Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Convergent Syntheses of 2,3-Dihydrobenzofurans via a Catellani Strategy

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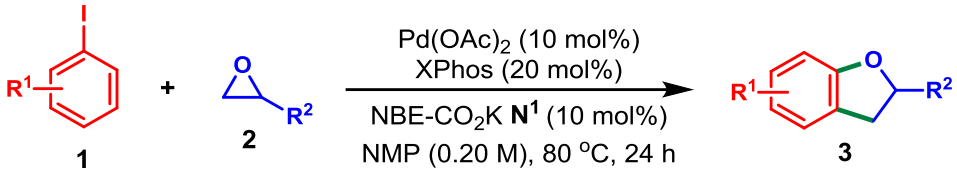
Table of Contents

1. General information

All reactions dealing with air- or moisture-sensitive compounds were performed in the argon-filled glove box or by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere. Unless noted otherwise, all solvents were dried by JC Meyer Solvent Drying System. Most reagents were purchased from commercial sources and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.2 mm commercial silica gel plates, using UV light as the visualizing agent or basic solution of $KMnO_4$ or acidic solution of *p*-anisaldehyde and heat as a developing agent. ^1H NMR spectra were recorded on a 400 MHz Bruker spectrometer. Chemical shifts (δ) were reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, brs = broad singlet. ^{13}C NMR spectra were recorded on 100 MHz with complete proton decoupling spectrophotometers ($CDCl_3$: 77.16 ppm). ^{19}F NMR were reported on 376 MHz or 564 MHz Bruker spectrometer. Gas chromatography (GC) were recorded on Agilent 7890 instrument and the biphenyl as internal standard. High resolution mass spectra (HRMS) were recorded on DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer. Enantiomeric ratio (*ee*) values were determined by chiral HPLC (Agilent 1260) with chiral OD-H column with hexane and *i*-PrOH as solvents. Optical rotations were measured with a polarimeter.

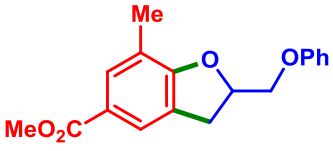
2. General procedure for the synthesis of 3



Unless otherwise noted, in an argon-filled glove box, an oven-dried 4.0 mL vial equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (2.2 mg, 10 mol%), XPhos (19.1 mg, 20 mol%), NBE-CO_2K **N^1** (3.5 mg, 10 mol%), aryl iodide **1** (0.20 mmol, 1.0 equiv.), epoxide **2** (0.6 mmol, 3.0 equiv.) and dry NMP (1.0 mL). The vial was sealed with a cap and stirred at r.t. for about 5 min, then the reaction mixture was heated at 80 ^oC for 24 h. After the reaction vessel was cooled to r.t., the mixture was washed with H_2O, extracted with MTBE, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was directly purified by column chromatography on silica gel or purified by PTLC to yield the desired product **3**.

3. Characterization data for 3

Methyl 7-methyl-2-(phenoxymethyl)-2,3-dihydrobenzofuran-5-carboxylate (3a)



3a

Physical state: white solid.

Melting point: 48-50 ℃.

Yield: 82%.

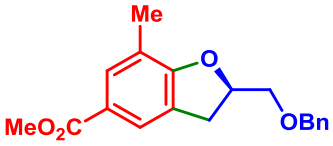
R$_f$ = 0.5 (silica gel, petroleum ether: ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.72 (s, 1H), 7.31-7.27 (m, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 2H), 5.25-5.18 (m, 1H), 4.22 (dd, *J* = 10.1, 5.6 Hz, 1H), 4.13 (dd, *J* = 10.1, 4.9 Hz, 1H), 3.87 (s, 3H), 3.41 (dd, *J* = 15.8, 9.6 Hz, 1H), 3.20 (dd, *J* = 15.8, 7.0 Hz, 1H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.27, 162.10, 158.65, 132.12, 129.63, 125.87, 124.42, 122.75, 121.37, 119.66, 114.78, 81.49, 69.66, 51.96, 32.14, 15.33.

HRMS (ESI-TOF): calc'd for $C_{18}H_{18}NaO_4$ [M+Na^+] 321.1097, found 321.1100.

(*R*)-Methyl 2-((benzyloxy)methyl)-7-methyl-2,3-dihydrobenzofuran-5-carboxylate (3b)



3b

Physical state: light yellow oil.

Yield: 93%.

***R**f* = 0.5 (silica gel, petroleum ether: ethyl acetate = 10:1).

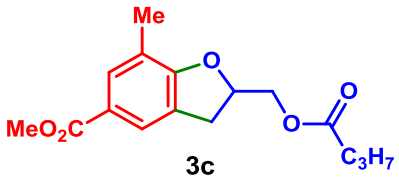
***Ee*:** >99%, the *ee* was determined by HPLC (Chiralpak OD-H column, hexane/*i*-PrOH, 95:5 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 ºC). t_R (major) = 13.190 min; t_R (minor), undetected. $[\alpha]_D^{23}$ = 34.2 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 2H), 7.37-7.27 (m, 5H), 5.08-5.01 (m, 1H), 4.66-4.58 (m, 2H), 3.86 (s, 3H), 3.72-3.63 (m, 2H), 3.28 (dd, *J* = 15.7, 9.6 Hz, 1H), 3.05 (dd, *J* = 15.7, 7.3 Hz, 1H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.33, 162.26, 137.98, 132.03, 128.58, 127.92, 127.86, 126.11, 124.40, 122.53, 119.53, 82.57, 73.61, 71.95, 51.94, 32.03, 15.38.

HRMS (ESI-TOF): calc'd for $C_{19}H_{20}NaO_4$ [M+Na^+] 335.1254, found 335.1259.

Methyl 2-((butyryloxy)methyl)-7-methyl-2,3-dihydrobenzofuran-5-carboxylate (3c)



3c

Physical state: light yellow oil.

Yield: 91%.

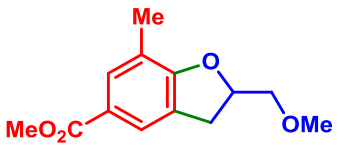
***R**f* = 0.3 (silica gel, petroleum ether: ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 2H), 5.09-5.03 (m, 1H), 4.35-4.23 (m, 2H), 3.86 (s, 3H), 3.33 (dd, *J* = 15.8, 9.7 Hz, 1H), 3.01 (dd, *J* = 15.8, 7.0 Hz, 1H), 2.30 (t, *J* = 8.0 Hz, 2H), 2.21 (s, 3H), 1.63-1.56 (m, 2H), 0.92 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.60, 167.24, 161.97, 132.14, 125.65, 124.30, 122.77, 119.64, 80.88, 65.52, 51.97, 36.09, 31.87, 18.48, 15.26, 13.72.

HRMS (ESI-TOF): calc'd for $C_{16}H_{20}NaO_5$ [M+Na^+] 315.1203, found 315.1206.

Methyl 2-(methoxymethyl)-7-methyl-2,3-dihydrobenzofuran-5-carboxylate (3d)



3d

Physical state: light yellow oil.

Yield: 72%.

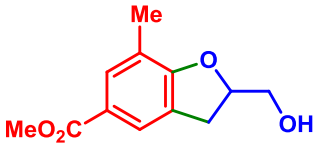
R_f = 0.3 (silica gel, petroleum ether: ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 2H), 5.04-4.97 (m, 1H), 3.85 (s, 3H), 3.65-3.56 (m, 2H), 3.43 (s, 3H), 3.27 (dd, *J* = 15.7, 9.5 Hz, 1H), 3.02 (dd, *J* = 15.7, 7.6 Hz, 1H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.29, 162.23, 132.04, 126.04, 124.37, 122.53, 119.57, 82.48, 74.67, 59.63, 51.92, 31.83, 15.39.

HRMS (ESI-TOF): calc'd for $C_{13}H_{16}NaO_4$ [M+Na^+] 259.0941, found 259.0942.

Methyl 2-(hydroxymethyl)-7-methyl-2,3-dihydrobenzofuran-5-carboxylate (3e)



3e

Physical state: colorless oil.

Yield: 73%.

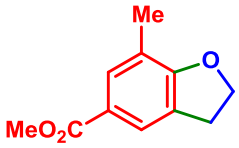
R_f = 0.5 (silica gel, petroleum ether: ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 2H), 5.02-4.95 (m, 1H), 3.92-3.88 (m, 1H), 3.86 (s, 3H), 3.78-3.73 (m, 1H), 3.27 (dd, *J* = 15.7, 9.5 Hz, 1H), 3.06 (dd, *J* = 15.7, 7.6 Hz, 1H), 2.22 (s, 3H), 2.01 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.27, 161.92, 132.09, 126.34, 124.47, 122.77, 119.54, 84.10, 64.95, 51.98, 31.07, 15.36.

HRMS (ESI-TOF): calc'd for $C_{12}H_{14}NaO_4$ [M+Na^+] 245.0784, found 245.0792.

Methyl 7-methyl-2,3-dihydrobenzofuran-5-carboxylate (3f)



3f

Physical state: yellow oil.

Yield: 83%.

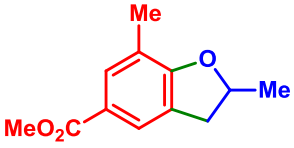
R_f = 0.5 (silica gel, petroleum ether: ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.70 (s, 1H), 4.64 (t, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 3.24 (t, *J* = 8.8 Hz, 2H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.35, 162.74, 131.97, 126.58, 124.37, 122.46, 119.44, 71.90, 51.94, 29.54, 15.29.

HRMS (ESI-TOF): calc'd for $C_{11}H_{12}NaO_3$ [M+Na^+] 215.0679, found 215.0683.

Methyl 2,7-dimethyl-2,3-dihydrobenzofuran-5-carboxylate (3g)



3g

Physical state: white solid.

Melting point: 42-44 ℃.

Yield: 97%.

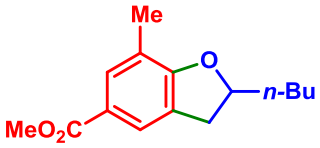
R_f = 0.5 (silica gel, petroleum ether: ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 2H), 5.03-4.94 (m, 1H), 3.85 (s, 3H), 3.33 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.82 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.21 (s, 3H), 1.48 (d, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.36, 162.27, 131.95, 126.65, 124.40, 122.18, 119.30, 80.60, 51.88, 36.88, 22.01, 15.31.

HRMS (ESI-TOF): calc'd for $C_{12}H_{15}O_3$ [M+H^+] 207.1016, found 207.1018.

Methyl 2-butyl-7-methyl-2,3-dihydrobenzofuran-5-carboxylate (3h)[1]



3h

Physical state: light yellow oil.

Yield: 71%.

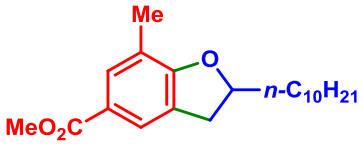
R_f = 0.5 (silica gel, petroleum ether: ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 2H), 4.87-4.80 (m, 1H), 3.86 (s, 3H), 3.29 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.86 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.21 (s, 3H), 1.89-1.80 (m, 1H), 1.71-1.64 (m, 1H), 1.53-1.44 (m, 4H), 0.93 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.41, 162.39, 131.92, 126.62, 124.38, 122.08, 119.28, 84.42, 51.89, 35.98, 35.24, 27.55, 22.73, 15.31, 14.17.

HRMS (ESI-TOF): calc'd for $C_{15}H_{20}NaO_3$ [M+Na$^+$] 271.1305, found 271.1312.

Methyl 2-decyl-7-methyl-2,3-dihydrobenzofuran-5-carboxylate (3i)



3i

Physical state: yellow oil.

Yield: 67%.

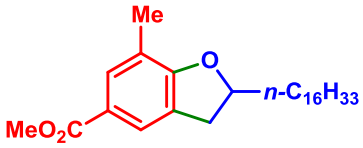
R_f = 0.65 (silica gel, petroleum ether: ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 2H), 4.87-4.80 (m, 1H), 3.86 (s, 3H), 3.29 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.86 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.21 (s, 3H), 1.88-1.79 (m, 1H), 1.71-1.62 (m, 1H), 1.47-1.26 (m, 16H), 0.88 (t, *J* = 8.0 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.42, 162.40, 131.93, 126.64, 124.38, 122.08, 119.29, 84.45, 51.90, 36.27, 35.25, 32.05, 29.75, 29.73, 29.68, 29.64, 29.48, 25.40, 22.84, 15.33, 14.29.

HRMS (ESI-TOF): calc'd for $C_{21}H_{32}NaO_3$ [M+Na$^+$] 355.2244, found 355.2245.

Methyl 2-hexadecyl-7-methyl-2,3-dihydrobenzofuran-5-carboxylate (3j)



3j

Physical state: white solid.

Melting point: 46-48 ℃.

Yield: 80%.

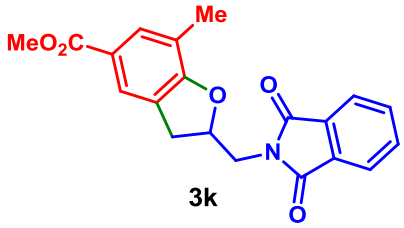
R_f = 0.7 (silica gel, petroleum ether: ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 2H), 4.87-4.80 (m, 1H), 3.86 (s, 3H), 3.29 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.86 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.21 (s, 3H), 1.88-1.79 (m, 1H), 1.71-1.63 (m, 1H), 1.42-1.25 (m, 28H), 0.88 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.42, 162.40, 131.93, 126.63, 124.39, 122.08, 119.28, 84.45, 51.89, 36.27, 35.25, 32.08, 29.85, 29.82, 29.80, 29.73, 29.68, 29.64, 29.52, 25.41, 22.85, 15.32, 14.29.

HRMS (ESI-TOF): calc'd for $C_{27}H_{44}NaO_3$ [M+Na^+] 439.3183, found 439.3184.

Methyl 2-((1,3-dioxoisoindolin-2-yl)methyl)-7-methyl-2,3-dihydrobenzofuran-5-carboxylate (3k)



3k

Physical state: white solid.

Melting point: 127-129 ℃.

Yield: 60%.

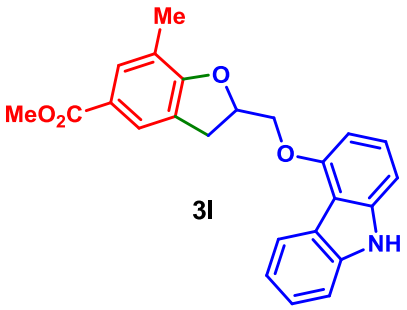
R_f = 0.5 (silica gel, petroleum ether: ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.85 (m, 2H), 7.74-7.72 (m, 2H), 7.70 (s, 1H), 7.68 (s, 1H) 5.20-5.13 (m, 1H), 4.01 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.85 (s, 3H), 3.82 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.38 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.04 (dd, *J* = 6.0, 8.0 Hz, 1H), 2.15 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.27, 167.21, 161.48, 134.25, 132.19, 132.02, 125.39, 124.48, 123.54, 122.93, 120.16, 80.37, 51.95, 42.00, 33.00, 15.18.

HRMS (ESI-TOF): calc'd for $C_{20}H_{17}NNaO_5$ [M+Na^+] 374.0999, found 374.1008.

Methyl 2-(((9H-carbazol-4-yl)oxy)methyl)-7-methyl-2,3-dihydrobenzofuran-5-carboxylate (3l)



3l

Physical state: white solid.

Melting point: 169-171 ℃.

Yield: 89%.

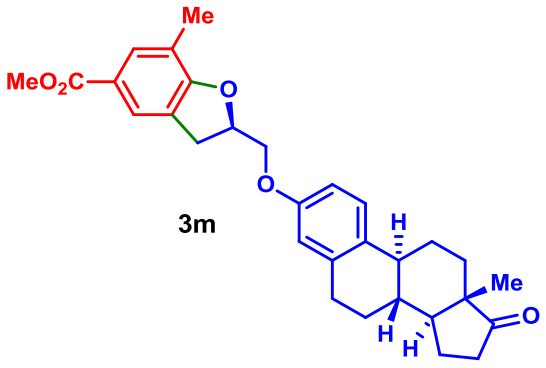
R_f = 0.45 (silica gel, petroleum ether: ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.36-7.30 (m, 3H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.00-6.96 (m, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.43-5.37 (m, 1H), 4.47 (dd, *J* = 12.0, 4.0 Hz, 1H), 4.42-4.38 (m, 1H), 3.91 (s, 3H), 3.55 (dd, *J* = 12.0, 8.0 Hz, 1H), 3.45 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.37, 162.48, 154.98, 140.96, 138.64, 132.16, 126.56, 126.11, 125.07, 124.45, 122.98, 122.68, 122.38, 119.69, 119.59, 112.81, 109.90, 104.09, 101.05, 81.21, 69.84, 51.94, 32.03, 15.31.

HRMS (ESI-TOF): calc'd for $C_{24}H_{21}NNaO_4$ [M+Na^+] 410.1357, found 410.1365.

Methyl 7-methyl-2-((((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)methyl)-2,3-dihydrobenzofuran-5-carboxylate (3m)



3m

Physical state: colorless oil.

Yield: 78%.

$[\alpha]_D^{23}$ = 12.8 (c = 1.0, CH_2Cl_2).

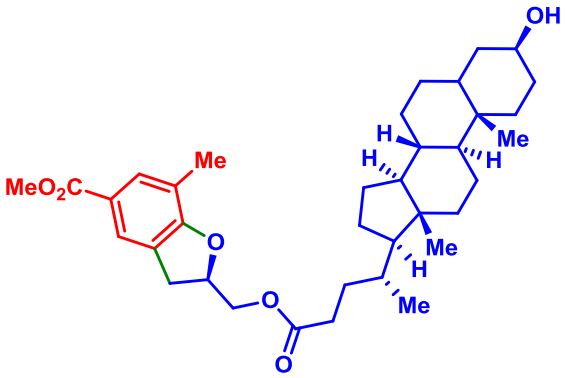
R_f = 0.3 (silica gel, dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.71 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 6.74 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.67 (d, *J* = 2.7 Hz, 1H), 5.23-5.17 (m, 1H), 4.19 (dd, *J* = 10.1, 5.6 Hz, 1H), 4.10 (dd, *J* = 10.2, 4.9 Hz, 1H), 3.87 (s, 3H), 3.40 (dd, *J* = 15.8, 9.6 Hz, 1H), 3.18 (dd, *J* = 15.8, 6.9 Hz, 1H), 2.90-2.86 (m, 2H), 2.54-2.47 (m, 1H), 2.42-2.38 (m, 1H), 2.28-2.22 (m, 4H), 2.19-1.94 (m, 4H), 1.68-1.62 (m, 1H), 1.57-1.40 (m, 5H), 0.91 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 221.14, 167.29, 162.12, 156.72, 138.01, 132.80, 132.11, 126.55, 125.90, 124.44, 122.75, 119.64, 114.89, 112.40, 81.52, 69.77, 51.98, 50.49, 48.14, 44.09, 38.45, 36.02, 32.17, 31.68, 29.76, 26.63, 26.06, 21.72, 15.35, 13.98.

HRMS (ESI-TOF): calc'd for $C_{30}H_{34}NaO_5$ [M+Na^+] 497.2298, found 497.2307.

(2*R*)-methyl 2-((((4*R*)-4-((3*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoyl)oxy)methyl)-7-methyl-2,3-dihydrobenzofuran-5-carboxylate (3n)



3n

Physical state: colorless oil.

Yield: 85%.

$[\alpha]_D^{23}$ = -18.6 (c = 1.0, CH_2Cl_2).

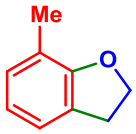
***R*$_f$** = 0.4 (silica gel, toluene: ethyl ether = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 2H), 5.09-5.02 (m, 1H), 4.33 (dd, *J* = 11.9, 3.8 Hz, 1H), 4.24 (dd, *J* = 11.9, 6.0 Hz, 1H), 3.86 (s, 3H), 3.66-3.58 (m, 1H), 3.33 (dd, *J* = 15.8, 9.7 Hz, 1H), 3.02 (dd, *J* = 15.8, 7.0 Hz, 1H), 2.39-2.31 (m, 1H), 2.25-2.17 (m, 4H), 1.96-1.91 (m, 1H), 1.85-1.67 (m, 6H), 1.55-1.52 (m, 2H), 1.40-1.33 (m, 6H), 1.30-1.16 (m, 6H), 1.11-0.95 (m, 6H), 0.91 (s, 3H), 0.87 (d, *J* = 6.5 Hz, 3H), 0.61 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.24, 167.23, 162.01, 132.17, 125.67, 124.31, 122.76, 119.62, 80.90, 71.96, 65.58, 56.56, 55.97, 51.97, 42.82, 42.18, 40.50, 40.24, 36.54, 35.93, 35.43, 34.67, 31.87, 31.20, 30.98, 30.64, 28.27, 27.30, 26.52, 24.29, 23.49, 20.91, 18.33, 15.29, 12.14.

