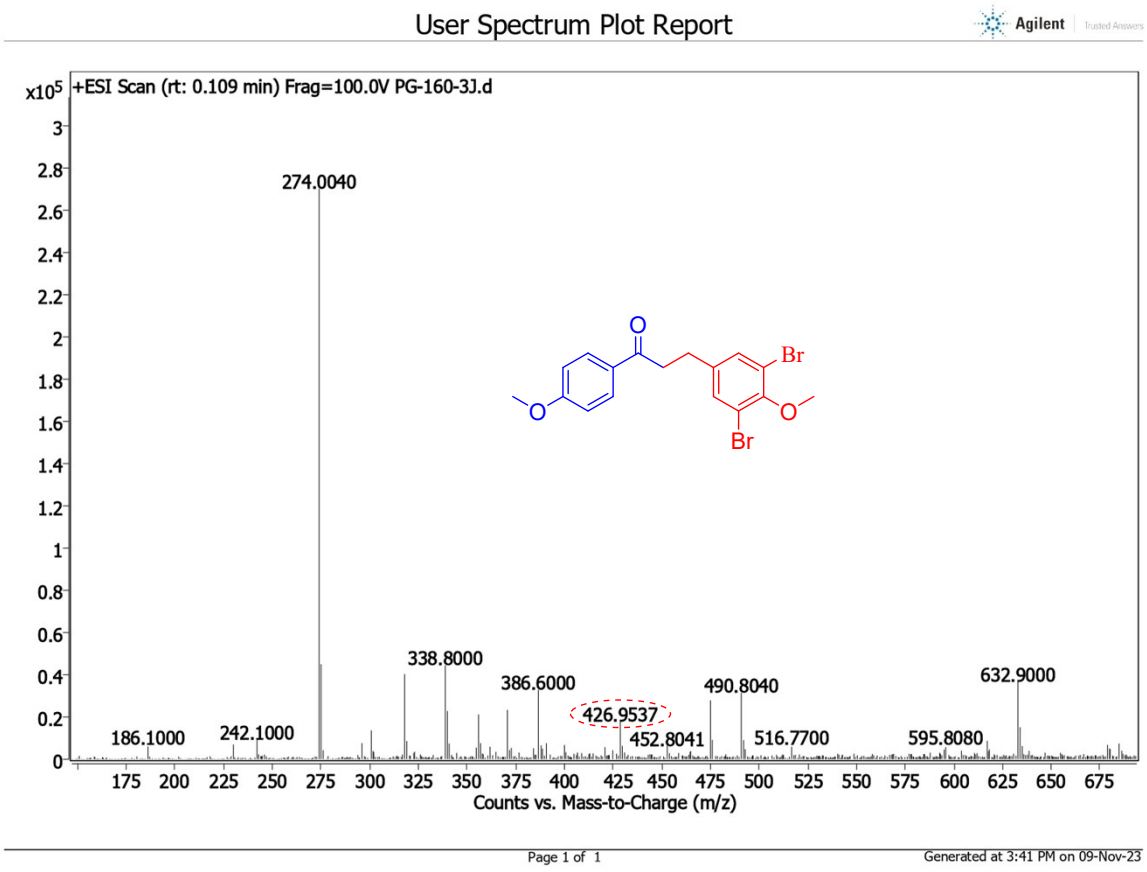

$^1$H NMR (400 MHz, Chloroform-*d*) Spectra of **3i**



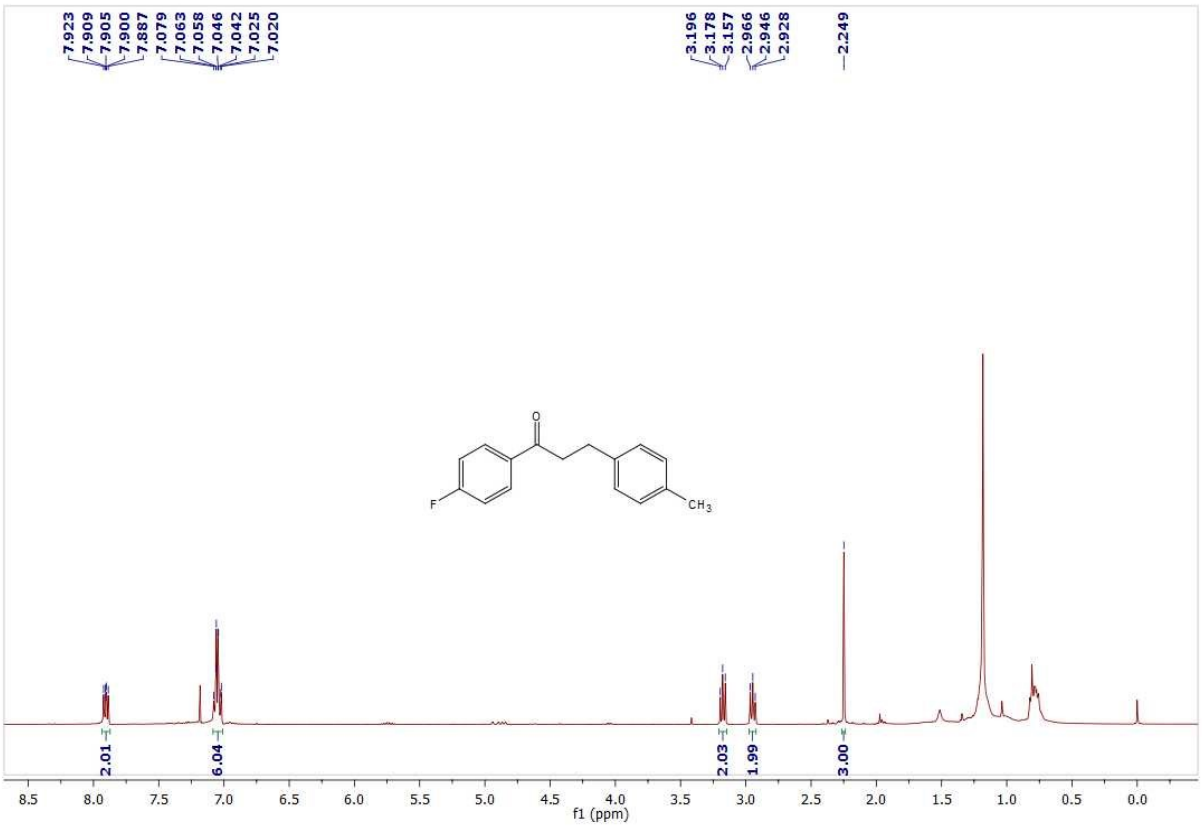

$^1$H NMR (400 MHz, Chloroform-*d*) Spectra of **3j**



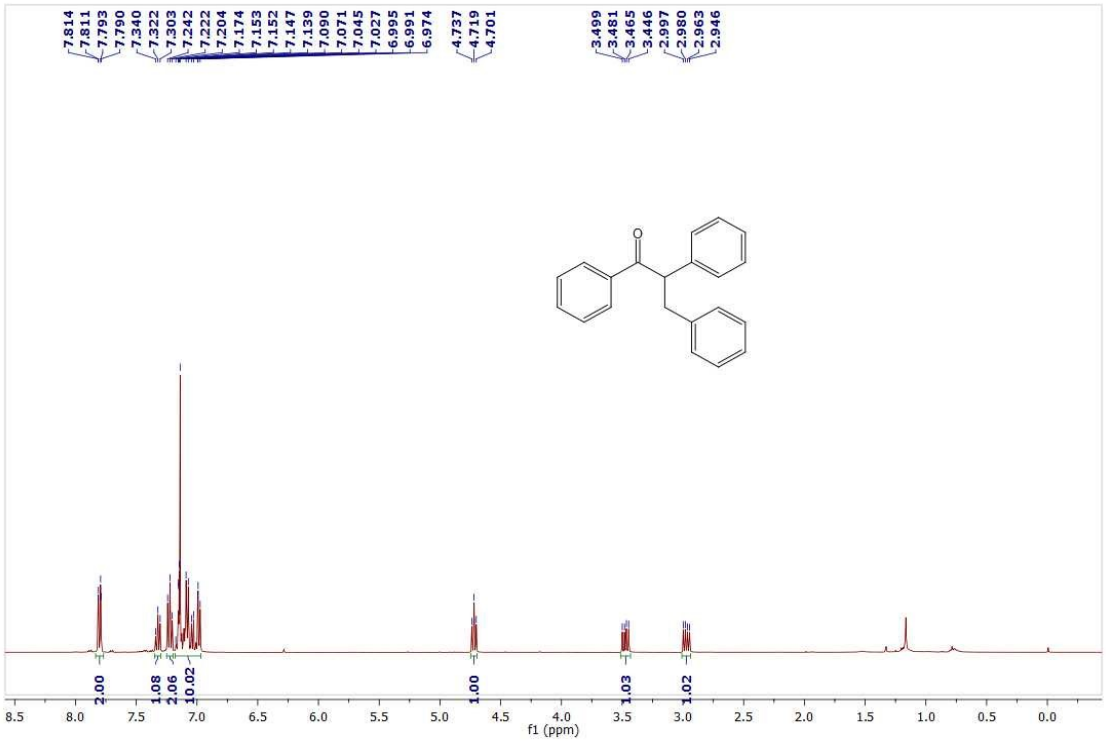

$^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) Spectra of **3j**



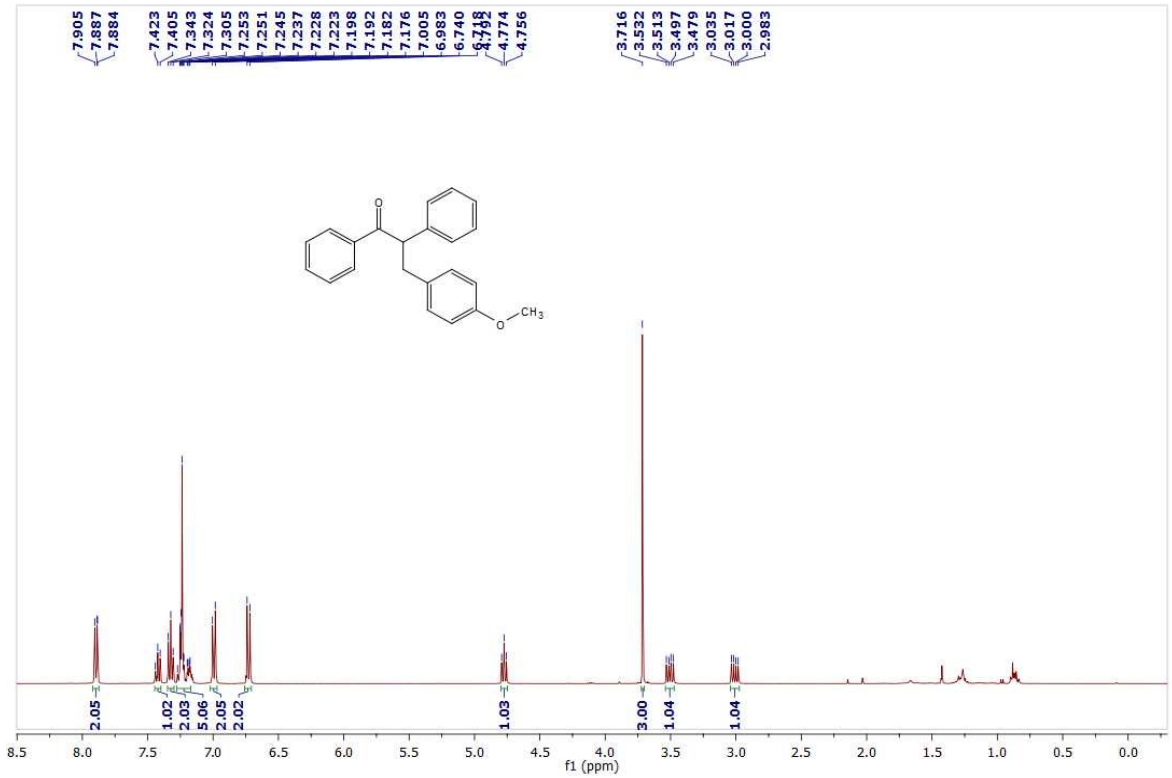

HRMS data of **3j**



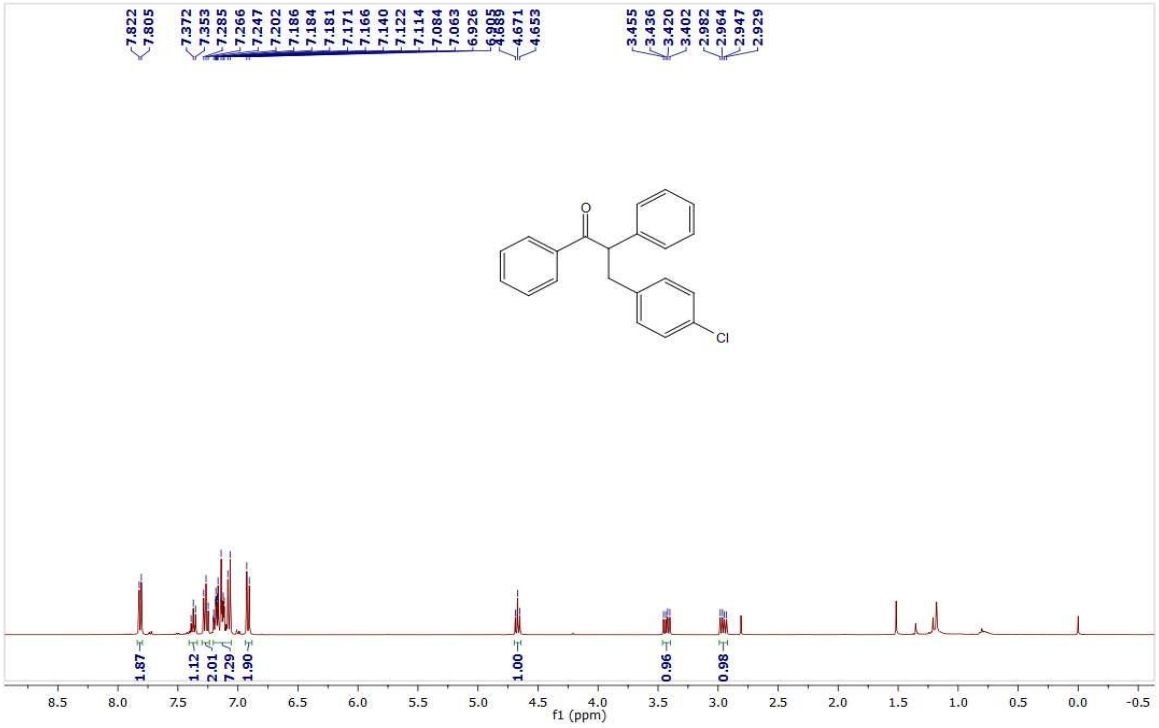

