

Supporting information

Polymer Supported Pd Catalyzed Carbonylation of Aryl Bromides for the Synthesis of Aryl esters and amides

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I. ^1H NMR Data of alkoxy carbonylation products

Ethyl Benzoate (Table 4, entry 1)

^1H NMR (400 MHz, CDCl_3): δ 8.03-8.06 (m, 2H), 7.52-7.57 (m, 1H), 7.41-7.46 (m, 2H), 4.38 (q, 2H, $J = 7.1$ Hz), 1.41 (t, 3H, $J = 7.2$ Hz),

Ethyl 2-methylbenzoate (Table 4, entry 2)

^1H NMR (400 MHz, CDCl_3): δ 7.91 (d, 1H, $J = 8.0$ Hz), 7.36 (t, 1H, $J = 7.6$ Hz), 7.21 (t, 2H, $J = 7.6$ Hz), 4.36 (q, 2H, $J = 7.3$ Hz), 2.58 (s, 3H), 1.38 (t, 3H, $J = 7.1$ Hz)

Ethyl 4-methylbenzoate (Table 4, entry 3)

^1H NMR (300 MHz, CDCl_3): δ 7.80 (d, 2H, $J = 7.8$ Hz), 7.09 (d, 2H, $J = 7.8$ Hz), 4.24 (q, 2H, $J = 7.2$ Hz), 2.26 (s, 3H), 1.26 (t, 3H, $J = 7.2$ Hz)

Ethyl 3-methylbenzoate (Table 4, entry 4)

^1H NMR (400 MHz, CDCl_3): δ 7.84-7.88 (m, 2H), 7.28-7.36 (m, 2H), 4.38 (q, 2H, $J = 7.3$ Hz), 2.41 (s, 3H), 1.38 (t, 3H, $J = 7.1$ Hz)

Ethyl 2-methoxybenzoate (Table 4, entry 5)

^1H NMR (400 MHz, CDCl_3): δ 7.78-7.80 (m, 1H), 7.44-7.49 (m, 1H), 6.96-6.98 (m, 2H), 4.37 (q, 2H, $J = 7.2$ Hz), 3.90 (s, 3H), 1.39 (t, 3H, $J = 7.1$ Hz)

Ethyl 4-methoxybenzoate (Table 4, entry 6)

^1H NMR (300 MHz, CDCl_3): δ 8.01 (d, 2H, $J = 8.8$ Hz), 6.92 (d, 2H, $J = 8.8$ Hz), 4.36 (q, 2H, $J = 7.3$ Hz), 3.85 (s, 3H), 1.39 (t, 3H, $J = 7.2$ Hz)

Ethyl 3-methoxybenzoate (Table 4, entry 7)

^1H NMR (300 MHz, CDCl_3): δ 7.66 (d, 1H, $J = 7.8$ Hz), 7.76 (s, 1H), 7.35 (dd, 1H, $J = 8.2$, 7.9 Hz), 7.11 (dd, 1H, $J = 8.1$, 1.8 Hz), 4.39 (q, 2H, $J = 6.9$ Hz), 3.86 (s, 3H), 1.41 (t, 3H, $J = 6.9$ Hz)

Ethyl 2-nitrobenzoate (Table 4, entry 8)

^1H NMR (300 MHz, CDCl_3): δ 7.93 (d, 1H, $J = 7.6$ Hz), 7.77 (d, 1H, $J = 7.2$ Hz), 7.72–7.62 (m, 2H), 4.40 (q, 2H, $J = 7.2$ Hz), 1.36 (t, 3H, $J = 7.2$ Hz)

Ethyl 4-nitrobenzoate (Table 4, entry 9)

^1H NMR (400 MHz, CDCl_3): δ 8.28-8.31 (m, 2H), 8.21-8.24 (m, 2H), 4.45 (q, 2H, $J = 7.2$ Hz), 1.45 (t, 3H, $J = 7.0$ Hz)

Ethyl 4-fluorobenzoate (Table 4, entry 10)

^1H NMR (400 MHz, CDCl_3): δ 8.04-8.09 (m, 2H), 7.08-7.14 (m, 2H), 4.38 (q, 2H, $J = 7.0$ Hz), 1.40 (t, 3H, $J = 7.0$ Hz)

Ethyl 4-(trifluoromethyl) benzoate (Table 4, entry 11)

^1H NMR (400 MHz, CDCl_3): δ 8.16 (dd, 2H, $J_1 = 0.5$ Hz, $J_2 = 8.9$ Hz), 7.70 (d, 2H, $J = 8.4$ Hz), 4.42 (q, 2H, $J = 7.1$ Hz), 1.43 (t, 3H, $J = 7.2$ Hz)

Ethyl 4-cyanobenzoate (Table 4, entry 12)

^1H NMR (300 MHz, CDCl_3): δ 8.16 (d, 2H, $J = 6.9$ Hz), 7.76 (d, 2H, $J = 6.8$ Hz), 4.43 (q, 2H, $J = 7.2$ Hz), 1.42 (t, 3H, $J = 7.2$ Hz)

Ethyl 4-Acetylbenzoate (Table 4, entry 13)

¹H NMR (300 MHz, CDCl₃): δ 8.15-8.12 (m, 2H), 8.03- 8.00 (m, 2H), 4.42 (q, 2H, *J* = 6.9 Hz), 2.65 (s, 3H), 1.42 (t, 3H, *J* = 6.9 Hz)

Diethyl terephthalate (Table 4, entry 14)

¹H NMR (300 MHz, CDCl₃): δ 8.11 (s, 4H), 4.40 (q, 2H, *J* = 7.2 Hz), 1.41 (t, 3H, *J* = 7.2 Hz)

Ethyl isonicotinate (Table 4, entry 15)

¹H NMR (400 MHz, CDCl₃): δ 9.23 (d, 1H, *J* = 2.0 Hz), 8.78 (m, 1H), 8.31 (m, 1H), 7.40 (m, 1H), 4.42 (q, 2H, *J* = 7.1 Hz), 1.43 (t, 3H, *J* = 7.0 Hz)

Ethyl thiophene-2-carboxylate (Table 4, entry 16)

¹H NMR (300 MHz, CDCl₃): δ 7.80 (d, 1H, *J* = 3.0 Hz), 7.55 (d, 1H, *J* = 4.5 Hz), 7.10 (dd, 1H, *J* = 3.0, 4.5 Hz), 4.36 (q, 2H, *J* = 7.2 Hz), 1.38 (t, 3H, *J* = 7.2 Hz)

Ethyl 1-naphthoate (Table 4, entry 17)

¹H NMR (300 MHz, CDCl₃): δ 8.93 (d, 1H, *J* = 8.4 Hz), 8.17 (d, 1H, *J* = 7.2 Hz), 7.98 (d, 1H, *J* = 8.2 Hz), 7.86 (d, 1H, *J* = 8.1 Hz), 7.60 (t, 1H, *J* = 7.2 Hz), 7.52–7.43 (m, 2H), 4.45 (q, 2H, *J* = 7.2 Hz), 1.44 (t, 3H, *J* = 7.2 Hz).

Ethyl biphenyl-4-carboxylate (Table 4, entry 18)

¹H NMR (300 MHz, CDCl₃): δ 8.12 (d, 2H, *J* = 8.7 Hz), 7.64 (t, 4H, *J*/₄ 8.8 Hz), 7.47 (t, 2H, *J* = 7.2 Hz), 7.40 (m, 1H), 4.41 (q, 2H, *J* = 7.2 Hz), 1.42 (t, 3H, *J* = 7.2 Hz)

II. ¹H NMR Data of amino carbonylation products

N-Phenylbenzamide (Table 7, entry 1)

¹H NMR (300 MHz, CDCl₃): δ 7.98 (br, s, 1H), 7.87-8.83 (m, 2H), 7.63 (d, 2H, *J* = 7.6 Hz), 7.32-7.53 (m, 5H), 7.16 (t, 1H, *J* = 7.3)

N-(4-methoxyphenyl)benzamide (Table 7, entry 2)

¹H NMR (300 MHz; *d*₆-DMSO): δ 10.12 (s, 1H), 7.94 (d, 2H, *J* = 6.8 Hz), 7.67 (d, 2H, *J* = 9.0 Hz), 7.46-7.62 (m, 3H), 6.92 (d, 2H, *J* = 9.0 Hz), 3.76 (s, 3H)

N-Benzylbenzamide (Table 7, entry 3)

¹H NMR (300 MHz, CDCl₃): δ 7.98–7.75 (d, 2H, *J* = 7.3 Hz), 7.40–7.29 (m, 8H), 6.70 (br, s, 1H), 4.60 (d, 2H, *J* = 5.7 Hz)

N-Cyclohexylbenzamide (Table 7, entry 4)

¹H NMR (300 MHz, CDCl₃): δ 7.78-7.75 (m, 2H), 7.36-7.46 (m, 3H), 6.18 (br, s, 1H), 3.98-3.95 (m, 1H), 2.03-1.98 (m, 2H), 1.77-1.61 (m, 3H), 1.43-1.15 (m, 5H)

N-[3-(Trifluoromethyl)phenyl]benzamide (Table 7, entry 5)

¹H NMR (400 MHz, CDCl₃): δ 8.09 (s, 1H), 7.97 (s, 1H), 7.90 (m, 3H), 7.60 (t, 1H, *J* = 7.40), 7.51 (m, 3H), 7.43 (d, 1H, *J* = 7.79 Hz)

N-Benzyl-4-methylbenzamide (Table 7, entry 6)

¹H NMR (300 MHz, CDCl₃): δ 7.79-7.66 (m, 2H), 7.36-7.12 (m, 7H), 6.93 (bs, 1H), 4.54 (d,

2H, $J = 4.8$ Hz), 2.34 (s, 3H)

***N*-Benzyl-4-methoxybenzamide (Table 7, entry 7)**

^1H NMR (300 MHz, CDCl_3): δ 7.78 (d, 2H, $J = 8.1$ Hz), 7.34 (bs, 5H), 6.92 (d, 2H, $J = 8.4$ Hz), 6.36 (bs, 1H), 4.64 (d, 2H, $J = 5.4$ Hz), 3.84 (s, 3H)

4-methoxy-N-phenylbenzamide (Table 7, entry 8)

^1H NMR (400 MHz, CDCl_3) δ : 7.83-7.85 (m, 2H), 7.62-7.64 (m, 2H), 7.34- 7.38 (m, 2H), 7.76 (bs, 1H), 7.12-7.16 (m, 1H), 6.96-6.98 (m, 2H), 3.88 (s, 3H).

