Supporting Information

Site-selective Phenol Acylation Mediated by Thioacids via Visible Light Photoredox Catalysis

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Abbreviations

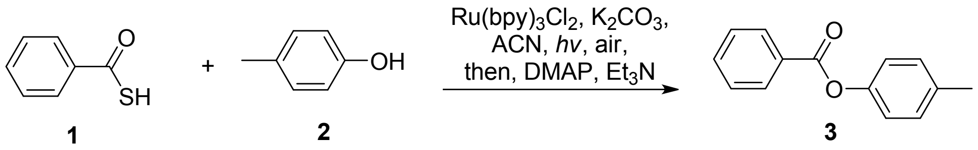
Ac	Acetyl
ACN	Acetonitrile
DMAP	*N*,*N*-Dimethyl-4-aminopyridine
DCE	1,2-Dichloroethane
DMSO	Dimethylsulfoxide
DCM	Dichloromethane
THF	Tetrahydrofuran
DMF	N,N-Dimethylformamide
NMR	Nuclear magnetic resonance
rt	Room temperature
TLC	Thin layer chromatography

General Information:

All reactions were carried out under an air atmosphere with dry solvents unless otherwise noted. All of reagents were purchased at highly commercial quality and used without further purification. Thin-layer chromatography (TLC) was conducted with 0.25 mm Tsingdao silica gel plates (60F-254) and visualized by exposure to UV light (254 nm) or stained with potassium permanganate. Silica gel (ZCX-II, 200-300 mesh) used for flash column chromatography was purchased from Qing Dao Hai Yang Chemical Industry Co. of China. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brüker Advance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz). Chemical shifts reported in parts per million relative to $CDCl_3$ (^{1}H NMR; 7.27 ppm, ^{13}C NMR; 77.00 ppm), CD_3OD (^{1}H NMR; 3.33 ppm, ^{13}C NMR; 47.60 ppm), and CD_3COCD_3 (^{1}H NMR; 2.88 ppm, ^{13}C NMR; 28.96 ppm). Acetonitrile (ACN) was distilled from calcium hydride. Yields referred to chromatographically purified products unless otherwise stated. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

For the preparation of thioacids, see reference 1.

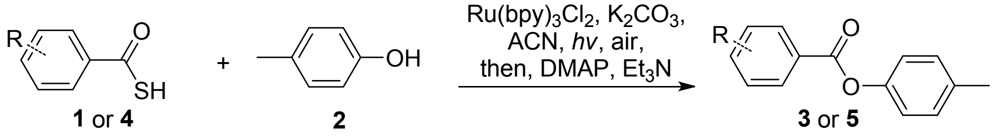
Control experiments



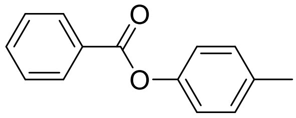
Entry	CFL intensity (W)	Time (h)	Yield (%)
1	darkness	3	<10
2	5	24	40
3	15	10	72
4	30	6	87
5	45	3	86
6	60	3	81

The effect of the intensity of the compact fluorescent lamp (CFL) was tested on phenol acylation between thioacid **1** and 4-methylphenol **2**. Low intensity (entry 2) led to only 40% yield of product after 24 h irradiation. Exposure to a 15 W CFL (entry 3) increased the yield to 72% within 10 h. Higher intensity showed progress both in reaction yield as well as efficiency (entry 4). A high-yielding (86%) acylation scenario was accessed just within 3 h when irradiated by a 45 W CFL (entry 5). Further increasing the intensity to 60 W reduced the reaction yield (entry 6). Thus, the optimized CFL intensity was 45 W for an overall consideration.

General procedure for visible light mediated phenol acylation A



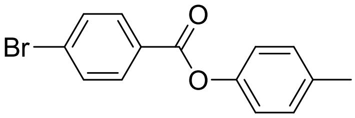
A flame-dried 10 mL flask was charged with thioacid **1** or **4** (1.0 mmol) and ACN (5 mL). $Ru(bpy)_3Cl_2\cdot 6H_2O$ (0.01 mmol, 7.5 mg) and K_2CO_3 (0.1 mmol, 13.8 mg) was added to the mixture. The mixture was allowed to stir at room temperature in the open air, and was irradiated with a 45 W household bulb for 1.5-3 h. Then phenol **2** (0.5 mmol, 54 mg), Et_3N (1.0 mmol, 101 mg) and DMAP (0.1 mmol, 12 mg) was added to the above mixture sequentially. Stirring for another 10 mins, and then the mixture was poured into water (10 mL), extracted with EtOAc (4 x 10 mL), washed with brine (15 mL), and dried over Na_2SO_4. The crude organic phase was concentrated in vacuo and purified with a short flash column chromatography (silica gel, hexane/EtOAc = 20:1) to afford the corresponding product **3** or **5**.



3

p-tolyl benzoate 3[2]

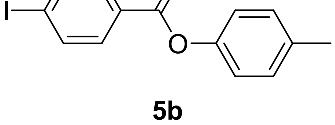
Following the typical procedure, **3** was obtained in 86% yield (91.2 mg) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.25 (dd, J = 8.3, 1.2 Hz, 2H), 7.66 (m, 1H), 7.54 (m, 2H), 7.26 (d, J = 8.2 Hz, 2H), 7.14 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.3, 148.7, 135.4, 133.4, 130.1, 130.0, 129.9, 128.5, 121.3, 20.8.



5a

p-tolyl-4-bromobenzoate 5a[2]

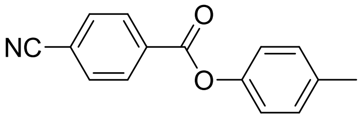
Following the typical procedure, **5a** was obtained in 92% yield (133.9 mg) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.08 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.5 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.7, 148.5, 135.7, 131.9, 131.6, 130.1, 128.7, 128.6, 121.3, 20.9.



5b

p-tolyl-4-iodobenzoate 5b[3]

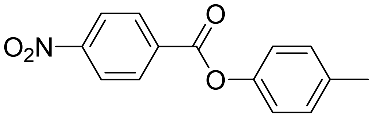
Following the typical procedure, **5b** was obtained in 89% yield (150.5 mg) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (m, 4H), 7.25 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.5 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.3, 148.9, 138.3, 136.1, 131.9, 130.5, 129.6, 121.7, 101.9, 21.3.



5c

p-tolyl-4-cyanobenzoate 5c[4]

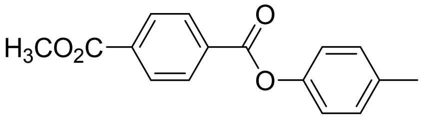
Following the typical procedure, **5c** was obtained in 93% yield (110.3 mg) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.3 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 7.35-7.22 (m, 2H), 7.12 (d, J = 8.5 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.8, 148.3, 136.1, 133.6, 132.4, 130.6, 130.2, 121.1, 117.9, 116.9, 20.9.



5d

p-tolyl-4-nitrobenzoate 5d[5]

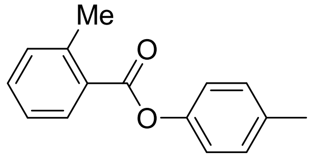
Following the typical procedure, **5d** was obtained in 85% yield (109.3 mg) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.47-8.29 (m, 4H), 7.27 (m, 2H), 7.14 (d, J = 8.5 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.5, 150.9, 148.3, 136.1, 135.1, 131.3, 130.2, 123.7, 121.1, 20.9.



5e

methyl p-tolyl terephthalate 5e[6]

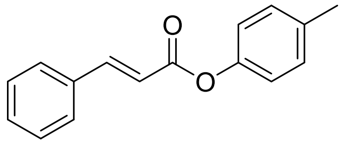
Following the typical procedure, **5e** was obtained in 76% yield (102.7 mg) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.30 (m, 2H), 8.19 (m, 2H), 7.26 (d, J = 8.2 Hz, 2H), 7.14 (m, 2H), 3.99 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.2, 164.6, 148.5, 135.8, 134.4, 133.5, 130.1, 130.1, 129.7, 121.2, 52.5, 20.9.



5f

***p-tolyl-2-methylbenzoate 5f*[7]**

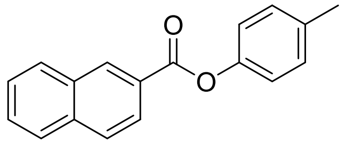
Following the typical procedure, **5f** was obtained in 88% yield (99.6 mg) as yellow oil. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.25 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.54 (m, 1H), 7.39 (ddd, *J* = 9.2, 7.6, 1.4 Hz, 2H), 7.29 (m, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 2.77 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 166.1, 148.8, 141.3, 135.5, 132.7, 132.0, 131.2, 130.1, 128.8, 126.0, 121.6, 22.0, 20.9.



5g

***p-tolyl cinnamate 5g*[8]**

Following the typical procedure, **5g** was obtained in 87% yield (103.6 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.93 (d, *J* = 16.0 Hz, 1H), 7.65 (m, 2H), 7.47 (m, 3H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.12 (m, 2H), 6.69 (d, *J* = 16.0 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 165.6, 148.6, 146.4, 135.4, 134.3, 130.7, 130.0, 129.0, 128.3, 121.4, 117.5, 20.9.



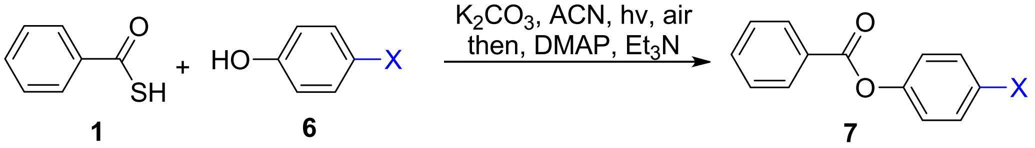
5h

***p-tolyl-2-naphthoate 5h*[9]**

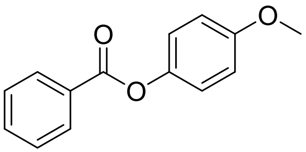
Following the typical procedure, **5h** was obtained in 96% yield (125.9 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.84 (m, 1H), 8.24 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.04 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.96 (m, 2H), 7.64 (m, 2H), 7.30 (m, 2H), 7.20 (d, *J* =

8.5 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.6, 148.8, 135.8, 135.6, 132.5, 131.9, 130.1, 129.5, 128.6, 128.4, 127.9, 126.9, 126.8, 125.5, 121.5, 20.9.

General procedure for visible light mediated phenol acylation reaction B.



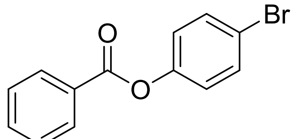
A flame-dried 10 mL flask was charged with thiobenzoic acid **1** (1.0 mmol, 138 mg) and ACN (5 mL). $Ru(bpy)_3Cl_2$•$6H_2O$ (0.01 mmol, 7.5 mg) and K_2CO_3 (0.1 mmol, 13.8 mg) was added to the mixture. The mixture was allowed to stir at room temperature in the open air, and was irradiated with a 45 W household bulb for 3 h. Then phenol **6** (0.5 mmol), Et_3N (1.0 mmol, 101 mg) and DMAP (0.1 mmol, 12 mg) was added to the above mixture sequentially. Stirring for another 10 mins, and then the mixture was poured into water (10 mL), extracted with EtOAc (4 x 10 mL), washed with brine (15 mL), and dried over Na_2SO_4. The crude organic phase was concentrated in vacuo and purified with a short flash column chromatography (silica gel, hexane/EtOAc = 20:1-5:1) to afford the corresponding product **7**



7a

4-methoxyphenyl benzoate 7a[2]

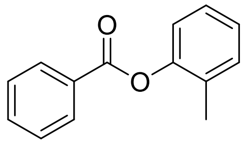
Following the typical procedure, **7a** was obtained in 92% yield (105.0 mg) as white solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.23 (dd, J = 8.3, 1.2 Hz, 2H), 7.65 (m, 1H), 7.53 (m, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.97 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): *δ* = 165.5, 157.3, 144.4, 133.5, 130.1, 129.7, 128.5, 122.4, 114.5, 55.6.



7b

4-bromophenyl benzoate 7b[10]

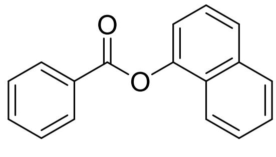
Following the typical procedure, **7b** was obtained in 90% yield (124.7 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): *δ* = 8.23 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.67 (m, 1H), 7.56 (m, 4H), 7.15 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): *δ* = 164.8, 150.0, 133.8, 132.5, 130.2, 129.2, 128.6, 128.6, 123.5, 119.0.



7c

2-methylphenyl benzoate 7c[2]

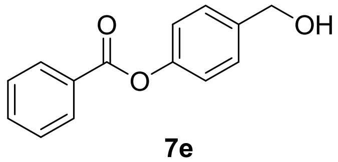
Following the typical procedure, **7c** was obtained in 84% yield (89.1 mg) as colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$): *δ* = 8.26 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.68 (m, 1H), 7.56 (dd, *J* = 11.0, 4.5 Hz, 2H), 7.32 (m, 2H), 7.21 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.18 (dd, *J* = 8.3, 1.0 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): *δ* = 164.9, 149.6, 133.6, 131.2, 130.9, 130.3, 130.2, 129.6, 128.9, 128.6, 127.0, 126.1, 122.0, 16.2.



7d

1-naphthyl benzoate 7d[10]

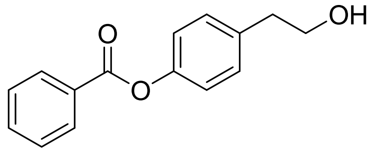
Following the typical procedure, **7d** was obtained in 93% yield (105.5 mg) as white solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.42 (m, 2H), 8.02 (m, 1H), 7.96 (m, 1H), 7.85 (dd, J = 8.3, 1.3 Hz, 1H), 7.74 (t, J = 7.5, 1H), 7.59 (m, 5H), 7.46 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ =165.2, 146.9, 134.8, 133.8, 130.3, 129.5, 128.8, 128.1, 127.1, 126.5, 126.5, 126.1, 125.5, 121.3, 118.3.



7e

***4-(hydroxymethyl)phenyl benzoate 7e*[8]**

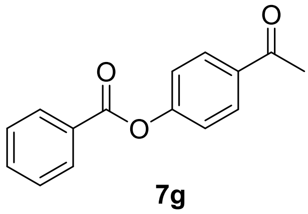
Following the typical procedure, **7e** was obtained in 87% yield (99.3 mg) as white solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.22 (m, 2H), 7.67 (m, 1H), 7.54 (t, J = 7.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.23 (m, 2H), 4.75 (d, J = 5.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.2, 150.4, 138.5, 133.6, 130.2, 129.5, 128.6, 128.1, 121.8, 64.8.



7f

***4-(2-hydroxyethyl)phenyl benzoate 7f*[8]**

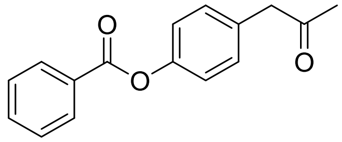
Following the typical procedure, **7f** was obtained in 83% yield (100.5 mg) as white solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.23 (dd, J = 8.5, 1.4 Hz, 2H), 7.66 (m, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.31 (m, 2H), 7.19 (d, J = 8.5 Hz, 2H), 3.91 (t, J = 6.5 Hz, 2H), 2.92 (t, J = 6.5Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.3, 149.6, 136.2, 133.6, 130.2, 130.1, 129.6, 128.6, 121.8, 63.6, 38.6.



7g

4-acetylphenyl benzoate 7g[8]

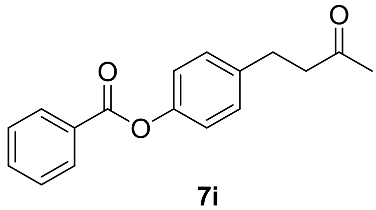
Following the typical procedure, **7g** was obtained in 97% yield (116.5 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.24 (dd, J = 8.3, 1.2 Hz, 2H), 8.09 (dd, J = 8.3, 1.2 Hz, 2H), 7.69 (m, 1H), 7.56 (m, 2H), 7.37 (m, 2H), 2.65 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 196.9, 164.6, 154.7, 134.8, 133.9, 130.3, 130.0, 129.0, 128.7, 121.9, 26.6.



7h

4-(2-oxopropyl)phenyl benzoate 7h[8]

Following the typical procedure, **7h** was obtained in 85% yield (108.1 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.23 (dd, J = 8.2, 1.0 Hz, 2H), 7.67 (m, 1H), 7.54 (dd, J = 8.5, 7.1 Hz, 2H), 7.31 (m, 2H), 7.22 (d, J = 8.6 Hz, 2H), 3.75 (s, 2H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 206.0, 165.1, 150.0, 133.6, 131.8, 130.4, 130.1, 129.5, 128.6, 122.0, 50.2, 29.3.

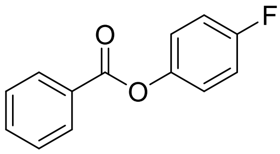


7i

4-(3-oxobutyl)phenyl benzoate 7i[11]

Following the typical procedure, **7i** was obtained in 92% yield (123.4 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.22 (m, 2H), 7.65 (d, J = 7.5 Hz, 1H), 7.53 (m, 2H), 7.28 (m, 2H), 7.15 (d, J = 8.5 Hz, 2H), 2.95 (t, J = 7.6, 7.6 Hz, 2H), 2.81 (t, J

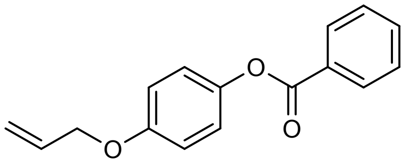
= 7.6 Hz, 2H), 2.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 207.7, 165.3, 149.2, 138.7, 133.6 130.2, 129.6, 129.4, 128.6, 121.7, 45.1, 30.1, 29.1.



7j

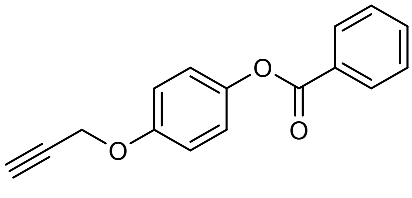
***4-fluorophenyl benzoate 7j*[2]**

Following the typical procedure, **7j** was obtained in 99% yield (132.8 mg) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.22 (dd, J = 8.3, 1.4 Hz, 2H), 7.68 (m, 1H), 7.54 (m, 2H), 7.21 (m, 2H), 7.14 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.2, 161.3, 159.3, 146.8, 146.8, 133.7, 130.2, 129.3, 128.6, 123.1, 123.1, 116.2, 116.0.



***4-(allyloxy)phenyl benzoate 7k*[12]**

Following the typical procedure, **7k** was obtained in 86% yield (109.3 mg) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.21 (m, 2H), 7.66 (td, J = 7.5, 7.3, 1.1 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 7.15 (m, 2H), 6.99 (m, 2H), 6.09 (ddd, J = 11.8, 10.3, 5.2 Hz, 1H), 5.46 (m, 1H), 5.33 (m, 1H), 4.58 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.5, 156.3, 144.5, 133.5, 133.1, 130.1, 129.6, 128.6, 122.4, 117.8, 115.4, 69.3.

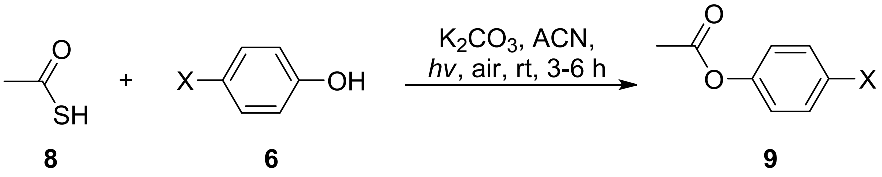


4-(prop-2-yn-1-yloxy)phenyl benzoate 7l

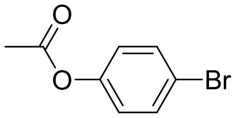
Following the typical procedure, **7l** was obtained in 93% yield (117.3 mg) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.23 (m, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.7 Hz, 2H), 7.18 (m, 2H), 7.06 (m, 2H), 4.73 (d, J = 2.4 Hz, 2H), 2.56 (t, J = 2.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.4, 155.3, 145.1, 133.6, 130.2, 129.6, 128.6, 122.5, 115.7, 78.4, 75.7, 56.3; MP: 90-92℃, HRMS (ESI): calculated for

$C_{16}H_{12}O_3Na^+$, [M+Na$^+$] 275.0684, found 275.0682.

General procedure for visible light mediated phenol acylation reaction C



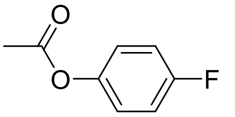
A flame-dried 10 mL flask was charged with thioacetic acid **8** (1.0 mmol, 76.1 mg), phenol **6** (0.5 mmol), and ACN (5 mL). $Ru(bpy)_3Cl_2{\bullet}6H_2O$ (0.01 mmol, 7.5 mg) and K_2CO_3 (1.0 mmol, 138 mg) was added to the mixture. The mixture was allowed to stir at room temperature in the open air, and was irradiated with a 45 W household bulb for 3-6 h. Then, the mixture was poured into water (10 mL), extracted with EtOAc (4 x 10 mL), washed with brine (15 mL), and dried over Na_2SO_4. The crude organic phase was concentrated in vacuo and purified with a short flash column chromatography (silica gel, hexane/EtOAc = 20:1) to afford the corresponding product **9**.



9a

4-bromophenyl acetate 9a [13]

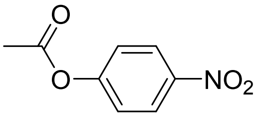
Following the typical procedure, **9a** was obtained in 56% yield (60.2 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50 (d, J = 9.0 Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.1, 149.7, 132.4, 123.4, 118.9, 21.0.



9b

***4-fluorophenyl acetate 9b*[13]**

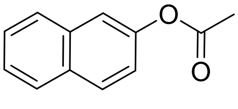
Following the typical procedure, **9b** was obtained in 56% yield (43.2 mg) as slight yellow oil. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.08 (m, 2H), 7.07 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 169.5, 161.2, 159.2, 146.5, 146.4, 122.9, 116.1, 21.0.



9c

***4-nitrophenyl acetate 9c*[14]**

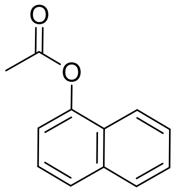
Following the typical procedure, **9c** was obtained in 67% yield (60.6 mg) as pale yellow solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.28 (m, 2H), 7.31 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 168.36, 155.37, 145.34, 125.19, 122.43, 21.09.



9d

***naphthalen-2-yl acetate 9d*[13]**

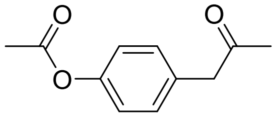
Following the typical procedure, **9d** was obtained in 82% yield (76.3 mg) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.90 (m, 2H), 7.85 (m, 1H), 7.62 (dd, J = 2.4, 0.7 Hz, 1H), 7.53 (m, 2H), 7.29 (dd, J = 8.9, 2.4 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 169.7, 148.3, 133.8, 131.5, 129.4, 127.8, 127.7, 127.7, 126.6, 125.7, 121.2, 118.6, 21.2.



9e

naphthalen-1-yl acetate 9e [15]

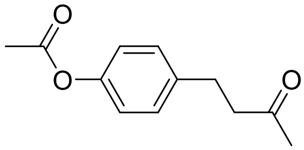
Following the typical procedure, **9e** was obtained in 66% yield (76.3 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.91 (m, 2H), 7.78 (m, 1H), 7.54 (m, 2H), 7.50 (dd, J = 8.2, 7.5 Hz, 1H), 7.28 (m, 1H), 2.50 (d, J = 0.7 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 169.5, 146.6, 134.6, 128.0, 126.7, 126.4, 126.0, 125.4, 121.1, 118.1, 21.0.



9f

4-(2-oxopropyl)phenyl acetate 9f [16]

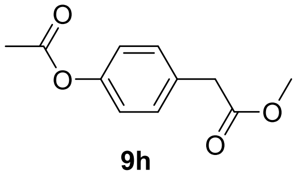
Following the typical procedure, **9f** was obtained in 56% yield (53.8 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.23 (m, 2H), 7.07 (m, 2H), 3.71 (s, 2H), 2.31 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 206.0, 169.4, 149.7, 131.7, 130.4, 121.8, 50.2, 29.4, 21.1.



9g

4-(4-acetoxyphenyl)butan-2-one 9g [17]

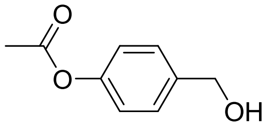
Following the typical procedure, **9g** was obtained in 69% yield (71.1 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.18 (m, 2H), 6.99 (m, 2H), 2.90 (t, J = 7.5 Hz, 2H), 2.77 (t, J = 7.5 Hz, 2H), 2.30 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 207.7, 169.6, 148.9, 138.6, 129.3, 121.5, 45.0, 30.1, 29.0, 21.1.



9h

***methyl 2-(4-acetoxyphenyl)acetate 9h*[18]**

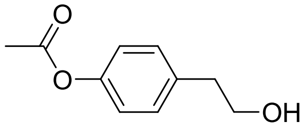
Following the typical procedure, **9h** was obtained in 69% yield (71.8 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.31 (m, 2H), 7.07 (m, 2H), 3.71 (d, J = 0.7 Hz, 3H), 3.63 (s, 2H), 2.30 (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 171.7, 169.5, 149.7, 131.5, 130.3, 121.7, 52.1, 40.5, 21.1



9i

***4-acetoxybenzyl alcohol 9i*[19]**

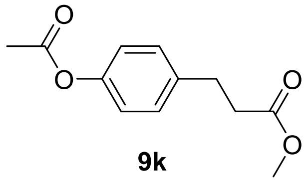
Following the typical procedure, **9i** was obtained in 73% yield (60.6 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.34 (m, 2H), 7.06 (m, 2H), 4.60 (s, 2H), 2.29 (s, 3H), 2.30 (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 169.8, 149.9, 138.6, 128.0, 121.5, 64.4, 21.1.



9j

***2-(4-acetoxyphenyl)ethanol 9j*[20]**

Following the typical procedure, **9j** was obtained in 80% yield (72.1 mg) as colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ = 7.22 (m, 2H), 7.02 (d, J = 8.5 Hz, 2H), 3.81 (t, J = 6.6 Hz, 2H), 2.84 (t, J = 6.6 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ = 169.8, 149.1, 136.3, 130.0, 121.5, 63.4, 38.5, 21.1.

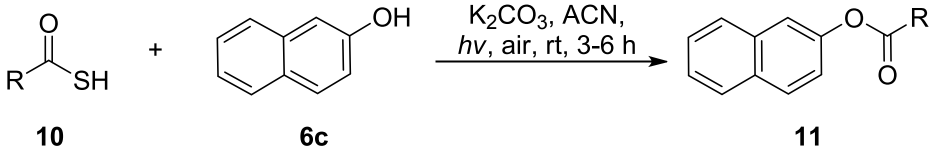


9k

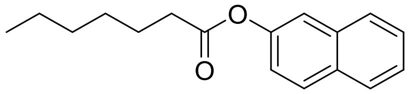
***methyl 3-(4-acetoxyphenyl)propanoate 9k*[21]**

Following the typical procedure, **9k** was obtained in 69% yield (76.7 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.22 (m, 2H), 7.02 (d, J = 8.5 Hz, 2H), 3.69 (s, 3H), 2.96 (t, J = 7.8 Hz, 2H), 2.64 (t, J = 7.8 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 173.2, 169.6, 149.1, 138.1, 129.2, 121.5, 51.6, 35.6, 30.3, 21.1.

General procedure for visible light mediated phenol acylation reaction D



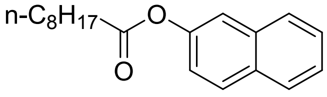
A flame-dried 10 mL flask was charged with thioacetic acid **10** (1.0 mmol, 76.1 mg) and ACN (5 mL). Ru(bpy)$_3$Cl$_2$•6H$_2$O (0.01 mmol, 7.5 mg), K$_2$CO$_3$ (1.0 mmol, 138 mg) and 2-naphthol (0.5 mmol, 72.1 mg) was added to the mixture sequentially. The mixture was allowed to stir at room temperature in the open air, and was irradiated with a 45 W household bulb for 3-6 h. After that, the mixture was poured into water (10 mL), extracted with EtOAc (4 x 10 mL), washed with brine (15 mL), and dried over Na$_2$SO$_4$. The crude organic phase was concentrated in vacuo and purified with a short flash column chromatography (silica gel, hexane/EtOAc = 20:1) to afford the corresponding product **11**.



11a

***2-naphthyl heptanoate 11a*[22]**

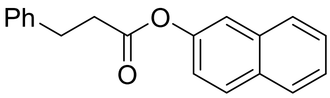
Following the typical procedure, **11a** was obtained in 81% yield (103.8 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.89 (m, 2H), 7.84 (m, 1H), 7.60 (d, J = 2.3 Hz, 1H), 7.51 (m, 2H), 7.27 (dd, J = 8.8, 2.3 Hz, 1H), 2.65 (m, 2H), 1.84 (m, 2H), 1.50 (m, 2H), 1.41 (m, 4H), 0.97 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 172.5, 148.4, 133.8, 131.4, 129.4, 127.8, 127.6, 126.5, 125.6, 121.2, 118.5, 34.5, 31.5, 28.8, 25.0, 22.5, 14.1.



11b

2-naphthyl nonanoate 11b[22]

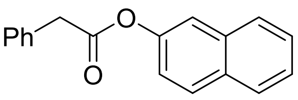
Following the typical procedure, **11b** was obtained in 84% yield (119.4 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.88 (dd, J = 8.2, 4.7 Hz, 2H), 7.84 (dd, J = 7.6, 1.8 Hz, 1H), 7.60 (d, J = 2.3 Hz, 1H), 7.50 (m, 2H), 7.27 (m, 1H), 2.65 (t, J = 7.5 Hz, 2H), 1.84 (m, 2H), 1.49 (t, J = 7.8 Hz, 2H), 1.38 (m, 8H), 0.95 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 172.5, 148.4, 133.8, 131.4, 129.4, 127.8, 127.6, 126.5, 125.6, 121.2, 118.5, 34.5, 31.8, 29.3, 29.2, 25.0, 22.7, 14.1.



11c

2-naphthyl-3-phenyl propanoate 11c[23]

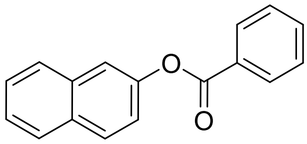
Following the typical procedure, **11c** was obtained in 94% yield (129.9 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.91 (m, 2H), 7.85 (m, 1H), 7.53 (m, 3H), 7.43 (m, 2H), 7.35 (m, 3H), 7.23 (m, 1H), 3.20 (m, 2H), 3.02 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 171.6, 148.3, 140.2, 133.8, 131.5, 129.4, 128.7, 128.5, 127.8, 127.7, 126.6, 126.5, 125.8, 121.2, 118.6, 36.1, 31.0.



11d

2-naphthyl-2-phenyl acetate 11d[24]

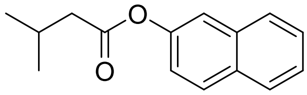
Following the typical procedure, **11d** was obtained in 90% yield (118.0 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.86 (m, 2H), 7.81 (m, 1H), 7.57 (dd, J = 2.3, 0.6 Hz, 1H), 7.50 (m, 2H), 7.44 (m, 4H), 7.37 (s, 1H), 7.22 (dd, J = 8.9, 2.3 Hz, 1H), 3.95 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 170.2, 148.3, 133.7, 133.4, 131.4, 129.4, 129.3, 128.8, 127.7, 127.6, 127.4, 126.5, 125.7, 121.0, 118.4, 41.5.