$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **3k**



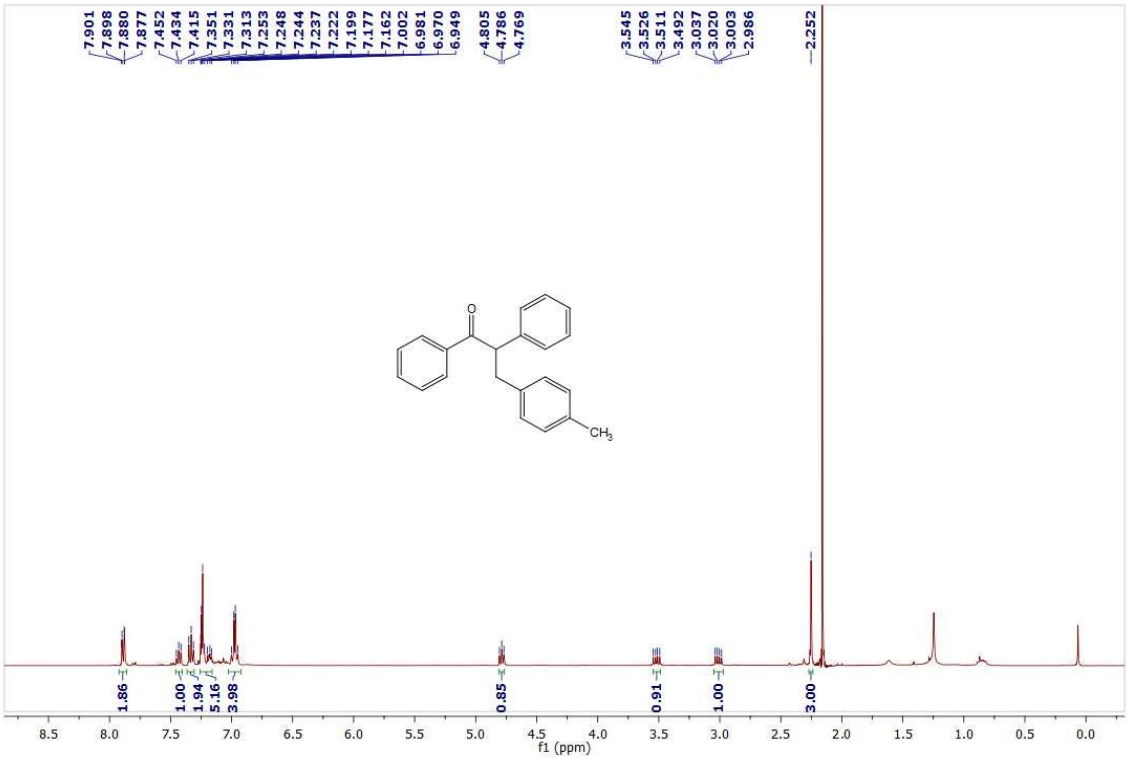

$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **3l**



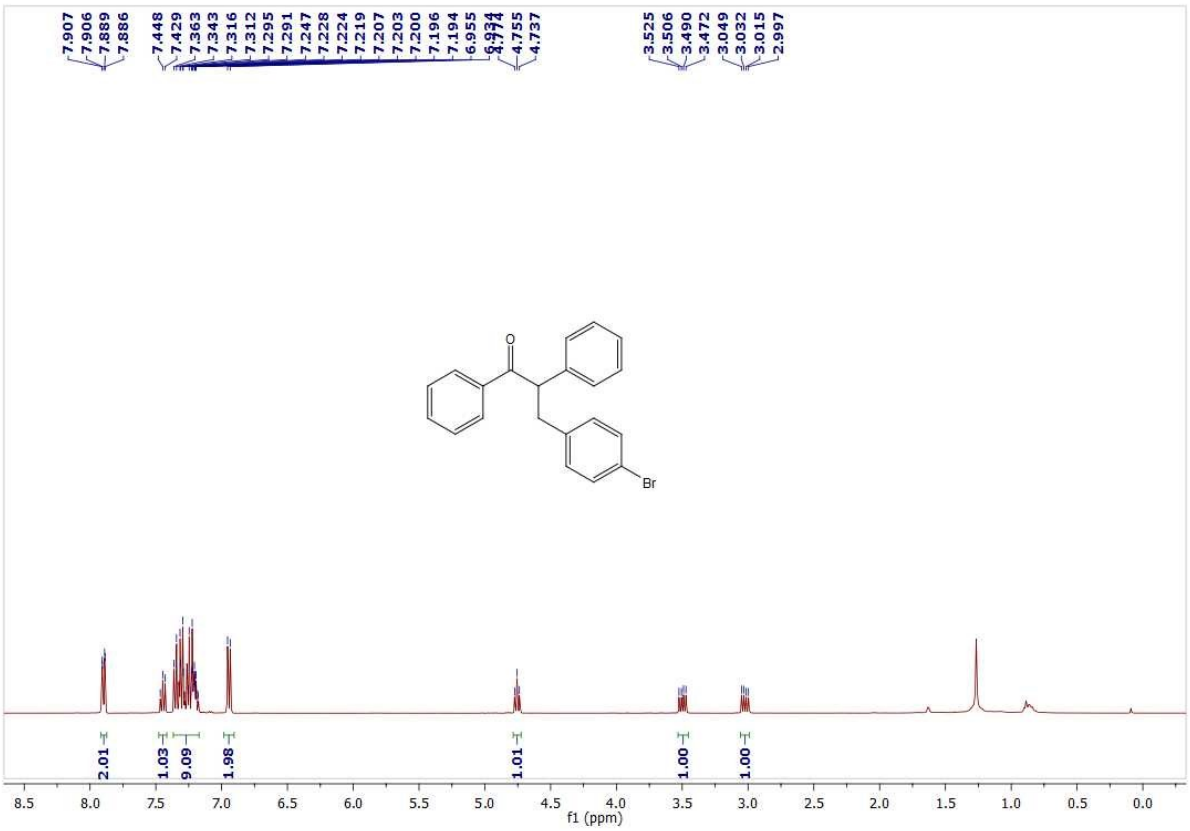

$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **3m**



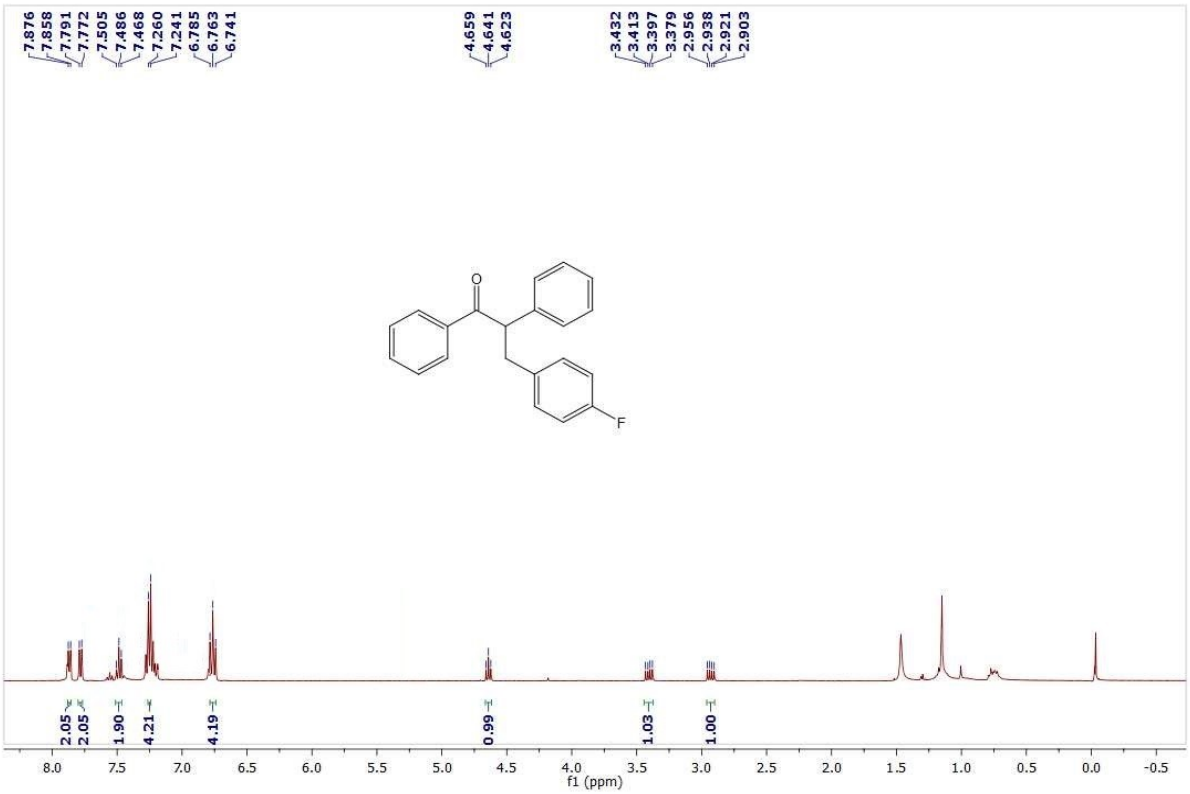

$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **3n**



