Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

TBA-OH Catalysed 1,4-Addition of Hydroxide into α,β-Unsaturated Ketone by Microwave Irradiation in Water

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Contents

1. General

Flash column chromatography was performed using E. Merck 230-400 mesh silica gel and column chromatography was monitored by analytical thin-layer chromatography (TLC) carried out on 0.25 Merck silica gel plates (60F-254) using UV light as a visualizing agent, *p*-anisaldehyde and $KMnO_4$ solution as staining solutions, and heat as developing agent. Microwave experiments were performed in a CEM Discover instrument with appropriate internal IR temperature control using 10 mL Pyrex vials. The reaction temperature and microwave power were monitored by computer, and a 10 mL thick walled Pyrex reaction vessel with Teflon septa with a crimp top was used as a reaction vessel. Gas chromatographic analyses were performed on Agilent 7890A instrument with FID detector and an Agilent HP-5 capillary column. Mass chromatography analyses were performed on Agilent 5975C instrument and an Agilent HP-5MS column. IR spectra were recorded using a Bruker Vertex 70 FT-IR spectrometer. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker Advance II/DPX 400(400 MHz ^{1}H, 100 MHz ^{13}C) spectrometers with chemical shifts reported relative to residual deuterated solvent peaks. ^{1}H NMR spectra were referenced to $CDCl_3$ (for ^{1}H, δ = 7.26) as internal standard, and are reported as follows: chemical shift multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). ^{13}C NMR spectra were referenced to the residual $CDCl_3$ (for ^{13}C, δ = 77.26) as internal standard]. High-resolution Mass spectra were provided by YCRF Yonsei university.

2. Materials

Most commercially available reagent grade chemicals [**1a-h**, **5**, **8a-c**, **9a-c**, NaOH, tetrabutylammonium hydroxide (TBA-OH), tetrabutyl ammonium chloride (TBA-Cl), K_2CO_3, amberlyst A26, HCl, moecular sieve, phosphotungstic acid, amberlyst 16, $AlCl_3$ and MeOH] were purchased from Aldrich Chemical Company, TCI, and Burdick and Jackson, and used as received without further purification unless otherwise stated.

3. Experimental

A. Microwave-assisted C-C double bond cleavage of various α,β-unsaturated compounds by TBA-OH catalyst in water (Table 2)

- C-C double bond cleavage of 3-(anthracen-9-yl)acrylaldehyde (1a) by TBA-OH (entry 1): To a 10 ml microwave vessel was added 3-(anthracen-9-yl)acrylaldehyde (**1a**, 92.9 mg, 0.40 mmol), TBA-OH (64.0 mg, 0.08 mmol) and H_2O (400 mg, 22.2 mmol). The mixture was heated at 150 ^oC for 10 min with stirring under microwave irradiation. After cooling the vessel to room temperature, the crude mixture was purified by column chromatography (*n*-hexane:ethyl acetate = 5:1) on silica gel to give anthracene-9-carbaldehyde (**3a**, 76.6 mg, 93 %) as a pale yellow powder.

B. A typical procedure for the formation of benzimidazole derivatives via trapping of aldehyde (Table 3)

- Formation of 2-methyl-benzimidazole (6a) and 2-(anthracen-9-yl)benzimidazole (7a) from 3-(anthracen-9-yl)acrylaldehyde (1a) with benzene-1,2-diamine (5) (entry 1): To a 10 ml microwave vessel was added 3-(anthracen-9-yl)acrylaldehyde (**1a**, 92.9 mg, 0.40 mmol), benzene-1,2-diamine (**5**, 95.2 mg, 0.88 mmol), TBA-OH (64.0 mg, 0.08 mmol) and H_2O (400 mg, 22.2 mmol). The mixture was heated at 150 ^oC for 10 min with stirring under microwave irradiation. After cooling the vessel to room temperature, the crude mixture was purified by column chromatography (*n*-hexane:ethyl acetate = 5:1) on silica gel to give 2-methyl-benzimidazole (**6a**, 32.7 mg, 62%) and 2-(anthracen-9-yl)benzimidazole (**7a**, 68.2 mg, 58%).

C. A typical procedure for the formation of multi-substituted phenol from alkyne and diketone with base catalyst (Table 4)

- Formation of (3-hydroxy-5-methyl-[1,1'-biphenyl]-2-yl)phenylmethanone (10a) from 4-phenylbut-3-yn-2-one (8a) and 1-phenylbutane-1,3-dione (9a) (entry 1): To a 10 ml microwave vessel was added (3-hydroxy-5-methyl-[1,1'-biphenyl]-2-yl)phenylmethanone (**8a**, 57.6 mg, 0.40 mmol), 1-phenylbutane-1,3-dione (**9a**, 71.3 mg, 0.44 mmol), TBA-OH (64.0 mg, 0.08 mmol) and H_2O (400 mg, 22.2 mmol). The mixture was heated at 100 ^oC for 10 min with stirring under microwave irradiation. After cooling the vessel to room temperature, the crude mixture was purified by column chromatography (*n*-hexane:ethyl acetate = 5:1) on silica gel to give (3-hydroxy-5-methyl-

[1,1'-biphenyl]-2-yl)phenylmethanone (**10a**, 103.7 mg, 90%).

D. Characterization data (2b, 2c, 3a-3d, 4a-4c, 6a-6c, 7a, 7b, 10a-10g)

Acetophenone (2b) [CAS No. 98-86-2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.96 (m, 2H), 7.53-7.58 (m, 1H), 7.44-7.47 (m, 2H), 2.60 (s, 3H).

1-(4-Methoxyphenyl)ethanone (2c) [CAS No. 100-06-1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.55 (s, 3H).

Anthracene-9-carbaldehyde (3a) [CAS No. 642-31-9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J* = 8.8 Hz, 2H), 8.65 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.66 (t, *J* = 6.8 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H).

6-Methylhept-5-en-2-one (3b) [CAS No. 110-93-8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.06 (t, *J* = 7.2 Hz, 1H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.29-2.24 (m, 2H), 2.14 (s, 3H), 1.68 (s, 6H).

Benzaldehyde (3c) [CAS No. 100-52-7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.0 (s, 1H), 7.87 (d, *J* = 6.8 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H).

4-Methoxybenzaldehyde (3d) [CAS No. 123-11-5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.82 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H).

1,3,5-Triphenylpentane-1,5-dione (4a) [CAS No. 6263-84-9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.92 (m, 4H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.42-7.38 (m, 4H), 7.30-7.23 (m, 4H), 7.18-7.14 (m, 1H), 4.12-4.05 (m, 1H), 3.48 (dd, *J* = 16.8 Hz, *J* = 6.8 Hz, 2H), 3.35 (dd, *J* = 16.4 Hz, *J* = 6.8 Hz, 2H).

3-(4-Methoxyphenyl)-1,5-diphenylpentane-1,5-dione (4b) [CAS No. 39659-76-2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.93 (m, 4H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.45-7.41 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.04-4.01 (m, 1H), 3.73 (s, 3H), 3.47 (dd, *J* = 16.4 Hz, *J* = 6.8 Hz, 2H), 3.31 (dd, *J* = 16.4 Hz, *J* = 7.2 Hz, 2H).

