Electronic Supplementary Information

Pt, Pd and Au Nanoparticles Supported on DNA-MMT Hybrid: Efficient Catalysts for Highly Selective Oxidation of Primary Alcohols to Aldehydes, Acids and Esters

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Contents:

General Remarks

All substrates were purchased commercially without further purification. Fish sperm DNA (CAS: 100403-24-5). The morphology and size of the Pd NPs were characterized on transmission electron microscopy (TEM) (JEOL–2010 and Hitachi H7650). The diluted solutions of the as-synthesized metal/DNA-MMT nanohybrid were used as samples directly and dried on the carbon-coated Cu grids. X-ray powder diffraction (XRD) experiments were carried out with a Philips X'Pert Pro Super diffractometer with Cu KR radiation ($\lambda = 1.54178$ Å). The accurate concentrations of metal/DNA-MMT nanohybrid and other supported metal catalysts were directly determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer) using Perkin Elmer Optima 7300 DV. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR were recorded on a Bruker AC-300 FT (^{1}H NMR 300 MHz, ^{13}C NMR 75 MHz) or Bruker AC-400 FT (^{1}H NMR 400 MHz, ^{13}C NMR 100 MHz) using TMS as internal reference. HRMS were recorded on a MicroMass GCT TOF-MS. GC-MS samples were recorded on a Shimadzu QP-5050 GC-MS system. And the yields were determined using 1,3,5-trimethylbenzene as an internal standard. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 electron spectrometer using monochromatized Al Kα excitation source (hν = 1486.6 eV).

General procedures for the synthesis of heterogeneous catalysts

Synthesis of metal/DNA

0.2 mmol of the corresponding metal salt ($PdCl_2$, $KAuCl_4$, K_2PtCl_6) and 20 mg of fish sperm DNA were dissolved in 24 ml Tris buffer (10 mM, pH = 7.4). The combined solution was stirred for 24 h to ensure the corresponding metal ion (Pd^{2+}, Au^{3+}, Pt^{4+}) thoroughly bind to DNA. After this aging process, 1.0 mmol of freshly dissolved $NaBH_4$ in 16 ml Tris buffer was added dropwise under N_2 atmosphere at 0 °C. After reduction, the solution was stirred for another 24 h in N_2 from 0 °C to room temperature to obtain the resulting M/DNA nanohybrids (c.a. 5 mM in Tris). This synthesis method can be scaled up to hundreds of millilitres easily at a time.

Synthesis of metal/MMT

0.2 mmol of the corresponding metal salt ($PdCl_2$, $KAuCl_4$, K_2PtCl_6) and 40 mg of Na-MMT were dissolved in 24 ml Tris buffer (10 mM, pH = 7.4). The combined solution was stirred for 24 h to ensure the corresponding metal ion (Pd^{2+}, Au^{3+}, Pt^{4+})

thoroughly bind to Na-MMT. After this aging process, 1.0 mmol of freshly dissolved $NaBH_4$ in 16 ml Tris buffer was added dropwise under N_2 atmosphere at 0 °C. After reduction, the solution was stirred for another 24 h in N_2 from 0 °C to room temperature to obtain the resulting M/ Na-MMT nanohybrids (c.a. 5 mM in Tris).

Synthesis of metal/DNA-MMT

To synthesize the hybrid of DNA-MMT, Na-MMT and fish sperm DNA were dispersed in deionized water with the desired concentration (MMT/DNA (w/w) = 2.0). After adjusting the pH value to 8 with 0.1 M Na_2CO_3, the above system was left under vigorous stirring for 12 h at 50 °C. Then the hybrid was centrifuged, washed with deionized water and dried under vacuum.

0.2 mmol of the corresponding metal salt ($PdCl_2$, $KAuCl_4$, K_2PtCl_6) and 60 mg of the as-synthesized DNA-MMT hybrid were dissolved in 36 ml Tris buffer (10 mM, pH = 7.4). The combined solution was stirred for 24 h to ensure the corresponding metal ion (Pd^{2+}, Au^{3+}, Pt^{4+}) thoroughly bind to DNA. After this aging process, 1.0 mmol of freshly dissolved $NaBH_4$ in 14 ml Tris buffer was added dropwise under N_2 atmosphere at 0 °C. After reduction, the solution was stirred for another 24 h in N_2 from 0 °C to room temperature to obtain the resulting M/DNA-MMT catalysts (c.a. 4 mM in Tris).

Detailed characterization of heterogeneous catalysts

XRD patterns for Na-MMT and DNA-MMT

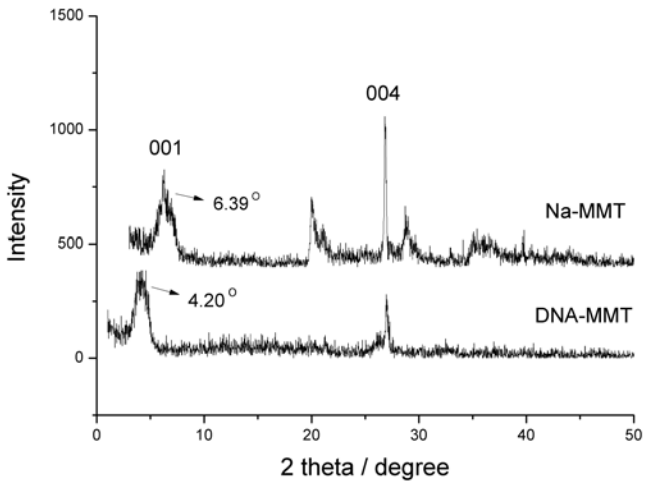


Figure S1 XRD patterns of Na-MMT and DNA-MMT hybrid

the XRD analyses for MMT and DNA-MMT show that 001 crystal face of origin Na-MMT'2θ is 6.39°, while DNA-MMT' 2θ is 4.20°. The layer spacing of MMT increases from 1.38 nm to 2.09 nm through the Bragg law. The hybrid of DNA-MMT has been obtained.

XRD patterns for matal/DNA-MMT heterogeneous catalysts

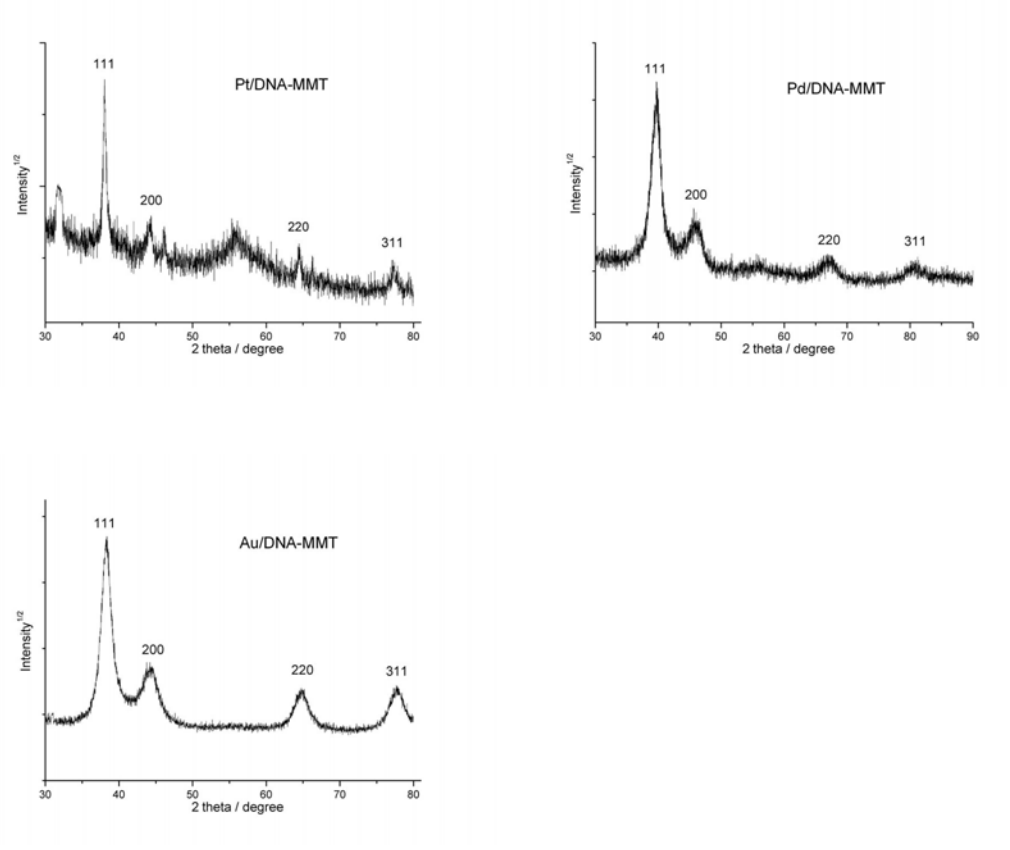
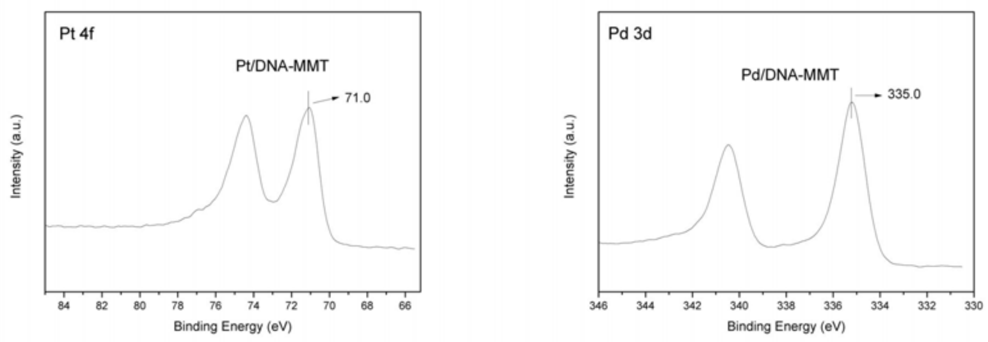
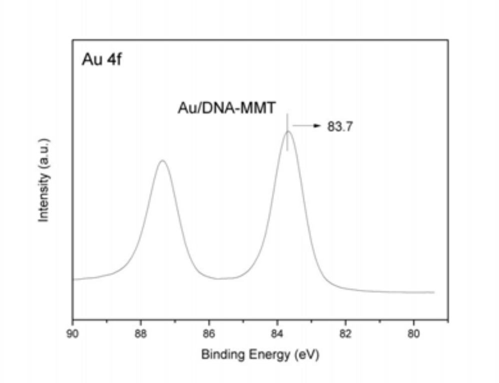


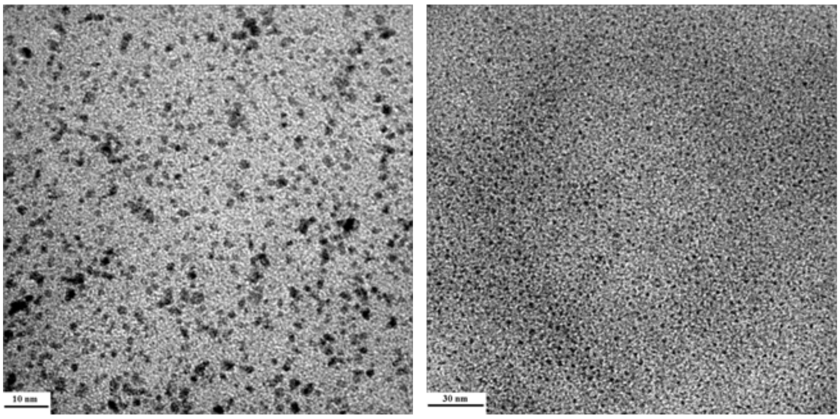
Figure S2 XRD patterns of Pt/DNA-MMT, Pd/DNA-MMT and Au/DNA-MMT heterogeneous catalysts

XPS experiments for matal/DNA-MMT heterogeneous catalysts



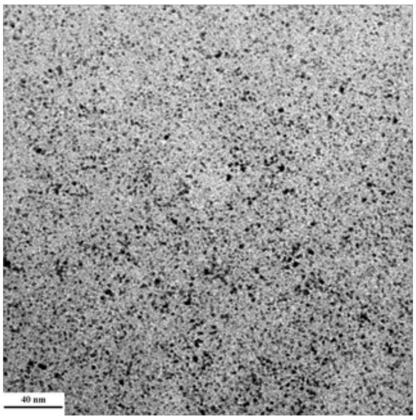


TEM analyses for metal/DNA-MMT heterogeneous catalysts



Pt/DNA-MMT

Pd/DNA-MMT



Au/DNA-MMT

Figure S3 TEM analyses for Pt/DNA-MMT, Pd/DNA-MMT and Au/DNA-MMT heterogeneous catalysts

General procedure for selective oxidation of alcohols

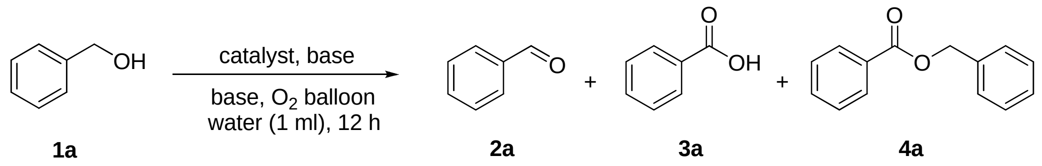
selective oxidation of primary alcohols to aldehydes: For Pt/DNA-MMT catalyst: To 3 ml of as-synthesized Pt/DNA-MMT catalyst was precipitated by adding excess EtOH (3 times of the volume). After sitting for 1 h and then centrifuged at 6000 r min^{-1} for 4 min, the decantate was poured off. The obtained solid residue was dried by N_2 flow and redispersed in a water solution (1 mL) containing $K_3PO_4•3H_2O$ (6.7 mg, 0.025 mmol). Benzyl alcohol (54.1 mg, 0.50 mmol) was then added to the solution. The air in the reaction mixture was removed under vacuum and the reaction vessel refilled with O_2. This procedure was repeated for three times. The reaction mixture was then stirred under an O_2 balloon at 60 °C for 12 h. After the reaction was finished, 3 times the volume of EtOH and 5 times the volume of EtOAc was added to the reaction mixture. This mixture was left undisturbed for 2 h to allow precipitation and then centrifuged at 6000 r min^{-1} for 4 min. The decantate was poured off. The solid residue was dried and used as the catalyst for the next round. The organic phase and the aqueous phase in the decantate were separated. The obtained aqueous phase was treated with hydrochloric acid and then extracted by EtOAc. The combined organic phase was evaporated with a rotary evaporator. The obtained residue was analyzed by GC-MS.

selective oxidation of primary alcohols to acids: For Pd/DNA-MMT catalyst: To 3 ml of as-synthesized Pd/DNA-MMT catalyst was precipitated by adding excess EtOH (3 times of the volume). After sitting for 1 h and then centrifuged at 6000 r min^{-1} for 4 min, the decantate was poured off. The obtained solid residue was dried by N_2 flow and redispersed in a water solution (1 mL) containing $LiOH•H_2O$ (31.4 mg, 0.750 mmol). Benzyl alcohol (54.1 mg, 0.50 mmol) was then added to the solution. The air in the reaction mixture was removed under vacuum and the reaction vessel refilled with O_2. This procedure was repeated for three times. The reaction mixture was then stirred under an O_2 balloon at 25 °C for 12 h. After the reaction was finished, 3 times the volume of EtOH and 5 times the volume of EtOAc was added to the reaction mixture. This mixture was left undisturbed for 2 h to allow precipitation and then centrifuged at 6000 r min^{-1} for 4 min. The decantate was poured off. The solid residue was dried and used as the catalyst for the next round. The organic phase and the aqueous phase in the decantate were separated. The obtained aqueous phase was treated with hydrochloric acid and then extracted by EtOAc. The combined organic phase was evaporated with a rotary evaporator. The obtained residue was analyzed by GC-MS and then purified with column chromatography over silica gel. The resulting products were characterized by ^{1}H NMR, ^{13}C NMR and HRMS.

selective oxidation of primary alcohols to esters: For Au/DNA-MMT catalyst: To 2 ml of as-synthesized Au/DNA-MMT catalyst was precipitated by adding excess EtOH (3 times of the volume). After sitting for 1 h and then centrifuged at 6000 r min^{-1} for 4 min, the decantate was poured off. The obtained solid residue was dried by N_2 flow and redispersed in a water solution (1 mL) containing Cs_2CO_3 (61.1 mg, 0.1875 mmol). Benzyl alcohol (54.1 mg, 0.50 mmol) was then added to the solution. The air in the reaction mixture was removed under vacuum and the reaction vessel refilled with O_2. This procedure was repeated for three times. The reaction mixture was then stirred under an O_2 balloon at 50 °C for 12 h. After the reaction was finished, 3 times the volume of EtOH and 5 times the volume of EtOAc was added to the reaction mixture. This mixture was left undisturbed for 2 h to allow precipitation and then centrifuged at 6000 r min^{-1} for 4 min. The decantate was poured off. The solid residue was dried and used as the catalyst for the next round. The organic phase and the aqueous phase in the decantate were separated. The obtained aqueous phase was treated with hydrochloric acid and then extracted by EtOAc. The combined organic phase was evaporated with a rotary evaporator. The obtained residue was analyzed by GC-MS and then purified with column chromatography over silica gel. The resulting products were characterized by ^{1}H NMR, ^{13}C NMR and HRMS.

Comparsion of different heterogenous catalysts in selective oxidation of benzyl alcohol[a]

Table S1

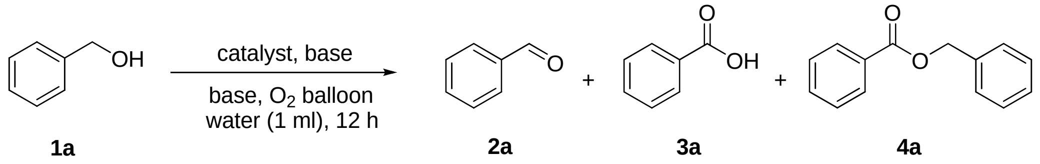


Entry	Catalyst	Base (equiv)	T (° C)	Yield (%)[b] 2a	3a	4a
1	Pd/DNA-MMT	$LiOH\cdot H_2O$ (1.5)	25	< 1	99	n.d.
2	Pd/DNA	$LiOH\cdot H_2O$ (1.5)	25	3	95	n.d.
3	Pd/MMT	$LiOH\cdot H_2O$ (1.5)	25	3	96	n.d.
4	Pt/DNA-MMT	$K_3PO_4\cdot H_2O$ (0.05)	60	86	7	n.d.
5	Pt/DNA	K_3PO4•H_2O (0.05)	60	75	20	n.d.
6	Pt/MMT	K_3PO4•H_2O (0.05)	60	50	35	n.d.
7	Au/DNA-MMT	Cs_2CO_3 (0.75)	50	3	< 1	95
8	Au/DNA	Cs_2CO_3 (0.75)	50	6	9	81
9	Au/MMT	Cs_2CO_3 (0.75)	50	10	21	68

[a] Reaction conditions: **1a** (0.50 mmol), Cat. (Pt: 1.5 mol%, Pd: 1.7 mol%, Au: 2.9 mol%). [b] Determined by GC-MS with an internal standard, n.d. = not detected.

Selective oxidation of alcohol catalyzed by different metal salt[a]

Table S2



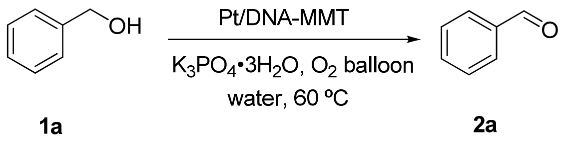
				Yield (%)[b]		
Entry	Catalyst	Base (equiv)	T (° C)	**2a**	**3a**	**4a**
1	$PdCl_2$	$LiOH•H_2O$ (1.5)	25	5	70	n.d.
4	K_2PtCl_6	$K_3PO_4•H_2O$ (0.05)	60	4	trace	n.d.
7	$KAuCl_4$	Cs_2CO_3 (0.75)	50	11	7	trace

[a] Reaction conditions: **1a** (0.50 mmol), Cat. (K_2PtCl_6: 1.5 mol%, $PdCl_2$: 1.7 mol%, $KAuCl_4$: 2.9 mol%). [b] Determined by GC-MS with an internal standard, n.d. = not detected.

