Supporting Information for

Catalytic Asymmetric Synthesis of 3-Aryl Phthalides Enabled by Arylation-Lactonization of 2-Formylbenzoates

Andressa M. M. Carlos,[a] Rafael Stieler,[a] and Diogo S. Lüdtke*[,a]

[a]*Instituto de Química, Universidade Federal do Rio Grande do Sul, UFRGS, Av. Bento Gonçalves 9500, 91501-970, Porto Alegre, RS, Brazil.*

e-mail: dsludtke@iq.ufrgs.br

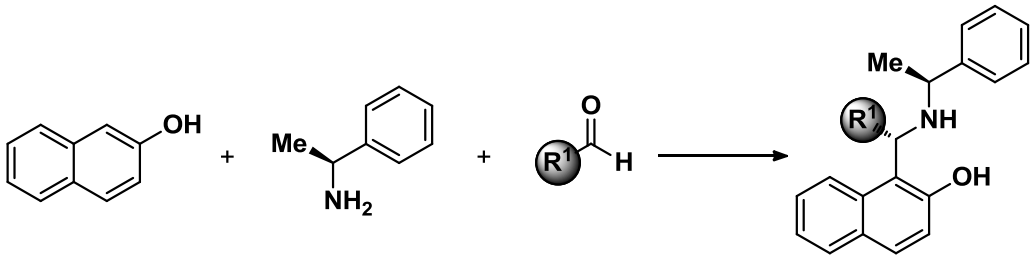
Phone: +55 51 3308 9637

Contents

1. General experimental information

Hydrogen Nuclear Magnetic Resonance spectra (^{1}H NMR) were obtained at 300 MHz and 400 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts (*δ*) are reported in ppm, referenced to the solvent peak of residual $CHCl_3$ or tetramethylsilane (TMS) as reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (*J*) in Hertz and integrated intensity. Carbon-13 Nuclear Magnetic Resonance spectra (^{13}C NMR) were obtained at 75 and 100 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak $CDCl_3$. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), dd (double doublet), m (multiplet) and bs (broad singlet). Optical rotations were obtained on a Perkin Elmer 341 Polarimeter. Column chromatography was performed using silica gel (230-400 mesh) following the methods described by Still.[1] Thin layer chromatography (TLC) was performed using silica gel GF254, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or phosphomolibdic acid, followed by heating. Air- and moisture-sensitive reactions were conducted in flame-dried or oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry argon. Reagents and solvents were handled using standard syringe techniques. Formyl benzoates **1** were prepared according to literature procedures.[2]

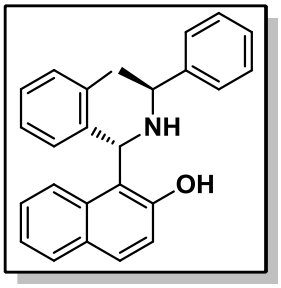
2. General procedure for synthesis of ligand L5[3]



In a flask, under an atmosphere of argon, 2-naphthol (1 eq.), 2-tolualdehyde (1.2 eq.) and (*S*)-(2)-1-phenylethylamine (1.05 eq.) were added at room temperature. The resulting reaction mixture was stirred for 8 h at 60 °C. After this period the reaction system was cooled to room temperature and ethanol (5 mL) was added and the resulted precipitate was collected by filtration, washed with ethanol (3 × 5 mL) and

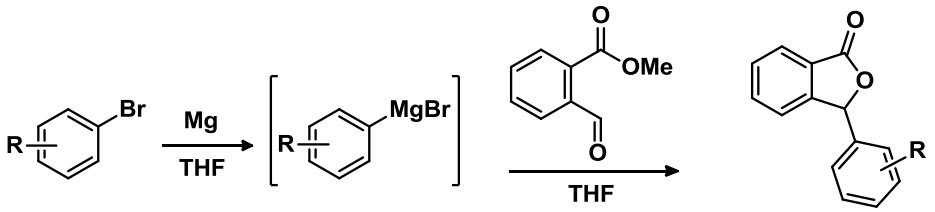
[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
[2] a) Bisai, V.; Suneja, A.; Singh, V. K. *Angew. Chem. Int. Ed.* **2014**, *53*, 10737. b) Zhang, Y. -H.; Shi, B. -F.; Yu, J. -Q. *Angew. Chem. Int. Ed.* **2009**, *48*, 6097. c) Dwight, S. J.; Levin, S. *Org. Lett*. **2016**, *18*, 5316. d) He, Y.; Cheng, C.; Chen, B.; Duan, K.; Zhuang, Y.; Yuan, B.; Zhang, M.; Zhou, Y.; Zhou, Z.; Su,Y. -J.; Cao, R.; Qiu, L. *Org. Lett.* **2014**, *16*, 6366.
[3] Wei, H.; Yin, L.; Haibin, L.; Xingshu, L.; Chan, A. S. C. *Chirality* **2011**, *23*, 222.

purified by crystallization from hexane to give the pure compound. The product was obtained as white solid in 58% yield.



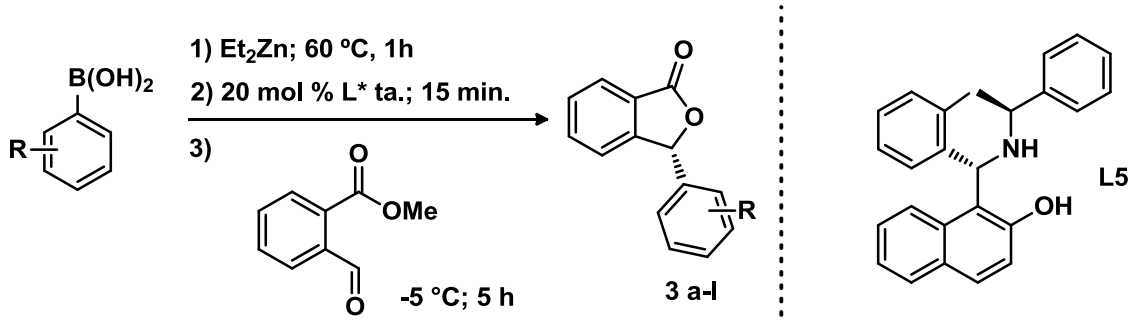
$[\alpha]_D^{20}$ = +312.49 (*c* = 1.2 in $CHCl_3$). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 1.53 (d, *J* = 6.9 Hz, 1 H); 1.90 – 1.93 (m, 2H); 3.85 – 3.92 (m, 1H); 5.66 (s, 1H); 6.98 – 7.38 (m,13H); 7.73 – 7.77 (m, 2H); 13.75 (s, 1H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 18.0; 21.5; 56.5; 56.7; 113.7; 120.0; 120.7; 122.3; 126.4; 126.7; 127.1; 127.9; 128.0; 128.6; 128.73; 128.77; 128.85; 129.5; 130.7; 132.5; 134.7; 138.7; 142.4; 157.7 ppm.

3. General procedure for the 1,2-addition of Grignard reagents to aldehydes:

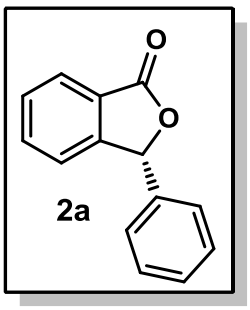


A solution of the aldehyde (5 mmol) in THF (5 mL) was added to a freshly prepared THF solution of the Grignard reagent (5.5 mmol, 1 M) at room temperature. The reaction mixture was stirred for 2 h and then quenched by the addition of NH_4Cl (10 mL). The aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layers were dried with anhydrous $MgSO_4$, filtered, and the solvent was evaporated in vacuum. The crude product was purified by flash chromatography using hexane:ethyl acetate (70:30) as the eluent to obtain the desired racemic alcohols.

4. General procedure for the aryl transfer reaction:



In an atmosphere of argon 1.5 M solution of Et_2Zn (7.2 equiv., 3.6 mmol, 2.4 mL) was slowly added to a solution of arylboronic acid (2.4 equiv., 1.2 mmol, 146 mg) in dry toluene (2 mL). The mixture was stirred at 60 ºC for 1 h and after this period, cooled at room temperature and a solution of 20 mol% of ligand **L5** in 1 mL of dry toluene was added. The reaction mixture was stirred for 15 min followed by addition of the aldehyde (0.5 mmol, 70 µL). After stirred at -5 °C for 5 h the reaction mixture was carefully quenched by the addition of HCl 1M. The aqueous layer was extracted with dichloromethane (3 × 30 mL). The combined organic layers were dried with anhydrous $MgSO_4$, filtered, and the solvent was evaporated in vacuum. The crude product was purified by flash chromatography using hexane:ethyl acetate (85:15).



(*R*)-3-Phenylisobenzofuran-1(3*H*)-one $C_{14}H_{10}O_2$ (2a). White solid. ***Rf*** = 0.4. **$[\alpha]_D^{20}$** = - 45.4 (*c* = 0.34 in DCM). **Melting point** = 152 - 154 °C. Purified by column chromatography (hexane/EtOAc 90:10) to give the product in 80% yield and 91% *ee*. **HPLC:** (Chiralcel OD, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 8.63 min, t_R (*R*) = 11.14 min.

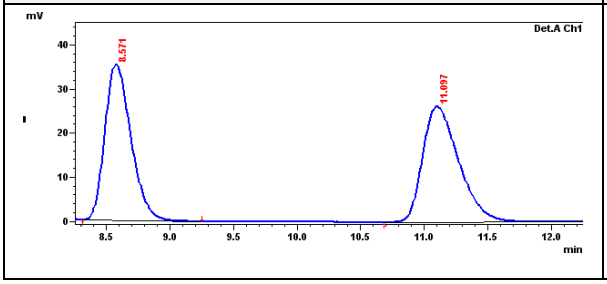
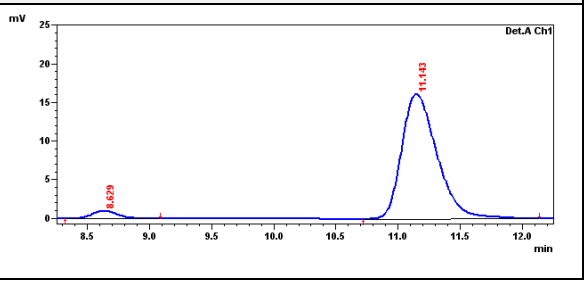
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.40 (s, 1H); 7.26 – 7.41 (m, 6H); 7.55 (t, *J* = 7.5 Hz, 1H); 7.64 (td, *J* = 7.5 Hz; *J* = 1.2 Hz, 1H); 7.96 (d, *J* = 7.6 Hz, 1H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 82.6; 122.8; 125.50; 125.55; 126.9; 128.9; 129.23; 129.29; 134.2; 136.3; 149.6; 170.4 ppm.

HRMS (ESI^+): Calcd for $C_{14}H_{10}O_2$ $[M + H]^+$ requires 211.0759; found 211.0758.

Ent-2a: Purified by column chromatography (hexane/EtOAc 90:10) to give the product in 87% yield and 97% *ee*. **$[\alpha]_D^{20}$** = + 43.98 (*c* = 0.98 in DCM). **HPLC:** (Chiralcel OD,

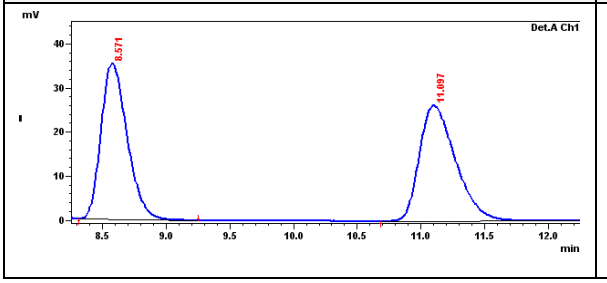
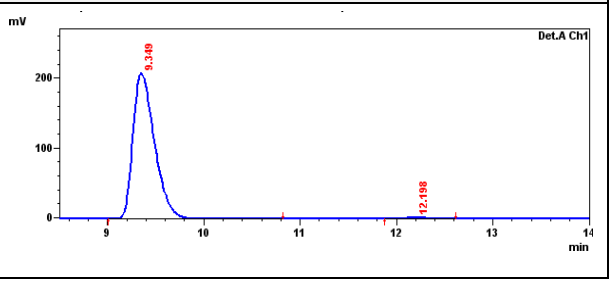
hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 9.34 min, t_R (*R*) = 12.19 min.

- **HPLC Chromatograms - Enantiomer *R***

Racemic Standard	Catalytic Reaction Product
	

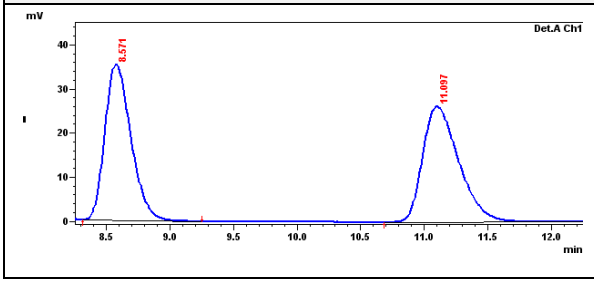
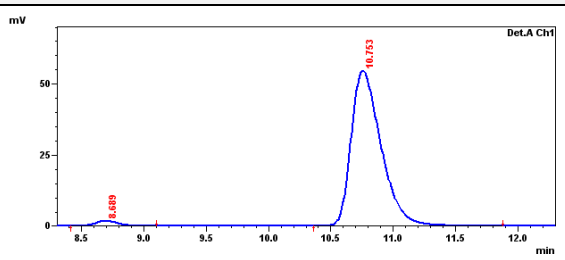
Peak	Retention time (min)	Area (%)	
1	8.629	4.412	**91% *ee***
2	11.143	95.588	

- **Enantiomer *S***

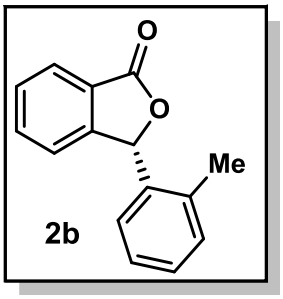
Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	9.349	98.367	**97% *ee***
2	12.198	1.633	

- **After recrystallization - Enantiomer *R***

Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	8.689	2.292	**95% *ee***
2	10.753	97.708	



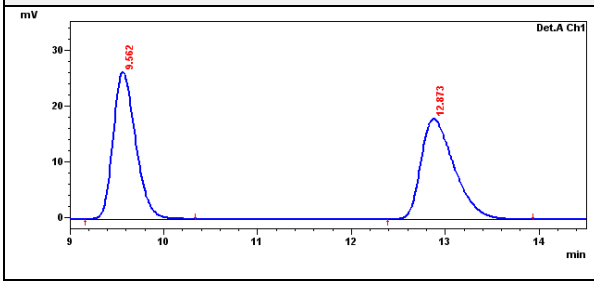
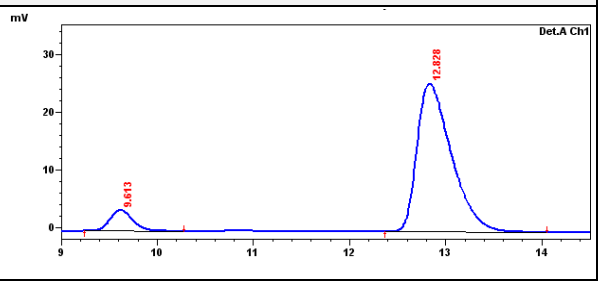
(*R*)-3-*o*-tolylisobenzofuran-1(3*H*)-one $C_{15}H_{12}O_2$ (2b). White solid. ***Rf*** = 0.3. $[\alpha]_D^{20}$ = + 27.4 (*c* = 0.94 in EtOAc). **Melting point** = 118 - 120 °C. Purified by column chromatography (hexane/EtOAc 85:15) to give the product in 86% yield and 83% *ee*. **HPLC:** (Chiralcel OD, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 9.61 min, t_R (*R*) = 12.82 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.50 (s, 3H); 6.69 (s, 1H); 6.92 (d, *J* = 7,6 Hz, 1H); 7.11 – 7.15 (m, 1H); 7.26-7.28 (m, 2H); 7.34 (dd, *J* = 7.6 Hz, *J* = 0.8 Hz, 1H); 7.57 (t, *J* = 7.5 Hz, 1H); 7.67 (td, *J* = 7.5 Hz, *J* = 1.1 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H) ppm.

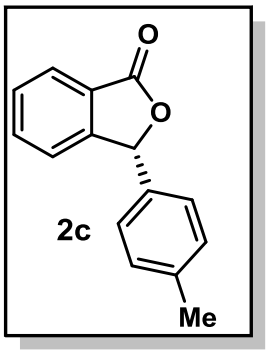
^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2; 80.4; 122.9; 125.6; 126.32; 126.35; 127.1; 129.25; 129.29; 131.0; 134.0; 134.1; 137.0; 149.2; 170.5 ppm.

HRMS (ESI^+): Calcd for $C_{15}H_{12}O_2$ $[M + H]^+$ requires 225.0916; found 225,0918.

- **HPLC Chromatograms - Enantiomer *R***

Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	9.613	8.591	**83% *ee***
2	12.828	91.409	



(*R*)-3-*p*-tolylisobenzofuran-1(3*H*)-one $C_{15}H_{12}O_2$ (2c). White solid. ***Rf*** =0.3. **$[\alpha]_D^{20}$** = - 7.72 (*c* = 0.22 in DCM). **Melting point** = 127 - 130 °C. Purified by column chromatography (hexane/EtOAc 85:15) to give the product in 91% yield and 91% *ee*. **HPLC:** (Chiralcel OD, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 7.82 min, t_R (*R*) = 9.61 min.

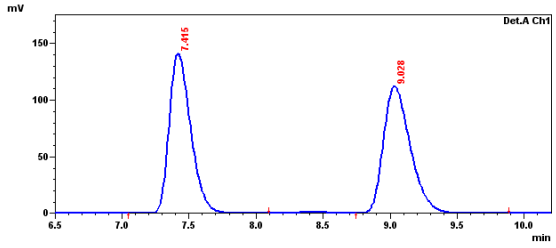
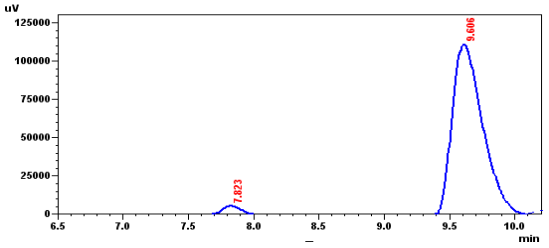
^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 2.35 (s, 3H); 6.37 (s, 1H); 7.14 – 7.19 (m, 4H); 7.32 (d, *J* = 7.6 Hz, 1H); 7.54 (t, *J* = 7.5 Hz, 1H); 7.64 (td, *J* = 7.5 Hz; 1.1 Hz; 1H); 7.95 (d, *J* = 7.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 21.3; 82.6; 122.8; 125.5; 125.6; 126.9; 129.2; 129.5; 133.3; 134.2; 139.3; 149.7; 170.5 ppm.

HRMS (ESI^+): Calcd for $C_{15}H_{12}O_2$ $[M + H]^+$ requires 225,0916; found 225,0918.

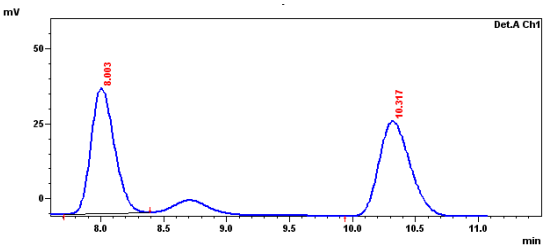
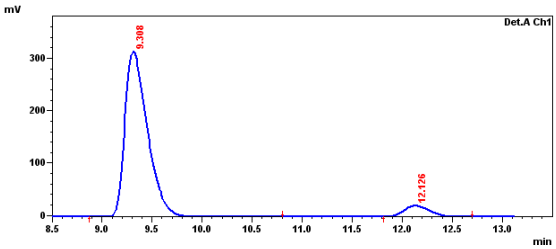
***Ent*-2f:** Purified by column chromatography (hexane/EtOAc 85:15) to give the product in 78% yield and 84% *ee*. **$[\alpha]_D^{20}$** = + 50.12 (*c* = 0.78 in DCM). **HPLC:** (Chiralcel OD, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 9.30 min, t_R (*R*) = 12.12 min.

- **HPLC Chromatograms - Enantiomer *R***

Racemic Standard	Catalytic Reaction Product
	

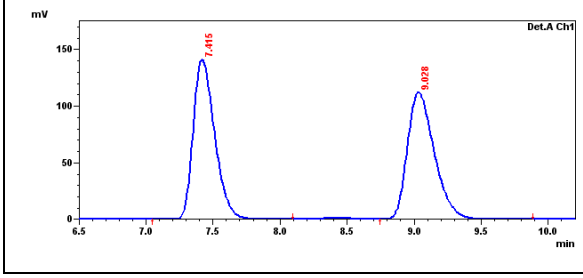
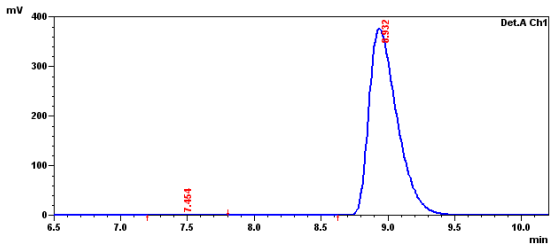
Peak	Retention time (min)	Area (%)	
1	7.823	4.279	**91% *ee***
2	9.606	95.721	

- **Enantiomer *S***

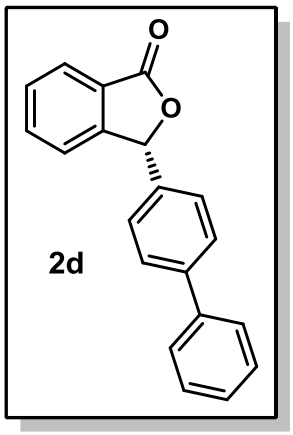
Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	9.308	92.070	**84% *ee***
2	12.126	7.930	

- **After recrystallization - Enantiomer *R***

Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	7.454	0.183	**99% *ee***
2	8.932	99.817	



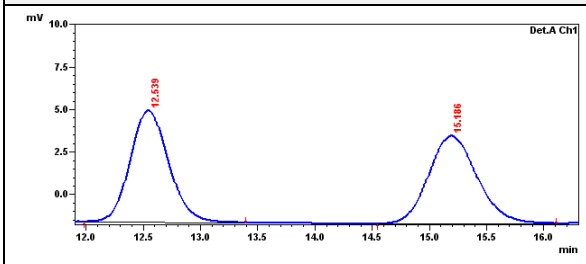
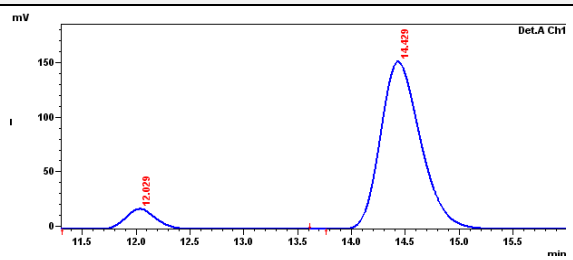
(*R*)-3-(*p*-bifhenyl)isobenzofuran-1(3*H*)-one $C_{20}H_{14}O_2$ (2d). White solid. ***Rf*** = 0.3. **$[\alpha]_D^{20}$** = + 23.6 (*c* = 0.22 in DCM). **Melting point** = 209 – 212 °C. Purified by column chromatography (hexane/EtOAc 85:15) to give the product in 72% yield and 81% *ee*. **HPLC:** (Chiralcel OD-H, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 12.02 min, t_R (*R*) = 14.43 min.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 6.45 (s, 1H); 7.34 – 7.39 (m, 4H); 7.44 (t, *J* = 7.5 Hz, 2H); 7.55 – 7.61 (m, 5H); 7.67 (td, *J* = 7.5 Hz; *J* = 0.9 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 82.4; 122.8; 125.66; 125.70; 127.1; 127.4; 127.67; 127.69; 128.8; 129.4; 134.4; 135.2; 140.2; 149.9; 170.4 ppm.

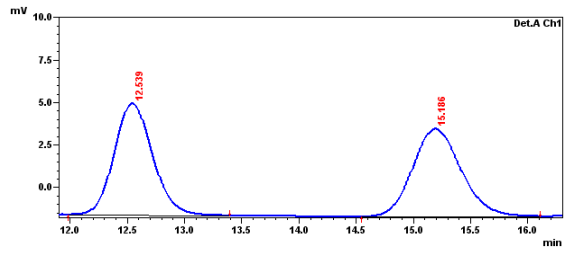
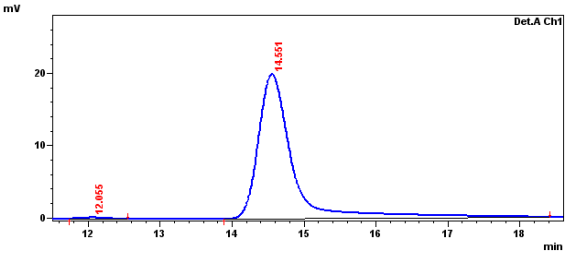
HRMS (ESI^+): Calcd for $C_{20}H_{14}O_2$ $[M + H]^+$: requires 287.1072; found 287.1072.

- **HPLC Chromatograms - Enantiomer *R***

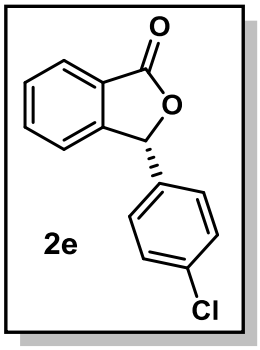
Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	12.029	9.251	**81% *ee***
2	14.429	90.749	

- **After recrystallization - Enantiomer *R***

Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	12.055	0.489	**99% *ee***
2	14.551	99.511	



(*R*)-3-(*p*-Chlorophenyl)isobenzofuran-1(3*H*)-one $C_{14}H_9ClO_2$ (2e). White solid. ***Rf*** = 0.3. **$[\alpha]_D^{20}$** = - 34.7 (*c* = 0.22 in DCM). **Melting point** = 156 - 159 °C. Purified by column chromatography (hexane/EtOAc 85:15) to give the product in 58% yield and 85% *ee*. **HPLC:** (Chiralcel OD-H, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 9.13 min, t_R (*R*) = 10.36 min.

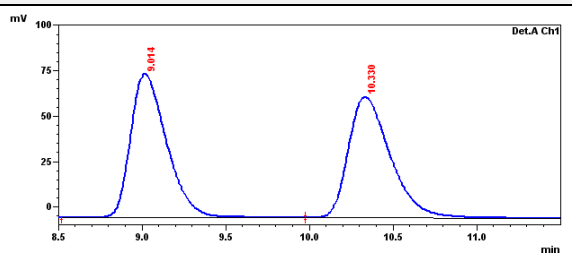
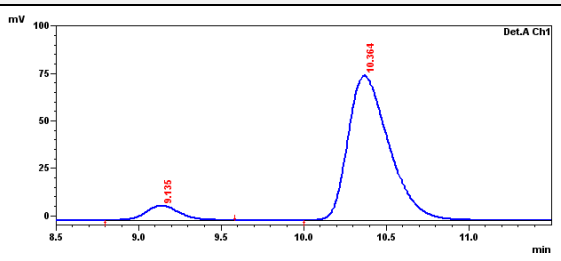
^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 6.38 (s, 1H); 7.20 – 7.24 (m, 2H); 7.32 (d, *J* = 7.6 Hz, 1H); 7.34 – 7.38 (m, 2H); 7.58 (t, *J* = 7.5 Hz 1H); 7.67 (t, *J* = 7.5 Hz, 1H); 7.96 (d, *J* = 7.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 81.7; 122.7; 125.4; 125.7; 128.3; 129.1; 129.5; 134.4; 134.8; 135.2; 149.1; 170.2 ppm.

HRMS (ESI^+): Calcd for $C_{14}H_9ClO_2$ $[M + H]^+$: requires 245.0369; found 245.0370.

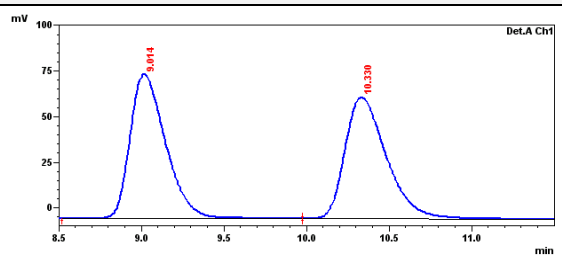
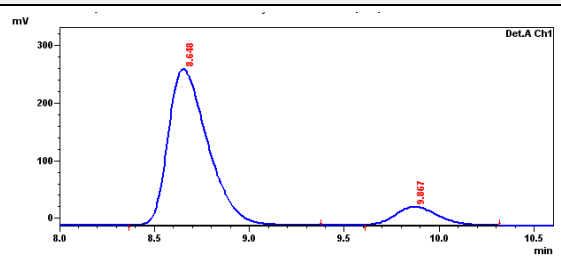
***Ent*-2b:** Purified by column chromatography (hexane/EtOAc 85:15) to give the product in 74% yield and 77% *ee*. **$[\alpha]_D^{20}$** = + 40.88 (*c* = 0.56 in DCM). **HPLC:** (Chiralcel OD-H, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 8.64 min, t_R (*R*) = 9.86 min.

- **HPLC Chromatograms - Enantiomer *R***

Racemic Standard	Catalytic Reaction Product
	

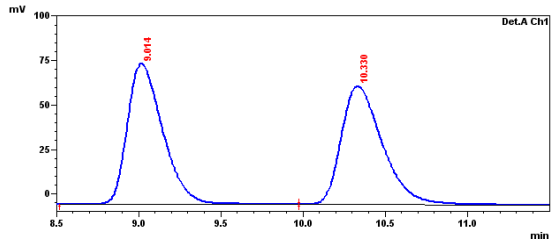
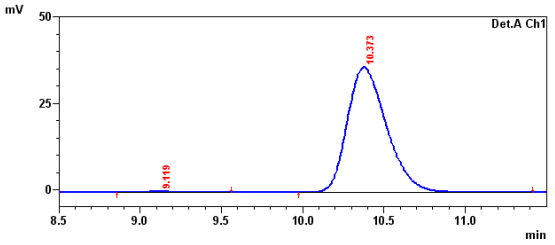
Peak	Retention time (min)	Area (%)	
1	9.135	7.517	**85% *ee***
2	10.364	92.483	

- **Enantiomer *S***

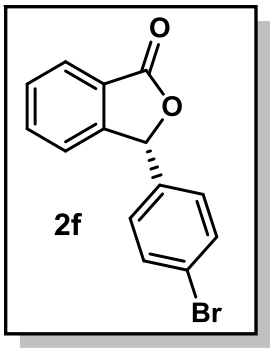
Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	8.648	88.592	**77% *ee***
2	9.867	11.408	

- **After recrystallization - Enantiomer *R***

Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	9.119	0.317	**99% *ee***
2	10.373	99.683	



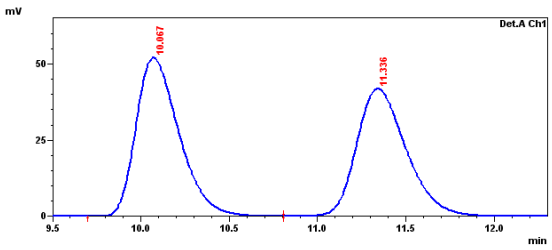
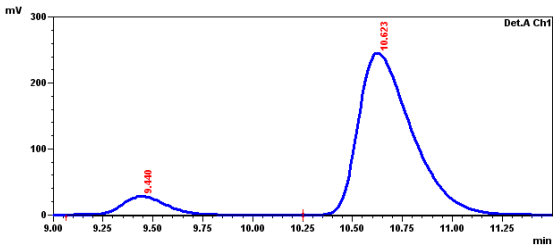
(*R*)-3-(*p*-bromophenyl)isobenzofuran-1(3*H*)-one $C_{14}H_9BrO_2$ (2f). White solid. ***Rf*** = 0.3. $[\alpha]_D^{20}$ = - 20.7 (*c* = 0.72 in DCM). **Melting point** = 169 – 172 °C. Purified by column chromatography (hexane/EtOAc 90:10) to give the product in >95% yield and 83% *ee*. **HPLC:** (Chiralcel OD-H, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 9.44 min, t_R (*R*) = 10.62 min.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 6.37 (s, 1H); 7.17 – 7.19 (m, 2H); 7.33 (dq, *J* = 7.7 Hz; *J* = 0.8 Hz, 1H); 7.52 – 7.54 (m, 2H); 7.57 – 7.61 (m, 1H); 7.68 (td, *J* = 7.5 Hz; *J* = 1.2 Hz, 1H); 7.98 (d, *J* = 7.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 81.7; 122.6; 123.3; 125.33; 125.65; 128.5; 129.5; 132.0; 134.4; 135.4; 149.0; 170.1 ppm.

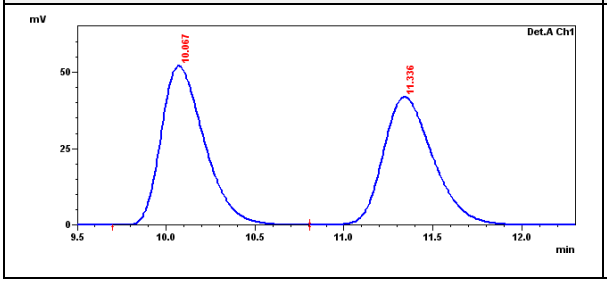
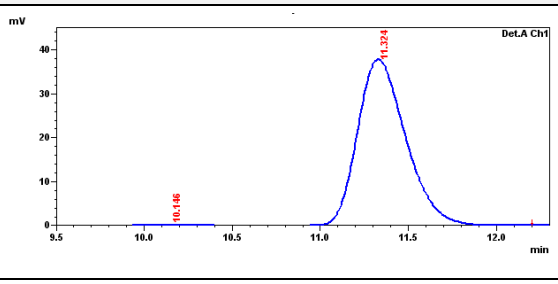
HRMS (ESI^+): Calcd for $C_{14}H_9{}^{79}BrO_2$ $[M + H]^+$: requires 288.9864; found 288.9864; calcd for $C_{14}H_9{}^{81}BrO_2$ $[M + H]^+$: requires 290.9845; found 290.9822.

- **HPLC Chromatograms**

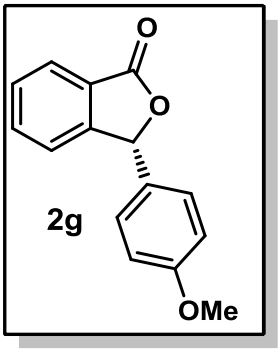
Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	9.440	8.600	**83% *ee***
2	10.623	91.400	

- **After recrystallization - Enantiomer *R***

Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	10.146	0.557	**99% *ee***
2	11.324	99.443	



(*R*)-3-(*p*-Methoxyphenyl)isobenzofuran-1(3*H*)-one $C_{15}H_{12}O_3$ (2g). White solid. ***Rf*** = 0.4. **$[\alpha]_D^{20}$** = + 28.5 (*c* = 0.53 in DCM). **Melting point** = 144 - 147 °C. Purified by column chromatography (hexane/EtOAc 85:15) to give the product in 71% yield and 91% *ee*. **HPLC:** (Chiralcel OD, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 13.63 min, t_R (*R*) = 16.58 min.

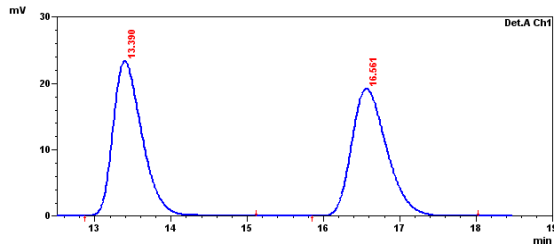
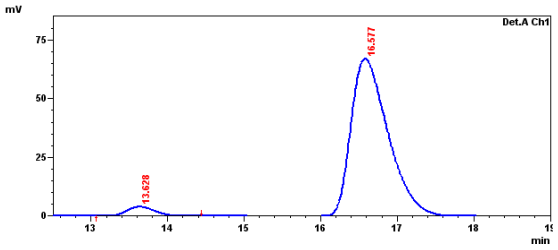
^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 3.81 (s, 3H); 6.37 (s, 1H); 6.89 (d, *J* = 8.4 Hz, 2H); 7.17 (d, *J* = 8.4 Hz, 2H); 7.31 (d, *J* = 7.6 Hz, 1H); 7.56 (t, *J* = 7.5 Hz, 1H); 7.64 (t, *J* = 7.5 Hz, 1H); 7.96 (d, *J* = 7.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 55.2; 82.6; 114.2; 122.8; 125.3; 125.7; 128.1; 128.6; 129.1; 134.1; 149.6; 160.3; 170.4 ppm.

HRMS (ESI^+): Calcd for $C_{15}H_{12}O_3$ $[M + H]^+$: requires 241.0865; found 241.0862.

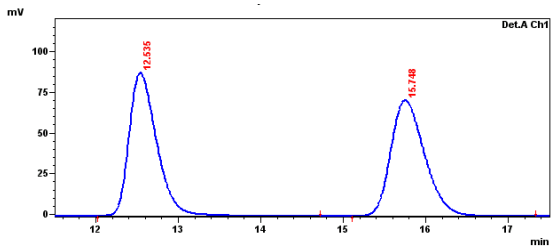
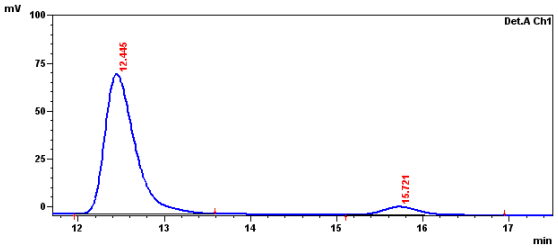
Ent-2g: Purified by column chromatography (hexane/EtOAc 85:15) to give the product in 87% yield and 87% *ee*. **$[\alpha]_D^{20}$** = -6.76 ° (*c* = 0.69 in DCM). **HPLC:** (Chiralcel OD, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 12.44 min, t_R (*R*) = 15.72 min.

- **HPLC Chromatograms - Enantiomer *R***

Racemic Standard	Catalytic Reaction Product
	

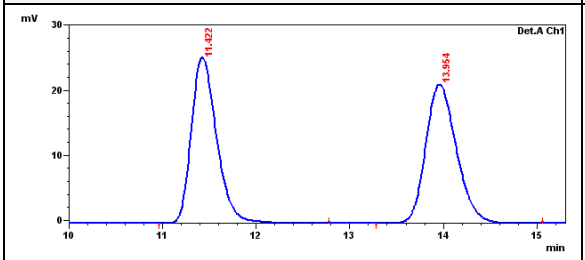
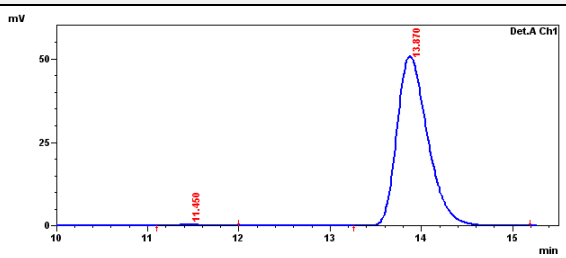
Peak	Retention time (min)	Area (%)	
1	13.628	4.638	**91% *ee***
2	16.577	95.362	

- **Enantiomer *S***

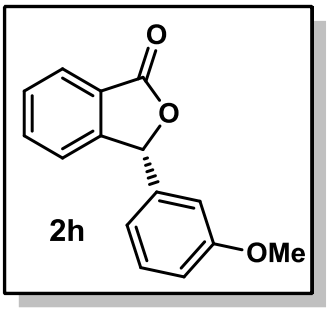
Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	12.445	93.683	**87% *ee***
***I*2**	15.721	6.317	

- **After recrystallization - Enantiomer *R***

Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	11.450	1.000	**98% *ee***
2	13.870	99.000	



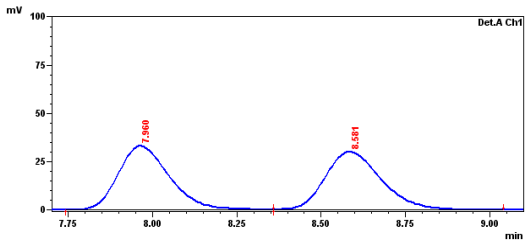
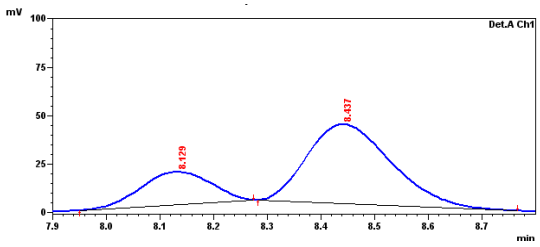
(*R*)-3-(*m*-Methoxyphenyl)isobenzofuran-1(3*H*)-one $C_{15}H_{12}O_3$ (2h). Yellow oil. ***Rf*** = 0.2. $[\alpha]_D^{20}$ = - 26.95 (*c* = 1.52 in DCM). Purified by column chromatography (hexane/EtOAc 85:15) to give the product in 80% yield and 48% *ee*. **HPLC:** (Chiralcel OD-H, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 8.13 min, t_R (*R*) = 8.44 min.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 3.77 (s, 3H); 6.37 (s, 1H); 6.78 – 6.80 (m, 1H); 6.87 – 6.91 (m, 2H); 7.28 – 7.36 (m, 2H); 7.53 – 7.57 (m, 1H); 7.64 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H); 7.95 (d, *J* = 7.96 Hz, 1H) ppm.

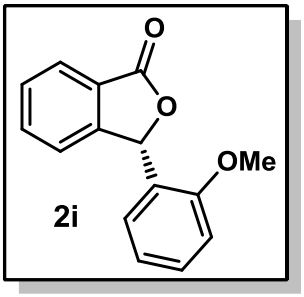
^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 55.2; 82.4; 112.3; 114.5; 118.9; 122.7; 125.3; 125.4; 129.2; 129.9; 134.2; 137.8; 149.4; 159.8; 170.4 ppm.

HRMS (ESI^+): Calcd for $C_{15}H_{12}O_2$ [M + H]+: requires 241.0865; found 241.0866.

- **HPLC Chromatograms - Enantiomer *R***

Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	8.129	25.769	**48% *ee***
2	8.437	74.231	



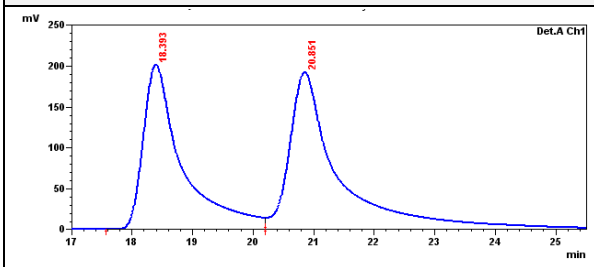
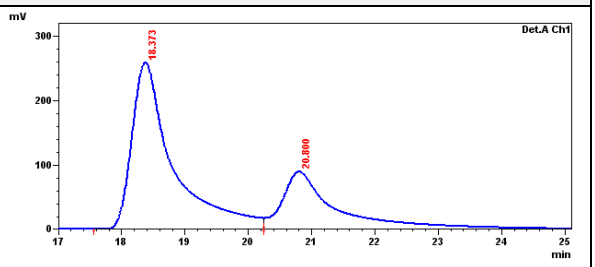
(*R*)-3-(*o*-methoxyphenyl)isobenzofuran-1(3*H*)-one $C_{15}H_{12}O_3$ (2i). White solid. ***Rf*** = 0.3. $[\alpha]_D^{20}$ = - 95.9 (*c* = 0.50 in DCM). **Melting point** = 100 - 103 °C. Purified by column chromatography (hexane/EtOAc 85:15) to give the product in 72% yield and 34% *ee*. **HPLC:** (Chiralcel AS-H, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 20.80 min, t_R (*R*) = 18.37 min.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 3.91 (s, 3H); 6.85 (s, 1H); 6.91 (td, *J* = 7.5 Hz, *J* = 0.9 Hz, 1H); 6.97 (d, *J* = 7.6 Hz, 1H); 7.08 (dd, *J* = 7.6 Hz, *J* = 1.7 Hz, 1H); 7.30 – 7.34 (m, 1H); 7.44 (dd, *J* = 7.6 Hz, *J* = 0.8 Hz, 1H); 7.51 (t, *J* = 7.5 Hz, 1H); 7.61 (td, *J* = 7.5 Hz, *J* = 1.1 Hz, 1H); 7.92 (d, *J* = 7.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 55.5; 78.0; 110.9; 120.7; 122.8; 124.9; 125.3; 125.5; 126.8; 128.9; 130.0; 134.0; 150.3; 156.9; 170.9 ppm.

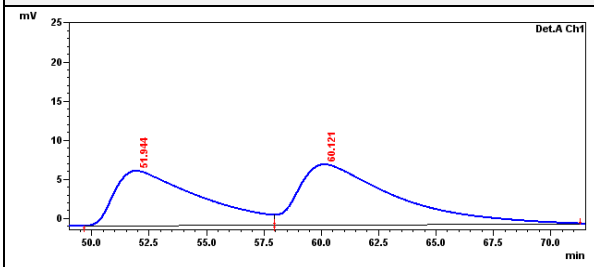
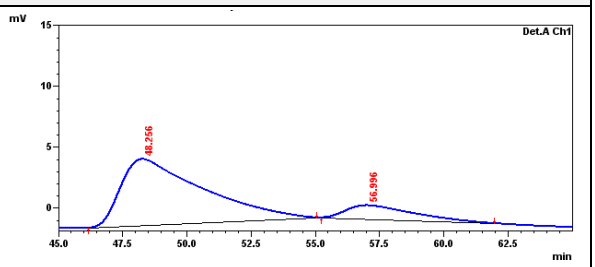
HRMS (ESI^+): Calcd for $C_{15}H_{12}O_3$ $[M + H]^+$: requires 241.0865; found 241.0865.

- **HPLC Chromatograms - Enantiomer *R***

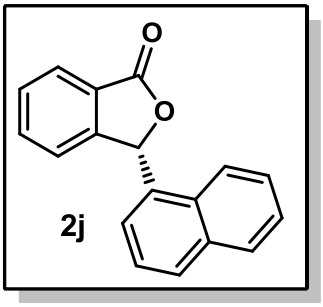
Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	18.373	67.190	**34% *ee***
2	20.800	32.810	

- **After recrystallization - Enantiomer *R***

Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	48.256	85.329	**71% *ee***
2	56.996	14.671	



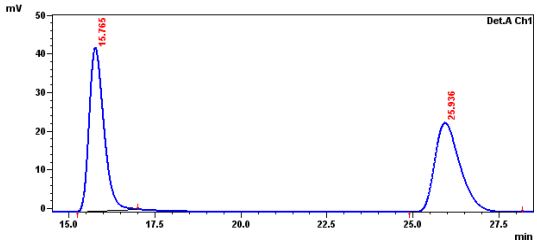
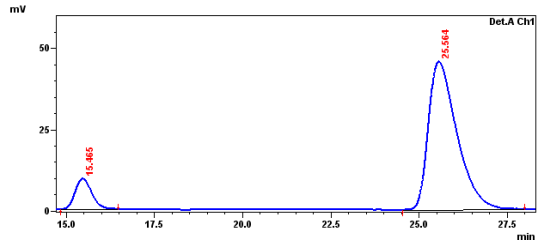
(*R*)-3-(naphthalen-1-yl)isobenzofuran-1(3*H*)-one $C_{18}H_{12}O_2$ (2j). White solid. ***Rf*** = 0.3. $[\alpha]_D^{20}$ = + 4.46 (*c* = 0.51 in DCM). **Melting point** = 154 - 157°C. Purified by column chromatography (hexane/EtOAc 85:15) to give the product in 88% yield and 79% *ee*. **HPLC:** (Chiralcel OD-H, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 15.46 min, t_R (*R*) = 25.56 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 – 7.27 (m, 2H); 7.38 (d, *J* = 8.1 Hz, 1H); 7.39 – 7.45 (m, 1H); 7.54 – 7.68 (m, 4H); 7.87 (d, *J* = 8.2 Hz, 1H); 7.92 (d, *J* = 8.0 Hz, 1H); 8.1 (d, *J* = 8.0 Hz, 1H); 8.23 (d, *J* = 8.3 Hz, 1H) ppm.

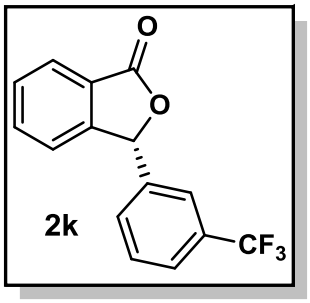
^{13}C NMR (100 MHz, $CDCl_3$): δ = 79.6; 122.8; 123.1; 124.4; 125.2; 125.9; 126.0; 126.1; 126.9; 129.0; 131.2; 131.8; 133.9; 134.1; 149.2; 170.5 ppm.

HRMS (ESI$^+$): Calcd for $C_{18}H_{12}O_2$ $[M + H]^+$ requires 261.0916; found 261.0918.

- **HPLC Chromatograms**

Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	15.465	10.701	**79% *ee***
2	25.564	89.299	



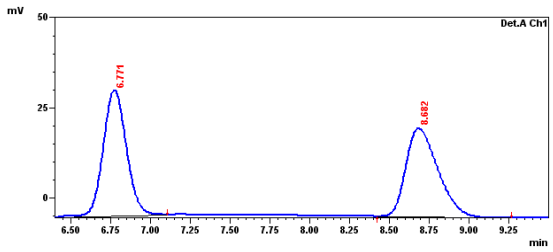
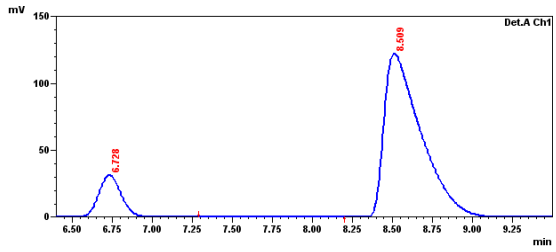
(*R*)-3-(*m*-(trifluoromethyl)phenyl)isobenzofuran-1(3*H*)-one $C_{15}H_9F_3O_2$ (2k). White solid. ***Rf*** = 0.3. **$[\alpha]_D^{20}$** = - 47.4 (*c* = 1.04 in EtOAc). **Melting point** = 98 – 100 °C. Purified by column chromatography (hexane/EtOAc 85:15) to give the product in 72% yield and 73% *ee*. **HPLC:** (Chiralcel OD-H, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 6.73 min, t_R (*R*) = 8.51 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.45 (s, 1H); 7.35 (dd, *J* = 7.7 Hz; *J* = 0.8 Hz, 1H); 7.47 – 7.55 (m, 2H); 7.58 – 7.71 (m, 4H); 8.00 (d, *J* = 7.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 81.5; 122.6; 123.62 (q, $^4J_{C\text{-}F}$ = 3.8 Hz); 123.64 (q, $J_{C\text{-}F}$ = 271.1 Hz); 125.3; 125.8; 126.0 (q, $J_{C\text{-}F}$ = 3.7 Hz); 129.5; 129.7; 130.1; 131.3 (q, $J_{C\text{-}F}$ = 32.6 Hz); 134.5; 137.5; 148.8; 170.0 ppm.

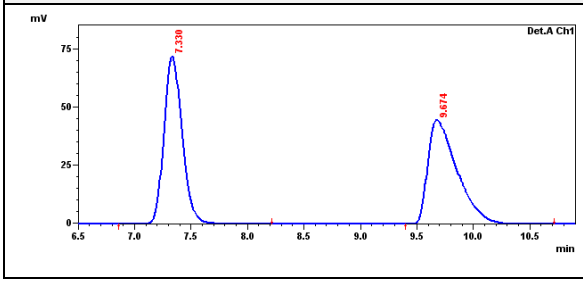
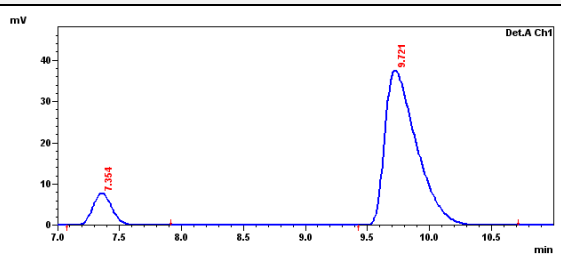
HRMS (ESI^+): Calcd for $C_{15}H_9F_3O_2$ [M + H]+: requires 279.0633; found 279.0639.

- **HPLC Chromatograms - Enantiomer *R***

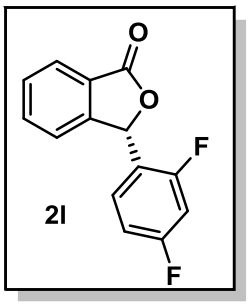
Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	6.728	13.634	**73% *ee***
2	8.509	86.366	

- **After recrystallization - Enantiomer *R***

Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	7.354	11.600	**77% *ee***
2	9.721	88.400	



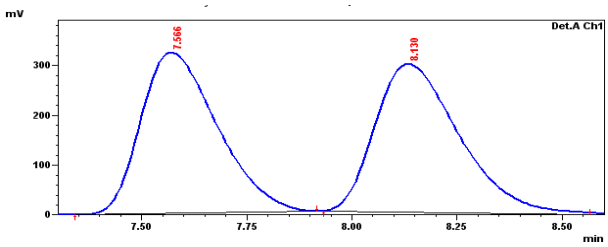
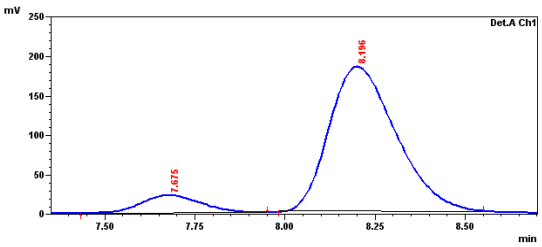
3-(2,4-difluorophenyl)isobenzofuran-1(3H)-one $C_{14}H_8F_2O_2$ (2l). White solid. ***Rf*** =0.3. **$[\alpha]_D^{20}$** = - 15.84 (*c* = 0.50 in DCM). **Melting point** = 113 – 116 °C. Purified by column chromatography (hexane/EtOAc 85:15) to give the product in 77% yield and 80% *ee*. **HPLC:** (Chiralcel OD-H, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 7.67 min t_R (*R*) = 8.19 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.70 (s, 1H); 6.81 – 6.96 (m, 2H); 7.11 (td, *J* = 8.4 Hz, *J* = 6.3 Hz, 1H); 7.41 (d, *J* = 7.7 Hz, 1H); 7.58 (t, *J* = 7.5 Hz, 1H); 7.69 (td, *J* = 7.6 Hz, *J* = 1.0 Hz, 1H) ; 7.97 (d, *J* = 7.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 76.1 (d, $^4J_{C\text{-}F}$ = 3.5 Hz); 104.4 (t, *J* = 25.3 Hz); 111.9 (dd, $^2J_{C\text{-}F}$ = 21.6Hz, $^1J_{C\text{-}F}$ = 3.7 Hz), 120.0 (d, $^3J_{C\text{-}F}$ = 13.2 Hz); 122.6 (d, $J_{C\text{-}F}$ = 2.0 Hz); 125.4; 125.8; 129.0 (dd, $^3J_{C\text{-}F}$ = 10.0 Hz, $^4J_{C\text{-}F}$ = 4.9 Hz) ; 129.6; 134.5; 148.8; 160.81 (dd, ^1J = 251.1 Hz, ^3J = 12.2 Hz ; 163.3 (dd, $^1J_{C\text{-}F}$ = 252.8, $^3J_{C\text{-}F}$ = 12.2 Hz); 170.1 ppm.

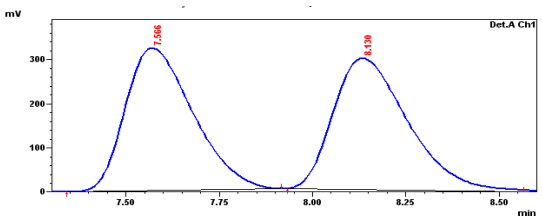
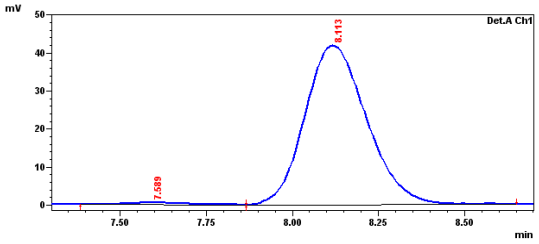
HRMS (ESI^+): Calcd for $C_{14}H_8F_2O_2$ $[M + H]^+$ requires 247.0571; found 247.0569.

- **HPLC Chromatograms - Enantiomer *S***

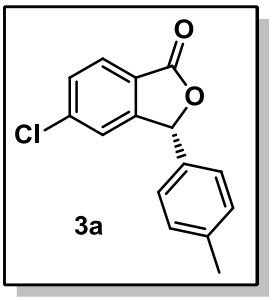
Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	7.675	9.845	**80% *ee***
2	8.196	90.155	

- **After recrystallization - Enantiomer *S***

Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	7.589	1.404	**97% *ee***
2	8.113	98.596	



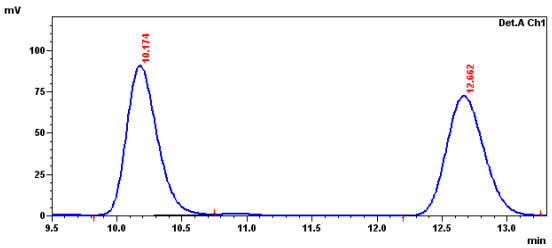
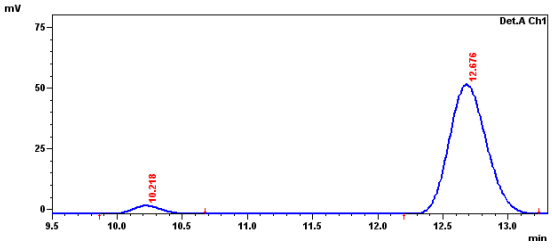
(*R*)-5-chloro-3-(*p*-tolyl)isobenzofuran-1(3*H*)-one $C_{15}H_{11}O_2Cl$ (3a). White solid. ***Rf*** =0.4. **$[\alpha]_D^{20}$** = + 71.50 (*c* = 0.40 in DCM). **Melting point** = 139 – 141 °C. Purified by column chromatography (hexane/EtOAc 85:15) to give the product in 66% yield and 90% *ee*. **HPLC:** (Chiralcel OD-H, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm): t_R (*S*) = 10.21 min, t_R (*R*) = 12.67 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 3H); 6.33 (s, 1H); 7.14 (d, *J* = 8.0 Hz, 2H); 7.20 (d, *J* = 8.0 Hz, 2H), 7.29 - 7.31 (m, 1H) 7.52 (dd, *J* = 8.2 Hz, J = 1.7 Hz, 1H); 7.88 (d, *J* = 8.2 Hz, 1H) ppm.

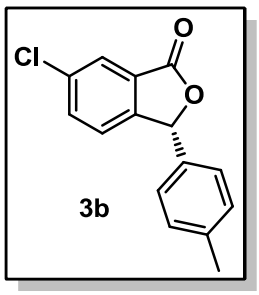
^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2; 82.1; 123.2; 124.1; 126.7; 126.9; 129.7; 130.1; 132.6; 139.6; 141.0; 151.4; 169.3 ppm.

HRMS (ESI^+): Calcd for $C_{15}H_{11}ClO_2$ $[M + H]^+$ requires 259.0526; found 259.0522. $[M + H - CH_3]^+$ requires 245.0369; found 245.0360.

- **HPLC Chromatograms - Enantiomer *R***

Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	10.218	5.081	**90% *ee***
2	12.676	94.919	



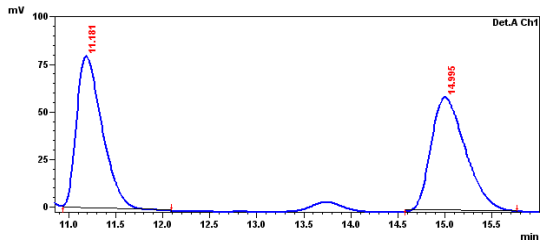
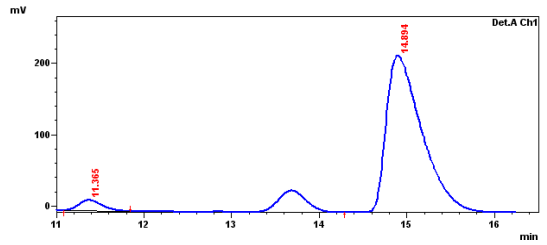
(*R*)-6-chloro-3-(*p*-tolyl)isobenzofuran-1(3*H*)-one $C_{15}H_{11}O_2Cl$ (3b). White solid. ***Rf*** = 0.4. $[\alpha]_D^{20}$ = - 4.07 (*c* = 0.59 in DCM). **Melting point** = 121 - 124 °C. Purified by column chromatography (hexane/EtOAc 85:15) to give the product in 63% yield and 92% *ee*. **HPLC:** (Chiralcel OD-H, hexane/i-PrOH = 85/15, flow rate = 0.8 mL/min, λ = 254 nm): t_R (*S*) = 11.36 min, t_R (*R*) = 14.89 min.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 2.35 (s, 3H); 6.35 (s, 1H); 7.13 (d, *J* = 8.1 Hz, 2H); 7.19 (d, *J* = 8.1 Hz, 2H); 7.26 (d, *J* = 1.7 Hz, 1H); 7.60 (dd, *J* = 8.2 Hz, *J* = 1.8 Hz, 1H); 7.91 (d, *J* = 1.8 Hz, 1H) ppm.

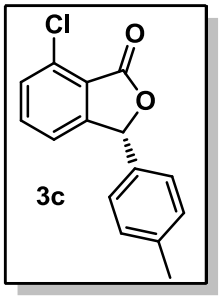
^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 21.2; 82.6; 124.1; 125.4; 127.0; 127.5; 129.7; 132.7; 134.5; 135.6; 139.6; 147.9; 169.0 ppm.

HRMS (ESI$^+$): Calcd for $C_{15}H_{11}ClO_2$: $[M + H]^+$ requires 259.0526; found 259.0527. $[M + H - CH_3]^+$ requires 245.0369; found 245.0371.

- **HPLC Chromatograms - Enantiomer *R***

• Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	11.365	4.039	**92% *ee***
2	14.894	95.961	



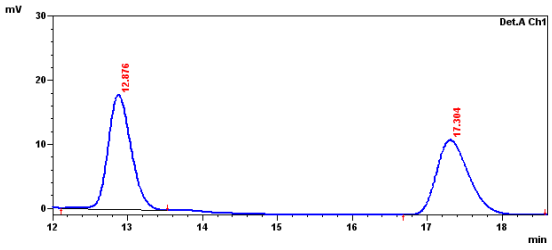
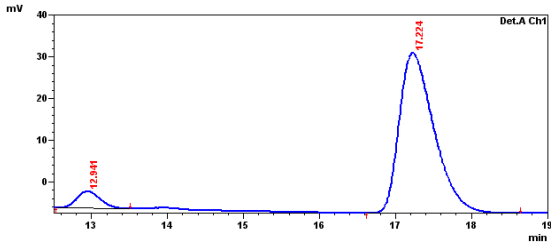
(*R*)-7-chloro-3-(*p*-tolyl)isobenzofuran-1(3*H*)-one $C_{15}H_{11}O_2Cl$ (3c). White solid. ***Rf*** = 0.3. **$[\alpha]_D^{20}$** = - 109.70 (*c* = 0.85 in DCM). **Melting point** = 97 - 100 °C. Purified by column chromatography (hexane/EtOAc 85:15) to give the product in 70% yield and 87% *ee*. **HPLC:** (Chiralcel OD-H, hexane/i-PrOH = 85/15, flow rate = 0.8 mL/min, λ = 254 nm): t_R (*S*) = 12.94 min, t_R (*R*) = 17.22 min.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 2.35 (s, 3H); 6.30 (s, 1H); 7.14 (d, *J* = 8.2 Hz, 2H); 7.18 – 7.21 (m, 3H); 7.48 (d, *J* = 7.8 Hz, 1H); 7.55 (t, *J* = 7.7 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 21.1; 81.3; 121.3; 122.2; 126.9; 129.6; 130.5; 132.8; 133.0; 135.1; 152.1; 139.5; 167.3 ppm.

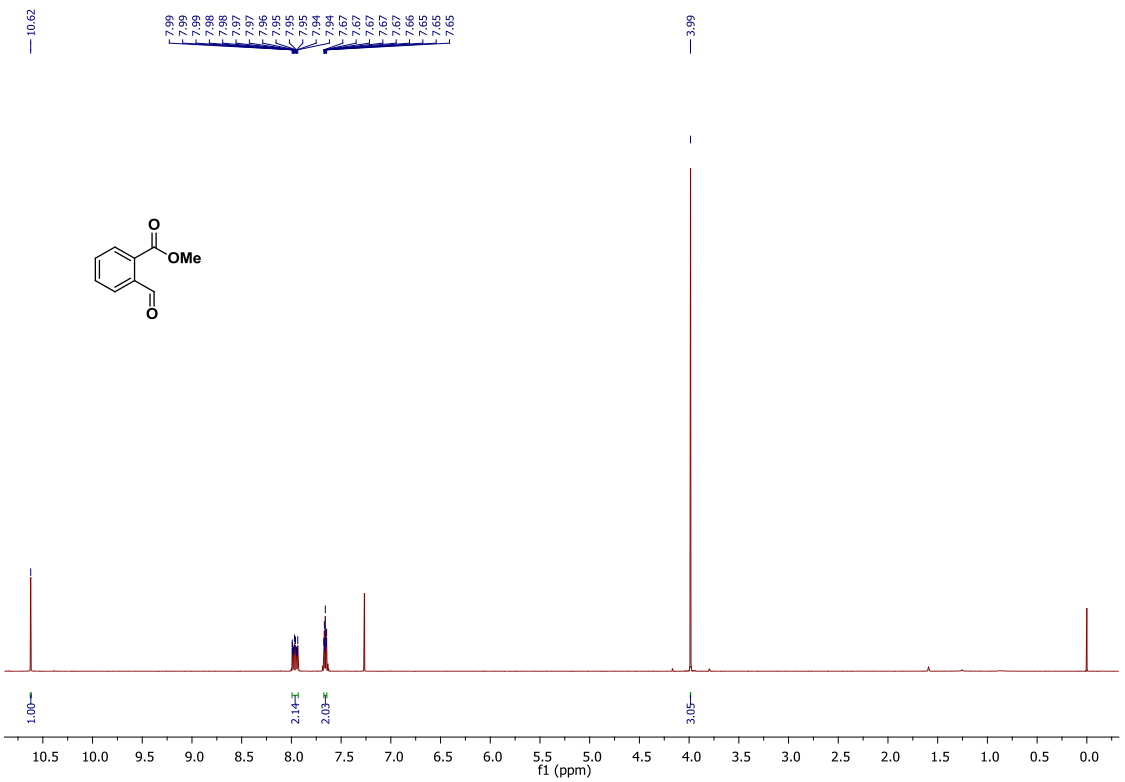
HRMS (ESI^+): Calcd for $C_{15}H_{11}ClO_2$ $[M + H]^+$ requires 259.0526; found 259.0520. $[M + H - CH_3]^+$ requires 245.0369; found 245.0361.

- **HPLC Chromatograms - Enantiomer *R***

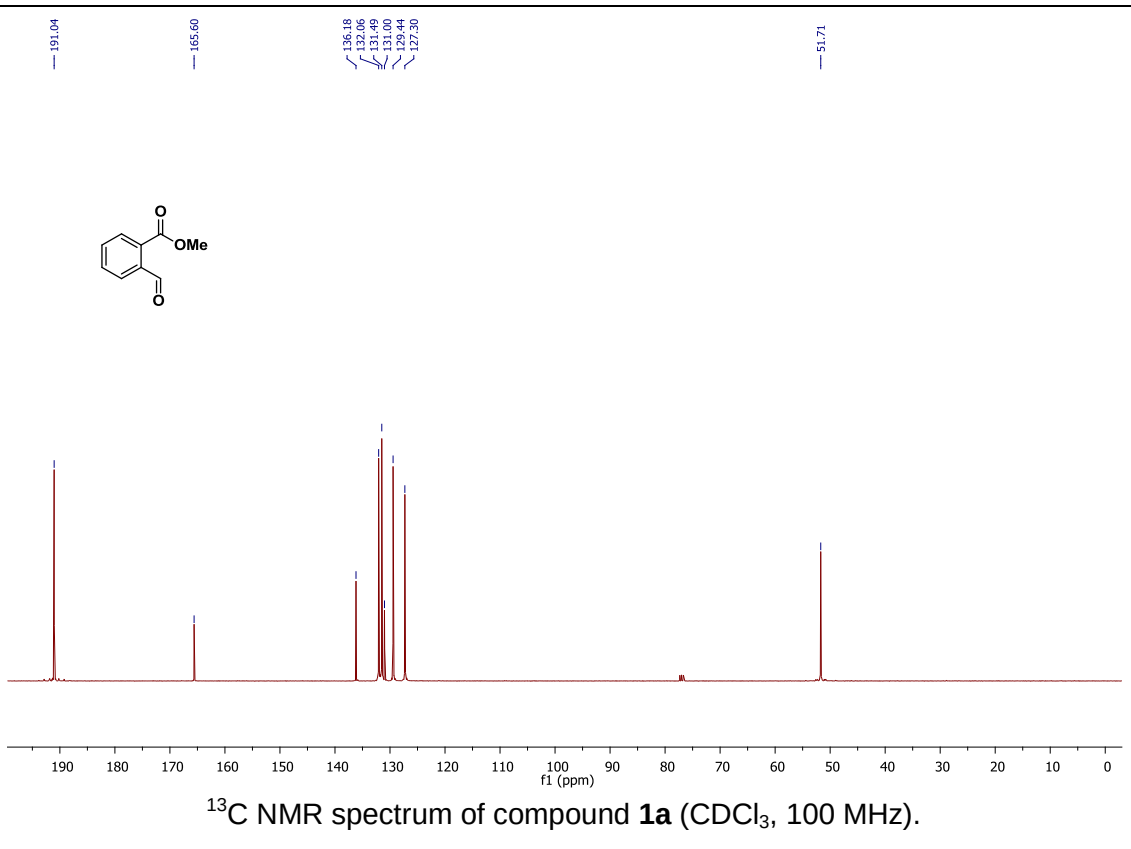
Racemic Standard	Catalytic Reaction Product
	

Peak	Retention time (min)	Area (%)	
1	12.941	6.677	**87% *ee***
2	17.224	93.323	

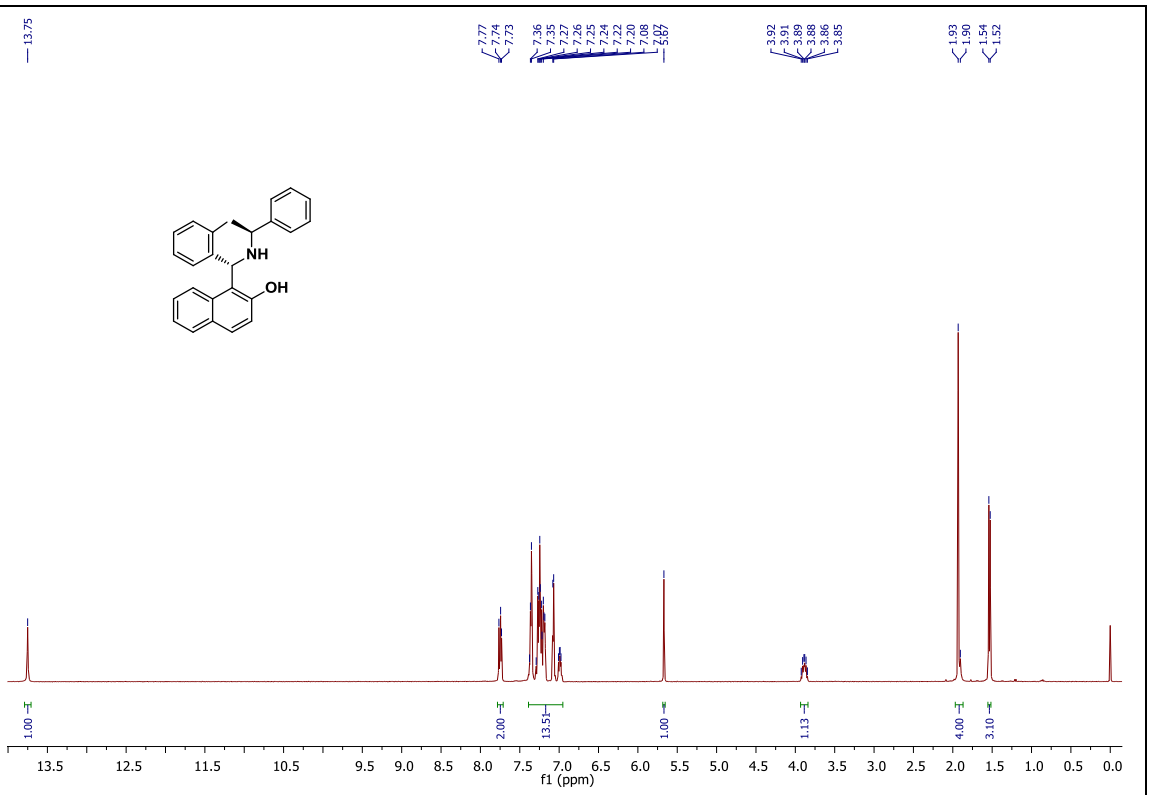
5. NMR Spectra



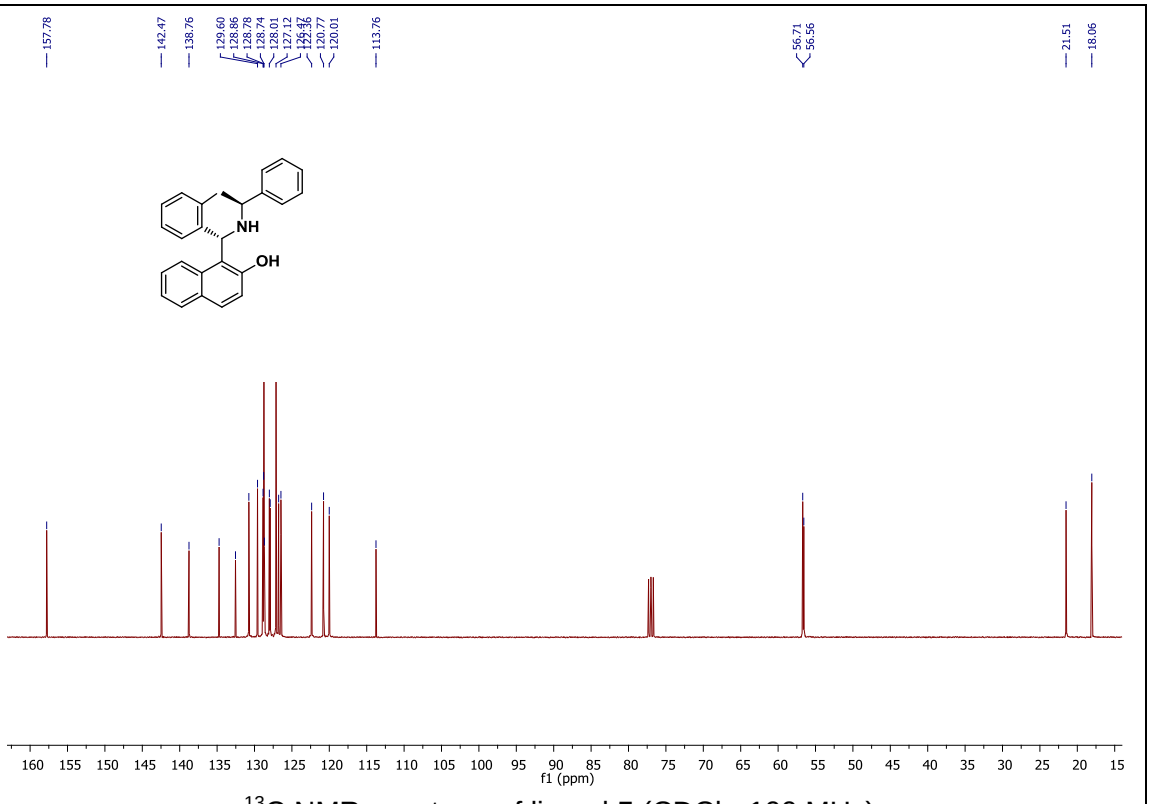
^{1}H NMR spectrum of compound **1a** ($CDCl_3$, 400 MHz).



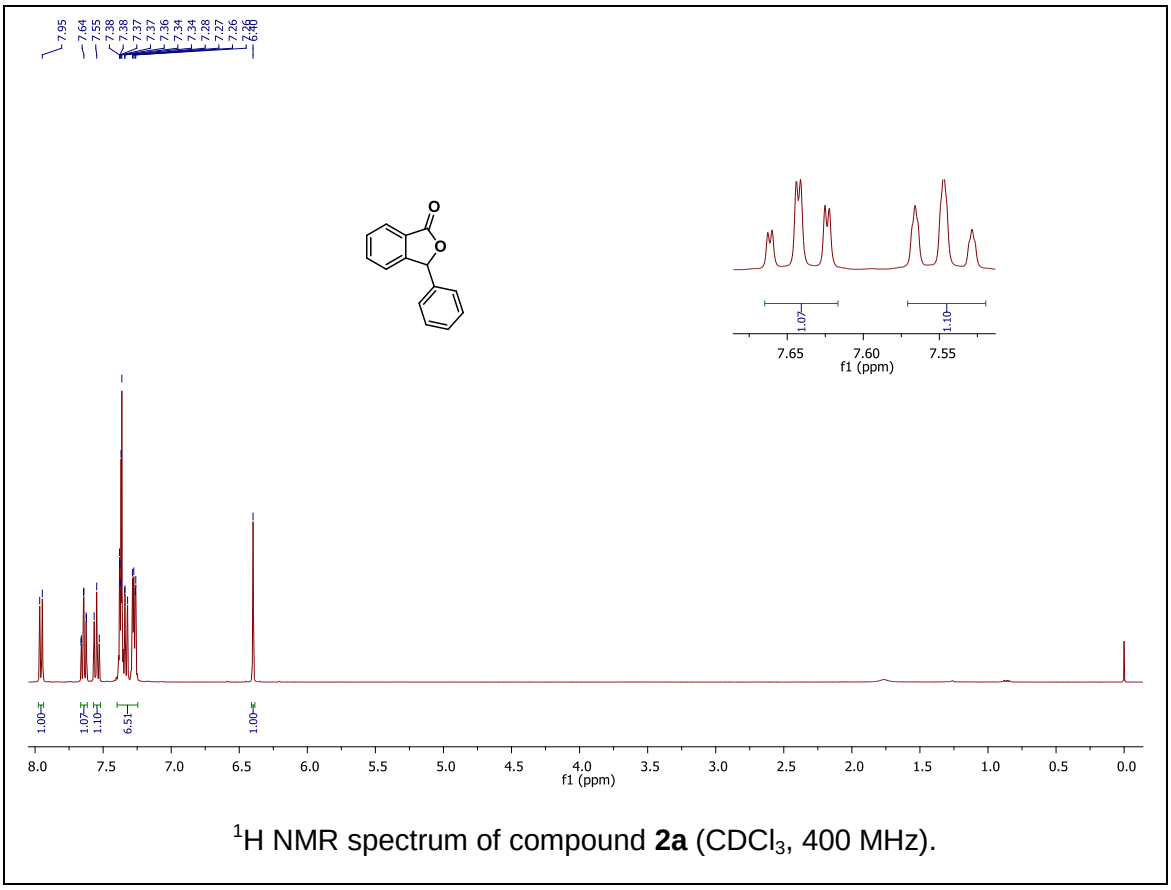
^{13}C NMR spectrum of compound **1a** ($CDCl_3$, 100 MHz).



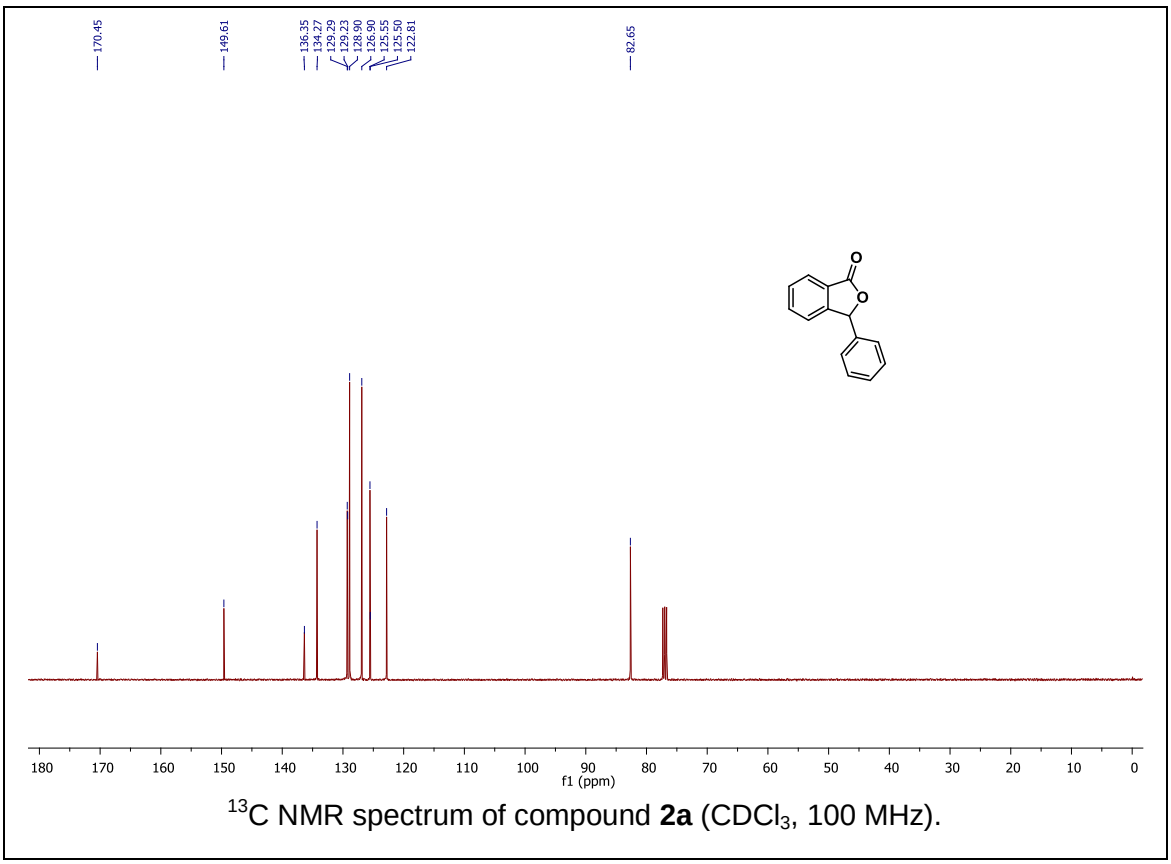
^{1}H NMR spectrum of ligand **L5** ($CDCl_3$, 400 MHz).



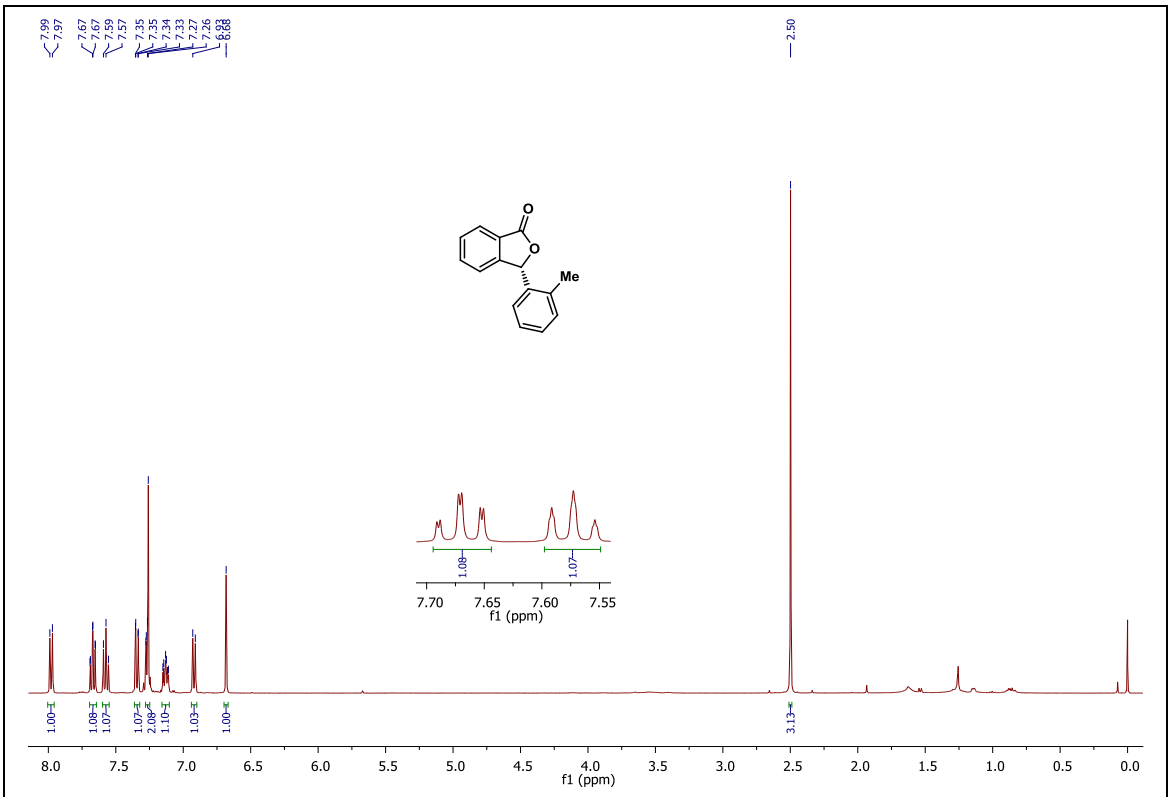
^{13}C NMR spectrum of ligand **5** ($CDCl_3$, 100 MHz).



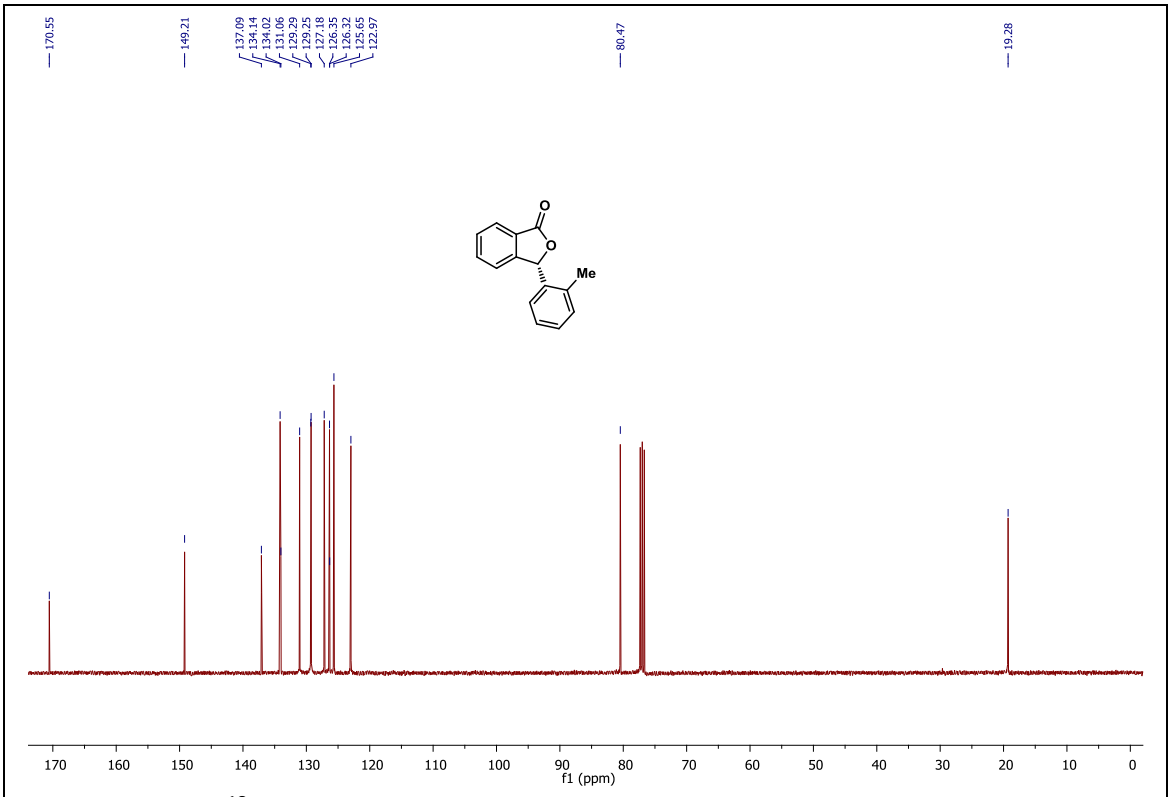
^{1}H NMR spectrum of compound **2a** ($CDCl_3$, 400 MHz).



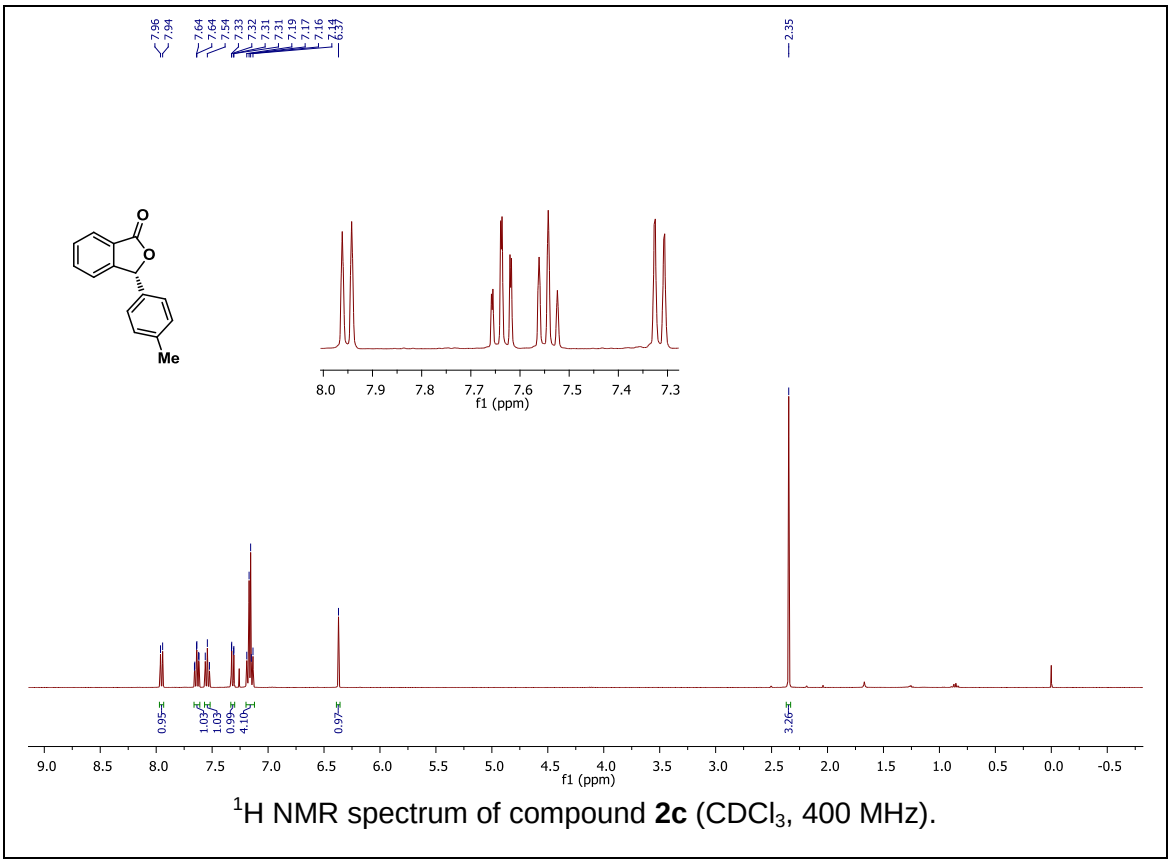
^{13}C NMR spectrum of compound **2a** ($CDCl_3$, 100 MHz).



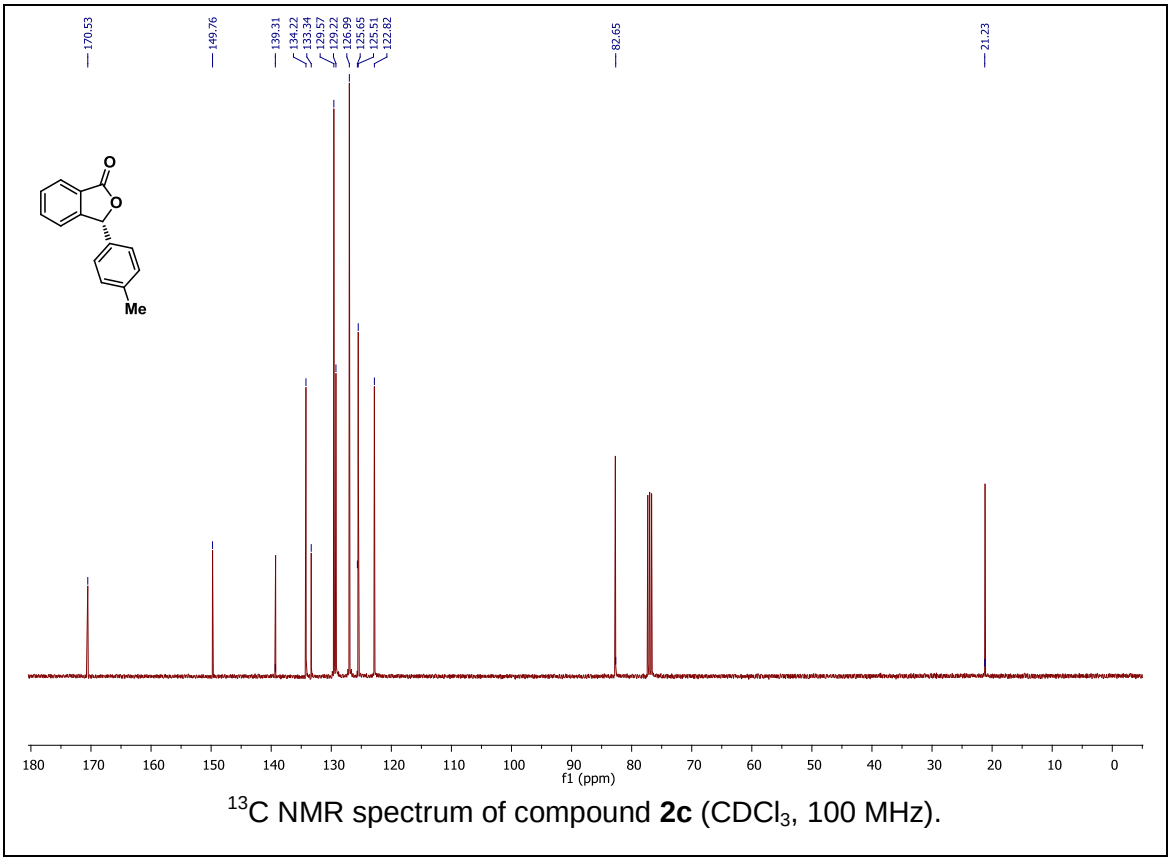
^{1}H NMR spectrum of compound **2b** ($CDCl_3$, 400 MHz).



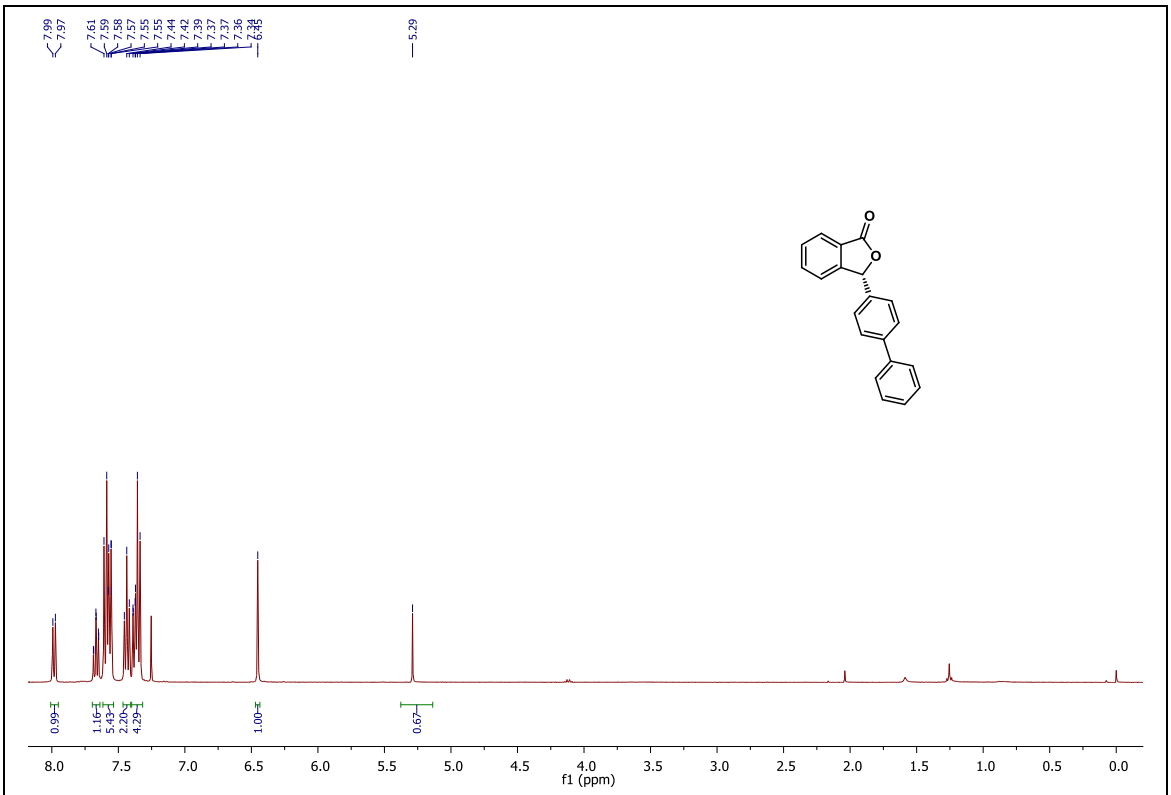
^{13}C NMR spectrum of compound **2b** ($CDCl_3$, 100 MHz).



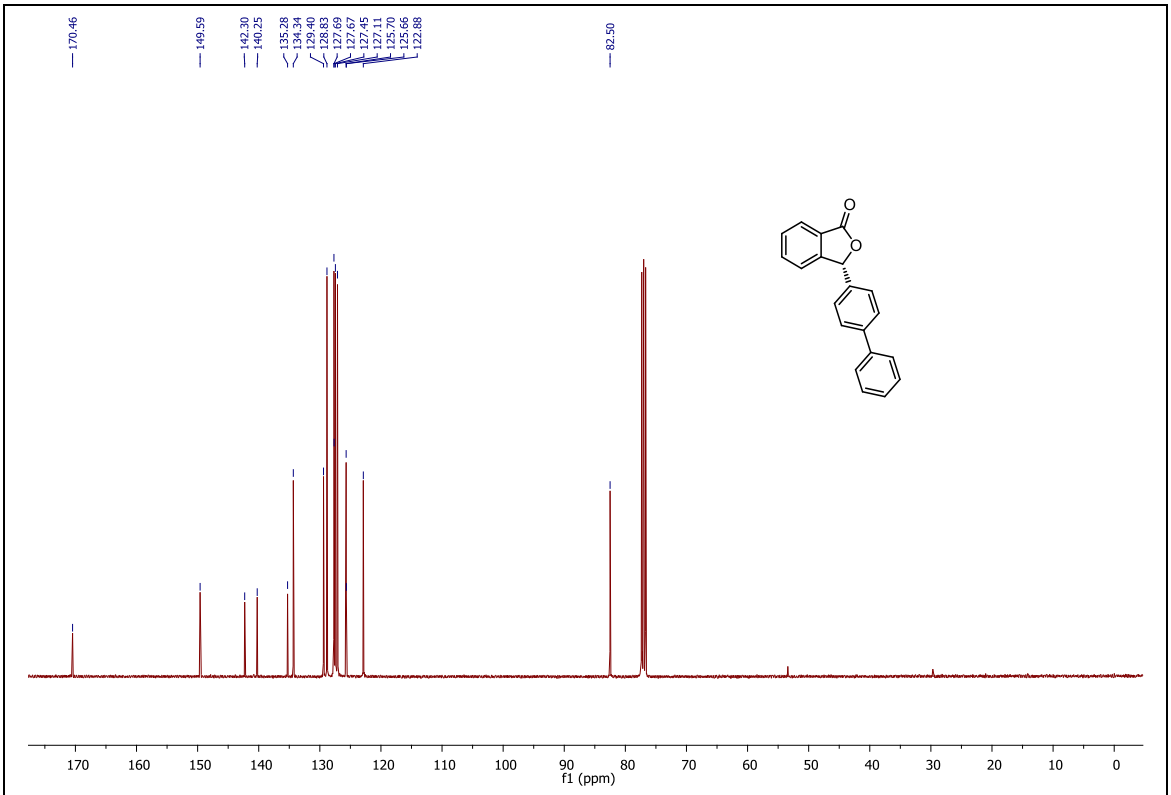
^{1}H NMR spectrum of compound **2c** ($CDCl_3$, 400 MHz).



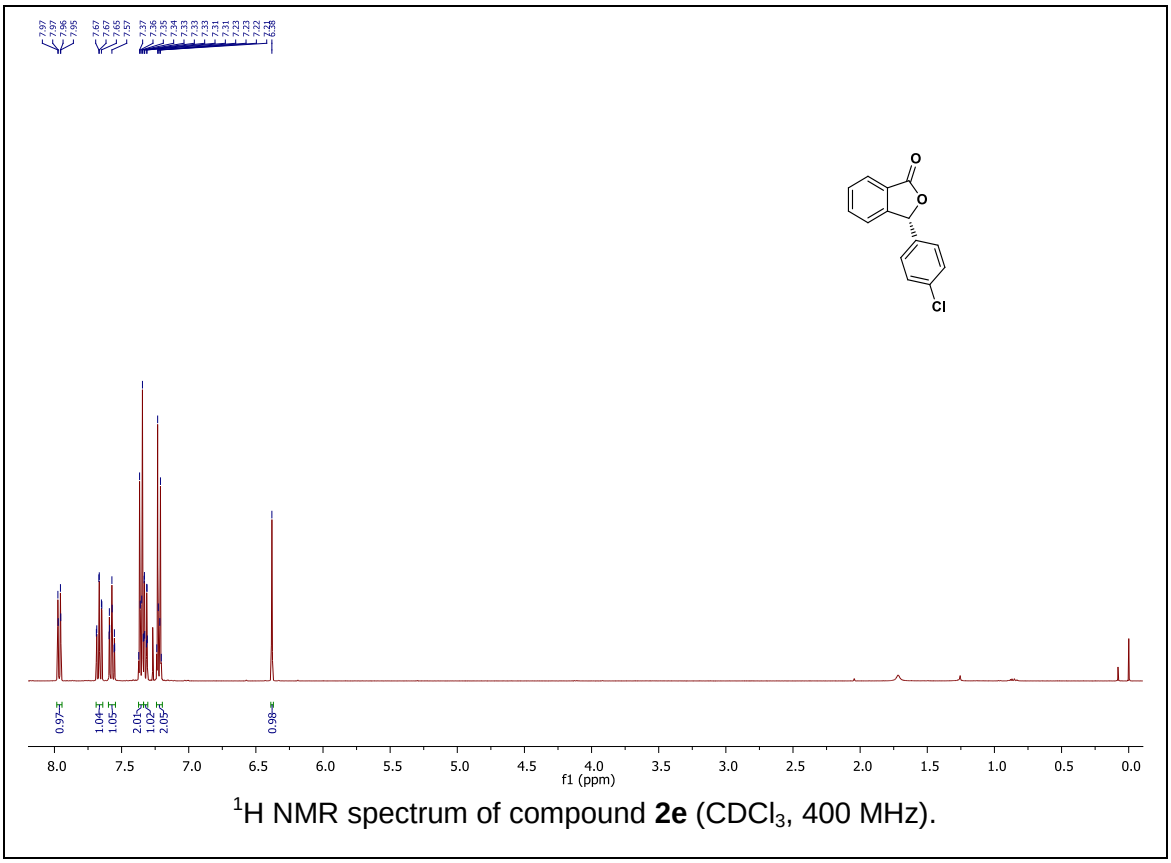
^{13}C NMR spectrum of compound **2c** ($CDCl_3$, 100 MHz).



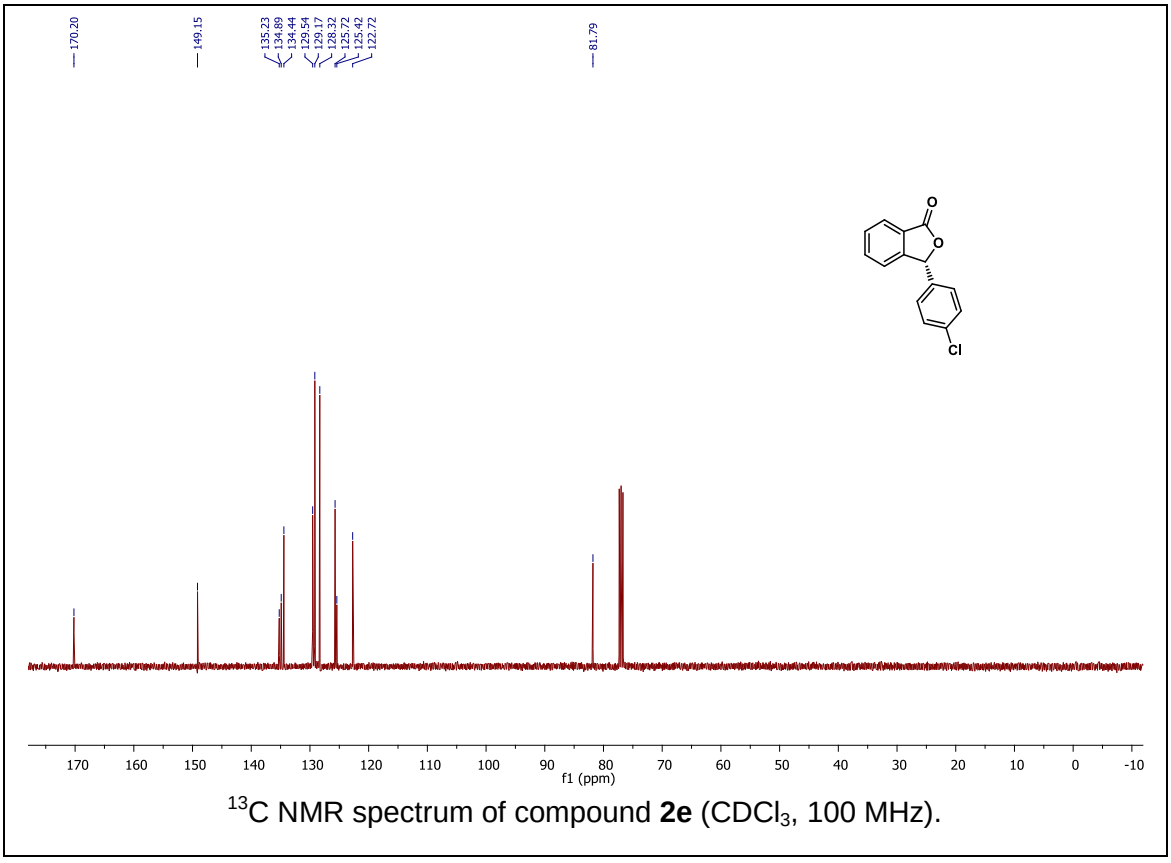
^{1}H NMR spectrum of compound **2d** ($CDCl_3$, 400 MHz).



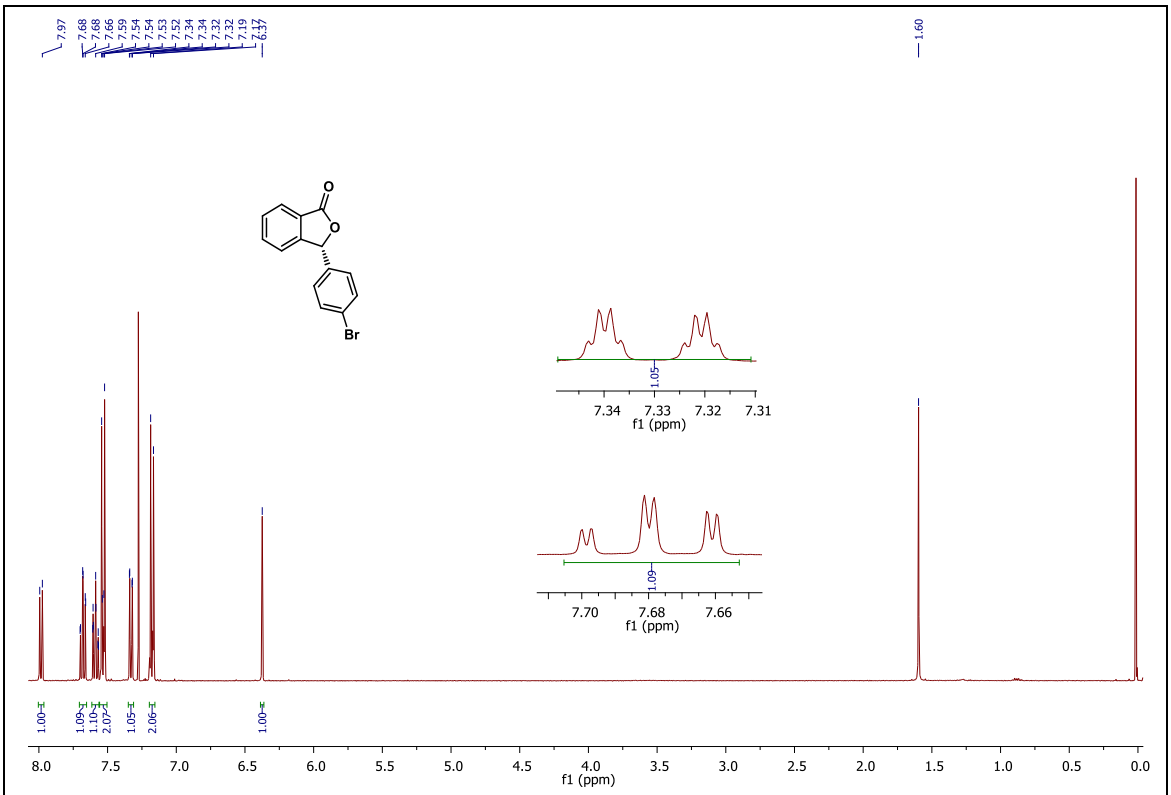
^{13}C NMR spectrum of compound **2d** ($CDCl_3$, 100 MHz).



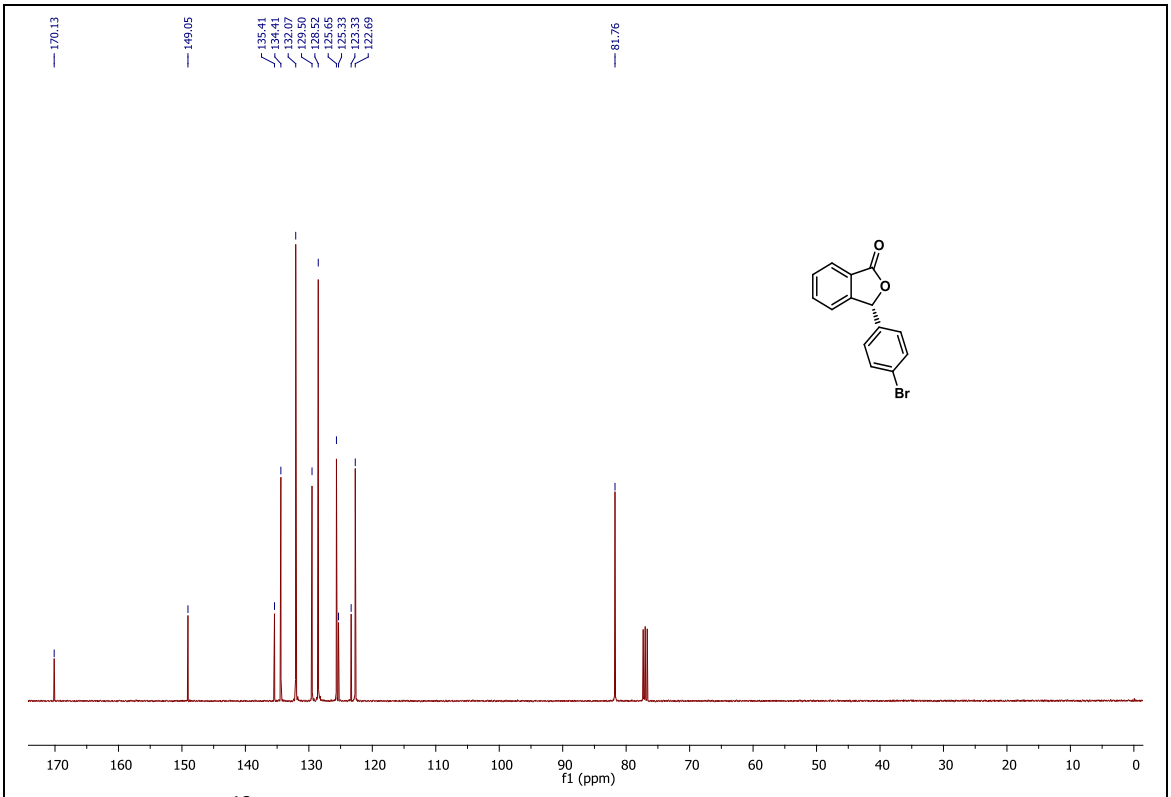
^{1}H NMR spectrum of compound **2e** ($CDCl_3$, 400 MHz).



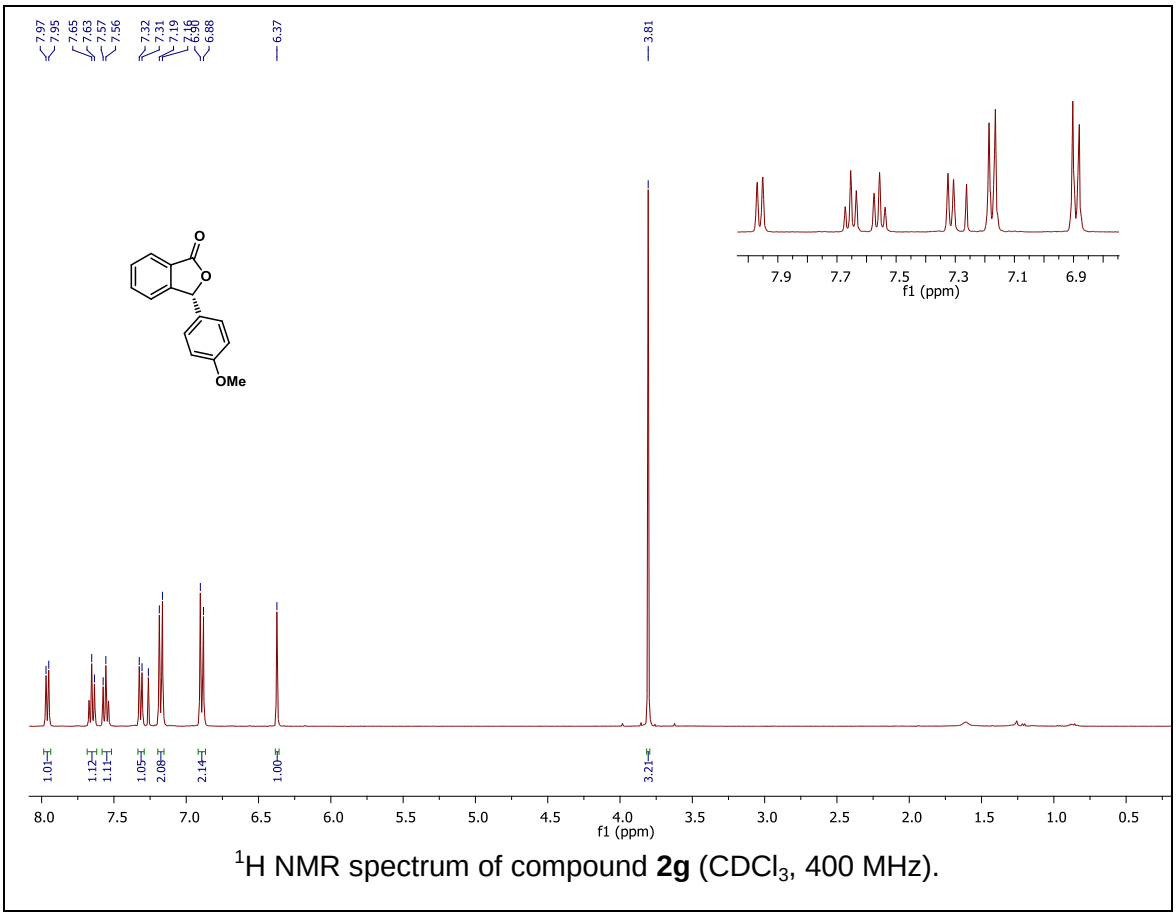
^{13}C NMR spectrum of compound **2e** ($CDCl_3$, 100 MHz).



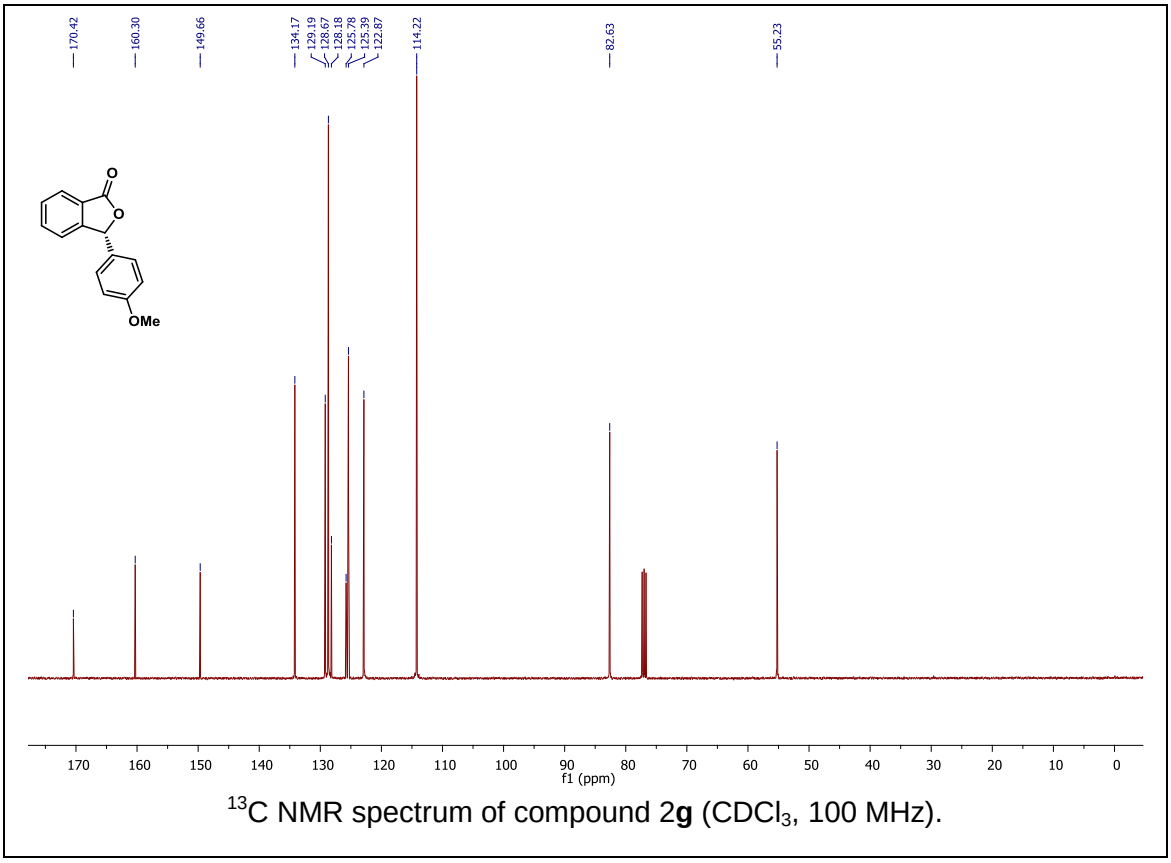
^{1}H NMR spectrum of compound **2f** ($CDCl_3$, 400 MHz).



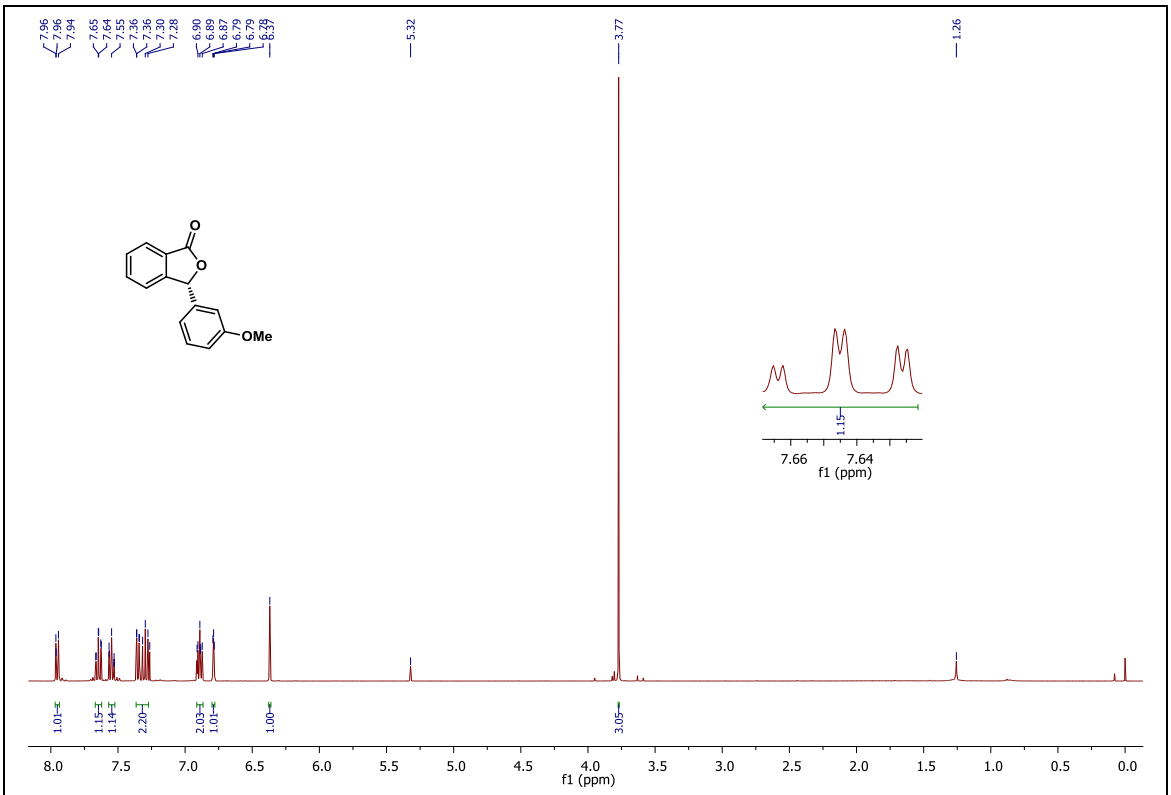
^{13}C NMR spectrum of compound **2f** ($CDCl_3$, 100 MHz).



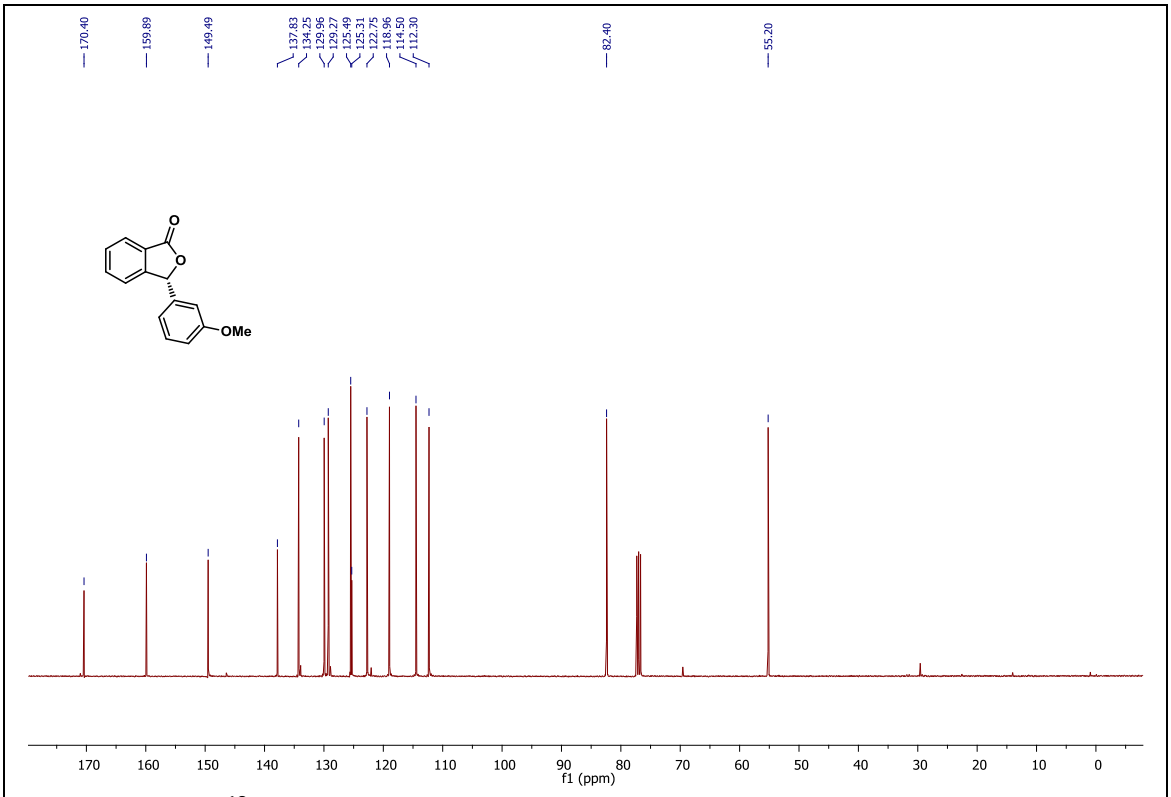
^{1}H NMR spectrum of compound **2g** ($CDCl_3$, 400 MHz).



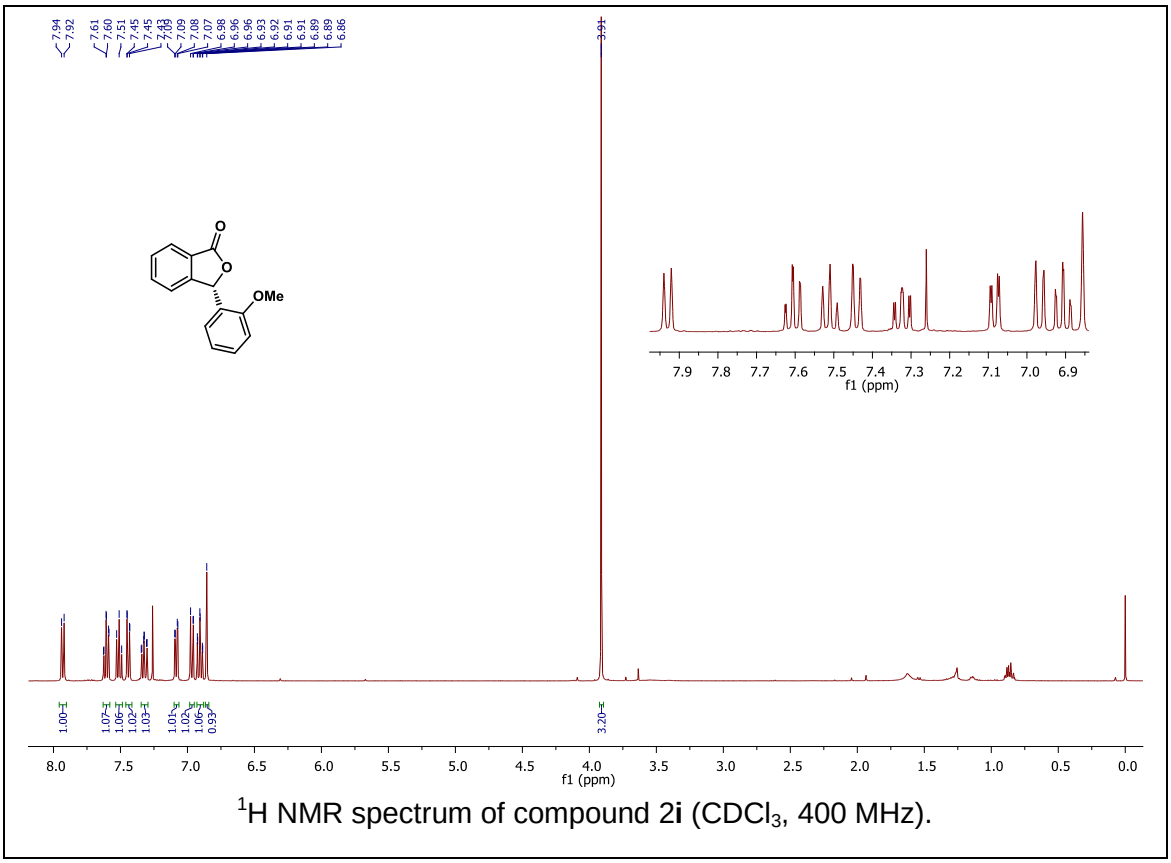
^{13}C NMR spectrum of compound 2**g** ($CDCl_3$, 100 MHz).



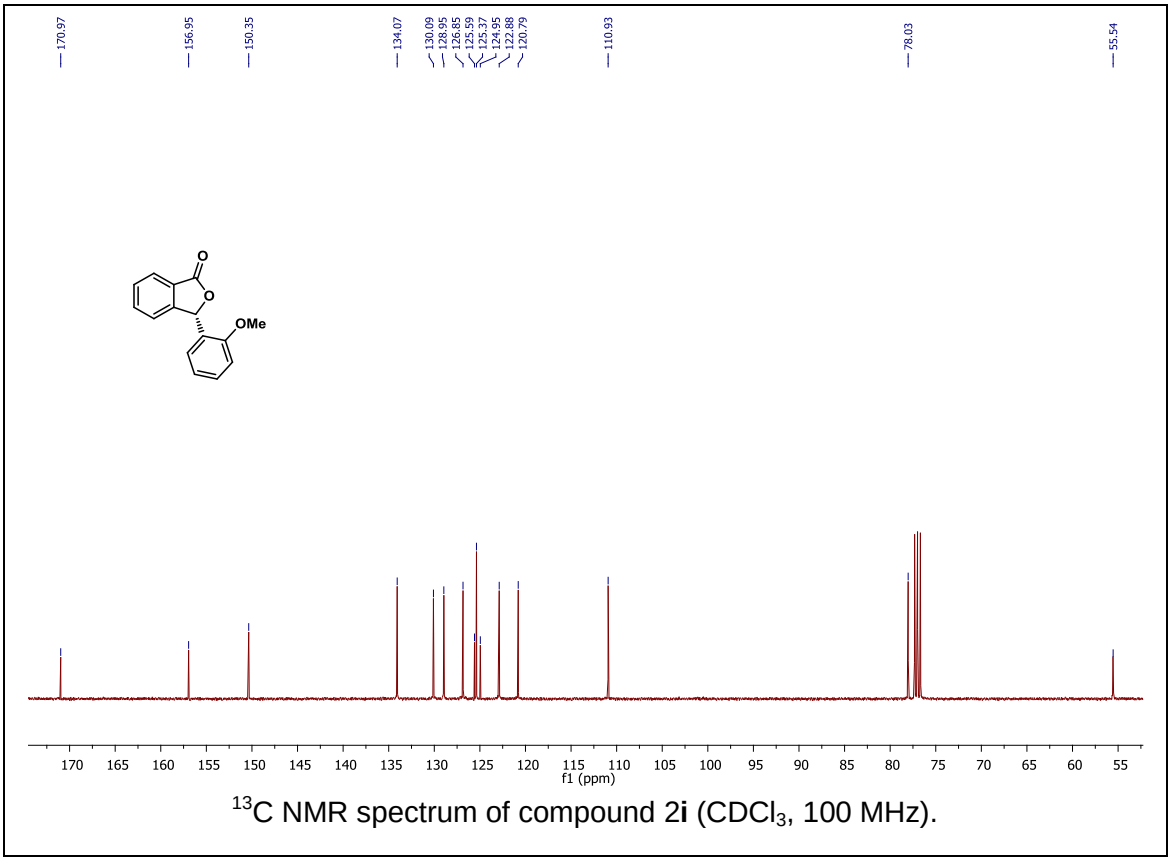
^{1}H NMR spectrum of compound 2**h** ($CDCl_3$, 400 MHz).



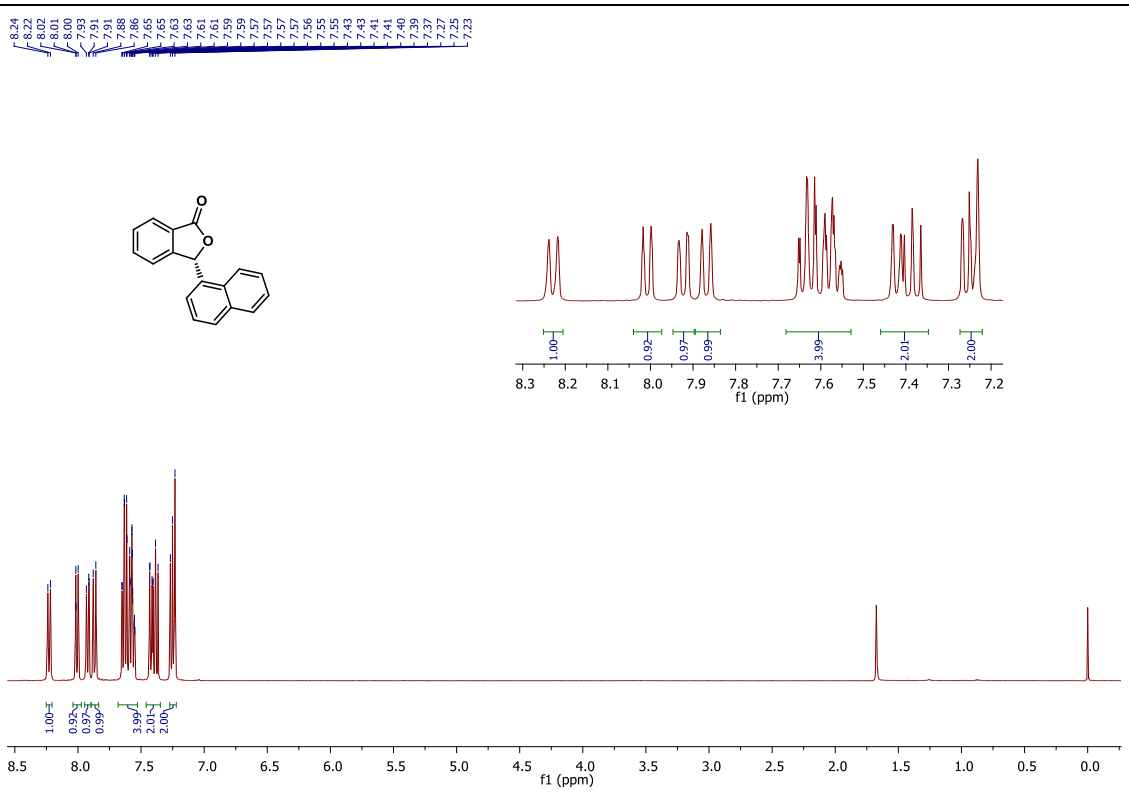
^{13}C NMR spectrum of compound 2**h** ($CDCl_3$, 100 MHz).



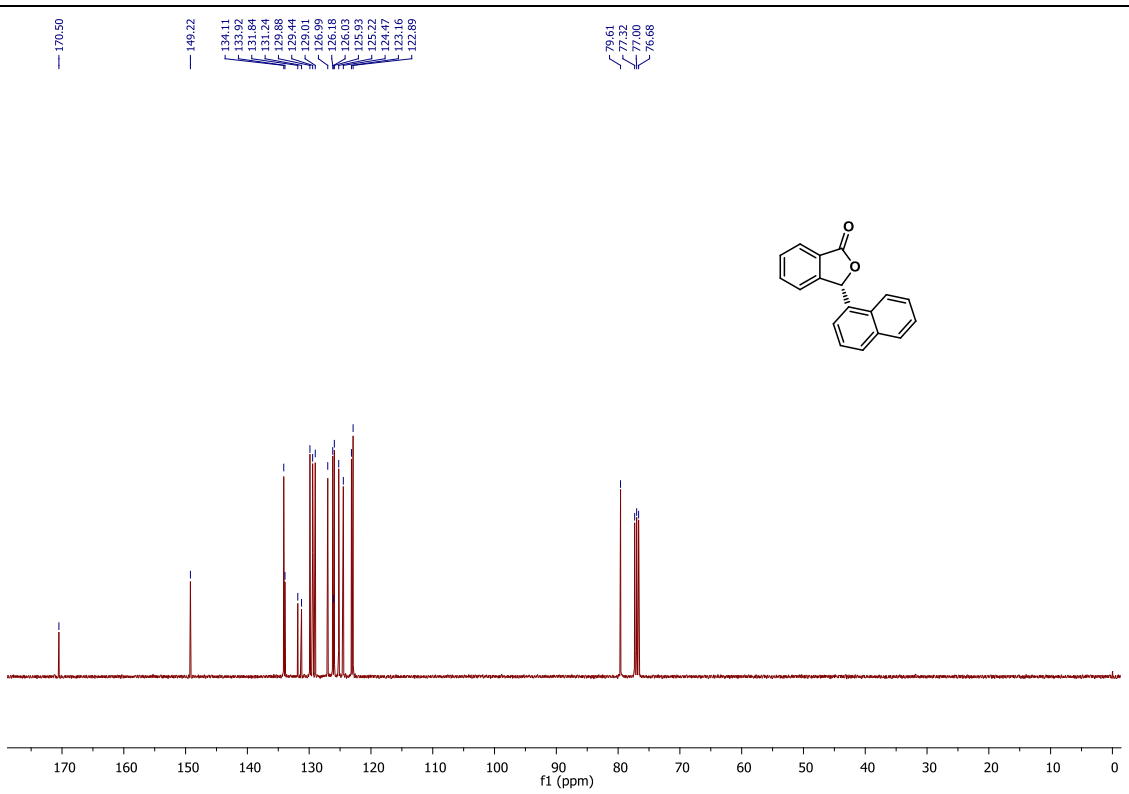
^{1}H NMR spectrum of compound 2**i** ($CDCl_3$, 400 MHz).



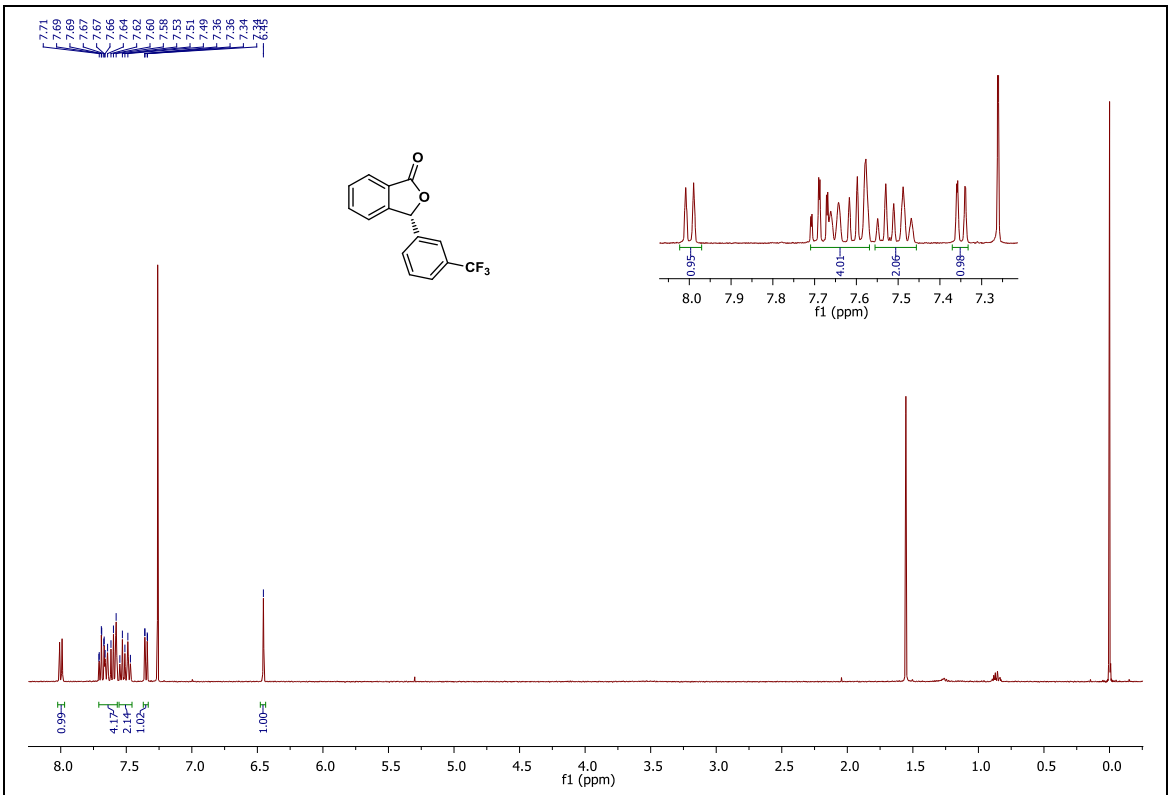
^{13}C NMR spectrum of compound 2**i** ($CDCl_3$, 100 MHz).



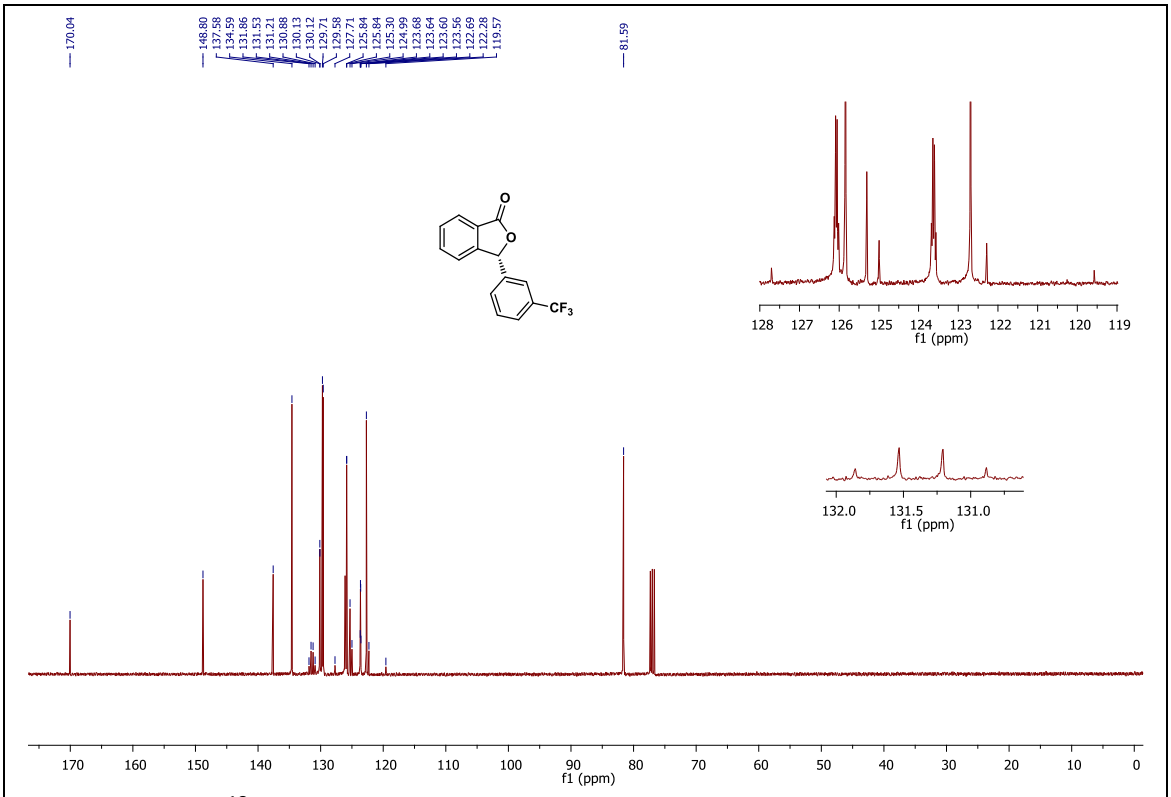
^{1}H NMR spectrum of compound **2j** ($CDCl_3$, 400 MHz).



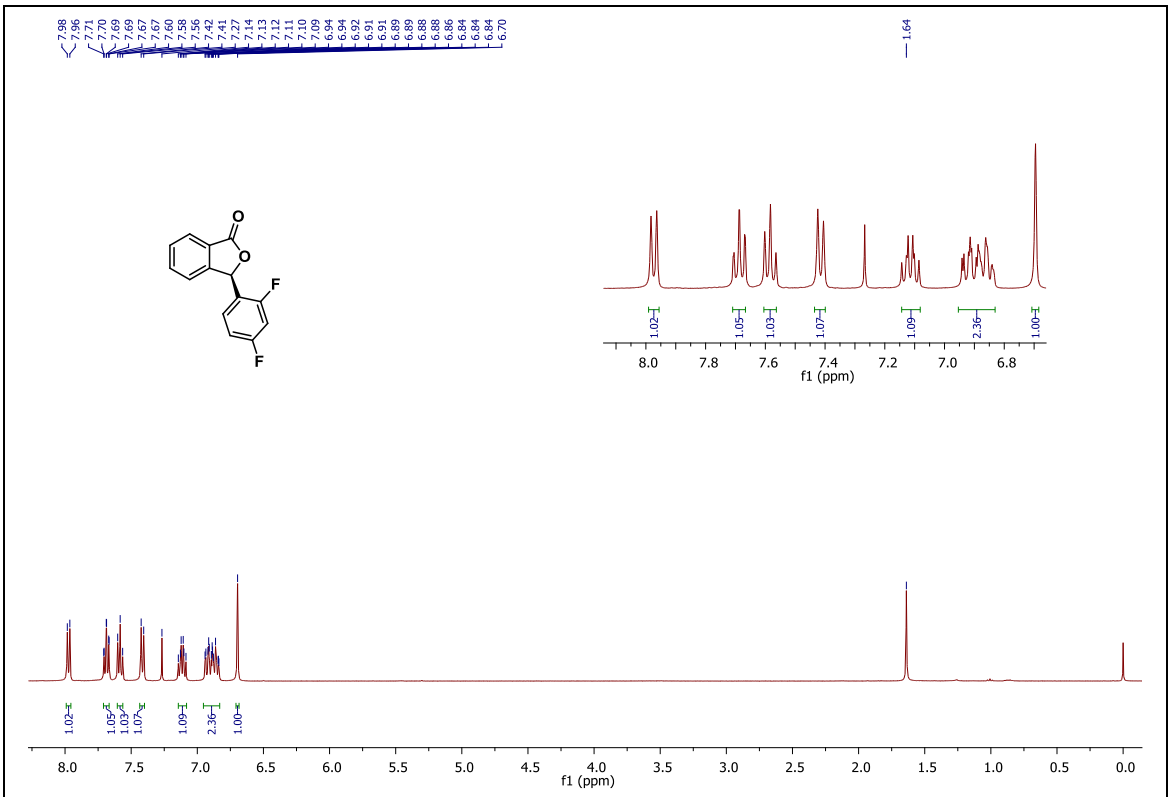
^{13}C NMR spectrum of compound **2j** ($CDCl_3$, 100 MHz).



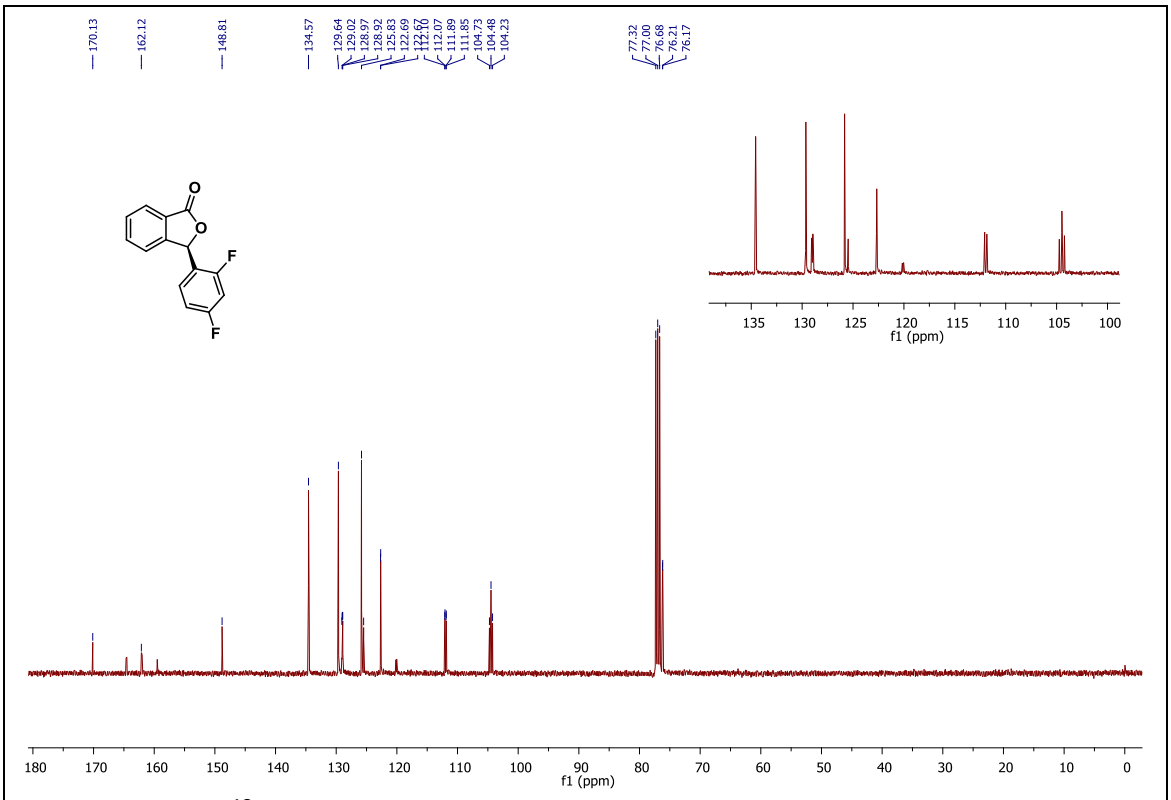
^{1}H NMR spectrum of compound 2**k** ($CDCl_3$, 400 MHz).



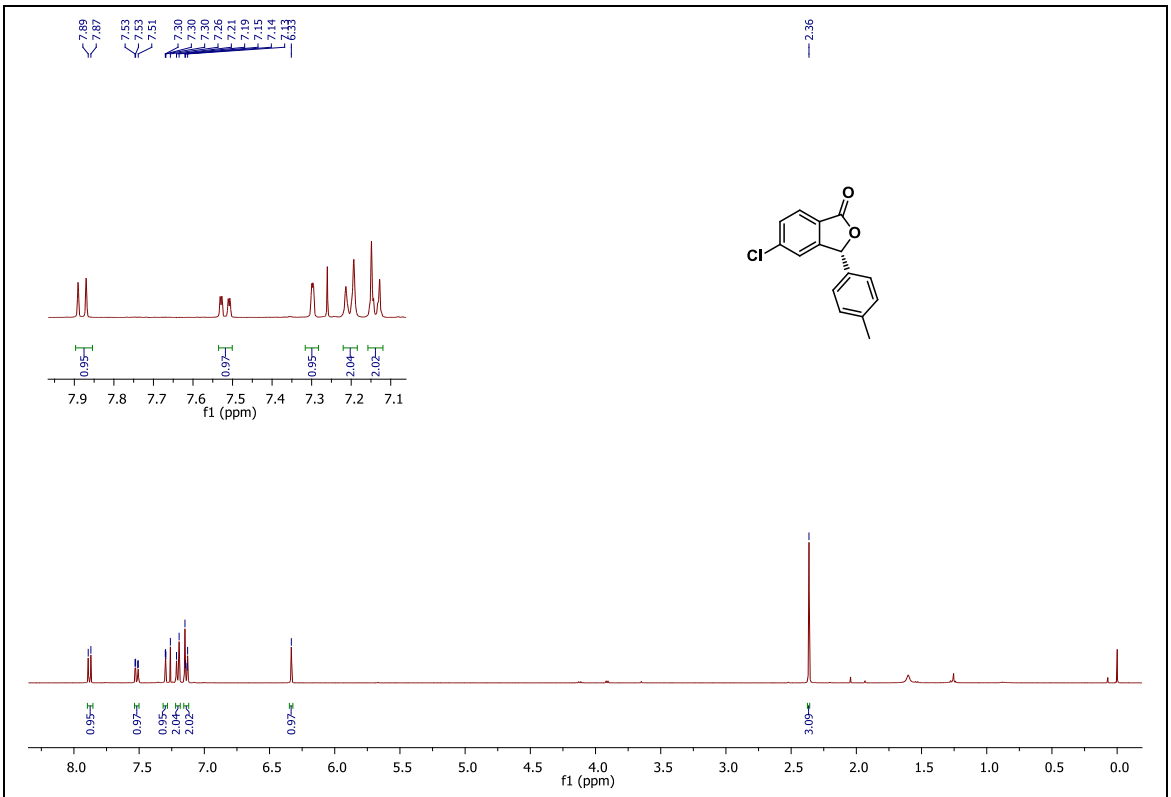
^{13}C NMR spectrum of compound 2**k** ($CDCl_3$, 100 MHz).



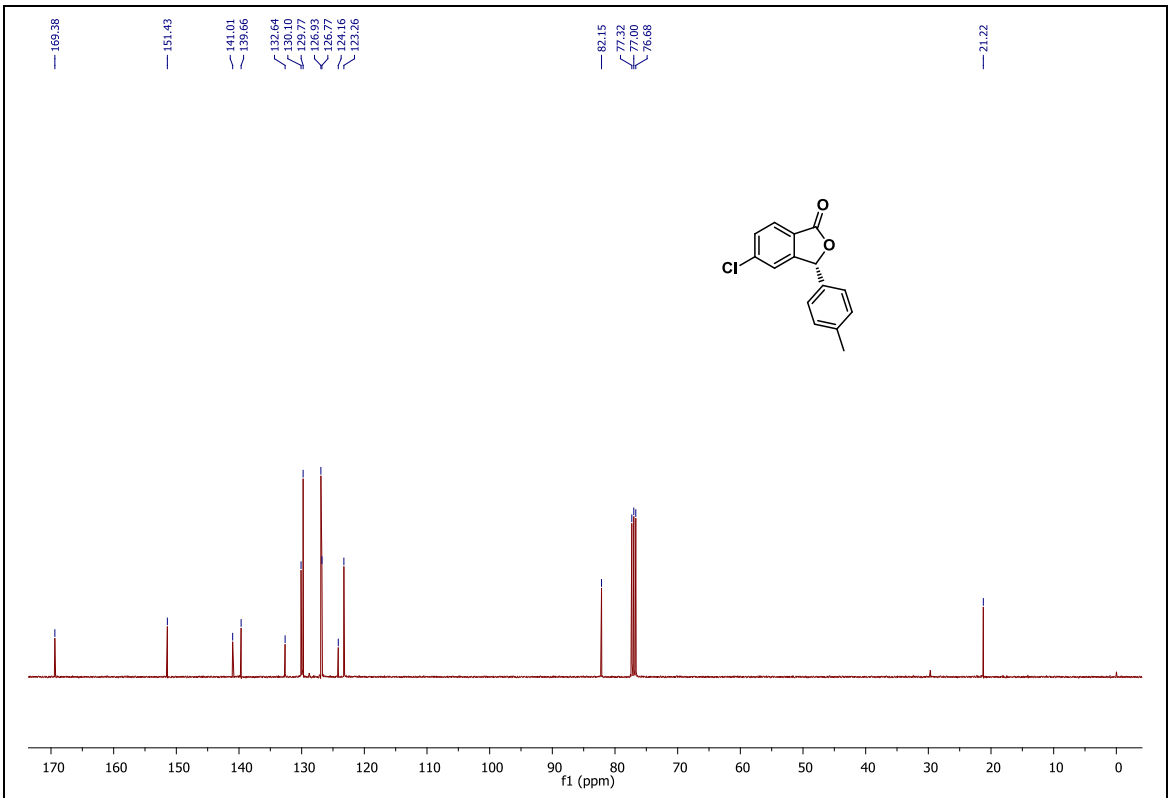
^{1}H NMR spectrum of compound **2l** ($CDCl_3$, 400 MHz).



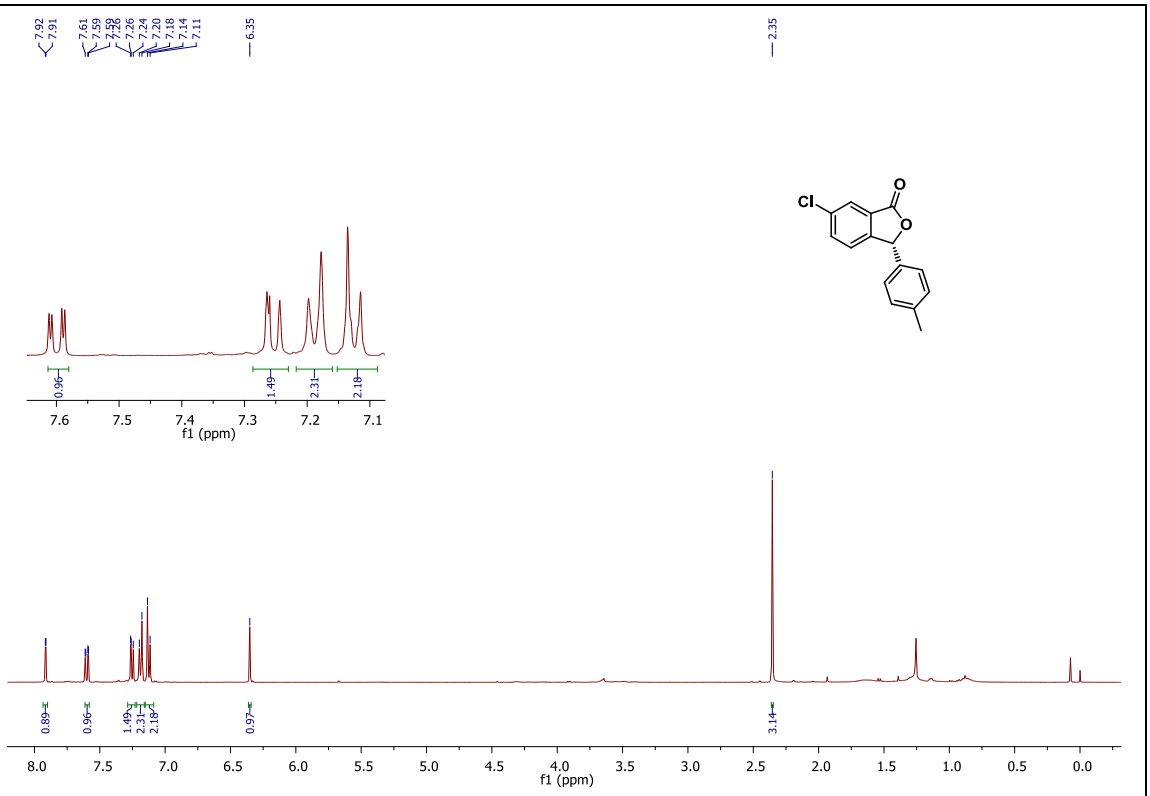
^{13}C NMR spectrum of compound **2l** ($CDCl_3$, 100 MHz).



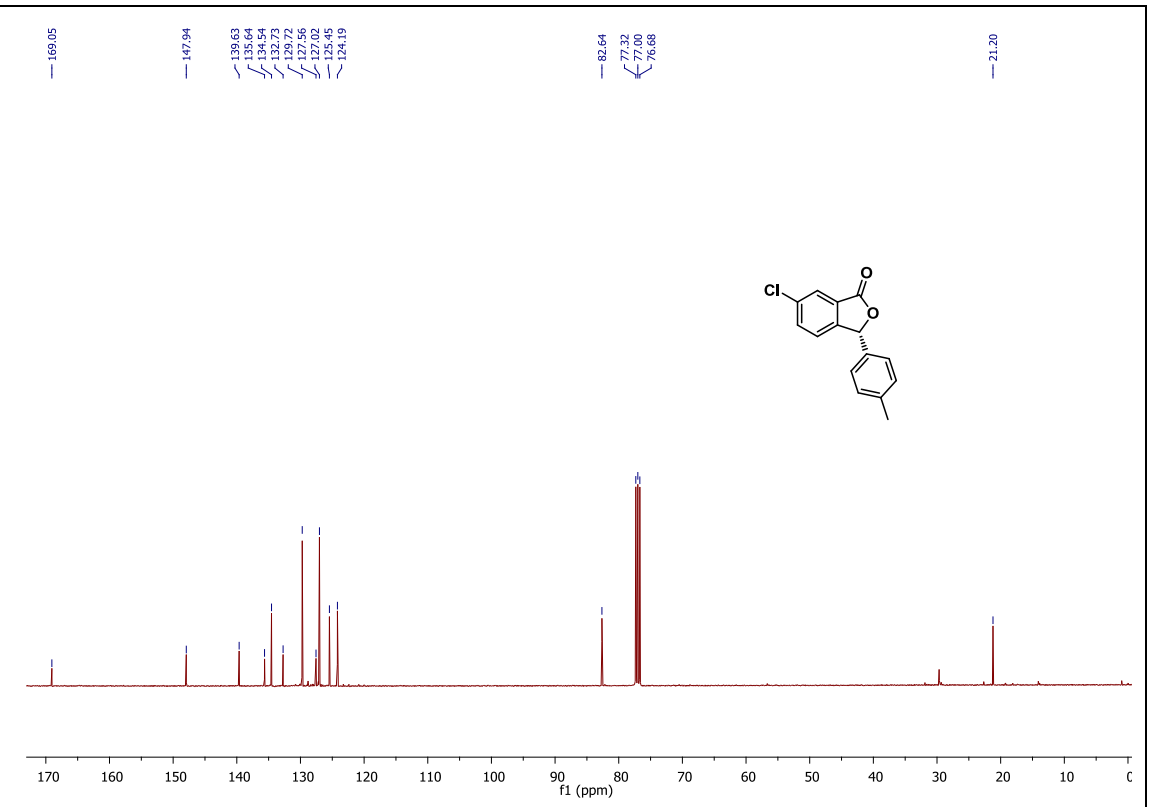
^{1}H NMR spectrum of compound **3a** ($CDCl_3$, 400 MHz).



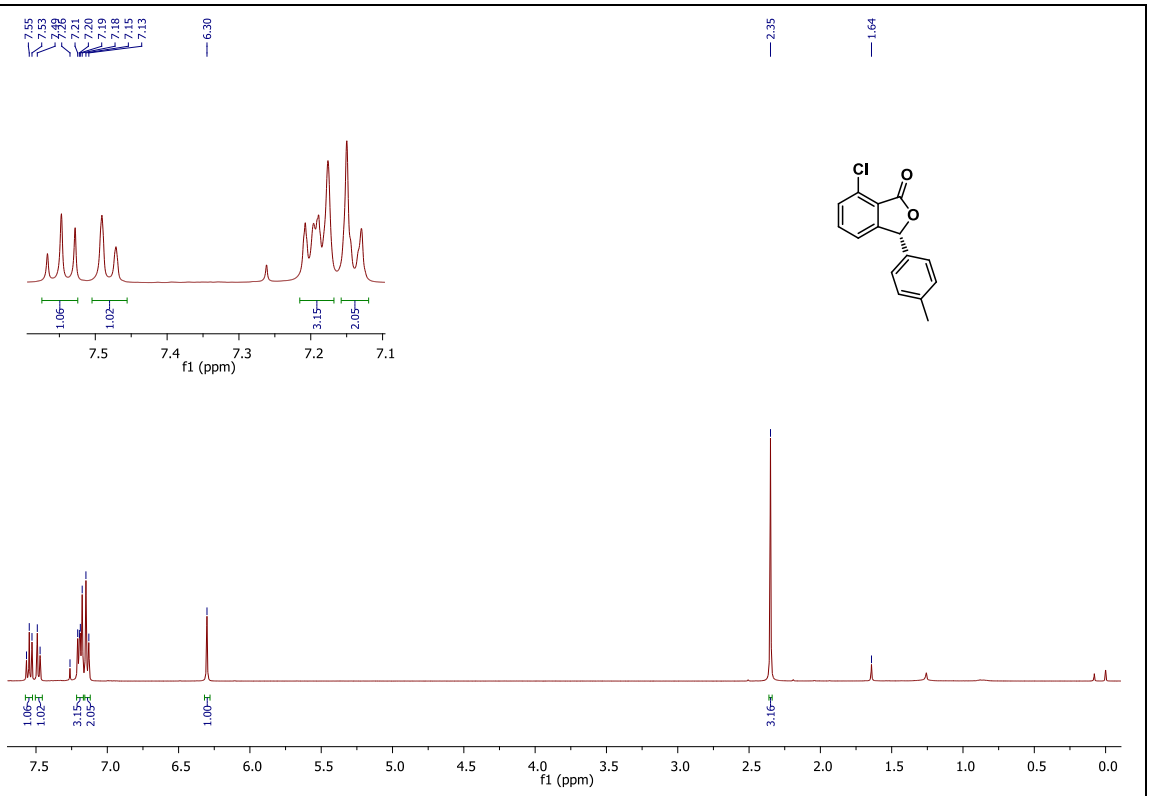
^{13}C NMR spectrum of compound **3a** ($CDCl_3$, 100 MHz).



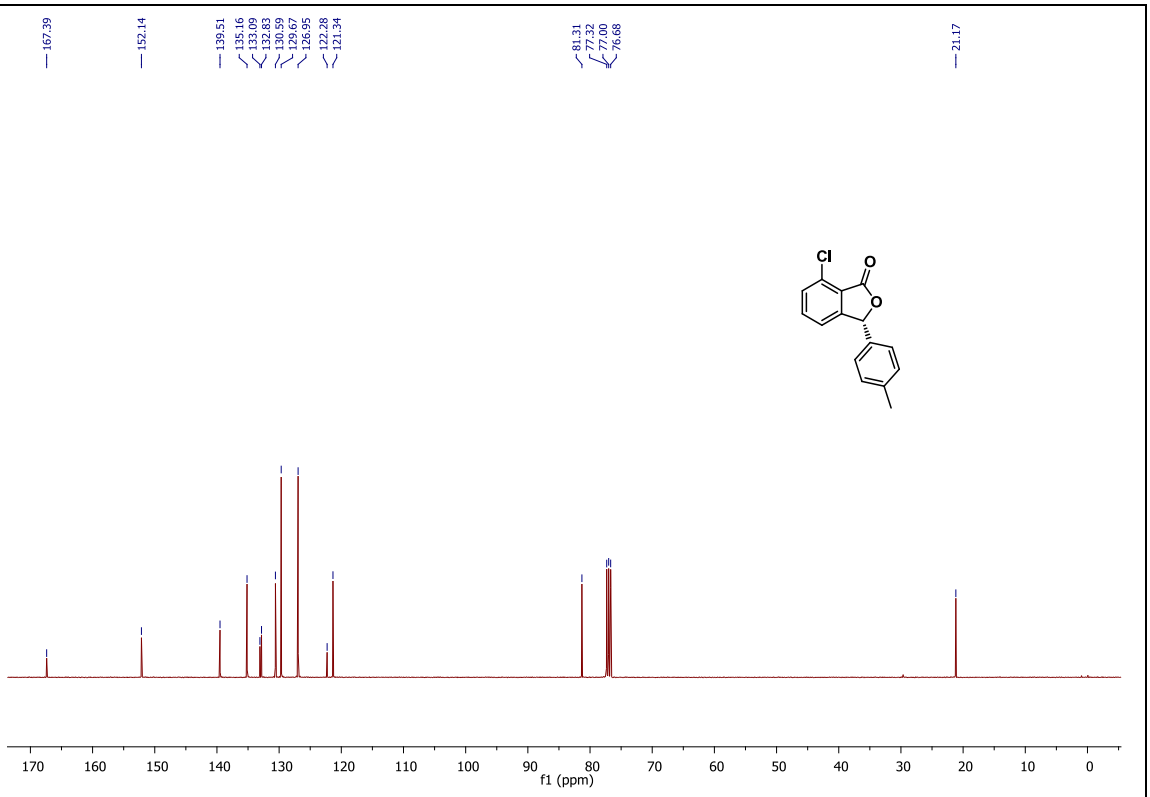
^{1}H NMR spectrum of compound **3b** ($CDCl_3$, 400 MHz).



^{13}C NMR spectrum of compound 3**b** ($CDCl_3$, 100 MHz).

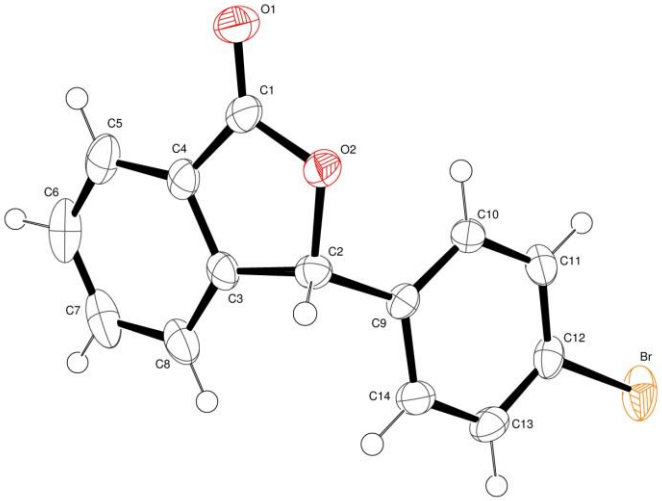


^{1}H NMR spectrum of compound **3c** ($CDCl_3$, 400 MHz).



^{13}C NMR spectrum of compound **3c** ($CDCl_3$, 100 MHz).

6. X-ray Crystal Structure of Compound 2f



Single crystals of **2f** suitable for X-ray diffraction studies were grown from a chloroform/petroleum ether solvent mixture. A Bruker D8 Venture Photon 100 dual source diffractometer was used to collect X-ray data for the structural analysis. Data were collected using Cu-Kα radiation and a combination of ϕ and ω scans was carried out to obtain at least one unique data set. The crystal structure was solved using direct methods with SHELXS.[4] The final structure was refined using SHELXL,[4] where the remaining atoms were located from difference Fourier synthesis. Anisotropic displacement parameters were applied to all non-hydrogen atoms followed by full-matrix least-squares refinement based on F^2. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters

Table S1. Crystallographic data and structure refinement parameters for **2f**.

Molecular formula	$C_{14}H_9BrO_2$
Formula weight (g mol^{-1})	289.12
T (K)	293(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	6.1663(3)
b (Å)	11.1767(6)
c (Å)	16.5802(8)

[4] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.

V (Å^3)	1142.69(10)
Z	4
Radiation type	Cu $K\alpha$
ρ_{calcd} (g cm^{-3})	1.681
μ (mm^{-1})	4.786
F(000)	576
Crystal size (mm)	0.61 × 0.29 × 0.24
θ range (°)	4.771 to 79.536
Limiting indices (*h, k, l*)	$-7 \le h \le 6$
	$-14 \le k \le 14$
	$-20 \le l \le 21$
Reflections collected	43921
Reflections unique (R_{int})	2474 (0.0319)
Completeness to θ_{max} (%)	99.6
Data / restraints / param.	2474 / 0 / 159
Absorption correction	Multiscan
Min. and max. transmission	0.4336 and 0.7542
R_1 [I > 2σ(I)]	0.0188
wR_2 [I > 2σ(I)]	0.0492
R_1 (all data)	0.0189
wR_2 (all data)	0.0492
S on F^2	1.071
Largest diff. peak and hole (e Å^{-3})	0.270 and −0.265
Absolute structure[5]	Flack *x* determined using 1006 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$
Absolute structure parameter[5]	0.008(4)

[5] S. Parsons, H. D. Flack, T. Wagner, *Acta Cryst.* **2013**, *B69*, 249.