***N*-Benzyl-3-chlorobenzamide (Table 7, entry 9)**

^1H NMR (300 MHz, CDCl_3): δ 7.79-7.76 (m, 1H), 7.67 -7.64 (m, 1H), 7.47- 7.34 (m, 7H), 6.44 (bs, 1H), 4.63 (d, 2H, $J = 5.4$ Hz)

***N*-Benzylnaphthalene-1-carboxamide (Table 7, entry 10)**

^1H NMR (400 MHz, CDCl_3) δ 8.33-8.35 (m, 1H) 7.85-7.91 (m, 2H), 7.49-7.60 (m, 3H), 7.28-7.43 (m, 6H), 6.40 (br s, 1H), 4.70 (d, 2H, $J = 5.6$ Hz).

***N*-benzylnicotinamide (Table 7, Entry 11)**

^1H NMR (400 MHz, DMSO) δ 9.26 (s, 1H), 9.05 (s, 1H), 8.71 (s, 1H), 8.22 (s, 1H), 7.52 (s, 1H), 7.33 (s, 4H), 7.25 (s, 1H), 4.50 (s, 2H)

***N*-Benzylthiophene-3-carboxamide (Table 7, entry 12)**

^1H NMR (400 MHz, CDCl_3) δ 7.87-7.8 (m, 1H), 7.39-7.41 (m, 1H), 7.26-7.35 (m, 6H), 6.62 (br s, 1H), 4.58 (d, 2H, $J = 5.5$ Hz).

***N*-Methyl-N-phenyl-benzamide (Table 7, entry 13)**

^1H NMR (400MHz, CDCl_3): δ 7.27-7.32 (m, 2H), 7.21-7.26 (m, 6H), 7.04-7.19 (m, 2H), 3.52 (s, 3H)

***N*-benzoylmorpholine (Table 7, entry 14)**

^1H NMR (400MHz, CDCl_3): δ 7.96 (d, $J = 8.0\text{Hz}$, 2H), 7.66 (t, $J = 7.6$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 2H), 3.84-3.75 (m, 4H), 3.65 (t, $J = 4.8$ Hz, 2H), 3.38 (t, $J = 4.8$ Hz, 2H);

***N*-(4-toluoyl)morpholine (Table 7, entry 15)**

^1H NMR (400MHz, CDCl_3): δ 7.85 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 3.76 (s, 4H), 3.62 (t, $J = 4.4$ Hz, 2H), 3.35 (t, $J = 4.4$ Hz, 2H), 2.42 (s, 3H);

***N*-(4-methoxybenzoyl)morpholine (Table 7, entry 16)**

^1H NMR (400MHz, CDCl_3): δ 7.92 (dt, $J = 8.8$ Hz, $J = 2.4$ Hz, 2H), 6.99 (dt, $J = 8.8$ Hz, $J = 2.4$ Hz, 2H), 3.88 (s, 3H), 3.81-3.76 (m, 4H), 3.65 (t, $J = 4.8$ Hz, 2H), 3.38(d, $J = 4.8\text{Hz}$, 2H)

***N*-(4-methoxybenzoyl)morpholine (Table 7, entry 17)**

^1H NMR (400MHz, CDCl_3): δ 7.68 (d, $J = 8.0\text{Hz}$, 2H), 7.53 (d, $J = 8.0\text{Hz}$, 2H), 3.89-3.71 (m, 4H), 3.70-3.56 (m, 2H), 3.50-3.30 (m, 2H)

III. ^1H NMR Spectra of alkoxy carbonylation products

Table 4, entry 1

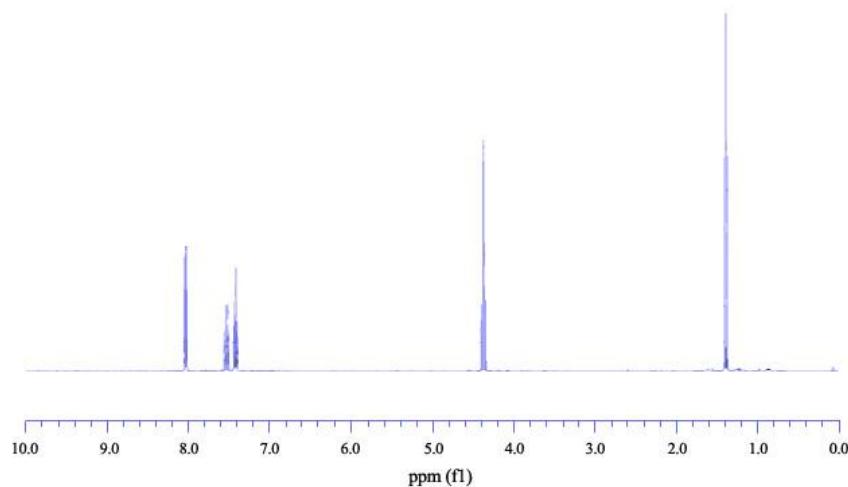
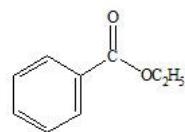


Table 4, entry 2

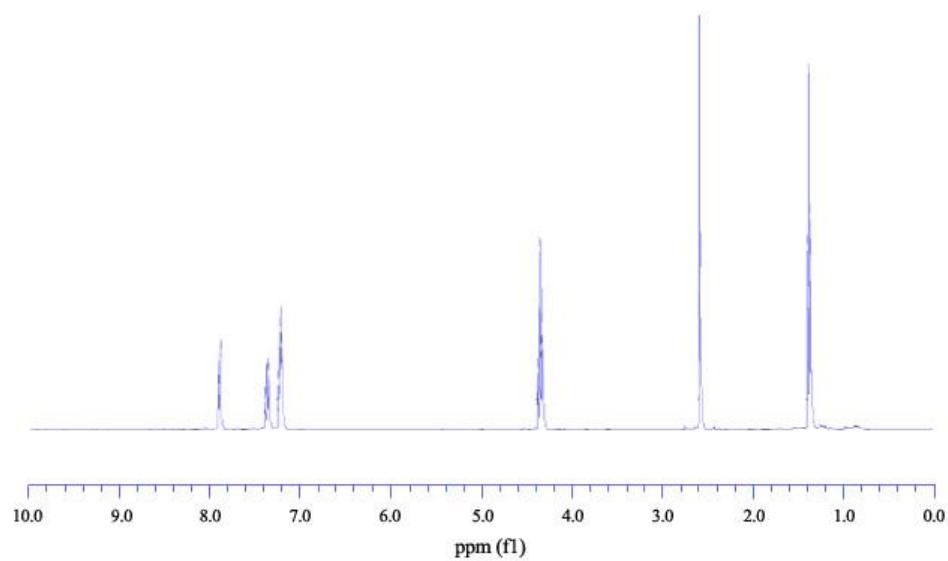
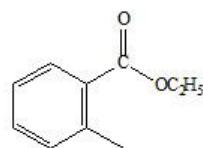


