Electronic Supplementary Material (ESI) for Chemical Communications
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Aerobic oxidation of NHC-catalysed aldehyde esterifications with alcohols: benzoin, not the Breslow intermediate, undergoes oxidation

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Supporting Information

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1 General Methods

Unless otherwise noted, all commercially available compounds were used as provided without further purification.

Melting points were determined using a standard melting point apparatus and are uncorrected. Proton NMR spectra were recorded on a Bruker Avance III 400 MHz (400.23 MHz) spectrometer using the solvent peak as internal reference ($CDCl_3$: δ H 7.26; δ C 77.0 and DMSO-d_6: δ H 2.51; δ C 39.5). Multiplicities are indicated, s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septet), m (multiplet); coupling constants (*J*) are in Hertz (Hz). Carbon NMR were recorded on the previously mentioned instrument (100.61 Hz) with total proton decoupling. Fluorine NMR spectra were recorded on the previously mentioned instrument at 376.5 Hz. Mass spectra (MS ESI) were recorded using a Finnigan MAT 95 or Varian MAT 311A. Electron Impact mass spectra were recorded on the same machine in EI mode. TLC analysis was performed on precoated silica gel 60F_{254} slides, and visualised by $KMnO_4$ staining. Flash chromatography was carried out using silica gel, particle size 0.2-0.063 mm and using the indicated mobile phase as correlated with TLC analysis. Infrared spectra were obtained on a Perkin Elmer Spectrum 100 FT-IR spectrometer equipped with a universal ATR sampling accessory.

Tetrahydrofuran was distilled from sodium/benzophenone under argon. Methanol, ethanol, *iso*propanol and allyl alcohol were distilled from sodium under argon. Benzyl alcohol was purified *via* flash chromatography using a gradual solvent gradient of CH_2Cl_2:MeOH to remove residual benzaldehyde and benzyl benzoate. All reactions were carried out using oven-dried 25 mL vials, equipped with a plastic lid perforated by 4 holes 2 mm in diameter, unless otherwise specified.

Liquid aldehydes were distilled under vacuum prior to use. Solid aldehydes were washed acid-free with 10% aq. K_2CO_3-solution prior to use.

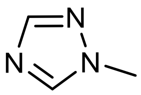
2 General Procedures

General Procedure 1 (Esterification of Benzaldehyde by Triazolium Precatalyst Using Various Alcohols, Table 1)

To a 25 mL vial equipped with a magnetic stirring bar was charged the triazolium precatalyst **2** (36 mg, 0.15 mmol, 15 mol%). Dry THF (2.5 mL) and the relevant alcohol were added. DBU (170 μL, 1.1 mmol, 110 mol%) was added and the solution stirred for 2 minutes. Benzaldehyde (102 μL, 1 mmol) was then added. The vessel was sealed with a plastic lid perforated by 4 holes 2 mm in diameter and the reaction mixture was stirred for the indicated time at room temperature unless stated otherwise. The solvent was then removed *in vacuo* and the resulting residue subjected to flash chromatography to yield the ester product.

3 Synthesis of 4-Ethyl-1-methyl-4*H*-[1,2,4]triazol-1-ium iodide (2)

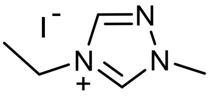
1-Methyl-1*H*-1,2,4-triazole (S1)



$C_3H_5N_3$
83.09 g/mol

To a flame-dried 250 mL round-bottomed flask equipped with a magnetic stirring bar was charged MeOH (80 mL) and sodium (3.30 g). The solution was stirred for 5 minutes before 1,2,4-triazole (10 g, 1.55 mol, 1 equiv) was added and the mixture stirred at room temperature until the solid had dissolved. The vessel was then placed under a protective atmosphere of argon and cooled to 0 ^{o}C in a H_2O/ice bath. Iodomethane (9.04 mL, 20.61 g, 1.55 mol, 1 equiv) was added dropwise *via* syringe. Stirring was continued for 5 minutes at 0 ^{o}C before warming to room temperature and stirring for a further 2 hours under argon before refluxing at 60 ^{o}C for 20 h. Upon cooling, the solvent was removed *in vacuo* and H_2O (60 mL) was added. The product was extracted with CH_2Cl_2 (3 x 50 mL), the combined organic layers dried over $MgSO_4$ and concentrated *in vacuo* to yield the title product as a yellow liquid (4.67 g, 39%) that was dried under vacuum for several hours. δ_H (400 MHz, $CDCl_3$): 3.80 (s, 3H, CH_3), 7.78 (s, 1H, CH), 7.93 (s, 1H, CH). HRMS (*m/z* –ESI$^+$): Found 84.0564 ($C_3H_6N_3^+$ requires 84.0562).

4-Ethyl-1-methyl-4*H*-[1,2,4]triazol-1-ium iodide (2)



$C_5H_{10}IN_3$
239.06 g/mol

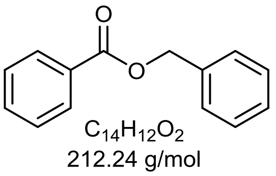
To a flame-dried 50 mL round-bottomed flask equipped with a magnetic stirring bar was charged 1-methyl-1*H*-1,2,4-triazole (**S1**) (4.2 g, 0.051 mol, 1 equiv). The vessel was placed under a protective atmosphere of argon and ethyl iodide (17.3 g, 8.9 mL, 0.111 mol, 2.17 equiv) was added *via* syringe. The flask was covered with aluminium foil and the reaction mixture stirred for 96 h at room temperature under argon. The resulting precipitate was filtered, washed with Et_2O (3 x 20 mL) and recrystallised from 1% CH_2Cl_2/MeOH to yield the title product as a white crystalline solid (3.07g, 0.0128 mol, 23%).

m.p.: 137 – 139 ^{o}C. R_F (CH_2Cl_2:MeOH, 4:1): 0.41. $\tilde{\nu}$ (cm^{-1}): 3423, 3028, 1773, 1583, 1164, 990, 730, 720, 653. δ_H (400 MHz, DMSO-d_6): 10.03 (s, 1H, CH), 9.18 (s, 1H, CH), 4.20 (q, J = 7.32 Hz, 2H, CH_2), 4.03 (s, 3H, CH_3), 1.42 (t, J = 7.32 Hz, 3H, CH_3). δ_C (100 MHz, DMSO-d_6): 144.7, 143.1, 43.4, 39.0472, 15.0. HRMS (*m/z* –ESI$^+$): Found 112.0874 ($C_5H_{10}N_3^+$ requires 112.0875).