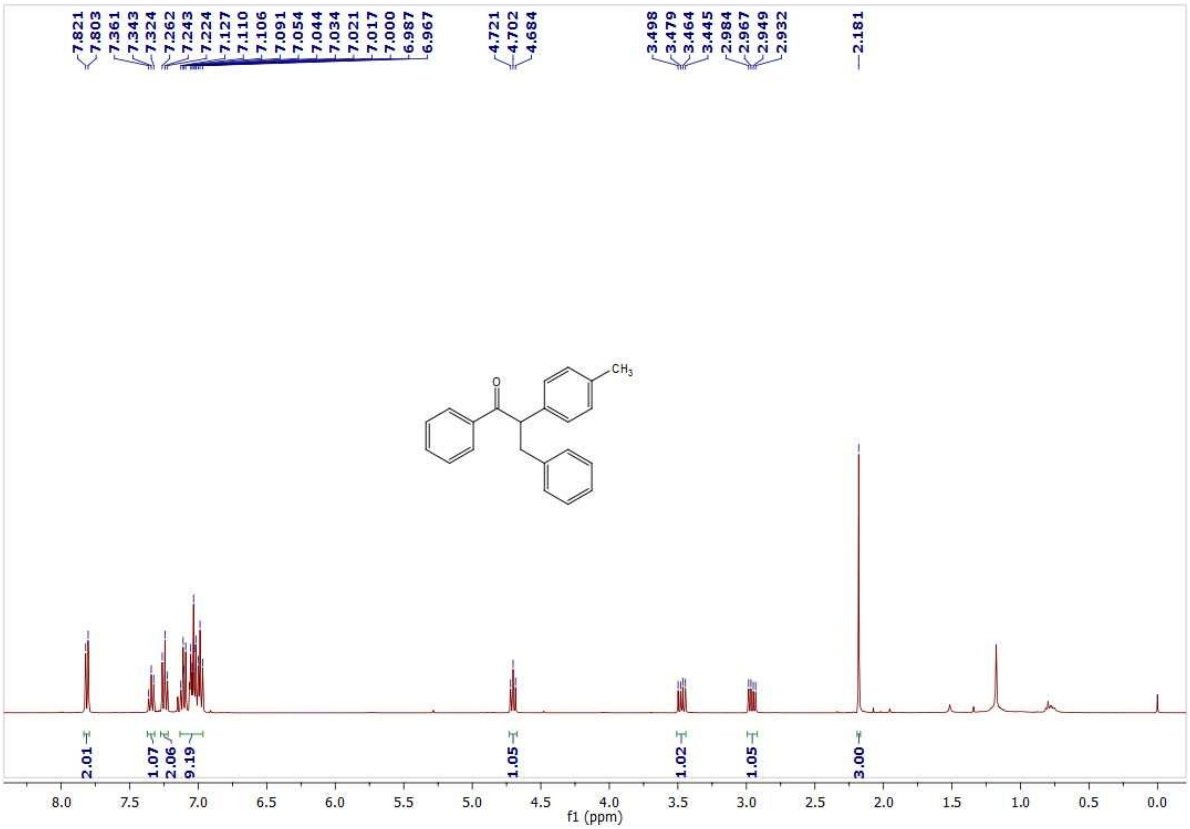

$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **3o**



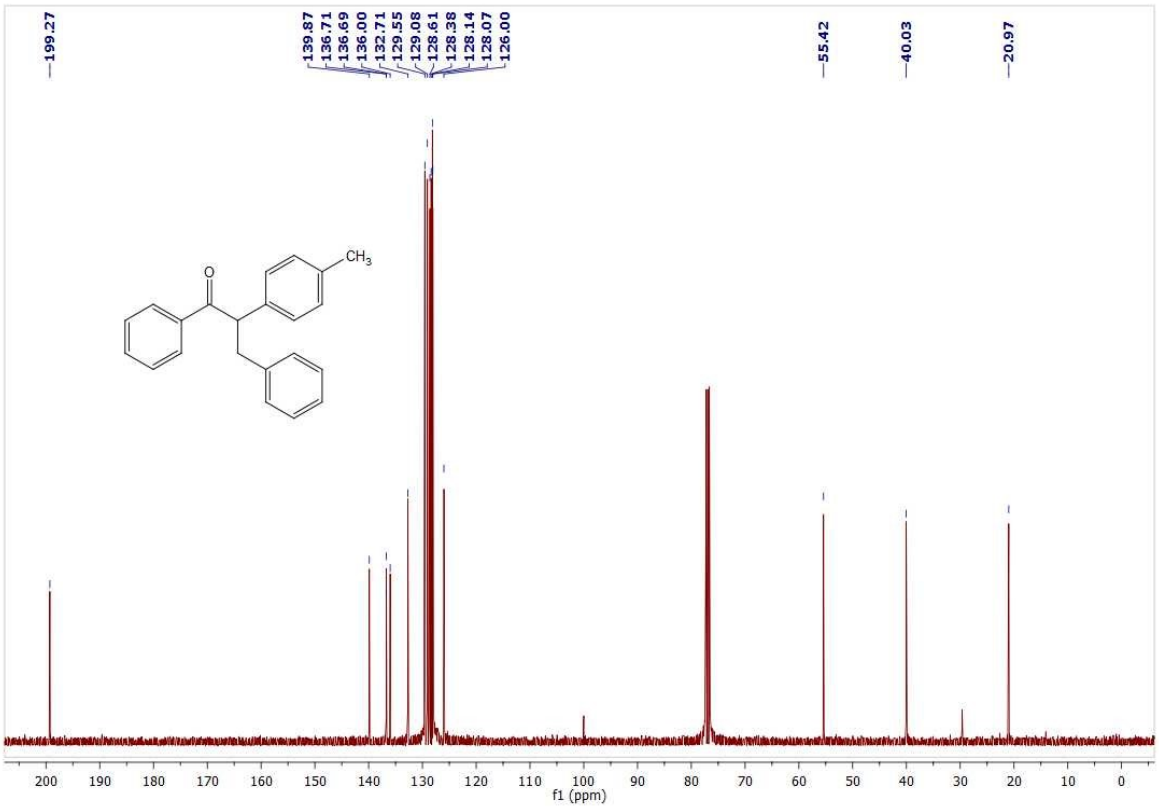

$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **3p**




$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **3q**

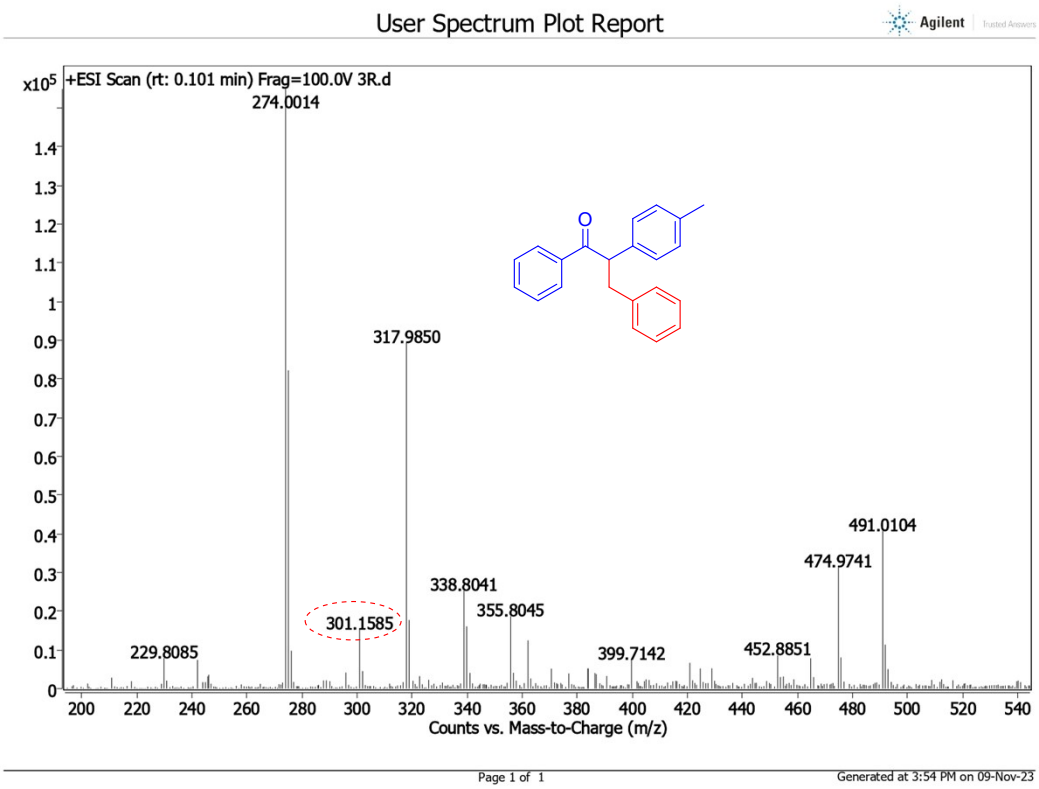



$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **3r**

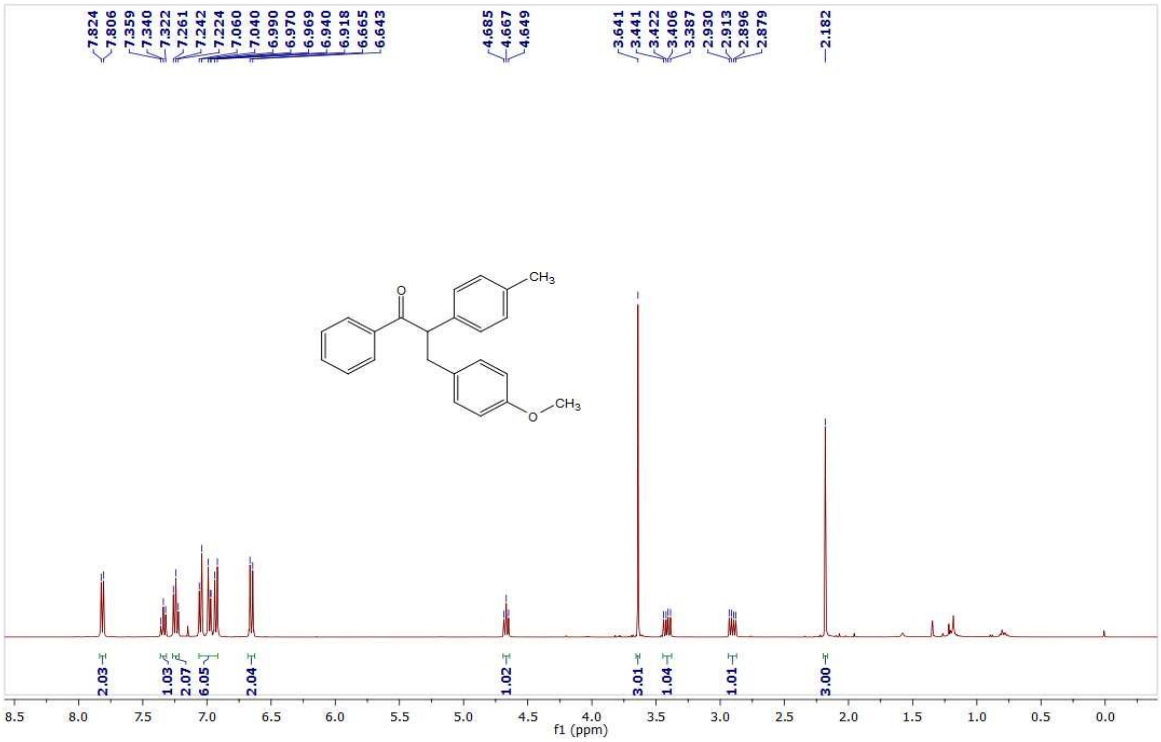