1,5-bis(4-Methoxyphenyl)-3-phenylpentane-1,5-dione (4c) [CAS No. 82672-13-7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.93 (m, 4H), 7.27-7.26 (m, 4H), 7.19-7.14 (m, 1H), 6.92-6.89 (m, 4H), 4.05-4.02 (m, 1H), 3.84 (s, 6H), 3.43 (dd, *J* = 16.0 Hz, *J* = 6.8 Hz, 2H), 3.27 (dd, *J* = 16.0 Hz, *J* = 6.8 Hz, 2H).

2-methyl-benzimidazole (6a) [CAS No. 615-15-6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.94 (s, 1H), 7.51 (dd, *J* = 5.6 Hz, *J* = 3.2 Hz, 2H), 7.18 (dd, *J* = 5.6 Hz, *J* = 2.8 Hz, 2H), 2.58 (s, 3H).

2-Ethyl-benzimidazole (6b) [CAS No. 1848-84-6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.49 (s, 1H), 7.57 (dd, *J* = 4.9 Hz, *J* = 3.0 Hz, 2H), 7.21 (dd, *J* = 5.3 Hz, *J* = 3.0 Hz, 2H), 3.03 (q, *J* = 7.5 Hz, 2H), 1.45 (t, *J* = 7.6 Hz, 3H).

2-Hexyl-benzimidazole (6c) [CAS No. 5851-48-9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.82 (s, 1H), 7.77 (dd, *J* = 6.0 Hz, *J* = 3.2 Hz, 2H), 7.37 (dd, *J* = 6.0 Hz, *J* = 3.2 Hz, 2H), 3.25 (t, *J* = 7.6 Hz, 2H), 2.00-1.94 (m, 2H), 1.36-1.21 (m, 6H), 0.78 (t, *J* = 7.2 Hz, 3H).

2-(Anthracen-9-yl)benzimidazole (7a) [CAS No. 81410-32-4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57

(s, 1H), 8.63 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.44-7.35 (m, 6H), 7.16 (d, *J* = 7.6 Hz, 2H).

2-Phenyl-benzimidazole (7b) [CAS No. 716-79-0] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 2H), 7.65 (s, 1H), 7.52-7.47 (m, 3H), 7.30-7.26 (m, 3H).

(3-Hydroxy-5-methyl-[1,1'-biphenyl]-2-yl)phenylmethanone (10a) [CAS No. 1470369-40-4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.17-7.11 (m, 3H), 7.06-6.97 (m, 5H), 6.92 (s, 1H), 6.80 (s, 1H), 2.43 (s, 3H).

1-(3-Hydroxy-5-methyl-[1,1'-biphenyl]-2-yl)ethanone (10b) [CAS No. 65053-04-5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.67 (s, 1H), 7.58 (d, *J* = 6.8 Hz, 2H), 7.44-7.37 (m, 3H), 7.06 (s, 1H), 6.94 (s, 1H), 2.65 (s, 3H), 2.62 (s, 3H).

(5'-Hydroxy-[1,1':3',1''-terphenyl]-2'-yl)phenylmethanone (10c) ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.42-7.39 (m, 3H), 7.34 (d, *J* = 1.6 Hz, 1H), 7.23 (d, *J* = 1.6 Hz, 1H), 7.21-7.17 (m, 3H), 7.08-6.98 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 160.5, 146.5, 145.1, 141.1, 139.8, 139.4, 132.2, 129.9, 129.6, 129.2, 128.7, 128.3, 127.9, 127.7, 127.5, 121.3, 120.0, 114.9; IR spectrum (CH_2Cl_2) 3331, 3082, 3060, 3030, 1735, 1669, 1623, 1440, 1401, 1268, 949 cm-1; HR-MS(ESI) calcd for $C_{25}H_{19}O_2^+$ $[M+H]^+$ 351.1380; found 351.1377.

(5'-Hydroxy-[1,1':3',1''-terphenyl]-4'-yl)phenylmethanone (10d) [CAS No. 7593-13-7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.42-7.40 (m, 3H), 7.34 (d, *J* = 1.6 Hz, 1H), 7.23 (d, *J* = 1.2 Hz, 1H), 7.20-7.18 (m, 3H), 7.08-6.98 (m, 5H).

1-(5'-Hydroxy-[1,1':3',1''-terphenyl]-4'-yl)ethanone (10e) [CAS No. 51522-45-3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.97 (s, 1H), 7.99 (d, *J* = 6.8 Hz, 2H), 7.55-7.37 (m, 8H), 7.24 (s, 1H), 6.86 (s, 1H), 1.87 (s, 3H).

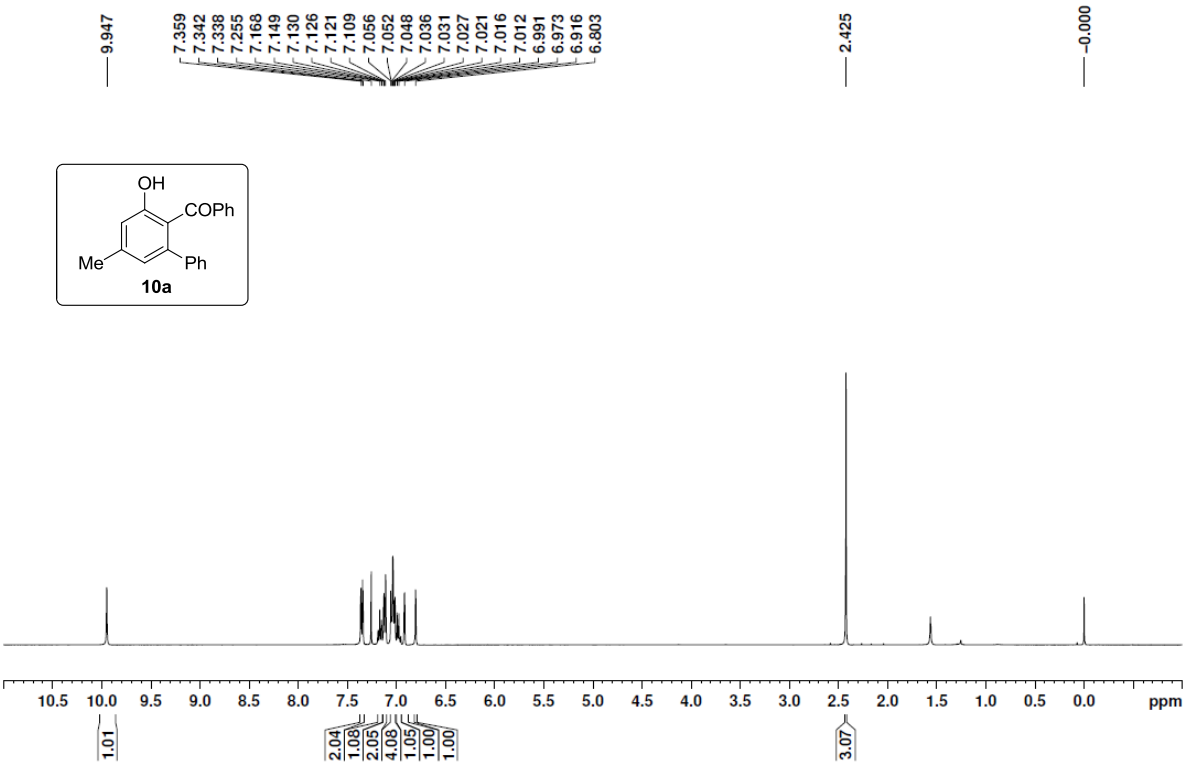
(3-Butyl-5-hydroxy-[1,1'-biphenyl]-4-yl)phenylmethanone (10f) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.76 (d, *J* = 6.8 Hz, 2H), 7.64-7.56 (m, 3H), 7.46 (t, *J* = 8.0 Hz, 4H), 7.41-7.37 (m, 1H),