11e

***naphthalene-2-yl benzoate 11e*[8]**

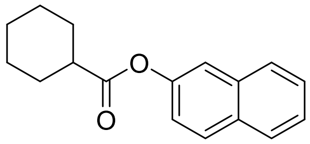
Following the typical procedure, **11e** was obtained in 86% yield (99.2 mg) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.31 (dd, J = 8.3, 1.2 Hz, 2H), 7.94-7.88 (m, 3H), 7.75 (d, J = 2.3 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.56 (m, 4H), 7.42 (dd, J = 8.8, 2.3 Hz, 1H); ^{13}C NMR (126 MHz, CDCl$_3$): δ = 165.4, 148.6, 133.9, 133.7, 131.6, 130.2, 129.6, 129.5, 128.6, 127.8, 127.7, 126.6, 125.8, 121.3, 118.7.



11f

***2-naphthyl-3-methyl butanoate 11f*[23]**

Following the typical procedure, **11f** was obtained in 77% yield (87.9 mg) as colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.89 (m, 2H), 7.84 (m, 1H), 7.60 (d, J = 2.3 Hz, 1H), 7.51 (m, 2H), 7.27 (dd, J = 8.8, 2.3 Hz, 1H), 2.54 (d, J = 7.2 Hz, 2H), 2.35 (m, 1H), 1.15 (d, J = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 171.7, 148.4, 133.8, 131.4, 129.4, 127.8, 127.6, 126.5, 125.7, 121.3, 118.5, 43.4, 25.9, 22.5.

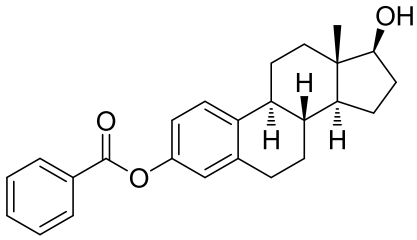


11g

2-naphthyl cyclohexanecarboxylate 11g[13]

Following the typical procedure, **11g** was obtained in 78% yield (99.2 mg) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.86 (m, 3H), 7.59 (d, J = 2.2 Hz, 1H), 7.50 (m, 2H), 7.25 (m, 1H), 2.67 (m, 1H), 2.15 (m, 2H), 1.89 (dt, J = 13.1, 3.9 Hz, 2H), 1.71 (m, 3H), 1.40 (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 174.7, 148.6, 133.8, 131.4, 129.3, 127.7, 127.6, 126.5, 125.6, 121.2, 118.5, 43.3, 29.0, 25.8, 25.4.

Characterization spectra data of compound **12**



12

Following the typical catalytic K$_2$CO$_3$ procedure, **12** was obtained in 89% yield (167.5 mg) as white solid. The gram scale (0.1 g and 1.0 g) experiments were proceeded using 0.37 mmol and 3.7 mmol Estradiol, affording 12 in 86% and 88% yield, respectively. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.21 (m, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.36 (dd, J = 8.5, 1.1 Hz, 1H), 7.00 (dd, J = 8.4, 2.6 Hz, 1H), 6.95 (d, J = 2.5 Hz, 1H), 3.76 (m, 1H), 2.92 (dt, J = 6.7, 1.9 Hz, 2H), 2.38 (dt, J = 13.6, 2.2 Hz, 1H), 2.28 (d, J = 4.4 Hz, 1H), 2.15 (m, 1H), 1.98 (m, 1H), 1.93 (m, 1H), 1.74 (m, 1H), 1.65 (s, 1H), 1.59 (m, 1H), 1.53 (m, 1H), 1.43 (m, 1H), 1.38 (m, 1H), 1.33 (d, J = 4.2 Hz, 1H), 1.24 (m, 1H), 0.82 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 165.47, 148.70, 138.32, 138.06, 133.47, 130.15, 129.75, 128.52, 126.45, 121.61, 118.68, 81.88, 50.12, 44.19, 43.24, 38.54, 36.72, 30.60, 29.58, 27.08, 26.21, 23.16, 11.07. [8]

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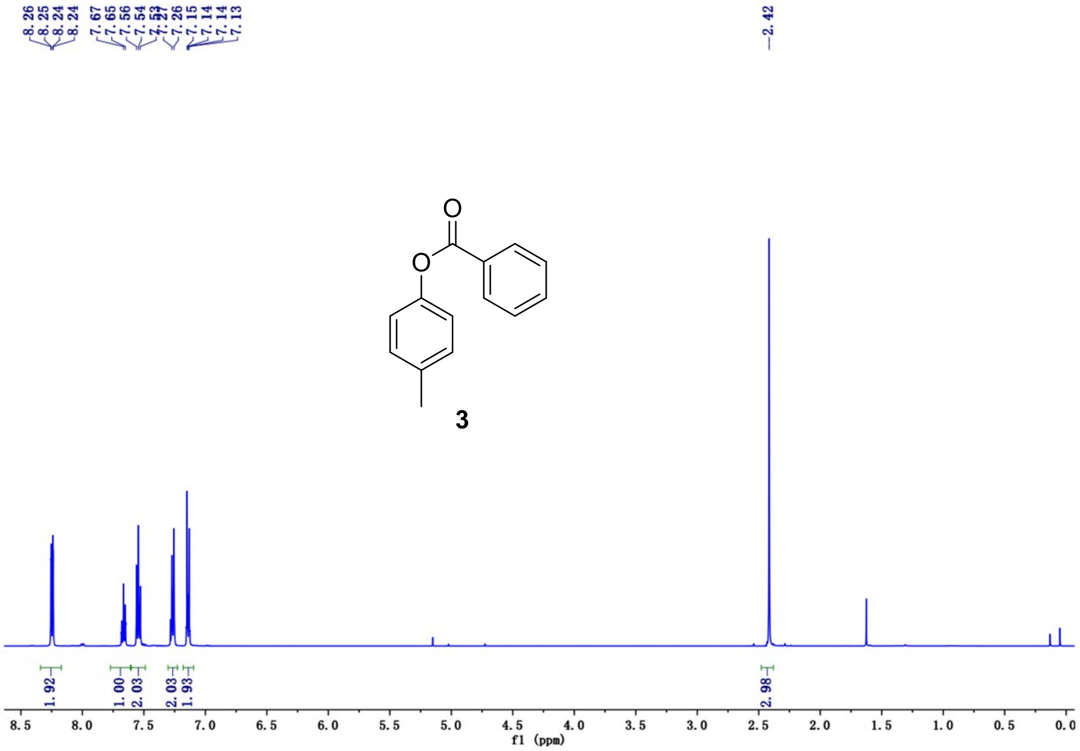
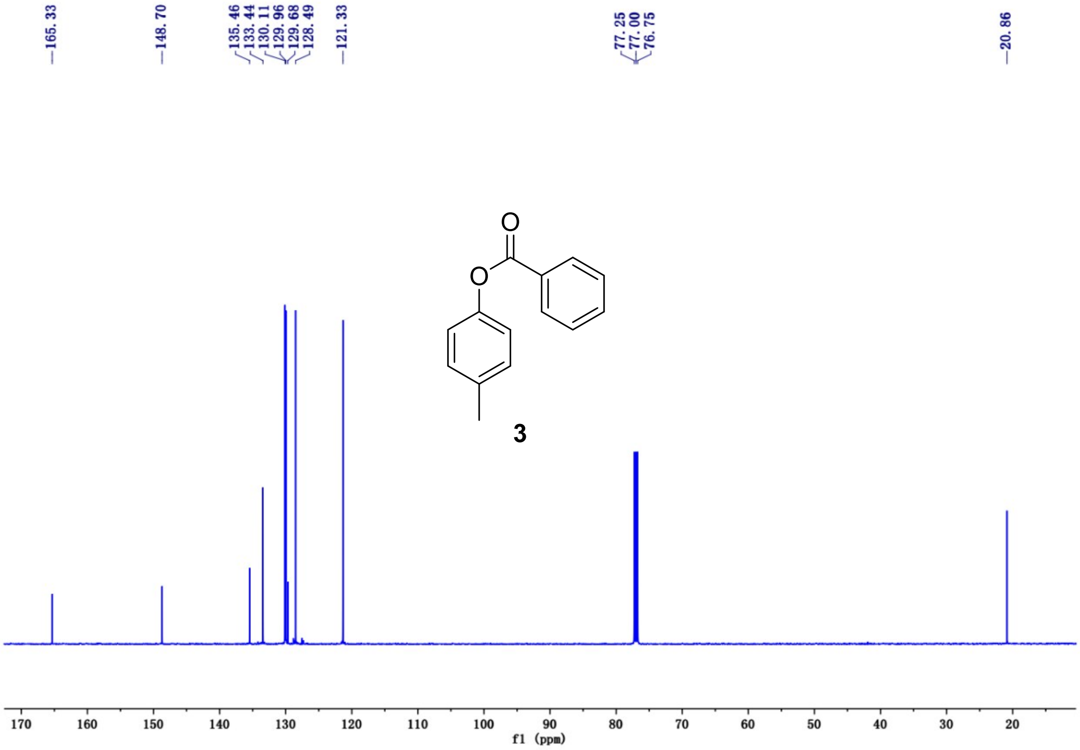
Spectral data





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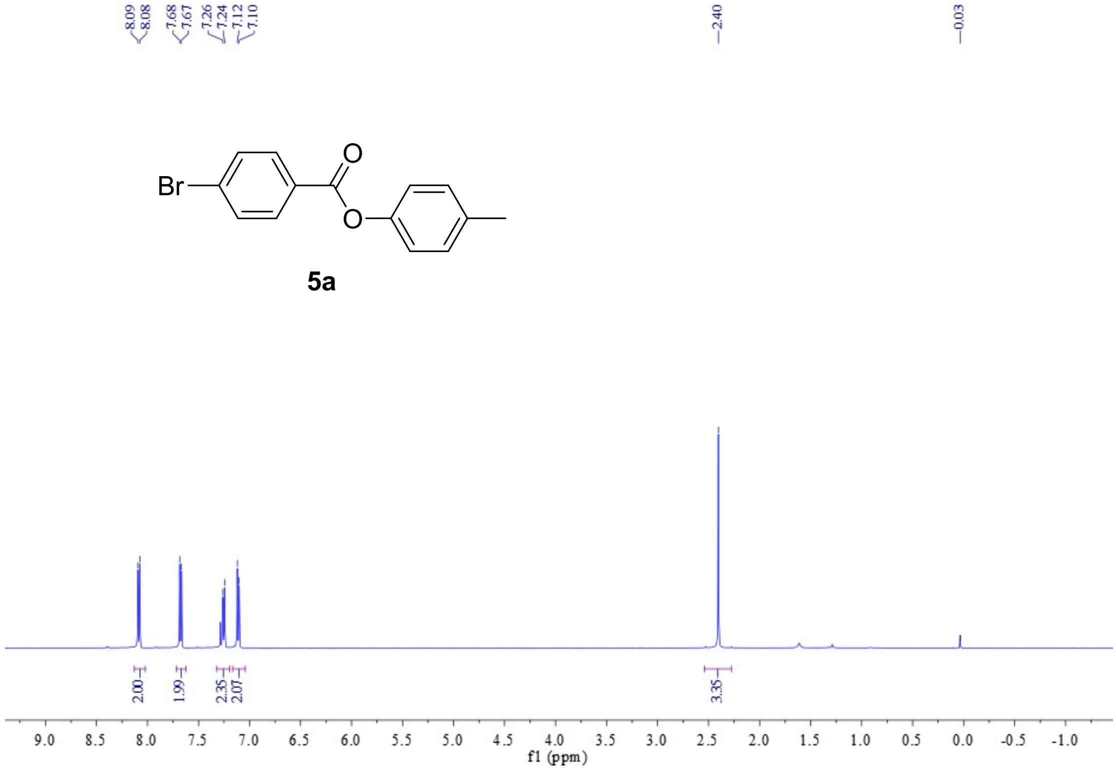

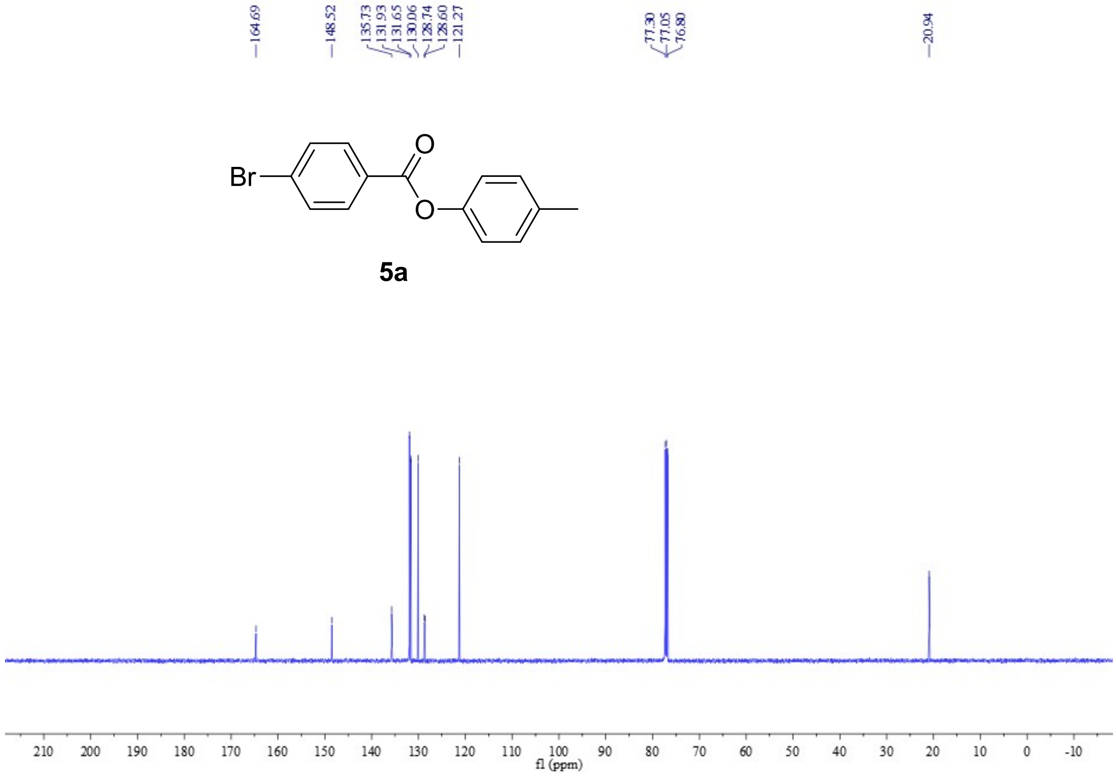

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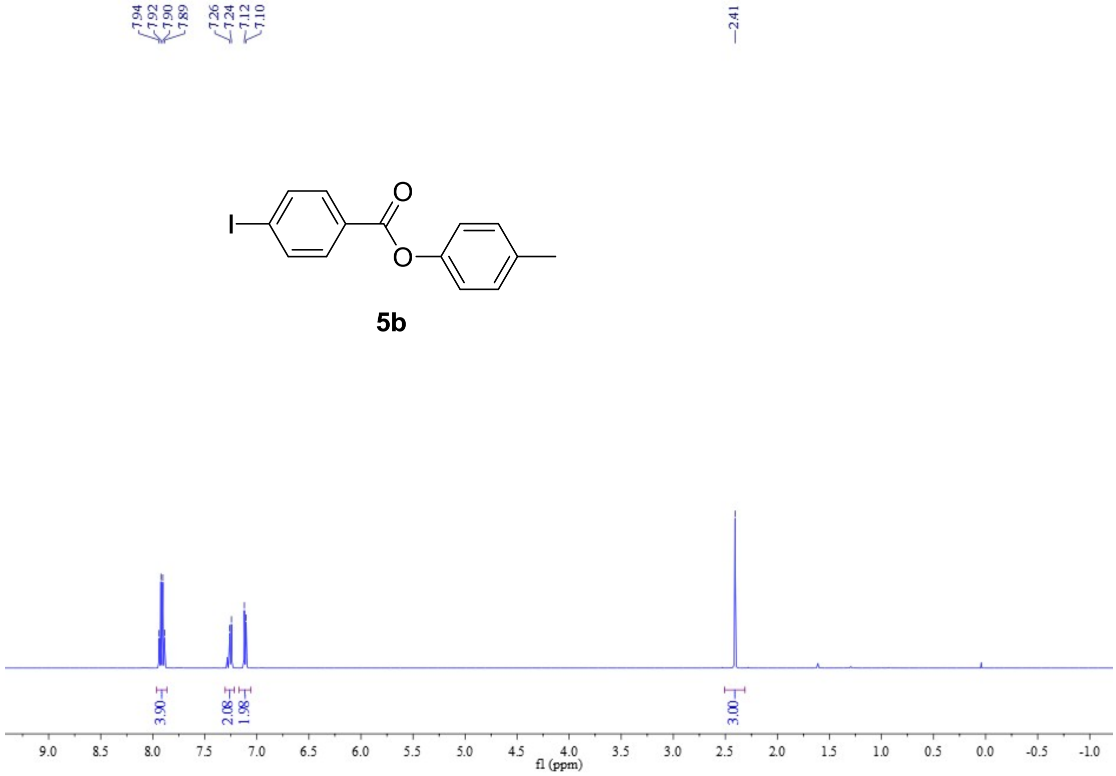

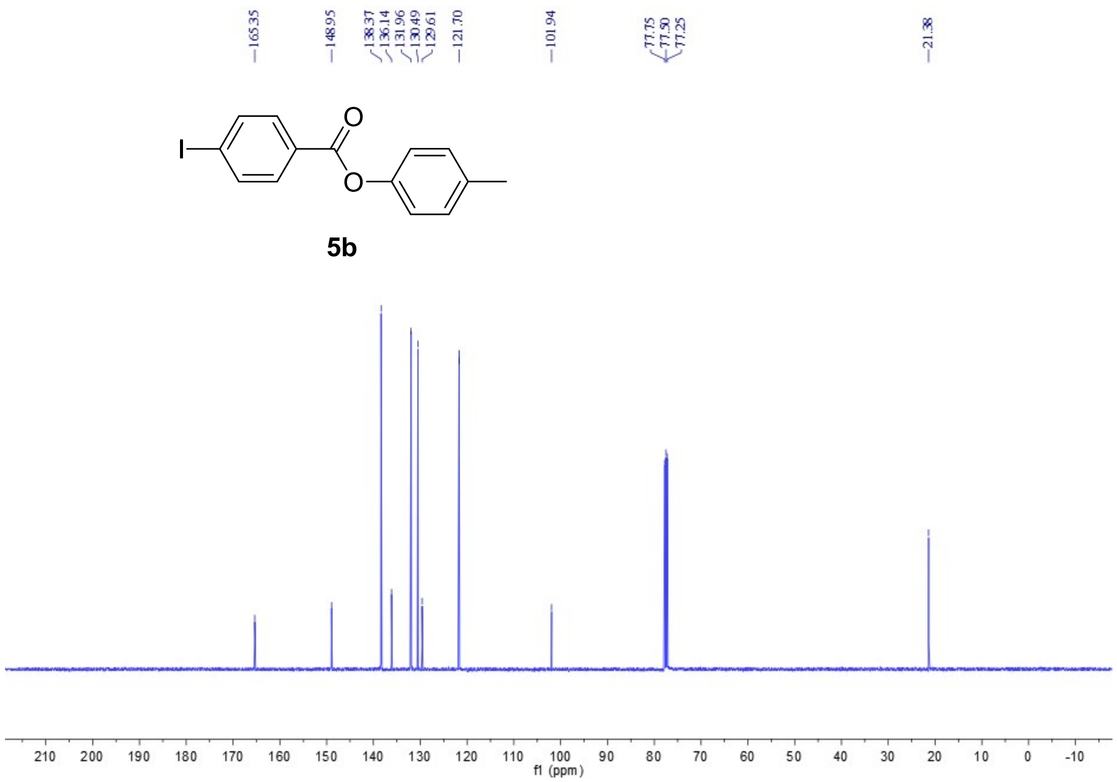

5b

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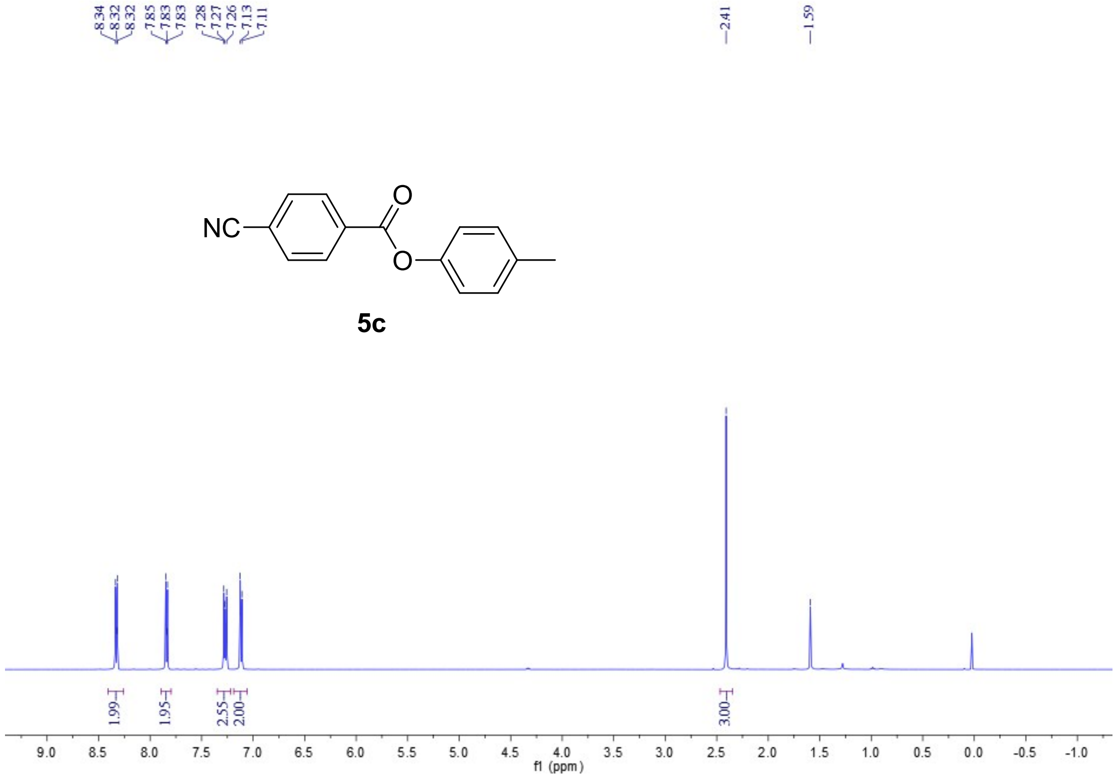
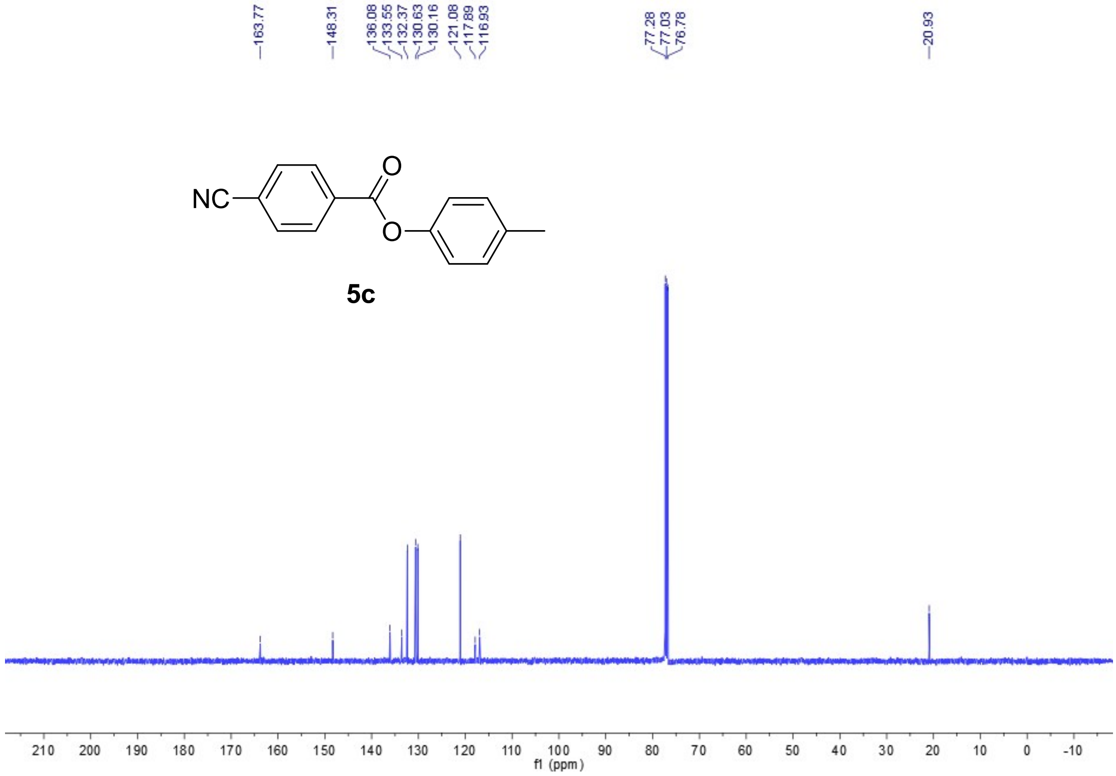


5c



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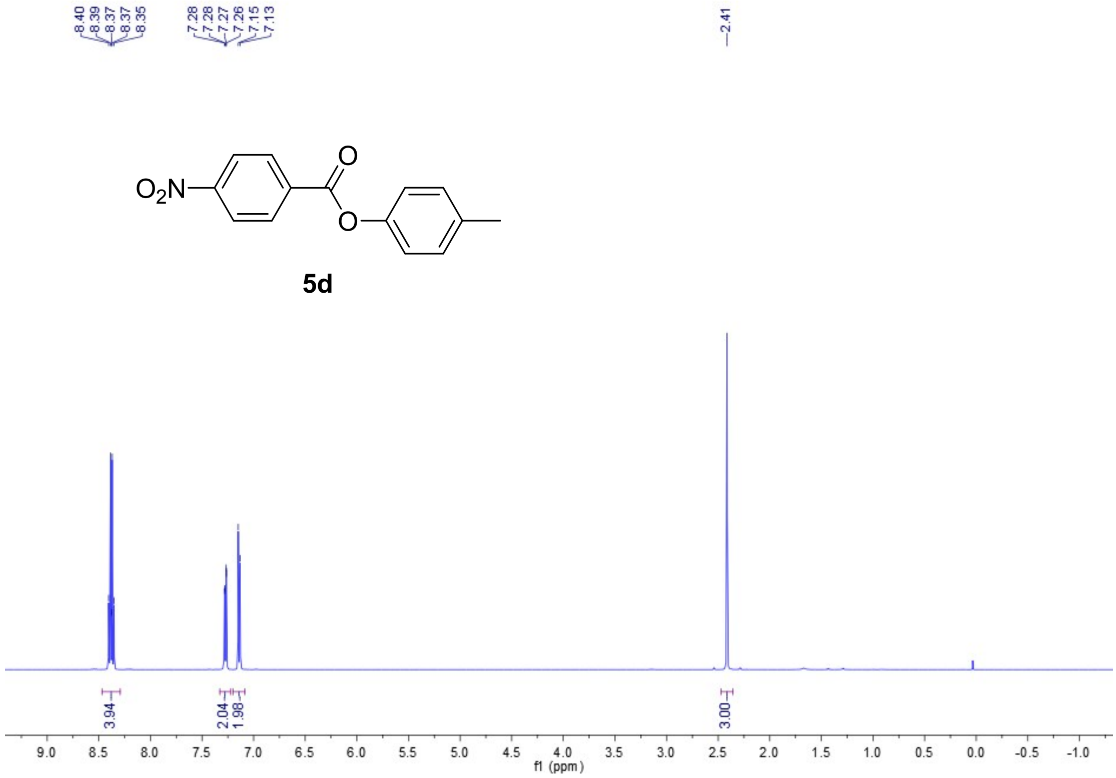

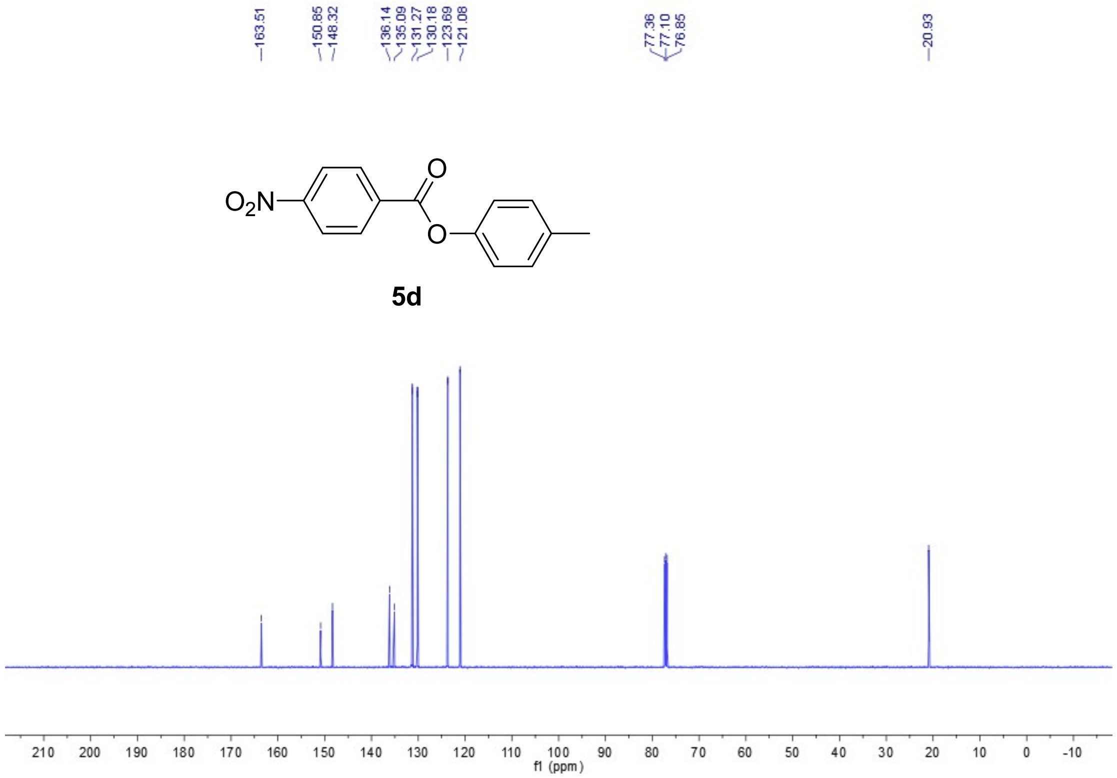

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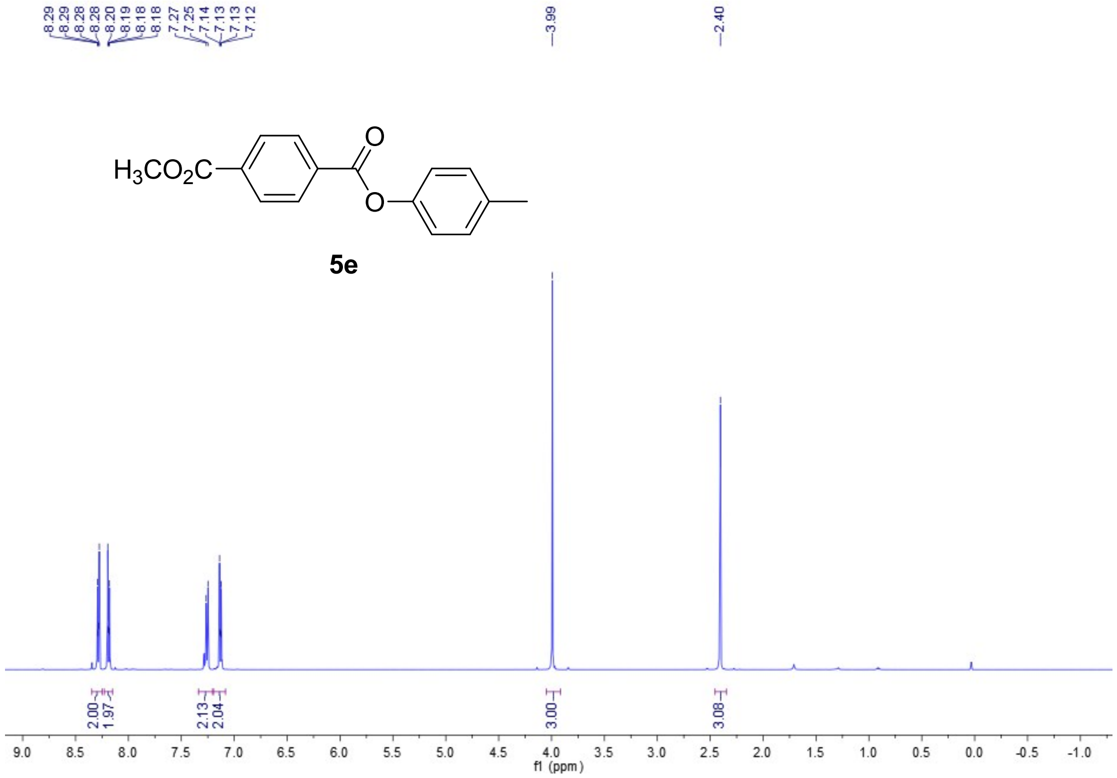
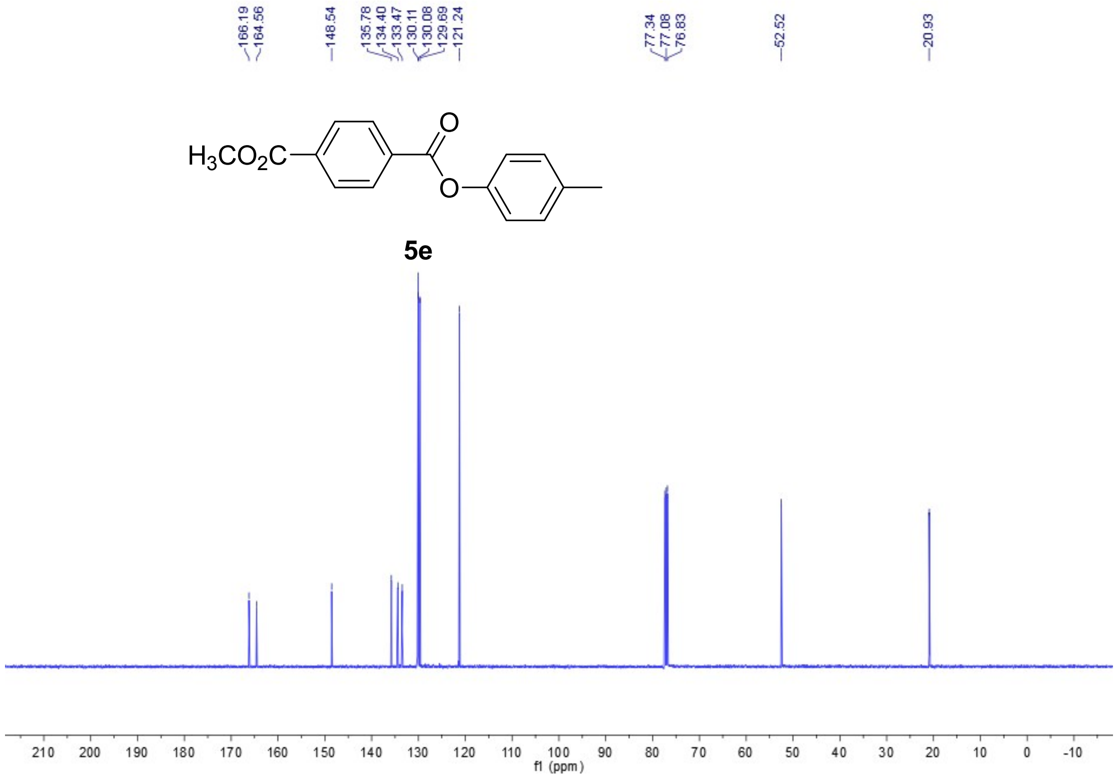


5e



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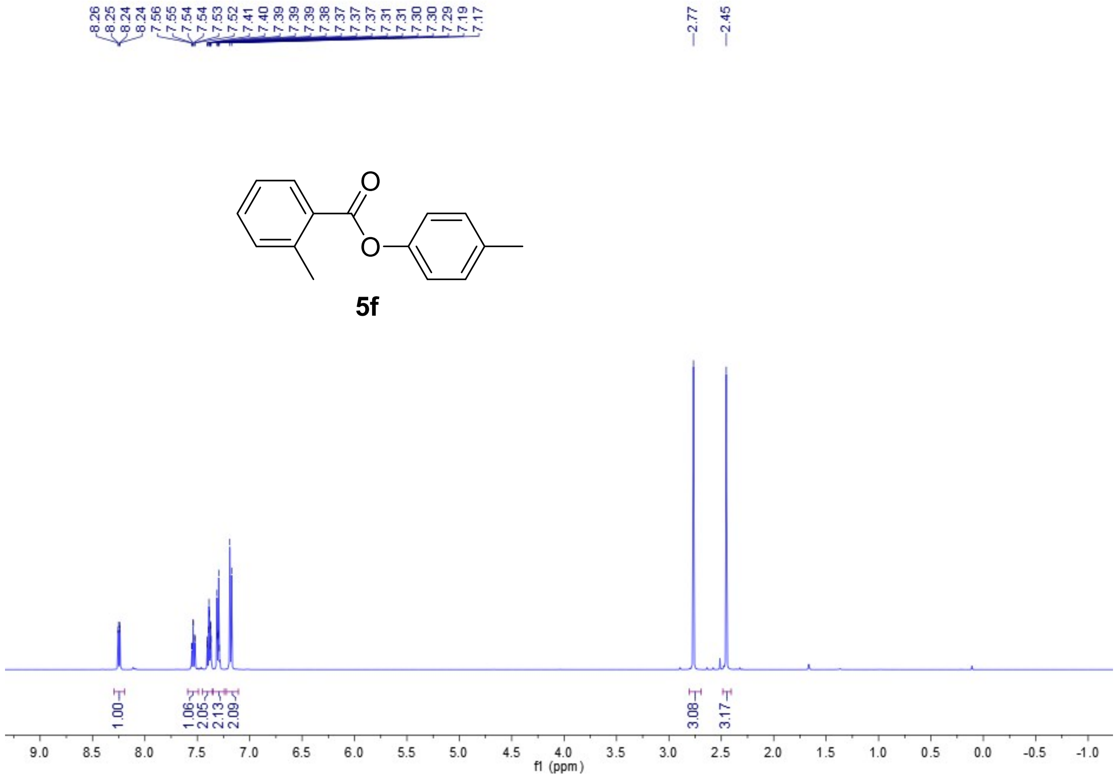

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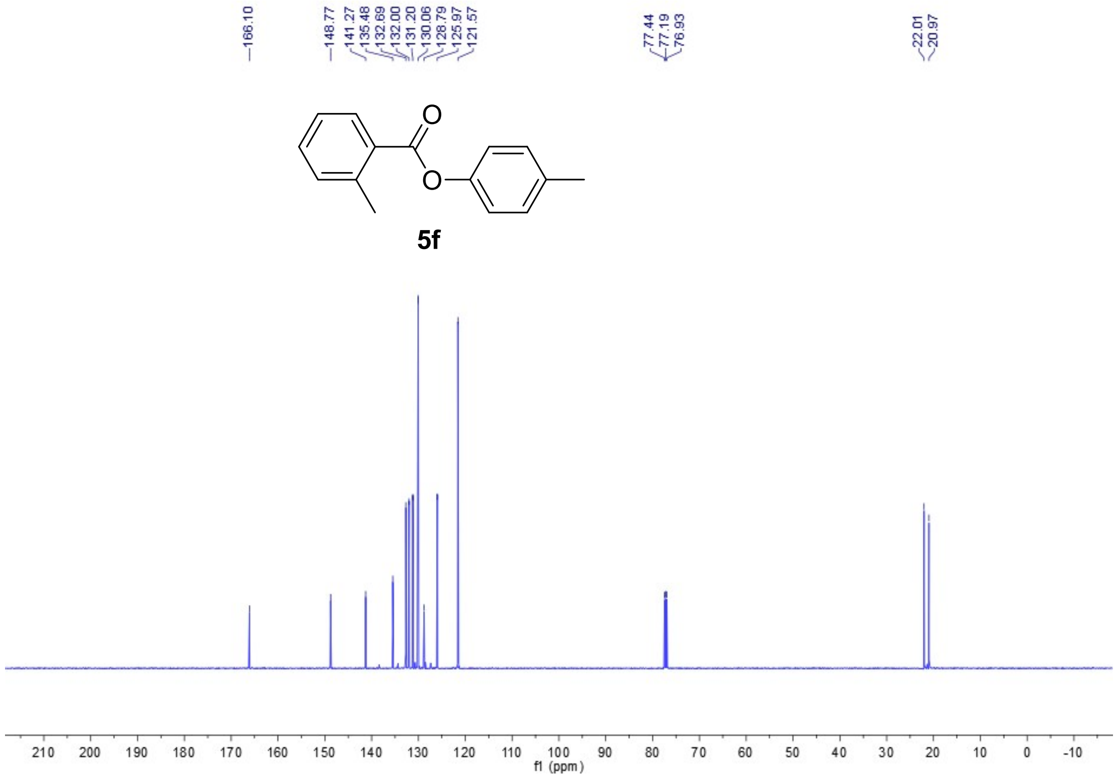

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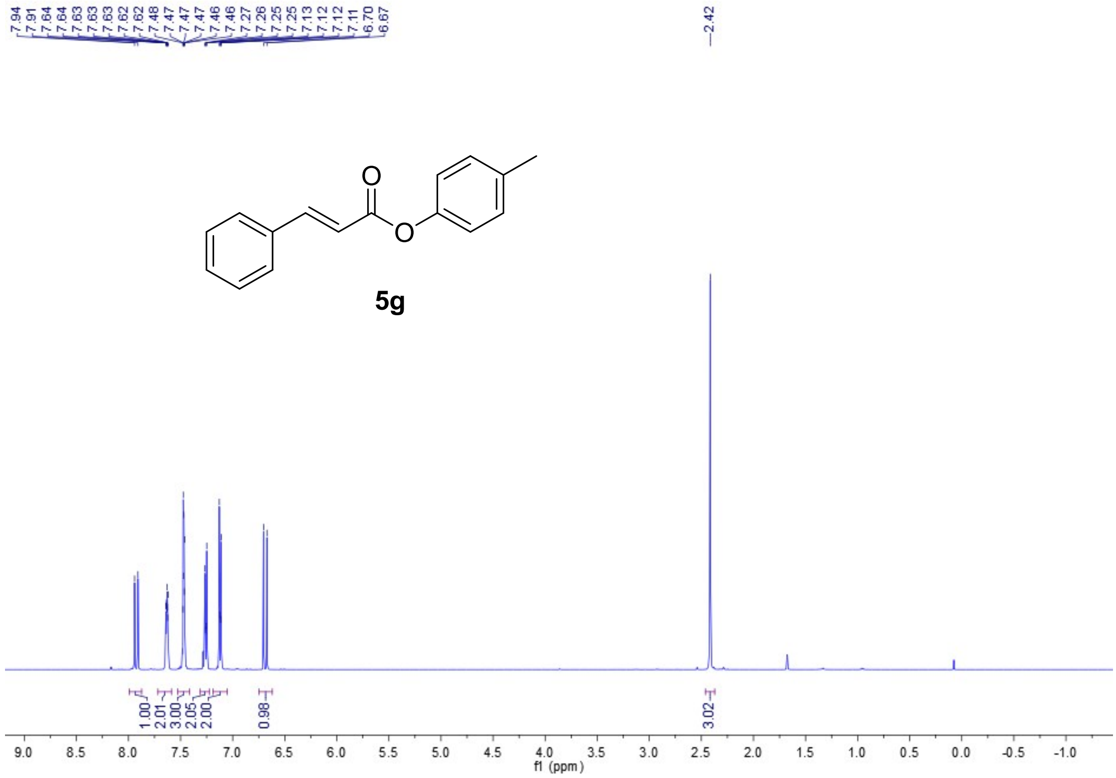

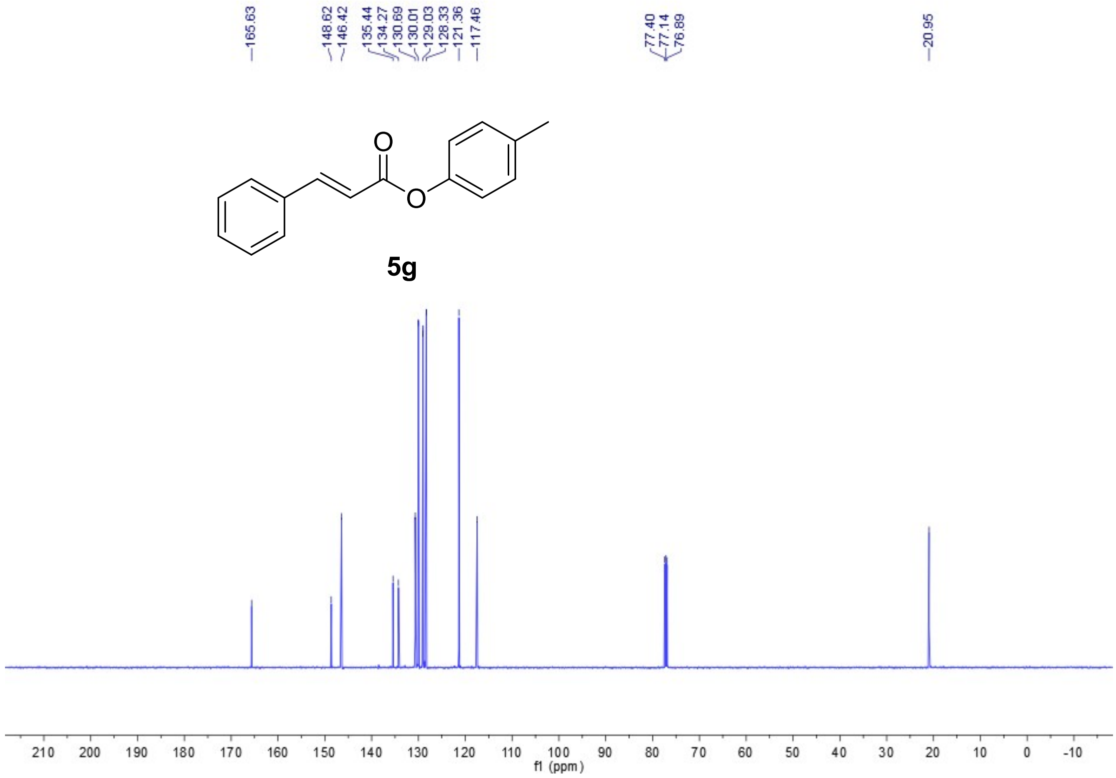

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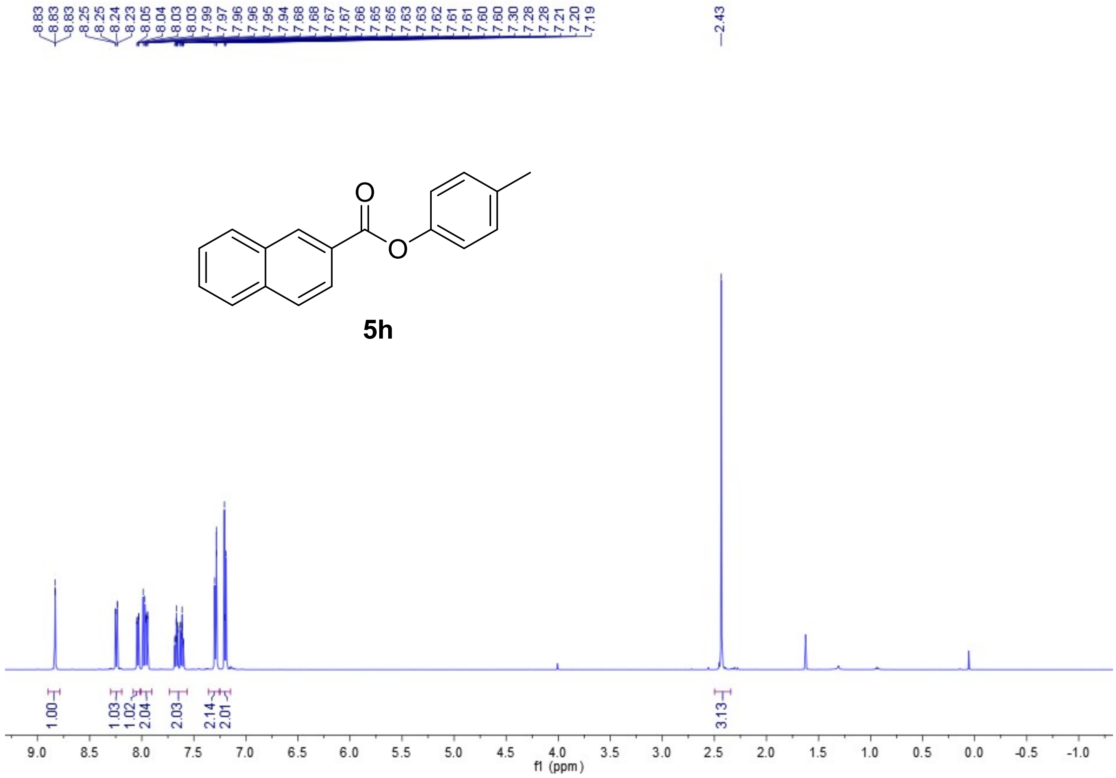

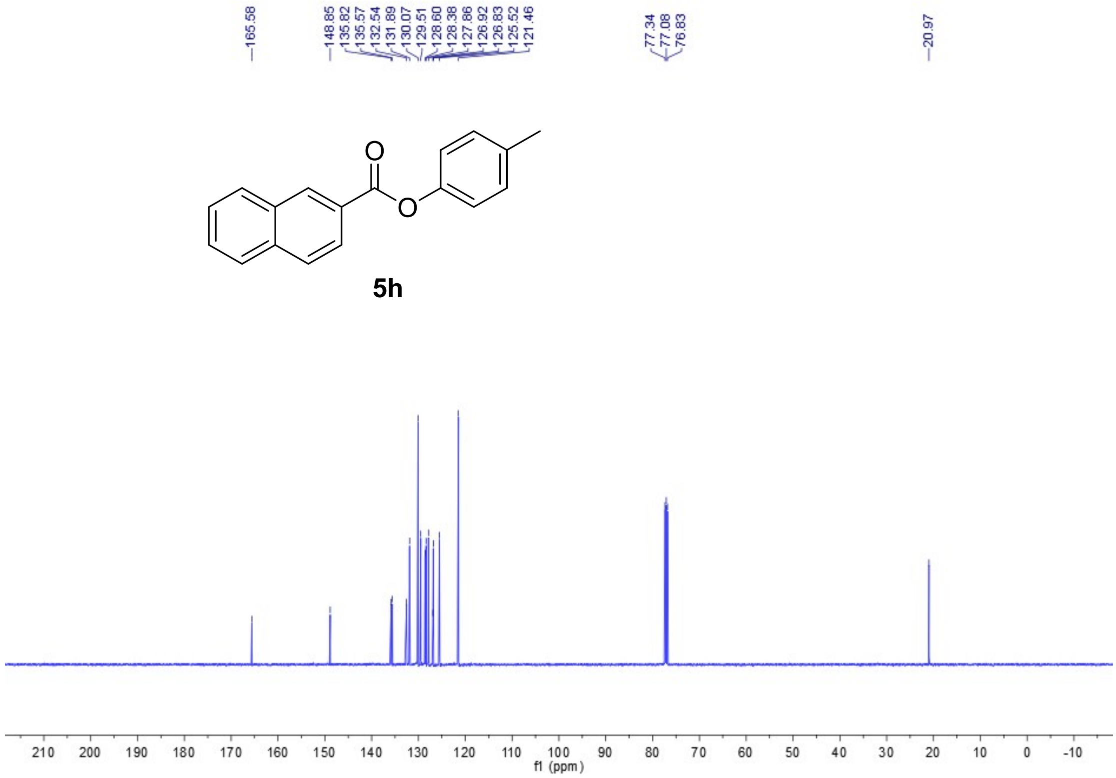

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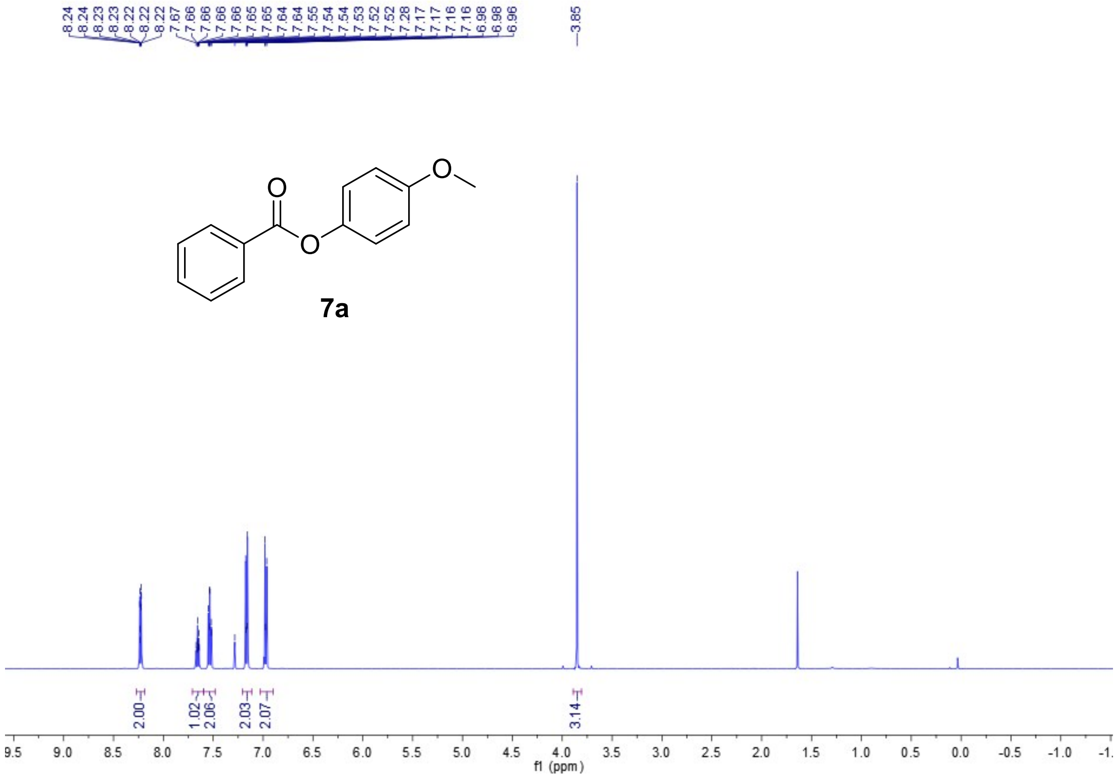
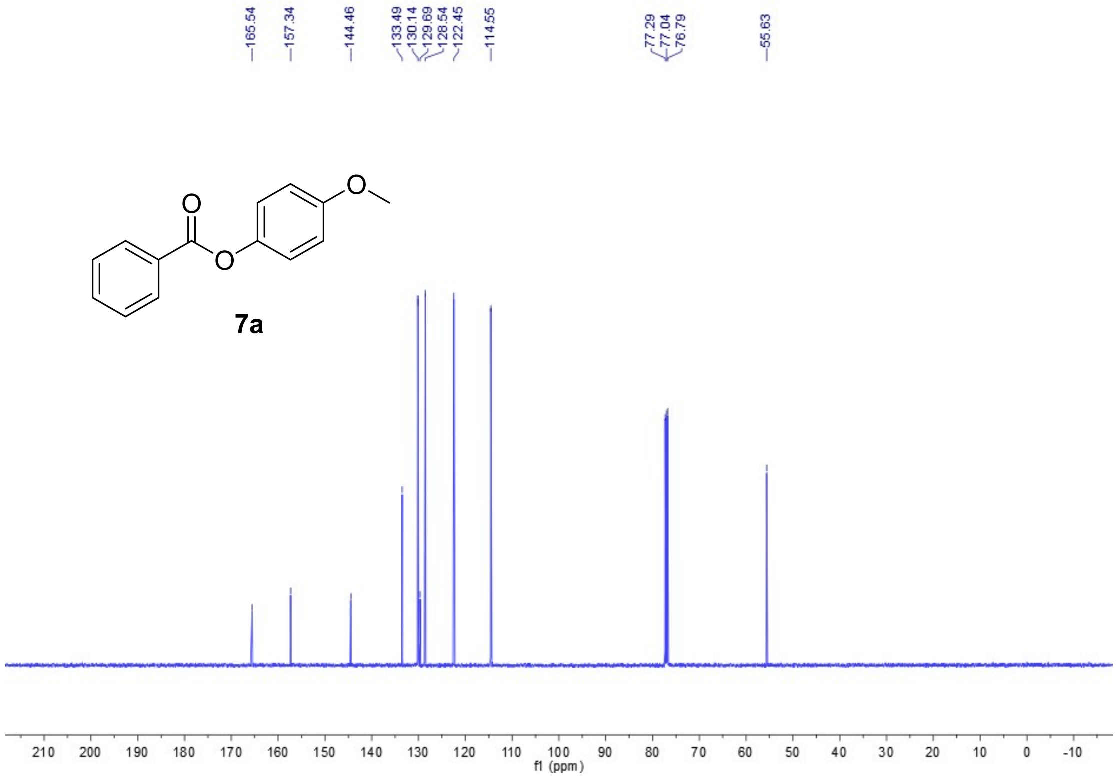
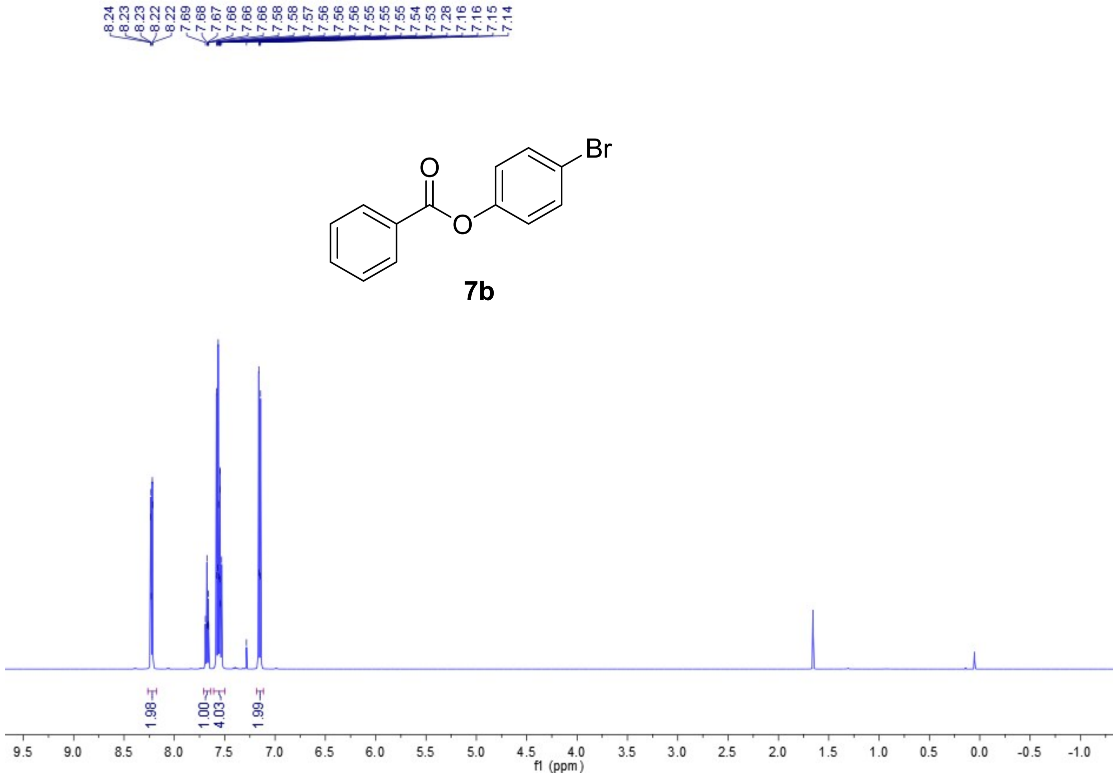


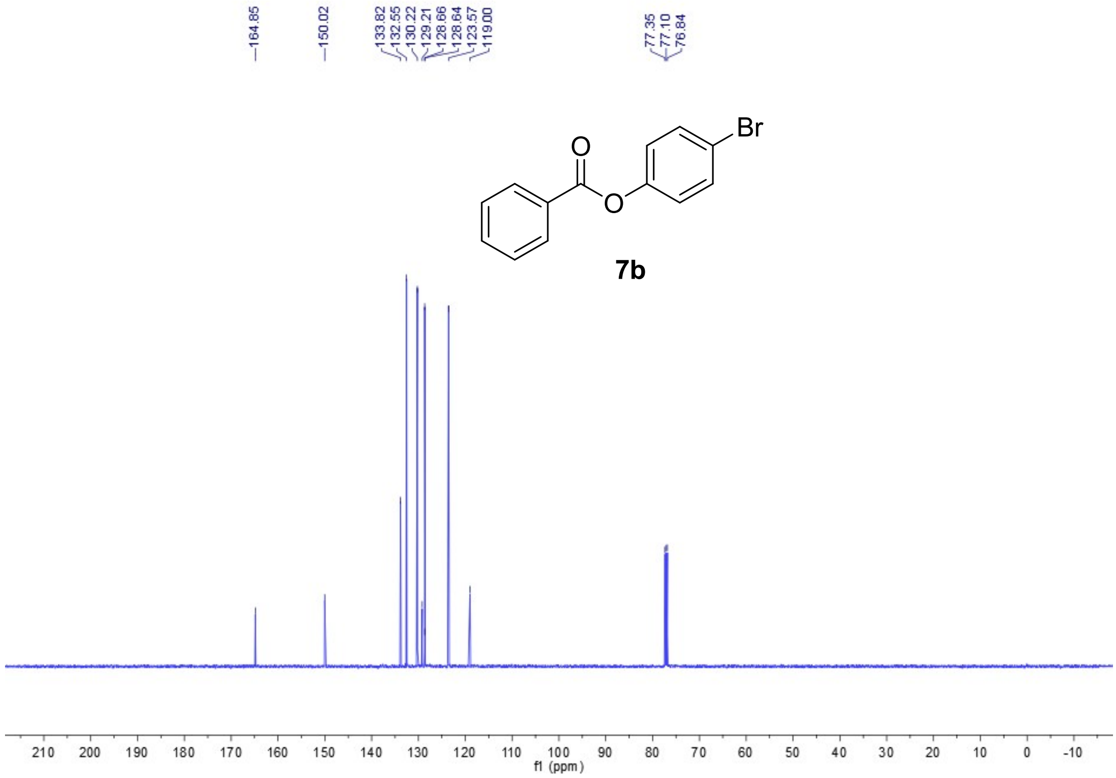


7a

^{1}H and ^{13}C NMR spectra of **7a**



7b



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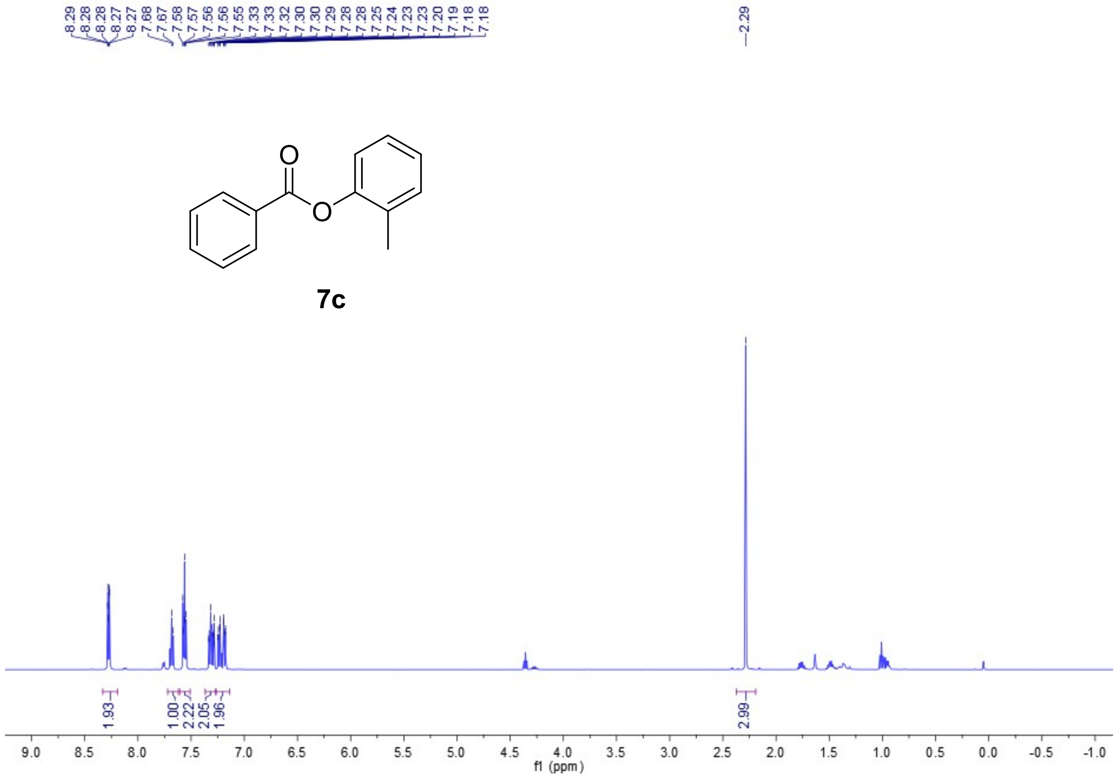

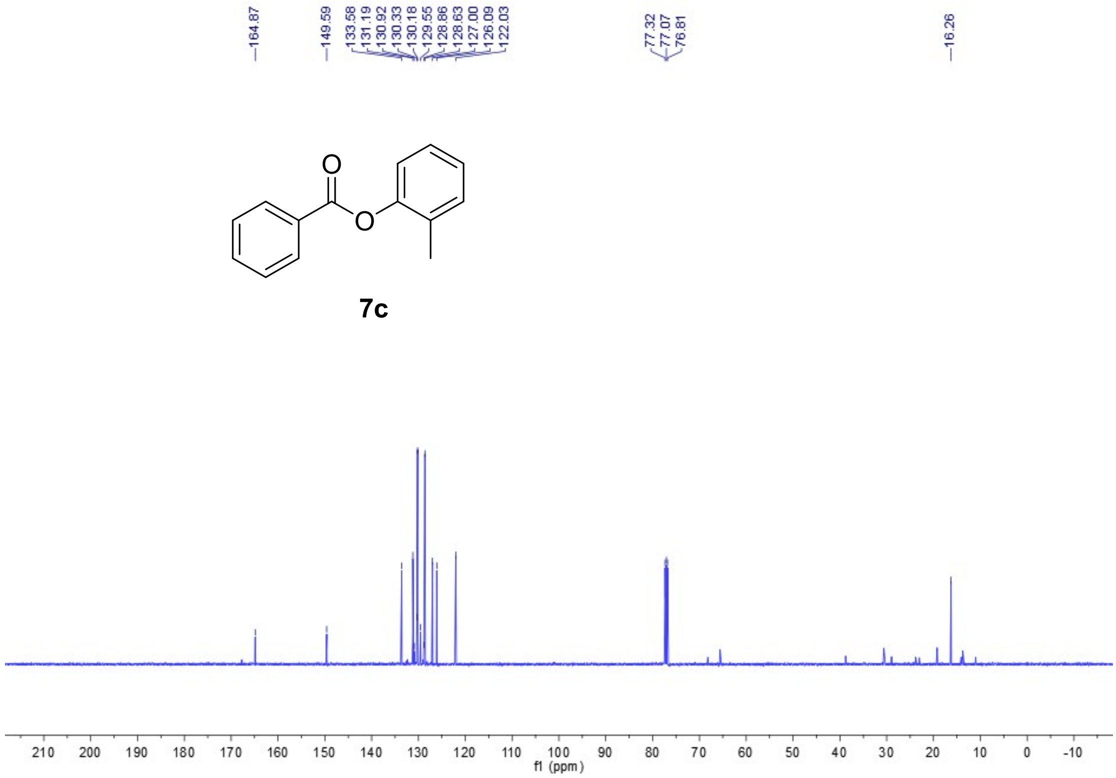

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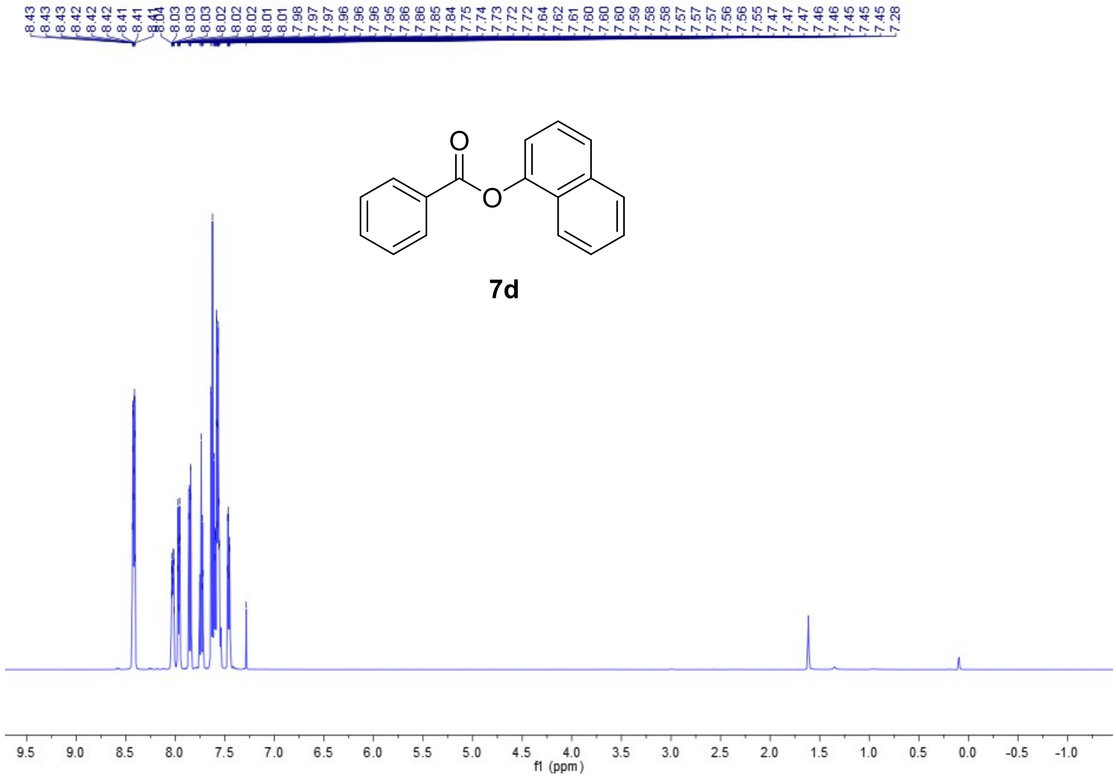

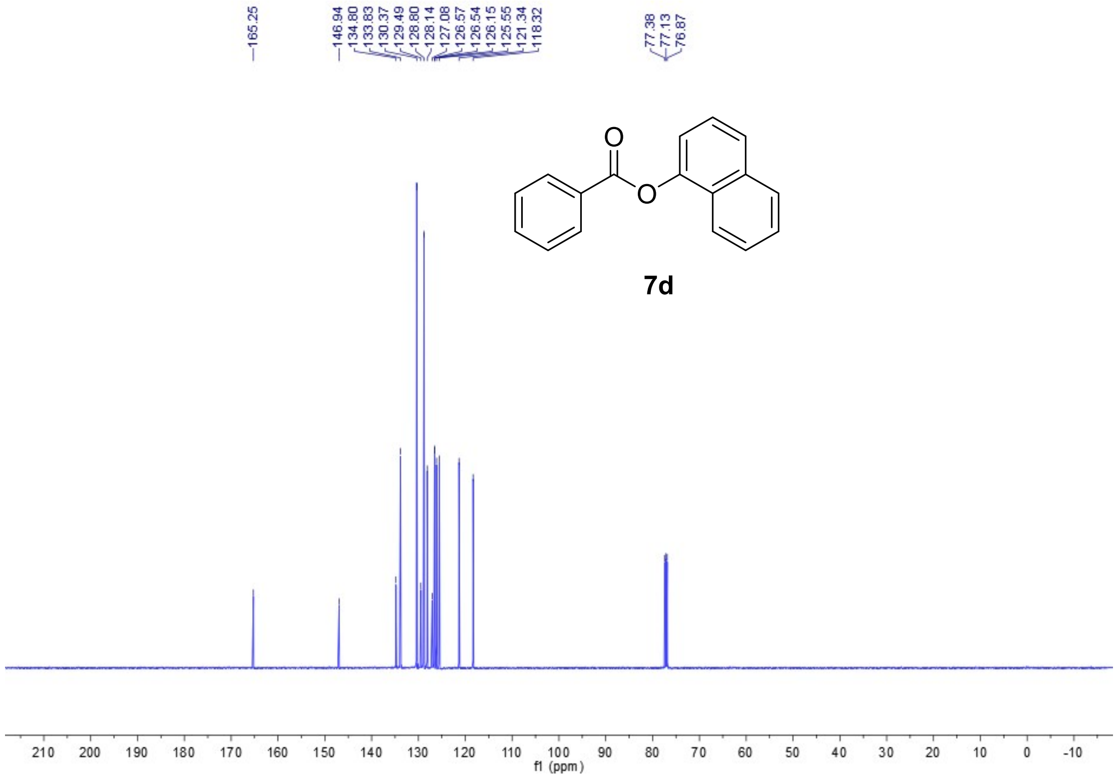

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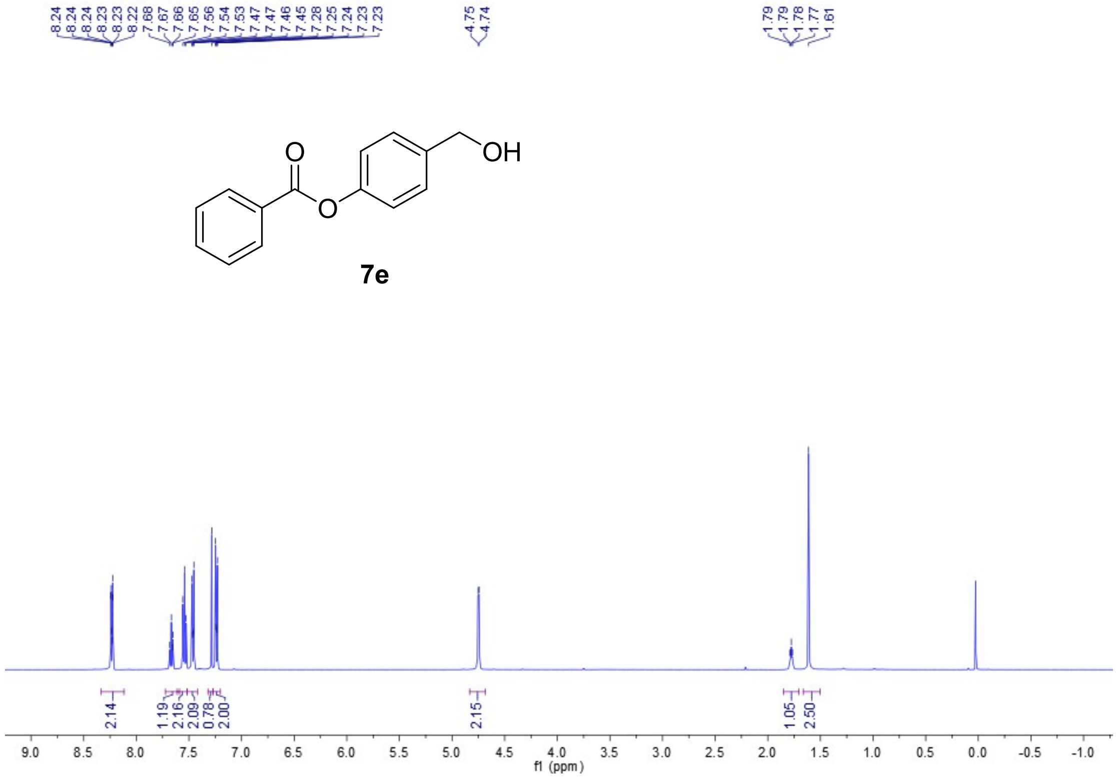

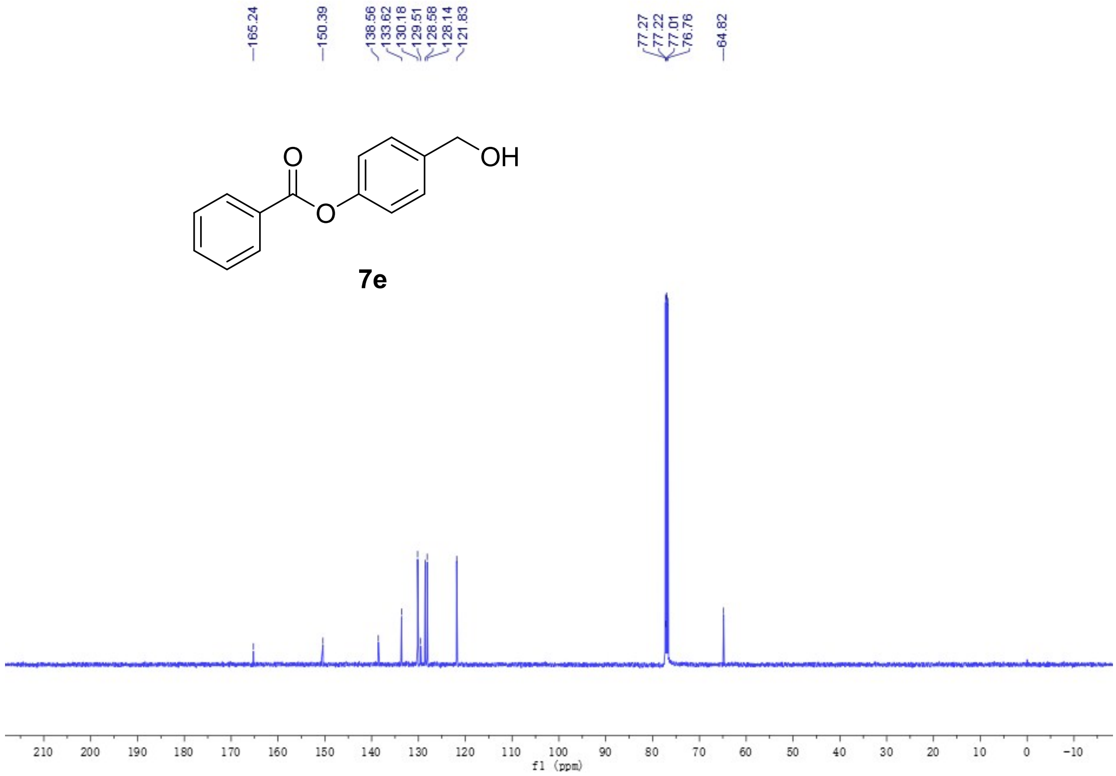

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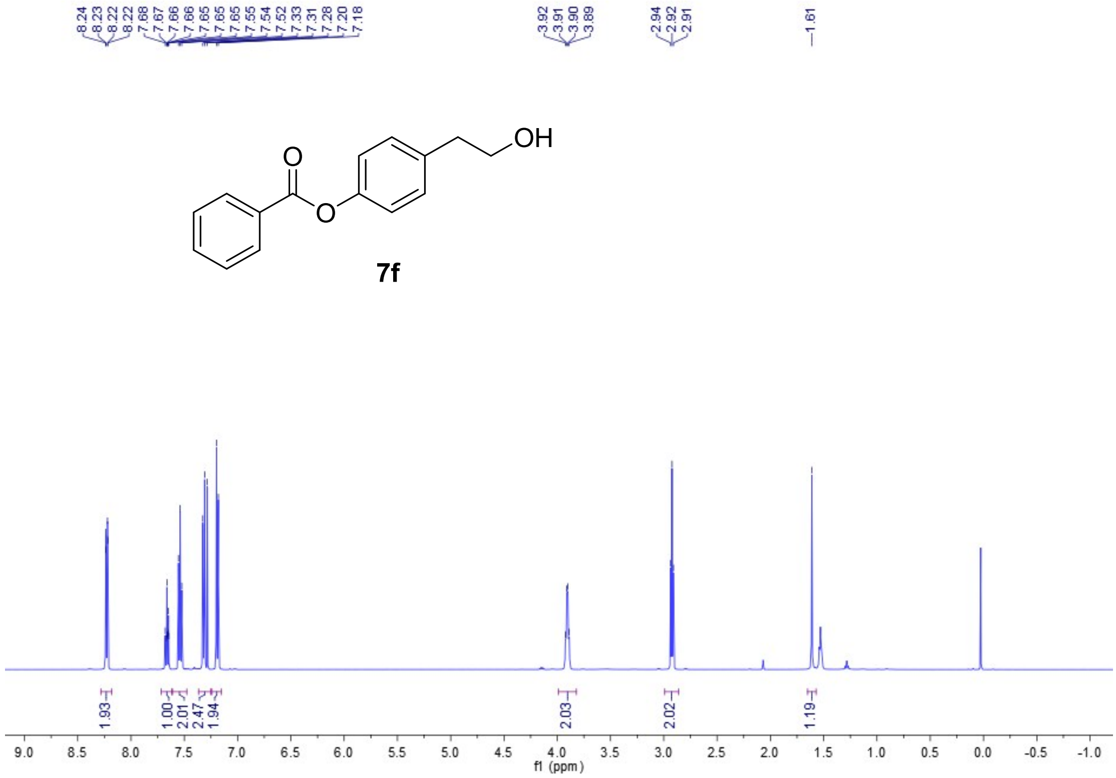

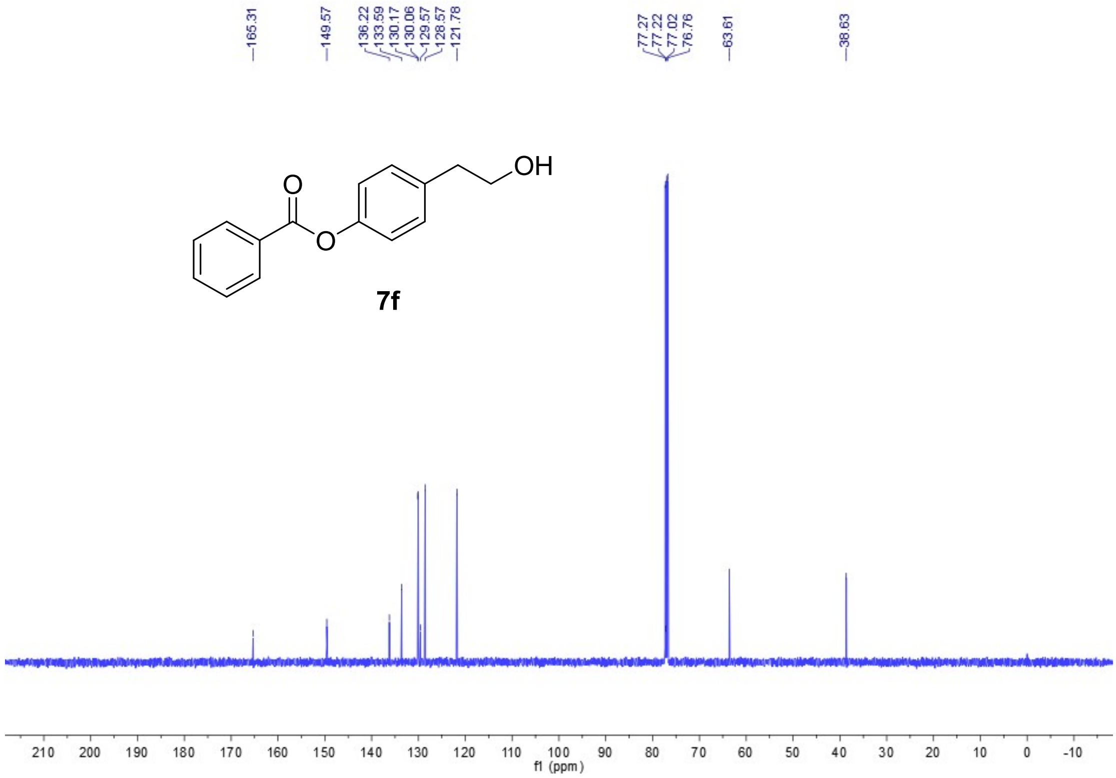

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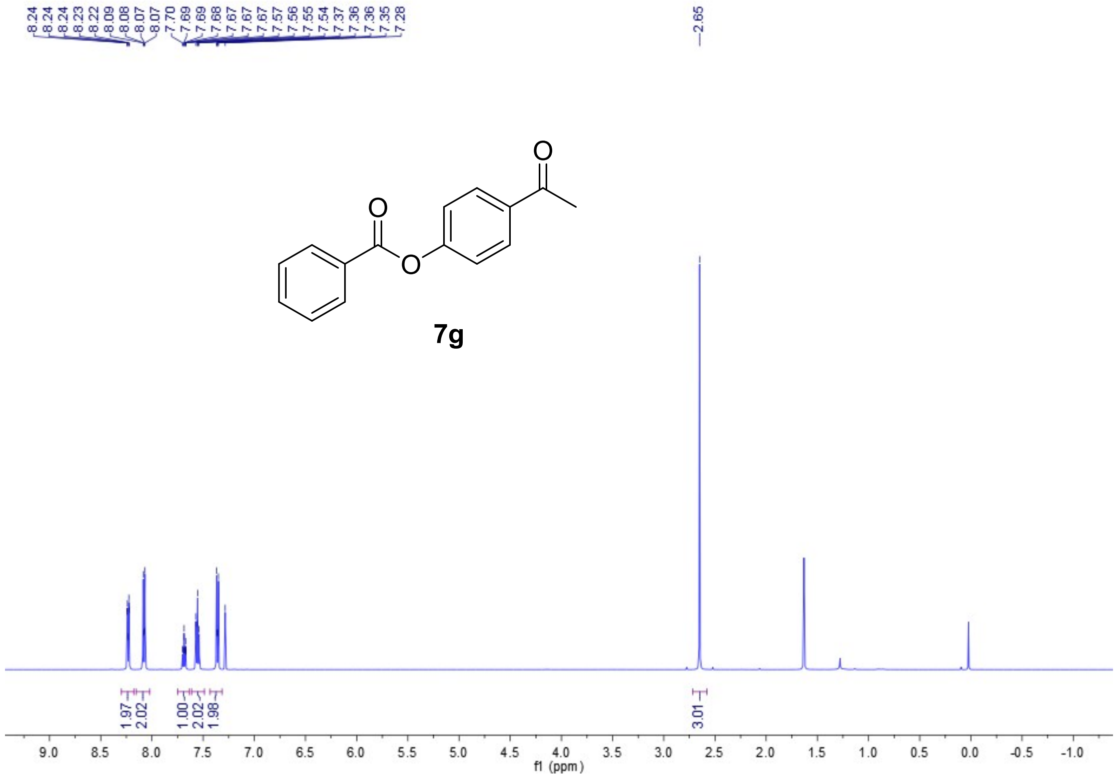
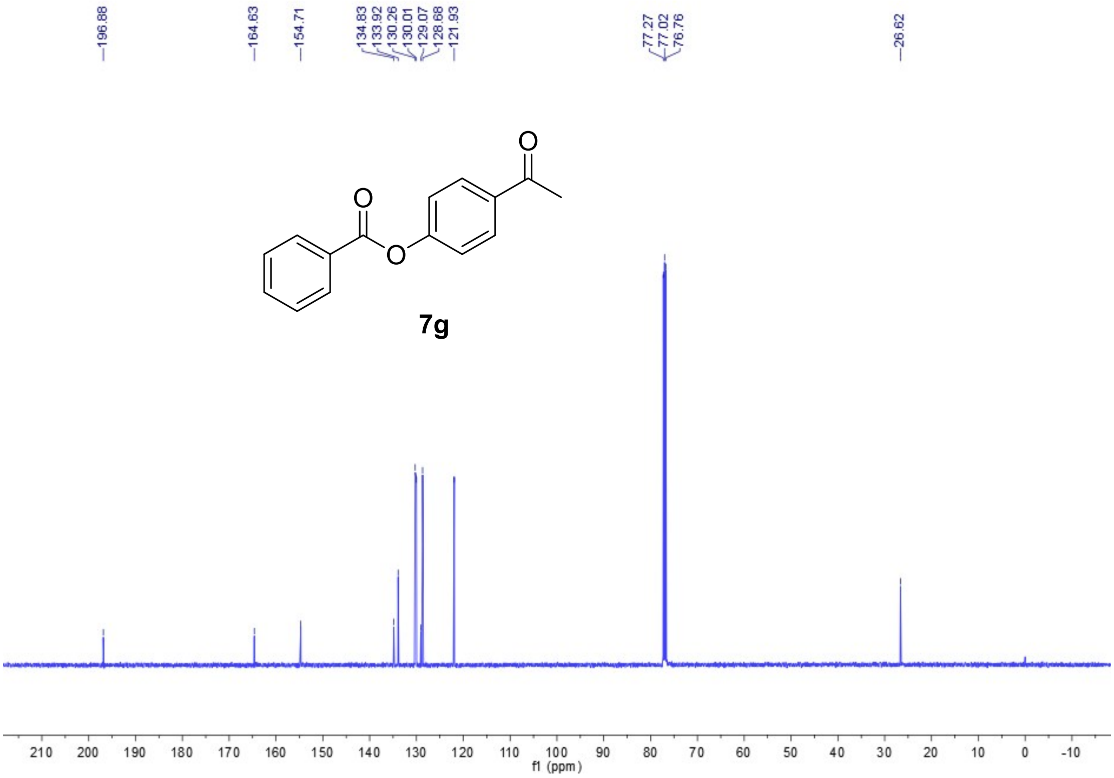
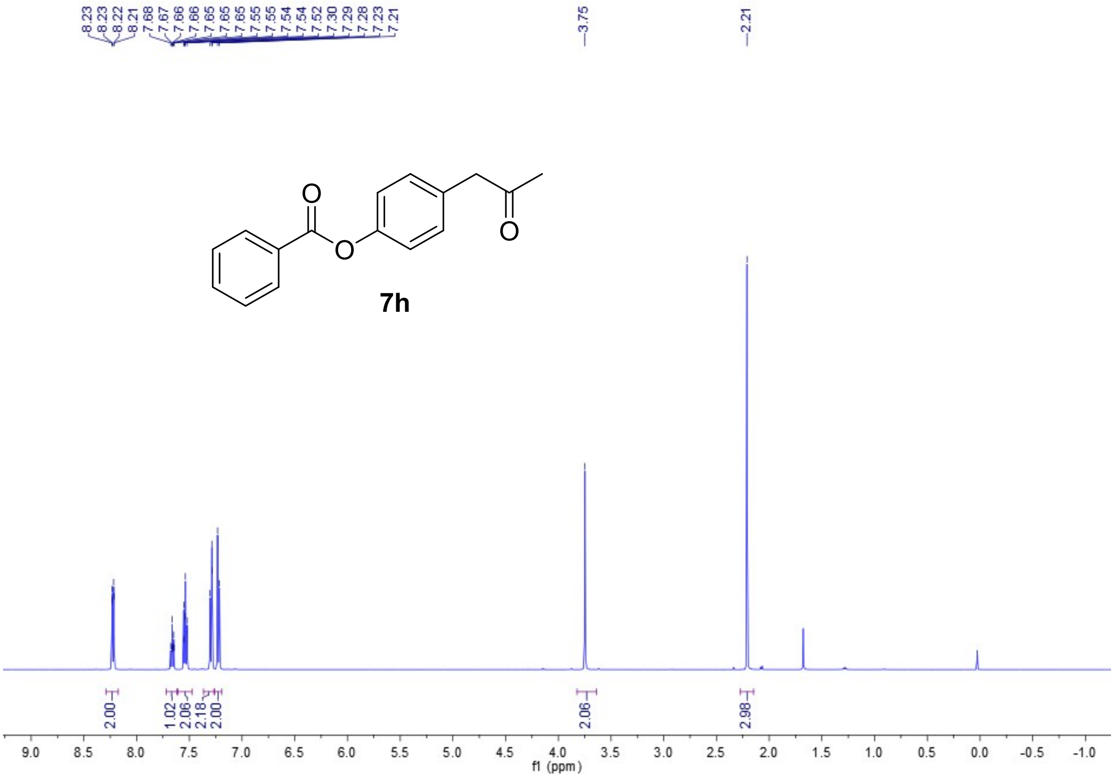


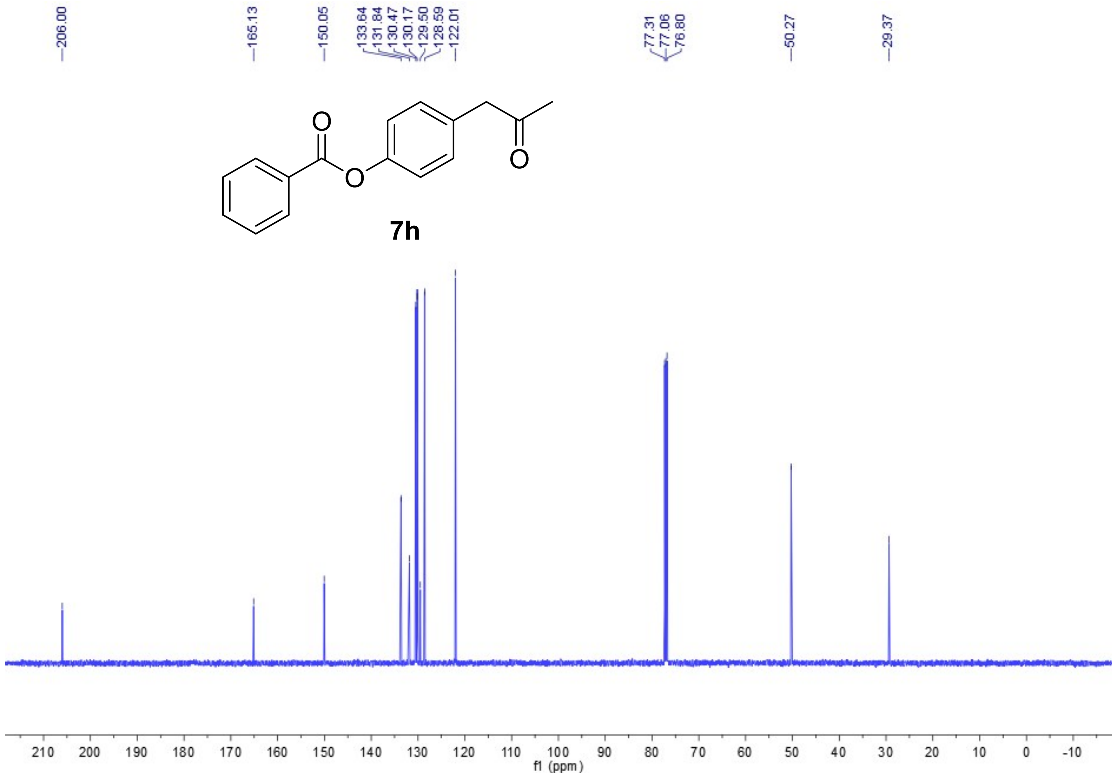


7g

^{1}H and ^{13}C NMR spectra of **7g**



7h



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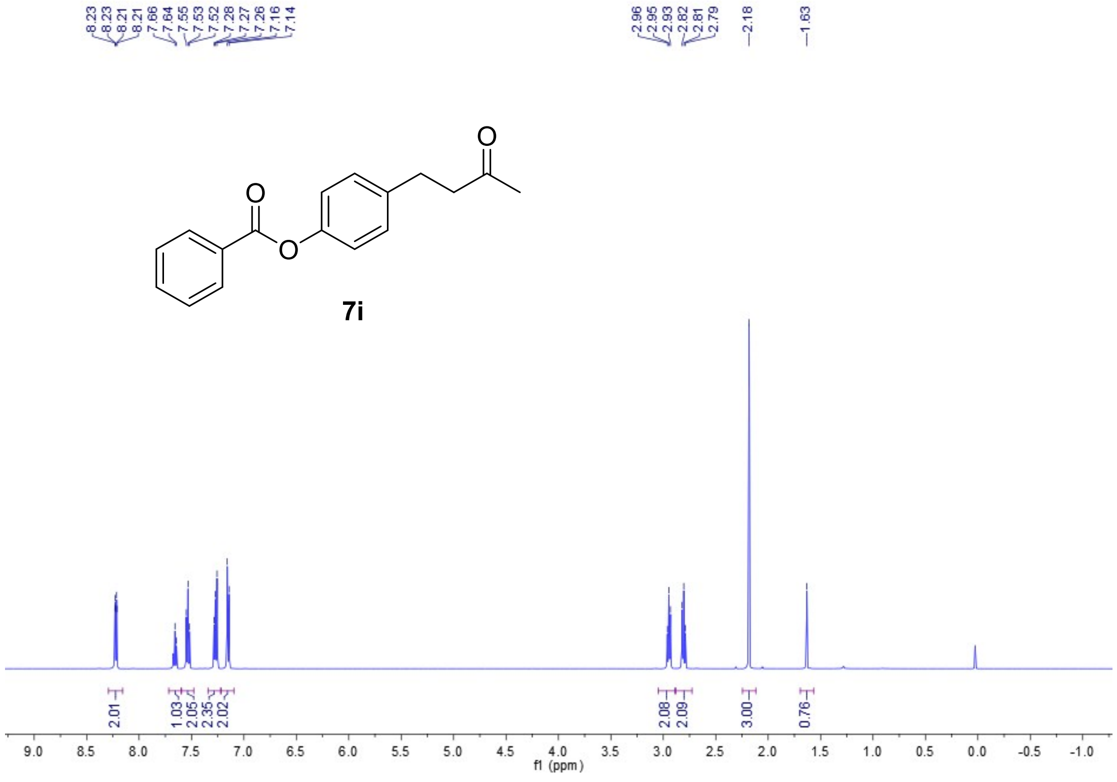

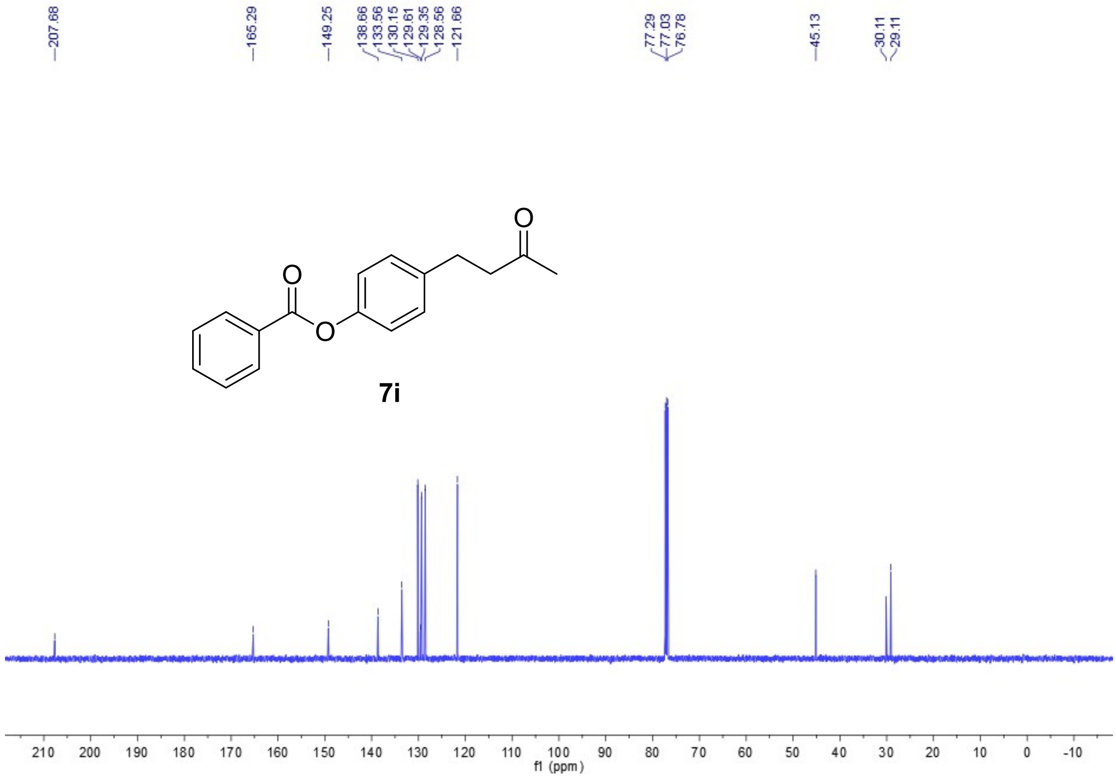

7i

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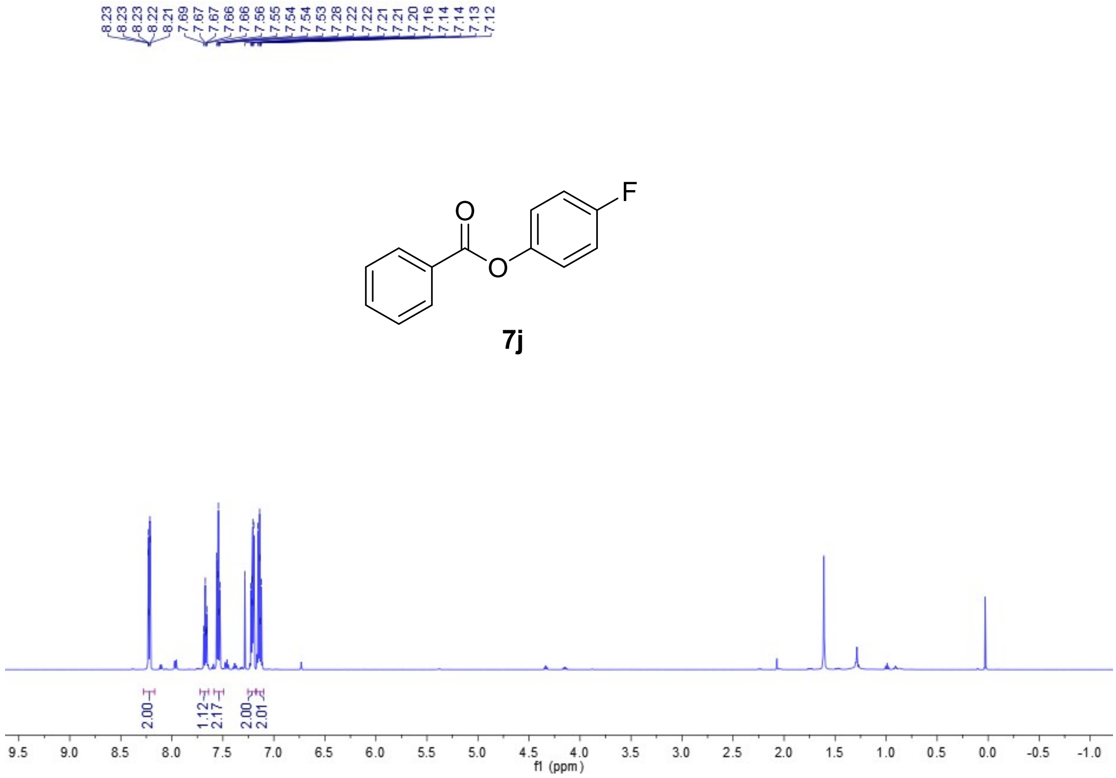
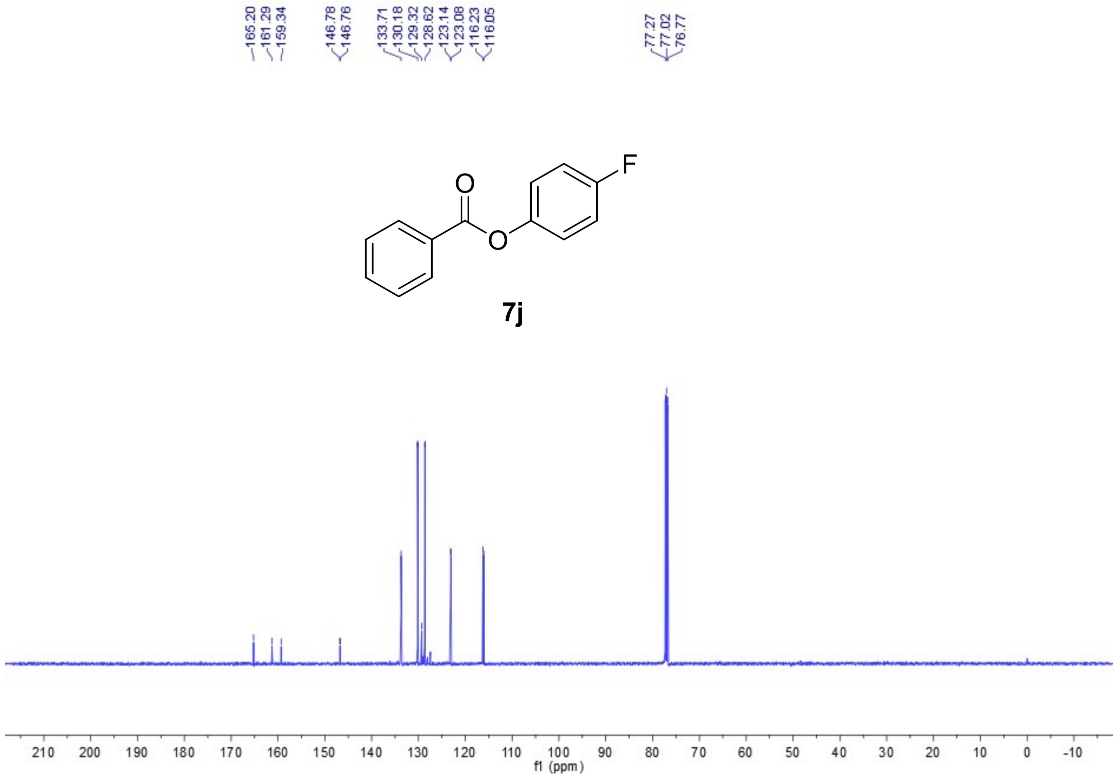


7j



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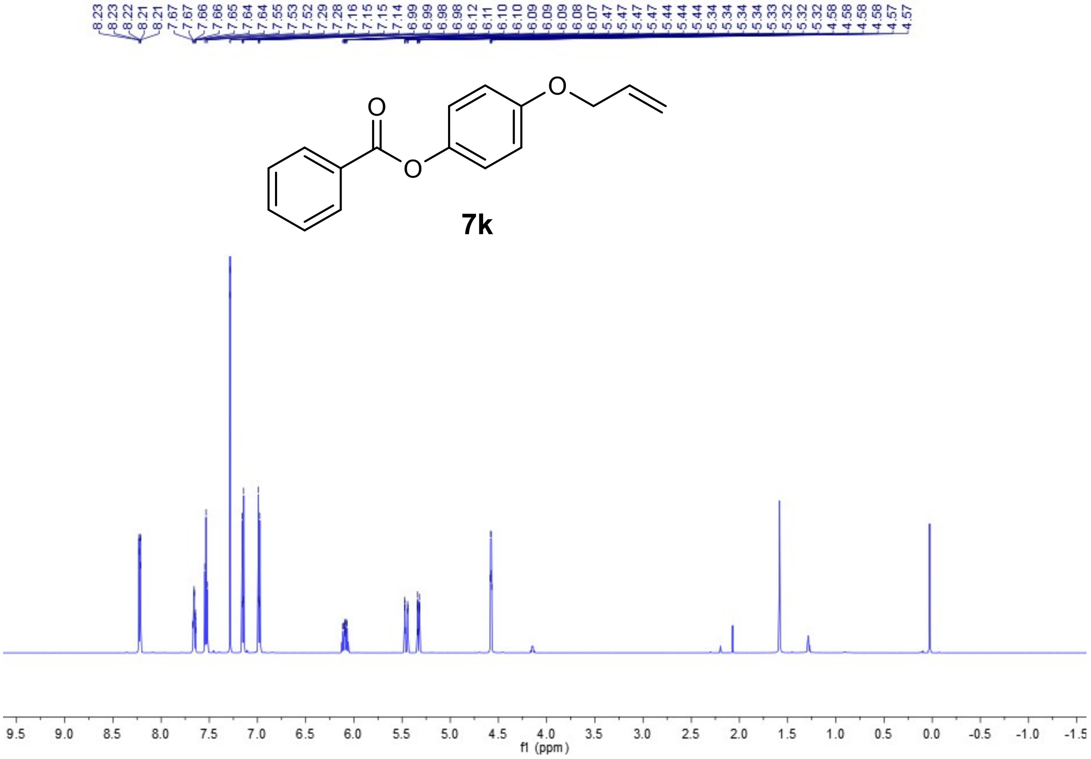

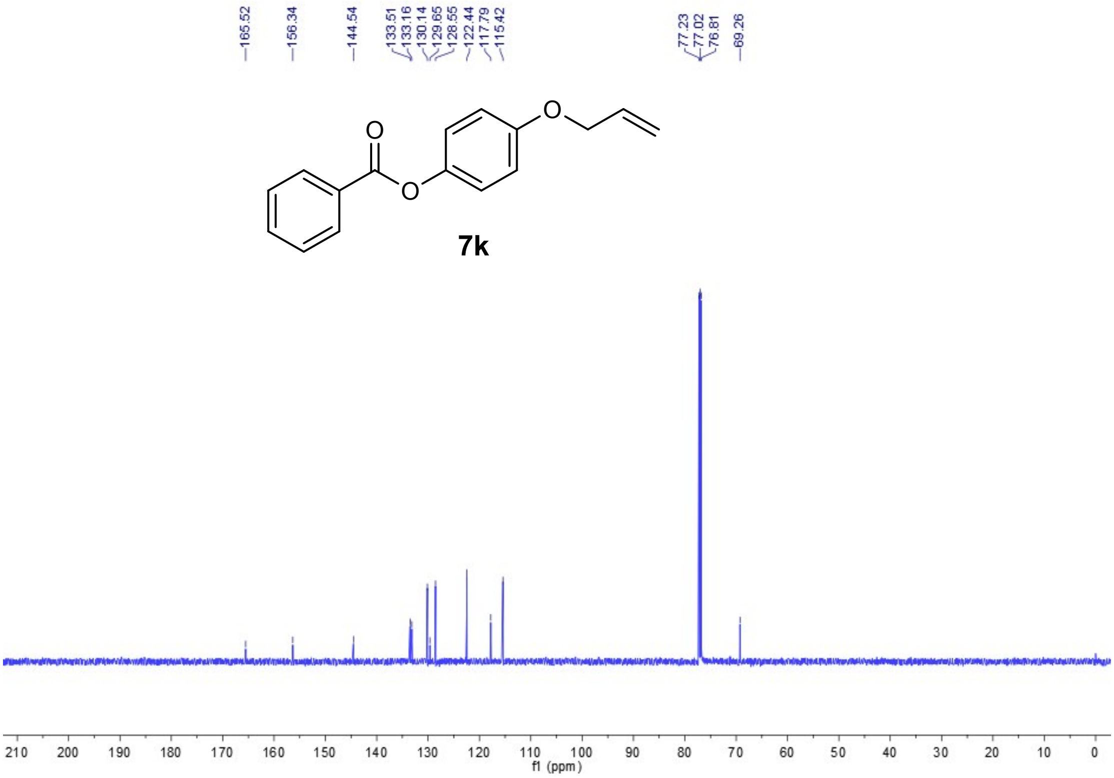

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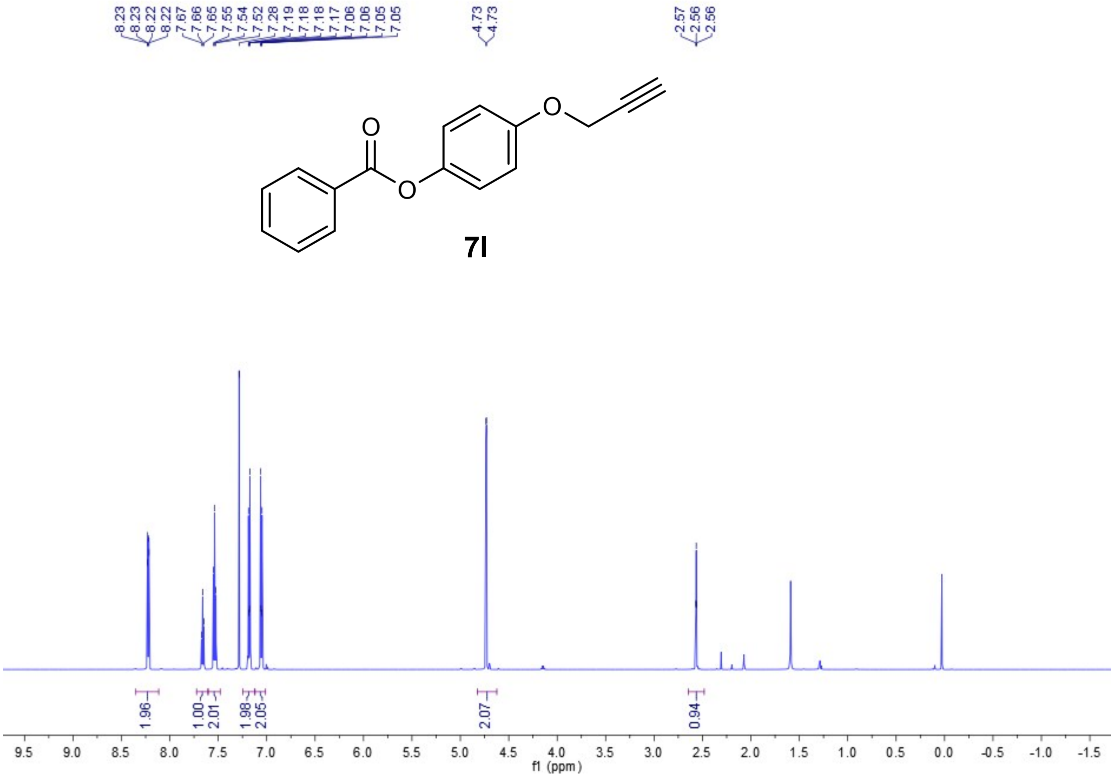

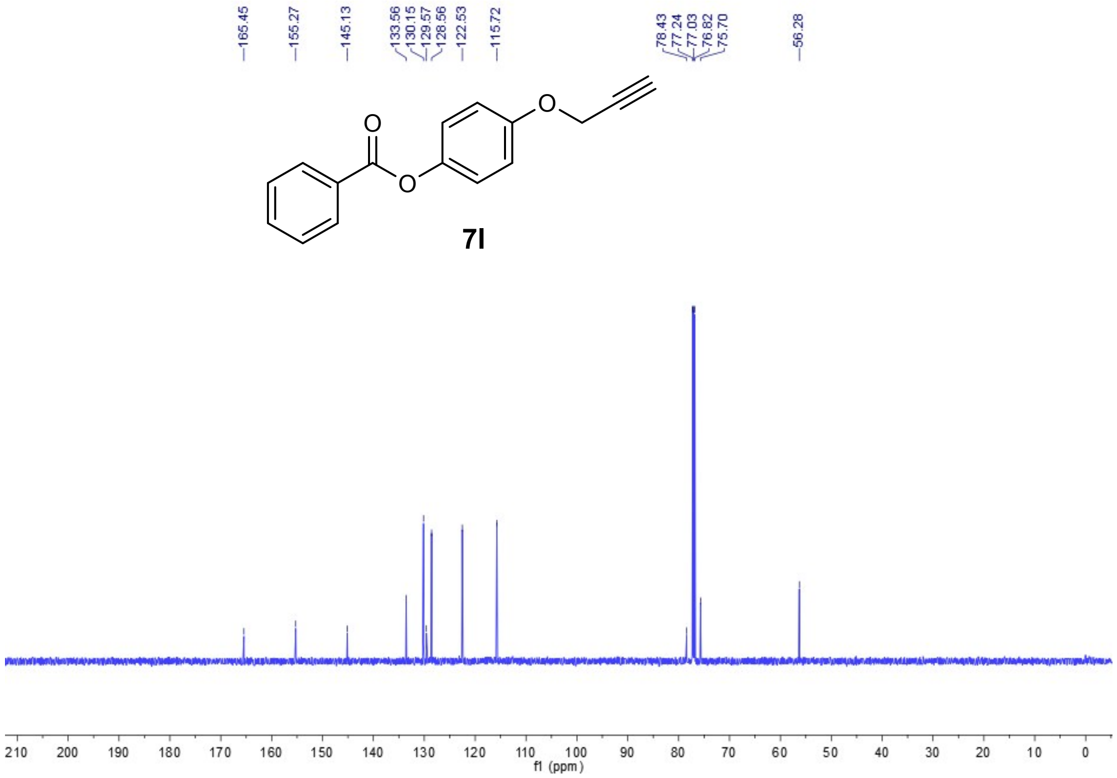

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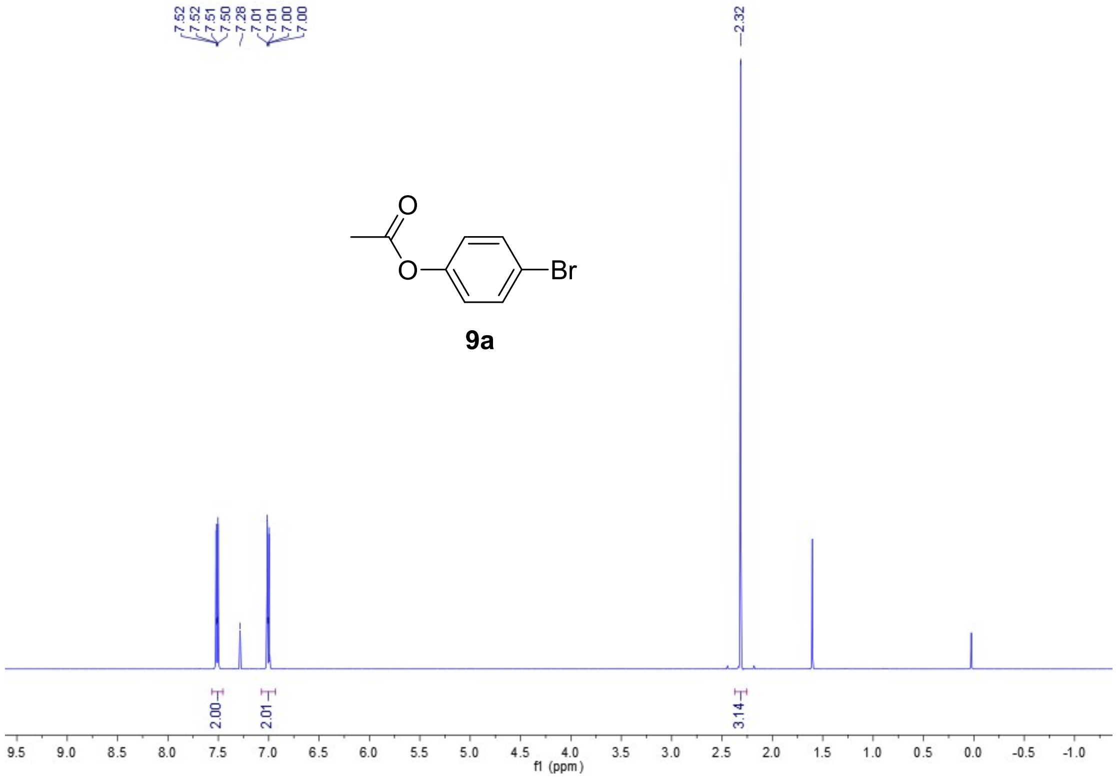

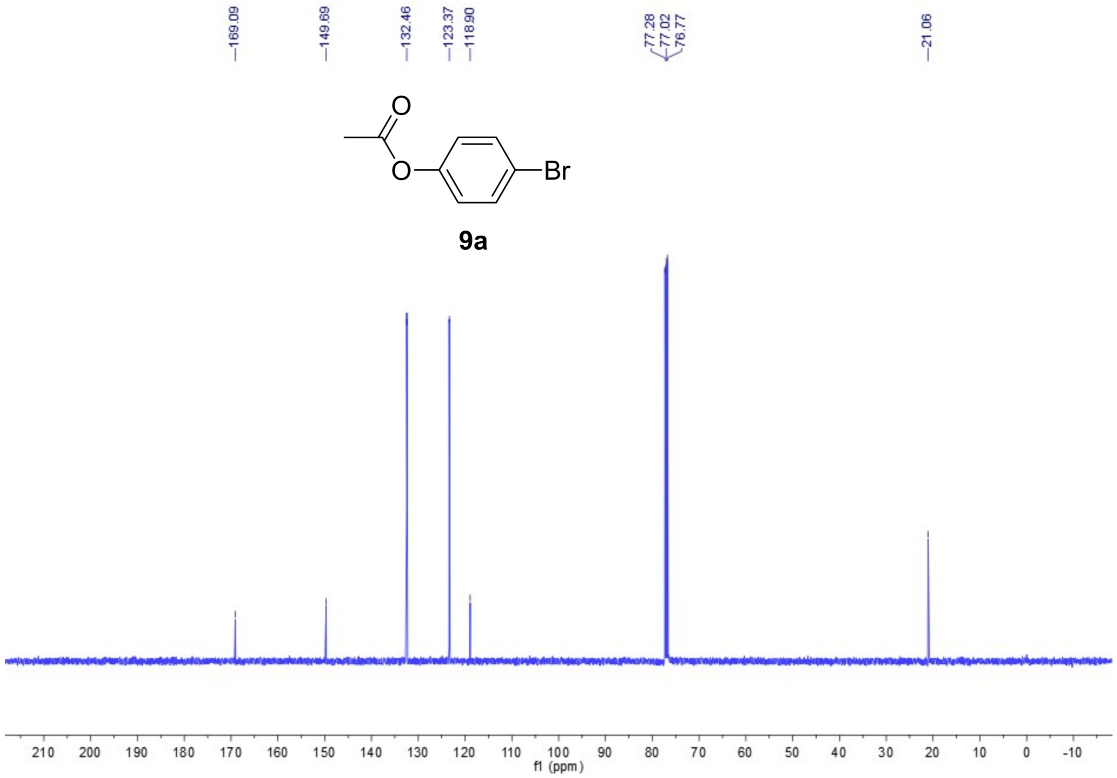

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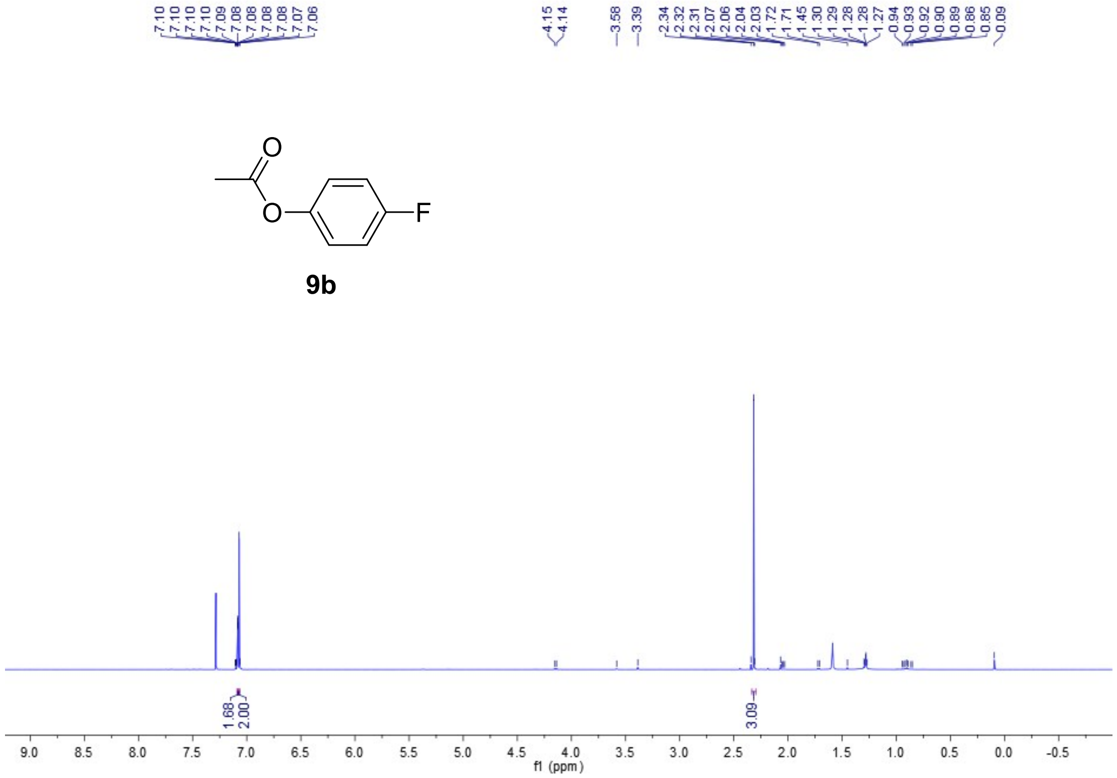

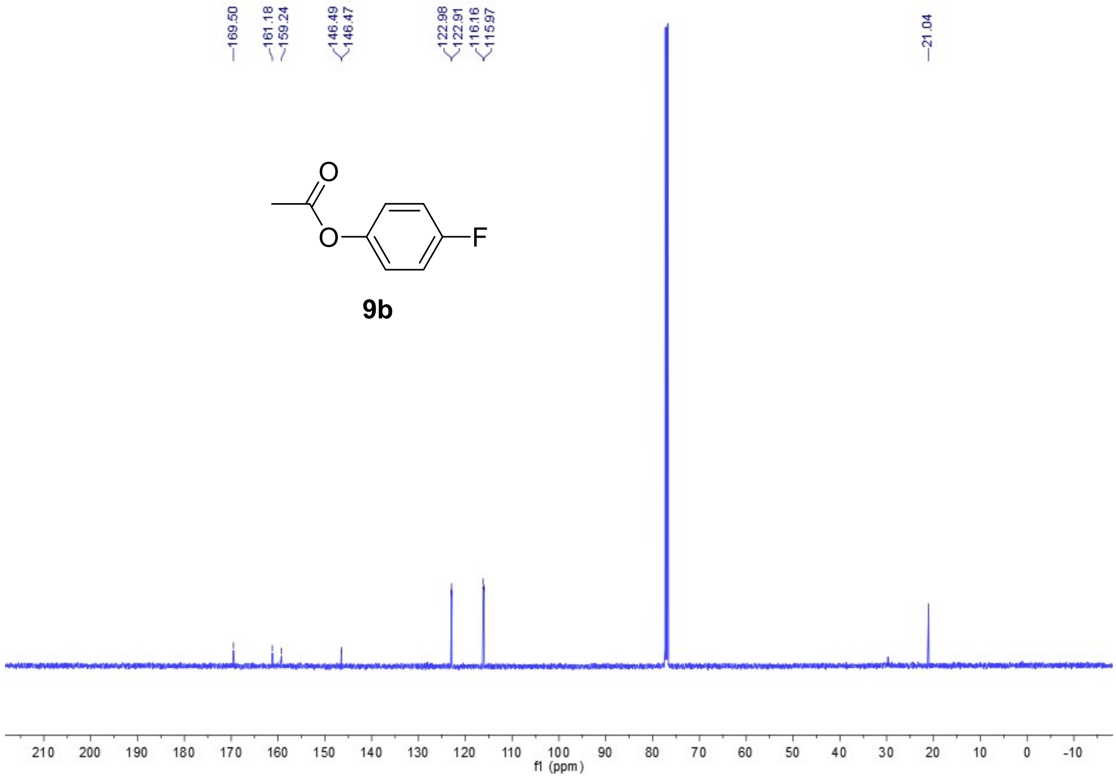

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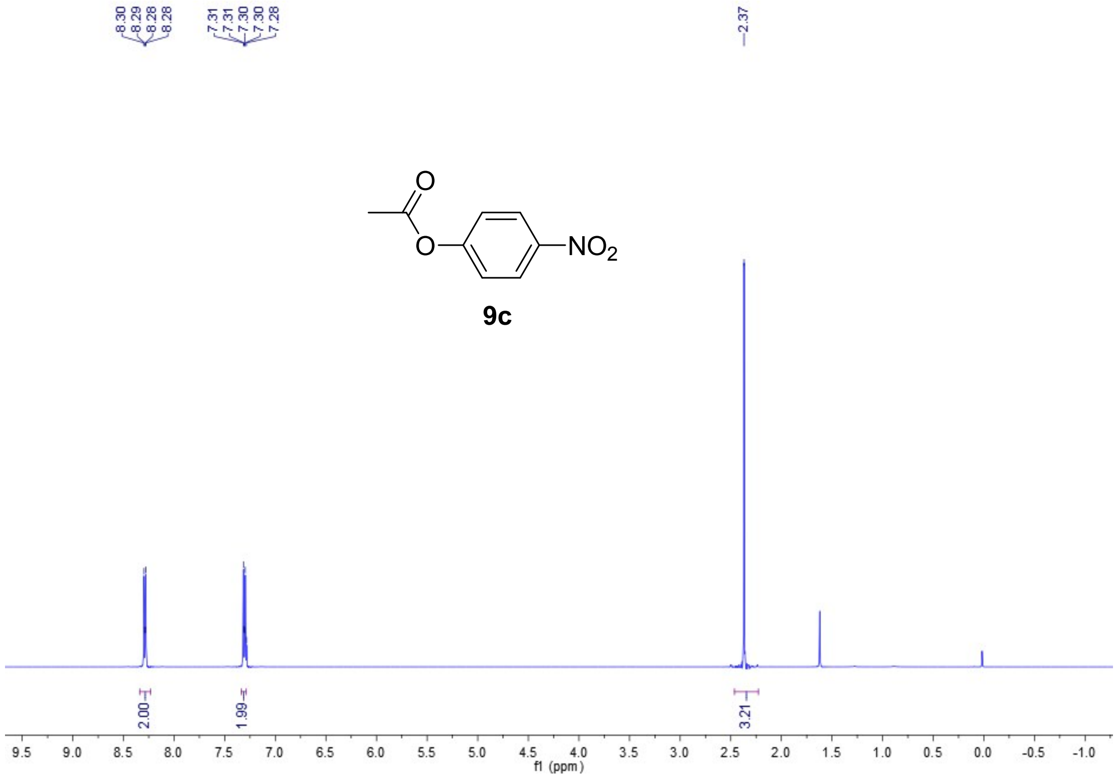

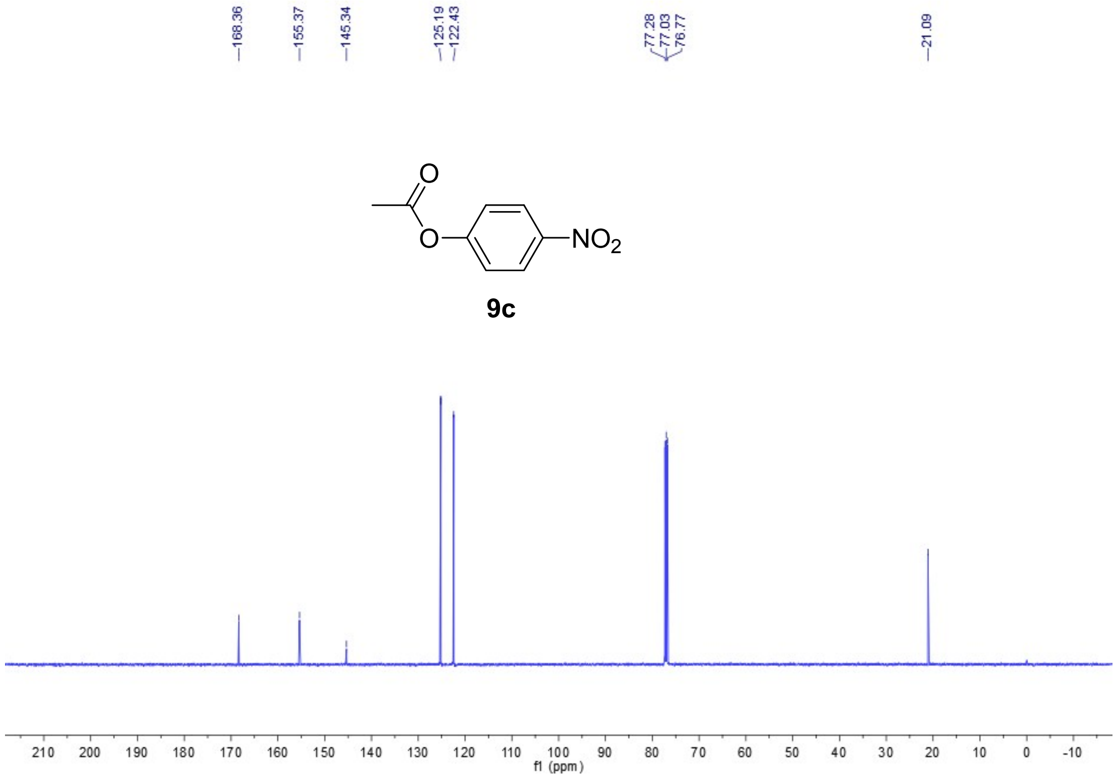

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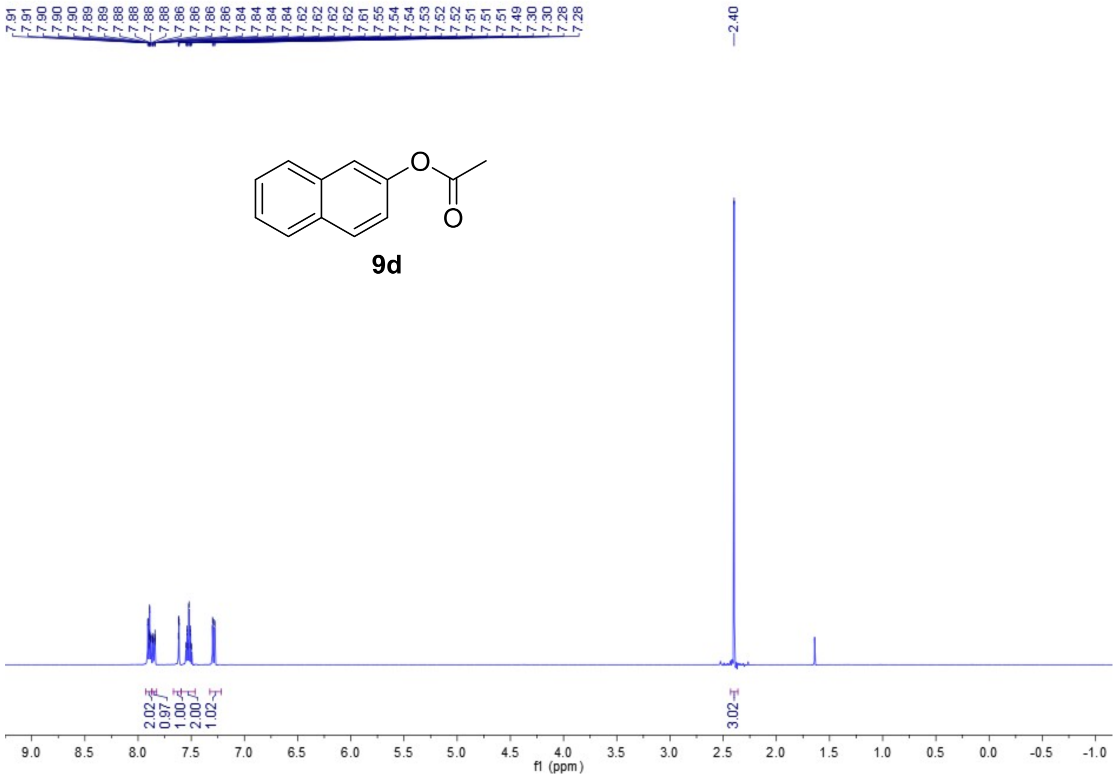

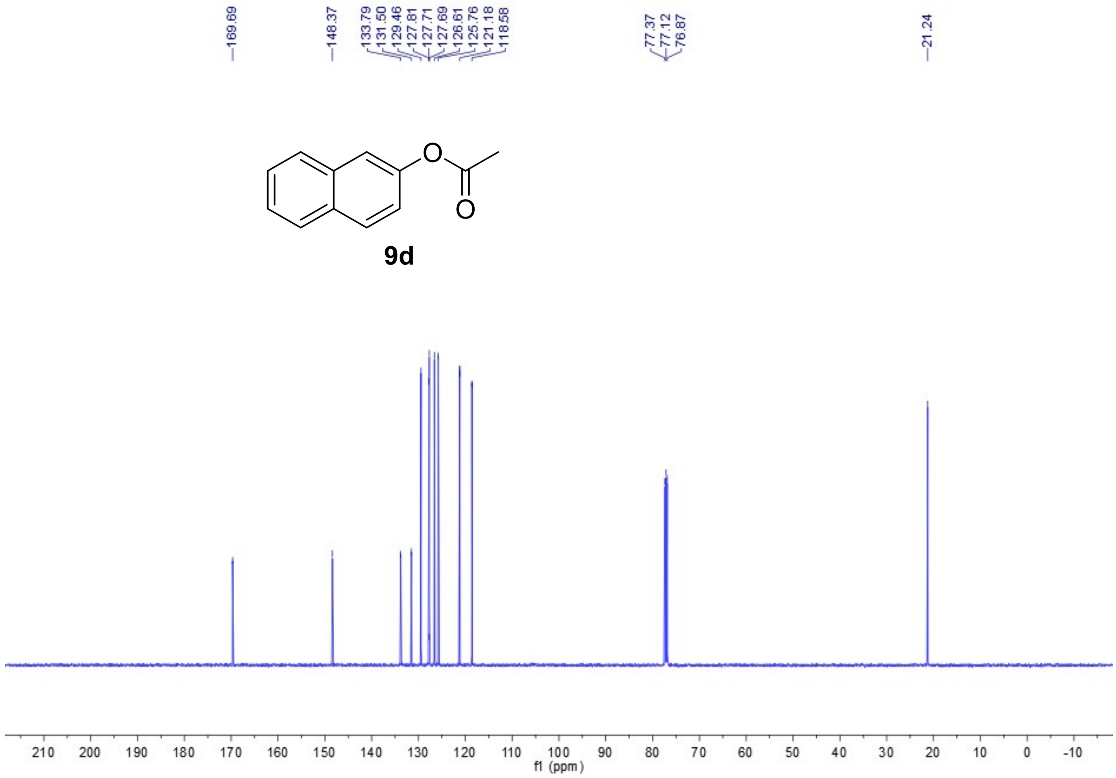

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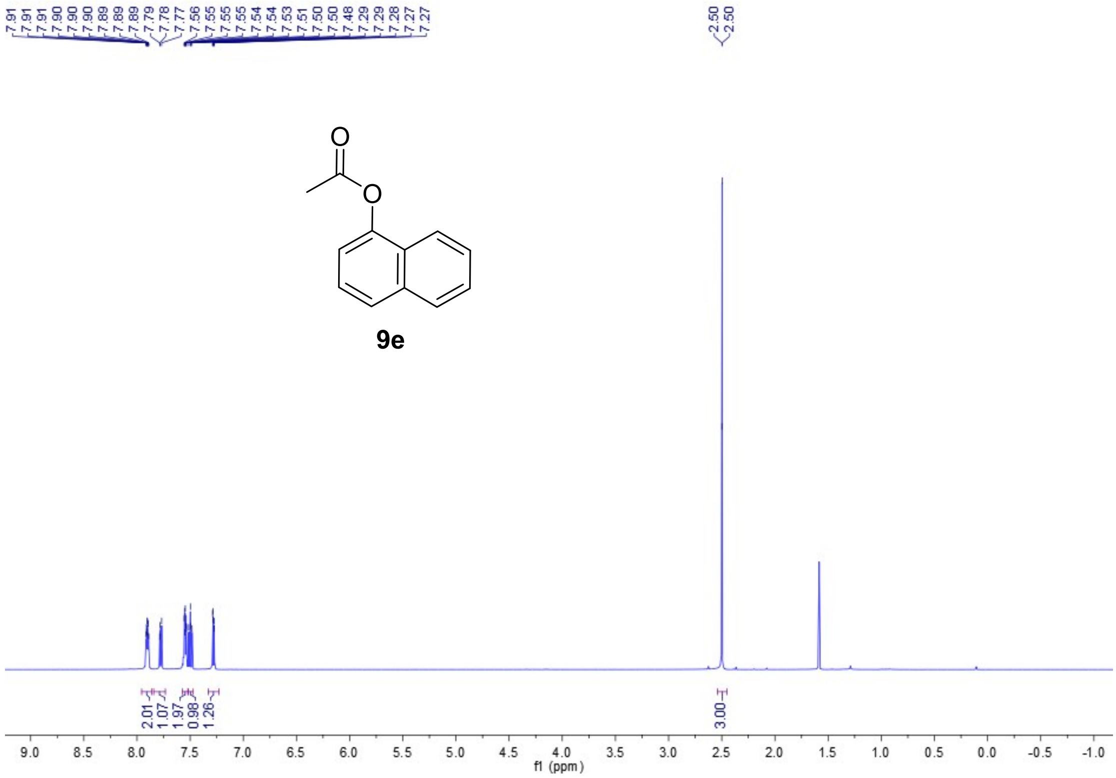

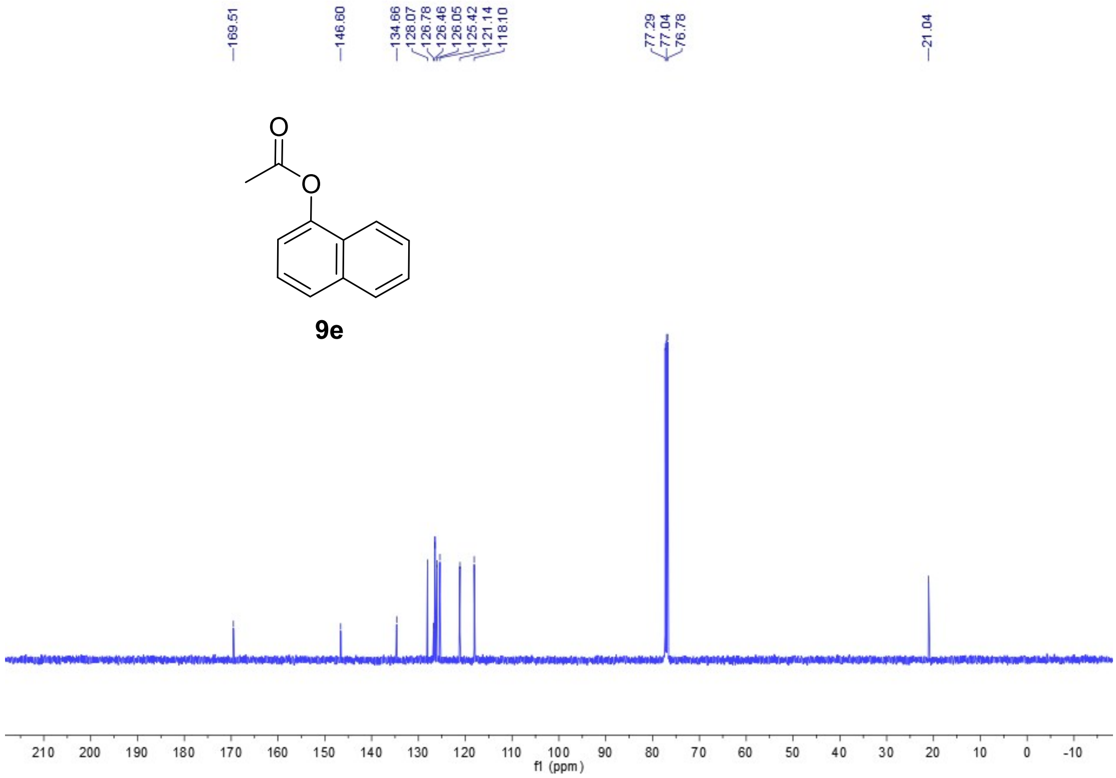
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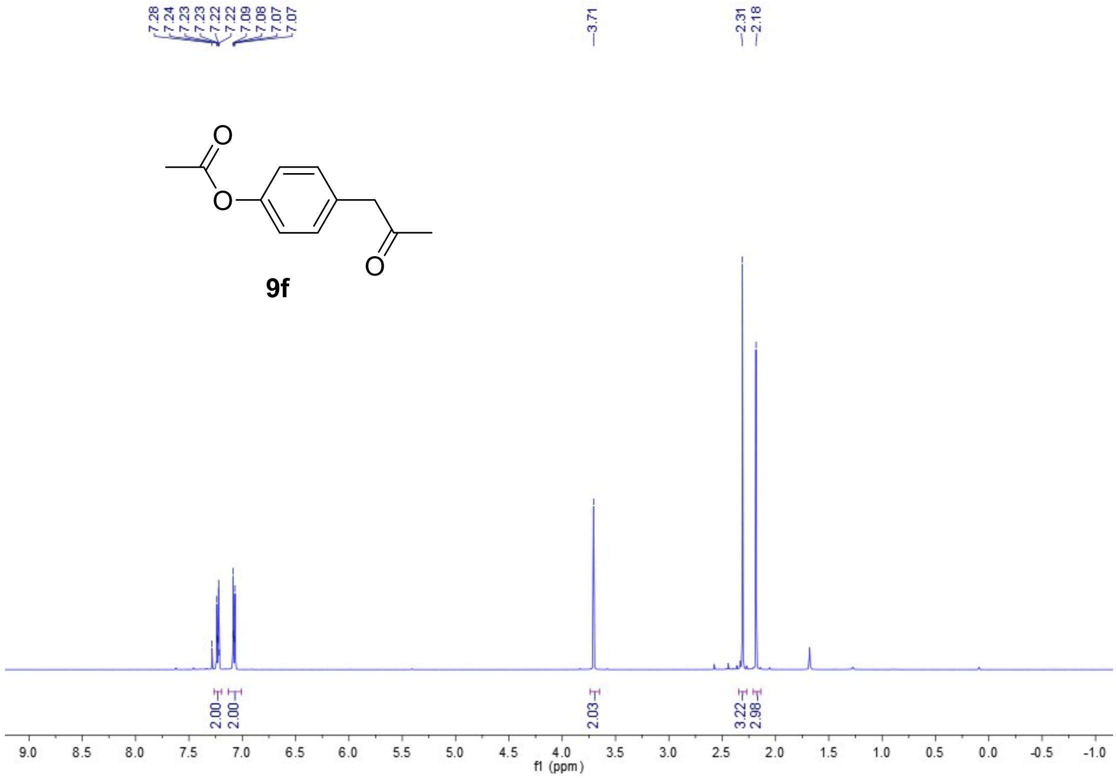
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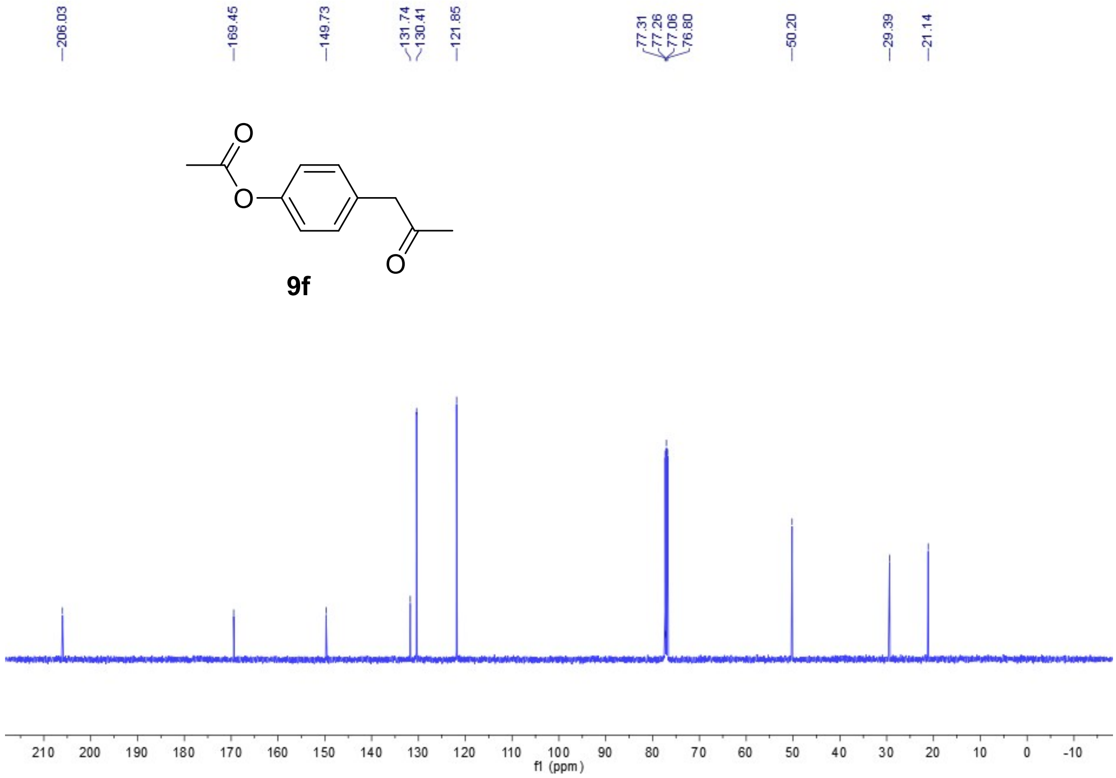

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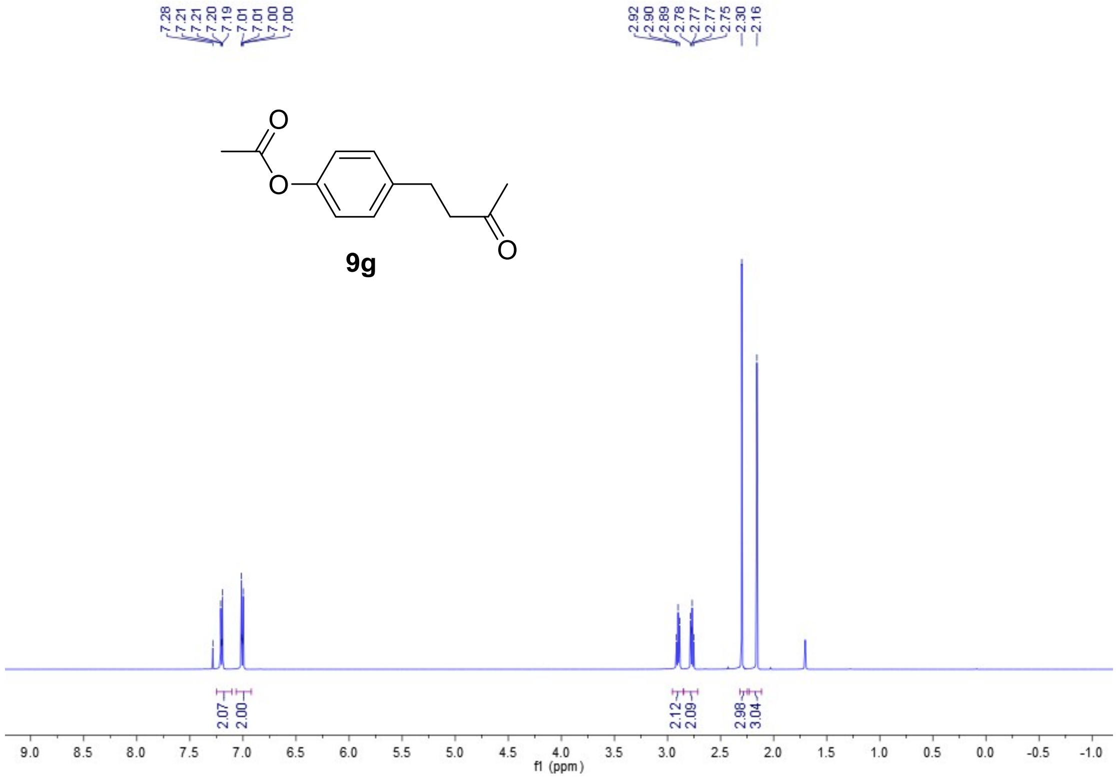

