Supplementary Materials

PPh_3-Assisted Esterification of Acyl Fluorides with Ethers via C(sp^3)-O Bond Cleavage Accelerated by TBAT

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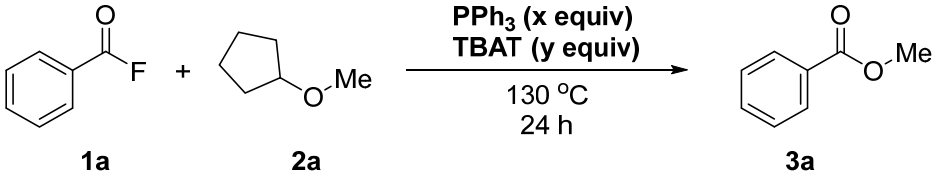
Table S1. Screening the Amounts of TBAT and PPh_3

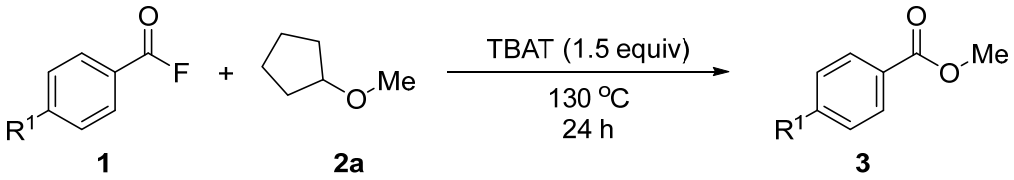


1a **2a** **3a**

entry[a]	**PPh_3 (x equiv)**	**TBAT (y equiv)**	yield (%)[b]
1	-	0	0
2	-	0.2	27
3	-	1.0	53
4	-	1.5	61
5	0.2	1.0	70
6	0.3	1.0	74
7	0.5	1.0	73
8	1.0	1.0	74

[a]**1a** (0.2 mmol), PPh_3, and TBAT in CPME (2 mL) at 130 °C for 24 h. [b]Determined by GC analysis of the crude mixture, using dodecane as an internal standard.

Table S2. Effect of PPh_3



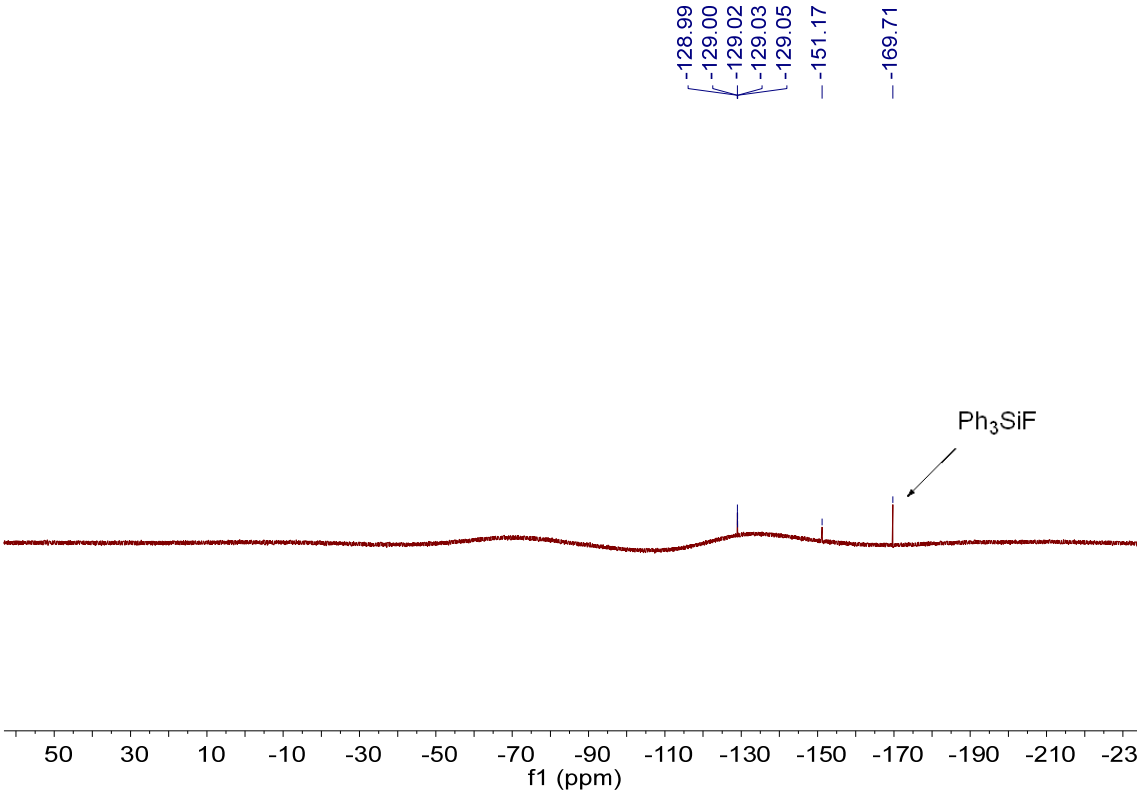
1 **2a** **3**

entry[a]	R^1	yield (%)
1	H	60[b]
2[c]	H	71[b]
3	Ph	69[d]
4[c]	Ph	92[d]

[a]**1a** (0.2 mmol), and TBAT (0.3 mmol) in CPME (2 mL) at 130 °C for 24 h. [b]Determined by GC analysis of the crude mixture, using dodecane as an internal standard. [c]30 mol % of PPh_3 was added. [d]Determined by NMR analysis of the crude mixture, using dibromomethane as an internal standard.

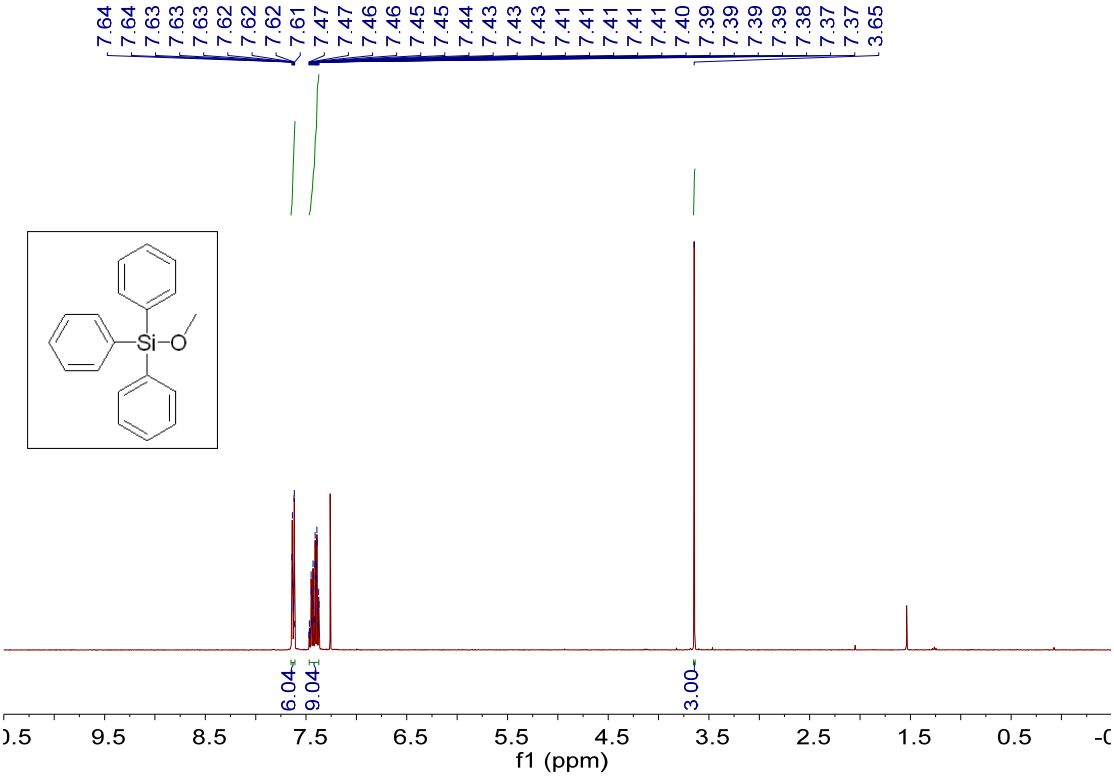
Detection of Ph_3SiF

To a 20 mL Schlenk tube containing PPh_3 (15.7 mg, 0.06 mmol, 30 mol %) and TBAT (108 mg, 0.2 mmol, 1 equiv), were added [1,1'-biphenyl]-4-carbonyl fluoride (**1b**) (40.0 mg, 0.2 mmol) and CPME (2.0 mL). Subsequently, the resulting mixture was heated at 130 ºC for 24 h. After the reaction mixture was cooled down to room temperature. The $^{19}F\{^1H\}$ NMR spectrum was measured in $CDCl_3$.