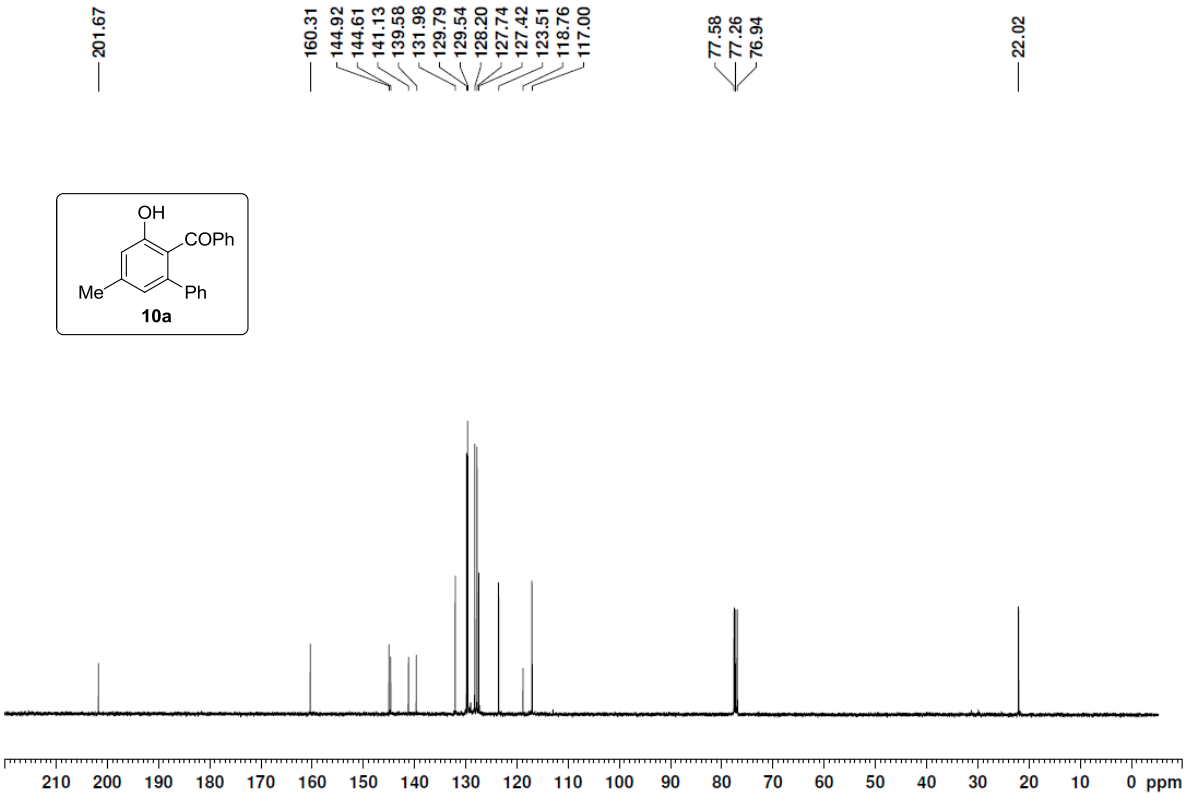
7.11 (d, *J* = 1.6 Hz, 1H), 7.05 (d, *J* = 1.6 Hz, 1H), 2.37 (t, *J* = 7.6 Hz, 2H), 1.42-1.35 (m, 2H), 1.09-1.00 (m, 2H), 0.70 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 158.1, 145.8, 144.5, 140.1, 139.8, 133.3, 129.4, 129.1, 128.8, 128.4, 127.4, 122.4, 120.9, 113.4, 34.9, 34.2, 22.6, 13.8; IR spectrum (CH_2Cl_2) 3403, 3061, 3033, 2927, 1668, 1450, 1407, 1268, 1001 cm-1; HR-MS(ESI) calcd for $C_{23}H_{23}O_2^+$ $[M+H]^+$ 331.1693; found 331.1690.

1-(3-Butyl-5-hydroxy-[1,1'-biphenyl]-4-yl)ethanone (10g) ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.8 (s, 1H), 7.62 (d, *J* = 1.6 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.41-7.37 (m, 1H), 7.07 (d, *J* = 2.0 Hz, 1H), 7.00 (d, *J* = 1.6 Hz, 1H), 2.95 (t, *J* = 8.0 Hz, 2H), 2.71 (s, 3H), 1.68-1.60 (m, 2H), 1.47-1.38 (m, 2H), 0.96 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 162.4, 147.1, 145.1, 139.7, 129.1, 128.7, 127.4, 121.3, 120.8, 114.5, 36.2, 34.9, 32.7, 23.1, 14.1; IR spectrum (CH_2Cl_2) 3363, 2957, 2929, 2870, 1682, 1622, 1554, 1405, 1358, 1263, 1209, 1028 cm-1; HR-MS(ESI) calcd for $C_{18}H_{21}O_2^+$ $[M+H]^+$ 269.1536; found 269.1533.

(3-butoxy-5-methyl-[1,1'-biphenyl]-2-yl)phenylmethanone (11a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.3 (t, *J* = 7.6 Hz, 2H), 7.26-7.24 (m, 2H), 7.21-7.16 (m, 3H), 6.85 (s, 1H), 6.77 (s, 1H), 3.89 (t, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 1.49-1.42 (m, 2H), 1.11-0.97 (m, 2H), 0.72 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 156.8, 141.8, 140.6, 140.2, 138.8, 132.8, 129.4, 129.1, 128.3, 128.2, 127.4, 126.1, 123.2, 111.7, 68.3, 31.1, 22.0, 19.0, 13.8; IR spectrum (CH_2Cl_2) 3083, 3060, 3029, 2958, 2933, 2872, 1668, 1602, 1568, 1449, 927 cm-1; HR-MS(ESI) calcd for $C_{24}H_{25}O_2^+$ $[M+H]^+$ 345.1849; found 345.1948.

