New Journal of Chemistry

Supporting Informations

Copper Porphyrin Catalyzed Esterification of C (sp^3)−H via Cross-Dehydrogenative Coupling Reaction

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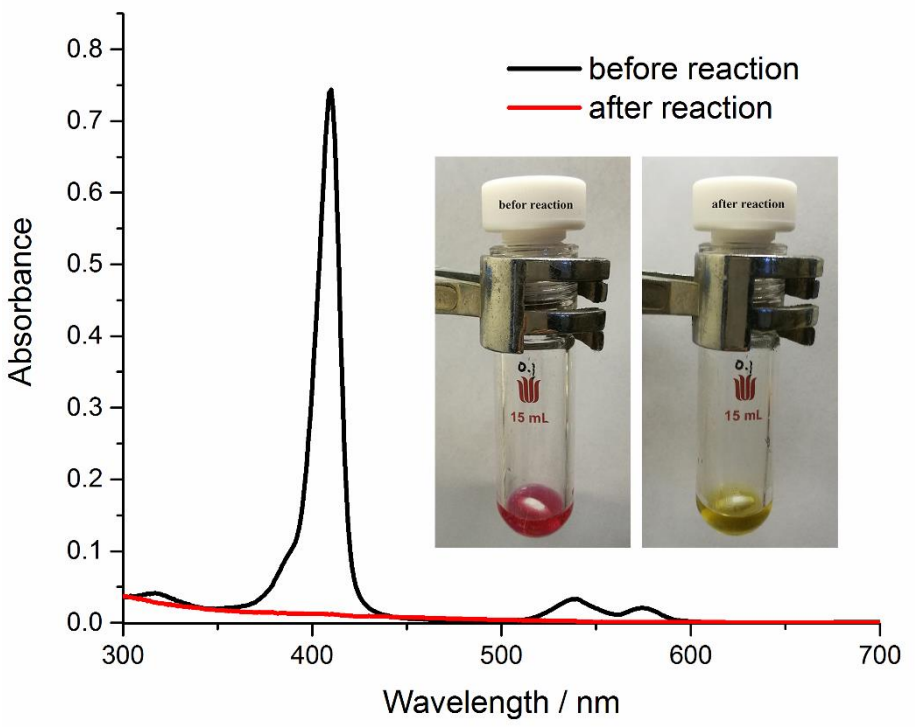


Figure S1. UV-vis spectra of CuTECP (0.1 mol % vs 0.5 mmol) react with DTBP (1.0 mmol) at 120 ºC for 5 min

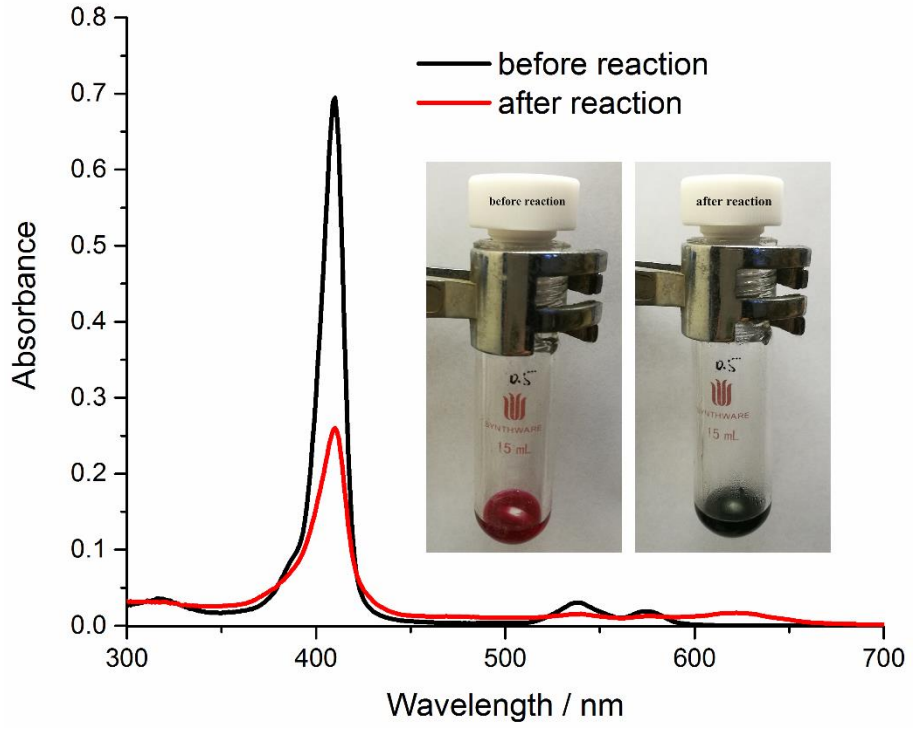


Figure S2. UV-vis spectra of CuTECP (0.5 mol % vs 0.5 mmol) react with DTBP (1.0

mmol) at 120 ºC for 5 min

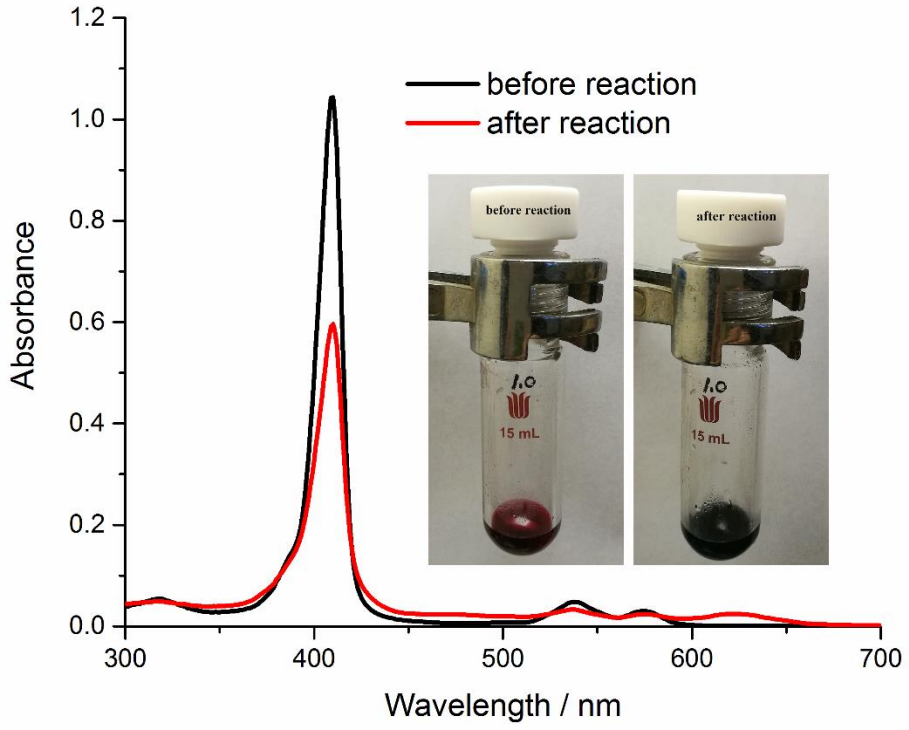


Figure S3. UV-vis spectra of CuTECP (1.0 mol % vs 0.5 mmol) react with DTBP (1.0 mmol) at 120 ºC for 5 min

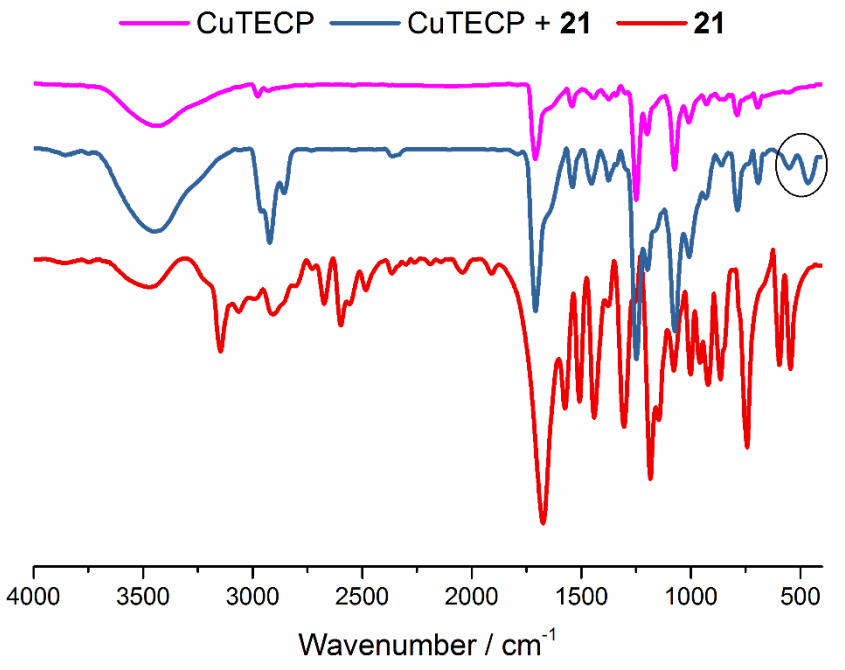
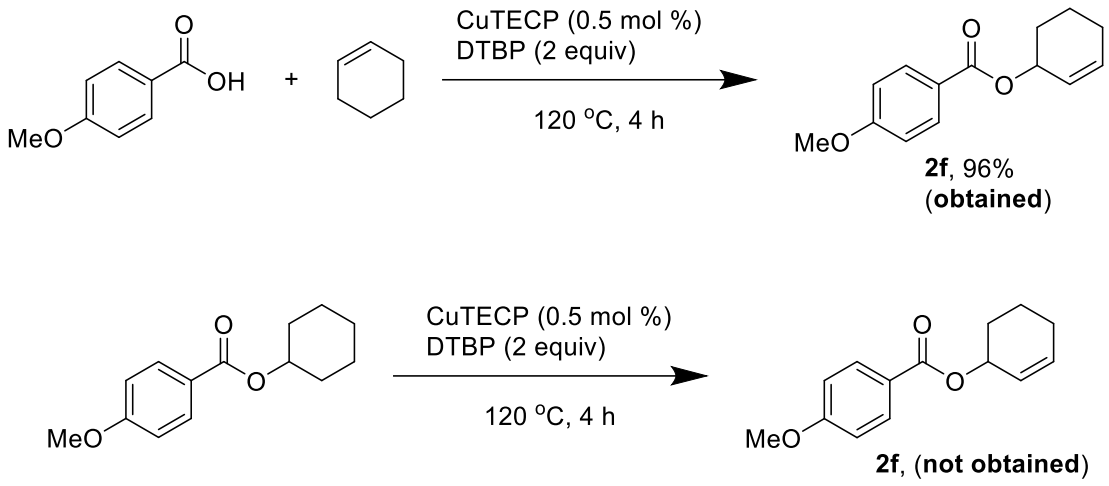
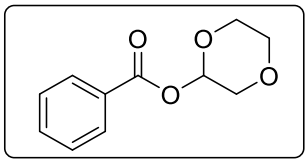


Figure S4. IR spectra of CuTECP, furan-3-carboxylic acid (**21**) and mixture of both


CuTECP (0.5 mol %)
DTBP (2 equiv)
120 °C, 4 h
MeO
OH
O
2f, 96%
(obtained)
CuTECP (0.5 mol %)
DTBP (2 equiv)
120 °C, 4 h
2f, (not obtained)

Scheme S1

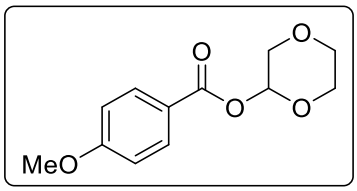
1,4-Dioxan-2-yl benzoate (1a)[1]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 6.7 Hz, 1H), 7.32 (t, *J* = 6.6 Hz, 2H), 5.99 (s, 1H), 4.17 – 3.99 (m, 1H), 3.84 – 3.70 (m, 2H), 3.66 (d, *J* = 4.1 Hz, 2H), 3.57 – 3.42 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.17, 133.38, 129.89, 129.78, 128.45, 89.85, 67.84, 66.11, 61.79.

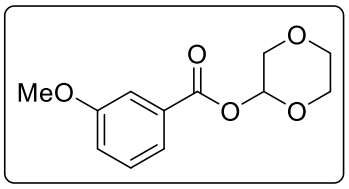
1,4-Dioxan-2-yl 4-methoxybenzoate (2a)[1]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.06 (s, 1H), 4.36 – 4.06 (m, 1H), 3.86 (d, *J* = 5.3 Hz, 5H), 3.81 (dd, *J* = 6.4, 2.3 Hz, 2H), 3.66 (dt, *J* = 11.7, 2.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.91, 163.77, 132.01, 122.07, 113.72, 89.53, 67.95, 66.14, 61.85, 55.45.

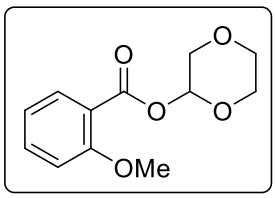
1,4-Dioxan-2-yl 3-methoxybenzoate (3a)[1]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.62 (s, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.12 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.08 (s, 1H), 4.27 – 4.12 (m, 1H), 3.88 (d, *J* = 1.4 Hz, 2H), 3.84 (s, 3H), 3.81 (dd, *J* = 6.5, 2.3 Hz, 2H), 3.67 (dd, *J* = 11.7, 2.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.12, 159.64, 131.05, 129.48, 122.31, 119.80, 114.45, 89.95, 67.82, 66.11, 61.84, 55.47.

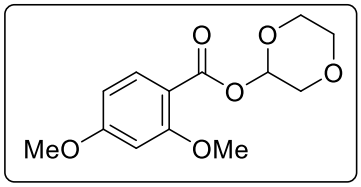
1,4-Dioxan-2-yl 2-methoxybenzoate (4a)[1]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 6.99 (dd, *J* = 7.9, 6.0 Hz, 2H), 6.08 (s, 1H), 4.23 (td, *J* = 12.5, 6.5 Hz, 1H), 3.91 (s, 3H), 3.87 (s, 2H), 3.84 – 3.75 (m, 2H), 3.67 (dd, *J* = 11.7, 2.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.59, 159.68, 134.03, 131.95, 120.13, 119.44, 112.16, 89.66, 67.87, 66.16, 61.81, 56.03.

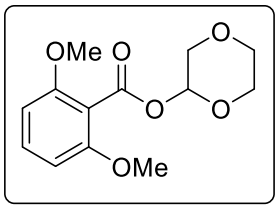
1,4-dioxan-2-yl 2,4-dimethoxybenzoate (5a)[1]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 1H), 6.57 – 6.41 (m, 2H), 6.04 (s, 1H), 4.31 – 4.12 (m, 1H), 3.87 (s, 3H), 3.83 (s, 5H), 3.81 – 3.75 (m, 2H), 3.64 (dt, *J* = 11.6, 2.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.72, 163.80, 161.99, 134.16, 111.60, 104.68, 98.97, 89.30, 67.97, 66.16, 61.87, 56.00, 55.50.