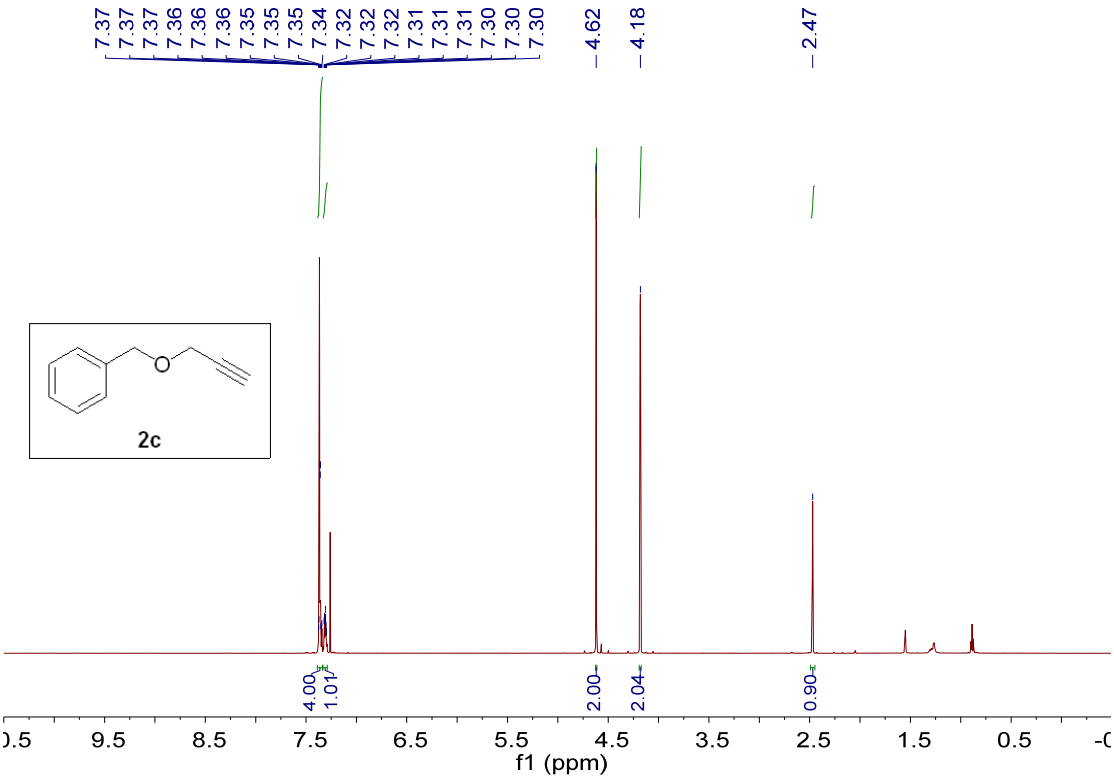


$^{19}F\{^1H\}$ NMR (376 MHz) spectrum of the reaction mixture ($CDCl_3$, rt)

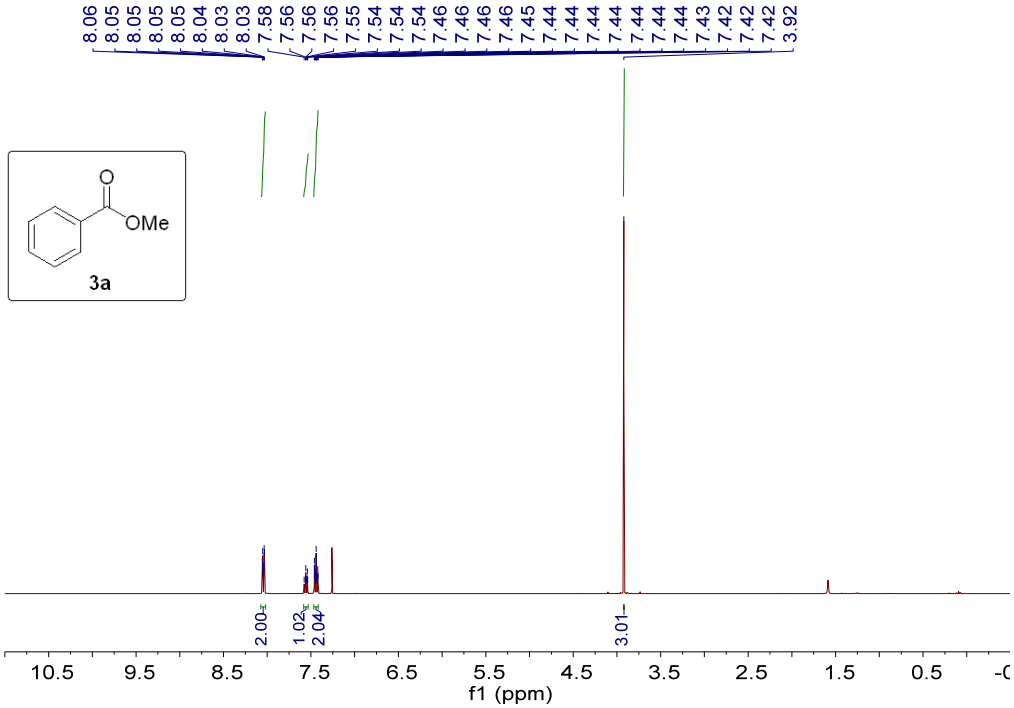
Copies of NMR Spectra



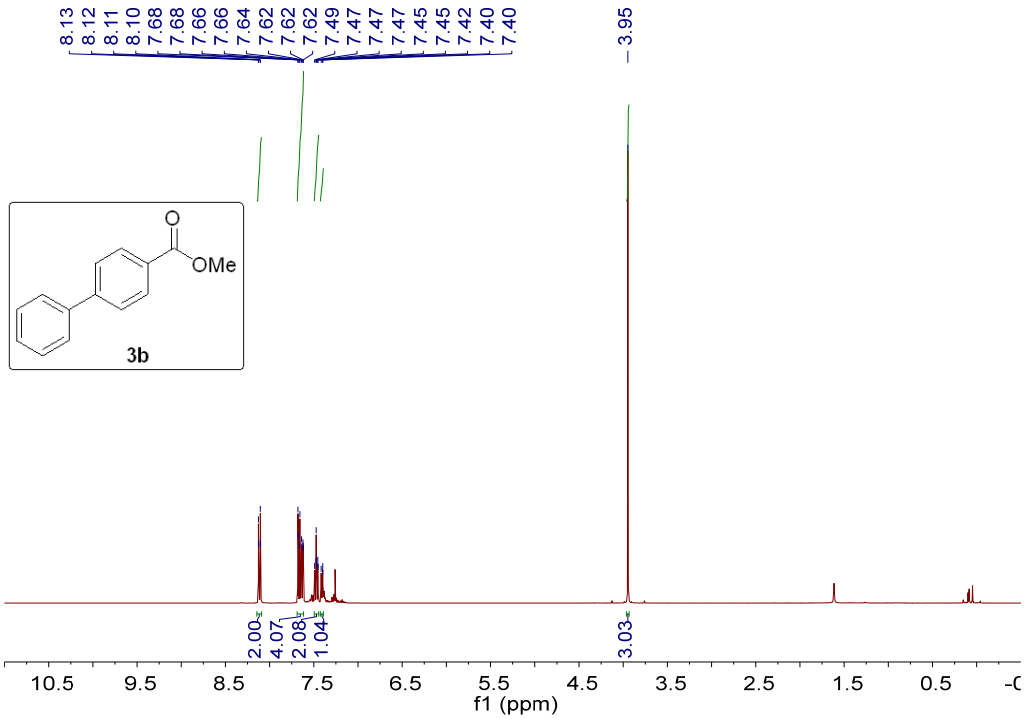
^{1}H NMR (400 MHz) spectrum of methoxytriphenylsilane ($CDCl_3$, rt).



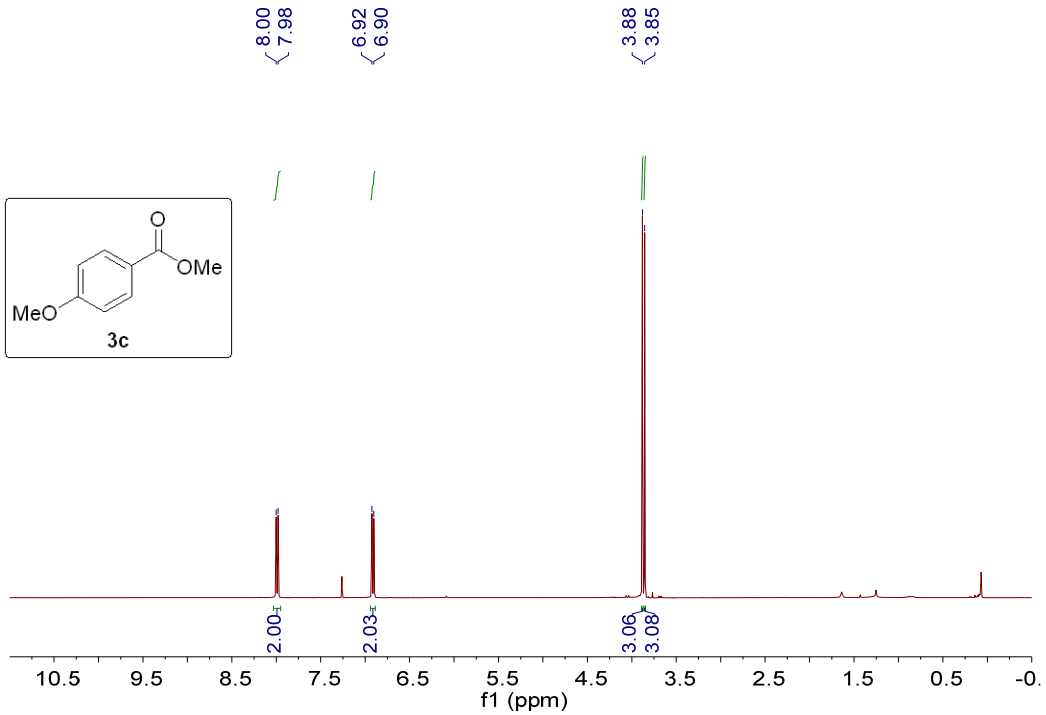
^{1}H NMR (600 MHz) spectrum of **2c** ($CDCl_3$, rt).