HRMS (ESI-TOF): calc'd for $C_{36}H_{52}NaO_6$ [M+Na$^+$] 603.3656, found 603.3658.

7-Methyl-2,3-dihydrobenzofuran (3a')[1]



3a'

CAS: 17359-45-4

Physical state: colorless oil.

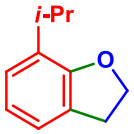
Yield: 85%.

***R*$_f$** = 0.3 (silica gel, petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 4.56 (t, *J* = 8.0 Hz, 2H), 3.22 (t, *J* = 8.0 Hz, 2H), 3.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.46, 129.25, 126.21, 122.38, 120.34, 119.69, 70.86, 30.20, 15.40.

7-Isopropyl-2,3-dihydrobenzofuran (3b')



3b'

Physical state: colorless oil.

Yield: 77%.

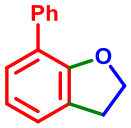
***R*$_f$** = 0.43 (silica gel, petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06-7.01 (m, 2H), 6.84-6.81 (m, 1H), 4.57 (t, *J* = 8.7 Hz, 2H), 3.21 (t, *J* = 8.7 Hz, 2H), 3.15-3.05 (m, 1H), 1.26 (s, 3H), 1.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.51, 130.62, 126.53, 124.85, 122.32, 120.52, 70.80, 30.15, 28.33, 22.48.

HRMS (ESI-TOF): calc'd for $C_{11}H_{15}O$ [M+H$^+$] 163.1123, found 163.1126.

7-Phenyl-2,3-dihydrobenzofuran (3c')



3c'

Physical state: colorless oil.

Yield: 65%.

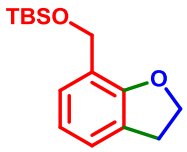
***R*$_f$** = 0.3 (silica gel, petroleum ether: ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.33-7.26 (m, 2H), 7.19 (d, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 4.62 (t, *J* = 8.8 Hz, 2H), 3.28 (t, *J* = 8.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.28, 137.45, 128.48, 128.47, 127.96, 127.86, 127.19, 124.12, 123.67, 120.99, 71.16, 29.99.

HRMS (ESI-TOF): calc'd for $C_{14}H_{12}NaO$ [M+Na^+] 219.0780, found 219.0770.

tert-Butyl((2,3-dihydrobenzofuran-7-yl)methoxy)dimethylsilane (3d′)



3d'

Physical state: colorless oil.

Yield: 55%.

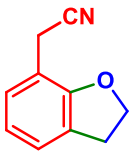
R_f = 0.3 (silica gel, petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 7.1 Hz, 1H), 7.10 (d, *J* = 7.3 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 4.74 (s, 2H), 4.57 (t, *J* = 8.7 Hz, 2H), 3.20 (t, *J* = 8.7 Hz, 2H), 0.95 (s, 9H), 0.11 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.52, 126.30, 125.84, 123.44, 123.36, 120.45, 71.32, 59.99, 29.87, 26.13, 18.61, -5.15.

HRMS (ESI-TOF): calc'd for $C_{15}H_{24}NaO_2Si$ [M+Na^+] 287.1438, found 287.1440.

2-(2,3-Dihydrobenzofuran-7-yl)acetonitrile (3e')



3e'

Physical state: colorless oil.

Yield: 82%.

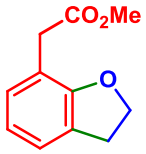
R_f = 0.4 (silica gel, petroleum ether: ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.13 (m, 2H), 6.86 (t, *J* = 7.5 Hz, 1H), 4.61 (t, *J* = 8.8 Hz, 2H), 3.66 (s, 2H), 3.24 (t, *J* = 8.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.84, 127.50, 127.37, 124.97, 121.00, 117.74, 117.71, 7.68, 29.99, 18.22.

HRMS (ESI-TOF): calc'd for $C_{10}H_{10}NO$ [M+H^+] 160.0762, found 160.0761.

Methyl 2-(2,3-dihydrobenzofuran-7-yl)acetate (3f')



3f'

Physical state: colorless oil.

Yield: 65%.

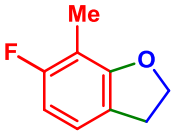
R_f = 0.5 (silica gel, petroleum ether: ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 6.5 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.81 (t, *J* = 7.5 Hz, 1H), 4.57 (t, *J* = 8.7 Hz, 2H), 3.70 (s, 3H), 3.61 (s, 2H), 3.22 (t, *J* = 8.7 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.99, 158.51, 129.14, 126.94, 124.06, 120.55, 115.87, 71.26, 52.18, 35.18, 30.11.

HRMS (ESI-TOF): calc'd for $C_{11}H_{12}NaO_3$ [M+Na^+] 215.0679, found 215.0677.

6-Fluoro-7-methyl-2,3-dihydrobenzofuran (3g')



3g'

Physical state: light yellow oil.

Yield: 63%.

R_f = 0.3 (silica gel, petroleum ether).

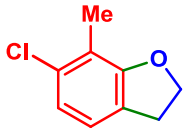
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94-6.90 (m, 1H), 6.54-6.49 (m, 1H), 4.61 (t, *J* = 8.0 Hz, 2H), 3.17 (t, *J* = 8.0 Hz, 2H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.45 (d, *J* = 240.0 Hz), 159.75 (d, *J* = 10.0 Hz), 121.66 (d, *J* = 10.0 Hz), 121.40 (d, *J* = 3.0 Hz), 107.84 (d, *J* = 22.0 Hz), 102.67 (d, *J* = 24.0 Hz), 72.24, 29.73, 7.95 (d, *J* = 4.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -121.16.

HRMS (APCI-TOF): calc'd for $C_9H_{10}FO$ [M+H^+] 153.0710, found 153.0720.

6-Chloro-7-methyl-2,3-dihydrobenzofuran (3h')



3h'

Physical state: yellow oil.

Yield: 64%.

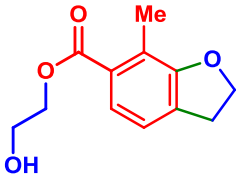
R_f = 0.3 (silica gel, petroleum ether: ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.59 (t, *J* = 8.0 Hz, 2H), 3.21-3.16 (m, 2H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.52, 133.56, 124.75, 122.34, 120.92, 118.44, 71.74, 30.04, 12.66.

HRMS (APCI-TOF): calc'd for $C_9H_{10}ClO$ [M+H$^+$] 169.0420, found 169.0422.

2-Hydroxyethyl 7-methyl-2,3-dihydrobenzofuran-6-carboxylate (3i')



3i'

Physical state: light yellow oil.

Yield: 50%.

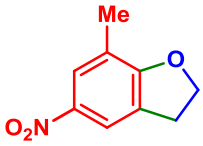
R_f = 0.4 (silica gel, petroleum ether: ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 4.59 (t, *J* = 8.8 Hz, 2H), 4.42-4.40 (m, 2H), 3.95-3.92 (m, 2H), 3.25 (t, *J* = 8.8 Hz, 2H), 2.43 (s, 3H), 2.18 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.03, 159.47, 130.86, 129.33, 123.47, 121.91, 121.64, 70.97, 66.49, 61.56, 30.48, 13.32.

HRMS (ESI-TOF): calc'd for $C_{12}H_{14}NaO_4$ [M+Na$^+$] 245.0784, found 245.0790.

7-Methyl-5-nitro-2,3-dihydrobenzofuran (3j')



3j'

Physical state: yellow solid.

Melting point: 82-84 ℃.

Yield: 60%.

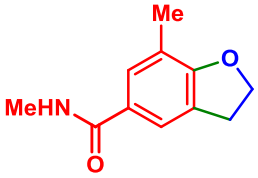
R_f = 0.6 (silica gel, petroleum ether: ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 2H), 4.73 (t, *J* = 8.8 Hz, 2H), 3.29 (t, *J* = 8.8 Hz, 2H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.21, 141.70, 127.41, 126.40, 120.08, 118.96, 72.72, 29.32, 15.34.

HRMS (ESI-TOF): calc'd for $C_9H_9NNaO_3$ [M+Na^+] 202.0475, found 202.0477.

***N*,7-dimethyl-2,3-dihydrobenzofuran-5-carboxamide (3k')**



3k'

Physical state: white solid.

Melting point: 115-118 ℃.

Yield: 76%.

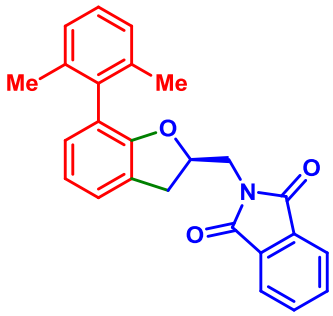
R_f = 0.5 (silica gel, petroleum ether: ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (s, 1H), 7.37 (s, 1H), 6.25 (s, 1H), 4.60 (t, *J* = 8.8 Hz, 2H), 3.19 (t, *J* = 8.8 Hz, 2H), 2.96 (d, *J* = 4.8 Hz, 3H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.40, 161.26, 128.72, 127.05, 126.66, 121.66, 119.32, 71.65, 29.68, 26.90, 15.33.

HRMS (ESI-TOF): calcd for $C_{11}H_{14}NO_2$ [M+H^+] 192.1019, found 192.1022.

(*R*)-2-((7-(2,6-dimethylphenyl)-2,3-dihydrobenzofuran-2-yl)methyl)isoindoline-1,3-dione (3m′)



3m'

Physical state: colorless oil.

Yield: 53%.

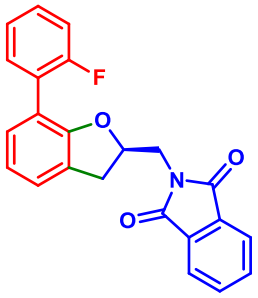
***R*$_f$** = 0.55 (silica gel, petroleum ether: ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.82 (m, 2H), 7.74-7.69 (m, 2H), 7.19-7.16 (m, 1H), 7.13-7.11 (m, 2H), 7.04-7.00 (m, 2H), 6.92 (m, 1H), 5.18-5.10 (m, 1H), 4.11 (dd, *J* = 13.8, 7.6 Hz, 1H), 3.83 (dd, *J* = 13.8, 5.5 Hz, 1H), 3.42 (dd, *J* = 15.8, 9.5 Hz, 1H), 3.13 (dd, *J* = 15.8, 6.2 Hz, 1H), 2.34 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.26, 156.22, 136.69, 134.91, 134.16, 133.26, 132.09, 131.13, 130.10, 129.92, 128.34, 125.86, 124.38, 124.05, 123.45, 120.71, 78.95, 42.27, 33.71, 21.02, 19.80.

HRMS (ESI-TOF): calc'd for $C_{25}H_{21}NNaO_3$ [M+Na$^+$] 406.1414, found 406.1415.

(*R*)-2-((7-(2-fluorophenyl)-2,3-dihydrobenzofuran-2-yl)methyl)isoindoline-1,3-dione (3n′)



3n'

Physical state: yellow oil.

Yield: 48%.

***R*$_f$** = 0.3 (silica gel, petroleum ether: ethyl acetate = 5:1).

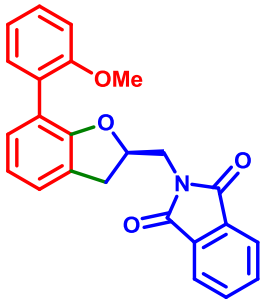
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.82 (m, 2H), 7.74-7.71 (m, 2H), 7.58-7.53 (m, 1H), 7.28-7.18 (m, 2H), 7.21-7.18 (m, 1H), 7.15-7.05 (m, 2H), 6.84 (m, 1H), 5.18-5.11 (m, 1H), 4.10 (dd, *J* = 13.9, 7.5 Hz, 1H), 3.88 (dd, *J* = 13.9, 5.4 Hz, 1H), 3.42 (dd, *J* = 15.7, 9.4 Hz, 1H), 3.14 (dd, *J* = 15.8, 6.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.29, 159.77 (d, *J* = 246.0 Hz), 156.37, 134.17, 132.06, 132.02, 129.82 (d, *J* = 4.0 Hz), 129.05 (d, *J* = 8.0 Hz), 126.40, 124.86, 124.61 (d, *J* = 14.0 Hz), 123.82 (d, *J* = 4.0 Hz), 123.42, 120.89, 118.26, 115.82 (d, *J* = 23.0 Hz), 79.29, 42.04, 35.53.

^{19}F NMR (564 MHz, $CDCl_3$): δ -115.54.

HRMS (ESI-TOF): calc'd for $C_{23}H_{16}FNNaO_3$ [M+Na^+] 396.1006, found 396.1007.

(*R*)-2-((7-(2-methoxyphenyl)-2,3-dihydrobenzofuran-2-yl)methyl)isoindoline-1,3-dione (3o′)



3o'

Physical state: yellow oil.

Yield: 62%.

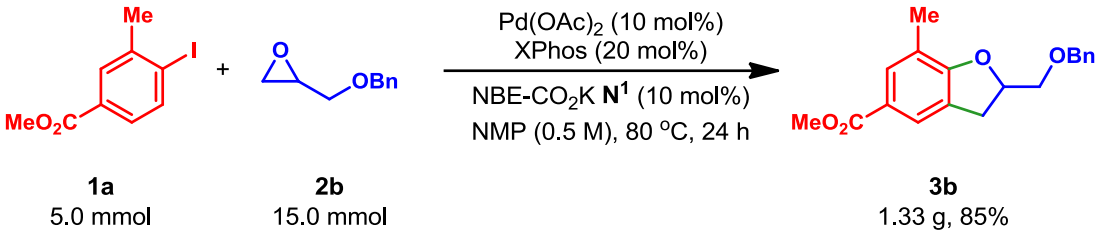
***R*$_f$** = 0.4 (silica gel, petroleum ether: ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.84 (m, 2H), 7.73-7.70 (m, 2H), 7.28-7.22 (m, 1H), 7.28-7.22 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.97-6.89 (m, 3H), 5.17-5.17 (m, 1H), 4.09 (dd, *J* = 13.8, 7.5 Hz, 1H), 3.87 (dd, *J* = 13.8, 5.7 Hz, 1H), 3.77 (s, 3H), 3.39 (dd, *J* = 15.7, 9.4 Hz, 1H), 3.12 (dd, *J* = 15.7, 6.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.33, 156.69, 156.56, 134.18, 132.12, 131.85, 130.32, 128.82, 126.02, 125.83, 124.20, 123.43, 120.89, 120.51, 120.42, 111.13, 78.93, 55.67, 42.16, 33.68.

HRMS (ESI-TOF): calc'd for $C_{24}H_{19}NNaO_4$ [M+Na^+] 408.1206, found 408.1213.

4. Experimental procedure for gram-scale synthesis of 3b



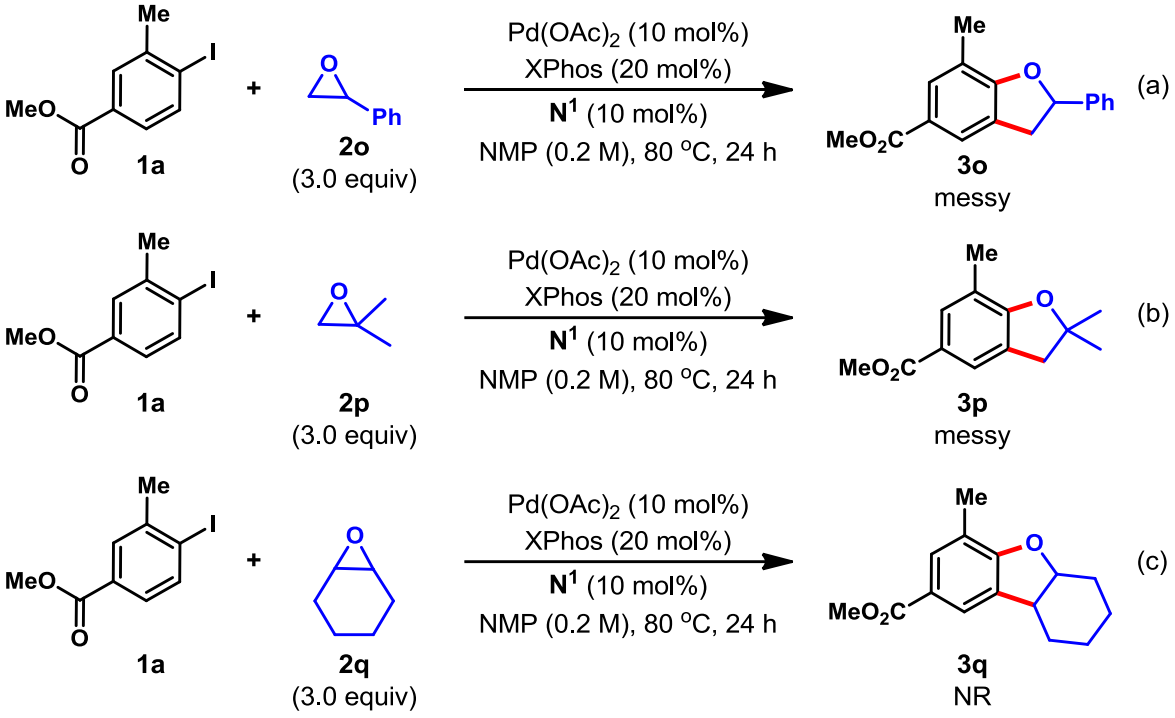
1a 5.0 mmol

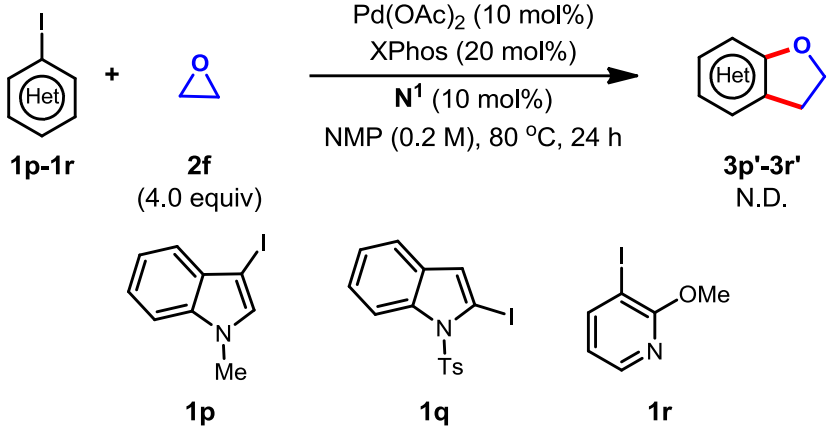
2b 15.0 mmol

3b 1.33 g, 85%

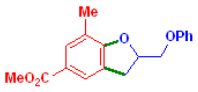
In an argon-filled glove box, an oven-dried 50 mL vial equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (112.3 mg, 0.5 mmol), XPhos (476.7 mg, 1.0 mmol), NBE-CO_2K **N1** (88.1 mg, 0.5 mmol), methyl 4-iodo-3-methylbenzoate **1a** (1.38 g, 5.0 mmol), 2-((benzyloxy)methyl)oxirane **2b** (2.46 g, 15.0 mmol), and dry NMP (10 mL). The vial was sealed with a cap and stirred at r.t. for about 5 min, then the reaction mixture was heated at 80 °C for 24 h. After the reaction vessel was cooled to r.t., the mixture was washed with H_2O, extracted with MTBE, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was directly purified by column chromatography on silica gel to yield the product **3b** (1.33 g, 85% yield) as a light yellow oil.

5. Failed substrates archive

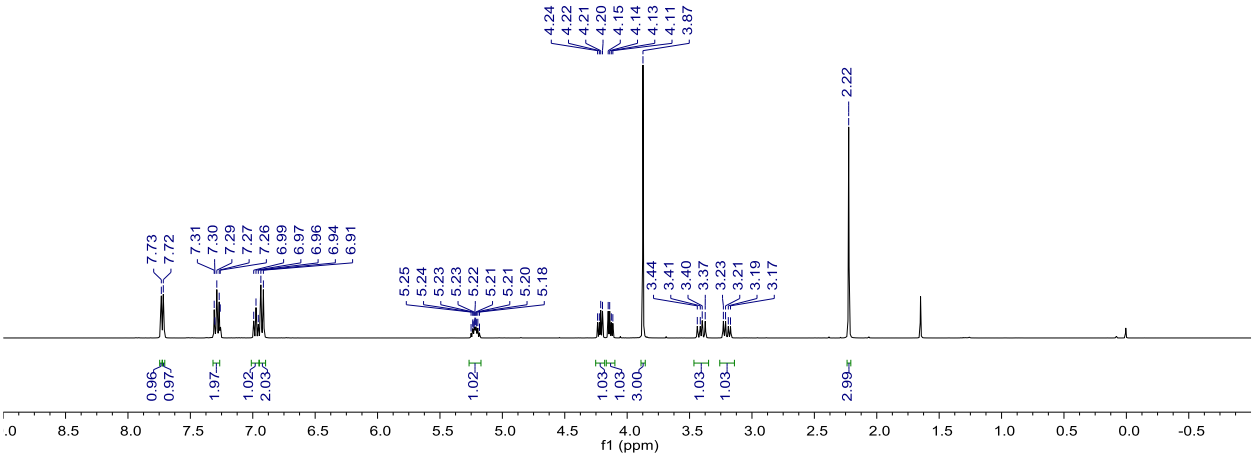


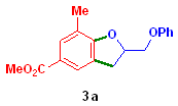


6. The spectra of products

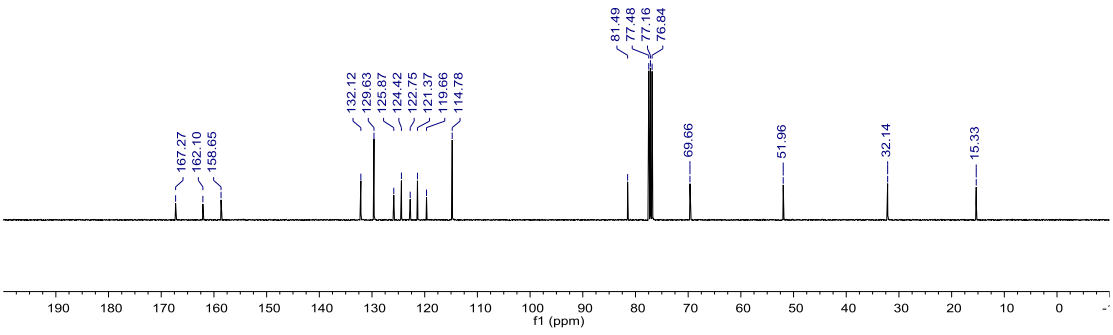


3a



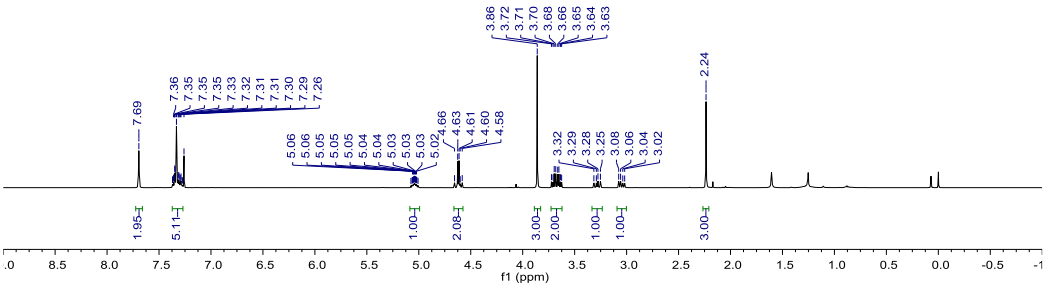


3a



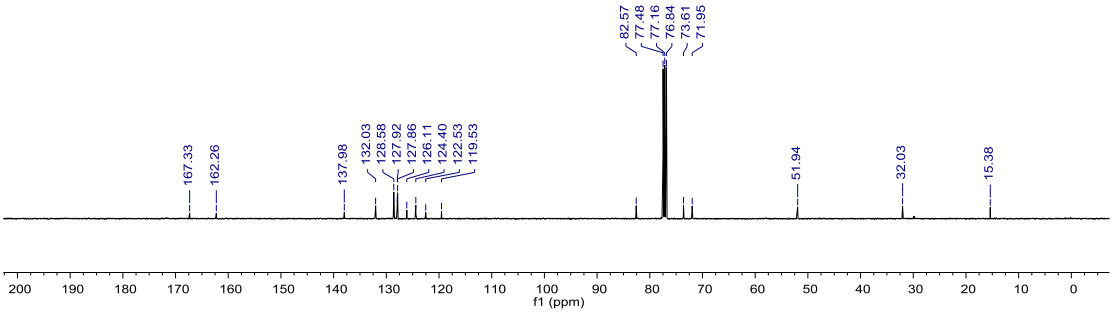

Me
O
MeO2C
OBn

3b


7.69
7.36
7.35
7.35
7.35
7.33
7.32
7.31
7.31
7.30
7.29
7.26
5.06
5.06
5.05
5.05
5.04
5.04
5.03
5.03
5.03
5.02
4.66
4.63
4.61
4.60
4.58
3.86
3.72
3.71
3.70
3.68
3.66
3.65
3.64
3.63
3.32
3.29
3.28
3.25
3.08
3.06
3.04
3.02
2.24
1.95
5.11
1.00
2.08
3.00
2.00
1.00
1.00
3.00
f1 (ppm)


Me
O
MeO2C
OBn

3b


82.57
77.48
77.16
76.84
73.61
71.95
167.33
162.26
137.98
132.03
128.58
127.92
127.86
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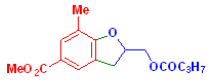
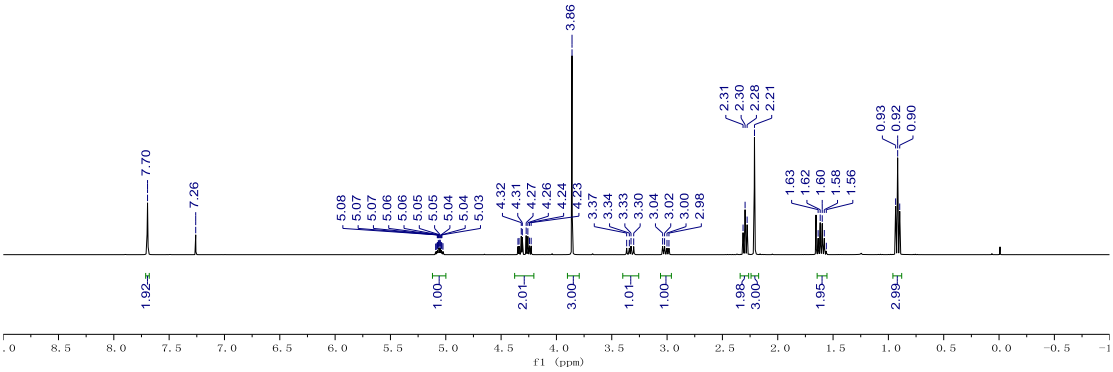
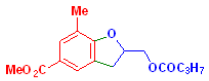
119.53
51.94
32.03
15.38
f1 (ppm)

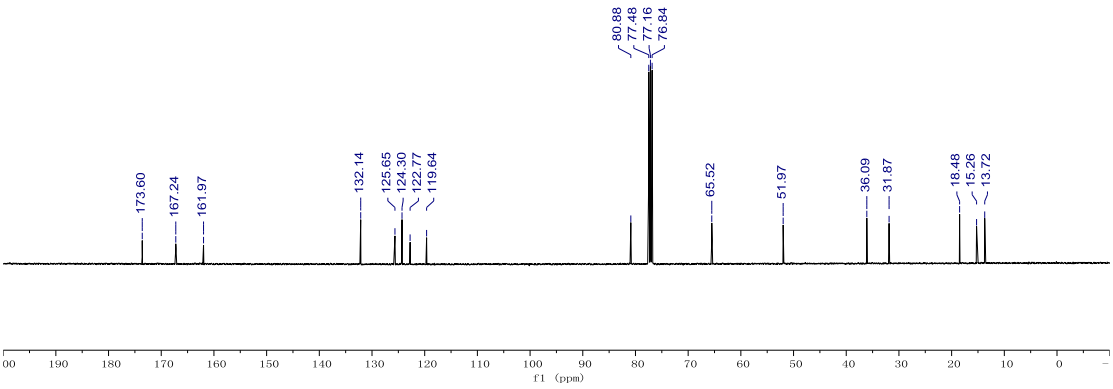

Me
MeO2C
OCOC3H7

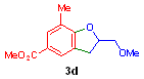
3c


7.70
7.26
5.08
5.07
5.07
5.06
5.06
5.05
5.05
5.04
5.04
5.03
4.32
4.31
4.27
4.26
4.24
4.23
3.86
3.37
3.34
3.33
3.30
3.04
3.02
3.00
2.98
2.31
2.30
2.28
2.21
1.63
1.62
1.60
1.58
1.56
0.93
0.92
0.90
1.92
1.00
2.01
3.00
1.01
1.00
1.98
3.00
1.95
2.99
f1 (ppm)

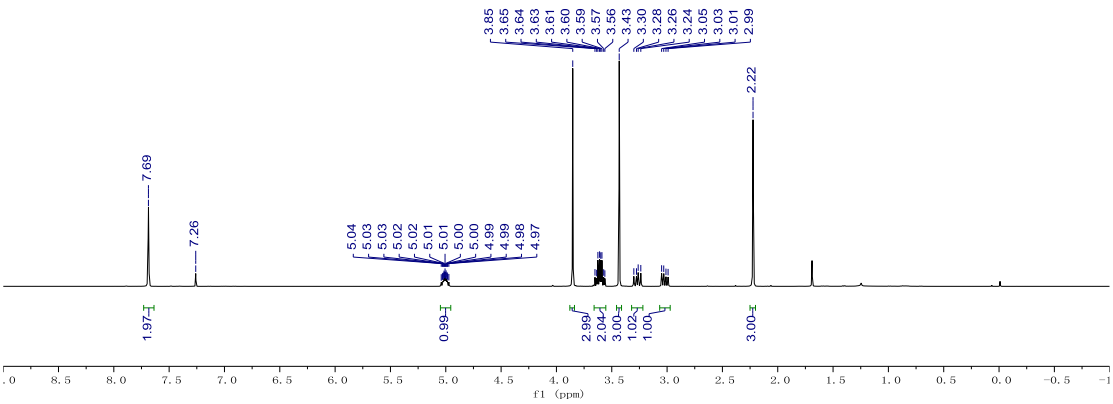

Me
MeO2C
OCOC3H7

3c


80.88
77.48
77.16
76.84
173.60
167.24
161.97
132.14
125.65
124.30
122.77
119.64
65.52
51.97
36.09
31.87
18.48
15.26
13.72
f1 (ppm)


Me
O
MeO2C
OMe

3d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3.65
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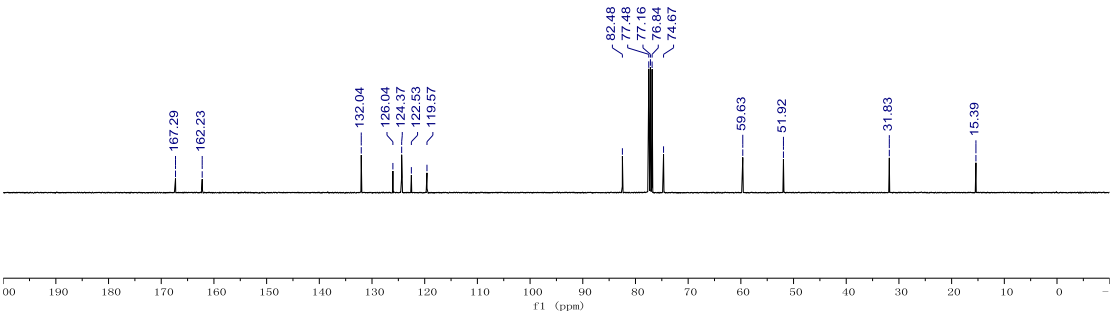
3.63
3.61
3.60
3.59
3.57
3.56
3.43
3.30
3.28
3.26
3.24
3.05
3.03
3.01
2.99
2.22
7.69
7.26
5.04
5.03
5.03
5.02
5.02
5.01
5.01
5.00
5.00
4.99
4.99
4.98
4.97
1.97
0.99
2.99
2.04
3.00
1.02
1.00
3.00
f1 (ppm)

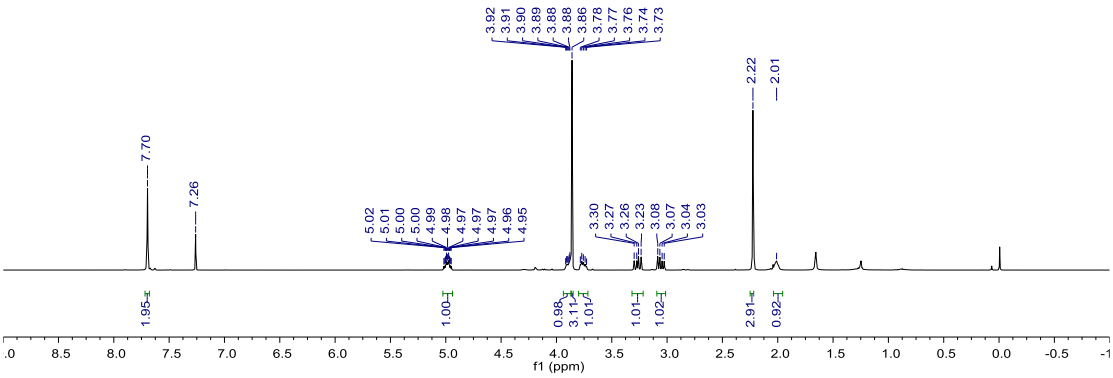

Me
O
MeO2C
OMe

3d


82.48
77.48
77.16
76.84
74.67
167.29
162.23
132.04
126.04
124.37
122.53
119.57
59.63
51.92
31.83
15.39
f1 (ppm)


Me
O
MeO2C
OH

3e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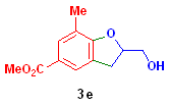
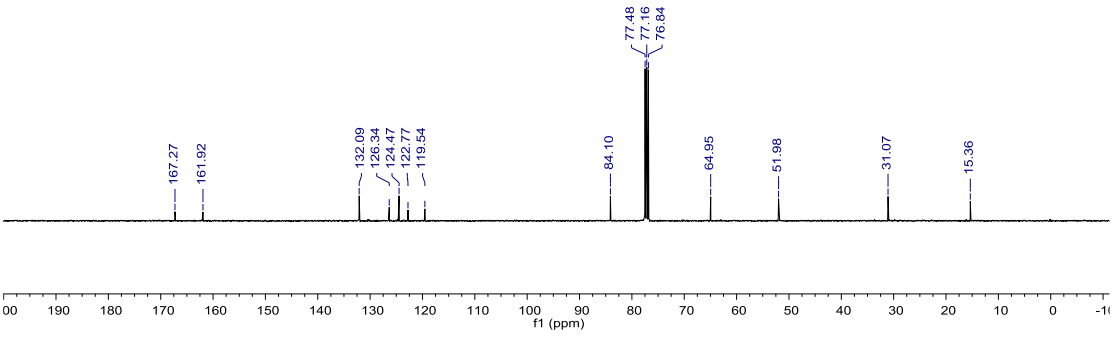
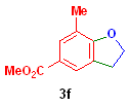
7.26
5.02
5.01
5.00
5.00
4.99
4.98
4.97
4.97
4.97
4.96
4.95
3.92
3.91
3.90
3.89
3.88
3.88
3.86
3.78
3.77
3.76
3.74
3.73
3.30
3.27
3.26
3.23
3.08
3.07
3.04
3.03
2.22
2.01
1.95
1.00
0.98
3.11
1.01
1.01
1.02
2.91
0.92
f1 (ppm)

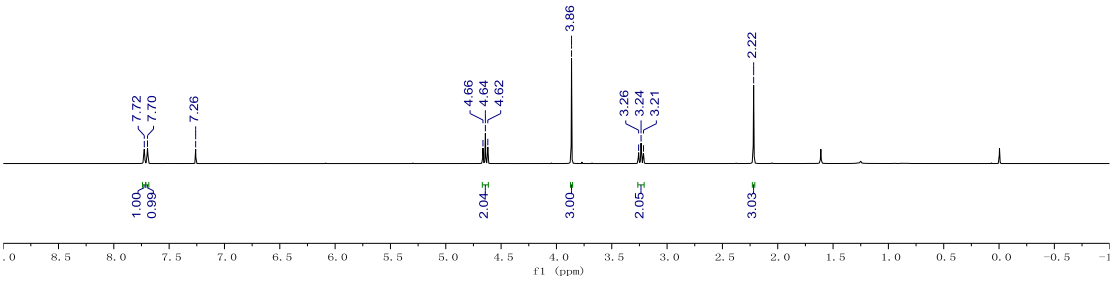

Me
O
MeO2C
OH

3e


77.48
77.16
76.84
167.27
161.92
132.09
126.34
124.47
122.77
119.54
84.10
64.95
51.98
31.07
15.36
f1 (ppm)

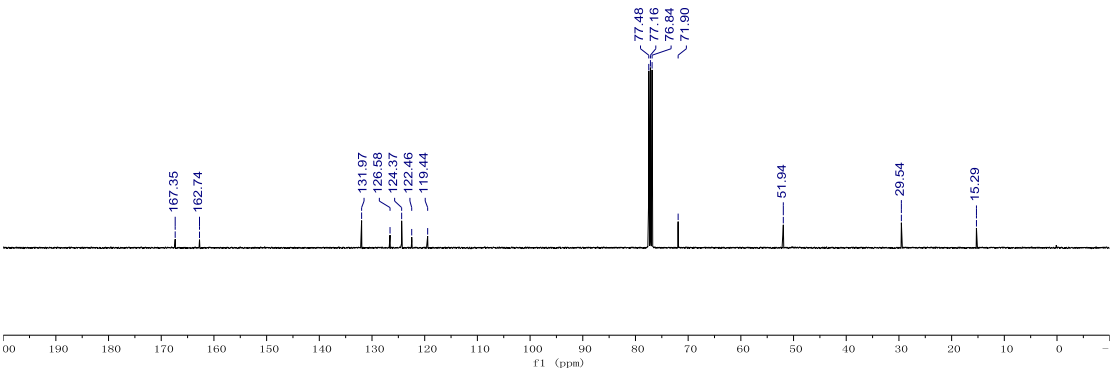

Me
O
MeO2C

3f


7.72
7.70
7.26
4.66
4.64
4.62
3.86
3.26
3.24
3.21
2.22
1.00
0.99
2.04
3.00
2.05
3.03
f1 (ppm)

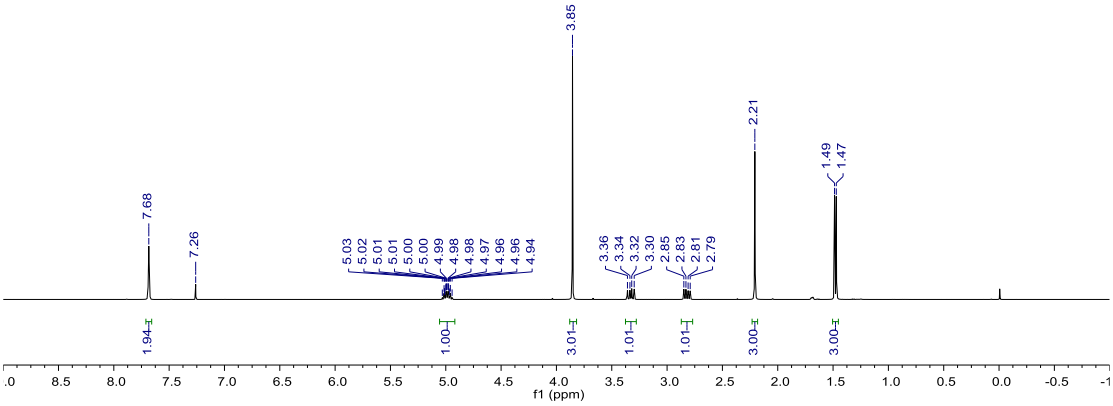

Me
O
MeO2C

3f


77.48
77.16
76.84
71.90
167.35
162.74
131.97
126.58
124.37
122.46
119.44
51.94
29.54
15.29
f1 (ppm)


