Supplementary Material

Enantioselective synthesis of 3-aryl-phthalides through a nickel-catalyzed stereoconvergent cross-coupling reaction

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1. General Information

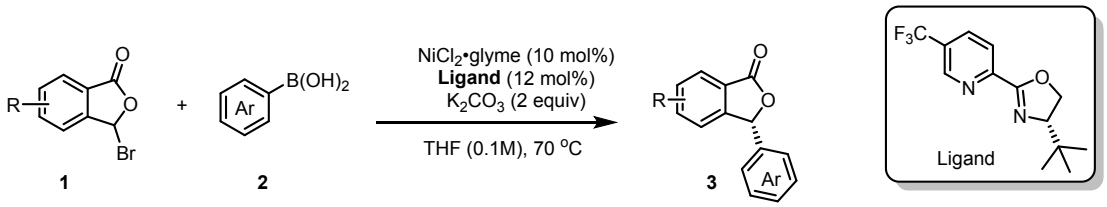
All reagents were obtained commercially unless otherwise noted. Anhydrous solvents were obtained using standard drying techniques. Commercial grade reagents were used without further purification. Flash chromatography was performed on 300-400 mesh silica gel with the indicated solvent systems. High-resolution mass spectra were determined on a Aglient 6545 Accurate-Mass Q-TOF spectrometer. Nuclear Magnetic Resonance(NMR) spectras were acquired on a Brüker Avance-600 HD instrument operating at 600, 150 and 565 MHz for ^{1}H, ^{13}C and ^{19}F. Chemical shifts are reported in δ ppm referenced to an internal SiMe4 standard for 1H NMR, chloroform-d (δ 77.00) for ^{13}C NMR. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad resonance.

2. Preparation of 3-Bromoisobenzofuran-1(3H)-ones 1

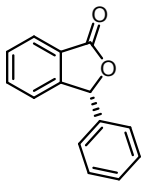
All 3-bromoisobenzofuran-1(3H)-ones **3** were prepared as the following general procedures according to the known literature:[1, 2]

Under N_2 atmosphere, a mixture of alkylbenzoic acid (20.0 mmol), $Na_2S_2O_8$ (60.0 mmol) and TBAB (40.0 mmol) in MeCN (250 mL) was stirred at 80 °C for 18 h in a 500 mL three-necked, round-bottomed flask. The reaction mixture was diluted with water and extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography to afford isobenzofuran-1(3H)-one. Isobenzofuran-1(3H)-one (15.0 mmol), *N*-bromosuccinimide (18 mmol) and azo-bisisobutyronitrile (1.5 mmol) were combined in 100 mL of CCl_4 and refluxed under N_2 atmosphere for 4 h. The reaction mixture was cooled to room temperature, filtered and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (petroleum ether/EtOAc = 10/1) to yield 3-bromoisobenzofuran-1(3H)-one.

3. Asymmetrice Nickel-Catalyzed Cross-Coupling of 3-Bromophthalides and Arylboronic Acids

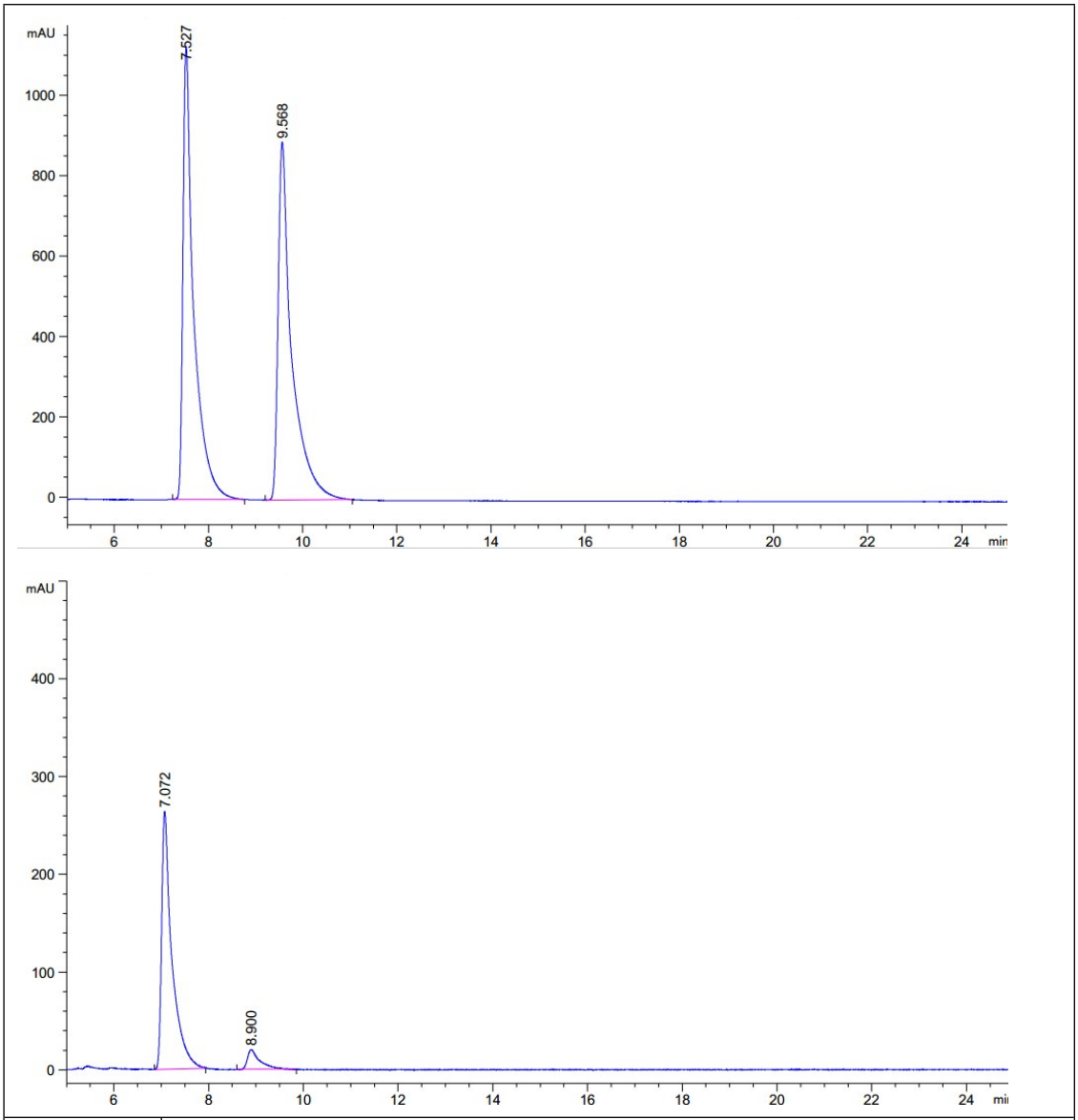


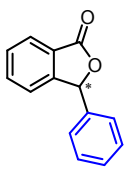
General Procedures: A 20 mL Schlenk tube was charged with 3-bromophthalide **1** (0.30 mmol), aryboronic acids **2** (0.6 mmol), K_2CO_3 (0.6 mmol), $NiCl_2$•glyme (0.03 mmol, 10 mol%), chiral ligand (0.036 mmol, 12 mol%) under N_2 atmosphere. THF (3 mL) was added and the mixture was stirred at rt for 10 min. The reaction mixture was then heated at 70 °C for additional 12 h. The mixture was concentrated under reduced pressure, and the residue was purified by silica-gel column chromatography (petroleum ether/EtOAc = 10/1 to 3/1) to afford pure 3-aryl-phthalides **3**.



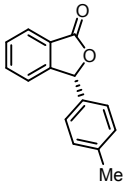
(*R*)-3-phenylisobenzofuran-1(*3H*)-one (3a)[3]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.28 (dd, *J* = 6.7, 2.9 Hz, 2H), 6.41 (s, 1H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.48, 149.66, 136.39, 134.29, 129.33, 129.27, 128.94, 126.94, 125.62, 125.58, 122.83, 82.69. **$[\alpha]^{25}_D$**= -37.30 (*c*=1.0 in $CHCl_3$, 84% ee sample). **HRMS** (ESI): calcd for $C_{14}H_{11}O_2$ ([M+ H]$^+$) 211.0754, found 211.0756. **HPLC analysis**: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 7.07 min (major) and 8.90 min (minor), 84% ee.





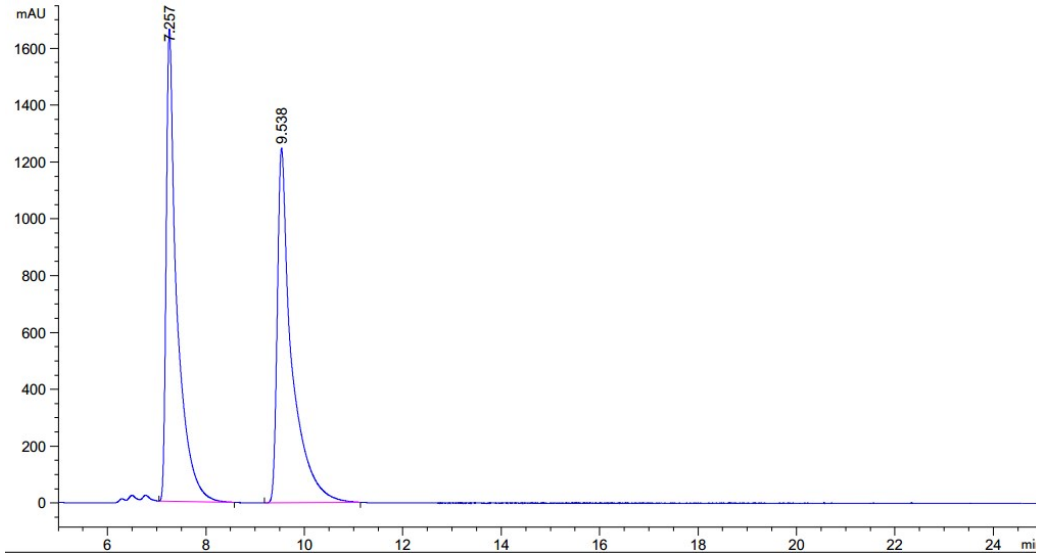
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.072	MM R	0.2150	3993.58569	263.65421	91.9856
2	8.900	MM R	0.2902	347.94998	19.98214	8.0144

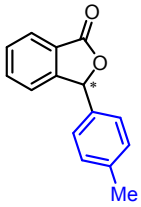


(*R*)-3-(p-tolyl)isobenzofuran-1(*3H*)-one (3b)[3]

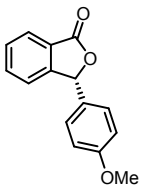
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H),

7.55 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.21 – 7.13 (m, 4H), 6.38 (s, 1H), 2.35 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.55, 149.81, 139.32, 134.23, 133.40, 129.62, 129.26, 127.04, 125.74, 125.59, 122.85, 82.75, 21.21 **$[\alpha]^{25}_{D}$**= -16.22 (*c*=1.0 in $CHCl_3$, 79% ee sample). **HRMS** (ESI): calcd for $C_{15}H_{13}O_2$ ([M+ H]$^+$) 225.0910, found 225.0912. **HPLC analysis**: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 7.12 min (major) and 9.33 min (minor), 79% ee.



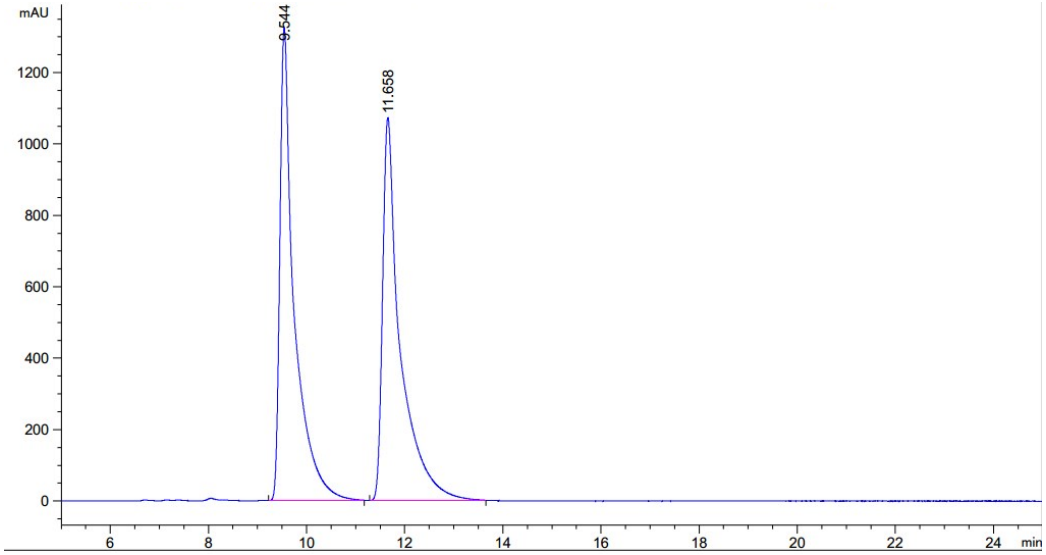


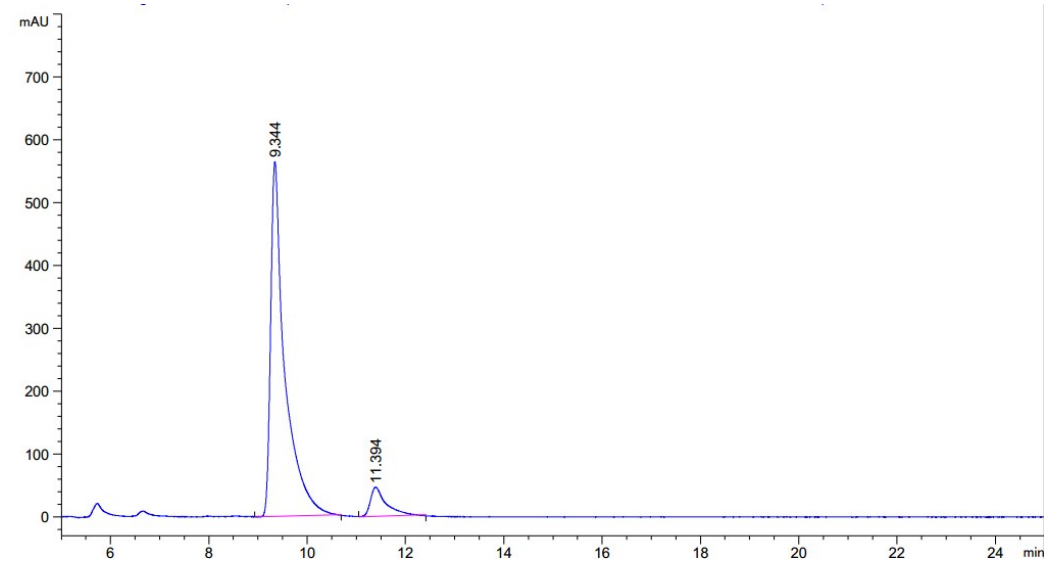
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.117	BV R	0.1879	2.98791e4	1884.93481	89.3953
2	9.333	BV R	0.2612	3544.47388	181.19560	10.6047

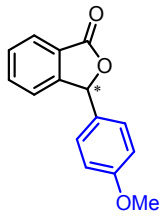


(*R*)-3-(4-methoxyphenyl)isobenzofuran-1(*3H*)-one (3c)[3]

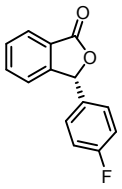
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.37 (s, 1H), 3.81 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.49, 160.42, 149.75, 134.22, 129.28, 128.78, 128.29, 125.95, 125.57, 122.92, 114.32, 82.71, 55.33. **$[\alpha]^{25}_D$**= +7.08 (*c*=1.0 in $CHCl_3$, 85% ee sample). **HRMS** (ESI): calcd for $C_{15}H_{13}O_3$ ([M+ H]$^+$) 241.0859, found 241.0863. **HPLC analysis**: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 9.34 min (major) and 11.39 min (minor), 85% ee.





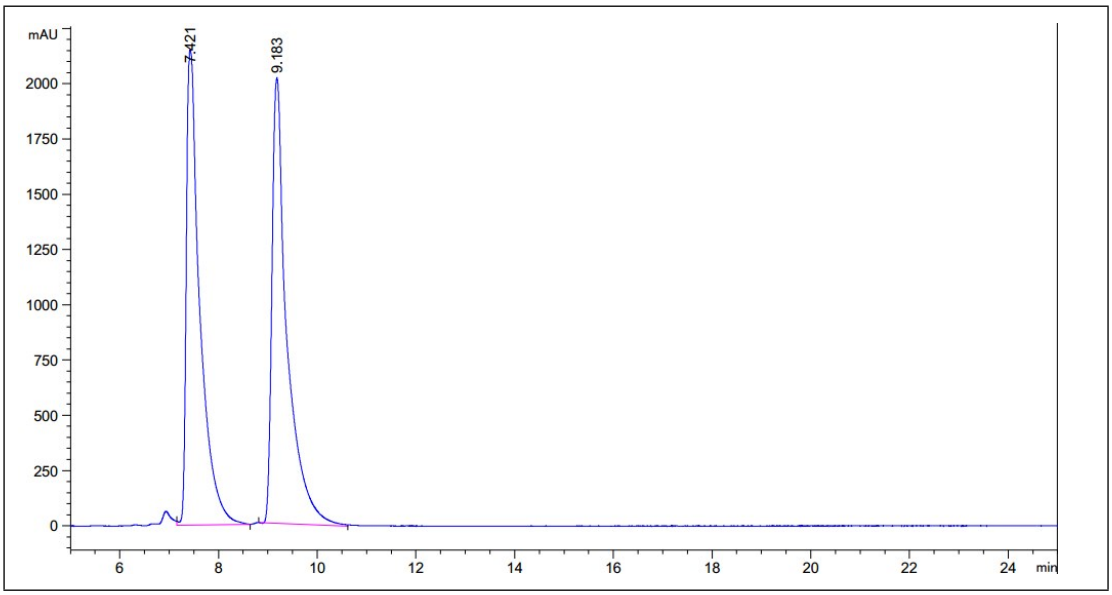


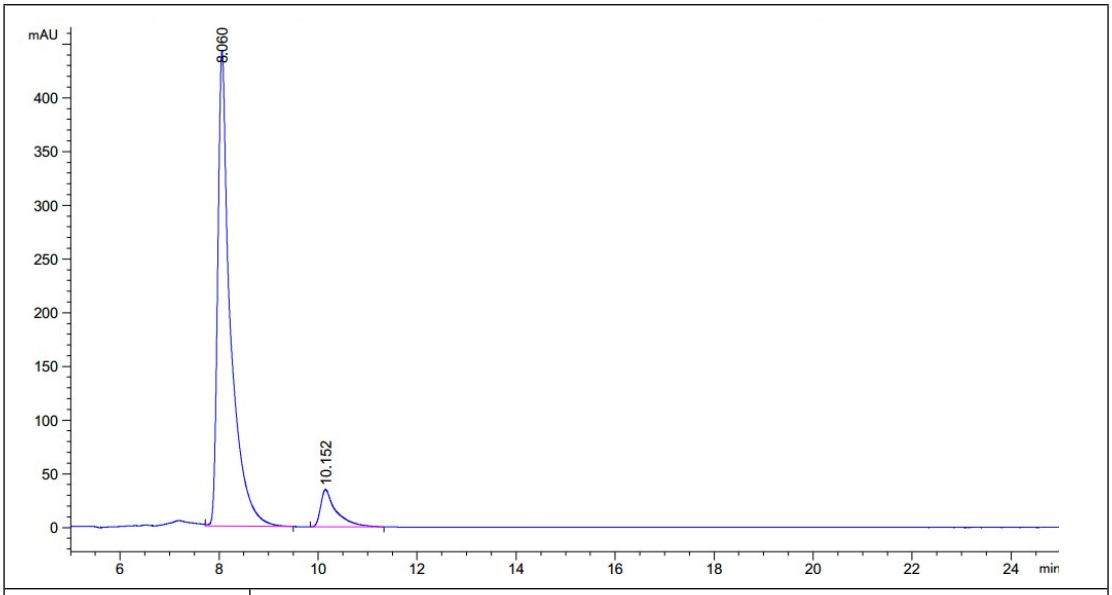
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.344	VV R	0.2675	1.12484e4	564.50293	92.4334
2	11.394	BV R	0.2391	920.79205	45.49445	7.5666

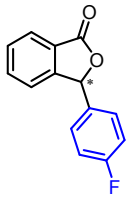


(*R*)-3-(4-fluorophenyl)isobenzofuran-1(*3H*)-one (3d)[4]

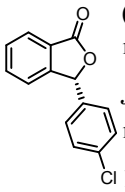
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.7 Hz, 1H), 7.67 (td, *J* = 7.5, 1.1 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.32 (dq, *J* = 7.7, 0.9 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.10 – 7.03 (m, 2H), 6.40 (s, 1H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.22, 163.19 (d, J = 248.6 Hz), 149.35, 134.39, 132.25 (d, J = 3.2 Hz), 129.50, 129.06 (d, J = 8.4 Hz), 125.70, 125.63, 122.80, 116.00 (d, J = 21.8 Hz), 81.97. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -111.77. **[α]$^{25}_{D}$**= -25.1 (*c*=1.0 in $CHCl_3$, 82% ee sample). **HRMS** (ESI): calcd for $C_{14}H_{10}FO_2$ ([M+ H]$^+$) 229.0659, found 229.0660. **HPLC analysis**: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 8.06 min (major) and 10.15 min (minor), 82% ee.





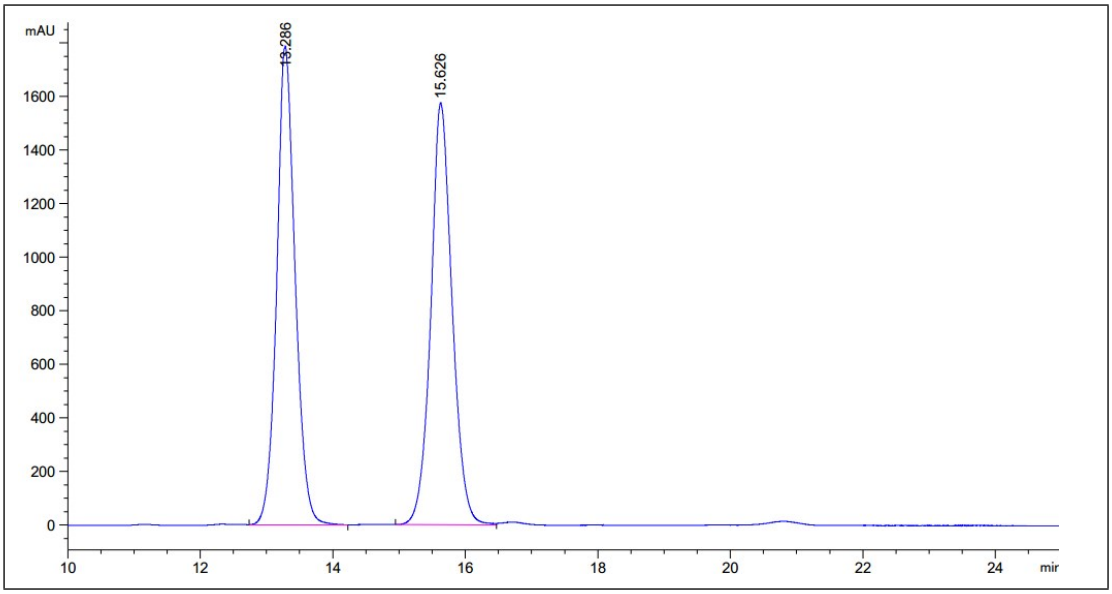


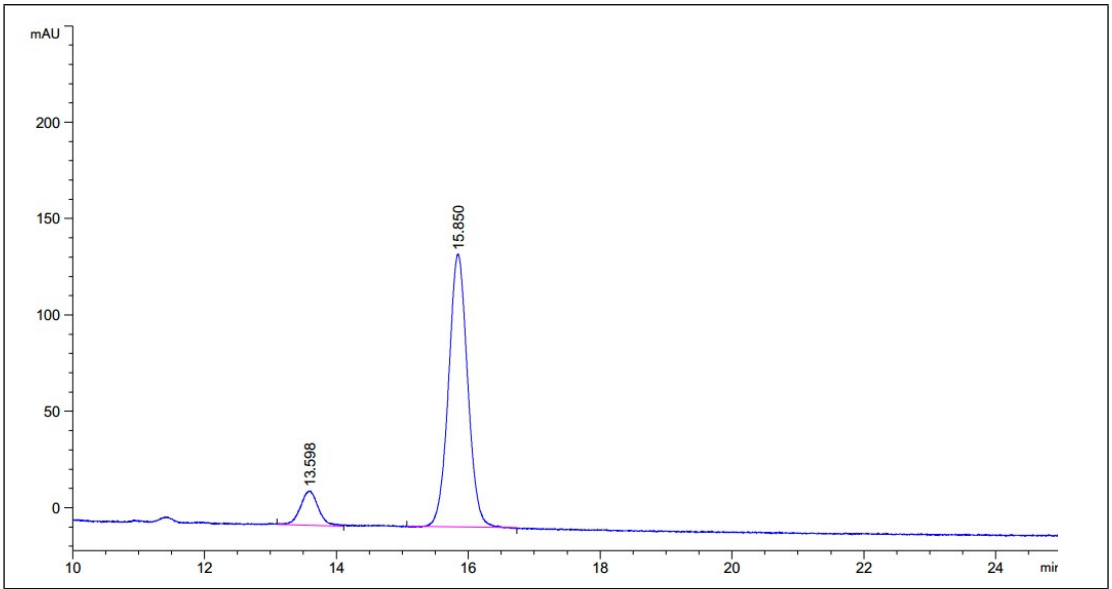
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.060	FM R	0.2973	7894.65967	442.62589	91.2178
2	10.152	BB	0.3035	760.07886	34.77905	8.7822

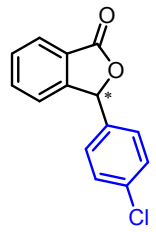


(*R*)-3-(4-chlorophenyl)isobenzofuran-1(*3H*)-one (3e)[3]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.6 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.34 – 7.30 (m, 1H), 7.25 – 7.19 (m, 2H), 6.38 (s, 1H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.19, 149.19, 135.26, 134.95, 134.44, 129.56, 129.20, 128.34, 125.76, 125.47, 122.74, 81.80. **[α]$^{25}_D$**= -34.52 (*c*=1.0 in $CHCl_3$, 79% ee sample). **HRMS** (ESI): calcd for $C_{14}H_{10}ClO_2$ ([M+ H]$^+$) 245.0364, found 245.0368. **HPLC analysis**: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 13.60 min (minor) and 15.85 min (major), 79% ee.







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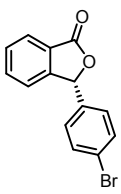
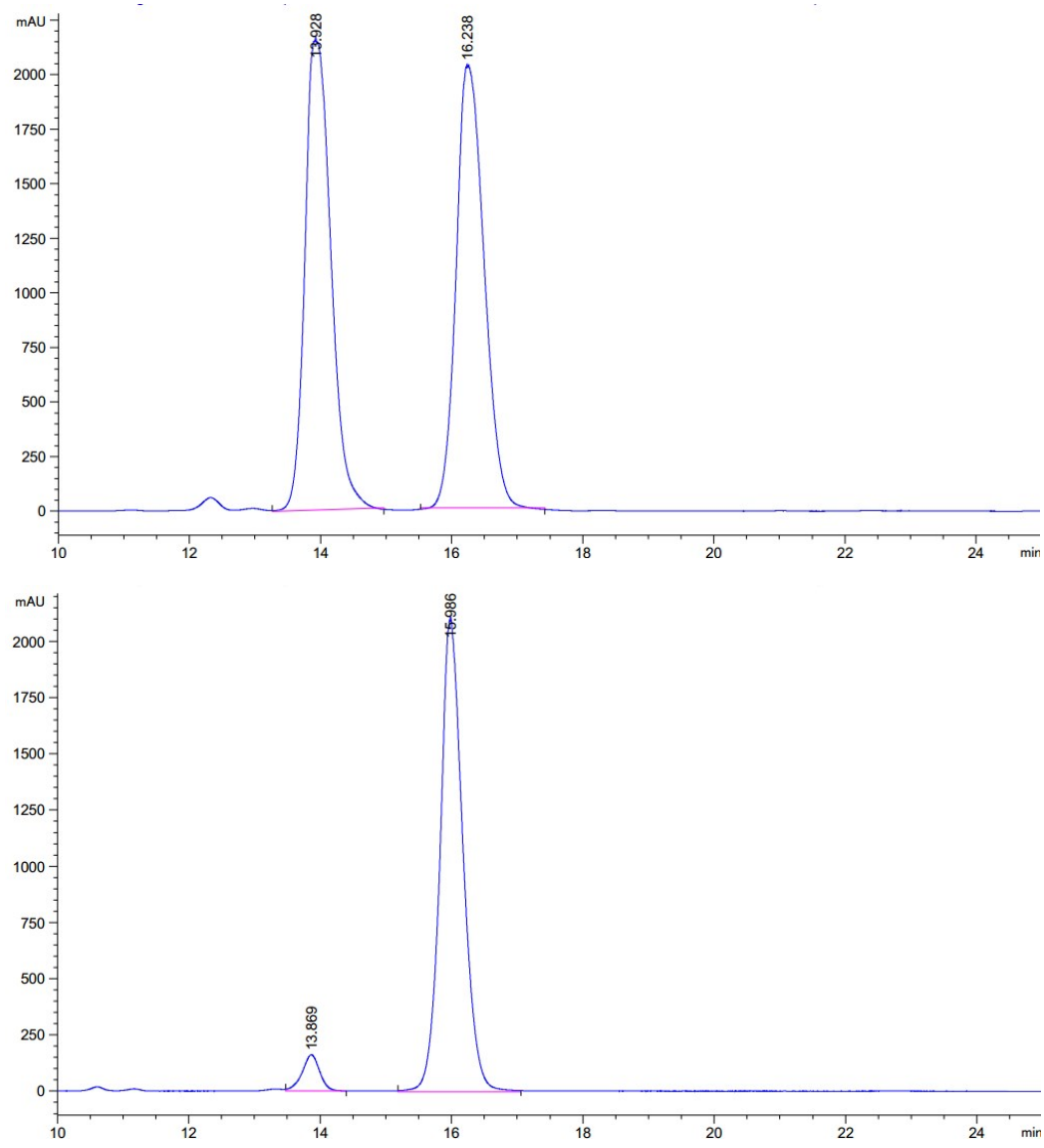
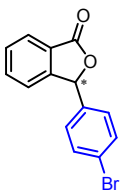
1	13.598	MM R	0.3161	339.75607	17.91339	10.7013
2	15.850	MM R	0.3338	2835.13403	141.54086	89.2987



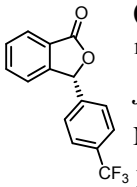
(R)-3-(4-bromophenyl)isobenzofuran-1(3H)-one (3f)[3]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 6.8 Hz, 2H), 6.36 (s, 1H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.17, 149.11, 135.46, 134.44, 132.15, 129.56, 128.57, 125.75, 125.43, 123.42, 122.72, 81.82. **$[\alpha]^{25}_D$**= -25.10 (*c*=1.0 in $CHCl_3$, 88% ee sample). **HRMS** (ESI): calcd for $C_{14}H_{10}BrO_2$ ([M+ H]$^+$) 288.9859, found 288.9861. **HPLC analysis**: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 13.87 min (minor) and 15.99 min (major), 88% ee.



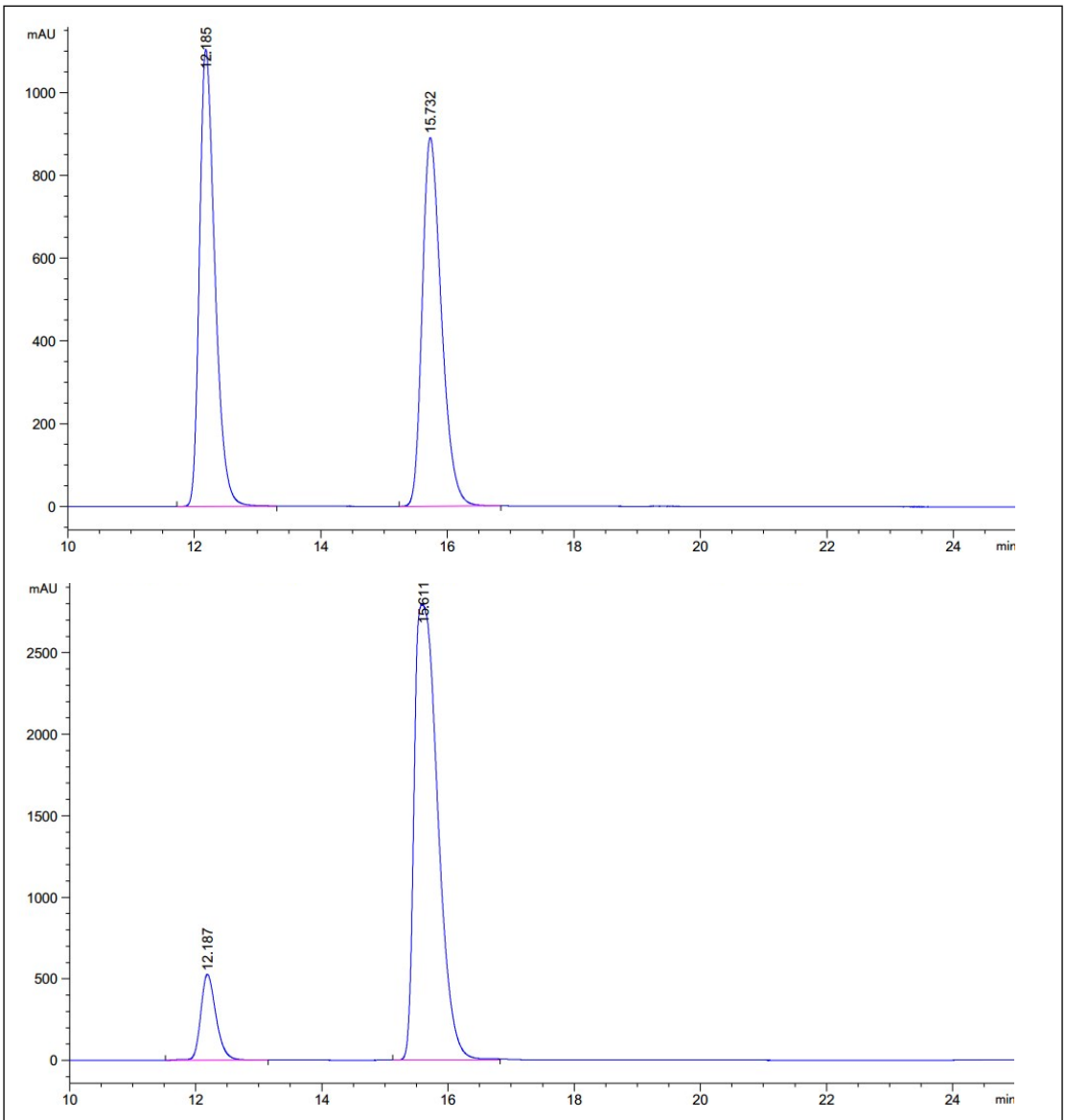


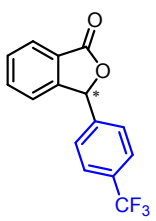
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.869	VV R	0.2367	3115.43384	160.59442	5.8921
2	15.986	MM	0.3942	4.97596e4	2103.61060	94.1079



(*R*)-3-(4-(trifluoromethyl)phenyl)isobenzofuran-1(*3H*)-one (3g)[4]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 7.7 Hz, 1H), 7.71 – 7.64 (m, 3H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.34 (dd, *J* = 7.7, 0.9 Hz, 1H), 6.46 (s, 1H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.08, 148.94, 140.27, 134.60, 131.46 (q, *J* = 32.6 Hz), 129.74, 127.09, 126.03 (q, *J* = 3.8 Hz), 125.96, 125.30, 123.74 (q, *J* = 272.4 Hz), 122.67, 81.54. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -62.77. **$[\alpha]^{25}_D$**= -57.30 (*c*=1.0 in $CHCl_3$, 78% ee sample). **HRMS** (ESI): calcd for $C_{15}H_{10}F_3O_2$ ([M+ H]$^+$) 279.0627, found 279.0629. **HPLC analysis**: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 12.19 min (minor) and 15.61 min (major), 78% ee.





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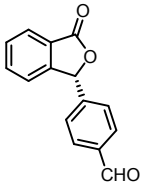
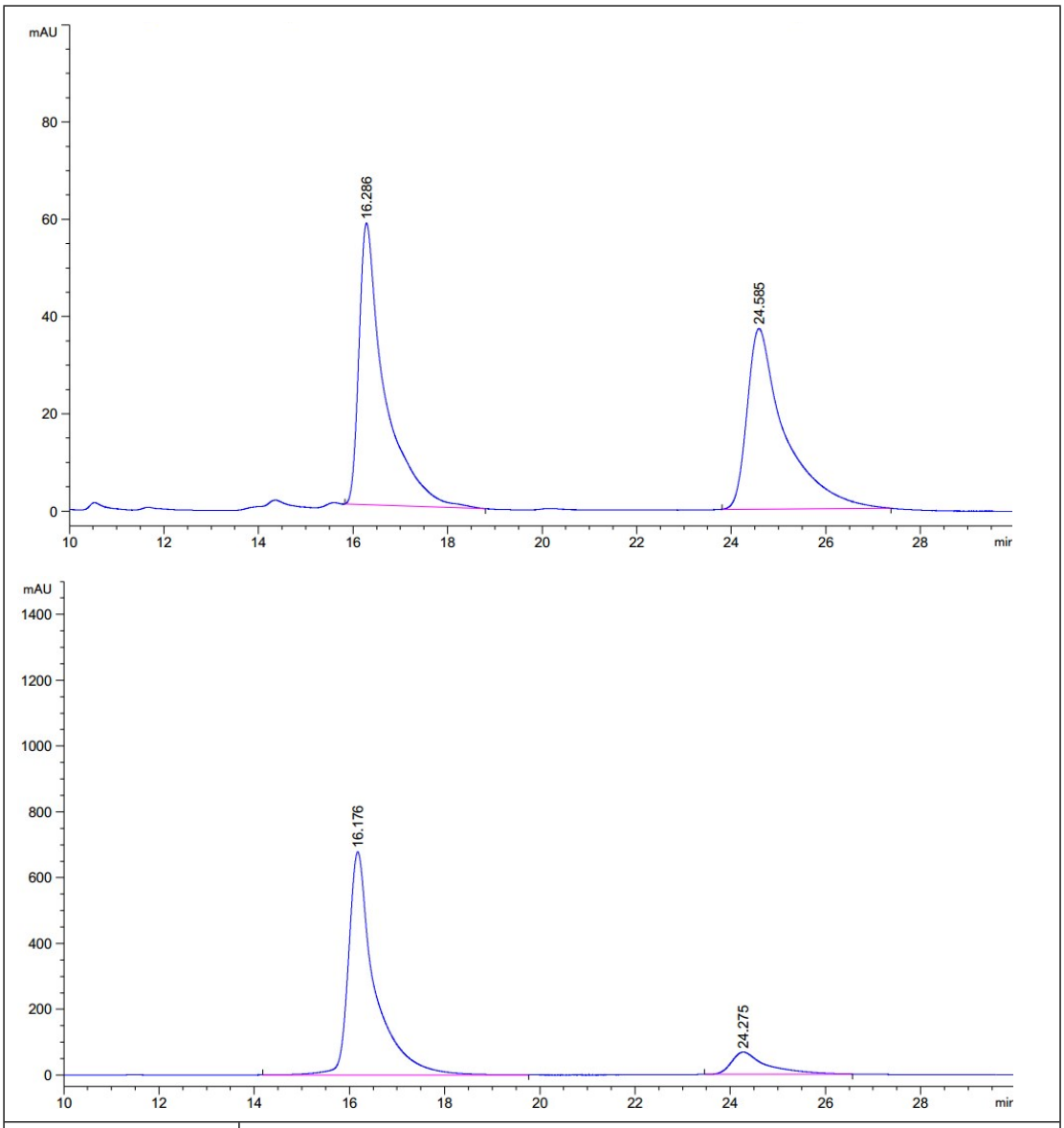
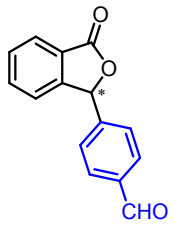
1	12.187	VB R	0.2537	8834.08594	525.94617	10.9389
2	15.611	MM R	0.4293	7.19240e4	2792.57861	89.0611



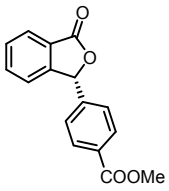
(*R*)-4-(3-oxo-1,3-dihydroisobenzofuran-1-yl)benzaldehyde (3h)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.03 (s, 1H), 7.99 (dd, *J* = 7.6, 2.7 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.7 Hz, 1H), 6.47 (s, 1H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 191.43, 170.07, 148.87, 142.89, 136.87, 134.58, 130.30, 129.73, 127.22, 125.96, 125.20, 122.63, 81.60. **$[\alpha]^{25}_D$**= -108.56 (*c*=1.0 in $CHCl_3$, 77% ee sample). **HRMS** (ESI): calcd for $C_{15}H_{11}O_3$ ([M+ H]$^+$) 239.0703, found 239.0705. **HPLC analysis**: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 16.18 min (major) and 24.28 min (minor), 77% ee.



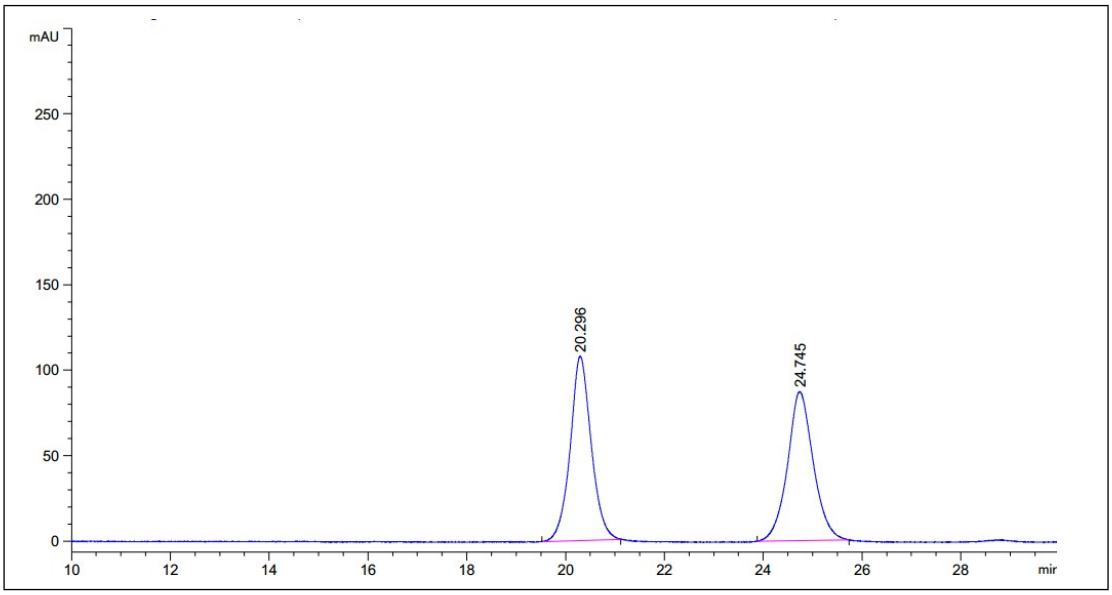


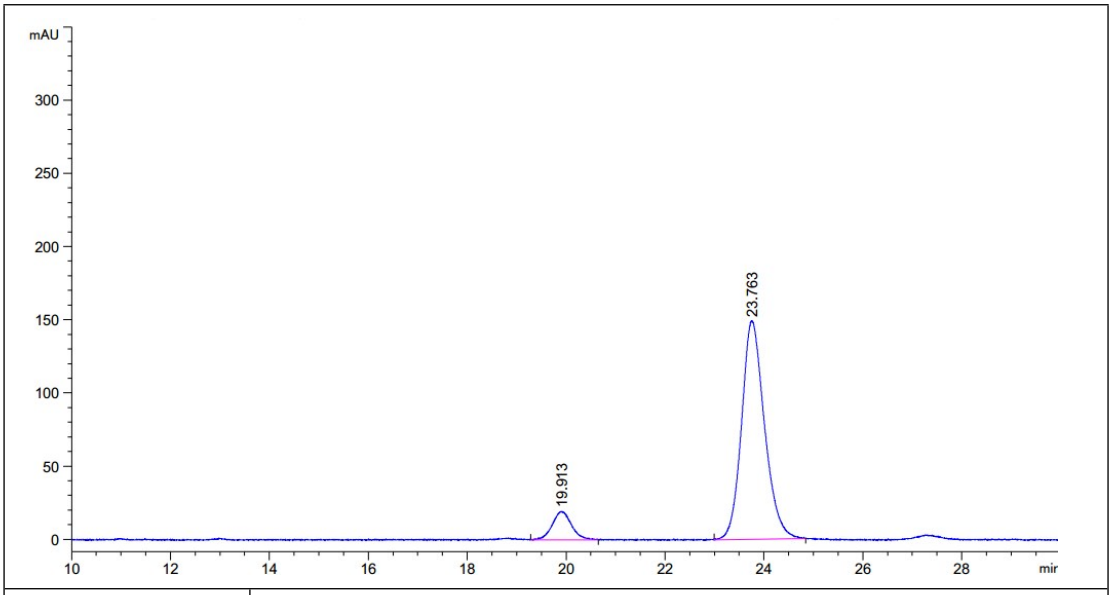
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.176	MM R	0.6409	2.60865e4	678.34863	88.2856
2	24.275	BB	0.6174	3461.33838	67.25989	11.7144

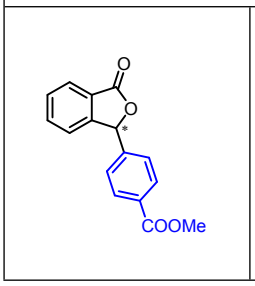


methyl (*R*)-4-(3-oxo-1,3-dihydroisobenzofuran-1-yl)benzoate (3i)[4]

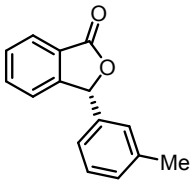
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.06 (dt, *J* = 8.5, 1.6 Hz, 2H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.67 (td, *J* = 7.5, 1.2 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 1H), 6.45 (s, 1H), 3.92 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.20, 166.38, 149.12, 141.30, 134.50, 131.01, 130.28, 129.63, 126.65, 125.90, 125.32, 122.68, 81.81, 52.27. **$[\alpha]^{25}_D$**= -79.48 (*c*=1.0 in $CHCl_3$, 81% ee sample). **HRMS** (ESI): calcd for $C_{16}H_{13}O_4$ ($[M+ H]^+$) 269.0808, found 269.0811. **HPLC analysis**: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 19.91 min (minor) and 23.76 min (major), 81% ee.





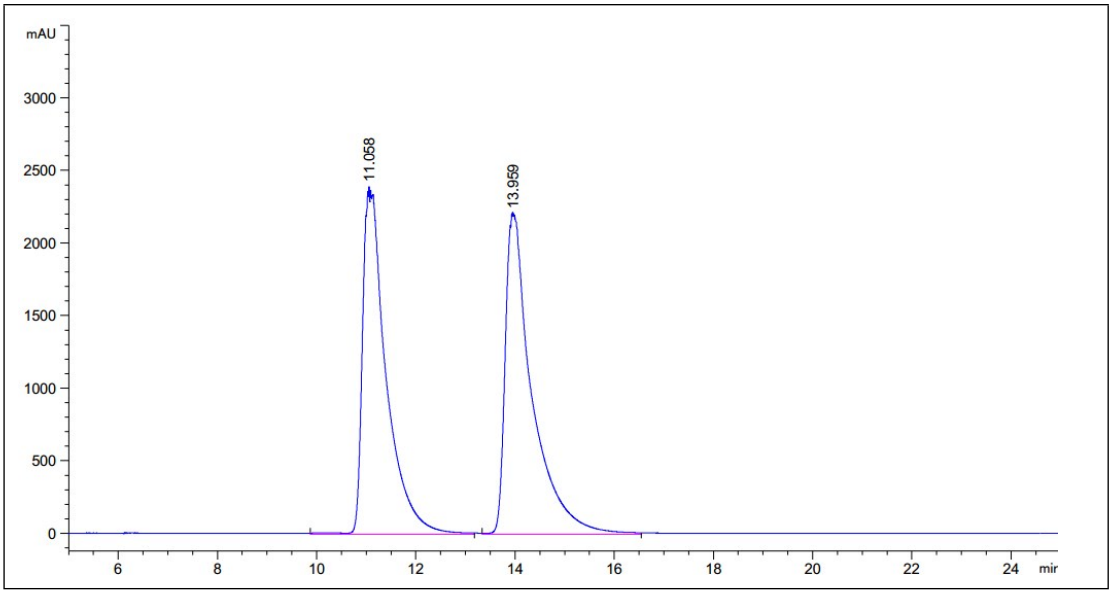


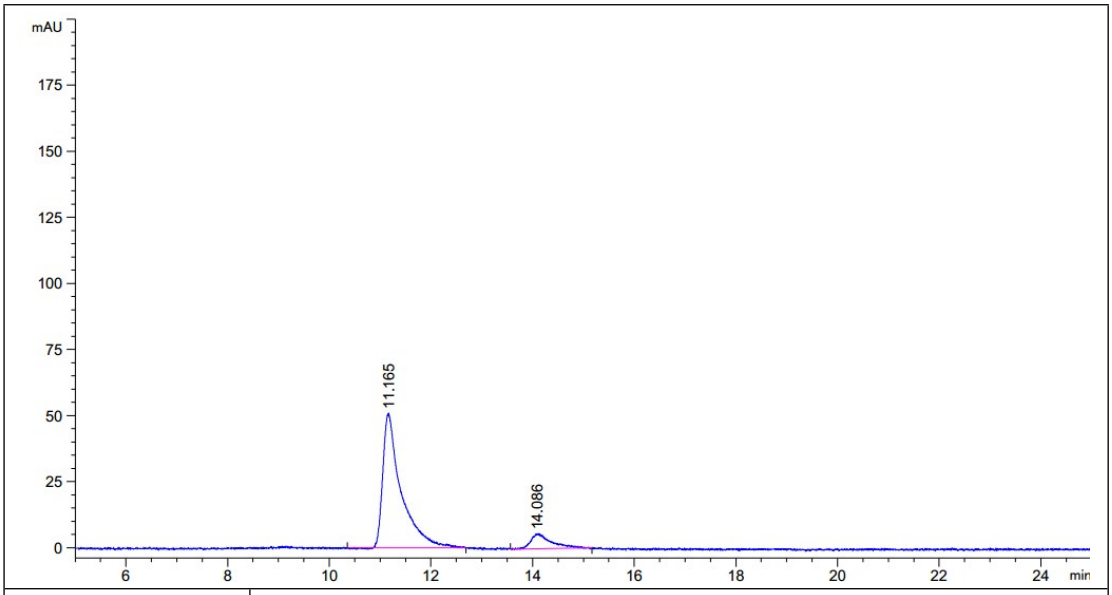
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.913	MM	0.4410	511.58978	19.33561	9.5397
2	23.763	MM	0.5413	4851.16113	149.36121	90.4603

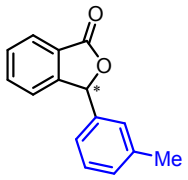


(*R*)-3-(m-tolyl)isobenzofuran-1(*3H*)-one (3j)[5]

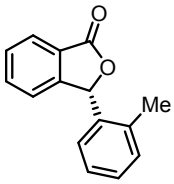
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.7 Hz, 1H), 7.65 (td, *J* = 7.5, 1.1 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1 H), 7.11 – 7.05 (m, 2H), 6.37 (s, 1H), 2.33 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.57, 149.79, 138.82, 136.31, 134.26, 130.04, 129.28, 128.81, 127.45, 125.61, 125.58, 124.04, 122.83, 82.79, 21.34. **$[\alpha]^{25}_{D}$**= -42.26 (*c*=1.0 in $CHCl_3$, 82% ee sample). **HRMS** (ESI): calcd for $C_{15}H_{13}O_2$ ([M+ H]$^+$) 225.0910, found 225.0912. **HPLC analysis**: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 11.17 min (minor) and 14.09 min (major), 82% ee.





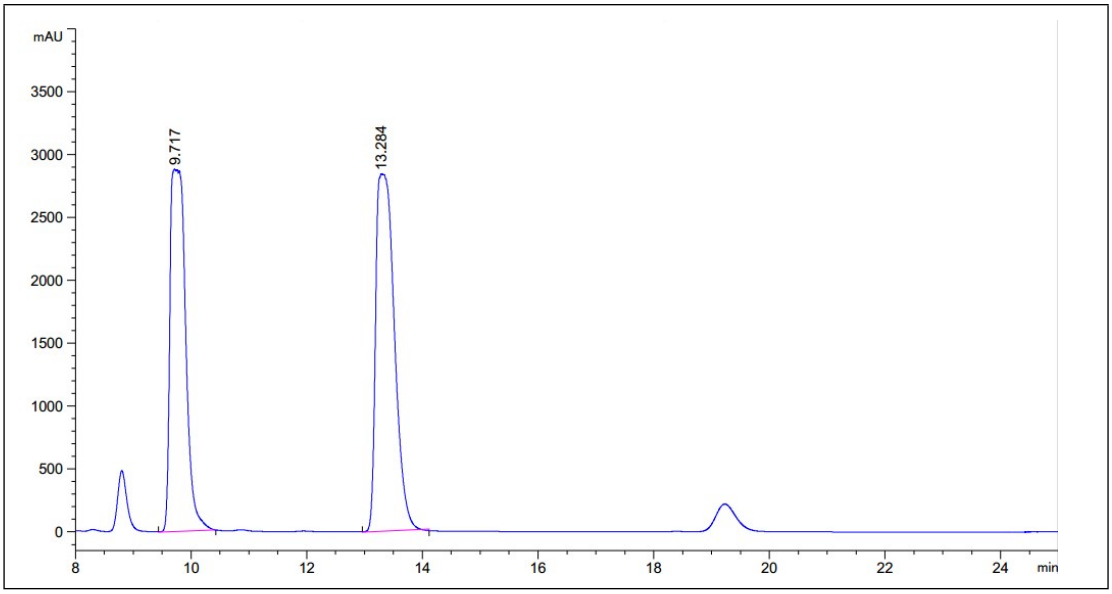


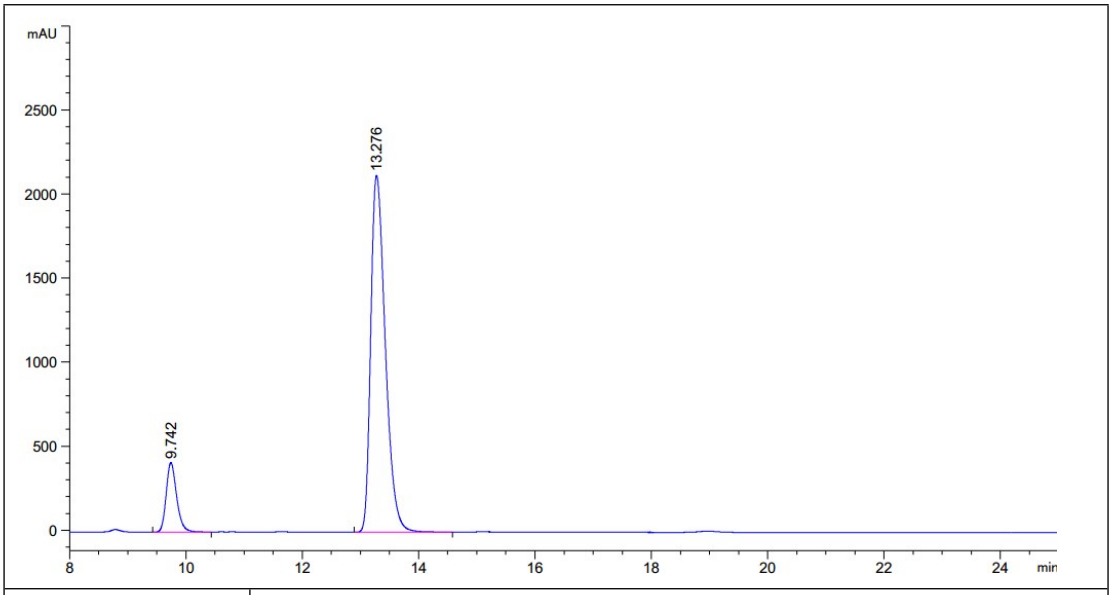
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.165	MM R	0.4055	1237.20959	50.84691	91.0735
2	14.086	MM R	0.3802	121.26366	5.31584	8.9265

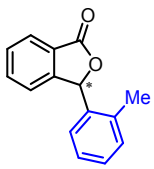


(*R*)-3-(o-tolyl)isobenzofuran-1(*3H*)-one (3k)[4]

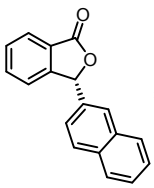
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.7 Hz, 1H), 7.67 (td, *J* = 7.5, 1.1 Hz, 1H), 7.58 (tt, *J* = 7.5, 0.8 Hz, 1H), 7.35 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.16 – 7.10 (m, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.69 (s, 1H), 2.50 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.58, 149.27, 137.15, 134.16, 134.08, 131.11, 129.35, 129.30, 127.25, 126.43, 126.40, 125.74, 123.00, 80.51, 19.32. **$[\alpha]^{25}_{D}$**= +48.28 (*c*=1.0 in $CHCl_3$, 75% ee sample). **HRMS** (ESI): calcd for $C_{15}H_{13}O_2$ ($[M+ H]^+$) 225.0910, found 225.0912. **HPLC analysis**: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 90:10; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 9.74 min (minor) and 13.28 min (major), 75% ee.





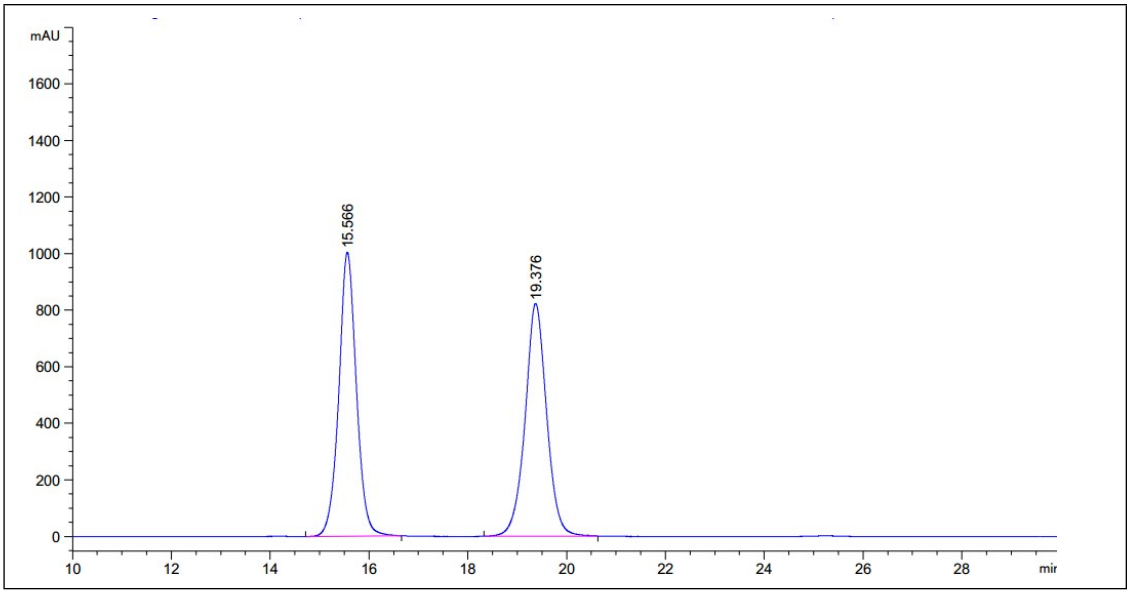


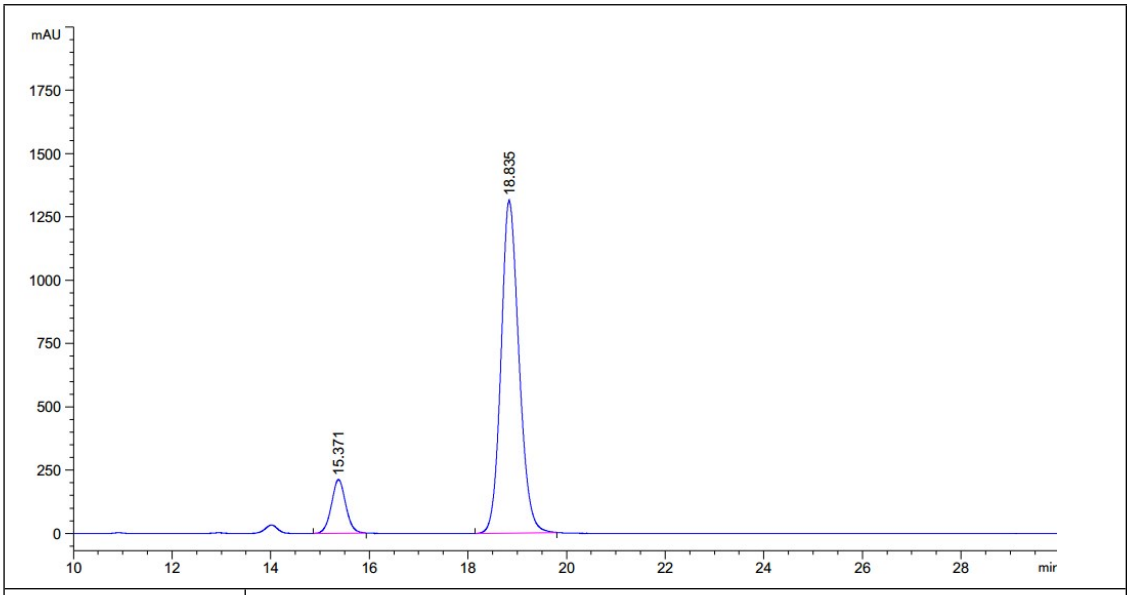
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.742	BB	0.1929	5175.66895	412.54684	12.3136
2	13.276	BB	0.2606	3.68566e4	2121.86963	87.6864

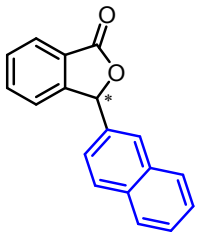


(*R*)-3-(naphthalen-2-yl)isobenzofuran-1(*3H*)-one (3l)[4]

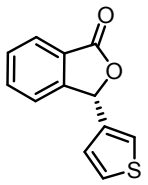
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.84 (m, 4H), 7.64 (td, *J* = 7.5, 1.2 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.34 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.23 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.56 (s, 1H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.55, 149.70, 134.35, 133.67, 133.57, 133.06, 129.41, 129.06, 128.06, 127.78, 126.81, 126.68, 126.67, 125.70, 125.61, 123.76, 122.90, 82.89. **$[\alpha]^{25}_D$**= -52.72 (*c*=1.0 in $CHCl_3$, 77% ee sample). **HRMS** (ESI): calcd for $C_{16}H_{13}O_2$ ([M+ H]$^+$) 261.0910, found 261.0913. **HPLC analysis**: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 15.37 min (minor) and 18.84 min (major), 77% ee.





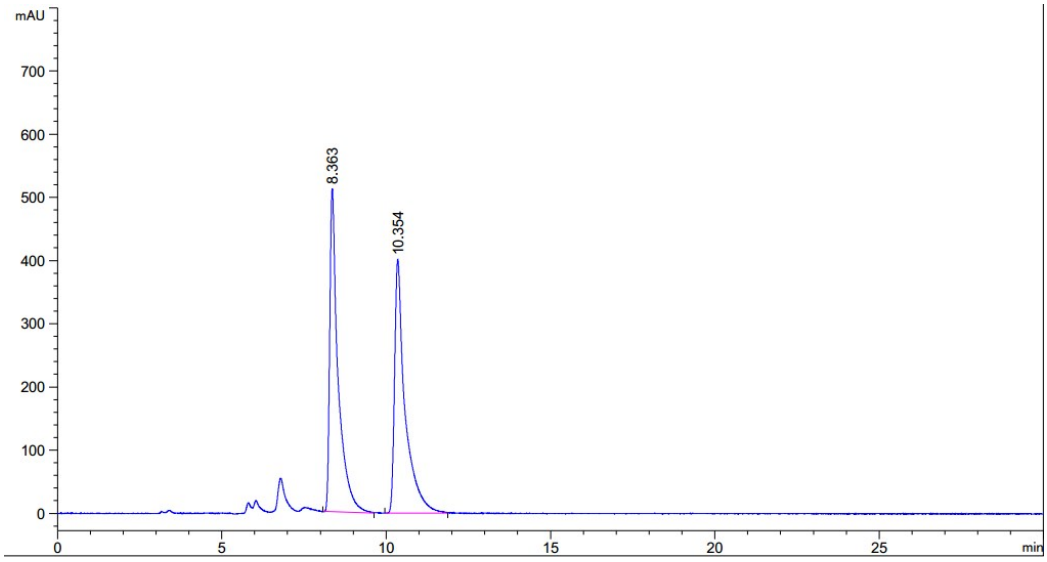


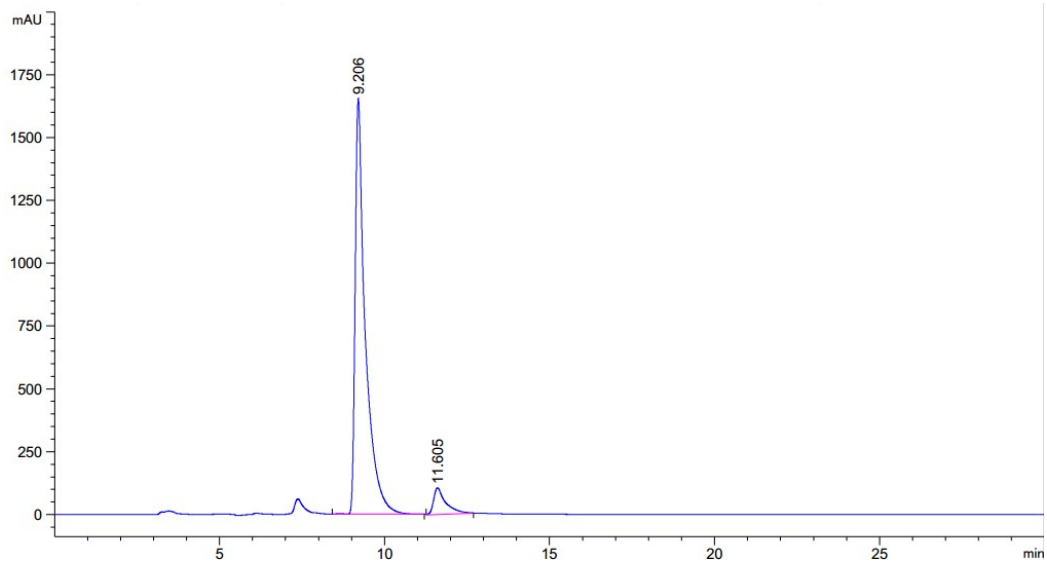
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.371	VV R	0.2381	4261.25830	211.86884	11.3801
2	18.835	VV R	0.2978	3.31837e4	1315.64355	88.6199

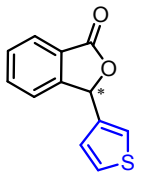


(*S*)-3-(thiophen-3-yl)isobenzofuran-1(*3H*)-one (3m)

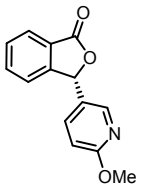
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.32 (m, 2H), 6.94 (d, *J* = 4.9 Hz, 1H), 6.51 (s, 1H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.17, 148.99, 137.19, 134.25, 129.45, 127.19, 125.89, 125.80, 125.73, 124.45, 122.81, 78.41. **$[\alpha]^{25}_D$**= +59.36 (*c*=1.0 in $CHCl_3$, 85% ee sample). **HRMS** (ESI): calcd for $C_{12}H_9O_2S$ ($[M+H]^+$) 217.0318, found 217.0320. **HPLC analysis**: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:10; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 9.21 min (major) and 11.61 min (minor), 85% ee.





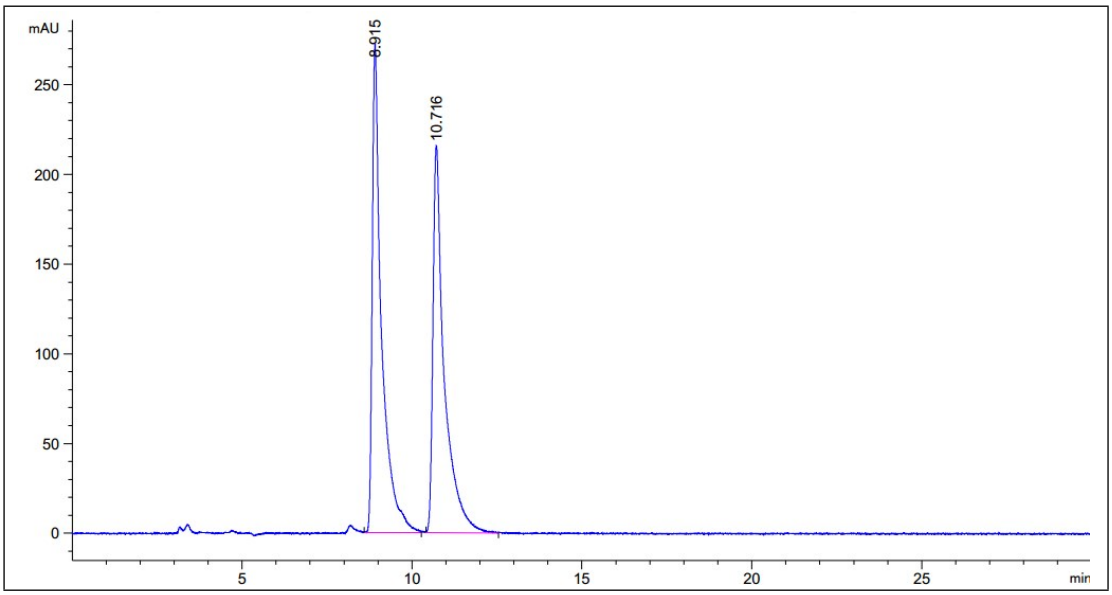


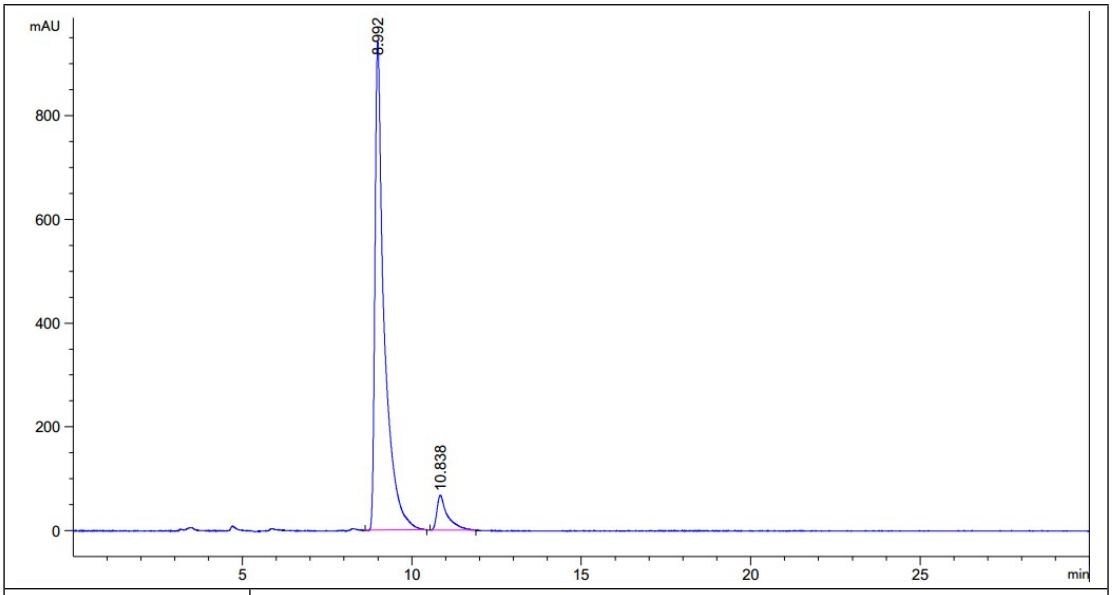
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.206	VB R	0.2968	3.55379e4	1654.22009	92.3880
2	11.605	BB	0.3816	2928.02173	105.55782	7.6120



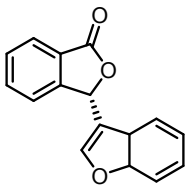
(*S*)-3-(6-methoxypyridin-3-yl)isobenzofuran-1(*3H*)-one (3n)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 2.5 Hz, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.69 (td, *J* = 7.5, 1.1 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.32 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.28 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 6.39 (s, 1H), 3.95 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.11, 164.98, 148.92, 146.48, 137.39, 134.46, 129.64, 125.97, 125.78, 124.91, 122.86, 111.72, 80.40, 53.69. **$[\alpha]^{25}_{D}$**= +17.12 (*c*=1.0 in $CHCl_3$, 85% ee sample). **HRMS** (ESI): calcd for $C_{14}H_{12}NO_3$ ($[M+H]^+$) 242.0812, found 242.0814. **HPLC analysis**: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 9.00 min (major) and 10.84 min (minor), 85% ee.



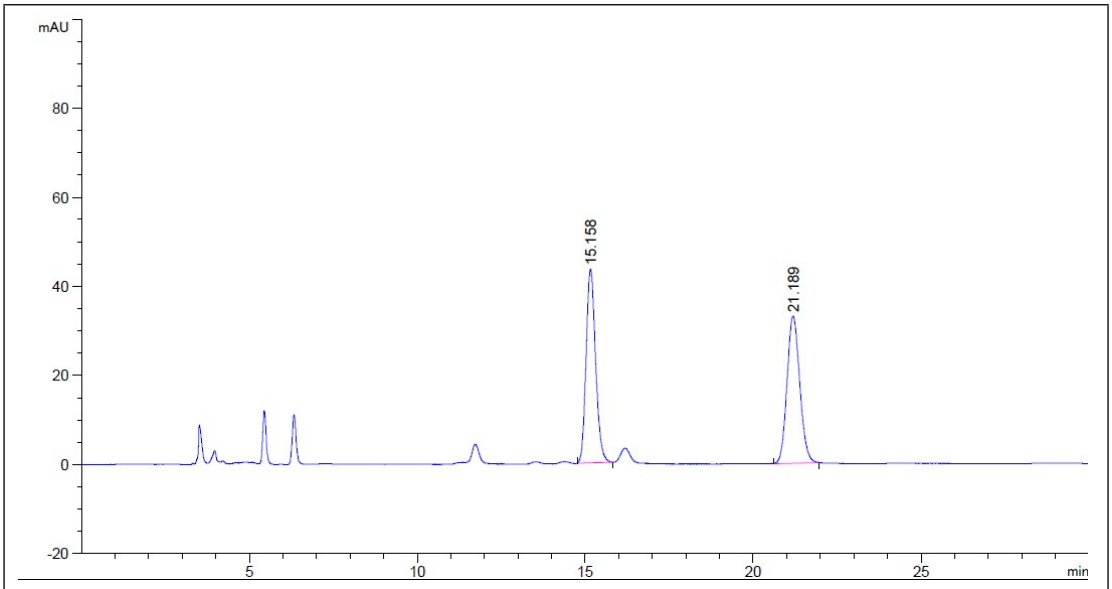


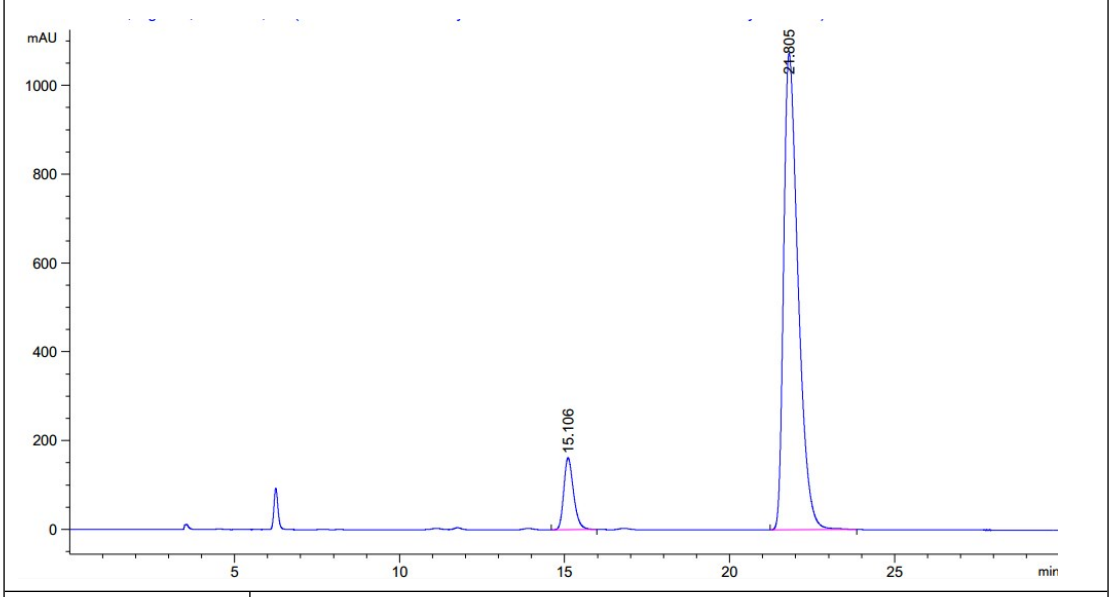
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.992	MM R	0.3193	1.80136e4	940.24683	92.4421
2	10.838	MM R	0.3646	1472.75452	67.31718	7.5579

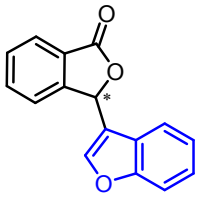


(3S)-3-(3a,7a-dihydrobenzofuran-2-yl)isobenzofuran-1(3H)-one (3o)

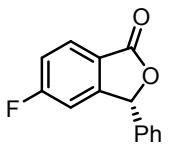
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 7.7 Hz, 1H), 7.73 (td, *J* = 7.5, 1.1 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.44 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.32 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.24 (td, *J* = 7.6, 1.0 Hz, 1H), 6.79 (s, 1H), 6.58 (s, 1H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 169.72, 155.49, 151.21, 146.28, 134.39, 129.97, 127.34, 126.06, 125.95, 125.35, 123.22, 123.04, 121.54, 111.58, 106.74, 75.83. **$[\alpha]^{25}_D$**= +77.46 (*c*=1.0 in $CHCl_3$, 82% ee sample). HRMS (ESI): calcd for $C_{16}H_{11}O_3$ ($[M+H]^+$) 251.0703, found 251.0705. **HPLC analysis**: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 15.11 min (minor) and 21.81 min (major), 82% ee.





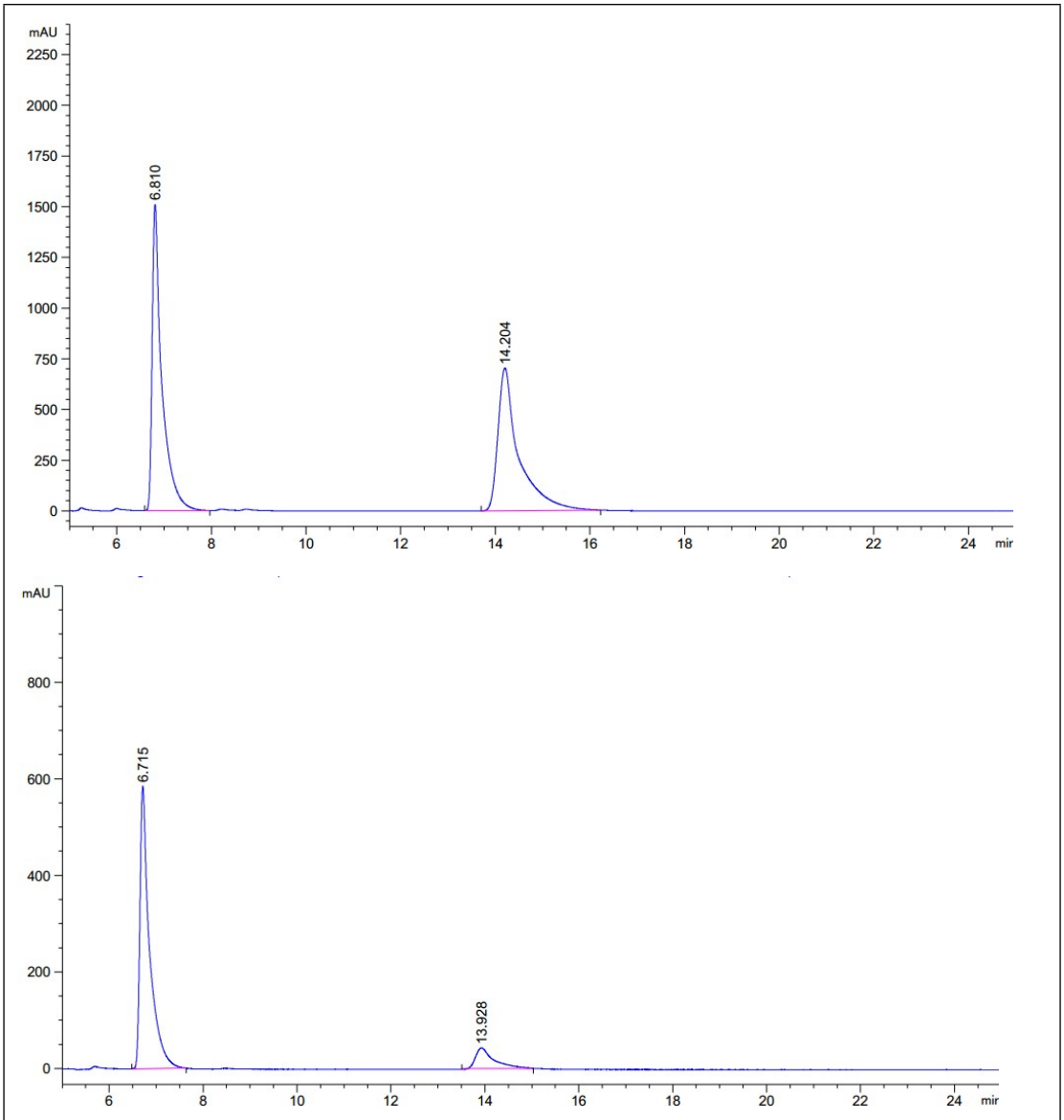


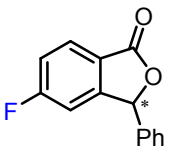
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.106	BB	0.2999	3322.05713	161.91768	9.2332
2	21.805	BB	0.4506	3.26576e4	1072.97095	90.7668



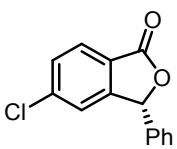
(*R*)-5-fluoro-3-phenylisobenzofuran-1(*3H*)-one (3p)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 8.3, 4.8 Hz, 1H), 7.38 – 7.41 (m, 3H), 7.28 – 7.23 (m, 3H), 7.00 (dd, *J* = 7.7, 2.2 Hz, 1H), 6.36 (s, 1H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 169.22, 166.65 (d, J = 256.7 Hz), 152.46 (d, J = 9.96 Hz), 135.76, 129.50, 129.07, 128.00 (d, J = 10.4 Hz), 126.82, 121.60, 117.65 (d, J = 24.1 Hz), 110.14 (d, J = 24.5 Hz), 81.97 (d, J = 2.7 Hz). **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -102.15. **$[\alpha]^{25}_D$**= -41.00 (*c*=1.0 in $CHCl_3$, 76% ee sample). **HRMS** (ESI): calcd for $C_{14}H_{10}FO_2$ ([M+ H]$^+$) 229.0659, found 229.0667. **HPLC analysis**: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 6.72 min (major) and 13.93 min (minor), 76% ee.



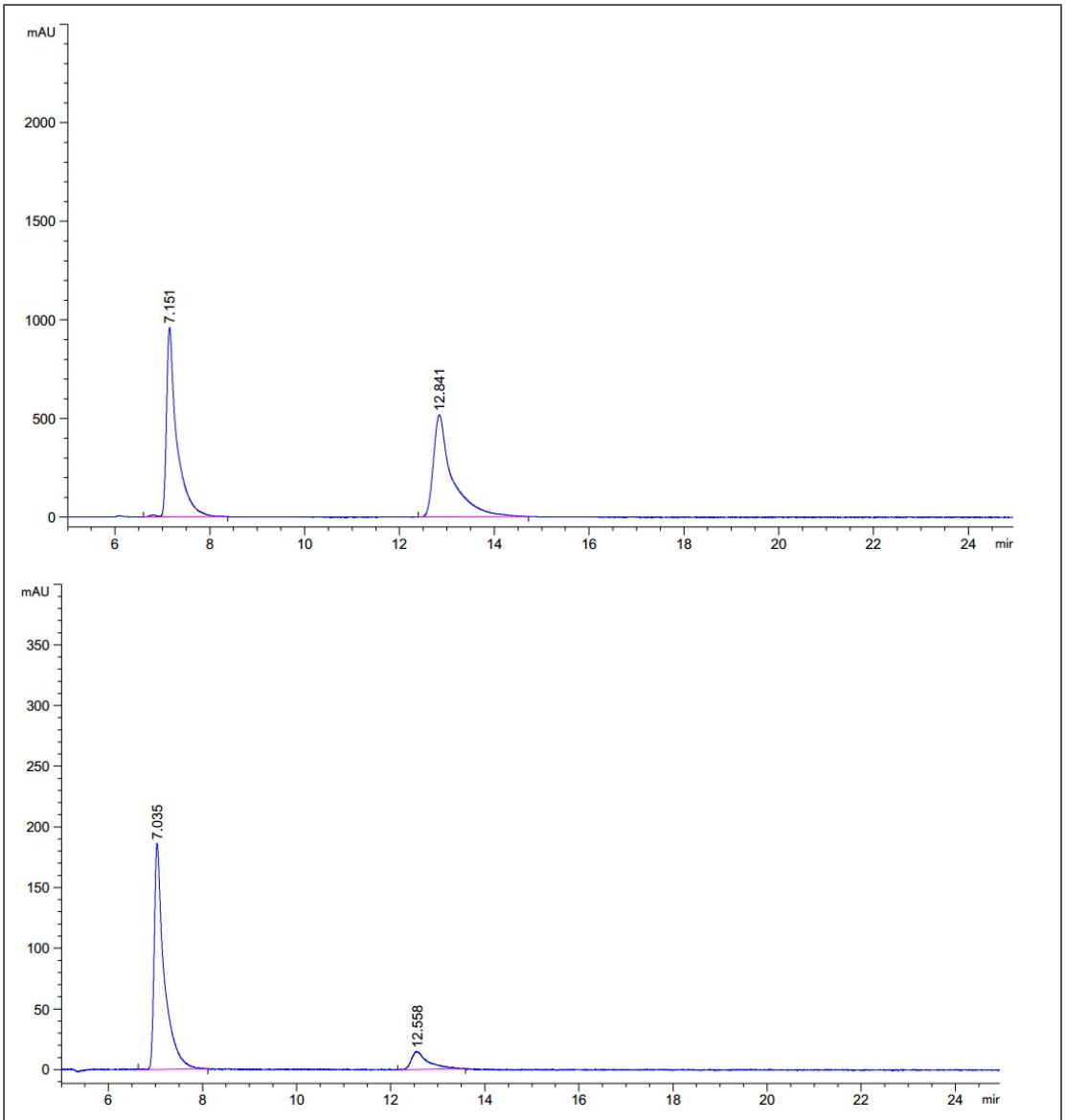


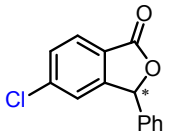
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.715	VV R	0.1969	8280.09863	585.64166	87.7905
2	13.928	MM	0.4380	1151.56104	43.81990	12.2095



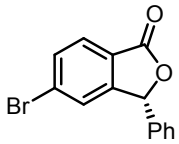
(*R*)-5-chloro-3-phenylisobenzofuran-1(*3H*)-one (3q)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.52 (ddd, *J* = 8.2, 1.7, 0.7 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.33 – 7.30 (m, 1H), 7.32 – 7.26 (m, 2H), 6.37 (s, 1H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 169.28, 151.27, 141.05, 135.67, 130.17, 129.54, 129.10, 126.85, 126.81, 124.03, 123.24, 82.07. **$[\alpha]^{25}_D$**= +30.52 (*c*=1.0 in $CHCl_3$, 77% ee sample). **HRMS** (ESI): calcd for $C_{14}H_{10}ClO_2$ ($[M+H]^+$) 245.0364, found 245.0371. **HPLC analysis**: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 7.04 min (major) and 12.56 min (minor), 77% ee.



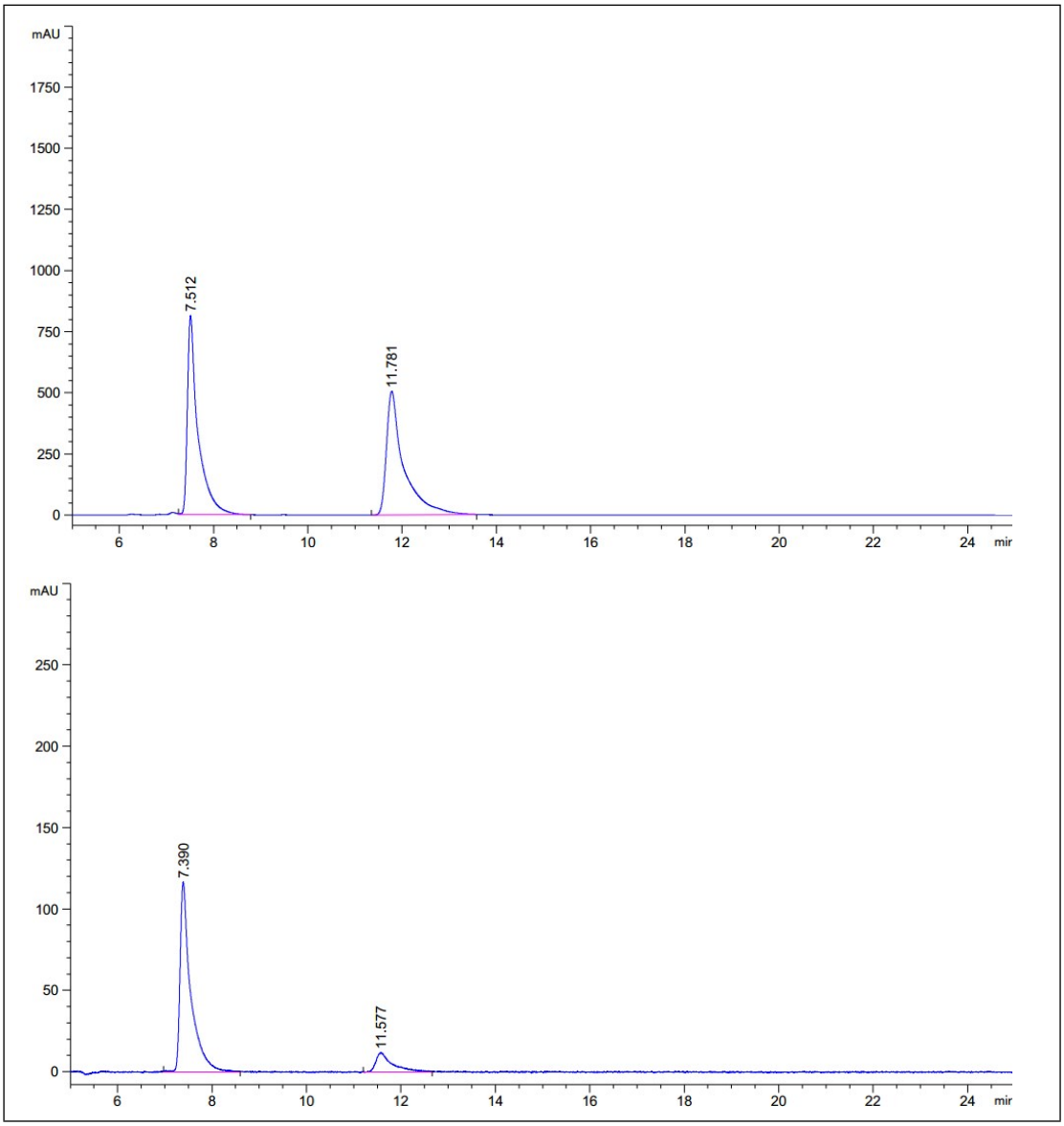


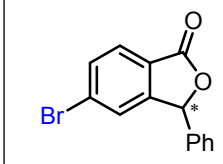
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.035	MM R	0.2445	2735.52173	186.43620	88.3015
2	12.558	MM R	0.4031	362.41345	14.98612	11.6985



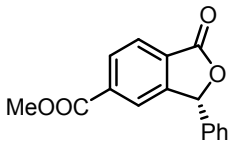
(*R*)-5-bromo-3-phenylisobenzofuran-1(*3H*)-one (3r)[6]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.1 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.49 (dt, *J* = 1.5, 0.7 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.29 – 7.23 (m, 2H), 6.37 (s, 1H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 169.41, 151.36, 135.63, 133.00, 129.56, 129.54, 129.10, 126.90, 126.85, 126.25, 124.48, 82.03. **$[\alpha]^{25}_{D}$**= +50.16 (*c*=1.0 in $CHCl_3$, 74% ee sample). **HRMS** (ESI): calcd for $C_{14}H_{10}BrO_2$ ($[M+ H]^+$) 288.9859, found 288.9868. **HPLC analysis**: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 7.39 min (major) and 11.58 min (minor), 74% ee.



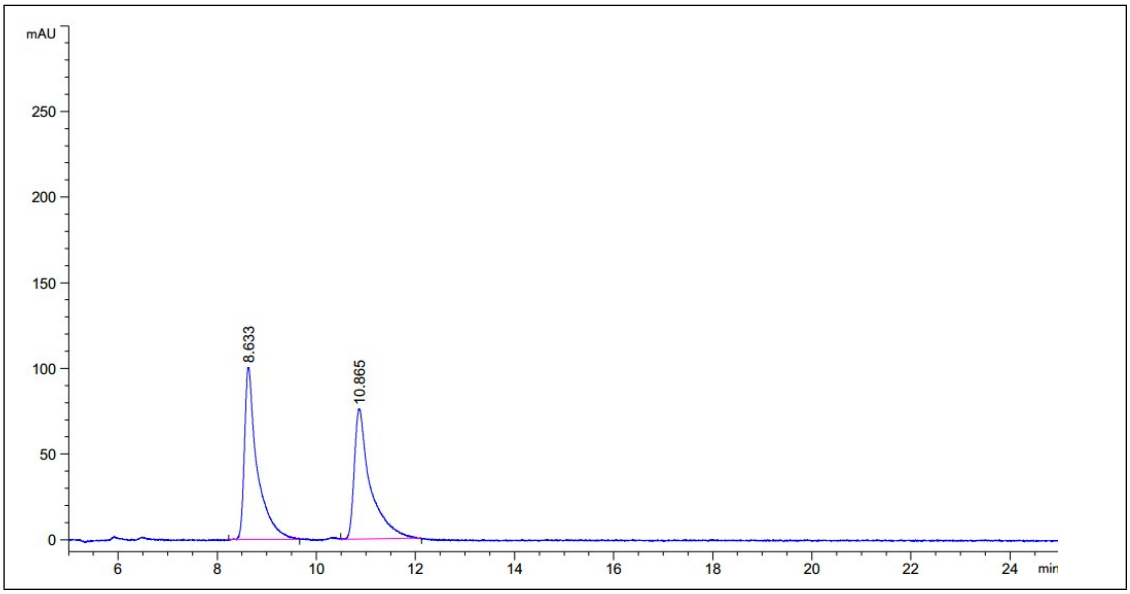


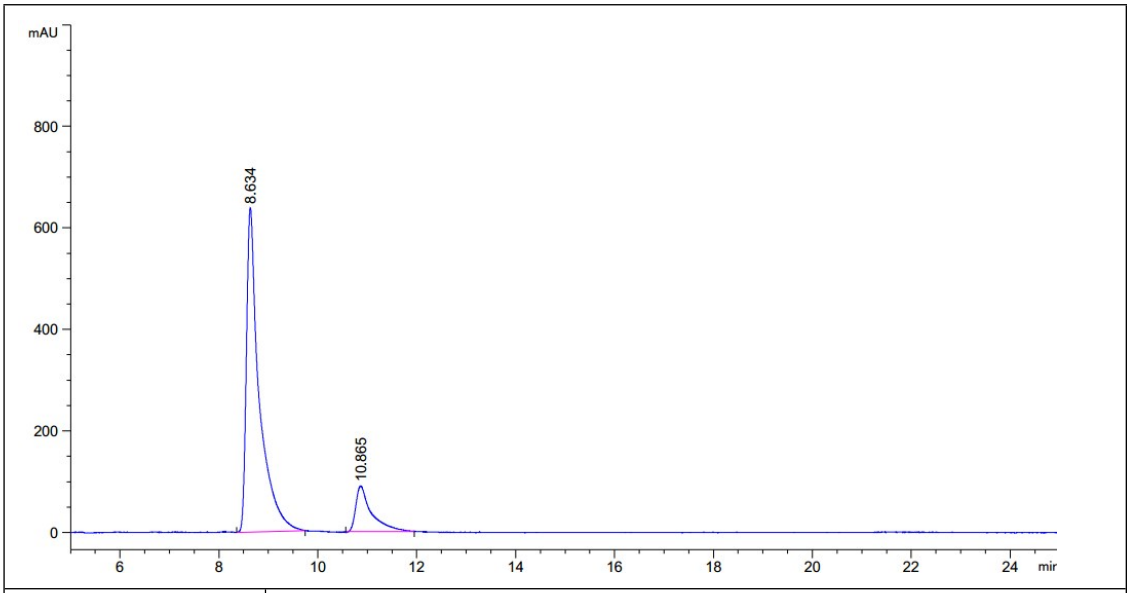
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.390	MM	0.2562	1788.86877	116.36292	87.0299
2	11.577	MM	0.3767	266.59537	11.79366	12.9701

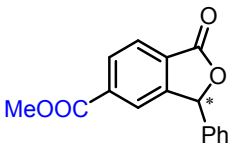


methyl (*R*)-1-oxo-3-phenyl-1,3-dihydroisobenzofuran-5-carboxylate (3s)

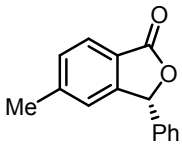
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 (dd, *J* = 8.2, 3.8 Hz, 1H), 8.05 – 8.01 (m, 1H), 8.00 (s, 1H), 7.42 – 7.38 (m, 3H), 7.29 – 7.27 (m, 2H), 6.46 (s, 1H), 3.93 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 169.39, 165.59, 149.65, 135.69, 135.63, 130.62, 129.50, 129.14, 129.07, 126.90, 125.67, 124.20, 82.73, 52.68. **$[\alpha]^{25}_{D}$**= +43.38 (*c*=1.0 in $CHCl_3$, 74% ee sample). **HRMS** (ESI): calcd for $C_{16}H_{13}O_4$ ([M+H]$^+$) 269.0808, found 269.0818. **HPLC analysis**: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 8.63 min (major) and 10.87 min (minor), 74% ee.





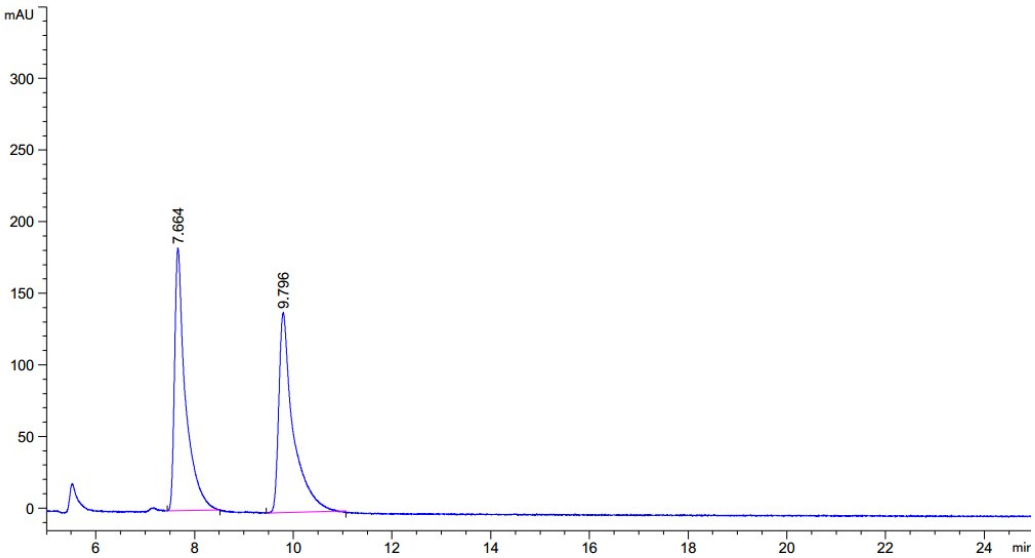


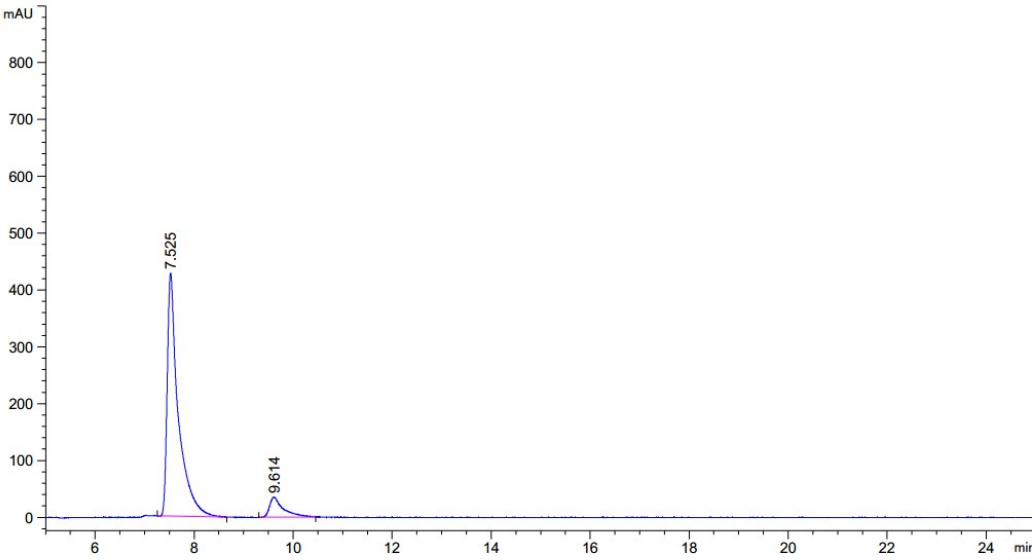
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.634	VV R	0.2437	1.14786e4	638.70135	86.3955
2	10.865	BV R	0.2441	1807.50037	89.39657	13.6045

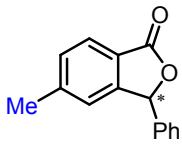


(*R*)-5-methyl-3-phenylisobenzofuran-1(*3H*)-one (3t)[6]

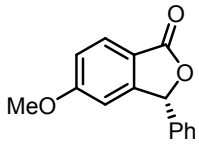
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.37 – 7.32 (m, 1H), 7.31 – 7.25 (m, 2H), 7.11 (d, *J* = 0.7 Hz, 1H), 6.34 (s, 1H), 2.43 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.54, 150.26, 145.60, 136.65, 130.51, 129.18, 128.92, 126.90, 125.36, 123.06, 122.98, 82.41, 22.02. **$[\alpha]^{25}_D$**= +3.16 (*c*=1.0 in $CHCl_3$, 83% ee sample). **HRMS** (ESI): calcd for $C_{15}H_{13}O_2$ ($[M+H]^+$) 225.0910, found 225.0914. **HPLC analysis**: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 7.53 min (major) and 9.61 min (minor), 83% ee.





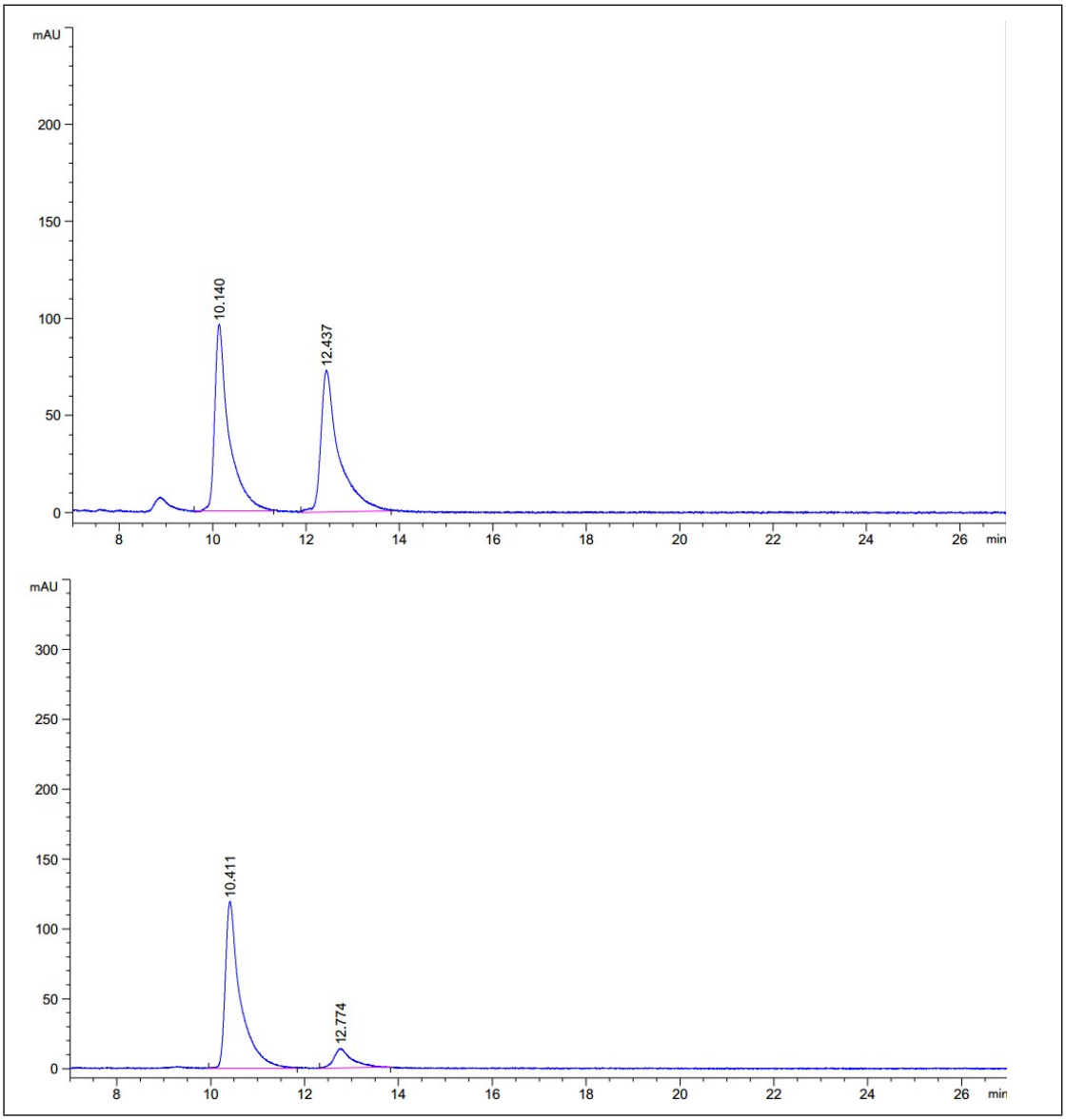


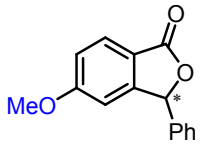
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.525	BV R	0.2099	6527.70068	426.89026	91.4560
2	9.614	MM	0.2896	609.82953	35.09508	8.5440



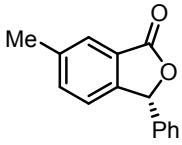
(*R*)-5-methoxy-3-phenylisobenzofuran-1(*3H*)-one (3u)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.5 Hz, 1H), 7.38 (dd, *J* = 5.2, 1.9 Hz, 3H), 7.32 – 7.25 (m, 2H), 7.05 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.72 (d, *J* = 2.0 Hz, 1H), 6.31 (s, 1H), 3.83 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.20, 164.90, 152.50, 136.58, 129.25, 128.96, 127.12, 127.01, 117.89, 116.84, 106.64, 82.08, 55.82. **$[\alpha]^{25}_D$**= +34.44 (*c*=1.0 in $CHCl_3$, 76% ee sample). **HRMS** (ESI): calcd for $C_{15}H_{13}O_3$ ($[M+H]^+$) 241.0859, found 241.0860. **HPLC analysis**: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 10.41 min (major) and 12.77 min (minor), 76% ee.



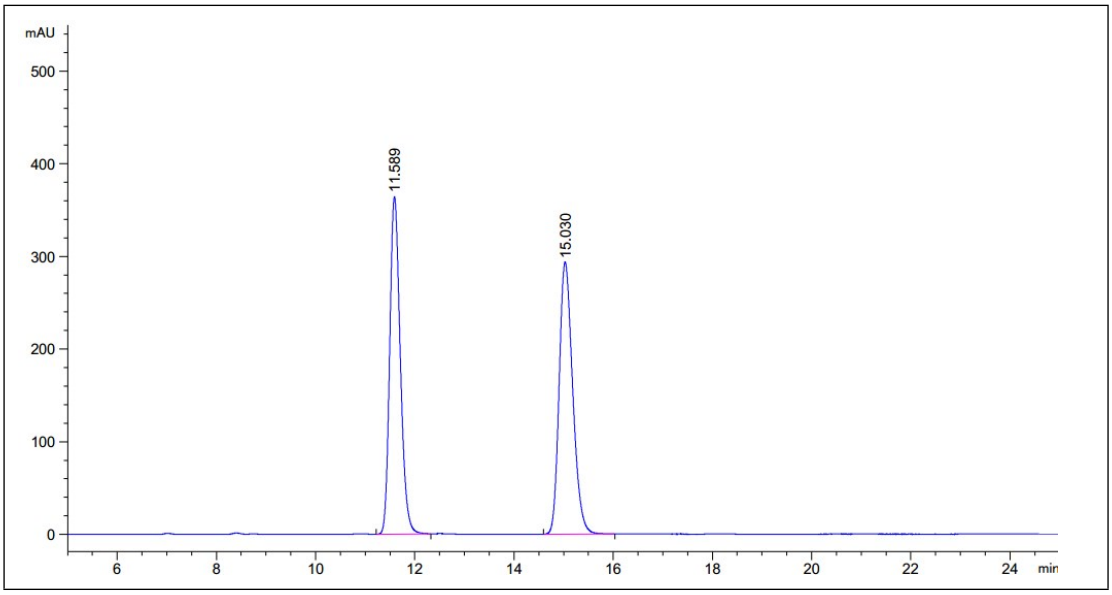


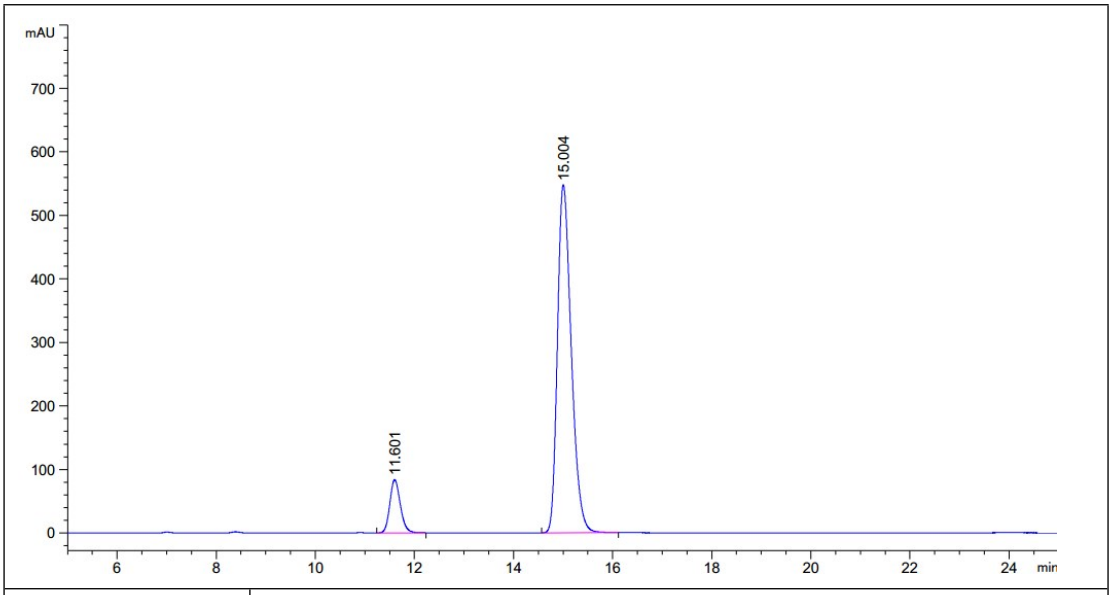
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.411	MM	0.3664	2620.24463	119.19129	87.7760
2	12.774	MM	0.4397	364.90543	13.83232	12.2240

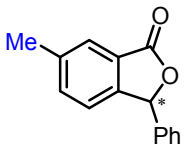


(*R*)-6-methyl-3-phenylisobenzofuran-1(*3H*)-one (3v)[6]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 (dt, *J* = 1.7, 0.8 Hz, 1H), 7.45 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.41 – 7.33 (m, 3H), 7.29 – 7.24 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 1H), 6.37 (s, 1H), 2.47 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.64, 147.11, 139.66, 136.67, 135.46, 129.19, 128.91, 126.94, 125.80, 125.57, 122.53, 82.61, 21.24. **$[\alpha]^{25}_D$**= -31.14 (*c*=1.0 in $CHCl_3$, 81% ee sample). **HRMS** (ESI): calcd for $C_{15}H_{13}O_2$ ($[M+H]^+$) 225.0910, found 225.0914. **HPLC analysis**: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 11.60 min (minor) and 15.00 min (major), 81% ee.







Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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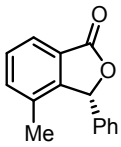
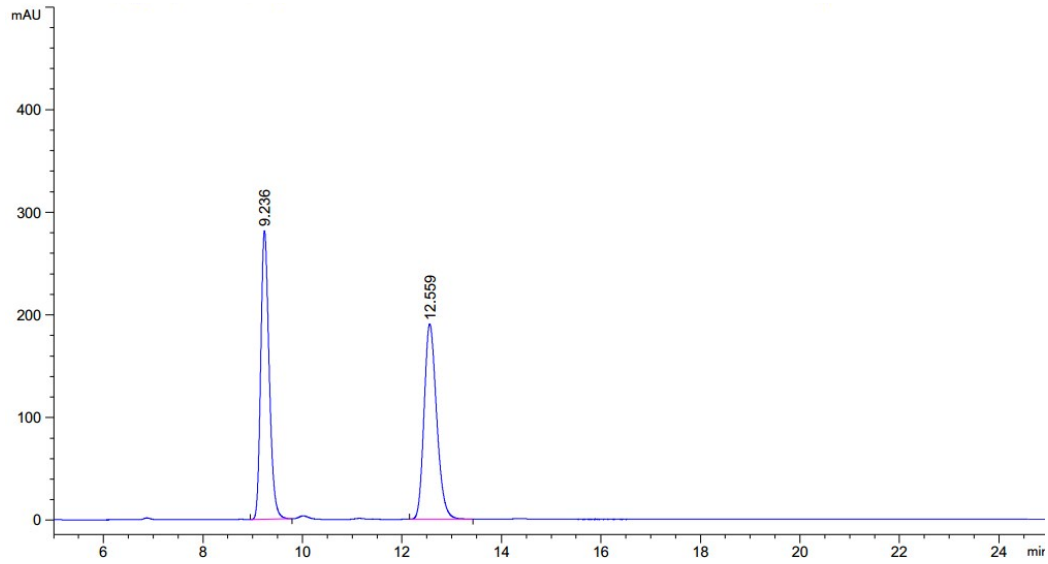
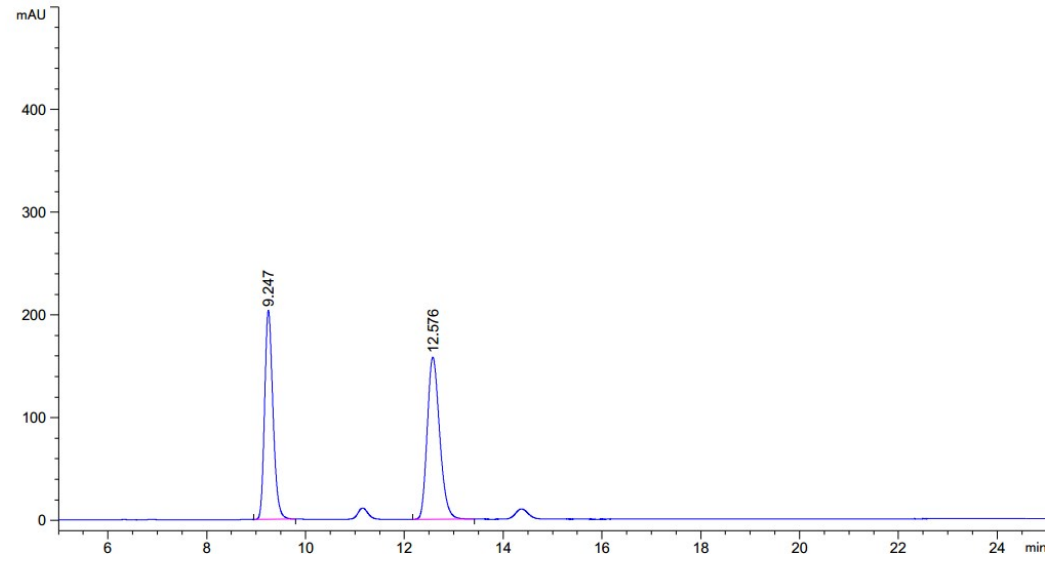
2	15.004	BB	0.2966	1.05971e4	547.98724	90.5527

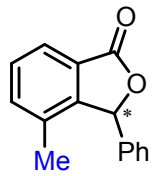


(*R*)-4-methyl-3-phenylisobenzofuran-1(*3H*)-one (3w)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.42 – 7.31 (m, 3H), 7.22 – 7.17 (m, 2H), 6.33 (s, 1H), 2.03 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.72, 147.55, 135.57, 135.27, 133.43, 129.77, 129.50, 128.92, 128.14, 126.12, 123.05, 82.98, 17.87. **$[\alpha]^{25}_D$**= +1.66 (*c*=1.0 in $CHCl_3$, 7% ee sample). **HRMS** (ESI): calcd for $C_{15}H_{13}O_2$ ($[M+H]^+$) 225.0910, found 225.0912. **HPLC analysis**: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 90:10; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R =9.25 min (minor) and 12.58 min (major), 7% ee.







Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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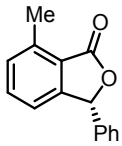
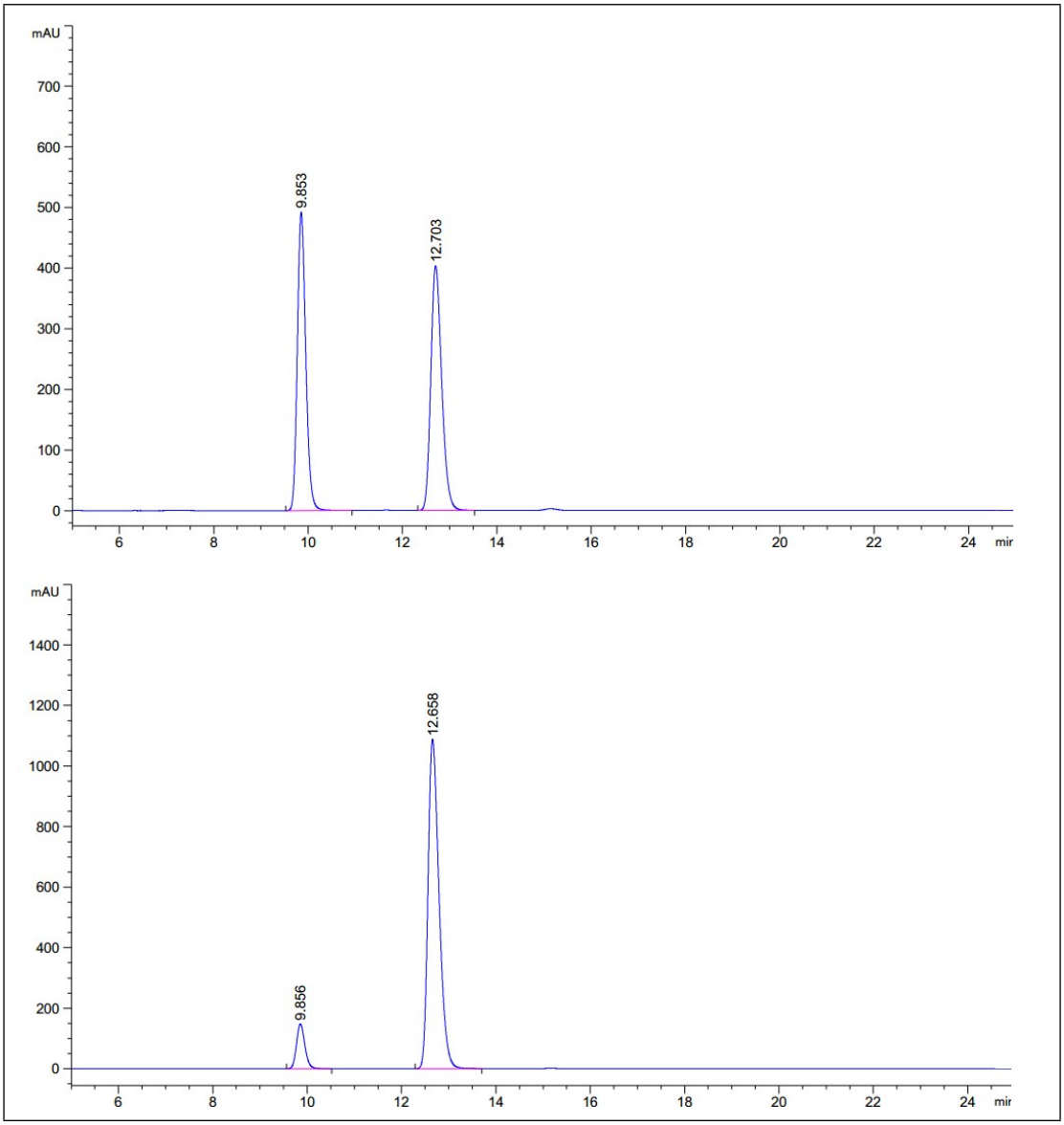
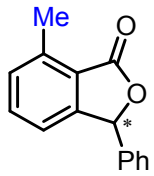
2	12.576	BB	0.2669	2752.87988	157.91391	53.5447



(*R*)-7-methyl-3-phenylisobenzofuran-1(*3H*)-one (3x)[6]

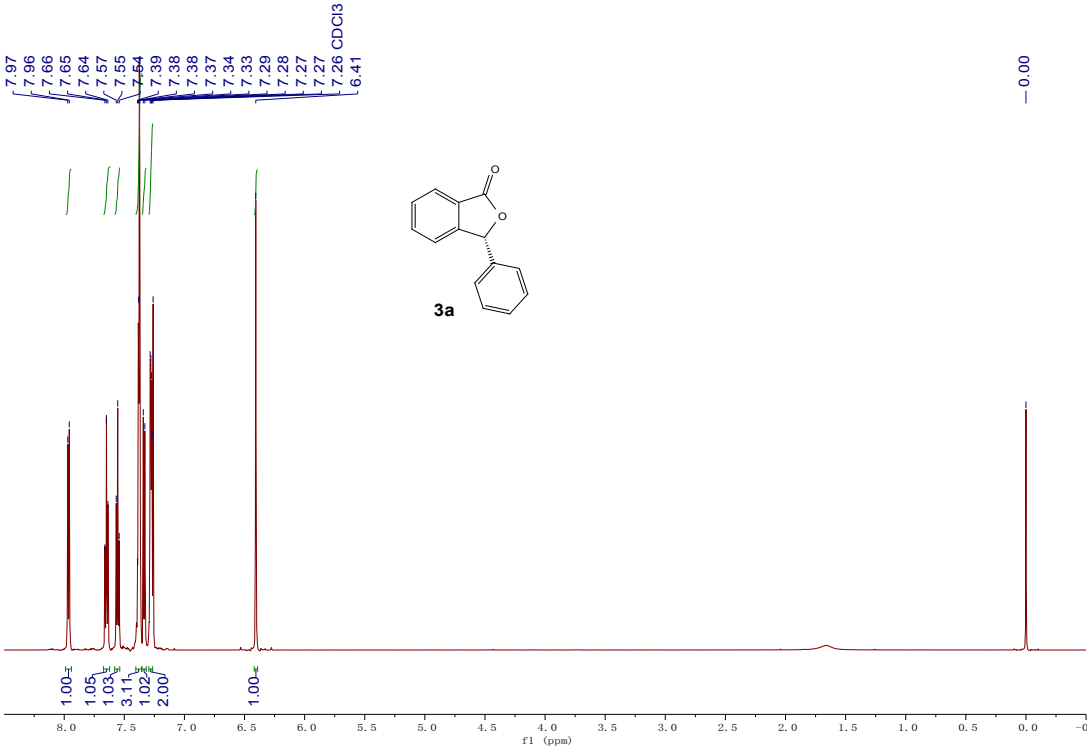
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 (t, *J* = 7.6 Hz, 1H), 7.41 – 7.33 (m, 3H), 7.32 – 7.25 (m, 3H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.33 (s, 1H), 2.75 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.68, 150.21, 139.68, 136.84, 133.97, 130.89, 129.14, 128.90, 126.95, 123.03, 120.17, 81.79, 17.38. **$[\alpha]^{25}_D$**= -90.18 (*c*=1.0 in $CHCl_3$, 81% ee sample). **HRMS** (ESI): calcd for $C_{15}H_{13}O_2$ ($[M+H]^+$) 225.0910, found 225.0912. **HPLC analysis**: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 9.86 min (minor) and 12.66 min (major), 81% ee.

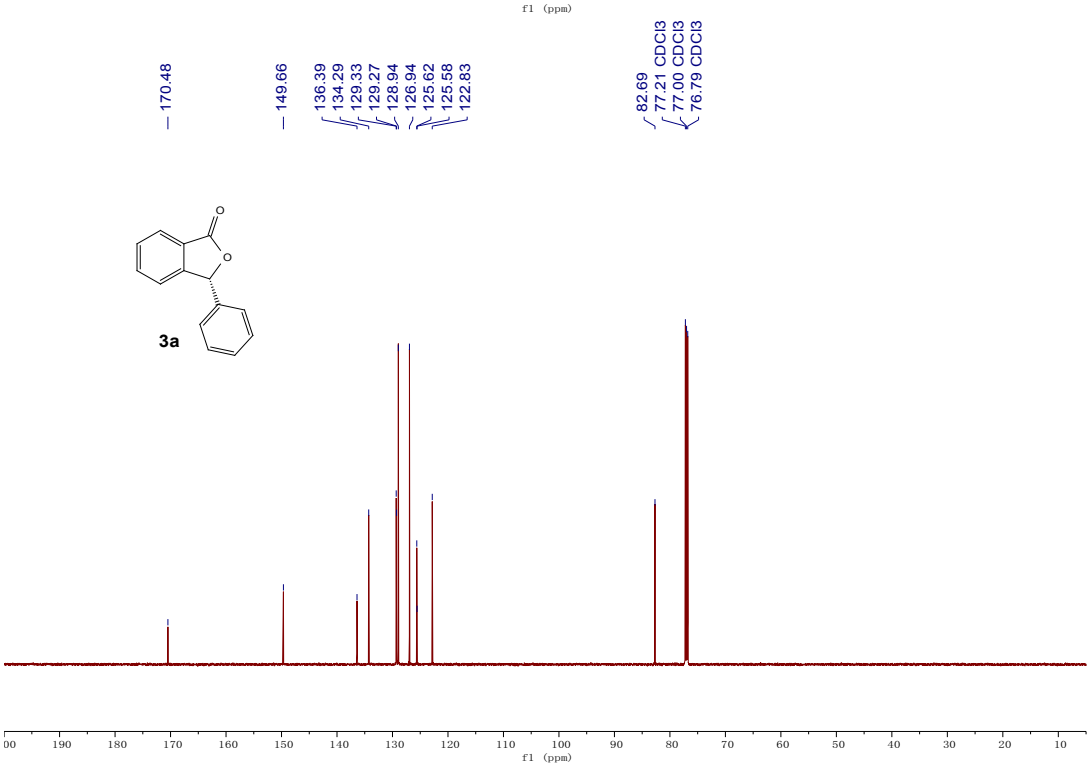


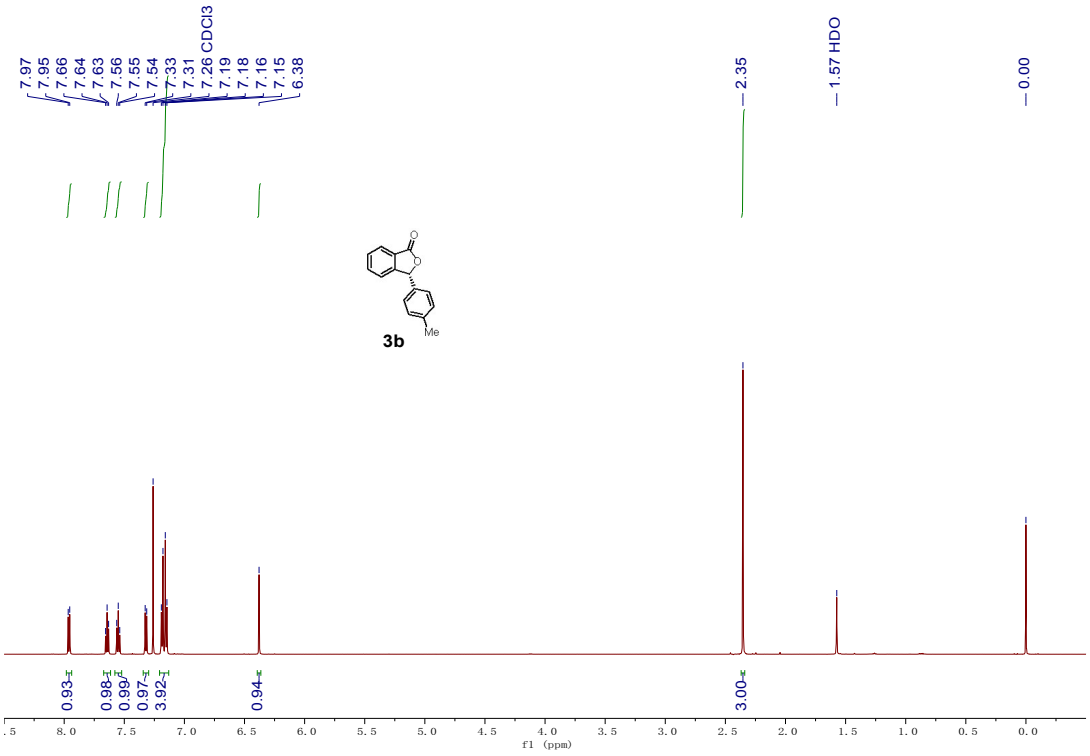


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.856	BB	0.1899	1827.01855	148.11800	9.3975
2	12.658	BB	0.2485	1.76145e4	1087.42371	90.6025

4. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectras



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7.54
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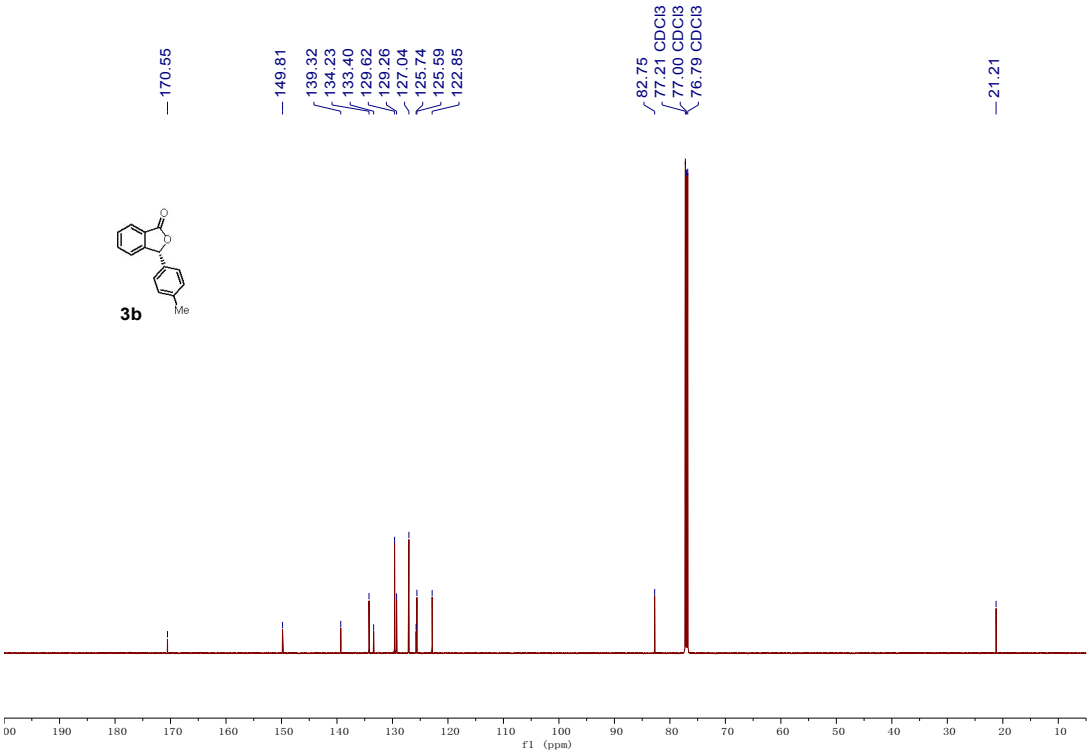
7.31
7.26 CDCl3
7.19
7.18
7.16
7.15
6.38
2.35
1.57 HDO
0.00
3b
Me
0.93
0.98
0.99
0.97
3.92
0.94
3.00
f1 (ppm)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149.81
139.32
134.23
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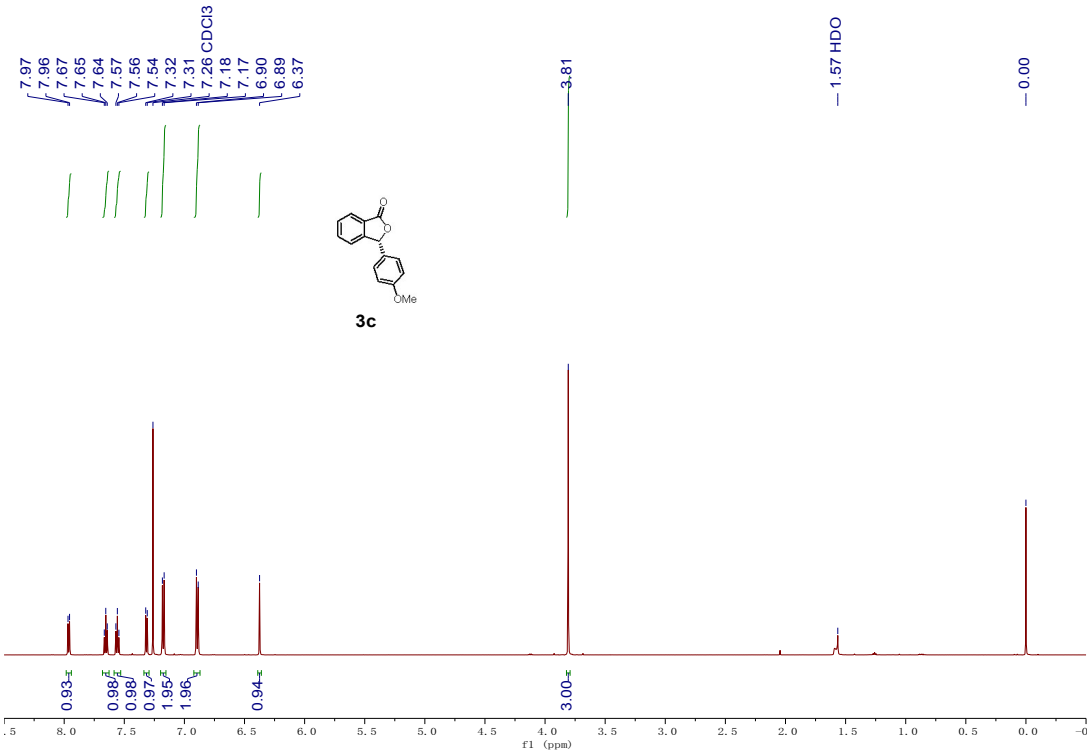
129.62
129.26
127.04
125.74
125.59
122.85
82.75
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
21.21
3b
Me
f1 (ppm)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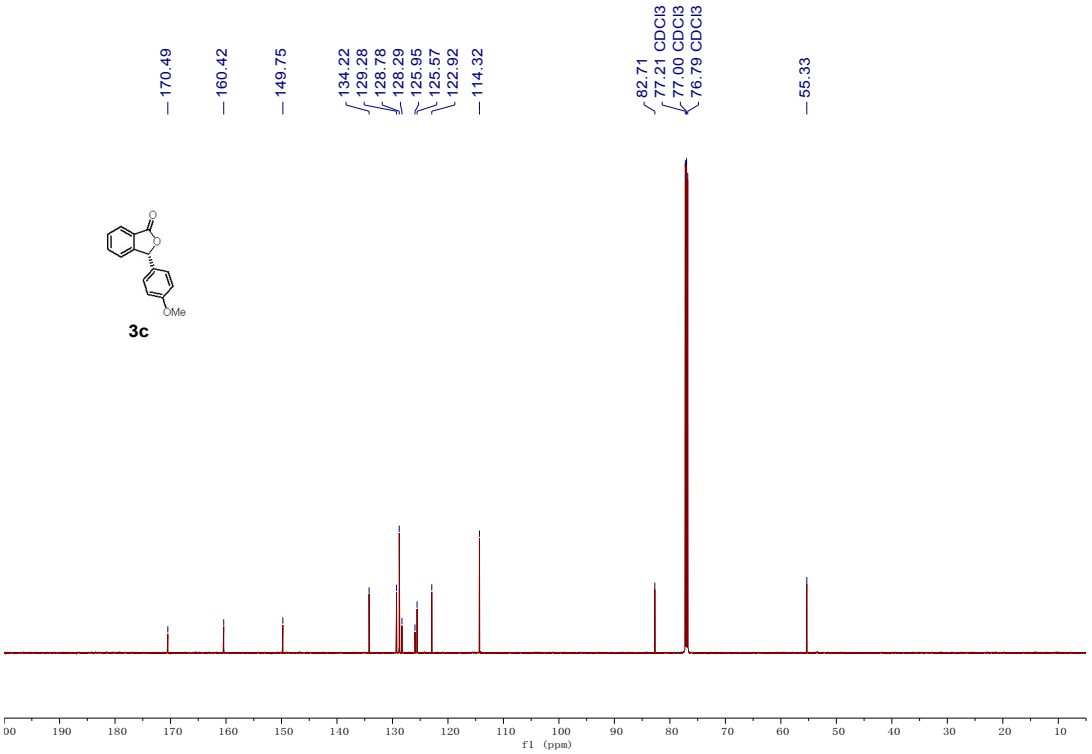
7.31
7.26 CDCl3
7.18
7.17
6.90
6.89
6.37
3.81
1.57 HDO
0.00
OMe
3c
0.93
0.98
0.98
0.97
1.95
1.96
0.94
3.00
f1 (ppm)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128.29
125.95
125.57
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82.71
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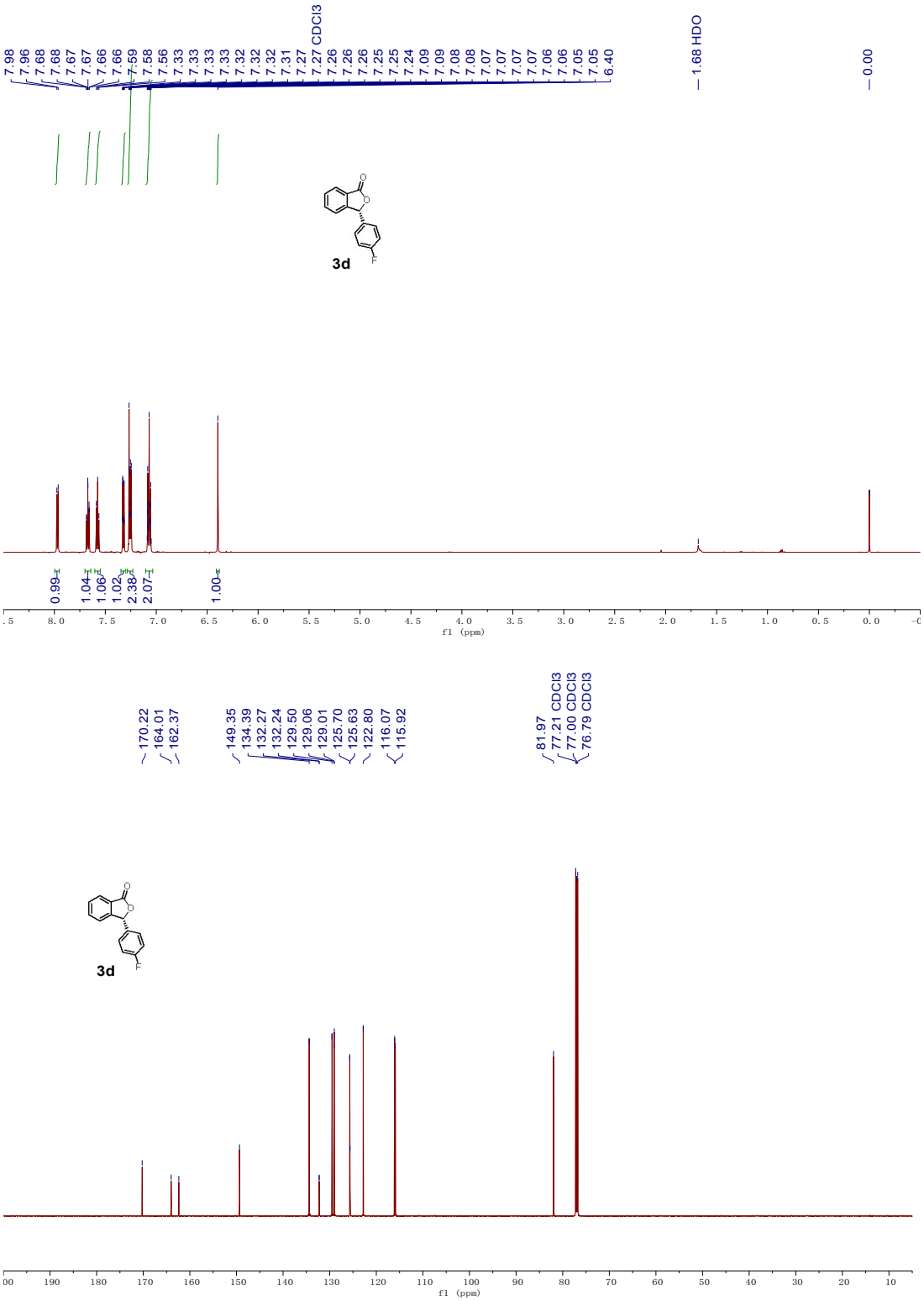
77.00 CDCl3
76.79 CDCl3
55.33
OMe
3c
f1 (ppm)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7.67
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7.66
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7.56
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7.33
7.33
7.32
7.32
7.31
7.27
7.27 CDCl3
7.26
7.26
7.25
7.24
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7.09
7.08
7.08
7.07
7.07
7.07
7.07
7.06
7.06
7.05
7.05
6.40
1.68 HDO
0.00
3d
0.99
1.04
1.06
1.02
2.38
2.07
1.00
f1 (ppm)
170.22
164.01
162.37
149.35
134.39
132.27
132.24
129.50
129.06
129.01
125.70
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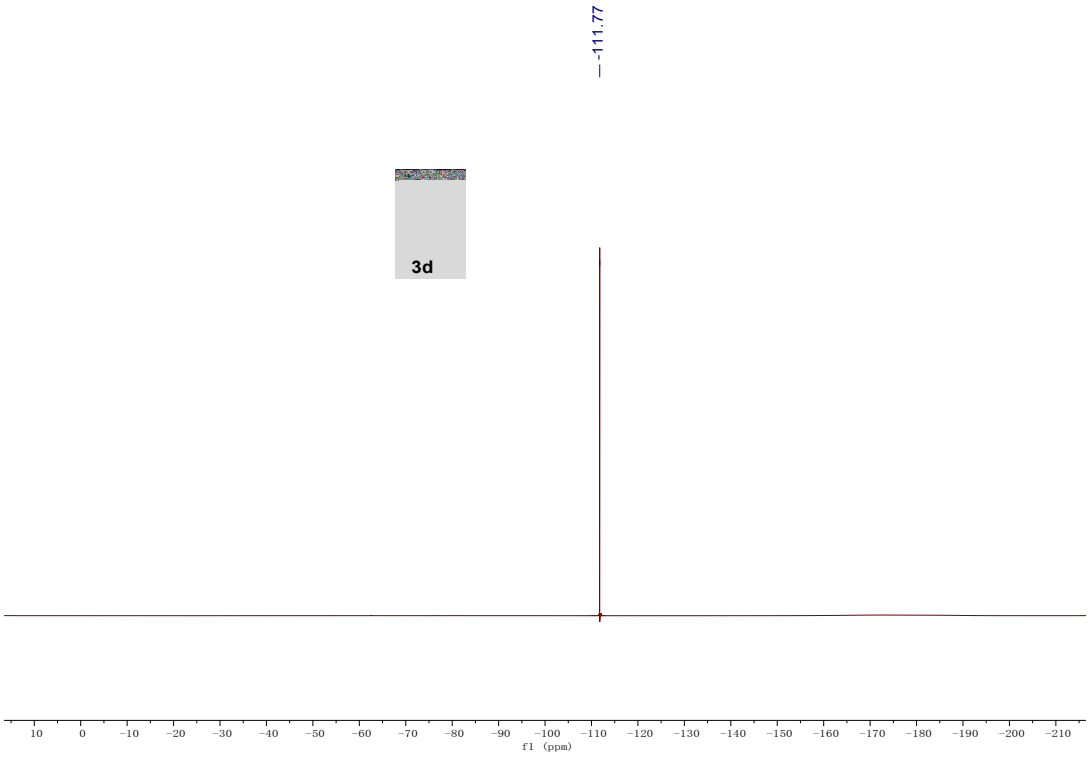
122.80
116.07
115.92
81.97
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
3d
f1 (ppm)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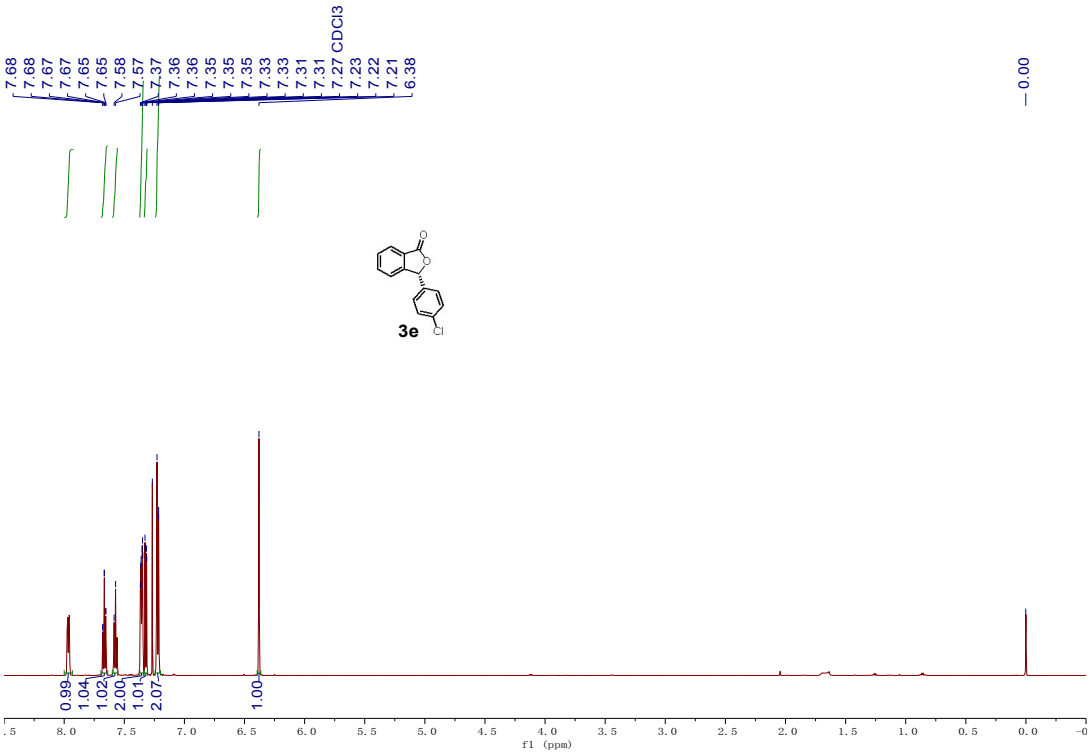
3d
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)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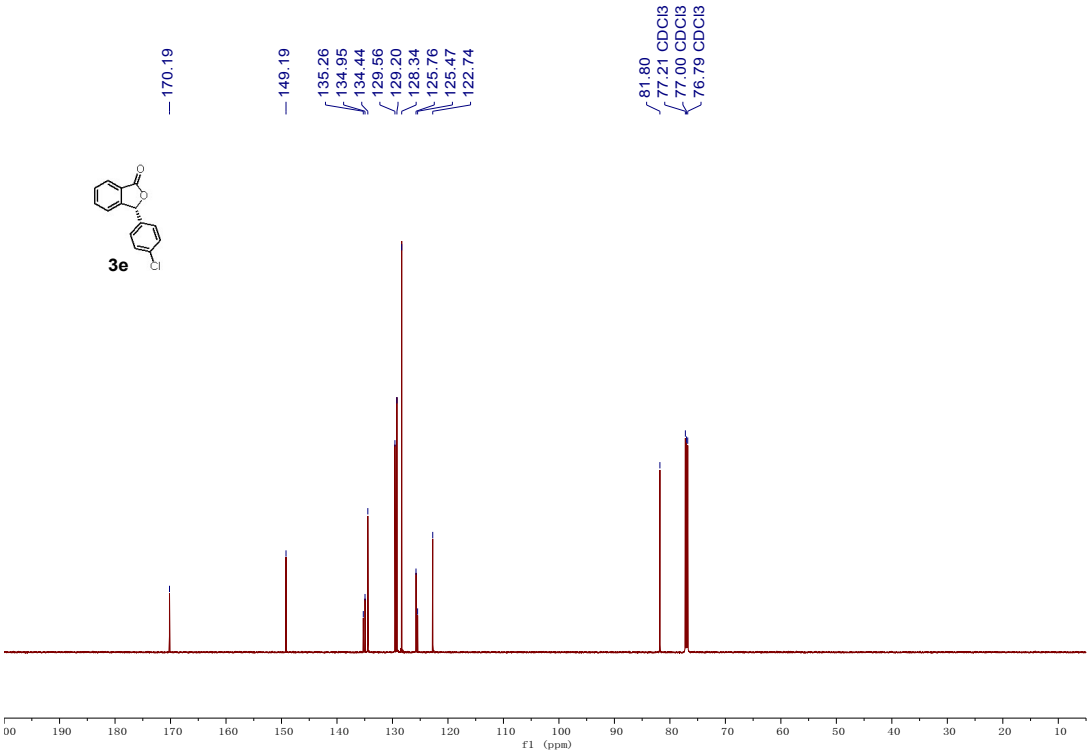
7.35
7.33
7.33
7.31
7.31
7.27 CDCl3
7.23
7.22
7.21
6.38
0.00
3e
Cl
0.99
1.04
1.02
2.00
1.01
2.07
1.00
f1 (ppm)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129.20
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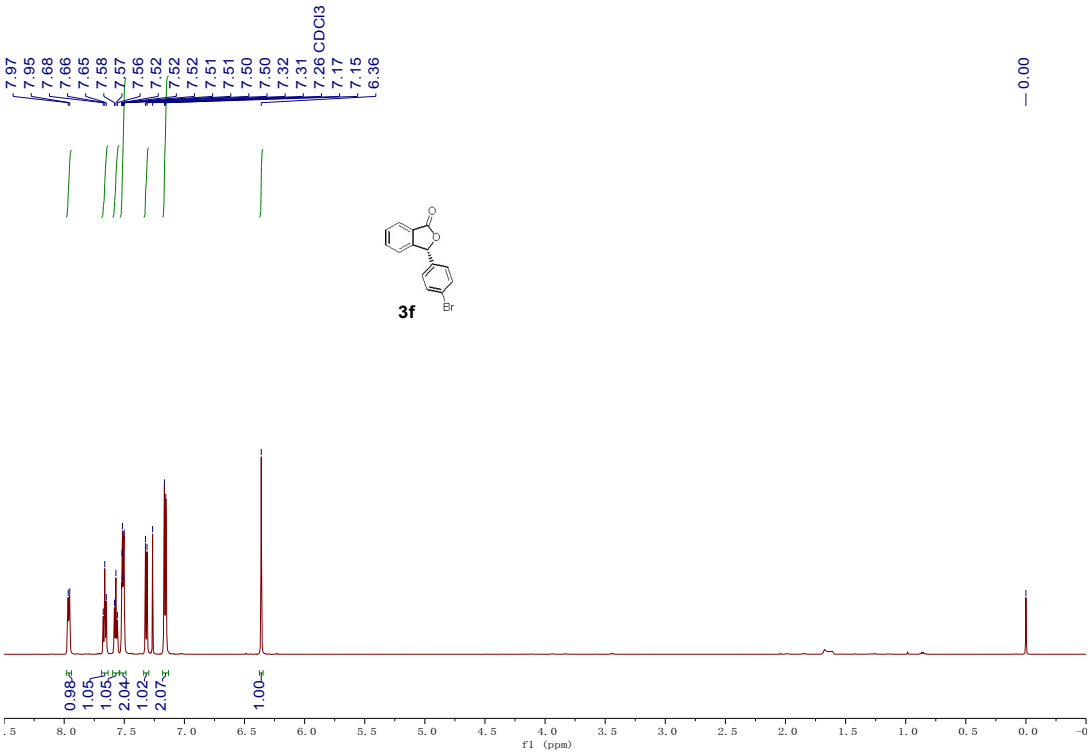
122.74
81.80
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
3e
Cl
f1 (ppm)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7.57
7.56
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7.52
7.51
7.51
7.50
7.50
7.32
7.31
7.26 CDCl3
7.17
7.15
6.36
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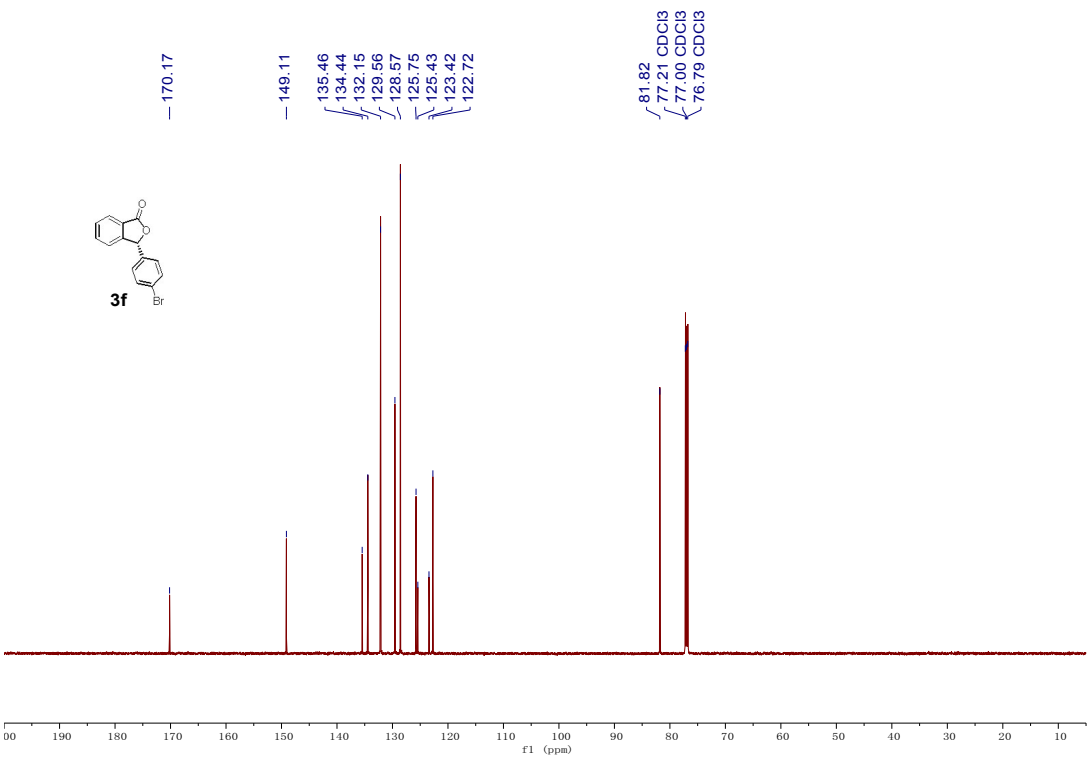
Br
0.98
1.05
1.05
2.04
1.02
2.07
1.00
f1 (ppm)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129.56
128.57
125.75
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81.82
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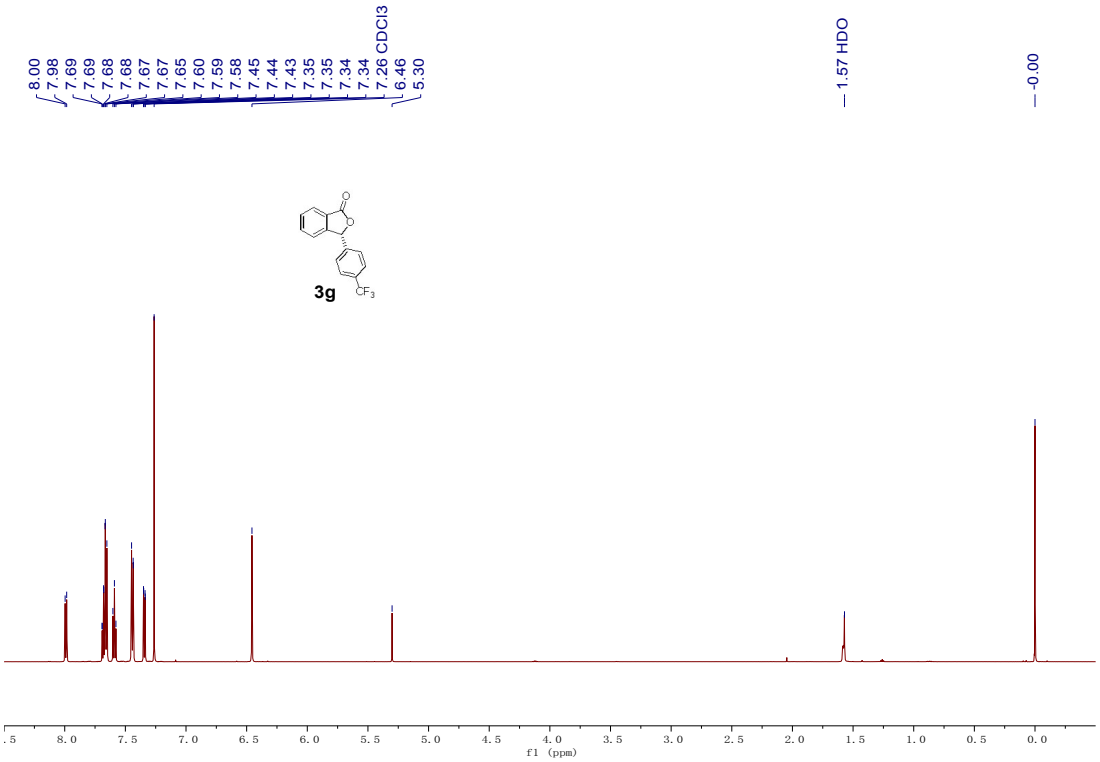
77.00 CDCl3
76.79 CDCl3
3f
Br
f1 (ppm)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7.68
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7.67
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7.59
7.58
7.45
7.44
7.43
7.35
7.35
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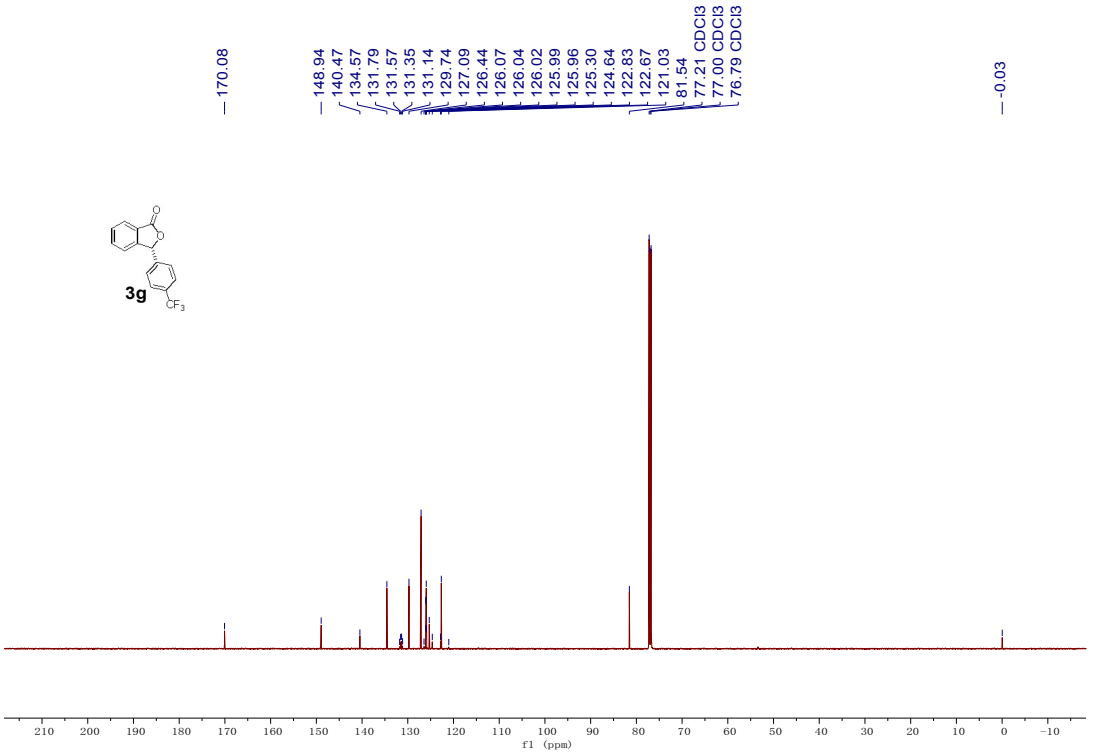
7.34
7.26 CDCl3
6.46
5.30
1.57 HDO
0.00
3g
f1 (ppm)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125.96
125.30
124.64
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121.03
81.54
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77.00 CDCl3
76.79 CDCl3
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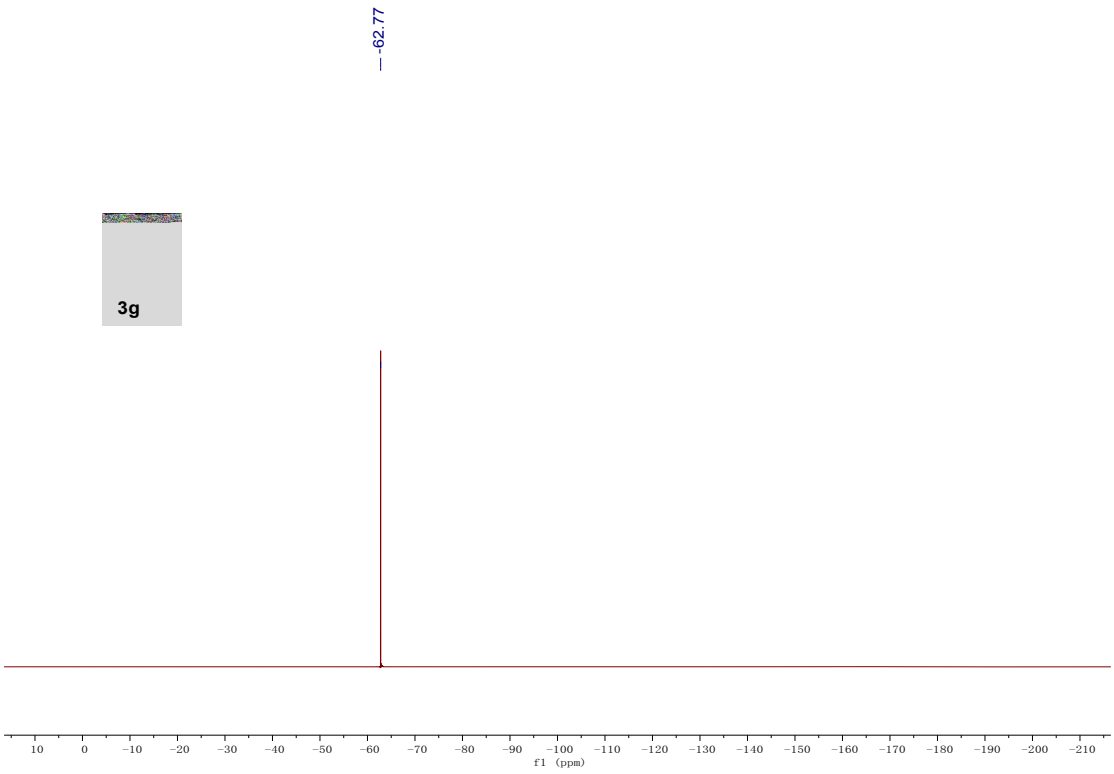
f1 (ppm)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-60
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-200
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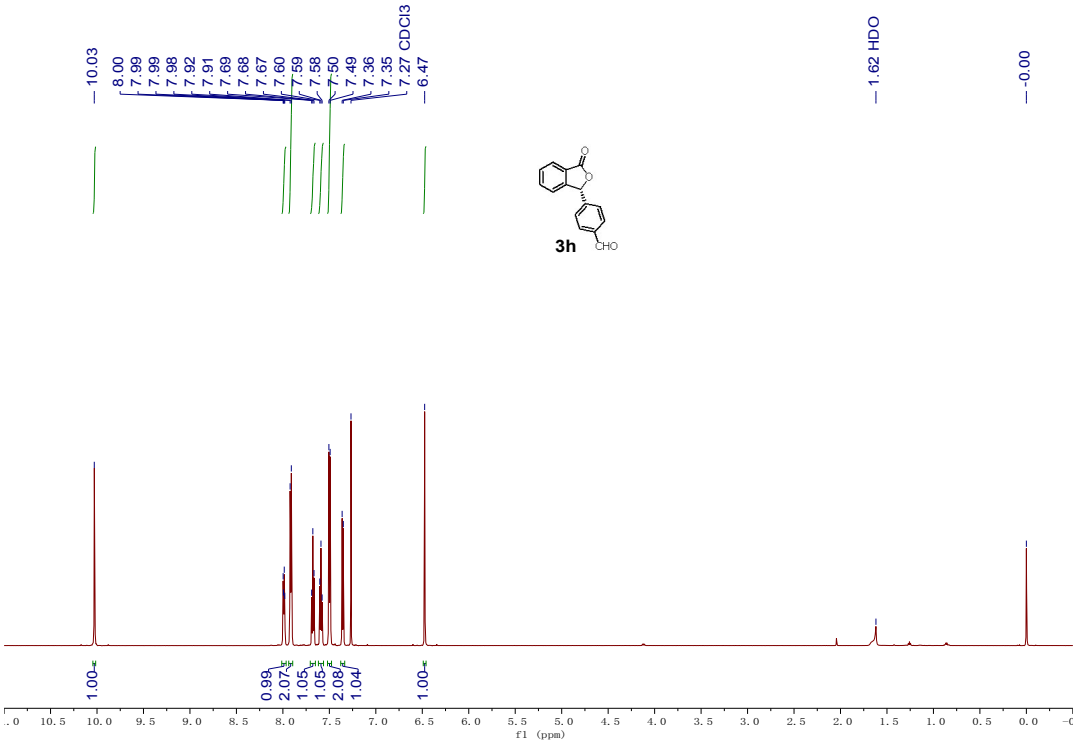
f1 (ppm)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7.91
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7.67
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7.58
7.50
7.49
7.36
7.35
7.27 CDCl3
6.47
1.62 HDO
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CHO
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2.08
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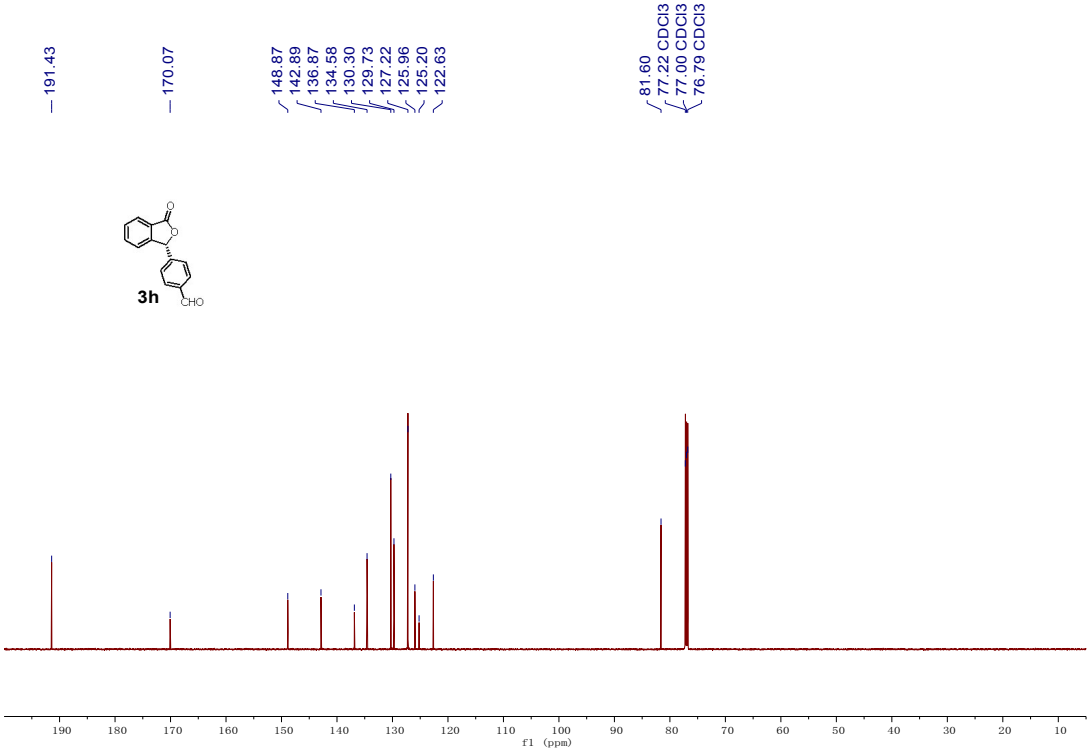
1.00
f1 (ppm)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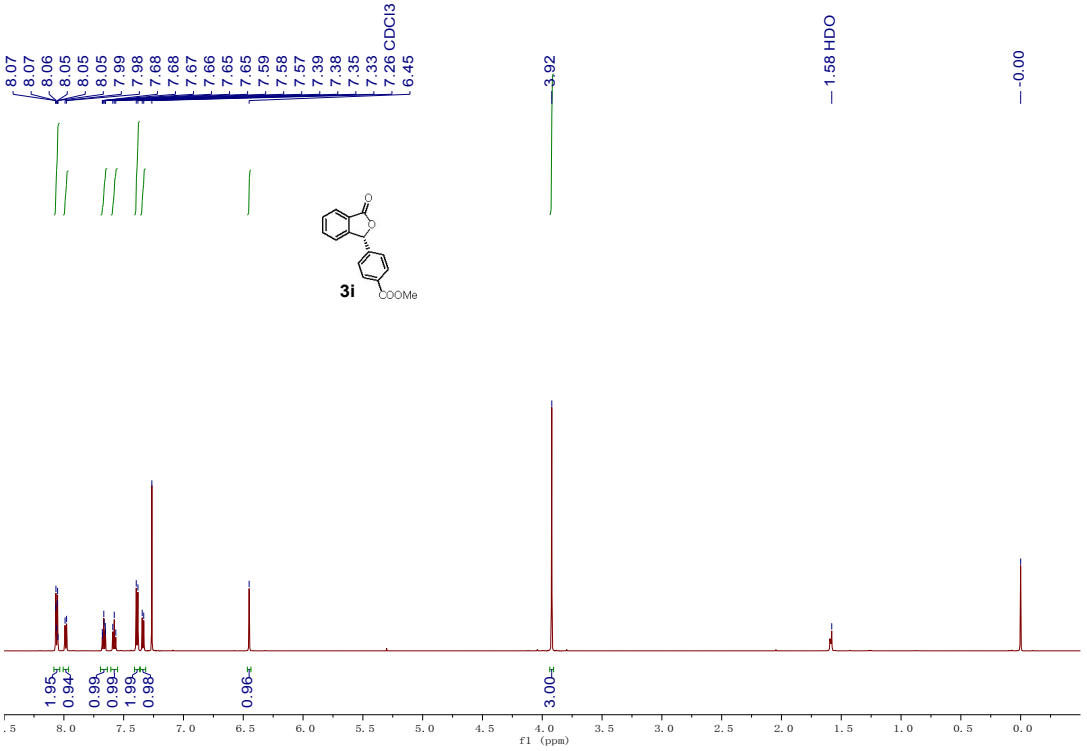
76.79 CDCl3
3h
CHO
f1 (ppm)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8.06
8.05
8.05
8.05
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7.98
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7.68
7.67
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7.65
7.59
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7.57
7.39
7.38
7.35
7.33
7.26 CDCl3
6.45
3.92
1.58 HDO
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COOMe
1.95
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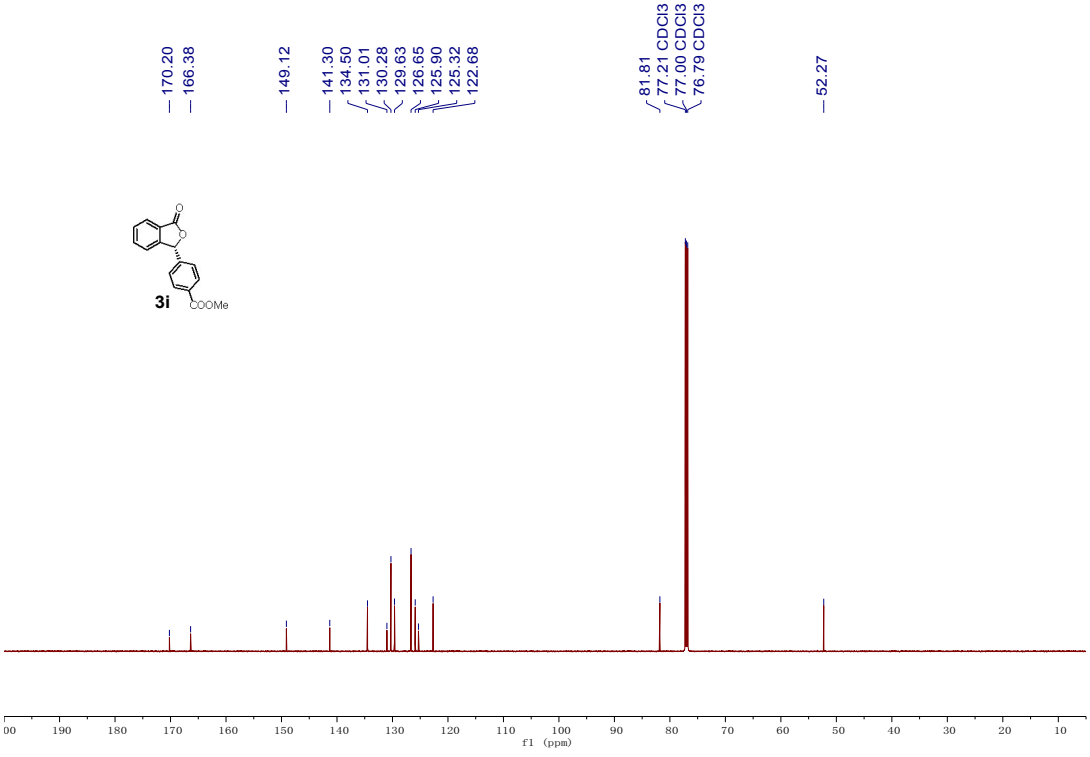
0.99
0.99
1.99
0.98
0.96
3.00
f1 (ppm)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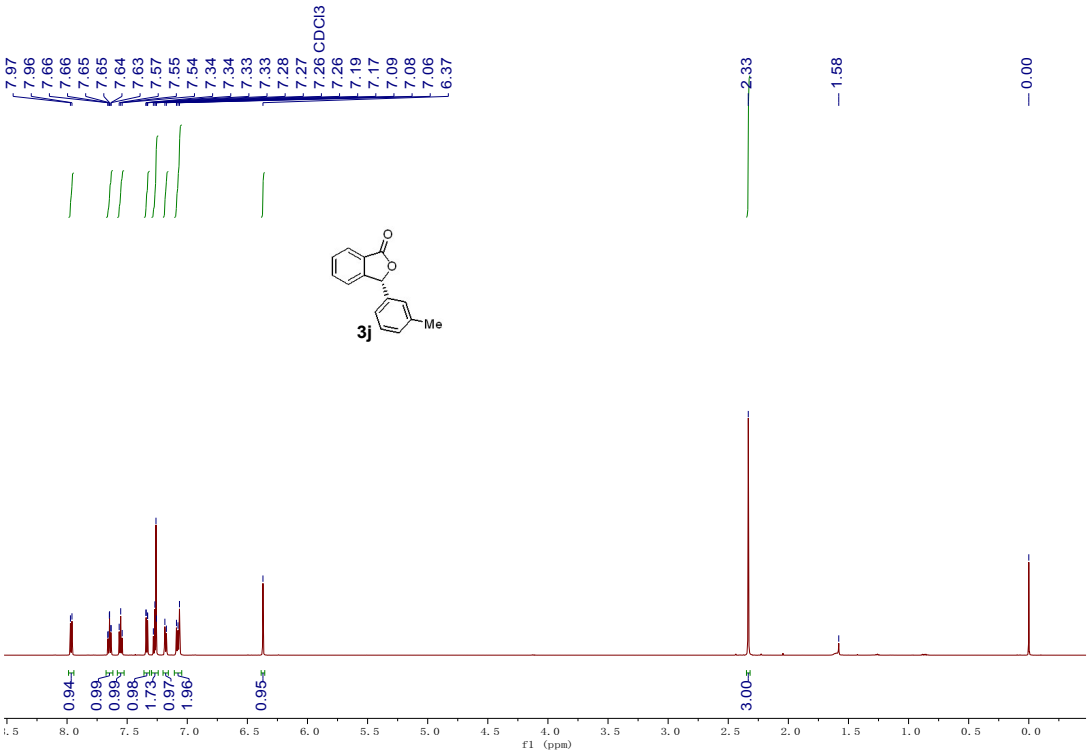
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
52.27
3i
COOMe
f1 (ppm)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7.34
7.33
7.33
7.28
7.27
7.26 CDCl3
7.26
7.19
7.17
7.09
7.08
7.06
6.37
2.33
1.58
0.00
Me
3j
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0.99
0.99
0.98
1.73
0.97
1.96
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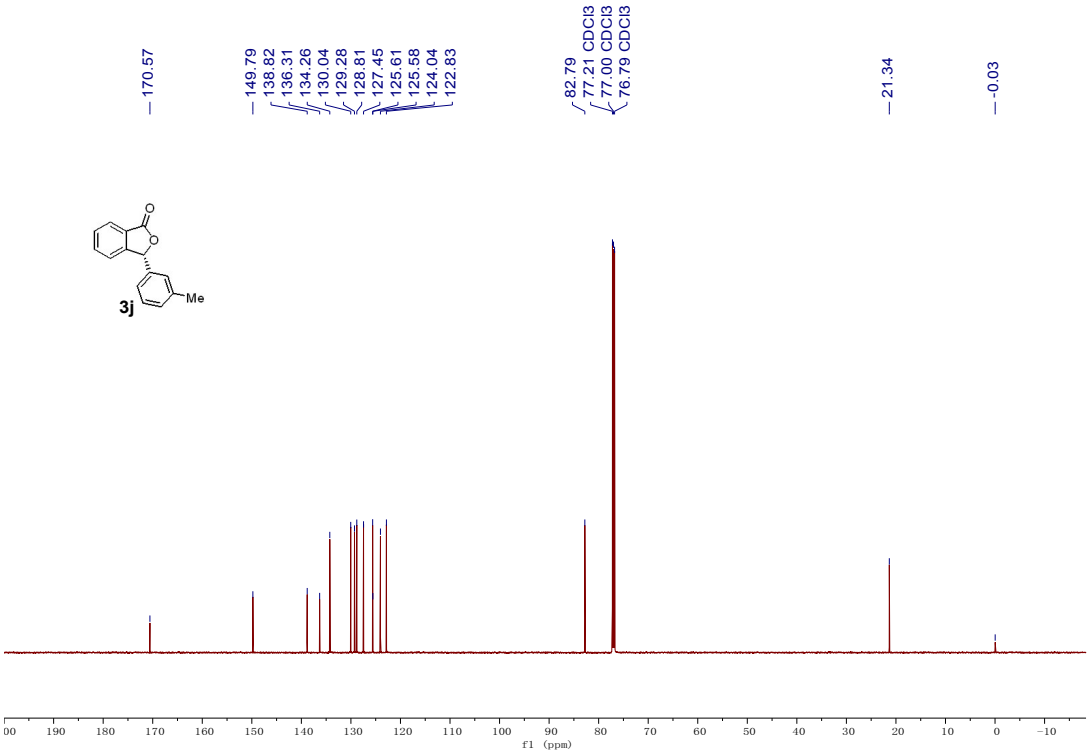
3.00
f1 (ppm)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76.79 CDCl3
21.34
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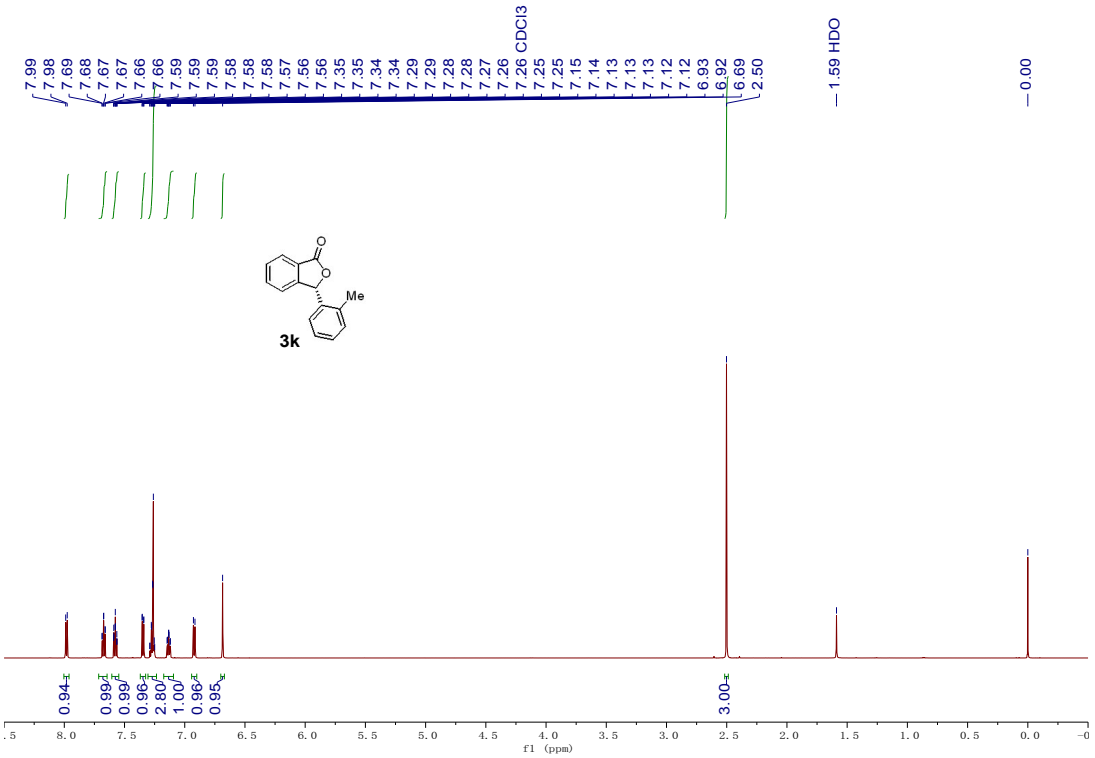
Me
3j
f1 (ppm)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7.26 CDCl3
