**Electronic Supplementary Information**

# The Enantioselective Construction of γ-substituted *anti*-Butenolides via The Vinylogous Makaiyama-Michael Reaction Catalyzed by Chiral Scandium(III)-*N*,*N*′-Dioxide Complex

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**Contents:**



**1. General remarks:** $^{1}$H NMR spectra were recorded on commercial instruments (400 MHz or 600 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Spectra are 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 or 150 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). The enantiomeric excess was determined by HPLC analysis on commercial chiral columns. Optical rotations were measured on a commercial polarimeter and reported as follows: $[\alpha]^{T}_{D}$ (c = g/100 mL, solvent). HR-ESIMS spectra were recorded using a commercial apparatus and methanol or acetonitrile was used to dissolve the sample. Unless otherwise indicated, reagents obtained from commercial sources were used without further purification. Solvents were dried and distilled prior to use

according to the standard methods. The *N*,*N*′-dioxide ligands was prepared according to the previous reports.[1] TBSOF **1**, 2-(tert-butyldimethylsilyloxy)furan, was prepared according to reported procedures[2] and immediately used due to its unstability.

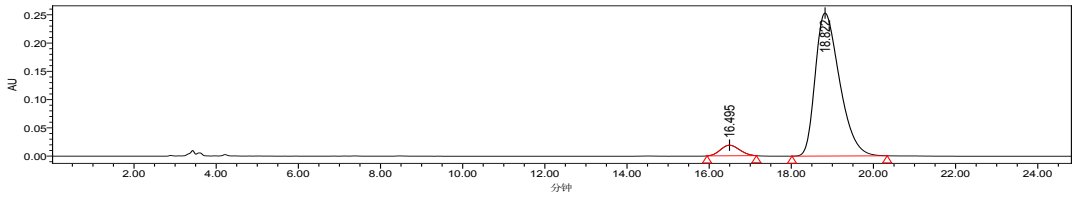
**2. Typical experimental procedure for racemic vinylogous Mukaiyama-Michael product:** TBSOF **1** (0.25 mmol, 60 μL) was added to a dry reaction tube containing $Sc(OTf)_3$ (0.005 mmol, 2.5 mg), chalcone **2a** (0.1 mmol, 20.8 mg), ethyl propionate (0.3 mL) at room temperature under air. After complete consumption of starting materials, the mixture was direct purified by column chromatography on silica gel (ethyl acetate/petroleum ether 1/5 - 1/3).

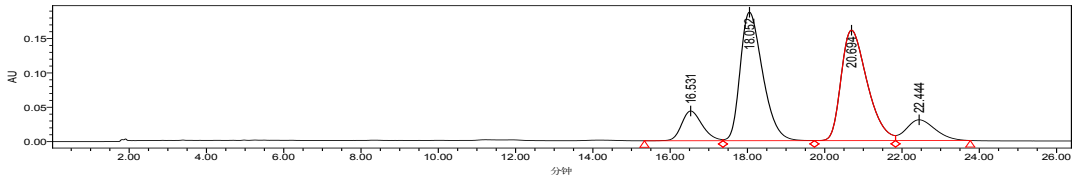
**3. Typical experimental procedure for catalytic VMMR**: *N*,*N*′-dioxide **L3** (0.005 mmol, 2.9 mg), $Sc(OTf)_3$ (0.005 mmol, 2.5 mg), chalcone **2a** (0.1 mmol, 20.8 mg), *t*-BuOH (0.15 mL) and ethyl propionate (0.15 mL) were stirred in a dry reaction tube under air at 30 °C for 0.5 h. Subsequently, TBSOF **1** (0.25 mmol, 60 μL) was added under 0 °C. The reaction was stirred at 0 °C and monitored by TLC. After complete consumption of starting materials, the mixture was direct purified by column chromatography on silica gel (ethyl acetate/petroleum ether 1/5 - 1/3).

**4. Characterization of the products:**

**5-(3-oxo-1,3-diphenylpropyl)furan-2(5H)-one (3a)**

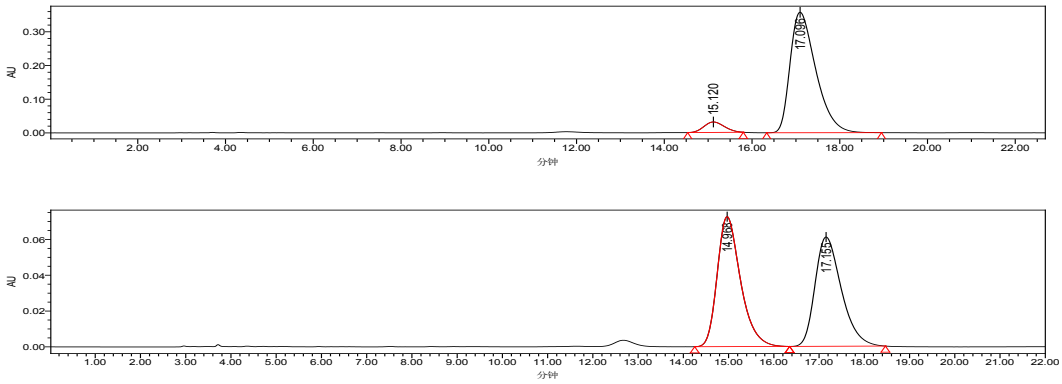
This is a known compound.[3] After 3 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white solid in 99% yield, as a mixture of diastereomers (90% ee, >99:1 dr; >99% ee was obtained after a single recrystallization in ethyl acetate/petroleum ether). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (major) = 16.495 min, $t_r$ (minor) = 18.822 min] and $^1$H NMR spectroscopy. m.p. 99-102 °C. $[\alpha]_D^{25}$ = -75.5° (c = 0.58 in $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.88 (d, *J*=7.5, 2H), 7.55 (t, *J*=7.4, 1H), 7.43 (t, *J*=7.7, 2H), 7.36-7.25 (m, 6H), 5.27 (dd, *J*=7.3, 1.4, 1H), 3.70 (td, *J*=7.7, 5.0, 1H), 3.58 (dd, *J*=17.7, 5.0, 1H), 3.48 (dd, *J*=17.7, 8.2, 1H) ppm.





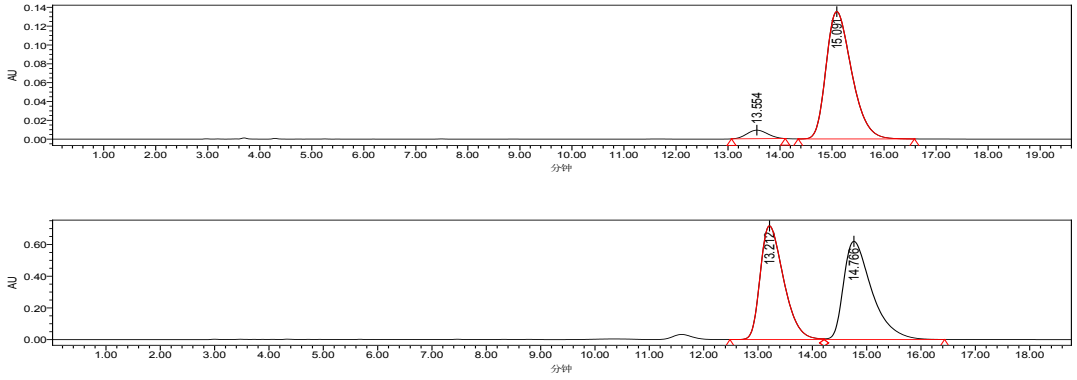

**5-(3-oxo-3-phenyl-1-(p-tolyl)propyl)furan-2(5H)-one (3b)**

After 3 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white solid in 99% yield, as a mixture of diastereomers (87% ee, >99:1 dr, 93 % ee was obtained after a single recrystallization in ethyl acetate/petroleum ether). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min: $t_r$ (minor) = 15.120 min, $t_r$ (major) = 17.096 min] and $^1$H NMR spectroscopy. m.p. 95-98 $^o$C. $[\alpha]_D^{25}$ = -63.6$^o$ (c = 0.61 in $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.07 (dd, *J* = 5.7, 1.7 Hz, 1H), 5.24 (d, *J* = 7.5 Hz, 1H), 3.64 (td, *J* = 7.9, 5.0 Hz, 1H), 3.56 (dd, *J* = 17.5, 4.8 Hz, 1H), 3.47 (dd, *J* = 17.5, 8.4 Hz, 1H), 2.31 (s, 3H) ppm. $^{13}$C NMR (150 MHz, $CDCl_3$) δ = 197.5, 172.8, 155.7, 137.4, 136.6, 136.5, 133.3, 129.6, 128.7, 128.0, 121.9, 85.98, 44.1, 40.3, 21.1 ppm. ESI-HRMS Calcd for ($C_{20}H_{18}O_3$ + $Na^+$): 329.1154, Found: 329.1152.



**5-(3-oxo-3-phenyl-1-(m-tolyl)propyl)furan-2(5H)-one (3c)**

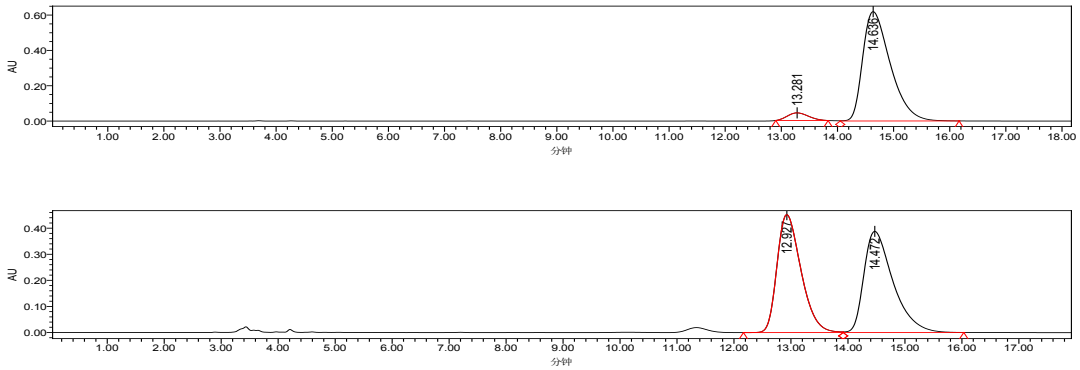
After 3 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white oil in 97% yield, as a mixture of diastereomers (90% ee, >99:1 dr). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 13.554 min , $t_r$ (major) = 15.091 min] and $^1$H NMR spectroscopy. $[\alpha]_D^{25}$ = -58.5$^o$ (c = 0.61 in $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.17 – 7.11 (m, 2H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.07 (dd, *J* = 5.7, 1.8 Hz, 1H), 5.25 (d, *J* = 7.4 Hz, 1H), 3.65 (td, *J* = 7.8, 5.1 Hz, 1H), 3.56 (dd, *J* = 17.6, 4.9 Hz, 1H), 3.47 (dd, *J* = 17.6, 8.2 Hz, 1H), 2.33 (s, 3H) ppm. $^{13}$C NMR (150 MHz, $CDCl_3$) δ = 197.4,172.8, 155.8, 139.6 , 138.6, 136.6, 133.3, 129.0,128.8, 128.7, 128.5, 128.0, 125.1, 121.9, 85.9, 63.7, 44.4, 40.2, 21.5 ppm. ESI-HRMS Calcd for ($C_{20}H_{18}O_3$ + $K^+$): 345.0893, Found: 345.0898.




**5-(3-oxo-3-phenyl-1-(o-tolyl)propyl)furan-2(5H)-one (3d)**

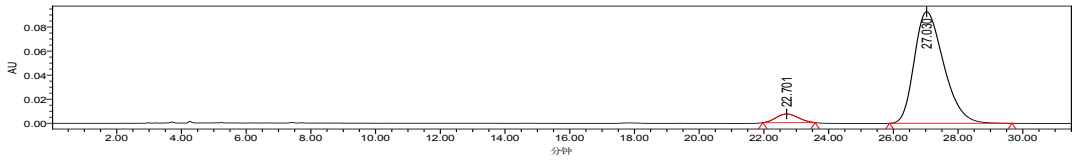
After 2.5 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white oil in 99% yield, as a mixture of diastereomers (90% ee, >99:1 dr). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min;

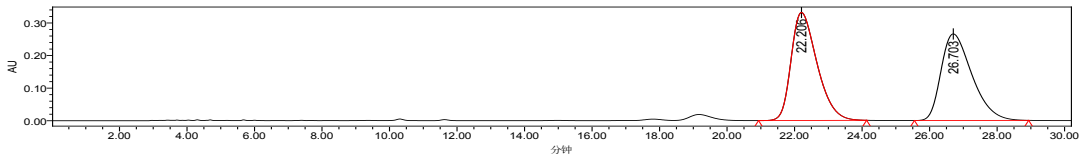
$t_r$ (minor) = 13.281 min, $t_r$ (major) = 14.636 min] and $^1$H NMR spectroscopy. $[\alpha]_D^{25}$ = 60.7$^o$ (c = 0.61 in $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.26 (m, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.16 – 7.10 (m, 2H), 7.07 (d, *J* = 7.5 Hz,1H), 6.07 (dd, *J* = 5.7, 1.9 Hz, 1H), 5.25 (d, *J* = 7.4 Hz, 1H), 3.65 (td, *J* = 7.8, 5.0 Hz, 1H), 3.56 (dd, *J* = 17.6, 4.9 Hz, 1H), 3.47 (dd, *J* = 17.6, 8.2 Hz, 1H), 2.33 (s, 3H) ppm. $^{13}$C NMR (150 MHz, $CDCl_3$) δ = 197.4 , 172.8, 155.8, 139.6, 138.66, 136.7, 133.4, 128.9, 128.8, 128.7, 128.5, 128.0, 125.1, 121.9, 85.9, 63.7, 44.4, 40.2, 21.5 ppm. ESI-HRMS Calcd for ($C_{20}H_{18}O_3$ + $H^+$): 307.1334 Found: 307.1339.




**5-(1-(4-methoxyphenyl)-3-oxo-3-phenylpropyl)furan-2(5H)-one (3e)**

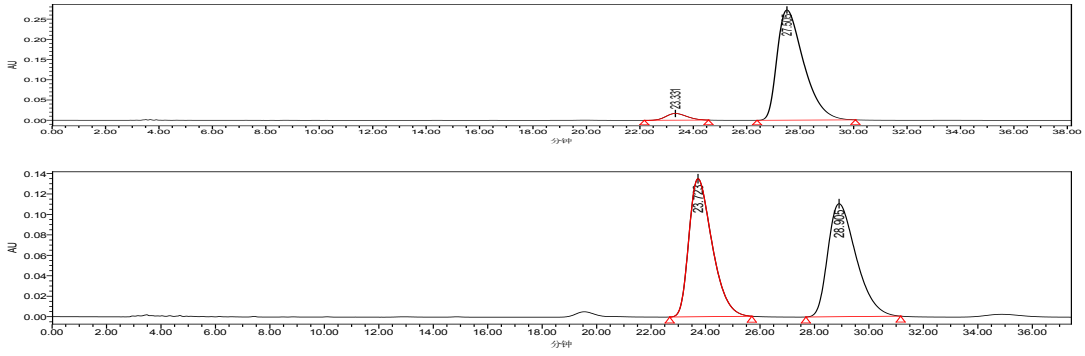
After 6 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white oil in 98% yield, as a mixture of diastereomers (90% ee, >99:1 dr). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 22.701 min, $t_r$ (major) = 27.030 min] and $^1$H NMR spectroscopy. $[\alpha]_D^{25}$ = 55.2$^o$ (c = 0.63 in $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) δ = 7.88 (d, *J*=7.5, 2H), 7.54 (t, *J*=7.4, 1H), 7.43 (t, *J*=7.7, 2H), 7.30-7.22 (m, 3H), 6.86 (d, *J*=8.6, 2H), 6.08 (dd, *J*=5.7, 1.8, 1H), 5.23 (d, *J*=7.5, 1H), 3.77 (s, 3H), 3.64 (td, *J*=7.9, 4.9, 1H), 3.54 (dd, *J*=17.5, 4.9, 1H), 3.45 (dd, *J*=17.5, 8.4, 1H) ppm. $^{13}$C NMR (150 MHz, $CDCl_3$) δ = 197.5, 172.8, 158.9, 155.7, 136.6, 133.3, 131.5, 129.2, 128.7, 128, 121.9, 114.3, 86.1, 63.7, 55.3, 43.7, 40.4 ppm. ESI-HRMS Calcd for ($C_{20}H_{18}O_4$ + $Na^+$): 345.1097 Found: 345.1103.





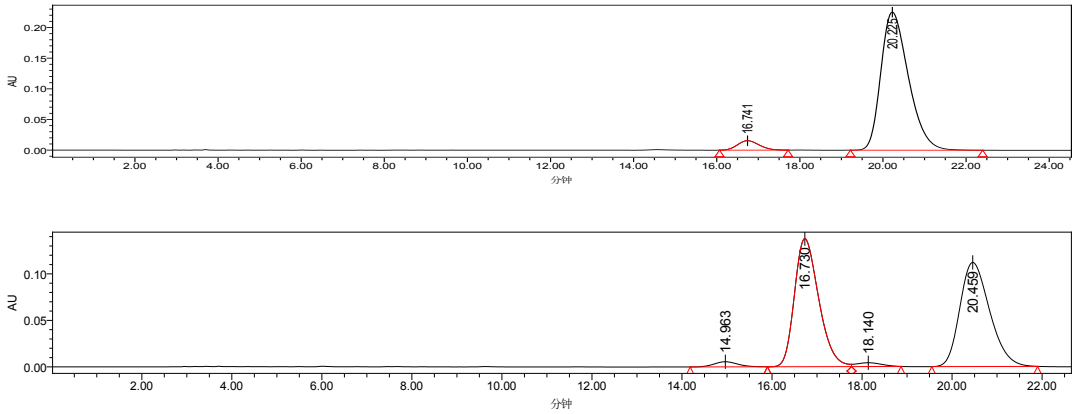

**5-(1-(3-methoxyphenyl)-3-oxo-3-phenylpropyl)furan-2(5H)-one (3f)**

After 3 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white oil in 99% yield, as a mixture of diastereomers (91% ee, >99:1 dr). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 1*n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 23.33 min, $t_r$ (major) = 27.050 min] and $^1$H NMR spectroscopy. $[\alpha]_D^{25}$ = -59.5$^o$ (c = 0.64 in $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.89 (d, *J*=7.7, 2H), 7.55 (t, *J*=7.4, 1H), 7.43 (t, *J*=7.7, 2H), 7.33 – 7.17 (m, 2H), 6.93 (d, *J*=7.7, 1H), 6.87 (s, 1H), 6.80 (dd, *J*=8.2, 2.3, 1H), 6.08 (dd, *J*=5.7, 1.7, 1H), 5.25 (d, *J*=7.4, 1H), 3.79 (s, 3H), 3.66 (td, *J*=7.8, 5.0, 1H), 3.57 (dd, *J*=17.6, 4.9, 1H), 3.48 (dd, *J*=17.6, 8.2, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 197.3, 172.7, 159.9, 155.6, 141.2, 136.6, 133.3, 130.0, 128.7, 128.0, 121.9, 120.3, 114.3, 112.7, 85.7, 63.7, 55.3, 44.5, 40.2 ppm. ESI-HRMS Calcd for ($C_{20}H_{18}O_4$ + $K^+$): 361.0842 Found: 361.0849.



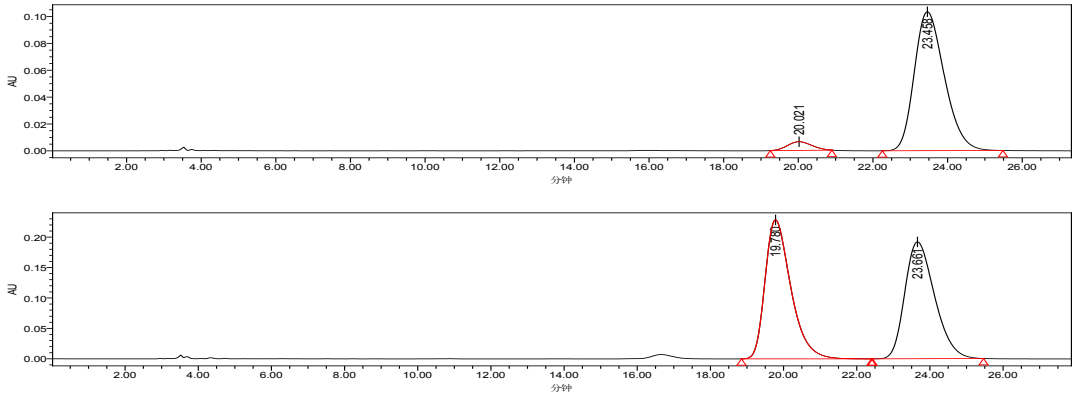

**5-(1-(4-fluorophenyl)-3-oxo-3-phenylpropyl)furan-2(5H)-one (3g)**

After 3 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white solid in 98% yield, as a mixture of diastereomers (90% ee, >99:1 dr; >99 % ee was obtained after a single recrystallization in ethyl acetate/petroleum ether). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 16.741 min, $t_r$ (major) = 20.225 min] and $^1$H NMR spectroscopy. m.p. 102-105 $^o$C. $[\alpha]_D^{25}$ = -55.7$^o$ (c = 0.61 in $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) δ = 7.88 (d, *J*=7.6, 2H), 7.55 (t, *J*=7.4, 1H), 7.44 (t, *J*=7.7, 2H), 7.38 – 7.25 (m, 3H), 7.02 (t, *J*=8.6, 2H), 6.10 (dd, *J*=5.7, 1.7, 1H), 5.25 (d, *J*=6.9, 1H), 3.74-3.71 (m, 1H), 3.51 (dd, *J*=17.7, 5.0, 1H), 3.43 (dd, *J*=17.7, 8.2, 1H) ppm. $^{13}$C NMR (150 MHz, $CDCl_3$) δ = 197.2, 172.6, 162.1, 155.3, 136.5, 135.5, 133.5, 129.8, 128.7, 128.0, 122.2, 115.8, 85.7, 63.7, 43.5, 39.9 ppm. ESI-HRMS Calcd for ($C_{19}H_{15}FO_3 + H^+$): 333.0902 Found: 333.0903.



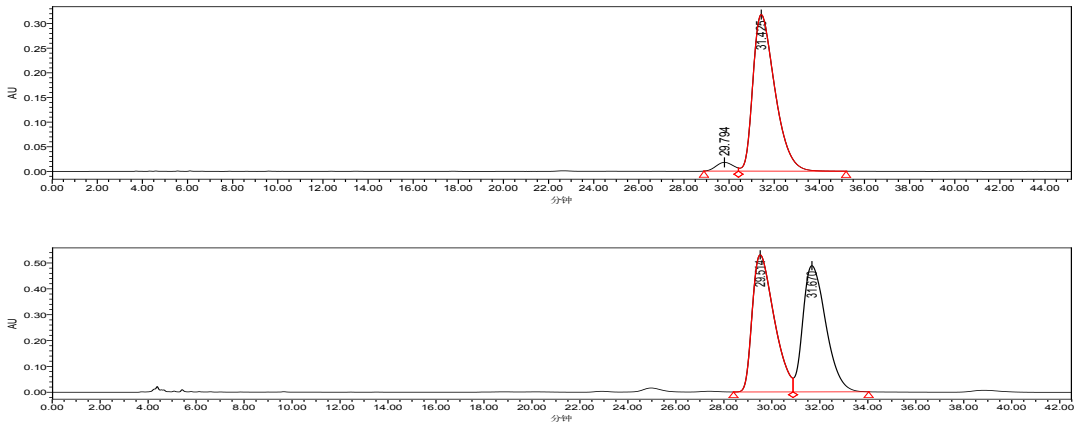

**5-(1-(4-chlorophenyl)-3-oxo-3-phenylpropyl)furan-2(5H)-one (3h)**

This is a known compound.[3a] After 3 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white solid in 92% yield, as a mixture of diastereomers (90% ee, >99:1 dr; >99 % ee was obtained after a single recrystallization in ethyl acetate/petroleum ether). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 20.021 min, $t_r$ (major) = 23.458 min] and $^1$H NMR spectroscopy. m.p. 111-113 $^o$C. $[\alpha]_D^{25}$ = -64.7$^o$ (c = 0.60 in $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.80 (d, *J*=7.6, 2H), 7.48 (t, *J*=7.4, 1H), 7.36 (t, *J*=7.6, 1H), 7.23 (s, 5H), 6.02 (dd, *J*=5.6, 1.5, 1H), 5.17 (d, *J*=6.7, 1H), 3.70 – 3.58 (m, 1H), 3.44 (dd, *J*=17.8, 5.0, 1H), 3.35 (dd, *J*=17.8, 8.2, 1H) ppm.



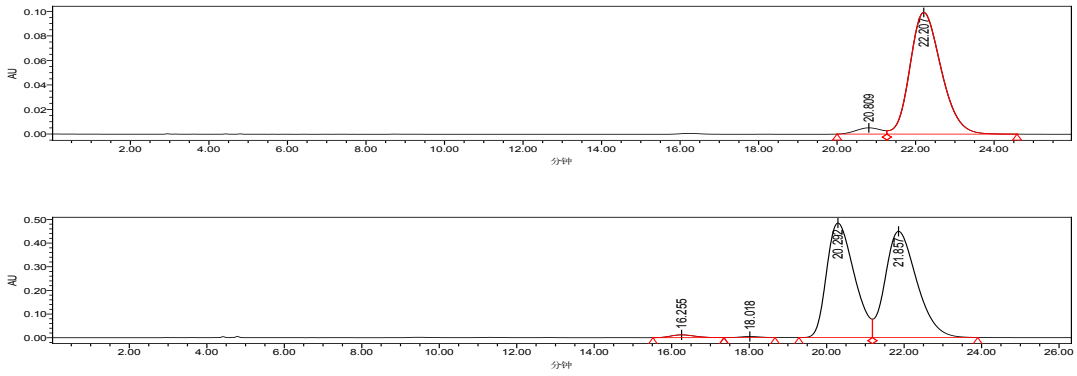

**5-(1-(3-chlorophenyl)-3-oxo-3-phenylpropyl)furan-2(5H)-one (3i)**

After 8 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white oil in 95% yield, as a mixture of diastereomers (92% ee, >99:1 dr).The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 85:15 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 29.794 min, $t_r$ (major) = 31.425 min] and $^1$H NMR spectroscopy. $[\alpha]_D^{25}$ = -52.3$^o$ (c = 0.62 in $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) δ = 7.89 (d, *J*=7.7, 2H), 7.56 (t, *J*=7.4, 1H), 7.44 (t, *J*=7.7, 2H), 7.36 (s, 1H), 7.31 (d, *J*=5.7, 1H), 7.30 – 7.22 (m, 3H), 6.11 (dd, *J*=5.7, 1.7, 1H), 5.26 (d, *J*=6.7, 1H),3.74-3.73 (m, 1H), 3.52 (dd, *J*=17.9, 5.0, 1H), 3.43 (dd, *J*=17.9, 8.0, 1H) ppm. $^{13}$C NMR (150 MHz, $CDCl_3$) δ = 197.0, 172.5, 155.3, 141.9, 136.4, 134.7, 133.5, 130.2, 128.7, 128.3, 128.0, 127.9, 126.6, 122.3, 85.4, 63.7, 43.8, 39.6 ppm. ESI-HRMS Calcd for ($C_{19}H_{15}ClO_3$ + $Na^+$): 349.0606 Found: 349.0607.



**5-(1-(3,4-dichlorophenyl)-3-oxo-3-phenylpropyl)furan-2(5H)-one (3j)**

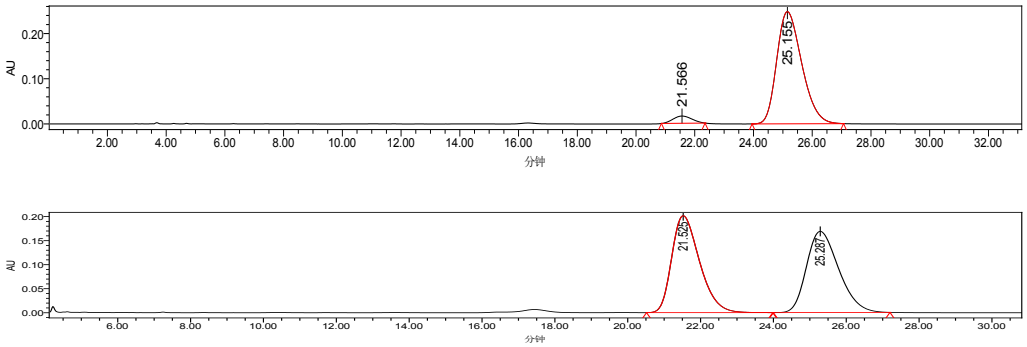
After 48 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white solid in 99% yield, as a mixture of diastereomers (92% ee, >99:1 dr; >99 % ee was obtained after a single recrystallization in ethyl acetate/petroleum ether). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 20.809 min, $t_r$ (major) = 22.207 min] and $^1$H NMR spectroscopy. m.p. 140-142 $^o$C. $[\alpha]_D^{25}$ = -44.8$^o$ (c = 0.71 in $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.88 (d, *J*=7.6, 2H), 7.57 (t, *J*=7.4, 1H), 7.50 – 7.38 (m, 4H), 7.33 (d, *J*=5.8, 1H), 7.27 – 7.20 (m, 1H), 6.13 (dd, *J*=5.7, 1.8, 1H), 5.24 (d, *J*=6.3, 1H), 3.80 – 3.69 (m, 1H), 3.49 (dd, *J*=18.0, 5.1, 1H), 3.39 (dd, *J*=18.0, 8.0, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 196.8, 172.3, 154.9, 140.2, 136.2, 133.7, 132.9, 131.9, 130.8, 130.2, 128.8, 128.0, 127.8, 122.5, 85.1, 63.72, 43.1, 39.3 ppm. ESI-HRMS Calcd for ($C_{19}H_{14}Cl_2O_3$ + $Na^+$): 383.0214 Found: 383.0218.




**5-(1-(4-bromophenyl)-3-oxo-3-phenylpropyl)furan-2(5H)-one (3k)**

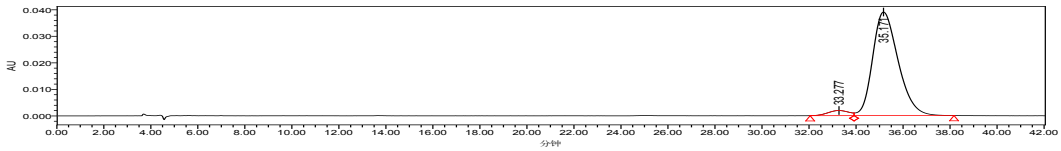
After 15 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white solid in 99% yield, as a mixture of diastereomers (91% ee, >99:1 dr; >99 % ee was obtained after a single recrystallization in ethyl acetate/petroleum ether). The ee and diastereoselectivity

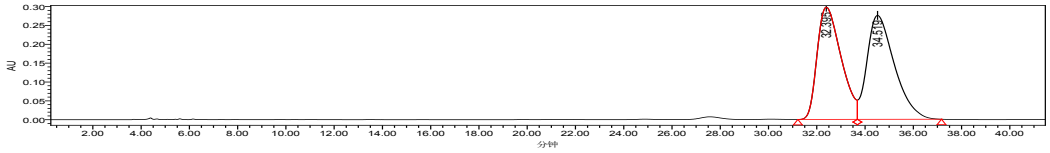
were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 21.566 min, $t_r$ (major) = 25.155 min] and $^1$H NMR spectroscopy. m.p. 138-141 $^o$C. $[\alpha]_D^{25}$ = -58.9$^o$ (c = 0.73 in $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) δ = 7.87 (d, *J*=7.3, 2H), 7.56 (t, *J*=7.4, 1H), 7.44 (dd, *J*=16.0, 8.1, 4H), 7.30 (dd, *J*=5.7, 1.4, 1H), 7.25 (t, *J*=9.9, 2H), 6.10 (dd, *J*=5.7, 2.0, 1H), 5.28 – 5.20 (m, 1H), 3.76 – 3.67 (m, 1H), 3.51 (dd, *J*=17.8, 5.0, 1H), 3.43 (dd, *J*=17.8, 8.2, 1H) ppm. $^{13}$C NMR (150 MHz, $CDCl_3$) δ = 197.1, 172.5, 155.2, 138.8, 136.4, 133.5, 132.0, 129.9, 128.7, 128.0, 122.3, 121.6, 85.4, 63.71, 43.6, 39.6 ppm. ESI-HRMS Calcd for ($C_{19}H_{16}BrO_3$ + $H^+$): 371.0285 Found: 371.0283.




**5-(1-(3-bromophenyl)-3-oxo-3-phenylpropyl)furan-2(5H)-one (3l)**

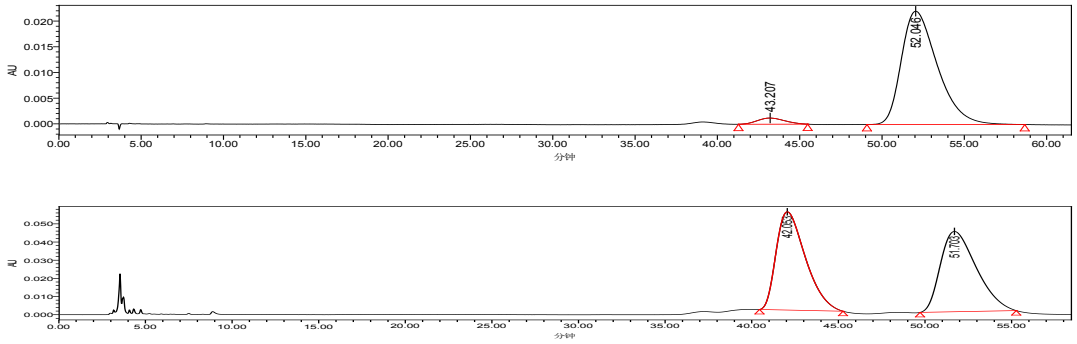
After 8 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white oil in 96% yield, as a mixture of diastereomers (92% ee, >99:1 dr). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 90:10 *n*-hexane/*i*PrOH, 0.8 mL/min; $t_r$ (minor) = 33.277 min, $t_r$ (major) = 35.171 min] and $^1$H NMR spectroscopy. $[\alpha]_D^{25}$ = -54.6$^o$ (c = 0.71 in $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, *J*=7.6, 2H), 7.47 (dd, *J*=16.1, 8.8, 2H), 7.41 – 7.30 (m, 3H), 7.28 – 7.08 (m, 3H), 6.03 (dd, *J*=5.7, 1.7, 1H), 5.18 (d, *J*=6.6, 1H), 3.72 – 3.58 (m, 1H), 3.45 (dd, *J*=17.9, 5.1, 1H), 3.35 (dd, *J*=17.9, 8.0, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 195.9, 171.5, 154.2, 141.2, 135.3, 132.5, 130.1, 129.8, 129.5, 127.7, 127.0, 126.0, 121.9, 121.3, 84.3, 62.7, 42.7, 38.5 ppm. ESI-HRMS Calcd for ($C_{19}H_{15}BrO_3$ + $H^+$): 371.0292 Found: 371.0283.





**4-(3-oxo-1-(5-oxo-2,5-dihydrofuran-2-yl)-3-phenylpropyl)benzonitrile (3m)**

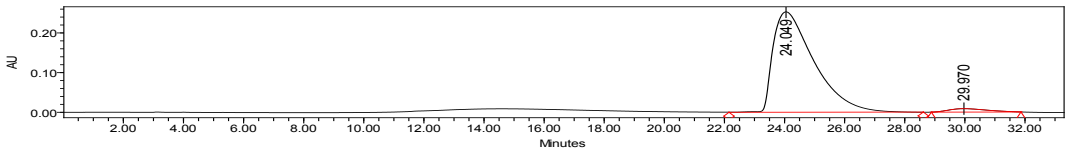
This is a known compound.[3a] After 18 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 1:1) to afford the white solid in 99% yield, as a mixture of diastereomers (92% ee, >99:1 dr; >99 % ee was obtained after a single recrystallization in ethyl acetate/petroleum ether). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 43.207 min, $t_r$ (major) = 52.046 min] and $^1$H NMR spectroscopy. m.p. 128-130 $^o$C. $[\alpha]_D^{25}$ = -50.8$^o$ (c = 0.63 in $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.80 (d, *J*=7.6, 2H), 7.56 (d, *J*=8.2, 2H), 7.50 (t, *J*=7.4, 1H), 7.44 (d, *J*=8.2, 2H), 7.37 (t, *J*=7.7, 2H), 7.26 (d, *J*=5.7, 1H), 6.06 (dd, *J*=5.7, 1.8, 1H), 5.21 (d, *J*=5.9, 1H), 3.79 (dd, *J*=13.2, 5.7, 1H), 3.47 – 3.31 (m, 2H) ppm.

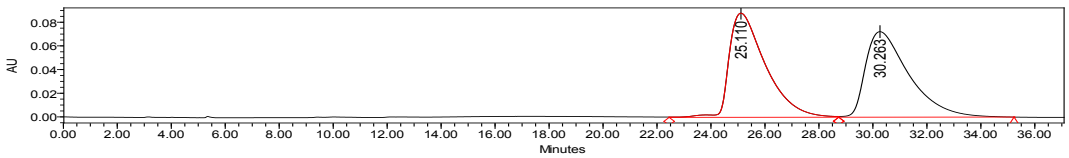


**5-(3-oxo-3-phenyl-1-(3-(trifluoromethyl)phenyl)propyl)furan-2(5H)-one (3n)**

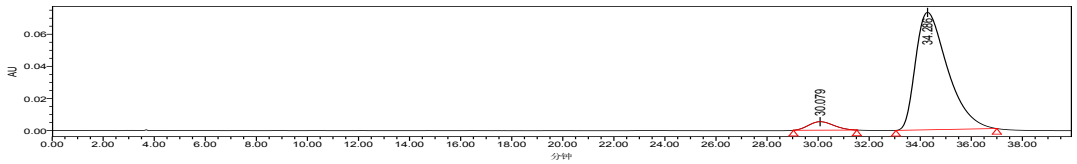
After 5 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white solid in 98% yield, as a mixture of diastereomers (94% ee, >99:1 dr; >99 % ee was obtained after a single recrystallization in ethyl acetate/petroleum ether). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OJ-H, 80:20 *n*-hexane/*i*PrOH, 1.0

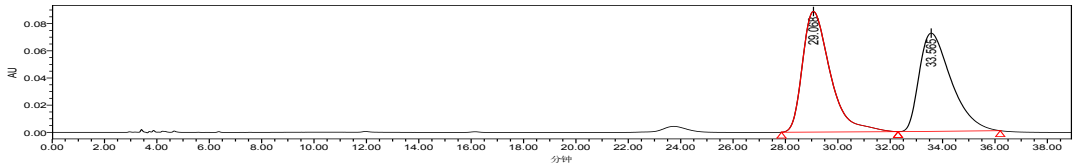
mL/min: $t_r$ (major) = 24.049 min, $t_r$ (minor) = 29.970 min] and $^1$H NMR spectroscopy. m.p. 108-110 $^o$C. $[\alpha]_D^{25}$ = -35.5$^o$ (c = 0.71 in $CH_2Cl_2$).
$^1$H NMR (400 MHz, $CDCl_3$) δ = 7.89 (d, *J*=7.7, 2H), 7.69 – 7.38 (m, 7H), 7.33 (d, *J*=5.6, 1H), 6.12 (dd, *J*=5.7, 1.7, 1H), 5.30 (d, *J*=6.2, 1H), 3.86 (dd, *J*=13.2, 6.0, 1H), 3.54 (dd, *J*=17.9, 5.2, 1H), 3.44 (dd, *J*=17.9, 7.8, 1H) ppm. ESI-HRMS Calcd for ($C_{20}H_{15}F_3O_3$ + $Na^+$): 383.0879 Found: 383.0871. $^{13}$C NMR (150 MHz, $CDCl_3$) δ = 197.0, 172.5, 155.3, 141.9, 136.4, 134.7, 133.5, 130.2, 128.7, 128.3, 128.0, 127.9, 126.6, 122.3, 85.4, 43.8, 39.6 ppm.



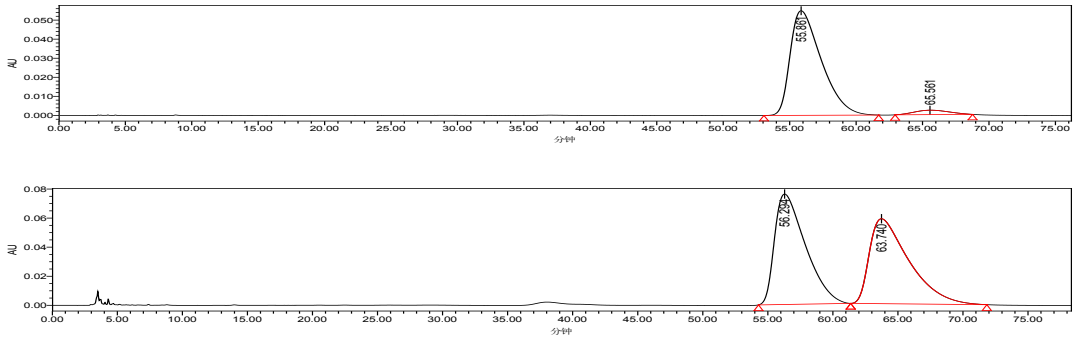

**5-(1-(benzo[*d*][1,3]dioxol-5-yl)-3-oxo-3-phenylpropyl)furan-2(5H)-one (3o)**
After 18 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 2:1) to afford the white oil in 99 % yield, as a mixture of diastereomers (91 % ee, >99:1 dr). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 30.077 min, $t_r$ (major) = 34.286 min] and $^1$H NMR spectroscopy. $[\alpha]_D^{25}$ = -57.3$^o$ (c = 0.67 in $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.89 (d, *J*=7.6, 2H), 7.55 (t, *J*=7.4, 1H), 7.44 (t, *J*=7.7, 1H), 7.38 – 7.23 (m, 1H), 6.83 (s, 1H), 6.80 – 6.67 (m, 2H), 6.09 (dd, *J*=5.7, 1.8, 1H), 5.93 (s, 2H), 5.21 (d, *J*=7.3, 1H), 3.61 (td, *J*=7.9, 4.9, 1H), 3.51 (dd, *J*=17.6, 4.8, 1H), 3.43 (dd, *J*=17.6, 8.4, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 197.4, 172.7, 155.6, 148.0, 147.0, 136.6, 133.4, 133.3, 128.7, 128.07, 122.07, 121.4, 108.6, 108.5, 101.2, 85.9, 44.2, 40.3 ppm. ESI-HRMS Calcd for ($C_{20}H_{16}O_5$ + $H^+$): 337.1076 Found: 337.1081.






**5-(3-oxo-1-(3-phenoxyphenyl)-3-phenylpropyl)furan-2(5H)-one (3p)**

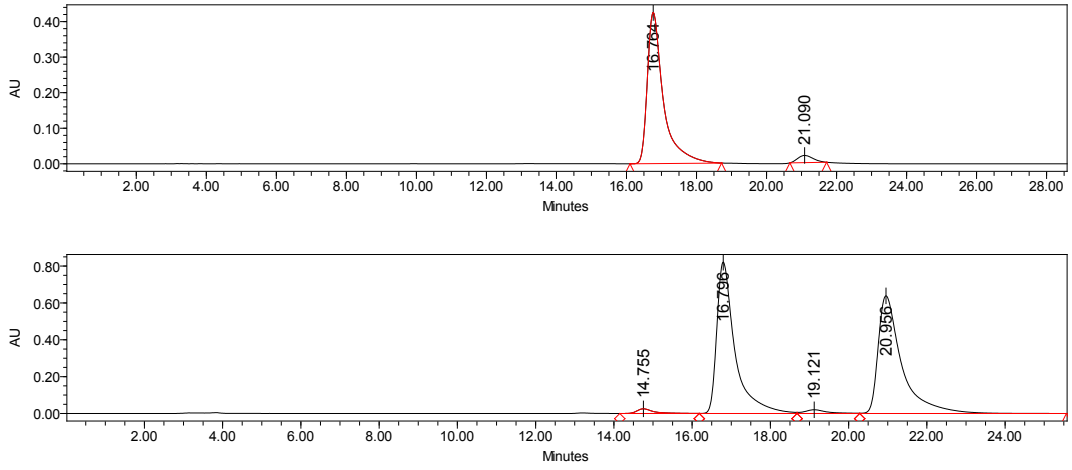
After 3 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white oil in 99% yield, as a mixture of diastereomers (91% ee, >99:1 dr). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (major) = 55.861 min, $t_r$ (minor) = 65.561 min] and $^1$H NMR spectroscopy. $[\alpha]_D^{25}$ = -55.5$^o$ (c = 0.76 in $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.88 (d, *J*=7.7, 2H), 7.55 (t, *J*=7.4, 1H), 7.44 (t, *J*=7.7,2H), 7.36 – 7.22 (m, 4H), 7.10 (dd, *J*=12.1, 7.5, 2H), 7.01 (s, 1H), 6.96 (d, *J*=8.2, 2H), 6.87 (dd, *J*=8.1, 2.1, 1H), 6.08 (dd, *J*=5.7, 1.7, 1H), 5.25 (d, *J*=7.1, 1H), 3.76 – 3.63 (m, 1H), 3.52 (dd, *J*=17.6, 5.2, 1H), 3.45 (dd, *J*=17.6, 8.0, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 197.3, 172.6, 157.6, 156.8, 155.4, 141.6, 136.6, 133.4, 130.2, 129.8, 128.7, 128.0, 123.5, 123.1, 122.1, 118.9, 118.5, 117.7, 85.6, 44.2, 39.9 ppm. ESI-HRMS Calcd for ($C_{25}H_{20}O_4$ + $H^+$): 385.1440 Found: 385.1444.




**5-(1-([1,1'-biphenyl]-4-yl)-3-oxo-3-phenylpropyl)furan-2(5H)-one (3q)**

After 24 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white solid in 94% yield, as a mixture of diastereomers (91% ee, >99:1 dr; >99 % ee was obtained after a single

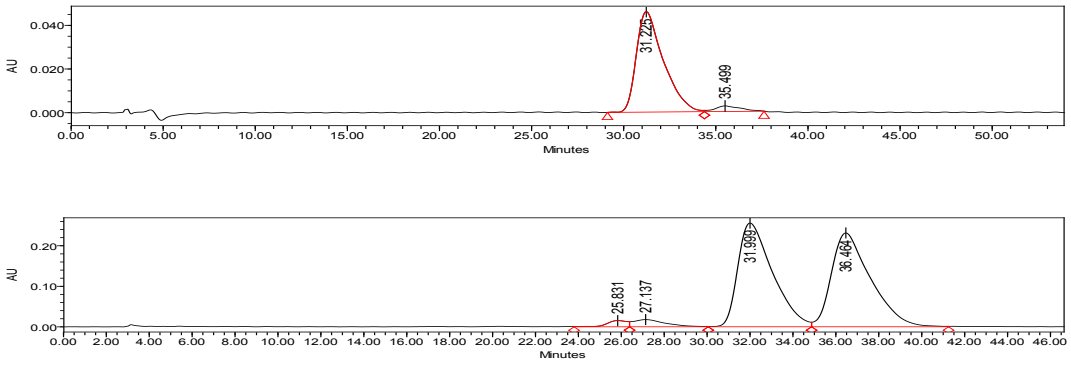
recrystallization in ethyl acetate/petroleum ether). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak IA, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (major) = 16.764 min, $t_r$ (minor) = 21.090 min] and $^1$H NMR spectroscopy. m.p. 149-151 $^o$C. $[\alpha]_D^{25}$ = -71.4$^o$ (c = 0.69 in $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.90 (d, *J*=7.7, 2H), 7.55 (t, *J*=7.4, 5H), 7.43 (td, *J*=7.9, 4.0, 6H), 7.34 (t, *J*=5.8, 2H), 6.10 (dd, *J*=5.7, 1.7, 1H), 5.30 (d, *J*=7.2, 1H), 3.82 – 3.69 (m, 1H), 3.60 (dd, *J*=17.7, 5.0, 1H), 3.52 (dd, *J*=17.7, 8.2, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 197.4, 172.8, 155.7, 140.6, 140.5, 138.7, 136.6, 133.4, 128.8, 128.7, 128.6, 128.0, 127.6, 127.5, 127.0, 122.1, 85.8, 44.0, 40.1 ppm. ESI-HRMS Calcd for ($C_{25}H_{20}O_3$ + $Na^+$): 391.1310 Found: 391.1306.




**5-(3-oxo-3-phenyl-1-(thiophen-2-yl)propyl)furan-2(5H)-one (3r)**

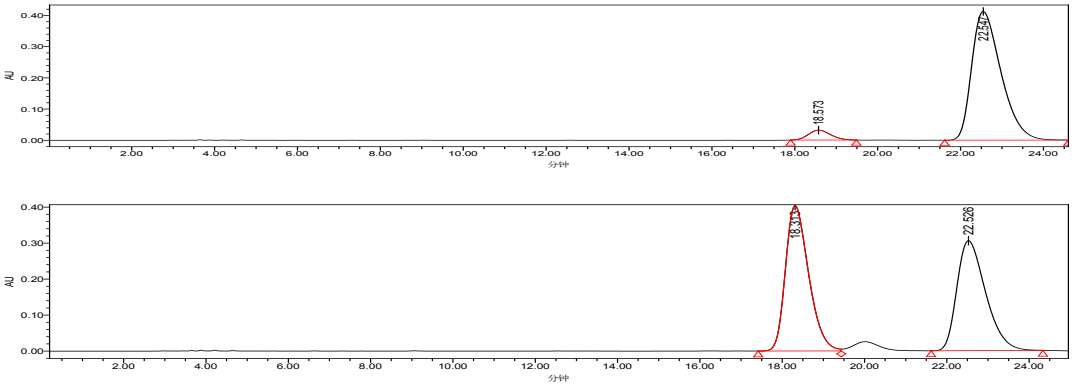
After 3 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white solid in 99% yield, as a mixture of diastereomers (92% ee, >99:1 dr; >99 % ee was obtained after a single recrystallization in ethyl acetate/petroleum ether). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak AD, 90:10 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (major) = 31.225 min, $t_r$ (minor) = 35.499 min] and $^1$H NMR spectroscopy. m.p. 83-85 $^o$C. $[\alpha]_D^{25}$ = -72.2$^o$ (c = 0.59 in $CH_2Cl_2$).

$^1$H NMR (400 MHz, $CDCl_3$) δ = 7.90 (d, *J*=7.6,2H), 7.56 (t, *J*=7.4, 1H), 7.45 (t, *J*=7.7,2H), 7.38 (d, *J*=5.7, 1H), 7.19 (d, *J*=5.0, 1H), 7.02 (d, *J*=3.2, 1H), 6.95 (dd, *J*=4.8, 3.7, 1H), 6.10 (dd, *J*=5.7, 1.8, 1H), 5.31 (d, *J*=7.1, 1H), 4.06 (dd, *J*=12.9, 7.2, 1H), 3.60 – 3.43 (m, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 195.9, 171.5, 154.1, 140.9, 135.4, 132.5, 127.7, 127.0, 126.1, 125.0, 123.6, 121.3, 84.4, 40.2, 38.6 ppm. ESI-HRMS Calcd for ($C_{17}H_{14}O_3S$ + $Na^+$): 321.0555 Found: 321.0561.



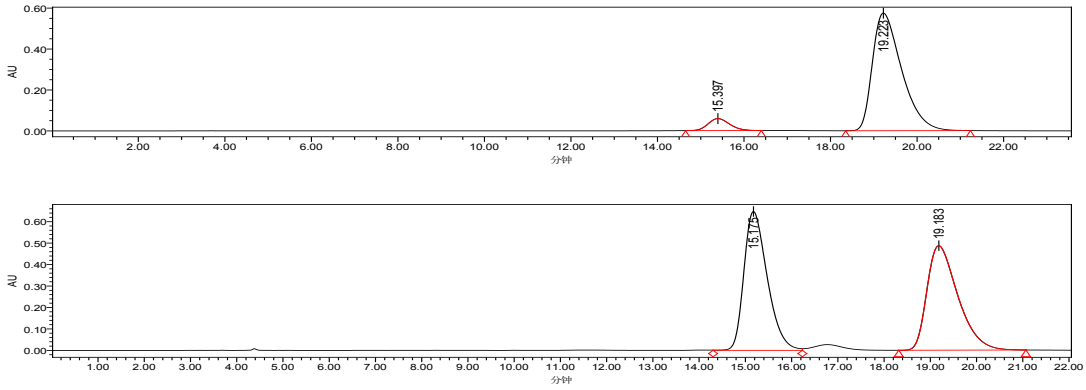

**5-(3-oxo-3-phenyl-1-(thiophen-3-yl)propyl)furan-2(5H)-one (3s)**

After 16 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white oil in 99% yield, as a mixture of diastereomers (90% ee, >99:1 dr).The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 18.573 min, $t_r$ (major) = 22.547 min] and $^1$H NMR spectroscopy. m.p. $[\alpha]_D^{25}$ = -58.8° (c = 0.59 in $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.87 – 7.74 (m, 2H), 7.48 (t, *J*=7.4, 1H), 7.36 (t, *J*=7.7, 2H), 7.27 (dd, *J*=5.7, 1.4, 1H), 7.22 (dd, *J*=4.9, 3.0, 1H), 7.13 (d, *J*=1.7, 1H), 7.02 (dd, *J*=5.0, 1.1, 1H), 6.01 (dd, *J*=5.7, 1.9, 1H), 5.28 – 5.19 (m, 1H), 3.83 (dd, *J*=12.6, 7.0, 1H), 3.39 (dd, *J*=17.6, 5.4, 1H), 3.32 (dd, *J*=17.6, 7.6, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 197.5, 172.7, 155.5, 140.2, 136.6, 133.4, 128.7, 128.0, 127.2, 126.4, 122.4, 122.1, 85.4, 40.0, 39.4 ppm. ESI-HRMS Calcd for ($C_{17}H_{14}O_3S + Na^+$): 321.0561 Found: 321.0567.



**5-(3-oxo-1-phenyl-3-(p-tolyl)propyl)furan-2(5H)-one (3t)**

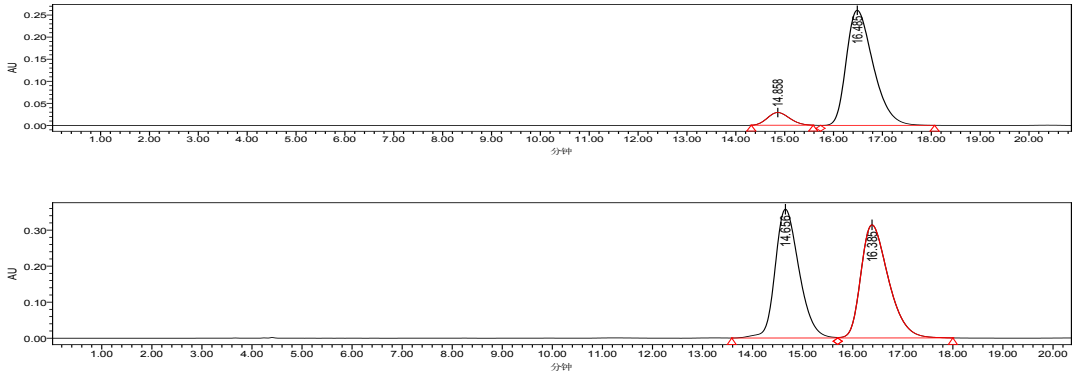
After 3 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white solid in 99% yield, as a mixture of diastereomers (88% ee, >99:1 dr; >99 % ee was obtained after a single recrystallization in ethyl acetate/petroleum ether).The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 15.397 min, $t_r$ (major) = 19.223 min] and $^1$H NMR spectroscopy. m.p. 104-106 $^o$C. $[\alpha]_D^{25}$ = -62.3$^o$ (c = 0.61 in $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, *J*=8.1, 2H), 7.39 – 7.16 (m, 8H), 6.07 (dd, *J*=5.7, 1.8, 1H), 5.27 (d, *J*=7.1, 1H), 3.75 – 3.67 (m, 1H), 3.53 (dd, *J*=17.5, 5.1, 1H), 3.44 (dd, *J*=17.6, 8.0, 1H), 2.39 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 197.0), 172.8, 155.7, 144.3, 139.7, 134.1, 129.3, 128.9, 128.2, 128.1, 127.6, 121.9, 85.9, 44.4, 39.7, 21.6 ppm. ESI-HRMS Calcd for ($C_{20}H_{18}O_3$ + $K^+$): 345.0893 Found: 345.0889.




**5-(3-oxo-1-phenyl-3-(p-tolyl)propyl)furan-2(5H)-one (3u)**

After 5 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white solid in 96% yield, as a mixture of diastereomers (84% ee, >99:1 dr; 93 % ee was obtained after a single recrystallization in ethyl acetate/petroleum ether). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 14.858 min, $t_r$ (major) = 16.485 min] and $^1$H NMR

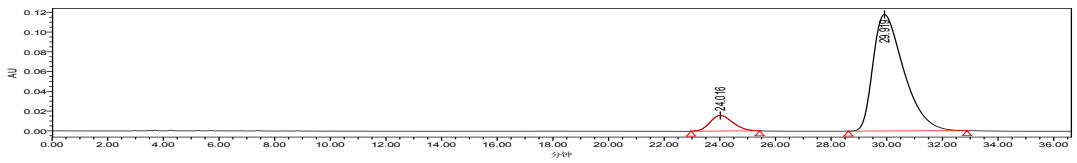
spectroscopy. m.p. 98-100 °C. $[\alpha]_D^{25}$ = -53.9° (c = 0.59 in $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) δ = 7.68 (d, *J*=5.9, 2H), 7.37 – 7.22 (m, 8H), 6.08 (dd, *J*=5.7, 1.8, 1H), 5.27 (d, *J*=7.2, 1H), 3.73-3.68 (m, 1H), 3.55 (dd, *J*=17.7, 5.1, 1H), 3.46 (dd, *J*=17.7, 8.1, 1H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 197.6, 172.8, 155.7, 139.7, 138.5, 136.6, 134.1, 128.9, 128.5, 128.2, 127.7, 125.2, 122.0, 85.9, 44.39, 40.1 ppm. ESI-HRMS Calcd for ($C_{20}H_{18}O_3 + H^+$): 307.1334 Found: 307.1333.

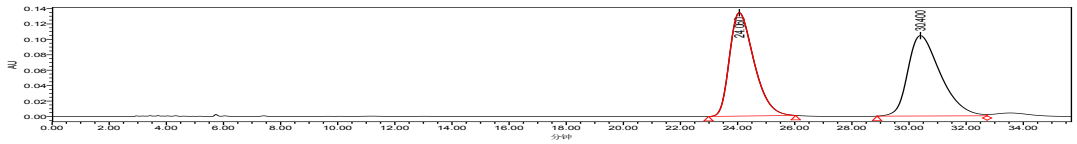



**5-(3-(4-methoxyphenyl)-3-oxo-1-phenylpropyl)furan-2(5H)-one (3v)**

After 24 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white solid in 99% yield, as a mixture of diastereomers (83 % ee, >99:1 dr; >99 % ee was obtained after a single recrystallization in ethyl acetate/petroleum ether). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 24.016 min, $t_r$ (major) = 29.919 min] and $^1H$ NMR spectroscopy. m.p. 139-141 °C. $[\alpha]_D^{25}$ = -32.8° (c = 0.64 in $CH_2Cl_2$).

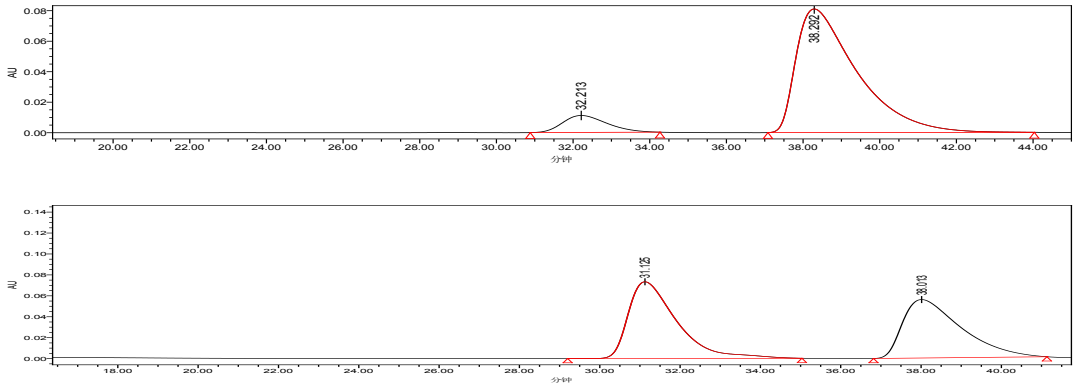
$^1H$ NMR (600 MHz, $CDCl_3$) δ = 7.87 (d, *J*=8.8, 2H), 7.38 – 7.21 (m, 6H), 6.90 (d, *J*=8.8, 2H), 6.07 (dd, *J*=5.7, 1.8, 1H), 5.27 (d, *J*=7.1, 1H), 3.85 (s, 3H), 3.76 – 3.65 (m, 1H), 3.50 (dd, *J*=17.4, 5.1, 1H), 3.41 (dd, *J*=17.4, 8.0, 1H) ppm. $^{13}C$ NMR (150 MHz, $CDCl_3$) δ = 195.8, 172.8, 163.7, 155.7, 139.8, 130.3, 129.7, 128.9, 128.2, 127.6, 121.9, 113.8, 85.9, 55.5, 44.4, 39.5 ppm. ESI-HRMS Calcd for ($C_{20}H_{18}O_4 + Na^+$): 345.1103 Found: 345.1106.





**5-(3-(benzo[*d*][1,3]dioxol-5-yl)-3-oxo-1-phenylpropyl)furan-2(5H)-one (3w)**

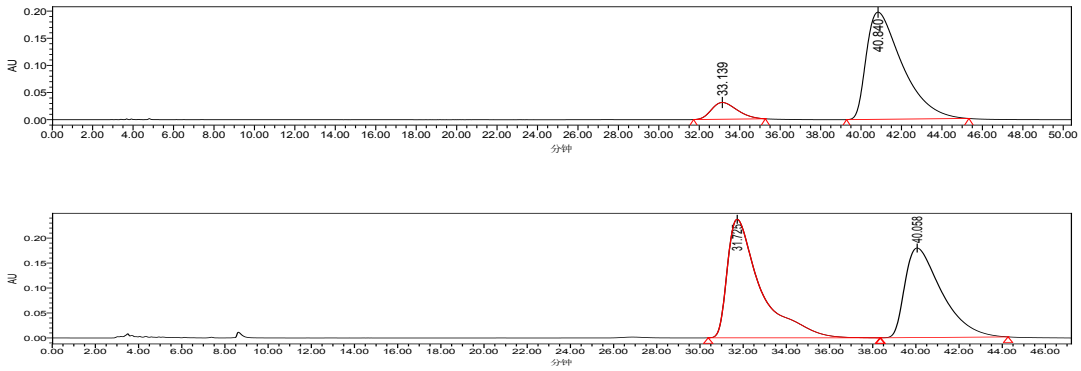
After 24 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white oil in 99% yield, as a mixture of diastereomers (83% ee, >99:1 dr). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 32.213 min, $t_r$ (major) = 38.292 min] and $^1$H NMR spectroscopy. $[\alpha]_D^{25}$ = -51.8$^o$ (c = 0.67 in $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.50 (d, *J*=8.2, 1H), 7.39 – 7.21 (m, 7H), 6.81 (d, *J*=8.2, 1H), 6.11 – 6.05 (m, 1H), 6.02 (s, 2H), 5.26 (d, *J*=7.2, 1H), 3.68 (dd, *J*=12.8, 7.6, 1H), 3.48 (dd, *J*=17.4, 5.1, 1H), 3.39 (dd, *J*=17.4, 8.1, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 172.8, 155.7, 152.0, 148.2, 139.7, 131.5, 128.9, 128.1, 127.7, 124.4, 121.9, 107.9, 107.8, 101.9, 85.9, 44.5, 39.8 ppm. ESI-HRMS Calcd for ($C_{20}H_{16}O_5$ + $H^+$): 337.1070 Found: 337.1076.



**5-(1,3-bis(4-methoxyphenyl)-3-oxopropyl)furan-2(5H)-one (3x)**

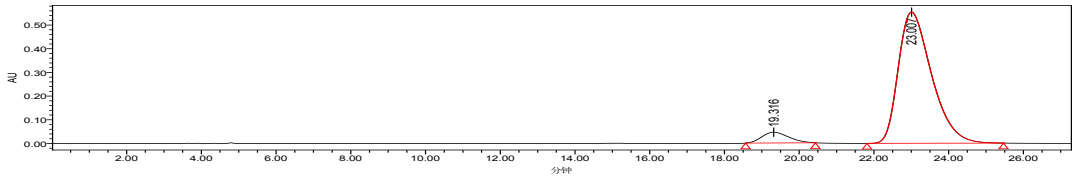
After 36 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white oil in 92% yield, as a mixture of diastereomers (82% ee, >99:1 dr). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min;

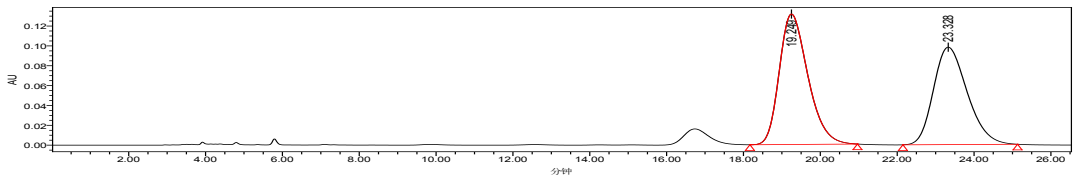
$t_r$ (minor) = 33.139 min, $t_r$ (major) = 40.840 min] and $^1$H NMR spectroscopy. $[\alpha]_D^{25}$ = -66.0$^o$ (c = 0.65 in $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.87 (d, *J*=8.8, 2H), 7.35 – 7.20 (m, 3H), 6.87 (dd, *J*=18.3, 8.6, 4H), 6.07 (dd, *J*=5.7, 1.4, 1H), 5.23 (d, *J*=7.2, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.64 (dd, *J*=12.7, 7.6, 1H), 3.47 (dd, *J*=17.3, 5.1, 1H), 3.38 (dd, *J*=17.3, 8.2, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 196.0, 172.9, 163.7, 158.9, 155.8, 131.7, 130.3, 129.7, 129.2, 121.9, 114.2, 113.8, 86.1, 55.5, 55.3, 43.7, 39.8 ppm. ESI-HRMS Calcd for ($C_{21}H_{20}O_5$ + $H^+$): 353.1389 Found: 353.1385.




**5-(1-(4-bromophenyl)-3-oxo-3-(p-tolyl)propyl)furan-2(5H)-one (3y)**

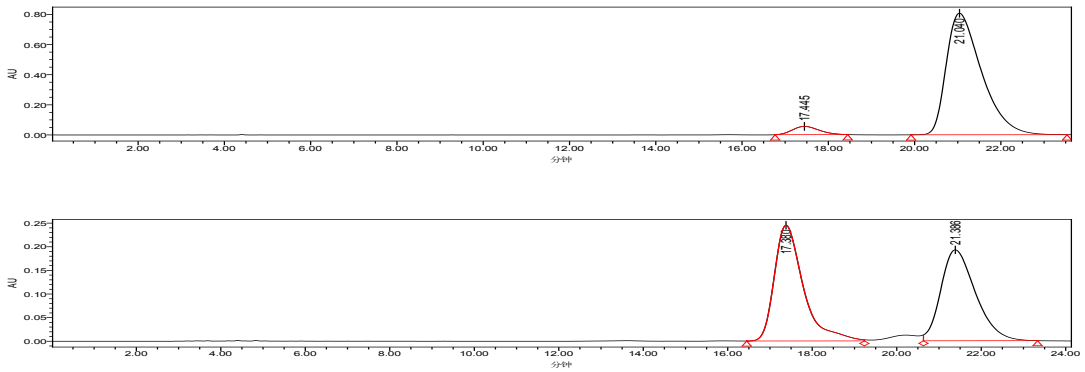
After 18 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white oil in 92% yield, as a mixture of diastereomers (88% ee, >99:1 dr). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 19.316 min, $t_r$ (major) = 23.007 min] and $^1$H NMR spectroscopy. $[\alpha]_D^{25}$ = -68.9$^o$ (c = 0.71 in $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J*=8.2, 2H), 7.38 (d, *J*=8.4, 2H), 7.27 – 7.13 (m, 5H), 6.02 (dd, *J*=5.7, 2.0, 1H), 5.16 (dt, *J*=6.6, 1.7, 1H), 3.68 – 3.60 (m, 1H), 3.40 (dd, *J*=17.7, 5.1, 1H), 3.31 (dd, *J*=17.7, 8.1, 1H), 2.32 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 196.7, 172.6, 155.3, 144.5, 138.9, 134.0, 132.0, 129.9, 129.4, 128.1, 122.3, 121.6, 85.4, 43.6, 39.4, 21.7 ppm. ESI-HRMS Calcd for ($C_{20}H_{17}BrO_3$ + $H^+$): 407.0259 Found: 407.0264.






**5-(1-(3-bromophenyl)-3-oxo-3-(p-tolyl)propyl)furan-2(5H)-one (3z)**

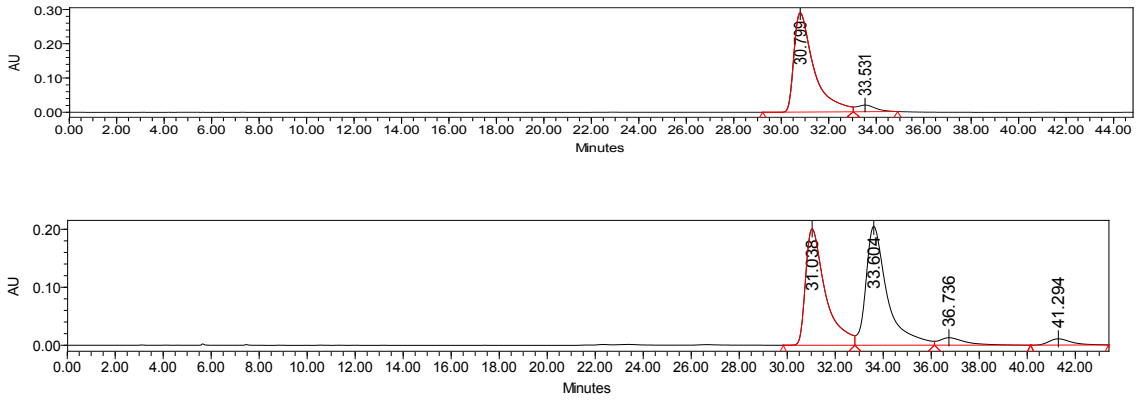
After 18 hours, the crude material was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white oil in 99% yield, as a mixture of diastereomers (91% ee, >99:1 dr). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 17.445 min, $t_r$ (major) = 21.040 min] and $^1$H NMR spectroscopy. $[\alpha]_D^{25}$ = -50.3$^o$ (c = 0.76 in $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, *J*=8.2, 2H), 7.44 (t, *J*=1.6, 1H), 7.35 – 7.29 (m, 1H), 7.27 – 7.21 (m, 2H), 7.20 – 7.09 (m, 3H), 6.02 (dd, *J*=5.7, 2.0, 1H), 5.17 (dt, *J*=6.5, 1.7, 1H), 3.69 – 3.59 (m, 1H), 3.41 (dd, *J*=17.8, 5.2, 1H), 3.31 (dd, *J*=17.8, 7.9, 1H), 2.32 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 196.6, 172.6, 155.3, 144.5, 142.3, 133.9, 131.1, 130.8, 130.5, 129.4, 128.1, 127.1, 122.9, 122.2, 85.4, 43.7, 39.3, 21.7 ppm. ESI-HRMS Calcd for ($C_{20}H_{17}BrO_3$ + $H^+$): 385.0439 Found: 385.0430.




**5-(3-oxo-3-(p-tolyl)-1-(3-(trifluoromethyl)phenyl)propyl)furan-2(5H)-one (3aa)**

After 48 hours, the crude material was directly purified by flash chromatography on

silica gel (petroleum ether/ethyl acetate, 3:1) to afford the white oil in 99% yield, as a mixture of diastereomers (89% ee, >99:1 dr). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak IA, 95:5 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 30.799 min, $t_r$ (major) = 33.531 min] and $^1$H NMR spectroscopy. $[\alpha]_D^{25}$ = -48.6$^o$ (c = 0.74 in $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, *J*=8.2, 2H), 7.57 – 7.50 (m, 2H), 7.46 (d, *J*=7.8, 1H), 7.39 (t, *J*=7.7, 1H), 7.25 (dd, *J*=5.7, 1.4, 1H), 7.21 – 7.13 (m, 2H), 6.03 (dd, *J*=5.7, 2.0, 1H), 5.26 – 5.22 (m, 1H), 3.79 (dd, *J*=13.3, 5.8, 1H), 3.43 (dd, *J*=17.8, 5.4, 1H), 3.38 – 3.28 (m, 1H), 2.32 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 196.5, 172.4, 155.0, 144.5, 141.1, 133.9, 131.9, 131.4, 131.0, 129.4, 128.1, 125.3, 124.9, 124.8, 124.6, 124.5, 122.4, 85.3, 43.7, 39.1, 21.6 ppm. ESI-HRMS Calcd for ($C_{21}H_{17}F_3O_3$ + $H^+$): 375.1208 Found:375.1202.

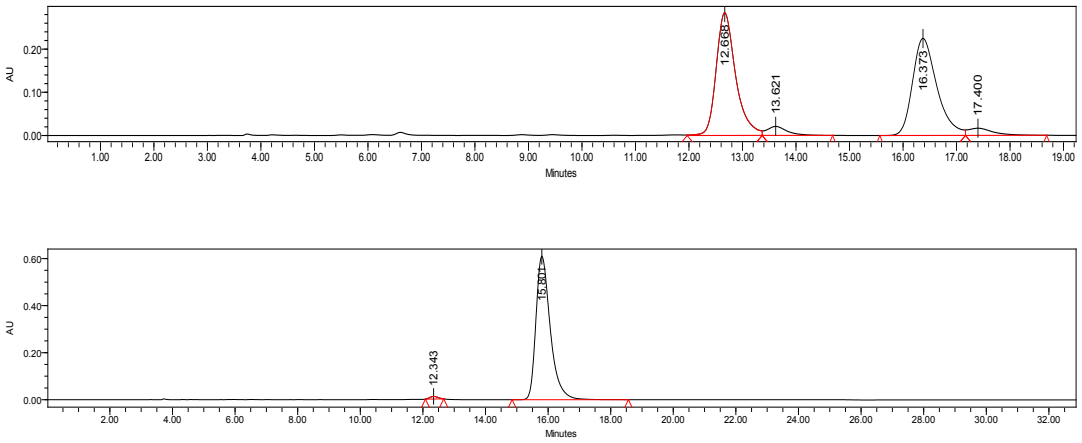



**5. Experimental procedure for the elaboration of adduct 3a:**

**3-(5-oxo-2,5-dihydrofuran-2-yl)-N,3-diphenylpropanamide (BV 7)**

To a solution of **3a** (58.4 mg, 0.2mmol, 99 ee, >99:1 dr) in ethanol (0.4 mL) was added hydroxylamine hydrochloride (41.4 mg, 0.6 mmol), pyridine (48.4 µL, 0.6 mmol). The reaction mixture was tirred at room temperature for 5 h, diluted with water (5.0 mL) and extracted ith $CH_2Cl_2$ (3×15 mL), organic layers were washed with brine, and dried over $MgSO_4$. After evaporation under reduced pressure, the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate =4/1) to give oxime **6** (55.3 mg, 90% yield) as a colorless oil. To a solution of oxime **6** (30.7 mg, 0.1mmol) in toluene (0.4 mL) was added $PCl_5$ (0.05 mmol, 10.4 mg) at 0$^o$C. After ambient temperature was reached, the reaction mixture was stirred for 5 h, diluted with water (5.0 mL) and extracted ith $CH_2Cl_2$ (3×15 mL). Organic layers were washed with 1 M $KHSO_4$ solution, saturated $NaHCO_3$ solution, brine, dried over anhydrous $Na_2SO_4$ and concentrated and purified through flash chromatograph (petroleum ether/ethyl acetate =3/2) to give butenolide **7** (21.5 mg,

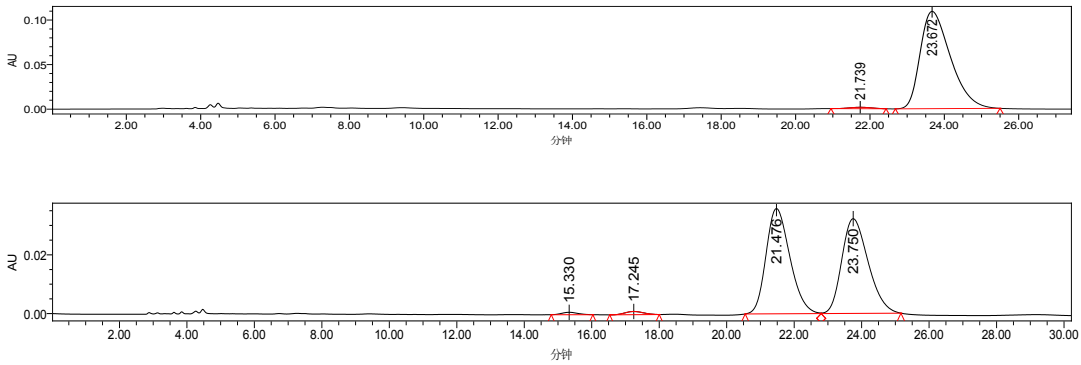
70% yield) as a colorless oil as a mixture of diastereomers (98% ee, >99:1 dr). The ee and diastereoselectivity were determined by HPLC analysis [Chiralpak AD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 12.343 min, $t_r$ (major) = 15.801 min] and $^1$H NMR spectroscopy. $[\alpha]_D^{25}$ = -32.3° (c = 0.43 in $CH_2Cl_2$). ESI-HRMS Calcd for ($C_{19}H_{17}NO_3$ + $H^+$): 308.1287 Found: 308.1284. $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.95 (s, 1H), 7.43 – 7.17 (m, 10H), 7.04 (t, *J*=7.4, 1H), 6.07 (dd, *J*=5.7, 1.9, 1H), 5.25 (d, *J*=6.3, 1H), 3.58 (dt, *J*=8.1, 6.1, 1H), 2.88 (dd, *J*=15.2, 5.8, 1H), 2.71 (ddd, *J*=15.1, 8.3, 3.1, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 173.2, 168.9, 155.9, 139.3, 137.7, 129.0, 128.8, 128.0, 127.8, 124.3, 121.8, 120.1, 86.0, 45.2, 38.5 ppm.




**phenyl 3-(5-oxotetrahydrofuran-2-yl)-3-phenylpropanoate (lacton 5)**

A solution of **3a** (58.4 mg, 0.2mmol, 99 ee, >99:1 dr) in anhydrous methanol (2.0 mL) containing 10% Pd/C (12 mg) was stirred under $H_2$ (1 atm) at room temperature overnight. The catalyst was removed by filtration through a pad of Celite, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate =2/1) to give lacton **4** (27.9 mg, 95% yield) as a colorless oil. To a stirred solution of **4** (58.8 mg, 0.2 mmol) in dichloroethane (2 mL) at room temperature were added $KH_2PO_4$ (272.2 mg, 2.0 mmol) and m-chloroperbenzoic acid (172.6 mg, 1.0 mmol). After being stirred for 3 h at 60 °C, the reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$. The resulting mixture was extracted with diethyl ether. The combined organic extracts were washed with ice-cooled saturated aqueous $NaHCO_3$ and brine, and then dried over $Na_2SO_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate =3/1) to give lacton **5** (40.3 mg, yield 65%) as a colorless solid as a mixture of diastereomers (98% ee, >99:1 dr). The ee and diastereoselectivity were

determined by HPLC analysis [Chiralpak OD-H, 80:20 *n*-hexane/*i*PrOH, 1.0 mL/min; $t_r$ (minor) = 21.793 min, $t_r$ (major) = 23.672 min] and $^1$H NMR spectroscopy. $[\alpha]_D^{25}$ = 9.1$^o$ (c = 0.81 in $CH_2Cl_2$). ESI-HRMS Calcd for ($C_{19}H_{18}O_4$ + $Na^+$): 333.1097 Found: 333.0950. $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.96 – 7.83 (m, 2H), 7.53 (t, *J*=7.4, 1H), 7.42 (t, *J*=7.6, 2H), 7.33 – 7.17 (m, 5H), 4.71 (dd, *J*=15.8, 7.4, 1H), 3.75 – 3.42 (m, 3H), 2.48 (dd, *J*=9.5, 6.8, 2H), 2.03 (td, *J*=13.7, 6.8, 1H), 1.96 – 1.81 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 197.7, 176.8, 139.4, 136.8, 133.2, 128.9, 128.6, 128.3, 128.0, 127.5, 82.9, 46.2, 41.7, 28.6, 26.6 ppm.




## 6. References:

1 (a) D. J. Shang, J. G. Xin, Y. L. Liu, X. Zhou, X. H. Liu, X. M. Feng, *J. Org. Chem.* **2008**, *73*, 630; (b) X. Li, X. H. Liu, Y. Z. Fu, L. J. Wang, L. Zhou, X. M. Feng, *Chem. Eur. J.* **2008**, *14*, 4796.

2 (a) G. Casiraghi and G. Rassu, *Synthesis* **1995**, 607; (b) G. Rassu, F. Zanardi, L. Battistini, E. Gaetani, G. Casiraghi, *J. Med. Chem.* **1997**, *40*, 168; (c) H. Näsman, K. G. Pensar, *Synthsis* **1985**, 786; (d) M. A. Brimble, M. T. Brimble, J. J. Gibson, *J. Chem. Soc. Perkin Trans I* **1989**, 179.

3 (a) Y. Zhang, C. Yu, Y. Ji, W. Wang, *Chem. Asian J.* **2010**, *5*, 1303; (b) H. C. Huang, F. Yu, Z. C. Jin, W. J. Li, W. B. Wu, X. M. Liang, J. X. Ye, *Chem. Commun.* **2010**, 5957.

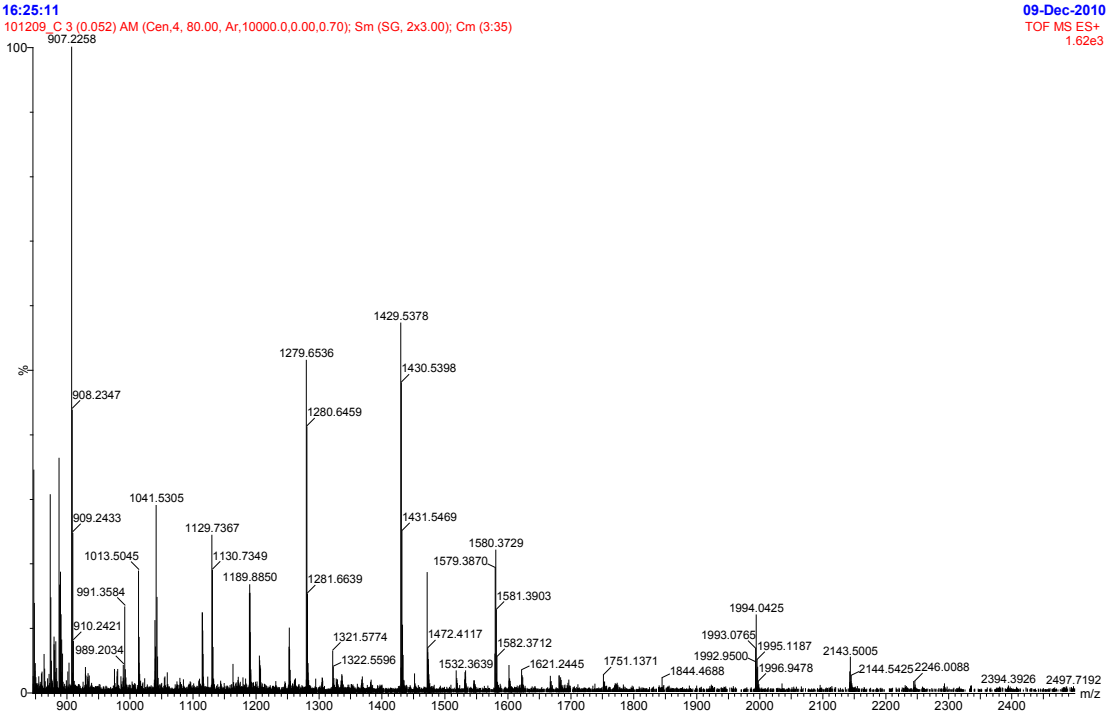
## 7. High Resolution Mass Spectrum (ES+) of the reaction mixture.

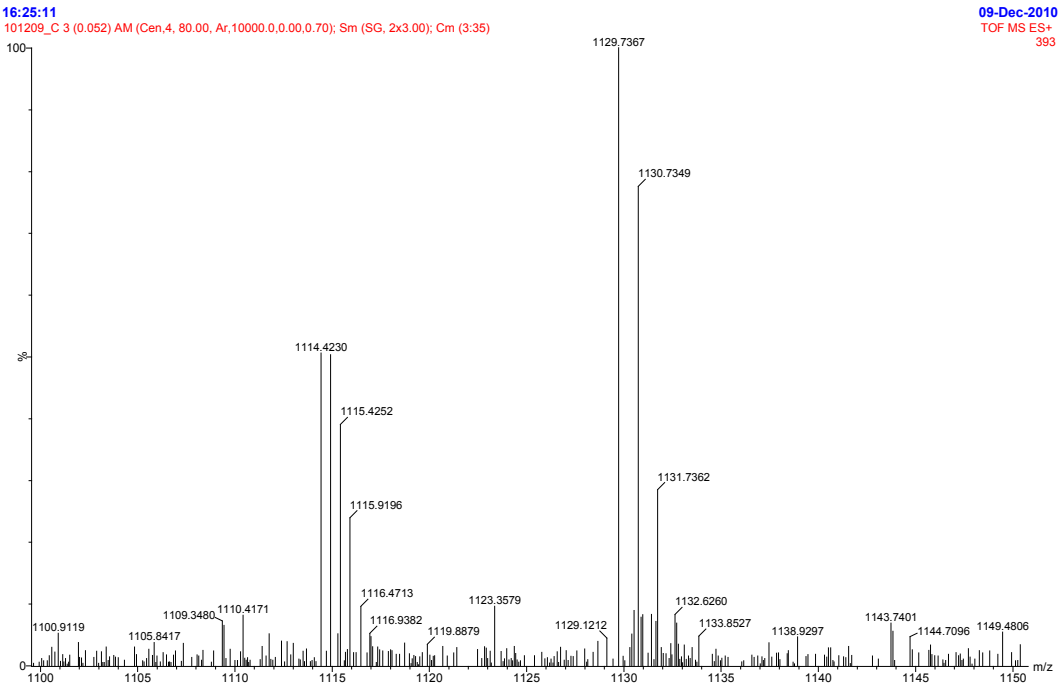
The preparation of the sample: *N*,*N*′-dioxide **L3** (0.02 mmol, 11.6 mg), $Sc(OTf)_3$ (0.02 mmol, 10.0 mg), chalcone **2a** (0.1 mmol, 20.8 mg), *t*-BuOH (0.3 mL) and ethyl propionate (0.3 mL) were stirred in a dry reaction tube under air at 30 $^o$C for 0.5 h. Subsequently, TBSOF **1** (0.25 mmol, 60 μL) was added and a sample of the mixture was taken to detect immediately.

**L3**+$Sc(OTf)_2$: calcd for $C_{35}H_{48}F_6N_4O_{10}S_2Sc$: 907.2259. $[M]^+$: 907.2258.

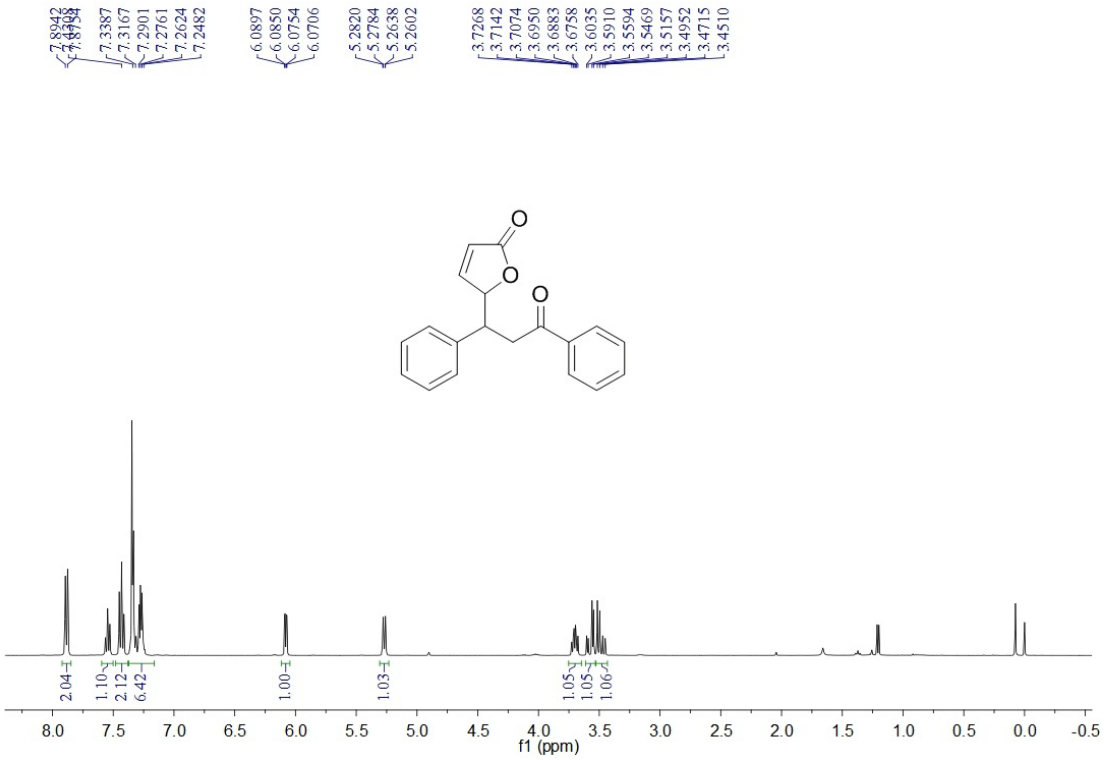
**L3**+$Sc(OTf)_2$+**2a**: calcd for $C_{50}H_{60}F_6N_4O_{11}S_2Sc$: 1115.3147. $[M]^+$: 1115.4252.

**L3**+$Sc^{III}$+**2a**+**1**-$2H^{+}$-$2TfO^{-}$: calcd for $C_{58}H_{76}N_4O_7Sc$: 1013.5026) at *m/z* 1013.5045




## 8. Copy of $^{1}$H NMR and $^{13}$C NMR spectrum for products: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7.8458
7.3387
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7.2901
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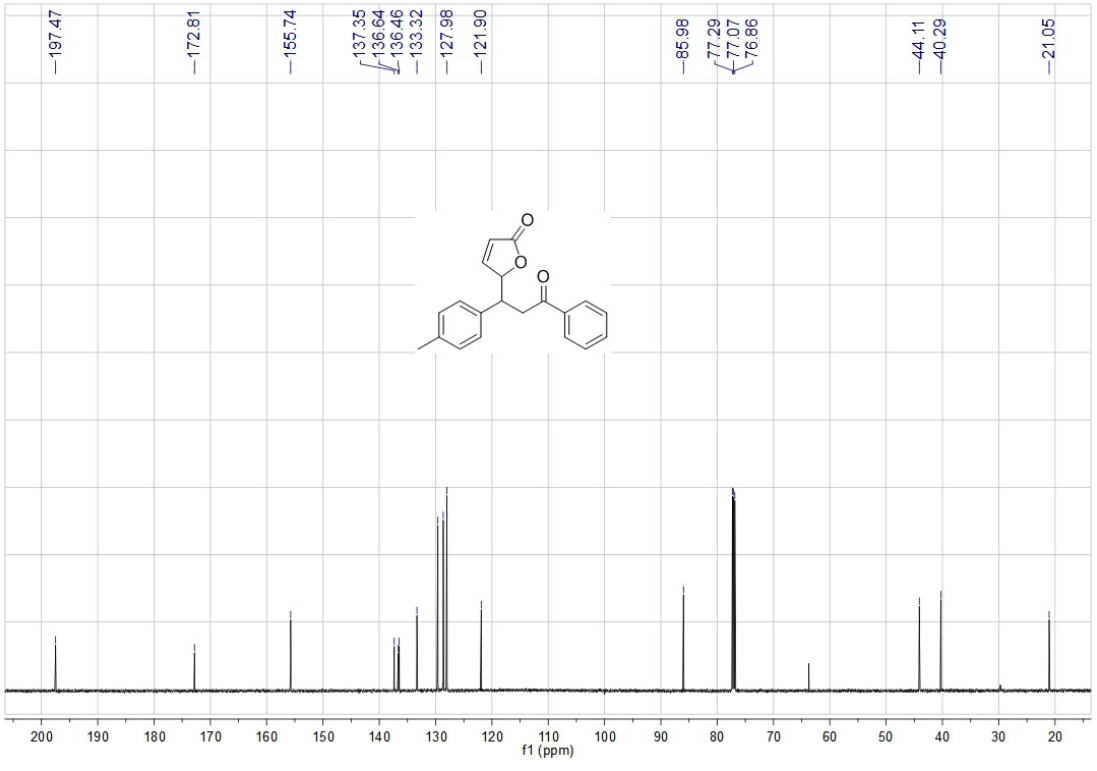
7.2624
7.2482
6.0897
6.0850
6.0754
6.0706
5.2820
5.2784
5.2638
5.2602
3.7268
3.7142
3.7074
3.6950
3.6883
3.6758
3.6035
3.5910
3.5594
3.5469
3.5157
3.4952
3.4715
3.4510
O
O
O
2.04
1.10
2.12
6.42
1.00
1.03
1.05
1.05
1.06
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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133.32
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85.98
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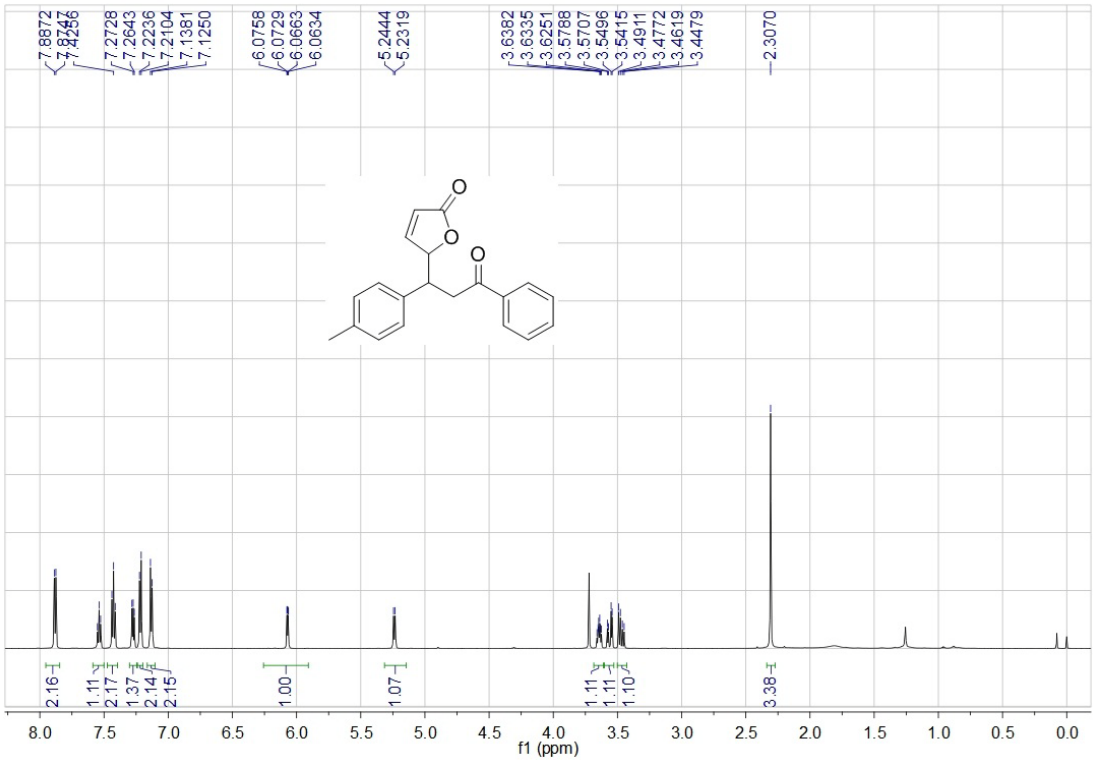
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)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1.11
1.11
1.10
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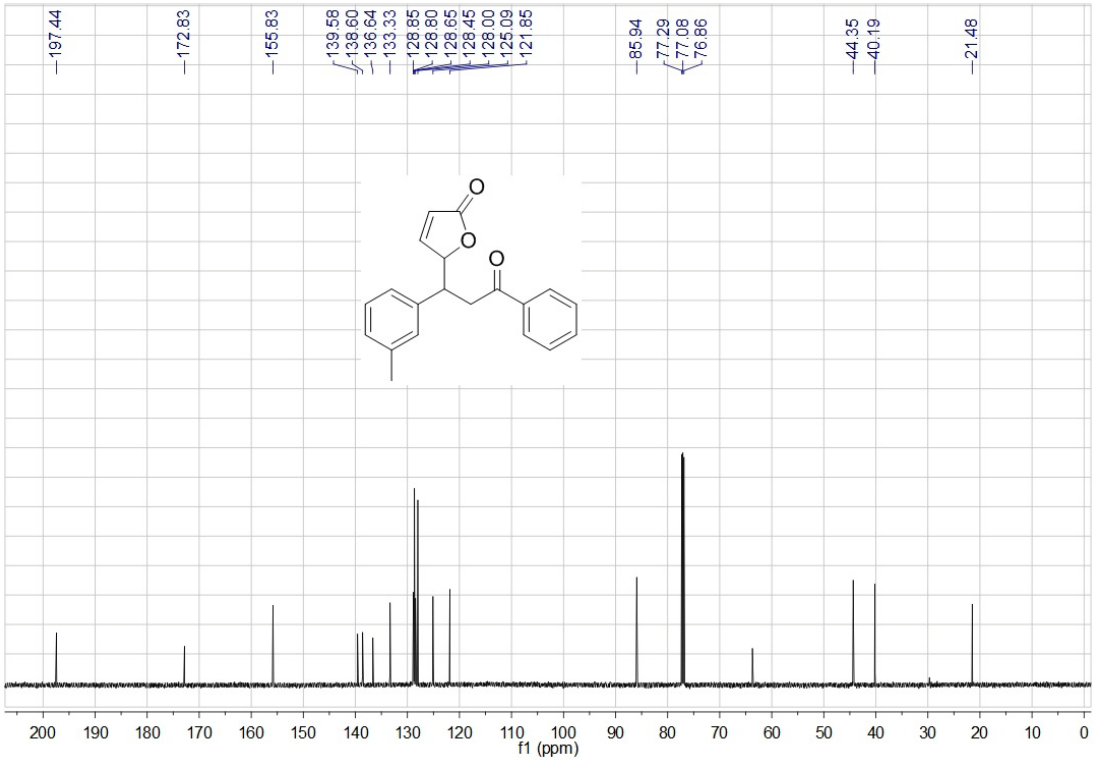
f1 (ppm)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172.83
155.83
139.58
138.60
136.64
133.33
128.85
128.80
128.65
128.45
128.00
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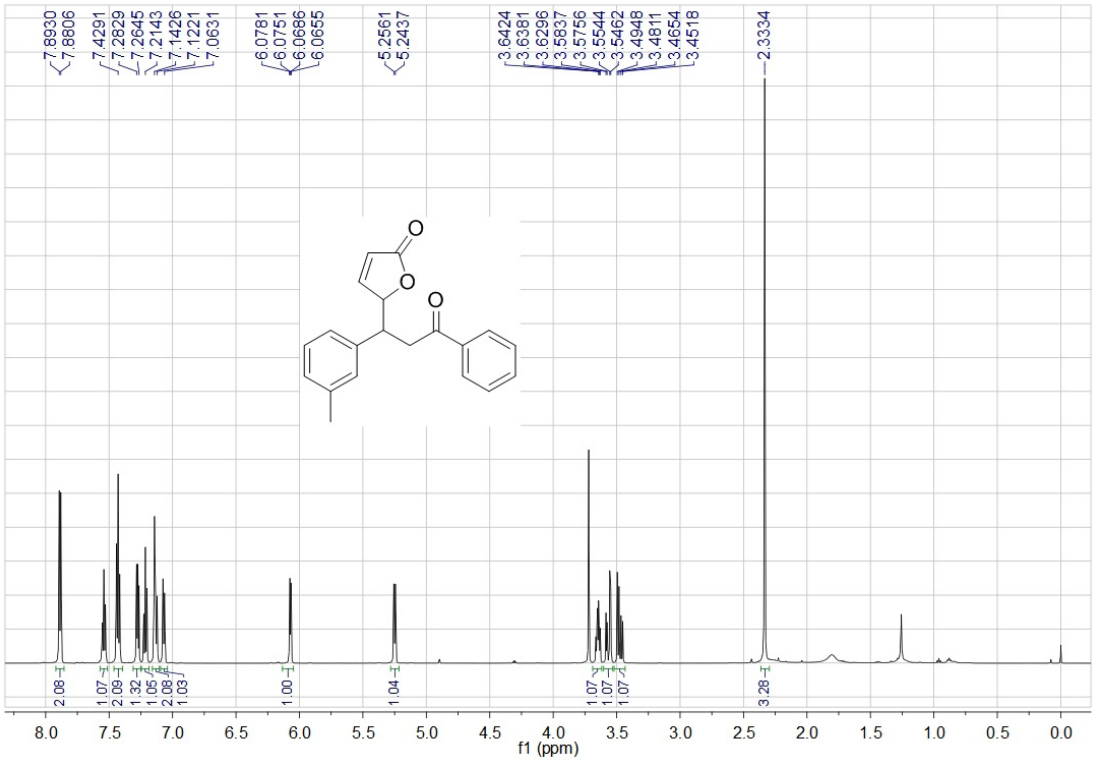
85.94
77.29
77.08
76.86
44.35
40.19
21.48
f1 (ppm)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7.1426
7.1221
7.0631
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6.0751
6.0686
6.0655
5.2561
5.2437
3.6424
3.6381
3.6296
3.5837
3.5756
3.5544
3.5462
3.4948
3.4811
3.4654
3.4518
2.3334
2.08
1.07
2.09
1.32
1.05
2.08
1.03
1.00
1.04
1.07
1.07
1.07
3.28
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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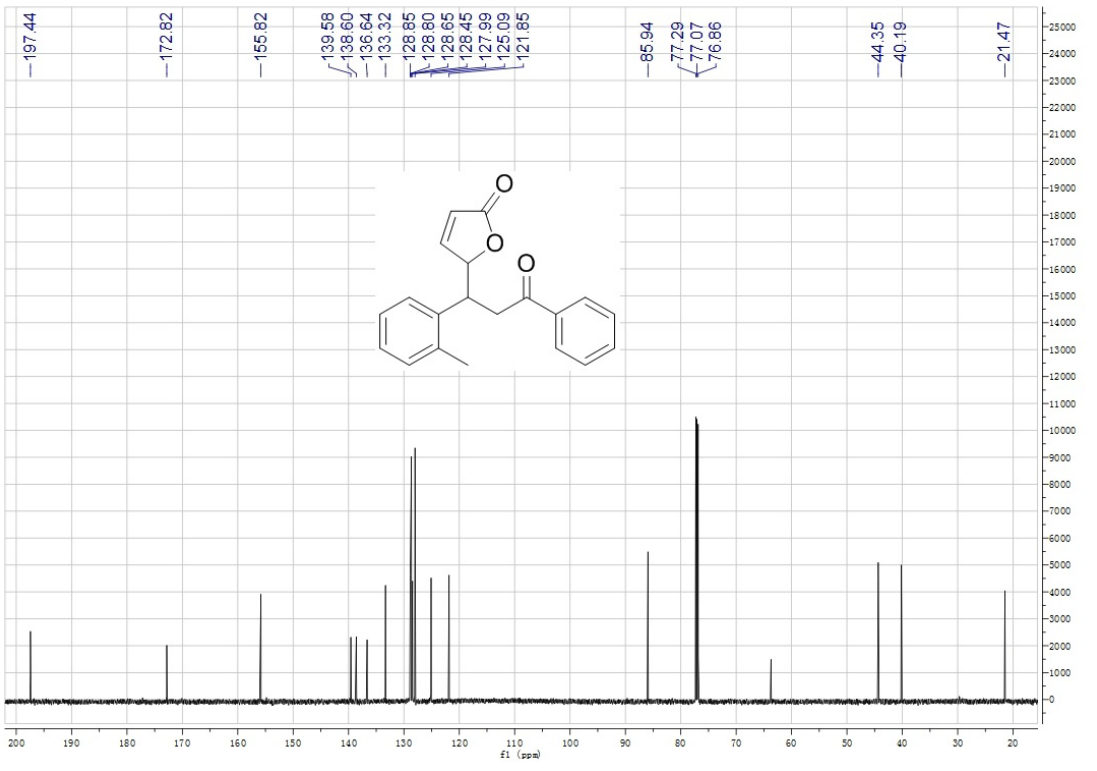
0.0
f1 (ppm)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128.85
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128.65
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127.99
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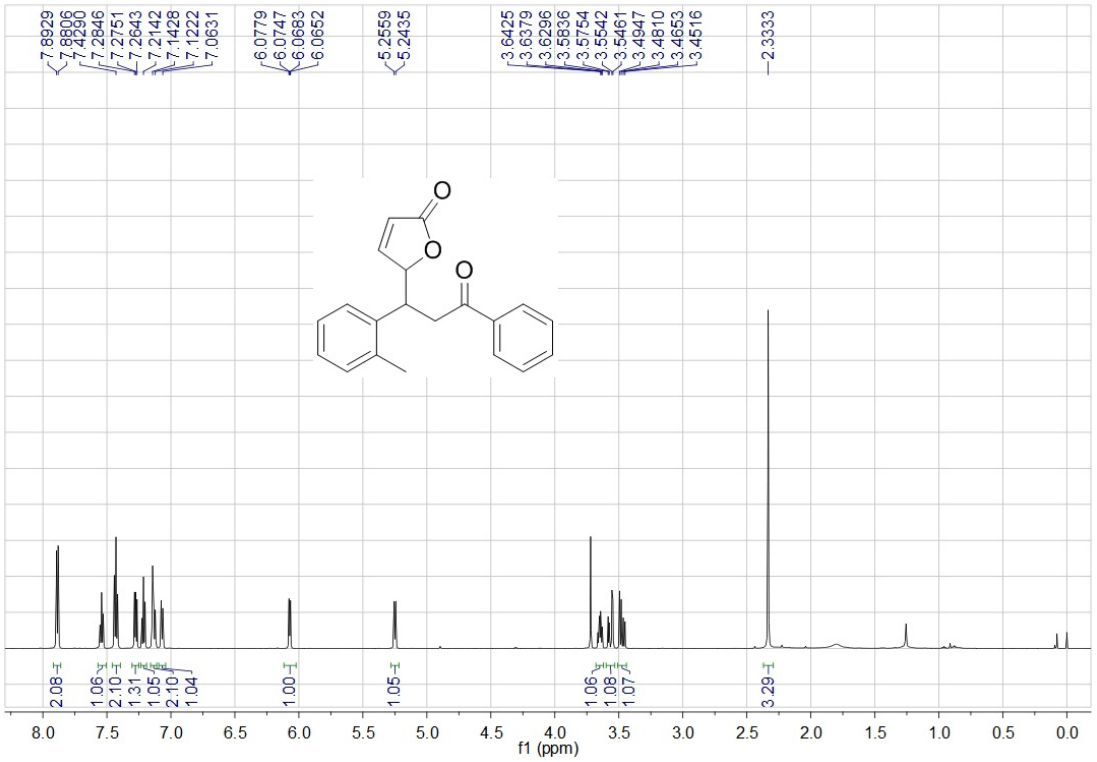
85.94
77.29
77.07
76.86
44.35
40.19
21.47
f1 (ppm)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7.1222
7.0631
6.0779
6.0747
6.0683
6.0652
5.2559
5.2435
3.6425
3.6379
3.6296
3.5836
3.5754
3.5542
3.5461
3.4947
3.4810
3.4653
3.4516
2.3333
O
O
O
2.08
1.06
2.10
1.31
1.05
2.10
1.04
1.00
1.05
1.06
1.08
1.07
3.29
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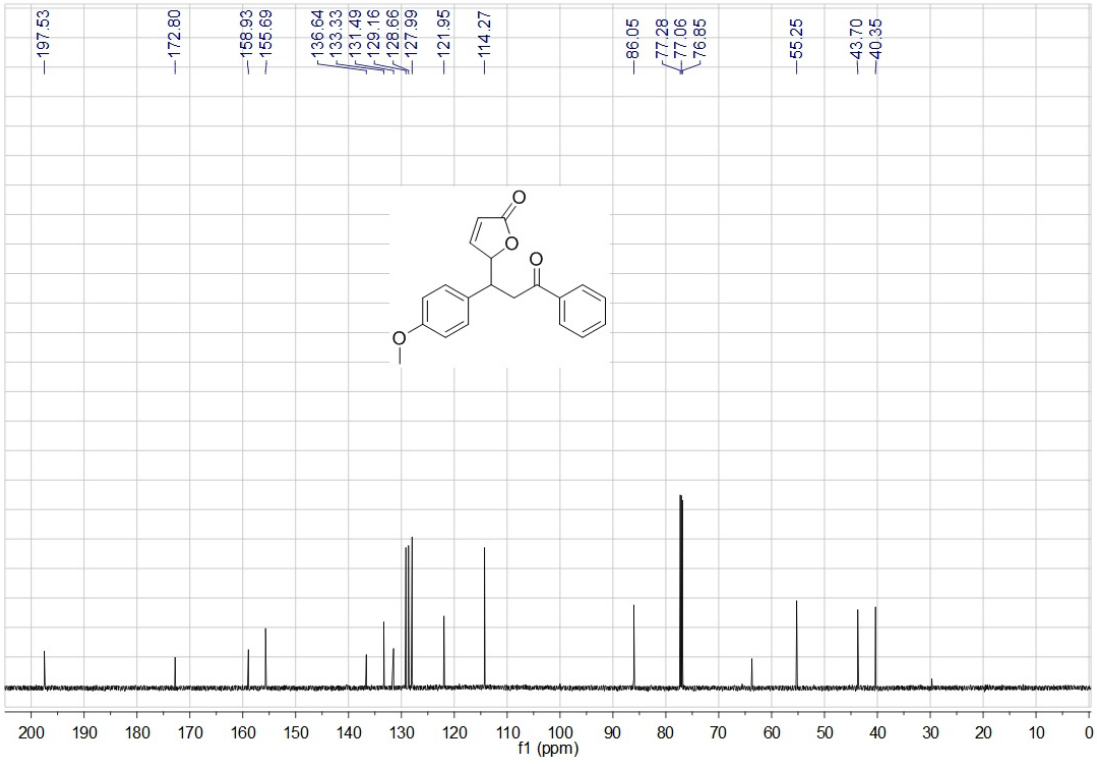
f1 (ppm)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133.33
131.49
129.16
128.66
127.99
121.95
114.27
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77.28
77.06
76.85
55.25
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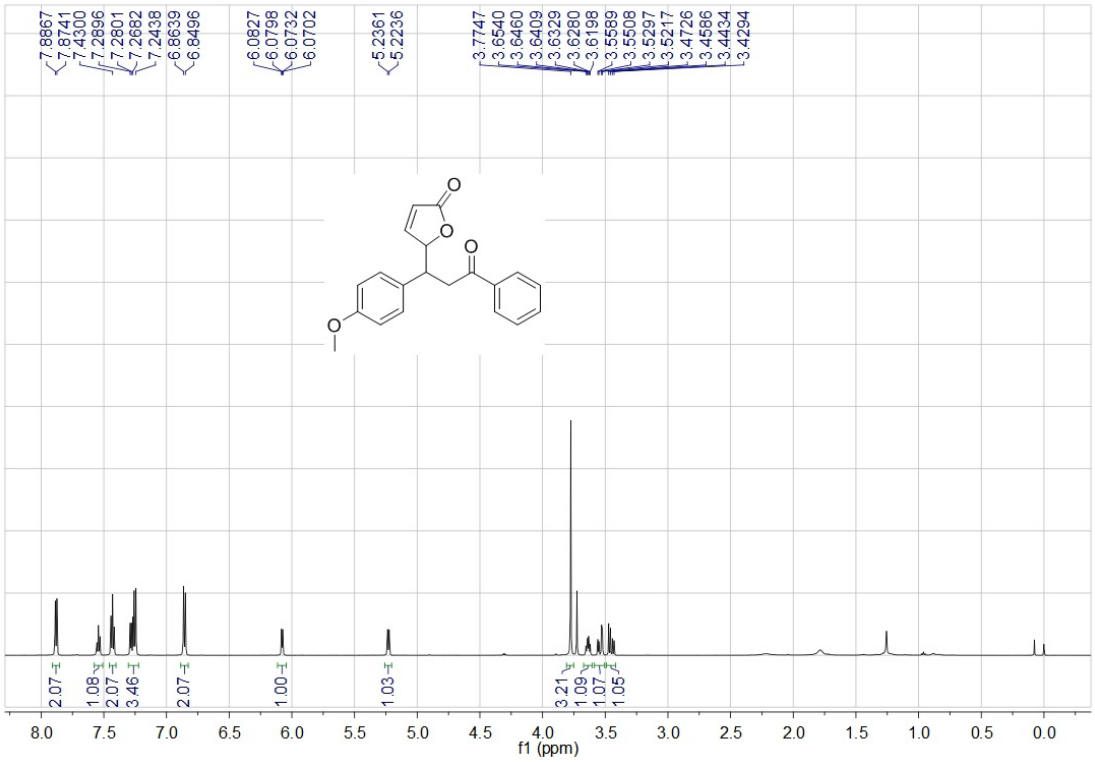
40.35
O
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.2438
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6.0732
6.0702
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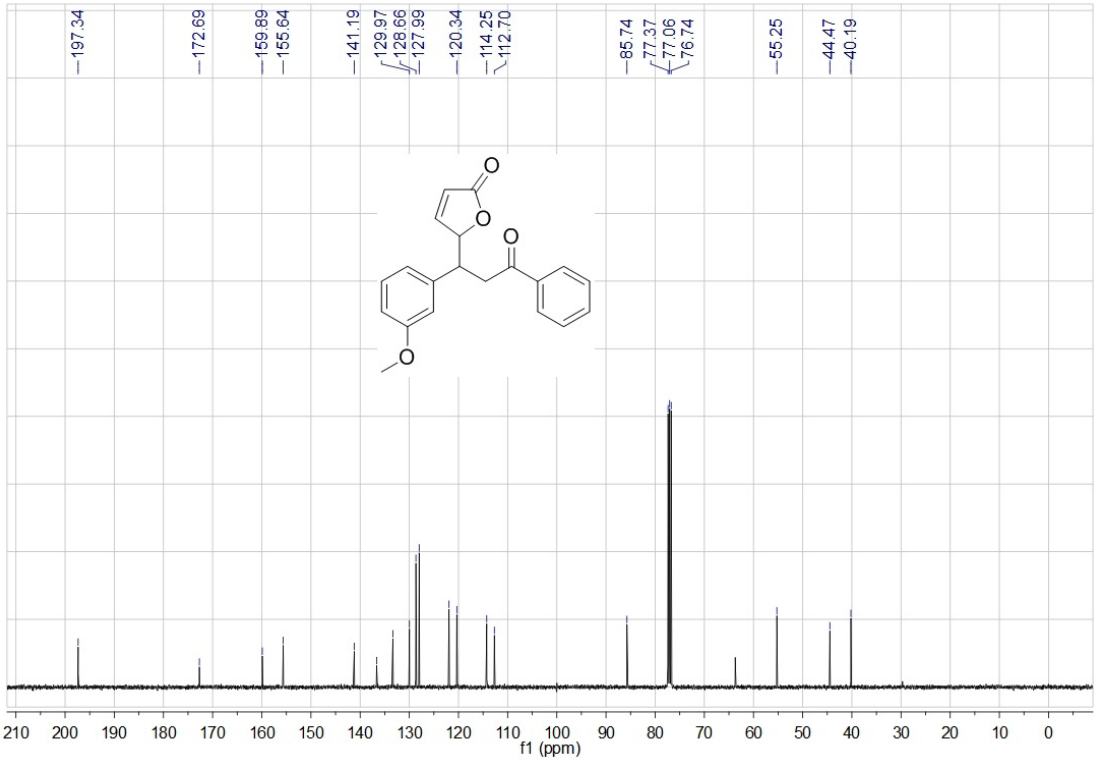
5.2236
3.7747
3.6540
3.6460
3.6409
3.6329
3.6280
3.6198
3.5589
3.5508
3.5297
3.5217
3.4726
3.4586
3.4434
3.4294
2.07
1.08
2.07
3.46
2.07
1.00
1.03
3.21
1.09
1.07
1.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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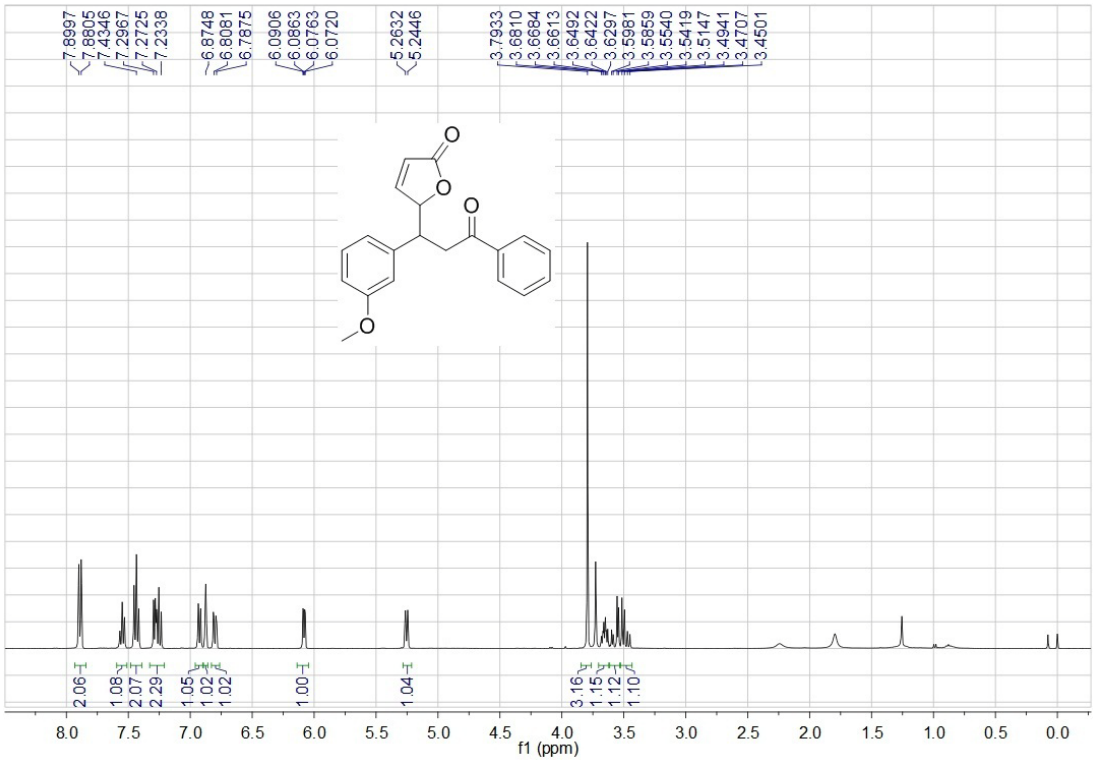
129.97
128.66
127.99
120.34
114.25
112.70
85.74
77.37
77.06
76.74
55.25
44.47
40.19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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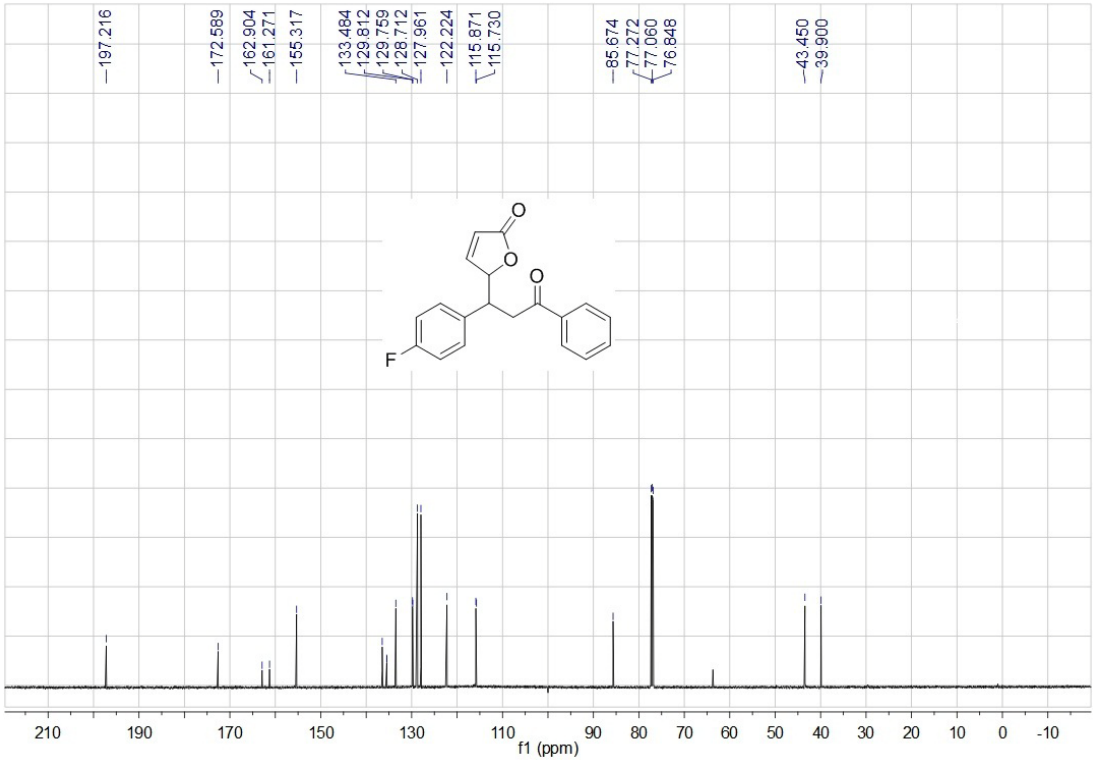
7.2967
7.2725
7.2338
6.8748
6.8081
6.7875
6.0906
6.0863
6.0763
6.0720
5.2632
5.2446
3.7933
3.6810
3.6684
3.6613
3.6492
3.6422
3.6297
3.5981
3.5859
3.5540
3.5419
3.5147
3.4941
3.4707
3.4501
O
O
O
O
2.06
1.08
2.07
2.29
1.05
1.02
1.02
1.00
1.04
3.16
1.15
1.12
1.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.759
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127.961
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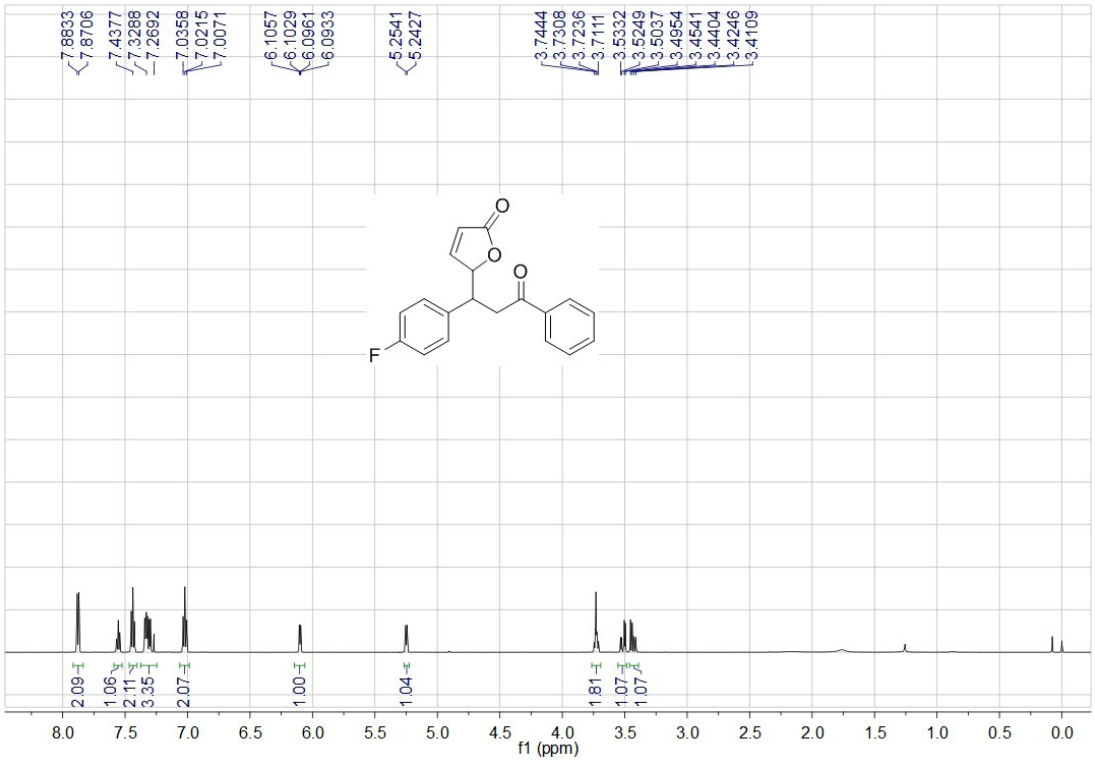
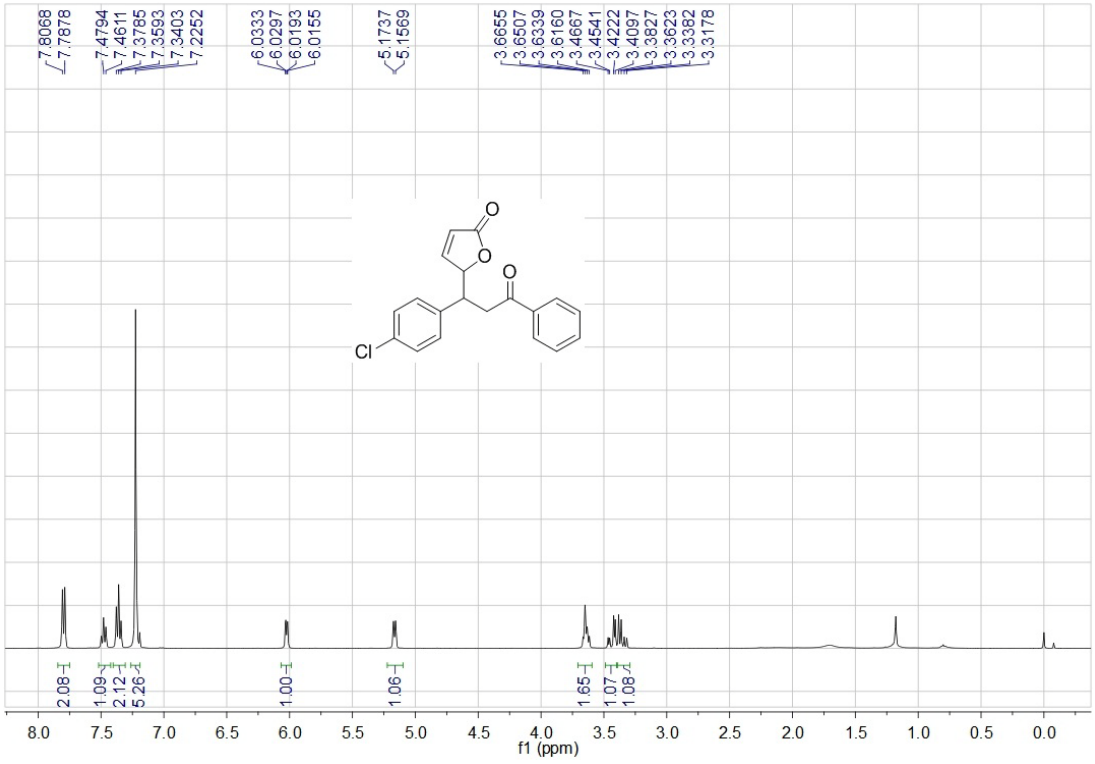
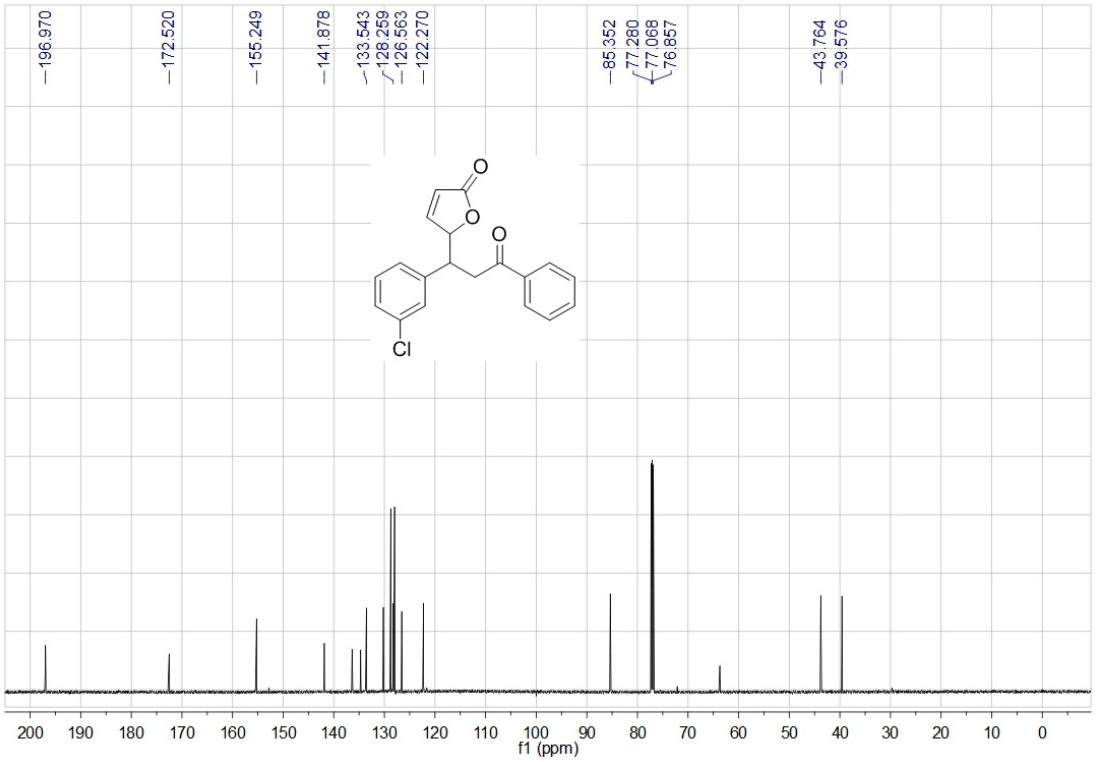
115.730
85.674
77.272
77.060
76.848
43.450
39.900
O
O
O
F
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

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122.270
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77.068
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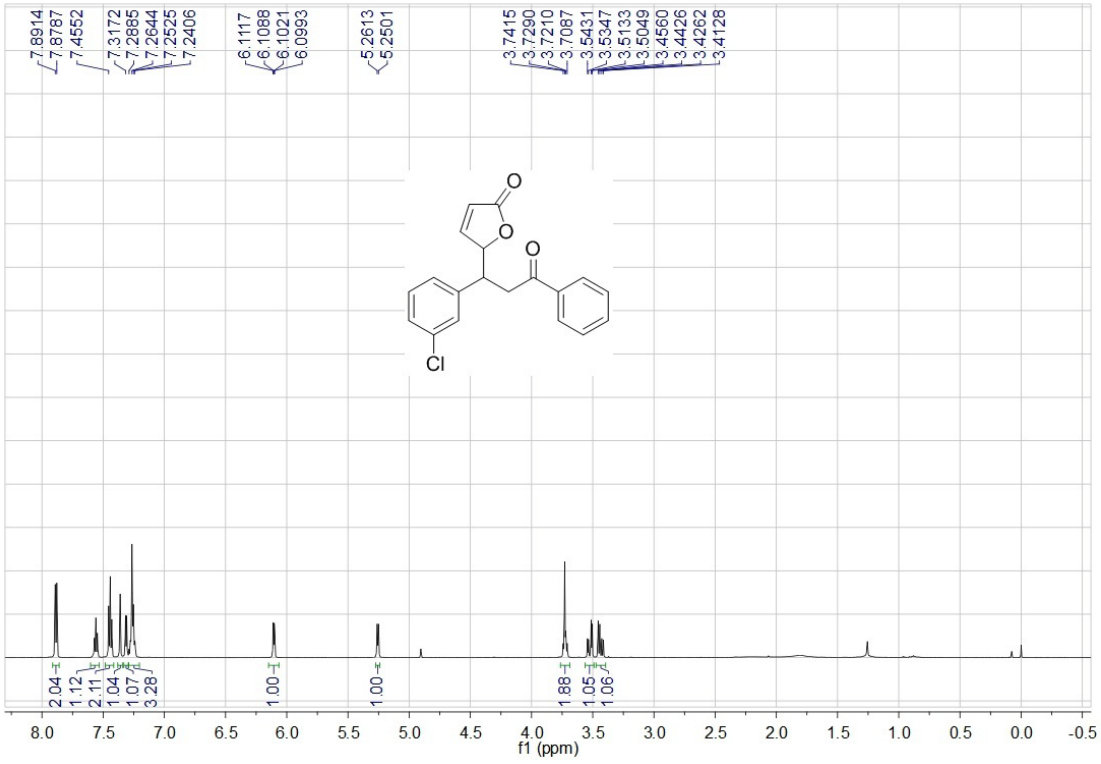
39.576
O
O
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.2644
7.2525
7.2406
6.1117
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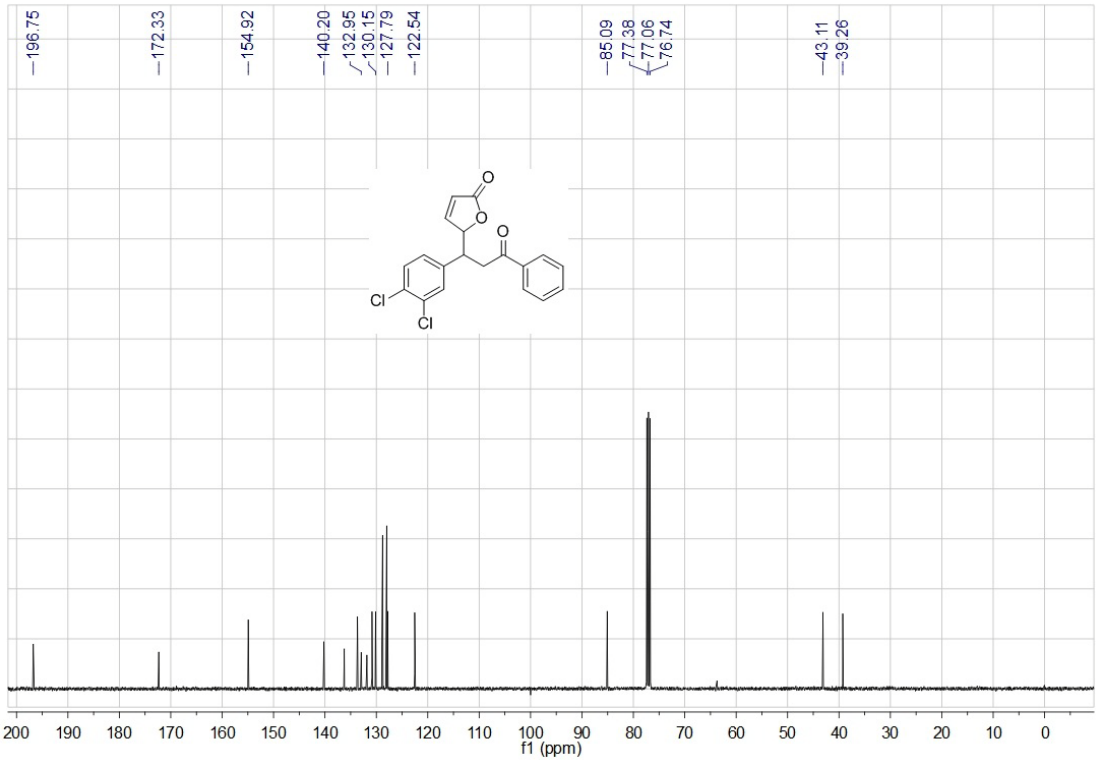
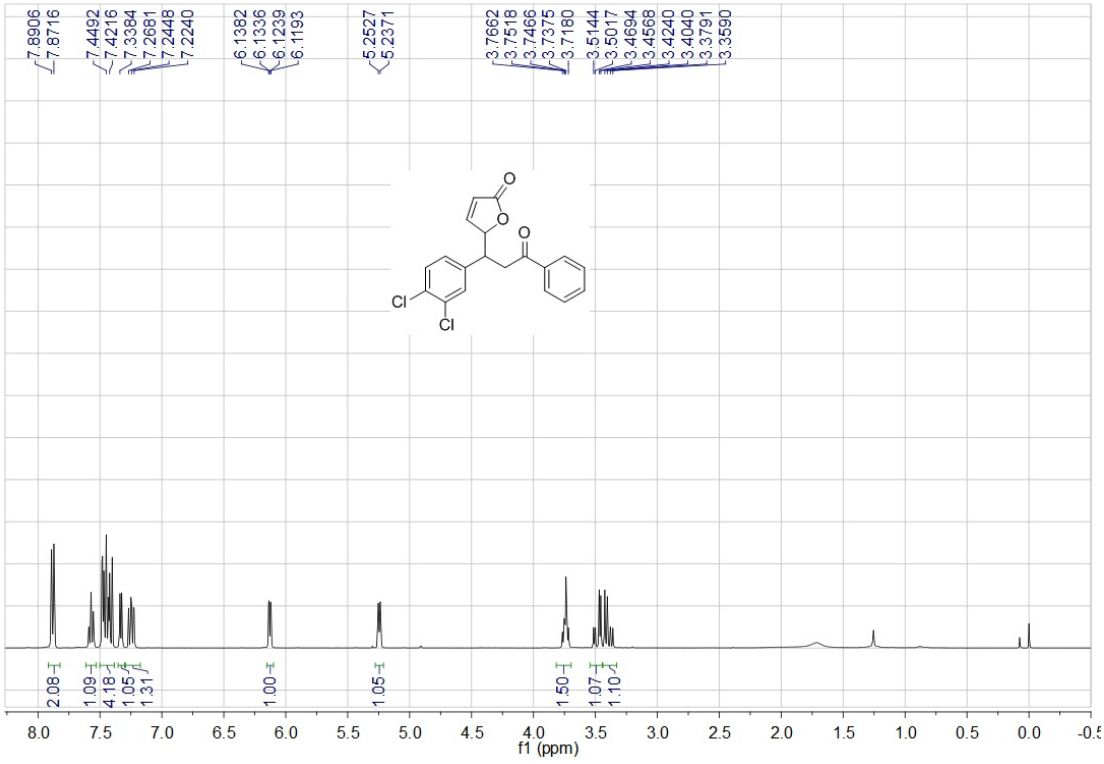
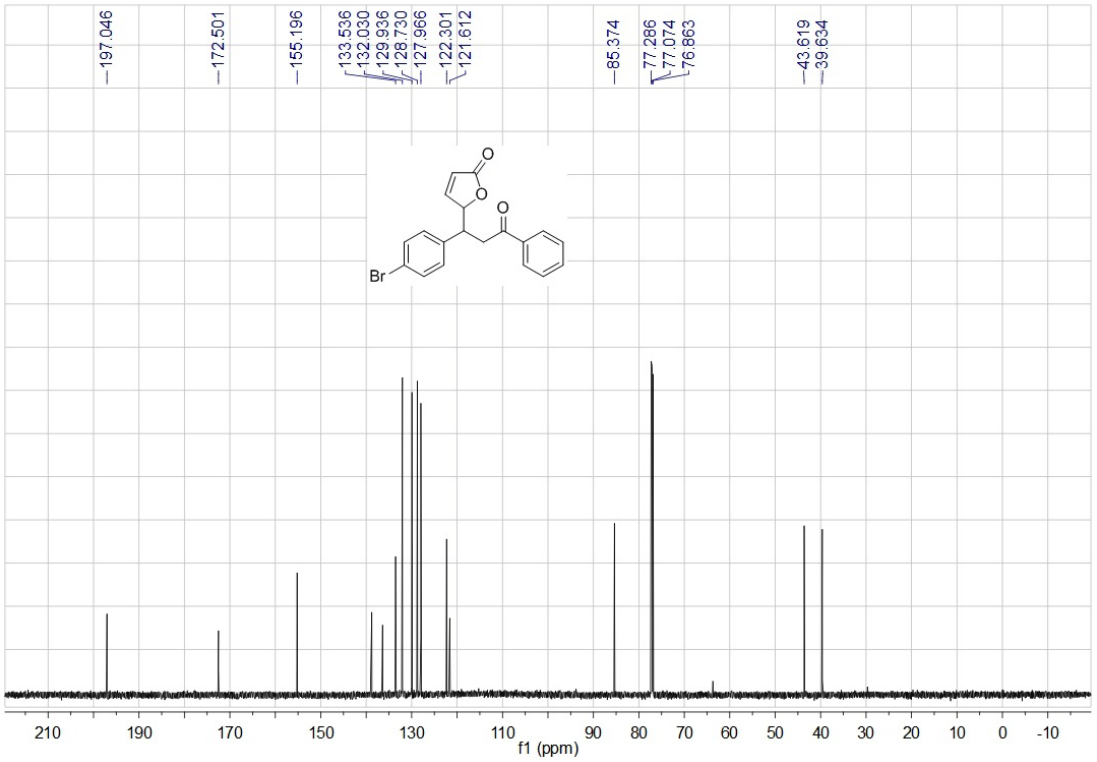
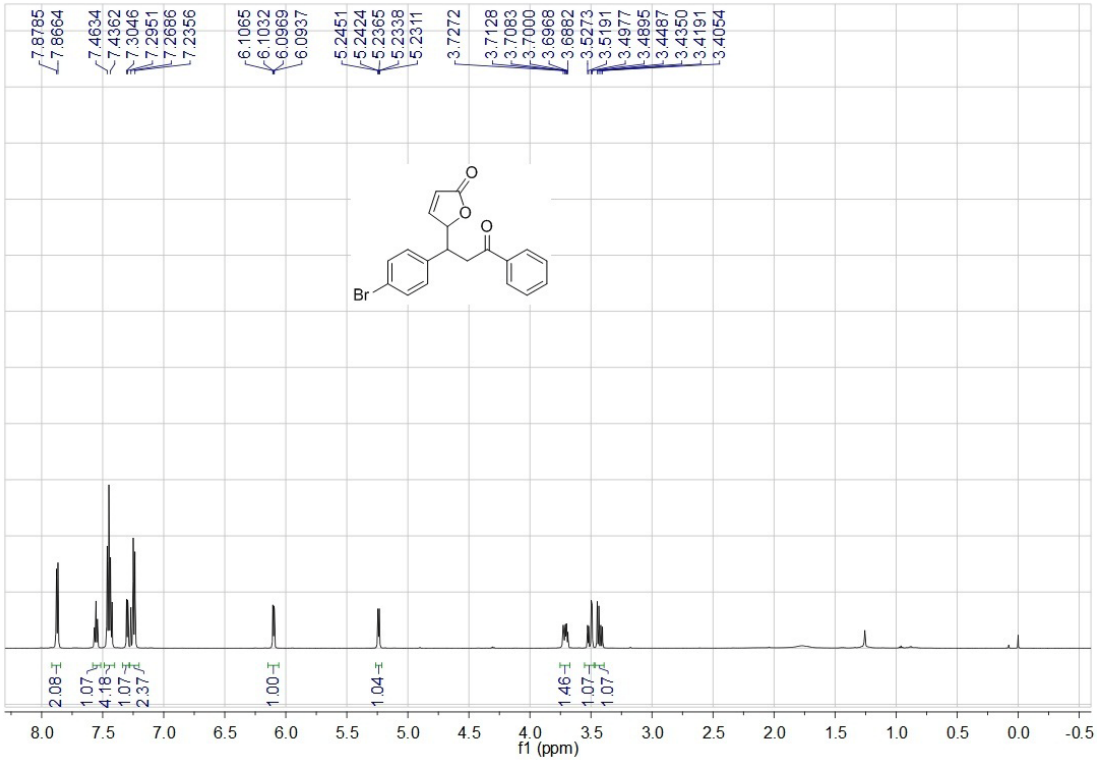
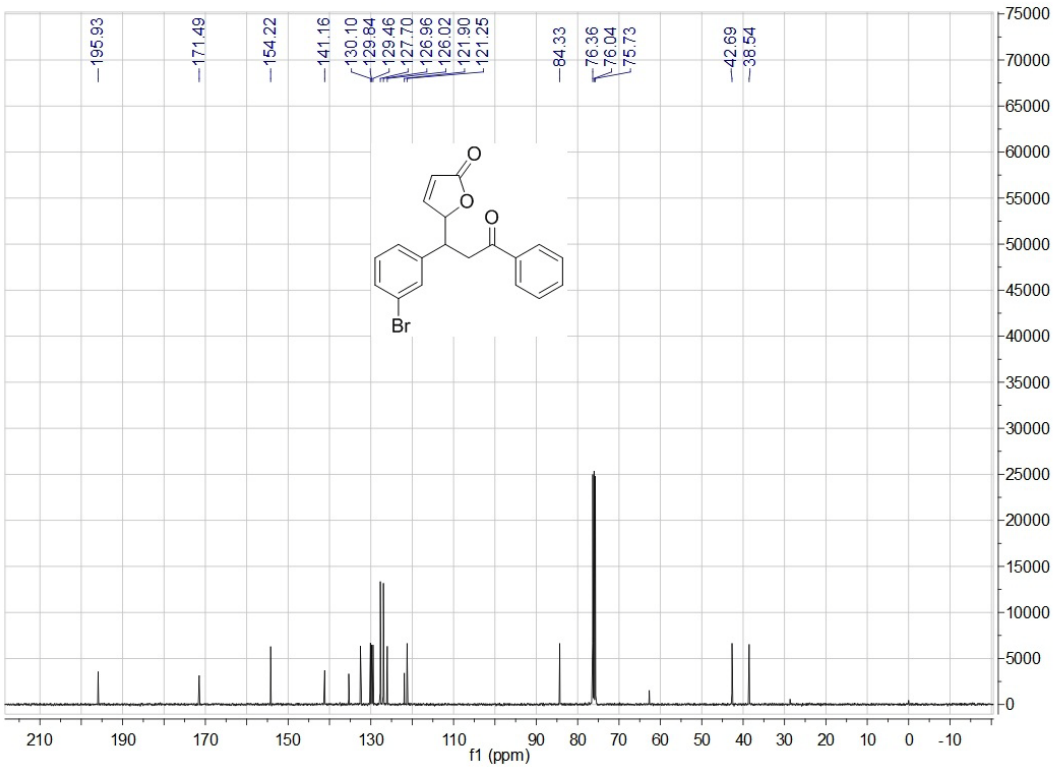
6.0993
5.2613
5.2501
3.7415
3.7290
3.7210
3.7087
3.5431
3.5347
3.5133
3.5049
3.4560
3.4426
3.4262
3.4128
O
O
O
Cl
2.04
1.12
2.11
1.04
1.07
3.28
1.00
1.00
1.88
1.05
1.06
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

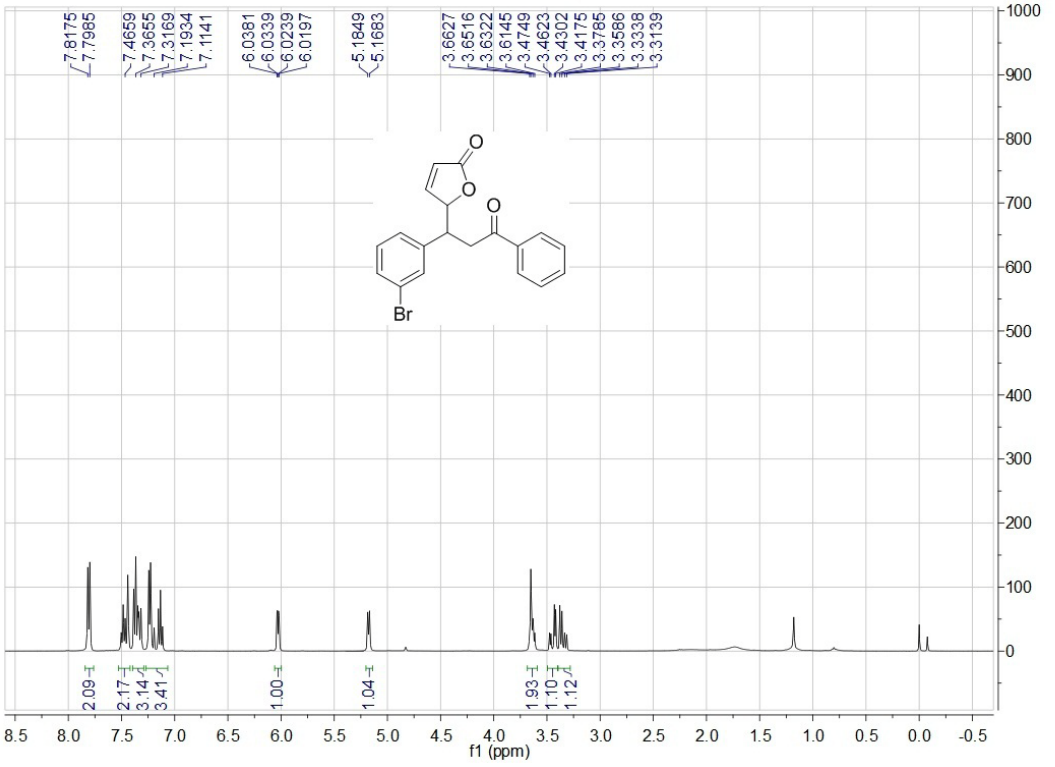


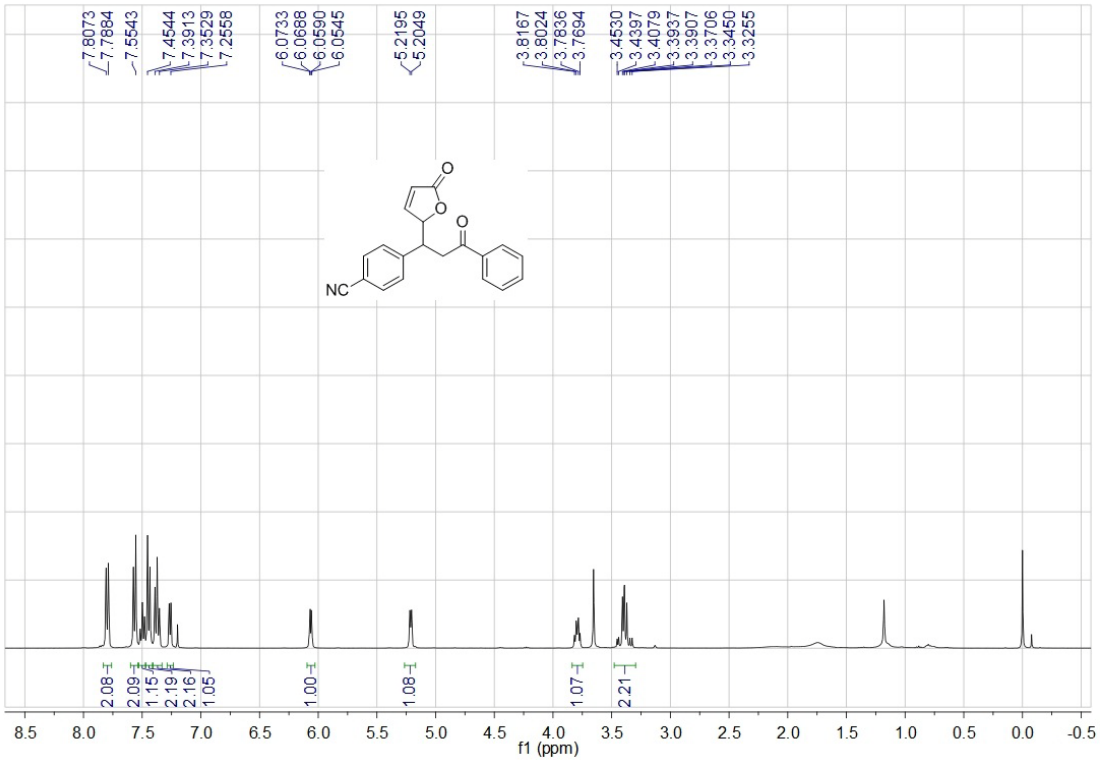



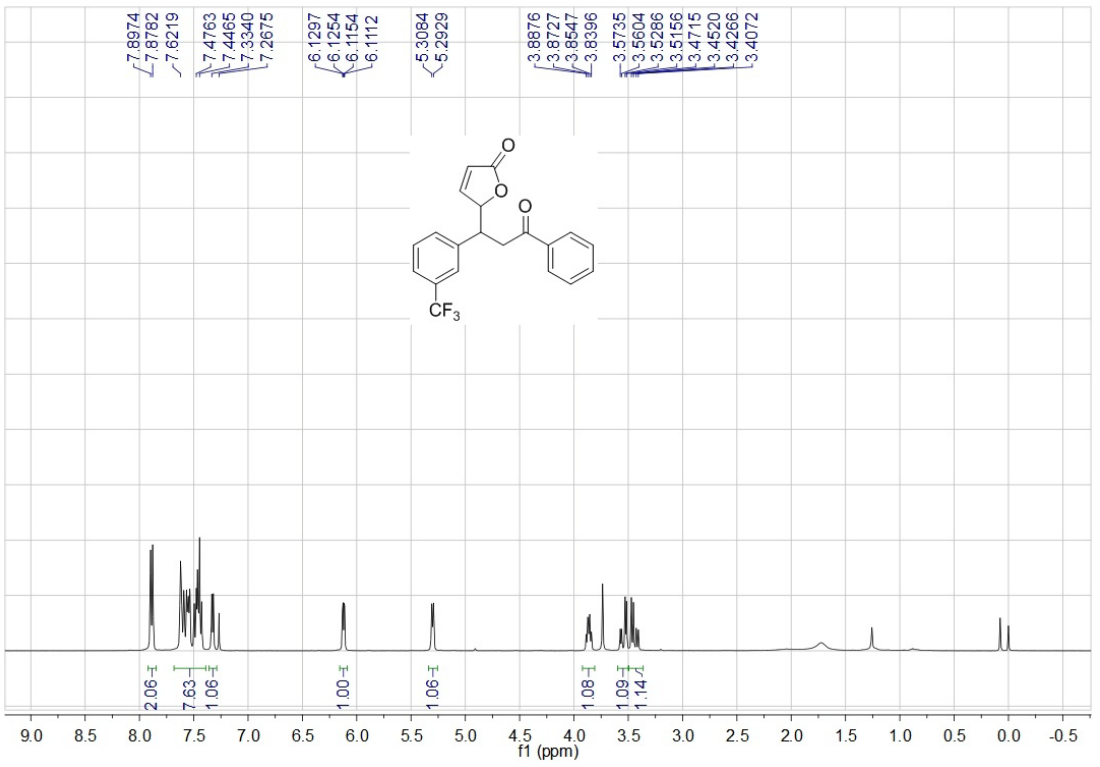


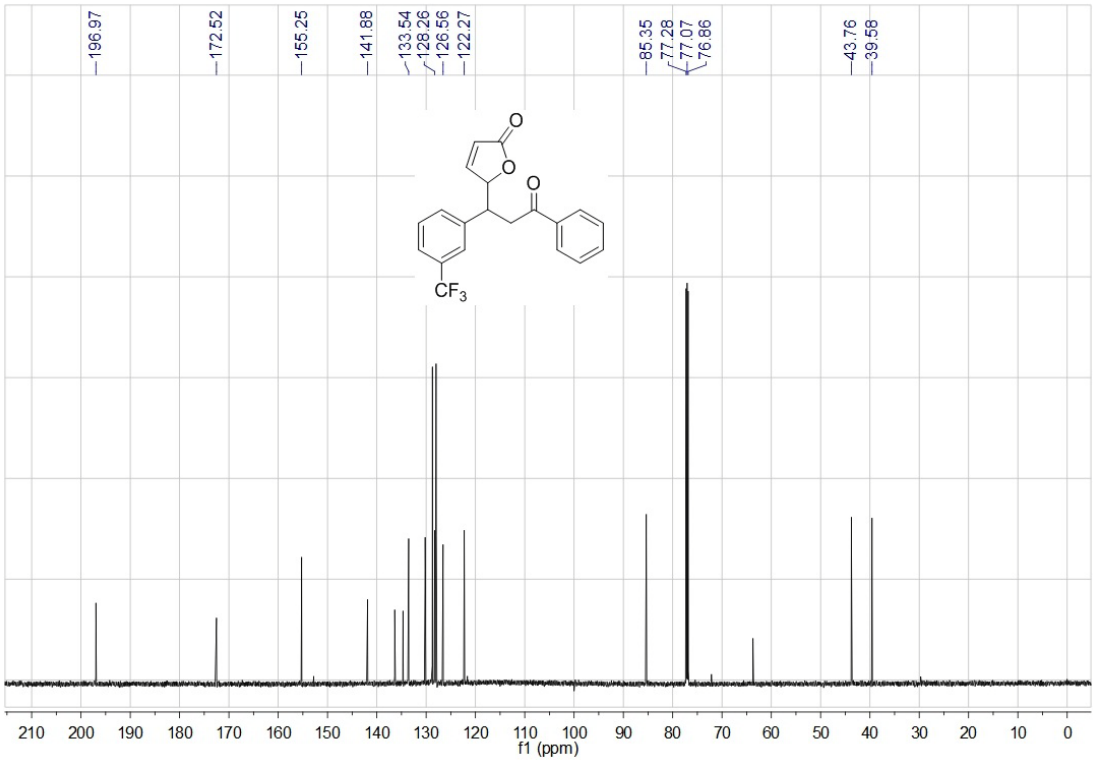



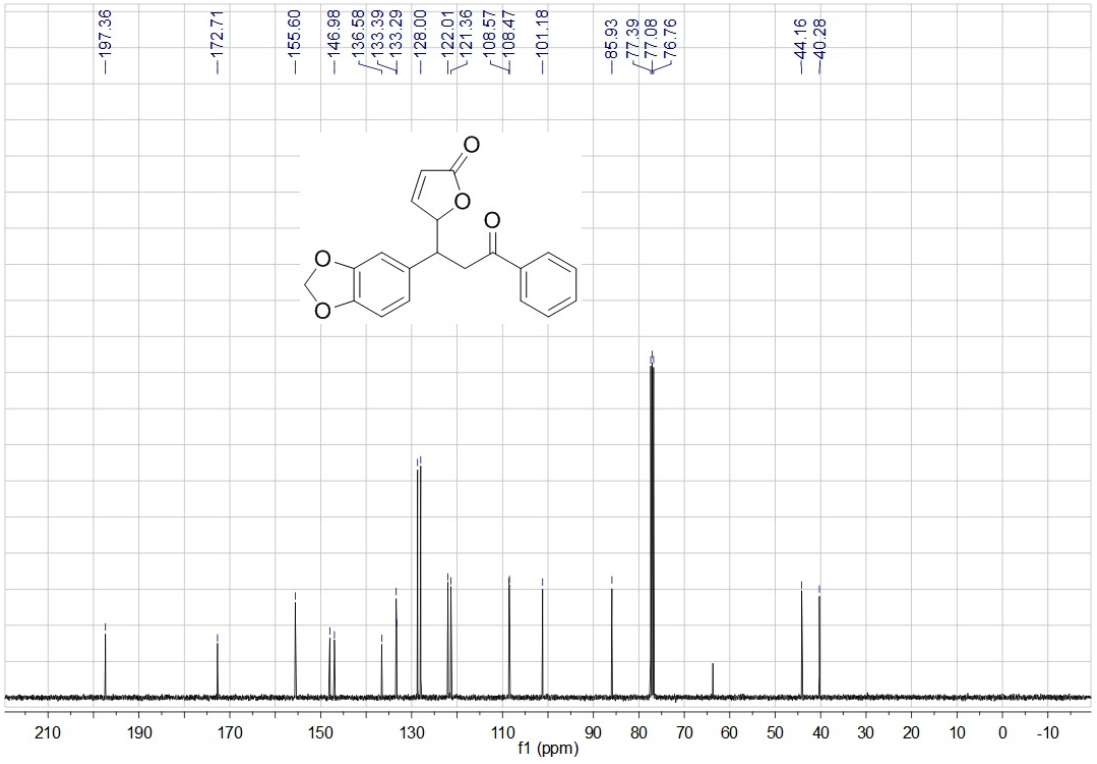


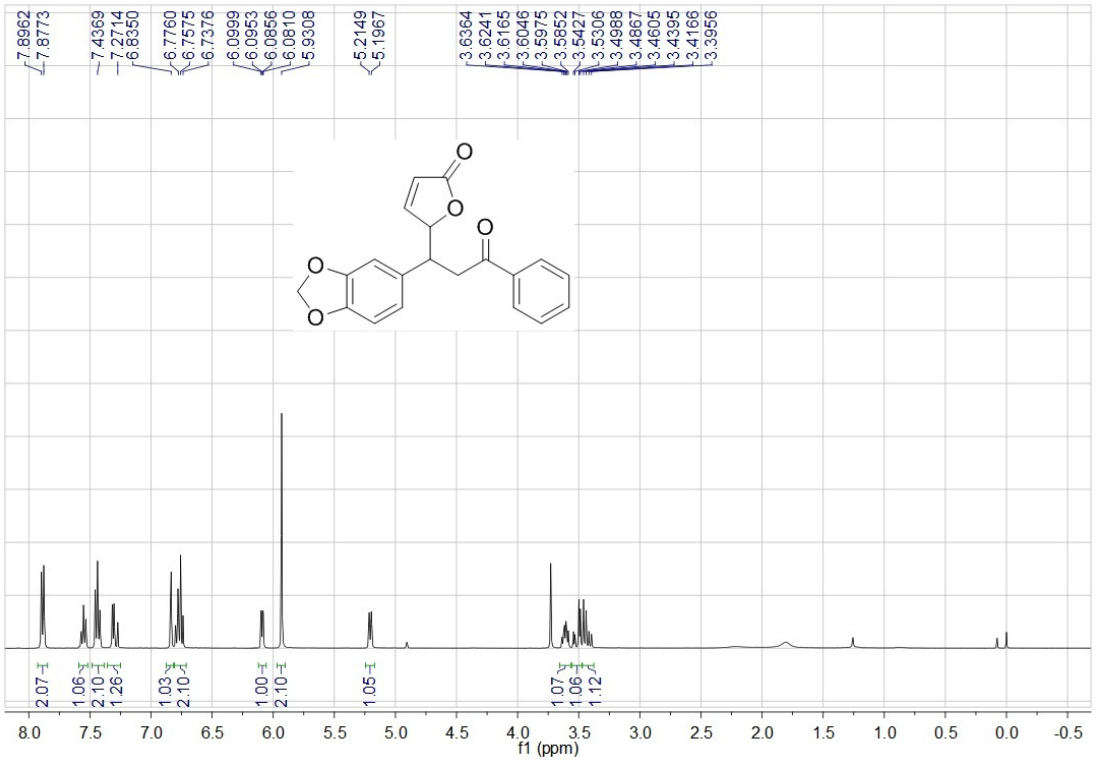





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6.0810
5.9308
5.2149
5.1967
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3.6241
3.6165
3.6046
3.5975
3.5852
3.5427
3.5306
3.4988
3.4867
3.4605
3.4395
3.4166
3.3956
2.07
1.06
2.10
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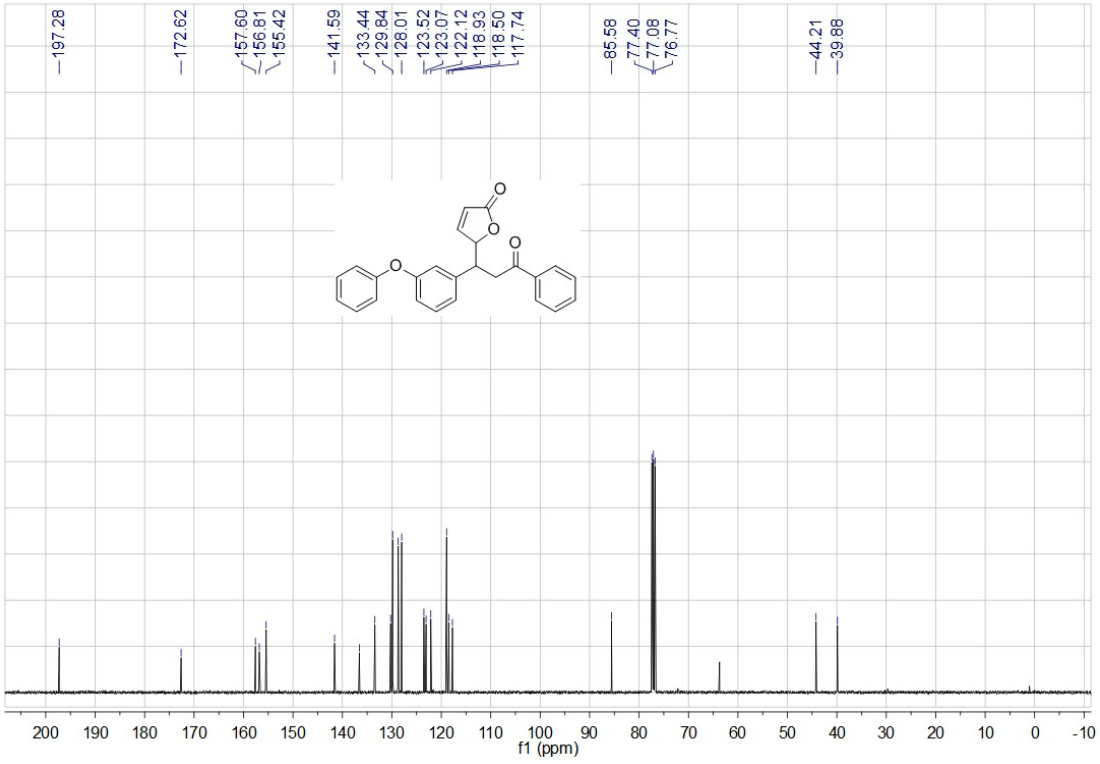
1.03
2.10
1.00
2.10
1.05
1.07
1.06
1.12
f1 (ppm)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141.59
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129.84
128.01
123.52
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122.12
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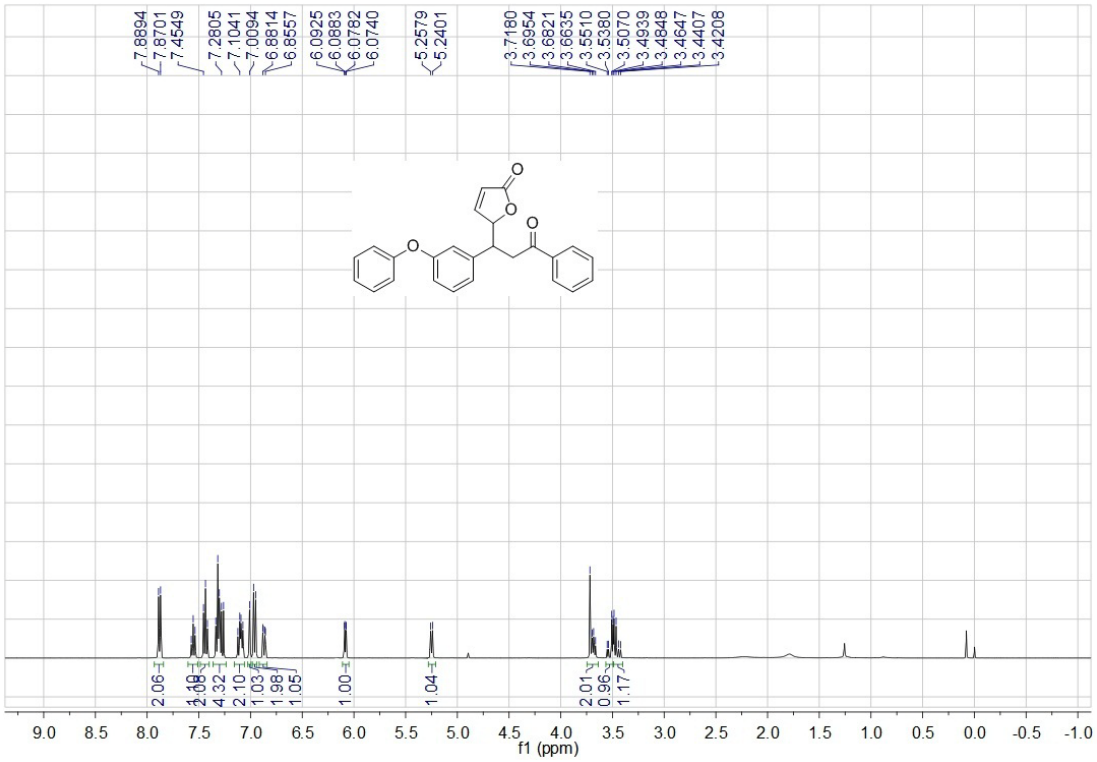
77.08
76.77
44.21
39.88
f1 (ppm)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6.0925
6.0883
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3.5380
3.5070
3.4939
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3.4208
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2.01
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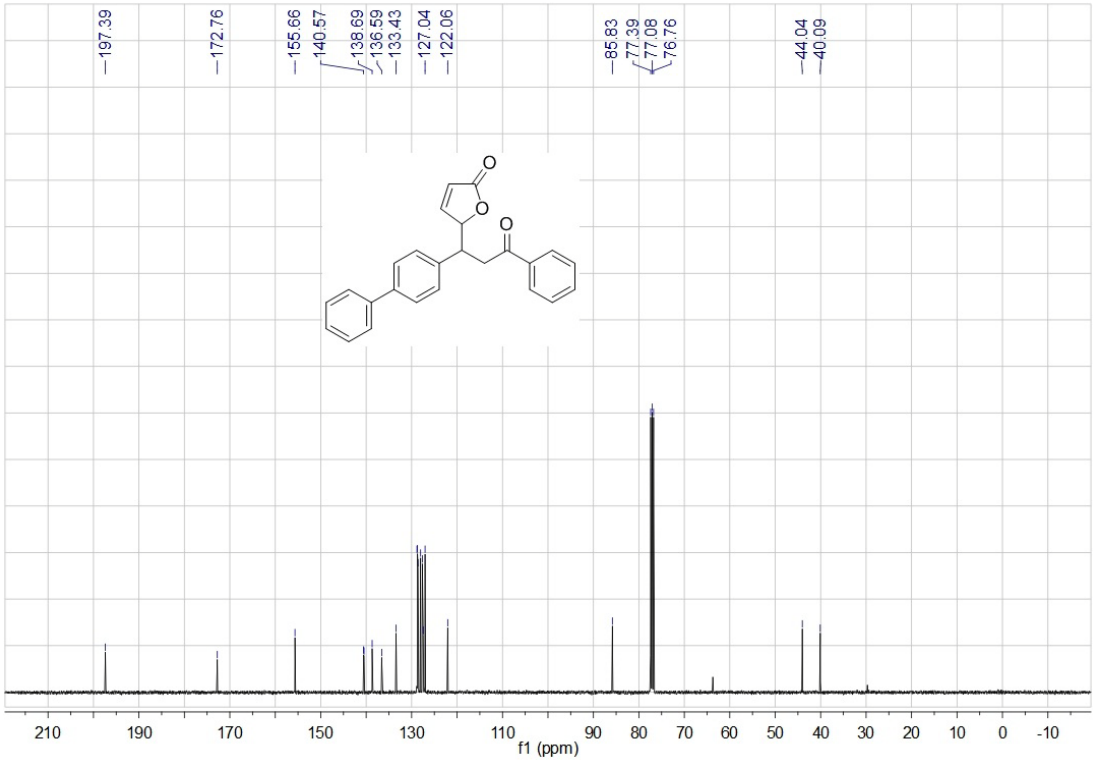
1.17
f1 (ppm)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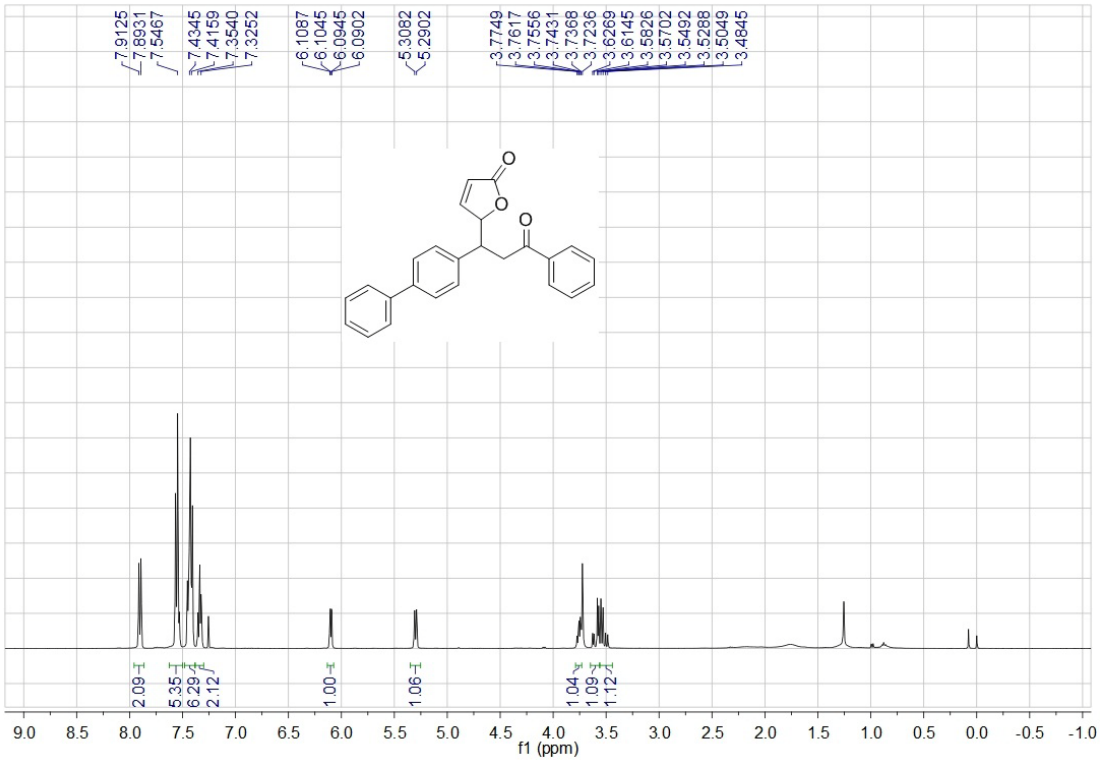
127.04
122.06
85.83
77.39
77.08
76.76
44.04
40.09
f1 (ppm)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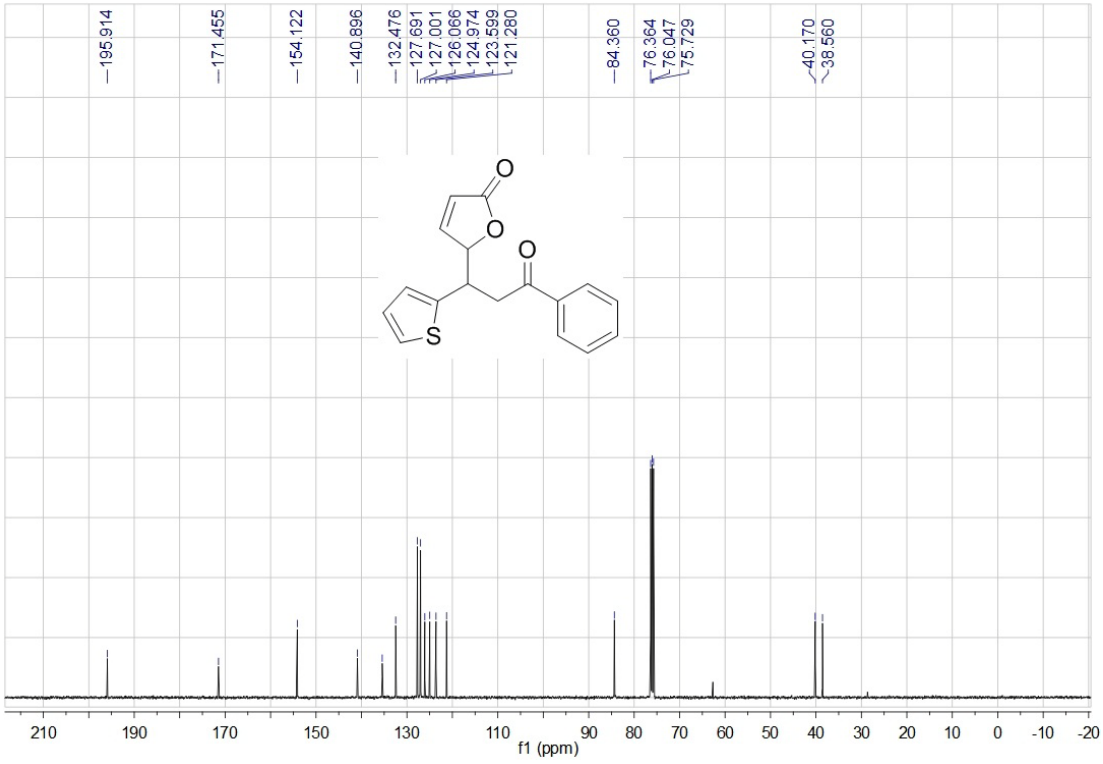
3.4845
O
O
O
2.09
5.35
6.29
2.12
1.00
1.06
1.04
1.09
1.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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84.360
76.364
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38.560
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O
O
S
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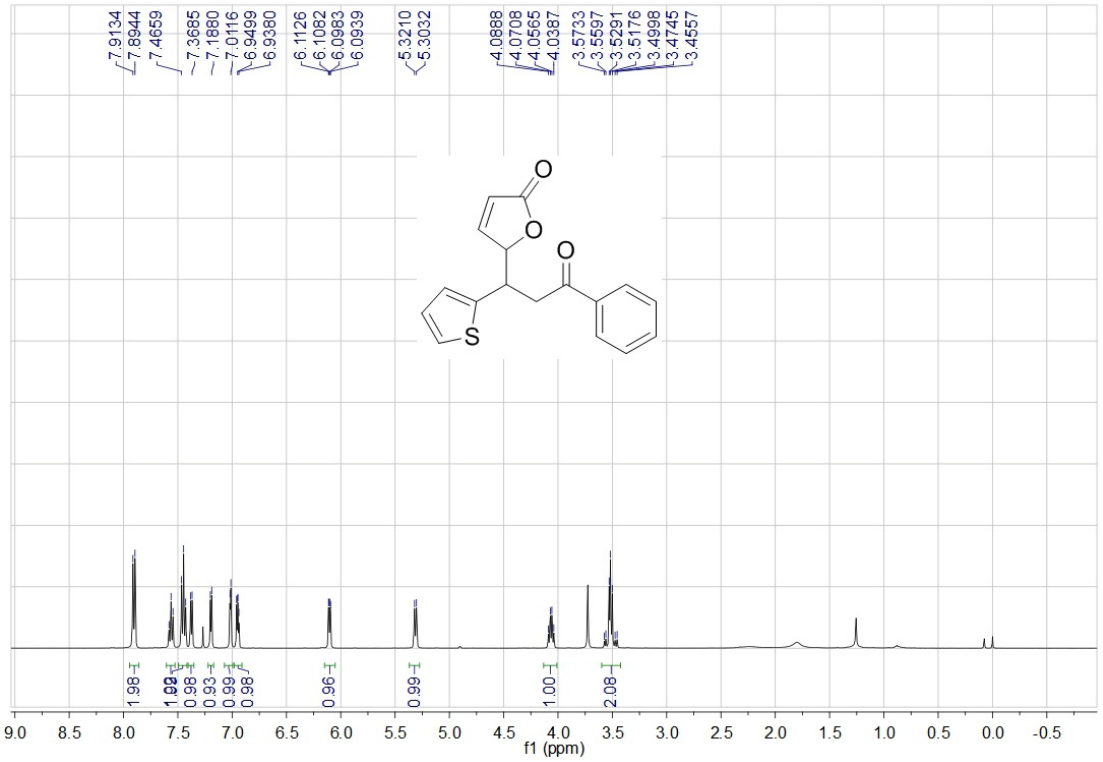
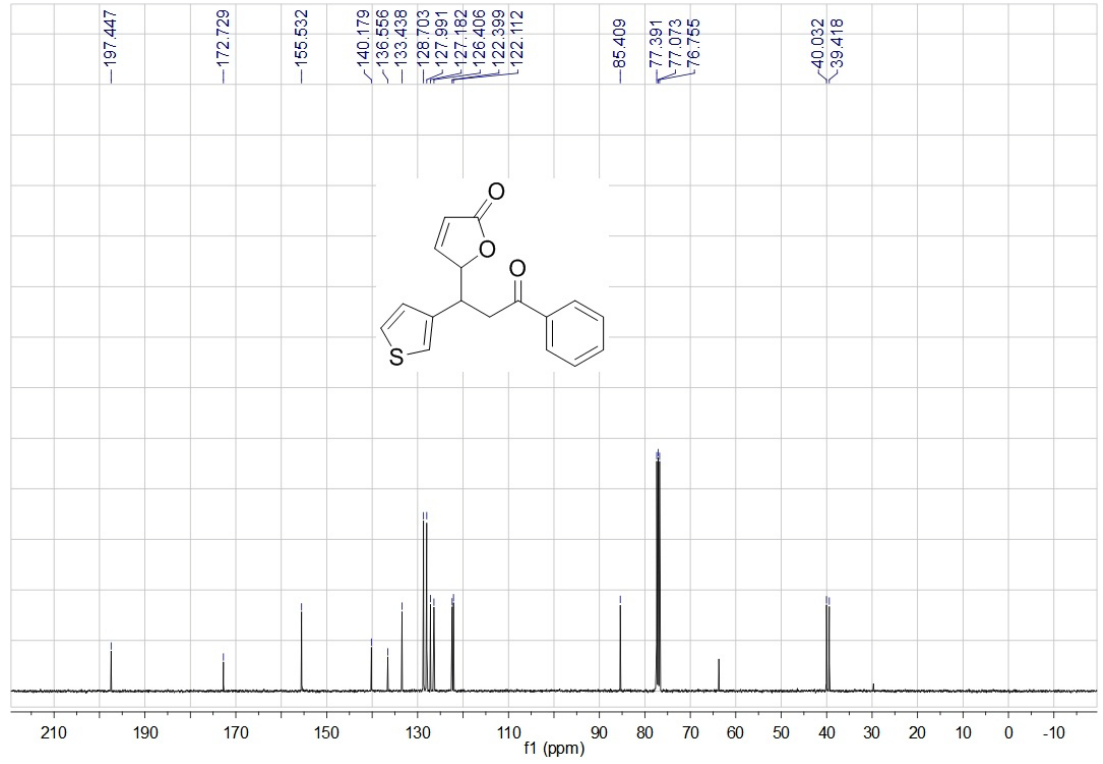
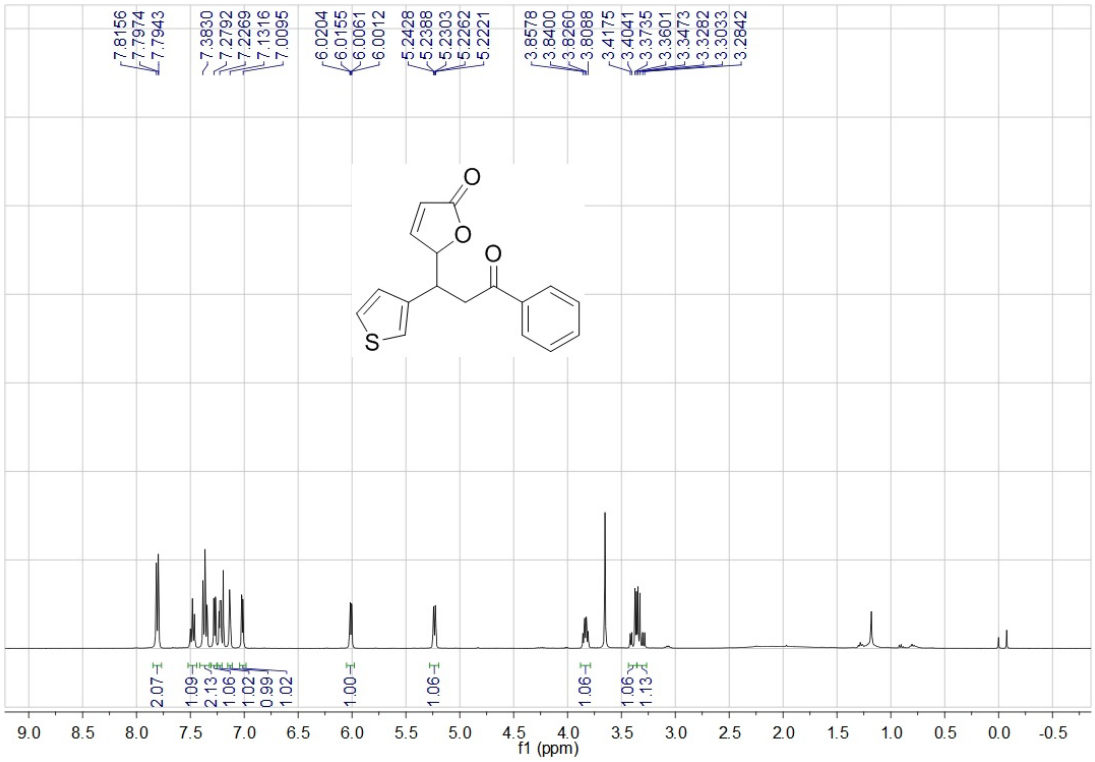
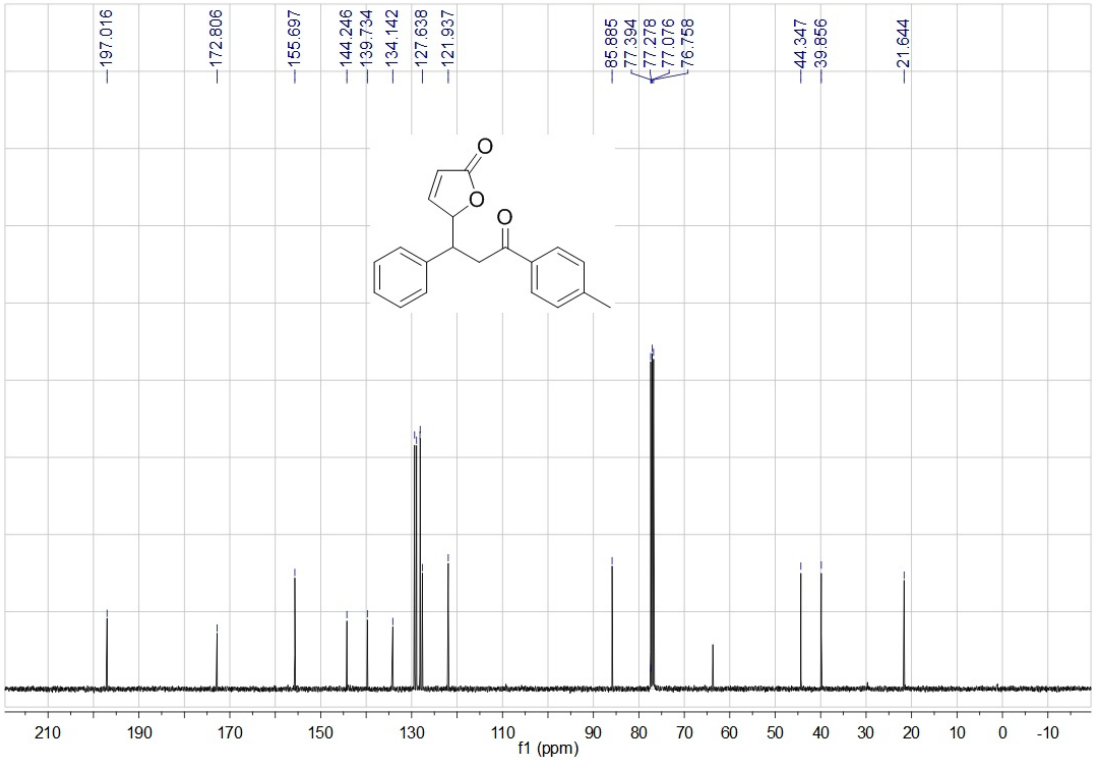
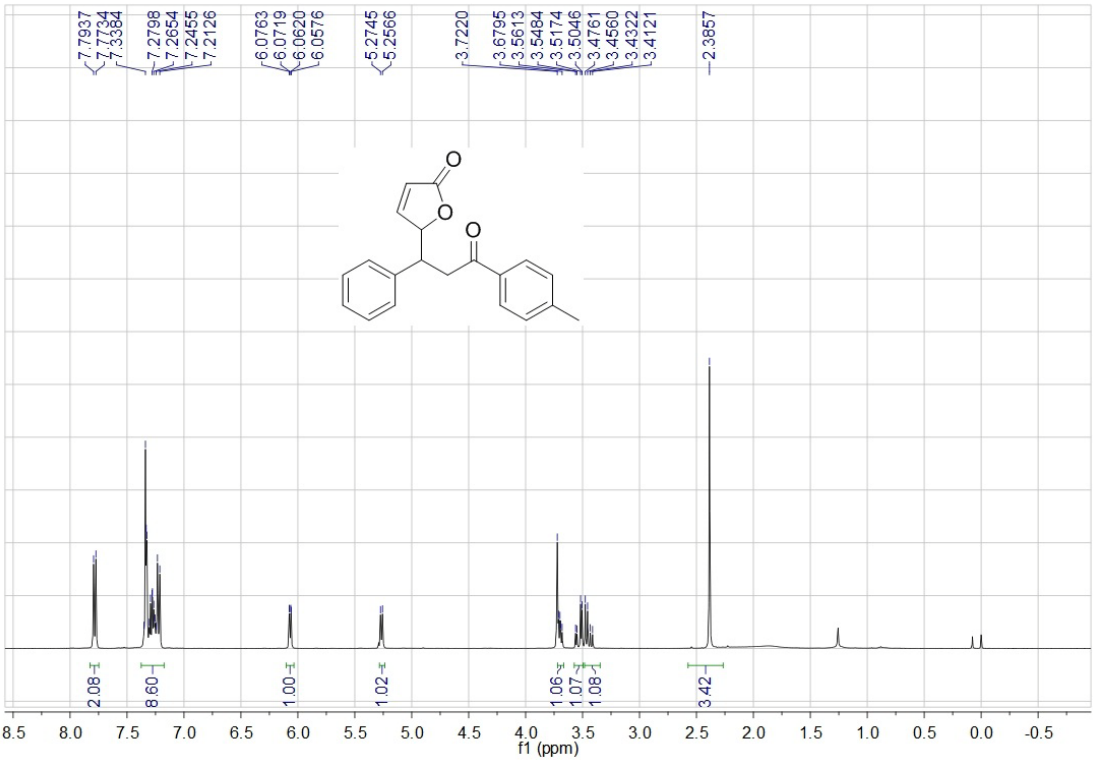
f1 (ppm)

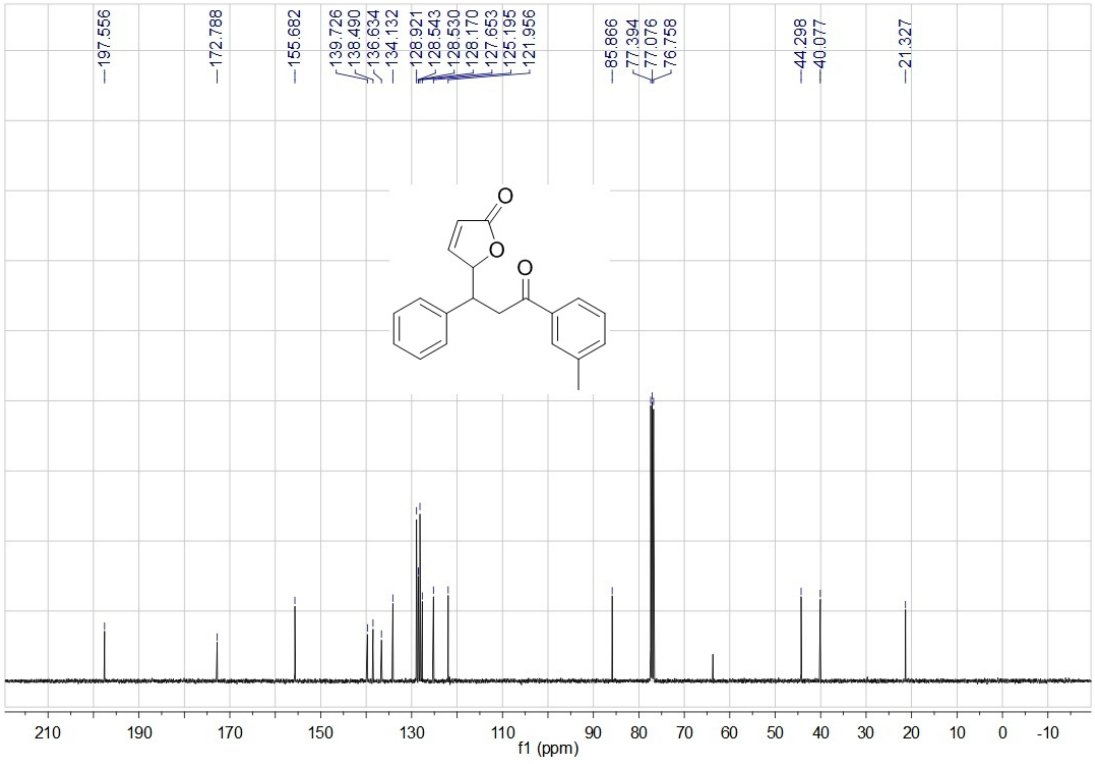


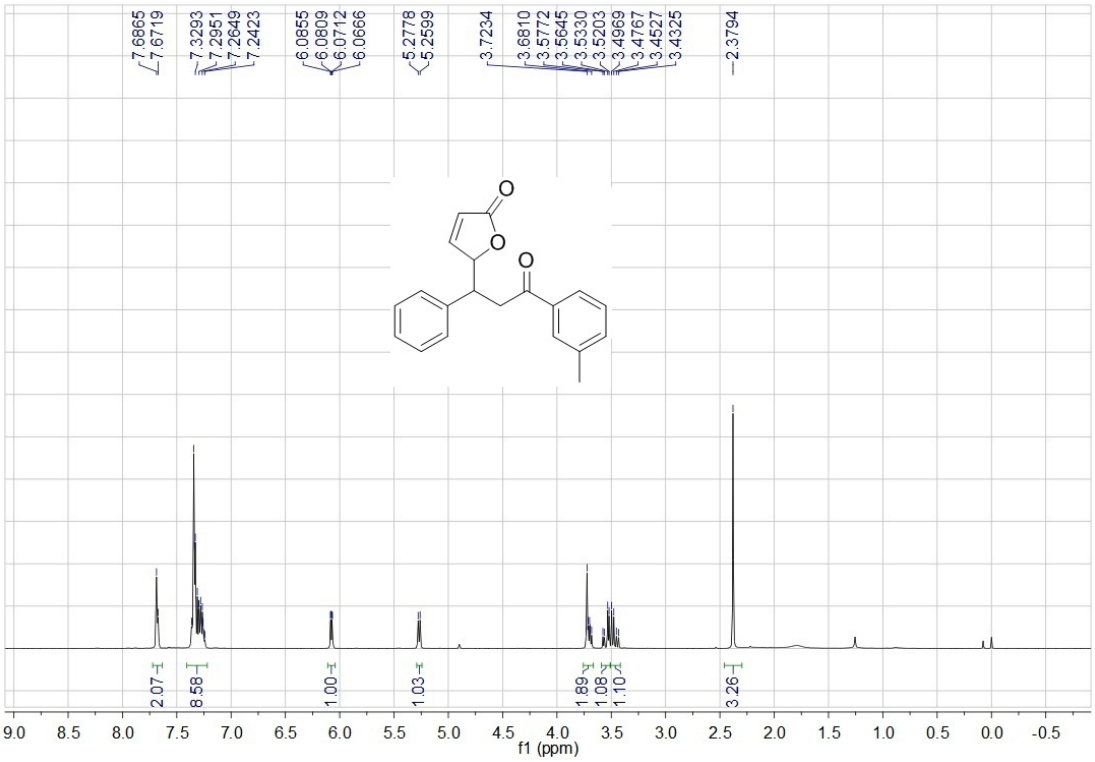





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3.7234
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3.5772
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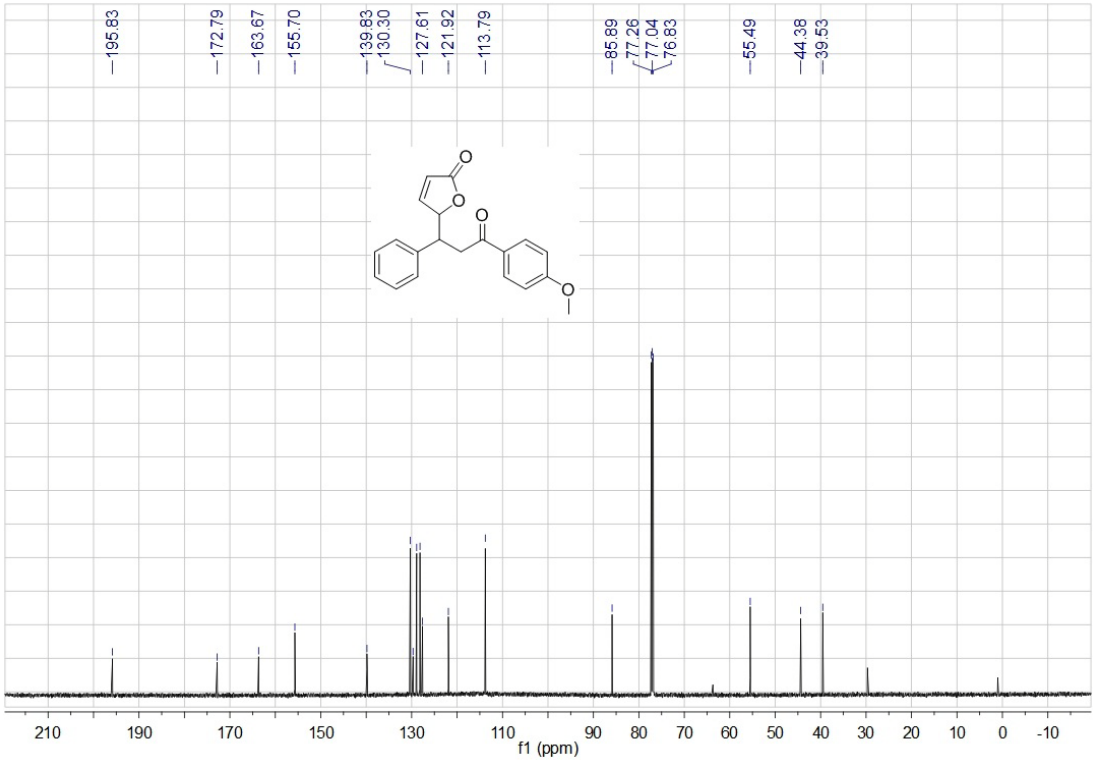
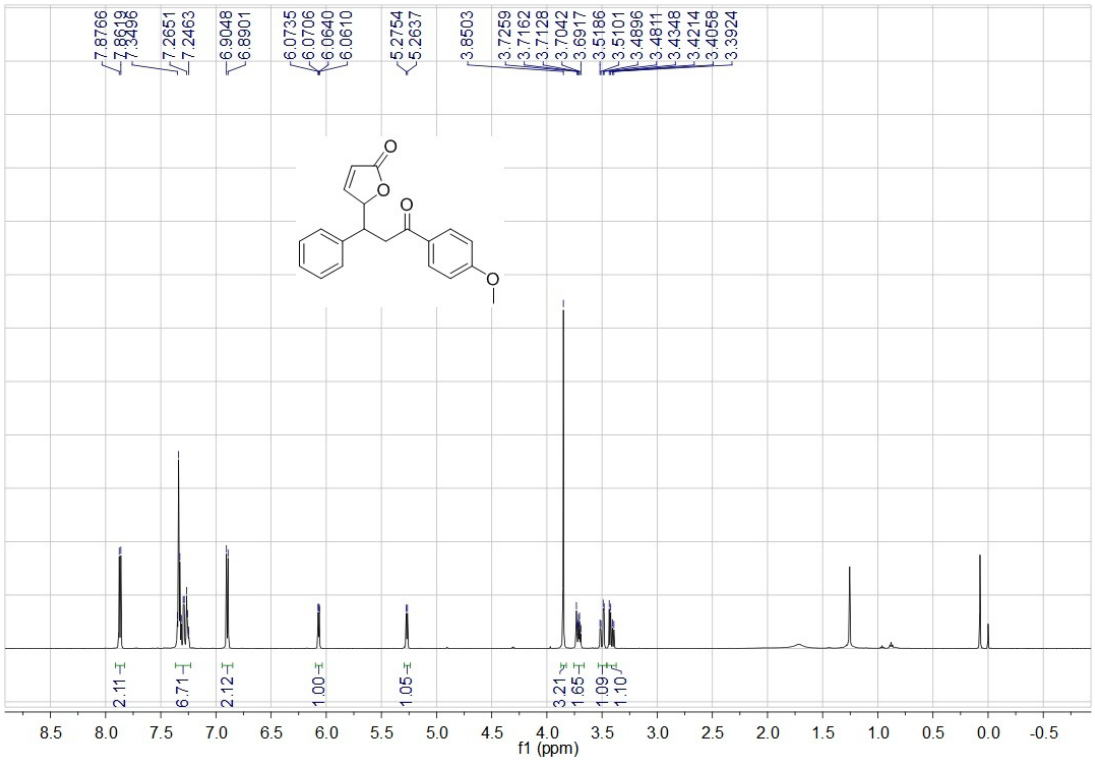
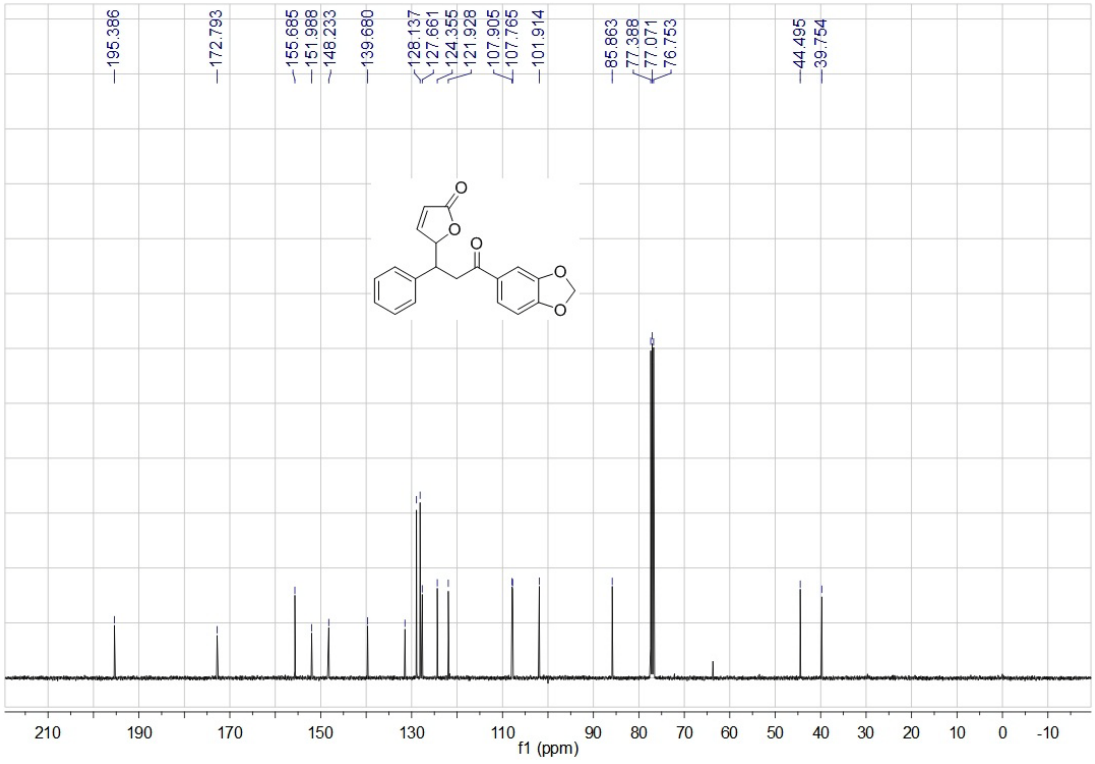
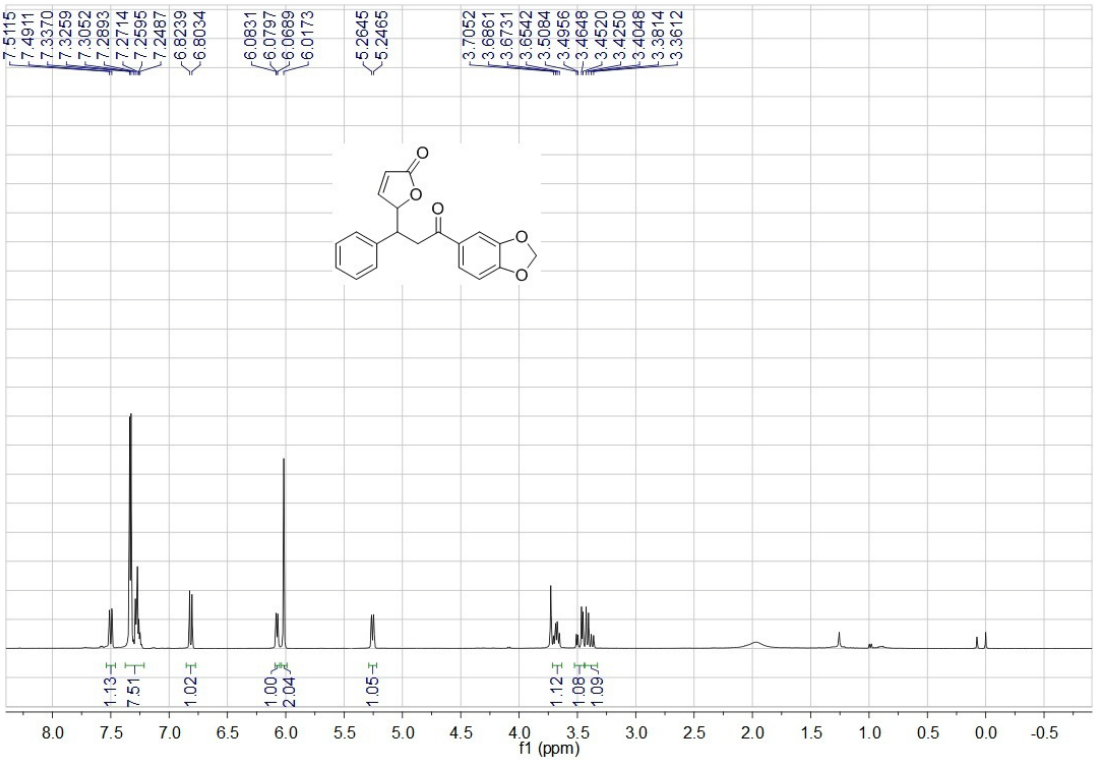
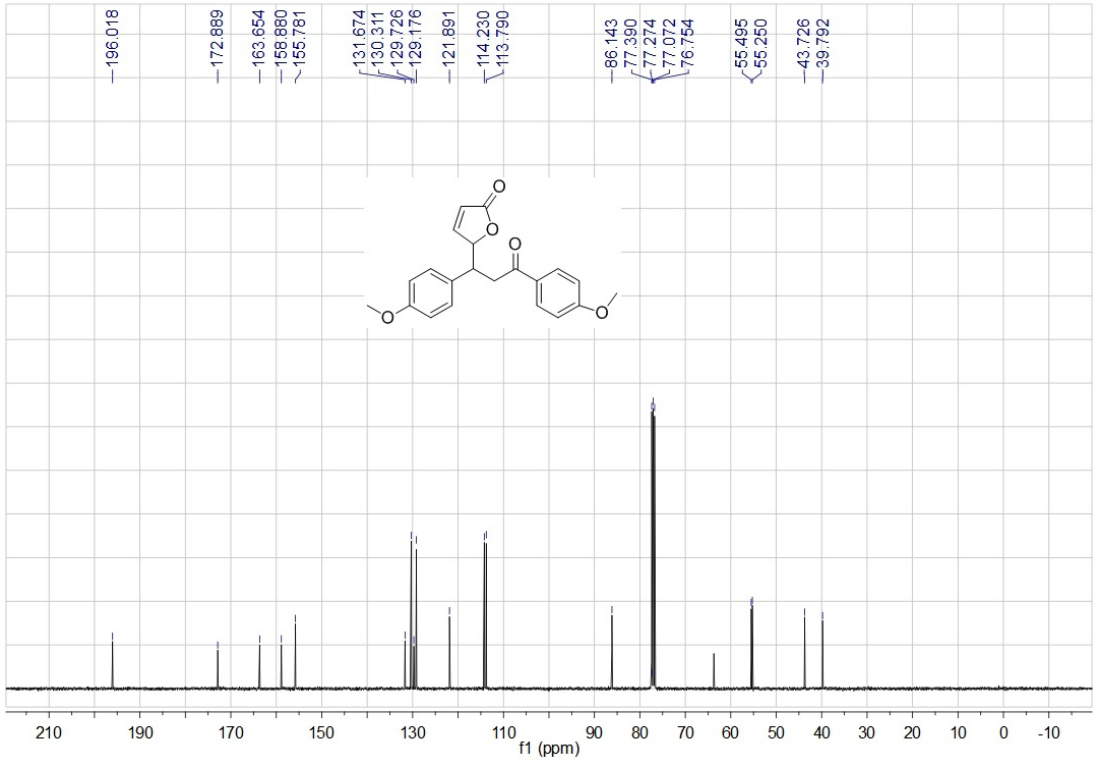
3.4969
3.4767
3.4527
3.4325
2.3794
2.07
8.58
1.00
1.03
1.89
1.08
1.10
3.26
f1 (ppm)

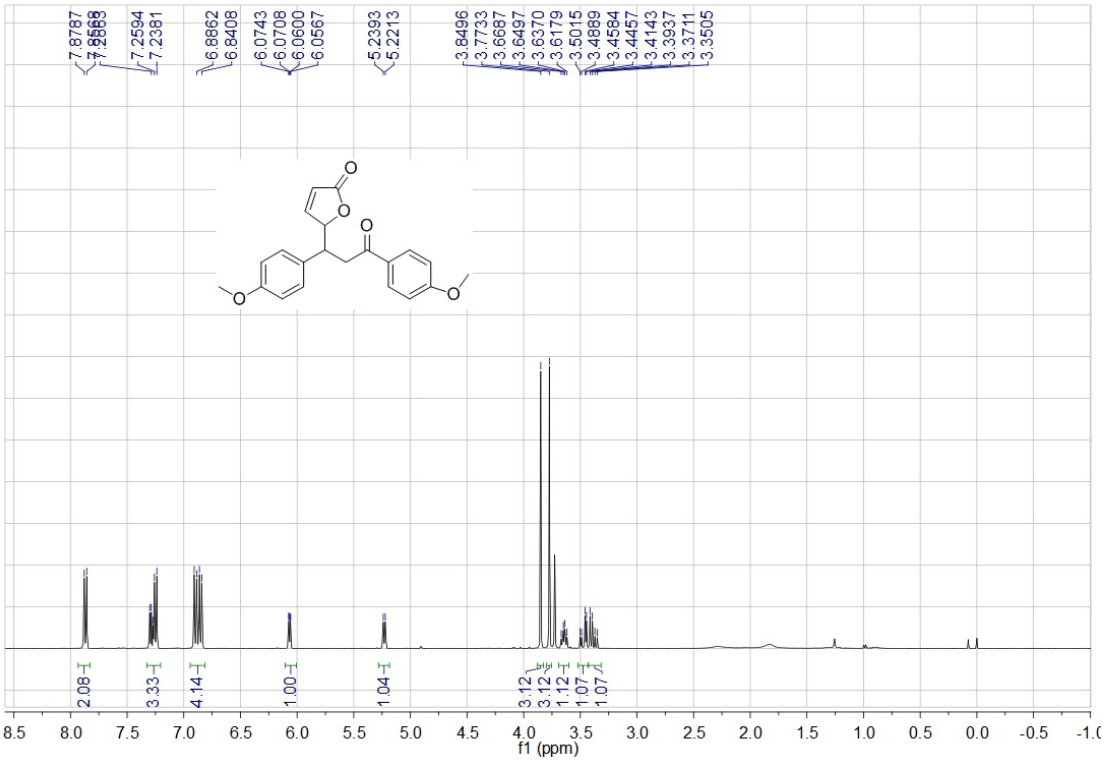

195.83
172.79
163.67
155.70
139.83
130.30
127.61
121.92
113.79
85.89
77.26
77.04
76.83
55.49
44.38
39.53
f1 (ppm)

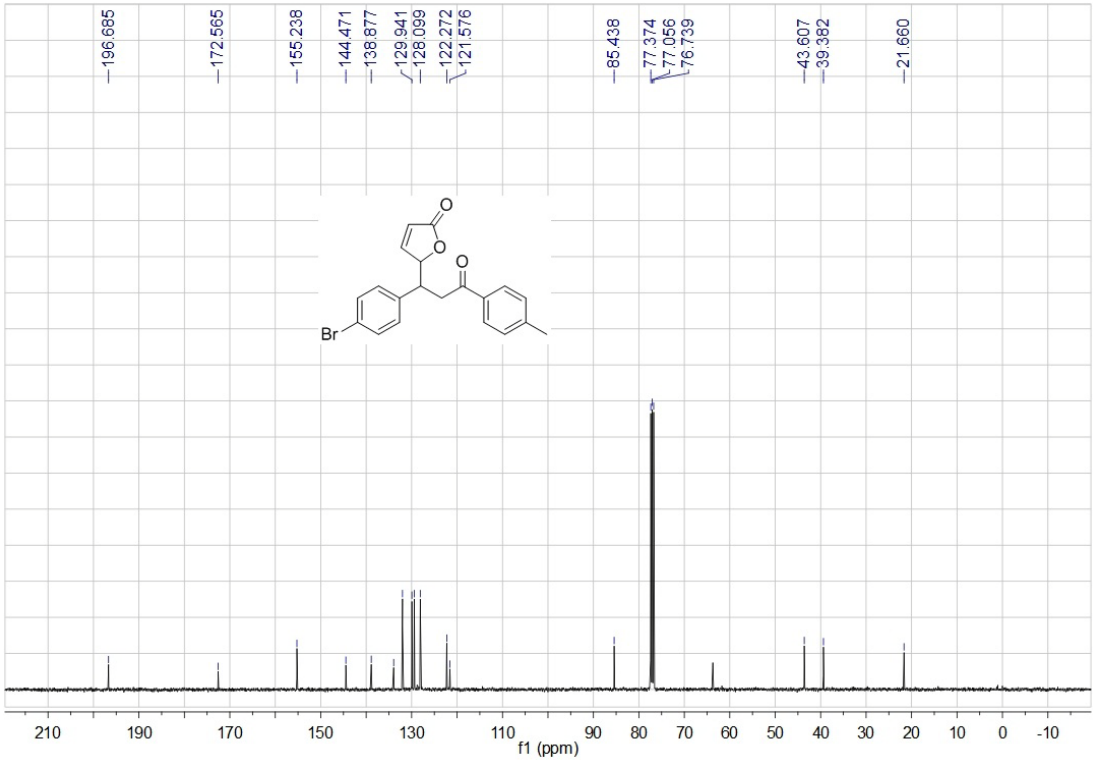





7.8787
7.8568
7.8563
7.2594
7.2381
6.8862
6.8408
6.0743
6.0708
6.0600
6.0567
5.2393
5.2213
3.8496
3.7733
3.6687
3.6497
3.6370
3.6179
3.5015
3.4889
3.4584
3.4457
3.4143
3.3937
3.3711
3.3505
O
O
O
O
2.08
3.33
4.14
1.00
1.04
3.12
3.12
1.12
1.07
1.07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


196.685
172.565
155.238
144.471
138.877
129.941
128.099
122.272
121.576
85.438
77.374
77.056
76.739
43.607
39.382
21.660
O
O
O
Br
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)