Table 4, entry 3

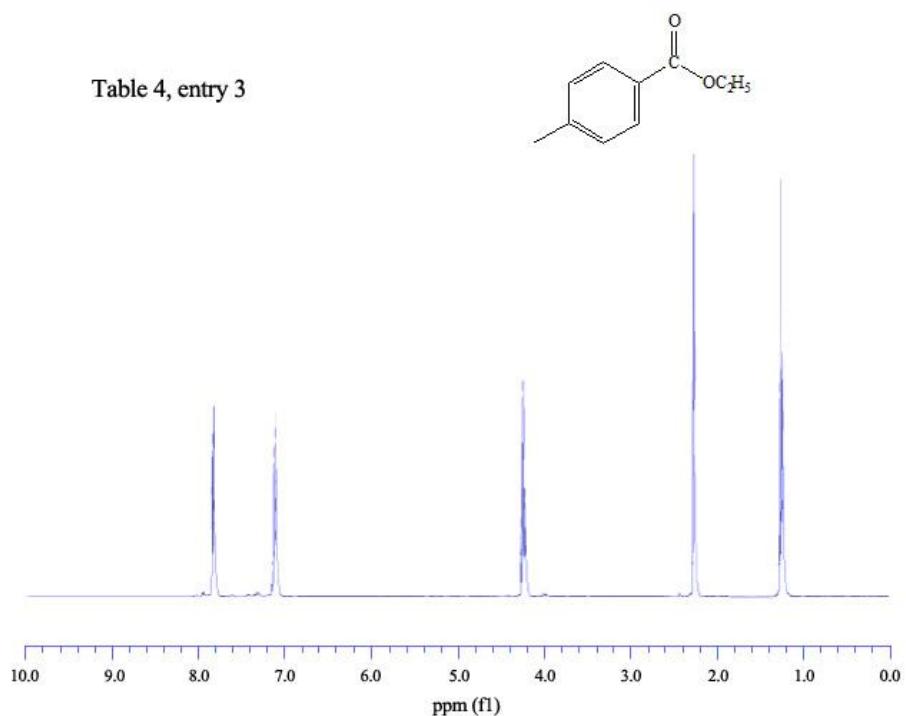


Table 4, entry 4

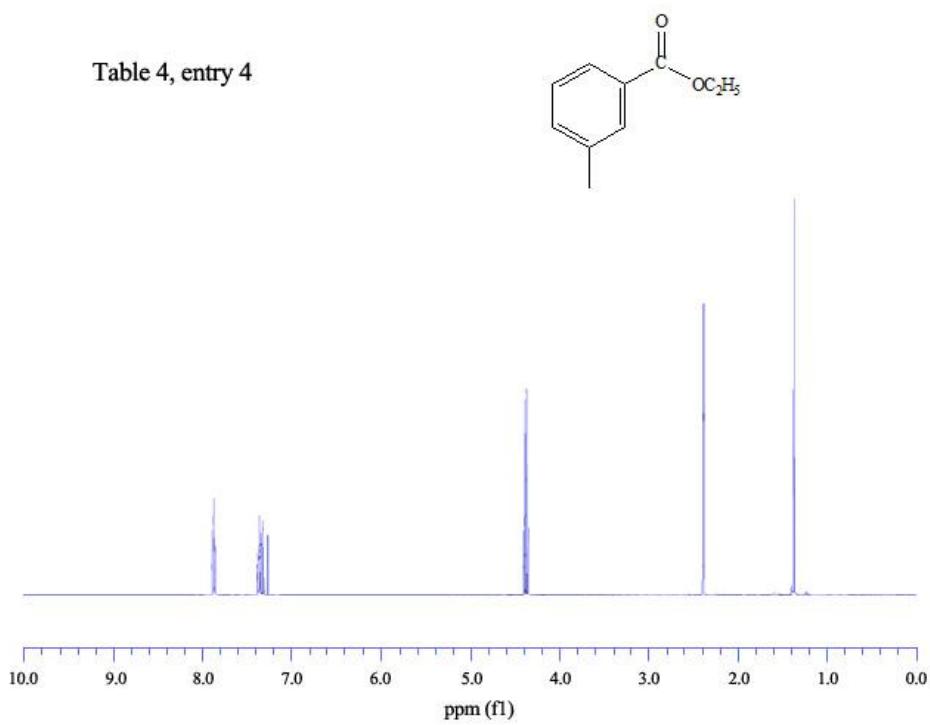


Table 4, entry 5

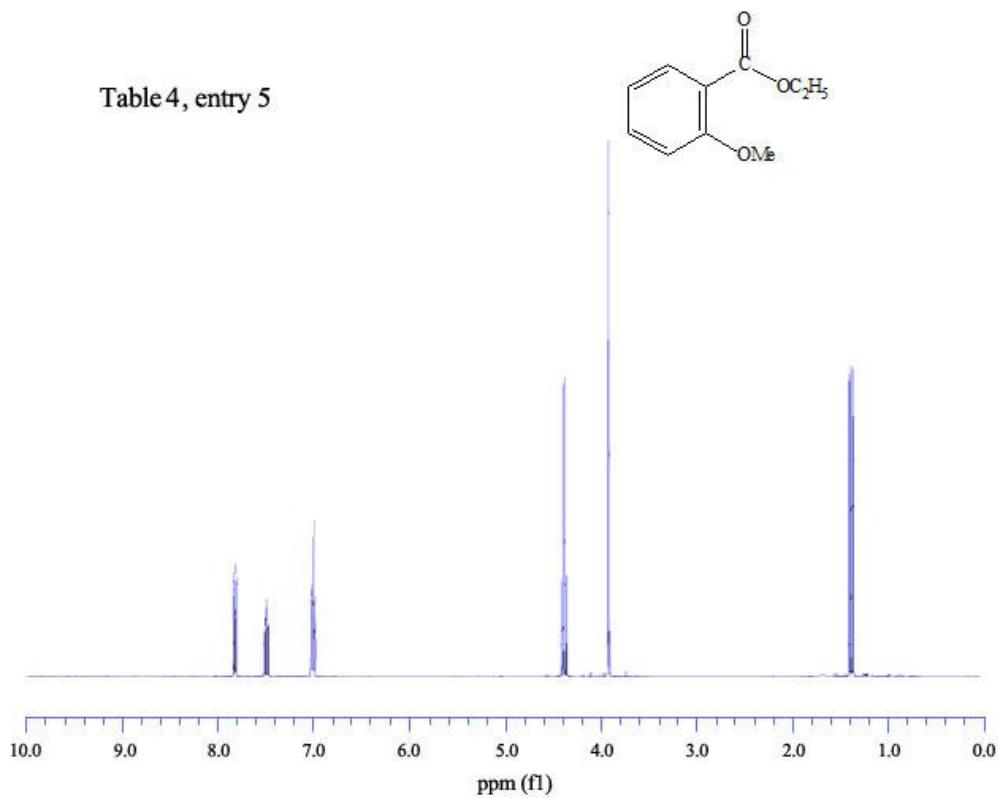


Table 4, entry 6

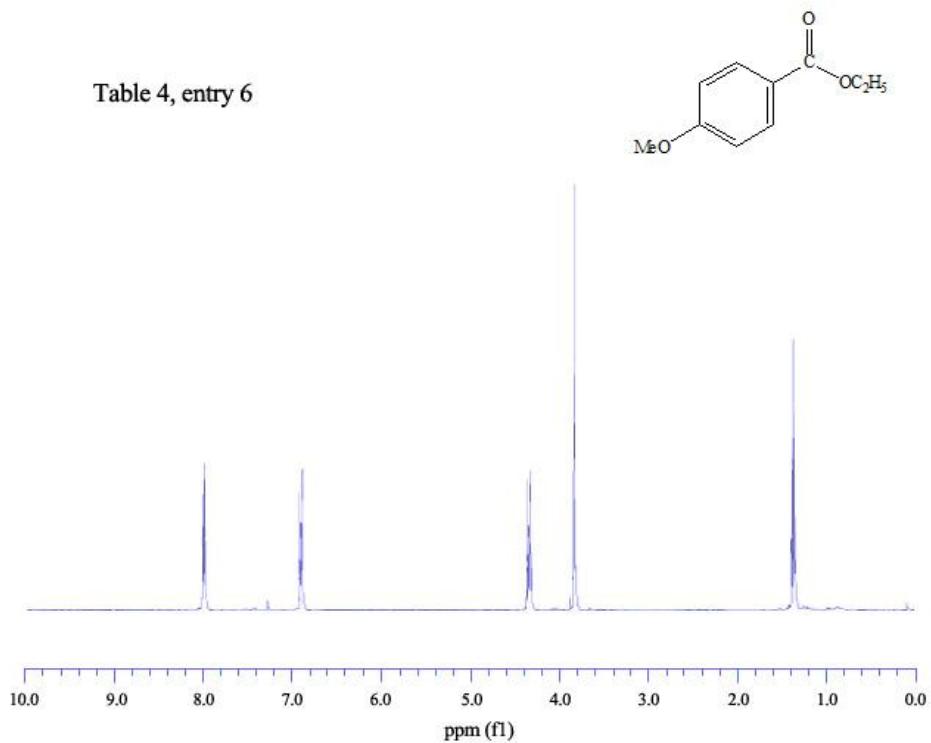


Table 4, entry 7

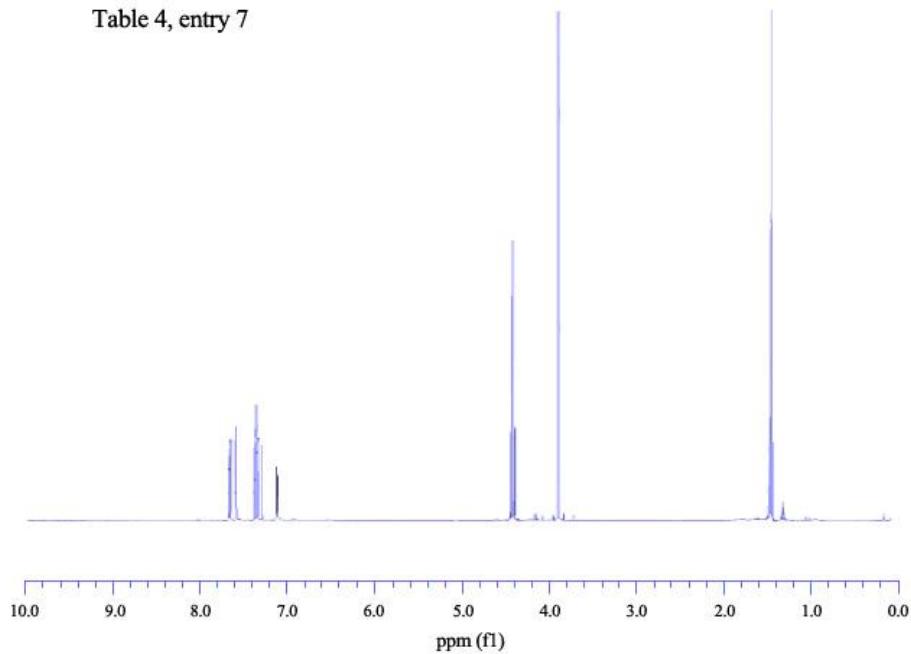


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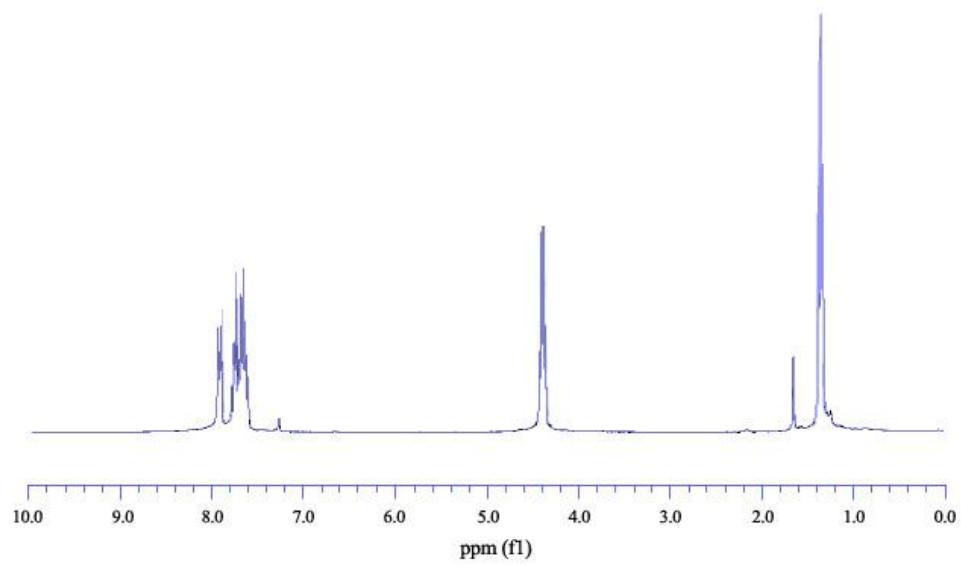
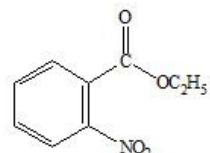


