Catalytic Asymmetric [3 + 2] Cycloaddition of Aromatic Aldehydes with Oxiranes by C–C Bond Cleavage of Epoxides: Highly Efficient Synthesis of Chiral 1,3-Dioxolanes

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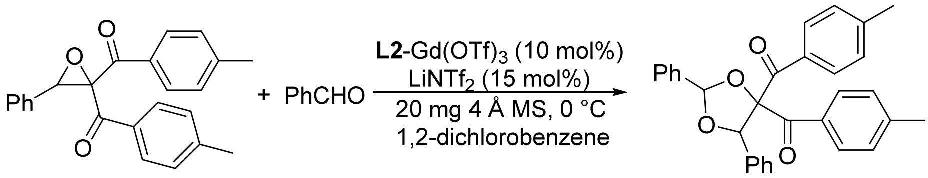
1. General remarks

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26; DMSO, δ = 2.49). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0; DMSO, δ = 39.6). Melting points (m.p.) were measured on electrothermal digital melting point apparatus and were uncorrected. Enantiomeric excesses (ee) were determined by HPLC analysis using the corresponding commercial chiral column as stated in the experimental procedures at 23 °C. Optical rotations were reported as follows: $[\alpha]^{T}_{D}$ (c g/100 mL, in ethyl acetate). HRMS was recorded on a commercial apparatus (ESI Source). All catalytic reactions were run in dried glassware using standard techniques. CH_2Cl_2, DCE, DCB (1,2-dichlorobenzene) was distilled over CaH_2. Toluene and THF were freshly distilled from sodium metal prior to use. All liquid aldehydes and ketones were freshly distilled prior to use and solid aldehydes were used after recrystallization.

2. Typical procedure for catalytic asymmetric [3+2] cycloaddition of oxiranes and adehydes

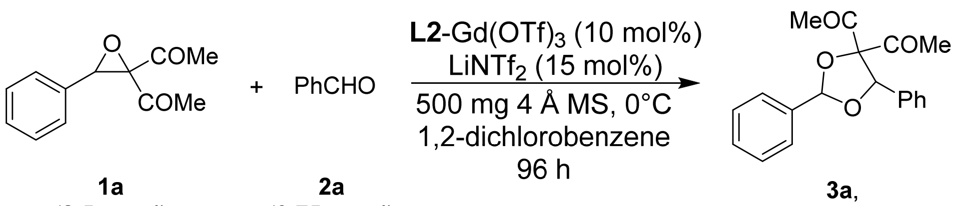
N,N'-dioxide **L2** (6.5 mg, 0.01 mmol), $Gd(OTf)_3$ (6.0 mg, 0.01 mmol), $LiNTf_2$ (15 mol%) and 4 Å MS (20.0 mg) were stirred in 0.5 mL 1,2-dichlorobenzene at 35 ^oC under N2 atmosphere for 0.5 h, then benzaldehyde (15.0 μL, 0.15 mmol) was added. After the temperature decreased to 0 °C, (3-phenyloxirane-2,2-diyl)bis(phenylmethanone) **1a** (32.8 mg, 0.1 mmol) was added. The mixture was stirred at 0 °C for 72 h. The reaction mixture was purified by flash chromatography (petroleum ether: ethyl acetate = 20:1) on silica gel to afford the desired product. (When 2-furaldehyde, 3-furaldehyde or 1,3-dihydroisobenzofuran-5-carbaldehyde was employed, 1.2 eq. aldehyde was added.)

3. The scope of oxiranes



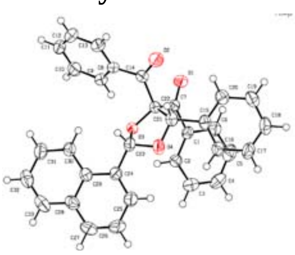
99% yield, 87% ee

4. Scale-up version of the reaction



1a (2.5 mmol)	**2a** (3.75 mmol)	**3a**, 1.05g, 97% yield, >95:5 dr. 89%ee

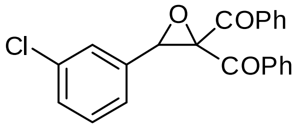
5. X-ray structure of 3h



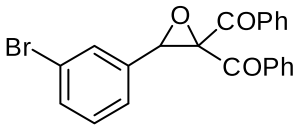
Single crystal of **3h** [$C_{33}H_{24}O_4$] was obtained from the mixed solvents of petroleum ether and ethyl acetate. The absolute configuration of **3h** is (1S, 3S). CCDC970252 contains the supplementary crystallographic data which can be obtained free of charge from The Cambrige Crystallographic Data Centere via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data. $C_{33}H_{24}O_4$, M = 484.52, orthorhombic, a = 10.5563(6), b = 13.0186(6), c = 18.3454(10) Å, U = 2521.2(2) $Å^3$, T = 170(2) K, space group P212121, Z = 4.

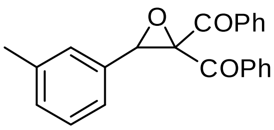
6. Characterization of the aryl oxiranyl diketones:[1,2]



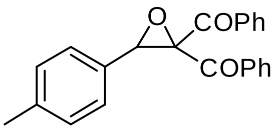
(3-(3-chlorophenyl)oxirane-2,2-diyl)bis(phenylmethanone): white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.13 (m, 2H), 7.97 – 7.91 (m, 2H), 7.63 – 7.58 (m, 1H), 7.54 – 7.46 (m, 3H), 7.42 – 7.43 (m, 3H), 7.25 – 7.16 (m, 3H), 4.66 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 191.69, 190.69, 134.60, 134.58, 134.54, 134.44, 134.40, 134.09, 130.11, 129.77, 129.65, 129.16, 128.87, 128.68, 126.64, 124.48, 73.81, 61.80 ppm; EI-HRMS: Calcd for $C_{22}H_{15}{}^{35}ClO_3$ $[M+H]^+$ 363.0788, Found 363.0789.



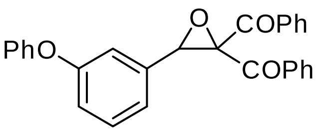
(3-(3-bromophenyl)oxirane-2,2-diyl)bis(phenylmethanone): white solid; ^{1}H NMR (400 MHz, DMSO) δ 8.07 (d, *J* = 7.2 Hz, 2H), 7.89 (d, *J* = 7.3 Hz, 2H), 7.76 – 7.69 (m, 1H), 7.66 – 7.57 (m, 3H), 7.56 – 7.43 (m, 4H), 7.40 – 7.32 (m, 1H), 7.30 – 7.22 (m, 1H), 5.07 (s, 1H) ppm; ^{13}C NMR (101 MHz, DMSO) δ 191.65, 190.62, 135.16, 134.78, 134.72, 134.12, 133.73, 131.74, 130.51, 129.41, 129.13, 129.08, 129.05, 128.95, 125.39, 121.55, 73.19, 60.94 ppm.



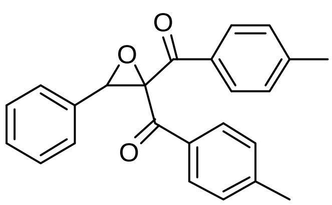
(3-(m-tolyl)oxirane-2,2-diyl)bis(phenylmethanone): white solid; 1H NMR (400 MHz, CDCl3) δ 8.21 – 8.15 (m, 2H), 7.99 – 7.93 (m, 2H), 7.64 – 7.55 (m, 1H), 7.52 – 7.44 (m, 3H), 7.41 – 7.32 (m, 2H), 7.18 – 7.11 (m, 3H), 7.07 – 7.01 (m, 1H), 4.65 (s, 1H), 2.27 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl3) δ = 192.13, 191.16, 138.17, 134.82, 134.44, 134.23, 134.16, 132.23, 130.14, 129.73, 129.72, 128.79, 128.54, 128.33, 127.00, 123.46, 73.98, 62.81, 21.34 ppm; EI-HRMS: Calcd for $C_{23}H_{18}O_3$ $[M+Na]^+$ 365.1154, Found 365.1152.



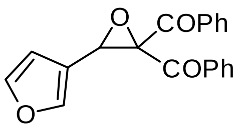
(3-(p-tolyl)oxirane-2,2-diyl)bis(phenylmethanone): white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.15 (m, 2H), 7.99 – 7.93 (m, 2H), 7.62 – 7.56 (m, 1H), 7.51 – 7.45 (m, 3H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 4.66 (s, 1H), 2.26 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.15, 191.21, 138.83, 134.79, 134.42, 134.25, 134.17, 130.13, 129.76, 129.28, 129.18, 128.78, 128.56, 126.30, 74.07, 62.84, 21.21 ppm; EI-HRMS: Calcd for $C_{23}H_{18}O_3$ $[M+H]^+$ 343.1334, Found 343.1332.



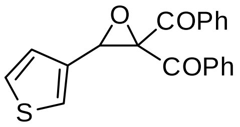
(3-(3-phenoxyphenyl)oxirane-2,2-diyl)bis(phenylmethanone): white solid; ^{1}H NMR (400 MHz, DMSO) δ 8.10 - 8.03 (m, 2H), 7.92 – 7.85 (m, 2H), 7.75 – 7.69 (m, 1H), 7.67 – 7.56(m, 3H), 7.52 - 7.45 (m, 2H), 7.40 – 7.30 (m, 3H), 7.20 – 7.12 (m, 2H), 6.96 – 6.87 (m, 2H), 6.84 – 6.75 (m, 2H), 5.02 (s, 1H) ppm; ^{13}C NMR (101 MHz, DMSO) δ = 191.90, 190.58, 156.45, 156.22, 134.70, 134.68, 134.66, 134.04, 133.75, 130.25, 130.01, 129.44, 129.21, 129.00, 128.85, 123.57, 121.61, 119.39, 118.38, 115.98, 73.16, 61.40 ppm; EI-HRMS: Calcd for $C_{28}H_{20}O_4$ $[M+H]^+$ 421.1440, Found 421.1436.



(3-phenyloxirane-2,2-diyl)bis(p-tolylmethanone): white solid; ^{1}H NMR (400 MHz, DMSO) δ 8.01 – 7.93 (m, 2H), 7.80 – 7.73 (m, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.24 (m, 7H), 4.96 (s, 1H), 2.38 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ = 191.21, 190.19, 145.62, 145.51, 132.56, 131.73, 131.31, 129.60, 129.44, 129.27, 128.79, 128.28, 126.26, 73.53, 61.66, 21.29, 21.20 ppm; EI-HRMS: Calcd for $C_{24}H_{20}O_3$ $[M+H]^+$ 357.1491, Found 357.1488.

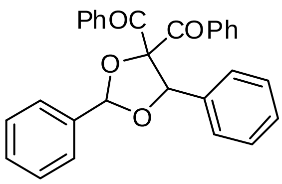


(3-(furan-3-yl)oxirane-2,2-diyl)bis(phenylmethanone): white solid; ^{1}H NMR (400 MHz, DMSO) δ 8.10 – 8.02 (m, 2H), 8.00 – 7.90 (m, 2H), 7.84 (s, 1H), 7.74 – 7.49 (m, 7H), 6.30 – 6.09 (m, 1H), 4.91 (s, 1H) ppm; ^{13}C NMR (101 MHz, DMSO) δ = 191.86, 191.43, 144.13, 143.18, 134.70, 134.18, 133.79, 129.37, 129.23, 129.03, 128.95, 118.52, 108.44, 72.58, 56.37 ppm; EI-HRMS: Calcd for $C_{20}H_{14}O_4$ $[M+H]^+$ 319.0970, Found 319.0966.

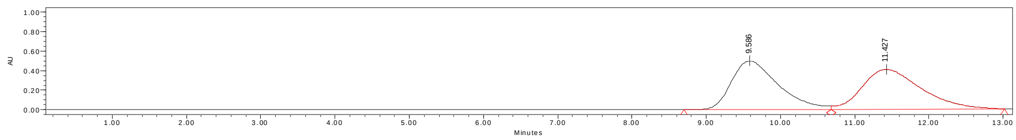


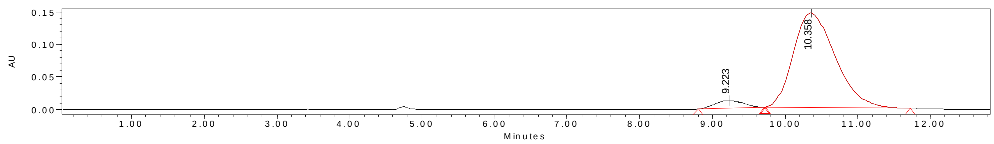
(3-(thiophen-3-yl)oxirane-2,2-diyl)bis(phenylmethanone): white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.13 (m, 2H), 8.02 – 7.94 (m, 2H), 7.62 – 7.56 (m, 1H), 7.54 – 7.44 (m, 3H), 7.41 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.21 – 7.16 (m, 1H), 7.01 – 6.96 (m, 1H), 4.75 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 191.95, 191.47, 134.66, 134.50, 134.28, 134.22, 133.90, 130.11, 129.71, 128.81, 128.61, 126.56, 125.75, 124.27, 73.73, 59.72 ppm; EI-HRMS: Calcd for $C_{20}H_{14}O_3S$ $[M+H]^+$ 335.0742, Found 335.0737.

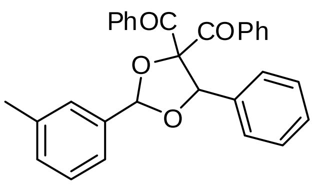
7. Characterization of the products



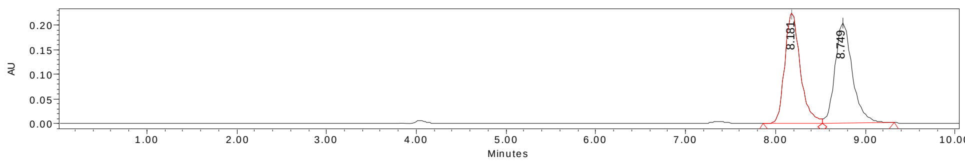
(2,5-diphenyl-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3a:[3] Viscous oil in 92% yield (petroleum ether : EtOAc = 20: 1); $[\alpha]^{26}_{D}$ = -119.52 (c 0.84, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ASH column (*i*PrOH/hexane = 2/98, 1.0 mL/min, 254 nm), t_r (minor) = 9.22 min, t_r (major) = 10.35 min, 90% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.02 (m, 2H), 7.76 – 7.66 (m, 4H), 7.52 – 7.46 (m, 4H), 7.43 – 7.34 (m, 5H), 7.19 – 7.09 (m, 5H), 6.59 (s, 1H), 6.06 (s, 1H) ppm.

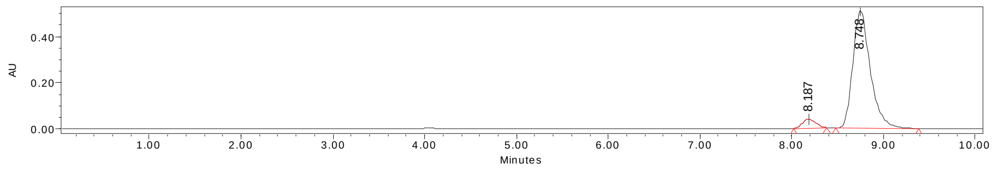


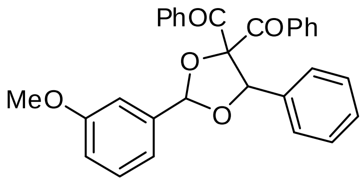




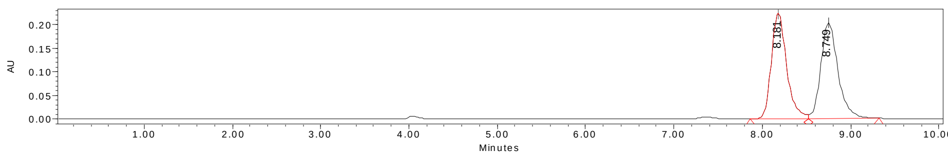
(5-phenyl-2-(m-tolyl)-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3b: Viscous oil in 97% yield (petroleum ether : EtOAc = 20: 1); $[\alpha]^{26}_{D}$ = -101.16 (c 0.60, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 8.19 min, t_r (major) = 8.75 min, 89% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 7.6 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.51 – 7.47(m, 1H), 7.43 – 7.35 (m, 6H), 7.31– 7.27 (m, 1H), 7.21 – 7.08 (m, 5H), 6.58 (s, 1H), 6.02 (s, 1H), 2.44 (s, 3H). ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.37, 194.27, 138.27, 135.61, 134.81, 134.57, 134.22, 133.46, 132.96, 130.70, 130.28, 129.96, 128.49, 128.44, 128.22, 127.94, 127.88, 127.72, 127.49, 124.28, 104.40, 94.89, 82.64, 21.52 ppm; EI-HRMS: Calcd for $C_{30}H_{24}O_4$ $[M+Na]^+$ 471.1572, Found 471.1571.

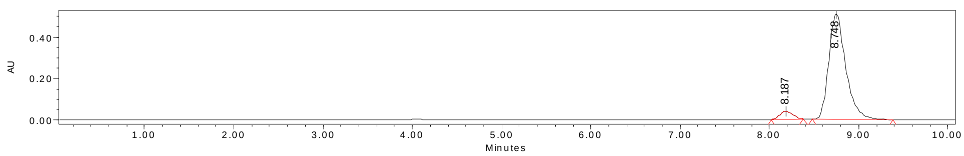


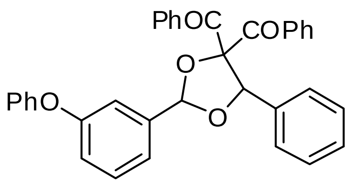




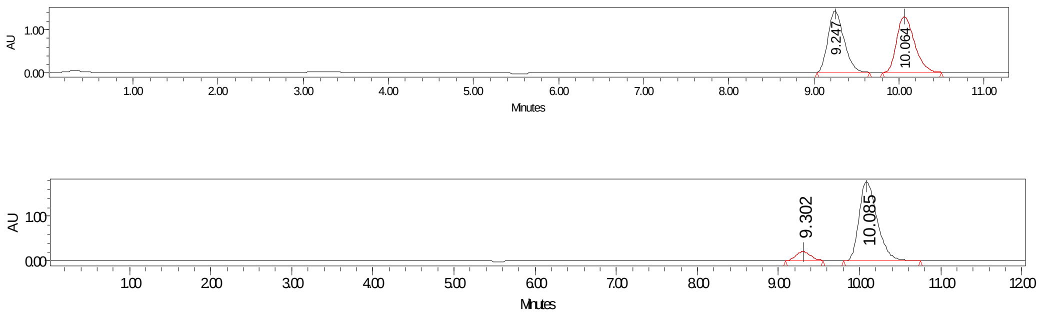
(2-(3-methoxyphenyl)-5-phenyl-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3c: Viscous oil in 90% yield (petroleum ether : EtOAc = 10: 1); $[\alpha]^{26}_{D}$ = -77.30 (c 0.89, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 8.19 min, t_r (major) =8.75 min, 88% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.51 – 7.47 (m, 1H), 7.43 – 7.35 (m, 6H), 7.32 – 7.28 (m, 1H), 7.20 – 7.12 (m, 5H), 6.58 (s, 1H), 6.02 (s, 1H), 2.44 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.37, 194.27, 138.27, 135.61, 134.81, 134.57, 134.22, 133.46, 132.96, 130.70, 130.28, 129.96, 128.49, 128.44, 128.22, 127.94, 127.88, 127.72, 127.49, 124.28, 104.40, 94.89, 82.64, 21.52 ppm; EI-HRMS: Calcd for $C_{30}H_{24}O_5$ $[M+Na]^+$ 487.1521, Found 487.1520.

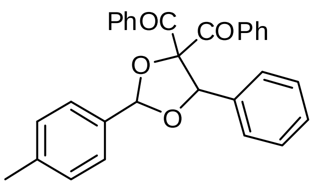




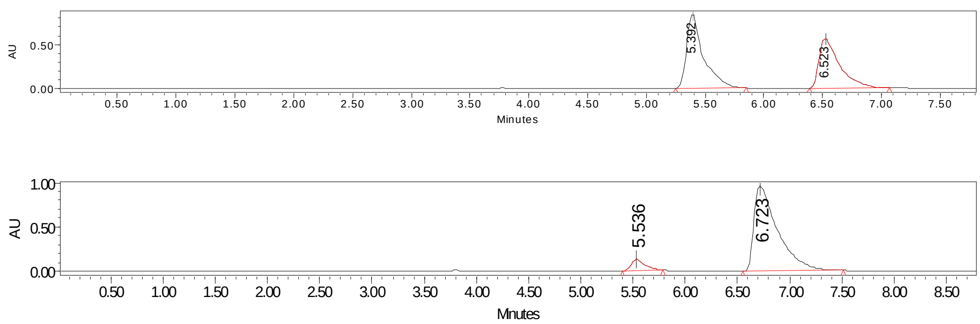


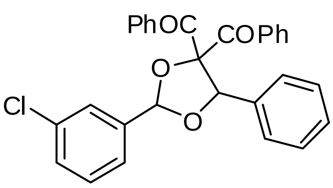
(2-(3-phenoxyphenyl)-5-phenyl-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3d: Viscous oil in 96% yield (petroleum ether : EtOAc = 10: 1); $[\alpha]^{26}_{D}$ = -70.68 (c 1.01, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 9.30min, t_r (major) =10.09 min, 83% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.54 – 7.41 (m, 5H), 7.40 – 7.34 (m, 6H), 7.21 – 7.04 (m, 9H), 6.58 (s, 1H), 6.03 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.10, 194.06, 157.58, 156.89, 136.98, 135.52, 134.47, 134.17, 133.53, 133.00, 130.26, 129.99, 129.88, 129.82, 128.52, 128.28, 127.96, 127.77, 127.50, 123.63, 121.97, 120.07, 119.18, 117.46, 103.76, 94.95, 82.66 ppm; EI-HRMS: Calcd for $C_{35}H_{26}O_5$ $[M+Na]^+$ 549.1678, Found 549.1677.



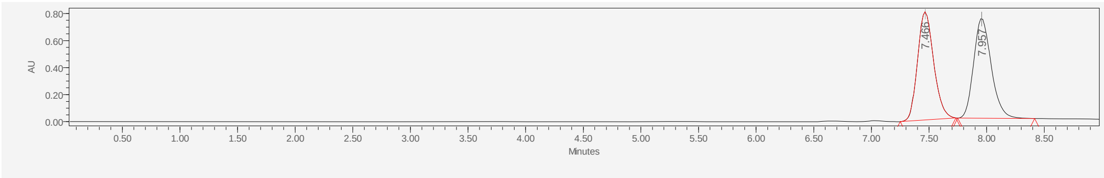


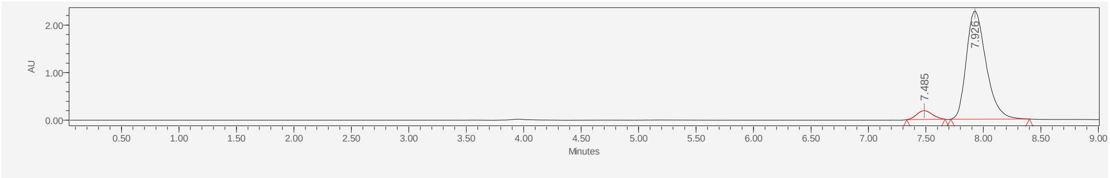
(5-phenyl-2-(p-tolyl)-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3e: Viscous oil in 95% yield (petroleum ether : EtOAc = 20: 1); $[\alpha]^{26}_{D}$ = -103.62 (c 0.41, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IB column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 5.54 min, t_r (major) = 6.72 min, 86% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.76 – 7.67 (m, 2H), 7.66 – 7.58 (m, 2H), 7.52 – 7.46 (m, 1H), 7.44 – 7.33 (m, 5H), 7.33 – 7.27 (m, 2H), 7.22 – 7.07 (m, 5H), 6.58 (s, 1H), 6.03 (s, 1H), 2.43 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.35, 194.30, 139.93, 135.62, 134.63, 134.24, 133.45, 132.95, 132.05, 130.28, 129.91, 129.20, 128.48, 128.20, 127.93, 127.74, 127.50, 127.19, 104.38, 94.89, 82.60, 21.45 ppm; EI-HRMS: Calcd for $C_{30}H_{24}O_4$ $[M+Na]^+$ 471.1572, Found 471.1572.

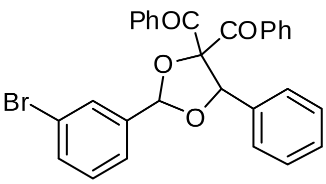




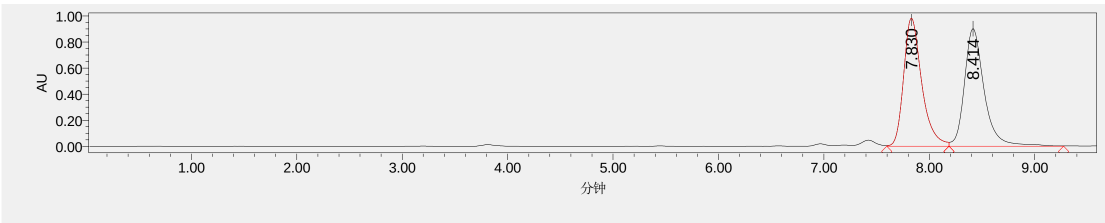
(2-(3-chlorophenyl)-5-phenyl-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3f: Viscous oil in 96% yield (petroleum ether : EtOAc = 20: 1); $[\alpha]^{26}_{D}$ = -95.90 (c 0.95, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 7.49 min, t_r (major) =7.93 min, 88% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.6Hz, 2H), 7.76 (s, 1H), 7.66 – 7.59 (m, 3H), 7.53 – 7.36 (m, 8H), 7.20 – 7.10 (m, 5H), 6.58 (s, 1H), 6.03 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.96, 194.04, 137.01, 135.43, 134.54, 134.19, 134.15, 133.63, 133.07, 130.25, 130.08, 129.89, 129.75, 128.57, 128.42, 128.04, 127.81, 127.53, 127.39, 125.47, 103.30, 94.74, 82.86 ppm; EI-HRMS: Calcd for $C_{29}H_{21}{}^{35}ClO_4$ $[M+Na]^+$ 491.1026, Found 491.1025.

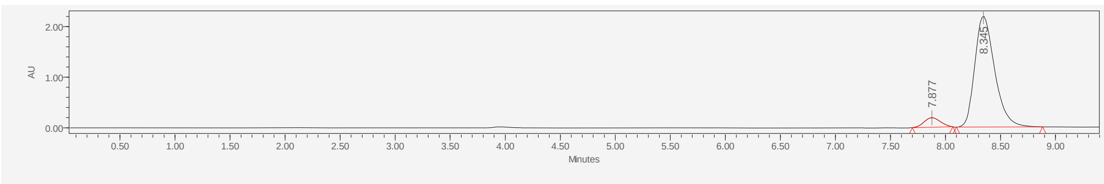


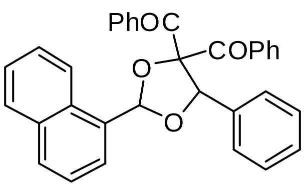




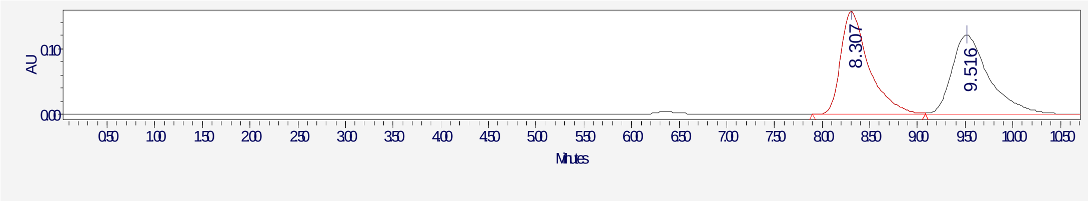
(2-(3-bromophenyl)-5-phenyl-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3g: Viscous oil in 99% yield (petroleum ether : EtOAc = 20: 1); $[\alpha]^{26}_{D}$ = -93.47 (c 0.81, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 7.88 min, t_r (major) = 8.35 min, 87% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.91 (s, 1H), 7.77 – 7.69(m, 4H), 7.53 – 7.48 (m, 1H), 7.42 – 7.33 (m, 6H), 7.21 – 7.10 (m, 5H), 6.58 (s, 1H), 6.02 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.98, 194.02, 137.20, 135.44, 134.17, 134.13, 133.65, 133.08, 133.04, 130.30, 130.26, 130.17, 129.76, 128.58, 128.43, 128.05, 127.83, 127.52, 125.97, 122.61, 103.24, 94.73, 82.86 ppm; EI-HRMS: Calcd for $C_{29}H_{21}{}^{79}BrO_4$ $[M+Na]^+$ 535.0521, Found 535.0518.

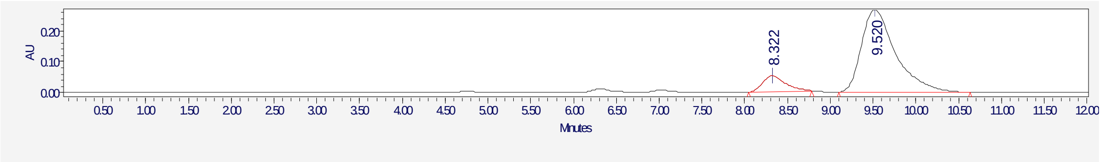


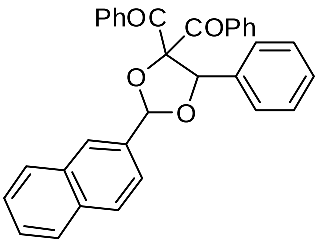




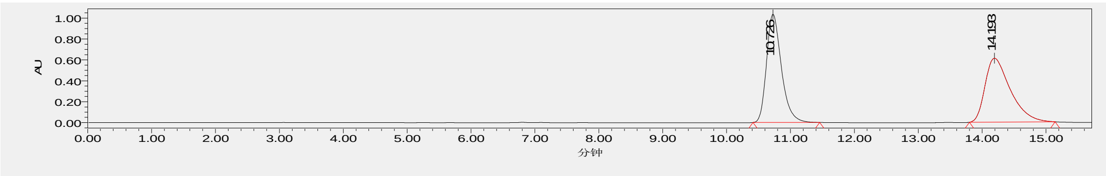
(2-(naphthalen-1-yl)-5-phenyl-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3h:[3] White solid in 97% yield (petroleum ether : EtOAc = 20: 1); $[\alpha]^{18}_{D}$ = -143.82 (c 0.94, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IC column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 8.32 min, t_r (major) = 9.52 min, 77% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.2 Hz, 1H), 8.16 – 8.08 (m, 2H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.94 – 7.86(m, 2H), 7.80 – 7.72 (m, 2H), 7.63 – 7.58 (m, 1H), 7.58 – 7.49 (m, 2H), 7.48 – 7.35 (m, 6H), 7.19 – 7.07 (m, 5H), 6.72 (s, 1H), 6.66 (s, 1H) ppm.

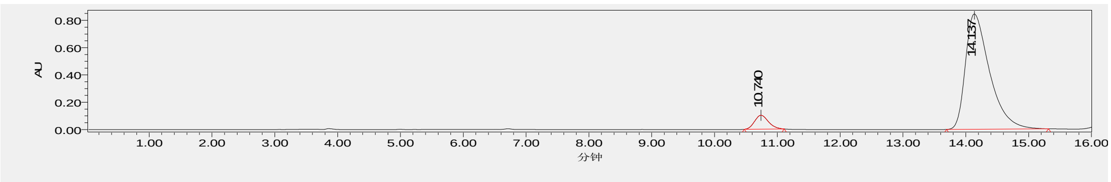


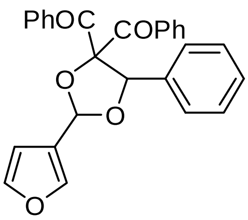




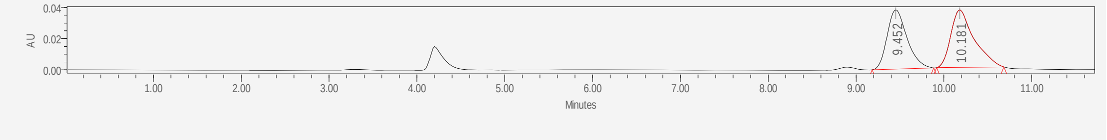
(2-(naphthalen-2-yl)-5-phenyl-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3i: White solid in 95% yield (petroleum ether : EtOAc = 20: 1); $[\alpha]^{26}_{D}$ = -94.19 (0.77, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 10.74 min, t_r (major) =14.14min, 87% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 8.01 – 7.97 (m, 1H), 7.95 – 7.86 (m, 3H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.51 – 7.44 (m, 3H), 7.42 – 7.36 (m, 3H) ,7.19 – 7.12 (m, 5H), 6.67 (s, 1H), 6.24 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 196.32, 194.23, 135.63, 134.57, 134.26, 134.15, 133.54, 133.00, 132.92, 132.36, 130.31, 129.92, 128.55, 128.49, 128.48, 128.31, 128.00, 127.89, 127.79, 127.56, 127.14, 126.93, 126.50, 124.23, 104.48, 94.99, 82.84 ppm; EI-HRMS: Calcd for $C_{33}H_{24}O_4$ $[M+Na]^+$ 507.1572, Found 507.1575.

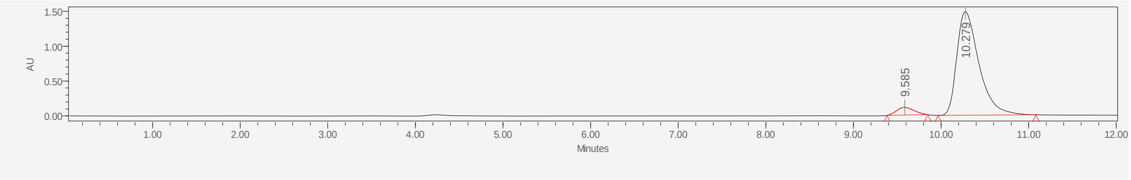


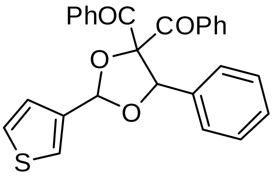




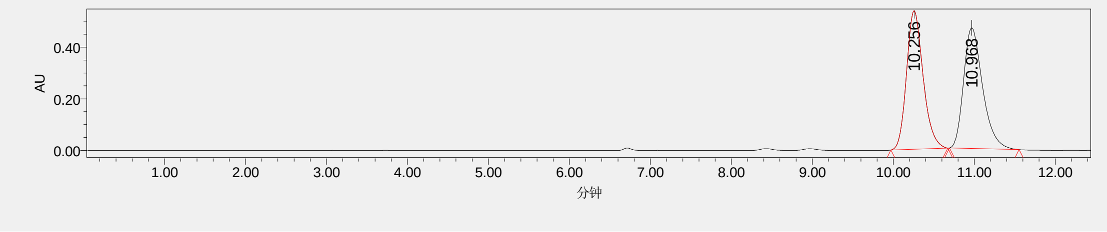
(2-(furan-3-yl)-5-phenyl-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3j: Viscous oil in 95% yield (petroleum ether : EtOAc = 10: 1); $[\alpha]^{26}_{D}$ = -140.47 (c 0.77, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 9.59 min, t_r (major) =10.28 min, 89% ee; ^{1}H NMR (400 MHz, DMSO) δ 8.08 (s, 1H), 7.91 (d, *J* = 7.4 Hz, 2H), 7.84 (s, 1H), 7.73 (d, *J* = 7.4 Hz, 2H), 7.63 – 7.58 (m, 1H), 7.57 – 7.52 (m, 1H), 7.50 – 7.44 (m, 2H), 7.40 – 7.34 (m, 4H), 7.23 – 7.13 (m, 3H), 6.88 (d, *J* = 0.9 Hz, 1H), 6.43 (s, 1H), 6.16 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 196.23, 194.09, 143.72, 142.34, 135.55, 134.37, 134.09, 133.52, 133.06, 130.26, 129.86, 128.50, 128.27, 127.96, 127.80, 127.38, 121.24, 109.02, 99.35, 94.71, 82.50 ppm; EI-HRMS: Calcd for $C_{27}H_{20}O_5$ $[M+Na]^+$ 447.1208, Found 447.1208.

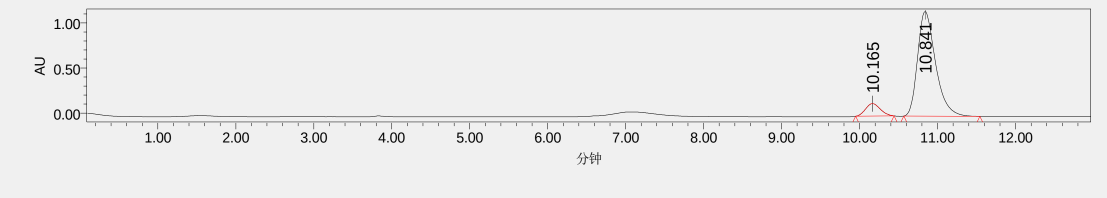


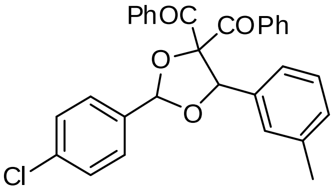




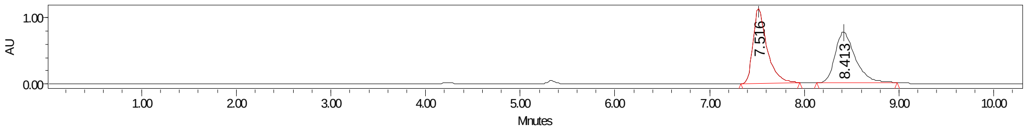
(5-phenyl-2-(thiophen-3-yl)-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3k: Viscous oil in 96% yield (petroleum ether : EtOAc = 20: 1); $[\alpha]^{26}_D$ = -99.19 (c 0.87, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 10.17 min, t_r (major) =10.84 min, 82% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.68 (s, 1H), 7.52 – 7.47 (m, 1H), 7.46 – 7.34 (m, 7H), 7.23 – 7.18 (m, 2H), 7.17 – 7.09 (m, 3H), 6.55 (s, 1H), 6.14 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.29, 194.14, 136.71, 135.53, 134.42, 134.15, 133.51, 133.03, 130.27, 129.89, 128.50, 128.27, 127.96, 127.79, 127.43, 126.54, 126.29, 125.48, 101.12, 94.79, 82.60 ppm; EI-HRMS: Calcd for $C_{27}H_{20}O_4S$ $[M+Na]^+$ 463.0980, Found 463.0976.

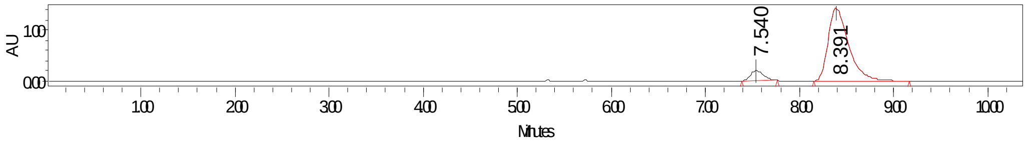


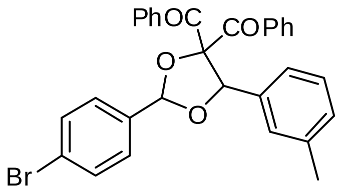




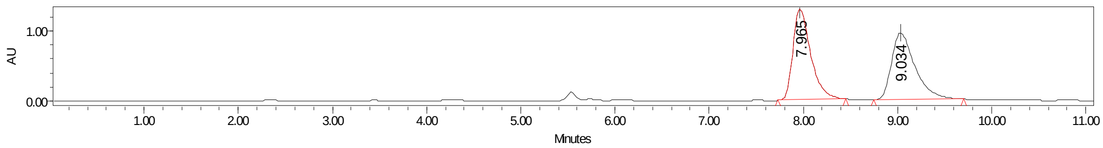
(2-(4-chlorophenyl)-5-(m-tolyl)-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3l: Viscous oil in 98% yield (petroleum ether : EtOAc = 20: 1); $[\alpha]^{26}_D$ = -86.78 (c 0.90, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 7.54 min, t_r (major) =8.39 min, 83% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.45 (m, 3H), 7.41 – 7.34 (m, 3H), 7.23 – 7.12 (m, 4H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.95 – 6.88 (m, 1H), 6.53 (s, 1H), 6.03 (s, 1H), 2.17 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.99, 194.09, 137.61, 135.86, 135.60, 134.25, 134.07, 133.68, 133.60, 132.95, 130.25, 129.73, 129.15, 128.78, 128.71, 128.55, 128.31, 127.96, 127.72, 124.63, 103.51, 94.66, 82.95, 21.27 ppm; EI-HRMS: Calcd for $C_{30}H_{23}{}^{35}ClO_4$ $[M+Na]^+$ 505.1183, Found 505.1185.

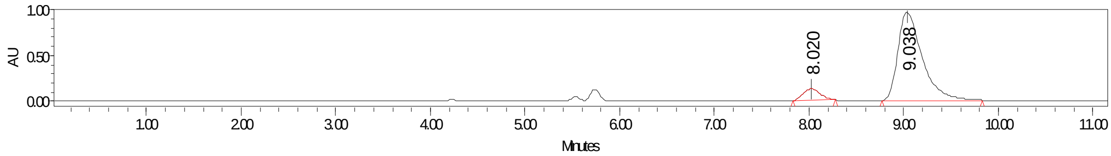


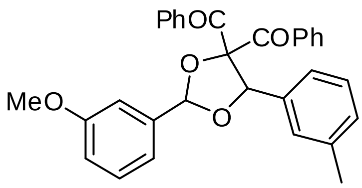




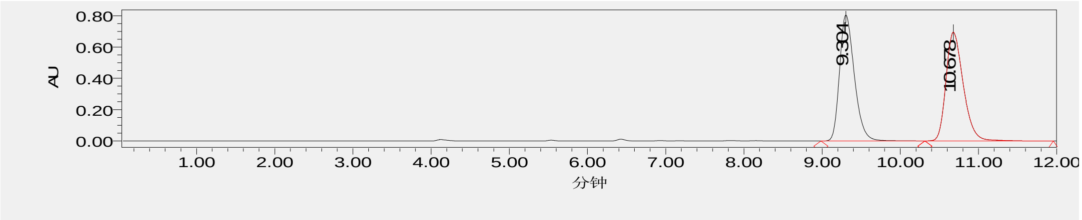
(2-(4-bromophenyl)-5-(m-tolyl)-1,3-dioxolane-4,4-diyl)bis(phenyl methanone) 3m: Viscous oil in 96% yield (petroleum ether : EtOAc = 20: 1); $[\alpha]^{26}_{D}$ = -74.85 (c 1.05, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 8.02 min, t_r (major) =9.04 min, 83% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 2H), 7.67 – 7.59 (m, 6H), 7.52 – 7.46 (m, 1H), 7.41 – 7.34 (m, 3H), 7.21 – 7.13 (m, 4H), 7.07 – 6.99 (m, 1H), 6.95 – 6.89 (m, 1H), 6.51 (s, 1H), 6.01 (s, 1H), 2.16 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.97, 194.07, 137.61, 135.59, 134.24, 134.18, 134.05, 133.61, 132.96, 131.74, 130.24, 129.72, 129.15, 128.97, 128.55, 128.30, 127.96, 127.73, 124.63, 124.15, 103.54, 94.66, 82.96, 21.27 ppm; EI-HRMS: Calcd for $C_{30}H_{23}{}^{79}BrO_4$ $[M+Na]^+$ 549.0677, Found 549.0676.

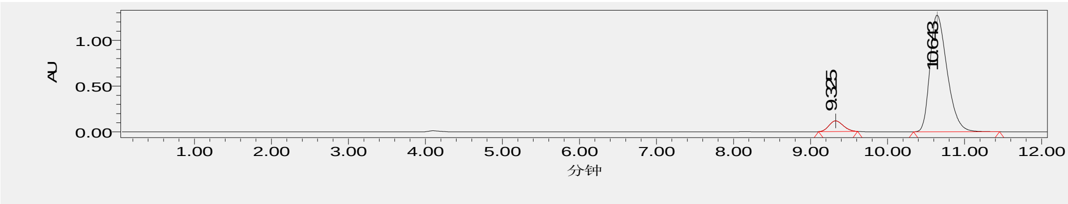


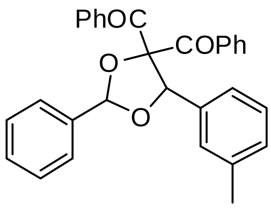




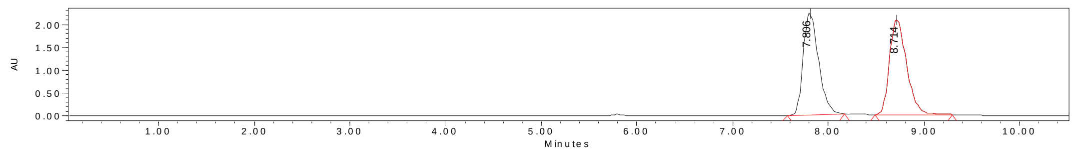
(2-(3-methoxyphenyl)-5-(m-tolyl)-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3n: Viscous oil in 93% yield (petroleum ether : EtOAc = 10: 1); $[\alpha]^{22}_{D}$ = -100.21 (c 0.93, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 9.32 min, t_r (major) = 10.64 min, 86% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.43 – 7.35 (m, 4H), 7.34 – 7.29 (m, 2H), 7.23 – 7.15 (m, 4H), 7.07 – 6.99 (m, 2H), 6.95 – 6.88 (m, 1H), 6.55 (s, 1H), 6.02 (s, 1H), 3.87 (s, 3H), 2.17 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 196.25, 194.20, 159.73, 137.51, 136.49, 135.74, 134.36, 134.26, 133.47, 132.90, 130.27, 129.90, 129.64, 129.00, 128.50, 128.28, 127.89, 127.70, 124.61, 119.56, 115.60, 112.63, 104.09, 94.83, 82.76, 55.38, 21.27 ppm; EI-HRMS: Calcd for $C_{31}H_{26}O_5$ $[M+Na]^+$ 501.1678, Found 501.1684.

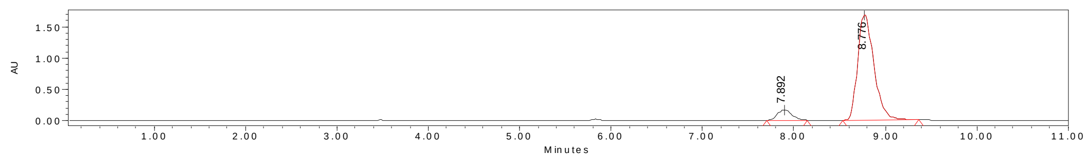


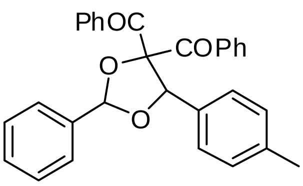




(2-phenyl-5-(m-tolyl)-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3o: Viscous oil in 98% yield (petroleum ether : EtOAc = 20: 1); $[\alpha]^{26}_{D}$ = -117.43 (c 0.61, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 7.89min, t_r (major) =8.78 min, 84% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.68 – 7.58 (m, 4H), 7.42 – 7.36(m, 4H), 7.32 – 7.24 (m, 3H), 7.16 – 7.05 (m, 4H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.86 – 6.79 (m, 1H), 6.46 (s, 1H), 5.96 (s, 1H), 2.07 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.32, 194.27, 137.54, 135.71, 135.04, 134.34, 134.27, 133.49, 132.92, 130.29, 129.93, 129.91, 129.02, 128.54, 128.51, 128.27, 127.90, 127.69, 127.25, 124.60, 104.27, 94.80, 82.81, 21.29 ppm; EI-HRMS: Calcd for $C_{30}H_{24}O_4$ $[M+Na]^+$ 471.1572, Found 471.1572.

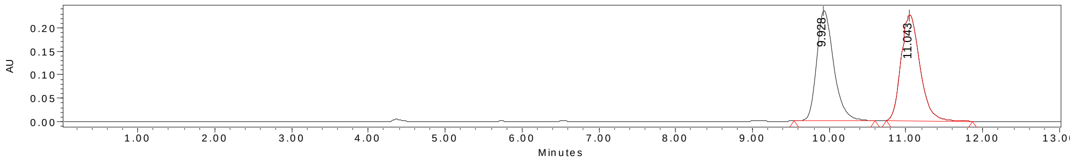


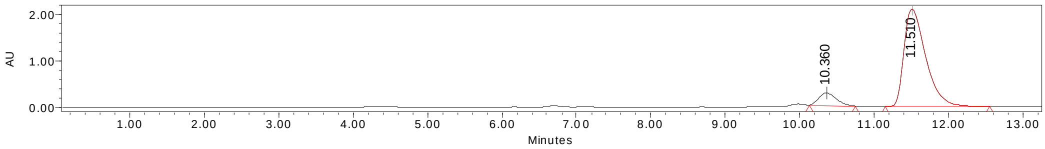


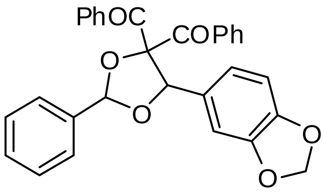


(2-phenyl-5-(p-tolyl)-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3p: Viscous oil in 92% yield (petroleum ether : EtOAc = 20: 1); $[\alpha]^{26}_{D}$ = -88.39 (c 0.62, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 10.36min, t_r (major) =11.52 min, 82% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.76 –7.68 (m, 4H), 7.52 – 7.45 (m, 4H), 7.42 – 7.34 (m, 3H), 7.32 – 7.27 (m, 2H), 7.20 – 7.13 (m, 2H), 6.99 – 6.89 (m, 2H), 6.56 (s, 1H), 6.05 (s, 1H), 2.20 (s, 3H) ppm;

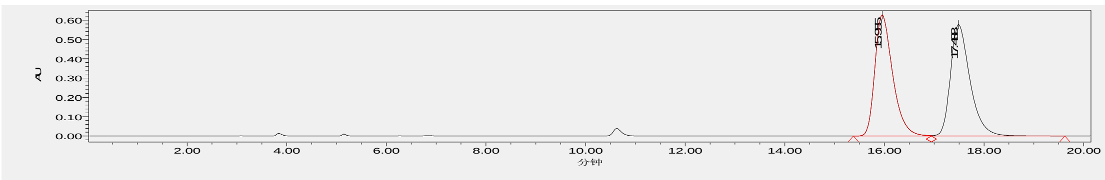
^{13}C NMR (101 MHz, $CDCl_3$) δ = 196.49, 194.29, 137.95, 135.54, 135.06, 134.23, 133.46, 132.91, 131.42, 130.27, 129.95, 129.86, 128.68, 128.50, 128.48, 127.71, 127.38, 127.17, 104.14, 94.82, 82.75, 21.14 ppm; EI-HRMS: Calcd for $C_{30}H_{24}O_4$ $[M+Na]^+$ 471.1572, Found 471.1572.

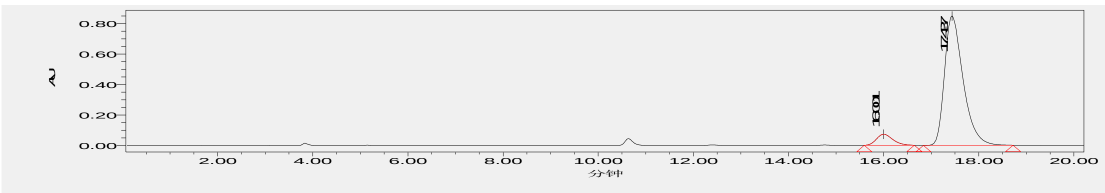


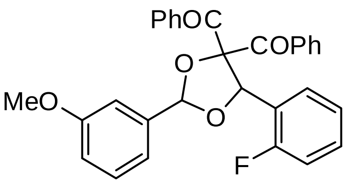




(5-(benzo[d][1,3]dioxol-5-yl)-2-phenyl-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3q: Viscous oil in 94% yield (petroleum ether : EtOAc = 10: 1); $[\alpha]^{22}_D$ = -94.48 (c 0.86, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 16.00 min, t_r (major) =17.44 min, 86% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.78 – 7.69 (m, 4.9 Hz, 4H), 7.52 – 7.45 (m, 4H), 7.44 – 7.34 (m, 3H), 7.24 – 7.17 (m, 2H), 6.95 – 6.85 (m, 2H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.50 (s, 1H), 6.03 (s, 1H), 5.86 – 5.77 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 196.14, 194.19, 147.46, 147.36, 135.57, 134.99, 134.22, 133.53, 133.03, 130.26, 129.91, 129.88, 128.53, 128.51, 128.25, 127.83, 127.14, 121.41, 108.13, 107.83, 104.09, 100.96, 94.74, 82.65 ppm; EI-HRMS: Calcd for $C_{30}H_{22}O_6$ $[M+Na]^+$ 501.1314, Found 501.1310.

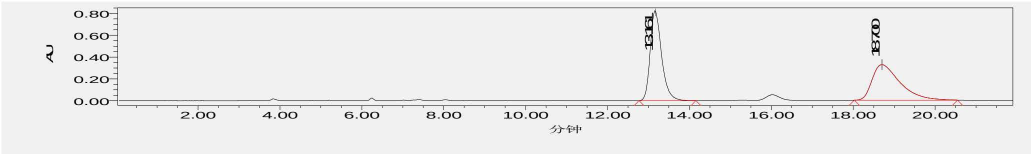


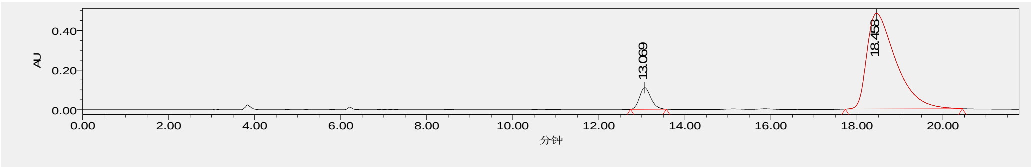


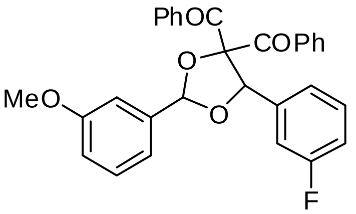


(5-(2-fluorophenyl)-2-(3-methoxyphenyl)-1,3-dioxolane-4,4-diyl) bis(phenylmethanone) 3r: Viscous oil in 93% yield (petroleum ether : EtOAc = 10: 1); $[\alpha]^{26}_D$ = -110.47 (c 0.90, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 13.07 min, t_r (major) =18.46 min, 84% ee; 1H NMR (400 MHz, CDCl3) δ 8.08 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.45 – 7.36 (m, 4H), 7.31 – 7.27 (m, 2H), 7.23 – 7.16 (m, 3H), 7.16

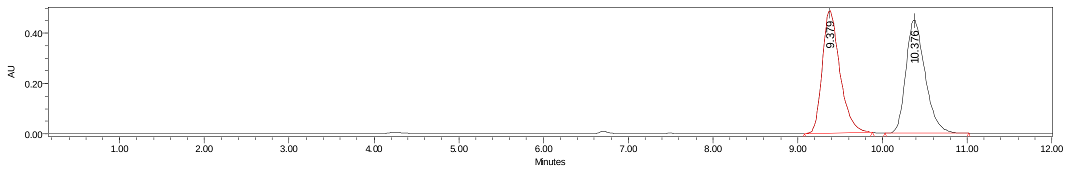
– 7.09 (m, 2H), 7.06 – 7.01 (m, 1H), 6.85 - 6.77 (m, 1H), 6.56 (s, 1H), 6.02 (s, 1H), 3.86 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 196.00, 193.98, 163.61, 161.16, 159.77, 137.20, 137.13, 136.15, 135.48, 134.02, 133.61, 133.22, 130.28, 129.86, 129.72, 129.61, 129.53, 128.55, 127.89, 123.30, 123.27, 119.38, 115.61, 115.26, 115.05, 114.58, 114.35, 112.58, 104.19, 94.93, 81.93, 55.39 ppm; EI-HRMS: Calcd for $C_{30}H_{23}FO_5$ $[M+Na]^+$ 505.1427, Found 505.1425.

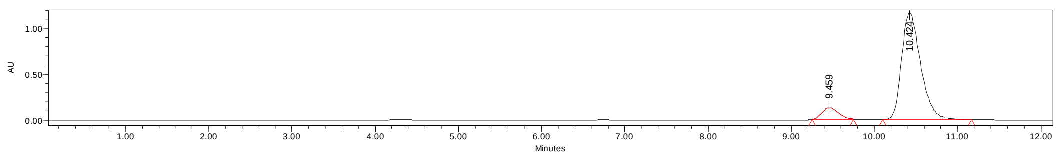


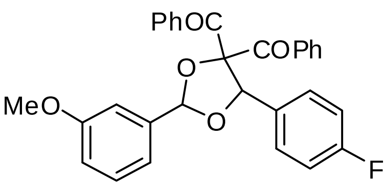




(5-(3-fluorophenyl)-2-(3-methoxyphenyl)-1,3-dioxolane-4,4-diyl) bis(phenylmethanone) 3s: Viscous oil in 93% yield (petroleum ether : EtOAc = 10: 1); $[\alpha]^{26}_{D}$ = -79.87 (c 0.92, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 9.46 min, t_r (major) =10.24 min, 83% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.44 – 7.36 (m, 4H), 7.31 – 7.26(m, 2H), 7.24 – 7.16 (m, 3H), 7.15 – 7.09 (m, 2H), 7.05 – 7.01 (m, 1H), 6.85 – 6.76 (m, 1H), 6.56 (s, 1H), 6.02 (s, 1H), 3.86 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.99, 193.98, 163.61, 161.16, 159.77, 137.21, 137.13, 136.15, 135.49, 134.03, 133.60, 133.21, 130.28, 129.86, 129.71, 129.61, 129.53, 128.55, 127.89, 123.29, 123.27, 119.38, 115.61, 115.25, 115.04, 114.58, 114.36, 112.58, 104.19, 94.93, 81.93, 55.38 ppm; EI-HRMS: Calcd for $C_{30}H_{23}FO_5$ $[M+Na]^+$ 505.1427, Found 505.1428.

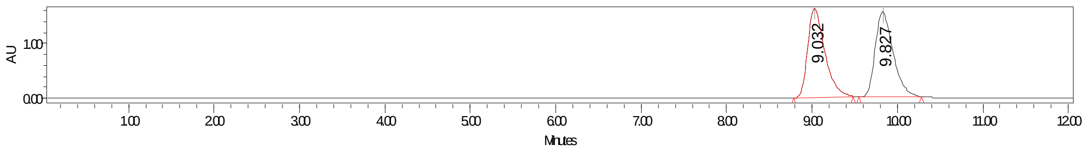


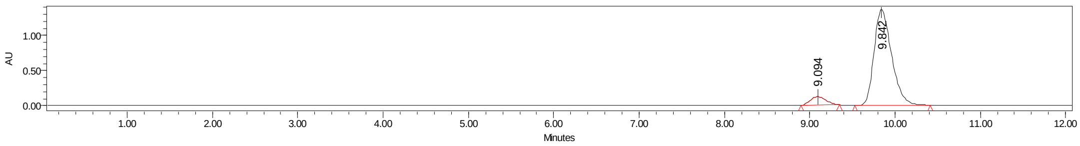


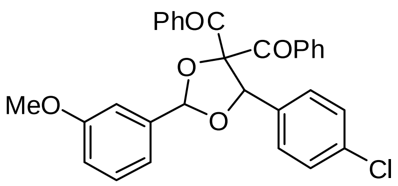


(5-(4-fluorophenyl)-2-(3-methoxyphenyl)-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3t: Viscous oil in 99% yield (petroleum ether : EtOAc = 10: 1); $[\alpha]^{26}_{D}$ = -109.94 (c 0.98, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral

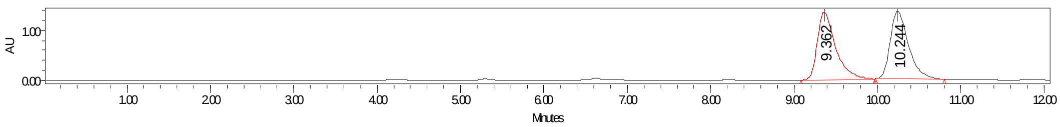
IE column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 9.09 min, t_r (major) =9.84 min, 85% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 753 – 7.48 (m, 1H), 7.44 – 7.35 (m, 6H), 7.32 – 7.28 (m, 2H), 7.23 – 7.17 (m, 2H), 7.05 – 7.00 (m, 1H), 6.87 – 6.79 (m, 2H), 6.56 (s, 1H), 6.03 (s, 1H), 3.86 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.13, 194.12, 163.75, 161.29, 159.75, 136.29, 135.47, 134.09, 133.61, 133.21, 130.39, 130.36, 130.27, 129.85, 129.70, 129.30, 129.22, 128.55, 127.91, 119.39, 115.49, 115.05, 114.84, 112.65, 104.08, 94.83, 82.09, 55.39 ppm; EI-HRMS: Calcd for $C_{30}H_{23}FO_5$ $[M+Na]^+$ 505.1427, Found 505.1431.

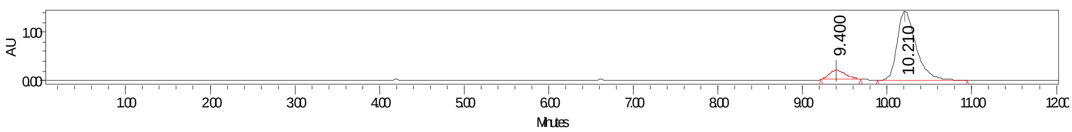


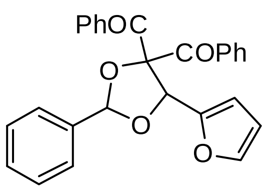




(5-(4-chlorophenyl)-2-(3-methoxyphenyl)-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3u: Viscous oil in 93% yield (petroleum ether : EtOAc = 10: 1); $[\alpha]^{26}_D$ = -70.39 (c 0.93, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 9.40 min, t_r (major) =10.21 min, 80% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* =8.0 Hz, 2H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.45 – 7.30 (m, 7H), 7.28 (s, 1H), 7.23 – 7.17 (m, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.04 – 6.99 (m, 1H), 6.53 (s, 1H), 6.01 (s, 1H), 3.85 (s, 3H) ppm; ^{13}C ^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.25, 191.34, 159.74, 136.17, 135.42, 134.09, 133.99, 133.64, 133.27, 133.14, 130.29, 129.90, 129.72, 128.78, 128.57, 128.16, 127.93, 119.35, 115.48, 112.64, 104.14, 94.90, 82.01, 55.40 ppm; EI-HRMS: Calcd for $C_{30}H_{23}{}^{35}ClO_5$ $[M+Na]^+$ 521.1132, Found 521.1129.

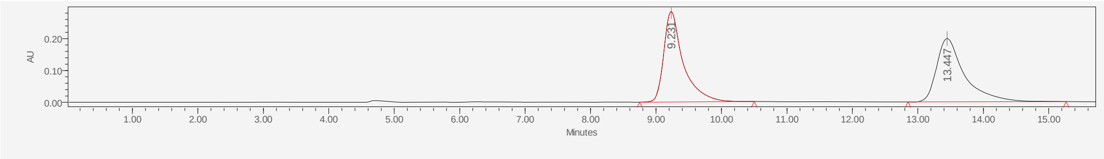


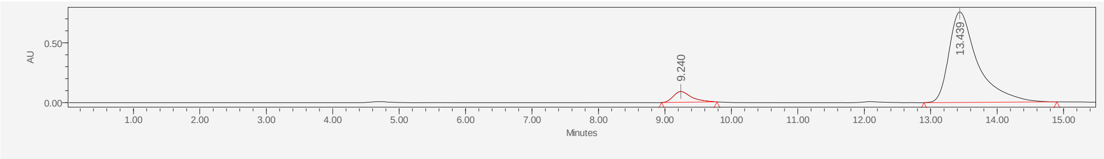


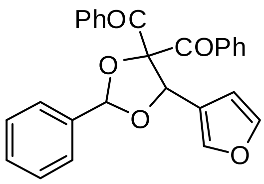


(5-(furan-2-yl)-2-phenyl-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3v: Viscous oil in 97% yield (petroleum ether : EtOAc = 10: 1); $[\alpha]^{26}_D$ = -101.94 (c 0.82, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IC column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 9.24 min, t_r (major) =13.44 min, 86% ee; ^{1}H NMR (400 MHz, DMSO) δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.78 – 7.72 (m, 4H), 7.62 – 7.54 (m, 2H), 7.53 – 7.49 (m, 3H), 7.48 – 7.43 (m, 3H), 7.39 – 7.34

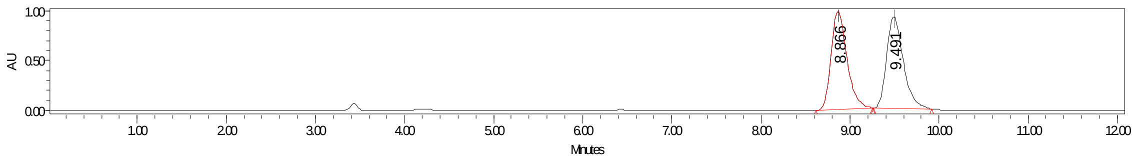
(m, 2H), 6.60 (s, 1H), 6.57 (d, J = 3.2 Hz, 1H), 6.30 – 6.24 (m, 1H), 6.03 (s, 1H) ppm; ^{13}C NMR (101 MHz, DMSO) δ 194.32, 192.46, 147.46, 143.98, 134.77, 134.16, 134.11, 133.58, 133.43, 130.16, 129.56, 129.11, 128.85, 128.46, 128.22, 127.44, 111.87, 110.57, 103.71, 93.20, 75.74 ppm; EI-HRMS: Calcd for $C_{27}H_{20}O_5$ $[M+Na]^+$ 447.1208, Found 447.1209.

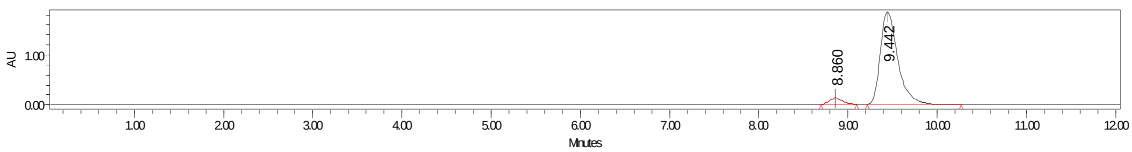


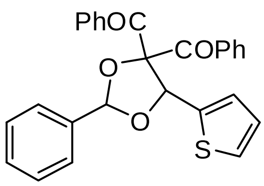




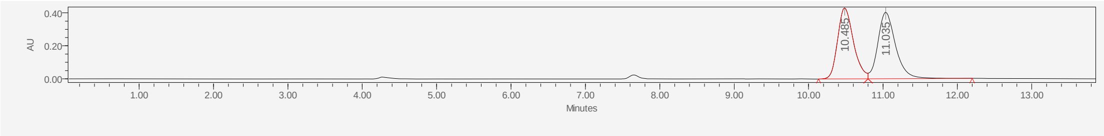
(5-(furan-3-yl)-2-phenyl-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3w: Viscous oil in 96% yield (petroleum ether : EtOAc = 10: 1); $[\alpha]^{26}_D$ = -132.14 (c 0.87, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE 90/10 column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 8.86 min, t_r (major) = 9.44 min, 90% ee; ^{1}H NMR (400 MHz, DMSO) δ 7.94 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.74 (s, 1H), 7.72 – 7.68 (m, 2H), 7.62 – 7.54 (m, 2H), 7.54 – 7.45 (m, 6H), 7.40 – 7.31 (m, 2H), 6.50 (s, 1H), 6.27 (s, 1H), 6.08 (s, 1H) ppm; ^{13}C NMR (101 MHz, DMS) δ = 195.72, 193.35, 143.73, 141.71, 134.58, 134.51, 133.94, 133.62, 133.53, 130.03, 129.55, 129.33, 128.82, 128.50, 128.25, 127.18, 120.06, 109.47, 103.61, 93.65, 75.93 ppm; EI-HRMS: Calcd for $C_{27}H_{20}O_5$ $[M+Na]^+$ 447.1208, Found 447.1211.

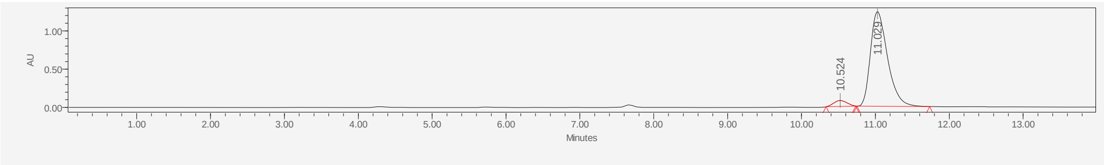


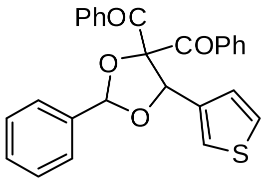




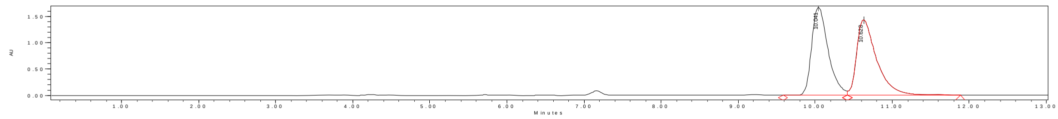
(2-phenyl-5-(thiophen-2-yl)-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3x: Viscous oil in 97% yield (petroleum ether : EtOAc = 20: 1); $[\alpha]^{26}_D$ = -155.39 (c 0.74, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE 90/10 column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 10.52 min, t_r (major) = 11.03 min, 91% ee; ^{1}H NMR (400 MHz, DMSO) δ 7.95 (d, J = 8.0 Hz, 2H), 7.77 – 7.70 (m, 4H), 7.63 – 7.57 (m, 1H), 7.56 – 7.50 (m, 4H), 7.50 – 7.44 (m, 2H), 7.40 – 7.36 (m, 1H), 7.36 – 7.30 (m, 2H), 7.09 – 7.04 (m, 1H), 6.89 – 6.84 (m, 1H), 6.82 (s, 1H), 6.10 (s, 1H) ppm; ^{13}C NMR (101 MHz, DMSO) δ = 195.01, 193.03, 137.27, 134.45, 134.44, 134.07, 133.67, 133.42, 130.19, 129.58, 129.32, 128.88, 128.56, 128.17, 127.61, 127.27, 126.88, 126.63, 103.69, 94.38, 78.79 ppm; EI-HRMS: Calcd for $C_{27}H_{20}O_4S$ $[M+Na]^+$ 463.0980, Found 463.0973.

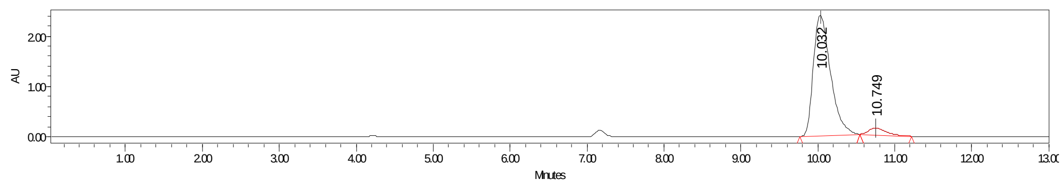


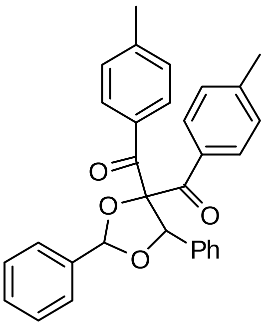




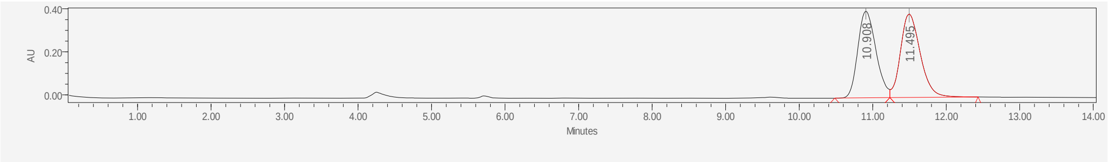
(2-phenyl-5-(thiophen-3-yl)-1,3-dioxolane-4,4-diyl)bis(phenylmethanone) 3y: Viscous oil in 97% yield (petroleum ether : EtOAc = 20: 1); $[\alpha]^{26}_D$ = -130.83 (c 0.92, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IE 90/10 column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 10.03 min, t_r (major) = 10.75 min, 90% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.73 – 7.69 (m, 2H), 7.51 – 7.46 (m, 4H), 7.42 – 7.35(m, 3H), 7.29 – 7.26 (m, 1H), 7.23 – 7.18 (m, 2H), 7.11 – 7.07 (m, 1H), 7.04 – 6.99 (m 1H), 6.64 (s, 1H), 6.03 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 196.13, 194.14, 135.79, 135.42, 135.01, 134.13, 133.59, 133.03, 130.27, 129.93, 129.73, 128.52, 127.85, 127.15, 126.93, 125.73, 123.90, 104.31, 94.49, 79.95 ppm; EI-HRMS: Calcd for $C_{27}H_{20}O_4S$ $[M+Na]^+$ 463.0980, Found 463.0981.

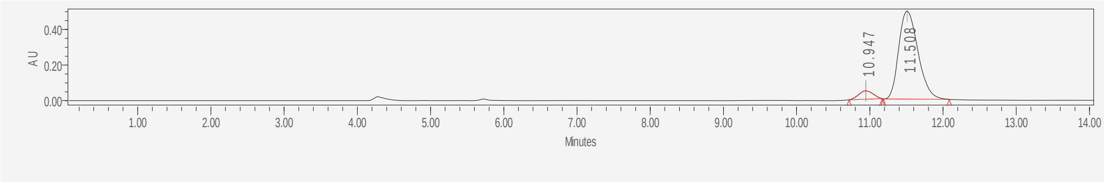






(2,5-diphenyl-1,3-dioxolane-4,4-diyl)bis(p-tolylmethanone) 3z: Viscous oil in 99% yield (petroleum ether : EtOAc = 20: 1); $[\alpha]^{26}_D$ = -89.82 (c 0.90, CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (*i*PrOH/hexane = 10/90, 1.0 mL/min, 254 nm), t_r (minor) = 10.92min, t_r (major) =11.51 min, 87% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2H), 7.79 – 7.73 (m, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.52 – 7.47 (m, 3H), 7.45 – 7.40 (m, 2H), 7.18 – 7.09 (m, 5H), 6.96 (d, J = 8.4 Hz, 2H), 6.59 (s, 1H), 6.04 (s, 1H), 2.34 (s, 3H), 2.29 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.49, 193.94, 144.45, 143.88, 135.18, 134.82, 132.95, 131.74, 130.43, 130.04, 129.84, 129.20, 128.51, 128.48, 128.19, 127.90, 127.63, 127.19, 104.05, 94.94, 82.56, 21.70, 21.65 ppm; EI-HRMS: Calcd for $C_{31}H_{26}O_4$ $[M+Na]^+$ 485.1729, Found 485.1731.

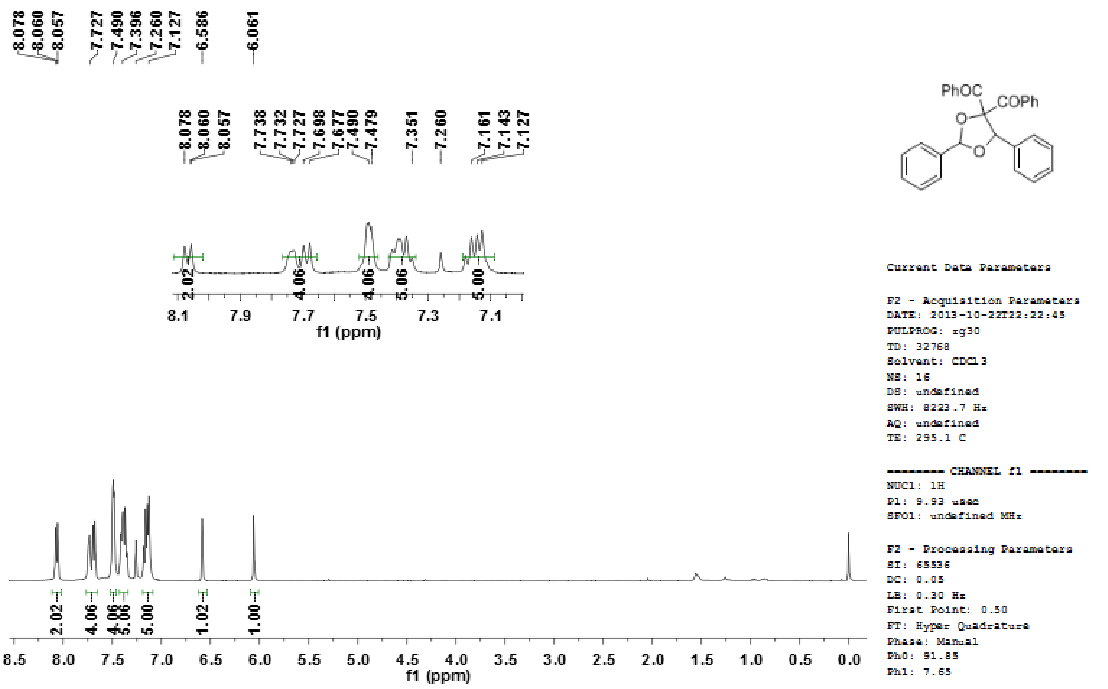




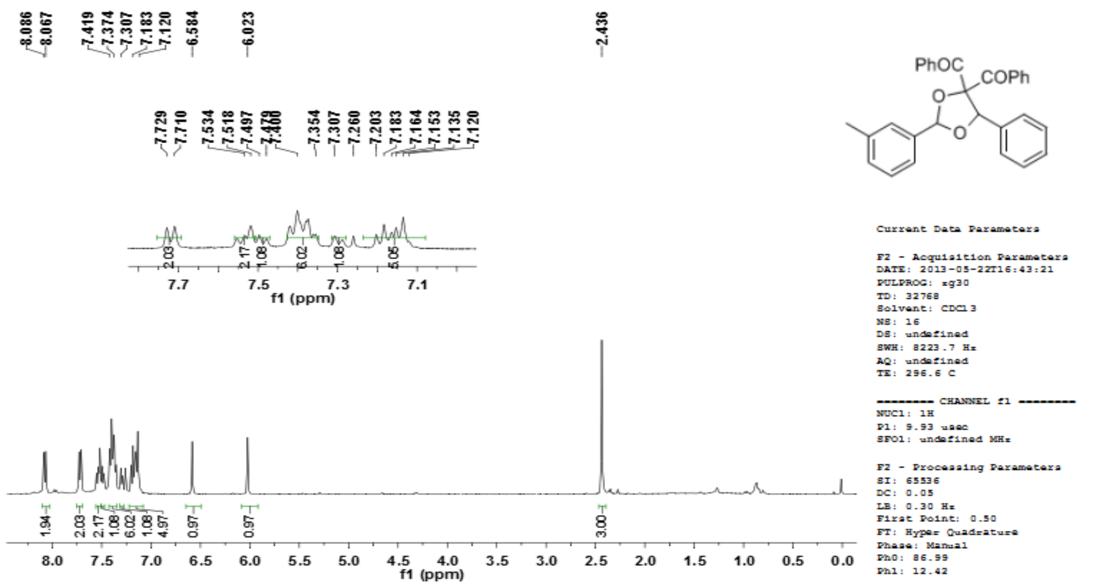
8. Refarence

1. Antonioletti, R.; Bovicelli, P.; Malancona, S. *Tetrahedron* 2002, **58**, 589.
2. Yadav, V.K.; Kapoor, K. K. *Tetrahedron* 1995, **51**, 8573.
3. Z. Chen, L. Wei and J. Zhang, *Org. Lett.*, 2011, **13**, 1170.

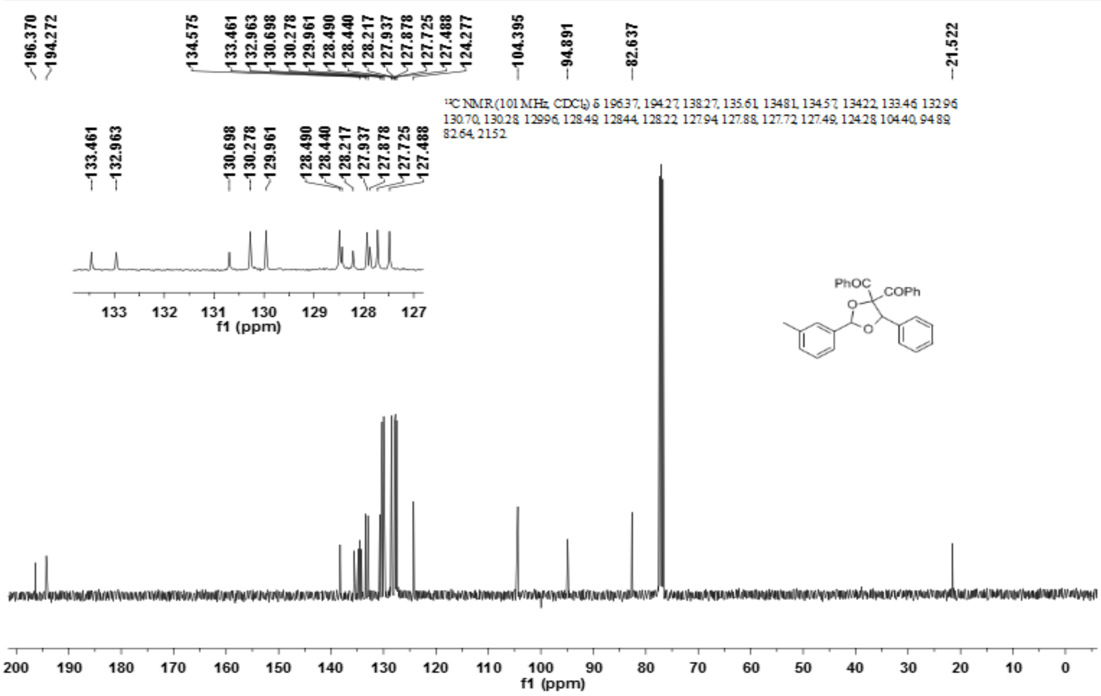
9. Copy of ^{1}H NMR and ^{13}C NMR spectra for products and subtrates

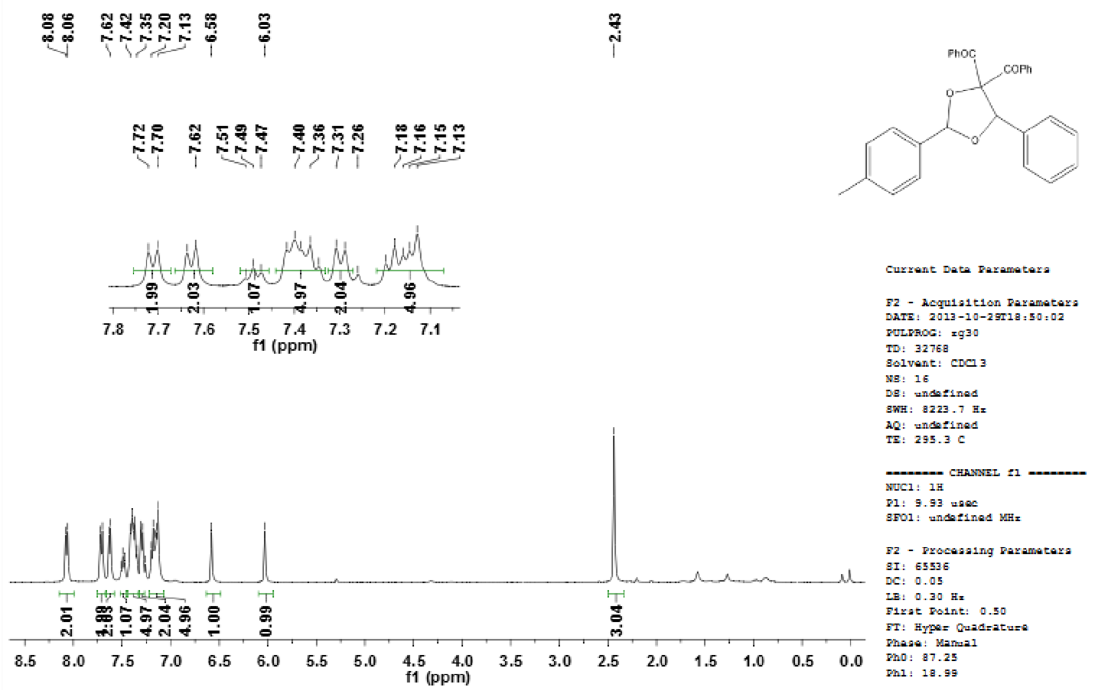


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.02 (m, 2H), 7.76 – 7.66 (m, 4H), 7.52 - 7.46 (m, 4H), 7.43 – 7.34 (m, 5H), 7.19 - 7.09 (m, 5H), 6.59 (s, 1H), 6.06 (s, 1H).

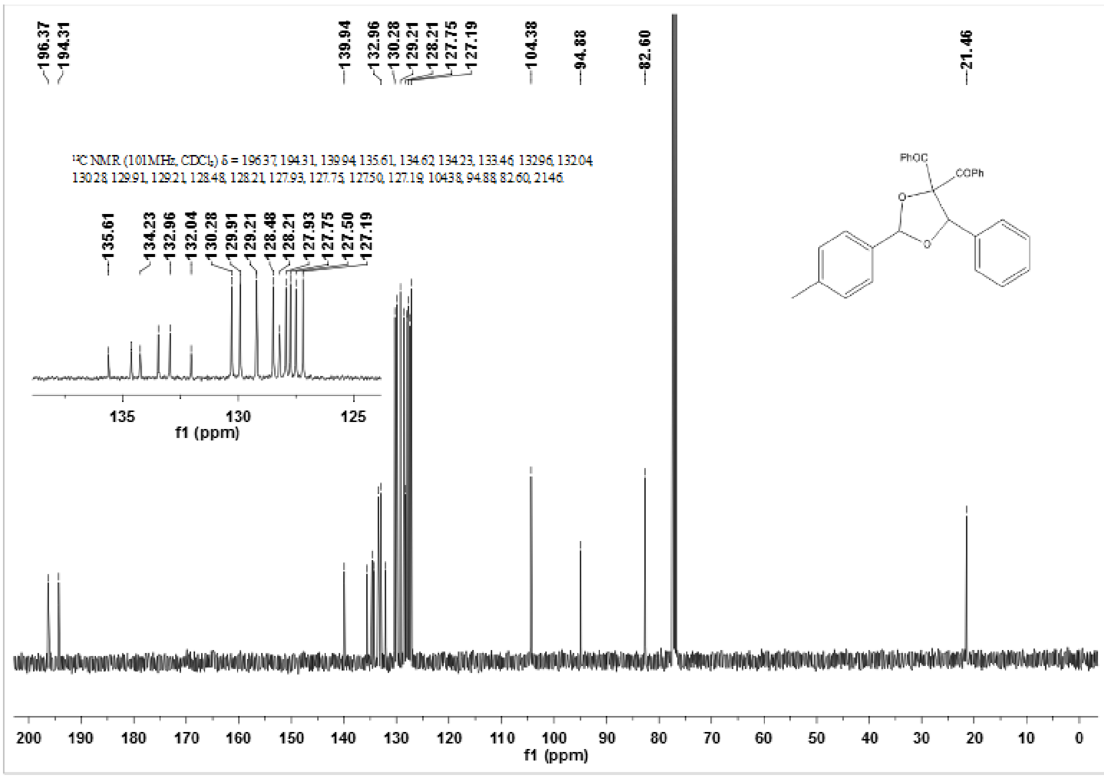


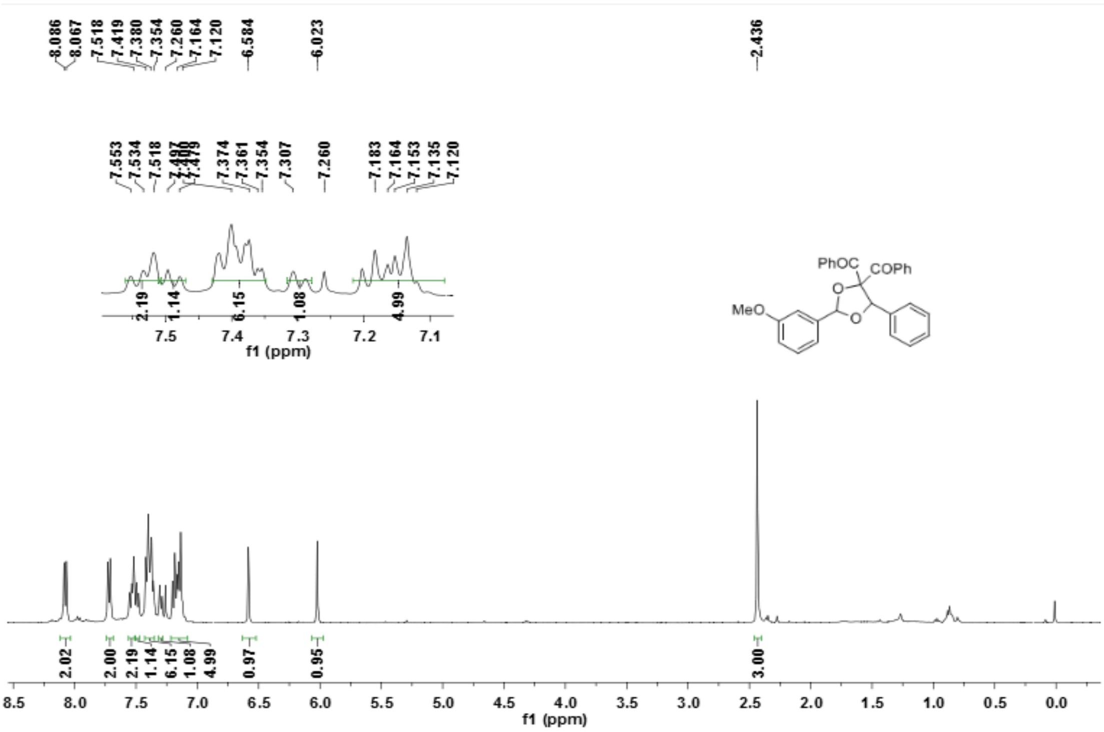
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 7.6 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.51-7.47 (m, 1H), 7.43 – 7.35 (m, 6H), 7.31-7.27 (m, 1H), 7.21-7.08 (m, 5H), 6.58 (s, 1H), 6.02 (s, 1H), 2.44 (s, 3H).

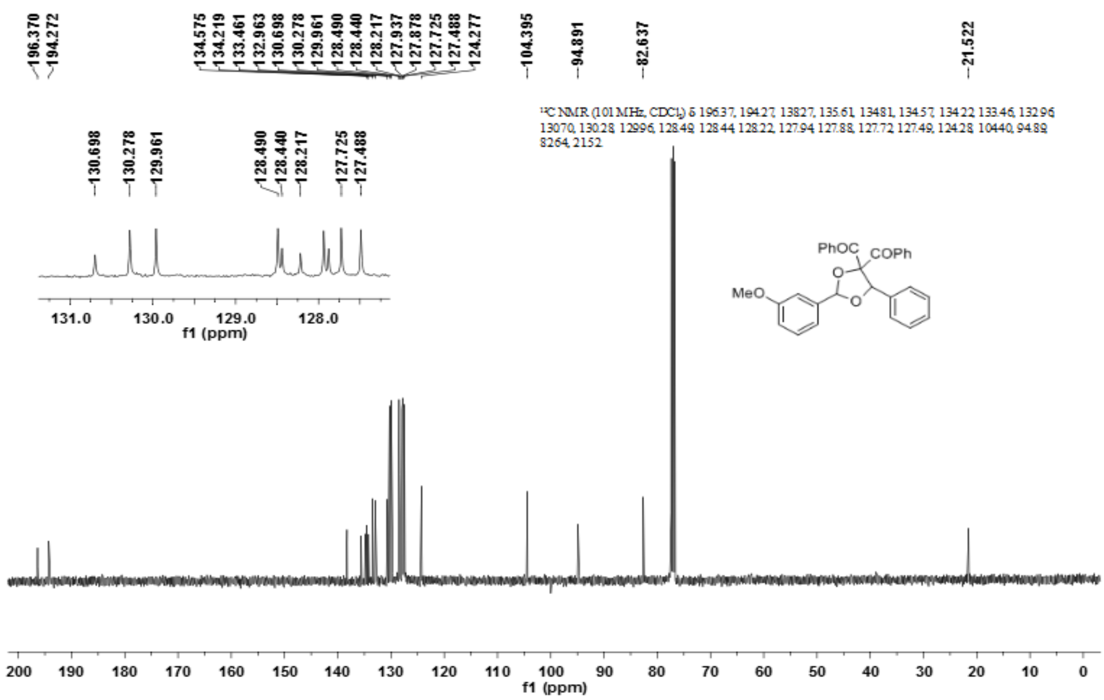


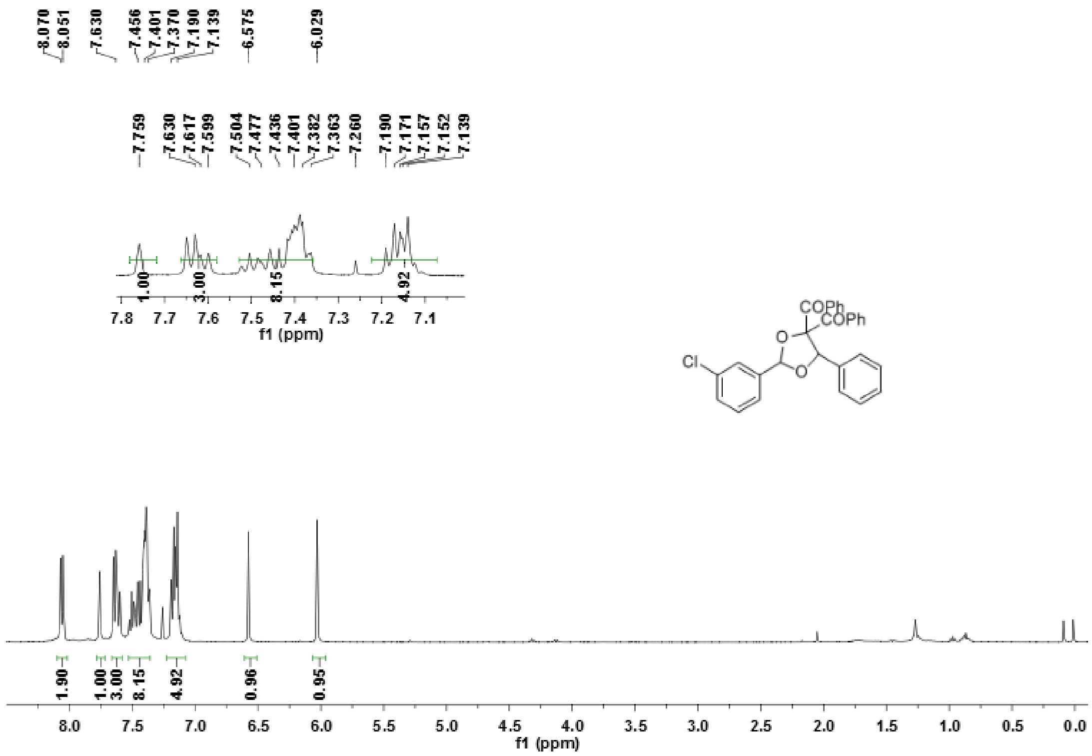


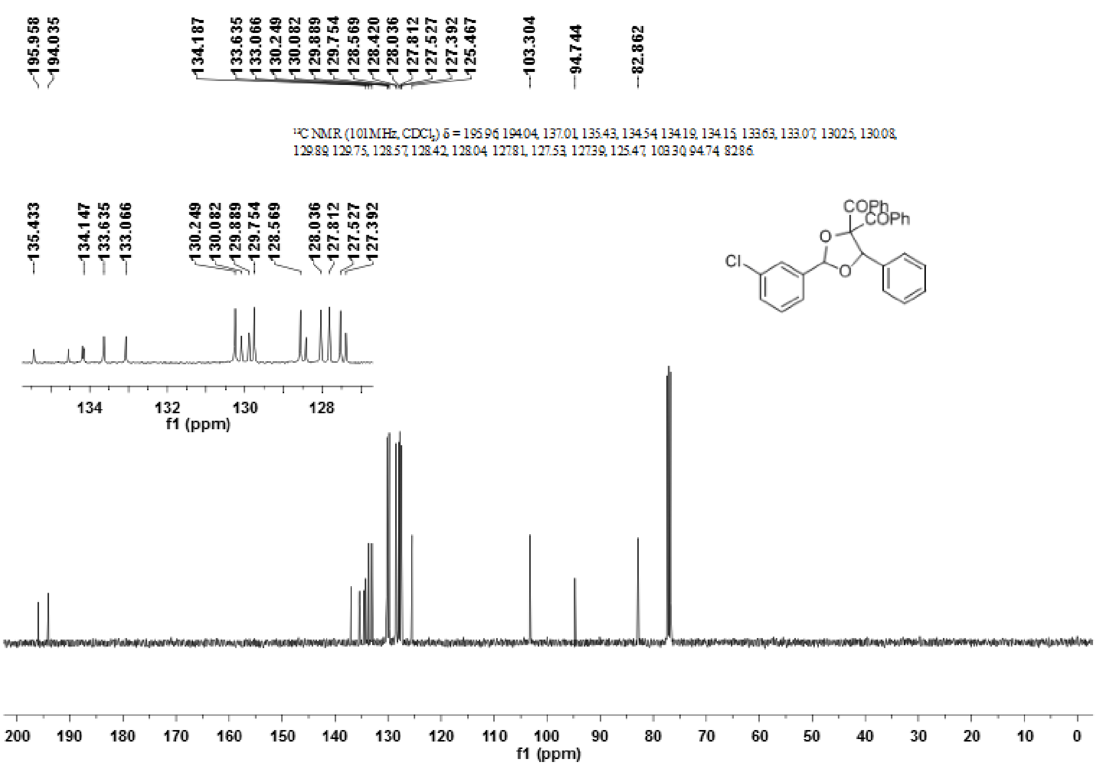
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.07 (d, J = 8.0 Hz, 2H), 7.76 - 7.67 (m, 2H), 7.66 - 7.58 (m, 2H), 7.52 - 7.46 (m, 1H), 7.44 – 7.33 (m, 5H), 7.33 - 7.27 (m, 2H), 7.22 – 7.07 (m, 5H), 6.58 (s, 1H), 6.03 (s, 1H), 2.43 (s, 3H).

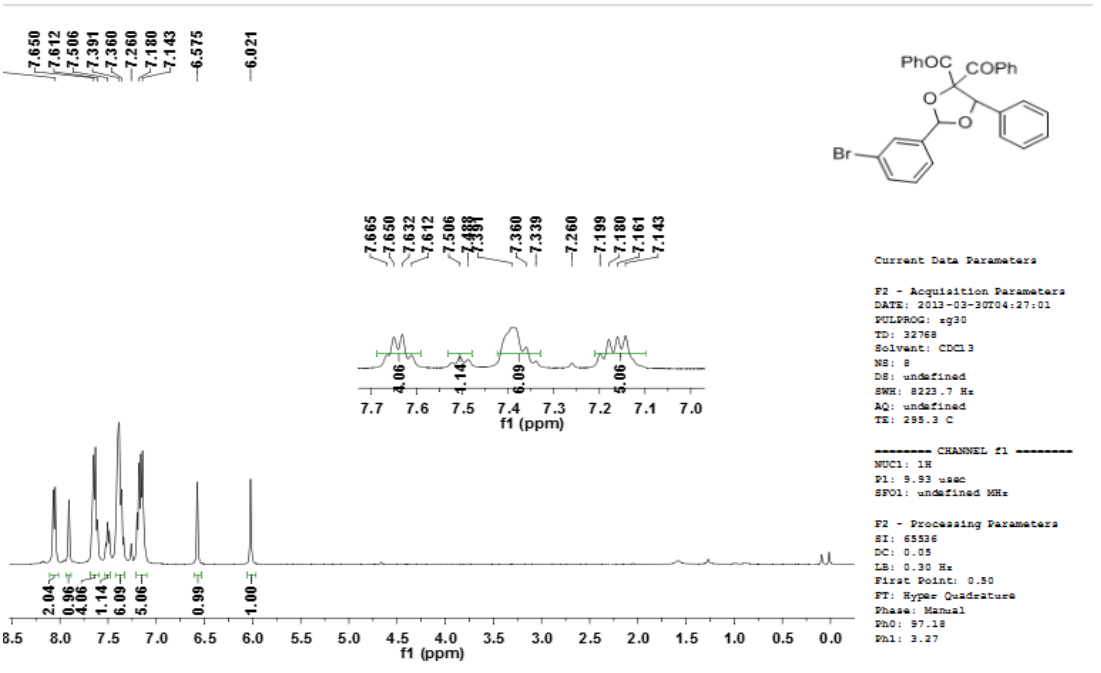

196.37
194.31
139.94
132.96
130.28
129.21
128.21
127.75
127.19
104.38
94.88
82.60
21.46
^{13}C NMR (101MHz, CDCl$_3$) δ = 196.37, 194.31, 139.94, 135.61, 134.62, 134.23, 133.46, 132.96, 132.04, 130.28, 129.91, 129.21, 128.48, 128.21, 127.93, 127.75, 127.50, 127.19, 104.38, 94.88, 82.60, 21.46.
135.61
134.23
132.96
132.04
130.28
129.91
129.21
128.48
128.21
127.93
127.75
127.50
127.19
135
130
125
f1 (ppm)
PhOC
COPh
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

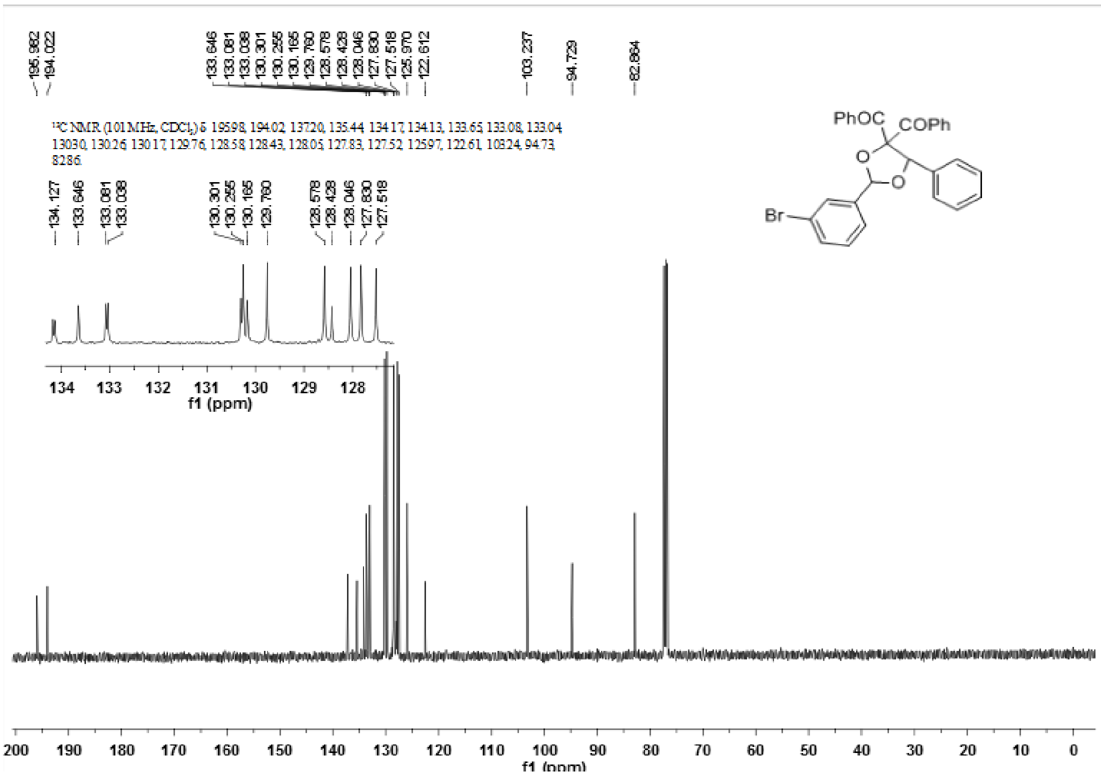

8.086
8.067
7.518
7.419
7.380
7.354
7.260
7.164
7.120
6.584
6.023
2.436
7.553
7.534
7.518
7.374
7.361
7.354
7.307
7.260
7.183
7.164
7.153
7.135
7.120
2.19
1.14
6.15
1.08
4.99
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
PhOC
COPh
MeO
O
O
2.02
2.00
2.19
1.14
6.15
1.08
4.99
0.97
0.95
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

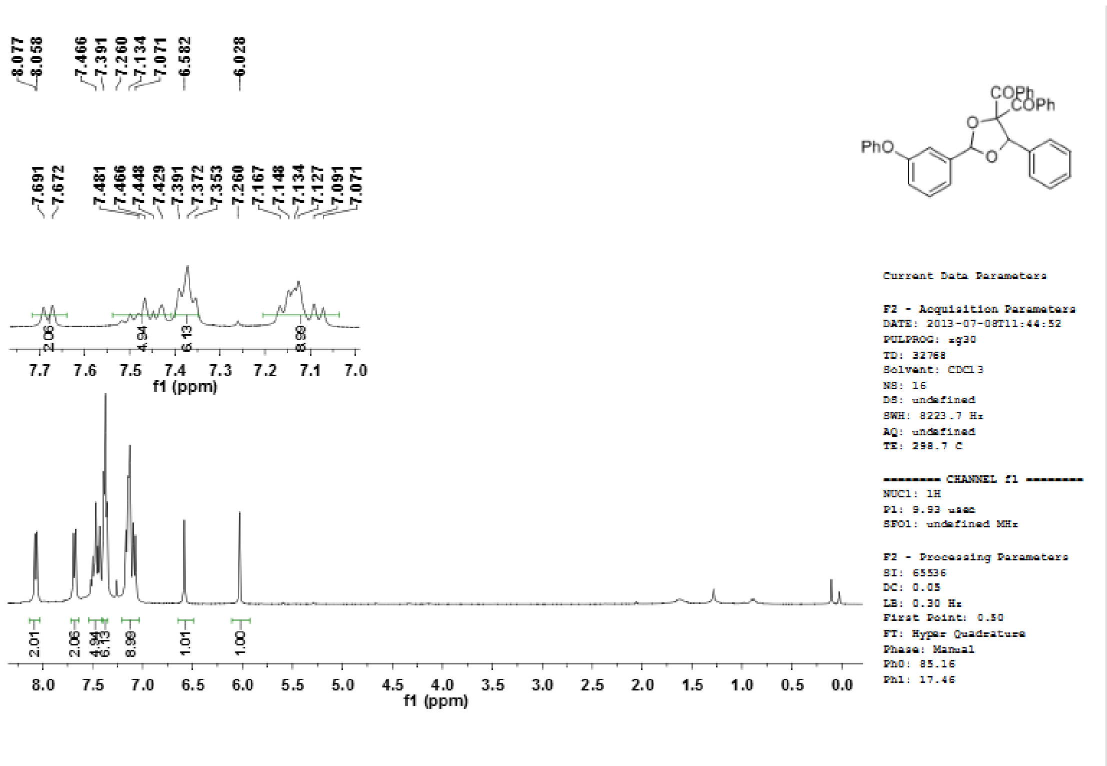

196.370
194.272
134.575
134.219
133.461
132.963
130.698
130.278
129.961
128.490
128.440
128.217
127.937
127.878
127.725
127.488
124.277
104.395
94.891
82.637
21.522
¹³C NMR (101 MHz, CDCl₃) δ 196.37, 194.27, 13827, 135.61, 13481, 134.57, 134.22, 133.46, 132.96, 13070, 130.28, 12996, 128.49, 128.44, 128.22, 127.94, 127.88, 127.72, 127.49, 124.28, 10440, 94.89, 8264, 2152
PhOC
COPh
MeO
O
O
f1 (ppm)


8.070
8.051
7.630
7.456
7.401
7.370
7.190
7.139
6.575
6.029
7.759
7.630
7.617
7.599
7.504
7.477
7.436
7.401
7.382
7.363
7.260
7.190
7.171
7.157
7.152
7.139
1.00
3.00
8.15
4.92
COPh
COPh
Cl
O
O
1.90
0.96
0.95
f1 (ppm)


13C NMR (101MHz, CDCl3) δ = 195.96, 194.04, 137.01, 135.43, 134.54, 134.19, 134.15, 133.63, 133.07, 130.25, 130.08, 129.89, 129.75, 128.57, 128.42, 128.04, 127.81, 127.53, 127.39, 125.47, 103.30, 94.74, 82.86.
COPh
COPh
O
O
Cl
f1 (ppm)
f1 (ppm)


PhOC
COPh
O
O
Br
f1 (ppm)
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2013-03-30T04:27:01
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 8
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 295.3 C
-------- CHANNEL f1 --------
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 97.18
Ph1: 3.27


^{13}C NMR (101 MHz, CDCl$_3$) δ 195.98, 194.02, 137.20, 135.44, 134.17, 134.13, 133.65, 133.08, 133.04, 130.30, 130.26, 130.17, 129.76, 128.58, 128.43, 128.05, 127.83, 127.52, 125.97, 122.61, 103.24, 94.73, 82.86.
PhOC
COPh
Br
f1 (ppm)


COPh
COPh
PhO
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
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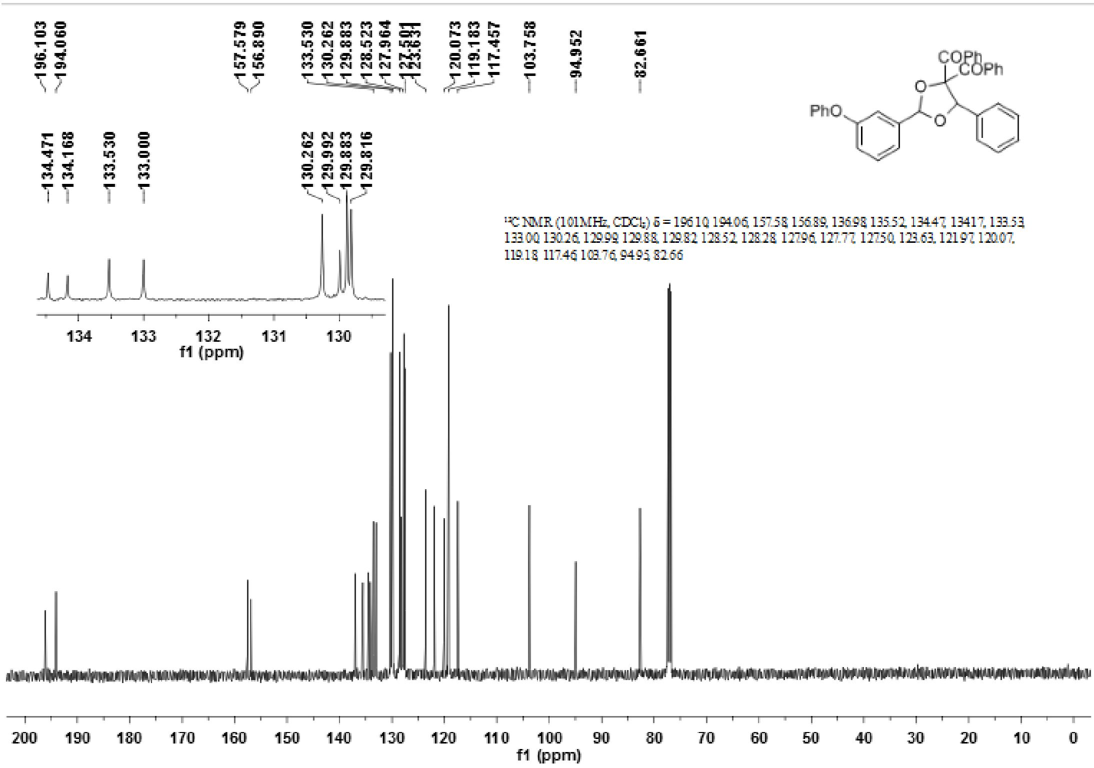
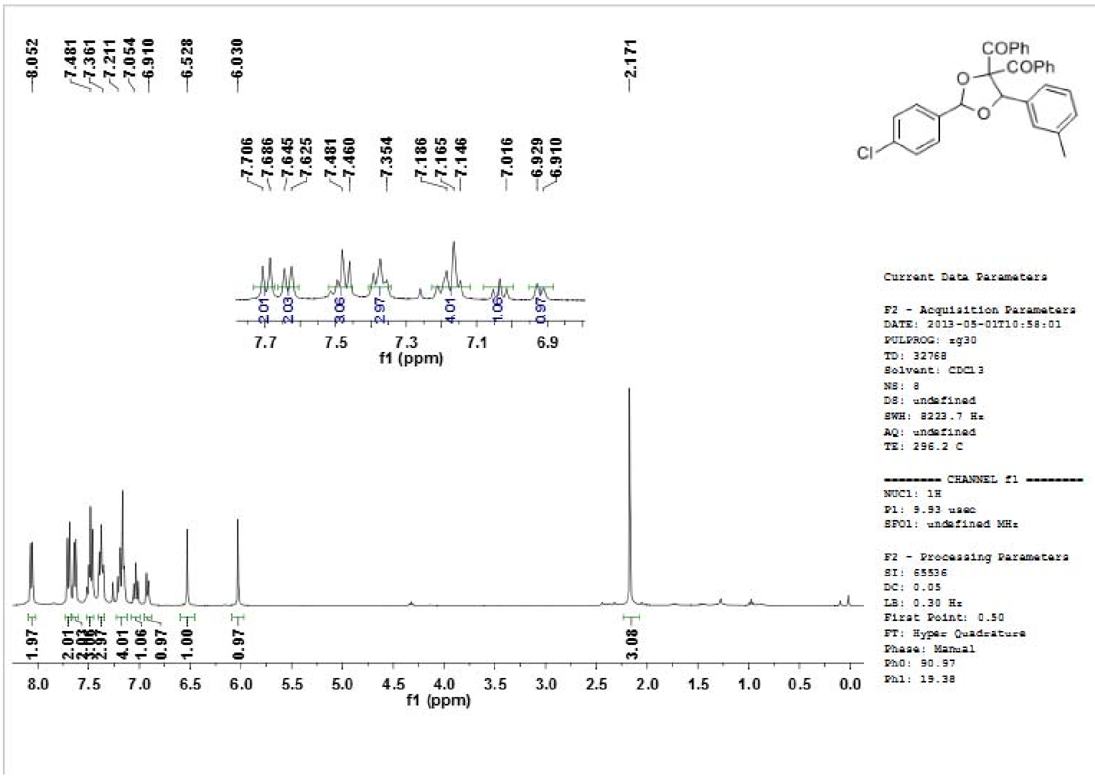
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
SWH: 8223.7 Hz
TE: 298.7 C
CHANNEL f1
NUC1: 1H
P1: 9.93 usec
F2 - Processing Parameters
SI: 65536
LB: 0.30 Hz
PHC0: 85.16
PHC1: 17.46


COPh
COPh
PhO
O
O
^{13}C NMR (101MHz, CDCl$_3$) δ = 196.10, 194.06, 157.58, 156.89, 136.98, 135.52, 134.47, 134.17, 133.53, 133.00, 130.26, 129.99, 129.88, 129.82, 128.52, 128.28, 127.96, 127.77, 127.50, 123.63, 121.97, 120.07, 119.18, 117.46, 103.76, 94.95, 82.66
f1 (ppm)


COPh
COPh
O
O
Cl
Current Data Parameters
F2 - Acquisition Parameters
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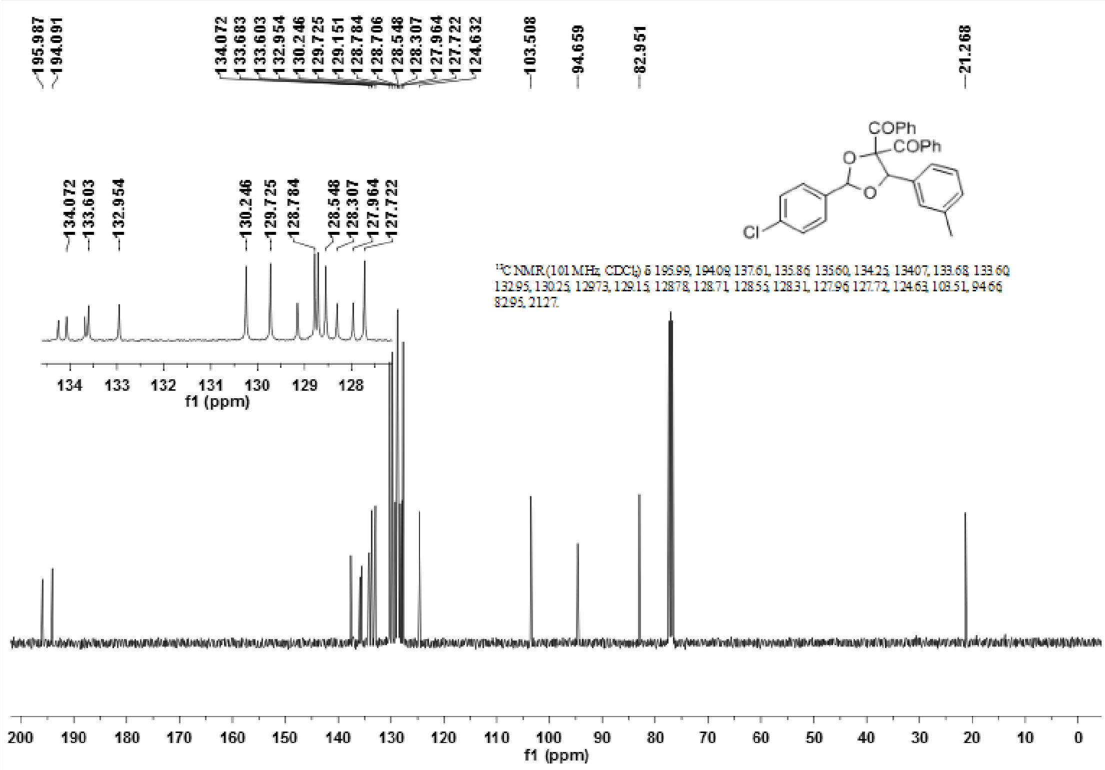
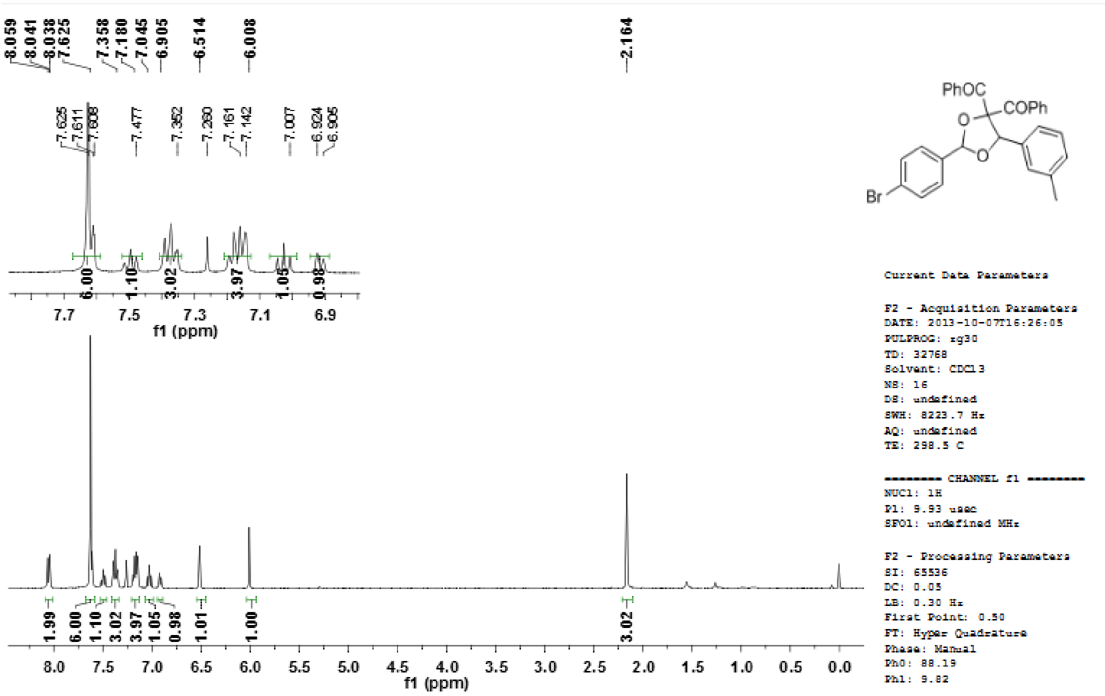
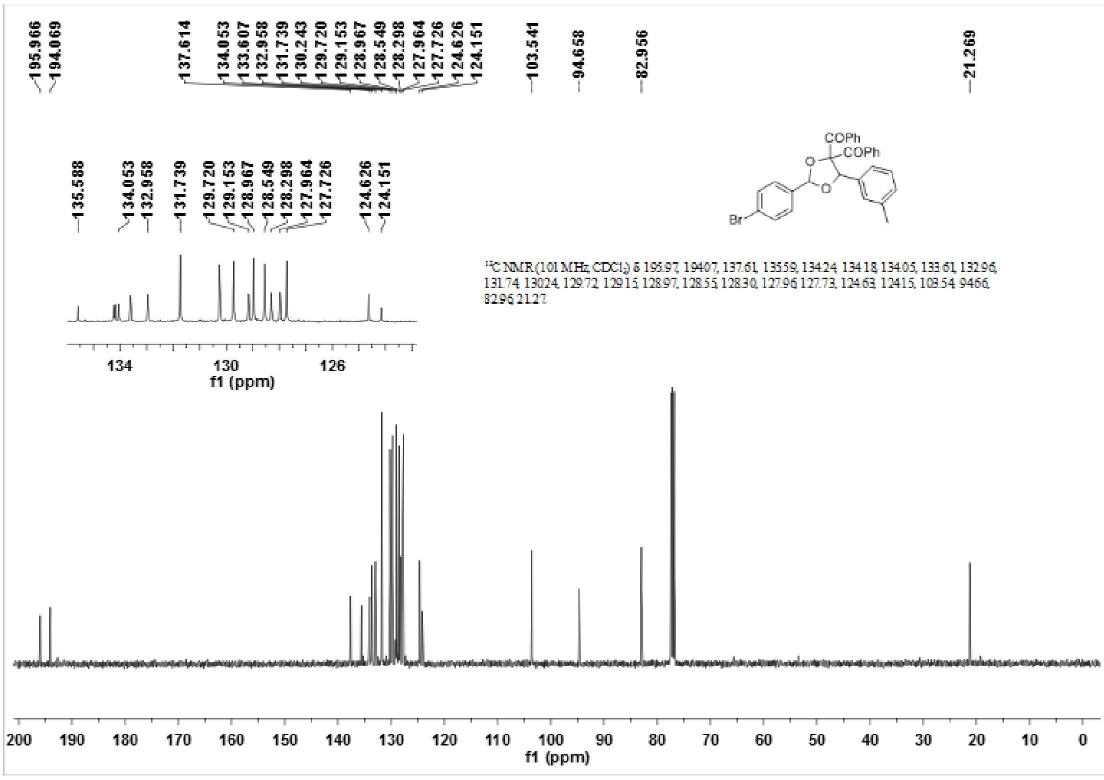
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 8
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 296.2 C
-------- CHANNEL f1 --------
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
SF: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 90.97
Ph1: 19.38
f1 (ppm)



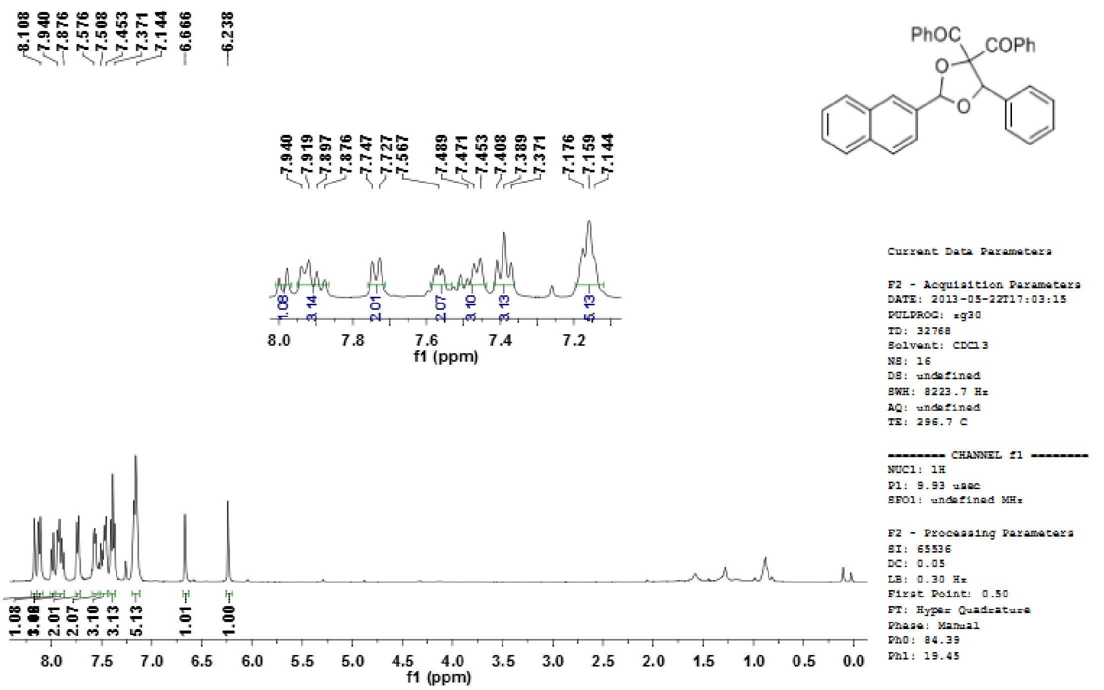
^{13}C NMR (101 MHz, CDCl$_3$) δ 195.99, 194.09, 137.61, 135.86, 135.60, 134.25, 134.07, 133.68, 133.60, 132.95, 130.25, 129.73, 129.15, 128.78, 128.71, 128.55, 128.31, 127.96, 127.72, 124.63, 103.51, 94.66, 82.95, 21.27.

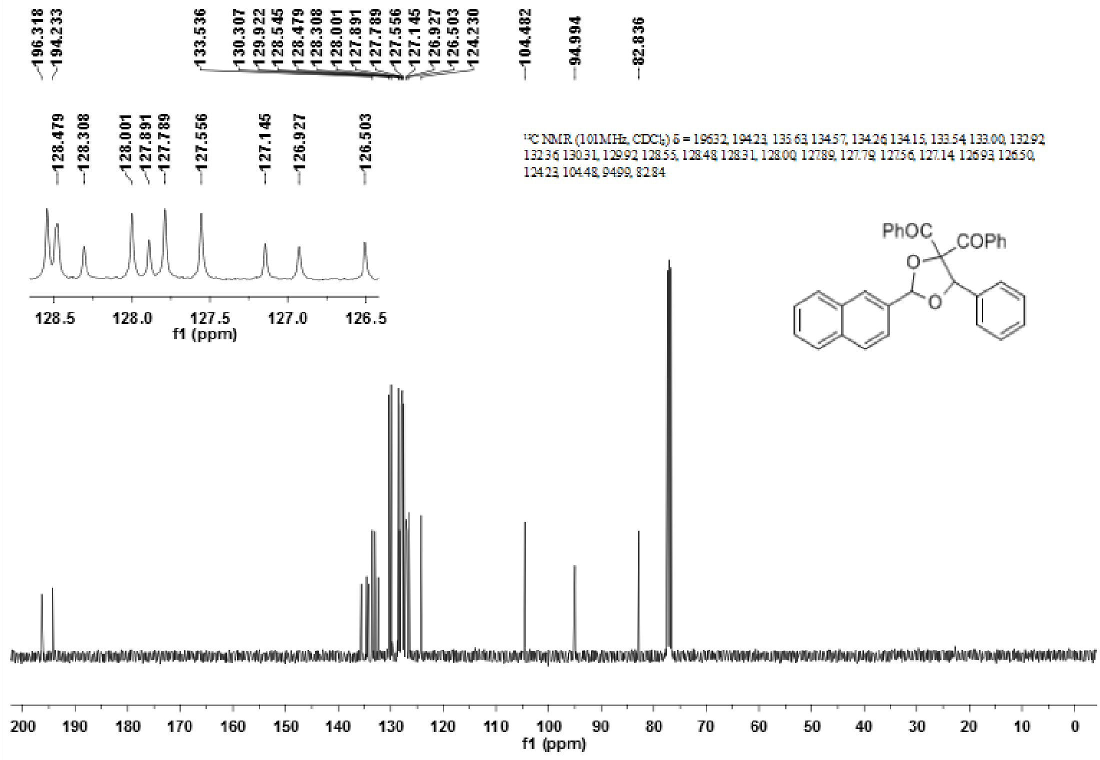


^{1}H NMR (400 MHz, CDCl$_3$) δ 8.09 – 8.01 (m, 2H), 7.67 – 7.59 (m, 6H), 7.52 - 7.46 (m, 1H), 7.41 - 7.34 (m, 3H), 7.21 – 7.13 (m, 4H), 7.07 - 6.99 (m, 1H), 6.95 - 6.89 (m, 1H), 6.51 (s, 1H), 6.01 (s, 1H), 2.16 (s, 3H).

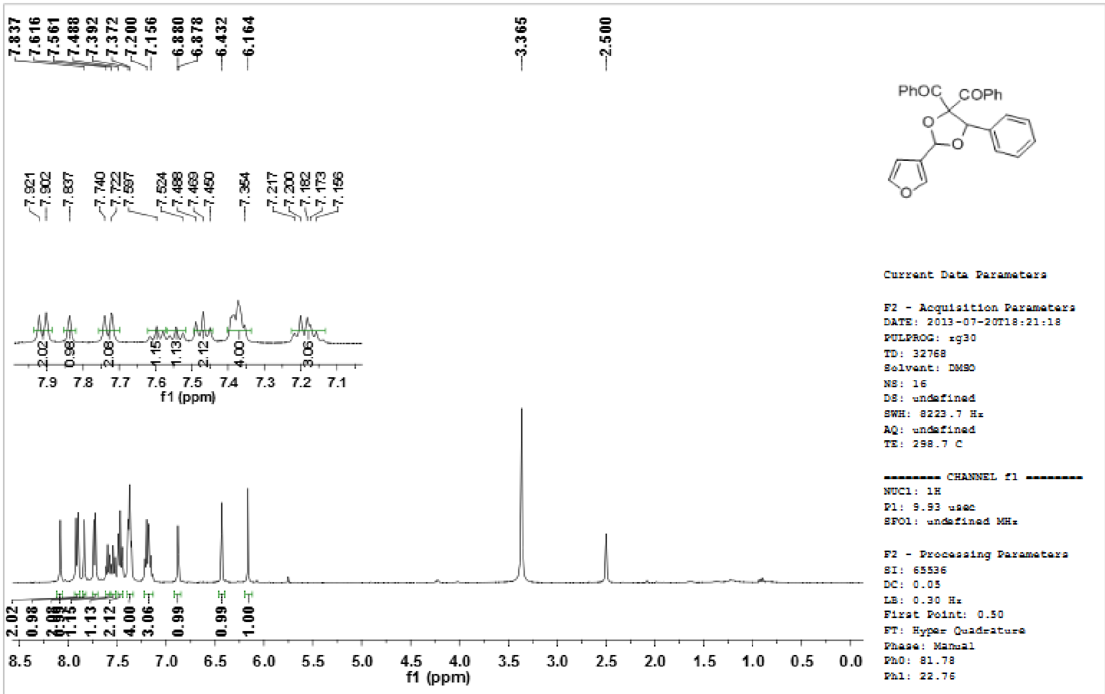


^{13}C NMR (101 MHz, $CDCl_3$) δ 195.97, 194.07, 137.61, 135.59, 134.24, 134.18, 134.05, 133.61, 132.96, 131.74, 130.24, 129.72, 129.15, 128.97, 128.55, 128.30, 127.96, 127.73, 124.63, 124.15, 103.54, 94.66, 82.96, 21.27.

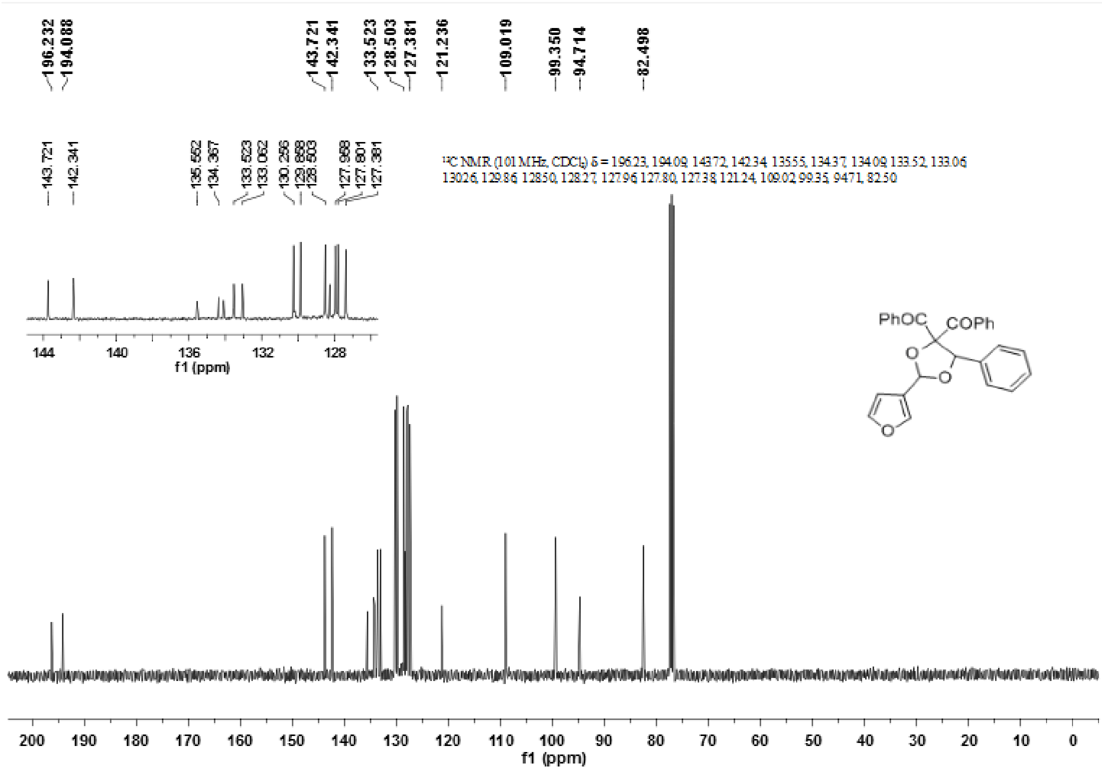


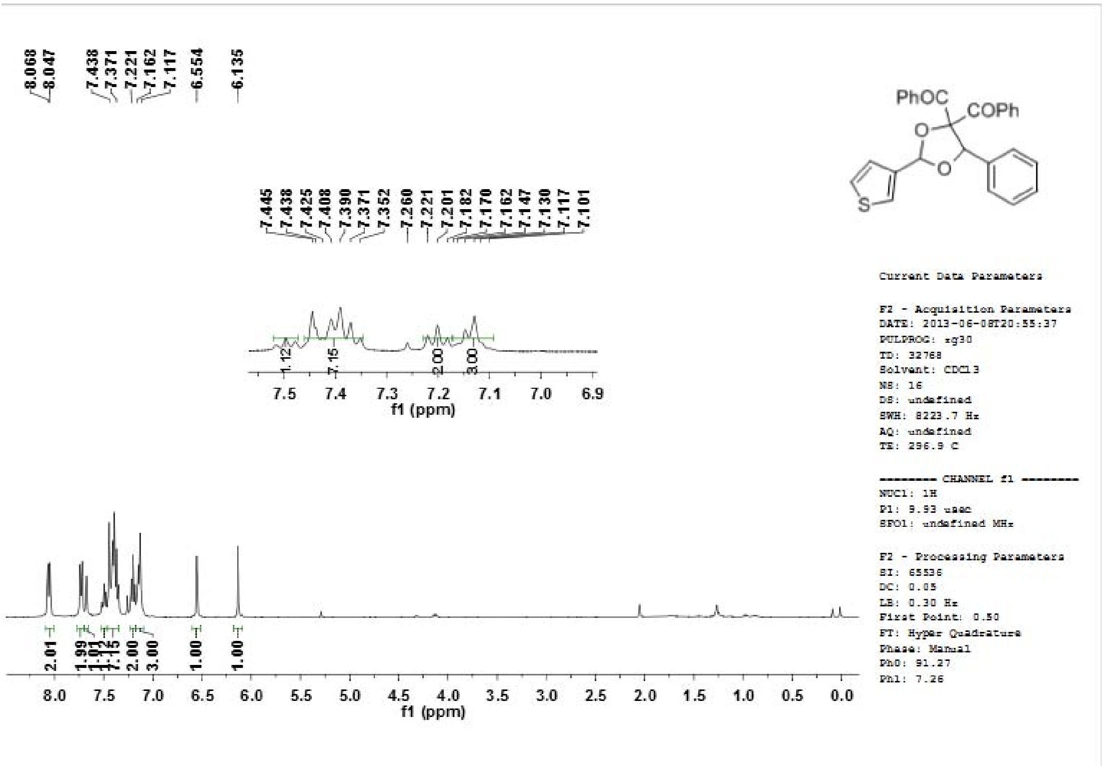


^{13}C NMR (101MHz, $CDCl_3$) δ = 196.32, 194.23, 135.63, 134.57, 134.26, 134.15, 133.54, 133.00, 132.92, 132.36, 130.31, 129.92, 128.55, 128.48, 128.31, 128.00, 127.89, 127.79, 127.56, 127.14, 126.93, 126.50, 124.23, 104.48, 94.99, 82.84



^{1}H NMR (400 MHz, DMSO) δ 8.08(s, 1H), 7.91(d, J = 7.4 Hz, 2H), 7.84(s, 1H), 7.73(d, J = 7.4 Hz, 2H), 7.63 - 7.58 (m, 1H), 7.57 - 7.52 (m, 1H), 7.50 - 7.44 (m, 2H), 7.40 – 7.34 (m, 4H), 7.23 – 7.13(m, 3H), 6.88(d, J = 0.9 Hz, 1H), 6.43 (s, 1H), 6.16(s, 1H).


196.232
194.088
143.721
142.341
133.523
128.503
127.381
121.236
109.019
99.350
94.714
82.498
^{13}C NMR (101 MHz, CDCl$_3$) δ = 196.23, 194.09, 143.72, 142.34, 135.55, 134.37, 134.09, 133.52, 133.06, 130.26, 129.86, 128.50, 128.27, 127.96, 127.80, 127.38, 121.24, 109.02, 99.35, 94.71, 82.50
PhOC
COPh
f1 (ppm)


PhOC
COPh
Current Data Parameters
F2 - Acquisition Parameters
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PULPROG: zg30
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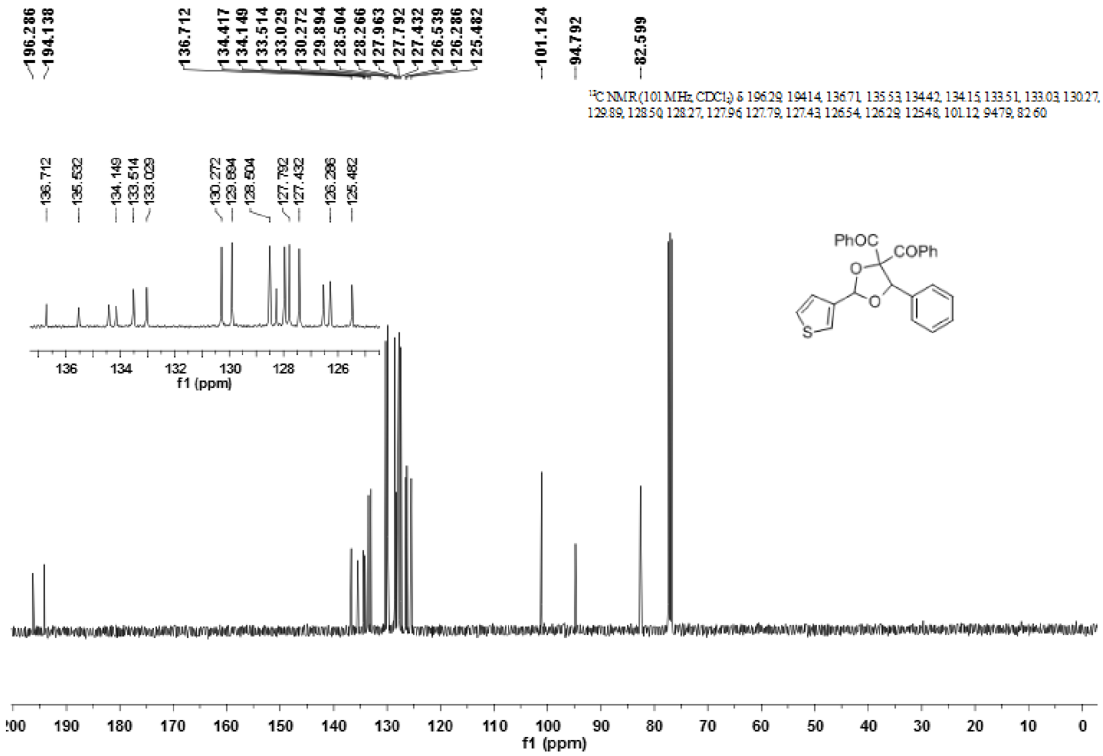
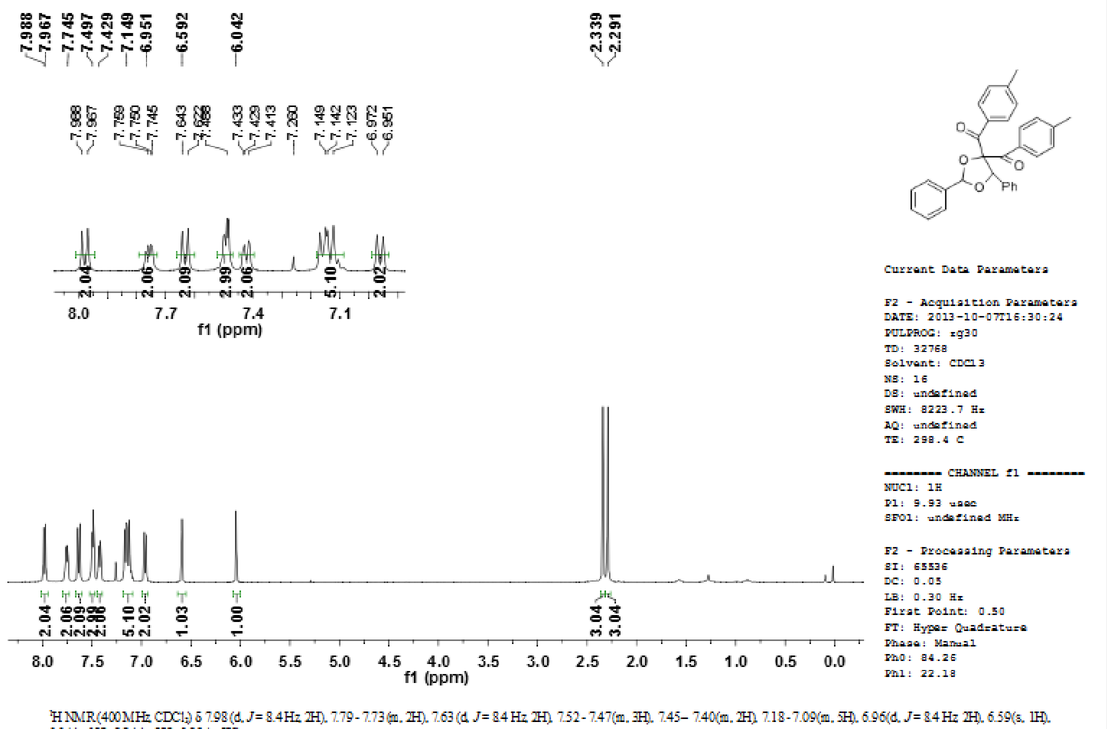
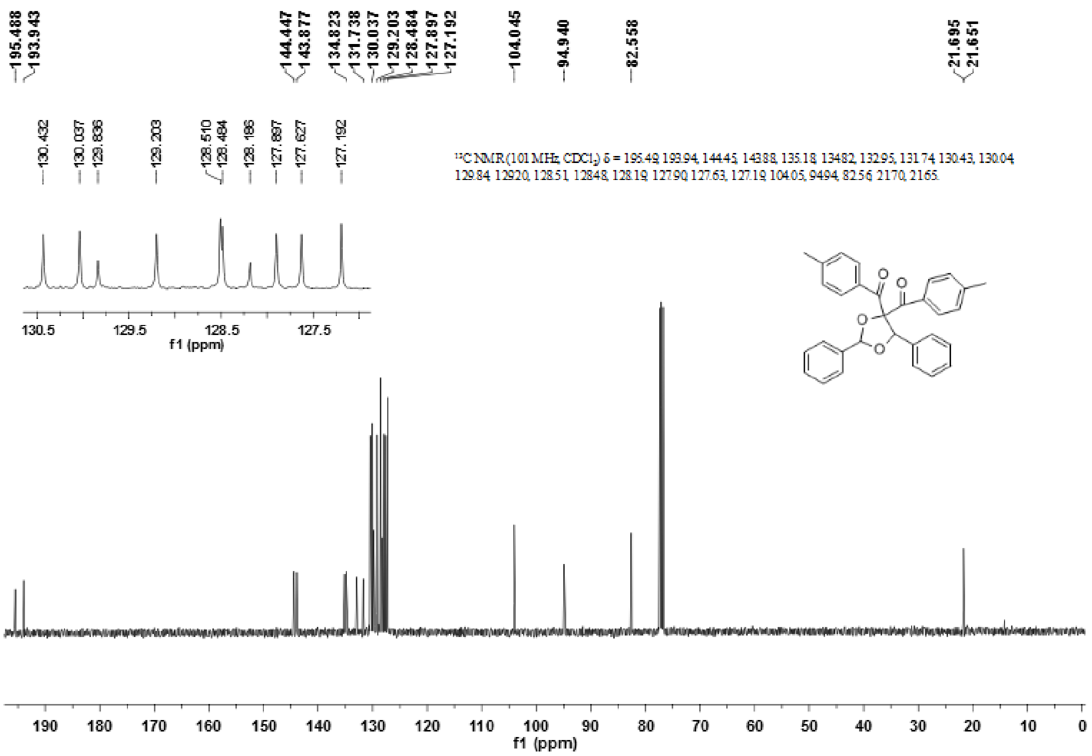
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 296.9 C
-------- CHANNEL f1 --------
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 91.27
Ph1: 7.26
f1 (ppm)

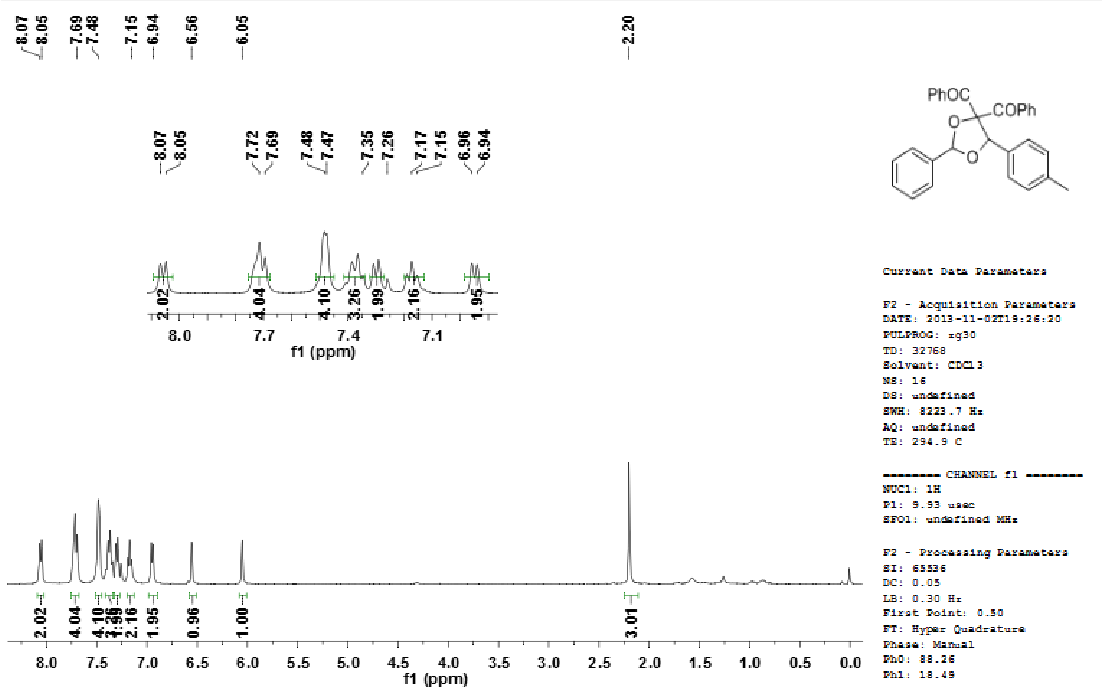


^{13}C NMR (101 MHz, $CDCl_3$) δ 196.29, 194.14, 136.71, 135.53, 134.42, 134.15, 133.51, 133.03, 130.27, 129.89, 128.50, 128.27, 127.96, 127.79, 127.43, 126.54, 126.29, 125.48, 101.12, 94.79, 82.60

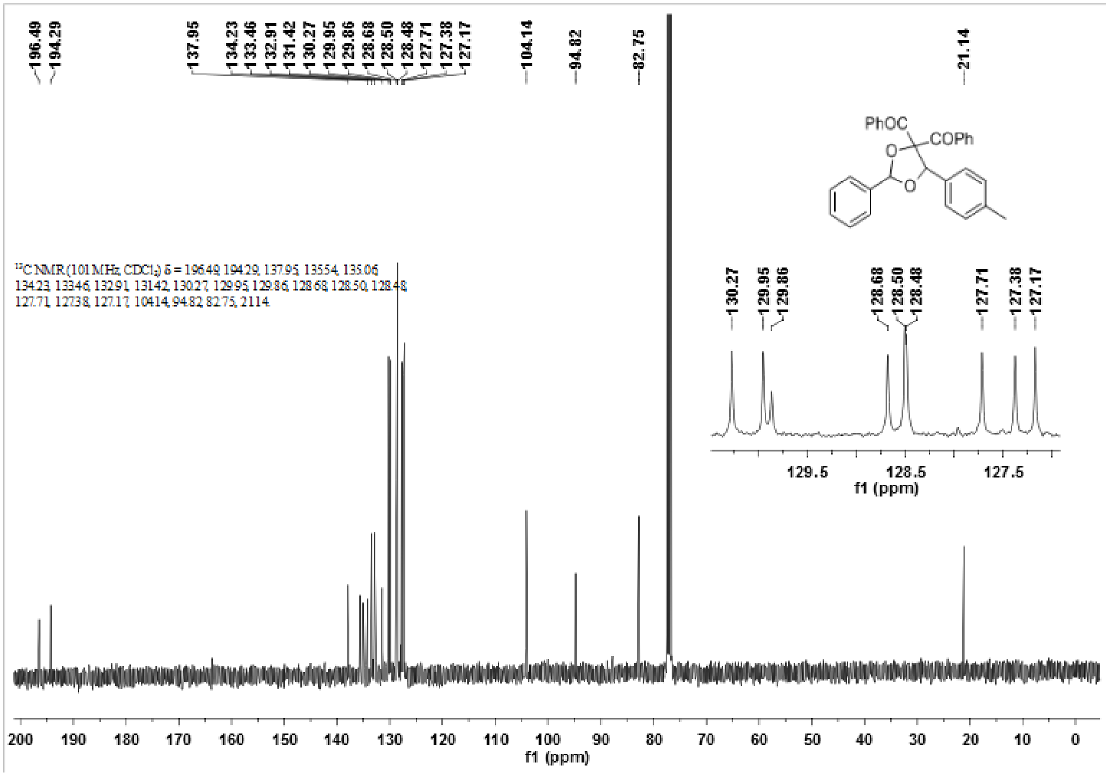


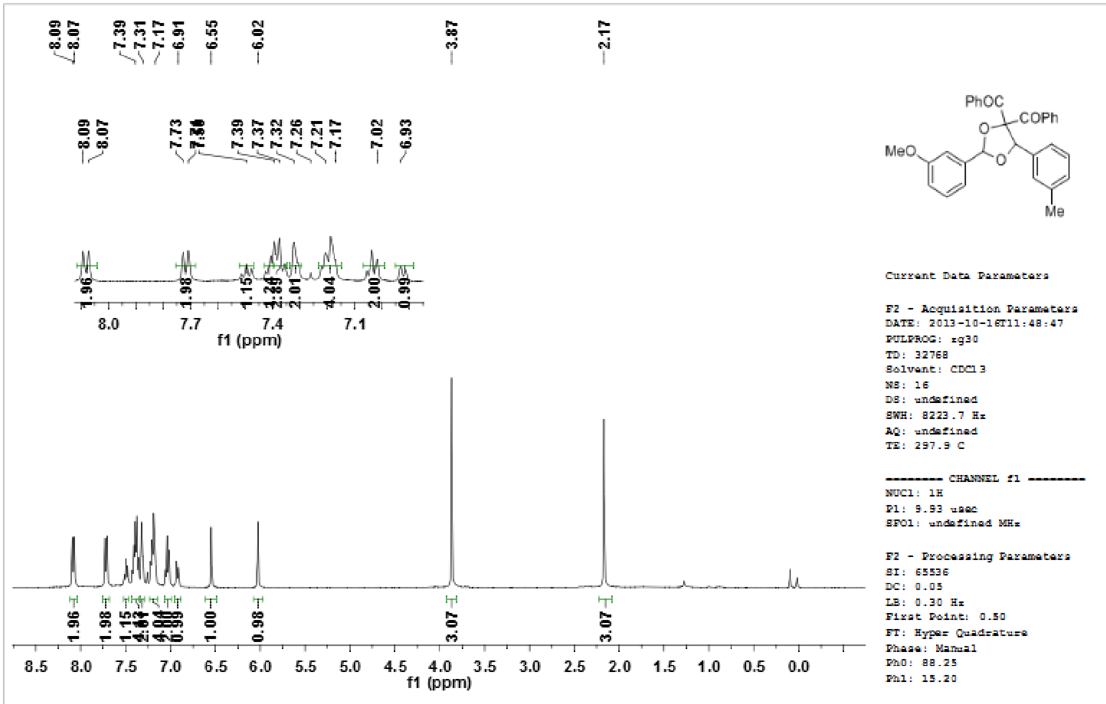
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2H), 7.79 - 7.73 (m, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.52 - 7.47 (m, 3H), 7.45 – 7.40 (m, 2H), 7.18 - 7.09 (m, 5H), 6.96 (d, J = 8.4 Hz, 2H), 6.59 (s, 1H), 6.04 (s, 1H), 2.34 (s, 3H), 2.29 (s, 3H).



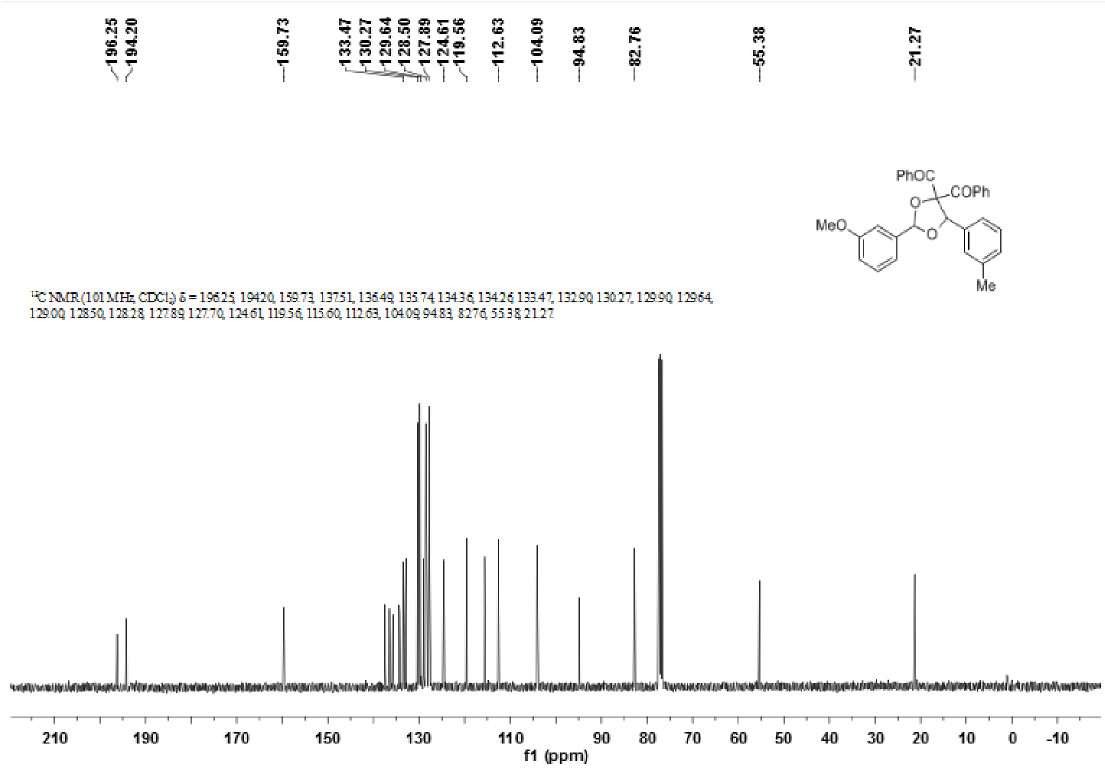


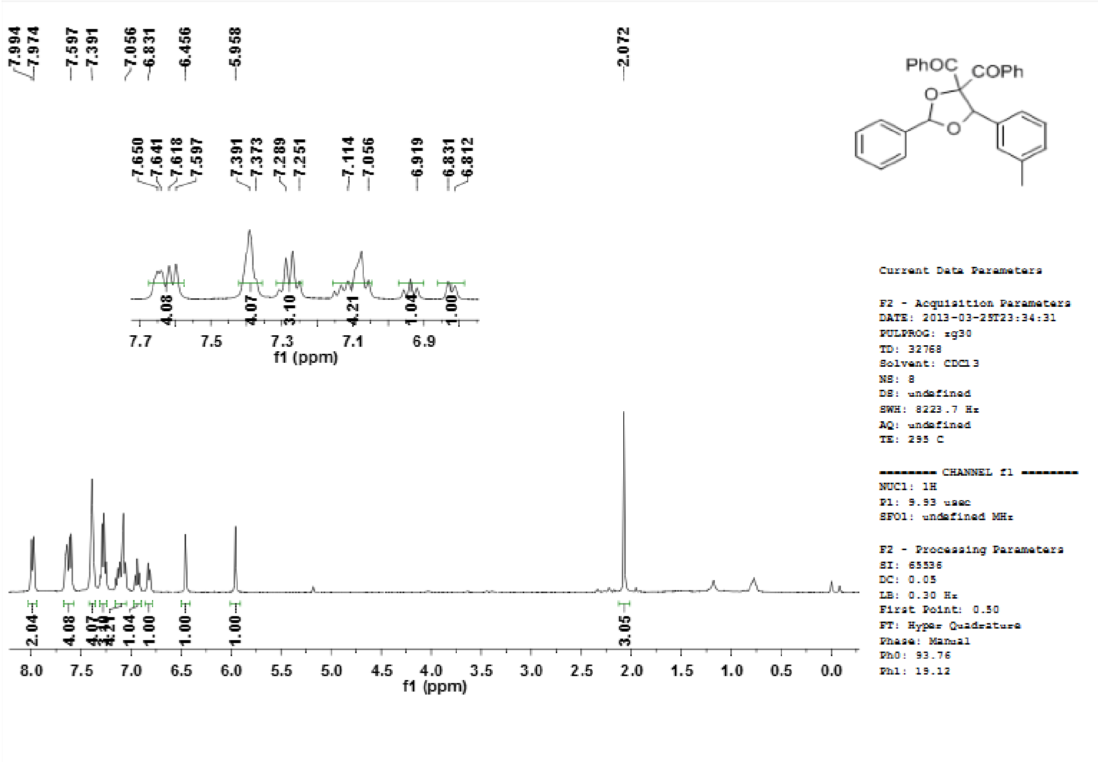
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.09 - 8.02 (m, 2H), 7.76-7.68 (m, 4H), 7.52 - 7.45 (m, 4H), 7.42 - 7.34 (m, 3H), 7.32 - 7.27 (m, 2H), 7.20 - 7.13 (m, 2H), 6.99 - 6.89 (m, 2H), 6.56 (s, 1H), 6.05 (s, 1H), 2.20 (s, 3H).





^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.52 - 7.47 (m, 1H), 7.43 - 7.35 (m, 4H), 7.34 - 7.29 (m, 2H), 7.23 - 7.15 (m, 4H), 7.07 - 6.99 (m, 2H), 6.95 - 6.88 (m, 1H), 6.55 (s, 1H), 6.02 (s, 1H), 3.87 (s, 3H), 2.17 (s, 3H).


196.25
194.20
159.73
133.47
130.27
129.64
128.50
127.89
124.61
119.56
112.63
104.09
94.83
82.76
55.38
21.27
PhOC
COPh
MeO
Me
^{13}C NMR (101 MHz, CDCl$_3$) δ = 196.25, 194.20, 159.73, 137.51, 136.49, 135.74, 134.36, 134.26, 133.47, 132.90, 130.27, 129.90, 129.64, 129.00, 128.50, 128.28, 127.89, 127.70, 124.61, 119.56, 115.60, 112.63, 104.09, 94.83, 82.76, 55.38, 21.27
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.994
7.974
7.597
7.391
7.056
6.831
6.456
5.958
2.072
PhOC
COPh
7.650
7.641
7.618
7.597
7.391
7.373
7.289
7.251
7.114
7.056
6.919
6.831
6.812
4.08
4.07
3.10
4.21
1.04
1.00
7.7 7.5 7.3 7.1 6.9
f1 (ppm)
Current Data Parameters
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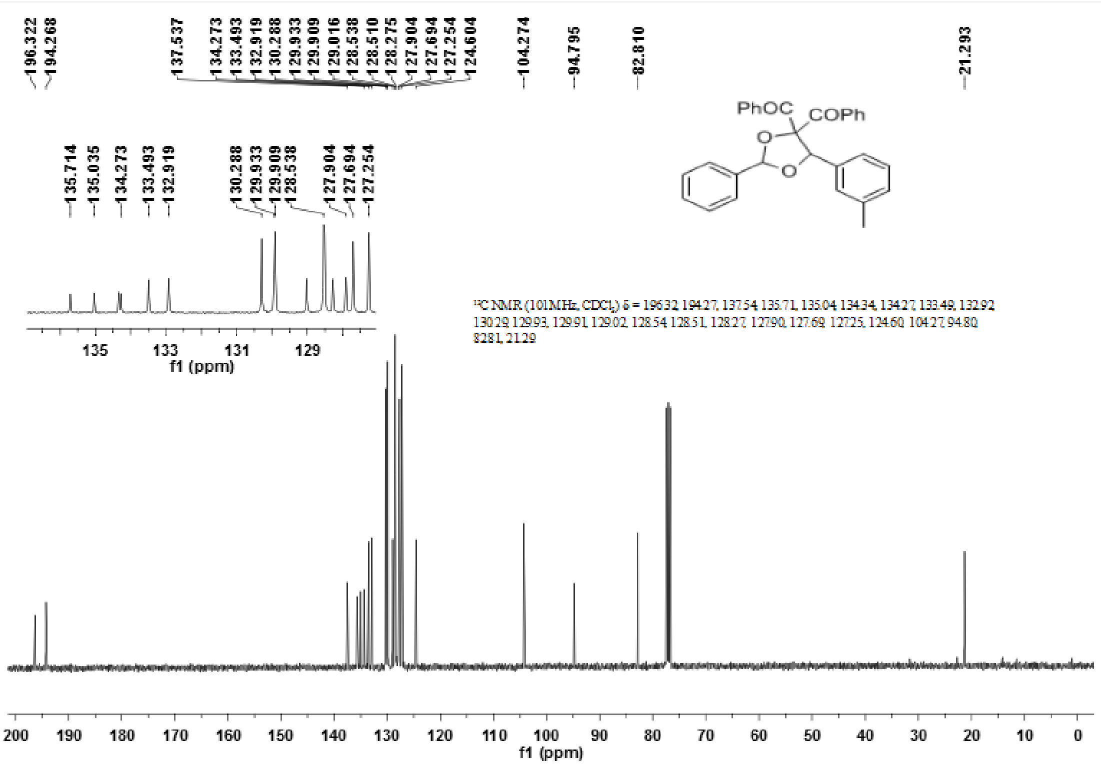
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 8
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 295 C
======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 93.76
Ph1: 19.12
2.04
4.08
4.07
3.10
4.21
1.04
1.00
1.00
1.00
3.05
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)


PhOC
COPh
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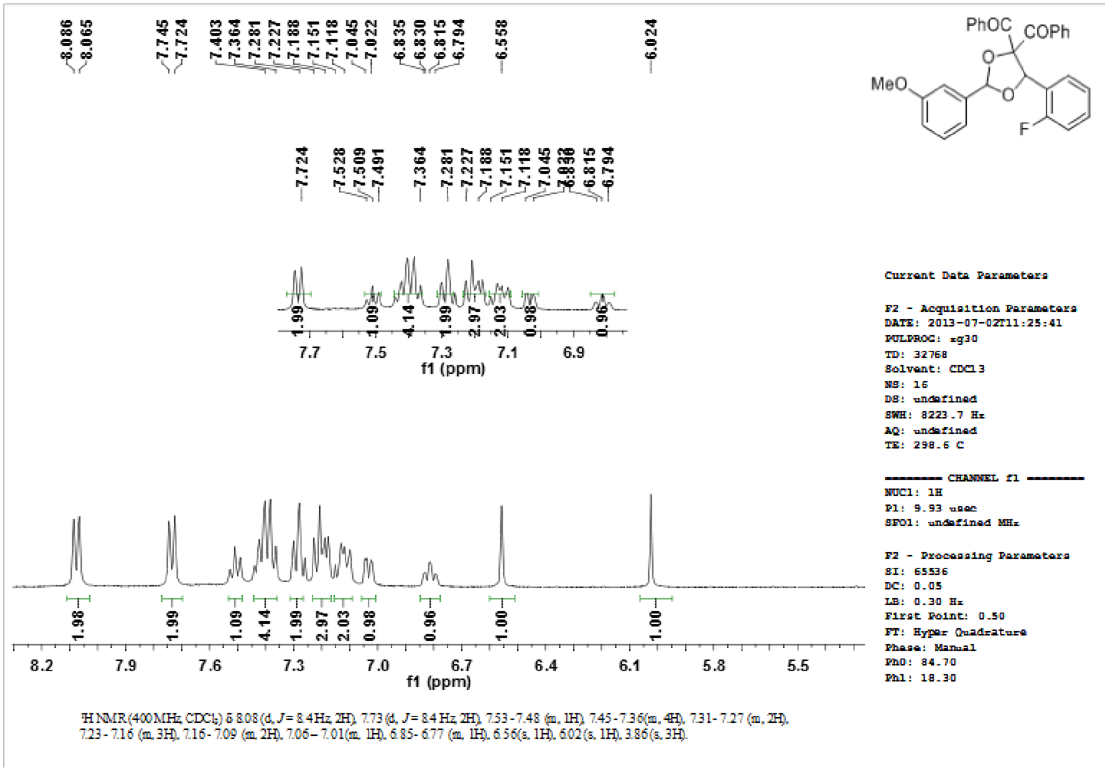
f1 (ppm)


PhOC
COPh
MeO
F
Current Data Parameters
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TD: 32768
Solvent: CDCl3
NS: 16
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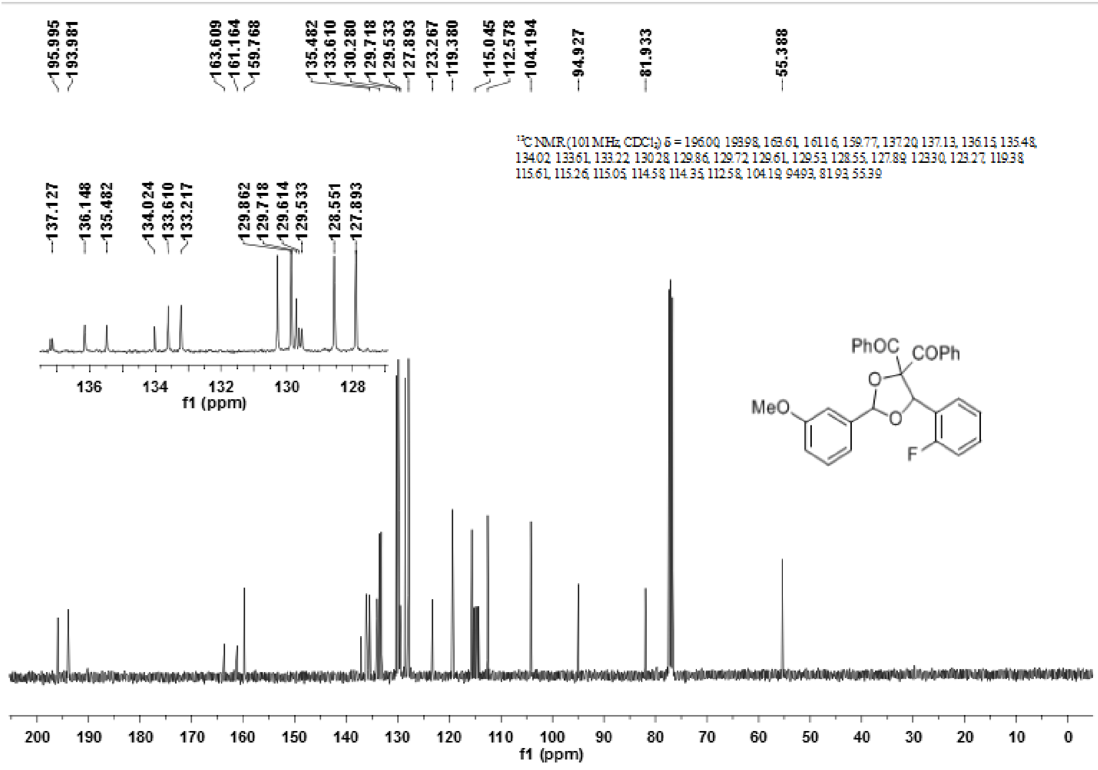
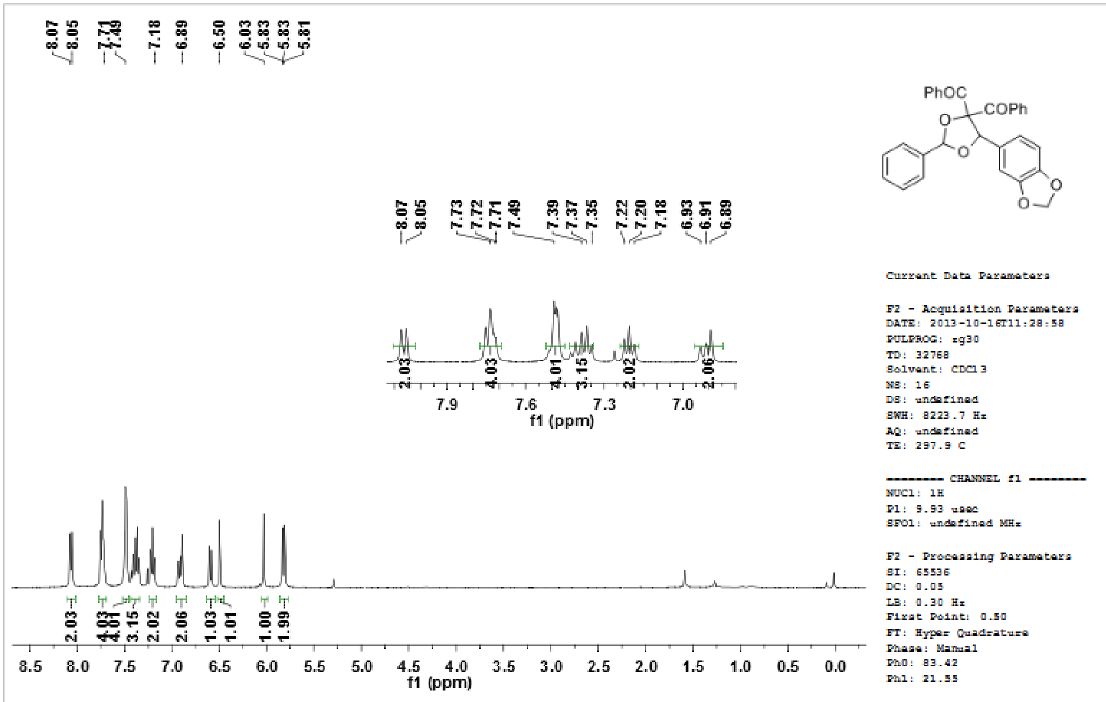
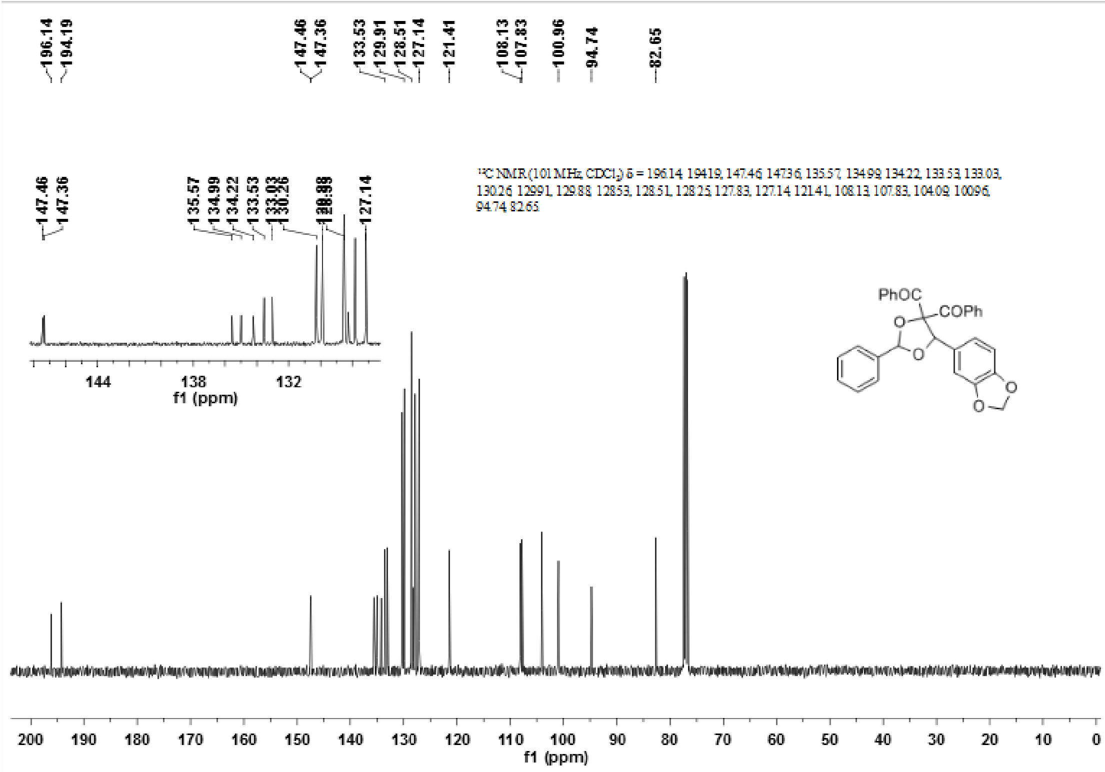
AQ: undefined
TE: 298.6 C
======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 84.70
Ph1: 18.30
f1 (ppm)
¹H NMR (400MHz, CDCl₃) δ 8.08 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.53 - 7.48 (m, 1H), 7.45 - 7.36(m, 4H), 7.31 - 7.27 (m, 2H), 7.23 - 7.16 (m, 3H), 7.16 - 7.09 (m, 2H), 7.06 – 7.01(m, 1H), 6.85 - 6.77 (m, 1H), 6.56(s, 1H), 6.02 (s, 1H), 3.86 (s, 3H).

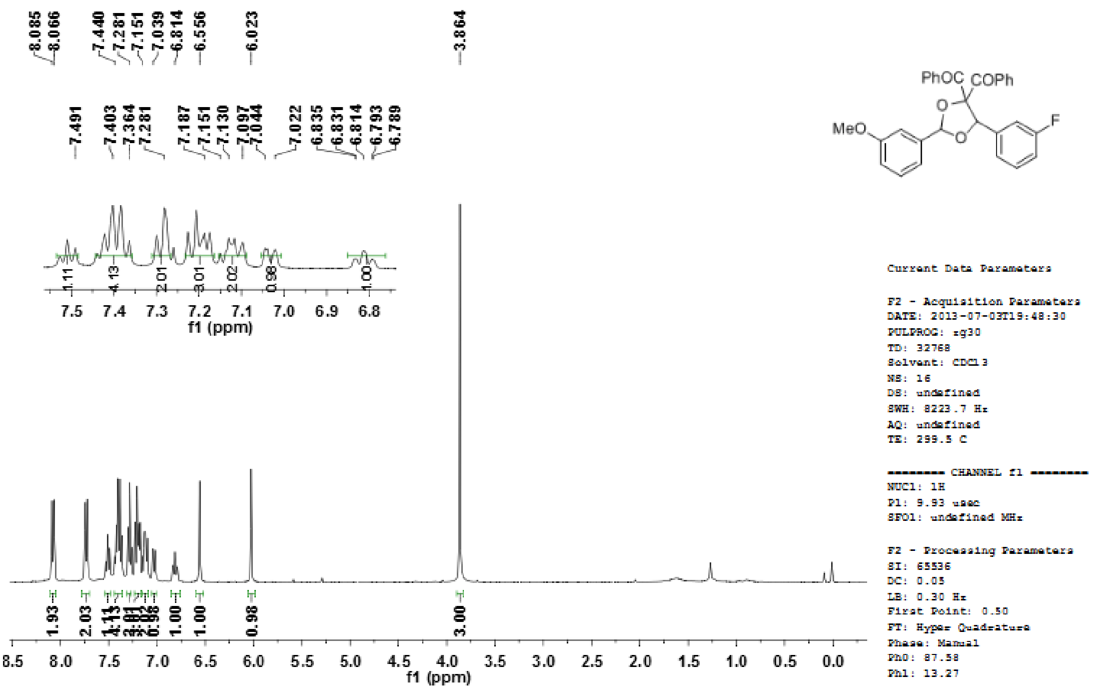


^{13}C NMR (101 MHz, $CDCl_3$) δ = 196.00, 193.98, 163.61, 161.16, 159.77, 137.20, 137.13, 136.15, 135.48, 134.02, 133.61, 133.22, 130.28, 129.86, 129.72, 129.61, 129.53, 128.55, 127.89, 123.30, 123.27, 119.38, 115.61, 115.26, 115.05, 114.58, 114.35, 112.58, 104.19, 94.93, 81.93, 55.39

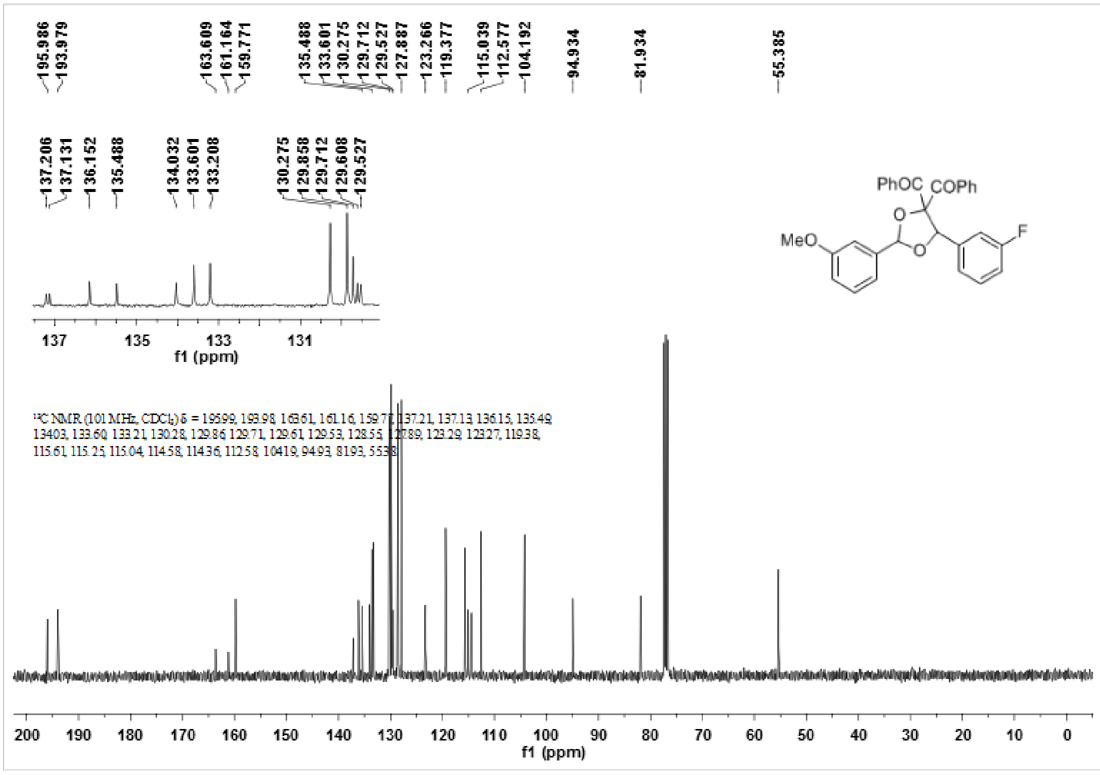


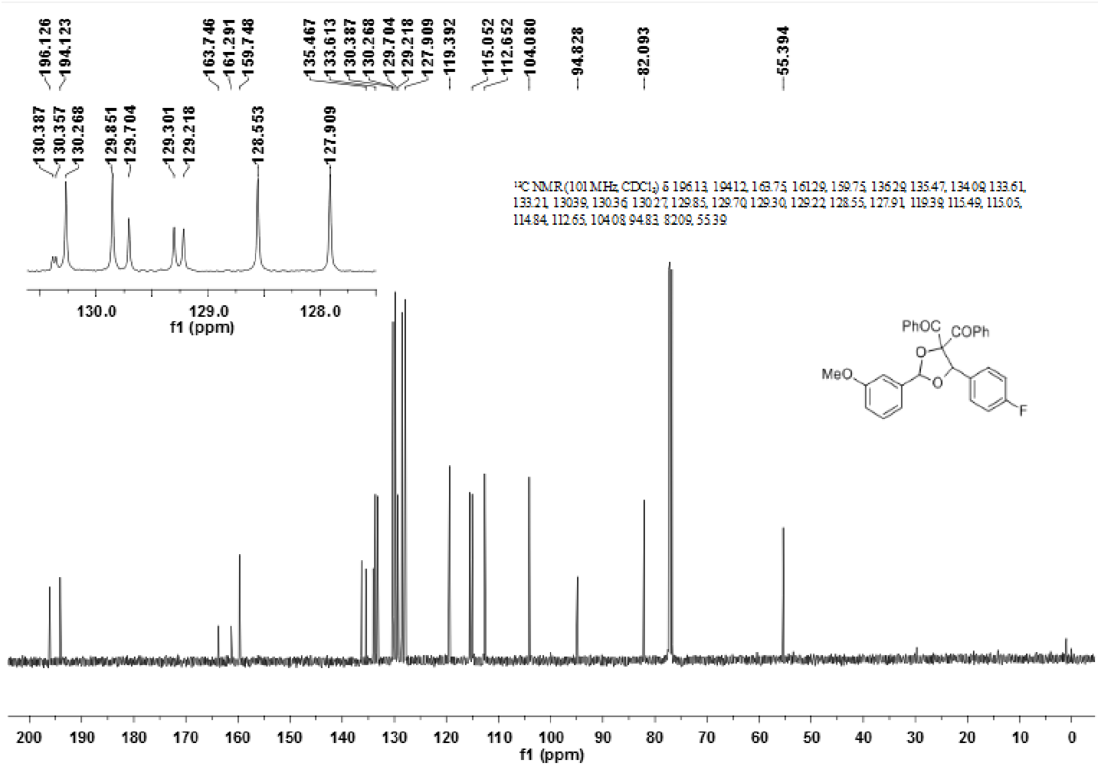
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.0 Hz, 2H), 7.78 - 7.69 (m, 4.9 Hz, 4H), 7.52 – 7.45 (m, 4H), 7.44 - 7.34 (m, 3H), 7.24 - 7.17 (m, 2H), 6.95 – 6.85 (m, 2H), 6.59 (d, J = 8.0 Hz, 1H), 6.50 (s, 1H), 6.03 (s, 1H), 5.86 – 5.77 (m, 2H).

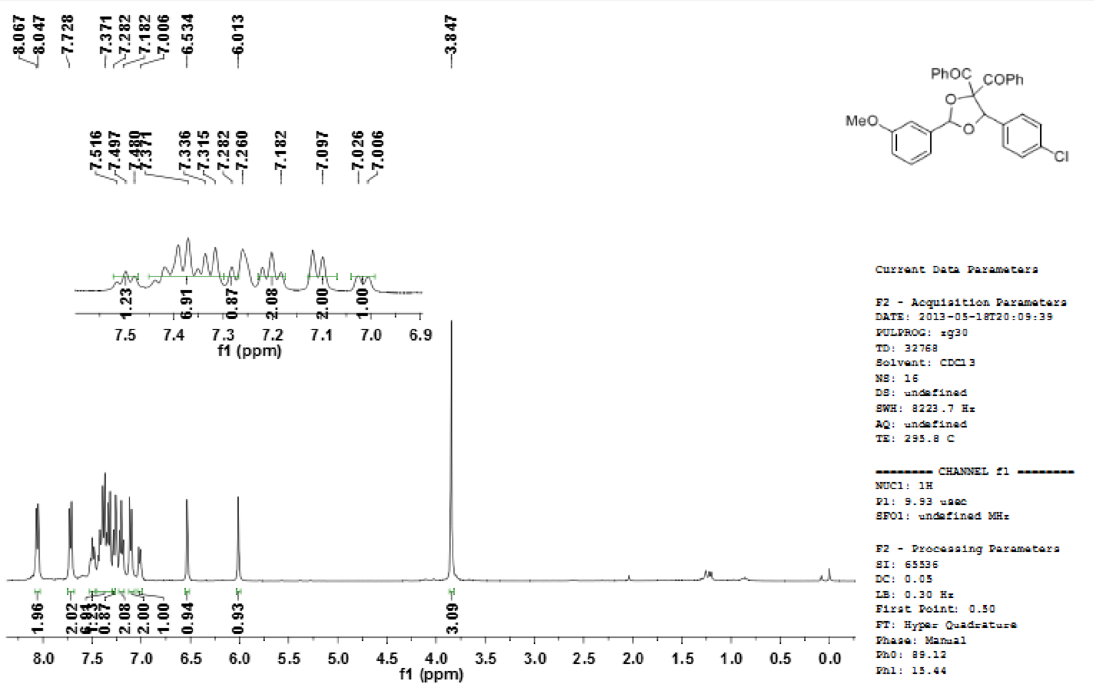




^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, J = 7.6 Hz, 2H), 7.73 (d, J = 7.6 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.44 – 7.36 (m, 4H), 7.31- 7.26 (m, 2H), 7.24-7.16 (m, 3H), 7.15 – 7.09 (m, 2H), 7.05 – 7.01 (m, 1H), 6.85 – 6.76 (m, 1H), 6.56 (s, 1H), 6.02 (s, 1H), 3.86 (s, 3H).

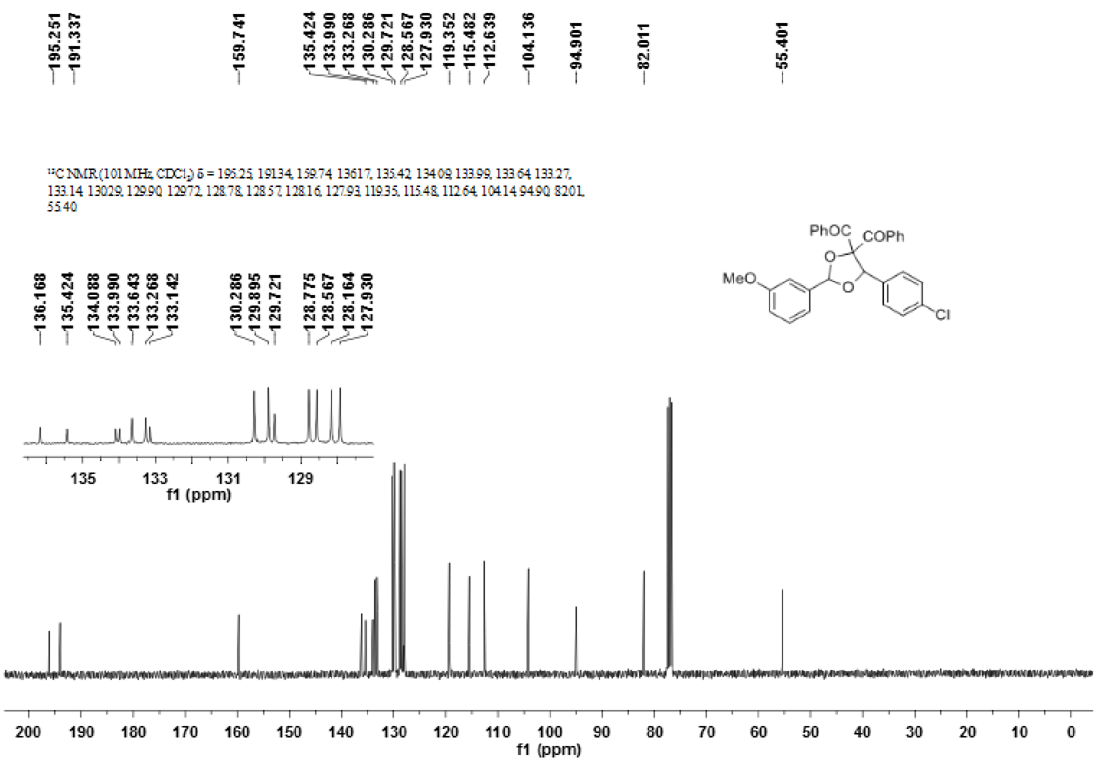

^{13}C NMR (101 MHz, CDCl$_3$) δ = 195.99, 193.98, 163.61, 161.16, 159.77, 137.21, 137.13, 136.15, 135.49, 134.03, 133.60, 133.21, 130.28, 129.86, 129.71, 129.61, 129.53, 128.55, 127.89, 123.29, 123.27, 119.38, 115.61, 115.25, 115.04, 114.58, 114.36, 112.58, 104.19, 94.93, 81.93, 55.38
PhOC
COPh
MeO
F
f1 (ppm)

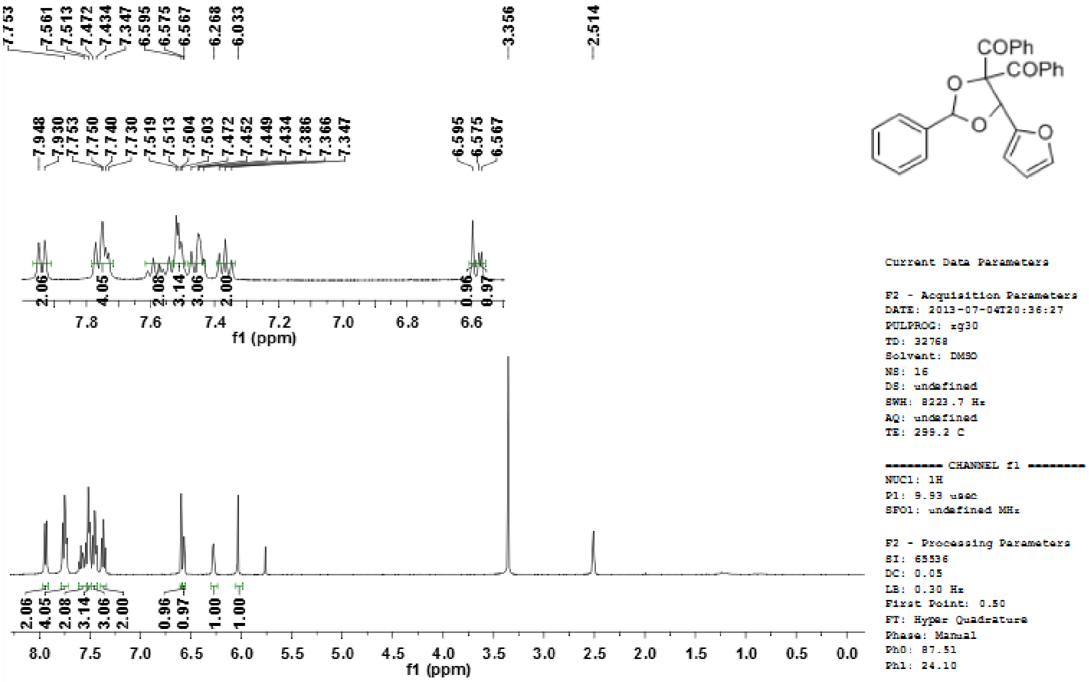

^{13}C NMR (101 MHz, CDCl$_3$) δ 196.13, 194.12, 163.75, 161.29, 159.75, 136.29, 135.47, 134.09, 133.61, 133.21, 130.39, 130.36, 130.27, 129.85, 129.70, 129.30, 129.22, 128.55, 127.91, 119.39, 115.49, 115.05, 114.84, 112.65, 104.08, 94.83, 82.09, 55.39
PhOC
COPh
MeO
F
f1 (ppm)



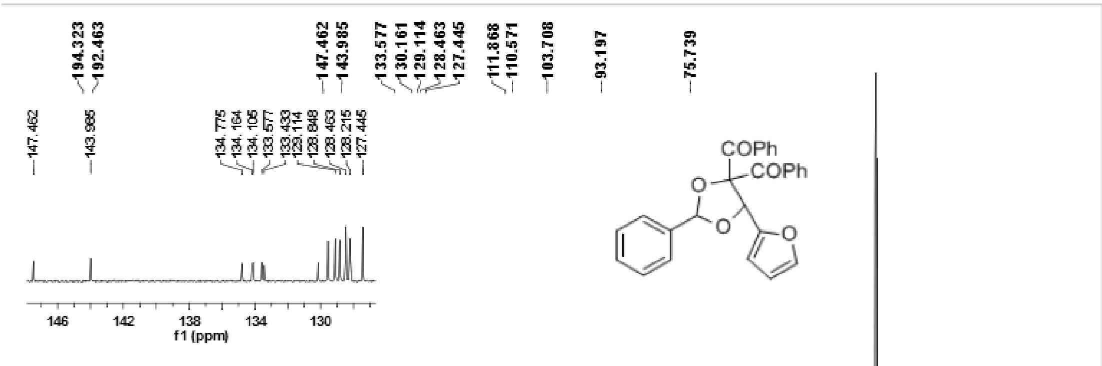
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 7.6 Hz, 2H), 7.52-7.47 (m, 1H), 7.45– 7.30 (m, 7H), 7.28 (s, 1H), 7.23-7.17 (m, 2H), 7.11 (d, J = 8.4 Hz, 2H), 7.04-6.99 (m, 1H), 6.53 (s, 1H), 6.01 (s, 1H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.25, 191.34, 159.74, 136.17, 135.42, 134.09, 133.99, 133.64, 133.27, 133.14, 130.29, 129.90, 129.72, 128.78, 128.57, 128.16, 127.93, 119.35, 115.48, 112.64, 104.14, 94.90, 82.01, 55.40

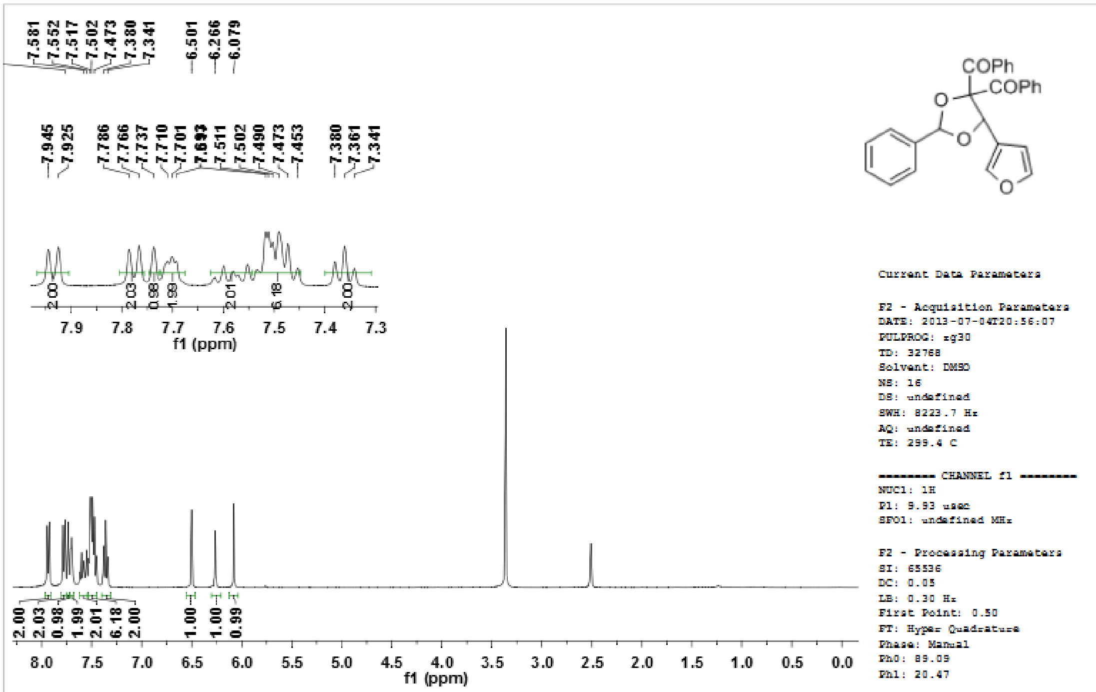




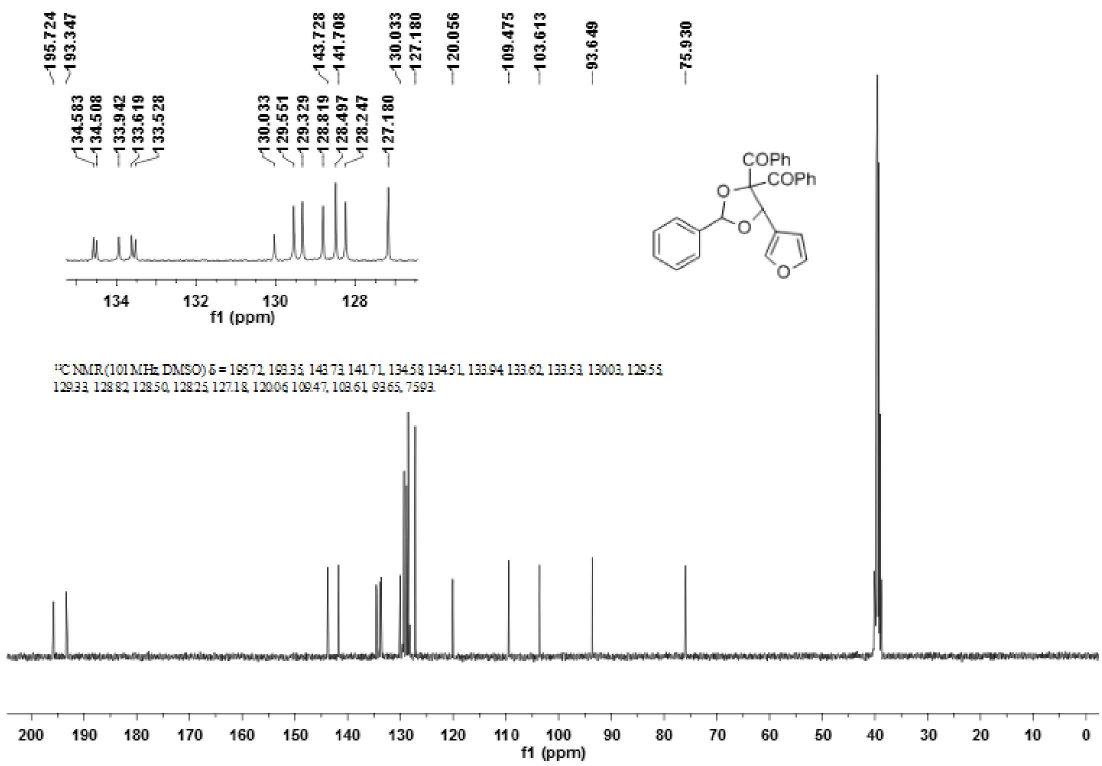
^{1}H NMR (400 MHz, DMSO) δ 7.94 (d, J = 7.2 Hz, 2H), 7.78 – 7.72 (m, 4H), 7.62-7.54 (m, 2H), 7.53-7.49 (m, 3H), 7.48-7.43 (m, 3H), 7.39-7.34 (m, 2H), 6.60 (s, 1H), 6.57 (d, J = 3.2 Hz, 1H), 6.30-6.24 (m, 1H), 6.03 (s, 1H).



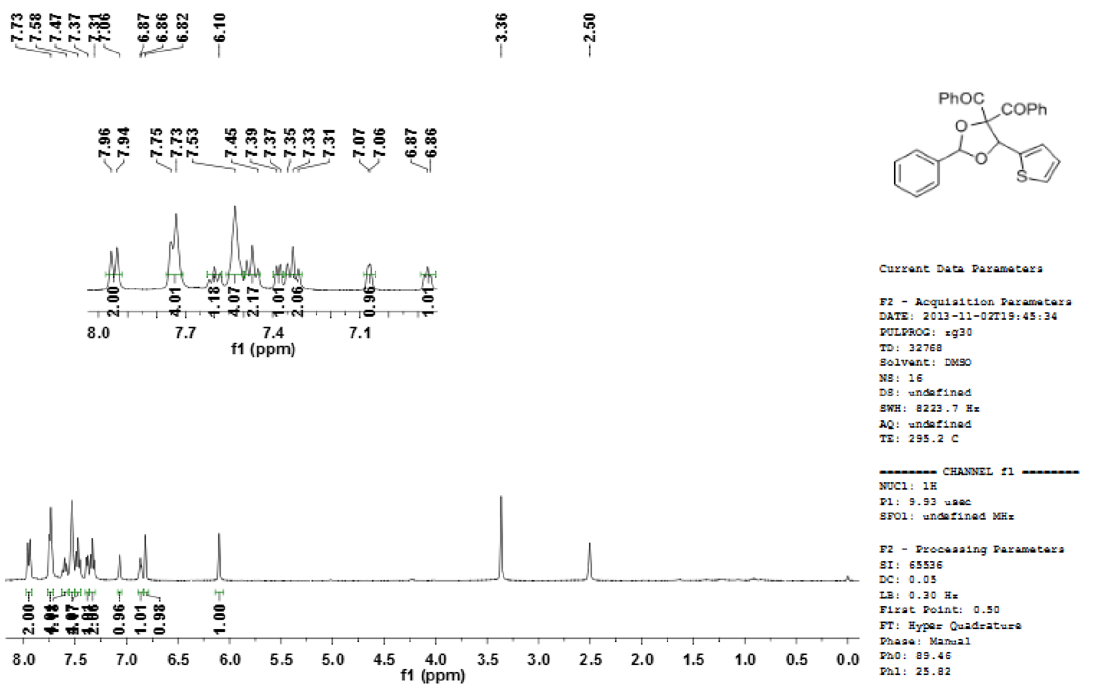
^{13}C NMR (101 MHz, DMSO) δ 194.32, 192.46, 147.46, 143.98, 134.77, 134.16, 134.11, 133.58, 133.43, 130.16, 129.56, 129.11, 128.85, 128.46, 128.22, 127.44, 111.87, 110.57, 103.71, 93.20, 75.74



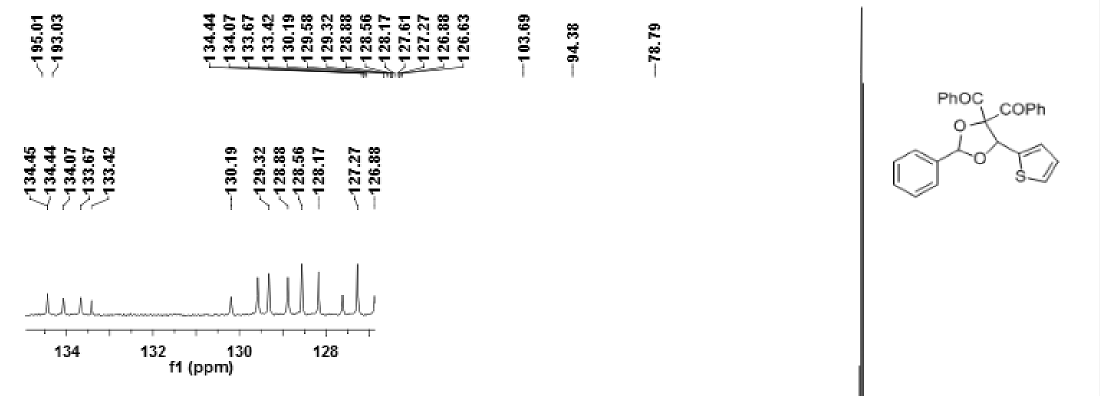
^{1}H NMR (400 MHz, DMSO) δ 7.94 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.74 (s, 1H), 7.72 – 7.68 (m, 2H), 7.62-7.54 (m, 2H), 7.54 – 7.45 (m, 6H), 7.40 - 7.31 (m, 2H), 6.50 (s, 1H), 6.27 (s, 1H), 6.08 (s, 1H)-



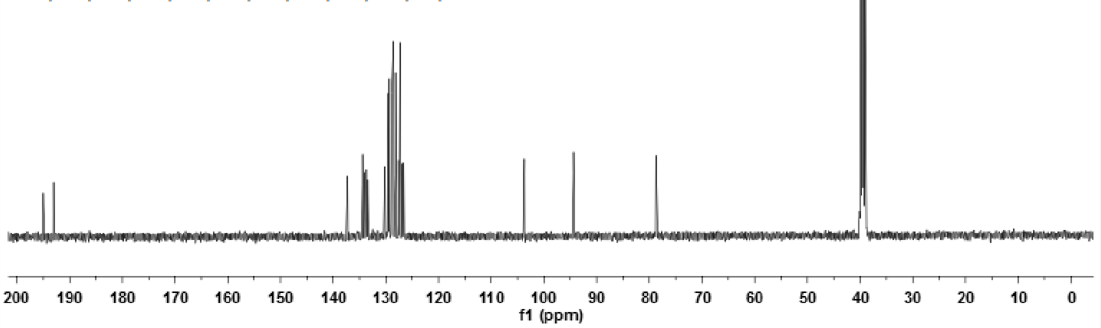
^{13}C NMR (101 MHz, DMSO) δ = 195.72, 193.35, 143.73, 141.71, 134.58, 134.51, 133.94, 133.62, 133.53, 130.03, 129.55, 129.33, 128.82, 128.50, 128.25, 127.18, 120.06, 109.47, 103.61, 93.65, 75.93.

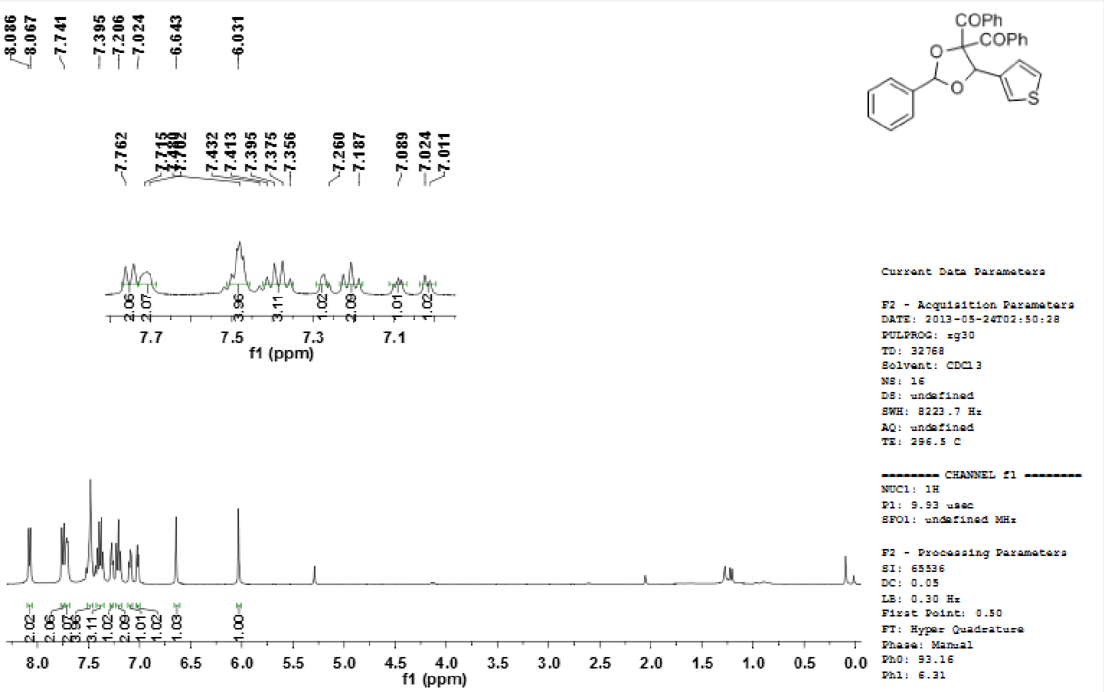


^{1}H NMR (400 MHz, DMSO) δ 7.95 (d, J = 8.0 Hz, 2H), 7.77 - 7.70 (m, 4H), 7.63 - 7.57 (m, 1H), 7.56 - 7.50 (m, 4H), 7.50 - 7.44 (m, 2H), 7.40 - 7.36 (m, 1H), 7.36 - 7.30 (m, 2H), 7.09 - 7.04 (m, 1H), 6.89 – 6.84 (m, 1H), 6.82 (s, 1H), 6.10 (s, 1H).

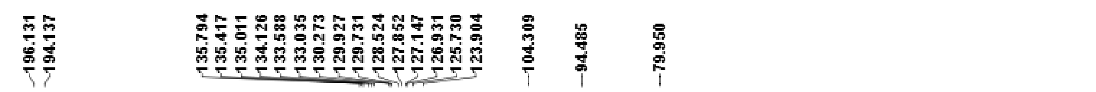


^{13}C NMR (101 MHz, DMSO) δ = 195.01, 193.03, 137.27, 134.45, 134.44, 134.07, 133.67, 133.42, 130.19, 129.58, 129.32, 128.88, 128.56, 128.17, 127.61, 127.27, 126.88, 126.63, 103.69, 94.38, 78.79

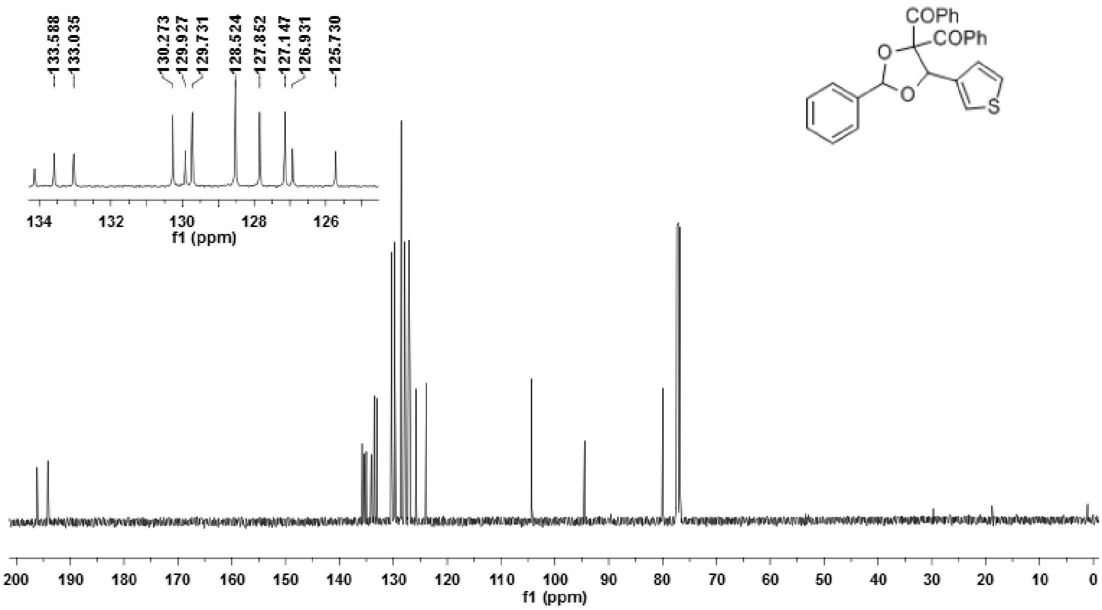


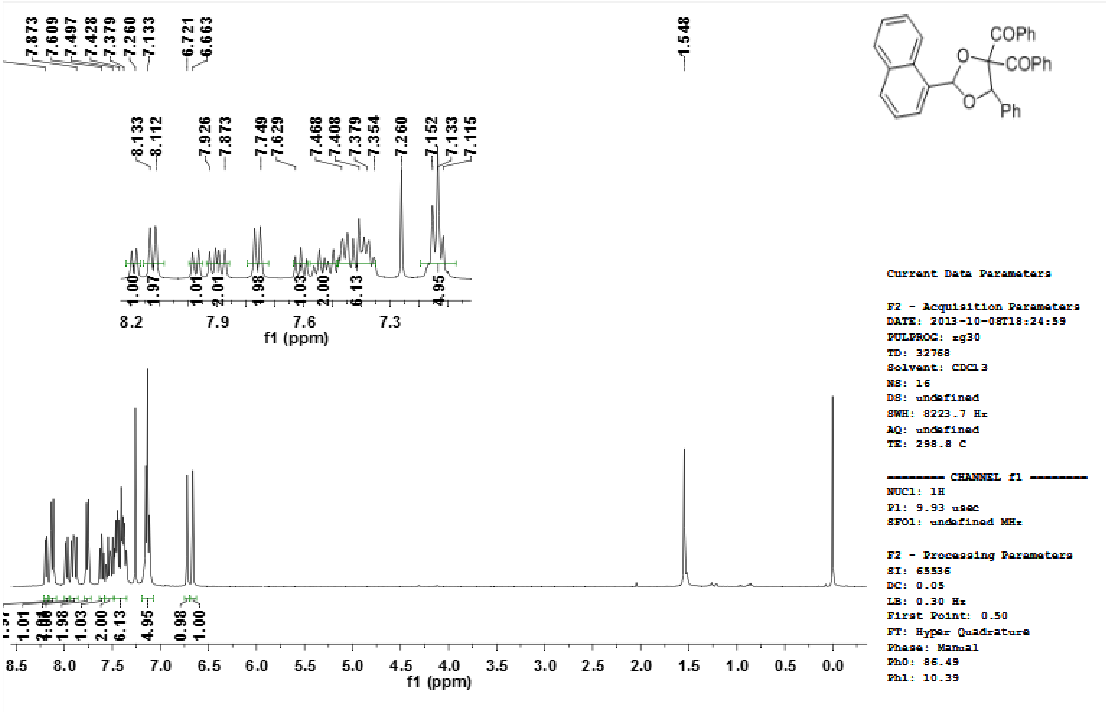


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.73 – 7.69 (m, 2H), 7.51-7.46 (m, 4H), 7.42735 (m, 3H), 7.29-7.26 (m, 1H), 7.21 (t, J = 7.8 Hz, 2H), 7.11-7.07 (m, 1H), 7.04699 (m 1H), 6.64 (s, 1H), 6.03 (s, 1H).