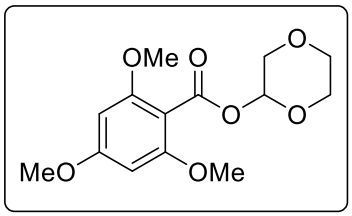
1,4-Dioxan-2-yl 2,6-dimethoxybenzoate (6a)[2]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 11.5, 5.3 Hz, 1H), 6.53 (d, *J* = 8.4 Hz, 2H), 6.07 (s, 1H), 4.24 (ddd, *J* = 12.0, 8.8, 4.8 Hz, 1H), 3.86 – 3.74 (m, 10H), 3.63 (dd, *J* = 11.7, 2.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.34, 157.55, 131.29, 112.63, 103.96, 89.84, 67.74, 66.11, 61.36, 56.00.

1,4-dioxan-2-yl 2,4,6-trimethoxybenzoate (7a):



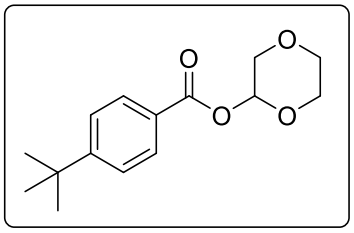
New compound.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (s, 2H), 6.07 (s, 1H), 4.32 – 4.22 (m, 1H), 3.85 – 3.79 (m, 13H), 3.65 (d, *J* = 11.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.14, 162.80, 158.93, 105.41, 90.63, 89.60, 67.74, 66.08, 61.37, 55.93, 55.41.

HRMS (ESI^+): m/z calcd for [$C_{14}H_{18}O_7$ + Na] 321.0945, found 321.0942.

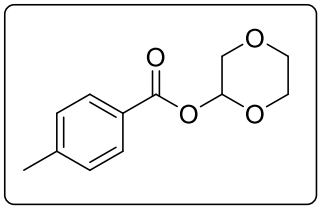
1,4-dioxan-2-yl 4-(*tert*-butyl)benzoate (8a)[1]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 6.07 (s, 1H), 4.26 – 4.14 (m, 1H), 3.86 (s, 2H), 3.79 (d, *J* = 5.7 Hz, 2H), 3.64 (d, *J* = 11.7 Hz, 1H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.16, 157.10, 129.82, 126.98, 125.42, 89.63, 67.88, 66.11, 61.76, 35.10, 31.09.

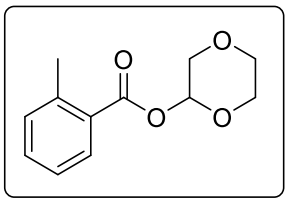
1,4-dioxan-2-yl 4-methylbenzoate (9a)[2]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.06 (s, 1H), 4.26 – 4.11 (m, 1H), 3.85 (d, *J* = 1.8 Hz, 2H), 3.81 – 3.73 (m, 2H), 3.64 (dt, *J* = 11.6, 2.2 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.23, 144.15, 129.94, 129.15, 127.00, 89.67, 67.86, 66.10, 61.79, 21.64.

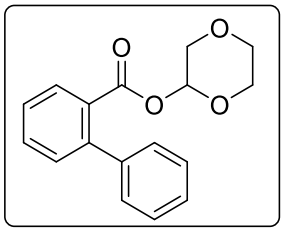
1,4-dioxan-2-yl 2-methylbenzoate (10a)[2]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 1H), 7.47 – 7.39 (m, 1H), 7.28 (t, *J* = 7.0 Hz, 2H), 6.10 (t, *J* = 1.8 Hz, 1H), 4.31 – 4.16 (m, 1H), 3.90 (d, *J* = 1.8 Hz, 2H), 3.83 (dd, *J* = 6.7, 2.6 Hz, 2H), 3.70 (dt, *J* = 11.8, 2.6 Hz, 1H), 2.67 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.97, 140.86, 132.49, 131.84, 131.04, 128.87, 125.80, 89.69, 67.93, 66.13, 61.89, 21.93.

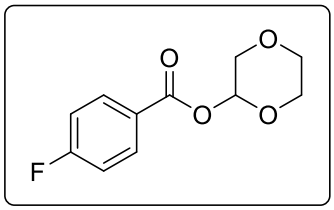
1,4-dioxan-2-yl [1,1'-biphenyl]-2-carboxylate (11a)[3]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.41 (dt, *J* = 23.1, 7.5 Hz, 7H), 5.84 (s, 1H), 3.70 – 3.54 (m, 4H), 3.41 (dt, *J* = 21.4, 11.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.52, 142.73, 141.42, 131.57, 130.89, 130.47, 130.15, 128.54, 128.20, 127.25, 90.14, 67.39, 65.85, 61.57.

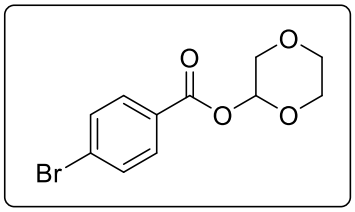
1,4-dioxan-2-yl 4-fluorobenzoate (12a)[3]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 7.2, 5.9 Hz, 2H), 7.10 (t, *J* = 8.4 Hz, 2H), 6.05 (s, 1H), 4.26 – 4.11 (m, 1H), 3.86 (s, 2H), 3.80 (d, *J* = 6.5 Hz, 2H), 3.65 (d, *J* = 11.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.29, 164.76, 164.23, 132.49, 125.98, 115.74, 115.52, 89.94, 67.78, 66.09, 61.77.

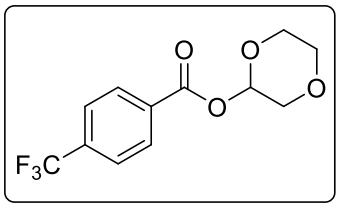
1,4-Dioxan-2-yl 4-bromobenzoate (13a)[3]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 6.04 (s, 1H), 4.15 (dd, *J* = 11.9, 6.1 Hz, 1H), 3.84 (s, 2H), 3.79 (s, 2H), 3.63 (d, *J* = 9.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.44, 131.81, 131.38, 128.67, 128.55, 90.09, 67.74, 66.08, 61.77.

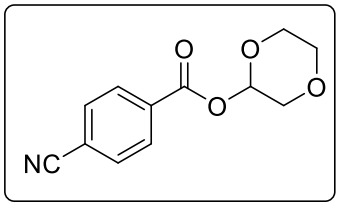
1,4-dioxan-2-yl 4-(trifluoromethyl)benzoate (14a)[4]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 6.10 (d, *J* = 1.9 Hz, 1H), 4.19 (dq, *J* = 12.7, 6.3 Hz, 1H), 3.89 (d, *J* = 1.8 Hz, 2H), 3.82 (dd, *J* = 7.0, 2.4 Hz, 2H), 3.67 (dt, *J* = 11.8, 2.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.03, 134.95, 134.62, 133.01, 130.27, 125.52, 125.48, 125.45, 125.41, 124.91, 122.20, 90.38, 67.68, 66.07, 61.75.

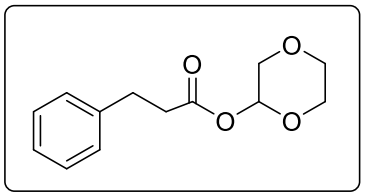
1,4-dioxan-2-yl 4-cyanobenzoate (15a):



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 6.10 (s, 1H), 4.19 (dt, *J* = 11.6, 6.7 Hz, 1H), 3.89 (d, *J* = 1.8 Hz, 2H), 3.83 (dd, *J* = 6.9, 2.3 Hz, 2H), 3.73 – 3.63 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.69, 133.58, 132.31, 130.37, 117.88, 116.82, 90.62, 67.64, 66.09, 61.77.

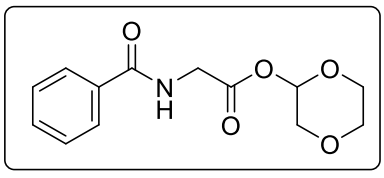
1,4-dioxan-2-yl 3-phenylpropanoate (17a)[3]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.13 (m, 5H), 5.83 (s, 1H), 4.12 – 3.88 (m, 1H), 3.83 – 3.62 (m, 4H), 3.56 (m, 1H), 2.98 (t, *J* = 7.7 Hz, 2H), 2.71 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.65, 140.24, 128.54, 128.33, 126.35, 89.31, 67.70, 66.02, 61.65, 35.86, 30.77.

1,4-dioxan-2-yl benzoylglycinate (18a):



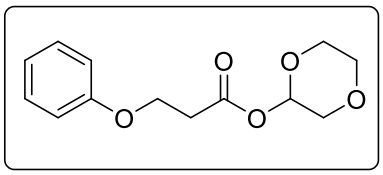
New compound.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 2H), 7.54 – 7.48 (m, 1H), 7.45 – 7.40 (m, 2H), 6.80 (s, 1H), 5.94 (s, 1H), 4.42 – 4.22 (m, 2H), 4.13 (m, 1H), 3.84 – 3.71 (m, 4H), 3.63 (dt, *J* = 11.7, 2.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.21, 167.60, 133.65, 131.84, 128.62, 127.09, 90.39, 67.48, 65.99, 61.63, 41.86 .

HRMS (ESI^+): m/z calcd for [$C_{13}H_{15}NO_5$ + Na] 288.0842, found 288.0842.

1,4-dioxan-2-yl 3-phenoxypropanoate (19a):



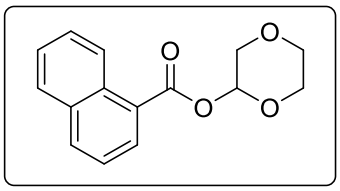
New compound.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.00 – 6.87 (m, 3H), 5.91 (t, *J* = 1.8 Hz, 1H), 4.34 – 4.23 (m, 2H), 4.17 – 4.06 (m, 1H), 3.80 – 3.71 (m, 4H), 3.61 (dt, *J* = 11.7, 2.6 Hz, 1H), 2.89 (t, *J* = 6.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.92, 158.47, 129.48, 121.13, 114.71, 89.57, 67.67, 66.05, 63.18, 61.65, 34.74.

HRMS (ESI^+): m/z calcd for [$C_{13}H_{16}O_5$ + Na] 275.0890, found 275.0886.

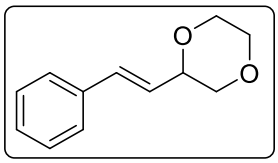
1,4-Dioxan-2-yl 1-naphthoate (20a)[1]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, *J* = 8.5 Hz, 1H), 8.36 (d, *J* = 7.0 Hz, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.54 (dd, *J* = 16.4, 8.1 Hz, 2H), 6.22 (s, 1H), 4.35 – 4.16 (m, 1H), 3.96 (s, 2H), 3.86 (d, *J* = 5.3 Hz, 2H), 3.73 (d, *J* = 11.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.95, 134.07, 133.89, 131.59, 130.97, 128.63, 128.06, 126.33, 126.20, 125.79, 124.49, 89.90, 67.99, 66.21, 61.94.

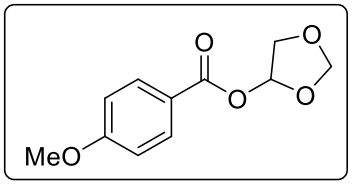
(E)-2-styryl-1,4-dioxane (22a)[5]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 5H), 6.68 (d, *J* = 16.1 Hz, 1H), 6.08 (dd, *J* = 16.1, 6.1 Hz, 1H), 4.25 (d, *J* = 6.7 Hz, 1H), 3.95 – 3.55 (m, 5H), 3.41 (t, *J* = 10.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.42, 132.67, 128.59, 127.93, 126.52, 125.15, 76.09, 70.97, 66.62, 66.32.

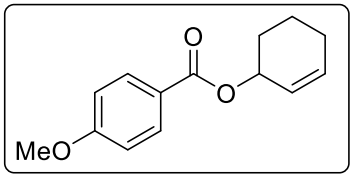
1,3-dioxolan-4-yl 4-methoxybenzoate (2b)[1]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.55 (s, 1H), 5.14 (d, *J* = 16.6 Hz, 2H), 4.12 (dt, *J* = 20.4, 6.6 Hz, 2H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.49, 163.82, 131.90, 121.76, 113.72, 95.82, 94.44, 70.69, 55.45.

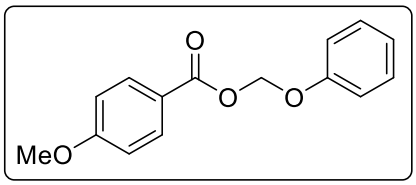
cyclohex-2-en-1-yl 4-methoxybenzoate (2f)[2]:



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.95 (d, *J* = 9.9 Hz, 1H), 5.80 (d, *J* = 9.6 Hz, 1H), 5.45 (s, 1H), 3.79 (s, 3H), 2.16 – 1.90 (m, 3H), 1.86 – 1.74 (m, 2H), 1.70 – 1.50 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.90, 163.24, 132.56, 131.55, 125.98, 123.19, 113.48, 68.21, 55.33, 28.47, 24.95, 19.00.

phenoxymethyl 4-methoxybenzoate (2g):



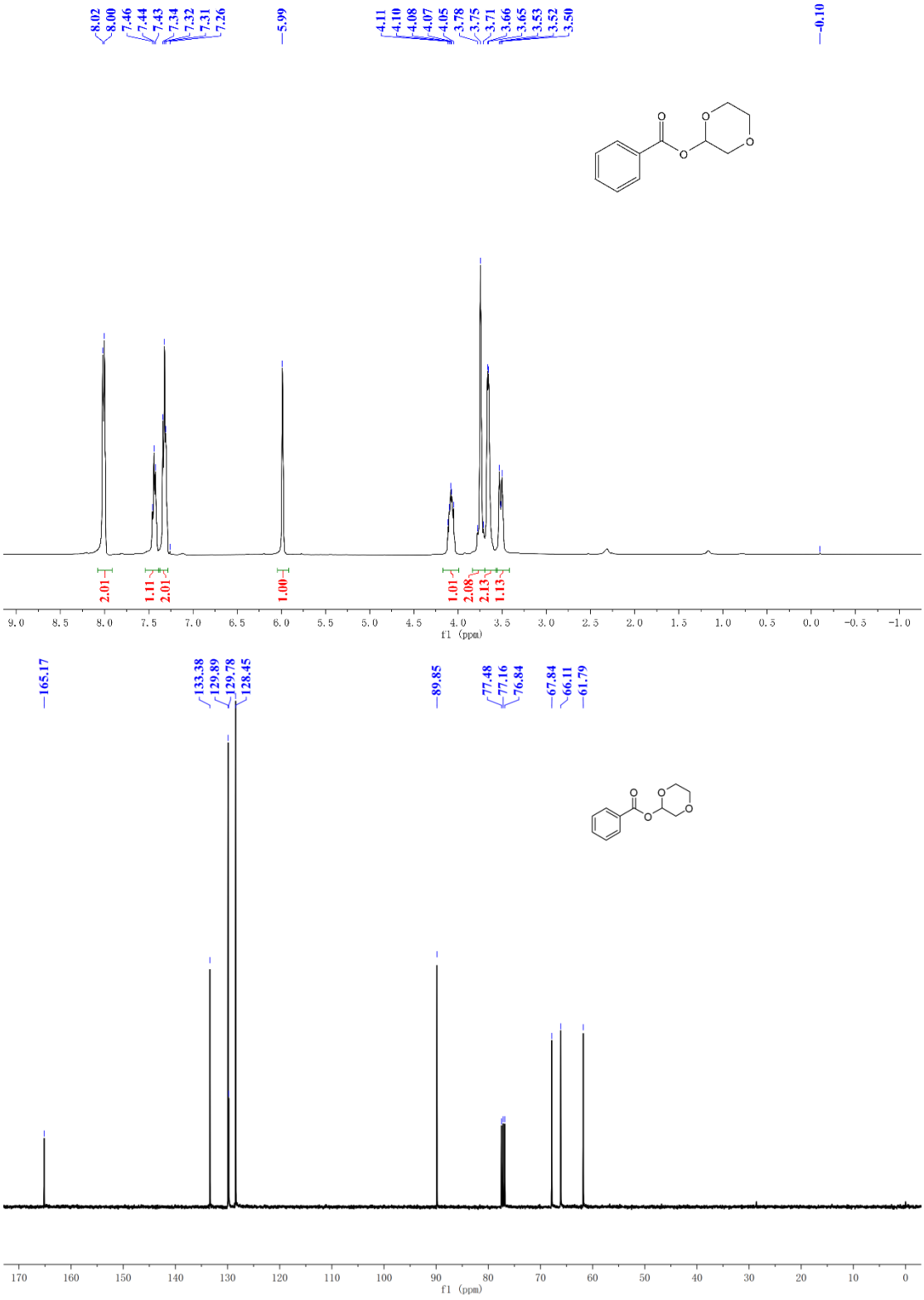
New compound.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.8 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.00 (s, 2H), 3.85 (s, 3H).

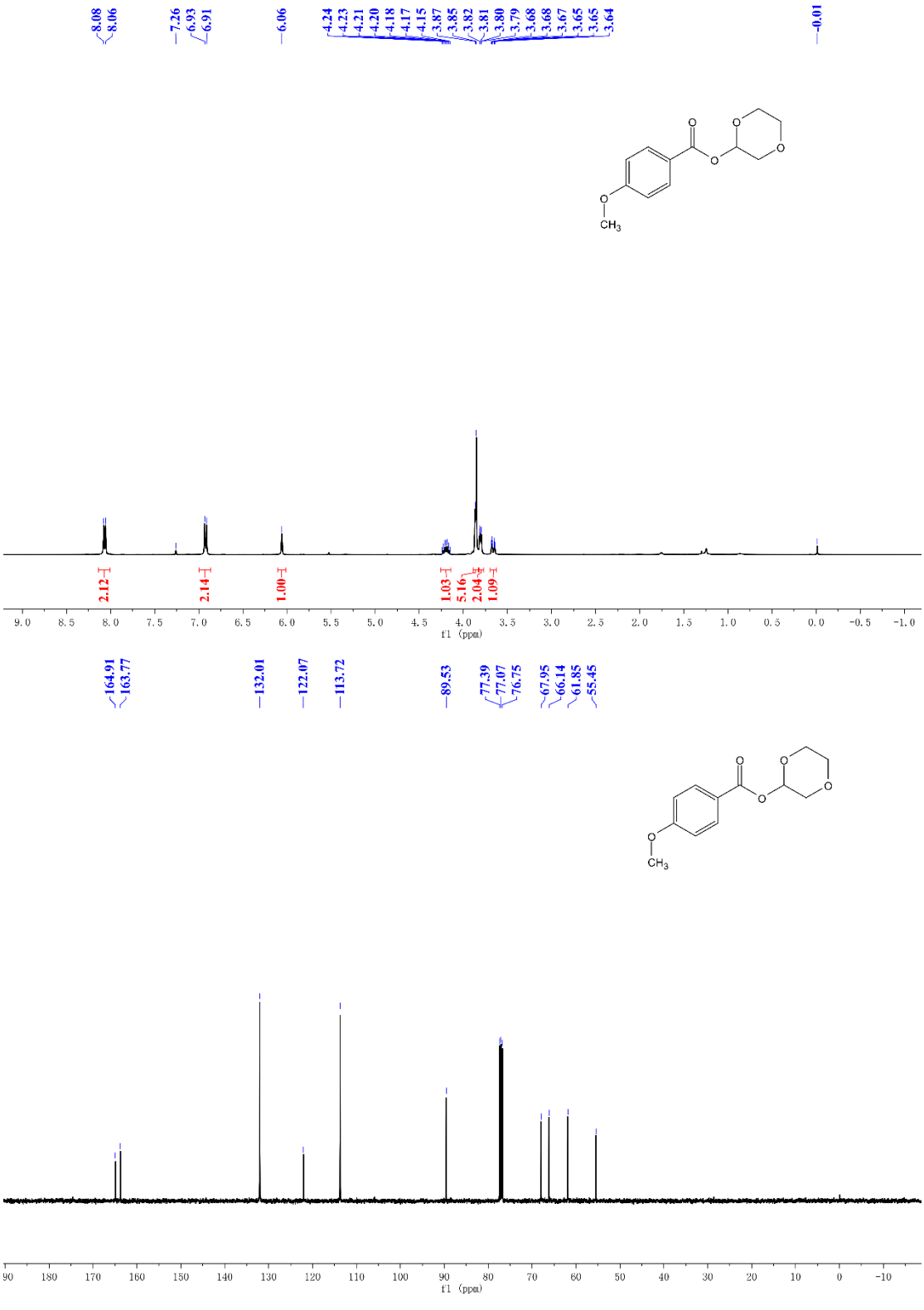
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.17, 163.85, 157.07, 132.02, 129.64, 122.73, 121.77, 116.21, 113.78, 86.15, 55.48.

HRMS (ESI^+): m/z calcd for [$C_{15}H_{14}O_4$ + Na] 281.0784, found 281.0790.

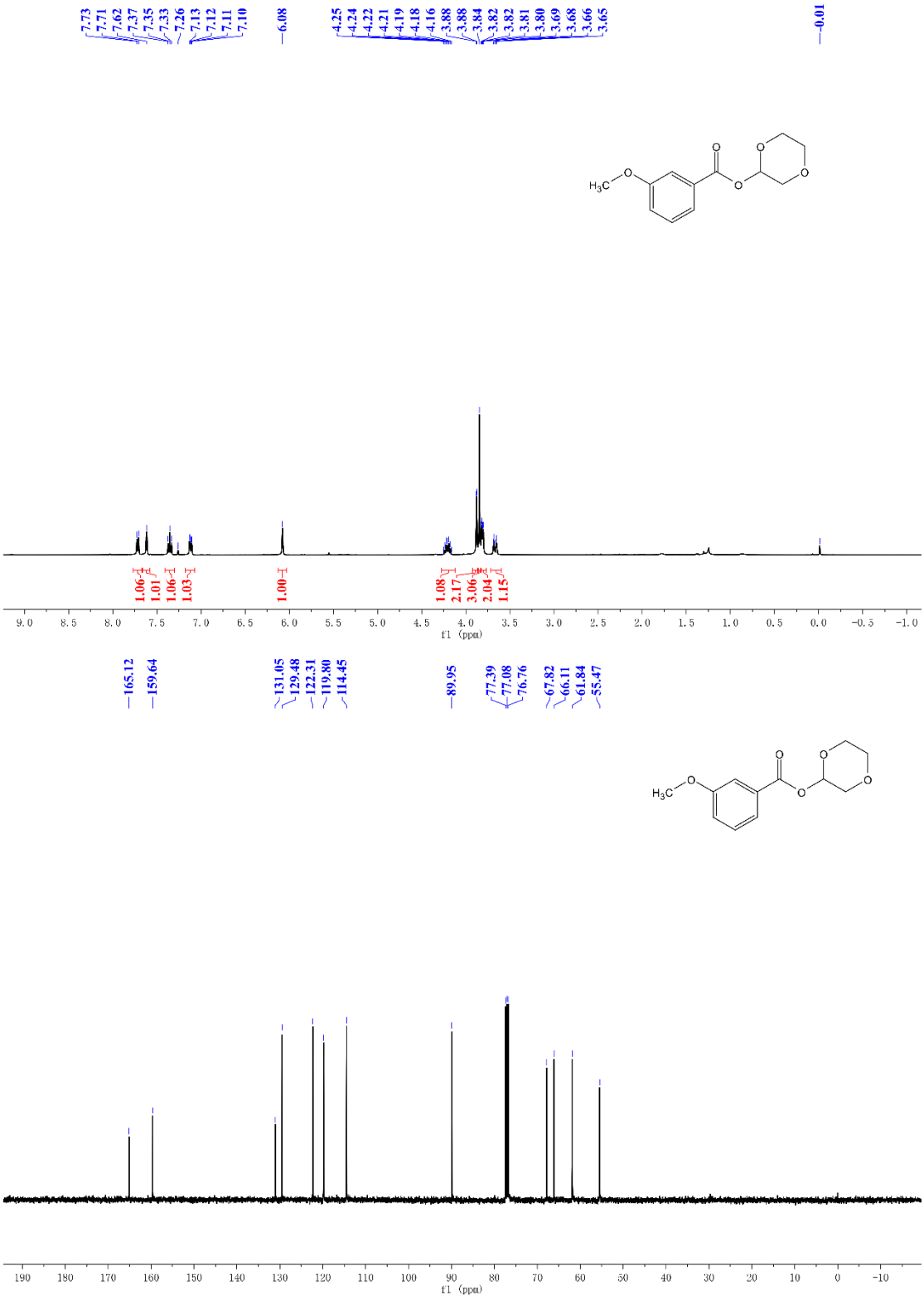
1,4-Dioxan-2-yl benzoate (1a)



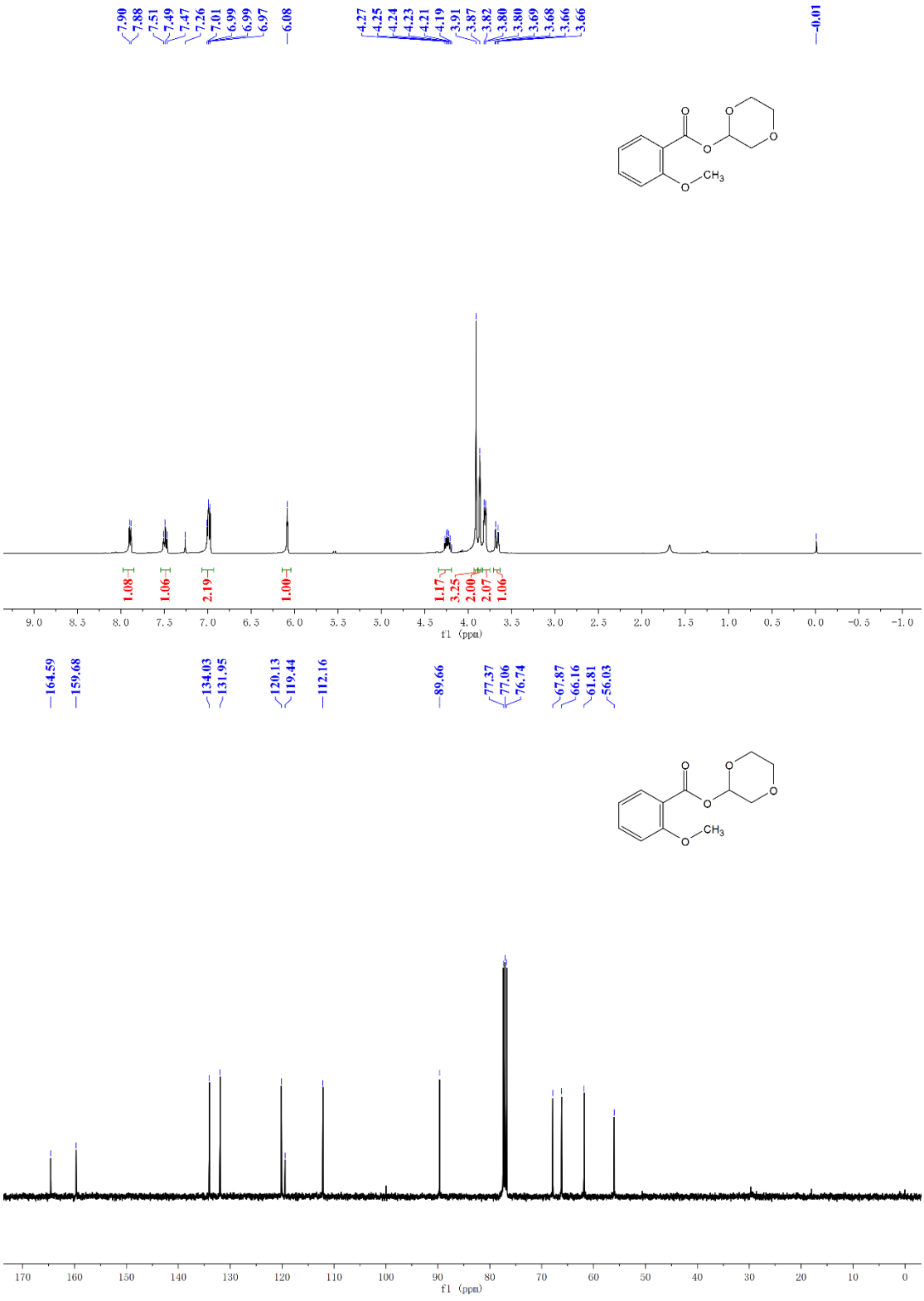
1,4-Dioxan-2-yl 4-methoxybenzoate (2a)



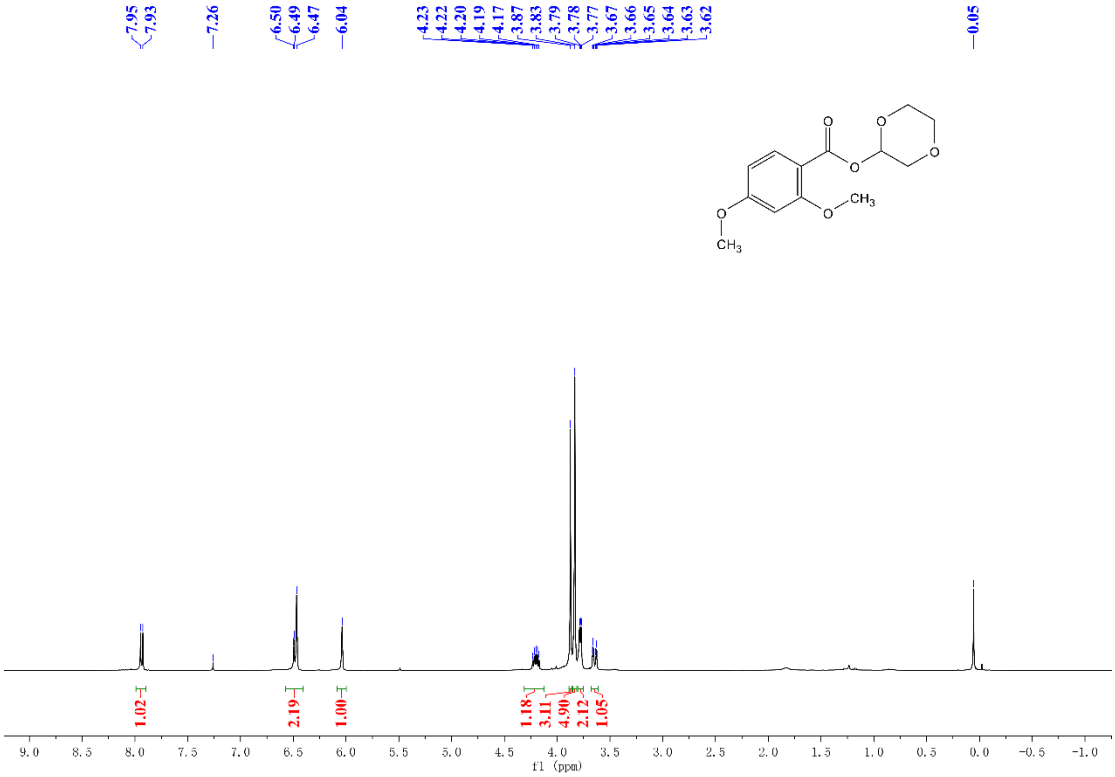
1,4-Dioxan-2-yl 3-methoxybenzoate (3a)