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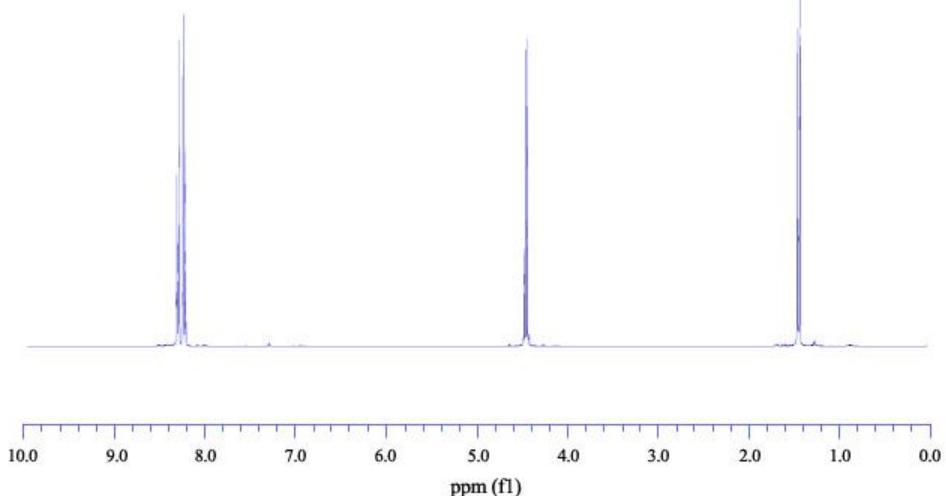
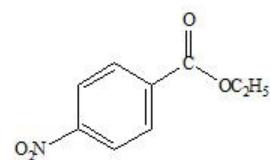


Table 4, entry 10

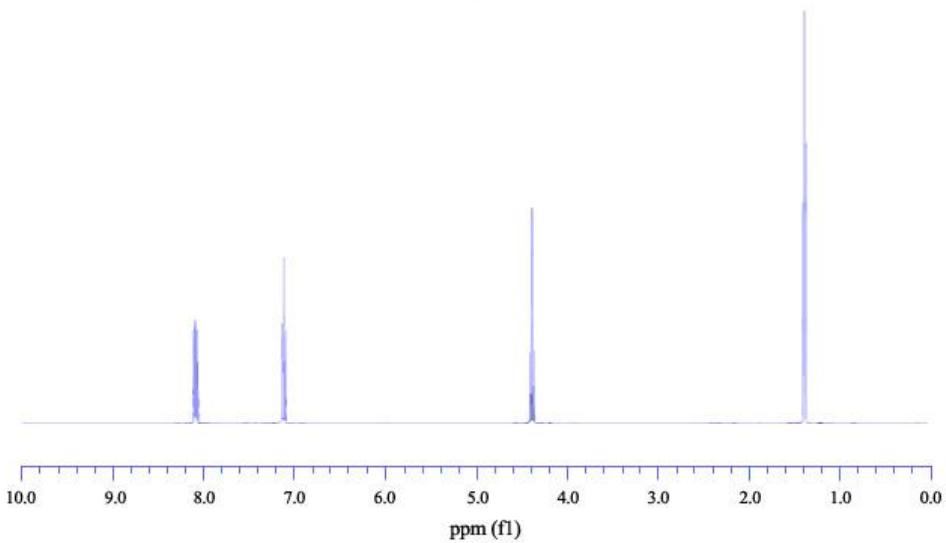
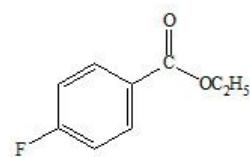


Table 4, entry 11

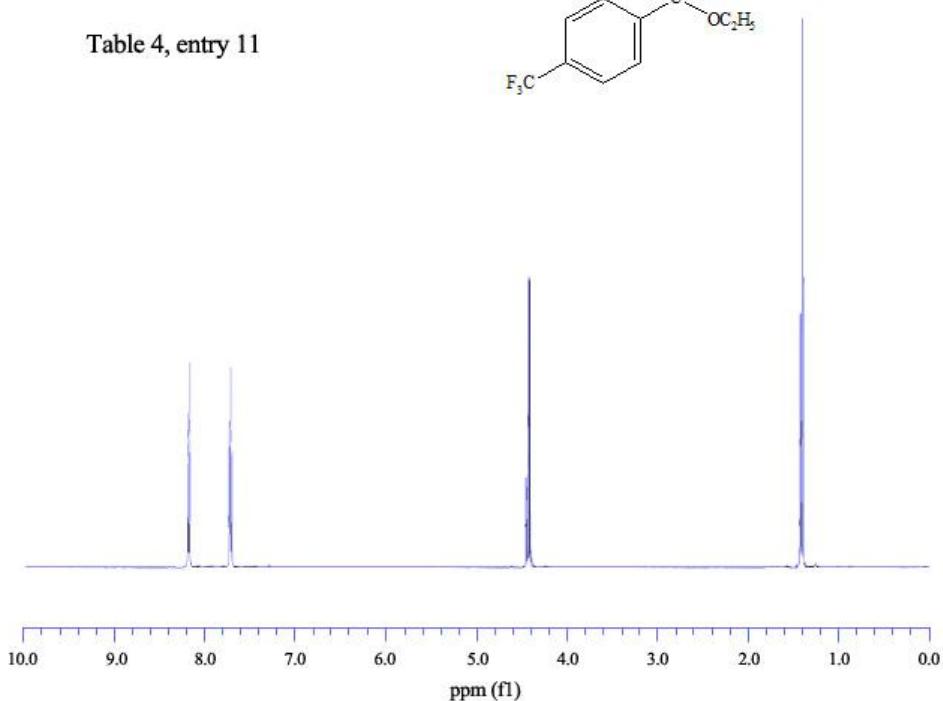
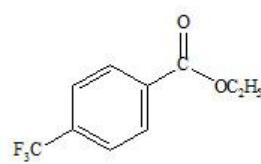


Table 4, entry 12

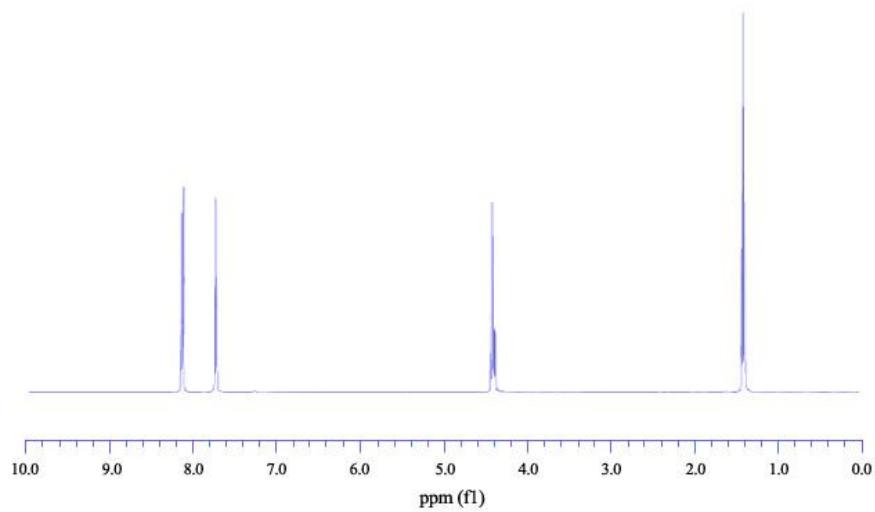
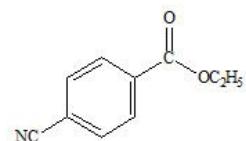


Table 4, entry 13

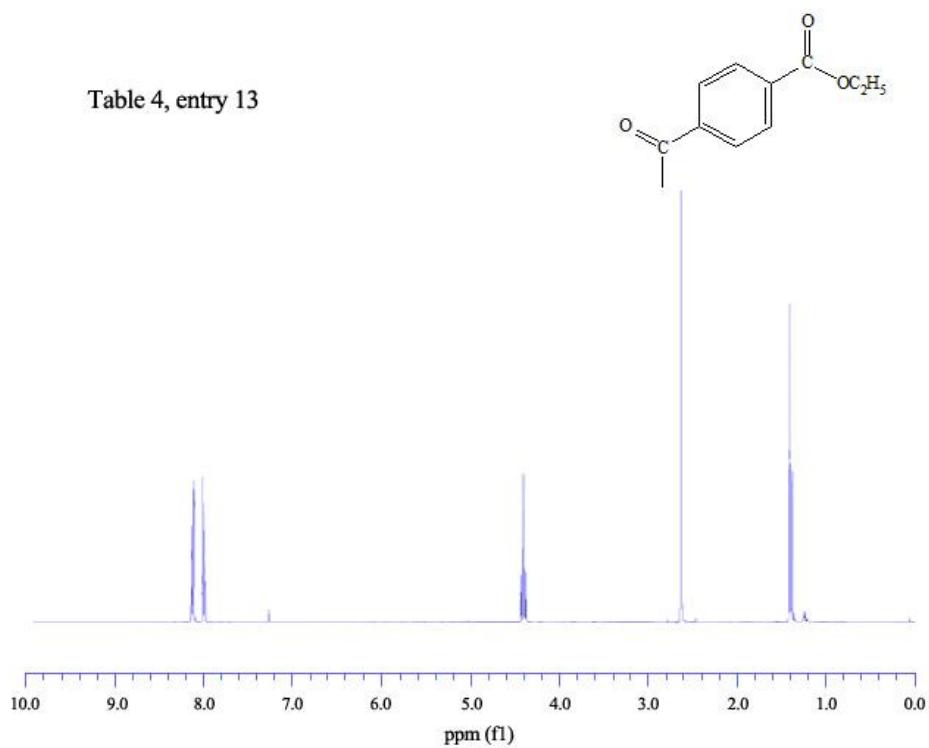


Table 4, entry 14

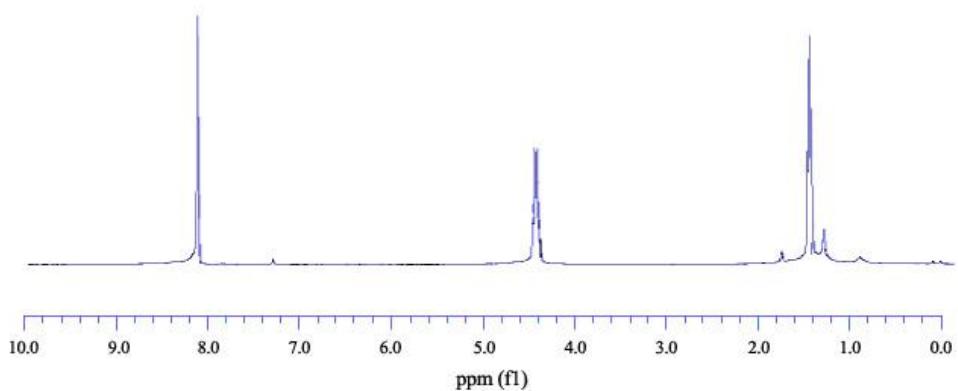
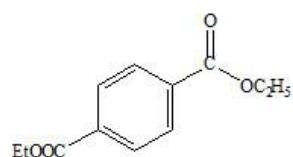


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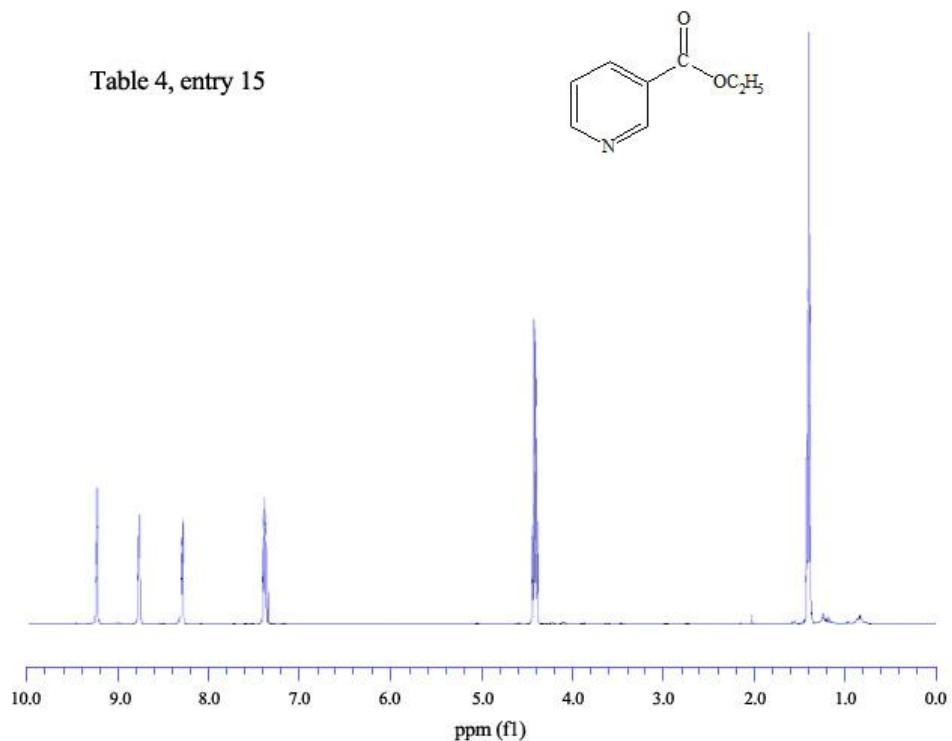
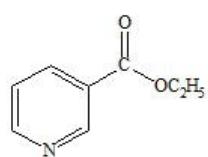


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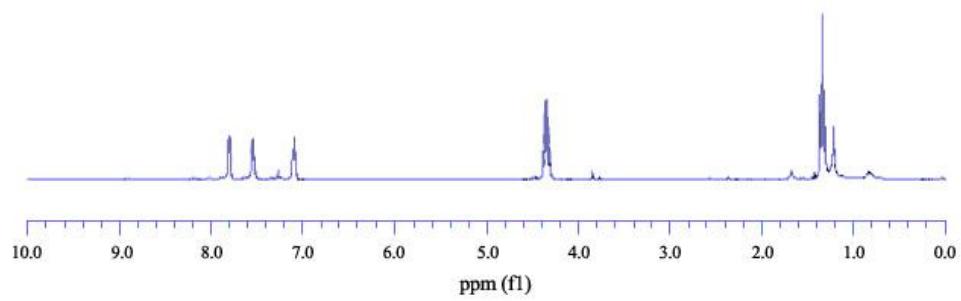
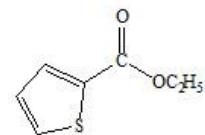


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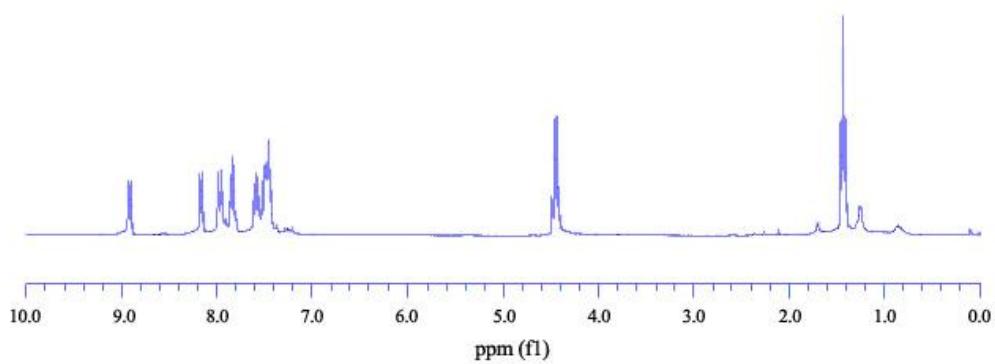
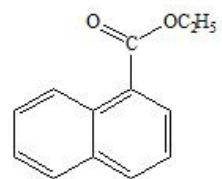
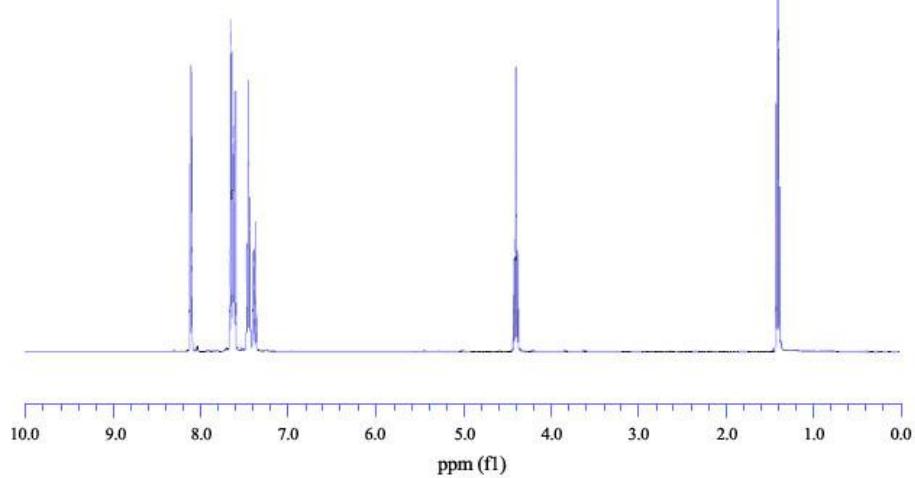
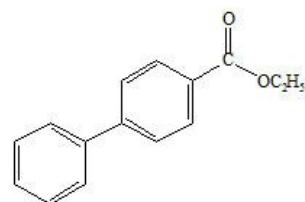


Table 4, entry 18



IV. ^1H NMR Spectra of amino carbonylation products

Table 7, entry 1

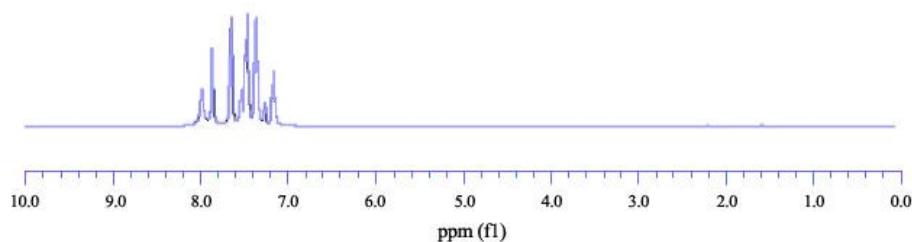
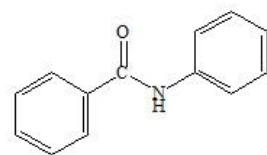


Table 7, entry 2

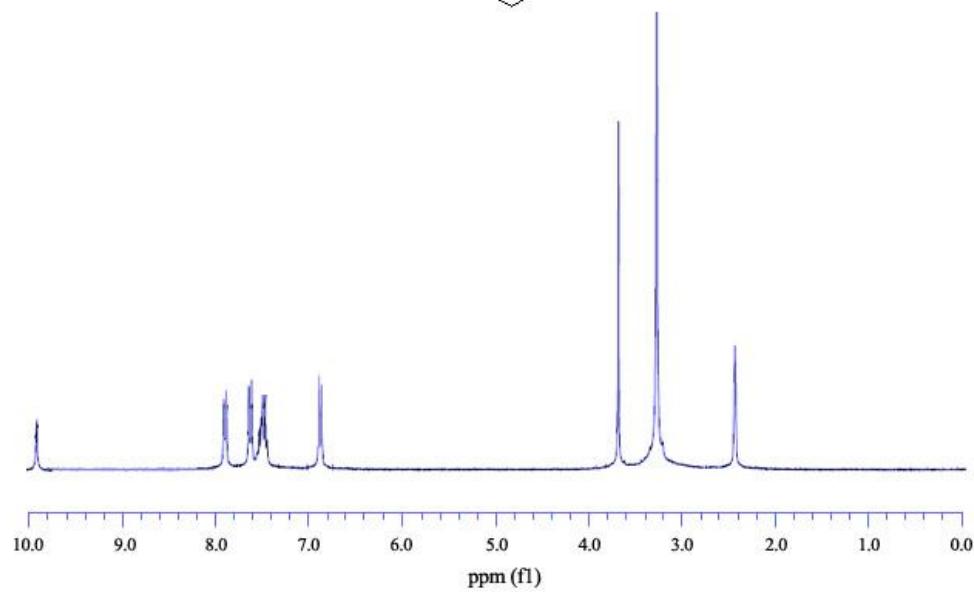
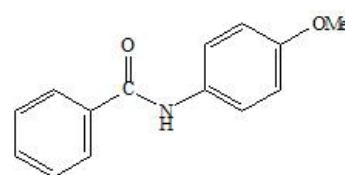


Table 7, entry 3

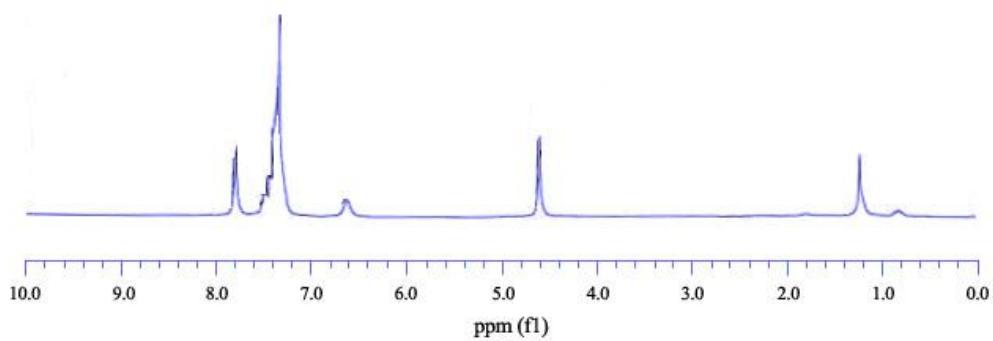
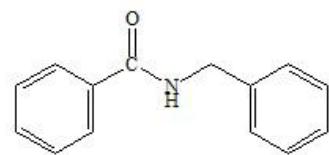


Table 7, entry 4

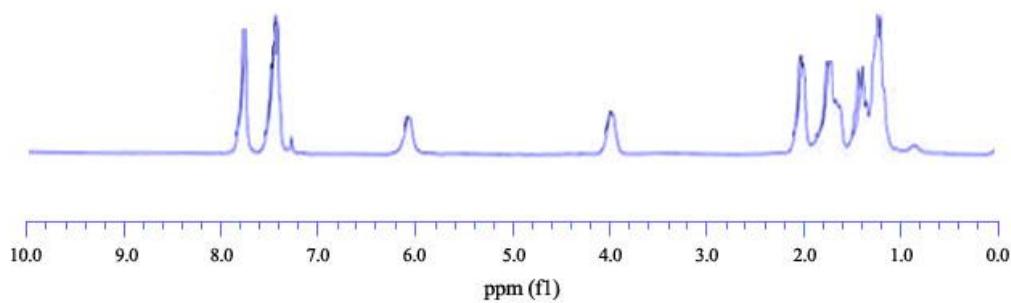
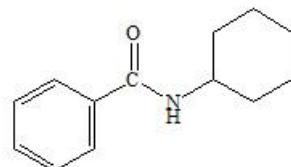


Table 7, entry 5

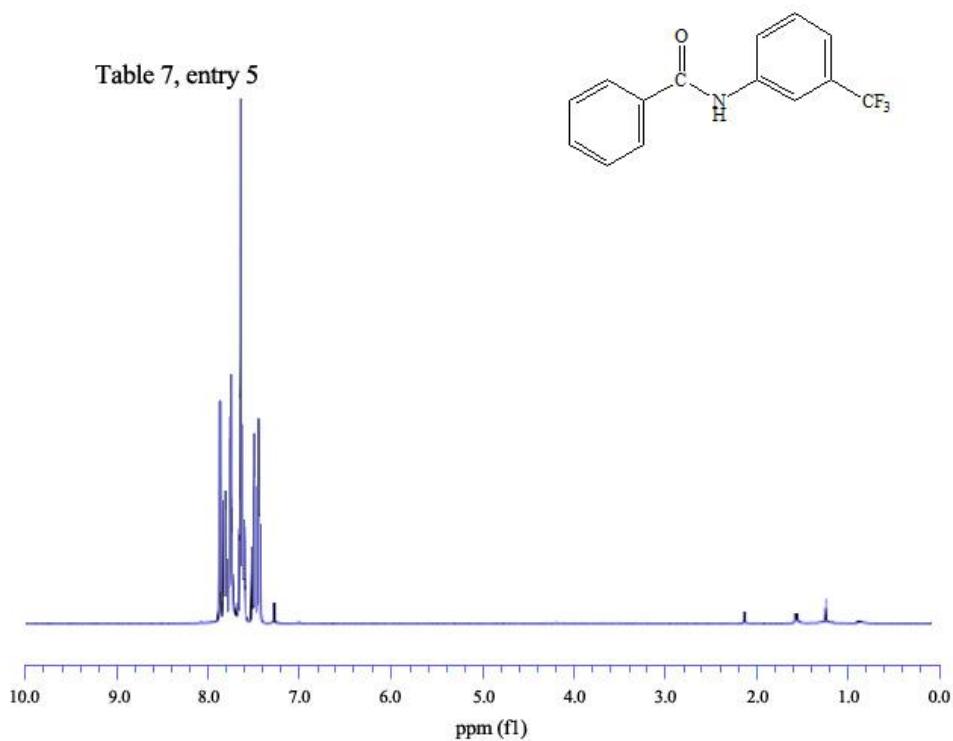


Table 7, entry 6

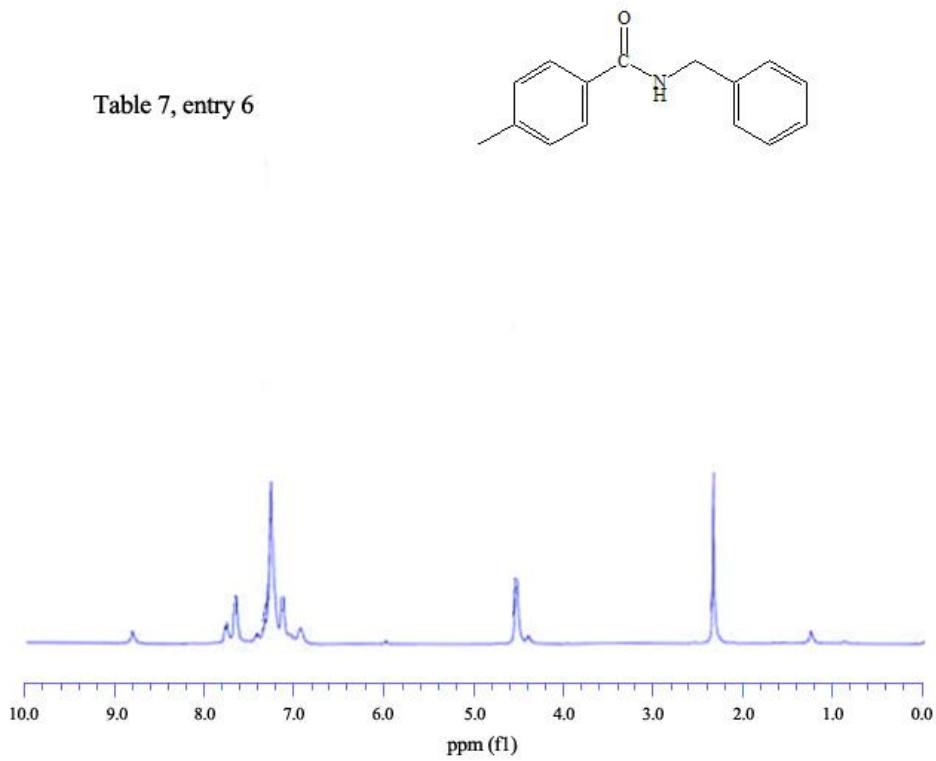


Table 7, entry 7

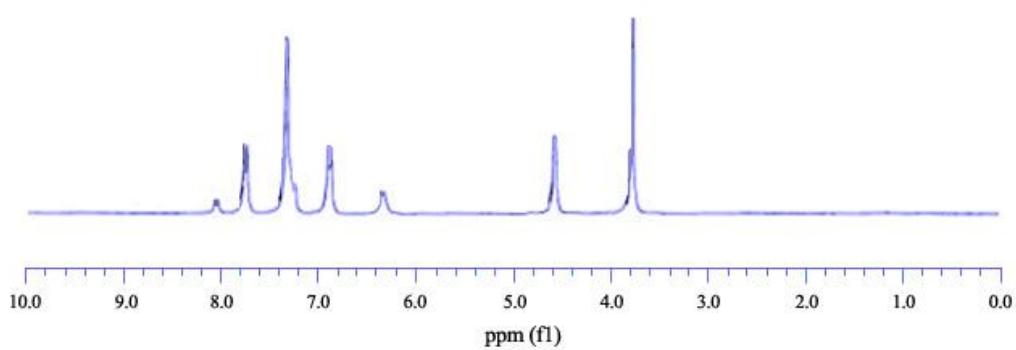
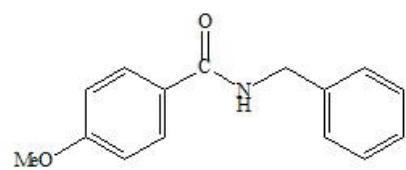


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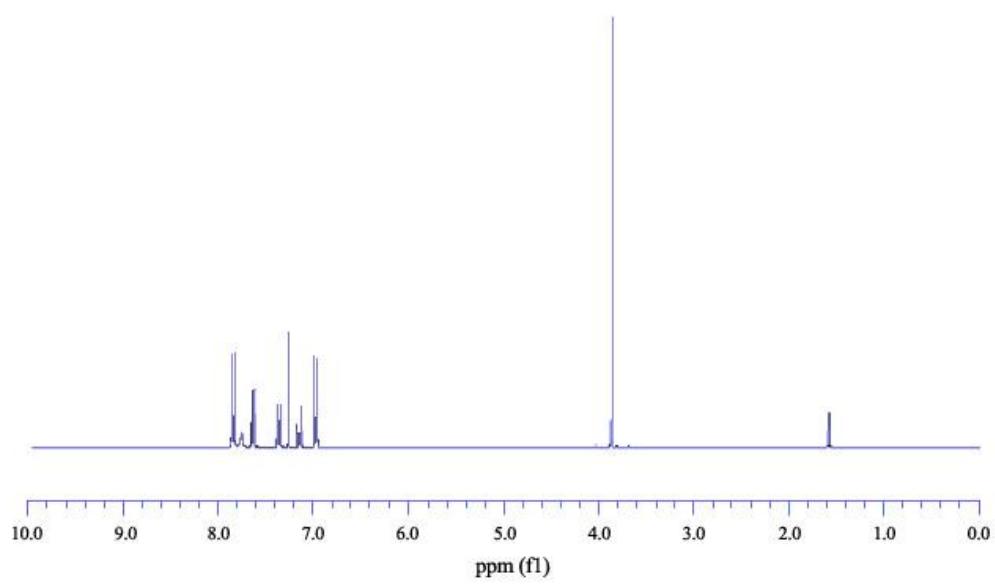
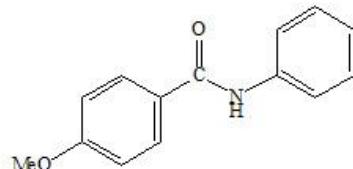


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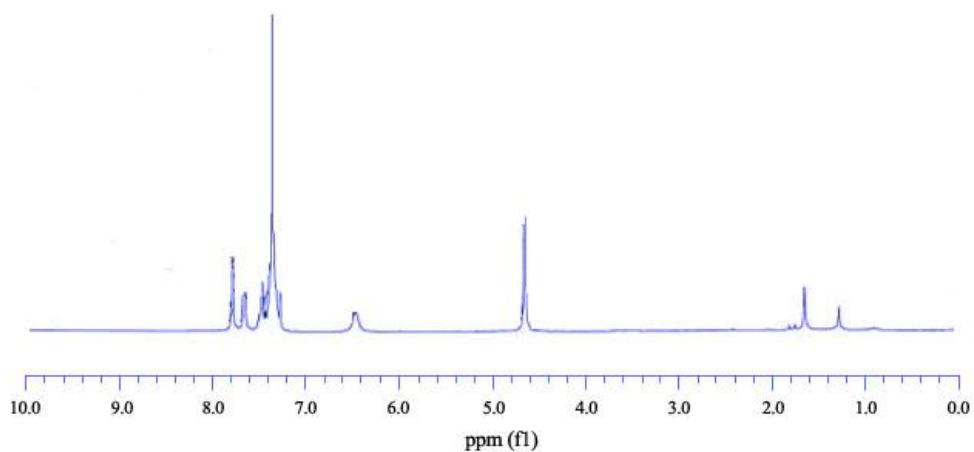
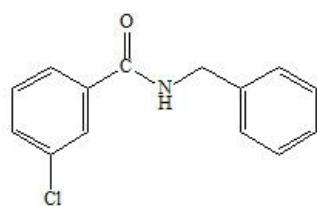


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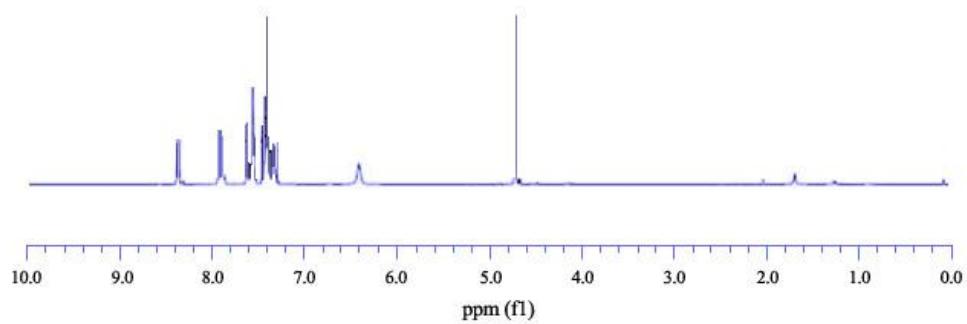
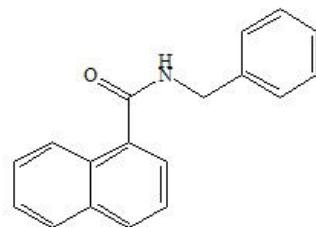


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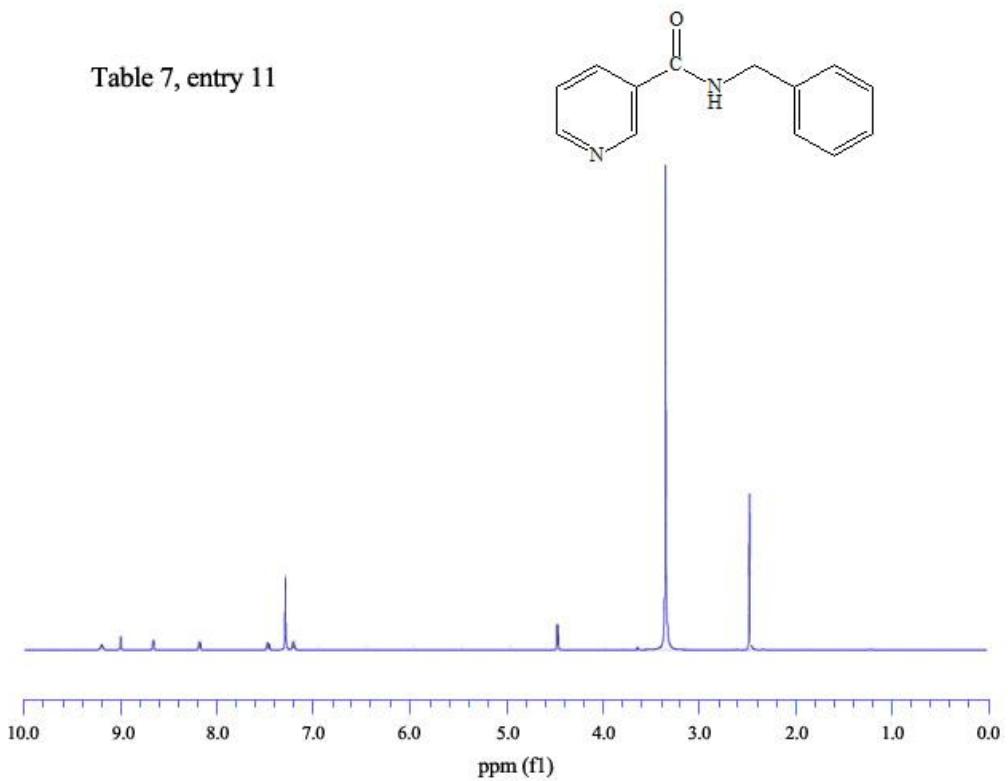


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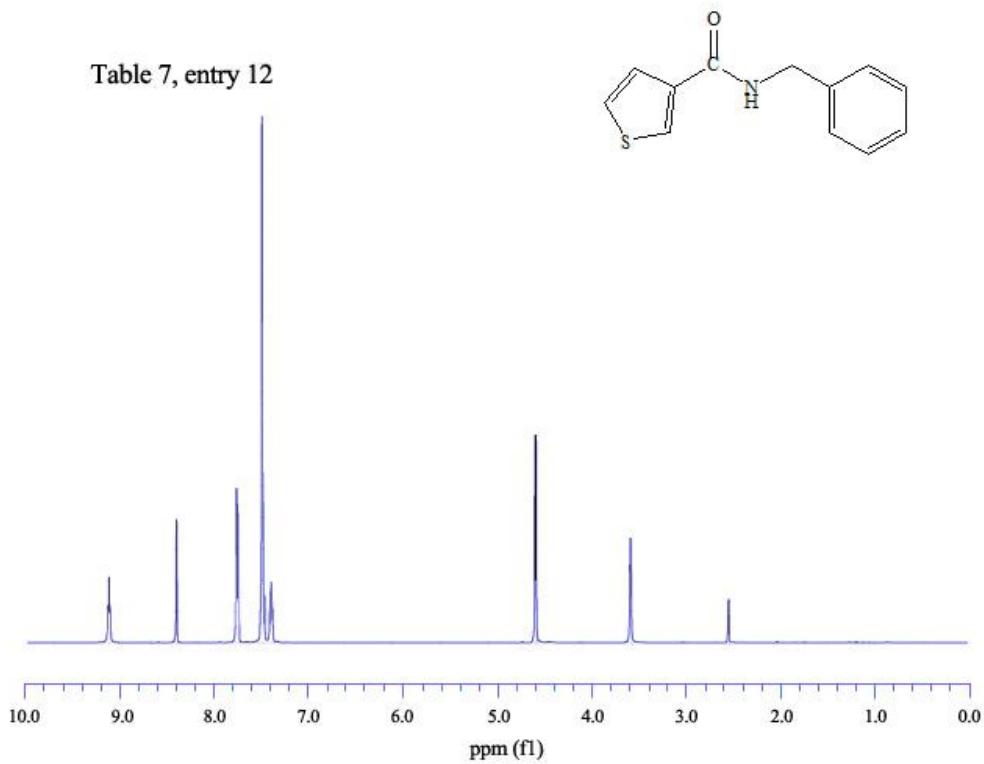


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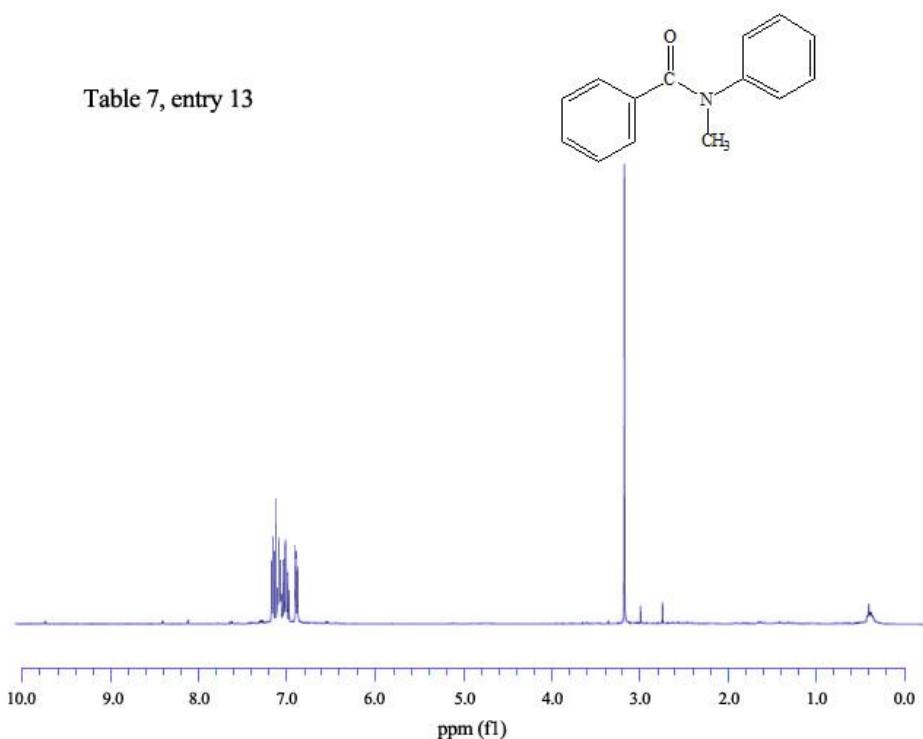


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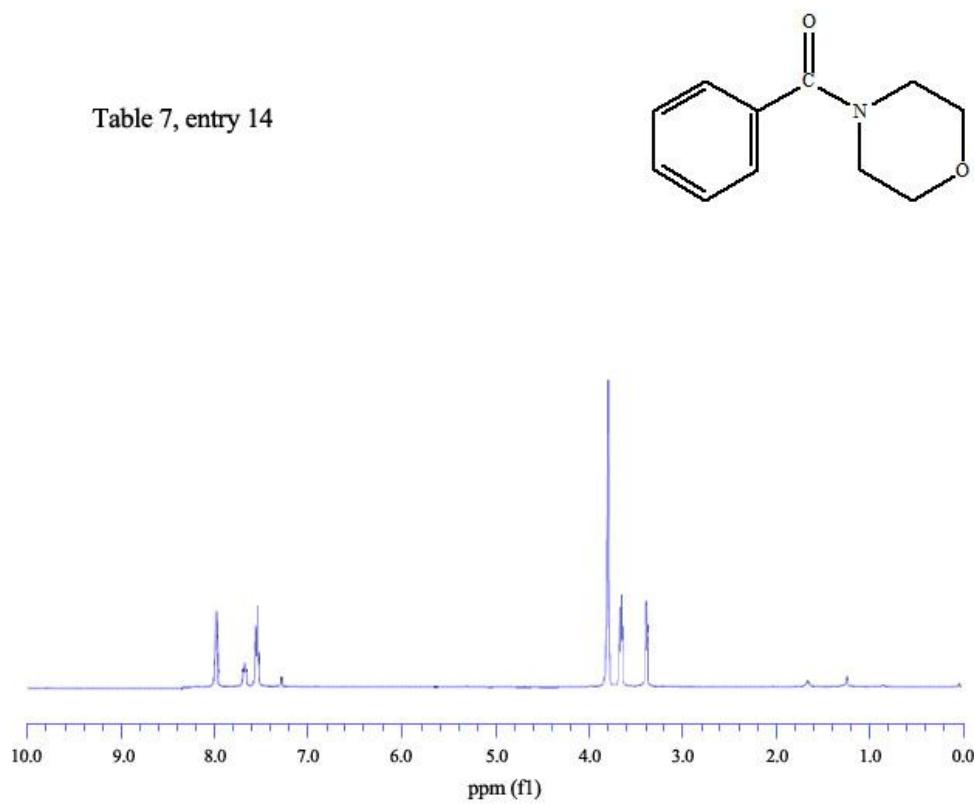


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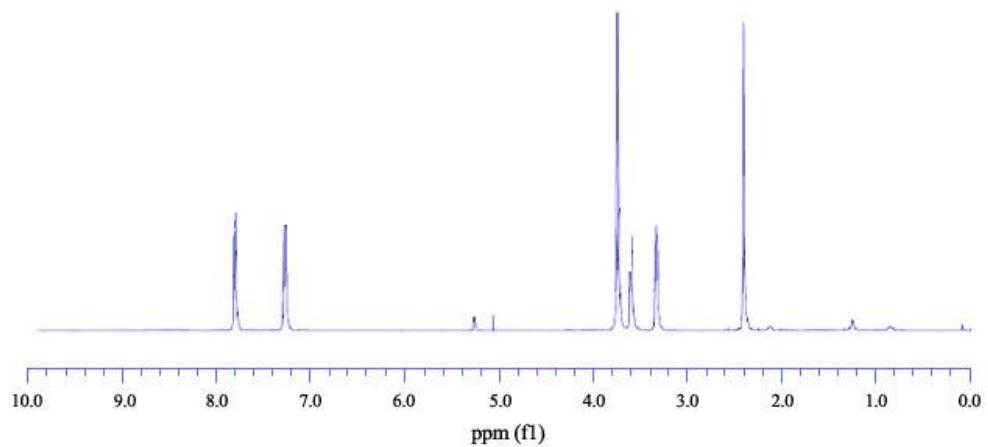
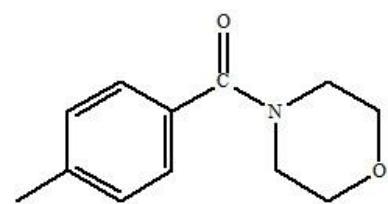


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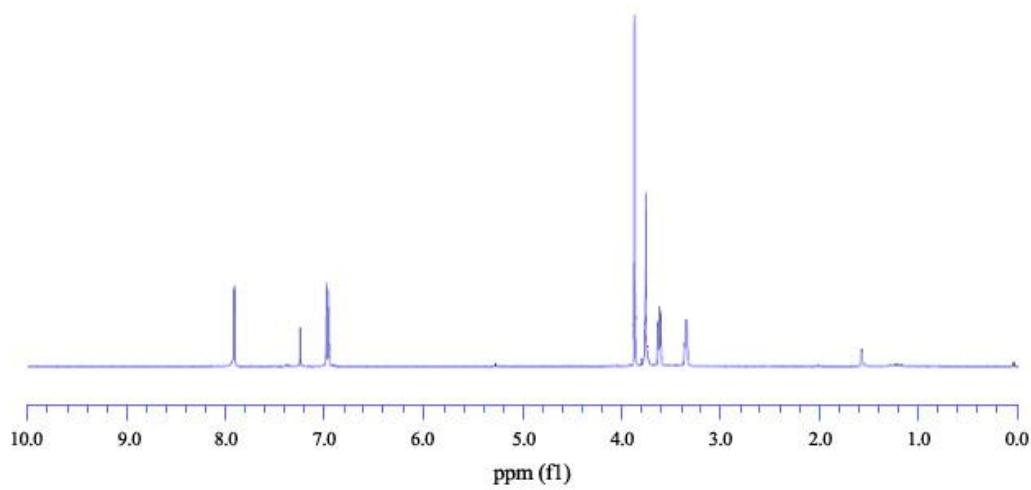
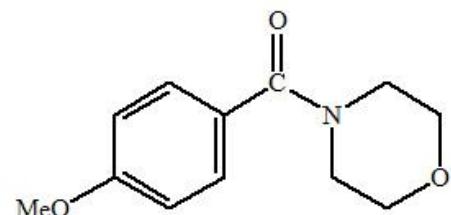
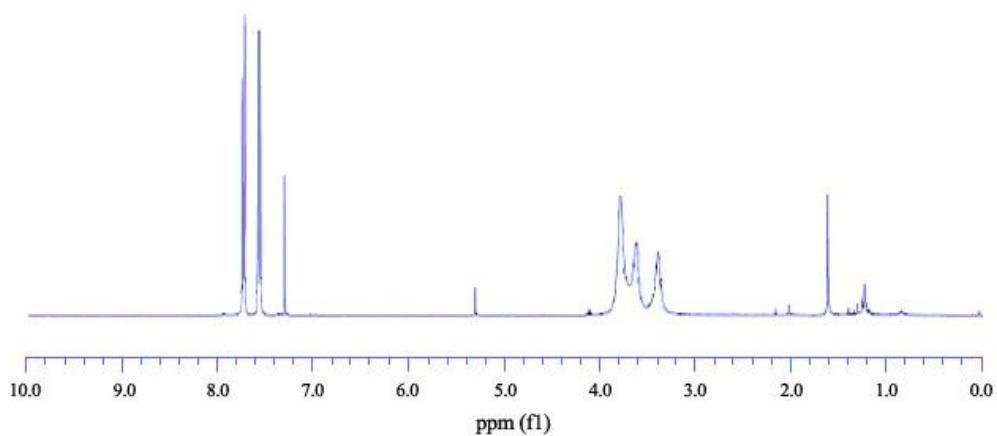
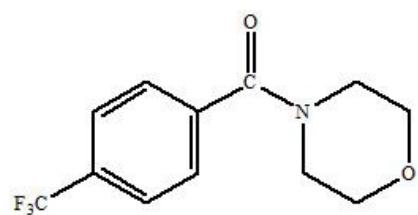


Table 7, entry 17



V.

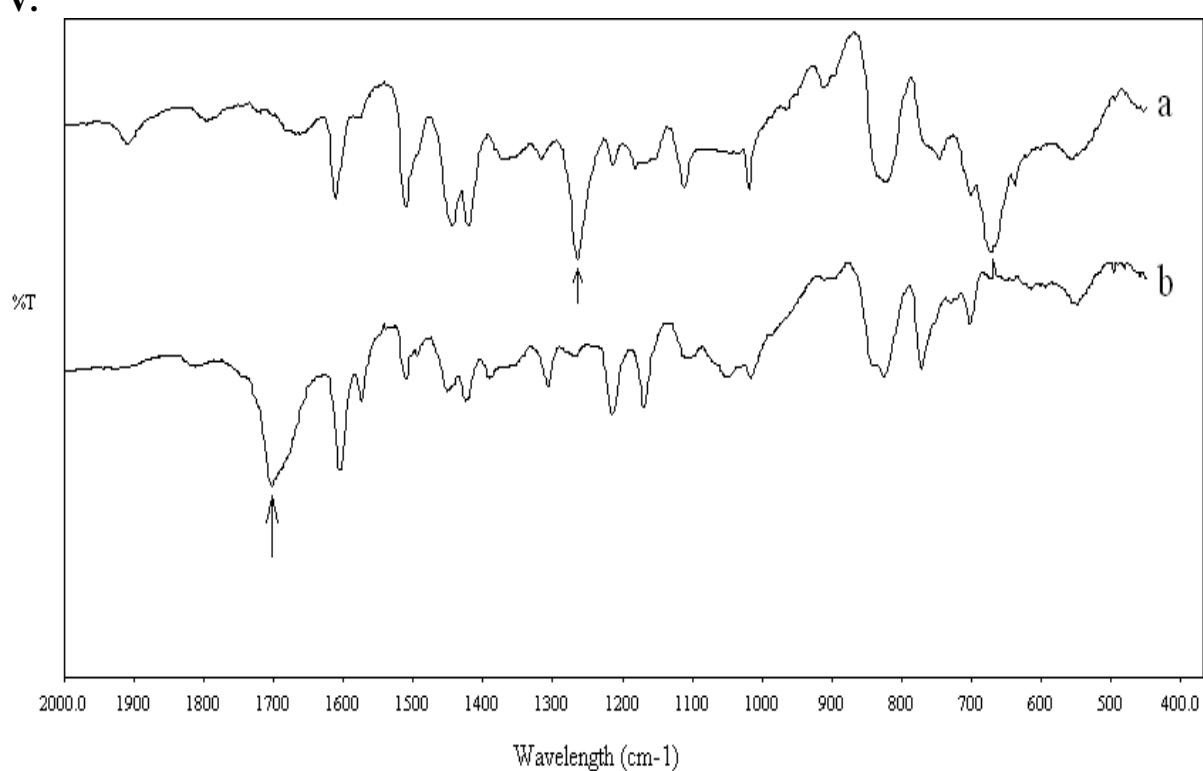


Fig. S1. FTIR spectra of chloromethylated polystyrene (a) and aldehyde functionalized polystyrene, PS-CHO (b)