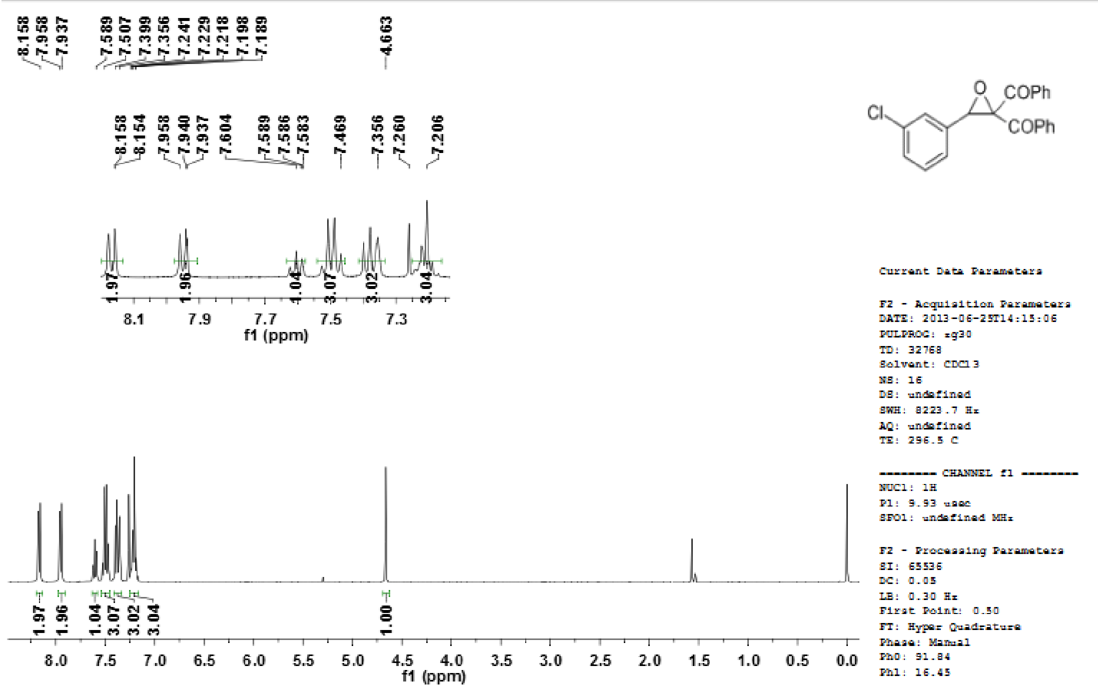


^{13}C NMR (101 MHz, $CDCl_3$) δ = 19613, 194.14, 135.79, 135.42, 135.01, 134.13, 133.59, 133.03, 130.27, 12993, 129.73, 12852, 127.85, 127.15, 126.93, 125.73, 12390, 104.31, 9449, 79.95

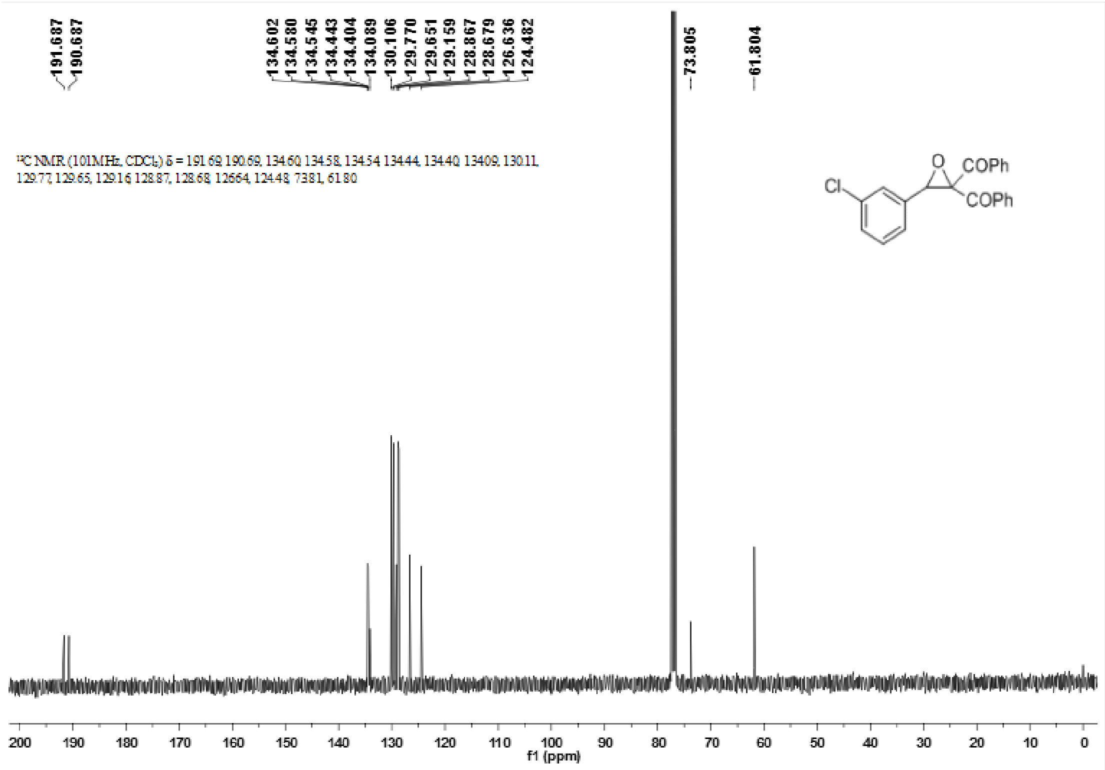




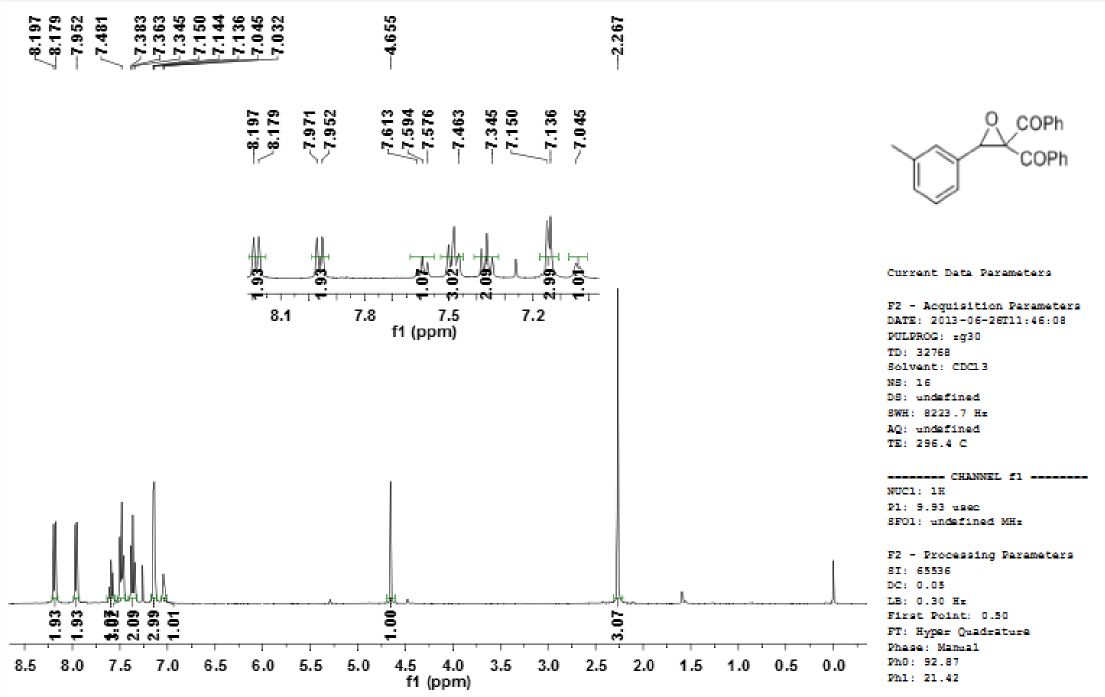
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.2 Hz, 1H), 8.16 – 8.08 (m, 2H), 7.98 (d, J = 8.4 Hz, 1H), 7.94 - 7.86 (m, 2H), 7.80 – 7.72 (m, 2H), 7.63 – 7.58 (m, 1H), 7.58 - 7.49 (m, 2H), 7.48 - 7.35 (m, 6H), 7.19 – 7.07 (m, 5H), 6.72 (s, 1H), 6.66 (s, 1H).



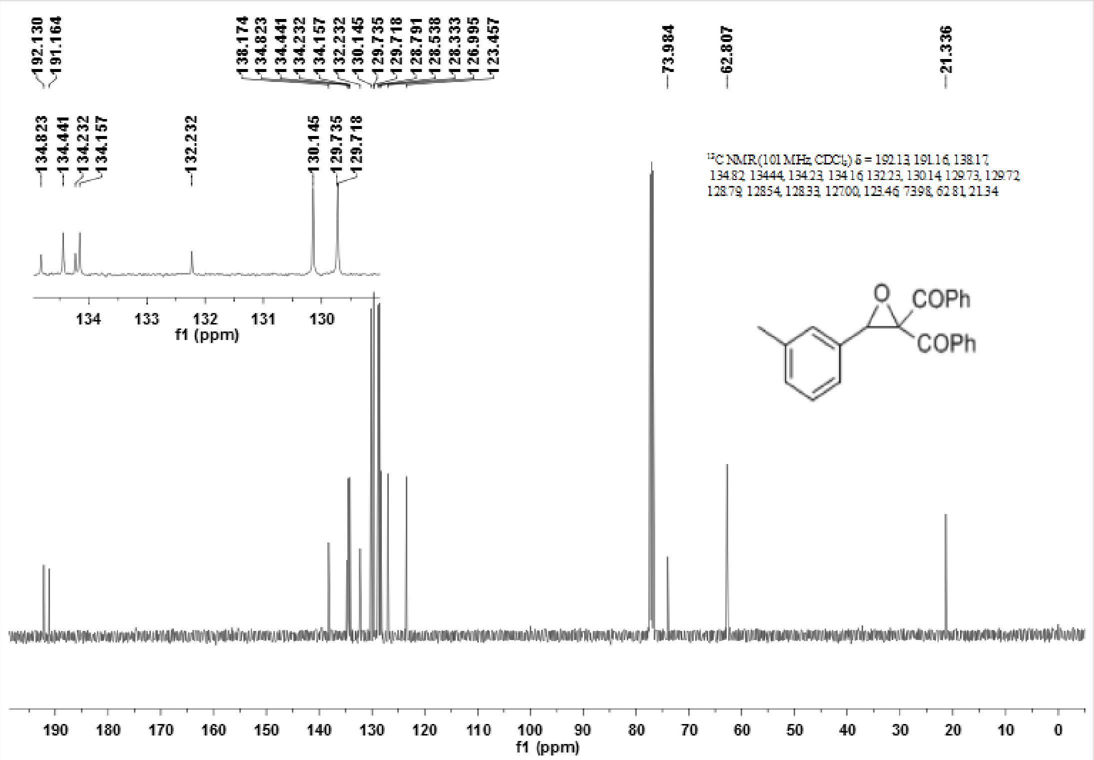
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.13 (m, 2H), 7.97 – 7.91 (m, 2H), 7.63 – 7.58 (m, 1H), 7.54 – 7.46 (m, 3H), 7.42 - 7.43 (m, 3H), 7.25 – 7.16 (m, 3H), 4.66 (s, 1H).

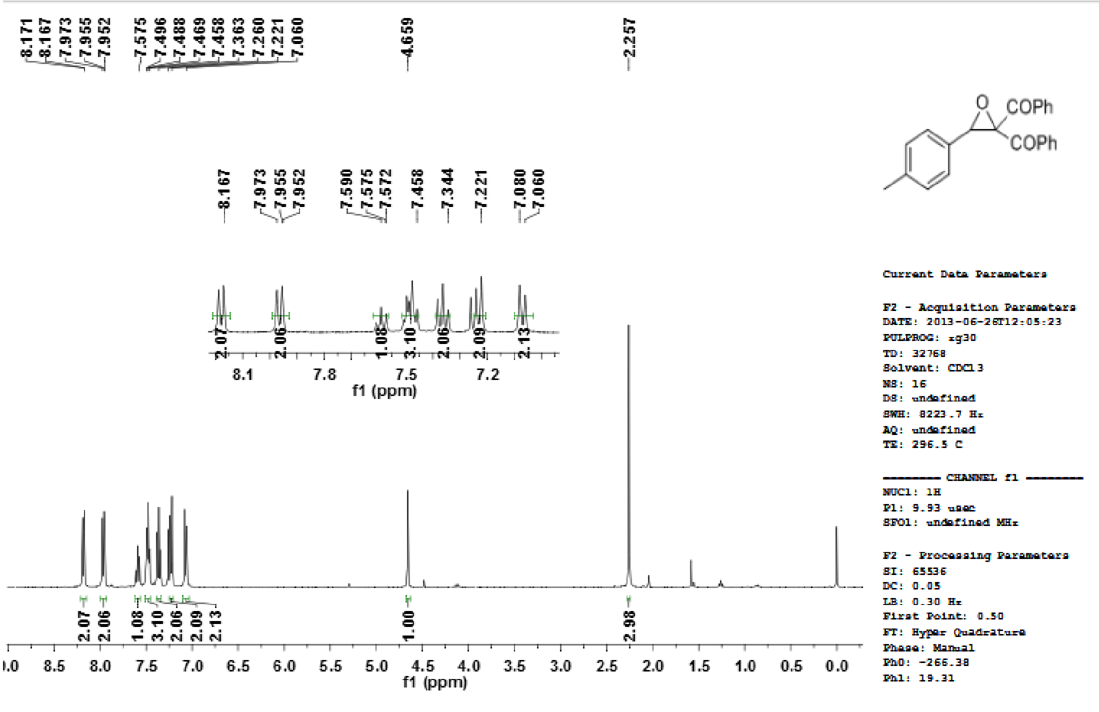


^{13}C NMR (101MHz, $CDCl_3$) δ = 191.69, 190.69, 134.60, 134.58, 134.54 134.44, 134.40, 134.09, 130.11, 129.77, 129.65, 129.16, 128.87, 128.68, 126.64, 124.48, 73.81, 61.80

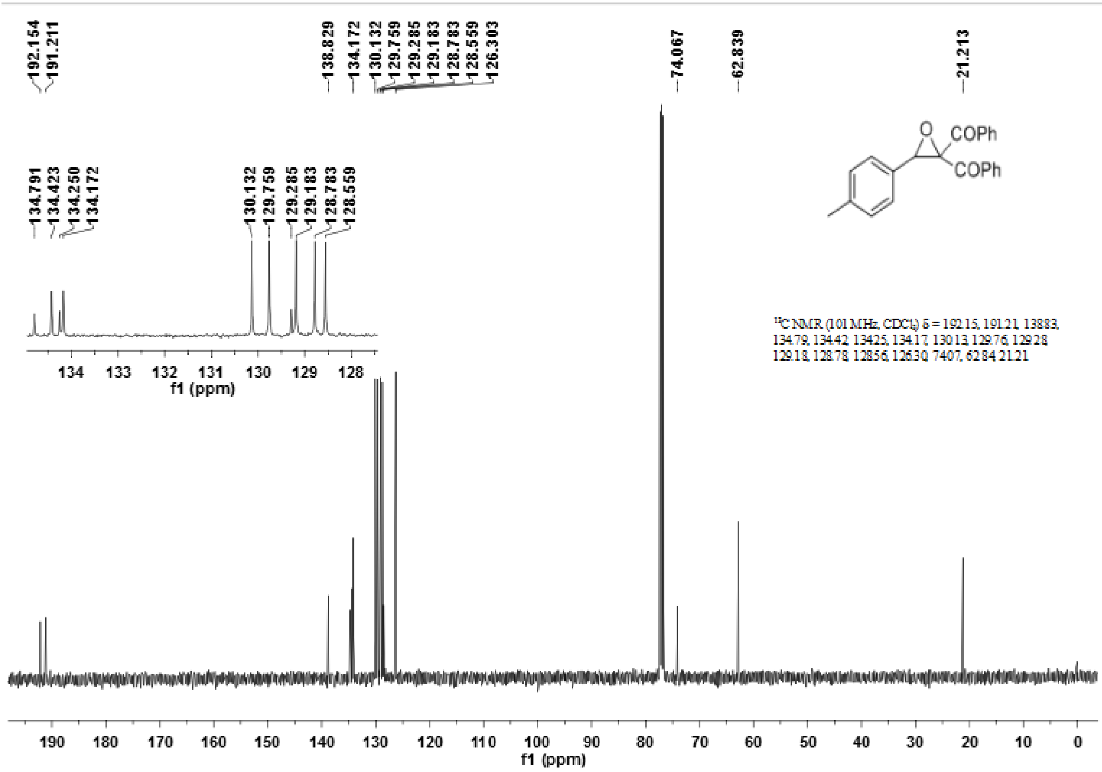


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 - 8.15 (m, 2H), 7.99 - 7.93 (m, 2H), 7.64 - 7.55 (m, 1H), 7.52 - 7.44 (m, 3H), 7.41 - 7.32 (m, 2H), 7.18 – 7.11 (m, 3H), 7.07- 7.01(m, 1H), 4.65(s, 1H), 2.27(s, 3H).

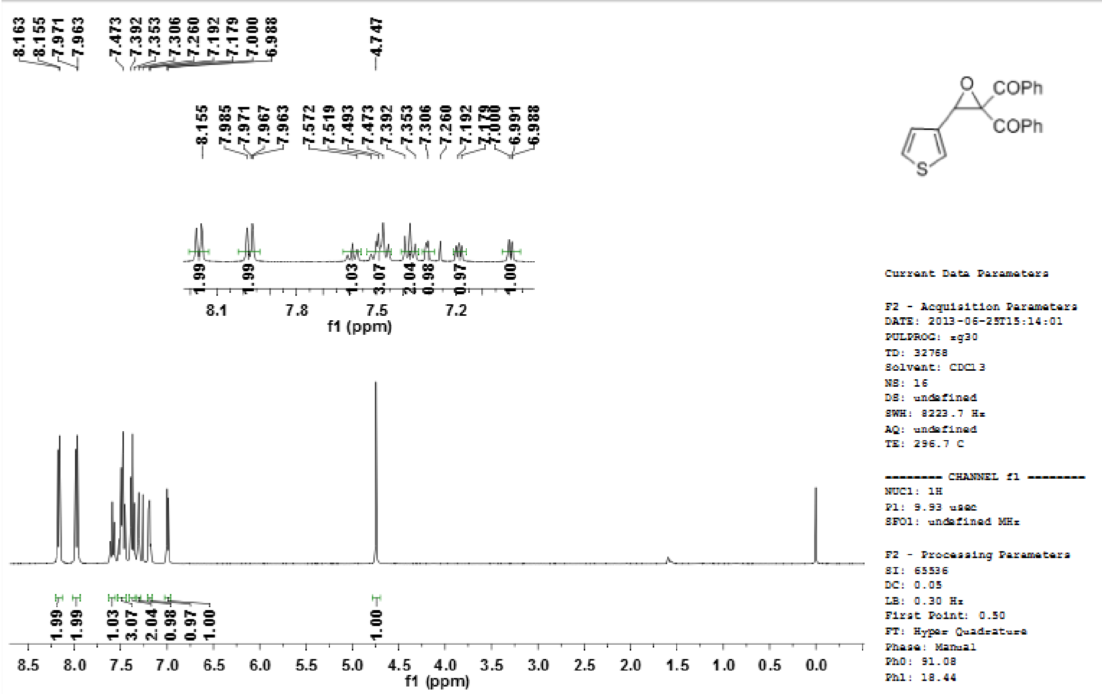




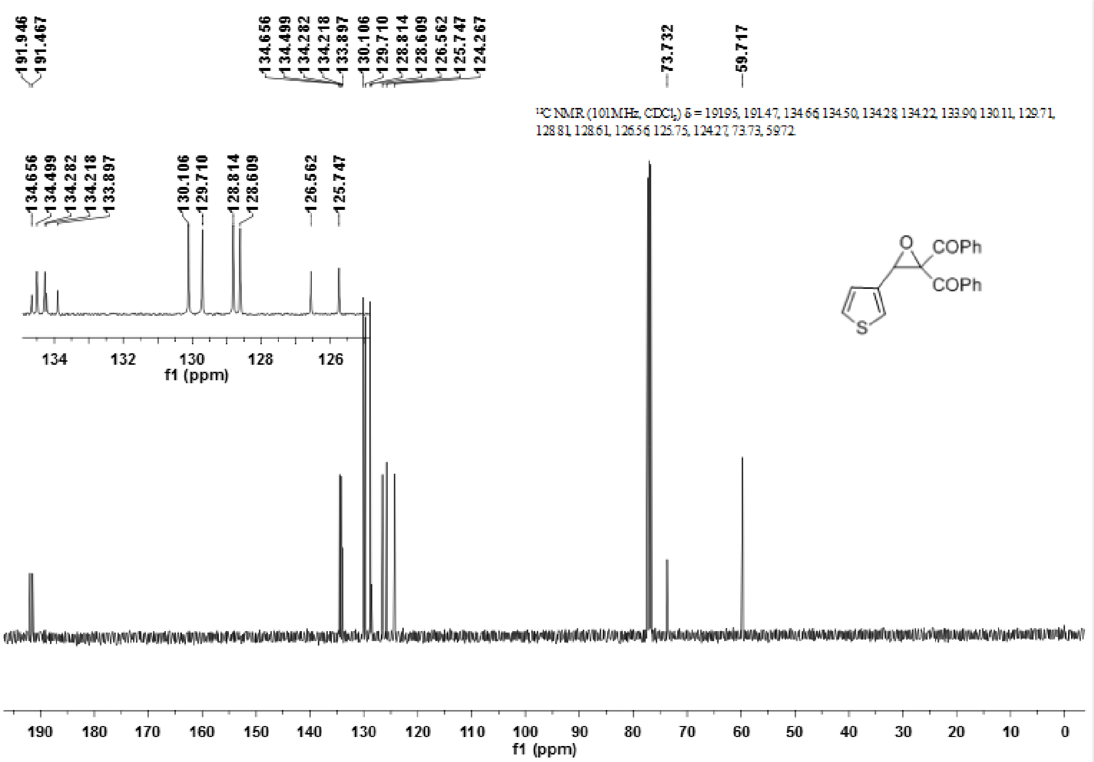
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.21 – 8.15 (m, 2H), 7.99 – 7.93 (m, 2H), 7.62 – 7.56 (m, 1H), 7.51 – 7.45 (m, 3H), 7.36 (t, J = 7.7 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 4.66 (s, 1H), 2.26 (s, 3H).



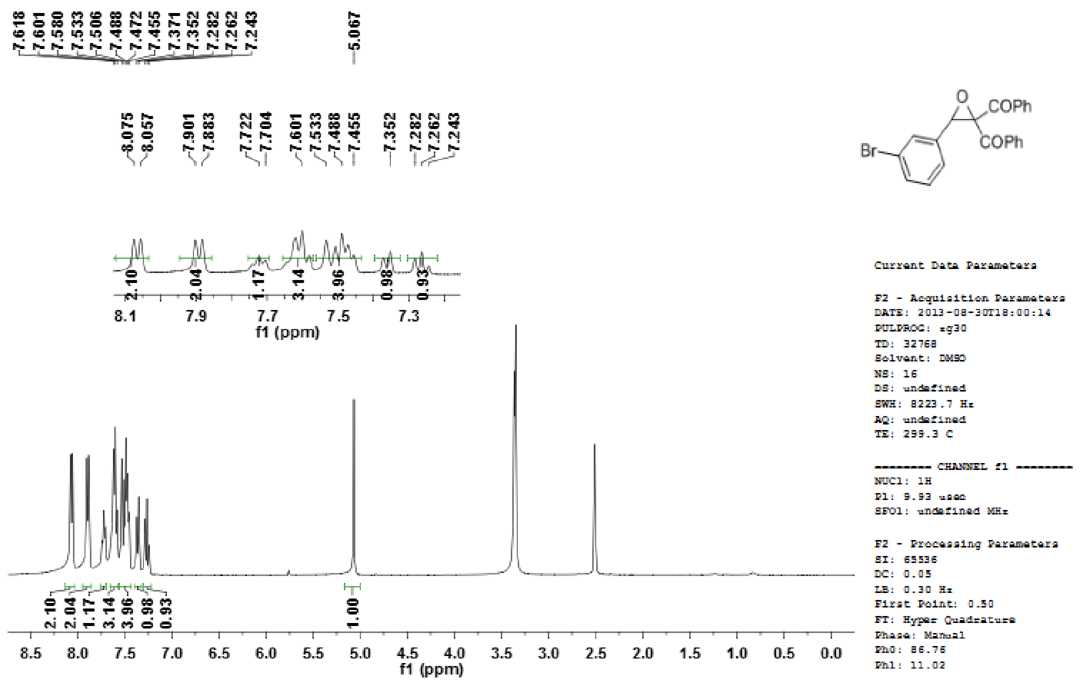
^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.15, 191.21, 138.83, 134.79, 134.42, 134.25, 134.17, 130.13, 129.76, 129.28, 129.18, 128.78, 128.56, 126.30, 74.07, 62.84, 21.21



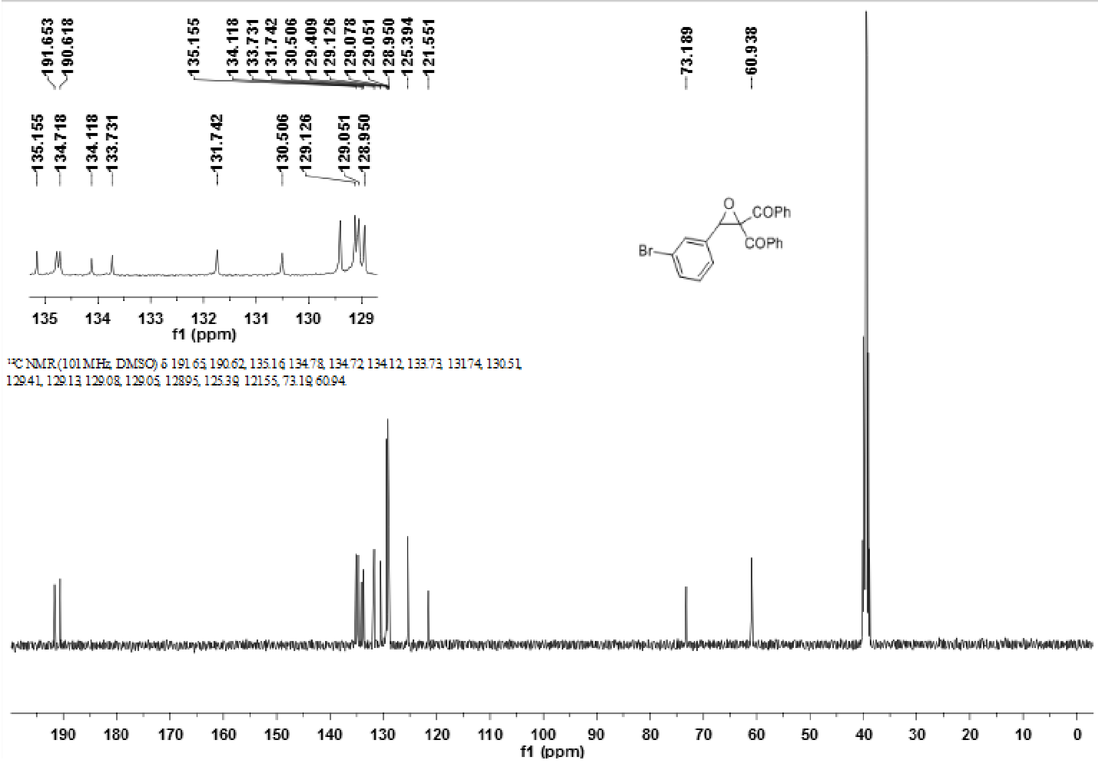
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 - 8.13 (m, 2H), 8.02 - 7.94 (m, 2H), 7.62 - 7.56 (m, 1H), 7.54 - 7.44 (m, 3H), 7.41 - 7.34 (m, 2H), 7.33 – 7.28(m, 1H), 7.21 - 7.16(m, 1H), 7.01 - 6.96(m, 1H), 4.75 (s, 1H).



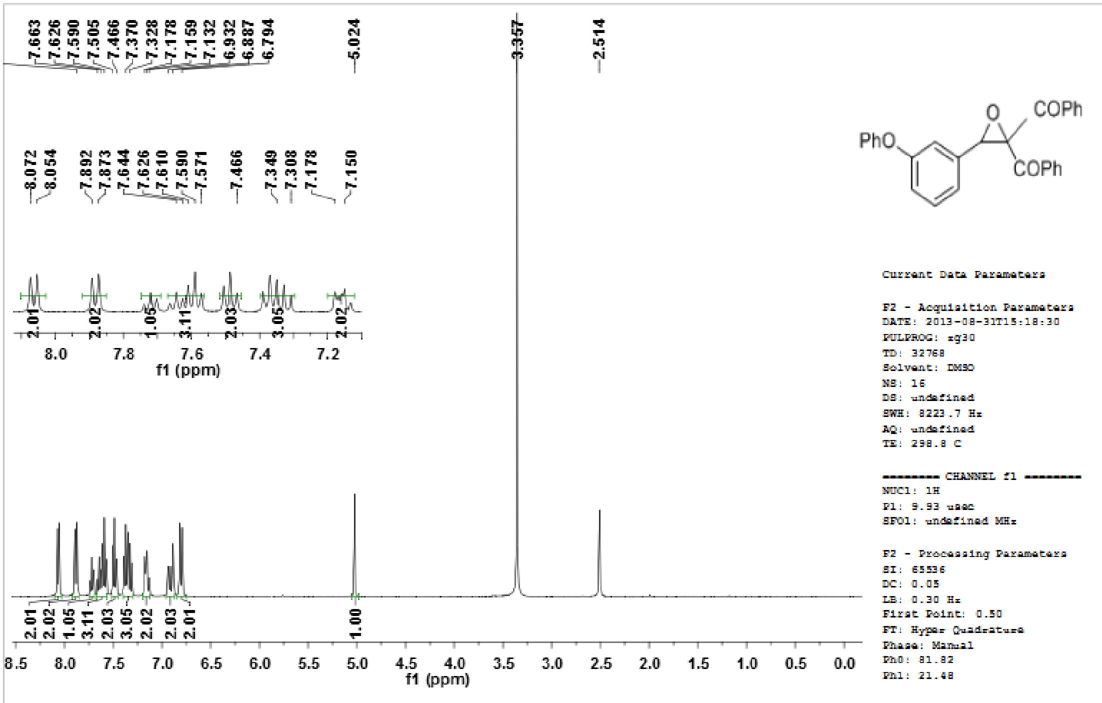
^{13}C NMR (101MHz, $CDCl_3$) δ = 191.95, 191.47, 134.66 134.50, 134.28 134.22 133.90 130.11, 129.71, 128.81 128.61, 126.56 125.75, 124.27, 73.73, 59.72



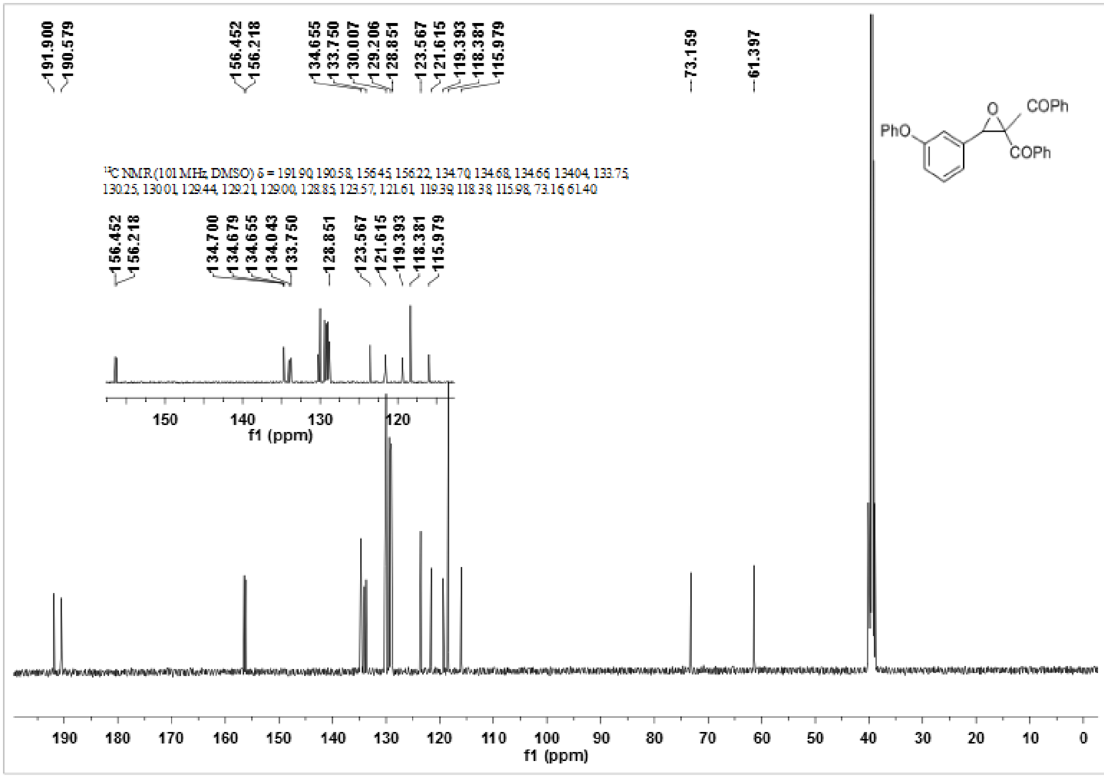
^{1}H NMR (400MHz, DMSO) δ 8.07 (d, J = 7.2 Hz, 2H), 7.89 (d, J = 7.3 Hz, 2H), 7.76 - 7.69 (m, 1H), 7.66 – 7.57 (m, 3H), 7.56 – 7.43 (m, 4H), 7.40 - 7.32 (m, 1H), 7.30 - 7.22 (m, 1H), 5.07 (s, 1H).



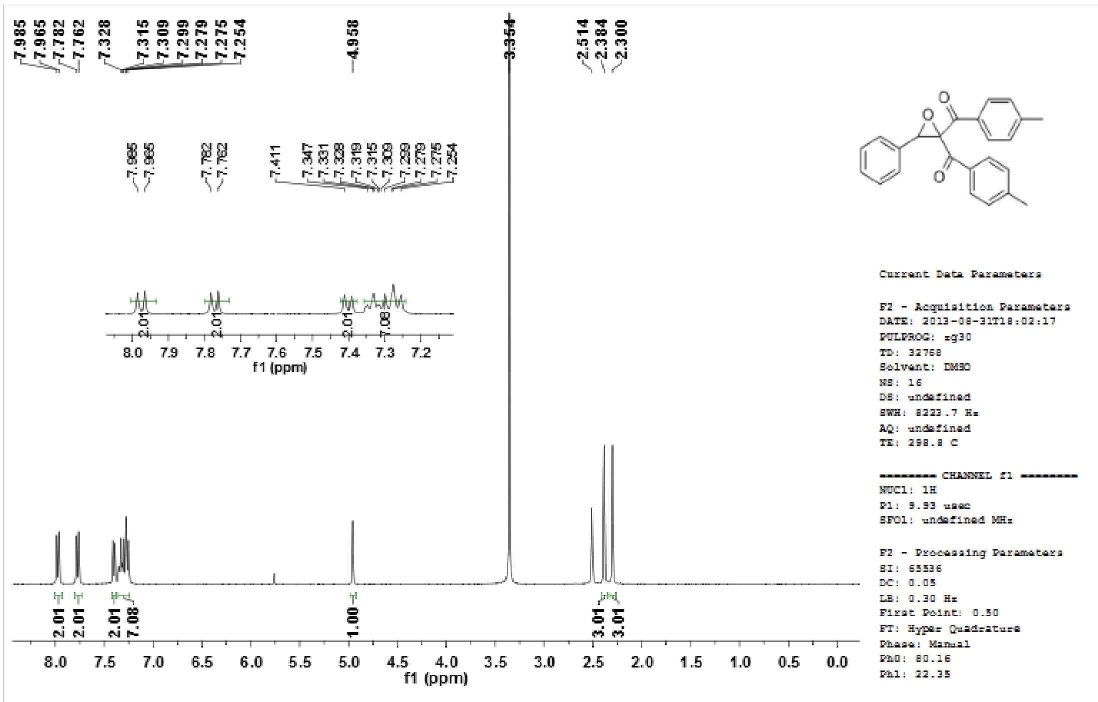
^{13}C NMR (101 MHz, DMSO) δ 191.65, 190.62, 135.16, 134.78, 134.72, 134.12, 133.73, 131.74, 130.51, 129.41, 129.13, 129.08, 129.05, 128.95, 125.39, 121.55, 73.19, 60.94.



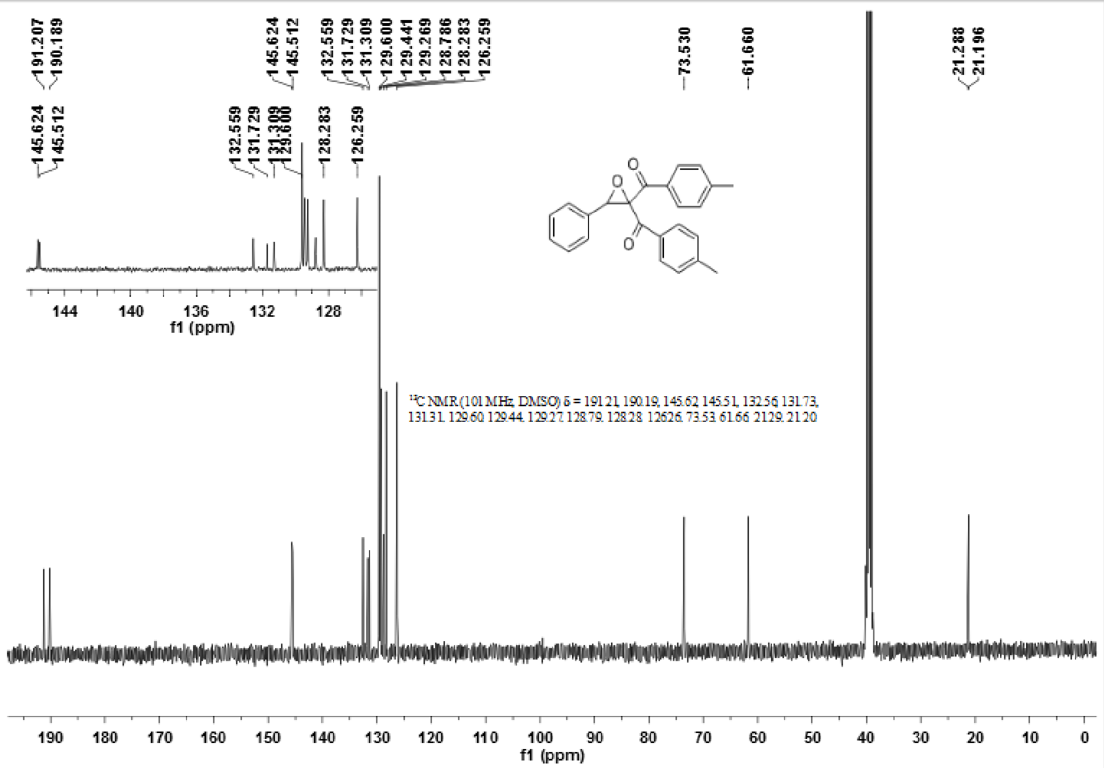
^{1}H NMR (400 MHz, DMSO) δ 8.10- 8.03(m, 2H), 7.92- 7.85(m, 2H), 7.75- 7.69(m, 1H), 7.67- 7.56(m, 3H), 7.52- 7.45 (m, 2H), 7.40 – 7.30 (m, 3H), 7.20 – 7.12 (m, 2H), 6.96- 6.87 (m, 2H), 6.84- 6.75(m, 2H), 5.02(s, 1H).



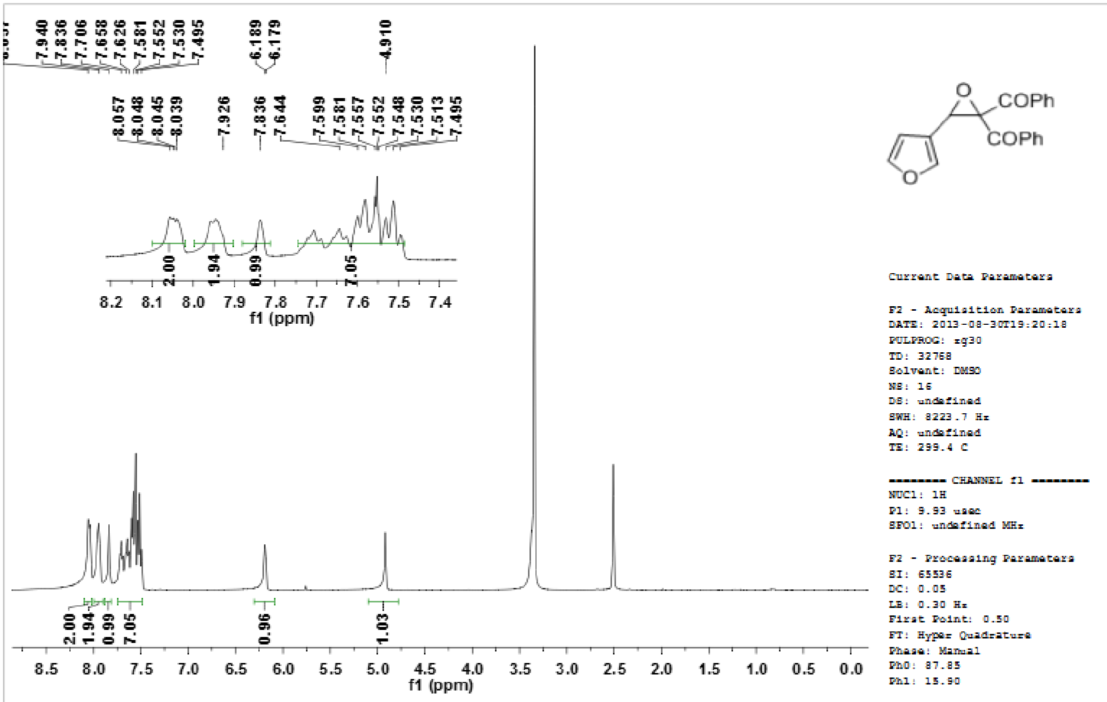
^{13}C NMR (101 MHz, DMSO) δ = 191.90, 190.58, 156.45, 156.22, 134.70, 134.68, 134.66, 134.04, 133.75, 130.25, 130.01, 129.44, 129.21, 129.00, 128.85, 123.57, 121.61, 119.39, 118.38, 115.98, 73.16, 61.40



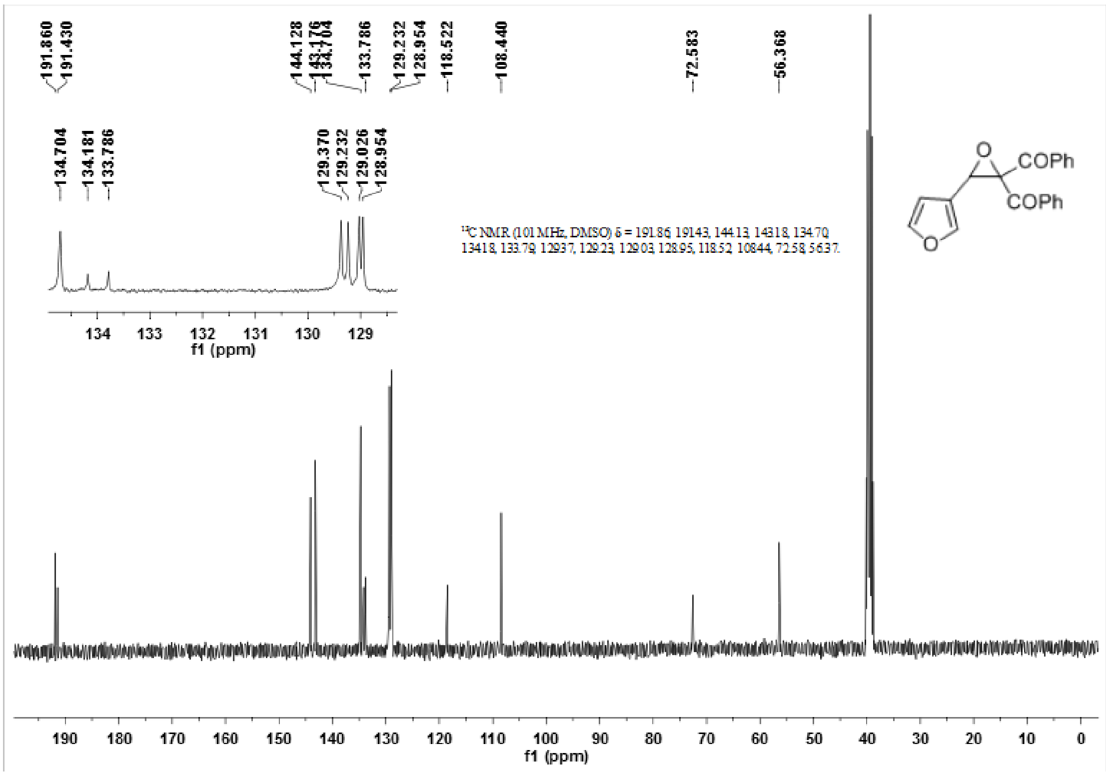
^{1}H NMR (400 MHz, DMSO) δ 8.01 - 7.93 (m, 2H), 7.80 - 7.73 (m, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.36 – 7.24 (m, 7H), 4.96 (s, 1H), 2.38 (s, 3H), 2.30 (s, 3H).



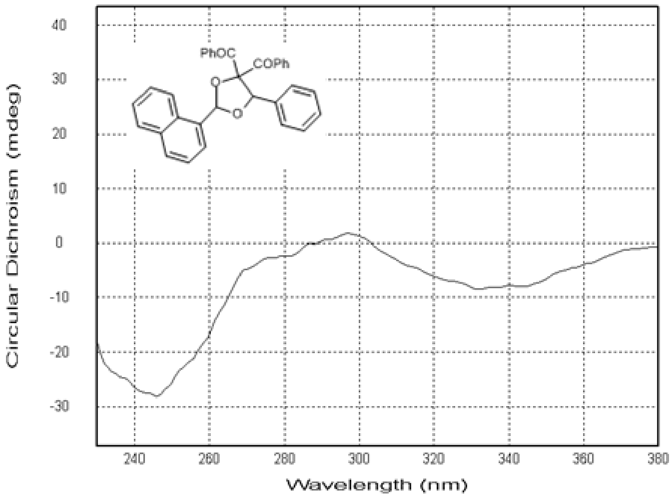
^{13}C NMR (101 MHz, DMSO) δ = 191.21, 190.19, 145.62, 145.51, 132.56, 131.73, 131.31, 129.60, 129.44, 129.27, 128.79, 128.28, 126.26, 73.53, 61.66, 21.29, 21.20

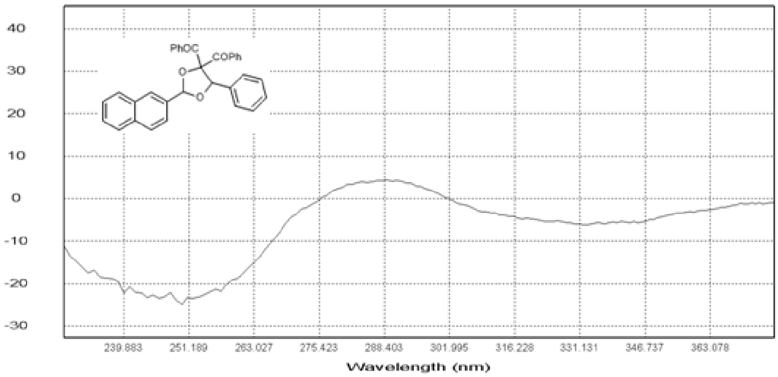


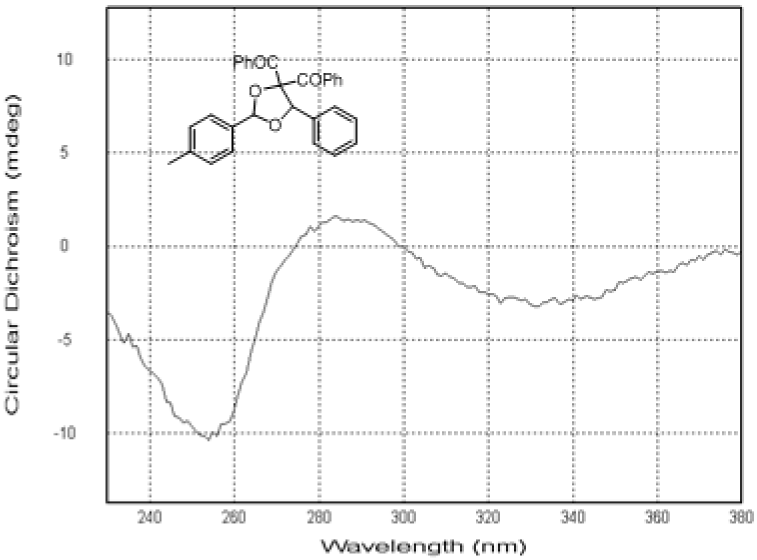
^{1}H NMR (400 MHz, DMSO) δ 8.10- 8.02(m, 2H), 8.00– 7.90(m, 2H), 7.84(s, 1H), 7.74– 7.49(m, 7H), 6.30- 6.09(m, 1H), 4.91(s, 1H).

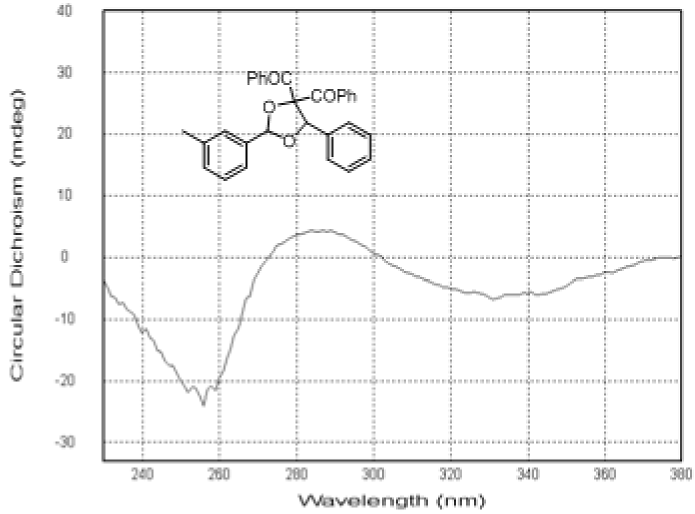

191.860
191.430
144.128
143.176
134.704
133.786
129.232
128.954
118.522
108.440
72.583
56.368
134.704
134.181
133.786
129.370
129.232
129.026
128.954
134 133 132 131 130 129
f1 (ppm)
13C NMR (101 MHz, DMSO) δ = 191.86, 191.43, 144.13, 143.18, 134.70, 134.18, 133.79, 129.37, 129.23, 129.03, 128.95, 118.52, 108.44, 72.58, 56.37.
O
COPh
COPh
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

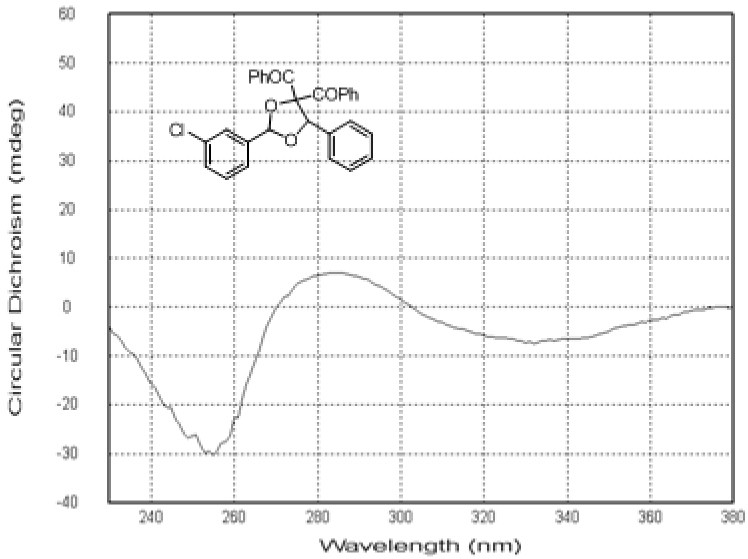
10. Copy of CD spectras for products

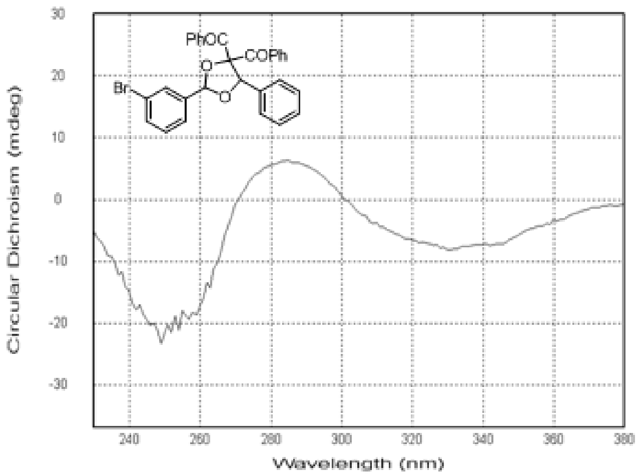


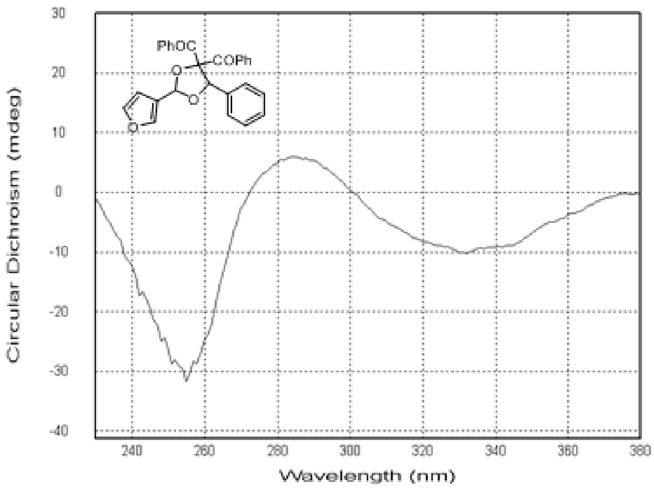


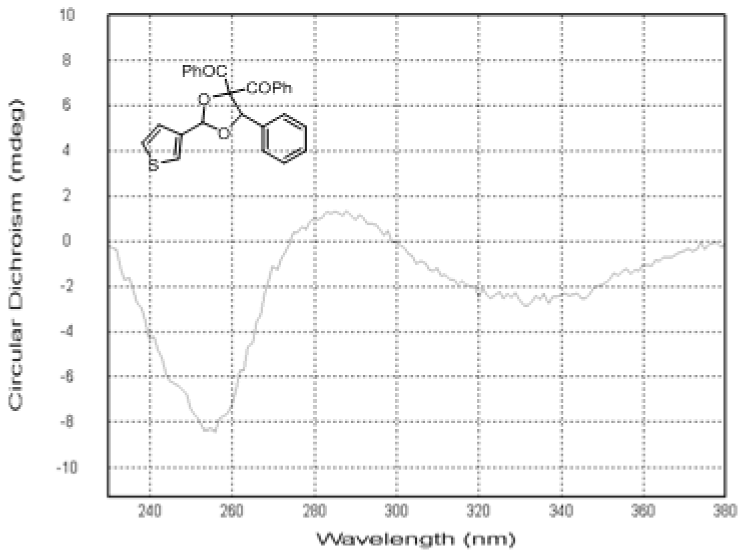


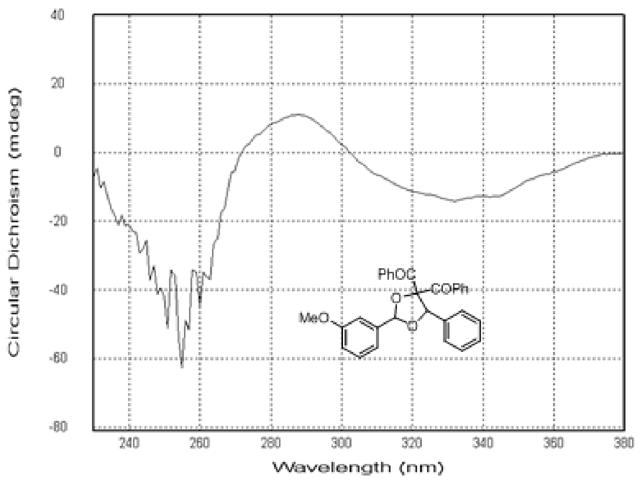

PhOC
COPh
O
O
Circular Dichroism (mdeg)
Wavelength (nm)

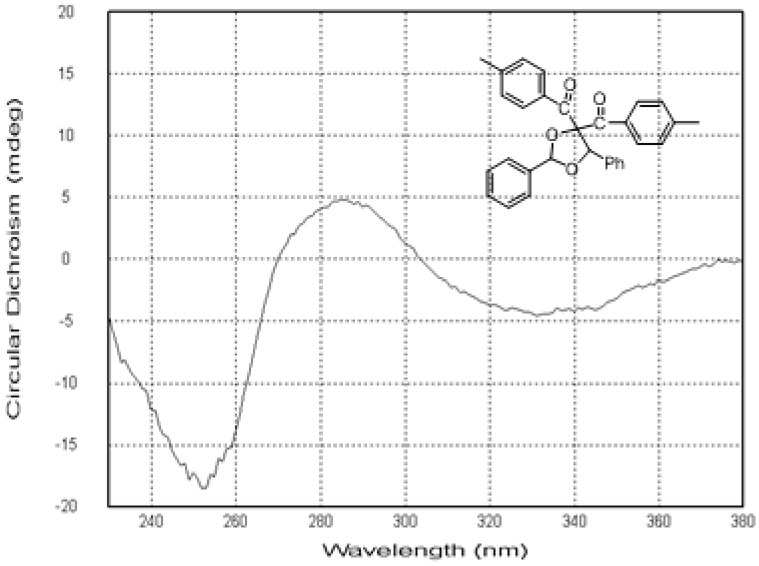

PhOC
COPh
O
O
Cl
Circular Dichroism (mdeg)
Wavelength (nm)

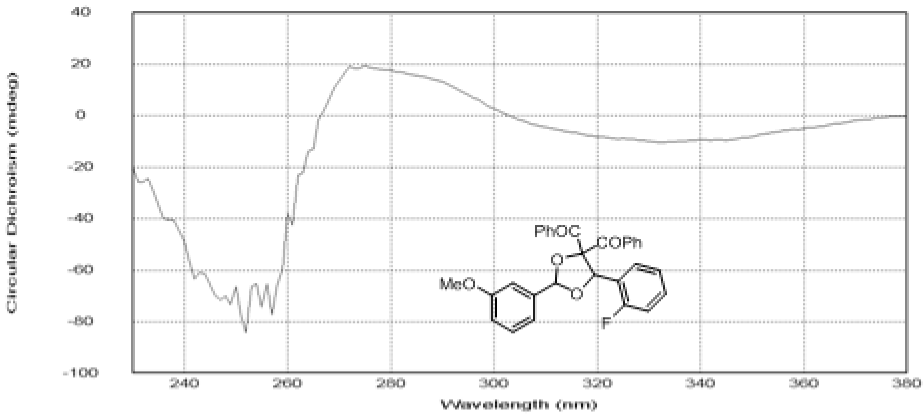

PhOC
COPh
O
O
Br
Circular Dichroism (mdeg)
Wavelength (nm)

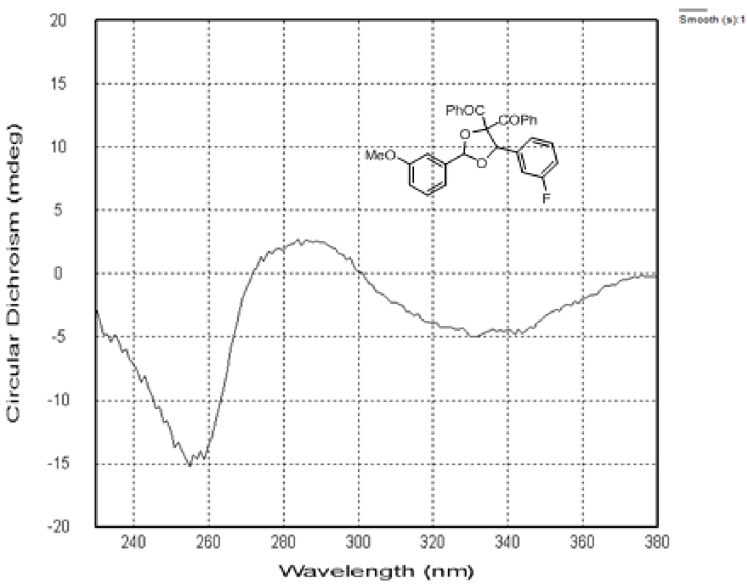

PhOC
COPh
O
O
O
Circular Dichroism (mdeg)
Wavelength (nm)
30
20
10
0
-10
-20
-30
-40
240
260
280
300
320
340
360
380

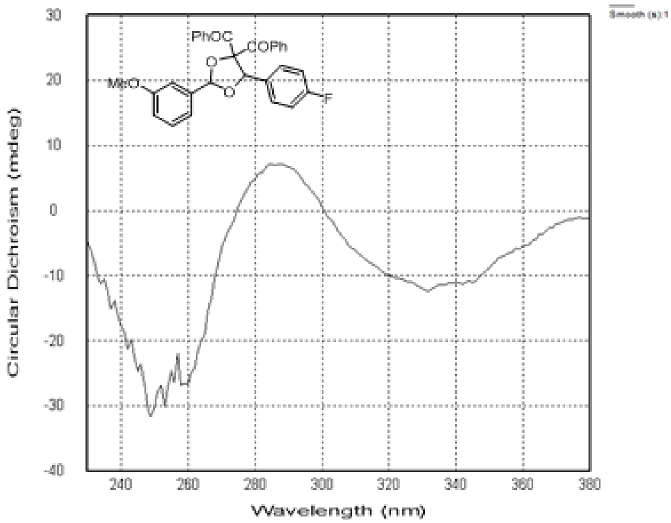

PhOC
COPh
O
O
S
Circular Dichroism (mdeg)
Wavelength (nm)
10
8
6
4
2
0
-2
-4
-6
-8
-10
240
260
280
300
320
340
360
380

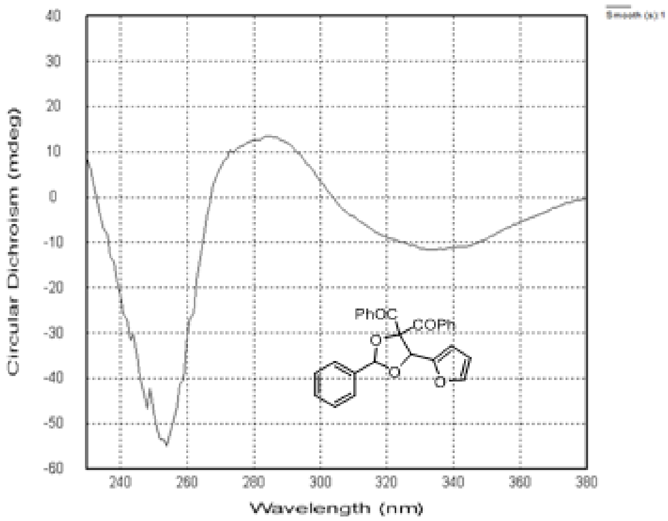

PhOC
COPh
MeO
O
O
Circular Dichroism (mdeg)
Wavelength (nm)
40
20
0
-20
-40
-60
-80
240
260
280
300
320
340
360
380

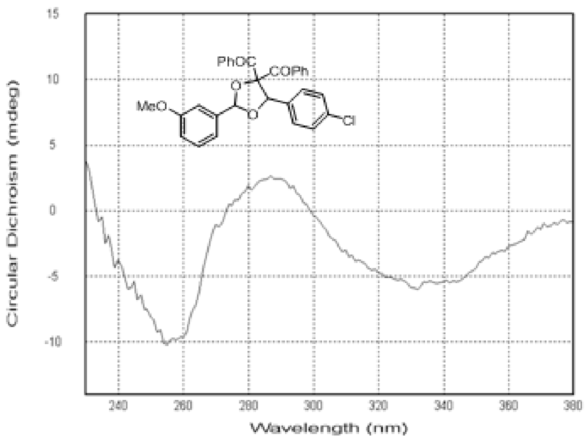

Circular Dichroism (mdeg)
Wavelength (nm)
Ph

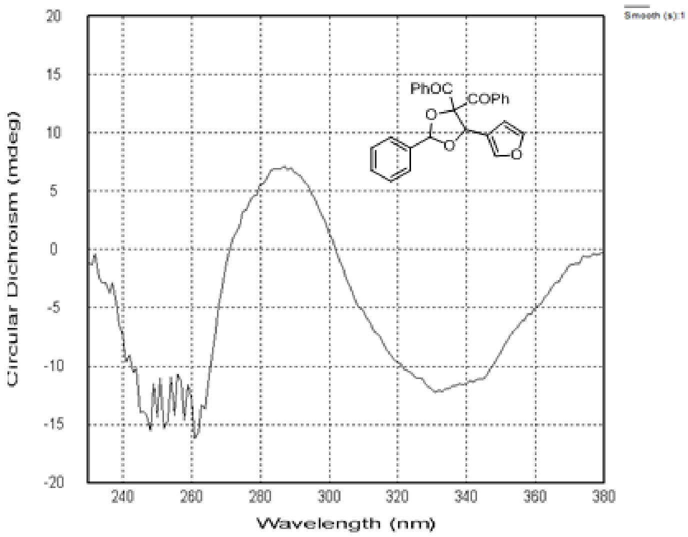

Circular Dichroism (mdeg)
Wavelength (nm)
PhOC
COPh
MeO
F

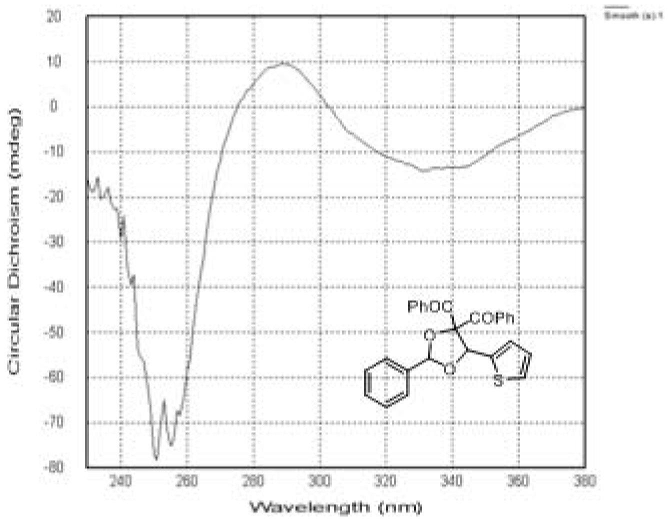

Smooth (s):1
Circular Dichroism (mdeg)
Wavelength (nm)
PhOC
COPh
MeO
F

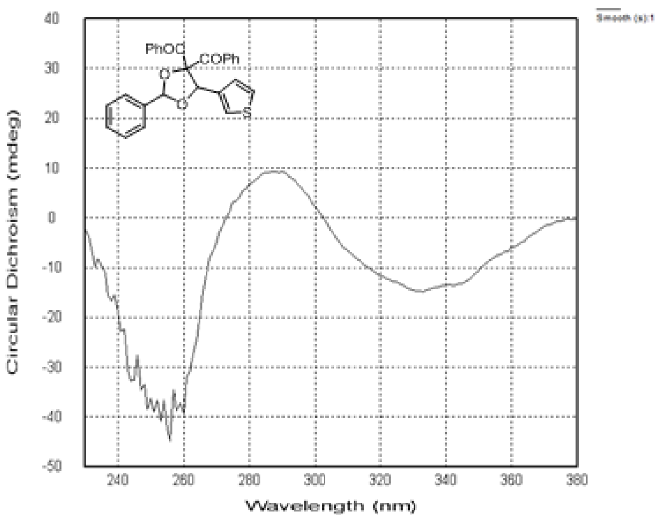

PhOC
COPh
MeO
F
Circular Dichroism (mdeg)
Wavelength (nm)

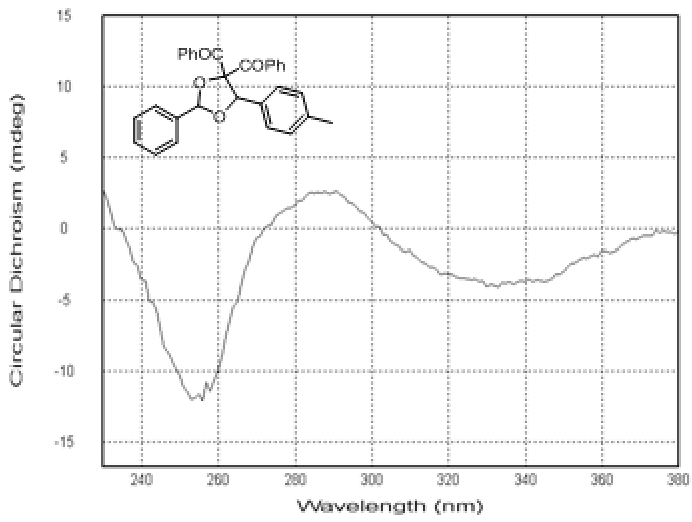

PhOC
COPh
Circular Dichroism (mdeg)
Wavelength (nm)

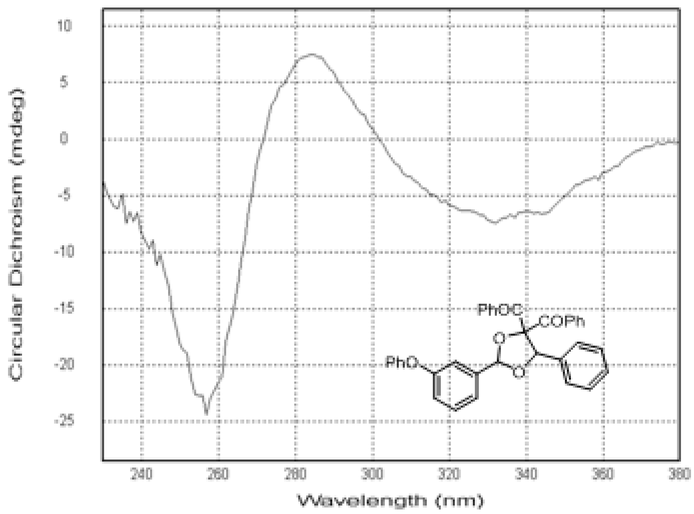

PhOC
COPh
MeO
Cl
Circular Dichroism (mdeg)
Wavelength (nm)

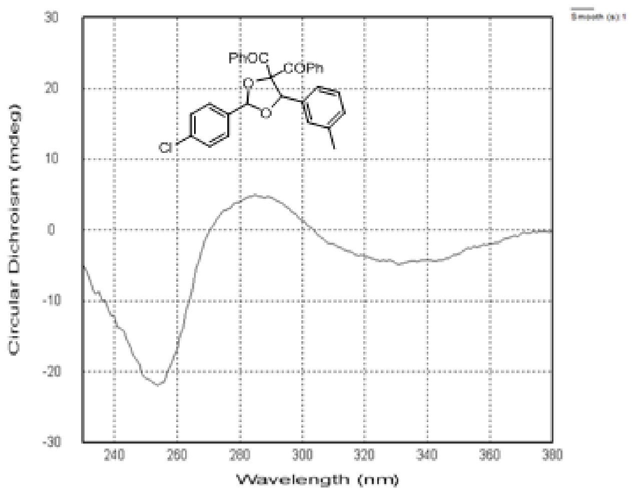

Circular Dichroism (mdeg)
Wavelength (nm)
PhOC
COPh
O
O
O

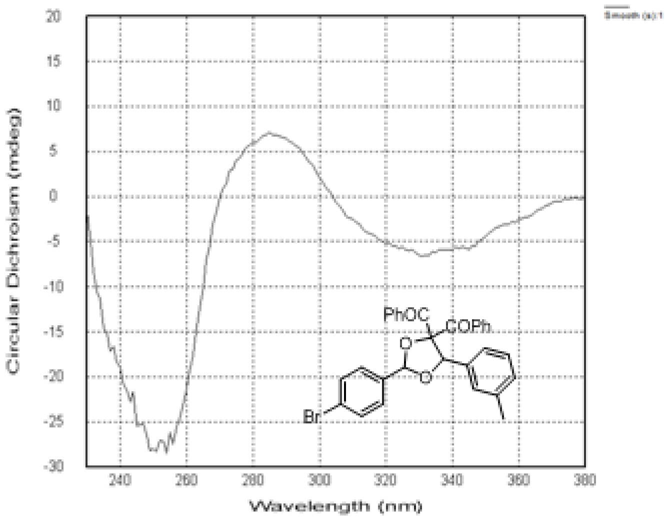

Circular Dichroism (mdeg)
Wavelength (nm)
PhOC
COPh
O
O
S


Circular Dichroism (mdeg)
Wavelength (nm)
PhOC
COPh
O
O
S


PhOC
COPh
O
O
Circular Dichroism (mdeg)
Wavelength (nm)


PhOC
COPh
PhO
O
O
Circular Dichroism (mdeg)
Wavelength (nm)


PhOC
COPh
Cl
O
O
Circular Dichroism (mdeg)
Wavelength (nm)


Smooth (s):1
Circular Dichroism (mdeg)
Wavelength (nm)
PhOC
COPh
O
O
Br