^{1}H and ^{13}C NMR spectra of new compounds





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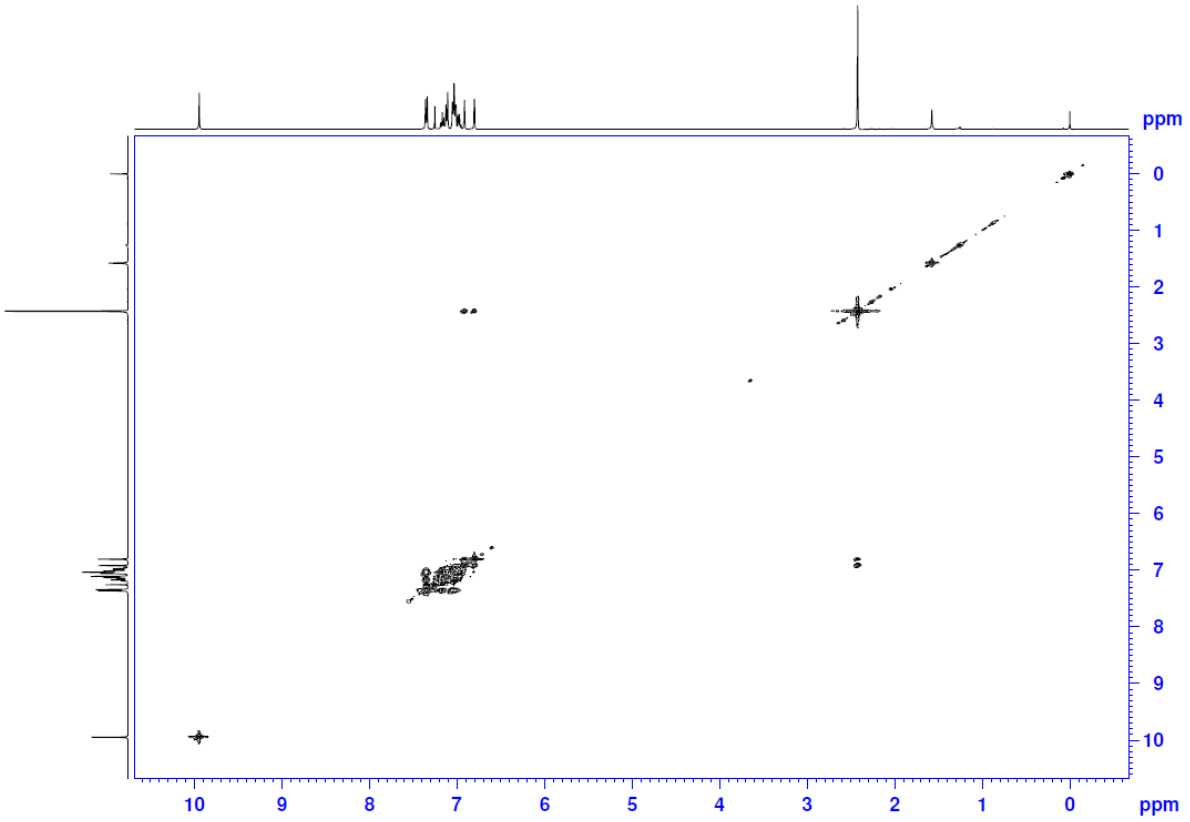

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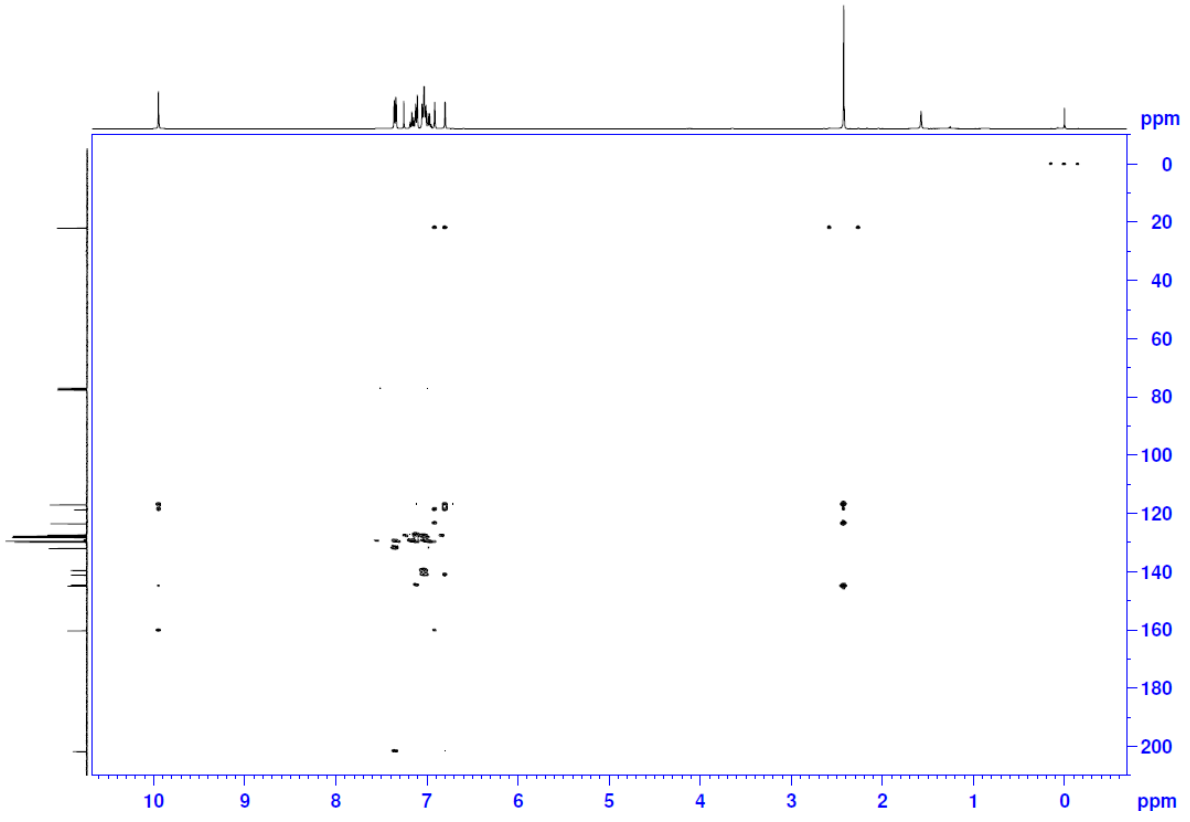