4 Experimental Data for Ester Products (Scheme 1)

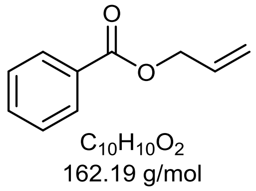
Benzyl benzoate (4, Scheme 1)

Prepared according to **general procedure 1** (24 h, 45°C in a 10 mL round-bottomed flask) using benzyl alcohol (311 µL, 3 mmol, 3 equiv). Purified *via* flash chromatography (*n*-hexane:Et_2O, 9:1): 153 mg (72%) as a pale yellow oil. δ_H (400 MHz, $CDCl_3$): 8.10 (app. d, 2H), 7.55 (app. t, 1H), 7.47 – 7.34 (m, 7H), 5.35 (app. d, 2H). HRMS (*m/z*-EI): Found 212.0845 ($C_{14}H_{12}O_2$ requires 212.0837).



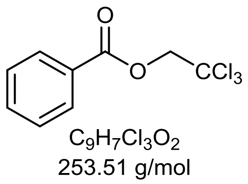
Allyl benzoate (5, Scheme 1)

Prepared according to **general procedure 1** (24 h, 45 °C in a 10 mL round-bottomed flask) using allyl alcohol (204 µL, 3 mmol, 3 equiv). Purified *via* flash chromatography (*n*-hexane:Et_2O, 9:1): 117 mg (69%) as a pale yellow oil. δ_H (400 MHz, $CDCl_3$): 8.05 (d, *J* = 7.48, 2H), 7.54 (t, *J* = 7.52 Hz, 1H), 7.43 (t, *J* = 7.72 Hz, 2H), 6.07 – 5.98 (m, 1H), 5.41 (d, *J* = 17.24 Hz, 1H), 5.27 (d, *J* = 10.44 Hz, 1H), 4.81 (d, *J* = 5.60 Hz, 2H). HRMS (*m/z*-EI): Found 162.0680 ($C_{10}H_{10}O_2$ requires 162.0681).



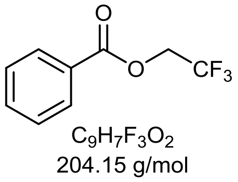
2,2,2-Trichloroethyl benzoate (6, Scheme 1)

Prepared according to **general procedure 1** (24 h, 45 °C in a 10 mL round-bottomed flask) using 2,2,2-trichloroethanol (288 µL, 3 mmol, 3 equiv). Purified *via* flash chromatography (*n*-hexane:Et_2O, 9:1): 155 mg (61%) as a pale yellow oil. δ_H (400 MHz, $CDCl_3$): 8.11 (d, *J* = 8.12 Hz, 2H), 7.59 (t, *J* = 7.80 Hz, 1H), 7.48 (t, *J* = 7.76 Hz, 2H), 4.95 (s, 2H) HRMS (*m/z*-EI): Found 251.9520 ($C_9H_7O_2Cl_3$ requires 251.9512).



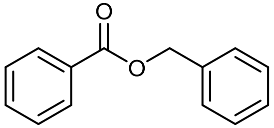
2,2,2-Trifluoroethyl benzoate (7, Scheme 1)

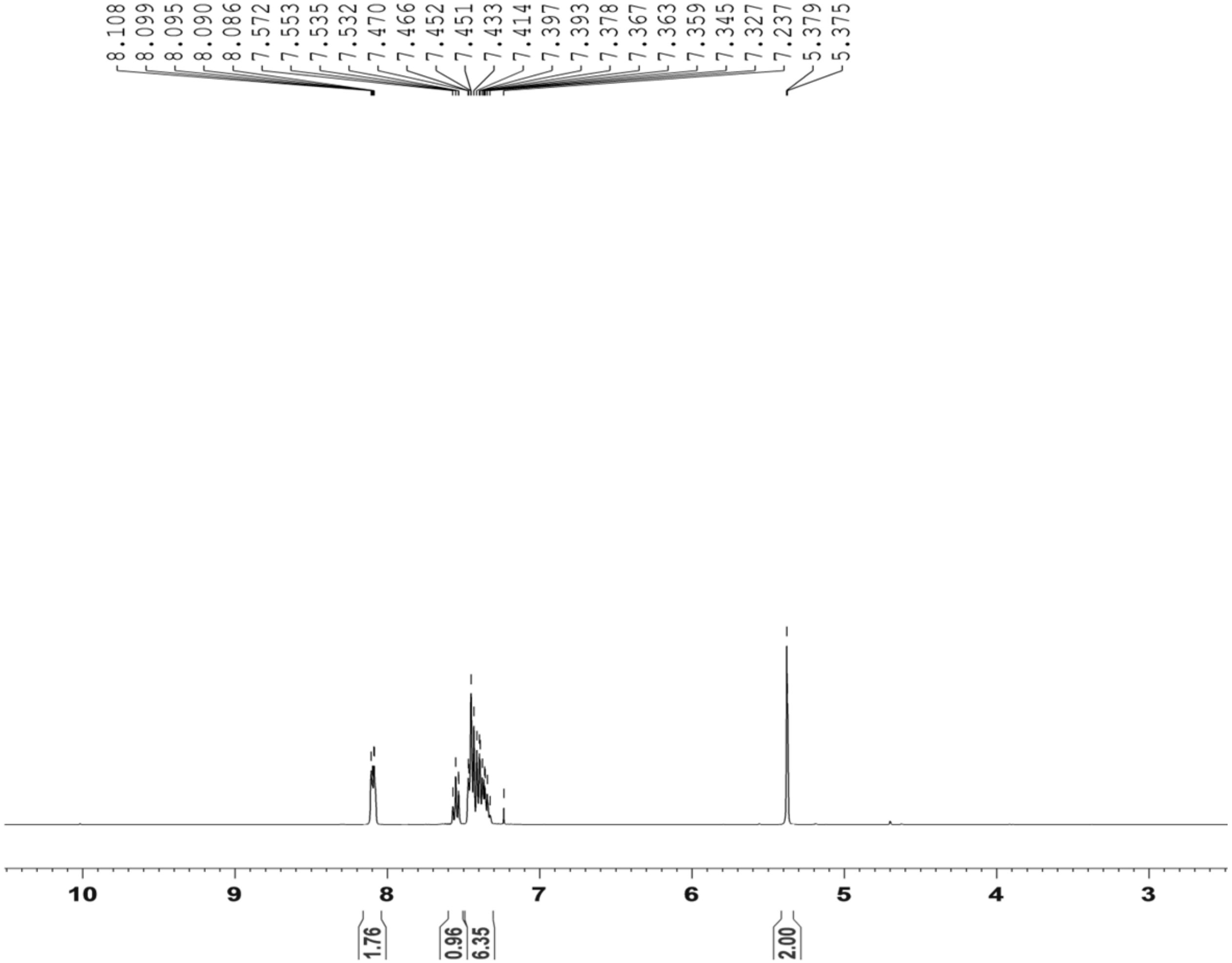
Prepared according to **general procedure 1** (24 h) using 2,2,2-trifluoroethanol (226 µL, 3 mmol, 3 equiv). Purified *via* flash chromatography (*n*-hexane:Et_2O, 9:1): 112 mg (55%) as a pale yellow oil. δ_H (400 MHz, $CDCl_3$): 8.06 (d, *J* = 7.56 Hz, 2H), 7.61 (t, *J* = 7.48 Hz, 1H), 7.47 (t, *J* = 7.72 Hz, 2H), 4.71 (q, $^3J_{FH}$ = 8.44 Hz, 2H). δ_F (375 MHz, $CDCl_3$): -73.71. HRMS (*m/z*-EI): Found 204.0397 ($C_9H_7F_3O_2$ requires 204.0398).