The recycling of heterogenous catalysts in selective oxidation of alcohol

The recycling of Pt/DNA-MMT[a]

Table S3

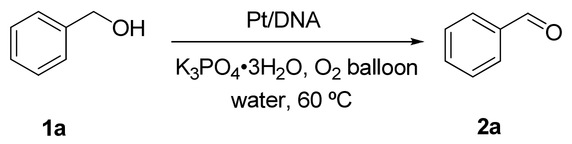


Run	1	2	3
Yield (%)[b]	86	83	80

[a] Reaction conditions: **1a** (0.50 mmol), Cat. (Pt: 1.5 mol%). [b] GC yield.

The recycling of Pt/DNA [a]

Table S4

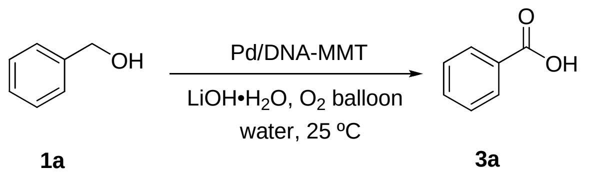


Run	1	2	3
Yield (%)[b]	75	70	67

[a] Reaction conditions: **1a** (0.50 mmol), Cat. (Pt: 1.5 mol%). [b] GC yield.

The recycling of Pd/DNA-MMT[a]

Table S5

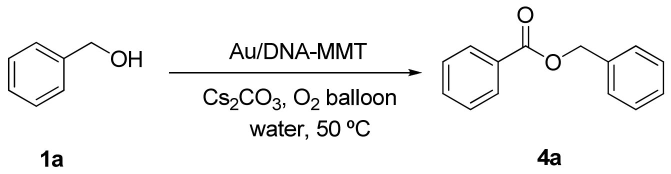


Run	1	2	3	4	5
Yield (%)[b]	98	95	93	91	89

[a] Reaction conditions: **1a** (0.50 mmol), Cat. (Pd: 1.7 mol%). [b] Isolated yield.

The recycling of Au/DNA-MMT[a]

Table S6



Run	1	2	3	4	5
Yield (%)[b]	94	90	87	84	81

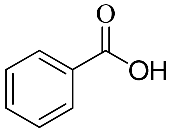
[a] Reaction conditions: **1a** (0.50 mmol), Cat. (Au: 2.9 mol%). [b] Isolated yield.

ICP-OES measurement of heterogenous catalysts

For the as-synthesized metal/DNA-MMT nanohybrids (2 mL), with the aid of centrifugation at 5000 r/min for 5 minutes, then the decantate were poured out. The residues were dried by N_2 flow and dissolved in aqua regia. Then the mixture was filtered and washed. Subsequently, the filtrate was transferred to a 50 ml volumetric flask. The accurate Pt, Pd and Au content in the corresponding metal/DNA-MMT was 1.463 mg, 0.905 mg and 1.428 mg respectively with ICP-OES measurement. After three cycles the Pt content was decreased to 1.287 mg, the Pd content was decreased to 0.830 mg and the Au content was decreased to 1.251 mg after five cycles, respectively. In contrast, the Pt content was decreased to 1.194 mg.from 1.463 mg in the Pt/DNA after three cycles

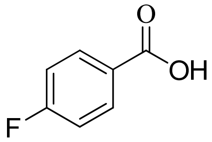
Characterization data of products

Benzoic acid **(3a)**



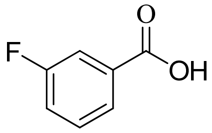
^{1}H NMR (300 MHz, d^6-DMSO): δ [ppm] = 12.919 (s, 1H), 7.948 (d, 7.2 Hz, 2H), 7.620 (t, 7.5 Hz, 1H), 7.497 (t, 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 172.6, 134.0, 130.4, 129.5, 128.6; HRMS (M+) calcd for $C_7H_6O_2$: 122.0368 found 122.0367.

4-Fluorobenzoic acid (**3b**)



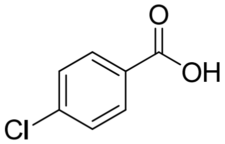
^{1}H NMR (300 MHz, d^6-DMSO): δ [ppm] = 13.021 (s, 1H), 8.002 (m, 2H), 7.316 (t, 9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 171.2, 166.5 (d, J_{CF} = 253.7 Hz), 133.1 (d, J_{CF} = 9.5 Hz), 125.7 (d, J_{CF} = 2.9 Hz), 115.9 (d, J_{CF} = 22.0 Hz); HRMS (M+) calcd for $C_7H_5FO_2$: 140.0274 found 140.0278.

3-Fluorobenzoic acid (**3c**)



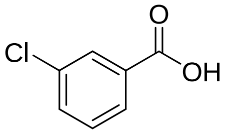
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 13.240 (s, 1H), 7.785 (d, 7.6 Hz, 1H), 7.664-7.631 (m, 1H), 7.577-7.523 (m, 1H), 7.492-7.444 (m, 1H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 166.2 (d, J_{CF} = 2.8 Hz), 162.0 (d, J_{CF} = 243.2 Hz), 133.3 (d, J_{CF} = 7.2 Hz), 130.8 (d, J_{CF} = 7.9 Hz), 125.4 (d, J_{CF} = 2.8 Hz), 119.8 (d, J_{CF} = 21.0 Hz), 115.7 (d, J_{CF} = 22.5 Hz); HRMS (M+) calcd for $C_7H_5FO_2$: 140.0274 found 140.0275.

4-Chlorobenzoic acid (**3d**)



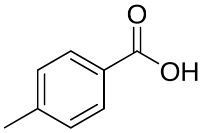
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 13.145 (s, 1H), 7.952-7.919 (m, 2H), 7.554 (d, 8.5 Hz, 2H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 166.5, 137.8, 131.1, 129.7, 128.7; HRMS (M+) calcd for $C_7H_5ClO_2$: 155.9978 found 155.9983.

3-Chlorobenzoic acid (**3e**)



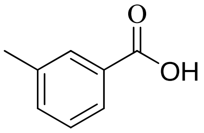
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 13.300 (s, 1H), 7.896-7.878 (m, 2H), 7.690-7.668 (m, 1H), 7.547-7.506 (m, 1H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 166.1, 133.4, 133.0, 132.7, 130.6, 128.8, 127.9; HRMS (M+) calcd for $C_7H_5ClO_2$: 155.9978 found 155.9985.

4-Methylbenzoic acid (**3f**)



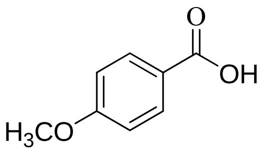
^{1}H NMR (300 MHz, d^6-DMSO): δ [ppm] = 12.822 (s, 1H), 7.745 (d, 10.7 Hz, 2H), 7.439-7.347 (m, 2H), 2.358 (s, 3H); ^{13}C NMR (75 MHz, d^6-DMSO): δ [ppm] = 167.3, 142.9, 129.3, 129.1, 128.0, 21.1; HRMS (M+) calcd for $C_8H_8O_2$: 136.0524 found 136.0521.

3-Methylbenzoic acid (**3g**)



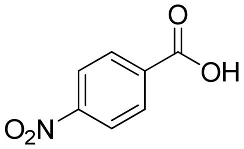
^{1}H NMR (300 MHz, d^6-DMSO): δ [ppm] = 12.749 (s, 1H), 7.848 (s, 1H), 7.821 (s, 1H), 7.304 (s, 1H), 7.277 (s, 1H), 2.362 (s, 3H); ^{13}C NMR (75 MHz, d^6-DMSO): δ [ppm] = 167.4, 137.9, 133.4, 130.7, 129.7, 128.4, 126.4, 20.8; HRMS (M+) calcd for $C_8H_8O_2$: 136.0524 found 136.0525.

4-Methoxybenzoic acid (**3h**)



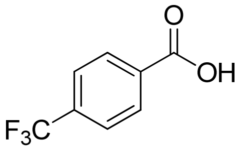
^{1}H NMR (400 MHz, d^{6}-DMSO): δ [ppm] = 12.590 (s, 1H), 7.910-7.870 (m, 2H), 7.03-6.99 (m, 2H), 3.820 (s, 1H); ^{13}C NMR (100 MHz, d^{6}-DMSO): δ [ppm] = 167.0, 162.8, 131.3, 123.0, 113.8, 55.4; HRMS (M+) calcd for $C_8H_8O_3$: 152.0473 found 152.0479.

4-Nitrobenzoic acid (**3i**)



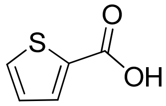
^{1}H NMR (400 MHz, d^{6}-DMSO): δ [ppm] = 13.644 (s, 1H), 8.316 (d, 8.6 Hz, 2H), 8.179-8.146 (m, 2H); ^{13}C NMR (100 MHz, d^{6}-DMSO): δ [ppm] = 165.8, 150.0, 136.4, 130.7, 123.7; HRMS (M+) calcd for $C_7H_5NO_4$: 167.0219 found 167.0222.

4-(Trifluoromethyl)benzoic acid (**3j**)



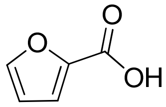
^{1}H NMR (400 MHz, d^{6}-DMSO): δ [ppm] = 13.444 (s, 1H), 8.130 (d, 8.3 Hz, 2H), 7.860 (d, 8.3 Hz, 2H); ^{13}C NMR (100 MHz, d^{6}-DMSO): δ [ppm] = 166.2, 134.6, 132.5 (q, J_{CF} = 31.7), 130.1, 125.6 (q, J_{CF} = 37 Hz), 123.8 (q, J_{CF} = 270.7 Hz); HRMS (M+) calcd for $C_8H_5F_3O_2$: 190.0242 found 190.0240.

Thiophene-2-carboxylic acid (**3k**)



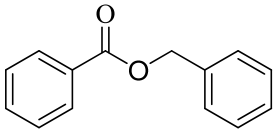
^{1}H NMR (300 MHz, d^{6}-DMSO): δ [ppm] = 13.006 (s, 1H), 7.878-7.857 (m, 1H), 7.734-7.718 (m, 1H), 7.190- 7.161 (m, 1H); ^{13}C NMR (75 MHz, d^{6}-DMSO): δ [ppm] = 162.9, 134.7, 133.22, 133.19, 128.2; HRMS (M+) calcd for $C_5H_4O_2S$: 127.9932 found 127.9936.

Furan-2-carboxylic acid (**3l**)



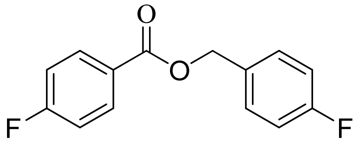
^{1}H NMR (400 MHz, d^{6}-DMSO): δ [ppm] = 12.972 (s, 1H), 7.907-7.901 (m, 1H), 7.211-7.200 (m, 1H), 6.652-6.638 (m, 1H); ^{13}C NMR (100 MHz, d^{6}-DMSO): δ [ppm] = 159.3, 147.0, 144.9, 117.7, 112.1; HRMS (M+) calcd for $C_5H_4O_3$: 112.0160 found 112.0161.

Benzyl benzoate (**4a**)



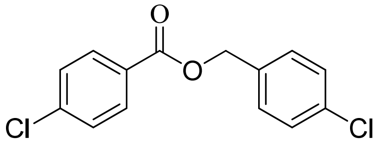
^{1}H NMR (400 MHz,CDCl$_3$): δ [ppm] = 8.110-8.082 (m, 2H), 7.588-7.544 (m, 1H), 7.476-7.444 (m, 3H), 7.430-7.332 (m, 4H), 5.382 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ [ppm] = 166.6, 136.2, 133.2, 130.3, 129.9, 128.7, 128.5, 128.4, 128.3, 66.8; HRMS (M+) calcd for $C_{14}H_{12}O_2$: 212.0837 found 212.0841.

4-Fluorobenzyl 4-fluorobenzoate (**4b**)



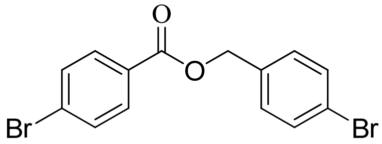
^{1}H NMR (400 MHz,CDCl$_3$): δ [ppm] = 8.093-8.050 (m, 2H), 7.441-7.406 (m, 2H), 7.135-7.045 (m, 4H), 5.316 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ [ppm] = 166.0 (d, J_{CF} = 252.7 Hz), 165.6, 162.9 (d, J_{CF} = 245.5 Hz), 132.4 (d, J_{CF} = 9.1 Hz), 131.9 (d, J_{CF} = 3.0 Hz), 130.4 (d, J_{CF} = 8.4 Hz), 126.4 (d, 2.9 Hz), 115.7 (d, J_{CF} = 21.8 Hz), 66.3; HRMS (M+) calcd for $C_{14}H_{10}F_2O_2$: 248.0649 found 248.0647.

4-Chlorobenzyl 4-chlorobenzoate (**4c**)



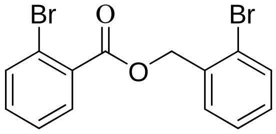
^{1}H NMR (400 MHz,CDCl$_3$): δ [ppm] = 8.008-7.974 (m, 2H), 7.428-7.391 (m, 2H), 7.382-7.343 (m, 4H), 5.316 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ [ppm] = 165.6, 139.8, 134.5, 134.4, 131.2, 129.8, 129.0, 128.9, 128.5, 66.3; HRMS (M+) calcd for $C_{14}H_{10}Cl_2O_2$: 280.0058 found 280.0063.

4-Bromobenzyl 4-bromobenzoate (**4d**)



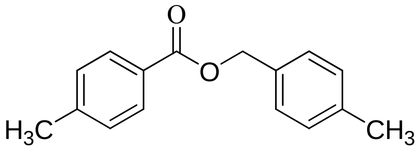
^{1}H NMR (400 MHz,CDCl$_3$): δ [ppm] = 7.930-7.896 (m, 2H), 7.598-7.565 (m, 2H), 7.534-7.501 (m, 2H), 7.326-7.293 (m, 2H), 5.297 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ [ppm] = 165.7, 134.9, 131.97, 131.95, 131.4, 130.1, 129.0, 128.5, 122.6, 66.3; HRMS (M+) calcd for $C_{14}H_{10}Br_2O_2$: 367.9048 found 367.9042.

2-Bromobenzyl 2-bromobenzoate (**4e**)



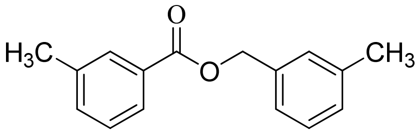
^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 7.884-7.860 (m, 1H), 7.688-7.665 (m, 1H), 7.624-7.587 (m, 1H), 7.553-7.530 (m, 1H), 7.394-7.316 (m, 3H), 7.241-7.198 (m, 1H), 5.465 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 165.8, 135.1, 134.6, 134.5, 133.1, 132.9, 131.7, 130.5, 130.1, 127.7, 127.4, 123.8, 122.1, 67.1; HRMS (M+) calcd for $C_{14}H_{10}Br_2O_2$: 367.9048 found 367.9044.

4-Methylbenzyl 4-methylbenzoate (**4f**)



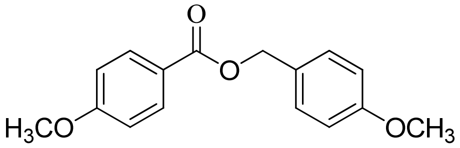
^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 7.967 (d, 7.6 Hz, 2H), 7.348 (d, 8.0 Hz, 2H), 7.240-7.190 (m, 4H), 5.318 (s, 2H), 2.407 (s, 3H), 2.371 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 166.7, 143.8, 138.1, 133.4, 129.9, 129.4, 129.2, 128.5, 127.7, 66.6, 21.8, 21.3; HRMS (M+) calcd for $C_{16}H_{16}O_2$: 240.1150 found 240.1155.

3-Methylbenzyl 3-methylbenzoate (**4g**)



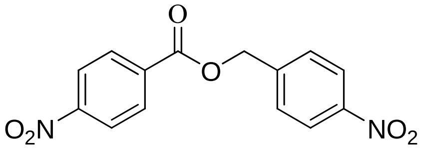
^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 7.886 (t, 8.6 Hz, 2H), 7.381-7.243 (m, 5H), 7.161 (d, 6.8 Hz, 1H), 5.329 (s, 2H), 2.400 (s, 3H), 2.381 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 166.8, 138.4, 138.3, 136.2, 133.9, 130.4, 130.3, 129.13, 129.10, 128.7, 128.4, 127.0, 125.4, 66.9, 21.5, 21.4; HRMS (M+) calcd for $C_{16}H_{16}O_2$: 240.1150 found 240.1153.

4-Methoxybenzyl 4-methoxybenzoate (**4h**)



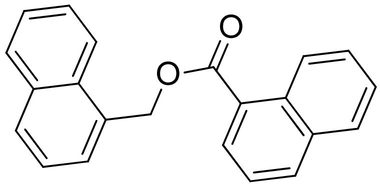
^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 8.023-8.000 (m, 2H), 7.381 (d, 8.8 Hz, 2H), 6.922-6.890 (m, 4H), 5.271 (s, 2H), 3.848 (s, 3H), 3.815 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 166.4, 163.6, 159.8, 131.9, 130.1, 128.6, 122.9, 114.1, 113.7, 66.4, 55.6, 55.4; HRMS (M+) calcd for $C_{16}H_{16}O_4$: 272.1049 found 272.1043.

4-Nitrobenzyl 4-nitrobenzoate (**4i**)



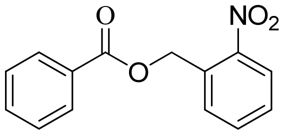
^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 8.318-8.292 (m, 2H), 8.273-8.232 (m, 4H), 7.622 (d, 8.8 Hz, 2H), 5.503 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 164.4, 151.0, 148.2, 142.5, 135.0, 131.0, 128.8, 124.1, 123.8, 66.2; HRMS (M+) calcd for $C_{14}H_{10}N_2O_6$: 302.0539 found 302.0544.

naphthalen-1-ylmethyl 1-naphthoate (**4k**)



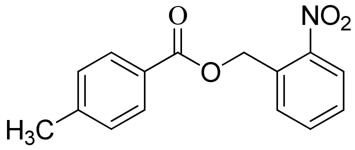
^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 8.881 (d, 8.7 Hz, 1H), 8.108-8.072 (m, 2H), 7.902 (d, 8.2 Hz, 1H), 7.835-7.762 (m, 3H), 7.603 (d, 6.8 Hz, 1H), 7.523-7.466 (m, 2H), 7.449-7.386 (m, 3H), 7.358-7.320 (m, 1H), 5.823 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 167.5, 134.5, 134.0, 133.7, 132.0, 131.7, 131.6, 130.6, 129.5, 128.9, 128.7, 128.0, 127.8, 127.0, 126.8, 126.4, 126.1, 126.0, 125.5, 124.6, 123.8, 65.3; HRMS (M+) calcd for $C_{22}H_{16}O_2$: 312.1150 found 312.1161.

2-Nitrobenzyl benzoate (**4l**)



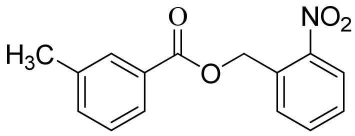
^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 8.148-8.0874 (m, 3H), 7.700-7.637 (m, 2H), 7.623-7.580 (m, 1H), 7.528-7.457 (m, 3H), 5.787 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 166.1, 147.8, 133.9, 133.5, 132.5, 129.9, 129.7, 129.1, 128.9, 128.7, 125.3, 63.5; HRMS (M+) calcd for $C_{14}H_{11}NO_4$: 257.0688 found 257.0694.

2-Nitrobenzyl 4-methylbenzoate (**4m**)



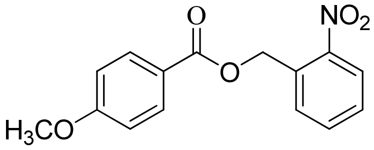
^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 8.108 (t, 8.6 Hz, 1H), 7.977-7.957 (m, 2H), 7.665-7.607 (m, 2H), 7.496-7.454 (m, 1H), 7.241 (s, 2H), 5.745 (s, 2H), 2.406 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 166.1, 147.8, 144.3, 133.9, 132.7, 129.9, 129.4, 129.0, 128.8, 127.0, 125.2, 63.3, 21.8; HRMS (M+) calcd for $C_{15}H_{13}NO_4$: 271.0845 found 271.0844.

2-Nitrobenzyl 3-methylbenzoate (**4n**)



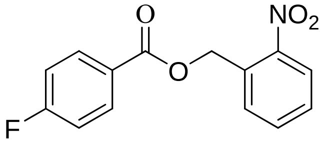
^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 8.149-8.127 (m, 1H), 7.909-7.889 (m, 2H), 7.687-7.634 (m, 2H), 7.524-7.482 (m, 1H), 7.421-7.358 (m, 2H), 5.778 (s, 2H), 2.421 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 166.3, 147.8, 138.6, 134.3, 133.9, 132.6, 130.5, 129.7, 129.1, 128.9, 128.6, 127.1, 125.3, 63.4, 21.4; HRMS (M+) calcd for $C_{15}H_{13}NO_4$: 271.0845 found 271.0841.