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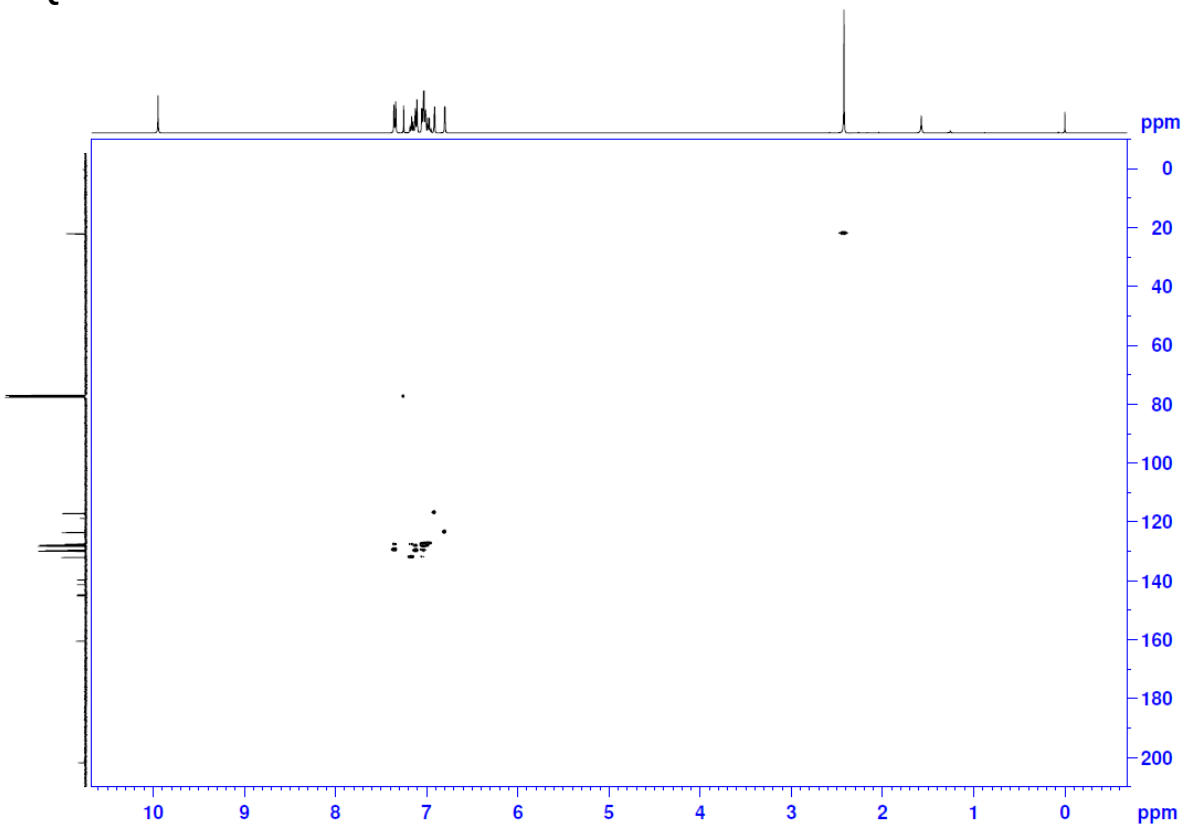