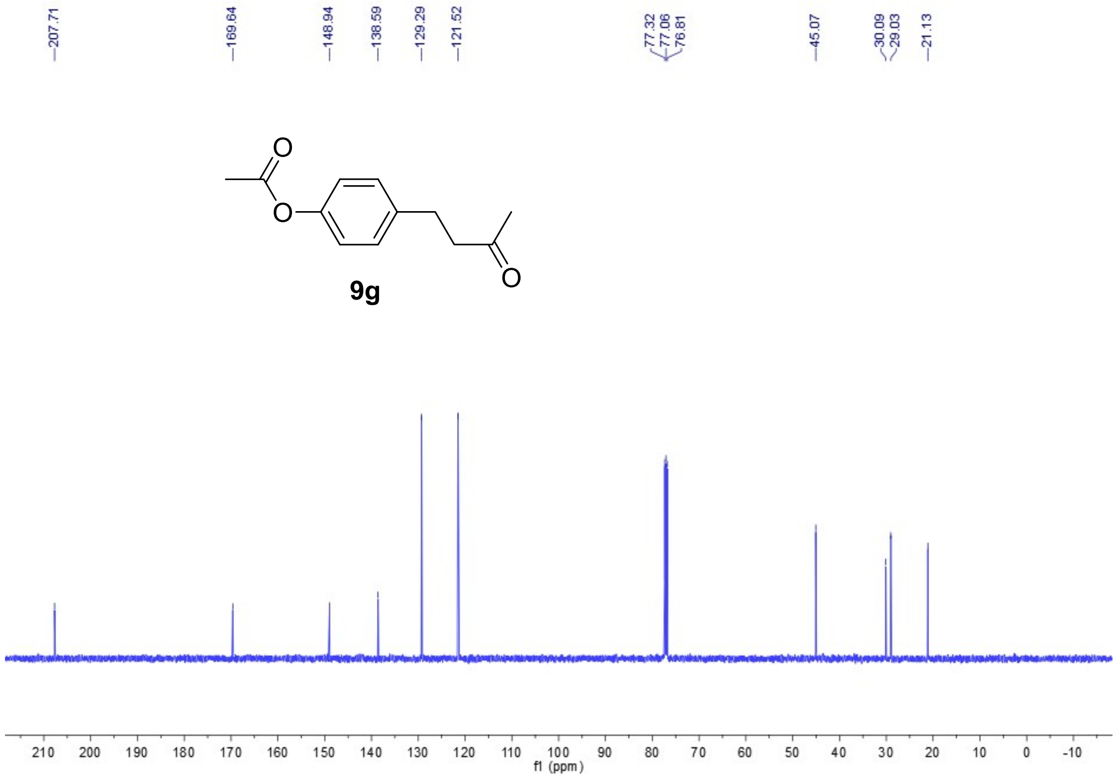

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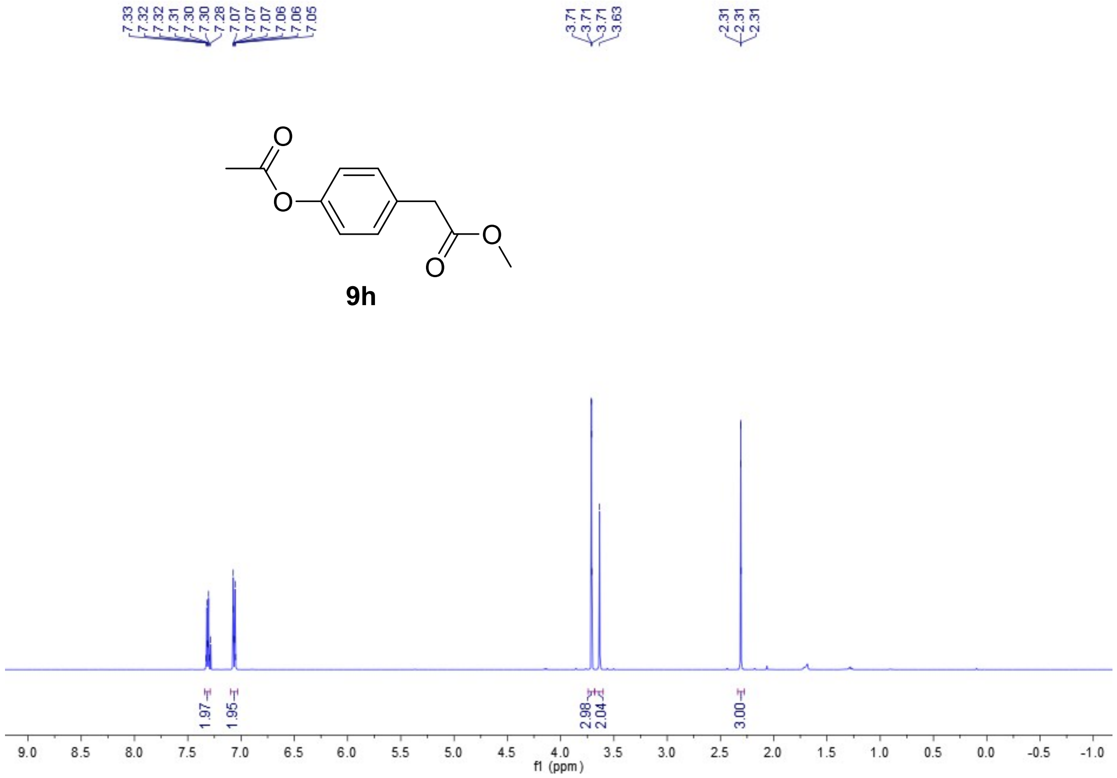
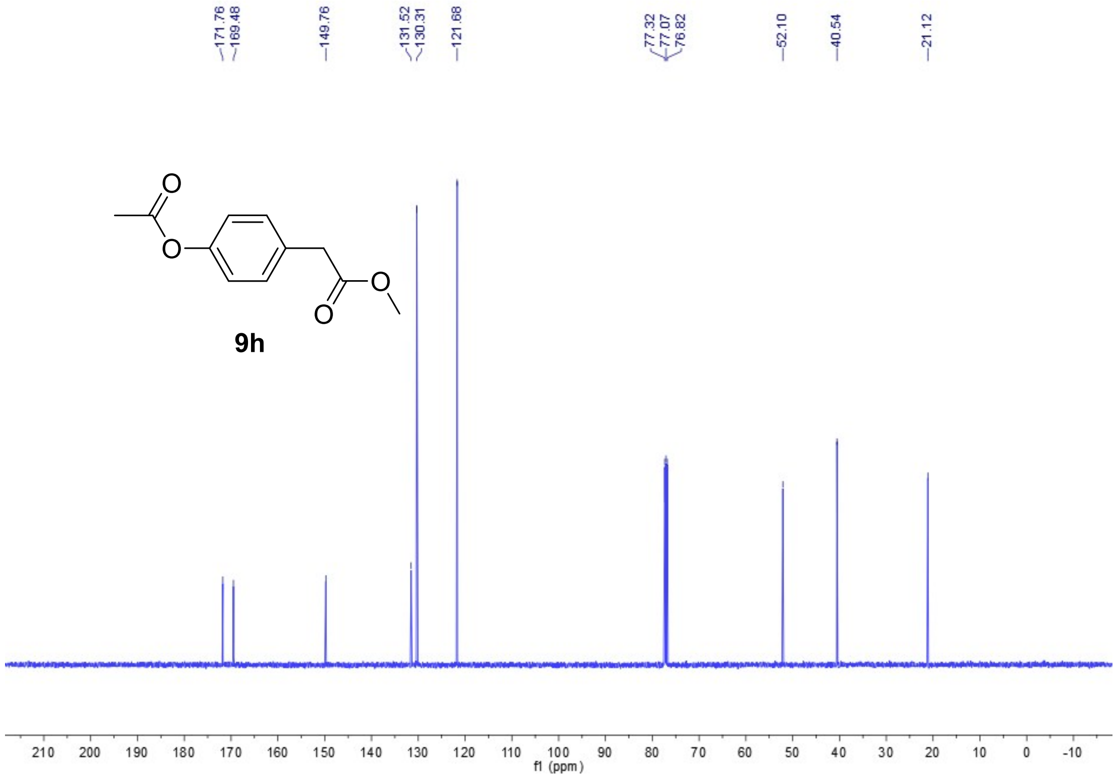
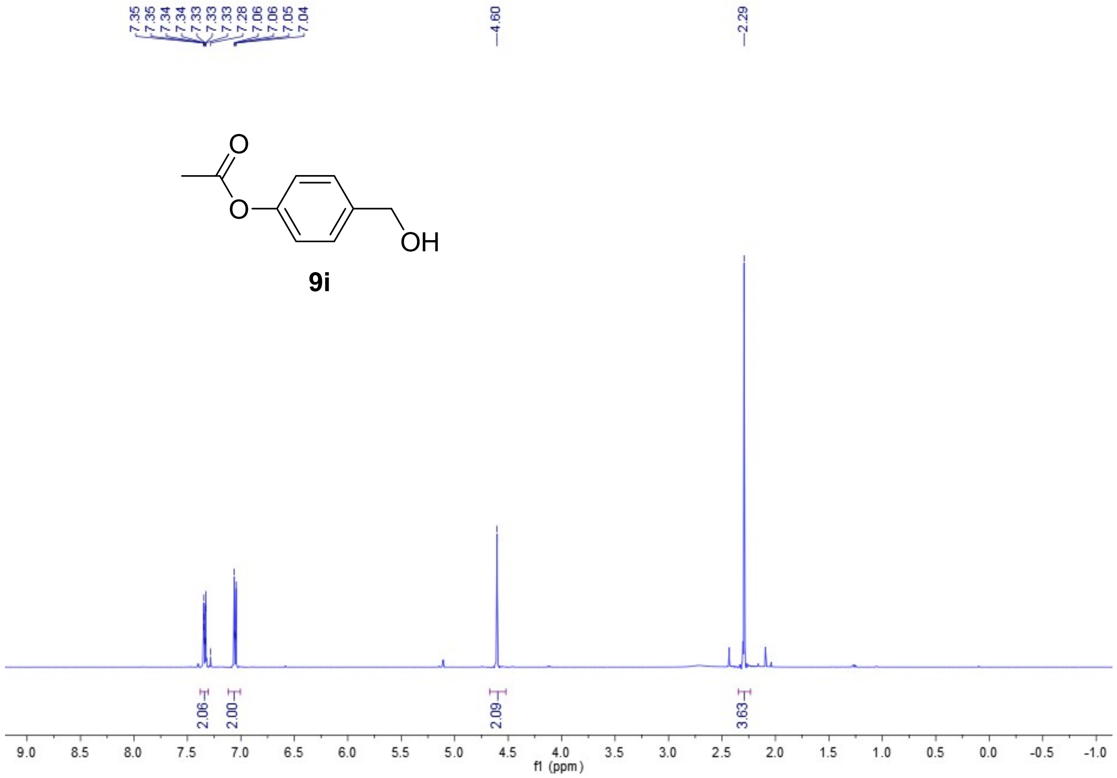
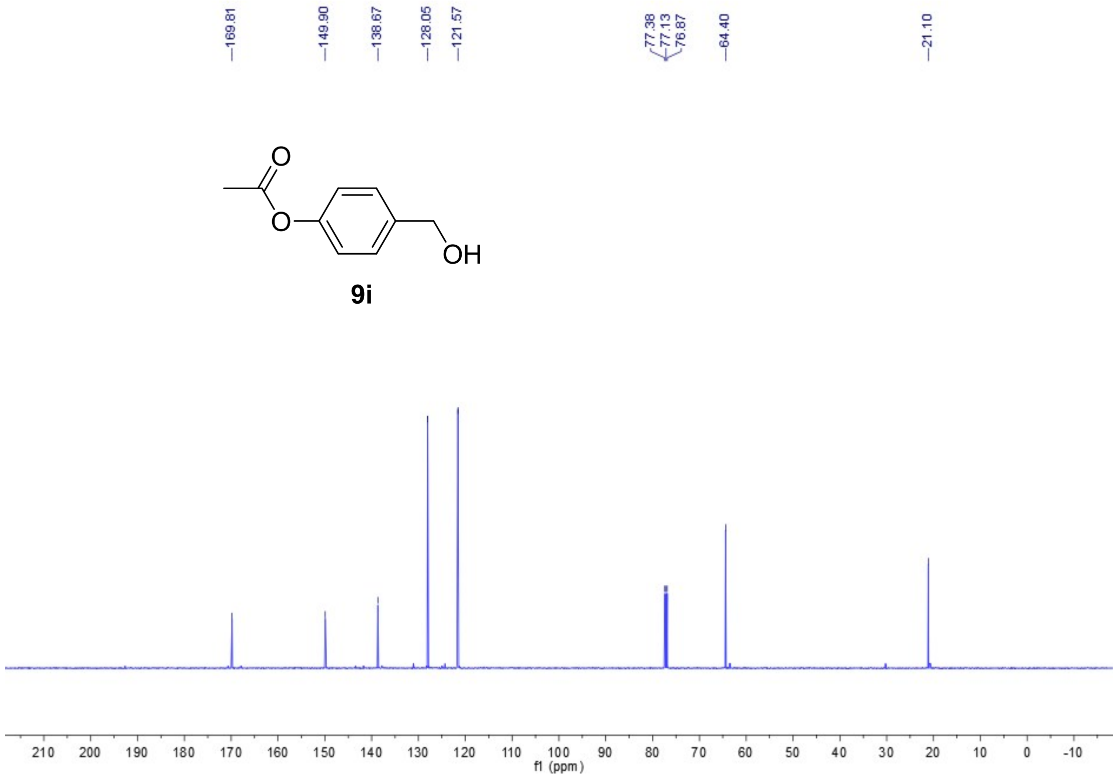




^{1}H and ^{13}C NMR spectra of **9h**





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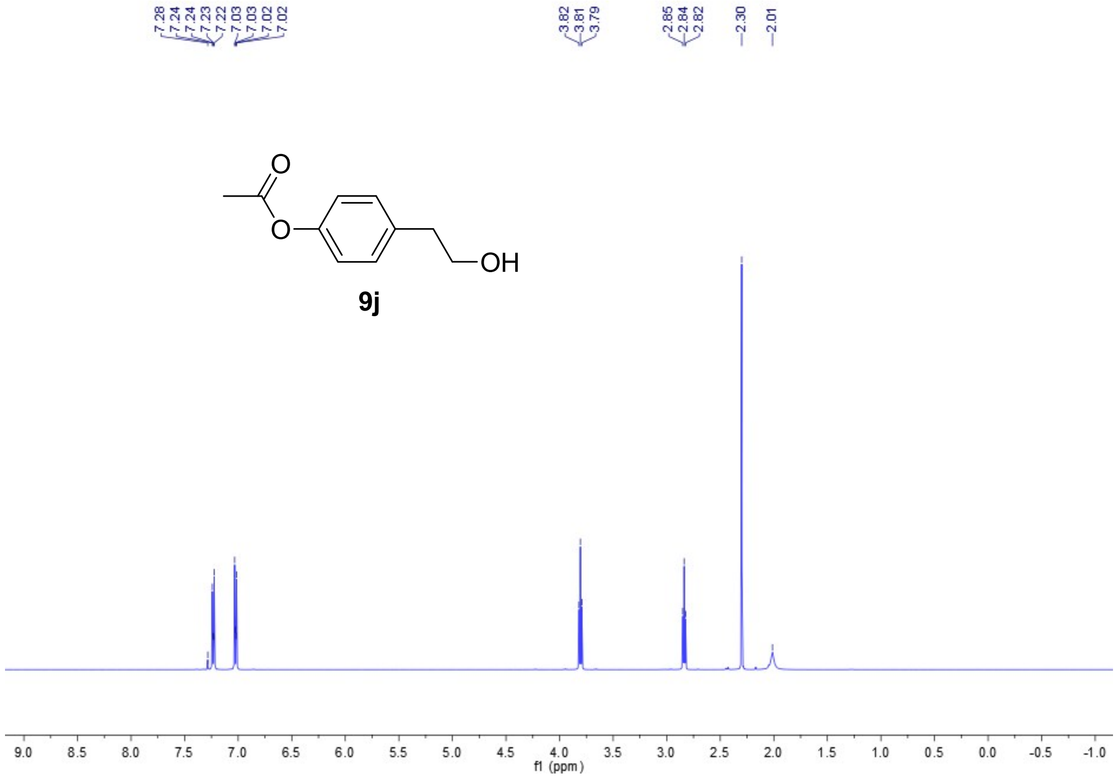

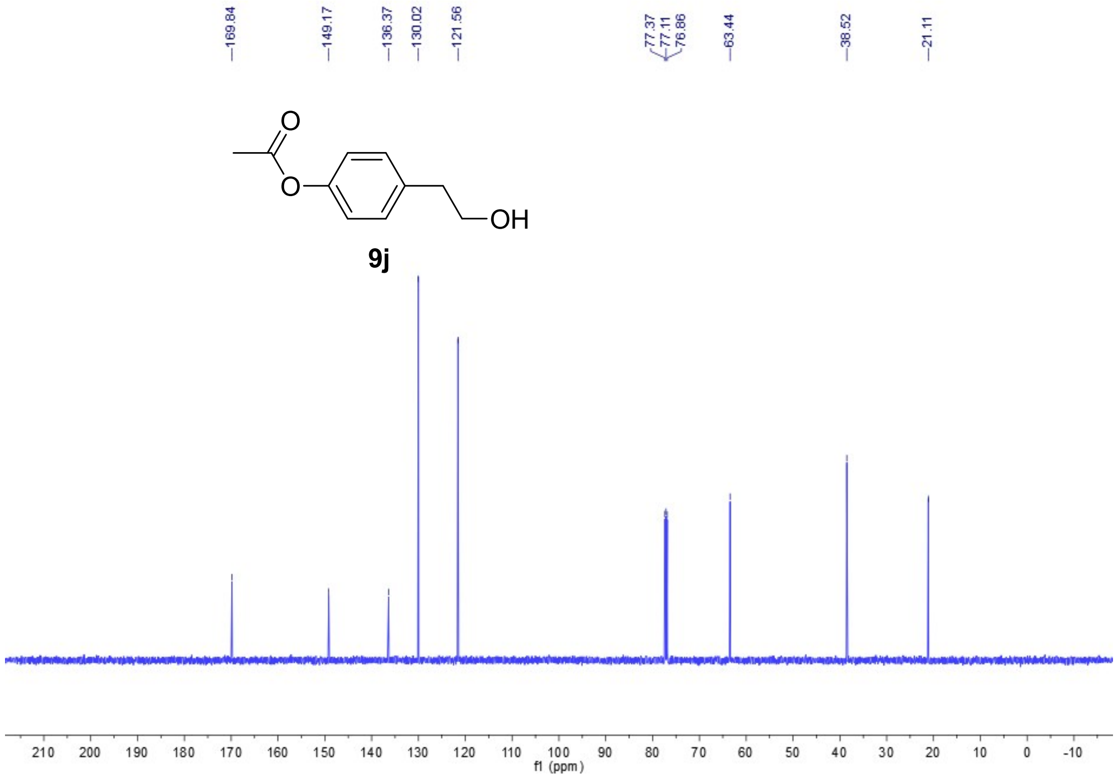

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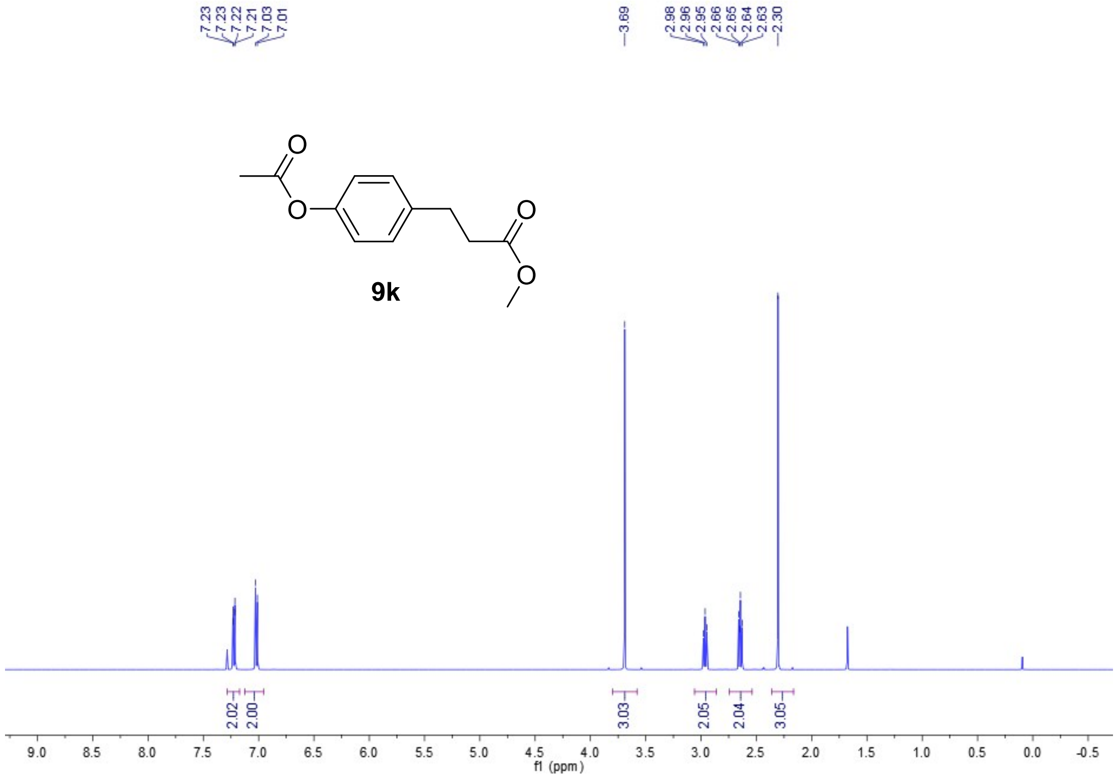
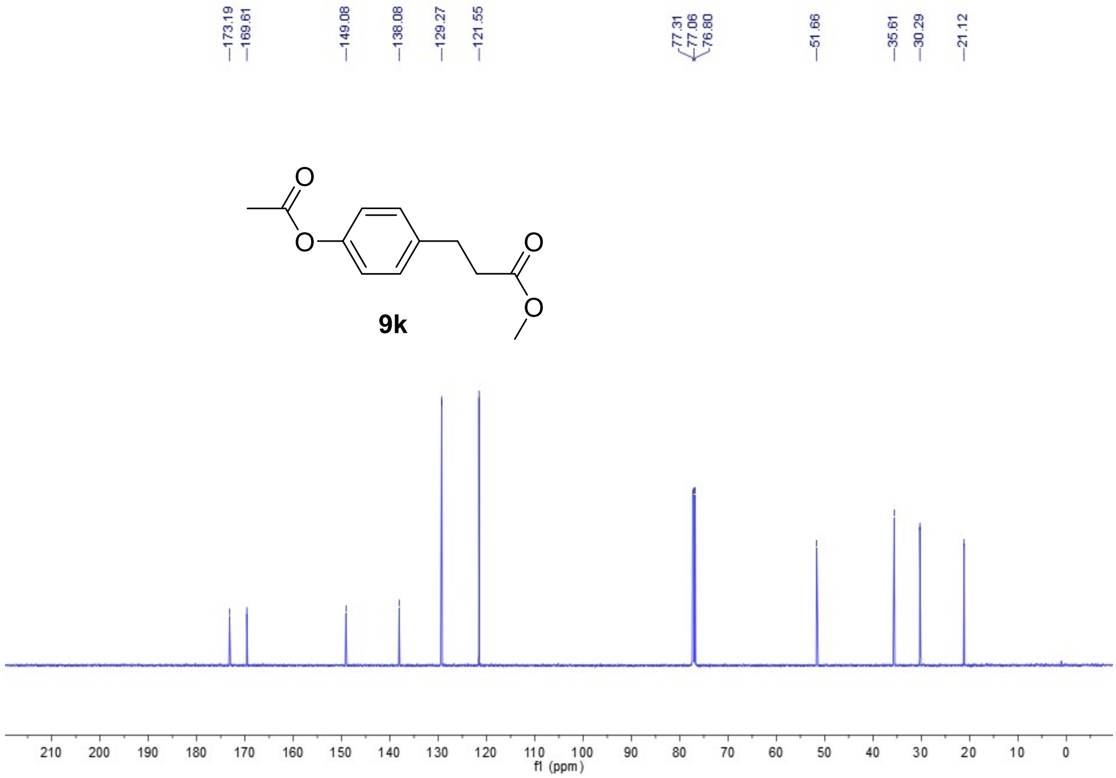
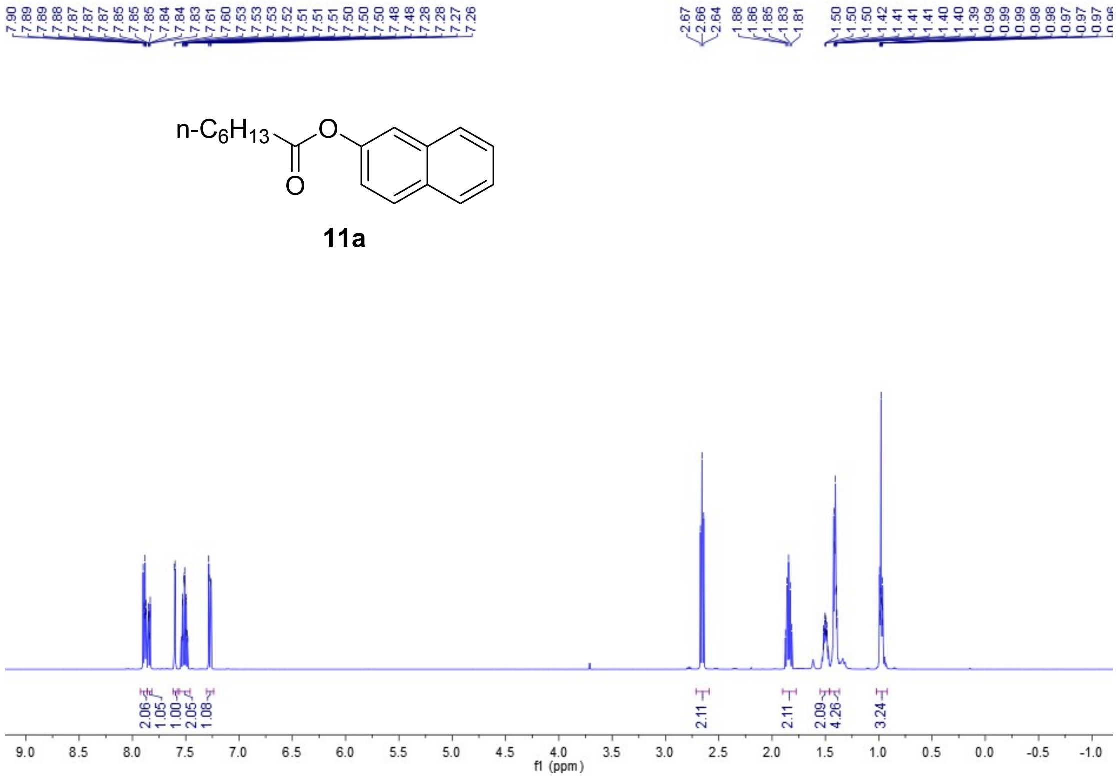
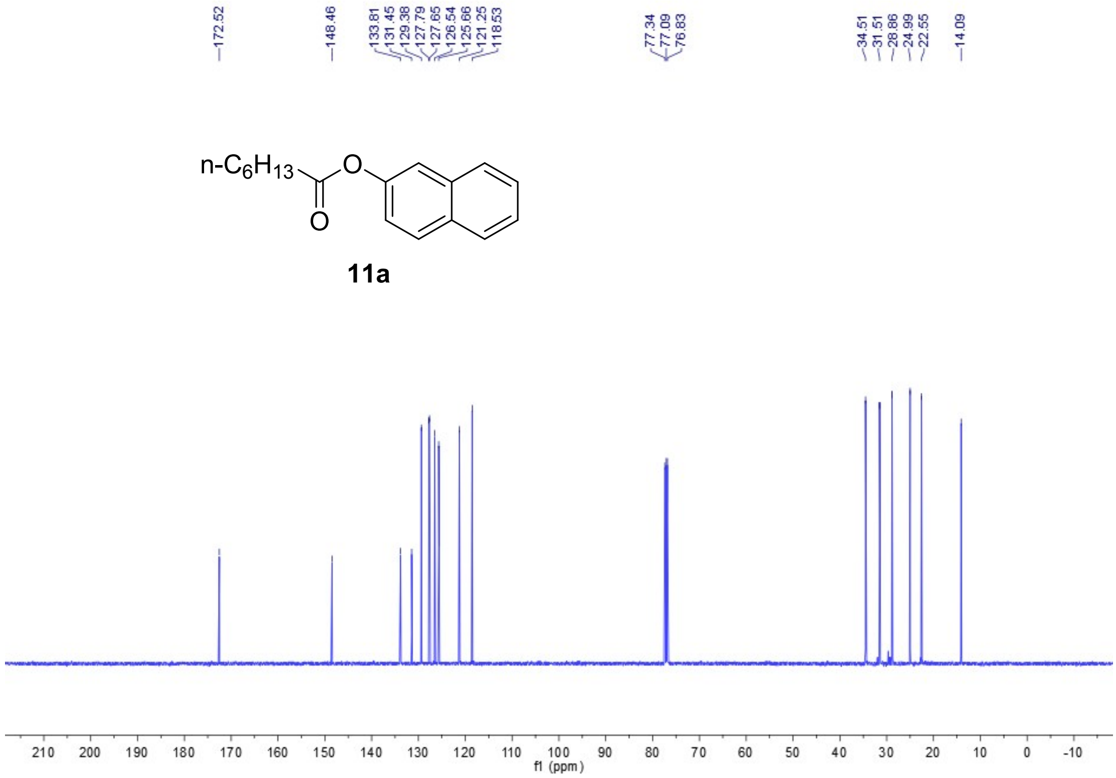




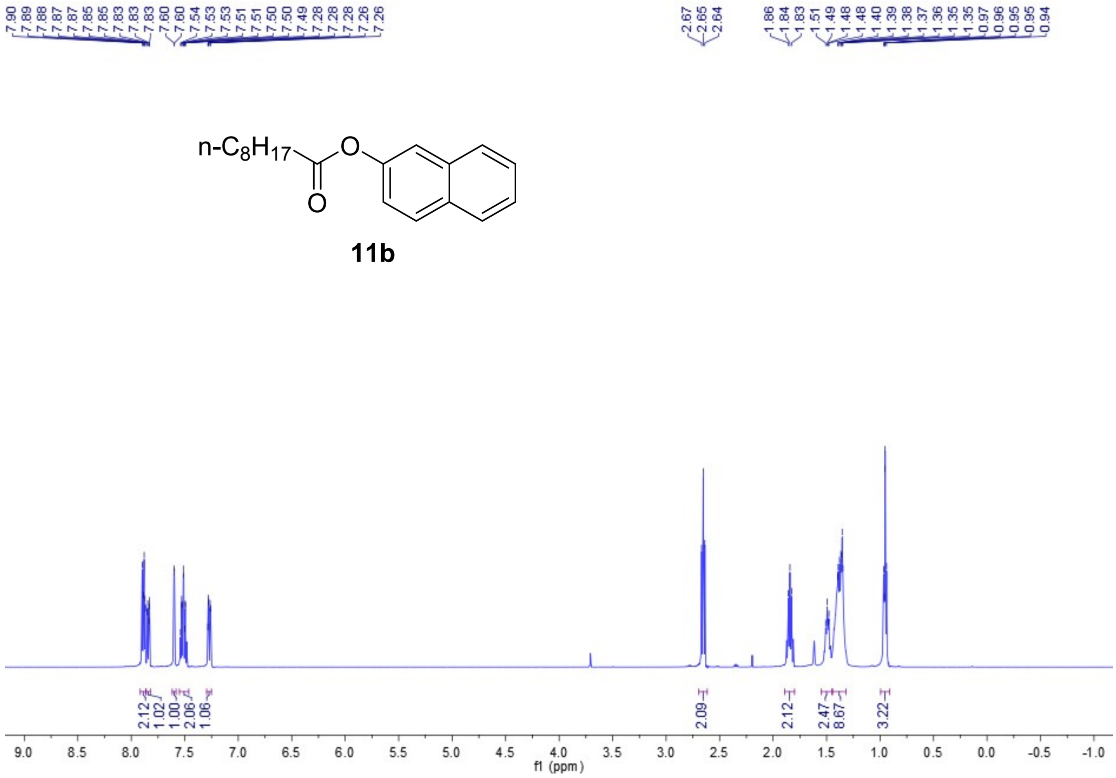
^{1}H and ^{13}C NMR spectra of **9k**



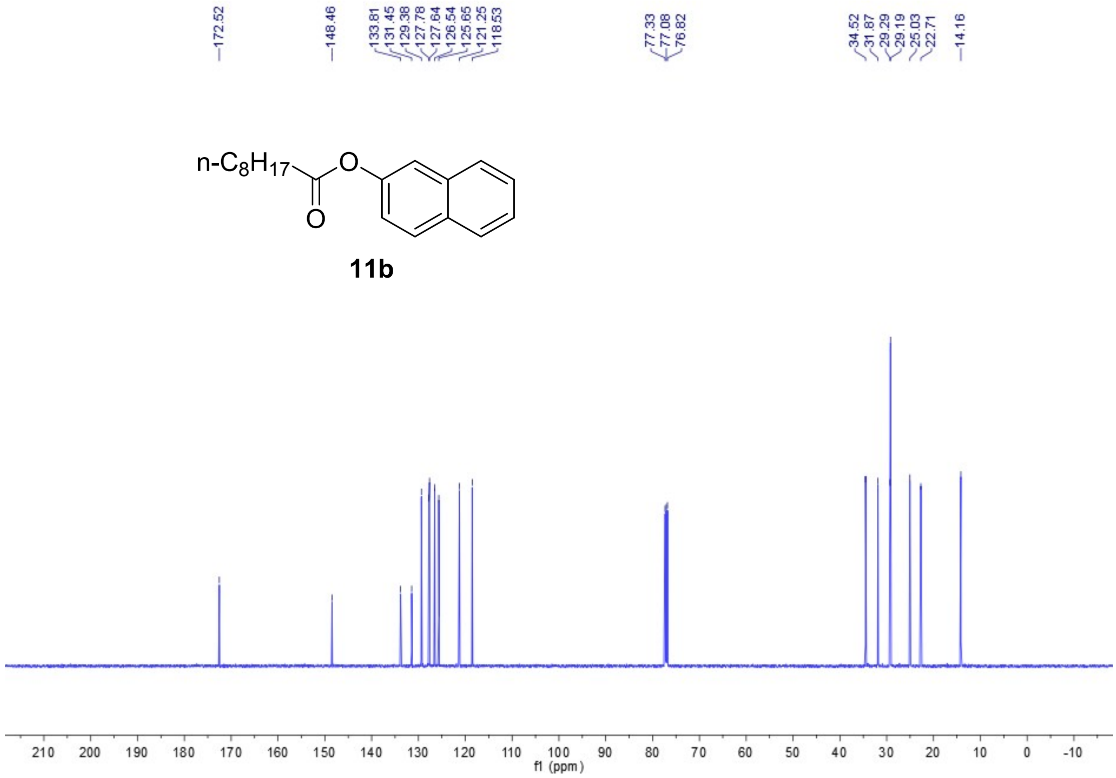


11a

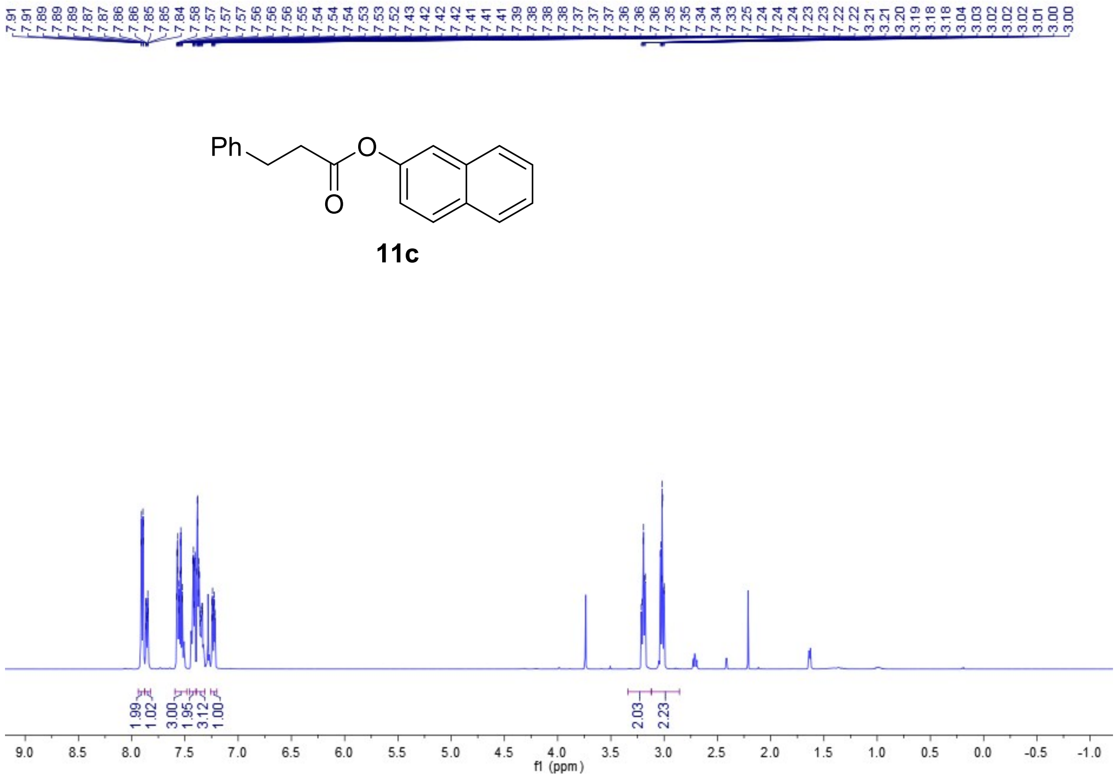
^{1}H and ^{13}C NMR spectra of **11a**

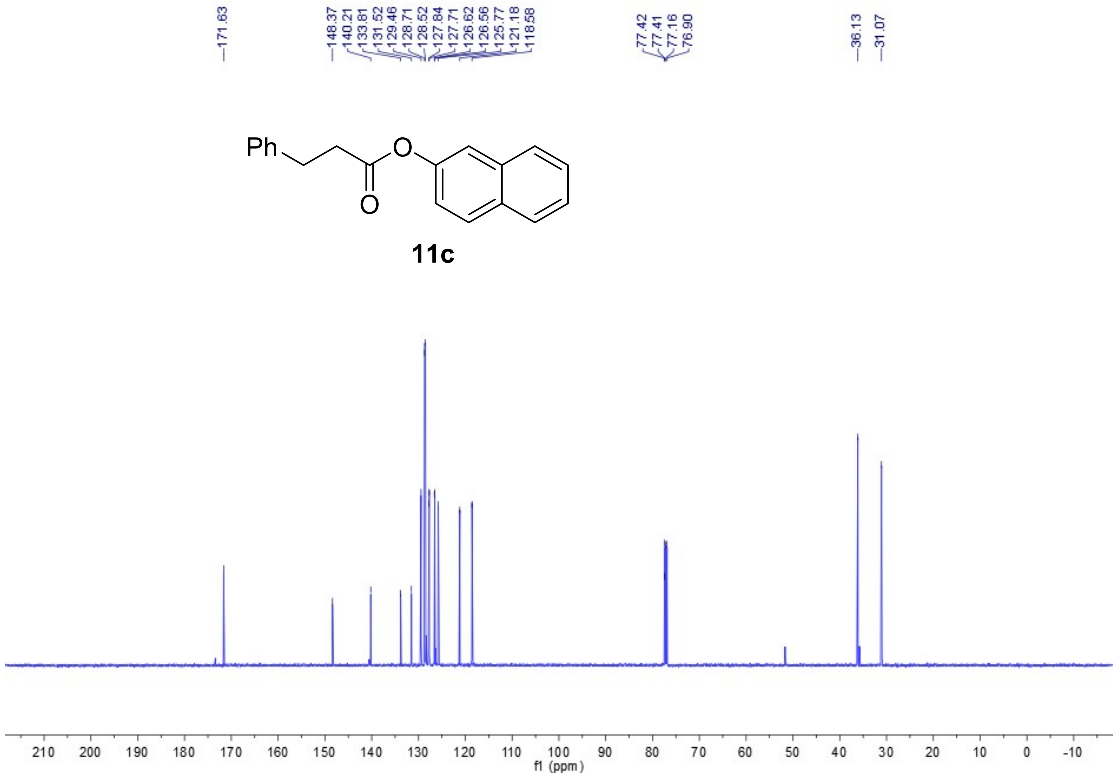


11b



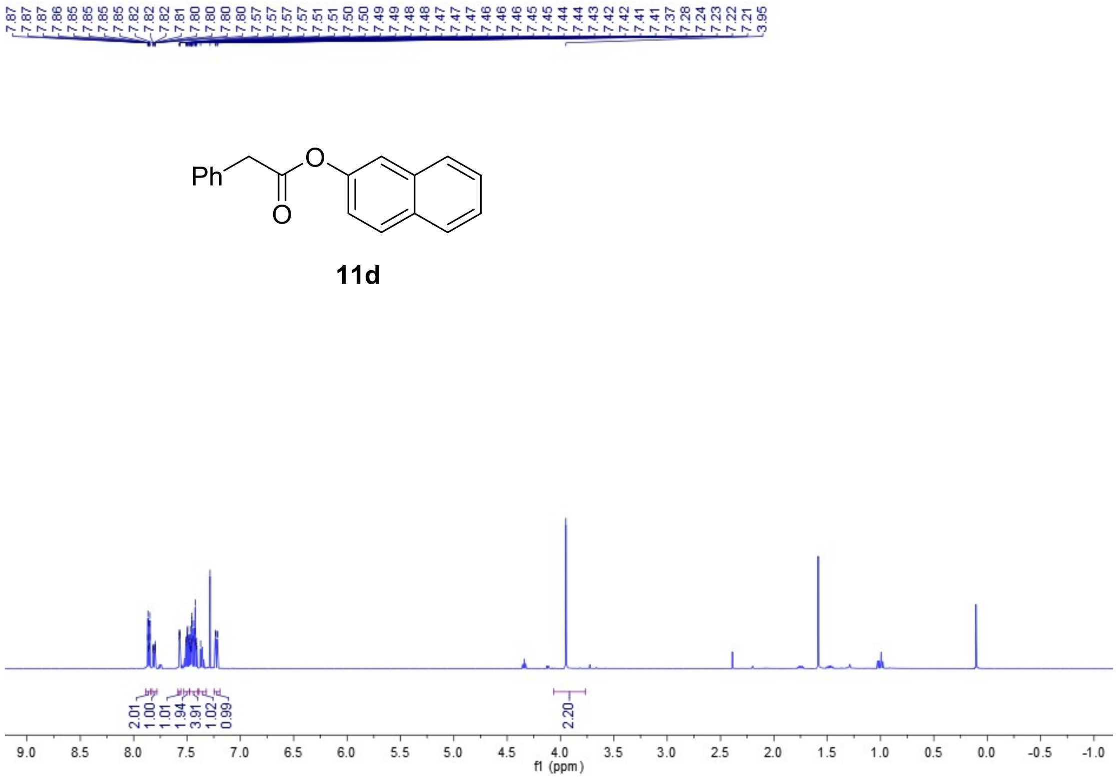
^{1}H and ^{13}C NMR spectra of **11b**



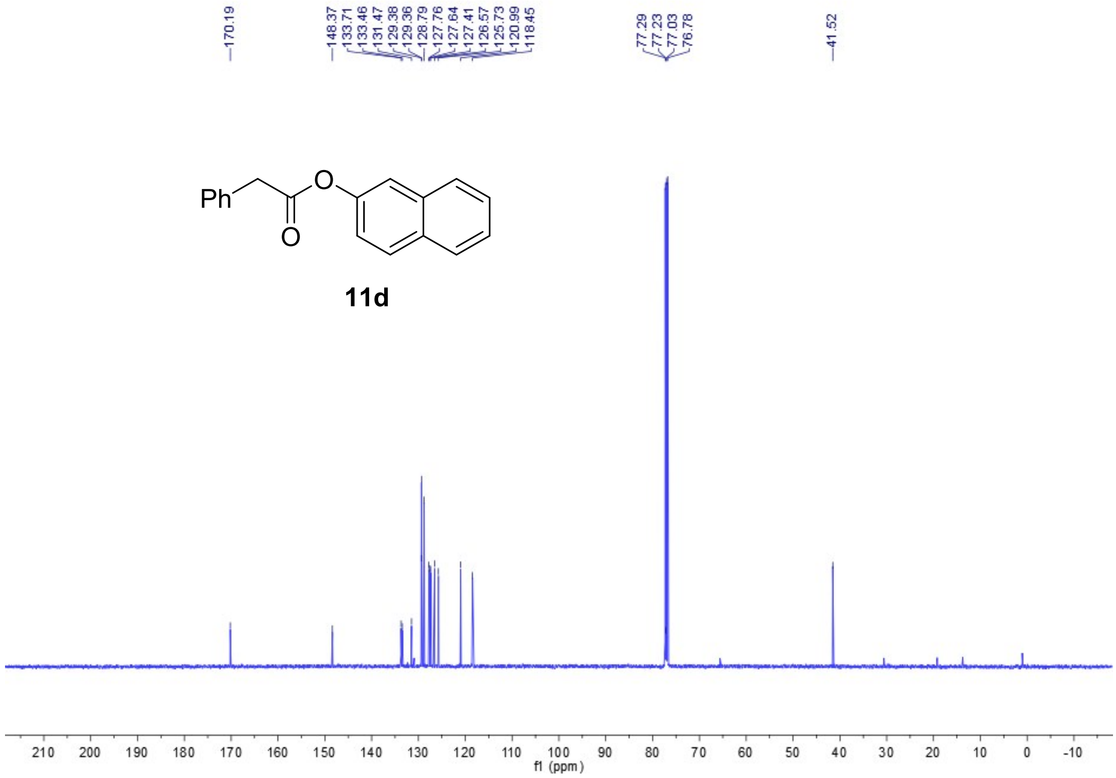


11c

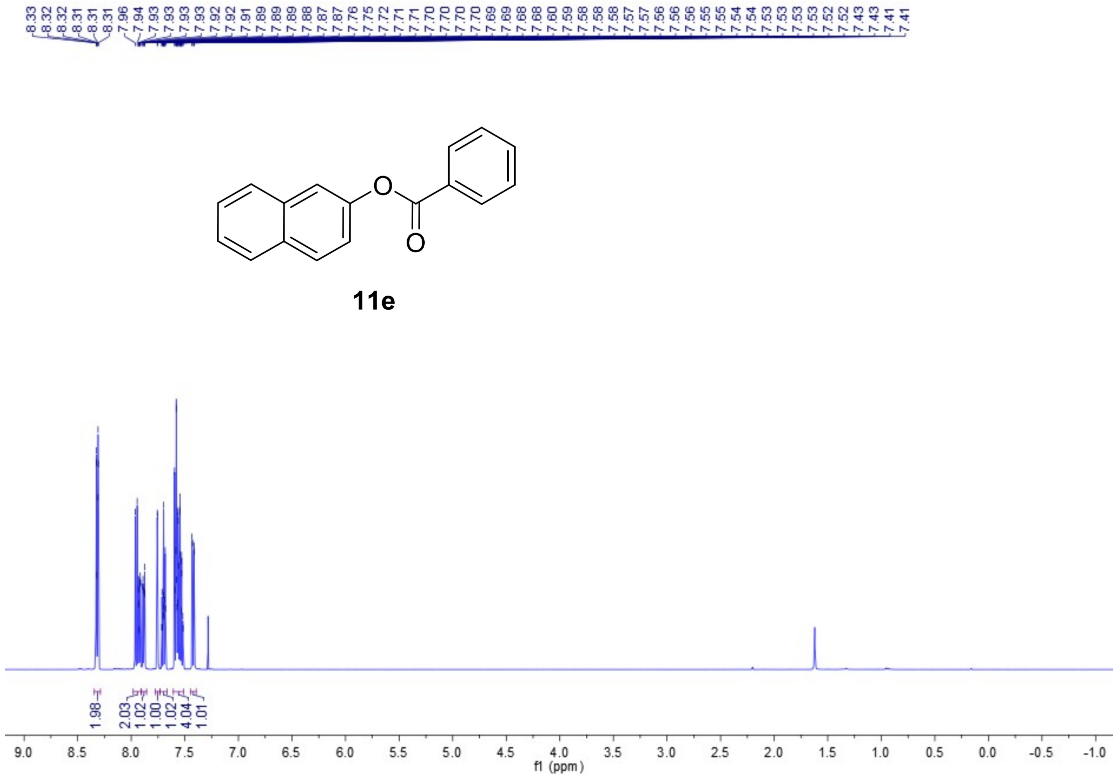
^{1}H and ^{13}C NMR spectra of **11c**

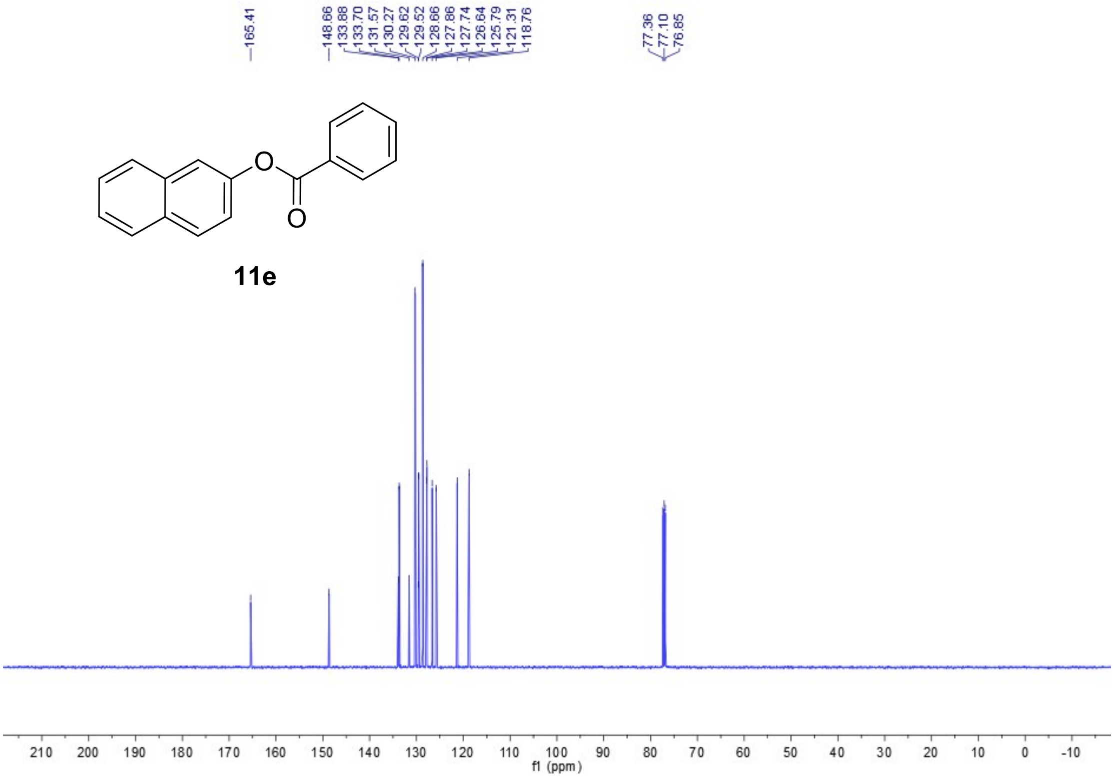


11d

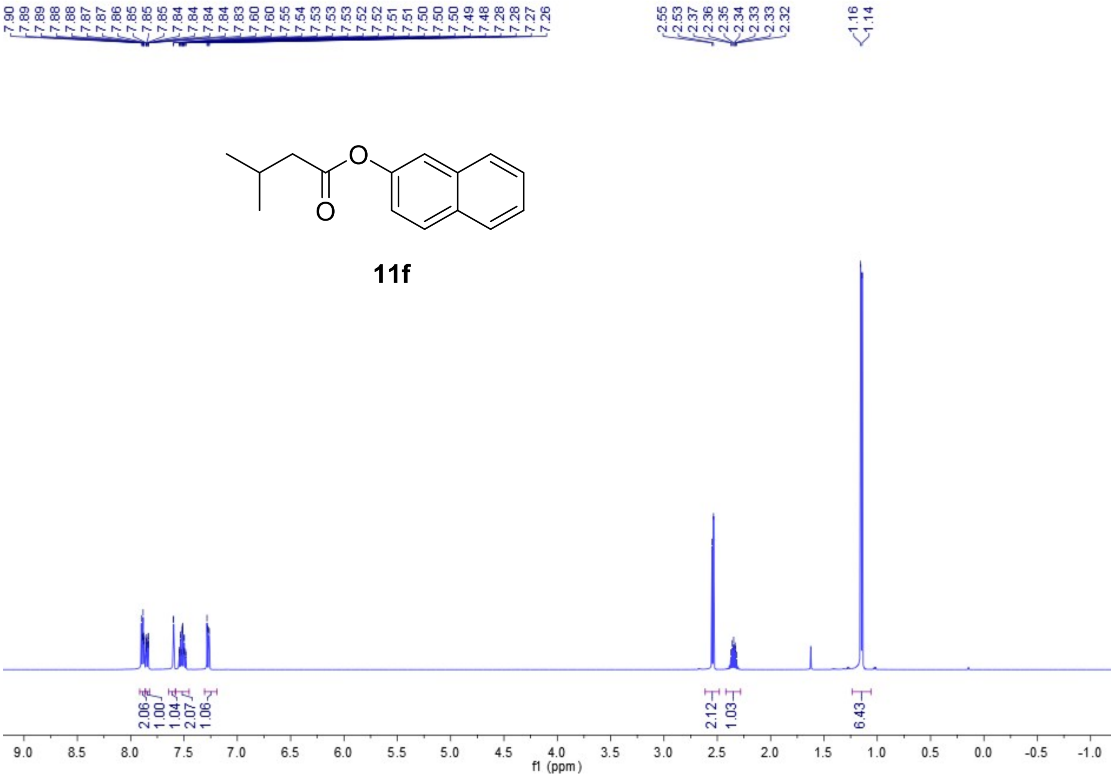


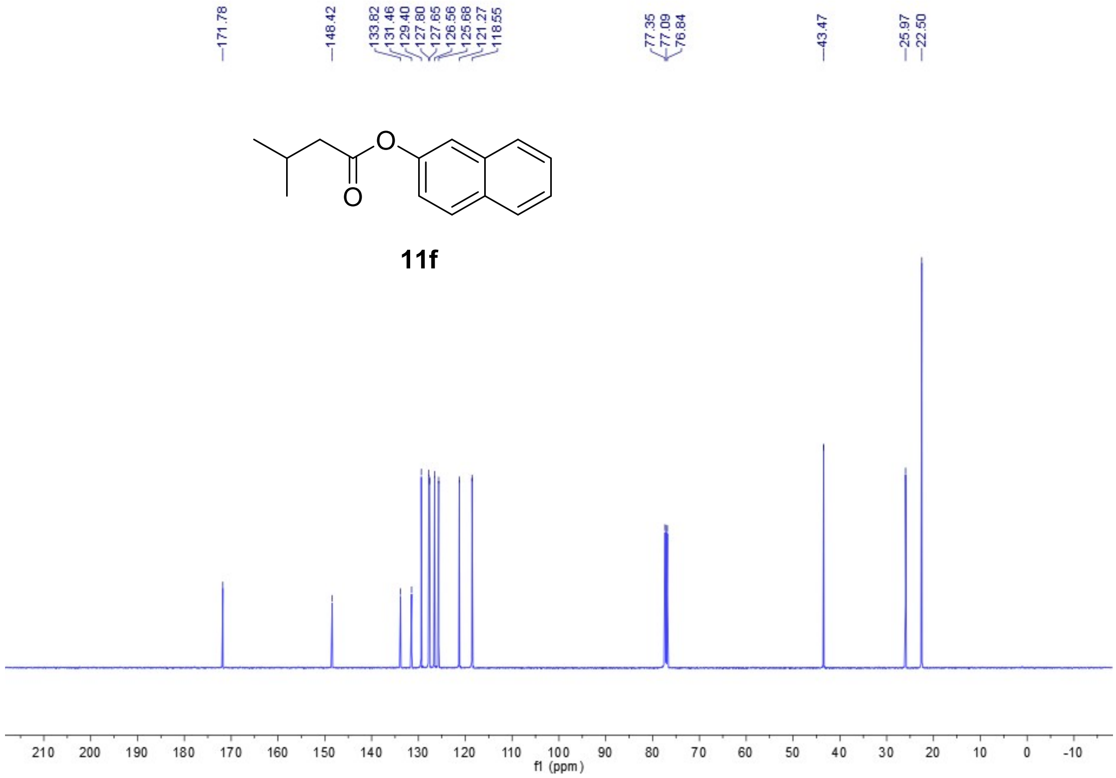
^{1}H and ^{13}C NMR spectra of **11d**




11e

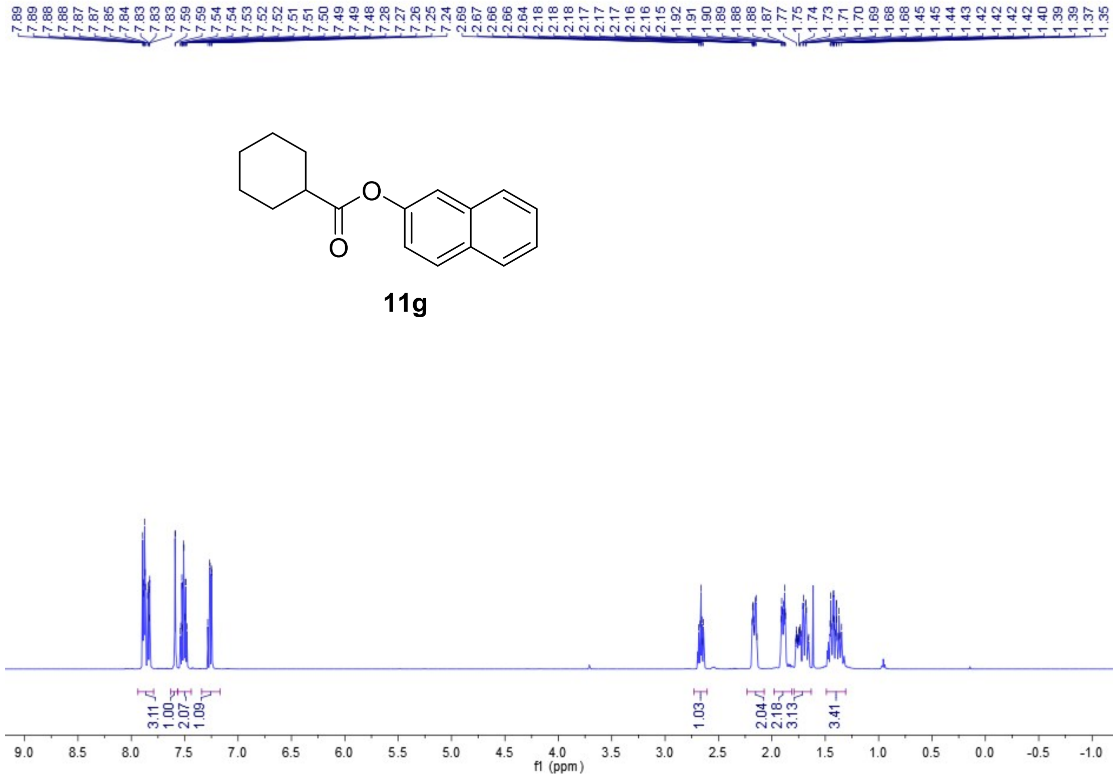
^{1}H and ^{13}C NMR spectra of **11e**


11f

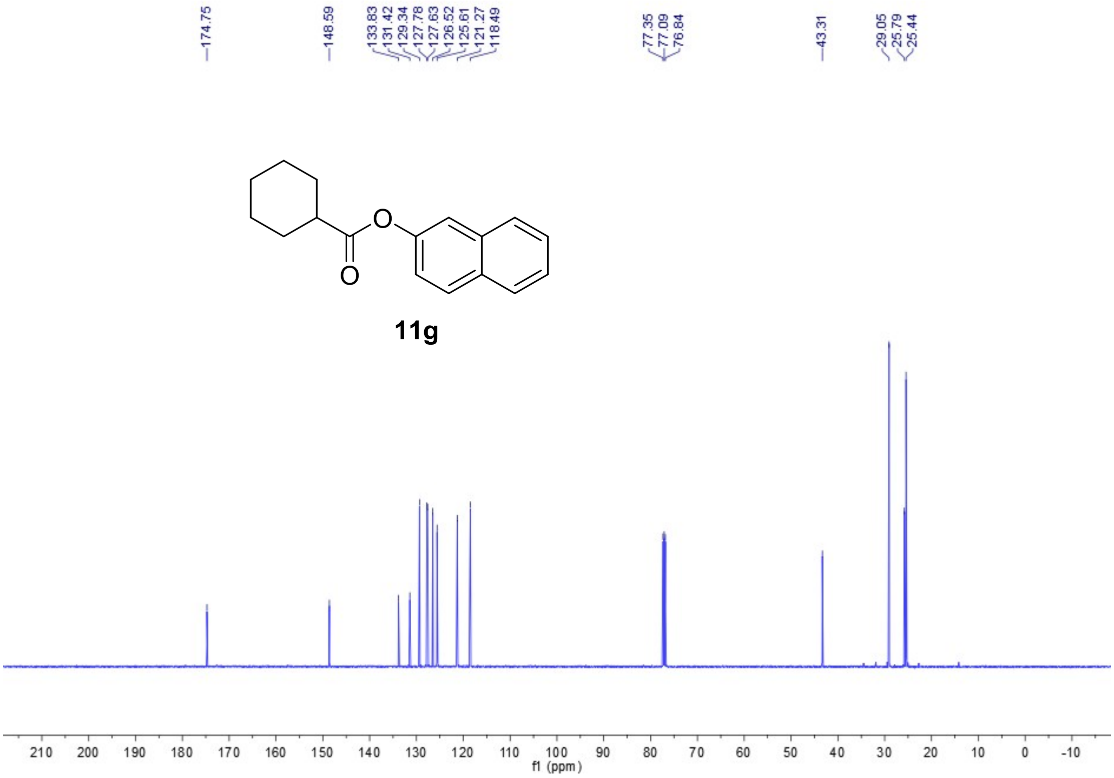


11f

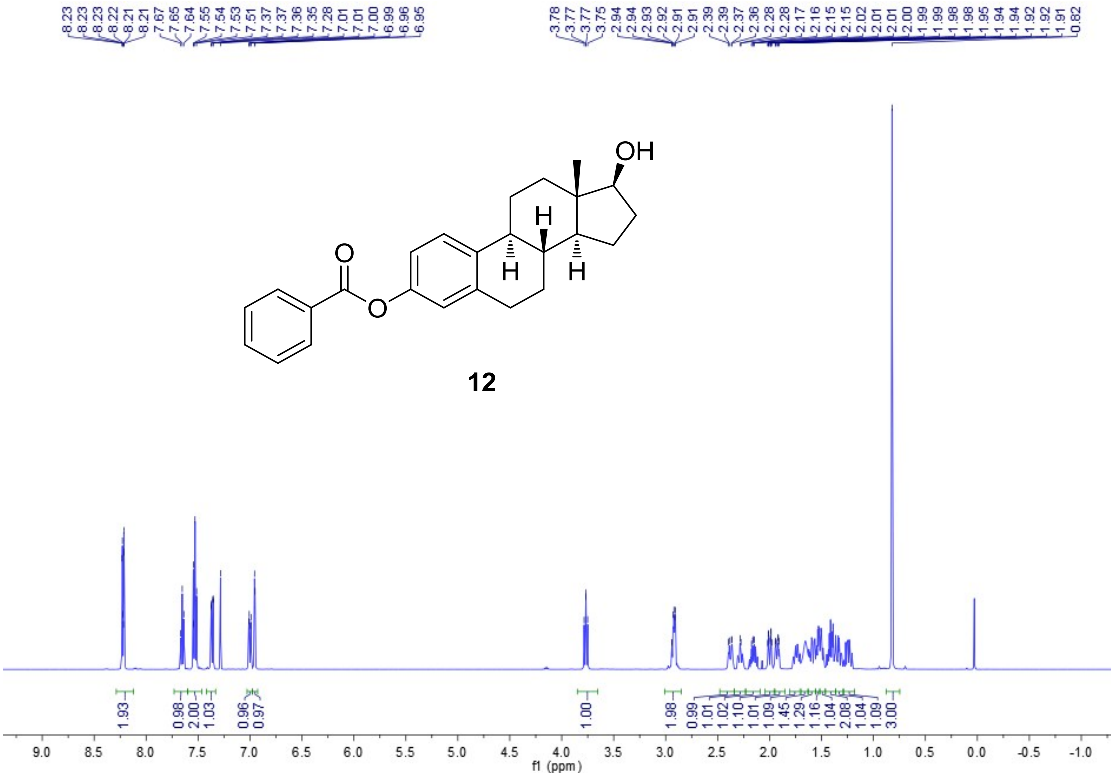
^{1}H and ^{13}C NMR spectra of **11f**

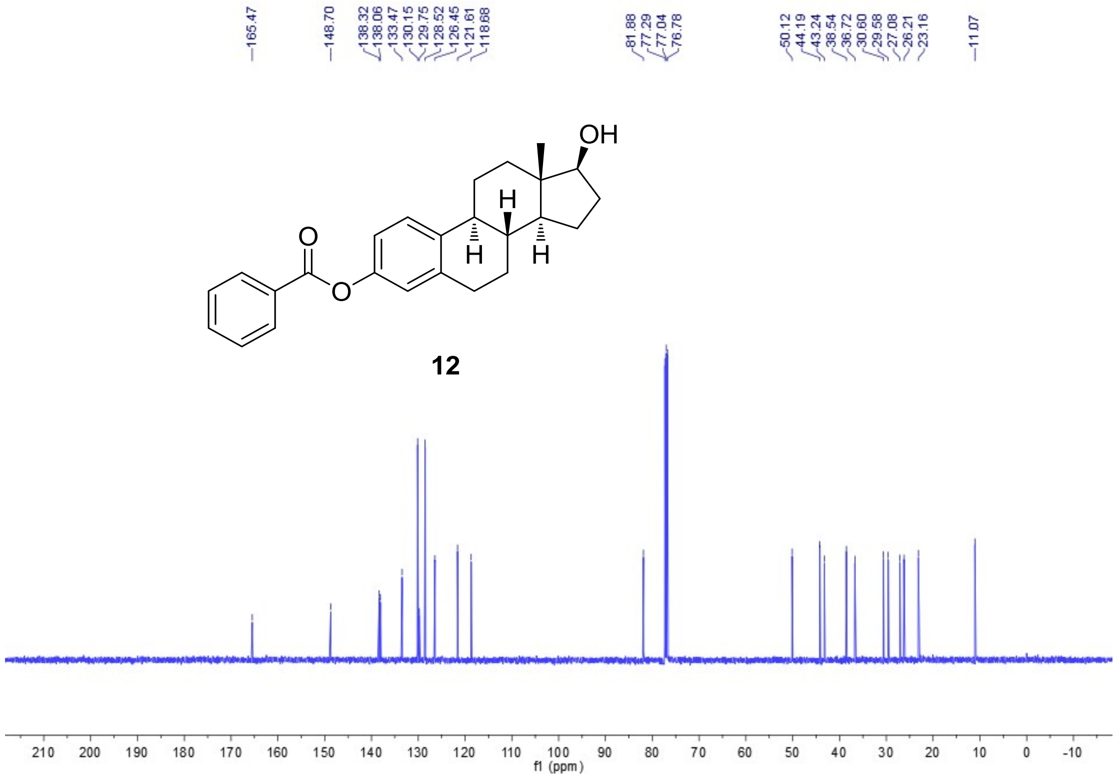


11g



^{1}H and ^{13}C NMR spectra of **11g**





^{1}H and ^{13}C NMR spectra of **12**