Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Ruthenium(II) oxidase catalysis for C–H alkenylations in biomass-derived γ-valerolactone

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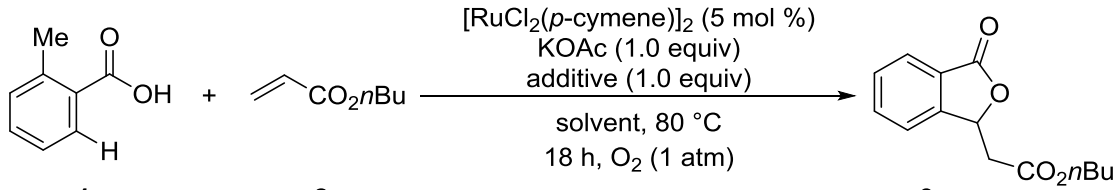
Table of Contents

General remarks

All catalytic reactions were carried out under an ambient O_2 atmosphere (1 atm) using pre-dried 25 mL Schlenk tubes or Schlenk flasks with 40±1 mL total volume. GVL was distilled prior to its use and stored over molecular sieves 4 Å. Acrylic esters and sulfonate esters were prepared by the slow addition of acryloyl chloride or sulfonyl chloride to a solution of the alcohol in CH_2Cl_2.[1] Other chemicals were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR and GC. TLC: Merck TLC Silica gel 60 F254, detection under UV light at 254 nm. Chromatographic separations were carried out on Merck Silica 60 (0.063–0.200 mm, 70–230 mesh ASTM). All IR spectra were recorded on a Bruker FT-IR Alpha device. MS: EI-MS: Finnigan MAT 95, 70 eV; ESI-MS: Finnigan LCQ. High resolution mass spectrometry (HR-MS): APEX IV 7T FTICR, Bruker Daltonic. Melting points (M.p.): Büchi 540 capillary melting point apparatus, values are uncorrected. NMR spectra were recorded on Varian Mercury VX 300, Inova-500, Inova-600 and Bruker Avance 300, Avance III 400 instruments in $CDCl_3$ solutions. If not otherwise specified chemical shifts (δ) are provided in ppm referenced versus $CDCl_3$ (7.26, 77.0 ppm).

Table S-1: Optimization studies for the synthesis of phthalide 3aa



1a **2a** **3aa**

Entry	Solvent	M	Additive	Yield [%][a]
1	GVL	0.3	-	75
2[b]	GVL	0.3	-	65
3[c]	GVL	0.3	-	49
4[d]	GVL	0.3	-	83
5	GVL	0.3	HOAc	81
6	GVL	1.0	-	88
7	GVL	1.0	HOAc	90
8[e]	GVL	0.3	-	-
9[f]	GVL	0.3	-	-
10[g]	GVL	1.0	-	-
11[h]	GVL	1.0	-	traces
12[i]	GVL	1.0	HOAc	30
13	L-Ethyllactate	1.0	HOAc	59
13	2-Me(THF)	1.0	HOAc	81
13	Tetrahydrofufuryl alcohol	1.0	HOAc	82

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5.0 mol %), KOAc (1.0 equiv), additive (1.0 equiv), solvent (M), 80 °C, 18 h, O_2 (1 atm), yield of isolated product. [b] KOAc (0.5 equiv.). [c] GVL (2 mL), H_2O (1 mL). [d] **1a** (2.0 mmol), **2a** (1.0 mmol). [e] Without KOAc. [f] Without [Ru]. [g] $RuCl_3 \cdot xH_2O$ (10 mol%) as catalyst. [h] $[RuCl_2(cod)]_n$ (10 mol%) as catalyst. [i] $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %).

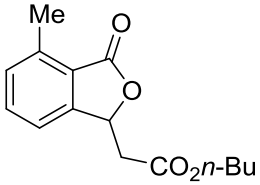
Synthesis of phthalides in biomass-derived GVL

Representative procedure A:

Benzoic acid **1** (1.00 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (30.6 mg, 0.05 mmol, 5.0 mol %) and KOAc (98 mg, 1.00 mmol, 1.0 equiv) were placed in a pre-dried 25 mL Schlenk tube. The flask was evacuated and flushed with ambient O_2 three times. GVL (1.0 mL) and acrylate **2** (1.50 mmol, 1.5 equiv) and HOAc (60 mg, 1.00 mmol, 1.0 equiv) were added and the reaction mixture was stirred at 80 °C for 18 h. At ambient temperature, the mixture was diluted with H_2O (10 mL) and extracted with *n*-hexane/MTBE (1/1, 3 × 10 mL). The combined organic layers were washed with H_2O (5 × 10 mL) and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography on silica gel.

Representative procedure B:

Benzoic acid **1** (5.00 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (150.0 mg, 0.25 mmol, 5.0 mol %) and KOAc (490 mg, 5.00 mmol, 1.0 equiv) were placed in a pre-dried 25 mL Schlenk flask. The flask was evacuated and flushed with ambient O_2 three times. GVL (5.0 mL) and acrylate **2** (7.50 mmol, 1.5 equiv) and HOAc (300 mg, 5.00 mmol, 1.0 equiv) were added and the reaction mixture was stirred at 80 °C for 18 h. At ambient temperature, the mixture was diluted with H_2O (25 mL) and extracted with *n*-hexane/MTBE (1/1, 3 × 25 mL). The combined organic layers were washed with H_2O (5 × 50 mL) and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography on silica gel.



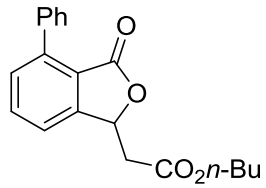
3aa

***n*-Butyl-2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3aa):**

The representative procedure **A** was followed using 2-methylbenzoic acid (**1a**) (136 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (192 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3aa** (237 mg, 0.90 mmol, 90%) as a colourless solid.

The representative procedure **B** was followed using 2-methylbenzoic acid (**1a**) (680 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (960 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3aa** (1265 mg, 4.85 mmol, 97%) as a colourless solid.

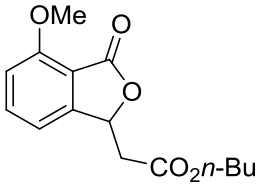
M.p.: 78-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (dd, J = 7.6, 7.6 Hz, 1H), 7.31–7.27 (m, 2H), 5.81 (t, J = 6.8 Hz, 1H), 4.16 (t, J = 6.7 Hz, 2H), 2.87 (dd, J = 6.5, 2.2 Hz, 2H), 2.69 (s, 3H), 1.67–1.56 (m, 2H), 1.43–1.32 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.2 (C_q), 169.6 (C_q), 149.4 (C_q), 140.1 (C_q), 134.1 (CH), 131.3 (CH), 123.6 (C_q), 119.4 (CH), 76.2 (CH), 65.3 (CH_2), 39.9 (CH_2), 30.7 (CH_2), 19.2 (CH_2), 17.5 (CH_3), 13.8 (CH_3). IR (ATR): 2960, 2933, 2874, 1755, 1731, 1602, 1167, 1088, 1046, 787 cm^{-1}. MS (EI) *m/z* (relative intensity): 262 (14) [M^+], 206 (74), 160 (82), 147 (100), 132 (25), 119 (33), 91 (35), 46 (13). HR-MS (ESI) *m/z* calcd for $C_{15}H_{19}O_4$, [M+H^+] 263.1287, found 263.1276. The spectral data are in accordance with those reported in the literature.[2]



3ba

***n*-Butyl-2-(4-phenyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3ba):**

The representative procedure **A** was followed using 2-phenylbenzoic acid (**1b**) (198 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (192 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3ba** (211 mg, 0.65 mmol, 65%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.49–7.42 (m, 2H), 7.42–7.30 (m, 5H), 5.78 (t, *J* = 6.5 Hz, 1H), 4.09 (t, *J* = 6.7 Hz, 2H), 2.85 (d, *J* = 6.7 Hz, 2H), 1.62–1.45 (m, 2H), 1.40–1.19 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.5 (C_q), 168.7 (C_q), 150.2 (C_q), 143.0 (C_q), 136.4 (C_q), 134.1 (CH), 131.4 (CH), 129.6 (CH), 128.5 (CH), 128.1 (CH), 122.1 (C_q), 120.8 (CH), 75.7 (CH), 65.3 (CH_2), 39.9 (CH_2), 30.6 (CH_2), 19.2 (CH_2), 13.8 (CH_3). IR (ATR): 2958, 1759, 1729, 1595, 1345, 1286, 1169, 1079, 1039, 817 cm^{-1}. MS (EI) *m/z* (relative intensity): 324 (28) [M^+], 268 (39), 250 (75), 223 (100), 209 (82), 181 (55), 152 (84), 76 (8). HR-MS (ESI) *m/z* calcd for $C_{20}H_{21}O_4$, [$M+H^+$] 325.1434, found 325.1438. The spectral data are in accordance with those reported in the literature.[2]

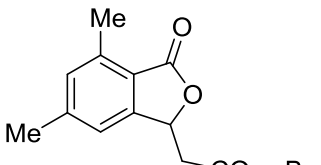


3ca

***n*-Butyl-2-(4-methoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3ca):**

The representative procedure **A** was followed using 2-methoxybenzoic acid (**1c**) (152 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (192 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3ca** (167 mg, 0.60 mmol, 60%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (dd, *J* = 8.3, 7.6 Hz, 1H), 7.00 (d, *J* = 7.6Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 7.07–6.93 (m, 2H), 5.79 (dd, *J* = 7.0, 6.2 Hz, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 3.99 (s, 3H), 2.96–2.76 (m, 2H), 1.70–1.50 (m, 2H), 1.44–1.25 (m, 2H), 0.93

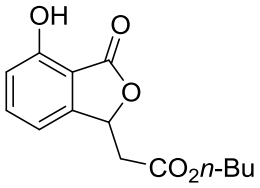
(t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.5 (C_q), 168.0 (C_q), 158.9 (C_q), 151.8 (C_q), 136.6 (CH), 113.7 (CH), 113.6 (C_q), 111.3 (CH), 76.1 (CH), 65.3 (CH_2), 56.2 (CH_3), 39.9 (CH_2), 30.7 (CH_2), 19.2 (CH_2), 13.8 (CH_3). IR (ATR): 2959, 1758, 1730, 1601, 1396, 1276, 1239, 1169, 777, 690 cm^{-1}. MS (EI) *m/z* (relative intensity): 278 (25) [M^+], 222 (62), 163 (100), 135 (33), 120 (11), 105 (25), 77 (26), 41 (18). HR-MS (ESI) *m/z* calcd for $C_{15}H_{19}O_5$, [M+H^+] 279.1228, found 279.1227.



3da

***n*-Butyl-2-(4,6-dimethyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3da):**

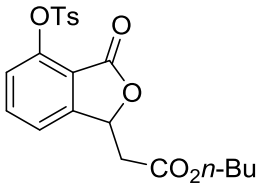
The representative procedure **A** was followed using 2,4-dimethylbenzoic acid (**1d**) (150 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (192 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3da** (261 mg, 0.95 mmol, 95%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10 (s, 1H), 7.05 (s, 1H), 5.76 (t, J = 6.5 Hz, 1H), 4.16 (t, J = 6.7 Hz, 2H), 2.85 (d, J = 6.5 Hz, 2H), 2.64 (s, 3H), 2.42 (s, 3H), 1.68 – 1.54 (m, 2H), 1.45 – 1.30 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2 (C_q), 169.7 (C_q), 150.0 (C_q), 145.3 (C_q), 139.7 (C_q), 132.4 (CH), 121.1 (C_q), 119.8 (CH), 76.0 (CH), 65.3 (CH_2), 40.0 (CH_2), 30.7 (CH_2), 22.1 (CH_3), 19.2 (CH_2), 17.4 (CH_3), 13.8 (CH_3). IR (ATR): 2960, 1754, 1731, 1613, 1310, 1270, 1203, 1170, 1013, 686 cm^{-1}. MS (EI) *m/z* (relative intensity): 276 (20) [M^+], 220 (60), 174 (95), 161 (100), 146 (35), 133 (40), 105 (25), 77 (15). HR-MS (EI) *m/z* calcd for $C_{16}H_{20}O_4$, [M^+] 276.1362, found 276.1359. The spectral data are in accordance with those reported in the literature.[2]



3ea

***n*-Butyl-2-(4-hydroxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3ea):**

The representative procedure **A** was followed using salicylic acid (**1e**) (138 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (192 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 1/1 + 1 % MeOH) yielded **3ea** (138 mg, 0.52 mmol, 52%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (s, 1H), 7.52 (dd, *J* = 8.3, 7.5 Hz, 1H), 6.98 – 6.87 (m, 2H), 5.86 (t, *J* = 6.6 Hz, 1H), 4.13 (t, *J* = 6.7 Hz, 2H), 2.88 (d, *J* = 6.6 Hz, 2H), 1.68 – 1.51 (m, 2H), 1.45 – 1.22 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.4 (C_q), 169.2 (C_q), 156.6 (C_q), 149.1 (C_q), 137.2 (CH), 116.0 (CH), 113.4 (CH), 111.0 (C_q), 78.3 (CH), 65.2 (CH_2), 39.3 (CH_2), 30.5 (CH_2), 19.1 (CH_2), 13.7 (CH_3). IR (ATR): 2960, 1727, 1615, 1464, 1280, 1158, 997, 801, 689, 436 cm^{-1}. MS (EI) *m/z* (relative intensity): 264 (15) [M^+], 208 (95), 165 (35), 162 (100), 149 (95), 134 (15), 121 (30), 65 (20). HR-MS (EI) *m/z* calcd for $C_{14}H_{16}O_5$, [M^+] 264.0998, found 264.1000.

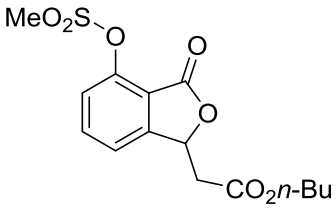


3fa

***n*-Butyl-2-(4-tosyloxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3fa):**

The representative procedure **A** was followed using 2-tosyloxybenzoic acid (**1f**) (292 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (192 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 1/1 + 1 % MeOH) yielded **3fa** (206 mg, 0.49 mmol,

49%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.5 Hz, 1H), 7.66 (m, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.75 (t, J = 6.5 Hz, 1H), 4.10 (t, J = 6.7 Hz, 2H), 2.83 (d, J = 6.5 Hz, 2H), 2.41 (s, 3H), 1.65–1.46 (m, 2H), 1.40–1.18 (m, 2H), 0.89 (m, J = 7.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.1 (C_q), 165.4 (C_q), 151.2 (C_q), 146.5 (C_q), 145.9 (C_q), 136.0 (CH), 132.0 (C_q), 129.8 (CH), 128.9 (CH), 123.7 (CH), 120.9 (CH), 118.7 (C_q), 76.0 (CH), 65.2 (CH_2), 39.3 (CH_2), 30.5 (CH_2), 21.8 (CH_3), 19.1 (CH_2), 13.7 (CH_3). IR (ATR): 2960, 1769, 1732, 1475, 1172, 997, 812, 748, 668, 548 cm^{-1}. MS (EI) *m/z* (relative intensity): 418 (5) [M^+], 354 (7), 303 (14), 263 (45), 207 (44), 163 (22), 155 (87), 91 (100). HR-MS (EI) *m/z* calcd for $C_{21}H_{22}O_7S$, [M^+] 418.1086, found 418.1071.

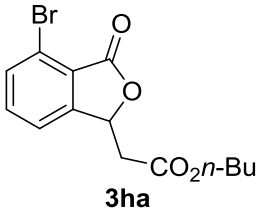


3ga

***n*-Butyl-2-(4-methylsulfonyloxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3ga):**

The representative procedure **A** was followed using 2-methylsulfonyloxybenzoic acid (**1g**) (192 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (192 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 1/1 + 1 % MeOH) yielded **3ga** (188 mg, 0.55 mmol, 55%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.74 (dd, J = 7.5, 7.5 Hz, 1H), 7.48–7.47 (m, 1H), 7.45–7.44 (m, 1H), 5.87 (t, J = 6.4 Hz, 1H), 4.15 (t, J = 6.7 Hz, 2H), 3.41 (s, 3H), 3.03–2.86 (m, 2H), 1.67–1.56 (m, 2H), 1.44–1.29 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.1 (C_q), 166.4 (C_q), 151.4 (C_q), 146.3 (C_q), 136.4 (CH), 124.9 (CH), 121.2 (CH), 118.8 (C_q), 76.6 (CH), 65.5 (CH_2), 39.3 (CH_2), 39.2 (CH_3), 30.6 (CH_2), 19.2 (CH_2), 13.8 (CH_3). IR (ATR): 2961, 2874, 1764, 1729, 1618, 1476, 1365, 1117, 1003, 787 cm^{-1}. MS (EI) *m/z* (relative intensity) 342 (22) [M^+], 286 (100), 240 (52), 227 (75), 207 (100),

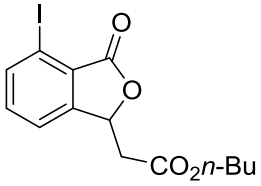
162 (82), 149 (81), 120 (32). HR-MS (ESI) *m/z* calcd for $C_{15}H_{18}O_7S$, $[M+H^+]$ 343.0846, found 343.0859.



3ha

***n*-Butyl-2-(4-bromo-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3ha):**

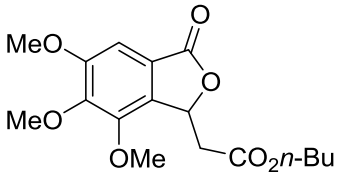
The representative procedure **A** was followed using 2-bromobenzoic acid (**1h**) (201 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (192 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 1/1 + 1 % MeOH) yielded **3ha** (227 mg, 0.70 mmol, 70%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCL_3$): δ = 7.64 (d, *J* = 7.6 Hz, 1H), 7.44 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 5.74 (t, *J* = 6.5 Hz, 1H), 4.09 (t, *J* = 6.7 Hz, 2H), 2.99–2.69 (m, 2H), 1.61–1.43 (m, 2H), 1.37–1.23 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.3 (C_q), 167.3 (C_q), 151.4 (C_q), 135.3 (CH), 134.4 (CH), 124.5 (C_q), 121.4 (C_q), 121.2 (CH), 75.4 (CH), 65.5 (CH_2), 39.6 (CH_2), 30.7 (CH_2), 19.2 (CH_2), 13.8 (CH_3). IR (ATR): 2957, 1735, 1599, 1456, 1340, 1204, 1079, 1043, 797, 677 cm^{-1}. MS (EI) *m/z* (relative intensity): 326 (5) [^{79}Br-M^+], 272 (91), 227 (88), 211 (100), 183 (30), 155 (18), 104 (10), 75 (30). HR-MS (ESI) *m/z* calcd for $C_{14}H_{16}{}^{79}BrO_4$, $[M+H^+]$ 327.0226, found 327.0228.



3ia

***n*-Butyl-2-(4-iodo-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3ia):**

The representative procedure **A** was followed using 2-iodobenzoic acid (**1i**) (201 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (192 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 1/1 + 1 % MeOH) yielded **3ia** (201 mg, 0.54 mmol, 54%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (d, J = 7.7 Hz, 1H), 7.48 (d, J = 7.7 Hz, 1H), 7.34 (dd, J = 7.7, 7.7 Hz, 1H), 5.76 (t, J = 6.9 Hz, 1H), 4.14 (t, J = 6.7 Hz, 2H), 3.08–2.75 (m, 2H), 1.69–1.52 (m, 2H), 1.44–1.20 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.3 (C_q), 168.0 (C_q), 151.1 (C_q), 141.1 (CH), 135.1 (CH), 127.2 (C_q), 122.0 (CH), 92.5 (C_q), 74.9 (CH), 65.4 (CH_2), 39.4 (CH_2), 30.6 (CH_2), 19.2 (CH_2), 13.8 (CH_3). IR (ATR): 2959, 1763, 1727, 1457, 1304, 1173, 1076, 968, 781, 678 cm^{-1}. MS (EI) *m/z* (relative intensity): 374 (22) [M^+], 318 (100), 273 (75), 259 (81), 231 (29), 203 (9), 104 (10), 76 (19). HR-MS (EI) *m/z* calcd for $C_{14}H_{15}IO_4$, [M^+] 374.0015, found 374.0026. The spectral data are in accordance with those reported in the literature.[2]

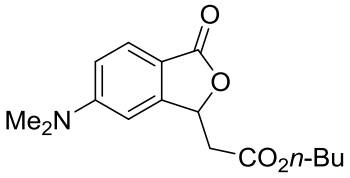


3ja

***n*-Butyl-2-(5,6,7-trimethoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3ja):**

The representative procedure **A** was followed using 3,4,5-trimethoxybenzoic-acid (**1j**) (212 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (192 mg, 1.50 mmol, 1.5 equiv). Purification by

column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3ja** (326 mg, 0.96 mmol, 96%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12 (s, 1H), 5.82 (dd, *J* = 8.6, 3.4 Hz, 1H), 4.12 (t, *J* = 6.7 Hz, 2H), 3.99 (s, 3H), 3.93 (s, 3H), 3.91 (s, 3H), 3.20 (dd, *J* = 16.3, 3.4 Hz, 1H), 2.64 (dd, *J* = 16.3, 8.6 Hz, 1H), 1.65–1.54 (m, 2H), 1.45–1.26 (m, 2H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.9 (C_q), 169.5 (C_q), 156.2 (C_q), 147.6 (C_q), 146.8 (C_q), 133.9 (C_q), 121.5 (C_q), 102.7 (CH), 75.9 (CH), 65.2 (CH_2), 61.3 (CH_3), 61.1 (CH_3), 56.6 (CH_3), 38.6 (CH_2), 30.7 (CH_2), 19.2 (CH_2), 13.8 (CH_3). IR (ATR): 2958, 2874, 1765, 1733, 1477, 1420, 1339, 1170, 1104, 765 cm^{-1}. MS (EI) *m/z* (relative intensity) 338 (42) [M^+], 282 (24), 237 (78), 236 (100), 223 (100), 195 (24), 180 (16), 165 (16). HR-MS (ESI) *m/z* calcd for $C_{17}H_{23}O_7$, [M+H^+] 339.1438, found 339.1448.

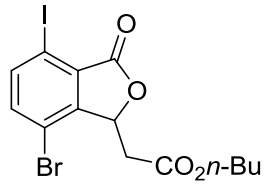


3ka

***n*-Butyl-2-(6-dimethylamino-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3ka):**

The representative procedure **A** was followed using 4-dimethylaminobenzoic acid (**1k**) (165 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (192 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 1/1 + 1 % MeOH) yielded **3ka** (169 mg, 0.59 mmol, 59%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.7 Hz, 1H), 6.76 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.54 (d, *J* = 2.3 Hz, 1H), 5.73 (t, *J* = 6.2 Hz, 1H), 4.16 (t, *J* = 6.7 Hz, 2H), 3.08 (s, 6H), 2.94 – 2.75 (m, 2H), 1.67 – 1.52 (m, 2H), 1.41 – 1.25 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.5 (C_q), 169.9 (C_q), 154.6 (C_q), 151.9 (C_q), 127.0 (CH), 113.2 (CH), 112.5 (C_q), 102.6 (CH), 76.3 (CH), 65.2 (CH_2), 40.5 (CH_3), 40.2 (CH_2), 30.7 (CH_2), 19.2 (CH_2), 13.8 (CH_3). IR (ATR): 2958, 1730, 1606, 1517, 1368, 1321, 1167, 1003, 691, 608

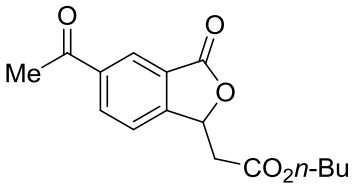
cm^{-1}. MS (EI) *m/z* (relative intensity): 291 (100) [M^+], 235 (25), 180 (70), 176 (100), 162 (10), 148 (40), 119 (15), 77 (10). HR-MS (EI) *m/z* calcd for $C_{16}H_{21}NO_4$, [M^+] 291.1471, found 291.1479.



3la

***n*-Butyl-2-(7-bromo-4-iodo-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3la):**

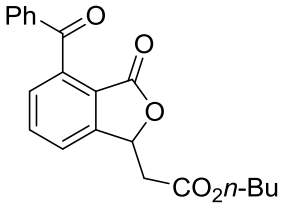
The representative procedure **A** was followed using 2-iodo-5-bromobenzoic-acid (**1l**) (327 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (192 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3la** (320 mg, 0.71 mmol, 71%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 5.70 (ddd, *J* = 8.0, 3.0, 0.6 Hz, 1H), 4.10 (t, *J* = 6.7 Hz, 2H), 3.46 (dd, *J* = 16.7, 3.0 Hz, 1H), 2.81 (dd, *J* = 16.8, 8.0 Hz, 1H), 1.63–1.52 (m, 2H), 1.41–1.26 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.5 (C_q), 166.6 (C_q), 149.2 (C_q), 142.3 (CH), 138.0 (CH), 129.5 (C_q), 116.5 (C_q), 91.0 (C_q), 75.5 (CH), 65.3 (CH_2), 36.7 (CH_2), 30.5 (CH_2), 19.1 (CH_2), 13.8 (CH_3). IR (ATR): 2958, 2932, 2872, 1769, 1730, 1449, 1338, 1172, 1060, 831 cm^{-1}. MS (EI) *m/z* (relative intensity): 452 (7) [^{79}Br-M^+], 396 (99), 350 (83), 337 (73), 309 (12), 154 (11), 75 (16), 41 (18). HR-MS (EI) *m/z* calcd for $C_{14}H_{14}{}^{79}BrIO_4$, [$M^+$] 451.9120, found 451.9136.