13

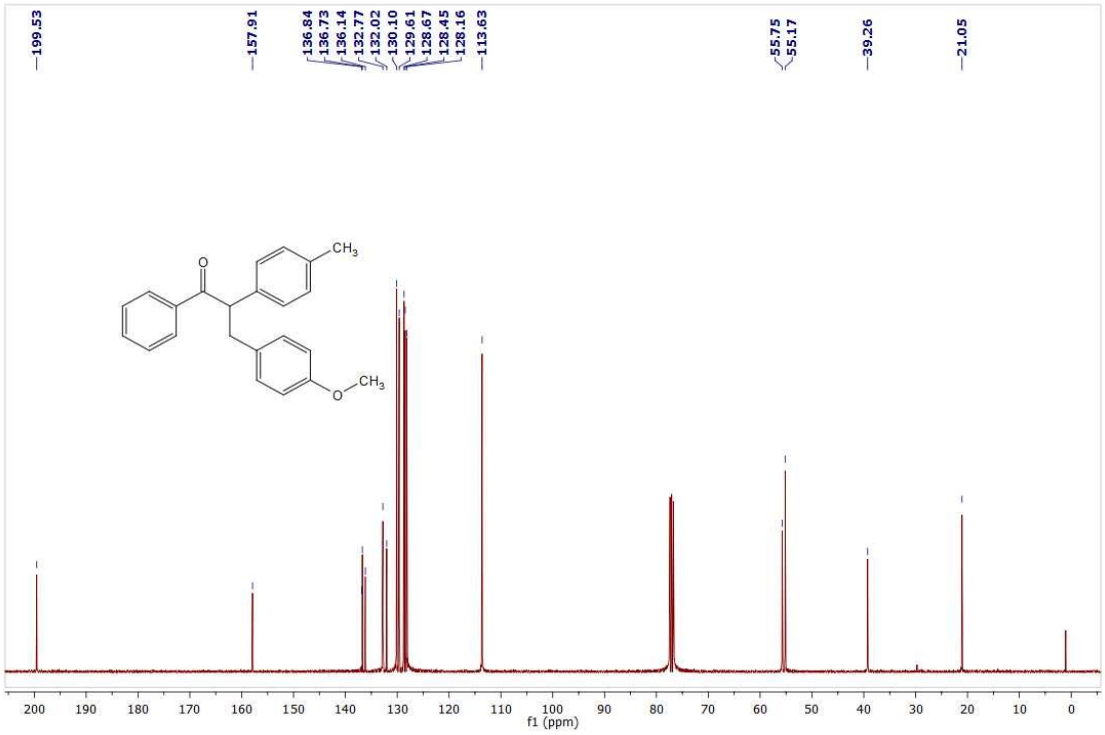
C{$^1$H} NMR (100 MHz, Chloroform-*d*) Spectra of **3r**



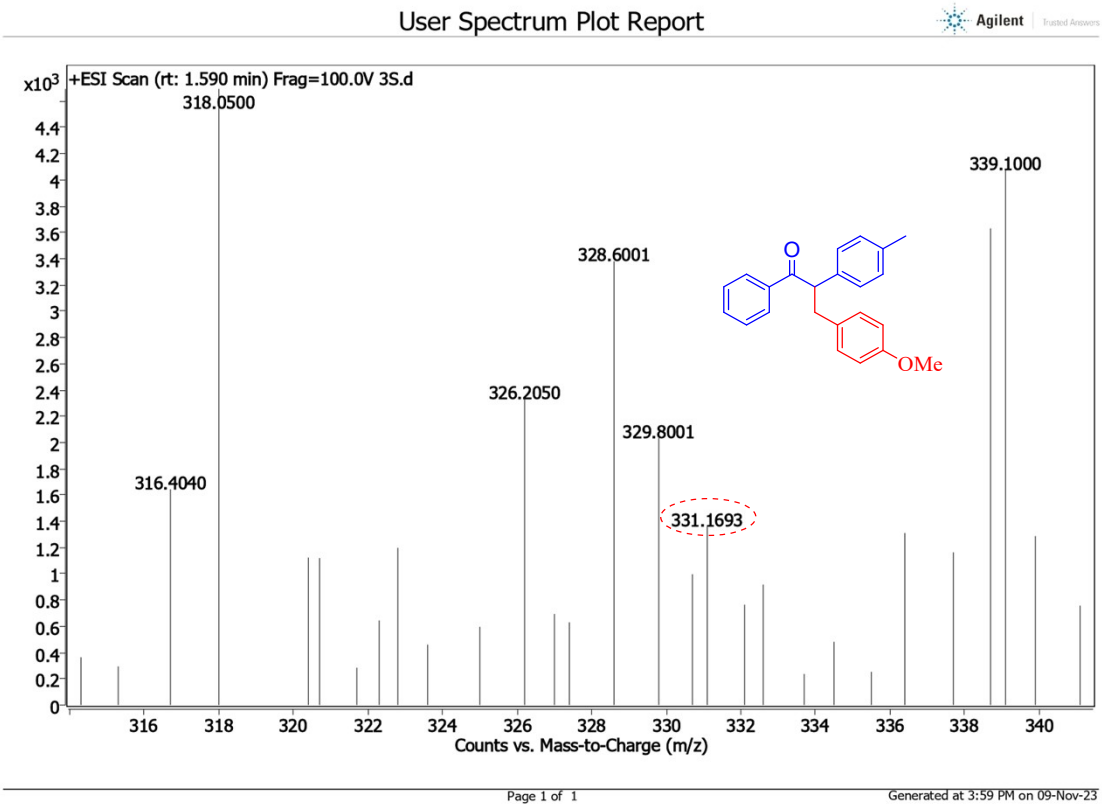

HRMS data of **3r**



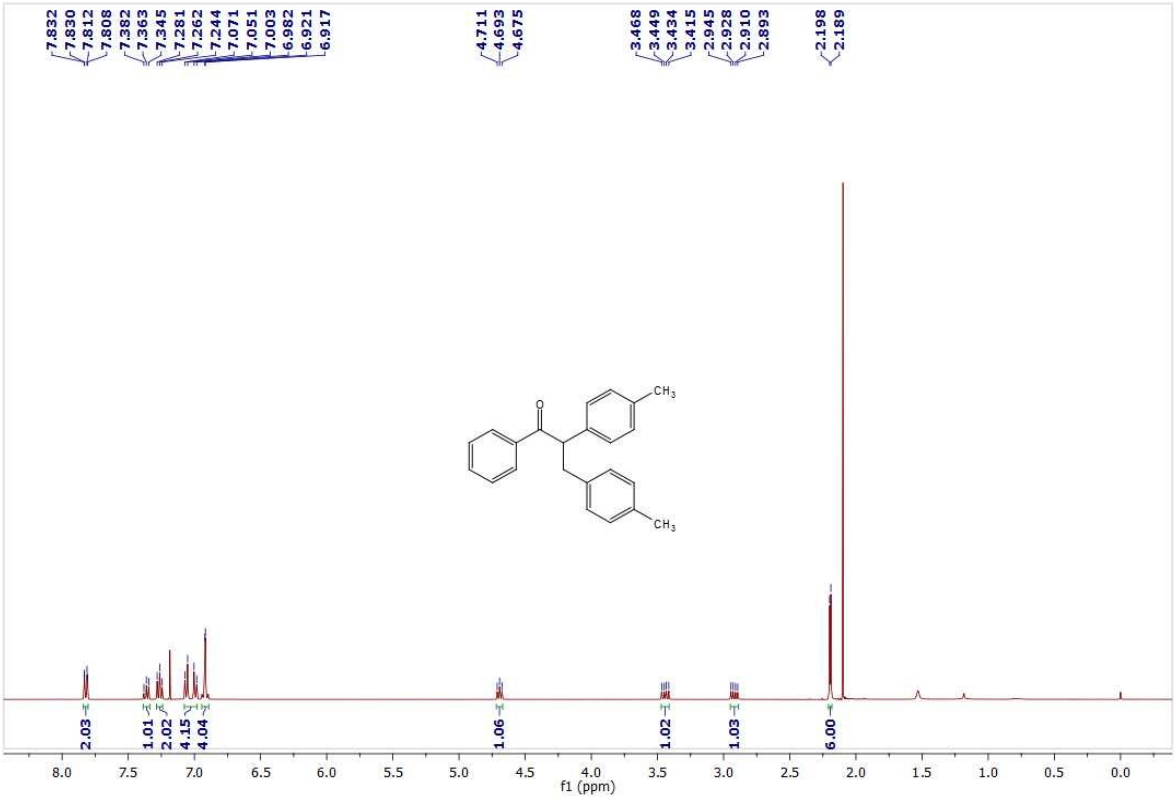

$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **3s**



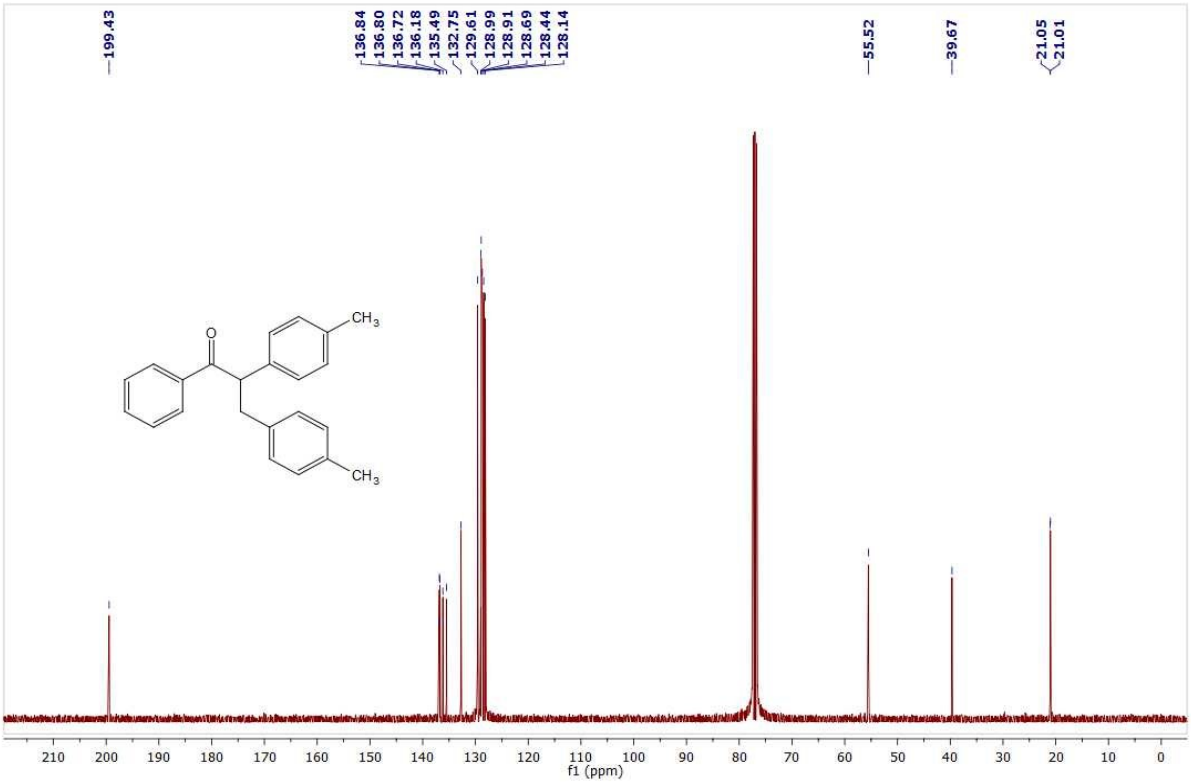
$^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) Spectra of **3s**



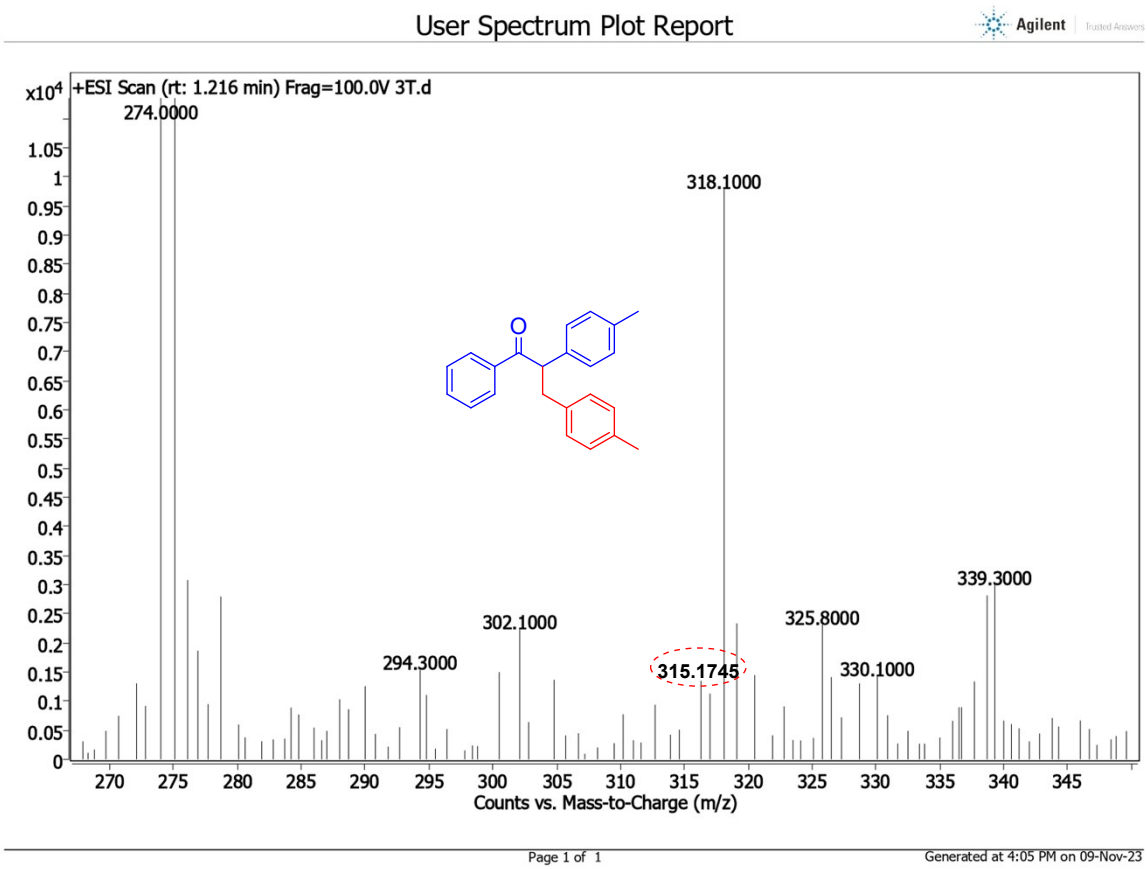

HRMS data of **3s**



$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **3t**




$^{13}$C{$^{1}$H} NMR (100 MHz, Chloroform-*d*) Spectra of **3t**



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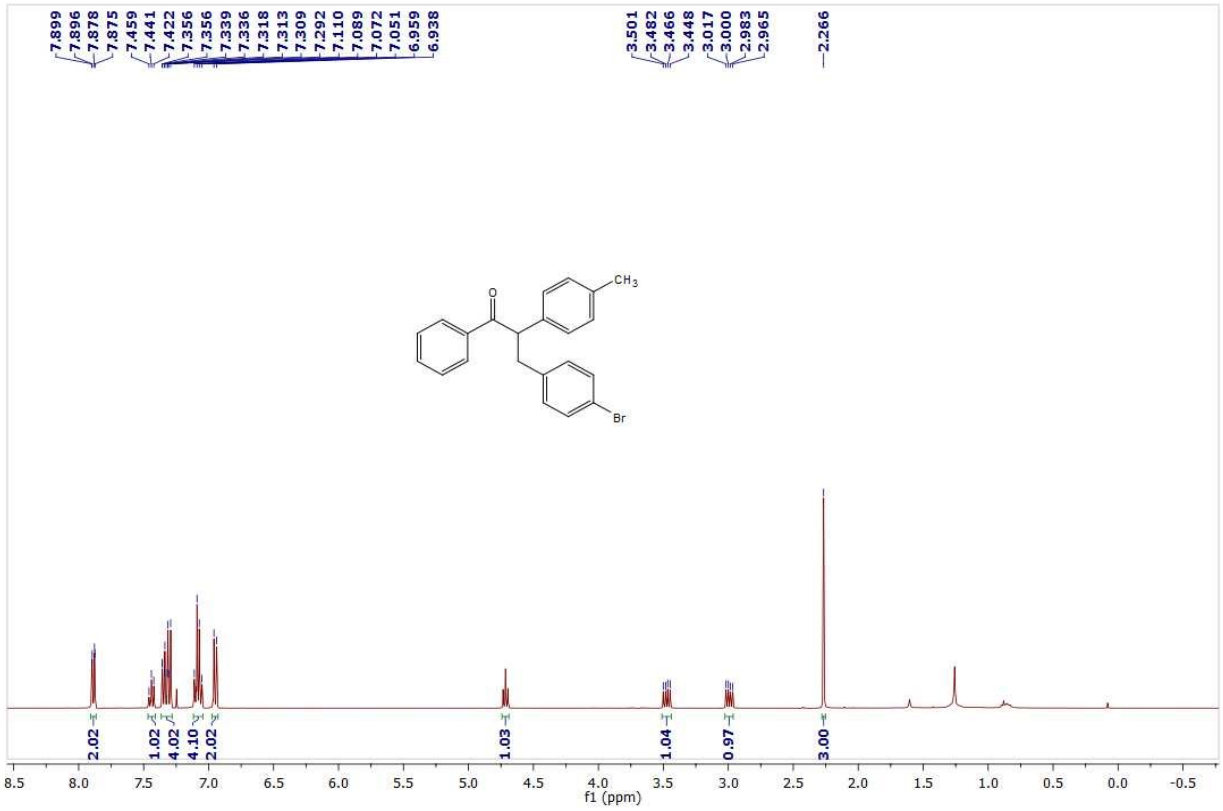
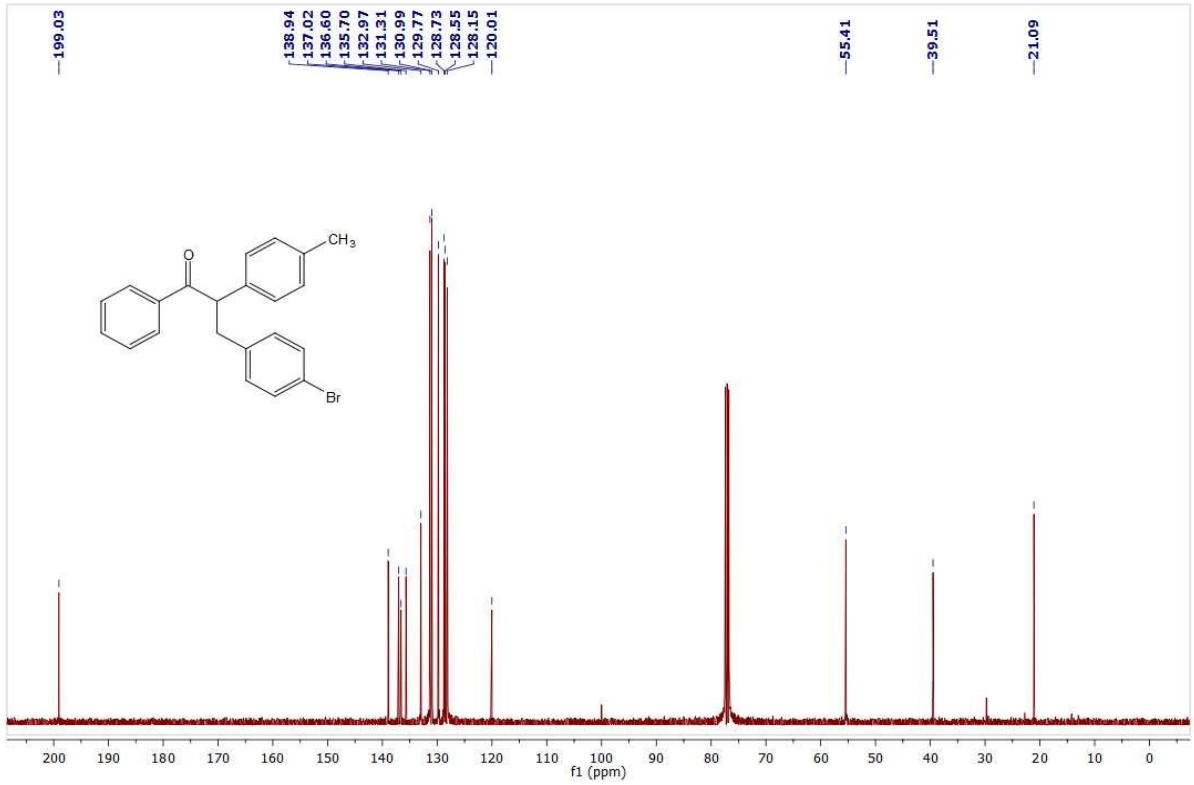
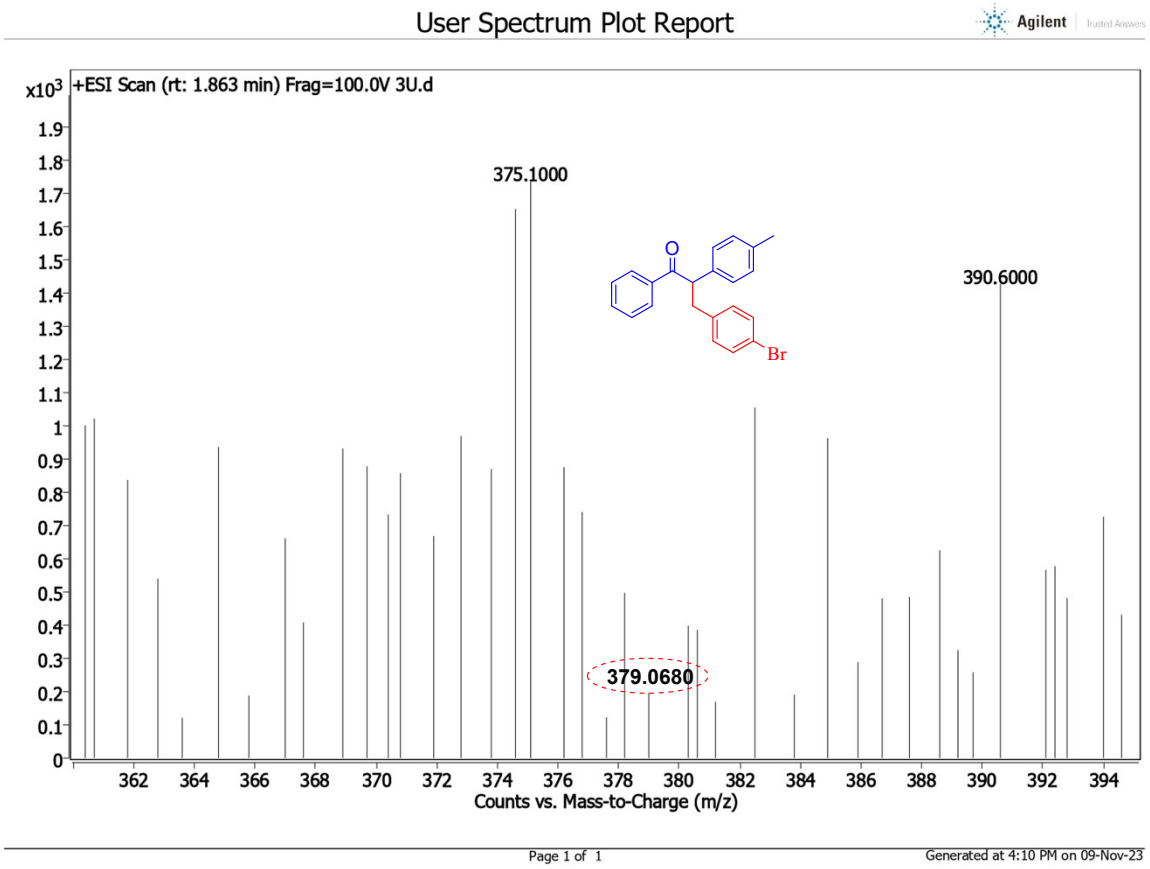