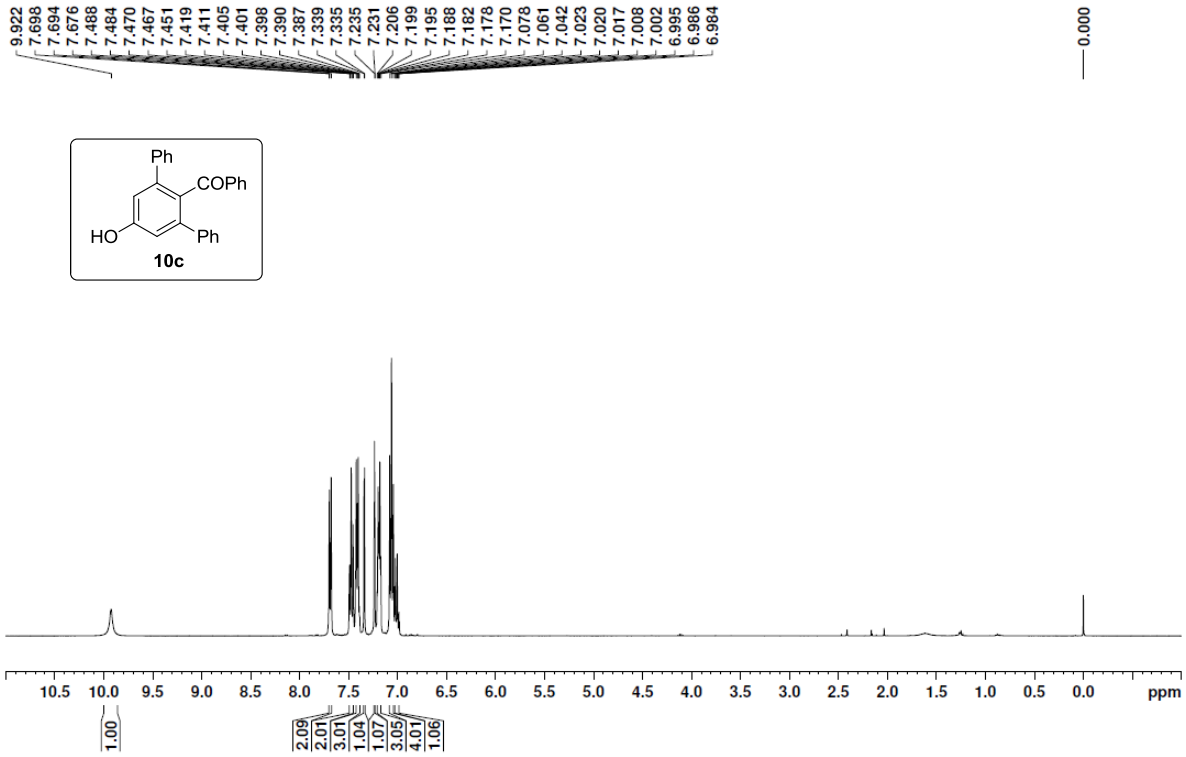
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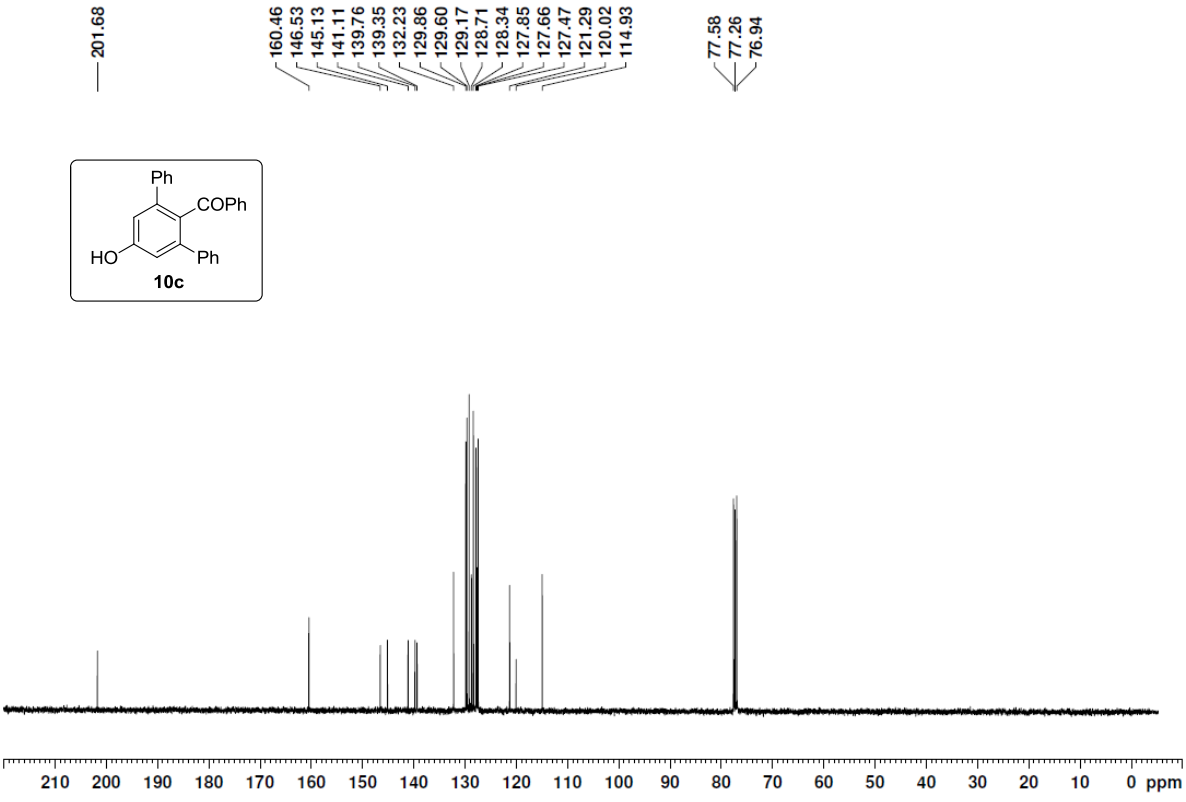
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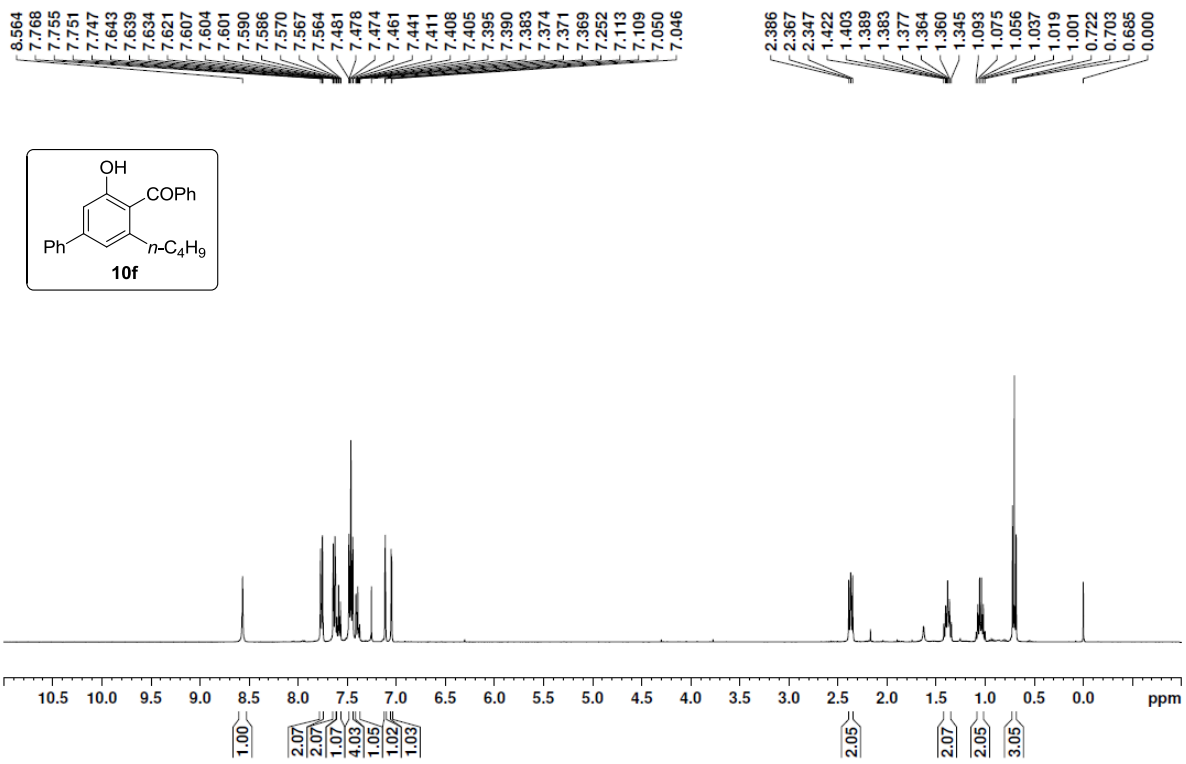
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