Supporting Information for：

COPPER CORROLE CATALYZED ESTERIFICATION OF C(sp^3)-H WITH CARBOXYLIC ACIDS VIA CROSS-DEHYDROGENATIVE COUPLING REACTION

Zhao-Yang Liu, Wei-Yu Peng, Waseem Akram, Jia-Wei Lai, Hao Zhang, and Hai-Yang Liu*

Department of Chemistry, The Key Laboratory of Fuel Cell Technology of Guangdong Province, South China University of Technology, Guangzhou 510640, China；E-mail address: chhyliu@scut.edu.cn

Crystallographic Description:

Single-crystal X-ray diffraction data were recorded on a Rigaku R-AXIS SPIDER IP diffractometer with Cu Kα radiation using a ω scan technique. The crystal was kept at 150 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine4 refinement package using Gauss-Newton minimisation. All atoms except for hydrogen atoms were refined anisotropically

Crystal structure determination of F_{10}C-Cu

$C_{37}H_{13}CuF_{10}N_4$ (*M*=767.05 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a*= 33.3260(12)Å, *b*= 6.49813(17)Å, *c*=28.7248(10)Å, *β*=110.569(4), *V*= 5824.0(4)Å^3, *Z*= 8,*T*= 100.00(10)K, μ(CuKα)= 1.989 mm^{-1}, *Dcalc*= 1.750g/cm^3, 21322 reflections measured (5.664° ≤ 2Θ ≤ 147.236°), 11344 unique (R_{int}= 0.0609, R_{sigma}= 0.0833) which were used in all calculations. The final R_1 was 0.0625 (I > 2σ(I)) and wR_2 was 0.1686 (all data)。CCDC 1936921 for compound F_{10}C-Cu contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Selected bond length（Å）and angels(。)of the F_{10}C-Cu

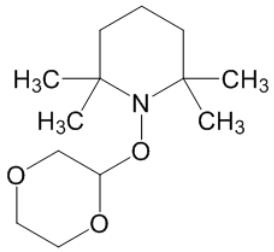
Bond Lengths/（Å）			
Cu1-N1	1.897(4)	Cu1-N2	1.896(4)
Cu1-N3	1.890(4)	Cu1-N4	1.884(4)
Bond angles (deg)			
N4-Cu1-N1	167.32(16)	N4-Cu1-N2	91.82(16)
N4-Cu1-N3	81.04(16)	N2-Cu1-N1	96.87(16)
N3-Cu1-N1	92.16(15)	N3-Cu1-N2	166.50(16)

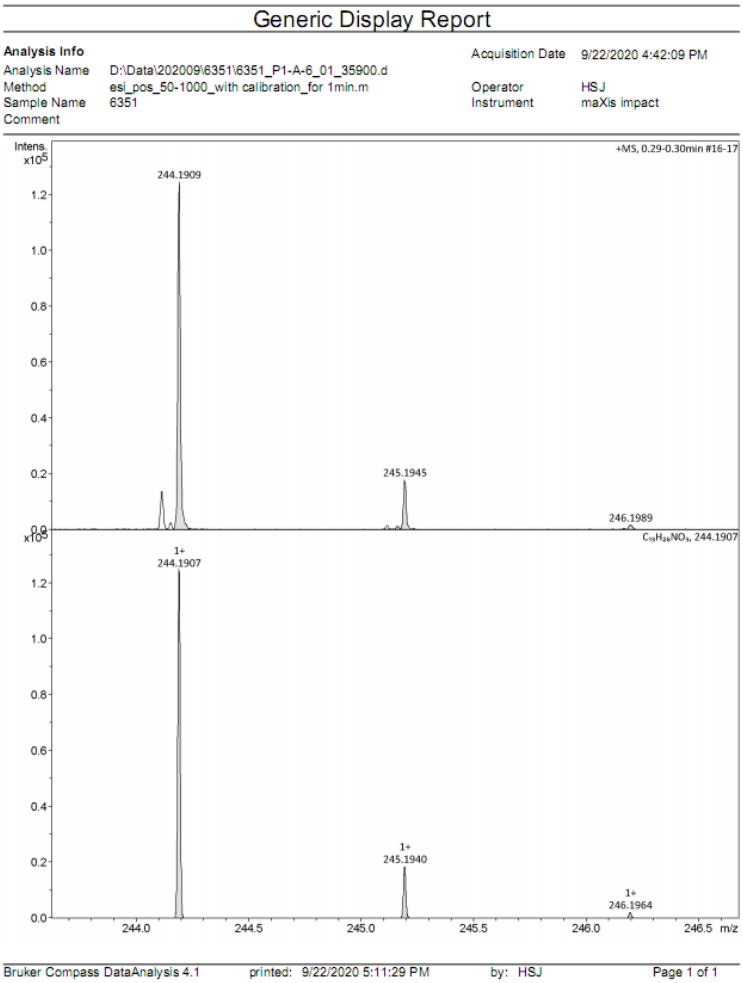
Synthesis of procedures

The synthesis of the 5,10,15-III (pentafluorophenyl) corrole (F_{15}), 5,15-II (pentafluorophenyl group), 10-phenyl corrole (F_{10}), 5,15-diphenyl ,10-pentafluorobenzyl corrole (F_5) and 5,10,15, triphenylcorrole (F_0) were performed using reported literature procedure [3]. Metallocorrole 5,10,15-III (pentafluorophenyl) corrole copper(F_{15}C-Cu), 5,15-II (pentafluorophenyl group),10-phenyl corrole copper (F_{10}C-Cu), 5,15-diphenyl,10-pentafluorobenzyl corrole copper(F_5C-Cu) and 5,10,15, triphenylcorrole copper(F_0C-Cu) were prepared using literature procedures [4].

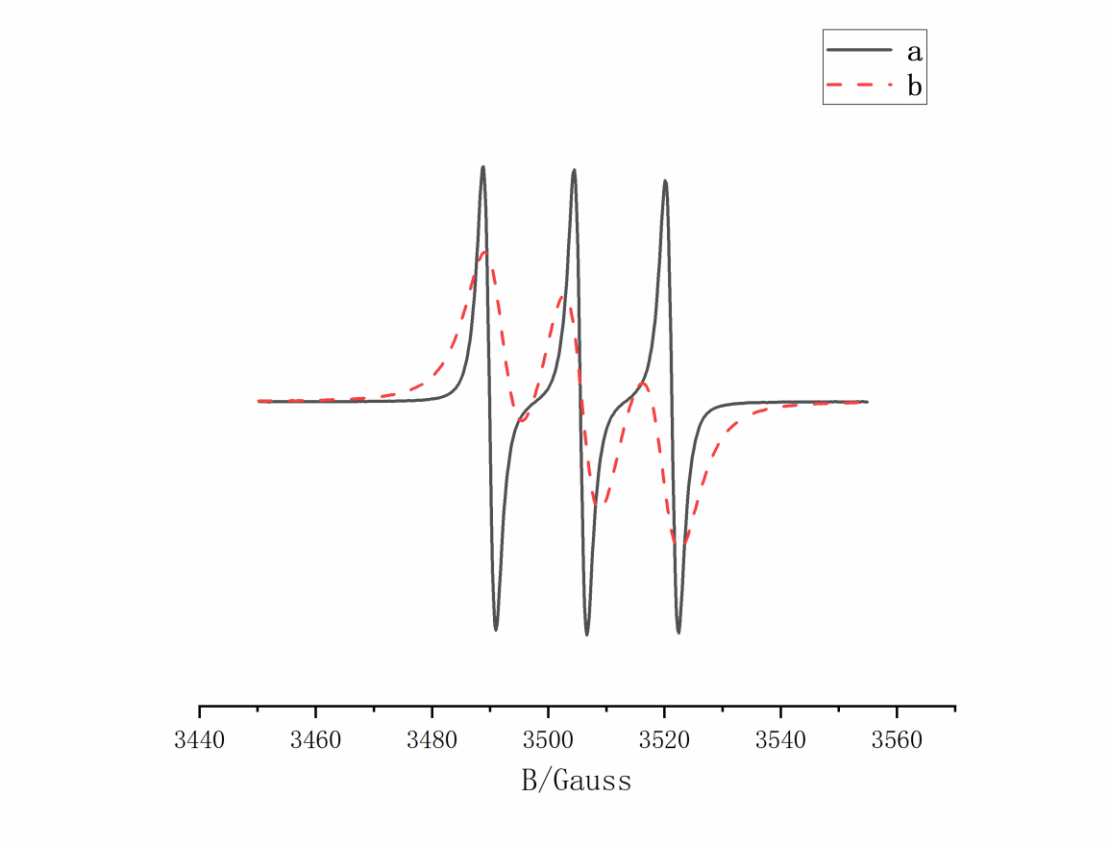
Synthesis of F_{15}C-Cu. F_{15}C-Cu was obtained by refluxing F_{15} with $Cu(OAc)_2 \cdot H_2O$ in DCM/CH_3OH(1:1 v/v) solution for 0.5 h. Then it was diluted with CH_2Cl_2 and washed with asaturated aqueous solution of NaCl several times. The organic layer was collected and dried over anhydrous Na_2SO_4. The filtrate was concentrated and the crude product was purified on silica gel (100–200 mesh) using CH_2Cl_2 as an eluent. Brown crystals were obtained after slow evaporation from CH_2Cl_2/hexane (1 : 1 v/v).

Other metallocorrles were synthesized using the same procedure for F_{15}C-Cu.



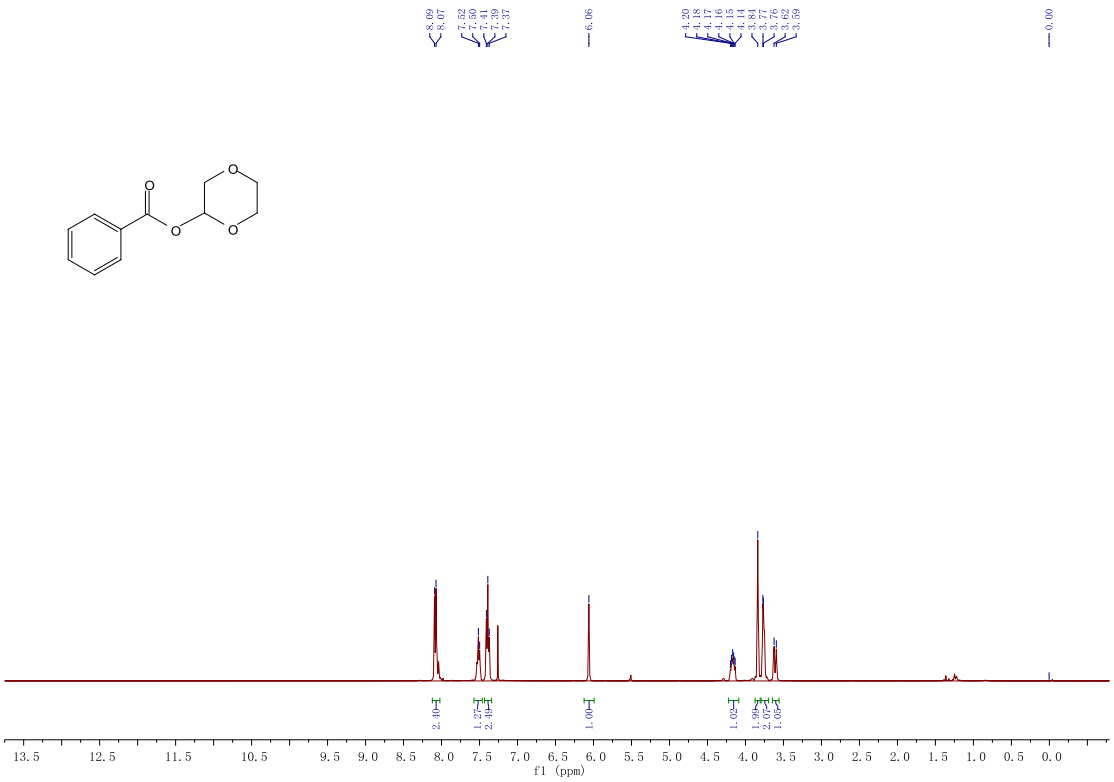


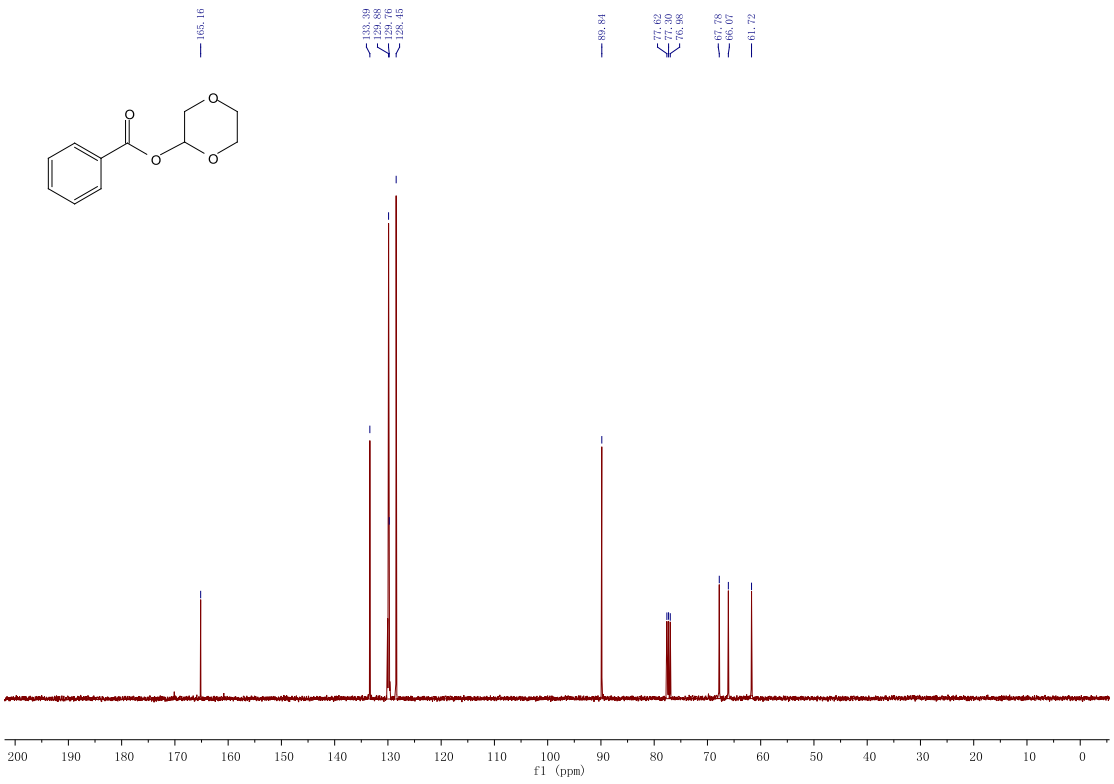
Scheme S1. ESI-MS of TEMPO-1,4-dioxane adduct