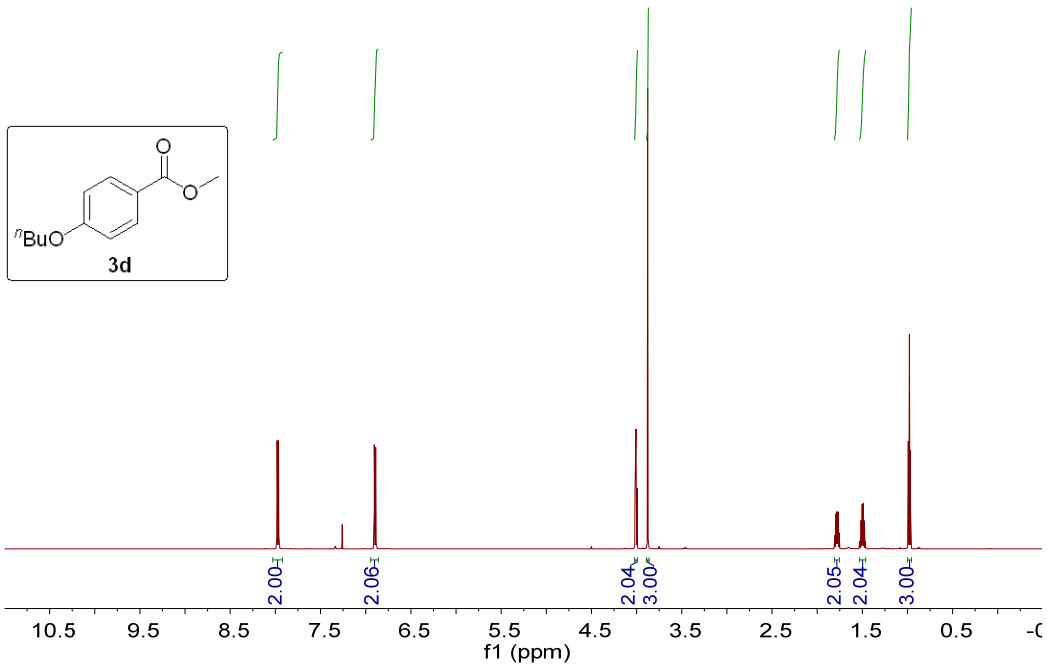
^{1}H NMR (400 MHz) spectrum of **3a** ($CDCl_3$, rt).



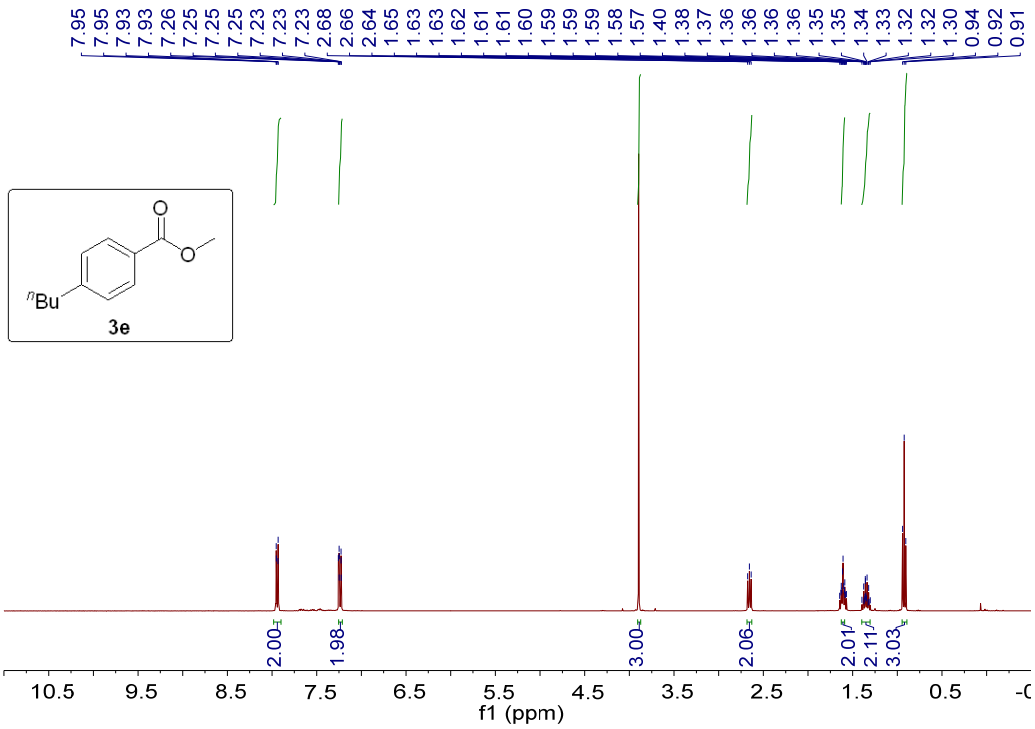
^{1}H NMR (400 MHz) spectrum of **3b** ($CDCl_3$, rt).



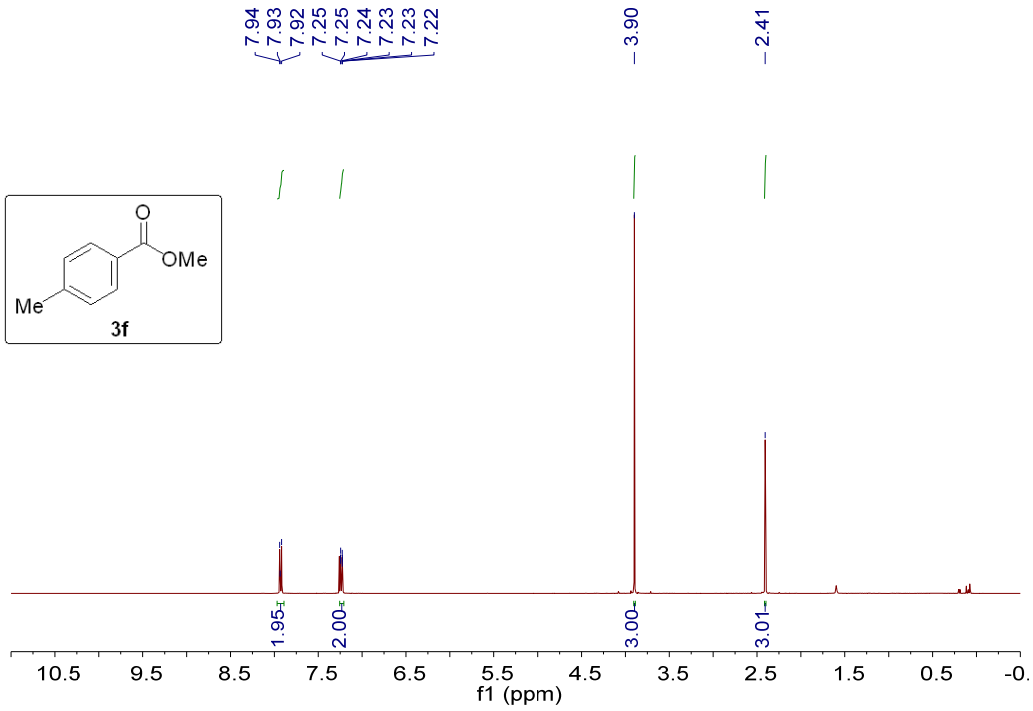
^{1}H NMR (400 MHz) spectrum of **3c** ($CDCl_3$, rt).



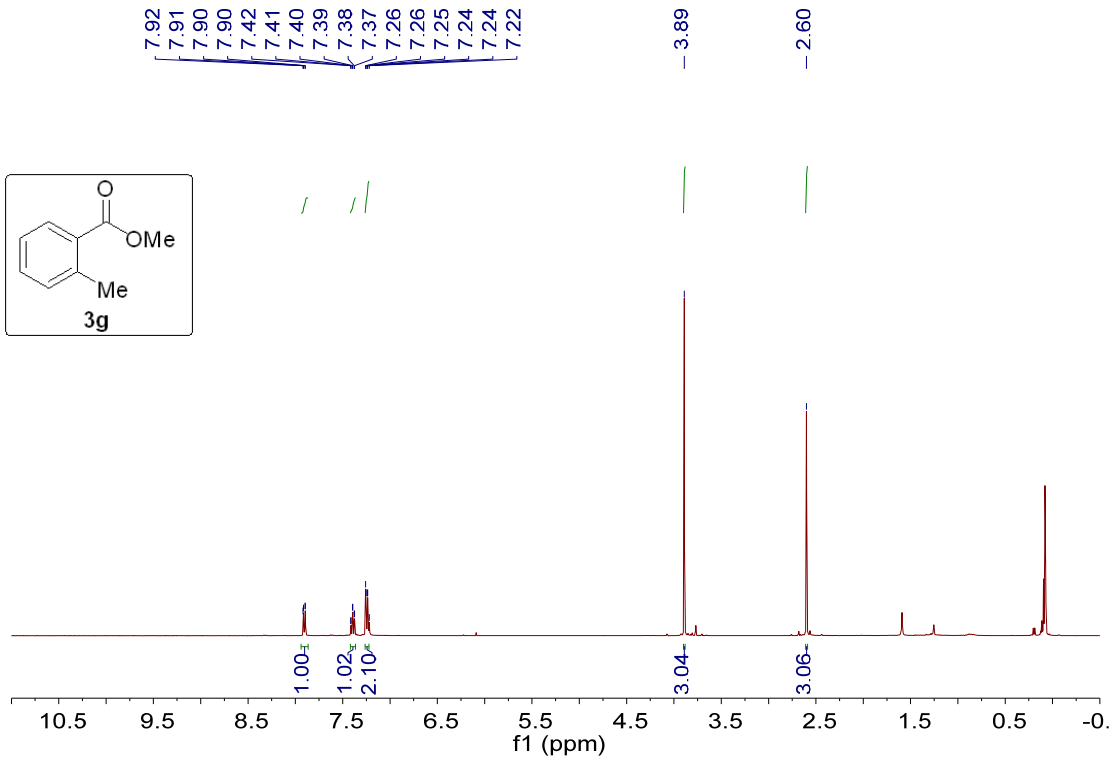
^{1}H NMR (600 MHz) spectrum of **3d** ($CDCl_3$, rt).