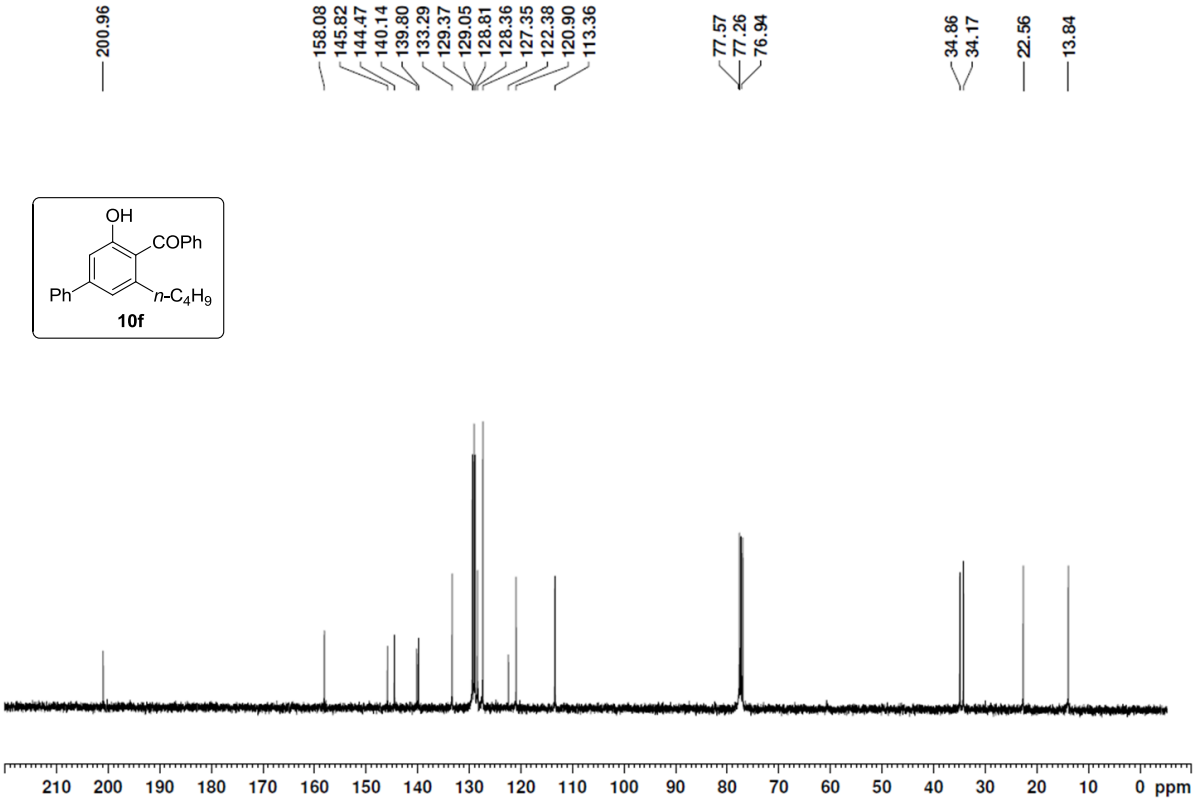
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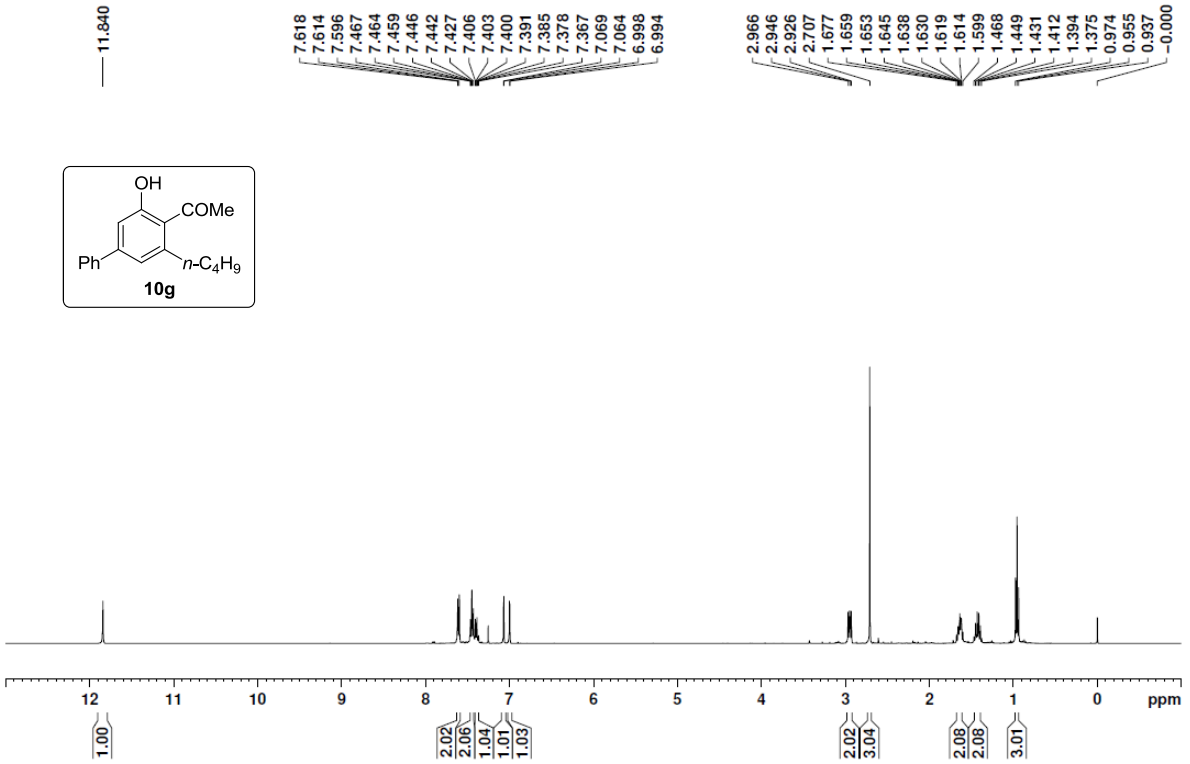
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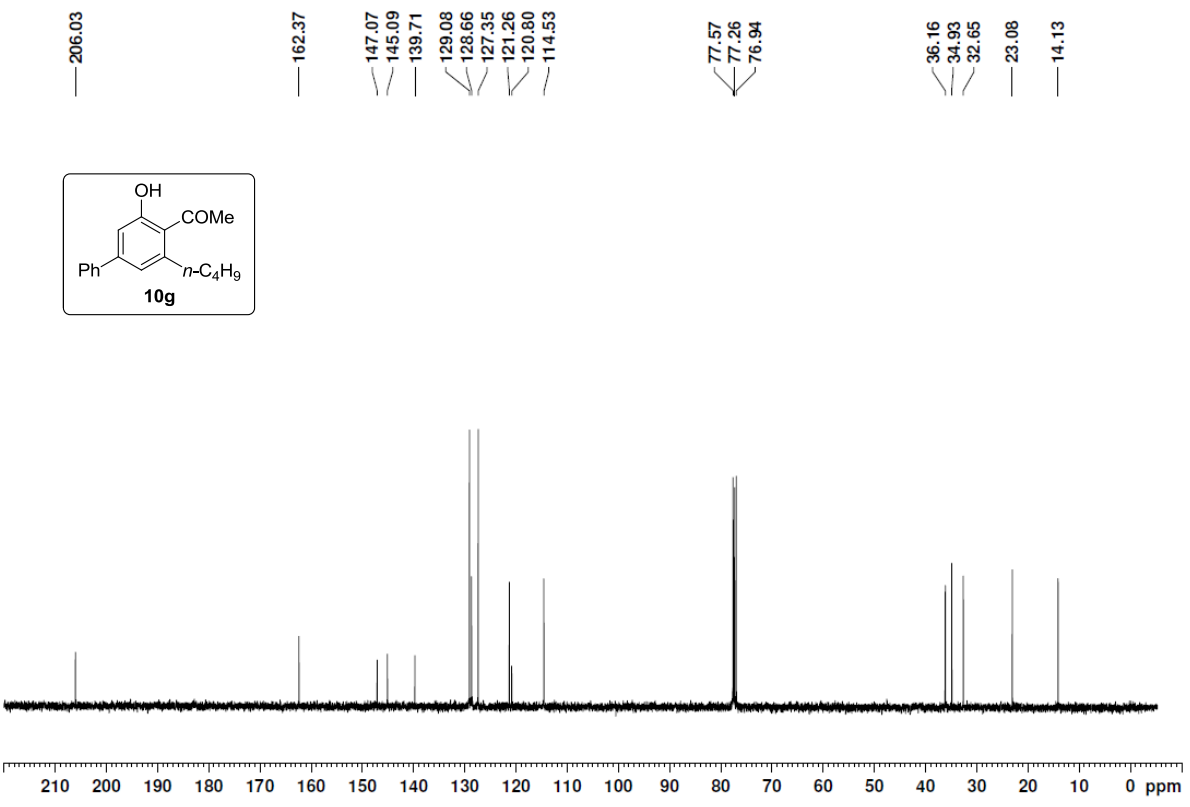
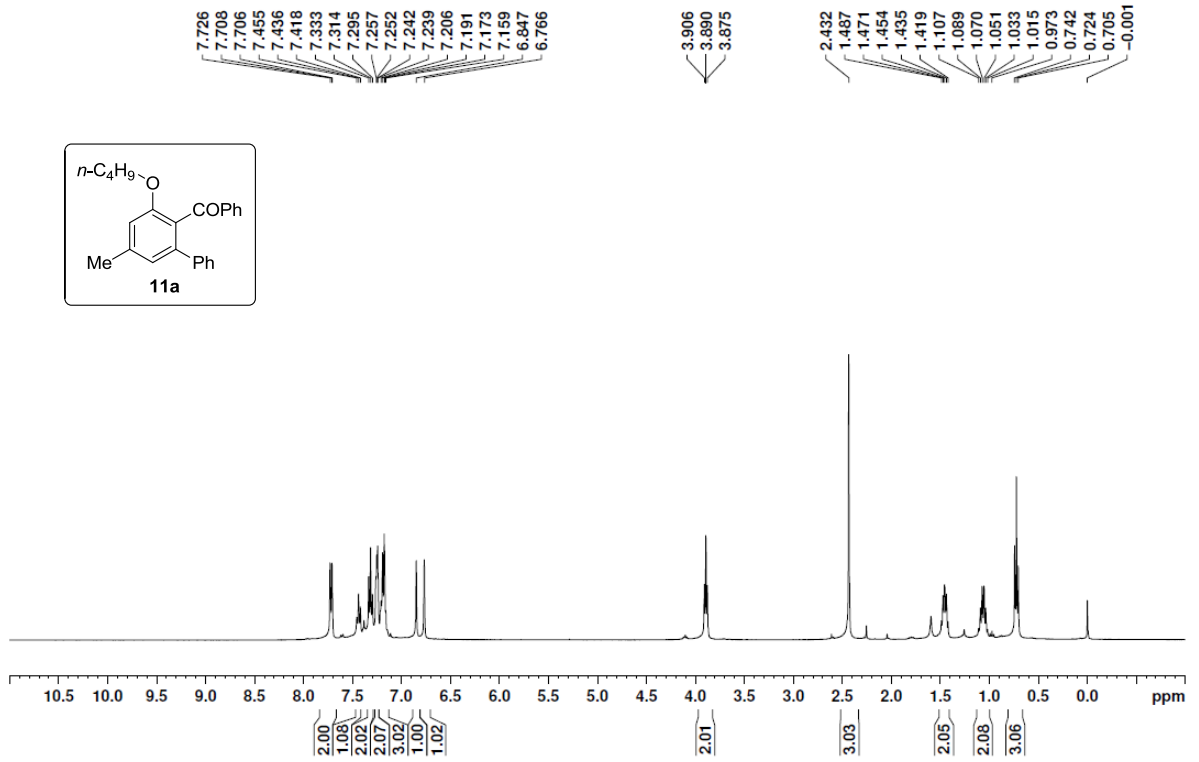
3.01