Me
O
Me
MeO2C

3g


7.68
7.26
5.03
5.02
5.01
5.01
5.00
5.00
4.99
4.98
4.98
4.97
4.96
4.96
4.94
3.85
3.36
3.34
3.32
3.30
2.85
2.83
2.81
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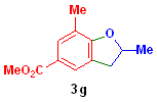
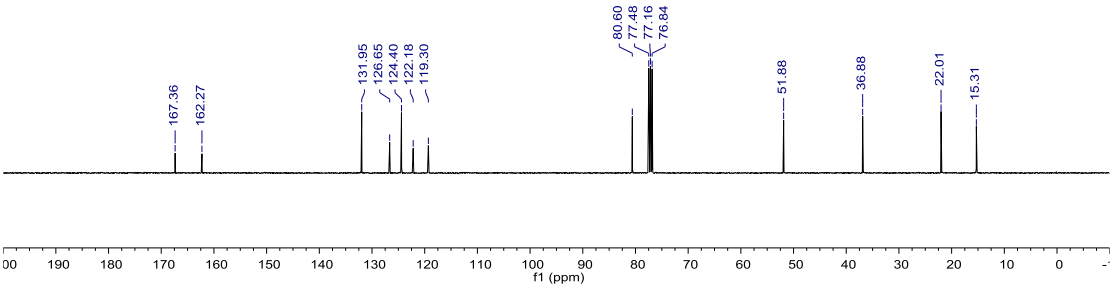
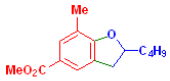
1.47
1.94
1.00
3.01
1.01
1.01
3.00
3.00
f1 (ppm)

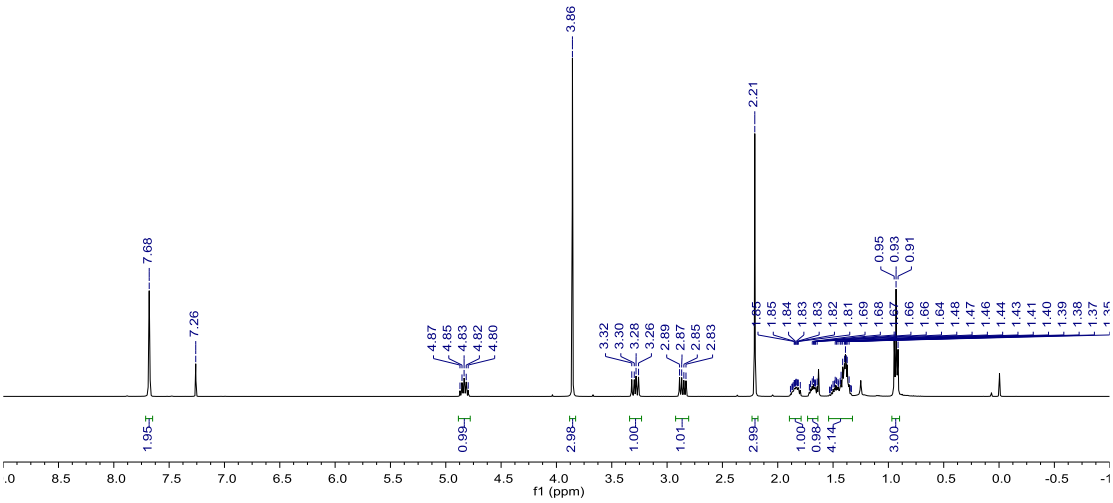

Me
O
Me
MeO2C

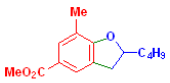
3g


167.36
162.27
131.95
126.65
124.40
122.18
119.30
80.60
77.48
77.16
76.84
51.88
36.88
22.01
15.31
f1 (ppm)

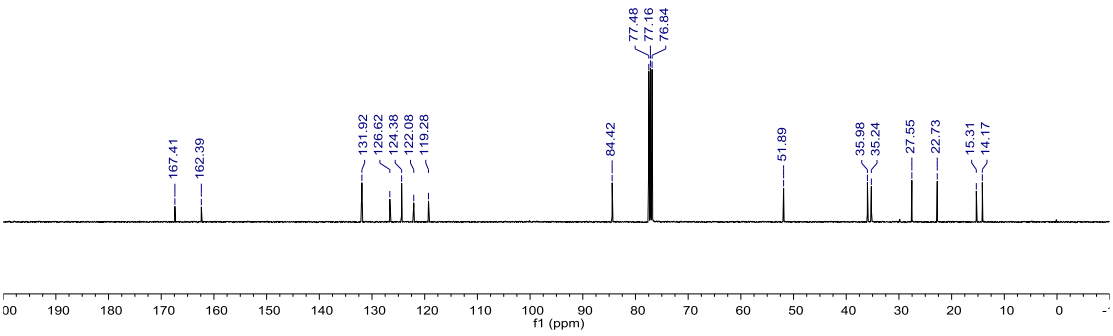

Me
O
C4H9
MeO2C

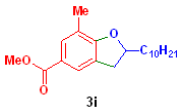
3h


7.68
7.26
4.87
4.85
4.83
4.82
4.80
3.86
3.32
3.30
3.28
3.26
2.89
2.87
2.85
2.83
2.21
1.85
1.84
1.83
1.82
1.81
1.69
1.68
1.67
1.66
1.64
1.48
1.47
1.46
1.44
1.43
1.41
1.40
1.39
1.38
1.37
0.95
0.93
0.91
1.95
0.99
2.98
1.00
1.01
2.99
1.00
0.98
4.14
3.00
f1 (ppm)

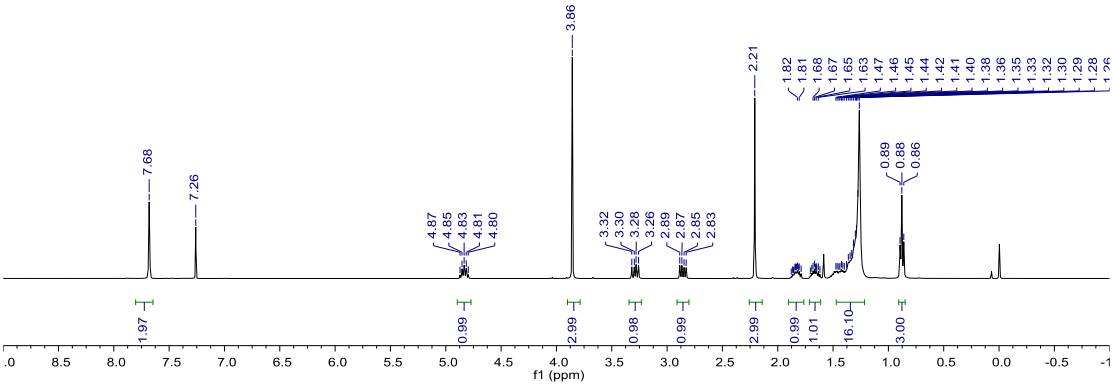

Me
O
C4H9
MeO2C

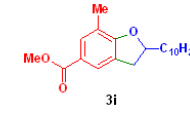
3h


167.41
162.39
131.92
126.62
124.38
122.08
119.28
84.42
77.48
77.16
76.84
51.89
35.98
35.24
27.55
22.73
15.31
14.17
f1 (ppm)

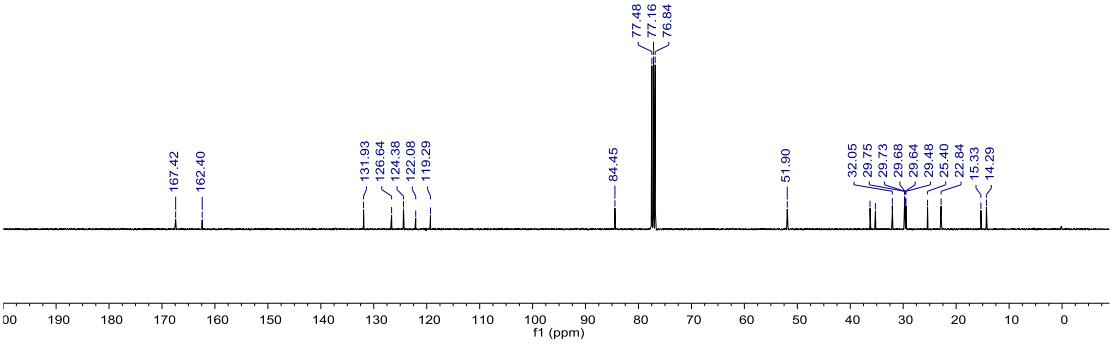

Me
O
MeO
O
$C_{10}H_{21}$

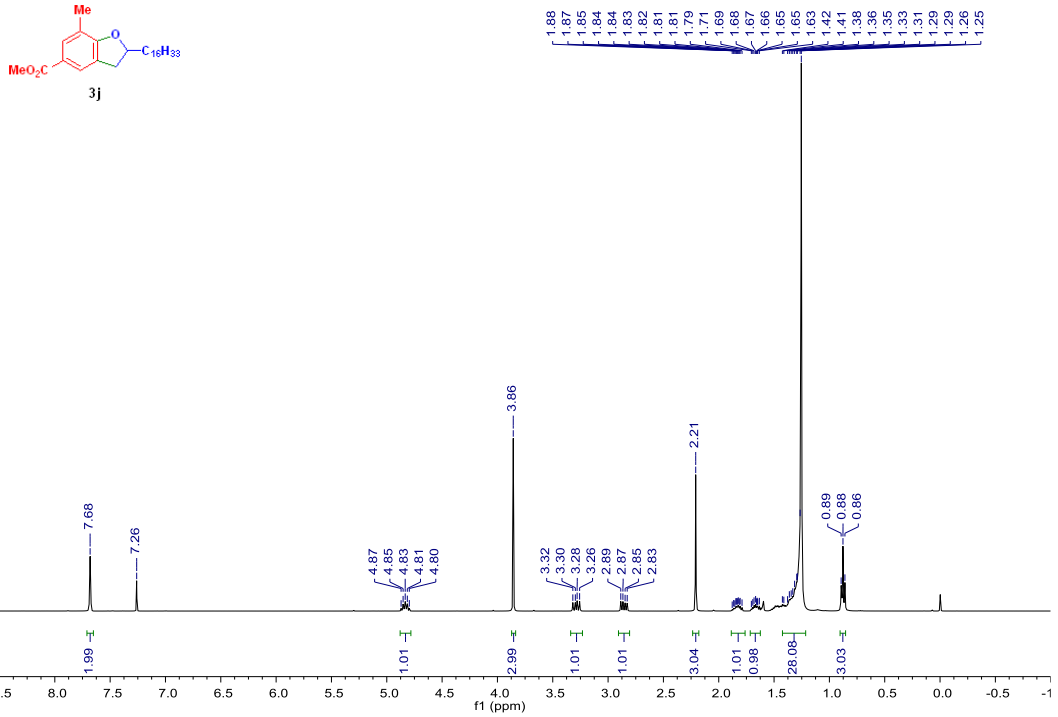
3i

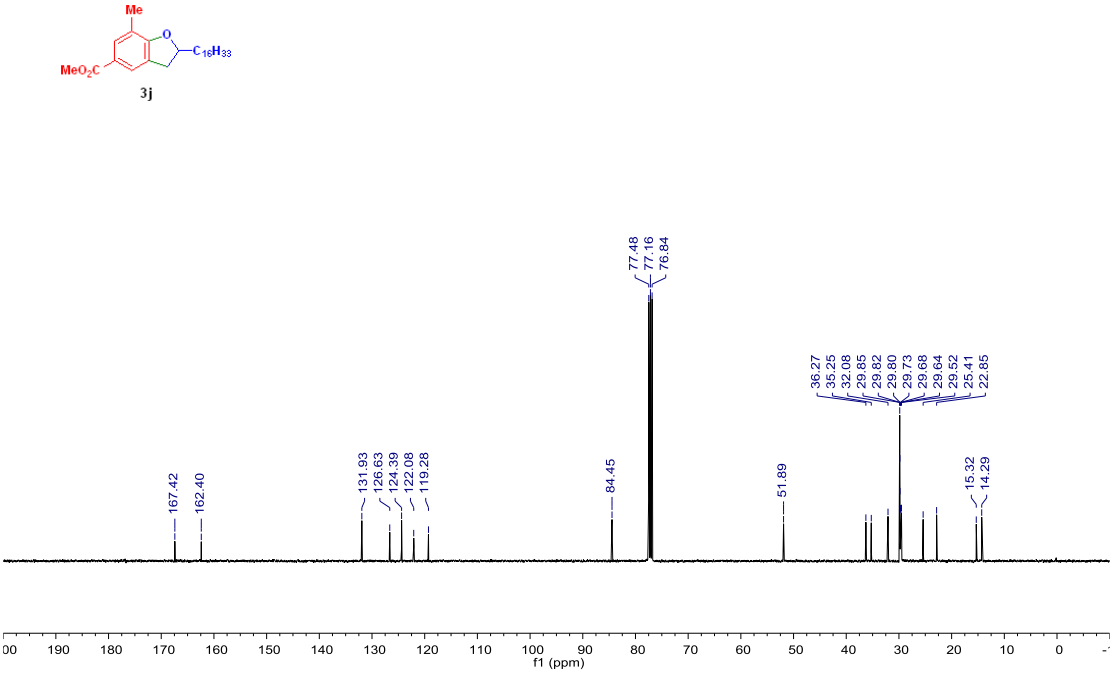

7.68
7.26
4.87
4.85
4.83
4.81
4.80
3.86
3.32
3.30
3.28
3.26
2.89
2.87
2.85
2.83
2.21
1.82
1.81
1.68
1.67
1.65
1.63
1.47
1.46
1.45
1.44
1.42
1.41
1.40
1.38
1.36
1.35
1.33
1.32
1.30
1.29
1.28
0.89
0.88
0.86
1.97
0.99
2.99
0.98
0.99
2.99
0.99
1.01
16.10
3.00
f1 (ppm)

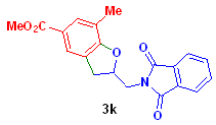

Me
O
MeO
O
$C_{10}H_{21}$

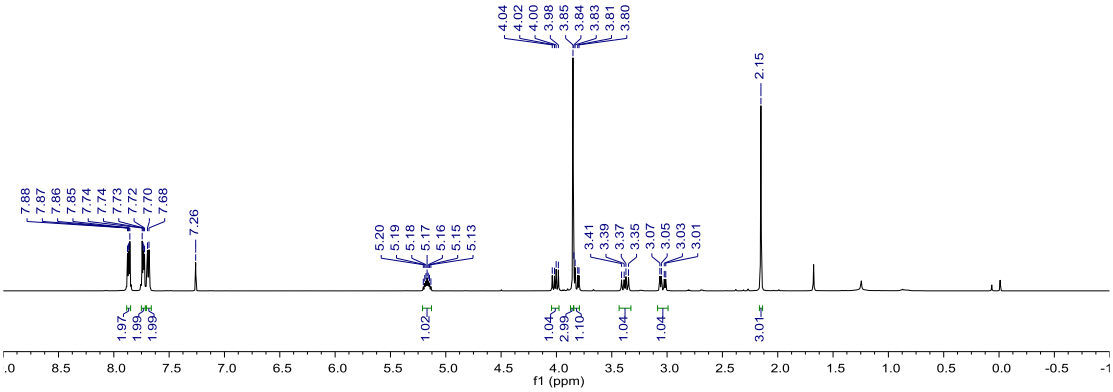
3i

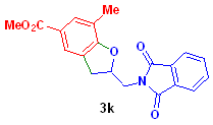

77.48
77.16
76.84
167.42
162.40
131.93
126.64
124.38
122.08
119.29
84.45
51.90
32.05
29.75
29.73
29.68
29.64
29.48
25.40
22.84
15.33
14.29
f1 (ppm)

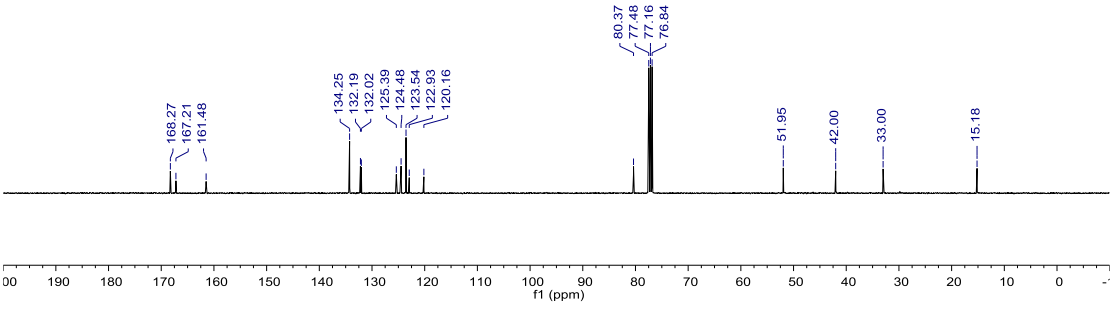

Me
MeO2C
C16H33
3j
1.88
1.87
1.85
1.84
1.84
1.83
1.82
1.81
1.81
1.79
1.71
1.69
1.68
1.67
1.66
1.65
1.65
1.63
1.42
1.41
1.38
1.36
1.35
1.33
1.31
1.29
1.29
1.26
1.25
7.68
7.26
4.87
4.85
4.83
4.81
4.80
3.86
3.32
3.30
3.28
3.26
2.89
2.87
2.85
2.83
2.21
0.89
0.88
0.86
1.99
1.01
2.99
1.01
1.01
3.04
1.01
0.98
28.08
3.03
f1 (ppm)

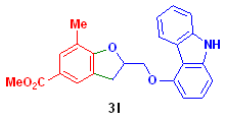

Me
MeO2C
C16H33
3j
77.48
77.16
76.84
36.27
35.25
32.08
29.85
29.82
29.80
29.73
29.68
29.64
29.52
25.41
22.85
167.42
162.40
131.93
126.63
124.39
122.08
119.28
84.45
51.89
15.32
14.29
f1 (ppm)


Me
MeO2C
O
N
O
O
3k

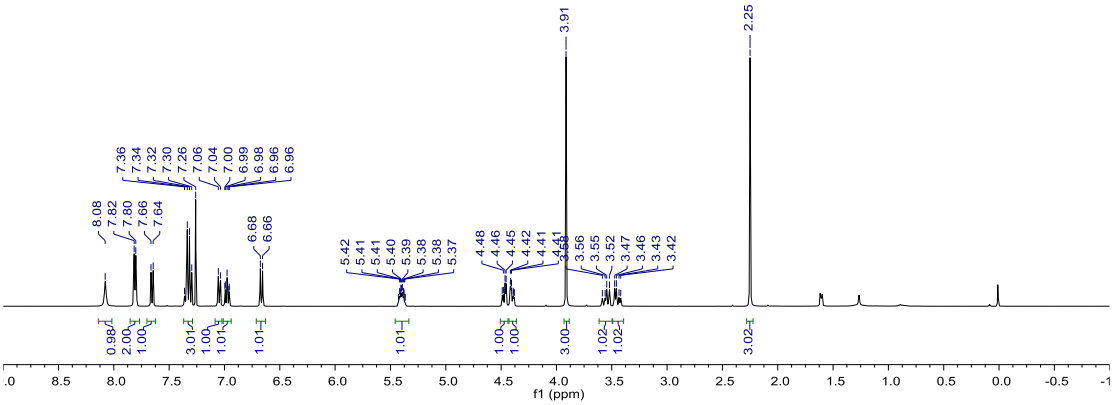

7.88
7.87
7.86
7.85
7.74
7.74
7.73
7.72
7.70
7.68
7.26
5.20
5.19
5.18
5.17
5.16
5.15
5.13
4.04
4.02
4.00
3.98
3.85
3.84
3.83
3.81
3.80
3.41
3.39
3.37
3.35
3.07
3.05
3.03
3.01
2.15
1.97
1.99
1.99
1.02
1.04
2.99
1.10
1.04
1.04
3.01
f1 (ppm)

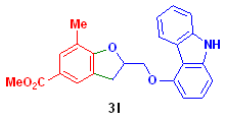

Me
MeO2C
O
N
O
O
3k


168.27
167.21
161.48
134.25
132.19
132.02
125.39
124.48
123.54
122.93
120.16
80.37
77.48
77.16
76.84
51.95
42.00
33.00
15.18
f1 (ppm)

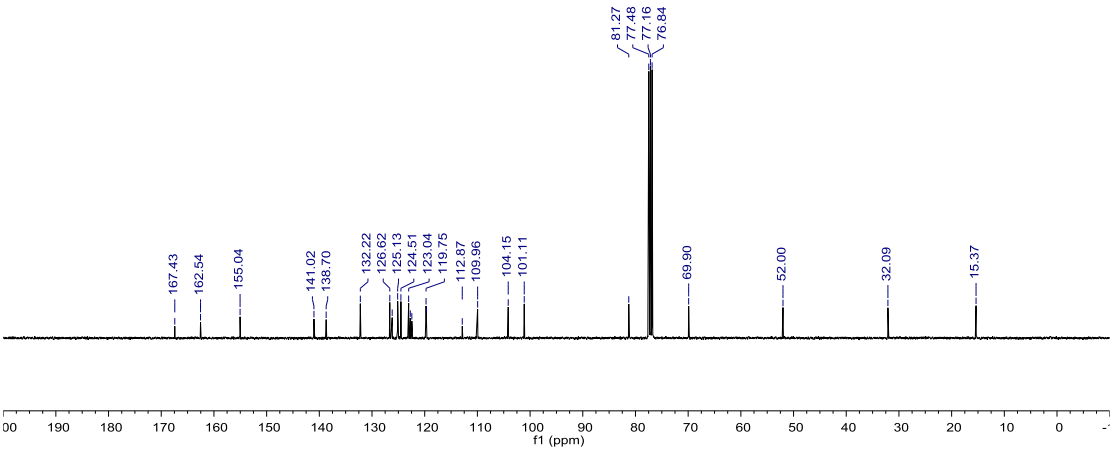

Me
MeO2C
O
O
NH

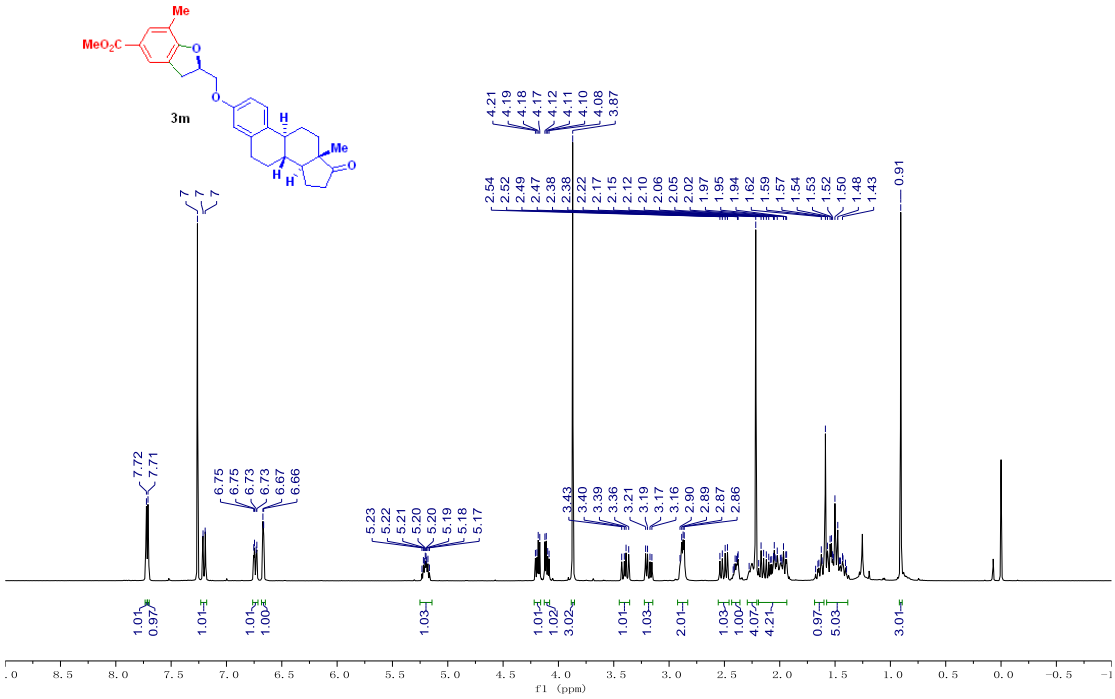
3l

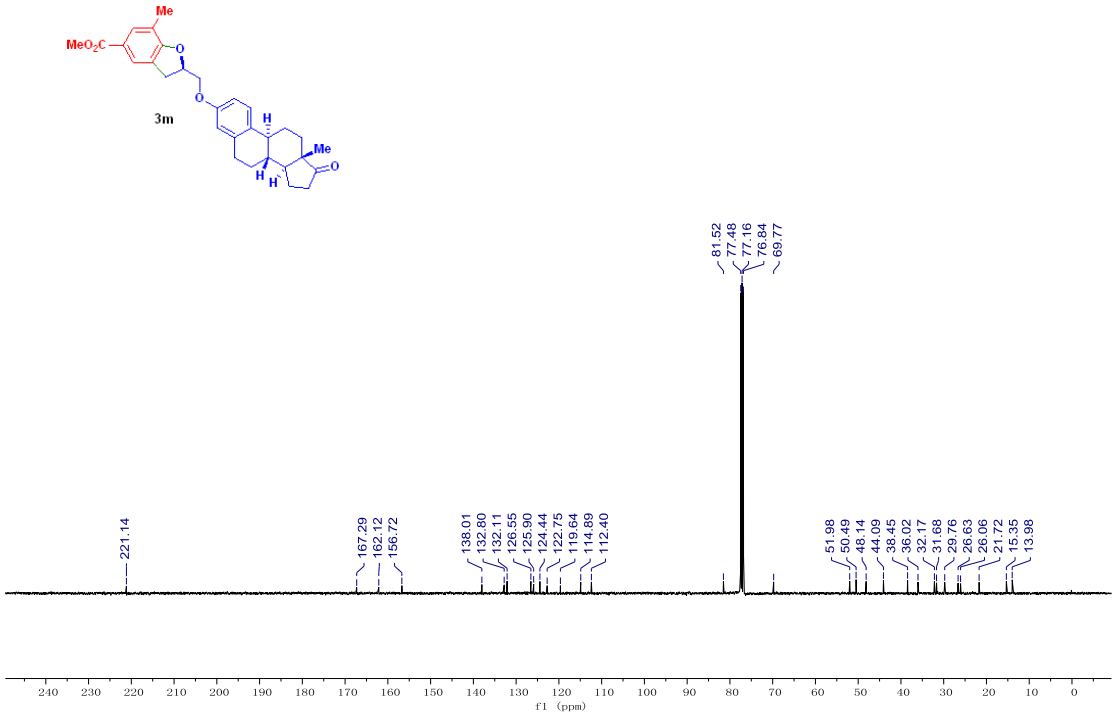

8.08
7.82
7.80
7.66
7.64
7.36
7.34
7.32
7.30
7.26
7.06
7.04
7.00
6.99
6.98
6.96
6.96
6.68
6.66
5.42
5.41
5.41
5.40
5.39
5.38
5.38
5.37
4.48
4.46
4.45
4.42
4.41
4.41
3.91
3.56
3.55
3.52
3.47
3.46
3.43
3.42
2.25
0.98
2.00
1.00
3.01
1.00
1.01
1.01
1.01
1.00
1.00
3.00
1.02
1.02
3.02
f1 (ppm)

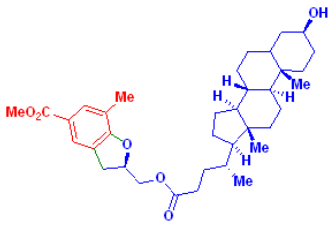

Me
MeO2C
O
O
NH

3l

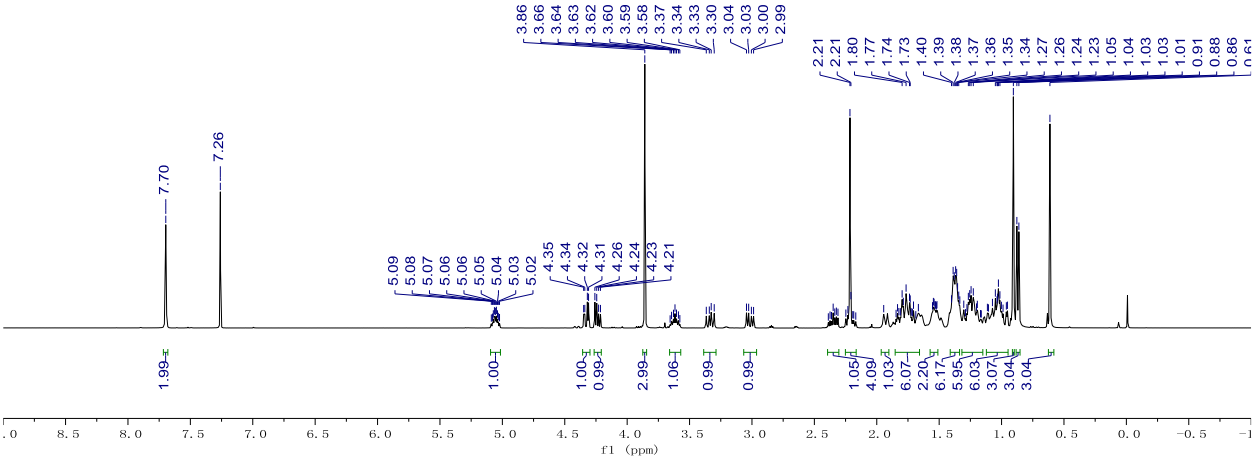

81.27
77.48
77.16
76.84
167.43
162.54
155.04
141.02
138.70
132.22
126.62
125.13
124.51
123.04
119.75
112.87
109.96
104.15
101.11
69.90
52.00
32.09
15.37
f1 (ppm)

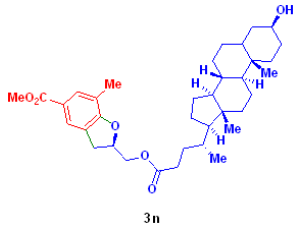

Me
MeO2C
O
3m
H
Me
O
H
H
7.72
7.71
6.75
6.75
6.73
6.73
6.67
6.66
5.23
5.22
5.21
5.20
5.20
5.19
5.18
5.17
4.21
4.19
4.18
4.17
4.12
4.11
4.10
4.08
3.87
3.43
3.40
3.39
3.36
3.21
3.19
3.17
3.16
2.90
2.89
2.87
2.86
2.54
2.52
2.49
2.47
2.38
2.38
2.22
2.17
2.15
2.12
2.10
2.06
2.05
2.02
1.97
1.95
1.94
1.62
1.59
1.57
1.54
1.53
1.52
1.50
1.48
1.43
0.91
1.01
0.97
1.01
1.01
1.00
1.03
1.01
1.02
3.02
1.01
1.03
2.01
1.03
1.00
4.07
4.21
0.97
5.03
3.01
f1 (ppm)


Me
MeO2C
O
3m
H
Me
O
H
H
81.52
77.48
77.16
76.84
69.77
221.14
167.29
162.12
156.72
138.01
132.80
132.11
126.55
125.90
124.44
122.75
119.64
114.89
112.40
51.98
50.49
48.14
44.09
38.45
36.02
32.17
31.68
29.76
26.63
26.06
21.72
15.35
13.98
f1 (ppm)

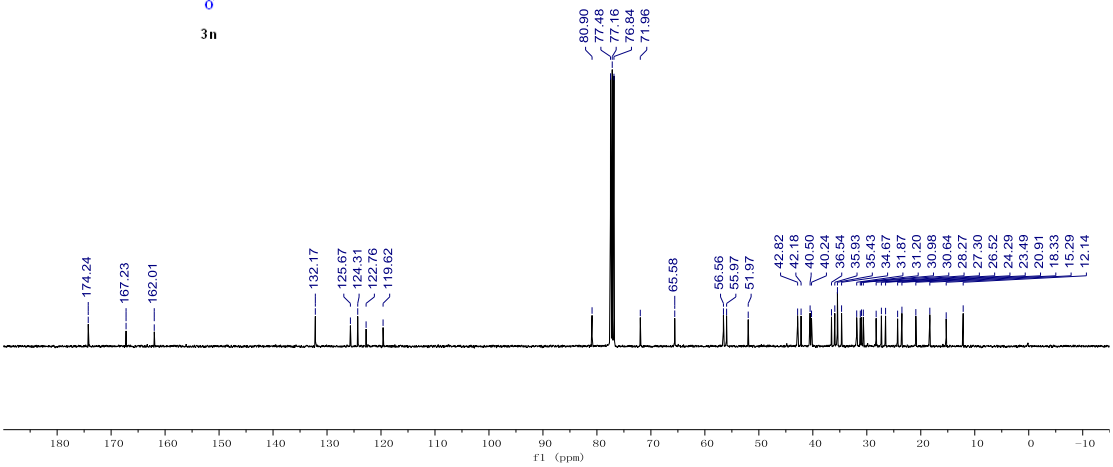

OH
Me
MeO2C
O
H
Me
H
Me
H
Me
O
O
O

3n


7.70
7.26
f1 (ppm)

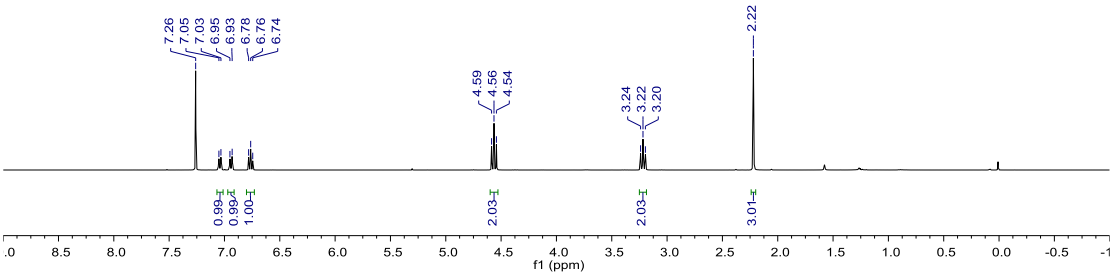

OH
Me
MeO2C
O
H
Me
H
Me
H
Me
O
O

3n


174.24
167.23
162.01
132.17
125.67
124.31
122.78
119.62
80.90
77.48
77.16
76.84
71.96
65.58
56.56
55.97
51.97
42.82
42.18
40.50
40.24
36.54
35.93
35.43
34.67
31.87
31.20
30.98
30.64
28.27
27.30
26.52
24.29
23.49
20.91
18.33
15.29
12.14
f1 (ppm)

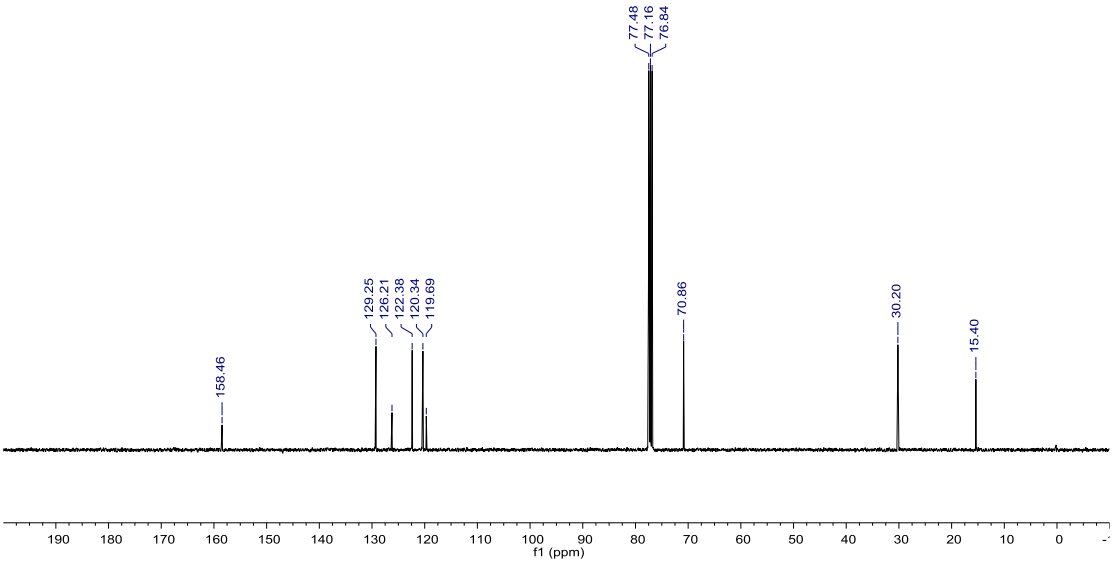

Me
O

3a'


7.26
7.05
7.03
6.95
6.93
6.78
6.76
6.74
4.59
4.56
4.54
3.24
3.22
3.20
2.22
0.99
0.99
1.00
2.03
2.03
3.01
f1 (ppm)

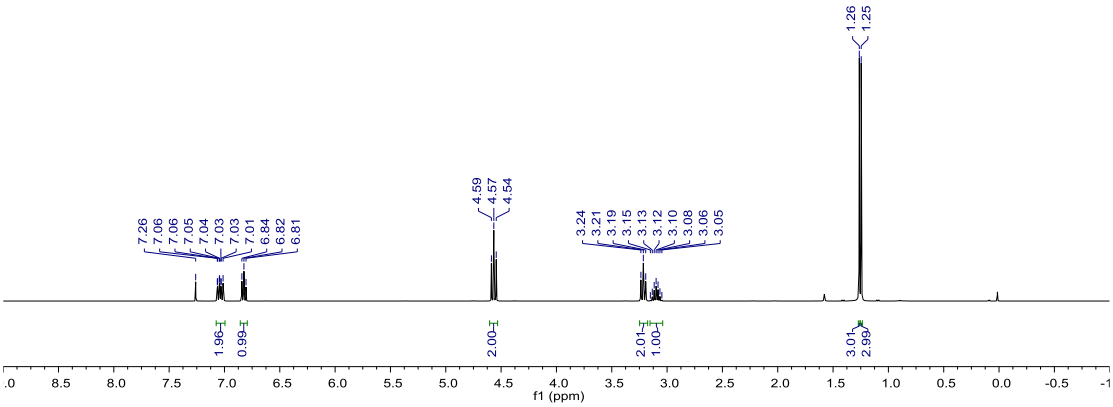

Me
O

3a'


77.48
77.16
76.84
158.46
129.25
126.21
122.38
120.34
119.69
70.86
30.20
15.40
f1 (ppm)

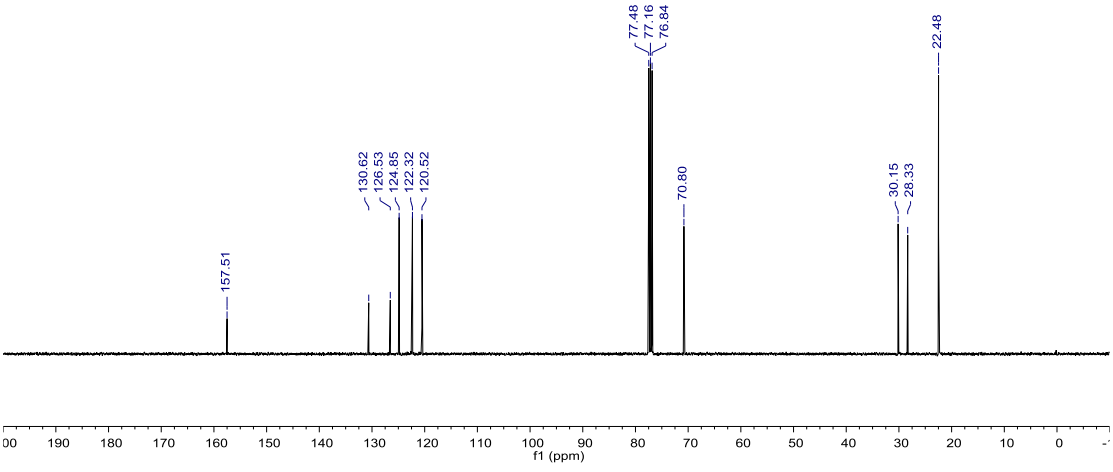

Me
Me
O

3b'

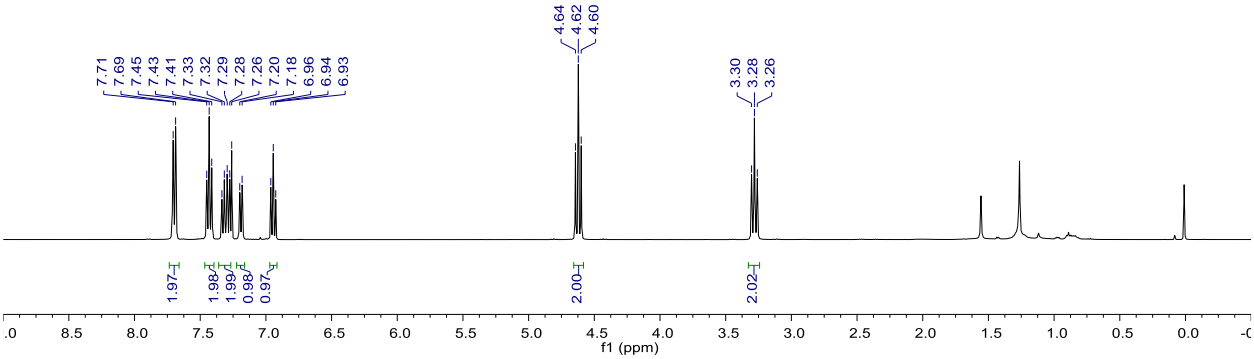

7.26
7.06
7.06
7.05
7.04
7.03
7.03
7.01
6.84
6.82
6.81
4.59
4.57
4.54
3.24
3.21
3.19
3.15
3.13
3.12
3.10
3.08
3.06
3.05
1.26
1.25
1.96
0.99
2.00
2.01
1.00
3.01
2.99
f1 (ppm)


Me
Me
O

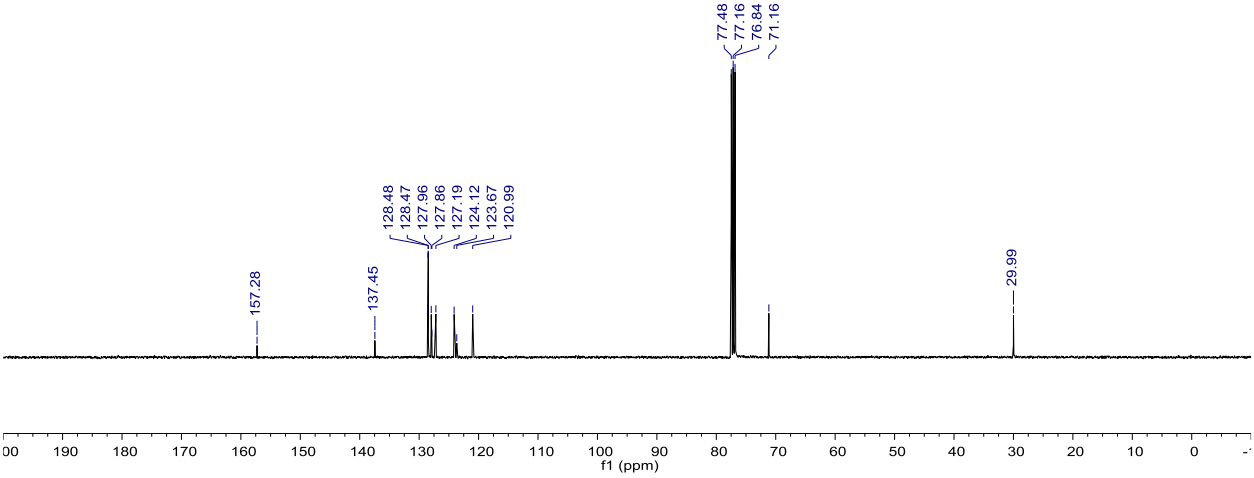
3b'

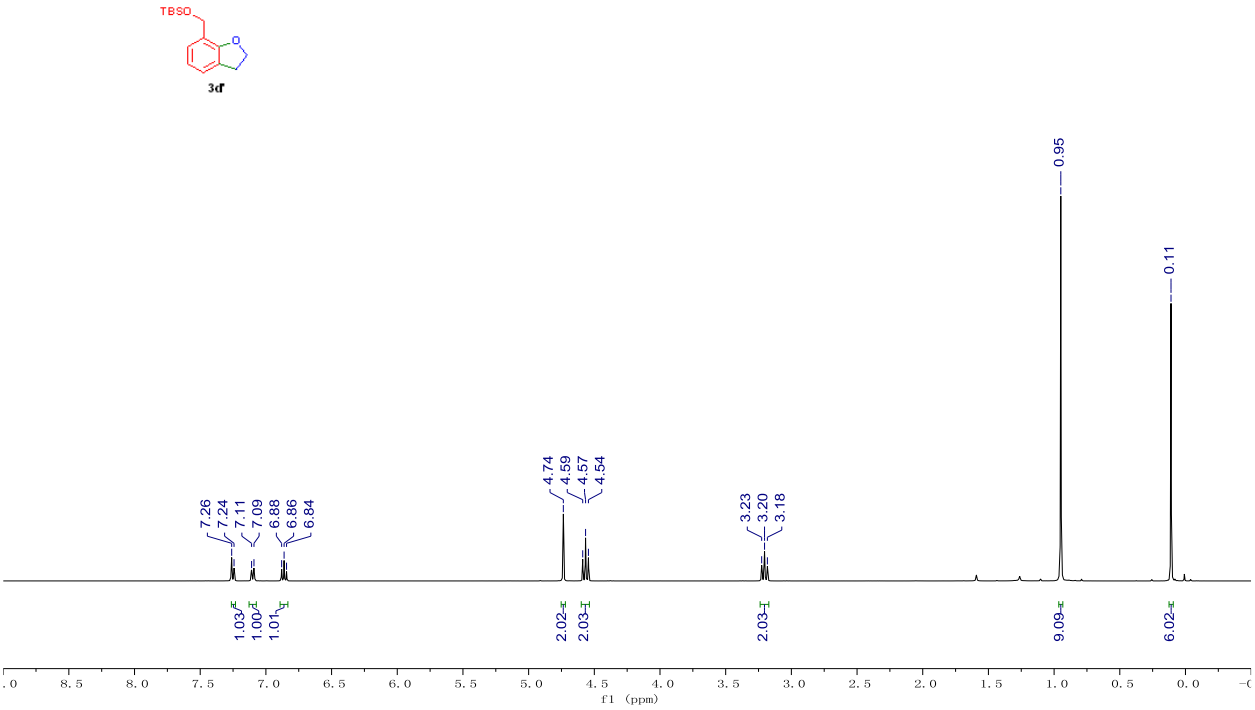

157.51
130.62
126.53
124.85
122.32
120.52
77.48
77.16
76.84
70.80
30.15
28.33
22.48
f1 (ppm)

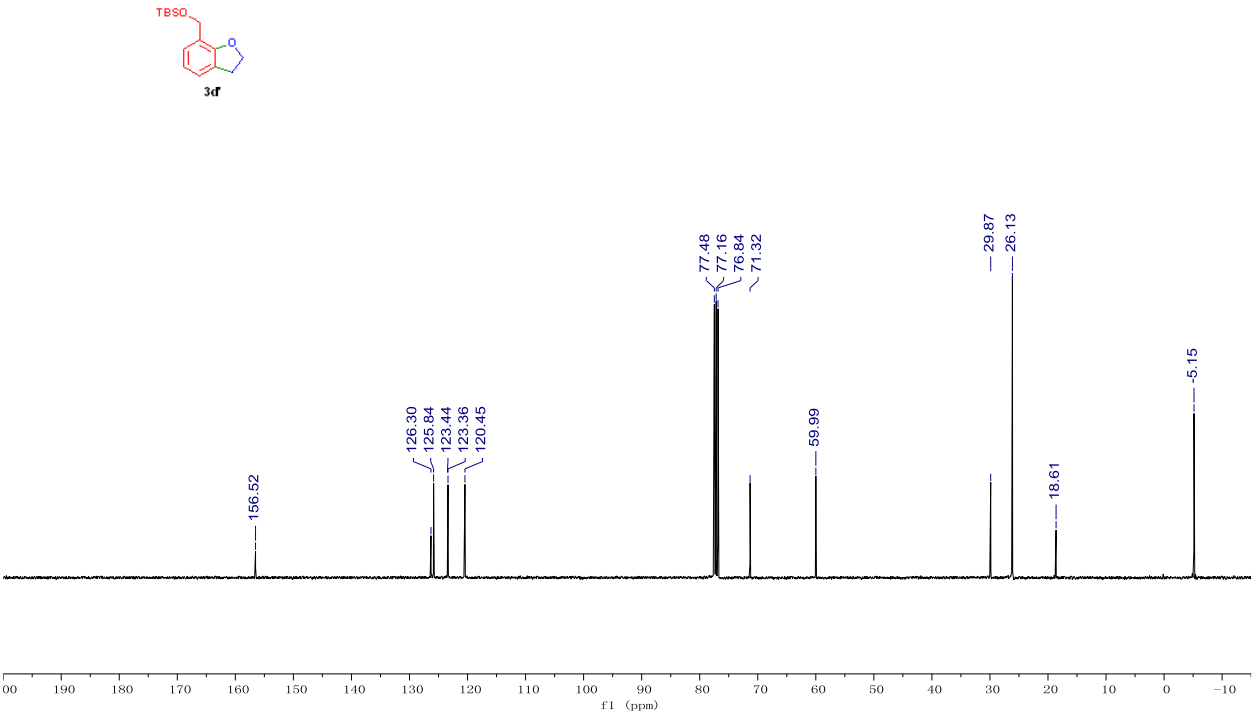

Ph
O
3c'

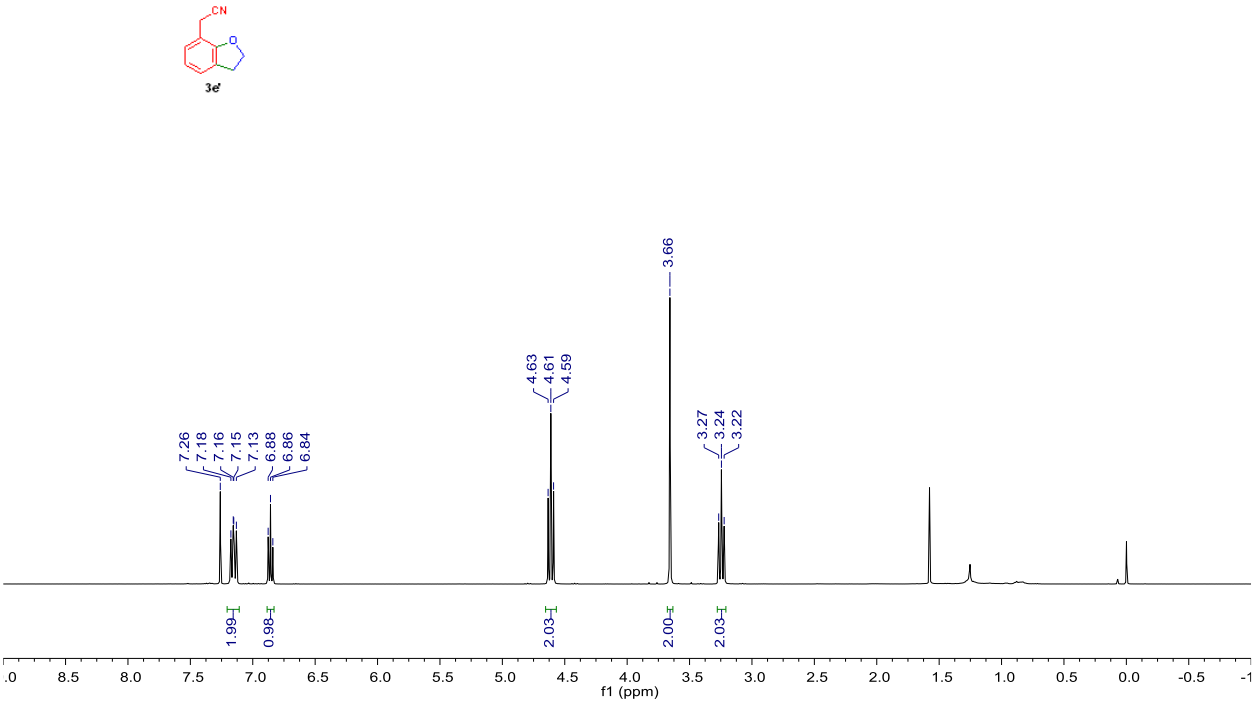

7.71
7.69
7.45
7.43
7.41
7.33
7.32
7.29
7.28
7.26
7.20
7.18
6.96
6.94
6.93
4.64
4.62
4.60
3.30
3.28
3.26
1.97
1.98
1.99
0.98
0.97
2.00
2.02
f1 (ppm)

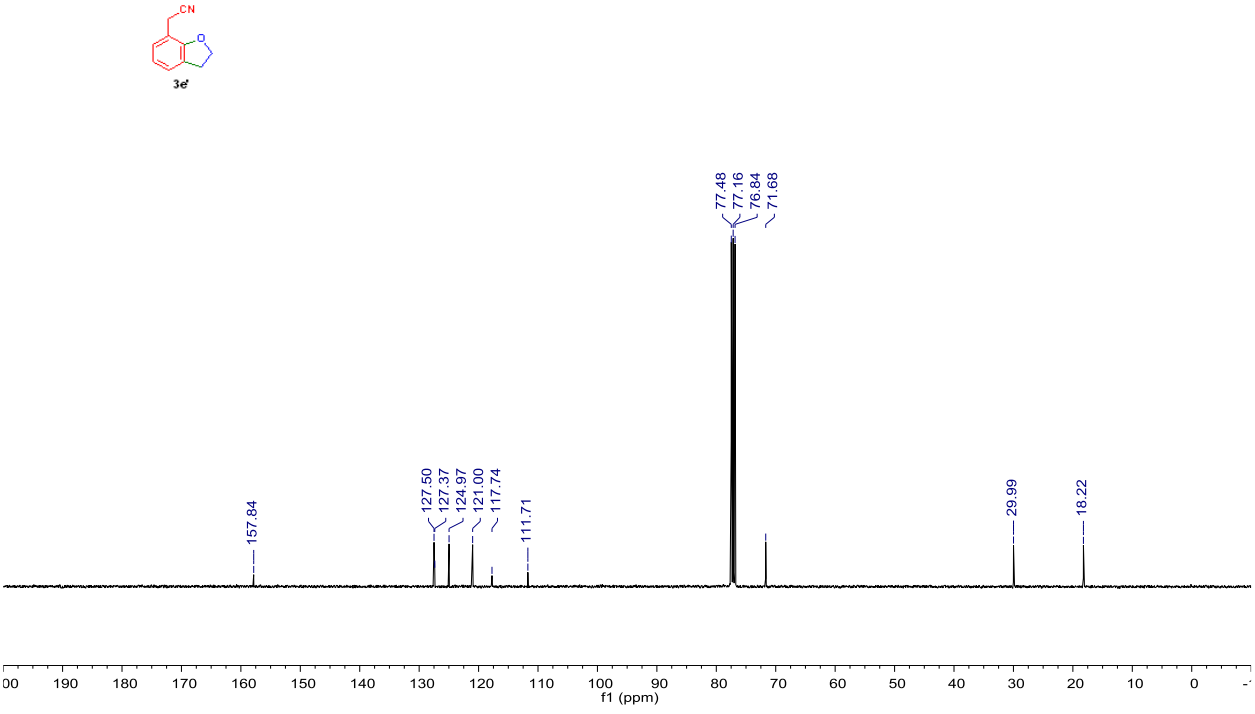

Ph
O
3c'

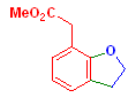

77.48
77.16
76.84
71.16
128.48
128.47
127.96
127.86
127.19
124.12
123.67
120.99
157.28
137.45
29.99
f1 (ppm)


TBSO
O
3df
7.26
7.24
7.11
7.09
6.88
6.86
6.84
4.74
4.59
4.57
4.54
3.23
3.20
3.18
0.95
0.11
1.03
1.00
1.01
2.02
2.03
2.03
9.09
6.02
f1 (ppm)

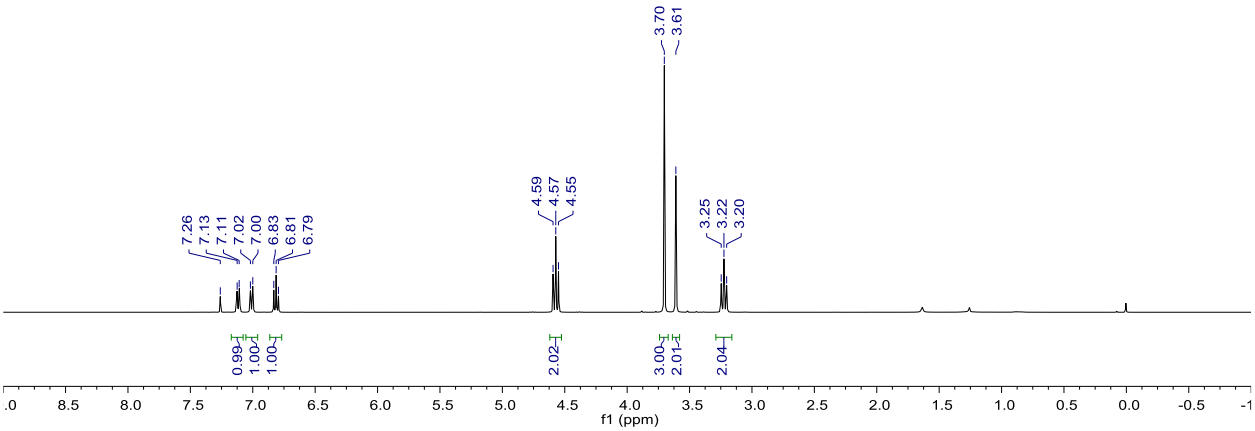

TBSO
O
3df
156.52
126.30
125.84
123.44
123.36
120.45
77.48
77.16
76.84
71.32
59.99
29.87
26.13
18.61
-5.15
f1 (ppm)

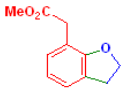

CN
O
3e'
7.26
7.18
7.16
7.15
7.13
6.88
6.86
6.84
4.63
4.61
4.59
3.66
3.27
3.24
3.22
1.99
0.98
2.03
2.00
2.03
f1 (ppm)


CN
O
3e'
77.48
77.16
76.84
71.68
157.84
127.50
127.37
124.97
121.00
117.74
111.71
29.99
18.22
f1 (ppm)

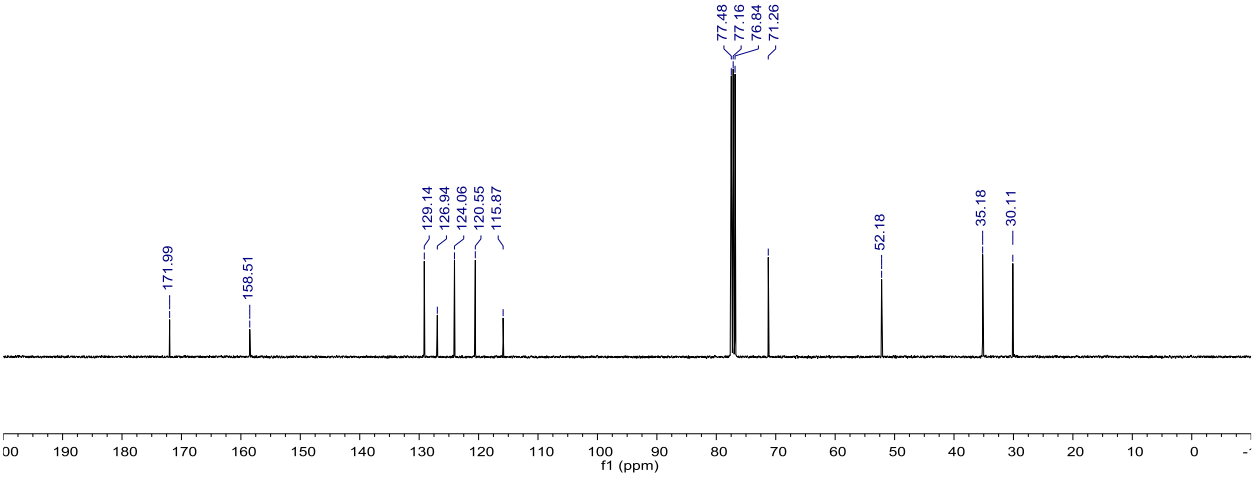

MeO2C
O

3f'


7.26
7.13
7.11
7.02
7.00
6.83
6.81
6.79
4.59
4.57
4.55
3.70
3.61
3.25
3.22
3.20
0.99
1.00
1.00
2.02
3.00
2.01
2.04
f1 (ppm)

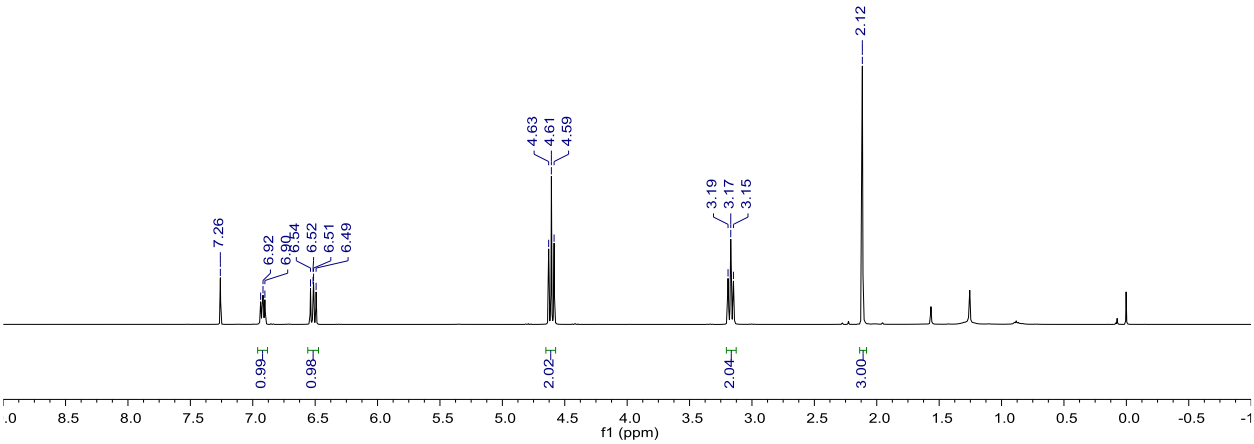

MeO2C
O

3f'


171.99
158.51
129.14
126.94
124.06
120.55
115.87
77.48
77.16
76.84
71.26
52.18
35.18
30.11
f1 (ppm)

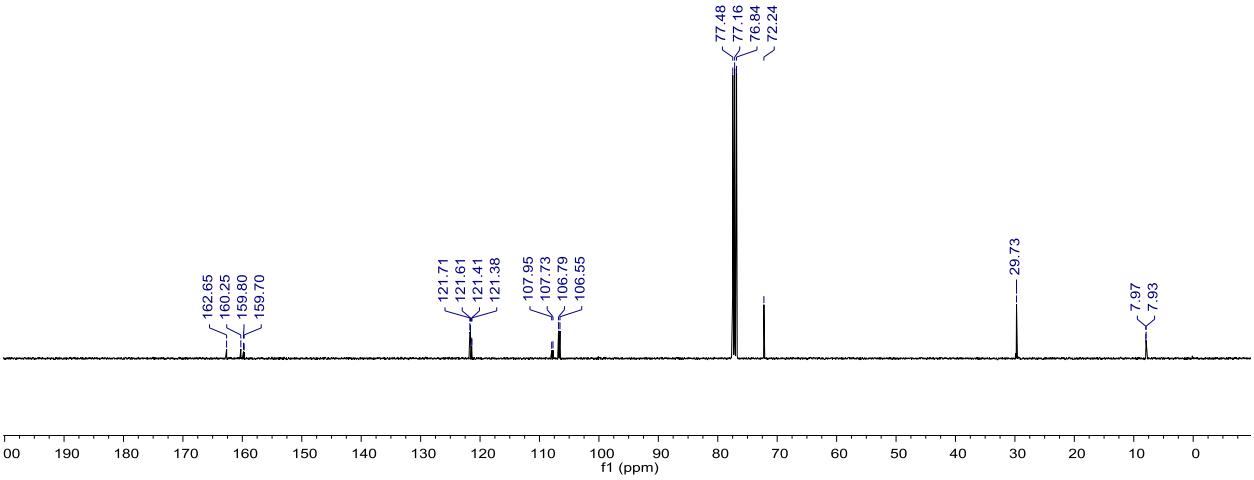

Me
F
O

3g'


7.26
6.92
6.90
6.54
6.52
6.51
6.49
4.63
4.61
4.59
3.19
3.17
3.15
2.12
0.99
0.98
2.02
2.04
3.00
f1 (ppm)

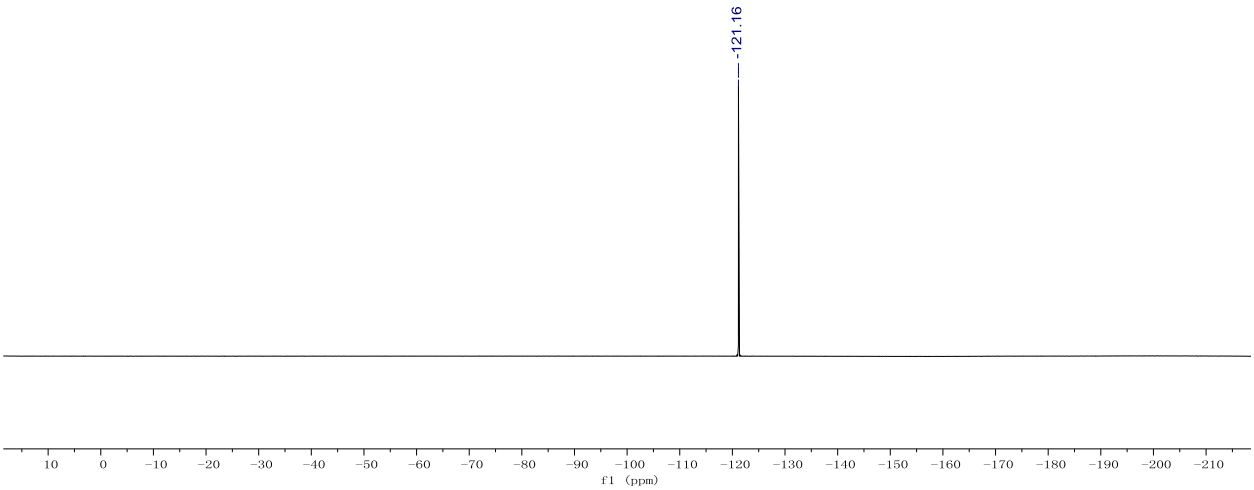

Me
F
O

3g'


77.48
77.16
76.84
72.24
162.65
160.25
159.80
159.70
121.71
121.61
121.41
121.38
107.95
107.73
106.79
106.55
29.73
7.97
7.93
f1 (ppm)

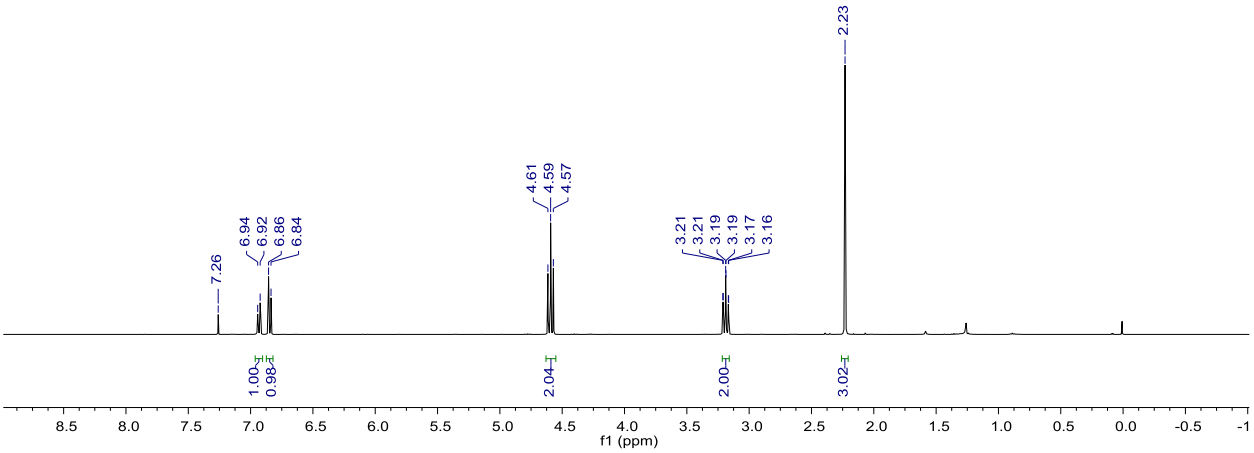

Me
F
O

3g'


-121.16
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

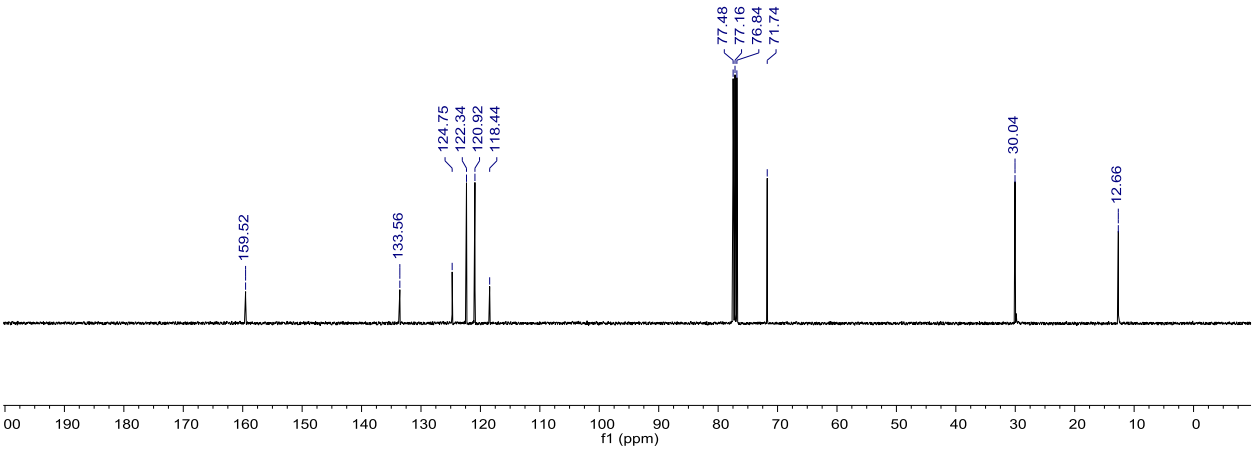

Me
Cl
O

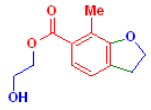
3h'


7.26
6.94
6.92
6.86
6.84
4.61
4.59
4.57
3.21
3.21
3.19
3.19
3.17
3.16
2.23
1.00
0.98
2.04
2.00
3.02
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 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

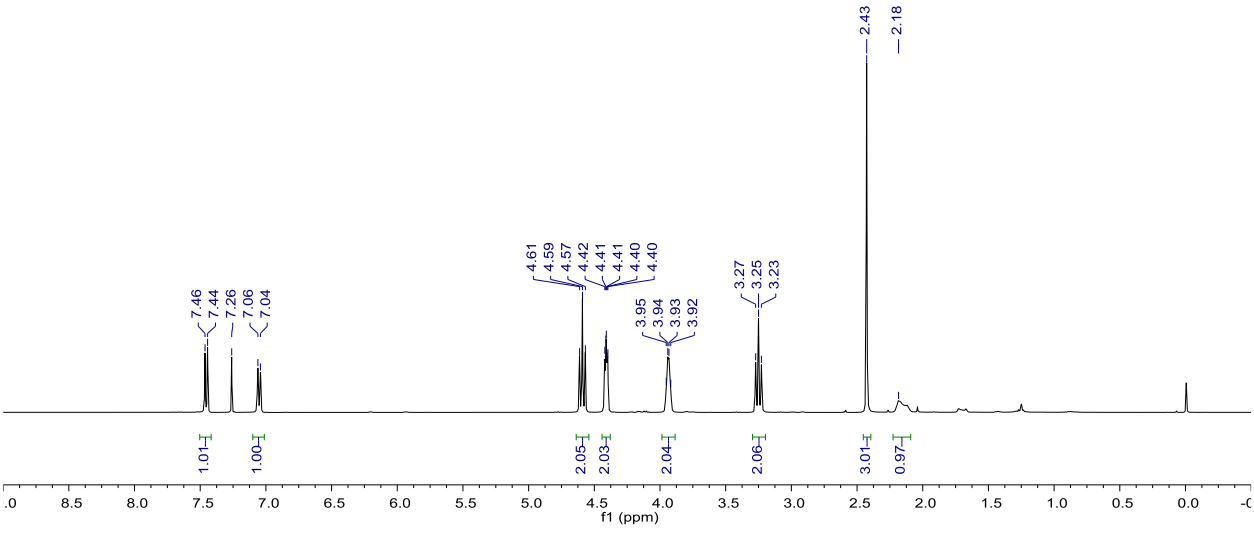

Me
Cl
O

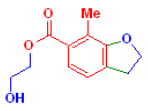
3h'


159.52
133.56
124.75
122.34
120.92
118.44
77.48
77.16
76.84
71.74
30.04
12.66
f1 (ppm)

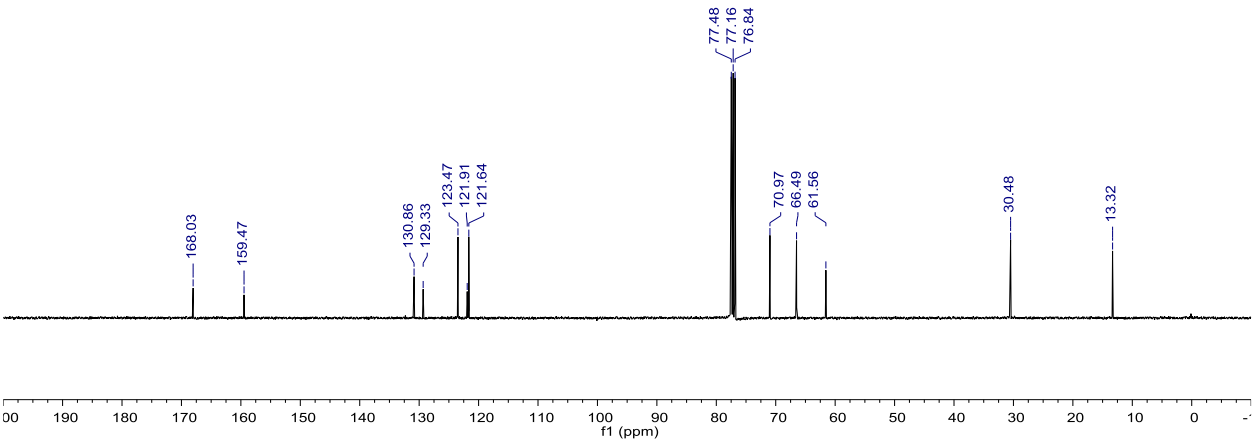

O
Me
O
O
OH

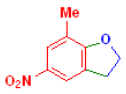
3i'


7.46
7.44
7.26
7.06
7.04
4.61
4.59
4.57
4.42
4.41
4.41
4.40
4.40
3.95
3.94
3.93
3.92
3.27
3.25
3.23
2.43
2.18
1.01
1.00
2.05
2.03
2.04
2.06
3.01
0.97
f1 (ppm)

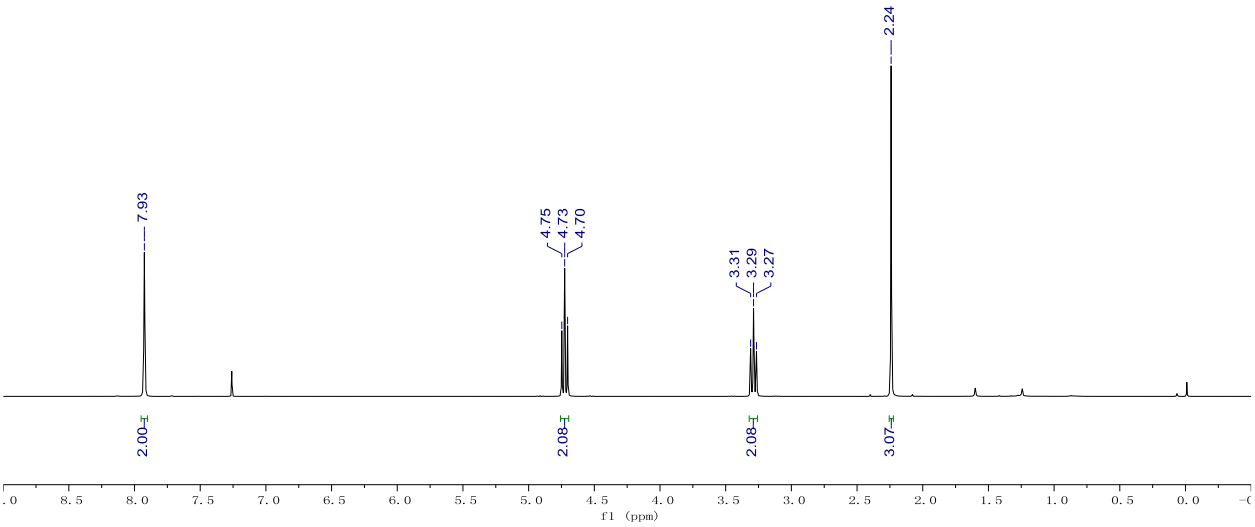

O
Me
O
O
OH

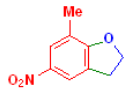
3i'


168.03
159.47
130.86
129.33
123.47
121.91
121.64
77.48
77.16
76.84
70.97
66.49
61.56
30.48
13.32
f1 (ppm)

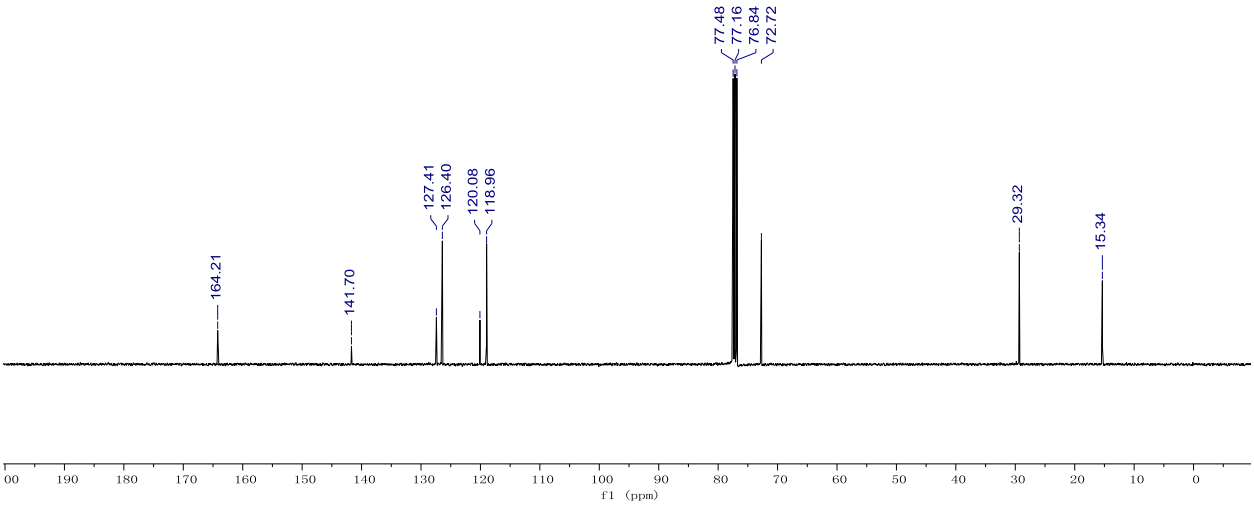

Me
O
O2N

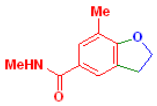
3j'


7.93
4.75
4.73
4.70
3.31
3.29
3.27
2.24
2.00
2.08
2.08
3.07
f1 (ppm)

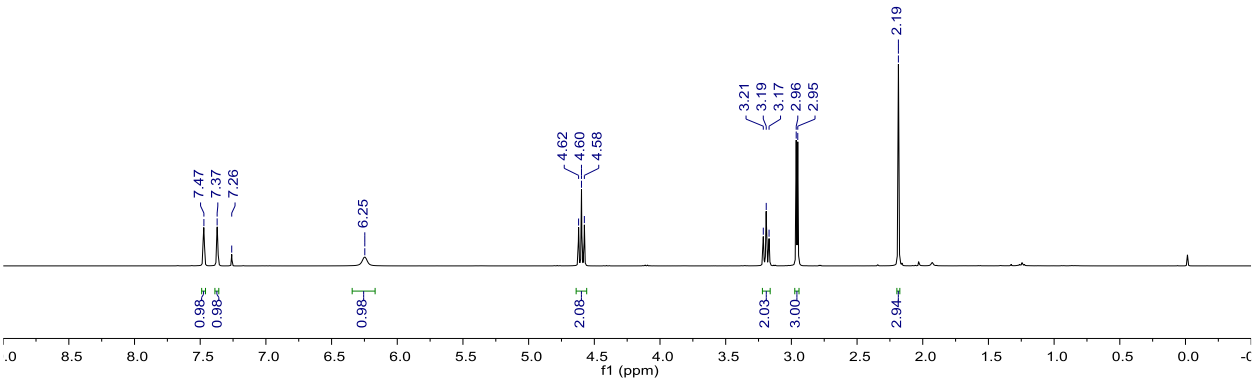

Me
O
O_2N

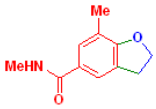
3j'


164.21
141.70
127.41
126.40
120.08
118.96
77.48
77.16
76.84
72.72
29.32
15.34
f1 (ppm)