3ma

***n*-Butyl-2-(5-acetyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3ma):**

The representative procedure **A** was followed using 2-acetylbenzoic acid (**1m**) (180 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (192 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 1/1 + 1 % MeOH) yielded **3ma** (244 mg, 0.84 mmol, 84%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.37 (s, 1H), 8.26 (d, J = 8.1 Hz, 1H), 7.60 (d, J = 8.1 Hz, 1H), 5.88 (t, J = 6.4 Hz, 1H), 4.09 (t, J = 6.7 Hz, 2H), 2.92 (dd, J = 6.4, 1.9 Hz, 2H), 2.62 (s, 3H), 1.63 – 1.45 (m, 2H), 1.39 – 1.19 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.3 (C_q), 169.0 (C_q), 169.0 (C_q), 152.9 (C_q), 138.6 (C_q), 133.9 (CH), 126.8 (C_q), 126.0 (CH), 122.8 (CH), 77.1 (CH), 65.3 (CH_2), 39.0 (CH_2), 30.5 (CH_2), 26.8 (CH_3), 19.0 (CH_2), 13.6 (CH_3). IR (ATR): 2961, 1772, 1734, 1690, 1345, 1397, 1288, 1181, 1075, 605 cm^{-1}. MS (EI) *m/z* (relative intensity): 264 (15) [M^+], 208 (95), 165 (35), 162 (100), 149 (95), 134 (15), 121 (30), 65 (20). HR-MS (EI) *m/z* calcd for $C_{16}H_{18}O_5$, [M^+] 290.1154, found 290.1159.

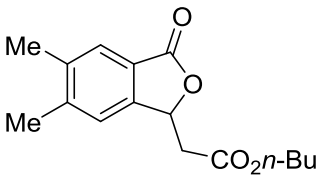


3na

***n*-Butyl-2-(4-benzoyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3na):**

The representative procedure **A** was followed using 2-benzoylbenzoic acid (**1n**) (226 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (192 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 1/1 + 1 % MeOH) yielded **3na** (287 mg, 0.82 mmol,

82%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 – 7.74 (m, 3H), 7.68 – 7.52 (m, 3H), 7.49 – 7.41 (m, 2H), 5.93 (t, *J* = 6.6 Hz, 1H), 4.17 (t, *J* = 6.7 Hz, 2H), 3.09 – 2.83 (m, 2H), 1.69 – 1.55 (m, 2H), 1.47 – 1.29 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.6 (C_q), 169.4 (C_q), 167.6 (C_q), 149.6 (C_q), 139.4 (C_q), 136.6 (C_q), 134.3 (CH), 134.0 (CH), 130.0 (CH), 128.7 (CH), 128.6 (CH), 123.9 (C_q), 123.7 (CH), 77.0 (CH), 65.4 (CH_2), 39.6 (CH_2), 30.7 (CH_2), 19.2 (CH_2), 13.8 (CH_3). IR (ATR): 2959, 1763, 1730, 1669, 1282, 1174, 1077, 1005, 711, 696 cm^{-1}. MS (EI) *m/z* (relative intensity): 352 (20) [M^+], 278 (75), 252 (30), 236 (75), 208 (45), 152 (30), 105 (100), 77 (65). HR-MS (EI) *m/z* calcd for $C_{21}H_{20}O_5$, [M^+] 352.1311, found 352.1302.

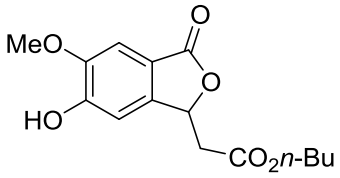


3oa

***n*-Butyl-2-(5,6-dimethyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3oa):**

The representative procedure **A** was followed using 3,4-dimethylbenzoic-acid (**1o**) (150 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (192 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3oa** (219 mg, 0.79 mmol, 79%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (s, 1H), 7.23 (s, 1H), 5.80 (t, *J* = 6.6 Hz, 1H), 4.16 (t, *J* = 6.7 Hz, 2H), 2.97–2.75 (m, 2H), 2.38 (s, 3H), 2.35 (s, 3H), 1.67–1.57 (m, 2H), 1.45–1.30 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.3 (C_q), 169.7 (C_q), 147.1 (C_q), 144.6 (C_q), 138.9 (C_q), 126.2 (CH), 123.9 (C_q), 122.9 (CH), 76.8 (CH), 65.3 (CH_2), 39.9 (CH_2), 30.7 (CH_2), 21.0 (CH_3), 20.1 (CH_3), 19.2 (CH_2), 13.8 (CH_3). IR (ATR): 2960, 2873, 1759, 1731, 1460, 1390, 1340, 1170, 1015, 990 cm^{-1}. MS (EI) *m/z* (relative intensity) 276 (13)

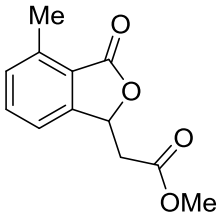
[M^+], 220 (51), 177 (44), 174 (100), 161 (84), 133 (34), 105 (16), 77 (12). HR-MS (ESI) *m/z* calcd for $C_{16}H_{21}O_4$, [M+H^+] 277.1434, found 277.1436.



3pa

***n*-Butyl 2-(6-hydroxy-5-methoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3pa):**

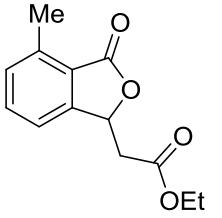
The representative procedure **A** was followed using vanillic acid (**1p**) (168 mg, 1.00 mmol, 1.0 equiv) and **2a** (192 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 1/1 + 1 % MeOH) yielded **3pa** (164 mg, 0.56 mmol, 56%) as colourless solid. M.p.: 118-120 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 (s, 1H), 6.97 (d, *J* = 0.8 Hz, 1H), 6.27 (s, 1H), 5.76 (ddd, *J* = 7.0, 6.2, 0.8 Hz, 1H), 4.16 (t, *J* = 6.7 Hz, 2H), 3.98 (s, 3H), 2.94–2.75 (m, 2H), 1.70–1.54 (m, 2H), 1.45–1.30 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.3 (C_q), 169.6 (C_q), 152.0 (C_q), 148.2 (C_q), 144.0 (C_q), 117.7 (C_q), 107.4 (CH), 106.3 (CH), 76.6 (CH), 65.3 (CH_2), 56.6 (CH_3), 39.8 (CH_2), 30.7 (CH_2), 19.2 (CH_2), 13.8 (CH_3). IR (ATR): 3300, 2961, 2927, 2874, 1737, 1707, 1600, 1498, 1062, 1043 cm^{-1}. MS (EI) *m/z* (relative intensity) 294 (16) [M^+], 238 (36), 195 (42), 193 (61), 192 (100), 179 (70), 164 (10), 151 (27). HR-MS (EI) *m/z* calcd for $C_{15}H_{18}O_6$, [M+H^+] 295.1176, found 295.1176.



3ab

Methyl 2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3ab):

The representative procedure **A** was followed using 2-methylbenzoic acid (**1a**) (136 mg, 1.00 mmol, 1.0 equiv) and methyl acrylate (**2b**) (129 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3ab** (135 mg, 0.61 mmol, 61%) as colourless solid. M.p.: 89-90 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.32–7.25 (m, 2H), 5.82 (t, *J* = 6.6 Hz, 1H), 3.77 (s, 3H), 2.87 (d, *J* = 6.6 Hz, 2H), 2.69 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.1 (C_q), 170.0 (C_q), 149.3 (C_q), 140.1 (C_q), 134.1 (CH), 131.3 (CH), 123.5 (C_q), 119.4 (CH), 76.1 (CH), 52.3 (CH_3), 39.8 (CH_2), 17.5 (CH_3). IR (ATR): 2952, 1757, 1732, 1600, 1441, 1400. 1199, 1086, 1007, 687 cm^{-1}. MS (EI) *m/z* (relative intensity) 220 (20) [M^+], 160 (100), 147 (90), 132 (37), 119 (38), 91 (39), 65 (16), 58 (38). HR-MS (ESI) *m/z* calcd for $C_{12}H_{13}O_4$, [M+H^+] 221.0808, found 221.0810. The spectral data are in accordance with those reported in the literature.[2]

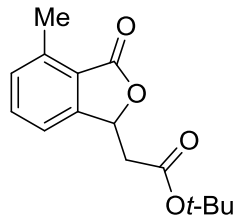


3ac

Ethyl 2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3ac):

The representative procedure **A** was followed using 2-methylbenzoic acid (**1a**) (136 mg, 1.00 mmol, 1.0 equiv) and ethyl acrylate (**2c**) (150 mg, 1.50 mmol, 1.5 equiv). Purification by

column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3ac** (195 mg, 0.83 mmol, 83%) as colourless solid. M.p.: 50-52 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.31–7.25 (m, 2H), 5.81 (t, *J* = 6.6 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.86 (d, *J* = 6.6 Hz, 2H), 2.69 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2 (C_q), 169.5 (C_q), 149.4 (C_q), 140.1 (C_q), 134.1 (CH), 131.3 (CH), 123.6 (C_q), 119.4 (CH), 76.2 (CH), 61.4 (CH_2), 40.0 (CH_2), 17.5 (CH_3), 14.3 (CH_3). IR (ATR): 2988, 2926, 1744, 1725, 1602, 1475, 1171, 1097, 1007, 689 cm^{-1}. MS (EI) *m/z* (relative intensity) 234 (18) [M^+], 160 (100), 147 (87), 132 (32), 119 (31), 91 (31), 65 (13), 43 (25). HR-MS (ESI) *m/z* calcd for $C_{13}H_{15}O_4$, [M+H^+] 235.0965, found 235.967. The spectral data are in accordance with those reported in the literature.[2]

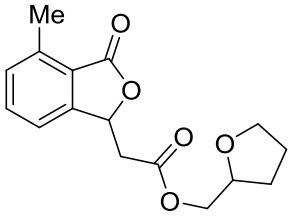


3ad

***tert*-Butyl-2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3ad):**

The representative procedure **A** was followed using 2-methylbenzoic acid (**1a**) (136 mg, 1.00 mmol, 1.0 equiv) and *tert*-butyl acrylate (**2d**) (192 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3ad** (178 mg, 0.68 mmol, 68%) as colourless solid. M.p.: 74-75 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.30–7.26 (m, 2H), 5.76 (t, *J* = 6.4 Hz, 1H), 2.81 (d, *J* = 6.4 Hz, 2H), 2.69 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.3 (C_q), 168.7 (C_q), 149.7 (C_q), 140.0 (C_q), 134.0 (CH), 131.1 (CH), 123.7 (C_q), 119.4 (CH), 82.0 (C_q), 76.5 (CH), 41.0 (CH_2), 28.2 (CH_3), 17.5 (CH_3). IR (ATR): 2980, 2929, 1740, 1598, 1478, 1049, 1003, 908, 828, 794 cm^{-1}. MS (EI) *m/z* (relative intensity) 206 (85), 189 (23), 161 (50), 147 (100), 119 (26), 91 (24), 57 (64), 43 (85). HR-MS (ESI)

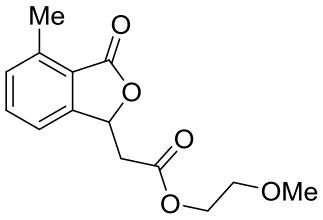
m/z calcd for $C_{15}H_{19}O_4$, $[M+H^+]$ 263.1278, found 263.1279. The spectral data are in accordance with those reported in the literature.[2]



3ae

(Tetrahydrofuran-2-yl)methyl-2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)-acetate (3ae):

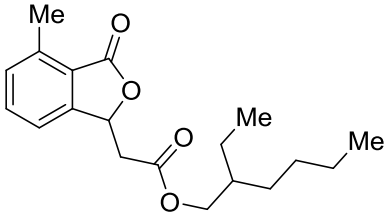
The representative procedure **A** was followed using 2-methylbenzoic acid (**1a**) (136 mg, 1.00 mmol, 1.0 equiv) and tetrahydrofurfuryl acrylate (**2e**) (234 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3ae** (237 mg, 0.82 mmol, 82%) as a colourless oil.^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (dd, J = 7.6, 7.6 Hz, 1H), 7.29 (m, 2H), 5.83 (t, J = 6.7 Hz, 1H), 4.29–4.21 (m, 1H), 4.18–4.06 (m, 2H), 3.93–3.75 (m, 2H), 2.92 (d, J = 6.7 Hz, 2H), 2.69 (s, 3H), 2.10–1.85 (m, 3H), 1.68–1.55 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.0 (C_q), 169.3 (C_q), 149.2 (C_q), 140.0 (C_q), 134.0 (CH), 131.2 (CH), 123.5 (C_q), 119.4 (CH), 76.5 (CH), 76.1 (CH), 68.6 (CH_2), 67.3 (CH_2), 40.0 (CH_2), 28.2 (CH_2), 25.9 (CH_2), 17.6 (CH_3). IR (ATR): 2953, 2872, 1753, 1734, 1380, 1167, 1005, 787, 687, 472 cm^{-1}. MS (EI) *m/z* (relative intensity) 290 (4) $[M^+]$, 247 (13), 220 (20), 207 (18), 162 (15), 147 (46), 84 (26), 71 (100). HR-MS (ESI) *m/z* calcd for $C_{16}H_{18}O_5$, $[M+H^+]$ 291.1227, found 291.1228.



3af

2-Methoxyethyl-2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3af):

The representative procedure **A** was followed using 2-methylbenzoic acid (**1a**) (136 mg, 1.00 mmol, 1.0 equiv) and 2-methoxyethyl acrylate (**2f**) (195 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3af** (224 mg, 0.85 mmol, 85%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (dd, J = 7.6, 7.6 Hz, 1H), 7.29 (m, 2H), 5.82 (t, J = 6.6 Hz, 1H), 4.37–4.27 (m, 2H), 3.66–3.56 (m, 2H), 3.39 (s, 3H), 2.92 (dd, J = 6.6, 1.6 Hz, 2H), 2.69 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.2 (C_q), 169.5 (C_q), 149.4 (C_q), 140.1 (C_q), 134.1 (CH), 131.3 (CH), 123.6 (C_q), 119.5 (CH), 76.1 (CH) 70.4 (CH_2), 64.3 (CH_2), 59.2 (CH_3), 39.9 (CH_2), 17.5 (CH_3). IR (ATR): 2927, 1753, 1733, 1382, 1238, 1127, 1045, 1005, 787, 687 cm^{-1}. MS (EI) *m/z* (relative intensity) 264 (16) [M^+], 160 (76), 147 (100), 132 (21), 119 (23), 91 (27), 58 (19), 45 (17). HR-MS (ESI) *m/z* calcd for $C_{14}H_{17}O_5$, [M+H^+] 265.1071, found 265.1071.

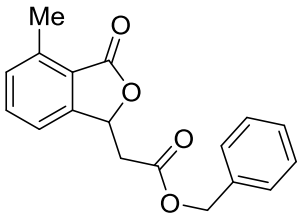


3ag

2-Ethylhexyl-2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3ag):

The representative procedure **A** was followed using 2-methylbenzoic acid (**1a**) (136 mg, 1.00 mmol, 1.0 equiv) and 2-ethylhexyl acrylate (**2g**) (276 mg, 1.50 mmol, 1.5 equiv). Purification

by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3ag** (196 mg, 0.61 mmol, 61%) as colourless solid. M.p.: 42-44 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52 (dd, J = 7.6, 7.6 Hz, 1H), 7.33–7.22 (m, 2H), 5.81 (t, J = 6.6 Hz, 1H), 4.08 (m, 2H), 2.88 (m, 2H), 2.69 (s, 3H), 1.63–1.51 (m, 1H), 1.43–1.22 (m, 8H), 0.93–0.85 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2 (C_q), 169.7 (C_q), 149.5 (C_q), 140.1 (C_q), 134.1 (CH), 131.3 (CH), 123.6 (C_q), 119.4 (CH), 76.2 (CH), 67.8 (CH_2), 39.9 (CH_2), 38.8 (CH), 30.5 (CH_2), 29.0 (CH_2), 23.8 (CH_2), 23.1 (CH_2), 17.5 (CH_3), 14.2 (CH_3), 11.1 (CH_3). IR (ATR): 2957, 2928, 2860, 1743, 1601, 1461, 1399, 1202, 1049, 1001 cm^{-1}. MS (EI) *m/z* (relative intensity) 318 (1) [M^+], 206 (100), 161 (52), 147 (90), 119 (18), 91 (20), 71 (12), 57 (19). HR-MS (ESI) *m/z* calcd for $C_{19}H_{27}O_4$, [M+H^+] 319.1904, found 319.1910.



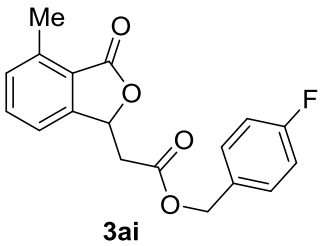
3ah

Benzyl 2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3ah):

The representative procedure **A** was followed using 2-methylbenzoic acid (**1a**) (136 mg, 1.00 mmol, 1.0 equiv) and benzyl acrylate (**2h**) (243 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3ah** (204 mg, 0.69 mmol, 69%) as colourless solid.

The representative procedure **B** was followed using **1a** (630 mg, 5.00 mmol, 1.0 equiv) and benzyl acrylate (**2h**) (1215 mg, 7.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3ah** (1367 mg, 4.60 mmol, 92%) as colourless solid.

M.p.: 58-61 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (dd, J = 7.6, 7.6 Hz, 1H), 7.36 (m, 5H), 7.29–7.25 (m, 1H), 7.20 (d, J = 7.6 Hz, 1H), 5.82 (t, J = 6.6 Hz, 1H), 5.20 (m, 2H), 2.92 (dd, J = 6.6, 2.9 Hz, 2H), 2.67 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.1 (C_q), 169.3 (C_q), 149.3 (C_q), 140.1 (C_q), 135.4 (C_q), 134.1 (CH), 131.3 (CH), 128.8 (CH), 128.6 (CH), 128.6 (CH), 123.5 (C_q), 119.4 (CH), 76.1 (CH), 67.2 (CH_2), 39.9 (CH_2), 17.5 (CH_3). IR (ATR): 3037, 2944, 1745, 1599, 1478, 1386, 1311, 1291, 1203, 1002 cm^{-1}. MS (EI) *m/z* (relative intensity) 296 (15) [M^+], 205 (54), 162 (71), 147 (55), 119 (40), 91 (100), 77 (11), 65 (23). HR-MS (EI) *m/z* calcd for $C_{18}H_{16}O_4$, [M^+] 296.1049, found 296.1054.

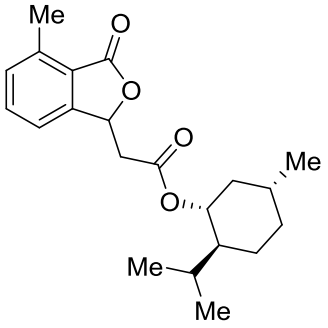


3ai

4-(Fluorobenzyl)-2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3ai):

The representative procedure **A** was followed using 2-methylbenzoic acid (**1a**) (136 mg, 1.00 mmol, 1.0 equiv) and 4-fluorobenzyl acrylate (**2i**) (249 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 1/1 + 5 % Net_3) yielded **3ai** (277 mg, 0.92 mmol, 92%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (dd, J = 7.6, 7.6 Hz, 1H), 7.38–7.25 (m, 3H), 7.20 (d, J = 7.6 Hz, 1H), 7.05 (dd, J = 8.8, 8.8 Hz, 2H), 5.81 (t, J = 6.5 Hz, 1H), 5.15 (m, 2H), 2.91 (d, J = 6.5 Hz, 2H), 2.67 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.1 (C_q), 169.2 (C_q), 162.9 (d, $^{1}J_{C\text{-}F}$ = 247.4 Hz, C_q), 149.2 (C_q), 140.2 (C_q), 134.1 (CH), 131.3 (CH), 131.3 (C_q), 130.6 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz, CH), 123.5 (C_q), 119.3 (CH), 115.7 (d, $^{2}J_{C\text{-}F}$ = 21.5 Hz, CH), 76.0 (CH), 66.4 (CH_2), 39.9 (CH_2), 17.5 (CH_3).^{19}F NMR (282 MHz, $CDCl_3$): δ = -113.18. IR (ATR): 2959, 2924, 1602, 1482, 1385, 1289, 1090, 1046, 787, 687 cm^{-1}. MS (EI) *m/z* (relative

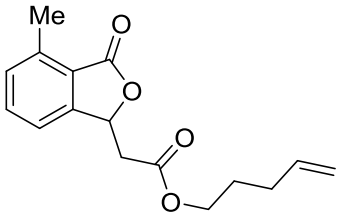
intensity): 314 (26) [M^+], 205 (52), 162 (68), 147 (53), 119 (42), 109 (100), 91 (28), 83 (16). HR-MS (EI) *m/z* calcd for $C_{18}H_{15}FO_4$, [M^+] 314.0954, found 314.0963.



3aj

(*1R,2S,5R*)-2-*iso*-Propyl-5-methylcyclohexyl-2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3aj):

The representative procedure **A** was followed using 2-methylbenzoic acid (**1a**) (136 mg, 1.00 mmol, 1.0 equiv) and *R*-(-)-menthyl acrylate (**2j**) (316 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3aj** (238 mg, 0.69 mmol, 69%) as colourless solid. The product was observed as a 57:43 mixture of two diastereomers. M.p.: 81-84 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.31–7.27 (m, 2H), 5.80 (m, 1H), 4.76 (m, 1H), 2.97–2.78 (m, 2H), 2.69 (s, 3H), 2.06–1.62 (m, 4H), 1.58–1.25 (m, 2H), 1.11–0.83 (m, 9H), 0.76 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2 (C_q), 169.1 (C_q), 149.4 (C_q), 140.0 (C_q), 134.0 (CH), 131.2 (CH), 119.4 (CH), 100.2 (C_q), 76.3 (CH), 75.5 (CH), 47.1 (CH), 40.9 (CH_2), 40.1 (CH_2), 34.3 (CH_2), 31.6 (CH), 26.4 (CH), 23.5 (CH_2), 22.1 (CH_3), 20.9 (CH_3), 17.5 (CH_3), 16.4 (CH_3). IR (ATR): 2938, 2864, 1751, 1725, 1601, 1481, 1288, 1199, 1175, 688 cm^{-1}. MS (EI) *m/z* (relative intensity) 344 (1) [M^+], 206 (70), 189 (16), 161 (18), 147 (100), 138 (21), 123 (14), 95 (33). HR-MS (ESI) *m/z* calcd for $C_{21}H_{29}O_4$, [M+H^+] 345.2060, found 345.2057.

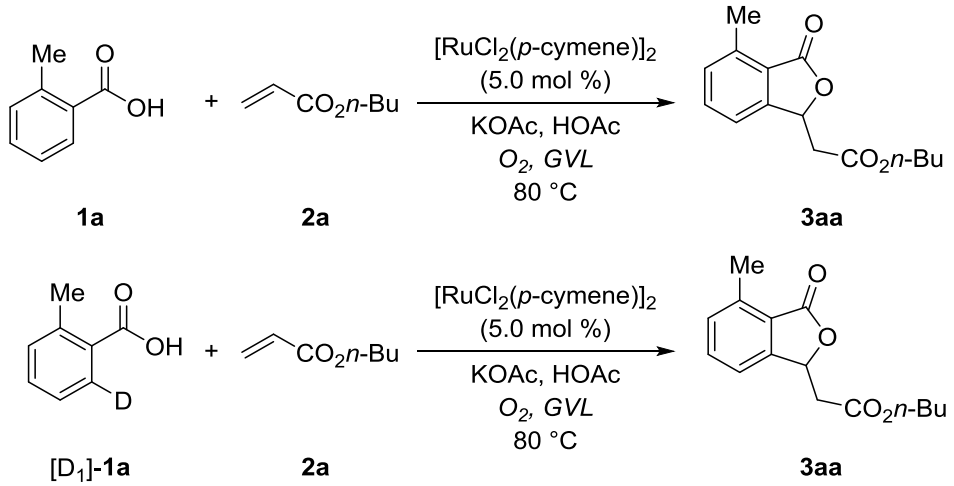


3ak

Pent-4-en-1-yl-2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (3ak):

The representative procedure **A** was followed using 2-methylbenzoic acid (**1a**) (136 mg, 1.00 mmol, 1.0 equiv) and pent-4-en-1-yl acrylate (**2k**) (210 mg, 1.50 mmol, 1.5 equiv). Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3ak** (169 mg, 0.62 mmol, 62%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (dd, J = 7.6, 7.6 Hz, 1H), 7.34–7.22 (m, 2H), 5.87–5.70 (m, 2H), 5.08–4.96 (m, 2H), 4.17 (t, J = 6.5 Hz, 2H), 2.87 (d, J = 6.5 Hz, 2H), 2.69 (s, 3H) 2.11 (m, 2H), 1.74 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2 (C_q), 169.5 (C_q), 149.4 (C_q), 140.1 (C_q), 137.4 (CH), 134.1 (CH), 131.3 (CH), 123.6 (C_q), 119.4 (CH), 115.6 (CH_2), 76.2 (CH), 64.8 (CH_2), 39.9 (CH_2), 30.1 (CH_2), 27.8 (CH_2), 17.5 (CH_3). IR (ATR): 3078, 2927, 1755, 1731, 1601, 1237, 1046, 912, 687, 630 cm^{-1}. MS (EI) *m/z* (relative intensity) 274 (3) [M^+], 207 (40), 189 (11), 160 (24), 147 (100), 119 (19), 91 (26), 68 (46). HR-MS (ESI) *m/z* calcd for $C_{16}H_{19}O_4$, [M+H^+] 275.1278, found 275.1281.