206.03
162.37
147.07
145.09
139.71
129.08
128.66
127.35
121.26
120.80
114.53
77.57
77.26
76.94
36.16
34.93
32.65
23.08
14.13
OH
COMe
Ph
n-C4H9
10g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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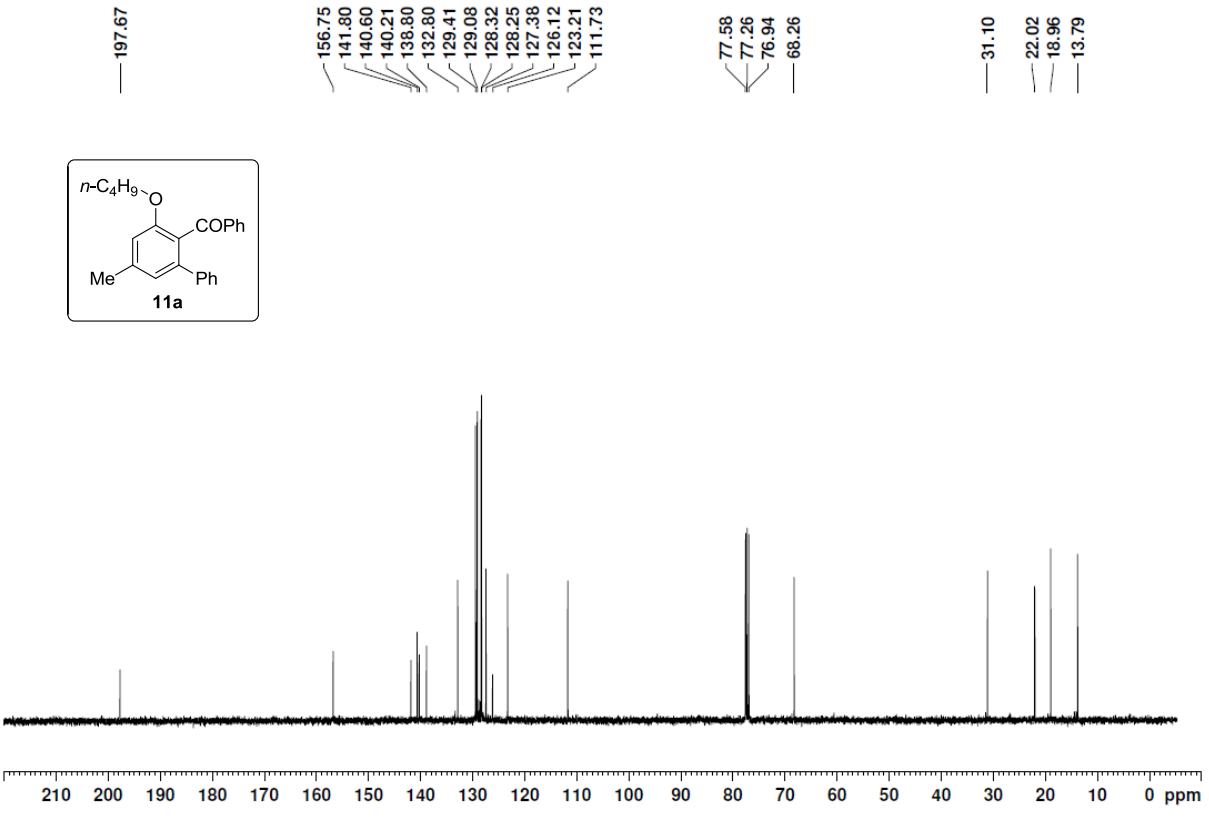
7.708
7.706
7.455
7.436
7.418
7.333
7.314
7.295
7.257
7.252
7.242
7.239
7.206
7.191
7.173
7.159
6.847
6.766
3.906
3.890
3.875
2.432
1.487
1.471
1.454
1.435
1.419
1.107
1.089
1.070
1.051
1.033
1.015
0.973
0.742
0.724
0.705
-0.001
n-C4H9
O
COPh
Me
Ph
11a
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
1.08
2.02
2.07
3.02
1.00
1.02
2.01
3.03
2.05
2.08
3.06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141.80
140.60
140.21
138.80
132.80
129.41
129.08
128.32
128.25
127.38
126.12
123.21
111.73
77.58
77.26
76.94
68.26
31.10
22.02
18.96
13.79
n-C4H9
O
COPh
Me
Ph
11a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm