Supporting Information

Copper-Catalyzed Borylative Aromatization of *p*-Quinone Methides: Enantioselective Synthesis of Dibenzylic Boronates.

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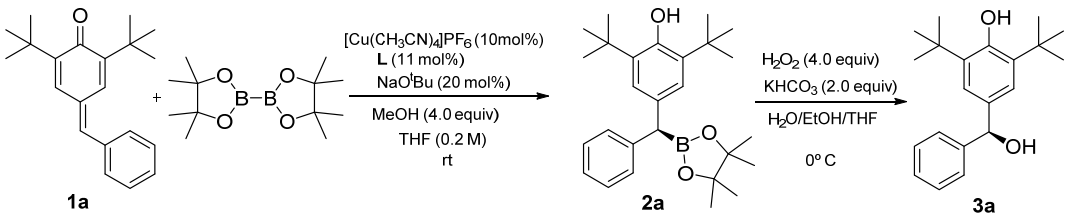
1.General Experimental Details

Tetrahydrofuran, toluene, acetonitrile and dichloromethane were purified by passing through a Pure Solv™ column drying system from Innovative Technology, Inc. Additionally, argon was bubbled through THF and methanol before used. Dry-DMF was acquired from commercial sources. Unless indicated otherwise, all reactions were conducted under an argon atmosphere using flame-dried glassware with standard vacuum-line techniques. NMR spectra were acquired on a Bruker 300 spectrometer, running at 300, and 75 MHz for ^{1}H and ^{13}C, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$, 7.26 ppm for ^{1}H-NMR and 77.0 ppm for ^{13}C-NMR respectively). ^{13}C-NMR spectra were acquired on a broad band decoupled mode. The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septuplet), m (multiplet), bs (broad singlet). Analytical thin layer chromatography (TLC) was performed using pre-coated aluminium-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation or phosphomolybdic acid dip, vainilline dip or potassium permanganate dip. Purification of reaction mixtures were carried out by flash chromatography (FC) using silica gel Merck-60 or Florisil® 100-200 mesh from Aldrich. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. The enantiomeric ratio (er) of the products was determined by stationary phase SFC using chiral columns or by stationary phase HPLC using chiral columns. Mass Spectrometry (MS) and High Resolution Mass Spectrometry (HRMS) were registered in a spectrometer GCT Agilent Technologies 6890N using Electronic Impact (E.I.) techniques at 70 eV, electrospray (ESI+) and Fast Atom Bombardment (FAB+). Melting points were determined in a GallenKamp apparatus in open capillary tubes. All ligands, $[Cu(CH_3CN)_4]PF_6$, NaO^tBu (2.0 M solution in THF), were acquired from commercial sources and were used without further purification. Bis(pinacolato)diboron was recrystrallized in *n*-pentane before used.

2.Optimization details

Table S1. Ligand Effect on the 1,6 Boron conjugate addition to *p*-quinone methide 1a.[a]

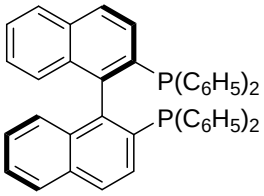


Entry	Ligand	Solvent	Yield[b] (%)	*Er* of **3a**
1	none	THF	35	-
2	L1	THF	47	54.5:45.5
3	L2	THF	52	65:35
4	L3	THF	76	77:23
5	L4	THF	68	83:17
6	L5	THF	41	66.5:33.5
7	***L6***	***THF***	***95***	***96:4***
8[c]	L6	THF	79	94:6
9[d]	L6	THF	54	74:26
10	L6	toluene	83	97:3
11	L7	THF	64	57:43
12	L8	THF	32	49:51
13	L9	THF	70	61:39
14	L10	THF	59	63:37
15	L11	THF	36	56:44
16	L12	THF	41	61:39
17	L13	THF	62	49:51
18	L14	THF	55	61:39
19	L15	THF	27	55:45
20	L16	THF	69	55:45
21	L17	THF	50	68:32
22	L18	THF	70	50:50
23	L19	THF	9	74:26

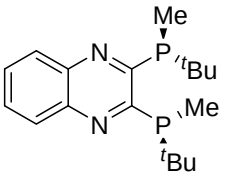
a:Reaction conditions: **1a** (0.2 mmol), B_2pin_2 (0.30 mmol), NaO^{t}Bu (20 mol%), $[Cu(CH_3CN)_4]PF_6$ (10 mol%), **L** (11 mol%), MeOH (0.8 mmol), THF (0.2 M). **b**: Yield of isolated **2a**. **c:** $[Cu(CH_3CN)_4]PF_6$ (5 mol%), **L6** (5.5 mol%). **d:** The reaction was carried out in the absence of MeOH.

When **1a** was treated in THF with $Cu(CH_3CN)_4PF_6$ (10 mol%), B_2pin_2 (1.5 equiv.), NaO*t*-Bu (0.2 equiv.) and MeOH (4 equiv.) in the absence of ligand, we observed the formation of product **2a** with moderate yield (Table S1, entry 1). This background reaction showed the feasibility of the transformation but also revealed a serious handicap for the development of an asymmetric version. We soon realized that the yields and stereoselectivities were highly dependent on the ligand. Commercially available (*R*)-DM-Segphos (**L6**) was superior to other chiral ligands affording the desired dibenzylic boronate **2a** in good yield and high enantiomeric ratio at room temperature (Table S1, entry 7, er = 96:4). The reaction can be carried out with 5 mol% of copper salt and 5.5 mol% of chiral phosphine (Table S1, entry 8) without affecting the enantioselectivity, although the yield observed under these conditions was slightly lower.

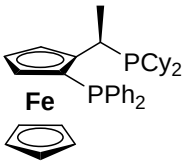
Interestingly, in the absence of MeOH we observed product formation but moderate enantiomeric ratio (Table S1, entry 9).



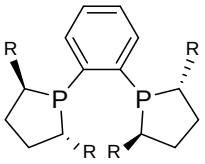
L1 : (*R*) BINAP



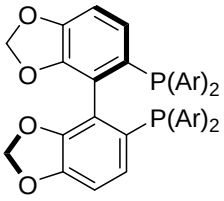
L2: (*R*,*R*)-QuinoxP*

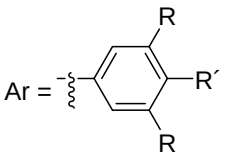


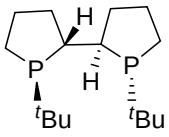
L3

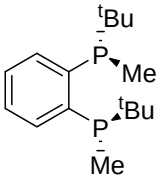


L4 R= ^{i}Pr (R,R)-^{i}Pr-Duphos
L7 R= Me (R,R)-Me-Duphos





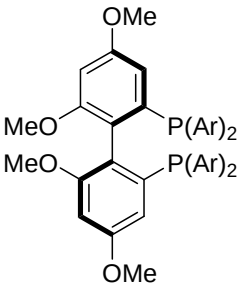


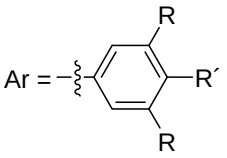


L5: R = R´= H (*R*)-(+)-Segphos
L6: R = Me, R´= H (*R)*-(+)-DM-Segphos
L8: R = ^{t}Bu, R´= OMe (*R)*-(+)-DTBM-Segphos

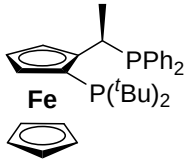
L9: (*S*,*S´*,*R*,*R´*)-Tangphos

L10: BenzP*

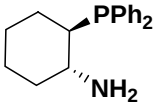




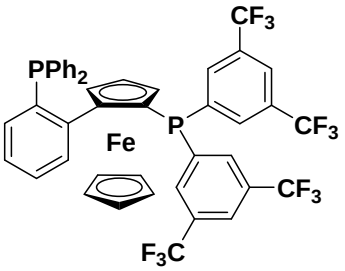
L11: R = CF_3 R´= H (*R*)-(+)-BTFM-Garphos^{TM}
L12: R = R´ = OMe



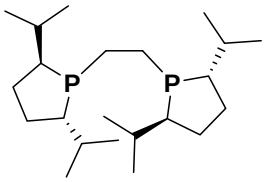
L13



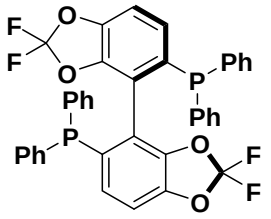
L14



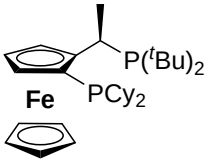
L15



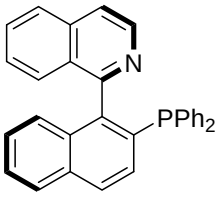
L16



L17: (*R*)-DIFLUORPHOS



L18



L19 (*R*)-OUINAP

Figure S1: Ligands used for optimization.

3. Synthesis of Starting Materials

3.1. General procedure for the synthesis of 2,6-di-*tert*-butyl *p*-quinone methides[1]

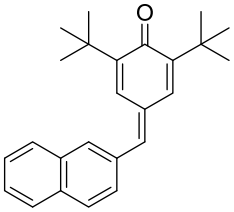
$R^1 = R^2 = {}^t$Bu	$R^3 = C_6H_5$	**1a**
$R^1 = R^2 = {}^t$Bu	R^3 = 2-naphthyl	**1b**
$R^1 = R^2 = {}^t$Bu	$R^3 = p$-OMe-C_6H_4	**1c**
$R^1 = R^2 = {}^t$Bu	$R^3 = p$-Me-C_6H_4	**1d**
$R^1 = R^2 = {}^t$Bu	$R^3 = m$-CF_3-C_6H_4	**1e**
$R^1 = R^2 = {}^t$Bu	$R^3 = p$-Br-C_6H_4	**1f**
$R^1 = R^2 = {}^t$Bu	$R^3 = o$-Br-C_6H_4	**1g**
R^1 = Me, $R^2 = {}^t$Bu	$R^3 = C_6H_5$	**1o**
R^1 = Me, $R^2 = {}^t$Bu	$R^3 = p$-Br-C_6H_4	**1p**

In a Dean–Stark apparatus, a solution of 2,6-di-*tert*-butylphenol (or 2-(*tert*-butyl)-6-methylphenol) and the corresponding benzaldehyde in toluene was heated at 140 ºC. Piperidine was added within 1 h and heating was continued for 12 h. After cooling to 115 ºC, acetic anhydride was added and stirring was continued for 15 min. Then the reaction mixture was poured on ice-water and extracted with CH_2Cl_2 (x3). The combined organic phases were dried over Mg_2SO_4, and the solvent was removed under reduced pressure. The crude products were purified by column chromatography (cyclohexane) and recrystallized from *n*-hexane.

Compounds **1a**[2], **1c**[2], **1d**[3], **1f**[2], **1g**[2], and **1o**[2] were synthesized using this method and obtained as reported previously in the literature.

[1] Chu,W.-D.; Zhang, L.-F; Bao, X.; Zhao, X.-Y.; Zeng, C.; Du, J.-Y.; Zhang, G.-B.; Wang, F.Z.; Ma, Z.-Y; Fan, C.-A. *Angew. Chem. Int. Ed.* **2013**, *52*, 9229.
[2] Koutek; B; Pavličková, L.; Souček, M. *Synthetic Commun.*, **1976**, *6*, 305.
[3] Roos, E.; Hugl, E. *DE 2734239 A 19770729*, **1979**.

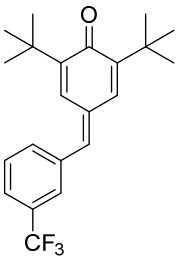
2,6-di-*tert*-Butyl-4-(naphthalen-2-ylmethylene)cyclohexa-2,5-dienone (1b)



From 2,6-di-*tert*-butylphenol (5.0 g, 24.3 mmol, 1.0 equiv) and 2-naphthaldehyde (3.8 g, 24.3 mmol, 1.0 equiv), following the general procedure described above, compound **1b** was obtained in 65% yield, as a yellow solid, after purification by column chromatography (cyclohexane). $\mathbf{R_f}$= 0.24 (hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.97-7.83 (m, 4H), 7.65 (d, *J* = 2.4 Hz, 1H), 7.62-7.50 (m, 3H), 7.34 (s, 1H), 7.08 (d, *J* = 2.4 Hz, 1H), 1.36 (s, 9H), 1.32 (s, 9H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 185.2, 148.2, 146.6, 141.1, 133.8, 132.2, 131.9, 130.9, 129.3, 127.2, 127.1, 126.6, 126.4, 126.0, 125.9, 125.5, 34.2, 33.7, 28.3, 28.2. **HRMS (EI$^+$)** calculated for $C_{25}H_{28}O$ [M^+]: 344.2140, found: 344.2133. **mp** = 112-114 ºC.

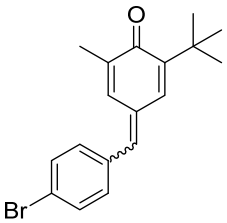
2,6-di-*tert*-Butyl-4-[3-(trifluoromethyl)benzylidene]cyclohexa-2,5-dien-1-one (1e)



From 2,6-di-*tert*-butylphenol (5.0 g, 24.3 mmol, 1.0 equiv) and 3-(trifluoromethyl)benzaldehyde (4.2 g, 24.3 mmol, 1.0 equiv), following the general procedure described above, compound **1e** was obtained in 70% yield, as an orange solid, after purification by column chromatography (cyclohexane). $\mathbf{R_f}$= 0.33 (hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.67-7.54 (m, 3H), 7.42 (s, 1H), 7.17 (s, 1H), 7.02 (s, 1H), 1.31 (s, 9H), 1.30 (s, 9H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 186.6, 150.3, 148.7, 139.8, 136.8, 134.7, 133.4, 133.3, 133.2, 131.5 (q, $J_{C\text{-}F}$ = 32.0 Hz), 129.4, 127.2, 127.1 (q, $J_{C\text{-}F}$ = 3.8 Hz), 125.5 (*q*, $J_{C\text{-}F}$ = 3.8 Hz), 124.0 (q, $J_{C\text{-}F}$ = 270.75 Hz), 35.7, 35.2, 29.6, 29.5.**^{19}F-NMR** (282 MHz, $CDCl_3$) δ -62.9 (s). **HRMS (EI$^+$)** calculated for $C_{22}H_{25}OF_3$ [M^+]: 362.1858, found: 362.1866. **mp** = 54-56 ºC.

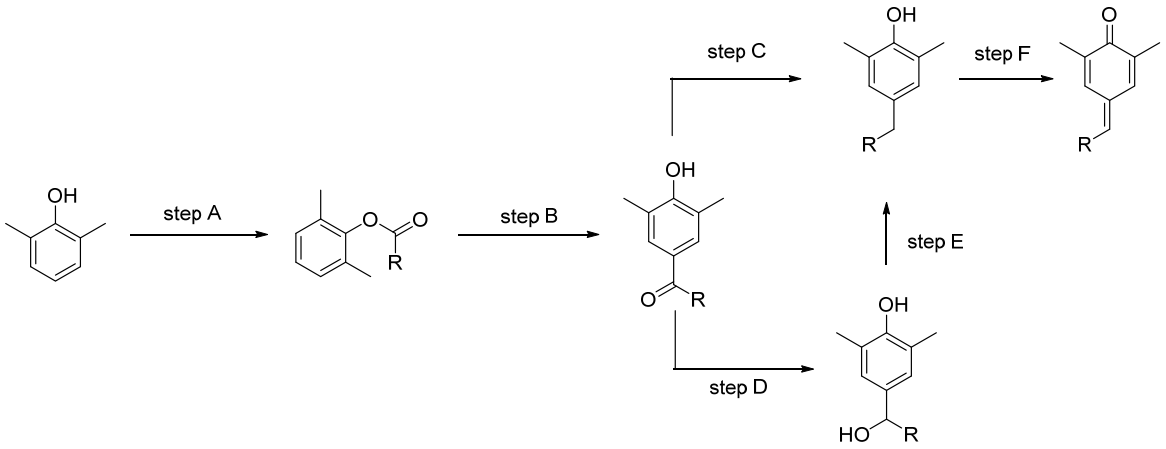
4-(4-Bromobenzylidene)-2-(*tert*-butyl)-6-methylcyclohexa-2,5-dien-1-one (1p)



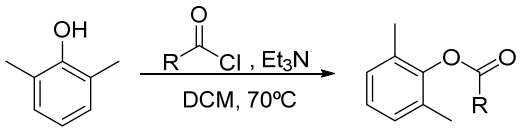
From 2-(*tert*-butyl)-6-methylphenol (4.0 g, 24.3 mmol, 1.0 equiv) and 4-bromobenzaldehyde (4.2 g, 24.3 mmol, 1.0 equiv), following the general procedure described above, compound **1p** was obtained in 32% yield after purification by column chromatography (cyclohexane) as a 1.7:1 mixture of A:B isomers and as a yellow solid (recrystallization of the product gave a 1.1:1 mixture of A:B isomers). $\mathbf{R_f}$= 0.12 (hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.5 Hz, 2H, isomer A), 7.54 (d, *J* = 8.5 Hz, 2H, isomer B), 7.48 (d, *J* = 2.4 Hz, 1H, isomer A), 7.38 (bs, 1H, isomer B), 7.29 (d, *J* = 8.5 Hz, 2H, isomers A and B), 7.07 (s, 1H, isomer B), 7.03 (s, 1H, isomer A), 7.02 (d, *J* = 2.6 Hz, 1H, isomer B), 6.97 (bs, 1H, isomer A), 2.01 (s, 3H, isomers A and B), 1.31 (s, 9H, isomer B), 1.28 (s, 9H, isomer A). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 186.7 (isomer A), 186.6 (isomer B), 148.3 (isomer B), 146.7 (isomer A), 140.9 (isomer A), 140.6 (isomer B), 139.5 (isomer A), 137.6 (isomer B), 137.0 (isomer B), 136.5 (isomer A), 134.6 (isomer A), 134.5 (isomer B), 132.3 (isomer A), 132.2 (isomer B), 132.0 (both), 131.8 (isomer B), 131.7 (isomer A), 129.5 (isomer A), 128.5 (isomer B), 123.6 (isomer B), 123.5 (isomer A), 35.2 (isomer B), 34.8 (isomer A), 29.3 (isomer B), 29.2 (isomer A), 17.1 (isomer A), 16.4 (isomer B).**HRMS (EI$^+$)** calculated for $C_{18}H_{19}OBr$ [M^+]: 330.0619, found: 330.0616. **mp** = 98-100 °C.

3.2. Synthesis of 2,6-dimethyl *p*-quinone methides



3.2.1. General procedure for the synthesis of 2,4-dimethylbenzoates, step A[4]



R = 2-naphthyl **SI-1**

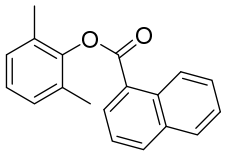
R = *p*-Br-C_6H_4 **SI-2**

R = *o*-Me-C_6H_4 **SI-3**

A round bottom flask was charged with 2,6-dimethylphenol (1.0 equiv), the corresponding acyl chloride (1.0 equiv) and triethylamine (1.4 equiv) in DCM (2.0 mL/1.0 mmol phenol). Then, the reaction mixture was stirred at 60 ºC until starting material disappearance was observed by TLC and allowed to cool at room temperature. Then the reaction mixture was washed with water (x3) and the combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The product was used in the next step without further purification.

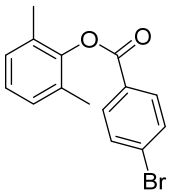
[4] Pews, R. *US 7141684*, **2006**.

Naphthalen-2-yl 2,6-dimethylbenzoate (SI-1)



This compound was synthesized using this method and obtained as previously described in the literature.[5]

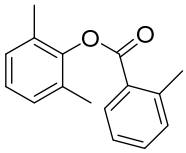
2,6-Dimethylphenyl 4-bromobenzoate (SI-2)



From 2,6-dimethylphenol (2.5 g, 20.5 mmol, 1.0 equiv) and *p*-bromobenzoyl chloride (4.5 g, 20.5 mmol, 1.0 equiv), following the general procedure described above, compound **SI-2** was obtained in 93% yield as a yellow oil. $\mathbf{R_f}$= 0.72 (33% hexanes/ethyl acetate).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.28 (s, 3H), 2.40 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 163.8, 148.5, 132.2, 131.8, 130.4, 129.0, 128.9, 128.4, 126.3, 16.6. **HRMS (EI$^+$)** calculated for $C_{15}H_{13}O_2$ [M^+]: 304.0099, found: 304.0100.

2,6-Dimethylphenyl 2-methylbenzoate (SI-3)

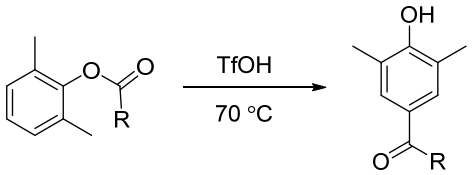


From 2,6-dimethylphenol (2.5 g, 20.5 mmol, 1.0 equiv) and *o*-toluoyl chloride (2.7 ml, 20.5 mmol, 1.0 equiv), following the general procedure described above, compound **SI-3** was obtained in 99% yield as a colorless oil. $\mathbf{R_f}$= 0.50 (10% ethyl acetate/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.30 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.46 – 7.35 (m, 2H), 7.22 – 7.14 (m, 3H), 2.76 (s, 3H), 2.29 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 165.1, 148.5, 141.3, 132.7, 132.1, 131.1, 130.4, 128.7, 128.6, 126.1, 125.9, 22.0, 16.6. **HRMS (EI$^+$)** calculated for $C_{16}H_{16}O_2$ [M^+]: 240.1150, found: 240.1152.

[5] Ren, W.; Emi, A.; Yamane. M. *Synthesis*, **2011**, *14*, 2303.

3.2.2. General procedure for the synthesis of (4-hydroxy-3,5-dimethylphenyl)arylmethanones, step B[6]



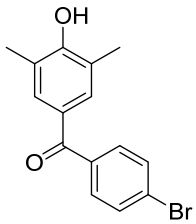
R = 2-naphthyl **SI-4**

R = *p*-Br-C_6H_4 **SI-5**

R = *o*-Me-C_6H_4 **SI-6**

Triflic acid (0.3 mL/ 1 mmol) was added to the corresponding ester (**SI-1-3**) at 0 ºC, and then it was stirred at 70 ºC until completion (checked by TLC). The reaction mixture was cooled at room temperature and then poured into an ice-water bath and the layers were separated. The aqueous phase was extracted with EtOAc (x3) and then neutralized with a saturated sodium bicarbonate solution. The resulting aqueous layer was extracted with EtOAc (x2) and the combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography (cyclohexane/EtOAc) as indicated in each case. In some cases crude products were used in the next step without further purification.

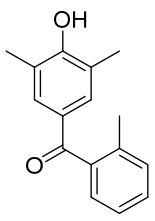
4-(4-Bromophenyl)-4-(hydroxy-3,5-dimethylphenyl)methanone (SI-4)



From **SI-2** (5.9 g, 19.1 mmol, 1.0 equiv) and triflic acid, following the general procedure described above, compound **SI-4** was obtained in 92% yield after purification by column chromatography (33% EtOAc/hexanes) as a white solid. $\mathbf{R_f}$= 0.28 (33% hexanes/ethyl acetate).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.62 (s, 4H), 7.48 (s, 2H), 2.28 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 194.8, 156.6, 137.2, 131.4, 131.4, 131.3, 129.3, 126.7, 123.0, 15.8. **HRMS (EI$^+$)** calculated for $C_{15}H_{13}O_2Br$ [M^+]: 304.0099, found: 304.0095. **mp** = 142-144 ºC.

(4-Hydroxy-3, 5-dimethylphenyl)(*o*-tolyl)methanone (SI-5)

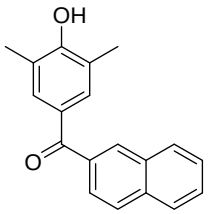


From **SI-3** (4.7 g, 19.5 mmol, 1.0 equiv) and triflic acid, following the general procedure described above, compound **SI-5** was obtained in 81% yield after purification by column chromatography (20% EtOAc/ hexanes) as a brown solid. $\mathbf{R_f}$= 0.12 (10% EtOAc/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.41 (s, 2H), 7.33–7.25 (m, 1H), 7.21 (s, 1H), 7.18 (s, 2H), 2.22 (s, 3H), 2.18 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 197.8, 157.0, 139.4, 136.1, 131.4, 130.8, 130.0, 129.6, 127.8, 125.1, 123.0, 19.7, 15.8. **HRMS (EI$^+$)** calculated for $C_{16}H_{16}O_2$ [M^+]: 240.1150, found: 240.1142. **mp** = 173-175 ºC.

[6] Olah , M. G.; Robbins, J. S.; Baker, M. S. and Phillips, S.T. *Macromolecules,* **2013**, *46*, 5924.

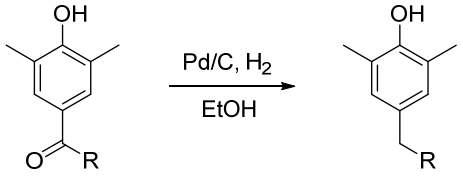
(4-Hydroxy-3,5-dimethylphenyl)(naphthalen-2-yl)methanone (SI-6)



From **SI-1** (5.1 g, 18.4 mmol, 1.0 equiv) and triflic acid, following the general procedure described above, compound **SI-6** was obtained in 98% yield as a yellow solid and used in the next step without further purification. $\mathbf{R_f}$= 0.21 (10% EtOAc/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.93 (t, *J* = 7.8 Hz, 3H), 7.87 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.66–7.51 (m, 4H), 2.31 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 196.5, 156.8, 136.1, 135.4, 132.7, 131.9, 131.4, 130.3, 129.6, 128.4, 128.3, 128.2, 127.0, 126.3, 123.2, 16.2. **HRMS (EI$^+$)** calculated for $C_{19}H_{16}O_2$ [M^+]: 276.1150, found: 276.1150. **mp** = 162-164 ºC.

3.2.3. General procedure for the synthesis of diaryl methanes, step C[6]

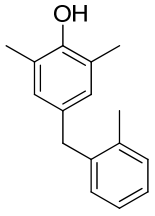


R = 2-naphtyl **SI-7**

R = *o*-Me-C_6H_4 **SI-8**

Palladium (10% by weight on carbon powder) (0.05 equiv) was added to a solution of the corresponding ketone (**SI-5-6**) (1.0 equiv) in ethanol (3.1 mL, 1.0 mmol) under argon atmosphere. The flask was evacuated and purged with H_2 gas (~1 atm, balloon). The reaction mixture was stirred vigorously at room temperature until completion by TLC. The reaction mixture was filtered through a pad of celite and concentrated. The crude of product was purified by flash column chromatography as indicated in each case.

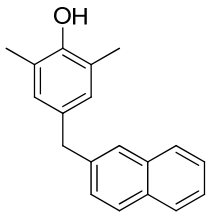
2,6-Dimethyl-4-(2-methylbenzyl)phenol (SI-7)



From **SI-5** (1.0 g, 4.2 mmol, 1.0 equiv) and Pd/C, following the general procedure described above, compound **SI-7** was obtained in 98% yield after purification by column chromatography (25% EtOAc/hexanes) as a white solid. $\mathbf{R_f}$= 0.77 (25% EtOAc/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.18-7.06 (m, 4H), 6.75 (s, 2H), 4.46 (s, 1H), 3.86 (s, 2H), 2.27 (s, 3H), 2.21 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 150.3, 139.5, 136.5, 131.9, 130.2, 129.8, 128.9, 126.2, 125.9, 122.9, 38.5, 19.7, 15.9. **HRMS (EI$^+$)** calculated for $C_{16}H_{18}O$ [M^+]: 226.1358, found: 226.1362. **mp** = 74-76 ºC.

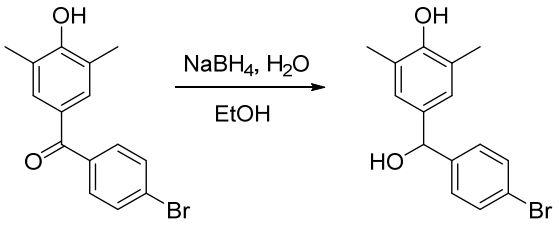
2,6-Dimethyl-4-(naphthalen-2-ylmethyl)phenol (SI-8)



From **SI-6** (1.0 g, 3.6 mmol, 1.0 equiv) and Pd/C, following the general procedure described above, compound **SI-8** was obtained in 50% yield as a yellow solid. $\mathbf{R_f}$= 0.56 (20% EtOAc/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.13–8.00 (m, 3H), 7.89 (s, 1H), 7.76–7.66 (m, 3H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.11 (s, 2H), 4.75 (s, 1H), 4.28 (s, 2H), 2.47 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 150.6, 139.3, 133.7, 132.6, 132.1, 129.2, 128.0, 127.7 (2C), 127.6, 126.9, 125.9, 125.3, 123.1, 41.3, 15.9. **HRMS (EI$^+$)** calculated for $C_{19}H_{18}O$ [M^+]: 262.1358, found: 262.1366. **mp** = 80-82 ºC.

3.2.4. Synthesis of 4-[(4-bromophenyl)(hydroxy)methyl]-2,6-dimethylphenol, step D

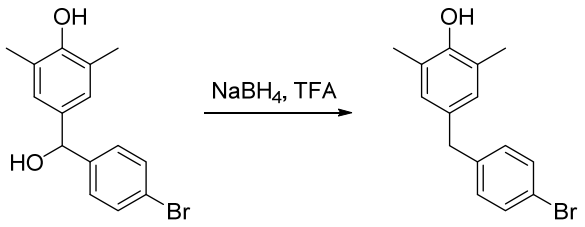


SI-4 **SI-9**

A solution of sodium borohydride (272.6 mg, 7.2 mmol, 1.1 equiv) in H_2O (1.1 mL/ 1.0 mmol) was added to a solution of **SI-4** (2.0 g, 6.6 mmol, 1.1 equiv) in EtOH (21 mL). After stirring 5 h, the reaction mixture was added to a mixture of ice-water and concentrated HCl, and the product was extracted with AcOEt (x3). The combined organic layers were subsequently washed with a saturated solution of $NaHCO_3$ (x2). The product was used in the next step without further purification. Compound **SI-9** was obtained in 70% yield as a white solid. $\mathbf{R_f}$= 0.30 (25% EtOAc/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.3 Hz, 2H), 7.31 (d, *J* = 5.6 Hz, 2H), 6.98 (s, 2H), 5.73 (s, 1H), 4.69 (s, 1H), 2.27 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 151.9, 143.1, 135.2, 131.4, 128.1, 127.0, 123.2, 121.1, 75.4, 15.9. **HRMS (ESI+)** calculated for $C_{15}H_{14}BrO$ [M-OH]$^+$: 289.0222, found: 289.0218. **mp** = 138-140 ºC.

3.2.5. Synthesis of 4-(4-bromobenzyl)-2,6-dimethylphenol, step E[7]



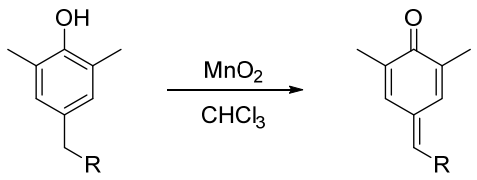
SI-9 **SI-10**

Sodium borohydride (695.5 mg, 18.4 mmol, 4.0 equiv) was slowly added to trifluoroacetic acid (61 mL) at 0 ºC. (*This addition must be done carefully: large amount of hydrogen gas is released in the process*). When the addition was completed, alcohol **SI-9** (1.4 g, 4.6 mmol, 1.0 equiv) was added and the reaction mixture stirred 1 hour at room temperature. Water was added and the reaction mixture was neutralized with $NaHCO_3$ and the aqueous layer extracted with Et_2O (x3). The combined organic layers were washed with saturated NaCl solution, dried over Na_2SO_4, filtered and concentrated. The product was used in the next step without further purification. Compound **SI-10** was obtained in 75% yield as an orange solid. $\mathbf{R_f}$= 0.65 (25% EtOAc/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.88 (s, 2H), 4.72 (s, 1H), 3.90 (s, 2H), 2.32 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 150.7, 140.8, 132.1, 131.5, 130.6, 129.0, 123.1, 119.8, 40.5, 15.9. **HRMS (EI$^+$)** calculated for $C_{15}H_{15}OBr$ [M^+]: 290.0306, found: 290.0303. **mp** = 58-60 °C.

[7] Bringmann, G.; Pabst, T.; Henschel, P; Michel, M. *Tetrahedron*, **2001**, 57, 1269.

3.2.6. General procedure for the synthesis of 2,6-dimethylquinometanes, step F[8,9]

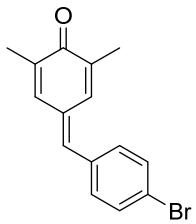


R = C_6H_5	**1i**
R = *p*-Me- C_6H_4	**1j**
R = *p*-Br-C_6H_4	**1k**
R = *o*-Me-C_6H_4	**1l**
R = 2-naphthyl	**1m**

Activated MnO_2 was added to a solution of the corresponding diarylmethane in $CHCl_3$ and the reaction mixture was stirred at room temperature until completion (checked by TLC). The crude product was filtered through a pad of celite and concentrated. The product was used in the next step without further purification.

Compounds **1i** and **1j** have been previously described in the literature.[6,9]

4-(4-Bromobenzylidene)-2,6-dimethylcyclohexa-2,5-dienone (1k)

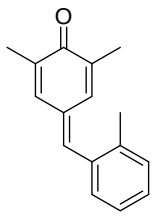


From **SI-10** (100.0 mg, 0.3 mmol, 1.0 equiv) and MnO_2 (1.4 g, 16.7 mmol, 48.5 equiv) in $CHCl_3$ (31.2 mL), following the general procedure described above, compound **1k** was obtained in 96% yield as a yellow solid. $\mathbf{R_f}$= 0.47 (33% Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.44 (bs, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.07 (s, 1H), 7.04 (bs, 1H), 2.06 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 187.2, 140.8, 138.6, 138.0, 136.0, 134.5, 132.2, 132.0, 131.8, 130.8, 123.8, 16.9, 16.2. **HRMS (EI$^+$)** calculated for $C_{15}H_{13}BrO$ [M^+]: 288.0150, found: 288.0156. **mp** = 98-100 ºC.

[8] Nagakawa, R; Takahiro, U; Kubo, M; Itoh, T; *Polym. Bull.* **2012**, *68*, 1831.
[9] Lin, L.-T. W.; Bromps, W.; Chin., T. Y. *J. Polym. Sci., Part A: Polym. Chem.*, **1993**, *31*, 3239.

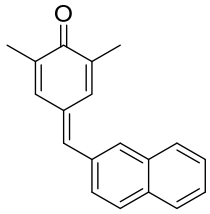
2,6-Dimethyl-4-(2-methylbenzylidene)cyclohexa-2,5-dien-1-one (1l)



From **SI-7** (235.8 mg, 1.0 mmol, 1.0 equiv) and MnO_2 (4.4 g, 50.4 mmol, 48.5 equiv) in $CHCl_3$ (95 mL), following the general procedure described above, compound **1l** was obtained in 99% yield as a yellow solid. $\mathbf{R_f}$= 0.39 (20% EtOAc/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.41-7.25 (m, 6H), 7.15 (s, 1H), 2.38 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 187.4, 141.8, 138.5, 137.7, 137.5, 135.8, 134.6, 132.0, 131.8, 130.9, 130.4, 129.3, 125.9, 20.1, 16.7, 16.2. **HRMS (EI$^+$)** calculated for $C_{16}H_{16}O$ [M^+]: 224.1201, found: 224.1207. **mp** = 80-82. ºC.

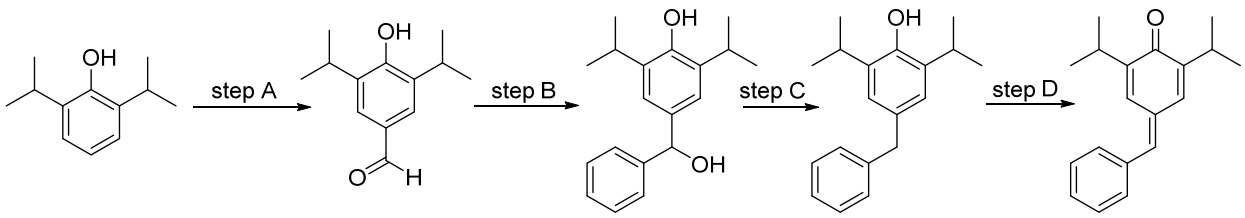
2,6-Dimethyl-4-(naphthalen-2-ylmethylene)cyclohexa-2,5-dien-1-one (1m)



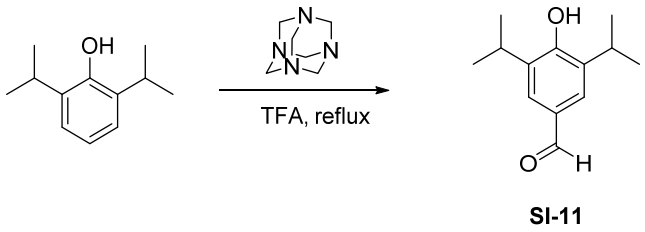
From **SI-8** (50.0 mg, 0.2 mmol, 1.0 equiv) and MnO_2 (801.2 mg, 9.2 mmol, 48.5 equiv) in $CHCl_3$ (7.0 mL), following the general procedure described above, compound **1m** was obtained in 98% yield as yellow solid. $\mathbf{R_f}$= 0.51 (20% EtOAc/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.97-7.83 (m, 4H), 7.62 (s, 1H), 7.61-7.52 (m, 2H), 7.32 (s, 1H), 7.12 (s, 1H), 2.10 (s, 3H), 2.09 (s, 3H).**^{13}C-NMR** (75 MHz, $CDCl_3$): δ 187.3, 142.7, 138.9, 137.8, 135.8, 133.4, 133.2 (2C), 132.0, 131.5, 130.8, 128.6, 128.5, 127.8, 127.4, 127.3, 126.9, 16.9, 16.3. **HRMS (EI$^+$)** calculated for $C_{19}H_{16}O$ [M^+]: 260.1201, found: 260.1205. **mp** = 88-90 ºC.

3.3. Synthesis of 2,6-diisopropyl *p*-quinone methide 1n



3.3.1. Synthesis of 4-hydroxy-3,5-diisopropylbenzaldehyde (SI-11), step A[10,11]

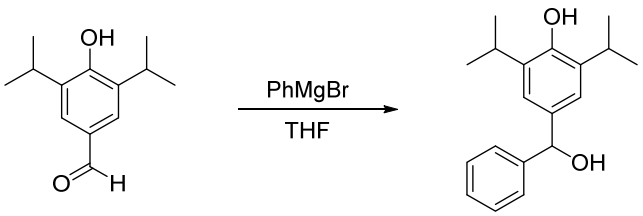


2,6-diisopropylphenol (8.0 g, 44.8 mmol, 1.0 equiv), hexamethylenetetramine (12.6 g, 89.6 mmol, 2.0 equiv) and trifluoroacetic acid were mixed in a round bottom flask (44 mL) and the solution was heated under reflux for 12 hours. The reaction mixture was cooled at room temperature and neutralized with $NaHCO_3$. The aqueous layer was extracted with EtOAc (x3) and the combined organic layers were concentrated. The crude product was dissolved in a solution of HCl 3.0M and stirred under reflux for 3 hours. The precipitated was filtered, washed with water and purified by recrystallization from EtOH. Compound **SI-11** was obtained in 98% yield as a white solid, as reported in the literature.[10] $\mathbf{R_f}$= 0.66 (25% hexanes/EtOAc).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.86 (s, 1H), 7.62 (s, 2H), 5.43 (s, 1H), 3.18 (sept, *J* = 6.9 Hz, 2H), 1.31 (d, *J* = 6.8 Hz, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 192.1, 156.4, 134.7, 129.7, 126.4, 27.2, 22.7.

[10] Kurlovich, A. L.; Terasevich, V. A.; Kozlov, N. G. *Russ. J. Org. Chem.* **2009**, *45*, 1503.
[11] Geurink, P. P.; Florea, B. I.; Li, N.; Witte, M. D.; Verasdonck, J., Kuo, C.-L.; van der Marel, G. A.; Overkleeft, H. S. *Angew. Chem. Int. Ed.* **2010**, 49, 6802.

3.3.2. Synthesis of 4-(hydroxy(phenyl)methyl)-2,6-diisopropylphenol (SI-12), step B[12]

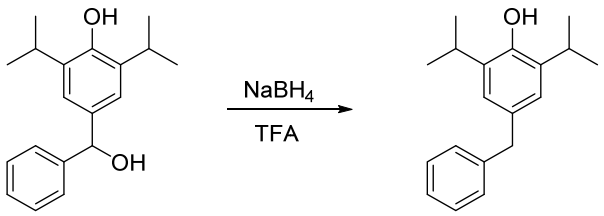


SI-11 **SI-12**

To magnesium turnings (302 mg, 12.6 mmol, 2.6 equiv) in dry THF (2 mL), a solution of bromobenzene (1.23 mL, 11.7 mmol, 2.4 equiv) in dry THF (10 mL) was added dropwise under argon atmosphere. After 2 hours of reflux, the mixture was cooled at room temperature and a solution of **SI-11** (1.0 g, 4.8 mmol, 1.0 equiv) in dry THF (10 mL) was added dropwise and stirred for 12 hours. Then, the reaction mixture was hydrolyzed with saturated aqueous NH_4Cl solution. The aqueous layer was extracted with Et_2O (x3) and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The product was obtained without further purification. Compound **SI-12** was obtained in 99% yield as a white solid. $\mathbf{R_f}$= 0.22 (20% Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.42–7.19 (m, 5H), 7.04 (s, 2H), 5.77 (s, 1H), 4.83 (s, 1H), 3.11 (sept, *J* = 6.9 Hz, 2H), 1.22 (d, *J* = 6.8 Hz, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 149.6, 144.2, 135.9, 133.8, 128.4, 127.3, 126.5, 122.1, 76.5, 27.4, 22.7. **HRMS (EI$^+$)** calculated for $C_{19}H_{24}O_2$ [M^+]: 284.1776, found: 284.1773. **mp** = 94–96 ºC.

3.3.3. Synthesis of 4-benzyl-2,6-diisopropylphenol (SI-13), step C[7]



SI-12 **SI-13**

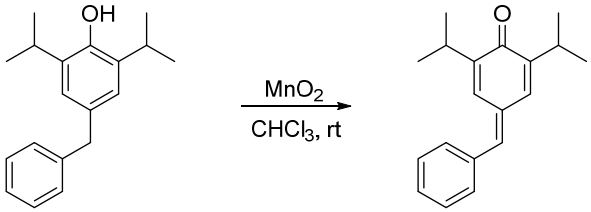
Sodium borohydride (680.4 mg, 18.0 mmol, 4.0 equiv) was added to trifluoroacetic acid (39 mL) in small portions at 0 ºC. *(This addition must be done carefully: large amount of hydrogen gas is released in the process).* Then the alcohol **SI-12** (1.3 g, 4.5 mmol, 1.0 equiv) was added and the reaction mixture was stirred 15 min at room temperature. Water was added, the aqueous layer was neutralized with $NaHCO_3$ and extracted with Et_2O (x3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The product was used in the next step without further purification. Compound **SI-13** was obtained in 85% yield as an orange solid. $\mathbf{R_f}$= 0.67 (25% EtOAc/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.41–7.16 (m, 5H), 6.94 (s, 2H), 4.75 (bs, 1H), 3.98 (s, 2H), 3.18 (sept, *J* = 6.9, 2H), 1.30 (d, *J* = 6.8 Hz, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 148.4, 142.0,

[12] Richter, D.; Hampel, N.; Singer, T.; Ofial, A. R.; Mayr, H. *Eur. J. Org. Chem.*, **2009**, 3203.

133.8, 132.9, 128.8, 128.4, 125.9, 124.2, 41.8, 27.4, 22.8. **HRMS (EI$^+$)** calculated for $C_{19}H_{24}O$ [M^+]: 268.1827, found: 268.1836. **mp** = 34-36 ºC.

3.3.4. Synthesis for 4-benzylidene-2,6-diisopropylcyclohexa-2,5-dienone 1n, step D[8]

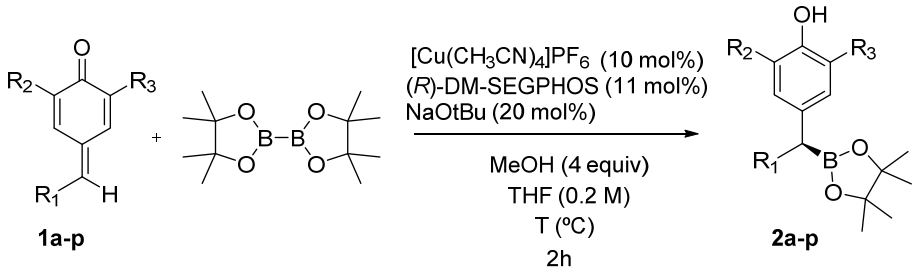


SI-13 **1n**

Activated MnO_2 (10 equiv) was added to solution of compound **SI-13** in $CHCl_3$ (16.4 mL) and the reaction mixture was stirred at room temperature for 15 min. The crude product was filtered through a pad of celite and concentrated. The product was used in the next step without further purification. Compound **1n** was obtained in 98% yield as an orange-red solid, as reported in literature.[3] $\mathbf{R_f}$= 0.66 (25% EtOAc/hexanes).

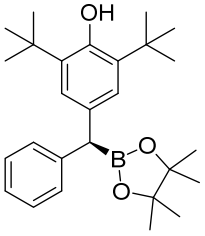
^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.51-7.45 (m, 5H), 7.26 (s, 1H), 7.23 (s, 1H), 6.99 (s, 1H), 3.28-3.11 (sept, *J* = 6.9 Hz, 2H), 1.17 (d, *J* = 6.9 Hz, 6H), 1.13 (d, *J* = 6.9 Hz, 6H).**^{13}C-NMR** (75 MHz, $CDCl_3$): δ 185.3, 147.5, 145.9, 142.7, 135.9, 134.9, 132.1, 130.5, 129.2, 128.8, 127.5, 27.0, 26.6, 22.0. **HRMS (EI$^+$)** calculated for $C_{19}H_{22}O$ [M^+]: 266.1671, found: 266.1668.

4. General Procedure for the synthesis of chiral dibenzylic boronates 2a-2p



An oven-dried vial was charged with $[Cu(CH_3CN)_4]PF_6$ (7.5 mg, 0.02 mmol, 10.0 mol%), (*R*)-DM-SEGPHOS (26 mg, 0.022 mmol, 11.0 mol%) and B_2pin_2 (76 mg, 0.3 mmol, 1.5 equiv) and sealed with a septum. The vial was connected to an argon-vacuum line, evacuated and backfilled with argon (x3). THF (0.5 mL) and NaO*t*-Bu solution (2M in THF, 20µL, 0.04 mmol, 20.0 mol%) was then added and the dark brown solution was stirred for 15 min. The *p*-quinone methide **1** (0.2 mmol, 1.0 equiv) was connected to an argon-vacuum line, evacuated and backfilled with argon (x3), dissolved in 0.5 mL of THF, and finally added to the reaction mixture at 0 ºC, followed by methanol (32 µL, 0.8 mmol, 4.0 equiv). Then, the reaction mixture was stirred for 2 hours at the optimized temperature for each case (rt or 0 ºC). Reaction was diluted with Et_2O and concentrated under reduced pressure. The crude product was purified by flash-column chromatography (eluents indicated in each case). *The racemic products were obtained using SIMes as ligand and following the procedure described above.*

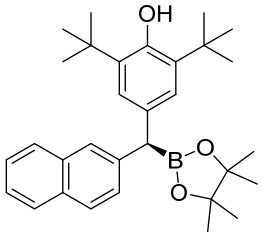
(*S*)-2,6-di-*tert*-Butyl-4-[phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]phenol (2a)



From **1a** (59 mg, 0.2 mmol), following the general procedure described above (rt), compound (*S*)-**2a** (80.5 mg, 0.19 mmol) was obtained in 95% yield after purification by column chromatography (6% Et_2O/hexanes) as a white solid. $\mathbf{R}_f$= 0.45 (6% Et_2O/hexanes).

^{1}H-NMR δ (75 MHz, $CDCl_3$): 7.25-7.18 (m, 4H), 7.17-7.09 (m, 1H), 7.06 (s, 2H), 4.99 (s, 1H), 3.76 (s, 1H), 1.39 (s, 18H), 1.23 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 151.8, 143.0, 136.5, 132.0, 128.8, 128.2, 126.0, 125.2, 83.5, 34.3, 30.3, 24.7, 24.6 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **HRMS (EI+):** calculated for [M^+], $C_{27}H_{39}BO_3$: 422.2992, found 422.2979. Compound (*S*)-**2a** was oxidized to compound (*S*)-**3a** (see general procedure below) to determine the enantiomeric ratio. Compound (*S*)-**3a** was obtained with a 96:4 enantiomeric ratio determined by HPLC using Chiralpak-IA column [Hexane/^{i}PrOH (98:2), 1.0 mL/min]: τ_{major}= 9.0 min, τ_{minor}= 7.9 min. $\mathbf{[\alpha]^{20}_D}$= +20.6 (*c*= 1.0, $CHCl_3$). **mp** = 105-107 ºC.

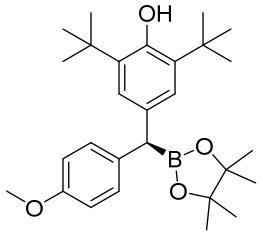
(*S*)-2,6-di-*tert*-Butyl-4-[naphthalen-2-yl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]phenol (2b)



From **1b** (69 mg, 0.2 mmol), following the general procedure described above (0 ºC), compound (*S*)-**2b** (79.1 mg, 0.16 mmol) was obtained in 78% yield after purification by column chromatography (3.33% Et_2O/hexanes) as a yellow oil. $\mathbf{R}_f$= 0.58 (3% Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.82-7.72 (m, 3H), 7.64 (s, 1H), 7.46-7.38 (m, 3H), 7.15 (s, 2H), 5.03 (s, 1H), 3.96 (s, 1H), 1.42 (s, 18H), 1.25 (s, 12H).**^{13}C-NMR** (75 MHz, $CDCl_3$): δ 151.9, 140.7, 135.6, 133.8, 132.0, 131.8, 128.8, 127.7, 127.6, 127.5, 126.7, 126.1, 125.5, 124.8, 83.6, 34.4, 30.4, 24.7, 24.6 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **HRMS (EI+):** calculated for $[M]^+$ $C_{31}H_{41}BO_3$: 472.3149, found 472.3171. Compound (*S*)-**2b** was oxidized to compound (*S*)-**3b** (see general procedure below) to determine the enantiomeric ratio. Compound (*S*)-**3b was** obtained with a 96:4 enantiomeric ratio determined by SFC using Chiralpak-IB column [CO_2/MeOH (95:5, 3.0 mL/min]: τ_{major}= 16.5 min, τ_{minor}= 15.2 min. $\mathbf{[\alpha]^{20}_D}$= +19.0 (*c*= 0.8, $CHCl_3$).

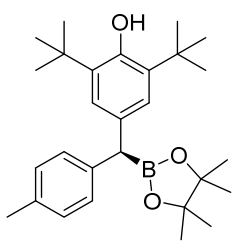
(*S*)-2,6-di-*tert*-Butyl-4-[(4-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]phenol (2c)



From **1c** (65 mg, 0.2 mmol), following the general procedure described above (rt), compound (*S*)-**2c** (38.6 mg, 0.086 mmol) was obtained in 65% yield after purification by column chromatography (10% Et_2O/hexanes) as a colorless oil. $\mathbf{R}_f$= 0.37 (10% Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.14 (d, *J* = 8.7 Hz, 2H), 7.04 (s, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.98 (s, 1H), 3.77 (s, 3H), 3.70 (s, 1H), 1.39 (s, 18H), 1.23 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 157.4, 151.7, 135.5, 135.0, 132.6, 129.8, 125.8, 113.7, 83.4, 55.2, 34.3, 30.4, 24.7, 24.6. [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **HRMS (ESI+, MeOH+NaI):** calculated for $[M+Na]^+$, $C_{28}H_{41}BO_4Na$: 475.2990, found 475.2974. Compound (*S*)-**2c** was oxidized to compound (*S*)-**3c** (see general procedure below) to determine the enantiomeric ratio. Compound (*S*)-**3c** was obtained with a 93:7 enantiomeric ratio determined by HPLC using Chiralpak-IA column [Hexane/^{i}PrOH (99.5:0.5, 1.0 mL/min]: τ_{major}= 35.9 min, τ_{minor}= 32.9 min. $\mathbf{[\alpha]^{20}_D}$= +12.3 (*c*= 0.8, $CHCl_3$).

(*S*)-2,6-di-*tert*-Butyl-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(*p*-tolyl)methyl]phenol (2d)

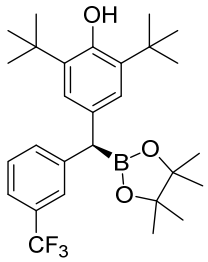


From **1d** (62 mg, 0.2 mmol), following the general procedure described above (rt), compound (*S*)-**2d** (57.6 mg, 0.154 mmol) was obtained in 77% yield after purification by column chromatography (3% Et_2O/hexanes) as a white solid. $\mathbf{R}_f$= 0.46 (3% Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.11 (d, *J* = 8.2 Hz, 2H), 7.06 (s, 2H),

7.05 (d, J = 8.1 Hz, 2H), 4.97 (s, 1H), 3.72 (s, 1H), 2.30 (s, 3H), 1.4 (s, 18H), 1.24 (s, 6H), 1.23 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 151.7, 140.0, 135.5, 134.5, 132.3, 128.9, 128.6, 125.9, 83.4, 34.3, 30.4, 24.7, 24.6, 21.0. [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **HRMS (ESI+MeOH+0.1% formic acid):** calculated for $[M+Na]^+$, $C_{28}H_{41}BO_3Na$: 459.3040, found 459.3035. Compound (*S*)-**2d** was oxidized to (*S*)-**3d** (see general procedure below) to determine the enantiomeric ratio. Compound (*S*)-**3d** was obtained with a 93:7 enantiomeric ratio determined by SFC using Chiralpak-IA column [CO_2/MeOH (95:5) 3.0 mL/min] τ_{major} : 5.8 min τ_{minor} : 5.4 min. **$[\alpha]^{20}_D$** = +14.5 (*c*= 1.0, $CHCl_3$). **mp** = 85-87 ºC.

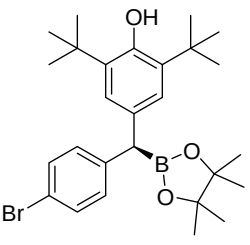
(*S*)-2,6-di-*tert*-Butyl-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)[(3-(trifluoromethyl)phenyl]methyl]phenol (2e)



From **1e** (72 mg, 0.2 mmol), following the general procedure described above (rt), compound (*S*)-**2e** (77.5 mg, 0.16 mmol) was obtained in 79% yield after purification by column chromatography (8.33% Et_2O/hexanes) as a colorless oil. **R_f**= 0.50 (8% Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.44-7.34 (m, 3H), 7.04 (s, 2H), 5.06 (s, 1H), 3.82 (s, 1H), 1.40 (s, 18H), 1.24 (s, 6H), 1.23 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 152.1, 144.1, 135.8, 132.2, 131.2, 130.3 (q, J = 31.5 Hz), 128.6, 125.8, 125.6 (q, J = 3.8 Hz), 124.4 (q, J = 272.2 Hz), 122.1 (q, J = 3.8 Hz), 83.8, 34.4, 30.3, 24.6 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **^{19}F-NMR** (282 MHz, $CDCl_3$): δ -62.6. **HRMS (EI+):** calculated for $[M]^+$, $C_{28}H_{38}BO_3F_3$: 490.2866, found 490.2877. Compound (*S*)-**2e** was oxidized to compound (*S*)-**3e** (see general procedure below) to determine the enantiomeric ratio. Compound (*S*)-**3e** was obtained with a 94:6 enantiomeric ratio determined by SFC using Chiralpak-IB column [CO_2/MeOH (98:2) 1.0 mL/min] τ_{major} : 19.0 min τ_{minor} : 17.9 min. **$[\alpha]^{20}_D$** = +17.4 (c= 1.0, $CHCl_3$).

(*S*)-4-[(4-Bromophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2,6-di-*tert*-butylphenol (2f)

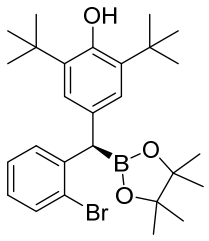


From **1f** (75 mg, 0.2 mmol), following the general procedure described above (rt), compound (*S*)-**2f** (84.4 mg, 0.17 mmol) was obtained in 84% yield after purification by column chromatography (5% Et_2O/hexanes) as a white solid. **R_f**= 0.55 (3% Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.36 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 7.03 (s, 2H), 5.02 (s, 1H), 3.71 (s, 1H), 1.40 (s, 18H), 1.24 (s, 6H), 1.23 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 152.3, 142.6, 136.1, 131.9, 131.6, 130.9, 126.2, 119.4, 84.0, 34.7, 30.7, 25.6, 25.0. [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **HRMS (ESI+, MeOH+NaI):** calculated for $[M+NaBr]^+$ $C_{27}H_{38}BO_3NaBr$: 523.1989, found 523.1977. Compound (*S*)-**2f** was oxidized to compound (*S*)-**3f** (see general procedure below) to determine the enantiomeric ratio. Compound (*S*)-**3f** was obtained with a 96:4 enantiomeric ratio determined by SFC using

Chiralpak-IA column [CO_2/MeOH (95:5, 3.0 mL/min]: τ_{major}= 7.4 min, τ_{minor}= 6.7 min. **[α]$^{20}_{D}$**= +20.3 (*c*= 1.0, $CHCl_3$). **mp** = 102-104 ºC.