Kinetic isotope effect (KIE) studies for the synthesis of phthalide 3aa



Two independent reactions of *n*-butyl acrylate (**2a**) with 2-methylbenzoic acids **1a** and [D_1]-**1a** respectively were performed to determine the KIE value by comparison of the initial rates. The representative procedure **A** was followed using **1a** (136 mg, 1.0 mmol) or [D_1]-**1a** (137 mg, 1.0 mmol), acrylate **2a** (192 mg, 1.0 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (30.6 mg, 5.0 mol %), *n*-dodecane (100 mg), HOAc (60 mg, 1.0 mmol) and KOAc (98 mg, 1.0 mmol) in GVL (2.0 mL) under an ambient atmosphere of O_2. The mixture was stirred at 80 °C, a periodic aliquot (10 μL) was removed by a syringe and analyzed by GC to provide the following data:

Table-S2: Formation of 3aa. r.i. = relative integral of 3as vs. *n*-dodecane

Time [min]	**Conversion (1a) [r.i.]**	**Conversion (1a) [%]**	**Conversion** [D_1]-**1a [r.i.]**	**Conversion** [D_1]-**1a** [%]
10	0.27252	6.22905	0.26618	6.08418
15	0.31989	7.31185	0.28758	6.57329
20	0.38549	8.81117	0.38211	8.73404
25	0.44963	10.27729	0.45262	10.34562
30	0.50417	11.52389	0.53759	12.28783
40	0.65753	15.02926	0.65206	14.90412
50	0.81280	18.57822	0.81391	18.60369
65	1.04867	23.96968	1.07684	24.61338

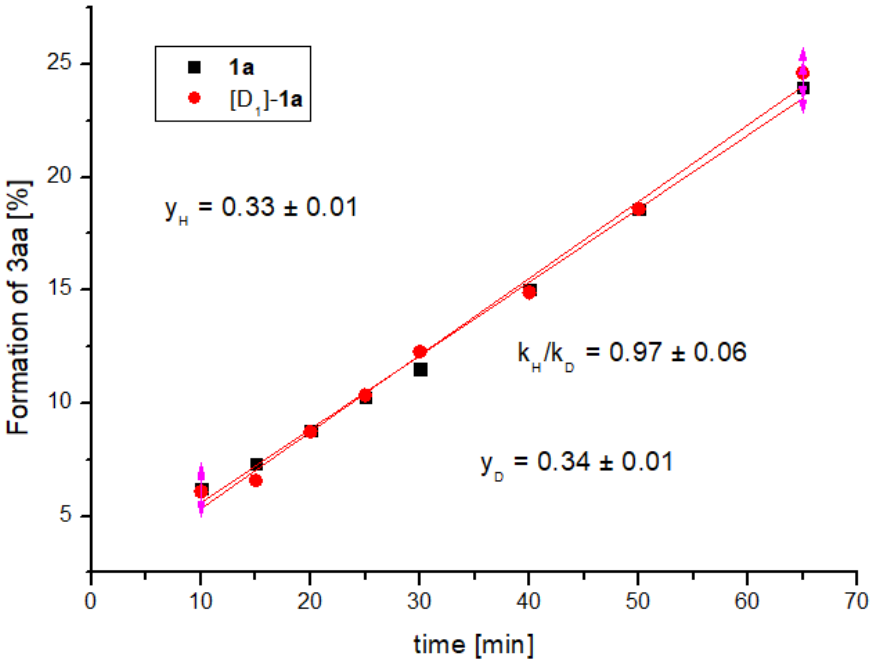
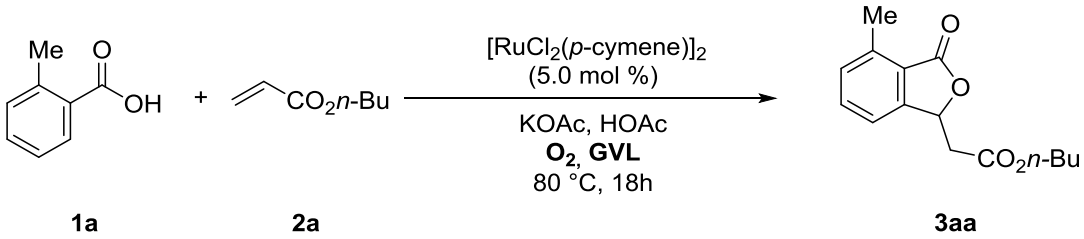


Figure-S1: Formation of 3aa.

O_2-uptake study for the synthesis of phthalide 3aa



1a **2a** **3aa**

2-Methylbenzoic acid (**1a**) (136 mg, 1.00 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (30.6 mg, 0.05 mmol, 5.0 mol %) and KOAc (108 mg, 1.10 mmol, 1.1 equiv) were placed in a predried 25 mL Schlenk tube. The flask was evacuated and flushed with ambient oxygen 3 times. *n*-Butyl acrylate (**2a**) (192 mg, 1.5 mmol, 1.5 equiv) and HOAc (60 mg, 1.0 mmol, 1.0 equiv) in oxygen saturated GVL (1.0 mL) were added. The Schlenk tube was connected to a burette with a reservoir filled with oxygen-saturated water. The mixture was stirred at 80 °C and the changes in volume were determined as shown in Table-S3. Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5% NEt_3) yielded **3aa** (229 mg, 0.87 mmol, 87%) as a colourless oil.

Table-S3: Oxygen uptake.

t / h	V / mL	ΔV / mL	n / mmol
0	23.2	0.00	0.00
2	22.6	0.6	0.02459
5	22.0	1.2	0.04918
8	21.5	1.7	0.06967
10	19.9	3.3	0.13525
16	18.3	4.9	0.20082
23	17.6	5.6	0.22951
29	16.2	7.0	0.28689
35	15.6	7.6	0.31148
41	15.1	8.1	0.33197
46	14.8	8.4	0.34426
55	14.5	8.7	0.35656
65	14.2	9.0	0.36885
95	13.5	9.7	0.39754
108	13.3	9.9	0.40574
134	13.2	10.0	0.40984
150	13.0	10.2	0.41803
180	12.7	10.5	0.43033
215	12.4	10.8	0.44262
257	12.0	11.2	0.45902
308	11.5	11.7	0.47951
366	11.3	11.9	0.4877
1344	10.0	13.2	0.54098

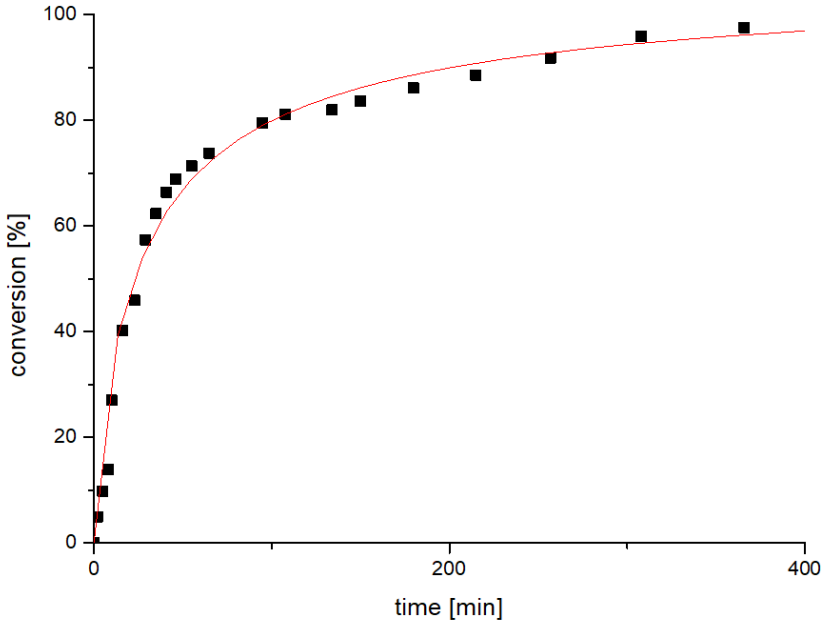
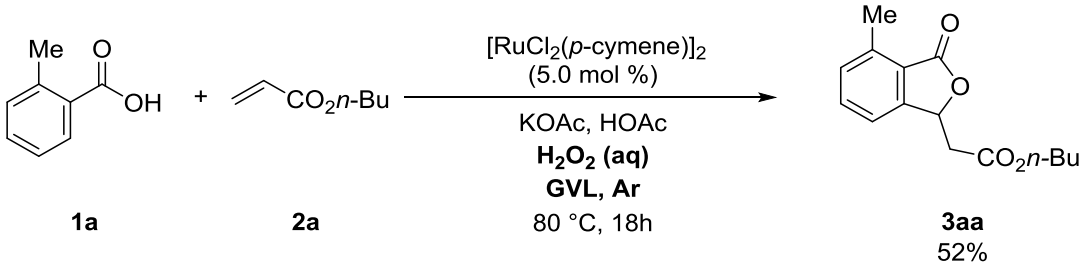


Figure-S2: Oxygen uptake.

Formation of 3aa with hydrogen peroxide as oxidant



1a **2a** **3aa**
52%

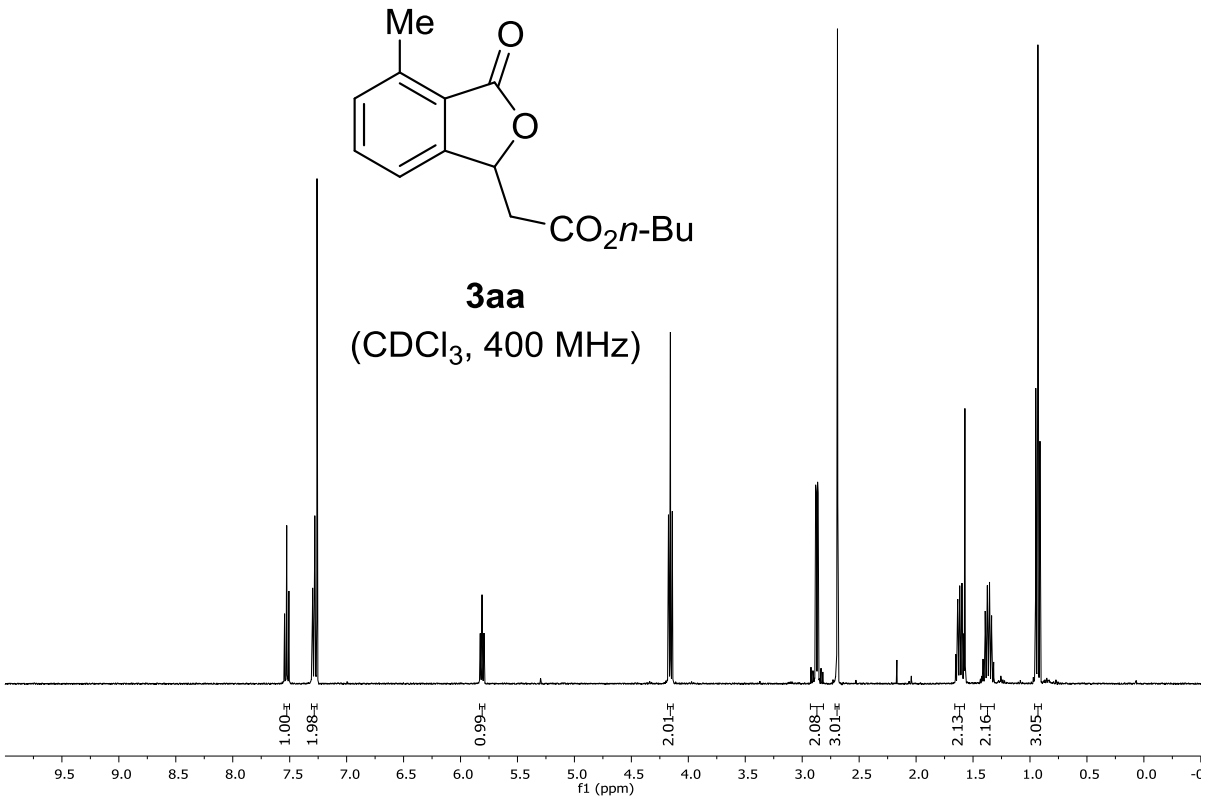
The representative procedure **A** was followed using 2-methylbenzoic acid (**1b**) (136 mg, 1.00 mmol, 1.0 equiv) and *n*-butyl acrylate (**2a**) (192 mg, 1.50 mmol, 1.5 equiv) under an Ar atmosphere instead of oxygen. Hydrogen peroxide (30 % aqueous solution, 0.3 mL) was added slowly before the mixture was warmed. Purification by column chromatography (*n*-hexane/EtOAc: 4/1 + 5 % NEt_3) yielded **3aa** (136 mg, 0.52 mmol, 52%) as a colourless solid.

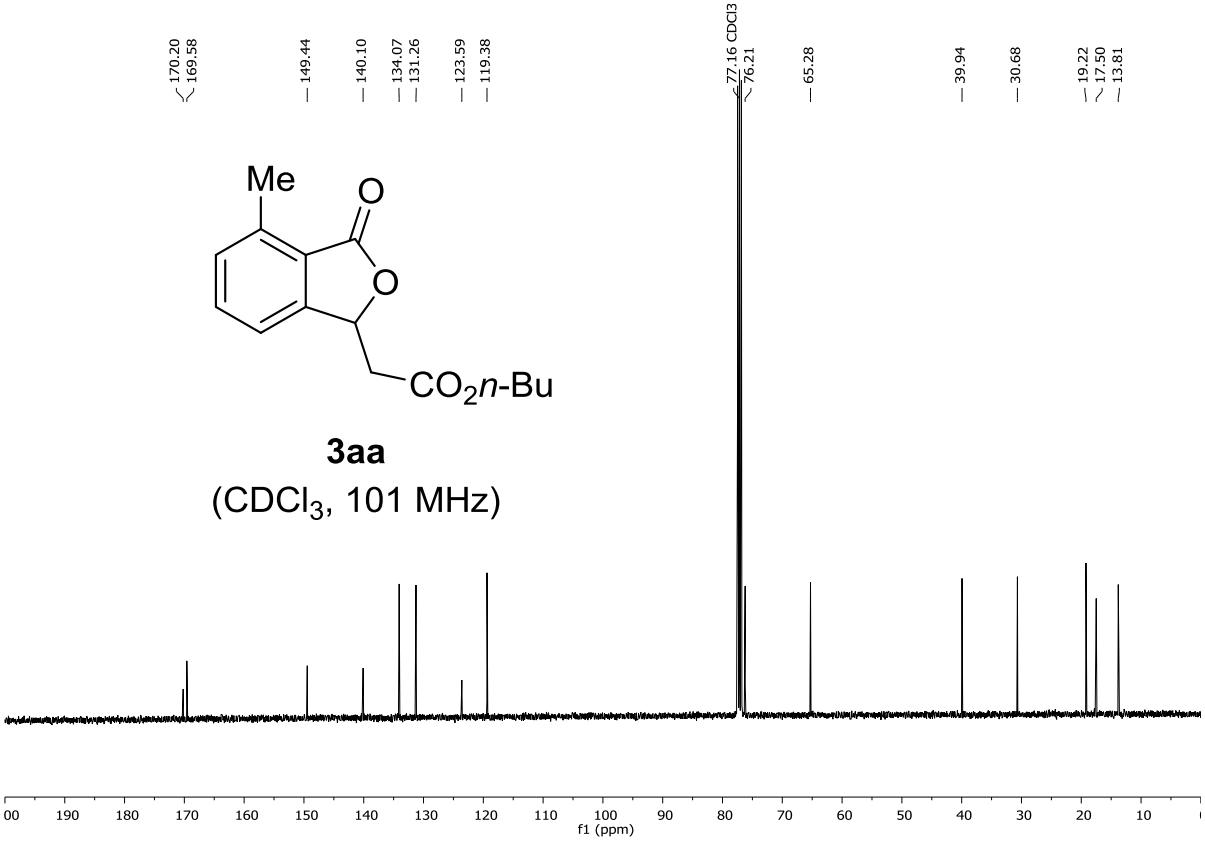
References

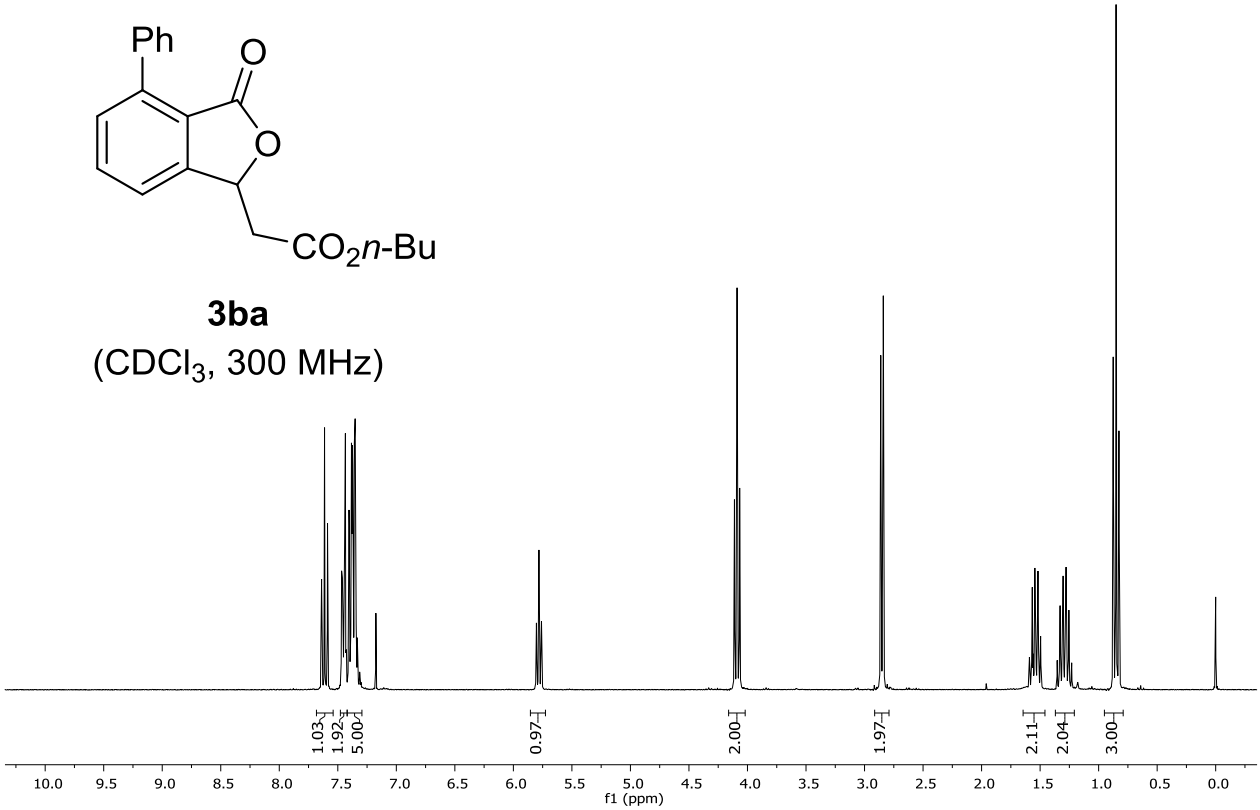
[1] S. B. Evans, J. E. Mulvaney and H.K. Hall, *J. Polym. Sci. Pol. Chem.*, 1990, **28**, 1073-1078.

[2] A. Bechtoldt, C. Tirler, K. Raghuvanshi, S. Warratz, C. Kornhaaß and L. Ackermann, *Angew. Chem. Int. Ed.*, 2016, **55**, 264-267.

NMR Spectra

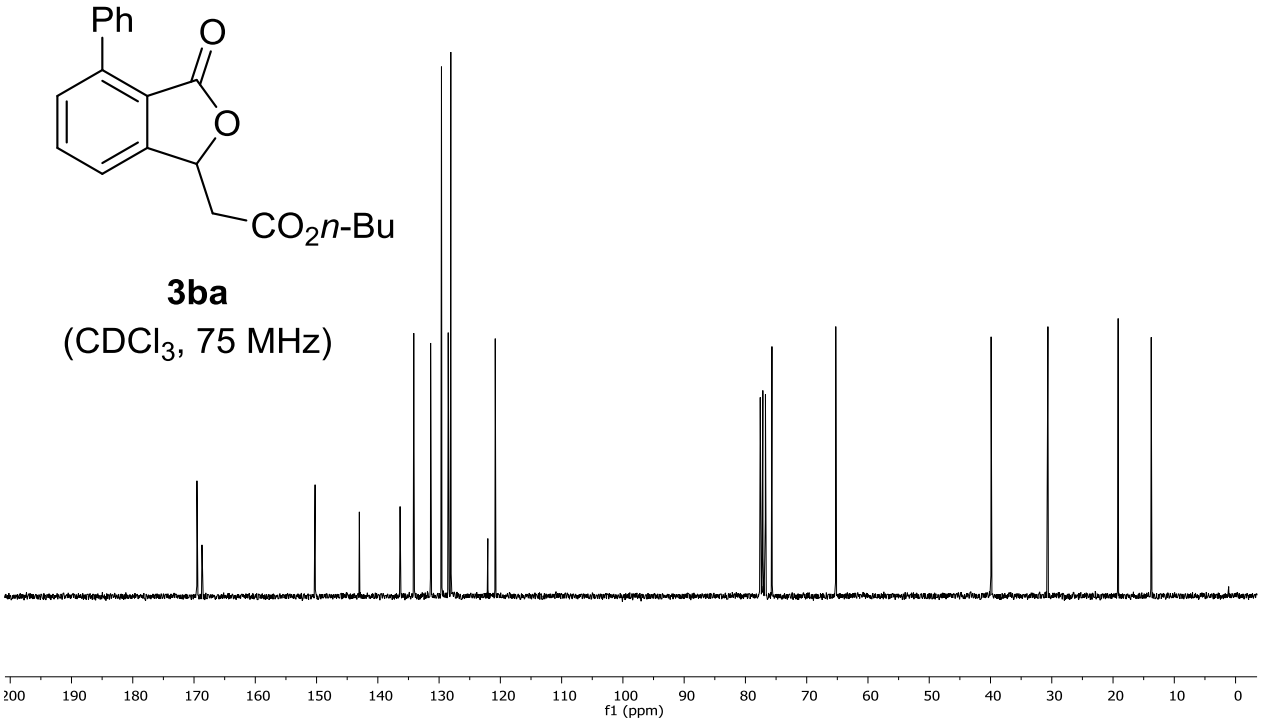

Me
O
O
CO2n-Bu
3aa
(CDCl3, 400 MHz)
1.00
1.98
0.99
2.01
2.08
3.01
2.13
2.16
3.05
f1 (ppm)


170.20
169.58
149.44
140.10
134.07
131.26
123.59
119.38
77.16 CDCl3
76.21
65.28
39.94
30.68
19.22
17.50
13.81
Me
O
O
CO2n-Bu
3aa
(CDCl3, 101 MHz)
f1 (ppm)



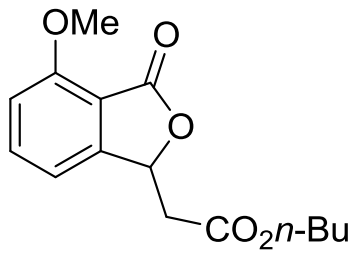
3ba

($CDCl_3$, 300 MHz)



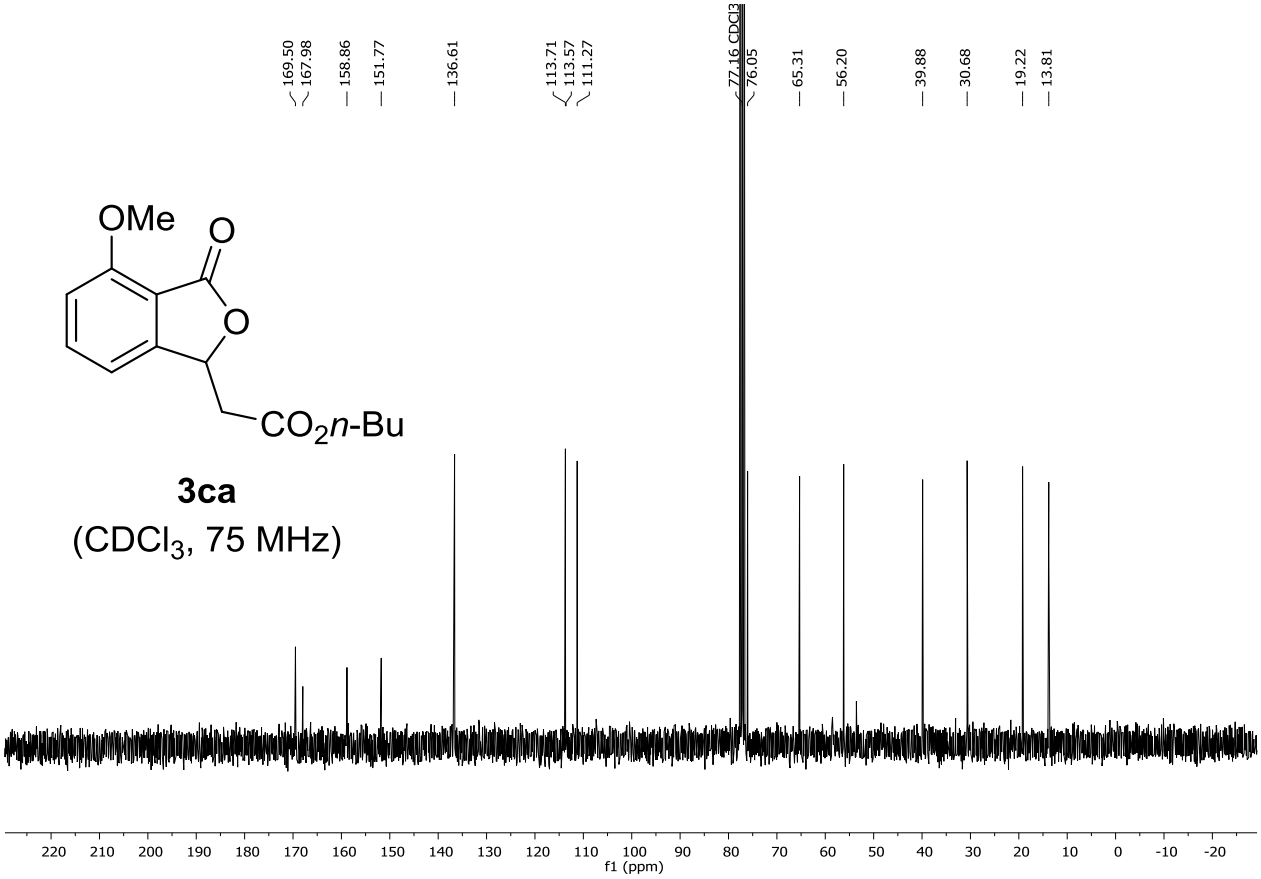
3ba

($CDCl_3$, 75 MHz)



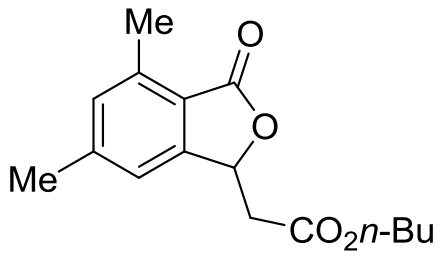
3ca

($CDCl_3$, 300 MHz)