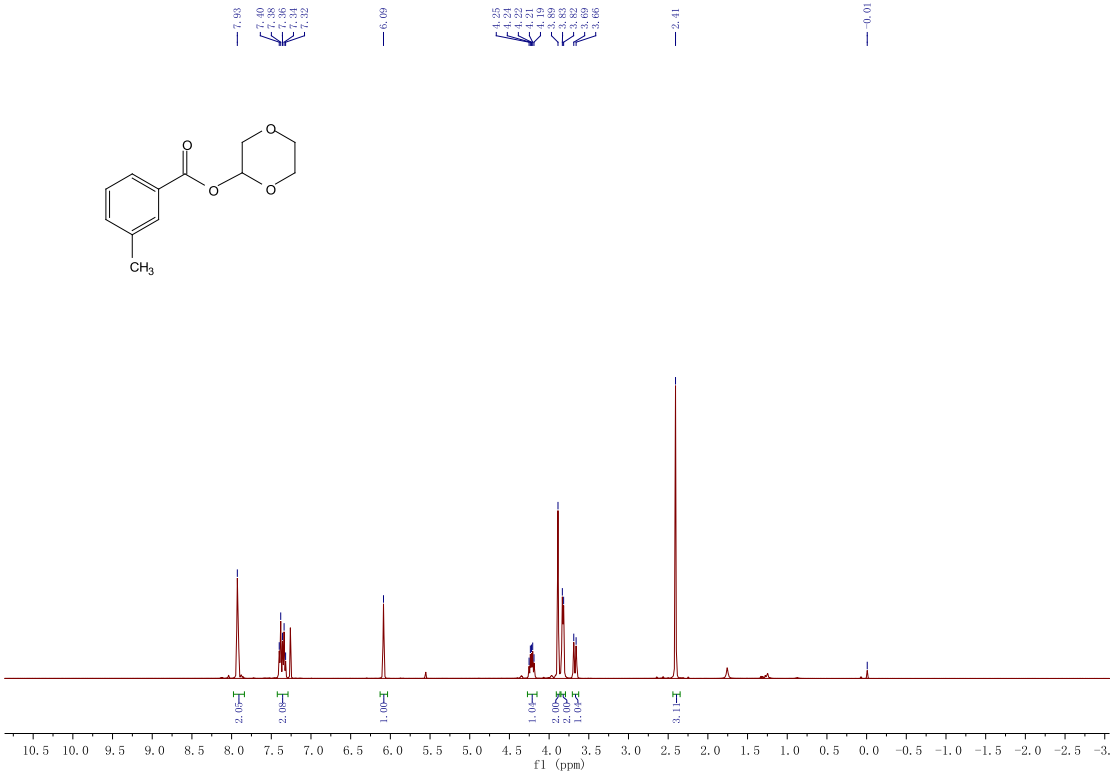
Scheme S2. EPR spectrum of (a) Benzoic acid (0.5 mmol), 1,4-dioxane (2 mL), CuTPFC (0.5 mol%) and TEMPO (0.5 mmol) in 120 ℃ after 2 h; (b) Followed by the addition of DTBP (2 equiv) in the mixture at 120 ℃ after 2 h.

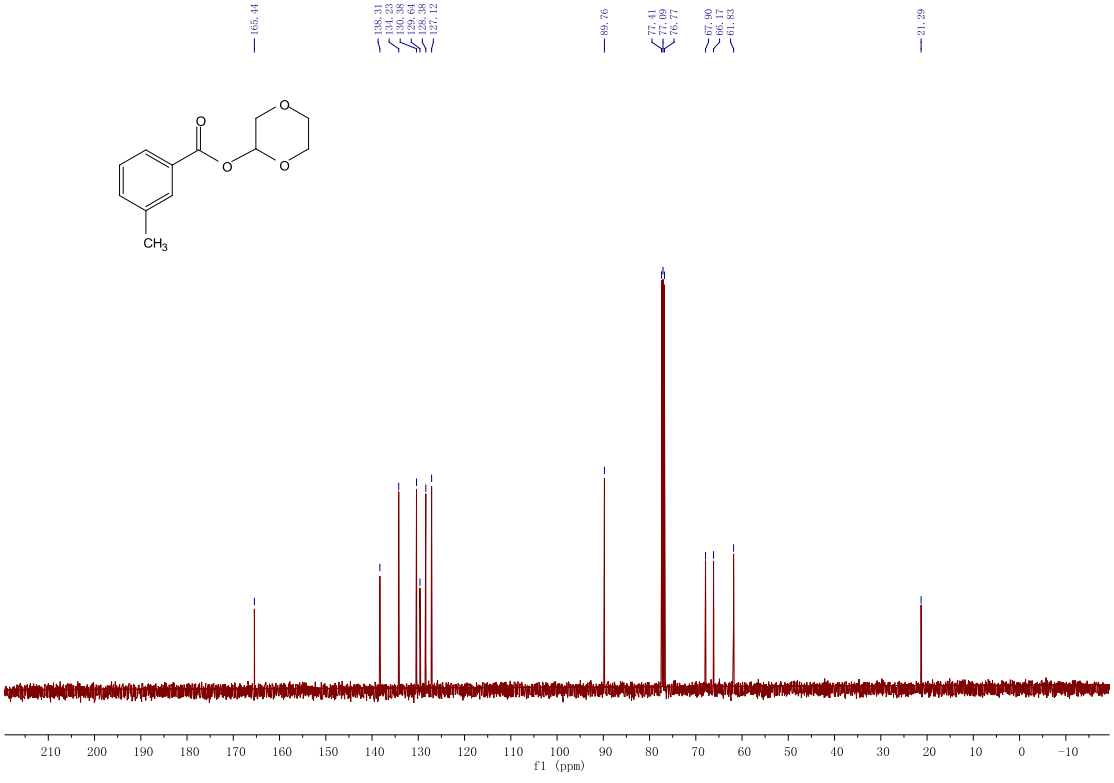
1,4-Dioxan-2-yl benzoate (1a):



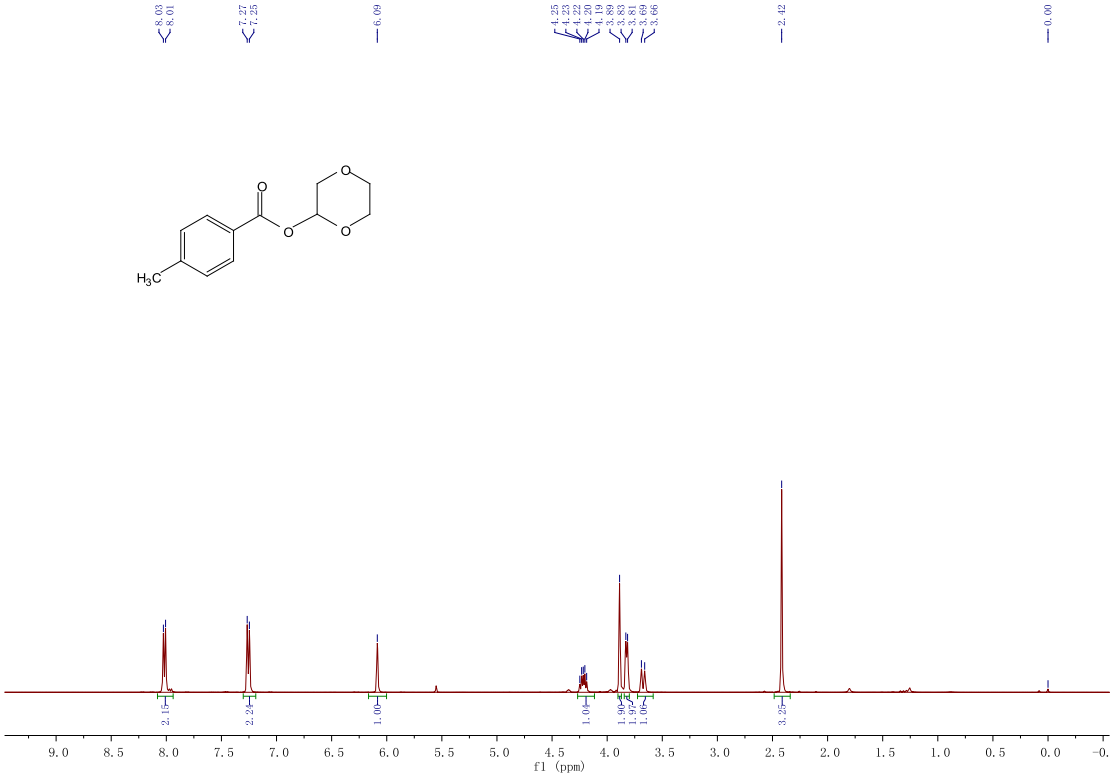


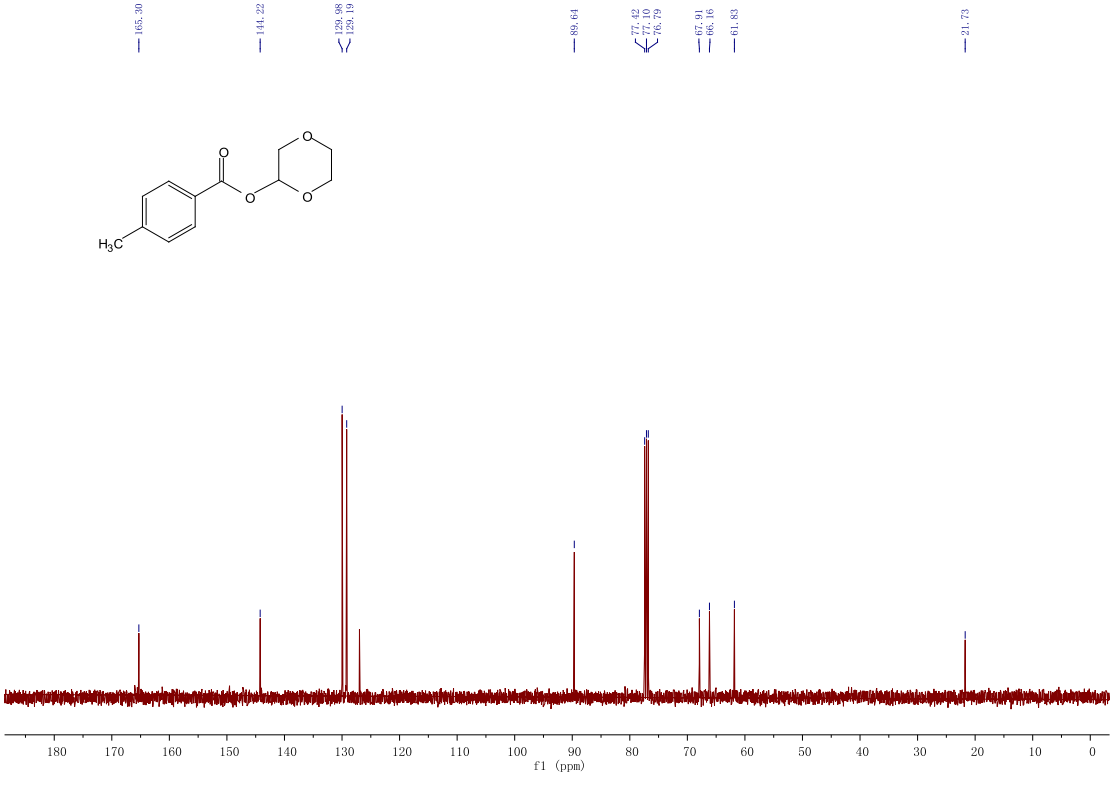
1,4-Dioxan-2-yl 3-methylbenzoate（2a）



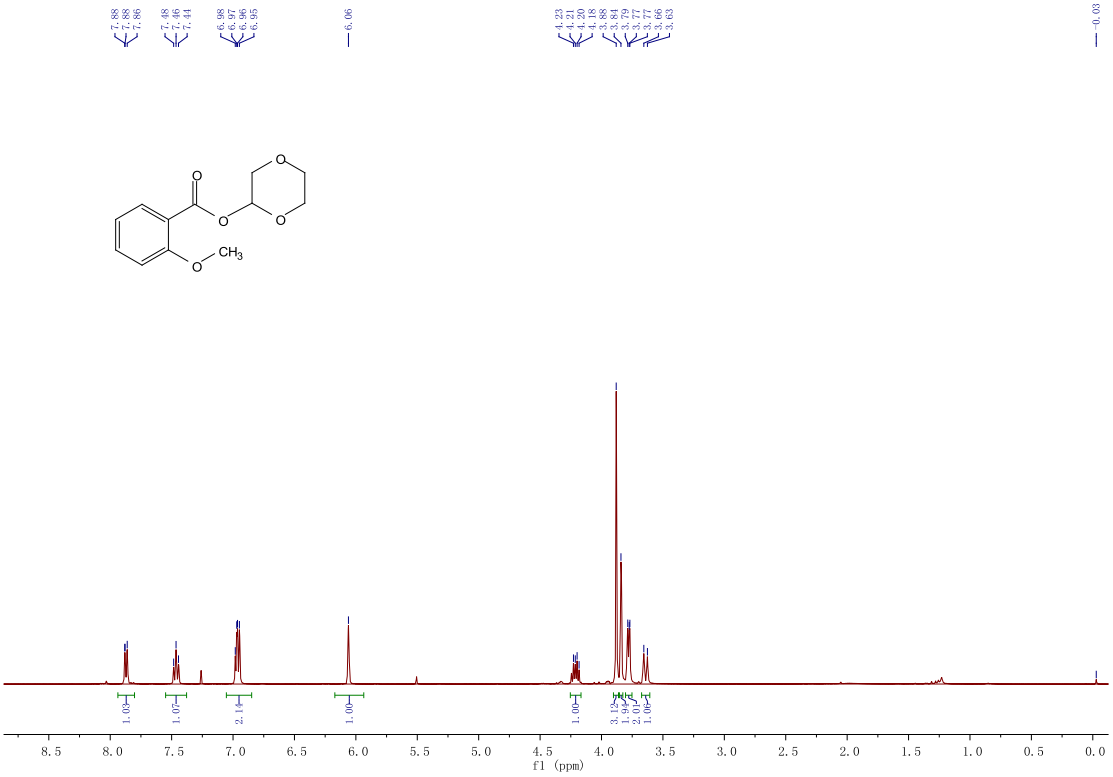


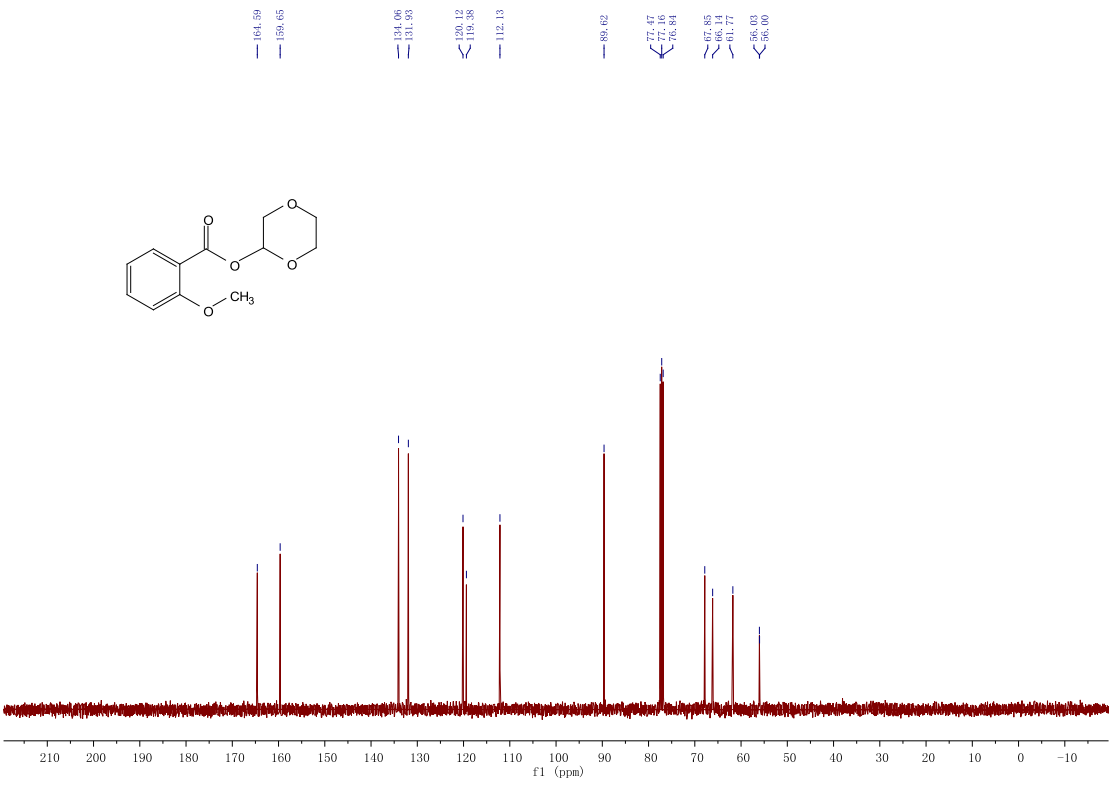
1,4-Dioxan-2-yl 4-methylbenzoate（3a）



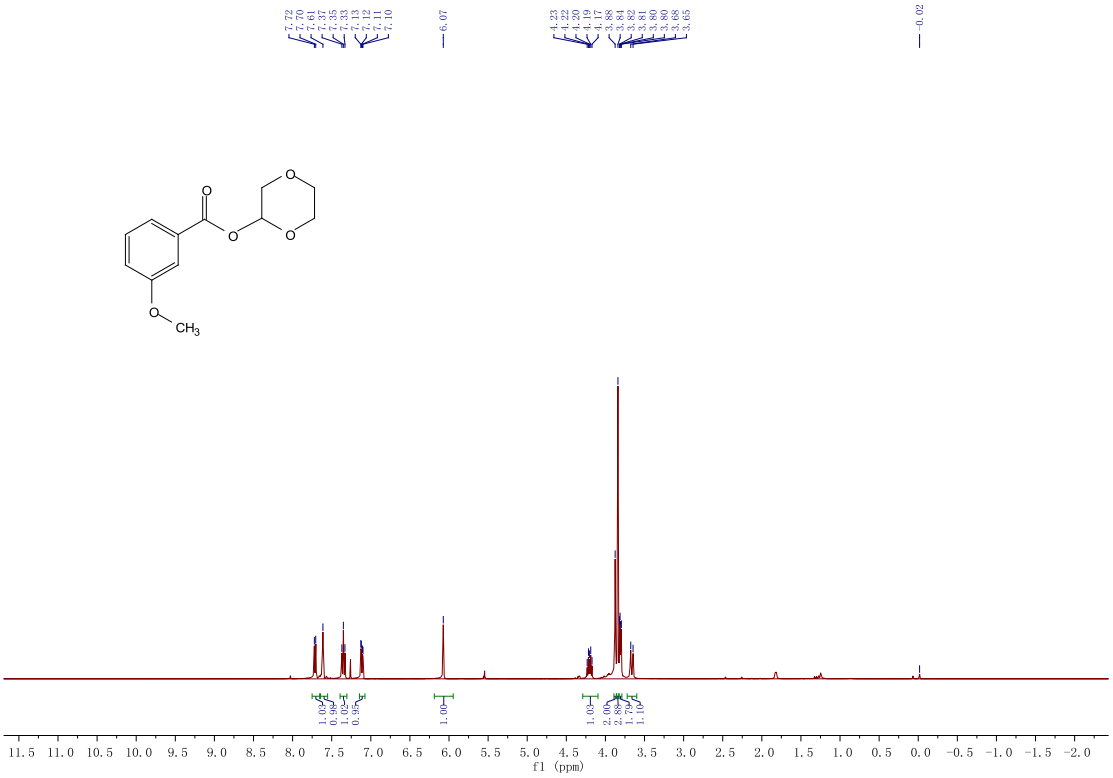


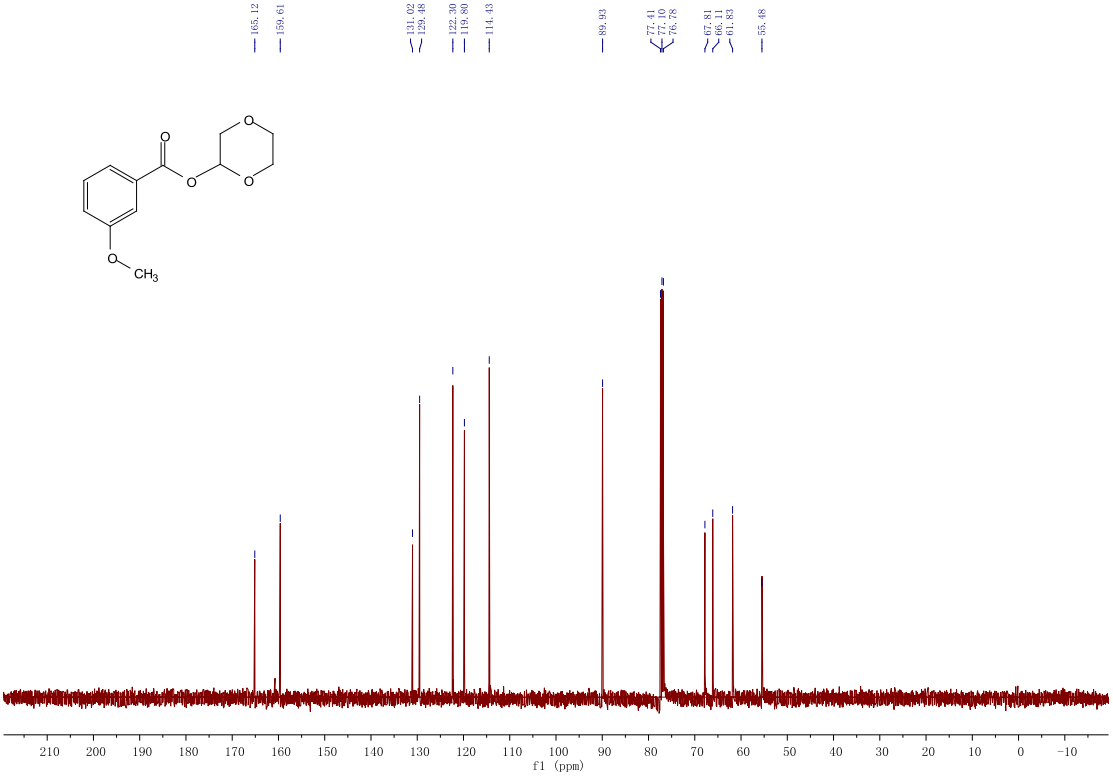
1,4-Dioxan-2-yl 2-methoxybenzoate（4a）



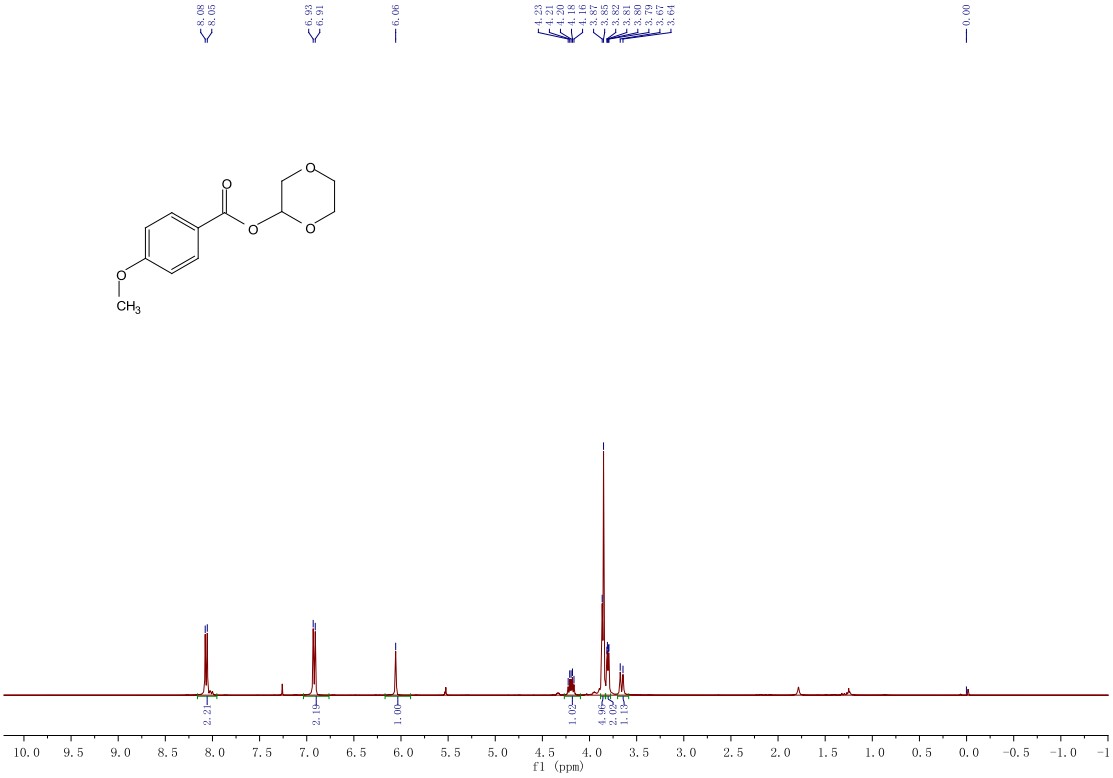


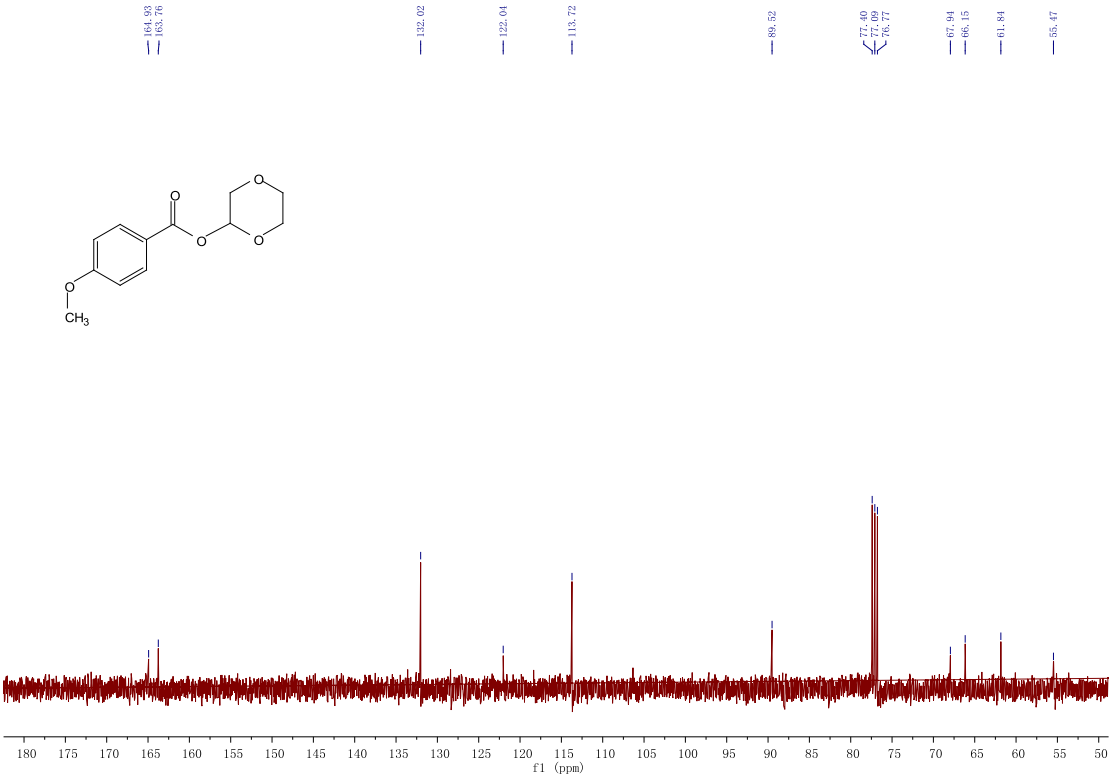
1,4-Dioxan-2-yl 3-methoxybenzoate（5a）



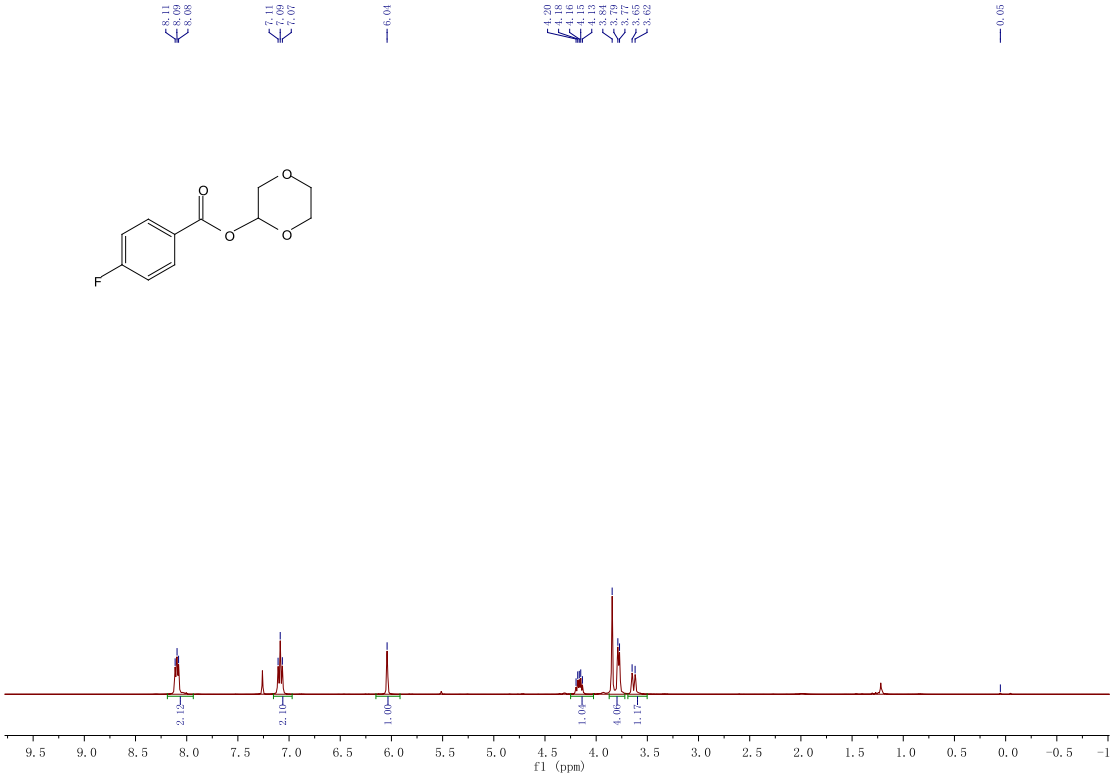


1,4-Dioxan-2-yl 4-methoxybenzoate（6a）

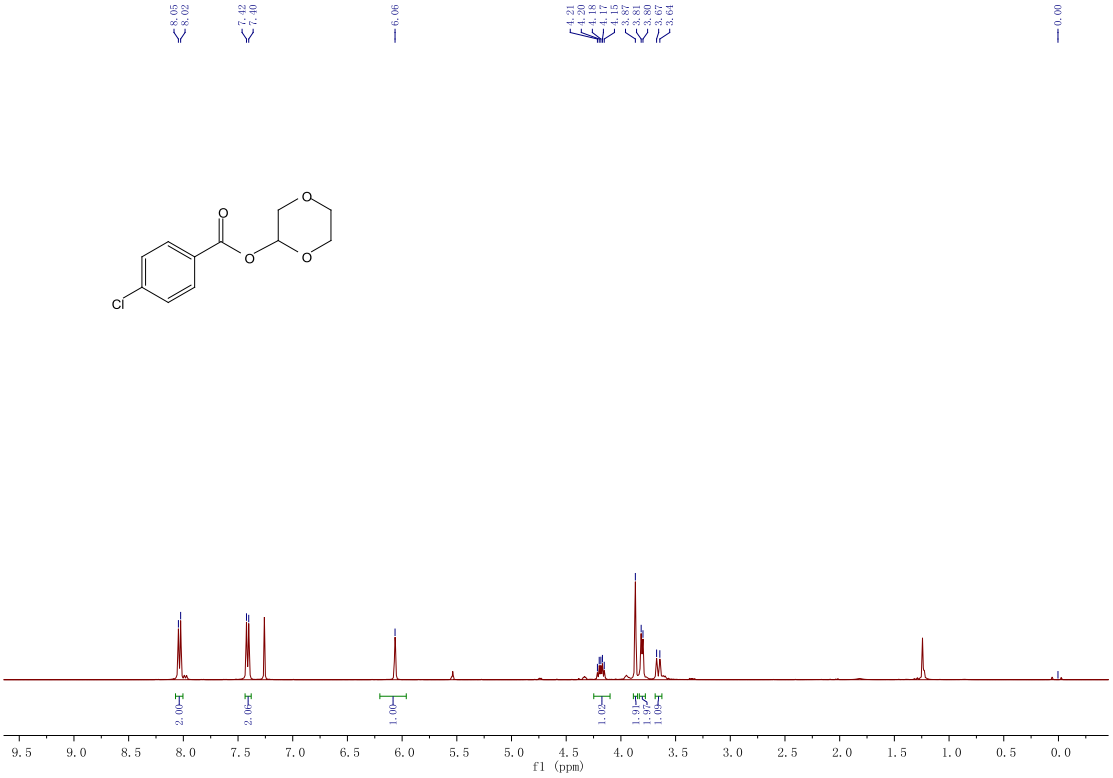


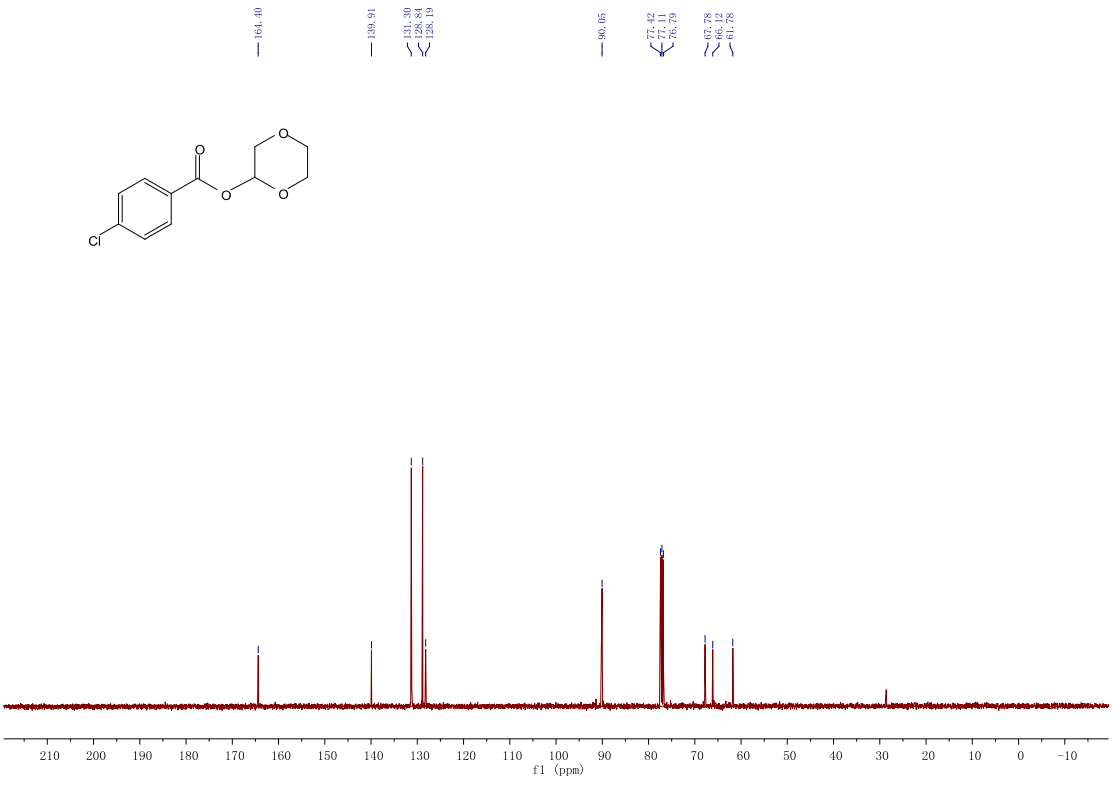


1,4-Dioxan-2-yl 4-fluorobenz（7a）

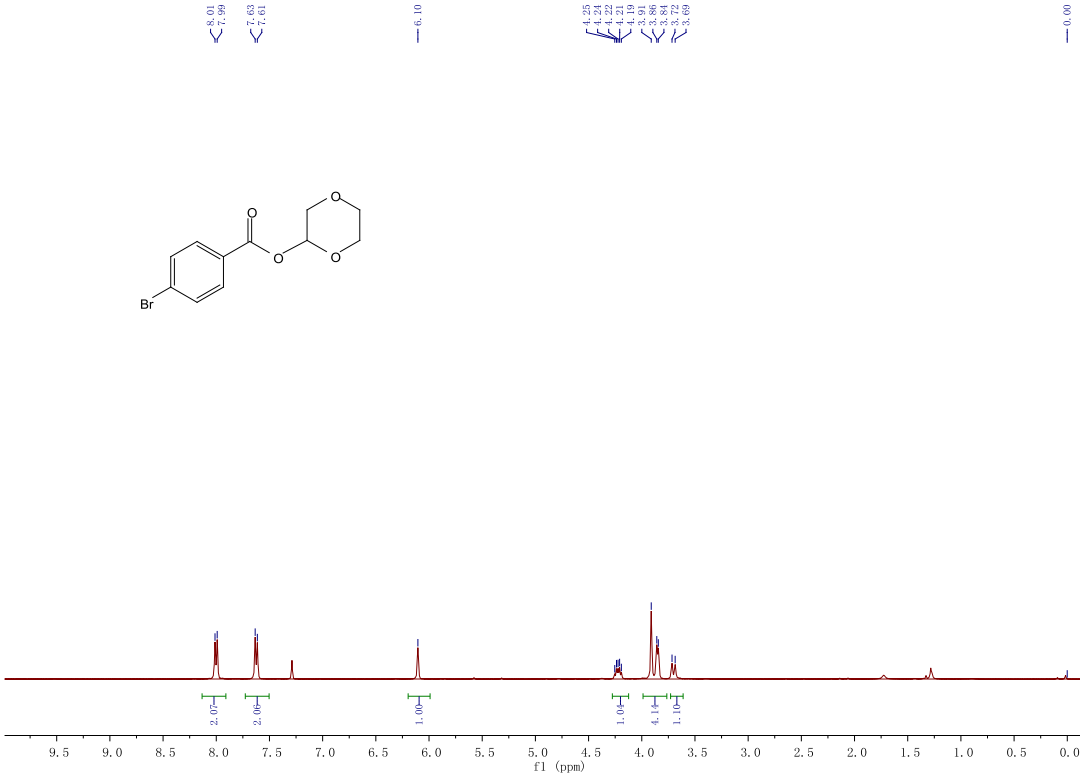


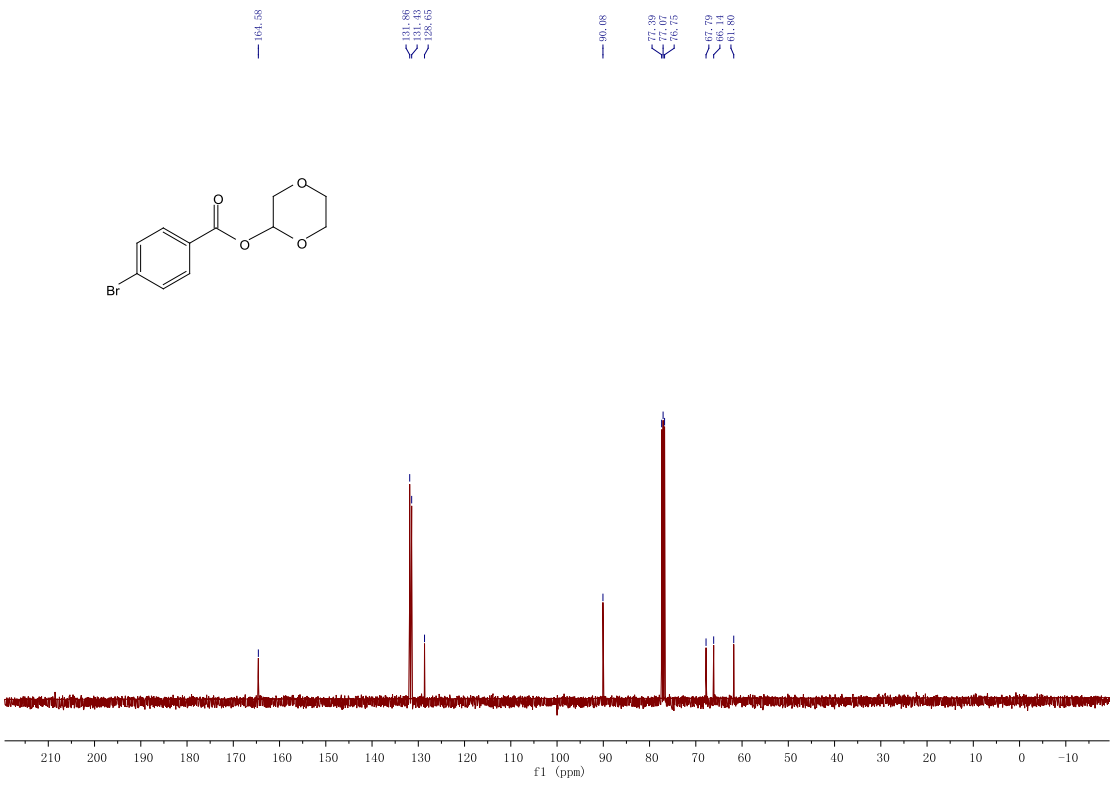
1,4-Dioxan-2-yl 4-chlorobenzoate（8a）



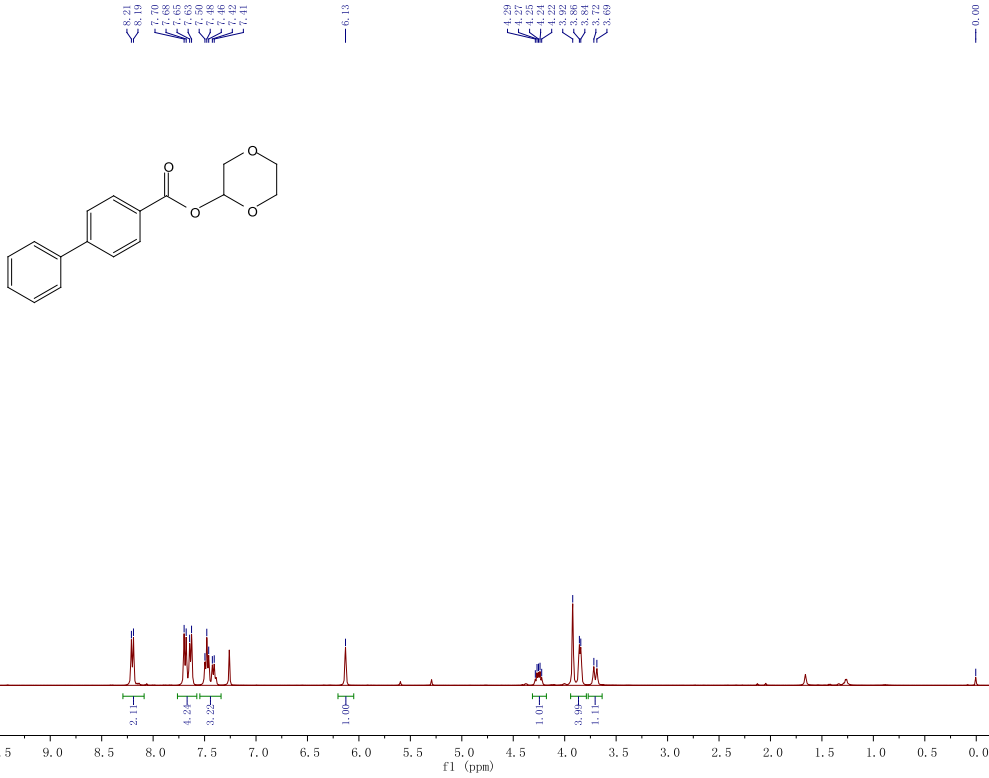


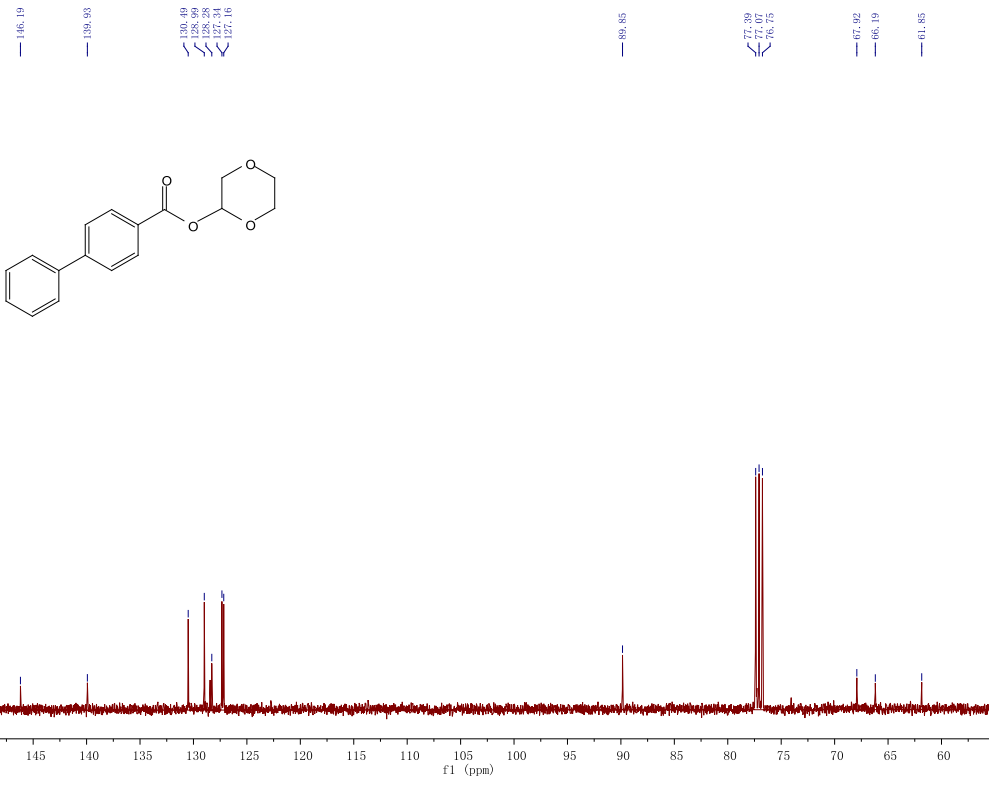
1,4-Dioxan-2-yl 4-bromobenzoate（9a）



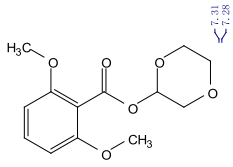


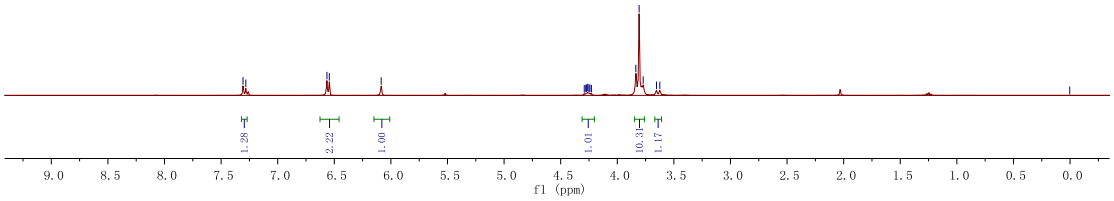
1,4-Dioxan-2-yl [1,1'-biphenyl]-4-carboxylate（10a）

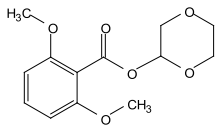


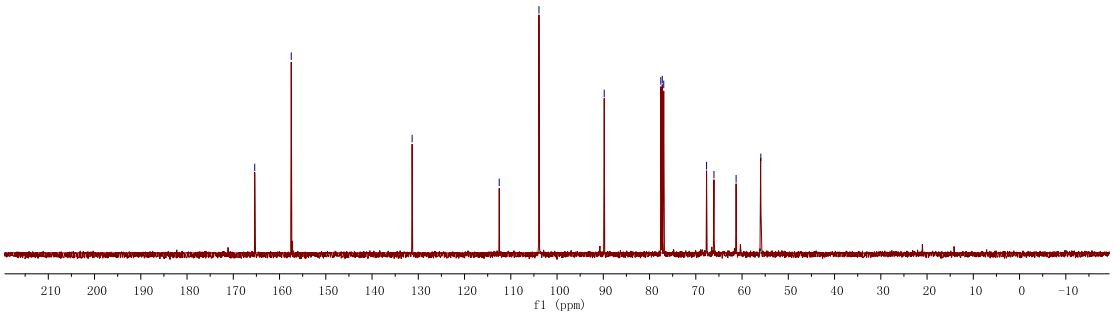


1,4-Dioxan-2-yl 2,6-dimethoxybenzoate（11a）

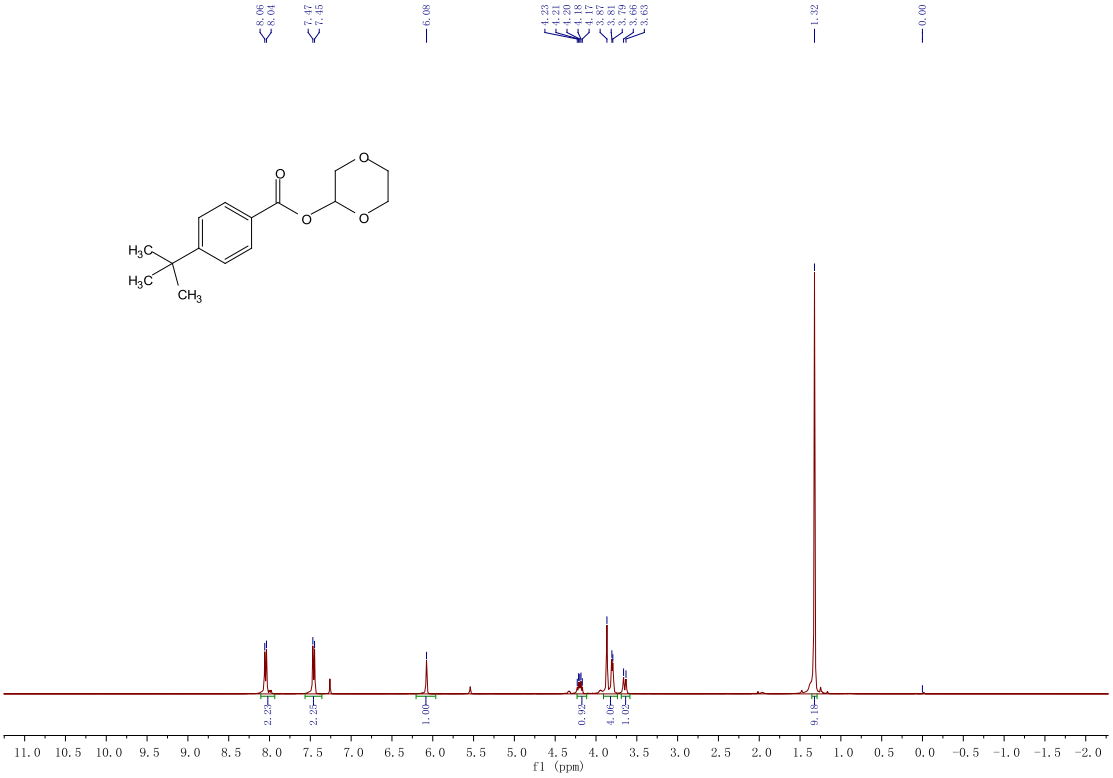


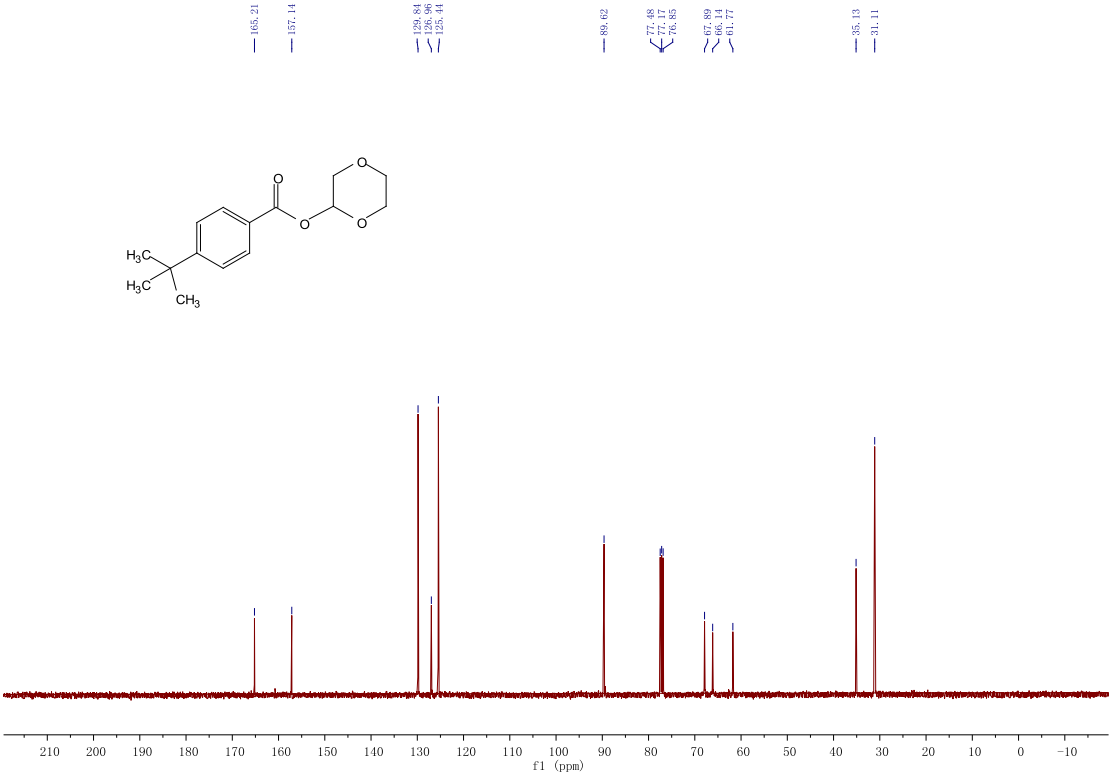




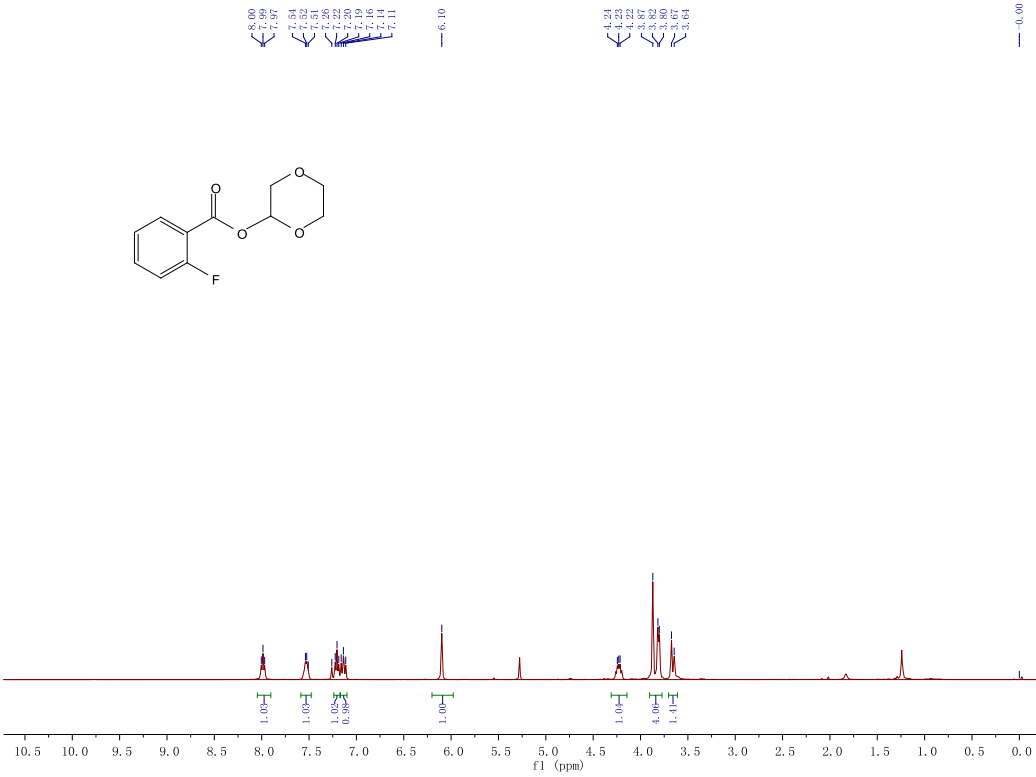


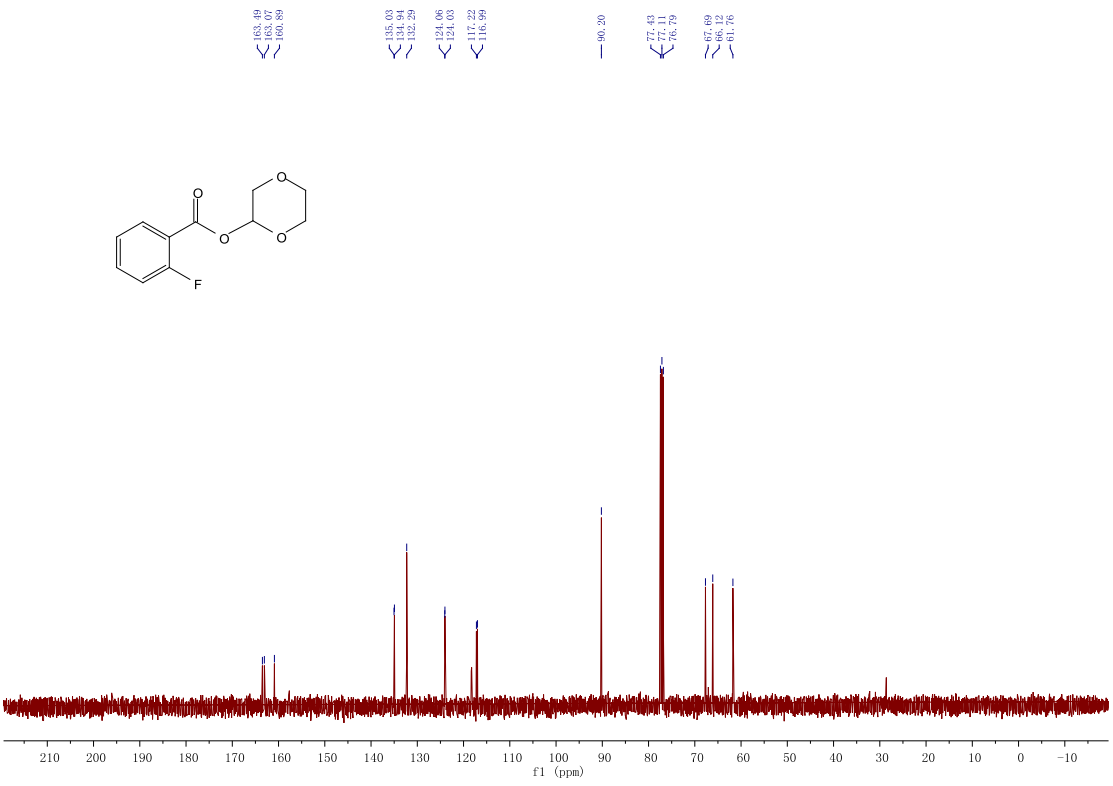
1,4-Dioxan-2-yl 4-(tert-butyl)benzoate（12a）



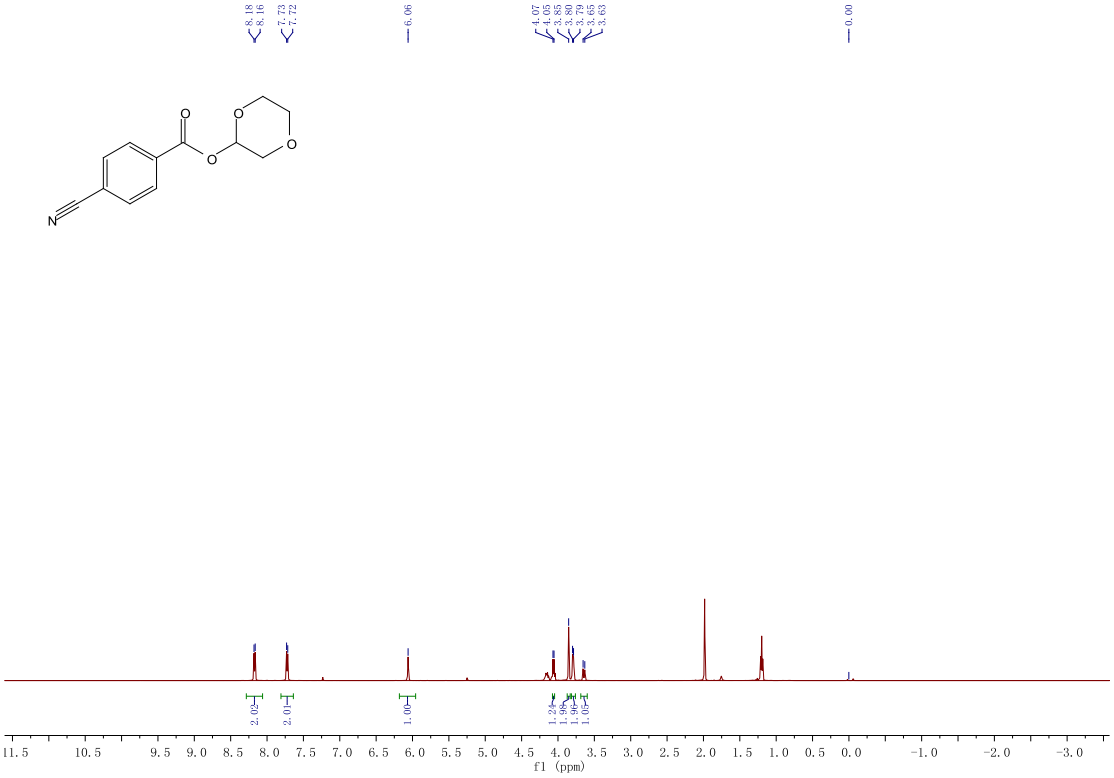


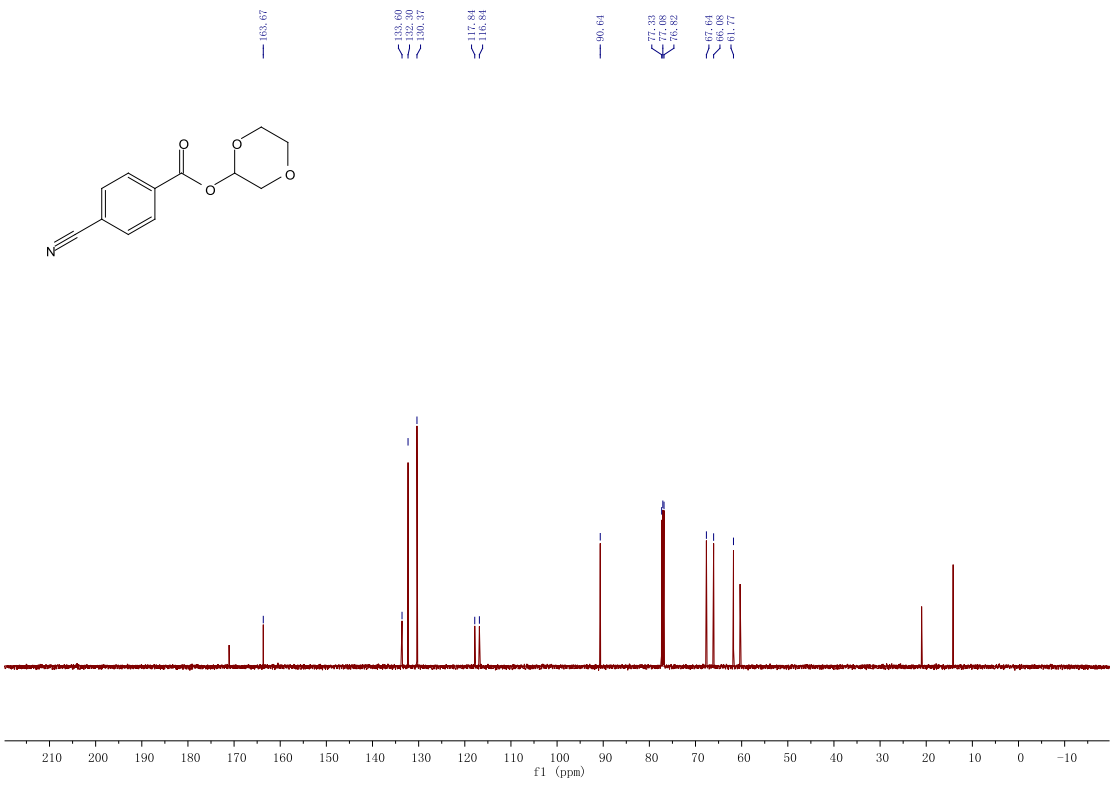
1,4-Dioxan-2-yl 2-fluorobenzoate（13a）



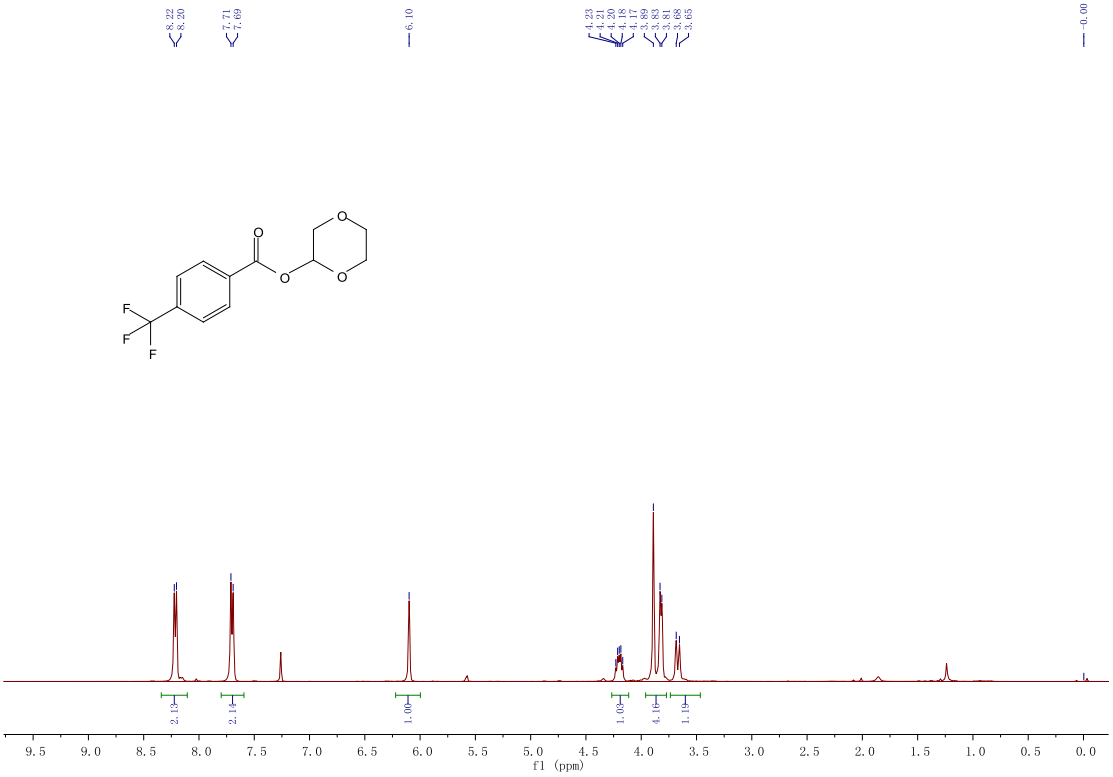


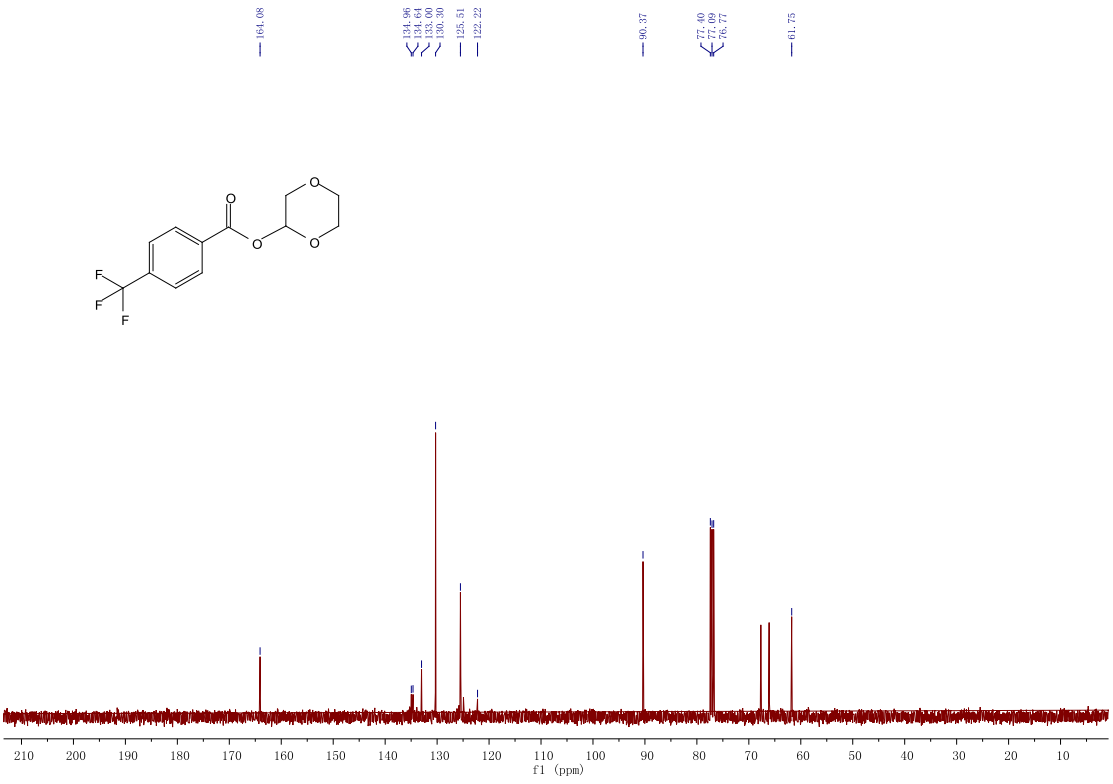
1,4-Dioxan-2-yl 4-cyanobenzoate（14a）



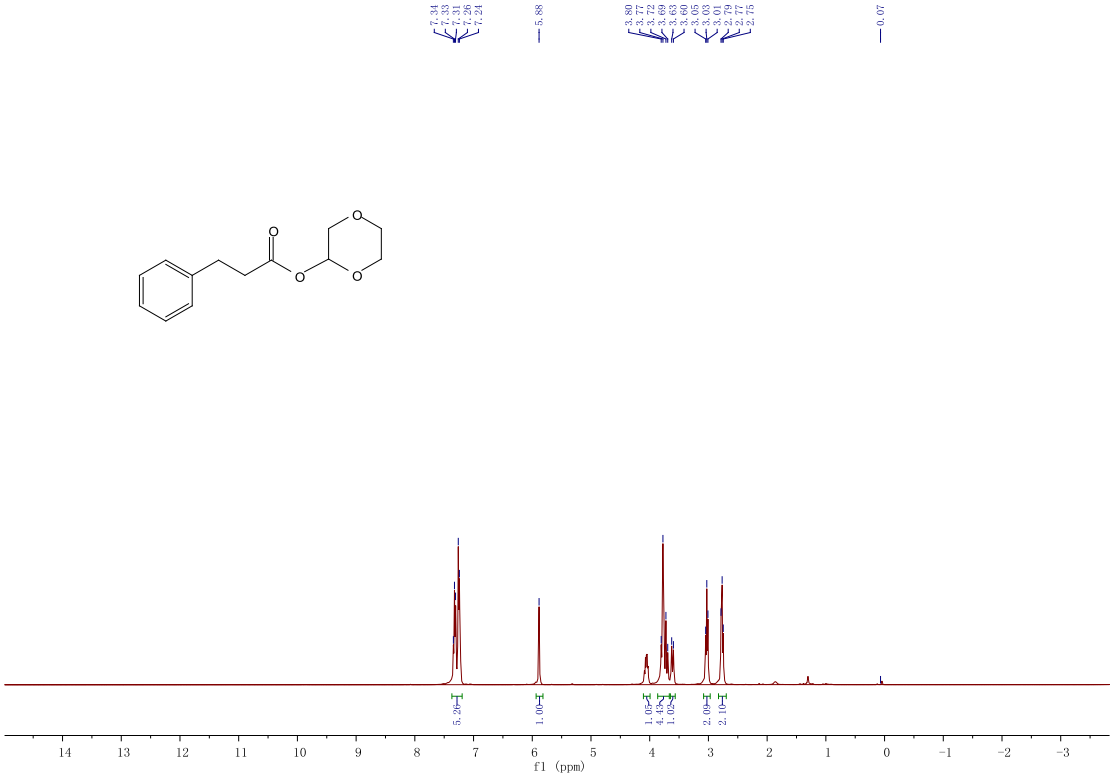


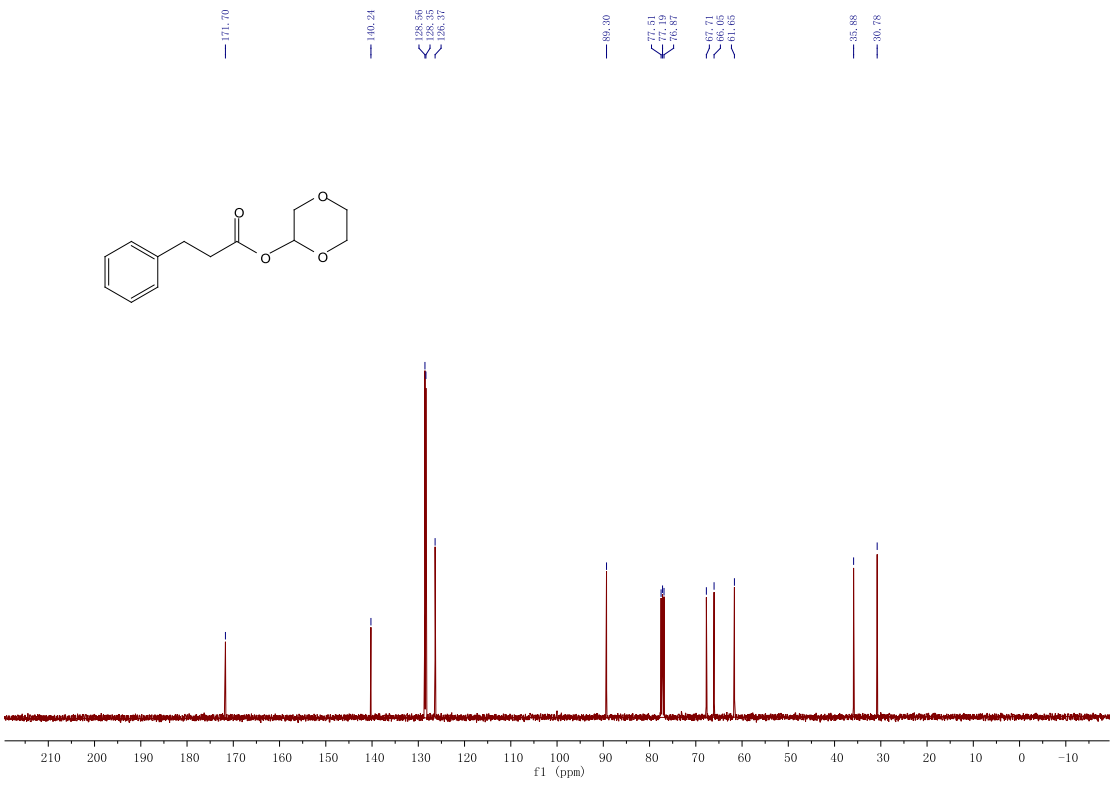
1,4-Dioxan-2-yl 4-(trifluoromethyl) benzoate（15a）



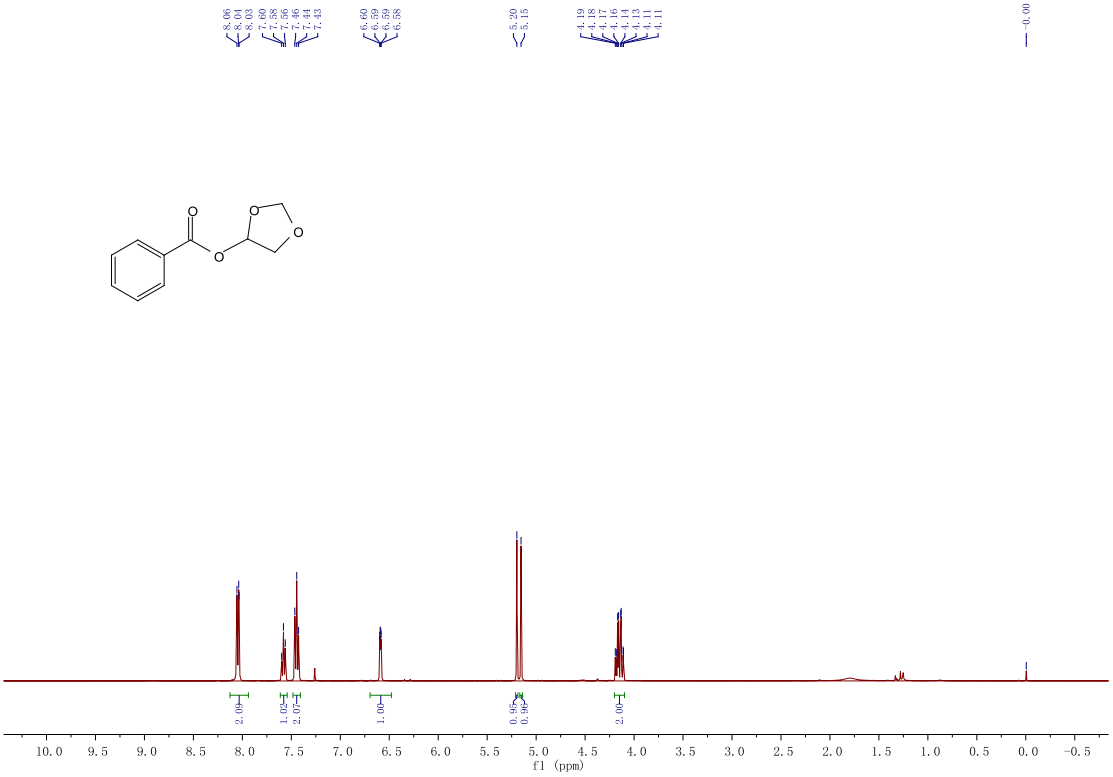


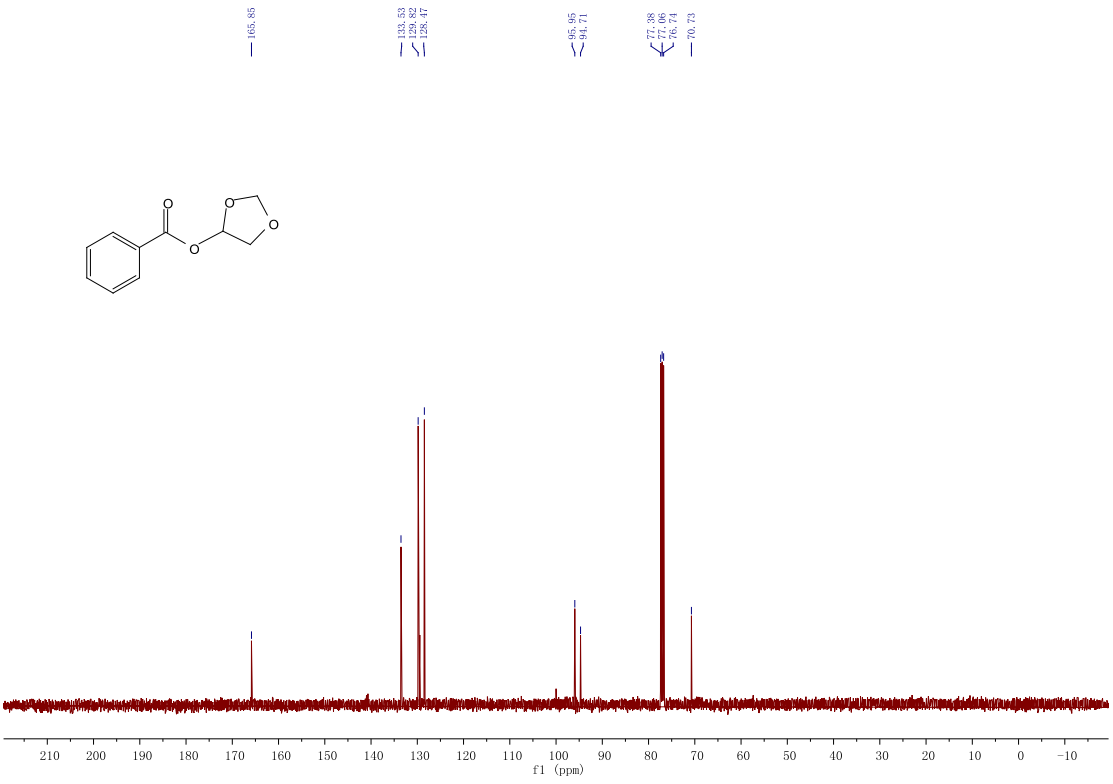
1,4-Dioxan-2-yl 3-phenylpropanoate（18a）



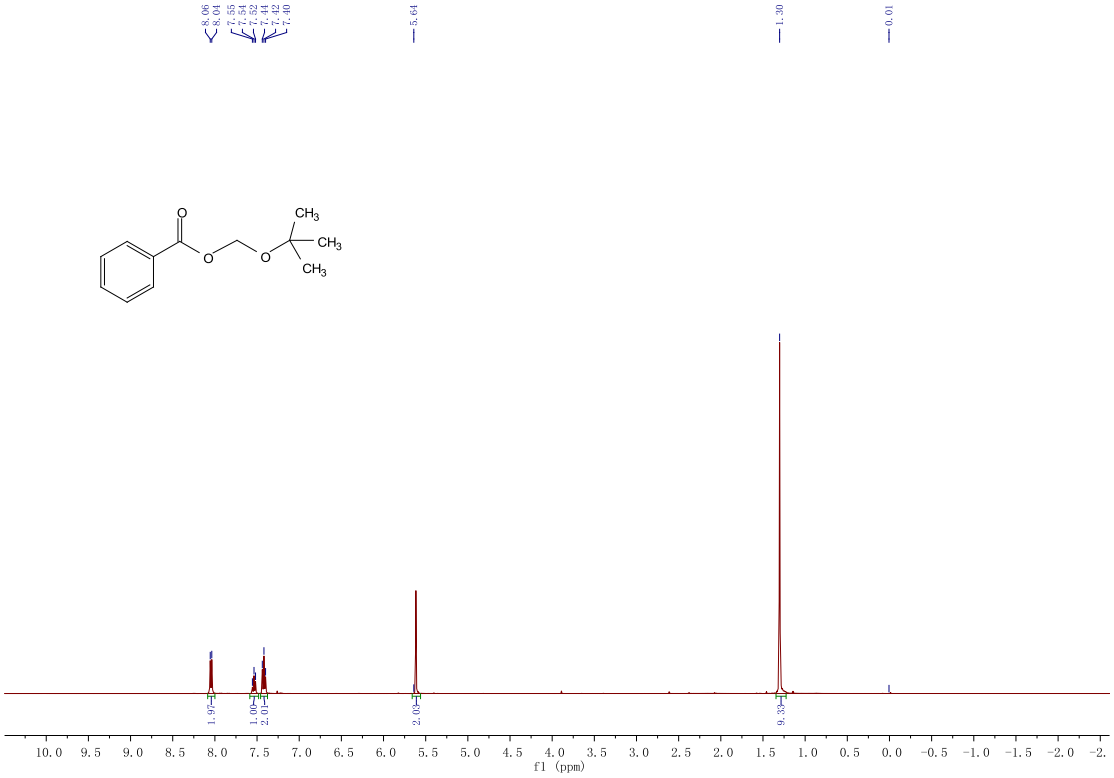


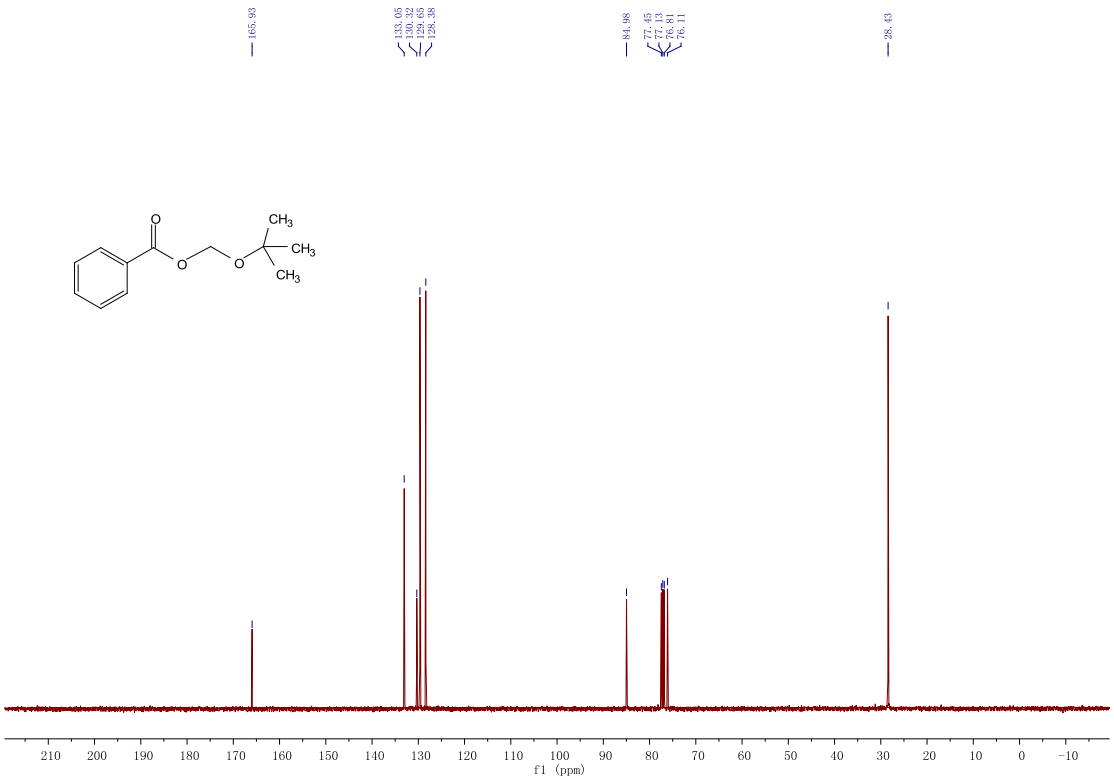
1,4-Dioxolan-4-yl -benzoate（1e）



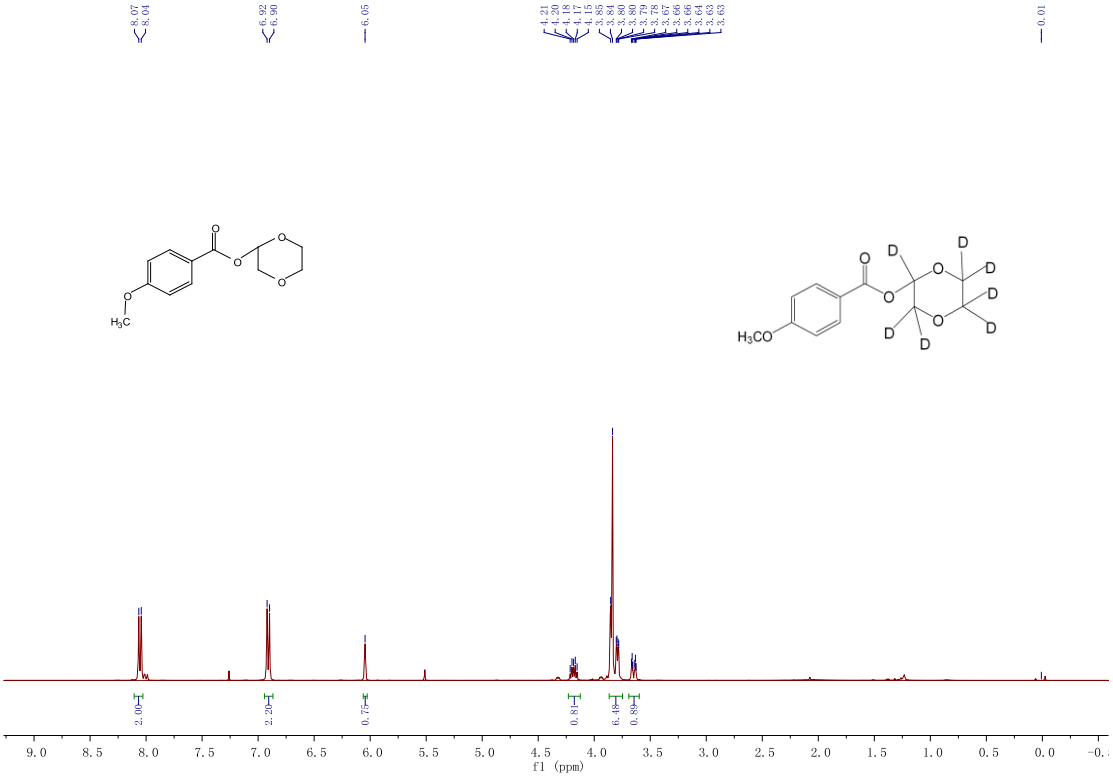


tert-butoxy methyl benzoate（1h）





^{1}H- NMR spectra for **9a** and **[D]9a**



Reference

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr.,42 (2009) 339–341.

[2] L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, Acta Crystallogr., Sect. A: Found. Adv.,71(2015) 59–75

[3] Gross, Z.; Galili, N.; Saltsman, I. Angew. Chem. Int. Ed. 38 (1999) 1427-1429.

[4] Wasbotten I H，Wondimagegn T，Ghosh A, J Am Chem Soc，124 (2002) 8104- 8116．