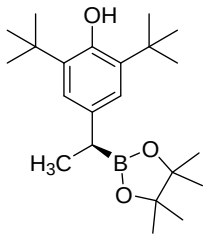
(*R*)-4-[(2-Bromophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2,6-di-*tert*-butylphenol (2g)



From **1g** (75 mg, 0.2 mmol), following the general procedure described above (rt), compound (*R*)-**2g** (69.2 mg, 0.14 mmol) was obtained in 69% yield after purification by column chromatography (3% Et_2O/hexanes) as a white solid. $\mathbf{R}_f$= 0.25 (3% Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.1 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 2H), 7.00 (m, 2H), 5.07 (s, 1H), 4.09 (s, 1H), 1.43 (s, 18H), 1.28 (s, 6H), 1.22 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 152.2, 143.5, 135.9, 132.2, 130.1, 129.8, 127.3, 126.8, 126.6, 124.7, 83.7, 34.4, 30.3, 24.8, 24.7. [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **HRMS (ESI+,MeOH+0.1% formic acid):** calculated for $[M+H]^+$, $C_{27}H_{39}BO_3Br$: 501.2170, found 501.2183. Compound (*R*)-**2g** was oxidized to compound (*R*)-**3g** (see general procedure below) to determine the enantiomeric ratio. Compound (*R*)-**3g** was obtained with a 96:4 enantiomeric ratio determined by SFC using Chiralpak-IB column [CO_2/MeOH (97:3) 3.0 mL/min] τ_{major} : 9.8 min τ_{minor} : 9.2 min. **[α]$^{20}_{D}$** = +90.6 (c= 1.0, $CHCl_3$). **mp** = 170-172 ºC.

(*S*)-2,6-di-*tert*-Butyl-4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]phenol (2h)

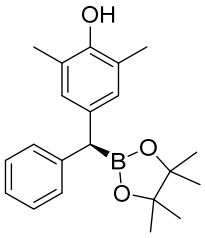


From **1h**[13] (47 mg, 0.2 mmol), following the general procedure described above (rt), compound (*S*)-**2h** (54 mg, 0.15 mmol) was obtained in 76% yield after purification by column chromatography (4% Et_2O/hexanes) as a yellow solid. $\mathbf{R}_f$= 0.62 (17% Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.01 (s, 2H), 4.94 (s, 1H), 2.33 (q, *J* = 7.4 Hz, 1H), 1.42 (s, 18H), 1.28 (d, *J* = 7.5 Hz, 3H), 1.24 (s, 6H),1.22 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 151.4, 135.5, 135.3, 124.5, 83.1, 34.4, 30.4, 24.7, 18.0. [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the nucleus]. **HRMS (ESI+,MeOH+0.1% formic acid+NaCl):** calculated for $[M+Na]^+$, $C_{22}H_{37}BO_3Na$: 383.2727, found 383.2735. Compound (*S*)-**2h** was oxidized to (*S*)-**3h** (see general procedure below) to determine the enantiomeric ratio. Compound (*S*)-**3h** was obtained with a 93:7 enantiomeric ratio determined by SFC using Chiralpak-IB column [CO_2/MeOH (99:1) 3 mL/min] τ_{major} : 6.8 min τ_{minor} : 6.1 min. **[α]$^{20}_{D}$** = +6.2 (*c*= 1.0, $CHCl_3$). **mp** = 46-48 ºC.

[13] Bacha, J. D.; Matthews, J. S., *US 4032547 A 19770628*, **1977**.

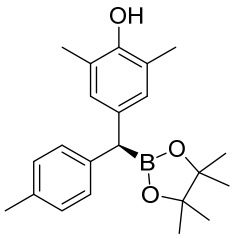
(*S*)-2,6-Dimethyl-4-[phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]phenol (2i)



From **1i** (42 mg, 0.2 mmol), following the general procedure described above (rt), compound (*S*)-**2i** (42.8 mg, 0.13 mmol) was obtained in 65% yield after purification by column chromatography (33% Et_2O/hexanes) as a colorless oil. $\mathbf{R_f}$= 0.34 (33% Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.28-7.20 (m, 4H), 7.18-7.08 (m, 1H), 6.83 (s, 2H), 4.45 (s, 1H), 3.72 (s, 1H), 2.18 (s, 6H), 1.22 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 150.6, 143.1, 133.7, 129.7, 129.2, 128.6, 125.7, 123.2, 84.0, 24.9, 24.8, 16.3. [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **HRMS (EI+):** calculated for [M^+], $C_{21}H_{27}BO_3$: 338.2053, found 338.2044. Compound (*S*)-**2i** was obtained with a 96:4 enantiomeric ratio determined by SFC using Chiralpak-IB column [CO_2/MeOH (98:2), 1.0 mL/min]: τ_{major}= 31.7 min, τ_{minor}= 30.4 min. $\mathbf{[\alpha]^{20}_D}$= +13.4 (*c*= 1.0, $CHCl_3$).

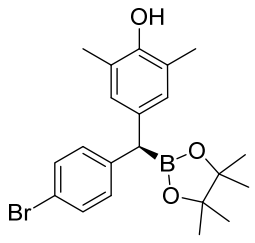
(*S*)-2,6-Dimethyl-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(*p*-tolyl)methyl]phenol (2j)



From **1j** (45 mg, 0.2 mmol), following the general procedure described above (rt), compound (*S*)-**2j** (66.8 mg, 0.19 mmol) was obtained in 95% yield after purification by column chromatography (20% Et_2O/hexanes) as a yellow solid. $\mathbf{R_f}$= 0.34 (20 % Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.86 (s, 2H), 4.40 (s, 1H), 3.67 (s, 1H), 2.29 (s, 3H), 2.18, (s, 6H), 1.23 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 150.2, 139.6, 134.7, 133.6, 129.2, 129.0, 128.7, 122.8, 83.5, 24.6, 24.5, 20.9, 15.9. [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the nucleus]. **HRMS (ESI+,MeOH+NaI):** calculated for [M+Na]$^+$, $C_{22}H_{29}BO_3Na$: 375.2101, found 375.2115. Compound (*S*)-**2j** was obtained with a 95:5 enantiomeric ratio determined by SFC using Chiralpak-IA column [CO_2/MeOH (98:2), 1.0 mL/min]: τ_{major} : 42.5 min, τ_{minor} : 38.0 min. $\mathbf{[\alpha]^{20}_D}$ = +25.0 (c= 1.0, $CHCl_3$). **mp** = 86-88 ºC.

(*S*)-[(4-Bromophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2,6-dimethylphenol (2k)

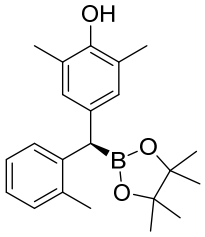


From **1k** (58 mg, 0.2 mmol), following the general procedure described above (rt), compound (*S*)-**2k** (48.0 mg, 0.12 mmol) was obtained in 58% yield after purification by column chromatography (33% Et_2O/hexanes) as a white solid. $\mathbf{R_f}$= 0.28 (33% Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.84 (s, 2H), 4.54 (s, 1H), 3.67 (s, 1H), 2.19 (s, 6H), 1.24 (s, 6H), 1.23 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 150.4, 141.9, 132.7, 131.3, 130.6, 129.3, 123.1, 119.2, 83.8, 24.6, 24.5, 15.9. [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the nucleus]. **HRMS (EI+):** calculated for [$M]^+$, $C_{21}H_{26}BO_3Br$: 416.1158, found 416.1157. Compound (*S*)-**2k** was obtained with a 95:5

enantiomeric ratio determined by HPLC using Chiralpak-IA column [Hexane/^{i}PrOH (99.5:0.5) 0.5 mL/min]: τ_{major} : 24.1 min, τ_{minor} : 20.7 min. **[α]$^{20}_{D}$** = +7.9 (c= 1.0, $CHCl_3$). **mp** = 70-72 ºC.

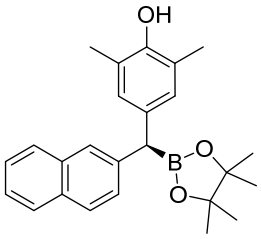
(*R*)-2,6-Dimethyl-4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(*o*-tolyl)methyl]phenol (2l)



From **1l** (45 mg, 0.2 mmol), following the general procedure described above (0 ºC), compound (*R*)-**2l** (44.2 mg, 0.126 mmol) was obtained in 63% yield after purification by column chromatography (20% Et_2O/hexanes) as a white solid. $\mathbf{R}_f$= 0.24 (20 % Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.21 (d, *J* = 6.4 Hz, 1H), 7.15-7.03 (m, 3H), 6.80 (s, 2H), 4.42 (s, 1H), 3.85 (s, 1H), 2.29 (s, 3H), 2.18 (s, 6H), 1.23 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 150.1, 140.8, 136.3, 132.8, 130.2, 129.5, 128.9, 125.9, 125.5, 122.8, 83.6, 24.7, 24.5, 20.13, 16.0 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the nucleus]. **HRMS (EI+):** calculated for $[M]^+$, $C_{22}H_{29}BO_3$: 352.2210, found 352.2198. Compound (*S*)-**2l** was oxidized to (*S*)-**3l** (see general procedure below) to determine the enantiomeric ratio. Compound (*S*)-**3l** was obtained with a 95.5:4.5 enantiomeric ratio determined by SFC using Chiralpak-IB column [CO_2/MeOH (95:5) 3.0 mL/min]: τ_{major} : 18.4 min, τ_{minor} : 17.6 min. **[α]$^{20}_{D}$** = +20.8 (c= 1.0, $CHCl_3$). **mp** = 102-104 ºC.

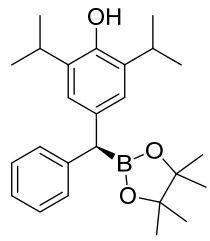
(*S*)-2,6-Dimethyl-4-[naphthalen-2-yl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]phenol (2m)



From **1m** (52 mg, 0.2 mmol), following the general procedure described above (rt), compound (*S*)-**2m** (49 mg, 0.13 mmol) was obtained in 63% yield after purification by column chromatography (33% Et_2O/hexanes) as a yellow solid. $\mathbf{R}_f$= 0.33 (33% Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.85–7.70 (m, 3H), 7.64 (s, 1H), 7.50-7.34 (m, 3H), 6.91 (s, 2H), 4.51 (s, 1H), 3.89 (s, 1H), 2.19 (s, 6H), 1.24 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 150.3, 140.3, 133.7, 133.2, 131.8, 129.4, 128.1, 127.7, 127.6, 127.5, 126.8, 125.6, 124.9, 122.9, 83.6, 24.6, 15.9. [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the nucleus]. **HRMS (EI+):** calculated for $[M]^+$, $C_{25}H_{29}BO_3$: 388.2210, found 388.2220. Compound (*S*)-**2m** was obtained with a 96:4 enantiomeric ratio determined by SFC using Chiralpak-IA column [CO_2/MeOH (95:5) 3.0 mL/min]: τ_{major} : 11.2 min, τ_{minor} : 10.4 min. **[α]$^{20}_{D}$** = +13.4 (*c*= 1.0, $CHCl_3$). **mp** = 49-51 °C.

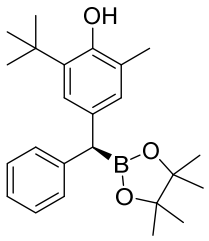
(*S*)-2,6-Diisopropyl-4-[phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]phenol (2n)



From **1n** (53 mg, 0.2 mmol), following the general procedure described above (0 ºC), compound (*S*)-**2n** (56.1 mg, 0.14 mmol) was obtained in 71% yield after purification by column chromatography (20% Et_2O/hexanes) as a yellow oil. $\mathbf{R_f}$= 0.55 (20 % Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.33-7.19 (m, 4H), 7.13 (t, *J* = 6.8 Hz, 1H), 6.96 (s, 2H), 4.65 (s, 1H), 3.79 (s, 1H), 3.19-3.04 (m, 2H), 1.28-1.19 (m, 24H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 148.0, 143.0, 133.4, 133.1, 128.7, 128.2, 125.2, 124.5, 83.5, 27.2, 24.7, 24.5, 22.8, 22.7 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the nucleus]. **HRMS (EI+):** calculated for $[M]^+$, $C_{25}H_{35}BO_3$: 394.2679, found 394.2673. Compound (*S*)-**2n** was oxidized to (*S*)-**3n** (see general procedure below) to determine the enantiomeric ratio. Compound (*S*)-**3n** was obtained with a 95:5 enantiomeric ratio determined by HPLC using Chiralpak-IA column [Hexane/^{i}PrOH (95:5) 1 mL/min]: τ_{major} : 15.8 min, τ_{minor} : 13.5 min. $\mathbf{[\alpha]^{20}_D}$ = +16.7 (*c*= 1.0, $CHCl_3$).

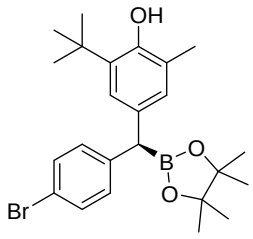
(*S*)-2-(*tert*-Butyl)-6-methyl-4-[phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]phenol (2o)



From **1o** (51 mg, 0.2 mmol), following the general procedure described above (rt), compound (*S*)-**2o** (49.6 mg, 0.14 mmol) was obtained in 71% yield after purification by column chromatography (14% Et_2O/hexanes) as a yellow oil. $\mathbf{R_f}$= 0.44 (14 % Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.31-7.22 (m, 4H), 7.20-7.15 (m, 1H), 7.13 (s, 1H), 6.85 (s, 1H), 4.61 (s, 1H), 3.78 (s, 1H), 2.19 (s, 3H), 1.42 (s, 9H), 1.26 (s, 6H), 1.25 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 150.1, 142.8, 135.3, 132.8, 129.2, 128.8, 128.2, 126.1, 125.3, 122.9, 83.5, 34.5, 29.8, 24.6, 24.5, 16.0 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the nucleus]. **HRMS (ESI+, MeOH+NaI):** calculated for $[M+Na]^+$, $C_{24}H_{33}BO_3Na$: 403.2414, found 403.2410. Compound (*S*)-**2o** was obtained with a 93:7 enantiomeric ratio determined by HPLC using Chiralpak-IA column [Hexane/^{i}PrOH (99.5:0.5) 1 mL/min]: τ_{major} : 7.6 min, τ_{minor} : 6.6 min. $\mathbf{[\alpha]^{20}_D}$ = +10.9 (c= 1.0, $CHCl_3$).

(*S*)-4-[(4-Bromophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2-(*tert*-butyl)-6-methylphenol (2p)



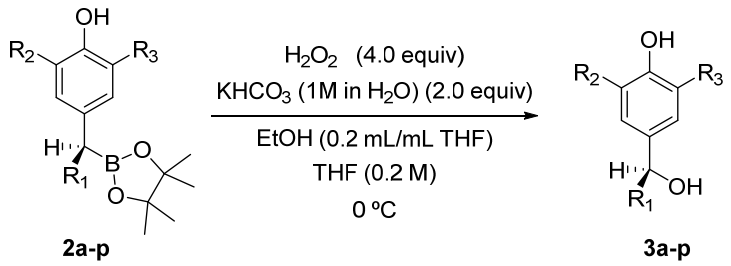
From **1p** (66 mg, 0.2 mmol), following the general procedure described above (rt), compound (*S*)-**2p** (49.5 mg, 0.108 mmol) was obtained in 54% yield after purification by column chromatography (20% Et_2O/hexanes) as a white solid. $\mathbf{R_f}$= 0.36 (20% Et_2O/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.06 (s, 1H), 6.78 (s, 1H), 4.79 (s, 1H), 3.68 (s, 1H), 2.17 (s, 3H), 1.37 (s, 9H), 1.25 (s, 6H), 1.24 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 150.8, 142.0, 135.5,

132.2, 131.3, 130.6, 129.1, 126.0, 123.1, 119.1, 83.7, 34.5, 29.8, 24.6, 24.5, 16.0 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the nucleus]. **HRMS (EI+):** calculated for $[M]^+$, $C_{24}H_{32}BO_3Br$: 458.1628, found 458.1629. Compound (*S*)-**2p** was oxidized to (*S*)-**3p** (see general procedure below) to determine the enantiomeric ratio. Compound (*S*)-**3p** was obtained with a 91:9 enantiomeric ratio determined by HPLC using Chiralpak-IC column [Hexane/^{i}PrOH (98:2) 1 mL/min]: τ_{major} : 9.3 min, τ_{minor} : 7.6 min. $\mathbf{[\alpha]^{20}_D}$ = +15.38 (c= 1.0, $CHCl_3$). **mp** = 123-125 ºC.

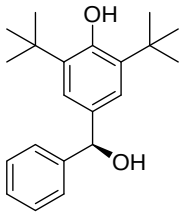
5. Functionalization of the C-B bond

5.1. General Procedure for the synthesis of chiral benzylic alcohols 3a-3p



A round bottom flask was charged with benzylic boronate **2** (0.1 mmol), a magnetic stir bar and 0.5 mL of THF and was cooled to 0 ºC. Then, EtOH (0.1 mL), potassium bicarbonate solution (1M in H_2O, 0.2 mL) and H_2O_2 (30%, 41 µL) were added. The reaction mixture was stirred for 1 hour at 0 ºC. The reaction was checked by TLC until completion. Ethyl acetate and water were added and the layers were separated. The aqueous phase was extracted with ethyl acetate (x3) and the combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash-column chromatography (eluents indicated in each case).

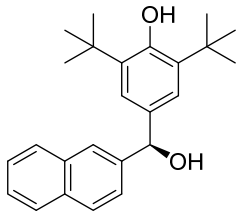
(*S*)-2,6-di-*tert*-Butyl-4-[hydroxy(phenyl)methyl]phenol (3a)



From **2a** (58 mg, 0.14 mmol), following the general procedure described above, compound (*S*)-**3a** (35 mg, 0.11 mmol) was obtained in 81% yield after purification by column chromatography (10% ethyl acetate/cyclohexane) as a white solid. $\mathbf{R}_f$= 0.27 (10% ethyl acetate/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.45-7.31 (m, 4H), 7.30-7.23 (m, 1H), 7.17 (s, 2H), 5.78 (s, 1H), 5.18 (s, 1H), 1.41 (s, 18H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 153.3, 144.1, 135.9, 134.6, 128.3, 127.2, 126.4, 123.6, 76.7, 34.4, 30.2. **HRMS (EI+):** calculated for $[M\text{-}H_2O]^+$, $C_{21}H_{26}O$: 294.1984, found 294.1986. Compound (*S*)-**3a** was obtained with a 96:4 enantiomeric ratio determined by HPLC using Chiralpak-IA column [Hexane/^{i}PrOH (98:2), 1.0 mL/min]: τ_{major}= 9.0 min, τ_{minor}= 7.9 min. **$[\alpha]^{20}_D$** = -18.33 (*c*= 0.67, $CHCl_3$). **mp** = 82-84 ºC.

(*S*)-2,6-di-*tert*-Butyl-4-[hydroxy(naphthalen-2-yl)methyl]phenol (3b)

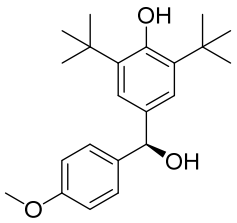


From **2b** (58 mg, 0.12 mmol), following the general procedure described above, compound (*S*)-**3b** (21.8 mg, 0.06 mmol) was obtained in 50% yield after purification by column chromatography (20% ethyl acetate/cyclohexane) as a white solid. $\mathbf{R}_f$= 0.28 (10% EtOAc/ hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.89-7.74 (m, 3H), 7.56-7.38 (m, 3H), 7.22 (s, 2H), 5.93 (s, 1H), 5.19 (s, 1H), 2.37 (bs, 1H), 1.41 (s, 18H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 153.4, 141.5, 136.0, 134.4, 133.3, 132.8, 128.1, 128.0, 127.6, 126.0, 125.7, 124.9, 124.7, 123.8, 76.8 34.4, 30.2. **HRMS (EI+):** calculated for $[M\text{-}H_2O]^+$, $C_{25}H_{28}O$: 344.2140, found 344.2142. Compound (*S*)-**3b** was obtained with a 96:4 enantiomeric ratio

determined by SFC using Chiralpak-IB column [CO_2/MeOH (95:5, 3.0 mL/min]: τ_{major}= 16.5 min, τ_{minor}= 15.2 min. **[α]$^{20}_{D}$** = –20.9 (*c*= 1.0, $CHCl_3$). **mp** = 153-155 ºC.

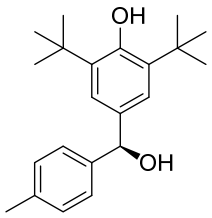
(*S*)-2,6-di-*tert*-Butyl-4-[hydroxy(4-methoxyphenyl)methyl]phenol (3c)



From **2c** (28 mg, 0.06 mmol), following the general procedure described above, compound (*S*)-**3c** (15 mg, 0,044 mmol) was obtained in 73% yield after purification by column chromatography (20% EtOAc/cyclohexane) as a yellow solid. **R$_f$**= 0.50 (20% EtOAc/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.6 Hz, 2H), 7.16 (s, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.74 (s, 1H), 5.16 (s, 1H), 3.80 (s, 3H), 2.05 (bs, 1H), 1.41 (s, 18H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 158.8, 153.2, 136.5, 135.8, 134.7, 127.7, 123.5, 113.7, 76.3, 55.3, 34.4, 30.3. **HRMS (EI+):** calculated for $[M\text{-}H_2O]^+$, $C_{22}H_{28}O_2$: 324.2089, found 324.2089. Compound (*S*)-**3c** was obtained with a 93:7 enantiomeric ratio determined by HPLC using Chiralpak-IA column [Hexane/^{i}PrOH (99.5:0.5, 1.0 mL/min]: τ_{major}= 35.9 min, τ_{minor}= 32.9 min. **[α]$^{20}_{D}$** = –15.9 (*c*= 1.0, $CHCl_3$). **mp** = 105-107 ºC.

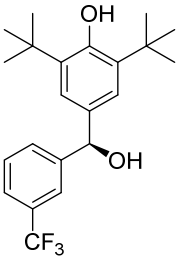
(*S*)-2,6-di-*tert*-Butyl-4-[hydroxy(*p*-tolyl)methyl]phenol (3d)



From **2d** (26 mg, 0.06 mmol), following the general procedure described above, compound (*S*)-**3d** (16.8 mg, 0,051 mmol) was obtained in 86% yield after purification by column chromatography (30% EtOAc/cyclohexane) as a yellow oil. **R$_f$**= 0.50 (31% EtOAc/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.17 (s, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.74 (s, 1H), 5.16 (s, 1H), 2.34 (s, 3H), 2.07 (bs, 1H), 1.41 (s, 18H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 153.2, 141.3, 136.8, 135.8, 134.7, 129.0, 126.3, 123.5, 76.6, 34.4, 30.2, 21.1. **HRMS (EI+):** calculated for $[M\text{-}H_2O]^+$, $C_{22}H_{28}O$: 308.2140, found 308.2133. (*S*)-**3d** was obtained with a 93:7 enantiomeric ratio determined by SFC using Chiralpak-IA column [CO_2/MeOH (95:5) 3.0 mL/min]: τ_{major} : 5.9 min, τ_{minor} : 5.4 min. **[α]$^{20}_{D}$** = –10.1 (*c*= 1.0, $CHCl_3$).

(*S*)-2,6-di-*tert*-Butyl-4-[hydroxyl[3-(trifluoromethyl)phenyl]methyl]phenol (3e)

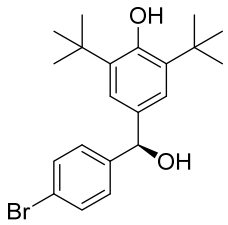


From **2e** (20 mg, 0.04 mmol), following the general procedure described above, compound (*S*)-**3e** (11.9 mg, 0,031 mmol) was obtained in 78% yield after purification by column chromatography (20% EtOAc/cyclohexane) as a yellow oil. **R$_f$**= 0.31 (17% EtOAc/hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.59-7.41 (m, 3H), 7.13 (s, 2H), 5.80 (s, 1H), 5.23 (s, 1H), 2.19 (bs, 1H), 1.41 (s, 18H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 153.7, 144.9, 136.2, 133.9, 130.6 (q, $J_{C\text{-}F}$ = 32.1 Hz), 129.7, 128.7 124.2 (q, $J_{C\text{-}F}$ = 271.8 Hz), 124.0 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.7, 123.1 (q, $J_{C\text{-}F}$ = 3.8 Hz), 76.2, 34.4, 30.2. **^{19}F-NMR** (282 MHz, $CDCl_3$): δ -62.6. **HRMS (EI+):** calculated for $[M\text{-}H_2O]^+$, $C_{22}H_{25}OF_3$: 362.1858, found 362.1849. Compound (*S*)-**3e** was obtained with a 94:6

enantiomeric ratio determined by SFC using Chiralpak-IB column [CO_2/MeOH (98:2) 1.0 mL/min]: τ_{major} : 19.0 min, τ_{minor} : 17.9 min. $[\alpha]^{20}_D$ = –10.5 (*c* = 1.0, $CHCl_3$).

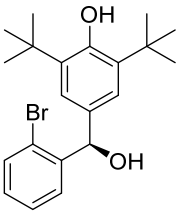
(*S*)-4-[(4-Bromophenyl)(hydroxy)methyl]-2,6-di-*tert*-butylphenol (3f)



From **2f** (50 mg, 0.1 mmol), following the general procedure described above, compound (*S*)-**3f** (31 mg, 0.08 mmol) was obtained in 79% yield after purification by column chromatography (20% EtOAc/cyclohexane) as a white solid. $\mathbf{R}_f$= 0.28 (10% EtOAc/ hexanes).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.13 (s, 2H), 5.73 (s, 1H), 5.21 (s, 1H), 2.13 (s, 1H), 1.42 (s, 18H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 153.4, 143.1, 136.0, 134.1, 131.3, 128.1, 123.5, 120.1, 76.1, 34.3, 30.2. **HRMS (EI+):** calculated for $[M]^+$, $C_{21}H_{27}O_2Br$: 390.1194, found 390.1206. Compound (*S*)-**3f** was obtained with a 96:4 enantiomeric ratio determined by SFC using Chiralpak-IA column [CO_2/MeOH (95:5, 3.0 mL/min]: τ_{major}= 7.4 min, τ_{minor}= 6.7 min. $[\alpha]^{20}_D$ = –23.4 (c = 1.0, $CHCl_3$). **mp =** 134-136 ºC.

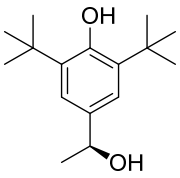
(*R*)-4-[(2-Bromophenyl)(hydroxy)methyl]-2,6-di-*tert*-butylphenol (3g)



From **2g** (69 mg, 0.14 mmol), following the general procedure described above, compound (*R*)-**3g** (28.3 mg, 0,072 mmol) was obtained in 52% yield after purification by column chromatography (25% EtOAc/cyclohexane) as a yellow oil. $\mathbf{R}_f$= 0.52 (25% EtOAc/hexanes).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.8, 1.6 Hz, 1H), 7.53 (d, *J* = 8.0, 1.1 Hz, 1H), 7.36 (t, *J* = 8.0, 1H), 7.24 (s, 2H), 7.13 (t, *J* = 7.8, 1H), 6.12 (s, 1H), 5.18 (s, 1H), 2.29 (bs, 1H), 1.42 (s, 18H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 153.4, 143.1, 135.8, 132.8, 132.7, 128.7, 128.0, 127.6, 123.9, 122.7, 75.2, 34.4, 30.2. **HRMS (EI+):** calculated for $[M]^+$, $C_{21}H_{27}O_2Br$: 390.1194, found 390.1190. Compound (*R*)-**3g** was obtained with a 96:4 enantiomeric ratio determined by SFC using Chiralpak-IB column [CO_2/MeOH (97:3) 3.0 mL/min] τ_{major} : 9.8 min, τ_{minor} : 9.2 min. $[\alpha]^{20}_D$ = +11.6 (*c* = 1.0, $CHCl_3$).

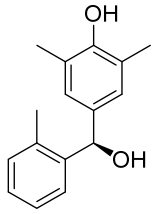
(*S*)-2,6-di-*tert*-Butyl-4-(1-hydroxyethyl)phenol (3h)



From **2h** (30 mg, 0.08 mmol), following the general procedure described above, compound (*S*)-**3h** (12.3 mg, 0,048 mmol) was obtained in 61% yield after purification by column chromatography (20% EtOAc/cyclohexane) as a white solid. $\mathbf{R}_f$= 0.14 (11% Et_2O/hexanes).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19 (s, 2H), 5.18 (s, 1H), 4.83 (q, *J* = 6.4 Hz, 1H), 1.70 (bs, 1H), 1.50 (d, *J* = 6.4 Hz, 3H), 1.46 (s, 18H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 153.2, 136.3, 135.9, 122.3, 70.9, 34.4, 30.3, 24.9. **HRMS (EI+):** calculated for $[M\text{-}H_2O]^+$, $C_{16}H_{24}O$: 232.1827, found 232.1822. Compound (*S*)-**3h,** obtained with a 93:7 enantiomeric ratio determined by SFC using Chiralpak-IB column [CO_2/MeOH (99:1) 3 mL/min]: τ_{major} : 6.8 min, τ_{minor} : 6.1 min. $[\alpha]^{20}_D$ = –14.1 (*c* = 1.0, $CHCl_3$). **mp =** 98-100 ºC.

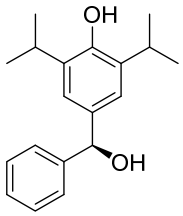
(*R*)-4-(Hydroxy(*o*-tolyl)methyl)-2,6-dimethylphenol (3l)



From **2l** (24 mg, 0.07 mmol), following the general procedure described above, compound (*R*)-**3l** (12 mg, 0,05 mmol) was obtained in 71% yield after purification by column chromatography (20% ethyl acetate/cyclohexane) as a white solid. $\mathbf{R}_f$= 0.11 (17% Et_2O/hexanes).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.7 Hz, 1H), 7.31-7.24 (m, 1H), 7.24-7.18 (m, 1H), 7.14 (t, *J* = 8.6 Hz, 1H), 6.91 (s, 2H), 5.88 (s, 1H), 4.60 (s, 1H), 2.22 (3H), 2.20 (s, 6H), 2.01 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 151.7, 141.6, 135.1, 134.5, 130.4, 127.5, 127.2, 126.0, 125.8, 123.0, 73.0, 19.4, 15.9. **HRMS (EI+):** calculated for $[M\text{-}H_2O]^+$, $C_{16}H_{16}O$: 224.1201, found 224.1206. Compound (*R*)-**3l** was obtained with a 95.5:4.5 enantiomeric ratio determined by SFC using Chiralpak-IB column [CO_2/MeOH (95:5) 3.0 mL/min]: τ_{major} : 18.4 min, τ_{minor} : 17.6 min. $\mathbf{[\alpha]^{20}_D}$ = +2.7 (*c*= 0.7, $CHCl_3$). **mp =** 135-137 °C.

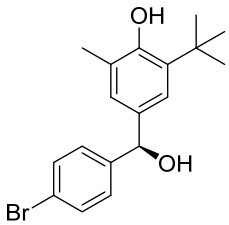
(*S*)-4-[Hydroxy(phenyl)methyl]-2,6-diisopropylphenol (3n)



From **2n** (34 mg, 0.084 mmol), following the general procedure described above, compound (*S*)-**3n** (19.5 mg, 0,068 mmol) was obtained in 82% yield after purification by column chromatography (20% EtOAc/cyclohexane) as an orange oil. $\mathbf{R}_f$ = 0.22 (20% Et_2O/hexanes).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.19 (m, 5H), 7.04 (s, 2H), 5.77 (s, 1H), 4.83 (s, 1H), 3.11 (sept, *J* = 6.9 Hz, 2H), 2.25 (bs, 1H), 1.22 (d, *J* = 6.8 Hz, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 149.6, 144.2, 135.9, 133.8, 128.4, 127.3, 126.5, 122.1, 76.5, 27.4, 22.7. **HRMS (EI+):** calculated for $[M\text{-}H_2O]^+$, $C_{19}H_{22}O$: 266.1671, found 266.1675. Compound (*S*)-**3n** was obtained with a 95:5 enantiomeric ratio determined by HPLC using Chiralpak-IA column [Hexane/^{i}PrOH (95:5) 1 mL/min]: τ_{major} : 15.8 min, τ_{minor} : 13.5 min. $\mathbf{[\alpha]^{20}_D}$ = –12.2 (*c*= 1.0, $CHCl_3$).

(*S*)-4-[(4-bromophenyl)(hydroxy)methyl]-2-(*tert*-butyl)-6-methylphenol (3p)

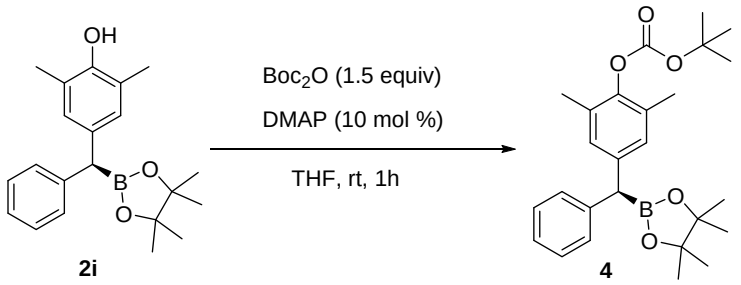


From **2p** (37 mg, 0.08 mmol), following the general procedure described above, compound (*S*)-**3p** (17 mg, 0,049 mmol) was obtained in 61% yield after purification by column chromatography (20% ethyl acetate/hexanes) as a yellow oil. $\mathbf{R}_f$= 0.20 (20% EtOAc/ hexanes).

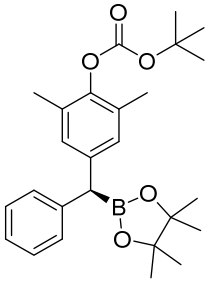
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.13 (s, 1H), 6.91 (s, 1H), 5.70 (s, 1H), 4.78 (s, 1H), 2.20 (s, 3H), 2.12 (bs, 1H), 1.39 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 152.4, 143.1, 135.8, 134.8, 131.4, 128.0, 126.8, 123.8, 123.3, 121.1, 75.7, 34.6, 29.7, 16.0. **HRMS (EI+):** calculated for $[M\text{-}H_2O]^+$, $C_{18}H_{19}OBr$: 330.0619, found 330.0615. Compound (*S*)-**3p**, was obtained with a 91:9 enantiomeric ratio determined by HPLC using Chiralpak-IC column [Hexane/^{i}PrOH (98:2) 1 mL/min]: τ_{major} : 9.3 min, τ_{minor} : 7.6 min. $\mathbf{[\alpha]^{20}_D}$ = –14.4 (*c*= 1.0, $CHCl_3$).

5.2. Synthesis of the diarylfurylmethane 6

5.2.1 (*S*)-*tert*-Butyl (2,6-dimethyl-4-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)phenyl) carbonate (4)

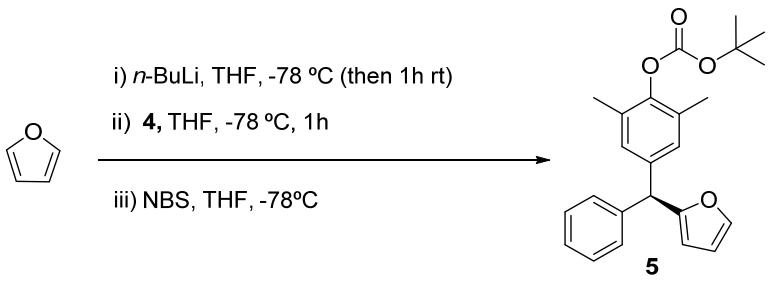


To a solution of boronate **2i** (580 mg, 1.7 mmol, 1.0 equiv) in THF (10 mL) was added Boc_2O (558 mg, 2.56 mmol, 1.5 equiv) followed by DMAP (21 mg, 0.1 mmol, 0.1 equiv). The resulting mixture was stirred at room temperature for 1 h. After this time, water (10 mL) and Et_2O (10 mL) were added. The organic layer was separated and the aqueous layers were extracted with Et_2O (2x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Purification by flash column chromatography (25% Et_2O/pentane), gave product **4** in 81% yield as a white solid. $\mathbf{R_f}$= 0.44 (20% Et_2O/hexanes).



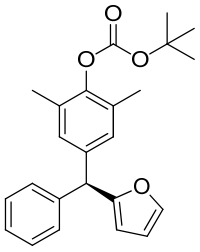
^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.32-7.23 (m, 4H), 7.21-7.13 (m, 1H), 6.96 (s, 2H), 3.78 (s, 1H), 2.17 (s, 6H), 1.57 (s, 9H), 1.25 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 151.5, 146.5, 142.1, 139.2, 129.9, 129.3, 129.1, 128.3, 125.5, 83.7, 82.8, 27.6, 24.6, 16.2. [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]. **HRMS (EI+):** calculated for [M^+], $C_{21}H_{27}BO_3$: 338.2053, found 338.2044. **$[\alpha]^{20}_D$**= +6.8 (*c*= 1.0, $CHCl_3$). **mp** = 70-72 °C.

5.2.2. Procedure for C(sp^3)-C (sp^2) coupling of boronic ester 4 with furan[14]



A solution of furan (10µL, 0.134 mmol, 1.0 equiv) in THF (0.3M) was cooled to -78 ºC and treated with *n*-BuLi (2.5M in hexanes, 57µL, 0.134 mmol, 1.0 equiv). The cooling bath was removed and the mixture was stirred at room temperature for 1 h. The mixture was cooled to -78 ºC and a solution of **4** (76 mg, 0.17 mmol, 1.3 equiv) in THF (0.5M) was added. The mixture was stirred at -78 ºC for 1 h. A solution of NBS (29 mg, 0.16 mmol, 1.2 equiv.) in THF (0.3M) was added dropwise. After 1 h at -78 ºC, a saturated solution of $Na_2S_2O_3$ was added and the reaction was allowed to warm to room temperature. Then Et_2O and water were added. The layers were separated and the aqueous layer was extracted with Et_2O. The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Purification by flash column chromatography (5% Et_2O/hexanes) gave product **5** in 75% yield as a colorless oil. $\mathbf{R}_f$= 0.31 (5% Et_2O/hexanes).

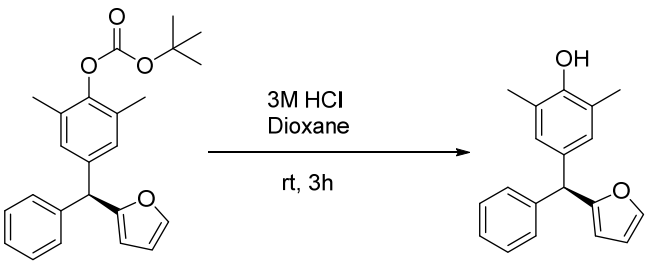
(*S*)-*tert*-Butyl-[4-(furan-2-yl(phenyl)methyl)-2,6-dimethylphenyl] carbonate (5)



^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.37 (s, 1H), 7.33-7.22 (m, 3H), 7.18-7.14 (m, 2H), 6.84 (s, 2H), 6.31 (m, 1H), 5.91 (m, 1H), 5.36 (s, 1H), 2.15 (s, 6H), 1.55 (s, 9H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 156.7, 151.4, 147.2, 141.9, 141.7, 139.0, 130.2, 128.9, 128.7, 128.4, 126.7, 110.1, 108.2, 83.1, 50.3, 27.6, 16.2. **HRMS (EI+):** calculated for [M^+], $C_{24}H_{27}O_4$: 379.1913, found 379.1909. **$[\alpha]^{20}_D$**= +13.8 (*c*= 1.0, $CHCl_3$).

[14] Bonet , A.; Odachowski, M.; Leonori, D.; Essafi, S.; Aggarwal, V. K. *Nat. Chem.*, **2014**, *6*, 584-589.

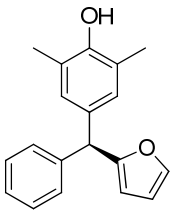
5.2.3 Procedure for Boc-deprotection of compound 5.



5 **SI-15**

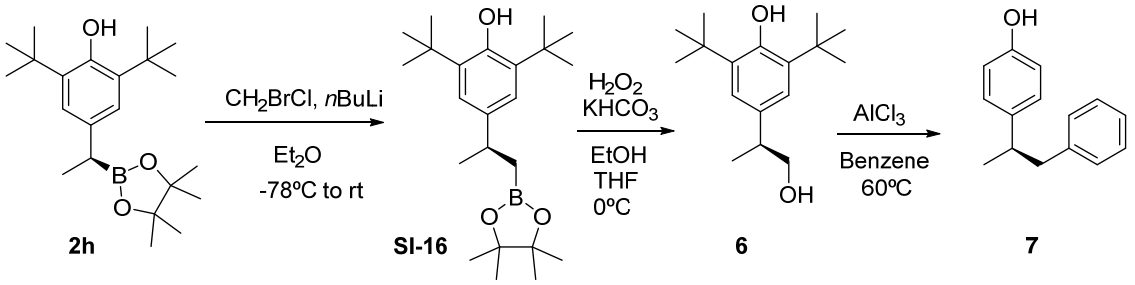
A round bottom flask was charged with **5** (38 mg, 0.1 mmol) and a solution 3M HCl in dioxane (2mL) was added. The reaction was stirred at room temperature for 3 h, after this time it was concentrated under reduced pressure. The reaction mixture was diluted with Et_2O and water. The layers were separated and the aqueous layers were extracted with Et_2O (2x10mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Purification by column chromatography on silica gel (25% Et_2O/pentane) to give product **SI-15** in 90% yield as a colorless oil. $\mathbf{R_f}$= 0.48 (25% Et_2O/pentane).

(*S*)-4-[Furan-2-yl(phenyl)methyl]-2,6-dimethylphenol (SI-15)



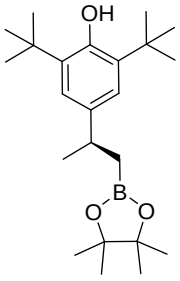
^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.37 (s, 1H), 7.32-7.22 (m, 3H), 7.20-7.14 (m, 2H), 6.79 (s, 2H), 6.30 (d, *J* = 3.1, 1H), 5.90 (d, *J* = 3.1 Hz, 1H), 5.32 (s, 1H), 4.52 (s, 1H), 2.20 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 157.3, 151.0, 142.3, 141.8, 133.4, 128.9, 128.7, 128.4, 126.6, 122.9, 110.0, 108.0, 50.2, 16.0. **HRMS (EI+):** calculated for [M^+], $C_{19}H_{18}O_2$: 278.1307, found 278.1303. Compound (*S*)-**SI-15** was obtained with a 92:8 enantiomeric ratio determined by SFC using Chiralpak-IB column [CO_2/MeOH (98:2), 2.0 mL/min]: τ_{major}= 23.5 min, τ_{minor}= 22.7 min. $\mathbf{[\alpha]^{20}_D}$= +21.9 (*c*= 1.0, $CHCl_3$).

5.3. Procedure for the synthesis of 1,2-diarylethane 7



5.3.1. Synthesis of (*R*)-2,6-di-*tert*-Butyl-4-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl]phenol (SI-16)

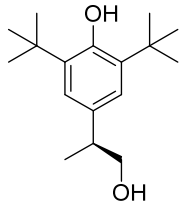
In an oven dried flask, benzylic boronate **2h** (72 mg, 0.2 mmol) and a magnetic stir bar were charged. Then, the flask was purged three times with vacuum/Ar cycles. Anhydrous diethyl ether (0.8 mL, 0.25M) was added and the reaction mixture was cooled to –78 ºC. Then *n*-BuLi (1.6M in hexanes, 2.5 equiv) was added dropwise to the reaction mixture. The mixture was stirred for 20 min at –78 ºC, and then it was warmed to room temperature and stirred for additional 4 h. The reaction mixture was filtered through a thin layer of silica gel. Solvent was removed and the crude mixture was purified by flash chromatography to give **SI-16** (58 mg, 0.154 mmol) in 77% yield as a colorless oil. $\mathbf{R}_f$= 0.62 (17% Et_2O/hexanes). This product was also synthesized in 0.5 mmol scale. **SI-16** can be purified or used directly in the oxidation step in a one-pot procedure.



^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.05 (s, 2H), 4.98 (s, 1H), 3.04-2.90 (m, 1H), 1.44 (s, 18H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.25 (d, *J* = 5.3 Hz, 1H) 1.17 (s, 12H), 1.14 (d, *J* = 5.3 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 151.6, 139.7, 135.3, 123.1, 82.8, 35.7, 34.3, 30.4, 25.3, 24.8, 24.6. [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the nucleus] **HRMS (EI+):** calculated for $[M]^+$, $C_{23}H_{39}O_3B$:374.2992, found 374.3001. **$[\alpha]^{20}_D$** = –6.43 (*c*= 1.0, $CHCl_3$).

5.3.2. Synthesis of (*S*)-2,6-di-*tert*-Butyl-4-(1-hydroxypropan-2-yl)phenol (6)

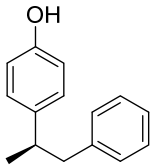
A solution of boronate **SI-16** (37 mg, 0.1 mmol) in THF (0,7 mL, 0.2M) was cooled to 0 ºC. Then, EtOH (0.13 mL, 0.2mL/mL THF), potassium bicarbonate solution (2.0 equiv, 1M in water) and hydrogen peroxide (4 equiv) were added and the mixture was stirred for 2 hours at this temperature. Water and EtOAc were added and the layers were separated. The aqueous layer was extracted with EtOAc and the combined organic layers were dried over Na_2SO_4 and filtered. Solvent was removed by rotary evaporation and the crude was purified by flash column chromatography to give **6** (22 mg, 0.083 mmol) with 83% yield as a white solid. This product was also synthesized in 0.5 mmol scale, from **2h**, in a one-pot homologation-oxidation sequence, to give **6** (93 mg, 0.35 mmol) in 71% overall yield.



^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.05 (s, 2H), 5.14 (s, 1H), 3.68 (d, *J* = 6.7 Hz, 2H), 2.89 (sext, *J* = 7.0 Hz, 1H), 1.48 (bs, 1H), 1.47 (s, 18H), 1.29 (d, *J* = 7.0 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 152.4, 136.0, 133.8, 123.8, 68.9, 42.2, 34.3, 30.3, 17.7. **HRMS (EI+):** calculated for $[M]^+$, $C_{17}H_{28}O_2$:264.2089, found 264.2096. **$[\alpha]^{20}_D$** = –10.6 (*c*= 1.0, $CHCl_3$). **mp** = 78-80 ºC.

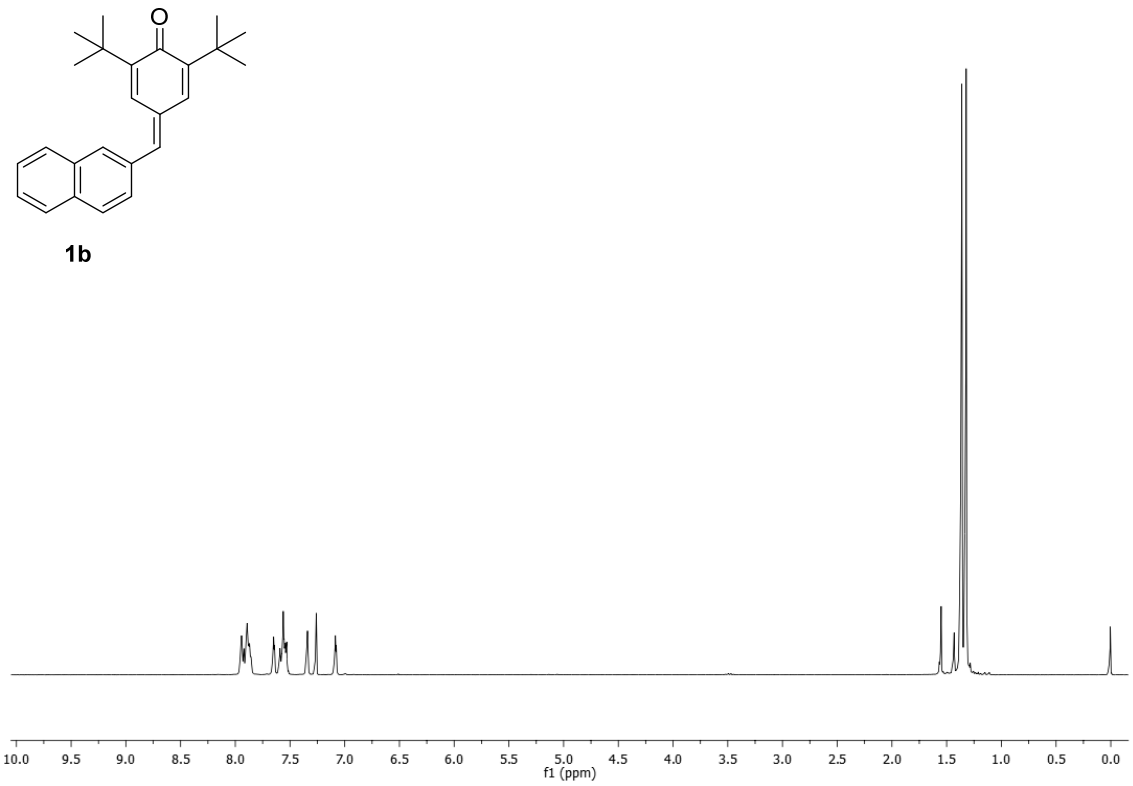
5.3.3. Synthesis of (*R*)-4-(1-Phenylpropan-2-yl)phenol (7)

A solution of alcohol **6** (50 mg, 0.2 mmol) and $AlCl_3$ (6 equiv) in dry benzene (0.018 M, 10.5 mL) was stirred at 60 ºC for one hour. Water and EtOAc were added and the layers were separated. The aqueous layer was extracted with EtOAc (x3) and the combined organic layers were dried over Na_2SO_4 and filtered. Solvent was removed by rotary evaporation and the crude product was purified by flash chromatography to give **7** (23 mg, 0.12 mmol) in 60% yield as a white solid. $\mathbf{R_f}$= 0.30 (20% Et_2O/hexanes)



^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.20 (dd, *J* = 7.6, 6.2 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 3H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 8.5 Hz, 2H), 4.61 (s,1H), 2.93-2.74 (m, 2H), 2.62 (dd, *J* = 13.1, 7.9 Hz, 1H), 1.15 (d, *J* = 6.7 Hz, 3H).**^{13}C-NMR** (75 MHz, $CDCl_3$): δ 153.6, 147.0, 133.1, 130.2, 128.2, 127.1, 125.9, 114.9, 44.1, 42.0, 21.1. **HRMS (EI+):** calculated for $[M]^+$, $C_{15}H_{16}O$:212.1201, found 212.1198. **$[\alpha]^{20}_D$ =** +52.7 (*c*= 1.0, $CHCl_3$). **mp =** 52-54 ºC.

6.NMR Spectra



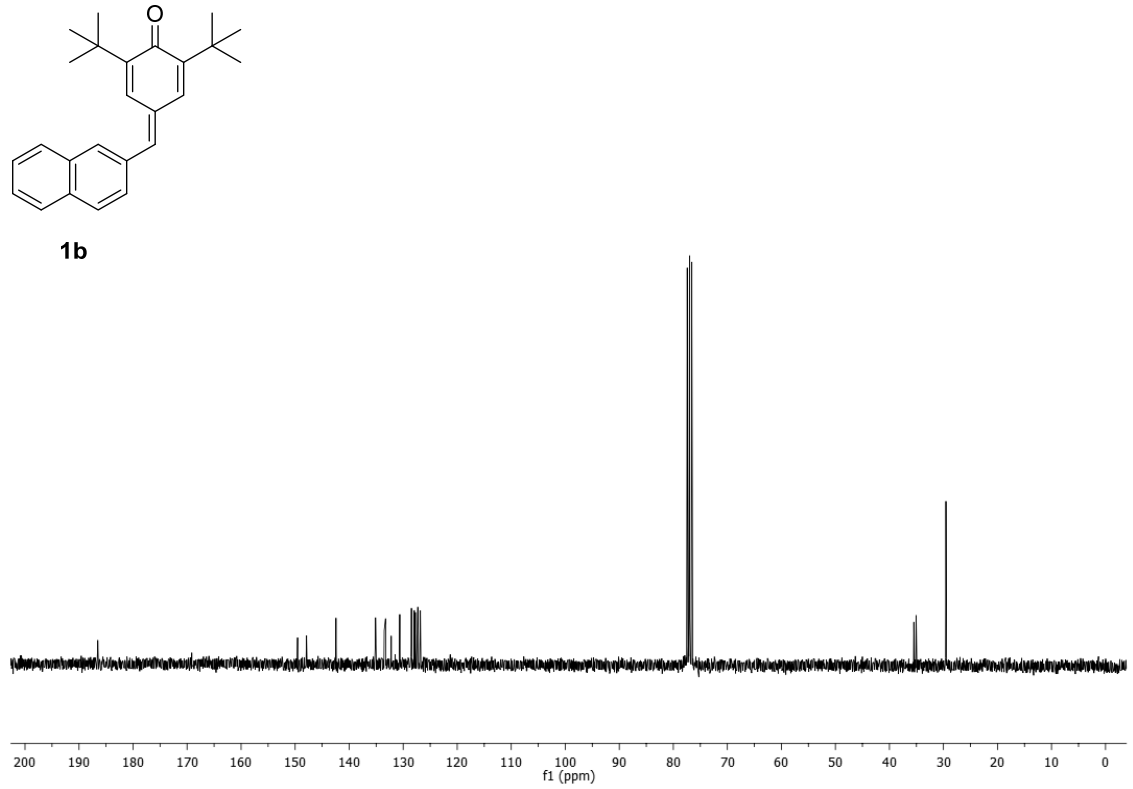
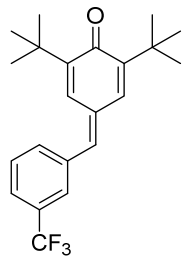
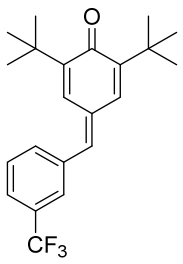


Figure S2: Spectra of compound **1b**.

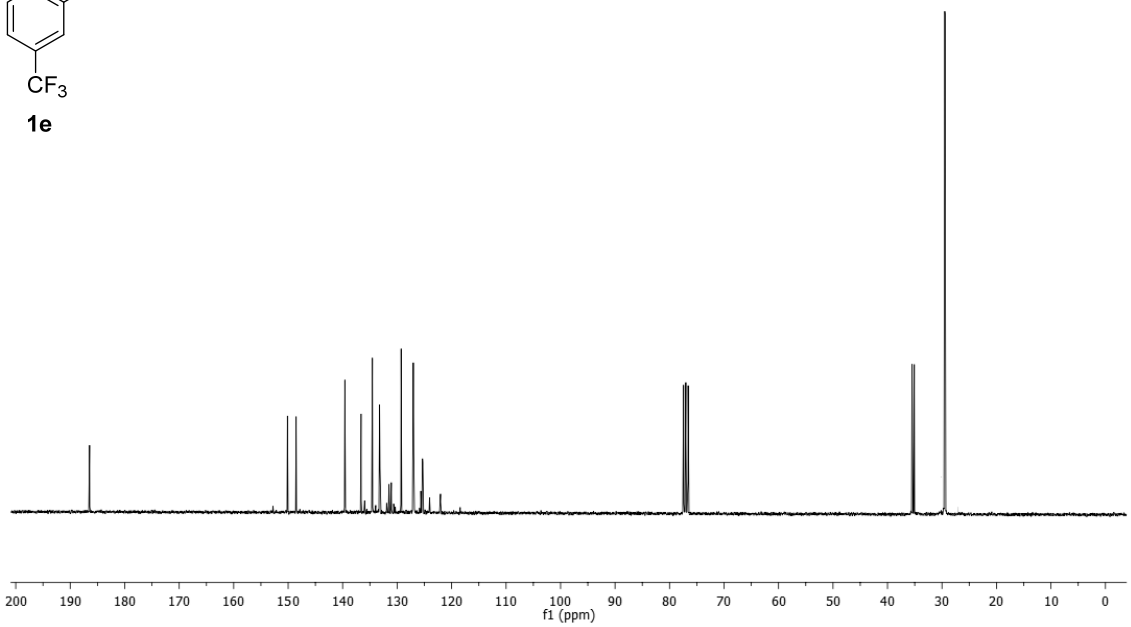

O
CF3

1e

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


O
CF3

1e


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

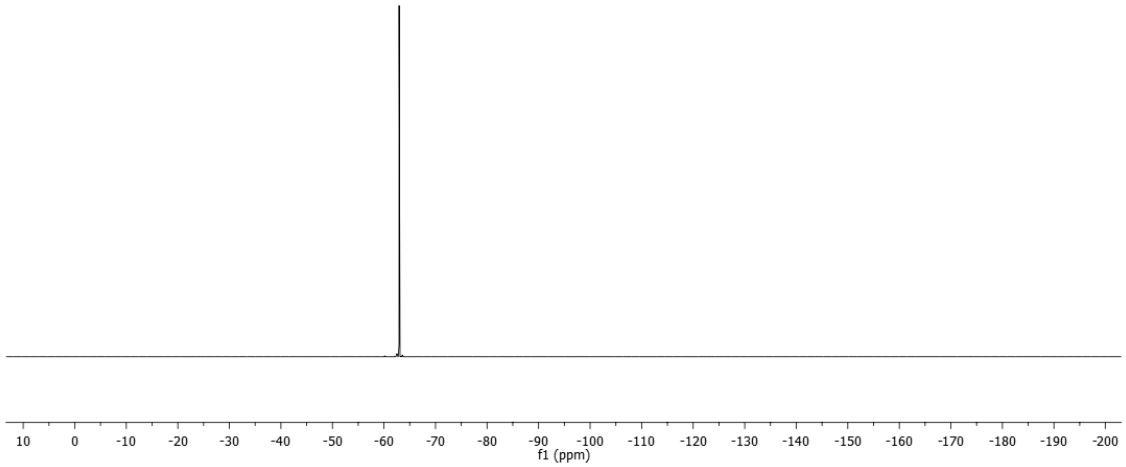
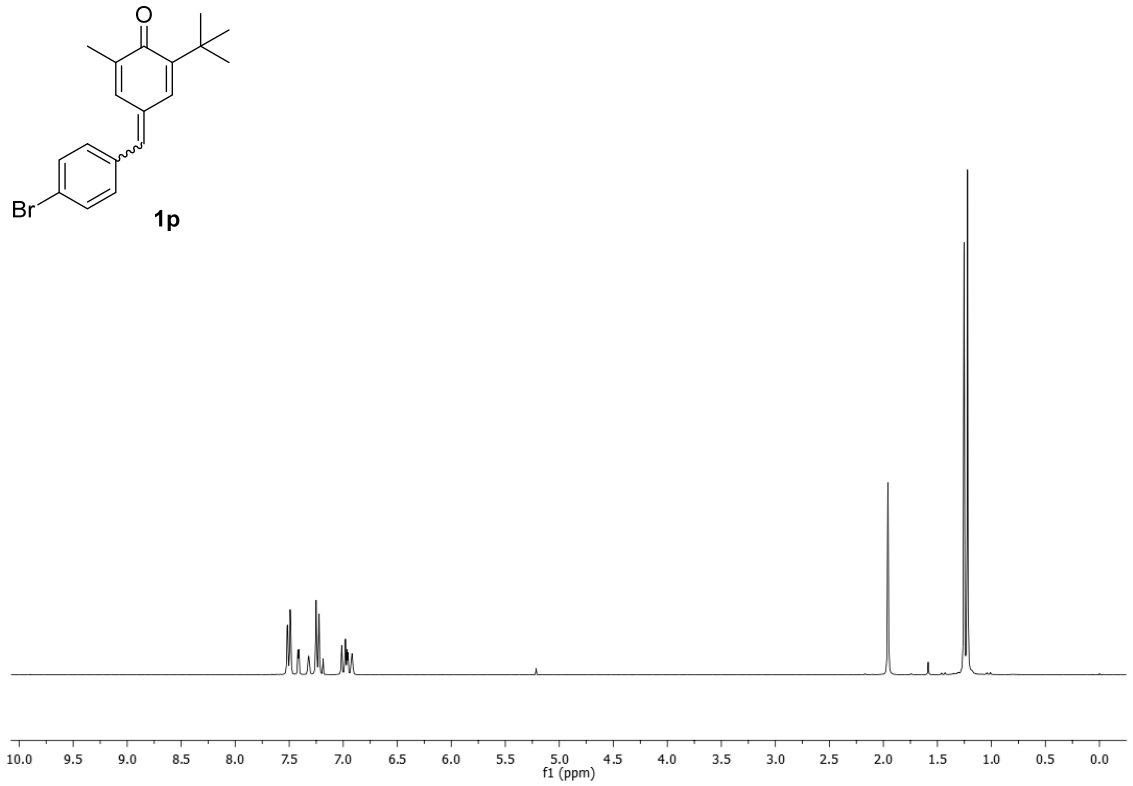


Figure S3: Spectra of compound **1e**.



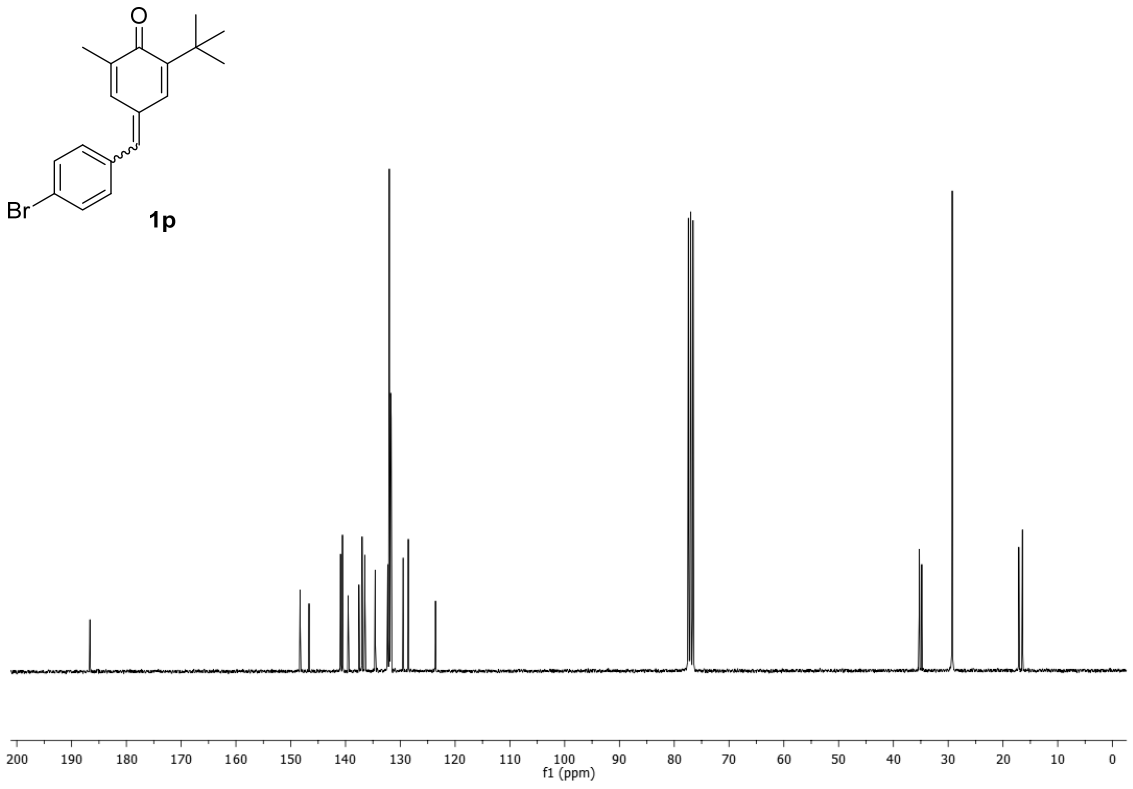
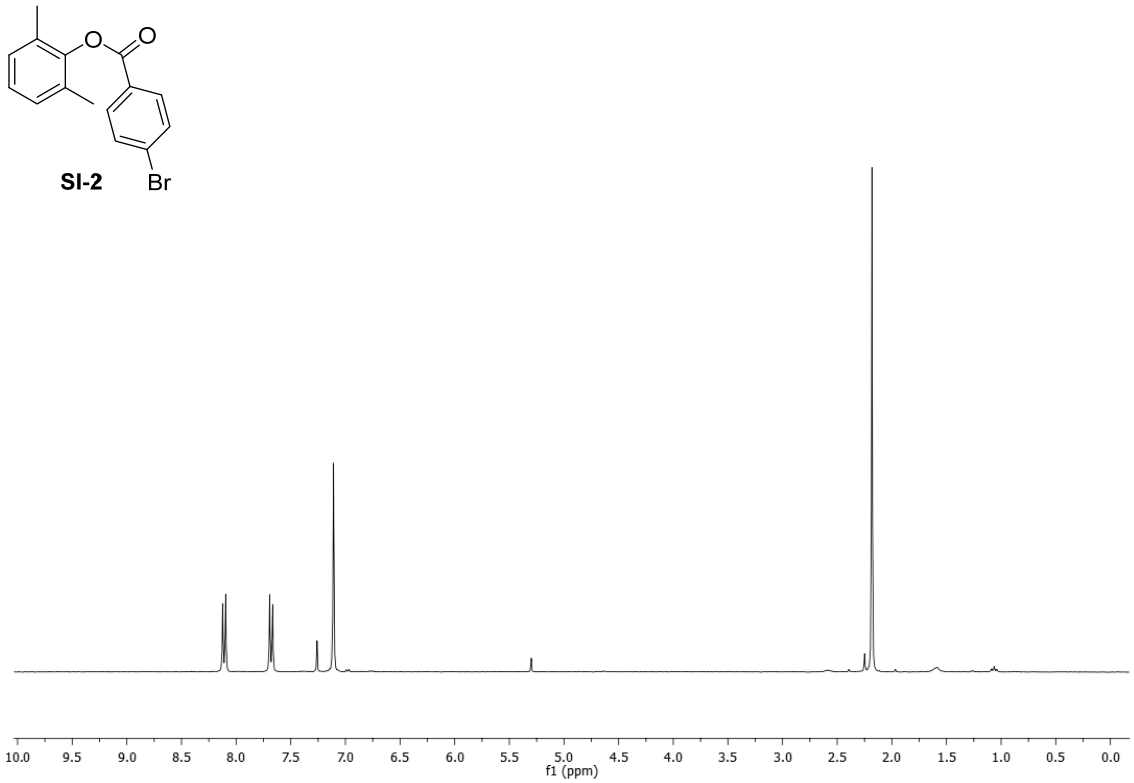


Figure S4: Spectra of compound **1p**.



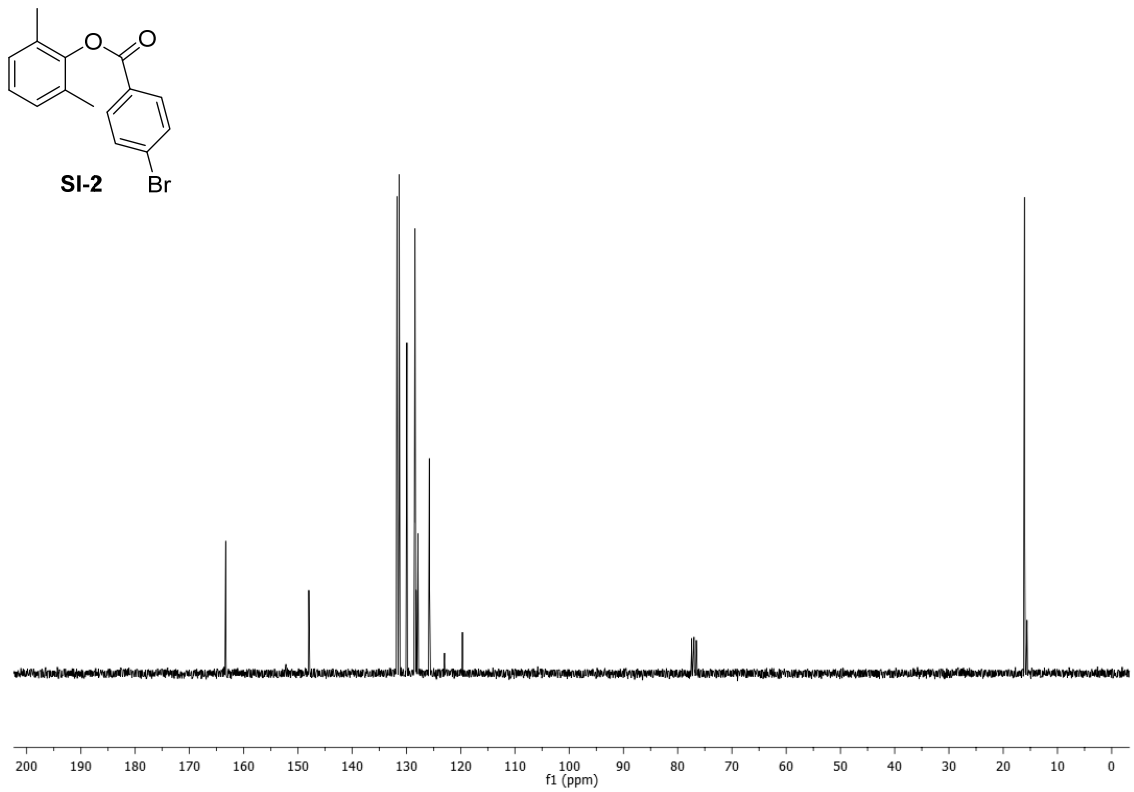
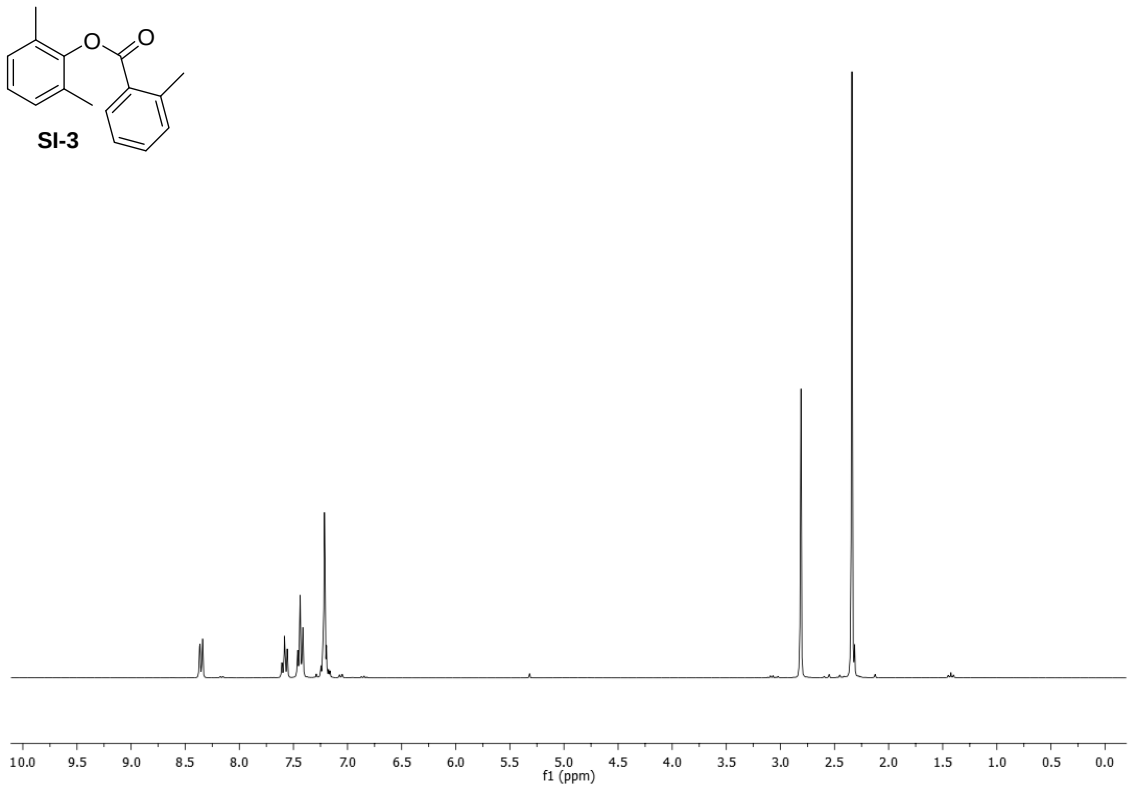


Figure S5: Spectra of compound **SI-2**.



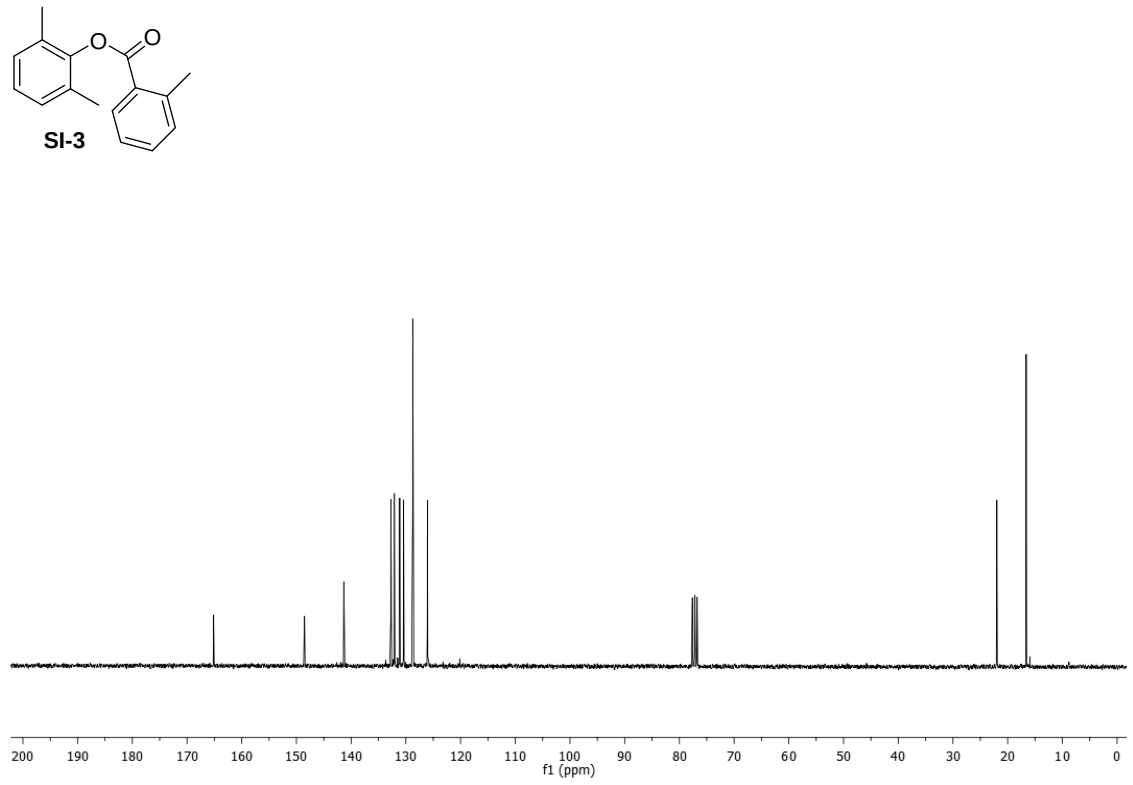
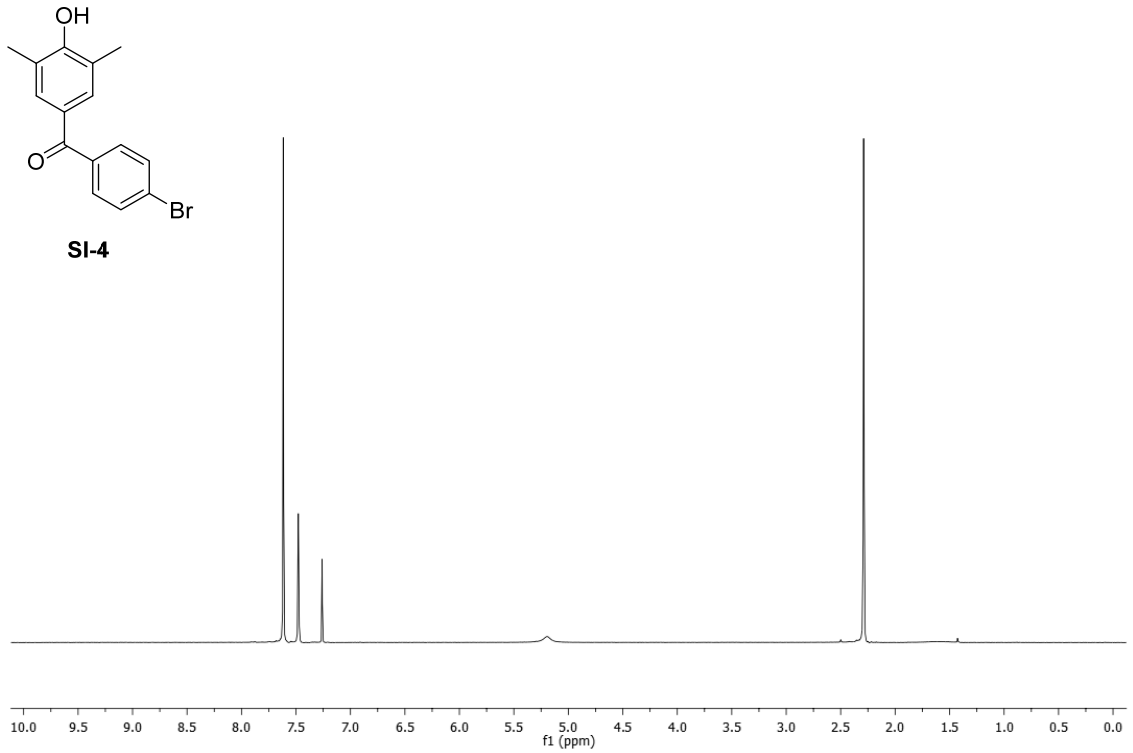


Figure S6: Spectra of compound **SI-3**.



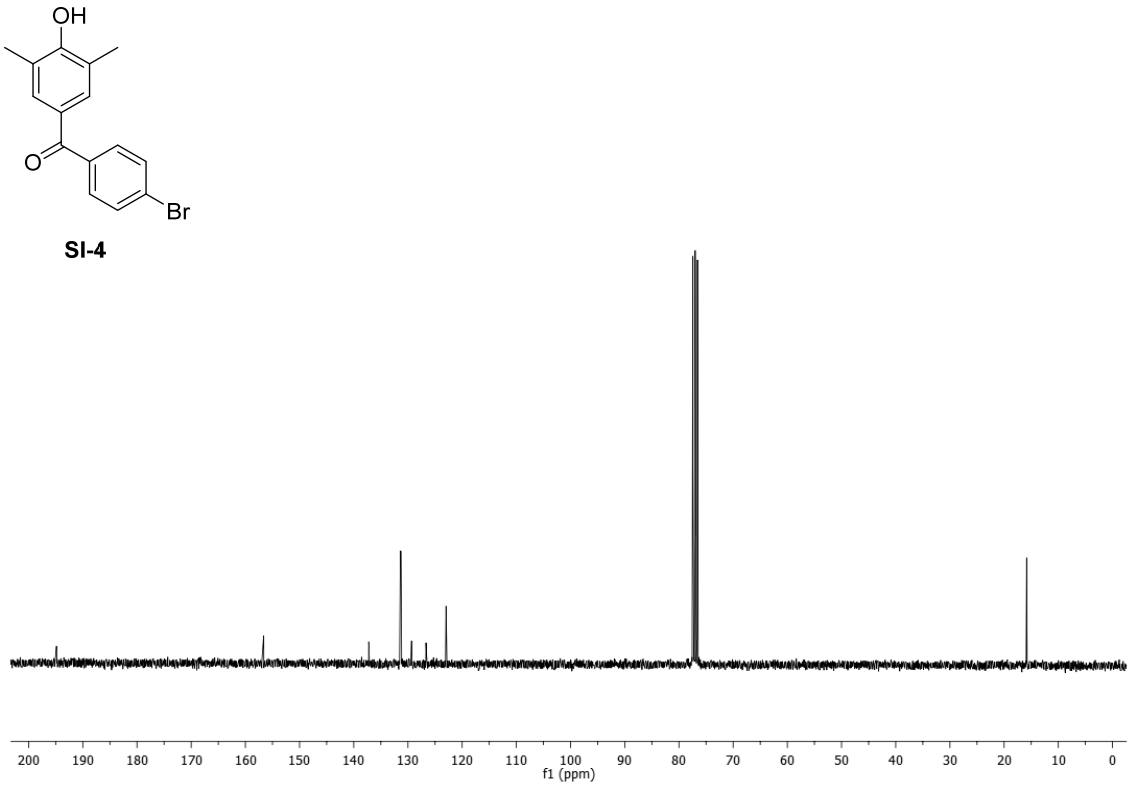
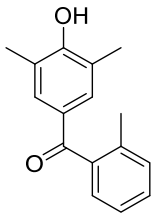
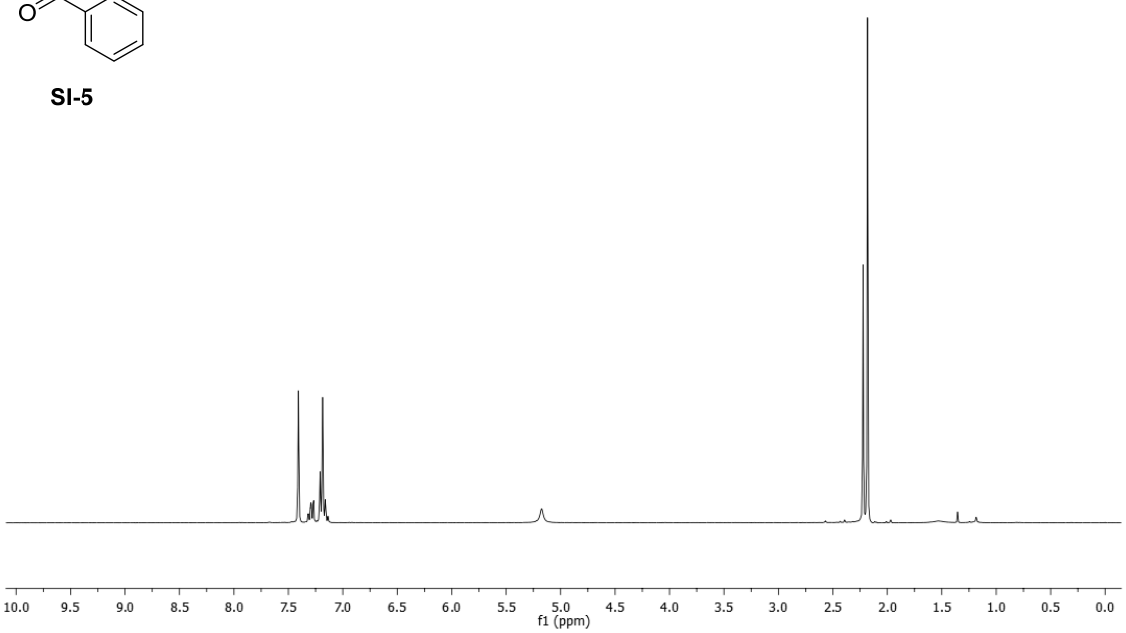
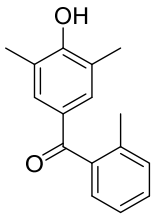


Figure S7: Spectra of compound **SI-4**.



SI-5





SI-5

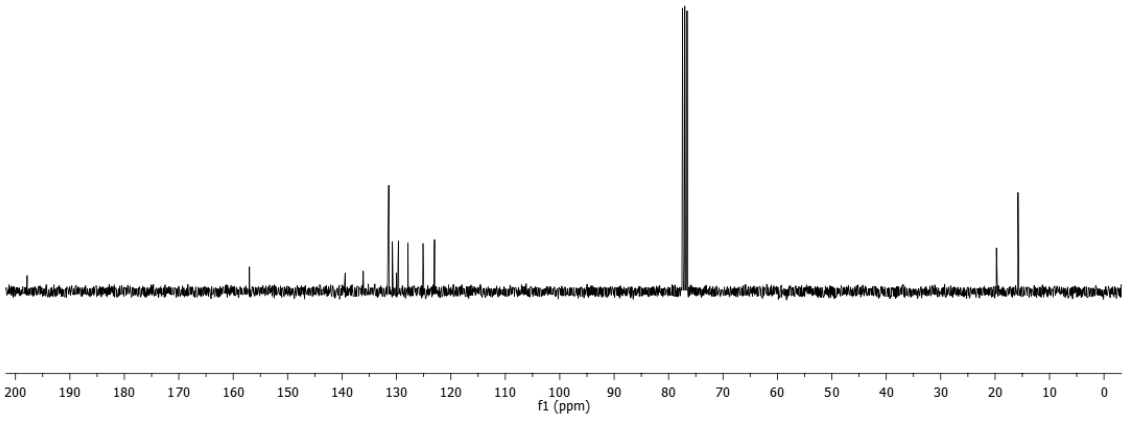
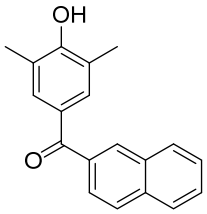
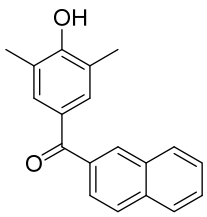


Figure S8: Spectra of compound **SI-5**.

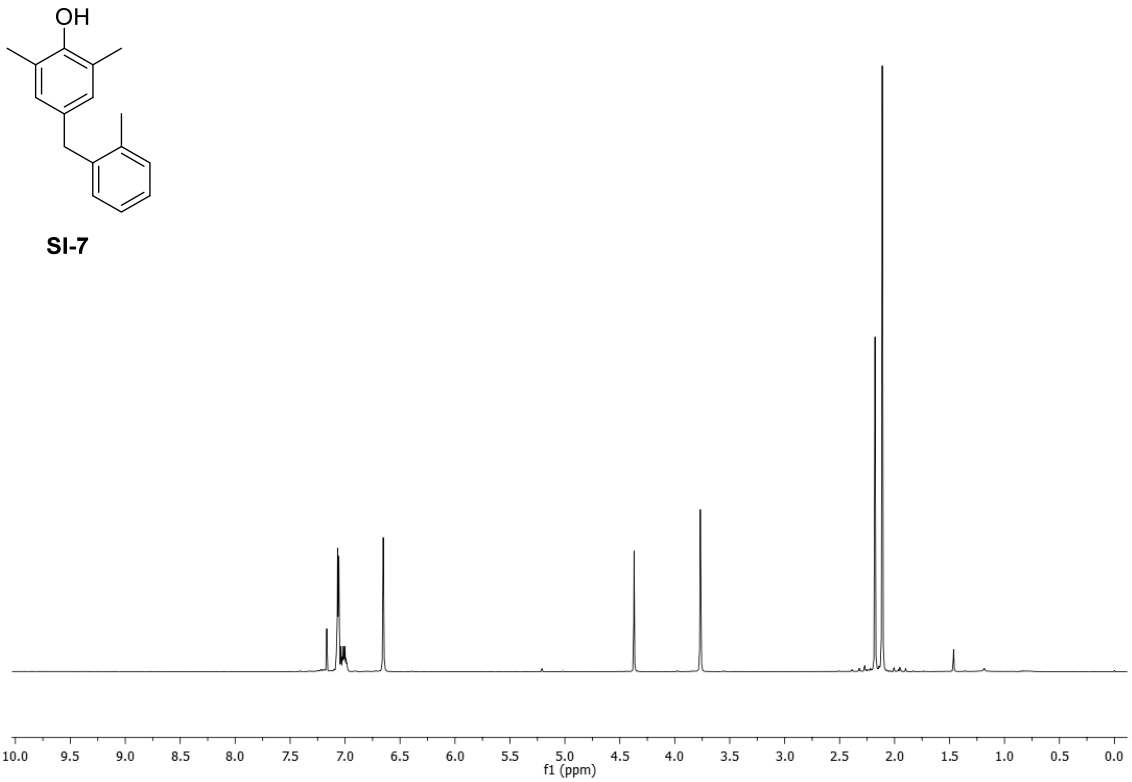


SI-6



SI-6

Figure S9: Spectra of compound **SI-6**.



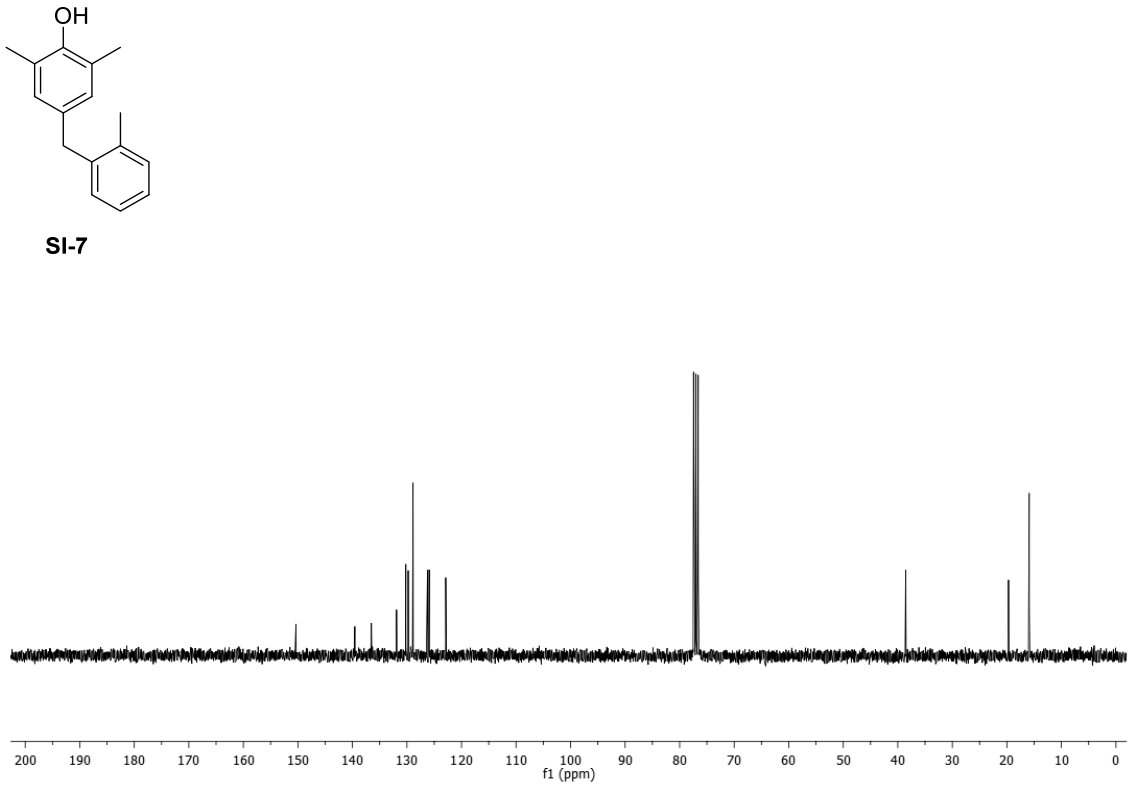
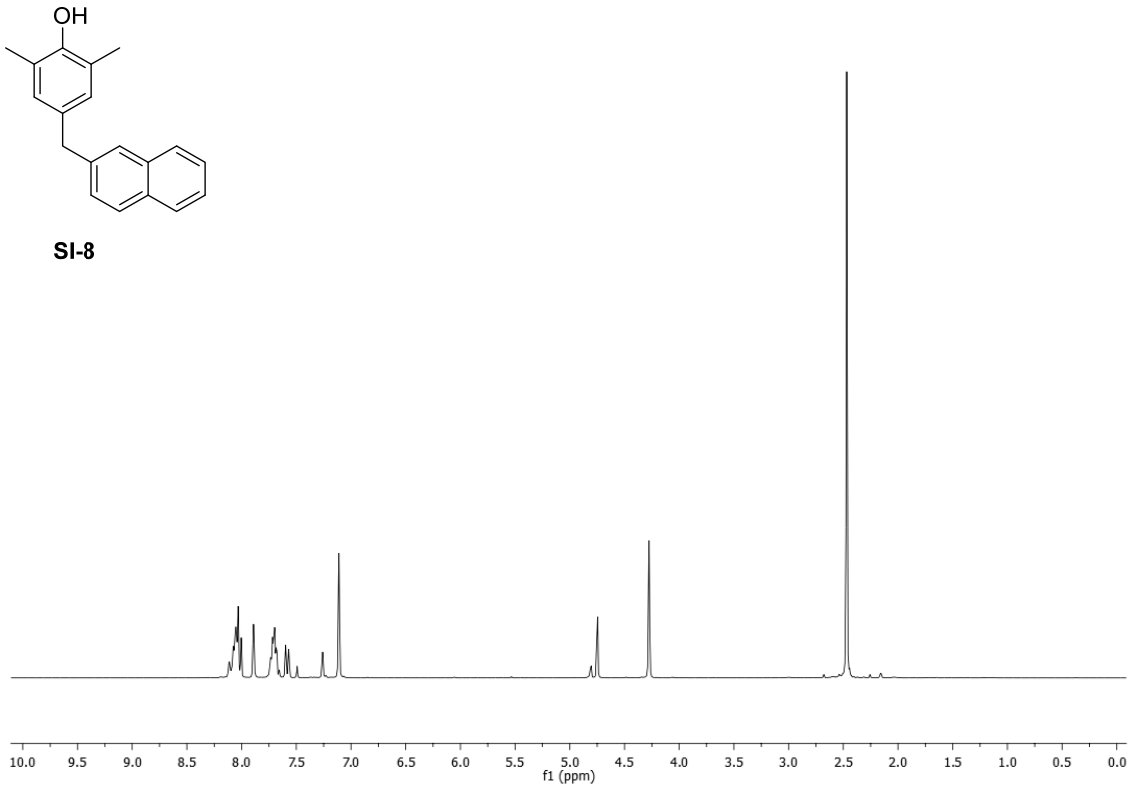


Figure S10. Spectra of compound **SI-7**.



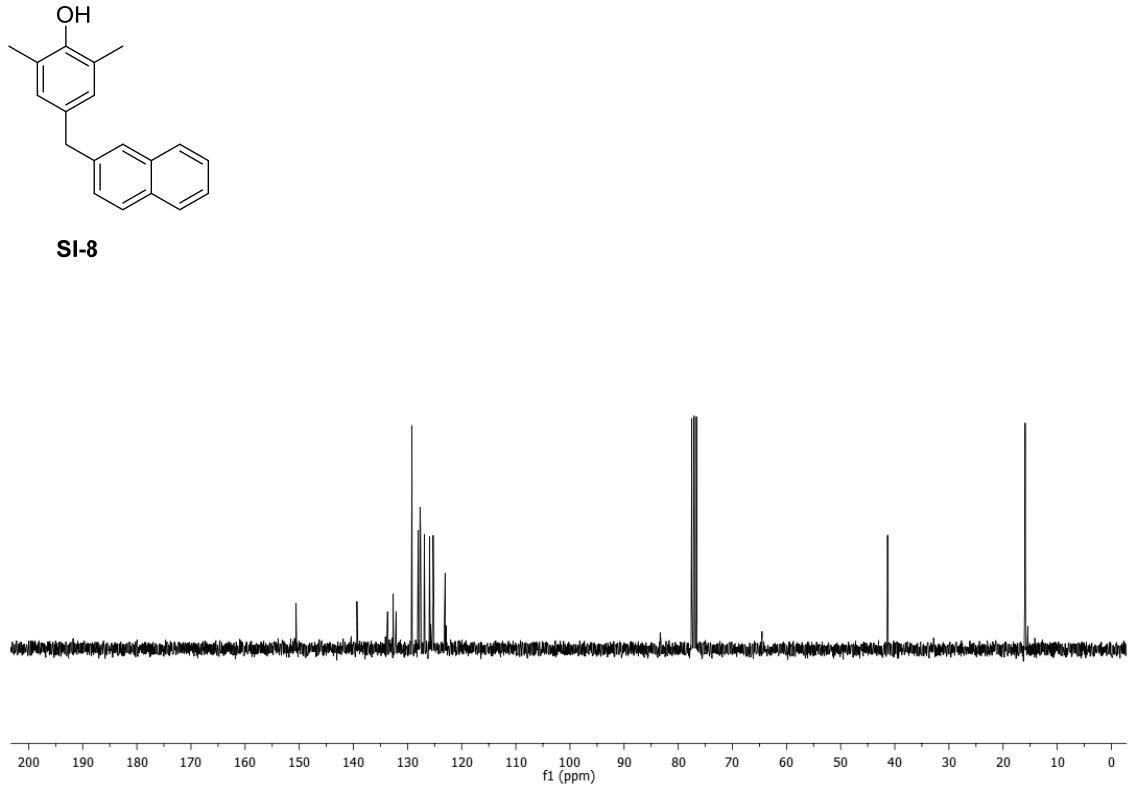
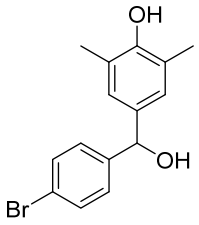
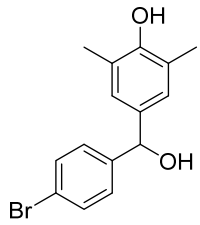


Figure S11: Spectra of compound **SI-8**.



SI-9



SI-9

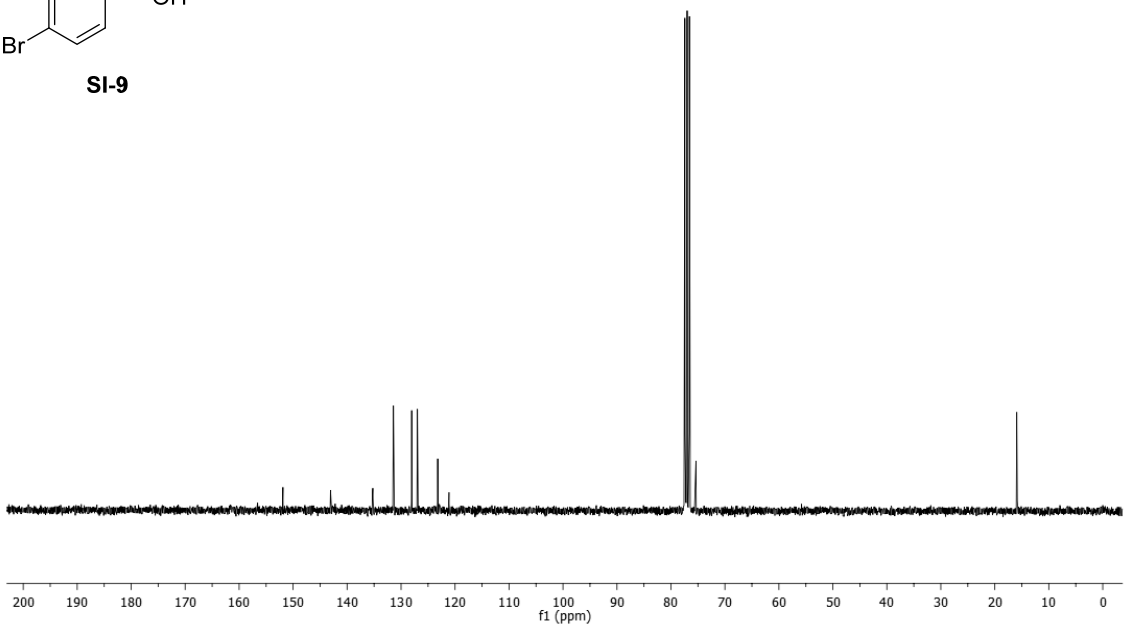
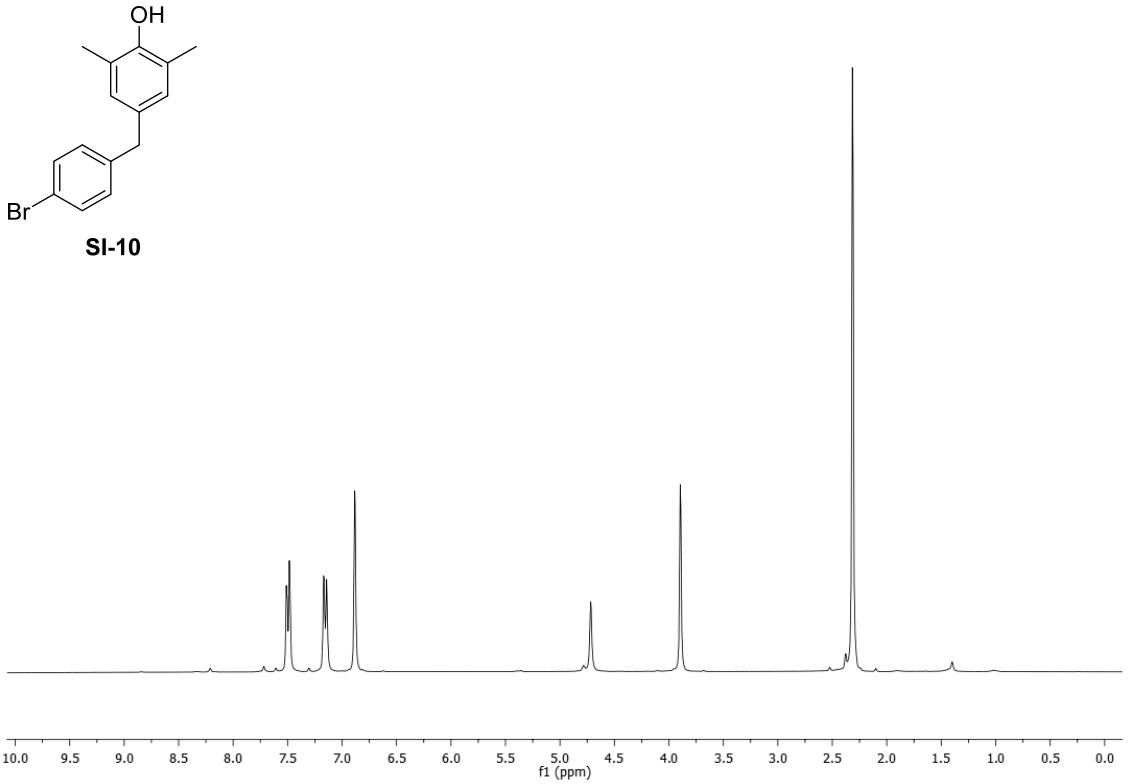


Figure S12. Spectra of compound **SI-9**.



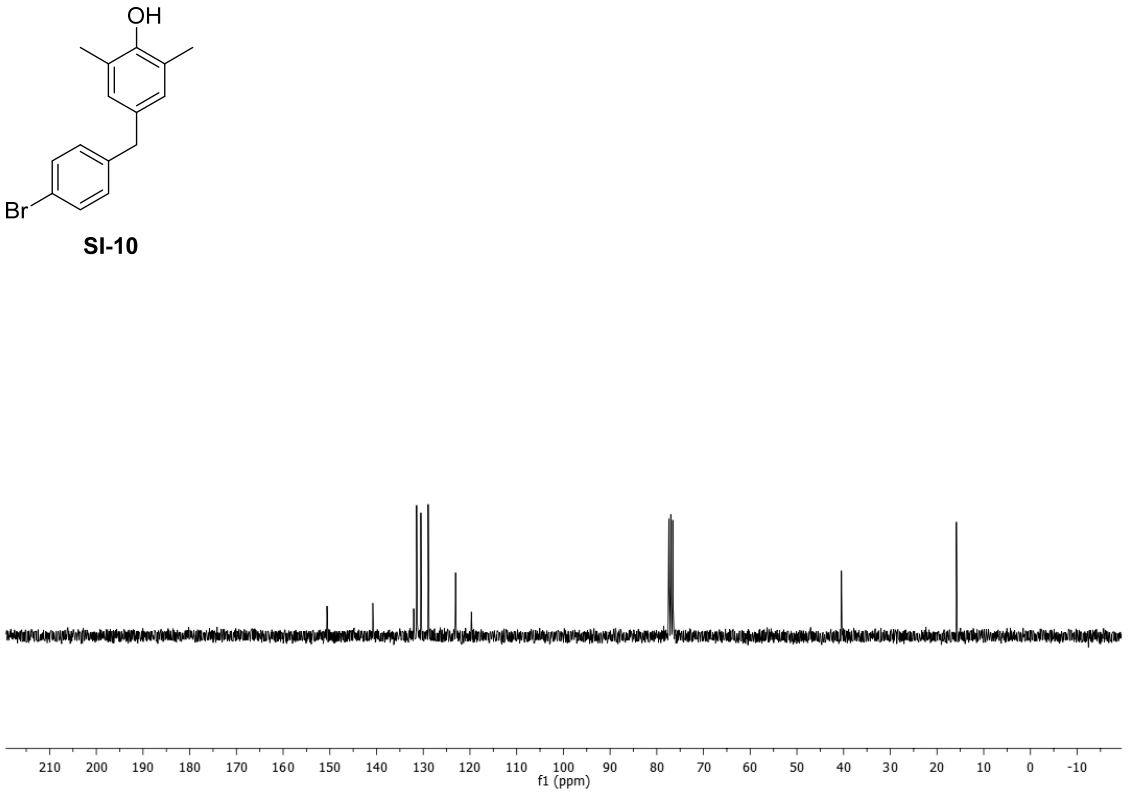
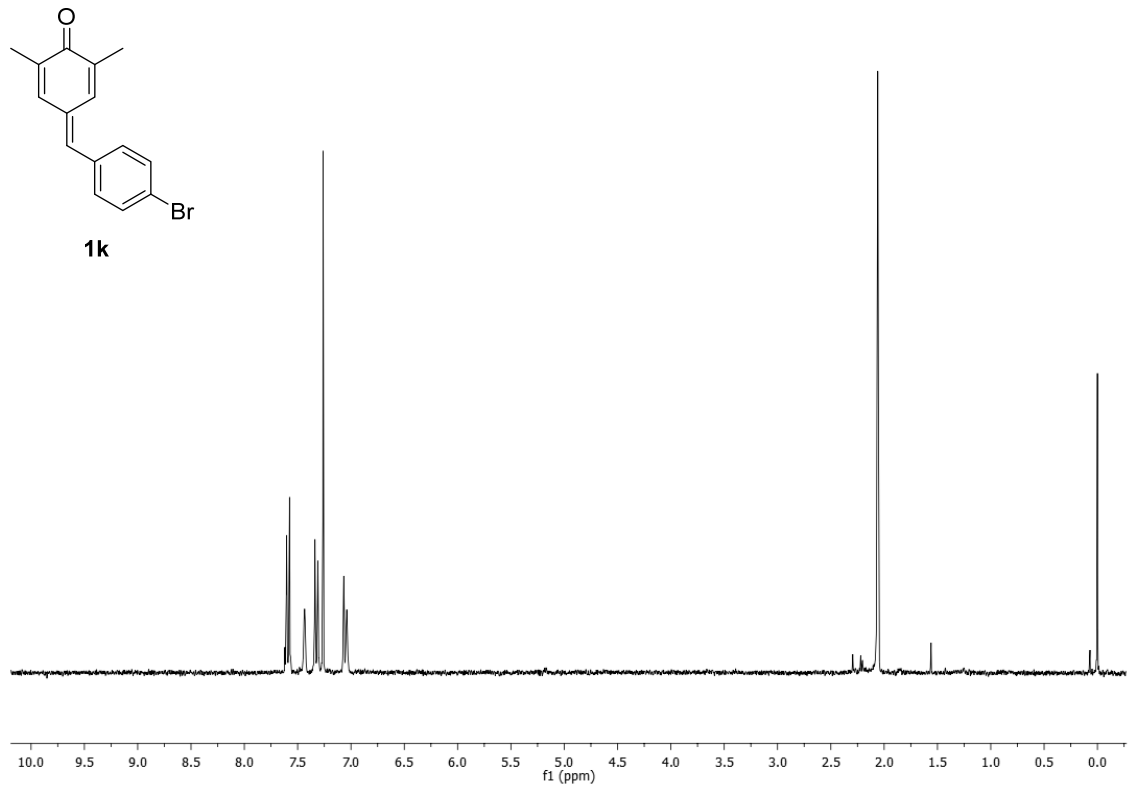


Figure S13. Spectra of compound **SI-10**.



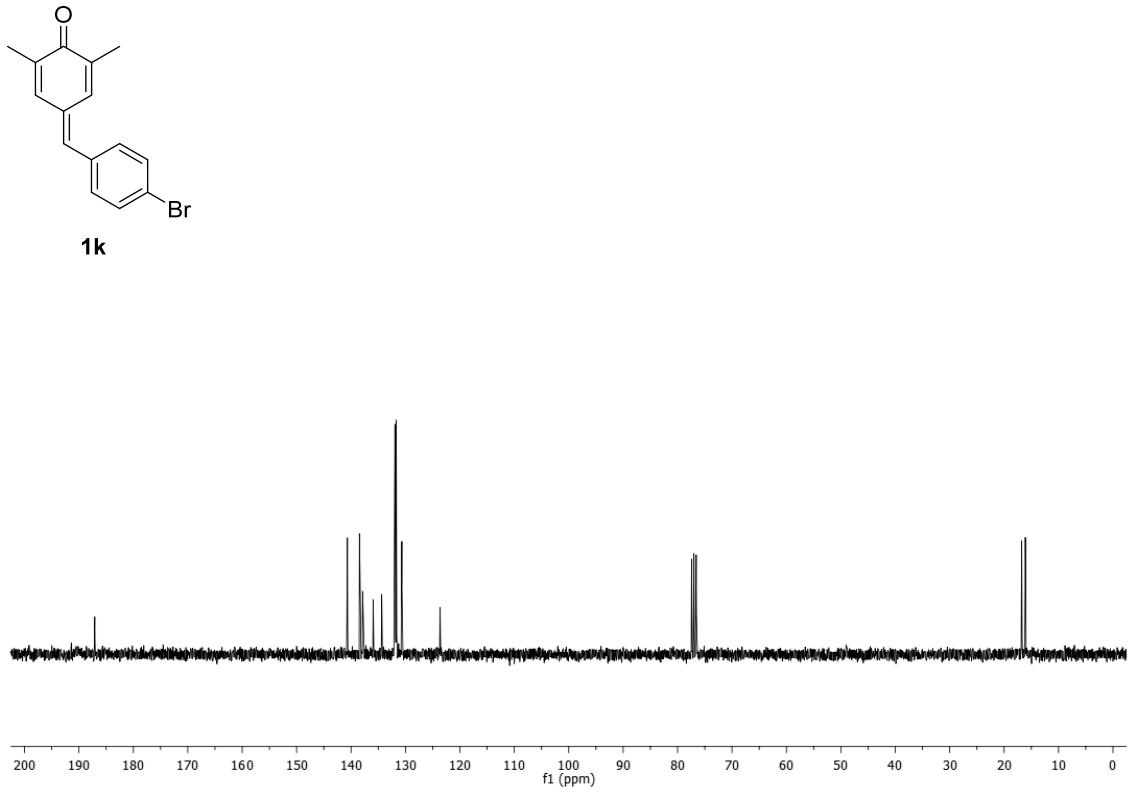
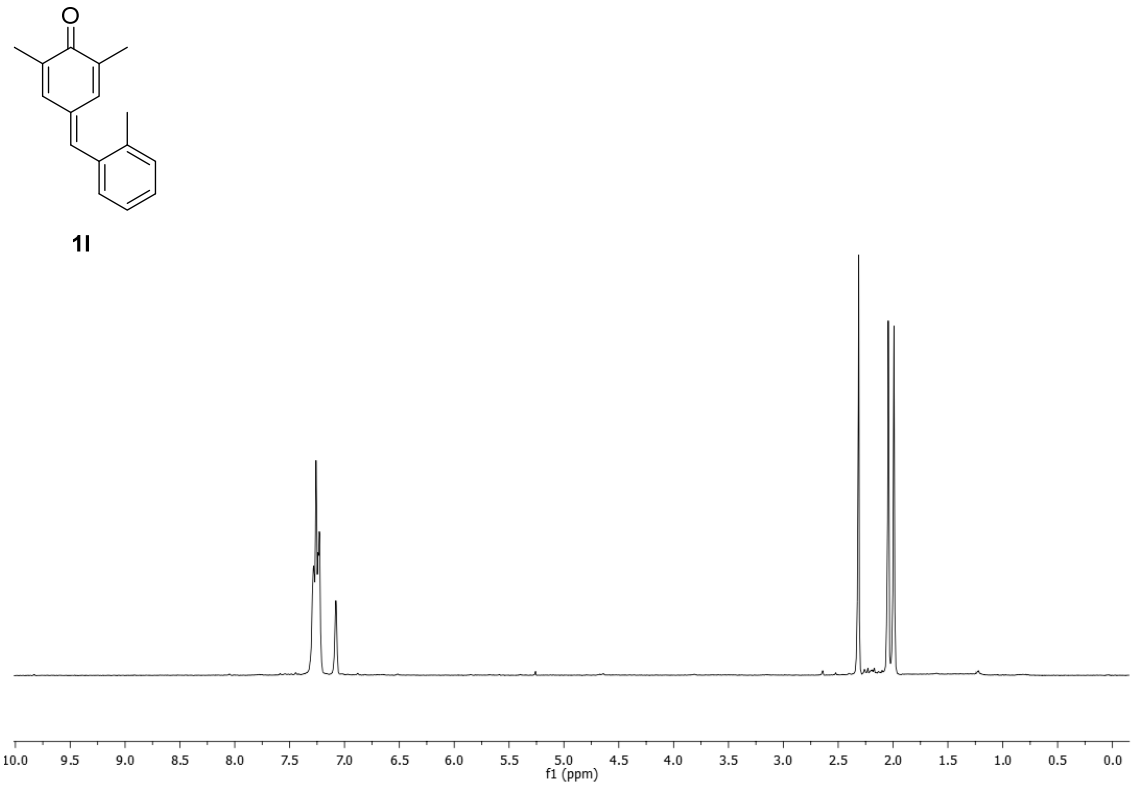


Figure S14. Spectra of compound **1k**.



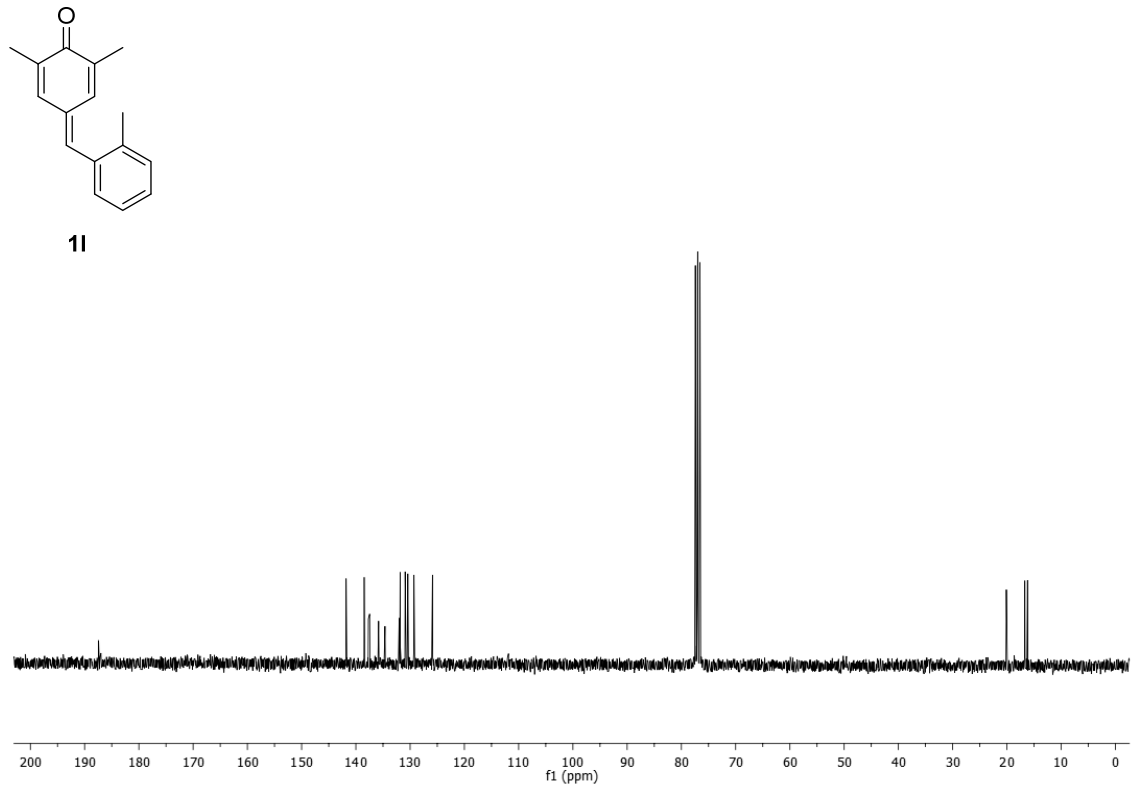
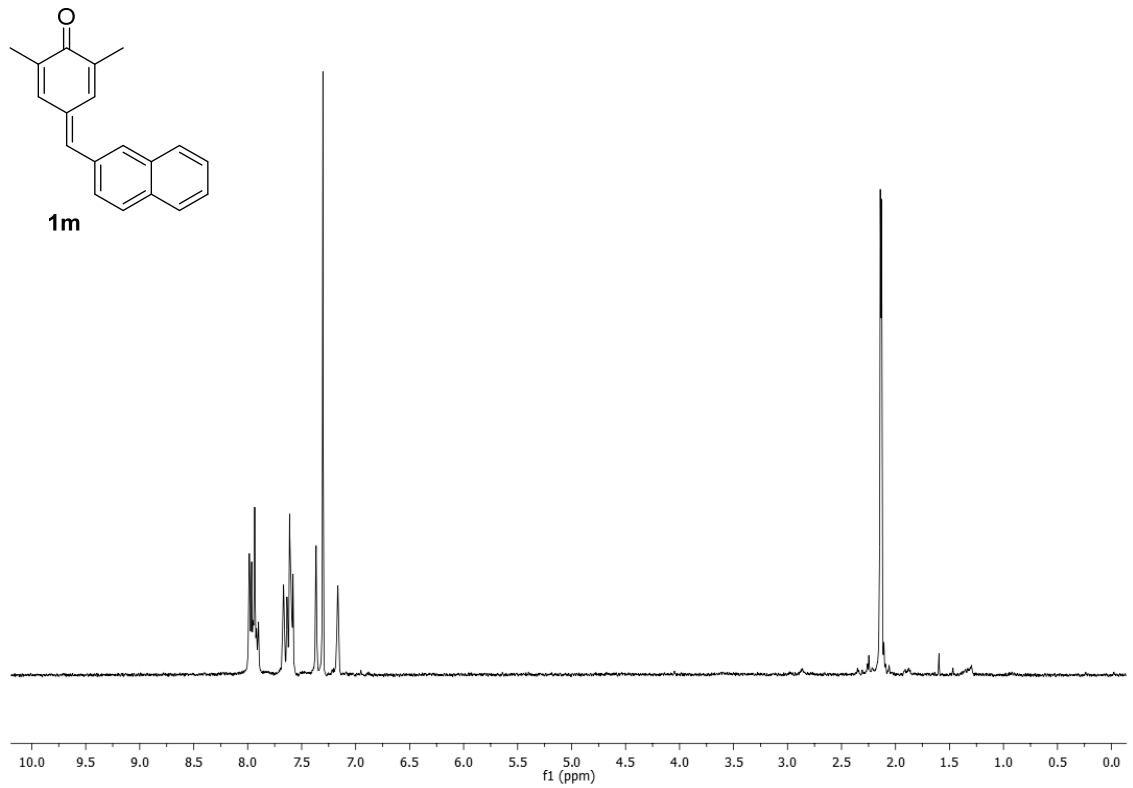


Figure S15. Spectra of compound **1l**.



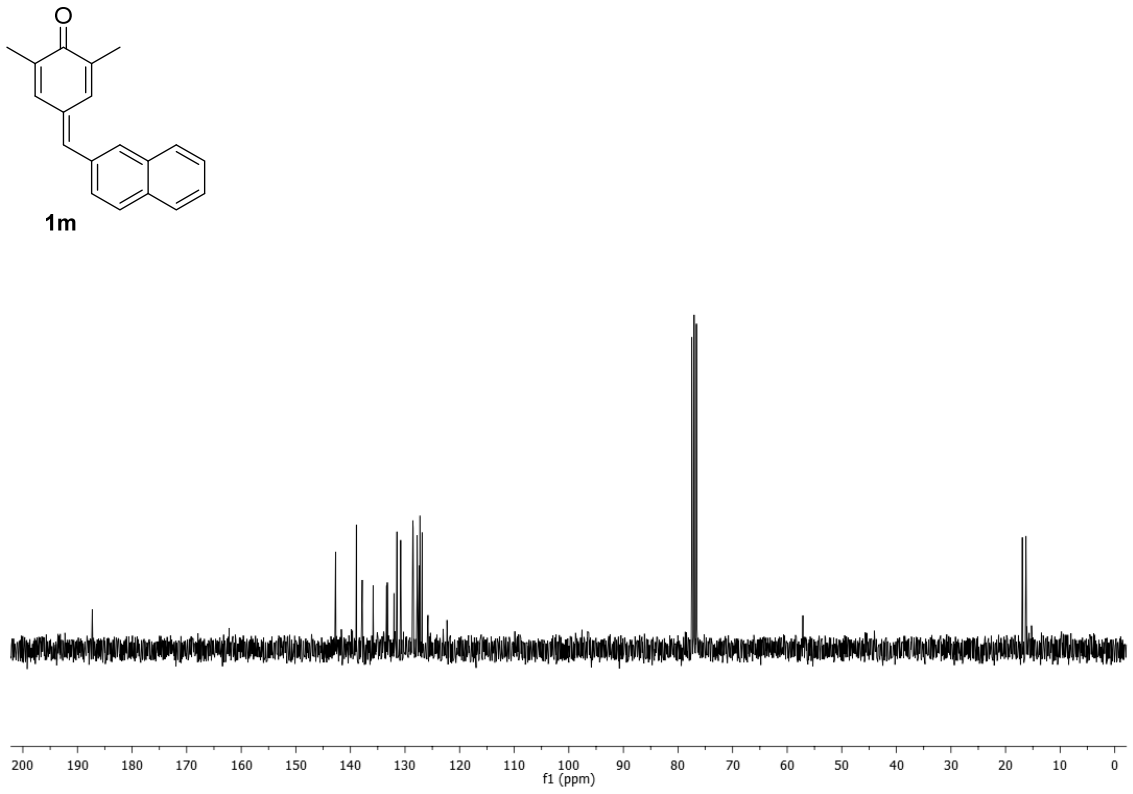
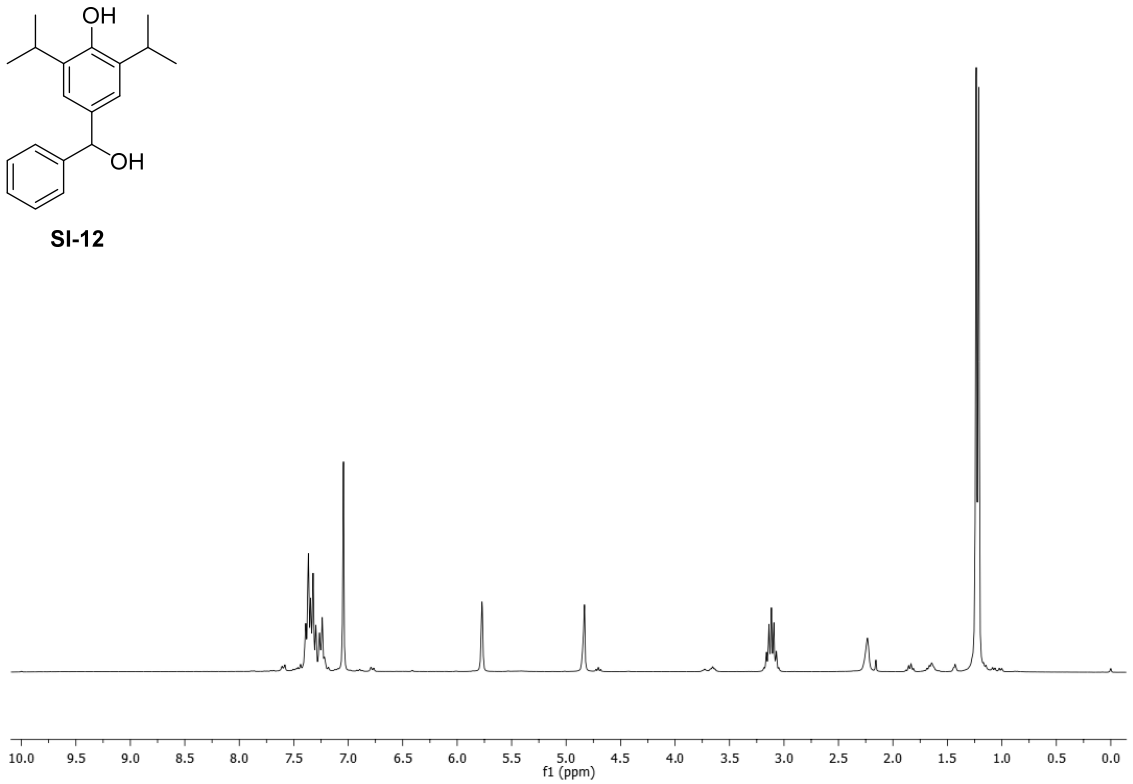


Figure S16. Spectra of compound **1m**.



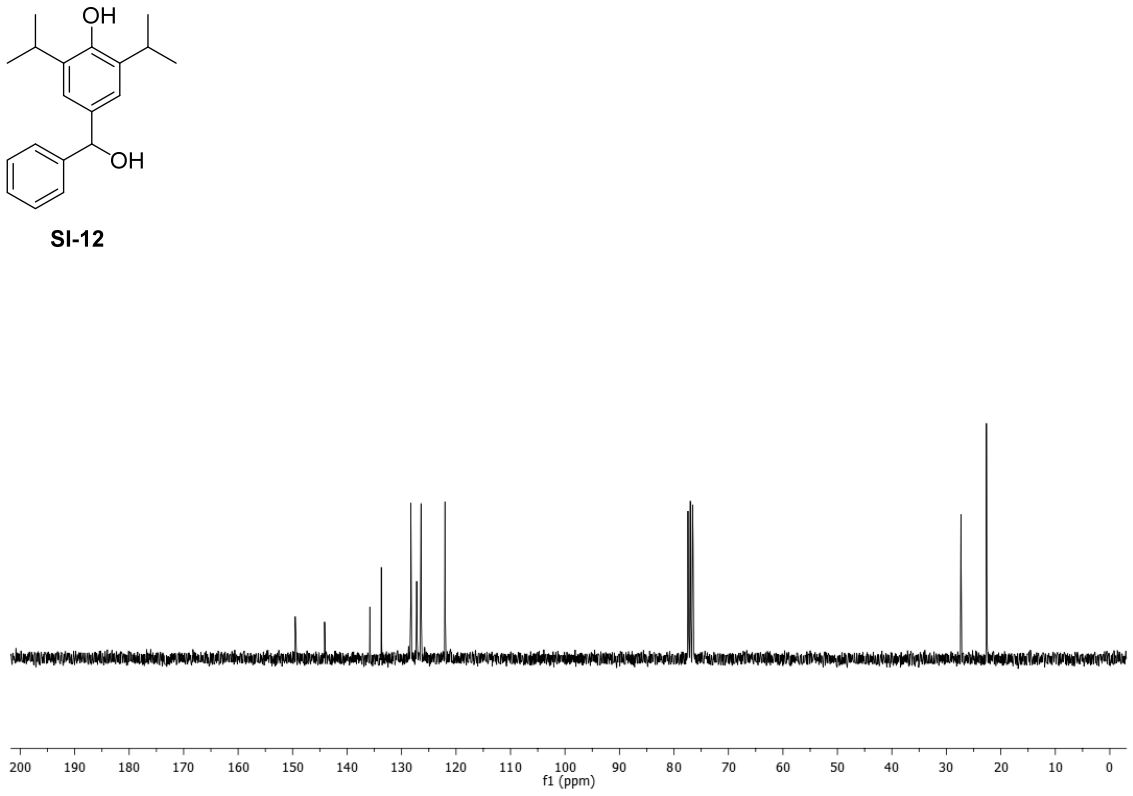
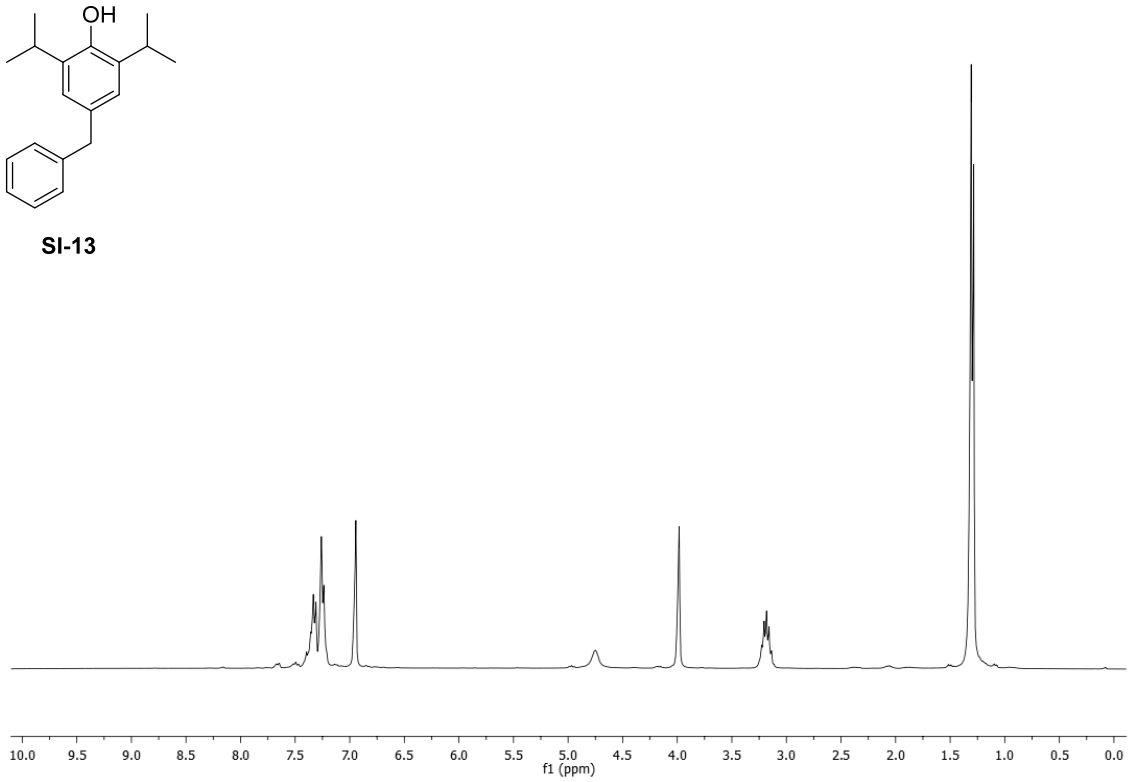


Figure S17. Spectra of compound **SI-12**.



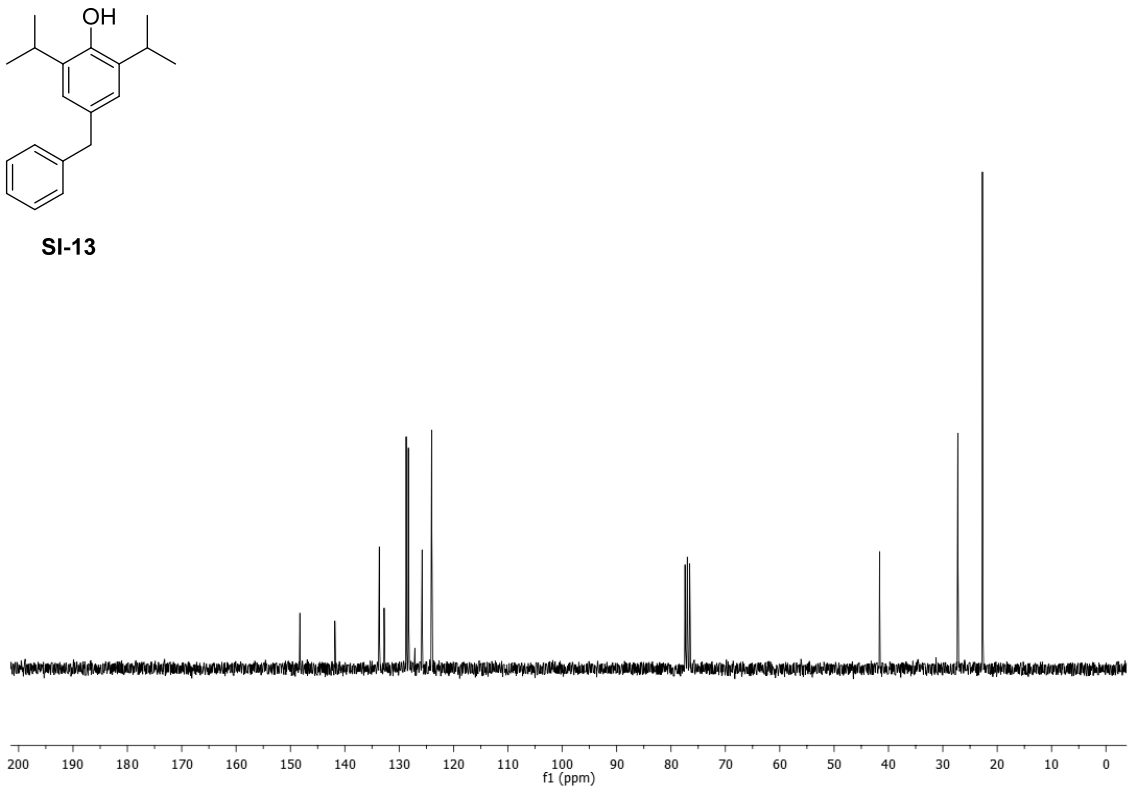
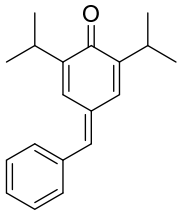
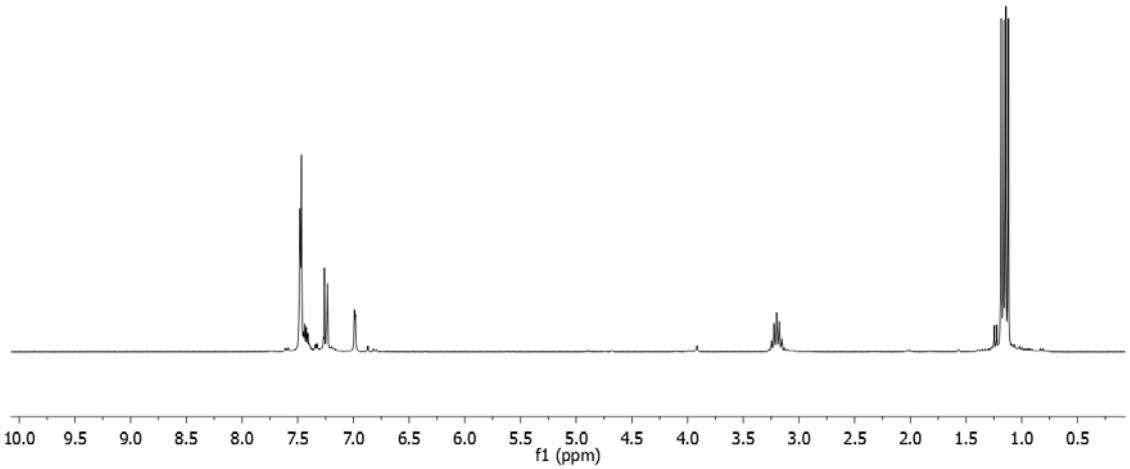
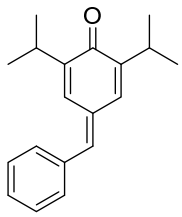


Figure S18. Spectra of compound **SI-13**.



1n





1n

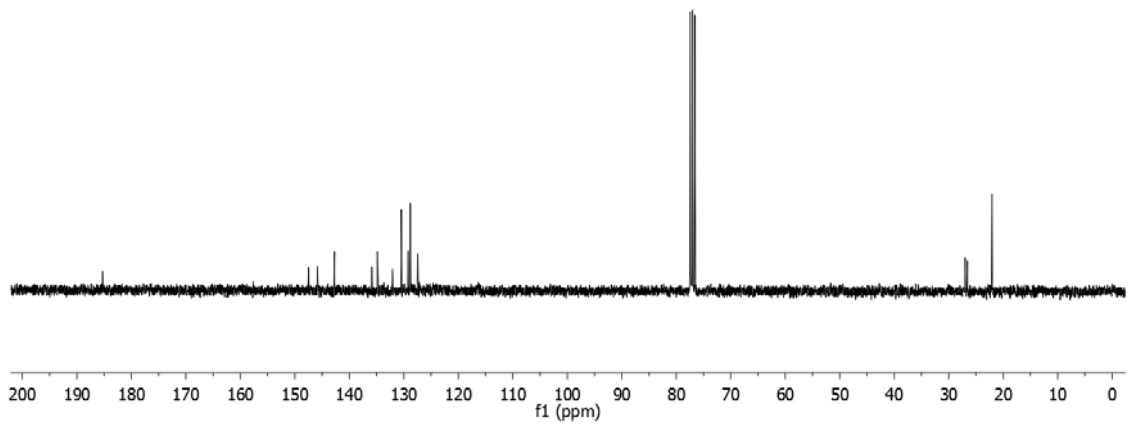
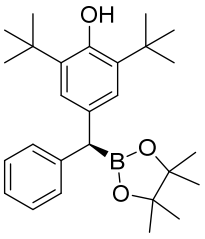
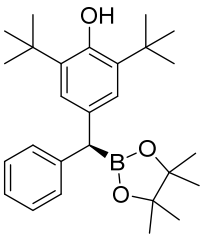


Figure S19. Spectra of compound **1n**.

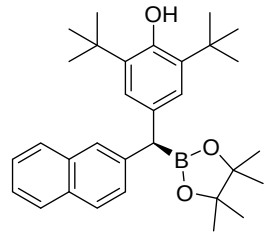


2a

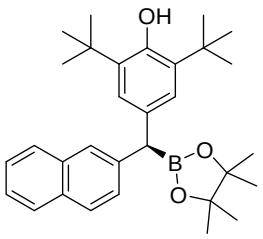


2a

Figure S20: Spectra of compound **2a**.

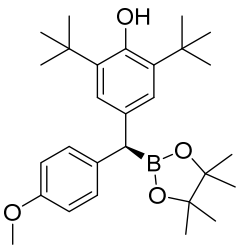


2b

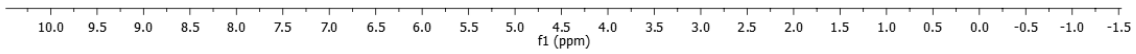


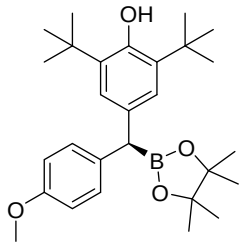
2b

Figure S21: Spectra of compound **2b**.



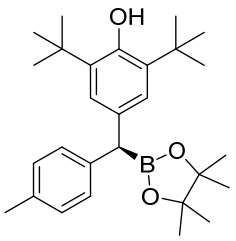
2c



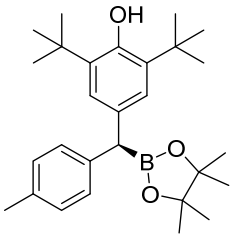


2c

Figure S22: Spectra of compound **2c**.



2d



2d

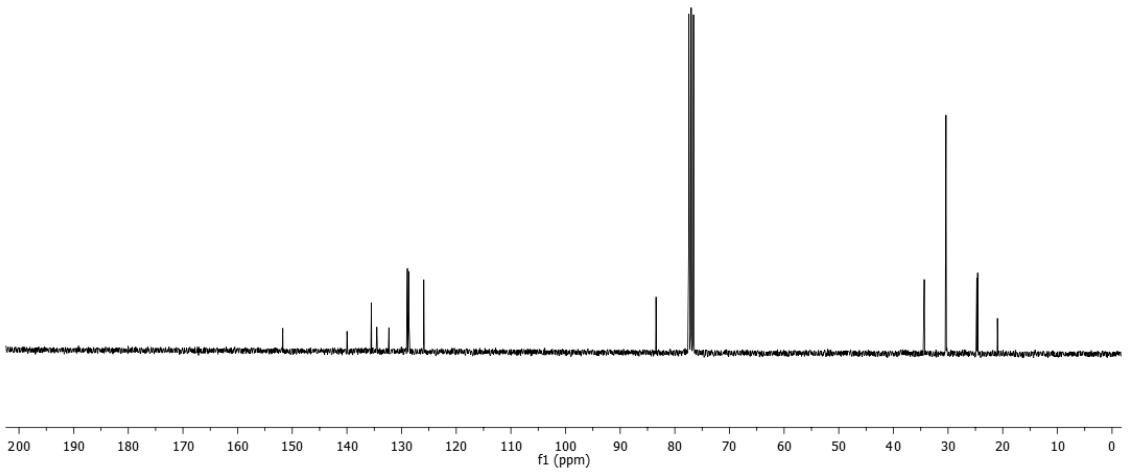
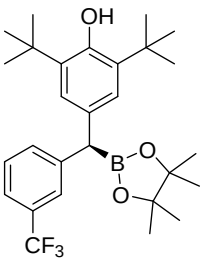
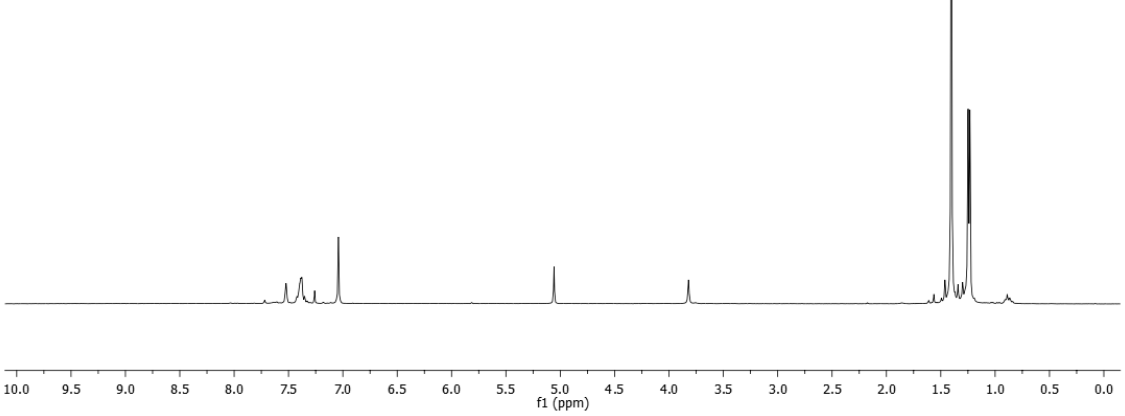
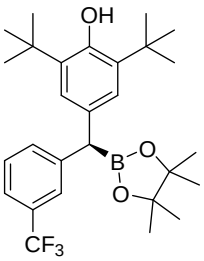


Figure S23: Spectra of compound **2d**.


OH
B
O
O
CF3

2e


10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


OH
B
O
O
CF3

2e

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

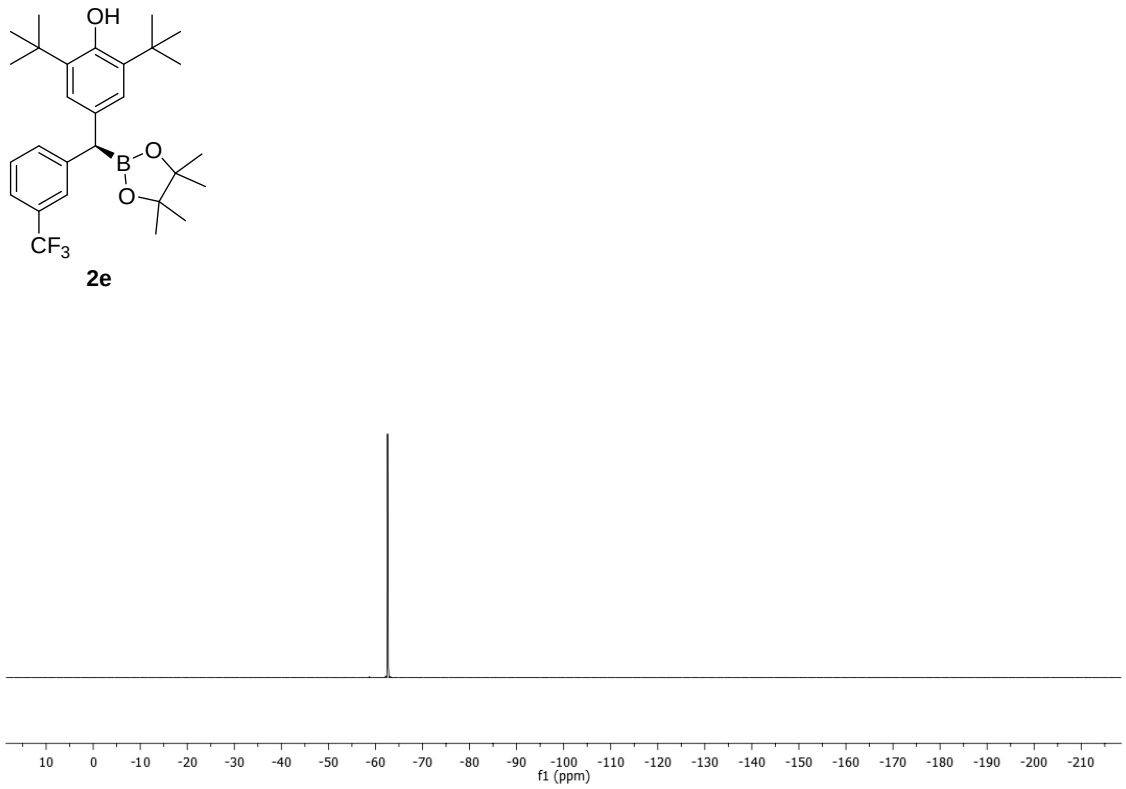
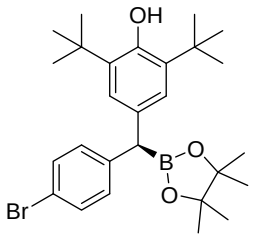
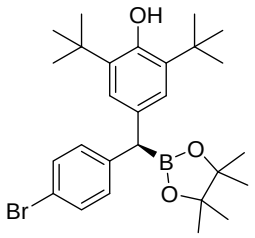


Figure S24: Spectra of compound **2e**.

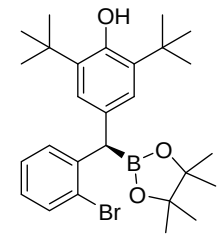


2f

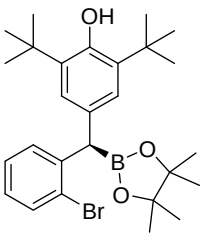


2f

Figure S25: Spectra of compound **2f**.

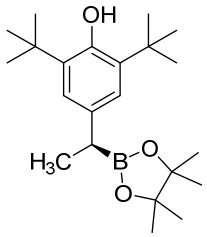


2g

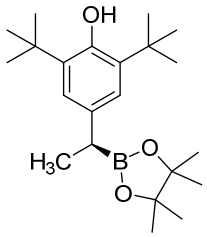


2g

Figure S26: Spectra of compound **2g**.

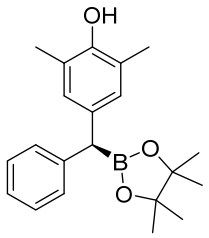


2h

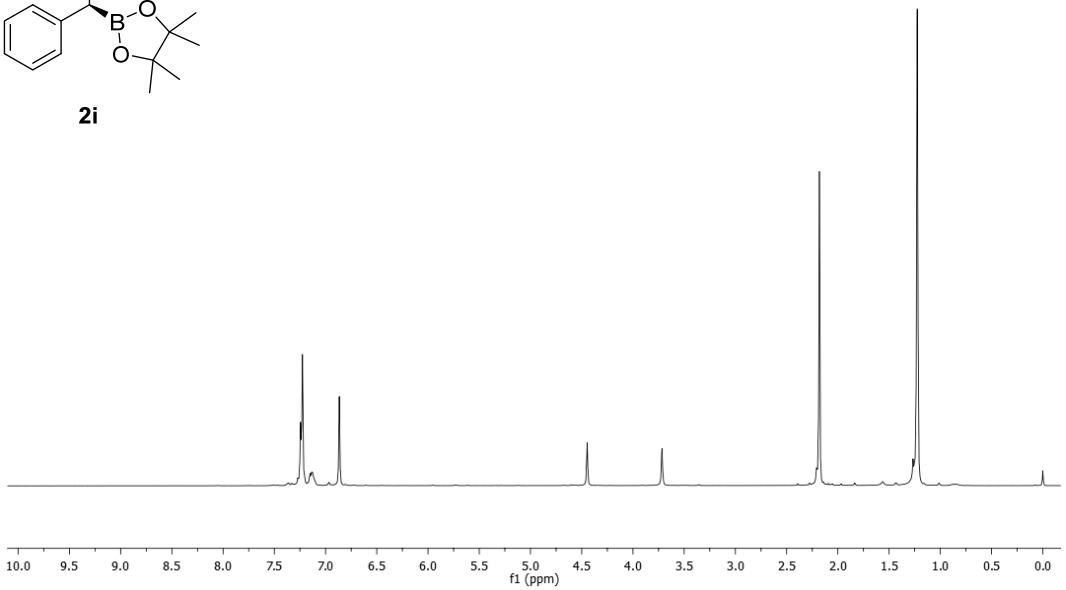


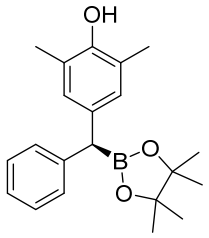
2h

Figure S27: Spectra of compound **2h**.



2i





2i

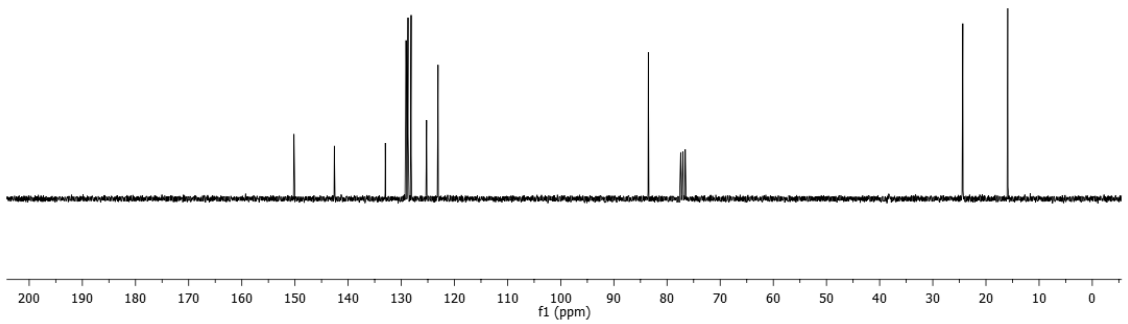
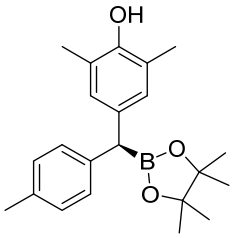
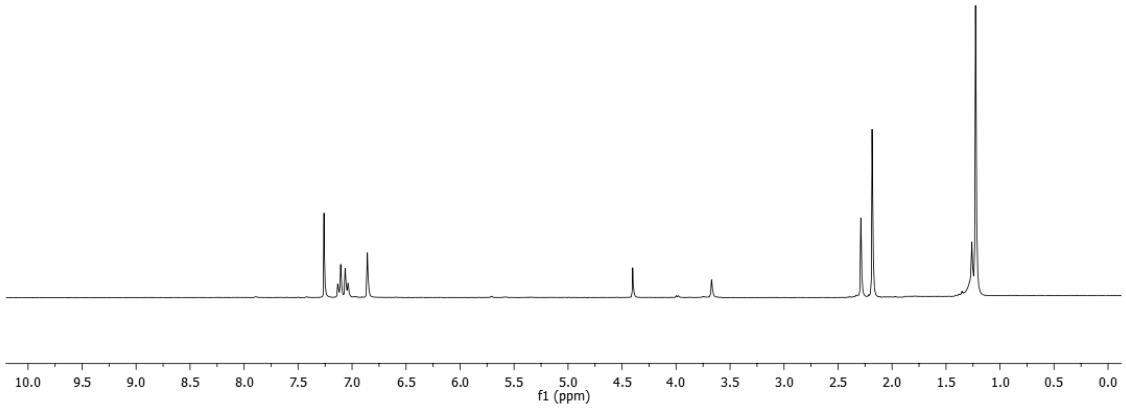
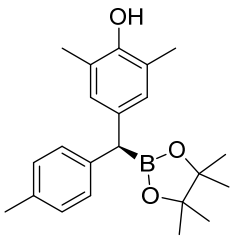


Figure S28: Spectra of compound **2i**.



2j





2j

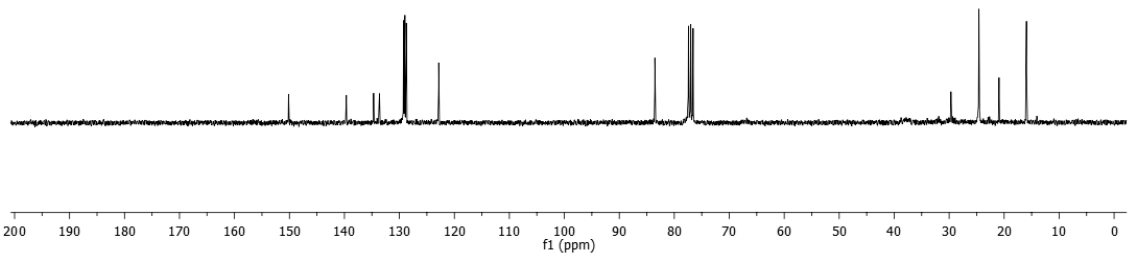
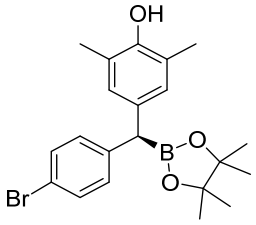
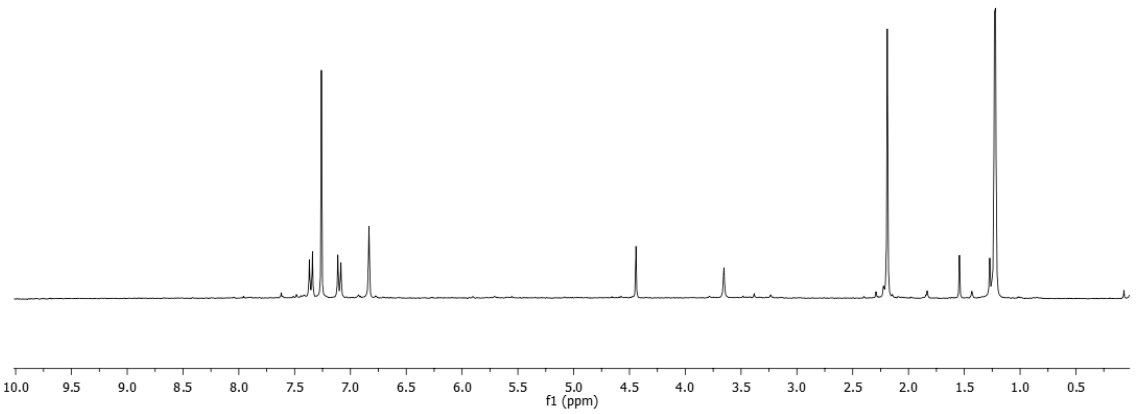
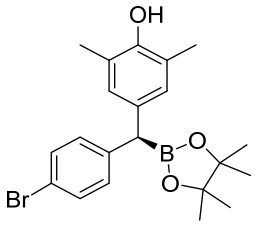


Figure S29: Spectra of compound **2j**.



2k





2k

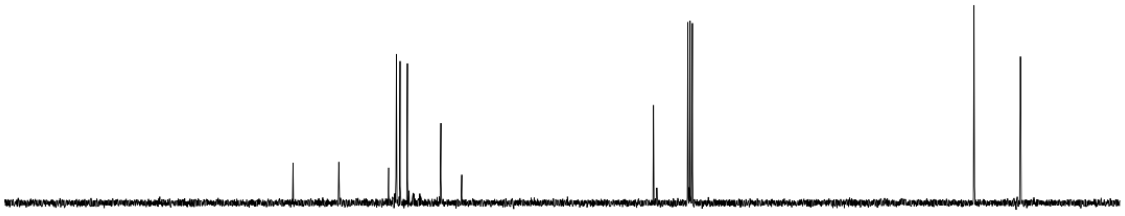
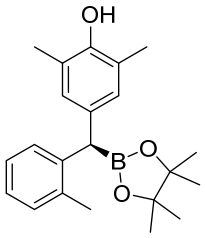
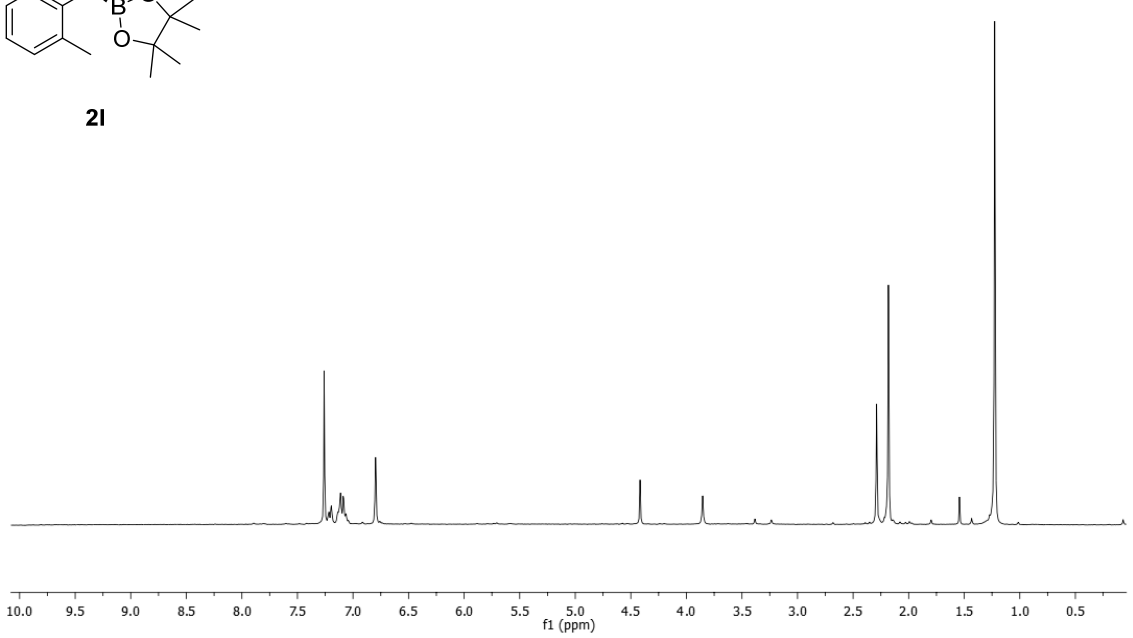
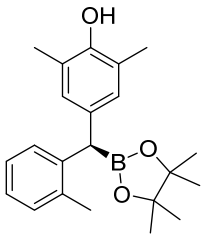


Figure S30: Spectra of compound **2k**.



2l





2l

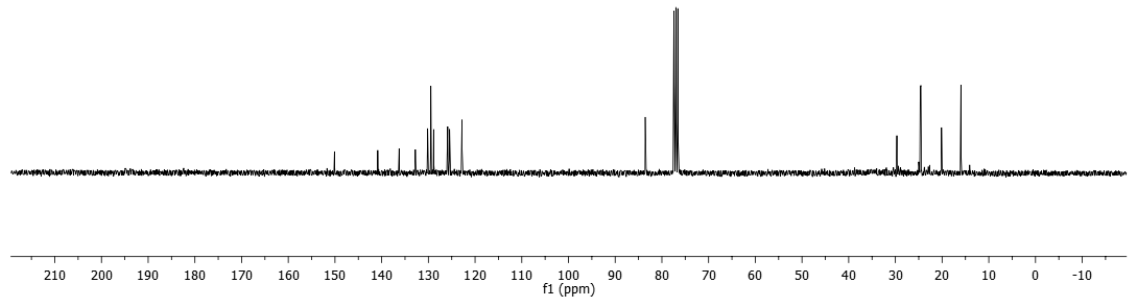
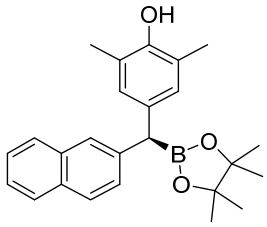
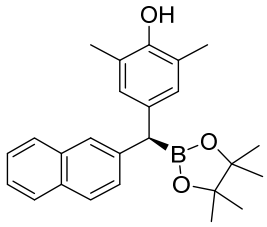


Figure S31: Spectra of compound **2l**.



2m



2m

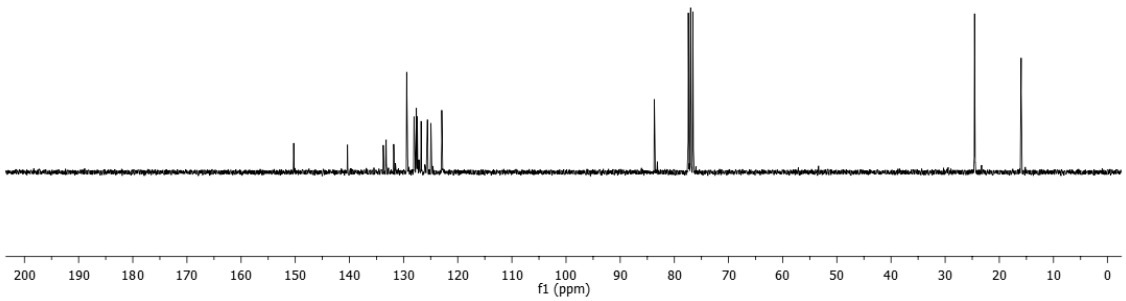
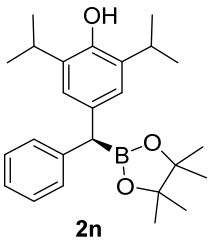
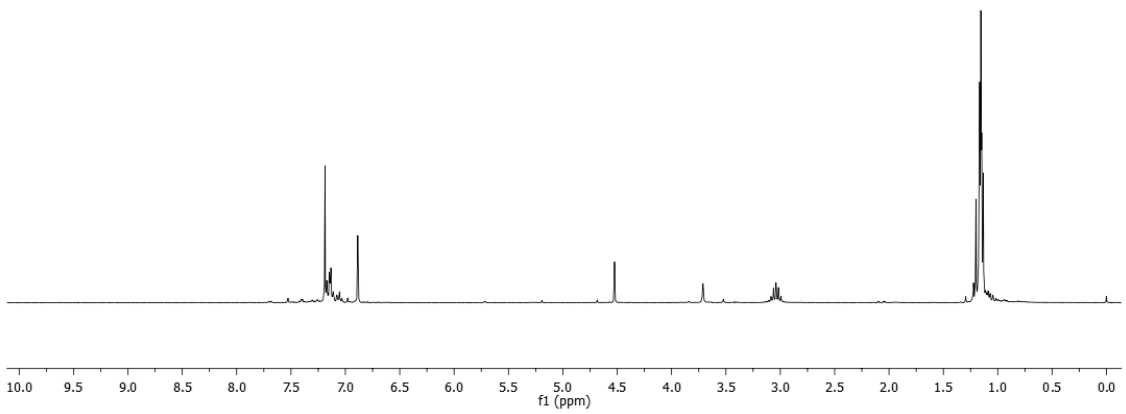
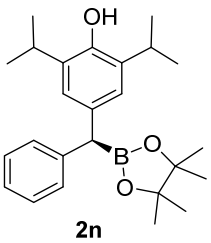


Figure S32: Spectra of compound **2m**.



2n





2n

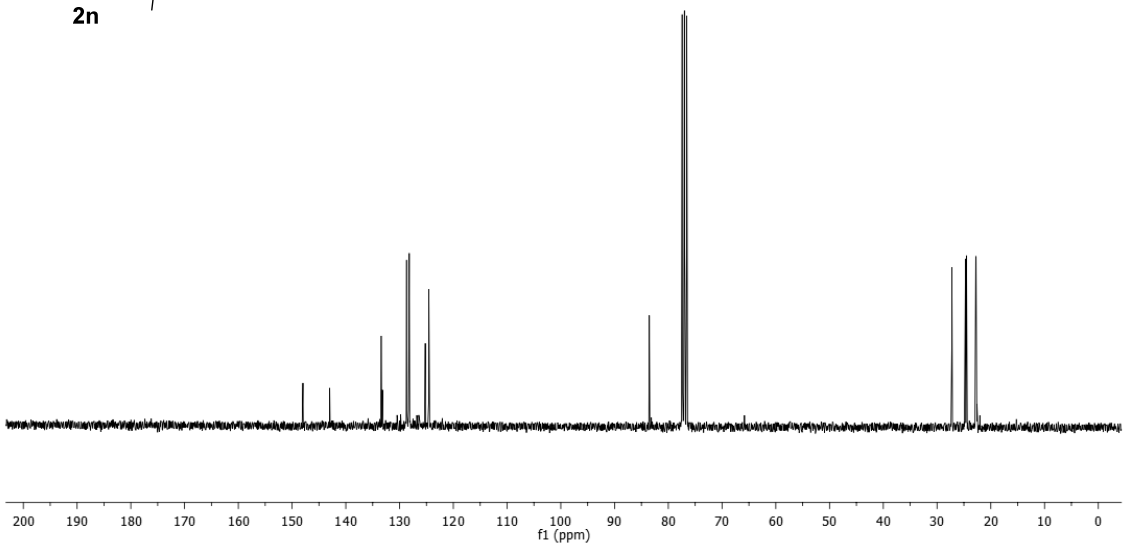
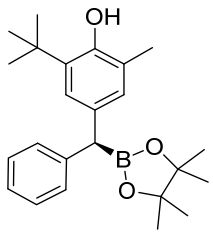
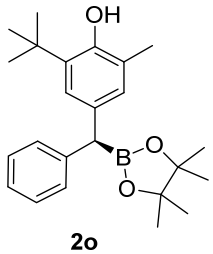


Figure S33: Spectra of compound **2n**.



2o



2o

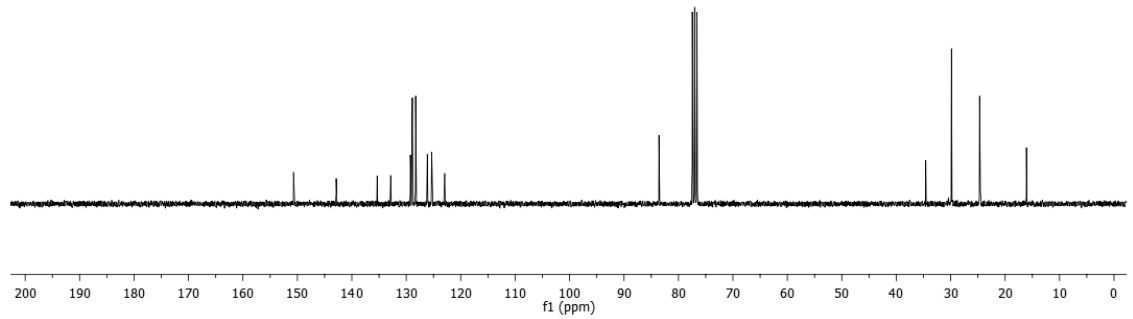
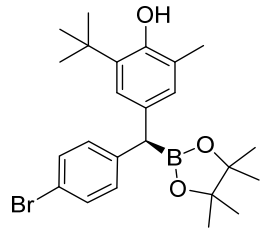
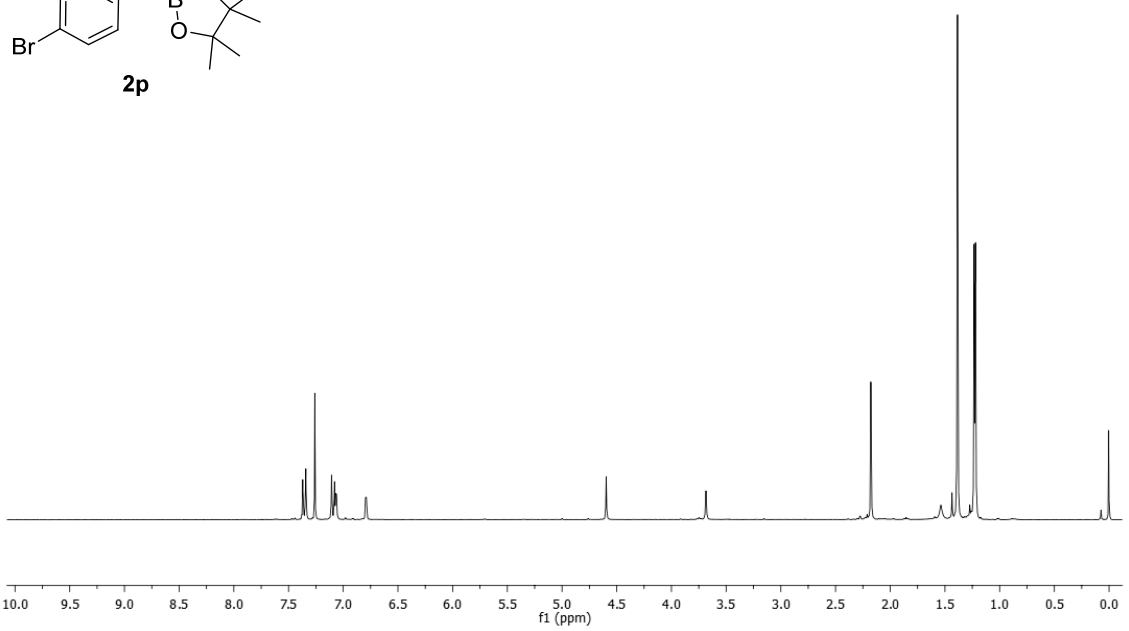
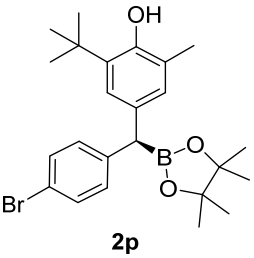


Figure S34: Spectra of compound **2o**.



2p





2p

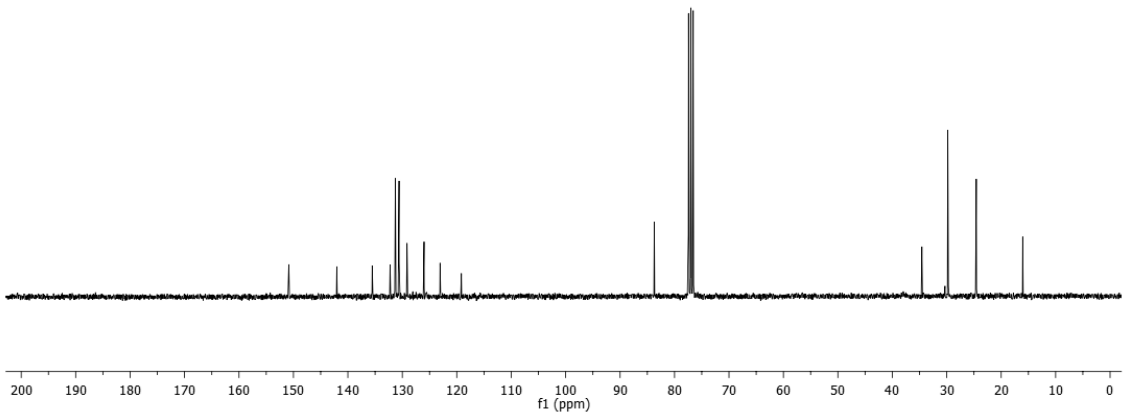
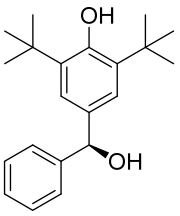
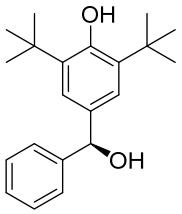


Figure S35: Spectra of compound **2p**.



3a



3a

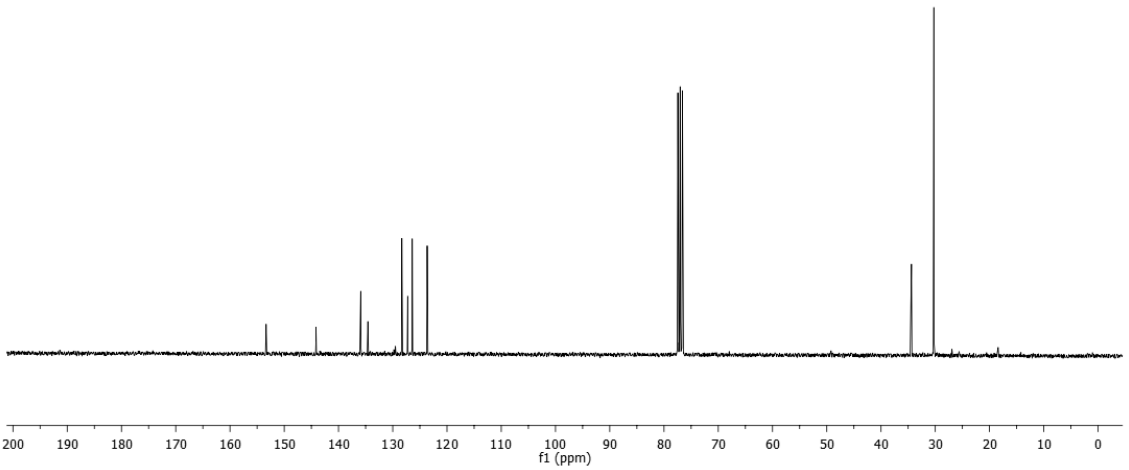
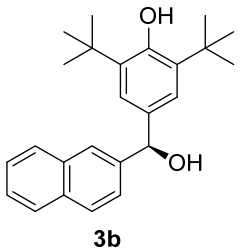
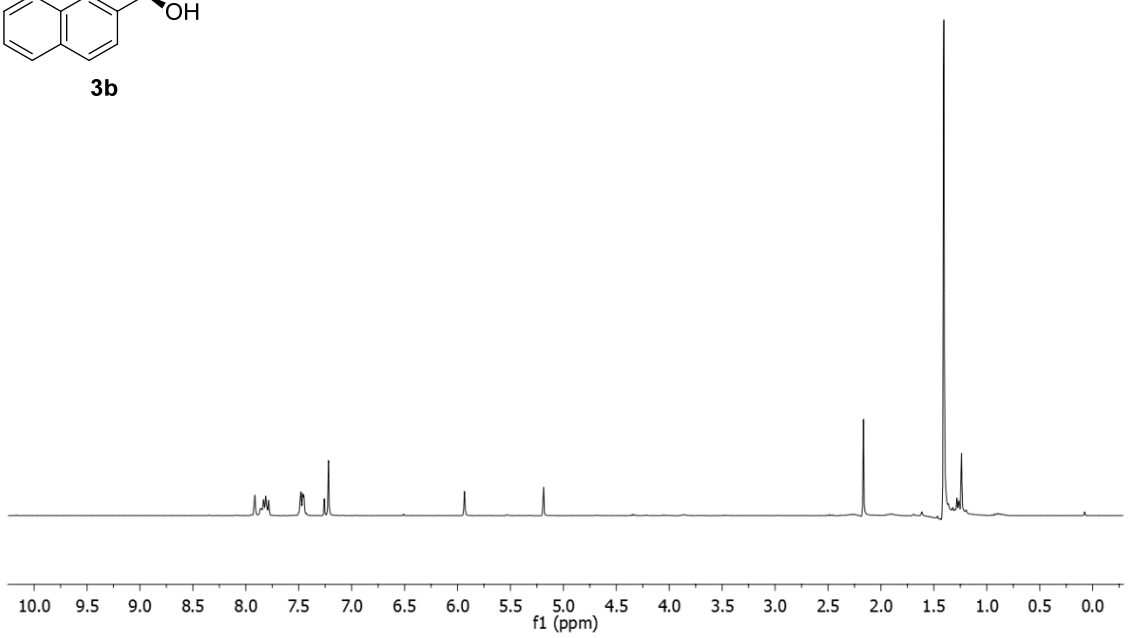
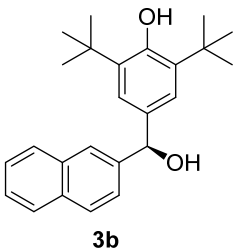


Figure S36: Spectra of compound **3a**.



3b





3b

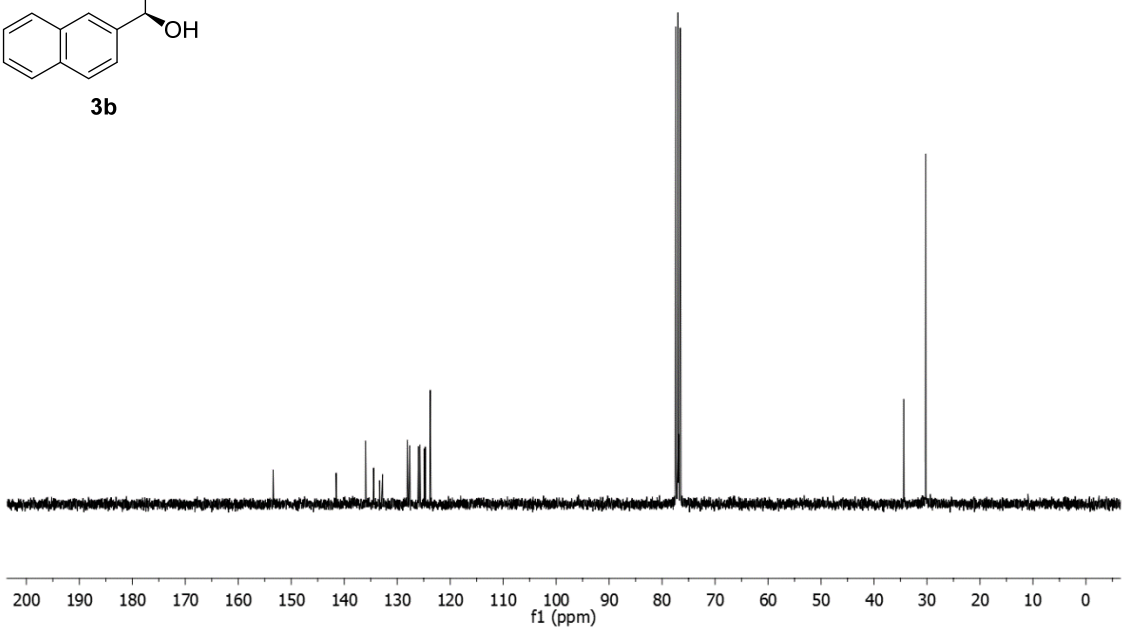
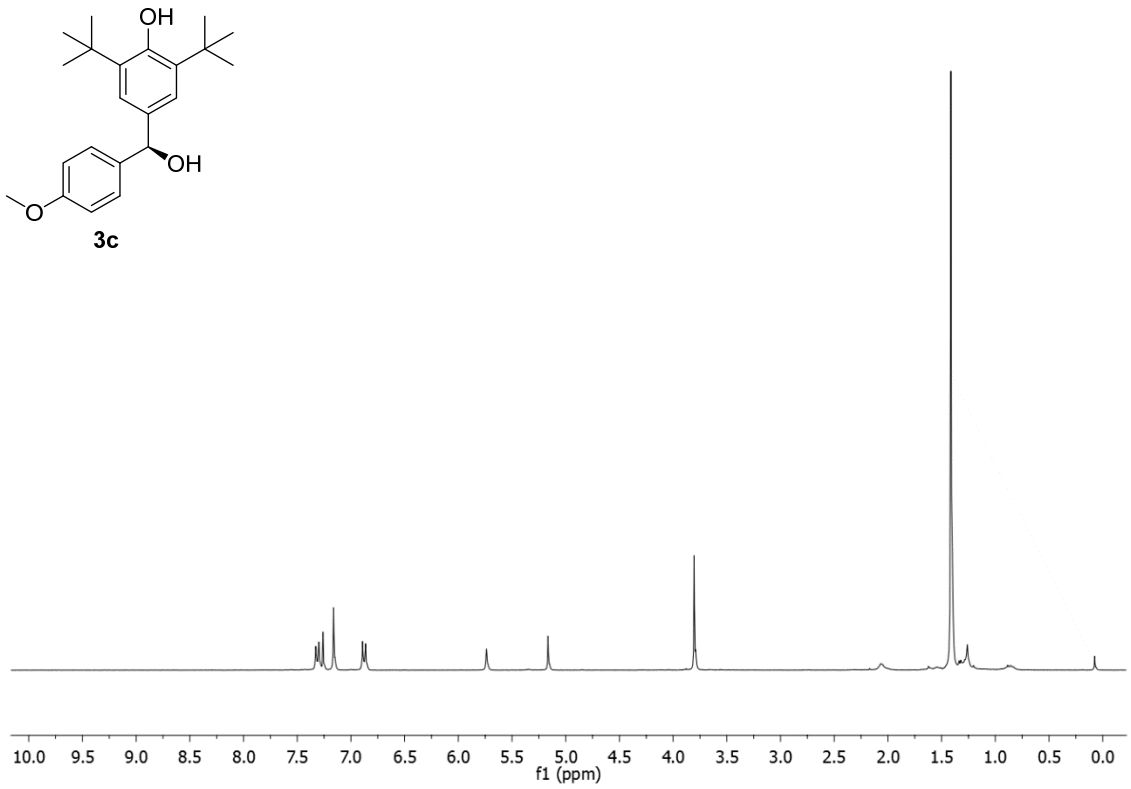


Figure S37: Spectra of compound **3b**.



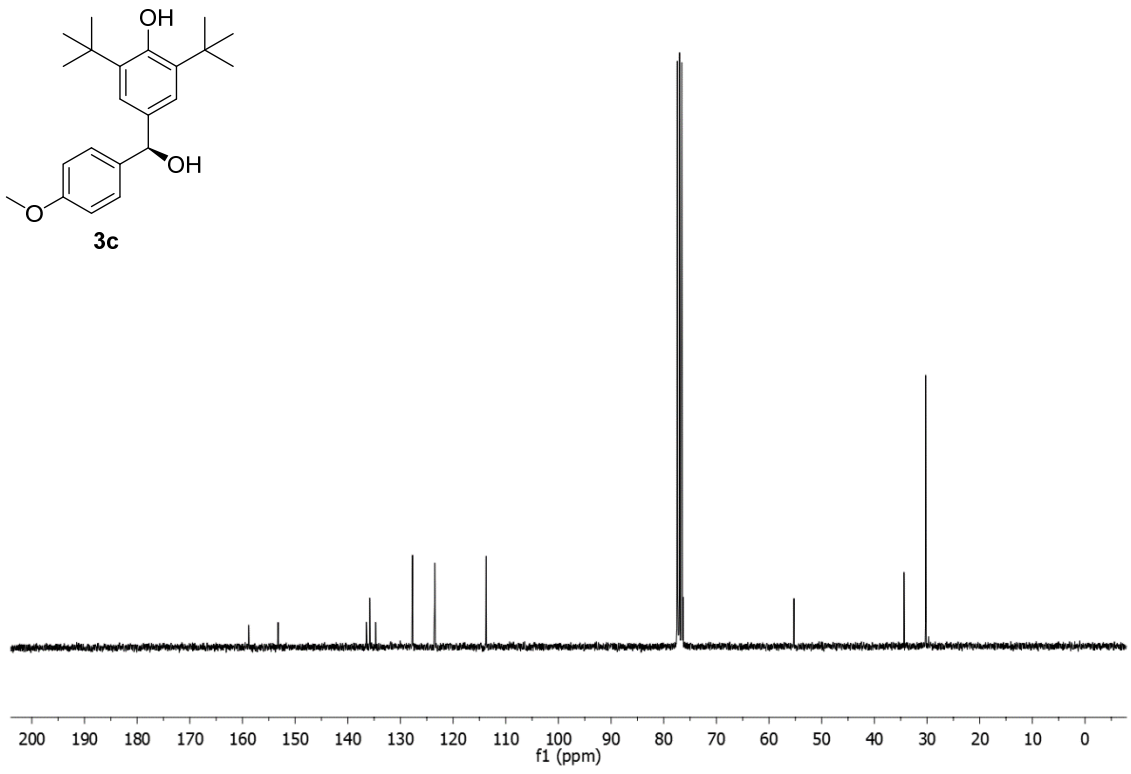
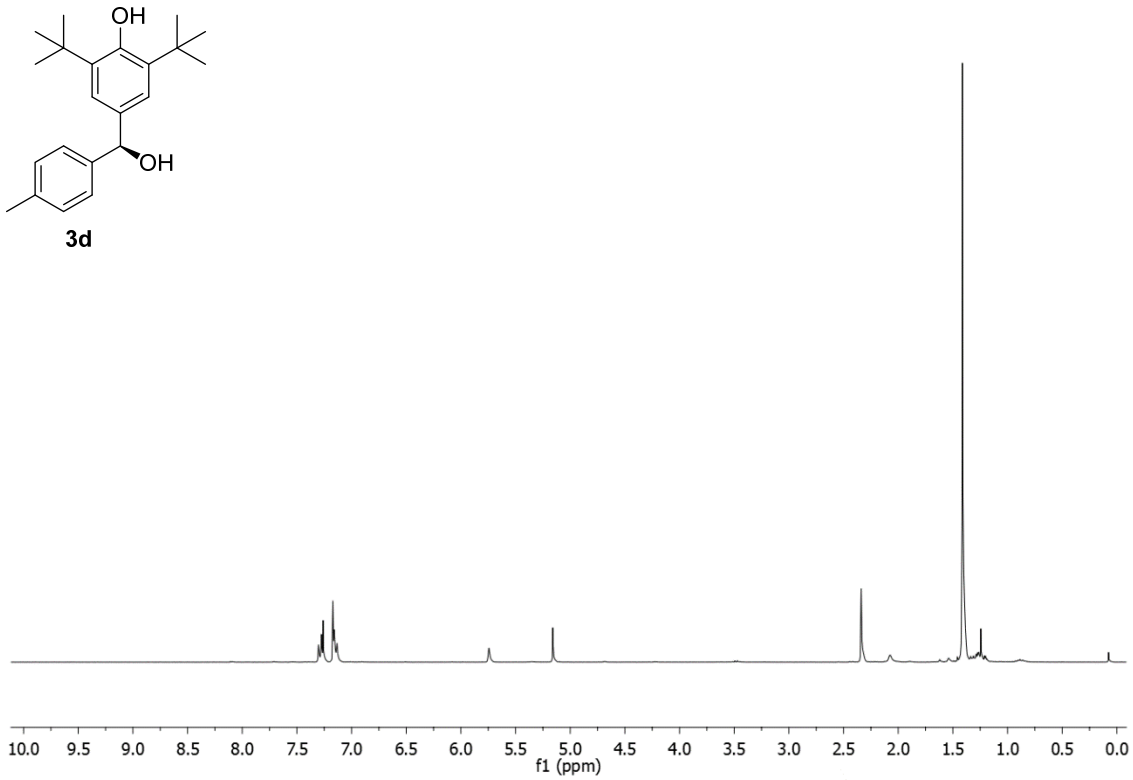


Figure S38: Spectra of compound **3c**.



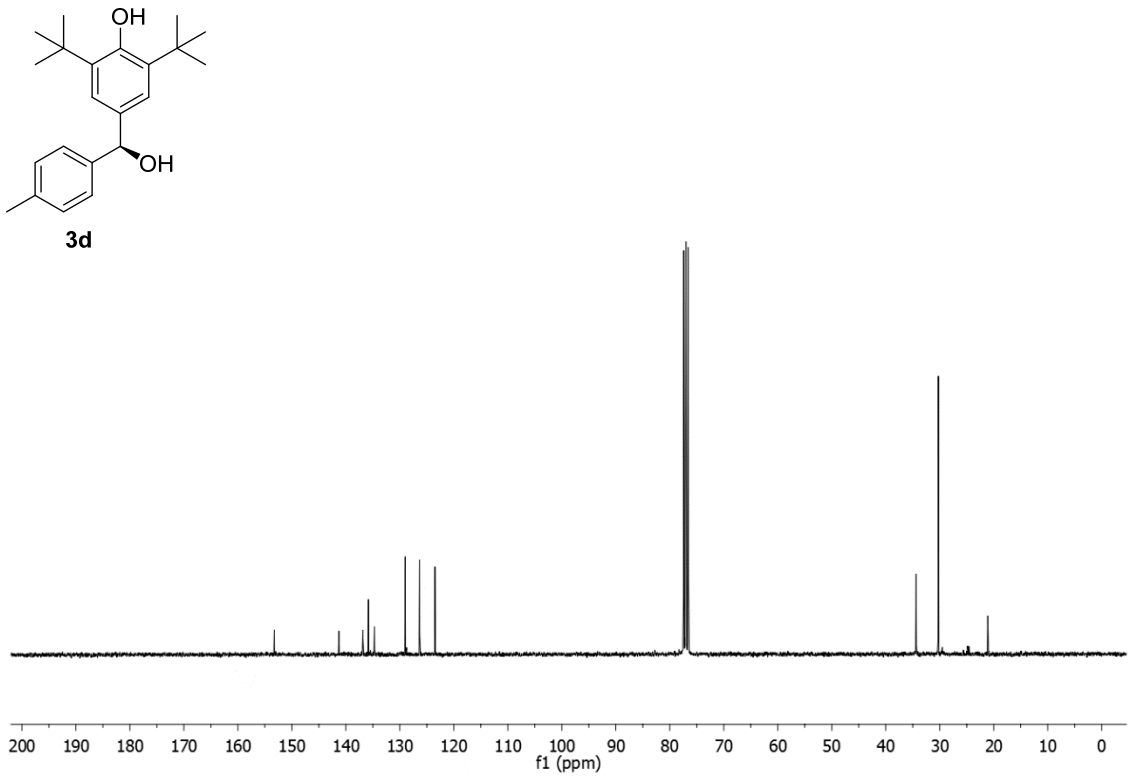
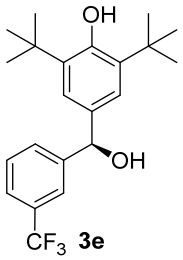
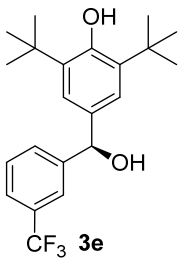


Figure S39: Spectra of compound **3d**.


OH
OH
CF3

3e

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


OH
OH
CF3

3e

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

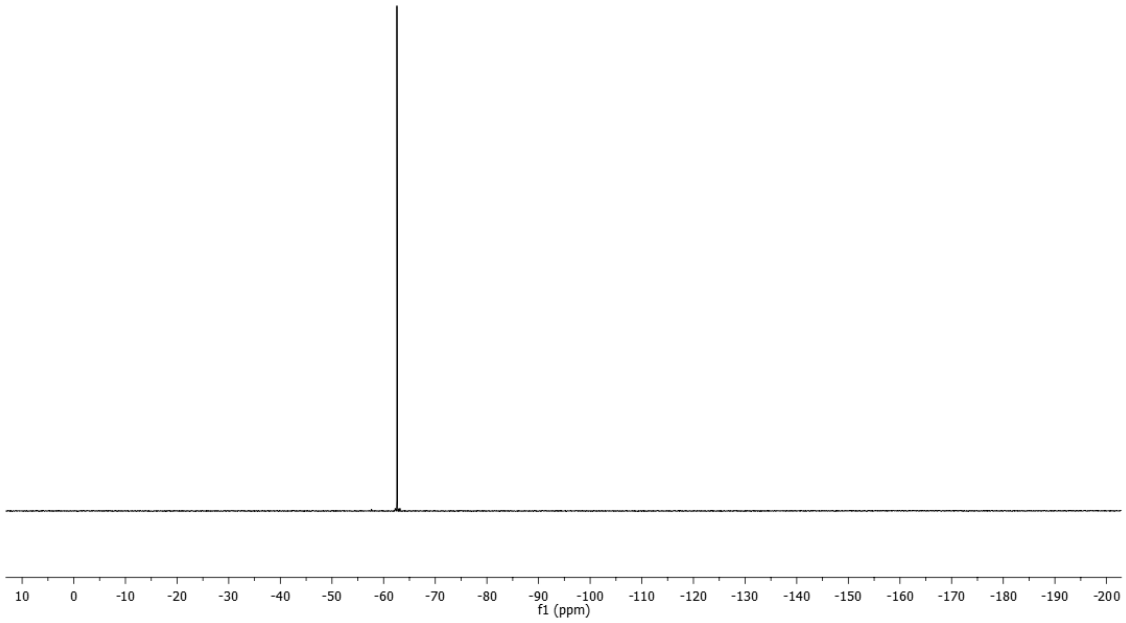
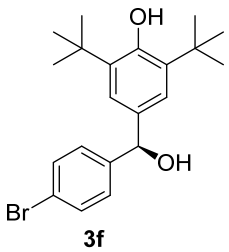
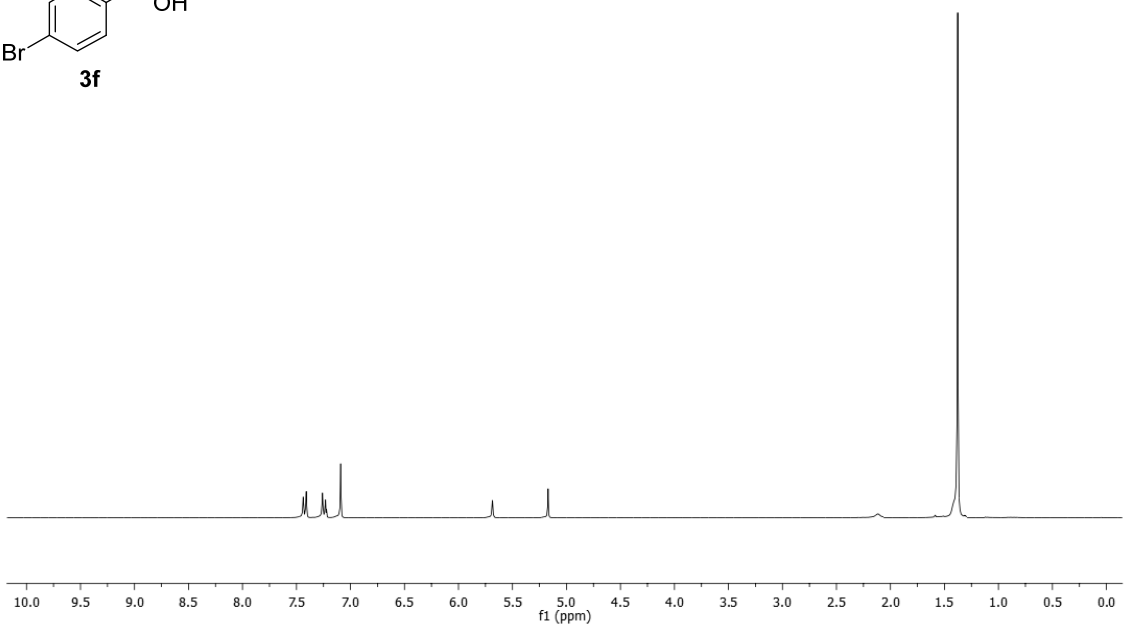
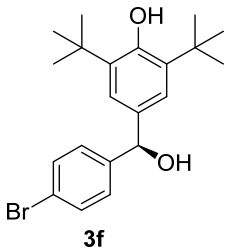


Figure S40: Spectra of compound **3e**.



3f





3f

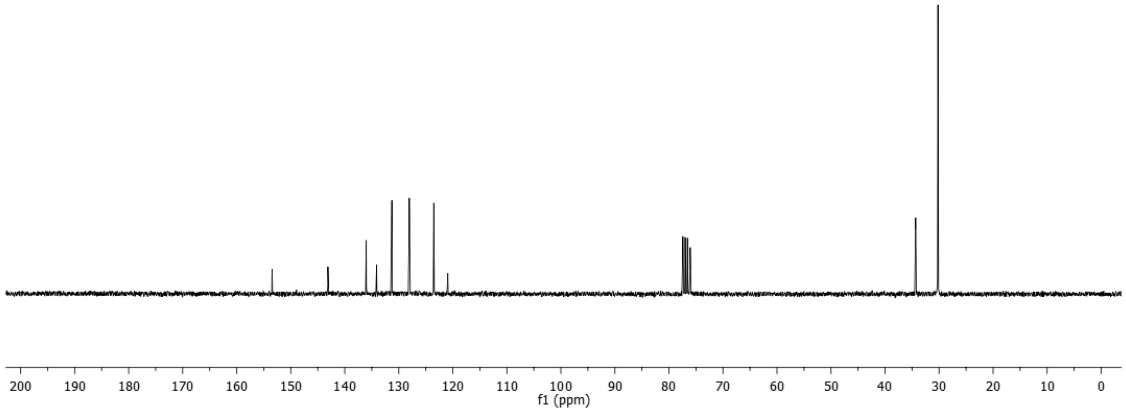
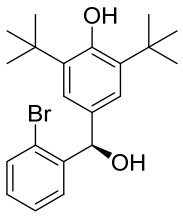
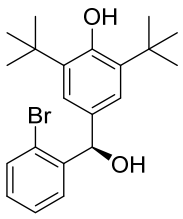


Figure S41: Spectra of compound **3f**.

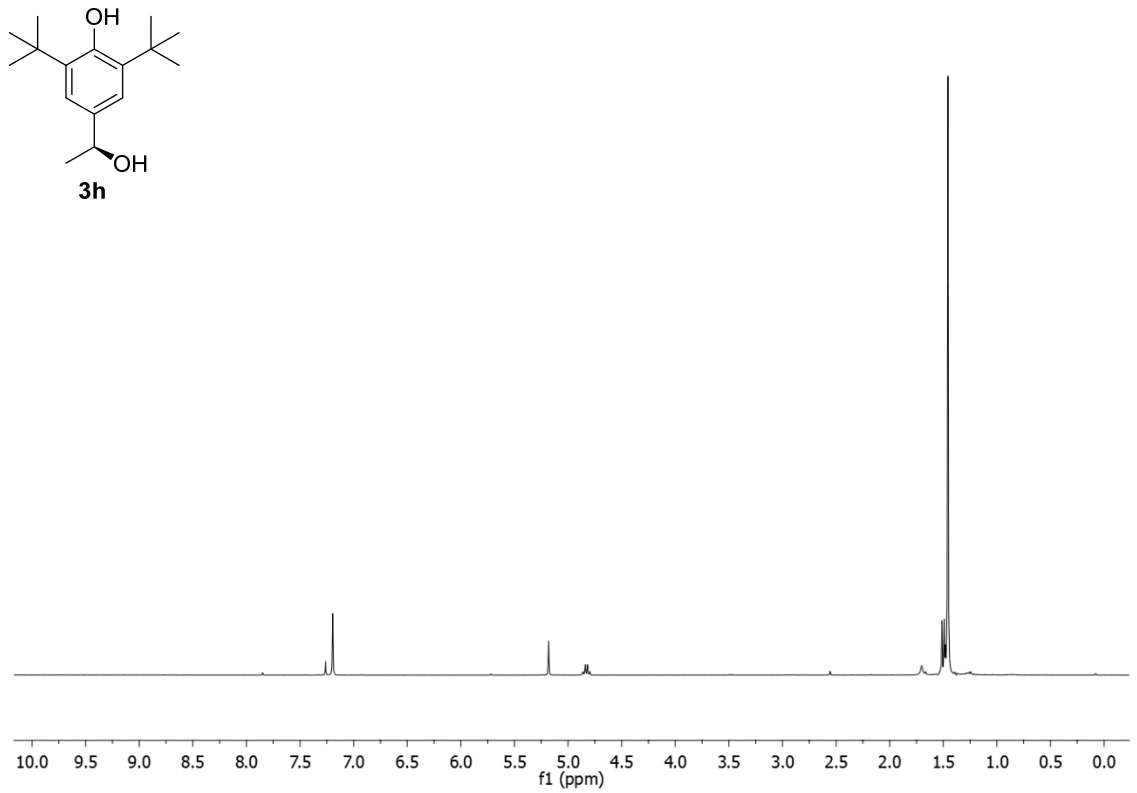


3g



3g

Figure S42: Spectra of compound **3g**.



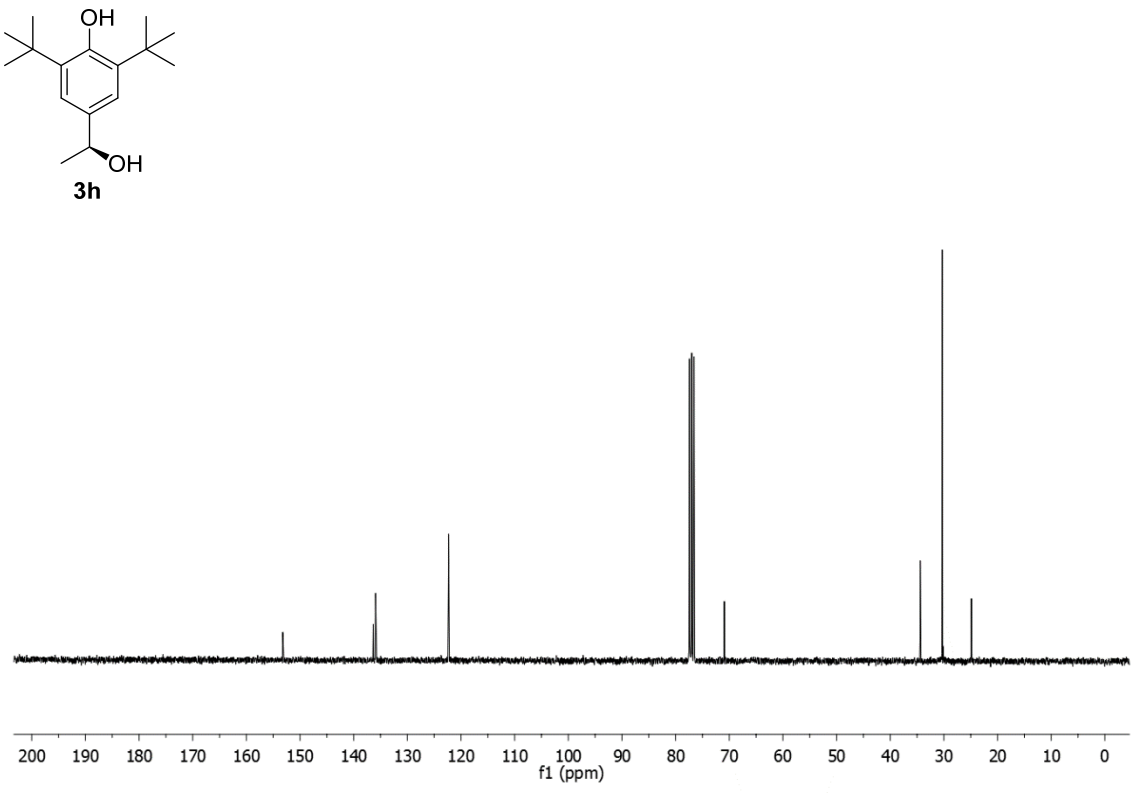
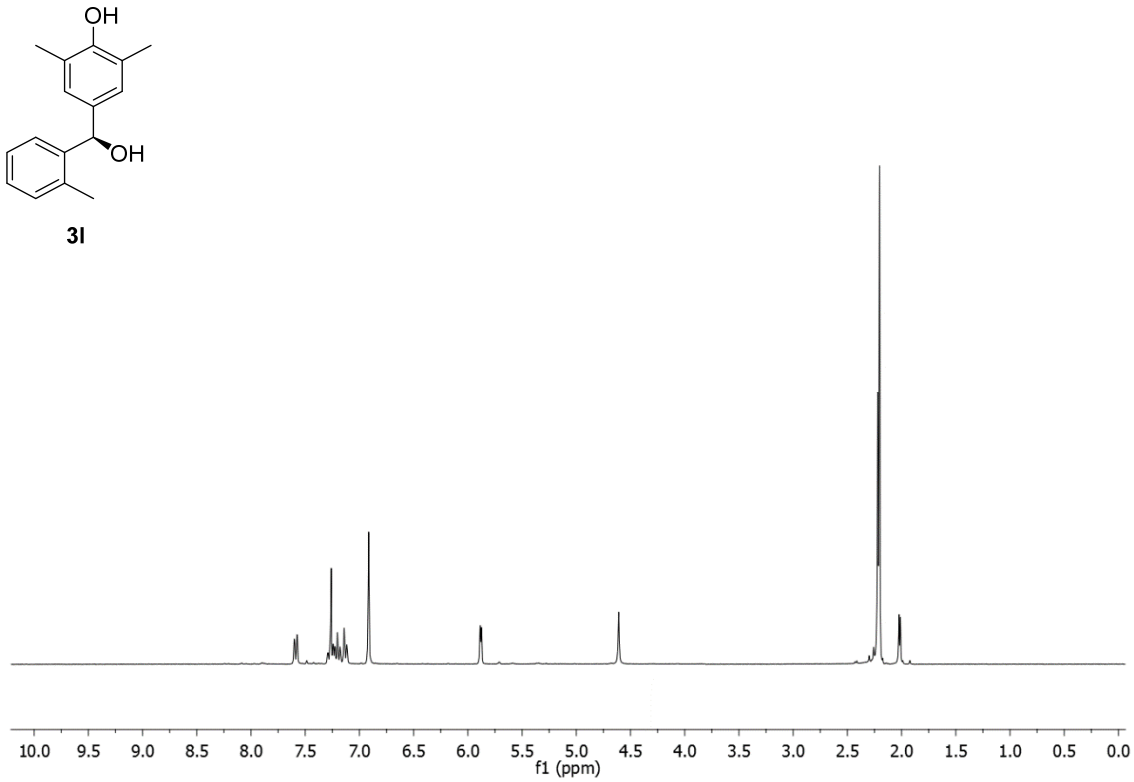


Figure S43: Spectra of compound **3h**.



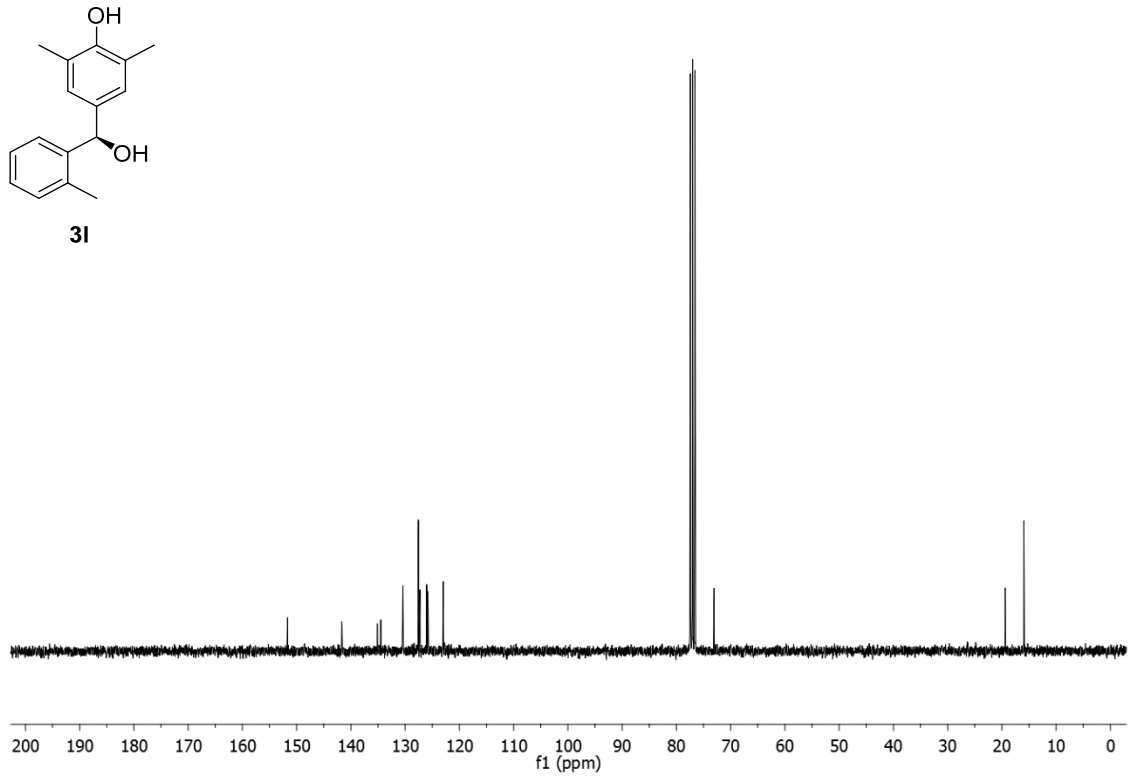
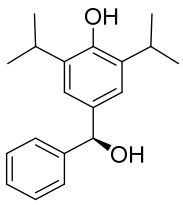
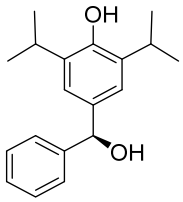


Figure S44: Spectra of compound **3l**.



3n



3n

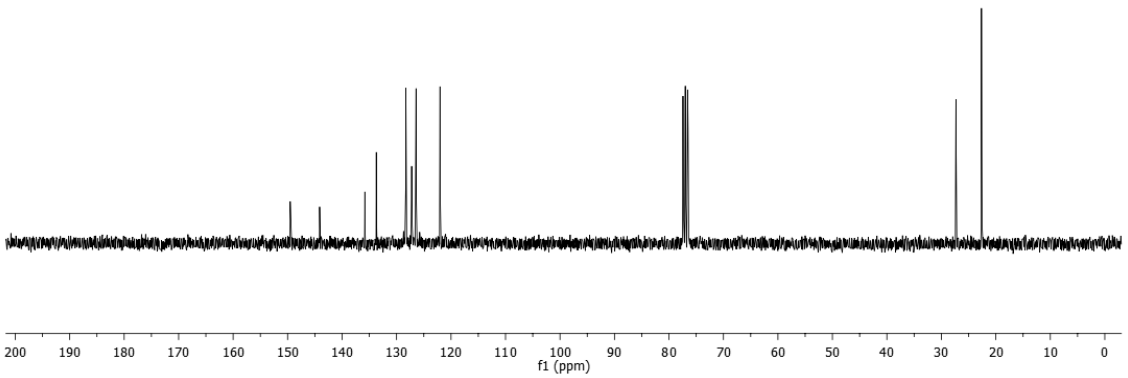
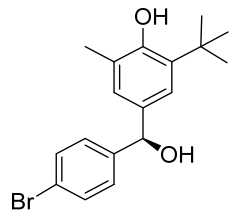
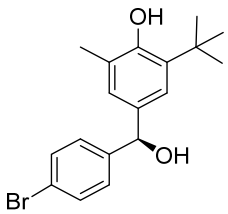


Figure S45: Spectra of compound **3n**.



3p



3p

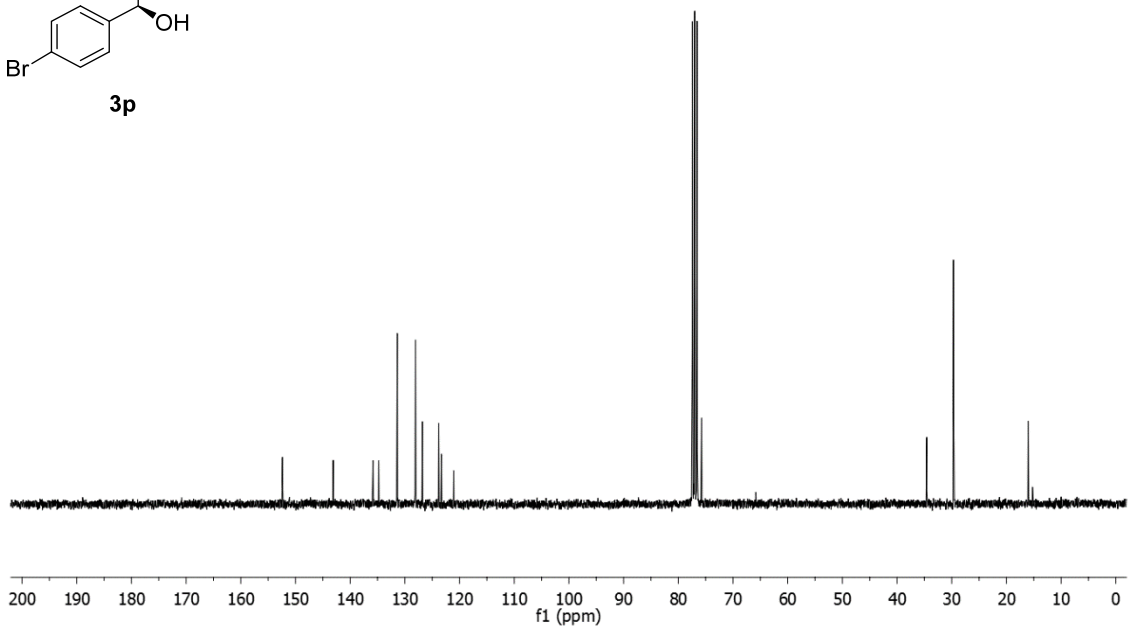
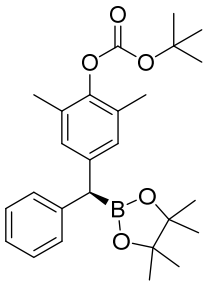
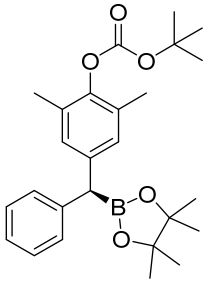


Figure S46: Spectra of compound **3p**.



4



4

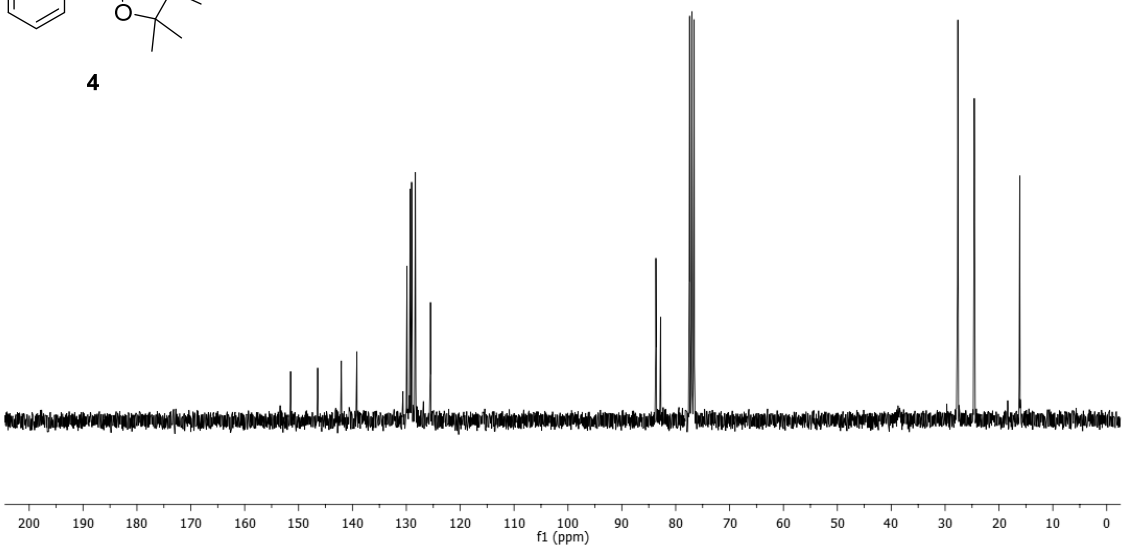
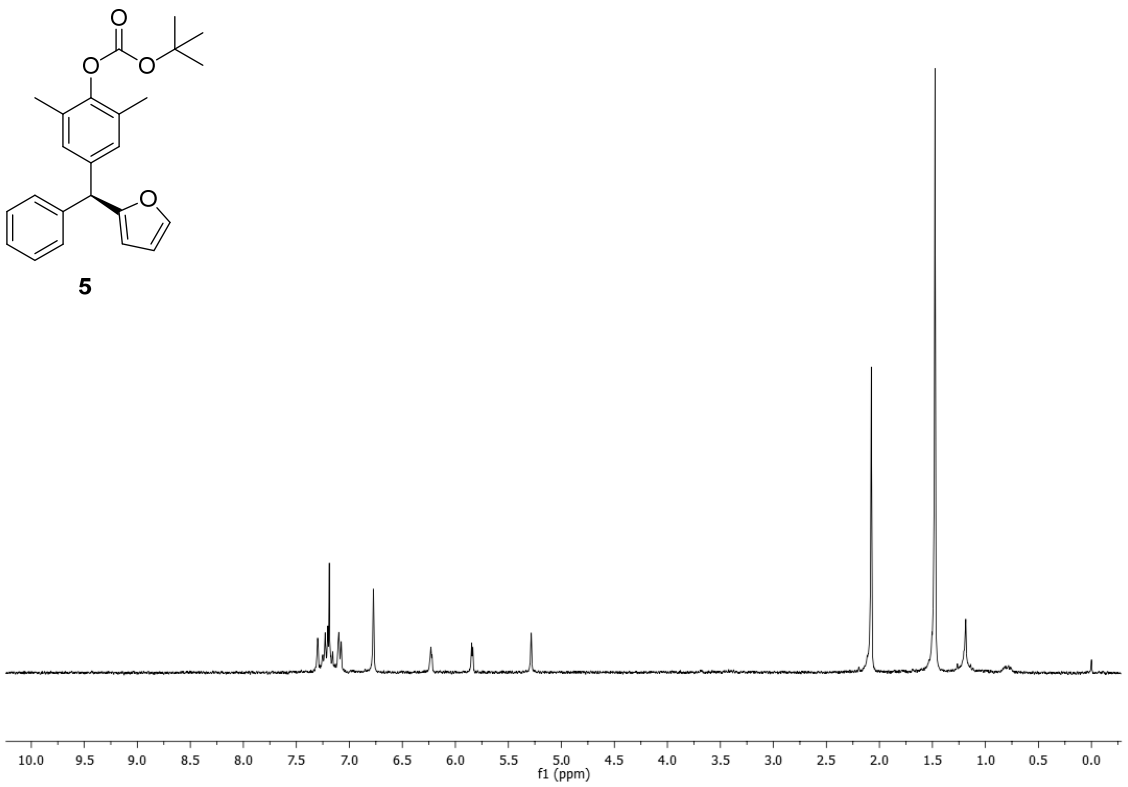


Figure S47: Spectra of compound **4**.



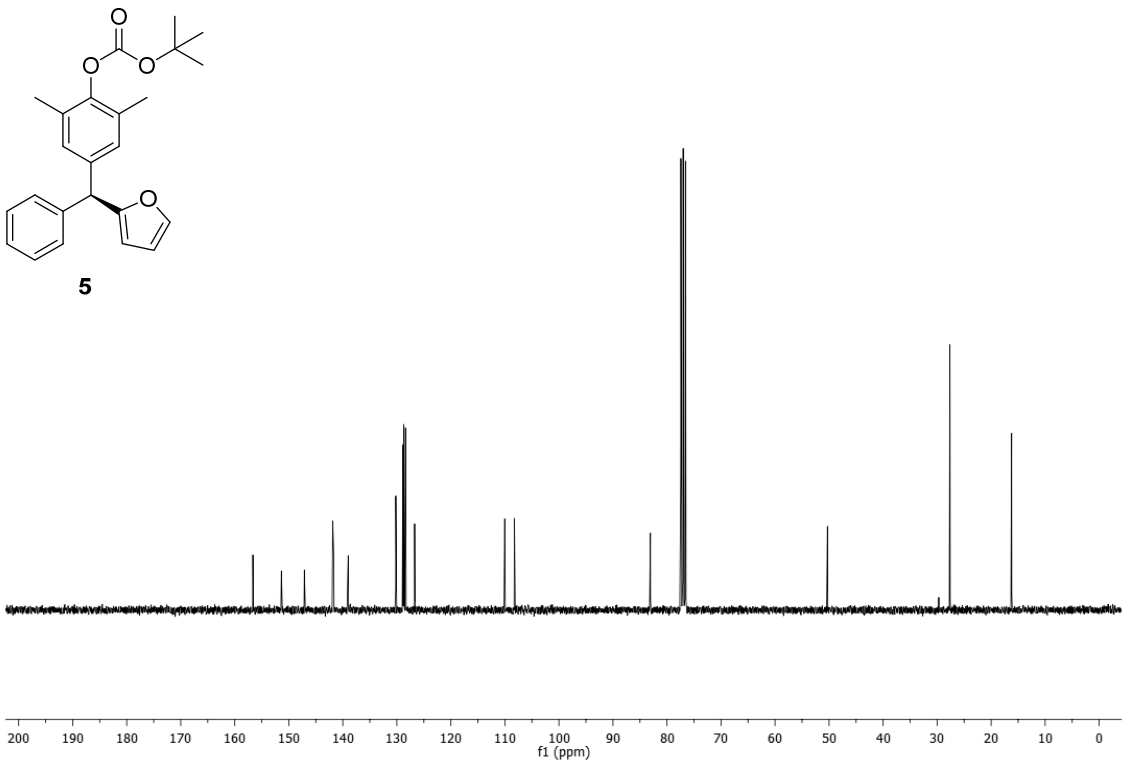


Figure S48: Spectra of compound **5**.

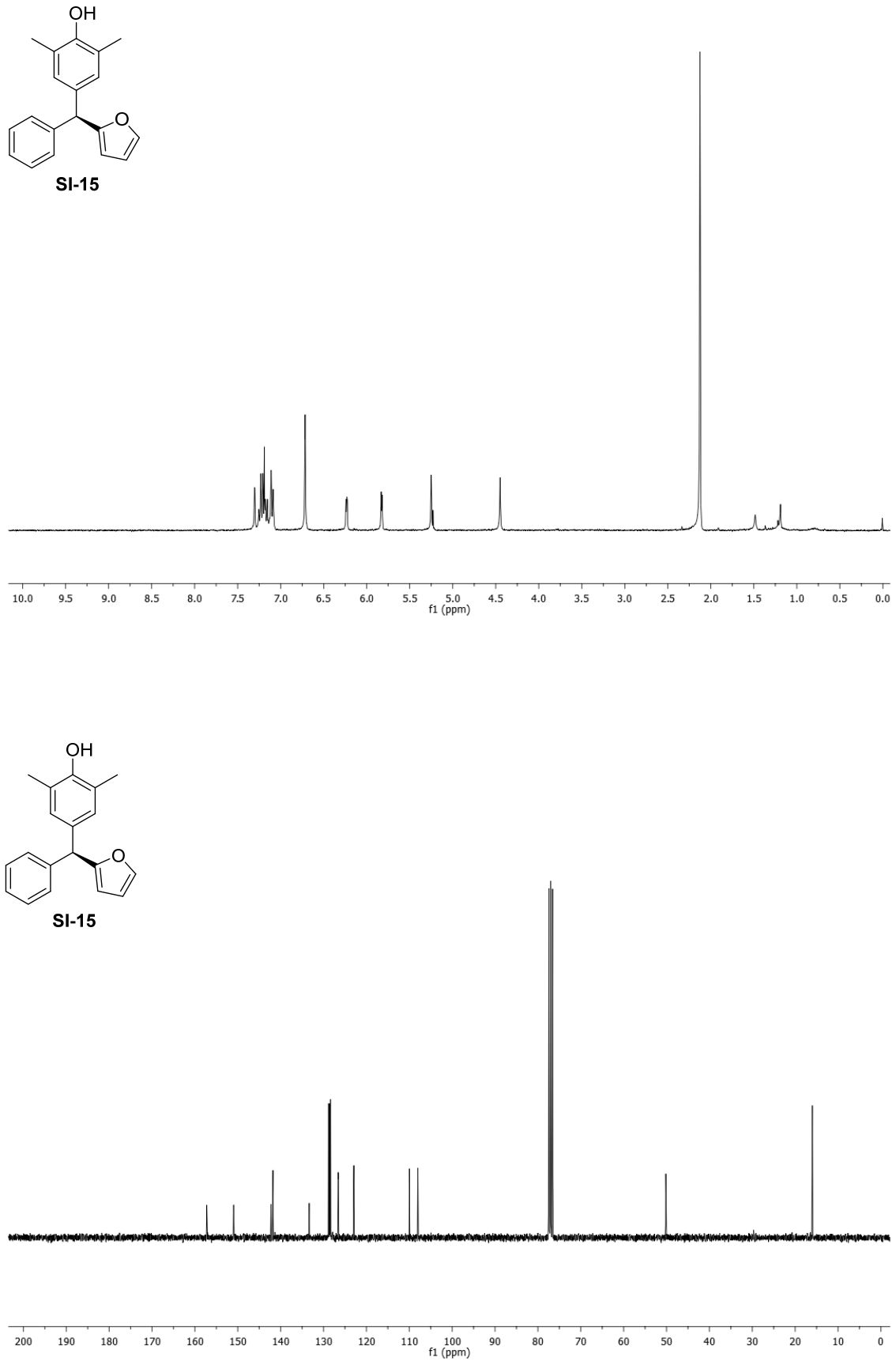
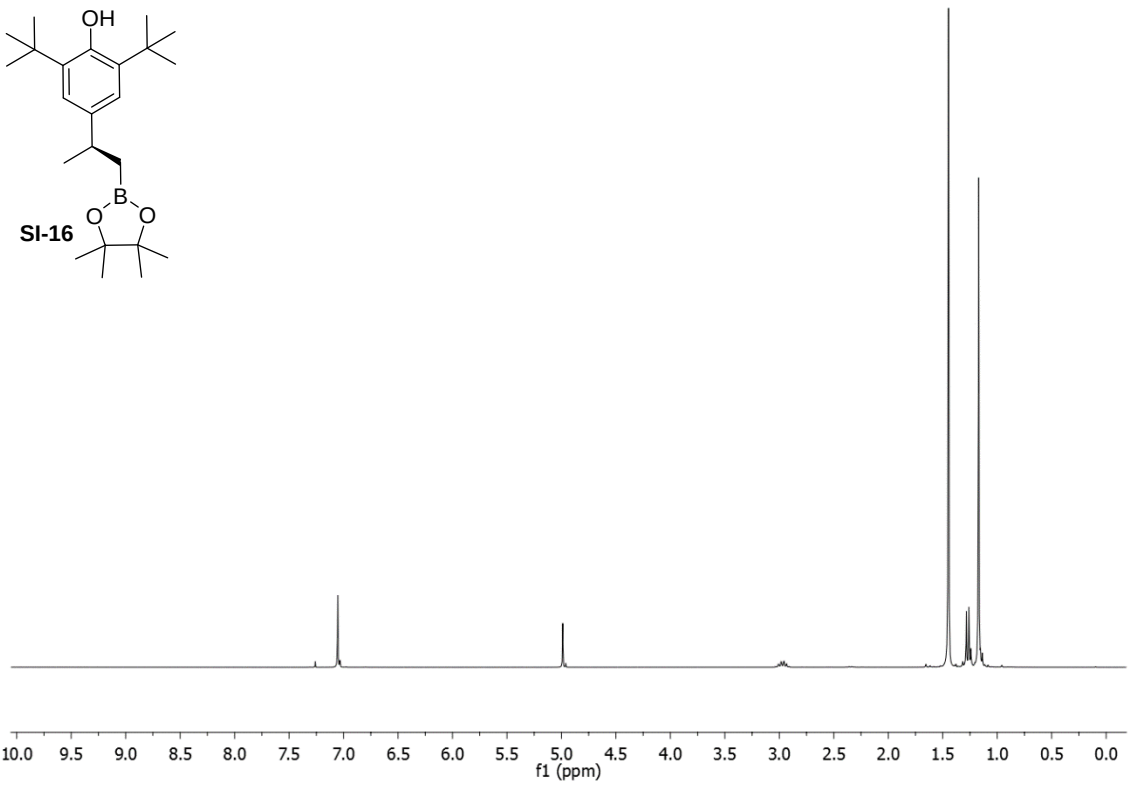


Figure S49: Spectra of compound **SI-15**.



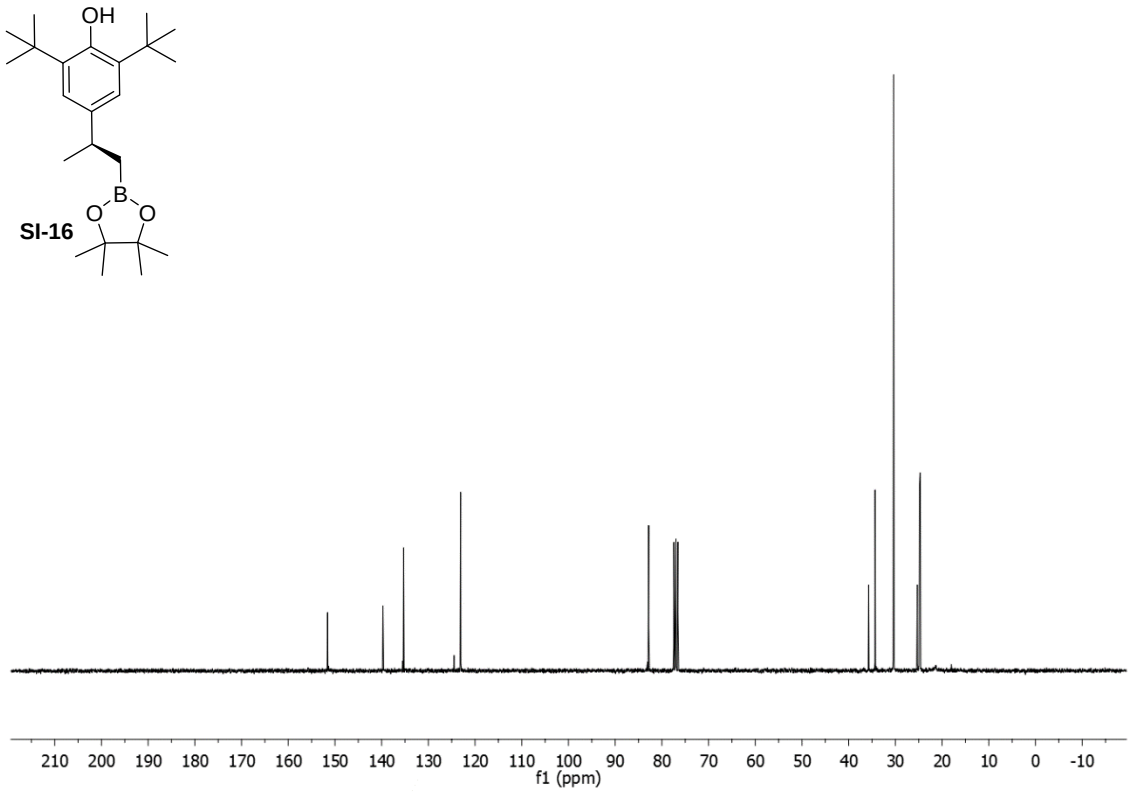
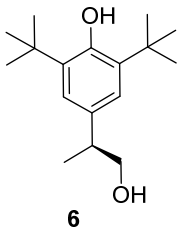
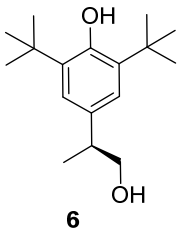


Figure S50: Spectra of compound **SI-16**.



6



6

Figure S51: Spectra of compound **6**.

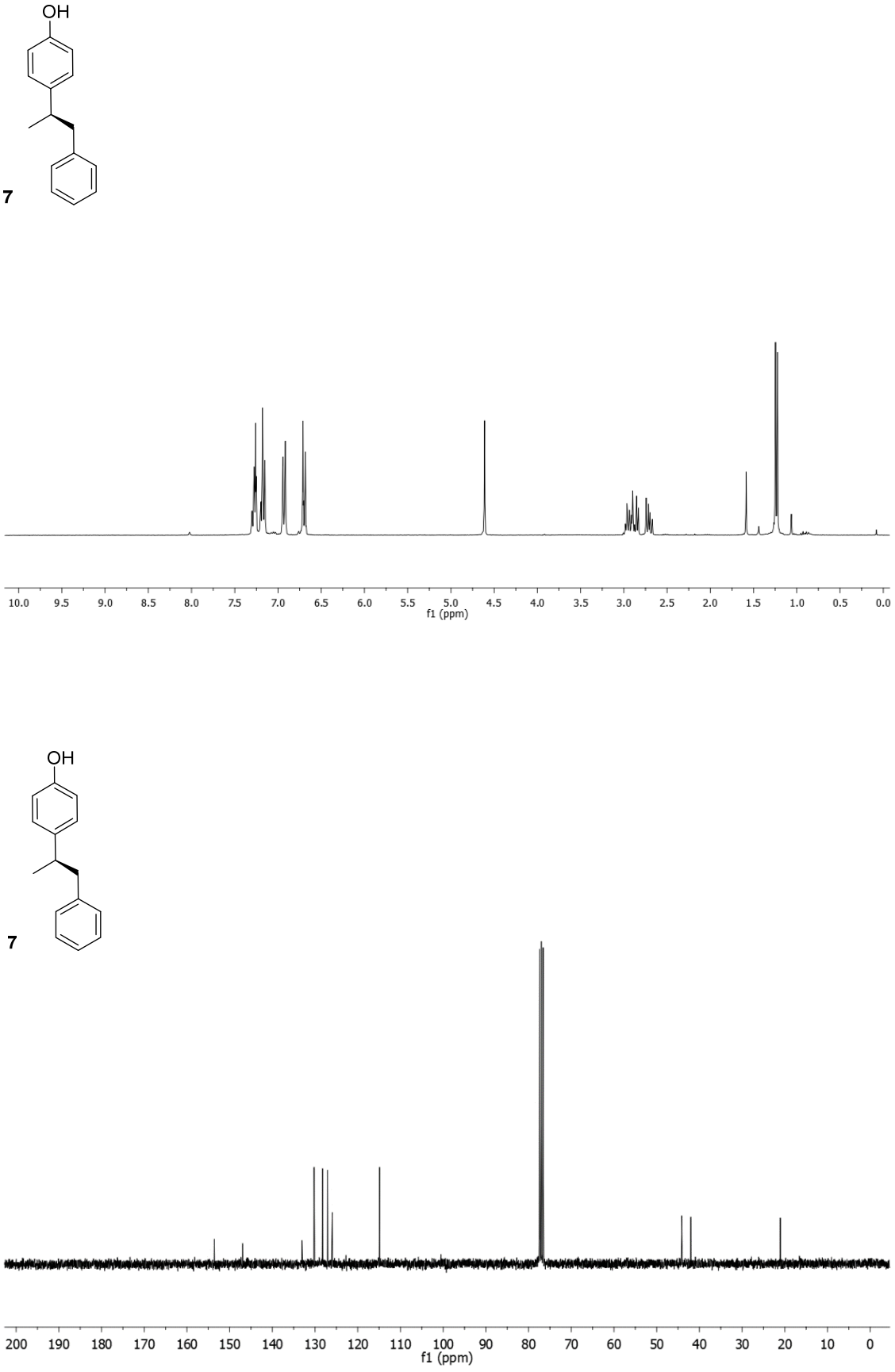
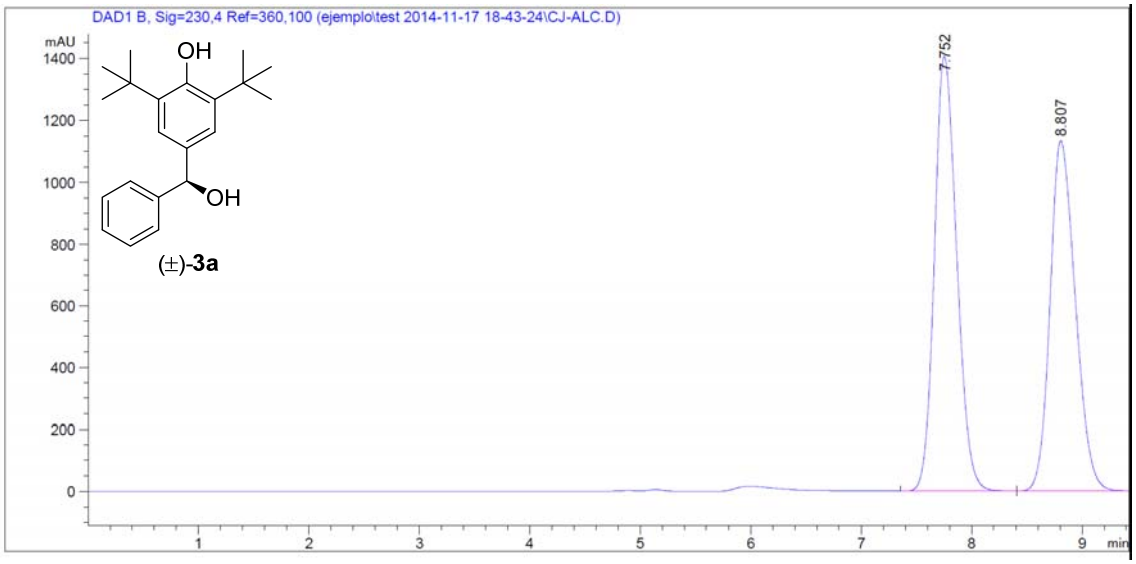
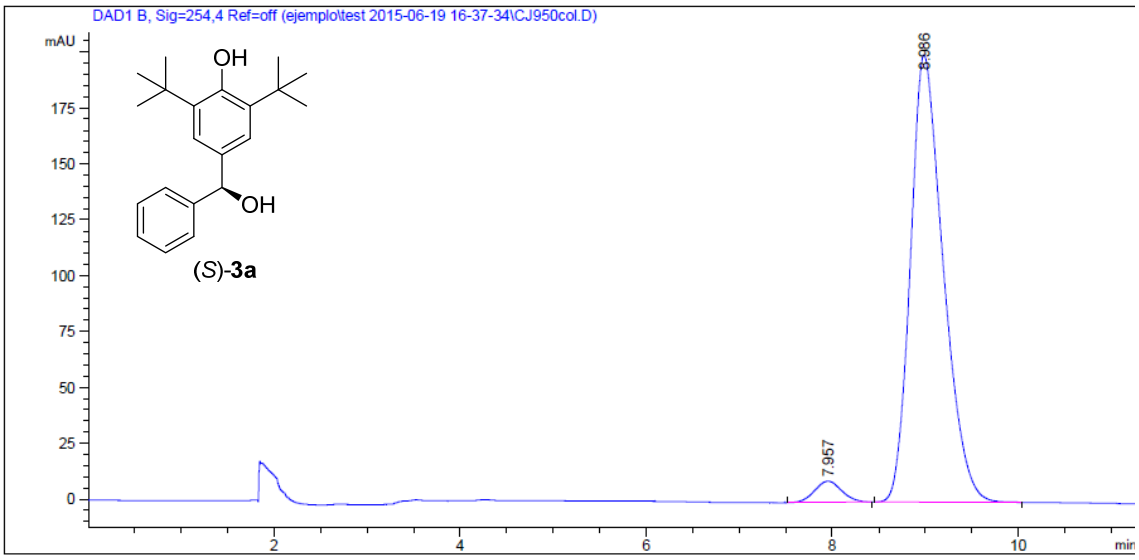


Figure S52: Spectra of compound **7**.

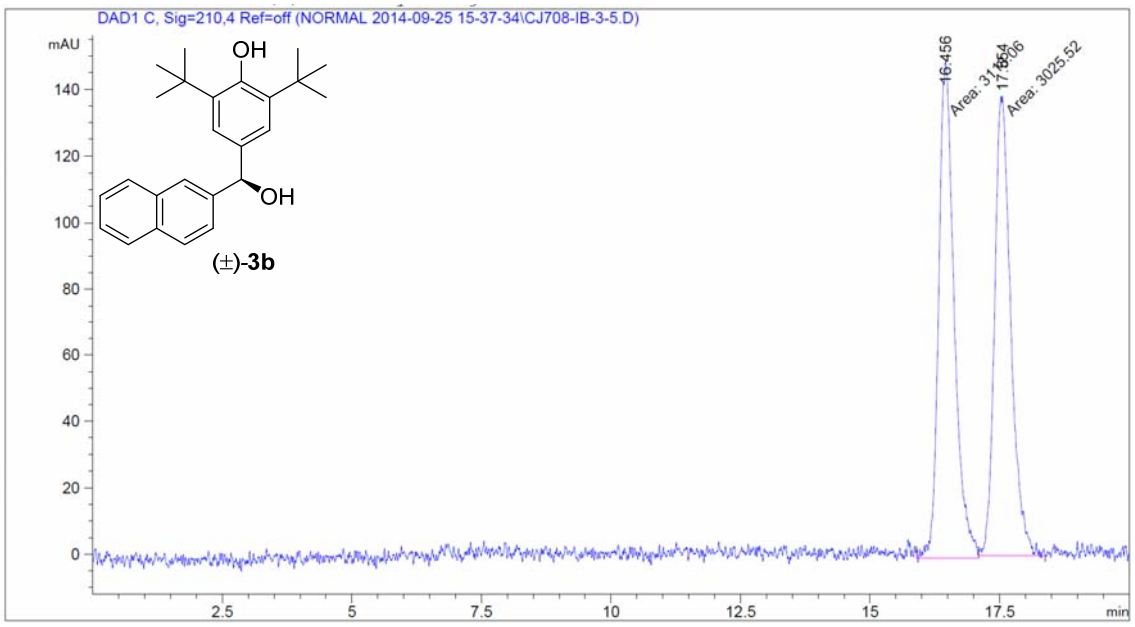
7. SFC and HPLC chromatograms

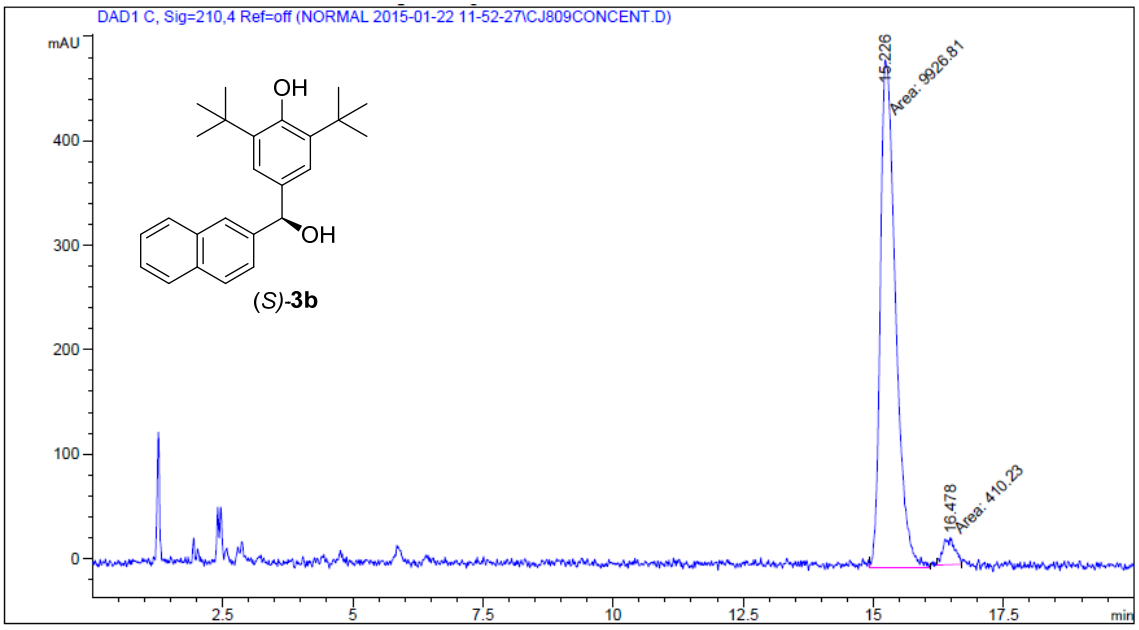




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.957	BB	0.2374	191.01881	9.46784	3.7523
2	8.986	BB	0.3512	4899.65430	200.04854	96.2477

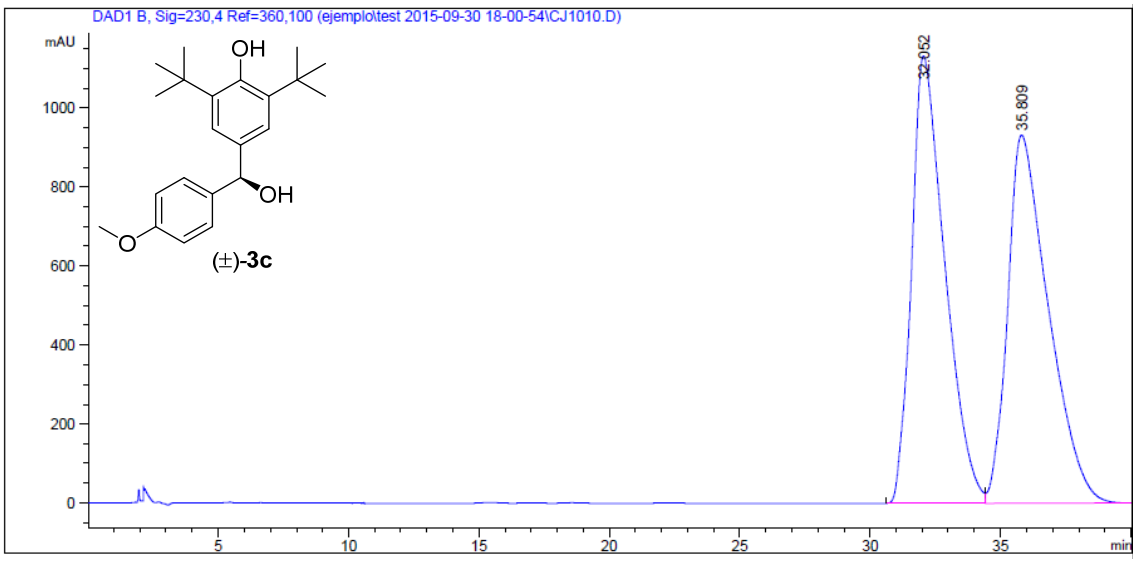
Figure S53: HPLC chromatogram of compound **3a**.

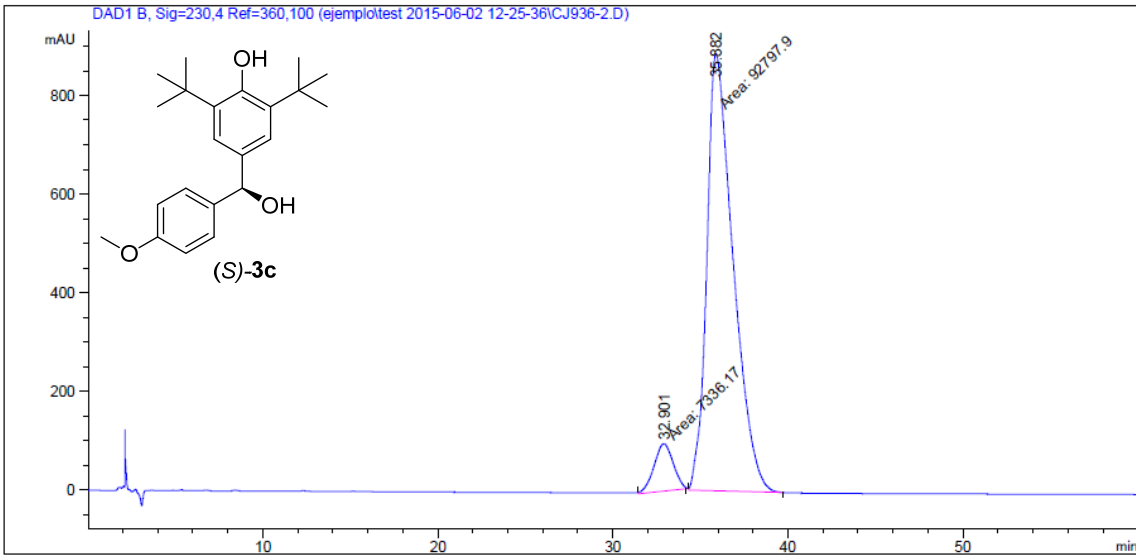




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.226	MM	0.3399	9926.80762	486.78424	96.0315
2	16.478	MM	0.2602	410.22952	26.27437	3.9685

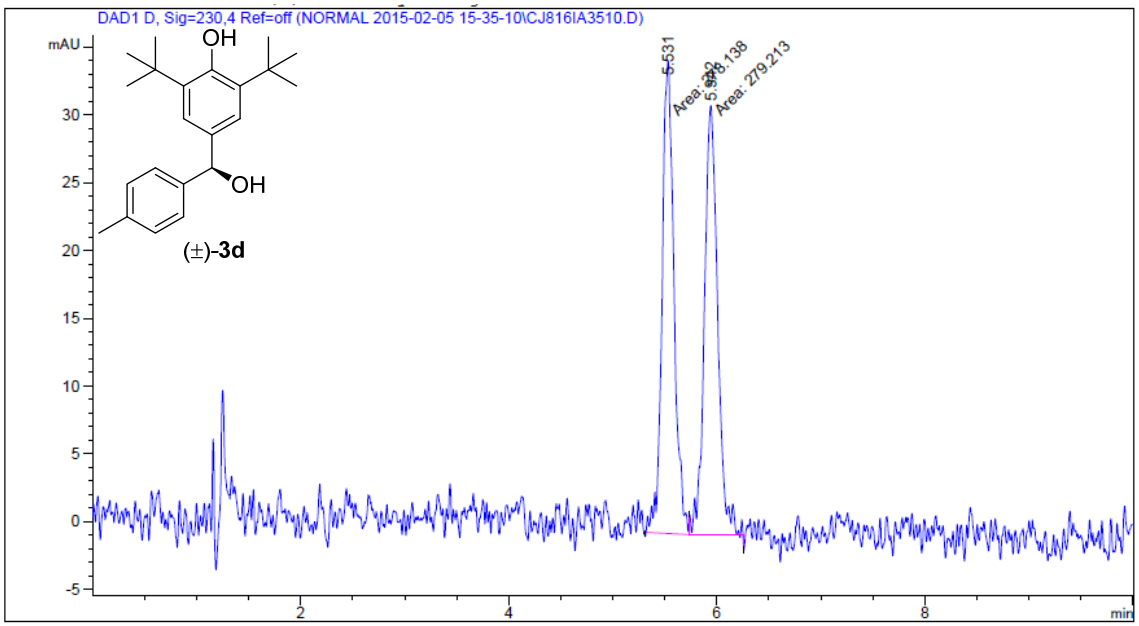
Figure S54: SFC chromatogram of compound **3b**.

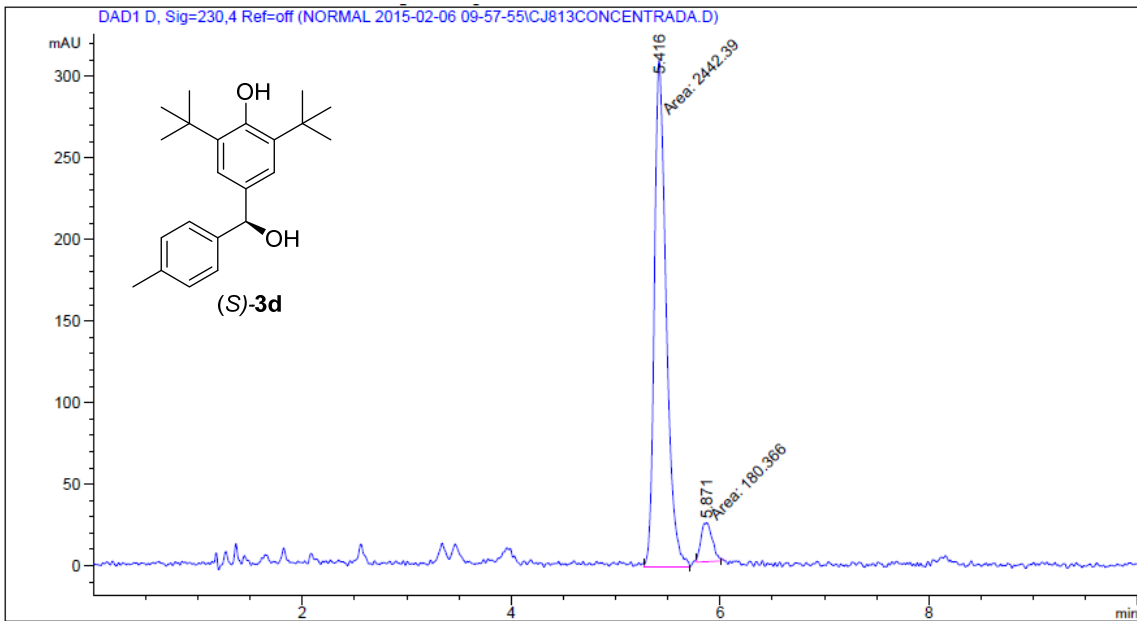




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.901	MM	1.2730	7336.17334	96.04536	7.3264
2	35.882	MM	1.7470	9.27979e4	885.28558	92.6736

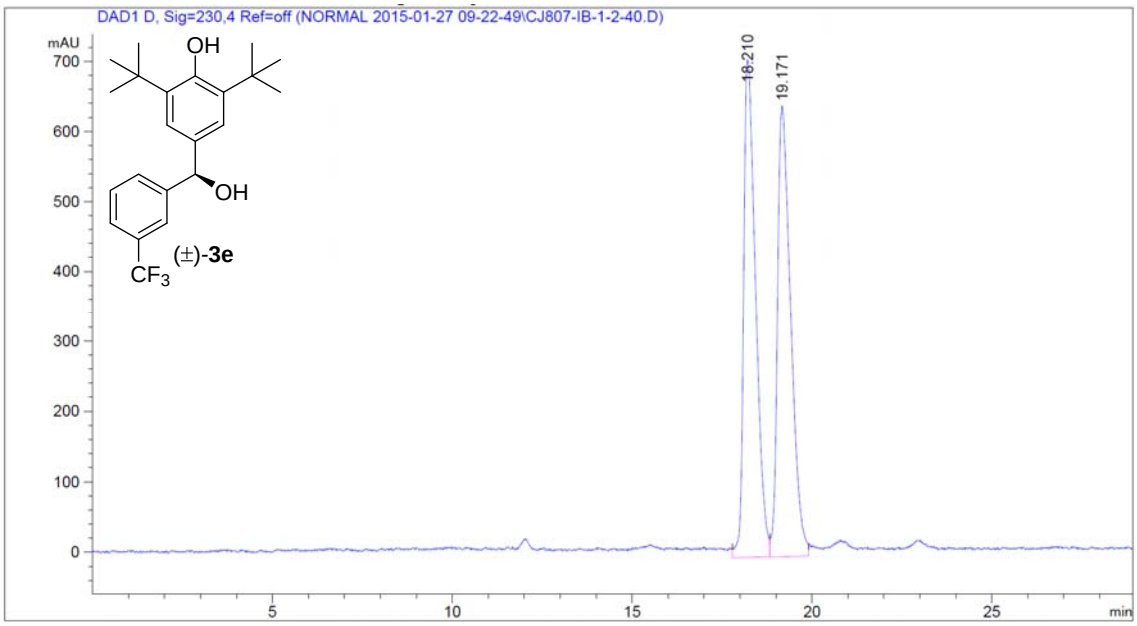
Figure S55: HPLC chromatogram of compound **3c**.

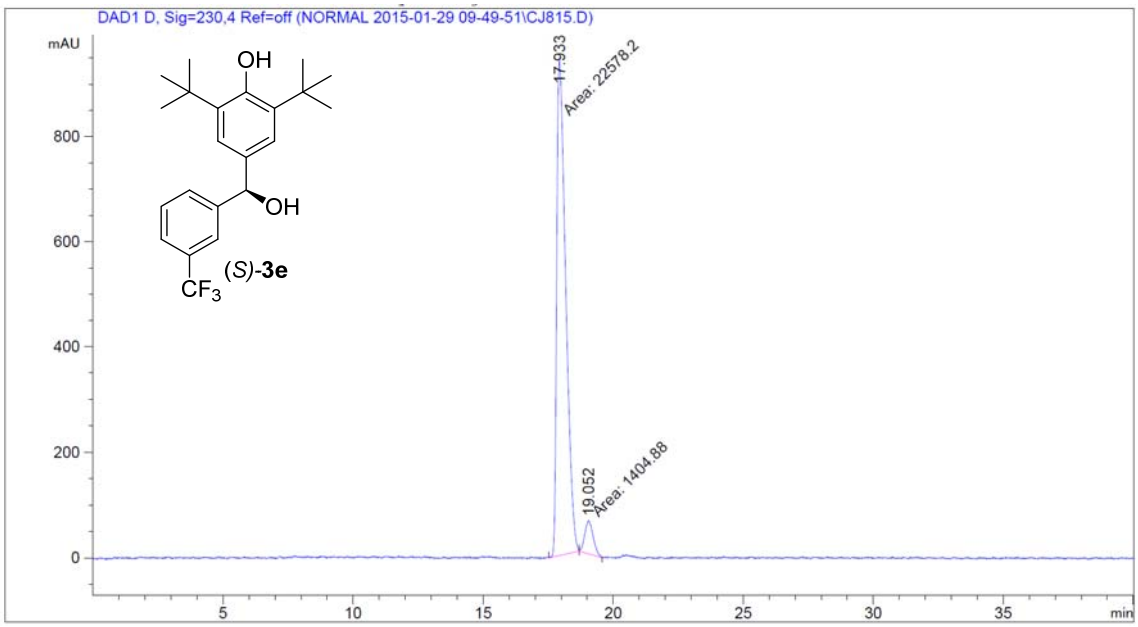




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.416	MM	0.1310	2442.38818	310.65051	93.1230
2	5.871	MM	0.1261	180.36591	23.84821	6.8770

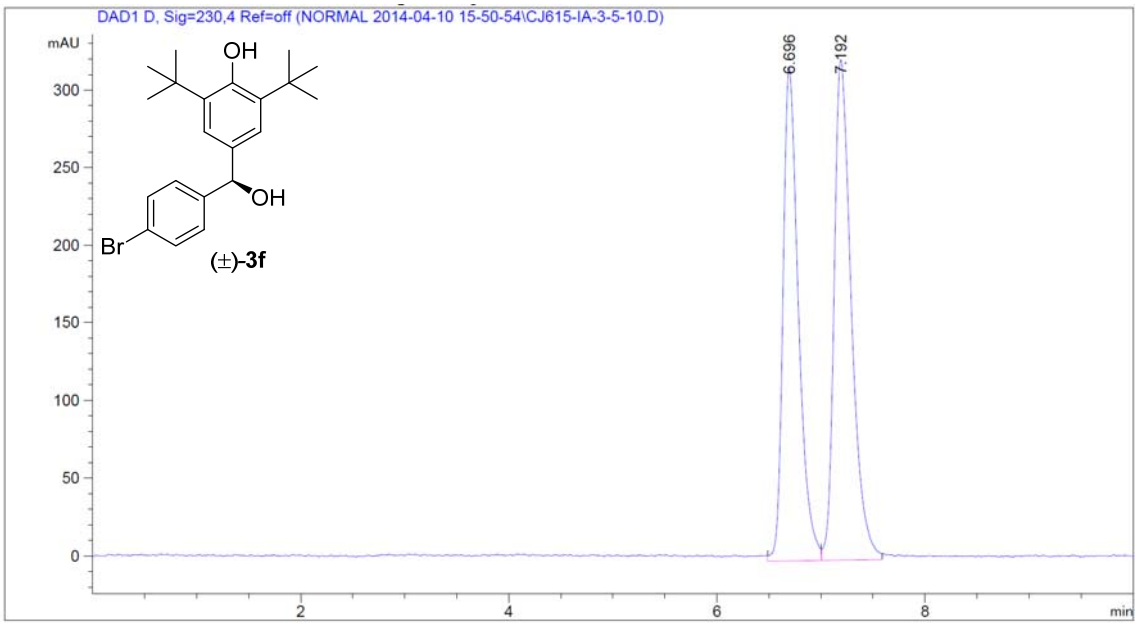
Figure S56: SFC chromatogram of compound **3d**.

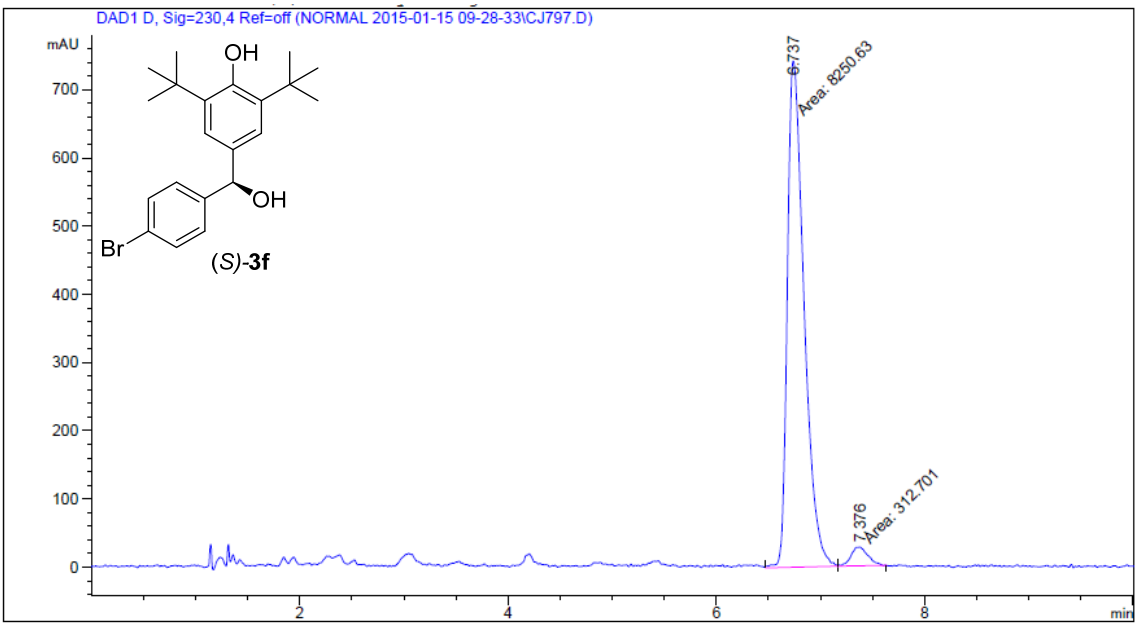




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.933	MM	0.3999	2.25782e4	940.91229	94.1422
2	19.052	MM	0.3715	1404.87708	63.02040	5.8578

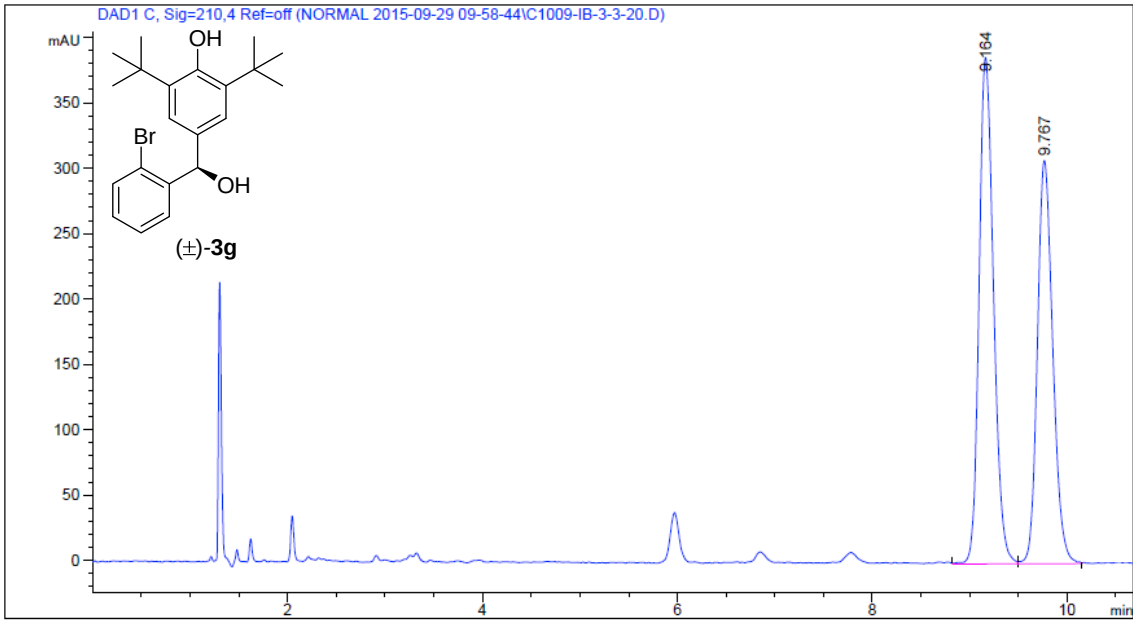
Figure S57: SFC chromatogram of compound **3e**.

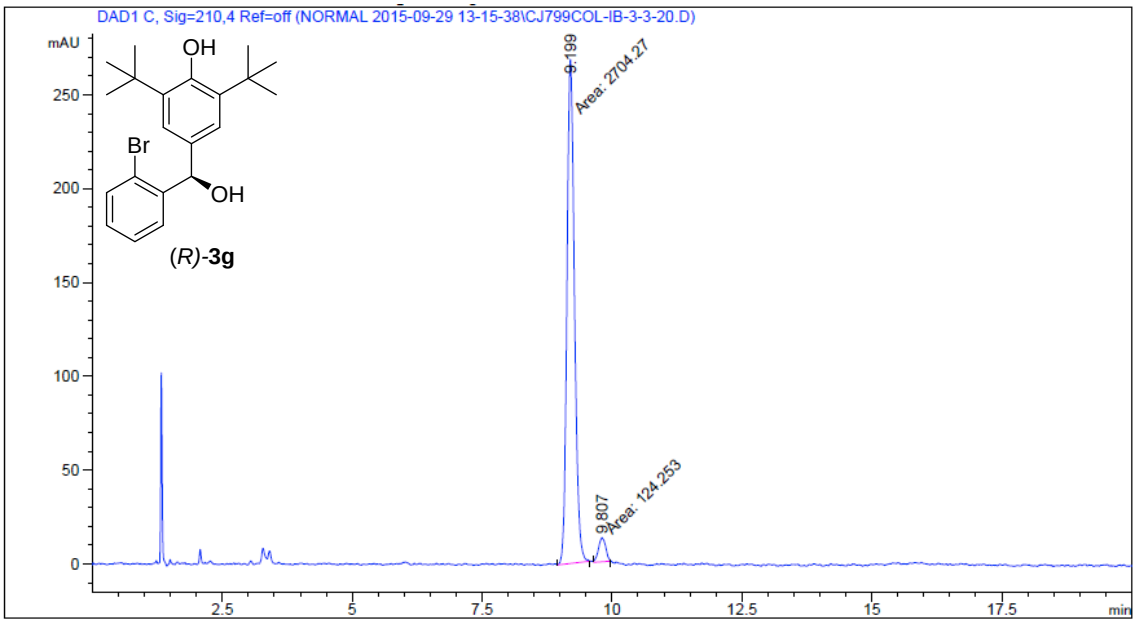




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.738	VV	0.1631	8290.87988	743.50781	95.4018
2	7.376	VV	0.1561	399.60156	31.26399	4.5982

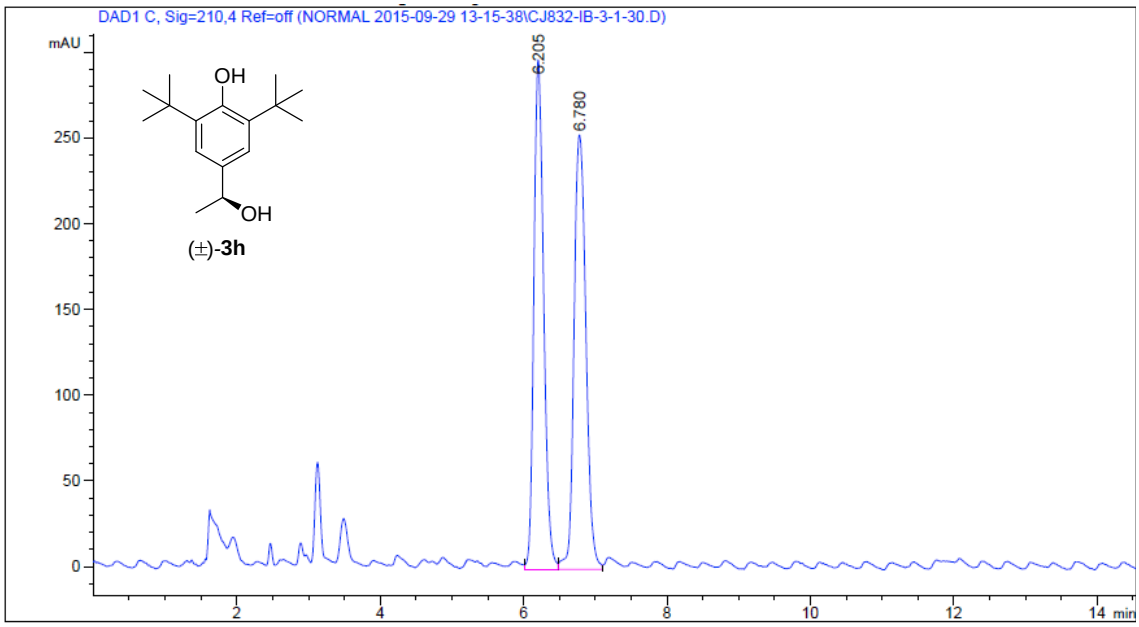
Figure S58: SFC chromatogram of compound **3f**.

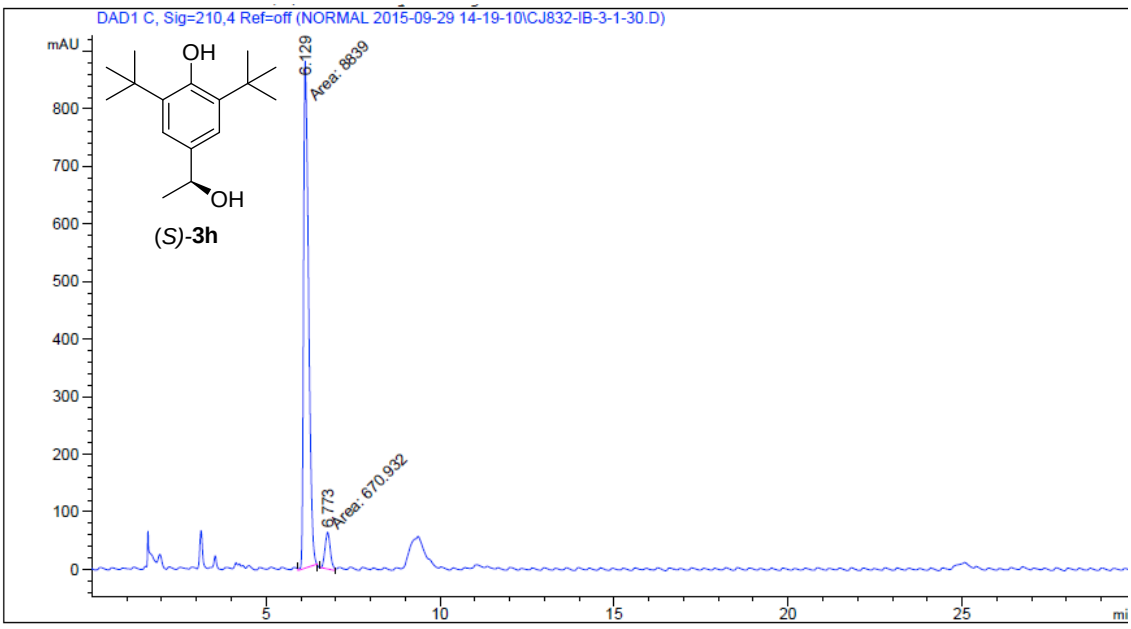




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.199	MM	0.1678	2704.26880	268.66586	95.6071
2	9.807	MM	0.1609	124.25291	12.87134	4.3929

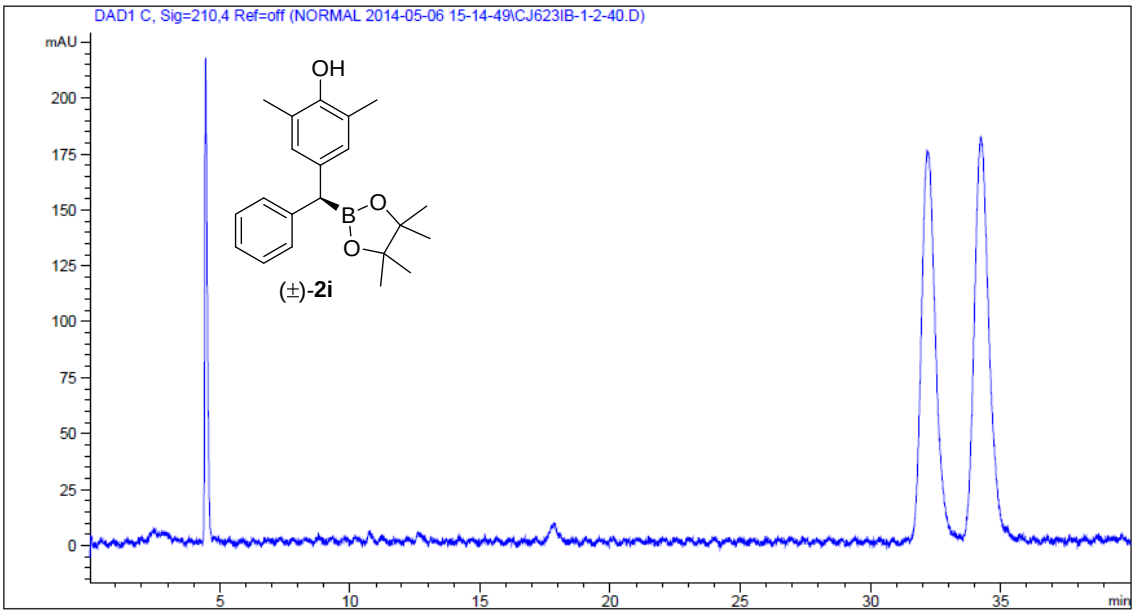
Figure S59: SFC chromatogram of compound **3g**.

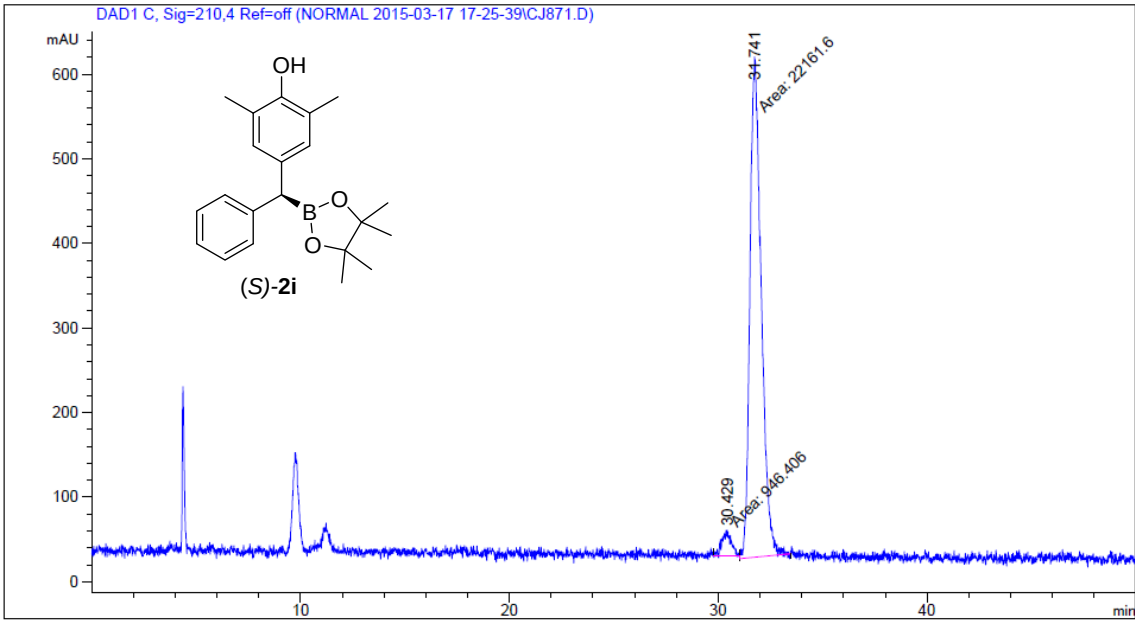




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.129	MM	0.1672	8839.00391	880.99493	92.9449
2	6.773	MM	0.1749	670.93164	63.93721	7.0551

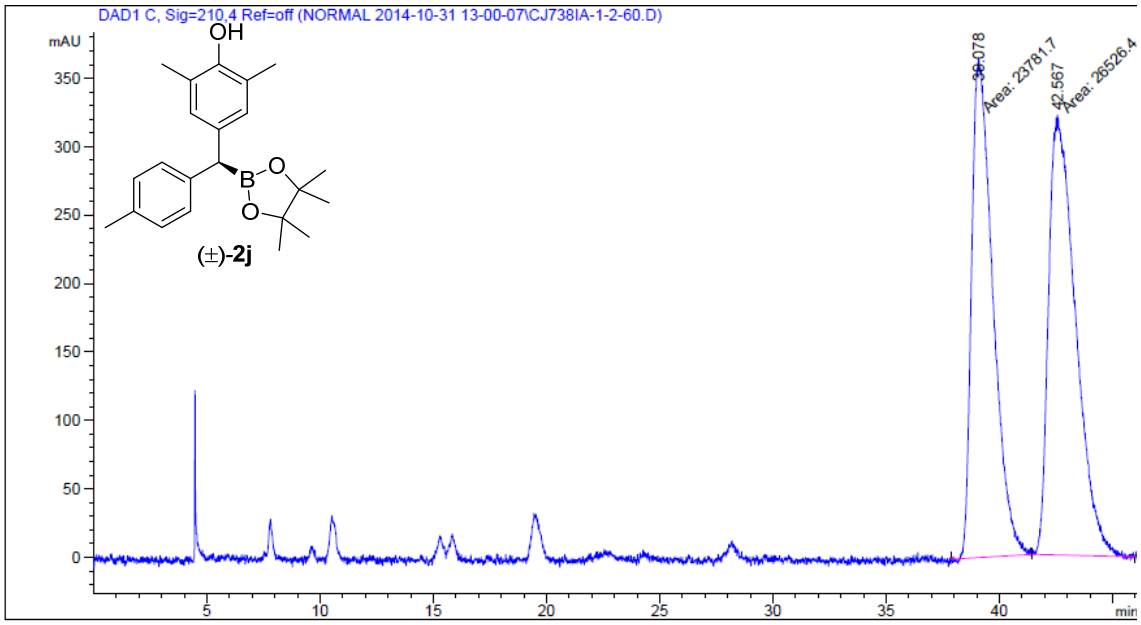
Figure S60: HPLC chromatogram of compound **3h**.

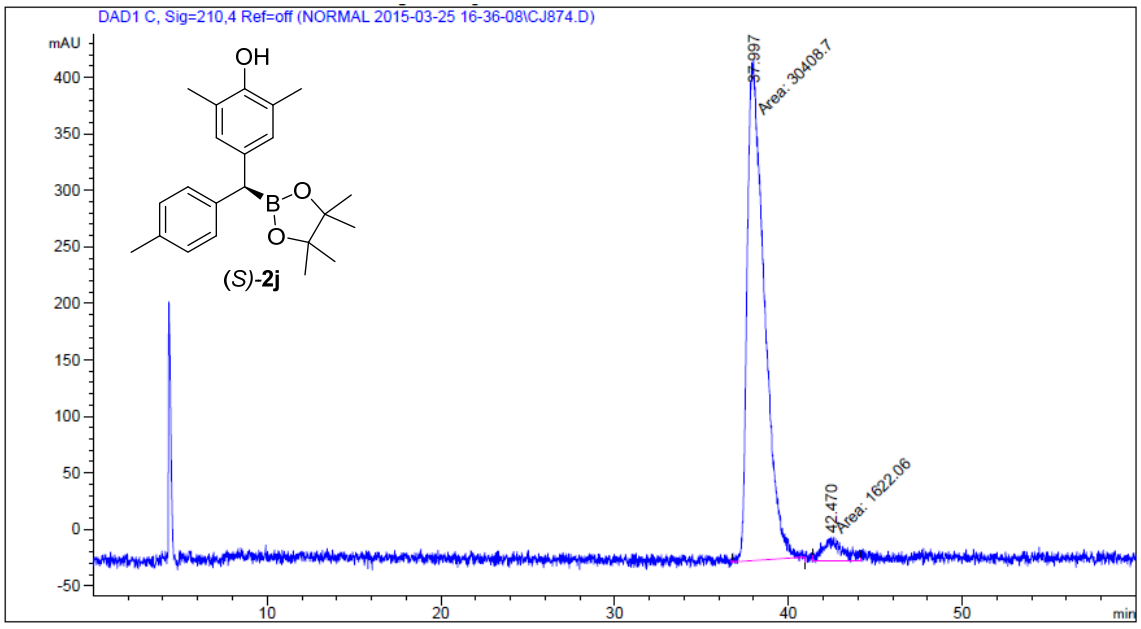




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.429	MM	0.5077	946.40619	31.06891	4.0956
2	31.741	MM	0.6241	2.21616e4	591.84839	95.9044

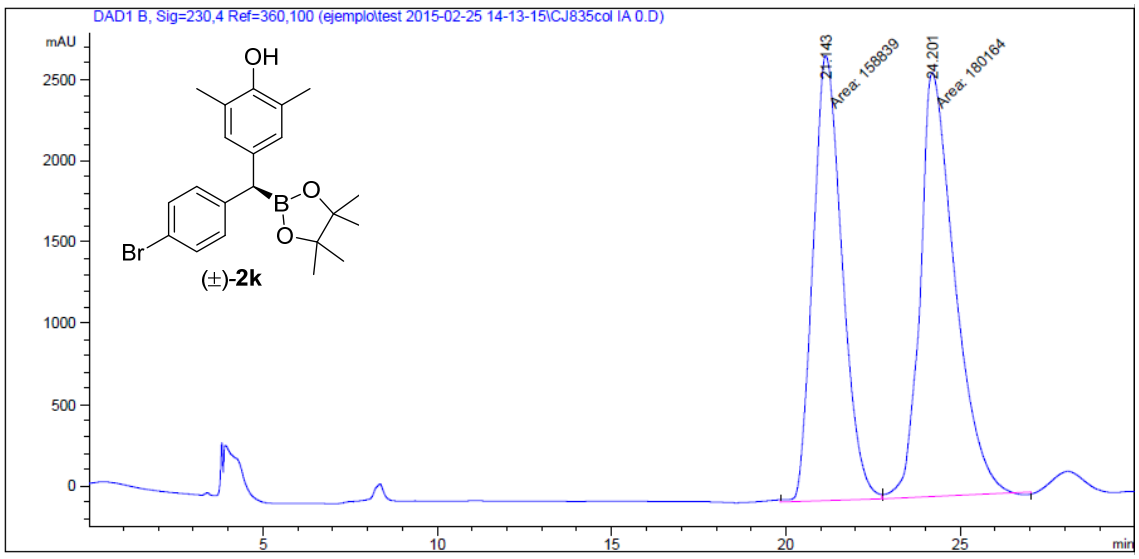
Figure S61: SFC chromatogram of compound **2i**.

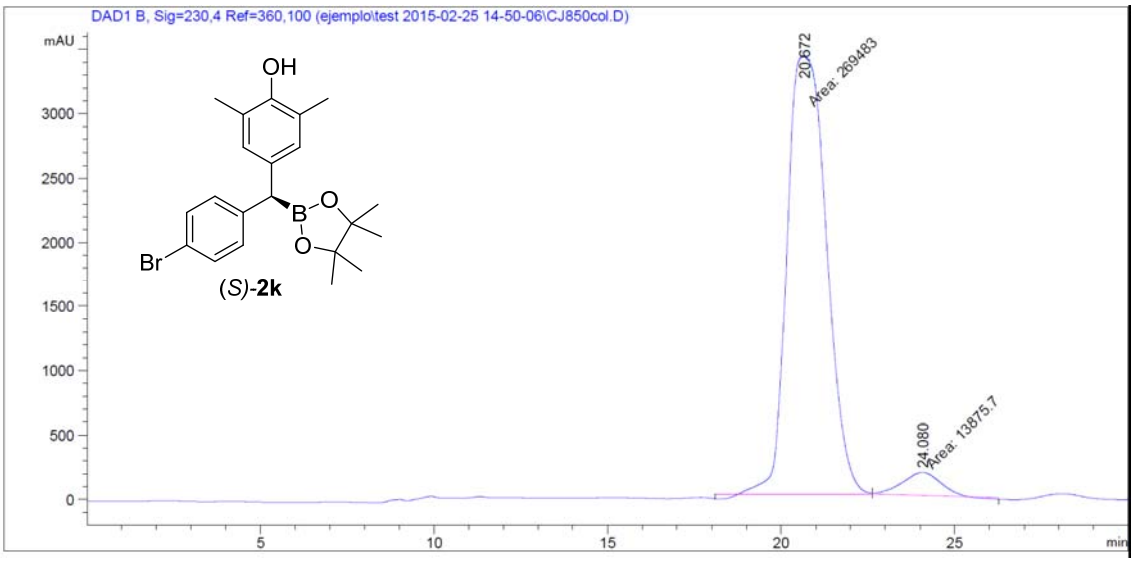




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.997	MM	1.1435	3.04087e4	443.20557	94.9359
2	42.470	MM	1.2396	1622.05969	21.80921	5.0641

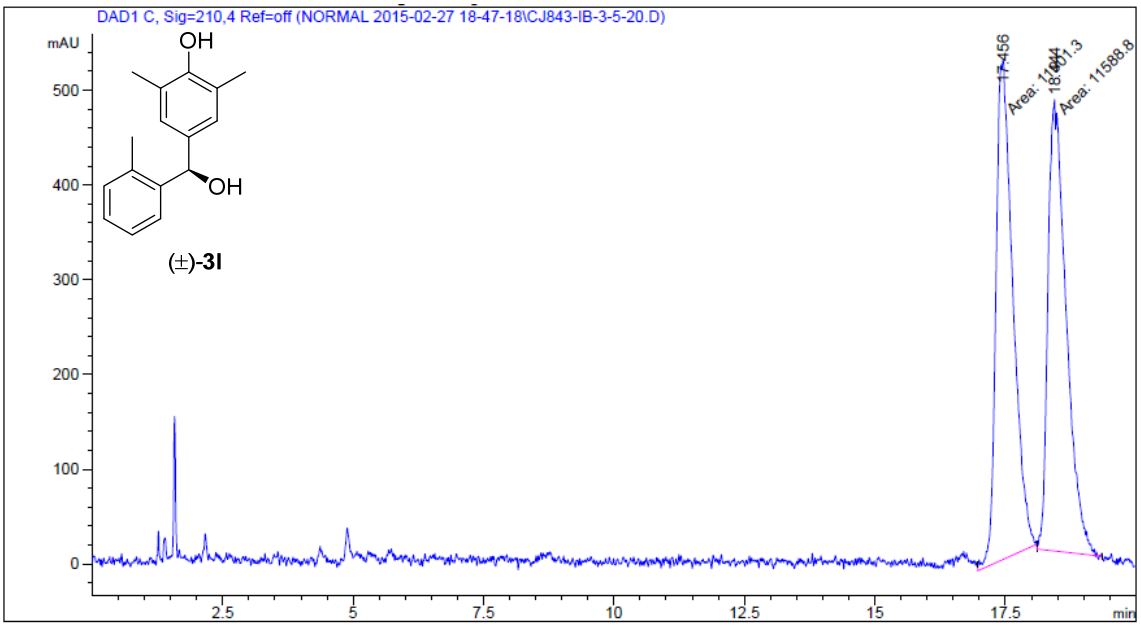
Figure S62: SFC chromatogram of compound **2j**.

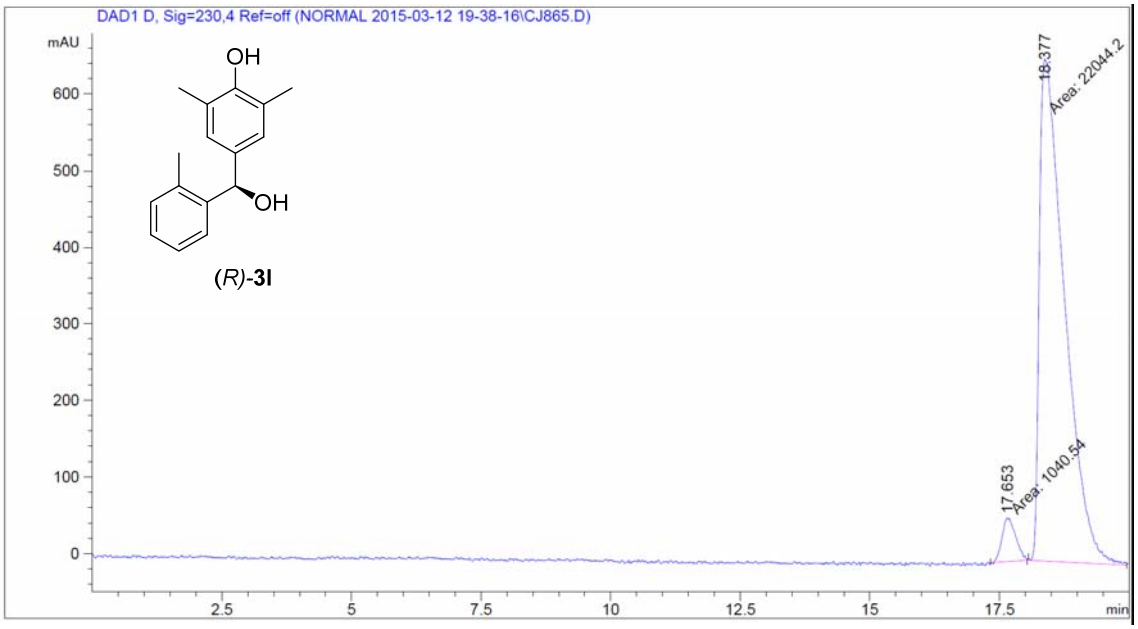




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.672	MM	1.3146	2.69483e5	3416.66016	95.1031
2	24.080	MM	1.2852	1.38757e4	179.94501	4.8969

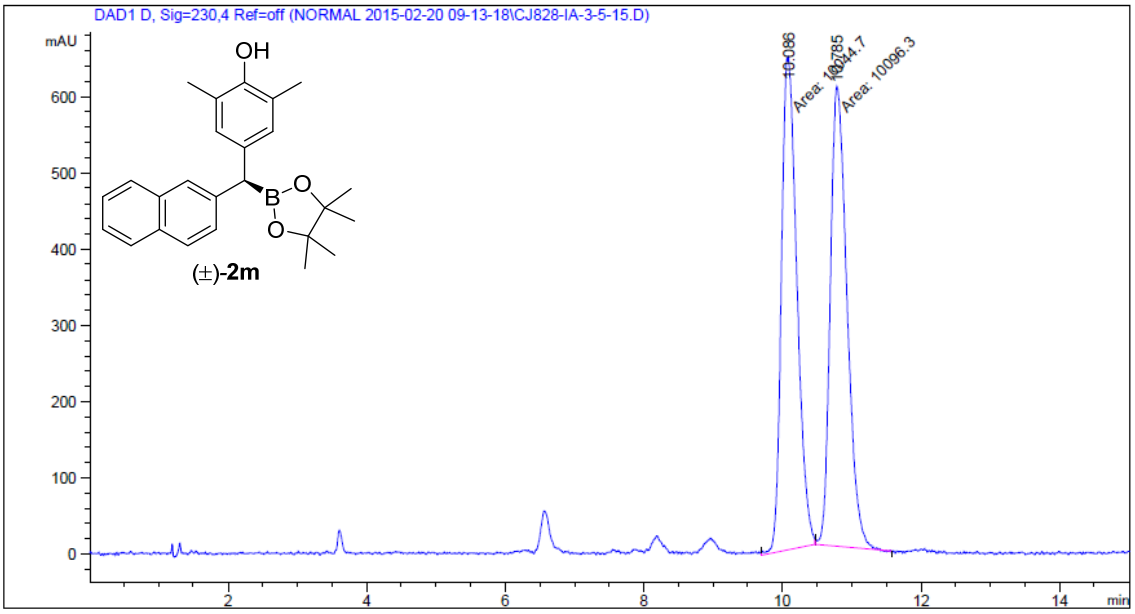
Figure S63: HPLC chromatogram of compound **2k**.

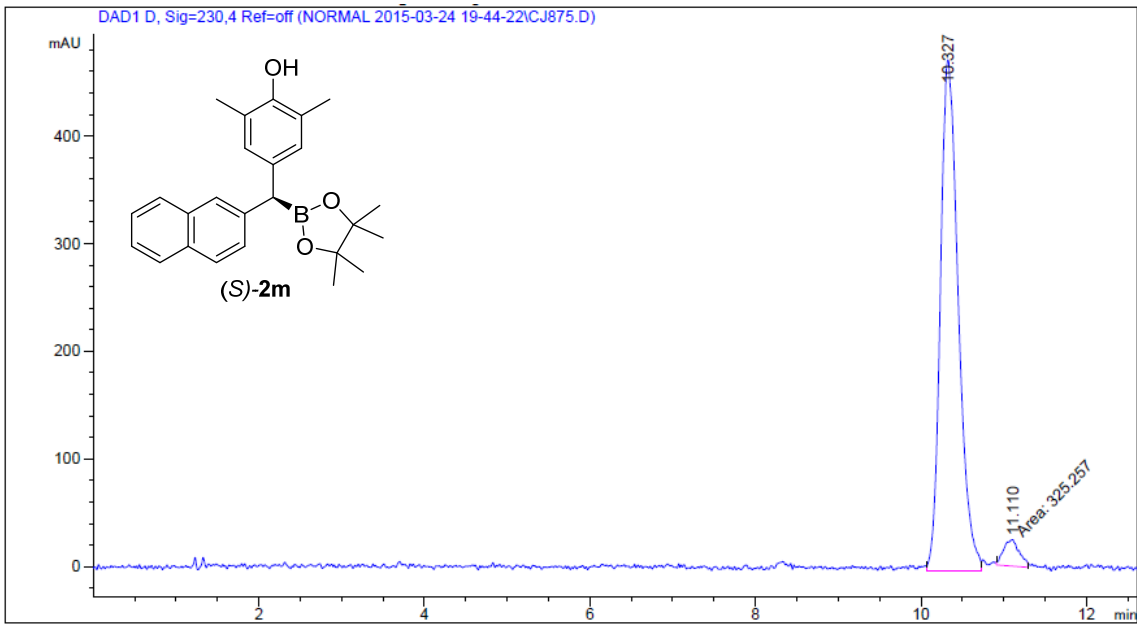




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.653	MM	0.3029	1040.53735	57.25291	4.5075
2	18.377	MM	0.5606	2.20442e4	655.36865	95.4925

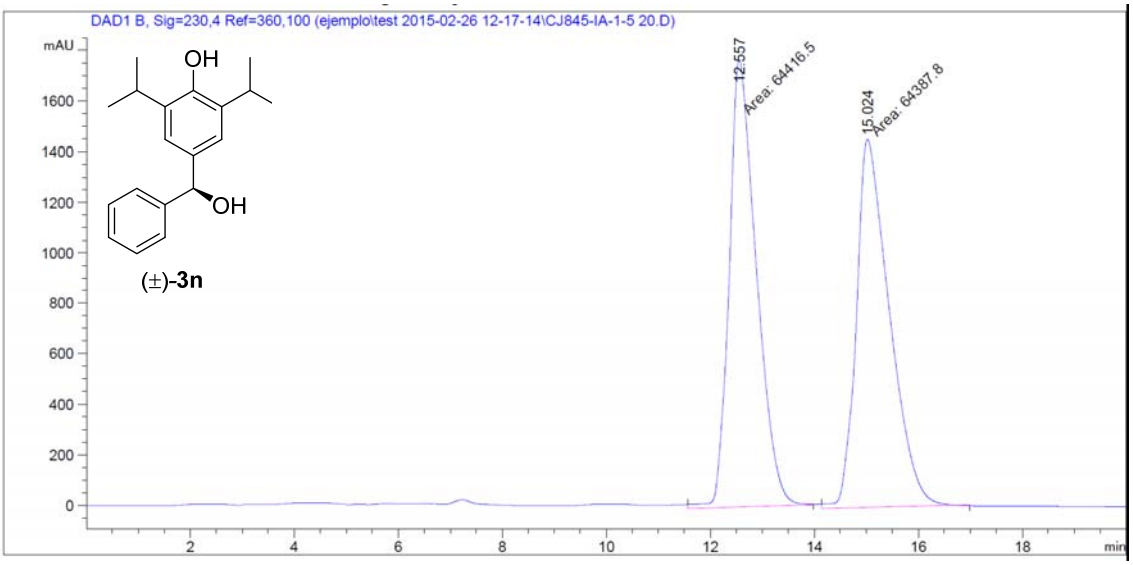
Figure S64: SFC chromatogram of compound **3l**.

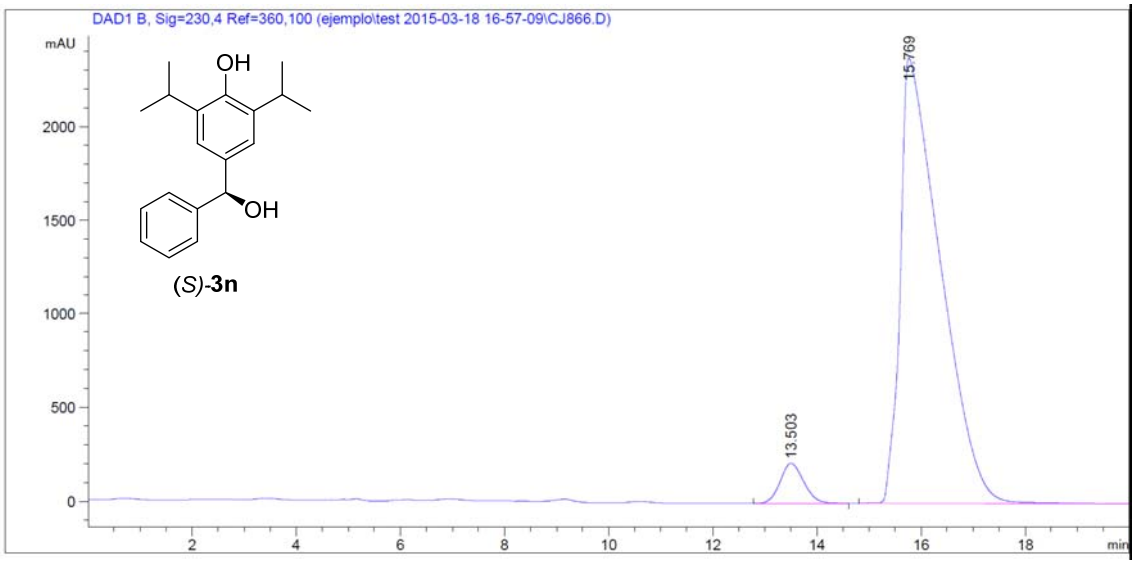




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.327	VV	0.1893	7134.89600	474.75522	95.6401
2	11.110	MM	0.2189	325.25656	24.76440	4.3599

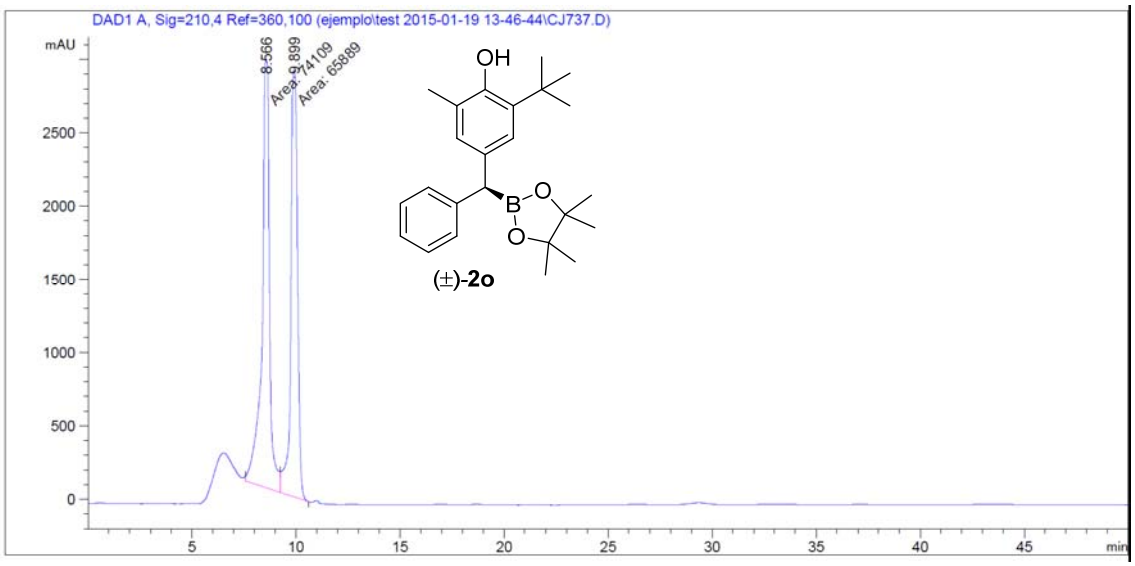
Figure S65: SFC chromatogram of compound **2m**.

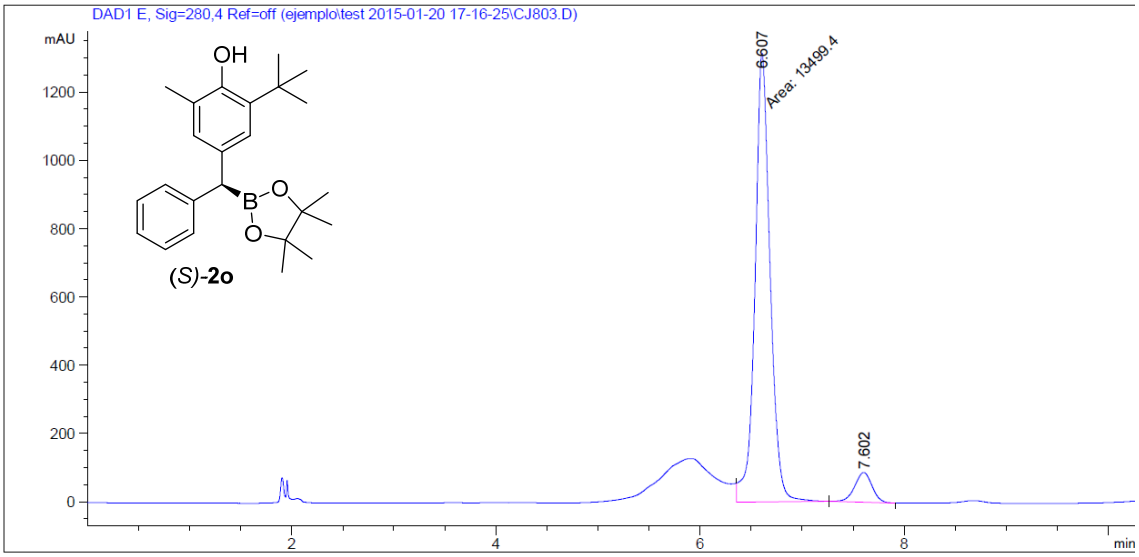




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.503	BB	0.4523	6639.08887	212.02979	4.9577
2	15.769	BBA	0.6273	1.27276e5	2374.75928	95.0423

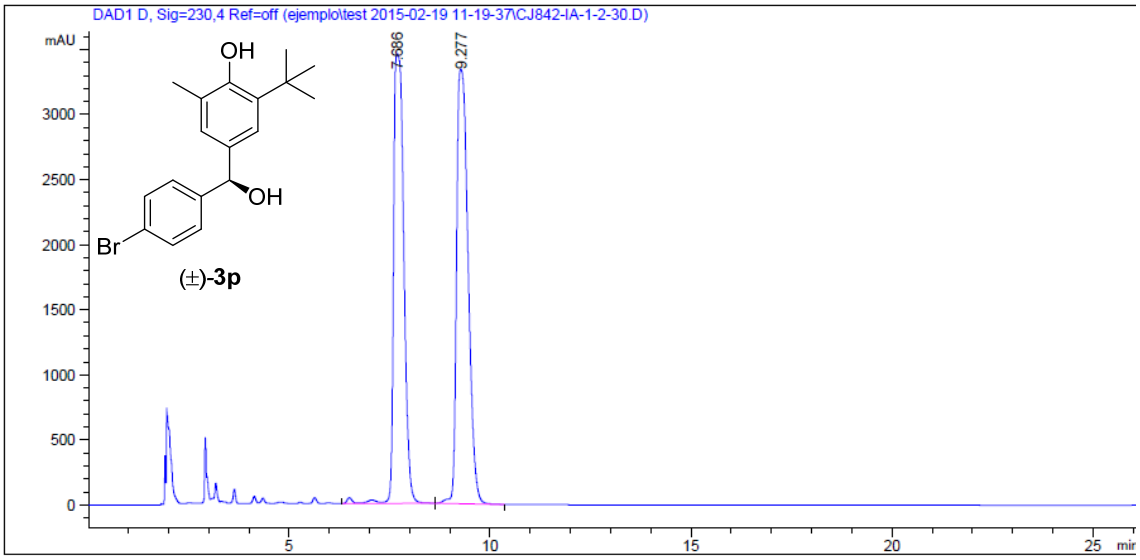
Figure S66: HPLC chromatogram of compound **3n.**

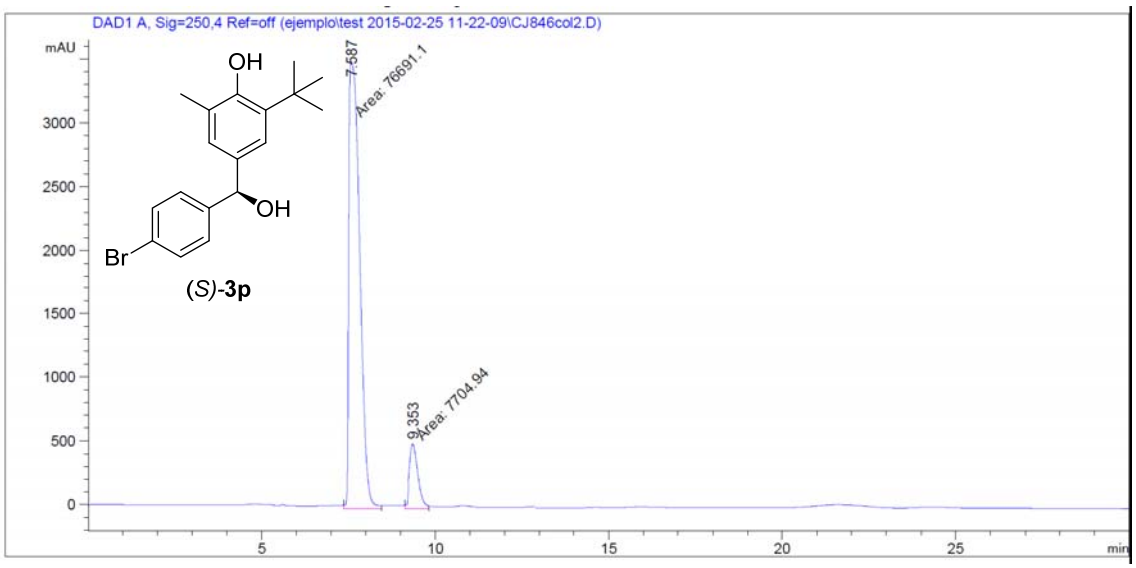




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.607	FM	0.1714	1.34994e4	1312.85229	92.8945
2	7.602	BB	0.1828	1032.57776	87.12360	7.1055

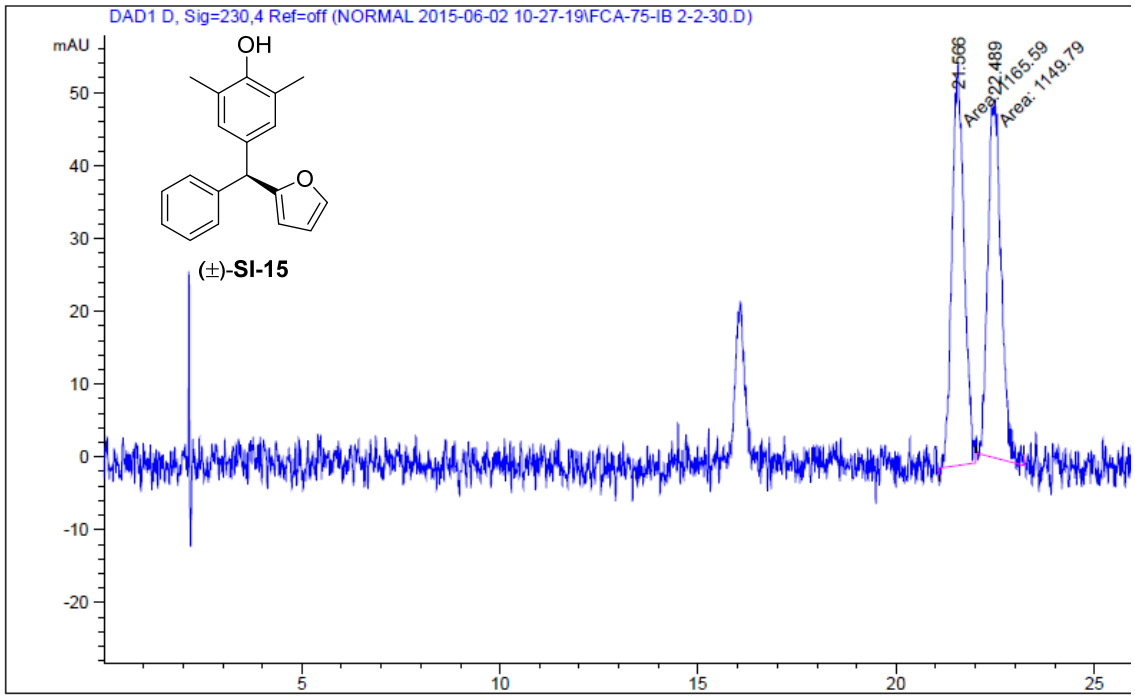
Figure S67: HPLC chromatogram of compound **2o**.

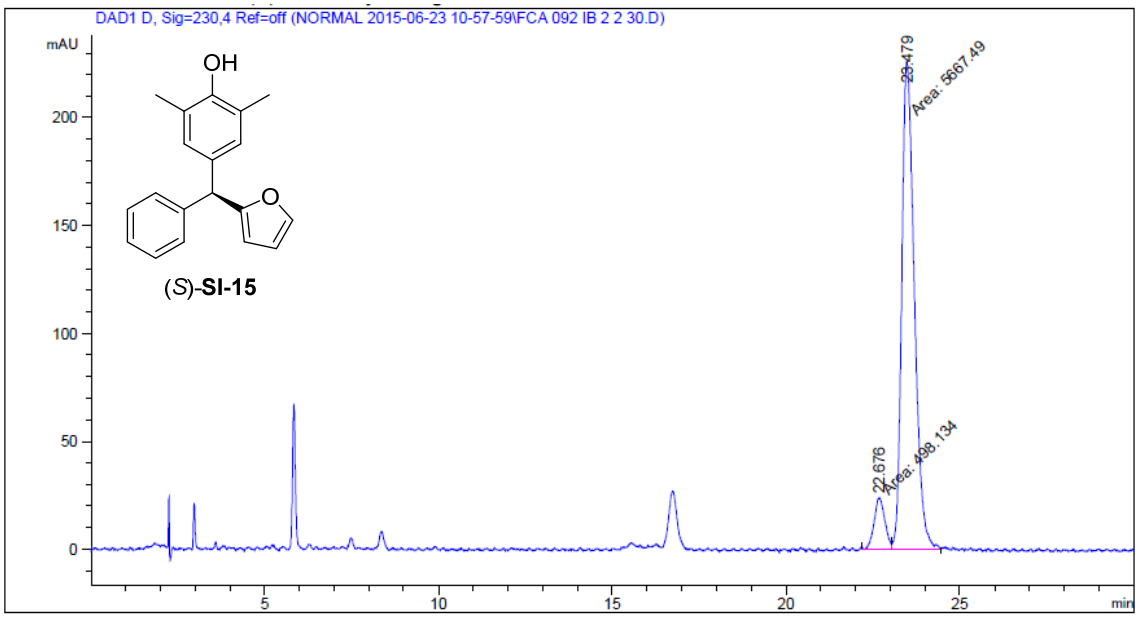




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.587	MM	0.3643	7.66911e4	3508.30688	90.8705
2	9.353	MM	0.2747	7704.94385	467.54684	9.1295

Figure S68: HPLC chromatogram of compound **3p.**





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.676	MF T	0.3526	498.13400	23.54592	8.0792
2	23.479	FM T	0.4178	5667.49414	226.08917	91.9208

Figure S69: SFC chromatogram of compound **SI-15**.

8. X-Ray Data

A clear colorless prismatic-like specimen of $C_{27}H_{38}BBrO_3$, approximate dimensions 0.21 mm x 0.24 mm x 0.30 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

Table S2: Data collection details for 2g.[15]

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°
Phi	34.827	18.00	-16.85	-283.14	30.74
Omega	34.827	-17.00	-55.25	-64.55	54.19
Omega	34.827	3.00	1.55	28.75	-87.66
Omega	34.827	-9.50	-5.74	-14.60	-56.93
Omega	34.827	-17.00	-62.26	-180.02	48.94
Phi	34.827	-14.50	18.90	-118.89	-69.99

Width/°	Frames	Time/s	Wavelength/Å	Voltage/kV	Current/mA	Temperature/K
0.50	611	10.00	0.71073	50	30.0	n/a
0.50	79	10.00	0.71073	50	30.0	n/a
0.50	77	10.00	0.71073	50	30.0	n/a
0.50	85	10.00	0.71073	50	30.0	n/a
0.50	93	10.00	0.71073	50	30.0	n/a
0.50	184	10.00	0.71073	50	30.0	n/a

A total of 1129 frames were collected. The total exposure time was 3.14 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a trigonal unit cell yielded a total of 35365 reflections to a maximum θ angle of 25.33 (0.83 Å resolution), of which 4945 were independent (average redundancy 7.152, completeness = 100.0%, R_{int} = 4.99%, R_{sig} = 3.83%) and 3510 (70.98%) were greater than $2\sigma(F^2)$. The final cell constants of a =13.3911(3) Å, b = 13.3911(3) Å, c = 26.1903(7) Å, volume =4067.28(17) $Å^3$, are based upon the refinement of the XYZ-centroids of 6881 reflections above 20 σ(I) with 4.670 < 2θ < 40.62. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.856. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6552 and 0.7381.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 32 2 1, with Z = 6 for the formula unit, $C_{27}H_{38}BBrO_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 300 variables converged at R1 = 3.88%, for the observed data and wR2 = 12.57% for all data. The goodness-of-fit was 1.093. The largest peak in the final difference electron density synthesis was 0.337 $e^-/Å^3$ and the largest hole was -0.303 $e^-/Å^3$ with an RMS deviation of 0.107 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.228g/cm^3 and F(000), 1584 e^-.

[15] **CCDC 1405406** contains the supplementary crystallographic data. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

Table S3. Sample and crystal data for 2k.

Identification code	**2k**	
Chemical formula	$C_{27}H_{38}BBrO_3$	
Formula weight	501.29	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.21 x 0.24 x 0.30 mm	
Crystal habit	clear colorless prismatic	
Crystal system	trigonal	
Space group	P 32 2 1	
Unit cell dimensions	a = 13.3911(3) Å	α = 90°
	b = 13.3911(3) Å	β = 90°
	c = 26.1903(7) Å	γ = 120°
Volume	4067.28(17) $Å^3$	
Z	6	
Density (calculated)	1.228 Mg/cm^3	
Absorption coefficient	1.540 mm^{-1}	
F(000)	1584	

Table S4. Data collection and structure refinement for 2k.

Theta range for data collection	1.76 to 25.33°	
Index ranges	-15<=h<=15, -16<=k<=16, -31<=l<=31	
Reflections collected	35365	
Independent reflections	4945 [R(int) = 0.0499]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7381 and 0.6552	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4945 / 0 / 300	
Goodness-of-fit on F^2	1.093	
Δ/σ_{max}	0.002	
Final R indices	3510 data; I>2σ(I)	R1 = 0.0388, wR2 = 0.0943
	all data	R1 = 0.0713, wR2 = 0.1257

Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0689P)^2+0.3054P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	-0.0(0)
Largest diff. peak and hole	0.337 and -0.303 eÅ^{-3}
R.M.S. deviation from mean	0.107 eÅ^{-3}

Table S5. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 2k. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Br1	0.60738(5)	0.46624(4)	0.06568(3)	0.0920(2)
B1	0.7201(4)	0.3822(4)	0.97446(16)	0.0428(10)
C1	0.5317(4)	0.3021(3)	0.06518(15)	0.0497(9)
C2	0.4200(4)	0.2421(5)	0.08450(18)	0.0699(13)
C3	0.3624(4)	0.1241(5)	0.0844(2)	0.0767(14)
C4	0.4154(4)	0.0683(4)	0.06597(19)	0.0736(13)
C5	0.5269(3)	0.1287(3)	0.04738(15)	0.0536(10)
C6	0.5883(3)	0.2475(3)	0.04595(12)	0.0389(8)
C7	0.7729(3)	0.2491(3)	0.01789(12)	0.0359(8)
C8	0.7435(3)	0.1711(3)	0.97810(13)	0.0403(8)
C9	0.7993(3)	0.1102(3)	0.96880(14)	0.0431(9)
C10	0.8916(3)	0.1322(3)	0.00135(15)	0.0495(10)
C11	0.9242(3)	0.2098(4)	0.04210(14)	0.0495(10)
C12	0.8630(3)	0.2670(3)	0.04898(13)	0.0426(9)
C13	0.7639(4)	0.0250(3)	0.92377(16)	0.0539(11)
C14	0.8586(5)	0.0730(4)	0.88344(18)	0.0776(15)
C15	0.7401(5)	0.9063(4)	0.9410(2)	0.0900(17)
C16	0.6517(5)	0.0072(5)	0.8989(2)	0.0912(17)
C17	0.0222(4)	0.2296(5)	0.07897(17)	0.0699(14)
C18	0.1343(5)	0.2709(7)	0.0512(2)	0.114(3)
C19	0.9862(7)	0.1139(7)	0.1072(3)	0.131(3)
C20	0.0415(5)	0.3197(6)	0.11907(19)	0.103(2)
C21	0.7111(3)	0.3173(3)	0.02575(12)	0.0371(7)
C22	0.6906(5)	0.4090(4)	0.89142(15)	0.0656(13)
C23	0.7877(4)	0.5221(4)	0.91349(17)	0.0663(13)
C24	0.7379(7)	0.3443(6)	0.8607(2)	0.119(2)
C25	0.5977(5)	0.4163(6)	0.8621(2)	0.106(2)
C26	0.7474(6)	0.6070(4)	0.9273(2)	0.0869(17)
C27	0.8972(5)	0.5838(6)	0.8827(3)	0.118(2)
O1	0.6384(2)	0.3377(2)	0.93709(9)	0.0542(7)
O2	0.8139(2)	0.4845(2)	0.96159(11)	0.0596(7)
O3	0.9516(3)	0.0762(4)	0.99056(13)	0.0844(11)

Table S6. Bond lengths (Å) for 2k

Br1-C1	1.906(4)	B1-O1	1.362(5)
B1-O2	1.359(5)	B1-C21	1.572(6)
C1-C6	1.385(5)	C1-C2	1.392(6)
C2-C3	1.369(7)	C3-C4	1.351(7)
C4-C5	1.383(6)	C5-C6	1.378(5)
C6-C21	1.523(5)	C7-C12	1.374(5)
C7-C8	1.386(5)	C7-C21	1.522(4)
C8-C9	1.374(5)	C9-C10	1.406(5)
C9-C13	1.542(5)	C10-O3	1.375(4)
C10-C11	1.398(5)	C11-C12	1.384(5)
C11-C17	1.542(5)	C13-C14	1.523(6)
C13-C16	1.542(7)	C13-C15	1.524(6)
C17-C18	1.503(7)	C17-C20	1.521(7)
C17-C19	1.559(8)	C22-O1	1.470(5)
C22-C25	1.506(7)	C22-C23	1.533(7)
C22-C24	1.532(7)	C23-O2	1.463(5)
C23-C27	1.508(7)	C23-C26	1.526(7)

Table S7. Bond angles (°) for 2k.

O1-B1-O2	113.4(3)	O1-B1-C21	123.3(4)
O2-B1-C21	123.1(3)	C6-C1-C2	122.8(4)
C6-C1-Br1	119.7(3)	C2-C1-Br1	117.5(3)
C3-C2-C1	119.2(4)	C4-C3-C2	119.4(4)
C3-C4-C5	121.0(5)	C4-C5-C6	122.1(4)
C5-C6-C1	115.5(3)	C5-C6-C21	123.8(3)
C1-C6-C21	120.7(3)	C12-C7-C8	118.1(3)
C12-C7-C21	120.6(3)	C8-C7-C21	121.3(3)
C9-C8-C7	123.1(3)	C8-C9-C10	116.7(3)
C8-C9-C13	121.2(3)	C10-C9-C13	122.1(3)
O3-C10-C11	120.8(3)	O3-C10-C9	116.9(3)
C11-C10-C9	122.2(3)	C12-C11-C10	117.3(3)
C12-C11-C17	120.8(3)	C10-C11-C17	121.9(3)
C7-C12-C11	122.5(3)	C14-C13-C16	108.2(4)
C14-C13-C15	110.0(4)	C16-C13-C15	106.5(4)
C14-C13-C9	109.6(3)	C16-C13-C9	110.6(3)
C15-C13-C9	111.9(4)	C18-C17-C20	107.4(5)
C18-C17-C11	111.6(4)	C20-C17-C11	111.2(3)
C18-C17-C19	110.5(5)	C20-C17-C19	107.9(5)
C11-C17-C19	108.2(4)	C7-C21-C6	115.0(3)
C7-C21-B1	107.6(3)	C6-C21-B1	113.4(3)
O1-C22-C25	108.5(4)	O1-C22-C23	103.1(3)
C25-C22-C23	116.6(4)	O1-C22-C24	104.9(4)
C25-C22-C24	111.0(5)	C23-C22-C24	111.7(5)

O2-C23-C27	108.4(4)	O2-C23-C26	106.7(4)
C27-C23-C26	109.2(4)	O2-C23-C22	102.4(3)
C27-C23-C22	116.8(5)	C26-C23-C22	112.6(4)
B1-O1-C22	106.5(3)	B1-O2-C23	107.5(3)

Table S8. Anisotropic atomic displacement parameters (Å^2) for 2k.

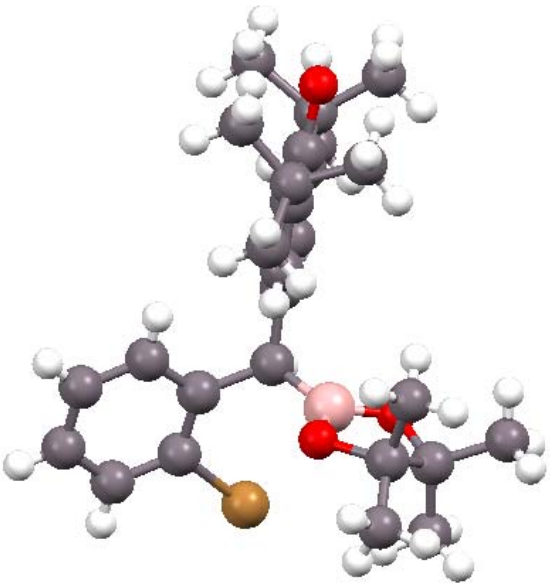
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

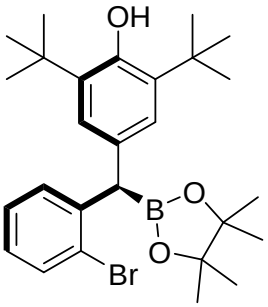
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	0.0949(4)	0.0625(3)	0.1358(5)	0.0029(3)	0.0423(4)	0.0522(3)
B1	0.044(2)	0.054(3)	0.044(2)	0.004(2)	0.007(2)	0.035(2)
C1	0.051(2)	0.057(2)	0.049(2)	0.0031(19)	0.0065(19)	0.034(2)
C2	0.058(3)	0.102(4)	0.067(3)	0.000(3)	0.015(2)	0.052(3)
C3	0.045(2)	0.078(4)	0.088(4)	0.009(3)	0.018(2)	0.017(3)
C4	0.062(3)	0.062(3)	0.084(3)	0.006(3)	0.015(3)	0.020(3)
C5	0.051(2)	0.049(2)	0.057(2)	0.0016(19)	0.009(2)	0.021(2)
C6	0.0415(19)	0.052(2)	0.0308(18)	0.0013(16)	-0.0026(15)	0.0290(18)
C7	0.0382(18)	0.0417(19)	0.0348(19)	0.0017(15)	0.0021(15)	0.0251(16)
C8	0.040(2)	0.044(2)	0.039(2)	-0.0033(16)	-0.0034(16)	0.0236(17)
C9	0.052(2)	0.048(2)	0.035(2)	-0.0022(17)	0.0006(17)	0.0291(19)
C10	0.056(2)	0.069(3)	0.044(2)	-0.0057(19)	-0.0034(18)	0.046(2)
C11	0.053(2)	0.073(3)	0.040(2)	-0.005(2)	-0.0040(18)	0.045(2)
C12	0.047(2)	0.058(2)	0.033(2)	-0.0080(17)	-0.0024(16)	0.0337(19)
C13	0.061(3)	0.044(2)	0.057(3)	-0.013(2)	-0.004(2)	0.027(2)
C14	0.096(4)	0.069(3)	0.060(3)	-0.023(2)	0.010(3)	0.035(3)
C15	0.112(5)	0.049(3)	0.105(4)	-0.008(3)	0.001(3)	0.037(3)
C16	0.093(4)	0.092(4)	0.094(4)	-0.055(3)	-0.047(3)	0.050(3)
C17	0.075(3)	0.115(4)	0.054(3)	-0.021(3)	-0.025(3)	0.073(3)
C18	0.070(3)	0.209(8)	0.093(4)	-0.053(4)	-0.028(3)	0.092(4)
C19	0.180(7)	0.169(7)	0.102(5)	-0.010(5)	-0.070(5)	0.130(6)
C20	0.102(4)	0.187(7)	0.064(3)	-0.060(4)	-0.049(3)	0.106(5)
C21	0.0393(18)	0.045(2)	0.0350(19)	-0.0019(16)	-0.0003(14)	0.0267(17)
C22	0.100(4)	0.076(3)	0.038(2)	0.012(2)	0.005(2)	0.057(3)
C23	0.070(3)	0.078(3)	0.055(3)	0.028(2)	0.010(2)	0.040(3)
C24	0.211(8)	0.135(6)	0.058(3)	0.010(4)	0.032(4)	0.122(6)
C25	0.116(5)	0.107(5)	0.090(4)	0.021(3)	-0.035(4)	0.052(4)
C26	0.127(5)	0.075(3)	0.081(4)	0.009(3)	-0.002(3)	0.068(3)
C27	0.098(4)	0.134(6)	0.118(5)	0.072(4)	0.054(4)	0.054(4)
O1	0.0595(17)	0.0620(15)	0.0428(15)	0.0072(13)	-0.0039(14)	0.0316(14)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	0.0477(16)	0.0666(18)	0.0619(19)	0.0228(15)	0.0033(13)	0.0266(15)
O3	0.102(3)	0.118(3)	0.088(2)	-0.033(2)	-0.023(2)	0.095(2)

Table S9. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 2k.

	x/a	y/b	z/c	U(eq)
H2	0.3849	0.2818	1.0973	0.084
H3A	0.2875	0.0827	1.0969	0.092
H4	0.3763	-0.0118	1.0658	0.088
H5	0.5615	0.0878	1.0355	0.064
H8	0.6832	0.1593	0.9567	0.048
H12	0.8837	0.3194	1.0757	0.051
H14A	0.8746	0.1487	0.8735	0.116
H14B	0.8336	0.0232	0.8542	0.116
H14C	0.9271	0.0775	0.8972	0.116
H15A	0.8049	-0.0859	0.9599	0.135
H15B	0.7276	-0.1414	0.9116	0.135
H15C	0.6726	-0.1285	0.9622	0.135
H16A	0.5923	-0.0183	0.9243	0.137
H16B	0.6283	-0.0499	0.8725	0.137
H16C	0.6649	0.0787	0.8845	0.137
H18A	1.1243	0.2169	1.0248	0.171
H18B	1.1920	0.2770	1.0748	0.171
H18C	1.1584	0.3450	1.0363	0.171
H19A	0.9613	0.0528	1.0826	0.197
H19B	0.9243	0.0972	1.1304	0.197
H19C	1.0509	0.1206	1.1259	0.197
H20A	1.1039	0.3316	1.1410	0.154
H20B	0.9726	0.2935	1.1390	0.154
H20C	1.0601	0.3909	1.1025	0.154
H21	0.7553	0.3766	1.0514	0.045
H24A	0.7985	0.3427	0.8797	0.178
H24B	0.7679	0.3829	0.8287	0.178
H24C	0.6771	0.2668	0.8544	0.178
H25A	0.5428	0.3413	0.8494	0.159
H25B	0.6316	0.4687	0.8340	0.159
H25C	0.5594	0.4436	0.8843	0.159
H26A	0.6742	0.5667	0.9444	0.13
H26B	0.7395	0.6421	0.8967	0.13
H26C	0.8029	0.6656	0.9494	0.13
H27A	0.9512	0.6534	0.8999	0.178
H27B	0.8802	0.6025	0.8496	0.178
H27C	0.9300	0.5348	0.8788	0.178
H3	0.9931	0.0826	1.0148	0.127





2g

Figure S70. X-ray Structure of (*R*)-**2g**

9. DFT Calculations

Calculations were performed with the GAUSSIAN 09 series of programs.[16] The geometries of all complexes were optimized at the DFT level using the B3LYP hybrid functional,[17] using the standard 6-31G* basis set for C, H, P, B and O. The LANL2DZ basis set, which includes the relativistic effective core potential (ECP) of Hay and Wadt and employs a split-valence (double-ζ) basis set, was used for Cu.[18] Harmonic frequencies were calculated at the same level of theory to characterize the stationary points and to determine the Free Energies (ΔG). The starting approximate geometries for the transition states (TS) were graphically located. Intrinsic reaction coordinate (IRC) studies using the default step

[16] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[17] a) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623-11627; b) W. Kohn, A. D. Becke, R. G. Parr, *J. Phys. Chem.* **1996**, *100*, 12974-12980; c) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270-283; d) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 284-298; e) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299-310.

[18] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648- 5653; b) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098-3100; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785- 789.

size were performed to confirm the relation of the transition states with the corresponding minima.

1i (Scheme 4, main manuscript)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.785545	-1.069302	0.111739
2	6	0	-1.508255	-1.518572	0.099513
3	6	0	-3.051140	0.382591	-0.020568
4	6	0	-0.357437	-0.633231	-0.007849
5	6	0	-3.981850	-1.966315	0.254570
6	8	0	-4.203552	0.825726	-0.004593
7	6	0	-1.887362	1.285670	-0.202819
8	6	0	0.895994	-1.186740	0.036272
9	6	0	-0.628167	0.784195	-0.190869
10	6	0	-2.194414	2.740176	-0.417829
11	6	0	2.210638	-0.548538	0.057106
12	6	0	3.295513	-1.232660	-0.531215
13	6	0	2.470664	0.689815	0.680640
14	6	0	4.572786	-0.680458	-0.546024
15	6	0	3.752212	1.236205	0.673417
16	6	0	4.805786	0.560985	0.052264
17	1	0	-1.307886	-2.584031	0.203566
18	1	0	-4.569942	-1.691927	1.138195
19	1	0	-3.685673	-3.016533	0.339086
20	1	0	-4.654920	-1.855511	-0.603672
21	1	0	0.931644	-2.276538	0.038436
22	1	0	0.211554	1.449015	-0.367064
23	1	0	-1.280248	3.326023	-0.554883
24	1	0	-2.753452	3.147084	0.432951
25	1	0	-2.837975	2.876186	-1.294868
26	1	0	3.119926	-2.200553	-0.994569
27	1	0	1.674283	1.201163	1.210367
28	1	0	5.388885	-1.220465	-1.018269
29	1	0	3.931868	2.187084	1.167715
30	1	0	5.803804	0.990284	0.049663

Zero-point correction= 0.247160
(Hartree/Particle)
Thermal correction to Energy= 0.261379
Thermal correction to Enthalpy= 0.262323
Thermal correction to Gibbs Free Energy= 0.205571
Sum of electronic and zero-point Energies= -654.981276
Sum of electronic and thermal Energies= -654.967057
Sum of electronic and thermal Enthalpies= -654.966112
Sum of electronic and thermal Free Energies= -655.022865

D (Scheme 4, main manuscript)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.306255	1.214765	-0.626671
2	8	0	4.079536	-0.794274	0.422675
3	6	0	5.591954	0.957098	-0.003388
4	6	0	5.510645	-0.580818	0.307650
5	6	0	6.697310	1.370116	-0.976299
6	6	0	5.659209	1.830620	1.259339
7	6	0	6.001241	-1.465475	-0.849301
8	6	0	6.177009	-1.020022	1.612442
9	5	0	3.395792	0.221430	-0.254602
10	29	0	1.390909	0.195382	-0.589418
11	15	0	-0.334177	1.936484	-0.405008
12	6	0	0.388137	3.604200	-0.047326
13	6	0	1.786500	3.729746	-0.055081
14	6	0	2.383027	4.969188	0.193884
15	6	0	-0.397299	4.742404	0.202949
16	6	0	-1.801610	2.373302	-1.439687
17	6	0	1.595574	6.091930	0.448198
18	6	0	0.202371	5.976318	0.451131
19	6	0	-1.636890	2.344122	-2.833304
20	6	0	-3.039986	2.771936	-0.913013
21	6	0	-4.084641	3.139516	-1.763186
22	6	0	-1.011721	1.361434	1.221363
23	6	0	-2.680103	2.716915	-3.682171
24	6	0	-3.906901	3.116030	-3.148294
25	6	0	-0.517237	1.949774	2.394876
26	6	0	-1.847654	0.199272	1.308601
27	6	0	-0.806632	1.459286	3.679913
28	6	0	-2.118514	-0.251076	2.591699
29	6	0	-1.609864	0.342656	3.744834
30	8	0	-2.067826	-0.325746	4.852287
31	8	0	-2.927568	-1.307028	2.945229
32	6	0	-2.698747	-1.506038	4.342529
33	15	0	-0.102103	-1.712189	-0.614875
34	6	0	0.274382	-2.798916	-2.057831
35	6	0	0.144293	-4.195965	-2.034983
36	6	0	0.461549	-4.954393	-3.163536
37	6	0	0.743628	-2.180641	-3.228397
38	6	0	0.121197	-2.819093	0.843172
39	6	0	0.912211	-4.327777	-4.327486
40	6	0	1.053182	-2.938738	-4.358234
41	6	0	1.400049	-2.870008	1.425796
42	6	0	-0.912374	-3.599300	1.384624
43	6	0	-0.669953	-4.425474	2.484858
44	6	0	-1.927355	-1.440957	-0.720215
45	6	0	1.636003	-3.701954	2.521897
46	6	0	0.604856	-4.479507	3.054039
47	6	0	-2.702820	-2.080256	-1.696875
48	6	0	-2.532573	-0.507024	0.177425
49	6	0	-4.084189	-1.858566	-1.835541
50	6	0	-3.899581	-0.333753	0.030639
51	6	0	-4.656823	-0.977156	-0.945061
52	8	0	-5.966040	-0.575848	-0.859244
53	8	0	-4.714668	0.497887	0.763909
54	6	0	-6.047243	0.220503	0.327382

55	1	0	6.595957	0.864752	-1.939495
56	1	0	7.690015	1.146428	-0.566232
57	1	0	6.642443	2.449116	-1.156882
58	1	0	4.868007	1.561367	1.965734
59	1	0	5.513523	2.877840	0.973776
60	1	0	6.626821	1.745291	1.767143
61	1	0	5.723204	-2.504105	-0.642495
62	1	0	7.089668	-1.418151	-0.970584
63	1	0	5.530398	-1.174107	-1.793119
64	1	0	6.037644	-2.097742	1.751276
65	1	0	5.743933	-0.511658	2.477316
66	1	0	7.255473	-0.820114	1.593446
67	1	0	2.408431	2.861073	-0.254922
68	1	0	3.466660	5.051669	0.182303
69	1	0	-1.480416	4.668888	0.195013
70	1	0	2.061811	7.055466	0.638037
71	1	0	-0.417492	6.848665	0.642302
72	1	0	-0.685240	2.028497	-3.254571
73	1	0	-3.195611	2.778482	0.161539
74	1	0	-5.038067	3.449261	-1.342010
75	1	0	-2.535849	2.690566	-4.759021
76	1	0	-4.721682	3.402694	-3.807891
77	1	0	0.124433	2.819492	2.316128
78	1	0	-0.413795	1.934571	4.571969
79	1	0	-3.655362	-1.653078	4.849975
80	1	0	-2.032366	-2.368543	4.483145
81	1	0	-0.197405	-4.692681	-1.131780
82	1	0	0.359929	-6.036121	-3.131426
83	1	0	0.880758	-1.102071	-3.246819
84	1	0	1.161702	-4.920520	-5.203626
85	1	0	1.416043	-2.445832	-5.256222
86	1	0	2.206589	-2.257660	1.028206
87	1	0	-1.908034	-3.556307	0.953576
88	1	0	-1.476280	-5.031105	2.891809
89	1	0	2.628037	-3.734062	2.964477
90	1	0	0.792429	-5.123377	3.909665
91	1	0	-2.227647	-2.783101	-2.371144
92	1	0	-4.669213	-2.360359	-2.598493
93	1	0	-6.580344	-0.339481	1.108544
94	1	0	-6.559448	1.159589	0.100065

Zero-point correction= 0.743302
(Hartree/Particle)
Thermal correction to Energy= 0.793201
Thermal correction to Enthalpy= 0.794145
Thermal correction to Gibbs Free Energy= 0.654149
Sum of electronic and zero-point Energies= -3055.114823
Sum of electronic and thermal Energies= -3055.064924
Sum of electronic and thermal Enthalpies= -3055.063980
Sum of electronic and thermal Free Energies= -3055.203976

$\mathbf{I}_S$ (Scheme 4, main manuscript)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.715523	-0.696650	1.712311
2	6	0	-0.418054	-0.150201	3.062800
3	6	0	-1.089782	1.071989	2.885107
4	6	0	-1.936731	1.568749	3.875531
5	6	0	-0.647896	-0.882553	4.236028
6	6	0	1.235130	-2.401769	2.187777
7	6	0	-2.152623	0.834655	5.045912
8	6	0	-1.514997	-0.394589	5.217548
9	6	0	0.609272	-3.485844	1.549204
10	6	0	2.234442	-2.650513	3.142827
11	6	0	2.590733	-3.960907	3.466628
12	6	0	2.230218	0.325397	2.013059
13	6	0	0.968620	-4.794781	1.879401
14	6	0	1.956192	-5.035534	2.836559
15	6	0	2.335582	1.161469	3.133142
16	6	0	3.285673	0.283486	1.051394
17	6	0	3.454825	1.978712	3.369419
18	6	0	4.381752	1.085873	1.325015
19	6	0	4.468371	1.916450	2.438640
20	8	0	5.653606	2.605389	2.417075
21	8	0	5.518085	1.225106	0.562421
22	6	0	6.387601	2.085249	1.303063
23	15	0	1.303552	0.767468	-1.581445
24	6	0	1.046382	0.900732	-3.412757
25	6	0	1.930786	1.584249	-4.263865
26	6	0	1.676034	1.668334	-5.632434
27	6	0	-0.103400	0.311283	-3.962288
28	6	0	1.977805	2.434472	-1.166752
29	6	0	0.531924	1.073876	-6.171751
30	6	0	-0.355601	0.397211	-5.334700
31	6	0	1.055613	3.385819	-0.703913
32	6	0	3.315854	2.819370	-1.345038
33	6	0	3.711695	4.131256	-1.076284
34	6	0	2.700520	-0.434912	-1.400580
35	6	0	1.446563	4.702090	-0.451245
36	6	0	2.779074	5.075066	-0.636649
37	6	0	2.950644	-1.330497	-2.451010
38	6	0	3.355066	-0.621629	-0.139969
39	6	0	3.827780	-2.422585	-2.334649
40	6	0	4.214412	-1.706868	-0.061119
41	6	0	4.440617	-2.592013	-1.112747
42	8	0	5.348161	-3.547196	-0.728076
43	8	0	4.988194	-2.075092	1.015774
44	6	0	5.499859	-3.368294	0.684969
45	1	0	-0.940871	1.643770	1.972517
46	1	0	-2.430610	2.525521	3.728002
47	1	0	-0.147064	-1.833262	4.388669
48	1	0	-2.814835	1.219225	5.817330
49	1	0	-1.683379	-0.974893	6.121061
50	1	0	-0.144786	-3.309906	0.785902
51	1	0	2.739001	-1.819507	3.626897
52	1	0	3.361550	-4.141959	4.211791
53	1	0	0.478738	-5.625512	1.378564
54	1	0	2.233963	-6.055724	3.089707

55	1	0	1.529374	1.182305	3.856494
56	1	0	3.517867	2.622026	4.240176
57	1	0	7.248726	1.509653	1.668775
58	1	0	6.713074	2.912424	0.664859
59	1	0	2.815854	2.063613	-3.857638
60	1	0	2.368813	2.202765	-6.277460
61	1	0	-0.801314	-0.213813	-3.315988
62	1	0	0.333006	1.143946	-7.238129
63	1	0	-1.251683	-0.062316	-5.743952
64	1	0	0.019330	3.098428	-0.549692
65	1	0	4.051394	2.093323	-1.678717
66	1	0	4.750348	4.419932	-1.219786
67	1	0	0.702964	5.422589	-0.122836
68	1	0	3.091650	6.097048	-0.438876
69	1	0	2.441418	-1.186286	-3.396638
70	1	0	4.007471	-3.098588	-3.163400
71	1	0	6.560245	-3.416959	0.944156
72	1	0	4.920205	-4.136048	1.216722
73	8	0	-2.715633	-1.616789	-2.266144
74	8	0	-1.594927	-3.290633	-1.201092
75	6	0	-3.402775	-2.841880	-2.642572
76	6	0	-2.367915	-3.952623	-2.233813
77	6	0	-4.707289	-2.899413	-1.834747
78	6	0	-3.729229	-2.772744	-4.135802
79	6	0	-2.975443	-5.227612	-1.646406
80	6	0	-1.384909	-4.317990	-3.357640
81	5	0	-1.700882	-1.902091	-1.339618
82	29	0	-0.383365	-0.633116	-0.453814
83	6	0	-2.761250	3.393548	-1.531311
84	6	0	-3.401841	2.213265	-1.339306
85	6	0	-2.770341	4.409926	-0.455918
86	6	0	-4.155718	1.910442	-0.131425
87	6	0	-2.029090	3.740683	-2.797887
88	8	0	-2.118681	5.458853	-0.552779
89	6	0	-3.600216	4.141016	0.744257
90	6	0	-4.780788	0.693371	-0.047609
91	6	0	-4.247268	2.955826	0.874196
92	6	0	-3.688303	5.245174	1.760509
93	6	0	-5.571326	0.121641	1.043379
94	6	0	-5.253356	0.289312	2.406120
95	6	0	-6.684866	-0.680260	0.716221
96	6	0	-6.042232	-0.291163	3.397531
97	6	0	-7.480111	-1.246015	1.708859
98	6	0	-7.164170	-1.049772	3.056115
99	1	0	-4.508005	-2.898484	-0.759104
100	1	0	-5.303448	-3.785644	-2.080576
101	1	0	-5.308775	-2.014528	-2.069129
102	1	0	-2.832823	-2.607426	-4.738578
103	1	0	-4.417862	-1.941487	-4.322975
104	1	0	-4.213604	-3.695033	-4.479339
105	1	0	-2.173170	-5.916451	-1.360342
106	1	0	-3.612441	-5.738807	-2.378644
107	1	0	-3.569791	-5.017262	-0.753920
108	1	0	-0.583635	-4.934921	-2.938093
109	1	0	-0.926066	-3.421615	-3.786038
110	1	0	-1.869405	-4.883446	-4.162154
111	1	0	-3.357773	1.436596	-2.100374
112	1	0	-2.012819	2.895474	-3.491972
113	1	0	-0.998739	4.046203	-2.590711
114	1	0	-2.506851	4.595254	-3.294024
115	1	0	-4.695807	0.057526	-0.927299

116	1	0	-4.882907	2.784778	1.737947
117	1	0	-2.692667	5.508883	2.136340
118	1	0	-4.324197	4.960979	2.605203
119	1	0	-4.090736	6.159834	1.308993
120	1	0	-4.354539	0.827687	2.684728
121	1	0	-6.931310	-0.840280	-0.330146
122	1	0	-5.767784	-0.162944	4.441199
123	1	0	-8.342045	-1.847295	1.432306
124	1	0	-7.776945	-1.500126	3.832309

Zero-point correction= 0.991469
(Hartree/Particle)
Thermal correction to Energy= 1.057798
Thermal correction to Enthalpy= 1.058742
Thermal correction to Gibbs Free Energy= 0.879965
Sum of electronic and zero-point Energies= -3710.100368
Sum of electronic and thermal Energies= -3710.034039
Sum of electronic and thermal Enthalpies= -3710.033095
Sum of electronic and thermal Free Energies= -3710.211873

$\underline{\mathbf{I}_R}$ (Scheme 4, main manuscript)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.259557	-2.906232	-1.321749
2	8	0	-1.422793	-3.604383	0.677878
3	6	0	-2.714825	-4.276656	-1.165435
4	6	0	-2.504084	-4.521983	0.370522
5	6	0	-4.161989	-4.374016	-1.649010
6	6	0	-1.812524	-5.151066	-2.051072
7	6	0	-3.707272	-4.096778	1.226861
8	6	0	-2.068314	-5.936727	0.753995
9	5	0	-1.378788	-2.585677	-0.280743
10	29	0	-0.115573	-0.994932	-0.131439
11	15	0	0.972018	0.455336	-1.796455
12	6	0	0.295237	0.167613	-3.498206
13	6	0	-0.679595	-0.833140	-3.649763
14	6	0	-1.235203	-1.092234	-4.905315
15	6	0	0.684803	0.911537	-4.624474
16	6	0	1.391046	2.252497	-1.823951
17	6	0	-0.837260	-0.352176	-6.019118
18	6	0	0.122453	0.652973	-5.874674
19	6	0	0.479398	3.139453	-1.231238
20	6	0	2.538749	2.775437	-2.441782
21	6	0	2.752957	4.154801	-2.477651
22	6	0	2.598427	-0.434941	-1.780461
23	6	0	0.690573	4.519953	-1.267126
24	6	0	1.829746	5.027606	-1.894800
25	6	0	2.828722	-1.437209	-2.733557
26	6	0	3.518442	-0.261932	-0.694556
27	6	0	3.937758	-2.299768	-2.685292
28	6	0	4.602369	-1.126204	-0.681983
29	6	0	4.808311	-2.123842	-1.632642
30	8	0	5.970812	-2.797982	-1.353843
31	8	0	5.642683	-1.136755	0.218967
32	6	0	6.370791	-2.335267	-0.058672
33	15	0	1.397923	-0.520961	1.716063

34	6	0	0.426477	-0.004071	3.197711
35	6	0	0.788569	-0.317780	4.516547
36	6	0	-0.007216	0.098065	5.586031
37	6	0	-0.754559	0.721676	2.973228
38	6	0	2.346474	-1.990737	2.302323
39	6	0	-1.171389	0.833070	5.351896
40	6	0	-1.544010	1.145300	4.042579
41	6	0	1.731983	-3.249863	2.181856
42	6	0	3.633618	-1.905040	2.855266
43	6	0	4.293311	-3.057768	3.289161
44	6	0	2.667880	0.807670	1.526886
45	6	0	2.394846	-4.396573	2.623028
46	6	0	3.674564	-4.305038	3.175476
47	6	0	2.789727	1.836783	2.469497
48	6	0	3.482981	0.810313	0.352252
49	6	0	3.705018	2.893924	2.324771
50	6	0	4.385880	1.856340	0.250352
51	6	0	4.494636	2.872482	1.196204
52	8	0	5.470322	3.759027	0.820718
53	8	0	5.295362	2.071477	-0.757848
54	6	0	5.942566	3.310339	-0.454536
55	1	0	-4.810243	-3.666274	-1.127243
56	1	0	-4.560129	-5.385435	-1.501060
57	1	0	-4.207255	-4.149155	-2.720688
58	1	0	-0.769358	-5.095357	-1.724916
59	1	0	-1.862264	-4.783238	-3.081330
60	1	0	-2.125843	-6.201521	-2.046460
61	1	0	-3.406845	-4.092964	2.279646
62	1	0	-4.555654	-4.781799	1.113118
63	1	0	-4.036642	-3.085915	0.967906
64	1	0	-1.913402	-5.991774	1.837077
65	1	0	-1.131151	-6.215152	0.265947
66	1	0	-2.834280	-6.674739	0.485655
67	1	0	-1.008869	-1.407379	-2.787727
68	1	0	-1.987420	-1.870545	-5.004140
69	1	0	1.418697	1.704875	-4.527112
70	1	0	-1.275650	-0.550714	-6.993976
71	1	0	0.432210	1.239985	-6.735688
72	1	0	-0.403948	2.748845	-0.732167
73	1	0	3.271740	2.104990	-2.880856
74	1	0	3.639397	4.548892	-2.969636
75	1	0	-0.039411	5.179507	-0.806954
76	1	0	2.000594	6.100561	-1.926640
77	1	0	2.120124	-1.565074	-3.543598
78	1	0	4.096555	-3.064885	-3.437274
79	1	0	7.441480	-2.116294	-0.067278
80	1	0	6.122426	-3.095219	0.695411
81	1	0	1.689953	-0.892425	4.707940
82	1	0	0.282576	-0.154531	6.602790
83	1	0	-1.062230	0.944540	1.954482
84	1	0	-1.789327	1.154304	6.186430
85	1	0	-2.452662	1.708401	3.847661
86	1	0	0.740443	-3.334021	1.742858
87	1	0	4.124450	-0.940410	2.939058
88	1	0	5.287543	-2.978391	3.722491
89	1	0	1.910159	-5.364670	2.527164
90	1	0	4.188301	-5.201116	3.514623
91	1	0	2.158891	1.822804	3.350509
92	1	0	3.787630	3.682937	3.064161
93	1	0	7.025754	3.153688	-0.407014
94	1	0	5.686789	4.054160	-1.219302

95	6	0	-3.588660	4.277748	1.862952
96	6	0	-4.536087	3.336966	2.096093
97	6	0	-3.113035	4.507405	0.479095
98	6	0	-5.095321	2.501894	1.043997
99	6	0	-2.971022	5.122132	2.941437
100	8	0	-2.229054	5.341392	0.243177
101	6	0	-3.750117	3.732532	-0.611731
102	6	0	-6.005164	1.535186	1.387571
103	6	0	-4.674675	2.784361	-0.318153
104	6	0	-3.341723	4.072170	-2.017580
105	6	0	-6.625762	0.501636	0.562815
106	6	0	-7.939793	0.092725	0.874252
107	6	0	-5.961703	-0.146355	-0.499933
108	6	0	-8.587003	-0.880621	0.119285
109	6	0	-6.609515	-1.127297	-1.248443
110	6	0	-7.925409	-1.490656	-0.950404
111	1	0	-4.888236	3.161852	3.112057
112	1	0	-1.888612	4.955796	2.993215
113	1	0	-3.408271	4.901511	3.920301
114	1	0	-3.105609	6.188228	2.725073
115	1	0	-6.335449	1.539870	2.426866
116	1	0	-5.157234	2.243560	-1.125985
117	1	0	-3.904276	3.481783	-2.747050
118	1	0	-2.272042	3.891130	-2.172312
119	1	0	-3.503972	5.137161	-2.221397
120	1	0	-8.456481	0.563231	1.707377
121	1	0	-4.922267	0.083537	-0.708146
122	1	0	-9.604726	-1.168949	0.367839
123	1	0	-6.076481	-1.618905	-2.056993
124	1	0	-8.425746	-2.256943	-1.536048

Zero-point correction=	0.991191
(Hartree/Particle)	
Thermal correction to Energy=	1.057629
Thermal correction to Enthalpy=	1.058574
Thermal correction to Gibbs Free Energy=	0.877962
Sum of electronic and zero-point Energies=	-3710.101333
Sum of electronic and thermal Energies=	-3710.034894
Sum of electronic and thermal Enthalpies=	-3710.033950
Sum of electronic and thermal Free Energies=	-3710.214561

TS$_S$ (Scheme 4, main manuscript)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-0.391191	-0.945089	-1.615502
2	6	0	0.180526	-0.722046	-3.365798
3	6	0	0.420259	0.583180	-3.830068
4	6	0	0.828342	0.804938	-5.145885
5	6	0	0.388030	-1.798255	-4.243121
6	6	0	-0.510015	-2.790964	-1.501341
7	6	0	1.031689	-0.272992	-6.010448
8	6	0	0.817787	-1.573373	-5.553260
9	6	0	0.630361	-3.515509	-1.121411
10	6	0	-1.668871	-3.492462	-1.870808
11	6	0	-1.686333	-4.888837	-1.858573
12	6	0	-2.176361	-0.435113	-1.695605

13	6	0	0.612229	-4.912543	-1.123798
14	6	0	-0.544677	-5.603427	-1.489062
15	6	0	-2.728498	0.013582	-2.904063
16	6	0	-2.997998	-0.517729	-0.529753
17	6	0	-4.074399	0.393187	-3.037835
18	6	0	-4.325918	-0.157557	-0.703178
19	6	0	-4.855657	0.291733	-1.908539
20	8	0	-6.179043	0.609916	-1.747702
21	8	0	-5.305892	-0.126337	0.262735
22	6	0	-6.521674	0.164705	-0.430753
23	15	0	-0.850207	1.179182	1.389504
24	6	0	-0.543510	2.012464	3.019018
25	6	0	-1.435760	2.948120	3.566779
26	6	0	-1.160287	3.561441	4.789379
27	6	0	0.636667	1.715140	3.719973
28	6	0	-1.956945	2.369944	0.529890
29	6	0	0.009936	3.252010	5.484855
30	6	0	0.905158	2.327026	4.946880
31	6	0	-1.351745	3.212612	-0.413030
32	6	0	-3.317699	2.543303	0.831170
33	6	0	-4.047621	3.555219	0.205305
34	6	0	-1.858809	-0.314432	1.816867
35	6	0	-2.076520	4.241117	-1.019488
36	6	0	-3.426746	4.411244	-0.710210
37	6	0	-1.709158	-0.862798	3.099251
38	6	0	-2.608257	-1.021945	0.824745
39	6	0	-2.263552	-2.098915	3.472551
40	6	0	-3.145288	-2.236359	1.229868
41	6	0	-2.971838	-2.773691	2.502023
42	8	0	-3.637776	-3.969263	2.598816
43	8	0	-3.948780	-3.073472	0.490620
44	6	0	-4.072602	-4.267898	1.267395
45	1	0	0.291509	1.430529	-3.163484
46	1	0	0.997339	1.821392	-5.487321
47	1	0	0.212360	-2.815182	-3.911020
48	1	0	1.359187	-0.098790	-7.031868
49	1	0	0.976522	-2.419391	-6.216961
50	1	0	1.528192	-2.994114	-0.807626
51	1	0	-2.560013	-2.951731	-2.169284
52	1	0	-2.590464	-5.416426	-2.152202
53	1	0	1.506549	-5.460174	-0.837271
54	1	0	-0.556254	-6.690326	-1.488677
55	1	0	-2.103789	0.064383	-3.786065
56	1	0	-4.474750	0.743311	-3.982720
57	1	0	-7.132603	-0.746450	-0.500038
58	1	0	-7.059660	0.958822	0.093367
59	1	0	-2.341635	3.216183	3.035393
60	1	0	-1.860358	4.287725	5.193856
61	1	0	1.346772	1.002734	3.315142
62	1	0	0.225156	3.734775	6.434525
63	1	0	1.823816	2.084889	5.475218
64	1	0	-0.303883	3.080734	-0.657622
65	1	0	-3.809930	1.882849	1.539858
66	1	0	-5.101653	3.682625	0.439970
67	1	0	-1.567096	4.908265	-1.709162
68	1	0	-3.997110	5.208624	-1.179394
69	1	0	-1.141293	-0.315896	3.842871
70	1	0	-2.146238	-2.496326	4.474836
71	1	0	-5.119836	-4.580037	1.289268
72	1	0	-3.430992	-5.050249	0.838436
73	8	0	2.546482	-0.632002	2.626858

74	8	0	2.691446	-2.150842	0.936904
75	6	0	3.270552	-1.765657	3.194761
76	6	0	2.947065	-2.907703	2.161765
77	6	0	4.753300	-1.372795	3.233177
78	6	0	2.756778	-2.004410	4.613722
79	6	0	4.092819	-3.879828	1.885093
80	6	0	1.664041	-3.679581	2.496749
81	5	0	2.340199	-0.862296	1.276036
82	29	0	1.009342	0.324034	0.111345
83	6	0	1.862758	4.310474	0.173077
84	6	0	2.242399	3.052133	0.563692
85	6	0	1.736881	4.636028	-1.249547
86	6	0	2.552655	2.001291	-0.366012
87	6	0	1.524977	5.400171	1.153076
88	8	0	1.311261	5.749604	-1.636975
89	6	0	2.141447	3.595662	-2.193801
90	6	0	3.154825	0.755173	0.160175
91	6	0	2.510530	2.344807	-1.754779
92	6	0	2.143134	3.978327	-3.649895
93	6	0	4.124437	-0.000871	-0.705922
94	6	0	3.738294	-0.751258	-1.825118
95	6	0	5.492741	0.070508	-0.397528
96	6	0	4.685963	-1.397362	-2.618364
97	6	0	6.443743	-0.581192	-1.184954
98	6	0	6.043769	-1.318136	-2.300796
99	1	0	5.145498	-1.188172	2.228736
100	1	0	5.363071	-2.151150	3.704793
101	1	0	4.862886	-0.452807	3.816757
102	1	0	1.673247	-2.139662	4.634627
103	1	0	3.003010	-1.143363	5.243929
104	1	0	3.228282	-2.889868	5.055810
105	1	0	3.777771	-4.614353	1.136667
106	1	0	4.372561	-4.425213	2.794235
107	1	0	4.974629	-3.364879	1.497953
108	1	0	1.399661	-4.326141	1.655563
109	1	0	0.823029	-3.001768	2.671740
110	1	0	1.797918	-4.308396	3.383771
111	1	0	2.323908	2.831506	1.628004
112	1	0	1.655172	5.067534	2.188829
113	1	0	0.488357	5.734554	1.018925
114	1	0	2.148820	6.286248	0.982244
115	1	0	3.588008	0.958675	1.138180
116	1	0	2.830255	1.605560	-2.484202
117	1	0	1.127644	4.193957	-4.011181
118	1	0	2.580277	3.190789	-4.273473
119	1	0	2.710128	4.904299	-3.802441
120	1	0	2.685356	-0.834344	-2.073248
121	1	0	5.815972	0.657624	0.459226
122	1	0	4.358995	-1.967829	-3.483898
123	1	0	7.497264	-0.507190	-0.927383
124	1	0	6.781765	-1.825494	-2.916412

Zero-point correction= 0.992079
(Hartree/Particle)
Thermal correction to Energy= 1.056695
Thermal correction to Enthalpy= 1.057639
Thermal correction to Gibbs Free Energy= 0.888256
Sum of electronic and zero-point Energies= -3710.079360
Sum of electronic and thermal Energies= -3710.014743
Sum of electronic and thermal Enthalpies= -3710.013799
Sum of electronic and thermal Free Energies= -3710.183182

$\underline{TS_R}$ (Scheme 4, main manuscript)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.604226	2.782959	3.288715
2	6	0	-1.303630	1.743882	2.720450
3	6	0	-0.578586	4.094763	2.648303
4	6	0	-2.027758	1.871848	1.486865
5	6	0	0.157629	2.640914	4.578688
6	8	0	0.103806	5.042891	3.109812
7	6	0	-1.387038	4.246515	1.437630
8	6	0	-2.931430	0.771498	1.073149
9	6	0	-2.043607	3.172721	0.888459
10	6	0	-1.434241	5.618660	0.822649
11	6	0	-4.176467	1.127225	0.306767
12	6	0	-5.416791	1.041985	0.960572
13	6	0	-4.155906	1.572281	-1.023709
14	6	0	-6.597127	1.411787	0.312782
15	6	0	-5.332781	1.949969	-1.669745
16	6	0	-6.558994	1.872234	-1.005213
17	1	0	-1.342545	0.786227	3.240630
18	1	0	-0.192014	3.367816	5.322395
19	1	0	1.223167	2.860309	4.430642
20	1	0	0.058611	1.633204	4.999603
21	1	0	-3.173476	0.155415	1.935901
22	1	0	-2.630778	3.329130	-0.012284
23	1	0	-2.109160	5.650934	-0.040203
24	1	0	-0.436160	5.940061	0.497920
25	1	0	-1.763028	6.362564	1.558427
26	1	0	-5.452249	0.695129	1.990488
27	1	0	-3.212851	1.604432	-1.558934
28	1	0	-7.544886	1.344285	0.840864
29	1	0	-5.289480	2.295939	-2.699255
30	1	0	-7.476133	2.163180	-1.510478
31	29	0	-0.975252	0.164843	0.322835
32	15	0	0.493890	1.003078	-1.478428
33	6	0	-0.453771	1.489941	-2.992294
34	6	0	-1.489346	0.637616	-3.417763
35	6	0	-2.258385	0.959647	-4.537353
36	6	0	-0.237490	2.687362	-3.690931
37	6	0	1.593736	2.435870	-1.120974
38	6	0	-2.025866	2.148028	-5.233501
39	6	0	-1.020759	3.013402	-4.800653
40	6	0	1.415968	3.113414	0.090733
41	6	0	2.594968	2.866863	-2.009508
42	6	0	3.371592	3.983211	-1.696531
43	6	0	1.698168	-0.282782	-2.069925
44	6	0	2.193862	4.231401	0.406429
45	6	0	3.166351	4.669920	-0.493272
46	6	0	1.574429	-0.840271	-3.347937
47	6	0	2.726064	-0.744667	-1.184987
48	6	0	2.429101	-1.851202	-3.823819
49	6	0	3.555209	-1.732524	-1.690535
50	6	0	3.413913	-2.281290	-2.962381
51	8	0	4.380007	-3.230890	-3.170824
52	8	0	4.620238	-2.320167	-1.054364
53	6	0	5.086277	-3.350330	-1.929398
54	15	0	0.690657	-1.271734	1.357632
55	6	0	0.431759	-1.872620	3.087522

56	6	0	1.464950	-2.213418	3.977255
57	6	0	1.172299	-2.729869	5.239889
58	6	0	-0.898940	-2.071751	3.490574
59	6	0	1.080078	-2.856889	0.472770
60	6	0	-0.154557	-2.921771	5.631601
61	6	0	-1.187736	-2.595119	4.753012
62	6	0	0.361121	-3.182752	-0.685575
63	6	0	2.057622	-3.750575	0.936926
64	6	0	2.307970	-4.943393	0.258071
65	6	0	2.278142	-0.333203	1.362739
66	6	0	0.618554	-4.372877	-1.370732
67	6	0	1.589248	-5.257539	-0.898894
68	6	0	2.653399	0.357252	2.524933
69	6	0	3.038239	-0.172027	0.161734
70	6	0	3.803945	1.159651	2.595919
71	6	0	4.185557	0.599349	0.277821
72	6	0	4.564261	1.246895	1.450448
73	8	0	5.732550	1.932230	1.248292
74	8	0	5.102110	0.867165	-0.708018
75	6	0	6.004902	1.829930	-0.154313
76	8	0	-2.933306	-1.474354	-1.245278
77	8	0	-3.297555	-1.934966	0.958022
78	6	0	-3.925037	-2.555482	-1.254813
79	6	0	-3.932281	-3.042214	0.255481
80	6	0	-5.247728	-1.937822	-1.724361
81	6	0	-3.465465	-3.604378	-2.268041
82	6	0	-5.325878	-3.232340	0.859285
83	6	0	-3.082587	-4.290178	0.525095
84	5	0	-2.694953	-1.083636	0.056212
85	1	0	-1.715461	-0.266283	-2.859505
86	1	0	-3.051033	0.286674	-4.853951
87	1	0	0.534081	3.375532	-3.366036
88	1	0	-2.631650	2.402878	-6.099105
89	1	0	-0.842251	3.948527	-5.324878
90	1	0	0.667621	2.765808	0.790905
91	1	0	2.769278	2.331488	-2.938972
92	1	0	4.132948	4.321983	-2.395392
93	1	0	2.011828	4.750374	1.343959
94	1	0	3.767834	5.544802	-0.259627
95	1	0	0.796595	-0.479597	-4.010510
96	1	0	2.321741	-2.264395	-4.820791
97	1	0	6.158425	-3.220201	-2.107607
98	1	0	4.875264	-4.330960	-1.483912
99	1	0	2.501431	-2.059348	3.695063
100	1	0	1.983440	-2.980895	5.918299
101	1	0	-1.711485	-1.834943	2.810611
102	1	0	-0.379758	-3.320941	6.616896
103	1	0	-2.223226	-2.740513	5.048939
104	1	0	-0.392726	-2.495882	-1.057608
105	1	0	2.625339	-3.521548	1.832800
106	1	0	3.060641	-5.630491	0.636610
107	1	0	0.062453	-4.604939	-2.275127
108	1	0	1.784177	-6.187032	-1.427326
109	1	0	2.035160	0.284417	3.411378
110	1	0	4.073400	1.686440	3.504376
111	1	0	7.033891	1.488195	-0.300248
112	1	0	5.833846	2.803545	-0.629815
113	1	0	-5.588950	-1.143004	-1.057914
114	1	0	-6.035003	-2.696195	-1.800012
115	1	0	-5.101202	-1.498545	-2.716006
116	1	0	-2.471427	-3.992386	-2.035214

117	1	0	-3.430778	-3.155697	-3.266319
118	1	0	-4.165975	-4.446679	-2.303211
119	1	0	-5.228803	-3.514550	1.912707
120	1	0	-5.872320	-4.031518	0.345500
121	1	0	-5.916397	-2.315218	0.807884
122	1	0	-3.038808	-4.461904	1.605441
123	1	0	-2.057591	-4.171358	0.166121
124	1	0	-3.516889	-5.180219	0.056768

Zero-point correction= 0.992511
(Hartree/Particle)
Thermal correction to Energy= 1.056833
Thermal correction to Enthalpy= 1.057777
Thermal correction to Gibbs Free Energy= 0.891208
Sum of electronic and zero-point Energies= -3710.080490
Sum of electronic and thermal Energies= -3710.016168
Sum of electronic and thermal Enthalpies= -3710.015224
Sum of electronic and thermal Free Energies= -3710.181793

II$_S$ (Scheme 4 and Figure 1, main manuscript)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-5.866600	-1.333254	0.691494
2	8	0	-3.795888	-0.562112	1.288407
3	6	0	-5.668158	-1.787128	2.056390
4	6	0	-4.475612	-0.875585	2.540425
5	6	0	-6.977762	-1.607585	2.823549
6	6	0	-5.307746	-3.277144	1.975399
7	6	0	-4.941189	0.460622	3.136225
8	6	0	-3.480625	-1.554775	3.479847
9	5	0	-4.711887	-0.721502	0.265922
10	6	0	-1.952913	-2.861036	-2.450032
11	6	0	-3.024957	-2.234540	-1.849189
12	6	0	-0.938908	-2.080473	-3.147080
13	6	0	-3.212331	-0.825974	-1.843406
14	6	0	-1.833301	-4.358535	-2.530087
15	8	0	-0.011987	-2.638451	-3.801140
16	6	0	-1.085288	-0.626954	-3.093850
17	6	0	-4.510817	-0.270443	-1.238971
18	6	0	-2.251850	-0.055272	-2.488671
19	6	0	-0.295032	0.139894	-4.147036
20	6	0	-4.714649	1.232789	-1.390140
21	6	0	-4.064333	2.164259	-0.564294
22	6	0	-5.583430	1.725201	-2.376037
23	6	0	-4.274679	3.535809	-0.719670
24	6	0	-5.799823	3.095221	-2.533211
25	6	0	-5.144984	4.007785	-1.704203
26	1	0	-7.340270	-0.578586	2.770125
27	1	0	-6.855486	-1.882237	3.877767
28	1	0	-7.745998	-2.256965	2.391755
29	1	0	-4.382201	-3.429681	1.411188
30	1	0	-6.109571	-3.807445	1.452451
31	1	0	-5.191071	-3.722046	2.969466
32	1	0	-4.075620	1.117801	3.264606
33	1	0	-5.417631	0.323935	4.112768
34	1	0	-5.646946	0.968066	2.471532

35	1	0	-2.673279	-0.860270	3.732805
36	1	0	-3.026510	-2.437336	3.023804
37	1	0	-3.969716	-1.856944	4.413280
38	1	0	-3.794269	-2.857695	-1.387066
39	1	0	-1.855331	-4.692216	-3.575401
40	1	0	-2.642673	-4.858081	-1.985390
41	1	0	-0.873176	-4.700598	-2.126012
42	1	0	-5.340448	-0.745435	-1.783492
43	1	0	-2.410535	1.015920	-2.589237
44	1	0	-0.587545	1.194982	-4.187503
45	1	0	-0.483944	-0.299130	-5.136306
46	1	0	0.789594	0.087224	-4.001747
47	1	0	-3.391738	1.809777	0.210737
48	1	0	-6.096245	1.021697	-3.027972
49	1	0	-3.753299	4.235791	-0.071818
50	1	0	-6.481218	3.448095	-3.303593
51	1	0	-5.311358	5.075386	-1.823301
52	29	0	-0.065217	-0.191627	-1.218273
53	15	0	0.522434	1.889750	-0.142284
54	6	0	-0.124602	3.489671	-0.816151
55	6	0	-0.639738	3.493116	-2.120920
56	6	0	-1.122718	4.668868	-2.697541
57	6	0	-0.125595	4.691101	-0.089058
58	6	0	0.342204	2.126790	1.675991
59	6	0	-1.112210	5.858258	-1.968450
60	6	0	-0.617233	5.864670	-0.662178
61	6	0	-0.773383	1.560954	2.311974
62	6	0	1.239363	2.901337	2.428845
63	6	0	1.018724	3.116055	3.789783
64	6	0	2.341355	1.957384	-0.494172
65	6	0	-0.991749	1.783128	3.673996
66	6	0	-0.100100	2.560657	4.414303
67	6	0	2.783884	2.793241	-1.529590
68	6	0	3.259562	1.054395	0.133837
69	6	0	4.109080	2.798204	-1.996141
70	6	0	4.562208	1.098721	-0.341286
71	6	0	4.979979	1.926225	-1.381589
72	8	0	6.319610	1.749369	-1.607861
73	8	0	5.640213	0.388844	0.131541
74	6	0	6.688395	0.613860	-0.815735
75	15	0	1.536824	-1.711685	-0.233757
76	6	0	0.780110	-3.307270	0.296403
77	6	0	1.490000	-4.517783	0.295306
78	6	0	0.881434	-5.694779	0.734070
79	6	0	-0.555830	-3.300041	0.727569
80	6	0	2.991883	-2.214000	-1.249150
81	6	0	-0.441187	-5.675396	1.180854
82	6	0	-1.157253	-4.477001	1.176001
83	6	0	2.808667	-2.377779	-2.632936
84	6	0	4.249387	-2.473381	-0.679743
85	6	0	5.313029	-2.888365	-1.483796
86	6	0	2.293301	-1.063532	1.331288
87	6	0	3.880439	-2.793486	-3.427456
88	6	0	5.130817	-3.045865	-2.860521
89	6	0	2.171562	-1.785807	2.526734
90	6	0	2.991318	0.183986	1.323009
91	6	0	2.724084	-1.349769	3.743211
92	6	0	3.549371	0.568534	2.532728
93	6	0	3.420268	-0.161985	3.710446
94	8	0	4.046458	0.496475	4.738649
95	8	0	4.261749	1.718674	2.788654

96	6	0	4.761702	1.570451	4.119682
97	1	0	-0.663684	2.569090	-2.686323
98	1	0	-1.518989	4.648357	-3.708758
99	1	0	0.249473	4.714660	0.928181
100	1	0	-1.494843	6.773910	-2.411334
101	1	0	-0.612281	6.786064	-0.085603
102	1	0	-1.469940	0.944337	1.748397
103	1	0	2.121230	3.322262	1.955370
104	1	0	1.720057	3.718627	4.361337
105	1	0	-1.858658	1.344312	4.159610
106	1	0	-0.272564	2.728312	5.474059
107	1	0	2.080306	3.468283	-2.001824
108	1	0	4.428009	3.457436	-2.795808
109	1	0	7.617958	0.830043	-0.283603
110	1	0	6.788851	-0.267560	-1.463014
111	1	0	2.517603	-4.541670	-0.052621
112	1	0	1.440699	-6.626509	0.722786
113	1	0	-1.133158	-2.380061	0.699359
114	1	0	-0.915859	-6.592620	1.519283
115	1	0	-2.193335	-4.462101	1.502980
116	1	0	1.828668	-2.230920	-3.092439
117	1	0	4.403061	-2.346565	0.386998
118	1	0	6.279669	-3.097711	-1.031470
119	1	0	3.726370	-2.925514	-4.494965
120	1	0	5.959091	-3.371081	-3.485363
121	1	0	1.641971	-2.730430	2.520986
122	1	0	2.616313	-1.925046	4.656158
123	1	0	5.832833	1.325466	4.084147
124	1	0	4.588175	2.492945	4.679501

Zero-point correction= (Hartree/Particle)	0.993692
Thermal correction to Energy=	1.058463
Thermal correction to Enthalpy=	1.059407
Thermal correction to Gibbs Free Energy=	0.889150
Sum of electronic and zero-point Energies=	-3710.142353
Sum of electronic and thermal Energies=	-3710.077583
Sum of electronic and thermal Enthalpies=	-3710.076639
Sum of electronic and thermal Free Energies=	-3710.246896

II$_R$ (Scheme 4, main manuscript)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	0.015539	0.492042	-1.151949
2	15	0	-0.267447	-1.806990	-0.407359
3	6	0	0.587313	-3.186382	-1.303551
4	6	0	0.840043	-3.037548	-2.676404
5	6	0	1.475019	-4.048279	-3.400790
6	6	0	0.999043	-4.368565	-0.668066
7	6	0	1.882382	-5.219049	-2.758140
8	6	0	1.644112	-5.374449	-1.391091
9	6	0	-2.070514	-2.177075	-0.648818
10	6	0	-2.433371	-3.031524	-1.700825
11	6	0	-3.090127	-1.494830	0.092508
12	6	0	-3.765563	-3.263288	-2.080018
13	6	0	-4.394366	-1.756781	-0.303847

14	6	0	-4.732384	-2.598598	-1.360250
15	8	0	-6.094481	-2.665689	-1.488320
16	8	0	-5.545495	-1.280216	0.278534
17	6	0	-6.609094	-1.672160	-0.594415
18	15	0	-1.847351	1.582279	-0.094029
19	6	0	-1.551559	3.293598	0.527367
20	6	0	-2.538141	4.291675	0.502597
21	6	0	-2.270719	5.560118	1.020416
22	6	0	-0.292400	3.596200	1.066681
23	6	0	-3.315265	1.764552	-1.190897
24	6	0	-1.020710	5.844970	1.574187
25	6	0	-0.031824	4.859855	1.597843
26	6	0	-3.086292	2.018306	-2.554426
27	6	0	-4.631755	1.718791	-0.704306
28	6	0	-5.708112	1.918889	-1.570957
29	6	0	-2.469552	0.691185	1.410374
30	6	0	-4.171624	2.217724	-3.412142
31	6	0	-5.479515	2.165321	-2.927592
32	6	0	-2.447381	1.341112	2.653617
33	6	0	-2.917716	-0.664277	1.328261
34	6	0	-2.861710	0.728665	3.848062
35	6	0	-3.345295	-1.227340	2.522350
36	6	0	-3.315011	-0.567554	3.746883
37	8	0	-3.766756	-1.401582	4.738709
38	8	0	-3.818510	-2.507767	2.710357
39	6	0	-4.289492	-2.547229	4.059688
40	1	0	0.533813	-2.129697	-3.183534
41	1	0	1.657386	-3.914286	-4.463618
42	1	0	0.819061	-4.507448	0.392611
43	1	0	2.384123	-6.003792	-3.317883
44	1	0	1.957076	-6.282884	-0.882993
45	1	0	-1.659489	-3.544505	-2.257299
46	1	0	-4.016459	-3.934474	-2.893822
47	1	0	-7.423161	-2.101370	-0.004682
48	1	0	-6.946540	-0.801612	-1.172185
49	1	0	-3.513480	4.082890	0.075403
50	1	0	-3.041089	6.326117	0.988804
51	1	0	0.493894	2.849404	1.064246
52	1	0	-0.815615	6.833643	1.976302
53	1	0	0.949086	5.072307	2.013618
54	1	0	-2.074087	2.107595	-2.954444
55	1	0	-4.818674	1.523339	0.346949
56	1	0	-6.723843	1.895686	-1.182709
57	1	0	-3.983388	2.422691	-4.462402
58	1	0	-6.318472	2.323309	-3.600778
59	1	0	-2.109378	2.368255	2.704558
60	1	0	-2.835121	1.254524	4.796059
61	1	0	-5.388177	-2.508191	4.066024
62	1	0	-3.926049	-3.455895	4.546155
63	6	0	0.134205	-2.196532	1.347000
64	6	0	1.314136	-1.645074	1.870734
65	6	0	-0.635762	-3.051700	2.148992
66	6	0	-0.238634	-3.334740	3.457549
67	6	0	1.708548	-1.932021	3.178757
68	6	0	0.930525	-2.773557	3.976351
69	1	0	1.942423	-1.012841	1.250400
70	1	0	-1.549741	-3.488919	1.760248
71	1	0	-0.843696	-3.996956	4.071689
72	1	0	2.620105	-1.489384	3.570834
73	1	0	1.233518	-2.992517	4.996837
74	8	0	6.202425	0.230486	-0.520755

75	8	0	4.199564	-0.829489	-0.200290
76	6	0	6.541947	-1.135201	-0.152931
77	6	0	5.180542	-1.893369	-0.394215
78	6	0	7.708626	-1.595273	-1.025493
79	6	0	6.967232	-1.101375	1.321696
80	6	0	5.012058	-2.395154	-1.834464
81	6	0	4.877184	-3.019815	0.591711
82	5	0	4.840549	0.373111	-0.400862
83	6	0	1.231283	3.630362	-2.050417
84	6	0	2.312561	3.302792	-1.260886
85	6	0	0.612269	2.628852	-2.911632
86	6	0	2.881753	1.999843	-1.199246
87	6	0	0.703627	5.035038	-2.156108
88	8	0	-0.318140	2.926109	-3.712849
89	6	0	1.166051	1.278113	-2.835368
90	6	0	4.161212	1.803589	-0.388763
91	6	0	2.307876	1.022256	-2.010021
92	6	0	0.853617	0.384347	-4.026752
93	6	0	4.045223	2.175547	1.095621
94	6	0	5.070479	2.889511	1.733936
95	6	0	2.946917	1.772053	1.869580
96	6	0	4.997900	3.198231	3.094123
97	6	0	2.869447	2.075756	3.229796
98	6	0	3.896089	2.793200	3.849737
99	1	0	7.482237	-1.495629	-2.089425
100	1	0	7.964072	-2.640907	-0.817755
101	1	0	8.590096	-0.982716	-0.810081
102	1	0	6.151486	-0.753639	1.963138
103	1	0	7.802703	-0.403371	1.434129
104	1	0	7.291515	-2.087389	1.671310
105	1	0	3.980960	-2.730459	-1.979851
106	1	0	5.679854	-3.237259	-2.045760
107	1	0	5.217254	-1.600434	-2.558830
108	1	0	3.904863	-3.463558	0.356008
109	1	0	4.843403	-2.658513	1.622135
110	1	0	5.635258	-3.808863	0.522991
111	1	0	2.773253	4.088833	-0.661196
112	1	0	0.788786	5.403168	-3.186415
113	1	0	1.241089	5.719650	-1.490887
114	1	0	-0.364836	5.074376	-1.911463
115	1	0	4.926172	2.476590	-0.804397
116	1	0	2.760499	0.034444	-2.063216
117	1	0	1.493954	-0.504212	-4.032938
118	1	0	1.036252	0.941467	-4.955465
119	1	0	-0.194887	0.066661	-4.077981
120	1	0	5.933755	3.208189	1.154071
121	1	0	2.142881	1.221075	1.391167
122	1	0	5.802599	3.760518	3.561708
123	1	0	2.004591	1.752092	3.804132
124	1	0	3.835929	3.035723	4.907535

Zero-point correction= 0.993684
(Hartree/Particle)
Thermal correction to Energy= 1.058488
Thermal correction to Enthalpy= 1.059432
Thermal correction to Gibbs Free Energy= 0.888183
Sum of electronic and zero-point Energies= -3710.143028
Sum of electronic and thermal Energies= -3710.078224
Sum of electronic and thermal Enthalpies= -3710.077280
Sum of electronic and thermal Free Energies= -3710.248529

III$_S$ (Figure 1, main manuscript)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-7.134614	-0.816721	-1.617635
2	8	0	-6.413269	-1.049825	0.542104
3	6	0	-7.096223	-2.248626	-1.370966
4	6	0	-7.063508	-2.309040	0.203094
5	6	0	-8.323362	-2.884497	-2.022206
6	6	0	-5.813262	-2.777912	-2.026990
7	6	0	-8.458594	-2.271367	0.843258
8	6	0	-6.249121	-3.458226	0.792613
9	5	0	-6.615877	-0.182126	-0.512654
10	6	0	-2.772176	1.207898	-2.124053
11	6	0	-4.147392	1.122559	-1.907879
12	6	0	-1.925260	1.691070	-1.090023
13	6	0	-4.740924	1.493624	-0.690177
14	6	0	-2.155447	0.816960	-3.442232
15	8	0	-0.617310	1.815727	-1.296218
16	6	0	-2.515123	2.074488	0.143410
17	6	0	-6.270119	1.361468	-0.533331
18	6	0	-3.899092	1.962780	0.322288
19	6	0	-1.635973	2.627045	1.237137
20	6	0	-6.872068	2.178022	0.601739
21	6	0	-6.908860	1.721122	1.929181
22	6	0	-7.407479	3.446882	0.330563
23	6	0	-7.458947	2.506931	2.944750
24	6	0	-7.961511	4.233001	1.341387
25	6	0	-7.989059	3.765478	2.656817
26	1	0	-9.250787	-2.424029	-1.673952
27	1	0	-8.365279	-3.959716	-1.812329
28	1	0	-8.270178	-2.753877	-3.107951
29	1	0	-4.922301	-2.320188	-1.585878
30	1	0	-5.829369	-2.522551	-3.091195
31	1	0	-5.730846	-3.866392	-1.935690
32	1	0	-8.351315	-2.100869	1.919109
33	1	0	-8.997332	-3.213722	0.696207
34	1	0	-9.063663	-1.457035	0.432780
35	1	0	-6.269079	-3.399018	1.886417
36	1	0	-5.206574	-3.424106	0.470197
37	1	0	-6.675187	-4.425410	0.501096
38	1	0	-4.782902	0.762328	-2.716920
39	1	0	-1.622446	1.659960	-3.900834
40	1	0	-2.914852	0.464307	-4.149086
41	1	0	-1.408387	0.020766	-3.315293
42	1	0	-6.709468	1.740551	-1.465965
43	1	0	-4.325793	2.277333	1.271395
44	1	0	-2.226301	2.909253	2.115808
45	1	0	-1.081414	3.510066	0.893591
46	1	0	-0.878402	1.897212	1.562787
47	1	0	-6.513140	0.738353	2.163779
48	1	0	-7.385528	3.822270	-0.690231
49	1	0	-7.475931	2.130060	3.964828
50	1	0	-8.371519	5.210955	1.100673
51	1	0	-8.419984	4.374596	3.447429
52	29	0	0.781082	0.744012	-0.535522
53	15	0	1.098737	-1.381194	0.323497
54	6	0	1.611689	-2.724856	-0.830668

55	6	0	1.177716	-2.639912	-2.162302
56	6	0	2.348796	-3.847688	-0.423838
57	6	0	2.629877	-4.871535	-1.329978
58	6	0	2.431002	-1.272872	1.598268
59	6	0	1.461178	-3.664571	-3.067211
60	6	0	2.185006	-4.783449	-2.651942
61	6	0	2.097040	-1.407277	2.952912
62	6	0	3.760642	-0.887784	1.224520
63	6	0	3.022513	-1.204353	3.991607
64	6	0	4.648757	-0.712035	2.274260
65	6	0	4.300242	-0.855727	3.615945
66	8	0	5.394880	-0.630975	4.408803
67	8	0	5.983116	-0.395475	2.183686
68	6	0	6.420446	-0.162195	3.525699
69	15	0	2.958188	1.703900	-0.613227
70	6	0	3.108162	2.966022	-1.950205
71	6	0	4.285380	3.695317	-2.193435
72	6	0	4.325457	4.654175	-3.204143
73	6	0	1.963043	3.232182	-2.719488
74	6	0	3.703534	2.549860	0.846277
75	6	0	3.187418	4.903387	-3.977821
76	6	0	2.010760	4.197049	-3.730824
77	6	0	2.833268	3.220500	1.719816
78	6	0	5.084947	2.598707	1.088294
79	6	0	5.584628	3.320014	2.174644
80	6	0	4.139724	0.353756	-1.052908
81	6	0	3.335100	3.939575	2.805804
82	6	0	4.711570	3.992681	3.033814
83	6	0	4.766871	0.350771	-2.305939
84	6	0	4.303359	-0.762657	-0.169121
85	6	0	5.587322	-0.703029	-2.746025
86	6	0	5.134048	-1.772575	-0.627983
87	6	0	5.753832	-1.756524	-1.875450
88	8	0	6.512505	-2.886613	-2.034908
89	8	0	5.488116	-2.919164	0.041864
90	6	0	6.256175	-3.696348	-0.882056
91	6	0	-0.367741	-2.109565	1.173356
92	6	0	-0.353259	-3.368617	1.799828
93	6	0	-1.510656	-3.876739	2.386106
94	6	0	-1.568187	-1.384801	1.129035
95	6	0	-2.701251	-3.143269	2.339990
96	6	0	-2.732465	-1.901122	1.706438
97	1	0	0.615363	-1.768771	-2.489755
98	1	0	2.718751	-3.915446	0.594793
99	1	0	3.190144	-5.743478	-1.000992
100	1	0	1.118145	-3.585856	-4.095174
101	1	0	2.404526	-5.582526	-3.355005
102	1	0	1.083123	-1.677281	3.222431
103	1	0	2.743409	-1.319024	5.033132
104	1	0	7.341901	-0.721351	3.709961
105	1	0	6.568159	0.914850	3.678641
106	1	0	5.170552	3.519703	-1.588836
107	1	0	5.241129	5.211477	-3.384296
108	1	0	1.028592	2.714619	-2.509648
109	1	0	3.218798	5.654542	-4.762887
110	1	0	1.118627	4.399351	-4.317298
111	1	0	1.760729	3.179274	1.546115
112	1	0	5.769025	2.063116	0.436824
113	1	0	6.657797	3.363773	2.344688
114	1	0	2.650317	4.455399	3.473367
115	1	0	5.102811	4.554285	3.877993

116	1	0	4.619082	1.193047	-2.971014
117	1	0	6.067175	-0.683427	-3.718281
118	1	0	7.205819	-3.979498	-0.417645
119	1	0	5.681216	-4.582255	-1.180384
120	1	0	0.561131	-3.953639	1.829344
121	1	0	-1.486892	-4.848578	2.872439
122	1	0	-1.609055	-0.420613	0.630625
123	1	0	-3.603389	-3.546078	2.792535
124	1	0	-3.656879	-1.333601	1.643421

Zero-point correction= 0.993511
(Hartree/Particle)
Thermal correction to Energy= 1.058456
Thermal correction to Enthalpy= 1.059400
Thermal correction to Gibbs Free Energy= 0.885099
Sum of electronic and zero-point Energies= -3710.176322
Sum of electronic and thermal Energies= -3710.111378
Sum of electronic and thermal Enthalpies= -3710.110434
Sum of electronic and thermal Free Energies= -3710.284734

$\underline{\mathbf{IV}_{\mathbf{R}}}$ (Reference 15, main manuscript)

Standard orientation:

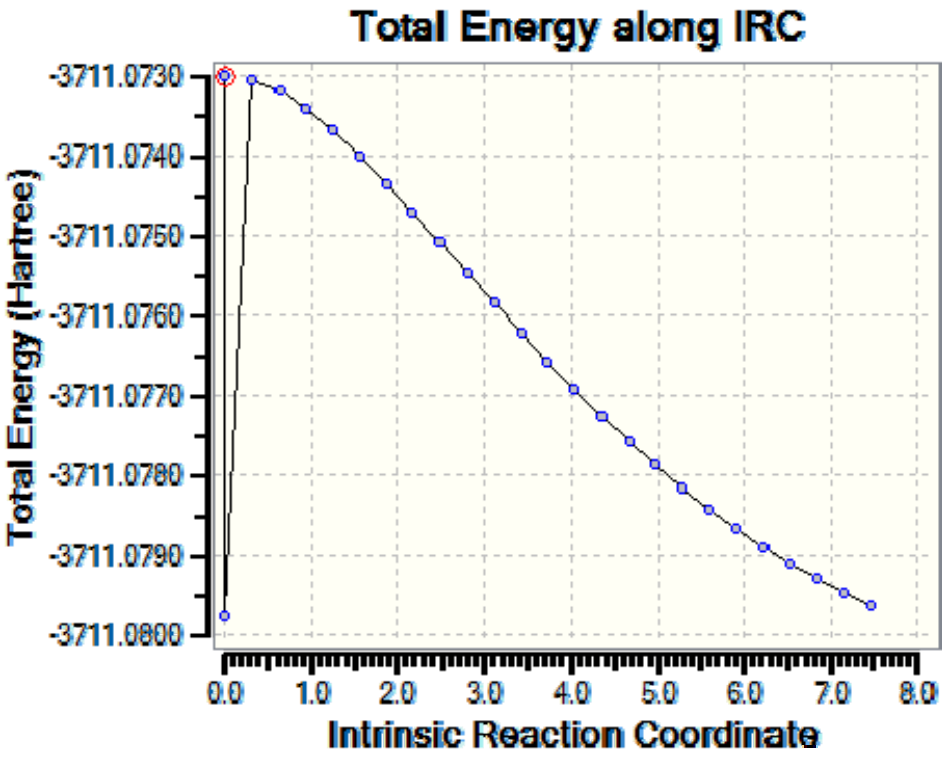
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-3.014240	-1.542623	-1.582009
2	8	0	-2.650586	-2.530480	0.442685
3	6	0	-3.544919	-2.893972	-1.719527
4	6	0	-3.632101	-3.382811	-0.224061
5	6	0	-4.883403	-2.809881	-2.453534
6	6	0	-2.533928	-3.678285	-2.568248
7	6	0	-4.986314	-3.102245	0.440798
8	6	0	-3.238759	-4.842000	0.007209
9	5	0	-2.417049	-1.411362	-0.341508
10	29	0	-1.322142	0.238819	0.198430
11	15	0	0.252710	0.765326	-1.584929
12	6	0	-0.666512	1.015366	-3.174406
13	6	0	-1.957754	1.552240	-3.081635
14	6	0	-2.685472	1.875157	-4.228409
15	6	0	-0.118644	0.805300	-4.451034
16	6	0	1.378120	2.234952	-1.621815
17	6	0	-2.133482	1.655229	-5.490152
18	6	0	-0.848689	1.117346	-5.597824
19	6	0	1.228980	3.178320	-0.598728
20	6	0	2.271726	2.501965	-2.671670
21	6	0	2.990981	3.696667	-2.692045
22	6	0	1.327032	-0.713312	-1.878672
23	6	0	1.944654	4.378951	-0.619902
24	6	0	2.825794	4.638383	-1.669541
25	6	0	0.887593	-1.695943	-2.778002
26	6	0	2.540979	-0.911353	-1.148620
27	6	0	1.631900	-2.853023	-3.064047
28	6	0	3.273040	-2.037881	-1.491249
29	6	0	2.840583	-2.984083	-2.415093
30	8	0	3.764407	-3.989054	-2.524053
31	8	0	4.487560	-2.420009	-0.978441
32	6	0	4.799504	-3.678953	-1.582152
33	15	0	1.008816	-0.899830	1.683143

34	6	0	0.951862	-0.916236	3.544127
35	6	0	2.072198	-1.005739	4.388414
36	6	0	1.918008	-1.115095	5.770228
37	6	0	-0.323543	-0.974910	4.127511
38	6	0	1.552379	-2.660570	1.435471
39	6	0	0.641208	-1.156301	6.336824
40	6	0	-0.480308	-1.094792	5.510876
41	6	0	0.574094	-3.598687	1.074144
42	6	0	2.856955	-3.104811	1.701591
43	6	0	3.175863	-4.460031	1.609514
44	6	0	2.510732	0.095636	1.239461
45	6	0	0.898088	-4.955143	0.979613
46	6	0	2.196707	-5.389651	1.246234
47	6	0	3.035855	1.040934	2.131504
48	6	0	3.061109	-0.007044	-0.079277
49	6	0	4.135519	1.859887	1.817459
50	6	0	4.168469	0.781982	-0.341968
51	6	0	4.695250	1.691300	0.570423
52	8	0	5.774733	2.331990	0.020764
53	8	0	4.893046	0.827829	-1.506615
54	6	0	5.867604	1.861259	-1.328803
55	1	0	-5.576855	-2.134915	-1.947161
56	1	0	-5.351351	-3.798420	-2.534337
57	1	0	-4.721238	-2.429180	-3.467482
58	1	0	-1.554712	-3.721850	-2.081664
59	1	0	-2.410235	-3.167586	-3.528937
60	1	0	-2.874071	-4.700973	-2.766455
61	1	0	-4.901610	-3.304488	1.513444
62	1	0	-5.775823	-3.743719	0.033077
63	1	0	-5.285928	-2.058288	0.319363
64	1	0	-3.268739	-5.063417	1.079261
65	1	0	-2.229701	-5.053704	-0.354333
66	1	0	-3.936569	-5.521282	-0.496951
67	1	0	-2.392027	1.723386	-2.102319
68	1	0	-3.684351	2.292466	-4.133332
69	1	0	0.874550	0.381143	-4.555935
70	1	0	-2.699297	1.900144	-6.385086
71	1	0	-0.410704	0.943284	-6.577278
72	1	0	0.547231	2.971054	0.217061
73	1	0	2.408474	1.783960	-3.473826
74	1	0	3.669752	3.901346	-3.516907
75	1	0	1.787387	5.104262	0.173500
76	1	0	3.378378	5.573919	-1.698369
77	1	0	-0.061068	-1.564805	-3.284417
78	1	0	1.276503	-3.599206	-3.766047
79	1	0	5.758136	-3.602670	-2.107294
80	1	0	4.830732	-4.455780	-0.809703
81	1	0	3.072956	-0.990970	3.969273
82	1	0	2.797847	-1.175863	6.405667
83	1	0	-1.202693	-0.948753	3.490202
84	1	0	0.524231	-1.242632	7.413742
85	1	0	-1.478426	-1.139055	5.938463
86	1	0	-0.443025	-3.270970	0.877679
87	1	0	3.630053	-2.392236	1.972037
88	1	0	4.187443	-4.791733	1.832386
89	1	0	0.130128	-5.672656	0.701772
90	1	0	2.445456	-6.445654	1.178152
91	1	0	2.585569	1.157075	3.109484
92	1	0	4.524270	2.584229	2.524660
93	1	0	6.867952	1.450493	-1.502632
94	1	0	5.651818	2.686820	-2.017174

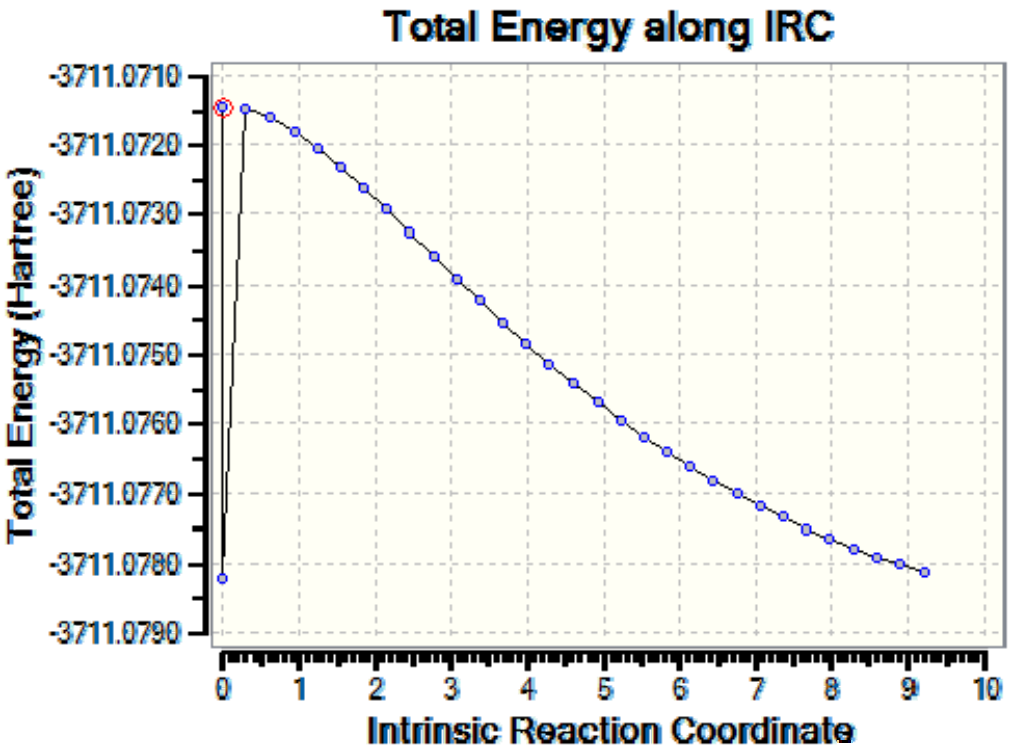
95	6	0	-0.449300	3.536943	2.606417
96	6	0	-1.075596	2.334923	2.447833
97	6	0	-0.800077	4.670486	1.739613
98	6	0	-2.125140	2.116940	1.475312
99	6	0	0.615246	3.775154	3.641880
100	8	0	-0.203887	5.761415	1.823085
101	6	0	-1.882748	4.462203	0.760992
102	6	0	-2.863659	0.896185	1.510638
103	6	0	-2.490700	3.246619	0.650861
104	6	0	-2.259335	5.643099	-0.088943
105	6	0	-4.299453	0.772232	1.124209
106	6	0	-5.219301	0.488420	2.150030
107	6	0	-4.801703	0.953409	-0.174491
108	6	0	-6.588800	0.414552	1.895776
109	6	0	-6.171613	0.883879	-0.430907
110	6	0	-7.073095	0.618637	0.602495
111	1	0	-0.819022	1.508925	3.107208
112	1	0	1.574887	4.017968	3.168260
113	1	0	0.752542	2.898320	4.283431
114	1	0	0.361078	4.637342	4.269324
115	1	0	-2.612307	0.257162	2.355597
116	1	0	-3.305808	3.124472	-0.057056
117	1	0	-3.094747	5.407396	-0.756489
118	1	0	-1.405269	5.970171	-0.694595
119	1	0	-2.533833	6.501297	0.535577
120	1	0	-4.853132	0.337266	3.162790
121	1	0	-4.112622	1.098611	-0.998065
122	1	0	-7.275912	0.197039	2.709360
123	1	0	-6.533084	1.025075	-1.446305
124	1	0	-8.139125	0.561433	0.399716

Zero-point correction= 0.991582
(Hartree/Particle)
Thermal correction to Energy= 1.057329
Thermal correction to Enthalpy= 1.058273
Thermal correction to Gibbs Free Energy= 0.884839
Sum of electronic and zero-point Energies= -3710.081102
Sum of electronic and thermal Energies= -3710.015356
Sum of electronic and thermal Enthalpies= -3710.014411
Sum of electronic and thermal Free Energies= -3710.187845

IRC TS_R



IRC TS_S



Formation of the copper-phenoxide complex

The Cu complexes formed after the alkene insertion show a long Cu-C distance with the carbon atom involved in the reaction ($\mathbf{II_S}$ and $\mathbf{II_R}$, Scheme 4, main manuscript). In fact, the structure is reminiscent of a (π–allyl)Cu complex. These complexes would become protonated in a subsequent step. We have also calculated the energy for isomer **IIIs** corresponding to the slipping of the borylated substrate to afford a copper-phenoxide complex (Figure S71). This process is highly exoergic, and for that reason, we propose that protonation most likely takes place at the Cu-O bond. We cannot rule out direct reaction of copper phenoxide **IIIs** with B_2pin_2 to generate a borylated phenol and a copper(I)-boryl complex that would start over the catalytic cycle.

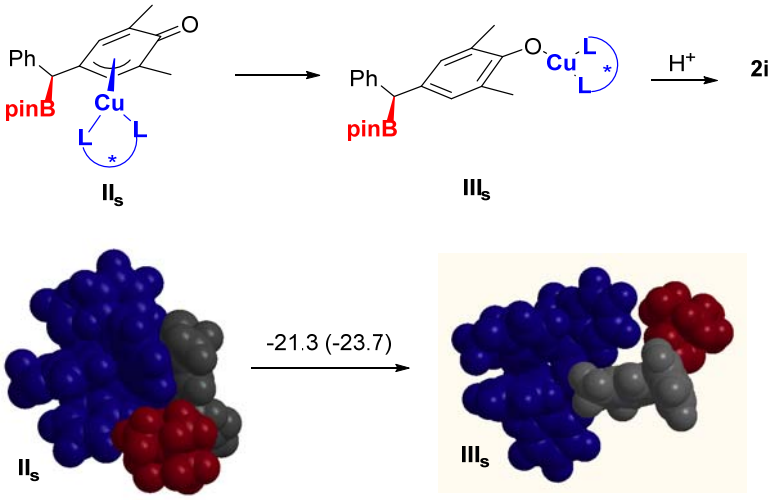
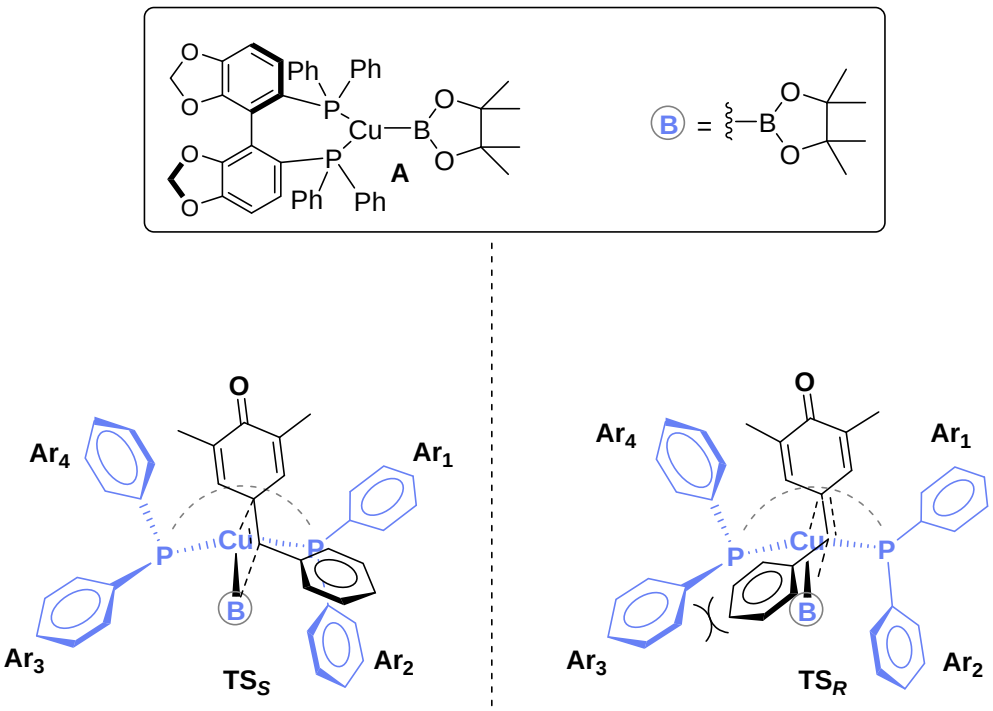


Figure S71. Calculated energy difference and equilibrium geometries for the formation of the copper-phenoxide complex at B3LYP/STO-3G (C,H,B,O,P) LANL2DZ (Cu) level. Δ(E+ZPE) and ΔG values (in brackets) in kcal mol^{-1}.

Stereochemical Model



The following rational, based on DFT-optimized geometries, was used to explain the enantioselectivity of the reaction. Gathering the substrate for either face to the (*R*)-Segphos-Cu-boryl complex gives rise to $\mathbf{TS}_{\boldsymbol{R}}$ (*Re*-face approach) and $\mathbf{TS}_{\boldsymbol{S}}$ (*Si*-face approach). To simplify the drawings we have only shown the part of the copper-boryl complex **A** that interacts directly with the *p*-quinone methide. For clarification, in $\mathbf{TS}_{\boldsymbol{S}}$ and $\mathbf{TS}_{\boldsymbol{R}}$ the *p*-quinone methide is approaching the catalyst complex from above the plane.

$\mathbf{TS}_{\boldsymbol{S}}$ is free from steric repulsion between the phenyl group of the exocyclic alkene and $\mathbf{Ar_1}$-$\mathbf{Ar_2}$ of the chiral ligand. However, $\mathbf{TS}_{\boldsymbol{R}}$ is destabilized by steric repulsion between the phenyl group and $\mathbf{Ar_3}$. This steric repulsion would also explain why both *E* and *Z* isomers of *p*-quinone methides **1o-1p** react through the *Si*-face, affording the same major enantiomer (Scheme 2, main manuscript).