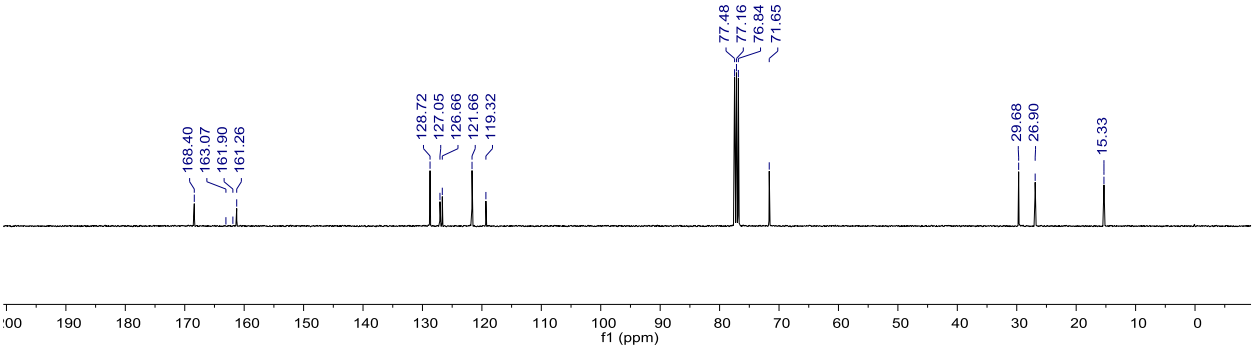

Me
O
MeHN
O

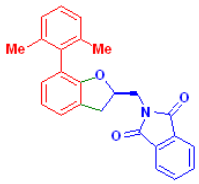
3k'


7.47
7.37
7.26
6.25
4.62
4.60
4.58
3.21
3.19
3.17
2.96
2.95
2.19
0.98
0.98
0.98
2.08
2.03
3.00
2.94
f1 (ppm)

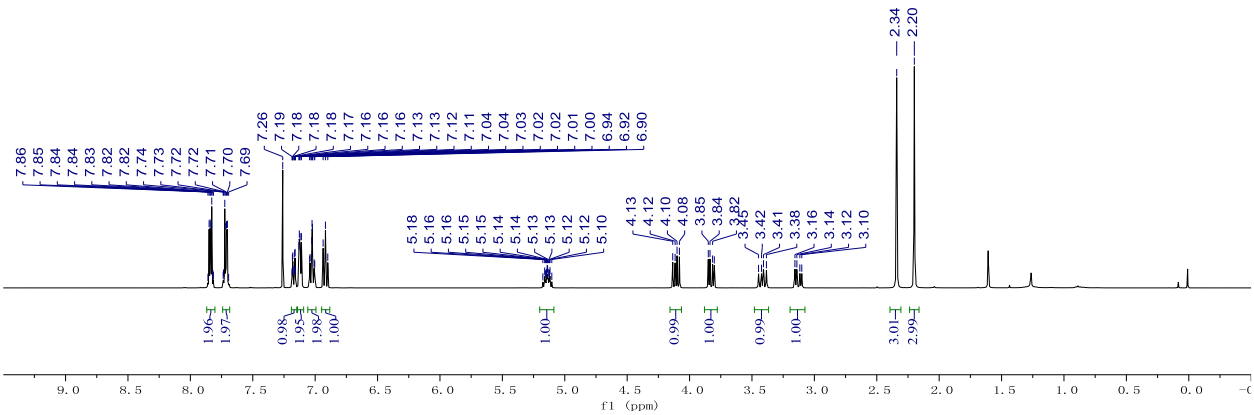

Me
MeHN
O
O

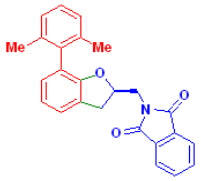
3k'


168.40
163.07
161.90
161.26
128.72
127.05
126.66
121.66
119.32
77.48
77.16
76.84
71.65
29.68
26.90
15.33
f1 (ppm)

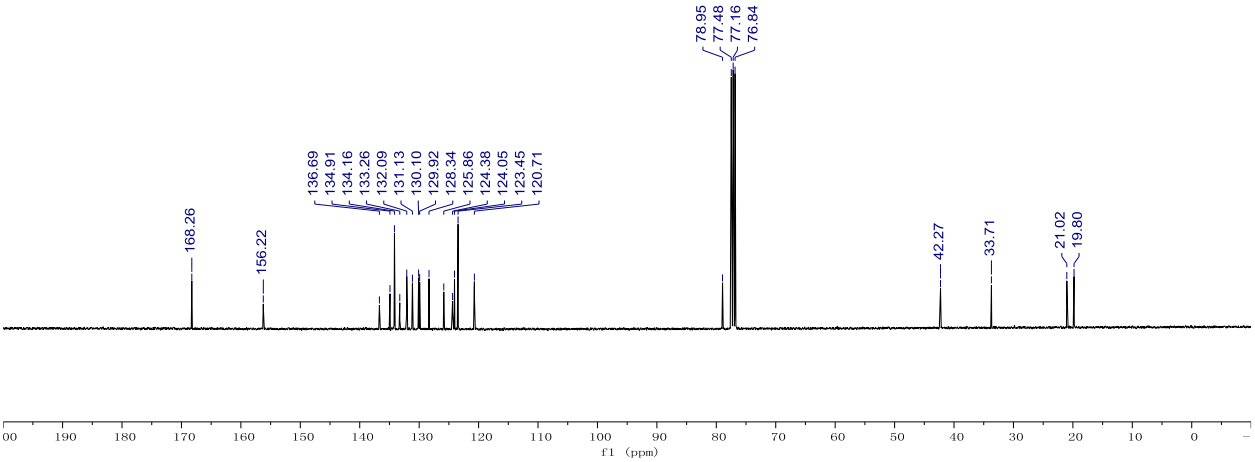

Me
Me
O
N
O
O

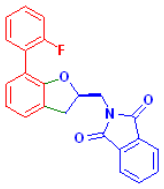
3m'


7.86
7.85
7.84
7.84
7.83
7.82
7.82
7.74
7.73
7.72
7.72
7.71
7.70
7.69
7.26
7.19
7.18
7.18
7.18
7.17
7.16
7.16
7.16
7.13
7.13
7.12
7.11
7.04
7.04
7.03
7.02
7.02
7.01
7.00
6.94
6.92
6.90
5.18
5.16
5.16
5.15
5.15
5.14
5.14
5.13
5.13
5.12
5.12
5.10
4.13
4.12
4.10
4.08
3.85
3.84
3.82
3.45
3.42
3.41
3.38
3.16
3.14
3.12
3.10
2.34
2.20
1.96
1.97
0.98
1.95
1.98
1.00
1.00
0.99
1.00
0.99
1.00
3.01
2.99
f1 (ppm)

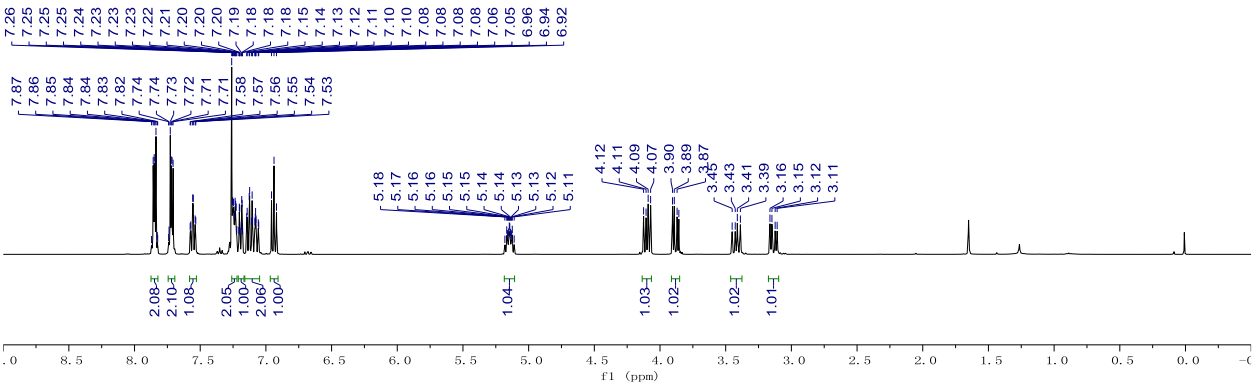

Me
Me
O
N
O
O

3m'


78.95
77.48
77.16
76.84
136.69
134.91
134.16
133.26
132.09
131.13
130.10
129.92
128.34
125.86
124.38
124.05
123.45
120.71
168.26
156.22
42.27
33.71
21.02
19.80
f1 (ppm)


F
O
N
O
O

3n'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7.25
7.25
7.25
7.24
7.23
7.23
7.23
7.22
7.21
7.20
7.20
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7.19
7.18
7.18
7.18
7.15
7.14
7.13
7.12
7.11
7.10
7.10
7.08
7.08
7.08
7.08
7.06
7.05
6.96
6.94
6.92
7.87
7.86
7.85
7.84
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7.82
7.74
7.74
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7.71
7.71
7.58
7.57
7.56
7.55
7.54
7.53
5.18
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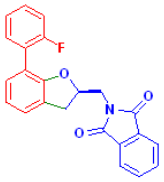
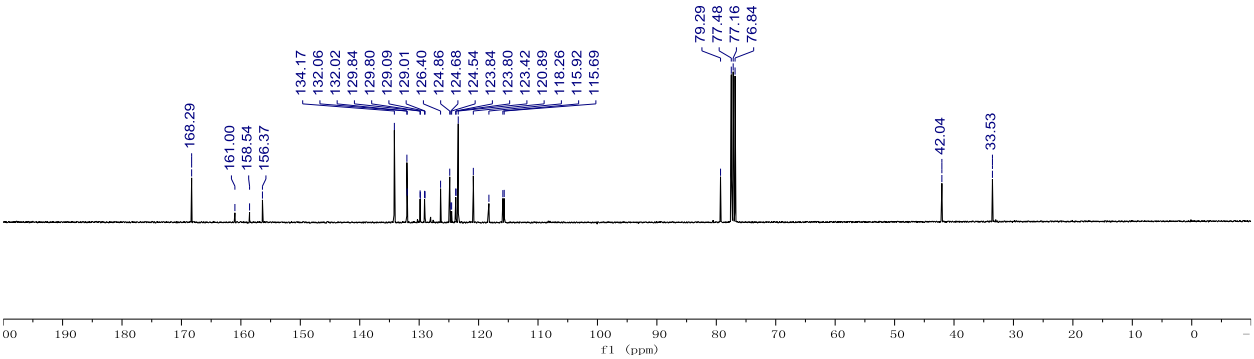
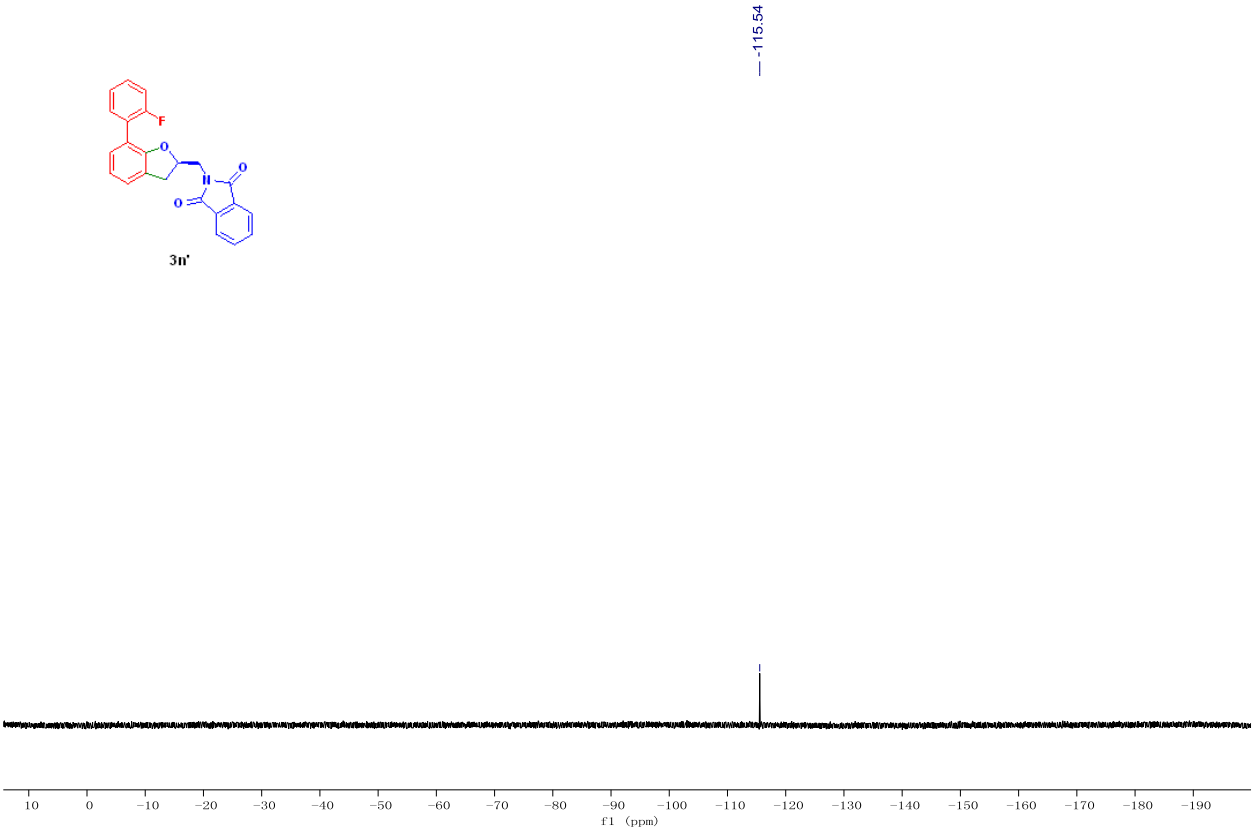
5.16
5.16
5.15
5.15
5.14
5.14
5.13
5.13
5.12
5.11
4.12
4.11
4.09
4.07
3.90
3.89
3.87
3.45
3.43
3.41
3.39
3.16
3.15
3.12
3.11
2.08
2.10
1.08
2.05
1.00
2.06
1.00
1.04
1.03
1.02
1.02
1.01
f1 (ppm)

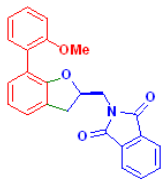

F
O
N
O
O

3n'

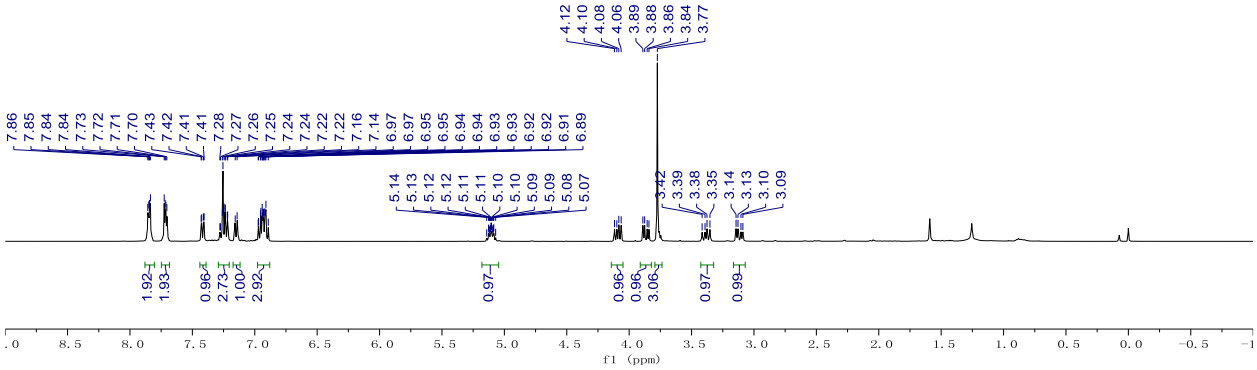

168.29
161.00
158.54
156.37
134.17
132.06
132.02
129.84
129.80
129.09
129.01
126.40
124.86
124.68
124.54
123.84
123.80
123.42
120.89
118.26
115.92
115.69
79.29
77.48
77.16
76.84
42.04
33.53
f1 (ppm)

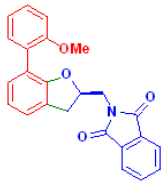

-115.54
F
O
N
O
O
f1 (ppm)

3n'

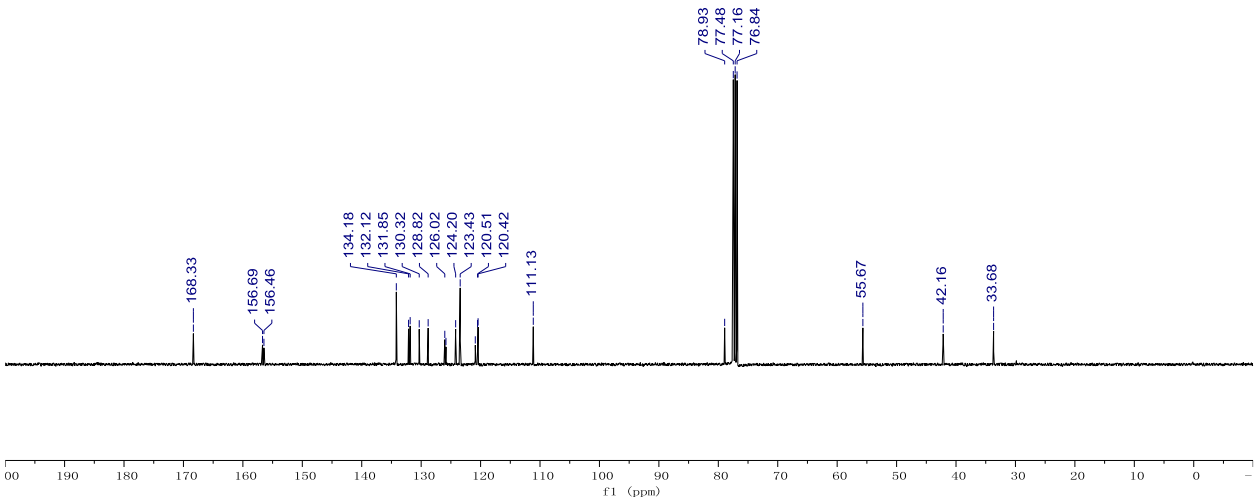

OMe
O
N
O
O

3o'

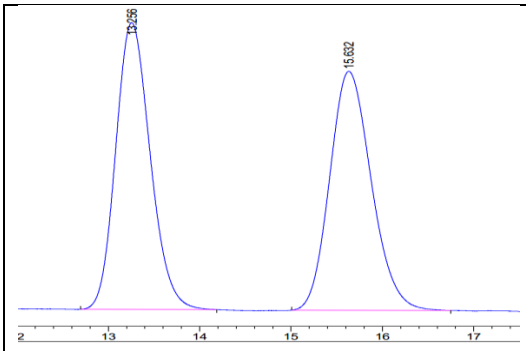

4.12
4.10
4.08
4.06
3.89
3.88
3.86
3.84
3.77
7.86
7.85
7.84
7.84
7.73
7.72
7.71
7.70
7.43
7.42
7.41
7.41
7.28
7.27
7.26
7.25
7.24
7.24
7.22
7.22
7.16
7.14
6.97
6.97
6.95
6.95
6.94
6.94
6.93
6.93
6.92
6.92
6.91
6.89
5.14
5.13
5.12
5.12
5.11
5.11
5.10
5.10
5.09
5.09
5.08
5.07
3.42
3.39
3.38
3.35
3.14
3.13
3.10
3.09
1.92
1.93
0.96
2.73
1.00
2.92
0.97
0.96
0.96
3.06
0.97
0.99
f1 (ppm)

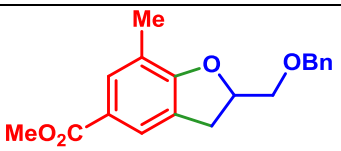

OMe
O
N
O
O

3o'


78.93
77.48
77.16
76.84
168.33
156.69
156.46
134.18
132.12
131.85
130.32
128.82
126.02
124.20
123.43
120.51
120.42
111.13
55.67
42.16
33.68
f1 (ppm)

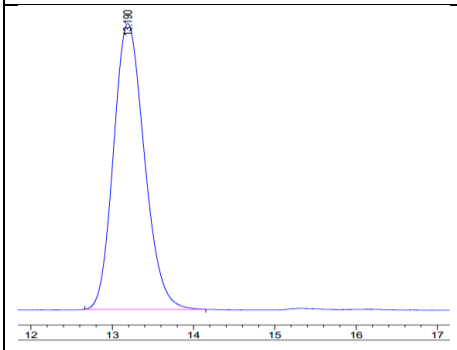
7. Copies of HPLC chromatograms

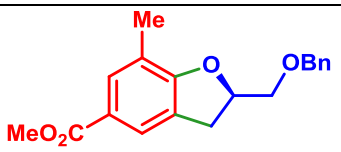




rac-3b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.256	BB	0.3945	1375.63452	52.36780	49.9054
2	15.632	BB	0.4402	1380.85071	43.63314	50.0946





3b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.190	BB	0.3802	1506.30591	57.20220	100.0000

8. Reference

[1] R. Li, G. Dong, *Angew. Chem. Int. Ed.* **2018**, *57*, 1697.