5 1H NMR Spectra for Isolated Ester Products

Benzyl benzoate (4, Scheme 1)





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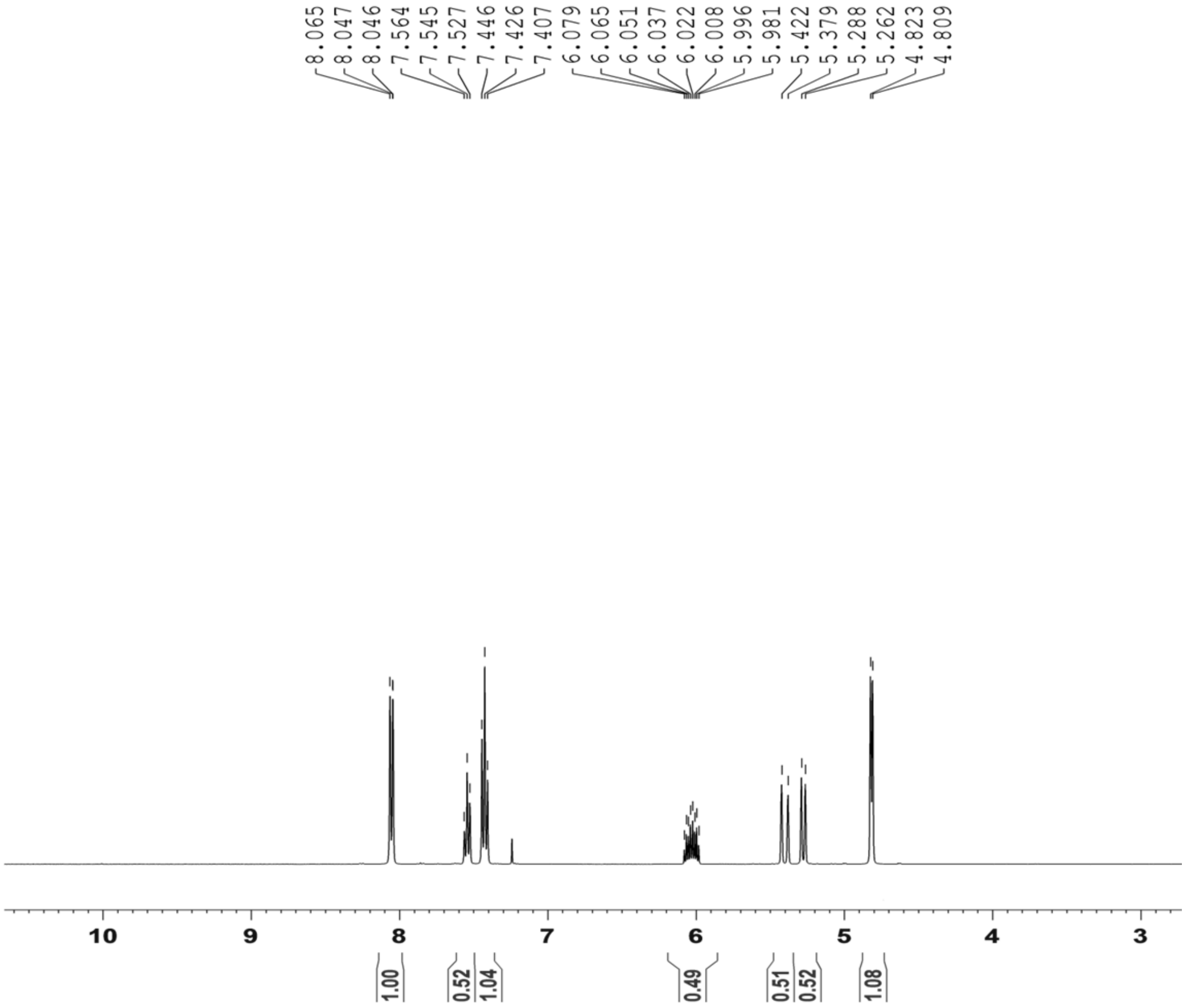
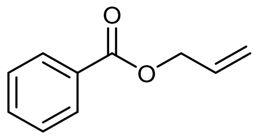
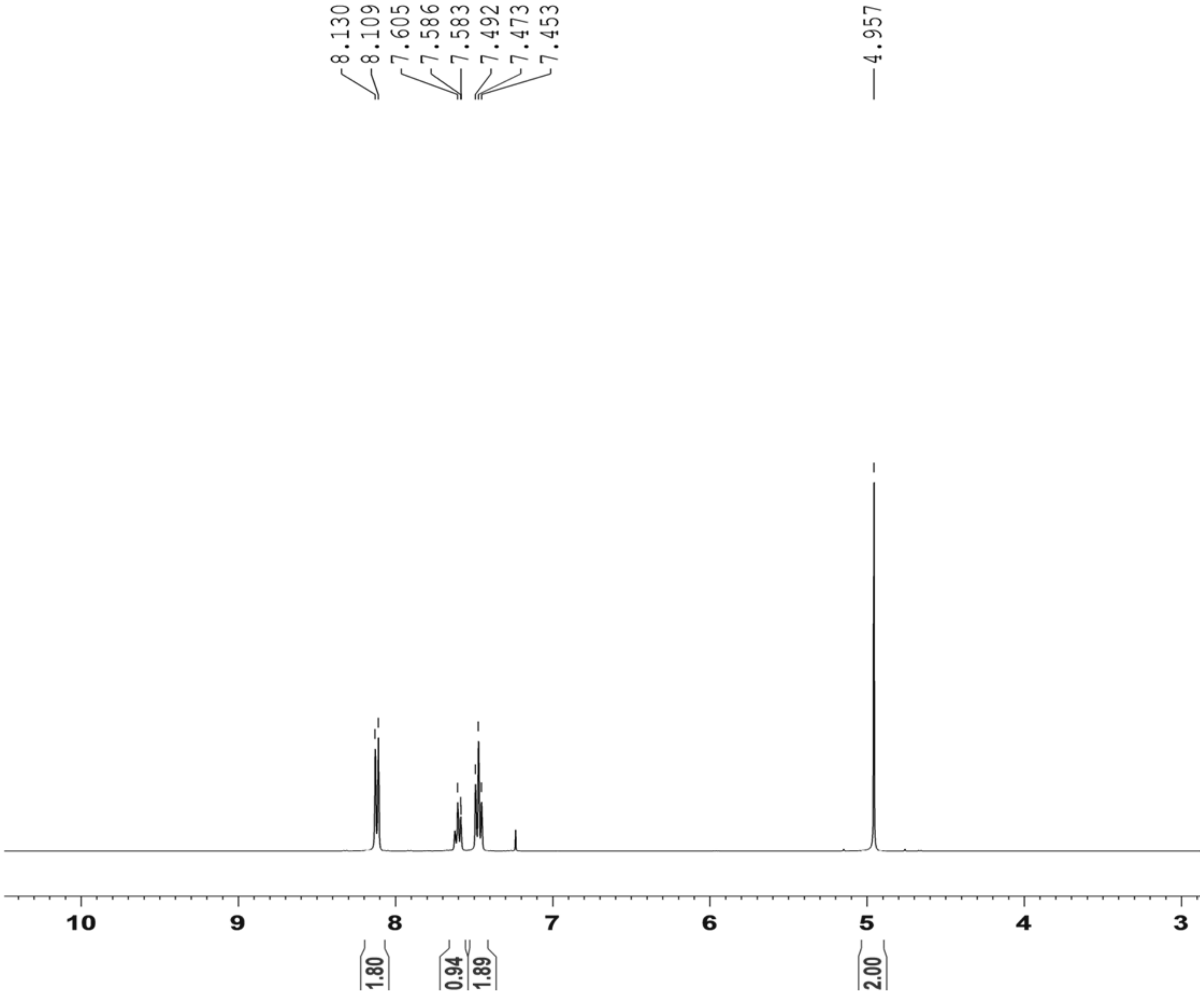
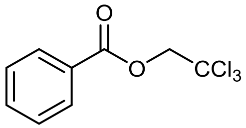
Allyl benzoate (5, Scheme 1)