2-Nitrobenzyl 4-methoxybenzoate (**4o**)



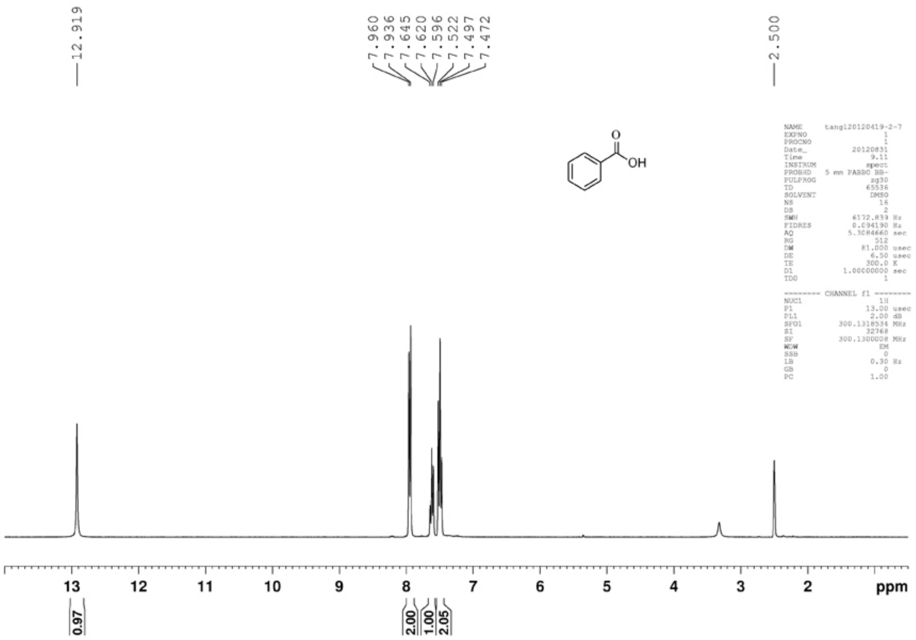
^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 8.119 (t, 8.4 Hz, 1H), 8.065-8.029 (m, 2H), 7.682-7.622 (m, 2H), 7.511-7.469 (m, 1H), 6.964-6.928 (m, 2H), 5.748 (s, 2H), 3.870 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 165.8, 163.9, 147.8, 133.9, 132.8, 132.0, 129.0, 128.8, 125.2, 122.1, 114.0, 63.2, 55.6; HRMS (M+) calcd for $C_{15}H_{13}NO_5$: 287.0794 found 287.0799.

2-Nitrobenzyl 4-fluorobenzoate (**4p**)



^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 8.143-8.089 (m, 3H), 7.669-7.642 (m, 2H), 7.538-7.495 (m, 1H), 7.164-7.121 (m, 2H), 5.468 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 166.2 (d, J_{CF} = 253 Hz), 165.1, 147.9, 133.9, 132.5 (d, J_{CF} = 9.0 Hz), 132.2, 129.2, 129.1, 126.0 (d, J_{CF} = 3.0 Hz), 125.3, 115.9 (d, J_{CF} = 22.0 Hz), 63.6; HRMS (M+) calcd for $C_{14}H_{10}FNO_4$: 275.0594 found 275.0591.

NMR Spectra of products



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SOLVENT                DMSO
NS                       16
DS                        2
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FIDRES             0.094190 Hz
AQ                5.3084660 sec
RG                      512
DW                   81.000 usec
DE                     6.50 usec
TE                    300.0 K
D1               1.00000000 sec
TD0                       1

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NUC1                     1H
P1                    13.00 usec
PL1                    2.00 dB
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WDW                      EM
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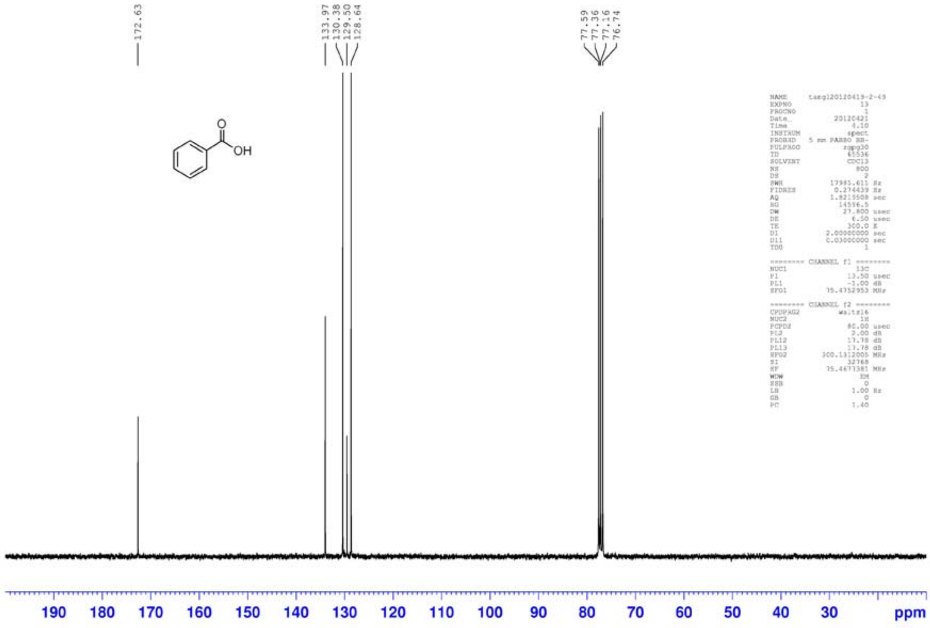

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PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      800
DS                        2
SWH               17985.611 Hz
FIDRES             0.274439 Hz
AQ                1.8215508 sec
RG                  14596.5
DW                   27.800 usec
DE                     6.50 usec
TE                    300.0 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    13.50 usec
PL1                   -1.00 dB
SFO1             75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                    2.00 dB
PL12                  17.78 dB
PL13                  17.78 dB
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SI                    32768
SF               75.4677381 MHz
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SSB                       0
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GB                        0
PC                     1.40
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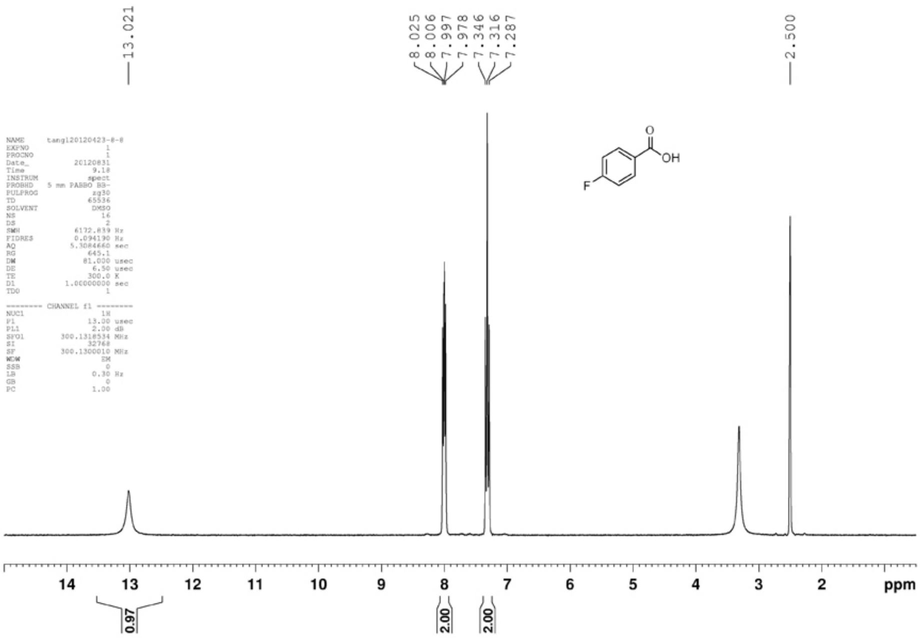

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PROCNO                  1
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TD                  65536
SOLVENT              DMSO
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                  645.1
DW                 81.000 usec
DE                   6.50 usec
TE                  300.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  13.00 usec
PL1                  2.00 dB
SFO1          300.1318534 MHz
SI                  32768
SF            300.1300010 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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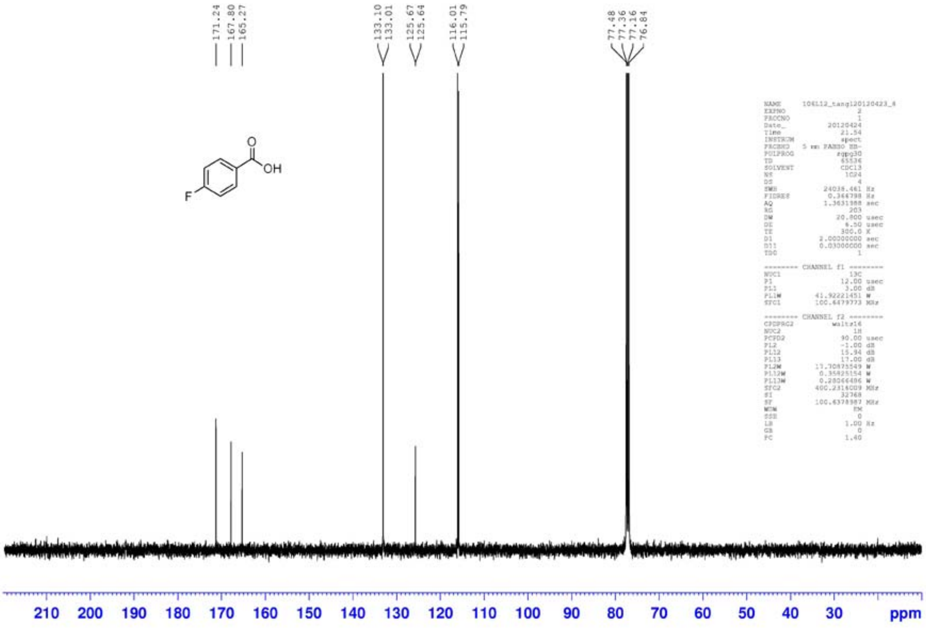

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PROCNO                  1
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PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1024
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SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
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P1                  12.00 usec
PL1                  3.00 dB
PL1W          41.92221451 W
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
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NUC2                   1H
PCPD2               90.00 usec
PL2                 -1.00 dB
PL12                15.94 dB
PL13                17.00 dB
PL2W          13.70875549 W
PL12W          0.35925154 W
PL13W          0.28066406 W
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SI                  32768
SF            100.6378987 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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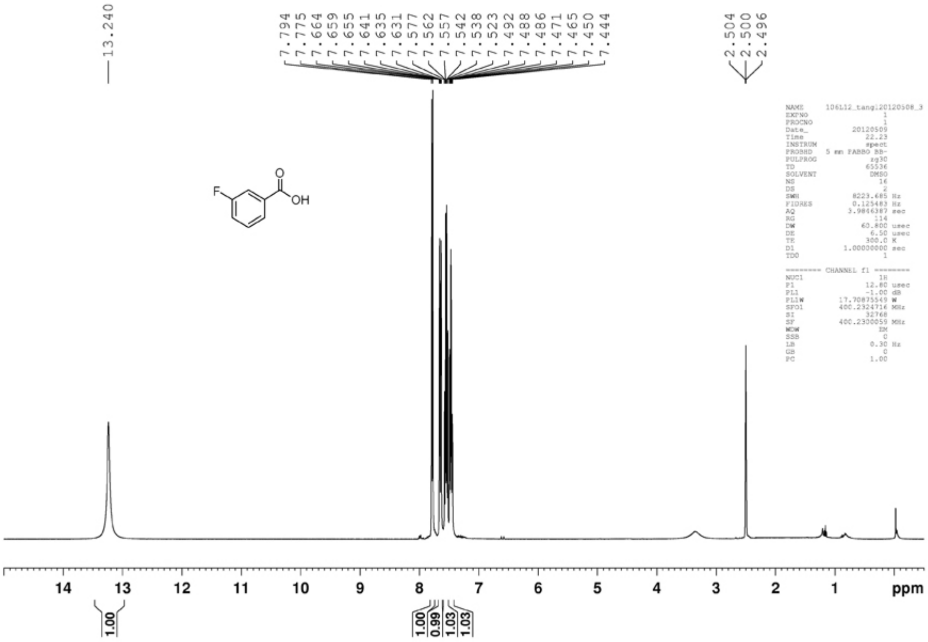
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7.444
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2.496
F
O
OH
14
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12
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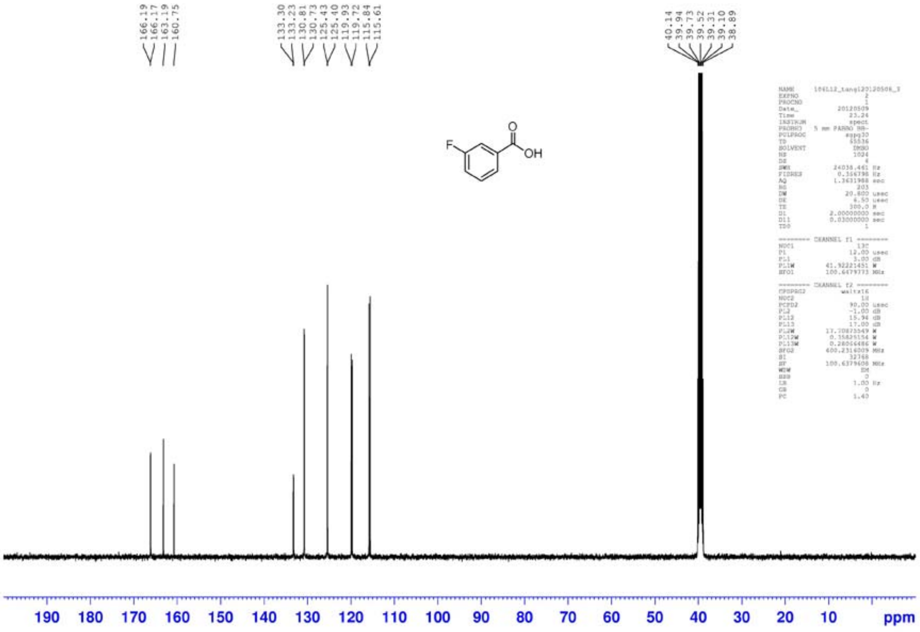
1.03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39.52
39.31
39.10
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O
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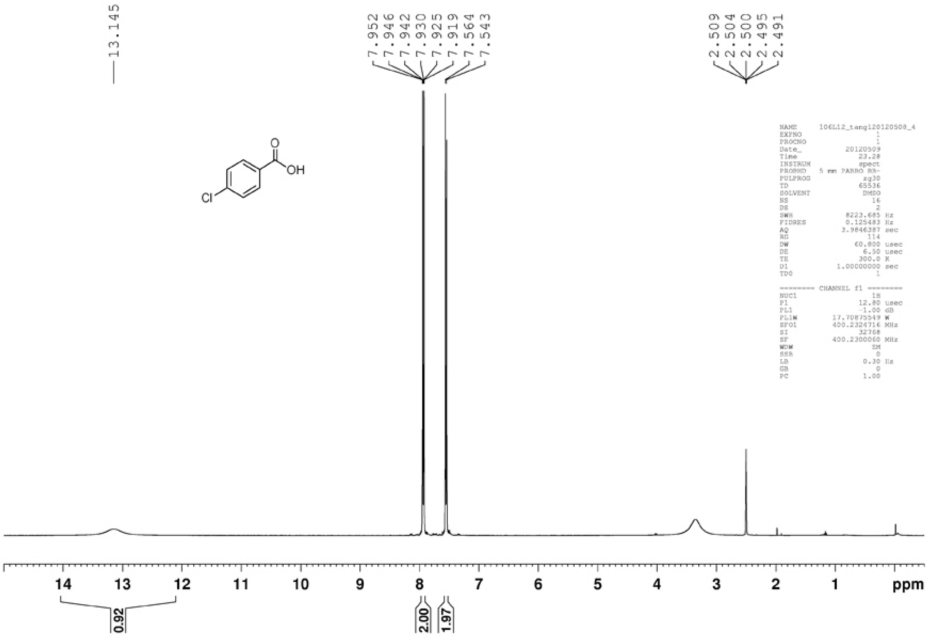
10
ppm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2.500
2.495
2.491
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OH
Cl
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EXPNO 1
PROCNO 1
Date_ 20120509
Time 23.28
INSTRUM spect
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PULPROG zg30
TD 65536
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DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
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PL1 -1.00 dB
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LB 0.30 Hz
GB 0
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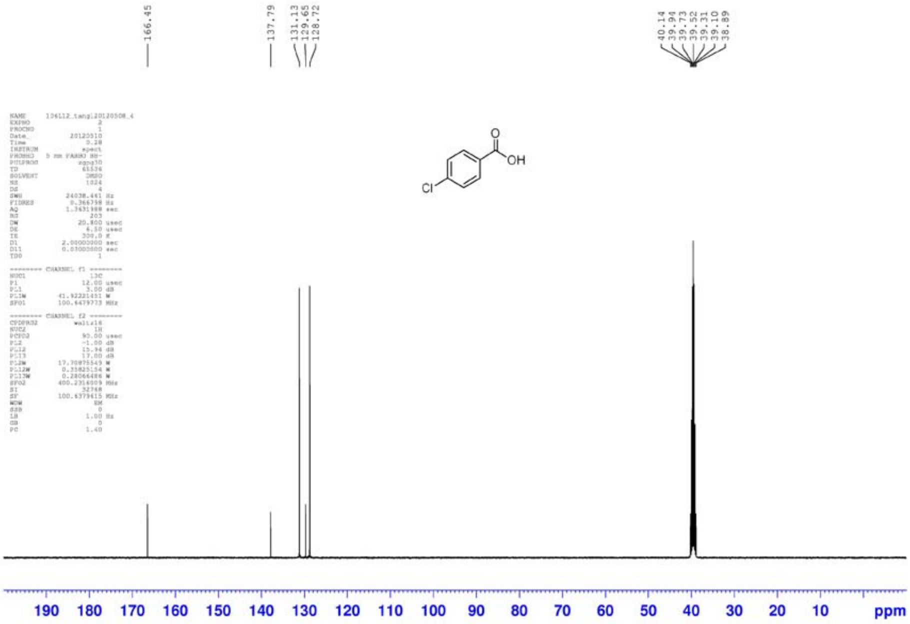
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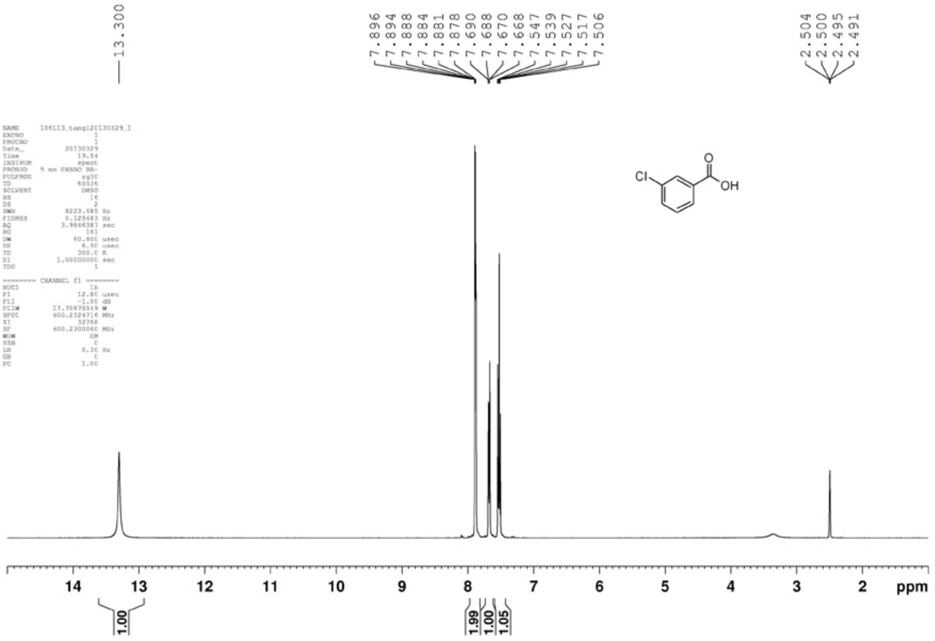
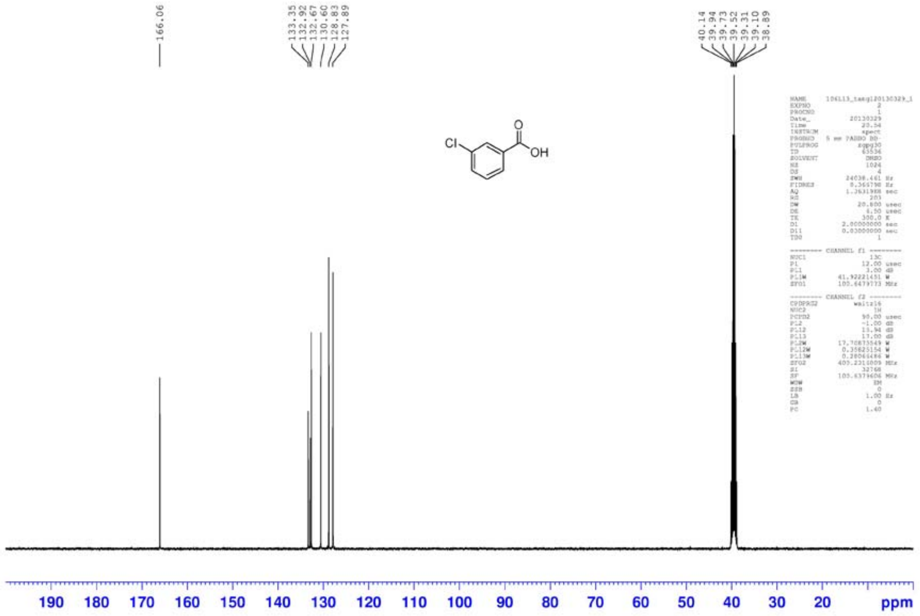
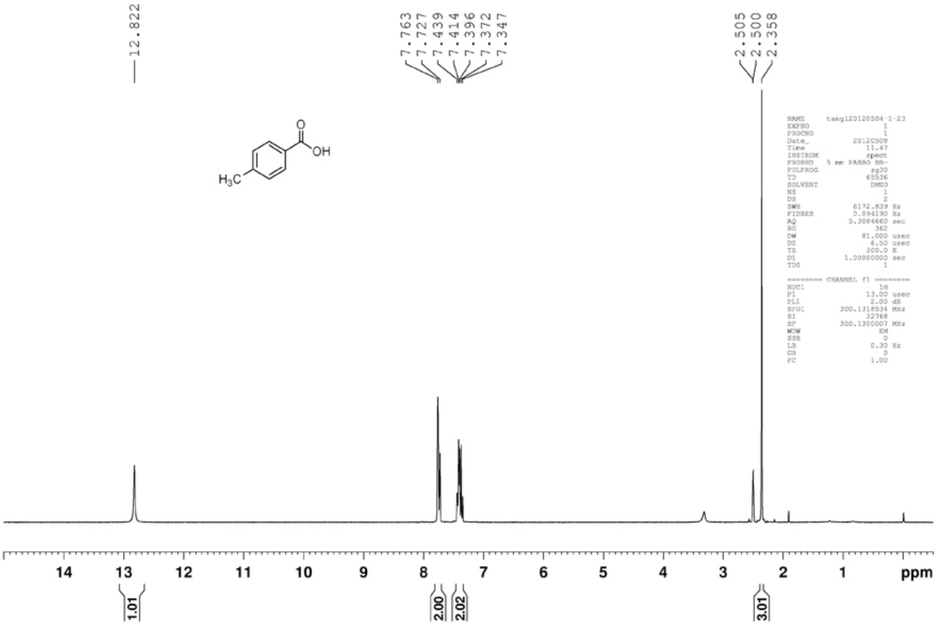
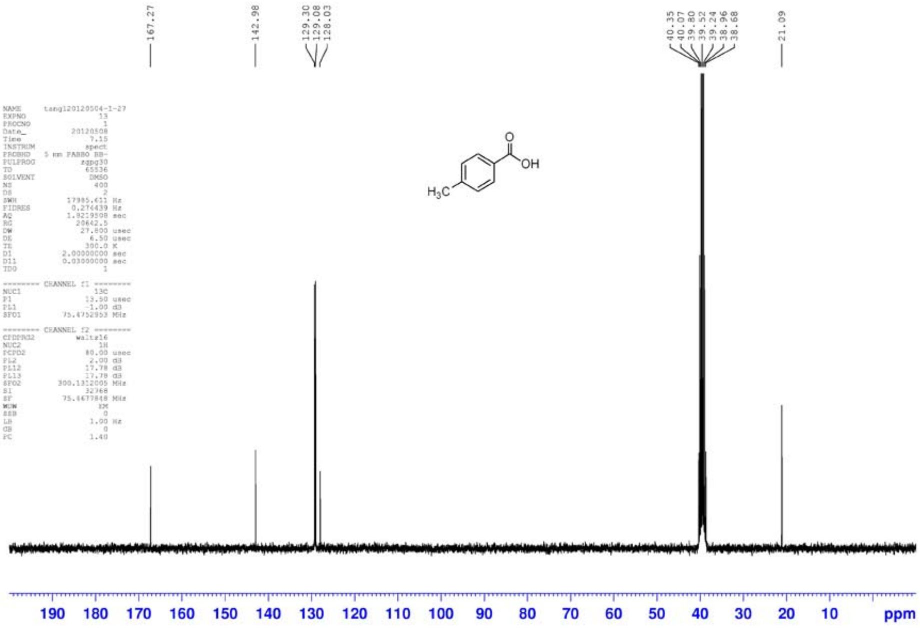
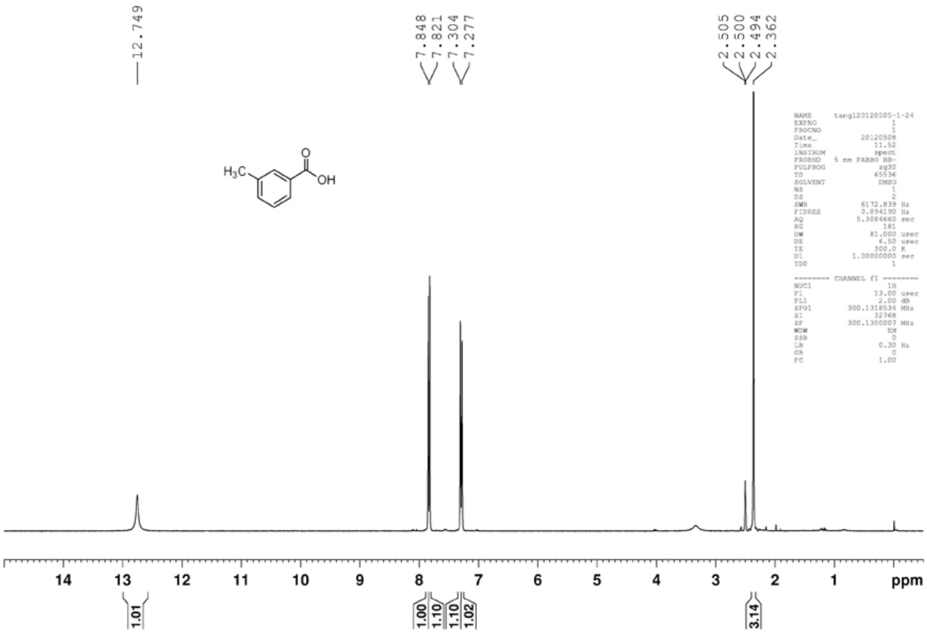
39.52
39.31
39.10
38.89
NAME 106L12_tang120120508_4
EXPNO 2
PROCNO 1
Date_ 20120510
Time 0.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 3.00 dB
PL1W 41.92221451 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.94 dB
PL13 17.00 dB
PL2W 17.70875549 W
PL12W 0.35825154 W
PL13W 0.28066486 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379615 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
OH
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