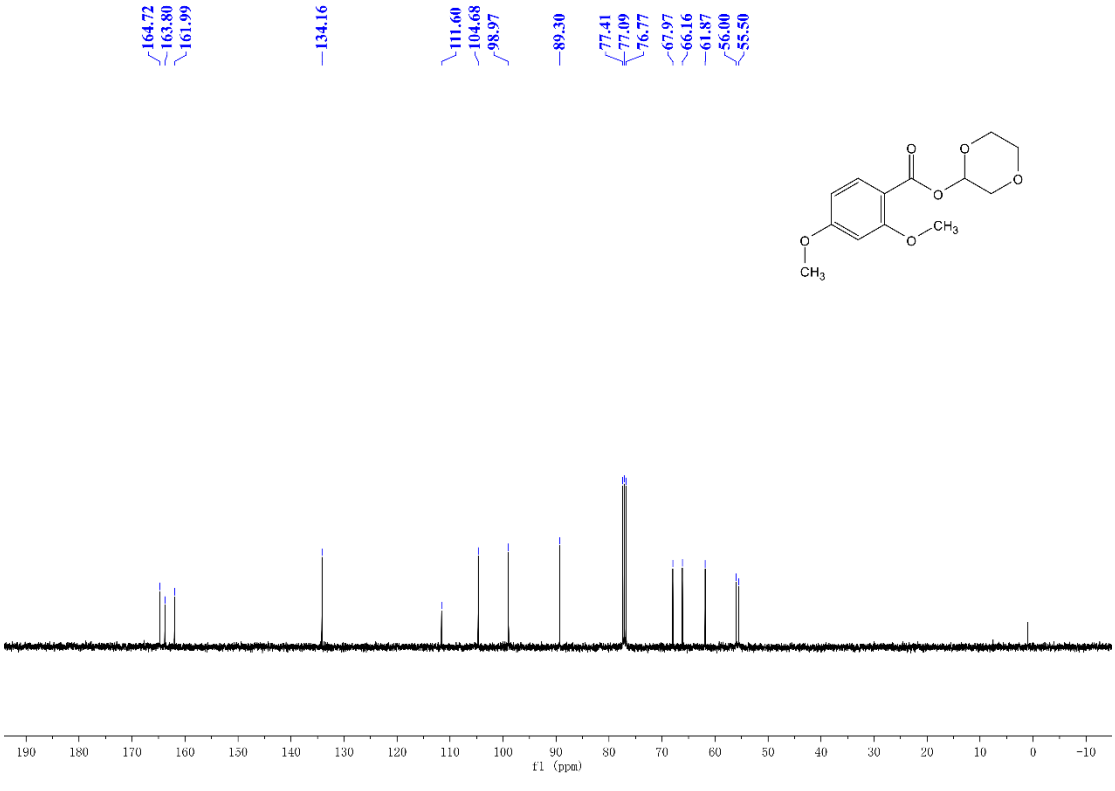


1,4-Dioxan-2-yl 2-methoxybenzoate (4a)

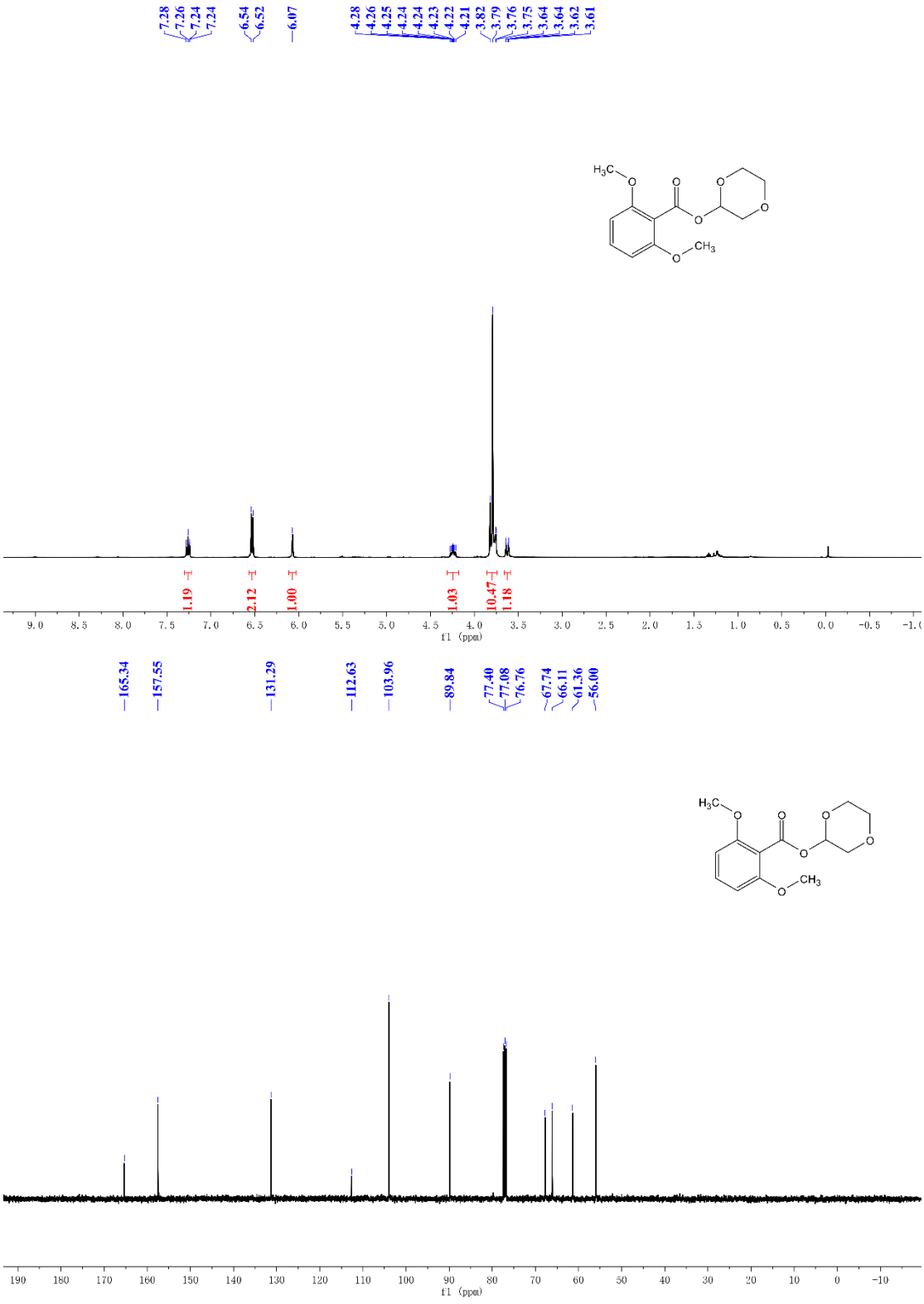


1,4-Dioxan-2-yl 2,4-dimethoxybenzoate (5a)

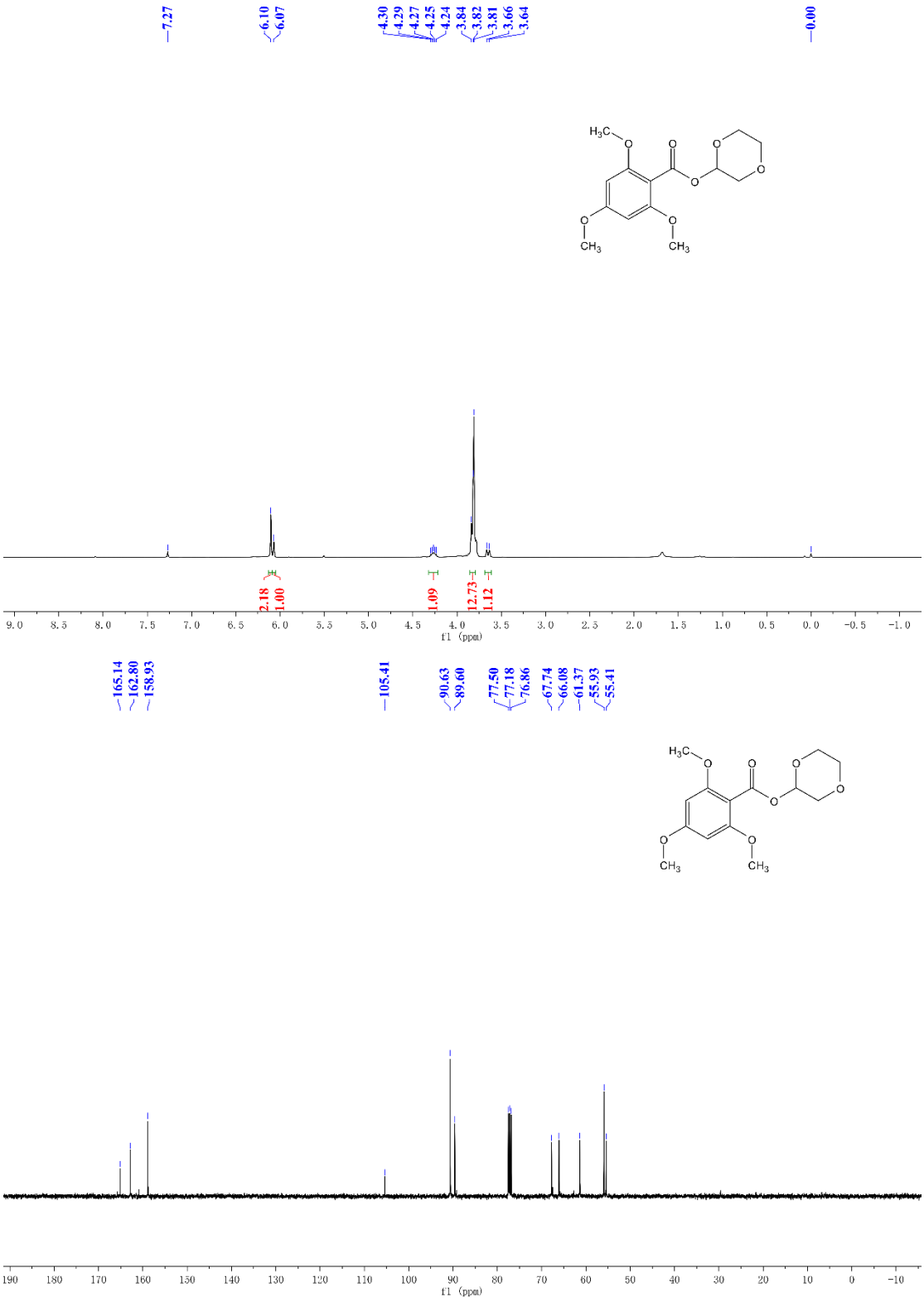




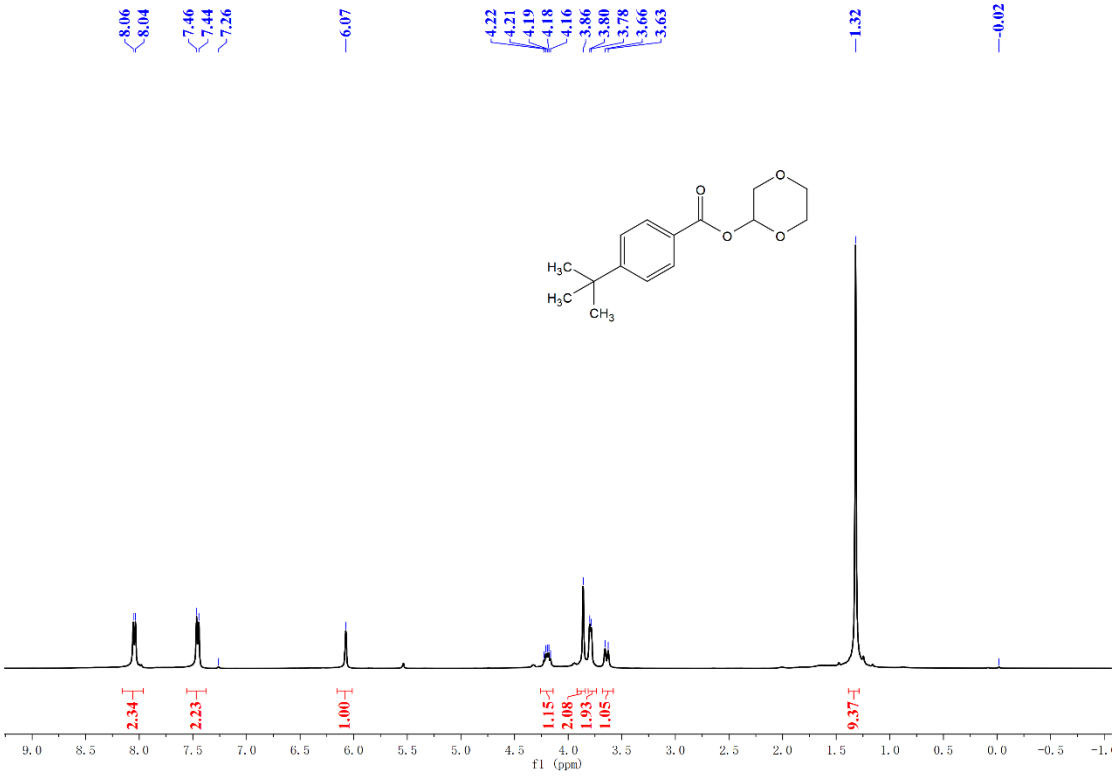
1,4-Dioxan-2-yl 2,6-dimethoxybenzoate (6a)

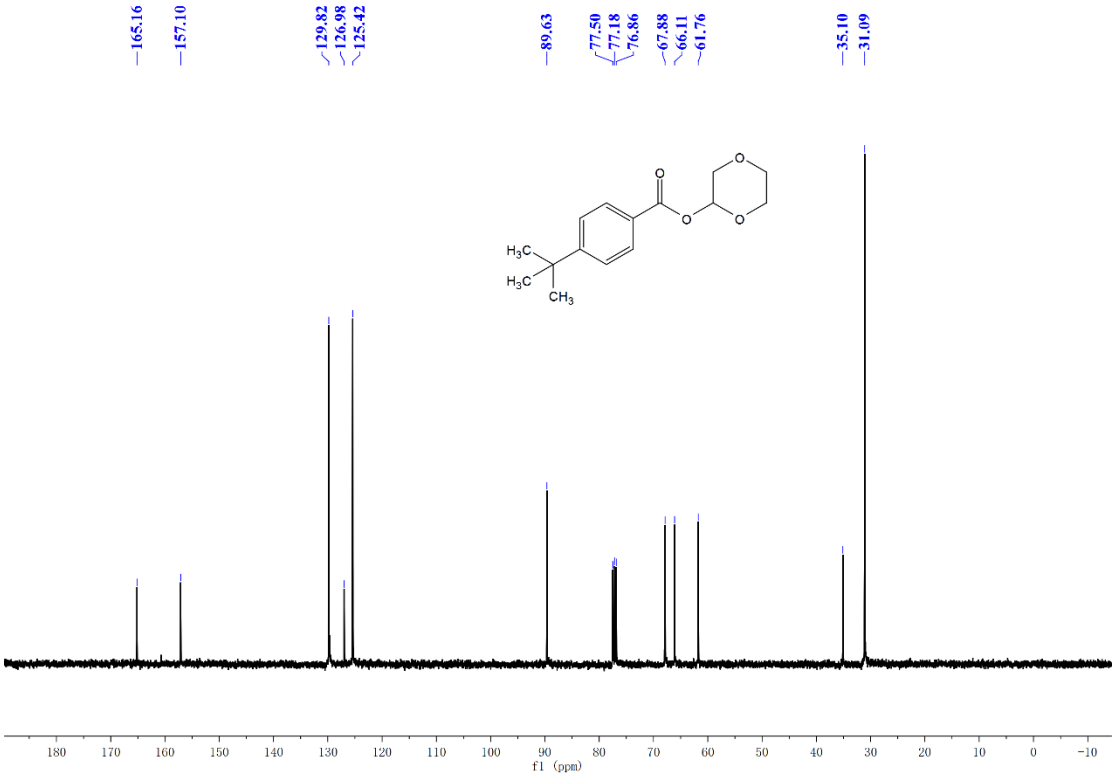


1,4-dioxan-2-yl 2,4,6-trimethoxybenzoate (7a):



1,4-dioxan-2-yl 4-(*tert*-butyl)benzoate (8a)

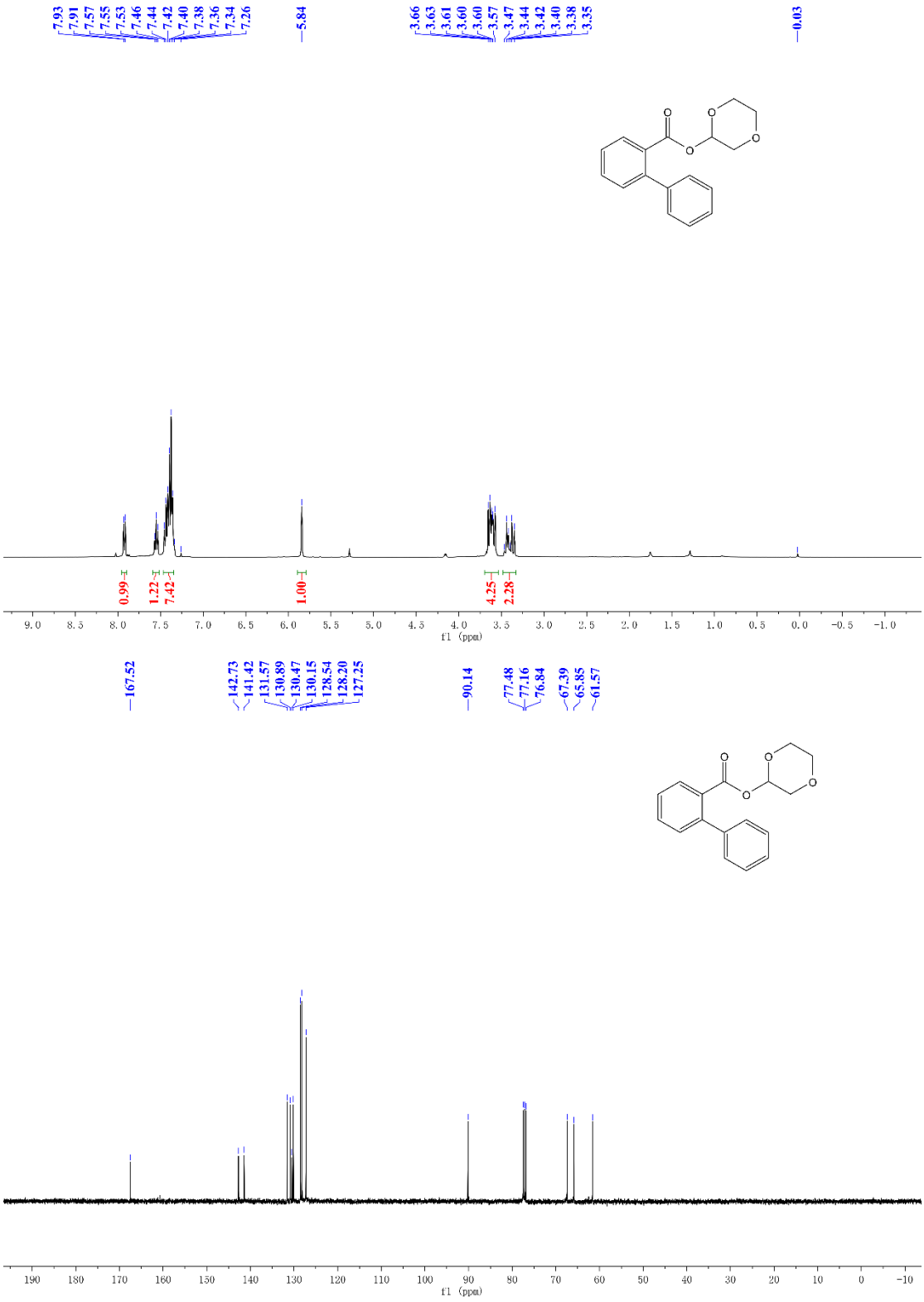




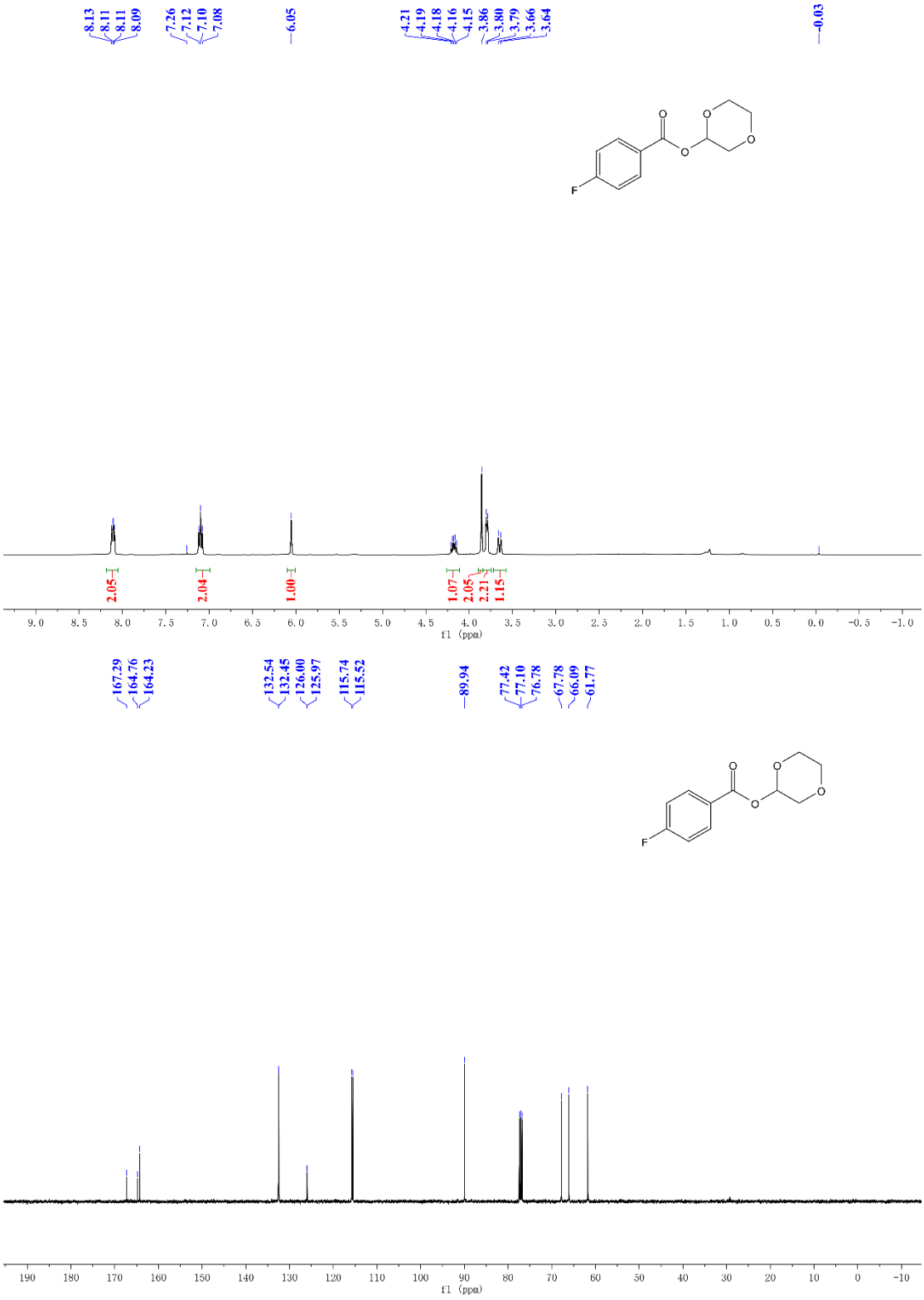
1,4-dioxan-2-yl 4-methylbenzoate (9a):

1,4-dioxan-2-yl 2-methylbenzoate (10a):

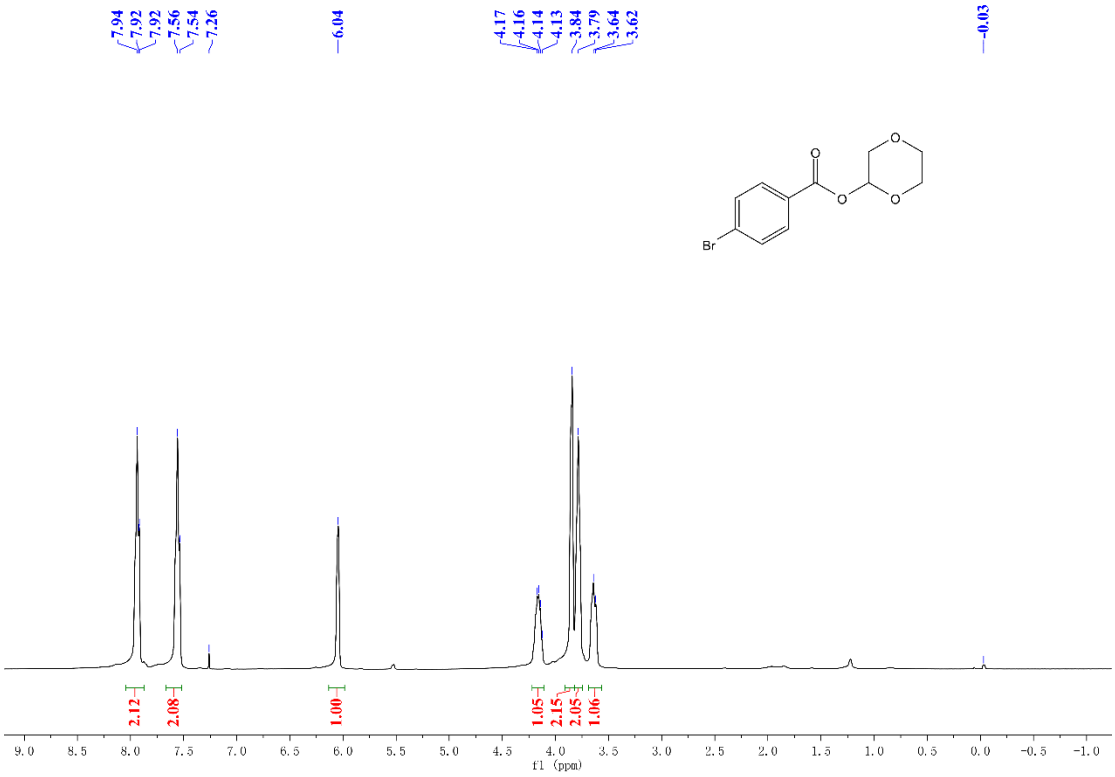
1,4-dioxan-2-yl [1,1'-biphenyl]-2-carboxylate (11a):

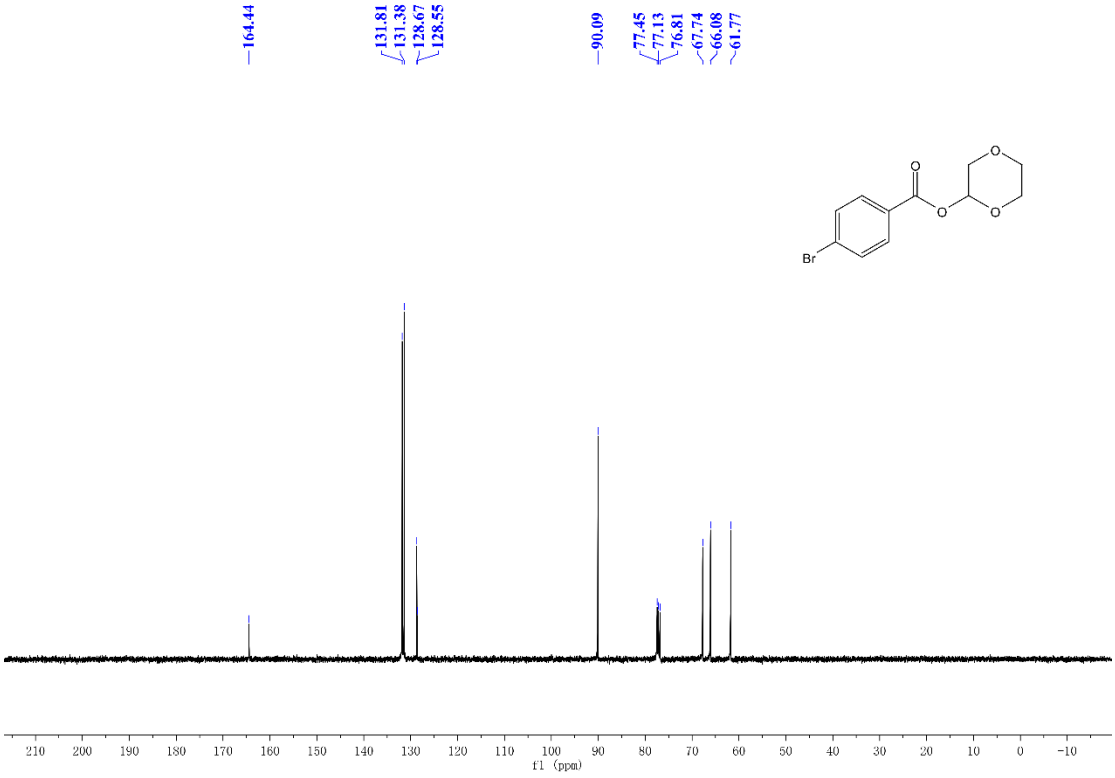


1,4-dioxan-2-yl 4-fluorobenzoate (12a):

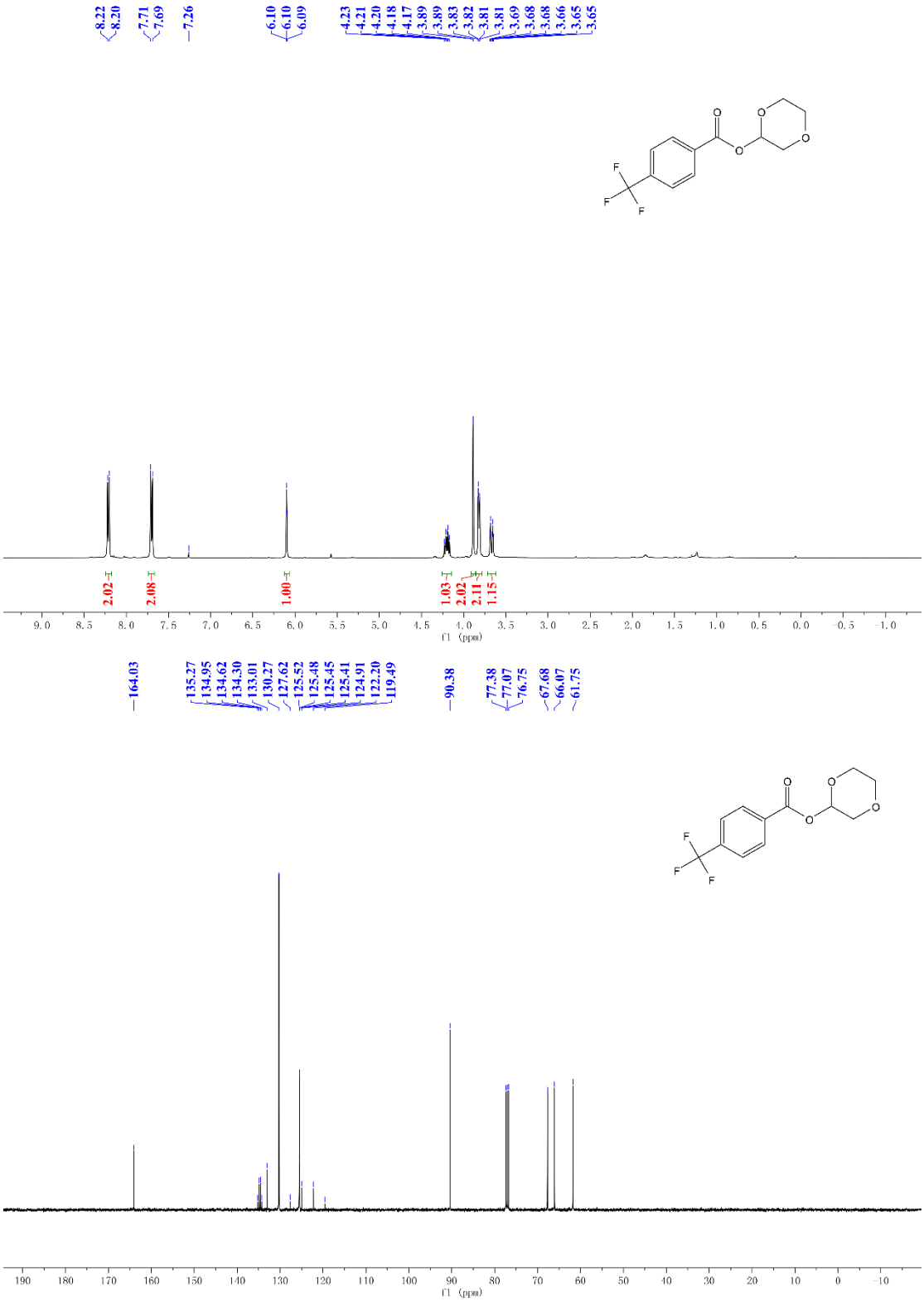


1,4-Dioxan-2-yl 4-bromobenzoate (13a)

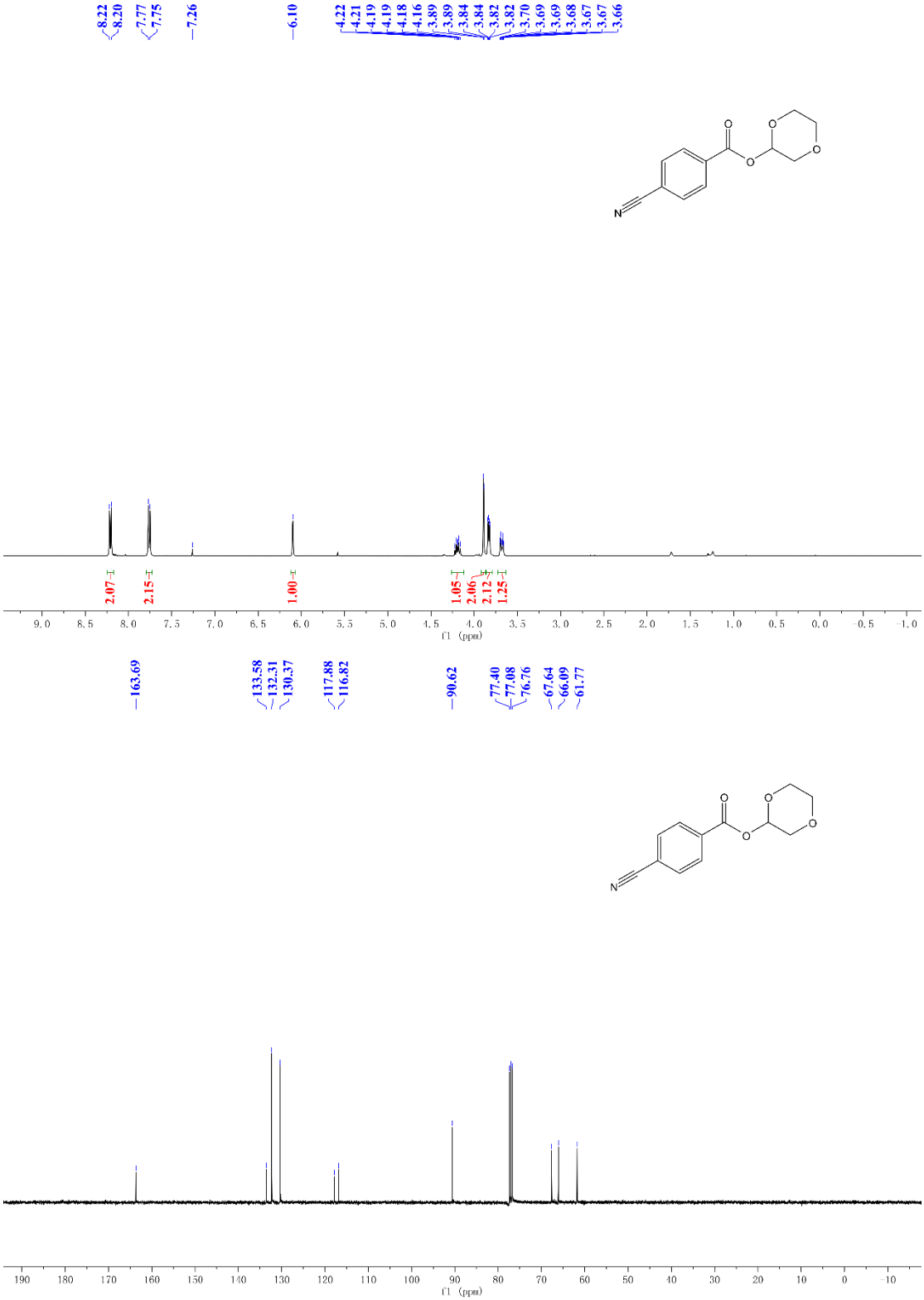




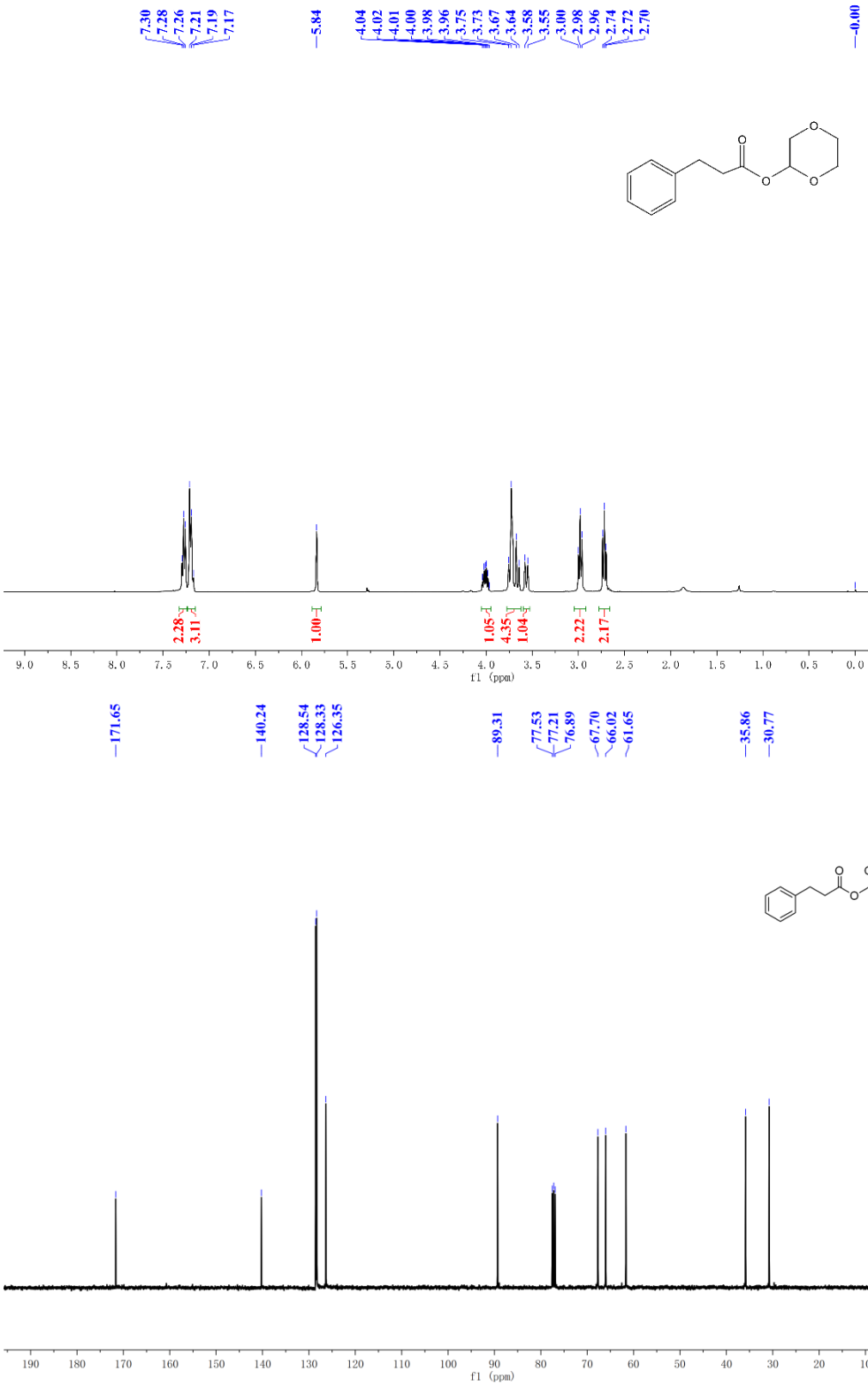
1,4-dioxan-2-yl 4-(trifluoromethyl)benzoate (14a)



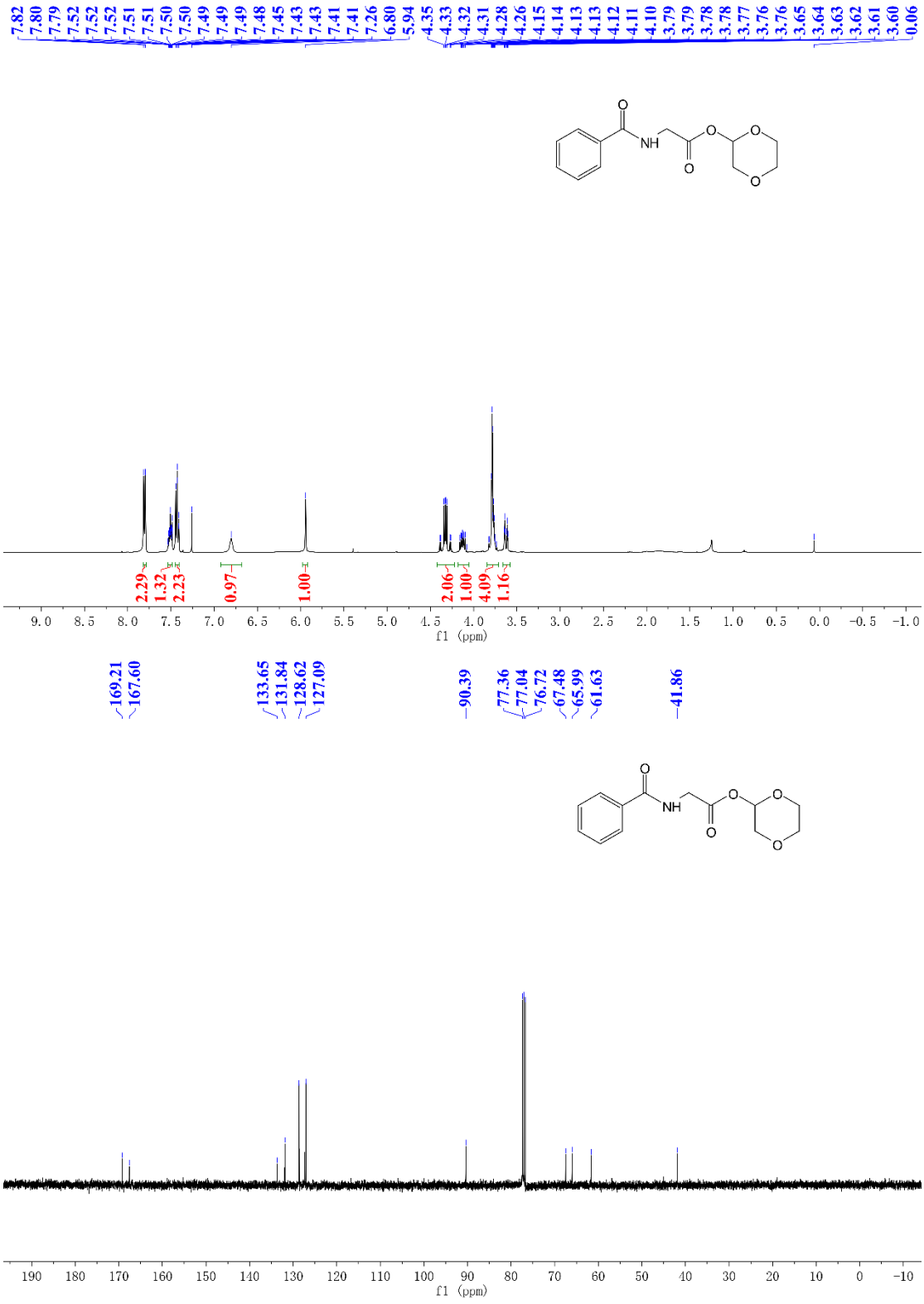
1,4-dioxan-2-yl 4-cyanobenzoate (15a)



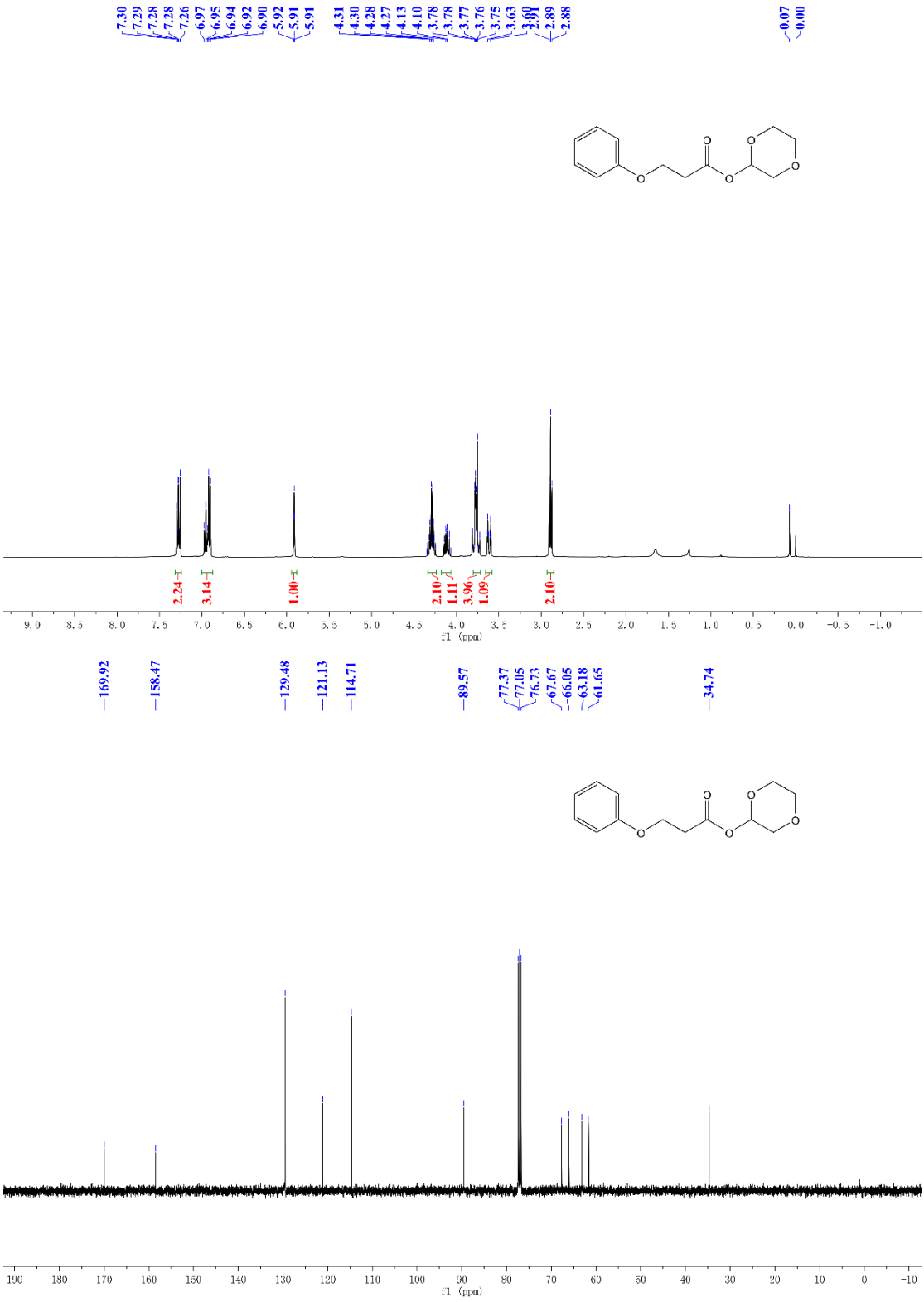
1,4-dioxan-2-yl 3-phenylpropanoate (17a)



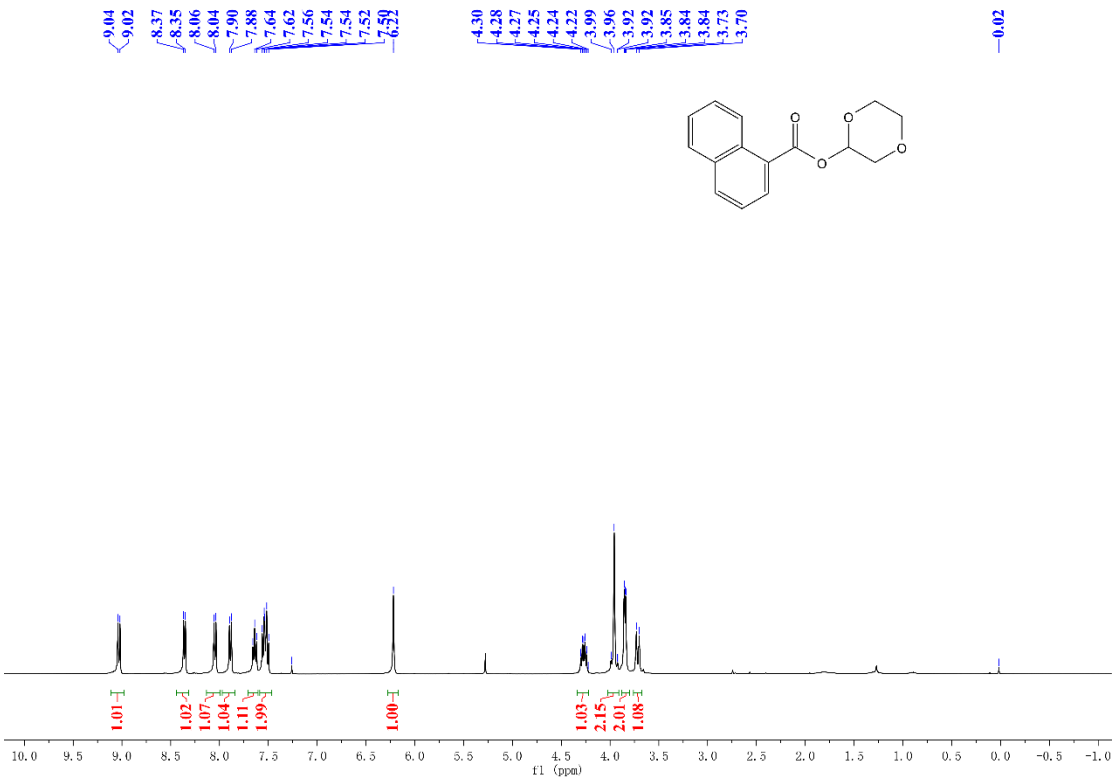
1,4-dioxan-2-yl benzoylglycinate (18a):

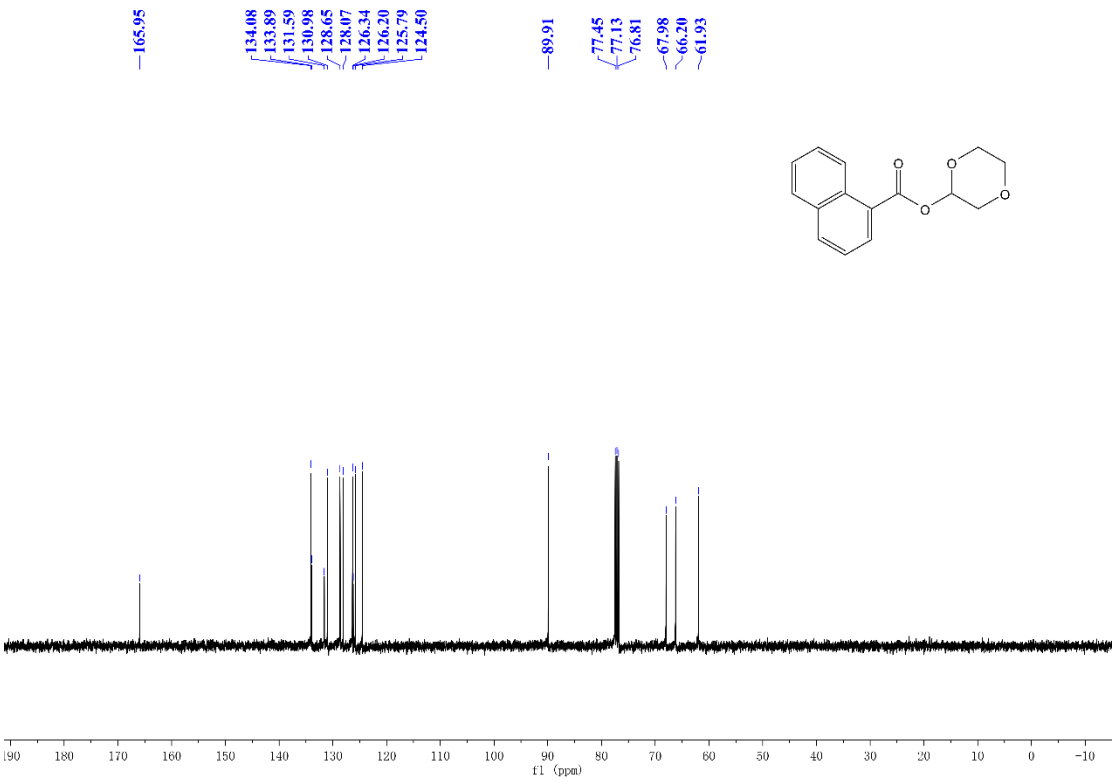


1,4-dioxan-2-yl 3-phenoxypropanoate (19a):

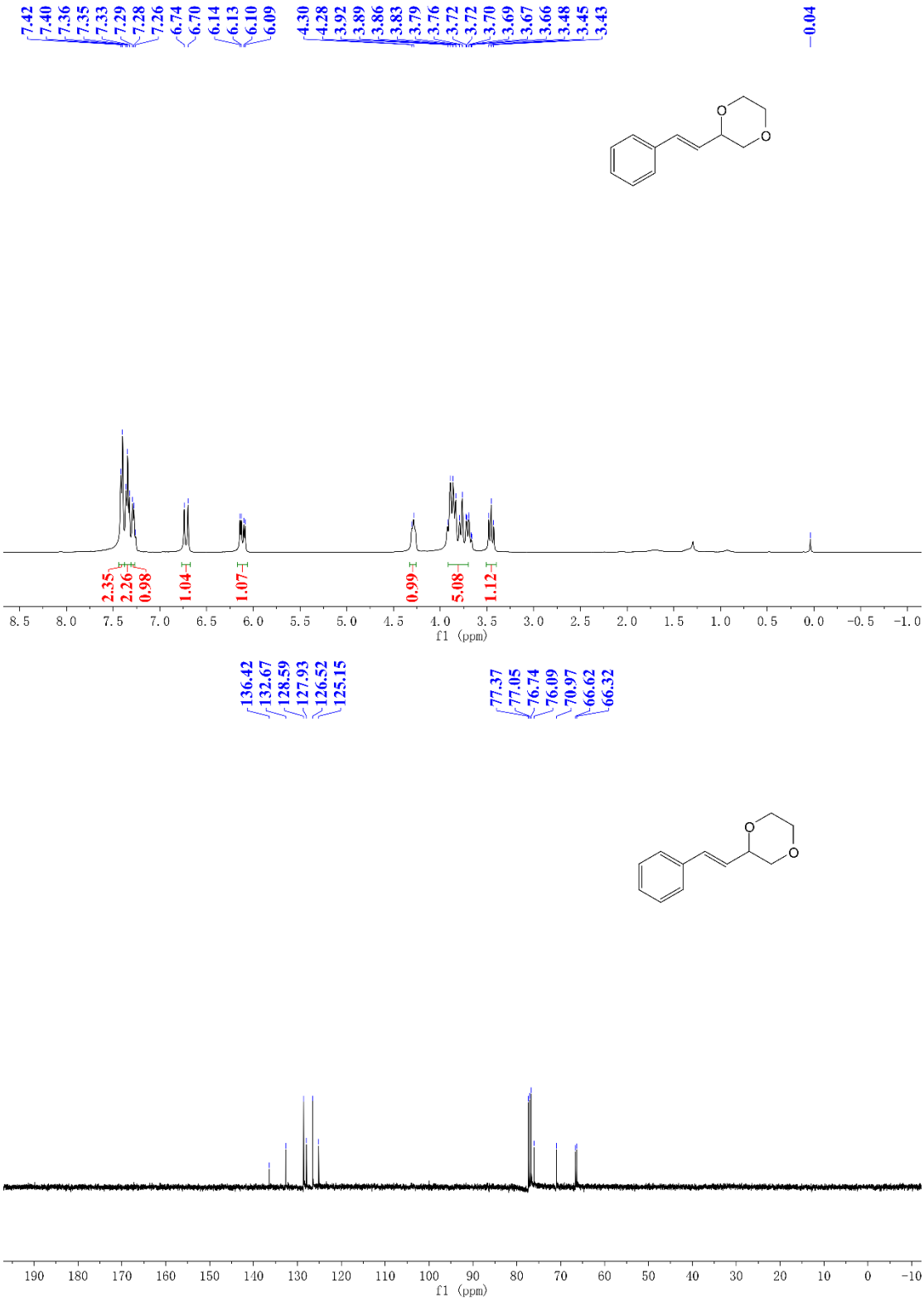


1,4-Dioxan-2-yl 1-naphthoate (20a)

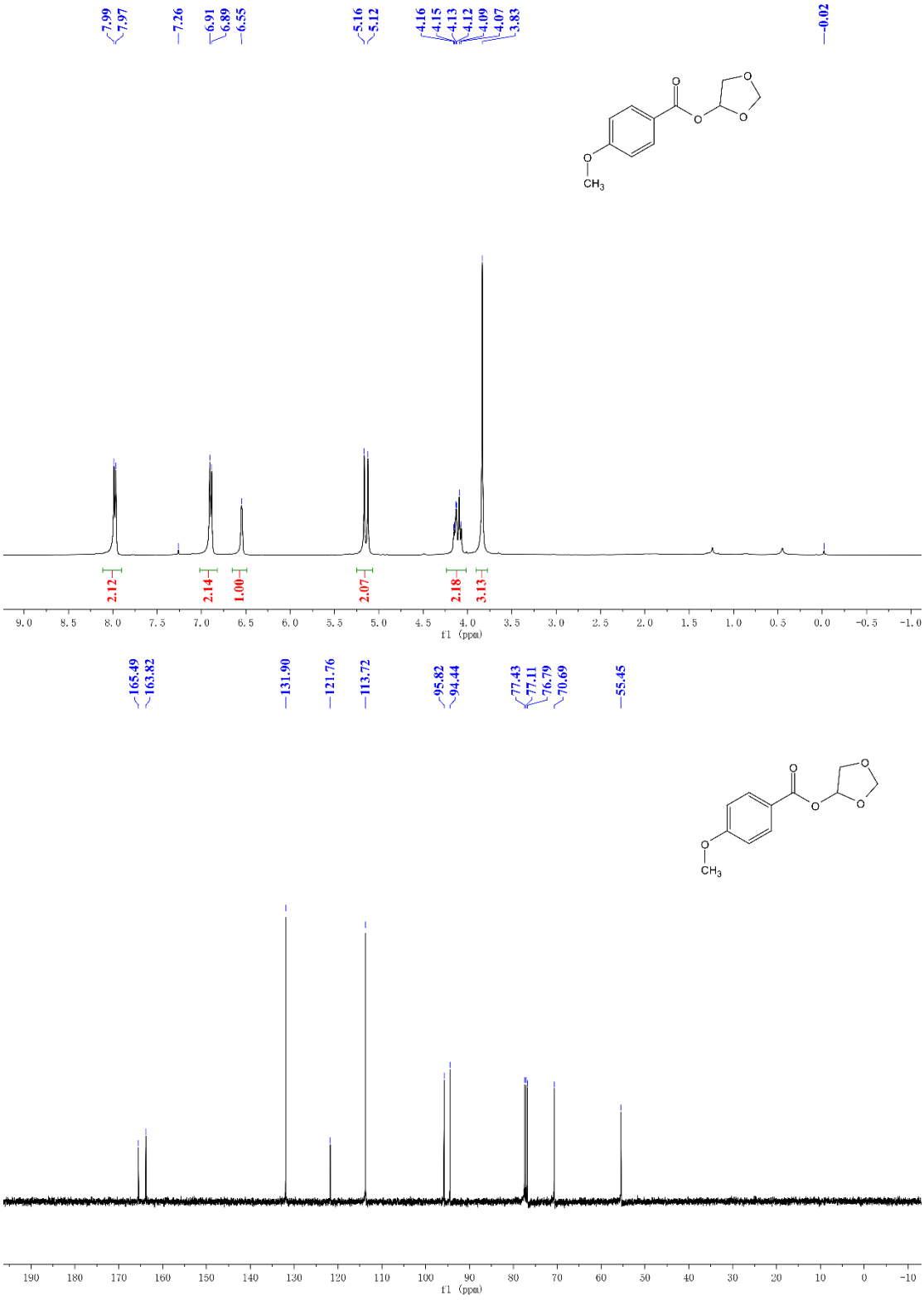




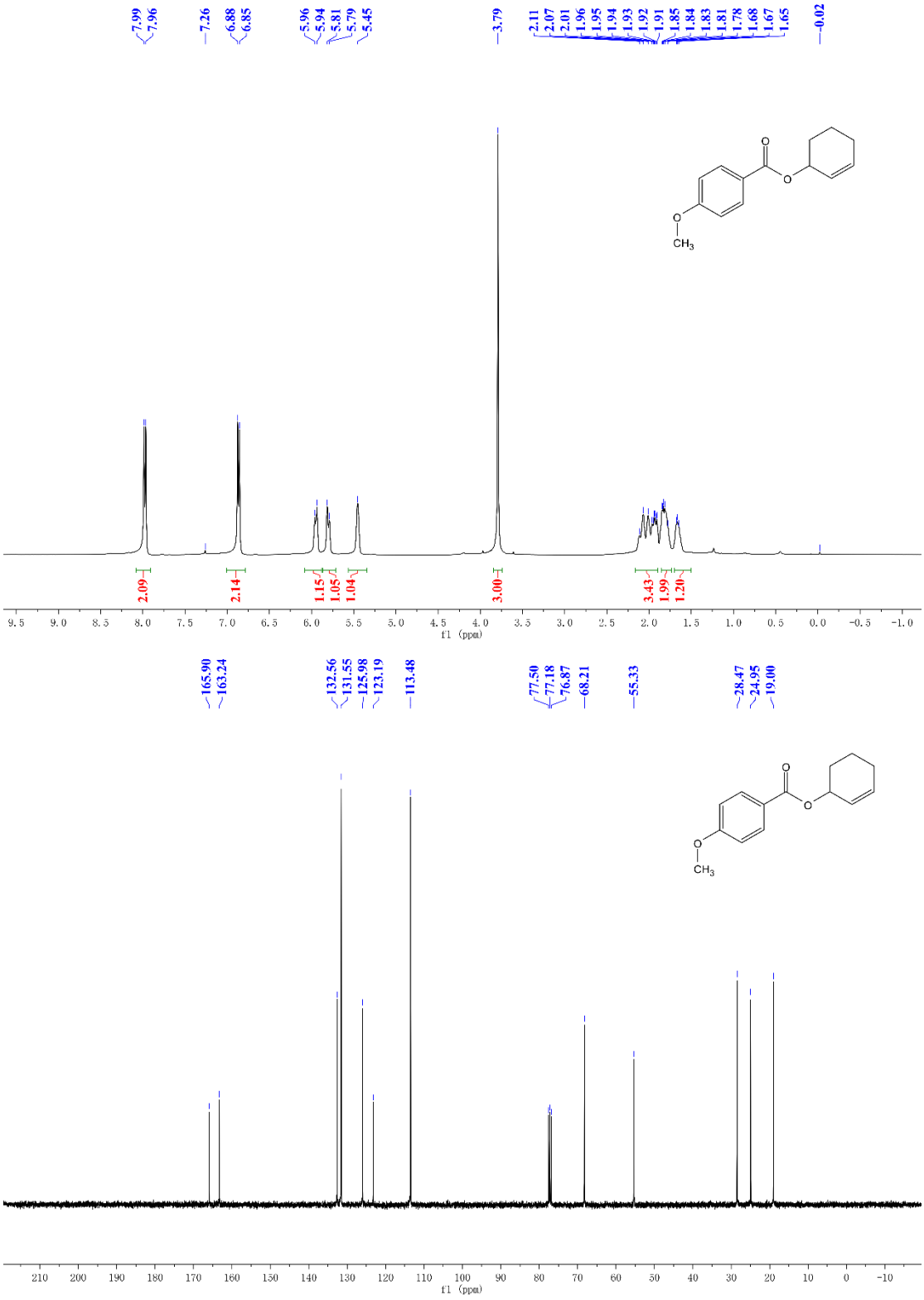
(E)-2-styryl-1,4-dioxane (22a)



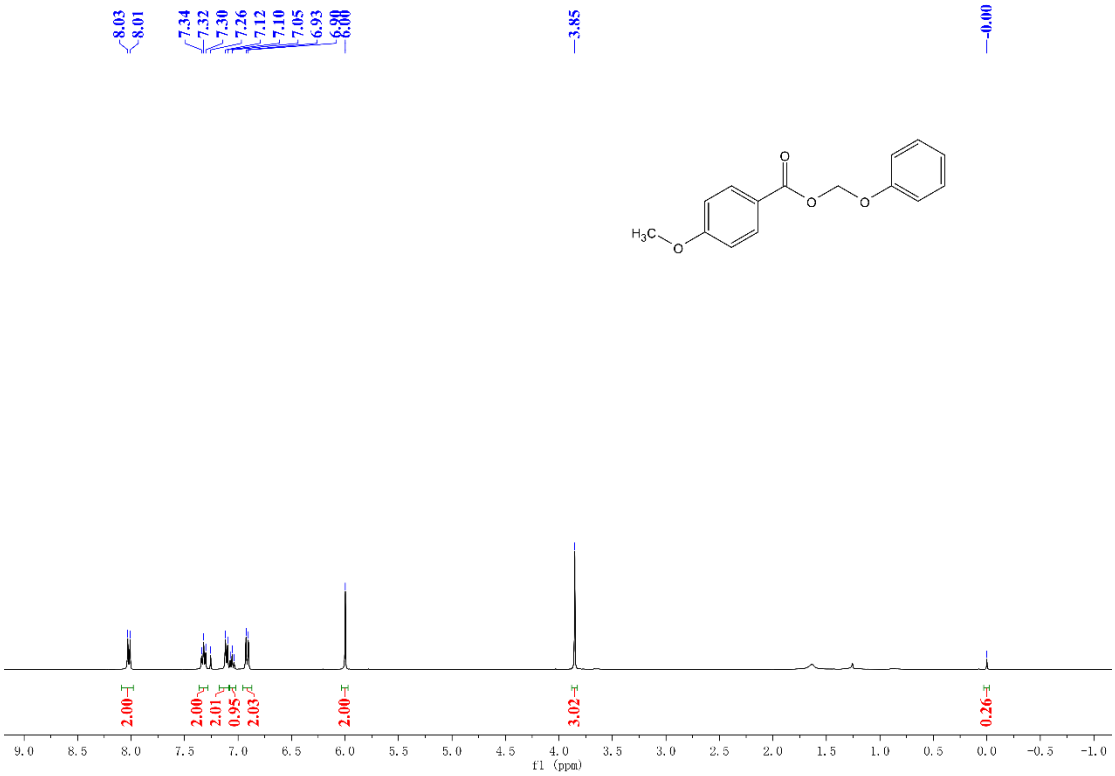
1,3-dioxolan-4-yl 4-methoxybenzoate (2b)

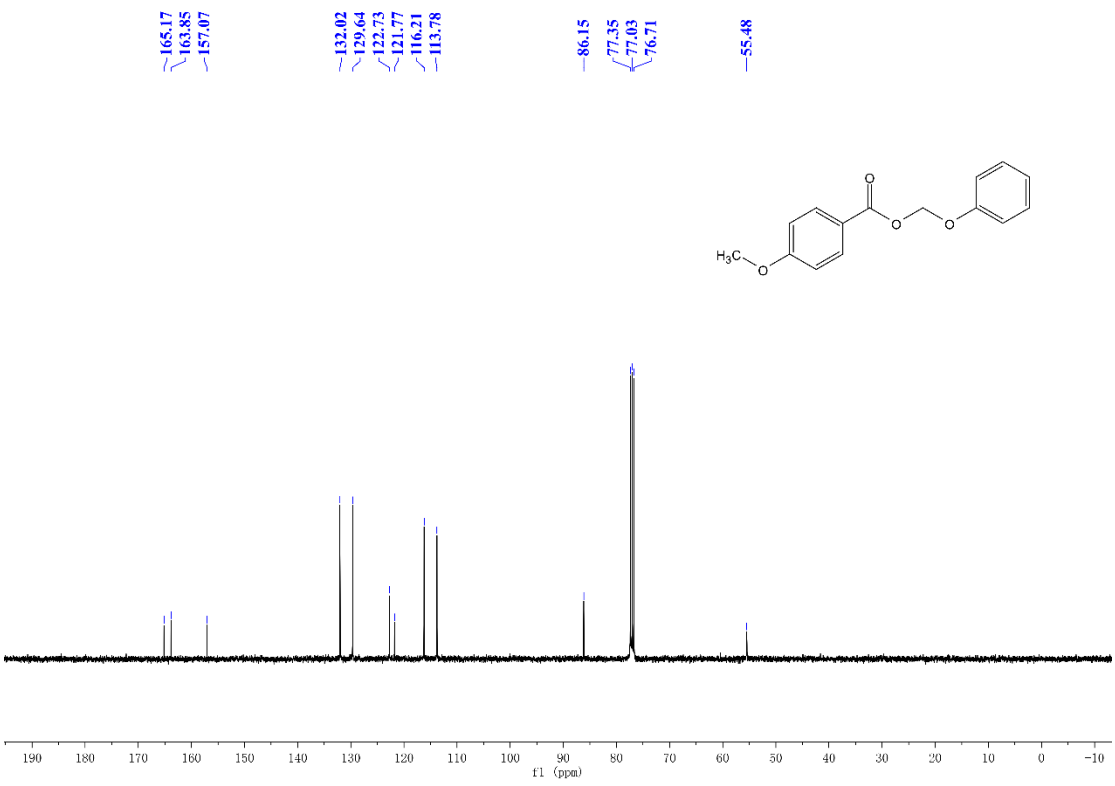


cyclohex-2-en-1-yl 4-methoxybenzoate (2f)

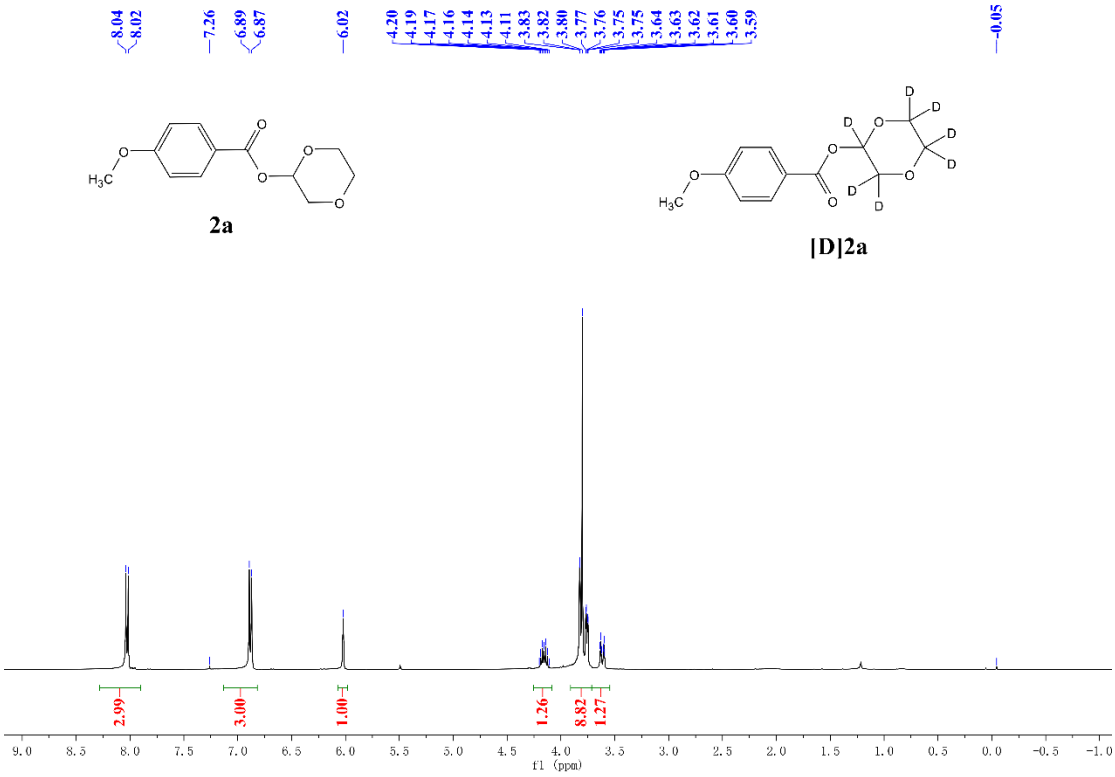


phenoxymethyl 4-methoxybenzoate (2g)





^{1}H- NMR spectra for **2a** and **[D]2a**



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2. S. K. Rout, S. Guin, W. Ali, A. Gogoi and B. K. Patel, *Org. Lett.*, 2014, **16**, 3086-3089.
3. L. Chen, E. B. Shi, Z. J. Liu, S. L. Chen, W. Wei, H. Li, K. Xu and X. B. Wan, *Chem. Eur. J.*, 2011, **17**, 4085-4089.
4. Y. Zheng, J. Mao, G. Rong, X. Xu, Chem. Commun. 2015, **51**, 8837-8840.
5. J. C. Zhao, W. Zhou, J. L. Han, G. G. Li and Y. Pan, *Tetrahedron Lett.*, 2013, **54**, 6507-6510.