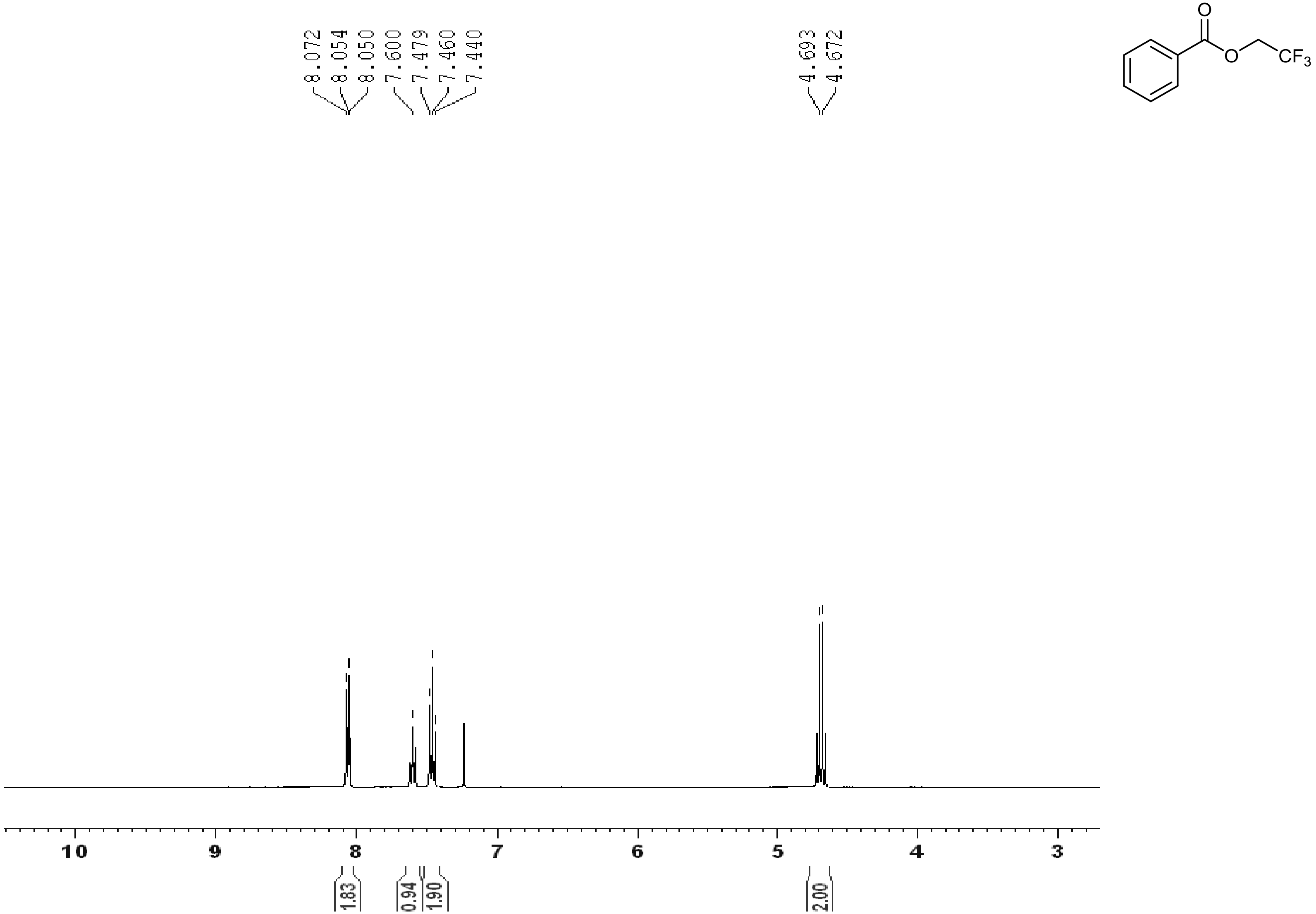


2,2,2-Trichloroethyl benzoate (6, Scheme 1)

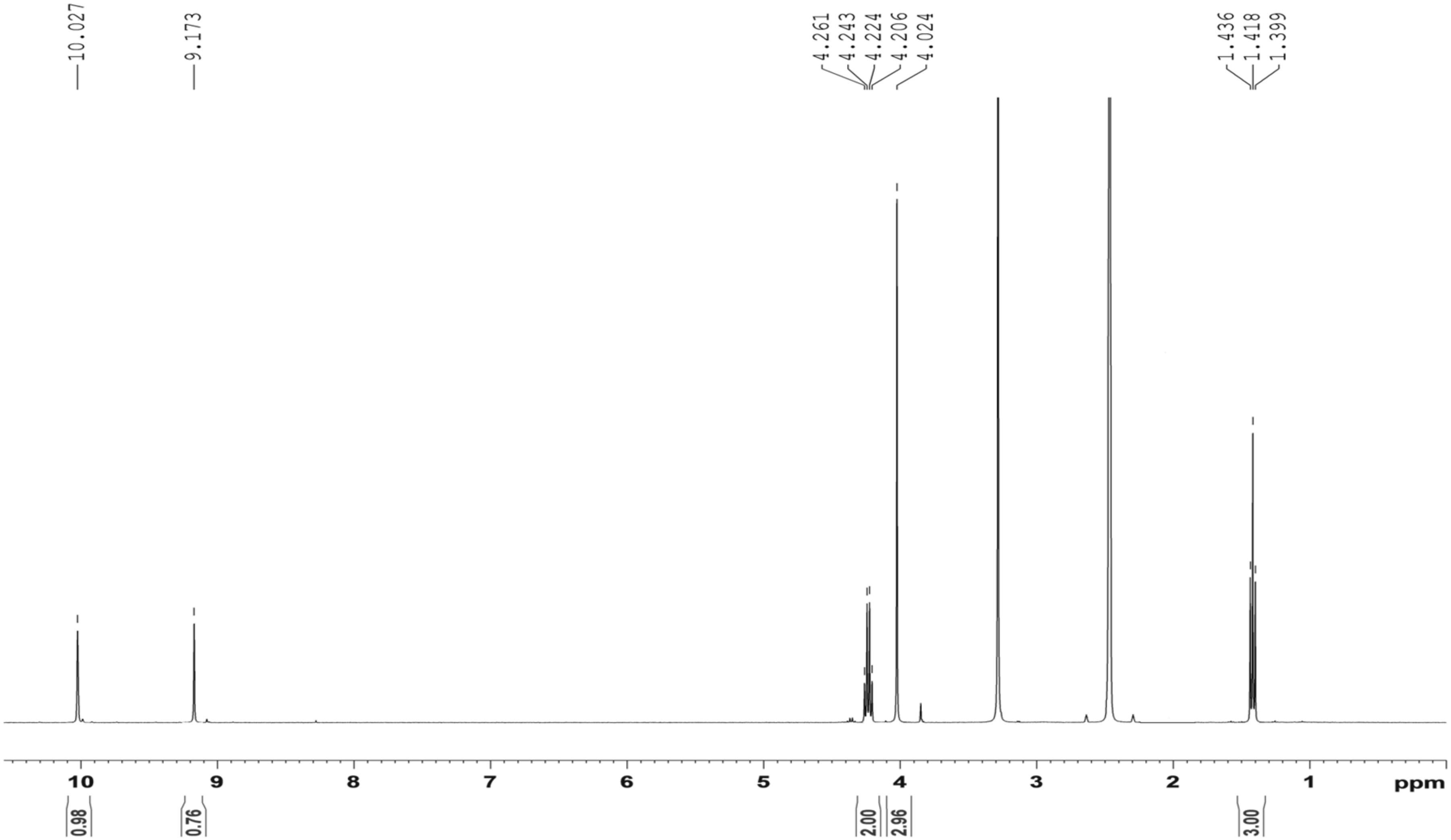


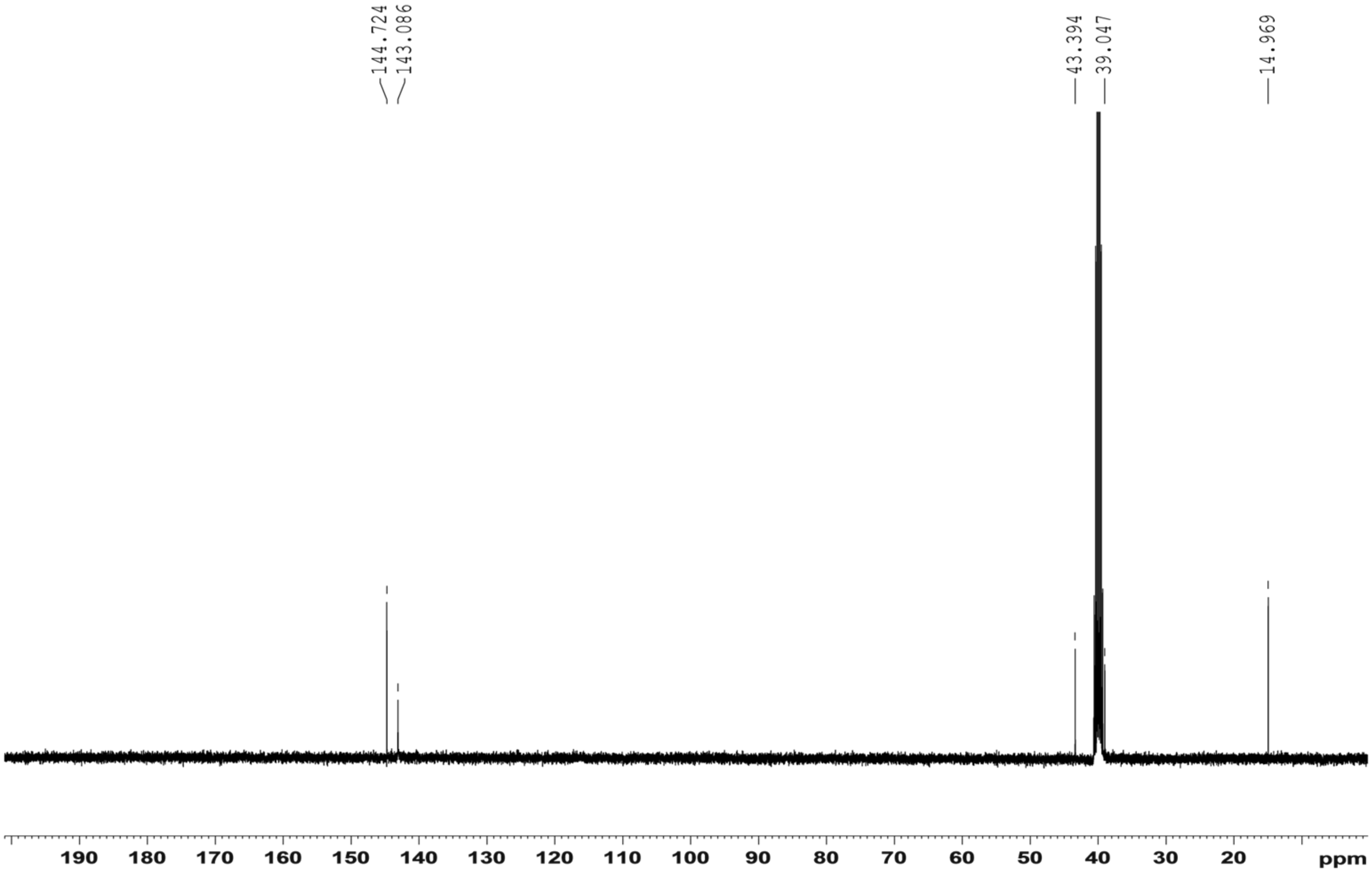


2,2,2-Trifluoroethyl benzoate (7, Scheme 1)



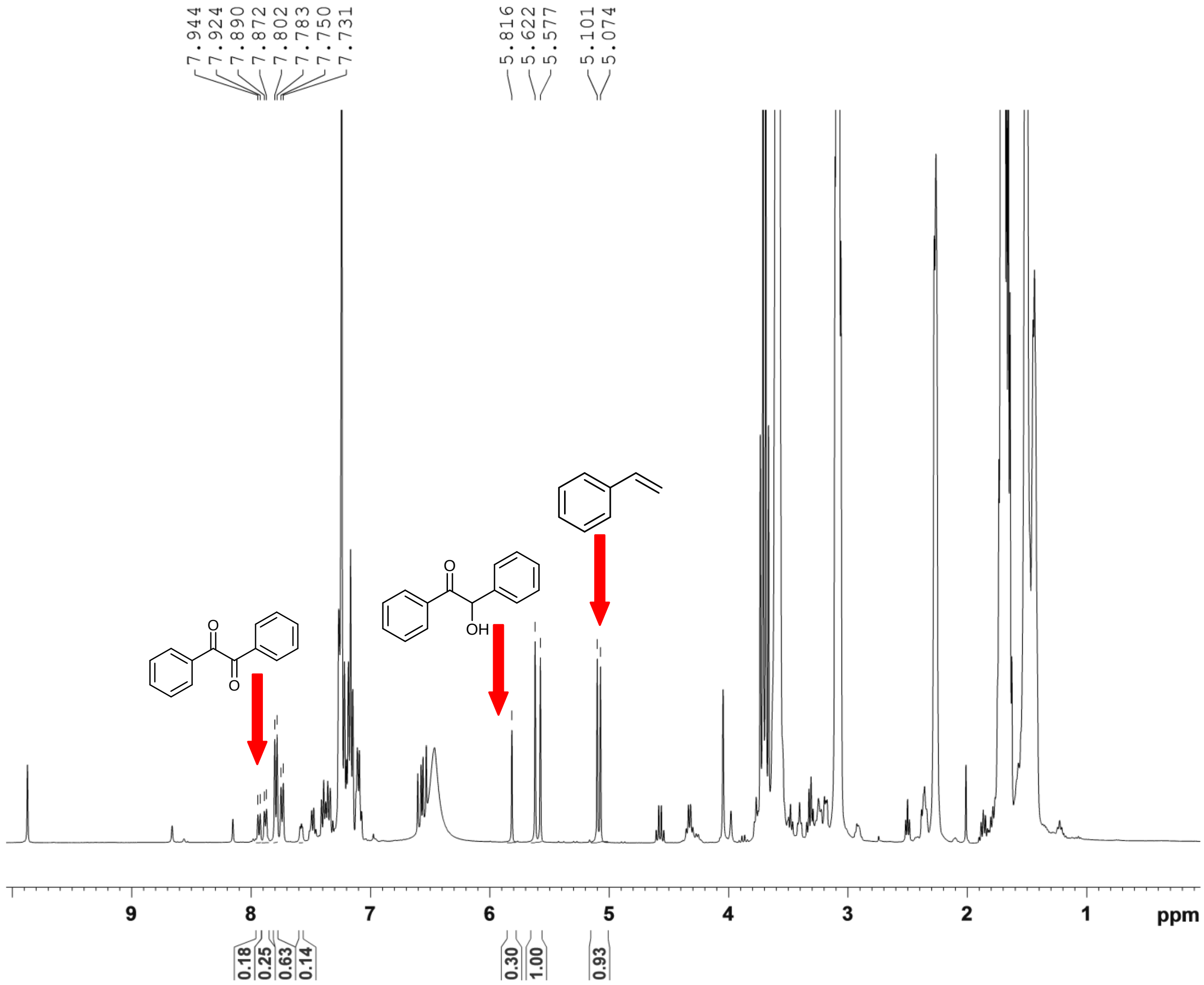
6 ^{1}H and ^{13}C NMR Spectral Data for Triazolium Precatalyst 2




144.724
143.086
43.394
39.047
14.969
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

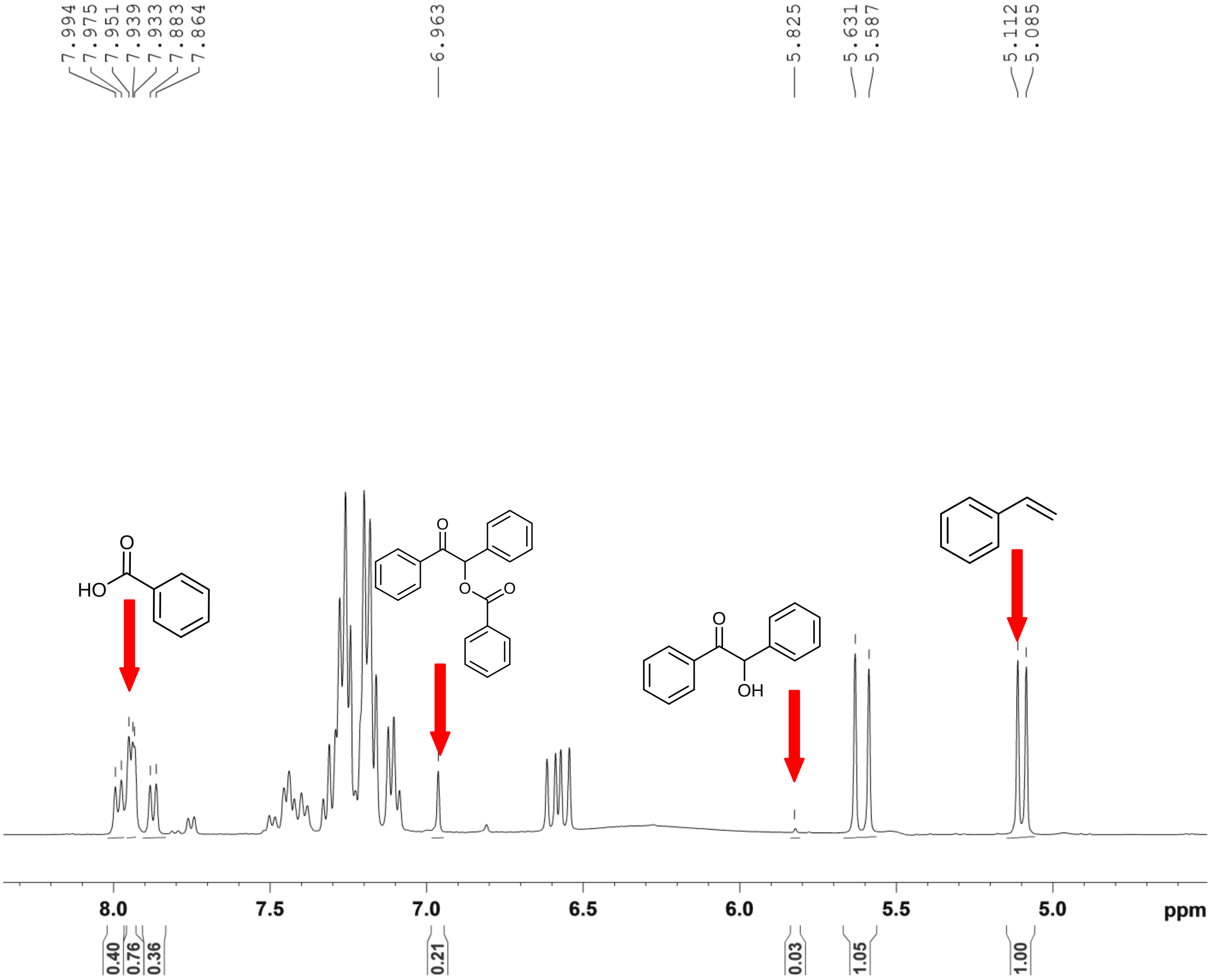
7 ^{1}H NMR Spectra Supporting Proposed Mechanism

t = 5 minutes

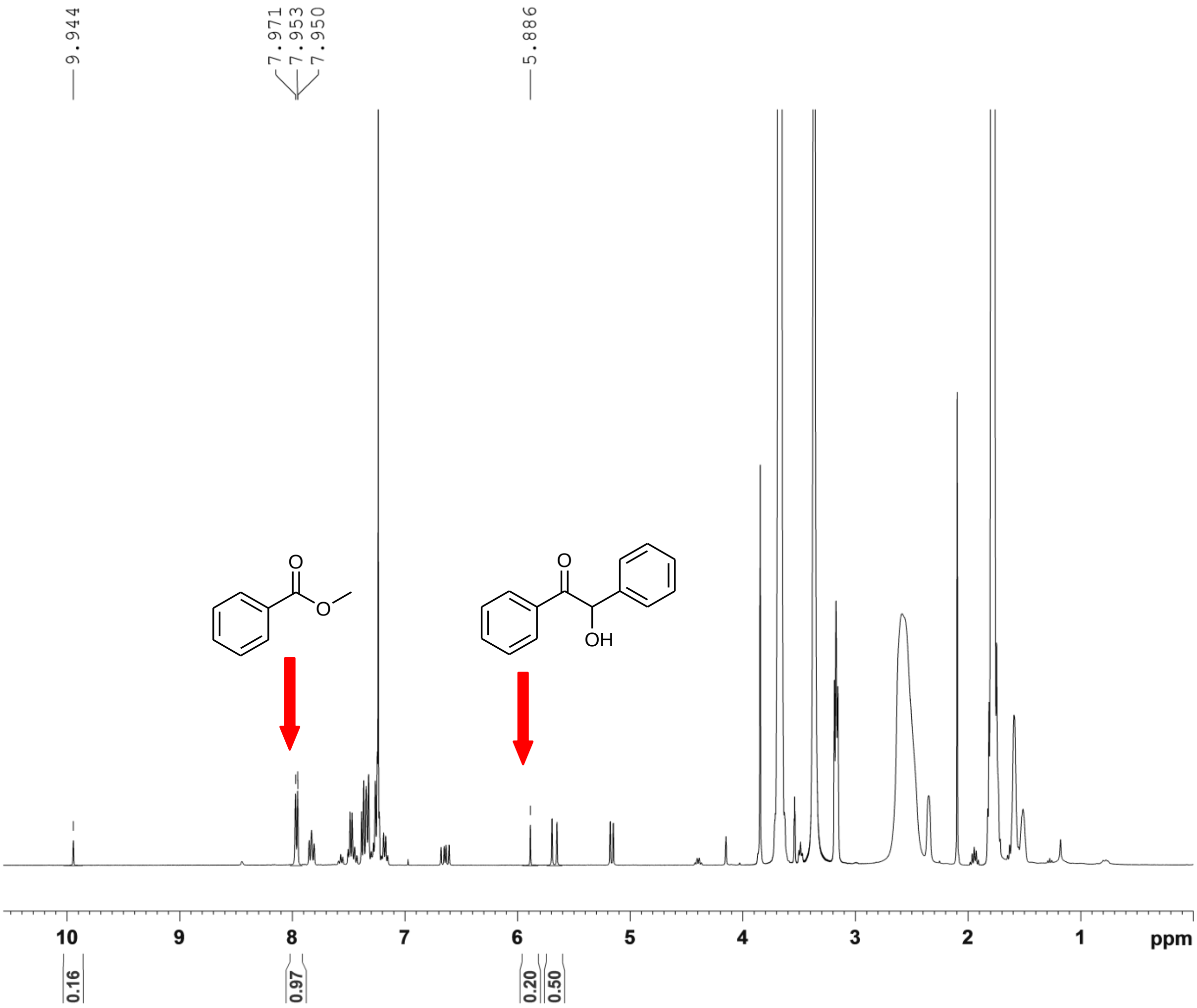


Reaction of benzaldehyde (**1**) under the conditions outlined in Scheme 2. t = 5 min. Styrene resonances are observed at 5.09 ppm, 5.60 ppm, 5.57 ppm and 7.05 ppm to 7.28 ppm.

t = 20 minutes

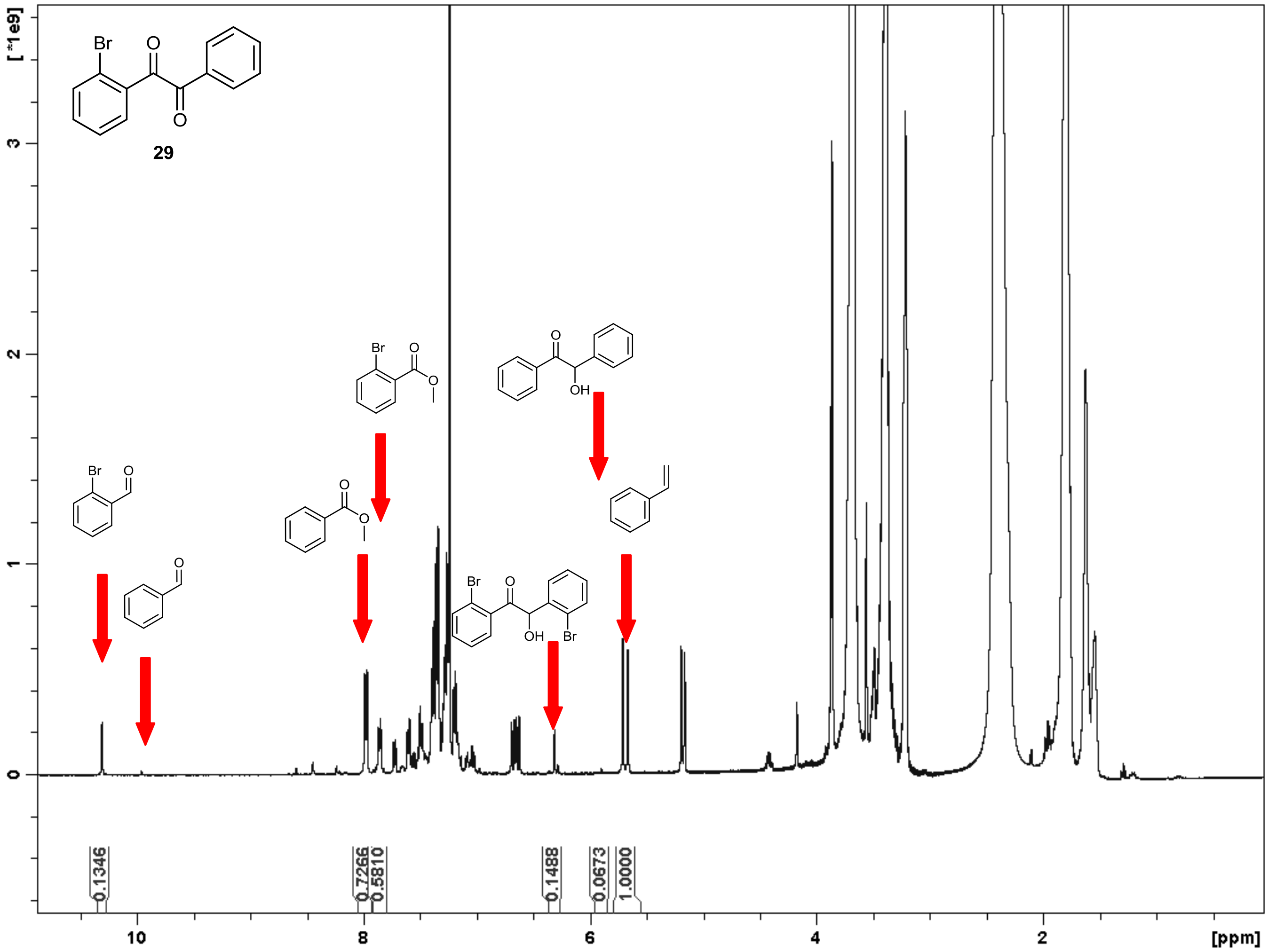


Reaction of benzaldehyde (**1**) under the conditions outlined in Scheme 2. t = 20 min. Styrene resonances are observed at 5.09 ppm, 5.60 ppm, 5.57 ppm and 7.05 ppm to 7.28 ppm.



Reaction of benzil **17** (1 mmol) with precatalyst **2** (15 mol%), DBU (110 mol%) in THF/MeOH (5.0 mL, 1:1 *v*/*v*) at room temperature under an argon atmosphere. t = 16 h. Styrene resonances are observed at 5.09 ppm, 5.60 ppm, 5.57 ppm and 7.05 ppm to 7.28 ppm.

8 ^{1}H NMR Spectrum for Esterification of an Unsymmetrical Benzil



Reaction of benzil **29** under the conditions outlined in Scheme 3. Styrene resonances are observed at 5.09 ppm, 5.60 ppm, 5.57 ppm and 7.05 ppm to 7.28 ppm.