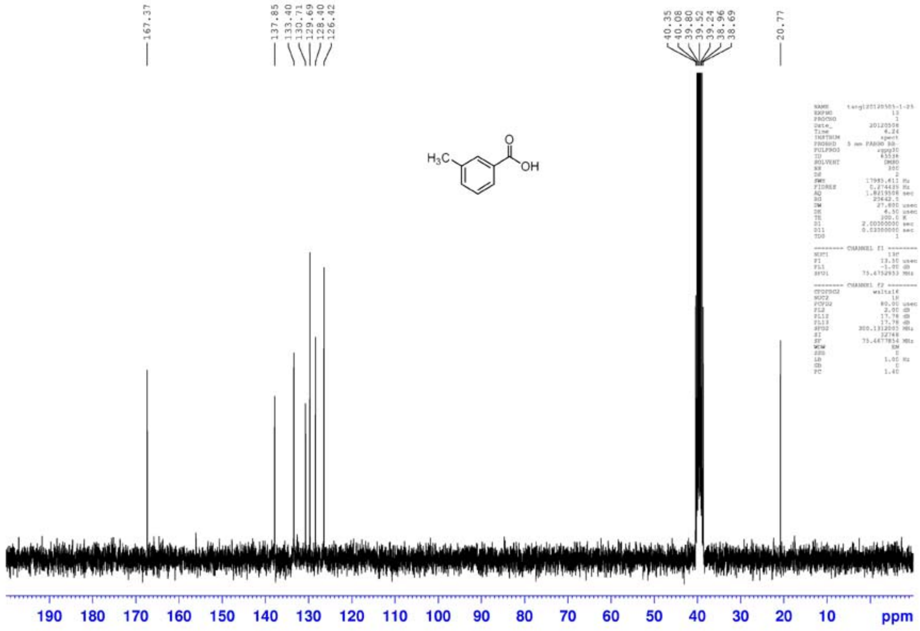

13.300
7.896
7.894
7.888
7.884
7.881
7.878
7.690
7.688
7.670
7.668
7.547
7.539
7.527
7.517
7.506
2.504
2.500
2.495
2.491
Cl
O
OH
14
13
12
11
10
9
8
7
6
5
4
3
2
ppm
1.00
1.99
1.00
1.05


166.06
133.35
132.92
132.67
130.60
128.83
127.89
40.14
39.94
39.73
39.52
39.31
39.10
38.89
Cl
O
OH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


12.822
7.763
7.727
7.439
7.414
7.396
7.372
7.347
2.505
2.500
2.358
OH
O
H3C
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.01
2.00
2.02
3.01


167.27
142.98
129.30
129.08
128.03
40.35
40.07
39.80
39.52
39.24
38.96
38.68
21.09
OH
O
H3C
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


12.749
7.848
7.821
7.304
7.277
2.505
2.500
2.494
2.362
H_3C
O
OH
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.01
1.00
1.10
1.10
1.02
3.14


167.37
137.85
133.40
130.71
129.69
128.40
126.42
40.35
40.08
39.80
39.52
39.24
38.96
38.69
20.77
H_3C
O
OH
190
180
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140
130
120
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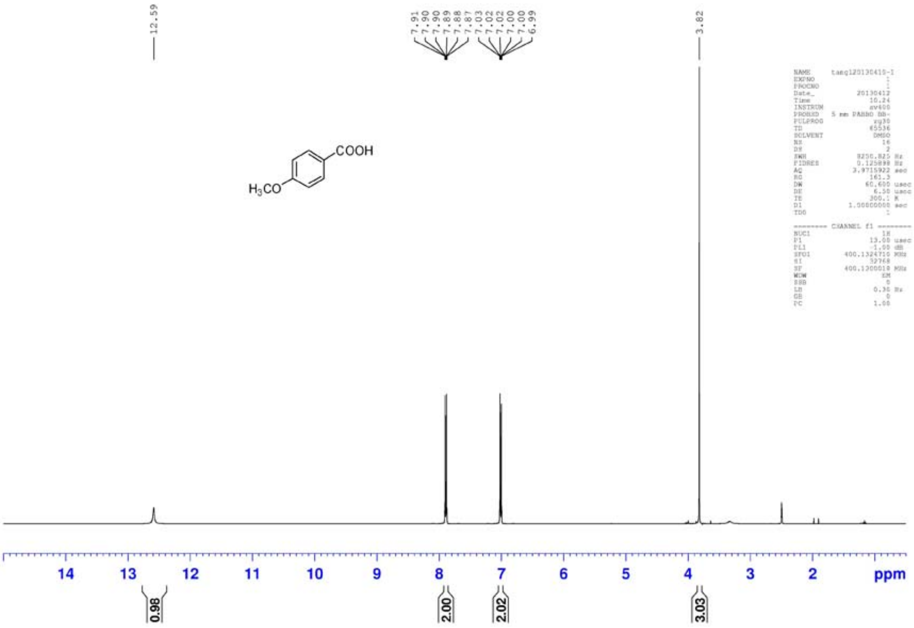
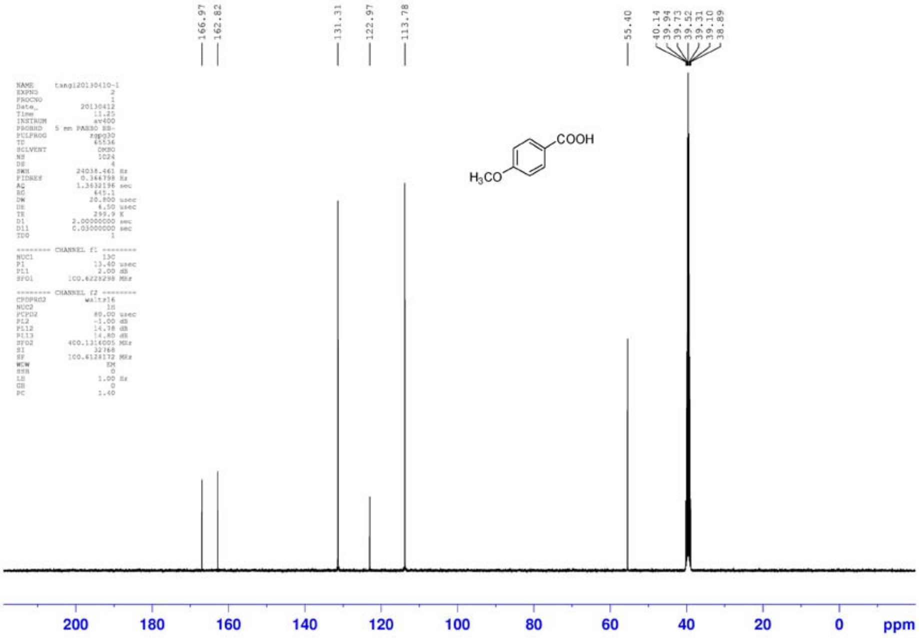
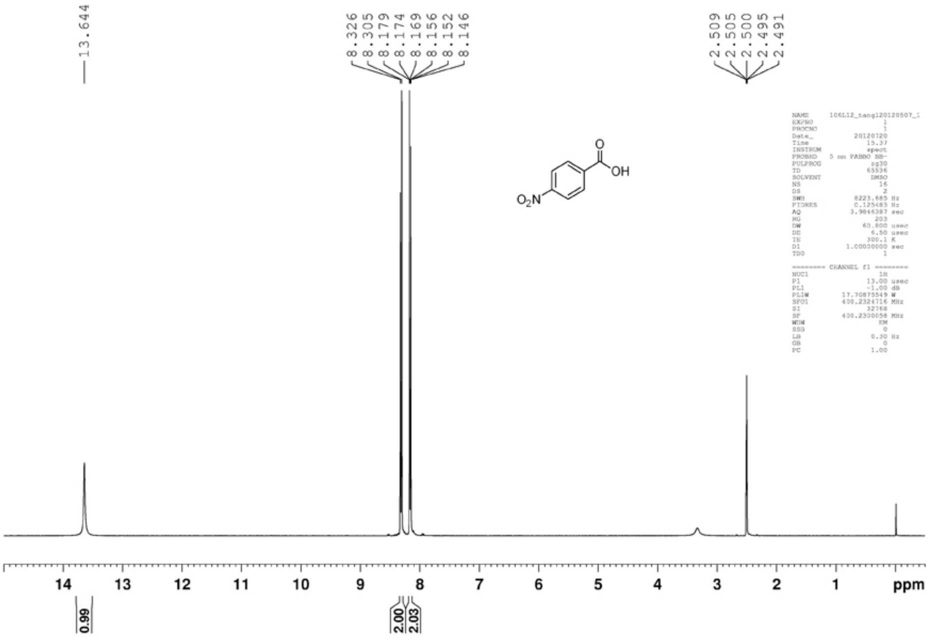
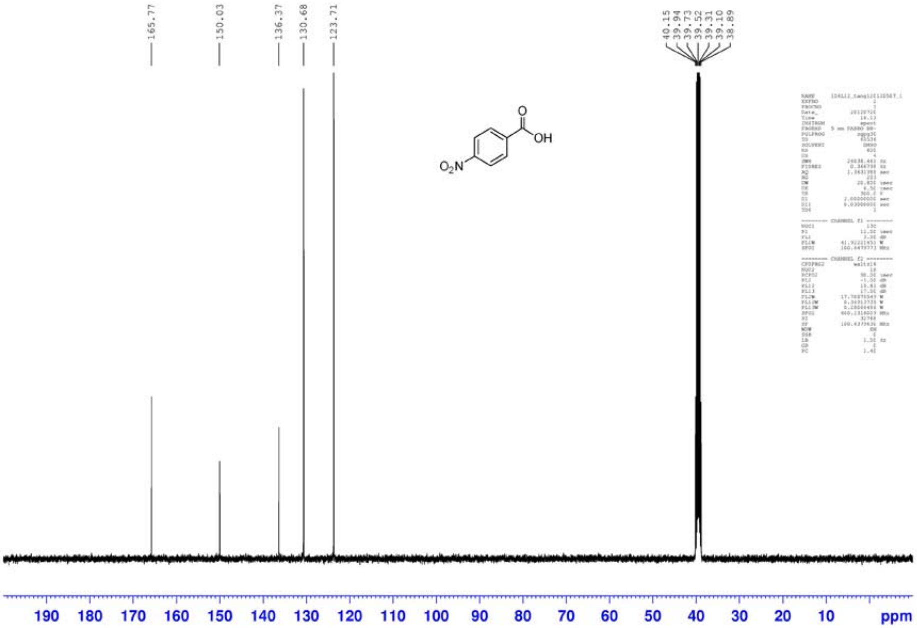
60
50
40
30
20
10
ppm


12.59
7.91
7.90
7.90
7.89
7.88
7.87
7.03
7.02
7.02
7.00
7.00
6.99
3.82
COOH
H3CO
NAME tang120130410-1
EXPNO 1
PROCNO 1
Date_ 20130412
Time 10.24
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8250.825 Hz
FIDRES 0.125898 Hz
AQ 3.9715922 sec
RG 161.3
DW 60.600 usec
DE 6.50 usec
TE 300.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 400.1324710 MHz
SI 32768
SF 400.1300018 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
14
13
12
11
10
9
8
7
6
5
4
3
2
ppm
0.98
2.00
2.02
3.03


166.97
162.82
131.31
122.97
113.78
55.40
40.14
39.94
39.73
39.52
39.31
39.10
38.89
NAME tang120130410-1
EXPNO 2
PROCNO 1
Date_ 20130412
Time 11.25
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3632196 sec
RG 645.1
DW 20.800 usec
DE 6.50 usec
TE 299.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 13.40 usec
PL1 2.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.78 dB
PL13 14.80 dB
SFO2 400.1316005 MHz
SI 32768
SF 100.6128172 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
COOH
H3CO
200
180
160
140
120
100
80
60
40
20
0
ppm


13.644
8.326
8.305
8.179
8.174
8.169
8.156
8.152
8.146
2.509
2.505
2.500
2.495
2.491
O
OH
O2N
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.99
2.00
2.03