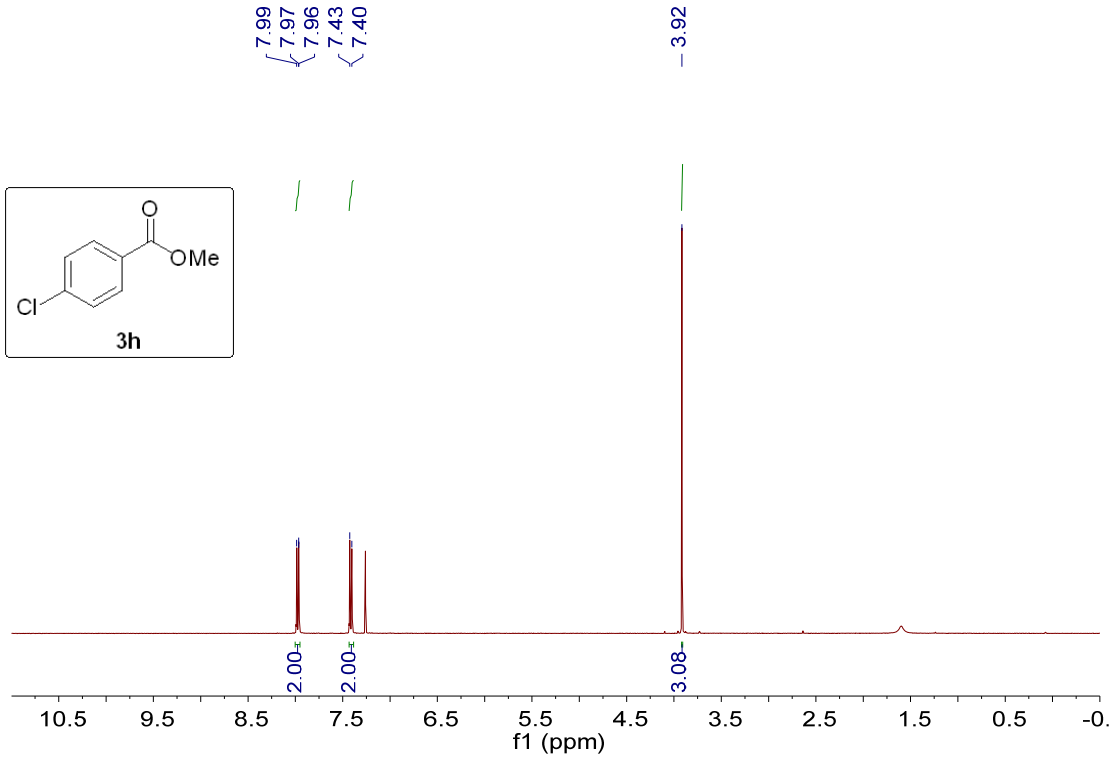
^{1}H NMR (400 MHz) spectrum of **3e** ($CDCl_3$, rt).



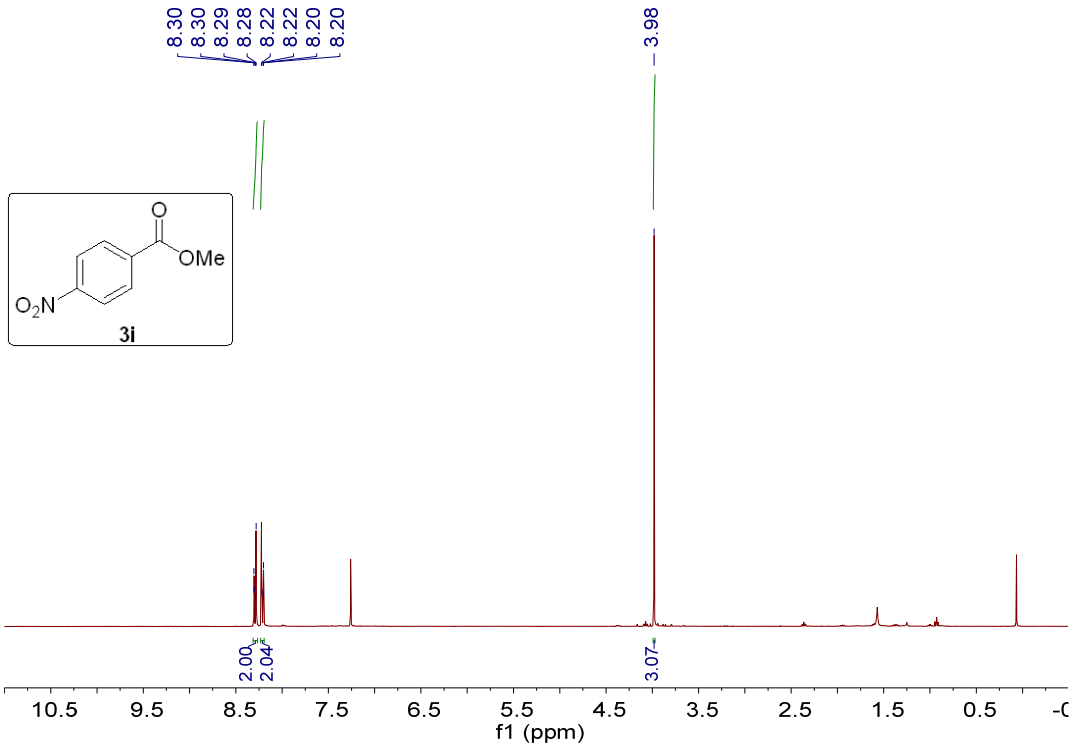
^{1}H NMR (400 MHz) spectrum of **3f** ($CDCl_3$, rt).



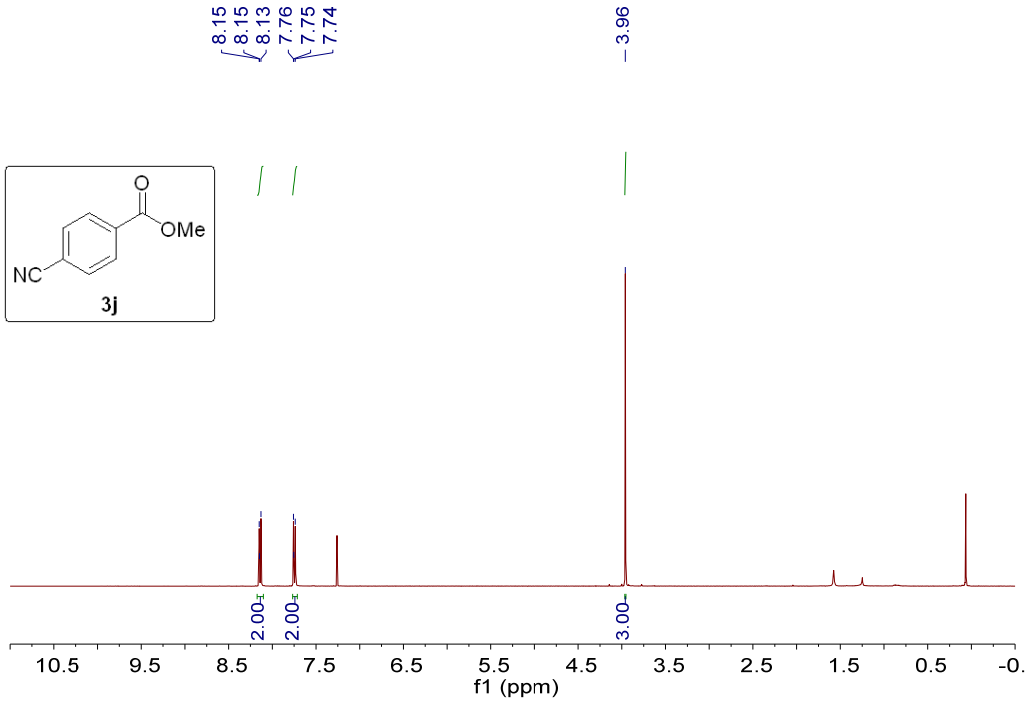
^{1}H NMR (400 MHz) spectrum of **3g** ($CDCl_3$, rt).



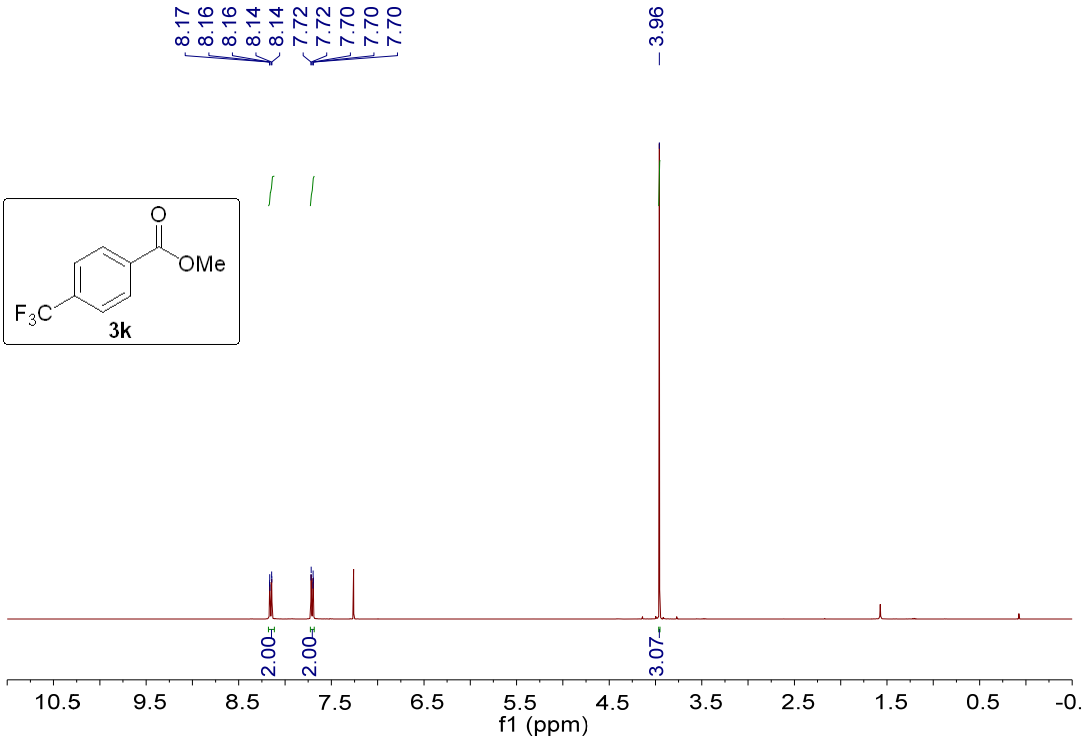
^{1}H NMR (400 MHz) spectrum of **3h** ($CDCl_3$, rt).



