Supporting Information

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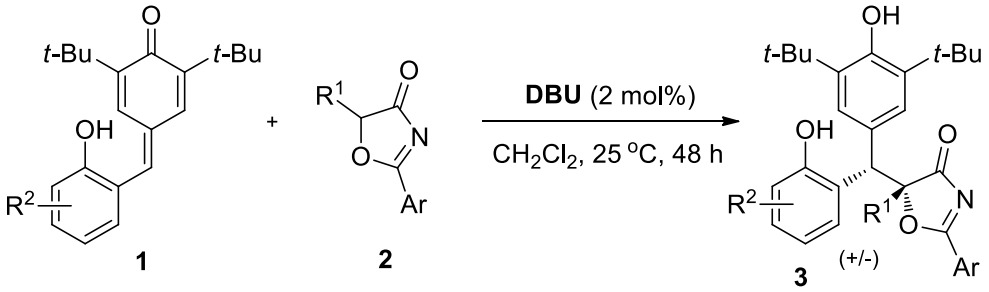
A: General Information and Starting Materials

General Information. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker ACF300 spectrometer (500 MHz and 125 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: δ 7.26; $(CD_3)_2SO$: δ 2.50). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.16; $(CD_3)_2SO$: δ 39.50). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T mass spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

Starting Materials. All solvents, inorganic reagents were from commercial sources and used without purification unless otherwise noted. The *o*-hydroxyphenyl-substituted *p*-QMs and 5*H*-oxazol-4-ones were prepared following the literature procedures.[1-2]

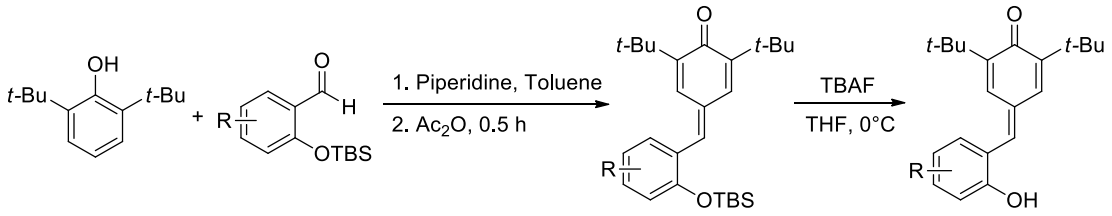
B: General Procedure for 1,4-Addition



To a solution of CH_2Cl_2 (0.3 mL) were added *ortho*-hydroxyphenyl substituted *p*-QMs **1** (0.05 mmol), 5*H*-oxazol-4-ones **2** (0.06 mmol) and catalyst **DBU** (0.001 mmol). The reaction mixture was stirred at 25 °C for 48 h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product **3**.

C: General Procedure for Synthesis of Starting Materials

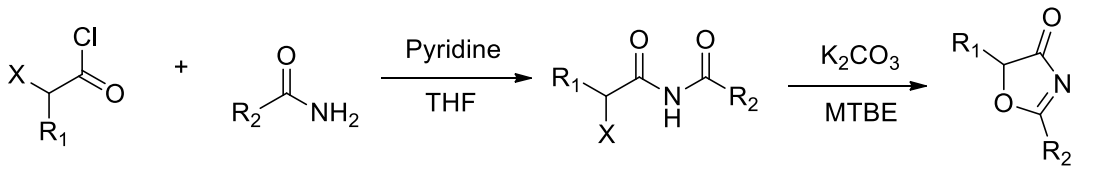
Synthesis of *o*-hydroxyphenyl-substituted *p*-QMs[1]



A solution of phenols (1.1 equiv.) and aldehydes (1.0 equiv.) in toluene (5 mL/mmol substrate) was placed in a Dean-Stark apparatus which was heated to reflux. Piperidine (2.0 equiv.) was added dropwise slowly. Then, the temperature was raised to 140 °C and stirred for 12 h. After that, the reaction mixture was cooled to 120 °C and acetic anhydride (2.0 equiv.) was dropwise added. The stirring was continued for 30 min and the solution was poured on ice-water and extracted with CH_2Cl_2 (3 × 50 mL). The organic phases were combined, washed with brine and dried over anhydrous Na_2SO_4. Then the solvent was evaporated under reduced pressure and the corresponding products were obtained after flash column chromatography (pentane/Et_2O = 100/1 to 30/1).

To a solution of product (1.0 equiv.) in THF (10 mL/mmol substrate) at 0 °C was added tetrabutylammonium fluoride trihydrate (1.1 equiv.). The reaction mixture was stirred for 10 min and a saturated NH_4Cl solution was added dropwise to quench the reaction. The resulting solution was extracted with Et_2O (3×20 mL). Then the combined organic phases were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed to give the crude product, which was purified by flash column chromatography (pentane/Et_2O = 10/1 to 4/1) to afford the desired compounds.

Synthesis of 5*H*-oxazol-4-ones[2]



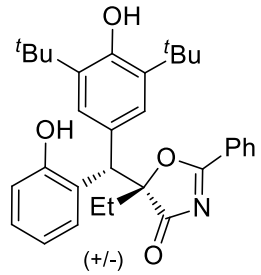
To a solution/suspension of benzamide (1.0 equiv.) and pyridine (1.0 equiv.) in THF (0.8 M) was added α-haloacylchloride dropwise over 5 min at 0 ℃. The resulting suspension was stirred overnight at rt and diluted with EtOAc. The mixture was acidified to pH=2 with 1N HCl aq. and the phases were separated. The aqueous phase was extracted with EtOAc and the combined organic layers were washed with water and brine, dried over Na_2SO_4, and filtered. Volatiles were removed under reduced pressure. The crude material was purified by either column chromatography on silica gel or recrystallization.

A suspension of K_2CO_3 in methyl *tert*-butylether (MTBE) was refluxed for 2 h to remove water using a Dean-Stark trap. The suspension was cooled to rt and animide was added in one portion. The resulting mixture was refluxed for the indicated time and cooled to room temperature. Inorganic salts were filtered through a celite pad

with suction and the filter cake was washed with EtOAc. The combined organic layers were concentrated in vacuo. The crude material was purified by flash chromatography on silica gel to give the desired product.

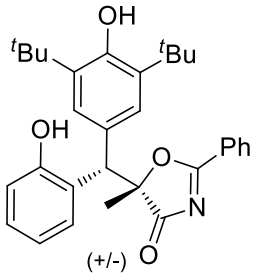
D: Characterization Data

5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3aa)



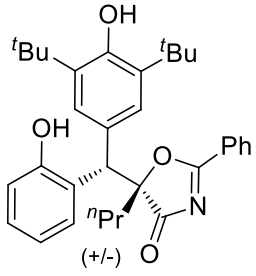
White solid, 22.6 mg, 91% yield. mp 221.1-222.0 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.59 (s, 1H), 8.16-8.15 (m, 2H), 7.87 (d, *J* = 5.0 Hz, 1H), 7.81-7.78 (m, 1H), 7.65-7.62 (m, 2H), 7.11-7.07 (m, 1H), 6.97-6.94 (m, 1H), 6.92 (s, 1H), 6.83-6.81 (m, 1H), 6.65 (s, 1H), 4.86 (s, 1H), 1.91-1.86 (m, 1H), 1.81-1.76 (m, 1H), 1.07 (s, 18H), 0.66 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 193.2, 185.3, 155.4, 153.0, 138.8, 135.9, 130.1, 129.8, 128.6, 128.2, 126.3, 125.9, 125.6, 119.8, 116.0, 110.0, 94.6, 47.5, 34.6, 30.5, 27.8, 7.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{32}H_{38}NO_4$) requires m/z 500.2795, found m/z 500.2792.

5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-methyl-2-phenyloxazol-4(5*H*)-one (3ab)



White solid, 29.5 mg, 99% yield. mp 181.2-181.9 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.22 (d, *J* = 5.0 Hz, 2H), 7.94 (d, *J* = 10.0 Hz, 1H), 7.72-7.69 (m, 1H), 7.62 (d, *J* = 10.0 Hz, 1H), 7.57-7.54 (m, 2H), 7.21-7.18 (m, 1H), 7.10 (s, 2H), 7.07-7.04 (m, 1H), 7.01 (d, *J* = 10.0 Hz, 1H), 5.42 (s, 1H), 4.91 (s, 1H), 1.64 (s, 3H), 1.10 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 185.4, 154.5, 152.9, 135.3, 130.1, 129.1, 129.0, 128.1, 127.3, 127.3, 125.9, 125.8, 125.8, 120.3, 116.3, 110.0, 92.4, 48.5, 33.9, 29.9, 21.1. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{31}H_{36}NO_4$) requires m/z 486.2639, found m/z 486.2633.

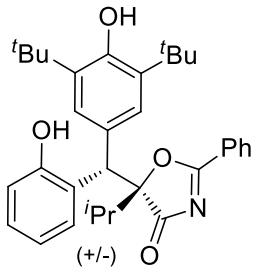
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-2-phenyl-5-propyloxazol-4(5*H*)-one (3ac)



White solid, 21.7 mg, 85% yield. mp 218.9-221.8 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.59 (s, 1H), 8.15 (d, *J* = 10.0 Hz, 2H), 7.88 (d, *J* = 5.0 Hz, 1H), 7.81-7.78 (m, 1H), 7.65-7.62 (m, 2H), 7.11-7.08 (m, 1H), 6.97-6.95 (m, 1H), 6.91 (s, 2H), 6.83-6.82 (m, 1H), 6.65 (s, 1H), 4.85 (s, 1H), 1.86-1.80 (m, 1H), 1.76-1.70 (m, 1H), 1.19-1.15 (m, 1H), 1.06 (s, 18H), 1.00-0.94 (m, 1H), 0.70 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 193.3, 185.2, 155.4, 153.0, 138.7, 135.9, 130.1,

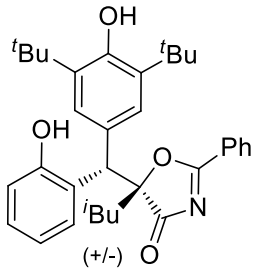
129.8, 129.2, 128.5, 128.2, 126.3, 125.9, 125.6, 119.8, 116.0, 94.3, 47.9, 36.7, 34.6, 30.5, 16.4, 14.2. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{33}H_{40}NO_4$) requires m/z 514.2952, found m/z 514.2949.

5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-isopropyl-2-phenyloxazol-4(5*H*)-one (3ad)



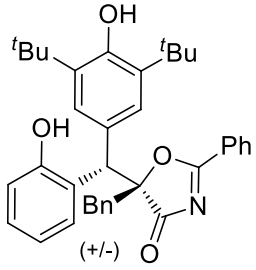
White solid, 28.9 mg, 99% yield. mp 153.1-154.1 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.63 (s, 1H), 8.13 (d, *J* = 10.0 Hz, 2H), 7.93 (d, *J* = 10.0 Hz, 1H), 7.79-7.76 (m, 1H), 7.63-7.60 (m, 2H), 7.11-7.08 (m, 1H), 6.98-6.95 (m, 1H), 6.91 (s, 2H), 6.84 (d, *J* = 5.0 Hz, 1H), 6.62 (s, 1H), 5.01 (s, 1H), 2.31-2.26 (m, 1H), 1.06 (s, 18H), 1.02 (d, *J* = 10.0 Hz, 3H), 0.67 (d, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 192.3, 184.9, 155.0, 152.9, 138.6, 135.8, 130.0, 129.7, 128.3, 128.2, 126.2, 126.0, 125.5, 119.6, 116.1, 96.4, 46.0, 34.6, 32.3, 30.5, 17.0, 14.7. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{33}H_{40}NO_4$) requires m/z 514.2952, found m/z 514.2948.

5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-isobutyl-2-phenyloxazol-4(5*H*)-one (3ae)



White solid, 25.8 mg, 98% yield. mp 219.2-221.5 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.57 (s, 1H), 8.14 (d, *J* = 10.0 Hz, 2H), 7.88 (d, *J* = 10.0 Hz, 1H), 7.81-7.78 (m, 1H), 7.65-7.62 (m, 2H), 7.11-7.07 (m, 1H), 6.98-6.95 (m, 1H), 6.88 (s, 2H), 6.82 (d, *J* = 5.0 Hz, 1H), 6.65 (s, 1H), 4.80 (s, 1H), 1.87-1.83 (m, 1H), 1.75-1.72 (m, 1H), 1.41-1.36 (m, 1H), 1.05 (s, 18H), 0.71 (d, *J* = 5.0 Hz, 6H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 193.5, 185.2, 155.5, 153.0, 138.7, 136.0, 130.0, 129.9, 128.3, 128.2, 126.5, 125.9, 125.7, 119.8, 116.0, 94.4, 49.0, 43.2, 34.6, 30.4, 24.6, 24.5, 23.7. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{34}H_{42}NO_4$) requires m/z 528.3108, found m/z 528.3106.

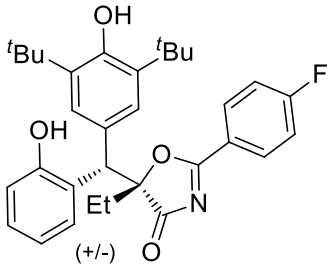
5-benzyl-5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-2-phenyloxazol-4(5*H*)-one (3af)



White solid, 26.5 mg, 94% yield. mp 140.8-142.3 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.68 (s, 1H), 8.05 (d, *J* = 5.0 Hz, 1H), 8.01 (d, *J* = 5.0 Hz, 2H), 7.75-7.72 (m, 1H), 7.58-7.55 (m, 2H), 7.15-7.12 (m, 1H), 7.08-7.03 (m, 6H), 6.95 (s, 2H), 6.87 (d, *J* = 10.0 Hz, 1H), 6.67 (s, 1H), 5.01 (s, 1H), 3.20 (d, *J* = 15.0 Hz, 1H), 3.03 (d, *J* = 15.0 Hz, 1H), 1.06 (s, 18H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 192.3, 184.8, 155.6, 153.0, 138.8, 135.8, 134.1, 130.2, 129.8, 129.7, 129.2, 128.7, 128.4, 128.3, 127.5, 126.4, 125.9, 125.5, 120.0, 116.1, 94.1, 48.0, 34.6, 30.5. HRMS (ESI): exact mass

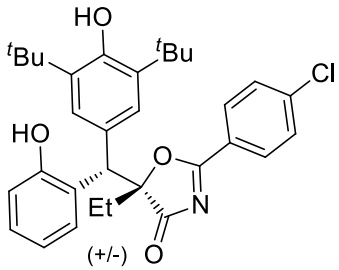
calculated for $[M+H]^+$ ($C_{37}H_{40}NO_4$) requires m/z 562.2952, found m/z 562.2947.

5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyl-2-(4-fluorophenyl)oxazol-4(5*H*)-one (3ag)



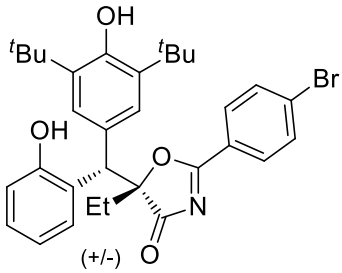
White solid, 22.7 mg, 88% yield. mp 229.1-230.7 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.60 (s, 1H), 8.26-8.23 (m, 2H), 7.87 (d, *J* = 10.0 Hz, 1H), 7.50-7.47 (m, 2H), 7.11-7.08 (m, 1H), 6.96-6.93 (m, 1H), 6.92 (s, 2H), 6.83 (d, *J* = 10.0 Hz, 1H), 6.67 (s, 1H), 4.87 (s, 1H), 1.92-1.87 (m, 1H), 1.81-1.77 (m, 1H), 1.09 (s, 18H), 0.67 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 193.0, 184.2, 166.9 (d, *J* = 1015.0 Hz), 155.4, 153.0, 138.8, 133.2 (d, *J* = 40.0 Hz), 129.2, 128.6, 128.2, 126.2, 125.8, 122.3, 119.7, 117.2 (d, *J* = 90.0 Hz), 116.0, 95.0, 60.2, 47.6, 34.6, 30.5, 27.8, 14.5, 7.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{32}H_{37}FNO_4$) requires m/z 518.2701, found m/z 518.2699.

2-(4-chlorophenyl)-5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyloxazol-4(5*H*)-one (3ah)



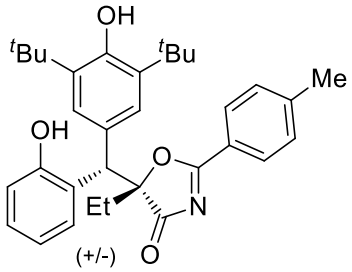
White solid, 28.1 mg, 99% yield. mp 200.1-202.6 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.60 (s, 1H), 8.16 (d, *J* = 10.0 Hz, 2H), 7.85 (d, *J* = 5.0 Hz, 1H), 7.73(d, *J* = 5.0 Hz, 2H), 7.11-7.07 (m, 1H), 6.96-6.93 (m, 1H), 6.90 (s, 2H), 6.82 (d, *J* = 10.0 Hz, 1H), 6.67 (s, 1H), 4.86 (s, 1H), 1.91-1.86 (m, 1H), 1.80-1.76 (m, 1H), 1.08 (s, 18H), 0.66 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 193.0, 184.3, 155.4, 153.0, 140.9, 138.8, 131.8, 130.0, 129.2, 128.5, 128.2, 126.1, 125.8, 124.5, 119.7, 116.0, 95.0, 47.6, 34.6, 30.5, 27.7, 7.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{32}H_{37}ClNO_4$) requires m/z 534.2406, found m/z 534.2405.

2-(4-bromophenyl)-5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyloxazol-4(5*H*)-one (3ai)



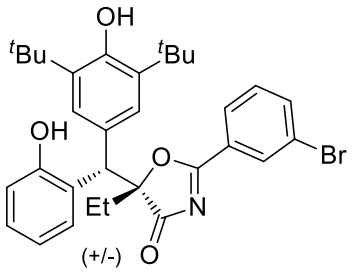
White solid, 28.4 mg, 98% yield. mp 149.1-150.3 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.60 (s, 1H), 8.07 (d, *J* = 10.0 Hz, 2H), 7.87-7.84 (m, 3H), 7.11-7.08 (m, 1H), 6.96-6.93 (m, 1H), 6.90 (s, 2H), 6.83 (d, *J* = 5.0 Hz, 1H), 6.67 (s, 1H), 4.87 (s, 1H), 1.91-1.87 (m, 1H), 1.81-1.76 (m, 1H), 1.08 (s, 18H), 0.66 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 193.1, 184.5, 155.4, 153.0, 138.8, 133.0, 131.8, 130.2, 129.2, 128.5, 128.2, 126.1, 125.8, 124.8, 119.7, 116.0, 95.0, 47.6, 34.6, 30.5, 27.7, 7.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{32}H_{37}BrNO_4$) requires m/z 578.1900, found m/z 578.1897.

5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyl-2-(*p*-tolyl)oxazol-4(5*H*)-one (3aj)



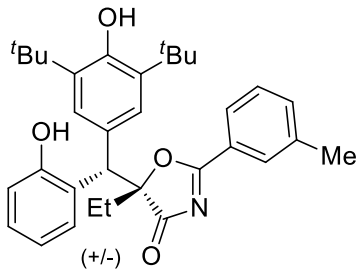
White solid, 27.9 mg, 99% yield. mp 231.9-233.2 ^{o}C. ^{1}H NMR ((CD$_3$)$_2$SO, 500 MHz): δ (ppm) 9.58 (s, 1H), 8.05 (d, *J* = 5.0 Hz, 2H), 7.86 (d, *J* = 5.0 Hz, 1H), 7.45 (d, *J* = 5.0 Hz, 2H), 7.10-7.07 (m, 1H), 6.96-6.93 (m, 1H), 6.92 (s, 2H), 6.83-6.81 (m, 1H), 6.65 (s, 1H), 4.86 (s, 1H), 2.42 (s, 3H), 1.89-1.84 (m, 1H), 1.79-1.75 (m, 1H), 1.08 (s, 18H), 0.65 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ((CD$_3$)$_2$SO, 125 MHz): δ (ppm) 193.2, 185.2, 155.4, 153.0, 146.9, 138.7, 130.3, 130.1, 129.2, 128.8, 128.1, 126.4, 125.8, 122.9, 119.8, 116.0, 94.4, 47.5, 34.6, 30.5, 27.9, 21.9, 7.4. HRMS (ESI): exact mass calculated for [M+H]$^+$ (C$_{33}$H$_{40}$NO$_4$) requires m/z 514.2952, found m/z 514.2951.

2-(3-bromophenyl)-5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyloxazol-4(5*H*)-one (3ak)



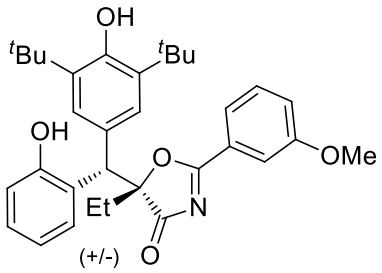
White solid, 28.2 mg, 98% yield. mp 150.2-152.3 ^{o}C. ^{1}H NMR ((CD$_3$)$_2$SO, 500 MHz): δ (ppm) 9.60 (s, 1H), 8.21 (s, 1H), 8.15 (d, *J* = 10.0 Hz, 1H), 8.00 (d, *J* = 10.0 Hz, 1H), 7.85 (d, *J* = 10.0 Hz, 1H), 7.61-7.58 (m, 1H), 7.11-7.08 (m, 1H), 6.98-6.95 (m, 1H), 6.90 (s, 2H), 6.83 (d, *J* = 10.0 Hz, 1H), 6.68 (s, 1H), 4.87 (s, 1H), 1.94-1.89 (m, 1H), 1.82-1.77 (m, 1H), 1.09 (s, 18H), 0.68 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ((CD$_3$)$_2$SO, 125 MHz): δ (ppm) 193.0, 184.0, 155.4, 153.0, 138.8, 138.5, 132.0, 132.0, 129.1, 128.3, 128.2, 127.8, 126.0, 125.9, 122.8, 119.8, 116.0, 110.0, 95.2, 47.7, 34.6, 30.4, 27.7, 7.4. HRMS (ESI): exact mass calculated for [M+H]$^+$ (C$_{32}$H$_{37}$BrNO$_4$) requires m/z 578.1900, found m/z 578.1901.

5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyl-2-(*m*-tolyl)oxazol-4(5*H*)-one (3al)



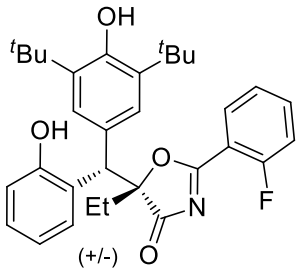
White solid, 31.2 mg, 99% yield. mp 143.2-145.1 ^{o}C. ^{1}H NMR ((CD$_3$)$_2$SO, 500 MHz): δ (ppm) 9.59 (s, 1H), 7.96-7.95 (m, 2H), 7.87 (d, *J* = 5.0 Hz, 1H), 7.60 (d, *J* = 10.0 Hz, 1H), 7.53-7.49 (m, 1H), 7.11-7.07 (m, 1H), 6.98-6.95 (m, 1H), 6.93 (s, 2H), 6.84-6.82 (m, 1H), 6.65 (s, 1H), 4.87 (s, 1H), 2.40 (s, 3H), 1.90-1.86 (m, 1H), 1.80-1.76 (m, 1H), 1.08 (s, 18H), 0.66 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ((CD$_3$)$_2$SO, 125 MHz): δ (ppm) 193.2, 185.4, 155.4, 153.0, 139.3, 138.7, 136.5, 130.3, 129.7, 129.2, 128.6, 128.2, 127.3, 126.3, 125.9, 125.6, 119.8, 116.0, 94.6, 47.6, 34.6, 30.5, 27.8, 21.2, 7.4. HRMS (ESI): exact mass calculated for [M+H]$^+$ (C$_{33}$H$_{40}$NO$_4$) requires m/z 514.2952, found m/z 514.2952.

5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyl-2-(3-methoxyphenyl)oxazol-4(5*H*)-one (3am)



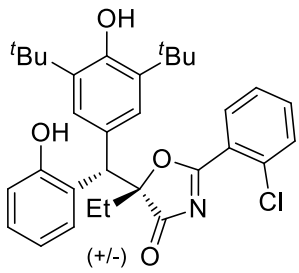
White solid, 32.8 mg, 99% yield. mp 180.2-182.5 ^{o}C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.60 (s, 1H), 7.84 (d, *J* = 10.0 Hz, 1H), 7.77 (d, *J* = 10.0 Hz, 1H), 7.58-7.55 (m, 2H), 7.38-7.36 (m, 1H), 7.10-7.07 (m, 1H), 6.97-6.94 (m, 1H), 6.92 (s, 2H), 6.83 (d, *J* = 5.0 Hz, 1H), 6.67 (s, 1H), 4.86 (s, 1H), 3.82 (s, 3H), 1.91-1.86 (m, 1H), 1.81-1.76 (m, 1H), 1.08 (s, 18H), 0.66 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 193.2, 185.2, 156.0, 155.4, 153.0, 138.8, 131.1, 129.2, 128.6, 128.2, 126.9, 126.3, 125.9, 122.3, 121.9, 119.8, 116.0, 114.6, 94.8, 56.0, 47.6, 34.6, 30.5, 27.8, 7.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{33}H_{40}NO_5$) requires m/z 530.2901, found m/z 530.2901.

5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyl-2-(2-fluorophenyl)oxazol-4(5*H*)-one (3an)



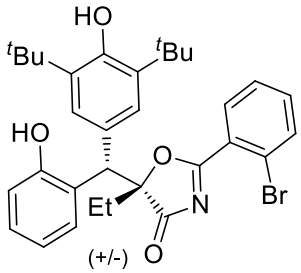
White solid, 28.2 mg, 99% yield. mp 190.1-192.2 ^{o}C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.60 (s, 1H), 8.08-8.04 (m, 1H), 7.85-7.82 (m, 2H), 7.53-7.49 (m, 1H), 7.44-7.41 (m, 1H), 7.10-7.07 (m, 1H), 6.93 (s, 2H), 6.92-6.91 (m, 1H), 6.83-6.82 (m, 1H) 6.69 (s, 1H), 4.87 (s, 1H), 1.90-1.85 (m, 1H), 1.81-1.76 (m, 1H), 1.09 (s, 18H), 0.68 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 192.9, 183.4, 162.1 (d, *J* = 1045.0 Hz), 155.4, 153.0, 138.8, 138.3 (d, *J* = 35.0 Hz), 133.0, 129.0, 128.4, 128.2, 126.1, 125.8, 119.6, 118.1 (d, *J* = 85.0 Hz), 116.0, 113.8 (d, *J* = 30.0 Hz), 94.3, 47.4, 34.6, 30.5, 27.8, 7.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{32}H_{37}FNO_4$) requires m/z 518.2701, found m/z 518.2700.

2-(2-chlorophenyl)-5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyloxazol-4(5*H*)-one (3ao)



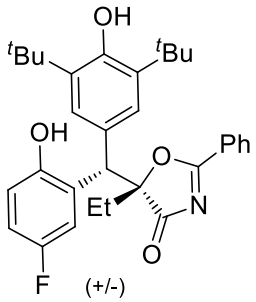
White solid, 21.8 mg, 82% yield. mp 145.9-147.5 ^{o}C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.59 (s, 1H), 8.01-7.99 (m, 1H), 7.82 (d, *J* = 5.0 Hz, 1H), 7.72-7.69 (m, 2H), 7.55-7.52 (m, 1H), 7.10-7.06 (m, 1H), 6.93-6.91 (m, 1H), 6.90 (s, 2H), 6.83-6.81 (m, 1H), 6.70 (s, 1H), 4.88 (s, 1H), 1.94-1.90 (m, 1H), 1.81-1.77 (m, 1H), 1.10 (s, 18H), 0.71 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 193.2, 184.7, 155.4, 153.1, 138.6, 136.2, 134.4, 133.7, 132.5, 129.2, 128.3, 128.2, 125.9, 125.8, 124.4, 119.6, 116.1, 94.8, 47.5, 34.6, 30.4, 27.8, 7.5. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{32}H_{37}ClNO_4$) requires m/z 534.2406, found m/z 534.2405.

2-(2-bromophenyl)-5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyloxazol-4(5*H*)-one (3ap)



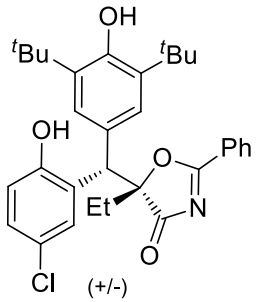
White solid, 26.7 mg, 93% yield. mp 210.3-212.5 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.59 (s, 1H), 7.92-7.90 (m, 1H), 7.89-7.87 (m, 1H), 7.86-7.74 (m, 1H), 7.63-7.59 (m, 1H), 7.57-7.54 (m, 1H), 7.10-7.06 (m, 1H), 6.93 (d, *J* = 5.0 Hz, 1H), 6.90 (s, 2H), 6.82 (d, *J* = 10.0 Hz, 1H), 6.70 (s, 1H), 4.88 (s, 1H), 1.96-1.91 (m, 1H), 1.81-1.77 (m, 1H), 1.10 (s, 18H), 0.73 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 193.2, 185.2, 155.4, 153.1, 138.6, 136.1, 135.9, 133.9, 129.3, 128.7, 128.2, 128.1, 126.3, 125.9, 122.6, 119.6, 116.1, 95.1, 47.5, 34.6, 30.5, 27.8, 7.6. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{32}H_{37}BrNO_4$) requires m/z 578.1900, found m/z 578.1902.

5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(5-fluoro-2-hydroxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3ba)



White solid, 24.1 mg, 93% yield. mp 177.4-179.9 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.69 (s, 1H), 8.14 (d, *J* = 10.0 Hz, 2H), 7.81-7.78 (m, 1H), 7.66-7.63 (m, 2H), 7.58-7.55 (m, 1H), 6.98-6.94 (m, 1H), 6.89 (s, 2H), 6.84-6.81 (m, 1H), 6.72 (s, 1H), 4.84 (s, 1H), 1.93-1.89 (m, 1H), 1.83-1.79 (m, 1H), 1.07 (s, 18H), 0.68 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 192.8, 185.3, 155.8 (d, *J* = 935.0 Hz), 153.2, 151.8, 138.9, 136.0, 130.0 (d, *J* = 90.0 Hz), 127.9, 127.6 (d, *J* = 25.0 Hz), 125.7, 125.5, 116.8 (d, *J* = 35.0 Hz), 115.3, 115.1, 114.5 (d, *J* = 90.0 Hz), 94.3, 47.7, 34.6, 30.4, 27.8, 18.5, 7.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{32}H_{37}FNO_4$) requires m/z 518.2701, found m/z 518.2700.

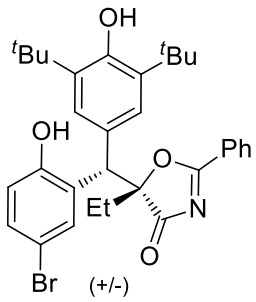
5-((5-chloro-2-hydroxyphenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3ca)



White solid, 23.4 mg, 88% yield. mp 140.1-141.7 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 10.02 (s, 1H), 8.10 (d, *J* = 5.0 Hz, 2H), 7.82-7.79 (m, 1H), 7.77-7.76 (m, 1H), 7.68-7.65 (m, 2H), 7.17-7.15 (m, 1H), 6.89 (s, 2H), 6.85 (d, *J* = 10.0 Hz, 1H), 6.74 (s, 1H), 4.83 (s, 1H), 1.91-1.87 (m, 1H), 1.84-1.79 (m, 1H), 1.07 (s, 18H), 0.68 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 192.7, 185.2, 154.4, 153.2, 139.0, 136.1, 129.9, 129.8, 128.7, 128.3, 128.0, 127.8, 125.7, 125.5, 123.0, 117.6, 94.3, 47.5, 34.6, 30.4, 27.8, 7.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{32}H_{37}ClNO_4$) requires m/z 534.2406, found m/z 534.2407.

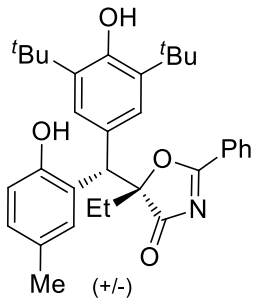
5-((5-bromo-2-hydroxyphenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-5-ethyl

-2-phenyloxazol-4(5*H*)-one (3da)



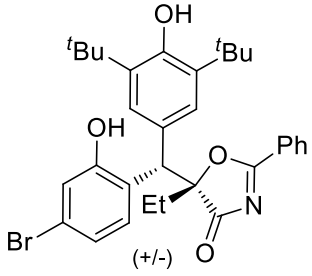
White solid, 25.1 mg, 87% yield. mp 235.2-237.7 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 10.05 (s, 1H), 8.09-8.08 (m, 2H), 7.92-7.91 (m, 1H), 7.81-7.78 (m, 1H), 7.67-7.64 (m, 2H), 7.29-7.27 (m, 1H), 6.90 (s, 2H), 6.82 (d, *J* = 10.0 Hz, 1H), 6.74 (s, 1H), 4.84 (s, 1H), 1.91-1.87 (m, 1H), 1.85-1.80 (m, 1H), 1.08 (s, 18H), 0.69 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 192.7, 185.2, 154.8, 153.2, 139.0, 136.1, 131.7, 130.8, 129.9, 129.8, 128.8, 127.9, 125.7, 125.5, 118.2, 110.6, 94.3, 47.5, 34.6, 30.4, 27.8, 7.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{32}H_{37}BrNO_4$) requires m/z 578.1900, found m/z 578.1900.

5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxy-5-methylphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3ea)



White solid, 29.6 mg, 99% yield. mp 134.2-136.6 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.37 (s, 1H), 8.14 (d, *J* = 5.0 Hz, 2H), 7.80-7.77 (m, 1H), 7.66-7.63 (m, 3H), 6.94 (s, 2H), 6.89 (d, *J* = 5.0 Hz, 1H), 6.73 (d, *J* = 5.0 Hz, 1H), 6.66 (s, 1H), 4.86 (s, 1H), 2.32 (s, 3H), 1.91-1.86 (m, 1H), 1.82-1.78 (m, 1H), 1.08 (s, 18H), 0.67 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 193.2, 185.2, 153.1, 153.0, 138.8, 135.9, 123.0, 129.8, 128.8, 128.5, 128.0, 126.0, 125.8, 125.6, 115.8, 94.7, 47.4, 34.6, 30.5, 27.8, 21.2, 14.5, 7.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{33}H_{39}NO_4$) requires m/z 514.2952, found m/z 514.2951.

5-((4-bromo-2-hydroxyphenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3fa)

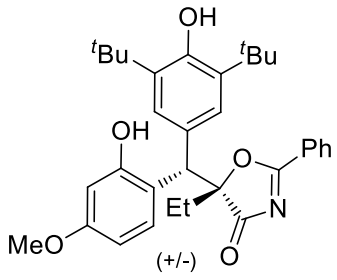


White solid, 25.3 mg, 88% yield. mp 207.0-208.3 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 10.19 (s, 1H), 8.17 (d, *J* = 5.0 Hz, 2H), 7.83-7.77 (m, 2H), 7.64-7.61 (m, 2H), 7.16-7.14 (m, 1H), 7.00-6.99 (m, 1H), 6.88 (s, 2H), 6.69 (s, 1H), 4.79 (s, 1H), 1.90-1.86 (m, 1H), 1.80-1.76 (m, 1H), 1.07 (s, 18H), 0.67 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 193.0, 185.3, 156.7, 153.1, 138.9, 136.0, 130.9, 130.1, 129.8, 128.0, 126.0, 125.8, 125.5, 122.6, 120.4, 118.6, 94.2, 47.4, 34.6, 30.5, 27.8, 7.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{32}H_{37}BrNO_4$) requires m/z 578.1900, found m/z 578.1902.

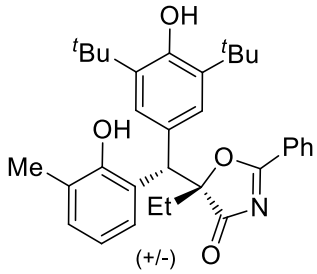
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxy-4-methoxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3ga)

White solid, 22.8 mg, 86% yield. mp 79.4-80.2 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ

(ppm) 9.65 (s, 1H), 8.15 (d, *J* = 10.0 Hz, 2H), 7.80-7.75 (m, 2H), 7.65-7.61 (m, 2H), 6.90 (s, 2H), 6.64 (s, 1H), 6.58-6.55 (m, 1H), 6.41-6.40 (m, 1H), 4.77 (s, 1H), 3.68 (s, 3H), 1.90-1.85 (m, 1H), 1.80-1.76 (m, 1H), 1.07 (s, 18H), 0.66 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 193.3, 185.2, 159.2, 156.4, 152.9, 138.7, 135.9, 130.0, 129.8, 129.2, 125.7, 125.6, 118.8, 105.4, 101.7, 94.9, 55.3, 47.1, 34.6, 30.5, 27.8, 7.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{33}H_{40}NO_5$) requires m/z 530.2901, found m/z 530.2901.

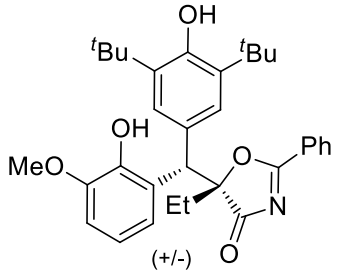


5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxy-3-methylphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3ha)



White solid, 23.2 mg, 92% yield. mp 223.1-224.5 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 8.46 (s, 1H), 8.15 (d, *J* = 5.0 Hz, 2H), 7.80-7.76 (m, 2H), 7.64-7.61 (m, 2H), 7.01 (d, *J* = 5.0 Hz, 1H), 6.94 (s, 2H), 6.92-6.91 (m, 1H), 6.64 (s, 1H), 4.99 (s, 1H), 2.16 (s, 3H), 1.93-1.89 (m, 1H), 1.82-1.78 (m, 1H), 1.07 (s, 18H), 0.66 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 193.3, 185.2, 153.2, 153.0, 138.7, 135.9, 130.0, 129.8, 129.6, 128.7, 127.6, 126.7, 126.0, 125.6, 125.6, 120.2, 94.8, 48.1, 34.6, 30.5, 27.8, 17.6, 7.5. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{33}H_{39}NO_4$) requires m/z 514.2952, found m/z 514.2950.

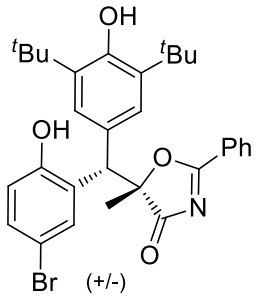
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxy-3-methoxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3ia)



White solid, 27.3 mg, 99% yield. mp 83.1-84.0 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 8.74 (s, 1H), 8.15 (d, *J* = 10.0 Hz, 2H), 7.80-7.77 (m, 1H), 7.65-7.62 (m, 2H), 7.50 (d, *J* = 10.0 Hz, 1H), 6.95-6.94 (m, 1H), 6.93 (s, 2H), 6.87 (d, *J* = 10.0 Hz, 1H), 6.65 (s, 1H), 4.91 (s, 1H), 3.76 (s, 3H), 1.90-1.86 (m, 1H), 1.80-1.76 (m, 1H), 1.07 (s, 18H), 0.66 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 193.2, 185.3, 153.0, 148.0, 144.5, 138.8, 135.9, 130.0, 129.8, 128.6, 126.6, 125.9, 125.6, 120.9, 119.5, 110.4, 94.6, 56.1, 47.7, 34.6, 30.5, 27.8, 7.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{33}H_{40}NO_5$) requires m/z 530.2901, found m/z 530.2897.

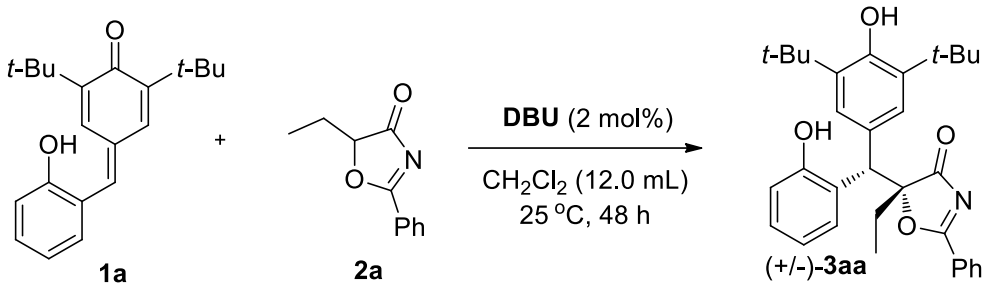
5-((5-bromo-2-hydroxyphenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-5-methyl-2-phenyloxazol-4(5*H*)-one (3db)

White solid, 27.3 mg, 99% yield. mp 166.4-168.8 °C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 10.05 (s, 1H), 8.07 (d, *J* = 5.0 Hz, 2H), 7.93-7.92 (m, 1H), 7.80-7.77 (m, 1H), 7.67-7.64 (m, 2H), 7.30-7.28 (m, 1H), 6.89 (s, 2H), 6.82 (d, *J* = 10.0 Hz, 1H), 6.74 (s,



1H), 4.79 (s, 1H), 1.45 (s, 3H), 1.08 (s, 18H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 193.4, 184.6, 155.0, 153.3, 139.0, 136.0, 131.7, 130.9 129.8, 128.7, 127.9, 125.8, 125.6, 118.2, 110.6, 90.7, 48.1, 34.6, 30.4, 21.2. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{31}H_{35}BrNO_4$) requires m/z 564.1744, found m/z 564.1743.

E: Large Scale Reaction



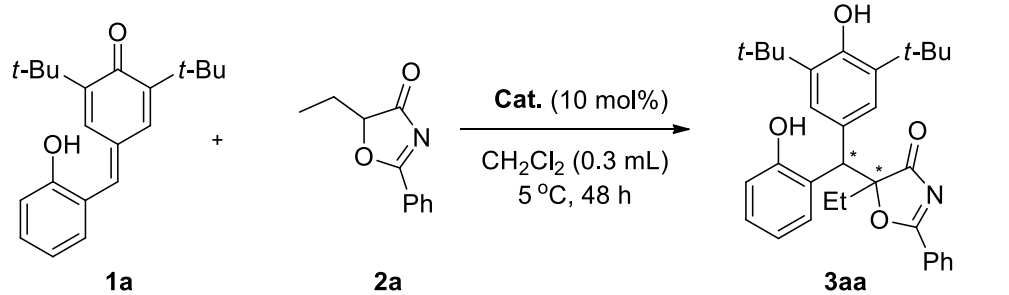
1a 620.0 mg, 2.0 mmol

2a 453.6 mg, 2.4 mmol

910.2 mg, 91% yield, >20:1 dr

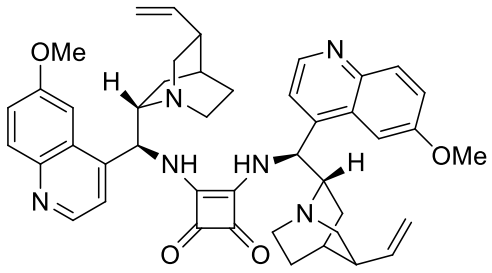
To a solution of CH_2Cl_2 (12.0 mL) were added *ortho*-hydroxyphenyl substituted *p*-QMs **1a** (620.0 mg, 2.0 mmol), 5*H*-oxazol-4-one **2a** (453.6 mg, 2.4 mmol) and **DBU** (6.08 mg, 0.04 mmol). The reaction mixture was stirred at 25 ^{o}C for 48 h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product **3aa** (910.2 mg, 91% yield, >20:1 dr).

F: Asymmetric Experiment



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

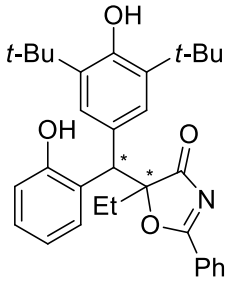
68% yield, 0% ee, >20:1 dr



Cat.

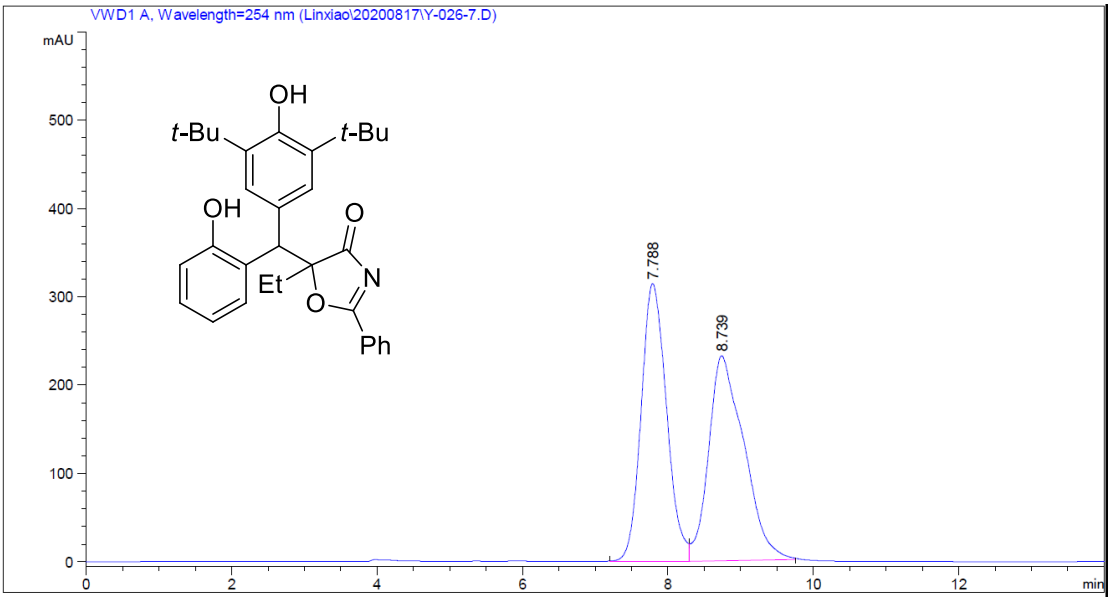
To a solution of CH_2Cl_2 (0.3 mL) were added *ortho*-hydroxyphenyl substituted *p*-QMs **1a** (0.05 mmol), 5*H*-oxazol-4-ones **2a** (0.06 mmol) and chiral catalyst (0.005 mmol). The reaction mixture was stirred at 5 ^{o}C for 48 h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product **3aa**.

5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3aa)

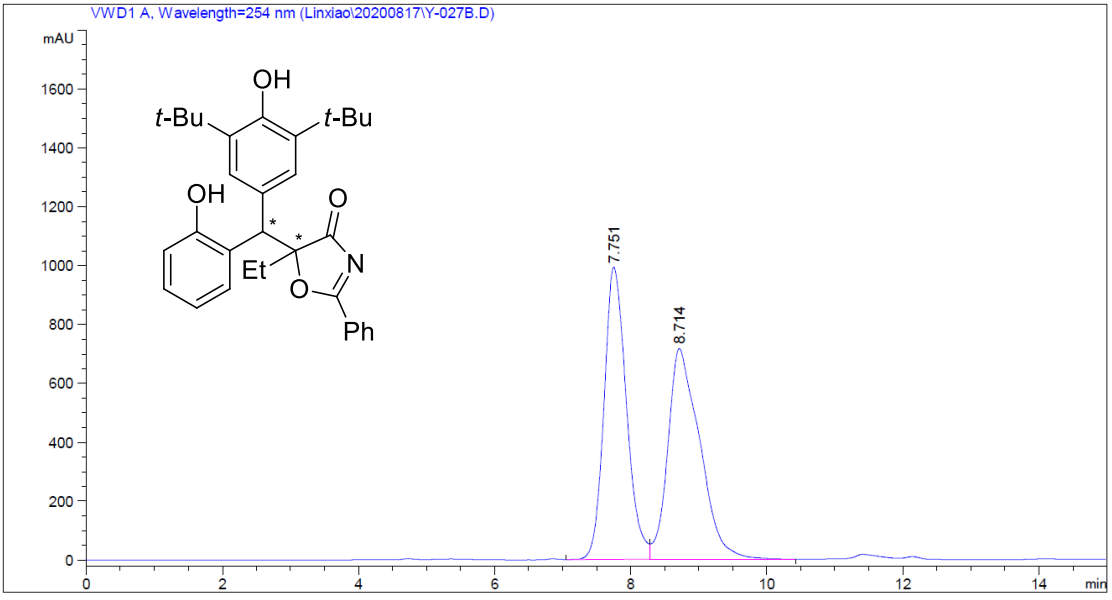


White solid, 17.0 mg, 68% yield. mp 221.1-222.0 ^{o}C. ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): δ (ppm) 9.59 (s, 1H), 8.16-8.15 (m, 2H), 7.87 (d, *J* = 5.0 Hz, 1H), 7.81-7.78 (m, 1H), 7.65-7.62 (m, 2H), 7.11-7.07 (m, 1H), 6.97-6.94 (m, 1H), 6.92 (s, 1H), 6.83-6.81 (m, 1H), 6.65 (s, 1H), 4.86 (s, 1H), 1.91-1.86 (m, 1H), 1.81-1.76 (m, 1H), 1.07 (s, 18H), 0.66 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz): δ (ppm) 193.2, 185.3, 155.4, 153.0, 138.8, 135.9, 130.1, 129.8, 128.6, 128.2, 126.3, 125.9, 125.6, 119.8, 116.0, 110.0, 94.6, 47.5, 34.6, 30.5, 27.8, 7.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{32}H_{38}NO_4$) requires m/z 500.2795, found m/z 500.2792. The enantiomeric excess was determined to be 0% by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 90:10, 0.8 mL/min]: 7.7 min (major), 8.7 min (minor).

5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3aa)

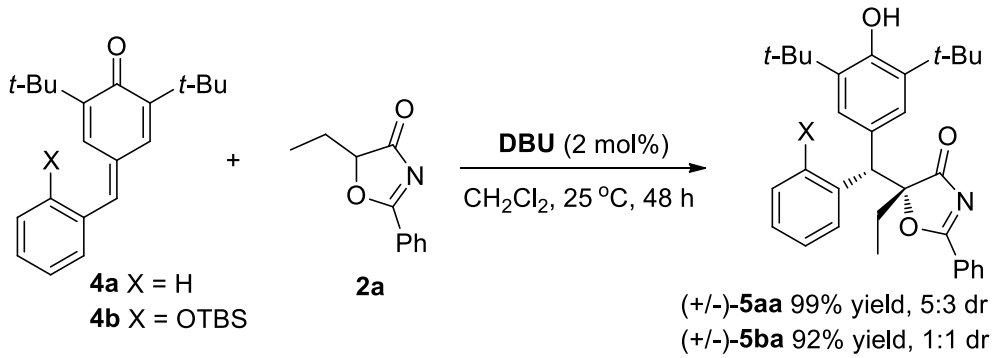


#	Time	Area	Height	Width	Symmetry	Area %
1	7.788	7618	314.3	0.404	0.802	49.307
2	8.739	7832.2	231.9	0.5628	0.585	50.693



#	Time	Area	Height	Width	Symmetry	Area %
1	7.751	22656.7	992.2	0.3544	0.747	49.306
2	8.714	23294.7	716.5	0.4503	0.546	50.694

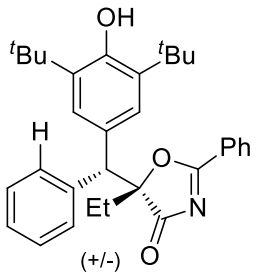
G: Control Experiments



To a solution of CH_2Cl_2 (0.3 mL) were added *para*-quinone methides **4a** (14.7 mg, 0.05 mmol), 5*H*-oxazol-4-one **2a** (11.34 mg, 0.06 mmol) and **DBU** (0.15 mg, 0.001 mmol). The reaction mixture was stirred at 25 ^oC for 48 h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product **5aa** (24.8 mg, 99% yield, 5:3 dr).

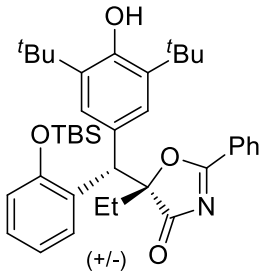
To a solution of CH_2Cl_2 (0.3 mL) were added TBS-protected quinone methides **4b** (21.2 mg, 0.05 mmol), 5*H*-oxazol-4-one **2a** (11.34 mg, 0.06 mmol) and **DBU** (0.15 mg, 0.001 mmol). The reaction mixture was stirred at 25 ^oC for 48 h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product **5ba** (28.3 mg, 92% yield, 1:1 dr).

5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (5aa)



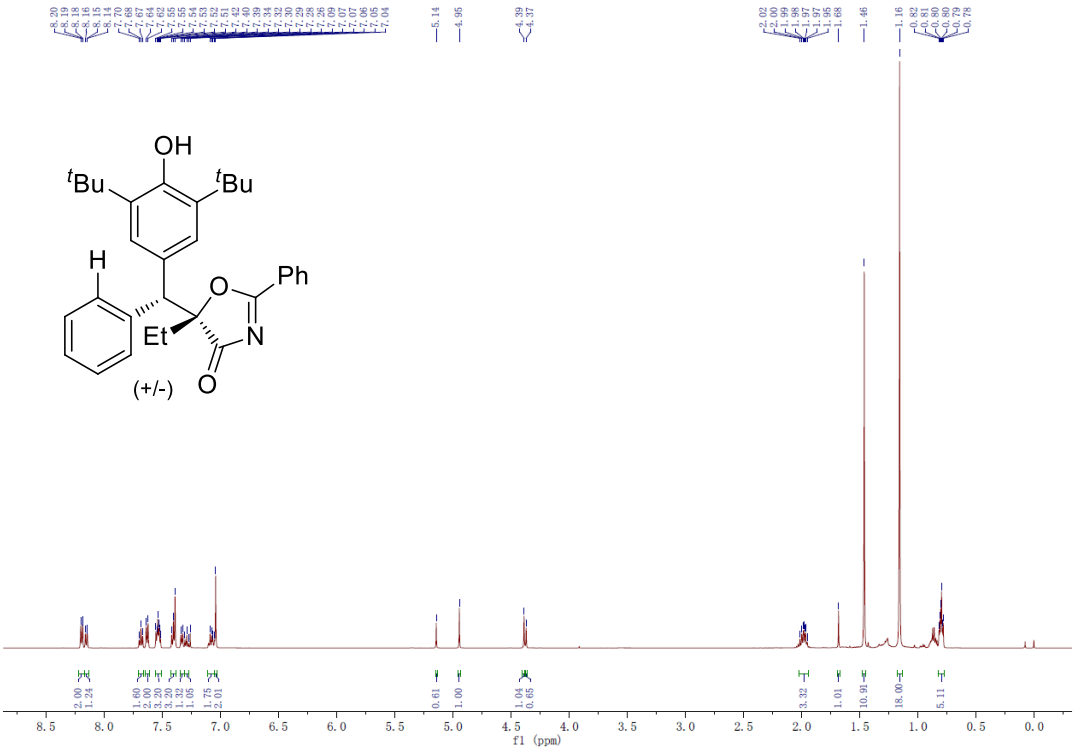
Colourless oil, 24.8 mg, 99% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.20-8.18 (m, 2H), 8.16-8.14 (m, 1.24H), 7.70-7.67 (m, 1.6H), 7.63 (d, *J* = 10.0 Hz, 2H), 7.55-7.51 (m, 3.2H), 7.42-7.39 (m, 3.2H), 7.33 (d, *J* = 10.0 Hz, 1.32H), 7.30-7.28 (m, 1H), 7.09-7.05 (m, 1.75H), 7.04 (s, 2H), 5.14 (s, 0.61H), 4.95 (s, 1H), 4.39 (s, 1H), 4.37 (s, 0.65H), 2.02-1.95 (m, 3.32H), 1.68 (s, 1H), 1.46 (s, 10.91H), 1.16 (s, 18H), 0.82-0.78 (m, 5.11H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 193.4, 185.5, 185.4, 152.9, 139.6, 138.2, 135.9, 135.3, 135.0, 134.9, 129.9, 129.7, 129.3, 129.1, 129.0, 128.9, 128.8, 128.3, 127.7, 127.1, 127.0, 125.8, 125.7, 94.9, 94.8, 57.5, 57.4, 34.4, 34.0, 30.3, 29.9, 28.4, 28.1, 7.5, 7.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{32}H_{38}NO_3$) requires m/z 484.2852, found m/z 484.2846.

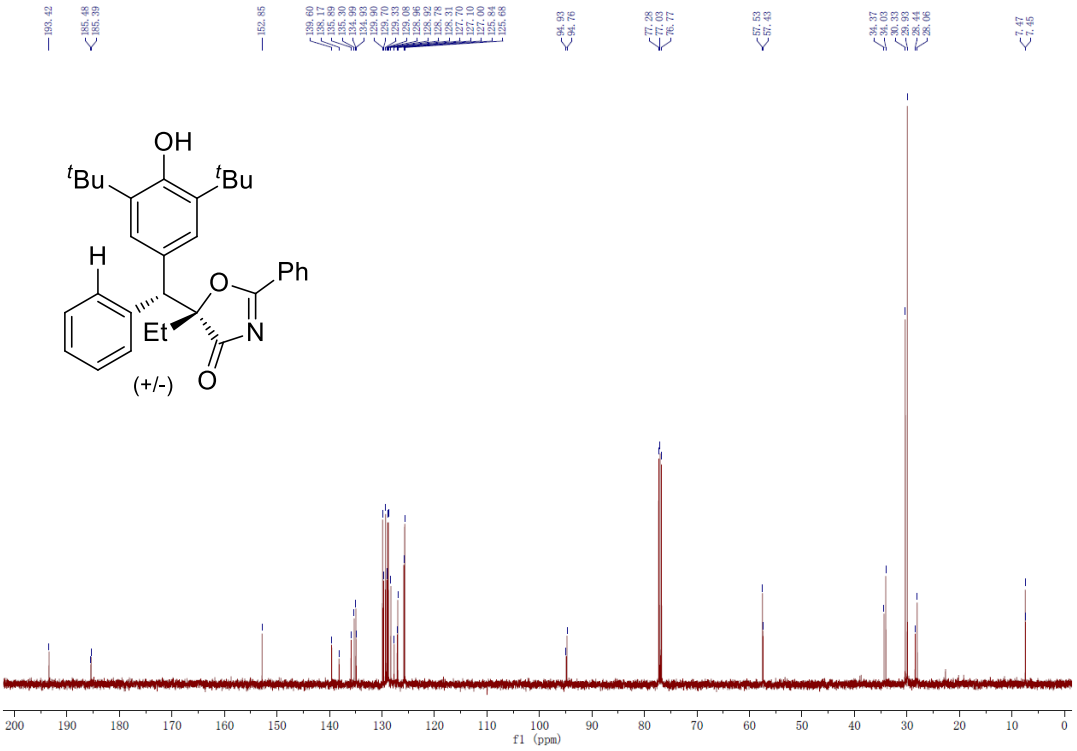
5-((2-((*tert*-butyldimethylsilyl)oxy)phenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (5ba)



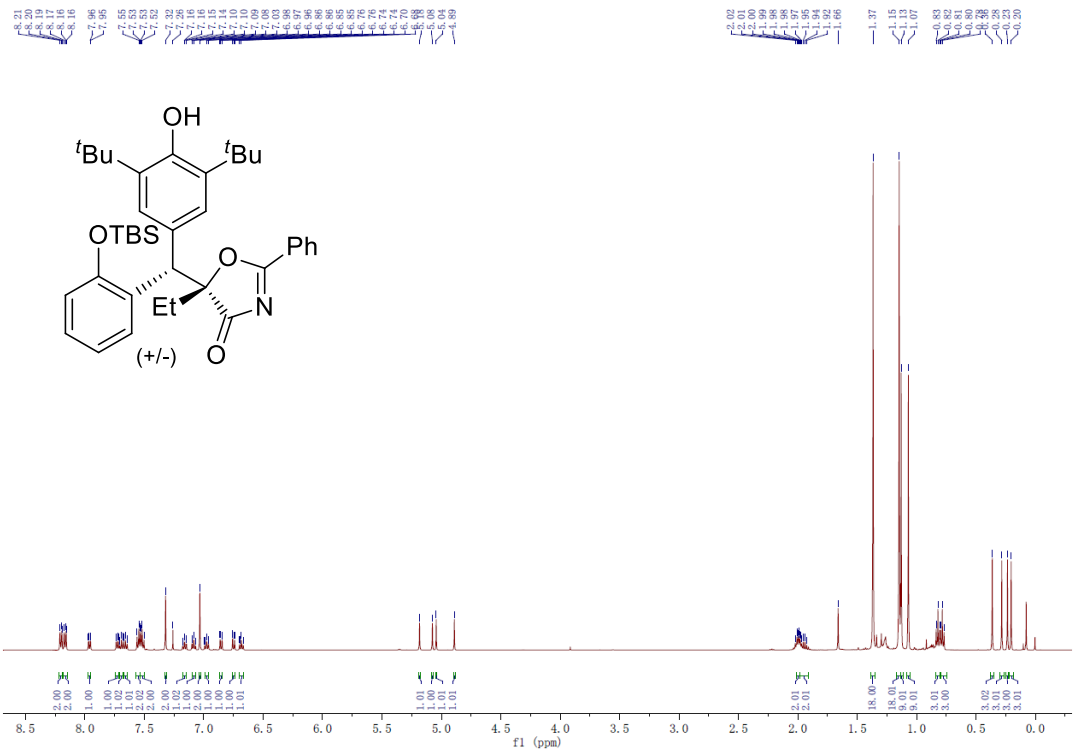
Colourless oil, 28.3 mg, 92% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.21-8.19 (m, 2H), 8.17-8.16 (m, 2H), 7.97-7.95 (m, 1H), 7.74-7.72 (m, 1H), 7.71-7.68 (m, 1H), 7.68-7.64 (m, 1H), 7.56-7.53 (m, 2H), 7.53-7.50 (m, 2H), 7.32 (s, 2H), 7.18-7.14 (m, 1H), 7.10-7.07 (m, 1H), 7.03 (s, 2H), 6.99-6.96 (m, 1H), 6.86-6.85 (m, 1H), 6.76-6.74 (m, 1H), 6.70-6.67 (m, 1H), 5.18 (s, 1H), 5.08 (s, 1H), 5.04 (s, 1H), 4.89 (s, 1H), 2.02-1.98 (m, 2H), 1.97-1.92 (m, 2H), 1.37 (s, 18H), 1.15 (s, 18H), 1.13 (s, 9H), 1.07 (s, 9H), 0.82 (t, *J* = 10.0 Hz, 3H), 0.78 (t, *J* = 10.0 Hz, 3H), 0.36 (s, 3H), 0.28 (s, 3H), 0.23 (s, 3H), 0.20 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 193.3, 192.4, 185.1, 184.8, 153.8, 152.9, 152.6, 152.6, 135.5, 134.9, 134.8, 130.1, 129.8, 129.7, 129.7, 129.6, 129.6, 128.9, 128.8, 127.7, 127.2, 126.3, 126.2, 126.0, 126.0, 120.9, 120.7, 118.7, 118.1, 95.3, 95.1, 48.2, 46.7, 34.3, 34.0, 30.2, 29.9, 29.5, 28.9, 27.7, 26.1, 26.0, 18.4, 18.4, 7.5, 7.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{38}H_{52}NO_4Si$) requires m/z 614.3666, found m/z 614.3660.

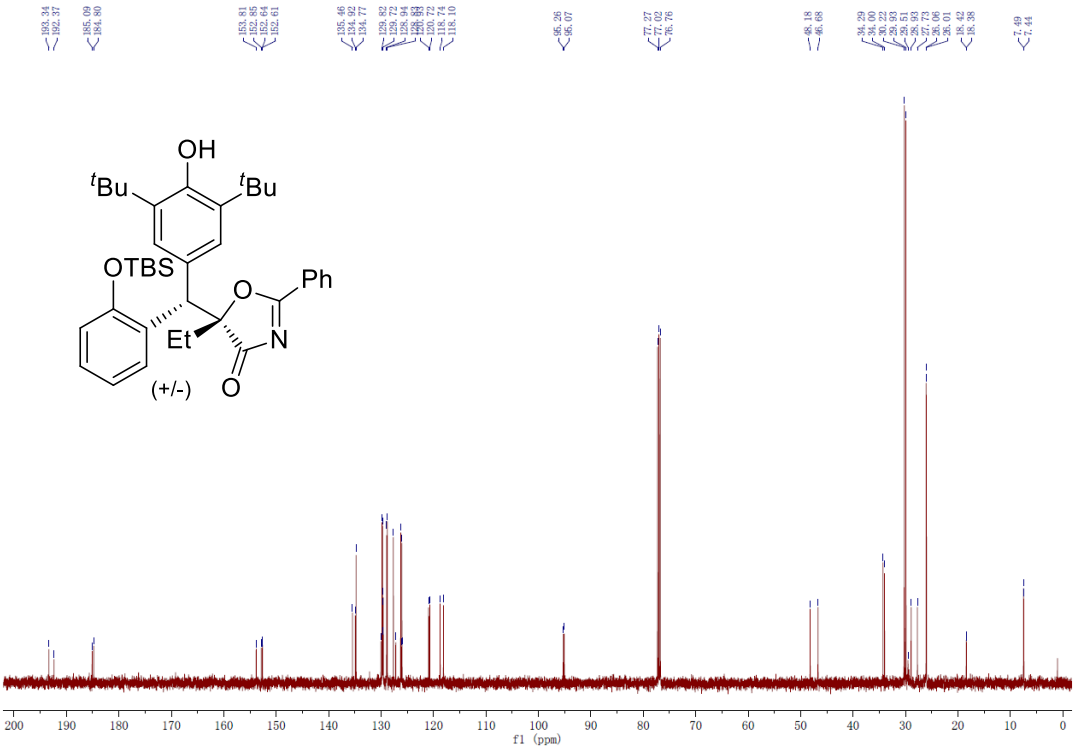
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (5aa)





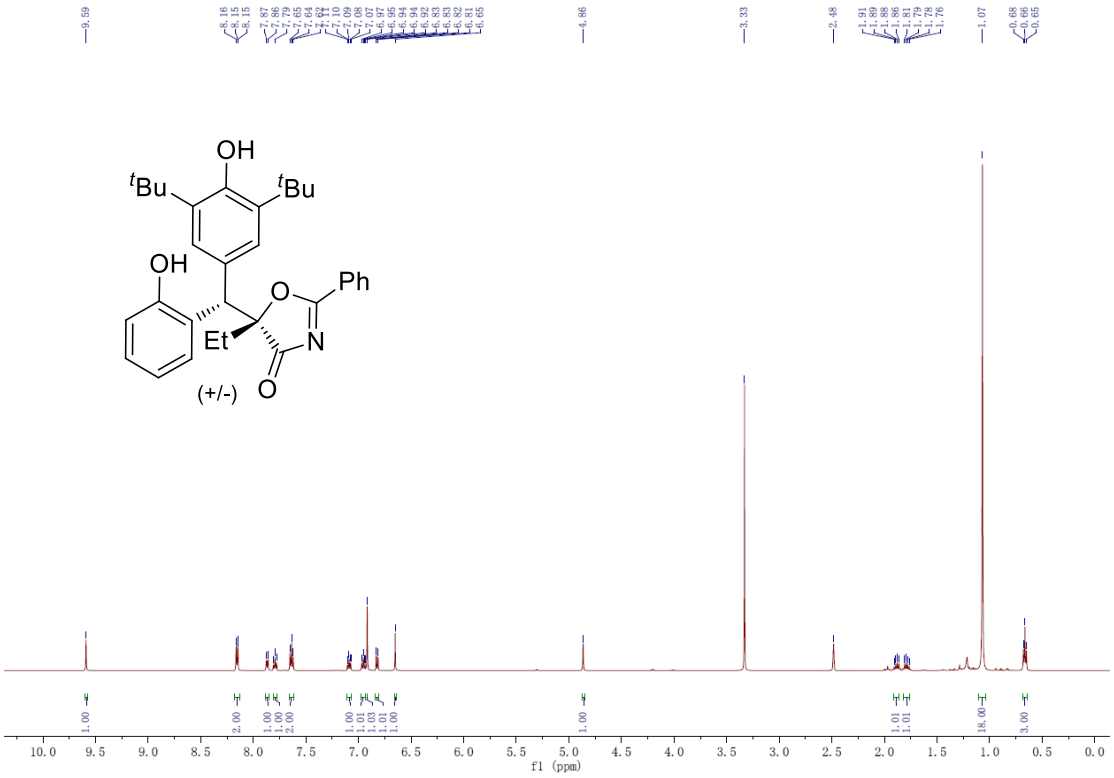
5-((2-((*tert*-butyldimethylsilyl)oxy)phenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (5ba)

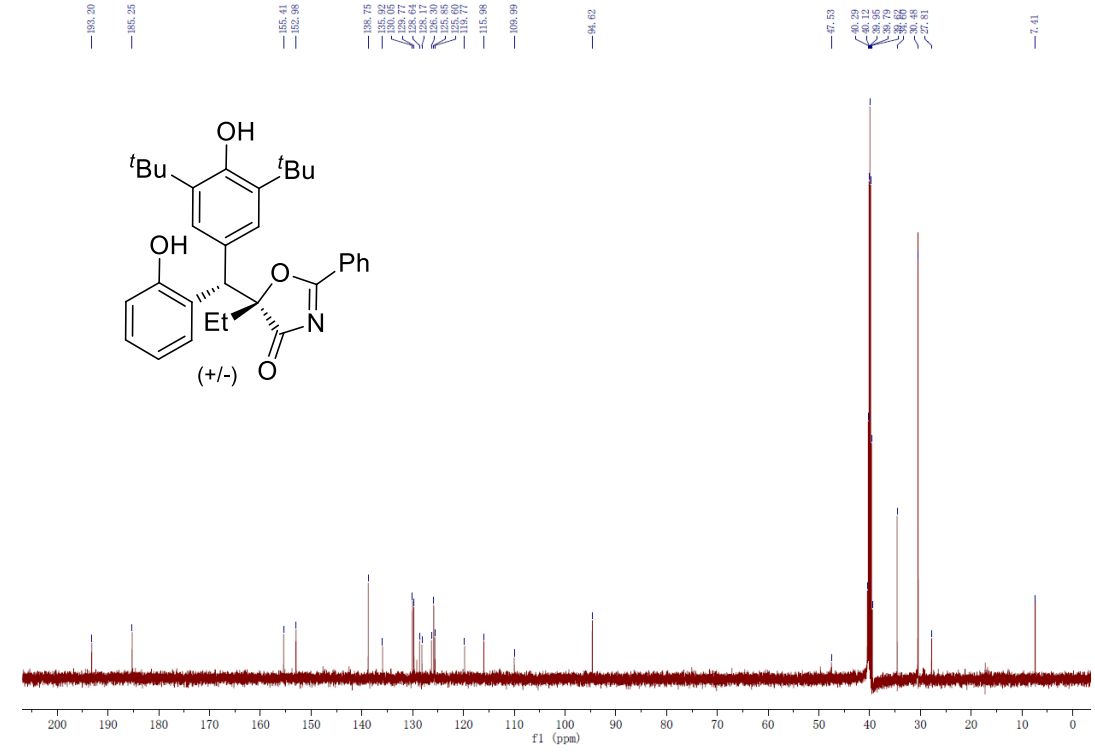




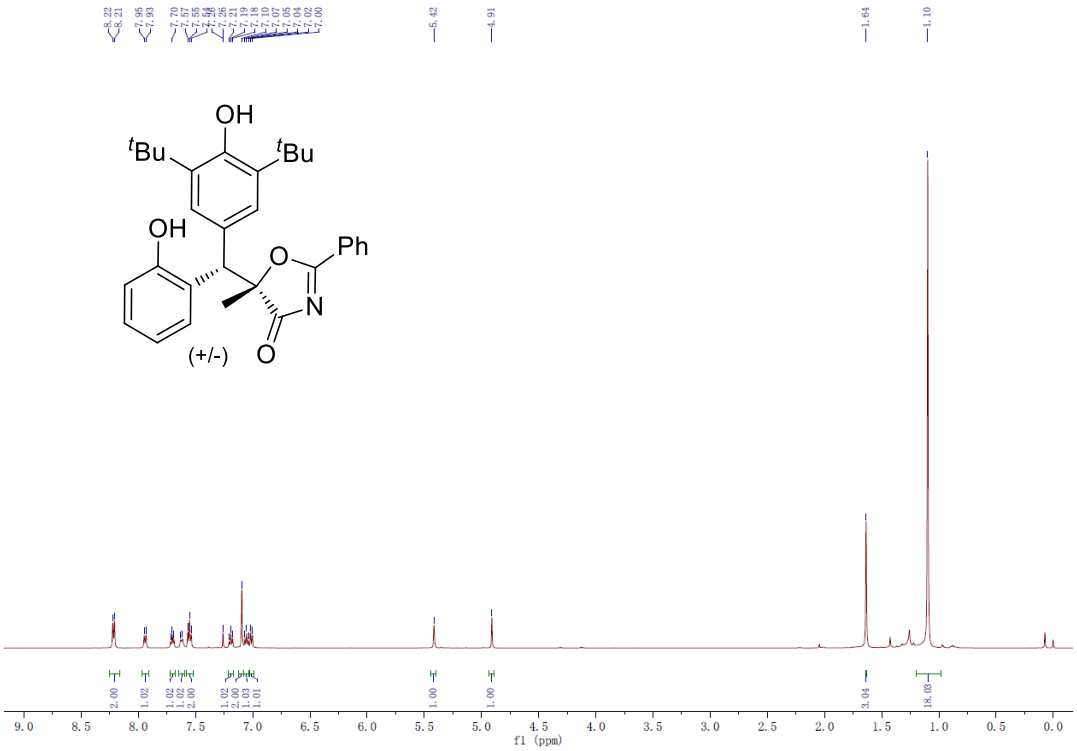
H: NMR Analysis

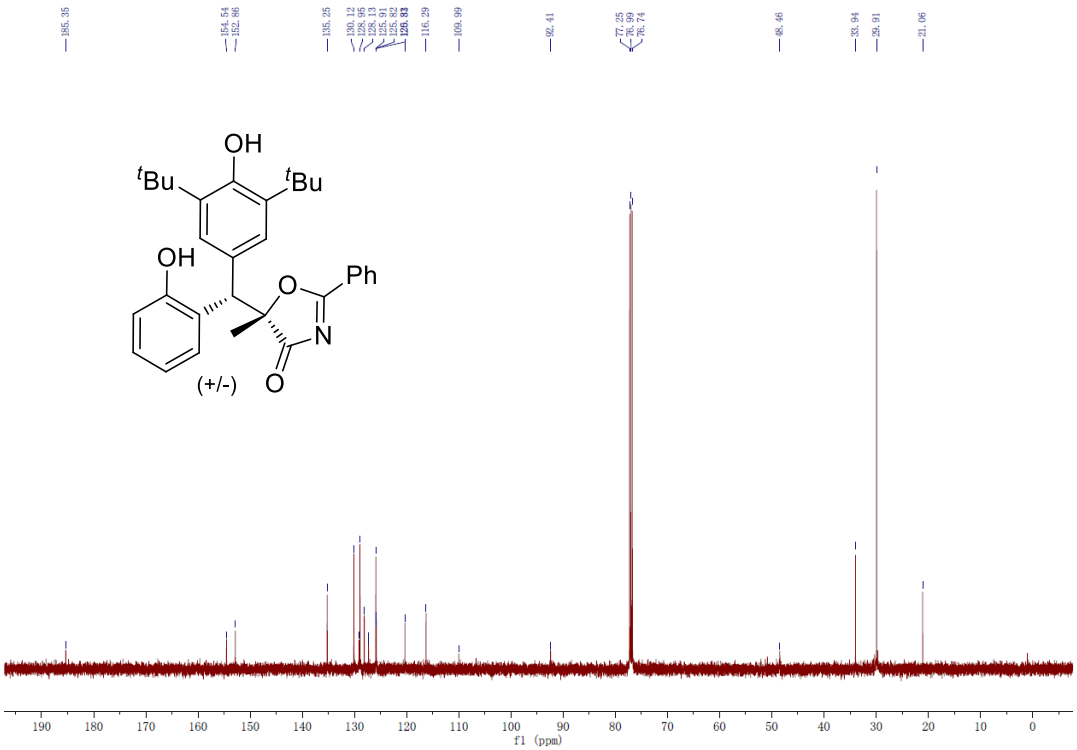
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3aa)



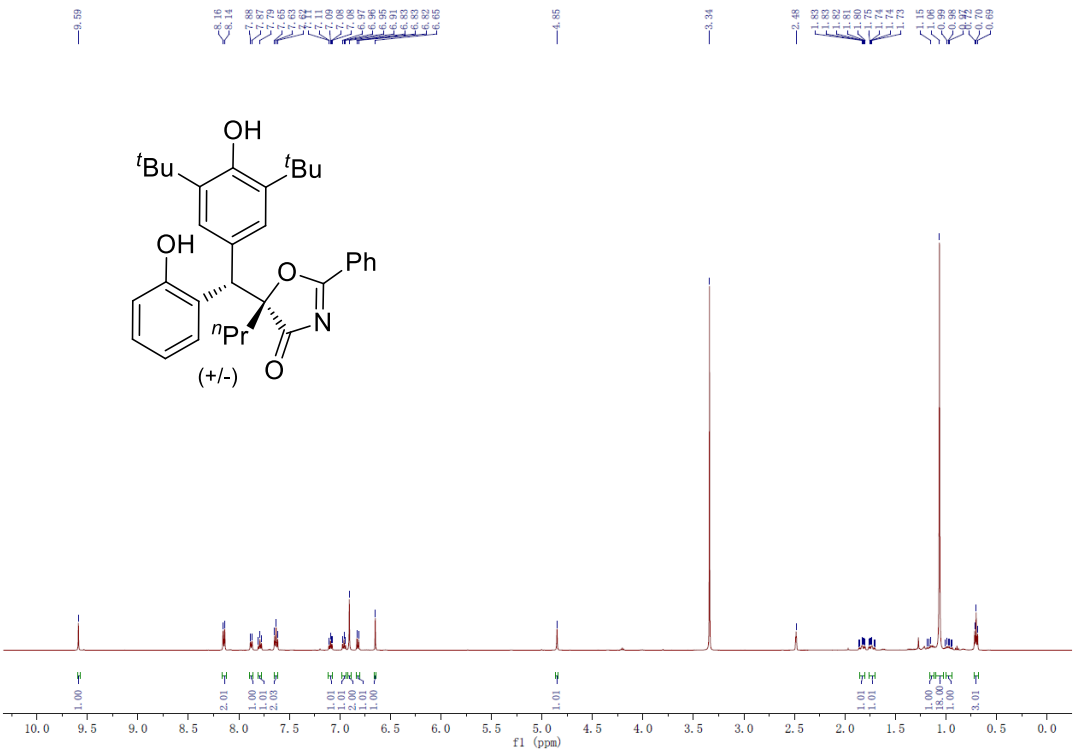


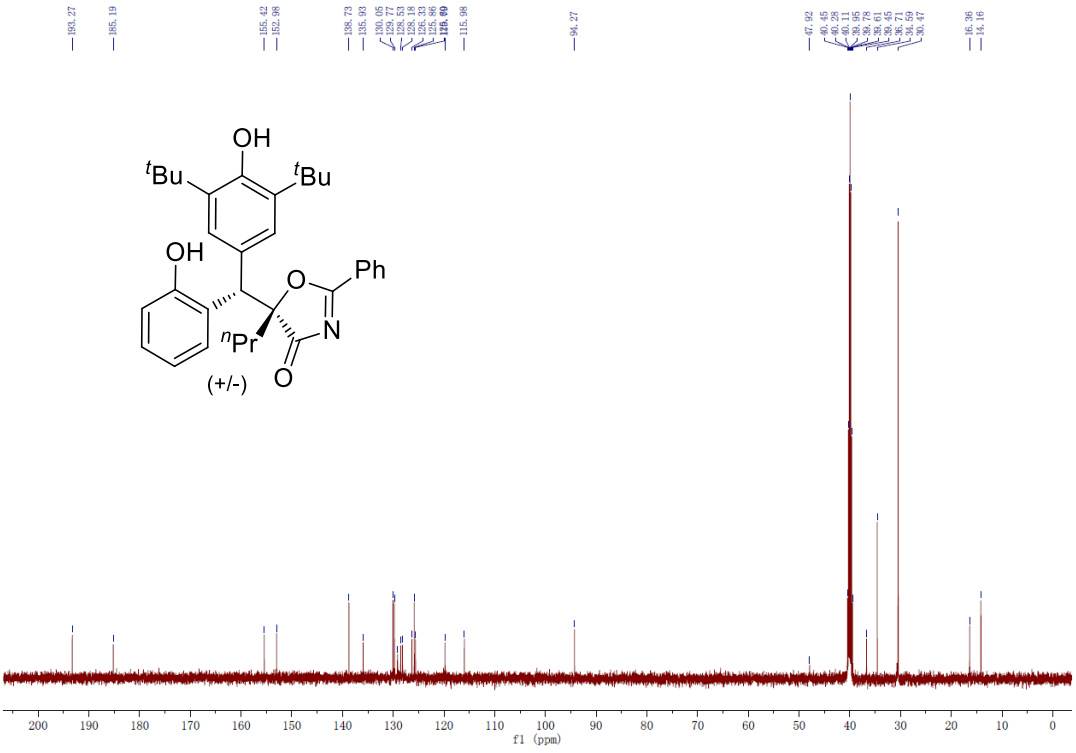
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-methyl-2-phenyloxazol-4(5*H*)-one (3ab)



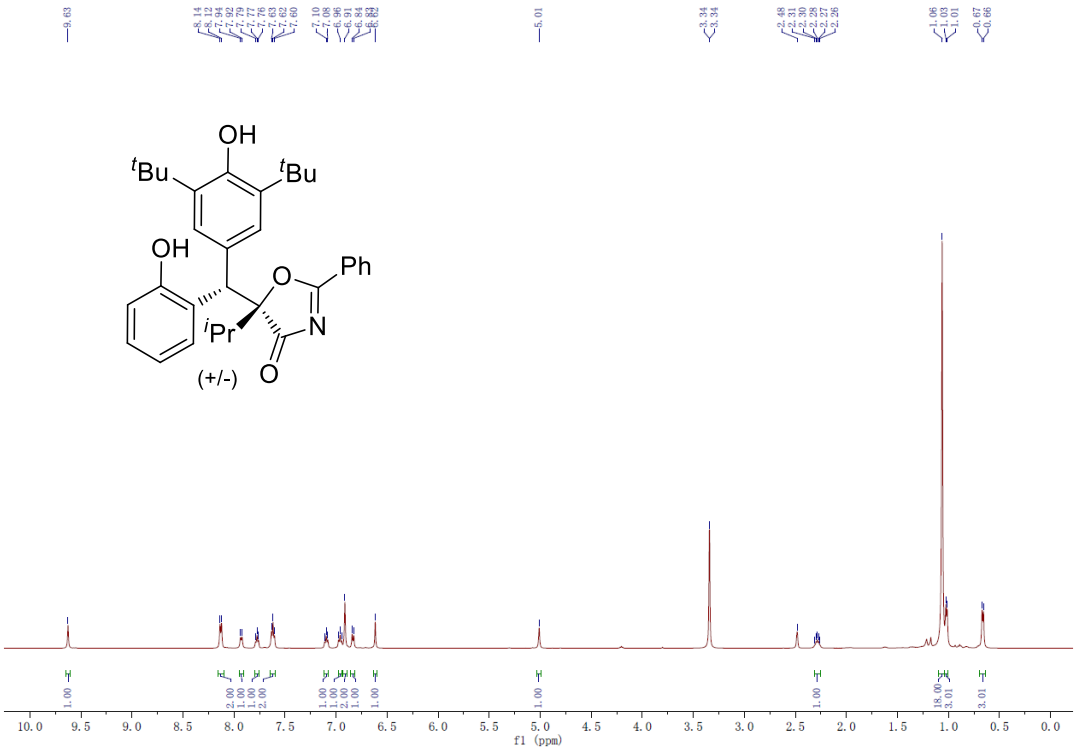


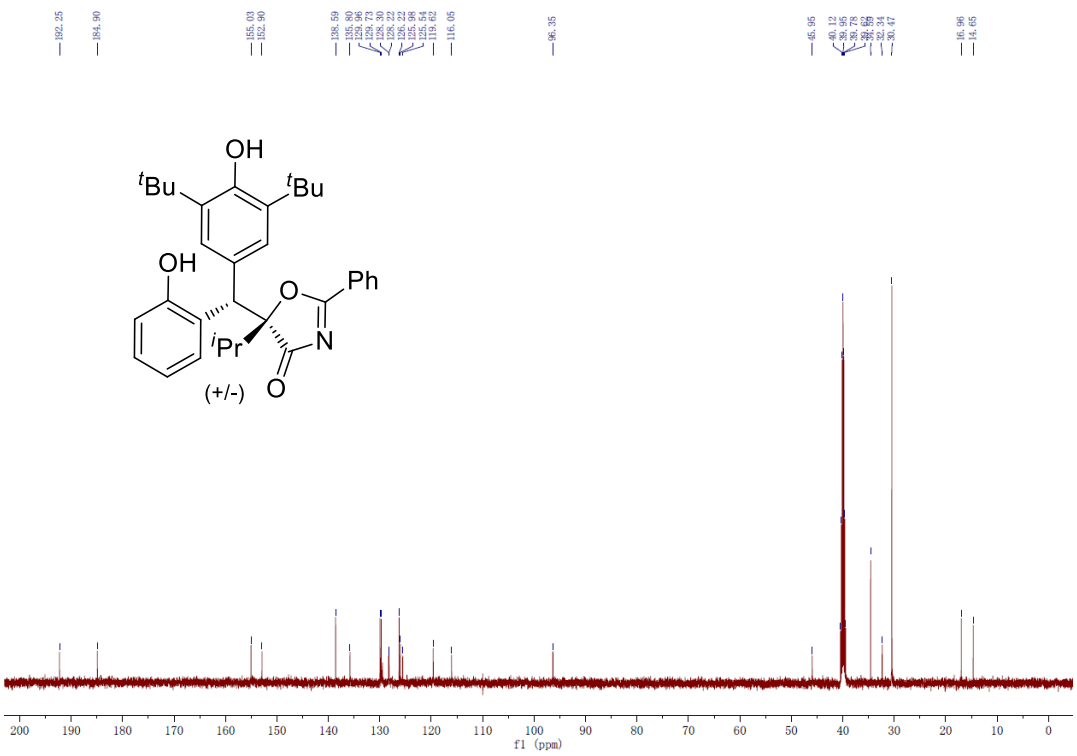
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-2-phenyl-5-propyloxazol-4(5*H*)-one (3ac)



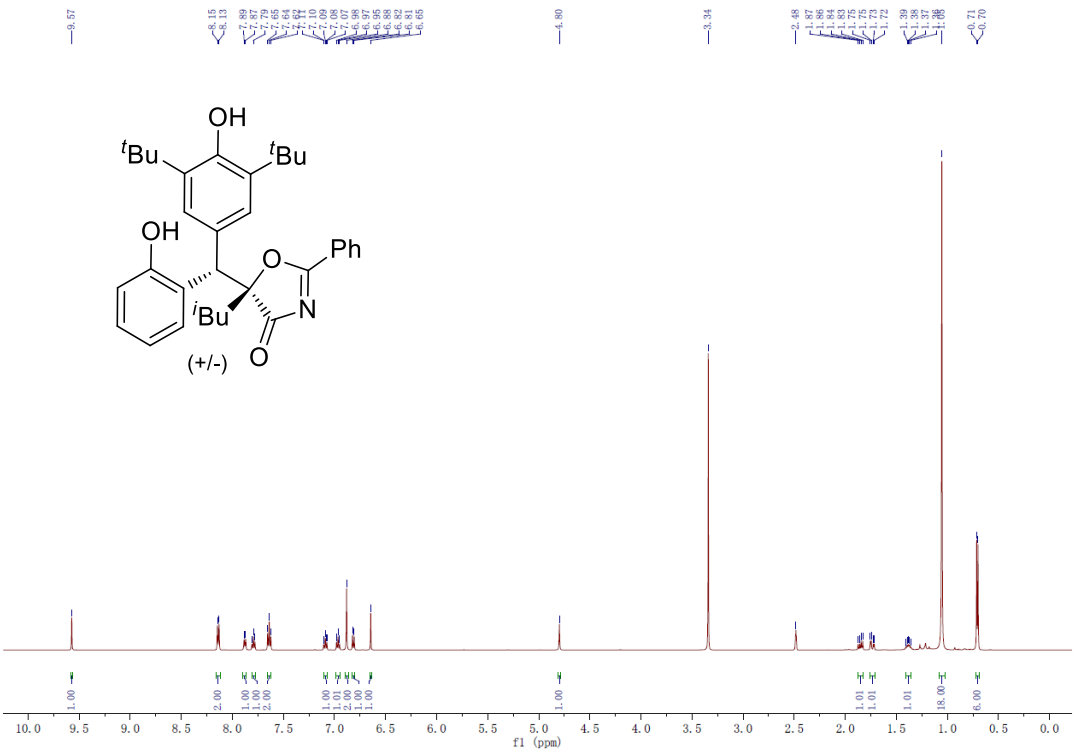


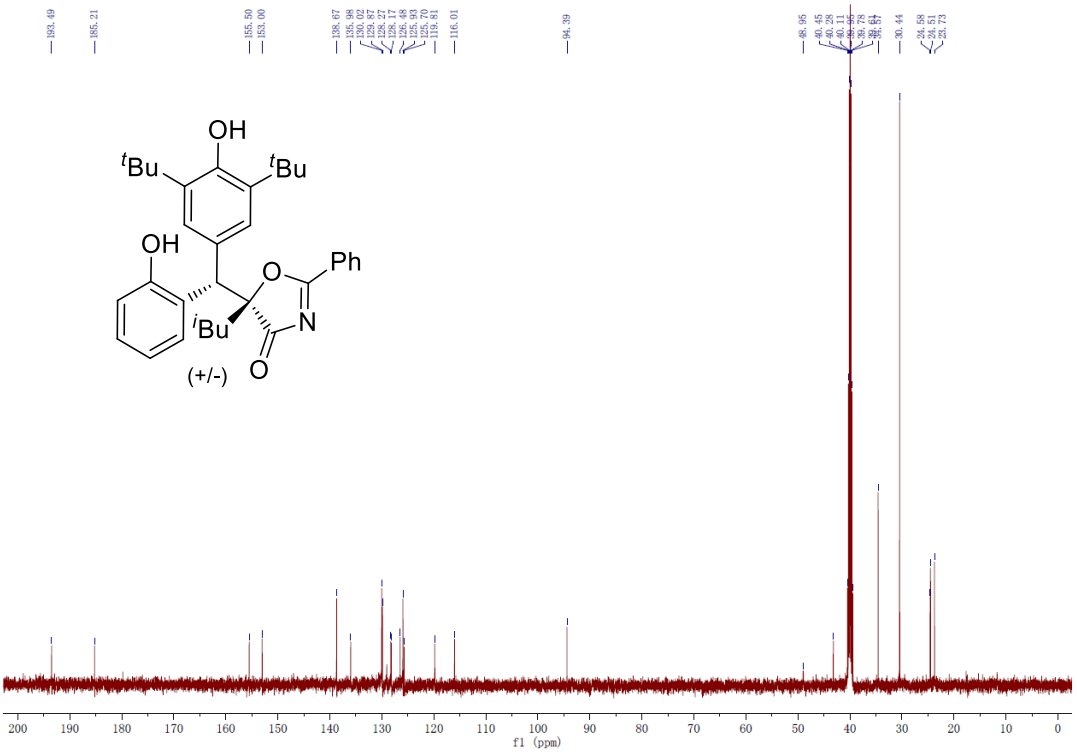
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-isopropyl-2-phenyloxazol-4(5*H*)-one (3ad)



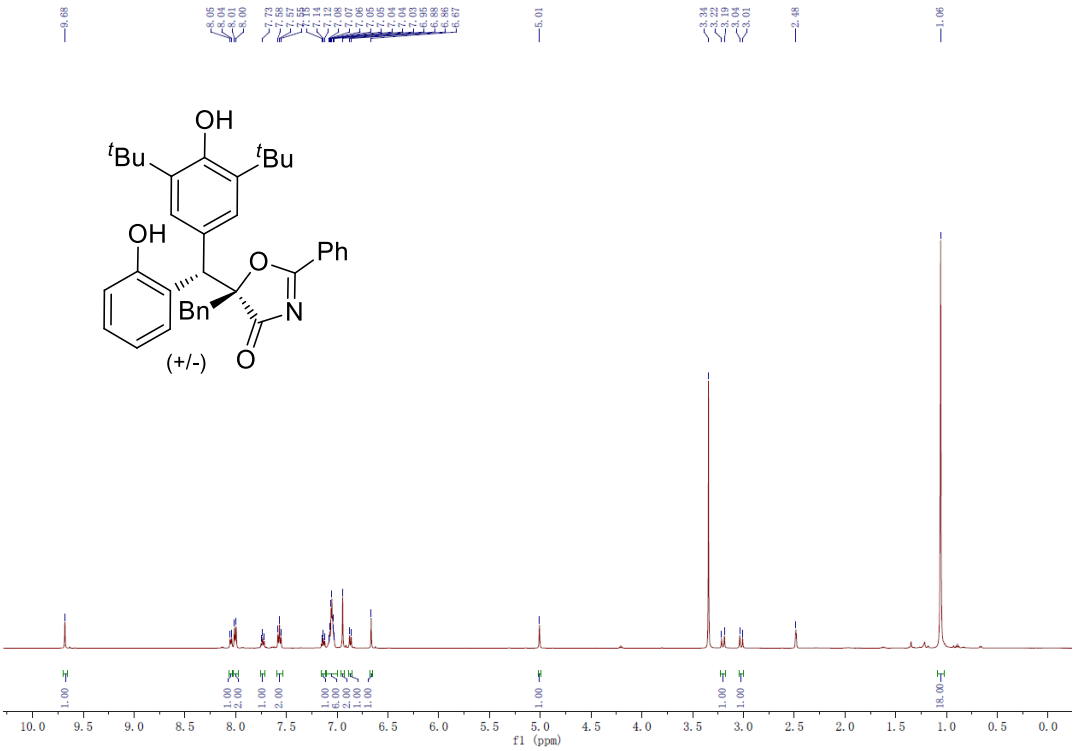


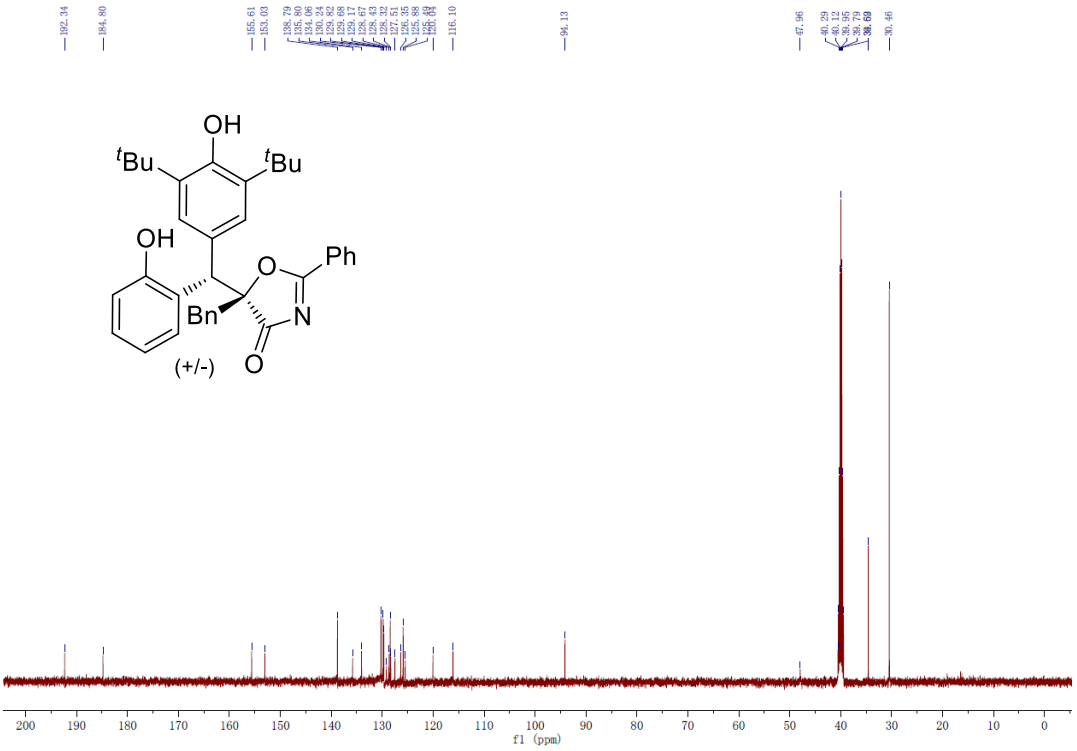
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-isobutyl-2-phenyloxazol-4(5*H*)-one (3ae)



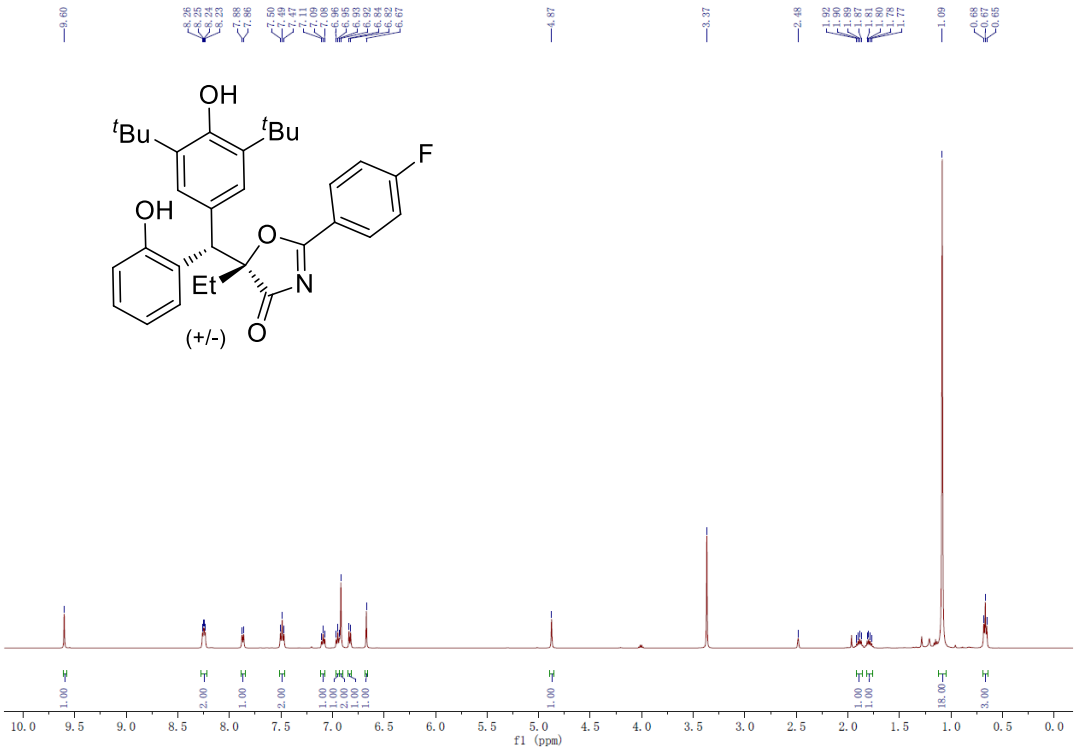


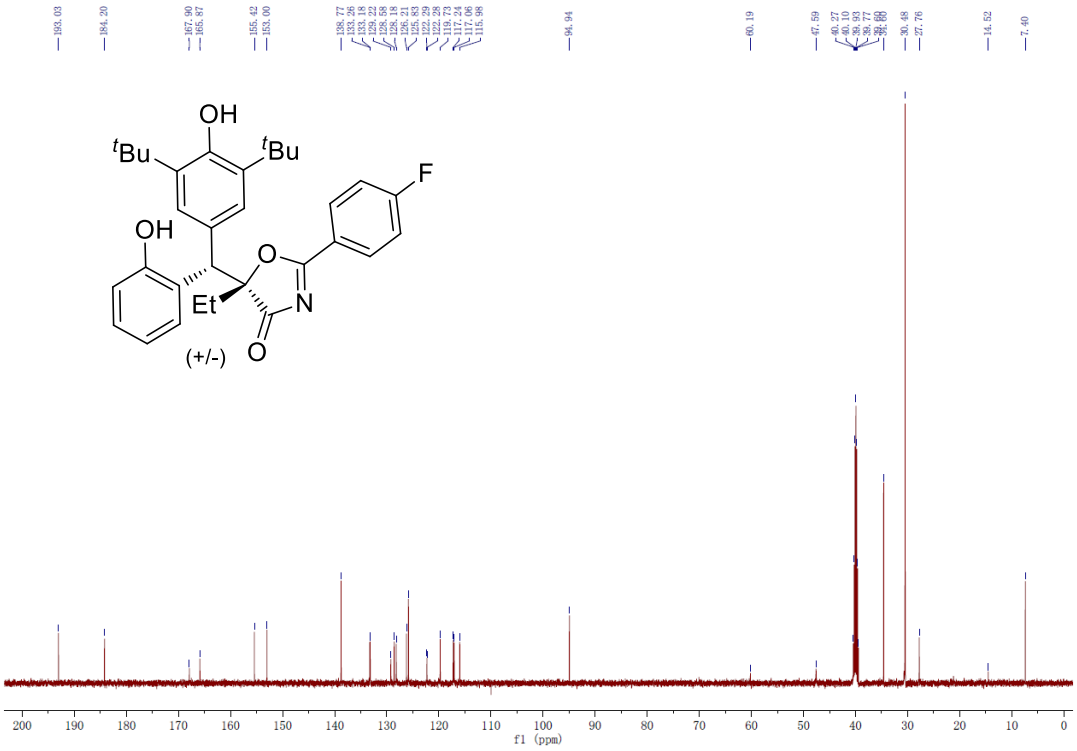
5-benzyl-5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-2-phenyloxazol-4(5*H*)-one (3af)



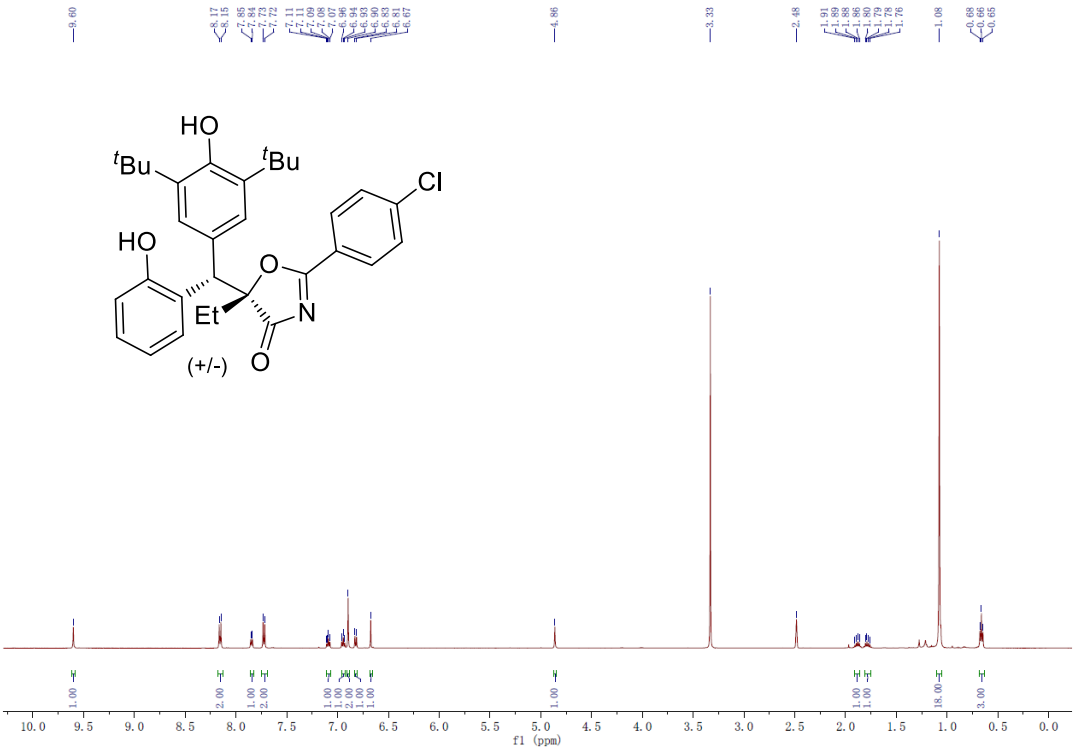


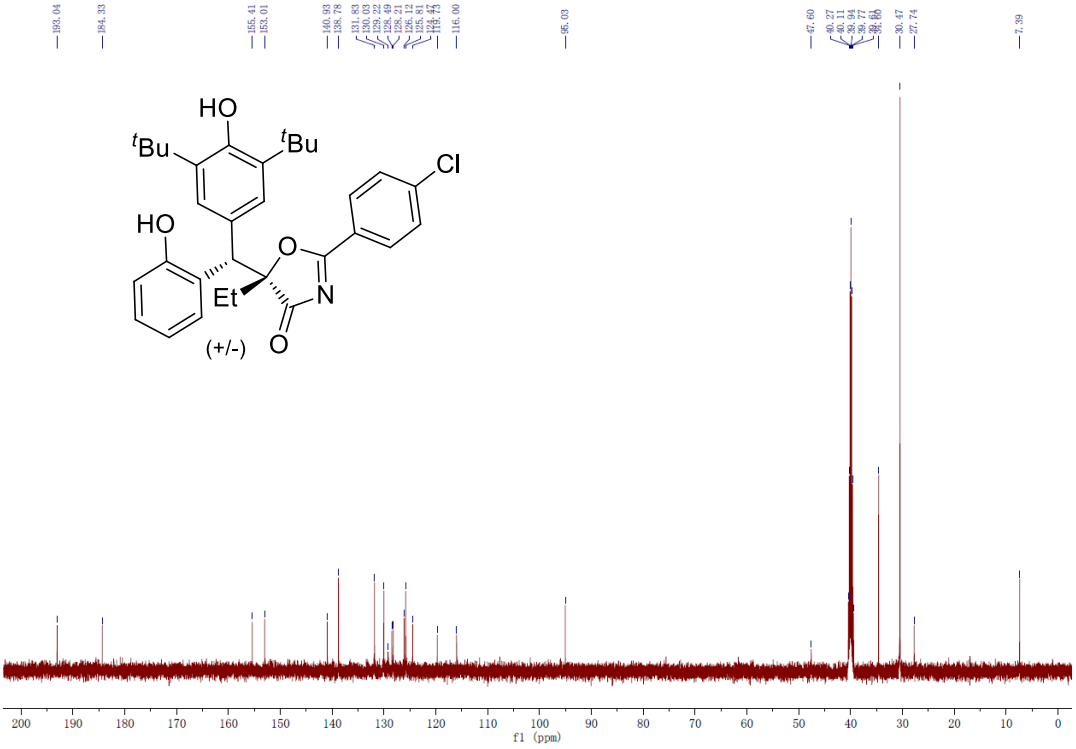
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyl-2-(4-fluorophenyl)oxazol-4(5*H*)-one (3ag)



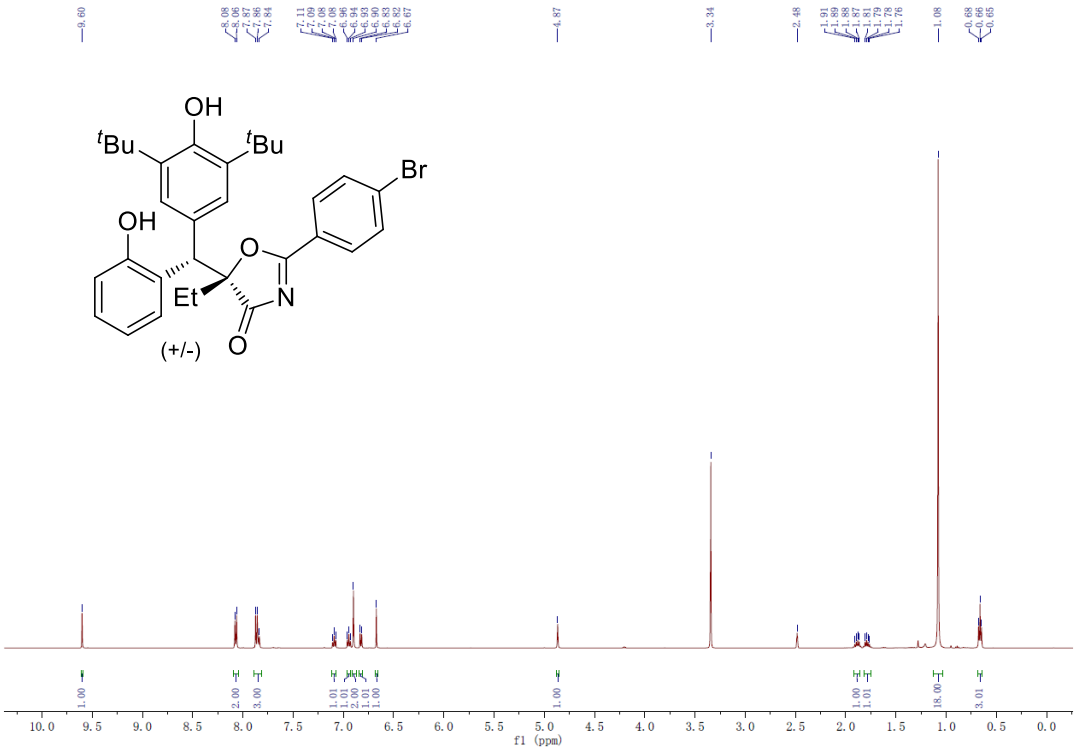


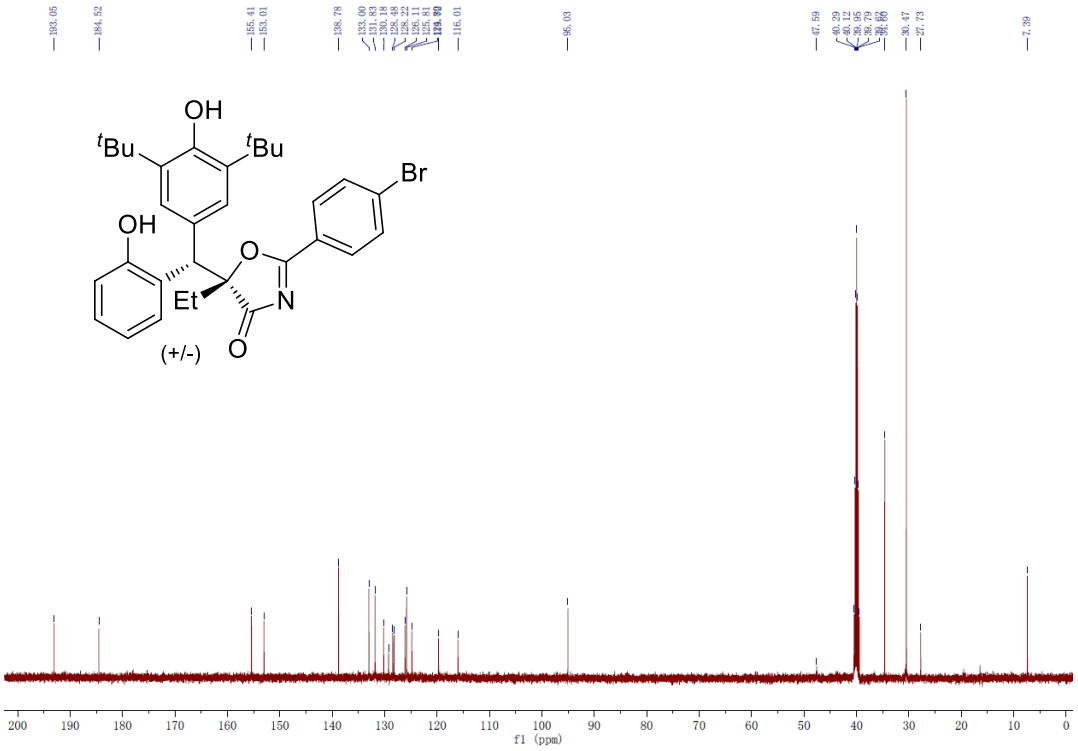
2-(4-chlorophenyl)-5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyloxazol-4(5*H*)-one (3ah)



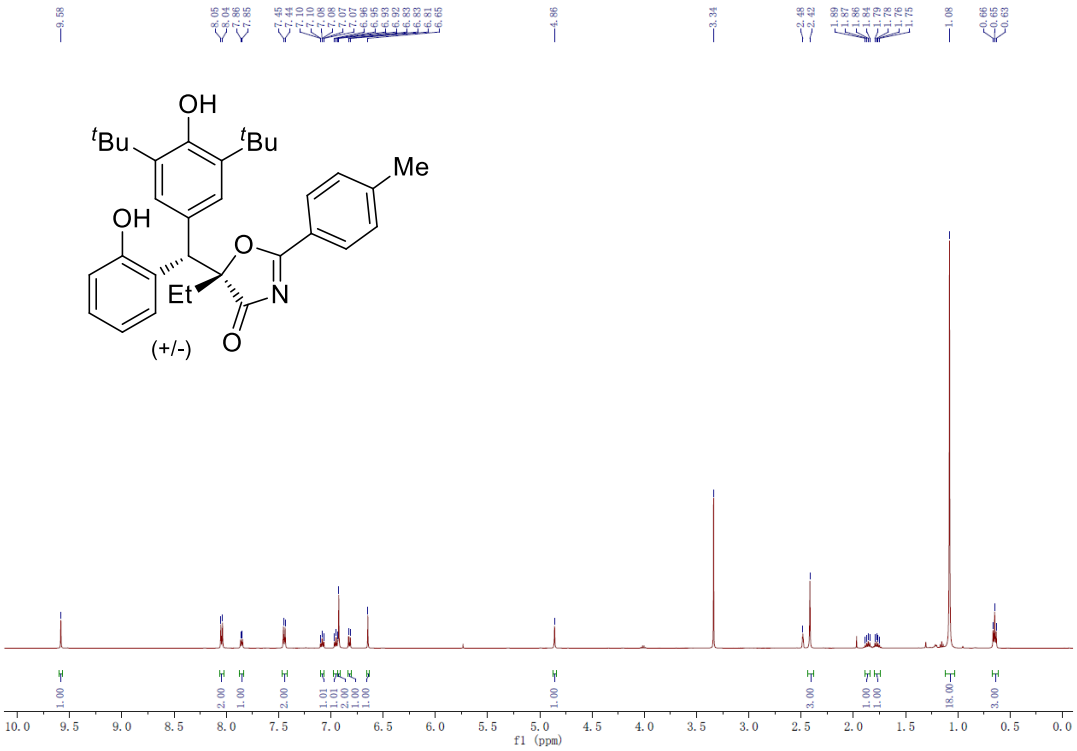


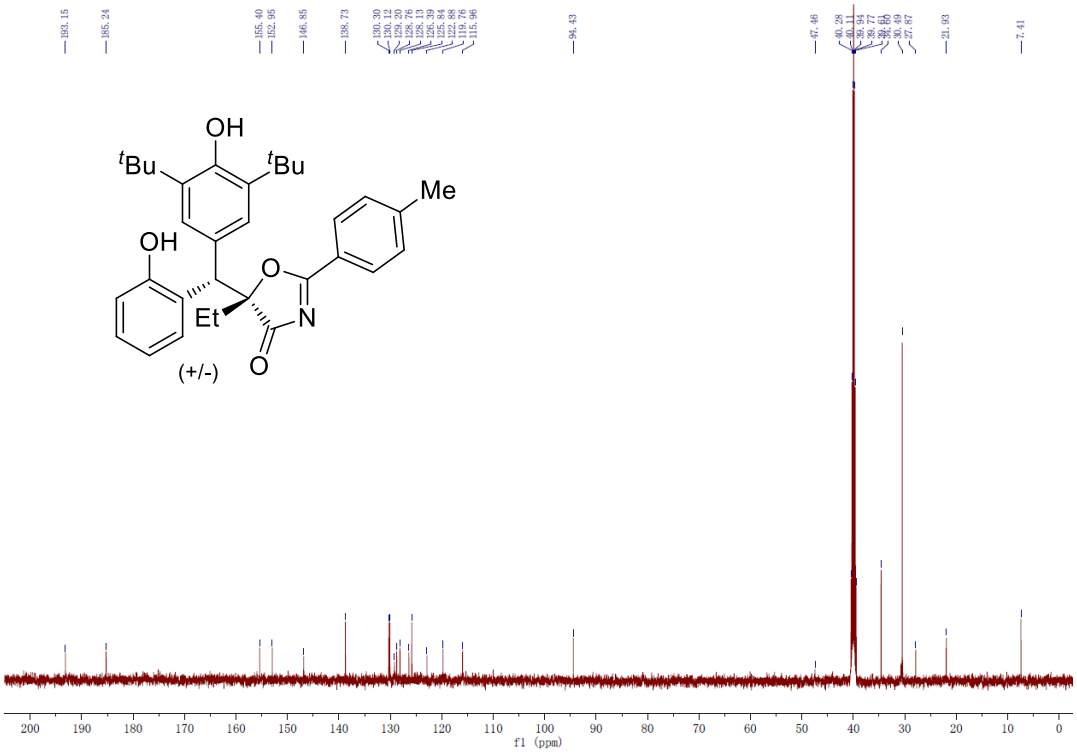
2-(4-bromophenyl)-5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyloxazol-4(5*H*)-one (3ai)



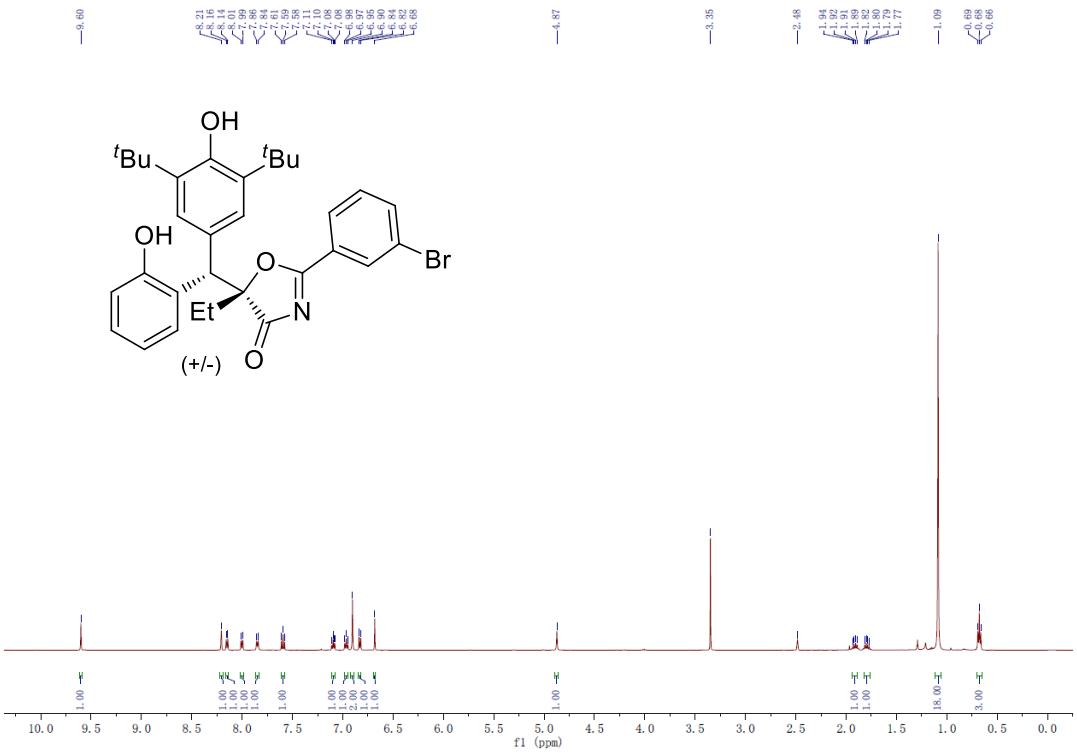


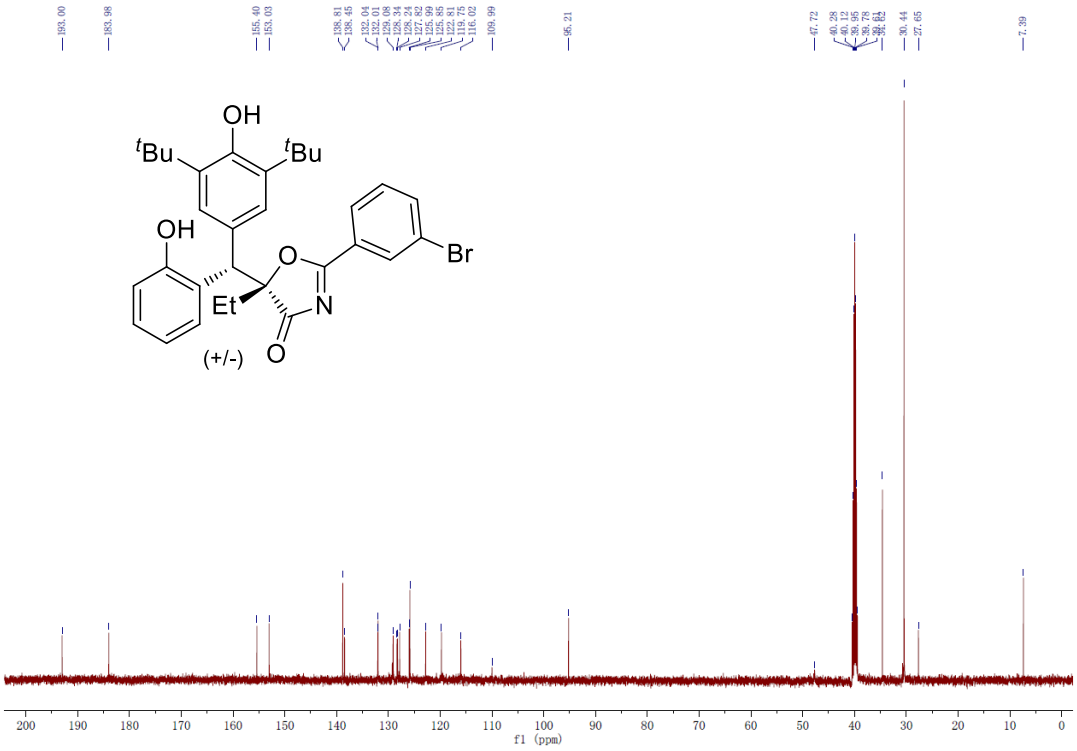
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyl-2-(*p*-tolyl)oxazol-4(5*H*)-one (3aj)



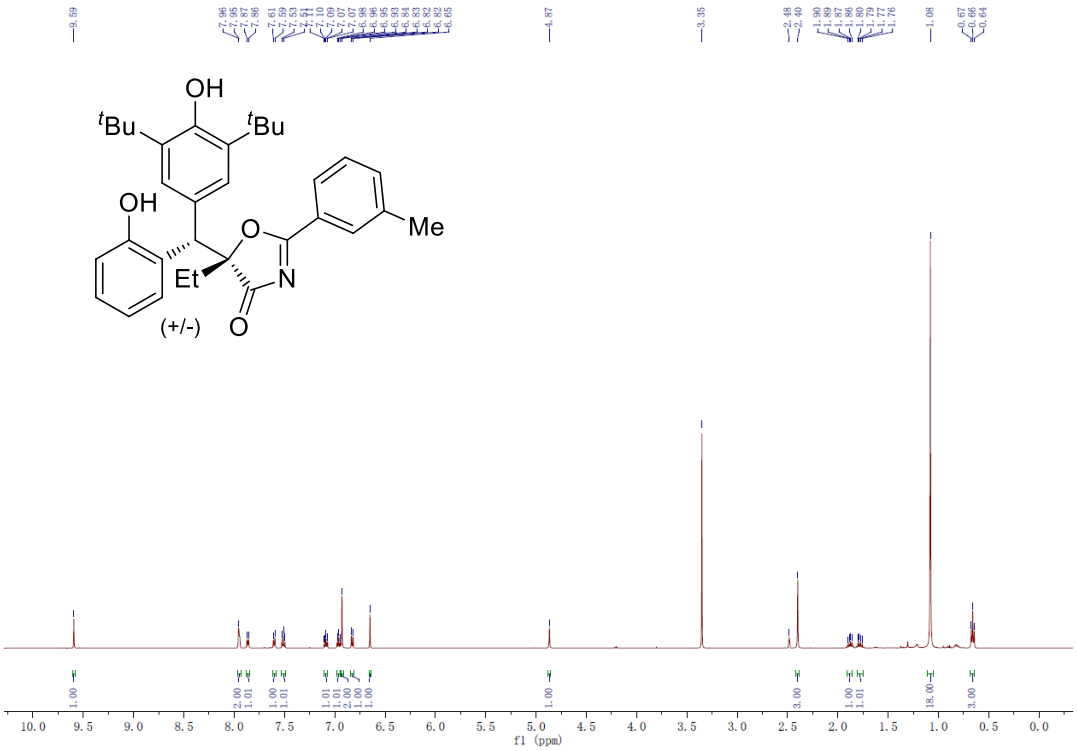


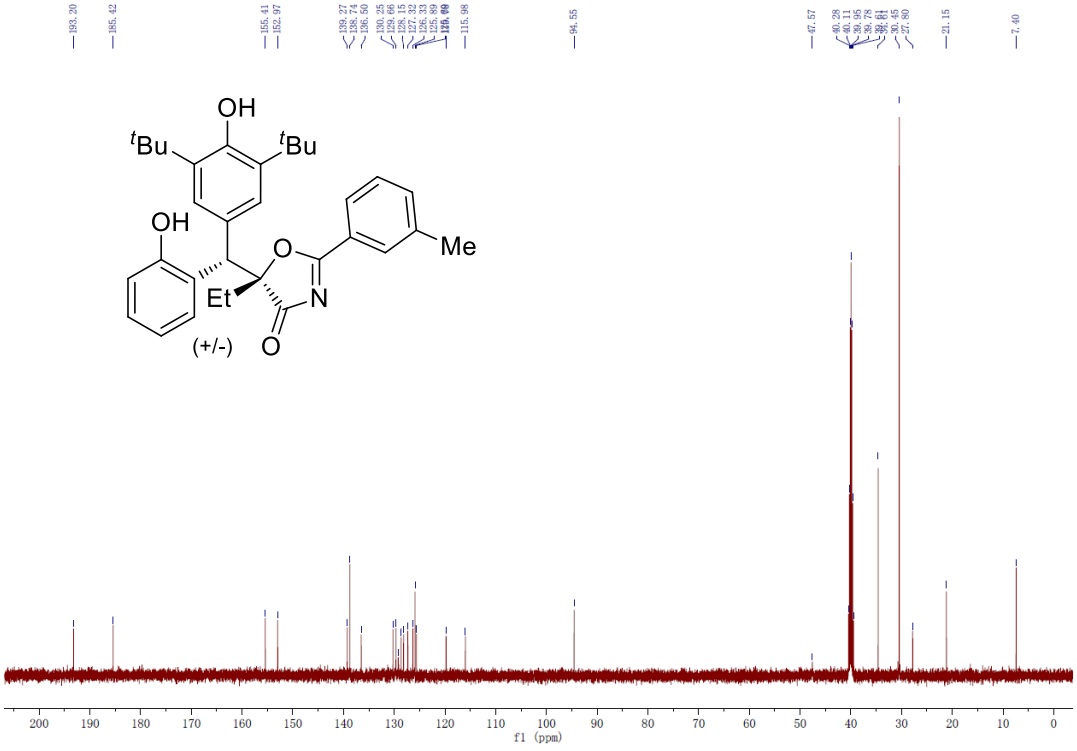
2-(3-bromophenyl)-5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyloxazol-4(5*H*)-one (3ak)



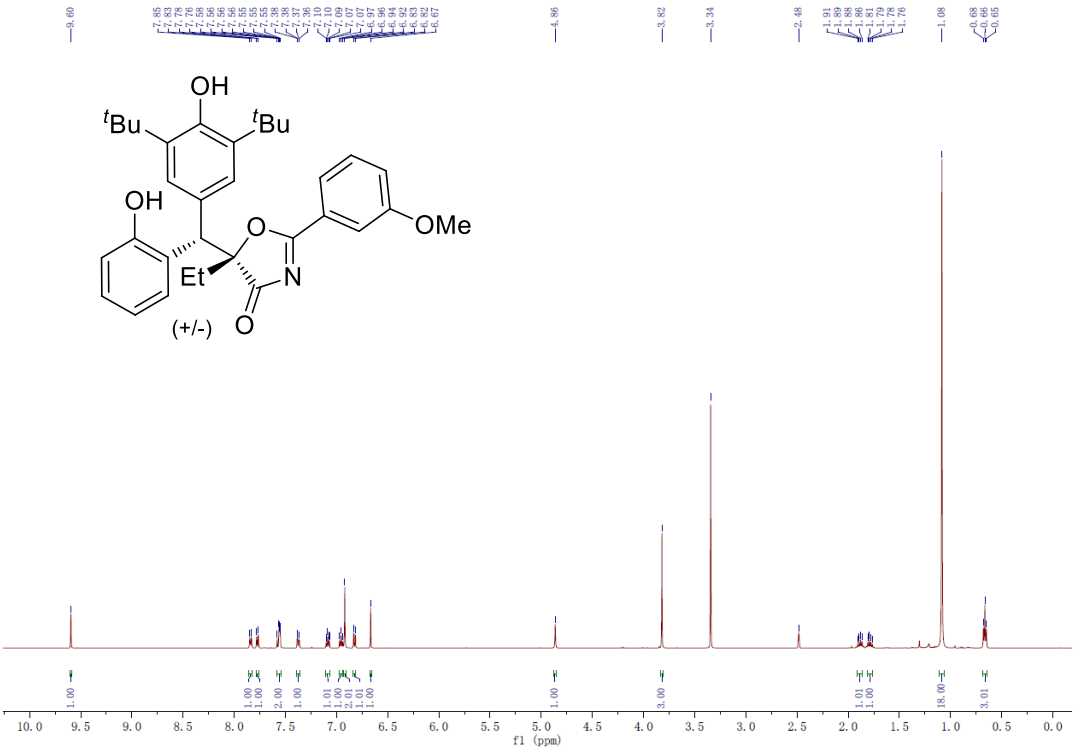


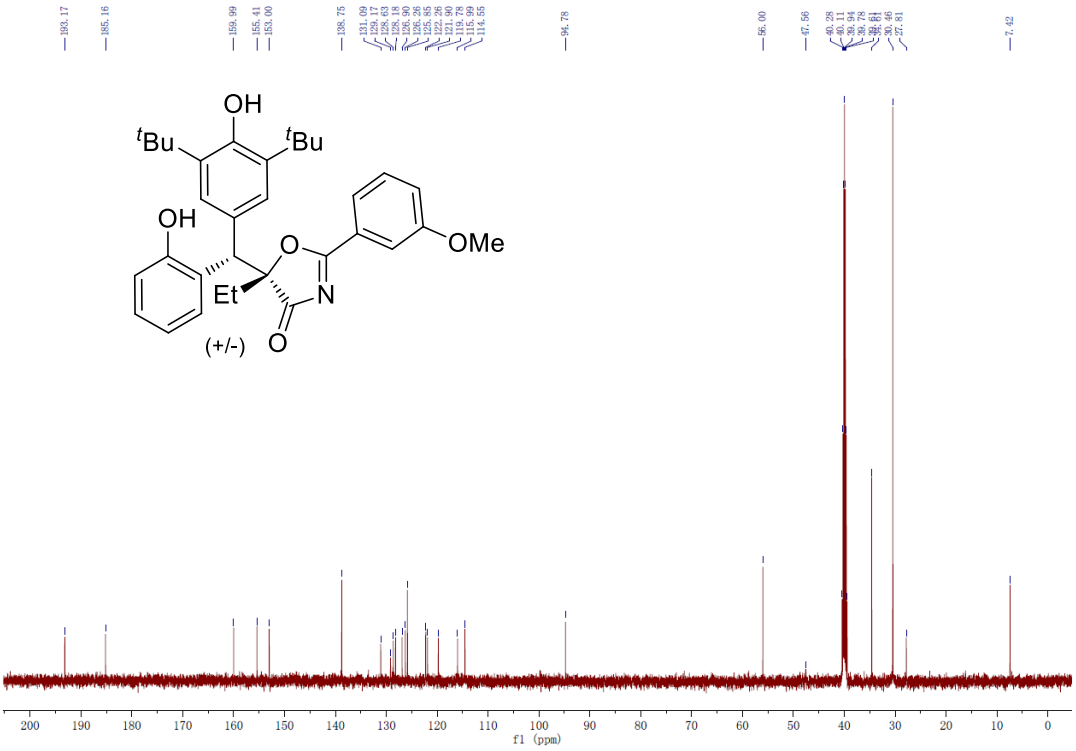
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyl-2-(*m*-tolyl)oxazol-4(5*H*)-one (3al)



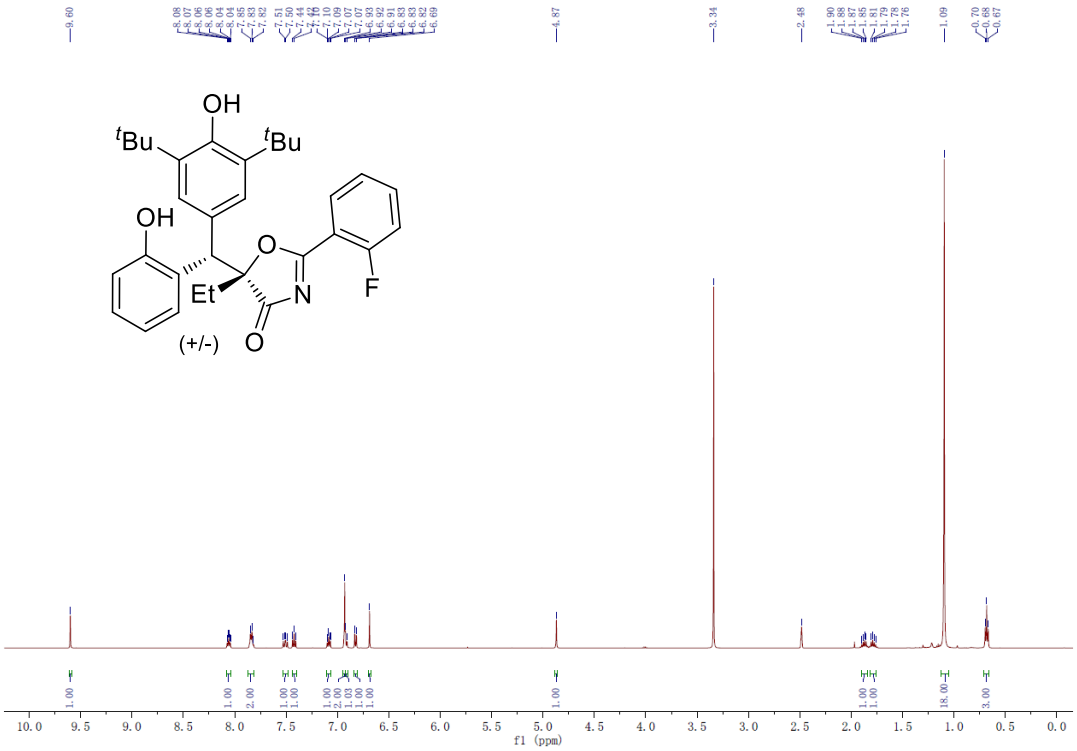


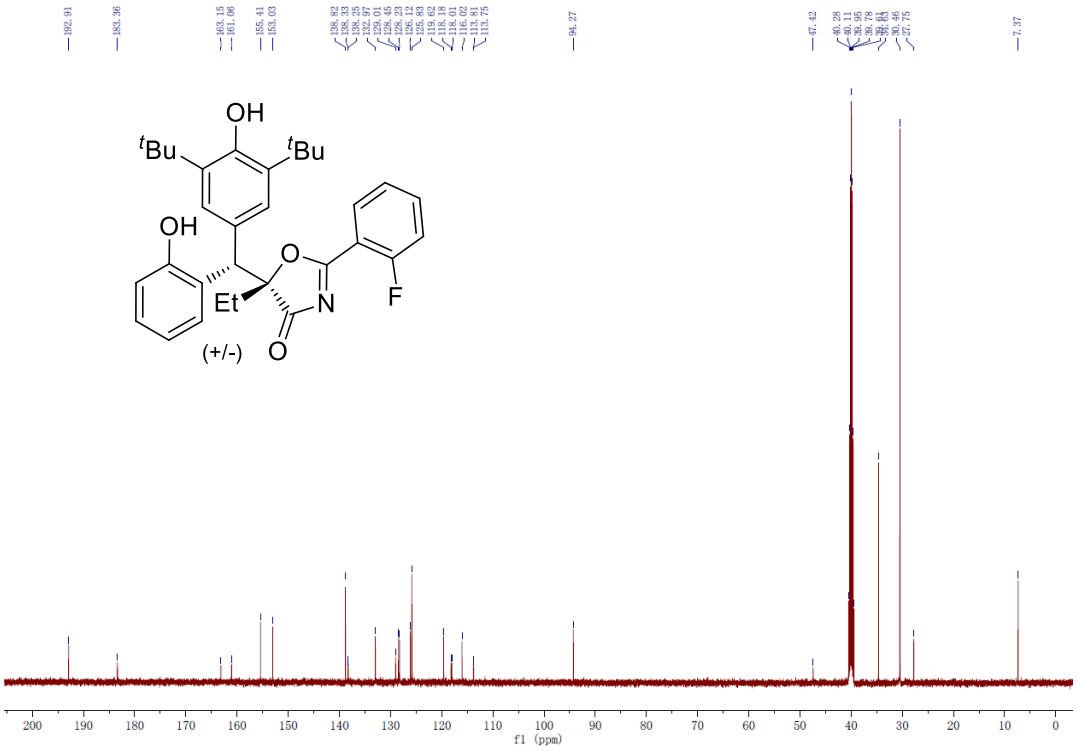
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyl-2-(3-methoxyphenyl)oxazol-4(5*H*)-one (3am)



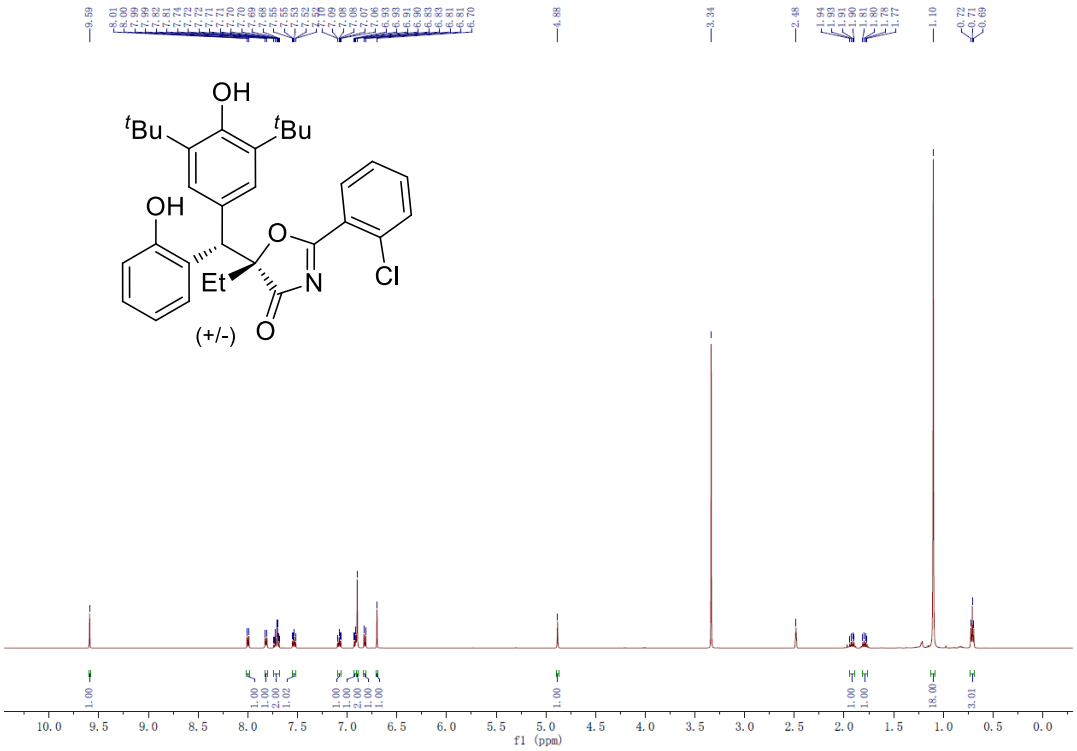


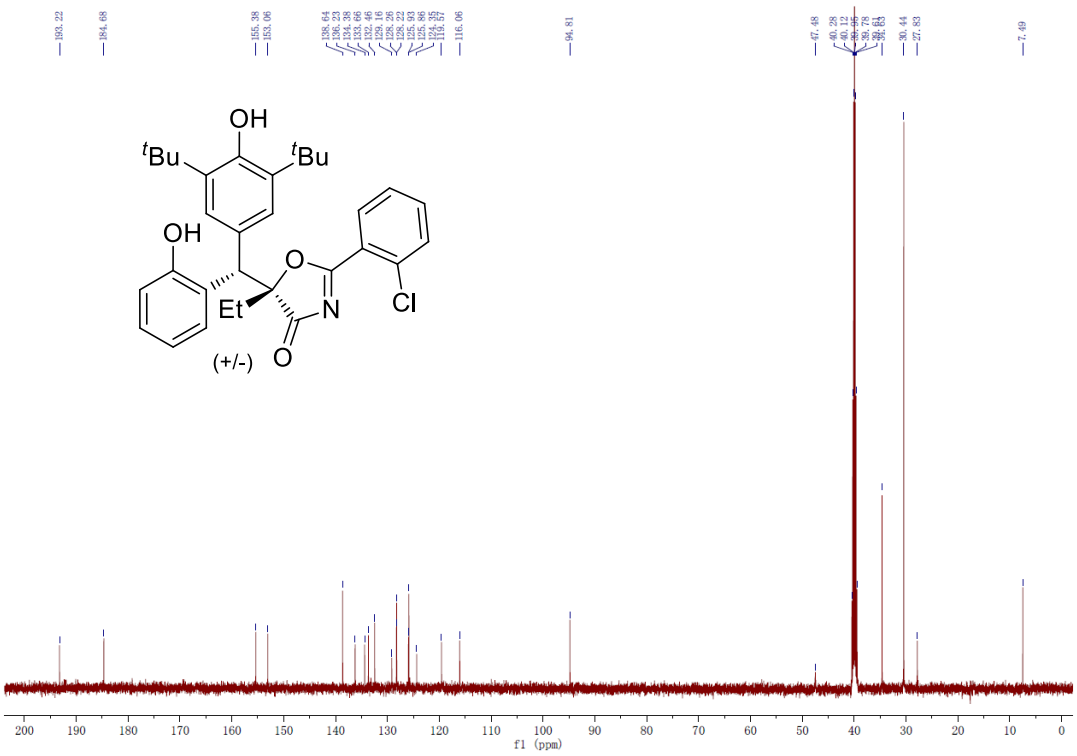
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyl-2-(2-fluorophenyl)oxazol-4(5*H*)-one (3an)



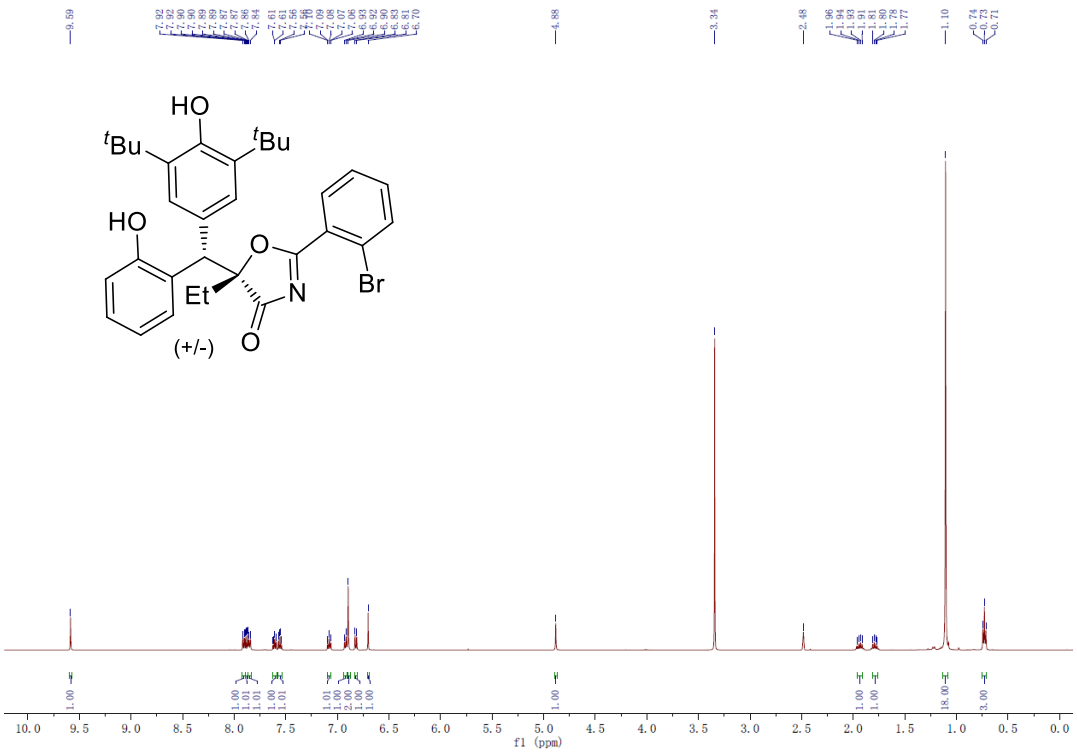


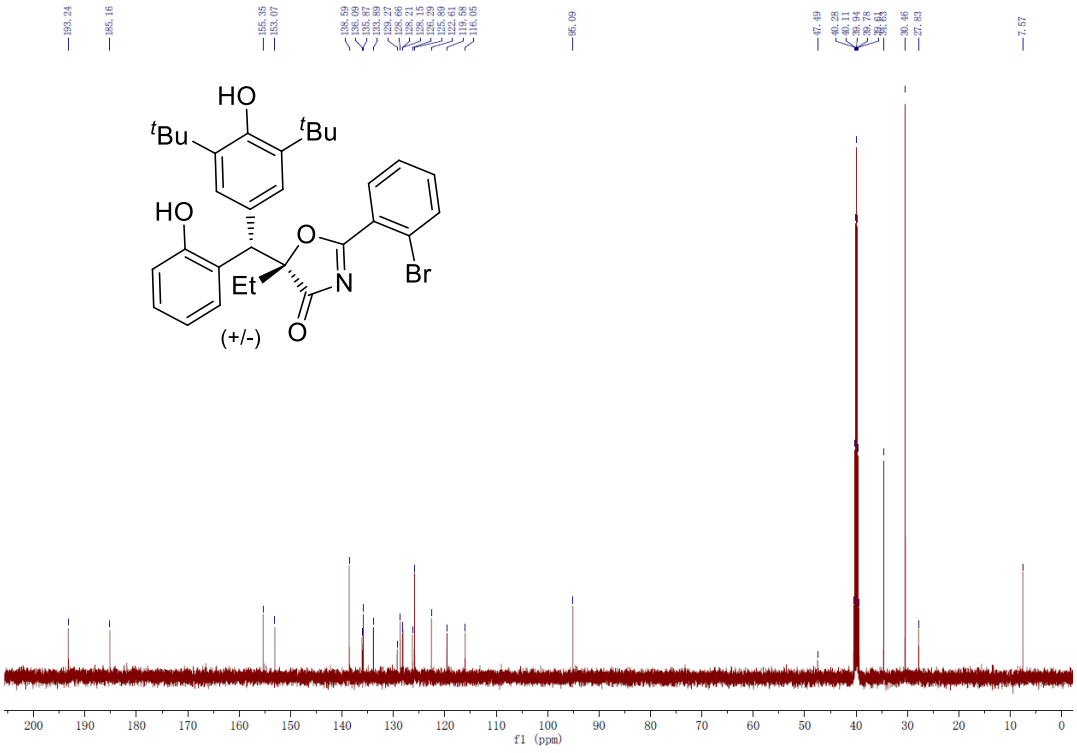
2-(2-chlorophenyl)-5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyloxazol-4(5*H*)-one (3ao)



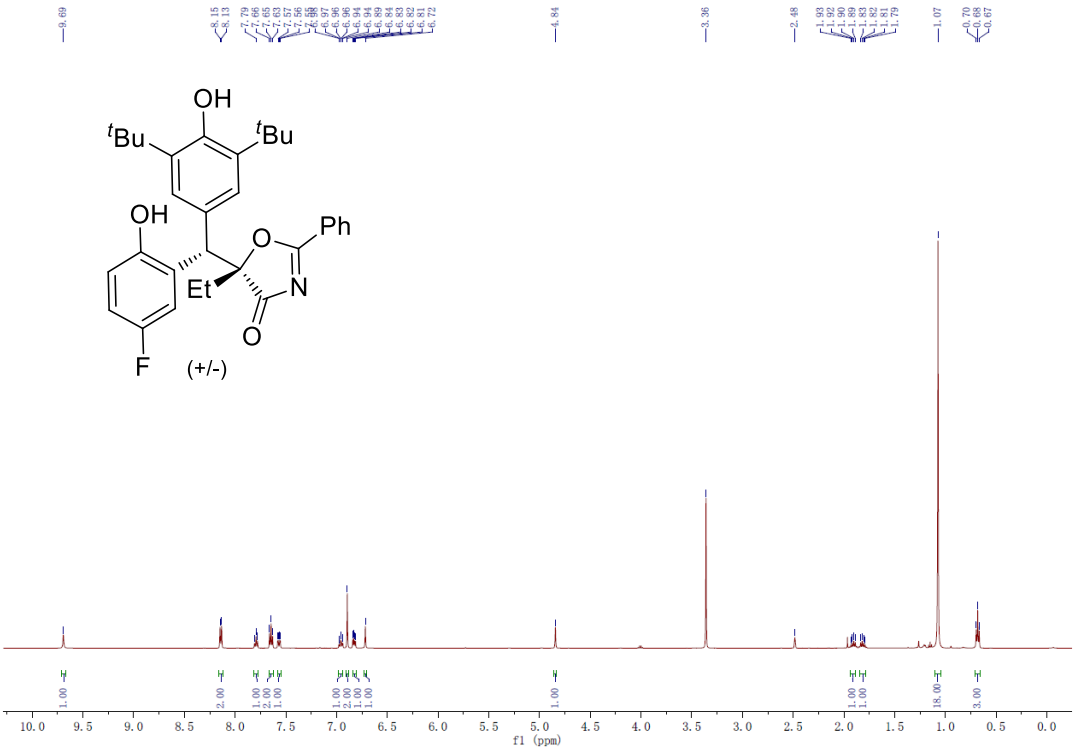


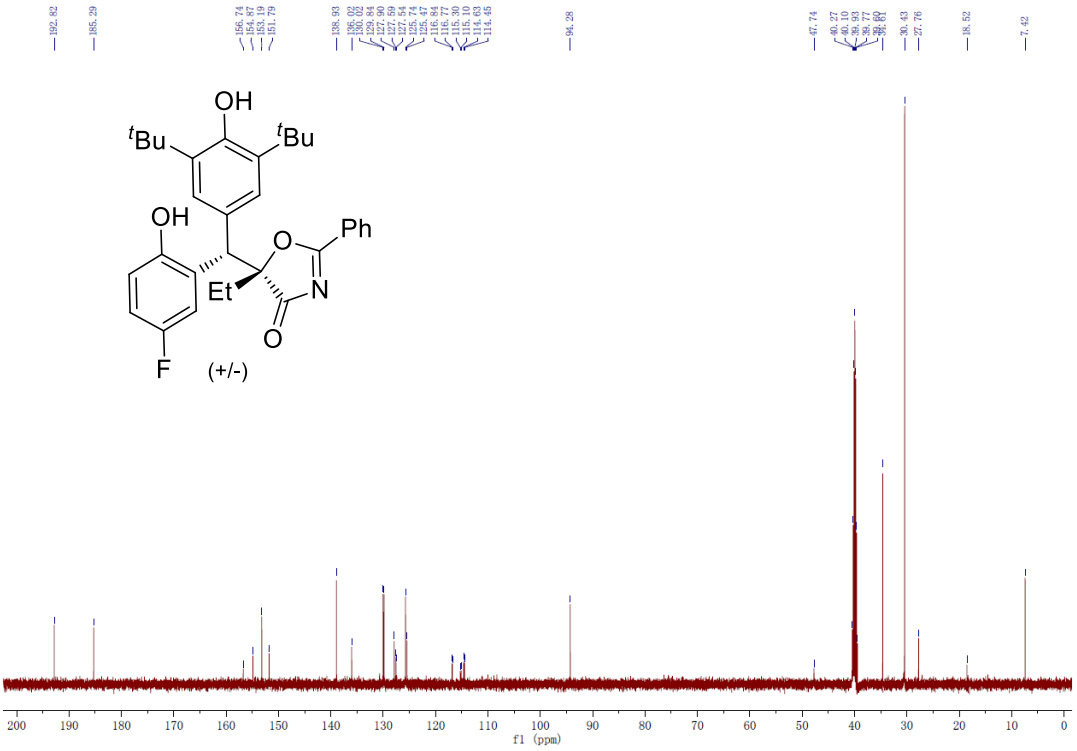
2-(2-bromophenyl)-5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxyphenyl)methyl)-5-ethyloxazol-4(5*H*)-one (3ap)



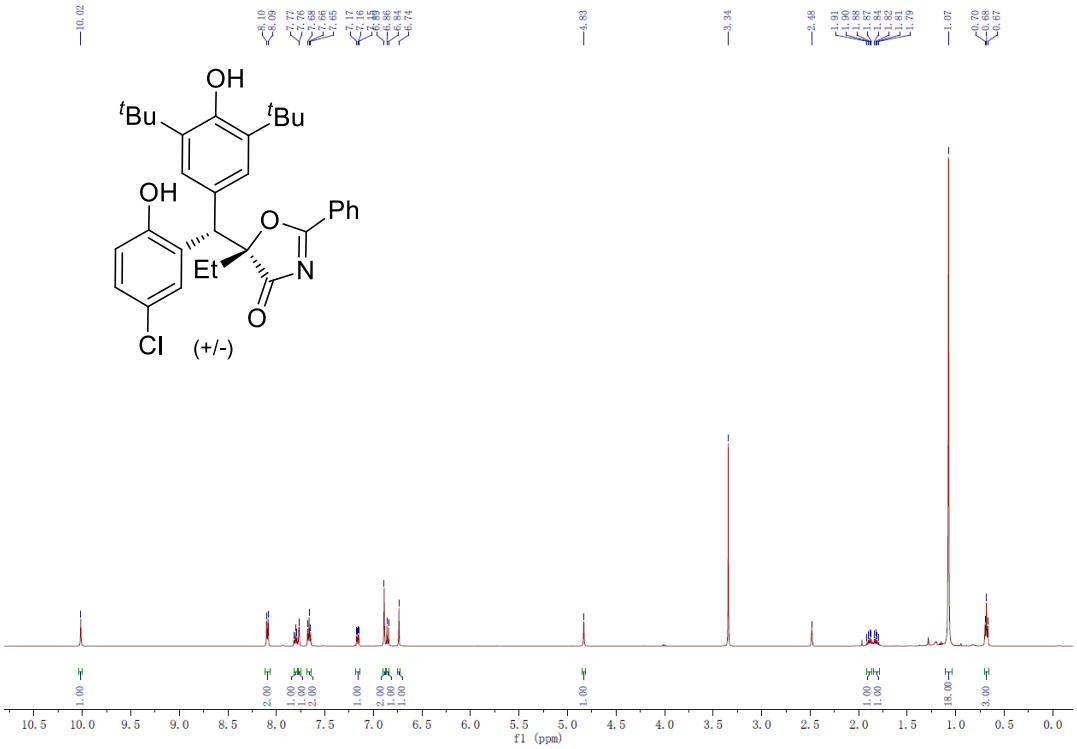


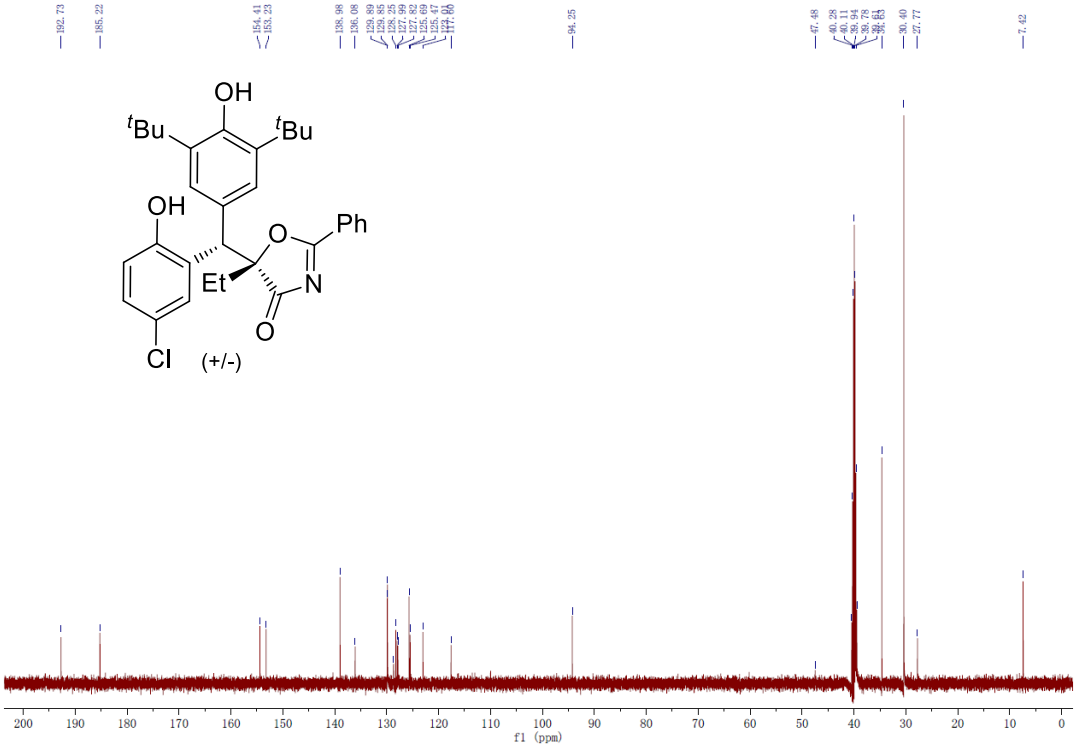
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(5-fluoro-2-hydroxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3ba)



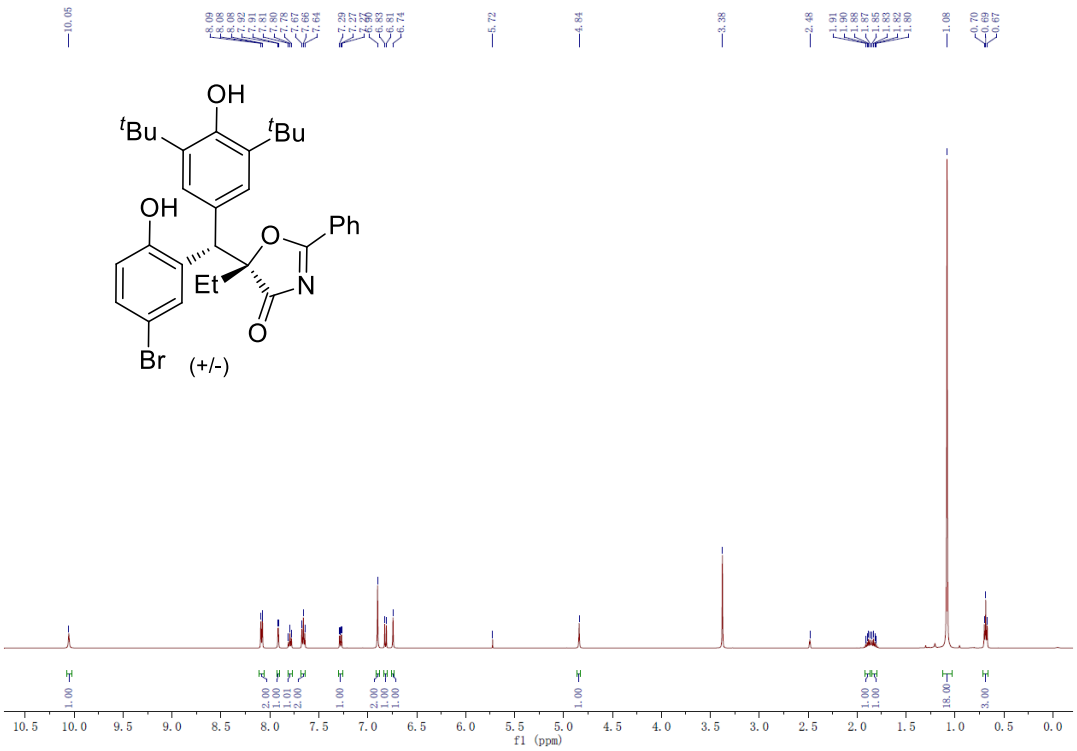


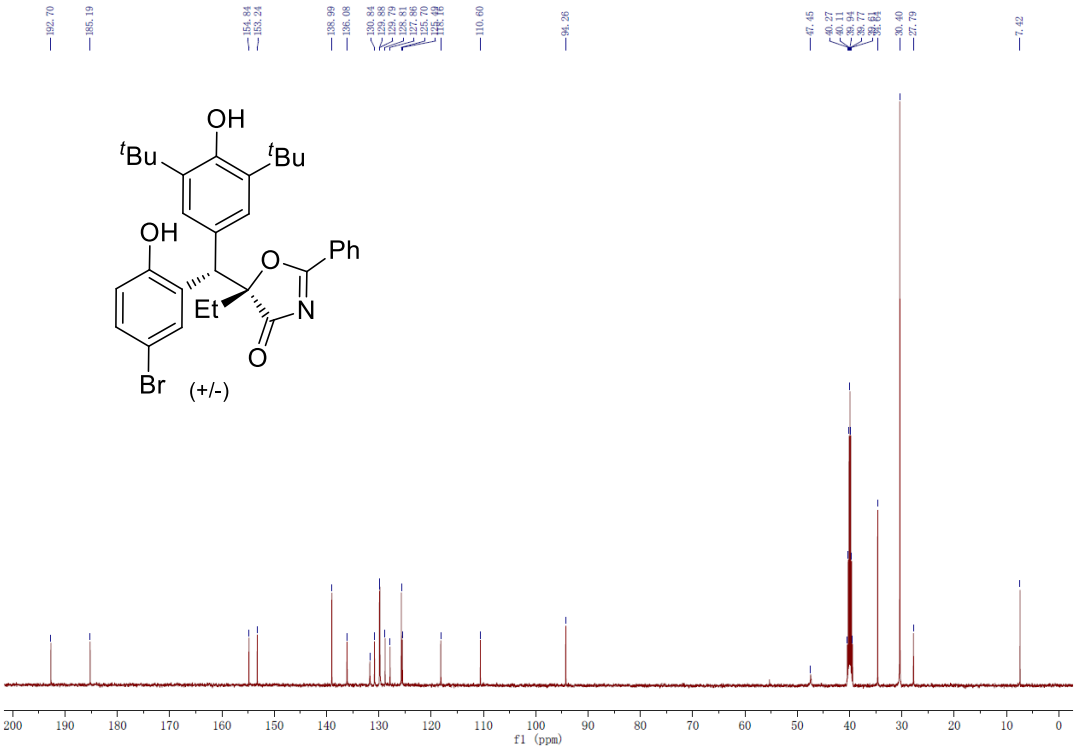
5-((5-chloro-2-hydroxyphenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3ca)



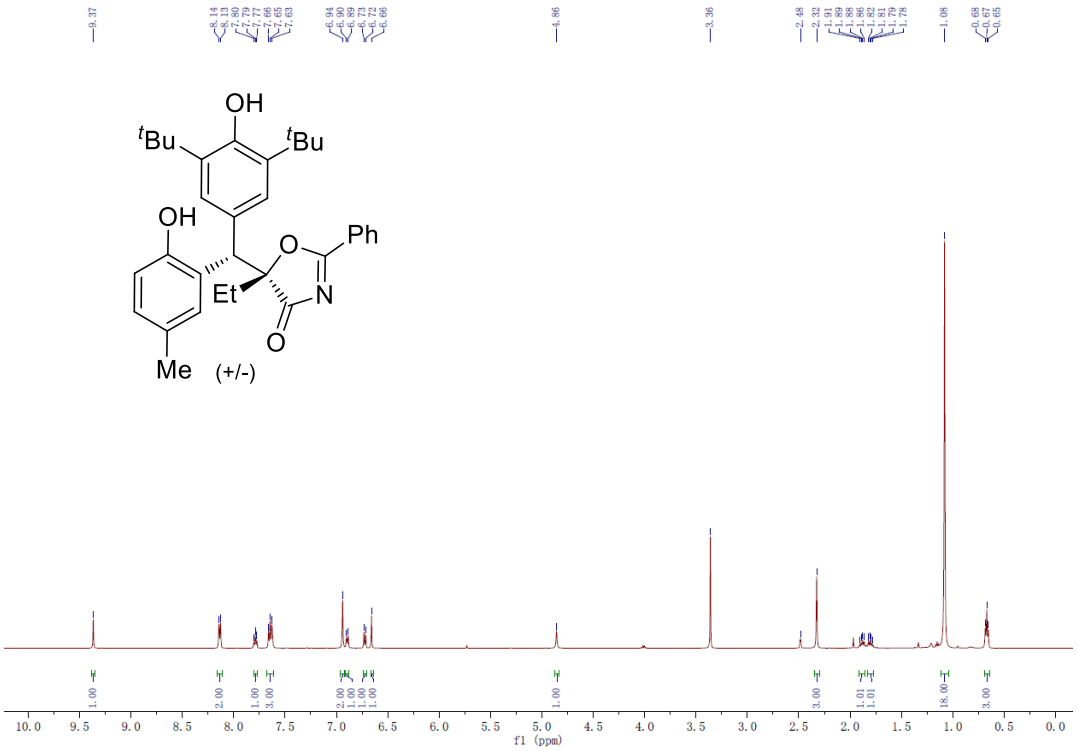


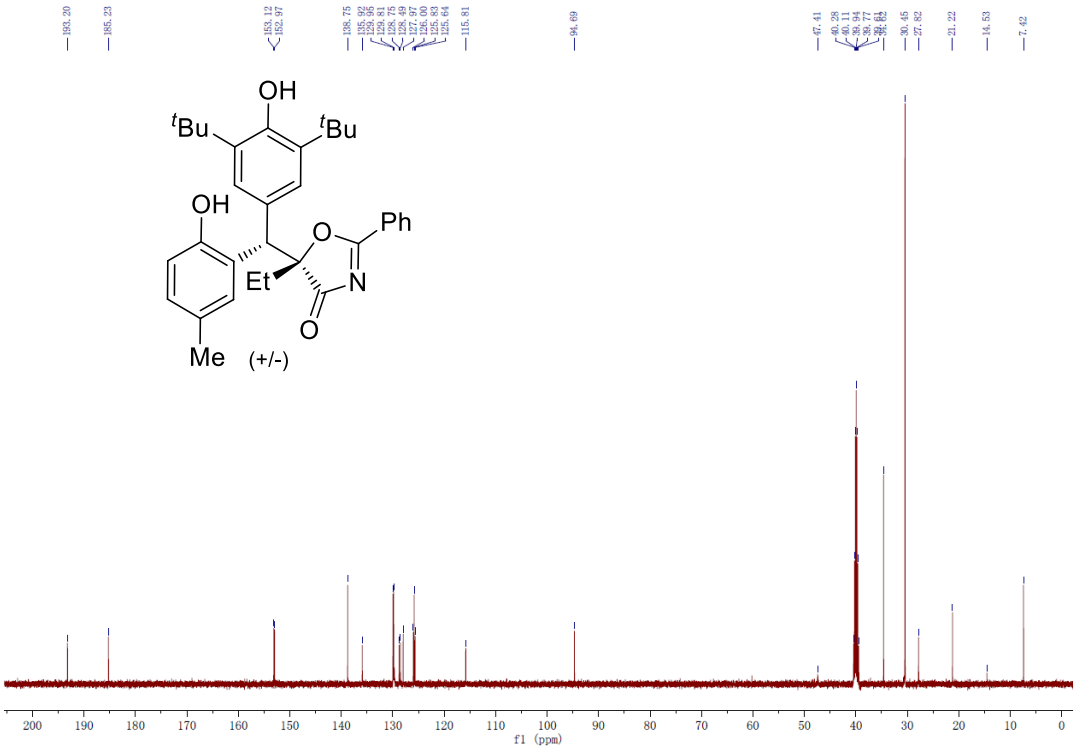
5-((5-bromo-2-hydroxyphenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3da)



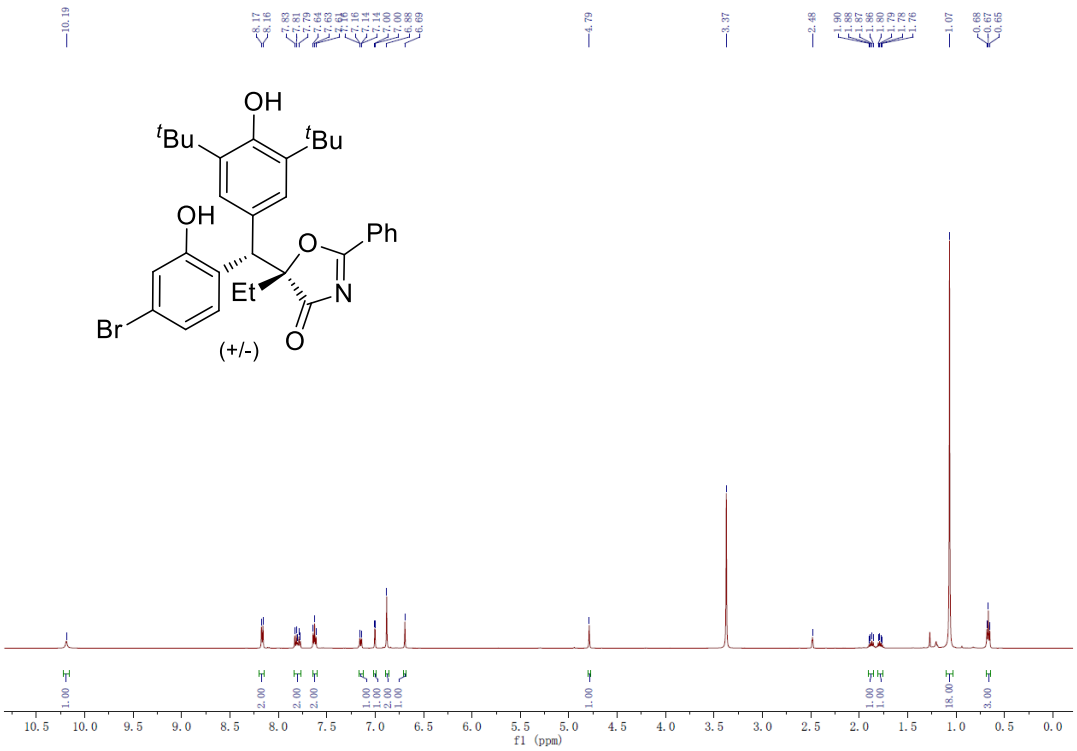


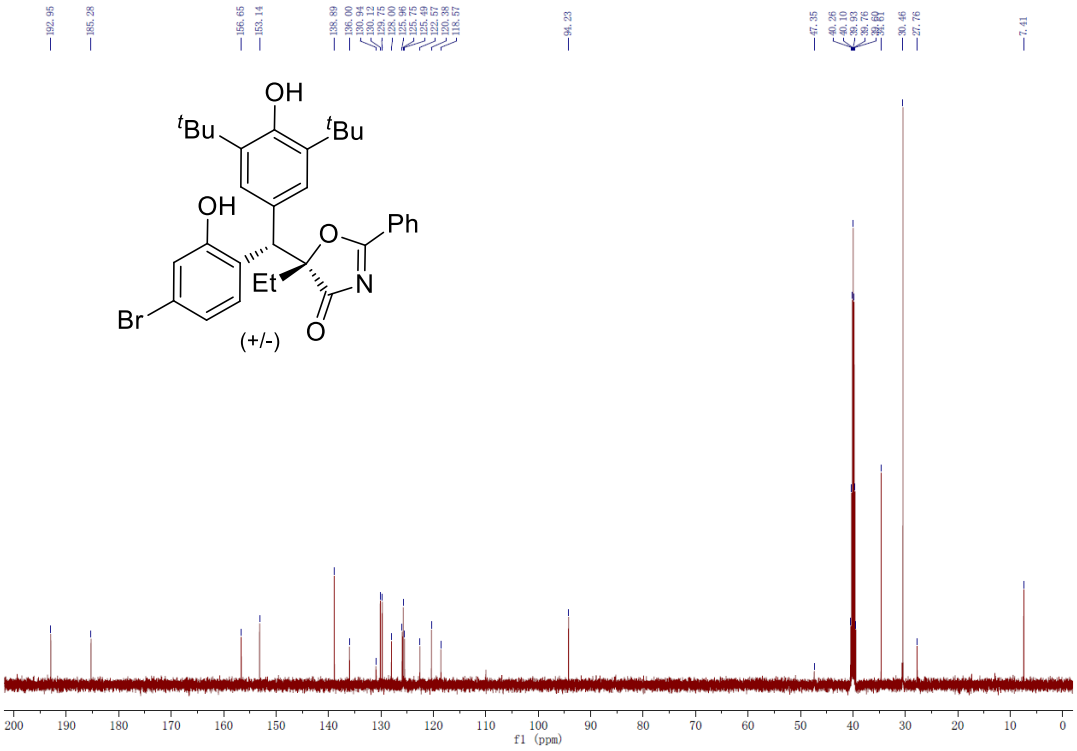
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxy-5-methylphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3ea)



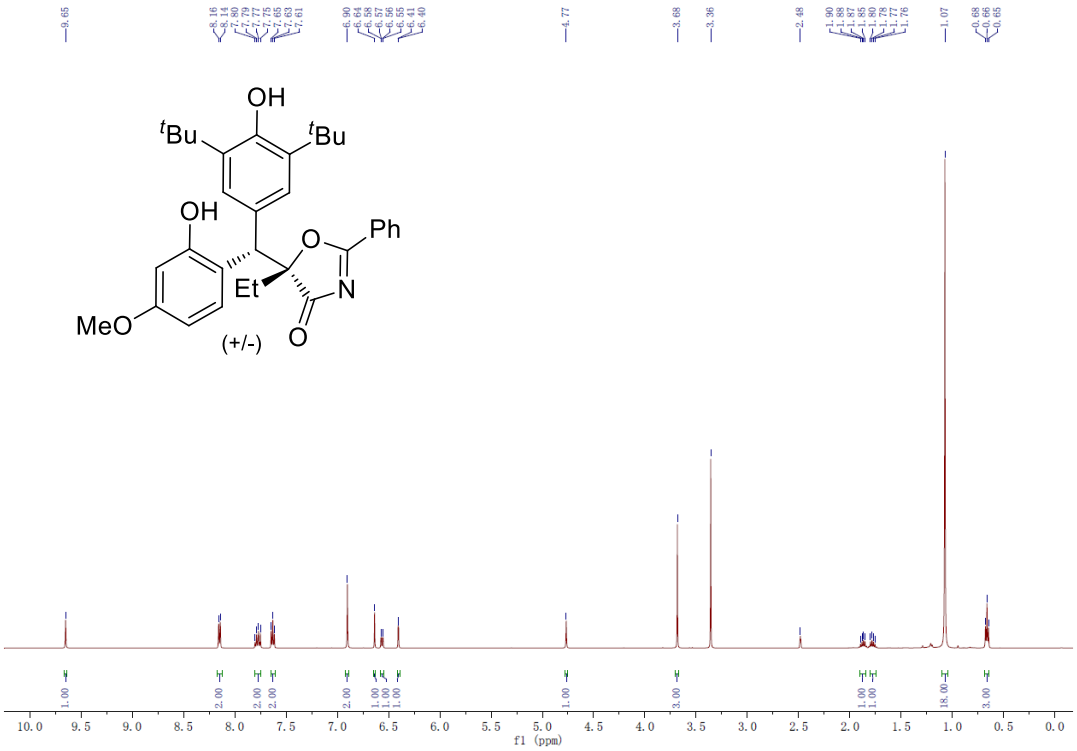


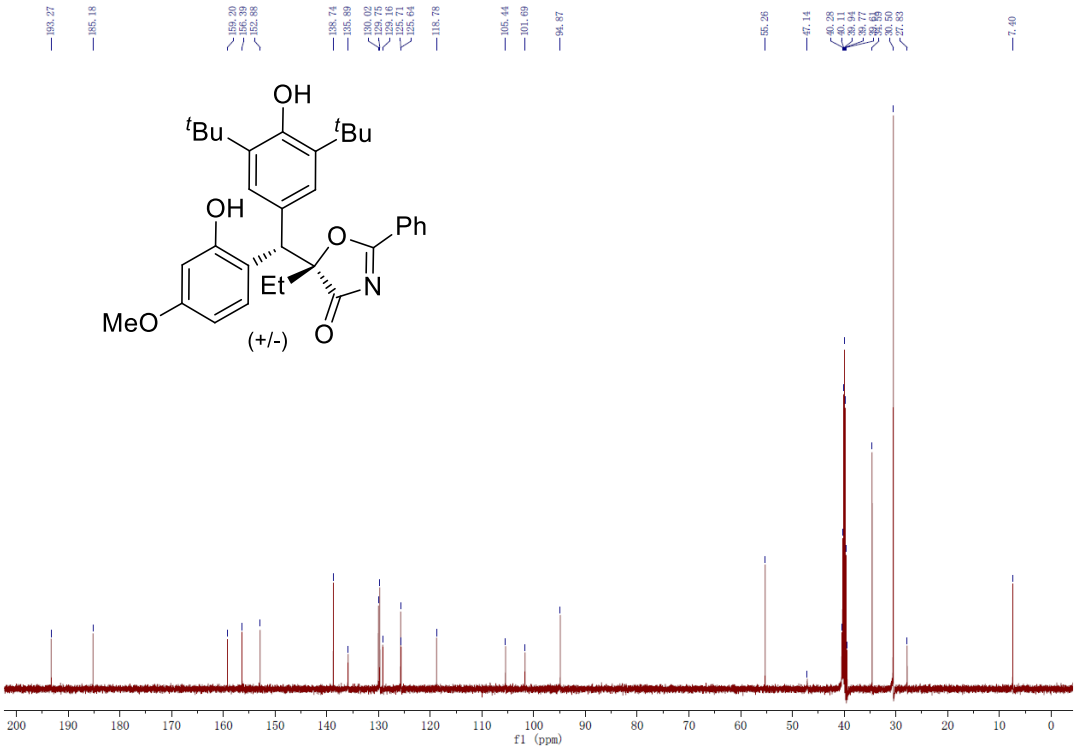
5-((4-bromo-2-hydroxyphenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3fa)



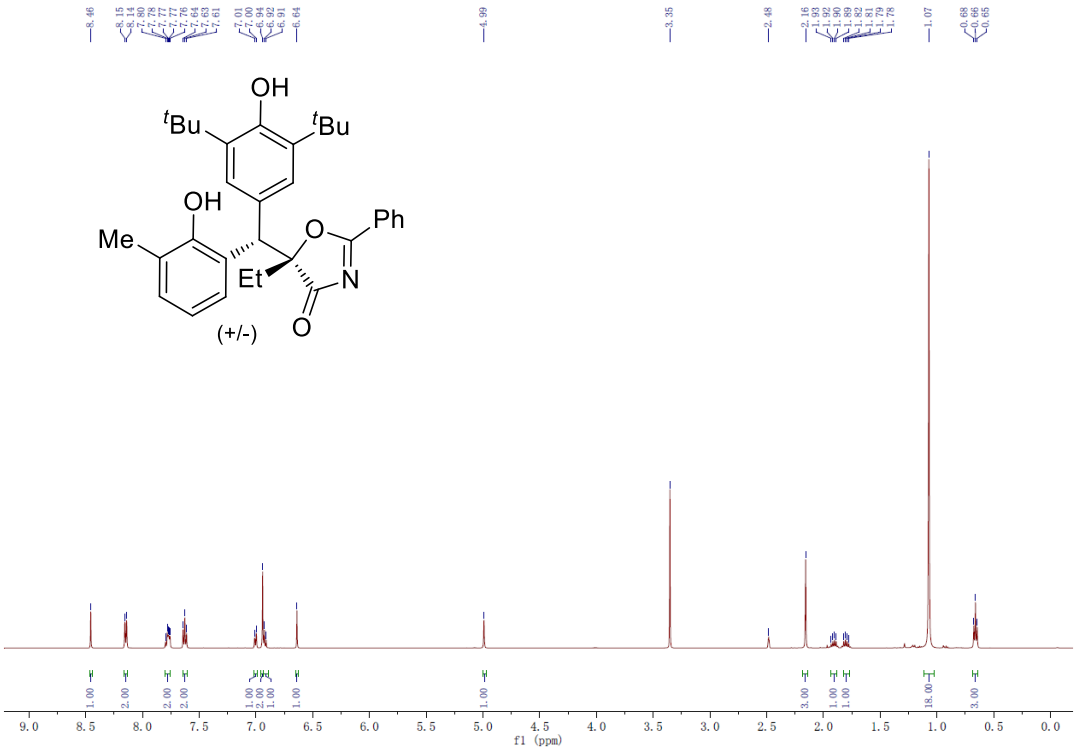


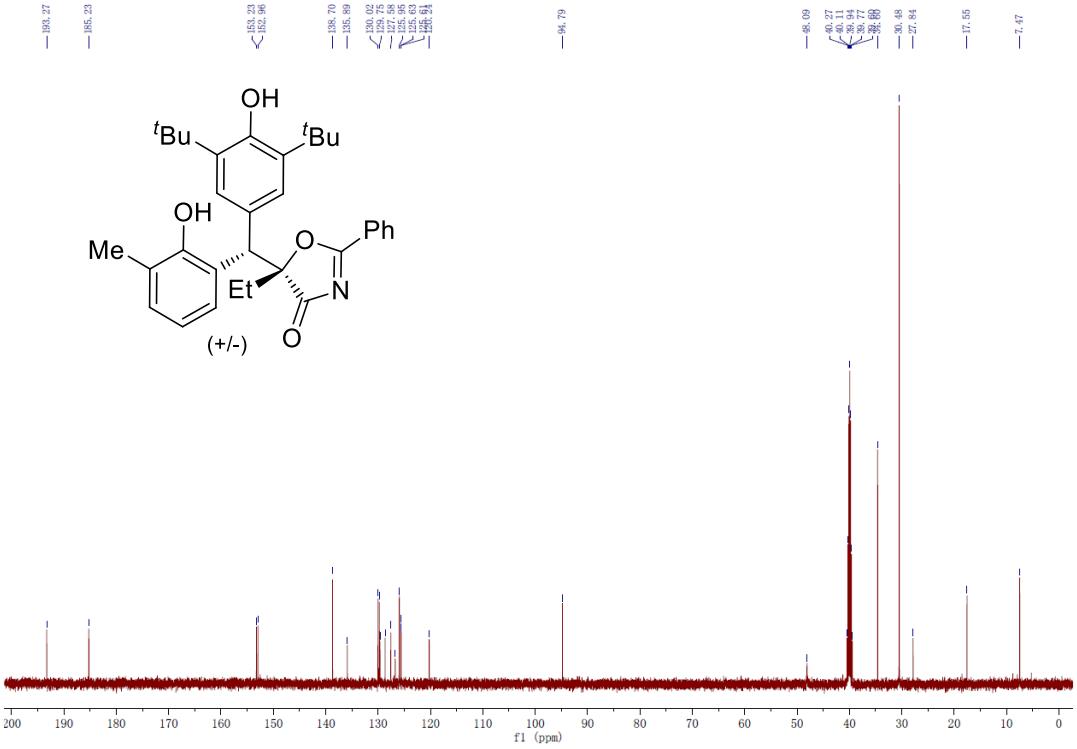
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxy-4-methoxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3ga)



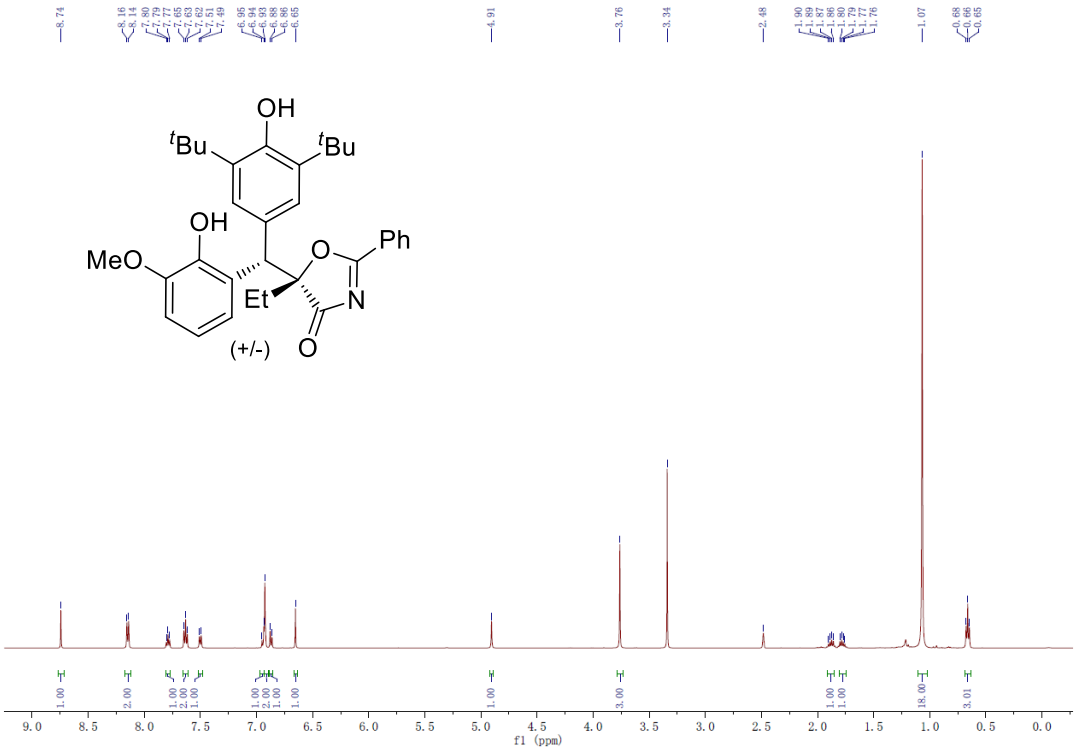


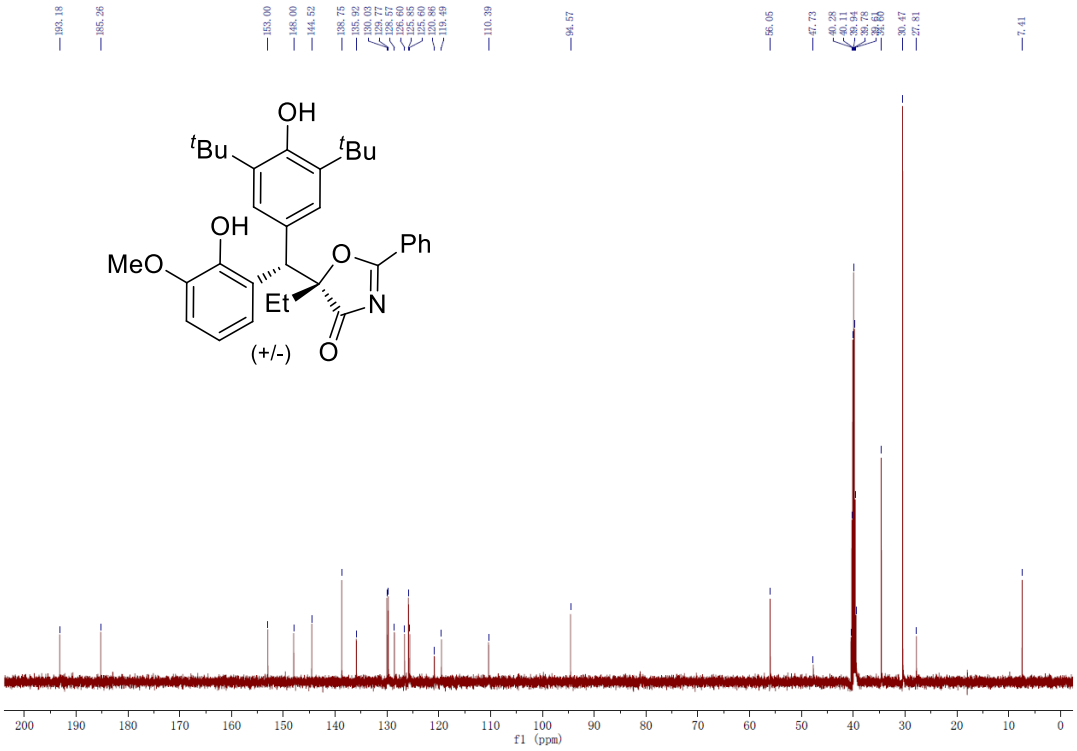
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxy-3-methylphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3ha)



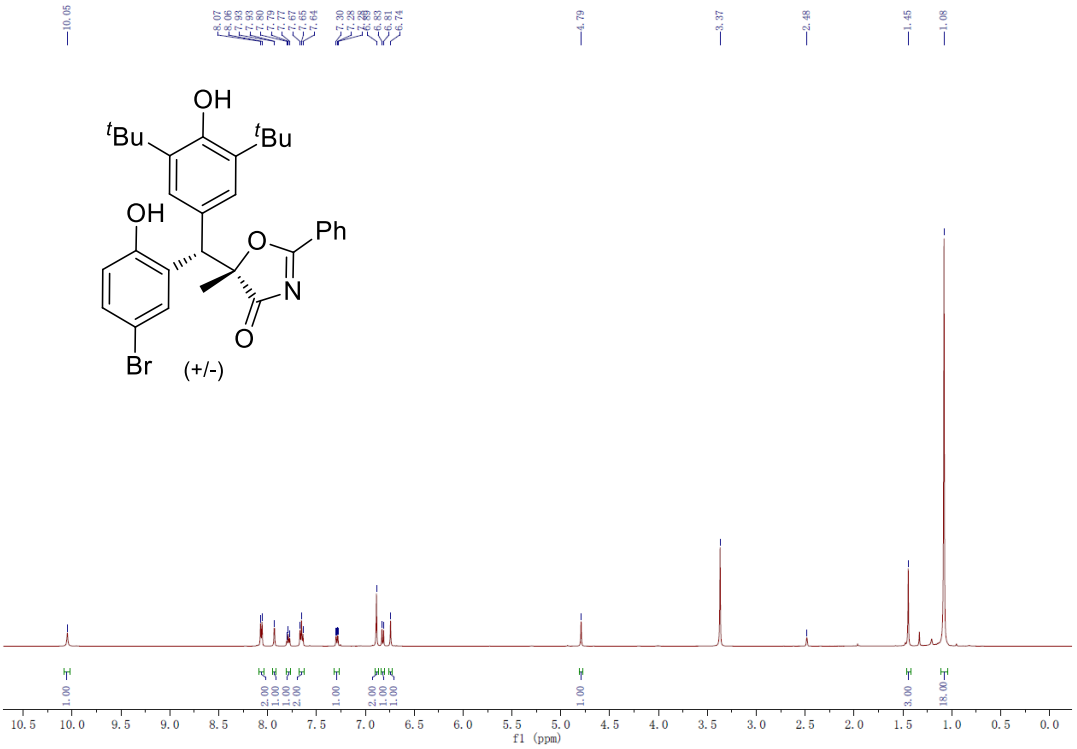


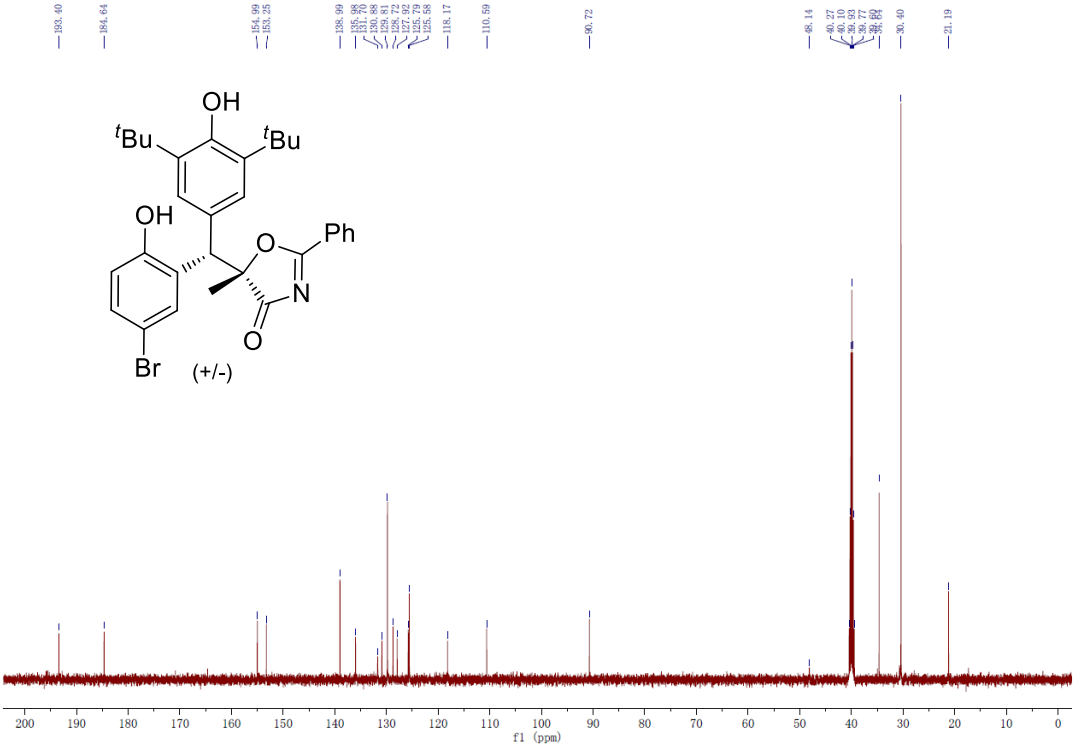
5-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2-hydroxy-3-methoxyphenyl)methyl)-5-ethyl-2-phenyloxazol-4(5*H*)-one (3ia)





5-((5-bromo-2-hydroxyphenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-5-methyl-2-phenyloxazol-4(5*H*)-one (3db)





I: X-Ray Analysis Data

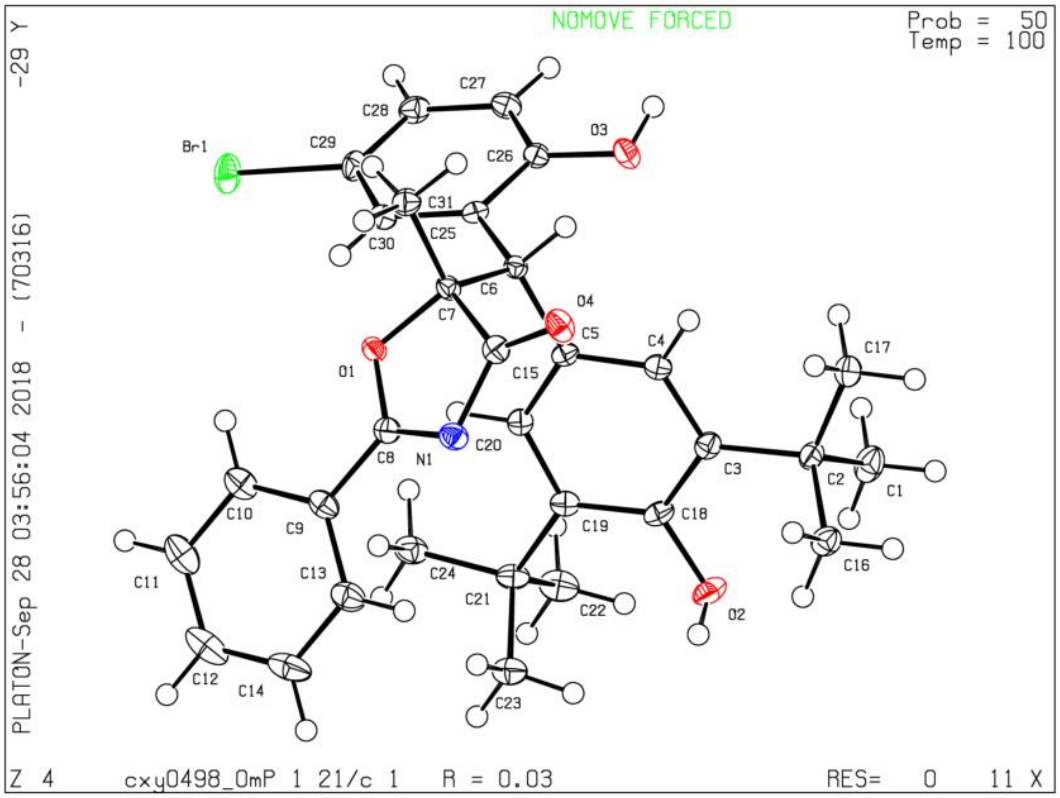


Table 1 Crystal data and structure refinement.

Identification code	**3db**
Empirical formula	$C_{31}H_{34}BrNO_4$
Formula weight	564.50
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.805(2)
b/Å	28.766(4)
c/Å	9.1158(16)
α/°	90
β/°	98.138(6)
γ/°	90
Volume/Å^3	2804.7(9)
Z	4
ρ_{calc}g/cm^3	1.337
μ/mm^{-1}	1.501
F(000)	1176.0
Crystal size/mm^3	0.48 × 0.45 × 0.39
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.73 to 55.118
Index ranges	$-13 \leq h \leq 14$, $-37 \leq k \leq 37$, $-11 \leq l \leq 10$
Reflections collected	43790
Independent reflections	6427 [R_{int} = 0.0548, R_{sigma} = 0.0324]
Data/restraints/parameters	6427/3/344
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0333, wR_2 = 0.0734
Final R indexes [all data]	R_1 = 0.0399, wR_2 = 0.0758
Largest diff. peak/hole / e Å^{-3}	0.63/-0.72

J: Reference

1. K. Zhao, Y. Zhi, T. Shu, A. Valkonen, K. Rissanen, D. Enders, *Angew. Chem. Int. Ed*. **2016**, *55*, 12104-12108.
2. B. M. Trost, K. Hirano, *Angew. Chem. Int. Ed*. **2012**, *51*, 6480-6483.