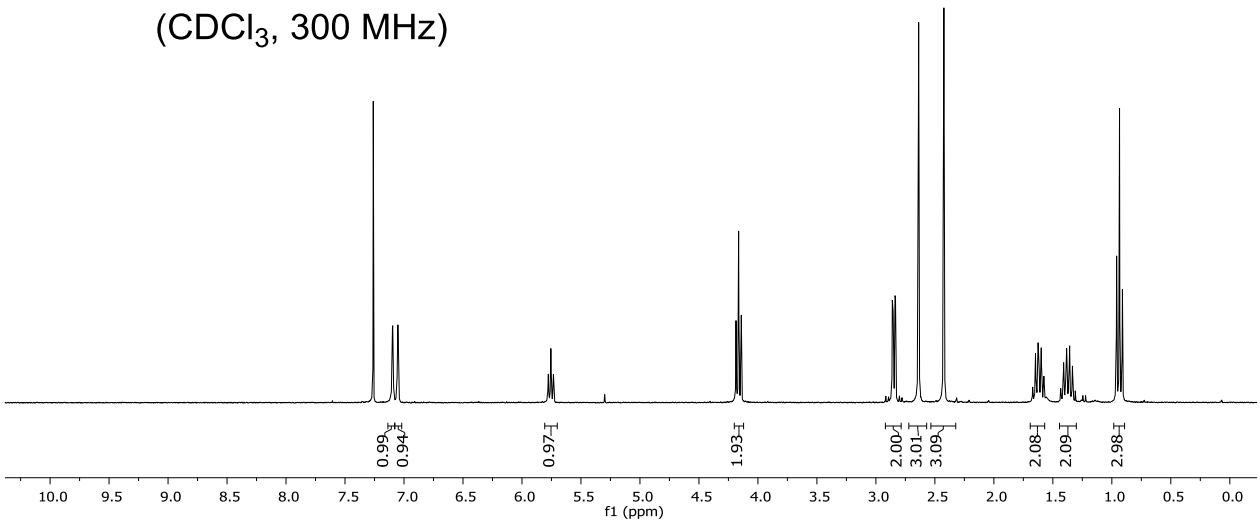
3ca

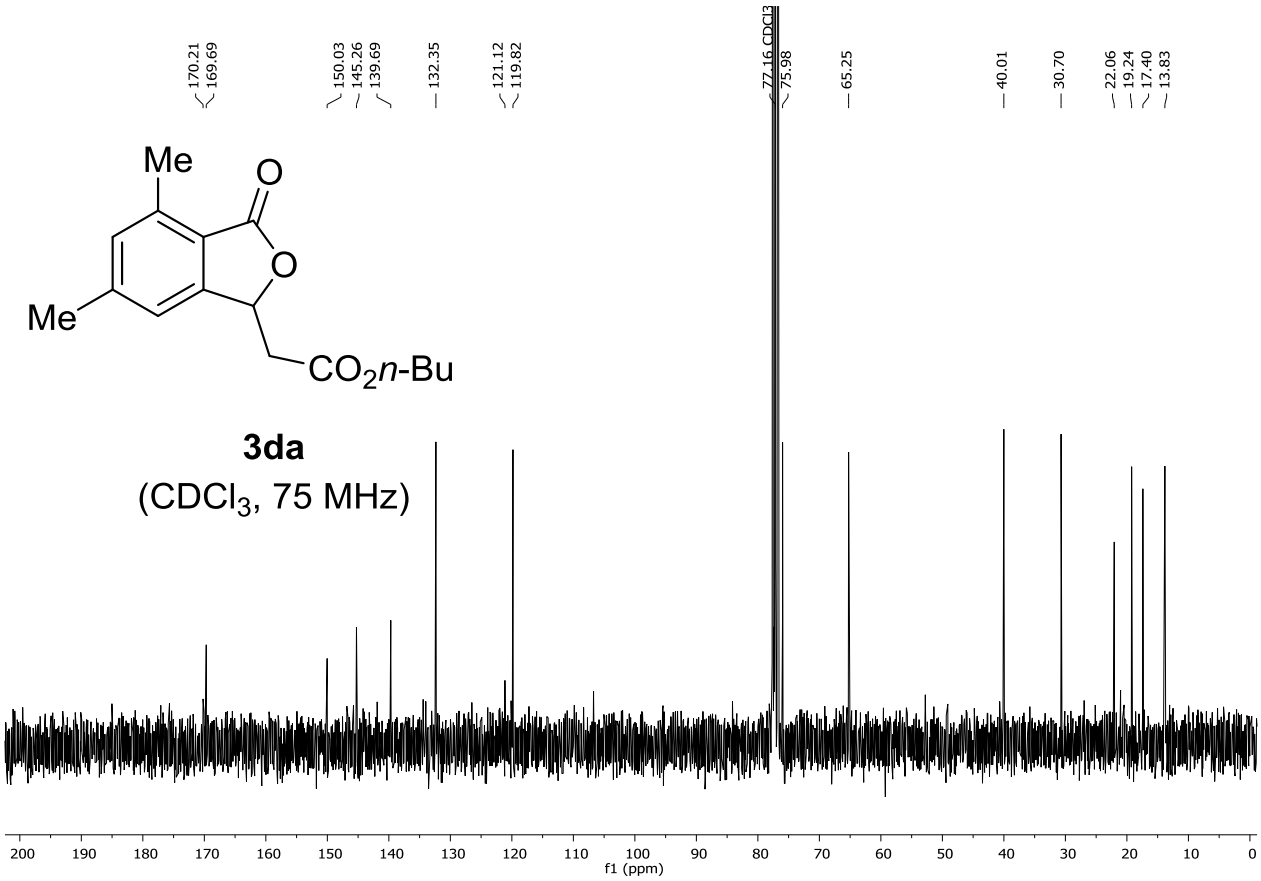
($CDCl_3$, 75 MHz)



3da

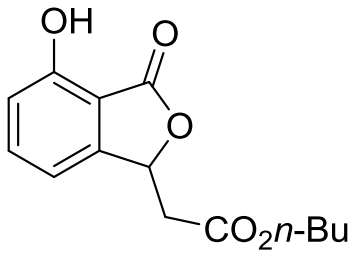
($CDCl_3$, 300 MHz)





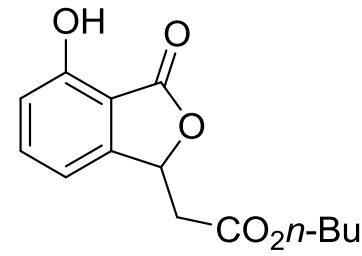
3da

($CDCl_3$, 75 MHz)



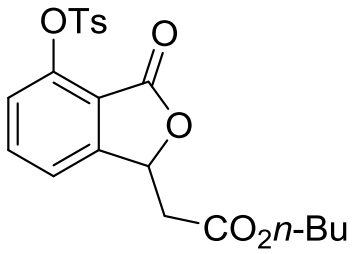
3ea

($CDCl_3$, 300 MHz)



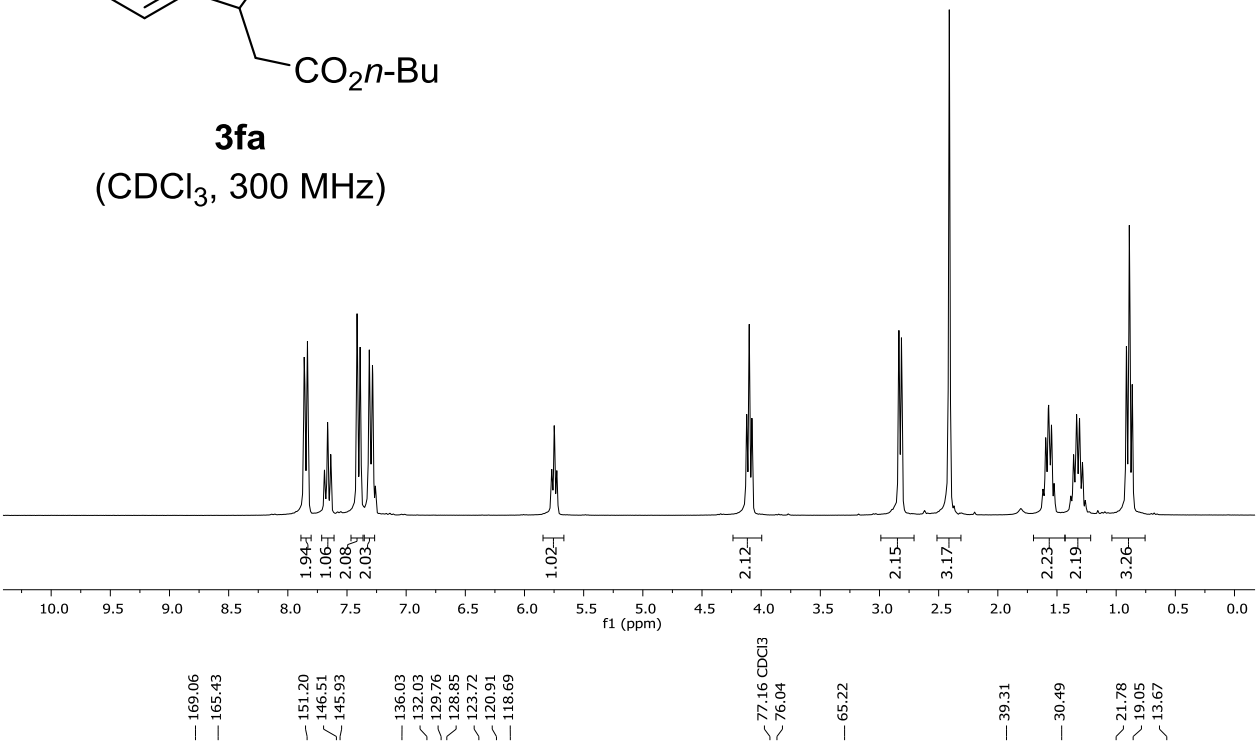
3ea

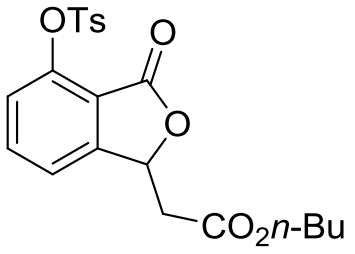
($CDCl_3$, 75 MHz)



3fa

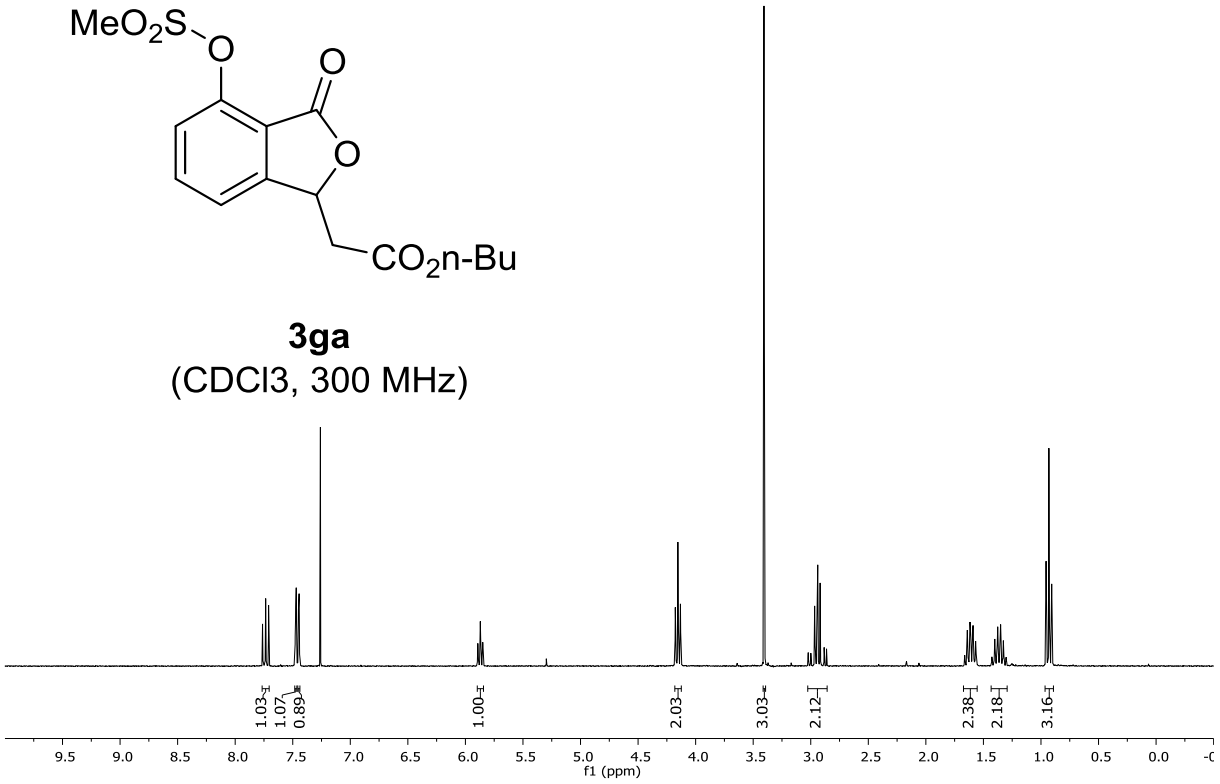
($CDCl_3$, 300 MHz)



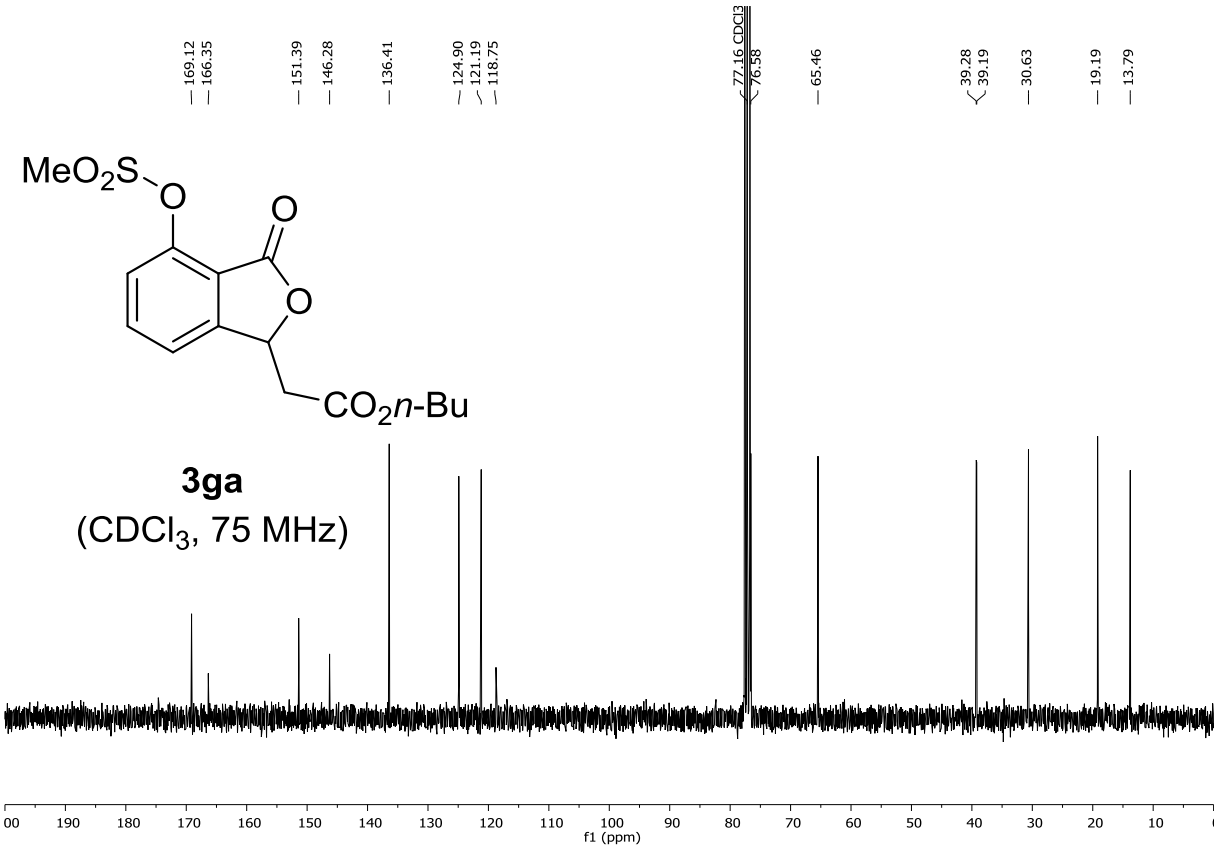


3fa

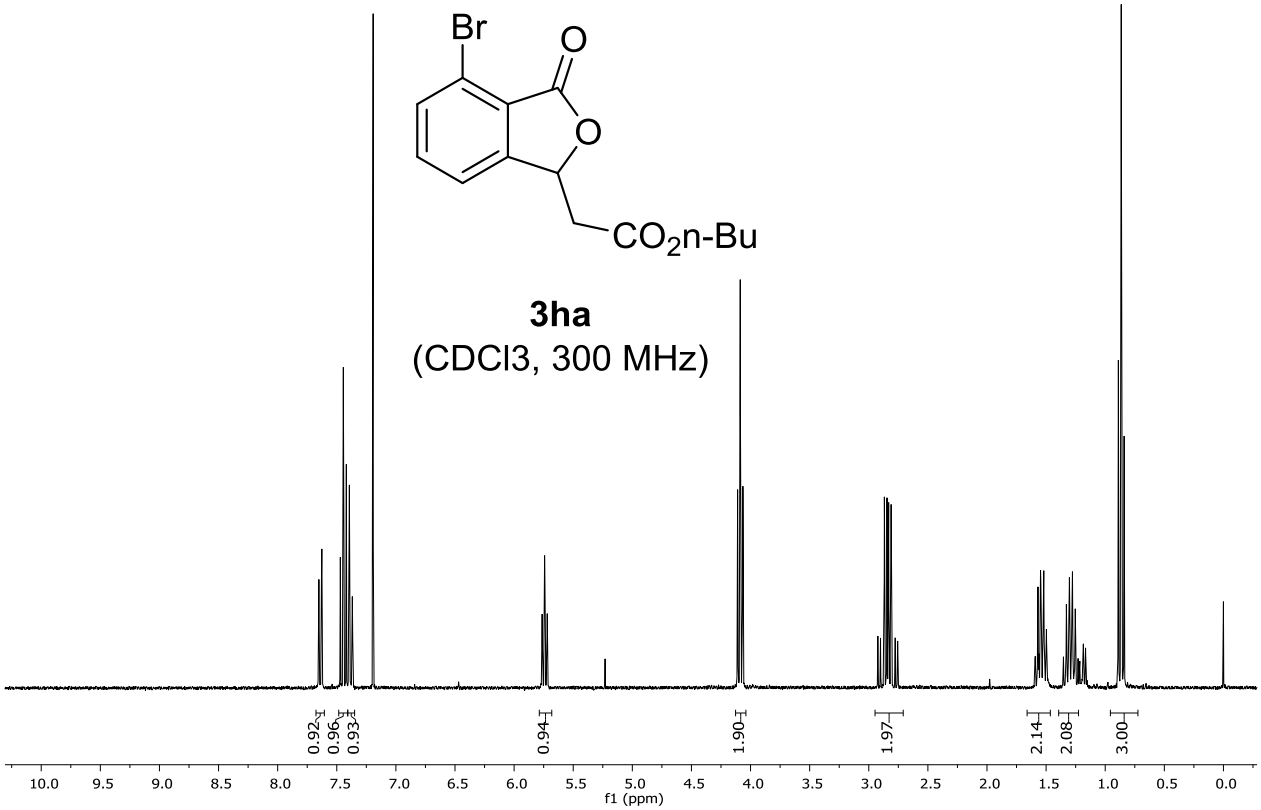
($CDCl_3$, 75 MHz)

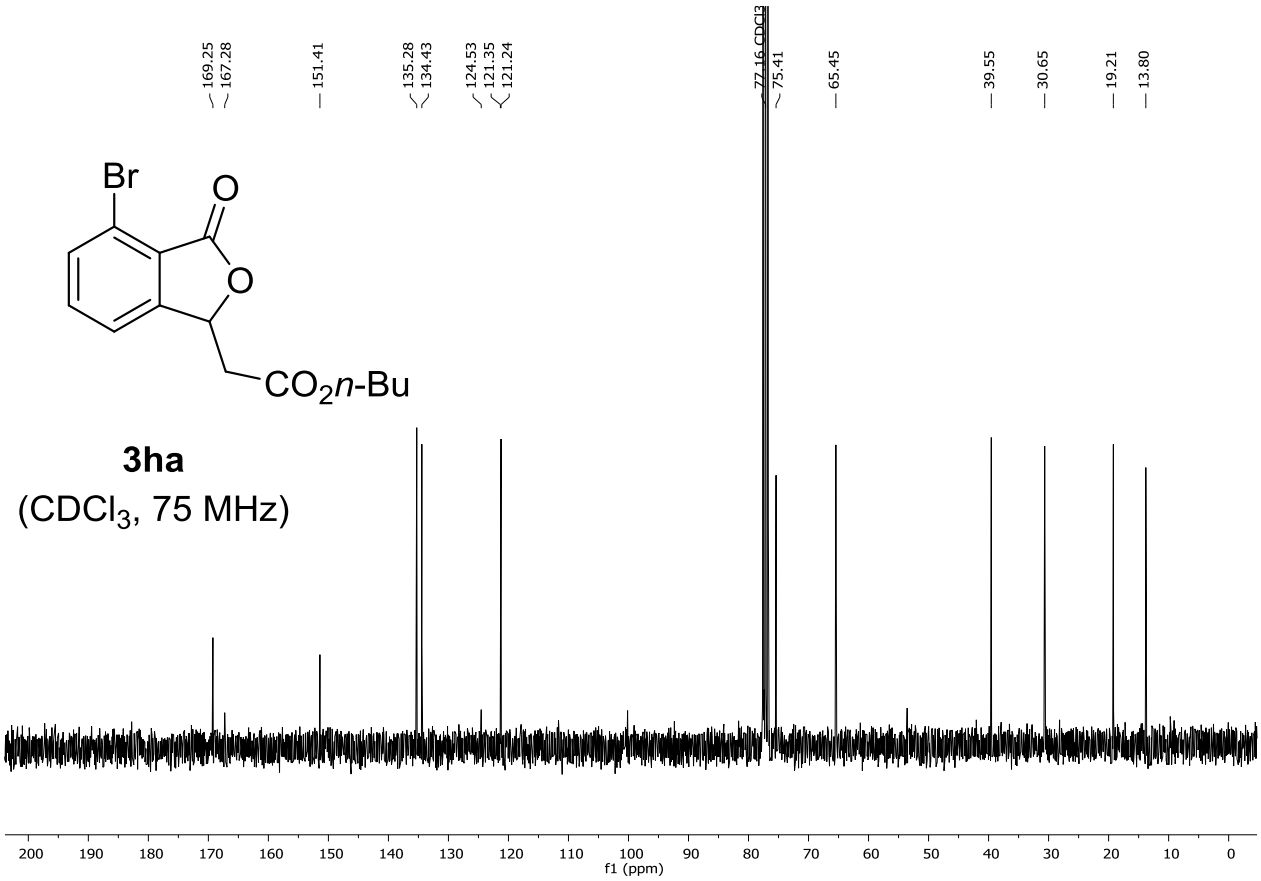


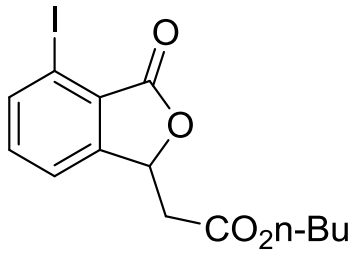
3ga
(CDCl3, 300 MHz)



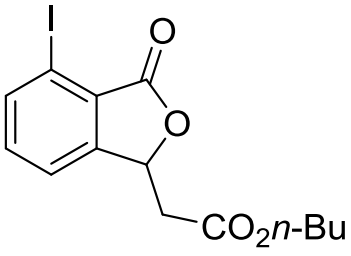
3ga
($CDCl_3$, 75 MHz)


Br
O
O
CO2n-Bu
3ha
(CDCl3, 300 MHz)
0.92
0.96
0.93
0.94
1.90
1.97
2.14
2.08
3.00
f1 (ppm)

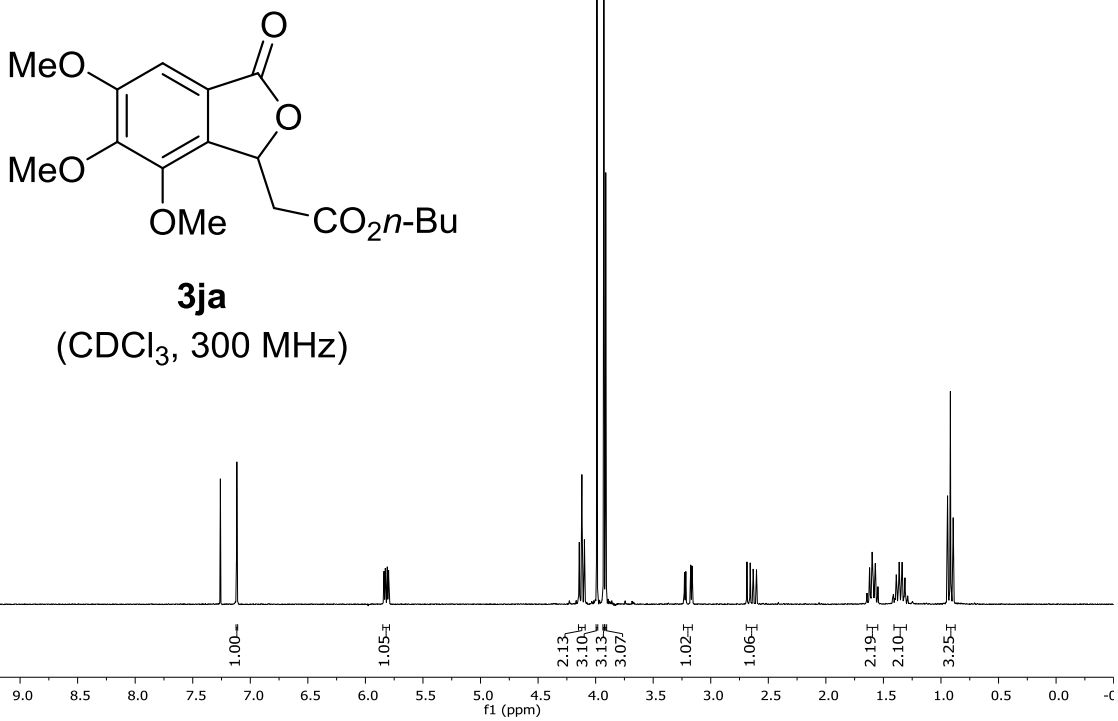

169.25
167.28
151.41
135.28
134.43
124.53
121.35
121.24
77.16 CDCl3
75.41
65.45
39.55
30.65
19.21
13.80
Br
O
O
CO2n-Bu
3ha
(CDCl3, 75 MHz)
f1 (ppm)



3ia
(CDCl3, 500 MHz)

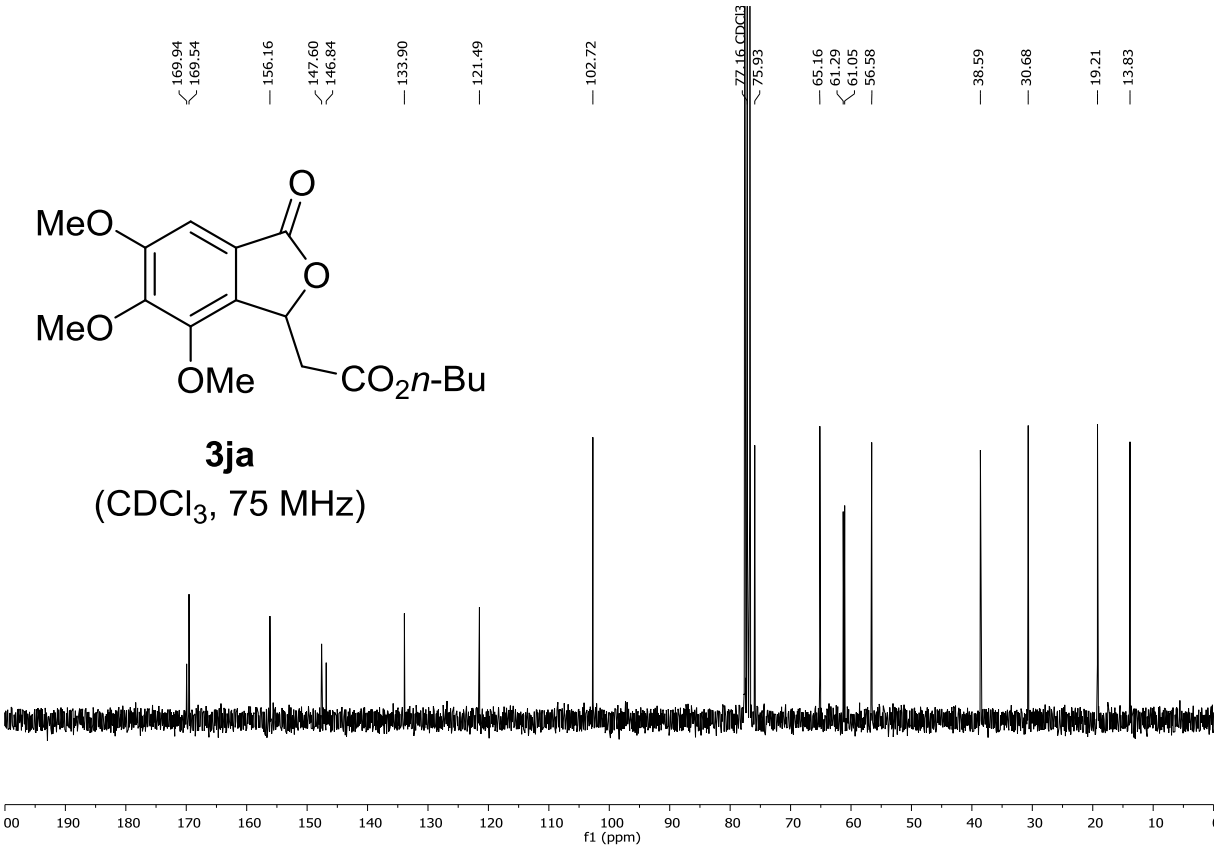


3ia
($CDCl_3$, 126 MHz)



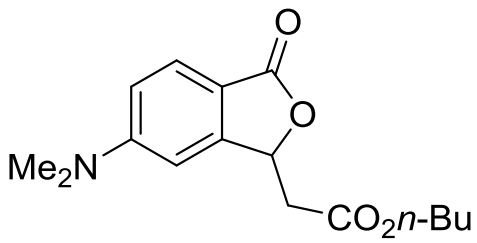
3ja

($CDCl_3$, 300 MHz)



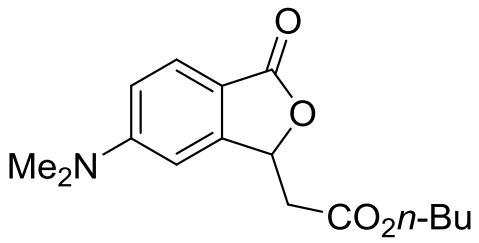
3ja

($CDCl_3$, 75 MHz)



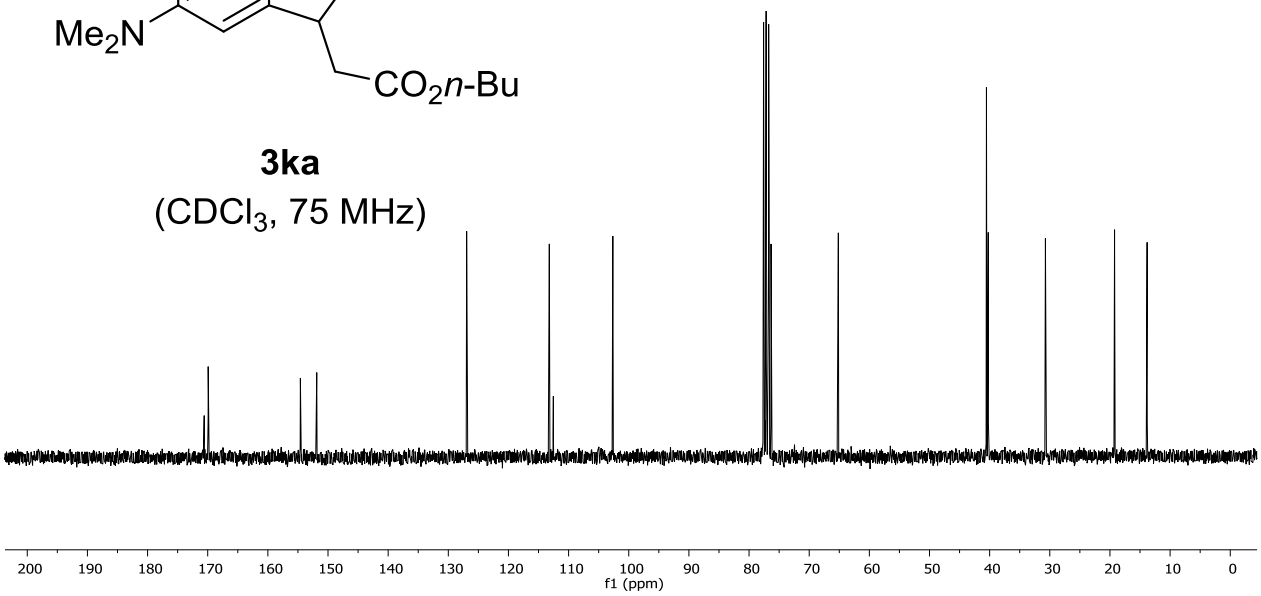
3ka

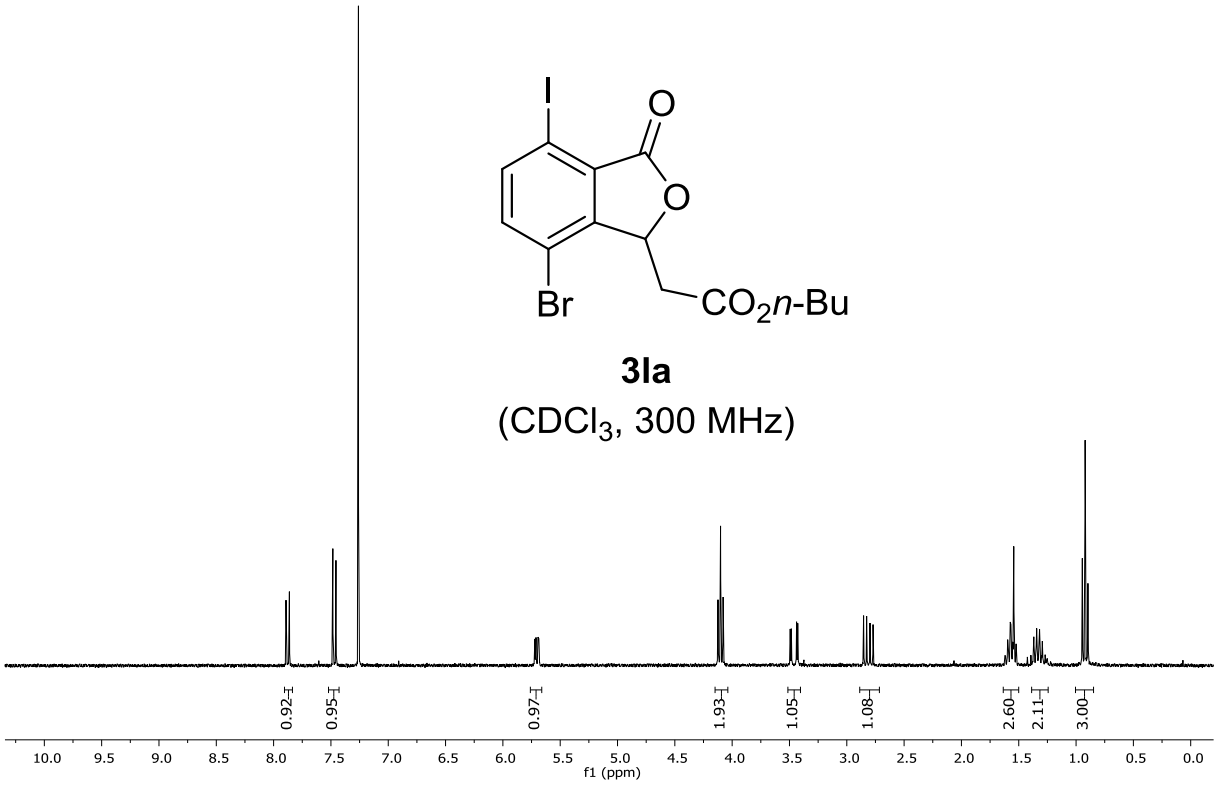
($CDCl_3$, 300 MHz)

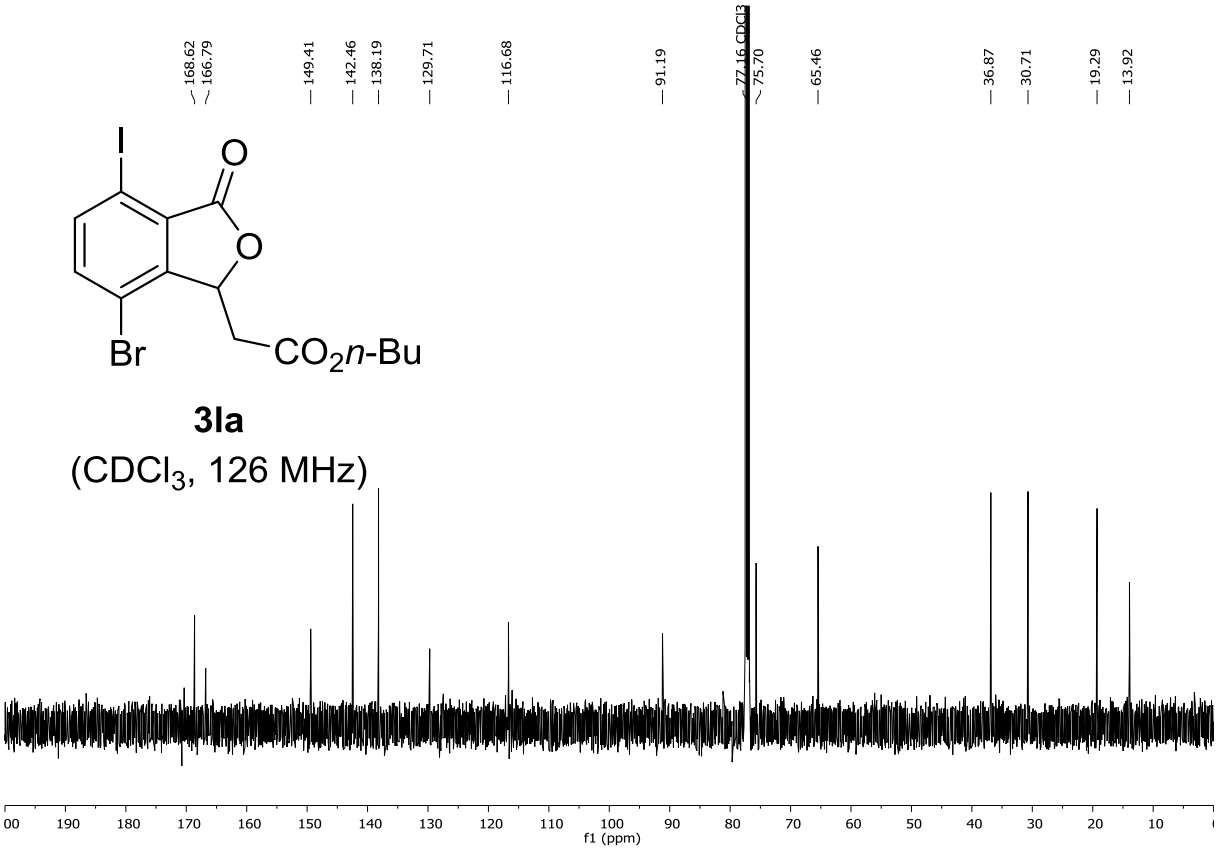


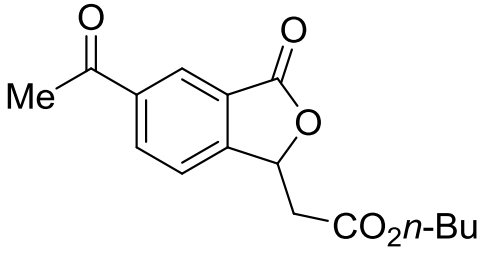
3ka

($CDCl_3$, 75 MHz)



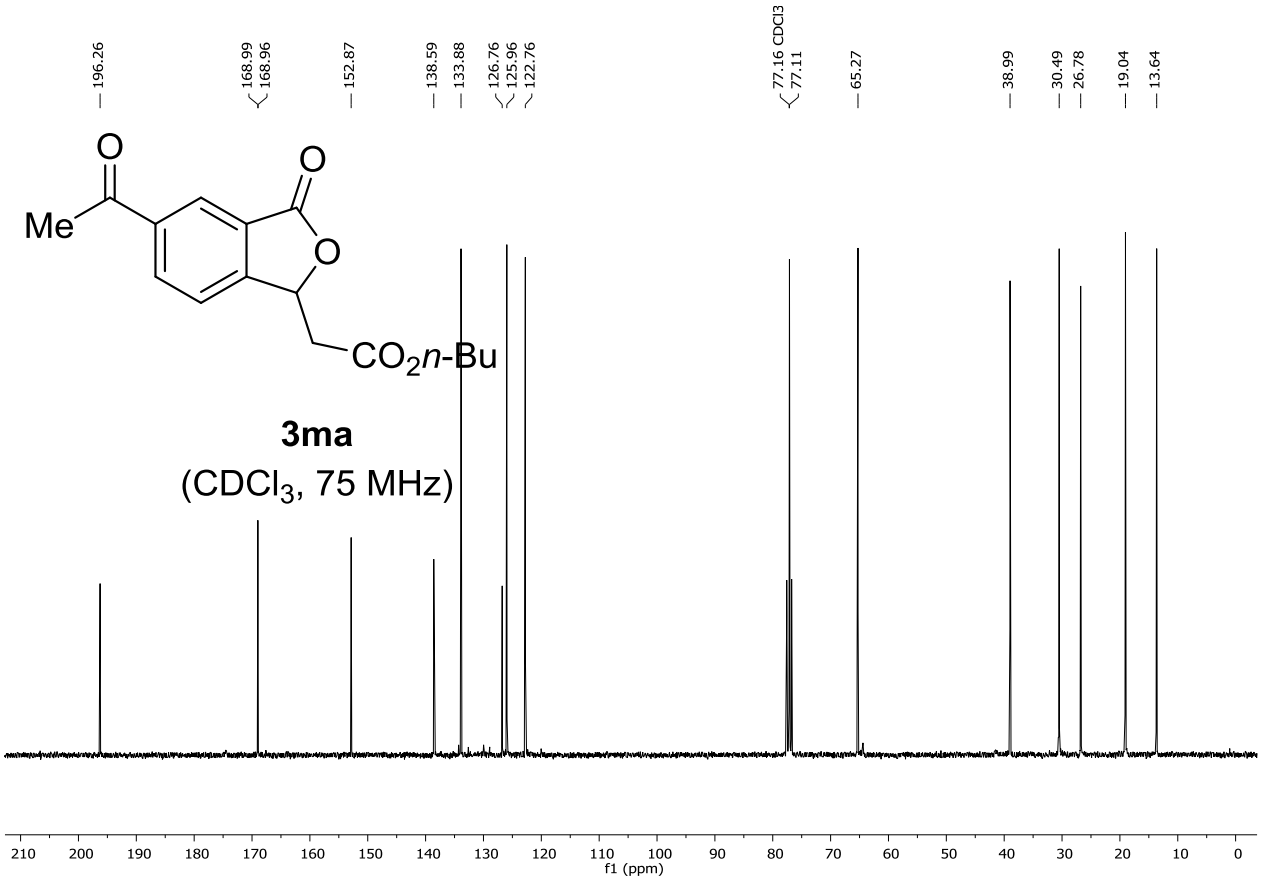

I
O
O
Br
CO2n-Bu
3Ia
(CDCl3, 300 MHz)
0.92
0.95
0.97
1.93
1.05
1.08
2.60
2.11
3.00
f1 (ppm)


168.62
166.79
149.41
142.46
138.19
129.71
116.68
91.19
77.16 CDCl3
75.70
65.46
36.87
30.71
19.29
13.92
I
O
O
Br
CO2n-Bu
3Ia
(CDCl3, 126 MHz)
f1 (ppm)



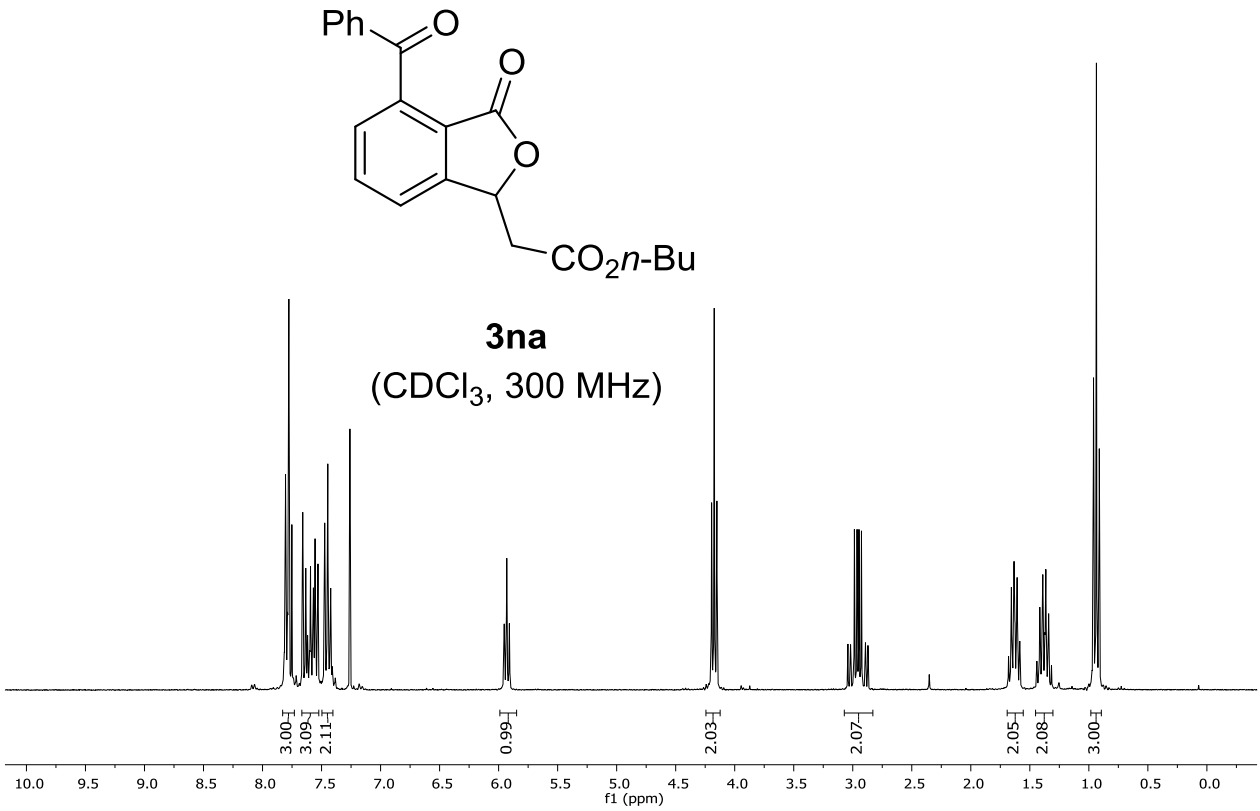
3ma

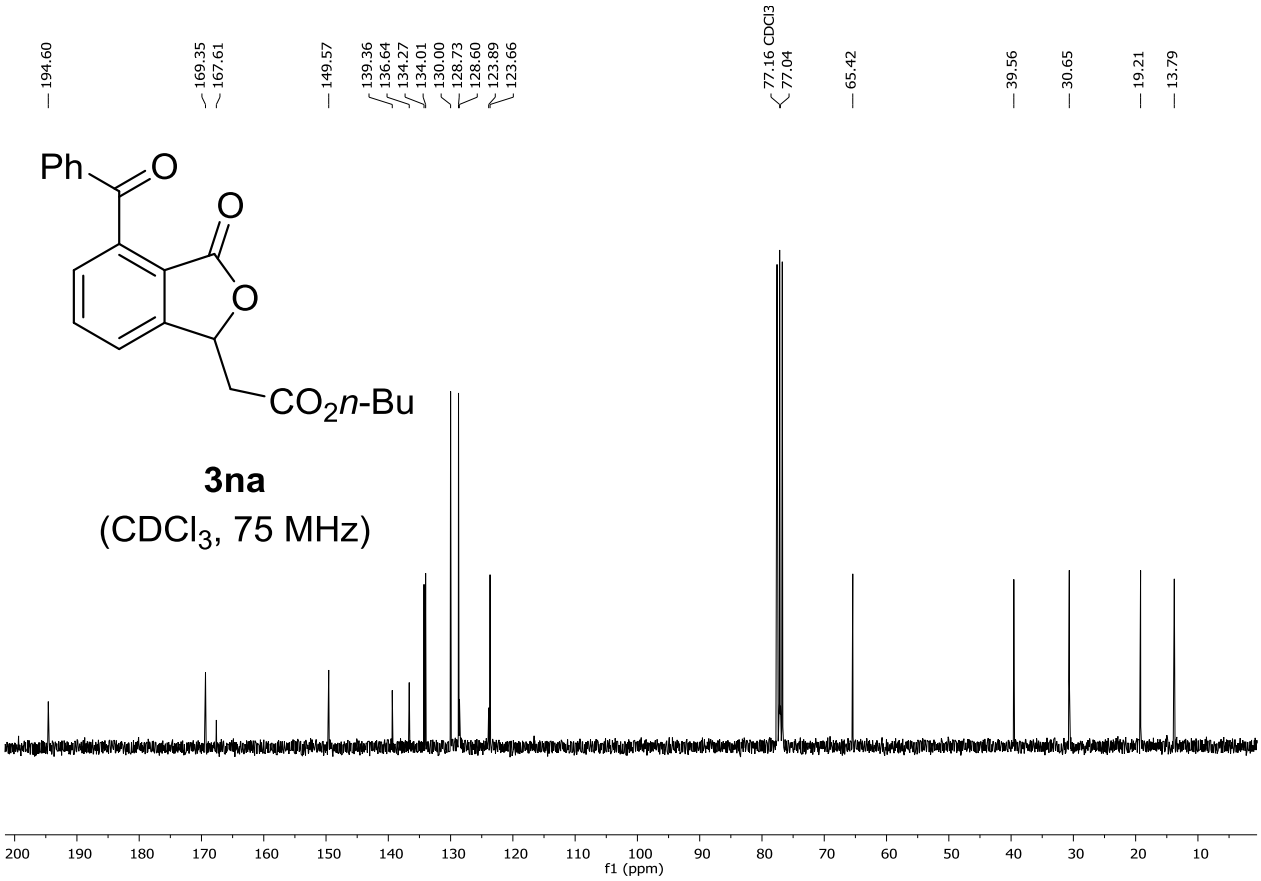
($CDCl_3$, 300 MHz)

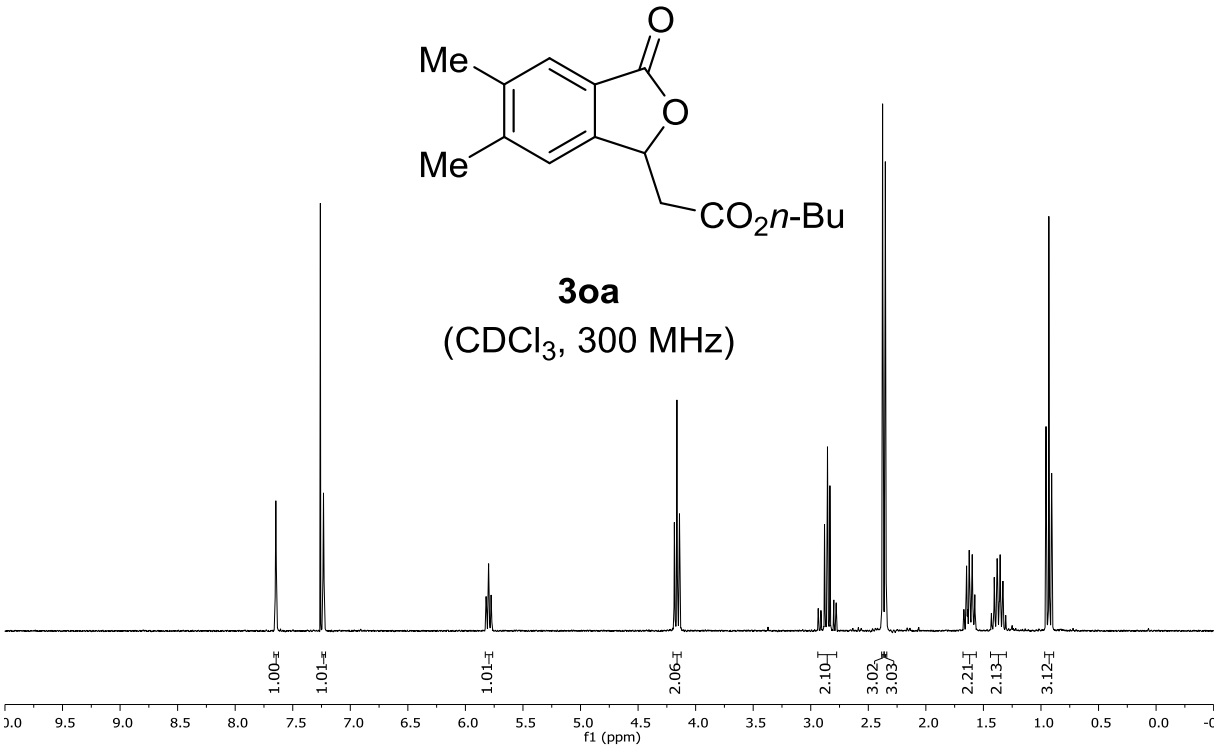


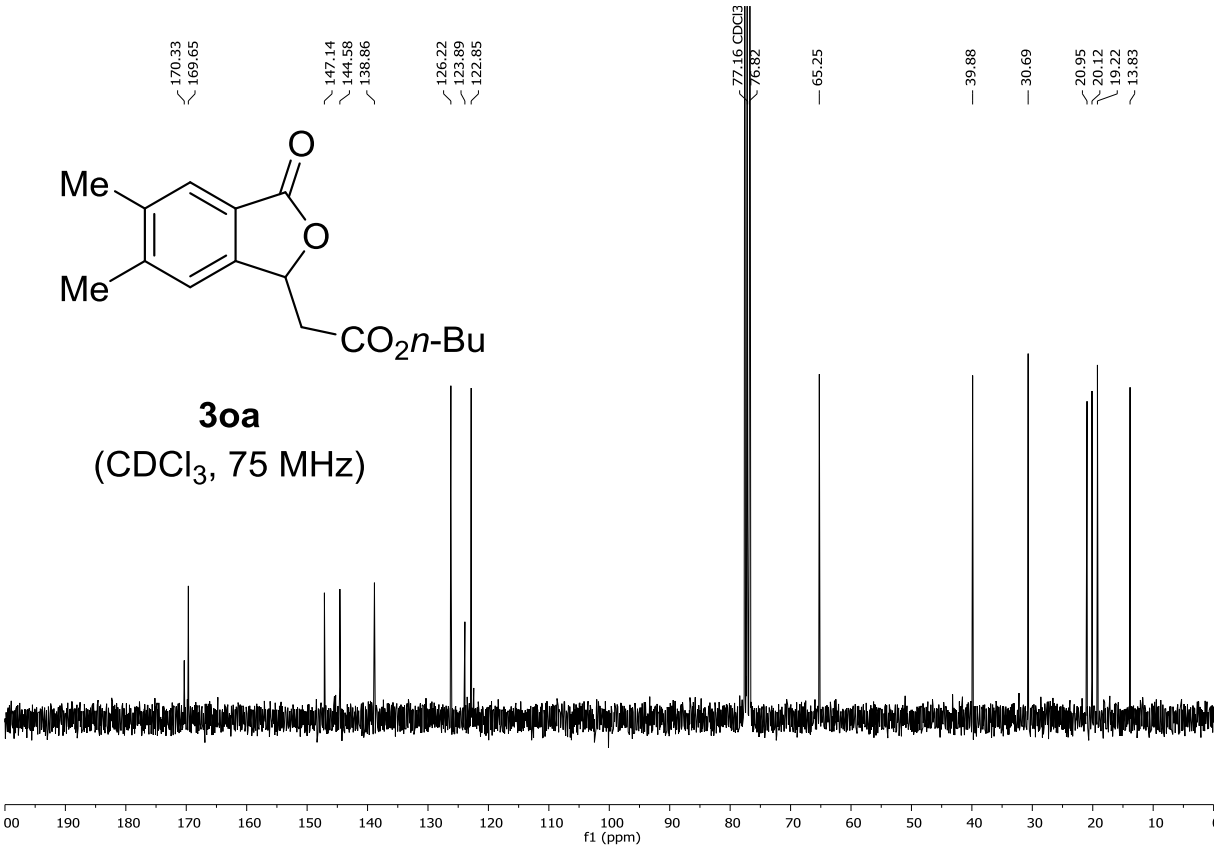
3ma

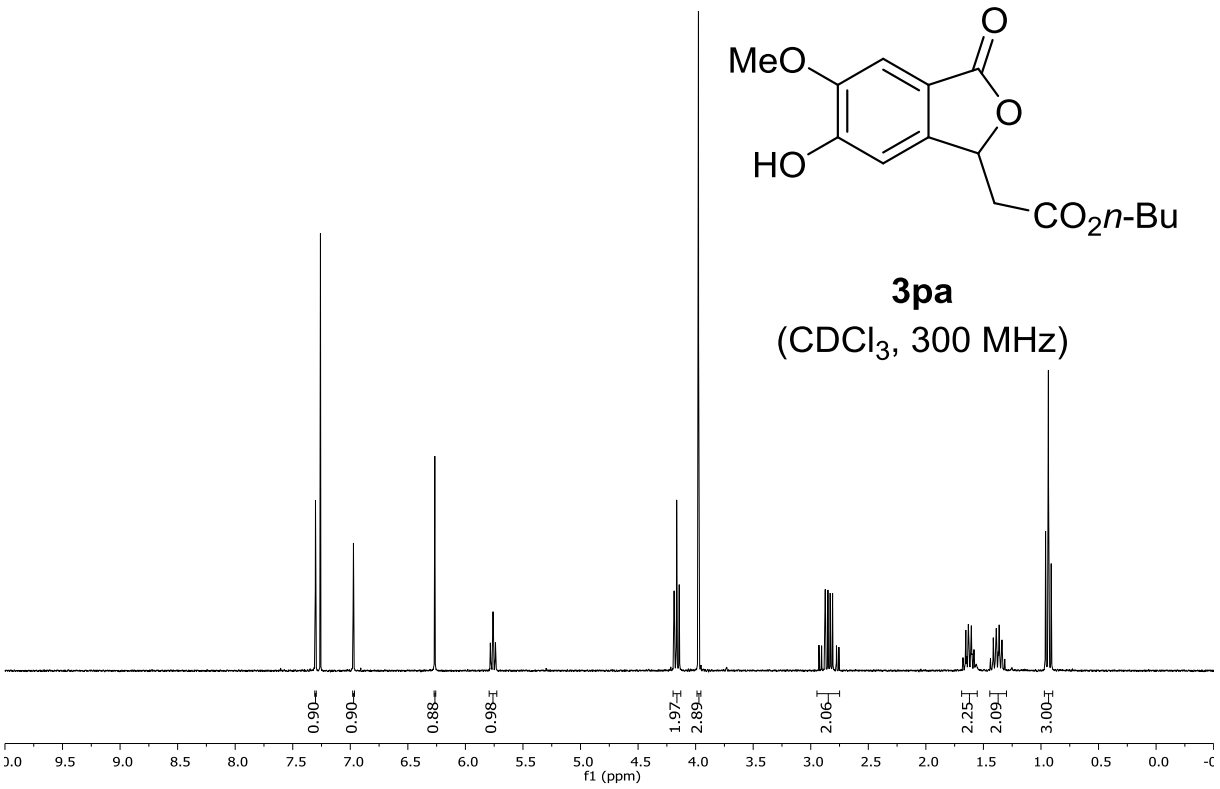
($CDCl_3$, 75 MHz)


Ph
O
O
O
CO2n-Bu
3na
(CDCl3, 300 MHz)
3.00
3.09
2.11
0.99
2.03
2.07
2.05
2.08
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


194.60
169.35
167.61
149.57
139.36
136.64
134.27
134.01
130.00
128.73
128.60
123.89
123.66
77.16 CDCl3
77.04
65.42
39.56
30.65
19.21
13.79
Ph
O
O
O
CO2n-Bu
3na
(CDCl3, 75 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

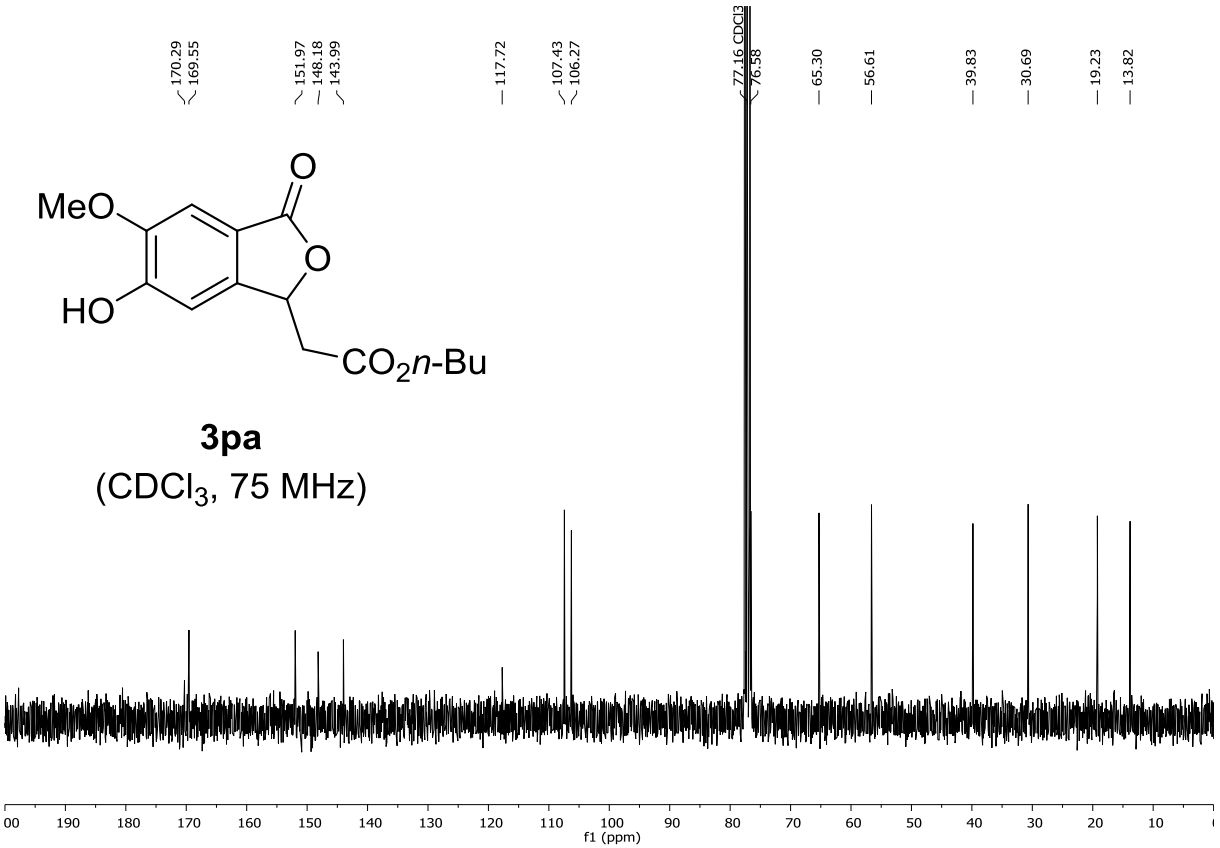

Me
Me
O
O
CO2n-Bu
3oa
(CDCl3, 300 MHz)
1.00
1.01
1.01
2.06
2.10
3.02
3.03
2.21
2.13
3.12
f1 (ppm)


170.33
169.65
147.14
144.58
138.86
126.22
123.89
122.85
77.16 CDCl3
76.82
65.25
39.88
30.69
20.95
20.12
19.22
13.83
Me
Me
O
O
CO2n-Bu
3oa
(CDCl3, 75 MHz)
f1 (ppm)



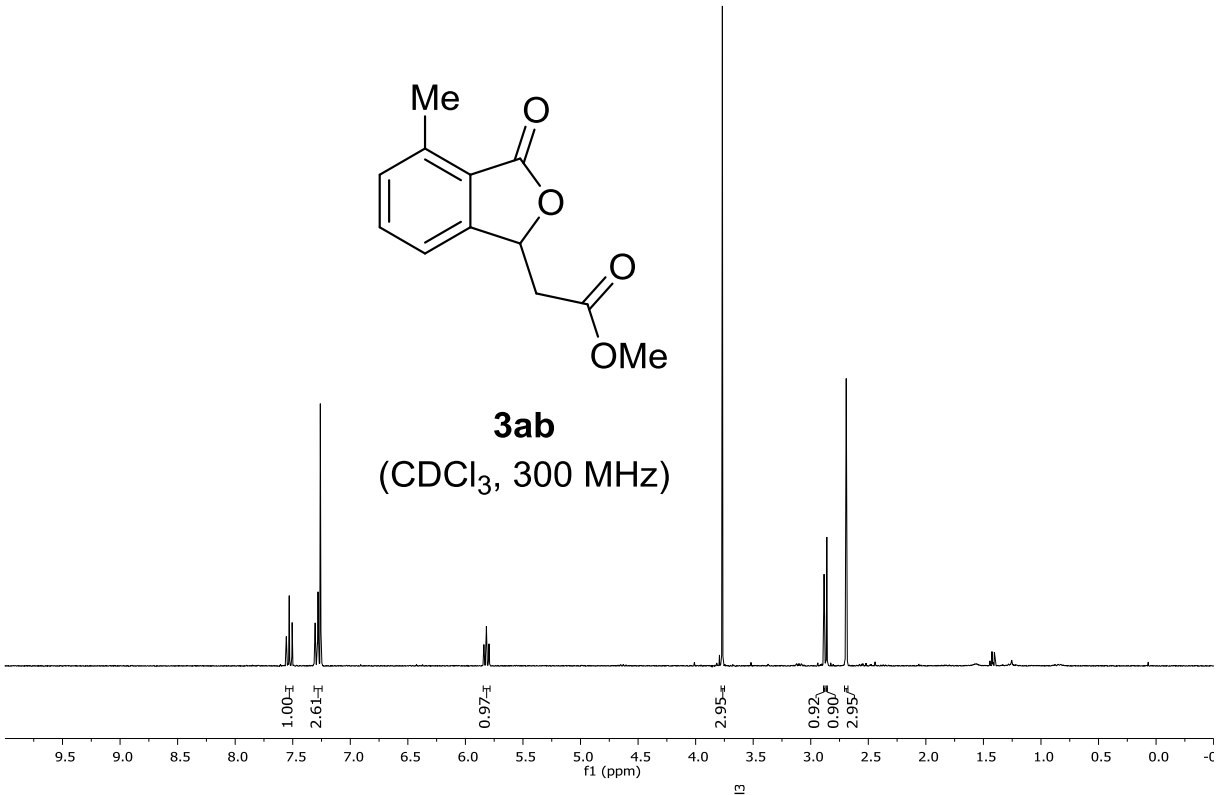
3pa

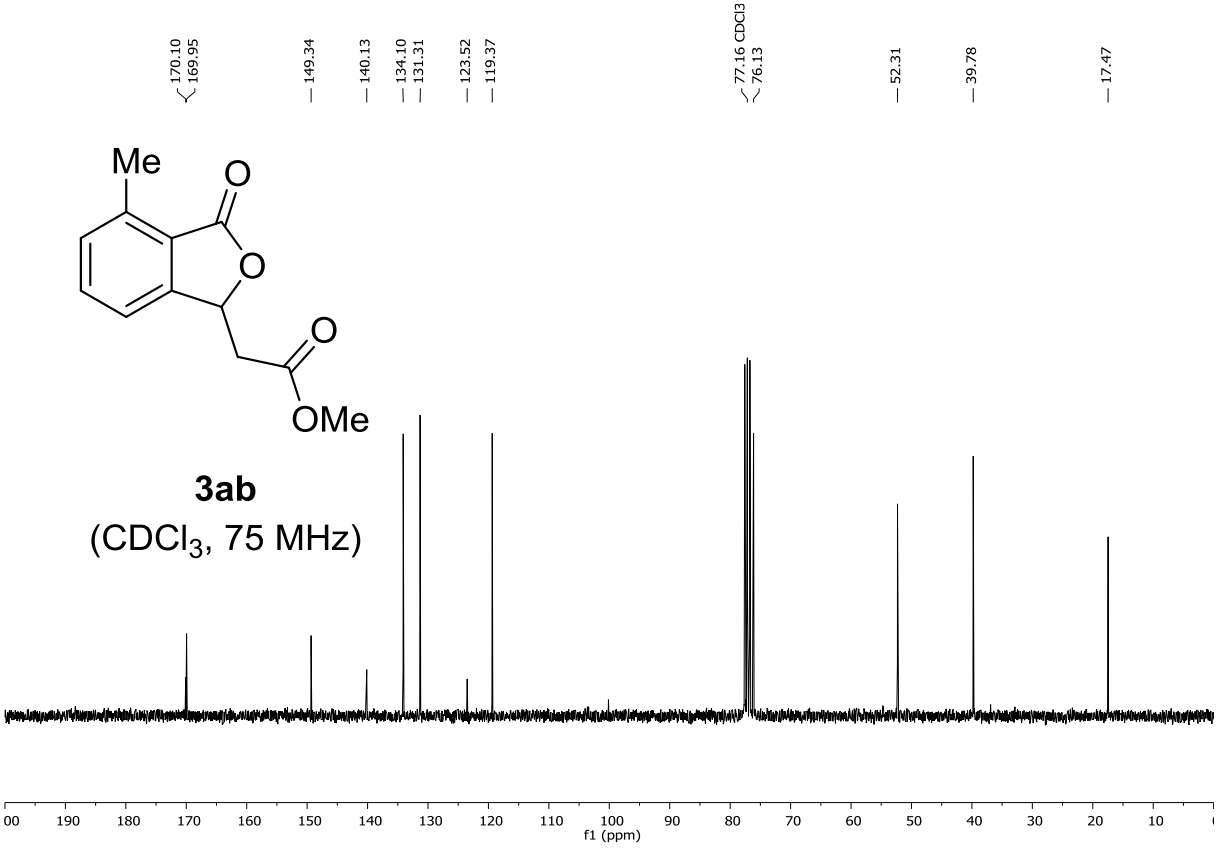
($CDCl_3$, 300 MHz)

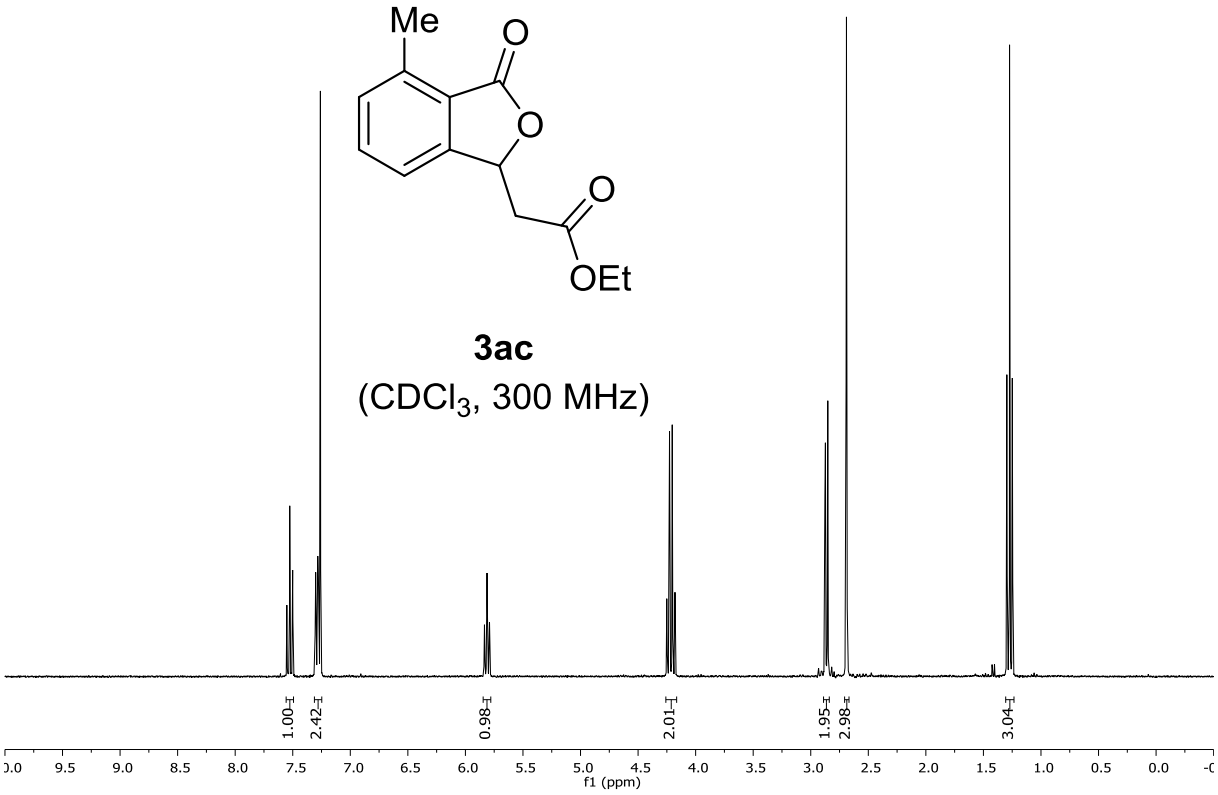


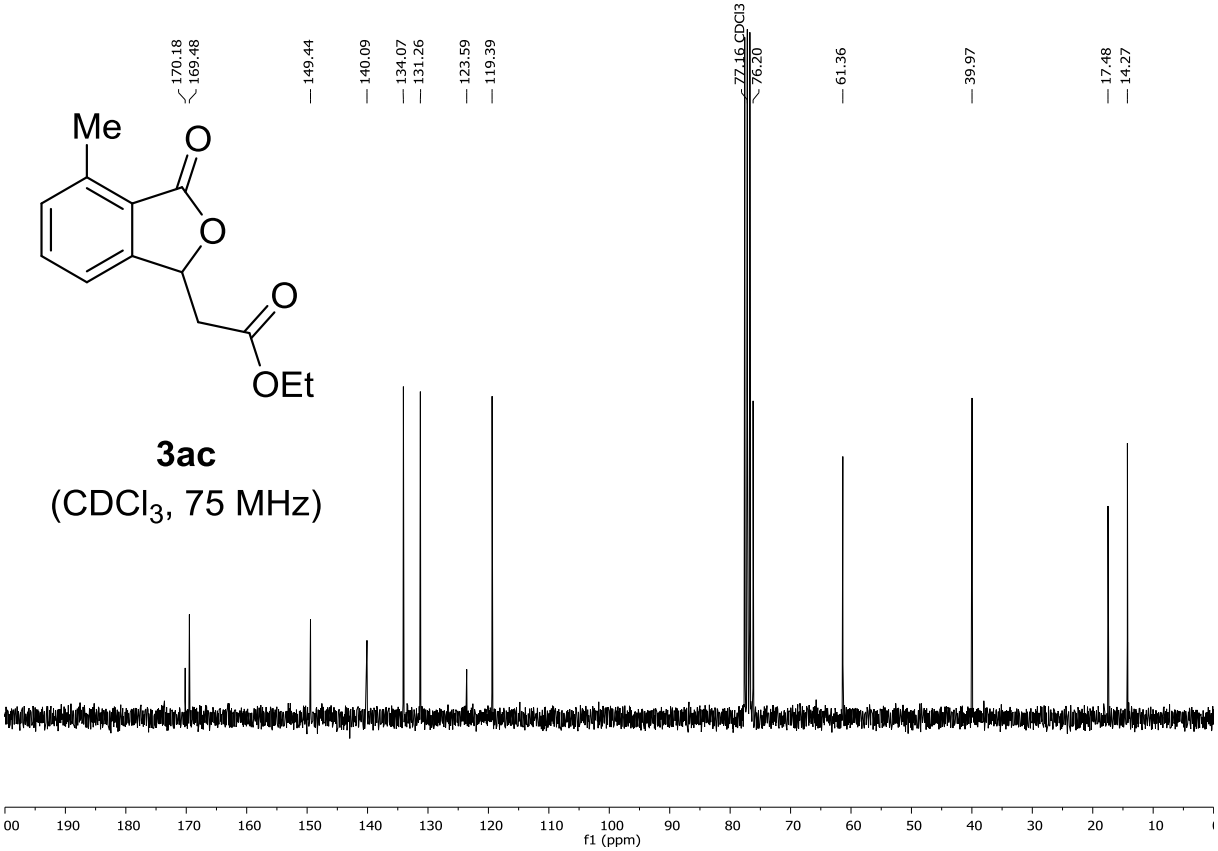
3pa

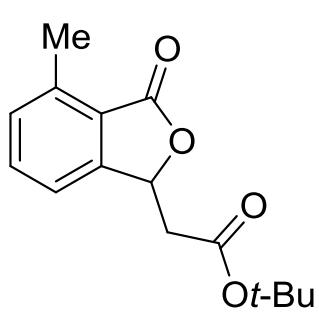
($CDCl_3$, 75 MHz)


Me
O
O
O
OMe
3ab
(CDCl3, 300 MHz)
1.00
2.61
0.97
2.95
0.92
0.90
2.95
f1 (ppm)


170.10
169.95
149.34
140.13
134.10
131.31
123.52
119.37
77.16 CDCl3
76.13
52.31
39.78
17.47
Me
O
O
O
OMe
3ab
(CDCl3, 75 MHz)
f1 (ppm)

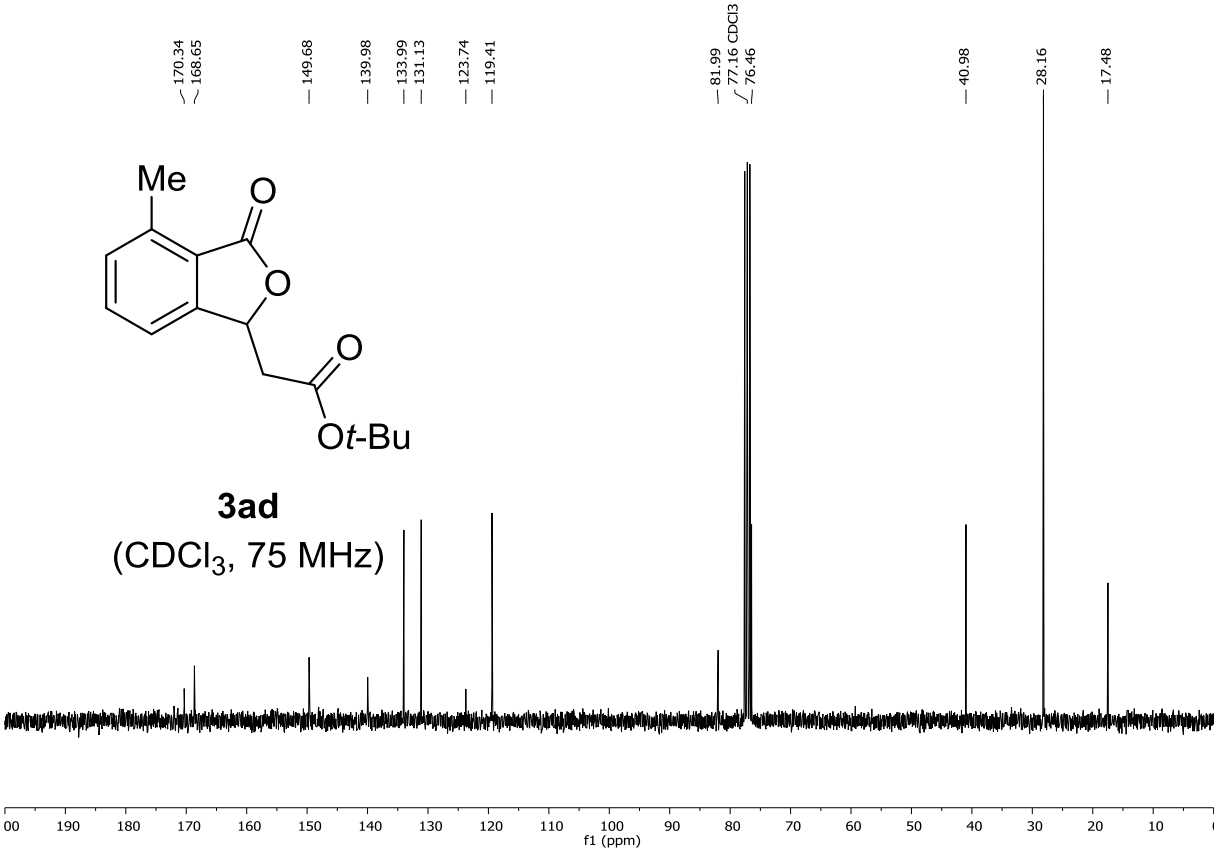

Me
O
O
O
OEt
3ac
(CDCl3, 300 MHz)
1.00
2.42
0.98
2.01
1.95
2.98
3.04
f1 (ppm)


170.18
169.48
149.44
140.09
134.07
131.26
123.59
119.39
77.16 CDCl3
76.20
61.36
39.97
17.48
14.27
Me
O
O
O
OEt
3ac
(CDCl3, 75 MHz)
f1 (ppm)



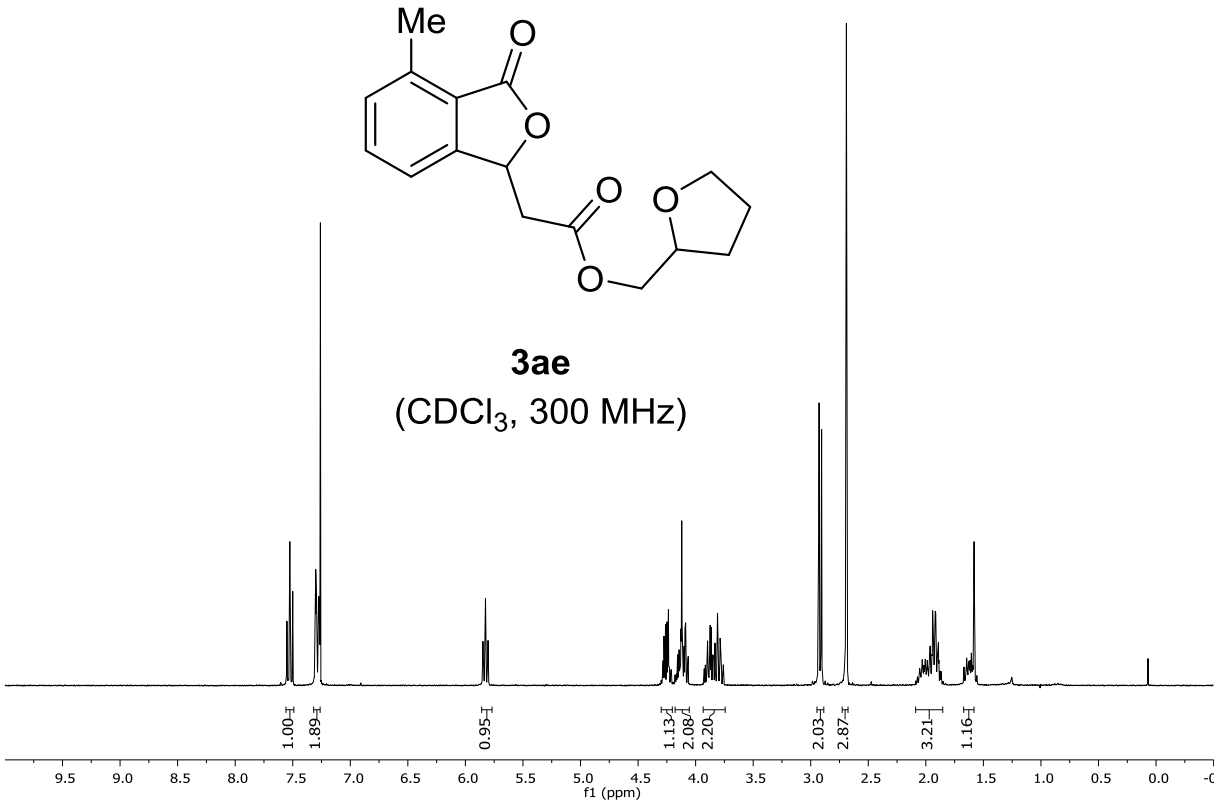
3ad

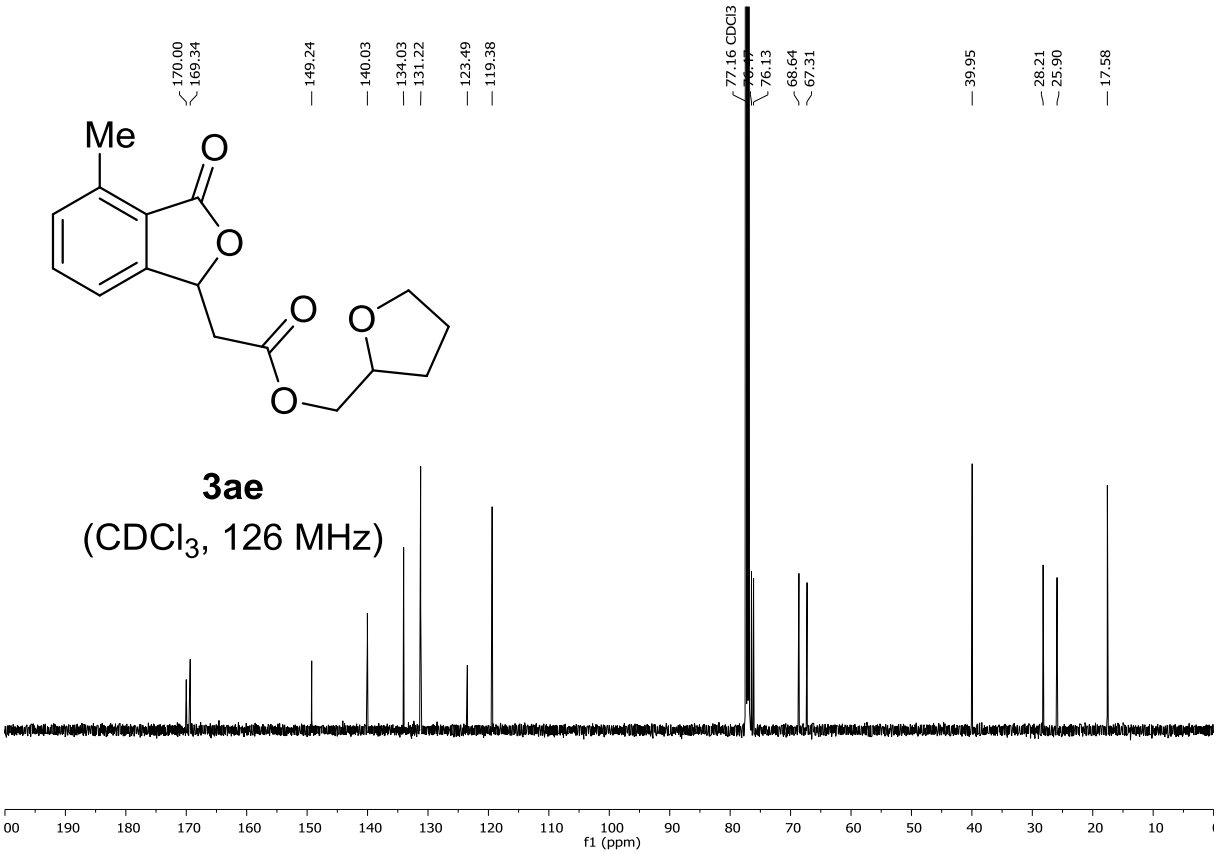
($CDCl_3$, 300 MHz)

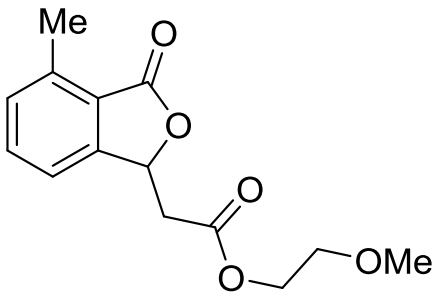


3ad

($CDCl_3$, 75 MHz)

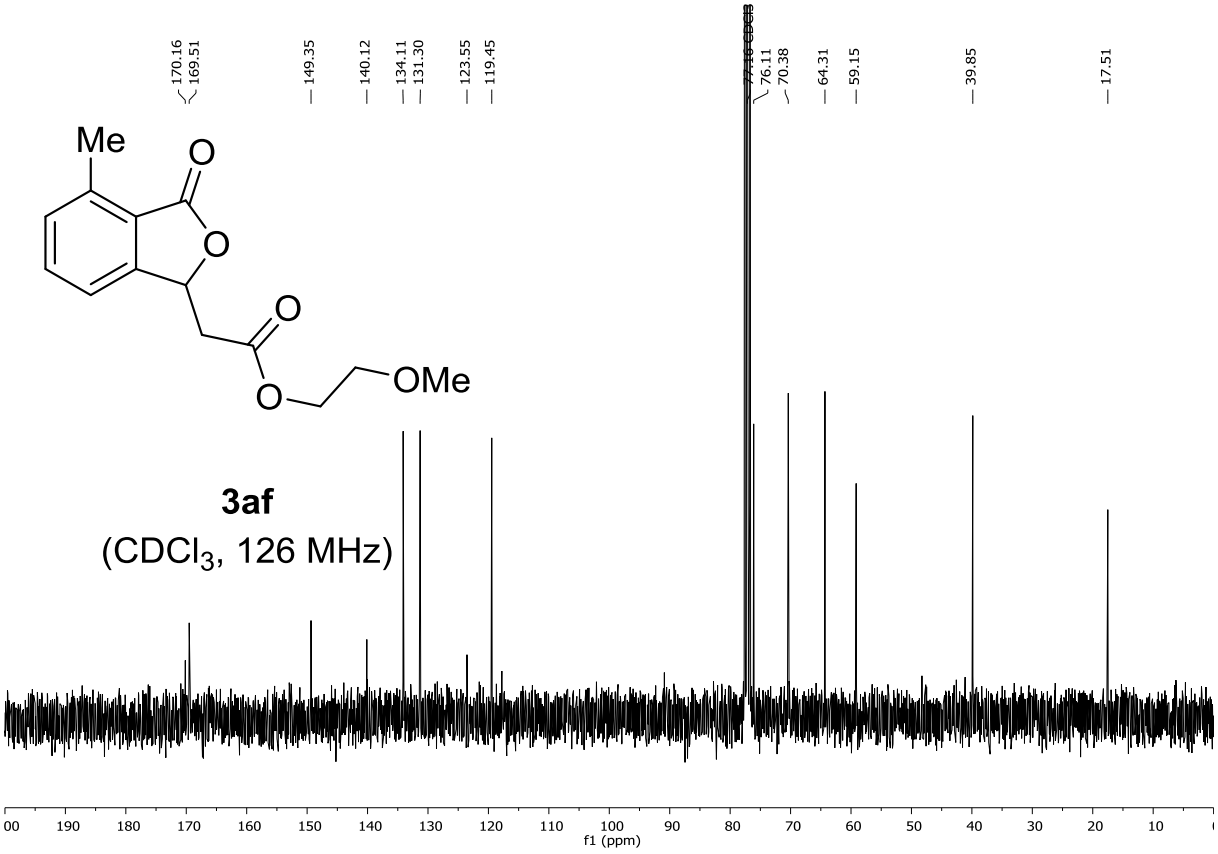

Me
O
O
O
O
O
3ae
(CDCl3, 300 MHz)
1.00
1.89
0.95
1.13
2.08
2.20
2.03
2.87
3.21
1.16
f1 (ppm)


170.00
169.34
149.24
140.03
134.03
131.22
123.49
119.38
77.16 CDCl3
76.13
68.64
67.31
39.95
28.21
25.90
17.58
Me
O
O
O
O
O
3ae
(CDCl3, 126 MHz)
f1 (ppm)



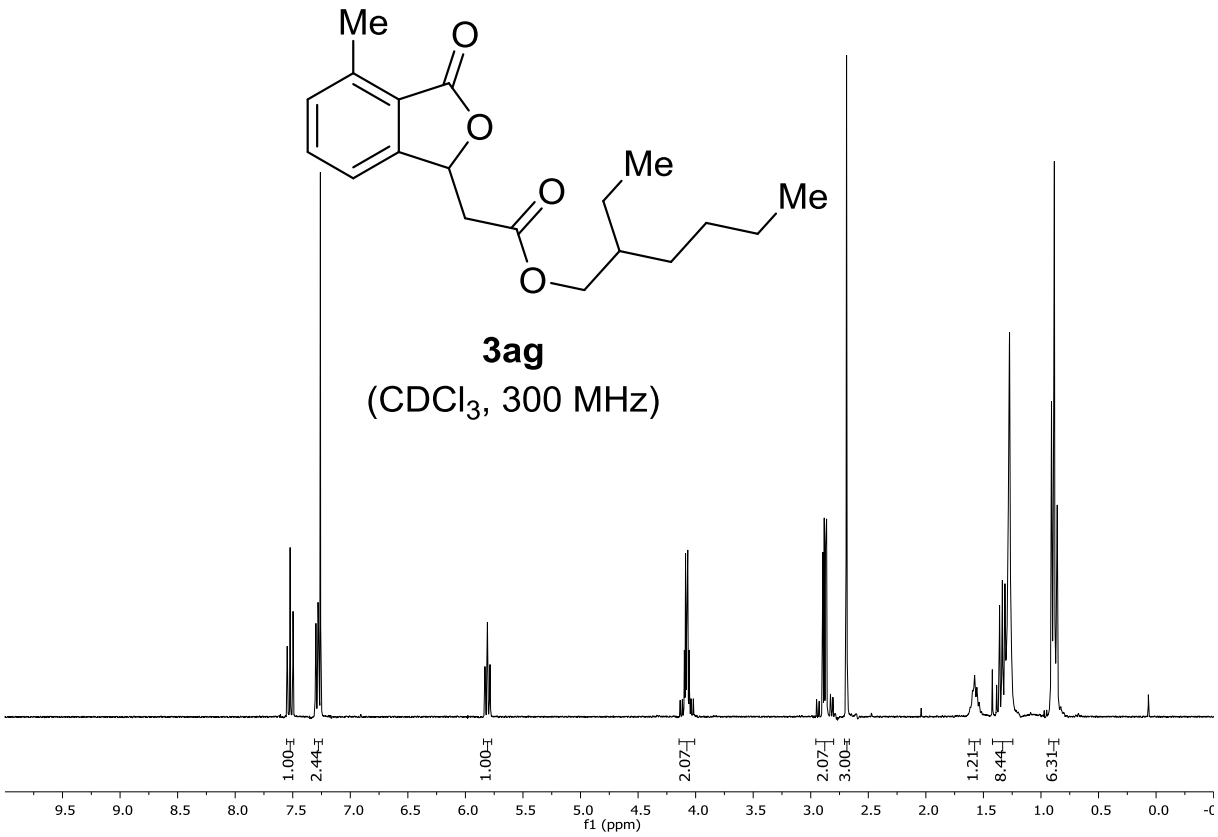
3af

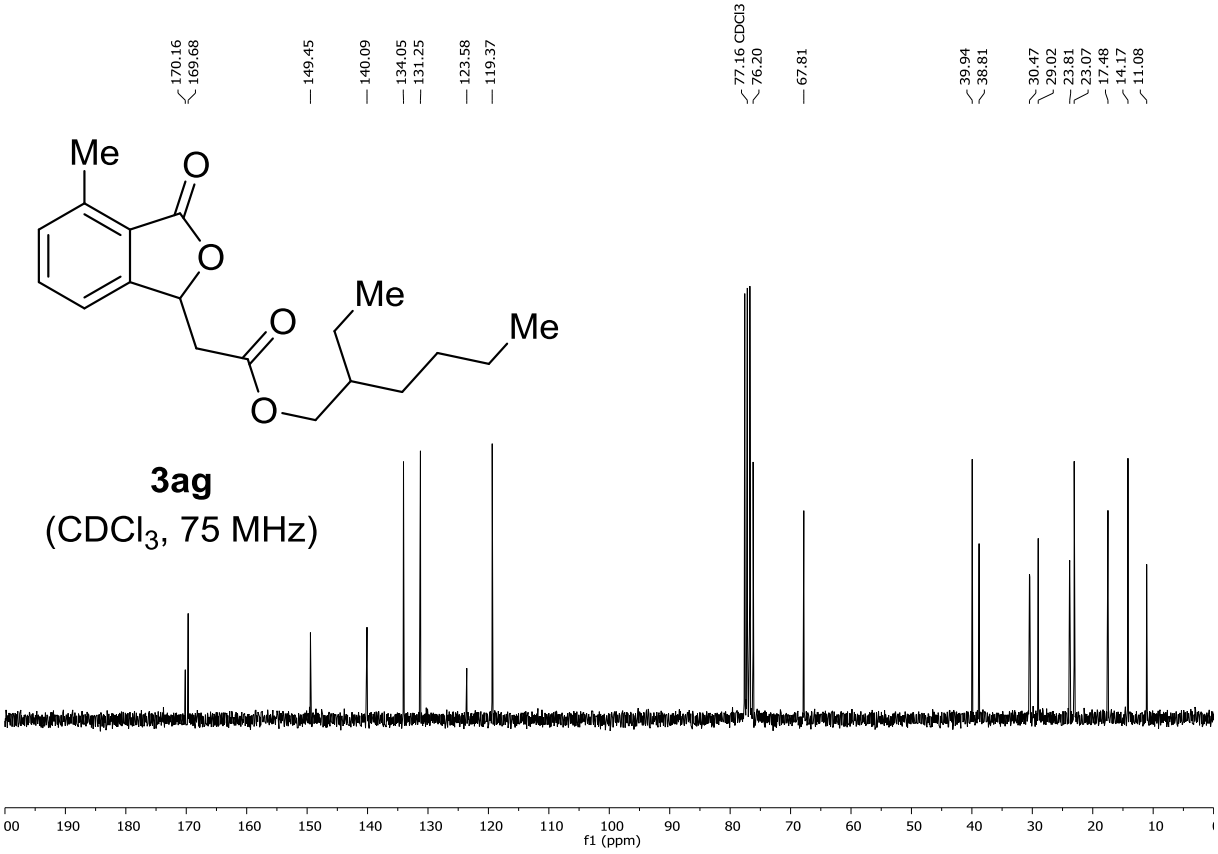
($CDCl_3$, 300 MHz)

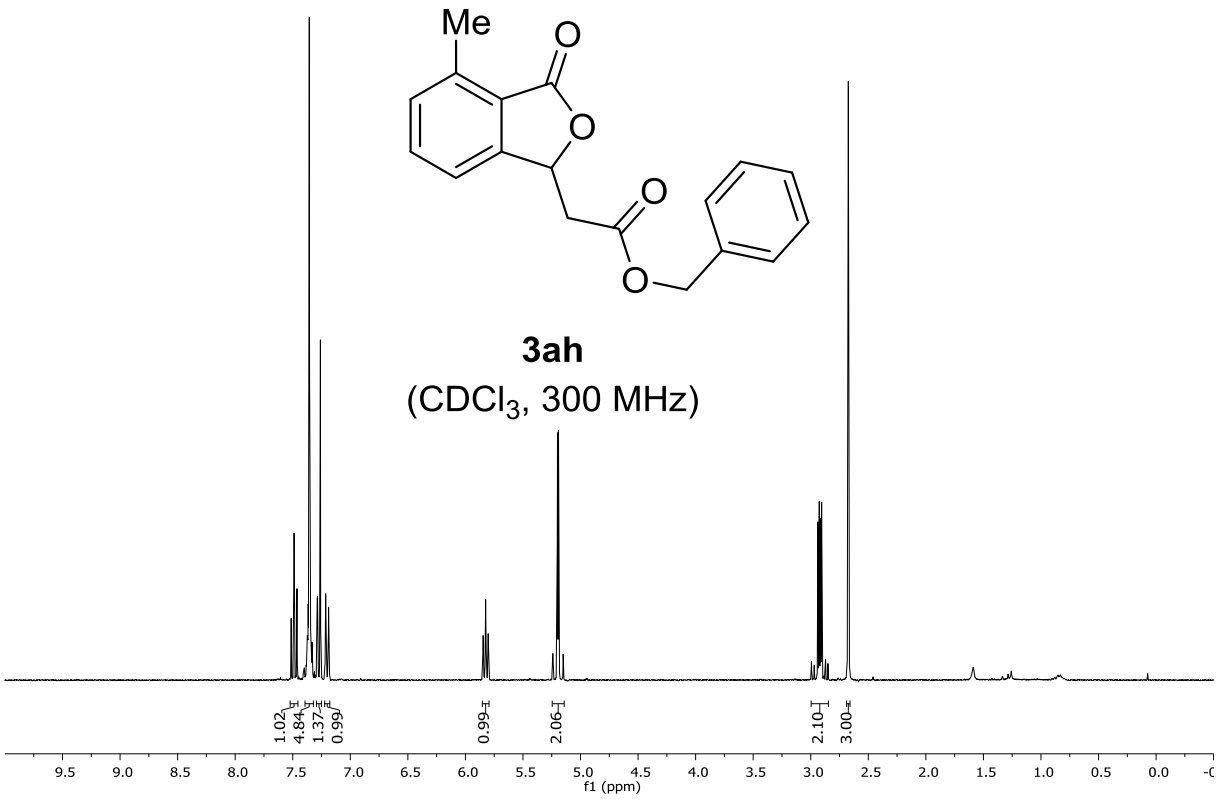


3af

($CDCl_3$, 126 MHz)

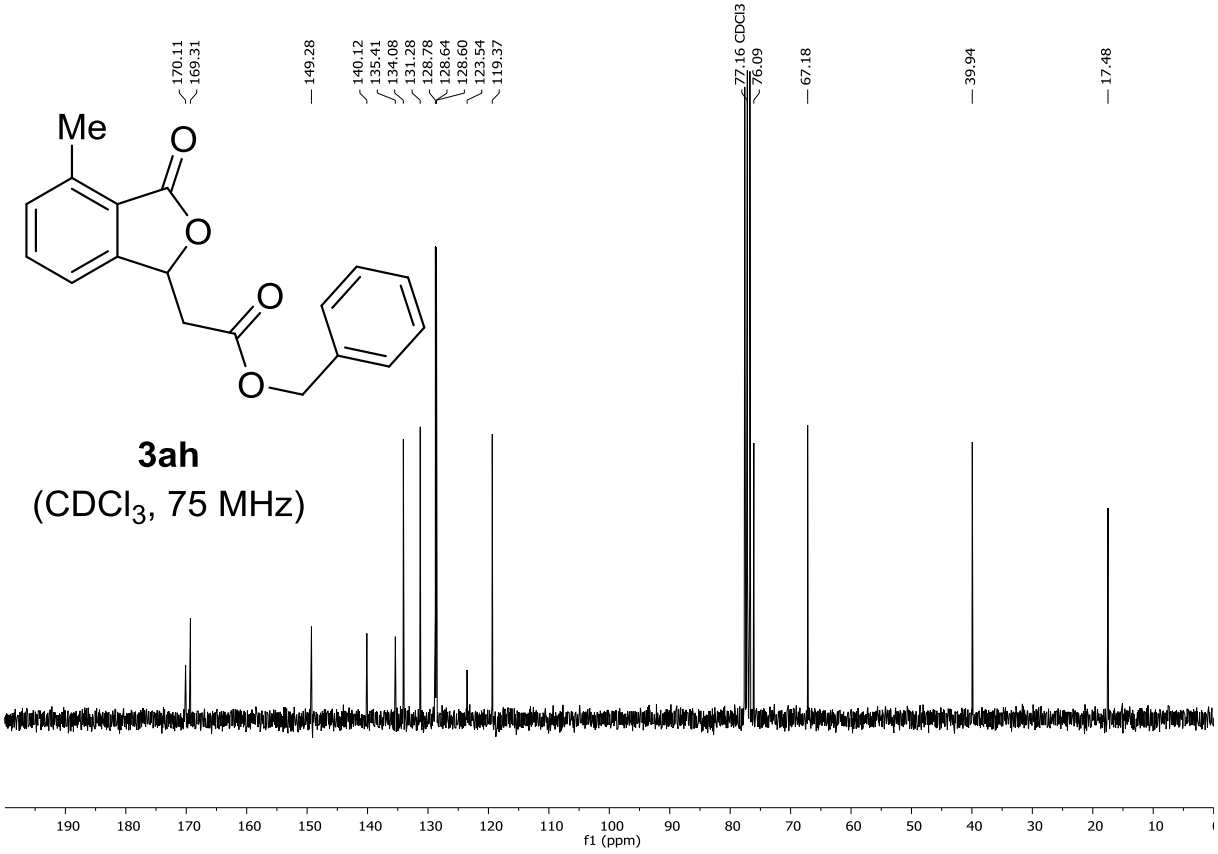

Me
O
O
O
Me
Me
O
3ag
(CDCl3, 300 MHz)
1.00
2.44
1.00
2.07
2.07
3.00
1.21
8.44
6.31
f1 (ppm)


170.16
169.68
149.45
140.09
134.05
131.25
123.58
119.37
77.16 CDCl3
76.20
67.81
39.94
38.81
30.47
29.02
23.81
23.07
17.48
14.17
11.08
Me
O
O
O
Me
Me
O
3ag
(CDCl3, 75 MHz)
f1 (ppm)



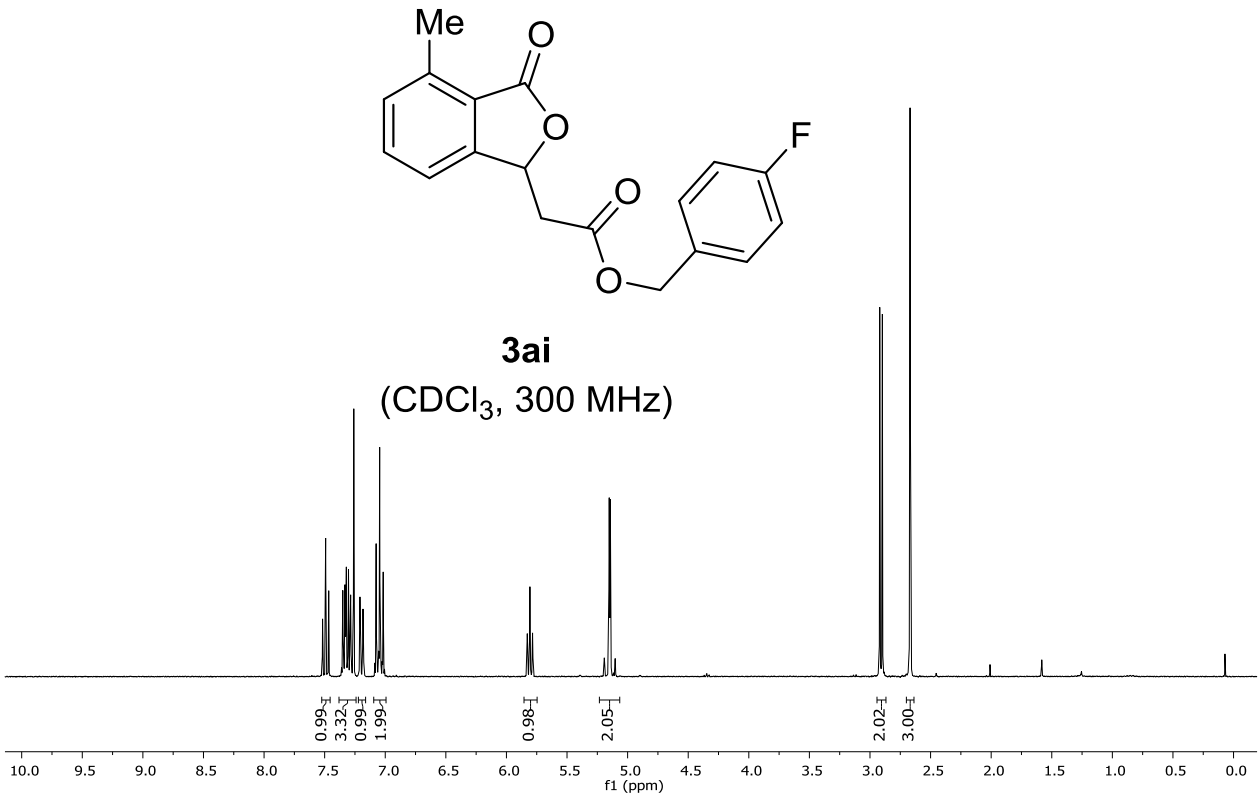
3ah

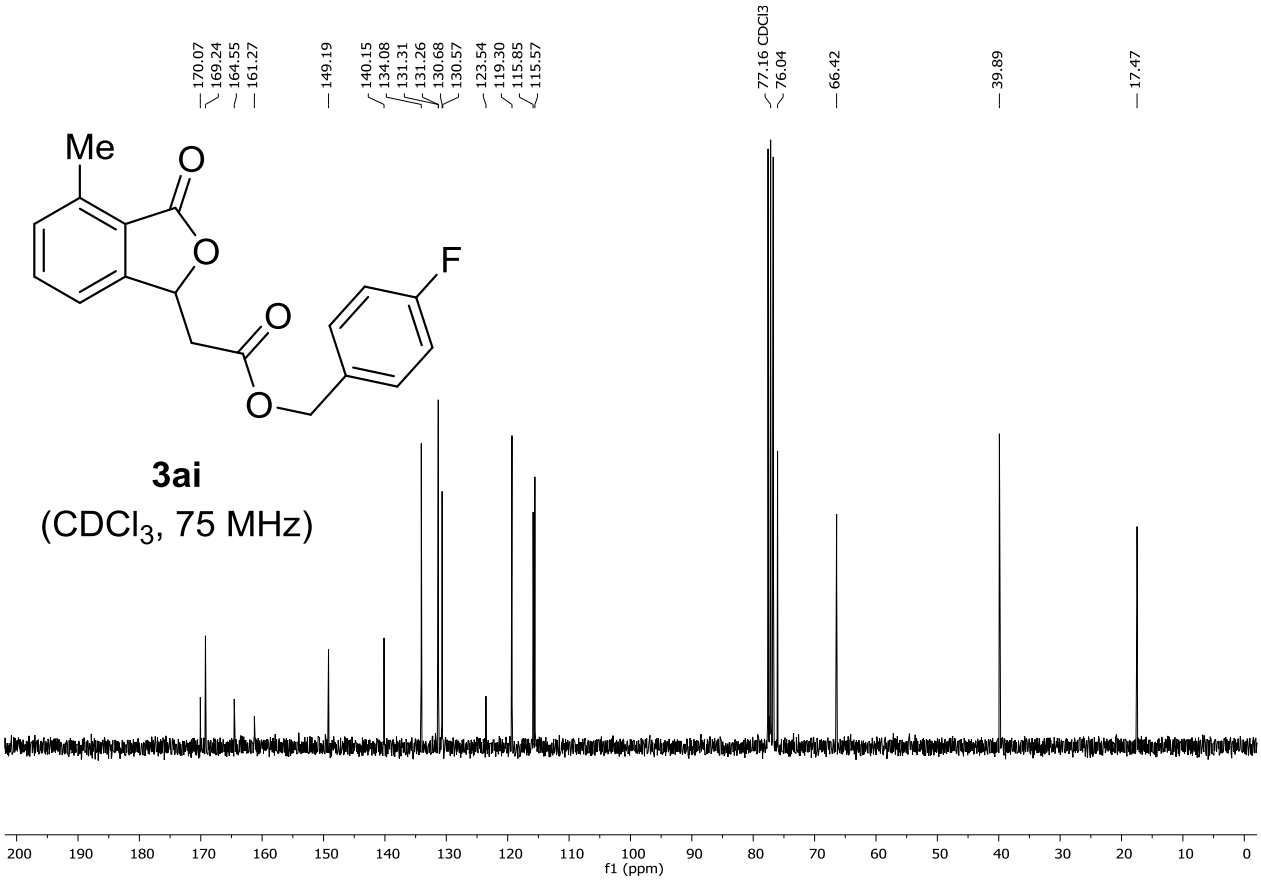
($CDCl_3$, 300 MHz)

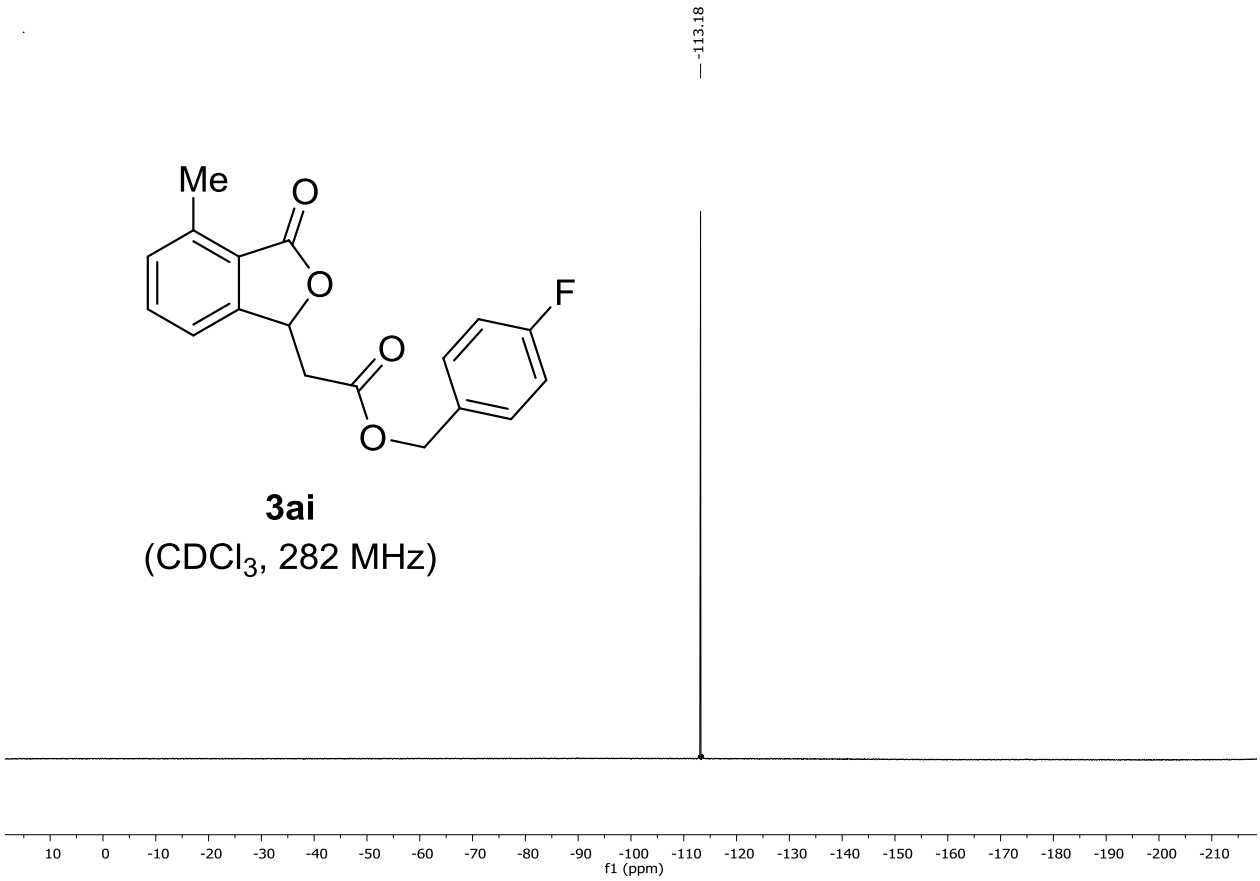


3ah

($CDCl_3$, 75 MHz)

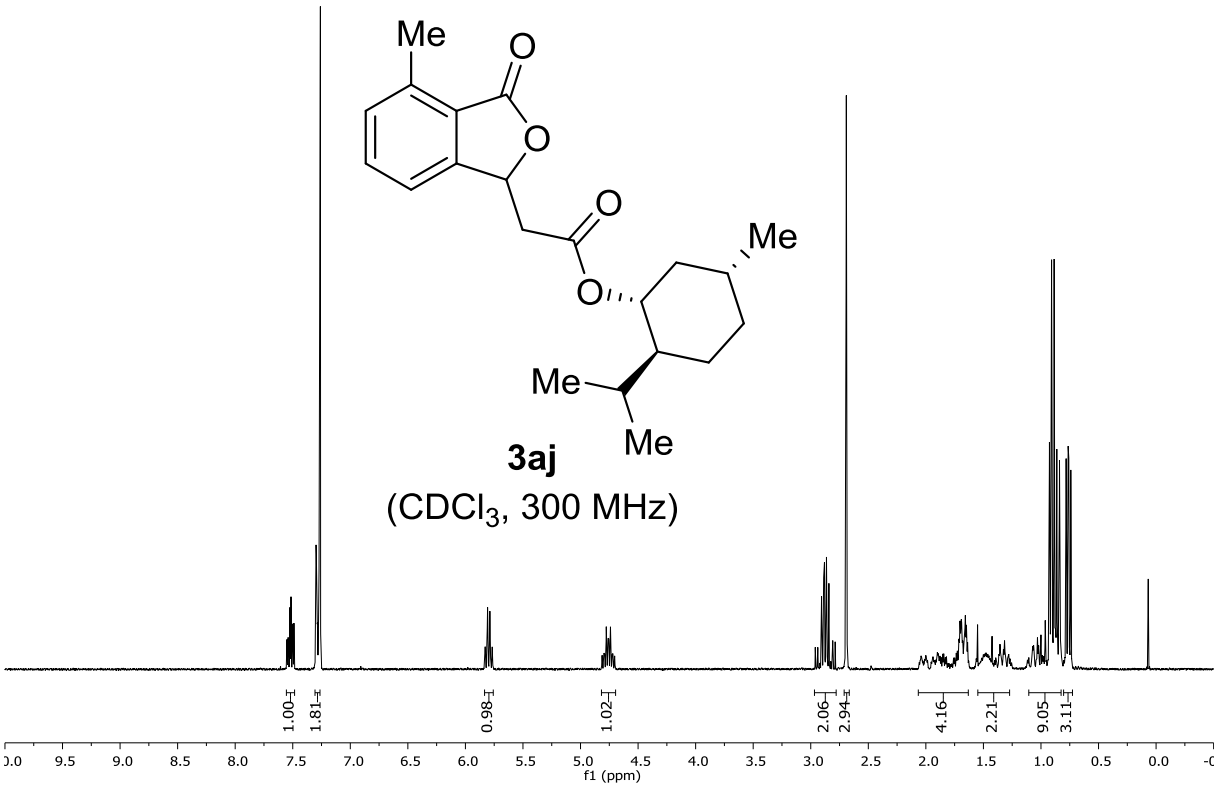

Me
O
O
O
O
F
3ai
(CDCl3, 300 MHz)
0.99
3.32
0.99
1.99
0.98
2.05
2.02
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

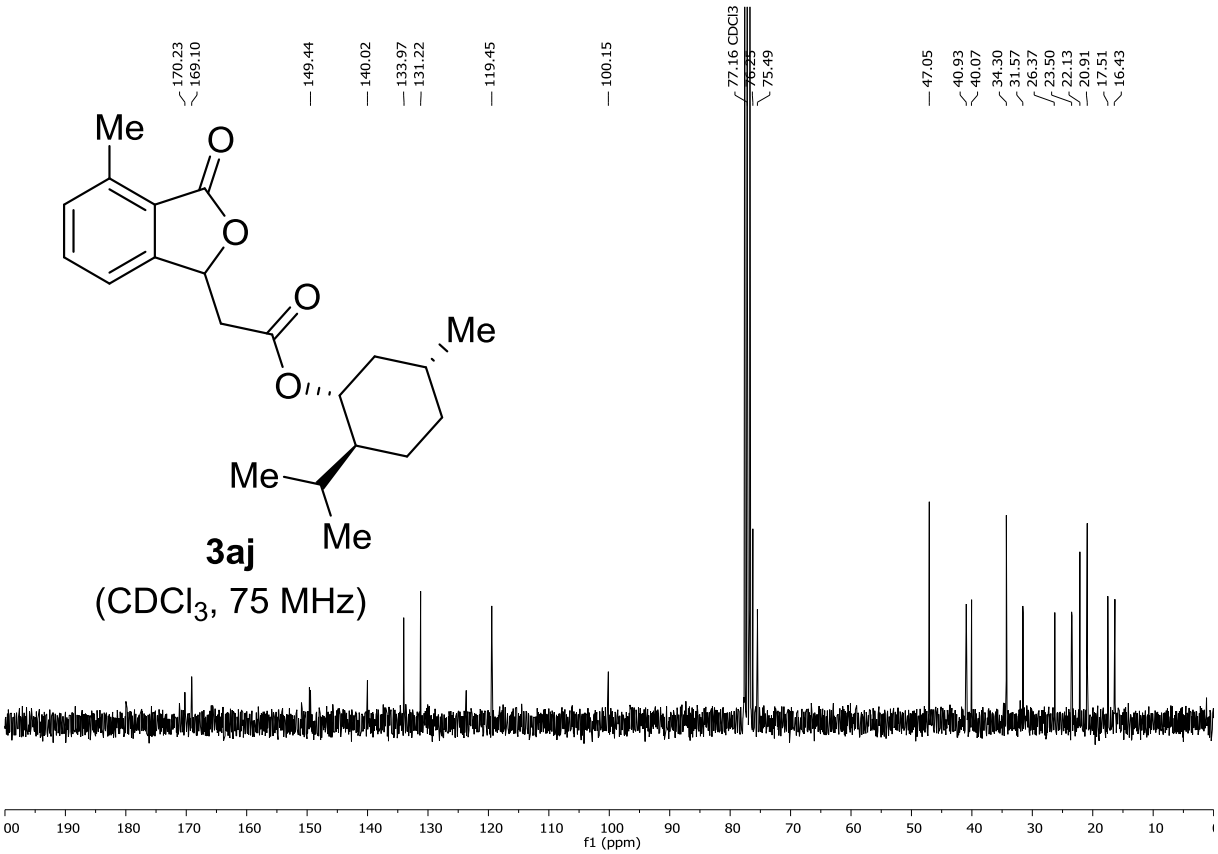

170.07
169.24
164.55
161.27
149.19
140.15
134.08
131.31
131.26
130.68
130.57
123.54
119.30
115.85
115.57
77.16 CDCl3
76.04
66.42
39.89
17.47
Me
O
O
O
O
F
3ai
(CDCl3, 75 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

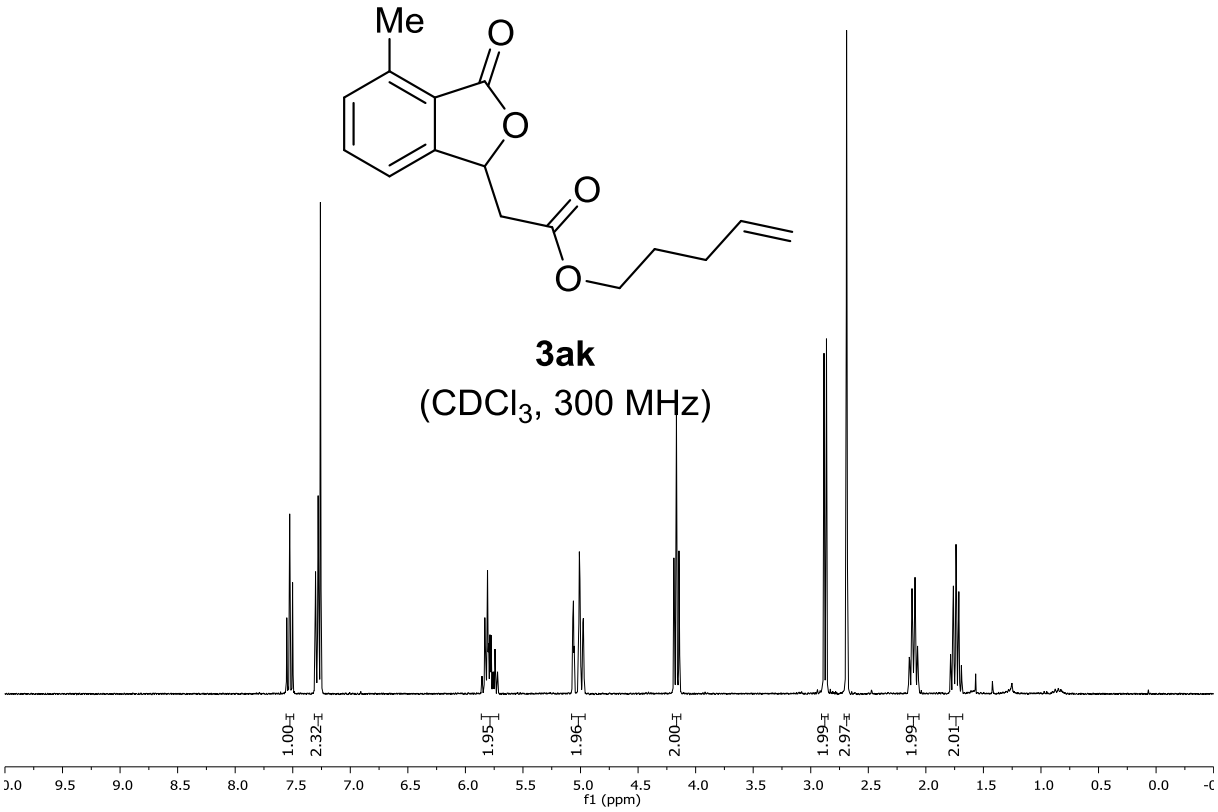


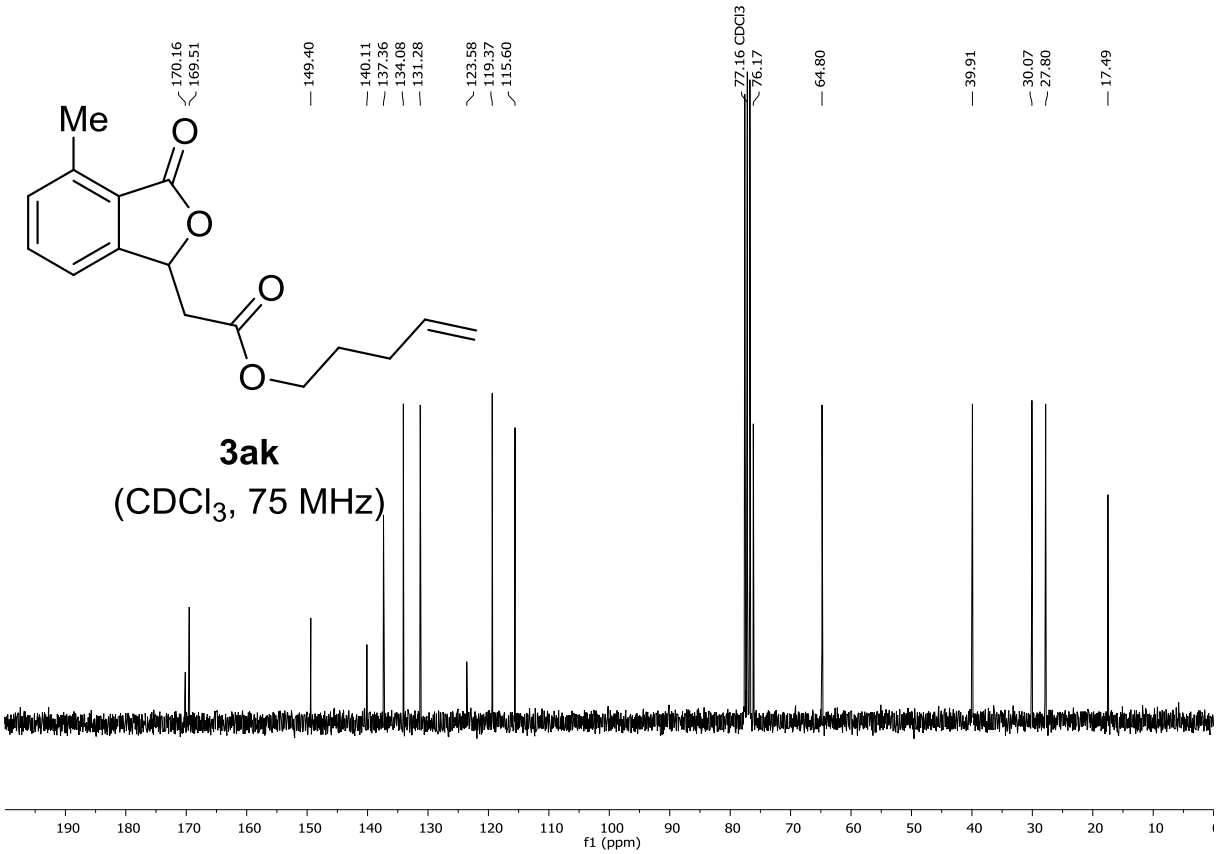
3ai

($CDCl_3$, 282 MHz)


Me
O
O
O
O
Me
Me
Me
3aj
(CDCl3, 300 MHz)
1.00
1.81
0.98
1.02
2.06
2.94
4.16
2.21
9.05
3.11
f1 (ppm)


170.23
169.10
149.44
140.02
133.97
131.22
119.45
100.15
77.16 CDCl3
76.25
75.49
47.05
40.93
40.07
34.30
31.57
26.37
23.50
22.13
20.91
17.51
16.43
Me
O
O
O
O
Me
Me
Me
3aj
(CDCl3, 75 MHz)
f1 (ppm)


Me
O
O
O
O
3ak
(CDCl3, 300 MHz)
1.00
2.32
1.95
1.96
2.00
1.99
2.97
1.99
2.01
f1 (ppm)


170.16
169.51
149.40
140.11
137.36
134.08
131.28
123.58
119.37
115.60
77.16 CDCl3
76.17
64.80
39.91
30.07
27.80
17.49
Me
O
O
O
O
3ak
(CDCl3, 75 MHz)
f1 (ppm)