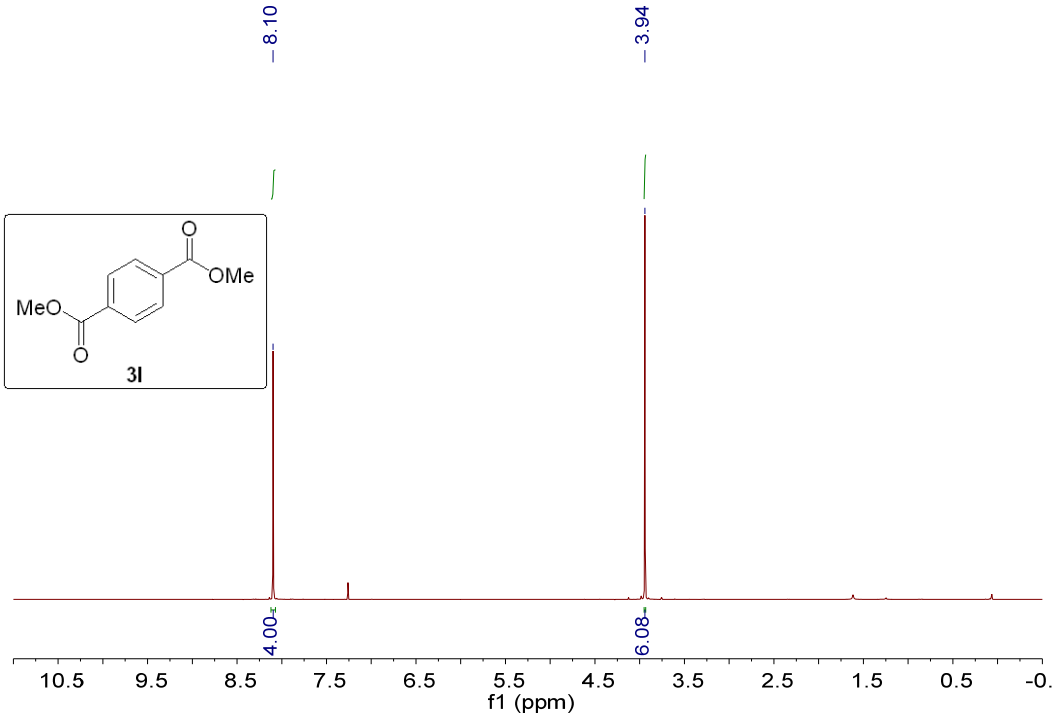
^{1}H NMR (400 MHz) spectrum of **3i** ($CDCl_3$, rt).



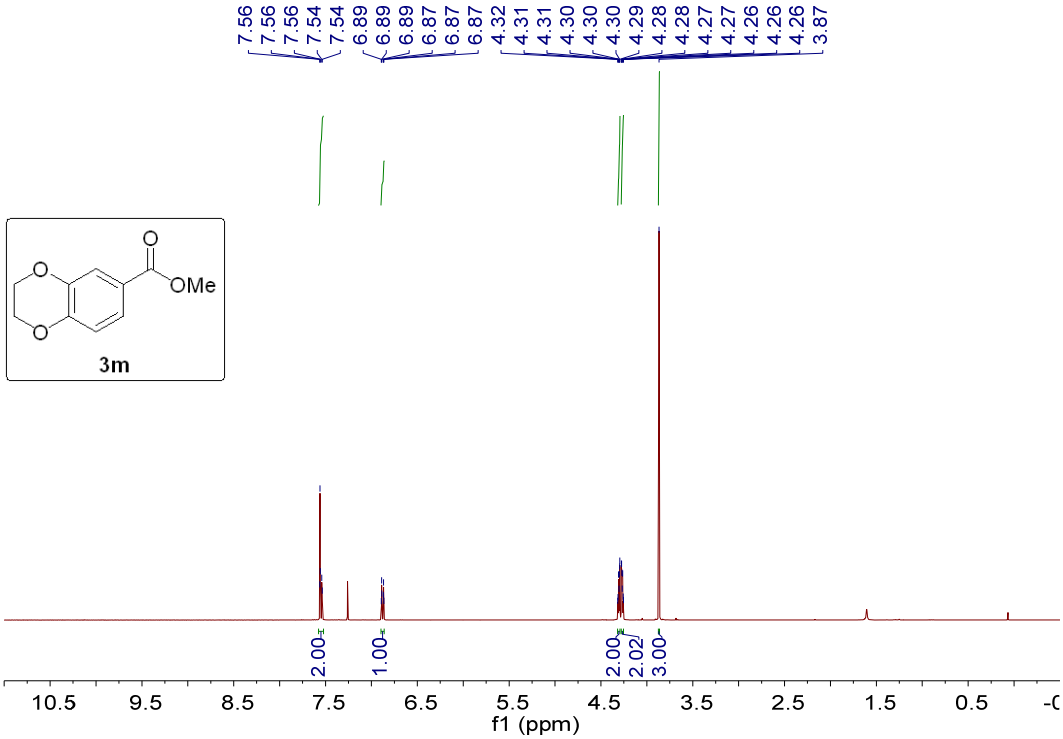
^{1}H NMR (400 MHz) spectrum of **3j** ($CDCl_3$, rt).



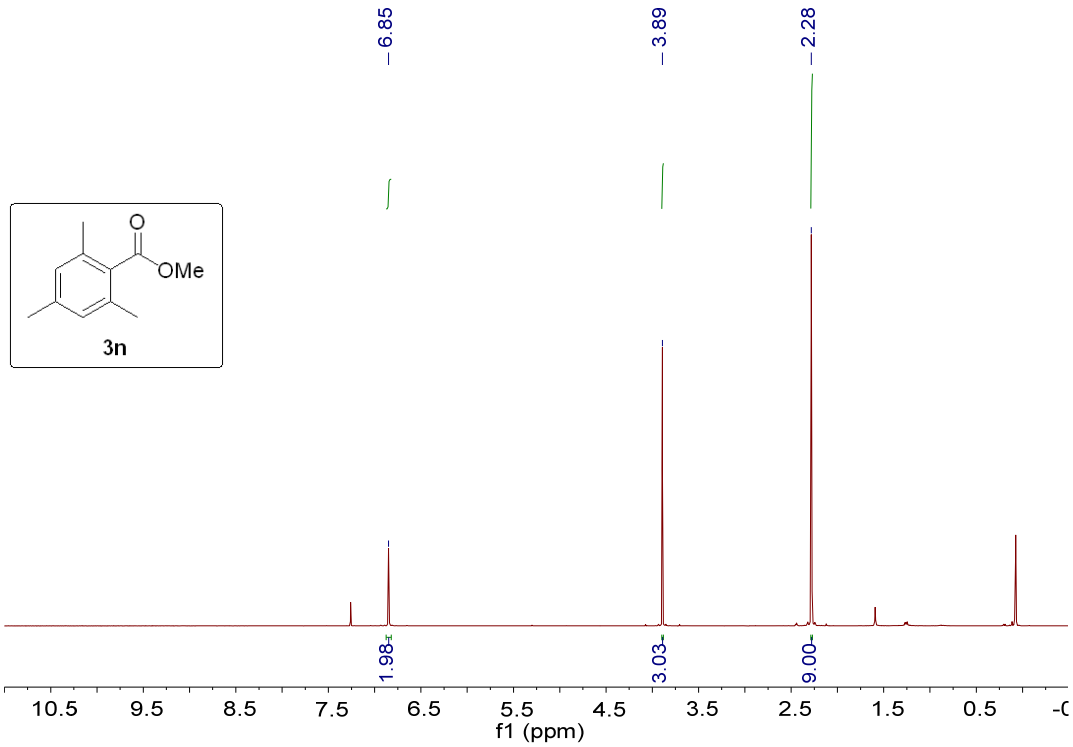
^{1}H NMR (400 MHz) spectrum of **3k** ($CDCl_3$, rt).



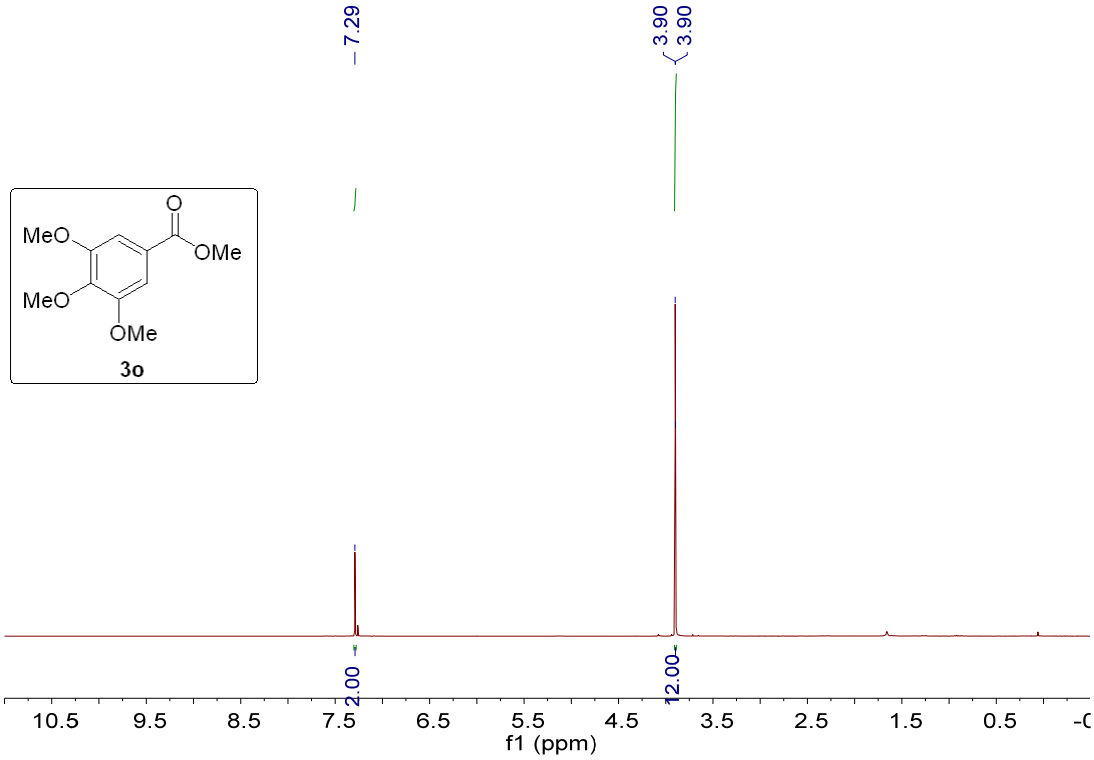
^{1}H NMR (400 MHz) spectrum of **3l** ($CDCl_3$, rt).



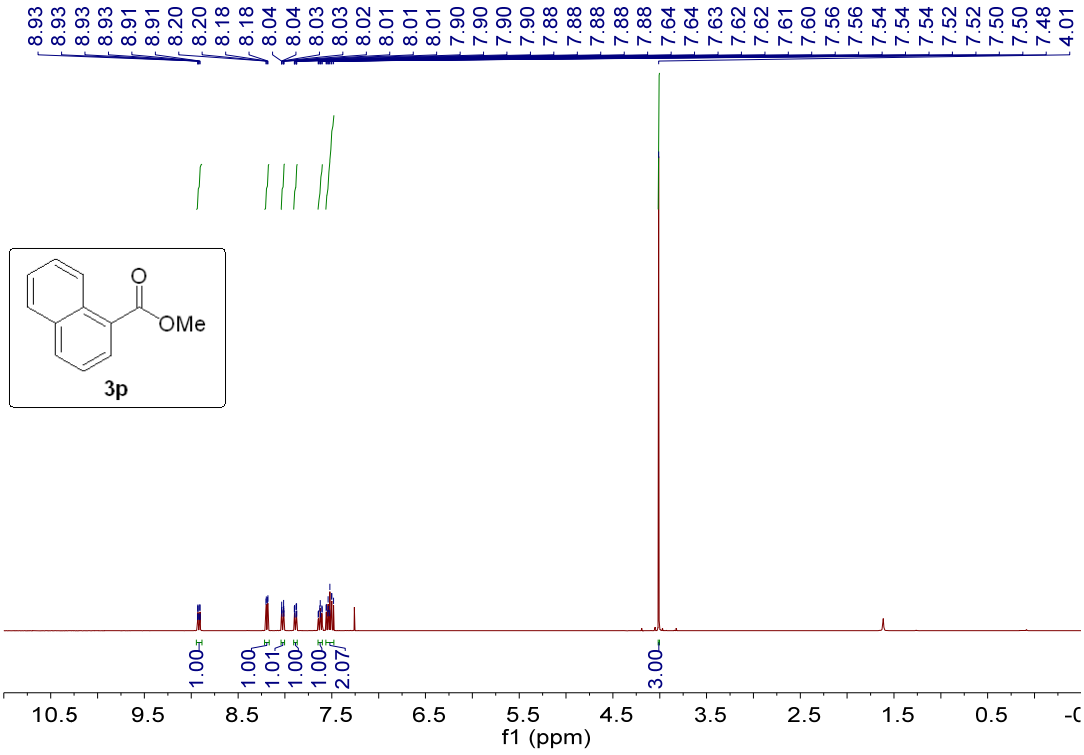
^{1}H NMR (400 MHz) spectrum of **3m** ($CDCl_3$, rt).



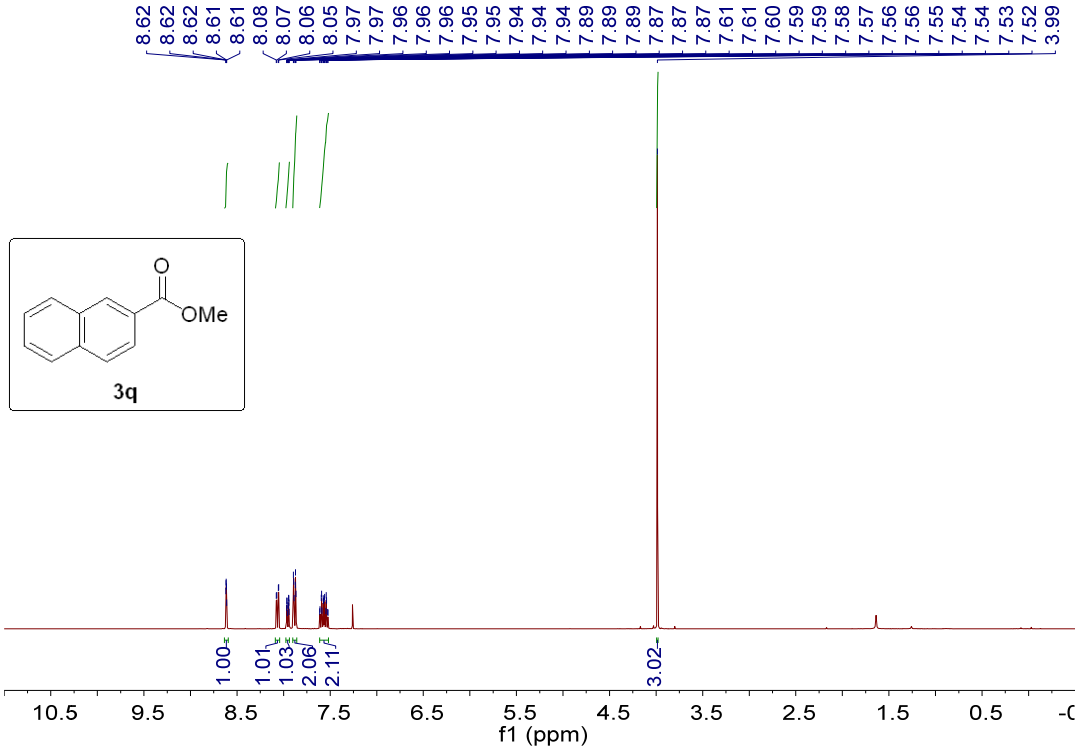
^{1}H NMR (400 MHz) spectrum of **3n** ($CDCl_3$, rt).



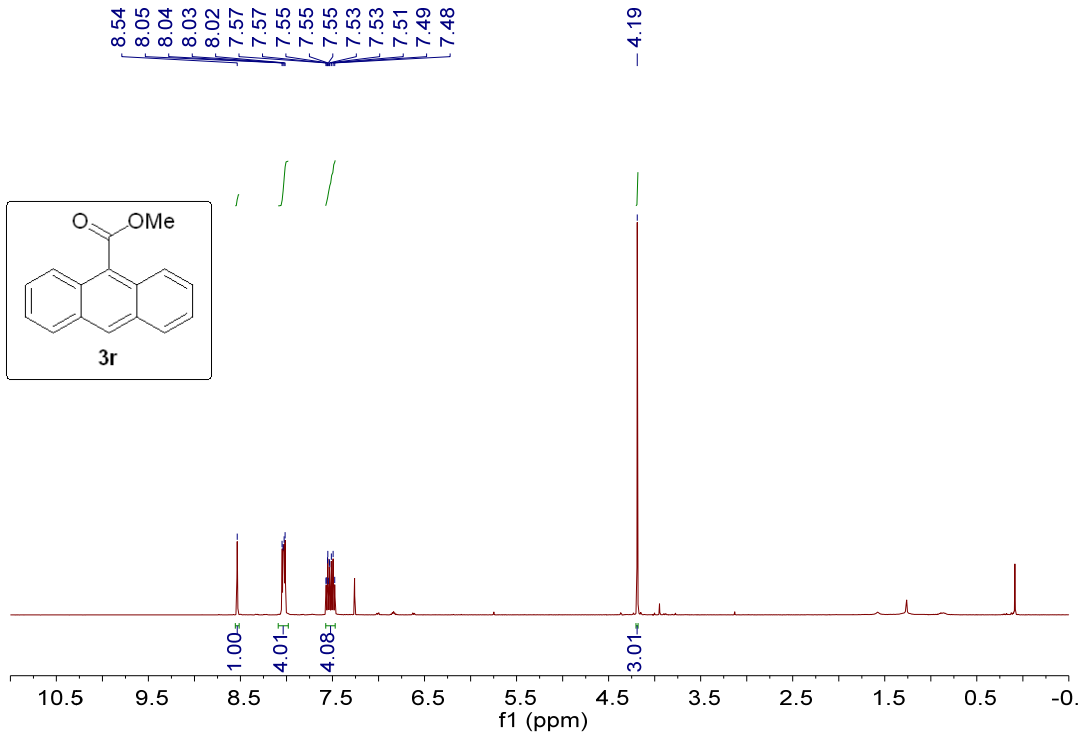
^{1}H NMR (400 MHz) spectrum of **3o** ($CDCl_3$, rt).



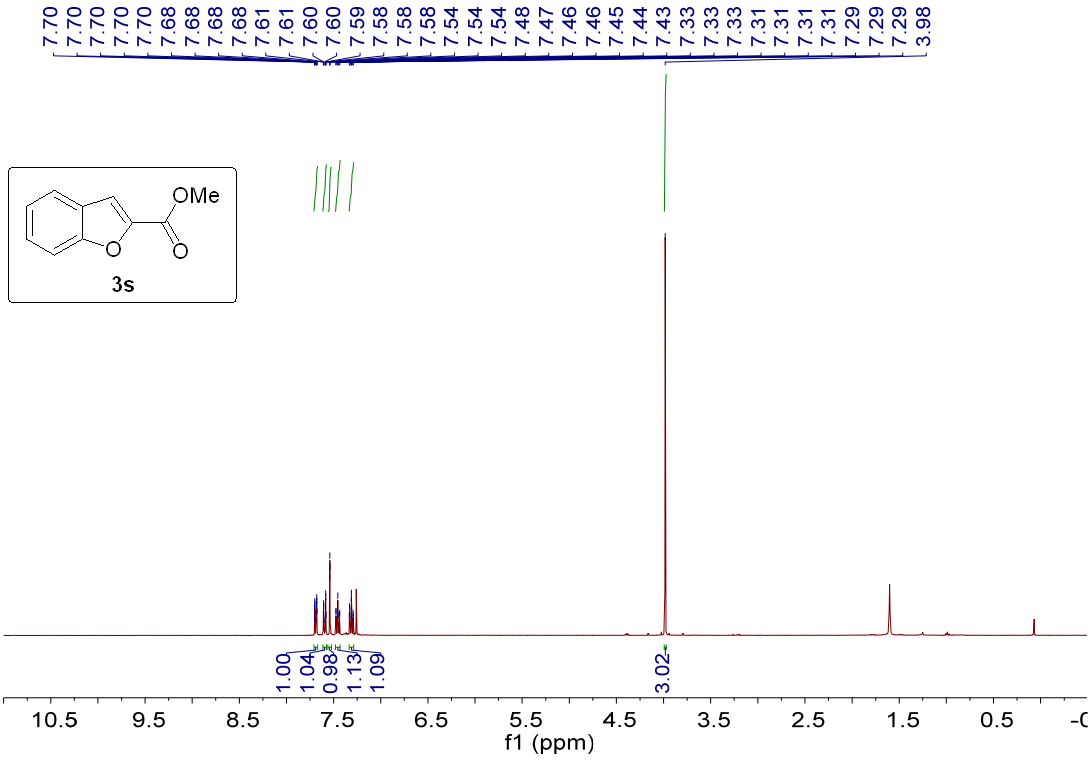
^{1}H NMR (400 MHz) spectrum of **3p** ($CDCl_3$, rt).



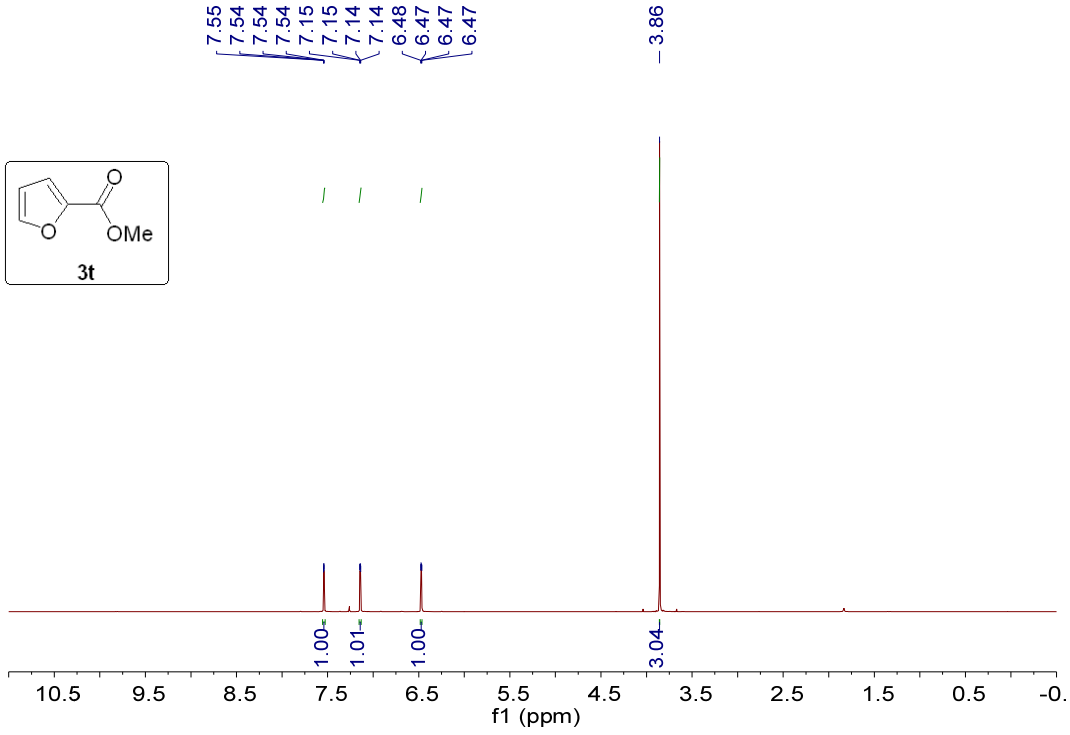
^{1}H NMR (400 MHz) spectrum of **3q** ($CDCl_3$, rt).



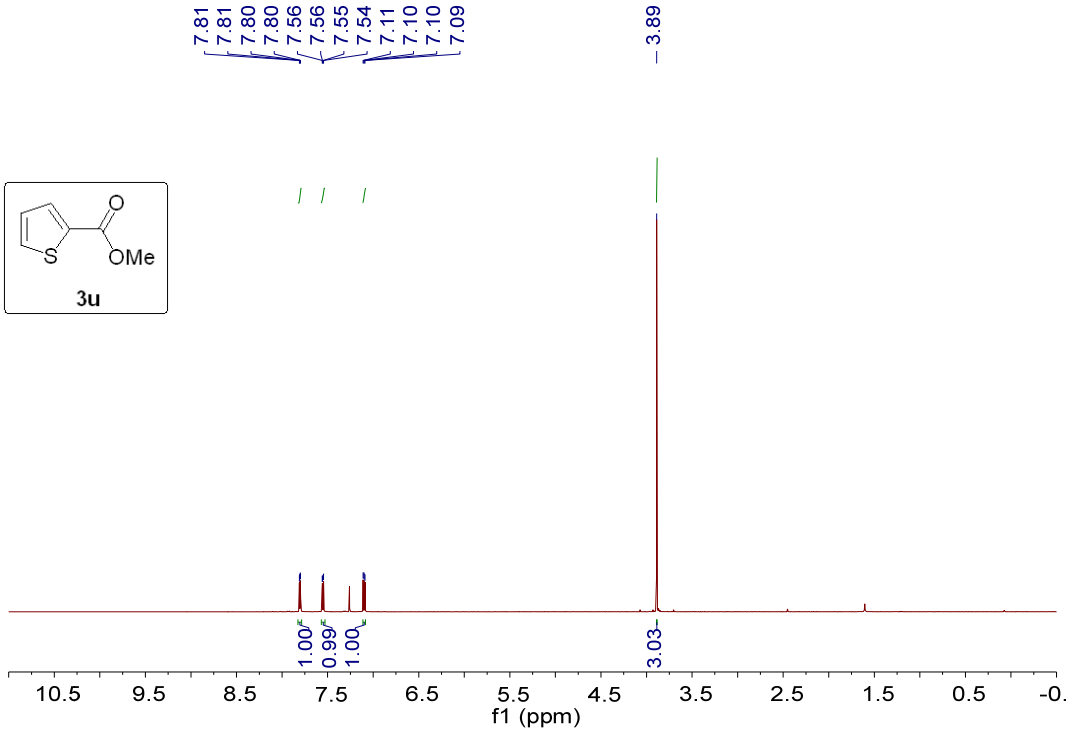
^{1}H NMR (400 MHz) spectrum of **3r** ($CDCl_3$, rt).



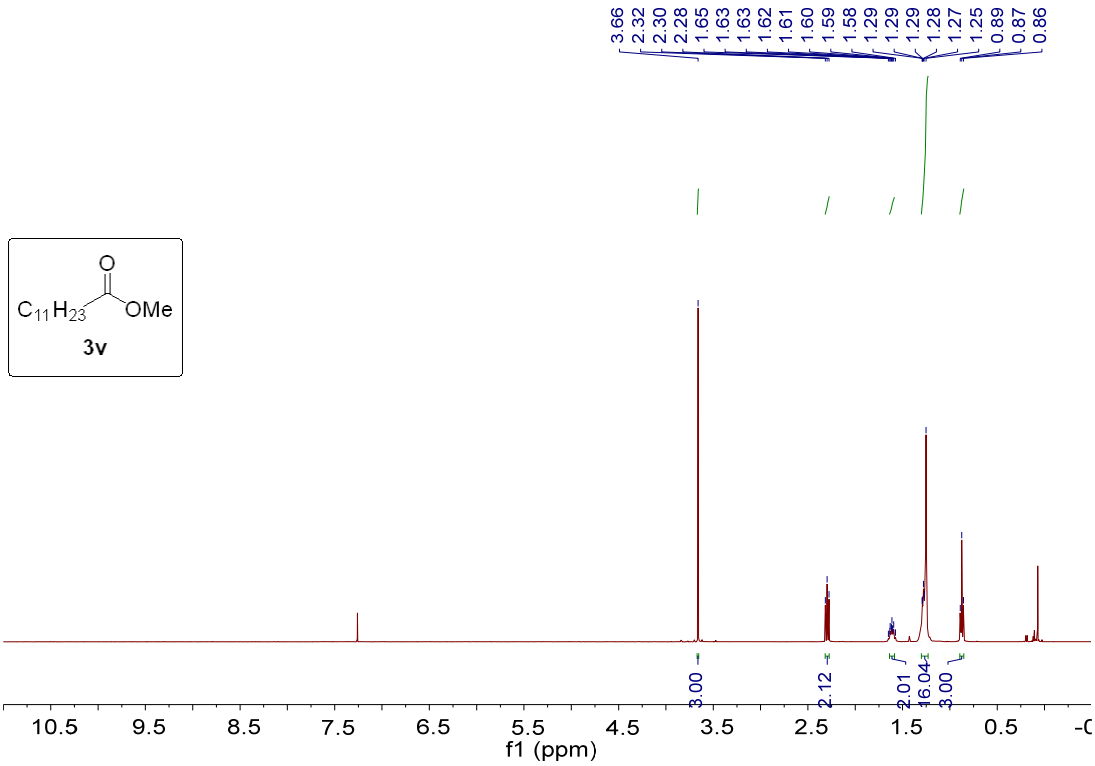
^{1}H NMR (400 MHz) spectrum of **3s** ($CDCl_3$, rt).



