

Supplementary Materials

Sustainable Room Temperature Conversion of *p*-Xylene to Terephthalic Acid using Ozone and UV Irradiation.

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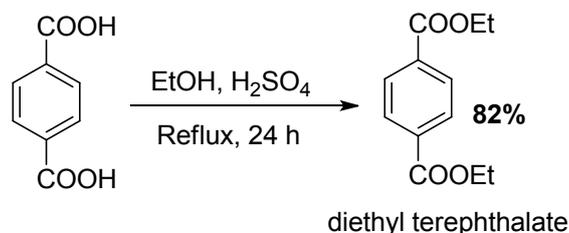
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Materials and Methods.

Purification of crude products and determination of the residual 4-CBA level in terephthalic acid: Both *p*-toluic acid and 4-carboxybenzaldehyde dissolve well in the CH₃CN-H₂O (3:2) co-solvent, whereas the terephthalic acid is barely soluble in this co-solvent. The as-produced crude solid terephthalic acid was washed with an equal volume of CH₃CN-H₂O (3:2) co-solvent for three times, followed by

centrifugation to remove solid (i.e., un-dissolved terephthalic acid) product. After three times washing, a known amount (100 ppm) of an external standard (i.e., 1,4-dicyanobenzene, 1,4-DCNB) was added to the final washed solid, and the suspension was sonicated to mix well the solid and the external standard. Finally, a small amount of a CH₃CN-MeOH (4:1 v/v) co-solvent was used to “dissolve” the final washed solid, and the un-dissolved solid was separated from the supernatant by centrifugation. The supernatant was subjected to high pressure liquid chromatography (HPLC) analysis (reverse phase HPLC, using water-acetonitrile as mobile phase) to measure the residual level of the 4-CBA (relative to the external standard) in the final “purified” terephthalic acid product.^{S1} The HPLC peak area was based on the uv absorbances of each components at 230 nm. The uv absorbance of 4-CBA, 1,4-dicyanobenzene, and *p*-toluic acid at 230 nm were determined to be 8.76 x 10³, 14.6 x 10³, and 5.1 x 10³ M⁻¹ cm⁻¹ (or 0.6 : 1 : 0.35), respectively. The integrated area ratios of HPLC chromatograph of 4-CBA, and *p*-toluic acid relative to the external standard were divided by the above absorbance ratio to normalize the HPLC response difference so that the residual levels of 4-CBA and *p*-toluic acid can be determined accurately. The residual level of 4-CBA in the crude solid product was measured to be ~160 ppm. Washing of the crude solid product can effectively remove (or dissolve) both *p*-toluic acid and 4-CBA. After 1, 2, and 3 times CH₃CN-H₂O (3:2 v/v) washing, the residual 4-CBA levels are reduced from 160 ppm to 34, 10, and 6 ppm, respectively. Note that in the HPLC measurements of crude PTA samples, the amount of external standard added to the samples is 250 ppm of 1,4-dicyanobenzene (1,4-DCNB), instead of 100 ppm used for all purified products.

General procedures for preparation of diethyl terephthalate and crystallization of diethyl terephthalate.



Although the ¹H and ¹³C NMR spectra of the above “purified TA” (pTA) are all the same as commercial TA sample, we are very cautious in determining the chemical structure of the “purified terephthalic acid” solid. To provide absolute chemical

structure determination, we adopted single crystal x-ray crystallography to determine the solid product obtained from the above ozone-uv irradiation of *p*-xylene experiments. It is proven difficult to grow big crystals from terephthalic acid itself. We, therefore, tried to prepare single crystals of esterification derivative of terephthalic acid; that is, diethyl terephthalate, which might be easier to grow big crystals of good quality. In the esterification process,^{S2} the crude solid product (1.0 g) of the above photo irradiation of *p*-xylene-acetonitrile-water-ozone system was added to a dry ethanol (50 mL) solution containing 8 mL of concentrated H₂SO₄. The mixture was heated to a reflux condition, and maintained for 24 h till all solids were dissolved. Then the reaction mixture was poured into ice-cold water. Immediately, a white solid starts to precipitate from the clear solution. Sodium bicarbonate was then used to neutralize the excess acid. Addition of sodium bicarbonate was continued till the effervescence ceases. The “presumed” terephthalate ester was dissolved in ethyl acetate, and washed with water for three times to remove any ionic salts. Organic solvent in the water-washed organic layer was evaporated, affording 1.1 gram of a white solid (after dried under vacuum. yield: 82%). The presumed crude diethyl terephthalate (1.1g) was added to 15 mL of ethyl acetate-hexane (1:1 v/v), slowly heated to a reflux condition, and continued stirred for 30 minutes. Then, the heater was switched off to allow slow cooling of the solution back to room temperature. During the cooling process, white crystalline solids gradually form. The crystalline white solids were isolated by filtration (1.0 g solid was obtained), and subjected to single crystal x-ray crystallography for chemical structure determination. The x-ray crystallography measurement unambiguously proves the chemical structure of the solid crystal to be diethyl terephthalate (see supplementary fig. S3). Supplementary crystallographic data for diethyl terephthalate (**4a**) can be obtained from the Cambridge crystallographic data Centre at www.ccdc.cam.ac.uk/data_request/cif on quoting registry no. **CCDC No:** 1034375. Likewise, the chemical structure of *p*-toluic acid was unambiguously confirmed by single crystal x-ray crystallography (see supplementary fig. S2). Supplementary crystallographic data for diethyl terephthalate (**2a**) can be obtained from the Cambridge crystallographic data Centre at www.ccdc.cam.ac.uk/data_request/cif on quoting registry no. **CCDC No:** 1034687.

EPR measurements of hydroxyl radical and benzyl radical. An acetonitrile-acidic

water (3: 2 v/v; pH= 4.5 using aqueous HCl) solution containing a radical trapping reagent, DMPO (2.5×10^{-2} M) was bubbled with ozone and concurrently irradiated with a 100 W Hg lamp irradiation or in the dark, and the EPR spectra were recorded (X band, 9.8 GHz). The parameters used in the simulation are the followings: $g=2.0070$, coupling constant $A_N=7.2$ G, and $A_{\alpha H}=A_{\beta H}=4.1$ G. All measurements were done at room temperature. In the case of detection of *p*-methylbenzyl radical, a *p*-xylene-acetonitrile-acidic water (5:3:2 volume ratio, pH= 4.5) containing a radical trapping reagent, DMPO (2.5×10^{-2} M) was bubbled with ozone and concurrently irradiated with a 100 W Hg lamp irradiation. After irradiation, EPR spectra were recorded from the solution in the dark. In the EPR spectrum simulation, the following parameters were used in the calculation: $g=2.00639$, $A_N=15.2$ G, and $A_{\beta H}=18.3$ G. All measurements were done at room temperature.

Dark reaction of ozone with “dry” p-xylene. In the literature, it was reported that ozone molecules can abstract hydrogen atom from alkanes to form HOOO· and alkyl radicals.^{S3} In the current system, a similar process might occur at the benzylic C-H bond selectively to generate 4-methylbenzyl radical. The 4-methylbenzyl radical can react with molecular oxygen to form alkylperoxyl radical (ROO·) radical, which can also abstract hydrogen atom from another *p*-xylene to regenerate 4-methylbenzyl radical. Such a peroxidation chain reaction is the same as that shown in the equations (5) and (6) in Figure 2(ii). Overall, *p*-xylene can be oxidatively converted to terephthalic acid by ozone molecules in the dark.

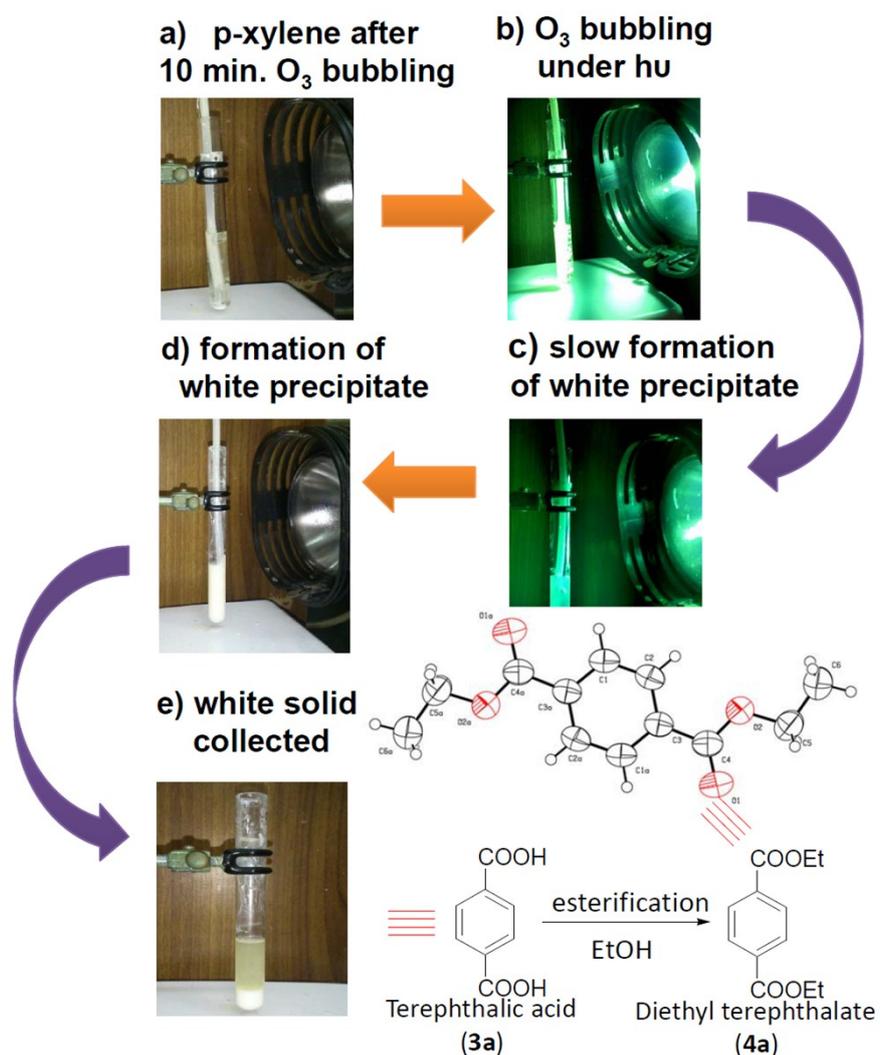


Figure S1. Ozonolysis conversion of *p*-xylene to terephthalic acid under photo irradiation. The composition of the solution is *p*-xylene:CH₃CN:H₂O= 5:3:2 (pH= 4.5).

Figure S2. ORTEP diagram of compound **2a** (CCDC No: 1034375)

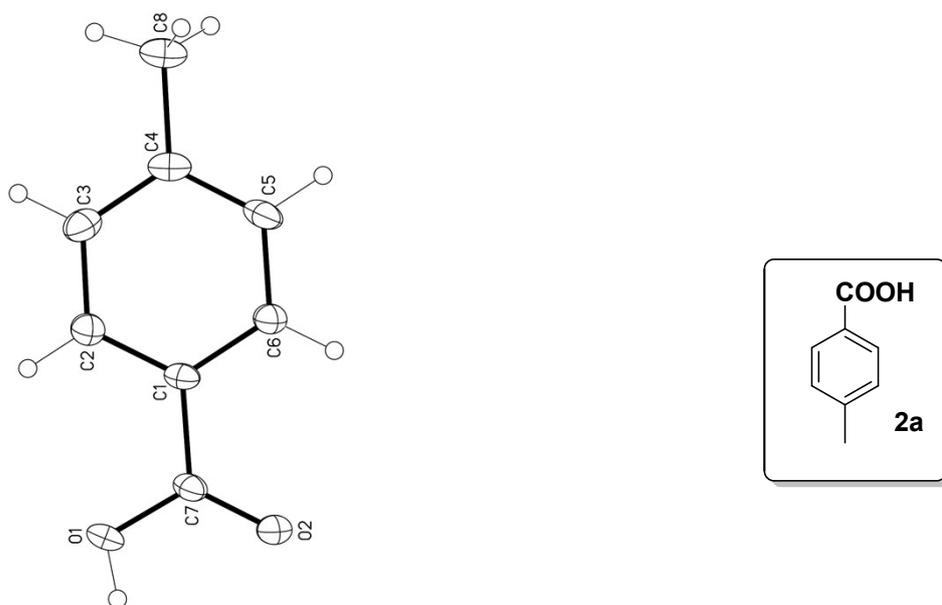


Table S1. Crystal data and structure refinement for TWIN5.

Identification code	twin5	
Empirical formula	C ₈ H ₈ O ₂	
Formula weight	136.14	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.308(6) Å	a = 96.059(14)°.
	b = 7.452(6) Å	b = 108.374(13)°.
	c = 7.833(7) Å	g = 117.853(14)°.
Volume	341.3(5) Å ³	
Z	2	
Density (calculated)	1.325 Mg/m ³	
Absorption coefficient	0.095 mm ⁻¹	
F(000)	144	
Crystal size	0.15 x 0.12 x 0.12 mm ³	
Theta range for data collection	2.874 to 26.592°.	
Index ranges	-9 ≤ h ≤ 8, -9 ≤ k ≤ 9, 0 ≤ l ≤ 9	
Reflections collected	1358	
Independent reflections	1358 [R(int) = 0.0508]	

Completeness to $\theta = 25.242^\circ$	98.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9484 and 0.7084
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1358 / 0 / 94
Goodness-of-fit on F^2	1.038
Final R indices [$I > 2 \sigma(I)$]	$R1 = 0.0602$, $wR2 = 0.1514$
R indices (all data)	$R1 = 0.0949$, $wR2 = 0.1717$
Extinction coefficient	n/a
Largest diff. peak and hole	0.337 and -0.234 e. \AA^{-3}

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for TWIN5. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	6855(4)	3236(4)	3635(3)	18(1)
C(2)	7054(4)	1469(4)	3300(3)	22(1)
C(3)	7781(4)	765(4)	4804(3)	24(1)
C(4)	8331(4)	1806(4)	6642(3)	23(1)
C(5)	8118(4)	3561(4)	6954(3)	24(1)
C(6)	7387(4)	4287(4)	5467(3)	20(1)
C(7)	6080(4)	4021(4)	2061(3)	19(1)
C(8)	9136(4)	1040(5)	8279(4)	30(1)
O(1)	5724(3)	3044(3)	392(2)	28(1)
O(2)	5775(3)	5525(3)	2334(2)	26(1)

Table S3. Bond lengths [\AA] and angles [$^\circ$] for TWIN5.

C(1)-C(6)	1.396(3)
C(1)-C(2)	1.398(4)
C(1)-C(7)	1.485(3)
C(2)-C(3)	1.393(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.394(4)

C(3)-H(3)	0.9500
C(4)-C(5)	1.393(4)
C(4)-C(8)	1.519(3)
C(5)-C(6)	1.395(3)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-O(2)	1.251(3)
C(7)-O(1)	1.309(3)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
O(1)-H(1)	0.8400
C(6)-C(1)-C(2)	120.1(2)
C(6)-C(1)-C(7)	119.2(2)
C(2)-C(1)-C(7)	120.8(2)
C(3)-C(2)-C(1)	119.6(2)
C(3)-C(2)-H(2)	120.2
C(1)-C(2)-H(2)	120.2
C(2)-C(3)-C(4)	121.0(2)
C(2)-C(3)-H(3)	119.5
C(4)-C(3)-H(3)	119.5
C(5)-C(4)-C(3)	118.8(2)
C(5)-C(4)-C(8)	120.4(2)
C(3)-C(4)-C(8)	120.9(2)
C(4)-C(5)-C(6)	121.1(2)
C(4)-C(5)-H(5)	119.5
C(6)-C(5)-H(5)	119.5
C(5)-C(6)-C(1)	119.5(2)
C(5)-C(6)-H(6)	120.2
C(1)-C(6)-H(6)	120.2
O(2)-C(7)-O(1)	122.53(19)
O(2)-C(7)-C(1)	121.1(2)
O(1)-C(7)-C(1)	116.4(2)
C(4)-C(8)-H(8A)	109.5
C(4)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(4)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5

H(8B)-C(8)-H(8C)	109.5
C(7)-O(1)-H(1)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for TWIN5. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^*2U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
C(1)	17(1)	24(2)	15(1)	8(1)	5(1)	12(1)
C(2)	23(1)	25(2)	19(1)	6(1)	7(1)	15(1)
C(3)	23(1)	25(2)	26(1)	10(1)	7(1)	15(1)
C(4)	18(1)	28(2)	21(1)	13(1)	7(1)	11(1)
C(5)	25(1)	35(2)	14(1)	9(1)	7(1)	17(1)
C(6)	22(1)	24(2)	18(1)	7(1)	7(1)	14(1)
C(7)	18(1)	24(2)	13(1)	6(1)	5(1)	12(1)
C(8)	28(2)	38(2)	22(1)	14(1)	6(1)	18(2)
O(1)	40(1)	34(1)	12(1)	9(1)	7(1)	24(1)
O(2)	36(1)	33(1)	19(1)	11(1)	11(1)	26(1)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for TWIN5.

	x	y	z	U(eq)
H(2)	6695	753	2055	26
H(3)	7904	-443	4573	29
H(5)	8477	4275	8199	29
H(6)	7253	5488	5699	25
H(8A)	10772	2030	9030	45
H(8B)	8838	-380	7790	45
H(8C)	8317	976	9072	45
H(1)	5292	3595	-402	42

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) twin5

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: twin5

Bond precision: C-C = 0.0038 A Wavelength=0.71073
Cell: a=7.308 (6) b=7.452 (6) c=7.833 (7)
 alpha=96.059(14) beta=108.374 (13) gamma=117.853 (14)
Temperature: 100 K

	Calculated	Reported
Volume	341.3 (5)	341.3 (5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C8 H8 O2	?
Sum formula	C8 H8 O2	C8 H8 O2
Mr	136.14	136.14
Dx, g cm-3	1.325	1.325
Z	2	2
Mu (mm-1)	0.095	0.095
F000	144.0	144.0
F000'	144.08	
h,k,lmax	9,9,9	9,9,9
Nref	1432	1358
Tmin,Tmax	0.986,0.989	0.708,0.948
Tmin'	0.986	

Correction method= MULTI-SCAN

Data completeness= 0.948 Theta(max)= 26.592
R(reflections)= 0.0602(919) wR2(reflections)= 0.1717(1358)
S = 1.038 Npar= 94

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G
 PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms 1 Report
 PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large. 0.11 Report

0 **ALERT level A** = Most likely a serious problem - resolve or explain
 0 **ALERT level B** = A potentially serious problem, consider carefully
 0 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
 2 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 1 ALERT type 2 Indicator that the structure model may be wrong or deficient
 0 ALERT type 3 Indicator that the structure quality may be low
 0 ALERT type 4 Improvement, methodology, query or suggestion
 1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 20/08/2014; check.def file version of 18/08/2014

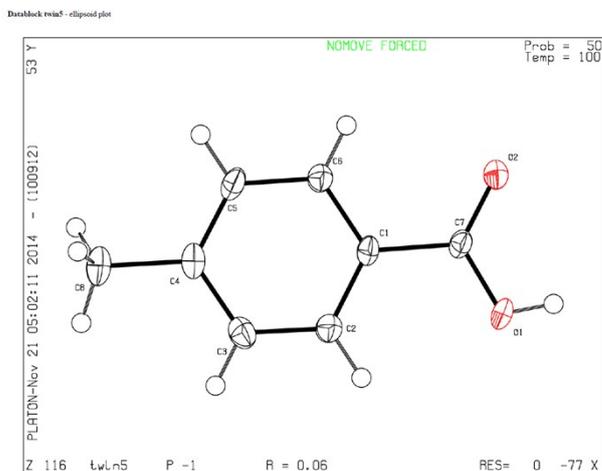


Figure S3.
(CCDC No:

ORTEP diagram of **diethyl terephthalate**
1034687)

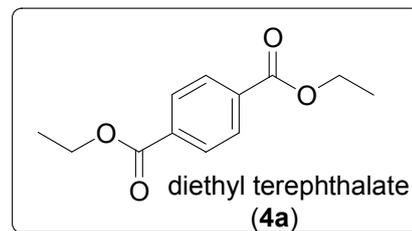
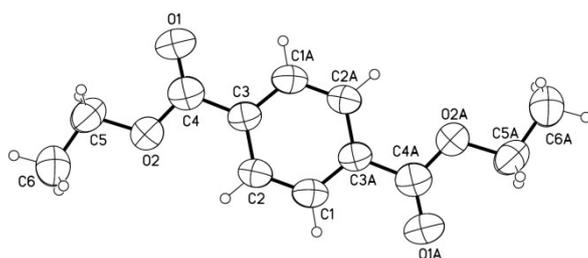


Table S6. Crystal data and structure refinement for mo_141114_0m.

Identification code	mo_141114_0m	
Empirical formula	C ₁₂ H ₁₄ O ₄	
Formula weight	222.23	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 4.206(2) Å	a = 90°.
	b = 15.399(9) Å	b = 92.854(10)°.
	c = 9.109(5) Å	g = 90°.
Volume	589.2(6) Å ³	
Z	2	
Density (calculated)	1.253 Mg/m ³	
Absorption coefficient	0.094 mm ⁻¹	
F(000)	236	
Crystal size	0.30 x 0.25 x 0.15 mm ³	
Theta range for data collection	2.600 to 26.391°.	
Index ranges	-3<=h<=5, -19<=k<=19, -11<=l<=9	
Reflections collected	4463	
Independent reflections	1173 [R(int) = 0.0412]	
Completeness to theta = 25.242°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9485 and 0.8135	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1173 / 0 / 74	

Goodness-of-fit on F^2	1.021
Final R indices [$I > 2 \sigma(I)$]	R1 = 0.0536, wR2 = 0.1257
R indices (all data)	R1 = 0.1046, wR2 = 0.1521
Extinction coefficient	n/a
Largest diff. peak and hole	0.149 and -0.144 e.Å ⁻³

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for mo_141114_0m. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3577(6)	5703(2)	9314(3)	66(1)
C(2)	5137(6)	5098(2)	8508(3)	65(1)
C(3)	6566(5)	4389(1)	9183(2)	56(1)
C(4)	8298(6)	3722(2)	8359(3)	63(1)
C(5)	9883(7)	3282(2)	6012(3)	78(1)
C(6)	9889(9)	3656(2)	4530(3)	110(1)
O(1)	9563(5)	3101(1)	8914(2)	90(1)
O(2)	8272(4)	3894(1)	6930(2)	72(1)

Table S8. Bond lengths [Å] and angles [$^\circ$] for mo_141114_0m.

C(1)-C(2)	1.374(3)
C(1)-C(3)#1	1.380(3)
C(1)-H(1)	0.9300
C(2)-C(3)	1.376(3)
C(2)-H(2)	0.9300
C(3)-C(1)#1	1.380(3)
C(3)-C(4)	1.485(3)
C(4)-O(1)	1.194(3)
C(4)-O(2)	1.328(3)
C(5)-O(2)	1.450(3)
C(5)-C(6)	1.467(4)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700

C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(2)-C(1)-C(3)#1	120.4(2)
C(2)-C(1)-H(1)	119.8
C(3)#1-C(1)-H(1)	119.8
C(1)-C(2)-C(3)	120.6(2)
C(1)-C(2)-H(2)	119.7
C(3)-C(2)-H(2)	119.7
C(2)-C(3)-C(1)#1	119.0(2)
C(2)-C(3)-C(4)	122.5(2)
C(1)#1-C(3)-C(4)	118.5(2)
O(1)-C(4)-O(2)	123.8(2)
O(1)-C(4)-C(3)	124.0(2)
O(2)-C(4)-C(3)	112.2(2)
O(2)-C(5)-C(6)	107.3(2)
O(2)-C(5)-H(5A)	110.3
C(6)-C(5)-H(5A)	110.3
O(2)-C(5)-H(5B)	110.3
C(6)-C(5)-H(5B)	110.3
H(5A)-C(5)-H(5B)	108.5
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(4)-O(2)-C(5)	117.0(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+2

Table S9. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mo_141114_0m. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^* 2U^{11} + \dots + 2 h k a^* b^* U^{12}]$

U11	U22	U33	U23	U13	U12
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C(1)	73(2)	57(1)	68(2)	14(1)	-2(1)	2(1)
C(2)	72(2)	65(2)	57(1)	12(1)	1(1)	-4(1)
C(3)	54(2)	54(1)	61(1)	6(1)	-2(1)	-10(1)
C(4)	59(2)	58(1)	72(2)	8(1)	-2(1)	-8(1)
C(5)	78(2)	69(2)	86(2)	-9(1)	1(2)	10(1)
C(6)	145(3)	97(2)	91(2)	4(2)	36(2)	31(2)
O(1)	107(2)	70(1)	92(1)	16(1)	2(1)	19(1)
O(2)	80(1)	68(1)	68(1)	0(1)	4(1)	10(1)

Table S10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mo_141114_0m.

	x	y	z	U(eq)
H(1)	2611	6178	8845	79
H(2)	5229	5168	7497	78
H(5A)	8777	2729	5988	93
H(5B)	12048	3188	6397	93
H(6A)	7745	3788	4193	165
H(6B)	10789	3246	3874	165
H(6C)	11136	4178	4555	165

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_141114_0m

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_141114_0m

Bond precision: C-C = 0.0034 A Wavelength=0.71073

Cell: a=4.206(2) b=15.399(9) c=9.109(5)
 alpha=90 beta=92.854(10) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	589.2(5)	589.2(6)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C12 H14 O4	?
Sum formula	C12 H14 O4	C12 H14 O4
Mr	222.23	222.23
Dx,g cm-3	1.253	1.253
Z	2	2
Mu (mm-1)	0.094	0.094
F000	236.0	236.0
F000'	236.14	
h,k,lmax	5,19,11	5,19,11
Nref	1208	1173
Tmin,Tmax	0.972,0.986	0.813,0.948
Tmin'	0.972	

Correction method= MULTI-SCAN

Data completeness= 0.971 Theta(max)= 26.391

R(reflections)= 0.0536(659) wR2(reflections)= 0.1521(1173)

S = 1.021 Npar= 74

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) . 1.13 Ratio

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
1 ALERT level G = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

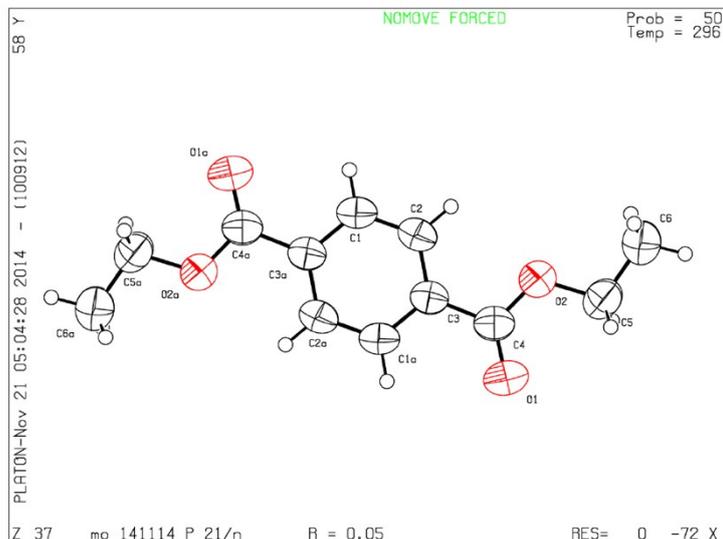
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 20/08/2014; check.def file version of 18/08/2014

DataBlock mo_141114_0m - ellipsoid plot



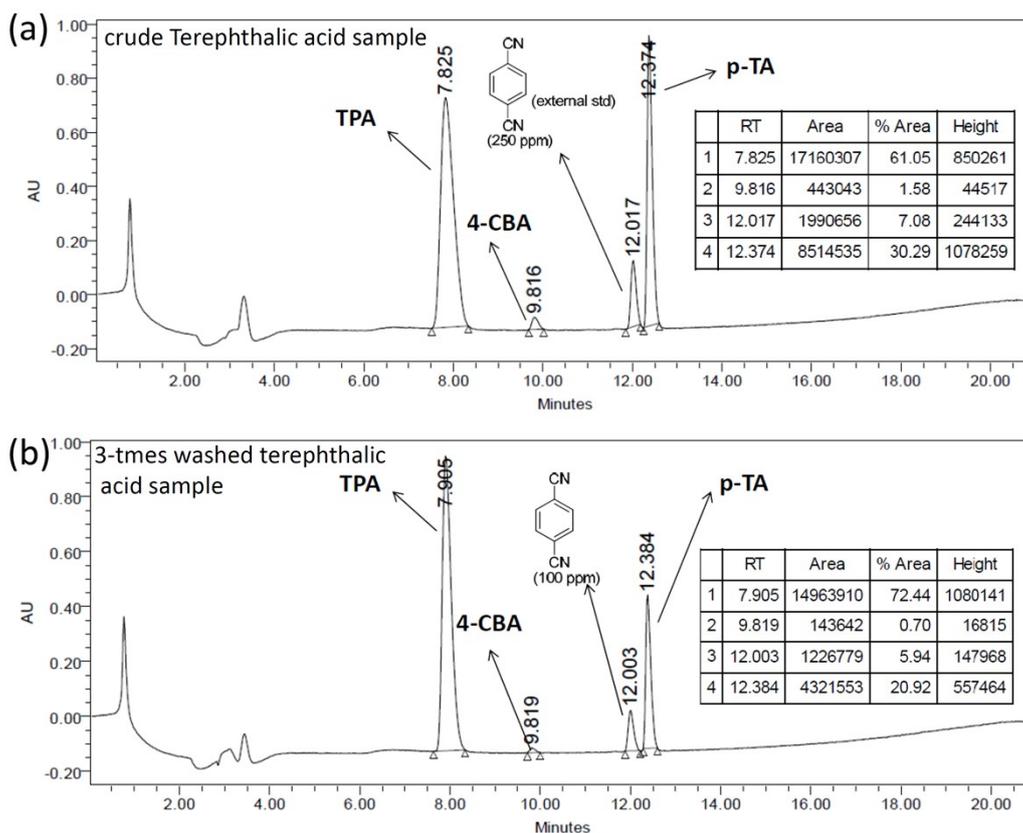


Fig. S4. HPLC chromatographs of (a) crude terephthalic acid and (b) 3-times washed terephthalic acid samples. The concentrations of the external standard, 1,4-dicyanobenzene are 250 ppm and 100 ppm, respectively, in the crude and washed terephthalic acid samples, as leveled in the figures. The signals within the retention times 0~4 mins are solvent signals. The integrated area of all peaks is shown in the inset tables. The assignments of all peaks are based on comparison of the retention times of known standard compounds.

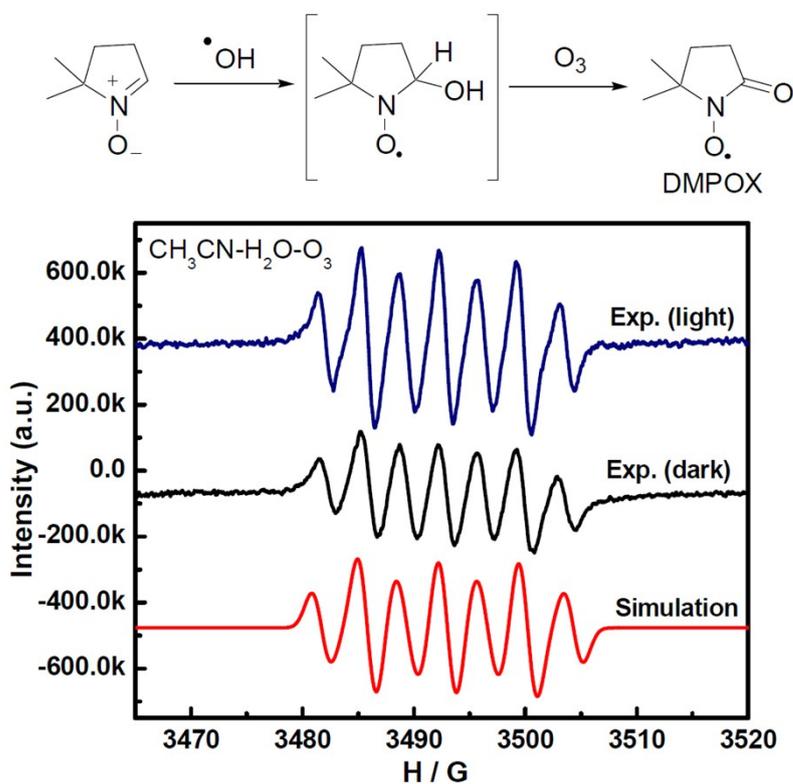


Figure S5. EPR spectra of hydroxyl radicals for acetonitrile-water in the presence of ozone under uv light irradiation (top) and in dark (middle). The bottom spectrum is a simulation one with the following parameters: parameters: $g= 2.0070$, coupling constant $A_{\text{N}}= 7.2$ G, and $A_{\text{rH}}= A_{\text{r}^{\cdot}\text{H}}= 4.1$ G. The top chemical reaction reveals the reaction of a spin trapping reagent, DMPO, with hydroxyl radical, followed by oxidation of the DMPO-OH adduct by ozone to form stable DMPOX radical, which is responsible for the observed EPR signal. The observed DMPOX EPR spectra are the same as those reported in the literature.^{S4}

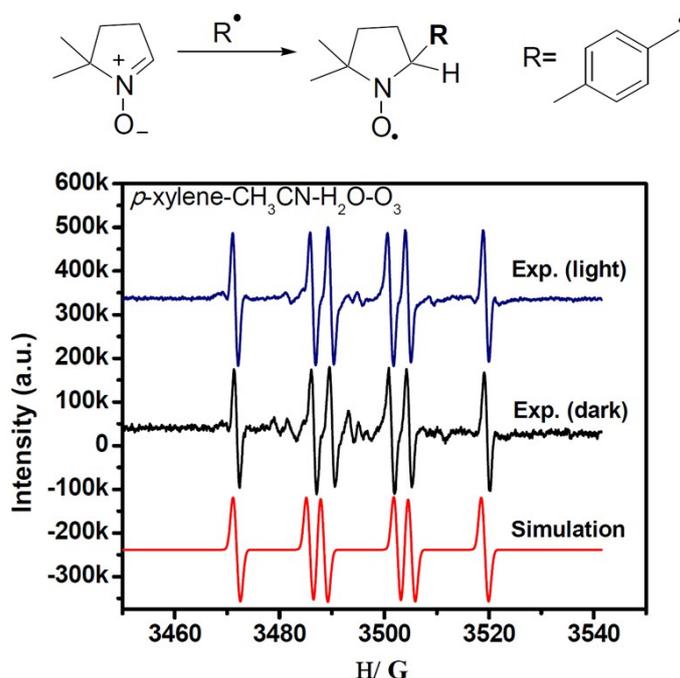


Figure S6. EPR spectra of benzyl radical for *p*-xylene-acetonitrile-water system in the presence of ozone under uv light irradiation (top) and in dark (middle). The bottom EPR spectrum is a simulation one using parameters: $g=2.00639$, $A_N=15.2$ G, and $A_{\beta H}=18.3$ G. The observed EPR spectra are the same as that reported in the literature for alkyl radical.³⁸

Green Chemistry Metric Evaluation.

In this section, we make side-by-side comparison of the Green Chemistry Metrics between the industrial process and the current work. The reaction conditions for the industrial AMOCO process and the current work are listed in Table S11. It is very clear that the reaction condition of the industrial Amoco process is far harsher than that described in the current work. In addition, the industrial process requires a high energy demanding hydropurification process to obtain purified terephthalic acid. This hydropurification process not only consumes a lot of energy (290 °C and H₂ 70-90 atm.), but also produce huge amount of waste water (3~10 kg waste water per kg terephthalic acid, or 210~700 million tons waste water for 70 million tons terephthalic acid.⁵ In the sharp contrast, the current work develops a simple solvent wash process to suppress the 4-CBA level down to 6 ppm. The washed acetonitrile-water solution

(containing the precursors of terephthalic acid, that is, p-toluic acid and 4-CBA) can be recycled. Therefore, nearly no waste was produced in the current work for the “purification” step of crude terephthalic acid. Based on a comparison of both the reaction conditions and the Green Chemistry Metrics (see Tables S11 and S12), one can see that the current work is greener than the industrial AMOCO process for the production of terephthalic acid.

Table S11. Comparison of reaction condition between the industrial AMOCO process and the current work for oxidative conversion of p-xylene to terephthalic acid.

oxidation reaction condition	Industrial process	Current process
temperature (°C)	190-200	RT (25-30)
pressure (bar)	15-30	1
catalysts/solvent	Co/Mn/Br ⁻ , acetic acid	no catalyst CH ₃ CN/H ₂ O
p-Xylene conversion (%)	98	98
selectivity of terephthalic acid	95	98
4-CBA content in crude (ppm)	1375	163
hydropurification condition		
temperature (°C)	270-290	---
pressure (bar)	70-90	---
catalysts/solvent	0.5 wt% Pd/C, H ₂ O	---
4-CBA conversion (%)	90	---
4-CBA content in purified (ppm)	7	6 (after 3 solvent washes)

From another aspect, one can compare the industrial process and the current work from the well accepted Green Chemistry Metrics point of view (see Table S12 below). Our process eliminates the use of a corrosive solvent acetic acid and bromides, avoids the generation/emission of greenhouse gases CO₂ and CH₃Br, and harsh reaction condition. In the high temperature industrial process, roughly ~5 % of the acetic acid is destroyed by oxidative burning process, resulting in significant solvent loss, CO₂ and CH₃Br emission to the atmosphere, causing serious global warming and ozone depletion problems; whereas, our room temperature process minimizes the evaporation of starting materials and solvents. Overall, our process eliminates number of processing steps resulting in a reduction in energy requirements as well as

the operation costs, and environmental benefits anticipated by omitting the hydropurification steps.

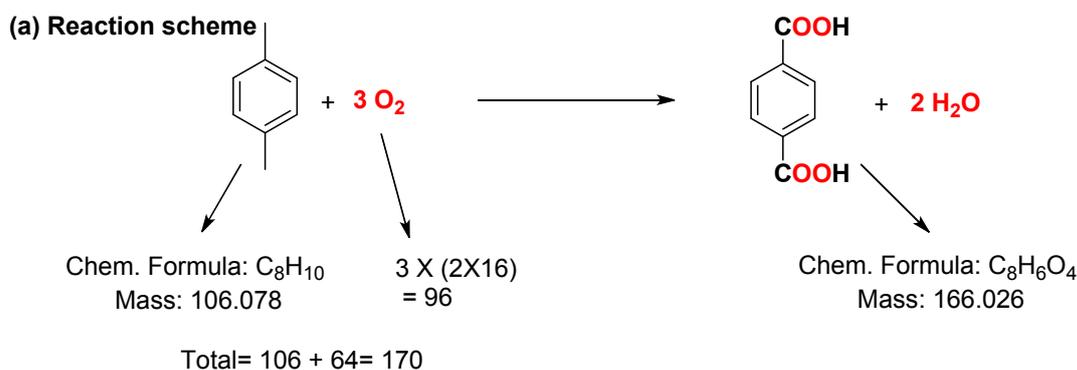
Table S12. Direct comparison of the industrial AMOCO process and the current work from the point of view of 12 Principles of Green Chemistry

No	Green chemistry principle	Industrial process	Current process
1	Prevent waste	evaporation of CO ₂ & CH ₃ Br, waste H ₂ O	nearly no waste
2	Maximize atom economy	82%	82%
3	Design less hazardous chemical syntheses	corrosive acetic acid & bromide were used	H ₂ O-ACN used
4	Design safer chemicals and products	---	---
5	Use safer solvents and reaction conditions	corrosive acetic acid & bromide, 190-200 °C, 15-30 atm.	H ₂ O-ACN used at RT
6	Increase energy efficiency	need harsh condition (190-200 °C)	R.T, uv light O ₃
7	Use renewable feedstocks	---	---
8	Avoid chemical derivatives	---	---
9	Use catalysts, not stoichiometric reagents	I. Co/Mn/Br ⁻ II Pd/C	no catalyst
10	Design chemicals and products that degrade after use	---	---
11	Analyze in real time to prevent pollution	release of greenhouse gases CO ₂ & CH ₃ Br, huge amount of waste H ₂ O	no gases evaporated
12	Minimize the potential for accidents	reaction at 190-200 °C may involve explosions and fire accidents	reaction at RT, less risk for explosions

Other green chemistry metrics, including E-factor, atom economy, atom efficiency, carbon efficiency and reaction mass efficiency, are calculated for the AMOCO industrial process and ours, respectively. These green chemistry metric values are listed in Table 3 (in the main text) for side by side comparison. The E factor for the industrial AMOCO process is 3.14~10.14, which is far higher than 0.118 for our new process. Due to prevention of thermal decomposition of terephthalic acid (to benzoic acid) at high temperatures (200~ 290 °C) in our process, both the carbon efficiency and reaction mass efficiency of our new process are also better than those for the industrial process.

Overall, from the above side-by-side comparison of Green Chemistry Metric values between the industrial process and ours, it is very clear that our new process is far greener than the industrial process. The industrial process was developed in

1960s. After nearly 60 years of research efforts and improvements, it has been proven to be very difficult to oxidatively convert p-xylene to terephthalic acid without using harsh conditions of high temperature, high pressure, using highly corrosive solvents/reagents and the generation/release of huge amount wastes/pollutants. Our new process avoids the use of high temperature, high pressure, and highly corrosive reagents. It is very clear that our work is a big breakthrough in Green Chemistry.



(1) Industrial process:

amounts of waste per kg terephthalic acid:
 CO₂ evaporation= 0.1 kg
 CH₃Br evaporation= 0.000032 kg
 Benzoic acid (5 mol%)= 0.037 kg
 waste water in hydrogenation step = 3 - 10 kg^c

$$\text{E-factor} = \frac{\text{mass of wastes}}{\text{mass of product}}$$

amount of wastes = 0.1 kg CO₂ + 0.000032 kg CH₃Br + 0.037 kg Benzoic acid
 + 3-10 kg waste water = 3.14-10.14 kg

$$\text{E-factor} = \frac{3.14-10.14 \text{ kg}}{1 \text{ kg TA}} = 3.14-10.14$$

(2) Current process:

$$\text{E-factor} = \frac{0.156\text{g}}{1.32\text{g}} = 0.118$$

amount of waste:
 2% substrate evaporation= 0.156 g

(b) Evaluation of Green metrics of the industrial process

Reactant A	p-xylene (1a)	0.672 kg	6.34mol	FW 106.08
Oxidant	O ₂	0.609 kg	19.02 mol	FW 32
Solvent	Acetic acid	1.545 kg	---	---
Product	Terephthalic acid (3a)	1.0 kg	6.023 mol	FW 166

Conversion= 100%; selectivity= 95% 5% solvent loss by burning

$$\text{E-factor} = \frac{3.14-10.14 \text{ kg}}{1.0 \text{ kg}} = 3.14-10.14$$

$$\text{Atom economy} = \frac{166}{166 + 18 \times 2} \times 100 = 82\%$$

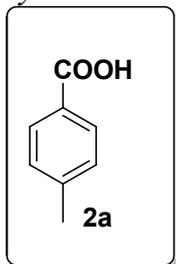
$$\text{Carbon efficiency (by mole)} = \frac{6.02 \times 8}{6.34 \times 8} \times 100 \times 0.95 = 90.2\%$$

$$\text{Reaction mass efficiency} = \frac{166 \times 6.023 \text{ g TA}}{106 \times 6.34 \text{ g pX} + 32 \times 0.609 \text{ g O}_2} \times 100 \times 0.95 = 74.1\%$$

Figure S7. Calculation of Green Chemistry Metric values for the industrial AMOCO process and the current work.

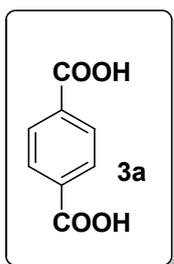
Spectroscopic Data:

4-methylbenzoic acid (2a) (CAS NO: 99-94-5)



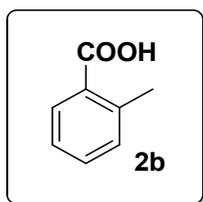
White solid; ¹H NMR (400 MHz, CDCl₃-DMSO): δ 10.83 (b, 1 H), 7.95 (d, *J*= 8.0 Hz, 2 H), 7.21 (d, *J*= 8.0 Hz, 2 H), 2.37 (s, 3 H); ¹³C NMR (100 MHz, DMSO): δ 170.2, 143.8, 129.8, 128.9, 21.5. *NMR data is in agreement with authentic commercially available sample*

Terephthalic acid (3a) (CAS NO: 100-21-0)



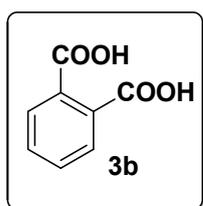
White solid; ¹H NMR (400 MHz, DMSO): δ 8.03 (s, 4 H); ¹³C NMR (100 MHz, DMSO): δ 166.7, 134.4, and 129.5. *NMR data is in agreement with authentic commercially available sample.*

2-methylbenzoic acid (2b) (CAS NO: 118-90-1)



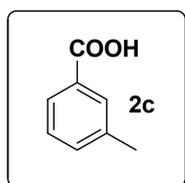
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3 -DMSO): δ 7.87 (m, 1 H), 7.30-7.14 (m, 3 H), 2.52 (s, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 -DMSO): δ 169.8, 140.0, 131.6, 131.4, 130.7, 129.8, 125.4, and 21.6. *NMR data is in agreement with authentic commercially available sample.*

Phthalic acid (3b) (CAS NO: 88-99-3)



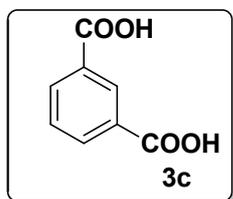
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.60 (dd, $J= 4.0\text{Hz}, 8.0\text{Hz}, 2\text{ H}$), 7.44 (dd, $J= 4.0\text{Hz}, 8.0\text{Hz}, 2\text{ H}$) 1; $^{13}\text{C NMR}$ (100 MHz, CDCl_3 -DMSO): δ 169.0, 132.8, 130.5, 128.3. *NMR data is in agreement with authentic commercially available sample.*

3-methylbenzoic acid (2c) (CAS NO: 99-04-7)



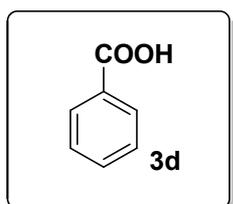
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.66-7.63 (m, 2 H), 7.15-7.08 (m, 2 H), 2.18 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 168.2, 137.4, 132.9, 130.2, 129.7, 127.6, 126.3, and 20.7. *NMR data is in agreement with authentic commercially available sample.*

Isophthalic acid (3c) (CAS NO: 121-91-5)



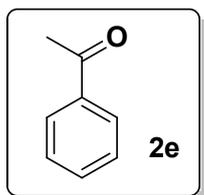
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.46 (d, $J= 4.0\text{Hz}$, 1H), 8.10 (d, $J= 8.0\text{Hz}$, 2H), 7.54 (t, $J= 8.0\text{ Hz}$, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.6, 133.3, 131.2, 130.1, and 128.8. *NMR data is in agreement with authentic commercially available sample.*

Benzoic acid (3d) (CAS NO: 65-85-0)



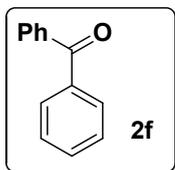
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 11.23 (b, 1 H), 8.14-8.13 (m, 2 H), 7.63-7.58 (m, 1 H), 7.48-7.44(m, 2 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.4, 133.7, 130.1, 129.3, and 128.4. *NMR data is in agreement with authentic commercially available sample*

Acetophenone (2e) (CAS NO: 98-86-2)

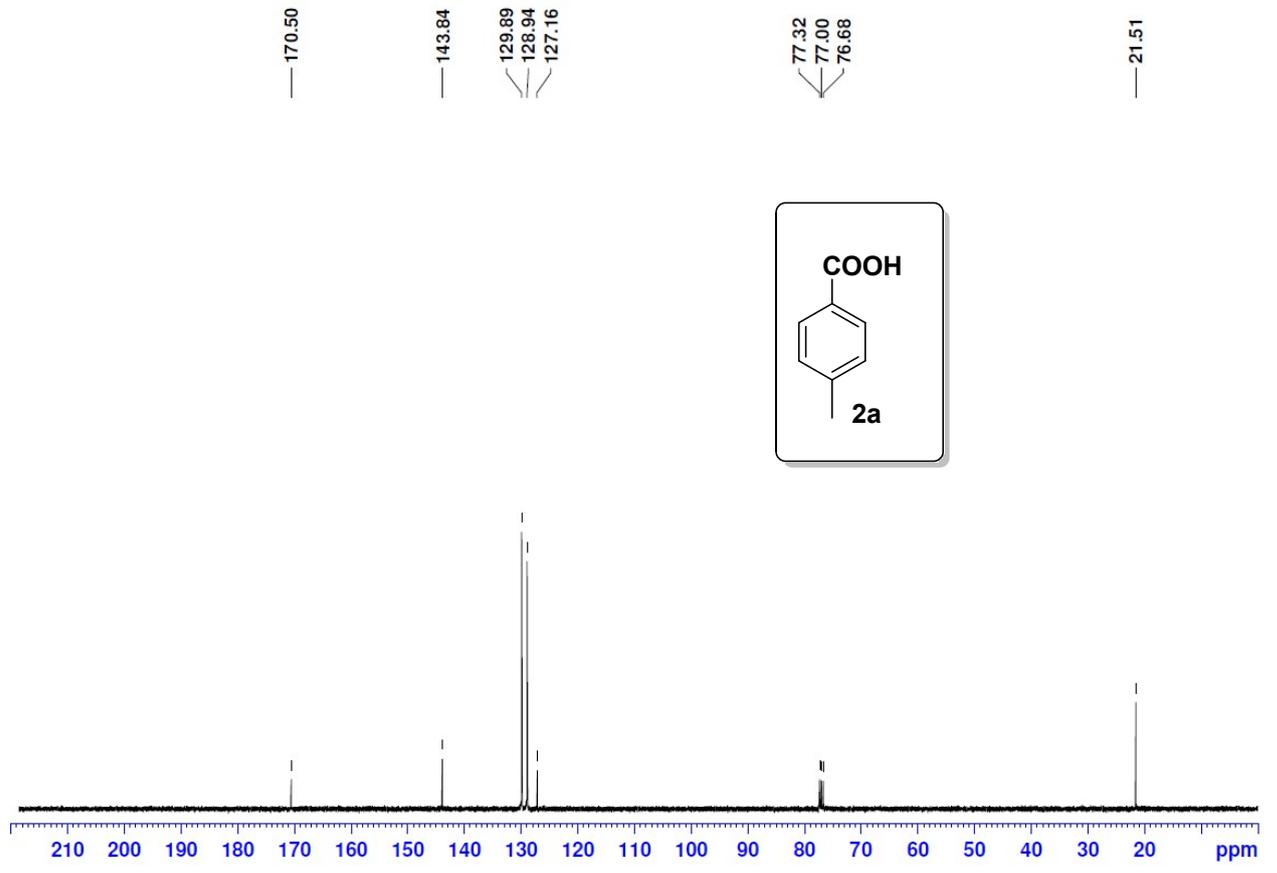
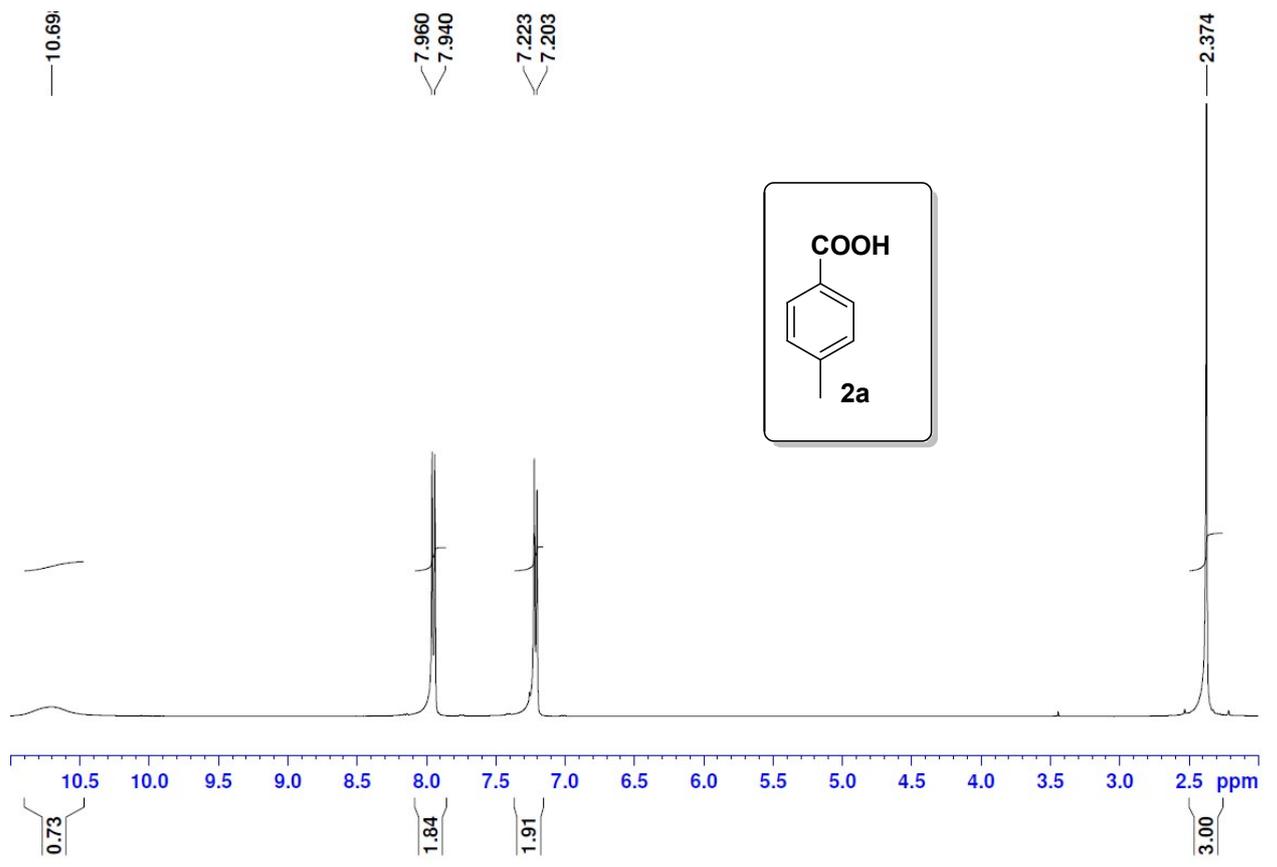


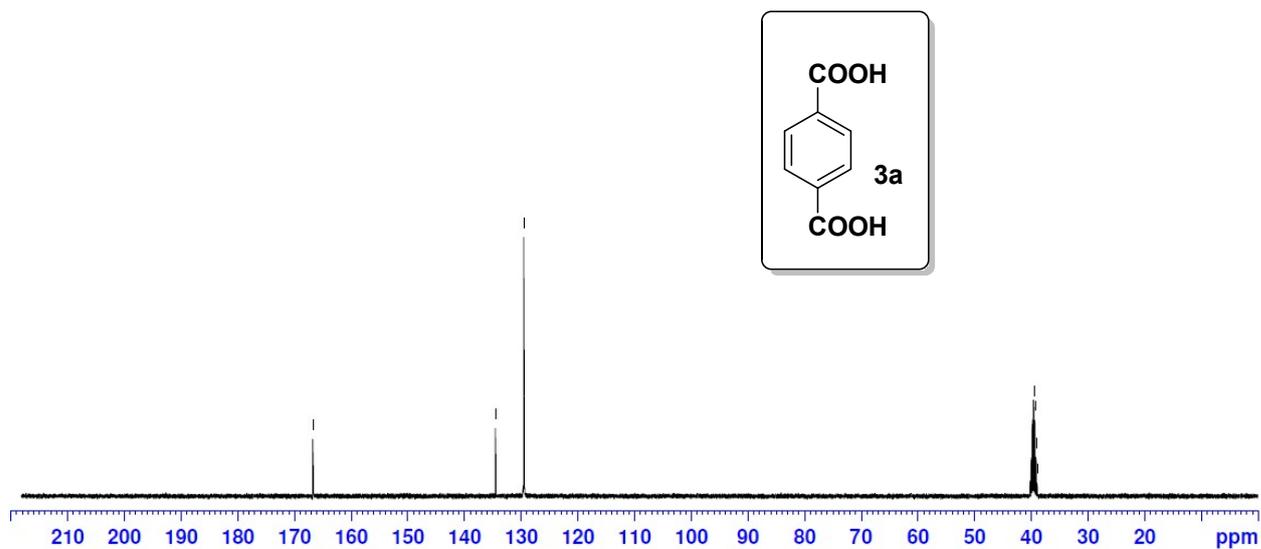
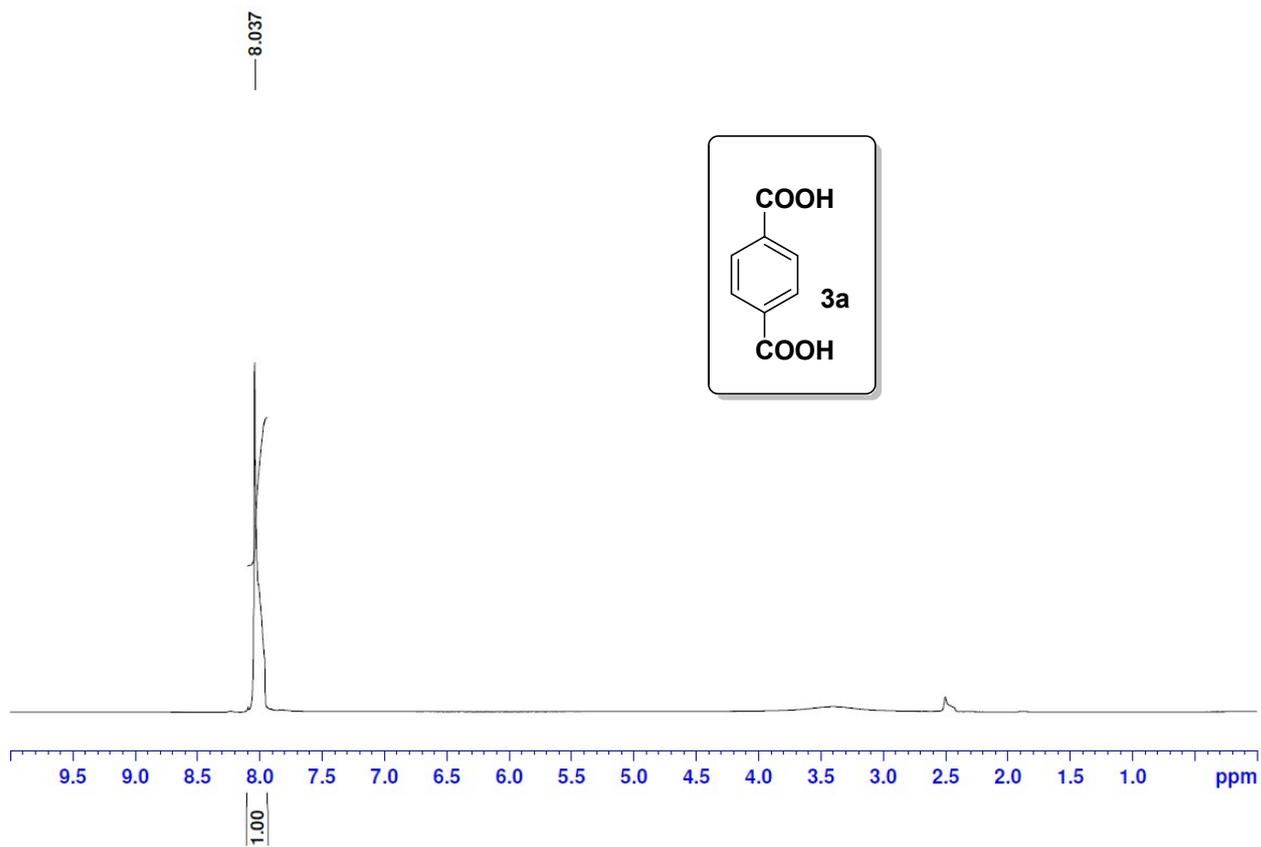
White solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.93 (dd, $J= 4.0\text{ Hz}$, 8.0Hz, 2 H), 7.55-7.51 (m, 2H), 7.45-7.41 (m, 2 H), 2.58 (s, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 198.1, 137.0, 133.0, 128.5, 128.2, and 26.5. *NMR data is in agreement with authentic commercially available sample*

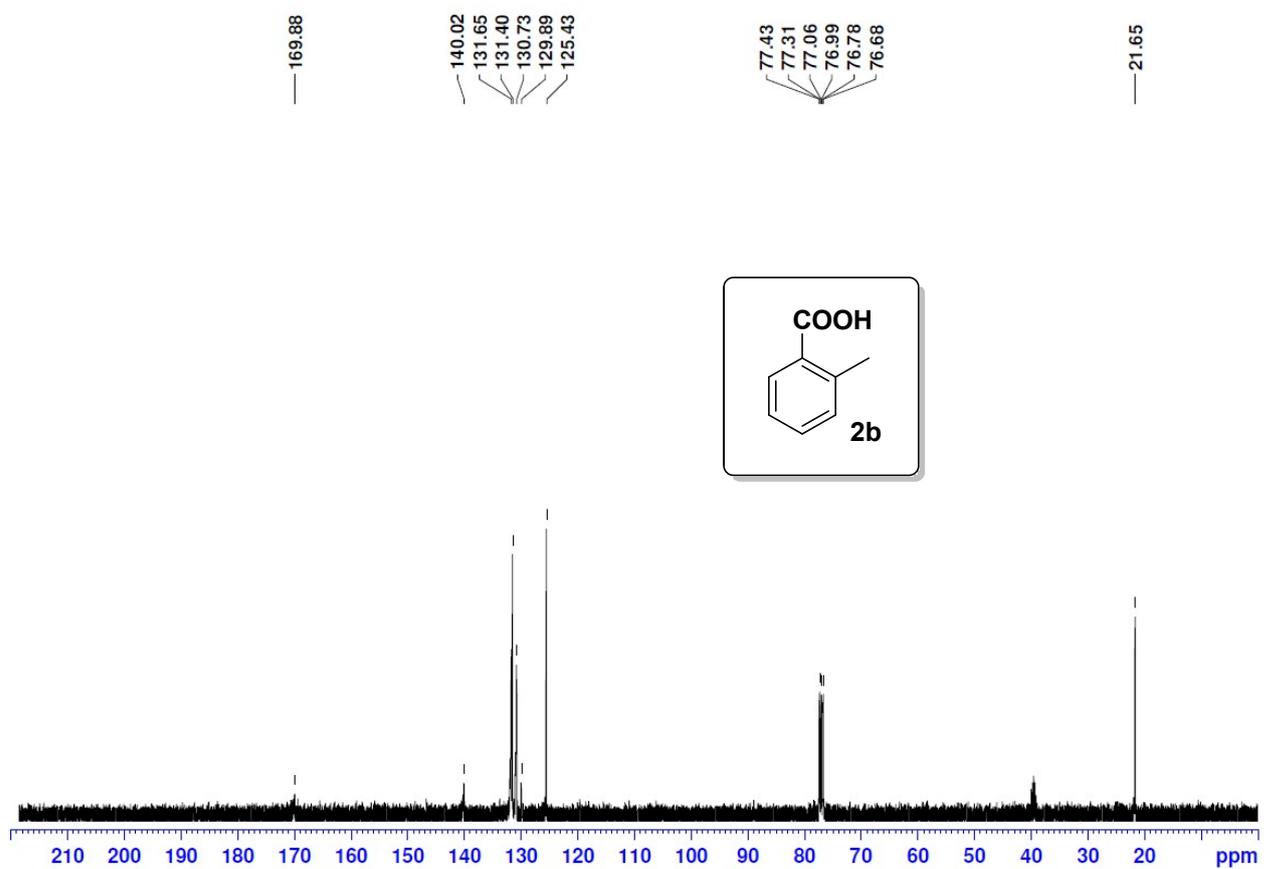
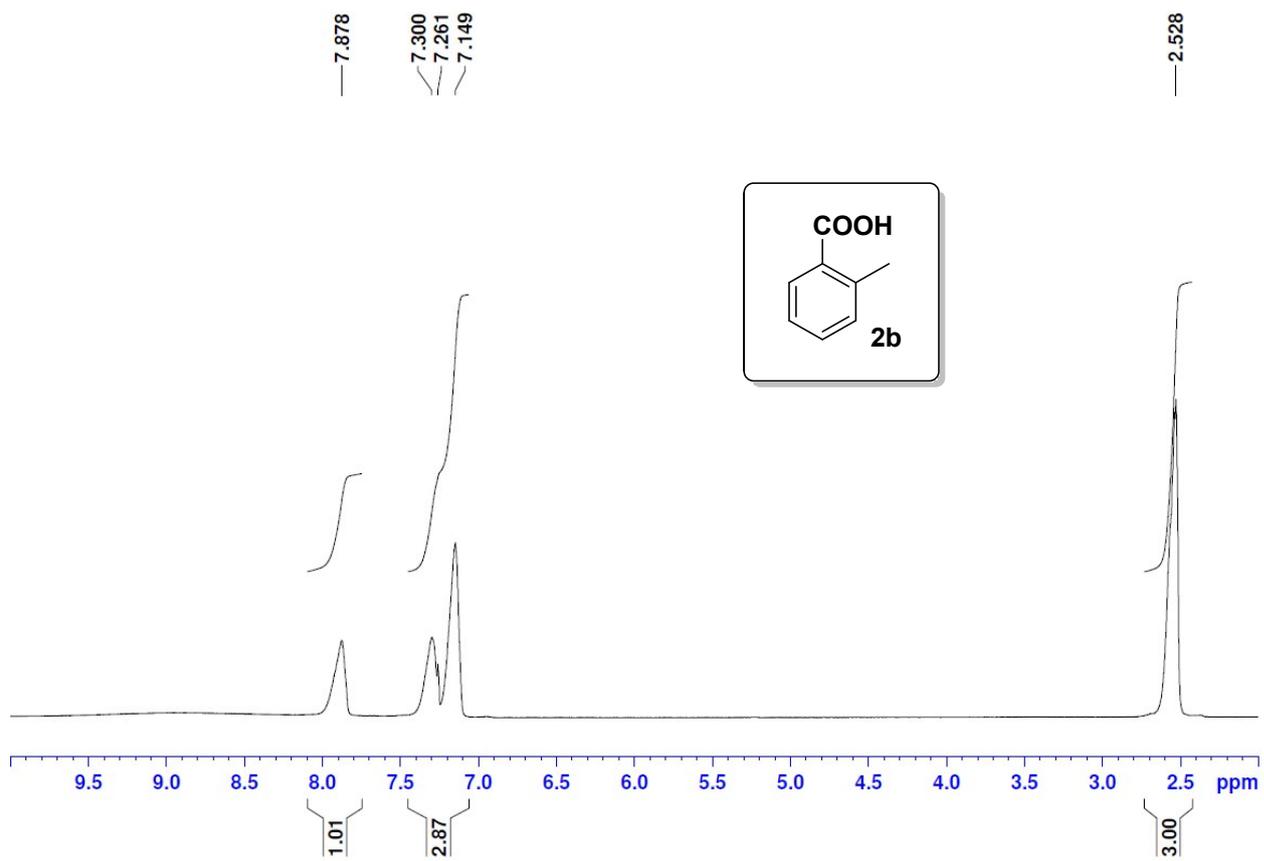
Benzophenone (2f) (CAS NO: 119-61-9)

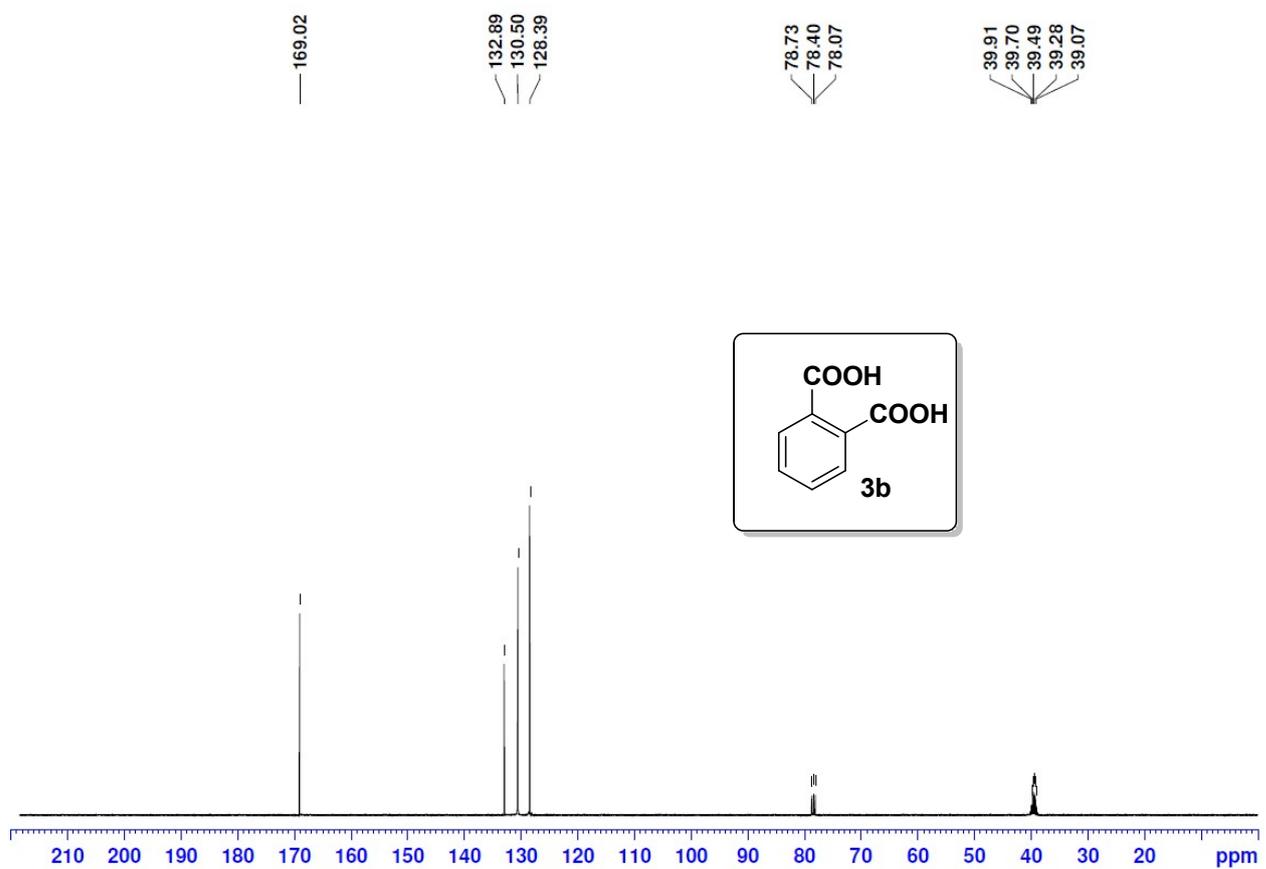
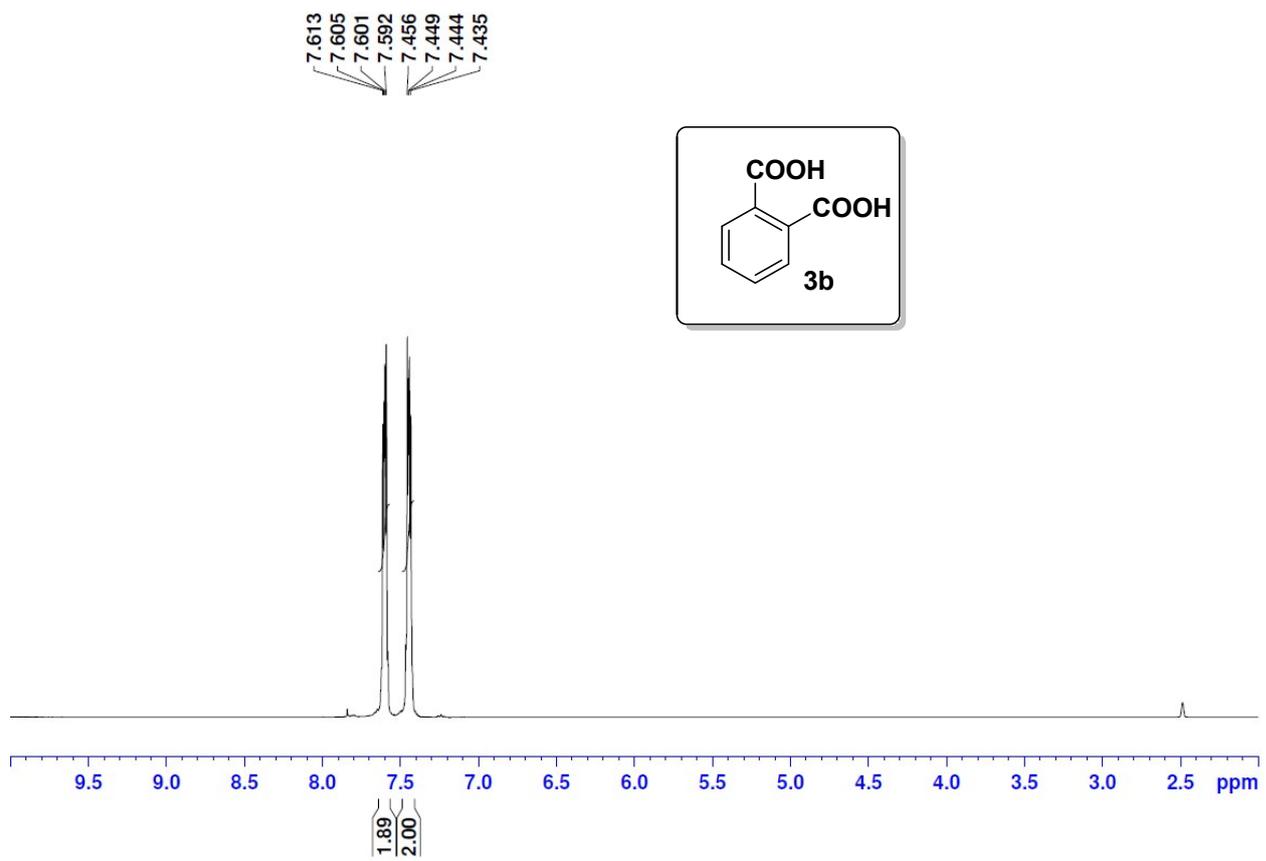


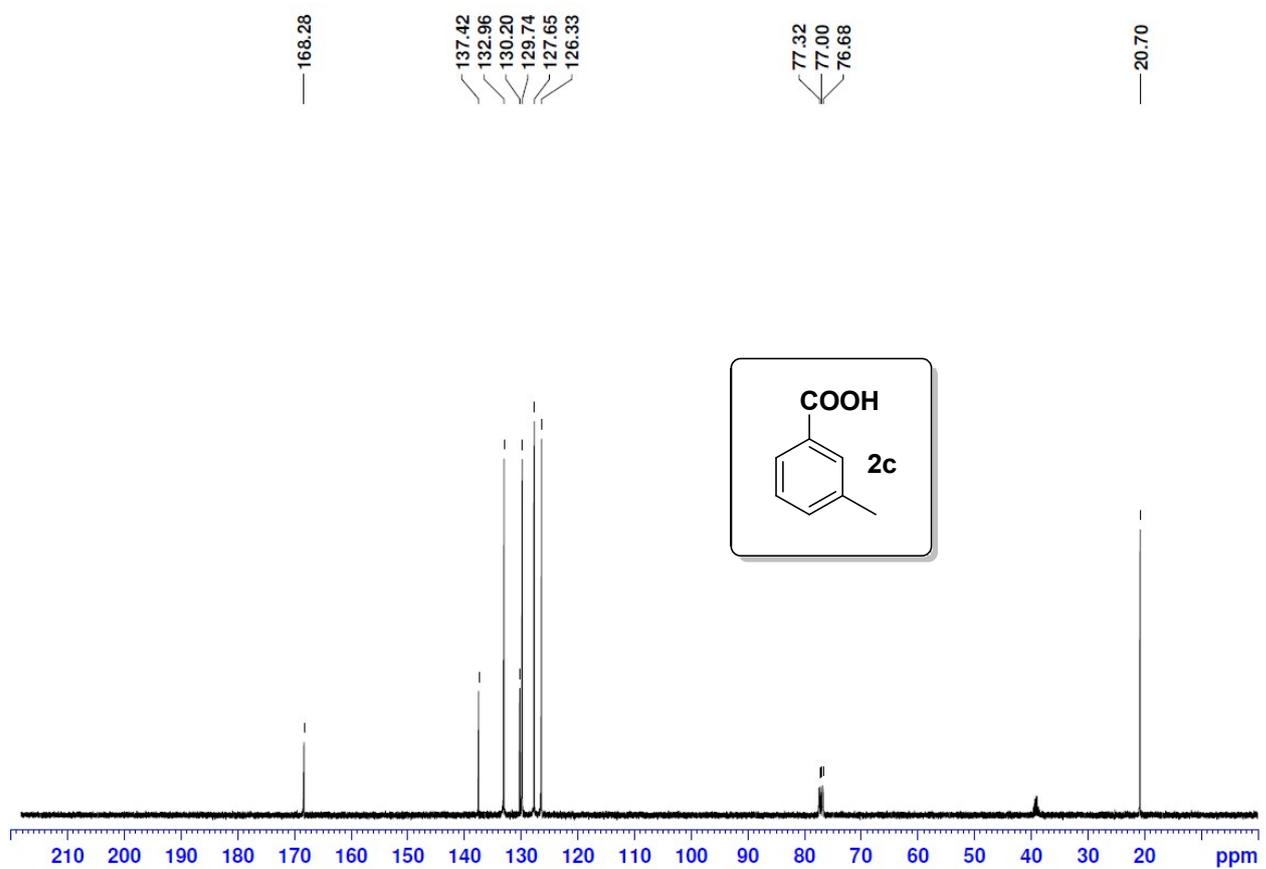
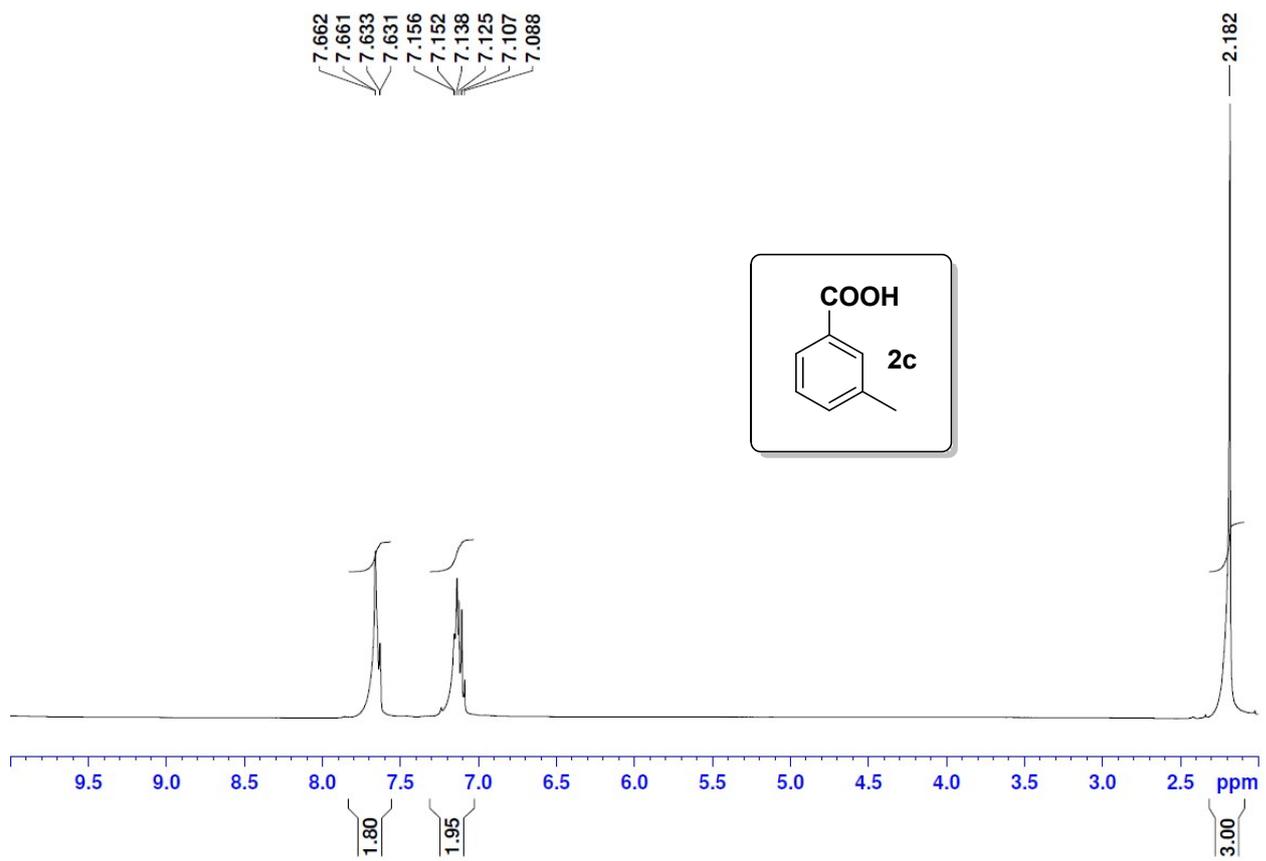
Brown liquid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.81-7.60 (m, 2 H), 7.60-7.56 (m, 1 H), 7.50-7.46 (m, 2 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 196.7, 137.5, 132.3, 130.0, and 128.2. *NMR data is in agreement with authentic commercially available sample.*

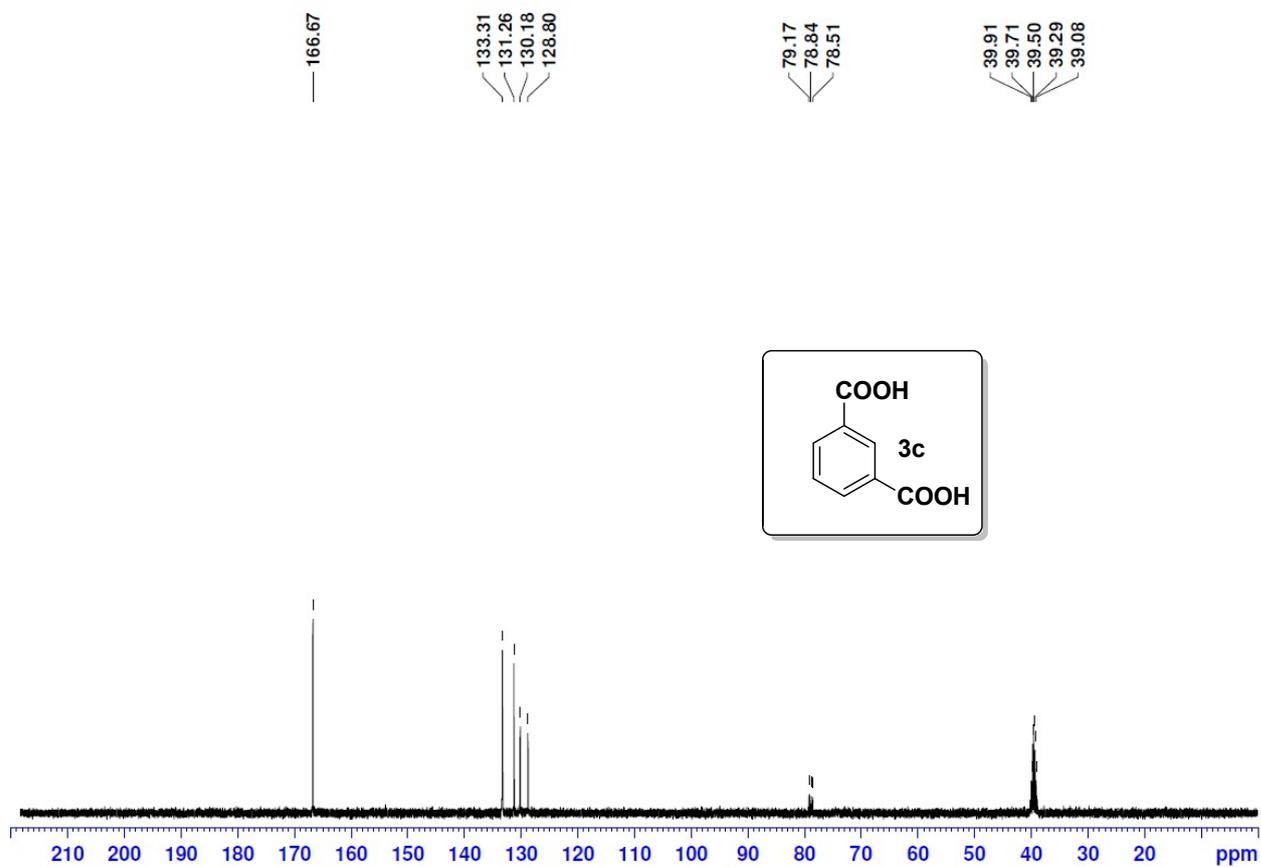
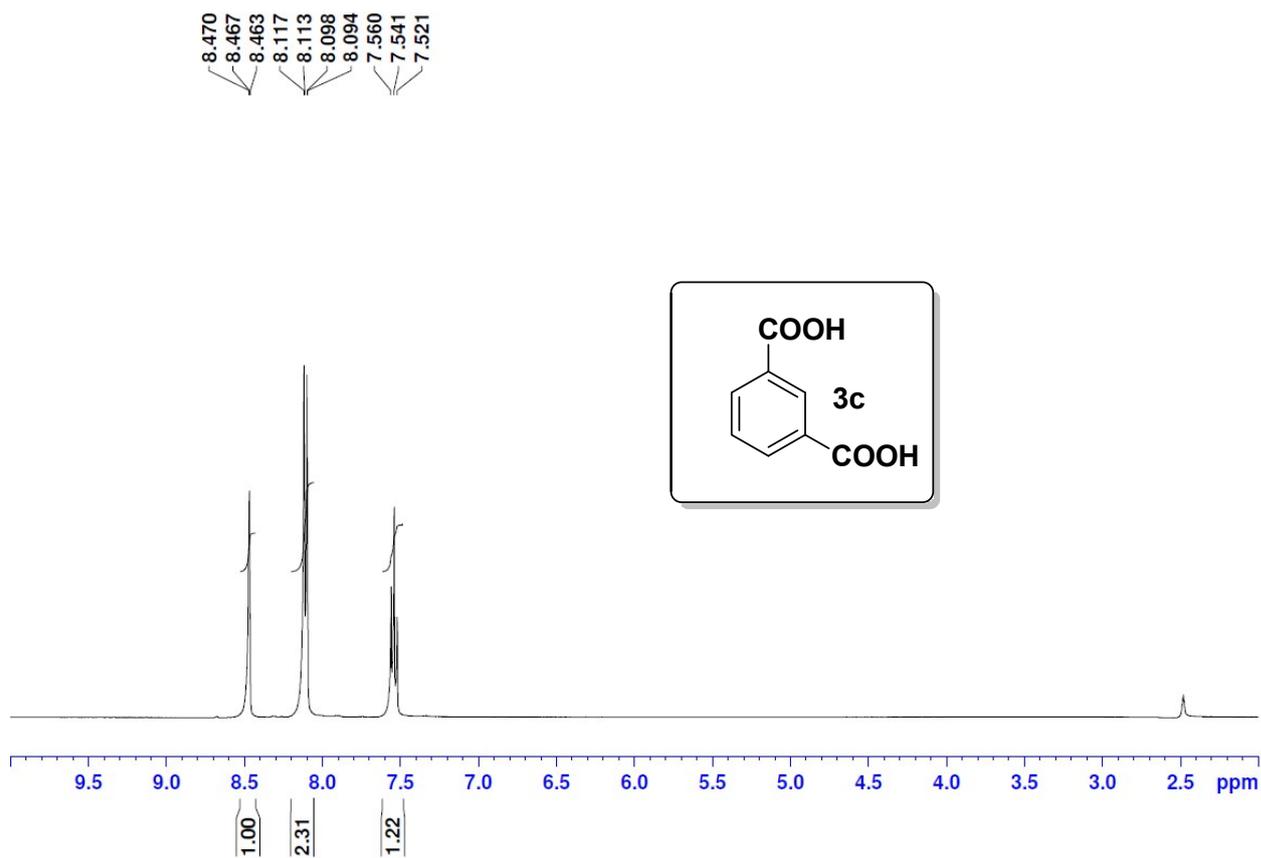


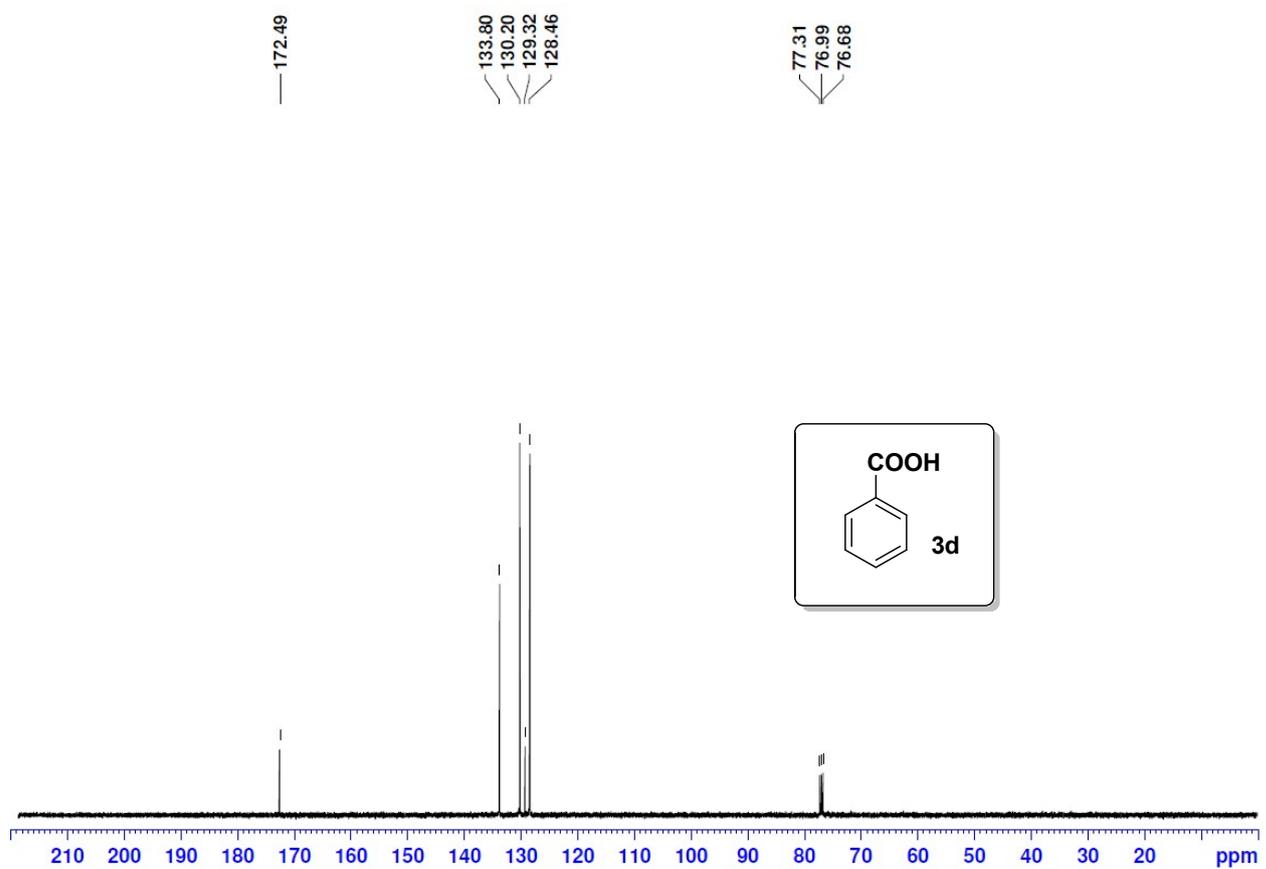
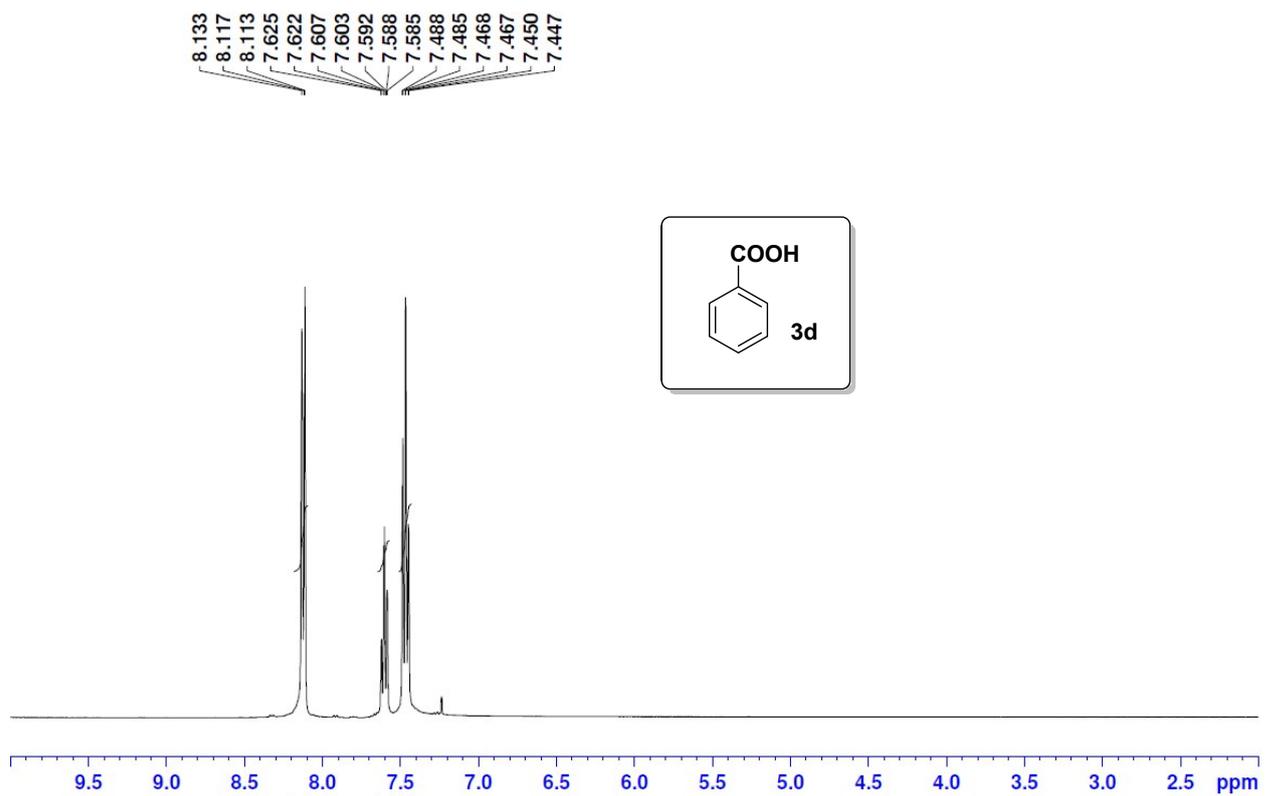


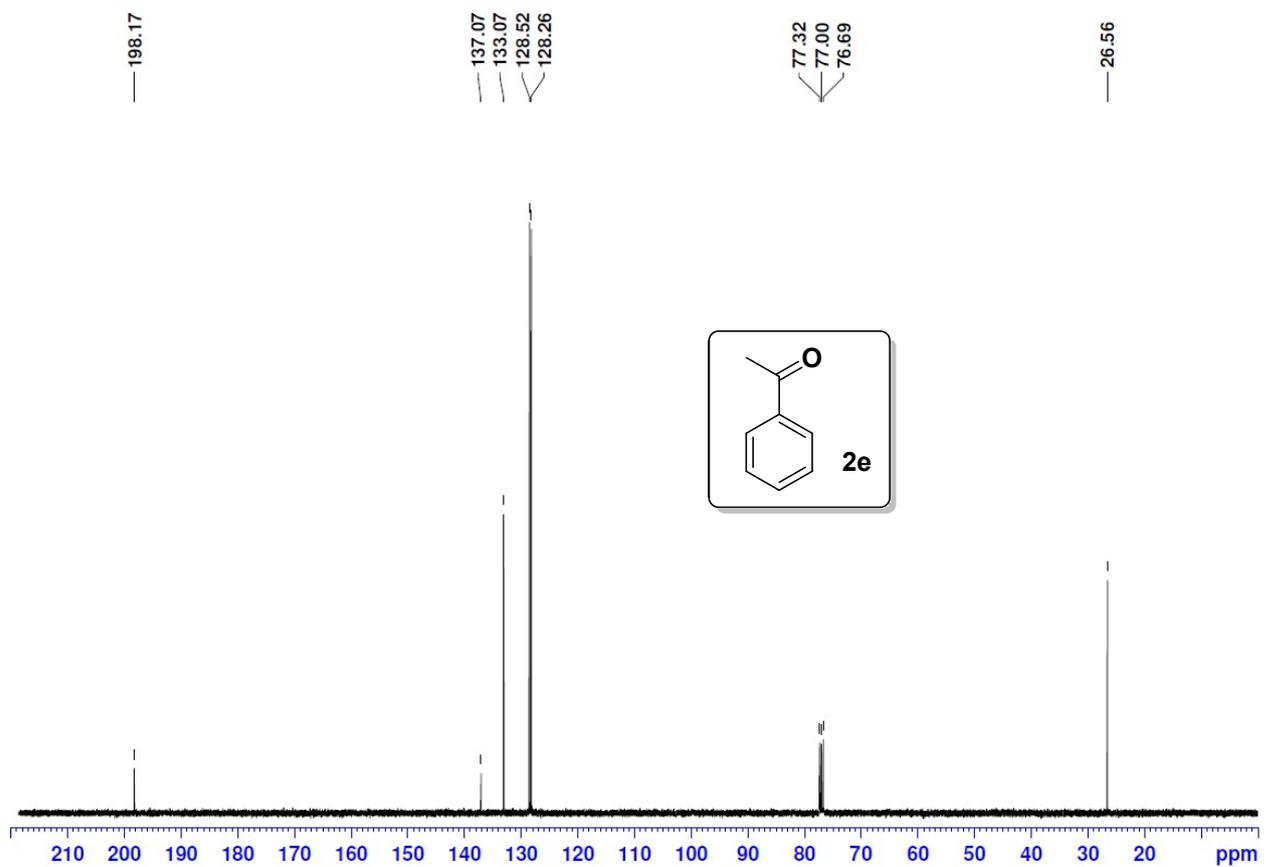
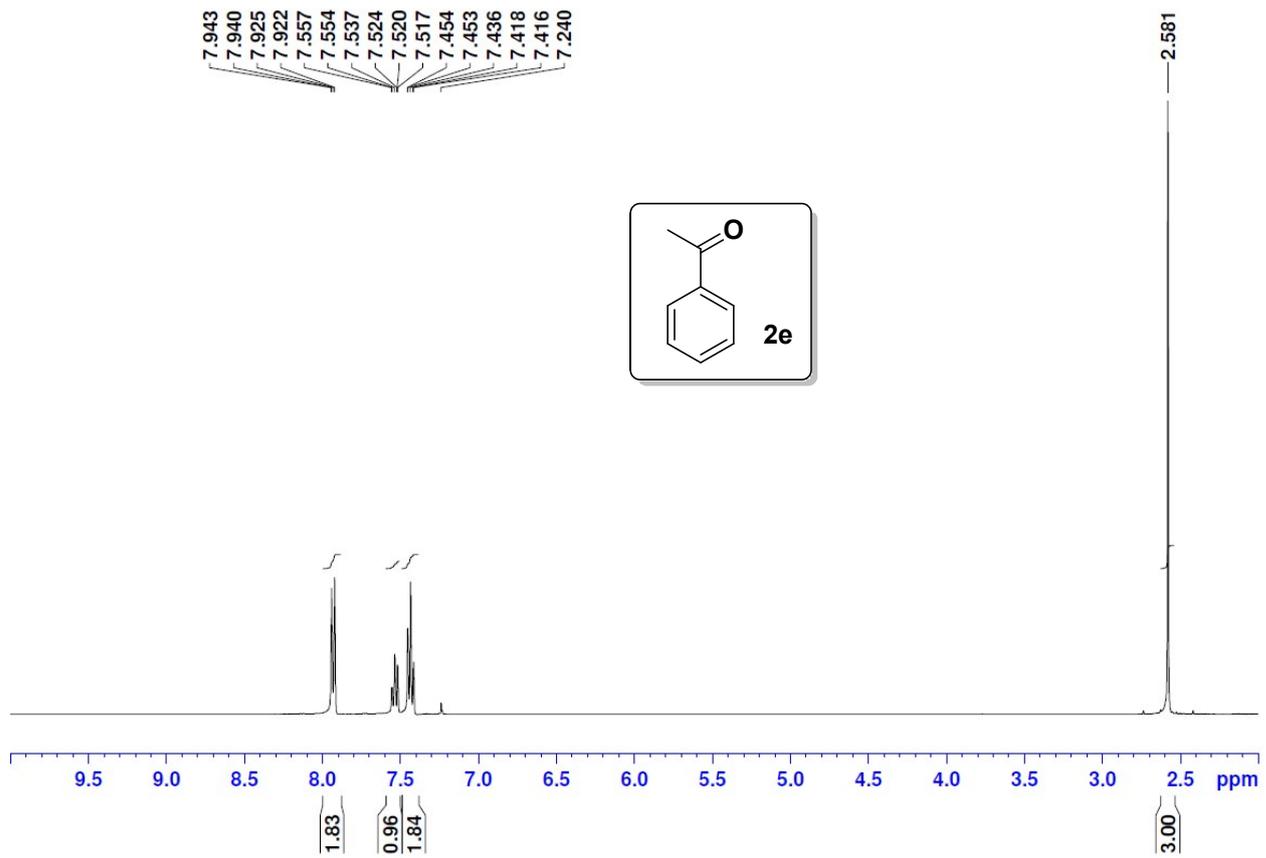


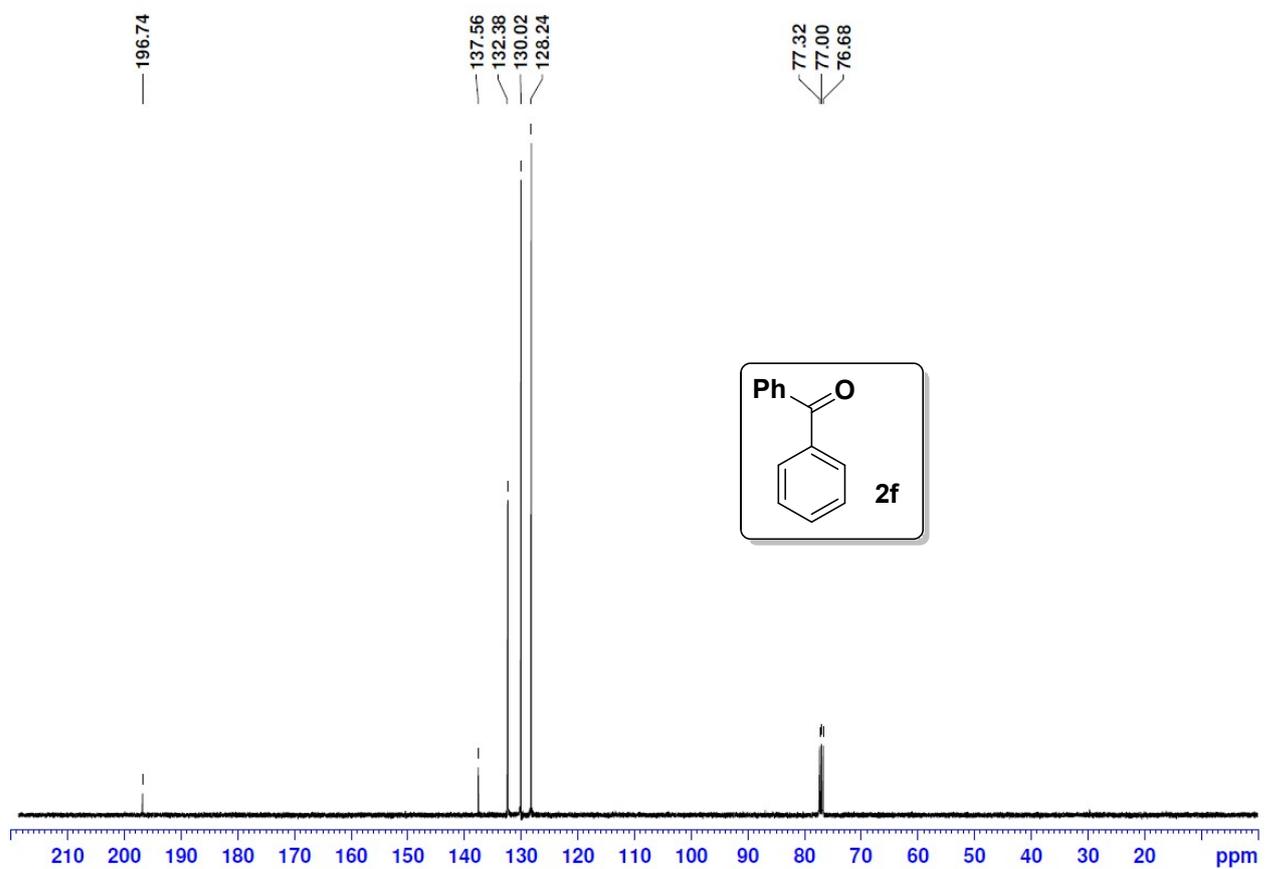
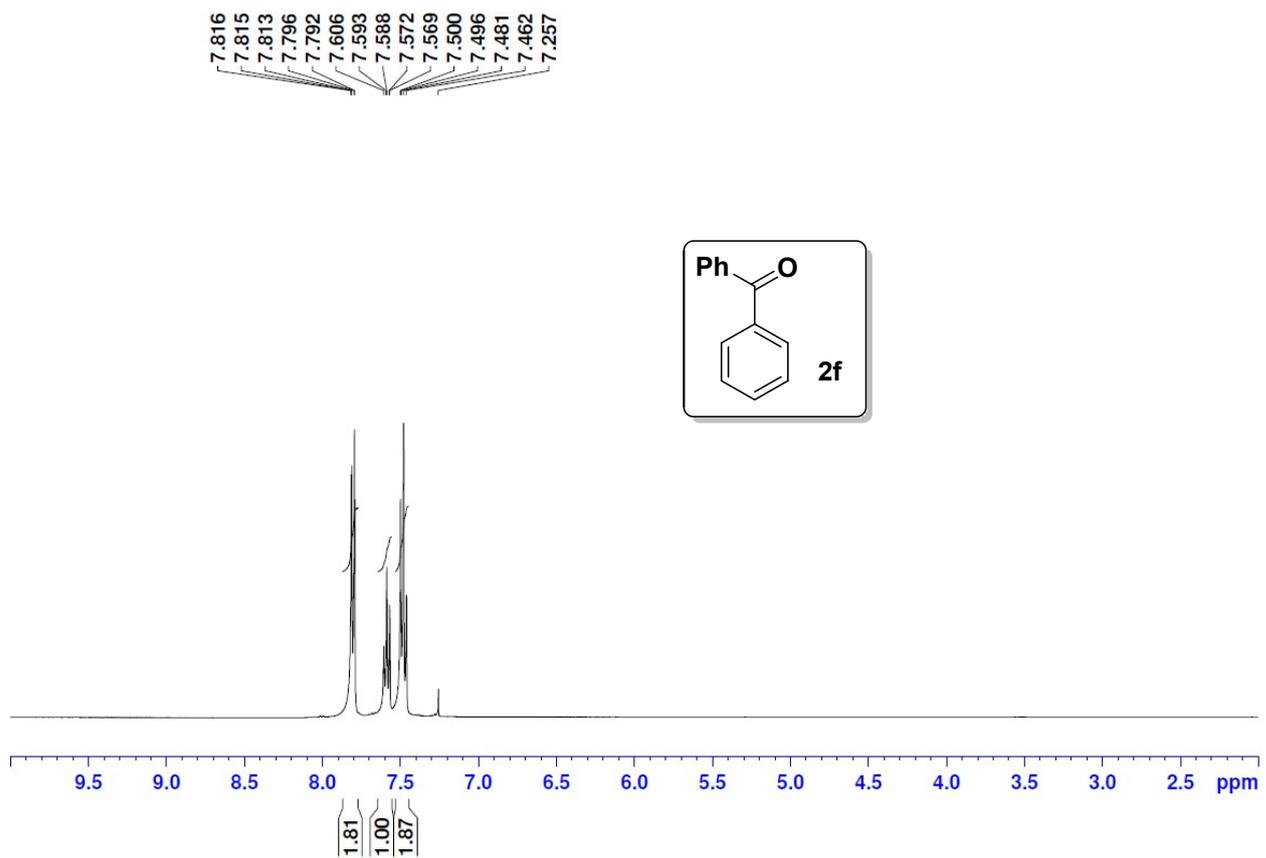












Supplemental references

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- S2.. Hosseini-Monfared, H.; Asghari-Lalami, N.; Pazio, A.; Wozniak, K.; Janiak, C. *Inorganica Chimica Acta*, **2013**, *406*, 241-244.
- S3. Cerkovnik, J.; Erzen, E.; Koller, J.; Plesnicar, B. *J. Am. Chem. Soc.*, **2002**, *124*, 404-409.
- S4. Finkelstein, E.; Rosen, G. M.; Rauckman, E. J. *Arch. Biochem. Biophys.*, **1980**, *200*, 1-16.