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7.15
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7.13
7.13
7.12
7.12
6.93
6.92
6.69
2.50
1.59 HDO
0.00
O
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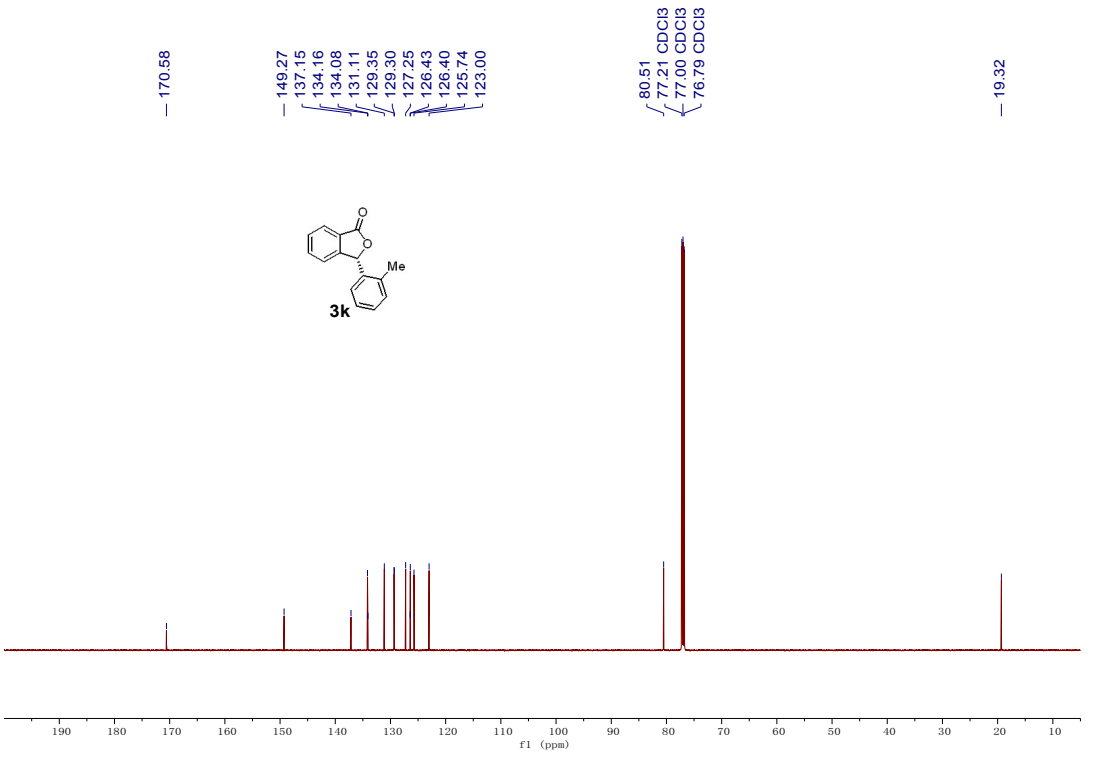
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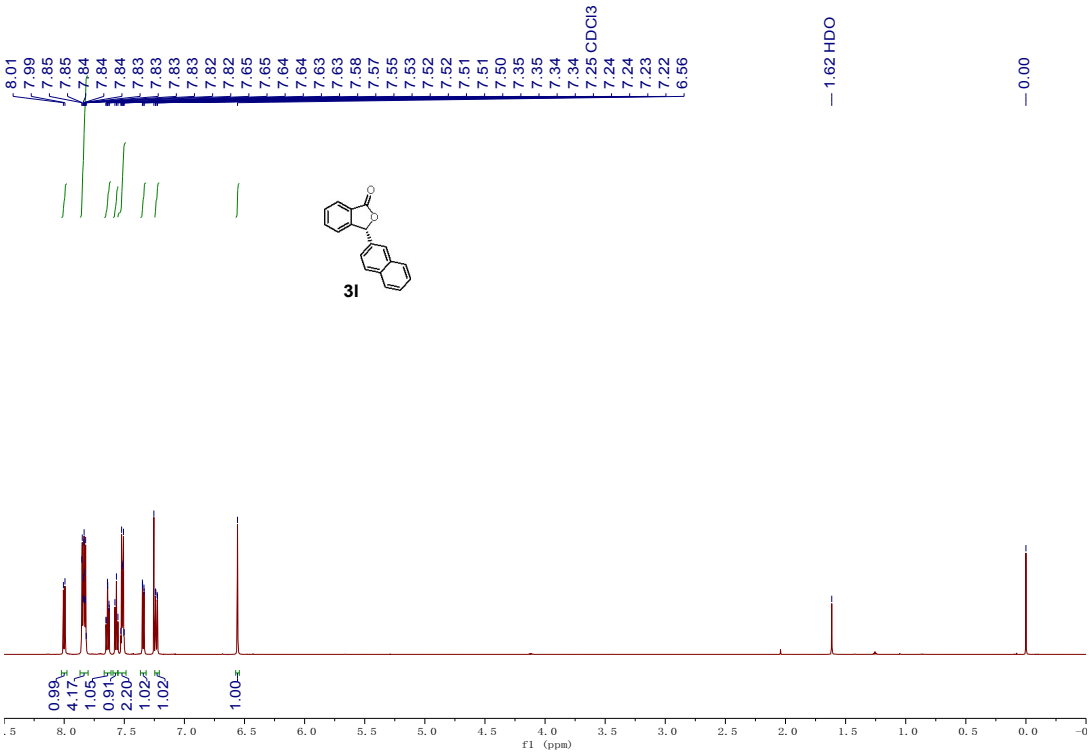
76.79 CDCl3
19.32
O
O
Me
3k
f1 (ppm)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7.34
7.34
7.25 CDCl3
7.24
7.24
7.23
7.22
6.56
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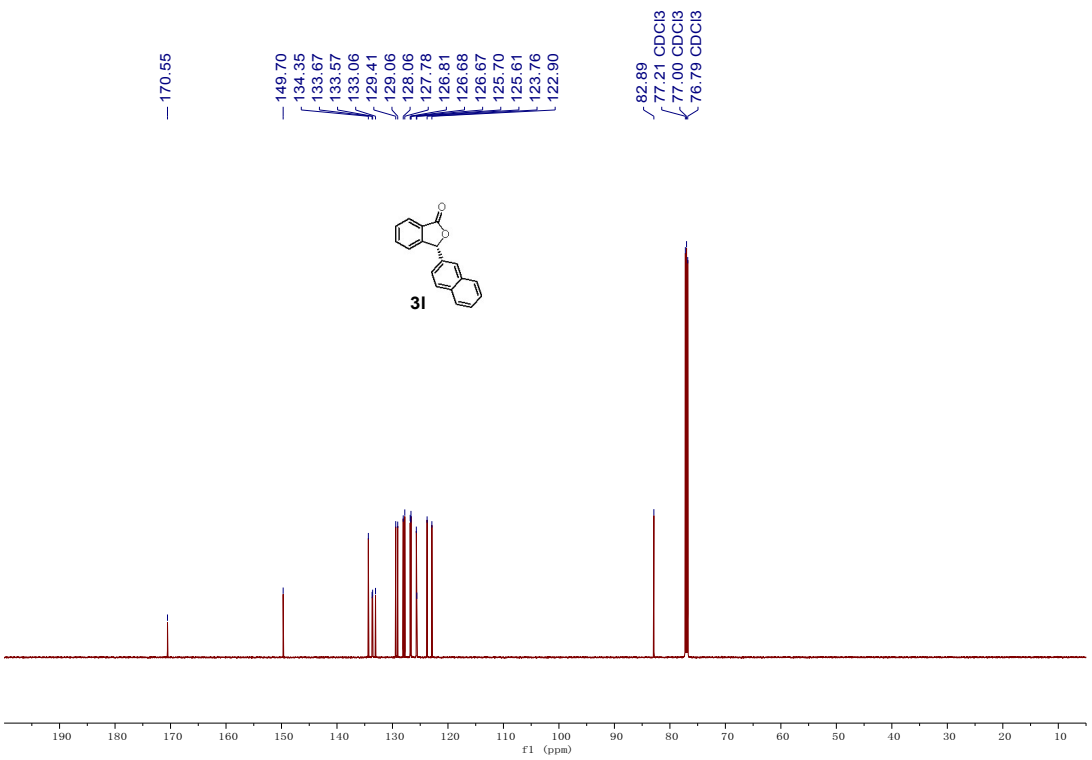
1.02
1.02
1.00
f1 (ppm)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126.67
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122.90
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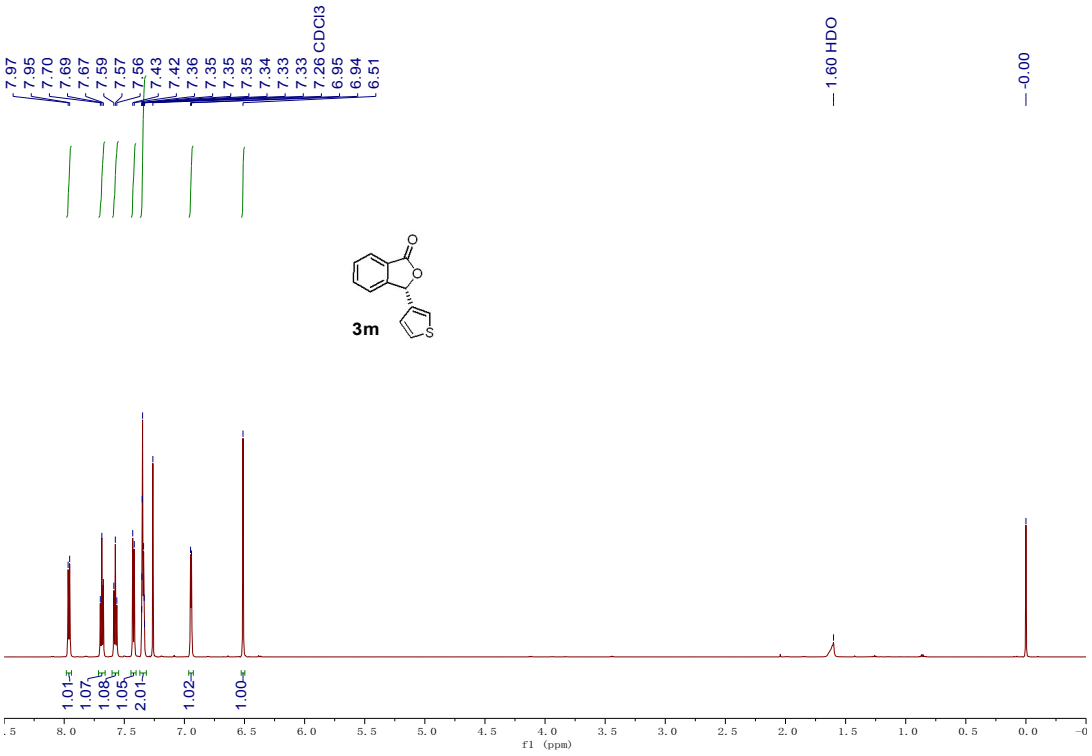
77.00 CDCl3
76.79 CDCl3
3l
f1 (ppm)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7.35
7.34
7.33
7.33
7.26 CDCl3
6.95
6.94
6.51
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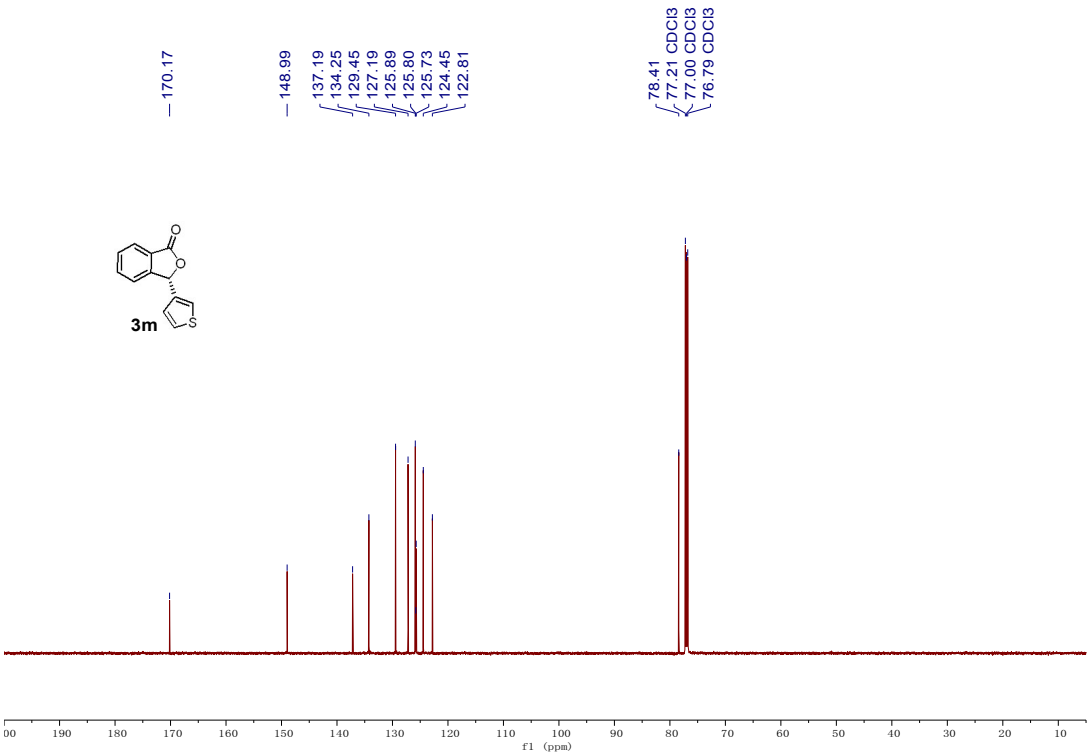
3m
1.01
1.07
1.08
1.05
2.01
1.02
1.00
f1 (ppm)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127.19
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125.73
124.45
122.81
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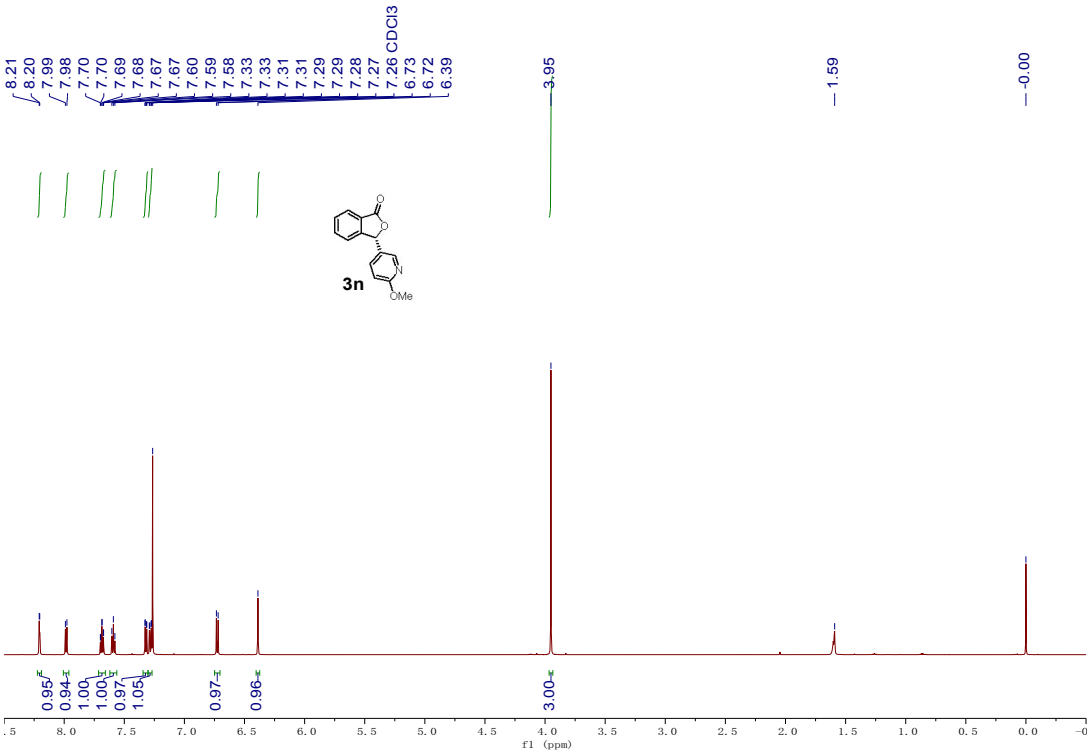
77.00 CDCl3
76.79 CDCl3
3m
f1 (ppm)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7.29
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7.28
7.27
7.26 CDCl3
6.73
6.72
6.39
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1.59
0.00
3n
0.95
0.94
1.00
1.00
0.97
1.05
0.97
0.96
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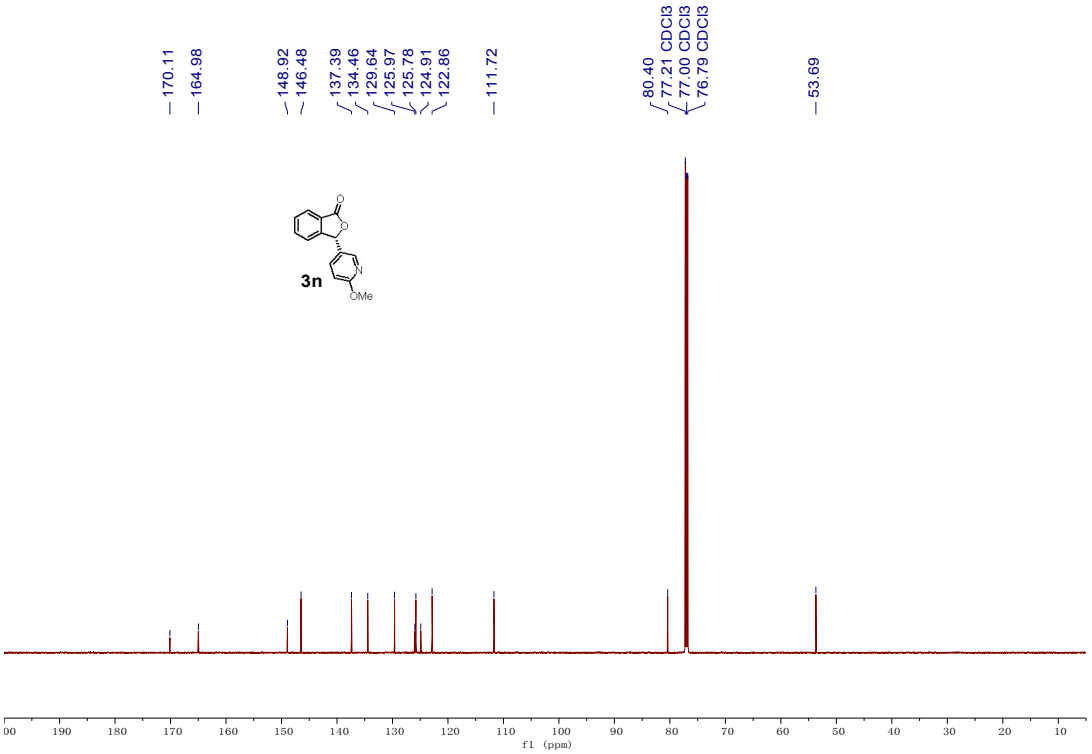
f1 (ppm)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76.79 CDCl3
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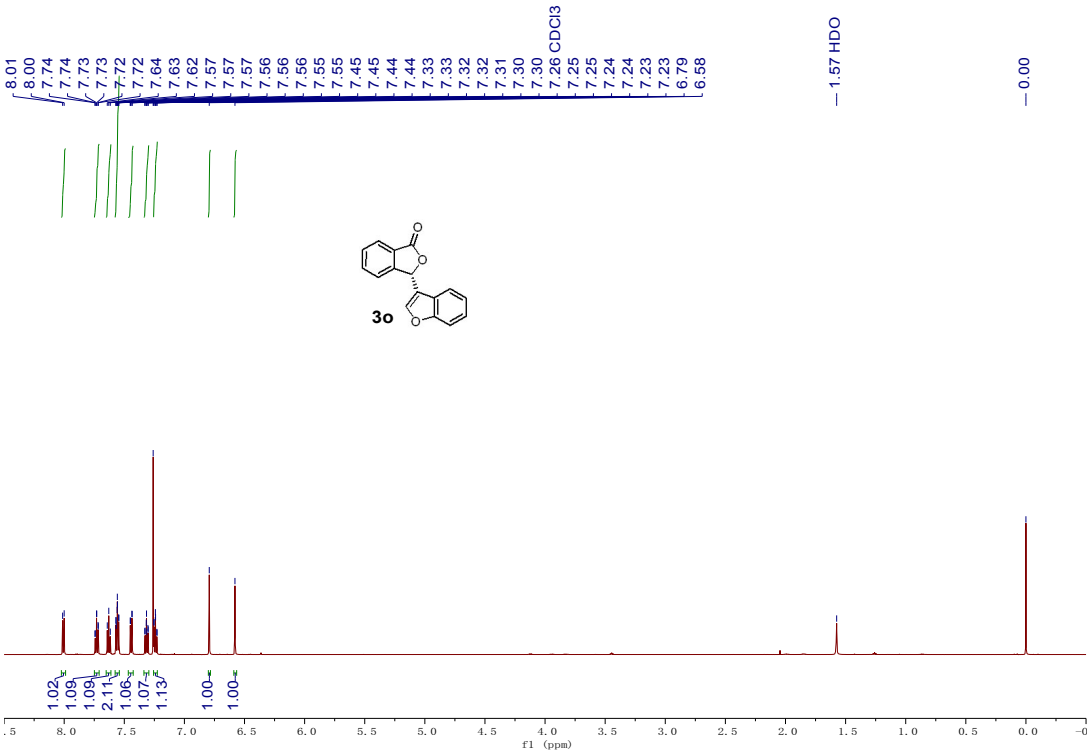
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7.24
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7.23
7.23
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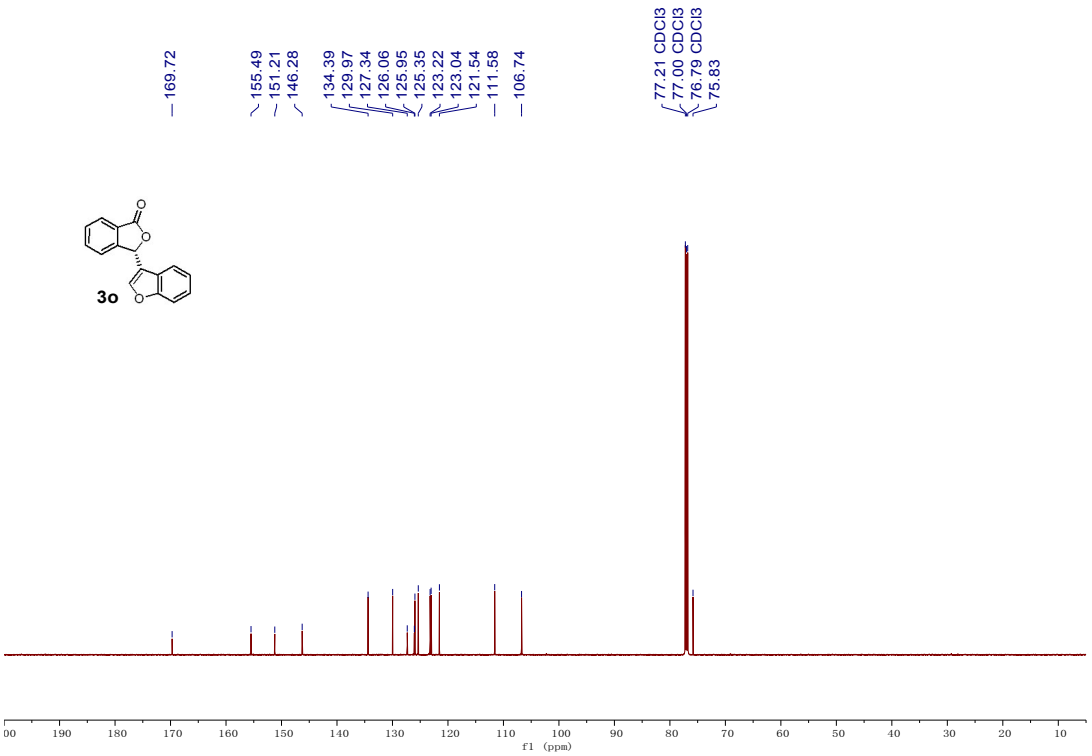
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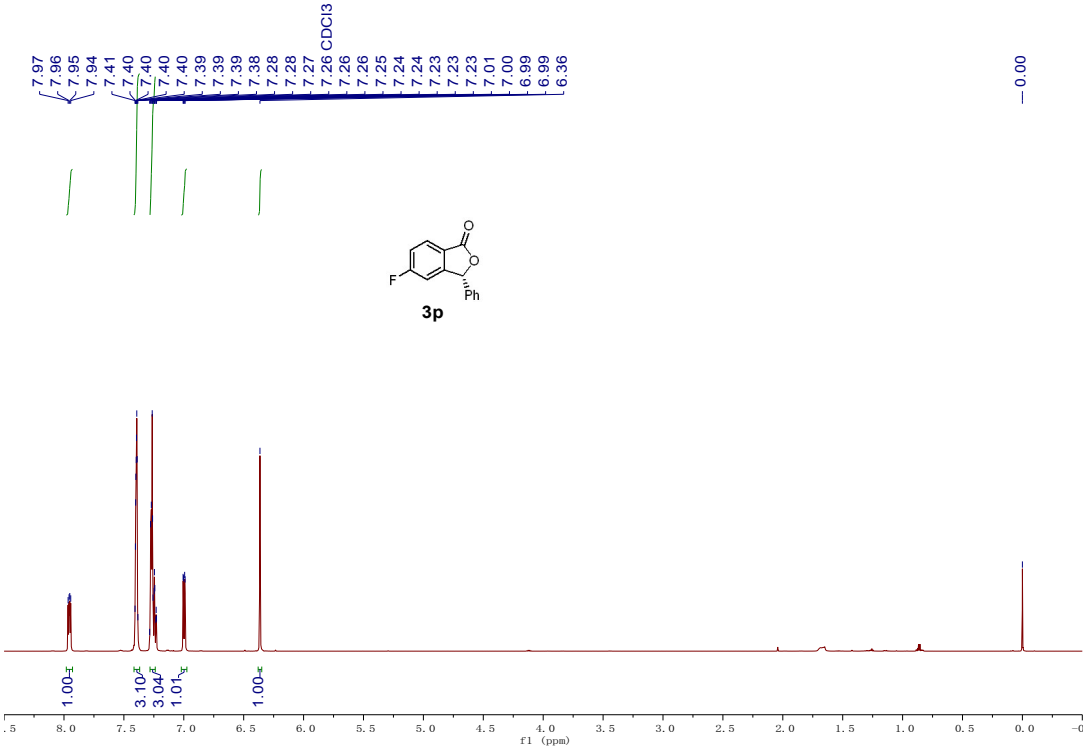
f1 (ppm)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7.28
7.27
7.26 CDCl3
7.26
7.26
7.25
7.24
7.24
7.23
7.23
7.23
7.01
7.00
6.99
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O
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Ph
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3.04
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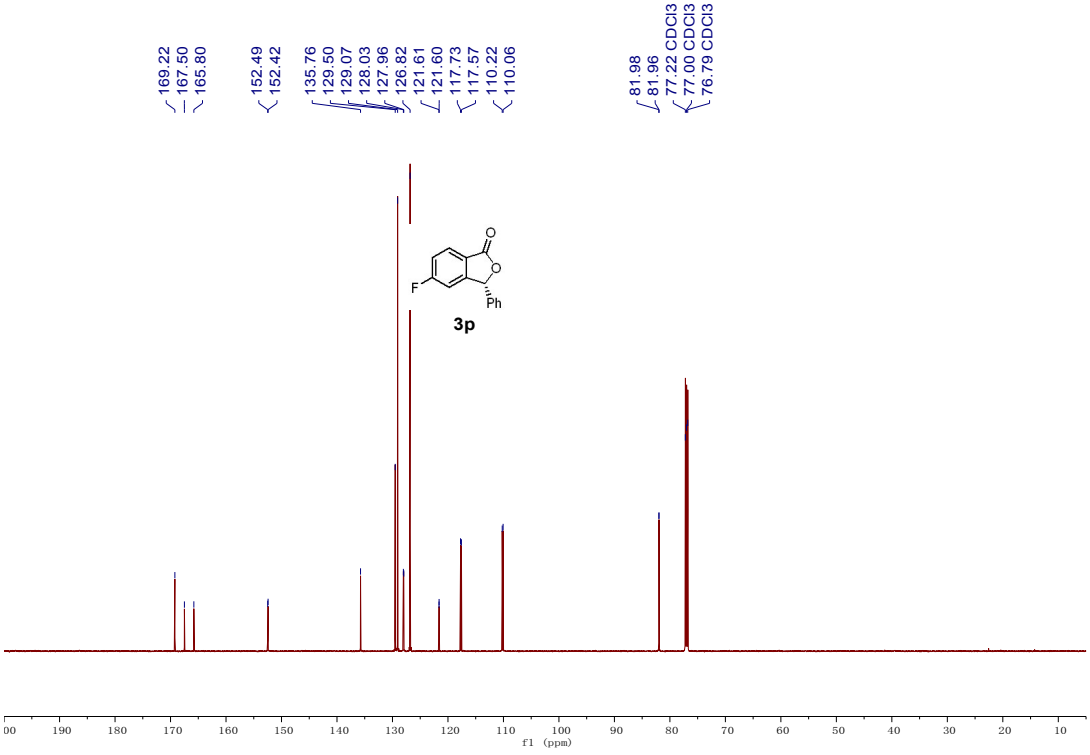
1.00
f1 (ppm)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117.73
117.57
110.22
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Ph
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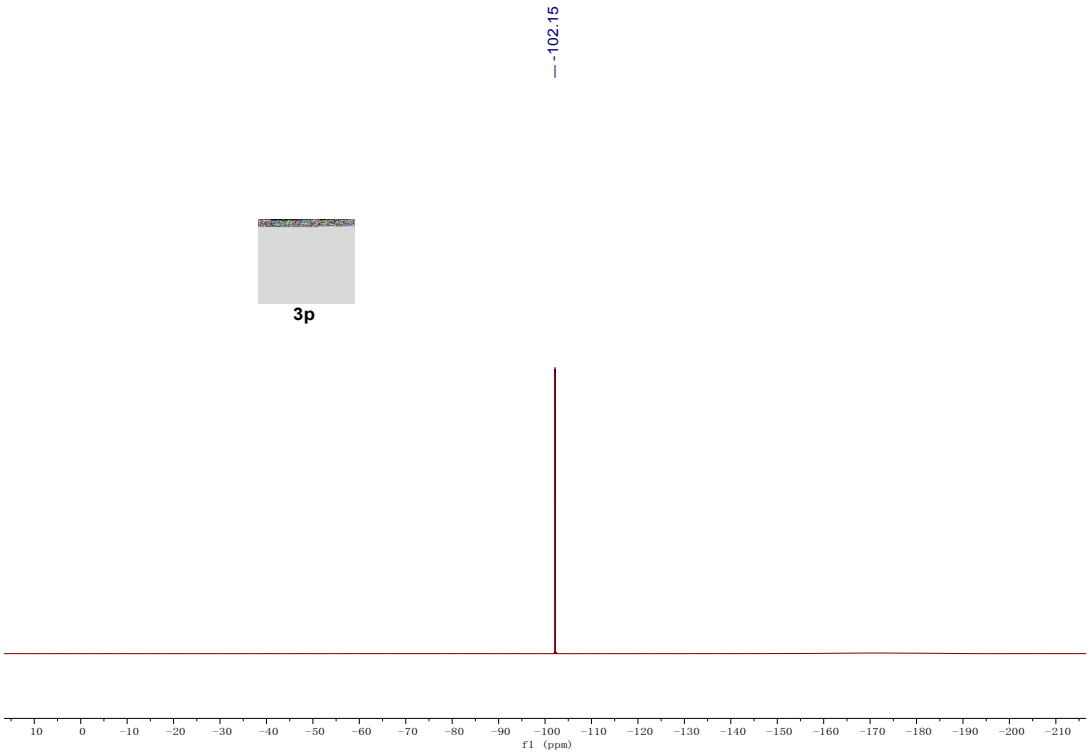
f1 (ppm)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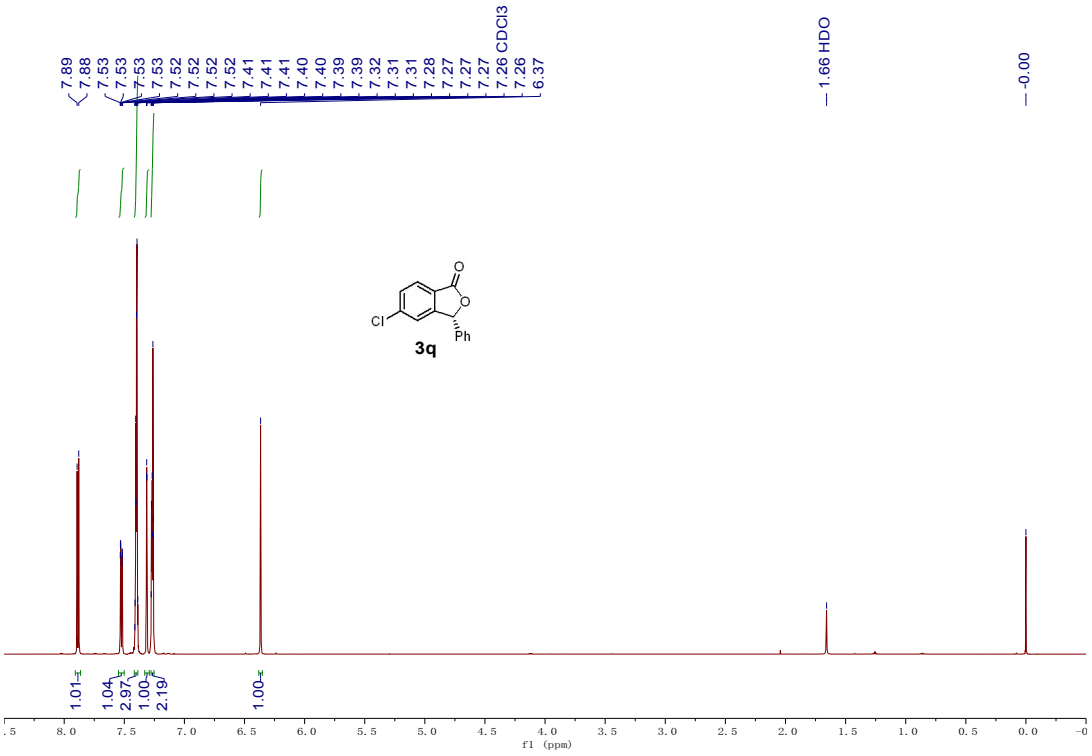
f1 (ppm)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7.27
7.27
7.27
7.26 CDCl3
7.26
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O
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Ph
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1.04
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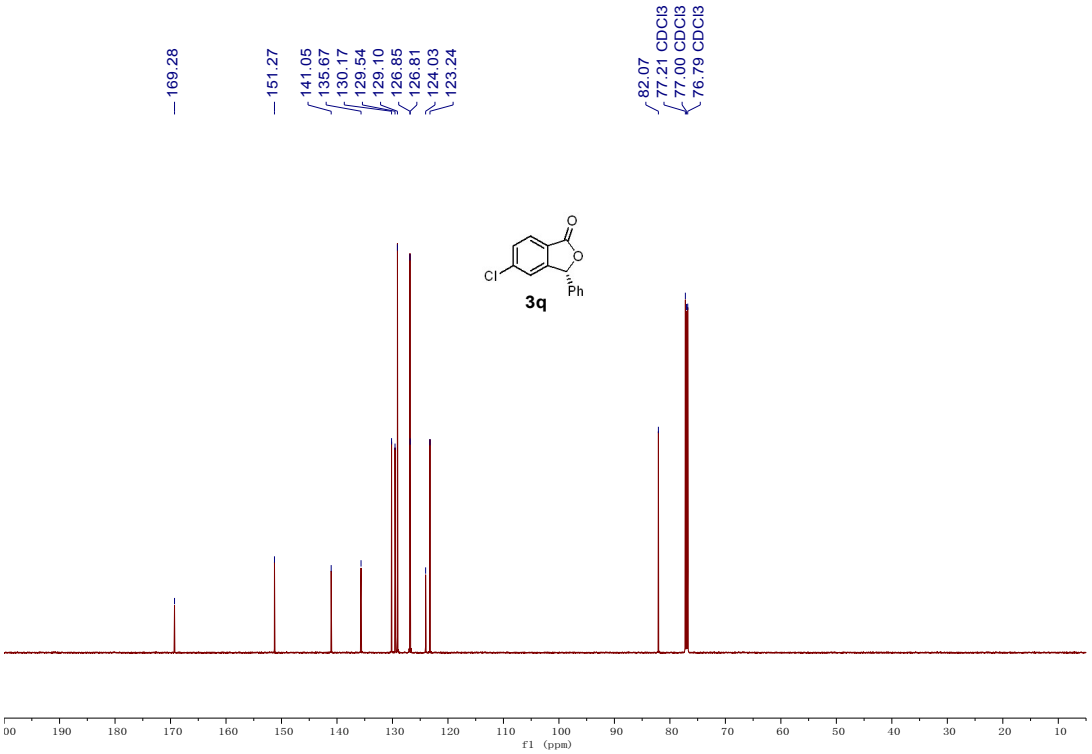
1.00
f1 (ppm)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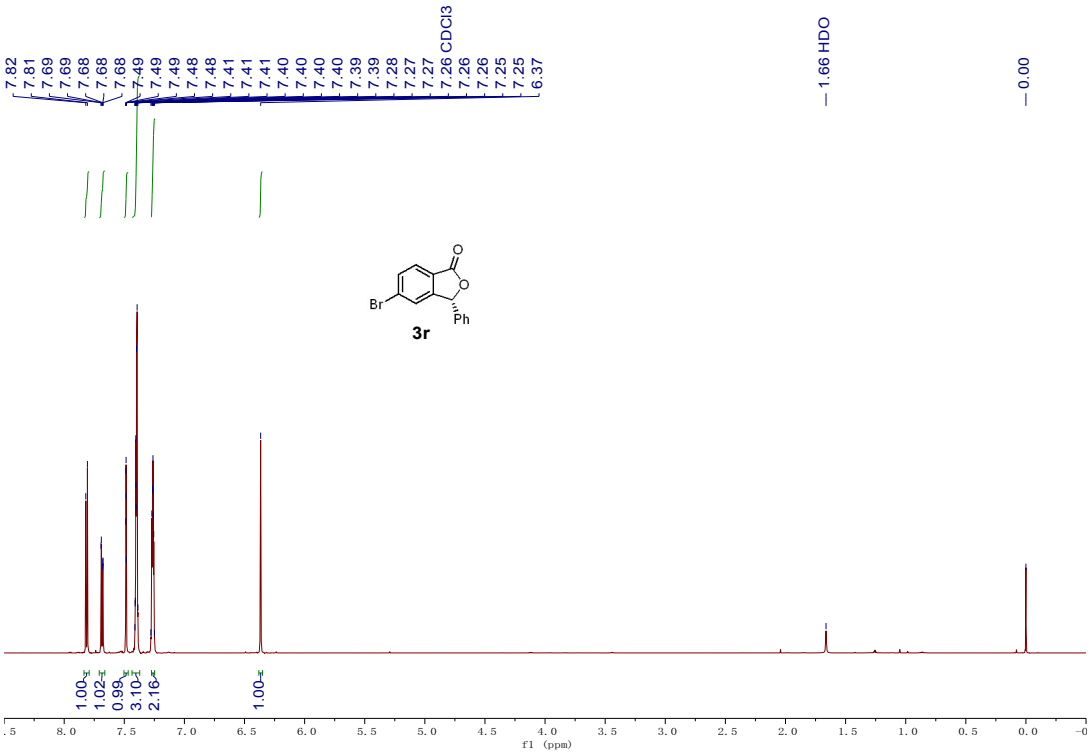
77.00 CDCl3
76.79 CDCl3
Cl
O
O
Ph
3q
f1 (ppm)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6.37
1.66 HDO
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O
Ph
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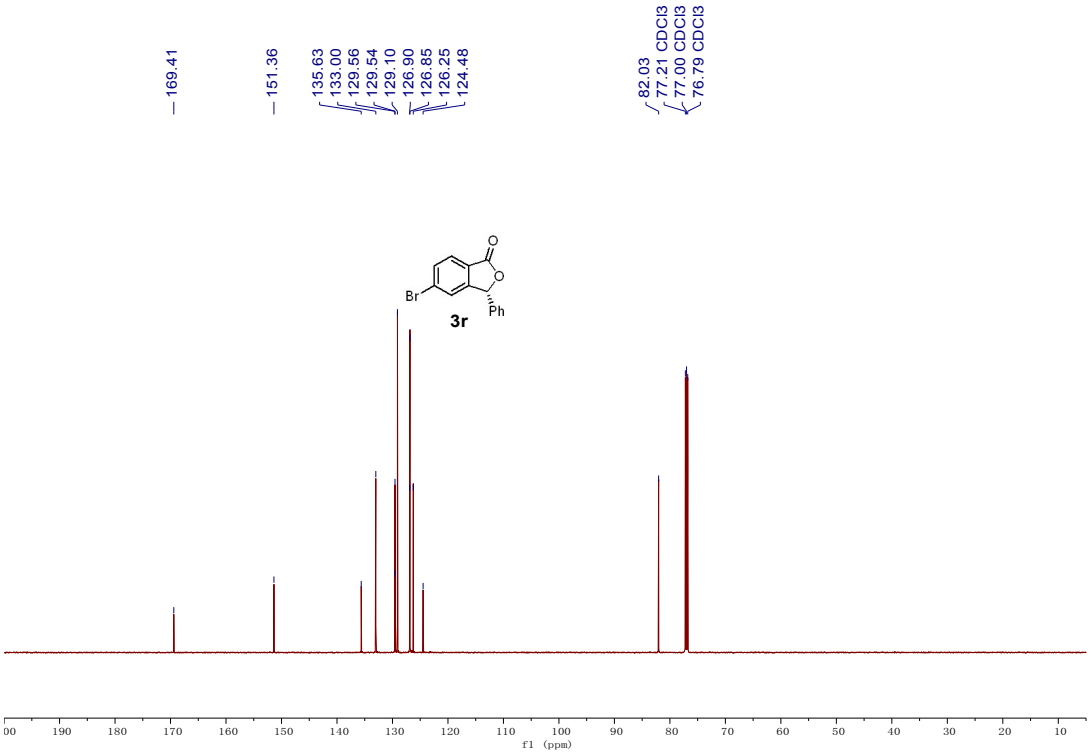
1.00
f1 (ppm)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Br
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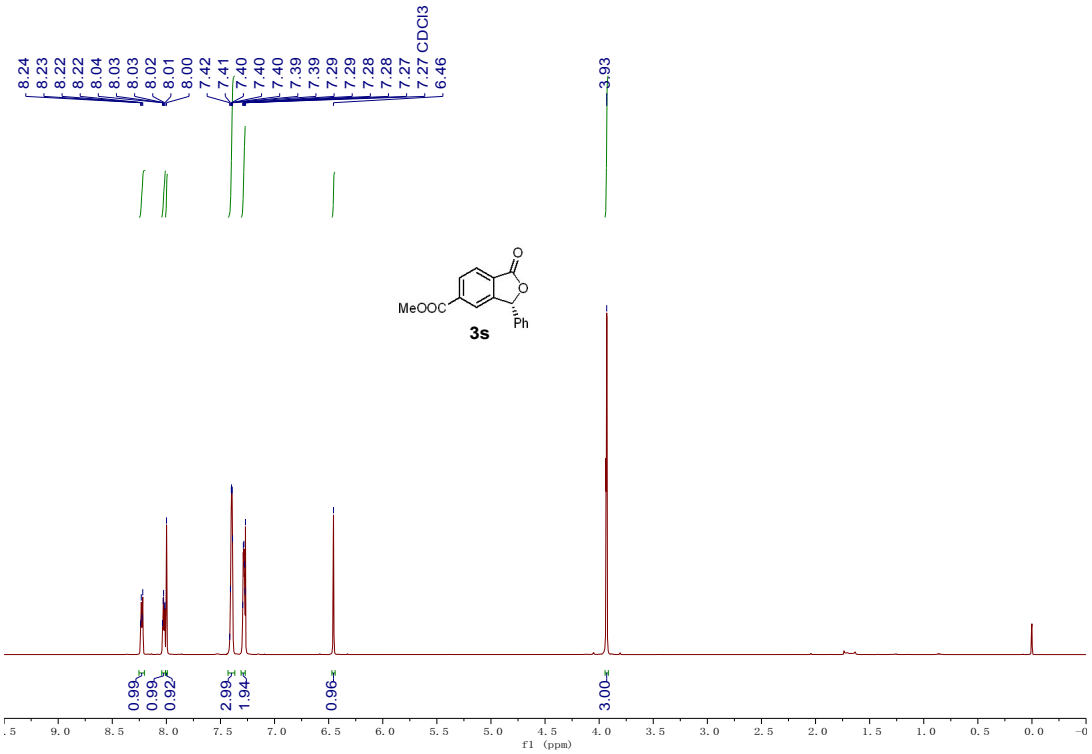
O
Ph
3r
f1 (ppm)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7.29
7.28
7.28
7.27
7.27 CDCl3
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Ph
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0.99
0.92
2.99
1.94
0.96
3.00
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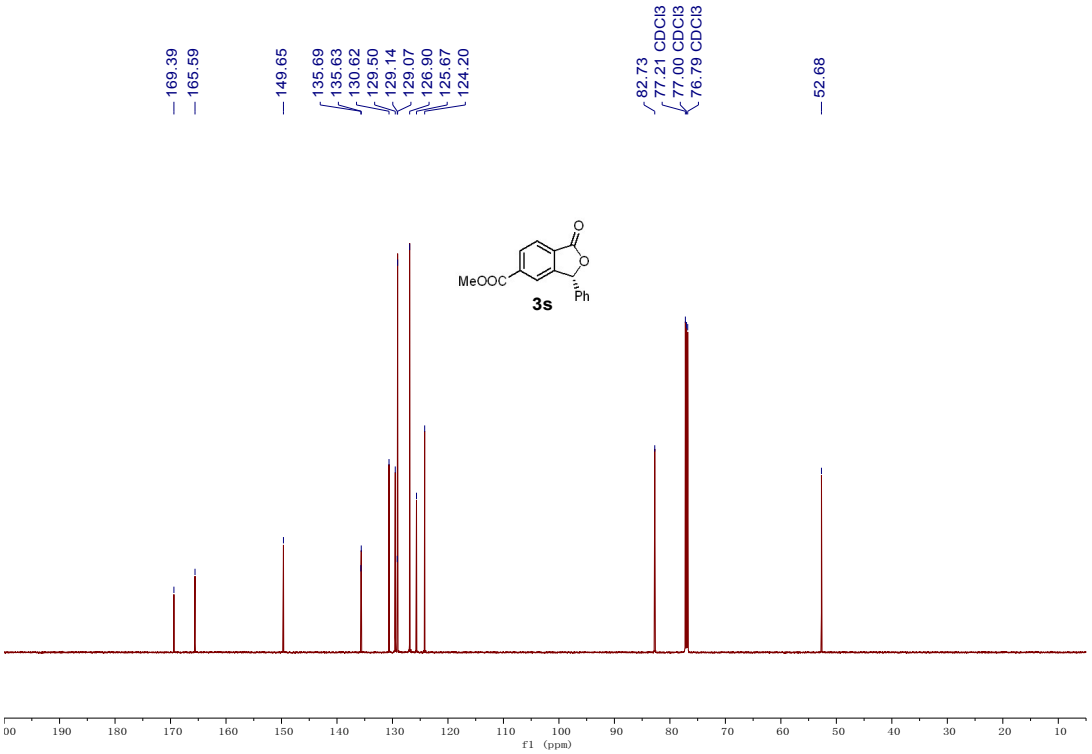
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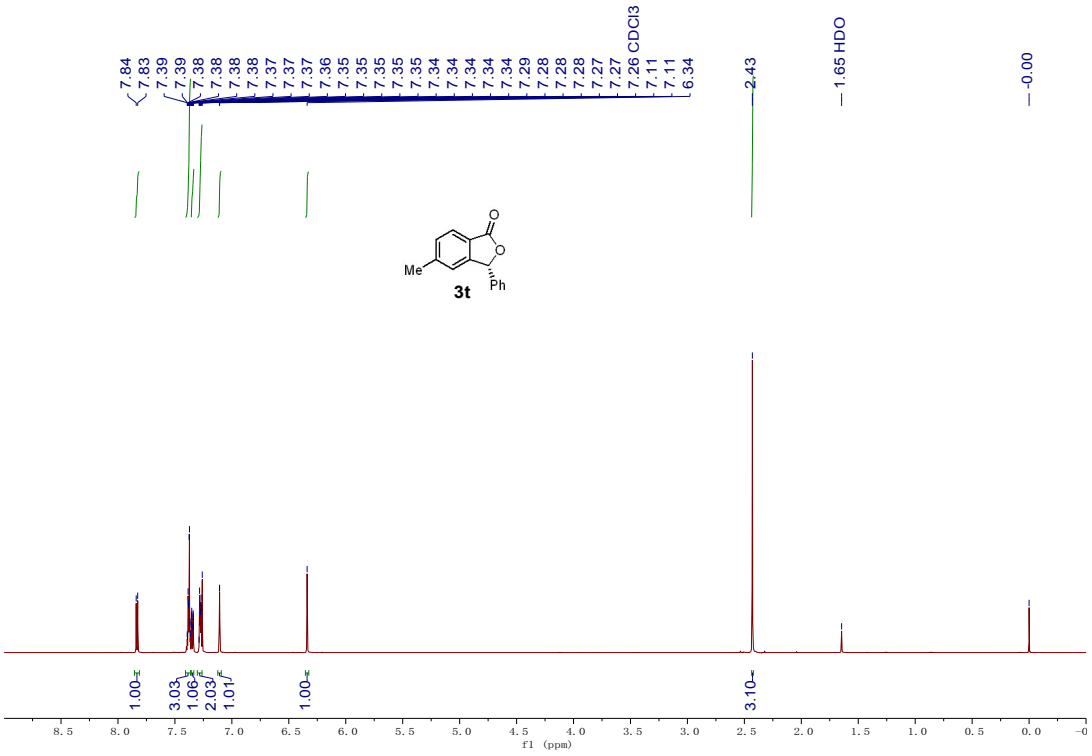
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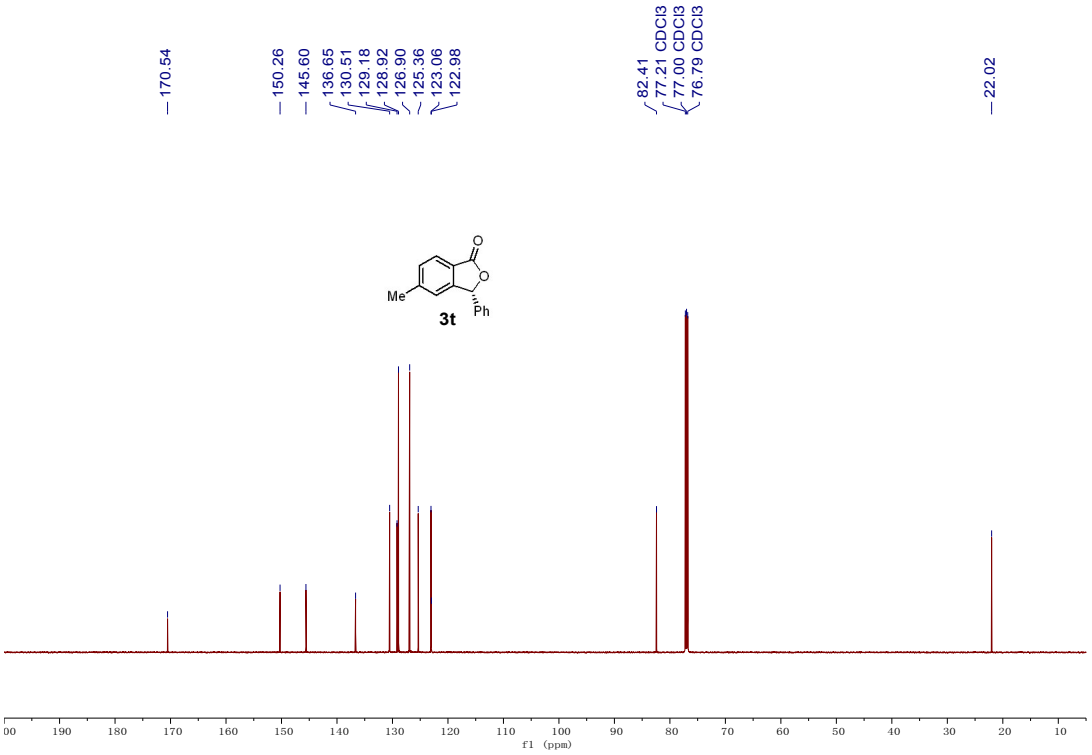
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3t
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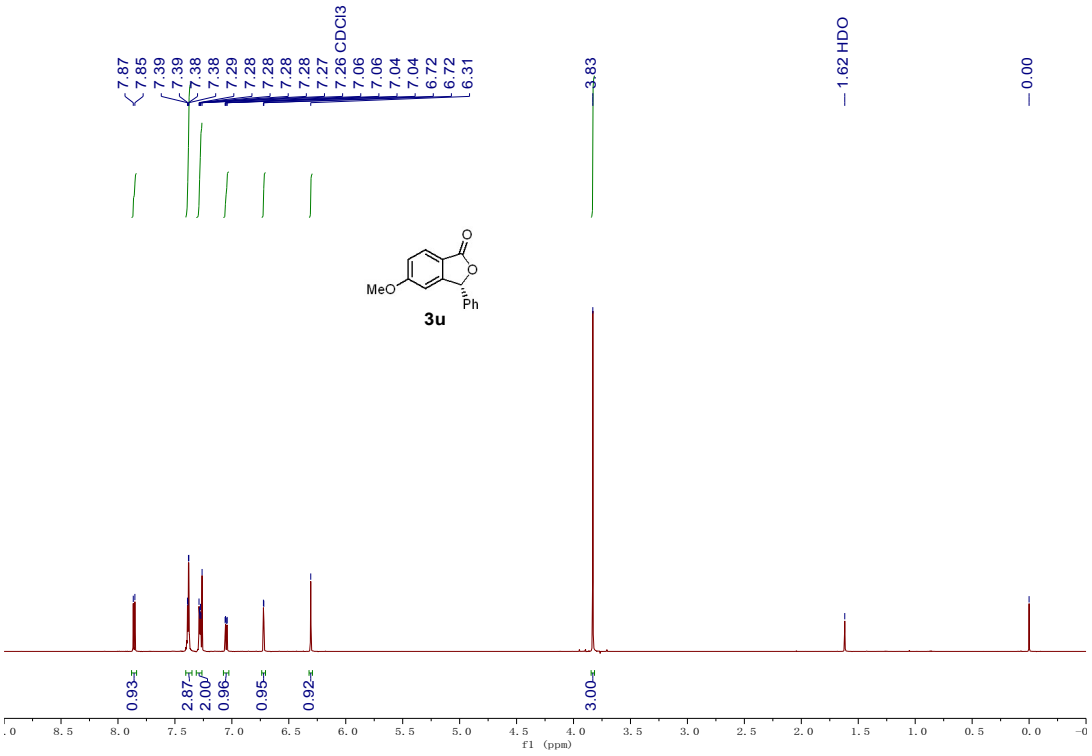
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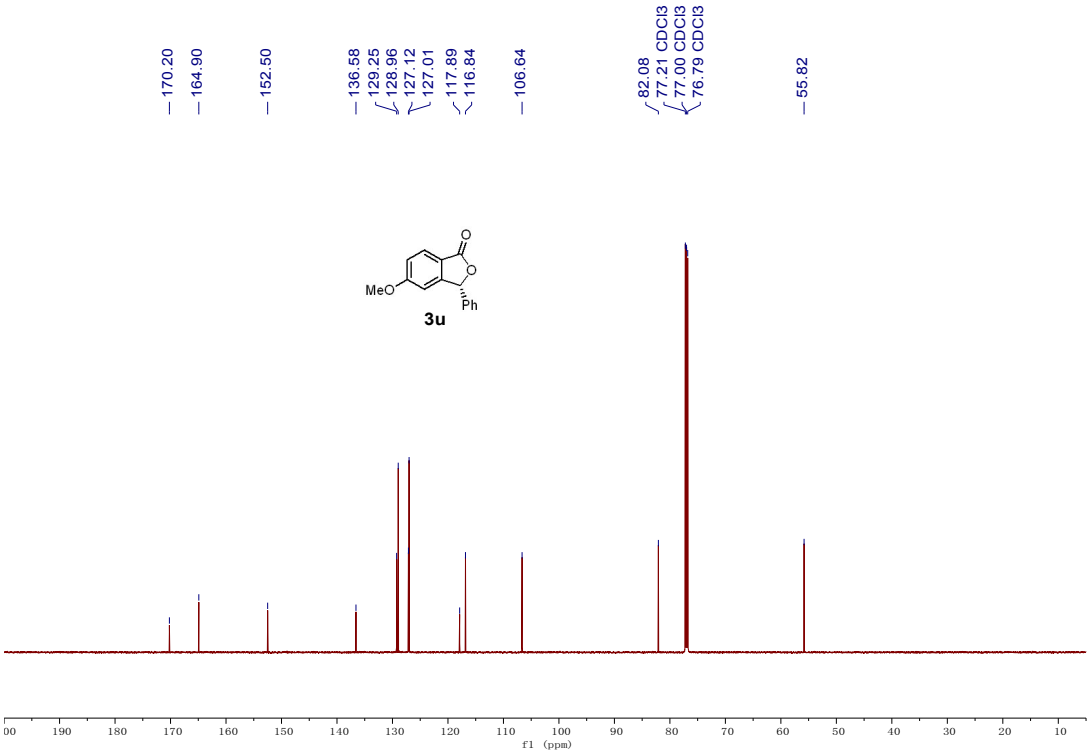
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MeO
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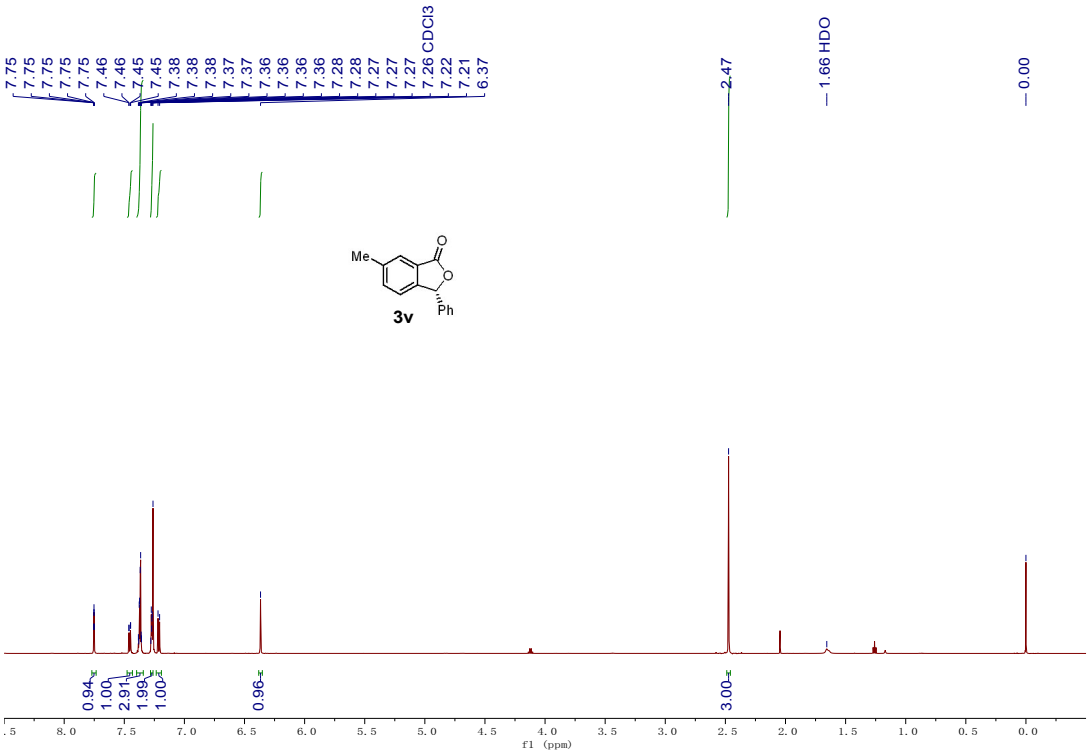
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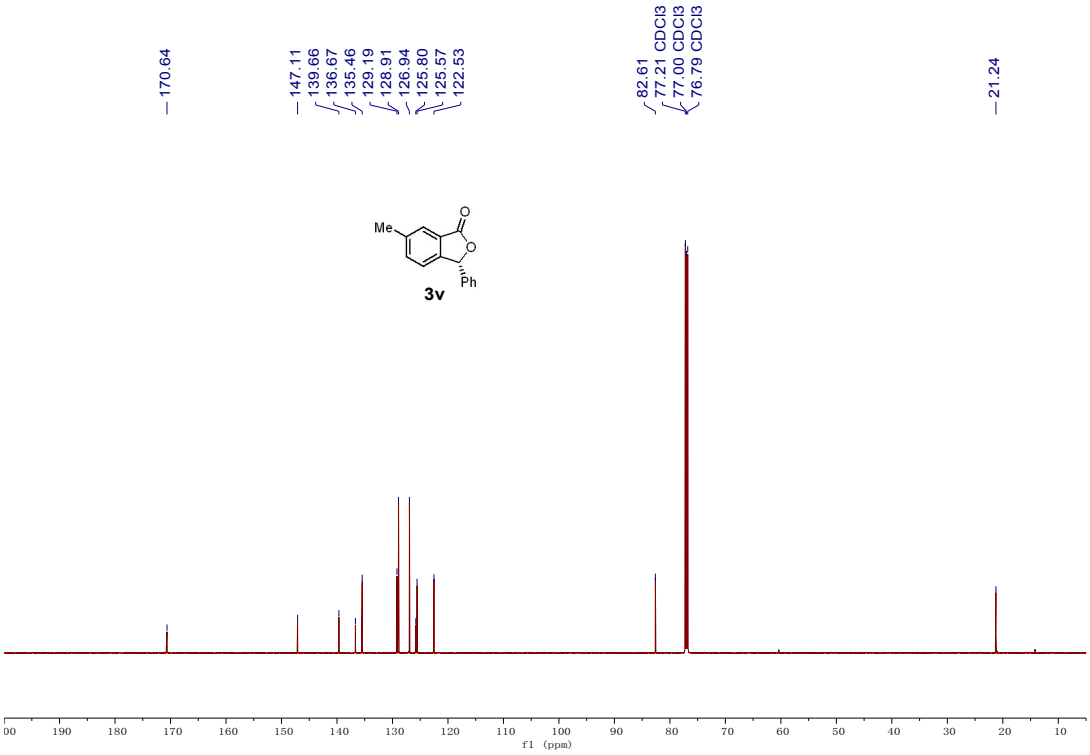
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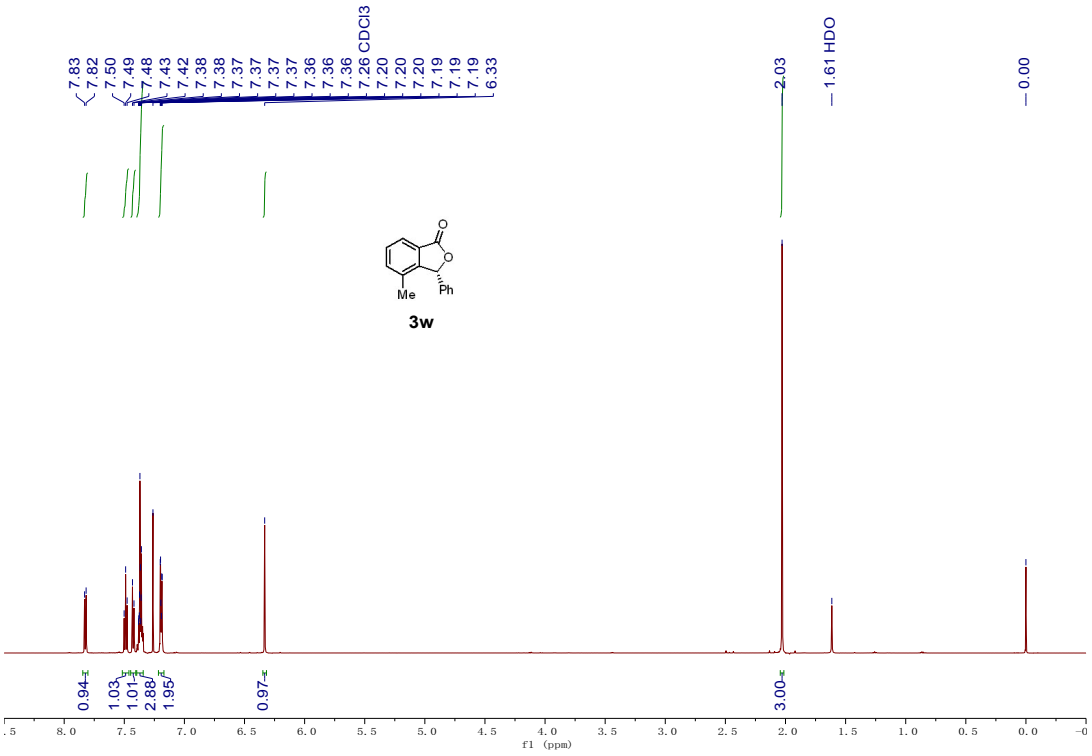
f1 (ppm)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7.36
7.36
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7.19
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7.19
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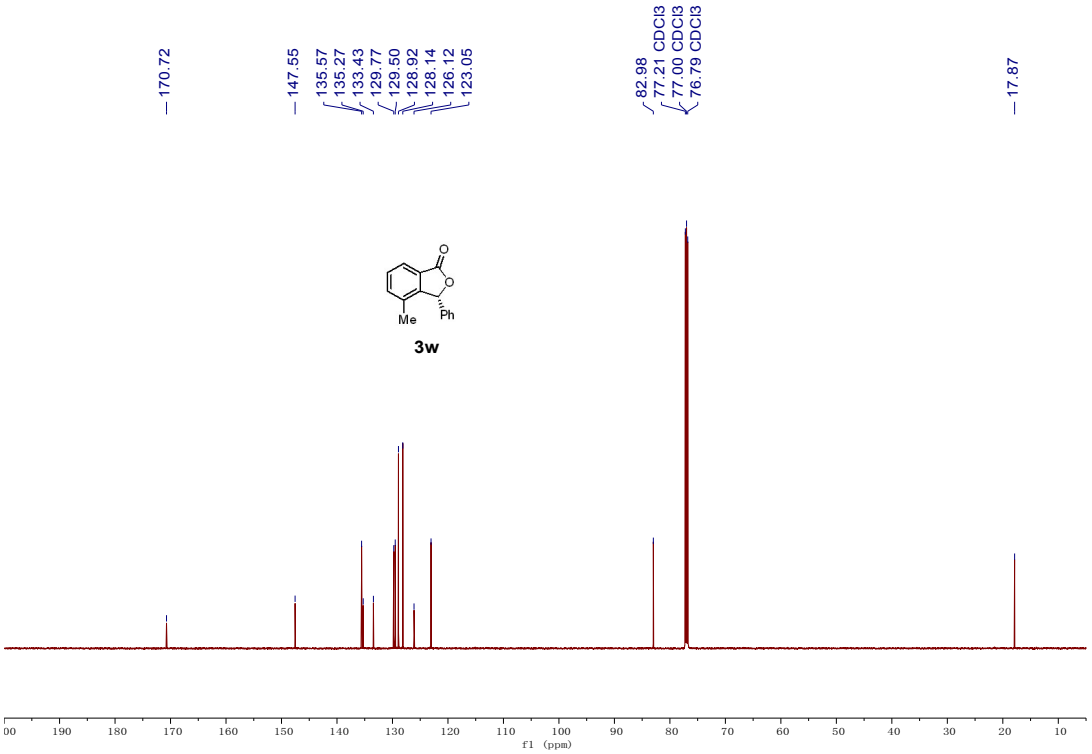
f1 (ppm)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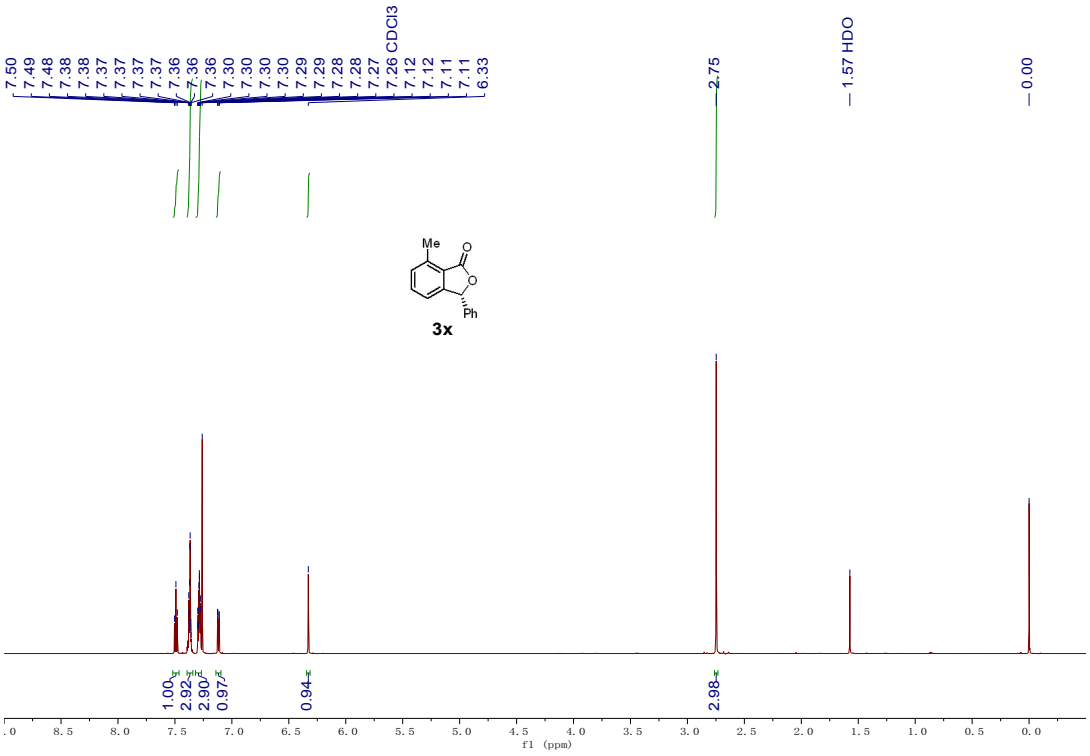
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7.12
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7.11
6.33
2.75
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Ph
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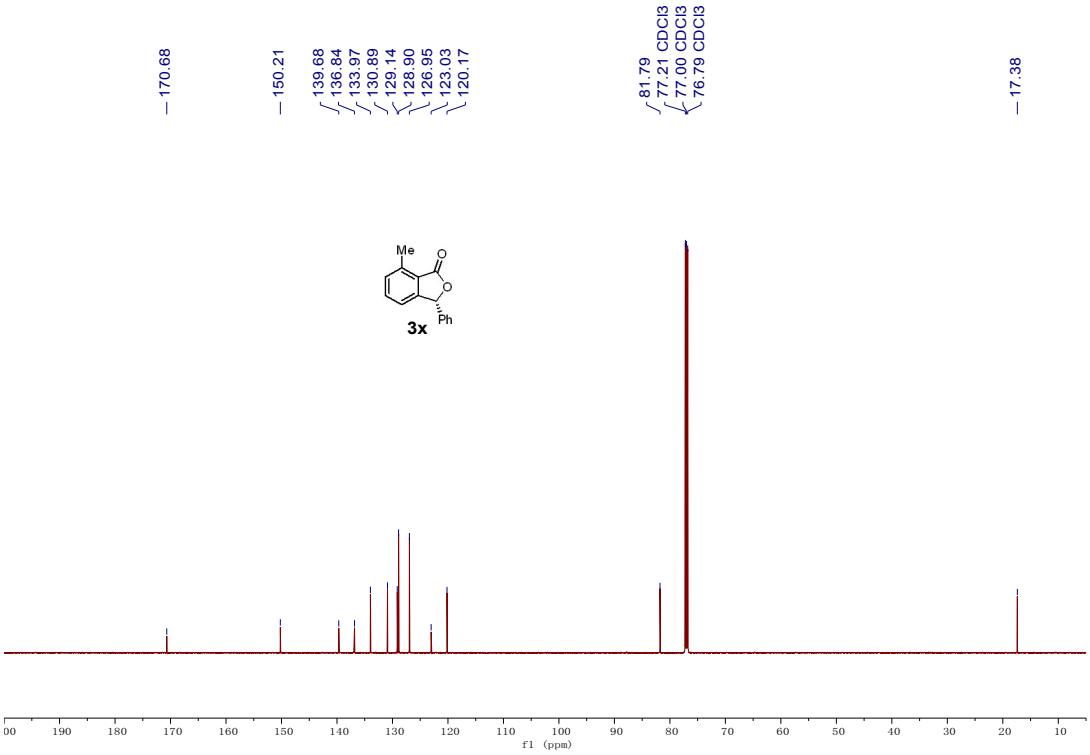
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120.17
81.79
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
17.38
Me
O
O
Ph
3x
f1 (ppm)

5. References

1) Nozawa-Kumada, K.; Kurosu, S.; Shigeno, M.; Kondo, Y., Peroxydisulfate-Mediated Transition-Metal-Free Oxidative C(sp^3)−H Bond Lactonization. *Asian J. Org. Chem.* **2019**, *8*, 1080.
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3) Carlos, A. M. M.; Stieler, R.; Ludtke, D. S., Catalytic Asymmetric Synthesis of 3-Aryl Phthalides Enabled by Arylation-Lactonization of 2-Formylbenzoates. *Org. Biomol. Chem.* **2019**, *17*, 283.
4) Chen, W.; Li, J.; Xie, H.; Wang, J., Rhodium(III)-Catalyzed Asymmetric Addition of Inert Arene C-H Bond to Aldehydes To Afford Enantioenriched Phthalides. *Org. Lett.* **2020**, *22*, 3586.
5) Yang, J.; Yoshikai, N., Cobalt-Catalyzed Enantioselective Intramolecular Hydroacylation of Ketones and Olefins. *J. Am. Chem. Soc.* **2014**, *136* , 16748.
6) Yohda, M.; Yamamoto, Y., Enantioselective Addition of Arylboronic Acids to Methyl 2-Formylbenzoates by Using a Ruthenium/Me-BIPAM Catalyst for Synthesis of Chiral 3-Aryl-Isobenzofuranones. *Org. Biomol. Chem.* **2015**, *13* , 10874.