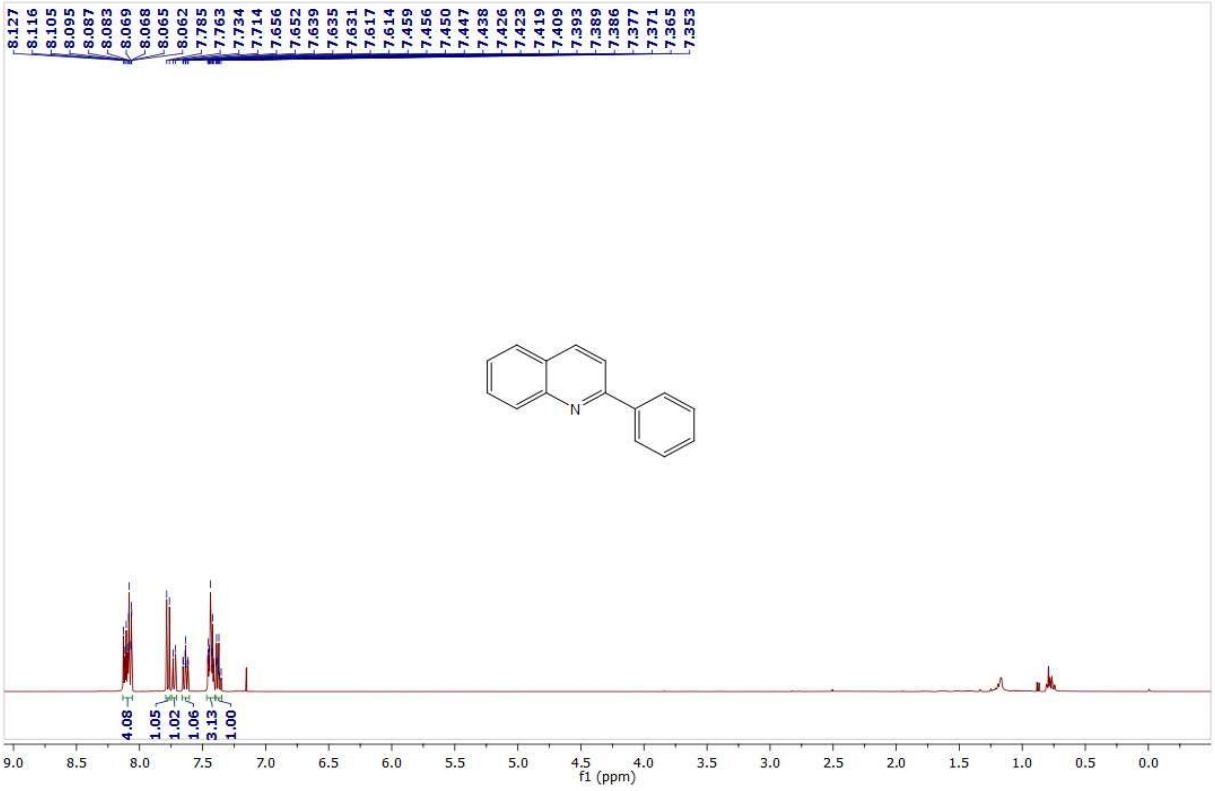

$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **3u**



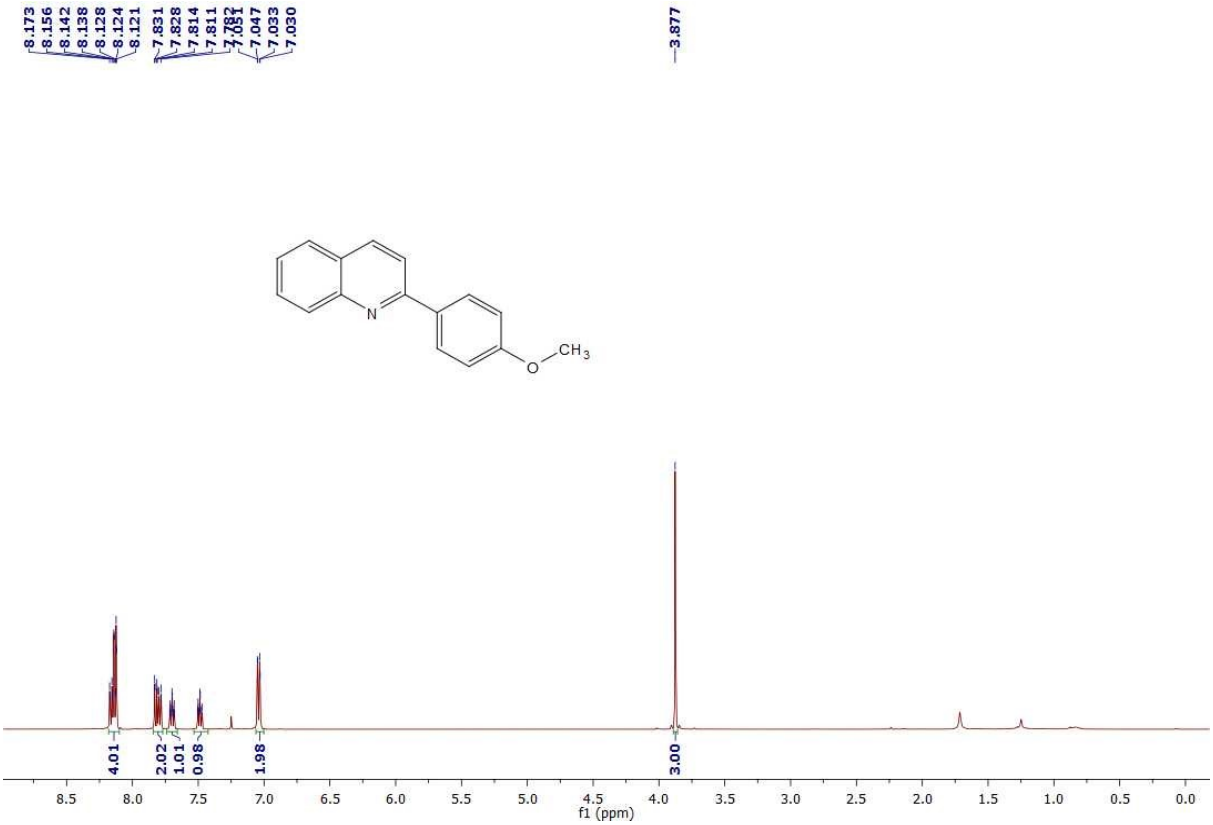

$^{13}$C{$^{1}$H} NMR (100 MHz, Chloroform-*d*) Spectra of **3u**



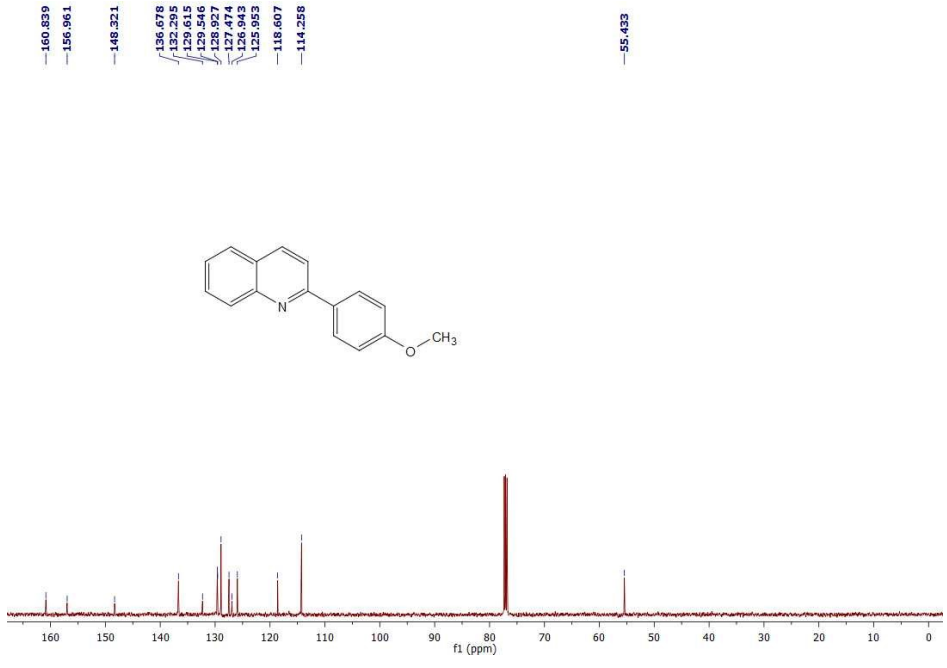

HRMS data of **3u**



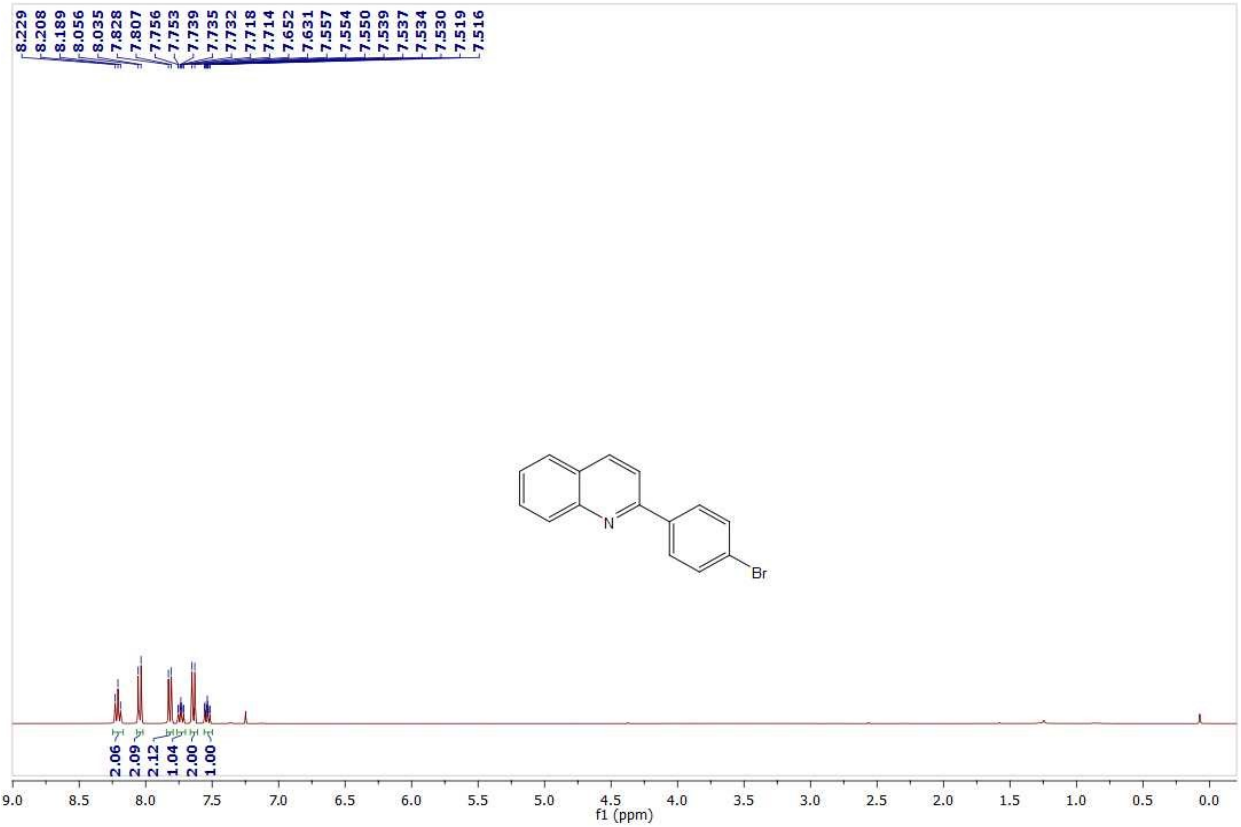
$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **5a**



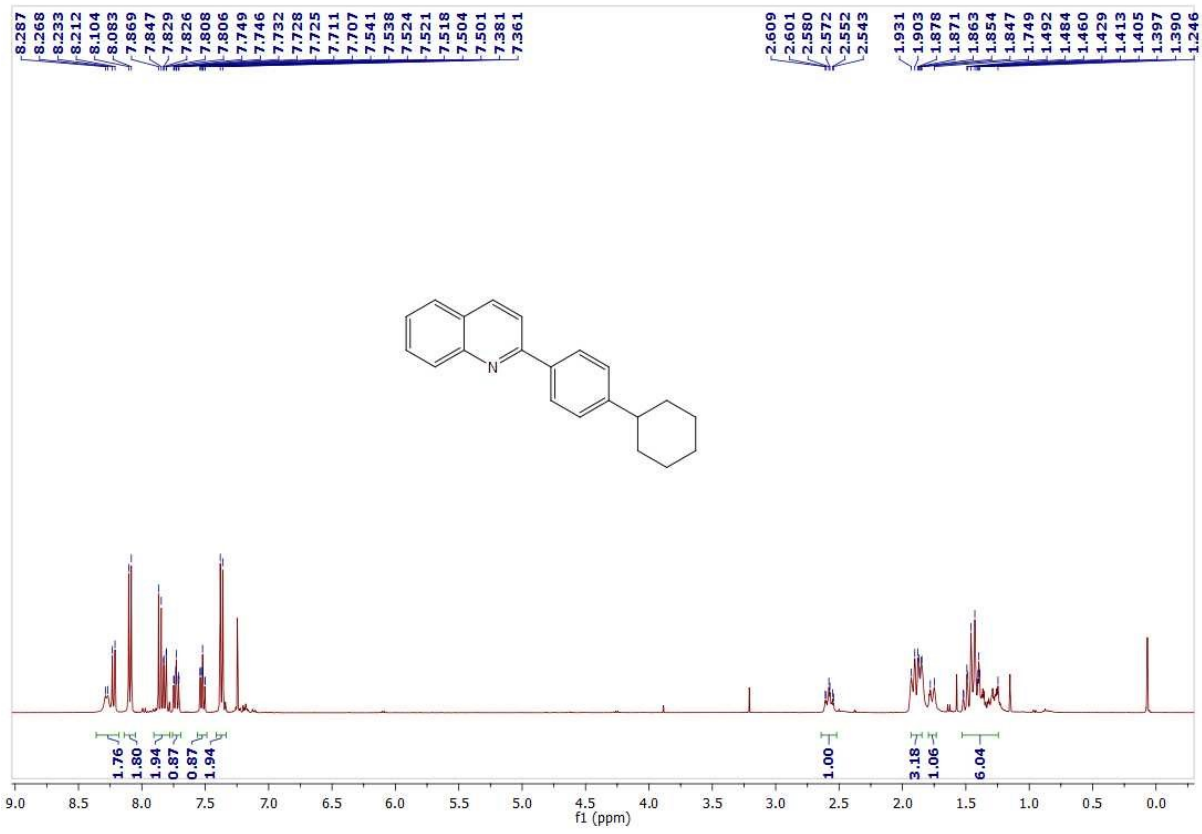

$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **5b**



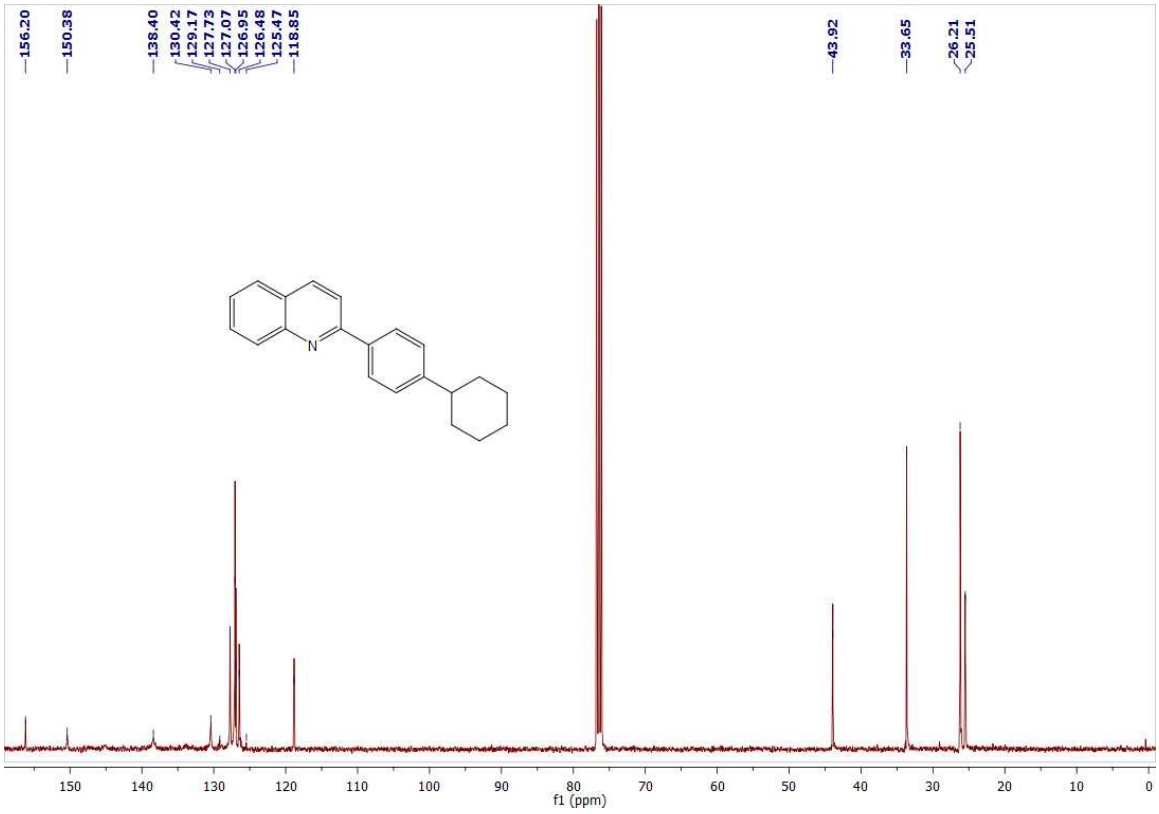

$^{13}$C{$^{1}$H} NMR (100 MHz, Chloroform-*d*) Spectra of **5b**



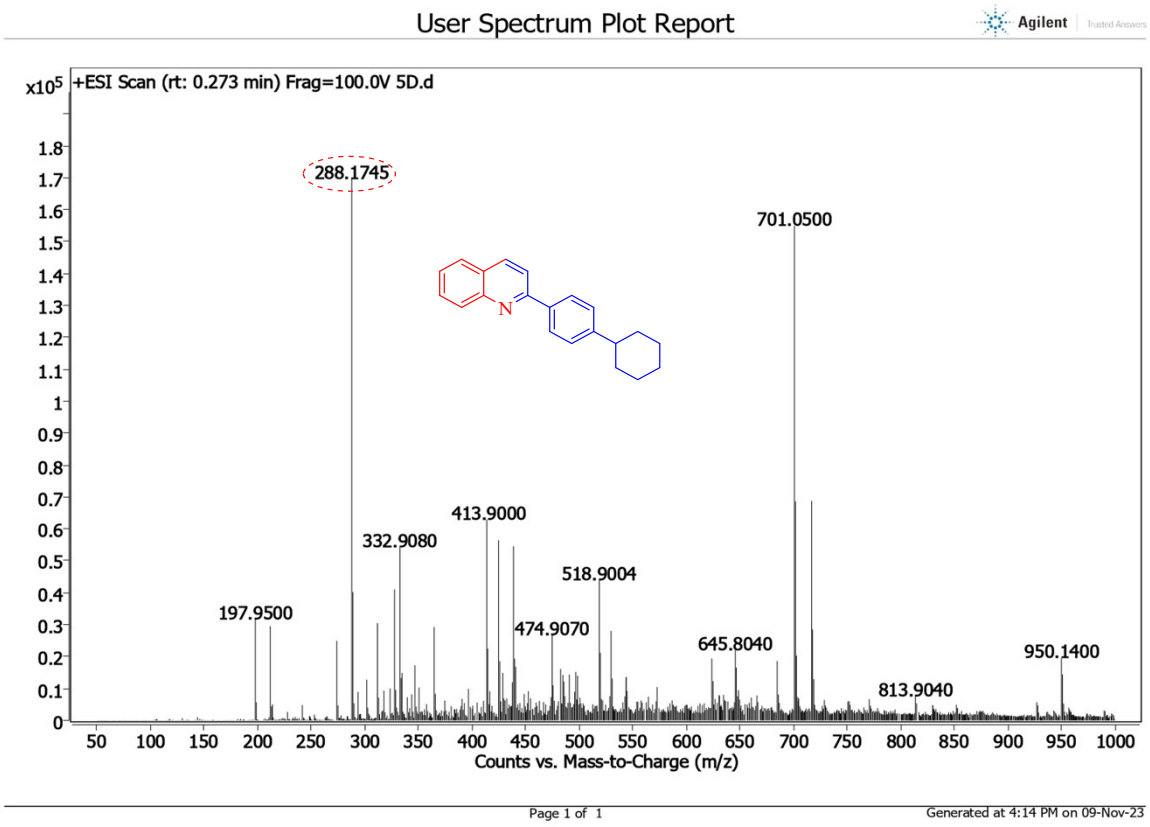

$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **5c**



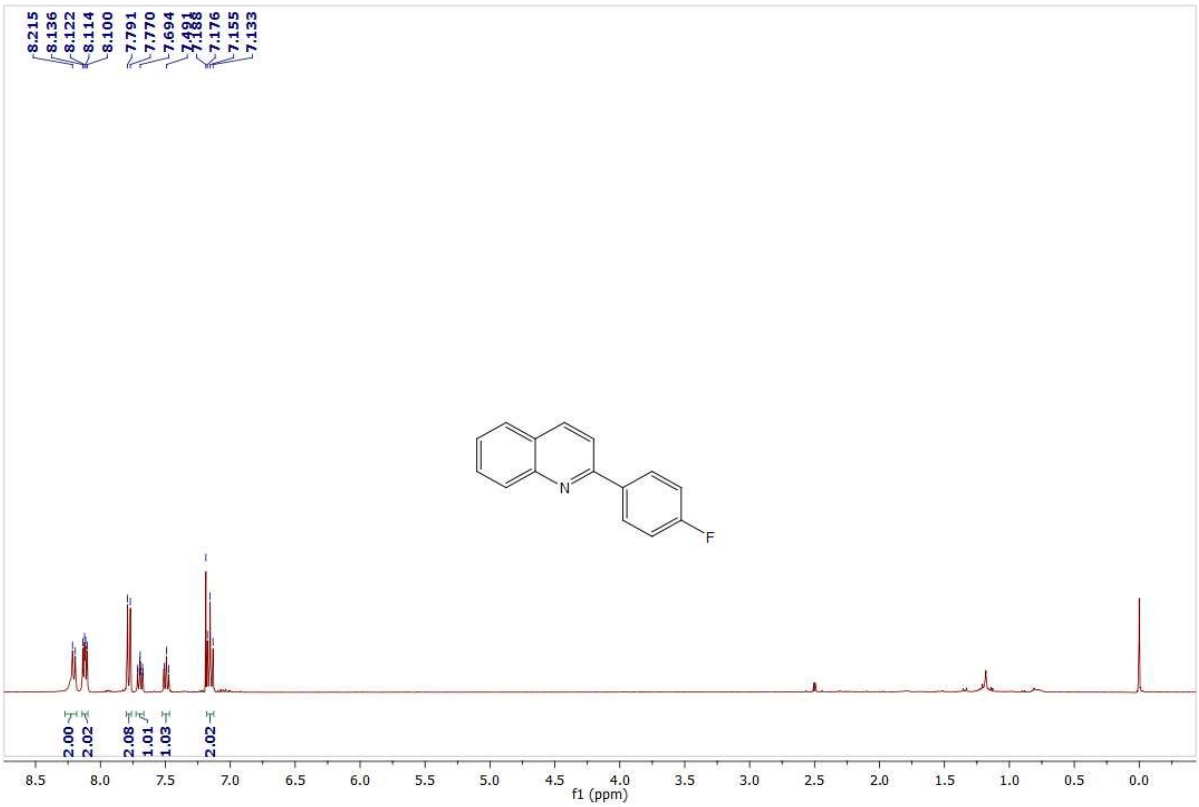

$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **5d**



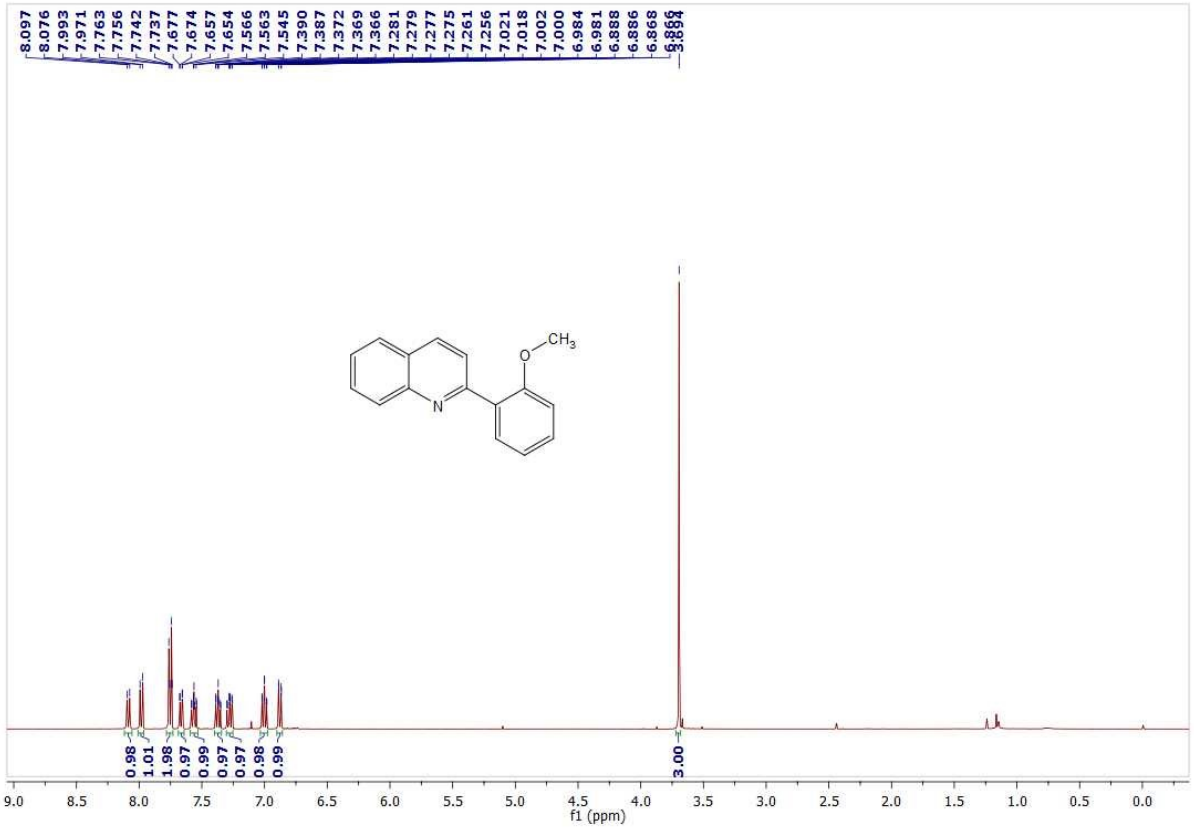

$^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) Spectra of **5d**



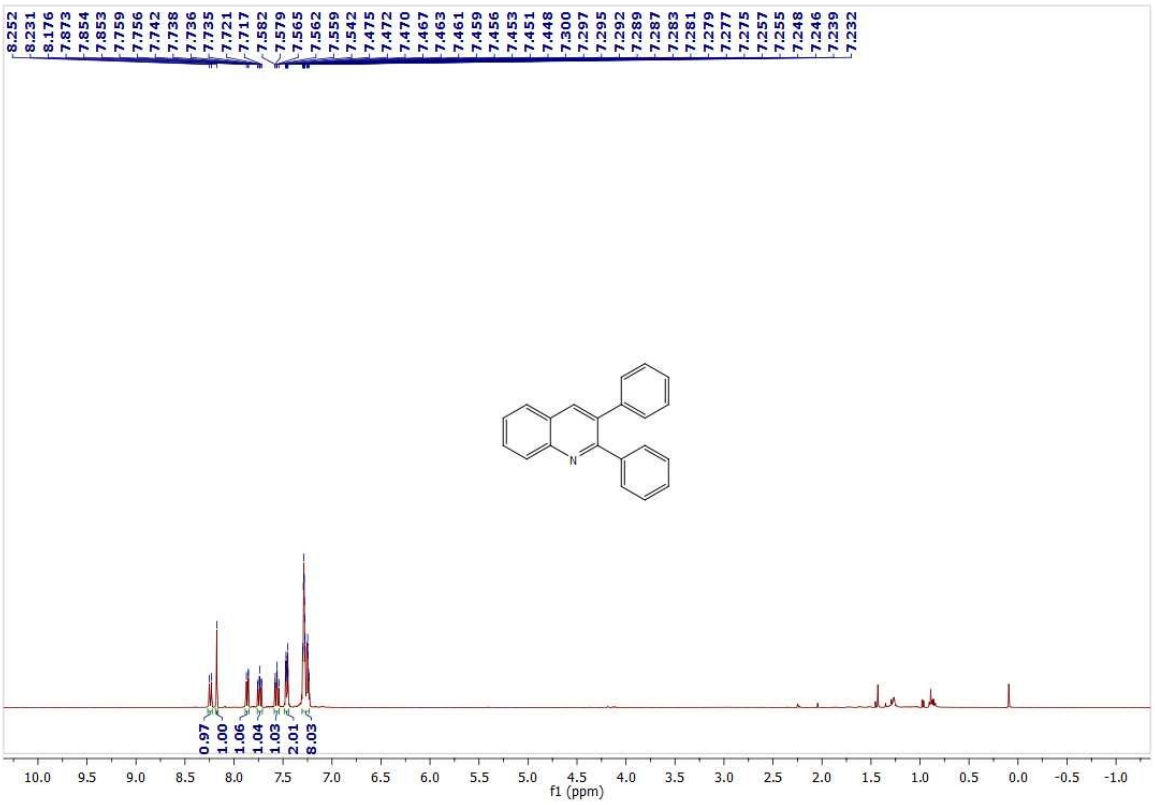

HRMS data of **5d**



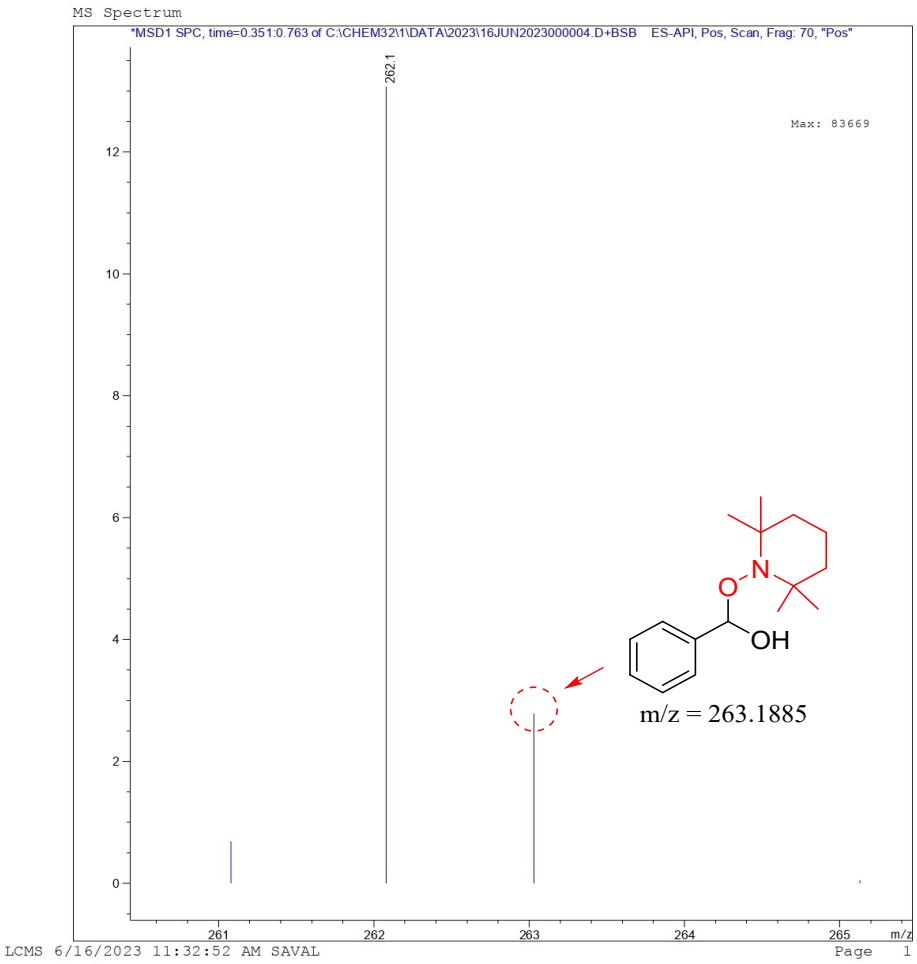

$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **5e**




$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **5f**




$^{1}$H NMR (400 MHz, Chloroform-*d*) Spectra of **5g**




HRMS data of the TEMPO trapped radical intermediate