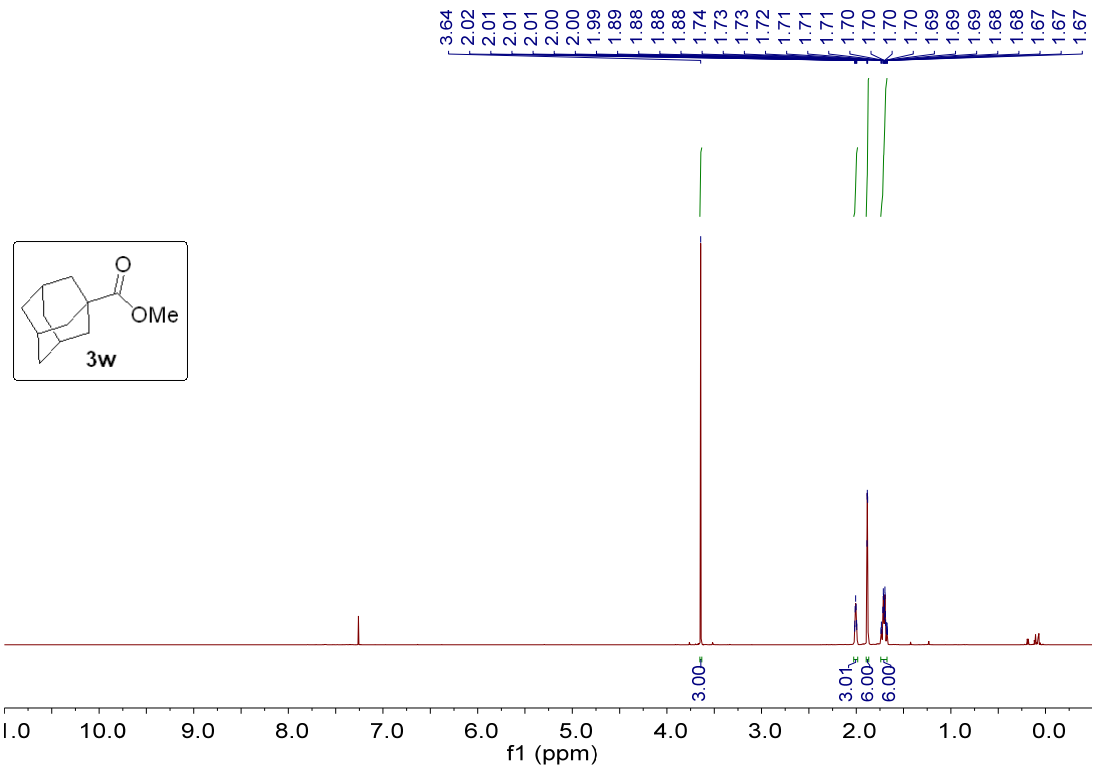
^{1}H NMR (400 MHz) spectrum of **3t** ($CDCl_3$, rt).



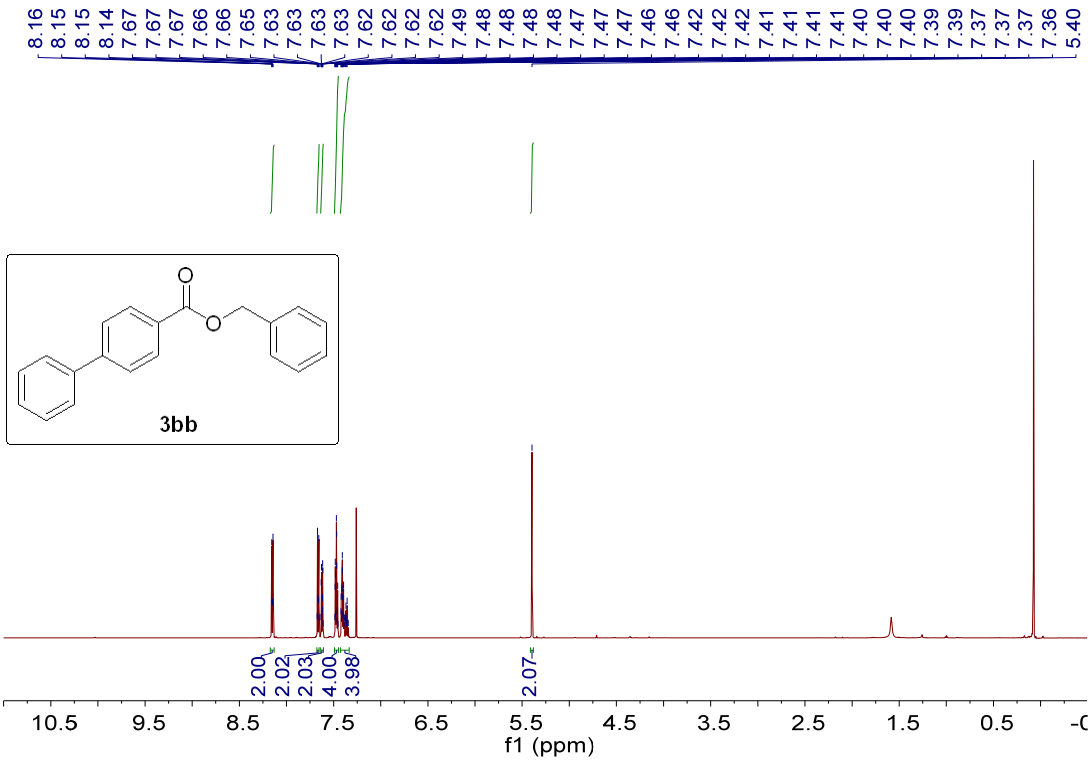
^{1}H NMR (400 MHz) spectrum of **3u** ($CDCl_3$, rt).



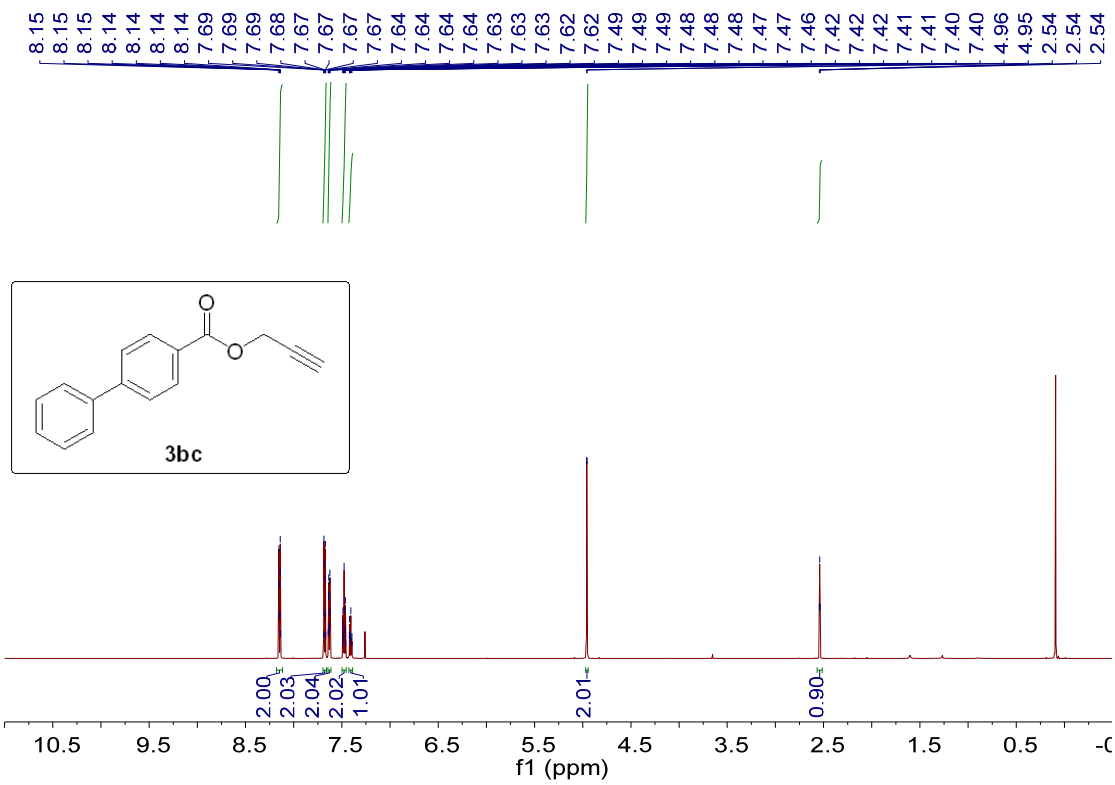
^{1}H NMR (400 MHz) spectrum of **3v** ($CDCl_3$, rt).



^{1}H NMR (600 MHz) spectrum of **3w** ($CDCl_3$, rt).



^{1}H NMR (600 MHz) spectrum of **3bb** ($CDCl_3$, rt).



^{1}H NMR (600 MHz) spectrum of **3bc** ($CDCl_3$, rt).