165.77
150.03
136.37
130.68
123.71
40.15
39.94
39.73
39.52
39.31
39.10
38.89
O
OH
O2N
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150
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130
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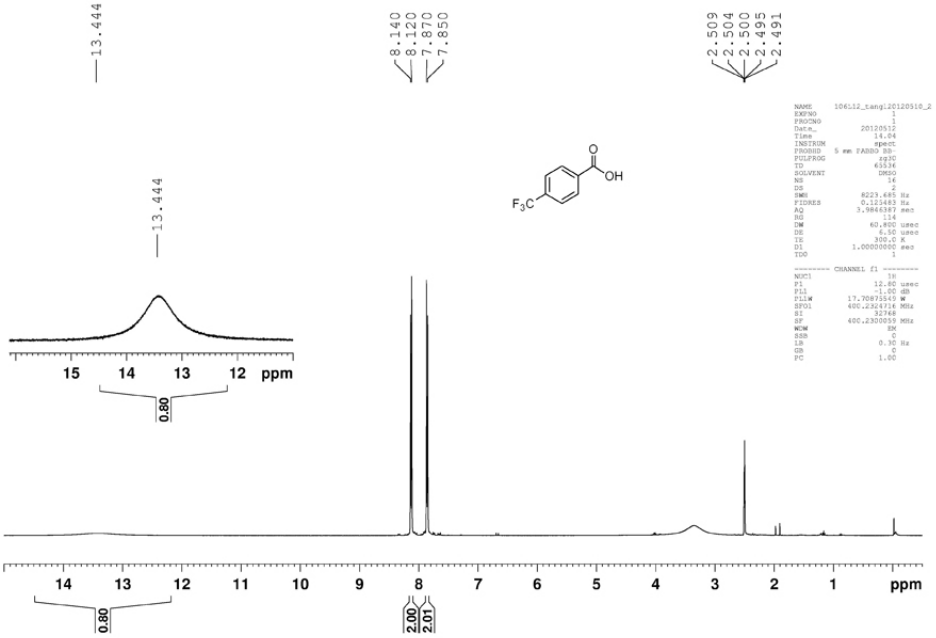
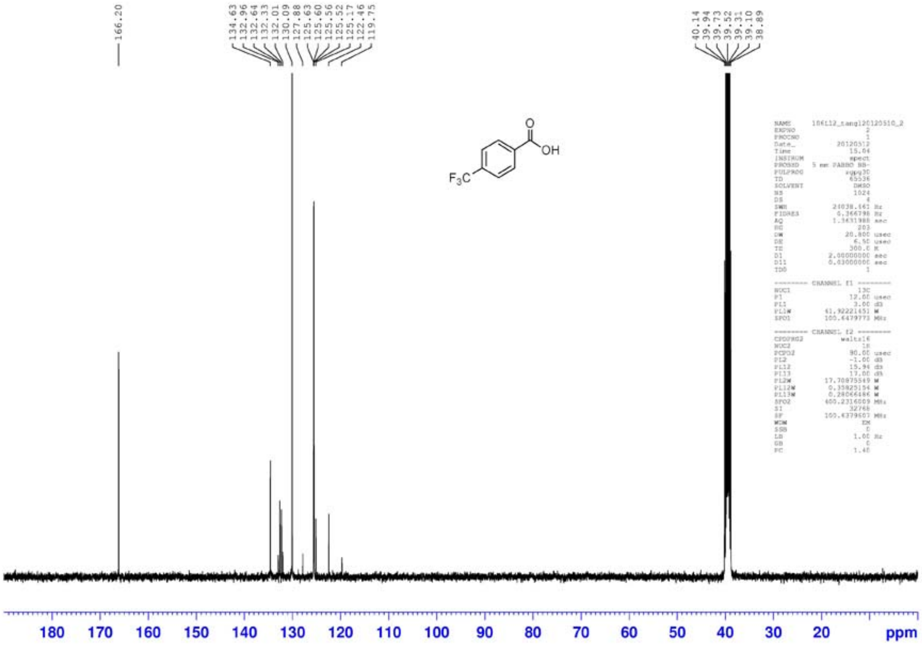
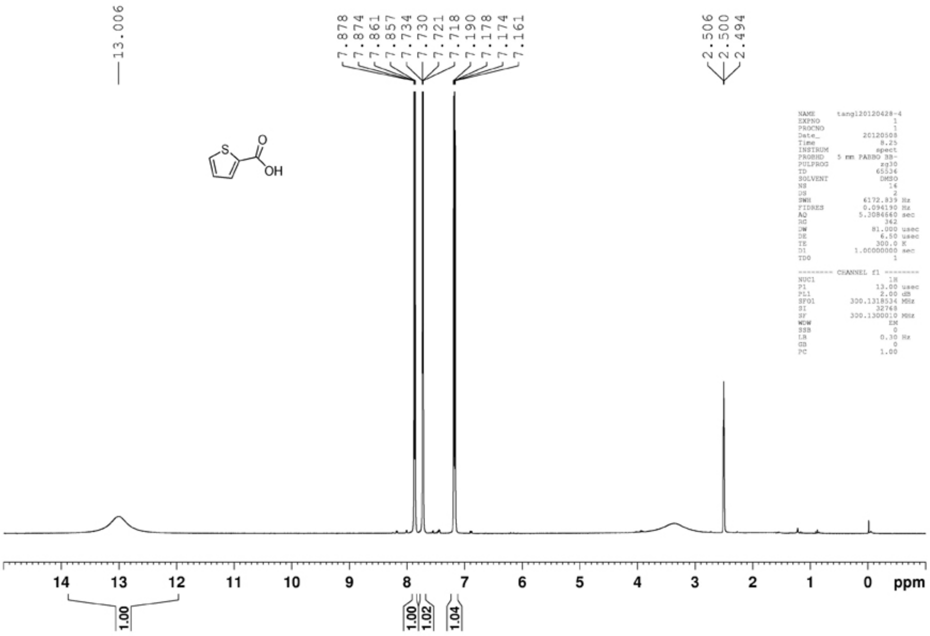
60
50
40
30
20
10
ppm

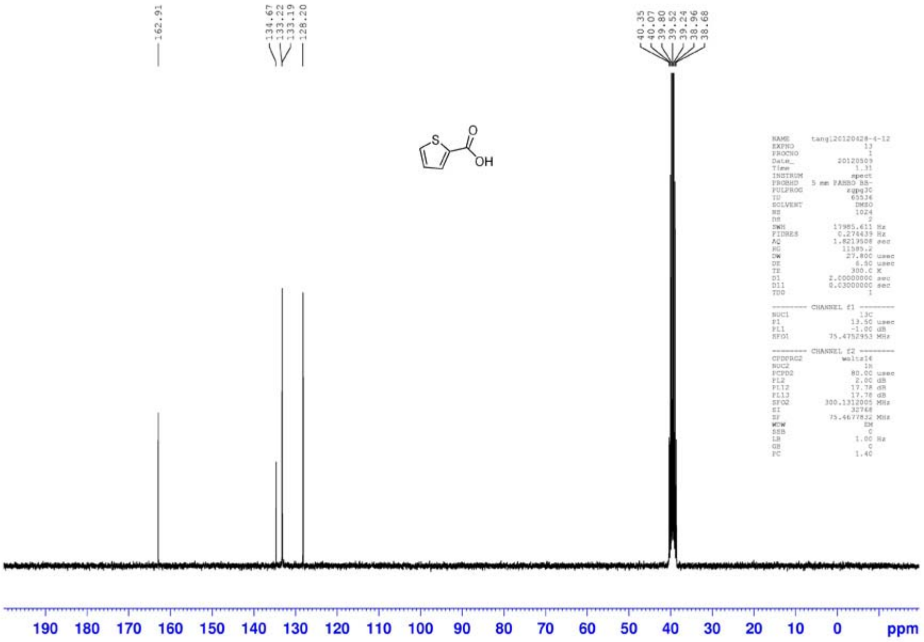


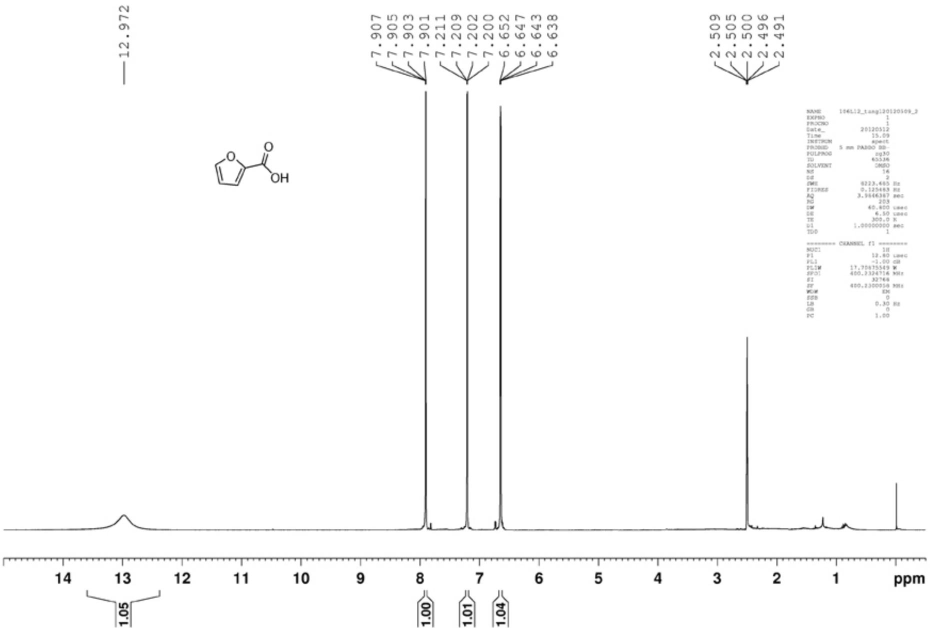
```
NAME       106L12_tang120120510_2
EXPNO                    1
PROCNO                   1
Date_             20120512
Time                 14.04
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      16
DS                       2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ               3.9846387 sec
RG                     114
DW                  60.800 usec
DE                    6.50 usec
TE                   300.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.80 usec
PL1                  -1.00 dB
PL1W           17.70875549 W
SFO1           400.2324716 MHz
SI                   32768
SF             400.2300059 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

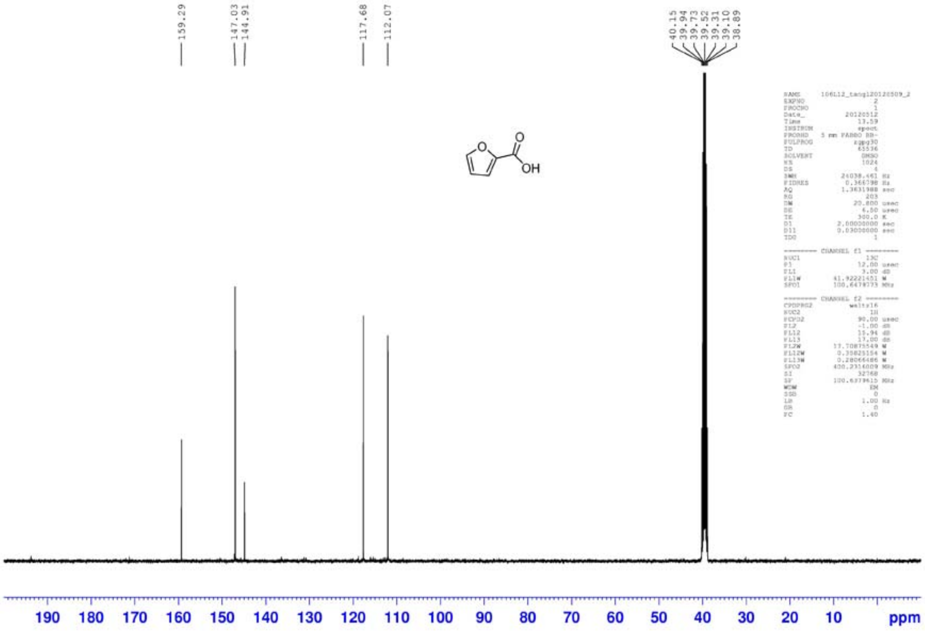


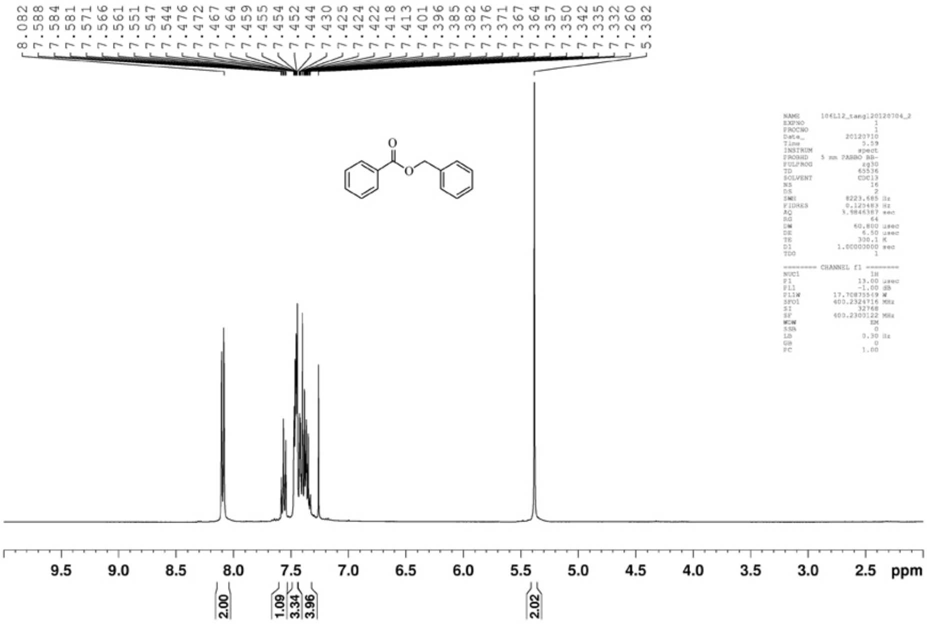
```
NAME       106L12_tang120120510_2
EXPNO                    2
PROCNO                   1
Date_             20120512
Time                 15.04
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT               DMSO
NS                    1024
DS                       4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                     203
DW                  20.800 usec
DE                    6.50 usec
TE                   300.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   12.00 usec
PL1                   3.00 dB
PL1W           41.92221451 W
SFO1           100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -1.00 dB
PL12                 15.94 dB
PL13                 17.00 dB
PL2W           17.70875549 W
PL12W           0.35825154 W
PL13W           0.28066486 W
SFO2           400.2316009 MHz
SI                   32768
SF             100.6379607 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

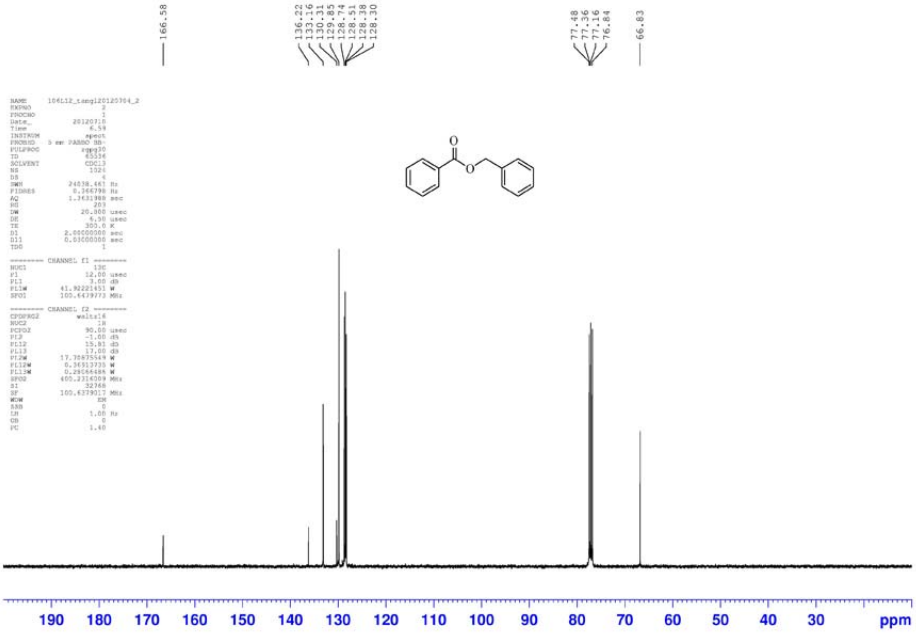

13.006
7.878
7.874
7.861
7.857
7.734
7.730
7.721
7.718
7.190
7.178
7.174
7.161
2.506
2.500
2.494
S
O
OH
NAME tang120120428-4
EXPNO 1
PROCNO 1
Date_ 20120508
Time 8.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 362
DW 81.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300010 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.02
1.04

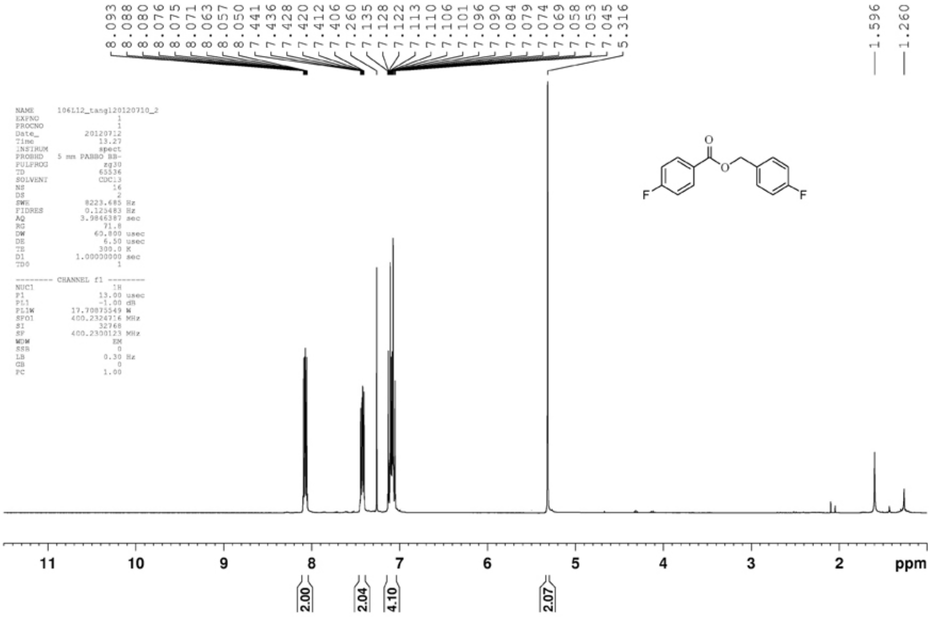

162.91
134.67
133.22
133.19
128.20
40.35
40.07
39.80
39.52
39.24
38.96
38.68
S
O
OH
NAME tang120120428-4-12
EXPNO 13
PROCNO 1
Date_ 20120509
Time 1.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1024
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 11585.2
DW 27.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 13.50 usec
PL1 -1.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 2.00 dB
PL12 17.78 dB
PL13 17.78 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677832 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

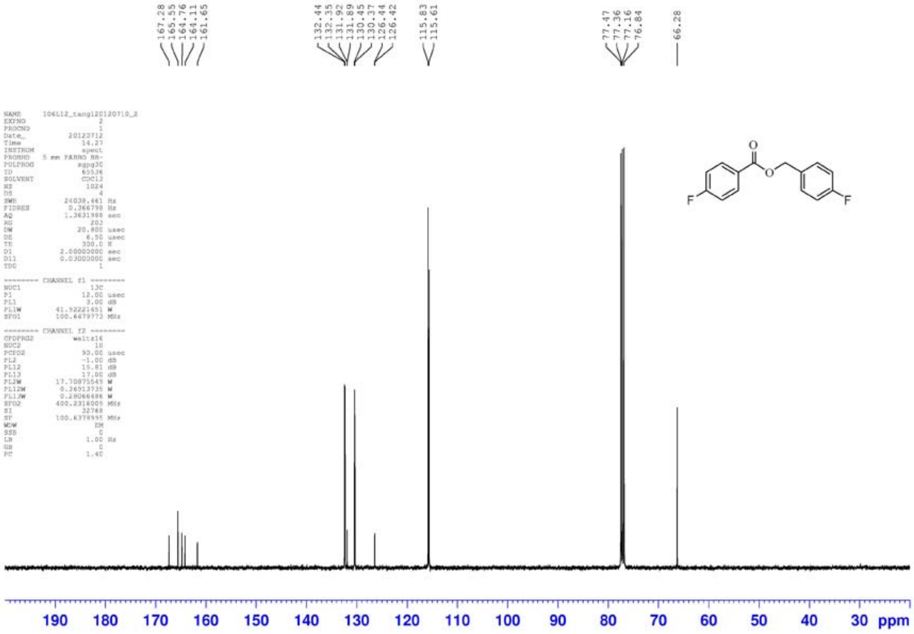

12.972
7.907
7.905
7.903
7.901
7.211
7.209
7.202
7.200
6.652
6.647
6.643
6.638
2.509
2.505
2.500
2.496
2.491
O
OH
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.05
1.00
1.01
1.04

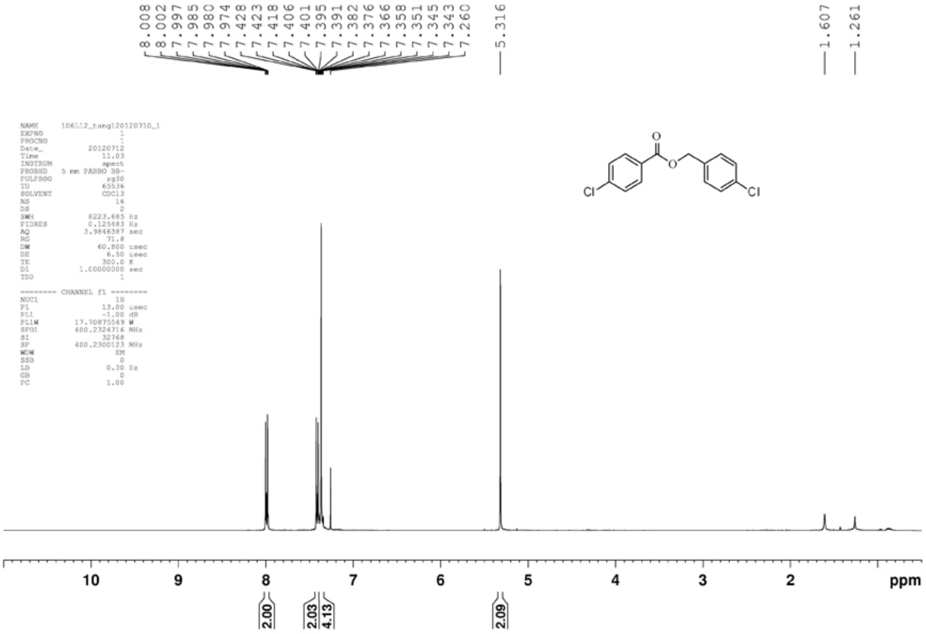

159.29
147.03
144.91
117.68
112.07
40.15
39.94
39.73
39.52
39.31
39.10
38.89
O
OH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.082
7.588
7.584
7.581
7.571
7.566
7.561
7.551
7.547
7.544
7.476
7.472
7.467
7.464
7.459
7.455
7.454
7.452
7.444
7.430
7.425
7.424
7.422
7.418
7.413
7.401
7.396
7.385
7.382
7.376
7.371
7.367
7.364
7.357
7.350
7.342
7.335
7.332
7.260
5.382
O
O
NAME 104L12_tang120120704_2
EXPNO 1
PROCNO 1
Date_ 20120710
Time 5.59
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 64
DW 60.800 usec
DE 6.50 usec
TE 300.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
PL1W 17.70875549 W
SFO1 400.2324716 MHz
SI 32768
SF 400.2300122 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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
ppm
2.00
1.09
3.34
3.96
2.02


166.58
136.22
133.16
130.31
129.85
128.74
128.51
128.38
128.30
77.48
77.36
77.16
76.84
66.83
NAME 104L12_tang120120704_2
EXPNO 2
PROCNO 1
Date_ 20120710
Time 6.59
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 3.00 dB
PL1W 41.92221451 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.81 dB
PL13 17.00 dB
PL2W 17.70875549 W
PL12W 0.36513735 W
PL13W 0.29566486 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379017 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


8.093
8.088
8.080
8.076
8.075
8.071
8.063
8.057
8.050
7.441
7.436
7.428
7.420
7.412
7.406
7.260
7.135
7.128
7.122
7.113
7.110
7.106
7.101
7.096
7.090
7.084
7.079
7.074
7.069
7.058
7.053
7.045
5.316
1.596
1.260
NAME 106L12_tang120120710_2
EXPNO 1
PROCNO 1
Date_ 20120712
Time 13.27
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 71.8
DW 60.800 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
PL1W 17.70875549 W
SFO1 400.2324716 MHz
SI 32768
SF 400.2300123 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
O
F
F
11
10
9
8
7
6
5
4
3
2
ppm
2.00
2.04
4.10
2.07


167.28
165.55
164.76
164.11
161.65
132.44
132.35
131.92
131.89
130.45
130.37
126.44
126.42
115.83
115.61
77.47
77.36
77.16
76.84
66.28
NAME 106L12_tang120120710_2
EXPNO 2
PROCNO 1
Date_ 20120712
Time 14.27
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 3.00 dB
PL1W 41.92221451 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.81 dB
PL13 17.00 dB
PL2W 17.70875549 W
PL12W 0.36913735 W
PL13W 0.28066486 W
SFO2 400.2316005 MHz
SI 32768
SF 100.6378995 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
O
F
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


8.008
8.002
7.997
7.985
7.980
7.974
7.428
7.423
7.418
7.406
7.401
7.395
7.391
7.382
7.376
7.366
7.358
7.351
7.345
7.343
7.260
5.316
1.607
1.261
O
O
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9
8
7
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5
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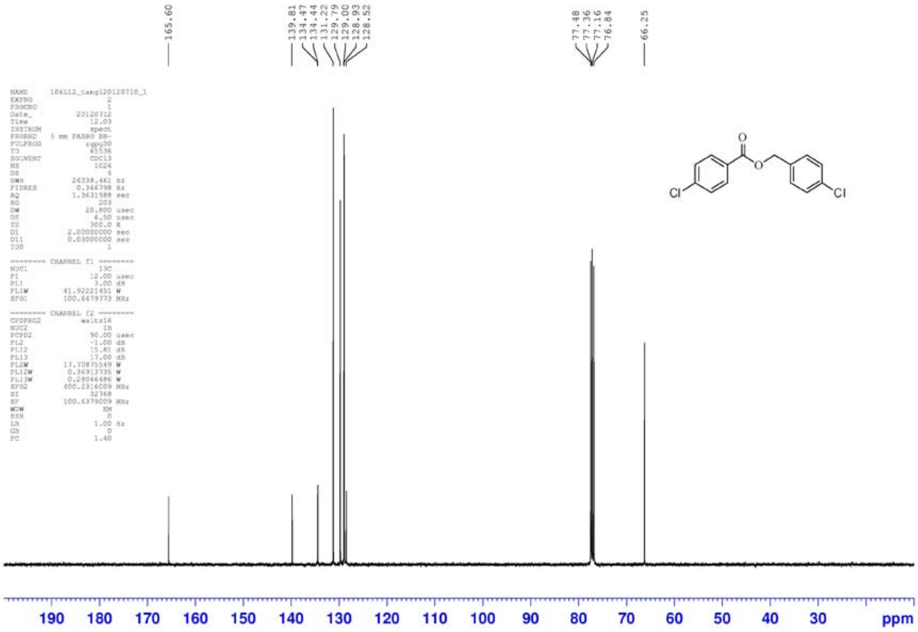
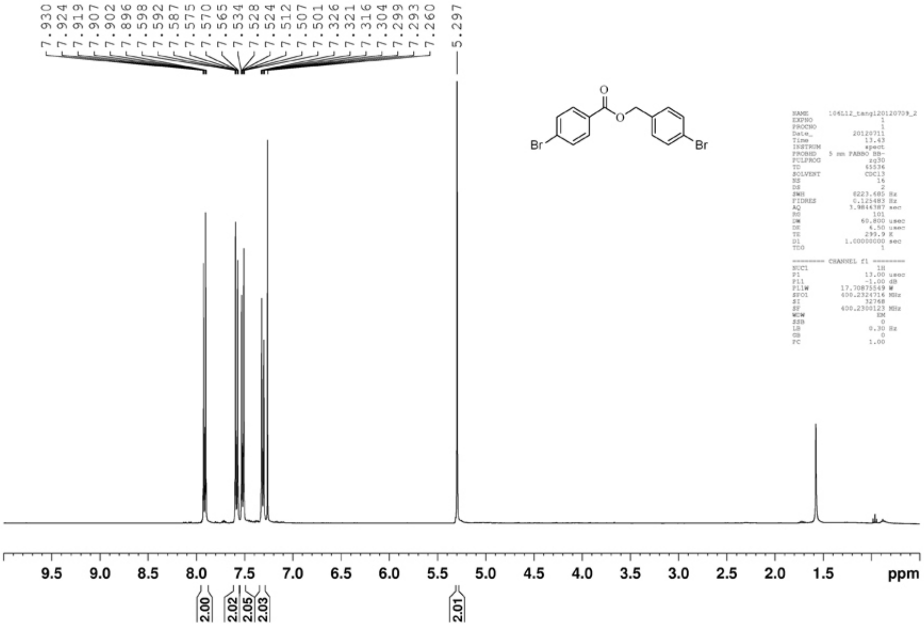
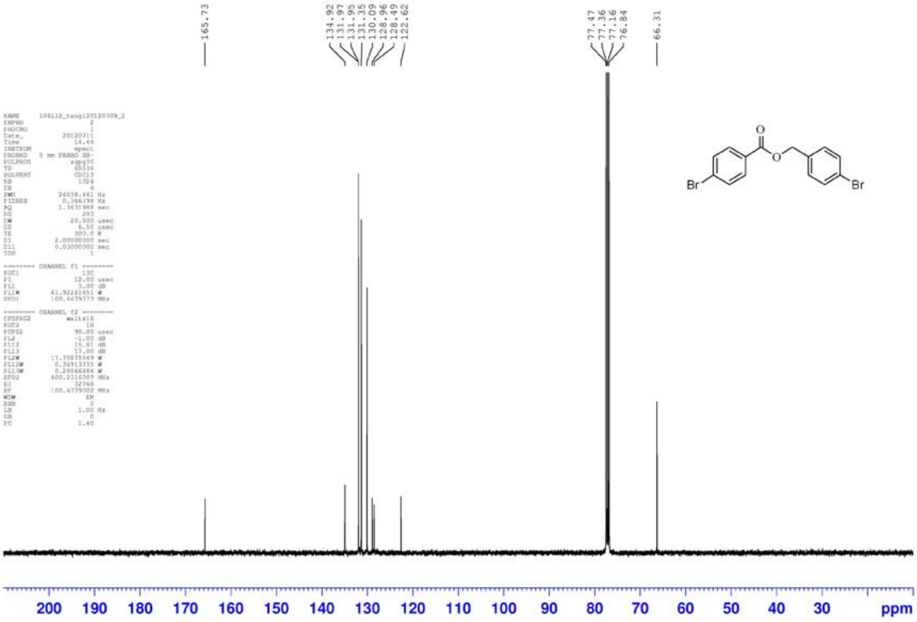
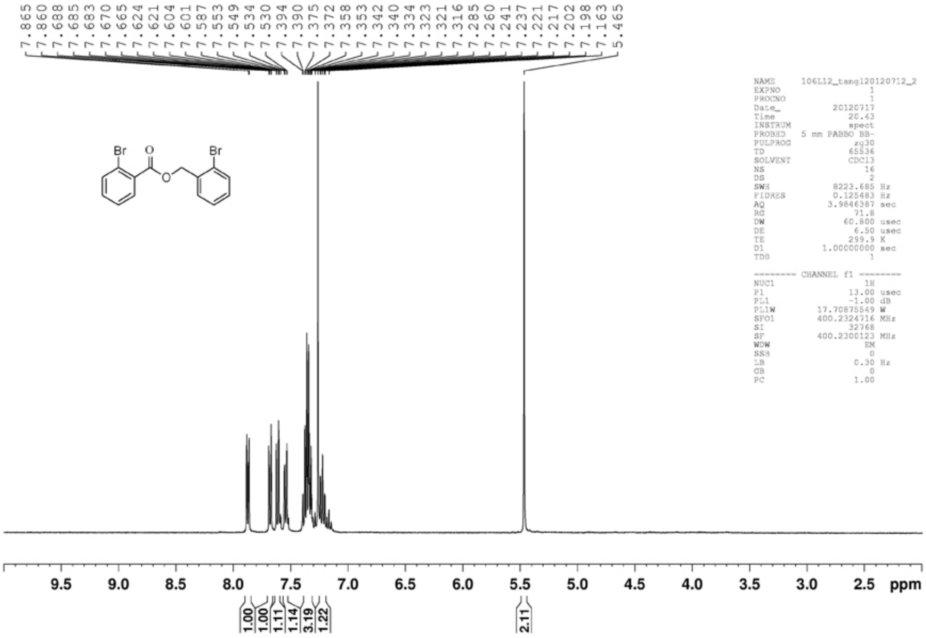
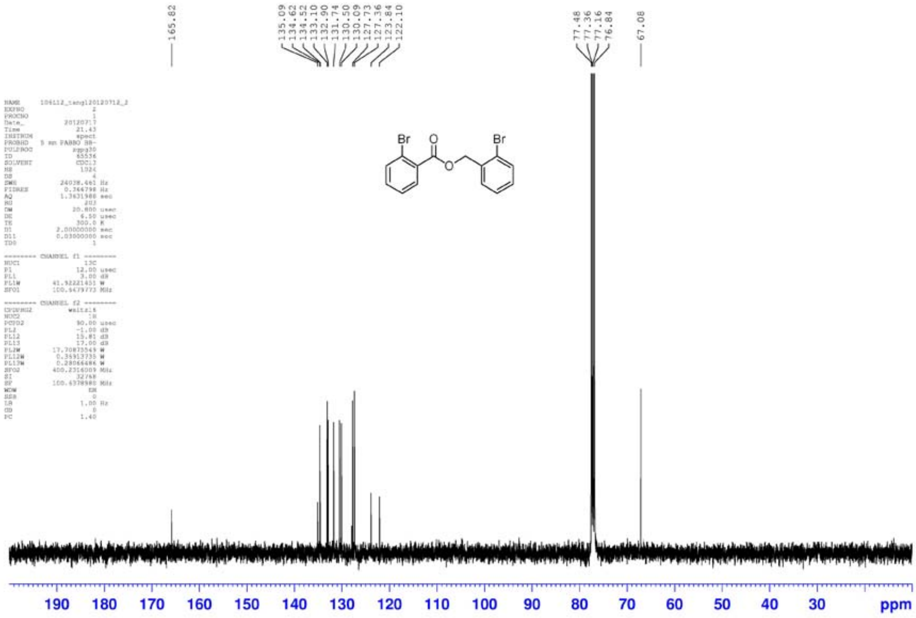
2.00
2.03
4.13
2.09

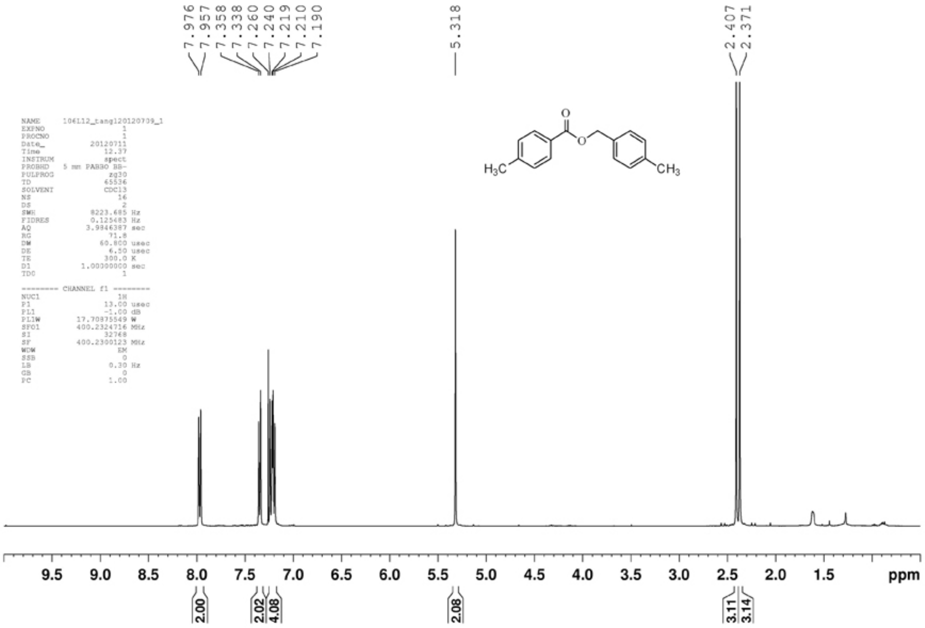

165.60
139.81
134.47
134.44
131.22
129.79
129.00
128.93
128.52
77.48
77.36
77.16
76.84
66.25
O
O
Cl
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


7.930
7.924
7.919
7.907
7.902
7.896
7.598
7.592
7.587
7.575
7.570
7.565
7.534
7.528
7.524
7.512
7.507
7.501
7.326
7.321
7.316
7.304
7.299
7.293
7.260
5.297
O
O
Br
Br
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
ppm
2.00
2.02
2.05
2.03
2.01

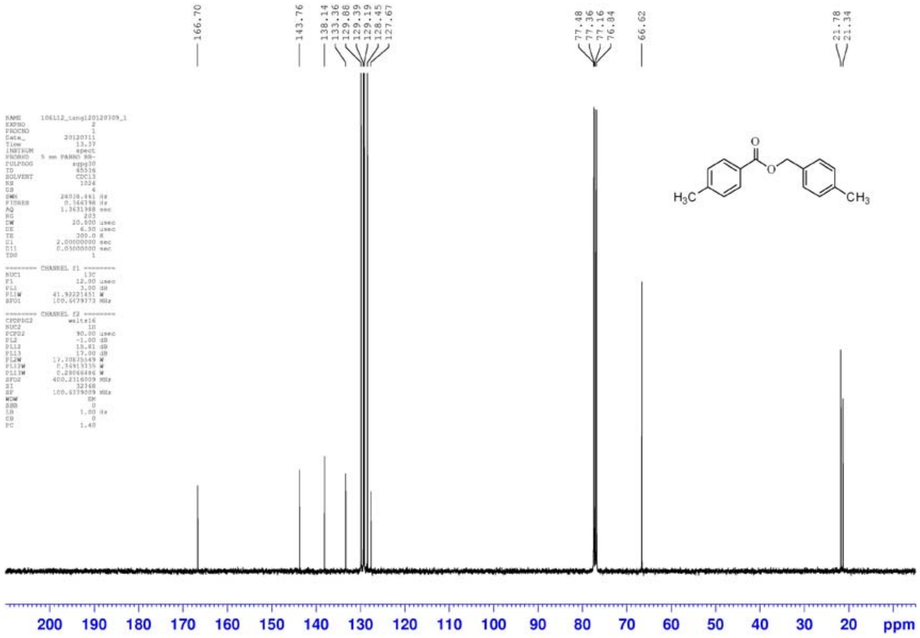

165.73
134.92
131.97
131.95
131.35
130.09
128.96
128.49
122.62
77.47
77.36
77.16
76.84
66.31
O
O
Br
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


7.865
7.860
7.688
7.685
7.683
7.670
7.665
7.624
7.621
7.604
7.601
7.587
7.553
7.549
7.534
7.530
7.394
7.390
7.375
7.372
7.358
7.353
7.342
7.340
7.334
7.323
7.321
7.316
7.285
7.260
7.241
7.237
7.221
7.217
7.202
7.198
7.163
5.465
Br
O
O
Br
NAME 106L12_tang120120712_2
EXPNO 1
PROCNO 1
Date_ 20120717
Time 20.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 71.8
DW 60.800 usec
DE 6.50 usec
TE 299.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
PL1W 17.70875549 W
SFO1 400.2324716 MHz
SI 32768
SF 400.2300123 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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
ppm
1.00
1.00
1.11
1.14
3.19
1.22
2.11

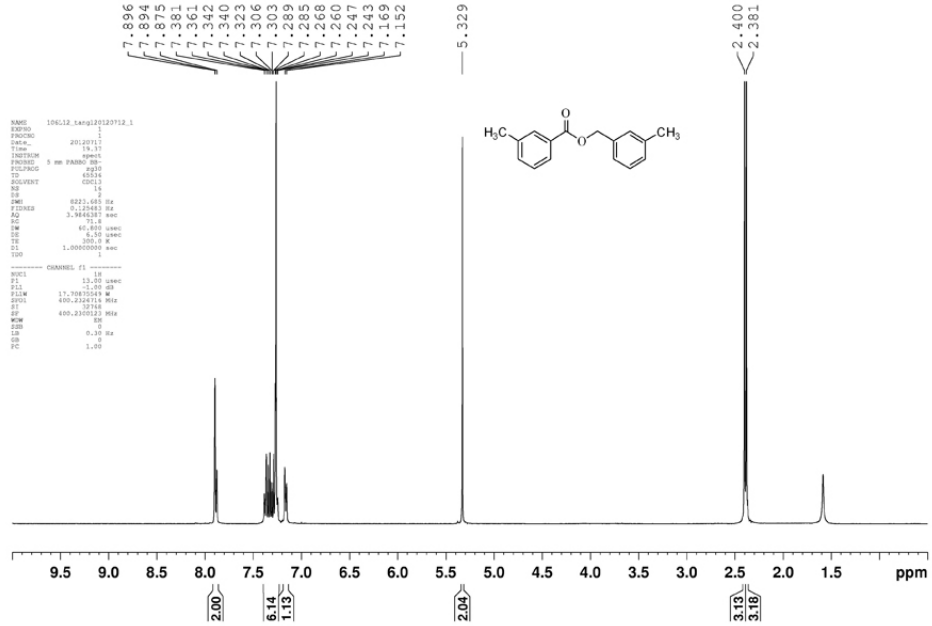

165.82
135.09
134.62
134.52
133.10
132.90
131.74
130.50
130.09
127.73
127.36
123.84
122.10
77.48
77.36
77.16
76.84
67.08
NAME 106L12_tang120120712_2
EXPNO 2
PROCNO 1
Date_ 20120717
Time 21.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 3.00 dB
PL1W 41.92221451 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.81 dB
PL13 17.00 dB
PL2W 17.70875549 W
PL12W 0.35913735 W
PL13W 0.28066486 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6378981 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Br
O
O
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

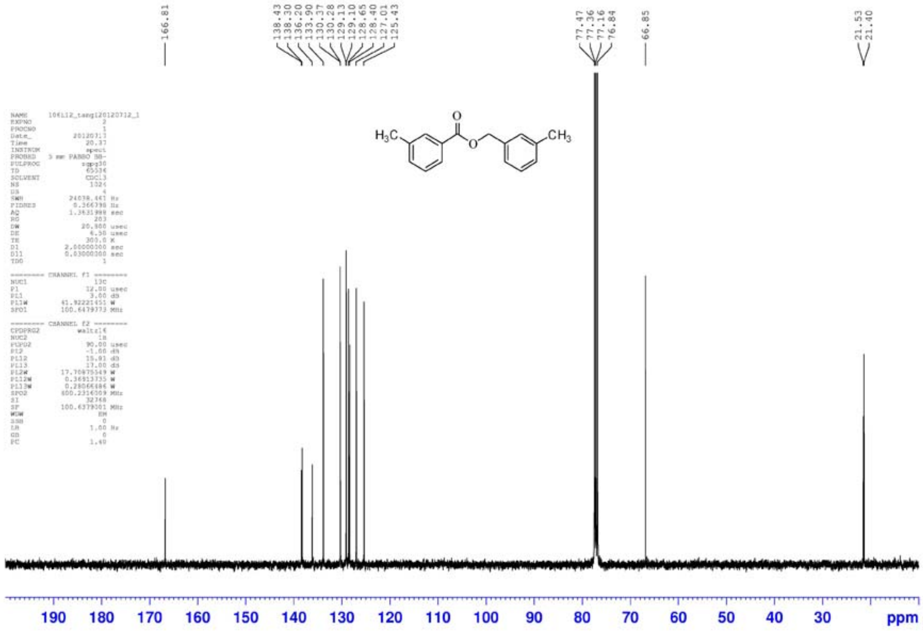


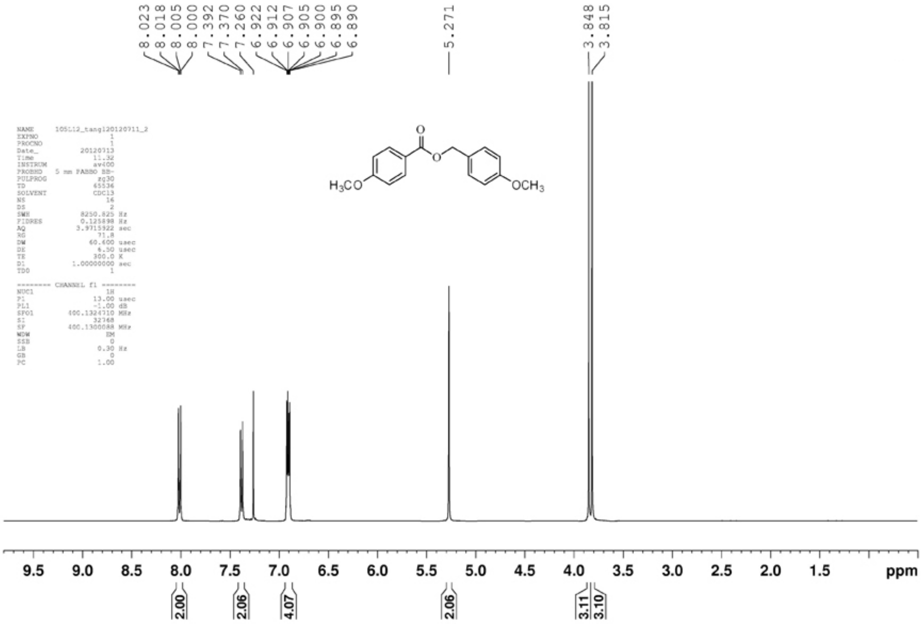
```
NAME      106L12_tang120120709_1
EXPNO                    1
PROCNO                   1
Date_             20120711
Time                 12.37
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ               3.9846387 sec
RG                    71.8
DW                  60.800 usec
DE                    6.50 usec
TE                   300.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.00 usec
PL1                  -1.00 dB
PL1W           17.70875549 W
SFO1           400.2324716 MHz
SI                   32768
SF             400.2300123 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

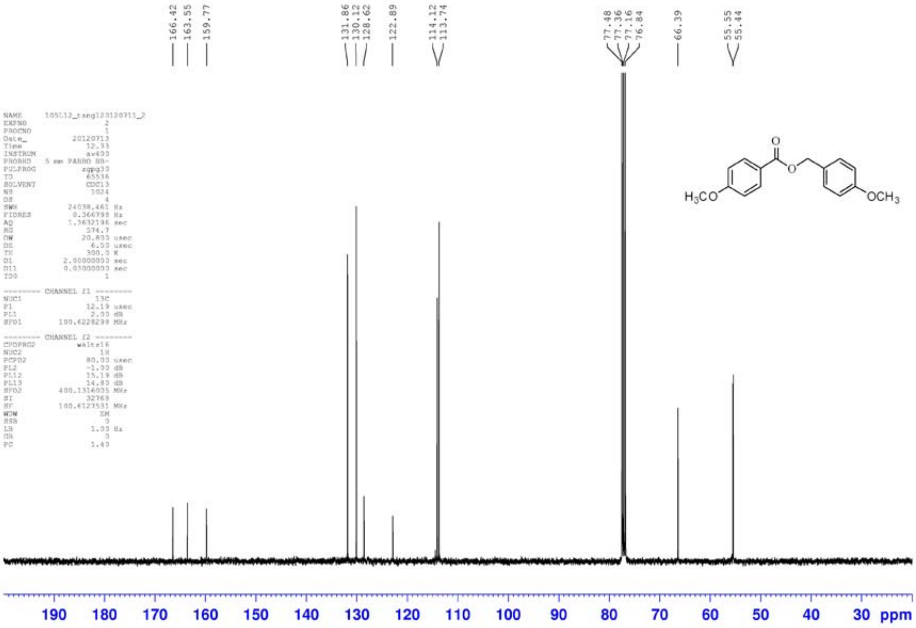


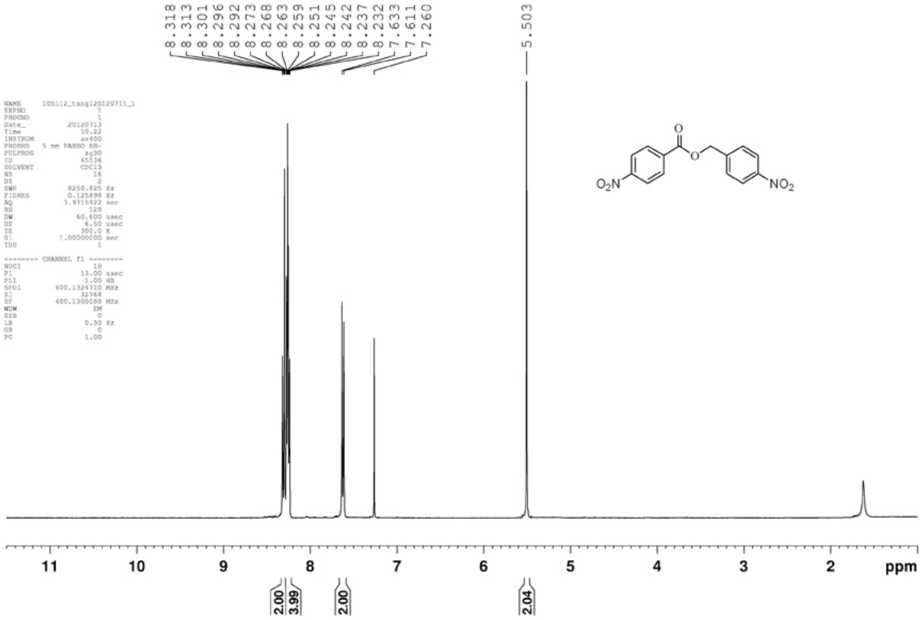
```
NAME      106L12_tang120120709_1
EXPNO                    2
PROCNO                   1
Date_             20120711
Time                 13.37
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                     203
DW                  20.800 usec
DE                    6.50 usec
TE                   300.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   12.00 usec
PL1                   3.00 dB
PL1W           41.92221451 W
SFO1           100.6479373 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -1.00 dB
PL12                 15.81 dB
PL13                 17.00 dB
PL2W           17.70875549 W
PL12W           0.36913335 W
PL13W           0.28066486 W
SFO2           400.2316009 MHz
SI                   32768
SF             100.6379009 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

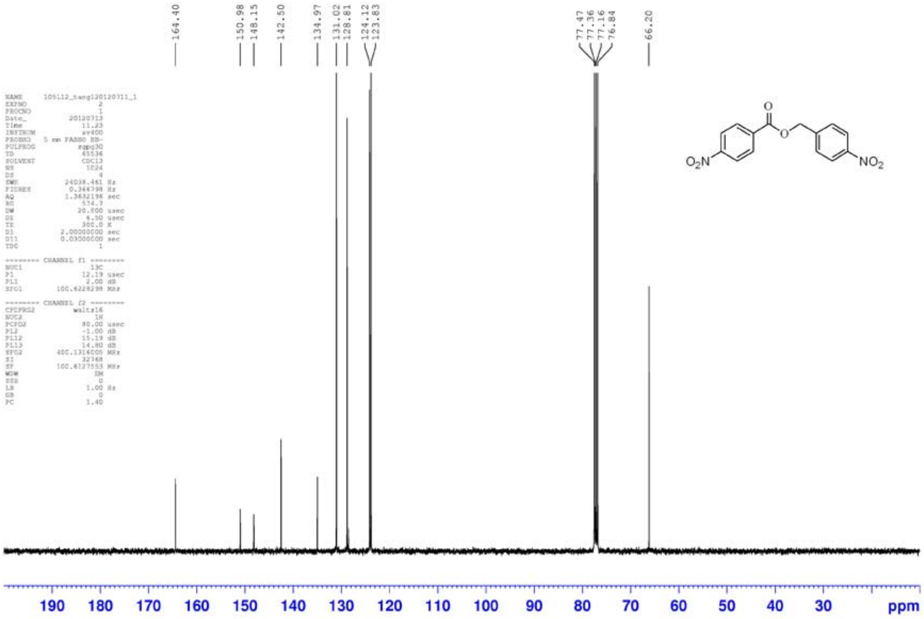

7.896
7.894
7.875
7.381
7.361
7.342
7.340
7.323
7.306
7.303
7.289
7.285
7.268
7.260
7.247
7.243
7.169
7.152
5.329
2.400
2.381
H_3C
O
O
CH_3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
2.00
6.14
1.13
2.04
3.13
3.18

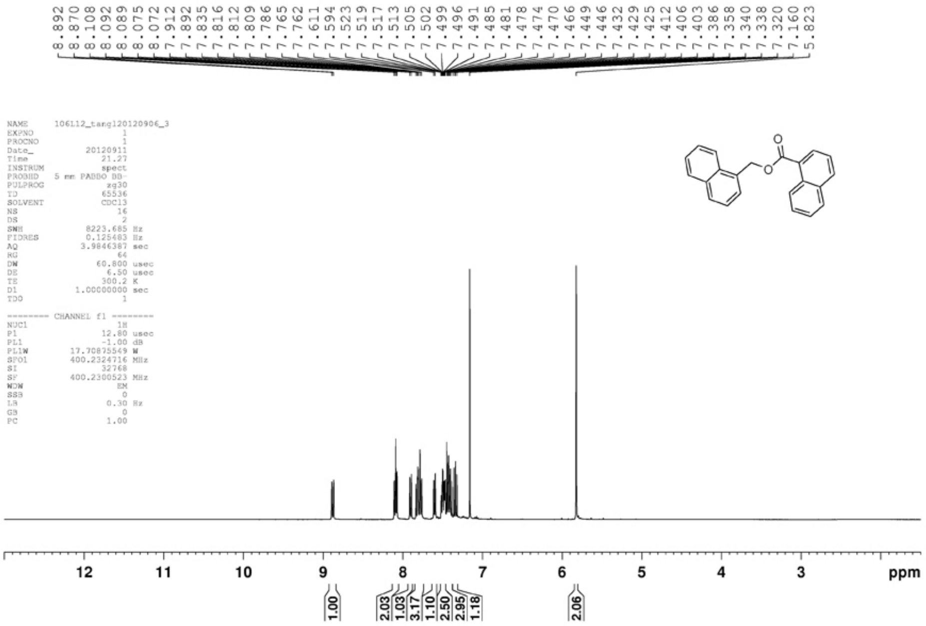

166.81
138.43
138.30
136.20
133.90
130.37
130.28
129.13
129.10
128.65
128.40
127.01
125.43
77.47
77.36
77.16
76.84
66.85
21.53
21.40
H_3C
O
O
CH_3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


8.023
8.018
8.005
8.000
7.392
7.370
7.260
6.922
6.912
6.907
6.905
6.900
6.895
6.890
5.271
3.848
3.815
NAME 105L12_tang120120711_2
EXPNO 1
PROCNO 1
Date_ 20120713
Time 11.32
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8250.825 Hz
FIDRES 0.125898 Hz
AQ 3.9715922 sec
RG 71.8
DW 60.600 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 400.1324710 MHz
SI 32768
SF 400.1300088 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
O
H3CO
OCH3
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
ppm
2.00
2.06
4.07
2.06
3.11
3.10


166.42
163.55
159.77
131.86
130.12
128.62
122.89
114.12
113.74
77.48
77.36
77.16
76.84
66.39
55.55
55.44
NAME 105L12_tang120120711_2
EXPNO 2
PROCNO 1
Date_ 20120713
Time 12.33
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3632196 sec
RG 574.7
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.19 usec
PL1 2.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 15.19 dB
PL13 14.80 dB
SFO2 400.1316005 MHz
SI 32768
SF 100.6127531 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
O
H3CO
OCH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


8.318
8.313
8.301
8.296
8.292
8.273
8.268
8.263
8.259
8.251
8.245
8.242
8.237
8.232
7.633
7.611
7.260
5.503
NAME 105L12_tang120120711_1
EXPNO 1
PROCNO 1
Date_ 20120713
Time 10.22
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8250.825 Hz
FIDRES 0.125898 Hz
AQ 3.9715922 sec
RG 128
DW 60.600 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 400.1324710 MHz
SI 32768
SF 400.1300088 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
O
O_2N
NO_2
11
10
9
8
7
6
5
4
3
2
ppm
2.00
3.99
2.00
2.04


164.40
150.98
148.15
142.50
134.97
131.02
128.81
124.12
123.83
77.47
77.36
77.16
76.84
66.20
NAME 105L12_tang120120711_1
EXPNO 2
PROCNO 1
Date_ 20120713
Time 11.23
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3632196 sec
RG 574.7
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.19 usec
PL1 2.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 15.19 dB
PL13 14.80 dB
SFO2 400.1316005 MHz
SI 32768
SF 100.6127553 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
O
O_2N
NO_2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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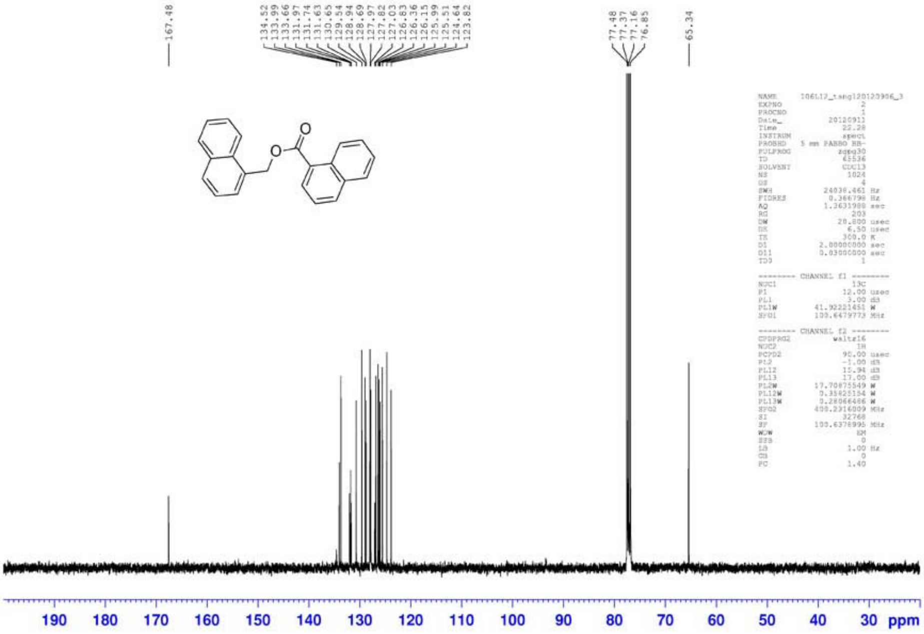
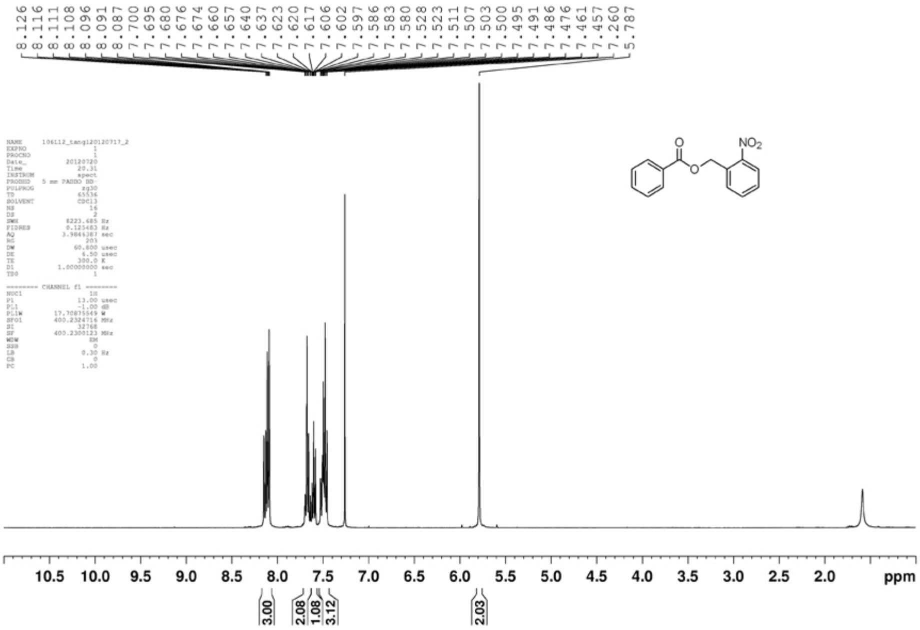
8.870
8.108
8.092
8.089
8.075
8.072
7.912
7.892
7.835
7.816
7.812
7.809
7.786
7.765
7.762
7.611
7.594
7.523
7.519
7.517
7.513
7.505
7.502
7.499
7.496
7.491
7.485
7.481
7.478
7.474
7.470
7.466
7.449
7.446
7.432
7.429
7.425
7.412
7.406
7.403
7.386
7.358
7.340
7.338
7.320
7.160
5.823
NAME 106L12_tang120120906_3
EXPNO 1
PROCNO 1
Date_ 20120911
Time 21.27
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 64
DW 60.800 usec
DE 6.50 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.80 usec
PL1 -1.00 dB
PL1W 17.70875549 W
SFO1 400.2324716 MHz
SI 32768
SF 400.2300523 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
O
12
11
10
9
8
7
6
5
4
3
ppm
1.00
2.03
1.03
3.17
1.10
2.50
2.95
1.18
2.06


167.48
134.52
133.99
133.66
131.97
131.74
131.63
130.65
129.54
128.94
128.69
127.97
127.82
127.03
126.83
126.46
126.15
125.99
125.51
124.64
123.82
77.48
77.37
77.16
76.85
65.34
O
O
NAME 106L12_tang120120906_3
EXPNO 2
PROCNO 1
Date_ 20120911
Time 22.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 3.00 dB
PL1W 41.92221451 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.94 dB
PL13 17.00 dB
PL2W 17.70875549 W
PL12W 0.35825154 W
PL13W 0.28066486 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6378995 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


8.126
8.116
8.111
8.108
8.096
8.091
8.087
7.700
7.695
7.680
7.676
7.674
7.660
7.657
7.640
7.637
7.623
7.620
7.617
7.606
7.602
7.597
7.586
7.583
7.580
7.528
7.523
7.511
7.507
7.503
7.500
7.495
7.491
7.486
7.476
7.461
7.457
7.260
5.787
NO2
O
O
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
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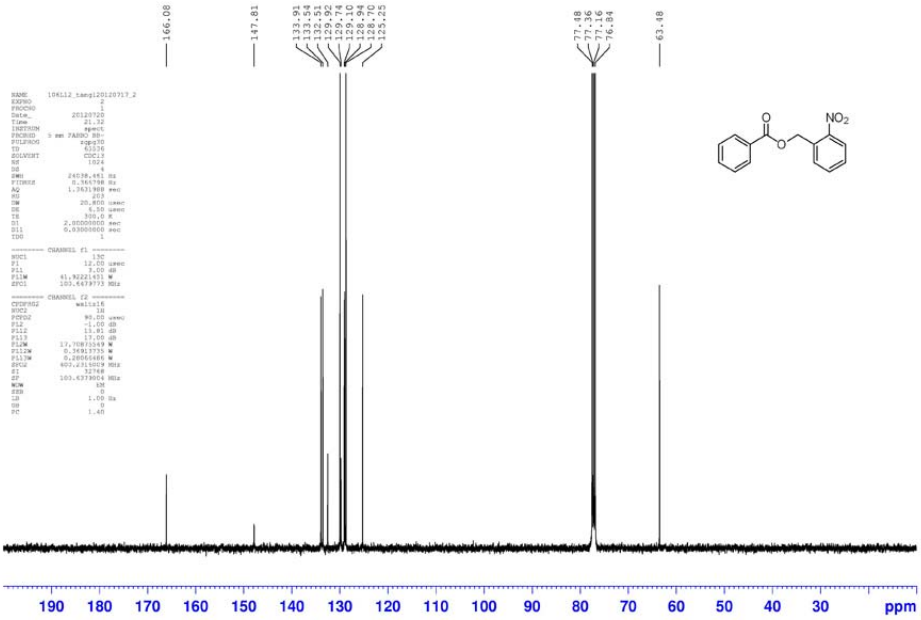
3.12
2.03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129.74
129.10
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128.70
125.25
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77.16
76.84
63.48
NO2
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O
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160
150
140
130
120
110
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90
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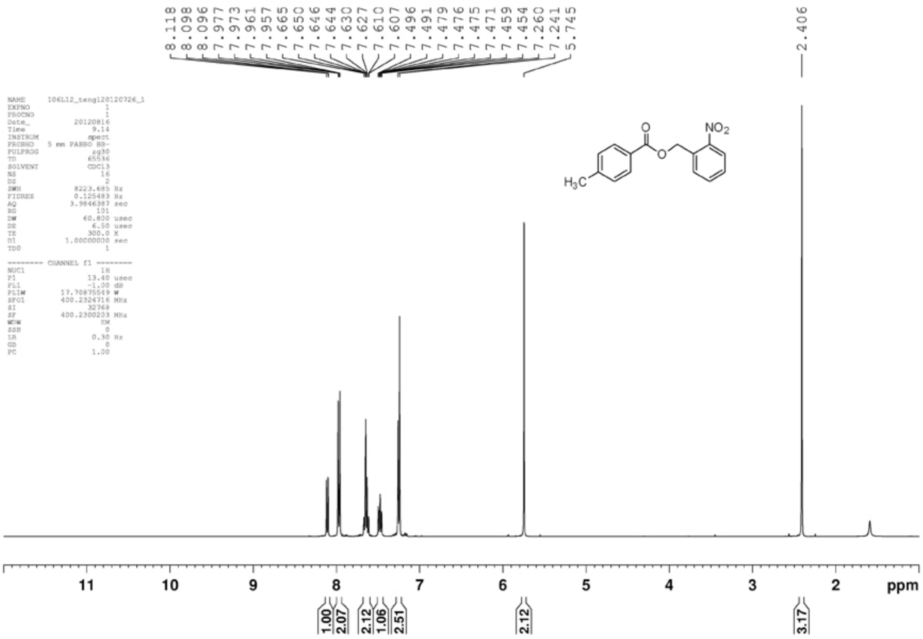
30
ppm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7.646
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7.630
7.627
7.610
7.607
7.496
7.491
7.479
7.476
7.475
7.471
7.459
7.454
7.260
7.241
5.745
2.406
NAME 104L12_teng120120726_1
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NO2
H3C
O
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10
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2.12
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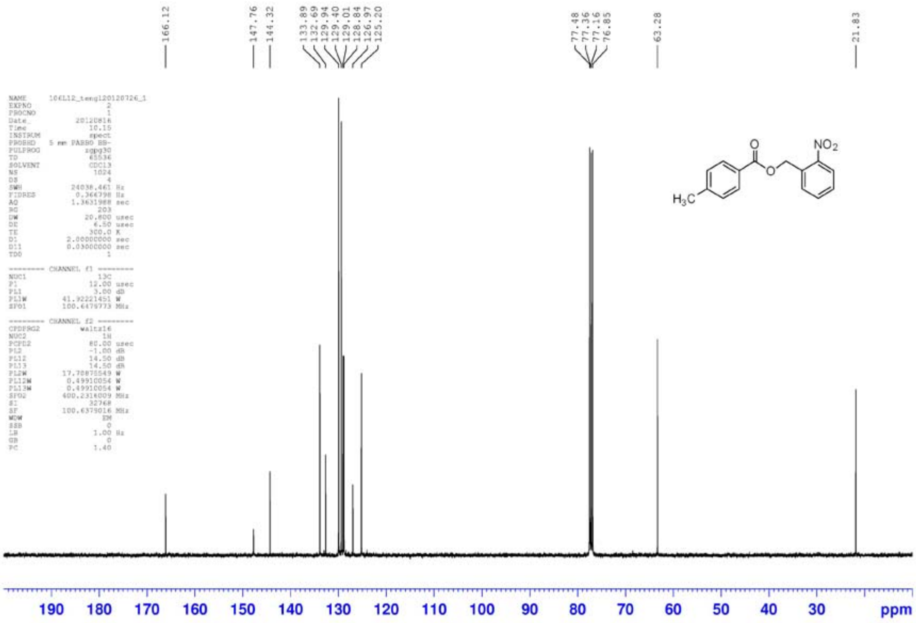
2.12
3.17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129.40
129.01
128.84
126.97
125.20
77.48
77.36
77.16
76.85
63.28
21.83
NAME 104L12_teng120120726_1
O
NO2
H3C
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180
170
160
150
140
130
120
110
100
90
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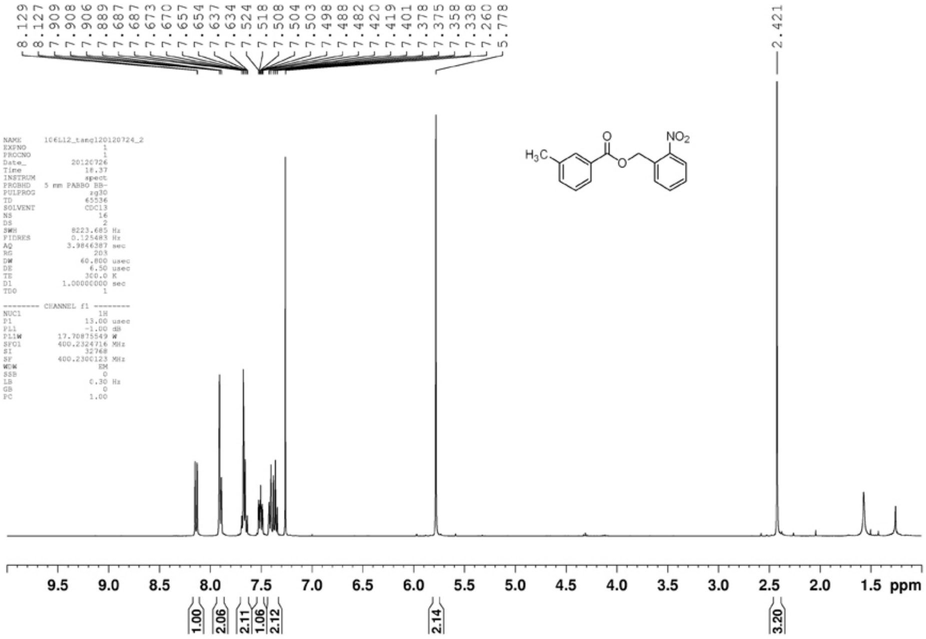
30
ppm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7.906
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7.673
7.670
7.657
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7.637
7.634
7.524
7.518
7.508
7.504
7.503
7.498
7.488
7.482
7.420
7.419
7.401
7.378
7.375
7.358
7.338
7.260
5.778
2.421
H_3C
O
O
NO_2
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
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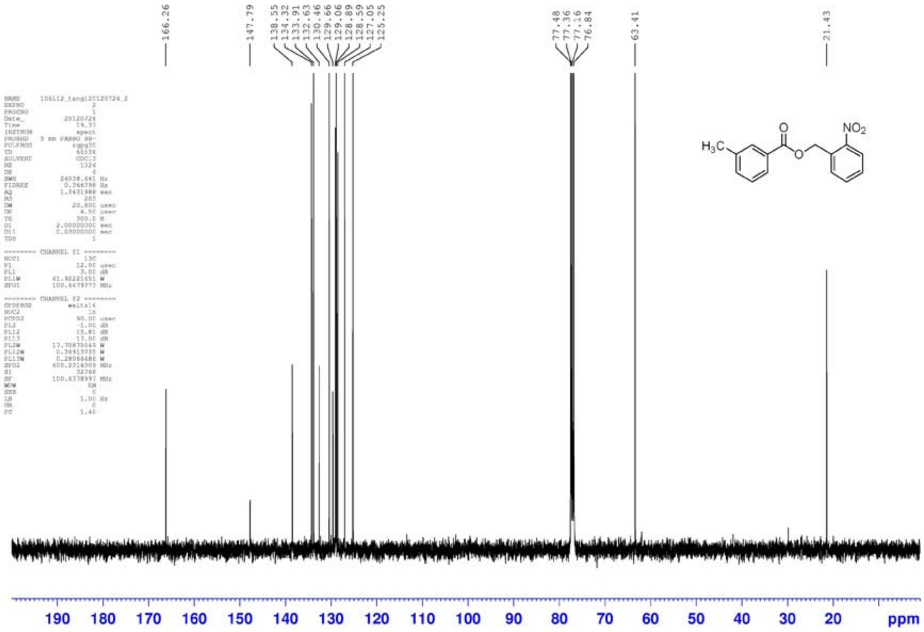
3.20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128.89
128.59
127.05
125.25
77.48
77.36
77.16
76.84
63.41
21.43
H_3C
O
O
NO_2
190
180
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160
150
140
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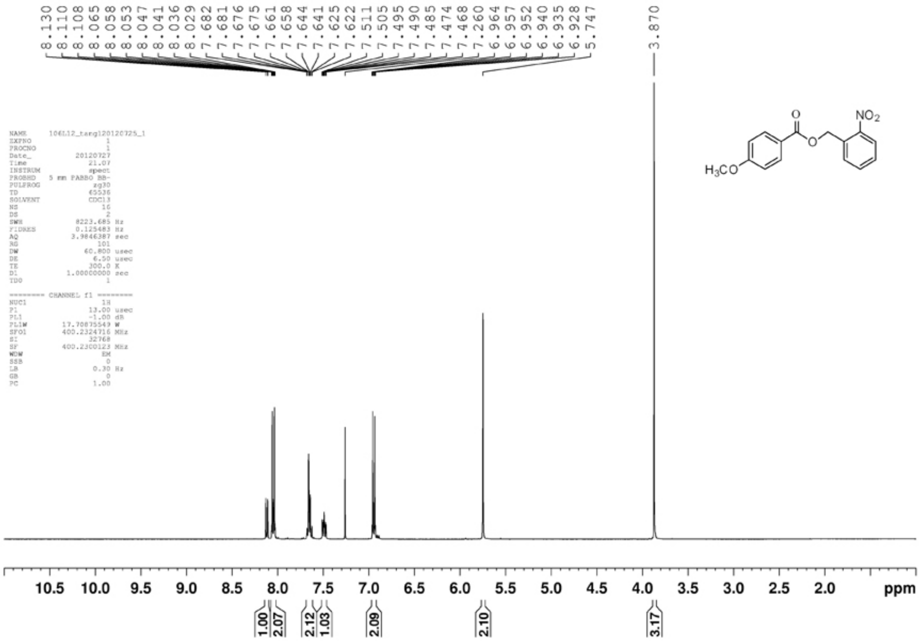
ppm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8.047
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7.681
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7.675
7.661
7.658
7.644
7.641
7.625
7.622
7.511
7.505
7.495
7.490
7.485
7.474
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7.260
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6.957
6.952
6.940
6.935
6.928
5.747
3.870
NAME 106L12_tang120120725_1
EXPNO 1
PROCNO 1
Date_ 20120727
Time 21.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 101
DW 60.800 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
PL1W 17.70875549 W
SFO1 400.2324716 MHz
SI 32768
SF 400.2300123 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
NO2
O
H3CO
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
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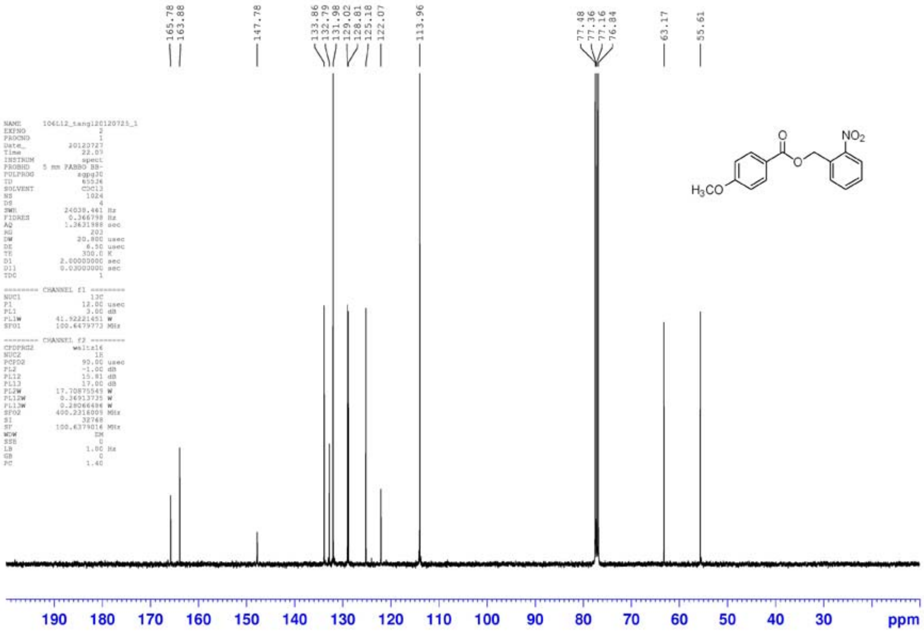
2.5
2.0
ppm
1.00
2.07
2.12
1.03
2.09
2.10
3.17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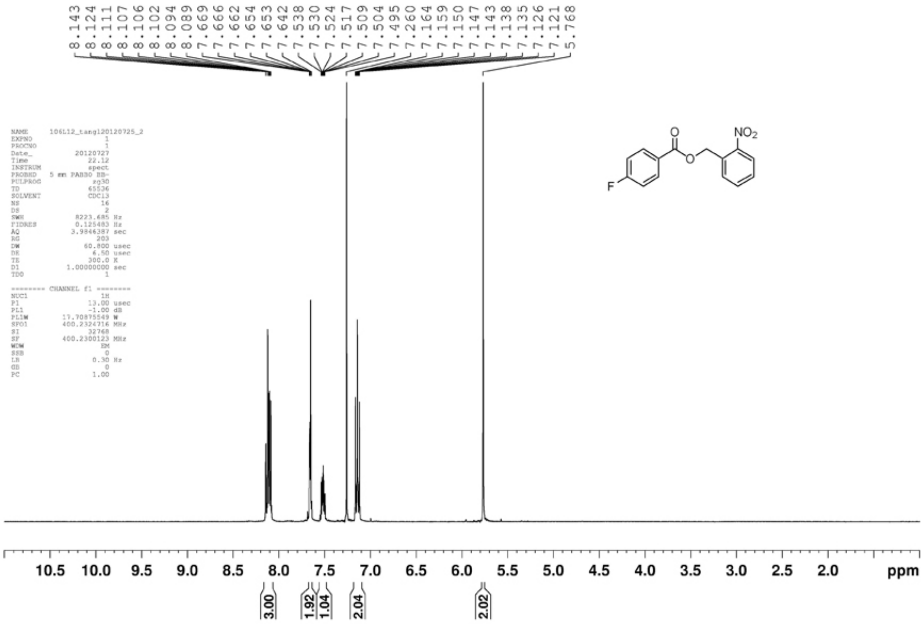
129.02
128.81
125.18
122.07
113.96
77.48
77.36
77.16
76.84
63.17
55.61
NAME 106L12_tang120120725_1
EXPNO 2
PROCNO 1
Date_ 20120727
Time 22.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 3.00 dB
PL1W 41.92221451 W
SFO1 100.6479773 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.81 dB
PL13 17.00 dB
PL2W 17.70875549 W
PL12W 0.36913735 W
PL13W 0.28066496 W
SFO2 400.2316009 MHz
SI 32768
SF 100.6379016 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
NO2
O
H3CO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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8.089
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7.642
7.538
7.530
7.524
7.517
7.509
7.504
7.495
7.260
7.164
7.159
7.150
7.147
7.143
7.138
7.135
7.126
7.121
5.768
F
O
O
NO2
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
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ppm
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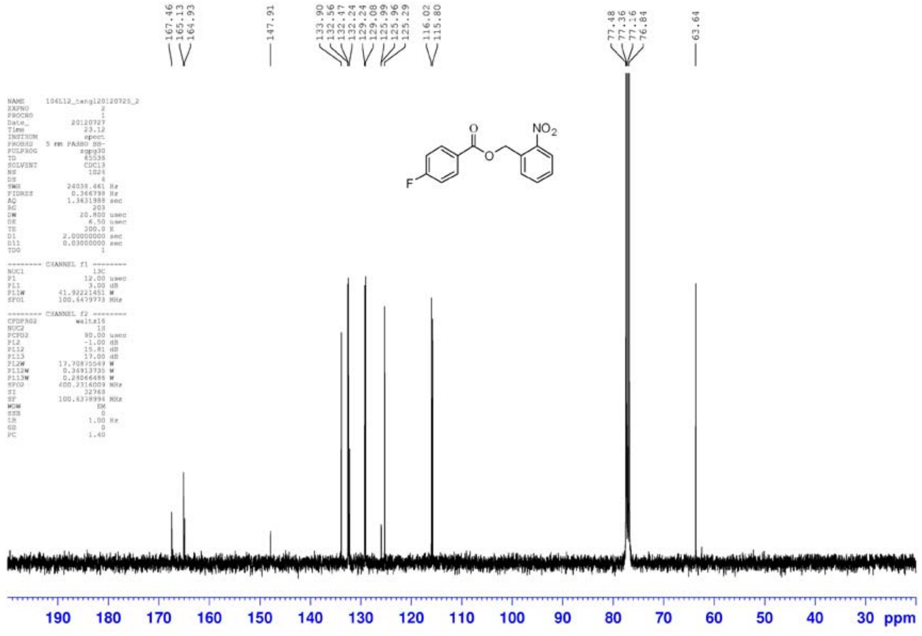
1.04
2.04
2.02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164.93
147.91
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132.56
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132.24
129.24
129.08
125.99
125.96
125.29
116.02
115.80
77.48
77.36
77.16
76.84
63.64
F
O
O
NO2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm